Electronic Supplementary Information

Characterization of heterogeneous aryl-Pd(II)-oxo clusters as active species for C-H arylation

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Contents:

1.	Characterization of Pd NPs	S2
2.	Reaction scope of C-H arylation of heterocyclic compounds	S5
3.	Characterization of the reaction intermediates	S14
4.	Control experiments	S16
5.	NMR spectra	S19

1. Characterization of Pd NPs

Chemicals. Palladium(II) acetylacetonate [Pd(acac)$_2$, 99%], oleylamine (OAm, 70%), and trioctylphosphine (TOP, 90%) were purchased from Aldrich. All substrates for direct C-H arylation and solvent were purchased from Sigma-Aldrich and used without further purification or drying. Other solvents were purchased from Aldrich, Samchun and Daejung co. Ltd. and all solvents were used as received without further purification or drying.

Preparation of Pd NPs. The Pd NPs were synthesized by a same procedure of the previous literature.[S1] A mixture of Pd(acac)$_2$ (91 mg), TOP (1.0 mL) and OAm (10.0 ml) was degassed at room temperature for 30 min and increased temperature to 503 K for 20 min under a nitrogen atmosphere, and maintained for 40 min at same temperature. The reaction mixture was cooled down to room temperature, and the Pd NPs were precipitated by centrifugation in ethanol.

Surface oxidation of Pd NPs. For the oxidation process, Pd NPs (3.0 mg) and Ph2IBF4 (2 equiv with respect to the Pd NPs) were dissolved in THF (2.0 mL) in a sealed vial equipped with a stirring bar. The mixture was heated to 333 K and allowed to stir for 1 h at the same temperature. After the oxidation, the mixture was cooled down to room temperature, and washed with hexane and acetone twice. The product was precipitated by centrifugation in ethanol.

XRD analysis. For the X-ray diffraction (XRD) analysis, the Pd NPs dissolved in ethanol were dropped on the glass substrates. XRD patterns were measured by a Rigaku SmartLab X-Ray Diffractometer.

Transmission electron microscopy (TEM). Pristine and oxidized Pd NPs were characterized by FEI Tecnai TF30 ST (300 kV, KAIST). TEM Samples were prepared by dropping a few samples on the carbon-coated 300 mesh copper grids (TED PELLA Inc.).

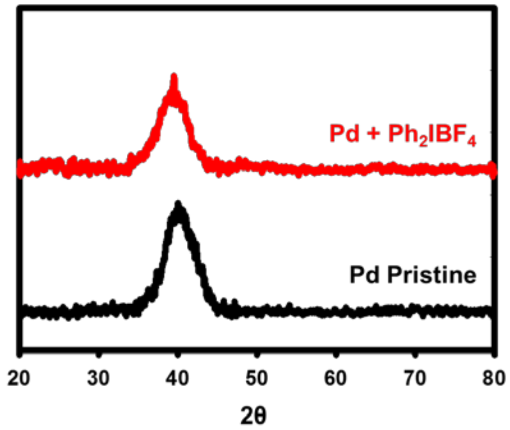


Fig. S1 XRD patterns of pristine Pd NPs and Pd NPs treated with $[Ph_2I]BF_4$.

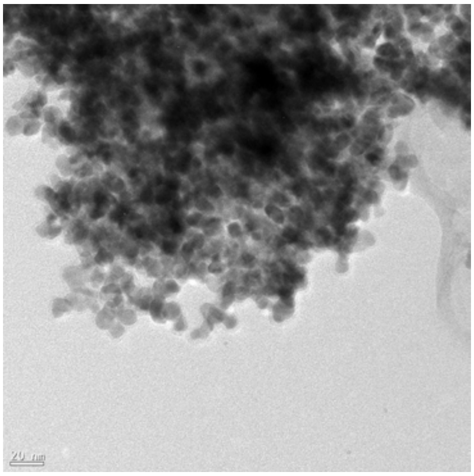


Fig. S2 TEM image of Pd NPs after the arylation reaction in EtOH.

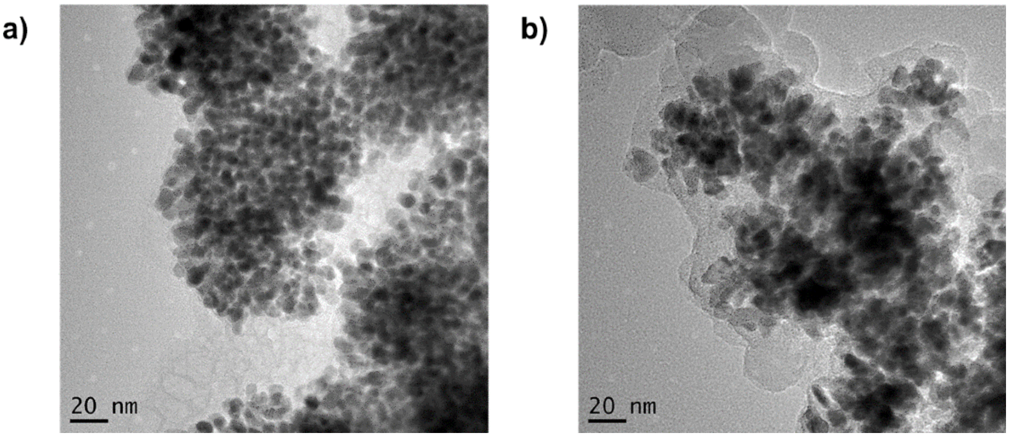


Fig. S3 TEM images of the precipitates formed after the reactions of (a) entry 4 and (b) entry 5 in Table 1.

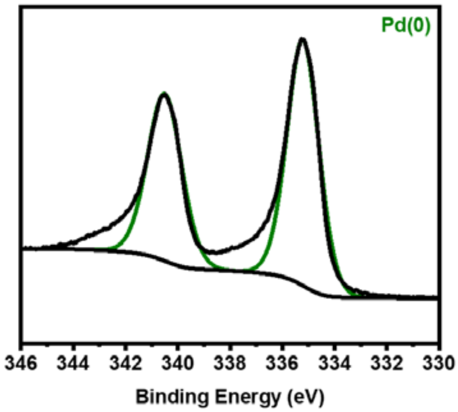
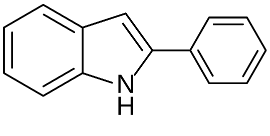


Fig. S4 XPS spectra at the Pd 3d level of Pd NPs after the treatment with PhI.

2. Reaction scope of C-H arylation of heterocyclic compounds

General procedure for Pd NPs C-H arylation. Diphenyliodonium tetrafluoroborate were synthesized according to the literatures.[1] To an vial equipped with a stir bar were added corresponding substrates (0.2 mmol), Pd NPs (5 mol% with respect to the substrate concentration), Ph_2IBF_4 (1.3 equiv), and THF (reagent grade, 99.5%) (2.0 mL) in air. The mixture was heated to 60 ^oC and stirred for 24 h. After 24 h, the crude mixture was directly analysed by GC-MS spectroscopy with mesitylene as an internal standard. Products were isolated with silica-gel column flash chromatography (Hex:EtOAc).

Analytical method. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 aluminum plates (Merck). TLC plates were visualized by exposure to short wave ultraviolet light (254 nm, 366 nm). Flash column chromatography was performed on Merck silica gel (40-63 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker Ascend 400 (400 MHz for ^1H and 100 MHz for ^{13}C) spectrometer and were reported in ppm, relative to residual protonated solvent peak ($CDCl_3$). GC-MS spectra were recorded on an Agilent Technologies 7890A GC-system with an Agilent 5977B MSD and a HP-5MS column(0.25 mm × 30 m, film: 0.25 Km). The major signals are quoted in m/z with the relative intensity in parentheses. The methods used start with the injection temperature T_0. After holding this temperature for 3 min, the column is heated to temperature T_1 (ramp) and this temperature is held for an additional time t (method : T_0 = 50 °C, T_1 = 290 °C, ramp = 10 °C/min, t = 5 min). The high-resolution mass spectra (HRMS) were obtained by ESI from KAIST Research Analysis Center (KARA).



1b

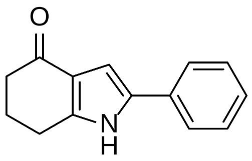
White solid, R_f(hexane/EtOAc 8:2) = 0.7;

^1H NMR ($CDCl_3$, 400 MHz) δ ppm 8.33 (bs, 1H, NH), 7.66 (m, 3H), 7.44 (m, 3H), 7.34 (m, 1H), 7.21 (m, 1H), 7.13 (ddd, J = 7.8, 7.1, 1.1 Hz, 1H), 6.84 (dd, J = 2.2, 0.9 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 138.0, 137.0, 132.5, 129.4, 129.2, 127.9, 125.3, 122.5, 120.8, 120.4, 111.0, 100.1.

HRMS (ESI) calculated for $C_{14}H_{11}N[M+H]^+$: 194.0971, Found : 194.0949.

Data is in accordance with the literature.[2]



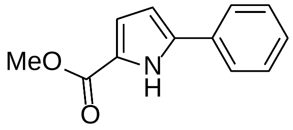
2b White solid, R_f(hexane/EtOAc 2:1) = 0.5;

^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 9.04 (bs, 1H, NH), 7.48 (m, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.24 (m, 1H), 6.80 (d, *J* = 2.5 Hz, 1H), 2.87 (t, *J* = 6.2 Hz, 2H), 2.51 (m, 1H), 2.18 (p, *J* = 6.4 Hz, 2H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 194.8, 144.7, 133.1, 131.8, 129.1, 128.0, 127.2, 124.3, 122.0, 102.5, 38.0, 24.0, 23.0.

HRMS (ESI) calculated for $C_{14}H_{13}NO[M+H]^+$: 211.1077, Found : 211.1066.

Data is in accordance with the literature.[3]



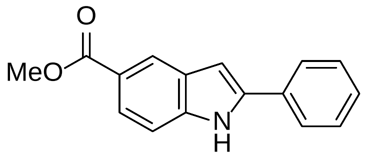
3b White solid, R_f(hexane/EtOAc 9:1) = 0.5;

^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.48 (brs, 1H, NH), 7.62 – 7.54 (m, 2H), 7.49 – 7.36 (m, 2H), 7.33 – 7.27 (m, 1H), 6.97 (dd, *J* = 3.9, 2.4 Hz, 1H), 6.55 (dd, *J* = 3.9, 2.7 Hz, 1H), 3.88 (s, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 161.8, 137.0, 131.5, 129.2, 127.9, 124.9, 123.2, 117.0, 108.2, 51.7.

HRMS (ESI) calculated for $C_{12}H_{11}NO_2[M+Na]^+$: 224.0688, Found : 224.0684.

Data is in accordance with the literature.[4]

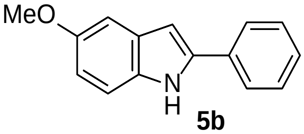


4b white solid, R_f(hex:EtOAc = 3:1) = 0.5;

^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 8.59 (br, 1H), 8.40 (s, 1H), 7.91 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.68 (m, 2H), 7.46 (dd, *J* = 8.6, 7.0 Hz, 2H), 7.39 (m, 2H), 6.90 (dd, J = 2.2, 0.9 Hz, 1H), 3.94 (s, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 168.3, 139.5, 139.5, 131.9, 129.3, 129.0, 128.3, 125.4, 123.9, 123.7, 122.5, 110.7, 101.1, 77.5, 77.2, 76.8, 52.1.

Data is in accordance with the literature.[5]

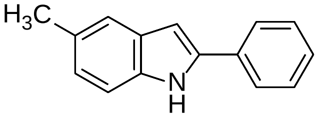


5b white solid, R_f(hex:EtOAc = 10:1) = 0.3;

^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 8.25 (br, 1H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.44 (m, 2H), 7.32 (m, 2H), 7.10 (d, *J* = 2.5 Hz, 1H), 6.87 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.77 (br, 1H), 3.88 (s, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 154.6, 138.8, 132.5, 132.2, 129.9, 129.1, 127.8, 125.2, 112.8, 111.8, 102.4, 99.9, 56.0.

Data is in accordance with the literature.[6]

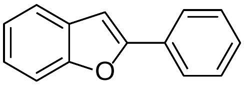


6b colorless oil, R_f(hex:EtOAc = 10:1) = 0.4;

^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 8.22 (br, 1H), 7.66 (m, 2H), 7.47-7.43 (m, 3H), 7.35-7.29 (m, 2H), 7.05 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.77 (s, 1H), 2.48 (s, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 138.1, 135.3, 132.6, 129.7, 129.6, 129.1, 127.7, 125.2, 124.1, 120.4, 110.7, 99.7, 21.6.

Data is in accordance with the literature.[7]



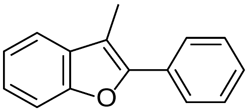
7b White solid, R_f(pentane) = 0.3;

^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 7.88 (m, 2H), 7.59 (ddd, *J* = 7.5, 1.5, 0.7 Hz, 1H), 7.54 (m, 1H), 7.46 (m, 2H), 7.37 (m, 1H), 7.29 (ddd, *J* = 8.1, 7.3, 1.5 Hz, 1H), 7.23 (m, 1H), 7.04 (d, *J* = 1.0 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.1, 155.0, 133.1, 130.6, 129.4, 128.9, 128.7, 125.1, 124.4, 123.1, 121.0, 111.3, 101.4

HRMS (ESI) calculated for $C_{14}H_{10}O[M+H]^+$: 195.0804, Found : 195.0805.

Data is in accordance with the literature.[8]

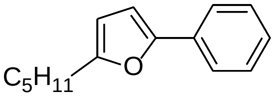


8b colorless, crystalline solid, R_f(hex:EtOAc = 10:1) = 0.65;

^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 7.82 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.55 (m, 1H), 7.49(m, 3H), 7.37(m, 1H), 7.29(m, 2H), 2.50(s, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 153.9, 150.8, 131.6, 131.3, 128.8, 128.0, 126.9, 124.5, 122.5, 119.4, 111.4, 111.1, 9.6.

Data is in accordance with the literature.[9]



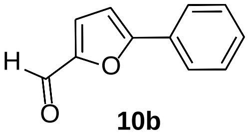
9b colorless oil, R_f(hexane/EtOAc 95:5) = 0.5;

^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 7.66 – 7.62 (m, 2H), 7.38 – 7.32 (m, 2H), 7.24 – 7.18 (m, 1H), 6.55 (d, *J* = 3.2 Hz, 1H), 6.06 (dt, *J* = 3.2, 0.9 Hz, 1H), 2.71 – 2.65 (m, 2H), 1.78 – 1.61 (m, 2H), 1.41 – 1.34 (m, 4H), 0.96 – 0.83 (m, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 156.6, 152.2, 131.4, 128.7, 126.8, 123.5, 107.0, 105.8, 31.5, 28.3, 27.9, 22.6, 14.2.

