Supplementary Materials for

Palladium-Catalyzed Reactions in Water Using Pd-catalysts Covalently Tethered on Thermo-responsive Polymer

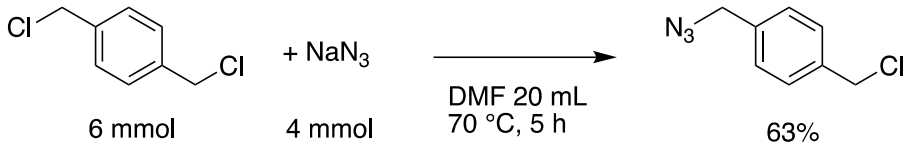
Noriyuki Suzuki[1,*], Nozomu Ebara[1], Rikito Arai[1], Chirika Takahashi[1], Tsai-Yu Hung[2], Yuko Takeoka[1], Masahiro Rikukawa[1], Yukie Yokota[1], Fu-Yu Tsai[2,*]

1. Materials and Methods

The preparation of RAFT agents and polymers were conducted under an argon atmosphere by using standard Schlenk techniques, unless otherwise mentioned. *N*-Isopropyl acrylamide (NIPAAm) was purchased from Kanto Chemical Co., Inc. and recrystallized from hexane/toluene prior to use. Bis(chloromethyl)benzene, (*tert*-butyldimethylsilyl)acetylene, sodium azide, potassium ethyl xanthogenate, 2-ethynyl pyridine, copper(I) bromide, *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA), tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA), sodium *p*-styrene sulfonate, bis(acetonitrile)dichloropalladium, dichloro(1,5-cyclooctadiene)palladium, tetrabutylammonium fluoride (1.0 M in tetrahydrofuran) were purchased from Tokyo Chemical Industry Co., Ltd. and used as received. 2,2'-Azobis(isobutyronitrile) (AIBN), dimethylacetamide (DMA) were purchased from Kanto Chemical Co., Inc. and used without further purification. 4,4'-Azobis(4-cyanovaleric acid) (V-501) was purchased from FUJIFILM Wako Pure Chemical Corporation. 1-Bromo-4-iodobenzene was purchased from Sigma-Aldrich Co. LLC. and used without further purification. The diblock copolymer **NS** was prepared as previously reported.[1-8] Dialysis was performed using Spectra/Por® RC tubing (MWCO: 1.0 kD, 3.5kD). Deionized water was obtained on WE-200 (Yamato Scientific Co., Ltd.). NMR spectra were recorded on JEOL ECA 500 and Bruker Avance III HD400 spectrometers. Gel permeation chromatography (GPC) was measured on PU-4580 and RI-4030 system (JASCO Corporation) equipped with Shodex GPC KD-802 and KD-803 columns (Showa Denko K.K.) using *N,N*-dimethylformamide (DMF) (0.1 wt% LiBr) as eluent; the molecular weight of the polymers was determined based on monodispersed poly(ethylene oxide) as standard, and ^{1}H NMR spectroscopy as well. Scanning transmission electron microscopy (STEM) was recorded on HITACHI Cs-corrected STEM HD-2700 with accelerating voltage of 200 kV, EDX on AMETEK EDAX Octane T Ultra W with 100 mm^2 SDD (Hitachi High-Tech Corporation) measured by CLEARIZE Co. Ltd. and JEM-ARM200F Thermal FE (STEM SDD) at The University of Tokyo.

2. Preparative methods for the compounds

2-1. 1-(Azidomethyl)-4-(chloromethyl)benzene [9]

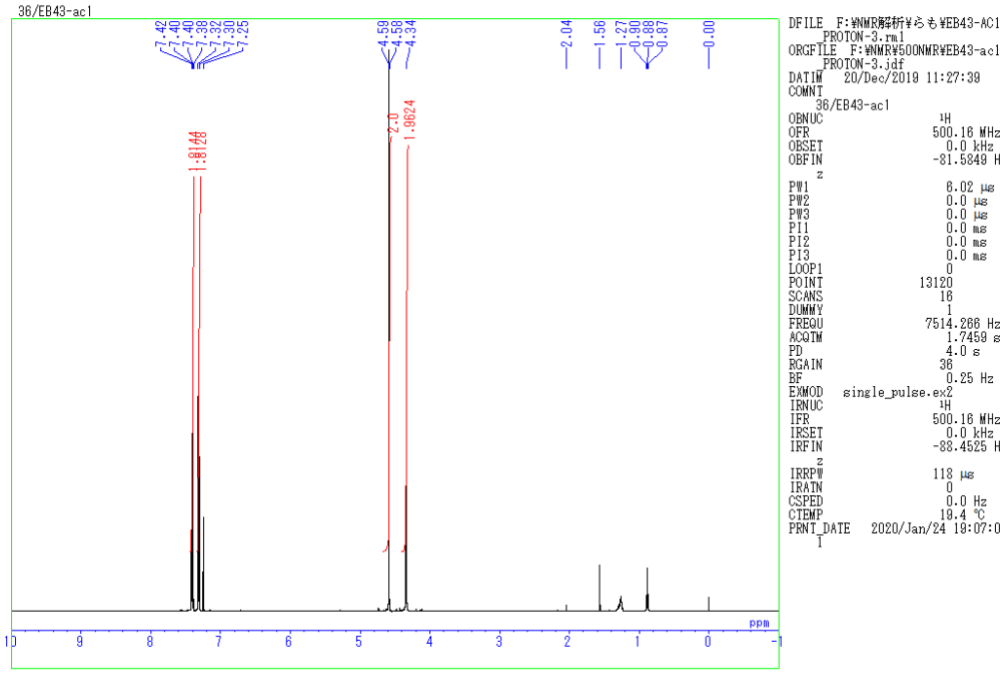


In a thoroughly dried Schlenk tube filled with argon, sodium azide (260 mg, 4.0 mmol), 1,4-bis(chloromethyl)benzene (1.05 g, 6.0 mmol) was dissolved in DMF (20 mL), and the mixture was stirred at 70 °C for 5 h. The mixture was filtered through Celite^{TM} and the volatile was removed in vacuo from the filtrate, and the residue was extracted dissolved in diethyl ether. The solution was washed with water and the organic layer was dried over magnesium sulfate. The desiccant was filtered off, and the filtrate was concentrated. The residue was purified by column chromatography on silica gel (chloroform/hexane = 1/9) to afford the title compound as colorless oil (460 mg, 63%).

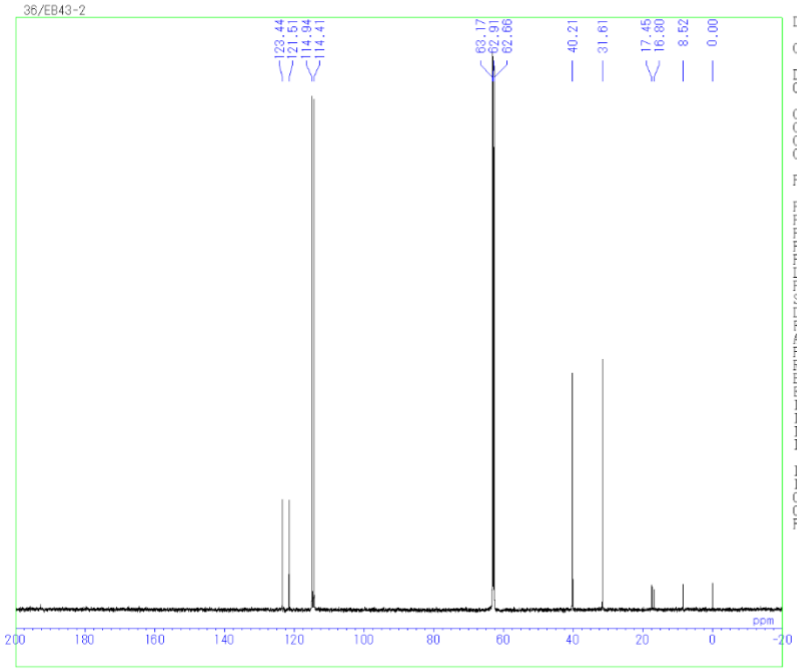
^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ = 4.34 (s, 2H, CH_2), 4.59 (s, 2H, CH_2), 7.31 (d, J = 10 Hz, 2H), 7.41 (d, J = 10 Hz, 2H).

^{13}C{^{1}H} NMR ($CDCl_3$, Me_4Si, 125 MHz): δ = 31.6, 40.2 (CH_2), 114.4, 114.9, 121.5 (q), 123.5 (q).

^{1}H NMR



$^{13}C\{^{1}H\}$ NMR

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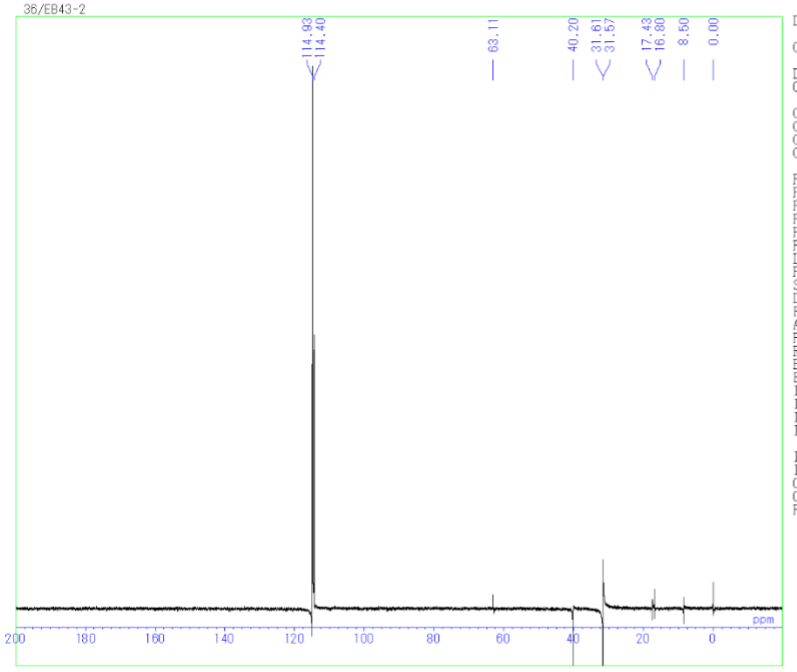


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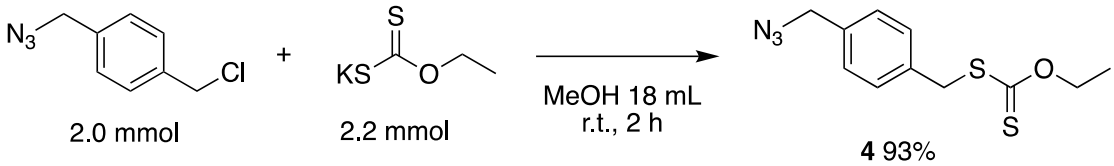
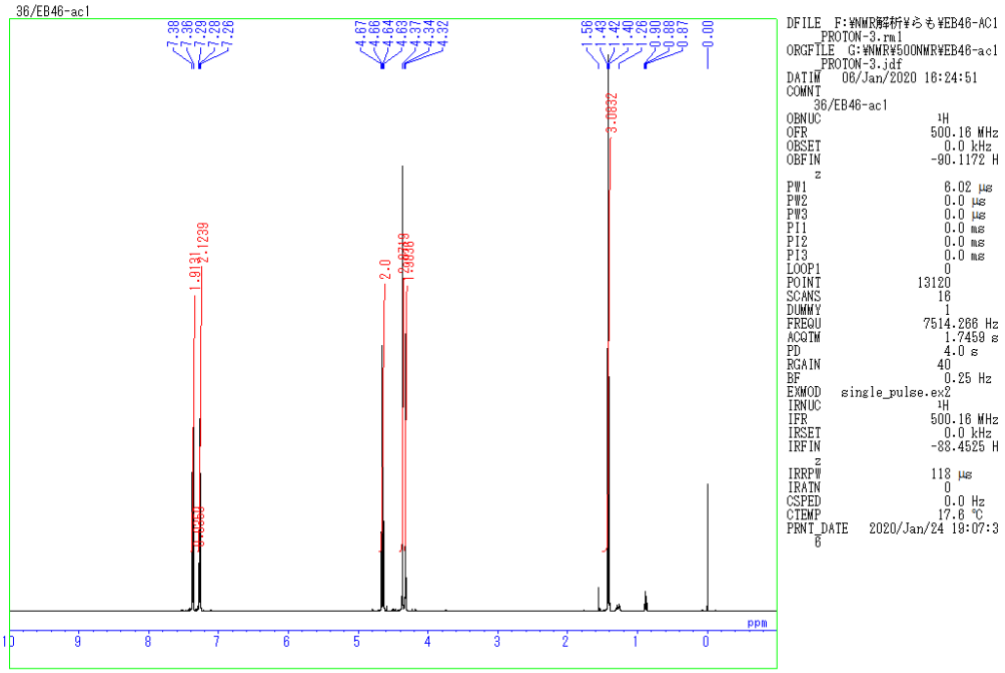
2-2. *S*-(4-(Azidomethyl)benzyl) *O*-ethyl carbonodithioate (**4**). [10]

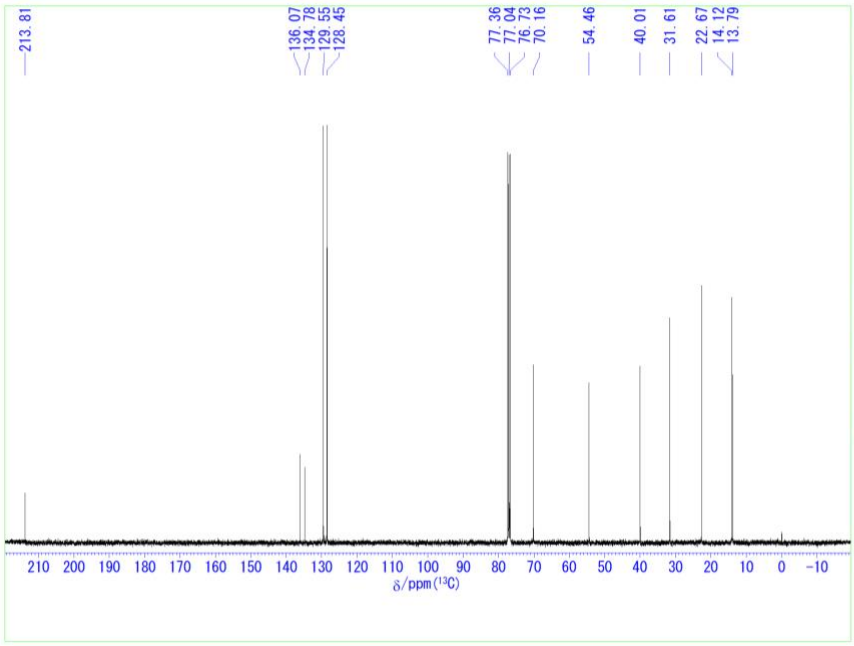


A 100 mL Schlenk tube was dried and filled with argon. In this tube, 1-(azidomethyl)-4-(chloromethyl)benzene (0.361 g, 2.0 mmol) in MeOH (9 mL) and potassium ethyl xanthogenate (0.358 g, 2.2 mmol) in MeOH (9 mL) were added and the mixture was stirred at r.t. for 2 h. To the reaction mixture was added water and extracted with diethyl ether (50 mL × 3). The organic layer was washed twice with water and dried over magnesium sulfate. The desiccant was filtered off and the volatile was removed in vacuo from the filtrate. The residue was purified with column chromatograph on silica gel ($CHCl_3$/hexane = 1/3) to give **4** as colorless oil (0.499 g, 93%).
^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ = 1.42 (t, *J* = 7 Hz, 3H, C*H*$_3$), 4.32 (s, 2H, C*H*$_2$), 4.37 (s, 2H, C*H*$_2$), 4.65 (qt, *J* = 7 Hz, 2H, OC*H*$_2$), 7.27 (d, *J* = 10 Hz, 2H), 7.37 (d, *J* = 10 Hz, 2H).
^{13}C{^{1}H} NMR ($CDCl_3$, Me_4Si, 100 MHz): δ = 13.8 (*C*H$_3$), 40.0, 54.5, 70.2 (*C*H$_2$), 128.5, 129.6, (*C*H), 134.9 (q), 136.1 (q), 213.8 (q).

^{1}H NMR



$^{13}C\{^{1}H\}$ NMR



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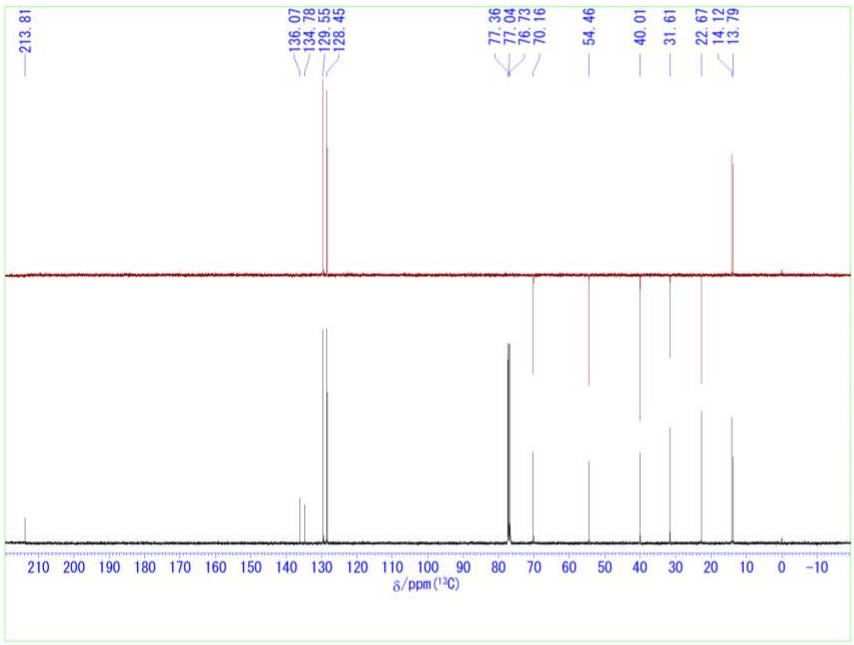

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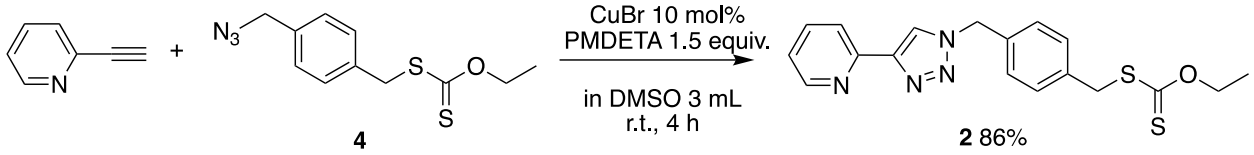
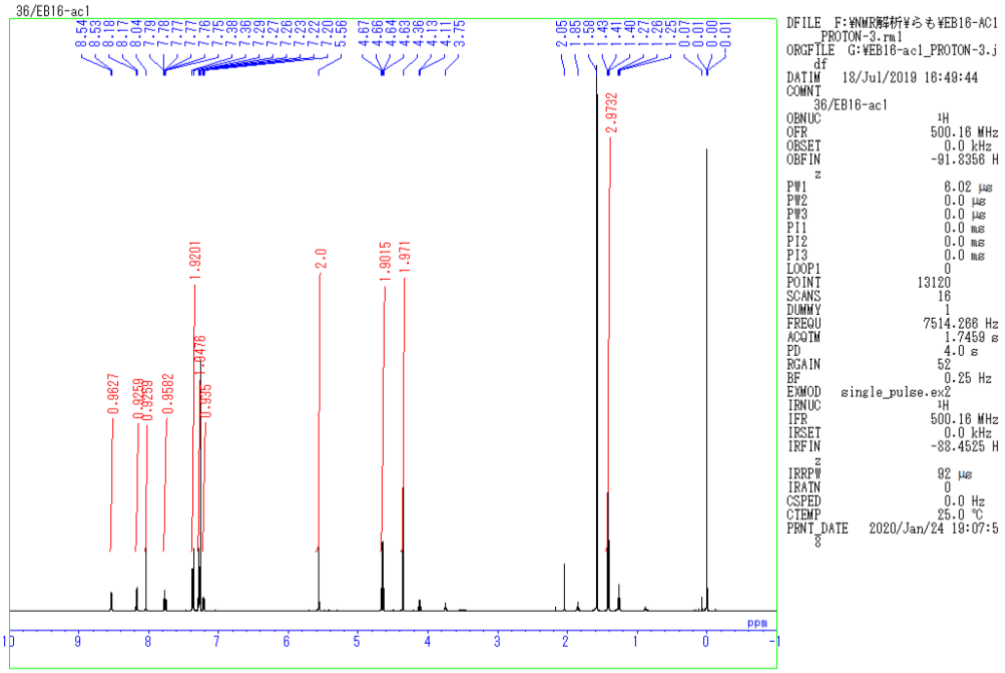
2-3. Preparation of the RAFT agent bearing *N*,*N*-ligand **2**.



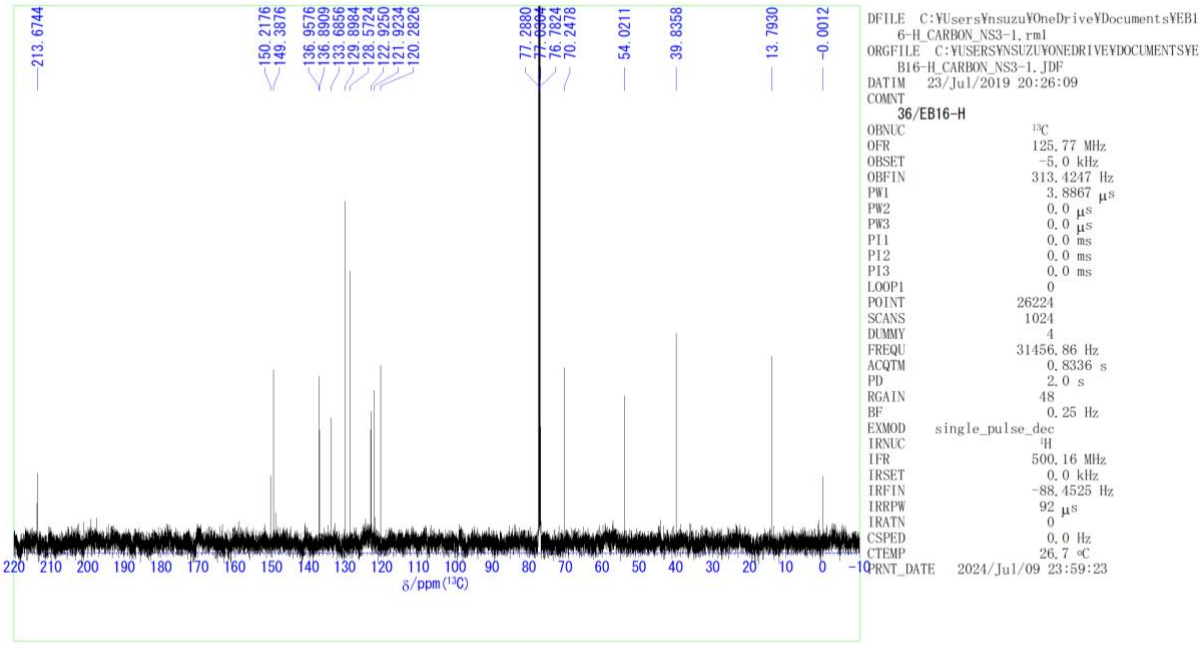
A Schlenk tube was dried, and the azide **4** (381 mg, 1.43 mmol), 2-ethynyl pyridine (147 mg, 1.43 mmol), copper(I) bromide (21 mg, 0.143 mmol), PMDETA (372 mg, 2.15 mmol) were dissolved in DMSO (5.8 mL), and the solution was stirred at r.t. for 4 h. The reaction mixture was extracted twice with ethyl acetate and water, and the organic layer was dried over magnesium sulfate. The desiccant was filtered off, and the filtrate was concentrated in vacuo to leave reddish solid. The residual solid was purified by column chromatograph on silica gel (chloroform/hexane = 1/1) to afford the title compound as light-yellow solid (458 mg, 86%).

^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ = 1.41 (t, *J* = 7 Hz, 3H, C*H*$_3$), 4.36 (s, 2H, SC*H*$_2$), 4.65 (qt, *J* = 7 Hz, 2H, OC*H*$_2$), 5.56 (s, 2H, NC*H*$_2$), 7.20–7.23 (m, 1H), 7.28 (d, *J* = 8 Hz, 2H), 7.37 (d, *J* = 8 Hz, 2H), 7.77 (td, *J* = 8, 1 Hz, 1H), 8.04 (s, 1H), 8.17 (d, *J* = 8 Hz, 1H), 8.54 (d, *J* = 5 Hz, 1H).
^{13}C{^{1}H} NMR ($CDCl_3$, Me_4Si, 125.8 MHz): δ = 13.8 (CH_3), 39.8, 54.0, 70.2 (CH_2), 120.3, 121.9, 122.9, 128.6, 129.9, 133.7 (q), 136.9 (q), 137.0, 149.4, 150.2 (q), 213.7 (q).
High resolution MS (ESI): calcd. for $C_{18}H_{18}N_4OS_2$ (M + Na) = 393.0820, found = 393.0809.

^{1}H NMR



$^{13}C\{^{1}H\}$ NMR



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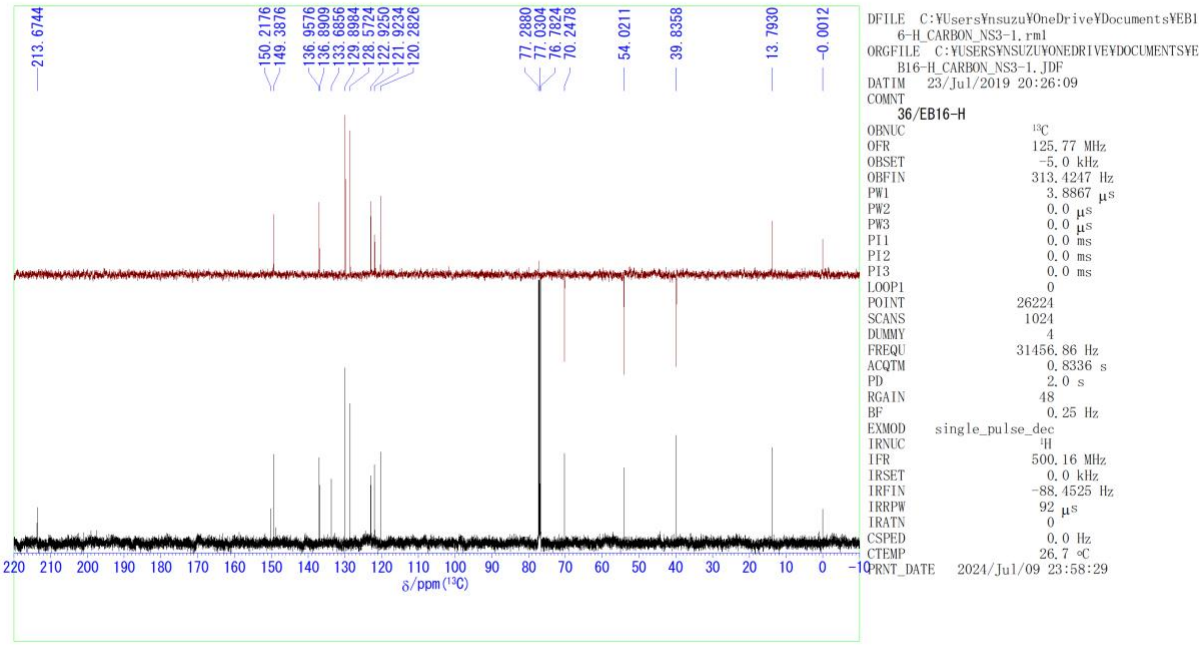
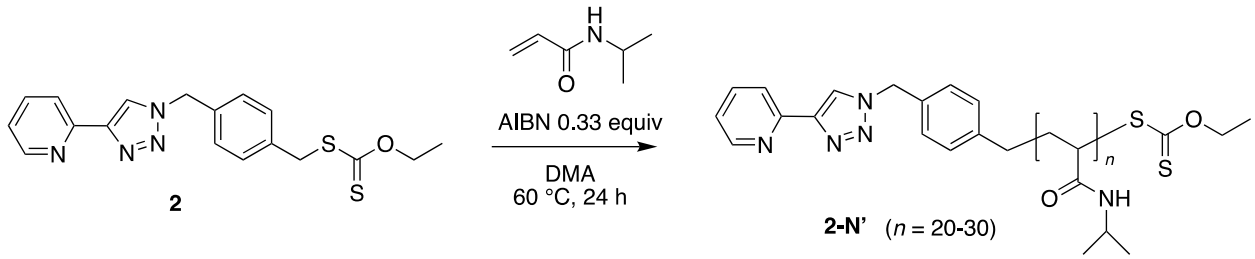


2-4. Preparation of the homopolymer PNIPAAm bearing pyridyl triazole end **2-N'**

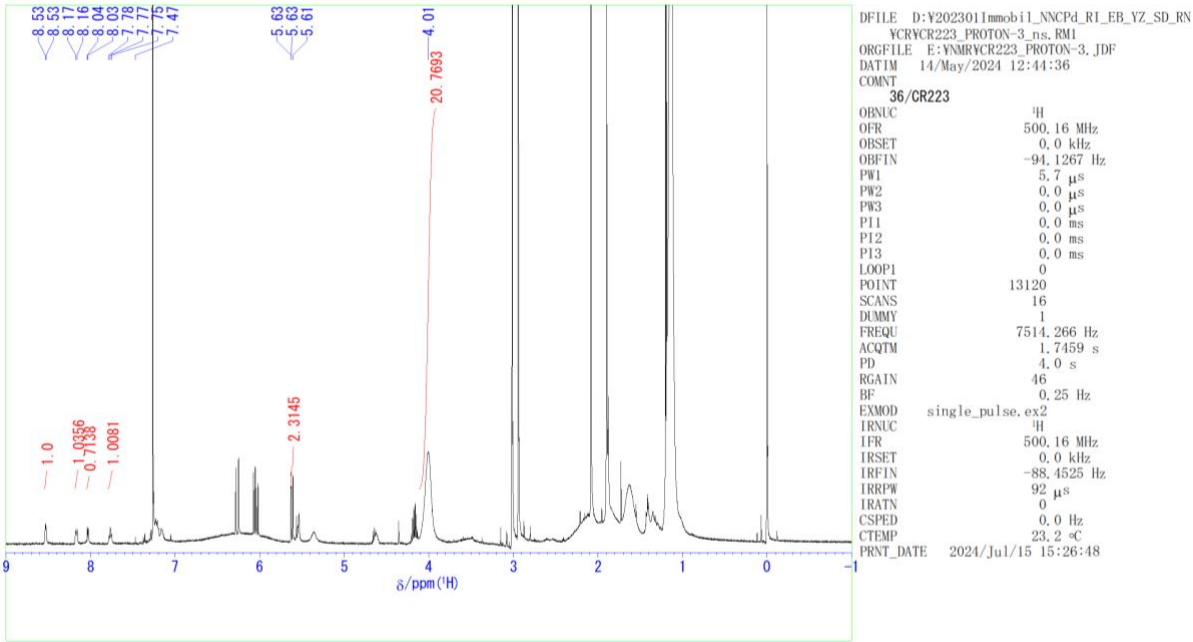


2 **2-N'** (*n* = 20-30)

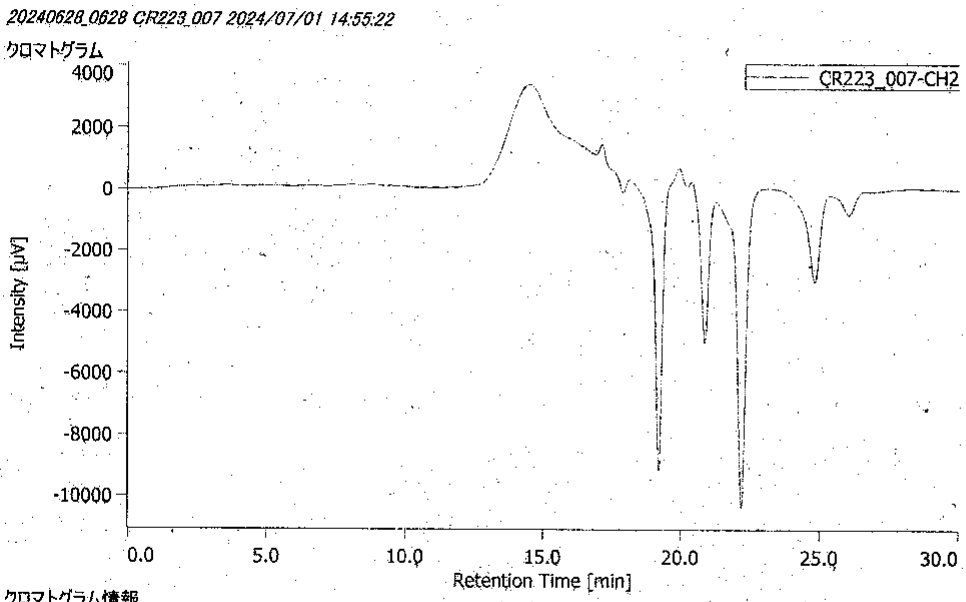
Typical procedure for polymerization of *N*-isopropylacrylamide (NIPAAm) using **2** as a RAFT agent is as follows. A thoroughly dried Schlenk tube (25 mL) was filled with argon. In this vessel, RAFT agent **2** (100 mg, 0.270 mmol), NIPAAm (0.611 g, 5.4 mmol), 2,2'-azobis(isobutyronitrile) (AIBN) (15 mg, 0.09 mmol) were dissolved in dimethylacetamide (DMA) (5 mL) and degassed in three freeze-pump-thaw cycles. The solution was stirred at 60 °C for 24 h, and the mixture was poured into hexane/diethyl ether (300/100 mL). Yellow precipitate was dried in vacuo to afford the title compound as pale yellow solid (752 mg, quant.). The polymer was characterized by ^{1}H NMR spectroscopy to determine polymerization degree (PD = 21, M_n = 2,745). GPC M_n = 2,578, M_w = 2,948, M_w/M_n = 1.14 (based on PEG standard).

