

Poly-Phenylene Jacketed Tailor-Made Dendritic Phenylazome-thine Ligand for Nanoparticle Synthesis

Ken Albrecht, ^{#*abcd} Maki Taguchi, ^{#b} Takamasa Tsukamoto, ^{abd} Tatsuya Moriai, ^a Nozomi Yoshida, ^a and Kimihisa Yamamoto^{*ab}

a. Laboratory for Chemistry and Life Science (CLS), Institute of Innovative Research (IIR), Tokyo Institute of Technology, Yokohama 226-8503 (Japan).

Email: yamamoto@res.titech.ac.jp

b. JST-ERATO, Yamamoto Atom Hybrid Project, Institute of Innovative Research (IIR), Tokyo Institute of Technology, 4259Nagatsuta, Midori-ku,Yokohama226-8503(Japan)

c. Institute for Materials Chemistry and Engineering Kyushu University, 6-1 Kasuga-Koen Kasuga-shi, 816-8580, Fukuoka, Japan

Email: albrecht@cm.kyushu-u.ac.jp

d. Present address: JST-PRESTO, Kawaguchi 332-0012(Japan)

[#] These authors contributed equally.

Electronic Supplementary Information

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1. Experimental section

Chemicals. Rhodium trichloride trihydrate was purchased from AlfaAesar. Ruthenium trichloride was purchased from Tokyo Chemical Industry Co., Ltd. Tin dibromide was purchased from Aldrich. High surface area graphene nanopowder (grade AO-1) was purchased from ALLIANCE Biosystems, Inc. All other chemicals were purchased from Kanto Kagaku Co., Ltd. or Aldrich, and used without further purification (all solvents for the UV-vis titration and cluster formation were of the dehydrated grade).

General. The NMR spectra were obtained using a Bruker AVANCE III 400 (400MHz). ^1H NMR and ^{13}C NMR were measured with TMS as the internal standard. The MALDI TOF-MS and APCI TOF-MS data were obtained using Shimadzu/ Kratos AXIMA CFR plus in the linear positive ion mode or Bruker MicrOTOF II, respectively. Dithranol was used as the matrix for MALDI-TOF-MS. The elemental analysis was performed at the Center for Advanced Materials Analysis, Technical Department, TIT. A preparative scale gel permeation chromatography, LC-908 (Japan Analytical Industry Co., Ltd.), was used to isolate each compound with THF as the eluent. The UV-vis spectra were recorded using a Shimadzu UV-3100, UV-3150, or UV-3600 spectrometer with a quartz cell having a 1cm optical length at 20°C in a glove box under Ar atmosphere. The STEM images were recorded using JEOL JEM-ARM200F equipped with an energy dispersive X-ray spectrometry (EDS) analyzer (acceleration voltage: 80 kV). XPS was recorded by a Shimadzu ESCA-3400 with Mg $\text{K}\alpha$ (10 kV, 20 mA) using as an X-ray source. The binding energy was standardized using the Au $4\text{f}_{7/2}$ peak at 84.0 eV.

Titration of complexation on dendrimers on UV-vis absorption spectra. A 5.0×10^{-6} M dendrimer solution in dichloromethane for RhCl_3 and RuCl_3 or 1.0×10^{-5} M solution in dichloromethane/acetonitrile=2:1 for SnBr_2 (3 mL, 20 °C) was prepared in a 1 cm optical quartz cell. A 3.0×10^{-3} M solution (acetonitrile for RuCl_3 and SnBr_2 , acetonitrile/methanol=250:1 for RhCl_3) was added to a 3 mL solution of dendrimer in a stepwise fashion from 0 to 20 equiv. of a dendrimer molecule, respectively. The absorption of metal salt was subtracted by adding the same amount to the reference cell.

Template synthesis of clusters. The preparation method of the complexes of dendrimers and metal salts (RhCl_3 and RuCl_3) was the same as those for the UV-vis absorption measurement mentioned above. 60 equiv of NaBH_4 (300 mM, methanol) on the accumulated metal salts was added to the complex solution with stirring. For the STEM observation and EDS analysis, a suspension of graphene nanopowder (1 mg in 2 mL of dichloromethane) was quickly added to the reaction mixture and stirred for 1 min. The clusters supported on graphene in solution were dropped onto a copper grid with a carbon film and dried overnight under a vacuum. For the XPS measurement, a 5 μL portion of the fresh cluster solution was then dropped 10 times (total 50 μL) onto a glassy carbon substrate (5 mm × 5 mm). After drying, the XPS analysis was conducted as soon as possible. All operations were carried out under an inert atmosphere (N_2).

2. Accumulation of Lewis acids to DPA

Accessible number of accumulated Lewis acids
(symmetric structure + closed shell accumulation)

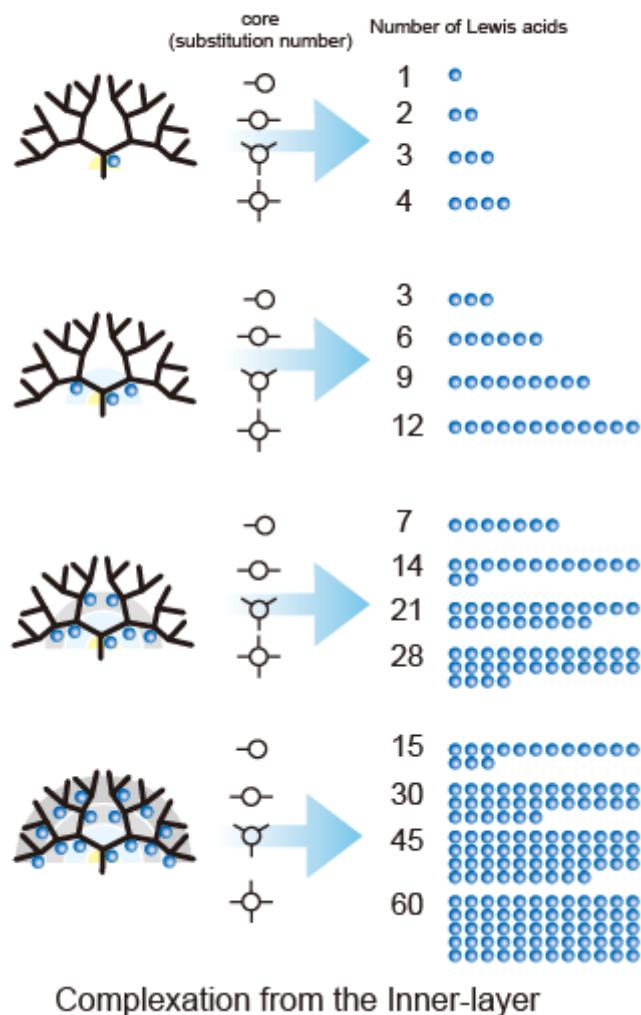


Figure S1. Accumulation of Lewis acids from the inner-layer to symmetric DPA with 1 to 4 substituted structures. Accessible numbers are 1, 2, 3, 4, 6, 7, 9, 12, 14, 15, 21, 28, 30, 45, and 60. Other numbers can be also accumulated, but the “closed shell” accumulation that is shown above will have a small statistical distribution compared to other multi-ligand systems that have equal binding sites. Note that in practical use the one and two substituted dendrimers have not enough shell effect to kinetically trap the formed nanoparticles.

3. Synthesis

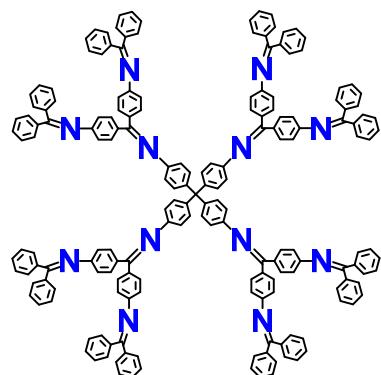
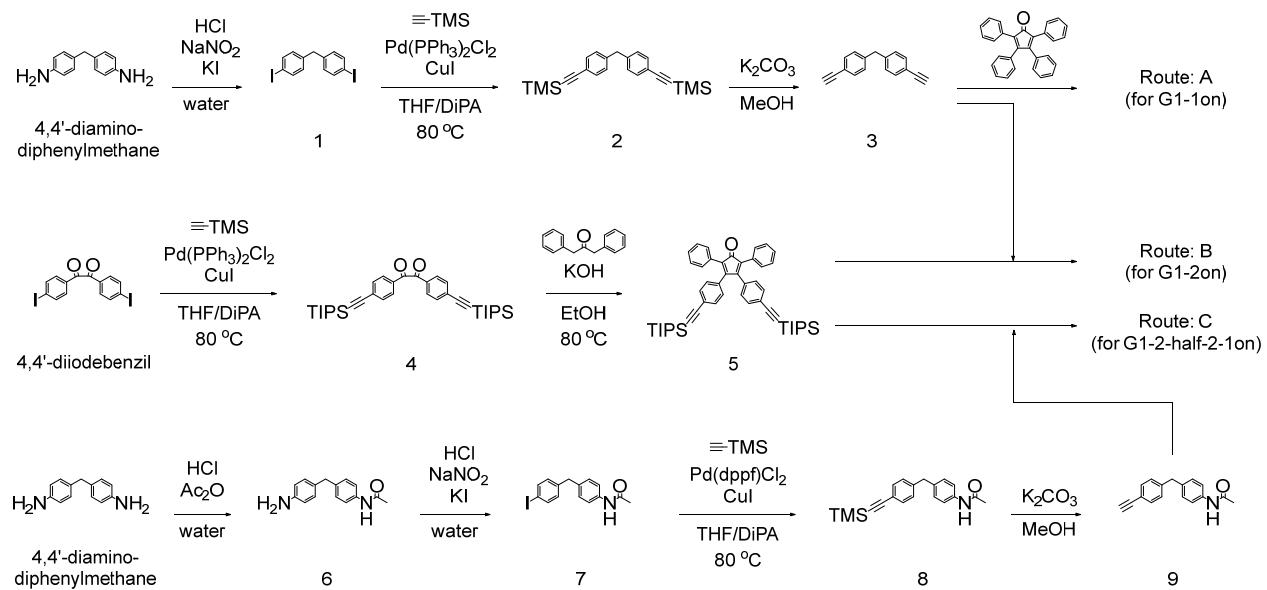
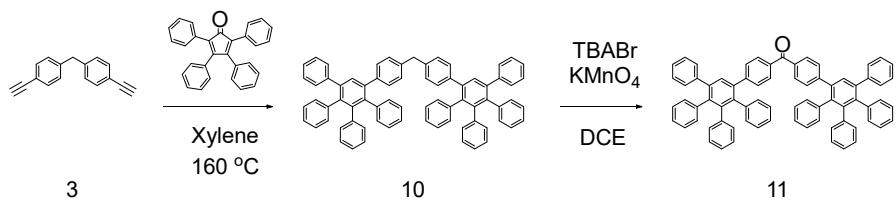


Figure S2. Structure of DPA12.

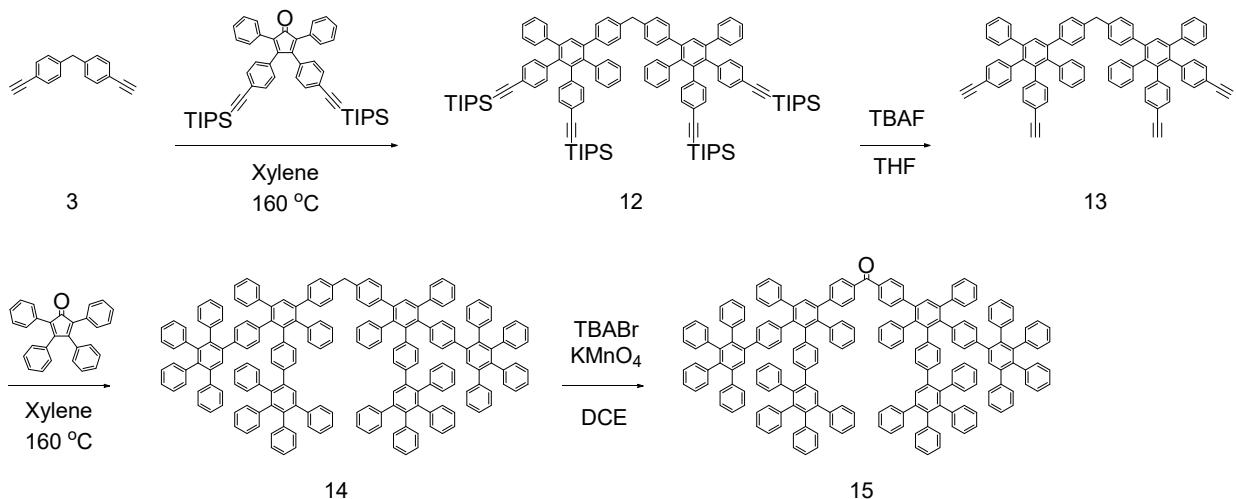


Scheme S1. Synthesis of starting materials.

Route: A

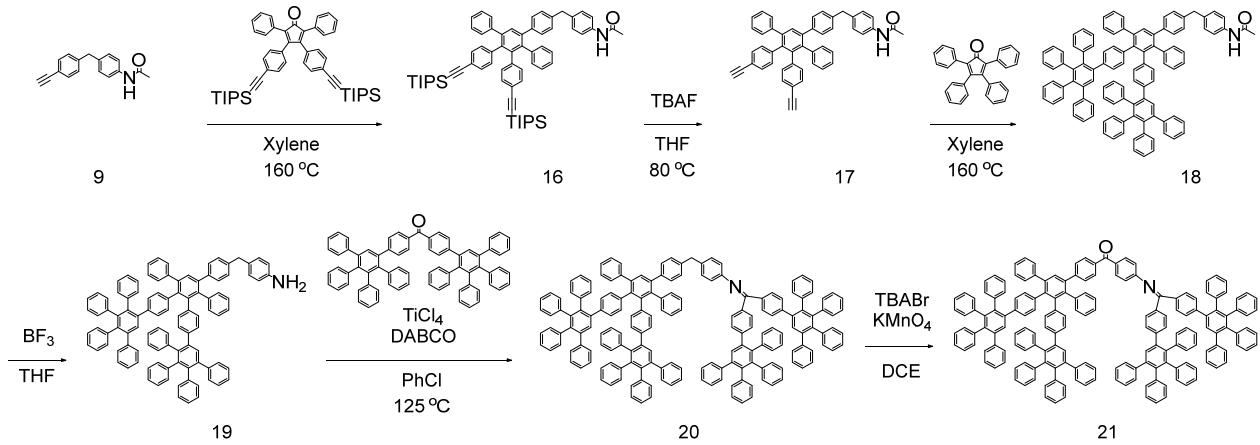


Route: B

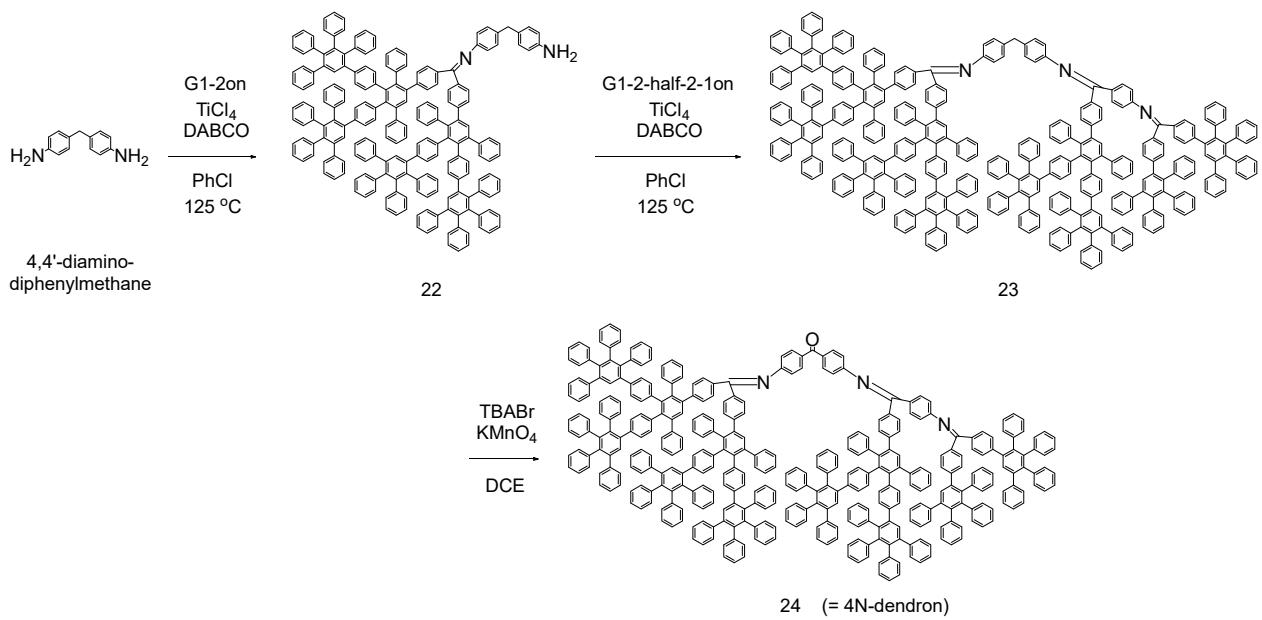


Scheme S2. Synthesis of polyphenylene jacketed dendrons G1-1on (Route: A) and G1-2on (Route: B).

Route: C



Scheme S3. Synthesis of polyphenylene jacketed dendron G1-1-half-2-1on (Route: C).



Scheme S4. Synthesis of polyphenylene jacketed dendron G2-2-quater-3-1on.

4,4'-Diiodo-diphenylmethane (**1**).

To 500 ml of distilled water in a 3000 ml beaker containing a stick-shaped magnetic stirrer tip which was completely cooled at 0 °C on the ice bath, 20 ml of Hydrochloride was added. 4,4'-diamino-diphenylmethane (10.0 g, 50.4 mmol) which was milled was added to the stirred mixture. The mixture was stirred at 0 °C for 30 min. Then, sodium nitrite (10.0 g, 145 mmol) was added slowly and the mixture was stirred for 60 min. And then, potassium iodide (50.0 g, 301 mmol) which was milled was added slowly to the mixture at 0 °C. After 15-20 min, agglomerated material on the side of a beaker was dissolved in dichloromethane. The mixture was stirred at r.t. overnight. The resulting solution was neutralized with aqueous potassium carbonate. The organic phase was extracted with dichloromethane, washed with aqueous sodium thiosulfate several times and with brine, respectively, and then dried with magnesium sulfate. The solution was filtrated and evaporated. The crude was adsorbed into Celite powder and then isolated through a silica-gel short column chromatography eluting with n-hexane to afford 12.5 g (yield 58.7%) of white powder.

¹H NMR (400 MHz, CDCl₃, 29.4 °C, TMS):

δ [ppm] = 7.6 (d, *J* = 8.3 Hz, 4H), 6.90 (d, *J* = 8.3 Hz, 4H), 3.85 (s, 2H).

MALDI TOF-MS (Matrix: Dithranol): Calcd: 420.89 ([M+H]⁺), Found: 420.70.

4,4'-Bis(trimethylsilyl ethynyl)-diphenylmethane (**2**).

A 300 ml flask (three-necked round-bottom flask) containing 4,4'-diiodo-diphenylmethane (**1**) (5.000 g, 11.90 mmol), copper (I) iodide (0.0906 g, 0.476 mmol) and bis(triphenylphosphine) palladium (II) dichloride (0.835 g, 1.190 mmol) was degassed and flushed with argon gas. 220 ml of tetrahydrofuran (anhydride grade) and 40 ml of diisopropylamine were added by using a syringe. To the stirred mixture, 3.6 ml of trimethylsilyl acetylene (2.57 g, 26.2 mmol) was added slowly by using a syringe. Then, the mixture was refluxed at 80 °C for

two nights. The resulting solution was evaporated. The crude was adsorbed into Celite powder and put on a silica gel column (round 10 cm, height 12 cm) packed with n-hexane. A purification with column chromatography eluting with n-hexane (which should not be pressured well) afforded 3.152 g (yield 73.4%) of ivory powder.

¹H NMR (400 MHz, CDCl₃, 27.4 °C, TMS):

δ [ppm] = 7.37 (d, *J* = 8.1 Hz, 4H), 7.07 (d, *J* = 8.1 Hz, 4H), 3.94 (s, 2H), 0.24 (s, 18H).

¹³C NMR (100 MHz, CDCl₃, 25.9 °C, TMS):

δ [ppm] = 140.92, 131.97, 128.66, 120.90, 104.87, 93.71, 41.49, -0.18.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 360.18 ([M+H]⁺), Found: 360.63.

Anal. Calcd. for C₂₃H₂₈Si₂: C, 76.60; H, 7.83. Found: C, 76.41; H, 7.92.

4,4'-Diethynyl-diphenylmethane (3).

A 300 ml flask (three-necked round-bottom flask) containing 4,4'-bis(trimethylsilylethynyl)-diphenylmethane (**2**) (0.420 g, 1.165 mmol) and potassium carbonate (0.966 g, 6.987 mmol) was degassed and flushed with argon gas. 150 ml of methanol was added. The mixture was stirred at r.t. for more than 5 hours and then evaporated. The crude was neutralized with dil. HCl, extracted with dichloromethane, washed with brine and then dried with magnesium sulfate. The solution was filtrated and evaporated to afford 0.362 g of yellow material (rough yield). The crude material was instantly used for the next step (Diels-Alder cycloaddition). The product can be purified by a silica gel column chromatography eluting with n-hexane to be white powder.

¹H NMR (400 MHz, CD₂Cl₂, 25.3 °C, TMS):

δ [ppm] = 7.41 (d, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 3.97 (s, 2H), 3.09 (s, 2H).

¹³C NMR (100 MHz, CD₂Cl₂, 26.6 °C, TMS):

δ [ppm] = 142.06, 132.65, 129.35, 120.40, 83.78, 77.21, 41.96.

APCI-MS (positive): Calcd: 217.10 ([M+H]⁺), Found: 217.20.

4,4'-Bis(triisopropylsilylethynyl)benzyl (4).

A 1000 ml flask (three-necked round-bottom flask) containing 4,4'-dibromobenzil (9.752 g, 26.50 mmol), copper (I) iodide (0.202 g, 1.06 mmol), and bis(triphenylphosphine) palladium (II) dichloride (1.862 g, 2.653 mmol) was degassed and flushed with argon gas. 400 ml of tetrahydrofuran (anhydrate grade) and 80 ml of diisopropylamine were added by using a syringe. To the stirred mixture, 13.0 ml of triisopropylsilyl acetylene (10.6 g, 58.3 mmol) was added slowly by using a syringe. Then, the mixture was refluxed at 75 °C for two nights. The resulting solution was evaporated. The crude was adsorbed into Celite particle for column and isolated by using a silica gel flash column chromatography [eluting with n-hexane and ethyl acetate mixture (98:2)]. It afforded 14.534 g (yield 96.0%) of yellow oil-like material.

¹H NMR (400 MHz, CDCl₃, 28.9 °C, TMS):

δ [ppm] = 7.92 (d, *J* = 8.5 Hz, 4H), 7.60 (d, *J* = 8.6 Hz, 4H), 1.16 (s, 42H).

APCI-MS (positive): Calcd: 589.36 ([M+H+H₂O]⁺), Found: 589.27.

3,4-Bis(4-triisopropylsilyl ethynyl)phenyl-2,5-diphenyl-cyclopenta-2,4-dien-1-one (5).

A 1000 ml flask (three-necked round-bottom flask) containing 4,4'-bis(triisopropylsilyl ethynyl) benzyl (**4**) (14.32 g, 25.08 mmol), 1,3-Diphenyl-2-propanone (4.800 g, 22.83 mmol), and ethyl alcohol (50 ml) was degassed and flushed with argon gas and reactant was completely dissolved in ethanol at 80 °C. To the mixture which had been stirred at room temperature, 140 ml of ethanol solution containing potassium hydroxide (0.769 g, 13.7 mmol) was added from a 200 ml dropping funnel. The mixture was stirred at 80 °C for 12 min and then cooled down in the refrigerator overnight. The resulting cold solution was filtrated to afford chocolate-like materials, which was washed well with 5% ethanol in water to afford cocoa-like powder 14.314 g (yield 84.0%). The filtrate solution was extracted with diethyl ether, washed with brine, and dried with magnesium sulfate. Then the solution was filtrated and evaporated. The crude was adsorbed into Celite particle for column and isolated by using a silica gel flush column chromatography [eluting with n-hexane and chloroform mixture (70:30)]. It afforded 1.748 g (yield 10.4%) of wine-red amorphous. cocoa-like powder and wine-red amorphous were identical materials by evaluation of NMR spectra. The total amount was 16.062 g (yield 94.4%).

¹H NMR (400 MHz, CD₂Cl₂, 25.2 °C, TMS):

δ [ppm] = 7.34-7.26 (m, 10H), 7.21-7.19 (m, 4H), 6.93-6.87 (m, 4H), 1.12 (s, 42H).

¹³C NMR (100 MHz, CD₂Cl₂, 26.2 °C, TMS):

δ [ppm] = 200.11, 153.94, 133.49, 133.40, 132.22, 132.02, 131.09, 130.98, 130.55, 130.25, 129.78, 129.74, 128.51, 128.10, 126.54, 126.47, 126.39, 124.13, 122.70, 107.00, 92.82, 78.73, 18.82, 11.74.

APCI-MS (positive): Calcd: 745.43 ([M+H]⁺), Found: 745.45.

4-Acetamide-4'-amino-diphenylmethane (6).

To a 1000 ml beaker containing a stick-shaped magnetic stirrer tip were added 200 ml of distilled water and 7.0 ml of hydrochloride. To the stirred mixture was added 4,4'-diamino-diphenylmethane (9.83 g, 49.58 mmol) which was milled, before it was rinsed with 50 ml of ethanol (99.5% grade). The mixture was heated at 80 °C. Acetic anhydride (4.2 g, 41.1 mmol) was extremely slowly dropwise added to the stirred mixture at 80 °C. When the pearl-rose material occurred in the reaction solution, 80 °C water was added to precipitate bi-acetylated derivative. The pink precipitate was removed by hot filtration and washed with ethanol 8 ml / water 50 ml solution. The yellow filtrate was heated at 70 °C. Potassium acetate (10.1 g, 0.103 mol) was dissolved in 20 ml of distilled water, and then dropwise added to the filtrated solution at 70 °C. The resulting solution was cooled to 0 °C and stirred for 2 hours. The precipitated white solid was collected by a cold filtration and washed with ethanol 7 ml / water 43 ml cold solution twice, and then dried at room temperature under diminished pressure. It afforded 5.83 g (yield 48.9%) of beige solid.

¹H NMR (400 MHz, CDCl₃, 31.4 °C, TMS):

δ [ppm] = 7.37 (d, *J* = 8.24 Hz, 2H), 7.18 (s, 1H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 2H), 6.61 (d, *J* = 8.24 Hz, 2H), 3.82 (s, 2H), 3.56 (br, 2H), 2.14 (s, 3H).

MALDI TOF-MS (Matrix: Dithranol): Calcd: 241.13 ([M+H]⁺), Found: 241.10.

4-Acetamide-4'-iodo-diphenylmethane (7).

10 ml of Hydrochloride was added to 500 ml of distilled water in a 3000 ml beaker containing a stick-shaped magnetic stirrer tip. 4-acetamide-4'-amino-diphenylmethane (**6**) (10.27 g, 42.73 mmol) was added to the mixture. The mixture was stirred at 0 °C for 30 min. Then, sodium nitrite (4.000 g, 57.96 mmol) was slowly added and then stirred for 60 min at 0 °C. To the 0 °C mixture was extremely slowly added potassium iodide (20.00 g, 120.5 mmol) which was milled. The reaction solution was gradually warmed to room temperature and stirred overnight. Chloroform was added to dissolve agglomerated material in the reaction solution. The resulting solution was neutralized with aqueous potassium carbonate. The organic phase was extracted with chloroform and washed with aqueous sodium thiosulfate several times, and then washed with brine. The solution was dried with magnesium sulfate before it was filtrated and evaporated. The product was purified by using a silica gel flush column chromatography [eluting with n-hexane and ethyl acetate mixture (gradient from 100:0 to 50:50)] and the precipitation with methanol to afford 10.78 g (yield 71.8%) of pale orange solid.

¹H NMR (400 MHz, CDCl₃, 27.9 °C, TMS):

δ [ppm] = 7.59 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.16 (s, 1H), 7.10 (d, *J* = 8.3 Hz, 2H), 6.91 (d, *J* = 8.2 Hz, 2H), 3.87 (s, 2H), 2.16 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, 26.6 °C, TMS):

δ [ppm] = 137.52, 130.93, 129.41, 120.15, 40.79.

APCI-MS (negative): Calcd: 350.00 ([M-H]⁺), Found: 349.36.

Anal. Calcd. for C₁₅H₁₄INO: C, 51.30; H, 4.02; N, 3.99. Found: C, 51.60; H, 4.10; N, 3.99.

4-Acetamide-4'-(trimethylsilylethynyl)-diphenylmethane (8).

A 1000 ml flask (three-necked round-bottom flask) containing 4-acetamide-4'-iodo-diphenylmethane (**7**) (7.600 g, 21.64 mmol), copper (I) iodide (0.370 g, 1.95 mmol) was degassed and flushed with argon gas. Under argon gas flowing, [1,1-bis(diphenylphosphino) ferrocene] palladium (II) dichloride: dichloromethane complex (Pd(dppf)Cl₂:CH₂Cl₂) (3.53 g, 4.34 mmol) was carefully added. To the mixture were added 200 ml of tetrahydrofuran (anhydrate grade) and 6.0 ml of trimethylsilyl acetylene (4.26 g, 43.4 mmol) by using a syringe. To the stirred mixture was added 40 ml of diisopropylamine by using a syringe. Then, the mixture was refluxed at 75 °C for two nights. The resulting solution was filtered and evaporated. The crude was dissolved in tetrahydrofuran and adsorbed into Celite particle for column and isolated by using a silica gel flush column chromatography [eluting with n-hexane and ethyl acetate mixture (gradient from 100:0 to 50:50)] and the precipitation with n-hexane to afford 6.30 g (yield 90.5%) of cream-color powder.

¹H NMR (400 MHz, CDCl₃, 25.3 °C, TMS):

δ [ppm] = 7.38 (t, *J* = 8.9 Hz, 4H), 7.17 (s, 1H), 7.09 (d, *J* = 7.9 Hz, 4H), 3.92 (s, 2H), 2.15 (s, 3H), 0.23 (s, 9H).

¹³C NMR (100 MHz, CDCl₃, 26.0 °C, TMS):

δ [ppm] = 168.15, 141.64, 136.59, 136.09, 132.10, 129.44, 128.79, 120.92, 120.14, 105.13, 93.75, 41.20, 24.54, 0.00.

APCI-MS (positive): Calcd: 322.16 ([M+H]⁺), Found: 322.16.

Anal. Calcd. for C₂₀H₂₃NOSi: C, 74.72; H, 7.21; N, 4.36. Found: C, 74.45; H, 6.95; N, 4.32.

4-Acetamide-4'-ethynyl-diphenylmethane (9).

A 25 ml schlenk flask containing 4-acetamide-4'-(trimethylsilylethynyl)-diphenylmethane (**8**) (0.159 g, 0.495 mmol) and potassium carbonate (0.205 g, 1.48 mmol) was degassed and flushed with argon gas. 10 ml of methanol was added. The mixture was stirred at r.t. overnight and then evaporated. The crude was dissolved in chloroform and neutralized with dil. HCl. The organic phase was extracted with chloroform and ethyl acetate. The organic phase was washed with brine, combined, and then dried with magnesium sulfate. The solution was filtered and evaporated. The product was isolated by twice silica gel flash column chromatography [eluting with n-hexane and toluene mixture (80:20)] and eluting with tetrahydrofuran. And then, the precipitation with n-hexane afforded 81.2 mg (yield 65%) of white powder.

¹H NMR (400 MHz, CD₂Cl₂, 25.2 °C, TMS):

δ [ppm] = 7.41-7.39 (m, 4H), 7.27-7.11 (m, 5H), 3.94 (s, 2H), 3.09 (s, 1H), 2.10 (s, 3H).

¹³C NMR (100 MHz, CD₂Cl₂, 26.4 °C, TMS):

δ [ppm] = 168.43, 142.85, 136.93, 136.83, 132.59, 129.72, 129.28, 120.38, 120.18, 83.88, 77.06, 41.52, 24.68.

APCI-MS (negative): Calcd: 248.11 ([M-H]⁻), Found: 248.19.

Anal. Calcd. for C₁₇H₁₅NO: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.55; H, 6.20; N, 5.58.

4,4'-Bis(2,3,4,5-tetraphenyl-phenyl)-diphenylmethane (; called as “pre-G1-1”) (10).

A 200 ml flask (three-necked round-bottom flask) containing 4,4'-diethynyl-diphenylmethane (**3**) (1.325 g, 6.128 mmol) and 2,3,4,5-tetraphenyl-cyclopenta-2,4-dien-1-one (4.97 g, 12.9 mmol) was degassed and flushed with argon gas. 60 ml of xylene (anhydrite grade, *o*-, *m*-, *p*-substituted mixture) was added by using a syringe. The mixture was refluxed at 160 °C for three nights then evaporated. The crude was dissolved in chloroform and spread into acetone. The white precipitate was filtered and washed with acetone to afford 5.09 g (yield 89%) of pearl-white powder.

¹H NMR (400 MHz, CD₂Cl₂, 26.9 °C, TMS):

δ [ppm] = 7.45 (s, 2H), 7.15 (s, 10H), 7.07 (d, *J* = 7.8 Hz, 4H), 6.94 (br, 16H), 6.87-6.86 (m, 14H), 6.82 (m, 4H), 3.82 (s, 2H).

¹³C NMR (100 MHz, CD₂Cl₂, 28.2 °C, TMS):

δ [ppm] = 142.27, 142.23, 141.18, 140.97, 140.67, 140.63, 140.02, 139.74, 139.62, 131.96, 131.88, 131.64, 130.39, 130.34, 128.48, 127.94, 127.23, 126.93, 126.63, 125.97, 125.69, 41.35.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 929.41 ([M+H]⁺), Found: 928.56.

Anal. Calcd. for C₇₃H₅₂: C, 94.36; H, 5.64. Found: C, 94.07; H, 5.53.

4,4'-Bis(2,3,4,5-tetraphenyl-phenyl)-diphenylmethanone (; called as “G1-1on”) (11).

Pre-G1-1 (**10**) (10.00 g, 10.76 mmol) and tetrabutylammonium bromide (138.8 g, 0.4305 mol) were dissolved in 570 ml of 1,2-dichloroethane. To the mixture stirred at 0 °C was added potassium permanganate (68.0 g, 0.430 mol). Then the mixture was stirred at r.t. for 8 days. The resulting solution was quenched with aqueous sodium hydrogen sulfite. The organic phase was extracted with chloroform and washed with brine and then dried with magnesium sulfate. The solution was filtrated and evaporated. The product was isolated by a

silica gel short column chromatography (eluting with chloroform) and purified by precipitation with methanol. It afforded 9.826 g (yield 96.8%) of white powder.

¹H NMR (400 MHz, CD₂Cl₂, 27.3 °C, TMS, chloroform):

δ [ppm] = 7.55 (m, 2H), 7.51 (d, *J* = 8.0 Hz, 4H), 7.25 (d, *J* = 8.0 Hz, 4H), 7.17 (s, 10H), 6.94 (m, 12H), 6.88 (m, 14H), 6.84 (m, 4H).

¹³C NMR (100 MHz, CD₂Cl₂, 28.2 °C, TMS):

δ [ppm] = 196.04, 146.48, 142.40, 142.08, 141.40, 140.70, 140.43, 140.41, 140.21, 139.78, 135.89, 131.92, 131.88, 131.84, 131.37, 130.31, 130.20, 129.63, 128.00, 127.42, 127.27, 127.00, 126.77, 126.27, 126.10, 125.83.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 943.39, Found: 943.63.

Anal. Calcd. for C₇₃H₅₀O: C, 92.96; H, 5.34. Found: C, 92.86; H, 5.55.

4,4'-Bis(3,4-bis(4-triisopropylsilylethynylphenyl)-2,5-diphenyl-phenyl)-diphenylmethane (12).

A 100 ml flask (three-necked round-bottom flask) containing 4,4'-diethynyl-diphenylmethane (**3**) (1.13 g, 5.22 mmol, crude material) and 3,4-bis(4-triisopropylsilylethynyl)phenyl-2,5-diphenyl-cyclopenta-2,4-dien-1-one (**5**) (10.00 g, 13.42 mmol) was degassed and flushed with argon gas. 100 ml of xylene (anhydrate grade, *o*-, *m*-, *p*-substituted mixture) was added by using a syringe. The mixture was refluxed at 175 °C for two nights then evaporated. The crude was dissolved in diethyl ether and adsorbed into Celite particle for column and isolated by using a silica gel flush column chromatography [eluting with n-hexane and toluene mixture (80:20)]. It afforded 5.002 g (yield 58%) of beige amorphous.

¹H NMR (400 MHz, CDCl₃, 26.1 °C, TMS):

δ [ppm] = 7.52 (s, 2H), 7.20-7.07 (m, 14H), 7.01 (t, *J* = 7.6 Hz, 8H), 6.96-6.91 (m, 6H), 6.88 (d, *J* = 8.1 Hz, 4H), 6.81-6.76 (m, 8H), 6.71 (d, *J* = 8.1 Hz, 4H), 3.81 (s, 2H), 1.08 (d, *J* = 3.6 Hz, 84H).

¹³C NMR (100 MHz, CDCl₃, 26.9 °C, TMS):

δ [ppm] = 141.42, 141.03, 140.82, 140.49, 140.09, 139.65, 139.31, 139.22, 139.00, 138.29, 131.90, 131.77, 131.46, 131.34, 131.26, 130.96, 130.68, 129.88, 129.34, 128.22, 127.79, 127.16, 126.44, 125.80, 120.78, 120.54, 107.41, 107.36, 90.17, 89.97, 40.98.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 1650.95 ([M+H]⁺), Found: 1650.93.

Anal. Calcd. for C₁₁₇H₁₃₂Si₄: C, 85.13; H, 8.06. Found: C, 84.80; H, 8.16.

4,4'-Bis(3,4-bis(4-ethynylphenyl)-2,5-diphenyl-phenyl)-diphenylmethane (13).

A 200 ml flask (three-necked round-bottom flask) containing 4,4'-Bis(3,4-bis(4-ethynylphenyl)-2,5-diphenyl-phenyl)-diphenylmethane (**12**) (1.350 g, 0.8178 mmol) was degassed and flushed with argon gas. 50 ml of tetrahydrofuran was added. To the stirred mixture was added 4.90 ml of 1.0M tetrabutylammonium fluoride solution in tetrahydrofuran (4.90 mmol) by using a syringe. After stirring for 2 hrs, the resulting solution was quenched with K₂CO₃ aq. The organic phase was extracted with dichloromethane. The organic phase was washed with brine and dried with magnesium sulfate. The solution was filtrated and evaporated. The crude was dissolved in tetrahydrofuran and precipitated in methanol to afford 0.83 g of beige material. The crude material was instantly used for the next step (Diels-Alder cycloaddition). The product can be purified by gel permeation chromatography (chloroform) to be pale beige powder.

¹H NMR (400 MHz, DMSO-d₆, 25.2 °C, TMS):

δ [ppm] = 7.41 (s, 2H), 7.21-7.13 (m, 10H), 7.06 (t, J = 6.7 Hz, 8H), 7.00-6.94 (m, 14H), 6.89-6.82 (m, 12H), 4.07 (s, 2H), 4.04 (s, 2H), 3.77 (s, 2H).

¹³C NMR (100 MHz, DMSO-d₆, 26.2 °C, TMS):

δ [ppm] = 140.71, 140.62, 140.61, 140.35, 140.20, 140.15, 139.11, 138.85, 138.47, 137.86, 131.34, 131.22, 130.97, 130.91, 130.37, 130.03, 129.53, 128.02, 127.75, 126.99, 126.57, 125.99, 119.13, 118.82, 83.40, 83.36, 80.79, 80.63.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 1025.41 ([M+H]⁺), Found: 1025.63.

APCI-MS (negative): Calcd: 1023.40 ([M-H]⁻), Found: 1023.45.

Pre-G1-2 (**14**).

A 200 ml flask (three-necked round-bottom flask) containing 4,4'-Bis(3,4-bis(4-ethynylphenyl)-2,5-diphenyl-phenyl)-diphenylmethane (**13**) (0.82 g, 0.80 mmol) and 2,3,4,5-tetraphenyl cyclopenta-2,4-dien-1-one (1.320 g, 3.435 mmol) was degassed and flushed with argon gas. 50 ml of xylene (anhydrate grade, *o*-, *m*-, *p*-substituted mixture) was added by using a syringe. The mixture was refluxed at 160 °C for two nights then evaporated. The crude was dissolved in dichloromethane and adsorbed into Celite particle for column and isolated by using a silica gel flush column chromatography [eluting with n-hexane and toluene mixture (gradient from 50:50 to 20:80)]. It afforded 1.557 g (yield 77.6%) of white amorphous. When the product was purified by precipitation with acetone without column chromatography, the yield was enhanced to 90%.

¹H NMR (400 MHz, CD₂Cl₂, 25.5 °C, TMS):

δ [ppm] = 7.45 (s, 2H), 7.41 (s, 2H), 7.37 (s, 2H), 7.14-7.13 (m, 25H), 7.07-7.06 (m, 4H), 7.00 (d, J = 8.0 Hz, 4H), 6.96-6.85 (m, 55H), 6.80-6.72 (m, 24H), 6.66 (d, J = 8.0 Hz, 4H), 6.55 (d, J = 8.0 Hz, 4H), 6.48 (d, J = 8.0 Hz, 4H), 3.79 (s, 2H).

¹³C NMR (100 MHz, CD₂Cl₂, 26.6 °C, TMS):

δ [ppm] = 142.30, 142.23, 142.12, 141.72, 141.11, 141.03, 140.99, 140.87, 140.80, 140.64, 140.58, 140.47, 140.44, 140.04, 139.70, 139.64, 139.60, 139.55, 139.48, 139.25, 139.09, 138.86, 138.70, 138.34, 131.92, 131.90, 131.84, 131.49, 131.46, 131.42, 131.34, 130.58, 130.36, 130.34, 130.31, 130.30, 129.00, 128.71, 128.43, 127.99, 127.89, 127.25, 127.21, 127.16, 126.86, 126.59, 125.96, 125.92, 125.64, 41.32.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 2452.05 ([M+H]⁺), Found: 2451.13.

Anal. Calcd. for C₁₉₃H₁₃₂: C, 94.57; H, 5.43. Found: C, 94.50; H, 5.40.

G1-2on (**15**).