HRMS (ESI) calculated for $C_{15}H_{18}O[M+Na]^+$: 237.1250, Found : 237.1254.

Data is in accordance with the literature.[10]



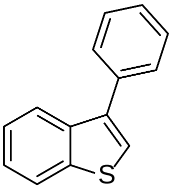
10b Pale-yellow solid, R_f(hexane/EtOAc 5:2) = 0.4;

^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 9.66 (s, 1H), 7.87 – 7.79 (m, 2H), 7.47 – 7.36 (m, 3H), 7.32 (d, *J* = 3.7 Hz, 1H), 6.85 (d, *J* = 3.7 Hz, 1H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 177.4, 159.6, 152.2, 129.8, 129.1, 125.5, 107.8.

HRMS (ESI) calculated for $C_{11}H_8O_2[M+Na]^+$: 195.0417, Found : 195.0400.

Data is in accordance with the literature.[11]



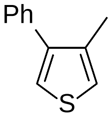
11c colorless oil, R_f(penatne) = 0.5;

^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 8.07 – 7.86 (m, 2H), 7.64 – 7.57 (m, 2H), 7.52 – 7.47 (m, 2H), 7.44 – 7.37 (m, 4H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 140.8, 138.3, 138.1, 136.2, 128.9, 127.7, 124.6, 124.5, 123.5, 123.1.

HRMS (ESI) calculated for $C_{14}H_{10}S[M+Na]^+$: 233.0395, Found : 233.0398.

Data is in accordance with the literature.[12]



12c colorless oil, R_f(pentane) = 0.7;

^{1}H NMR ($CDCl_3$, 400 MHz) δ ppm 7.42 – 7.40 (m, 4H), 7.34 – 7.32 (m, 1H), 7.20 (d, J = 3.3 Hz, 1H), (dd, J = 3.3, 1.0 Hz, 1H), 2.28(s, 3H)

^{13}C NMR ($CDCl_3$, 100 MHz) δ ppm 143.3, 137.2, 136.3, 128.8, 128.4, 127.1, 123.1, 122.1, 15.7.

Data is in accordance with the literature.[13]

The reaction with 5-chloro-3-methylbenzo[b]thiophene gave no product.

References

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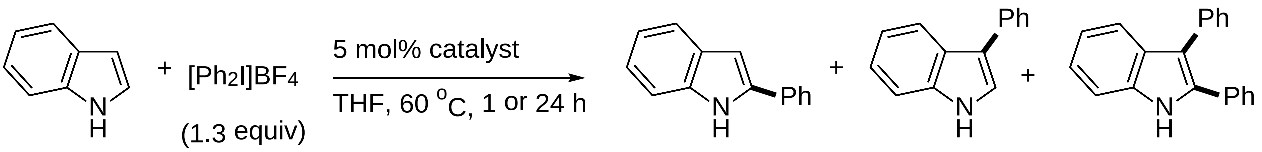
Compare the reactivity and regioselectivity with Pd NPs and homogeneous Pd catalysts.[a]

To an vial equipped with a stir bar were added indole (0.2 mmol), Pd NPs (5 mol%), Ph_2IBF_4 (1.3 equiv), and THF(reagent grade, 99.5%) (2.0 mL) in air. The mixture was heated to 60 °C and stirred 1 h. After 1 h, the crude mixture was directly analysed by GC-MS spectroscopy with mesitylene as internal standard. After check the conversion of 1 h reaction, the reaction mixture was heated to 60 °C and stirred until 24 h. After 24 h reaction time, the crude mixture was directly analysed by GC-MS spectroscopy with mesitylene as internal standard. Products were isolated with column flash chromatography (Hex:EtOAc).

Table S1 Arylation of indole with diaryliodonium salt catalyzed by homogeneous and heterogeneous Pd sources for 1 h and 24 h

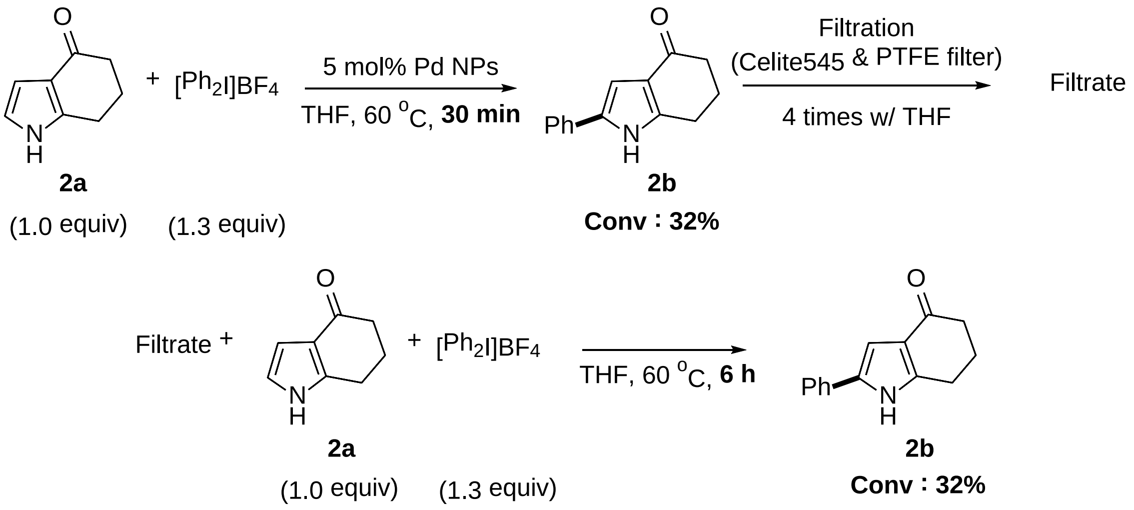


1a **1b** **1c** **1d**

Entry	Catalyst	Conv(%), 1 h	Conv(%), 24 h (yield)[a]	**1b**	**1c**	**1d**
1	Pd NPs	35	>99 (80%)	99%	-	-
2	$PdCl_2$	78	>99 (42%)	80%	10%	10%
3	$Pd(TFA)_2$	98	>99 (47%)	81%	18%	1%
4	$Pd(OAC)_2$	>99	>99 (65%)	76%	12%	12%

[a] No other side products were detected by ^1H NMR and GC-MS.

Filtration test. To an vial equipped with a stir bar were added Pd NPs (1.0 mg, 0.01 mmol, 5 mol%), $Ph_2I[BF_4]$ (95.7 mg, 0.26 mmol, 1.3 equiv.), indole (27 mg, 0.2 mmol, 1.0 equiv.), and THF (2.0 mL) in air. The crude mixture was stirred at 60 °C for 30 min, and the conversion of the crude mixture was determined by the GC-MS spectroscopy with mesitylene as internal standard. The reaction mixture was filtered through a layer of Celite 545 followed by a 0.2 μm PTFE filter. 0.6 mL of THF was used for the filtration. The filtrate was transferred to an vial, and then filtrate was stirred at 60 °C for 24 h, and the conversion of the crude mixture was determined by the GC-MS spectroscopy with mesitylene as internal standard.



	Conversion of 2a (2h)	Conversion of 2a (6h)
Control reaction	32%	>99%
Hot filtration test	32%	32%

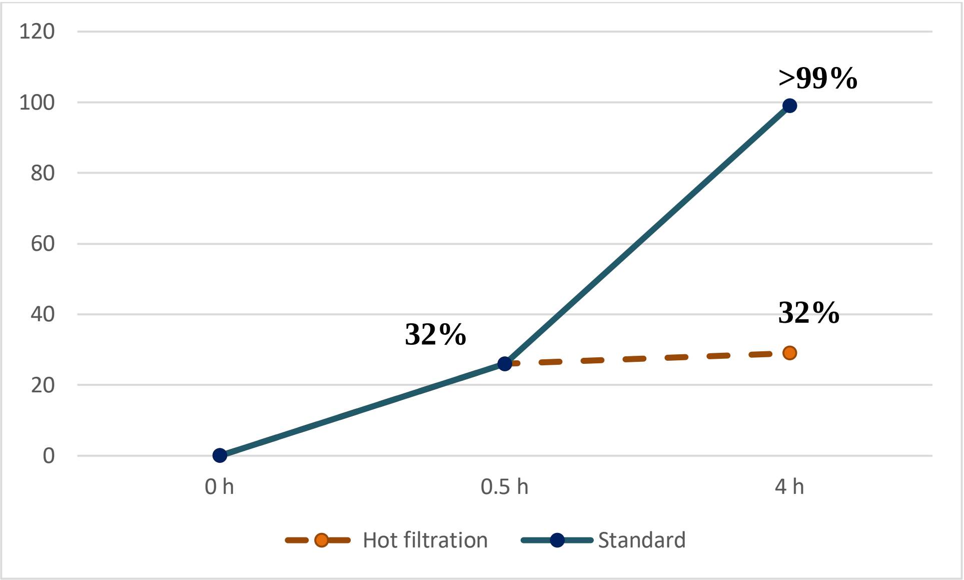


Fig. S5 The filtration experiment for the Pd NPs C-H arylation of **2**.

Mercury poisoning test. test. A drop of Hg was added to the Pd NPs-catalyzed C-H arylation. To an vial equipped with a stir bar were added Pd NPs (1.0 mg, 0.01 mmol, 5 mol%), Ph_2IBF_4 (95.7 mg, 0.26 mmol, 1.3 equiv), indole (27 mg, 0.2 mmol, 1.0 equiv), and THF (2.0 mL) in air. The crude mixture was stirred at 60 °C for 30 min, and the conversion of the crude mixture was determined by the GC-MS spectroscopy with mesitylene as internal standard. After check the conversion of crude mixture about 30 min reaction, Hg (10 μL, 0.70 mmol) was dropped into the reaction mixture. crude mixture was stirred at 60 °C for 24 h, and the conversion was determined by the GC-MS spectroscopy of the crude sample.

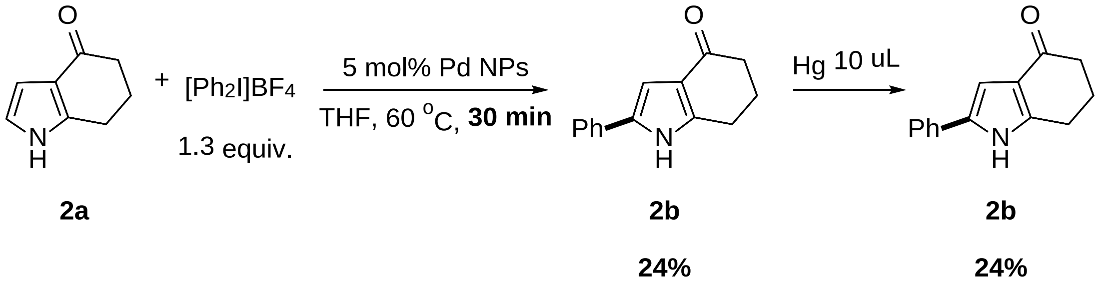
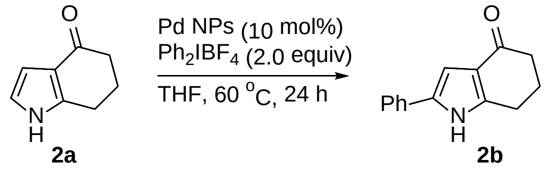


Fig. S6 Mercury test for the Pd NPs C-H arylation of **2**.

A typical procedure for recycling experiments.

To an vial equipped with a stir bar were added Pd NPs (4.0 mg, 0.04 mmol, 10 mol%), Ph_2IBF_4 (294 mg, 0.8 mmol, 2.0 equiv.), indole (54.0 mg, 0.4 mmol, 1.0 equiv.), and THF (reagent grade, 99.5%, 2.0 mL) in air. The crude mixture was stirred at 60 °C for 24 h, and the conversion was determined by ^1H NMR spectroscopy of the crude sample. When the reaction was completed, the reaction solution was centrifuged under 1500 rpm for 3 min. Then crude solution was decanted into vial and residue Pd NPs was washed with EtOH (2.0 mL) using sonicator equipment. Then washing solution was centrifuged under 1500 rpm for 3 min. The ethanol washing process repeat more than 4 times and final washing process was conducted with THF (2.0 mL). The recovered Pd NPs were used for the next run.



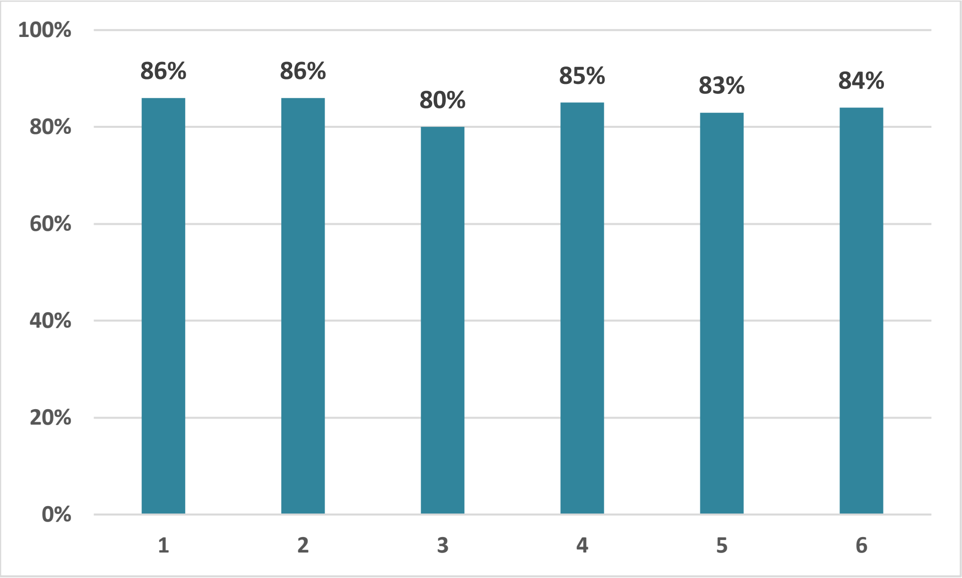


Fig. S7 Recycling test of Pd NPs C-H arylation of **2a**

3. Characterization of the reaction intermediates

XPS analysis. Pd NPs were characterized by X-ray photoelectron spectroscopy (XPS) to analyse the surface oxidation states. The Pd NP samples were dispersed in hexane, and were drop-casted on a Si wafer. The resulting wafer was immediately loaded in a UHV chamber. The measurements were performed with the XPS system.

IR spectroscopy measurement. The Pd NPs samples (2 mg) were mixed with KBr (100mg) and pelletized about 1.5 mm thickness. The IR spectroscopy was measured by AGILENT 660-IR spectrometer.