^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ = 4.01 (br, N*H*), 5.63 (s, 2H, NCH_2Ar), 7.77 (s, 1H), 8.03 (s, 1H), 8.16 (s, 1H), 8.53 (s, 1H).

^{1}H NMR



GPC chromatogram of **2-N'** (n = 21).



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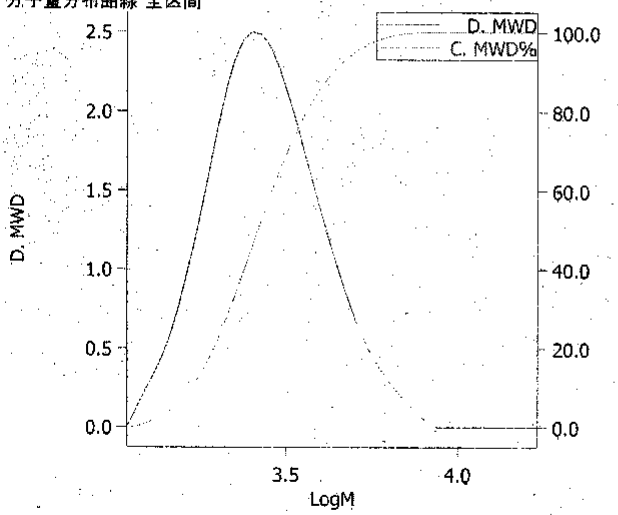

分子量計算結果

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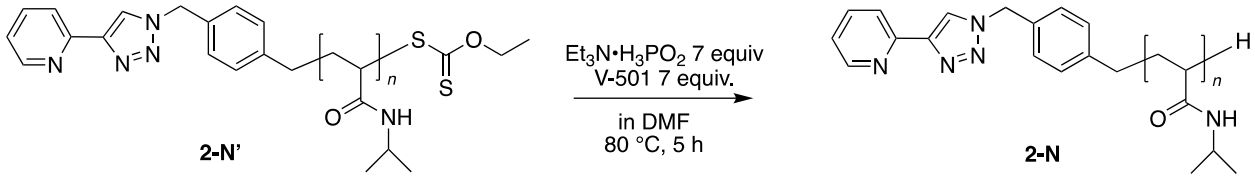
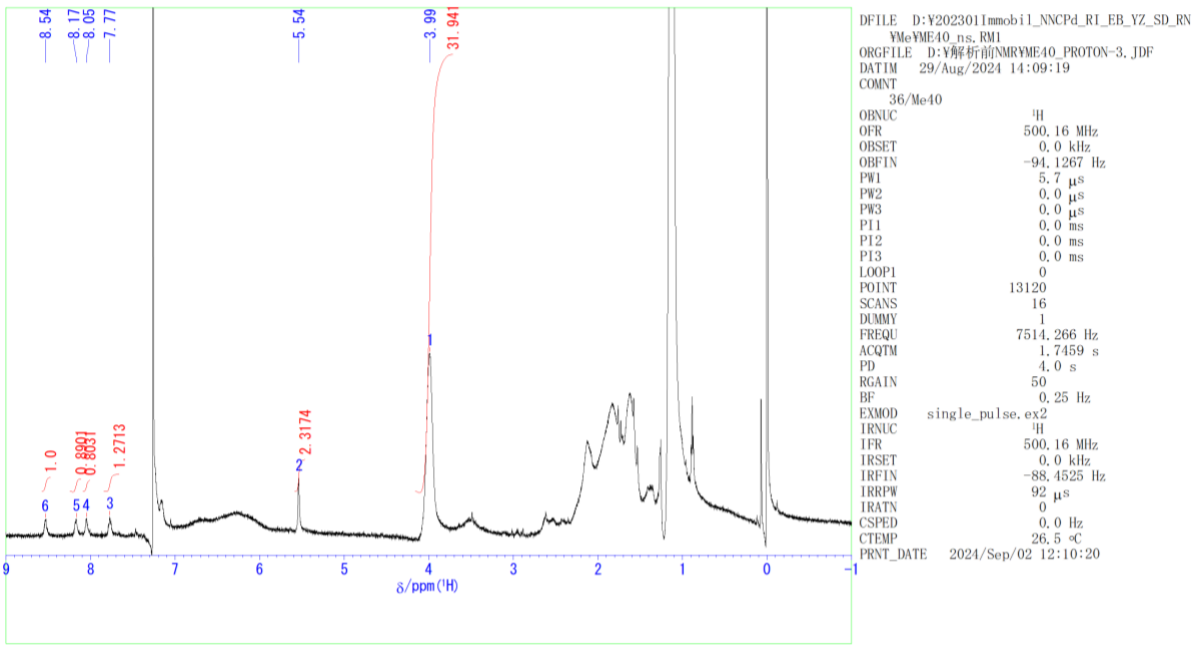
2-5. Preparation of **2-N**: Removal of the xanthogenate terminus of **2-N'** [11]



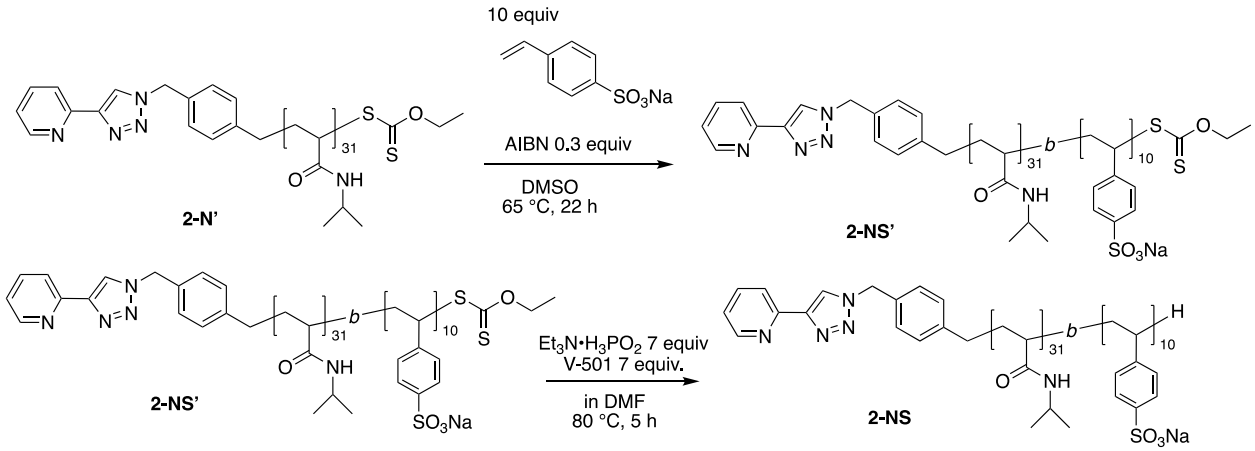
Typically, in a dried Schlenk tube, the polymer **2-N'** (710 mg 0.259 mmol), triethylammonium hypophosphite (376 mg, 1.82 mmol), V-501 (510 mg, 1.82 mmol) were dissolved in DMSO (14 mL). The mixture was degassed by three cycle of freeze-pump-thaw. The mixture was stirred at 80°C for 5 h. Yellowish solution was dialyzed (MWCO = 1.0 kD), and the solution was dried in vacuo to give **2-N** white-yellow solid (422 mg, n = 21, 62%). Elemental analysis showed that the amount of sulfur element in **2-N** was less than detection limit.

^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ = 3.99 (br, N*H*), 5.54 (s, 2H, NCH_2Ar), 7.77 (s, 1H), 8.05 (s, 1H), 8.17 (s, 1H), 8.54 (s, 1H).

^{1}H NMR (n = 32)



2-5. Preparation of ligand-tethered diblock copolymer **2-NS**.



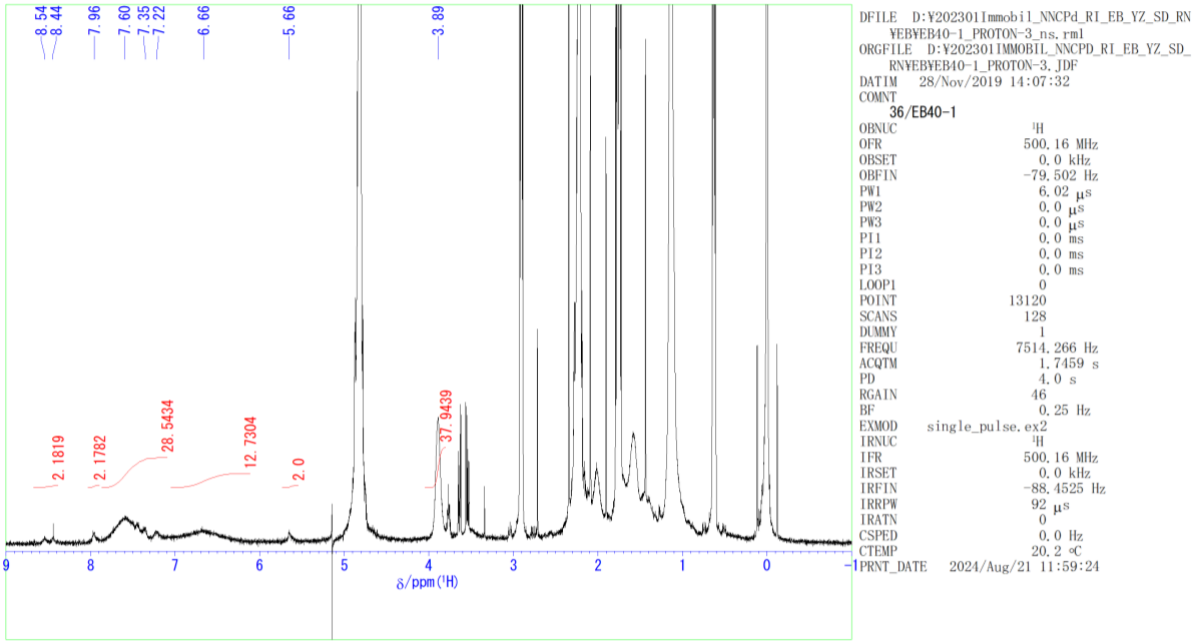
In a dried Schlenk tube filled with argon, the polymer **2-N'** PNIPAAm (200 mg, 0.0516 mmol), sodium p-styrene sulfonate (106 mg, 0.516 mmol), AIBN (14.1 mg, 0.0086 mmol) were dissolved in DMSO (5 mL) and the solution was degassed by freeze-pump-thaw for three times. The solution was stirred at 65 °C for 22 h. Yellow solution was dialyzed (MWCO = 3.5 kD) in water. The mixture was dried in vacuo to give yellowish solid (245 mg, 80%). The polymer **2-NS'** was identified by ^{1}H NMR and polymerization degree was determined (M_n = 5,900).

NMR (D_2O, $Me_3Si(CH_2)_3SO_3Na$, 500 MHz): δ = 3.89 (br, CO-N*H*-CH), 5.65 (s, 2H, N-CH_2-Ph), 6.08-8.10 (br, P*h*), 8.44 (s, 1H), 8.54 (s, 1H).

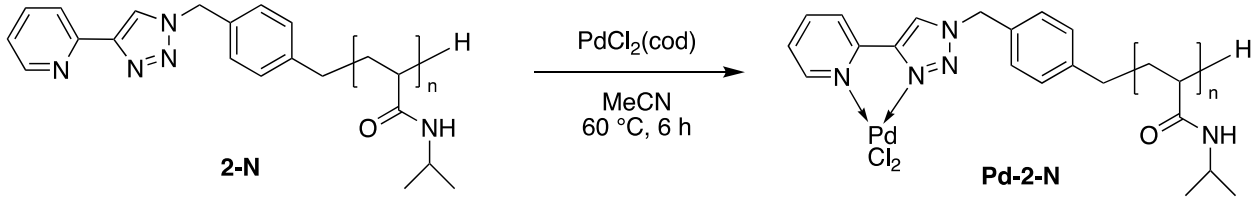
The xanthogenate terminus was removed in a similar manner to **2-N'** to furnish **2-NS**.

^{1}H NMR (D_2O, $Me_3Si(CH_2)_3SO_3Na$, 500 MHz): δ = 3.89 (br, CO-N*H*-CH), 5.65 (s, 2H, N-CH_2-Ph), 6.08-8.10 (br, P*h*), 8.44 (s, 1H), 8.54 (s, 1H).

^{1}H NMR



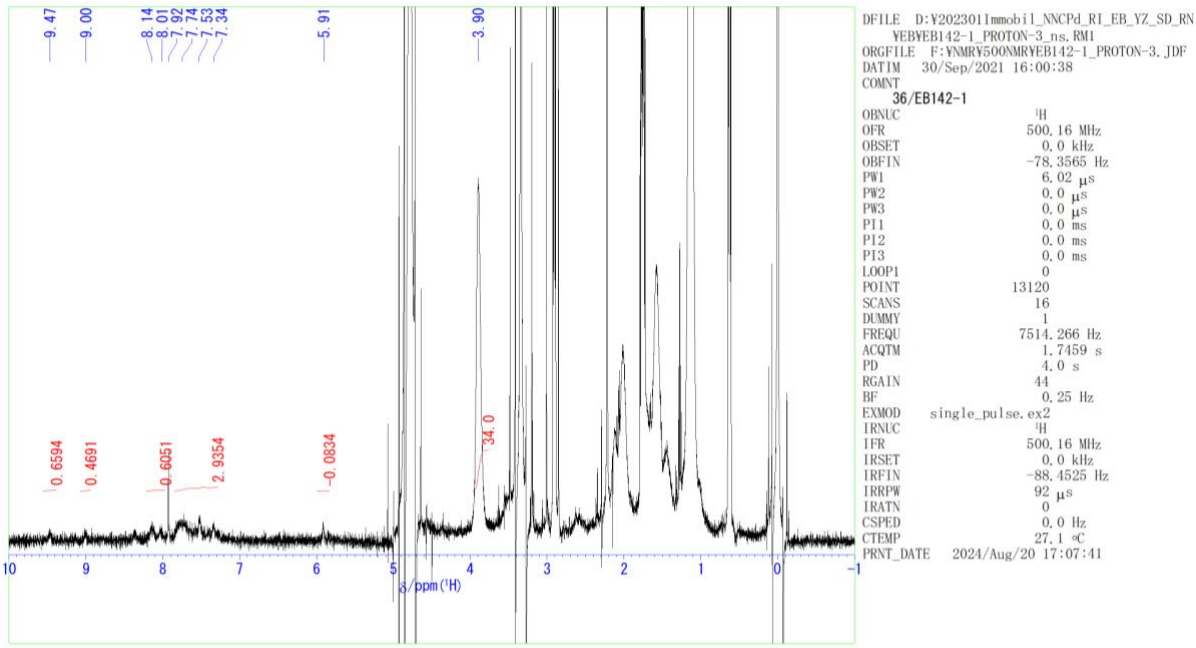
2-6. Preparation of polymer-immobilized Pd-complex **Pd-2-N**.



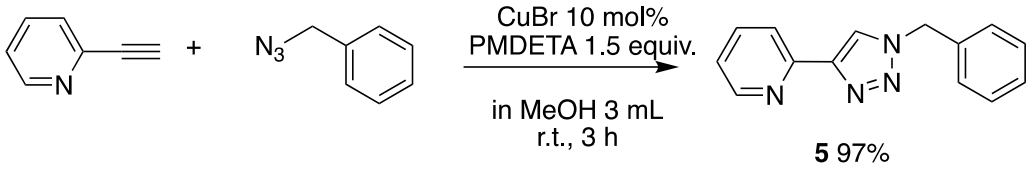
In a dried test tube with a screw cap, the polymer **2-N** (n = 21, 279 mg, 0.106 mmol), $PdCl_2$(cod) (30 mg, 0.106 mmol) were dissolved in acetonitrile (9 mL) and the mixture was stirred at 60 °C for 6 h. The yellow clear solution turned to reddish, and the mixture was poured into hexane/diethyl ether (4/1) to precipitate polymer. Solid was filtered and dried in vacuo to leave dark brown solid (299 mg). The product was identified by ^{1}H NMR and ICP analysis. ICP analysis showed 3.9 wt% of Pd content, which is consistent with the calculated value (3.8 wt% Pd).

^{1}H NMR (D_2O, $Me_3Si(CH_2)_3SO_3Na$, 500 MHz): δ = 3.89 (br, N*H*), 5.91 (s, 2H, NCH_2Ar), 6.14-8.27 (br, Ar), 9.00 (s, 1H), 9.47 (s, 1H).

^{1}H NMR



2-7. Preparation of **5**. [12]

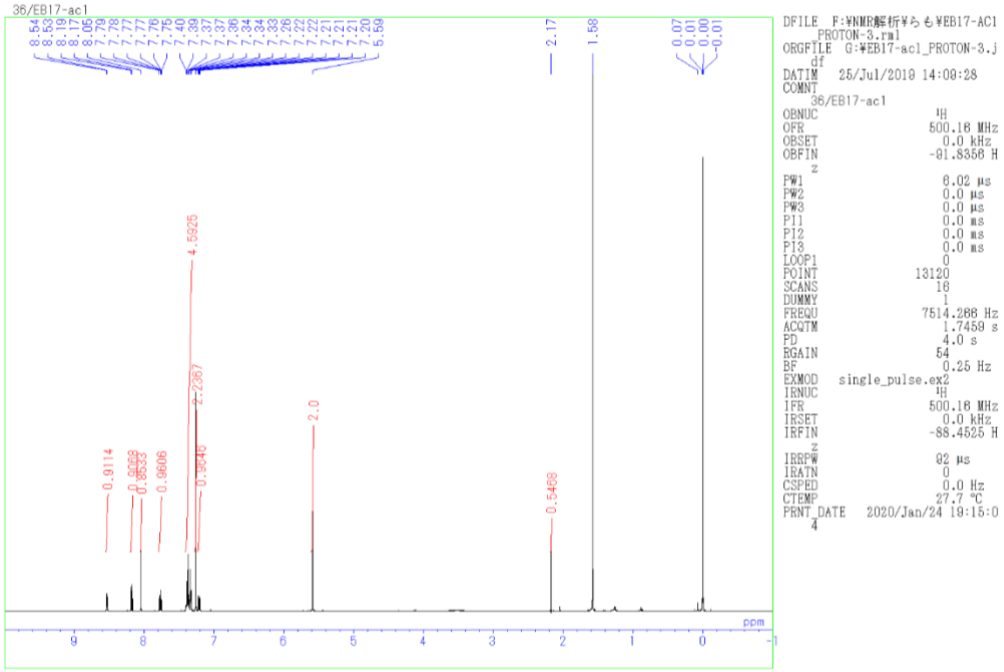


5 97%

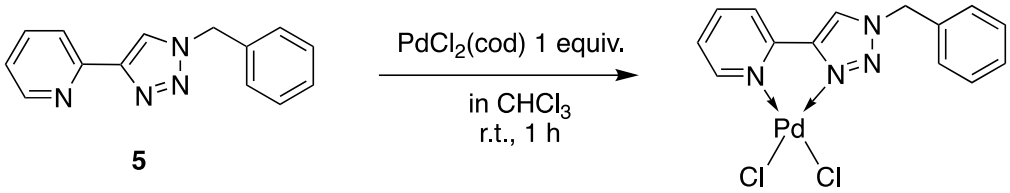
In a dried Schlenk tube filled with argon, and benzyl azide (133 mg, 1.0 mmol) and 2-ethynylpyridine (103 mg, 1.0 mmol), copper(I) bromide (14.3 mg, 0.1 mmol) and PMDETA (260 mg, 1.5 mmol) were dissolved in methanol (3 mL). The mixture was stirred at r.t. for 3 h, and concentrated in vacuo. The residual solid was purified by column chromatograph on silica gel (ethyl acetate/hexane = 1/2) to afford the title compound as white solid (228 mg, 97%).

^{1}H NMR ($CDCl_3$, Me_4Si, 500MHz): δ = 5.59 (s, 2H, N-C*H*$_2$-Ph), 7.21 (td, *J* = 5 Hz, 1H, P*y*), 7.33-7.40 (m, 5H, P*h*), 7.77 (td, *J* = 7.5 Hz, 1H, P*y*), 8.05 (s, 1H, T*az*), 8.18 (d, *J* = 10 Hz, 1H, P*y*), 8.54 (d, *J* = 5 Hz, 1H, P*y*).

^{1}H NMR



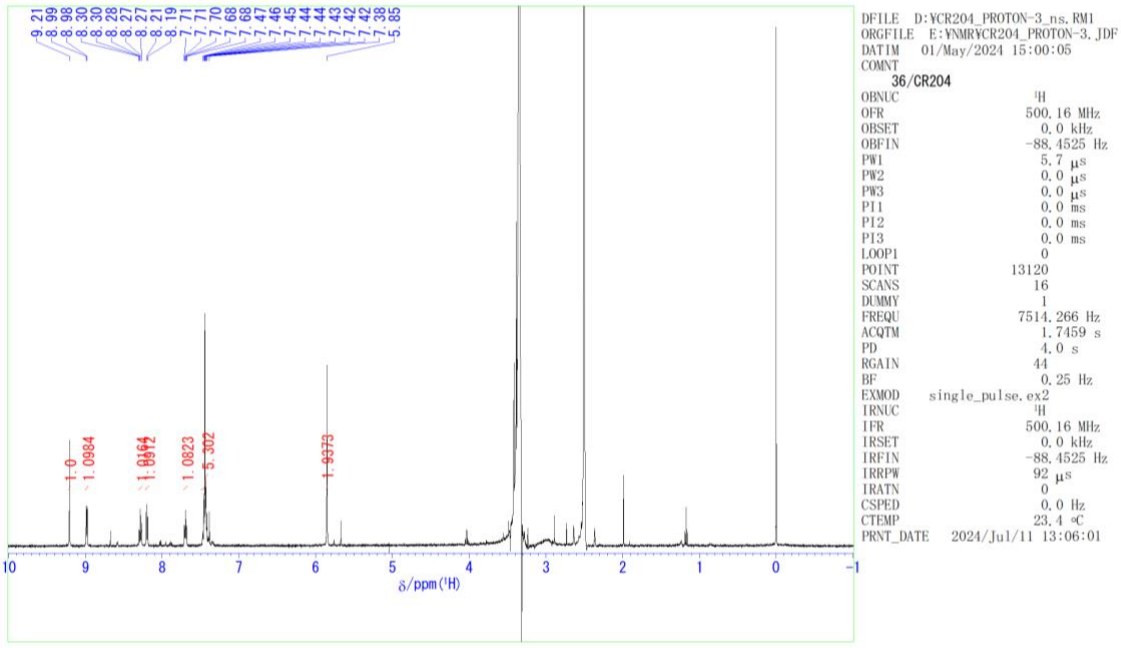
2-8. Preparation of small molecule Pd complex **Pd-5**.[12]



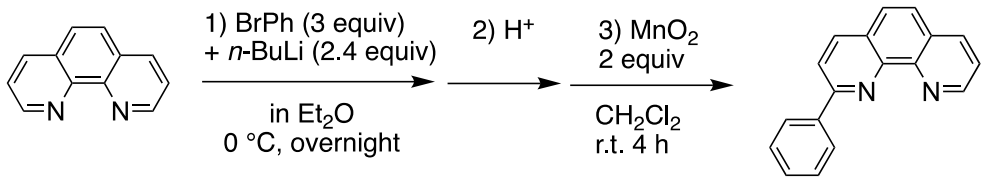
5 **Pd-5**

In a dried Schlenk tube, ligand **5** (76 mg, 0.32 mmol) and $PdCl_2$(cod) (92 mg, 0.32 mmol) were dissolved in chloroform (20 mL) and the mixture was stirred at r.t. for 1 h. Yellow suspension was filtered, and the collected solid was washed with hexane. The solid was dissolved in DMF to recover and the solvent was removed in vacuo to give dark orange solid (68 mg, 82%).
^{1}H NMR (DMSO-d_6, Me_4Si, 500 MHz): δ = 5.85 (s, 2H, CH_2), 7.36–7.49 (m, 5H), 7.70 (t, J = 6.5 Hz, 1H), 8.20 (d, J = 7.5 Hz, 1H), 8.30 (t, J = 8.3 Hz, 1H), 8.99 (d, J = 5.6 Hz, 1H), 9.21 (s, 1H).

^{1}H NMR



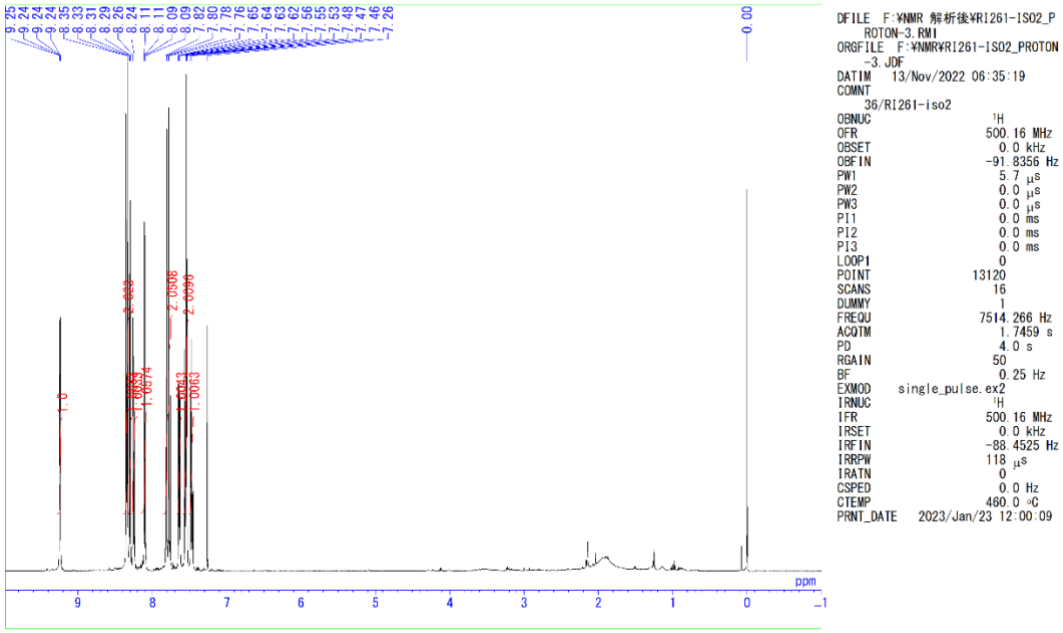
2-9. Preparation of 2-phenyl-1,10-phenanthroline.[13, 14]



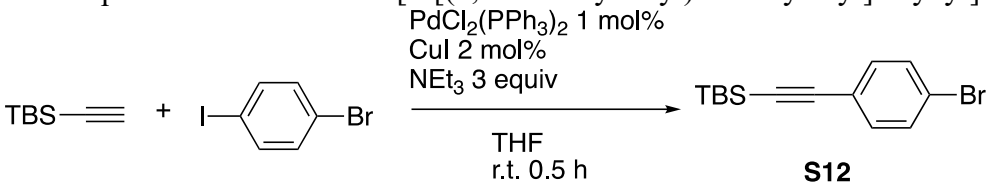
A Schlenk tube was thoroughly dried and filled with argon. In this tube, bromobenzene (942 mg, 6.0 mmol) was dissolved in anhydrous diethyl ether (10 mL) and the solution was cooled at –78 °C. To this solution was added *n*-butyllithium (1.6M in *n*-hexane, 3 mL, 4.8 mmol) dropwise and the mixture was allowed to warm to 0 °C and stirred for 1 h to prepare phenyllithium. Meanwhile, 1,10-phnenthroline (360 mg, 2.0 mmol) was dissolved in anhydrous diethyl ether (7 mL) in a dried Schlenk tube and the solution was cooled at –78 °C. To this solution, prepared phenyllithium solution was added dropwise and stirred at –78 °C for 3 h. The solution was then warmed up to 0 °C and stirred for additional 18 h. Aqueous sodium hydroxide (5 wt%, 50 mL) was added to the reaction mixture and extracted with dichloromethane (50 mL × 3), and combined organic layer was concentrated to ca. 100 mL. in vacuo. Manganese oxide (350 mg, 4.0 mmol) was added to this solution and stirred at r.t. for 4 h. The solution was dried over magnesium sulfate and filtered. The volatiles were removed in vacuo from the filtrate, and the residue was purified by column chromatograph on silica gel (ethyl acetate/hexane = 1/1 to 1/0) to afford the title compound as colorless liquid (365 mg, 71%). Recycling preparative HPLC may be applied for purification.

^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ = 7.47 (t, *J* = 7.0 Hz,1H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.64 (dd, *J* = 8.1, 4.6 Hz, 1H), 7.78 (d, *J* = 9 Hz, 1H), 7.81 (d, *J* = 9 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 8.25 (d, *J* = 8 Hz, 1H), 8.30 (d, *J* = 8 Hz, 1H), 8.34 (d, *J* = 8 Hz, 2H), 9.24 (d, *J* = 4.5 Hz, 1H).