Pre-G1-2 (**14**) (1.501 g, 0.612 mmol) and tetrabutylammonium bromide (7.898 g, 24.48 mmol) were dissolved in 150 ml of 1,2-dichloroethane. To the mixture stirred at 0 °C was added potassium permanganate (3.868 g, 24.48 mmol). Then the mixture was stirred at r.t. for 7 days. The resulting solution was quenched with aqueous sodium hydrogen sulfite. The organic phase was extracted with dichloromethane and washed with brine and then dried with magnesium sulfate. The solution was filtrated and evaporated. The crude was adsorbed into Celite particle for column and isolated by using a silica gel flush column chromatography [eluting with n-hexane and chloroform mixture (gradient from 100:0 to 0:100)]. Then, the product was purified

by a precipitation with methanol to afford 1.394 g (yield 92%) of white powder.

¹H NMR (400 MHz, CD₂Cl₂, 25.9 °C, TMS):

δ [ppm] = 7.52 (d, *J* = 7.7 Hz, 4H), 7.51 (s, 2H), 7.48 (s, 2H), 7.442 (s, 2H), 7.19-7.14 (m, 30H), 7.09-7.07 (m, 4H), 6.94-6.82 (m, 50H), 6.76-6.73 (m, 24H), 6.67 (d, *J* = 8.0 Hz, 4H), 6.55 (d, *J* = 8.0 Hz, 4H), 6.48 (d, *J* = 8.0 Hz, 4H).

¹³C NMR (100 MHz, CD₂Cl₂, 27.0 °C, TMS):

δ [ppm] = 196.17, 146.12, 141.79, 141.75, 141.59, 141.43, 141.43, 141.02, 140.75, 140.73, 140.40, 140.35, 140.02, 139.97, 139.74, 139.61, 139.44, 139.33, 139.27, 139.22, 139.10, 139.04, 138.80, 138.44, 135.38, 131.62, 131.52, 131.29, 131.21, 131.16, 131.04, 130.99, 129.43, 128.79, 128.53, 127.63, 127.55, 127.10, 126.87, 126.81, 126.57, 126.35, 126.22, 125.91, 125.55, 125.30.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 2466.03 ([M+H]⁺), Found: 2466.04.

Anal. Calcd. for C₁₉₃H₁₃₀O: C, 94.04; H, 5.32. Found: C, 93.86; H, 5.29.

4-Acetamide-4'-(3,4-bis(4-triisopropylsilyl ethynylphenyl)-2,5-diphenyl-phenyl)-diphenylmethane (16).

A 300 ml flask (three-necked round-bottom flask) containing 4-acetamide-4'-ethynyl-diphenylmethane (**9**) (4.88 g, 19.6 mmol) and 3,4-bis(4-triisopropylsilyl ethynylphenyl)-2,5-diphenyl-cyclopenta-2,4-dien-1-one (**5**) (16.4 g, 22.0 mmol) was degassed and flushed with argon gas. 100 ml of xylene (anhydride grade, *o*-, *m*-, *p*-substituted mixture) was added by using a syringe. The mixture was refluxed at 170 °C for 26 hours and then stirred at room temperature overnight before it was evaporated to afford brown amorphous. The crude was dissolved in ethyl acetate and adsorbed into Celite particle for column. The product was isolated by using a silica gel flush column chromatography [eluting with n-hexane and ethyl acetate mixture (gradient from 100:0 to 50:50)] and a gel permeation chromatography (chloroform). It afforded 10.86 g (yield 60%) of beige amorphous.

¹H NMR (400 MHz, CD₂Cl₂, 25.0 °C, TMS):

δ [ppm] = 7.49 (s, 1H), 7.45-7.42 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.18-7.12 (m, 5H), 7.09-6.95 (m, 13H), 6.87-6.82 (m, 4H), 6.78 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 2H), 2.07 (s, 3H), 1.08 (s, 42H).

¹³C NMR (100 MHz, CD₂Cl₂, 26.3 °C, TMS):

δ [ppm] = 168.51, 141.85, 141.35, 141.25, 141.18, 140.77, 140.22, 139.83, 139.71, 138.62, 137.38, 136.73, 132.02, 131.83, 131.75, 131.06, 130.79, 130.33, 130.22, 129.56, 128.46, 128.10, 127.41, 126.84, 126.23, 121.22, 120.94, 120.33, 107.35, 90.95, 90.79, 41.17, 24.60, 18.79, 11.72.

APCI-MS (positive): Calcd: 966.55 ([M+H]⁺), Found: 966.54.

Anal. Calcd. for C₆₇H₇₅NOSi₂: C, 83.26; H, 7.82; N, 1.45. Found: C, 83.16; H, 7.60; N, 1.51.

4-Acetamide-4'-(3,4-bis(4-ethynylphenyl)-2,5-diphenyl-phenyl)-diphenylmethane (17).

A 300 ml flask (three-necked round-bottom flask) containing 4-acetamide-4'-(3,4-bis(4-triisopropylsilyl ethynylphenyl)-2,5-diphenyl-phenyl)-diphenylmethane (**16**) (10.86 g, 11.24 mmol) was degassed and flushed with argon gas. 100 ml of tetrahydrofuran was added. To the stirred mixture was added 36.0 ml of 1.0M tetrabutylammonium fluoride solution in tetrahydrofuran (36.0 mmol) by using a syringe. After stirring for 160 min, the resulting solution was quenched with K₂CO₃ aq. The organic phase was extracted with ethyl acetate. The organic phase was washed with brine and dried with magnesium sulfate. The solution was filtrated and

evaporated to quantitatively afford 7.34 g of beige amorphous. The product can be purified by gel permeation chromatography (chloroform) and reprecipitation with n-hexane to be pale beige powder.

¹H NMR (400 MHz, CD₂Cl₂, 25.1 °C, TMS):

δ [ppm] = 7.51 (s, 1H), 7.43 (s, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.17-7.12 (m, 5H), 7.07-7.05 (m, 6H), 7.02-6.96 (m, 7H), 6.86-6.81 (m, 4H), 6.76 (d, *J* = 8.0 Hz, 2H), 3.85 (s, 2H), 3.02 (s, 1H), 3.00 (s, 1H), 2.09 (s, 3H).

¹³C NMR (100 MHz, CD₂Cl₂, 26.0 °C, TMS):

δ [ppm] = 168.52, 141.69, 141.65, 141.41, 141.26, 141.20, 141.16, 140.12, 139.94, 139.66, 138.55, 137.34, 136.82, 132.02, 131.93, 131.84, 131.19, 130.90, 130.36, 130.26, 129.58, 128.50, 128.12, 127.44, 126.90, 126.27, 120.31, 119.81, 119.50, 83.84, 77.42, 77.28, 41.19, 24.65.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 654.28 ([M+H]⁺), Found: 654.35.

APCI-MS (positive): Calcd: 654.28 ([M+H]⁺), Found: 654.12.

Pre-G1-2-half-NHAc (18).

A 300 ml flask (three-necked round-bottom flask) containing 4-acetamide-4'-(3,4-bis(4-ethynyl phenyl)-2,5-diphenyl-phenyl)-diphenylmethane (**17**) (7.34 g, 11.23 mmol) and 2,3,4,5-tetraphenyl cyclopenta-2,4-dien-1-one (14.00 g, 36.41 mmol) was degassed and flushed with argon gas. 200 ml of xylene (anhydride grade, *o*-, *m*-, *p*-substituted mixture) was added by using a syringe. The mixture was refluxed at 170 °C for two nights then evaporated. The crude was dissolvable in acetone which could be used for the precipitation as “pre-G1-2”. The crude was dissolved in chloroform and adsorbed into Celite particle for column. The product was isolated by using a silica gel flash column chromatography [eluting with n-hexane and toluene mixture (gradient from 50:50 to 0:100) and then eluting with toluene and ethyl acetate mixture (gradient from 100:0 to 0:100)]. It afforded 14.942 g (yield 91%) of orange amorphous.

¹H NMR (400 MHz, CDCl₃, 25.8 °C, TMS):

δ [ppm] = 7.48 (d, *J* = 3.4 Hz, 2H), 7.44 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.14 (s, 13H), 7.07-7.05 (m, 5H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.93-6.82 (m, 27H), 6.76-6.71 (m, 12H), 6.66 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 8.0 Hz, 2H), 6.47 (d, *J* = 8.0 Hz, 2H), 3.85 (s, 2H), 2.15 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, 27.1 °C, TMS):

δ [ppm] = 168.07, 141.81, 141.72, 141.14, 140.76, 140.73, 140.71, 140.60, 140.48, 140.44, 140.05, 140.01, 139.98, 139.62, 139.30, 139.21, 139.17, 139.10, 139.04, 138.83, 138.62, 138.25, 138.16, 137.78, 137.22, 135.86, 131.71, 131.63, 131.53, 131.51, 131.23, 131.14, 131.06, 130.05, 130.02, 129.95, 129.43, 128.73, 128.45, 128.14, 127.54, 126.86, 126.80, 126.56, 126.20, 125.57, 125.28, 120.03, 40.88, 24.56.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 1367.60 ([M+H]⁺), Found: 1368.02.

Anal. Calcd. for C₁₀₅H₇₅NO: C, 92.27; H, 5.53; N, 1.02. Found: C, 91.96; H, 5.28; N, 1.07.

Pre-G1-2-half-NH (19).

A 200 ml flask (three-necked round-bottom flask) containing pre-G1-2-half-NHAc (**18**) (3.630 g, 2.654 mmol) was degassed and flushed with argon gas. 80 ml of tetrahydrofuran and 5 ml of methanol were added. To the stirred mixture was added 10.0 ml of boron trifluoride: diethyl ether complex (BF₃:Et₂O) (11.3 g, 79.6

mmol) by using a hole pipette. The mixture was refluxed at 80 °C for 10 days. The resulting solution was quenched with water and neutralized with aqueous potassium carbonate. The organic phase was extracted with ethyl acetate and washed with sodium thiosulfate several times. The organic phase was washed brine and dried with magnesium sulfate. The solution was filtered and evaporated. The crude was dissolved in ethyl acetate and adsorbed into silica gel. The product was isolated by using a silica gel flash column chromatography [eluting with n-hexane and ethyl acetate mixture (gradient from 100:0 to 50:50)]. It afforded 3.485 g (yield 99%) of beige solid.

¹H NMR (400 MHz, CDCl₃, 25.5 °C, TMS):

δ [ppm] = 7.49 (d, *J* = 3.9 Hz, 2H), 7.44 (s, 1H), 7.14 (s, 13H), 7.07-7.05 (m, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.94-6.82 (m, 29H), 6.76-6.71 (m, 12H), 6.65 (d, *J* = 8.0 Hz, 2H), 6.60 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 8.0 Hz, 2H), 6.47 (d, 2H), 3.780 (s, 2H), 3.54 (br, 2H).

¹³C NMR (100 MHz, CDCl₃, 26.8 °C, TMS):

δ [ppm] = 144.42, 141.84, 141.80, 141.72, 141.12, 140.73, 140.70, 140.48, 140.44, 140.11, 140.05, 140.01, 139.98, 139.69, 139.32, 139.28, 139.20, 139.16, 139.10, 139.04, 138.60, 138.56, 138.22, 138.20, 137.80, 131.73, 131.63, 131.53, 131.51, 131.23, 131.20, 131.15, 131.07, 130.06, 129.95, 129.92, 129.75, 128.72, 128.44, 128.05, 127.54, 126.86, 126.80, 126.56, 126.20, 125.53, 125.28, 115.25, 40.61.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 1325.58 ([M+H]⁺), Found: 1325.85.

Anal. Calcd. for C₁₀₃H₇₃N: C, 93.39; H, 5.55; N, 1.06. Found: C, 93.31; H, 5.27; N, 1.12.

Pre-G1-2-half-2-1 (20).

A 100 ml flask (three-necked round-bottom flask) containing pre-G1-2-half-NH (**19**) (2.727 g, 2.058 mmol) and G1-1on (**11**) (2.030 g, 2.152 mmol) and 4-diazabicyclo[2.2.2]octane (DABCO) (1.645 g, 14.66 mmol) was degassed and flushed with argon gas. The mixture was dissolved in 60 ml of chlorobenzene at 100 °C. Titanium chloride (0.400 ml, 3.65 mmol) was dissolved in 5 ml of chlorobenzene, and then dropwise added to the stirred mixture by using a dropping funnel. The reaction mixture was stirred at 125 °C for 6 hours in an argon atmosphere and then stirred at room temperature in air overnight. The resulting solution was filtered through a pad of Celite and silica gel. The filtrate was concentrated. The product was isolated by a gel permeation chromatography (chloroform) and precipitation with methanol. It afforded 3.545 g (yield 76%) of yellow powder.

¹H NMR (400 MHz, CD₂Cl₂, 26.0 °C, TMS):

δ [ppm] = 7.54 (s, 1H), 7.49 (s, 1H), 7.45 (s, 1H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.41 (s, 1H), 7.37 (s, 1H), 7.19 (s, 1H), 7.16-7.11 (m, 24H), 7.06-6.97 (m, 10H), 6.94-6.84 (m, 53H), 6.82-6.77 (m, 11H), 6.74-6.72 (m, 5H), 6.65 (d, *J* = 8.0 Hz, 2H), 6.55 (d, *J* = 8.0 Hz, 4H), 6.48 (d, *J* = 8.0 Hz, 2H), 3.81 (s, 2H).

MALDI TOF-MS (Matrix: Dithranol): Calcd: 2249.96 ([M+H]⁺), Found: 2250.29.

Anal. Calcd. for C₁₇₆H₁₂₁N: C, 93.96; H, 5.42; N, 0.62. Found: C, 93.93; H, 5.41; N, 0.68.

G1-2-half-2-on (21).

Pre-G1-2-half-2-1 (**20**) (3.500 g, 1.556 mmol) and tetrabutylammonium bromide (20.04 g, 62.22 mmol) were dissolved in 200 ml of 1,2-dichloroethane. To the mixture stirred at 0 °C was added potassium permanganate (9.83 g, 62.2 mmol). Then the mixture was stirred at r.t. for 5 days. The resulting solution was quenched with aqueous sodium hydrogen sulfite and filtered through a pad of Celite. The organic phase was extracted with 10% trimethylamine-attached chloroform and washed with brine and then dried with magnesium sulfate. The solution was filtered and evaporated. The product was purified by precipitation with methanol to afford 3.446 g (yield 97.8%) of yellow powder.

¹H NMR (400 MHz, CD₂Cl₂, 26.3 °C, TMS):

δ [ppm] = 7.56-7.42 (m, 9H), 7.42 (s, 1H), 7.38 (s, 1H), 7.22-7.08 (m, 29H), 7.03-6.85 (m, 52H), 6.79-6.74 (m, 19H), 6.67 (t, *J* = 7.5 Hz, 4H), 6.57 (d, *J* = 7.3 Hz, 2H), 6.51 (d, *J* = 7.2 Hz, 2H).

¹³C NMR (100 MHz, CD₂Cl₂, 27.7 °C, TMS):

δ [ppm] = 195.41, 168.54, 155.94, 146.19, 145.16, 142.94, 142.40, 142.30, 142.14, 142.10, 141.90, 141.34, 141.12, 141.01, 140.83, 140.76, 140.72, 140.62, 140.45, 140.33, 140.16, 139.82, 139.77, 139.68, 139.64, 139.56, 139.49, 139.38, 139.02, 138.45, 138.18, 137.31, 136.32, 132.47, 131.99, 131.92, 131.90, 131.87, 131.81, 131.59, 131.44, 131.37, 131.31, 131.09, 130.29, 130.12, 129.91, 129.47, 129.08, 128.78, 128.05, 127.95, 127.90, 127.44, 127.24, 127.16, 126.96, 126.87, 126.73, 126.60, 126.28, 126.04, 125.93, 125.78, 125.65, 120.74.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 2263.94 ([M+H]⁺), Found: 2264.55.

Anal. Calcd. for C₁₇₆H₁₁₉NO: C, 93.38; H, 5.30; N, 0.63. Found: C, 92.98; H, 5.36; N, 0.68.

Pre-G2-2-half-NH (22).

A 200 ml flask (three-necked round-bottom flask) containing G1-2on (**15**) (2.500 g, 1.014 mmol) and 4,4'-diamino-diphenylmethane (4.020 g, 20.27 mmol) and 4-diazabicyclo[2.2.2]octane (DABCO) (1.640 g, 14.62 mmol) was degassed and flushed with argon gas. The mixture was dissolved in 100 ml of chlorobenzene at 80 °C. Titanium chloride (0.400 ml, 3.64 mmol) was dissolved in 8 ml of chlorobenzene, and then dropwise added to the stirred mixture by using a dropping funnel. The reaction mixture was stirred at 125 °C for 21 hours in an argon atmosphere and then stirred at room temperature for 3.5 hrs in air. The resulting solution was filtered through a pad of Celite and silica gel. The filtrate was concentrated. The product was isolated by a gel permeation chromatography (chloroform) and precipitation with methanol to afford 2.153 g (yield 80%) of beige solid.

¹H NMR (400 MHz, CDCl₃, 25.3 °C, TMS):

δ [ppm] = 7.51-7.41 (m, 8H), 7.14-7.08 (m, 32H), 6.96-6.72 (m, 80H), 6.68-6.63 (m, 6H), 6.57-6.53 (m, 8H), 6.49-6.47 (m, 4H), 3.79 (s, 2H), 3.46 (br, 2H).

¹³C NMR (100 MHz, CDCl₃, 26.4 °C, TMS):

δ [ppm] = 167.48, 149.09, 144.38, 144.11, 142.01, 141.78, 141.73, 141.69, 141.38, 141.08, 140.91, 140.80, 140.74, 140.41, 140.29, 140.07, 140.01, 139.78, 139.72, 139.43, 139.24, 139.09, 139.02, 138.71, 138.35, 137.98, 137.94, 137.70, 137.64, 137.61, 136.46, 134.04, 131.62, 131.51, 131.16, 131.07, 131.01, 130.03, 129.94, 129.67, 129.46, 129.33, 128.96, 128.90, 128.75, 128.62, 128.49, 127.54, 127.06, 126.86, 126.80, 126.56, 126.27, 126.21, 125.82, 125.55, 125.29, 121.27, 115.23, 40.44.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 2646.13 ($[M+H]^+$), Found: 2646.33.
Anal. Calcd. for $C_{206}H_{142}N_2$: C, 93.53; H, 5.41; N, 1.06. Found: C, 93.28; H, 5.42; N, 1.18.

Pre-G2-2-quarter-3-1 (23).

A 200 ml flask (three-necked round-bottom flask) containing G1-2-half-2-1on (**21**) (1.815 g, 0.8017 mmol) and pre-G2-2-half-NH (**22**) (2.100 g, 0.7938 mmol) and 4-diazabicyclo[2.2.2]octane (DABCO) (1.640 g, 14.62 mmol) was degassed and flushed with argon gas. The mixture was dissolved in 80 ml of chlorobenzene at 80 °C. Titanium chloride (0.200 ml, 1.82 mmol) was dissolved in 10 ml of chlorobenzene and dropwise added to the stirred mixture by using a dropping funnel. The reaction mixture was refluxed at 135 °C for 5 hours in an argon atmosphere. Additionally, titanium chloride (0.200 ml, 1.82 mmol) was dissolved in 5 ml of chlorobenzene and dropwise added to the reaction mixture by using a dropping funnel. The reaction mixture was refluxed at 135 °C for 15 hrs in an argon atmosphere and then stirred at room temperature for 3 hrs in air. The resulting solution was filtered through a pad of Celite and silica gel. The filtrate was concentrated. The product was isolated by a gel permeation chromatography (chloroform) and precipitation with methanol to afford 3.276 g (yield 84%) of yellow powder.

1H NMR (400 MHz, CD_2Cl_2 , 25.5 °C, TMS):

δ [ppm] = 7.55-7.35 (m, 17H), 7.21-7.02 (m, 62H), 6.98-6.65 (m, 160H), 6.61-6.44 (m, 18H), 3.83 (s, 1H), 3.66 (s, 1H).

^{13}C NMR (100 MHz, CD_2Cl_2 , 26.8 °C, TMS):

δ [ppm] = 168.31, 168.20, 149.61, 144.99, 144.91, 144.69, 142.80, 142.53, 142.30, 142.13, 141.90, 141.60, 141.28, 141.13, 141.02, 140.86, 140.79, 140.76, 140.72, 140.64, 140.47, 140.45, 140.36, 140.22, 139.84, 139.71, 139.67, 139.61, 139.56, 139.49, 139.35, 139.31, 138.97, 138.53, 138.25, 137.65, 136.48, 134.72, 134.48, 134.13, 133.73, 132.03, 131.93, 131.84, 131.71, 131.47, 131.39, 131.33, 130.31, 130.00, 129.82, 129.63, 129.32, 129.24, 129.04, 128.76, 128.04, 128.01, 127.97, 127.90, 127.42, 127.25, 127.22, 127.17, 126.98, 126.87, 126.70, 126.60, 126.24, 126.05, 125.97, 125.93, 125.78, 125.65, 121.66, 121.50, 120.82, 41.01

MALDI TOF-MS (Matrix: Dithranol): Calcd: 4892.06 ($[M+H]^+$), Found: 4892.39.

Anal. Calcd. for $C_{382}H_{259}N_3$: C, 93.80; H, 5.34; N, 0.86. Found: C, 93.56; H, 5.33; N, 0.92.

G2-2-quarter-3-1on (; also named as “4Non”) (24).

Pre-G2-2-quarter-3-1 (**23**) (3.275 g, 0.6695 mmol) and tetrabutylammonium bromide (8.640 g, 26.78 mmol) were dissolved in 210 ml of 1,2-dichloroethane. To the mixture stirred at 0 °C was added potassium permanganate (4.240 g, 26.78 mmol). Then the mixture was stirred at r.t. for 6 days. The resulting solution was quenched with aqueous sodium hydrogen sulfite. The organic phase was extracted with 10% trimethylamine-attached chloroform and washed with brine and then dried with magnesium sulfate. The solution was filtrated and evaporated. The product was isolated by a gel permeation chromatography (chloroform) and precipitation with methanol to afford 3.190 g (yield 97%) of yellow powder.

1H NMR (400 MHz, CD_2Cl_2 , 26.1 °C, TMS, drop of triethylamine was added as a stabilizer):

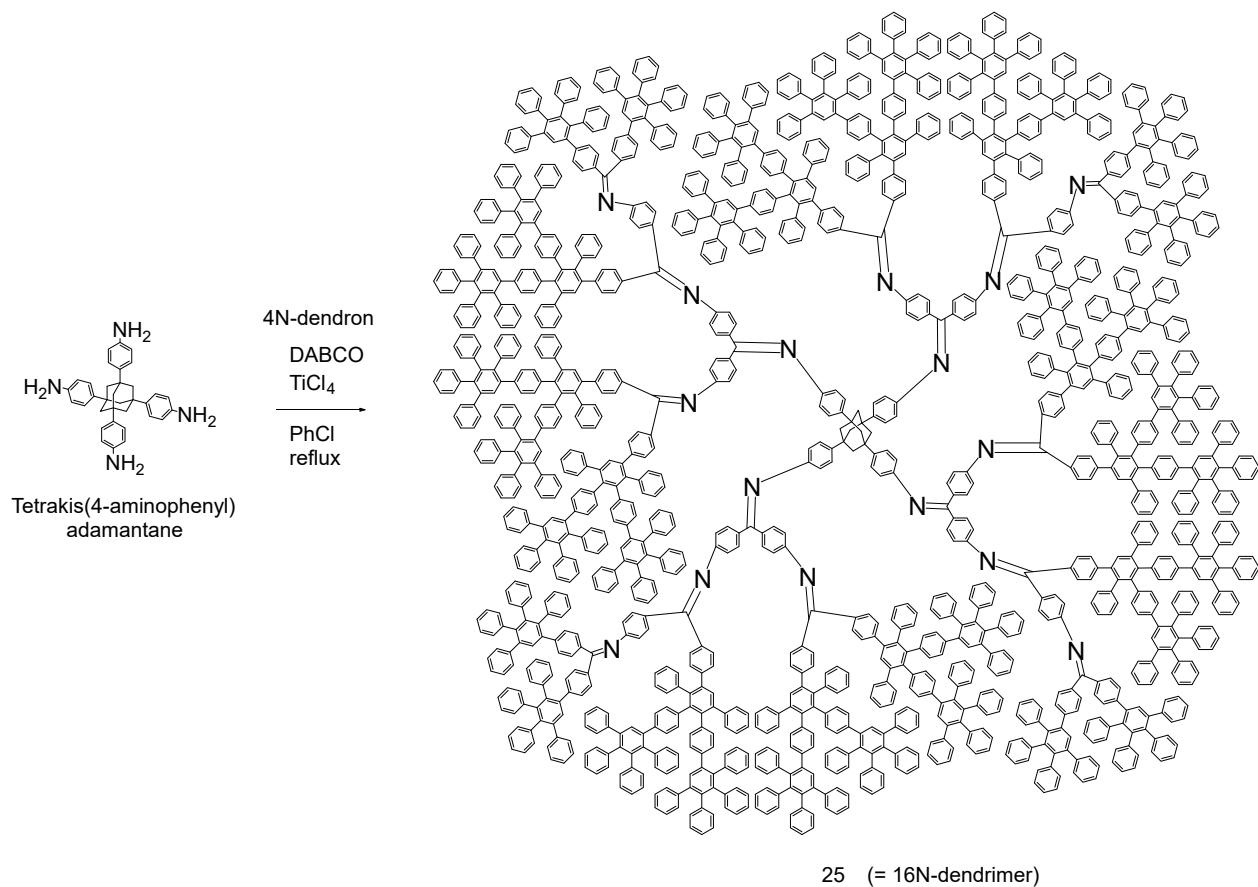
δ [ppm] = 7.58-7.35 (m, 21H), 7.22-7.03 (m, 61H), 6.98-6.63 (m, 162H), 6.58-6.45 (m, 13H).

^{13}C NMR (100 MHz, CD_2Cl_2 , 26.9 °C, TMS, drop of triethylamine was added as a stabilizer):

δ [ppm] = 194.85, 168.45, 168.33, 168.27, 155.89, 155.62, 154.52, 145.18, 145.03, 142.94, 142.87, 142.39, 142.28, 142.12, 142.09, 141.93, 141.60, 141.33, 141.12, 141.00, 140.83, 140.77, 140.73, 140.62, 140.58, 140.45, 140.37, 140.18, 140.06, 139.84, 139.71, 139.65, 139.60, 139.54, 139.48, 139.31, 138.97, 138.46, 138.20, 137.50, 137.32, 134.05, 133.77, 132.96, 132.76, 131.91, 131.82, 131.45, 131.36, 131.30, 131.10, 130.49, 130.30, 130.12, 129.91, 129.03, 128.75, 127.98, 127.89, 127.39, 127.24, 127.20, 127.16, 126.97, 126.86, 126.69, 126.58, 126.21, 126.03, 125.92, 125.78, 125.64, 120.89, 120.83, 120.66

MALDI TOF-MS (Matrix: Dithranol): Calcd: 4906.04 ([M+H]⁺), Found: 4906.49.

Anal. Calcd. for C₃₈₂H₂₅₇N₃O: C, 93.54; H, 5.28; N, 0.86. Found: C, 93.40; H, 5.34; N, 0.97.



Scheme S5. Synthesis of adamantine-core polyphenylene jacketed phenylazomethine dendrimer (PPDPA16).

PPDPA16 (16N dendrimer) (25).

A 100 ml flask (three-necked round-bottom flask) containing 1,3,5,7-Tetrakis(4-aminophenyl)adamantane (20.4 mg, 40.7 μ mol) and 4Non (**24**) (1.002 g, 204.2 μ mol) and 4-diazabicyclo[2.2.2]octane (DABCO) (1.23 g, 11.0 mmol) was degassed and flushed with argon gas. The mixture was dissolved in 35 ml of chlorobenzene at 100 °C. Titanium chloride (0.100 ml, 0.912 mmol) was dissolved in 5 ml of chlorobenzene and dropwise added to the stirred mixture by using a dropping funnel. The reaction mixture was refluxed at 130 °C for 27 hours in an argon atmosphere. Additionally, titanium chloride (0.100 ml, 0.912 mmol) was dissolved in 4 ml of chlorobenzene and dropwise added to the reaction mixture by using a dropping funnel. The reaction mixture was refluxed at 130 °C for 18 hrs in an argon atmosphere and then stirred at room temperature for 5 hrs in air. The resulting solution was filtered through a pad of Celite and silica gel. The filtrate was concentrated. The product was isolated by a gel permeation chromatography (chloroform) and precipitation with methanol to afford 153.9 mg (yield 19%) of yellow powder as PPDPA16 (**25**) and also 183.3 mg (yield 30%) of yellow powder as 4Non tri-substituent derivative.

^1H NMR (400 MHz, CD_2Cl_2 , 27.1 °C, TMS):

δ [ppm] = 7.55-7.25 (m, 80H), 7.21-6.63 (m, 882H), 6.52-6.47 (m, 82H), 1.79 (br, 12H).

^{13}C NMR (100 MHz, CD_2Cl_2 , 26.0 °C, TMS):

δ [ppm] = 168.03, 166.78, 154.16, 153.73, 152.11, 151.89, 149.58, 144.81, 142.63, 142.24, 142.08, 142.03, 141.84, 141.56, 141.10, 140.98, 140.83, 140.75, 140.60, 140.42, 140.21, 140.15, 139.82, 139.59, 139.53, 139.46, 139.36, 139.24, 138.95, 138.46, 138.22, 137.52, 135.14, 134.29, 134.03, 133.81, 131.89, 131.46, 131.35, 131.10, 130.27, 129.02, 128.76, 127.88, 127.39, 127.15, 126.96, 126.85, 126.66, 126.57, 126.22, 125.91, 125.62, 121.29, 120.86, 47.62, 39.07.

MALDI TOF-MS (Matrix: Dithranol): Calcd: 20049.37 ([M+H] $^+$), Found: 20049.37.

Anal. Calcd. for $\text{C}_{1562}\text{H}_{1056}\text{N}_{16}$: C, 93.57; H, 5.31; N, 1.22. Found: C, 93.30; H, 5.25; N, 1.23.

4. UV-vis titration

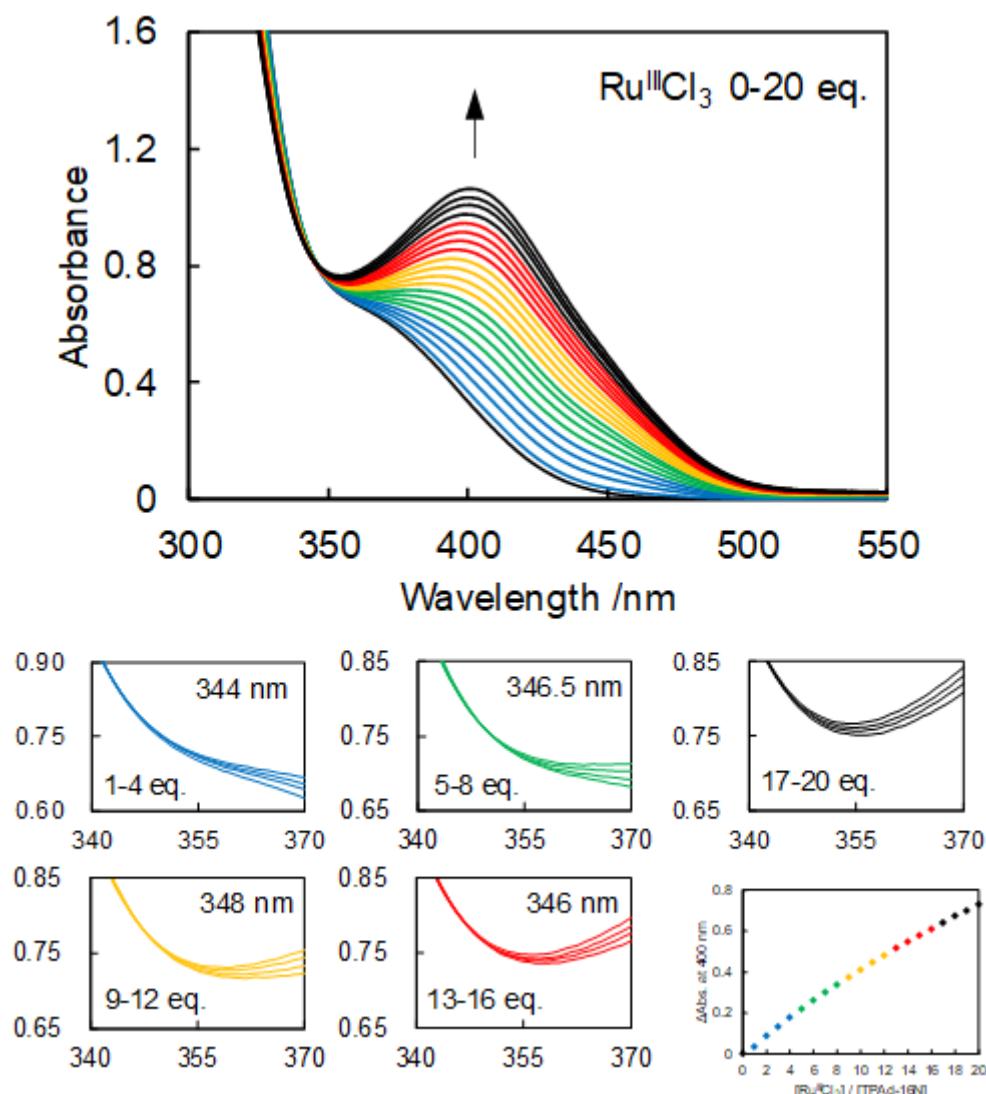


Figure S3. Accumulation of Ru to PPDPA16. (top) Change in UV-vis absorption spectra of PPDPA16 in DCM upon the addition of Ru^{III}Cl₃ in MeCN up to 20 equiv. ([PPDPA16] = ca. 5 μ M, 20 °C). (down) Enlarged views during complexation with Ru^{III}Cl₃ in respective positions 0–4, 5–8, 9–12, 13–16, and 17–20 equiv and the ΔAbs plot during the addition of Ru^{III}Cl₃.

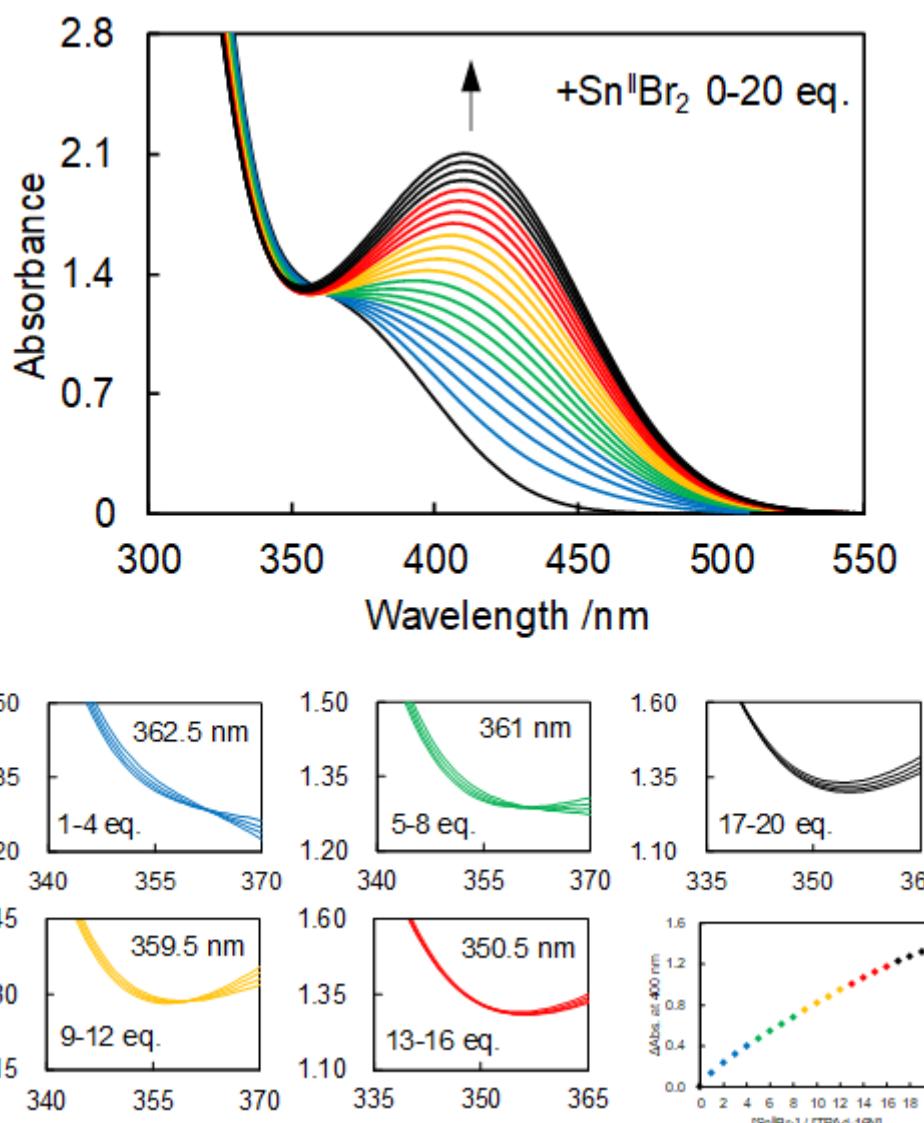


Figure S4 Accumulation of Sn to PPDPA16. (top) Change in UV-vis absorption spectra of PPDPA16 in DCM/MeCN = 2/1 upon the addition of Sn^{II}Br₂ in MeCN up to 20 equiv. ([PPDPA16] = ca. 10 μ M, 20 °C). (down) Enlarged views during complexation with Sn^{II}Br₂ in respective positions 0–4, 5–8, 9–12, 13–16, and 17–20 equiv and the Δ Ads plot during the addition of Sn^{II}Br₂.

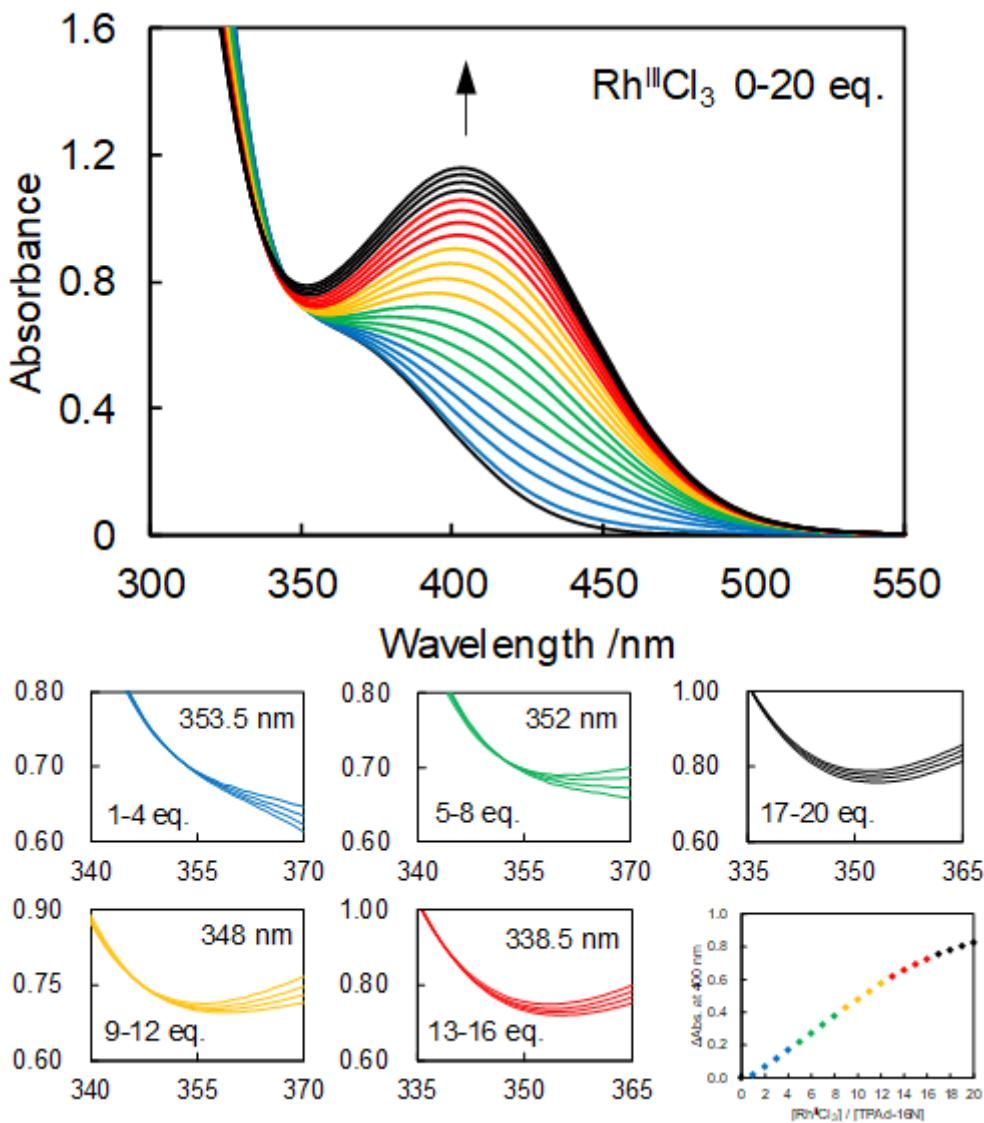


Figure S5 Accumulation of Rh to PPDPA16. (top) Change in UV-vis absorption spectra of PPDPA16 in DCM upon the addition of Rh^{III}Cl₃ in MeCN/MeOH = 250/1 up to 20 equiv. ([PPDPA16] = ca. 5 μ M, 20 °C). (down) Enlarged views during complexation with Rh^{III}Cl₃ in respective positions 0–4, 5–8, 9–12, 13–16, and 17–20 equiv and the Δ Ads plot during the addition of Rh^{III}Cl₃.

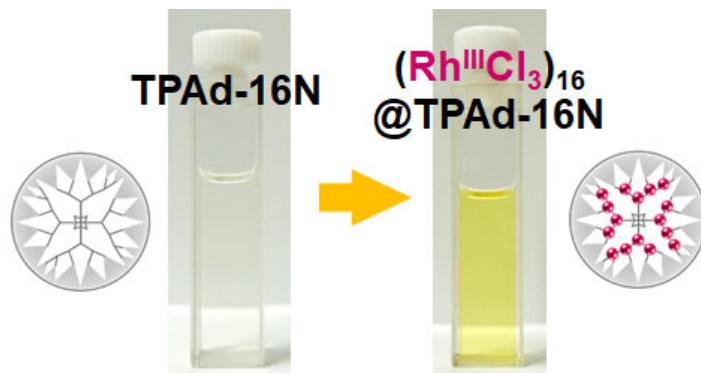


Figure S6. Photo of the PPDPA16 solution before and after the addition of 16 equivalent of Rh^{III}Cl₃.