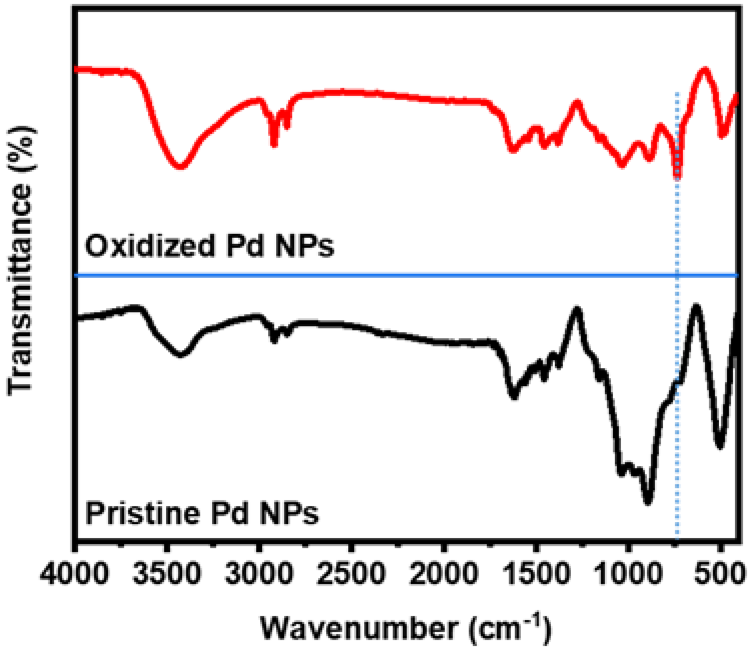
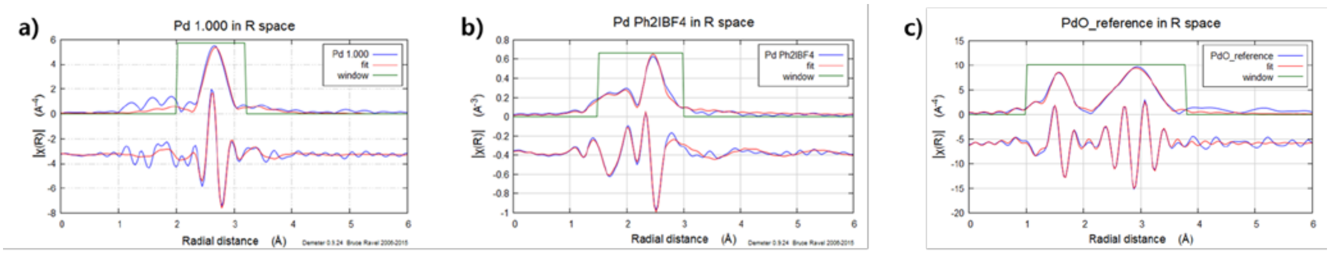


Fig. S8 IR spectra of pristine Pd NPs and Pd NPs treated by $[Ph_2I]BF_4$.

EXAFS analysis. X-ray absorption fine spectroscopy (XAFS) data of the catalysts were collected at Pd K-edge, 24350 eV with ambient condition in Pohang Accelerator Laboratory (7D-XAFS beamline in PLS-II) equipped Si(111) crystal as a monochromator. The beamline energy and ring current were 2.5 GeV and 300 mA, respectively. The step and duration time for X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were 1.0 eV and 2 s, and 0.30 nm^{-1} and 3 s, respectively. A total number of the points per an XAFS spectrum was 500, which were sufficient for the EXAFS analysis. For the EXAFS refinement, after the data processing using Athena, Artemis in Demeter program package (0.9.25) was employed. Using AUTOBK program for R_{bkg} = 0.1 nm, the background removal was performed to extract XAFS signals and subsequently the corresponding XAFS data in *k* space were Fourier transformed with the Kaiser-Bessel window function. The range for Fourier transformation of the Pd samples, Δk, were 30 – 115 nm^{-1} or 3 – 11.5 Å^{-1}. The phase shifts and amplitude functions of the reference was generated using *Feff* 6. Depending on the samples, the curve fitting ranges were varied in *r* space. The number of independent point of the data for the curve fit, N_{idp}, was decided from Nyquist theorem, which was always larger than the number of variables, ascribing the enough degree of freedom, N_{var}. The scattering path from the feasible model structure was acquired from the *Feff* calculation. Only the scatterings with large contribution were included in the multi-shell fitting. The many-body reduction factor was procured from a Pd foil under the same condition and was utilized further in the curve fit of the samples.



d)

	Path	C.N.	r (nm)	σ² (pm²)	R-factor
PdO_ref	Pd-O1	3.80±0.44	0.203±0.01	16±10	0.01
	Pd-Pd1	3.81±0.91	0.305±0.01	56±15	
	Pd-Pd2	5.42±1.66	0.344±0.02	42±17	

Fig. S9 EXAFS spectra and curve fitting in r and q spaces for (a) pristine, (b) [Ph_2I]BF_4-oxidized Pd NPs, and (c) commercial PdO. (d) Structural parameters of commercial PdO by EXAFS refinement.

4. Control experiments

Control experiments. For (a), to a vial equipped with a stir bar were added Pd NPs (1.0 mg, 0.01 mmol, 5 mol%), Ph_2IBF_4 (73.6 mg, 0.2 mmol, 1.0 equiv.), indole (117.2 mg, 1.0 mmol, 5.0 equiv.), and THF (2.0 mL). The vial was stirred at 60 °C for 24 h, and the conversion of the crude mixture was determined by the GC-MS spectroscopy with mesitylene as internal standard and isolated yield was given. For (b), to a vial equipped with a stir bar were added Pd NPs (1.0 mg, 0.01 mmol, 5 mol%), Ph2IBF4 (73.6 mg, 0.2 mmol, 1.0 equiv.) and THF (2.0 mL). The vial was stirred at 60 °C for 24 h, and isolated yield was given.

*all used chemical including solvent was used without further purification method.

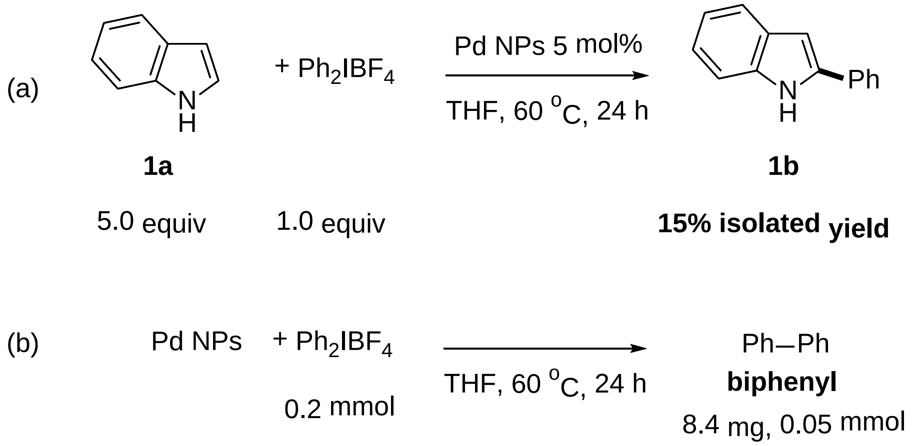


Fig. S10 (a) Catalytic arylation with excess indole (5 equiv). (b) Biphenyl generated without substrates.

Investigation of O_2 and H_2O effect

Procedure of scheme (1). In argon purged glove box, indole (0.2 mmol), Pd NPs (5 mol%), Ph_2IBF_4 (1.3 equiv), and THF(anhydrous and degassed, 99.9%) (2.0 mL) were added into an vial with stir bar. The crude mixture was heated to 60 °C and stirred 3 h. After 3 h, the crude mixture was directly isolated with flash column chromatography (Hex:EtOAc).

Procedure of scheme (2). In argon purged glove box, indole (0.2 mmol), Pd NPs (5 mol%), Ph_2IBF_4 (1.3 equiv), and THF(anhydrous and degassed, 99.9%) (2.0 mL) were added into an vial with stir bar. After taking out the crude mixture, insert an O_2 balloon, and stirred at 60 °C, for 3 h. After 3 h, the crude mixture was directly isolated with flash column chromatography (Hex:EtOAc).

Procedure of scheme (3). In argon purged glove box, indole (0.2 mmol), Pd NPs (5 mol%), Ph_2IBF_4 (1.3 equiv), and THF(anhydrous and degassed, 99.9%) (2.0 mL) were added into an vial with stir bar. After taking out the crude mixture, H_2O (10 μL) was added and stirred at 60 °C, for 3 h. After 3 h, the crude mixture was directly isolated with flash column chromatography (Hex:EtOAc).

Procedure of scheme (4). Procedure of scheme 4 followed the general procedure of Pd NPs catalysed C-H arylation of indole.To an vial equipped with a stir bar were added indole (0.2 mmol), Pd NPs (5 mol%), Ph_2IBF_4 (1.3 equiv), and THF(reagent grade, 99.5%) (2.0 mL). The mixture was heated to 60 °C and stirred for 3 h. After 3 h, the crude mixture was isolated with column flash chromatography (Hex:EtOAc).

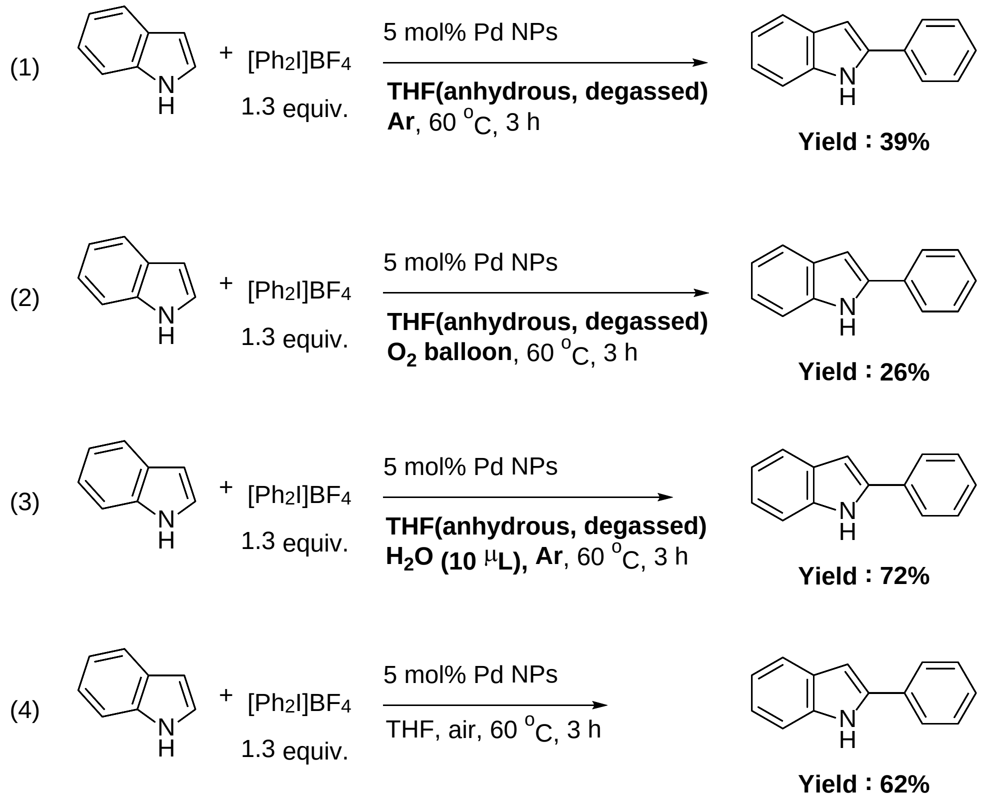


Fig. S11 Control experiments in anhydrous THF (1) in the absence of both H_2O and O_2, (2) in the presence of O_2, (3) in the presence of water but in the absence of O_2, (4) and in air with both H_2O and O_2.