^{1}H NMR



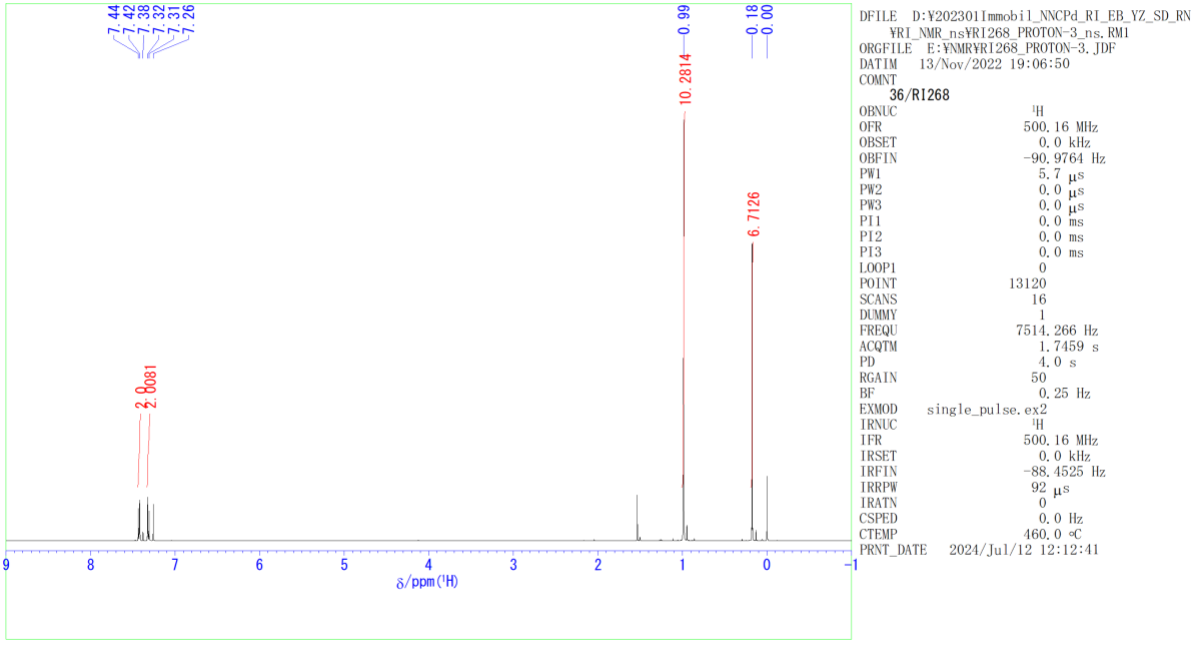
2-10. Preparation of 1-bromo-4-[2-[(1,1-dimethylethyl)dimethylsilyl]ethynyl]benzene (**S12**). [15]



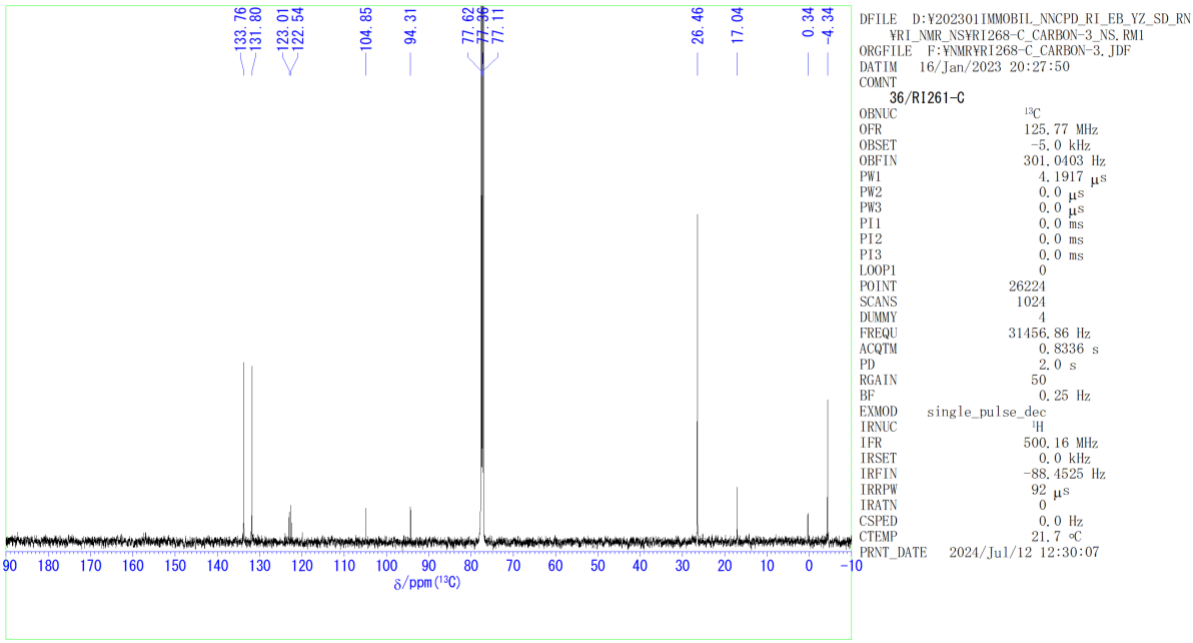
In a dried Schlenk tube, $PdCl_2(PPh_3)_2$ (35 mg, 0.05 mmol), copper(I) iodide (19 mg, 0.1 mmol), triethylamine (1.52 g, 15 mmol) were dissolved in THF (6.7 mL) and the solution was degassed by three freeze-pump-thaw cycles. To this solution, (*tert*-butyldimethylsilyl)acetylene (740 mg, 5.25 mmol) and 1-bromo-4-iodobenzen (1.42 g, 5.0 mmol) was added and stirred at r.t. for 0.5 h. The gray mixture was quenched by sat.NH_4Cl and extracted by diethyl ether. Combined organic layer was washed with deionized water and brine, and dried over magnesium sulfate. The desiccant was filtered off and the filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane) to afford **S12** as colorless liquid (1.38 g, 94%).

^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ = 0.18 (s, 6H, SiC*H*$_3$), 0.99 (s, 9H, C*H*$_3$), 7.32 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H).
^{13}C{^{1}H} NMR ($CDCl_3$, $CHCl_3$ = 77.36, Me_4Si, 100 MHz): δ = –4.3 (*C*H$_3$), 17.0 (q), 26.5 (*C*H$_3$), 94.3 (q), 104.9 (q), 122.5 (q), 123.0 (q), 131.8 (*C*H), 133.8 (*C*H).

^{1}H NMR



$^{13}C\{^{1}H\}$ NMR



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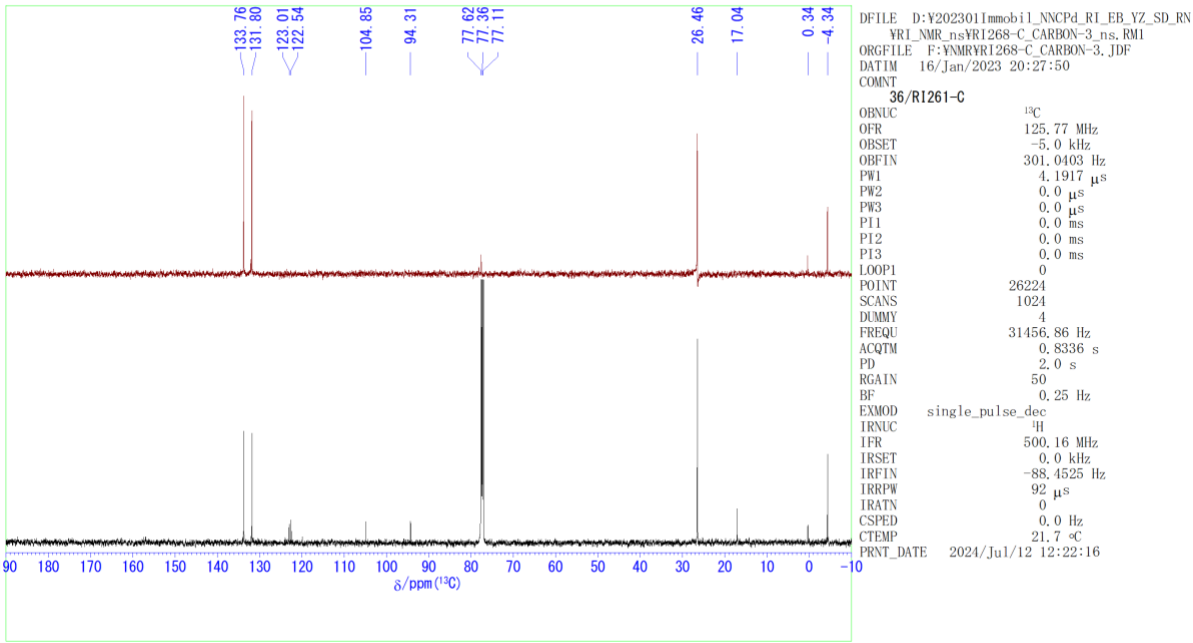
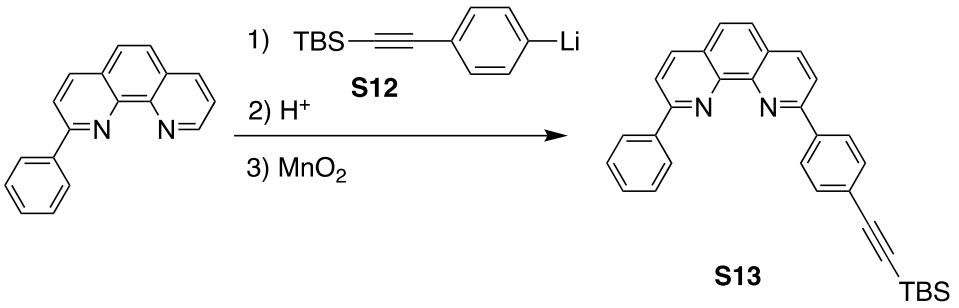
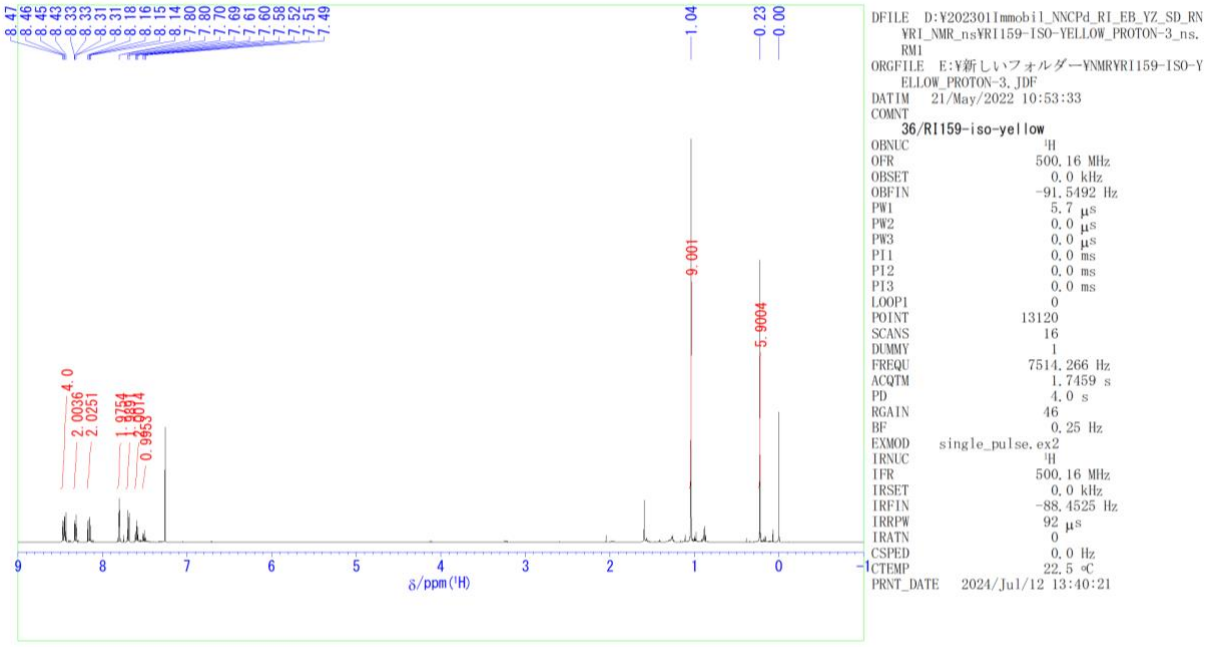


2-11. Preparation of 2-(4-((*tert*-butyldimethylsilyl)ethynyl)phenyl)-9-phenyl-1,10-phenanthroline (**S13**).

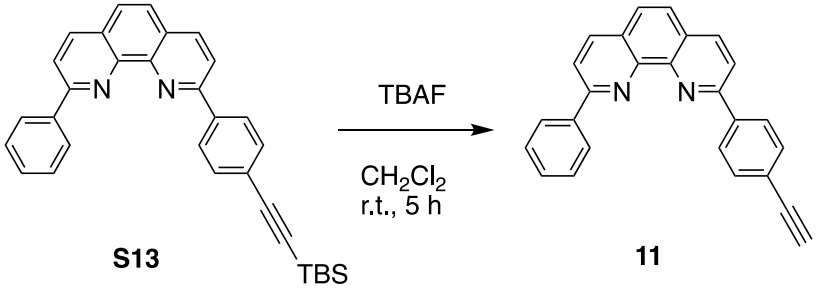


In a dried Schlenk tube, 2-phenyl-1,10-phenanthroline (858 mg, 2.92 mmol) was dissolved in anhydrous diethyl ether (5 mL) and the solution was cooled at –78 °C. To this solution, *n*-butyllithium (1.6 M in *n*-hexane, 1.83 mL, 2.92 mmol) was added dropwise and stirred at –78°C for 3 h. The mixture was kept at –40 °C and additionally stirred for 16 h to prepare an aryllithium reagent. Meanwhile, **S12** (374 mg, 1.46 mmol) was dissolved in diethyl ether (5.8 mL) in a Schlenk tube and cooled at –78 °C. To this solution, the prepared aryllithium was added dropwise at –78 °C. The mixture was allowed to warm up to 0 °C and stirred for 16 h. Aqueous sodium hydroxide (5 wt%, 50 mL) was added to the reaction mixture and extracted with dichloromethane (50 mL × 3), and combined organic layer was washed once with $NaOH_{aq}$ (10 wt%). The solution was filtered and the filtrate was concentrated to ca. 100 mL. in vacuo. Manganese oxide (250 mg, 2.9 mmol) was added to this solution and stirred at r.t. for 5 h. The solution was dried over magnesium sulfate and filtered. The volatiles were removed in vacuo from the filtrate, and the residue was purified by column chromatograph on silica gel (hexane/ethyl acetate = 9/1) to afford the title compound as colorless liquid (254 mg, 37%). Recycling preparative HPLC may be applied for purification.
^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ = 0.23 (s, 6H, Si(C*H*$_3$)$_2$), 1.04 (s, 9H, Si-C(C*H*$_3$)$_3$), 7.51 (t, *J* = 7.1 Hz,1H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.70 (d, *J* = 8.5, 2H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 8.15 (d, 8, 1H), 8.16 (d, 8, 1H), 8.32 (dd, *J* = 8.6, 2.2 Hz, 2H), 8.43-8.47 (m, 4H).

^{1}H NMR

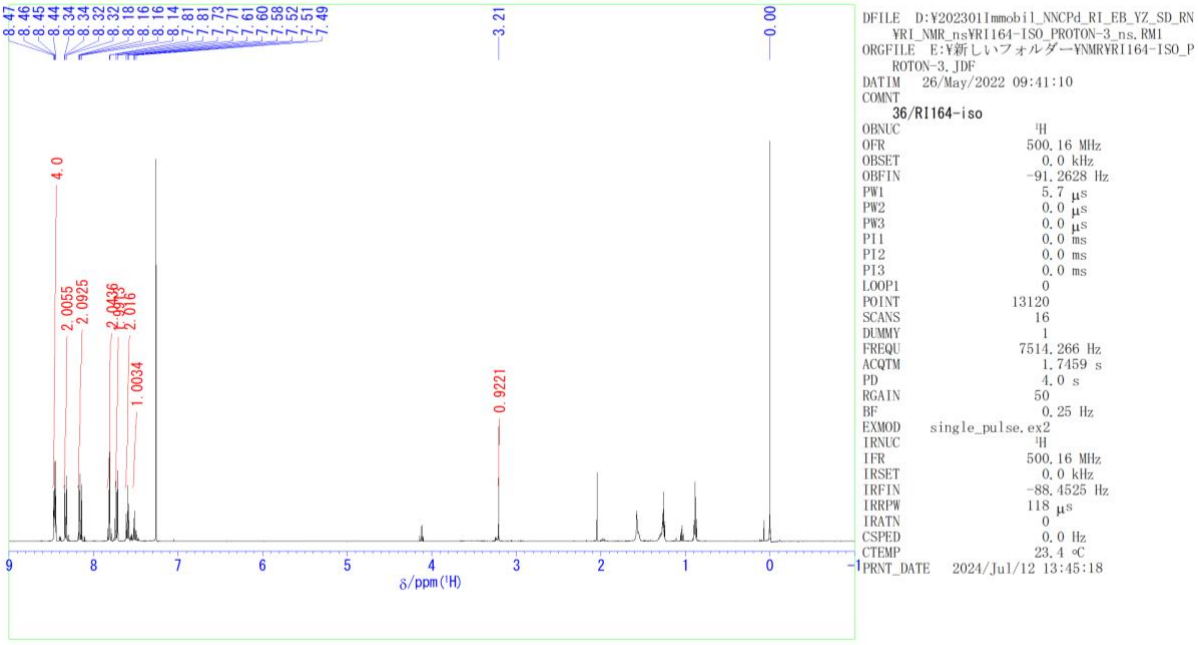


2-12. Deprotection of TBS group from **S13**: Preparation of **11**

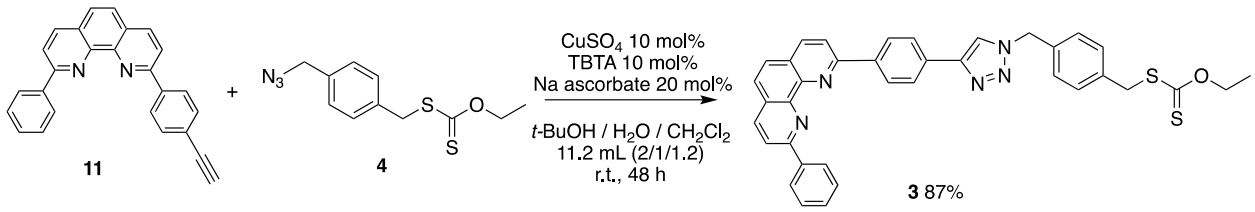


In dichloromethane (5 mL), **S13** (254 mg, 0.540 mmol) and tetrabutylammonium fluoride (1.0 M in tetrahydrofuran, 0.594 mL, 0.594 mmol) were dissolved. The solution was stirred at r.t. for 5 h, and volatiles were removed in vacuo. The residue was purified by column chromatograph on silica gel (hexane/ethyl acetate = 4/1) to furnish **11** as colorless oil (186 mg, 97%).
^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ = 3.21 (s, 1H, C≡C*H*), 7.51 (t, *J* = 7.1 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.72 (d, *J* = 8.5, 2H), 7.80 (d, *J* = 8.5 Hz, 1H),7.82 (d, *J* = 8.5 Hz, 1H), 8.14-8.18 (m, 2H), 8.33 (dd, *J* = 8.6, 2.2 Hz, 2H), 8.44-8.47 (m, 4H).

^{1}H NMR



2-13. RAFT agent with NNC-pincer ligand **3**.



The cycloaddition reaction condition was according to similar substrates. [16]

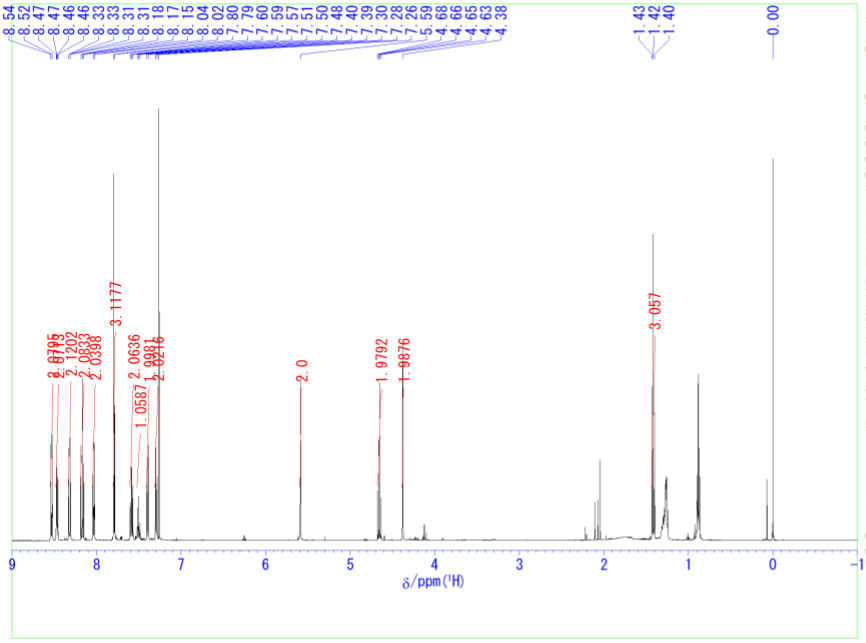
In a dried Schlenk tube, **11** (0.185 g, 0.52 mmol) and **4** (0.139 g, 0.52 mmol), tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA) (0.0275 g, 0.052 mmol), sodium *L*-ascorbate (0.0207 g, 0.104 mmol) were added in ^{t}BuOH (5.3 mL)/ H_2O (2.7 mL)/ CH_2Cl_2 (3.2 mL). After stirring until the substrates were dissolved, copper(II) sulfate (82.9 mg, 0.052 mmol) was added and the mixture was stirred at r.t. for 48 h. The solution immediately turned black. After the reaction completed, volatiles were removed in vacuo. Potassium cyanide (329 mg, 5.05 mmol) in water (50 mL) and methanol were added to the residue and sonicated for 1 h. The mixture with light yellow precipitate was concentrated in vacuo to remove volatiles, and the concentrated aqueous mixture was extracted with dichloromethane. The organic layer was washed twice with deionized water and dried over magnesium sulfate. The desiccant was filtered off and the filtrate was concentrated in vacuo. The residue was purified by column chromatograph on silica gel (hexane/ethyl acetate = 1/1) to afford the title compound as yellow solid (281 mg, 87%).

^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ = 1.42 (t, *J* = 7.3 Hz, 3H, C*H*$_3$), 4.38 (s, 2H, C*H*$_2$S), 4.66 (qt, *J* = 7.3 Hz, 2H, OC*H*$_2$), 5.59 (s, 2H, NC*H*$_2$), 7.29 (d, *J* = 8.1 Hz, 2H, CH_2), 7.40 (d, *J* = 8.1 Hz, 2H, CH_2), 7.50 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 2H), 7.79 (d, *J* = 6 Hz, 2H), 7.80 (s, 1H), 8.03 (d, *J* = 8.5 Hz, 2H), 8.17 (t, *J* = 8.5 Hz, 2H), 8.32 (dd, *J* = 8.5, 1.1 Hz, 2H), 8.47 (dd, *J* = 8.1, 1.1 Hz, 2H), 8.53 (d, *J* = 8.5 Hz, 2H).

^{13}C{^{1}H} NMR ($CDCl_3$, Me_4Si, 125.8 MHz): δ = 13.8 (*C*H$_3$), 39.9 (*C*H$_2$), 53.9 (*C*H$_2$), 70.3 (*C*H$_2$), 119.9 (*C*H×2), 120.1 (*C*H), 126.06 (*C*H), 126.10 (*C*H×2), 127.7 (*C*H×2), 127.99 (q), 128.03 (q), 128.11 (*C*H×2), 128.40 (*C*H×2), 128.87 (*C*H×2), 129.52 (*C*H), 129.91 (*C*H×2), 131.45 (q), 133.98 (q), 136.87 (q), 136.99 (*C*H×2), 139.09 (q), 139.42 (q), 146.07 (q), 146.12 (q), 148.00 (q), 156.12 (q), 156.86 (q), 213.69 (q).

High resolution MS (ESI): [M-H] cald for $C_{37}H_{30}N_5OS_2$ = 624.1892, found = 624.1866.

^{1}H NMR

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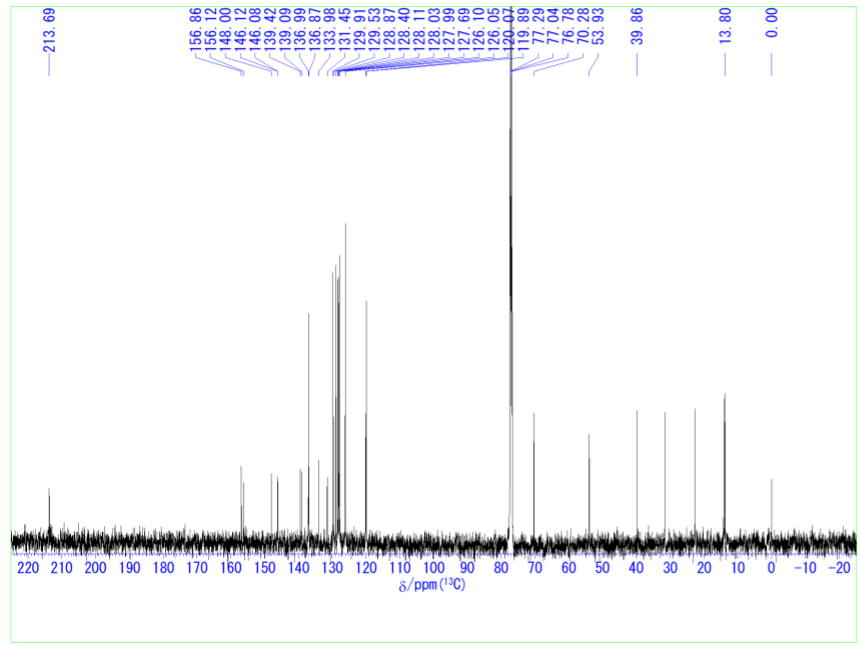
^{13}C{^{1}H} NMR

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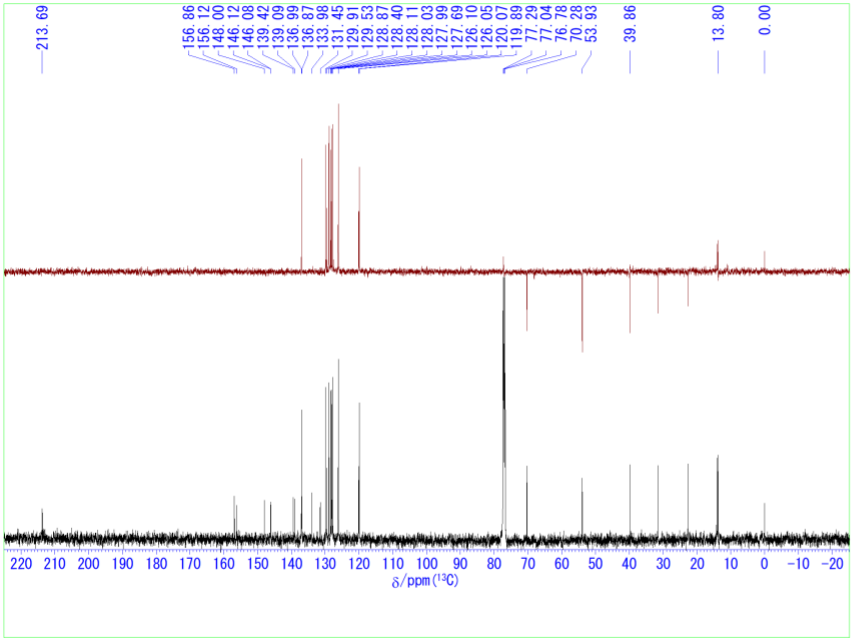

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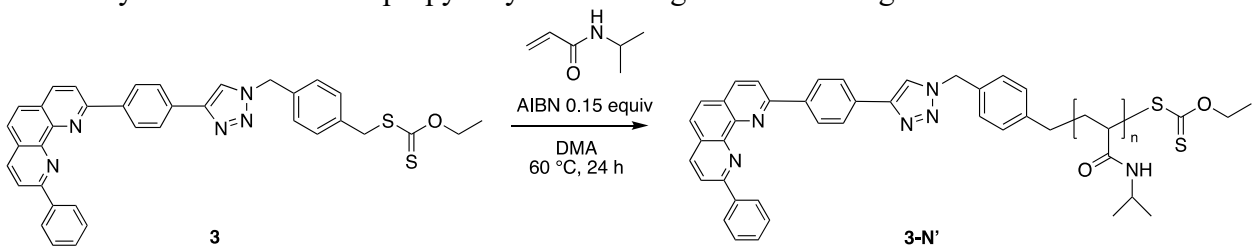
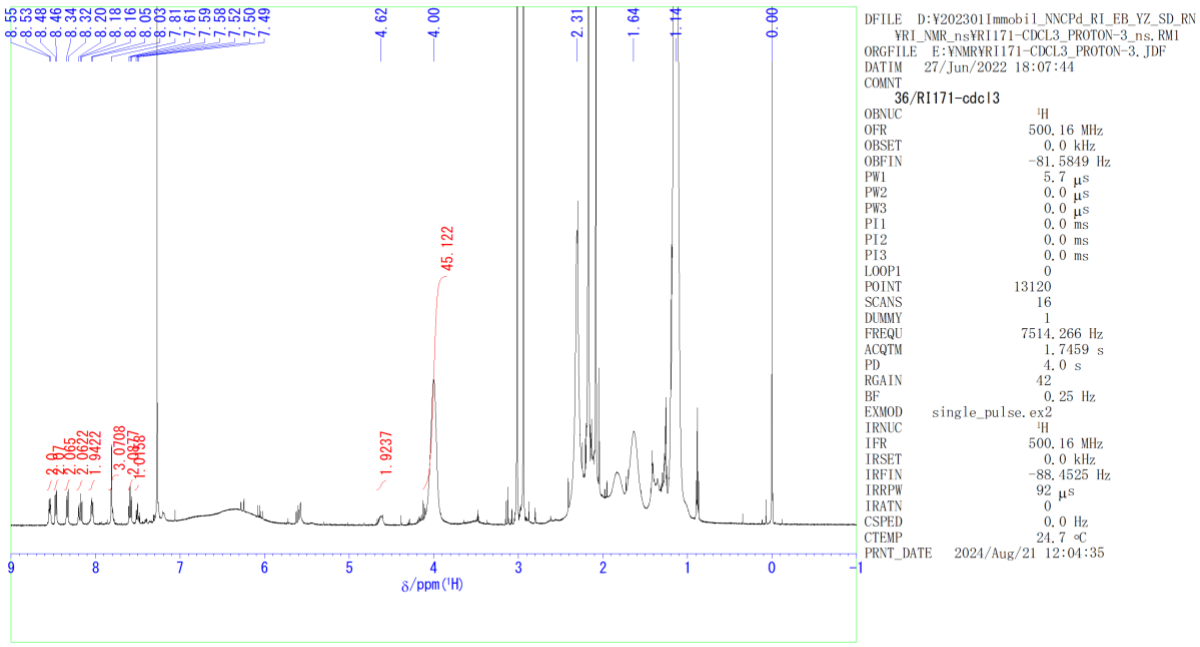
2-14. Polymerization of *N*-isopropylacrylamide using **3** as a RAFT agent.



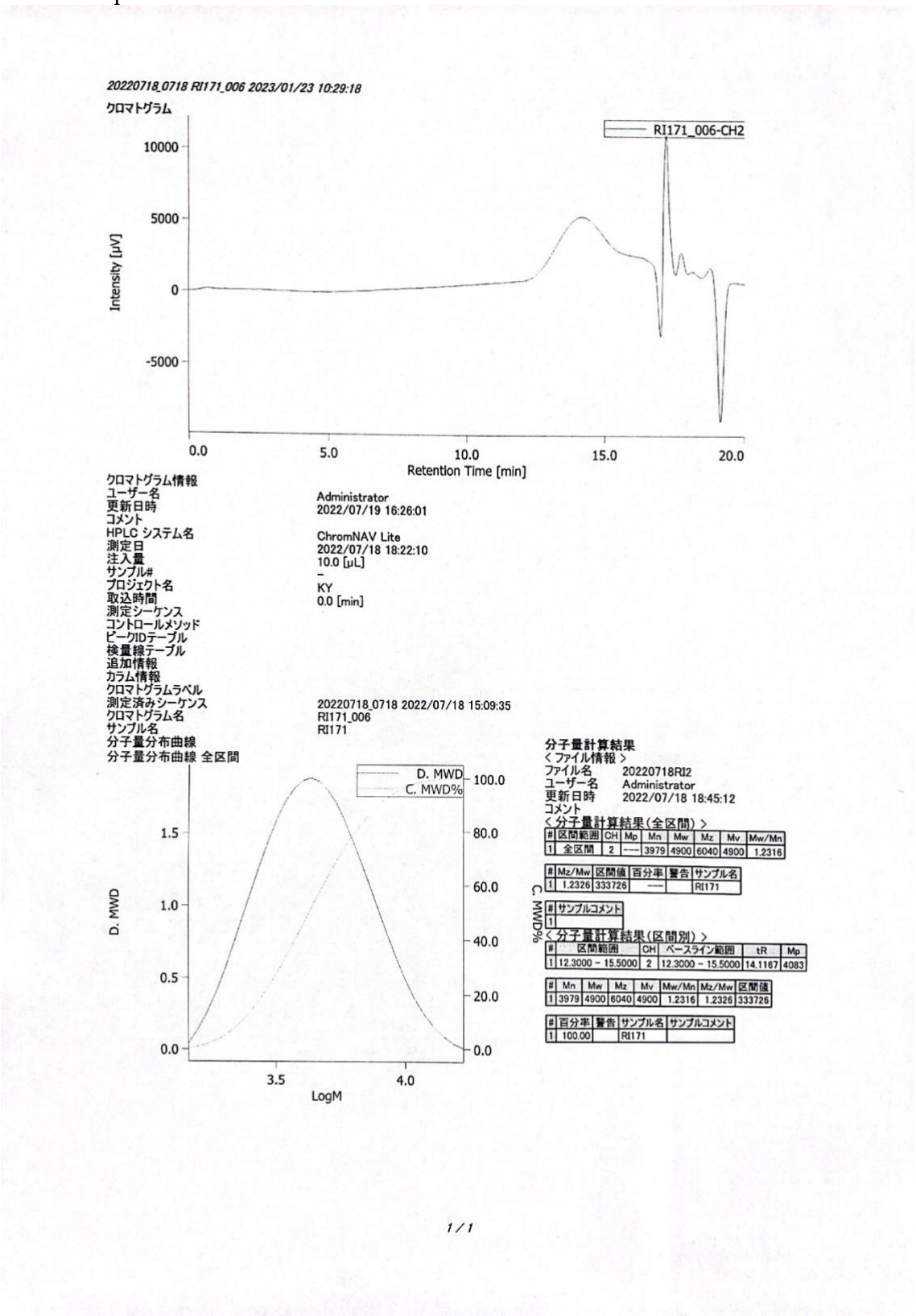
A Schlenk tube was thoroughly dried and fille with argon. In this tube, **3** (281 mg, 0.45 mmol), *N*-isopropylacrylamide (NIPAAm) (1.02 g, 9.0 mmol) and azobis(isobutyronitrile) (AIBN) (25 mg, 0.15 mmol) were dissolved in dimethylacetamide (DMA) (9 mL) and degassed by three cycles of freeze-pump-thaw. The solution was stirred at 60 °C for 24 h, and the mixture was poured into hexane/diethyl ether (250/100 mL). The yellow precipitate was dissolved in chloroform to recover and the volatile was removed in vacuo to afford the title compound as yellow solid (1.203 g, 92%). The polymerization degree was determined by ^{1}H NMR (n = 45, M_n = 5,700). Gel permeation chromatgraphy (GPC) was measured using polyethyele glycol as standard (M_w = 4,900, M_w/M_n = 1.23).