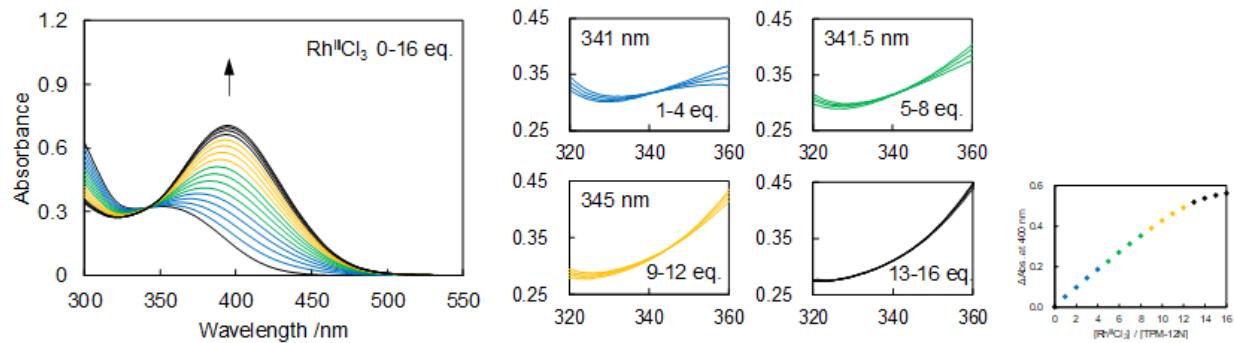


Figure S7 Accumulation of Rh to DPA12. (left) Change in UV-vis absorption spectra of DPA12 in DCM upon the addition of Rh^{III}Cl₃ in MeCN/MeOH = 250/1 up to 16 equiv. ([DPA12] = ca. 5 μ M, 20 °C). (right) Enlarged views during complexation with Rh^{III}Cl₃ in respective positions 0–4, 5–8, 9–12, and 13–16 equiv and the Δ Ads plot during the addition of Rh^{III}Cl₃.

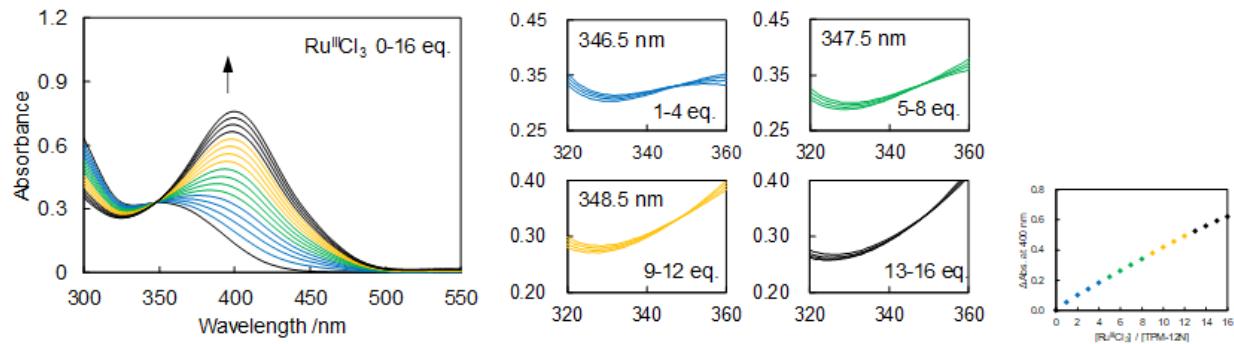


Figure S8 Accumulation of Ru to DPA12. (left) Change in UV-vis absorption spectra of DPA12 in DCM upon the addition of Ru^{III}Cl₃ in MeCN up to 16 equiv. ([DPA12] = ca. 5 μ M, 20 °C). (right) Enlarged views during complexation with Ru^{III}Cl₃ in respective positions 0–4, 5–8, 9–12, and 13–16 equiv and the Δ Ads plot during the addition of Ru^{III}Cl₃.

5. XPS Spectra

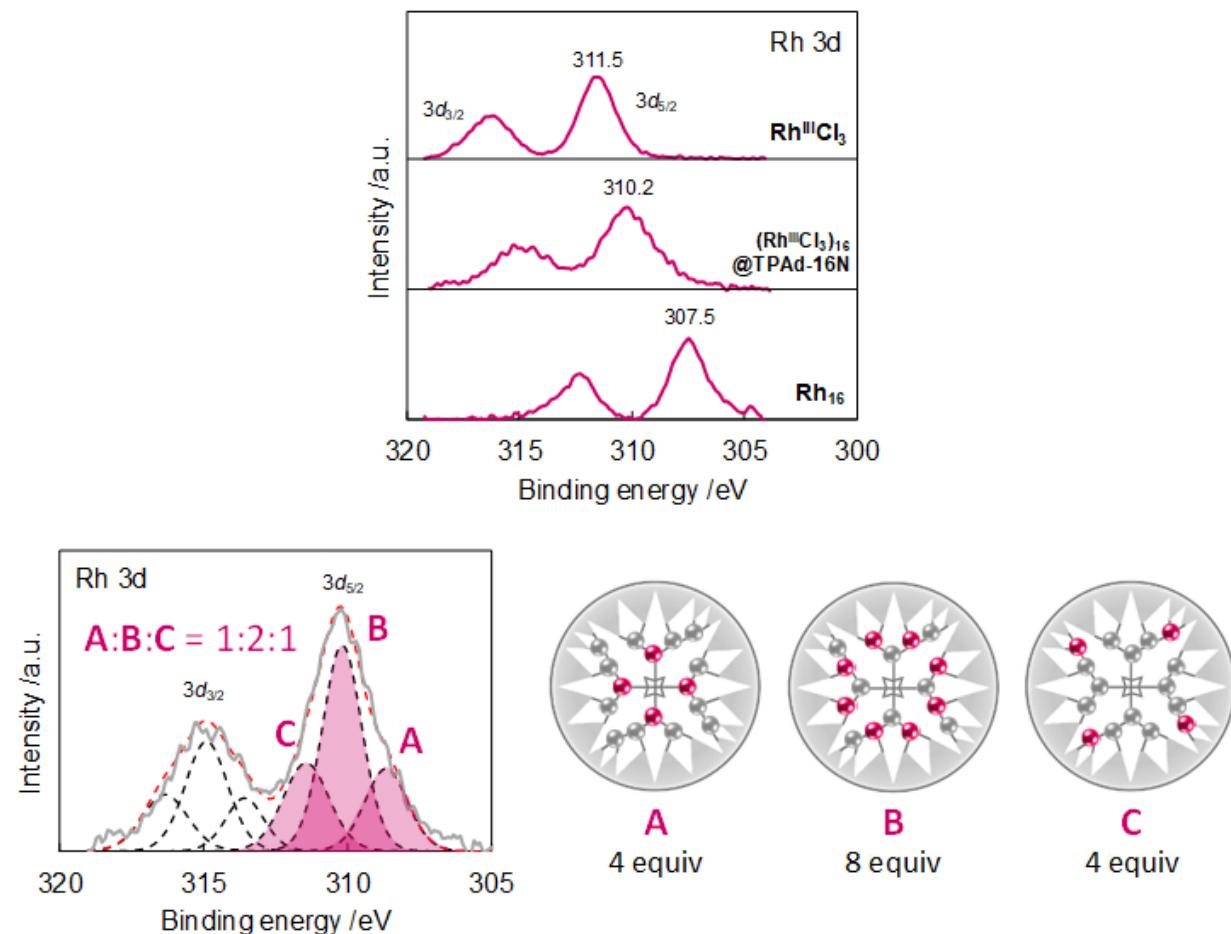


Figure S9 XPS spectra of $\text{Rh}^{III}\text{Cl}_3$, $(\text{Rh}^{III}\text{Cl}_3)_{16} @ \text{PPDPA16}$, and synthesized Rh cluster.

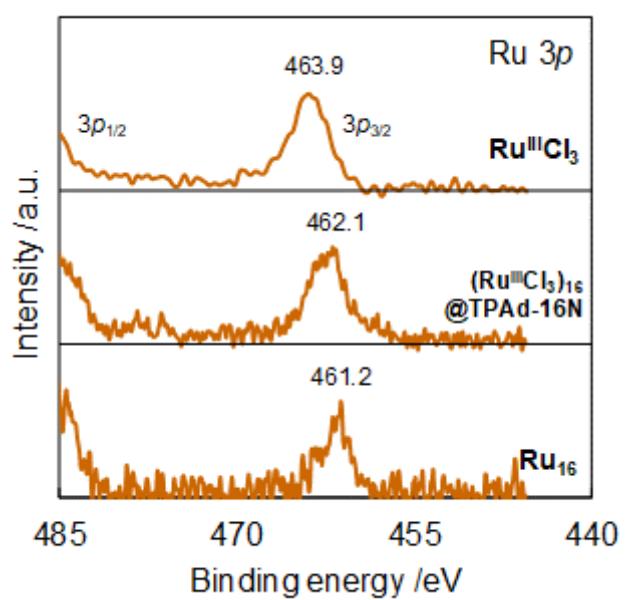


Figure S10 XPS spectra of $\text{Ru}^{\text{III}}\text{Cl}_3$, $(\text{Ru}^{\text{III}}\text{Cl}_3)_{16}$ @PPDPA16, and synthesized Ru cluster.

6. STEM Images

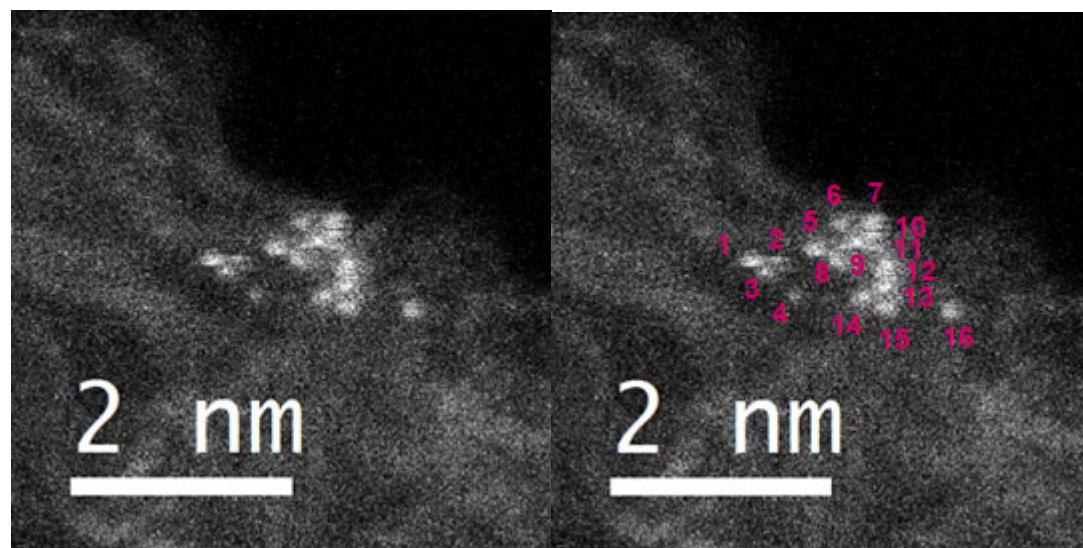


Figure S11 STEM image of Rh nanoparticle after disassembly. The numbers are the count of atoms

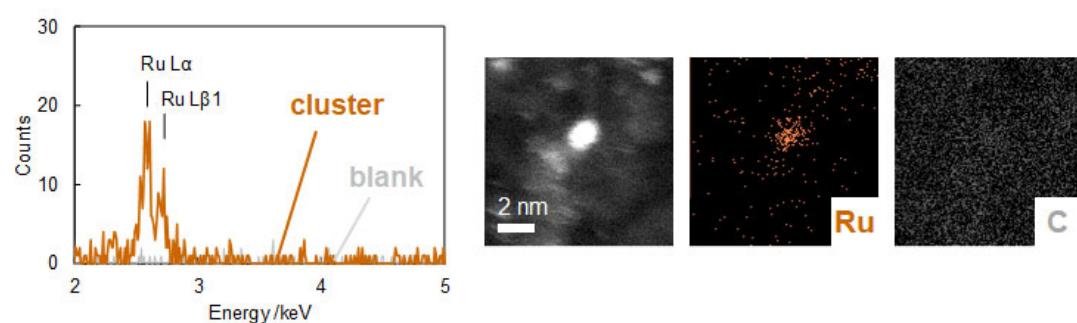
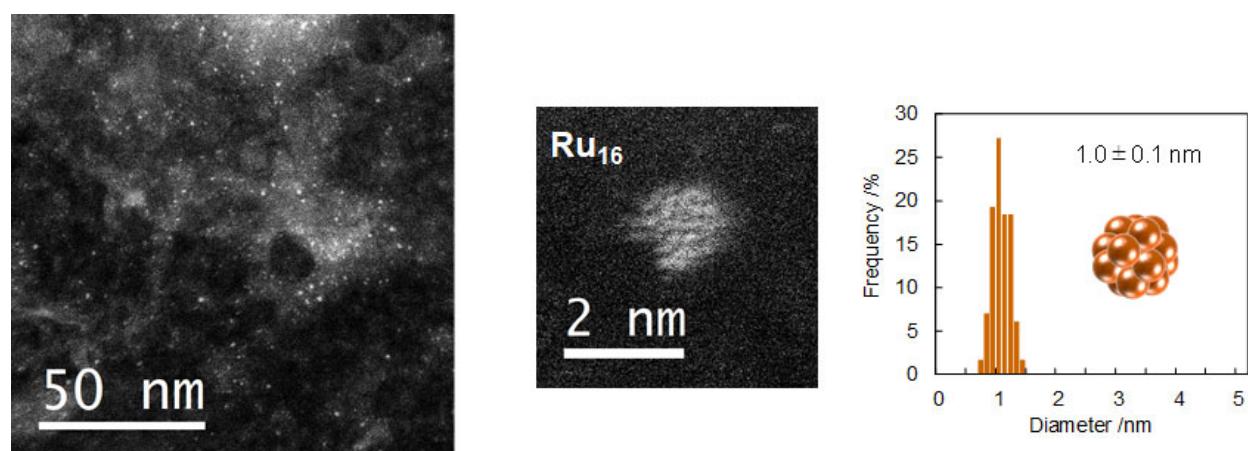


Figure S12. STEM image, histogram, and EDX analysis of the synthesized Ru nanoparticle.

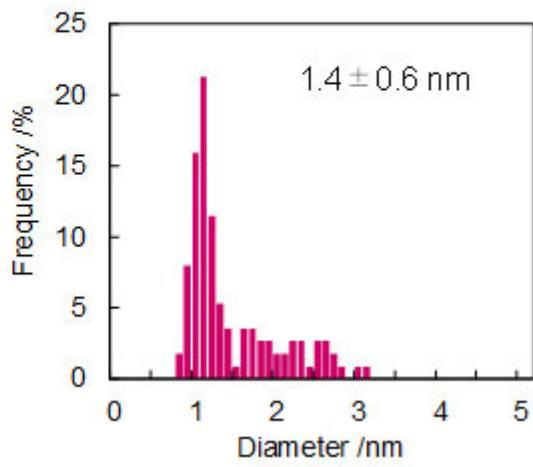
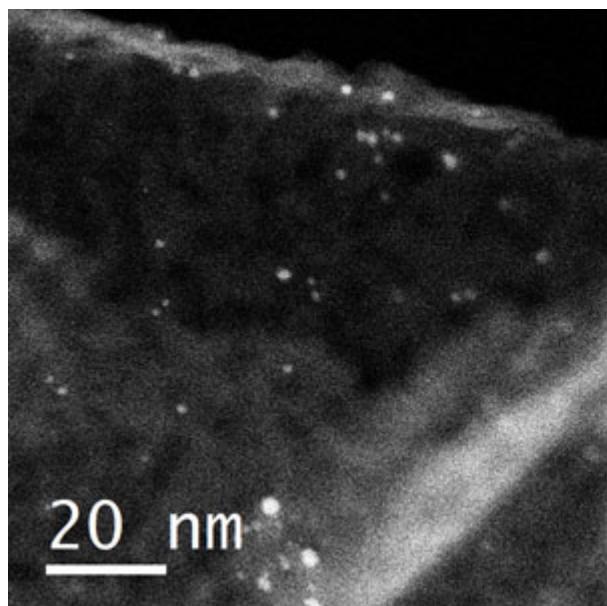


Figure S13 STEM image, and histogram of Rh nanoparticles synthesized with DPA12 with 12 equiv. RhCl_3 .

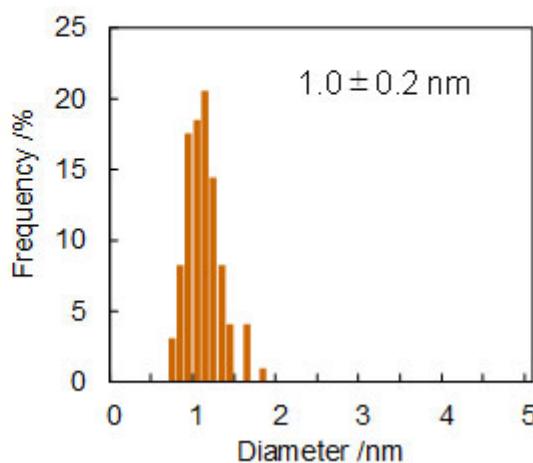
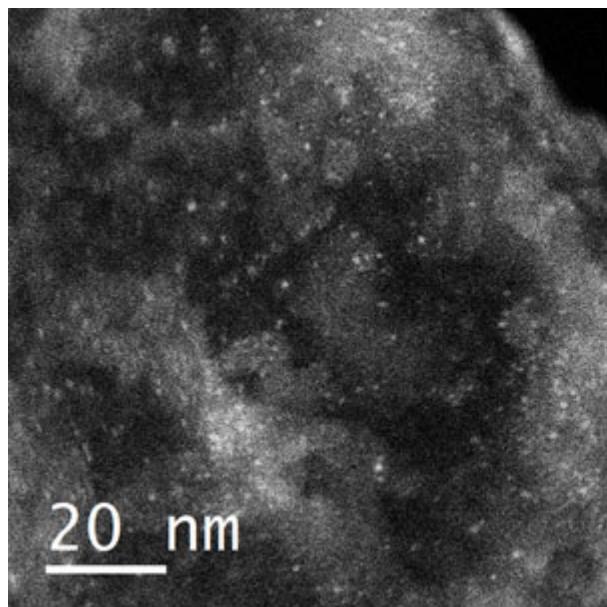
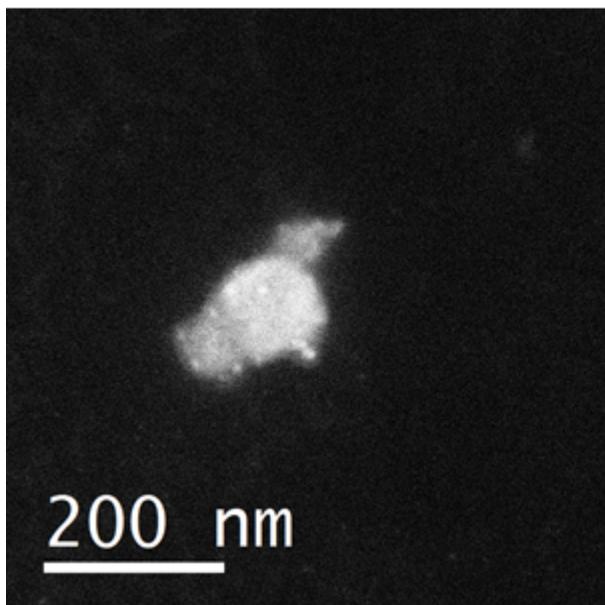


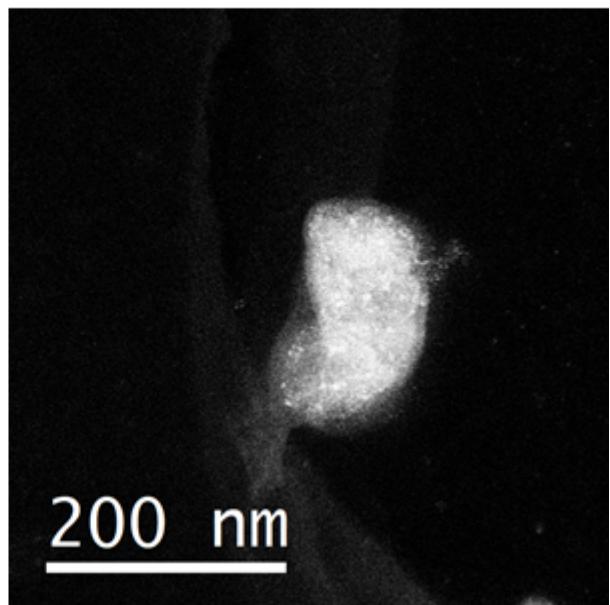
Figure S14 STEM image, and histogram of Ru nanoparticles synthesized with DPA12 with 12 equiv. RuCl_3 .

Rh₁₆ (non-template)



200 nm

Ru₁₆ (non-template)



200 nm

Figure S15 STEM image of Rh and Ru nanoparticles synthesized without any template dendrimer.

4,4'-Diododiphenylmethane 1H (CDCl₃, 400MHz, 302.5K)

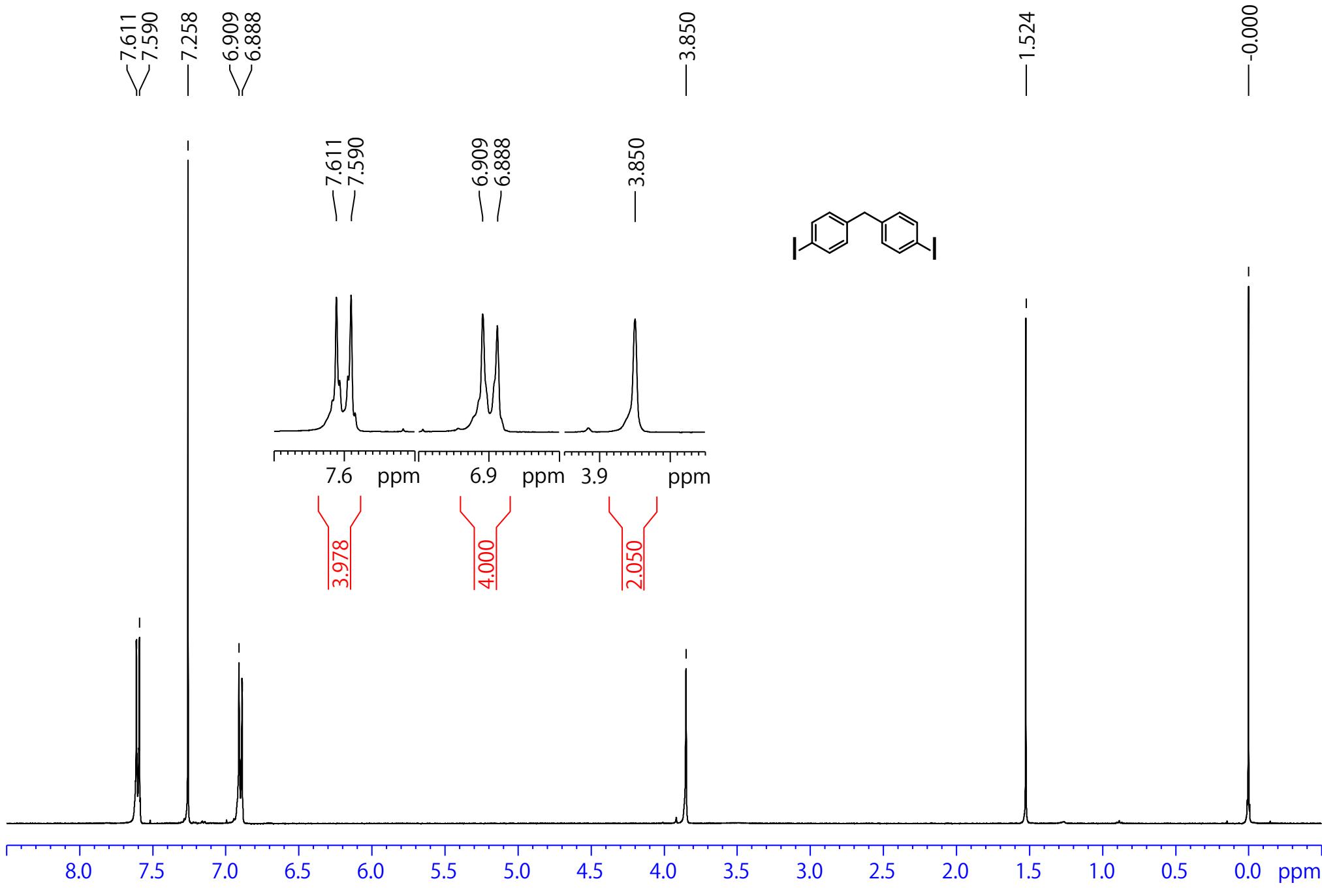


Fig C1. ¹H-NMR spectra of compound 1.

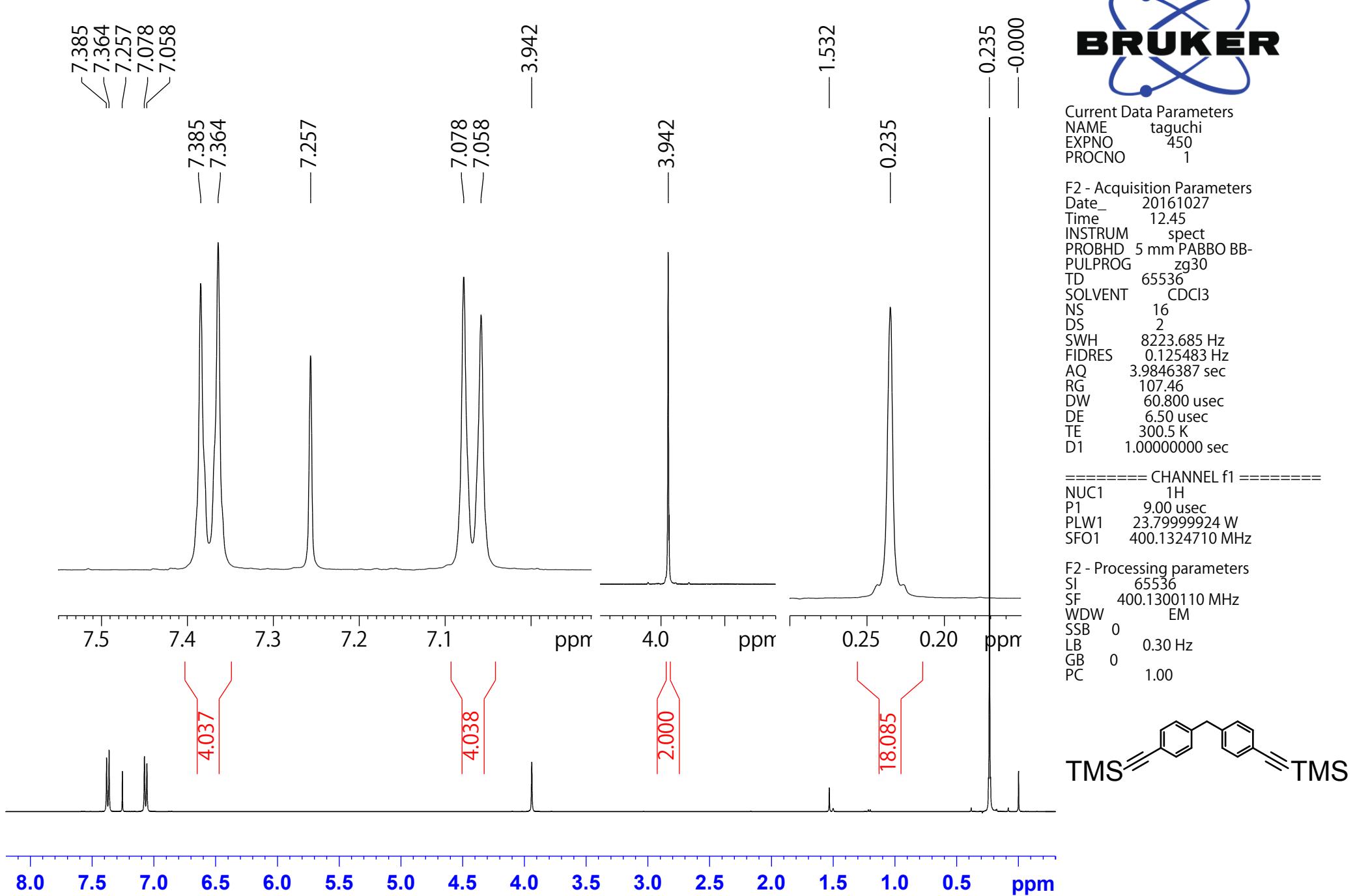


Fig C2. ¹H-NMR spectra of compound 2.

TMS-DPM 13C

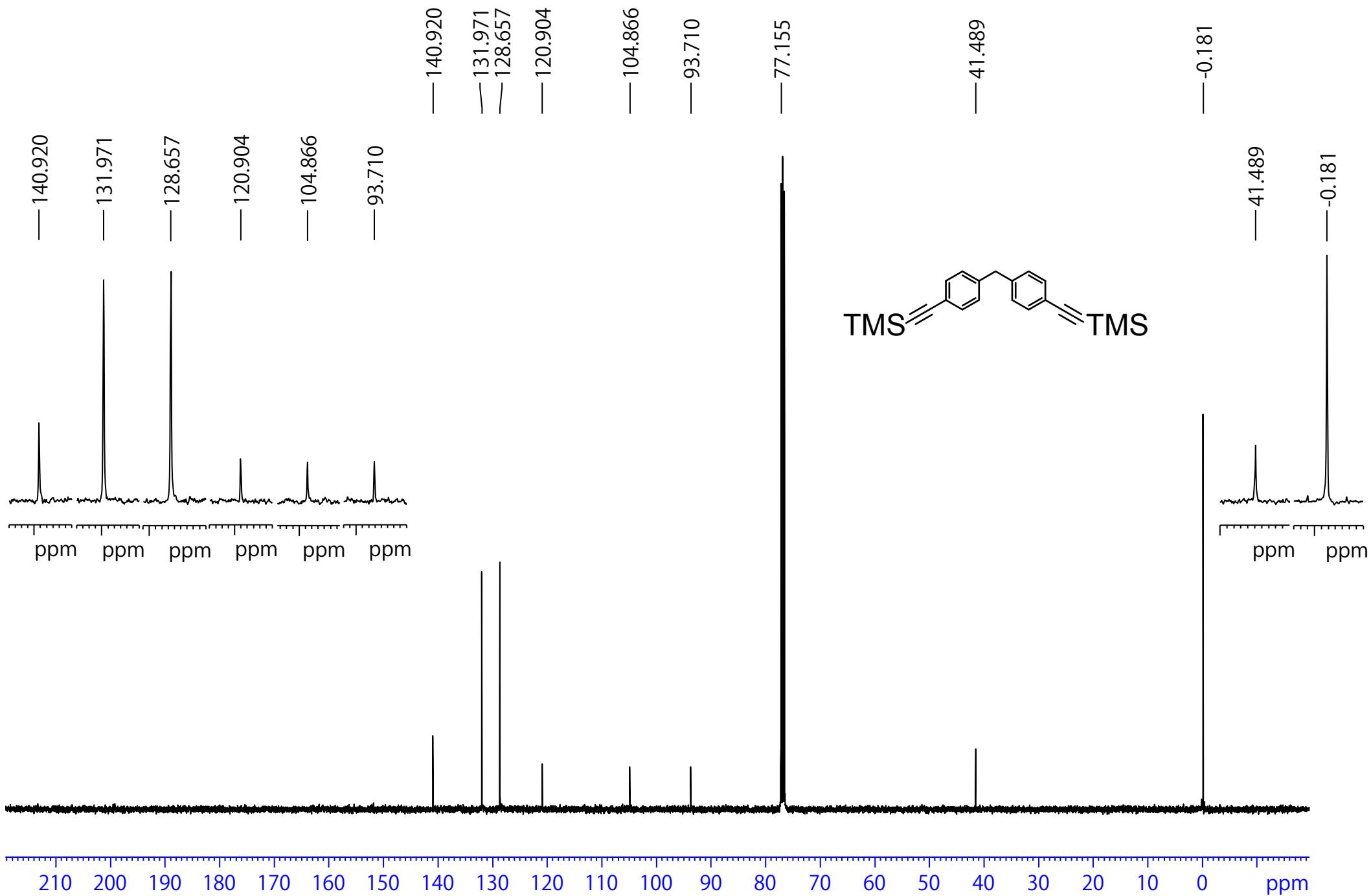
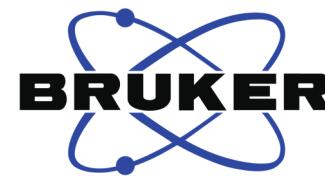
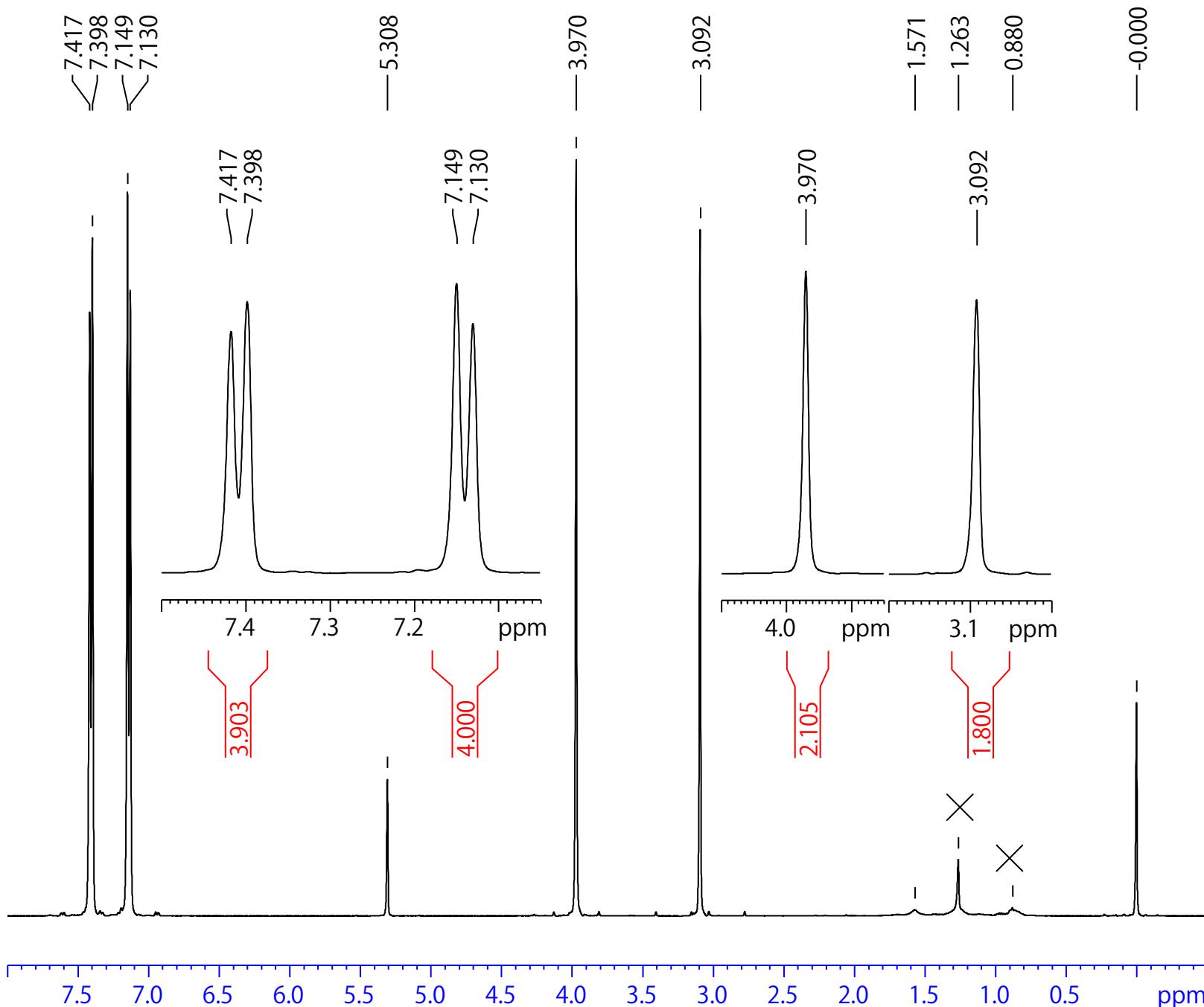


Fig C3. ¹³C-NMR spectra of compound 2.

Alkyn-DPM 1H (CD₂Cl₂, 400MHz, 298.4K)



Current Data Parameters
NAME taguchi
EXPNO 1500
PROCNO 1

F2 - Acquisition Parameters
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Time 18.34
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PULPROG zg30
TD 65536
SOLVENT CD₂Cl₂
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FIDRES 0.125483 Hz
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RG 70.37
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DE 6.50 usec
TE 298.4 K
D1 1.0000000 sec

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PLW1 23.79999924 W
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F2 - Processing parameters
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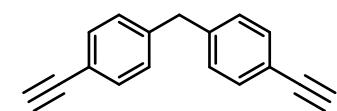


Fig C4. 1H-NMR spectra of compound 3.

Alkyn-DPM 13C (CD₂Cl₂, 100MHz, 299.7K)

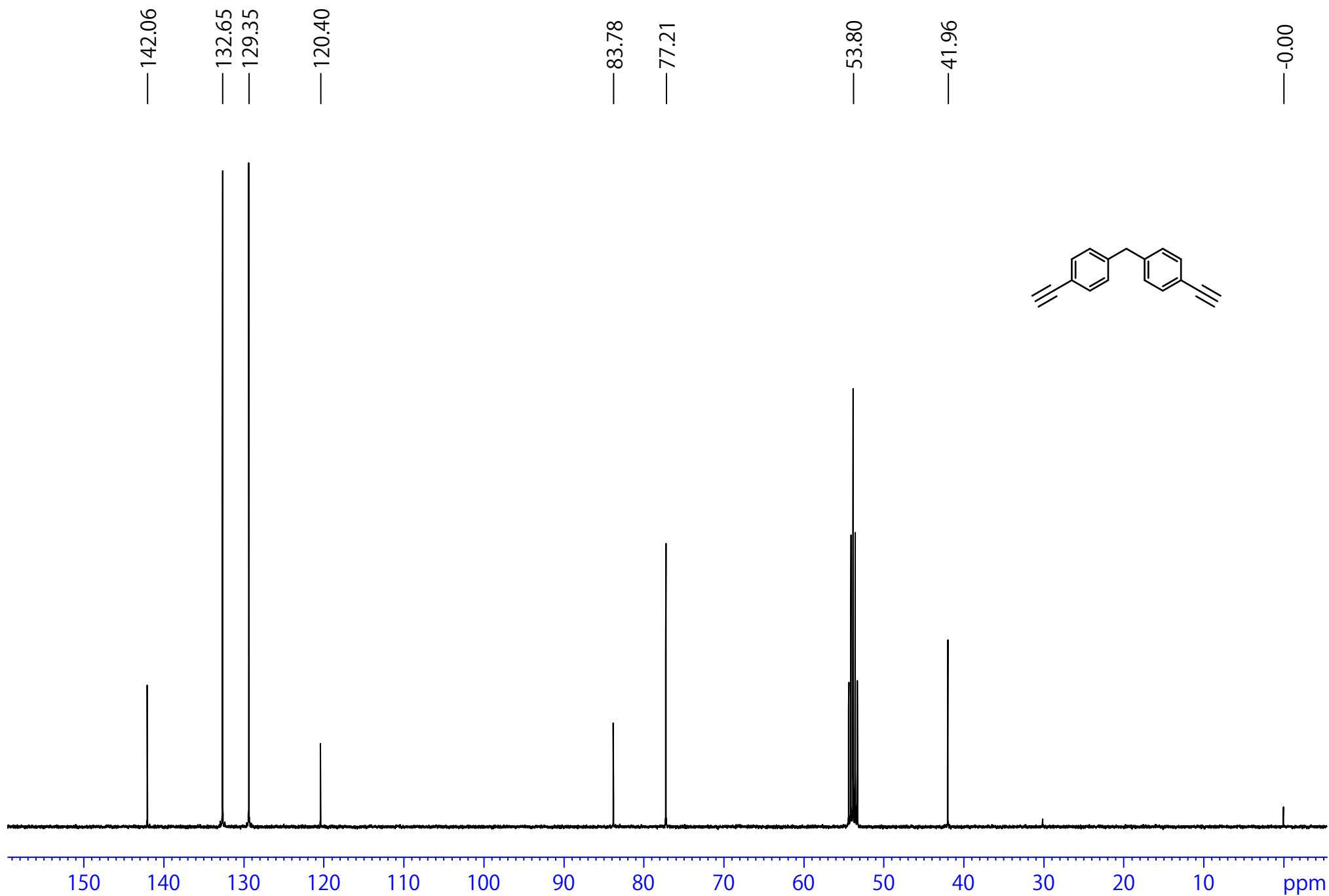


Fig C5. 13C-NMR spectra of compound 3.

TIPS-benzil 1H (CDCl₃, 400Mhz, 302.0K)

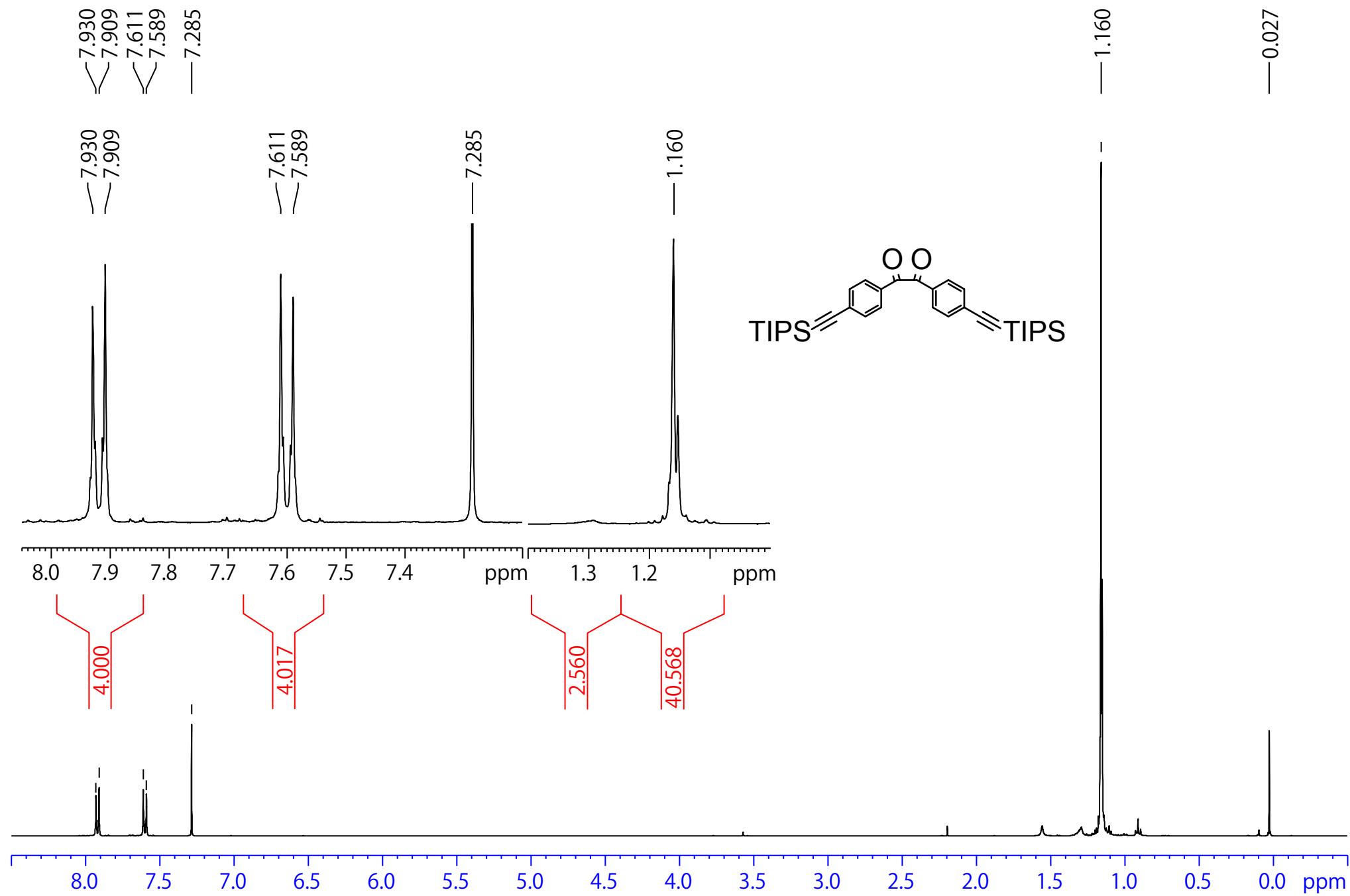


Fig C6. ¹H-NMR spectra of compound 4.