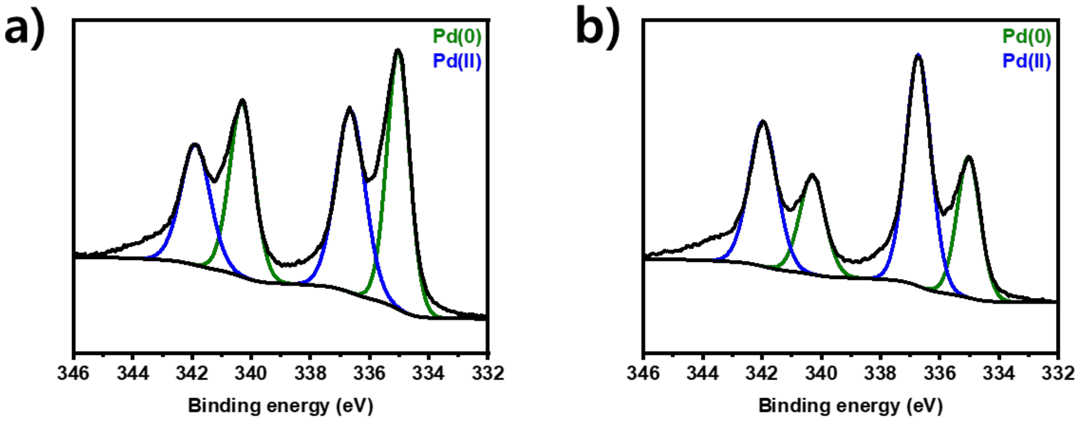
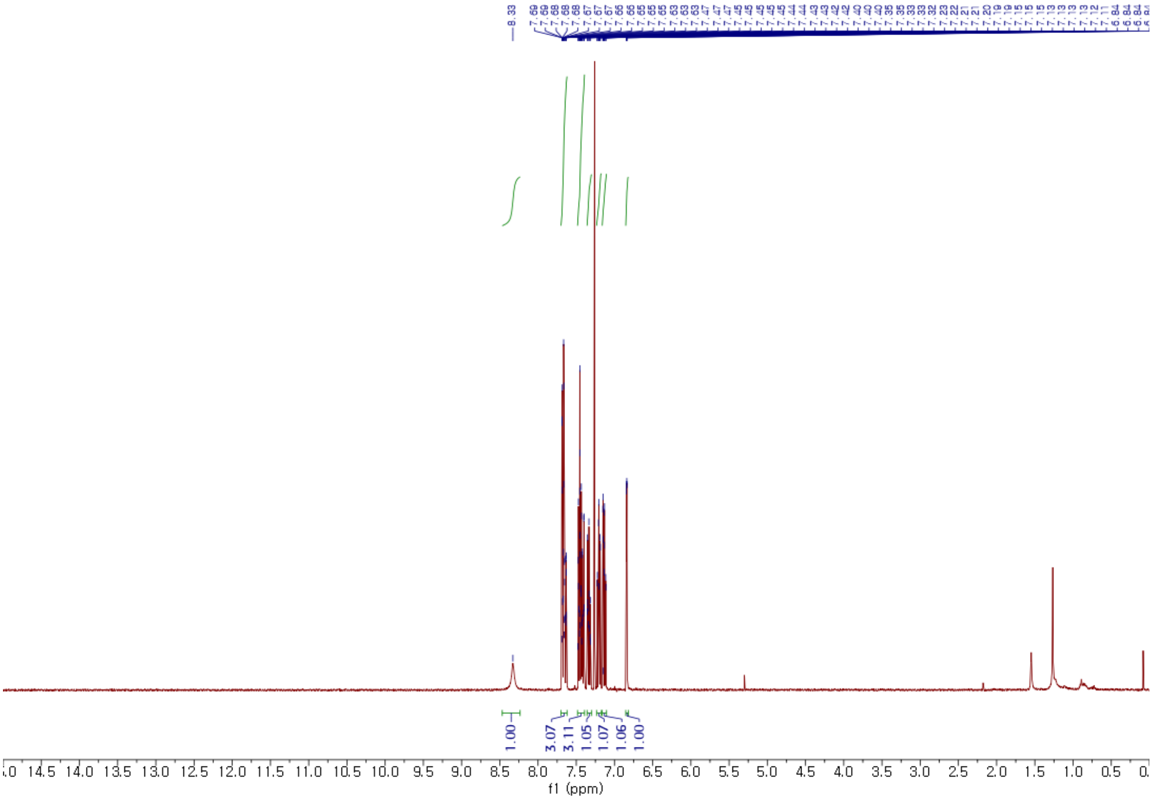
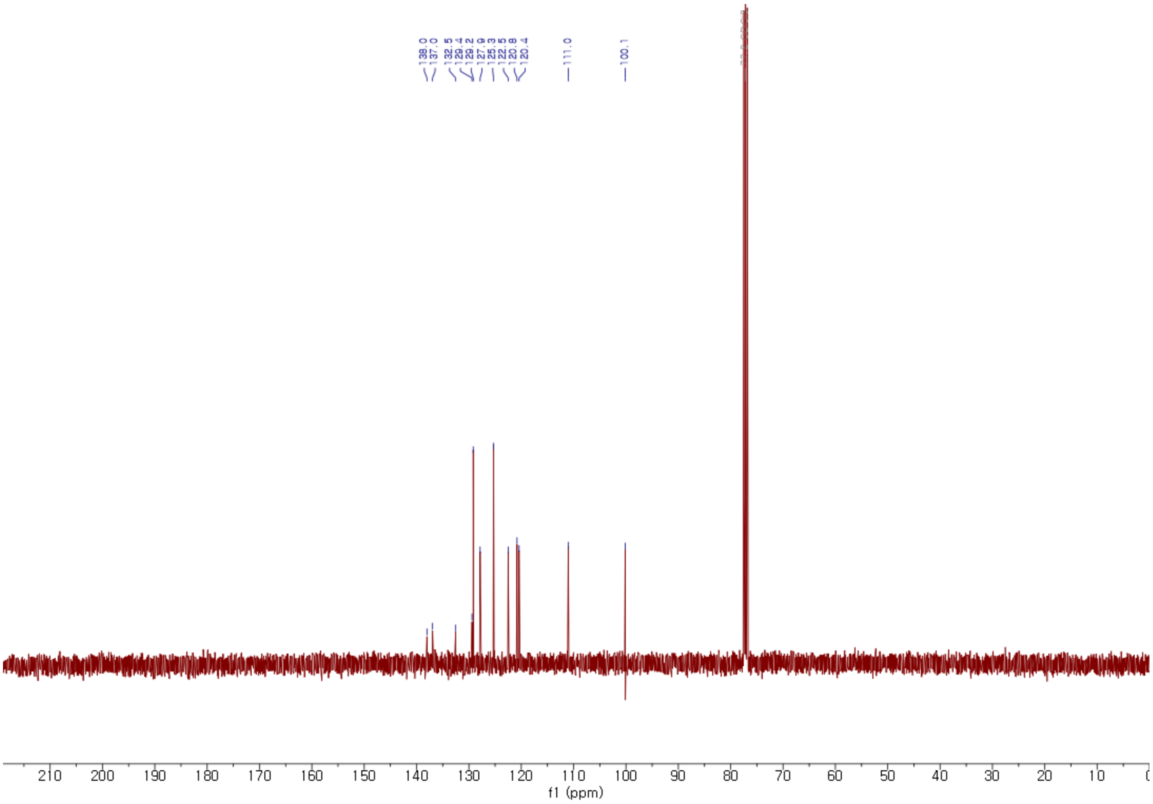


Fig. S12 XPS spectra at the Pd 3d level of (a) Pd NPs + [Ph_2I]BF_4 in anhydrous THF, (b) Pd NPs + [Ph_2I]BF_4 in THF in the presence of H_2O.

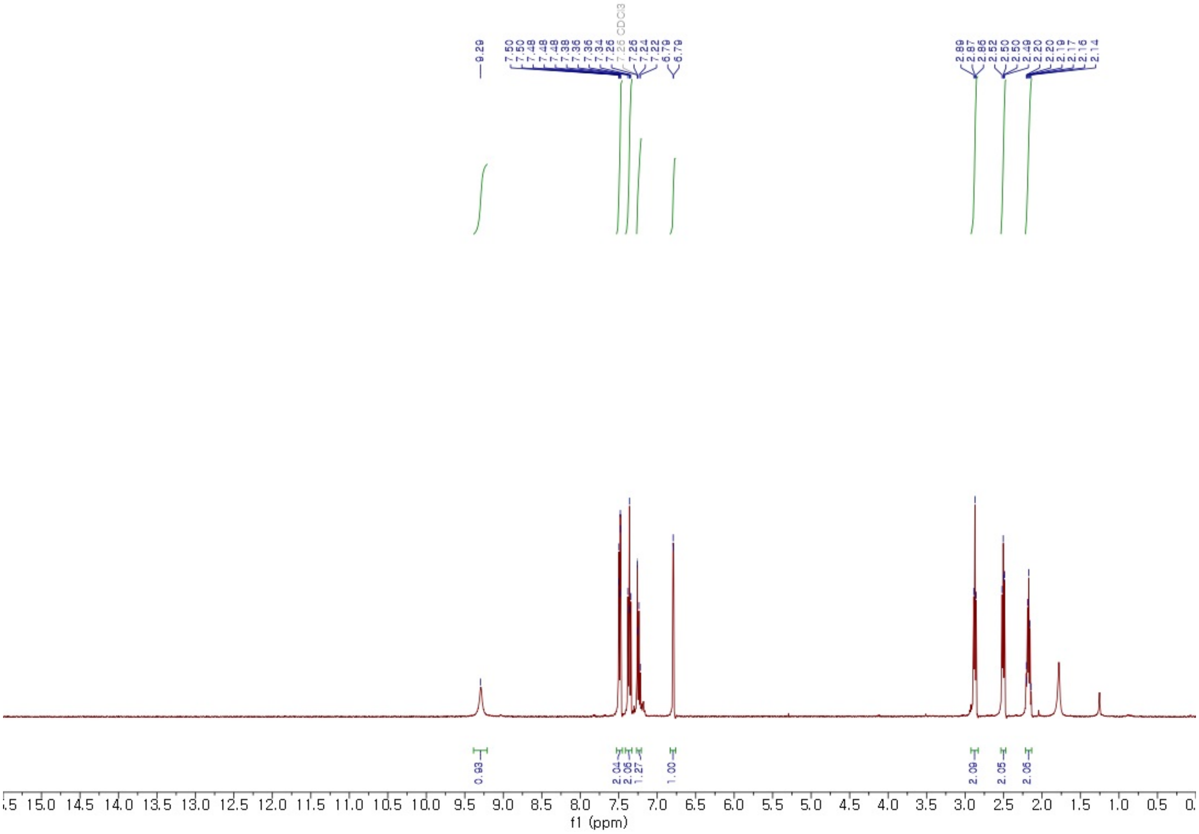
5. NMR Spectra



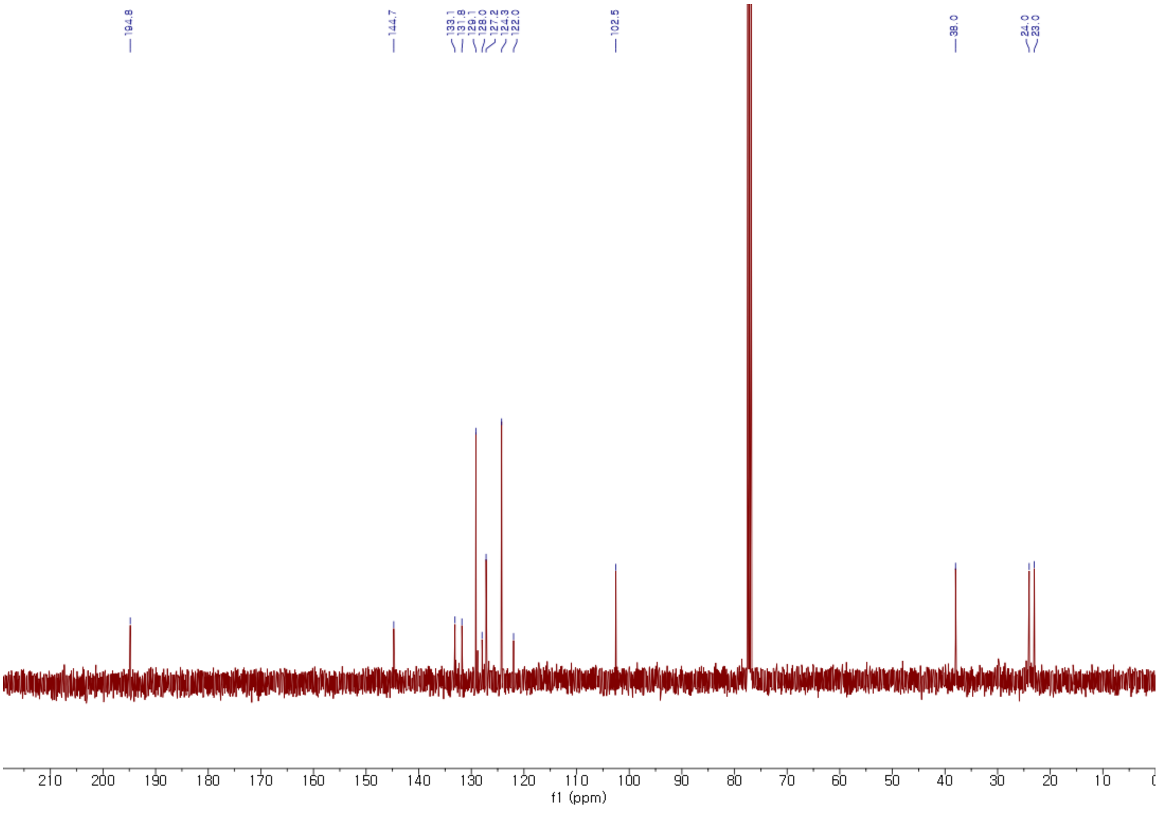
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **1b**



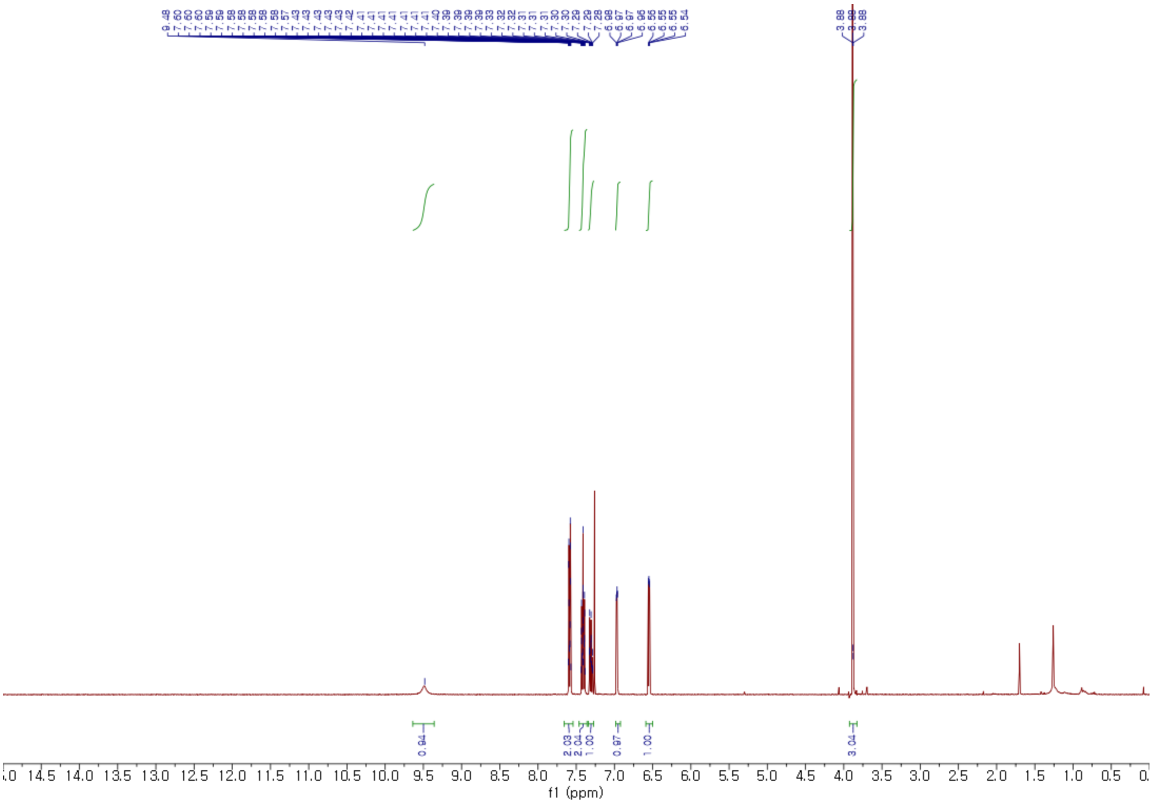
^{13}C{^{1}H} NMR spectrum (100 MHz, CDCl$_3$) of **1b**