^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ = 1.14 (br, $CH(CH_3)_2$), 1.64 (br, CH_2 in the main chain), 2.31 (br, CH in the main chain), 4.00 (br, $CH(CH_3)_2$), 4.62 (br, 2H, OCH_2CH_3), 7.50 (t, J = 7.1 Hz, 1H), 7.59 (t, J = 7.5 Hz, 2H), 7.81 (m, 3H), 8.04 (d, J = 8.1 Hz, 2H), 8.18 (t, J = 8.6 Hz, 2H), 8.33 (d, J = 8.6, 2H), 8.47 (d, J = 7.9 Hz, 2H), 8.54 (d, J = 8.5 Hz, 2H).

^{1}H NMR



The GPC spectrum for **3-N'**.



#	区間範囲	CH	Mp	Mn	Mw	Mz	Mv	Mw/Mn
1	全区間	2	----	3979	4900	6040	4900	1.2316

#	Mz/Mw	区間値	百分率	警告	サンプル名
1	1.2326	333726	----		RI171

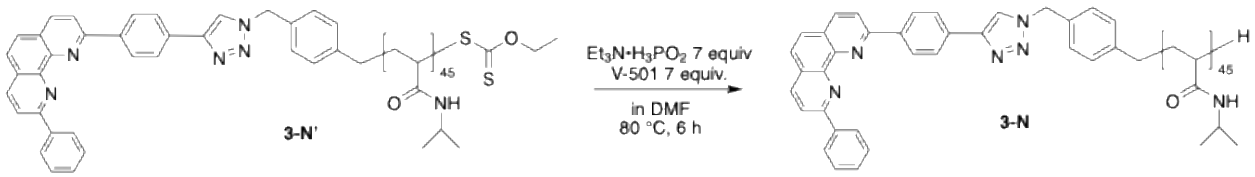
#	サンプルコメント
1	

#	区間範囲	CH	ベースライン範囲	tR	Mp
1	12.3000 – 15.5000	2	12.3000 – 15.5000	14.1167	4083

#	Mn	Mw	Mz	Mv	Mw/Mn	Mz/Mw	区間値
1	3979	4900	6040	4900	1.2316	1.2326	333726

#	百分率	警告	サンプル名	サンプルコメント
1	100.00		RI171	

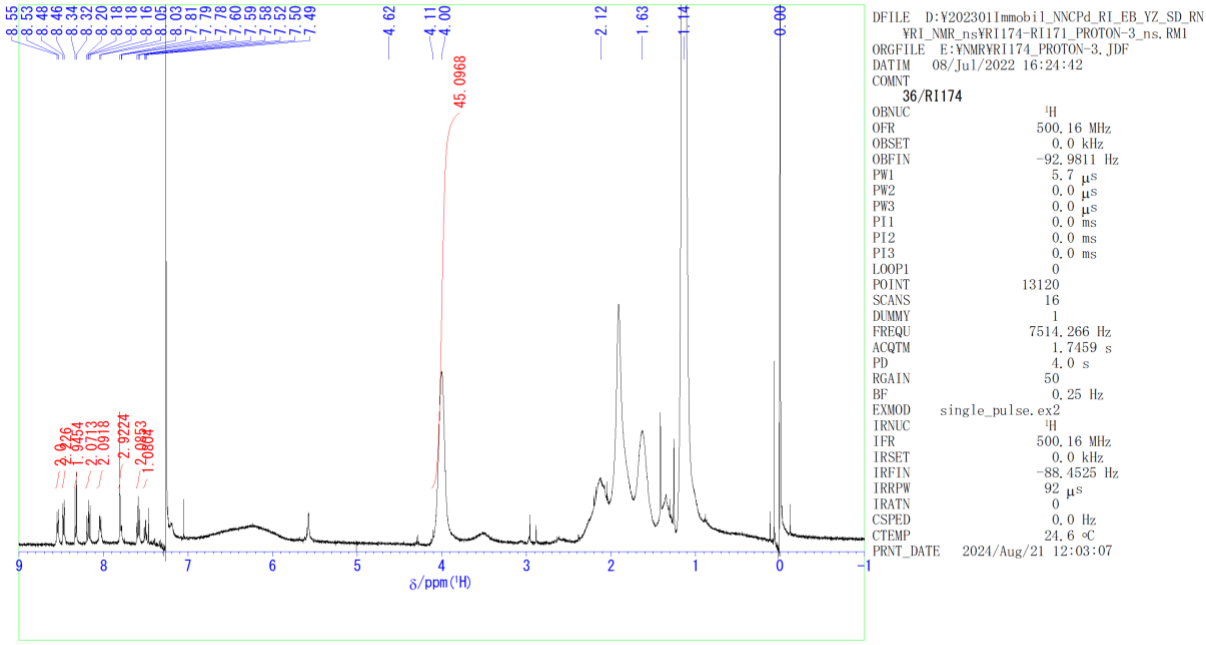
2-15. Preparation of **3-N**: Removal of xanthogenate terminus of **3-N'**



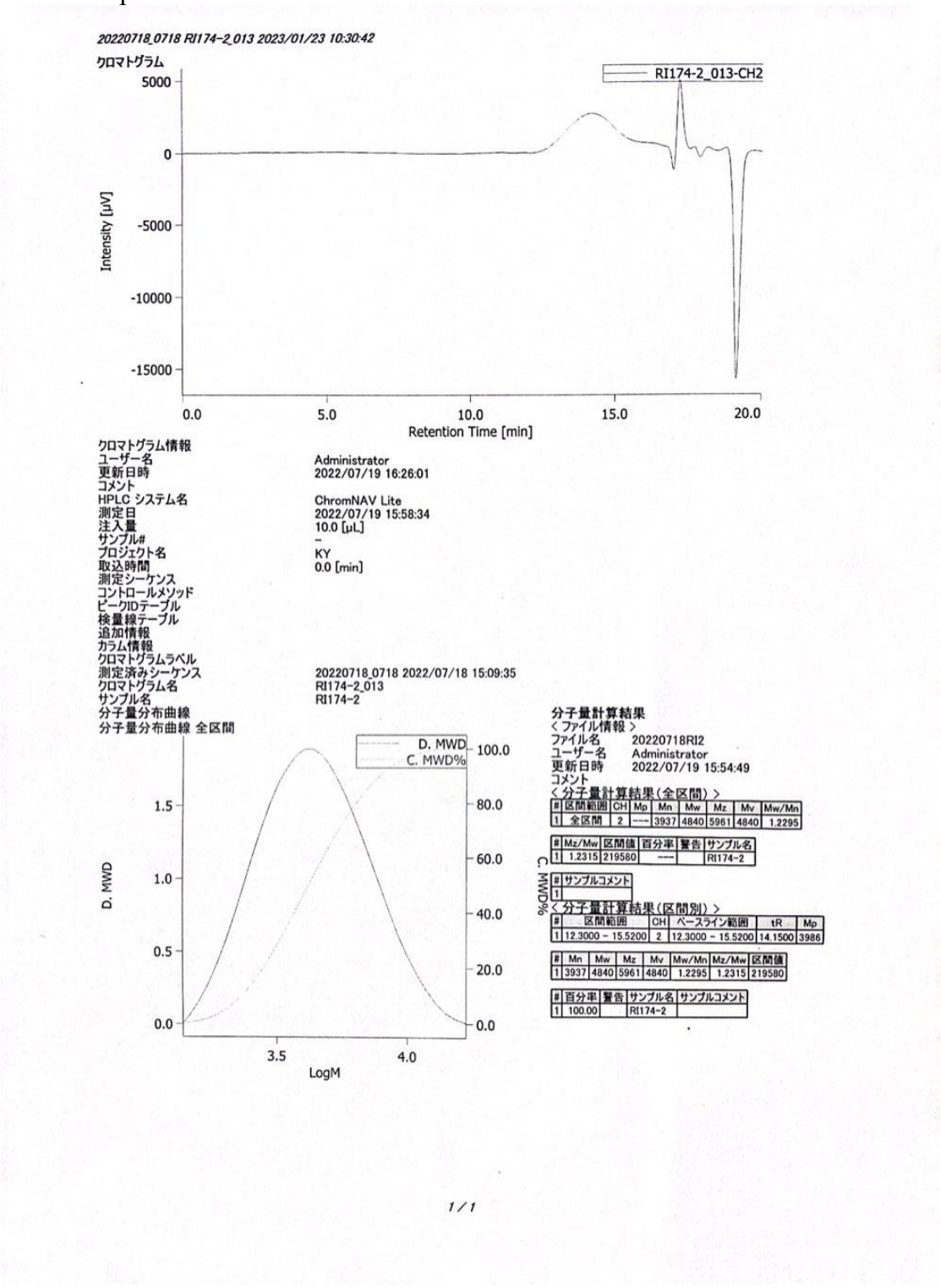
The xanthogenate terminus of **3-N'** (571 mg, 0.1 mmol) was removed in a similar manner to **2-N'** using 7 equiv of triethylammonium hypophosphite and V-501. Yellow solid, 425 mg, 76%. The polymerization degree was determined by ^{1}H NMR (PD = 45, M_n = 5,600). Gel permeation chromatgraphy (GPC) was measured using polyethyele glycol as standard (M_w = 4,800, M_w/M_n = 1.23).

^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ 1.14 (br, CH(CH_3)$_2$), 1.63 (br, CH_2 in the main chain), 2.12 (br, C*H* in the main chain), 4.00 (br, NC*H*), 7.50 (t, J = 7.1 Hz, 1H), 7.59 (t, J = 7.5 Hz, 2H), 7.78-7.81 (m, 3H), 8.04 (d, J = 8 Hz, 2H), 8.18 (t, J = 8.6 Hz, 2H), 8.33 (d, J = 8.6, 2H), 8.48 (d, J = 8 Hz, 2H), 8.54 (d, J = 8 Hz, 2H).

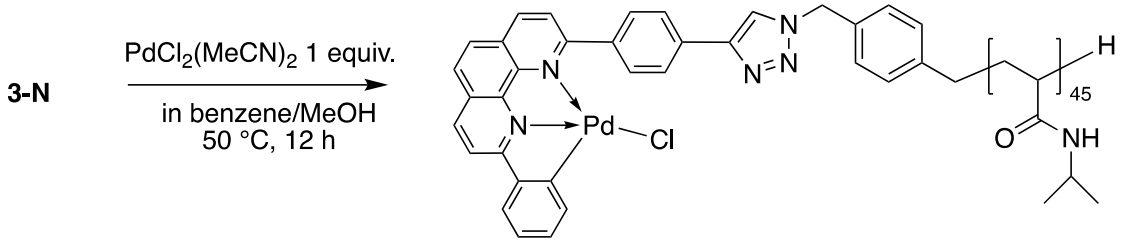
^{1}H NMR



The GPC spectrum of **3-N**



2-16. Preparation of polymer-immobilized Pd-complex **Pd-3-N**.

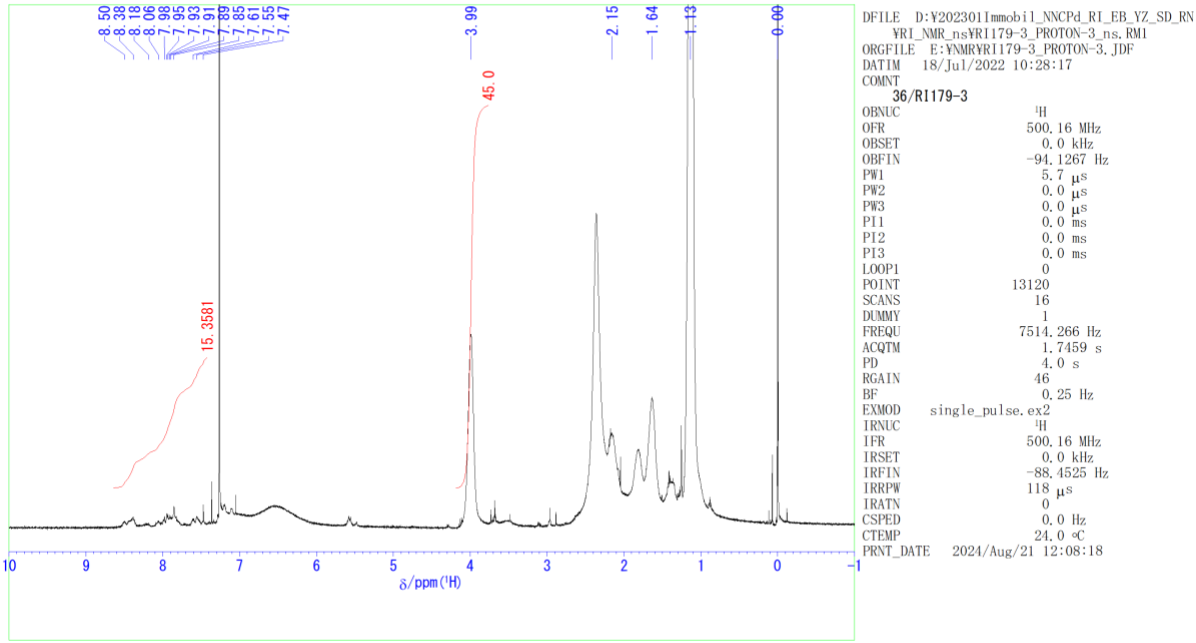


Pd-3-N

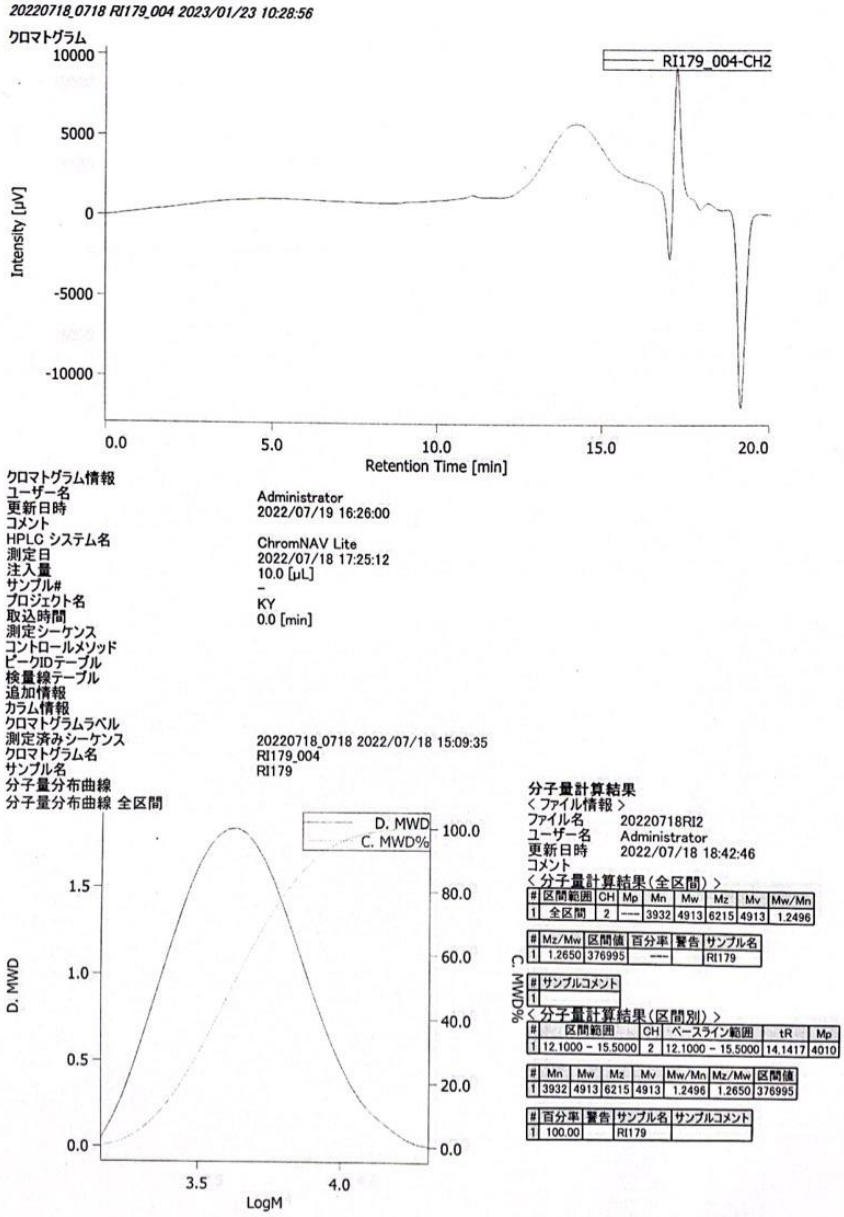
In a dried Schlenk tube filled with argon, **3-N** (140 mg, 0.025 mmol) and bis(acetonitrile)dichloropalladium (6.5 mg, 0.025 mmol) were dissolved in a mixture of benzene (1.2 mL) and methanol (1.5 mL), and the mixture was stirred at 50 °C for 12 h. The dark orange solution was filtered and washed with a small amount of dichloromethane, methanol and diethyl ether in this order. Recovered solid was dried in vacuo to give orange solid (164 mg). ICP analysis indicated that Pd content was 1.87 wt% (1.86 wt% calcd.)

^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ 1.13 (br, CH(CH_3)$_2$), 1.64 (br, CH_2 in the main chain), 2.15 (br, C*H* in the main chain), 3.99 (br, C*H*-(CH_3)$_2$), 7.47-8.50 (m, 16H).

^{1}H NMR



The GPC spectrum of **Pd-3-N**



3. Catalytic reactions using thermo-responsive Pd catalysts in water

3-1. Mizoroki-Heck reactions in water using **Pd-2-N**.

Typical procedure for Mizoroki-Heck reaction in water using the thermo-responsive catalysts in the presence of the thermo-responsive copolymer surfactant **NS** is as follows. In a test tube with a screw cap, **NS** (40 mg) was dissolved in deionized water (4 mL) and the solution was stirred. To this solution, iodobenzene (**6a**) (102 mg, 0.5 mmol), *n*-butyl acrylate (**7a**) (128 mg, 1.0 mmol), tri-*n*-butylamine (185 mg, 1.0 mmol), catalyst **Pd-2-N** (e.g. 22.5 mg, containing 0.005 mmol Pd), hydrazine monohydrate (2.5 mg, 50 μmol) were added, and the mixture was stirred at 70 °C for 48 h. Opaque suspension turned clear by heating, and became reddish solution through the reaction. Ethyl acetate (0.4 mL) was added and stirred for 5 min and centrifuged. The organic layer was separated and repeated the extraction until the product was not observed by thin layer chromatograph (TLC) in the extract. The combined organic layer was analyzed by ^{1}H NMR and gas chromatograph to determine yield of the product **8aa** (96%).

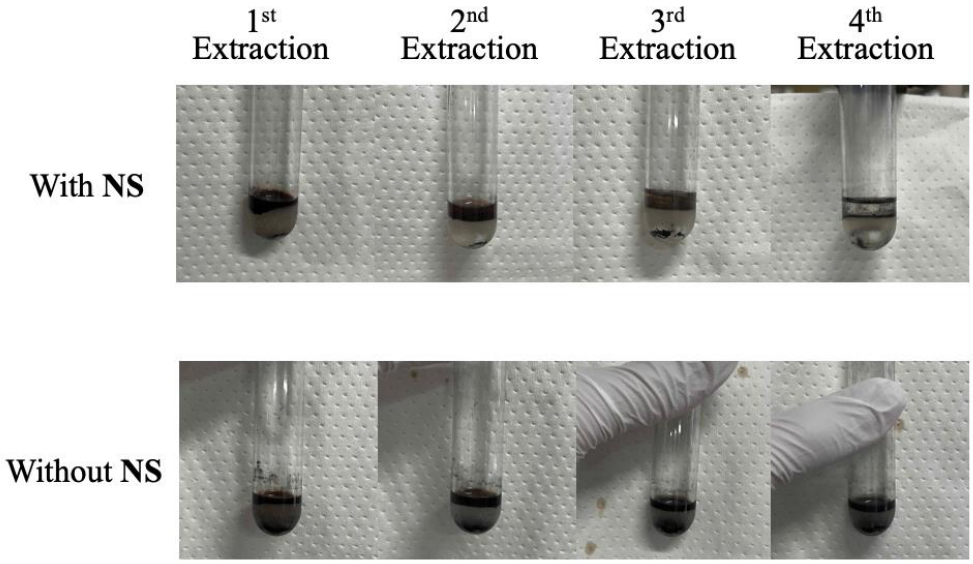
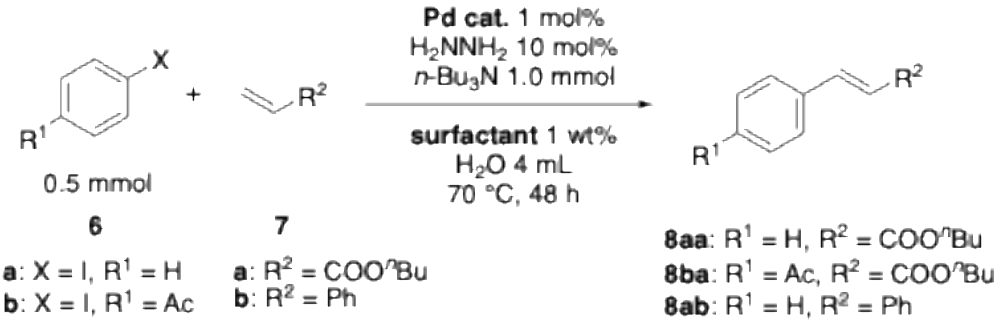
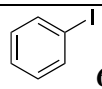
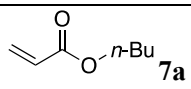
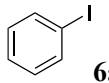
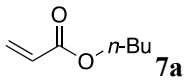
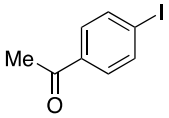


Figure S1. Appearance of extraction of the reaction mixture with ethyl acetate

Table S1. Mizoroki-Heck reactions in water using Pd catalysts.[a]



entry	ArI **6**	Alkenes **7**	surfactant	Catalysts	base	Products	Yield of **8**/%[b]
1	 **6a**	 **7a**	**NS**	**Pd-2-N**	*n*-Bu_3N	**8aa**	92
2	 **6a**	 **7a**	**NS**	**Pd-5** (small molecule)	*n*-Bu_3N	**8aa**	33
3	 **6b**	**7a**	**NS**	**Pd-2-N**	*n*-Bu_3N	**8ba**	>99
4	**6a**	**7b**	**NS**	**Pd-2-N**	*n*-Bu_3N	**8ab**	9
5	**6a**	**7a**	SDS	**Pd-2-N**	*n*-Bu_3N	**8aa**	>99
6	**6a**	**7a**	Triton X-100	**Pd-2-N**	*n*-Bu_3N	**8aa**	>99
7	**6a**	**7a**	Tween20	**Pd-2-N**	*n*-Bu_3N	**8aa**	>99
8	**6a**	**7a**	CTAB	**Pd-2-N**	*n*-Bu_3N	**8aa**	81
9	**6a**	**7a**	none	**Pd-2-N**	*n*-Bu_3N	**8aa**	86
10	**6a**	**7a**	**NS**	**Pd-2-N**	K_2CO_3	**8aa**	23
11	**6a**	**7a**	**NS**	**Pd-2-N**	NaOAc	**8aa**	12
12	**6a**	**7a**	**NS**	**Pd-2-N**	K_3PO_4	**8aa**	29
13	**6a**	**7a**	**NS** (2nd use)	**Pd-2-N** (2nd use)	*n*-Bu_3N	**8aa**	99
14	**6a**	**7a**	(3rd use)	(3rd use)	*n*-Bu_3N	**8aa**	>99
15	**6a**	**7a**	(4th use)	(4th use)	*n*-Bu_3N	**8aa**	>99
16	**6a**	**7a**	(5th use)	(5th use)	*n*-Bu_3N	**8aa**	>99
17	**6a**	**7a**	(6th use)	(6th use)	*n*-Bu_3N	**8aa**	>99
18	**6a**	**7a**	(7th use)	(7th use)	*n*-Bu_3N	**8aa** **8aa**	58
19	**6a**	**7a**	**Pd-2-NS**	**Pd-2-NS**	*n*-Bu_3N	**8aa**	93
20	**6a**	**7a**	**Pd-2-NS** (2nd use)	**Pd-2-NS** (2nd use)	*n*-Bu_3N	**8aa**	97
21	**6a**	**7a**	(3rd use)	(3rd use)	*n*-Bu_3N	**8aa**	75
22	**6a**	**7a**	(4th use)	(4th use)	*n*-Bu_3N	**8aa**	98
23	**6a**	**7a**	(5th use)	(5th use)	*n*-Bu_3N	**8aa**	107

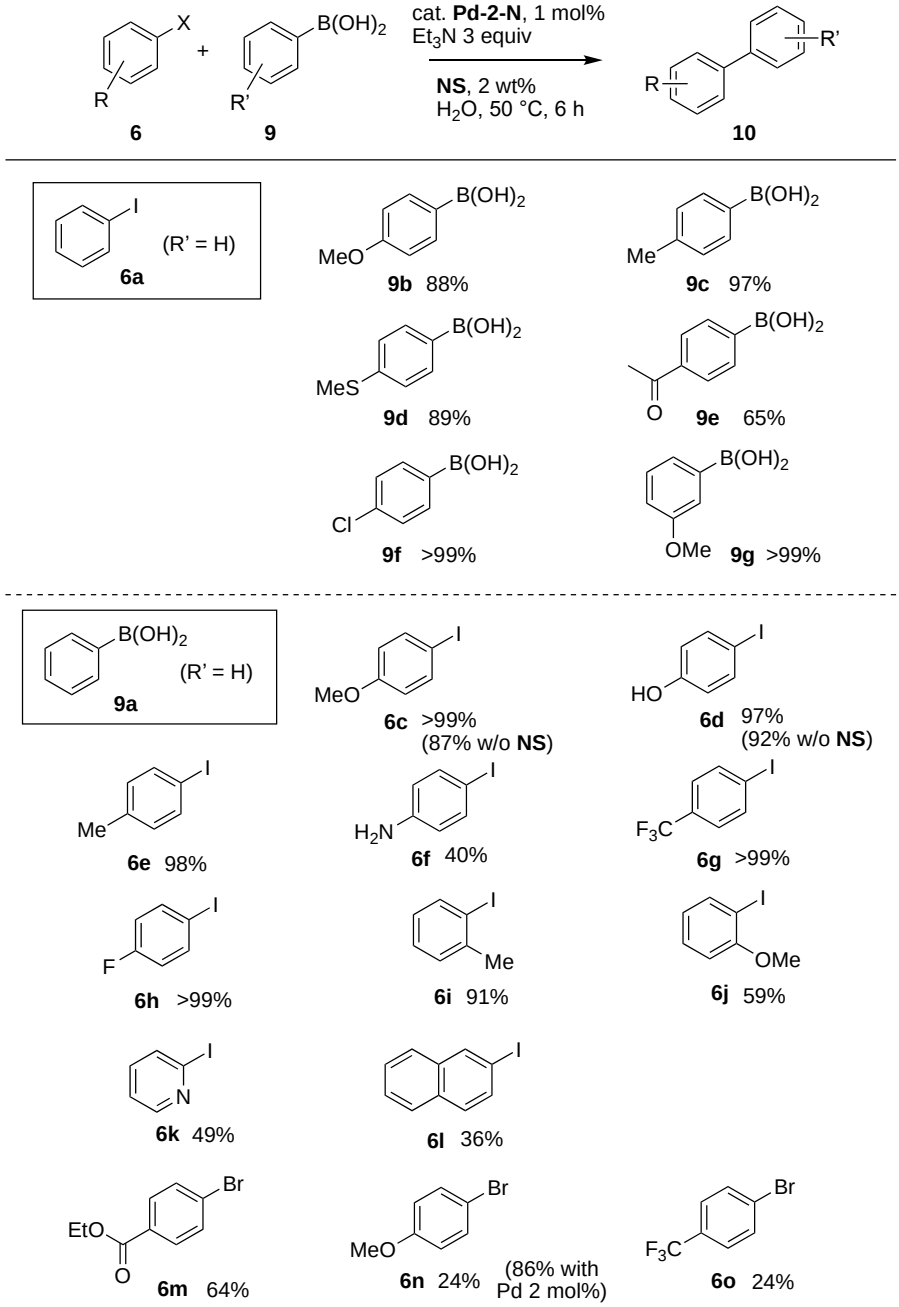
a) Conditions: iodoarene (0.5 mmol), alkene (1.0 mmol), catalyst (0.005 mol Pd atom), hydrazine (0.05 mol), surfactants (40 mg), H_2O (4 mL), 70 °C, 48 h.

b) determined by ^1H NMR.

3-2. Suzuki-Miyaura cross coupling reactions in water using **Pd-2-N**.

Typically, in a test tube with a screw cap, 4-iodoanisole (**6c**) (117 mg, 0.5 mmol) and phenylboronic acid (**9a**) (91 mg, 0.75 mmol), triethylamine (152 mg, 1.5 mmol), **NS** (20 mg) and **Pd-2-N** (e.g. 13 mg, containing 0.005 mmol of Pd) were suspended in water (1 mL). The mixture was stirred at 50 °C for 6 h. The reaction mixture was cooled to 0 °C, and then extracted with ethyl acetate (0.2 mL) followed by centrifugation (400 *g* for 2 min). The organic layer was analyzed by ^{1}H NMR using pyrene as an internal standard. Quantitative formation of **10ca** was observed.

Table S2. Suzuki-Miyaura coupling in water using Pd-catalysts.



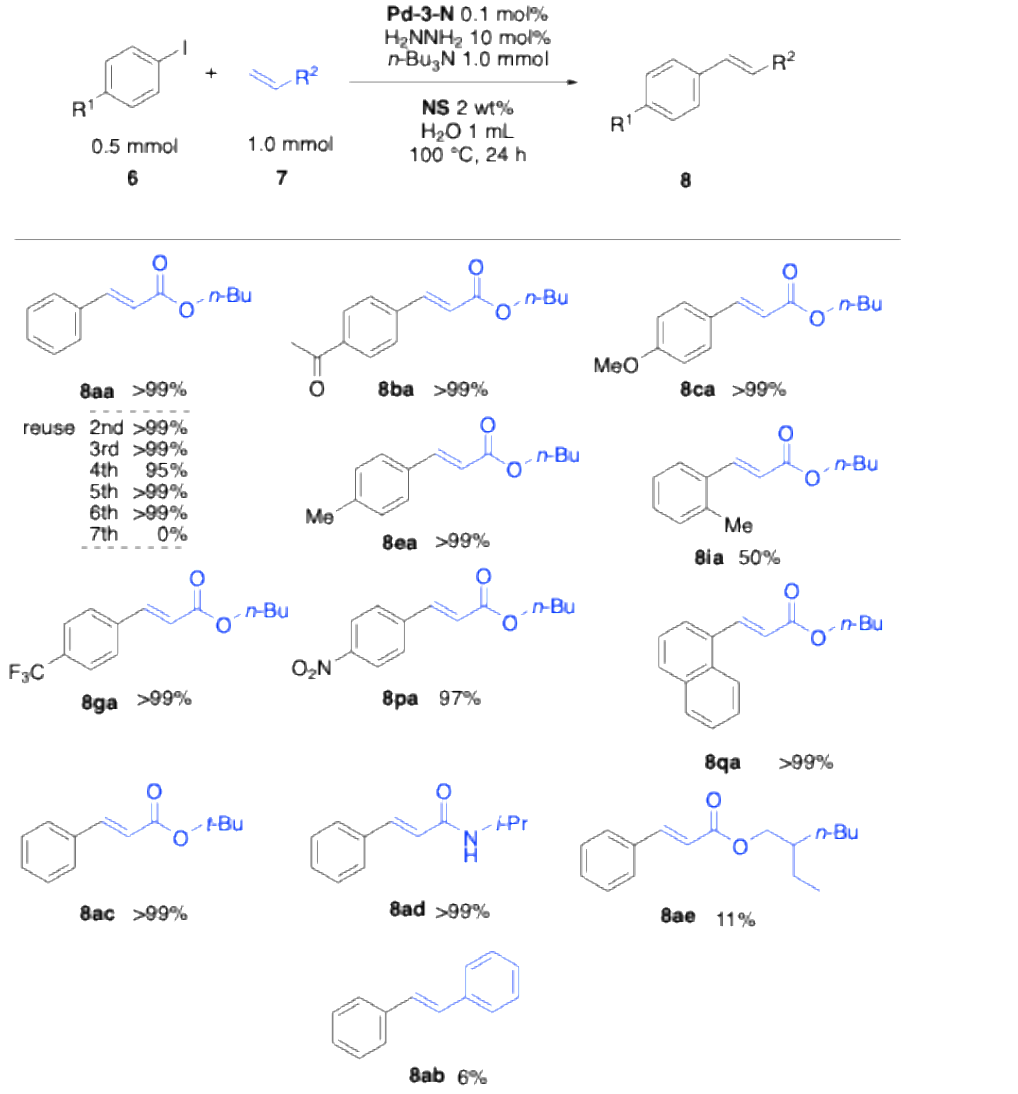
a) Conditions: aryl halide **6** (0.5 mmol), arylboronic acid **9** (0.75 mmol), **Pd-2-N** (containing 1 mol% Pd), Et_3N (1.5 mmol), **NS** (20 mg), H_2O (1 mL), yields were determined by ^{1}H NMR.