TIPS-Dienone 1H (CD₂Cl₂, 400MHz, 298.3K)

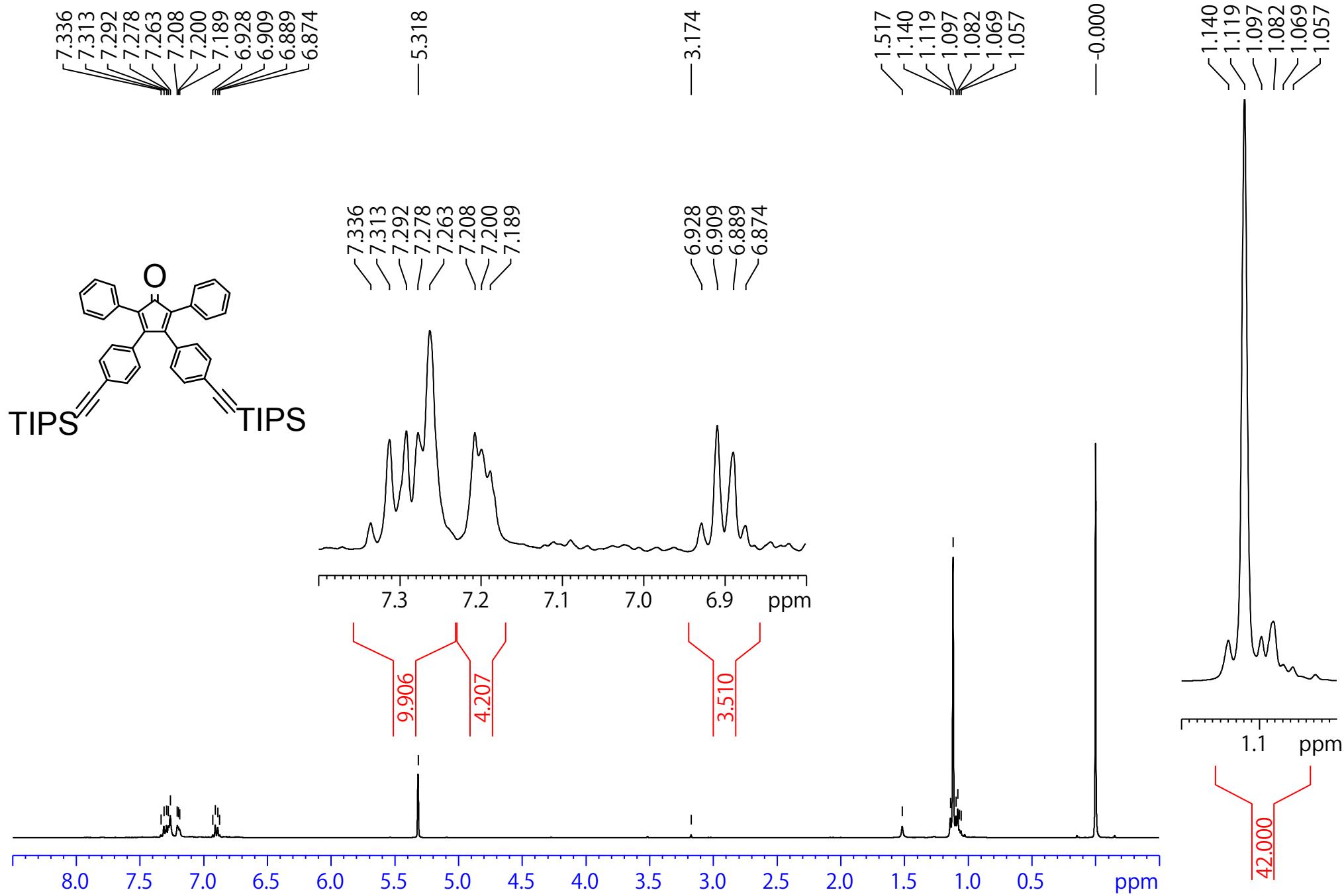
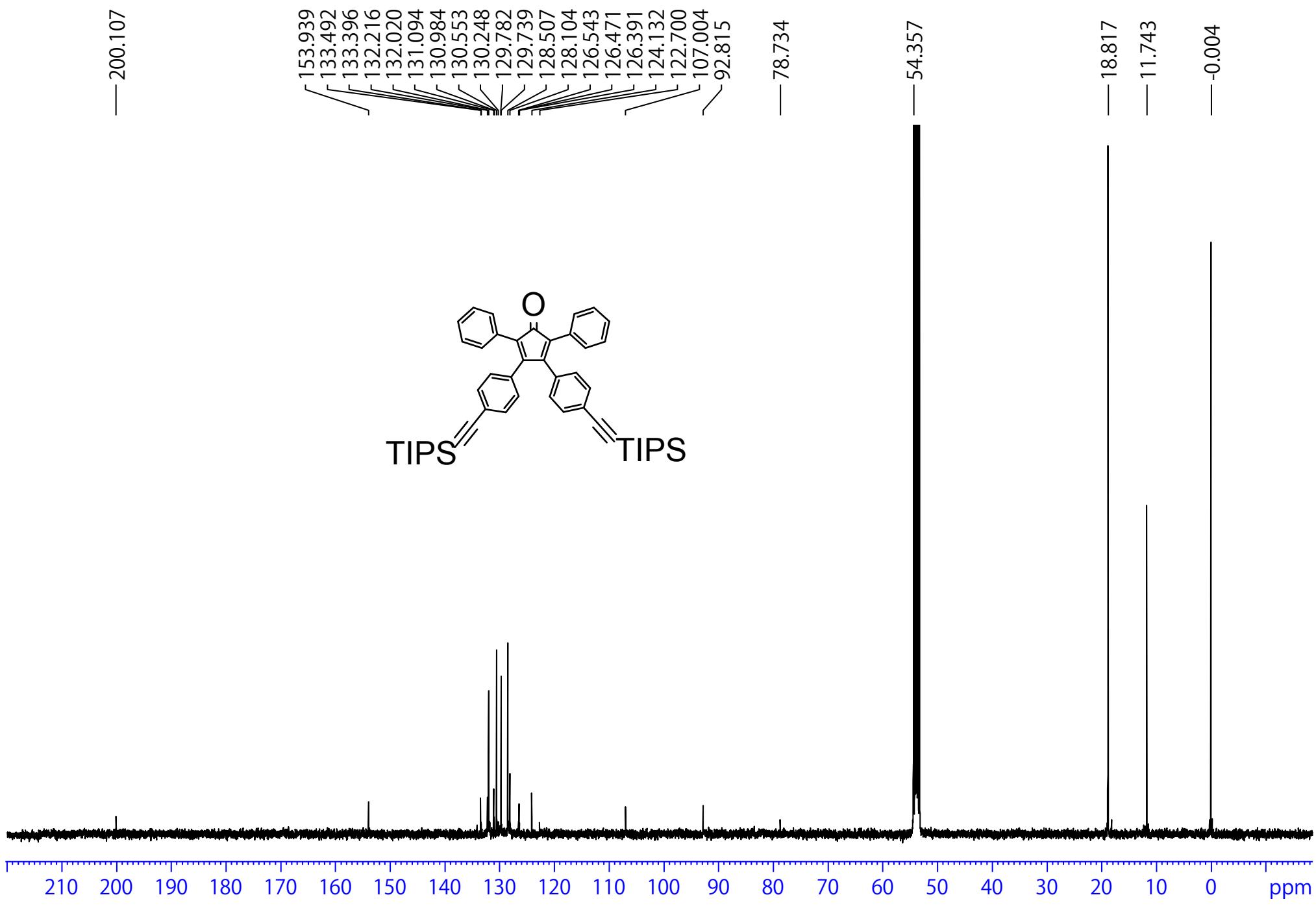


Fig C7. ¹H-NMR spectra of compound 5.

TIPS-Dienone 13C (CD₂Cl₂, 100MHz, 299.3K)



TIPS-Dienone 13C (CD₂Cl₂, 100MHz, 299.3K)

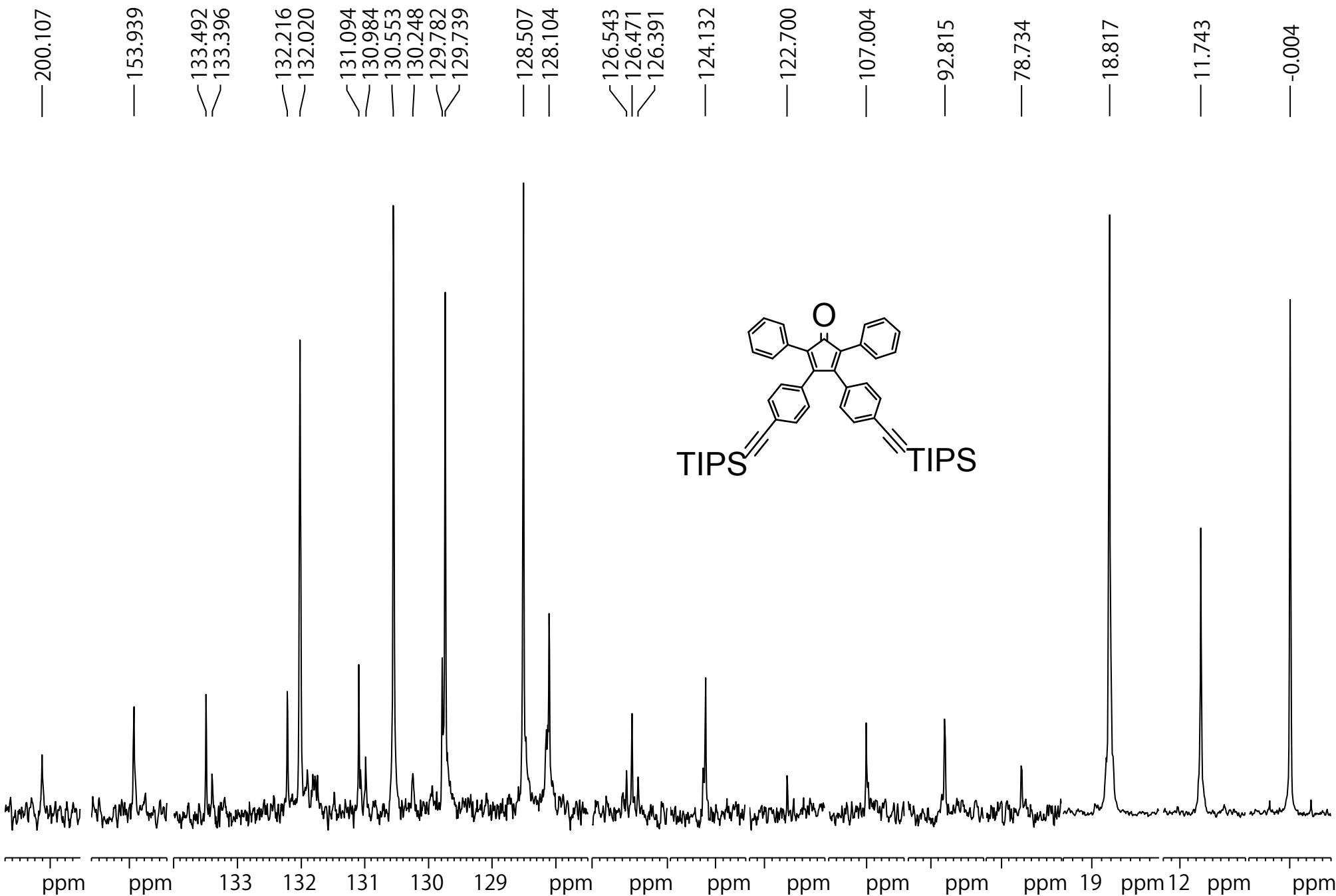
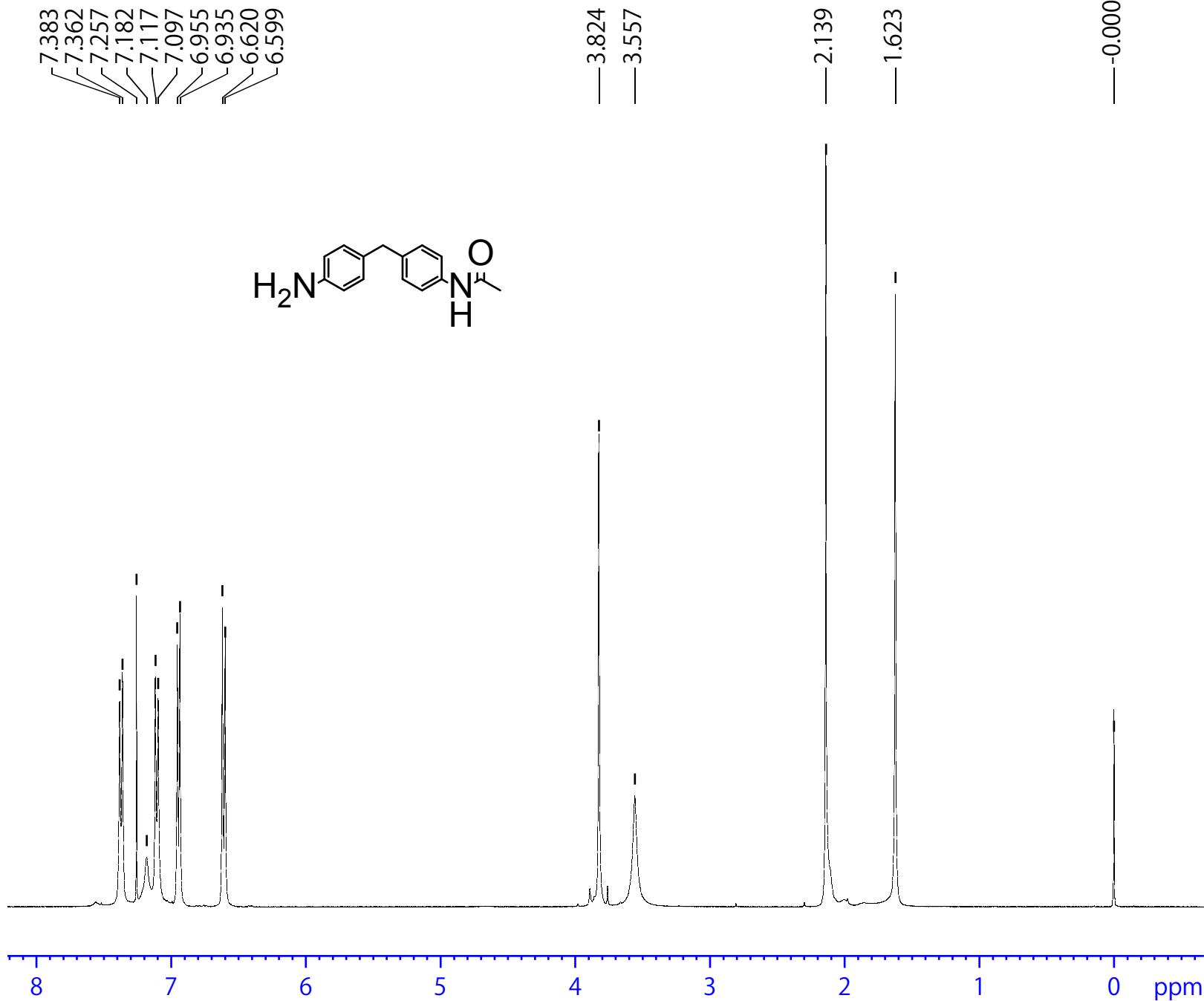


Fig C9. ¹³C-NMR spectra of compound 5.

TM53 monoacetyl-amino-DPM



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PROCNO 1

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Time 18.10
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DE 6.50 usec
TE 304.5 K
D1 1.0000000 sec

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SFO1 400.1324710 MHz

F2 - Processing parameters
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LB 0.30 Hz
GB 0
PC 1.00

Fig C10. 1H-NMR spectra of compound 6.

TM53 monoacetyl-amino-DPM

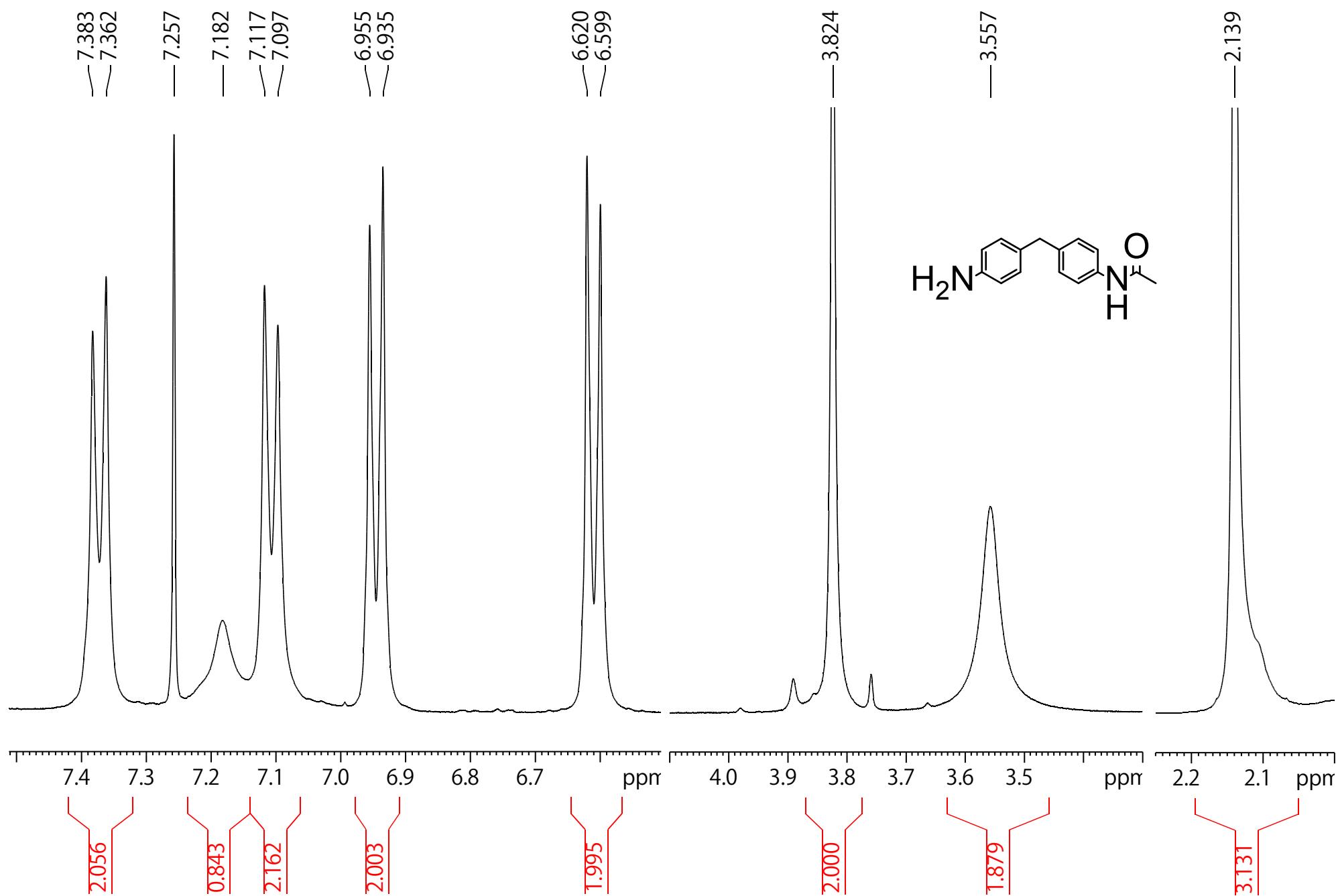


Fig C11. ¹H-NMR spectra of compound 6.

I-DPM-NHAc 1H (CDCl₃, 400MHz, 298.6K, 20181002)

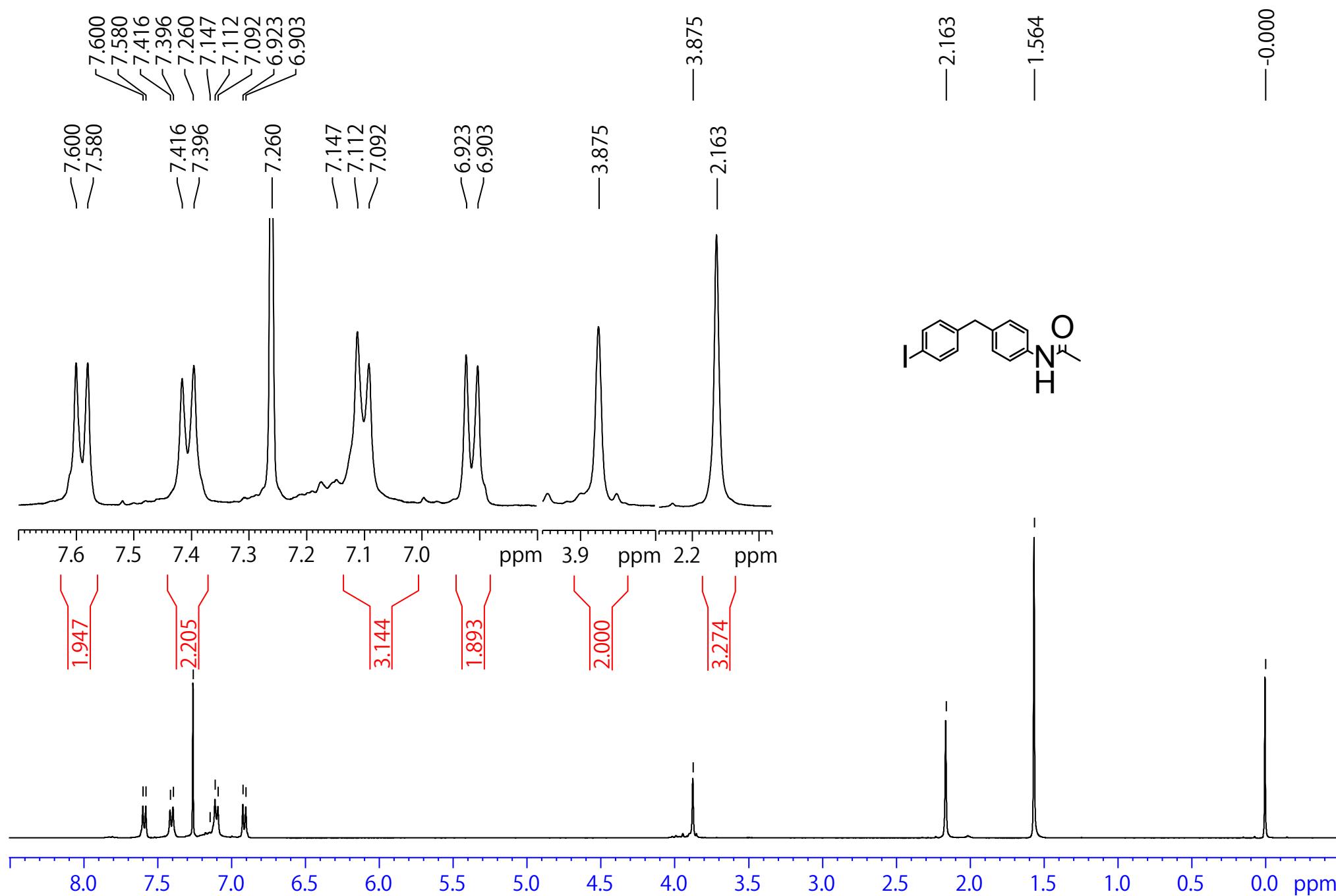


Fig C12. ¹H-NMR spectra of compound 7.

I-DPM-NHAc 13C (CDCl₃, 400MHz, 299.7K, 20181002)

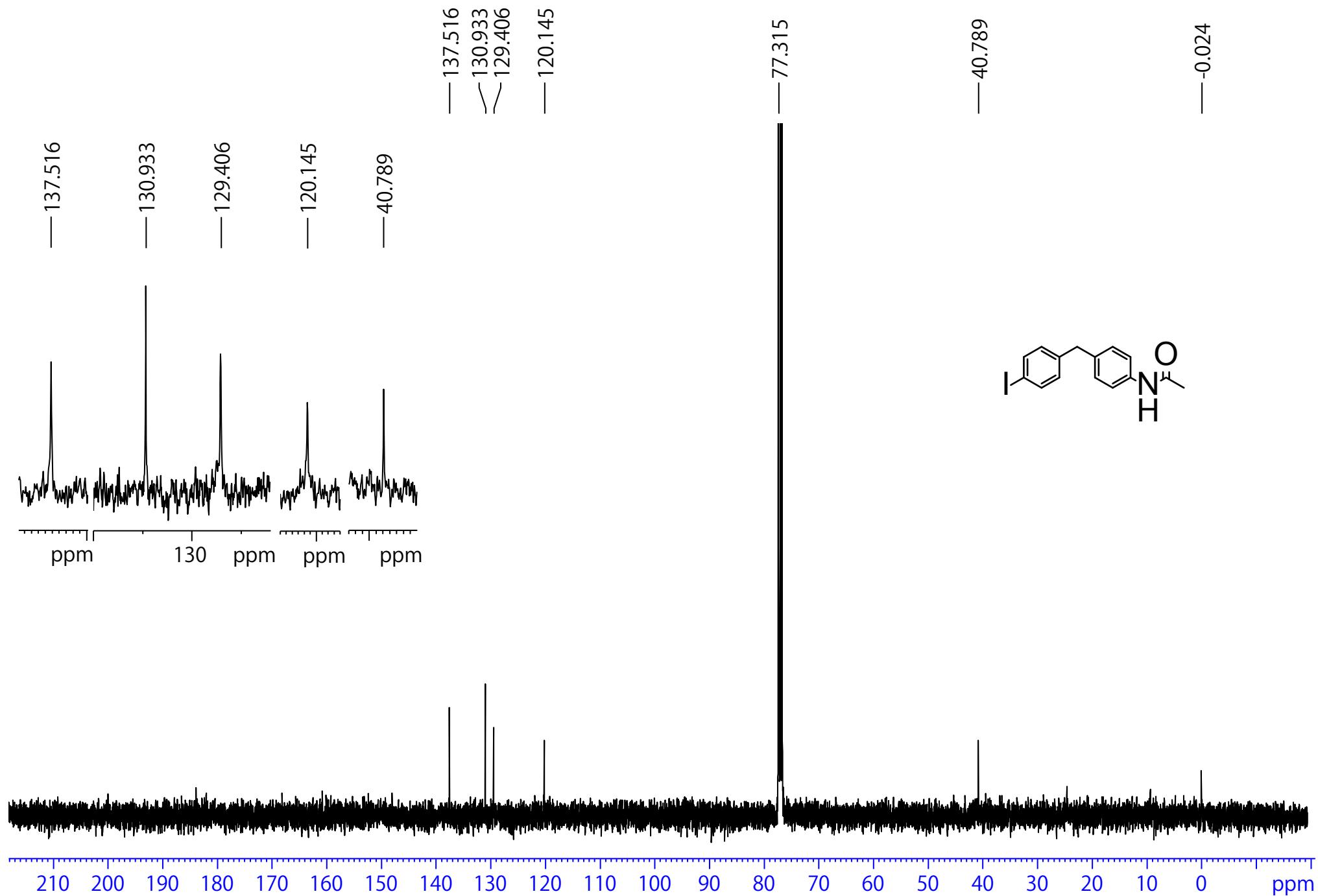
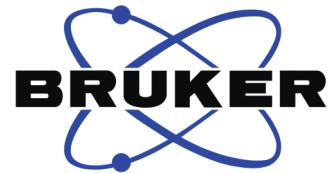
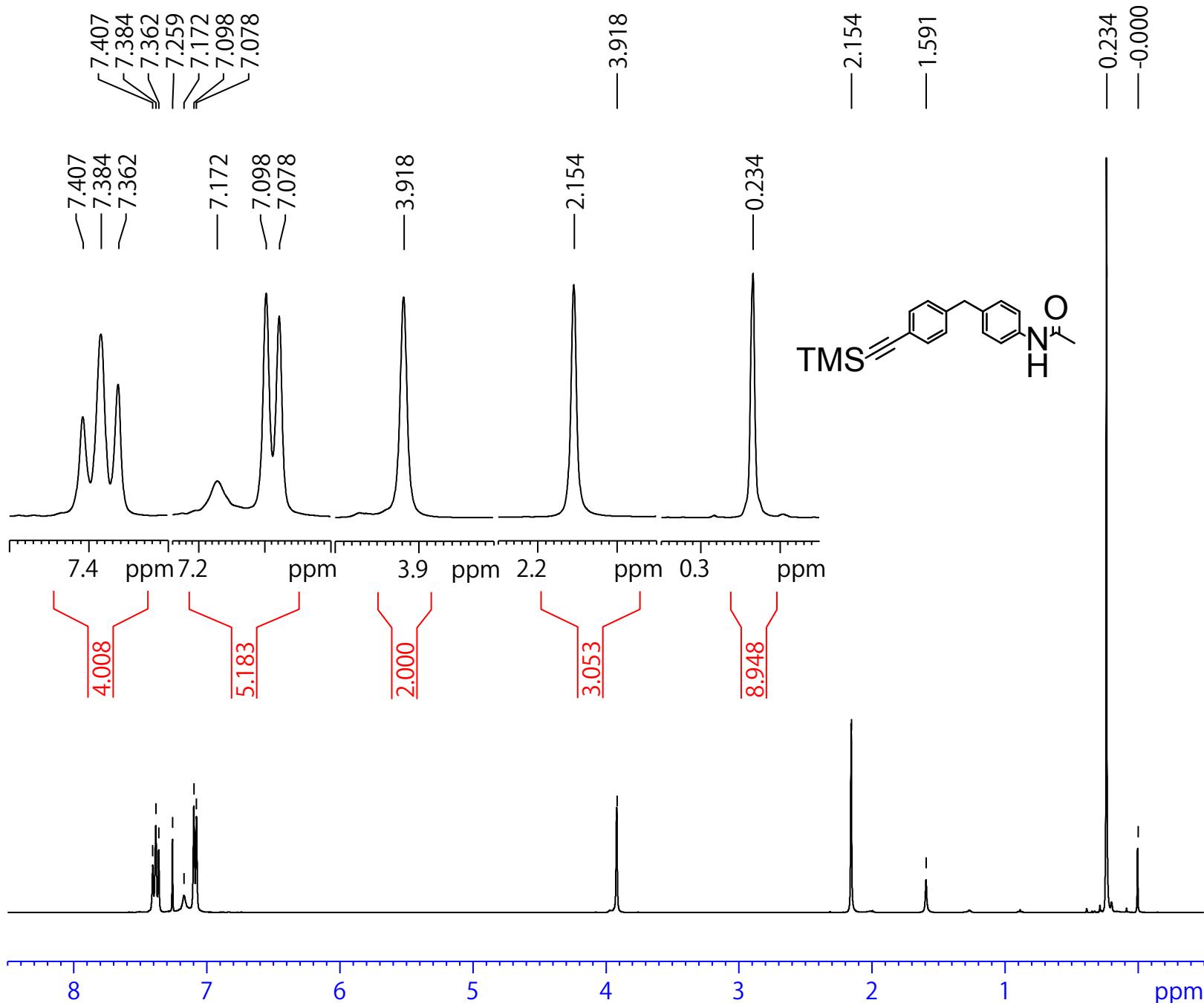


Fig C13. ¹³C-NMR spectra of compound 7.

TMS-DPM-NHAc 1H



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PROCNO 1

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FIDRES 0.125483 Hz
AQ 3.9845889 sec
RG 95.62
DW 60.800 usec
DE 6.50 usec
TE 298.4 K
D1 1.0000000 sec

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P1 9.00 usec
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F2 - Processing parameters
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WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig C14. ¹H-NMR spectra of compound 8.

TMS-DPM-NHAc ^{13}C (CDCl_3 , 100MHz, 299.1K)

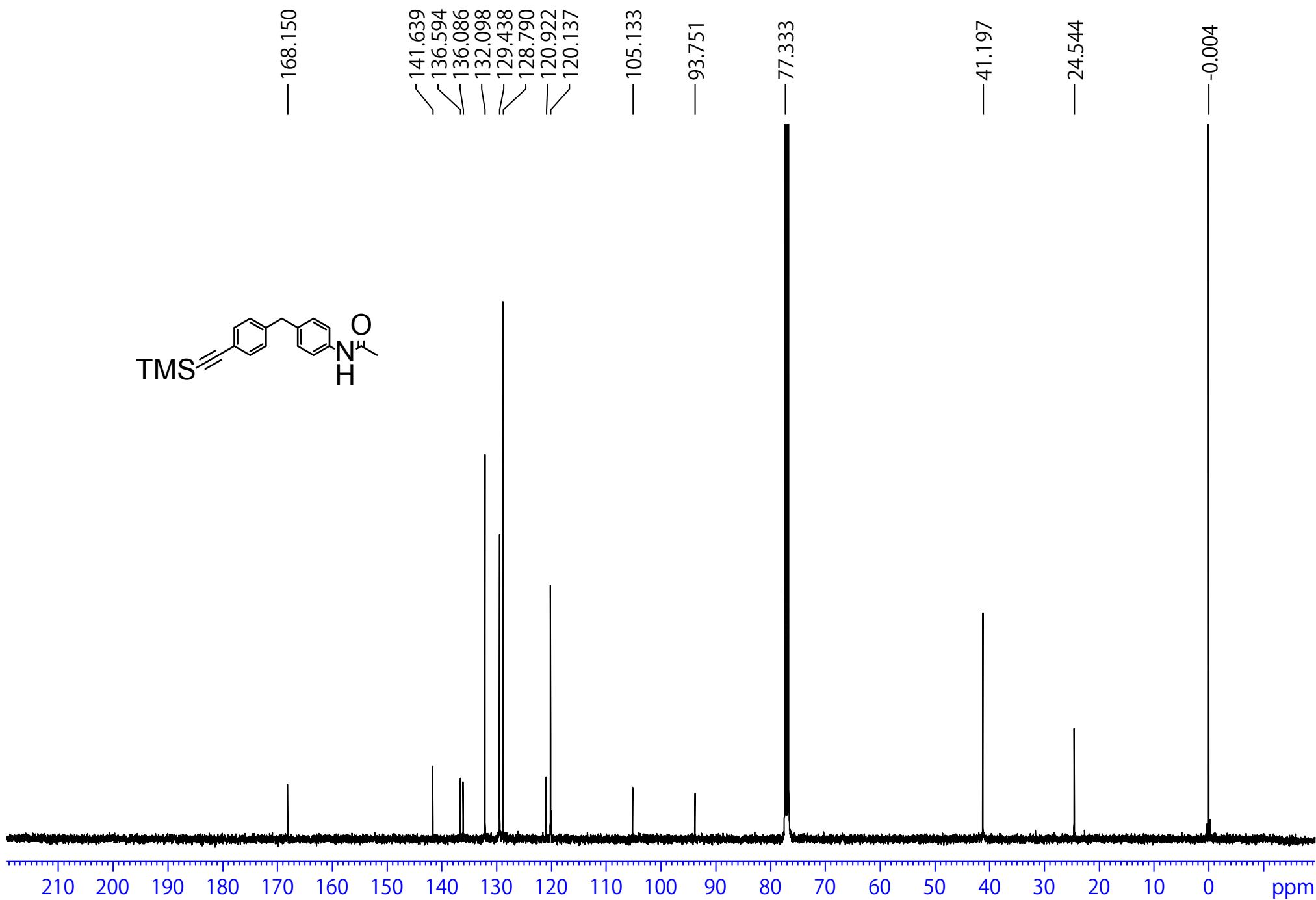


Fig C15. ^{13}C -NMR spectra of compound 8.

Alkyn-DPM-NHAc 1H (CD₂Cl₂, 400MHz, 298.3K)

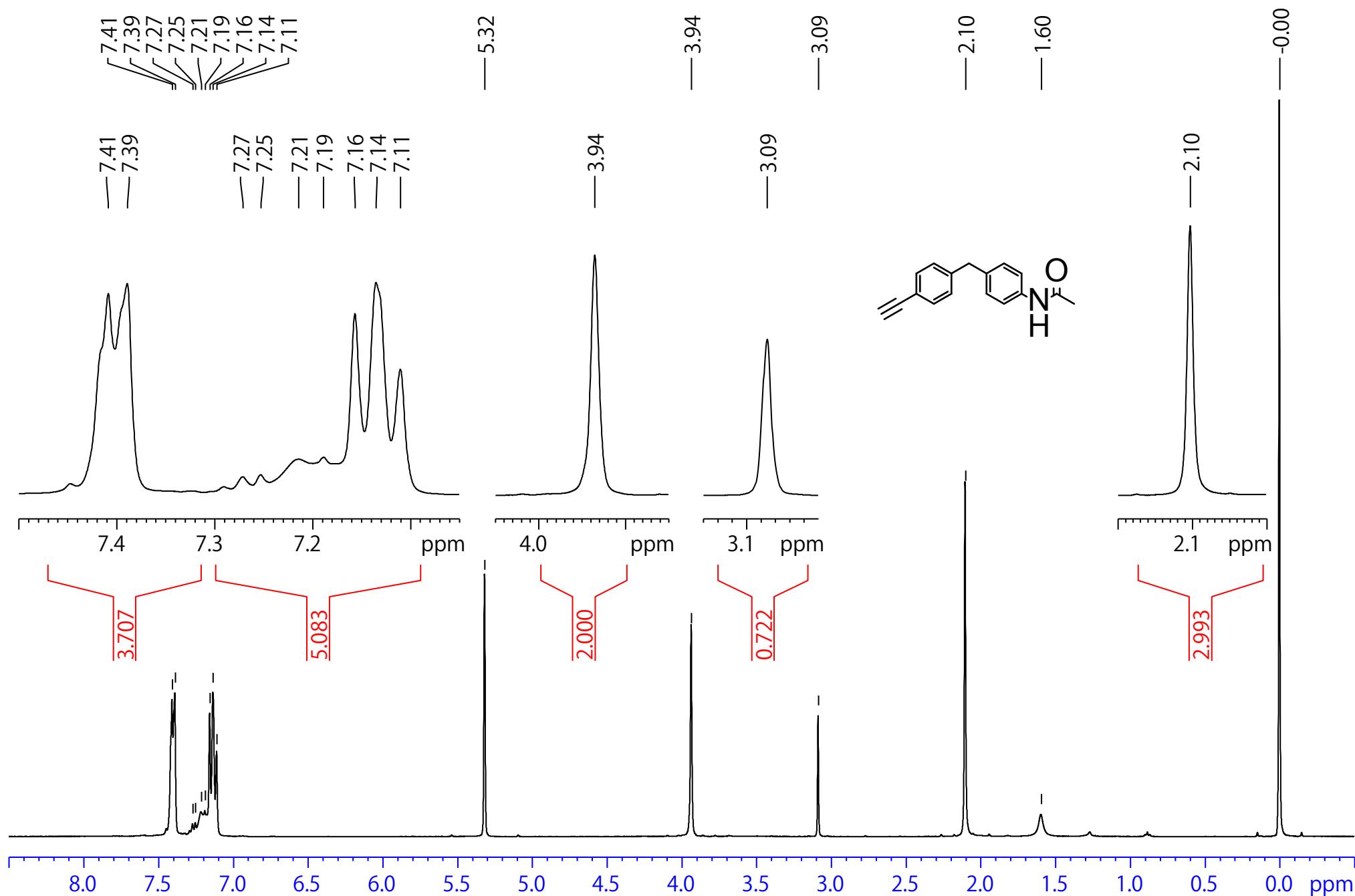


Fig C16. ¹H-NMR spectra of compound 9.