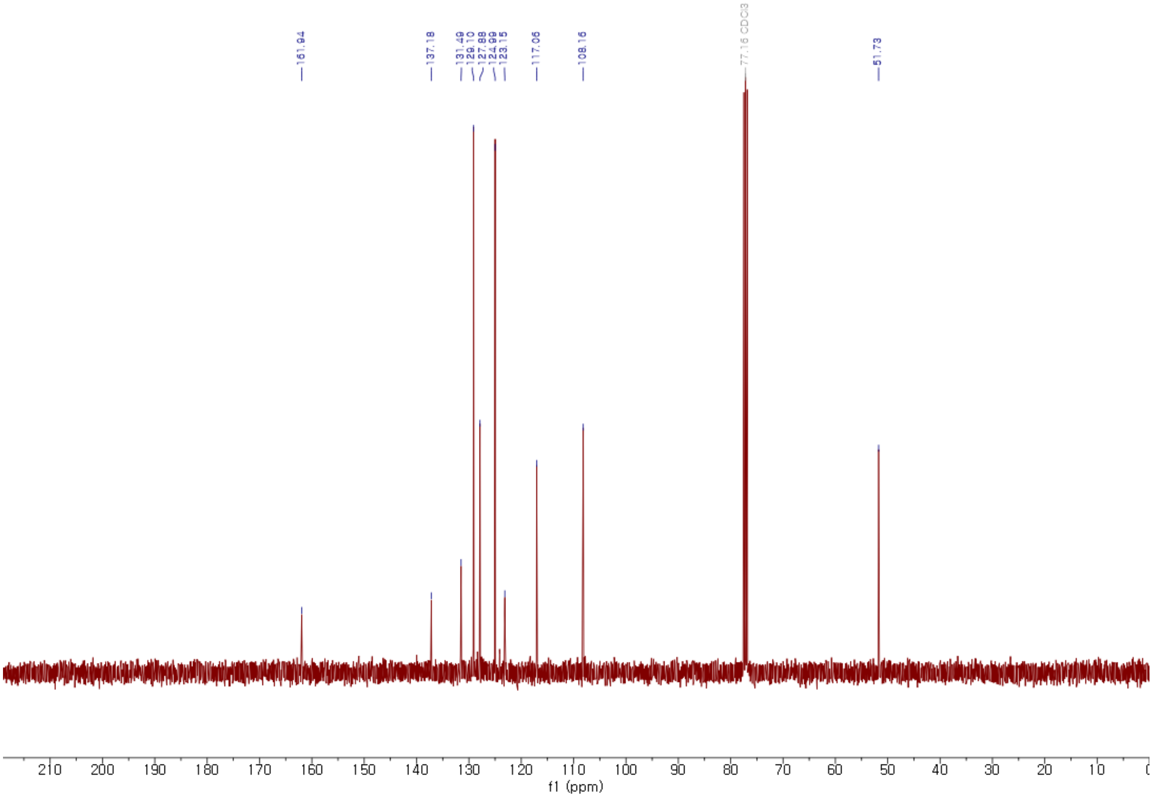
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **2b**



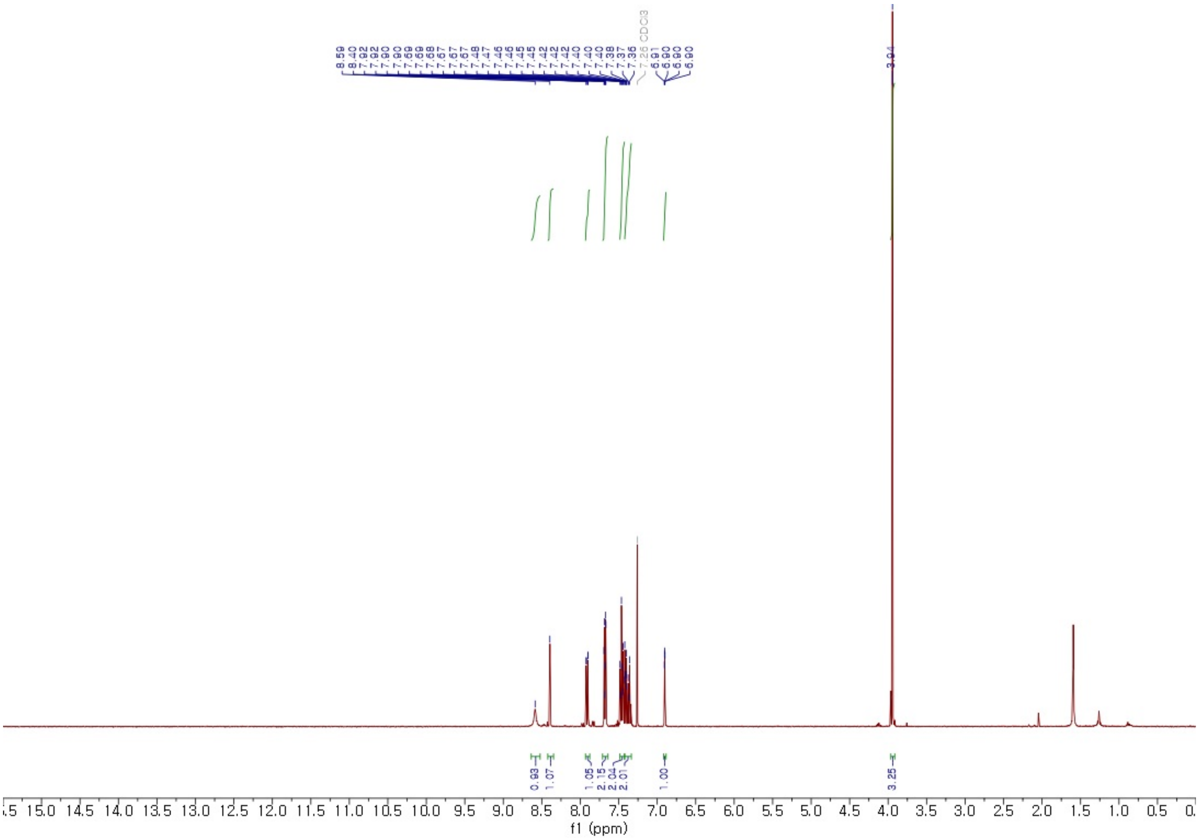
^{13}C{^{1}H} NMR spectrum (100 MHz, CDCl$_3$) of **2b**



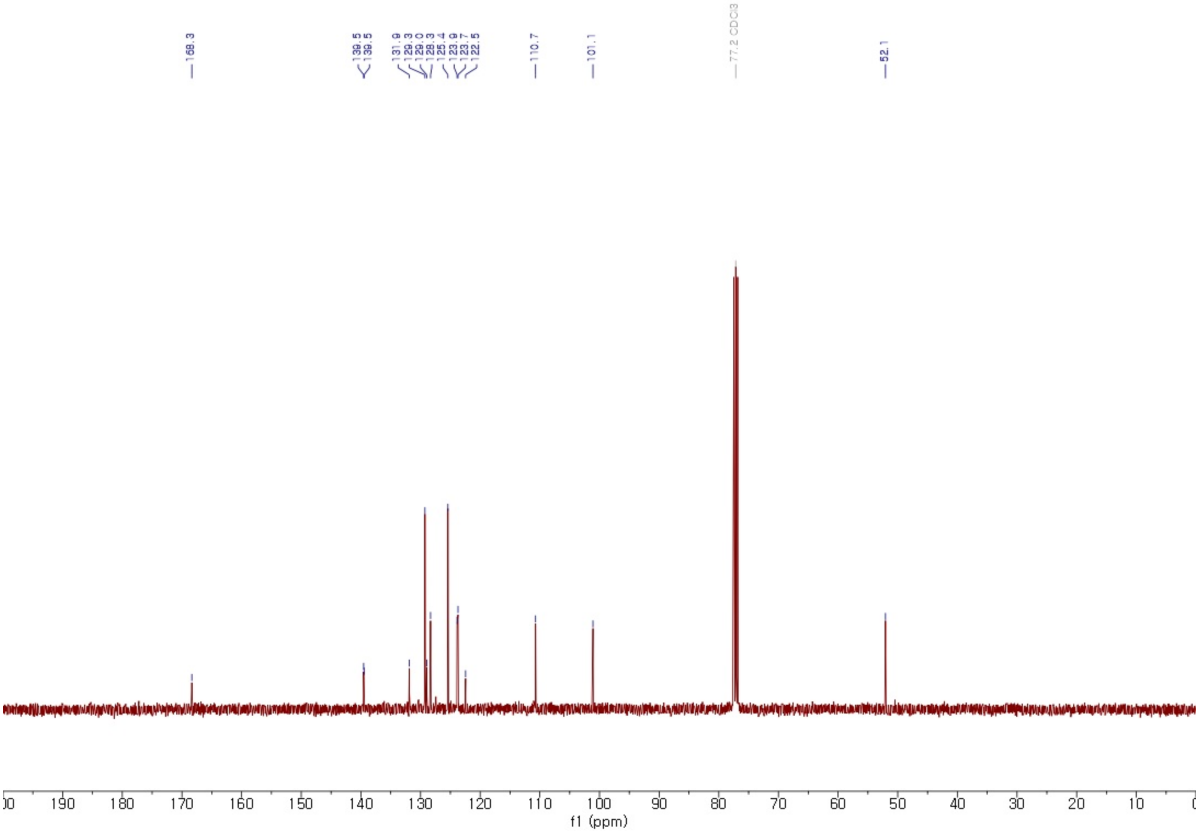
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **3b**



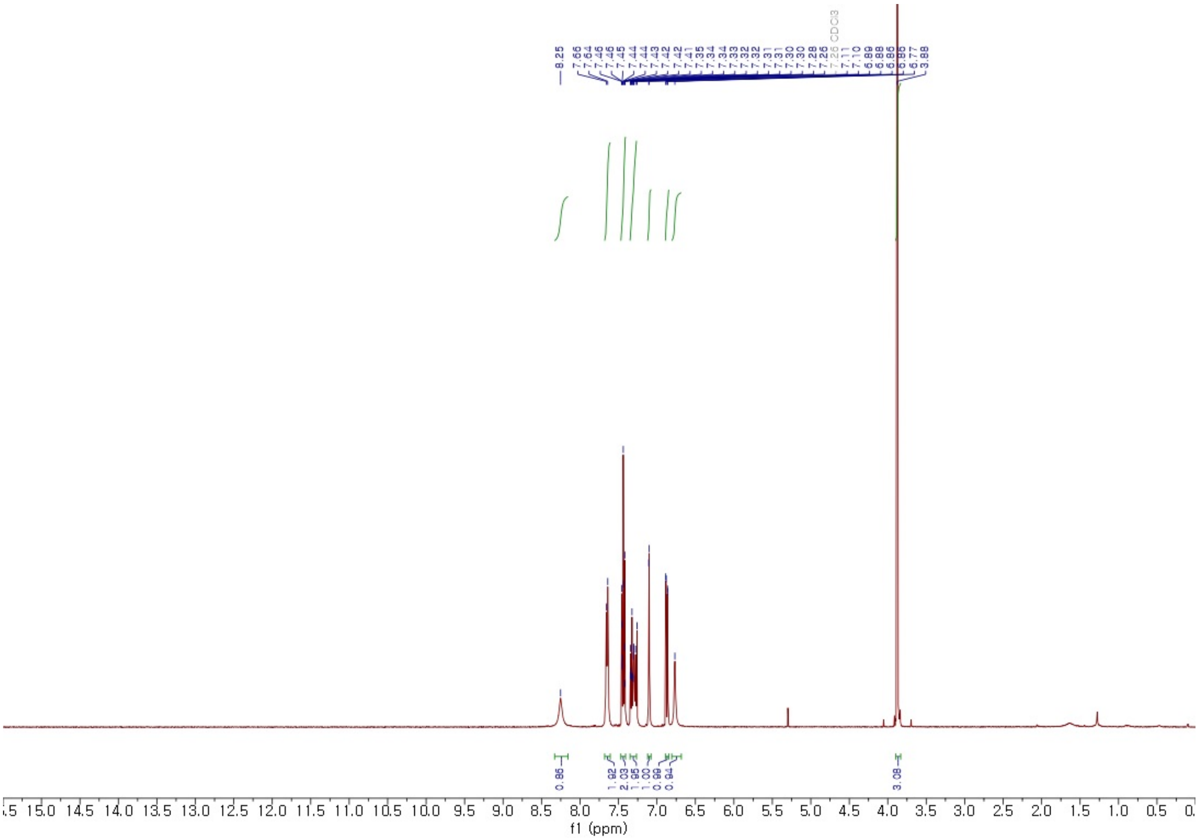
^{13}C{^{1}H} NMR spectrum (100 MHz, CDCl$_3$) of **3b**



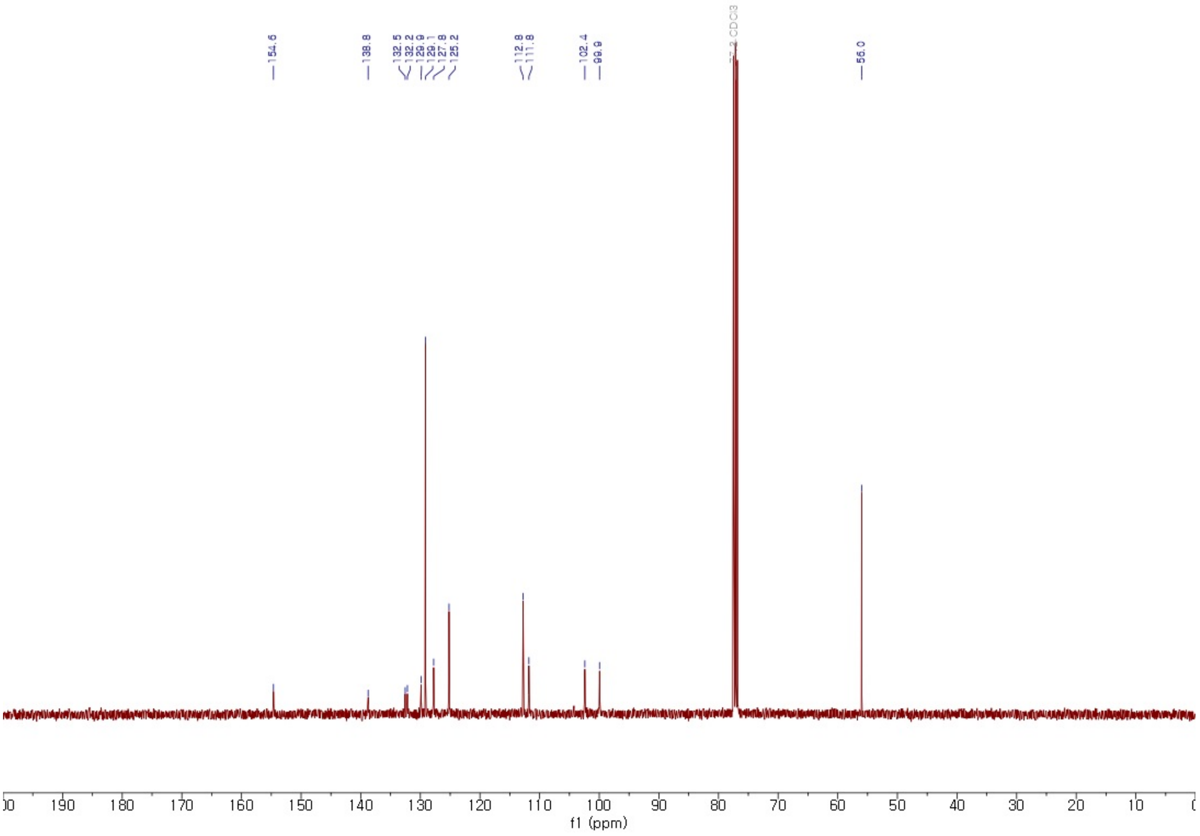
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **4b**