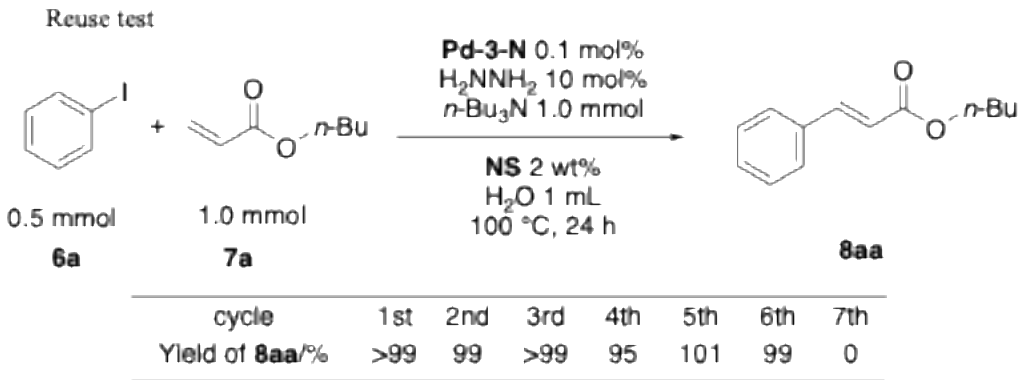
3-3. Mizoroki-Heck reactions in water using the copolymers using **Pd-3-N** in the *presence* of **NS**, and reuse of the catalyst solution.

Typical procedure for Mizoroki-Heck reaction in water using the thermo-responsive catalyst **Pd-3-N** in the presence of the thermo-responsive copolymer surfactant **NS** is as follows.

In a test tube with a screw cap, **Pd-3-N** (2.9 mg, 0.5 μmol) and **NS** (20 mg) was dissolved in deionized water (1 mL) and the solution was stirred at r.t. for 0.5 h. To this solution, iodobenzene (**6a**) (102 mg, 0.5 mmol), *n*-butyl acrylate (**7a**) (128 mg, 1.0 mmol), tri-*n*-butylamine (185 mg, 1.0 mmol), hydrazine monohydrate (2.5 mg, 50 μmol) were added, and the mixture was stirred at 100 °C for 24 h. Ethyl acetate (1 mL) was added and vigorously stirred and centrifuged. The organic layer was separated and repeated the extraction until the product was not observed by thin layer chromatograph (TLC) in the extract. The combined brownish organic layer was analyzed by ^{1}H NMR and/or gas chromatograph to determine yield of the product **8aa** (>99%). When the catalyst solution was reused, the aqueous layer after the extraction were added tributylamine (185 mg, 1.0 mmol), butyl acrylate (128 mg, 1.0 mmol) and Iodobenzene (102 mg, 0.5 mmol). The mixture was stirred at 100 °C for 24 h, and extracted with ethyl acetate (0.4 mL) for three times. The combined organic layer was analyzed by gas chromatography to determine the yield using tetradecane as internal standard.

Table S3. Mizoroki-Heck reactions in water using **Pd-3-N** in the presence of **NS**.



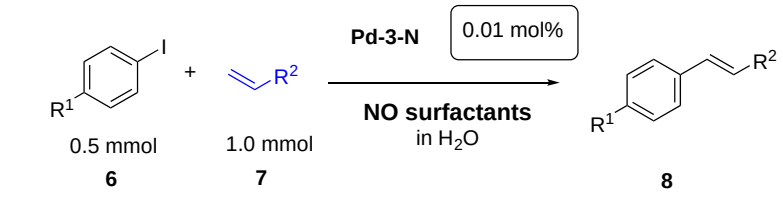


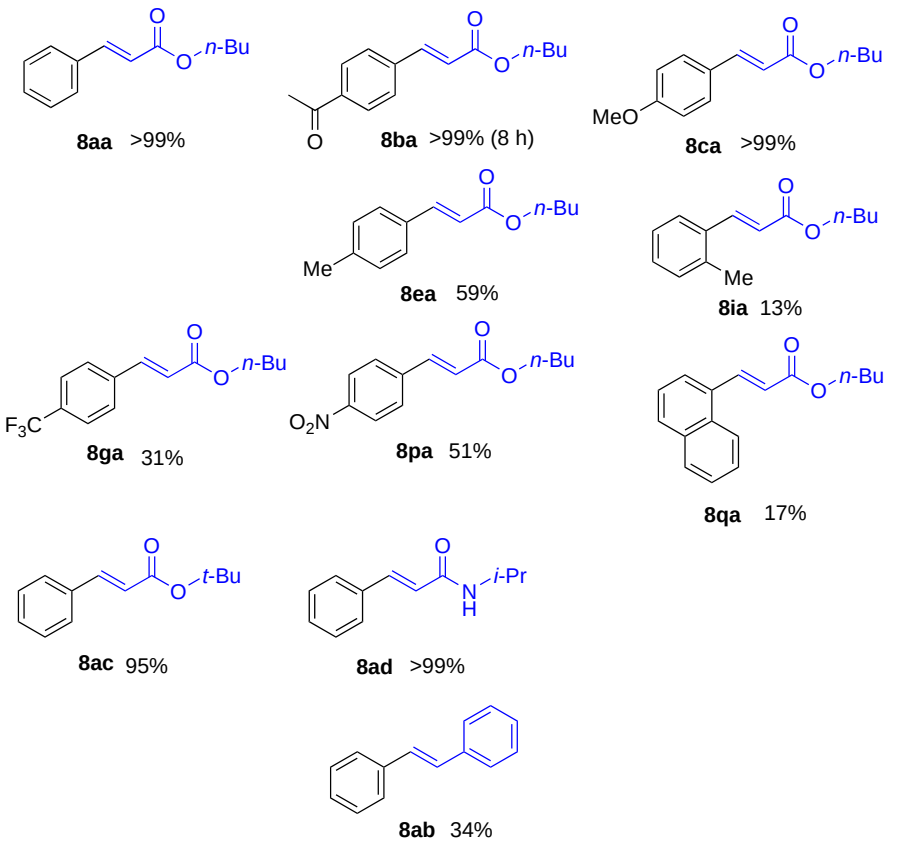
cycle	1st	2nd	3rd	4th	5th	6th	7th
Yield of **8aa**/%	>99	99	>99	95	101	99	0

Figure S2. Reuse of the aqueous solution of **Pd-3-N**, in the presence of **NS**.

3-4. Mizoroki-Heck reactions in water using the copolymers using **Pd-3-N** in the *absence* of **NS**.
Typical procedure for Mizoroki-Heck reaction in water using the thermo-responsive catalysts in the *absence* of **NS** is as follows.
Stock solution of the catalyst was prepared by dissolving **Pd-3-N** (2.9 mg, 0.5 μmol) in degassed water (1 mL) and stirred at r.t. for 10 min. The pale-yellow solution was stored in a refrigerator. In a dried test tube with a screw cap, the catalyst solution (0.1 mL) was added to water (0.9 mL) and the mixture was stirred for 10 min. To this solution, aryl halide (**6**) (0.5 mmol), alkene (**7**) (1.0 mmol), tri-*n*-burylamine (185 mg, 1.0 mmol), hydrazine monohydrate (2.5 mg, 50 μmol) were added, and the mixture was stirred at 100 °C for 24 h. The mixture was extracted with ethyl acetate (1 mL) and centrifuged. The organic layer was separated and repeated the extraction until the product was not observed by thin layer chromatograph (TLC) in the extract. The combined organic layer was analyzed by ^{1}H NMR and gas chromatograph to determine yield of the product **8**. Some of the products were isolated by column chromatograph on silica gel.

Table S4. Mizoroki-Heck reactions in water using **Pd-3-N** in the *absence* of **NS.**[a]

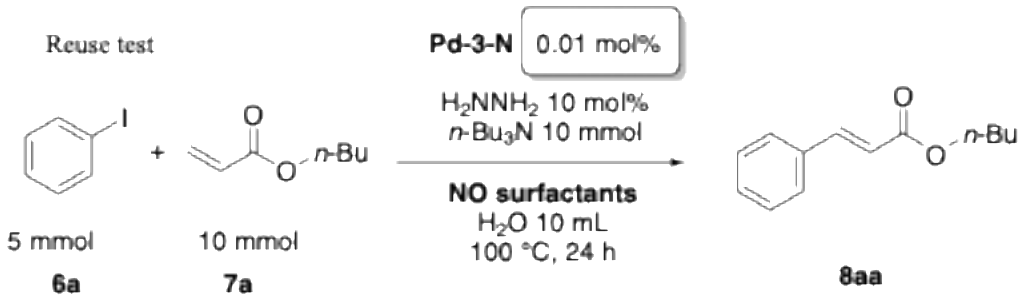




a) conditions: iodoarenes **6** (0.5 mmol), alkenes **7** (1.0 mmol), *n*-Bu_3N (1.5 mmol), **Pd-3-N** (0.29 mg, 0.05 μmol Pd), N_2H_4•H_2O (0.05 mmol), H_2O 1 mL, 100 °C, 24 h; Yields were determined by ^1H NMR.

3-5. Reuse of the aqueous solution of **Pd-3-N**, with no surfactants in 10 times scale.

In a dried test tube with a screw cap, the catalyst **Pd-3-N** (2.9 mg, 0.5 μmol) was dissolved in water (10 mL) and the mixture was stirred for 10 min. To this solution, iodobenzene (**6a**) (1.02 g, 5.0 mmol), *n*-butyl acrylate (**7a**) (1.28 g, 10 mmol), tri-*n*-burylamine (1.85 g, 10 mmol), hydrazine monohydrate (25 mg, 0.5 mmol) were added, and the mixture was stirred at 100 °C for 8 h. By keeping the solution rest, the mixture spontaneously separated into a brown organic layer, a yellowish aqueous layer and brown organic gel-like precipitate. The mixture was centrifuged to clearly separate them, and the upper organic layer and the bottom precipitate were taken up. The combined organic layer was analyzed by gas chromatography to determine yield of the product **8aa**. To the aqueous layer were added tri-*n*-butylamine (1.85 g, 10 mmol), *n*-butyl acrylate (1.28 g, 10 mmol) and iodobenzene (1.02 g, 5.0 mmol), and the second reaction was conducted.

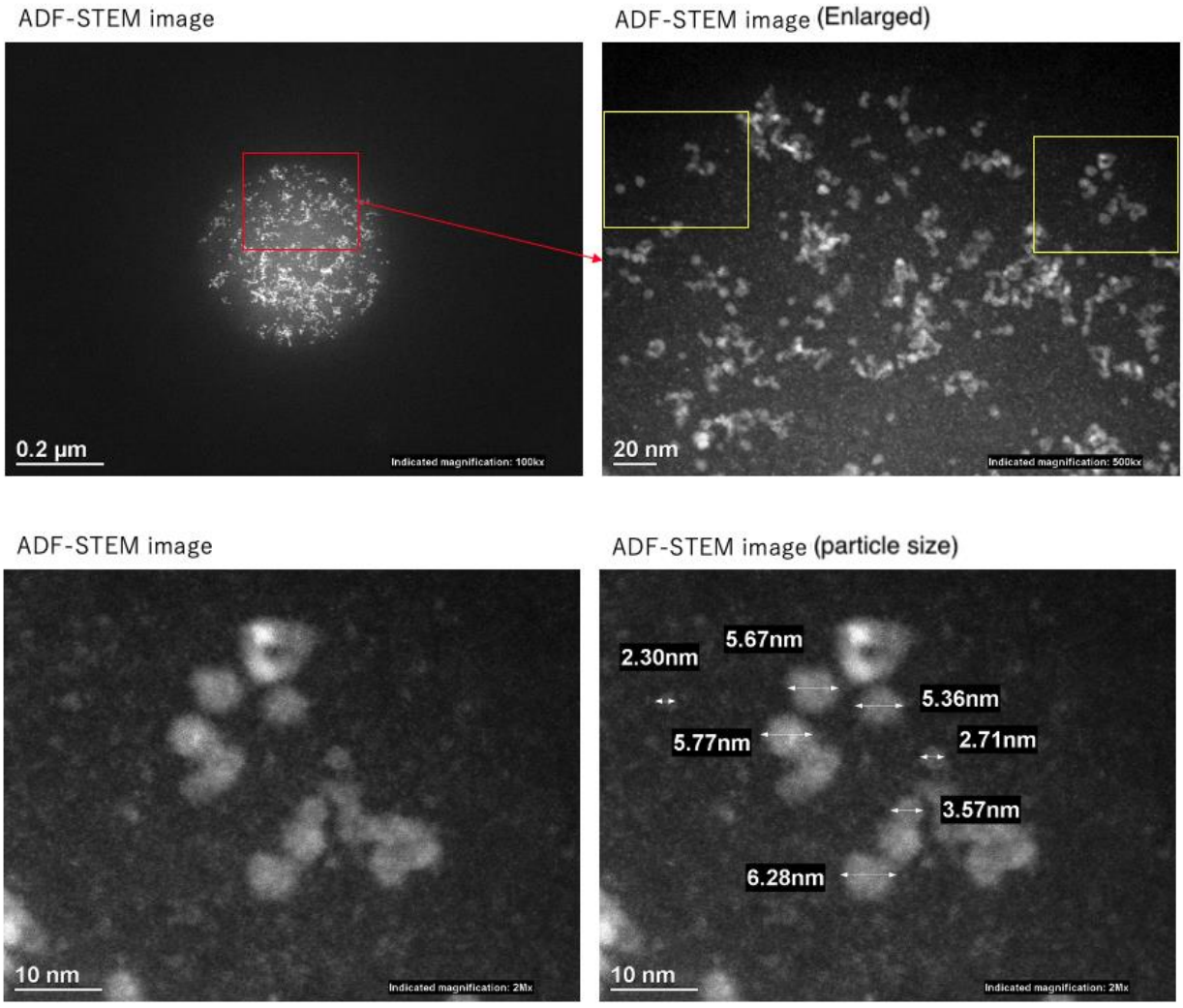


cycle	1st	2nd	3rd	4th	5th	6th	7th	6th	7th
Yield of **8aa**/%	73	78	125	118	101	106	103	98	26

Figure S3. Reuse of the aqueous solution of **Pd-3-N**, in the absence of **NS**.

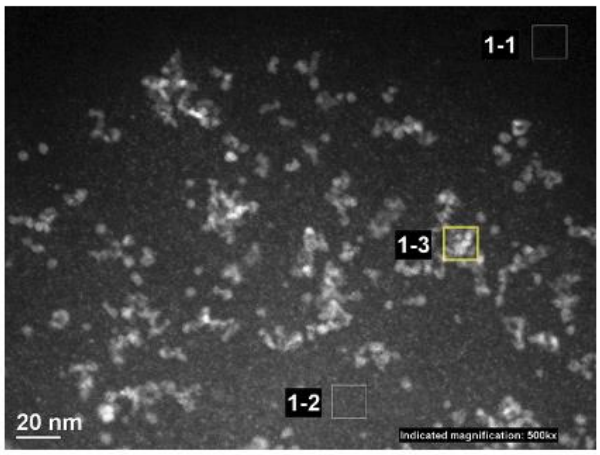
3-6. STEM analysis of the aqueous solution of the catalyst.
The catalytic reactions were carried out under the standard conditions using **Pd-2-N**, the aqueous solution was dried and observed by STEM.

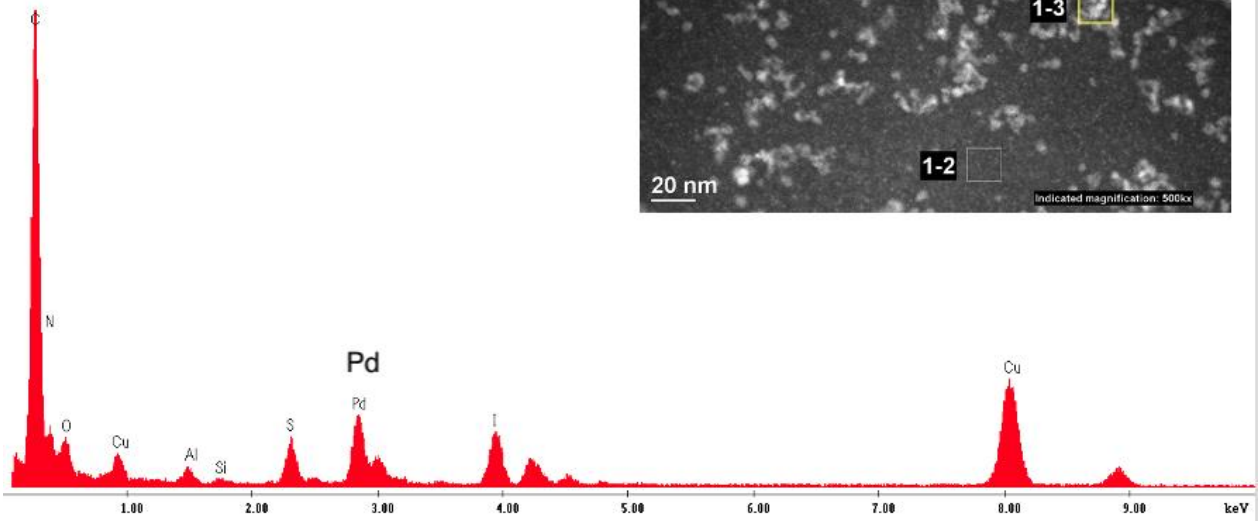
3-6-1. Mizoroki-Heck reaction



EDX spectrum for part 1-3

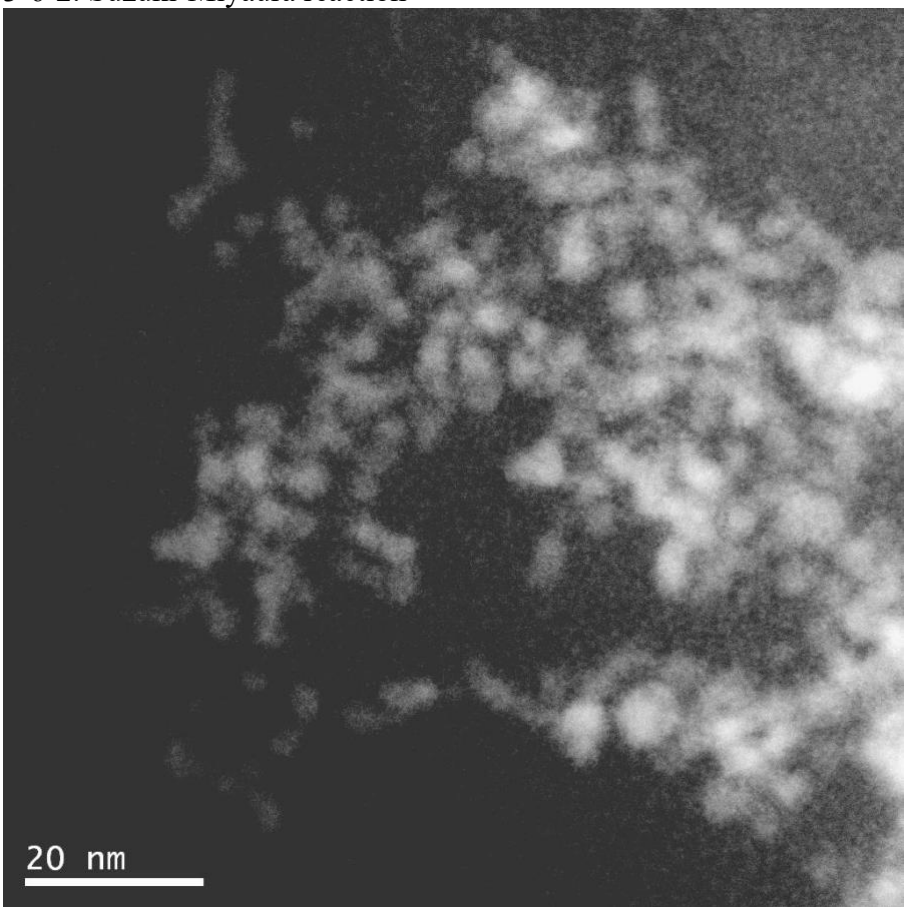
ADF-STEM image(EDX分析箇所)



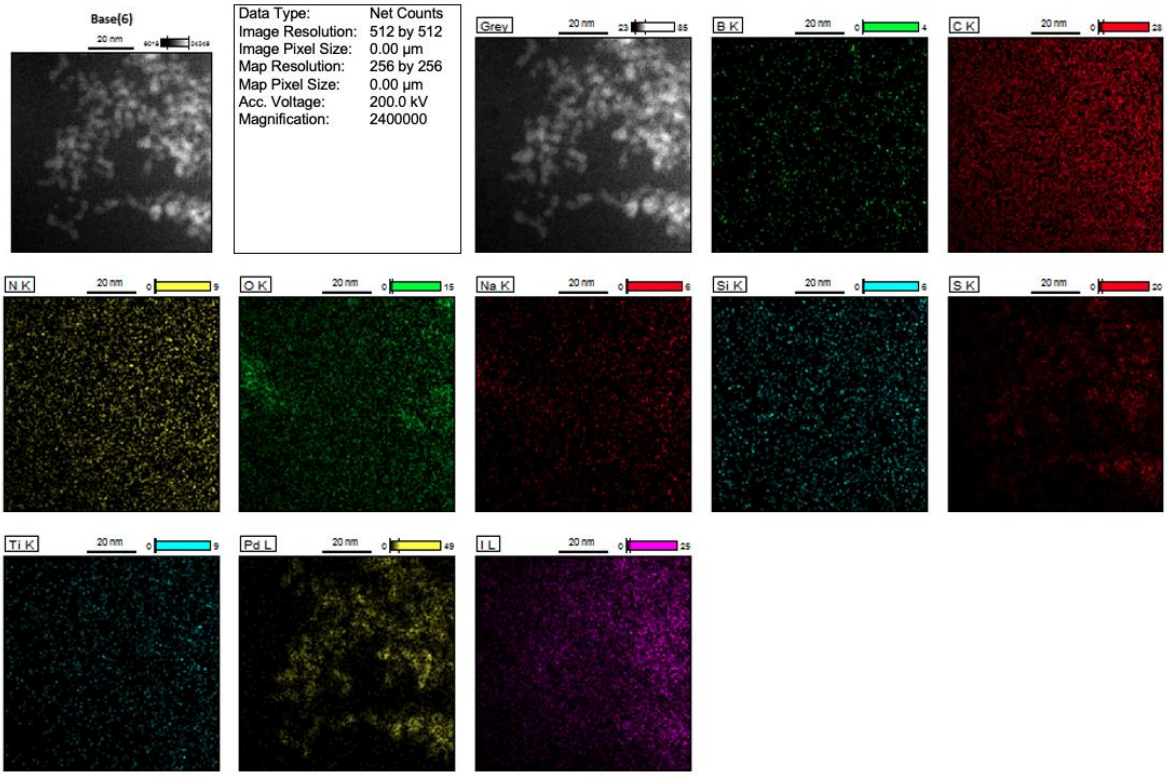


※Al,Si,Cuはシステムピーク

3-6-2. Suzuki-Miyaura reaction



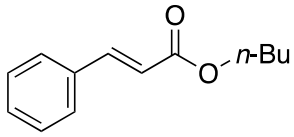
Project: 20240612



4. Spectroscopic data for the catalytic reactions in water.

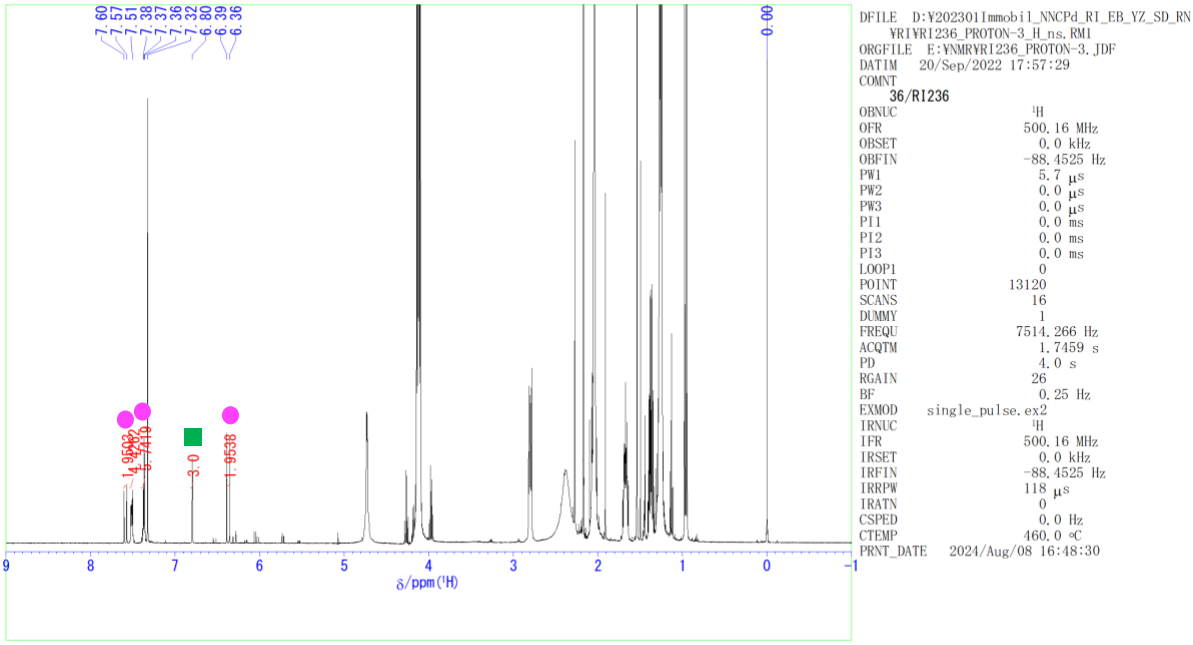
4.1. Mizoroki-Heck reactions in water.

Butyl (*E*)-3-phenylacrylate (**8aa**) [17]

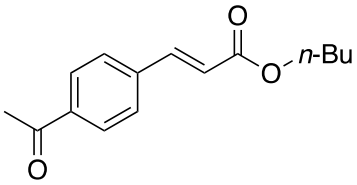


^{1}H NMR

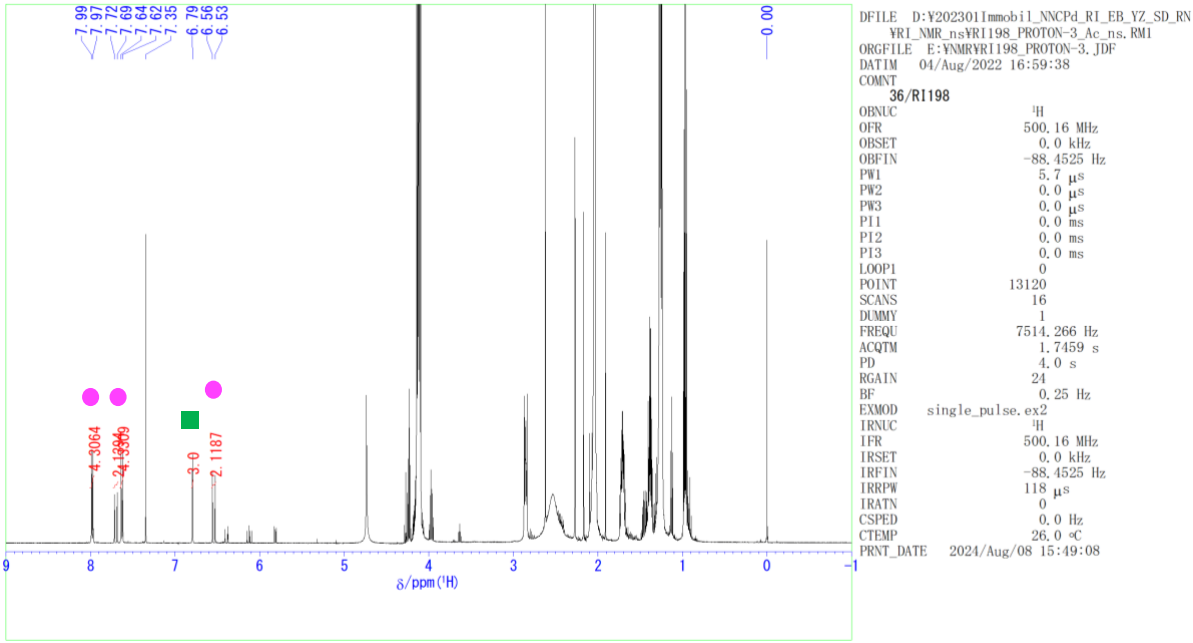
(Y >99%, Reaction mixture) ■ : internal standard (mesitylene), ● : the product



Butyl (E)-3-(4-acetylphenyl)acrylate (**8ba**) [17]

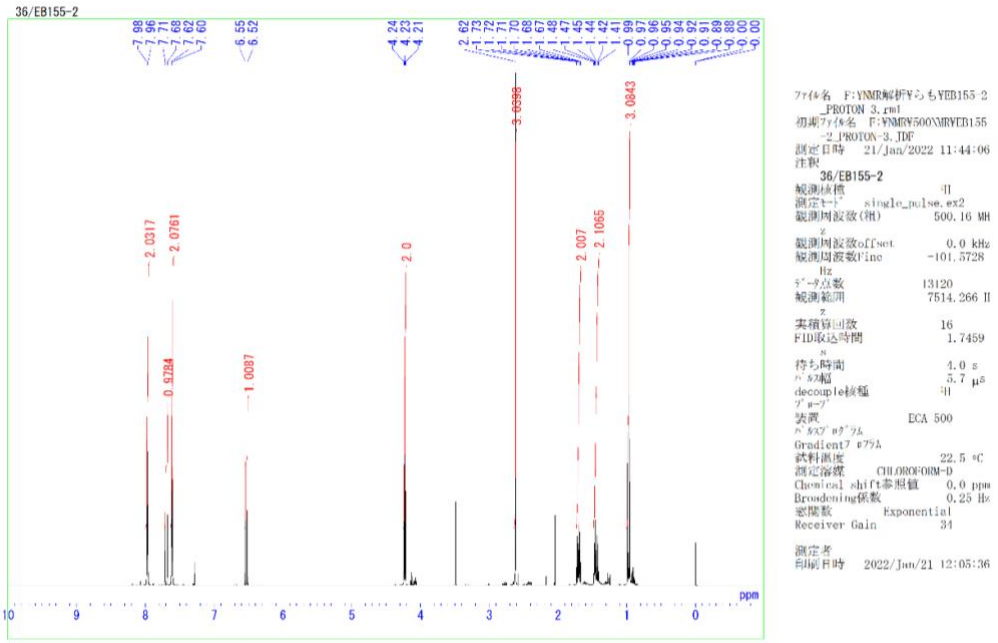


^{1}H NMR (Y >99%, reaction mixture) ■ : internal standard (mesitylene), ● : the product

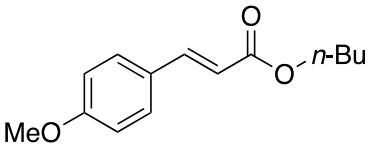


Isolated (ethyl acetate is contained).

^{1}H NMR ($CDCl_3$, Me_4Si, 500 MHz): δ = 0.97 (t, 3H, *J* = 7.3 Hz, C*H*$_3$), 1.40-1.49 (m, 2H, C*H*$_2$), 1.66-1.74 (m, 2H, C*H*$_2$), 2.62 (s, 3H, C*H*$_3$), 4.23 (t, 2H, *J* = 6.7 Hz, OC*H*$_2$), 6.54 (d, 1H, *J* = 16 Hz, C*H*), 7.61 (d, 2H, *J* = 8.2 Hz), 7.70 (d, 1H, *J* = 16 Hz, C*H*), 7.97 (d, 2H, *J* = 8.6 Hz).