Alkyn-DPM-NHAc 13C (CD₂Cl₂, 100MHz, 299.5K)

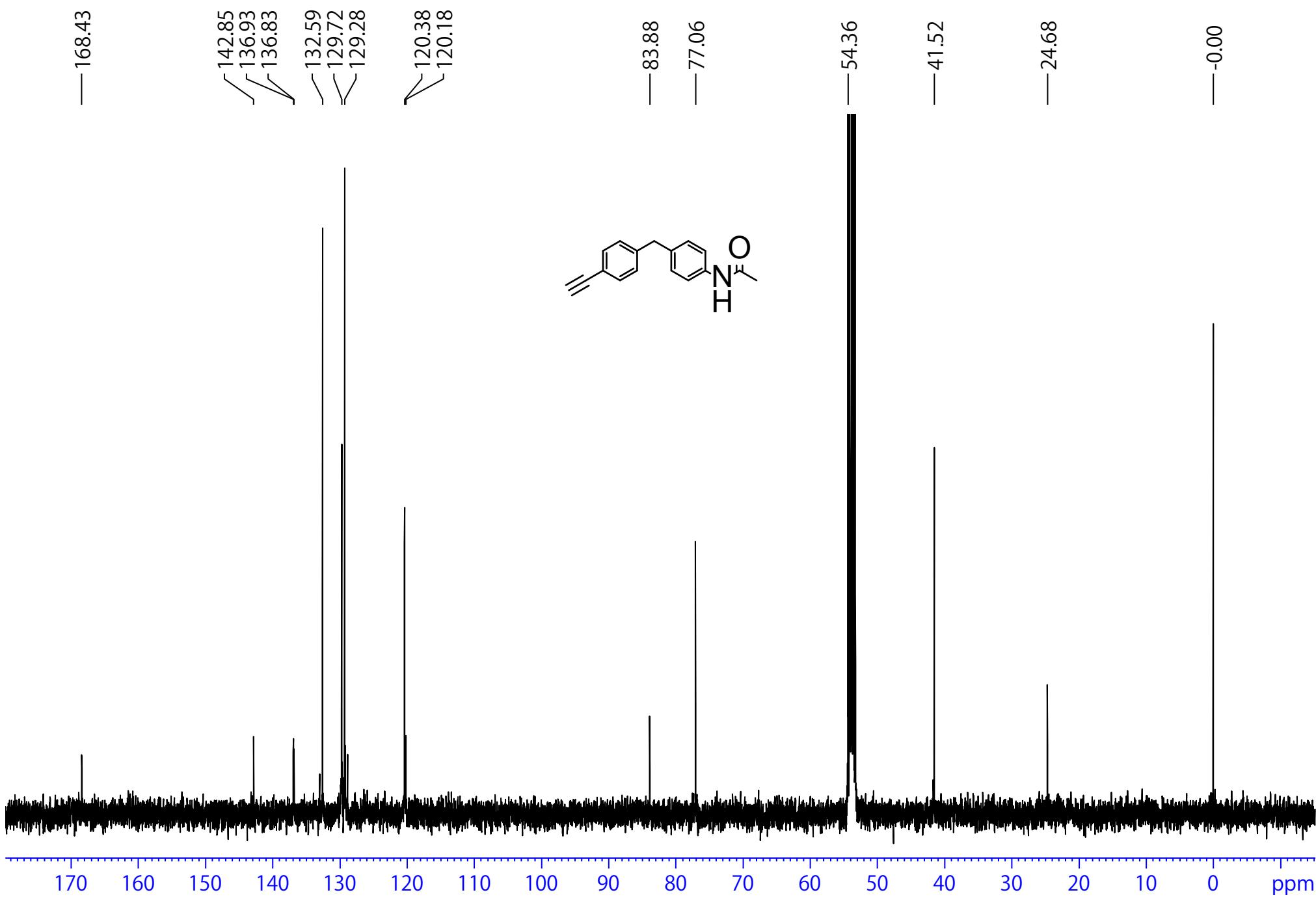
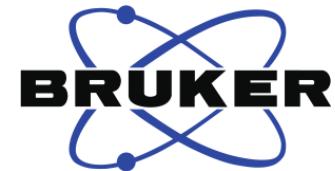
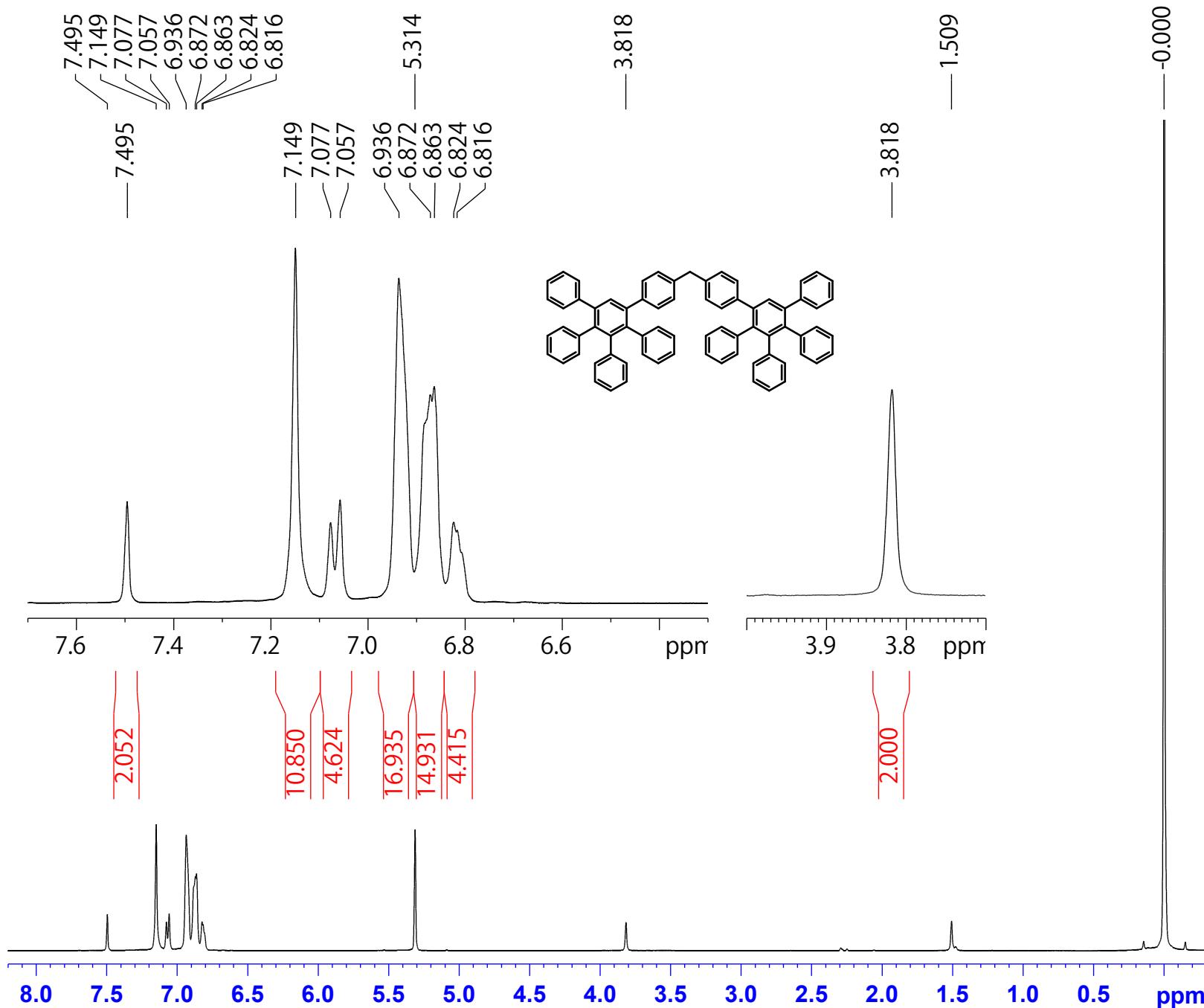


Fig C17. ¹³C-NMR spectra of compound 9.

preG1-1 1H



Current Data Parameters
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EXPNO 860
PROCNO 1

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TD 65536
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FIDRES 0.125483 Hz
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RG 95.62
DW 60.800 usec
DE 6.50 usec
TE 300.0 K
D1 1.0000000 sec

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SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300178 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig C18. ¹H-NMR spectra of compound 10.

preG1-1 13C

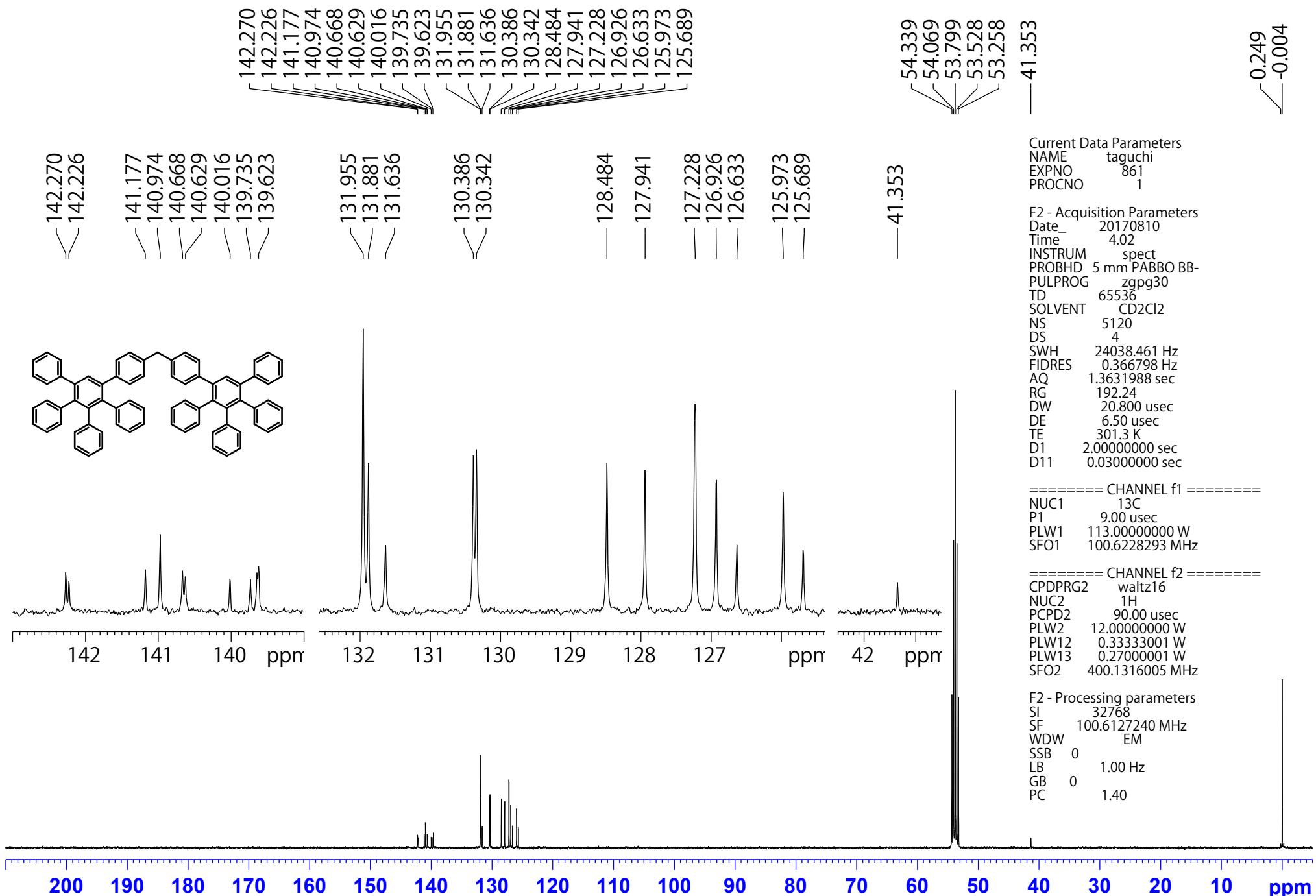
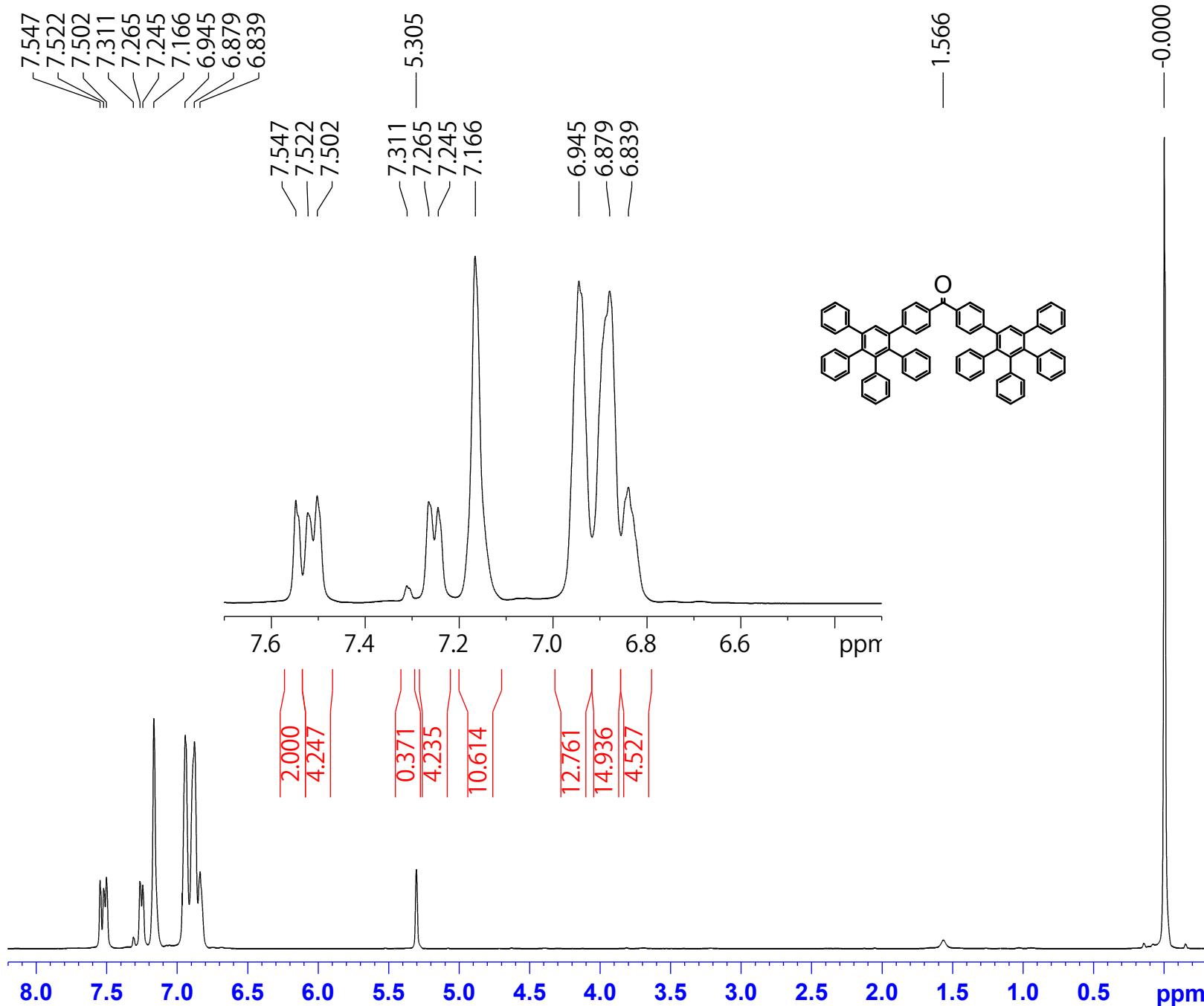


Fig C19. ¹³C-NMR spectra of compound 10.

G1-1on 1H



Current Data Parameters
NAME taguchi
EXPNO 870
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170810
Time 4.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CD2Cl₂
NS 64
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 78.21
DW 60.800 usec
DE 6.50 usec
TE 300.4 K
D1 1.0000000 sec

===== CHANNEL f1 ======
NUC1 1H
P1 9.00 usec
PLW1 23.79999924 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300214 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig C20. ¹H-NMR spectra of compound 11.

G1-1on 13C

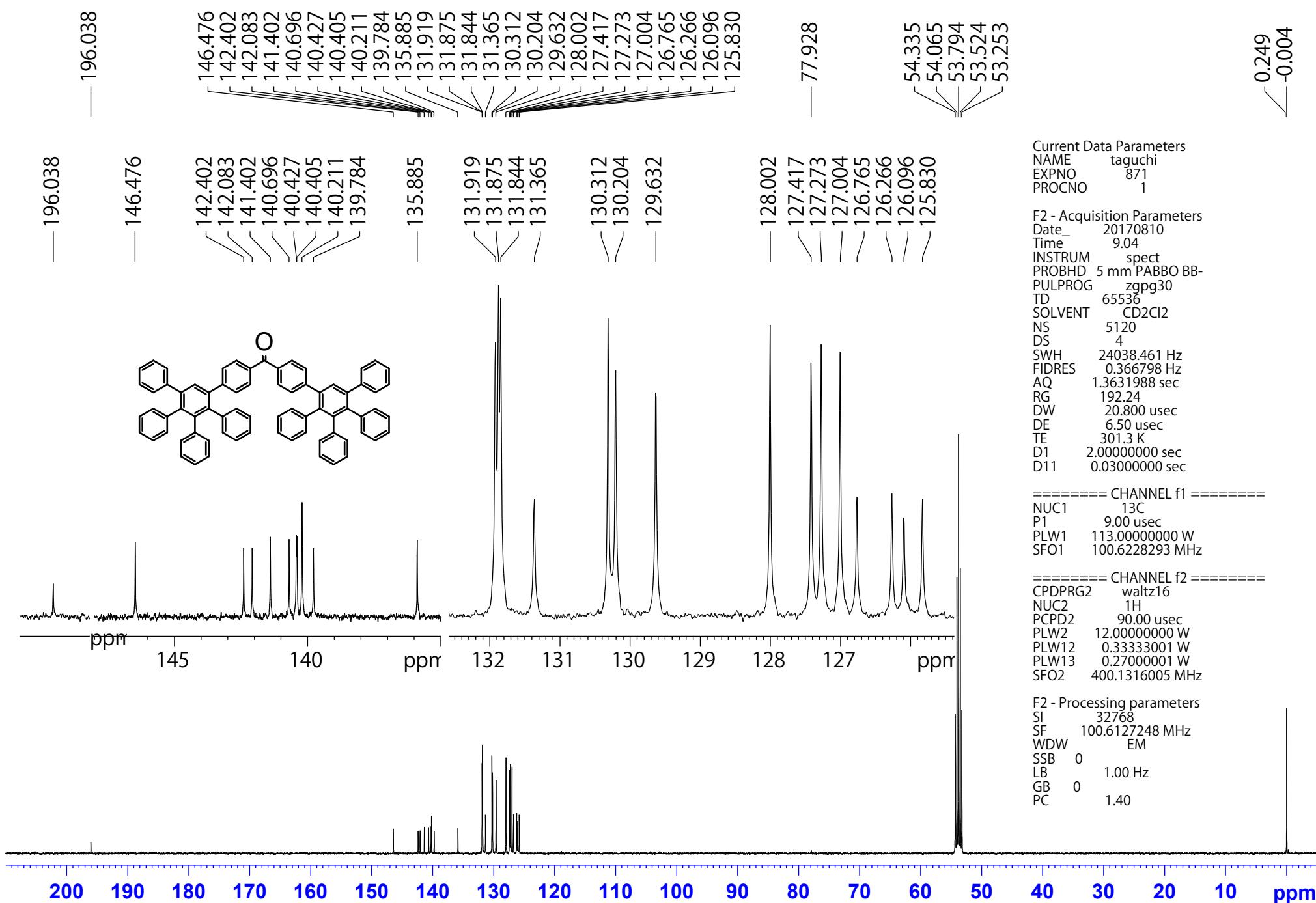
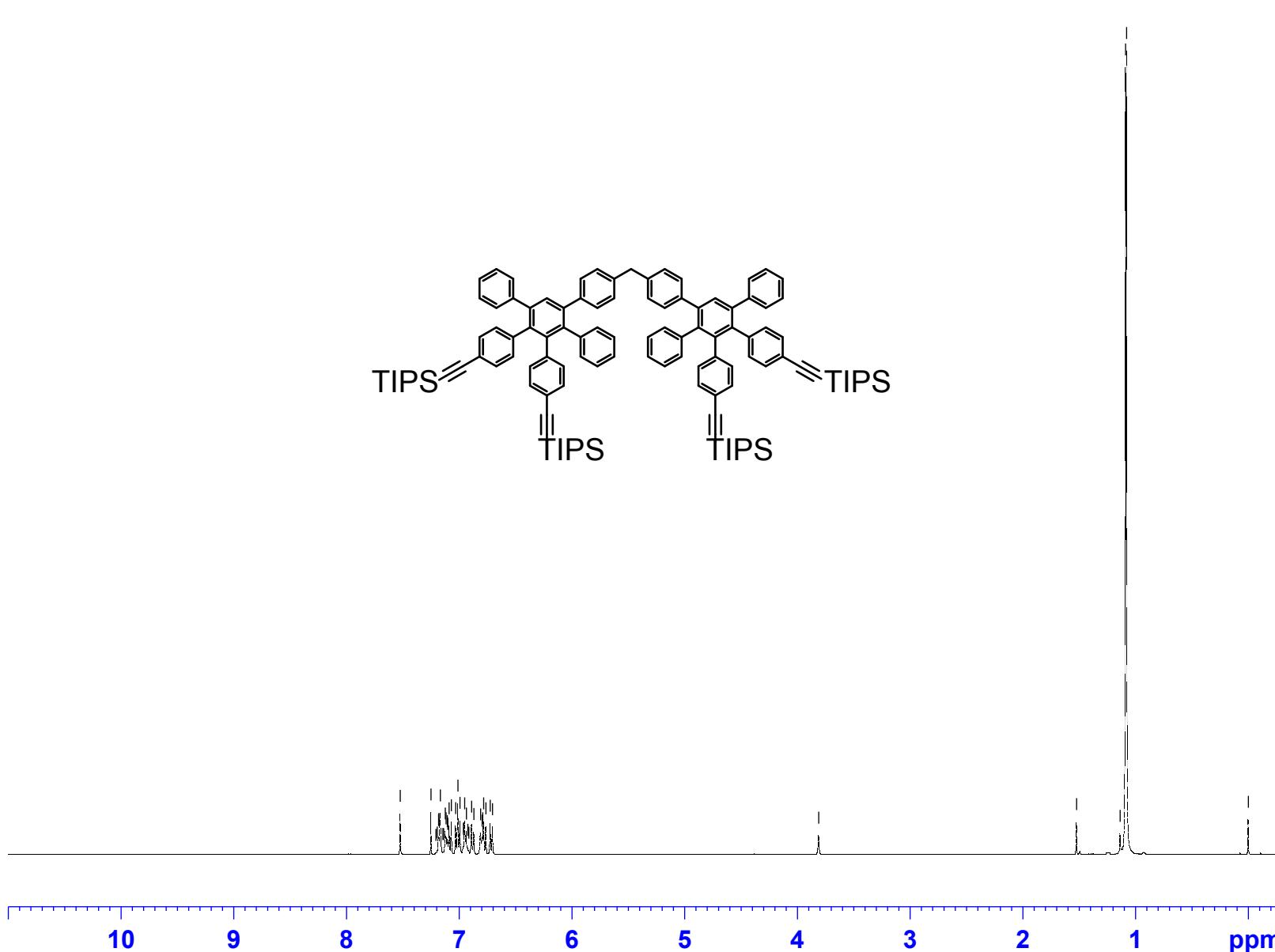
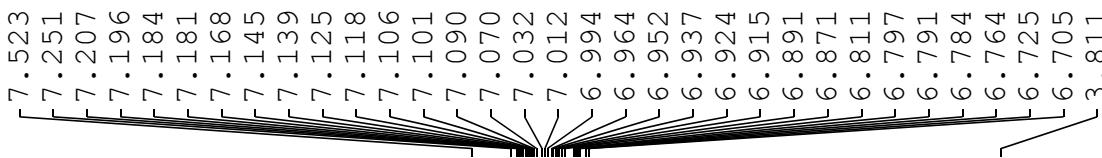


Fig C21. ¹³C-NMR spectra of compound 11.

TIPS-preG1-1 1H (CDC13)



Current Data Parameters
NAME NMR
EXPNO 1161
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180831
Time_ 21.33
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDC13
NS 256
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9845889 sec
RG 70.37
DW 60.800 usec
DE 6.50 usec
TE 299.2 K
D1 1.0000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 9.00 usec
PLW1 23.79999924 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300133 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig C22. 1H-NMR spectra of compound 12.

TIPS-preG1-1 1H (CDCl₃)

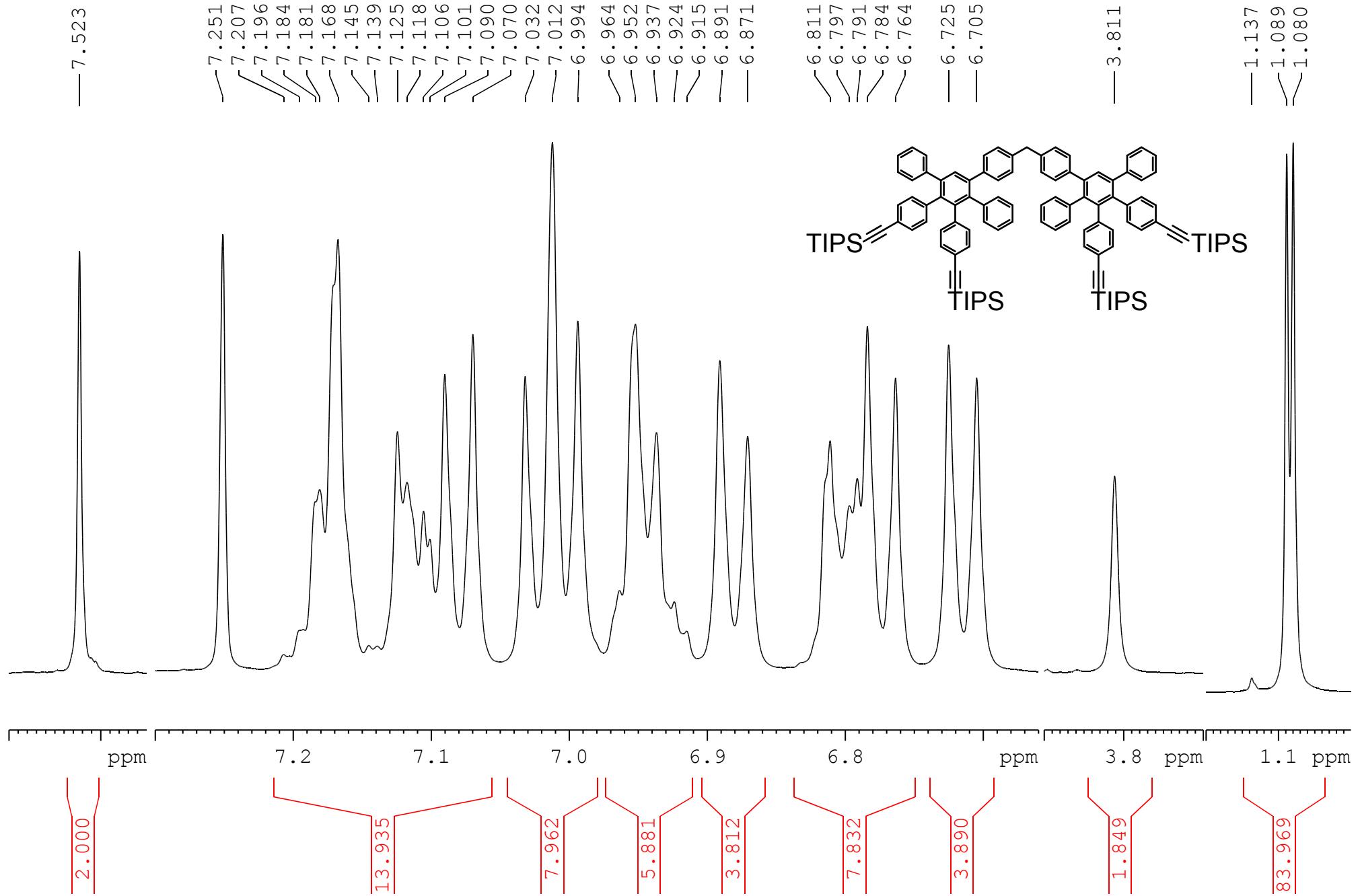


Fig C23. 1H-NMR spectra of compound 12.

TIPS-preG1-1 13C(CDCI3)

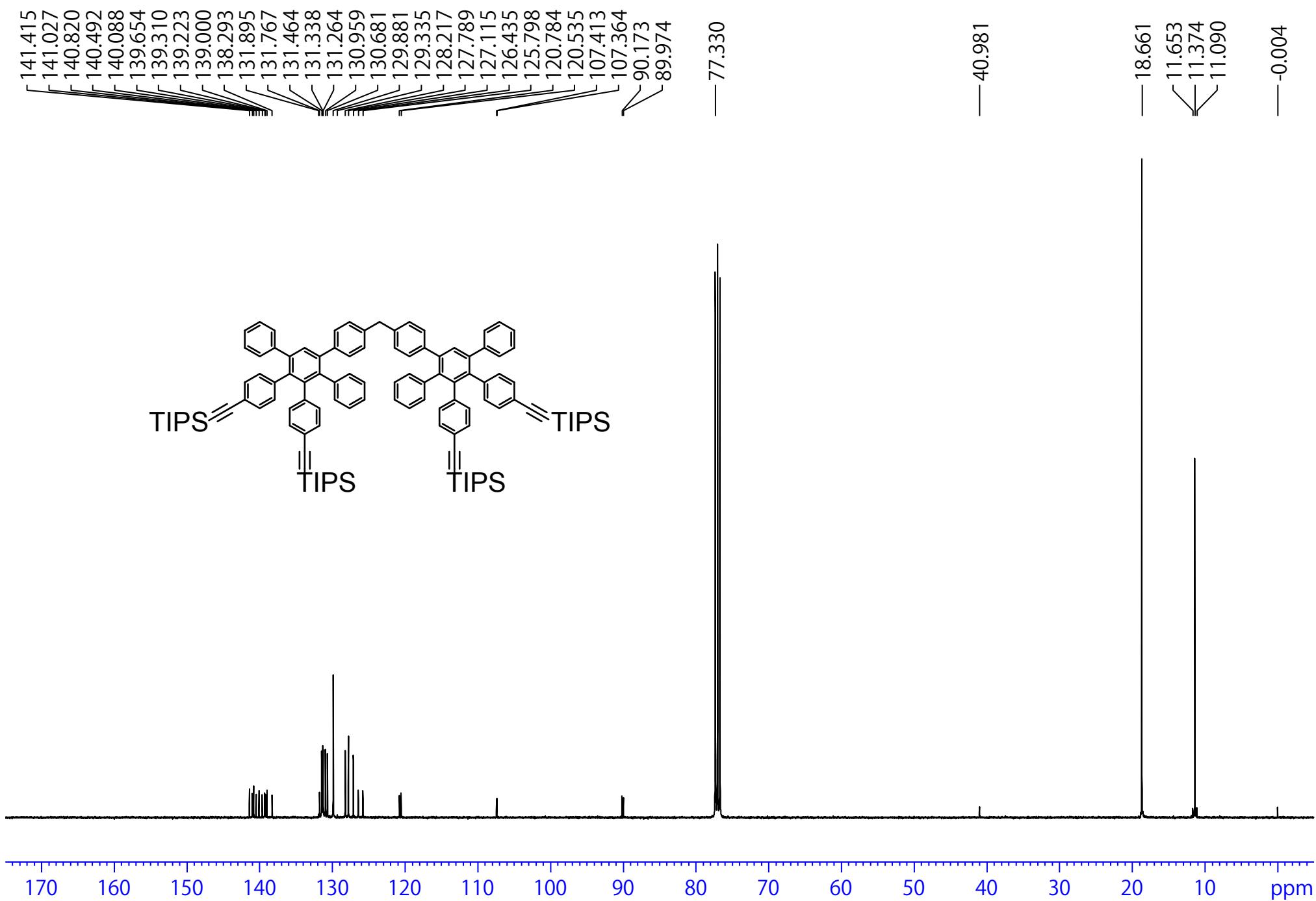


Fig C24. ¹³C-NMR spectra of compound 12.

TIPS-preG1-1 13C(CDCI3)

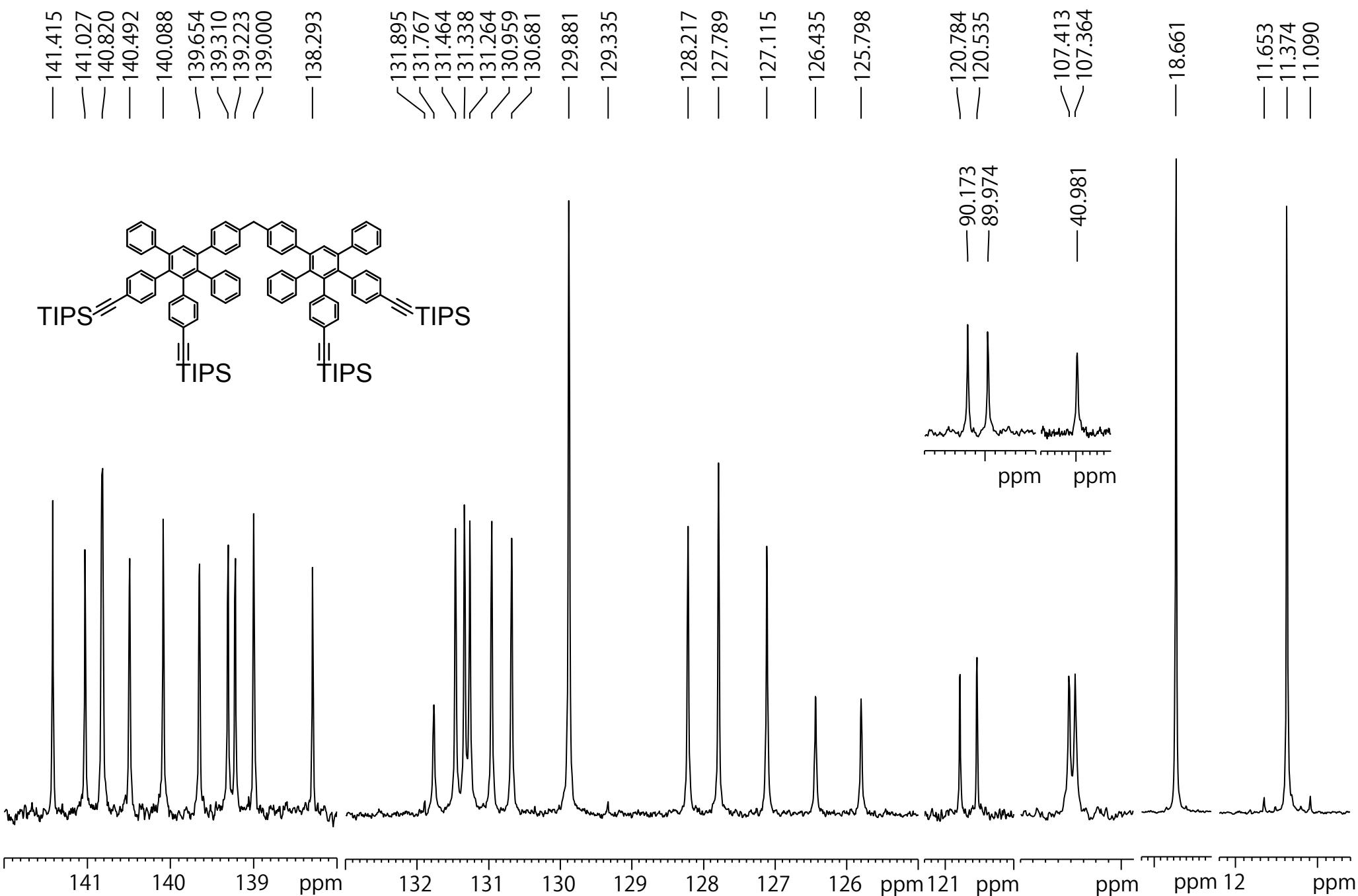


Fig C25. ¹³C-NMR spectra of compound 12.

Alkyn-G1-1 1H (DMSO, 400MHz, 298.3K)

8.312 ppm is corresponding to chloroform

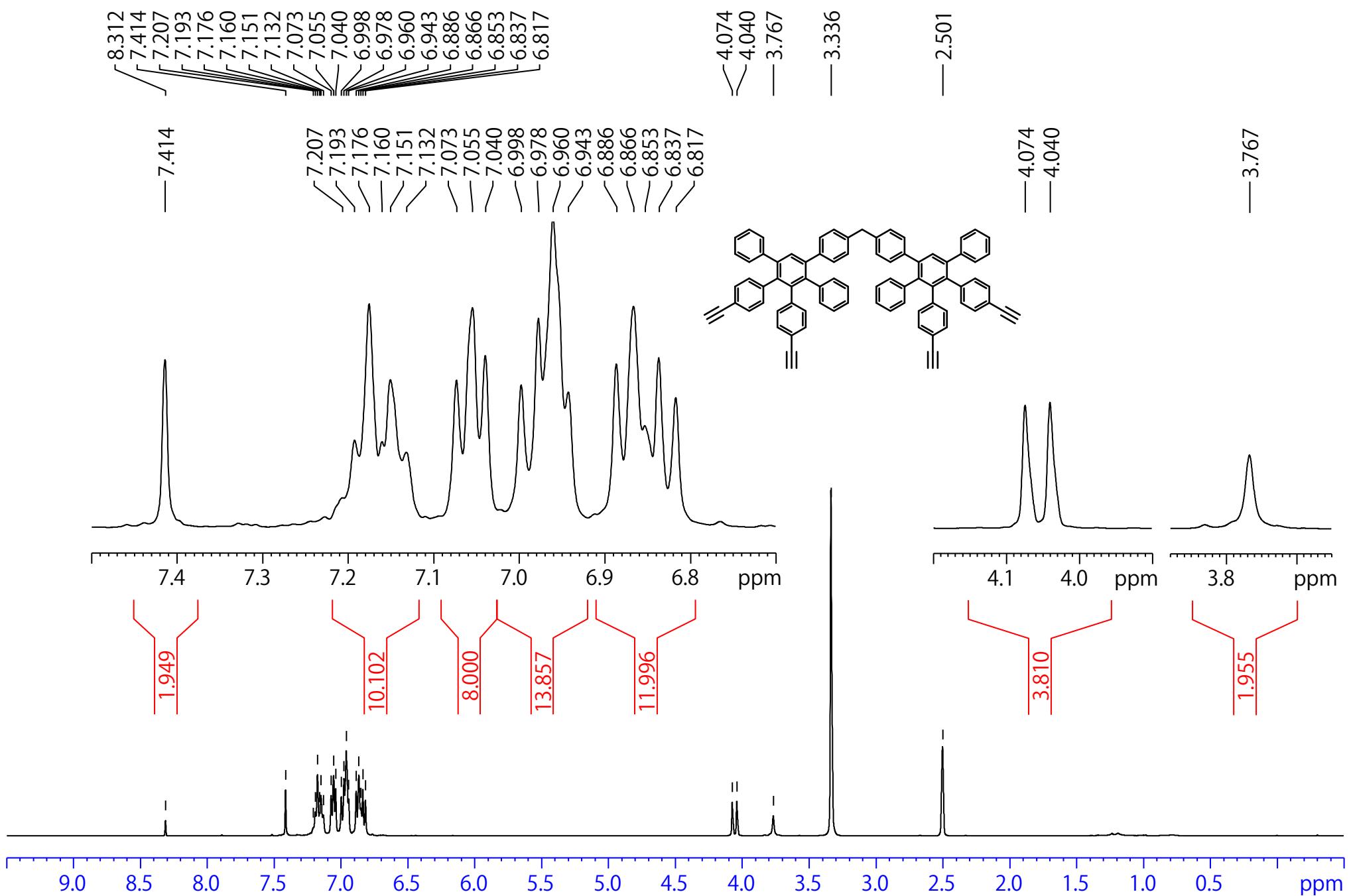
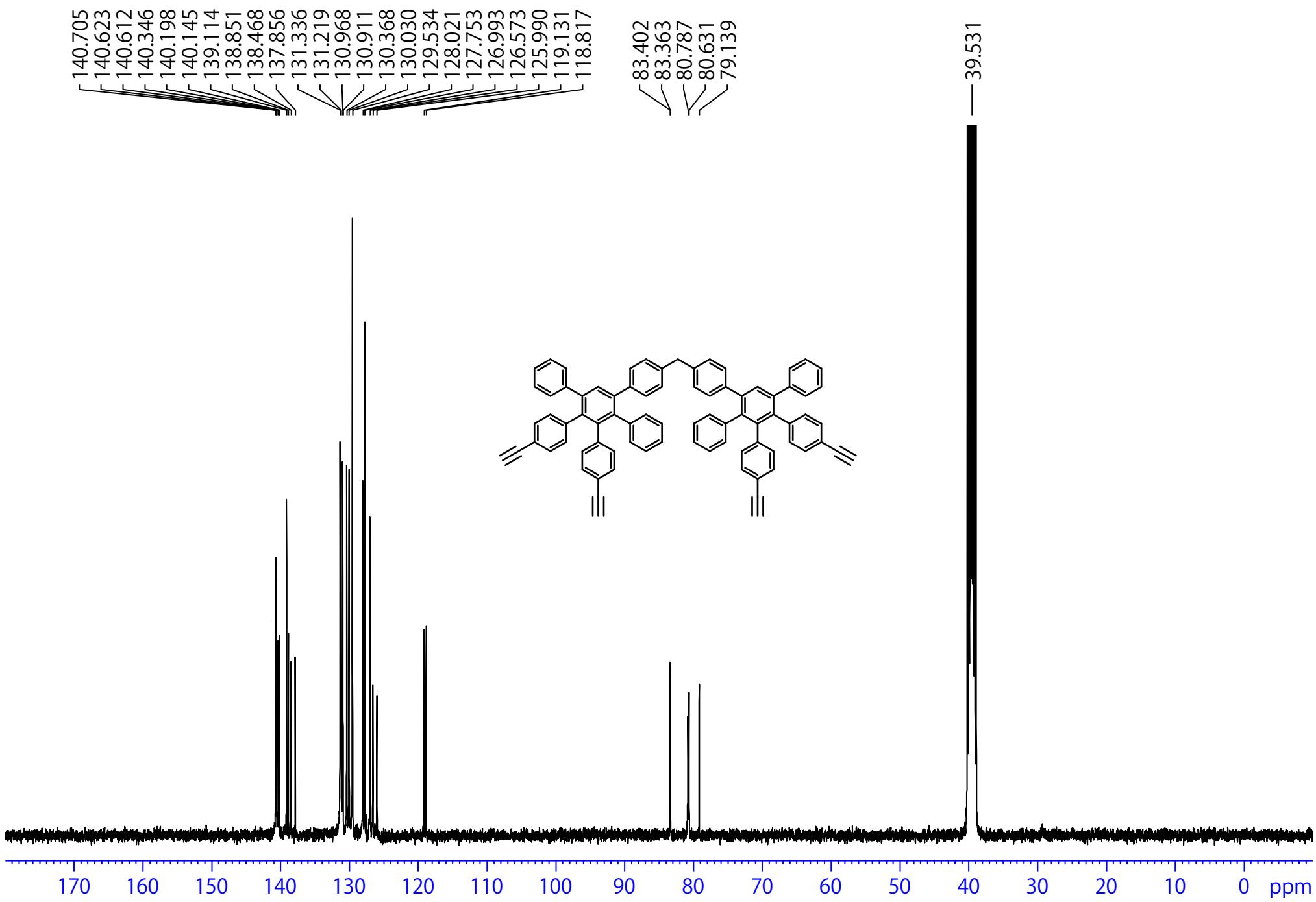
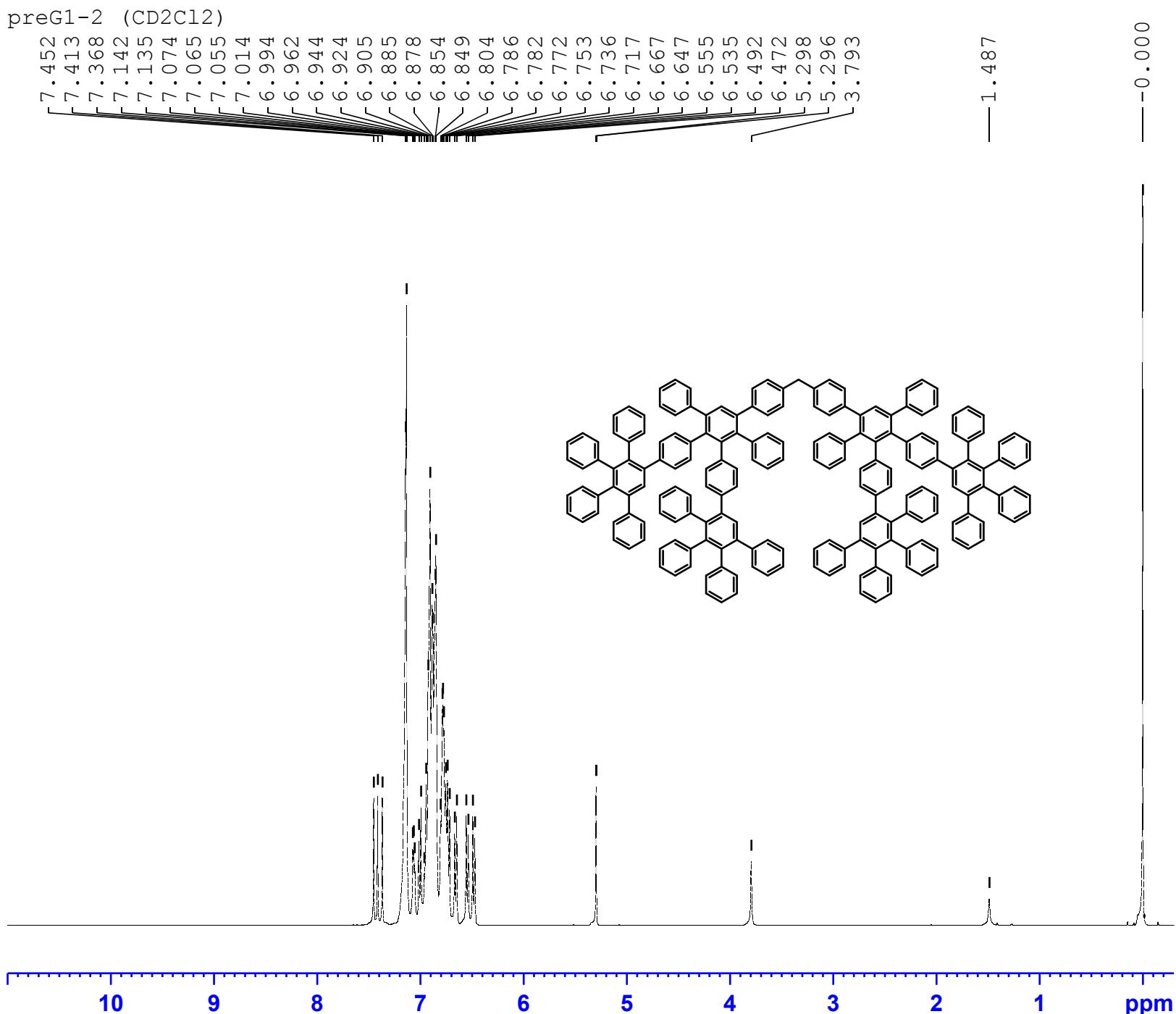


Fig C26. ¹H-NMR spectra of compound 13.