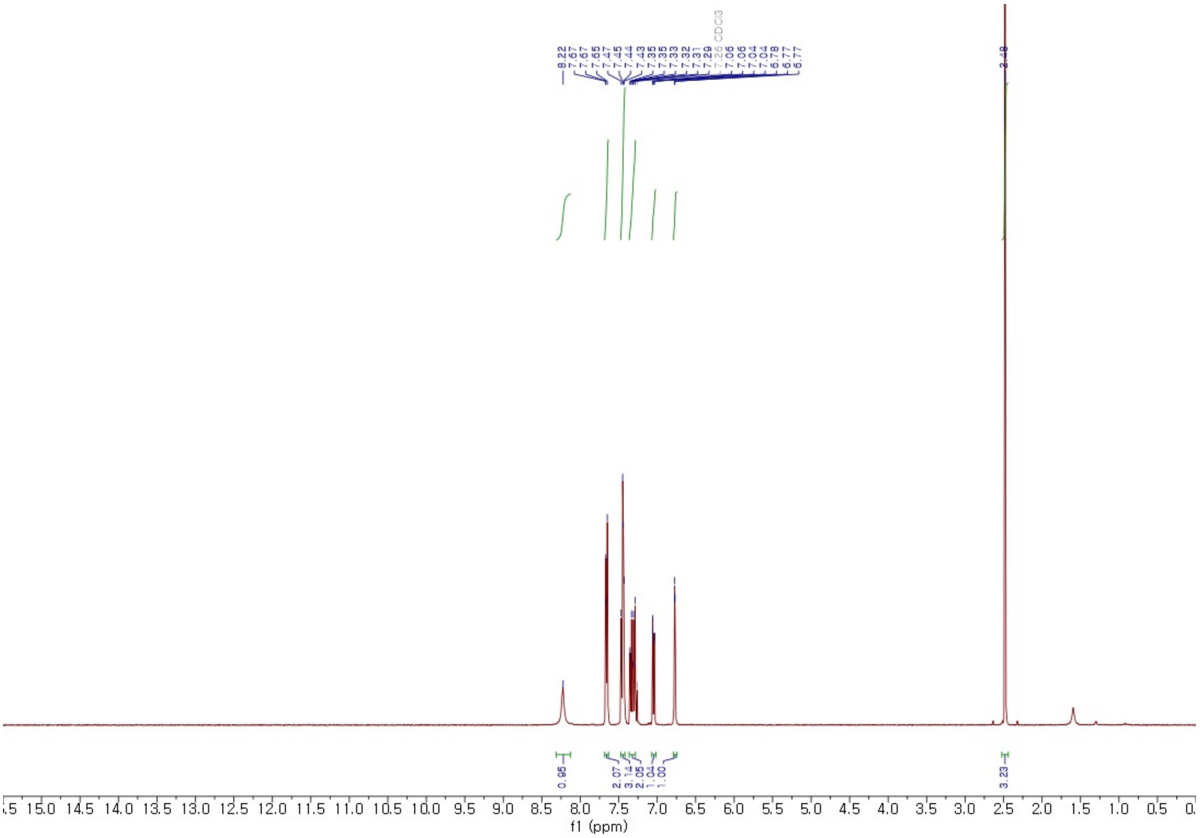
^{13}C{^{1}H} NMR spectrum (100 MHz, CDCl$_3$) of **4b**



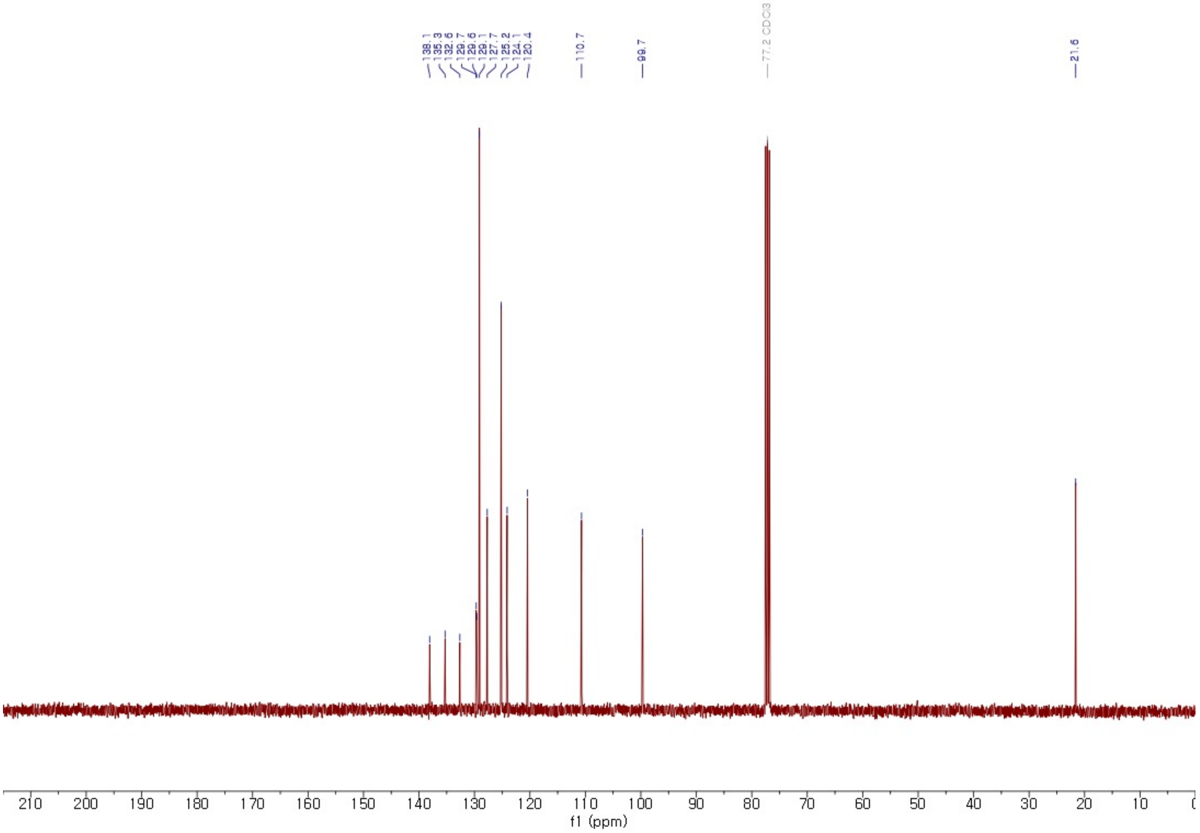
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **5b**



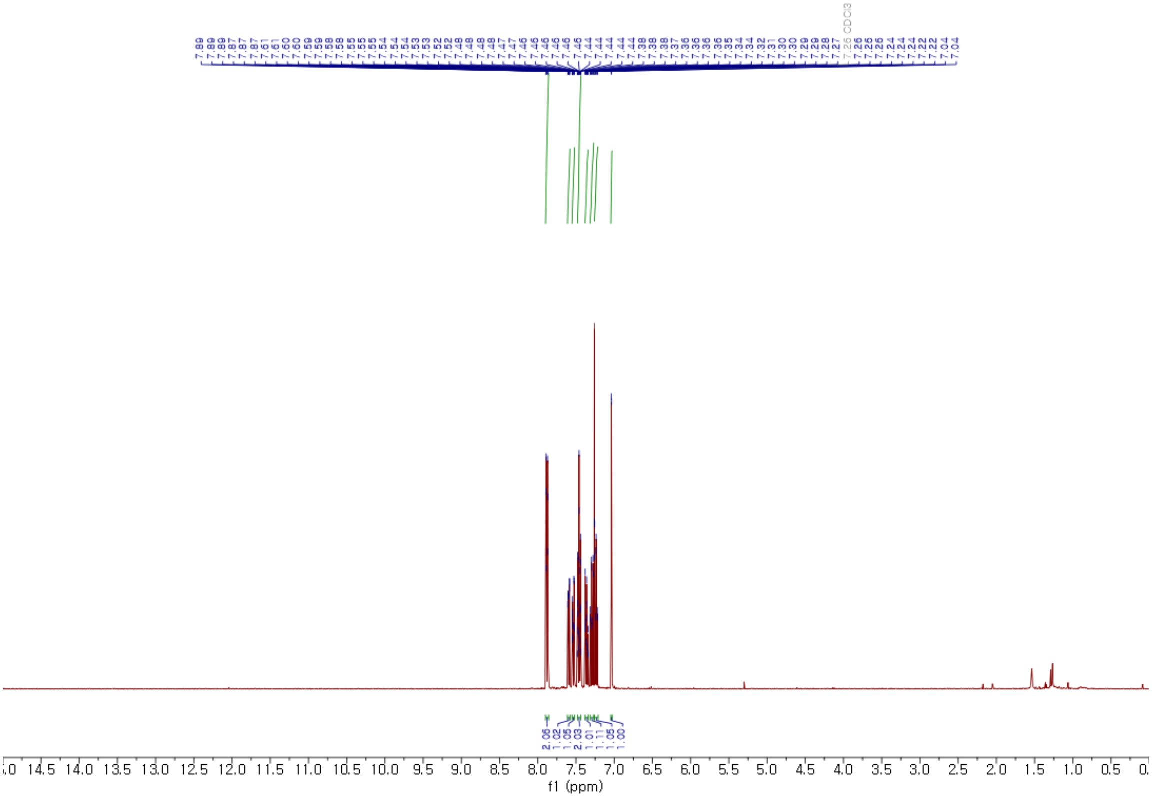
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **5b**



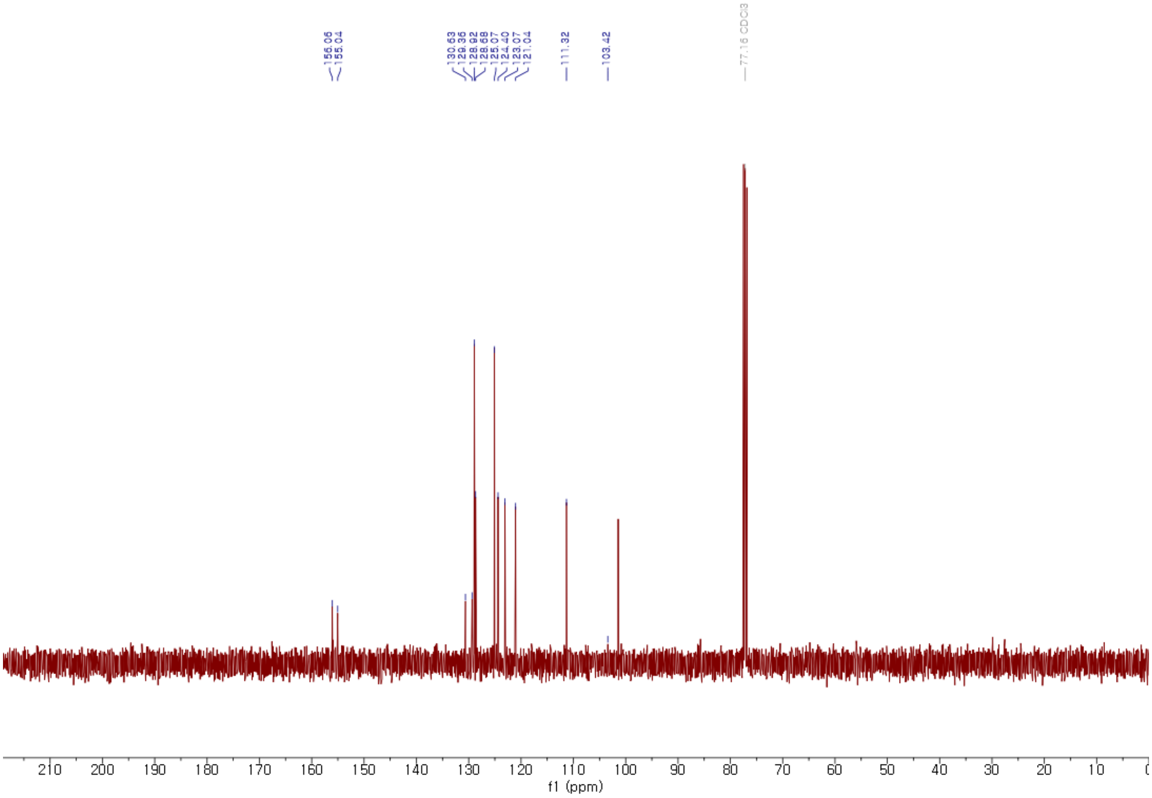
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **6b**



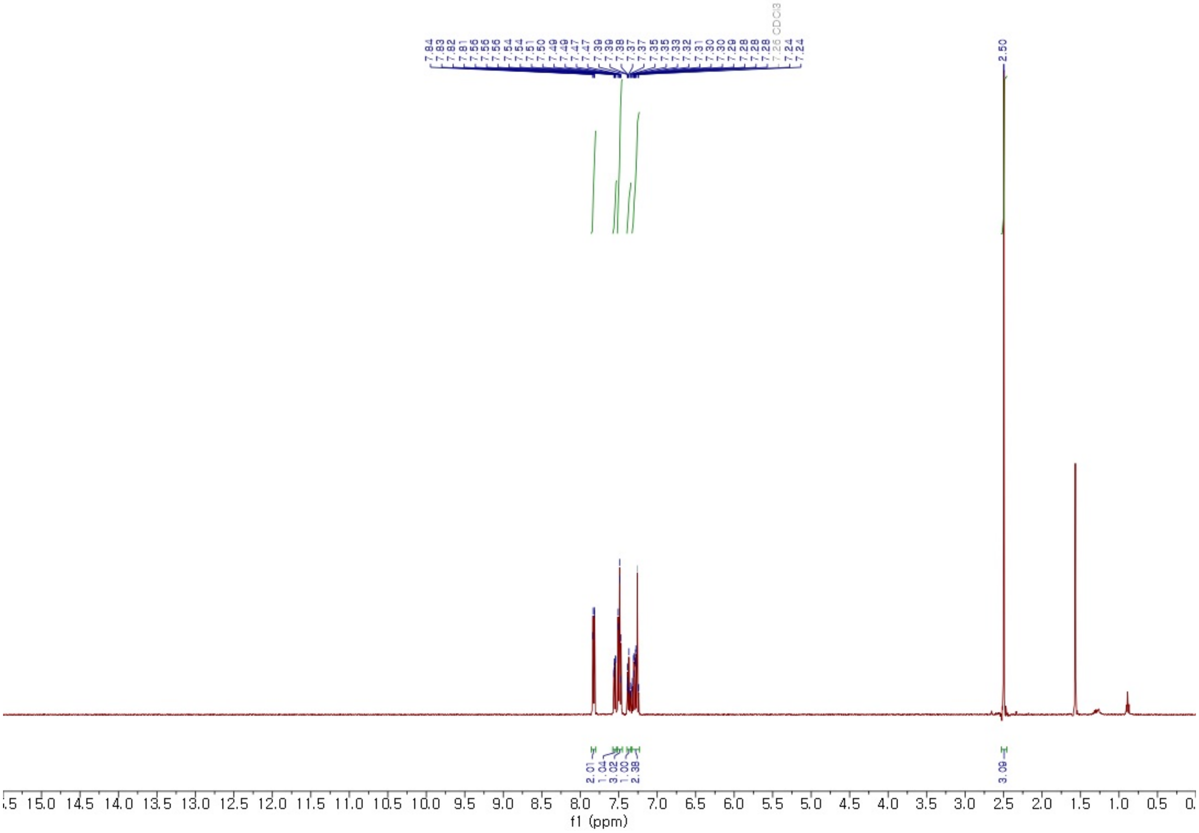
^{13}C{^{1}H} NMR spectrum (100 MHz, CDCl$_3$) of **6b**