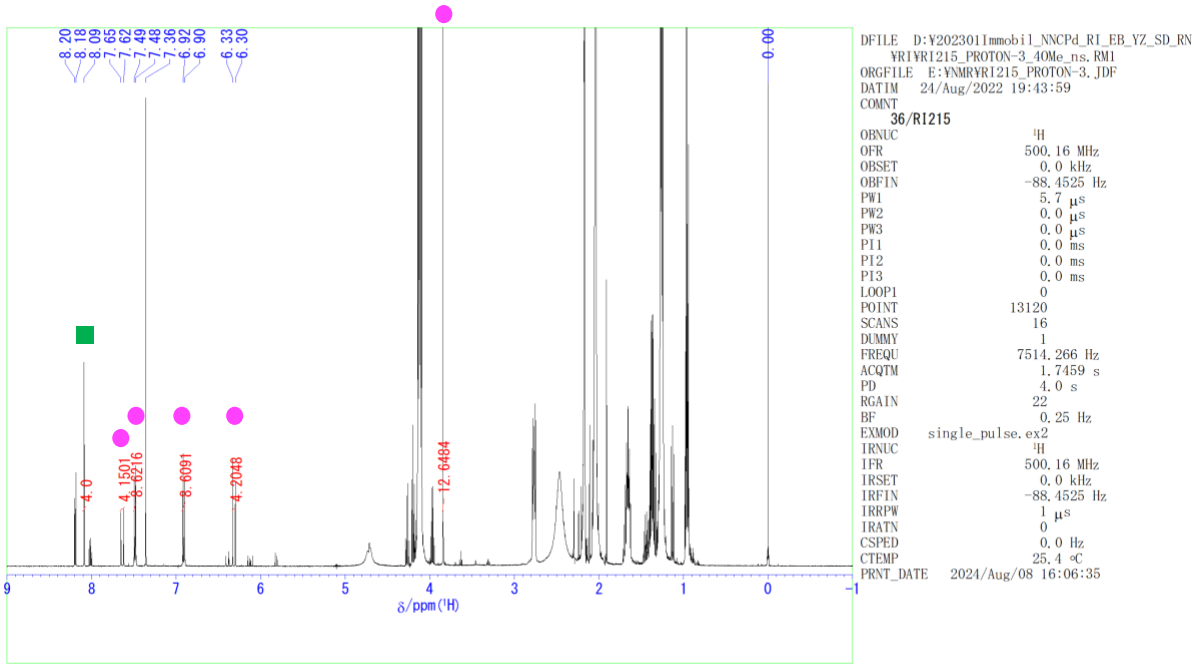


Butyl (E)-3-(4-methoxyphenyl)acrylate (**8ca**) [17]

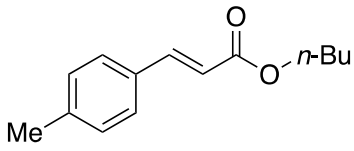


^{1}H NMR

(Y >99%, reaction mixture) ■ : internal standard (pyrene), ● : the product

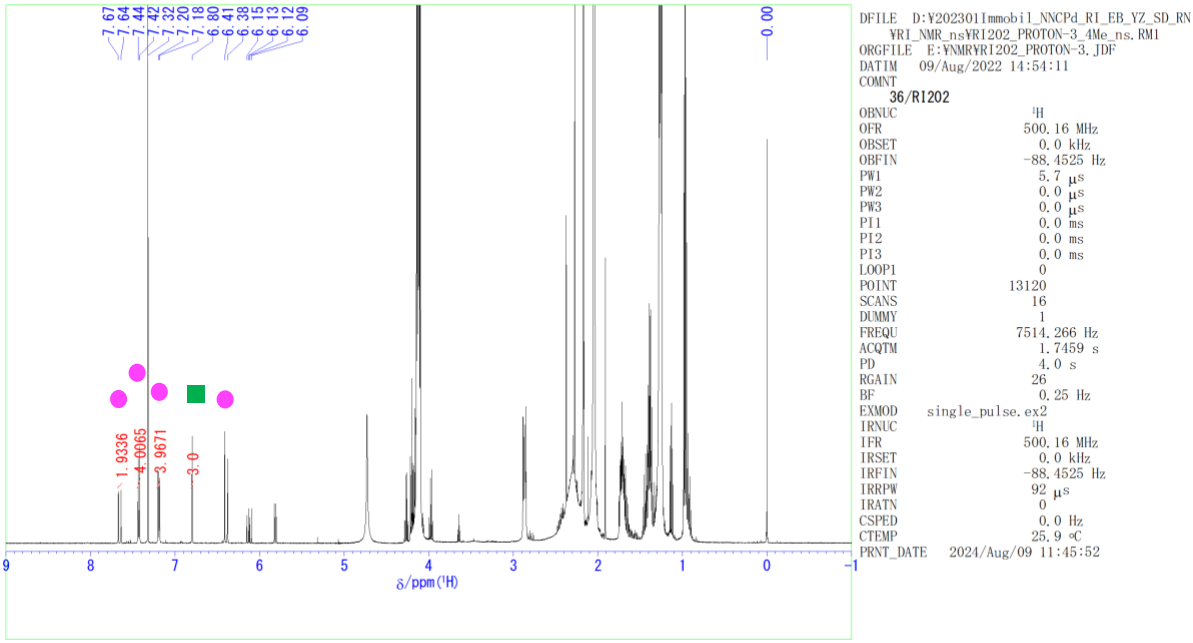


Butyl (E)-3-(4-methylphenyl)acrylate (**8ea**) [17]

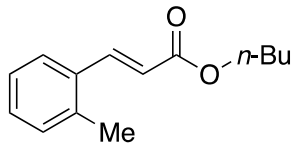


^{1}H NMR

(Y >99%, reaction mixture) ■ : internal standard (mesitylene), ● : the product

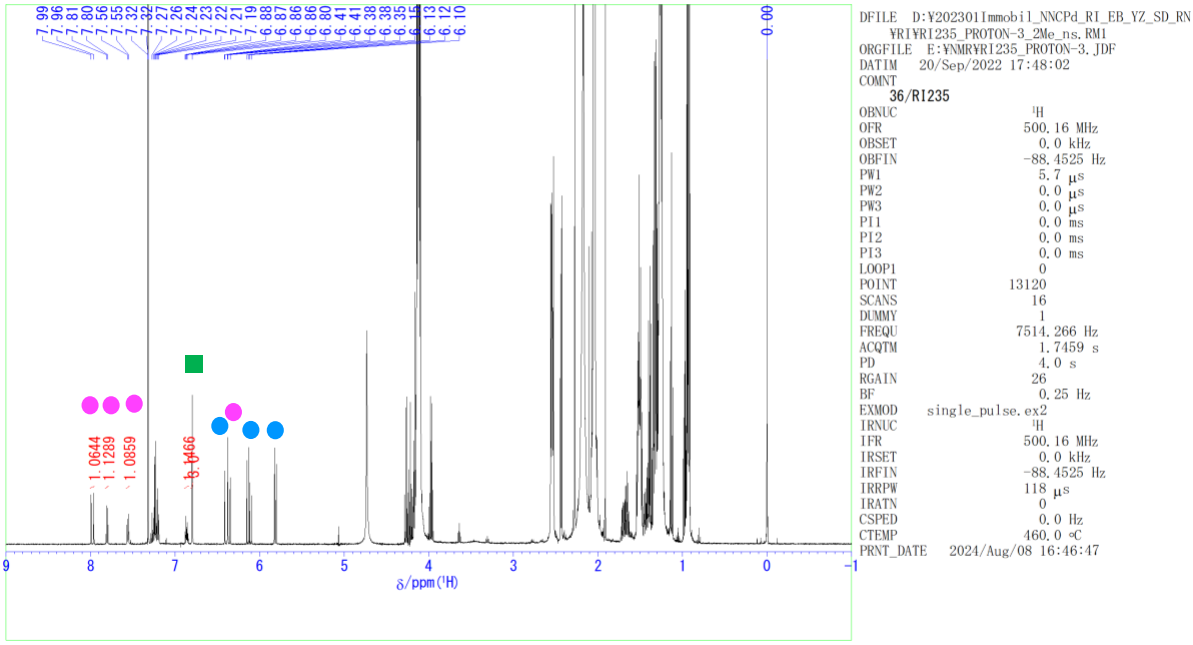


Butyl (E)-3-(2-methylphenyl)acrylate (**8ia**) [1]

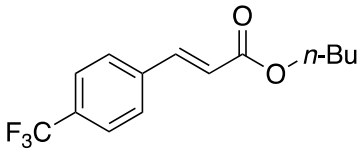


^{1}H NMR

(Y 50%, reaction mixture) ■ : internal standard (mesitylene), ● : the product, ● starting materials

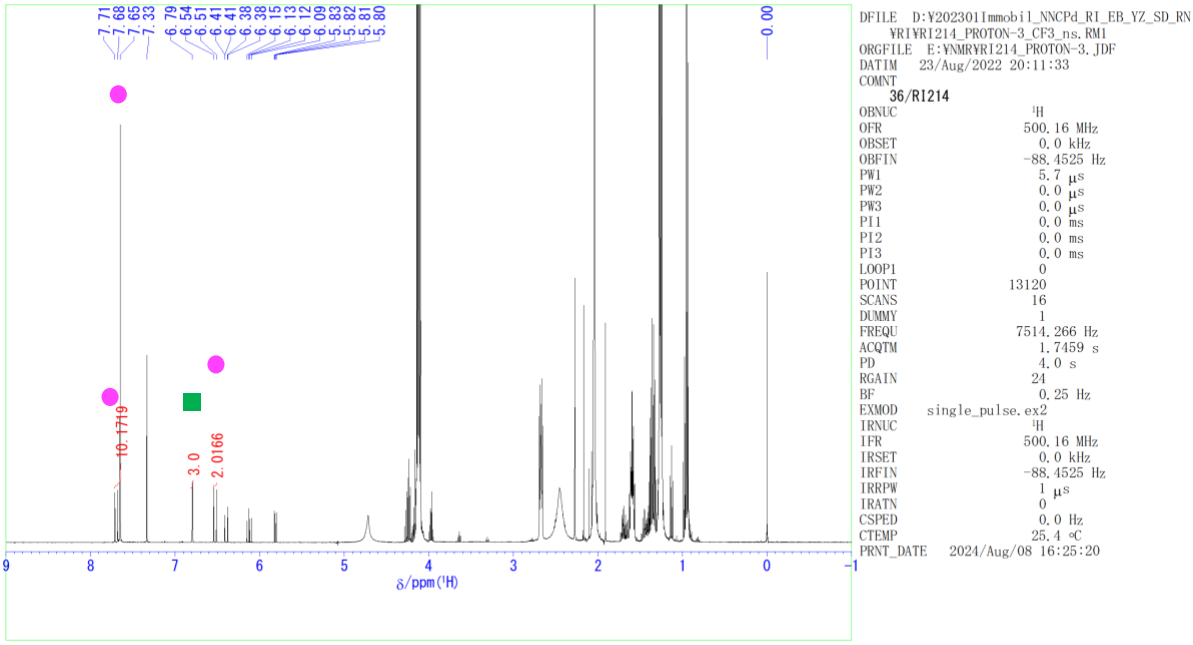


n-Butyl (*E*)-3-(4-trifluoromethylphenyl)acrylate (**8ga**) [17]

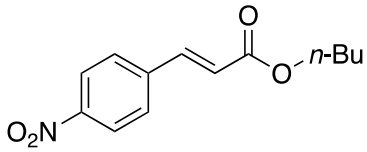


^{1}H NMR

(Y >99%, reaction mixture) ■ : internal standard (mesitylene), ● : the product

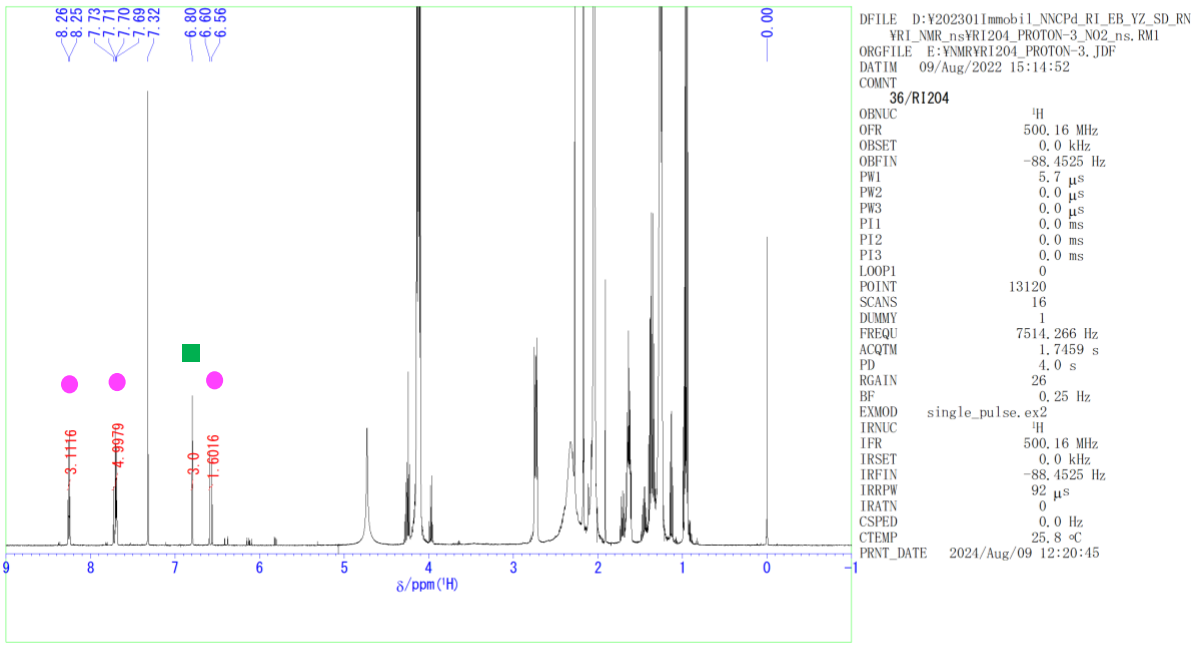


n-Butyl (*E*)-3-(4-nitrophenyl)acrylate (**8pa**) [17]

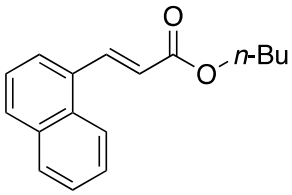


^{1}H NMR

(Y 97%, reaction mixture) ■ : internal standard (mesitylene), ● : the product

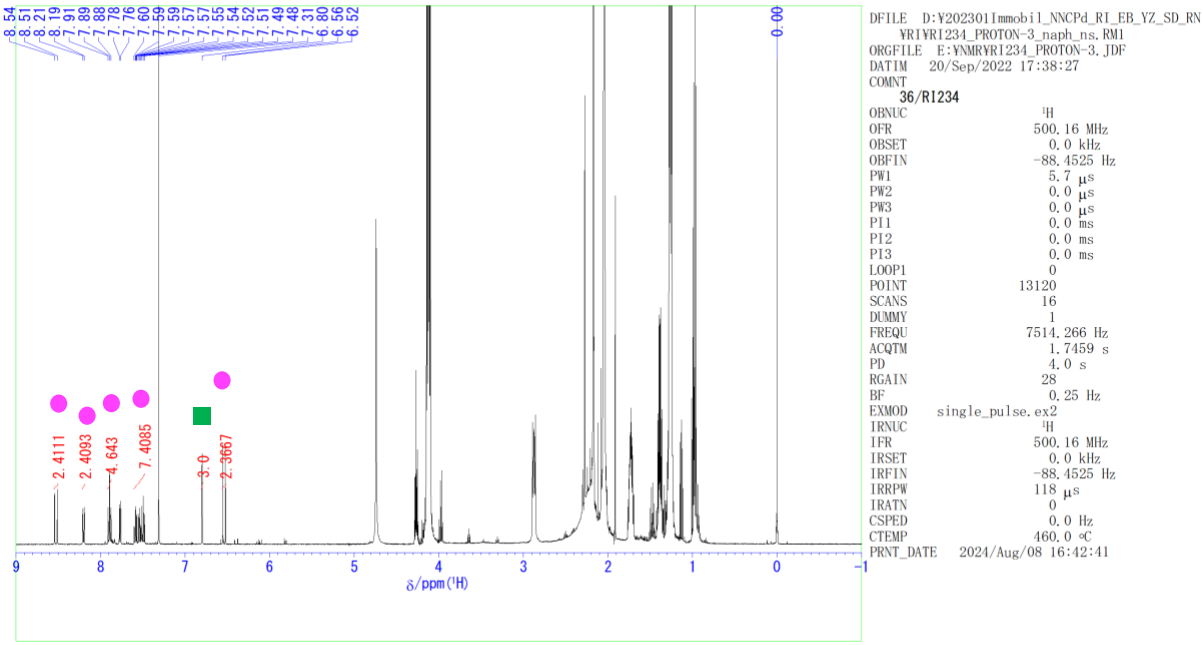


n-Butyl (*E*)-3-(1-naphthyl)acrylate (**8qa**) [1]

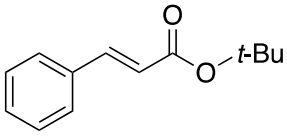


(Y >99%, reaction mixture) ■ : internal standard (mesitylene), ● : the product

^{1}H NMR

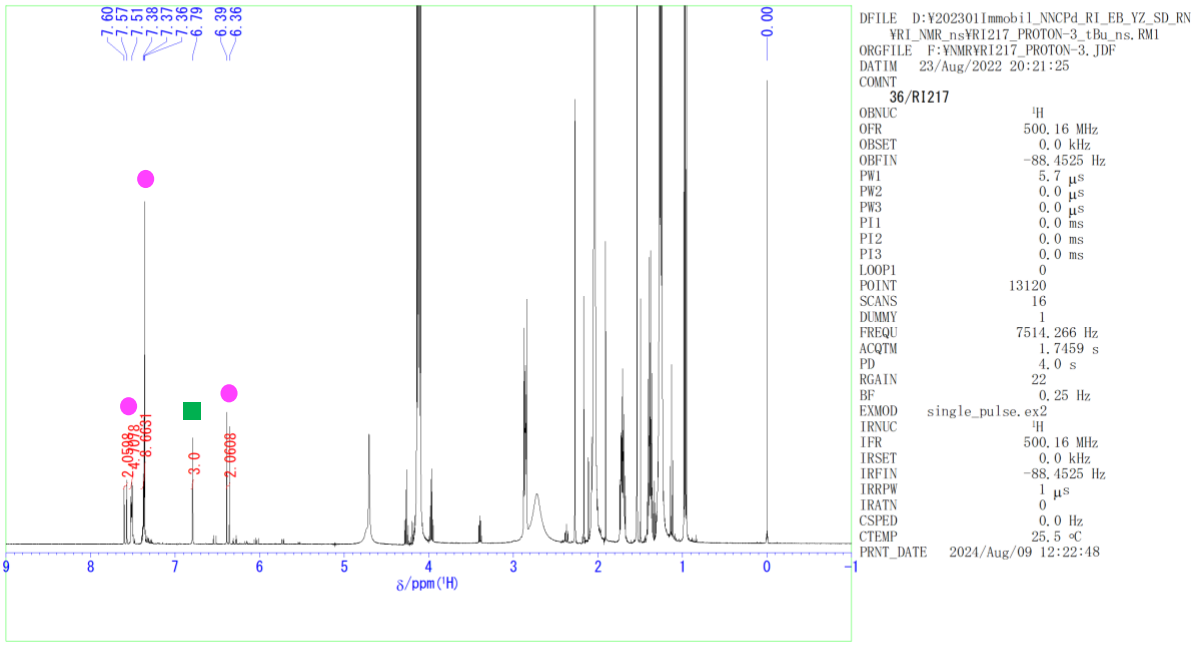


tert-Butyl (*E*)-3-phenylacrylate (**8ac**) [1]

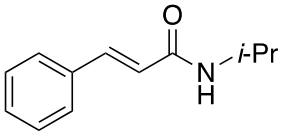


^{1}H NMR

(Y >99%, reaction mixture) ■ : internal standard (mesitylene), ● : the product

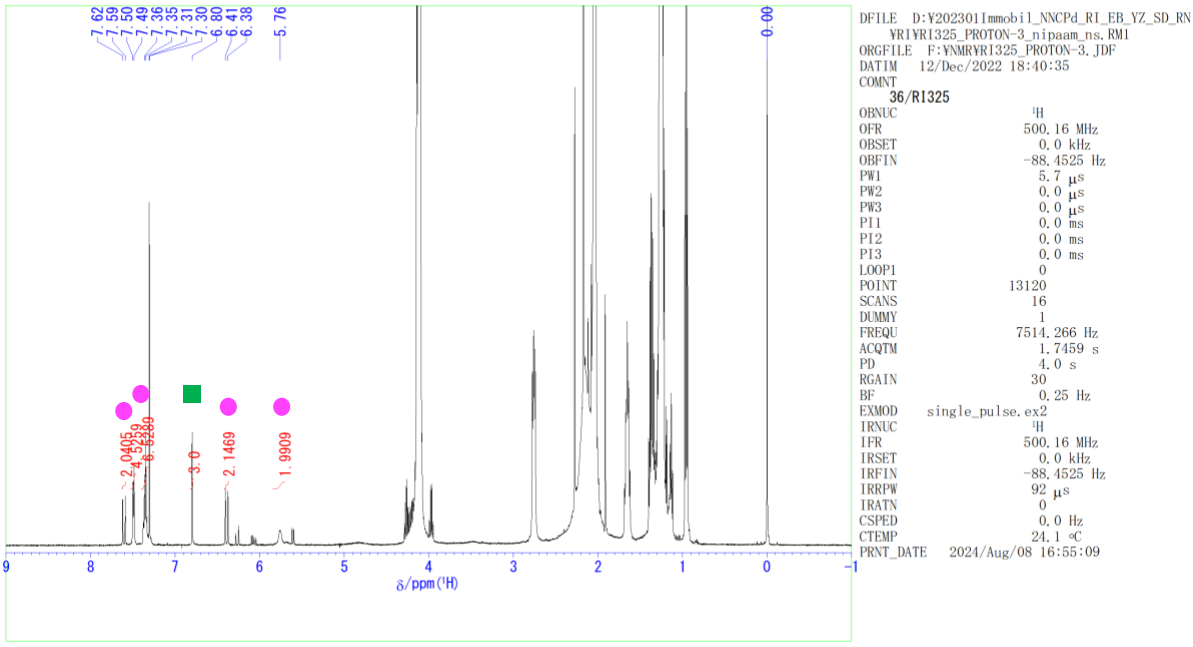


N-Isopropyl (*E*)-3-phenylacryliamide (**8ad**) [17]

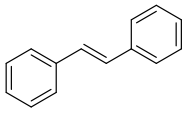


^{1}H NMR

(Y >99%, reaction mixture) ■ : internal standard (mesitylene), ● : the product

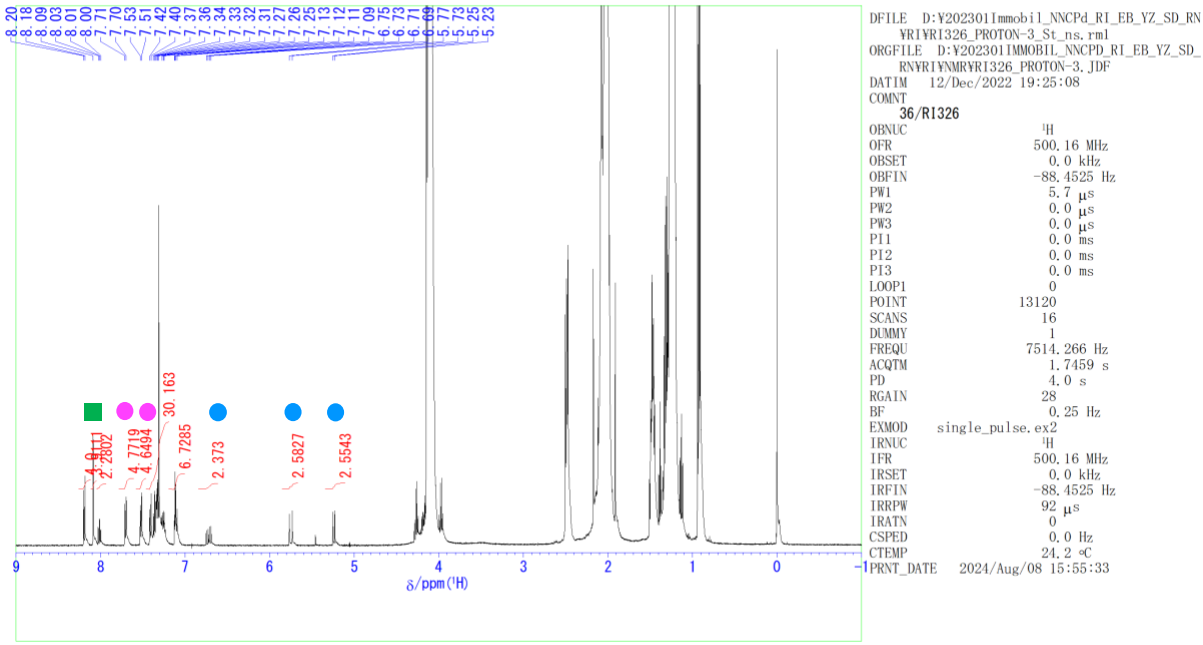


(E)-Stilbene (**8ab**) [17]



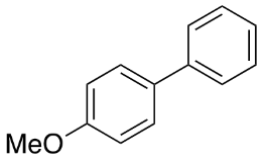
^{1}H NMR

(Y 34%, reaction mixture) ■ : internal standard (pyrene), ● : the product, ● starting materials

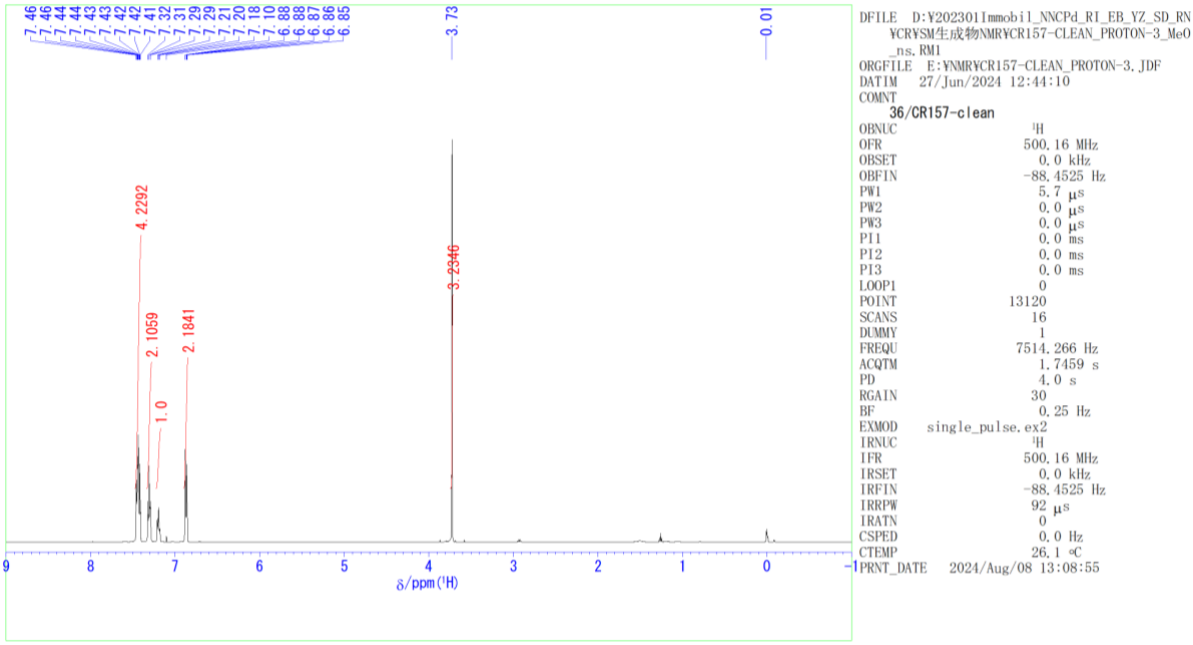


4.2. Suzuki-Miyaura cross coupling reactions in water.

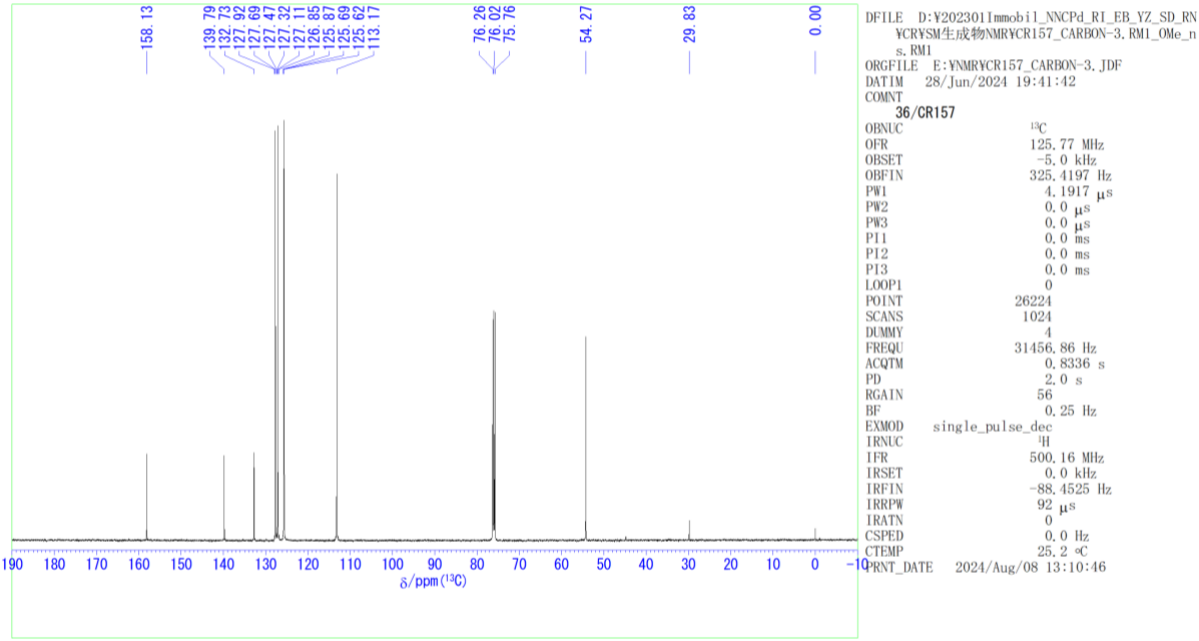
4-Methoxybiphenyl (**10ab**) [18, 19]



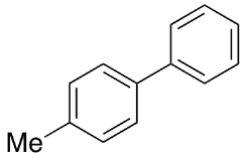
^{1}H NMR (isolated)



^{13}C{^{1}H} NMR

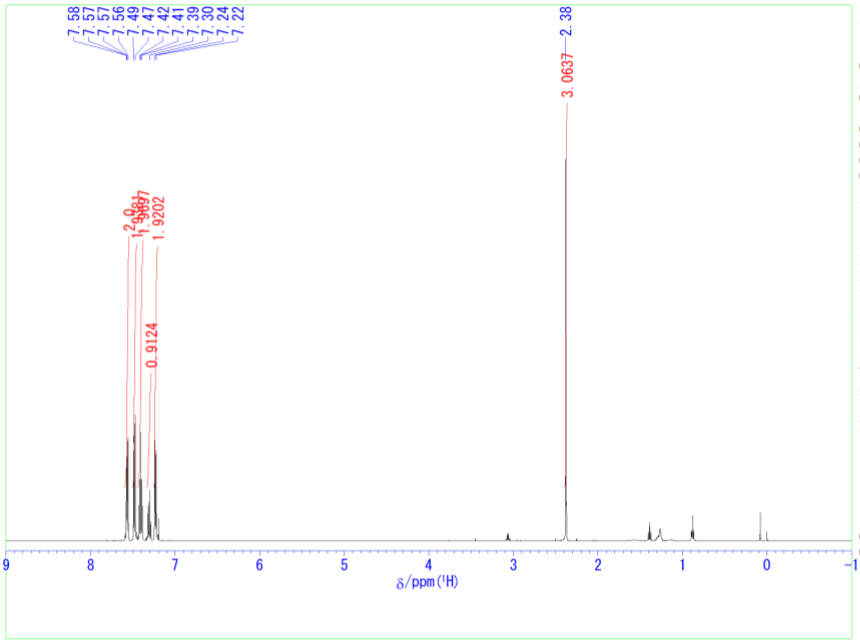


4-Methoxybiphenyl (**10ac**) [18, 19]