Alkyn-G1-1 13C (DMSO)





Current Data Parameters
 NAME NMR
 EXPNO 1252
 PROCNO 1

F2 - Acquisition Parameters
 Date 20180912
 Time 18.07
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CD2C12
 NS 256
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.125483 Hz
 AQ 3.9845889 sec
 RG 63.61
 DW 60.800 usec
 DE 6.50 usec
 TE 298.6 K
 D1 1.00000000 sec

===== CHANNEL f1 ======

NUC1 1H
 P1 9.00 usec
 PLW1 23.79999924 W
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 65536
 SF 400.1300249 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Fig C28. 1H-NMR spectra of compound 14.

preG1-2 (CD2C12)

— 7.452
— 7.413
— 7.368

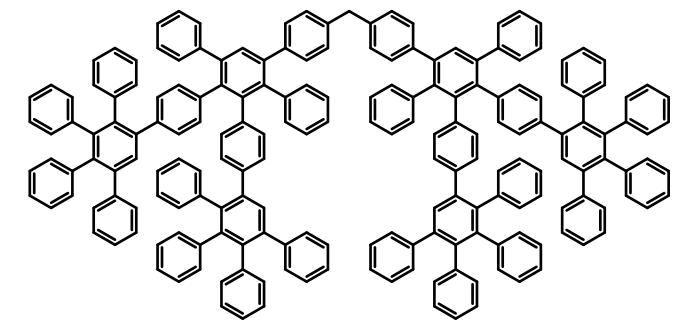
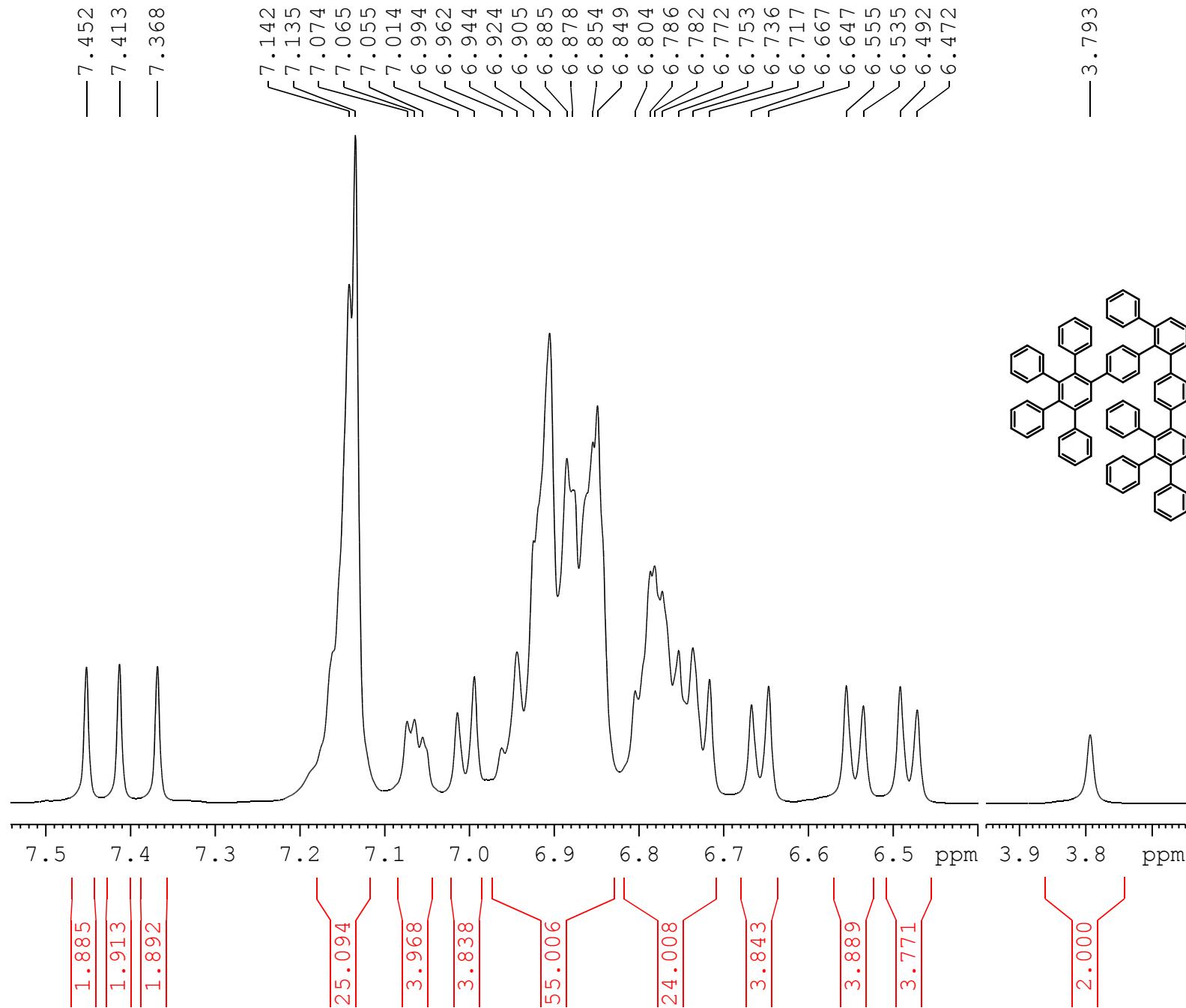


Fig C29. ¹H-NMR spectra of compound 14.

preG1-2 (CD₂Cl₂)

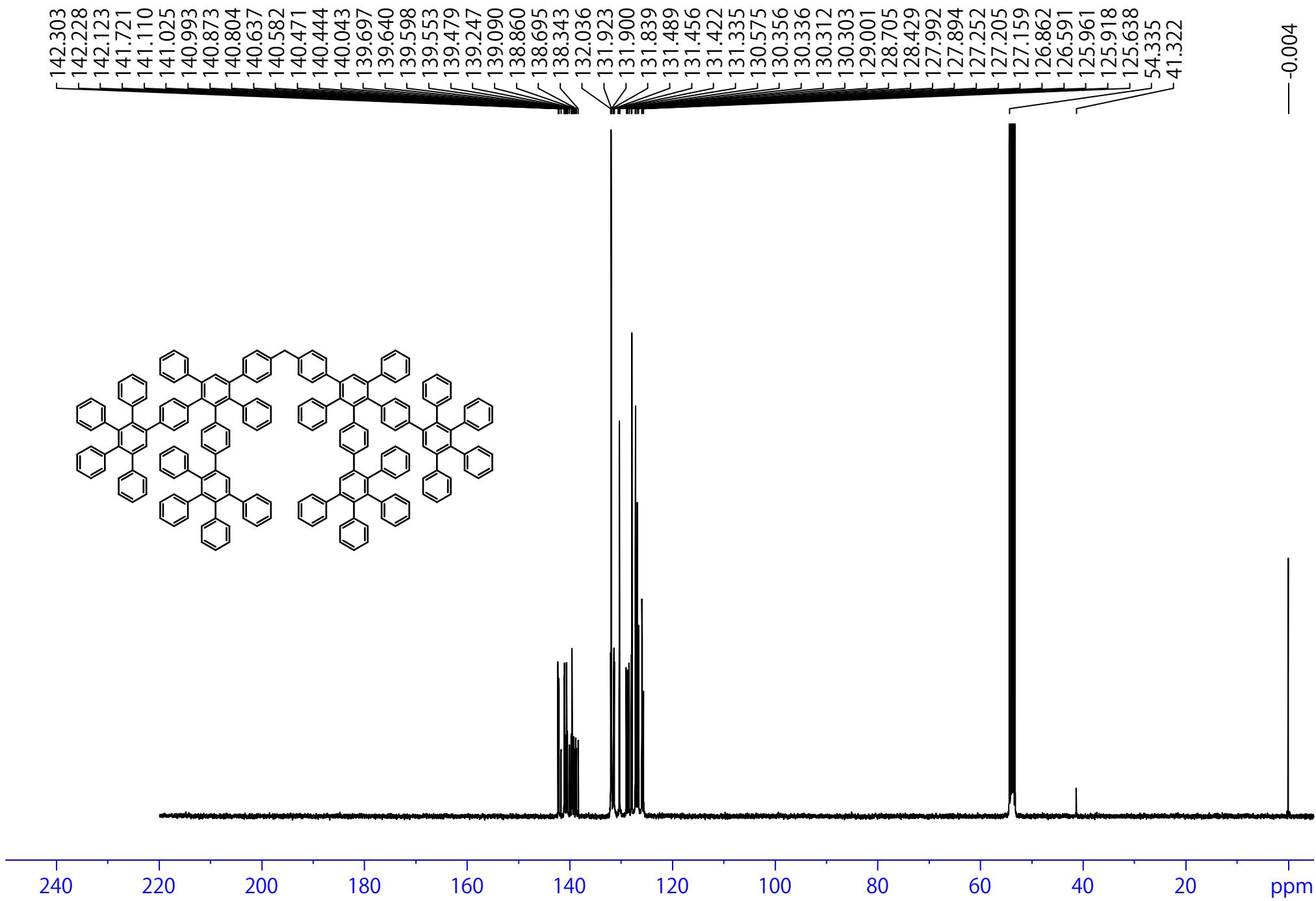


Fig C30. ¹³C-NMR spectra of compound 14.

preG1-2 (CD₂Cl₂)

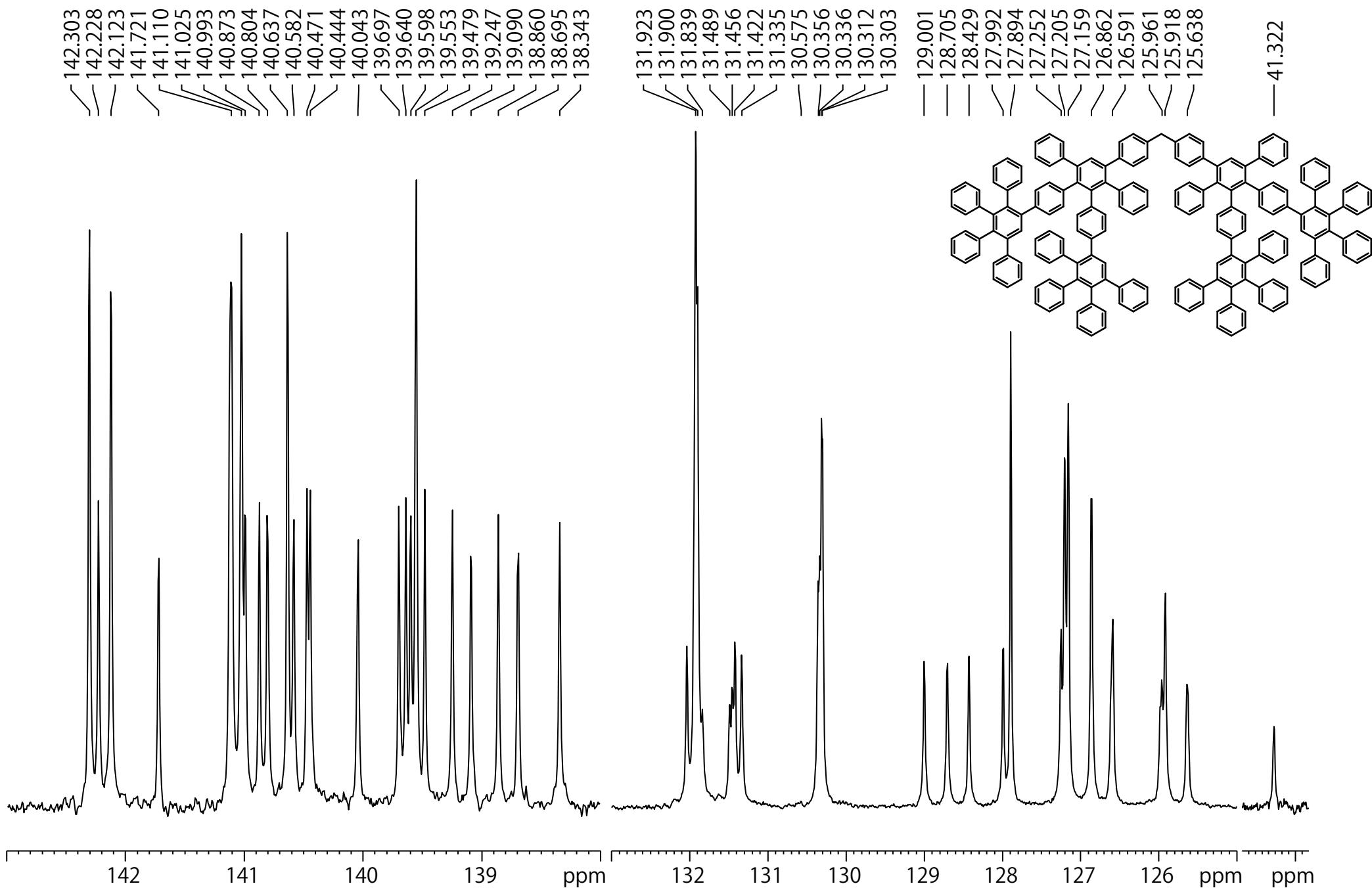
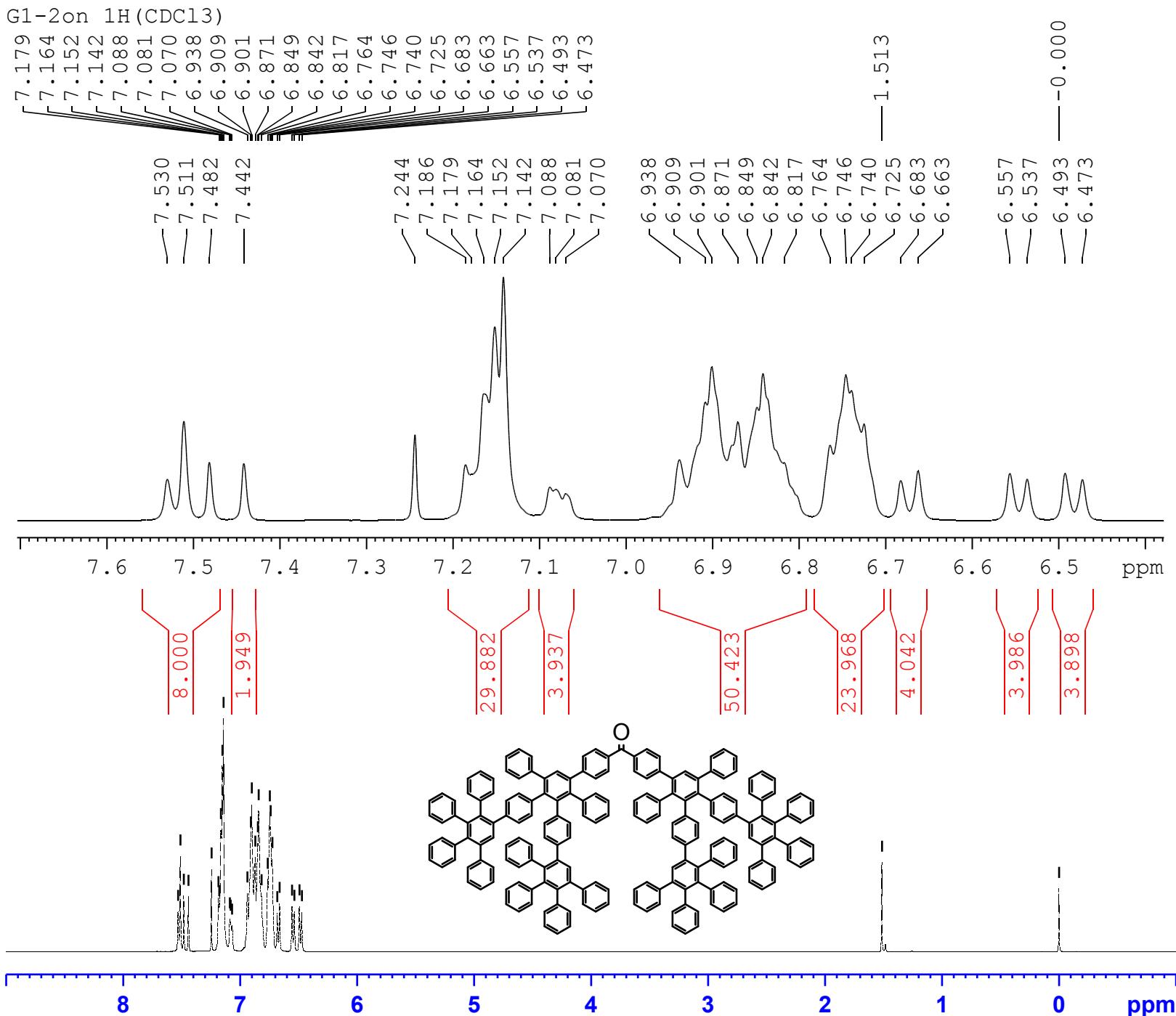


Fig C31. ¹³C-NMR spectra of compound 14.



Current Data Parameters
 NAME NMR
 EXPNO 1154
 PROCNO 1

F2 - Acquisition Parameters
 Date 20180831
 Time 18.20
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CDCl₃
 NS 256
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.125483 Hz
 AQ 3.9845889 sec
 RG 78.21
 DW 60.800 usec
 DE 6.50 usec
 TE 299.0 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 9.00 usec
 PLW1 23.79999924 W
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 65536
 SF 400.1300161 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

G1-2on 13C(CDCl₃)

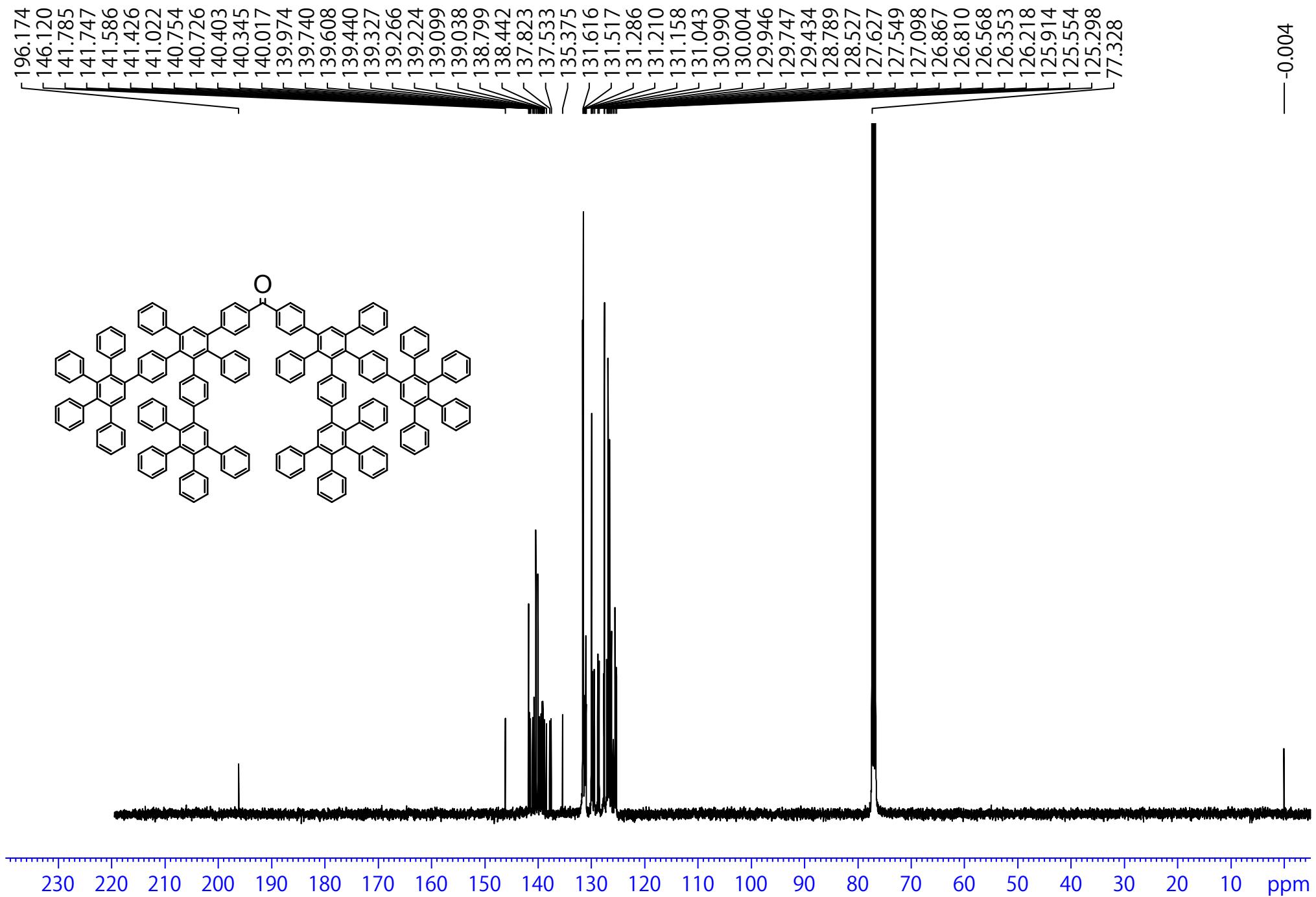


Fig C33. ¹³C-NMR spectra of compound 15.

G1-2on 13C(CDCl₃)

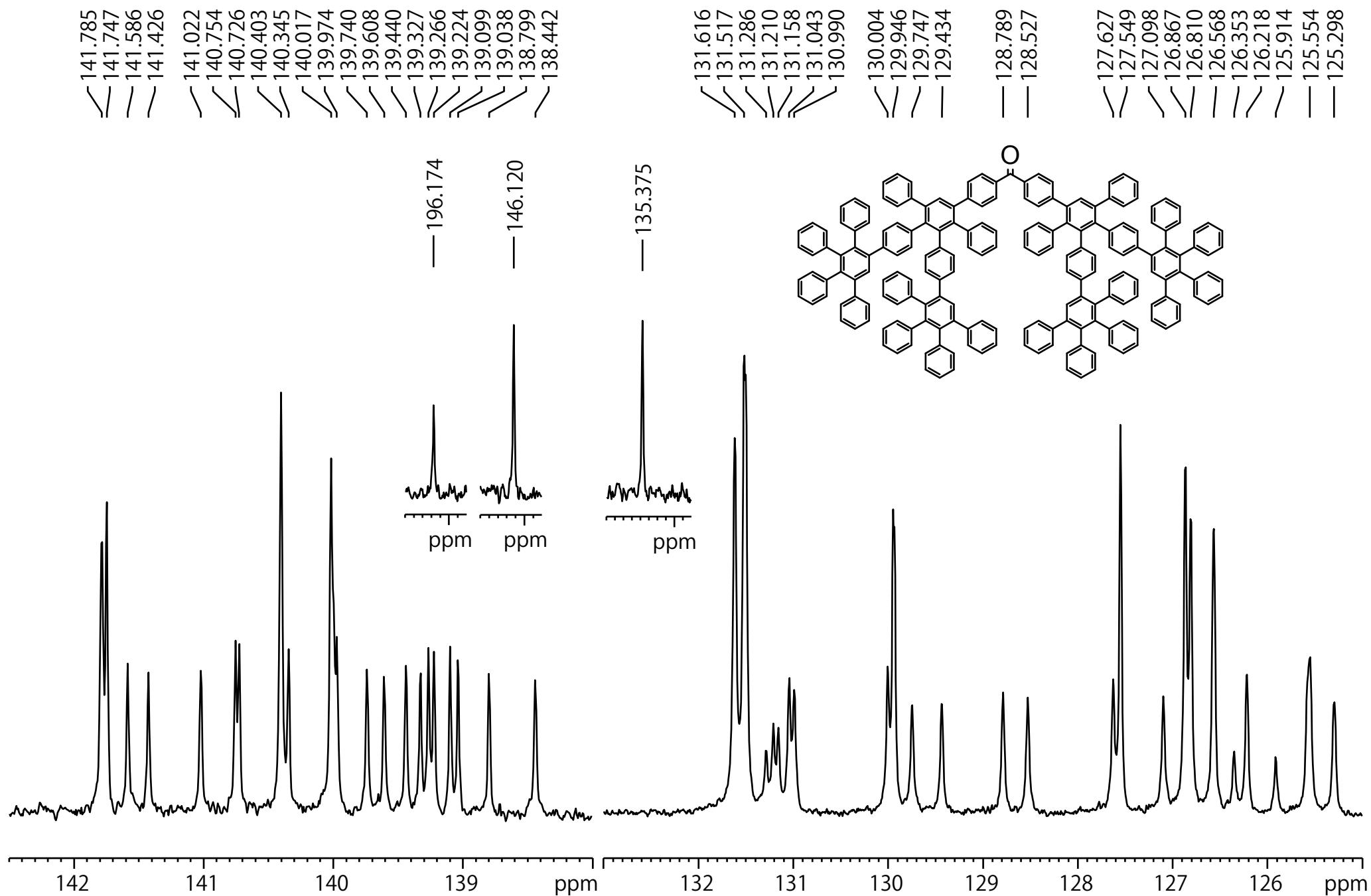


Fig C34. ¹³C-NMR spectra of compound 15.

TIPS-preG1-1half-NHAc 1H (CD₂Cl₂, 400MHz, 298.1K)

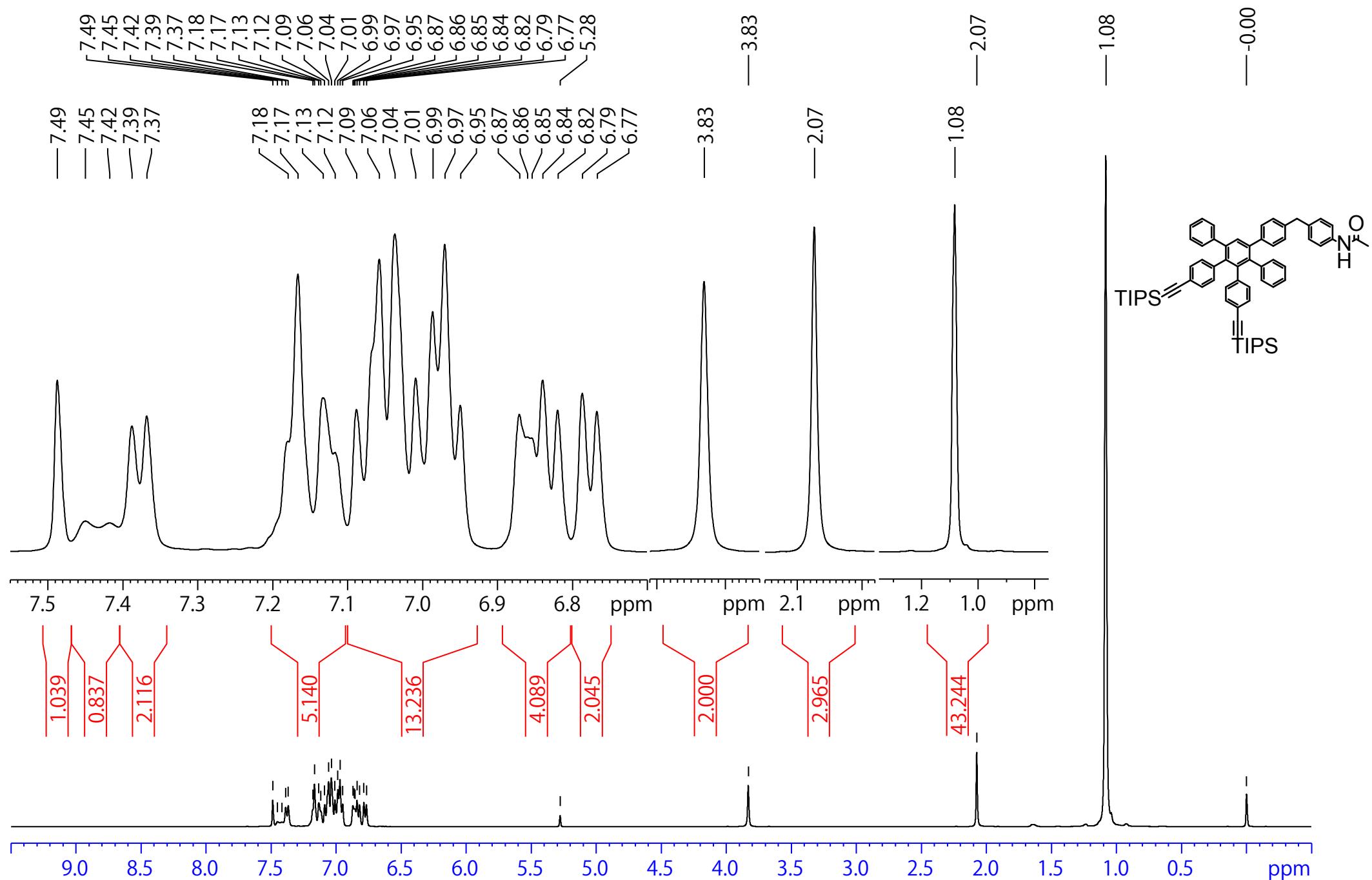


Fig C35. 1H-NMR spectra of compound 16.

TIPS-preG1-1half-NHAc 13C (CD₂Cl₂, 100MHz, 299.4K)

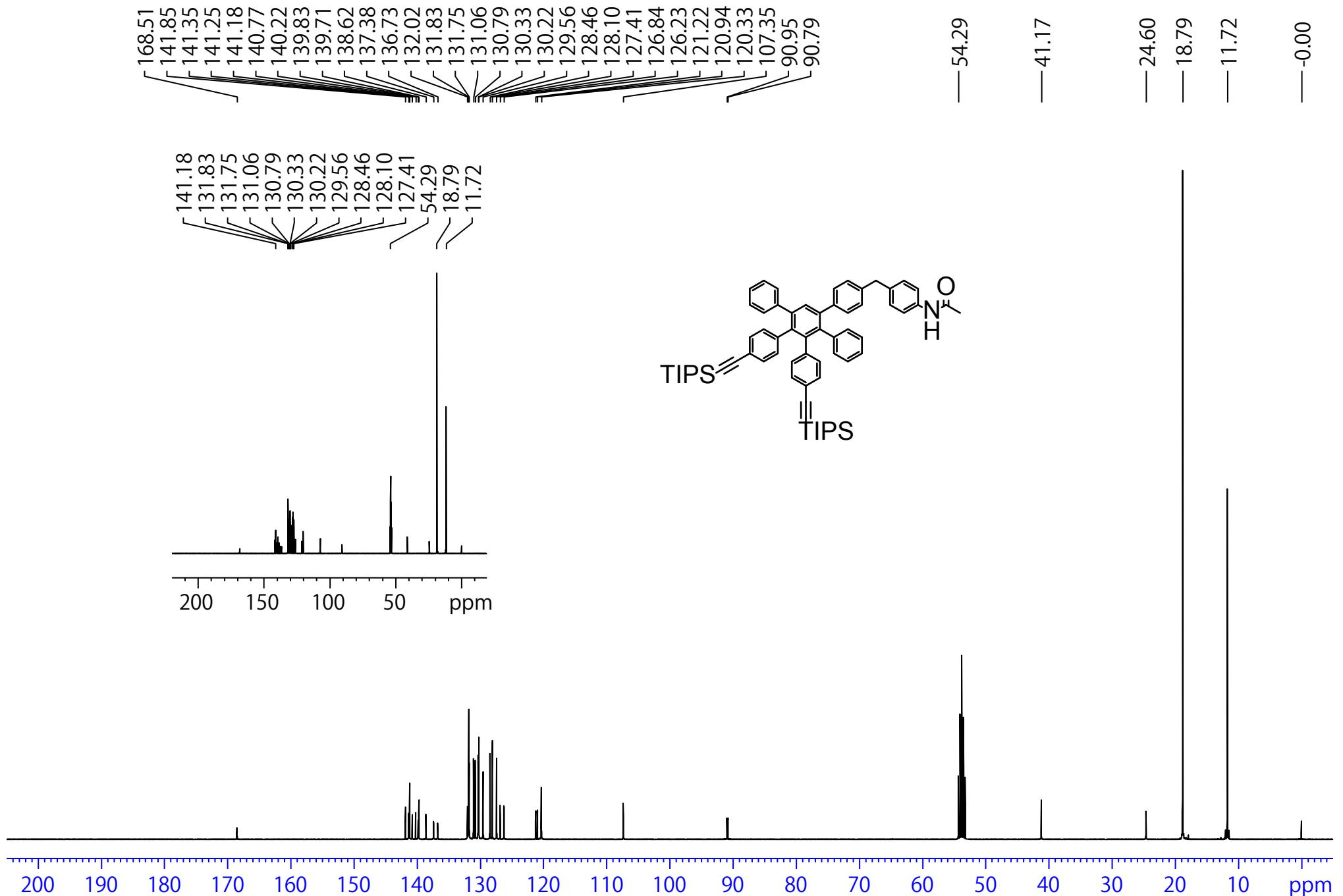


Fig C36. ¹³C-NMR spectra of compound 16.

Alkyn-preG1-1half-NHAc 1H (CD₂Cl₂, 400MHz, 298.2K)

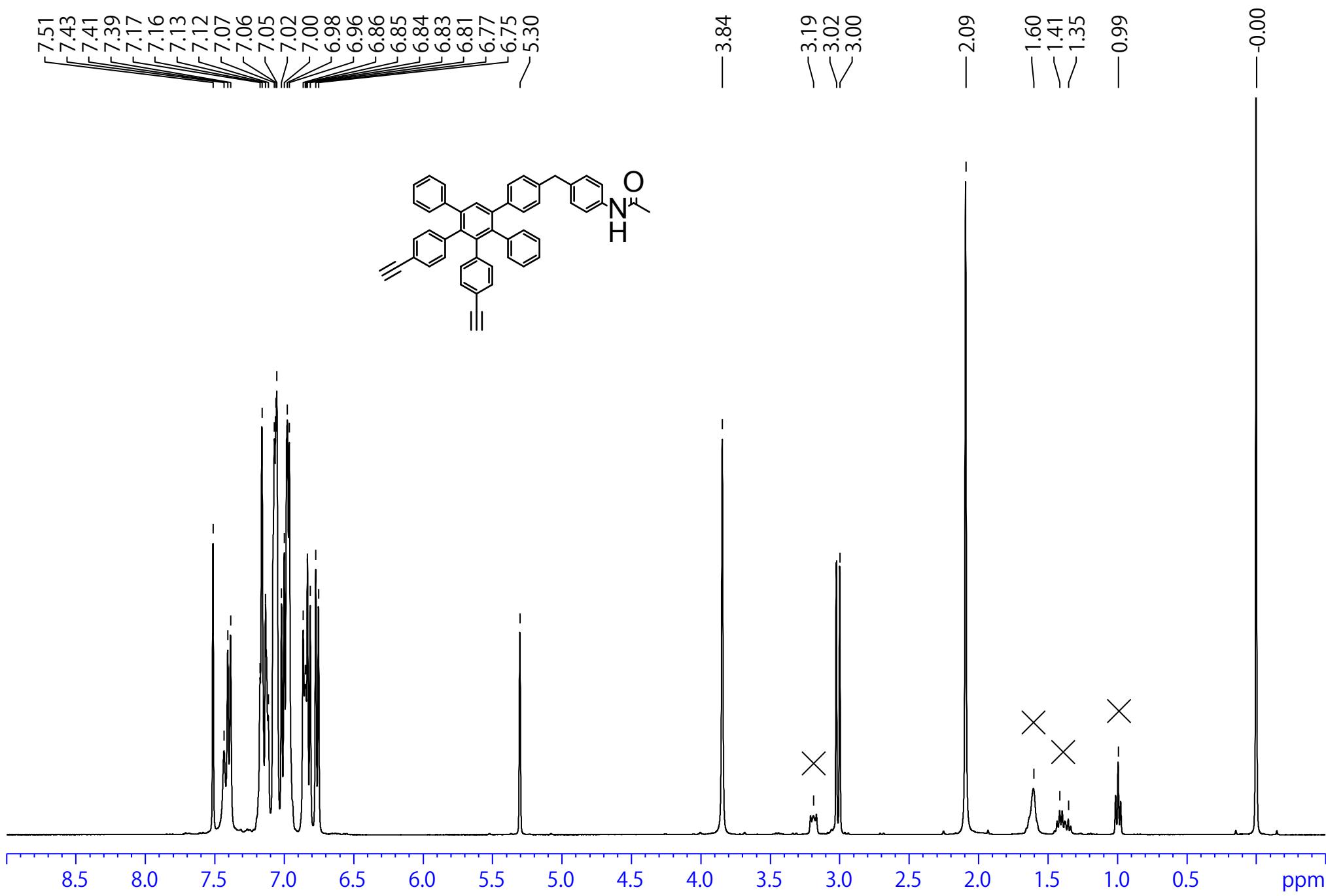


Fig C37. ¹H-NMR spectra of compound 17.

Alkyn-preG1-1half-NHAc 1H (CD₂Cl₂, 400MHz, 298.2K)

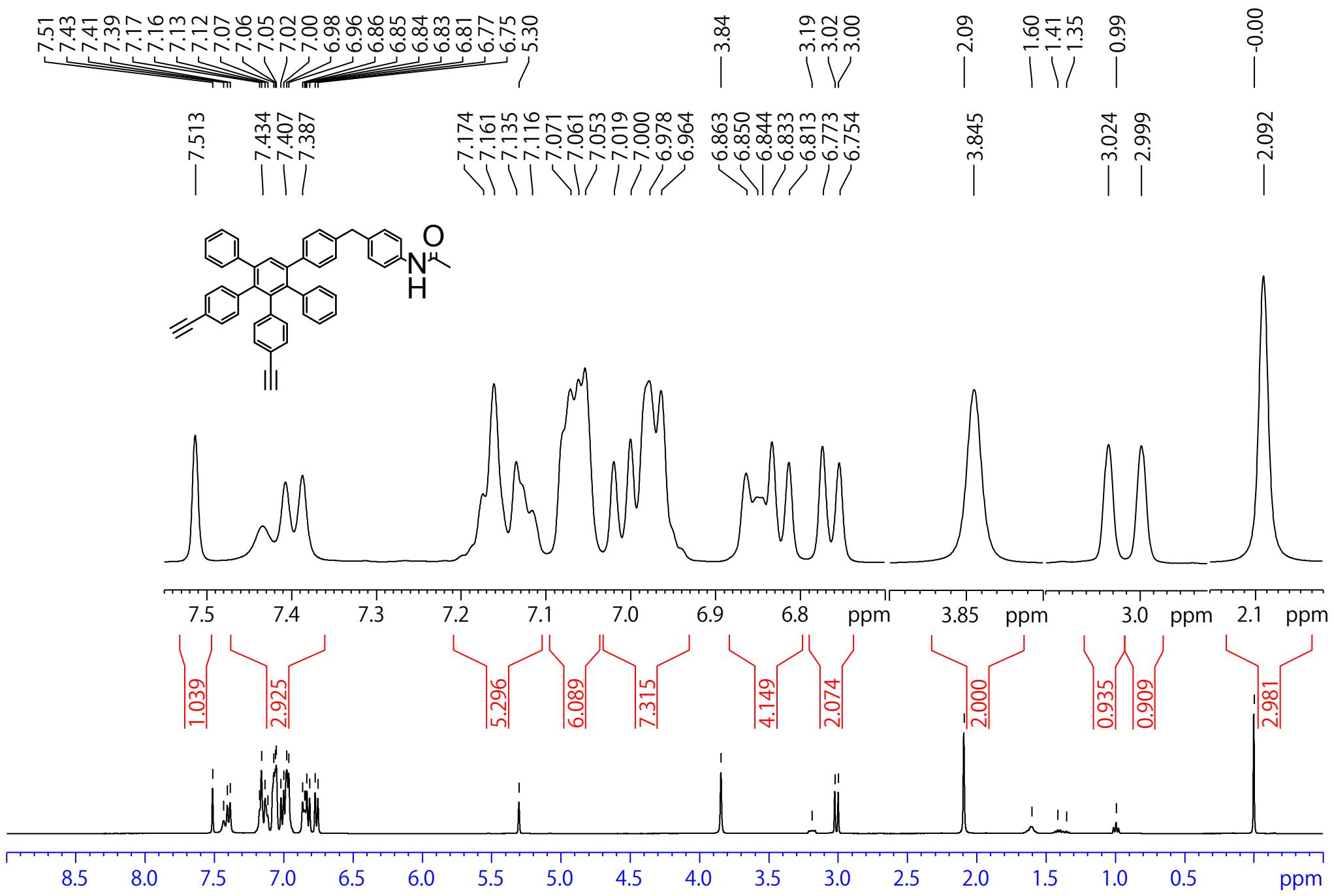


Fig C38. ¹H-NMR spectra of compound 17.