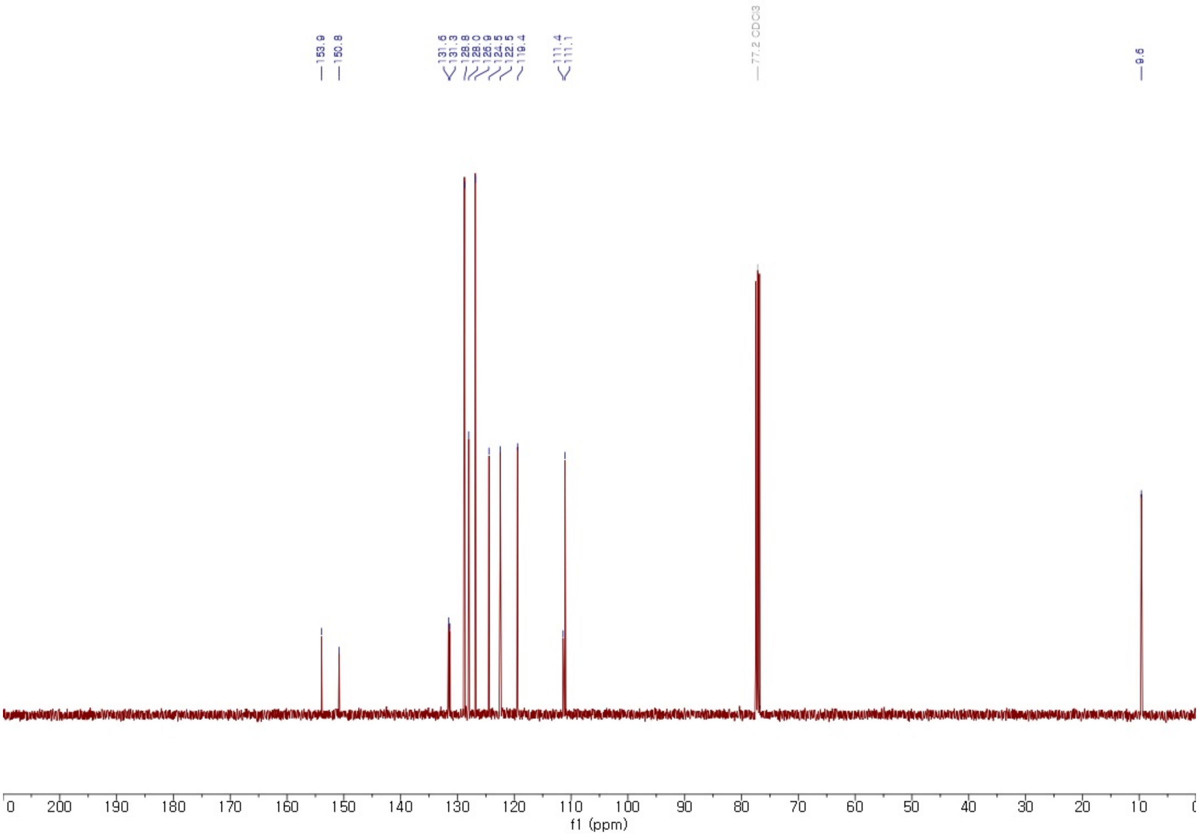
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **7b**



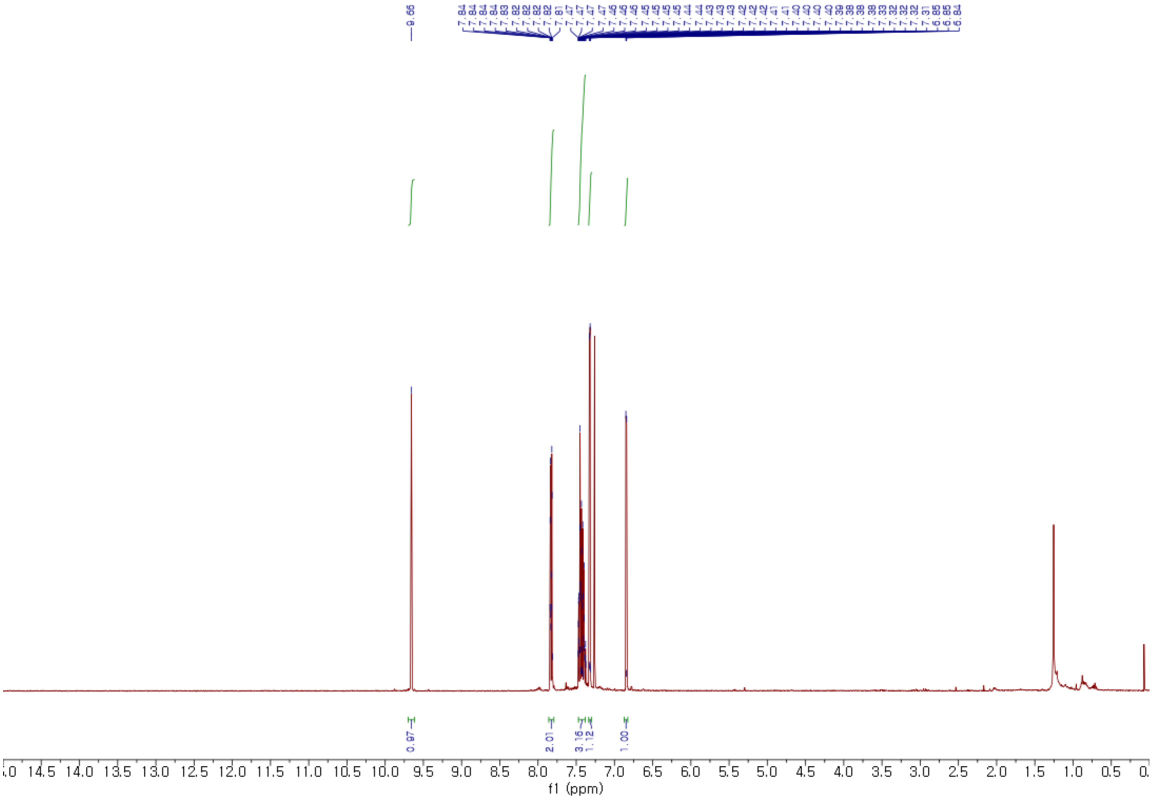
^{13}C{^{1}H} NMR spectrum (100 MHz, CDCl$_3$) of **7b**



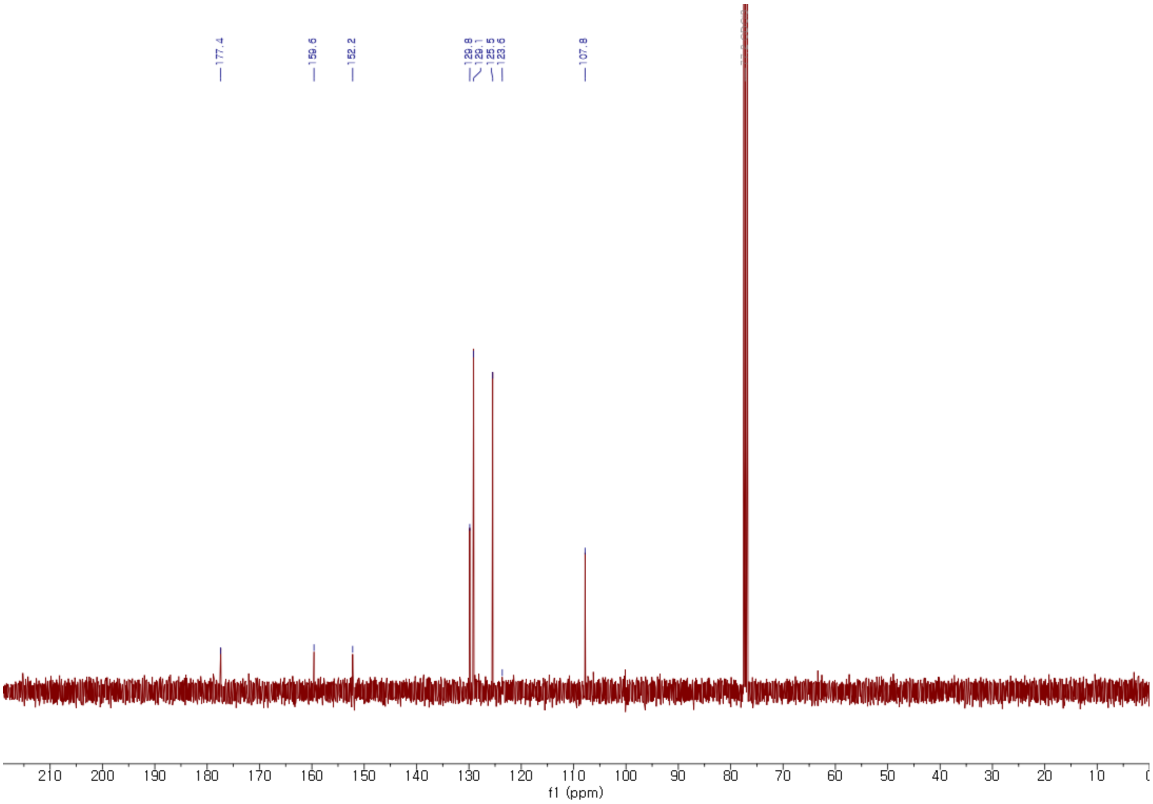
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **8b**



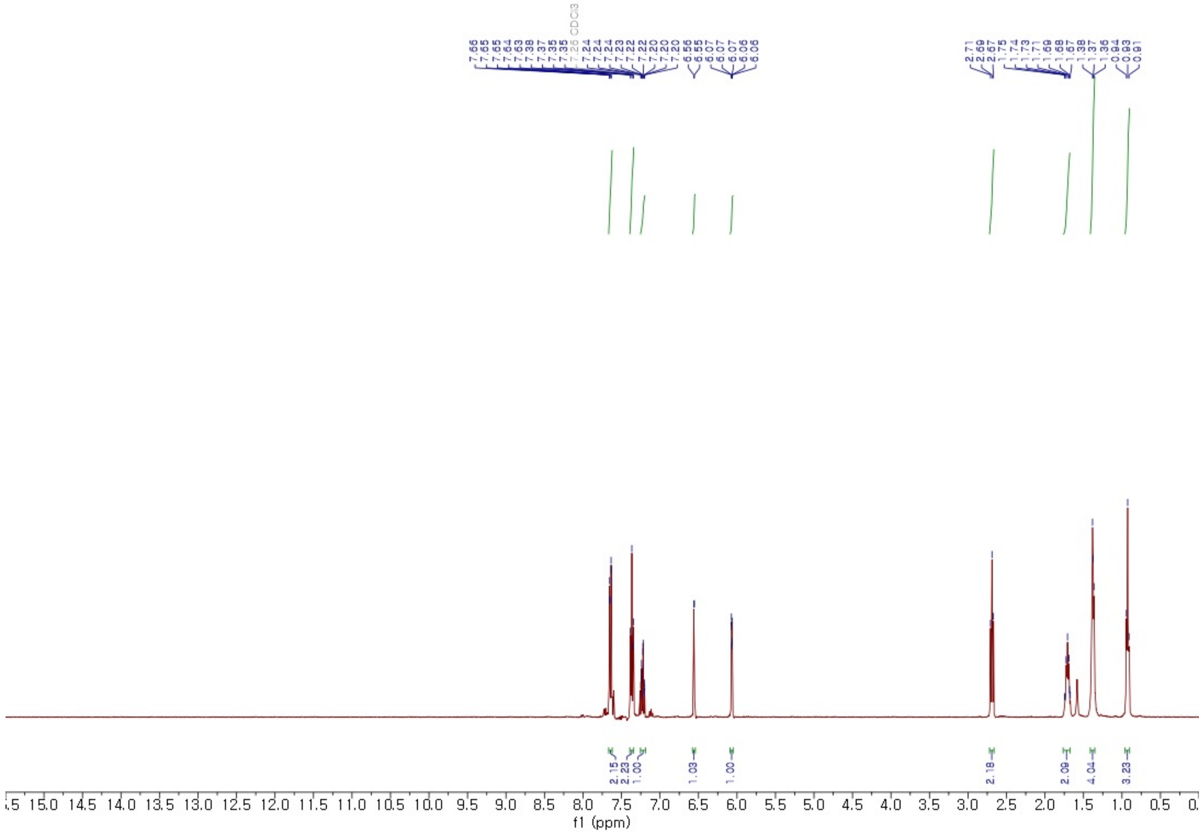
^{13}C{^{1}H} NMR spectrum (100 MHz, CDCl$_3$) of **8b**