98% by ^{1}H NMR isolated 56%

^{1}H NMR

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    M1
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     36/CR175-3
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OBSET                 0.0 kHz
OBFIN               -82.7305 Hz
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PW2                   0.0 μs
PW3                   0.0 μs
PI1                   0.0 ms
PI2                   0.0 ms
PI3                   0.0 ms
LOOP1                    0
POINT                13120
SCANS                   16
DUMMY                    1
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ACQTM                 1.7459 s
PD                    4.0 s
RGAIN                   32
BF                    0.25 Hz
EXMOD     single_pulse.ex2
IRNUC                    ¹H
IFR                 500.16 MHz
IRSET                 0.0 kHz
IRFIN               -88.4525 Hz
IRRPW                  92 μs
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CTEMP                 25.6 ℃
PRNT_DATE   2024/Aug/08 13:20:51
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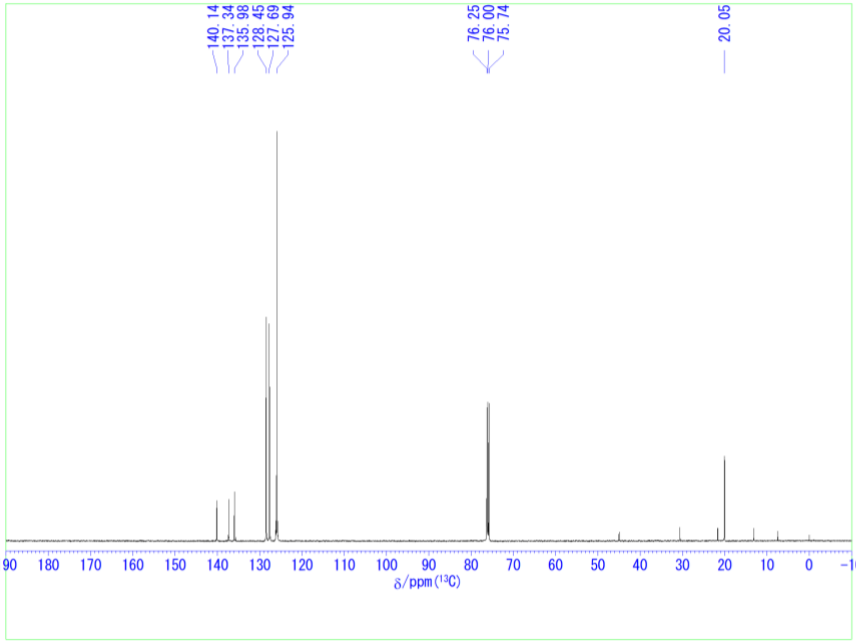
^{13}C{^{1}H} NMR

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OBSET                 -5.0 kHz
OBFIN               321.8213 Hz
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PW2                   0.0 μs
PW3                   0.0 μs
PI1                   0.0 ms
PI2                   0.0 ms
PI3                   0.0 ms
LOOP1                    0
POINT                26224
SCANS                 1024
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ACQTM                0.8336 s
PD                    2.0 s
RGAIN                   52
BF                    0.25 Hz
EXMOD     single_pulse_dec
IRNUC                    ¹H
IFR                 500.16 MHz
IRSET                 0.0 kHz
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CTEMP                 25.6 ℃
PRNT_DATE   2024/Aug/08 13:22:12
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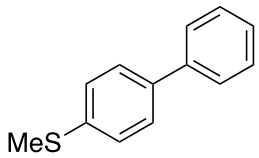
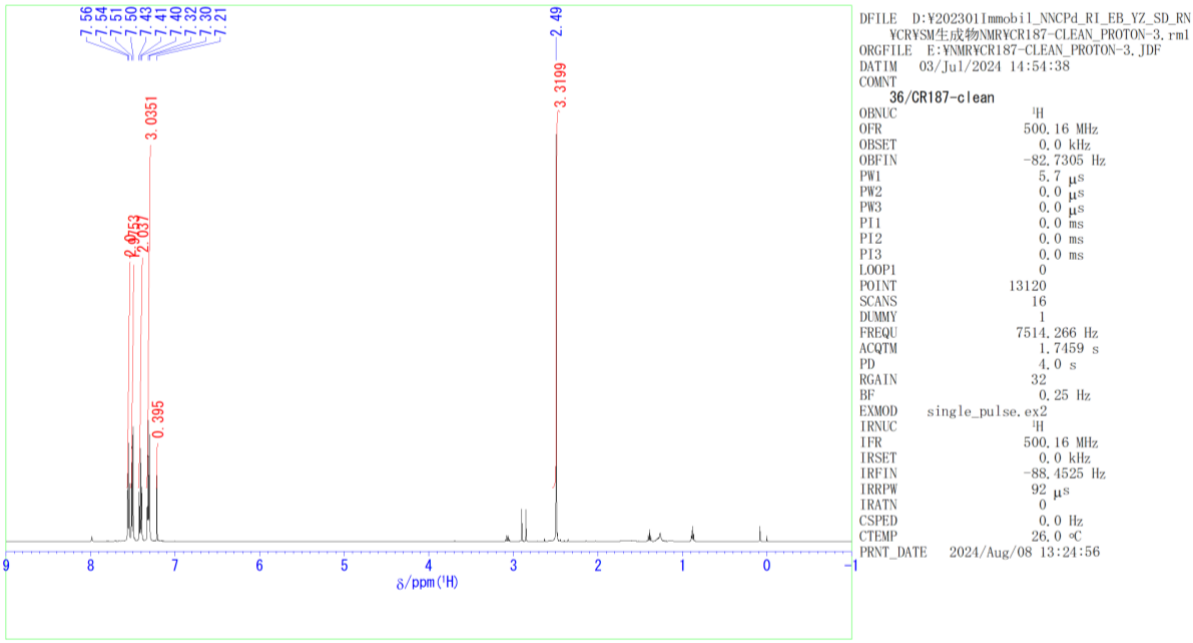
4-Methylsulfanylbiphenyl (**10ad**) [19]

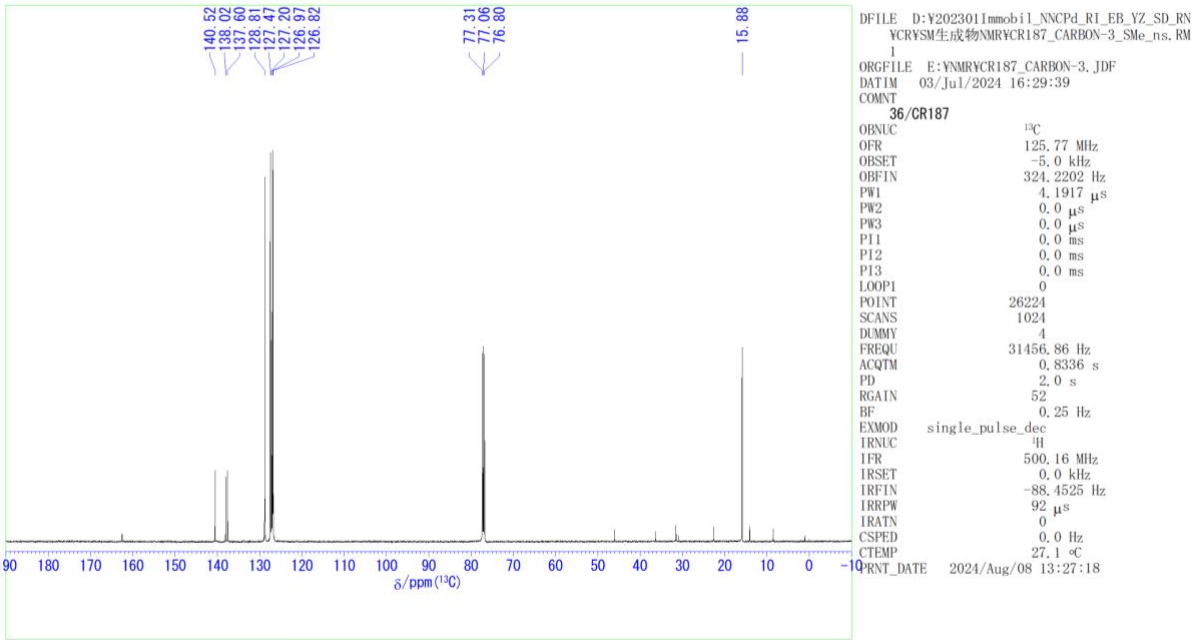


89% by ^{1}H NMR

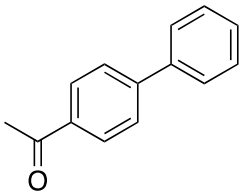
^{1}H NMR (isolated)



^{13}C{^{1}H} NMR

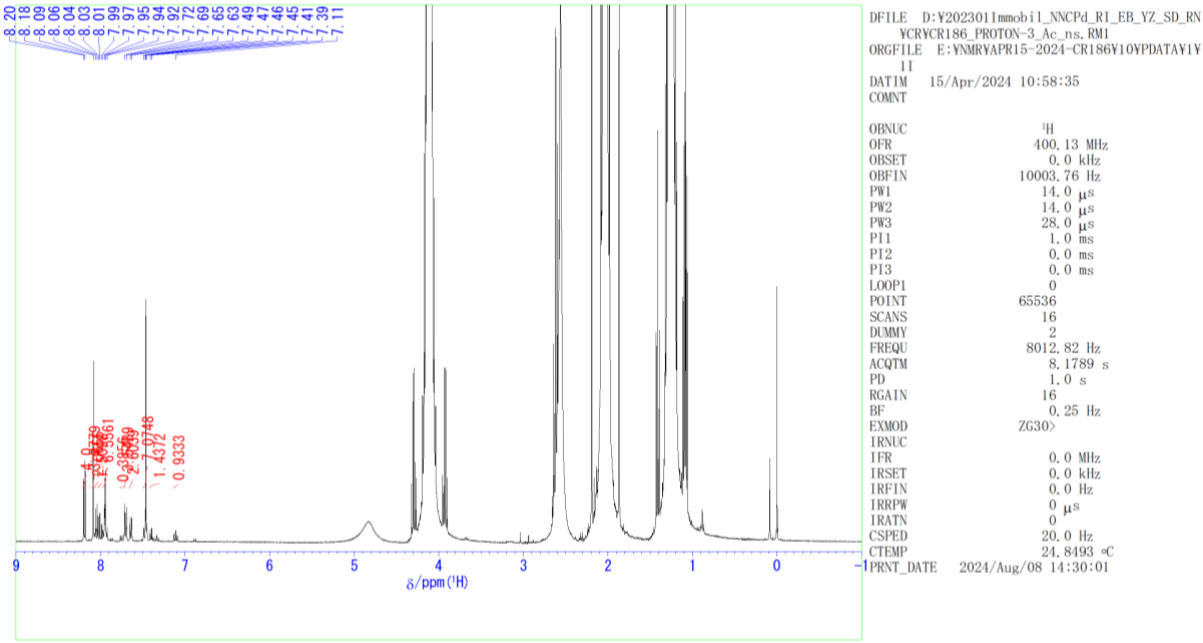


4-Acetylbiphenyl (**10ae**) [18, 20]

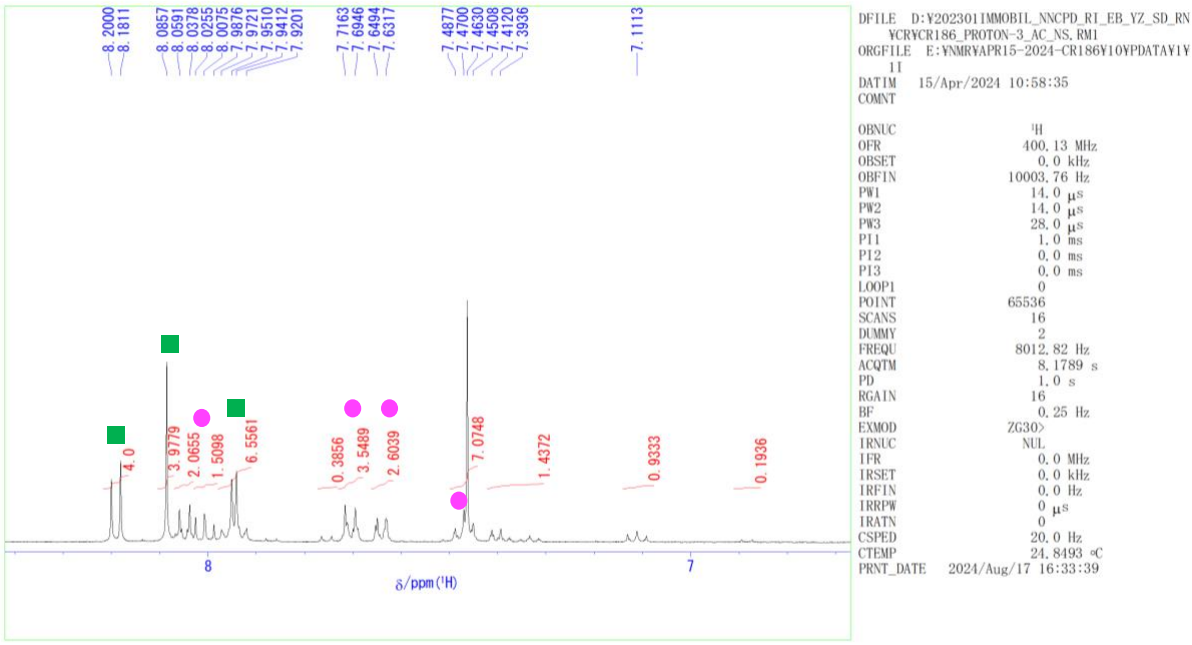


^{1}H NMR

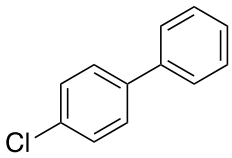
(Y 65%, reaction mixture)



Enlarged ■ : internal standard (pyrene), ● : the product

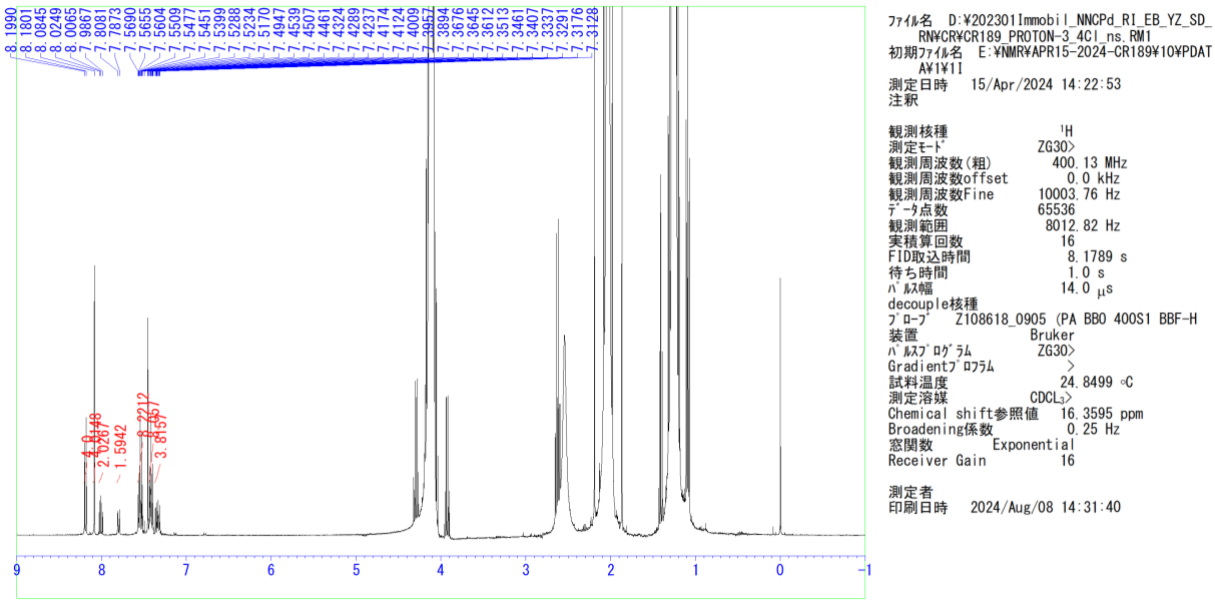


4-Chlorobiphenyl (**10af**) [19]

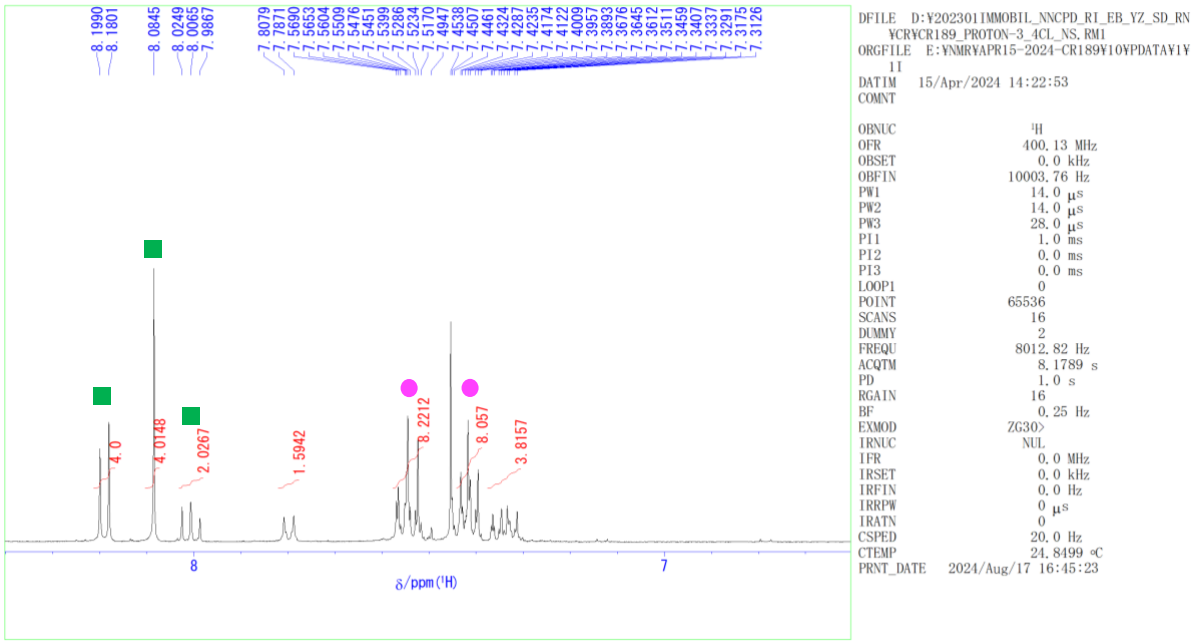


(Y >99%, reaction mixture)

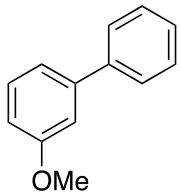
^{1}H NMR



Enlarged, ■ : internal standard (pyrene), ● : the product

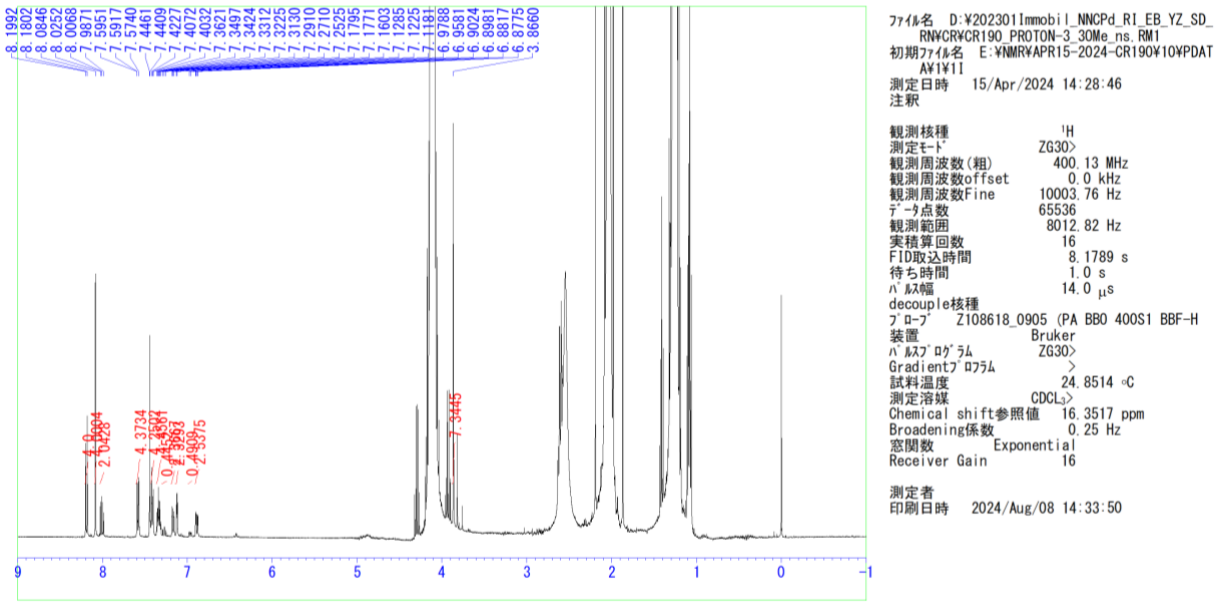


3-Methoxybiphenyl (**10ag**) [21]

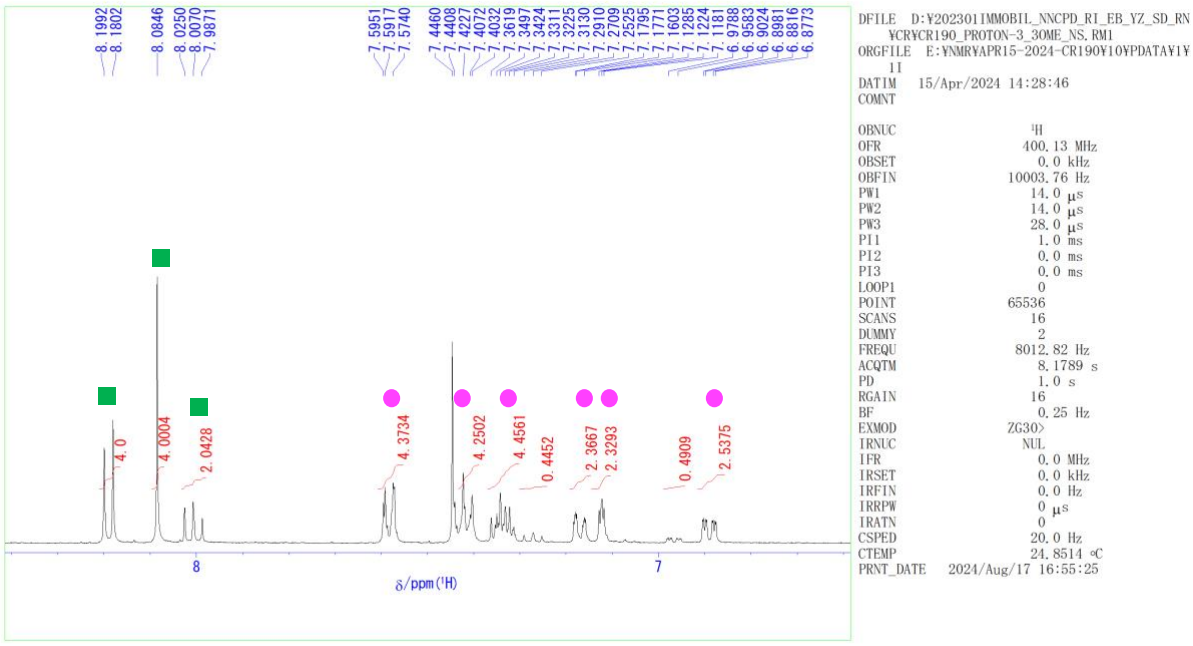


(>99%, reaction mixture)

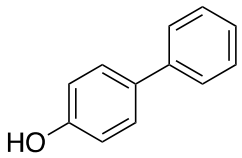
^{1}H NMR



Enlarged, ■ : internal standard (pyrene), ● : the product

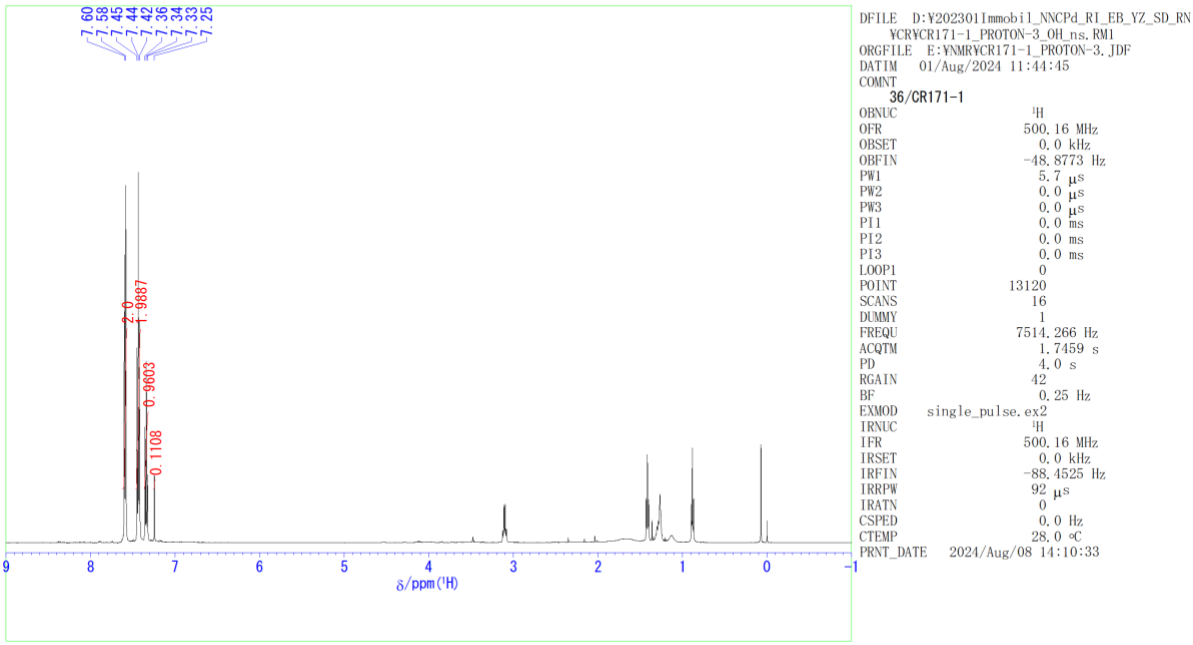


4-Hydroxybiphenyl (**10da**) [22]

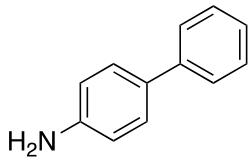


Isolated 97%

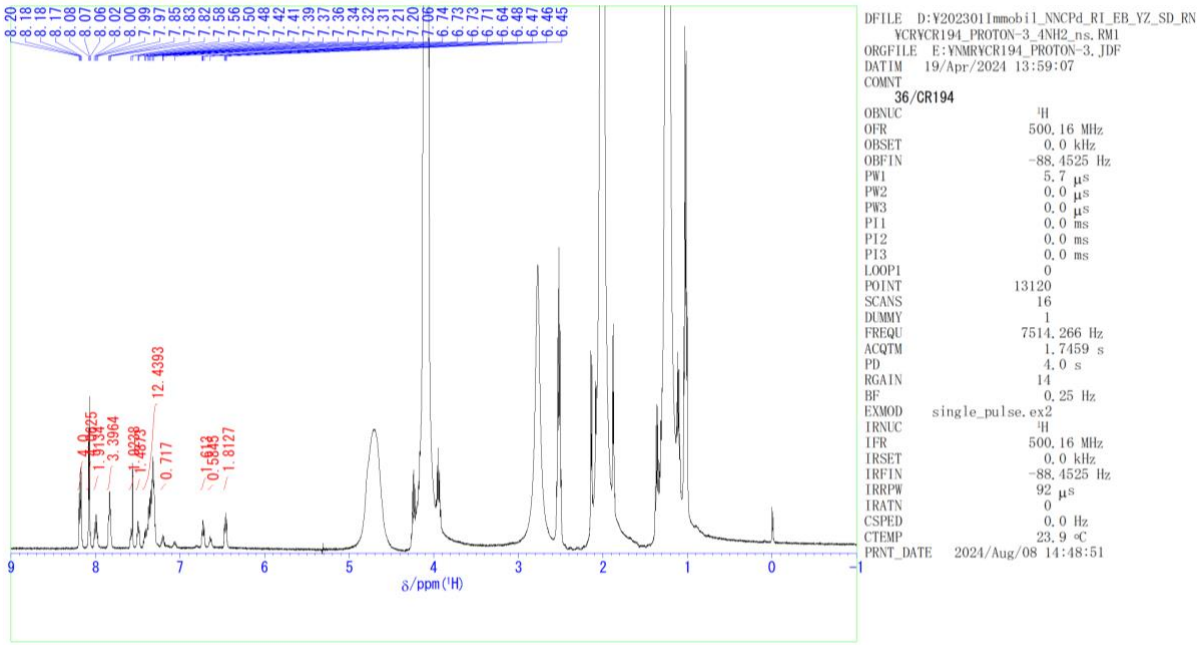
^{1}H NMR



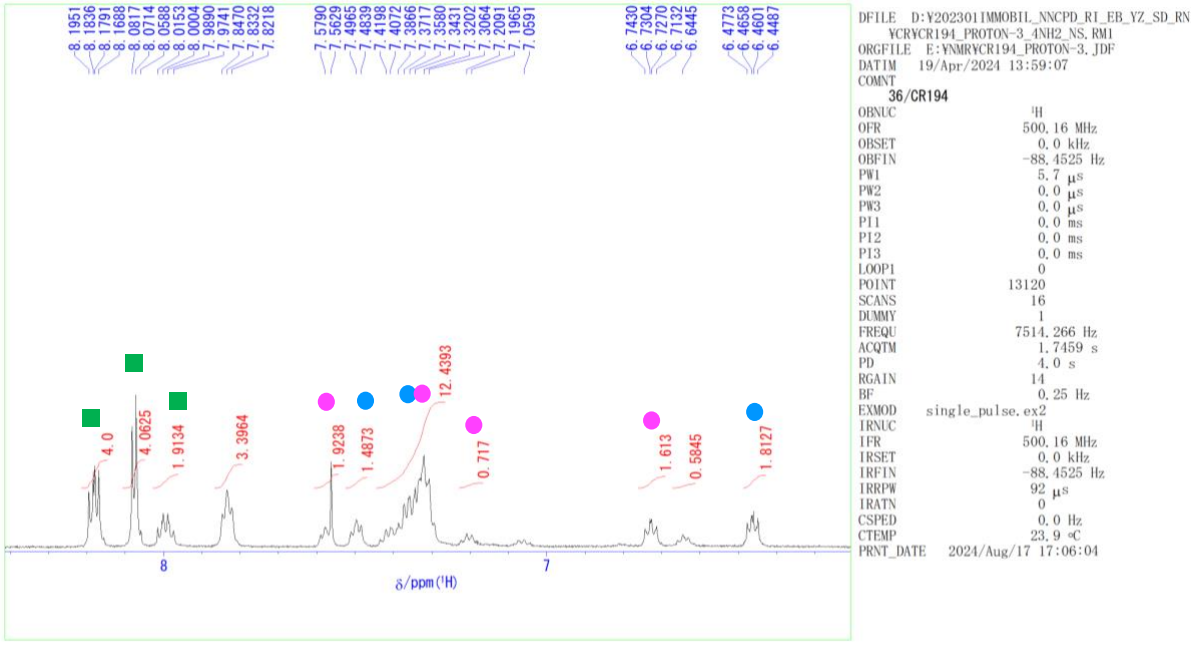
4-Aminobiphenyl (**10fa**) [22]



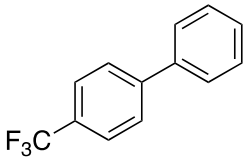
(Y 40%, reaction mixture)
^{1}H NMR



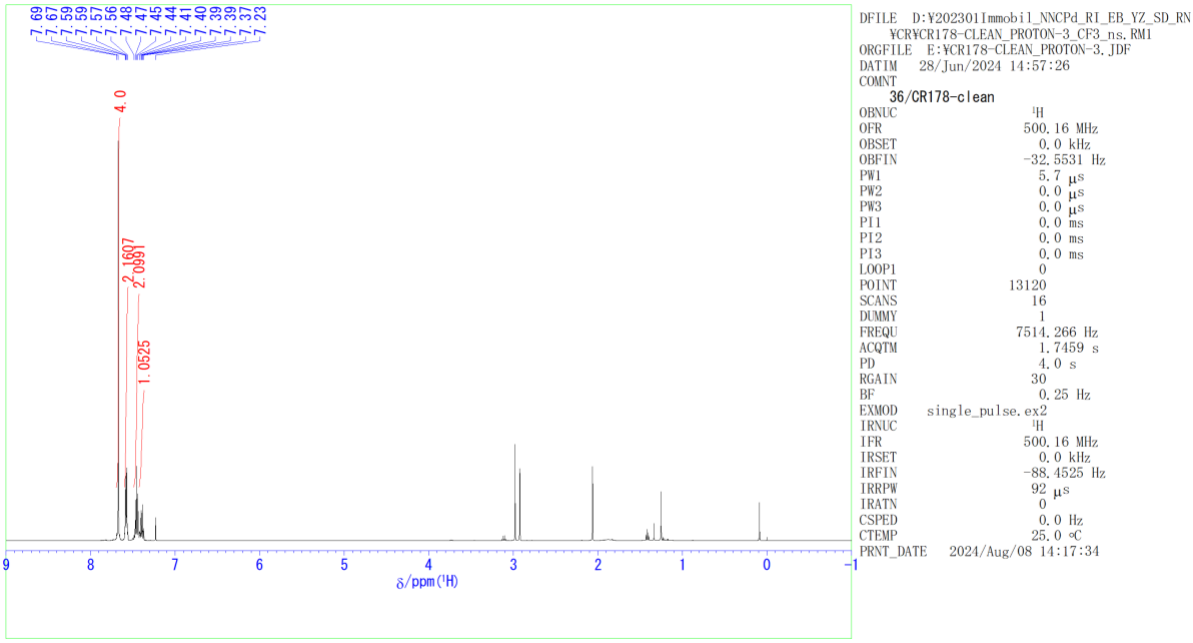
Enlarged, ■ : internal standard (pyrene), ● : the product, ● starting materials