Alkyn-preG1-1half-NHAc 13C (CD₂Cl₂, 100MHz, 299.1K)

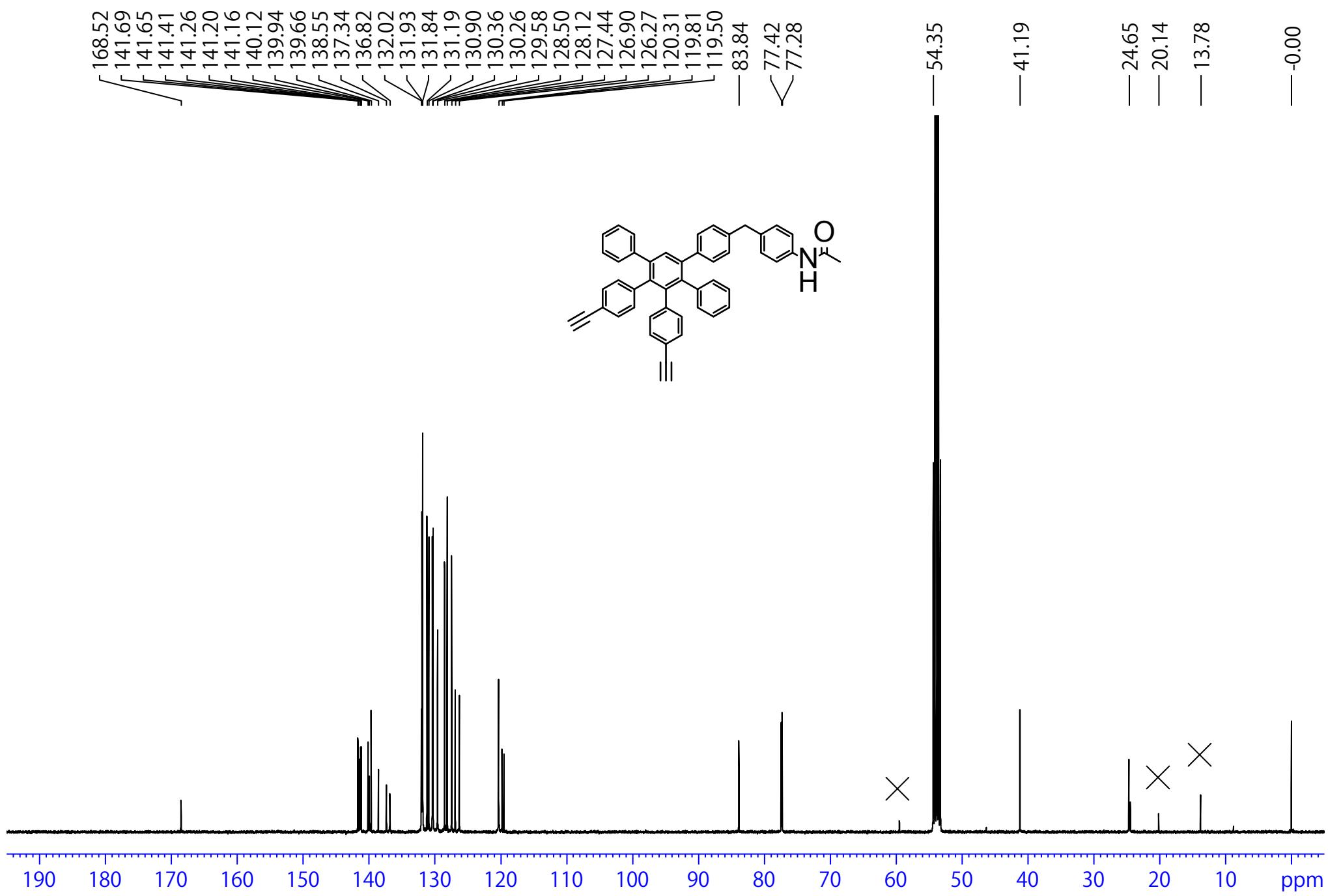
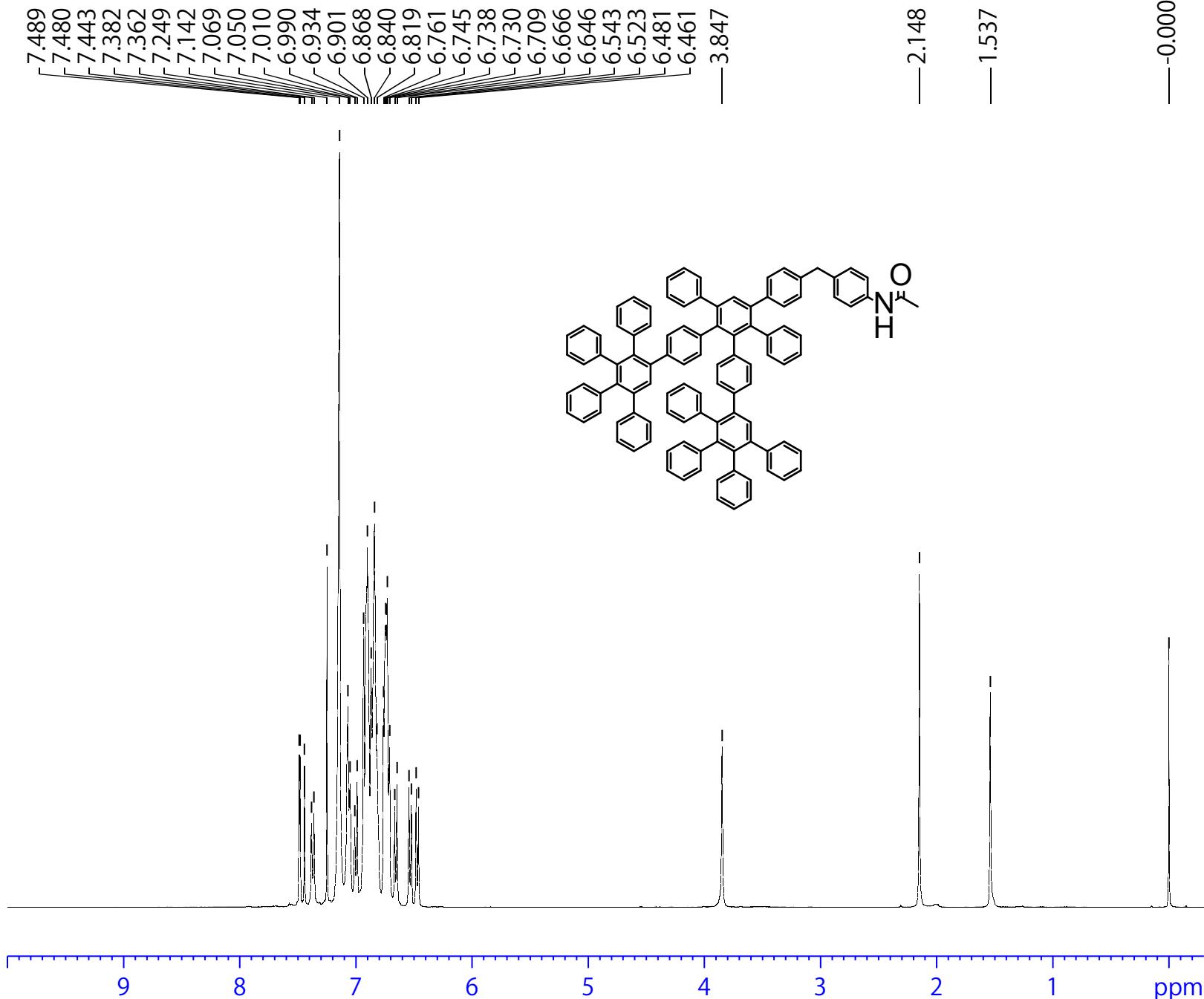


Fig C39. ¹³C-NMR spectra of compound 17.

preG1-2half-NHAc 1H(CDCI3)



Current Data Parameters
NAME NMR
EXPNO 1191
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180906
Time 5.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 256
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9845889 sec
RG 85.96
DW 60.800 usec
DE 6.50 usec
TE 298.9 K
D1 1.0000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 9.00 usec
PLW1 23.79999924 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300142 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig C40. 1H-NMR spectra of compound 18.

preG1-2half-NHAc 1H(CDCl₃)

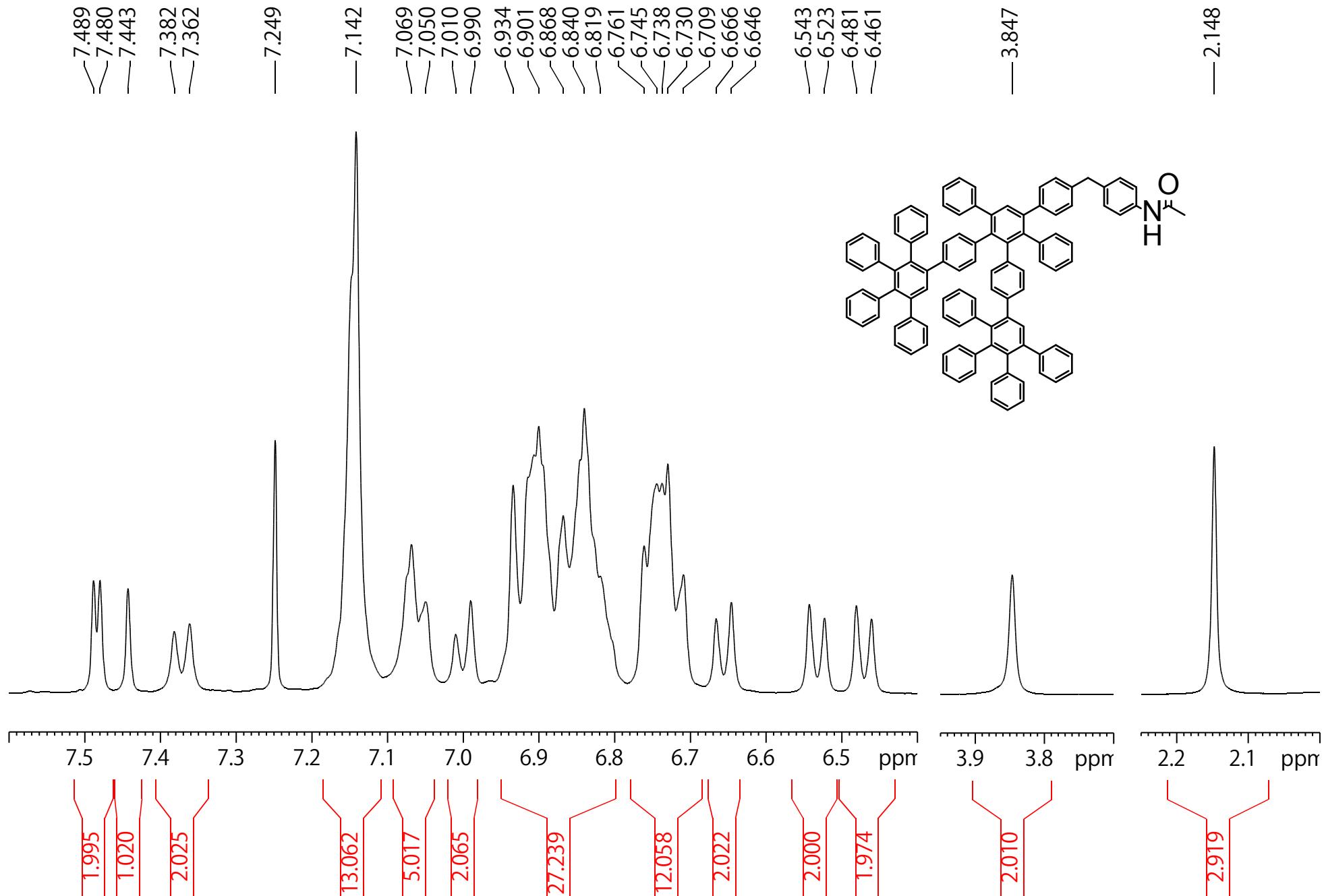


Fig C41. 1H-NMR spectra of compound 18.

preG1-2half-NHAc 13C(CDCl3)

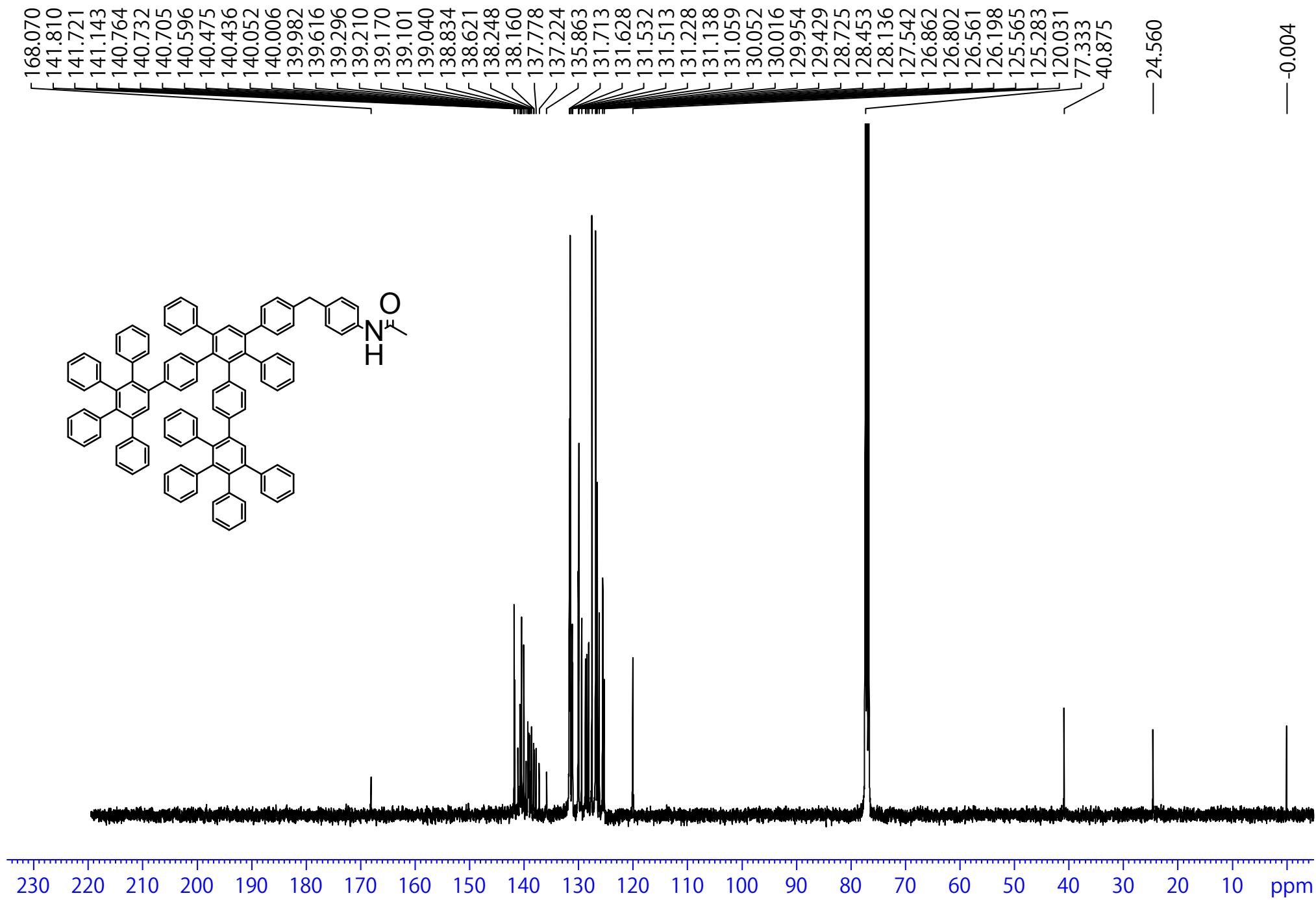


Fig C42. ¹³C-NMR spectra of compound 18.

preG1-2half-NHAc 13C(CDCl3)

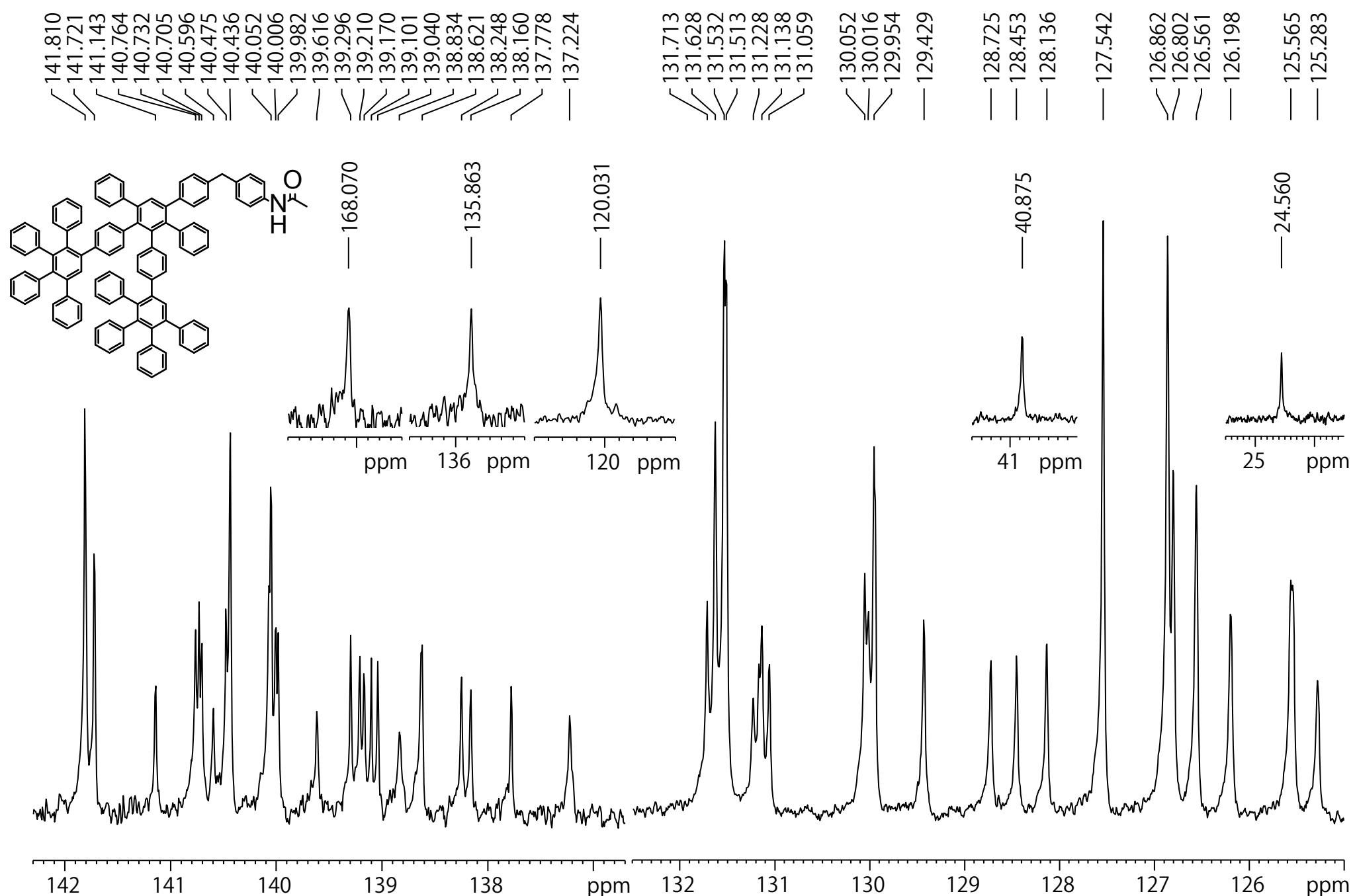
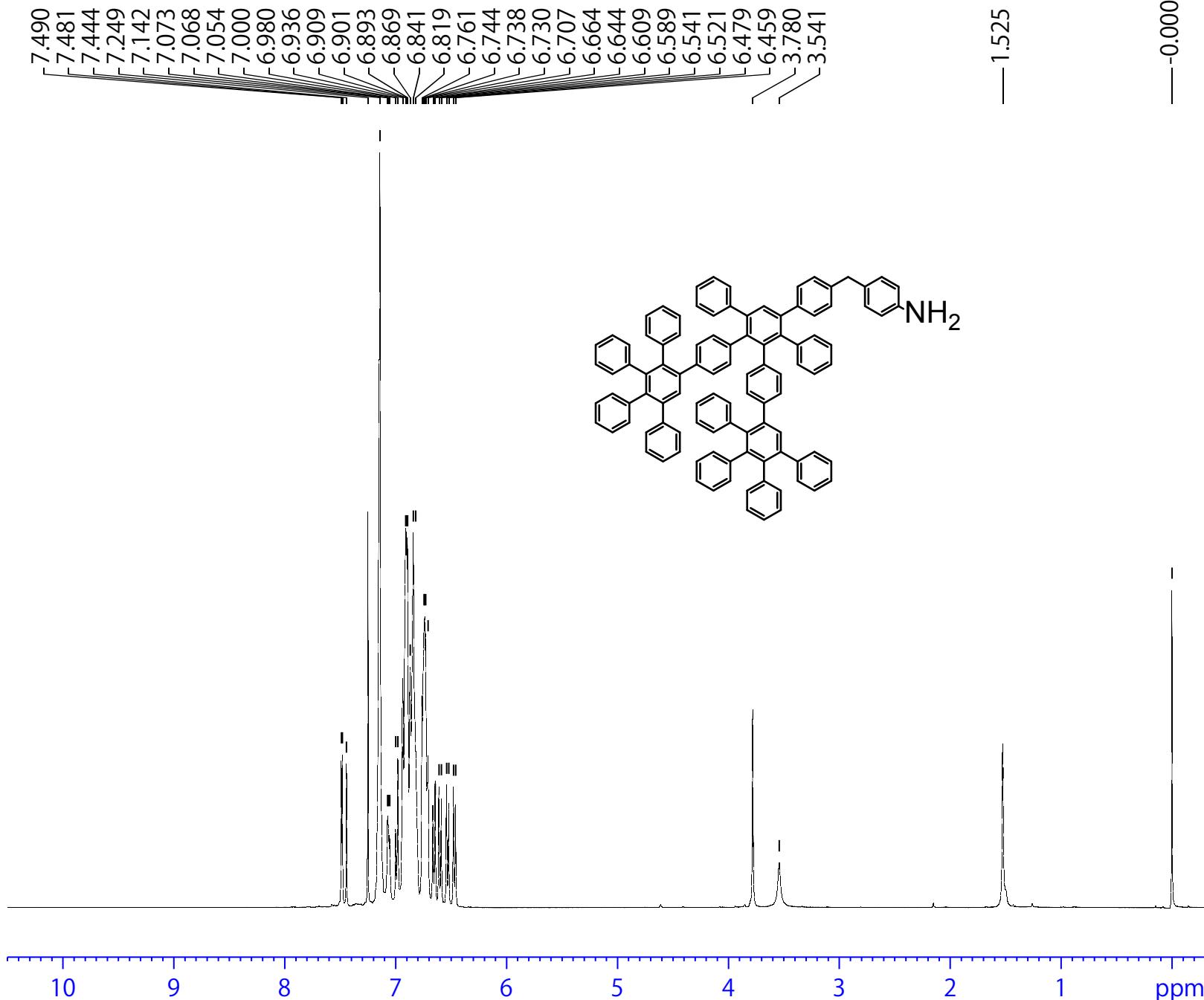


Fig C43. ¹³C-NMR spectra of compound 18.

preG1-2half-NH 1H(CDCl₃)



Current Data Parameters
NAME NMR
EXPNO 1201
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180907
Time 5.25
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl₃
NS 256
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9845889 sec
RG 95.62
DW 60.800 usec
DE 6.50 usec
TE 298.6 K
D1 1.0000000 sec

===== CHANNEL f1 ======

NUC1 1H
P1 9.00 usec
PLW1 23.79999924 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300140 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig C44. ¹H-NMR spectra of compound 19.

preG1-2half-NH 1H(CDCl₃)

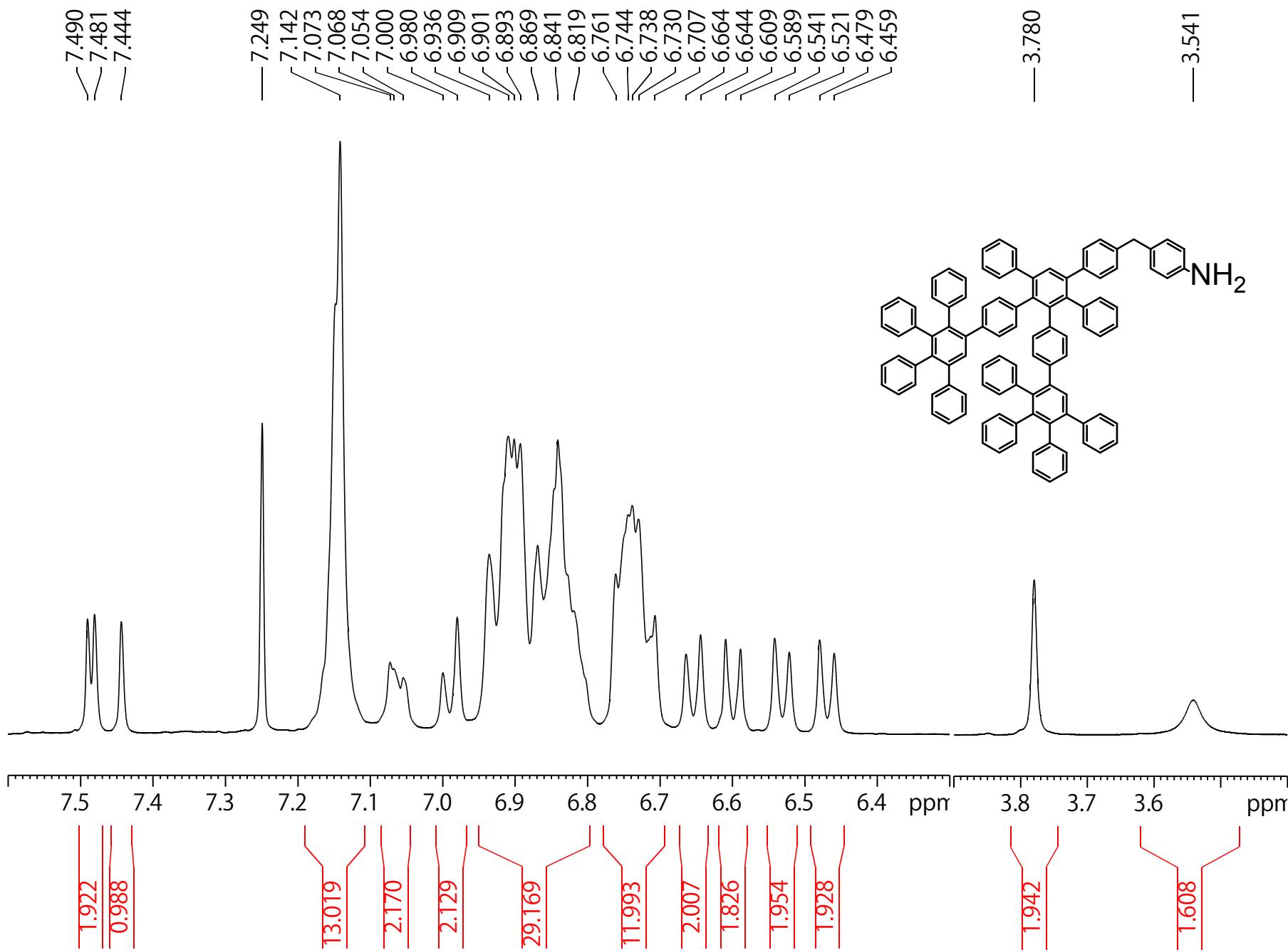


Fig C45. 1H-NMR spectra of compound 19.

preG1-2half-NH 1H(CDCl_3)

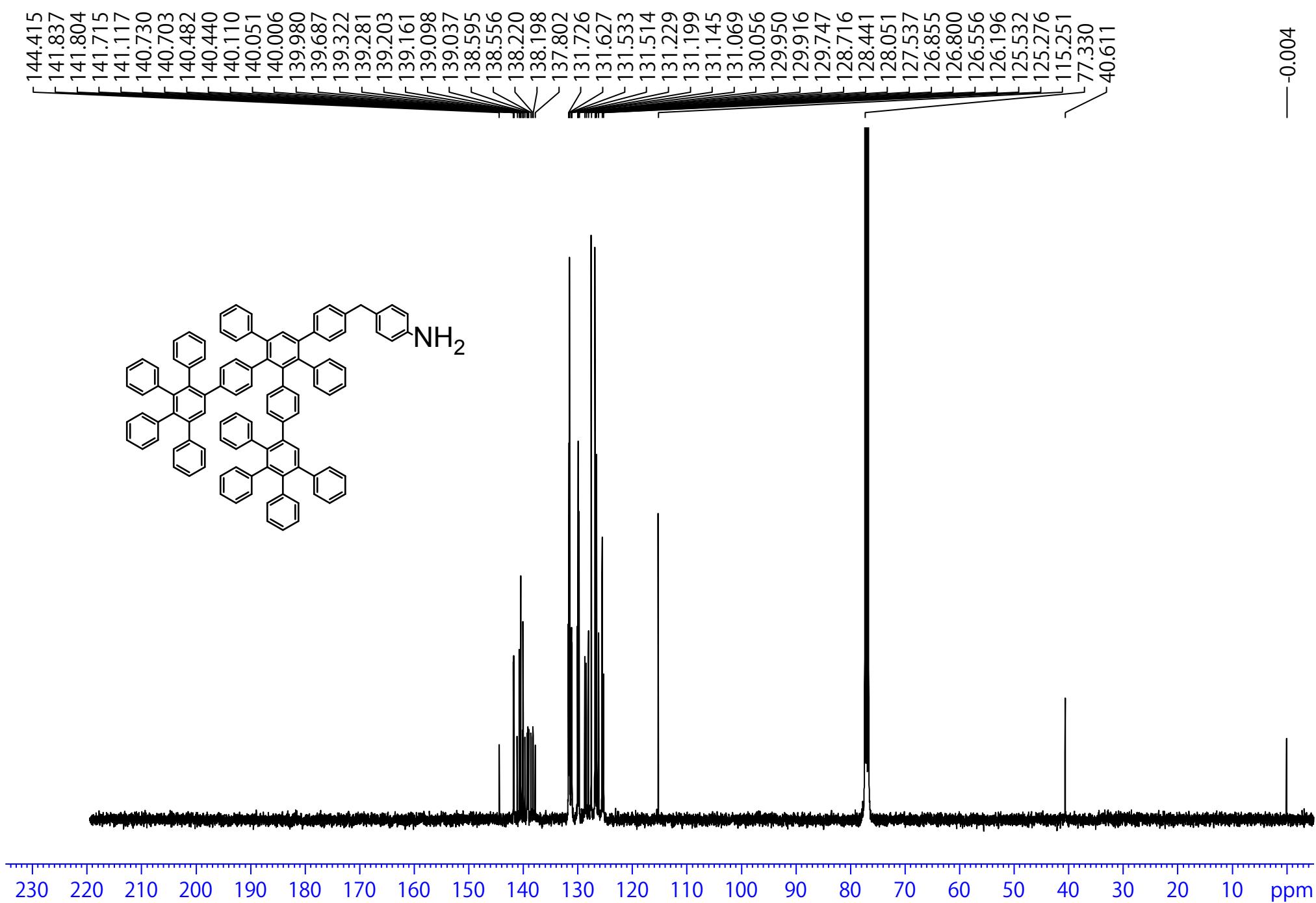


Fig C46. ^{13}C -NMR spectra of compound 19.

preG1-2half-NH 1H(CDCl₃)

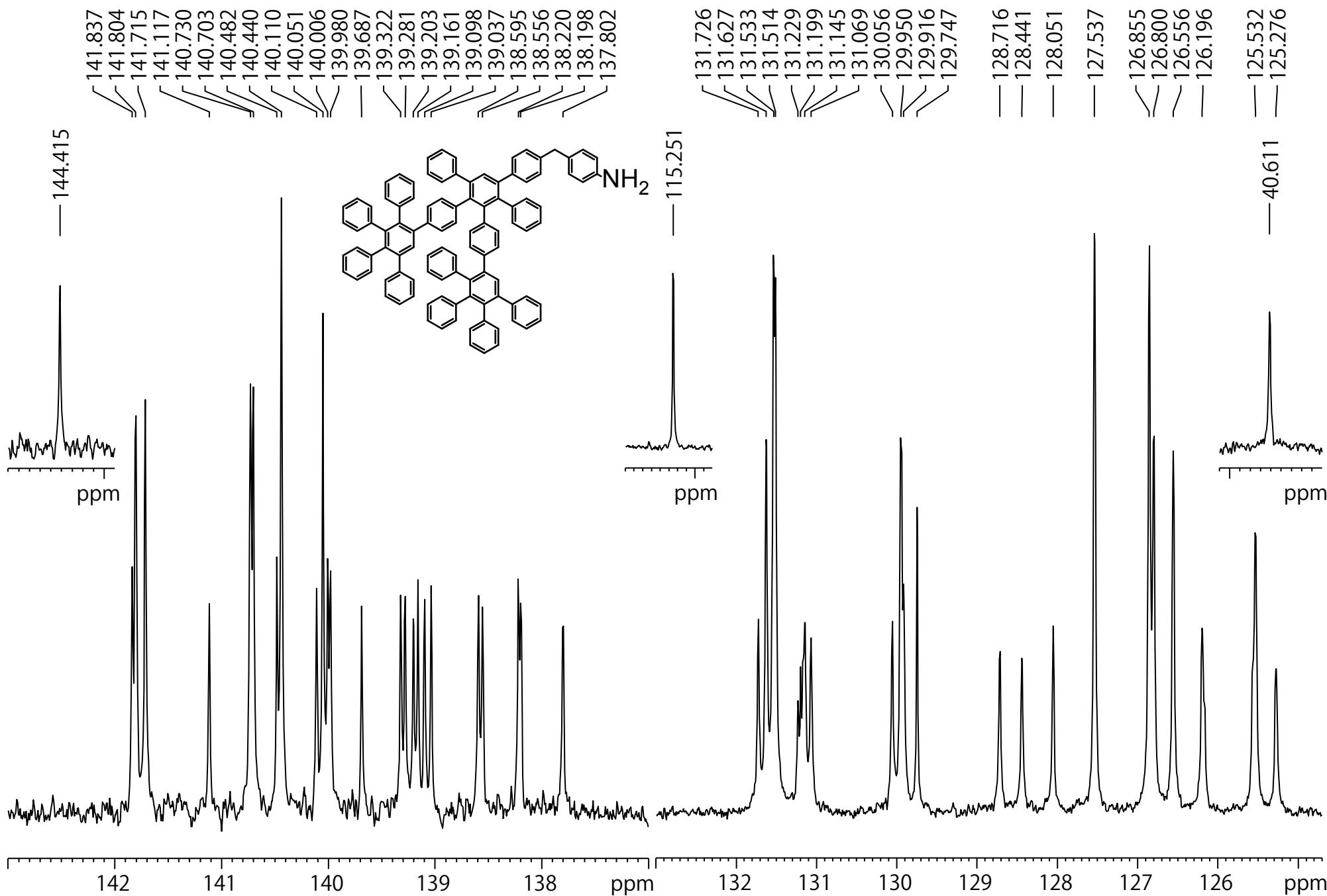
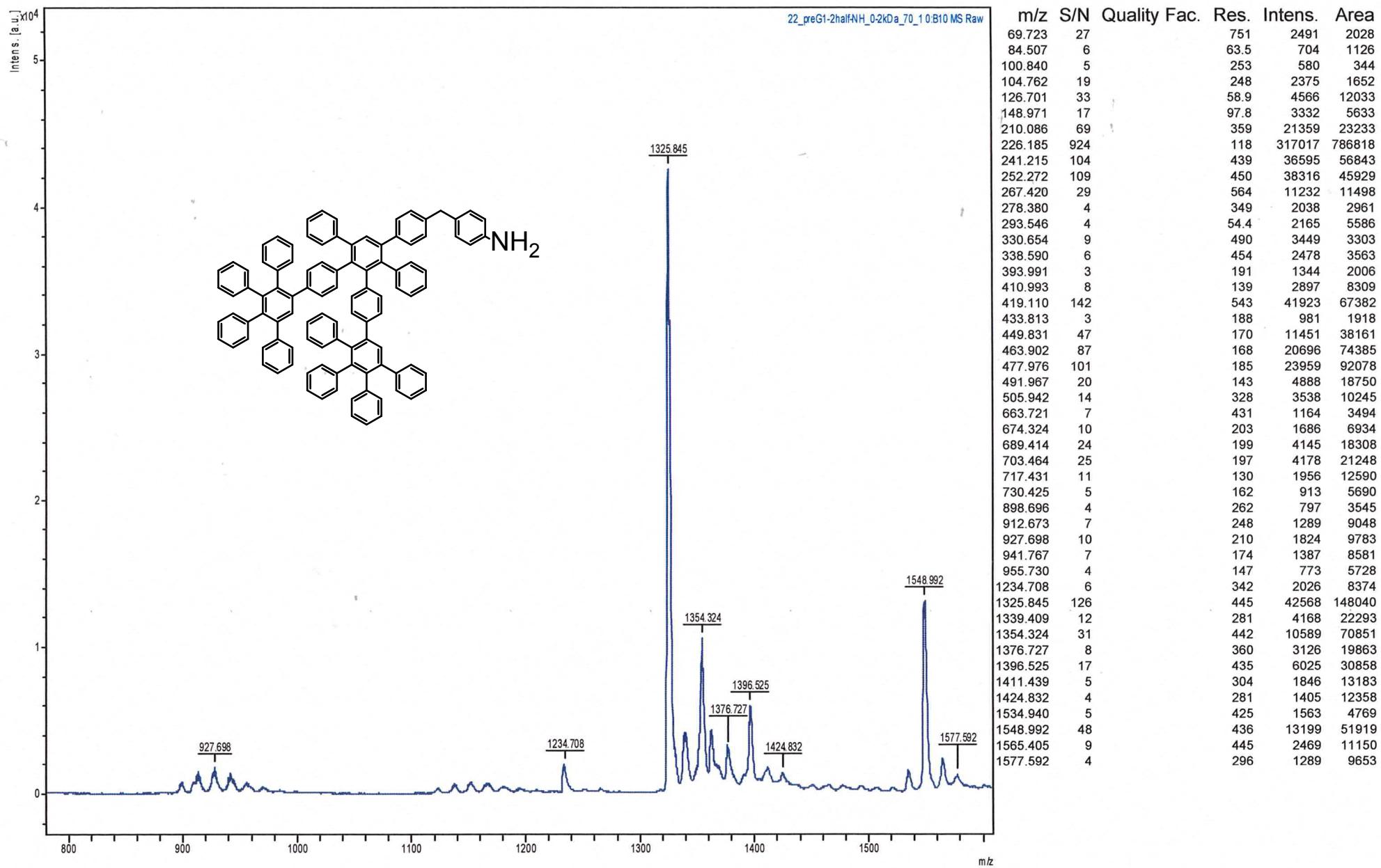


Fig C47. ¹³C-NMR spectra of compound 19.

[M+H] 1325.58

22



11/29/2018 4:55:21 PM

Fig C48. MALDI-TOF-MS spectra of compound 19.

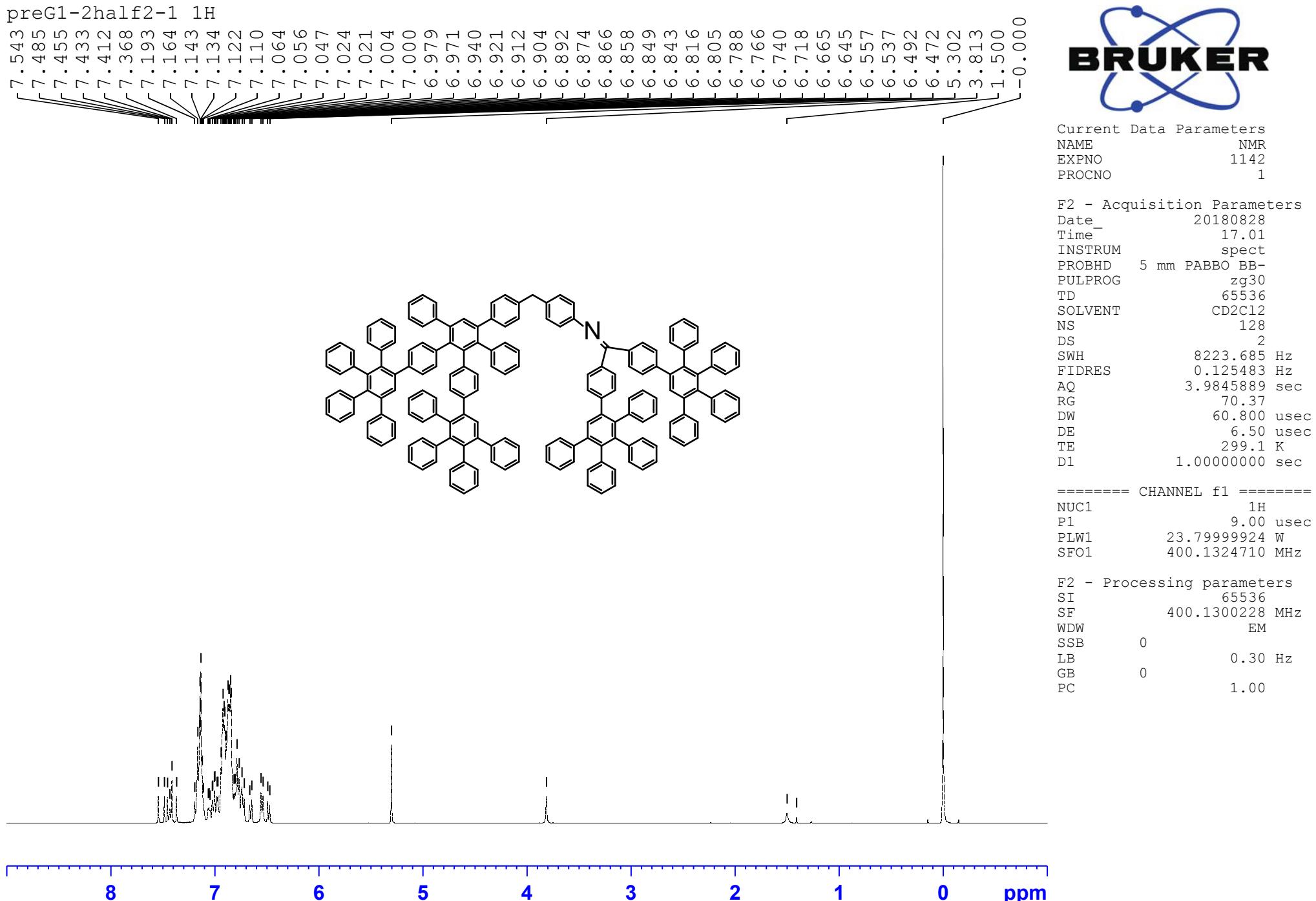


Fig C49. 1H-NMR spectra of compound 20.

preG1-2half2-1 1H

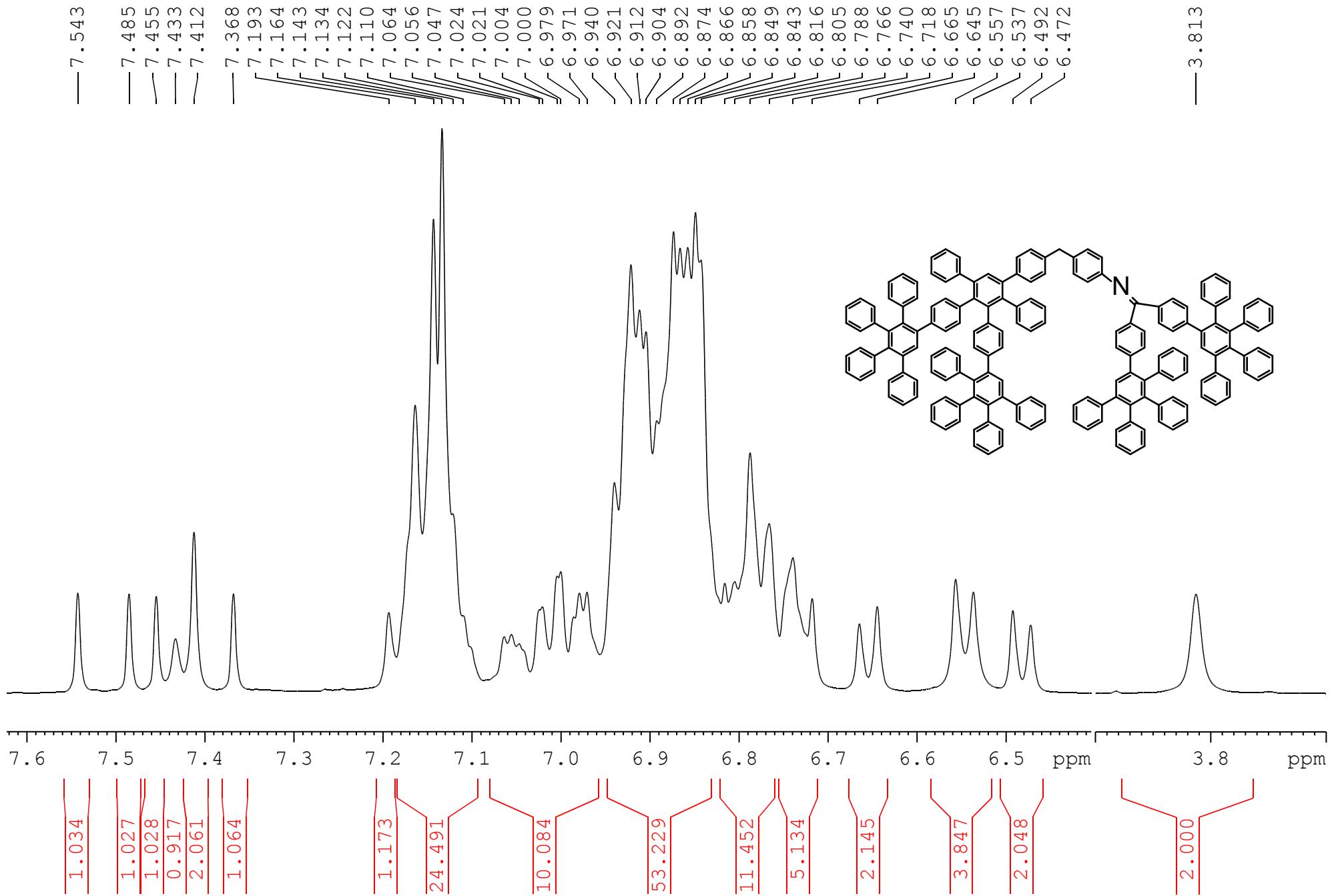


Fig C50. ¹H-NMR spectra of compound 20.