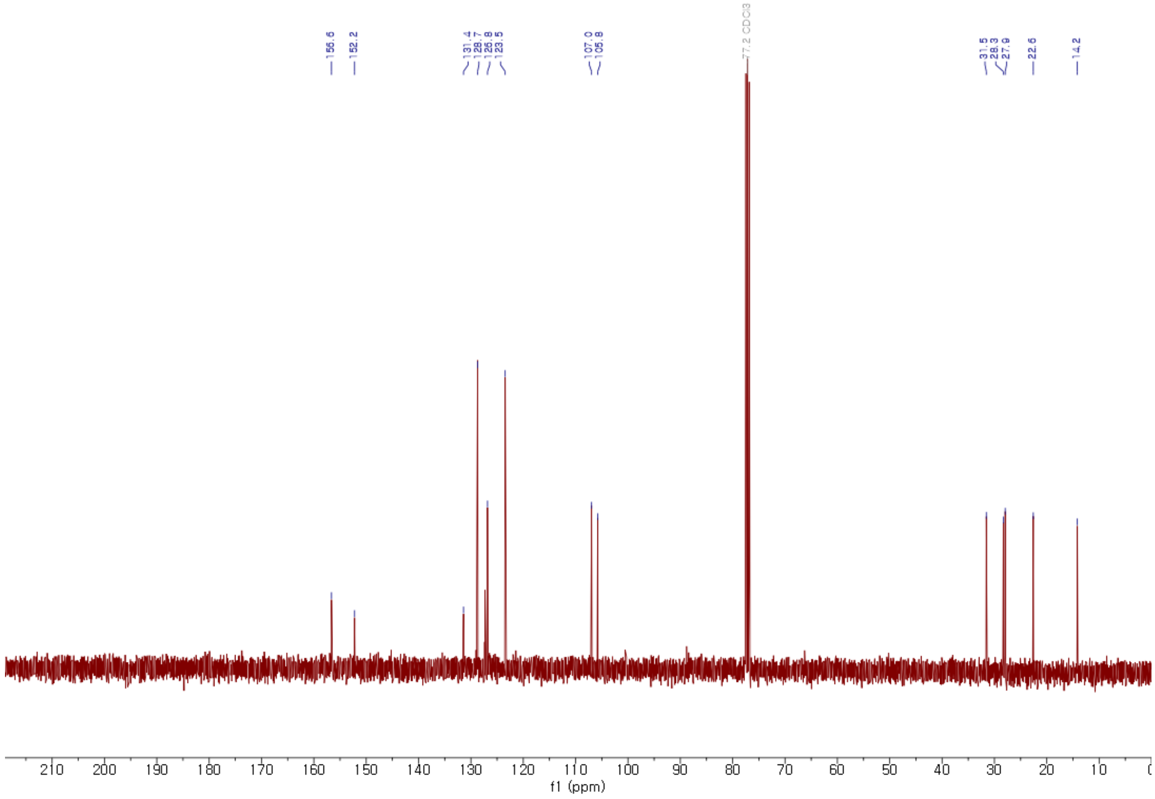
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **9b**



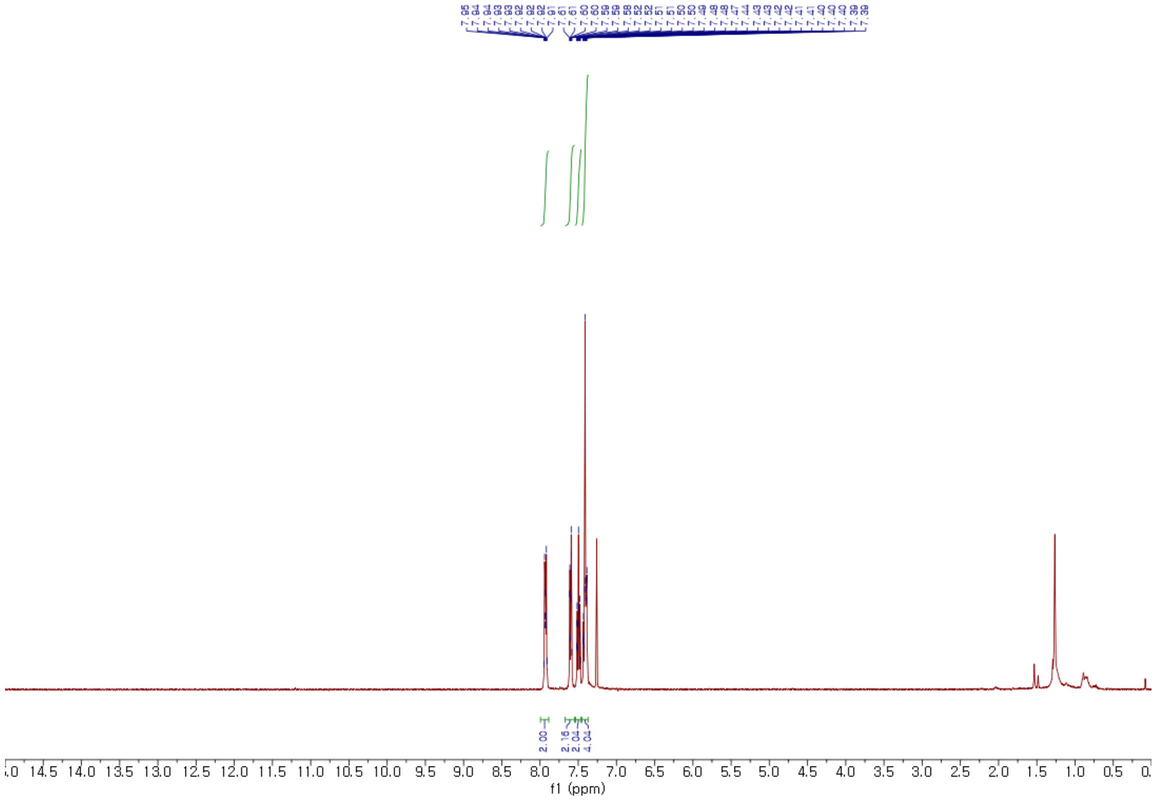
^{13}C{^{1}H} NMR spectrum (100 MHz, CDCl$_3$) of **9b**



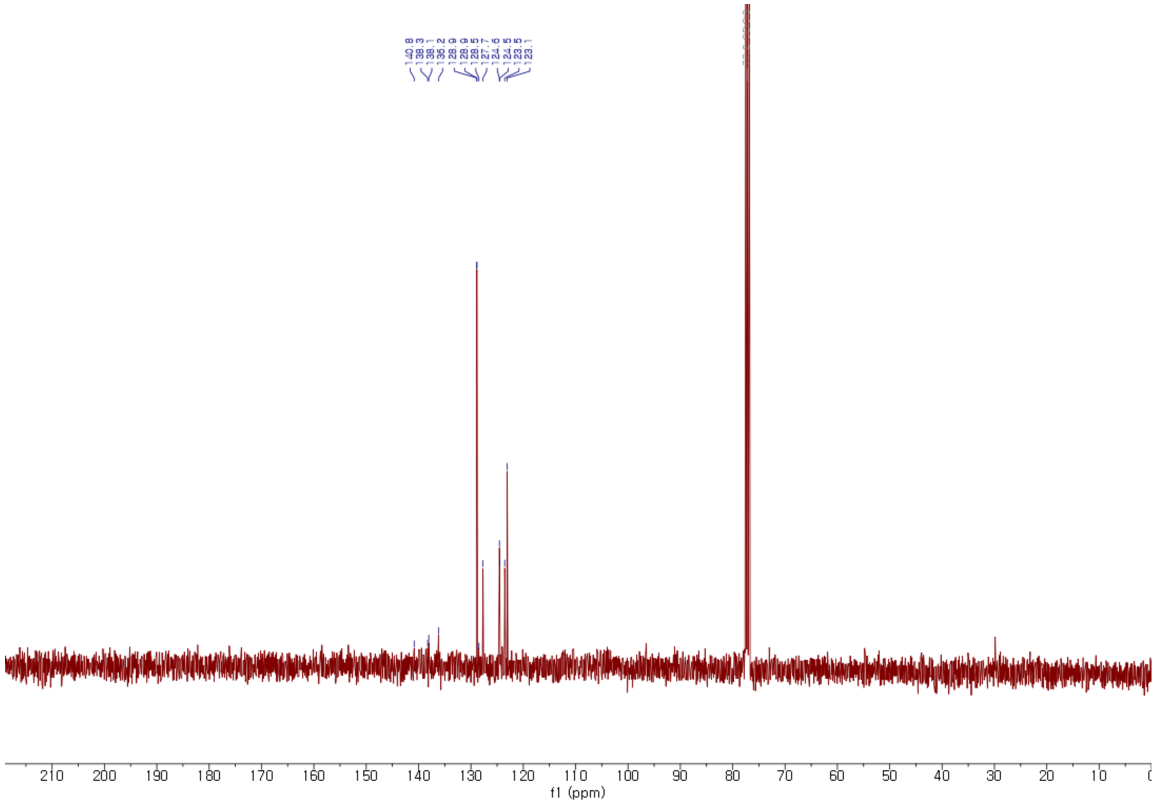
^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **10b**



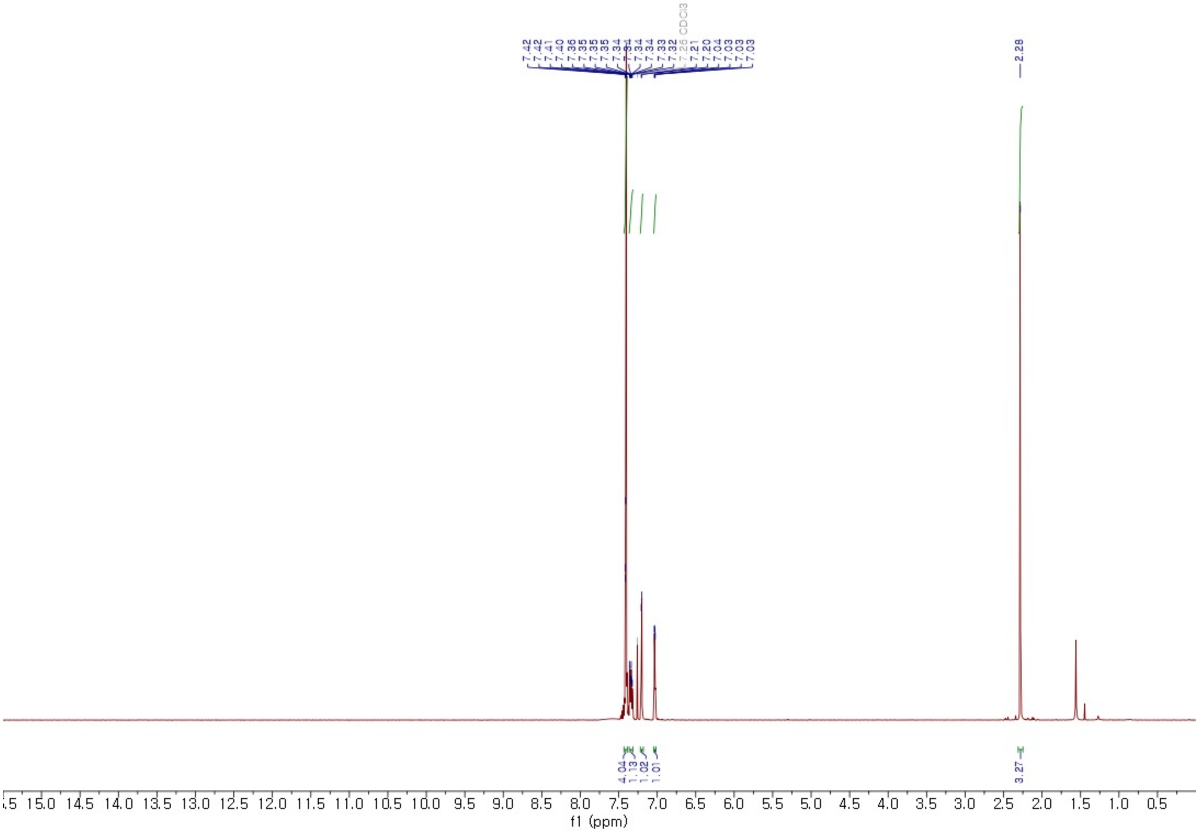
^{13}C{^{1}H} NMR spectrum (100 MHz, CDCl$_3$) of **10b**



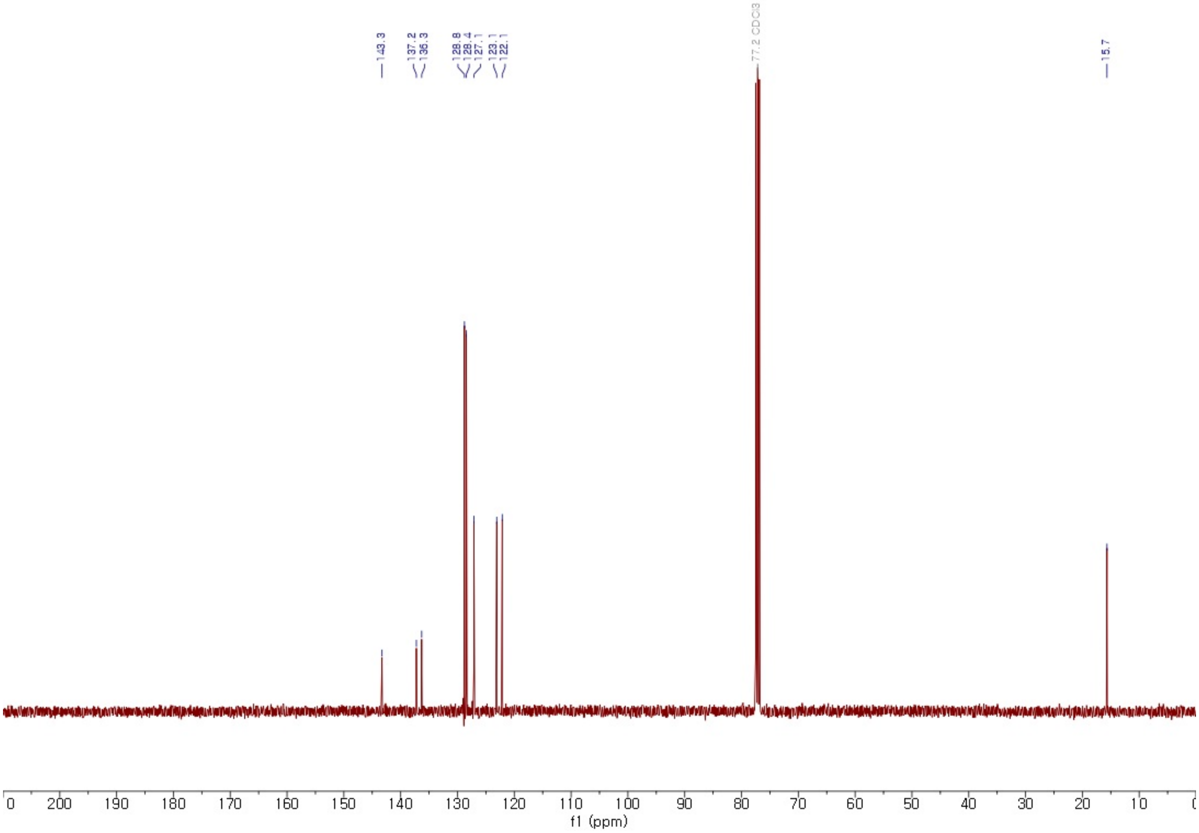
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of **11c**



^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of **11c**



^{1}H NMR spectrum (400 MHz, CDCl$_3$) of **12c**



^{13}C{^{1}H} NMR spectrum (100 MHz, CDCl$_3$) of **12c**