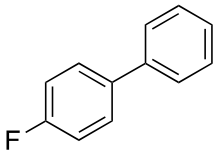
(4-trifluoromethyl)biphenyl (**10ga**) [23]



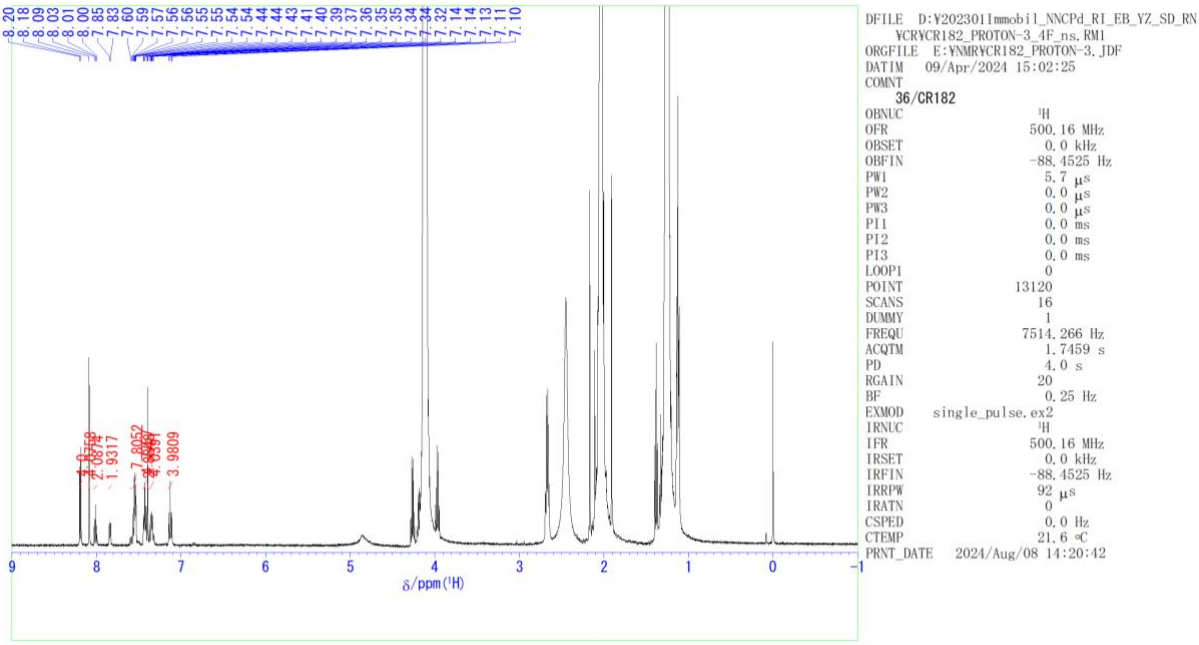
^{1}H NMR (>99%, 78% isolated yield)



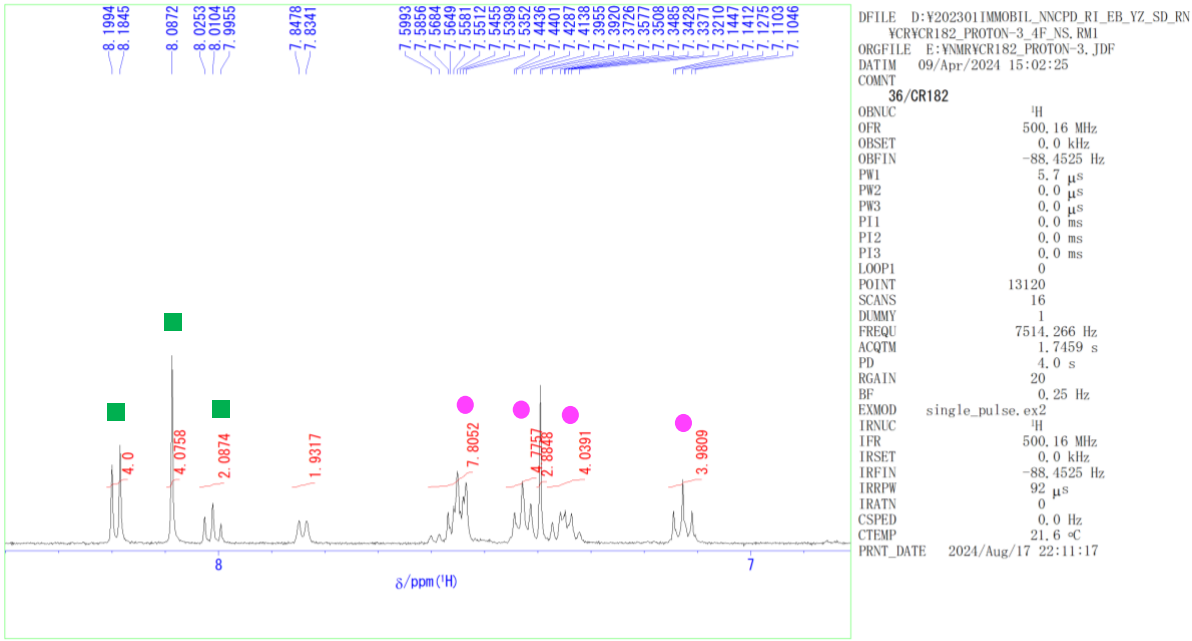
4-fluorobiphenyl (**10ha**) [19]



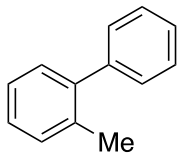
(Y >99%, reaction mixture)



Enlarged, ■ : internal standard (pyrene), ● : the product

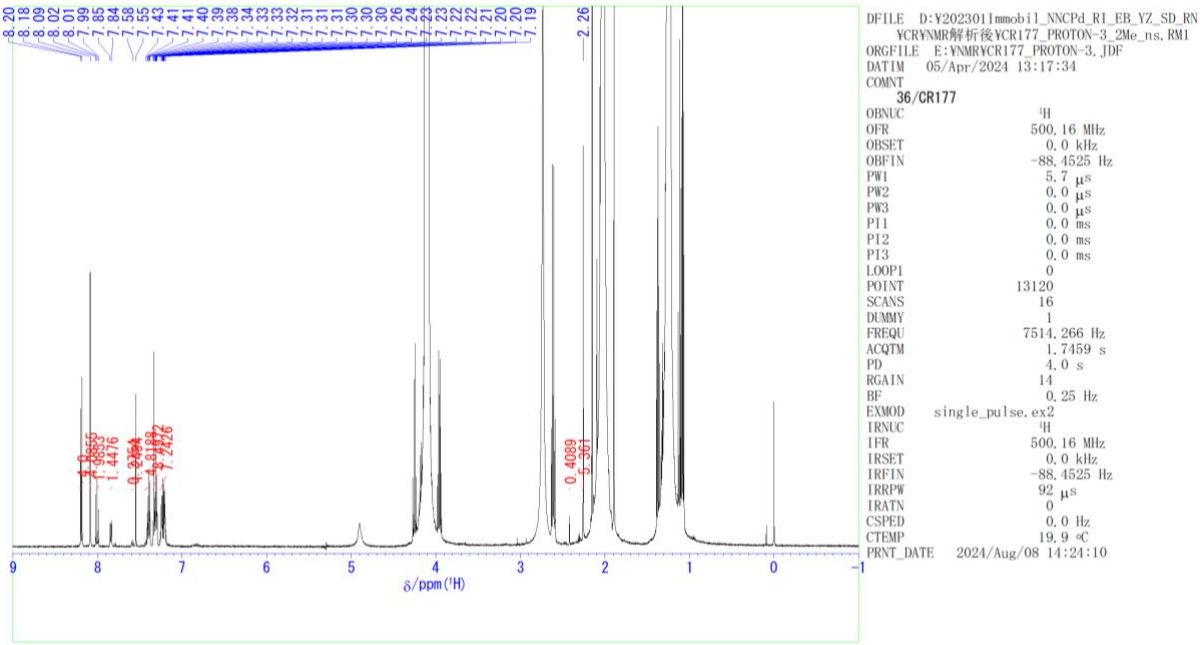


2-methylbiphenyl (**10ia**) [19]

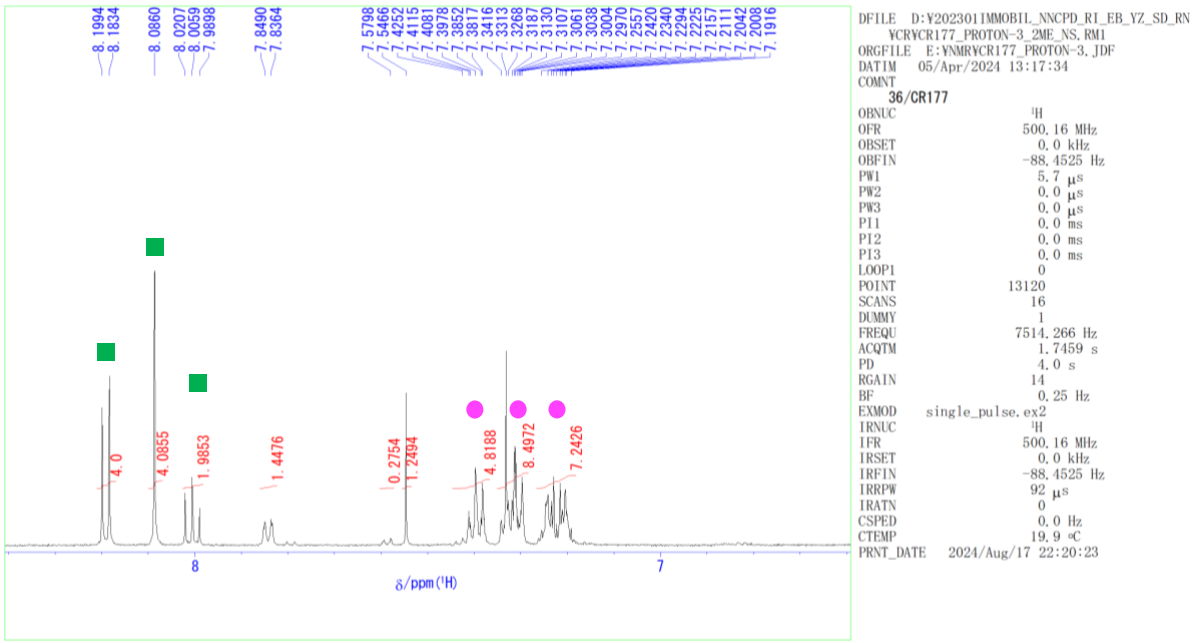


^{1}H NMR

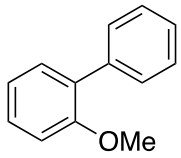
(Y 91%, reaction mixture)



Enlarged, ■ : internal standard (pyrene), ● : the product

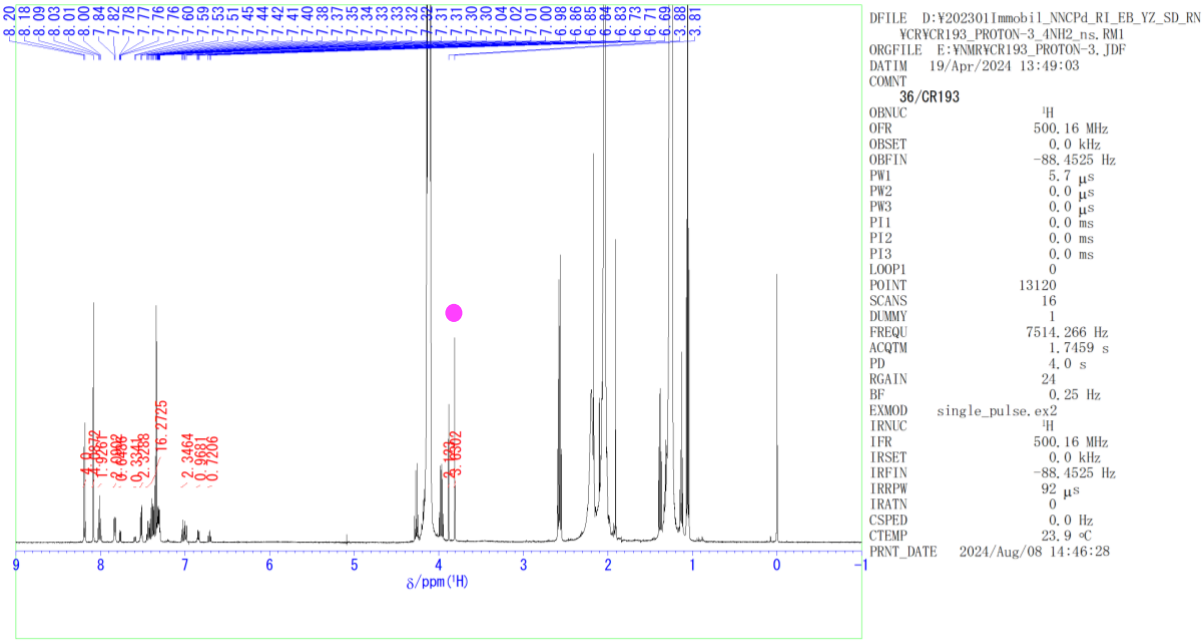


2-Methoxylbiphenyl (**10ja**) [21]

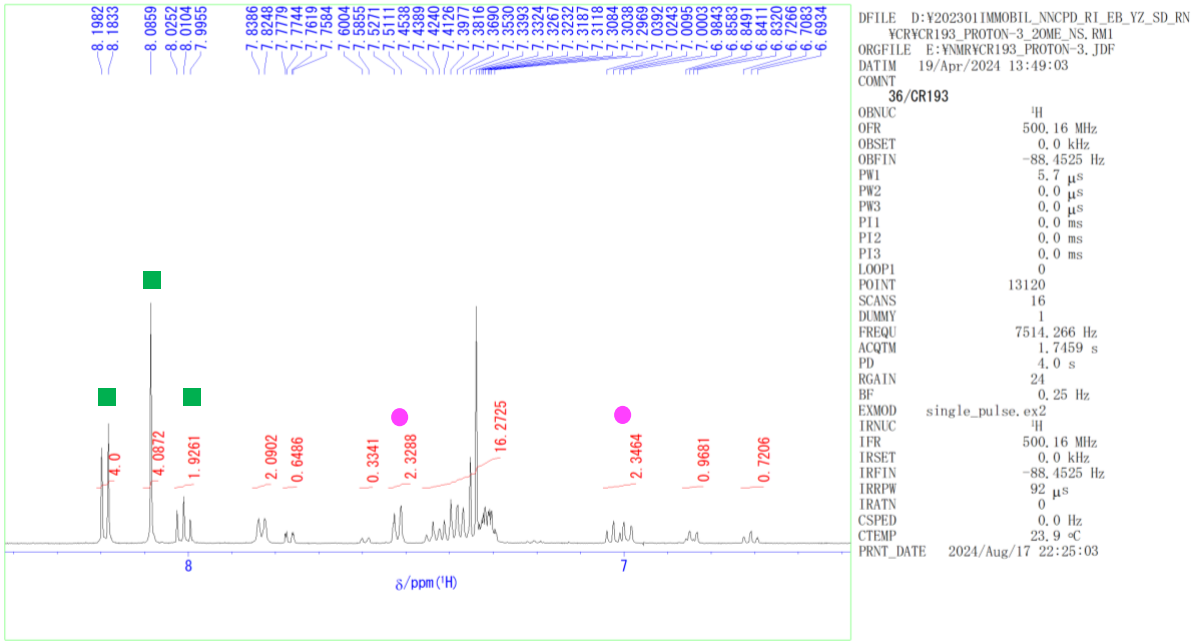


^{1}H NMR

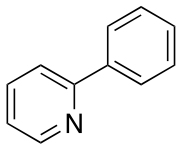
(Y 59%, reaction mixture)



Enlarged, ■ : internal standard (pyrene), ● : the product

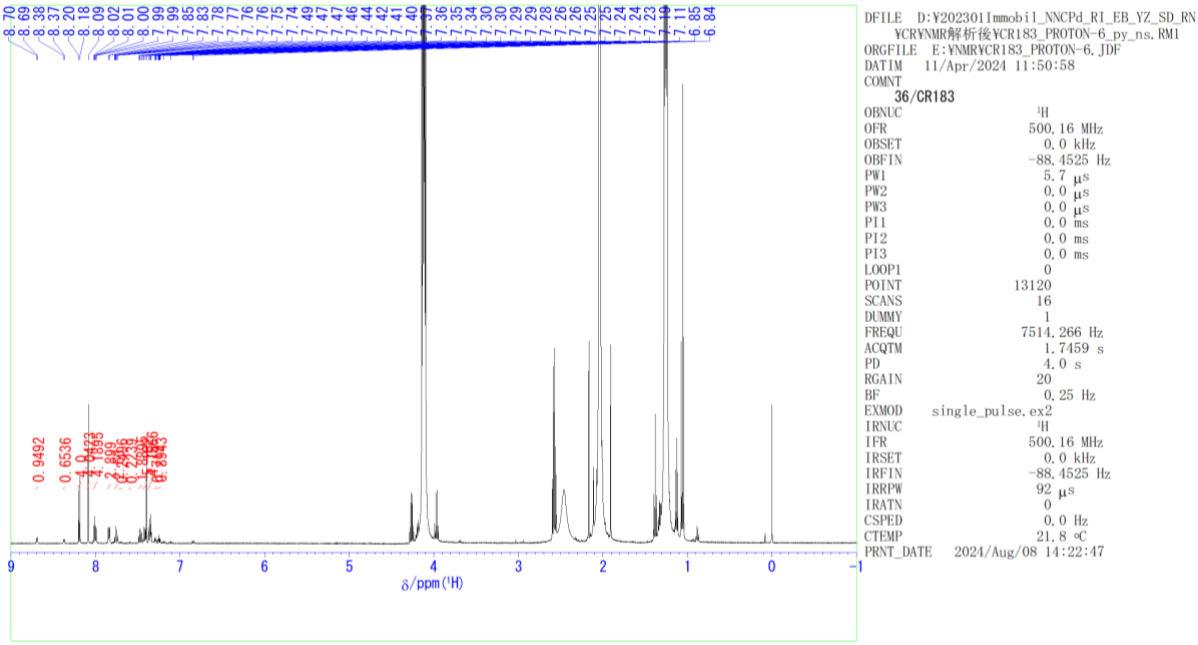


2-Phenylpyridine (**10ka**) [18, 19]

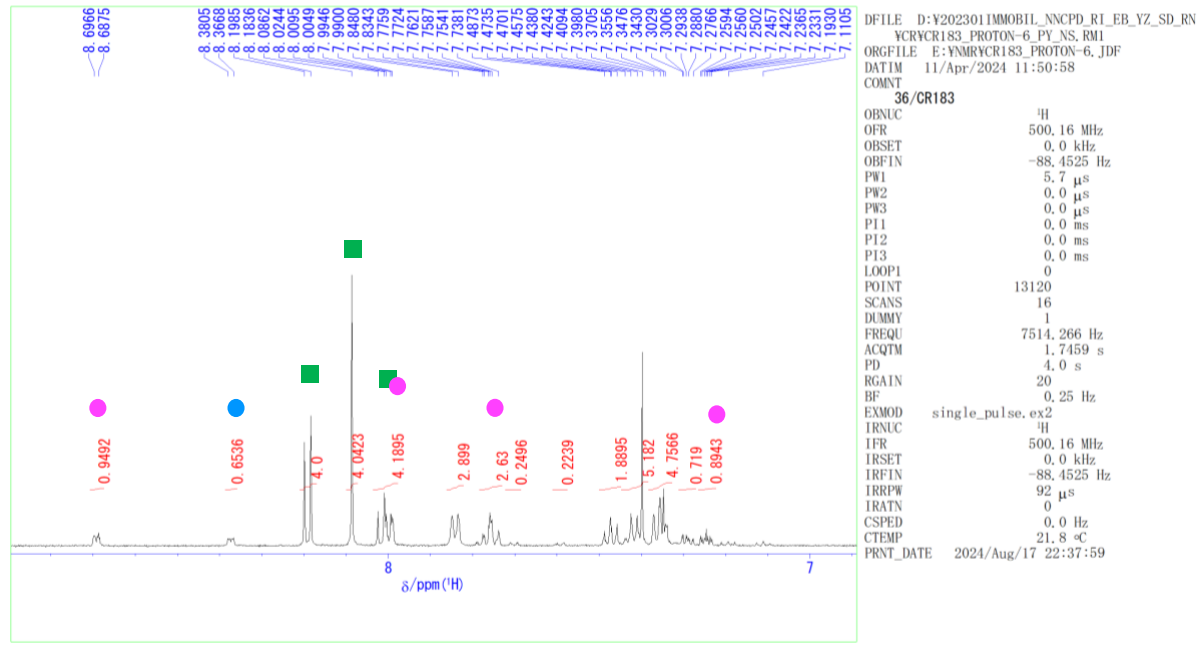


^{1}H NMR

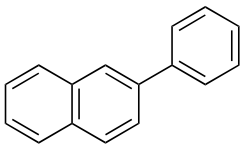
(Y 49%, reaction mixture)



Enlarged, ■ : internal standard (pyrene), ● : the product, ● starting materials

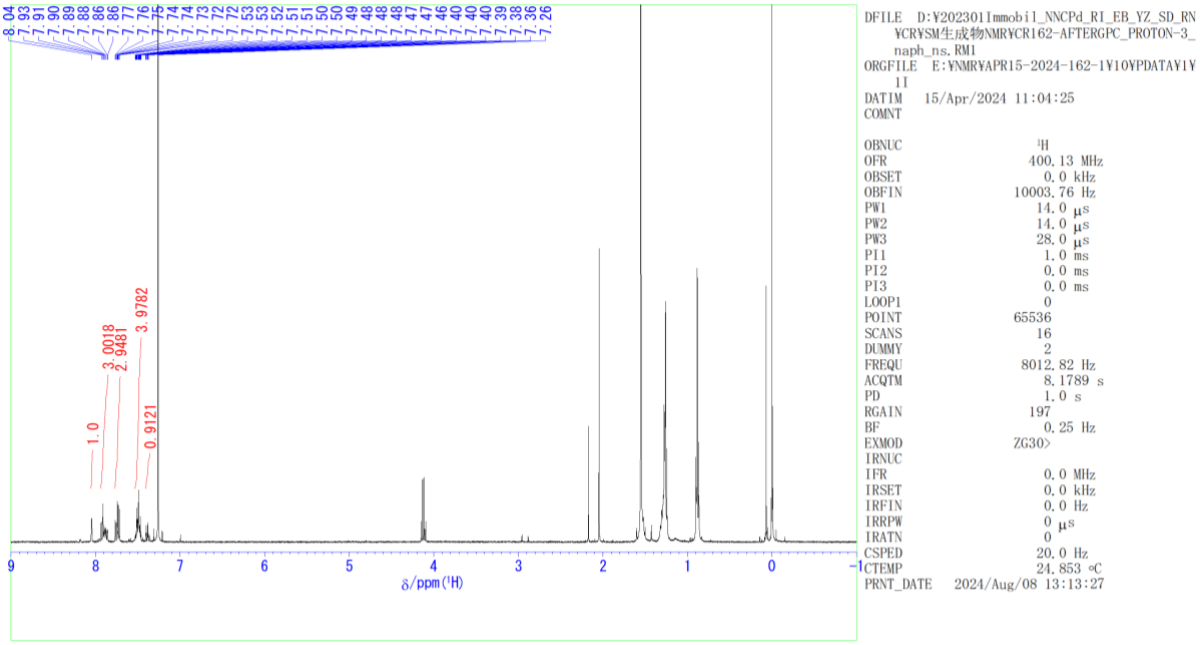


2-Phenylnaphthalene (**10la**) [19]

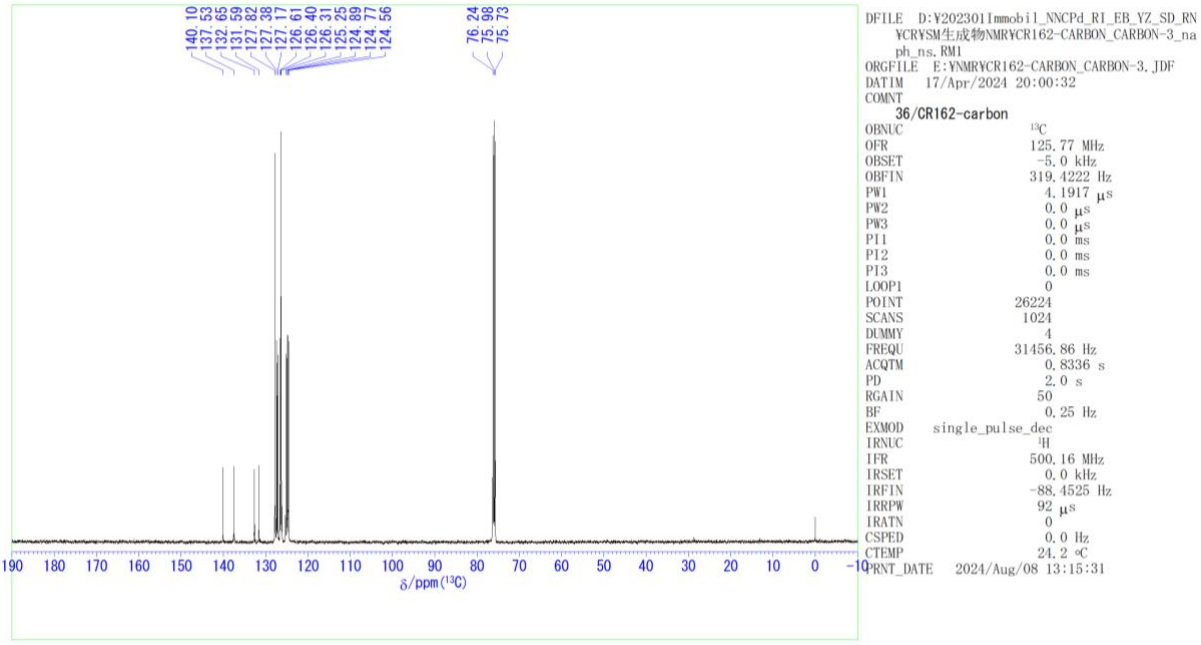


Isolated (crude 36%, containing solvents)

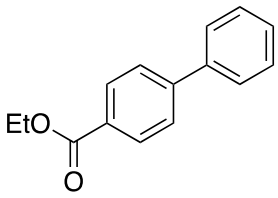
^{1}H NMR



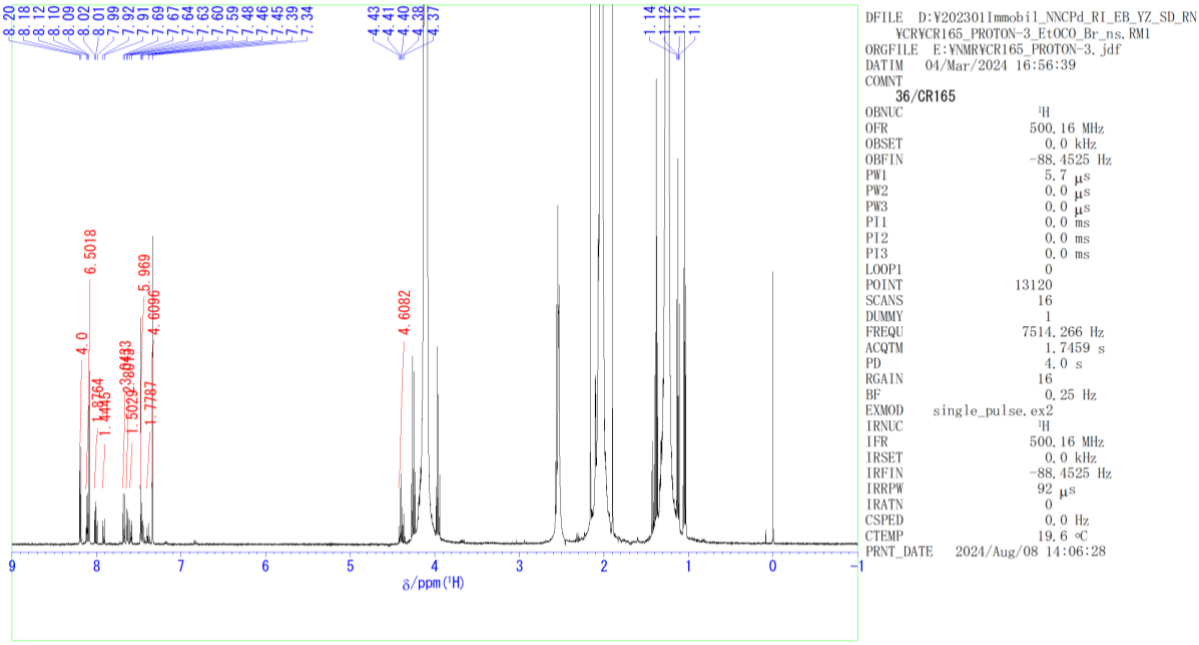
^{13}C{^{1}H} NMR



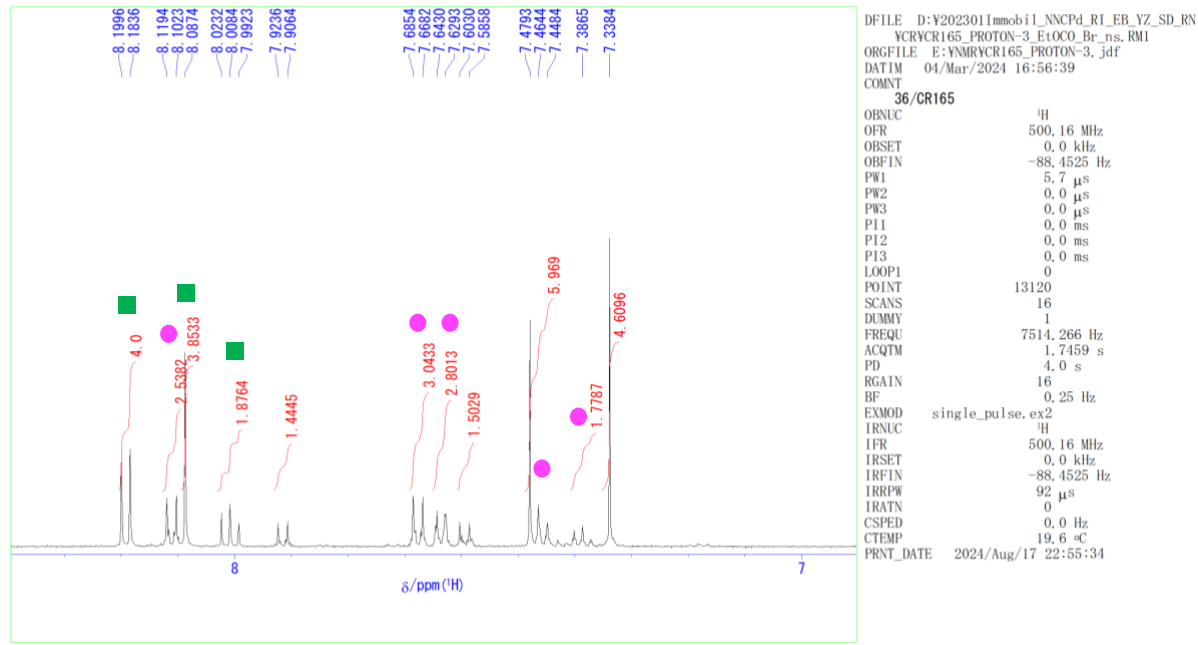
Ethyl 4-phenylbenzoate (**10ma**) [21]



^{1}H NMR (Y 64%, reaction mixture)



Enlarged ■ : internal standard (pyrene), ● : the product



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