[M+H]⁺ 2249.96

(23)

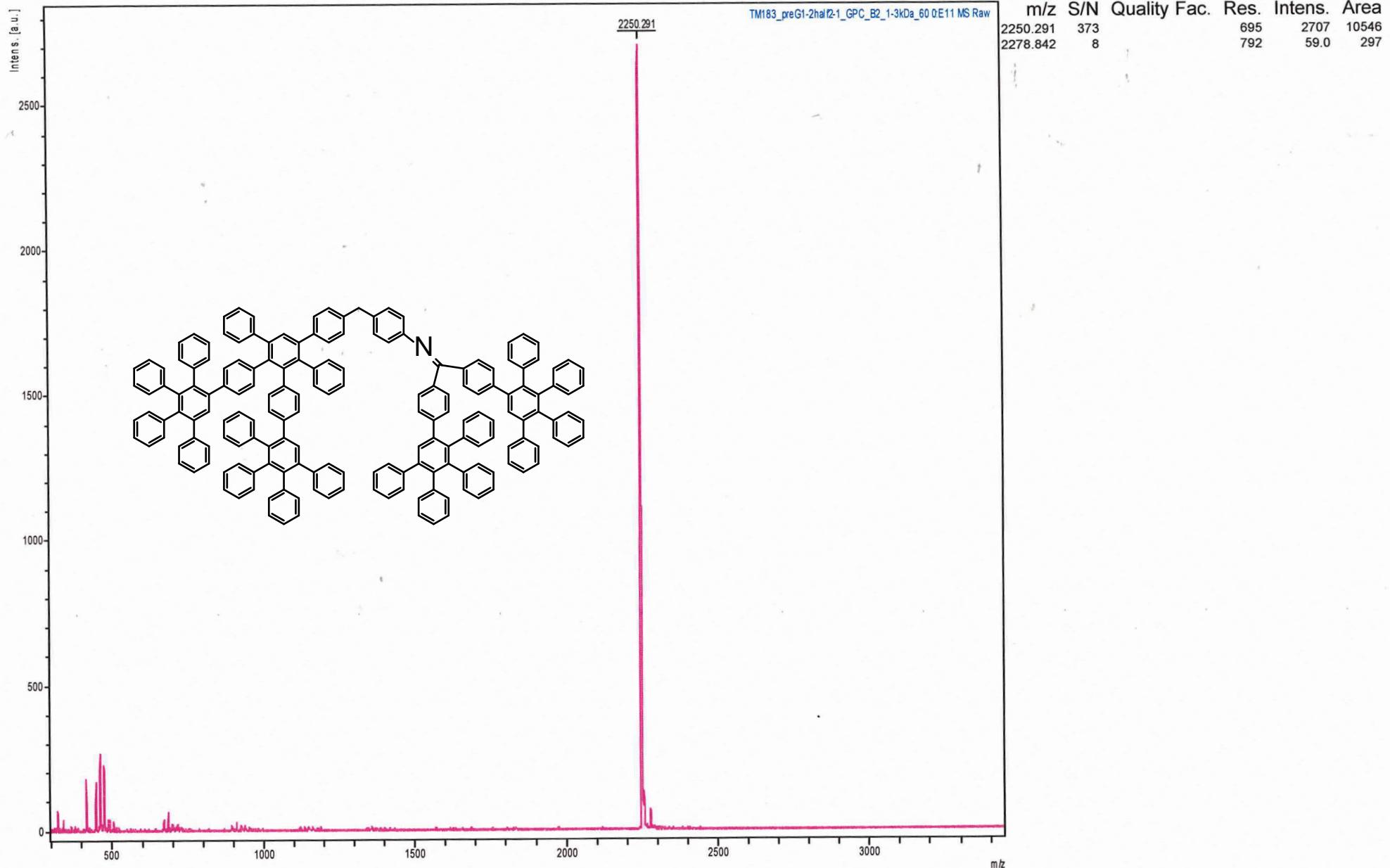


Fig C51. MALDI-TOF-MS spectra of compound 20.

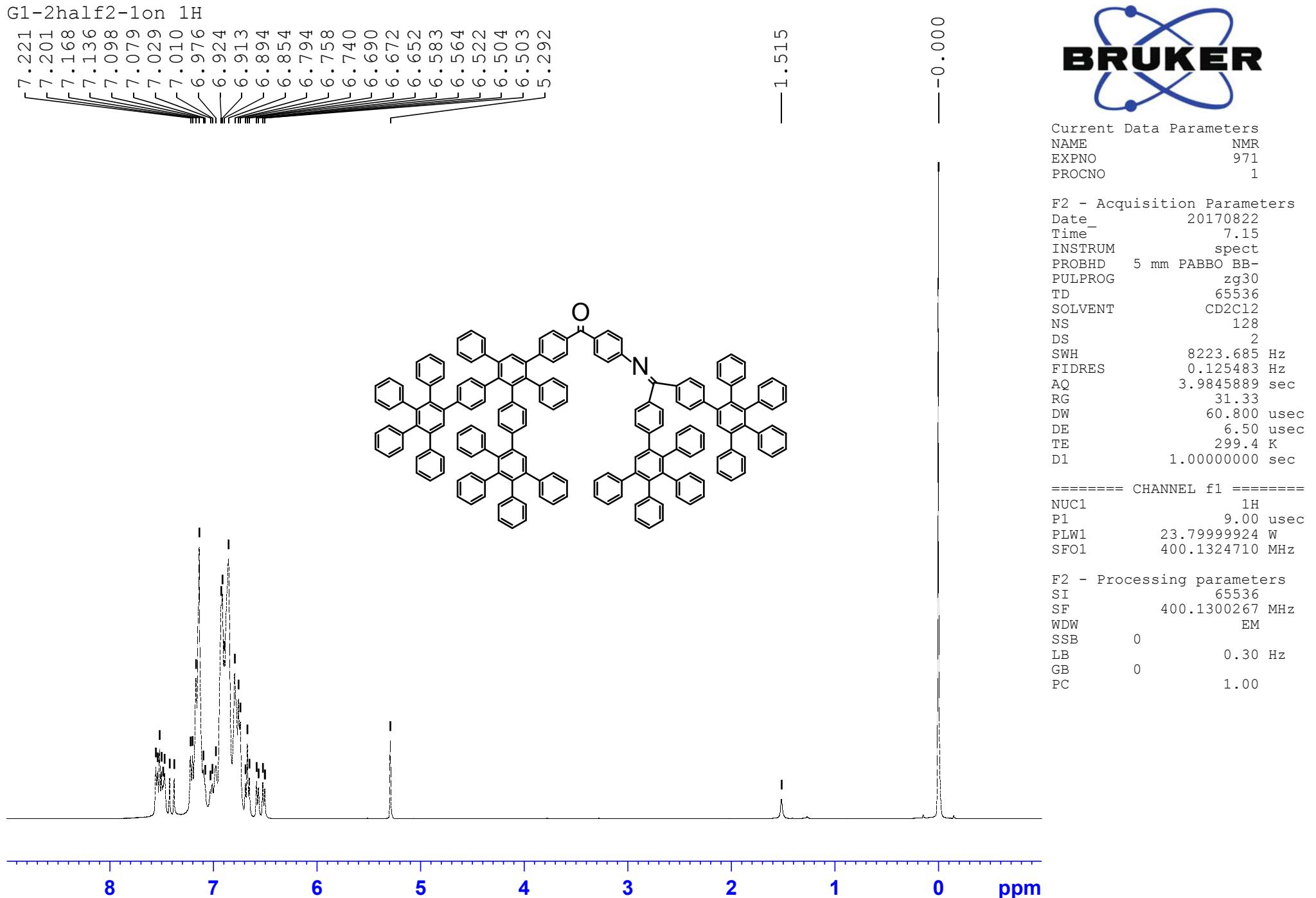
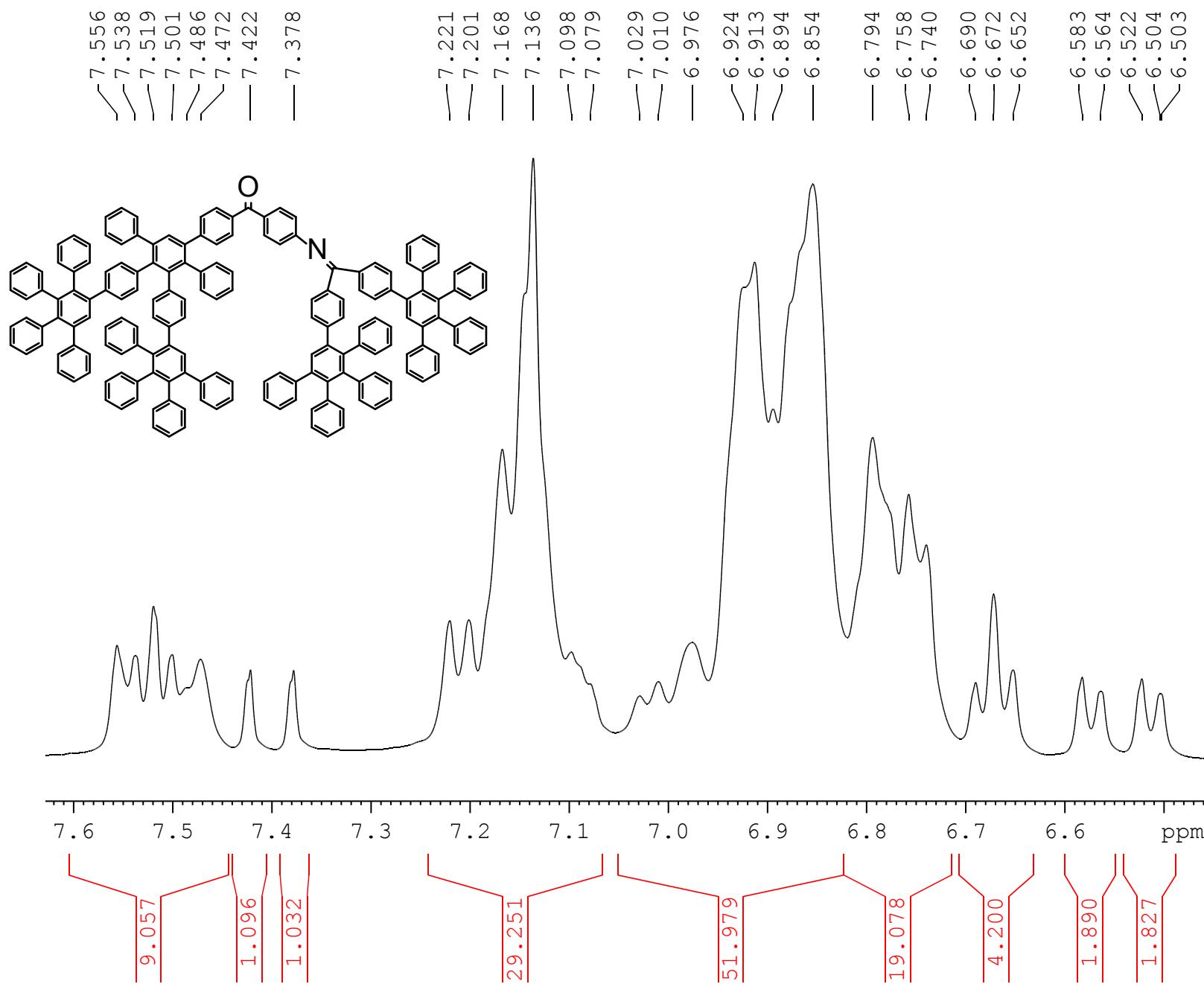


Fig C52. 1H-NMR spectra of compound 21.

G1-2half2-1on 1H



Current Data Parameters
NAME NMR
EXPNO 971
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170822
Time_ 7.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CD2C12
NS 128
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9845889 sec
RG 31.33
DW 60.800 usec
DE 6.50 usec
TE 299.4 K
D1 1.00000000 sec

===== CHANNEL f1 ======
NUC1 1H
P1 9.00 usec
PLW1 23.79999924 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300267 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig C53. ¹H-NMR spectra of compound 21.

G1-2half2-1on 13C

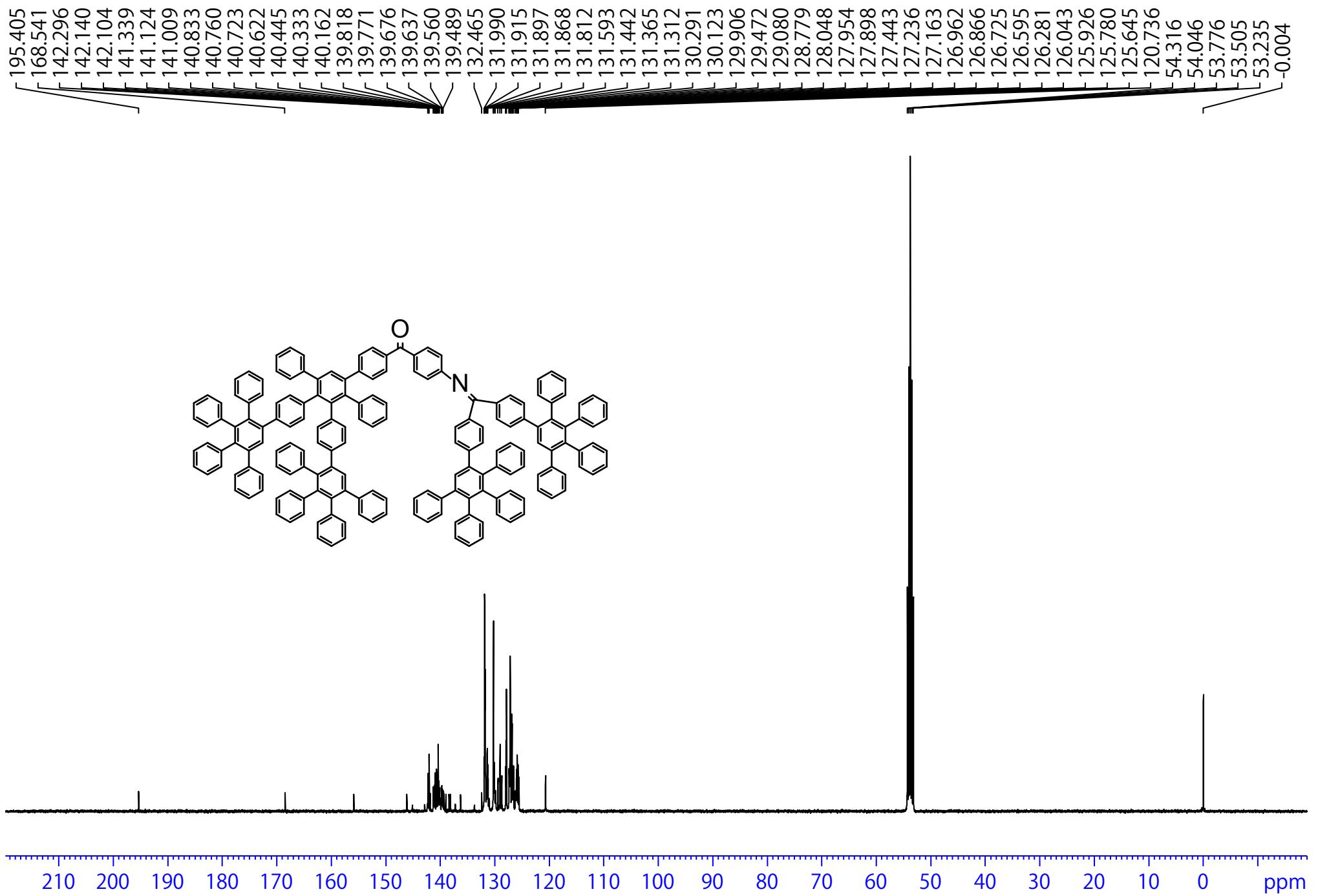


Fig C54. ¹³C-NMR spectra of compound 21.

G1-2half2-1on 13C

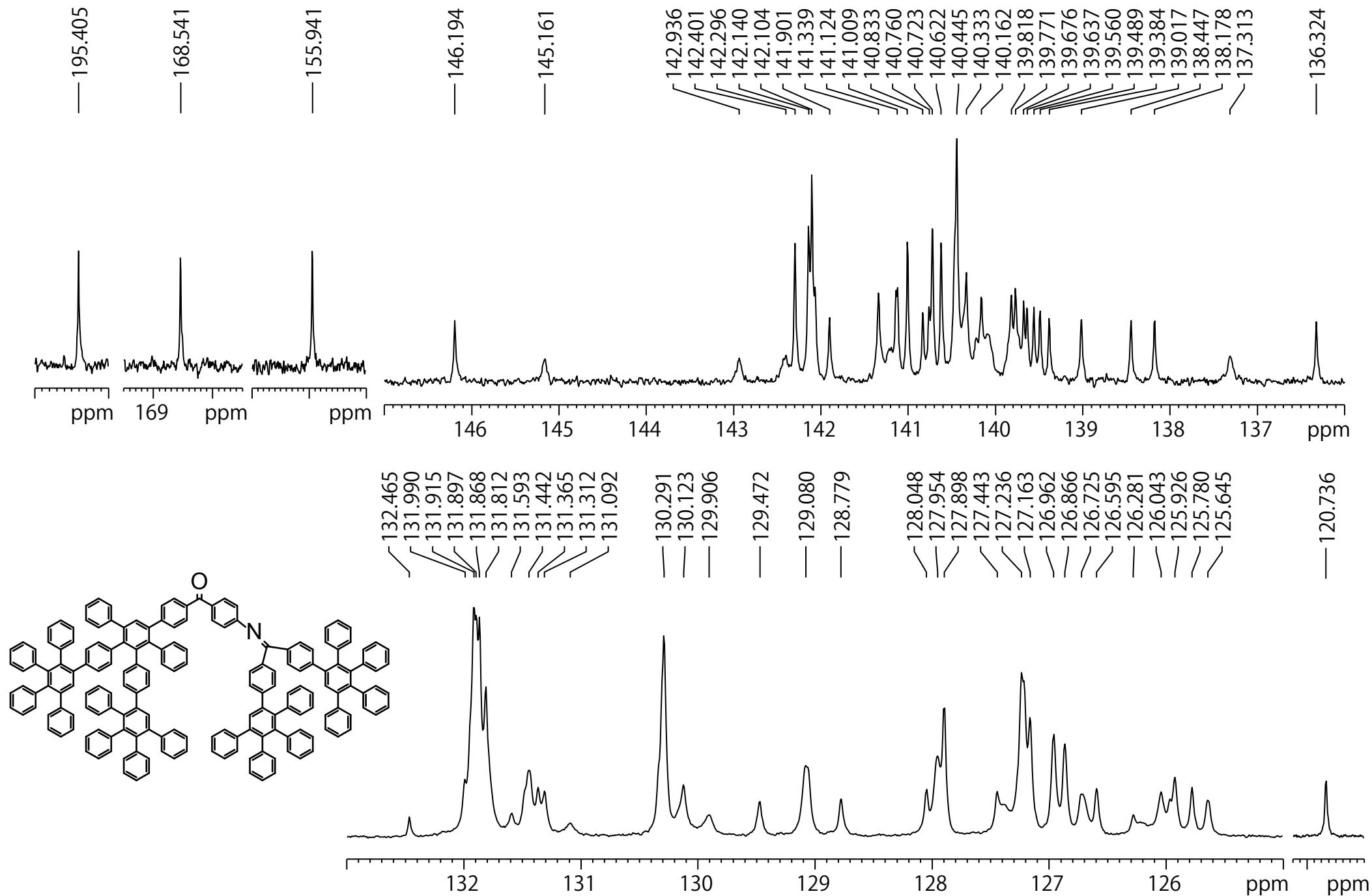


Fig C55. ¹³C-NMR spectra of compound 21.

[M+H] 2263.94

(24)

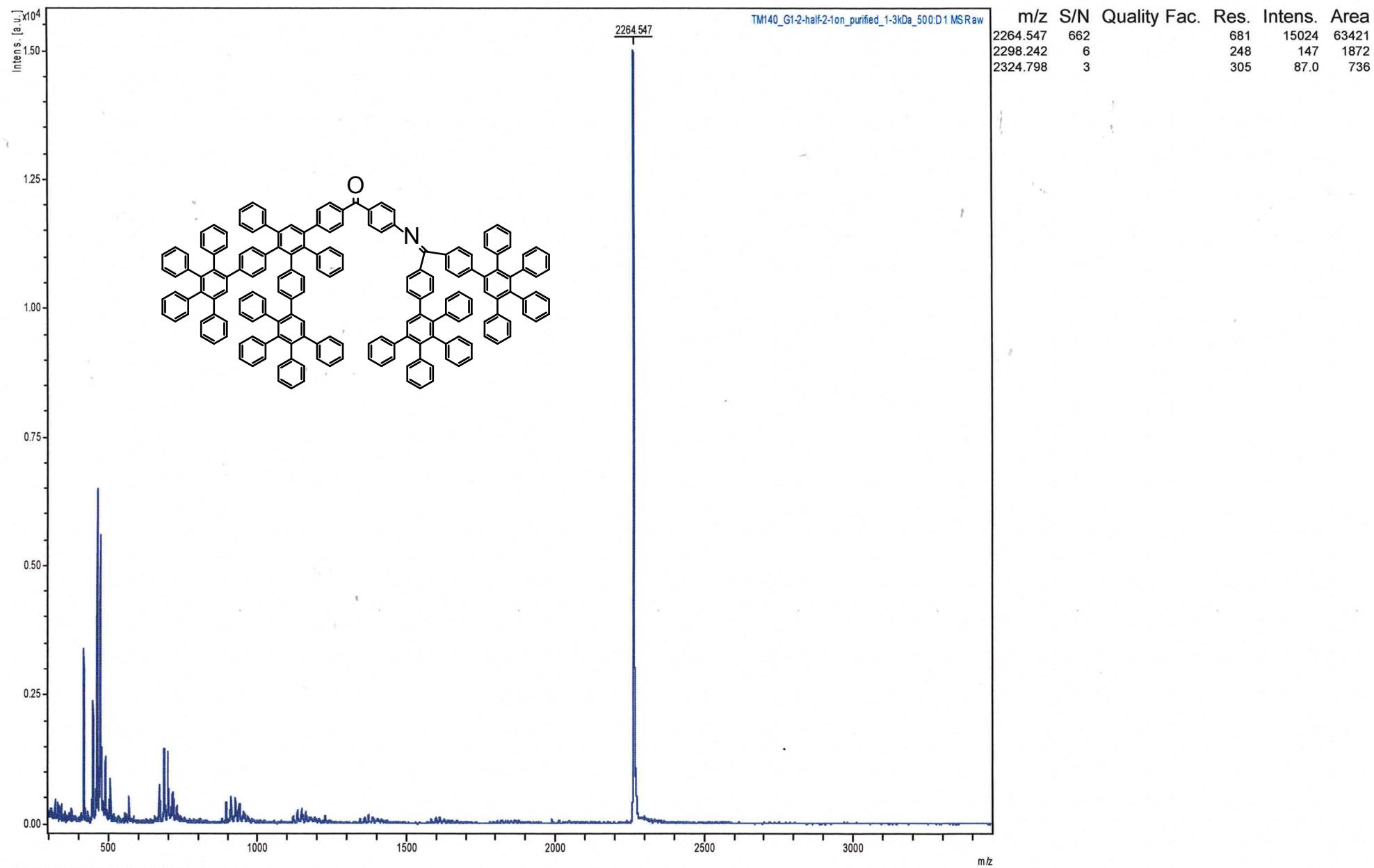


Fig C56. MALDI-TOF-MS spectra of compound 21.

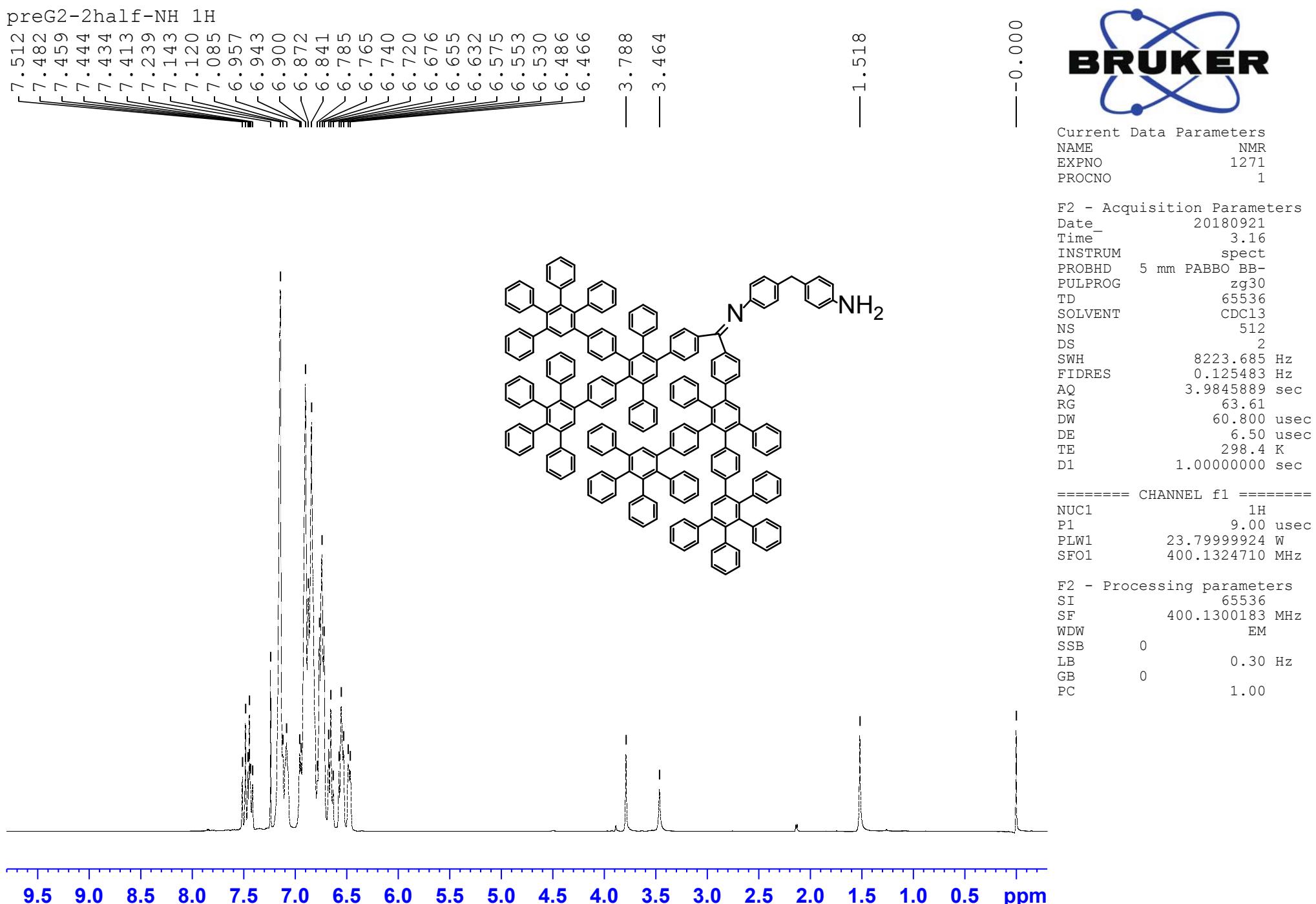


Fig C57 1H-NMR spectra of compound 22.

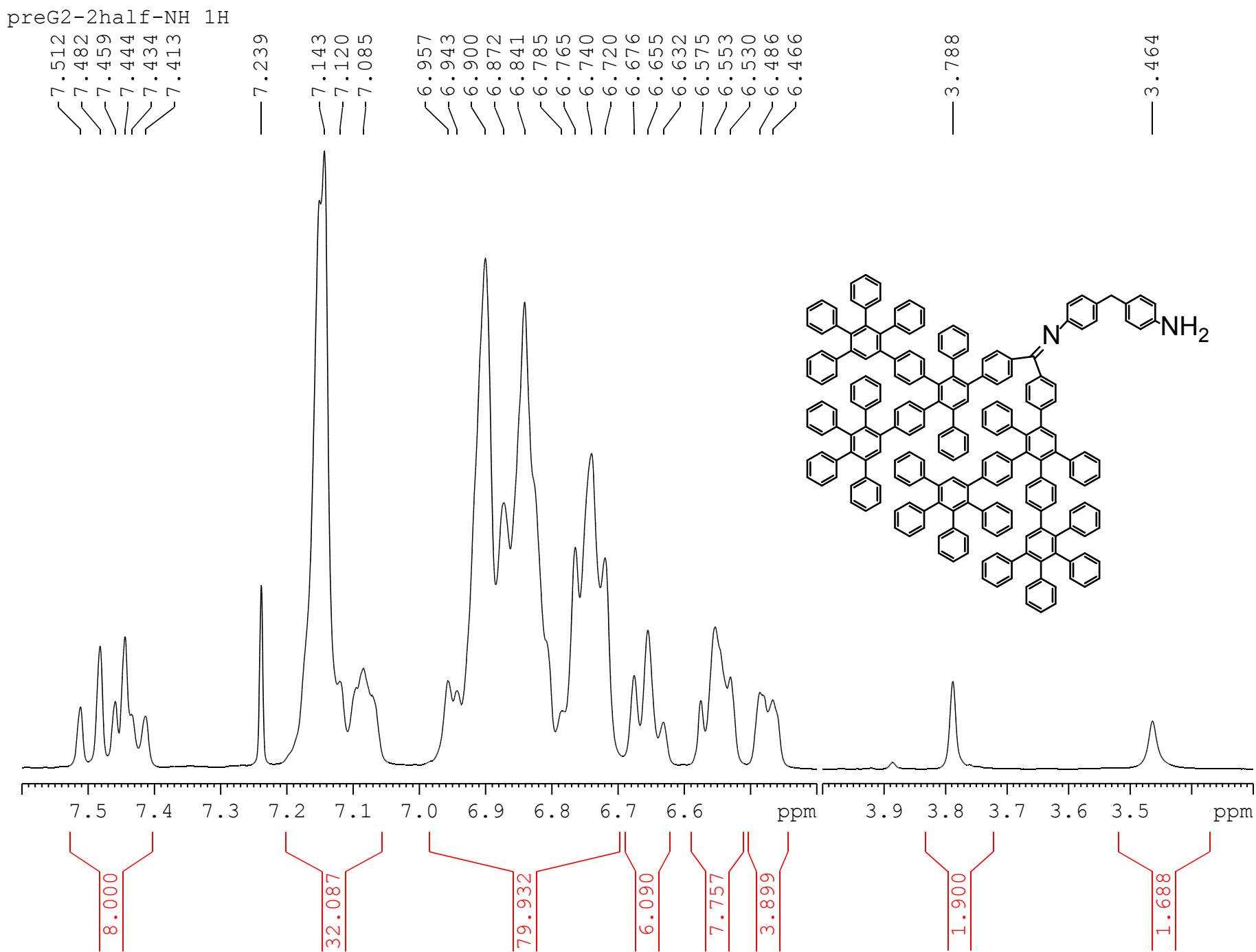


Fig C58. 1H-NMR spectra of compound 22.

preG2-2half-NH 13C

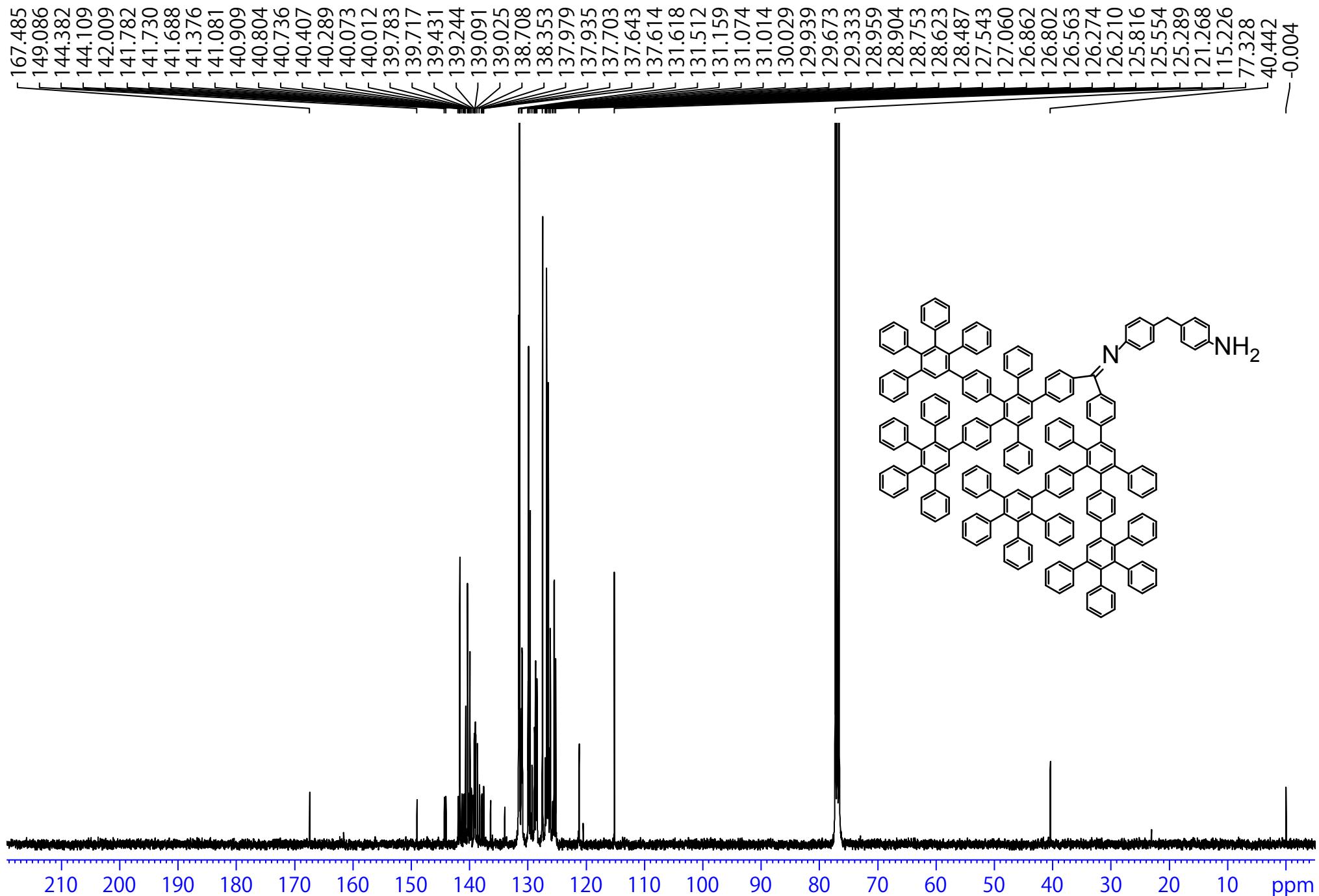
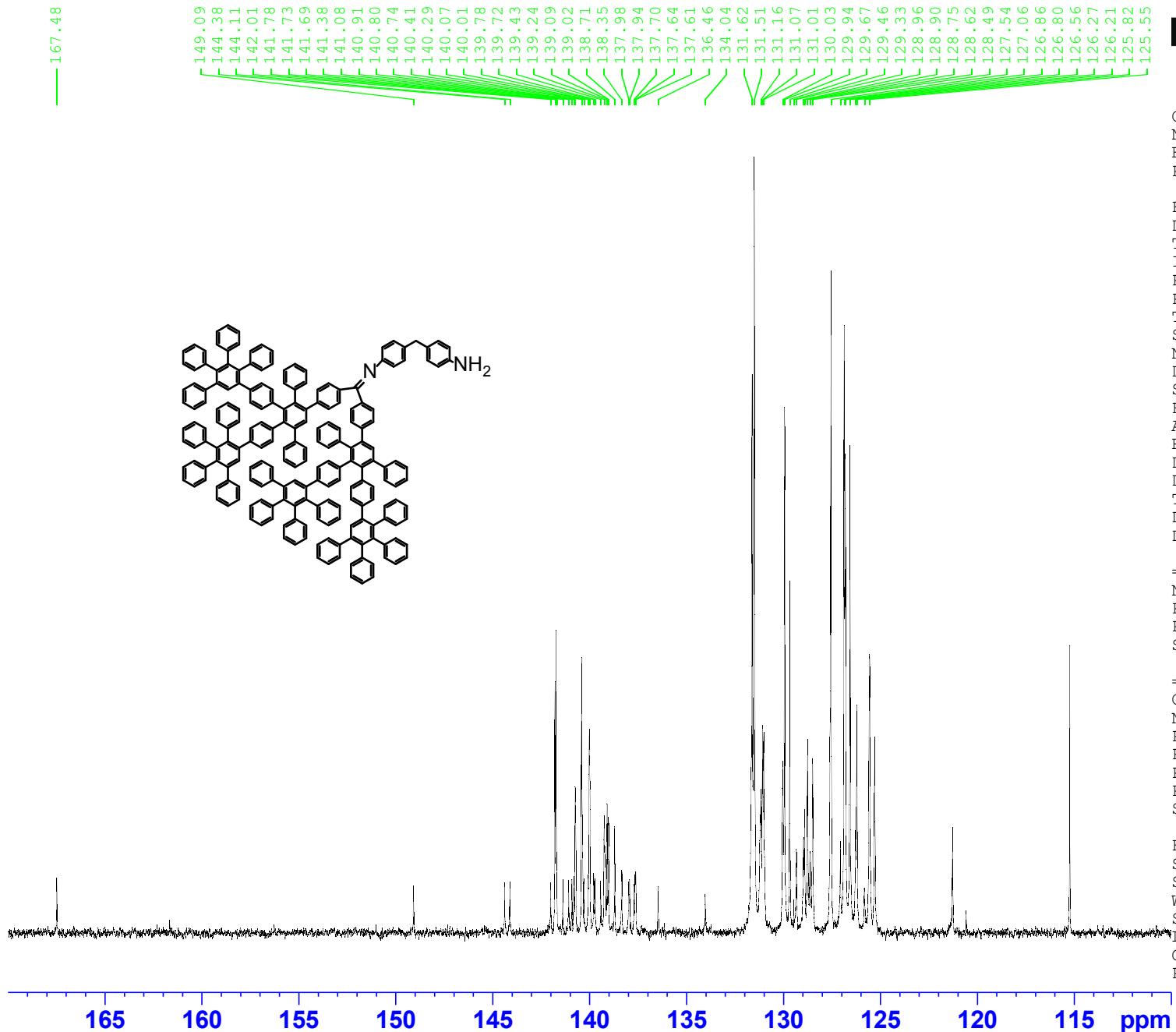


Fig C59. ¹³C-NMR spectra of compound 22.

preG2-2half-NH 13C



Current Data Parameters
NAME examdata
EXPNO 1272
PROCNO 1

F2 - Acquisition Parameters
Date 20180921
Time 17.02
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl₃
NS 14336
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 192.24
DW 20.800 usec
DE 6.50 usec
TE 299.5 K
D1 2.00000000 sec
D11 0.03000000 sec

===== CHANNEL f1 ======

NUC1	¹³ C
P1	9.00 usec
PLW1	113.00000000 W
SFO1	100.6228293 MHz

===== CHANNEL f2 ======

CPDPRG[2	waltz16
NUC2	¹ H
PCPD2	90.00 usec
PLW2	12.00000000 W
PLW12	0.33333001 W
PLW13	0.27000001 W
SFO2	400.1316005 MHz

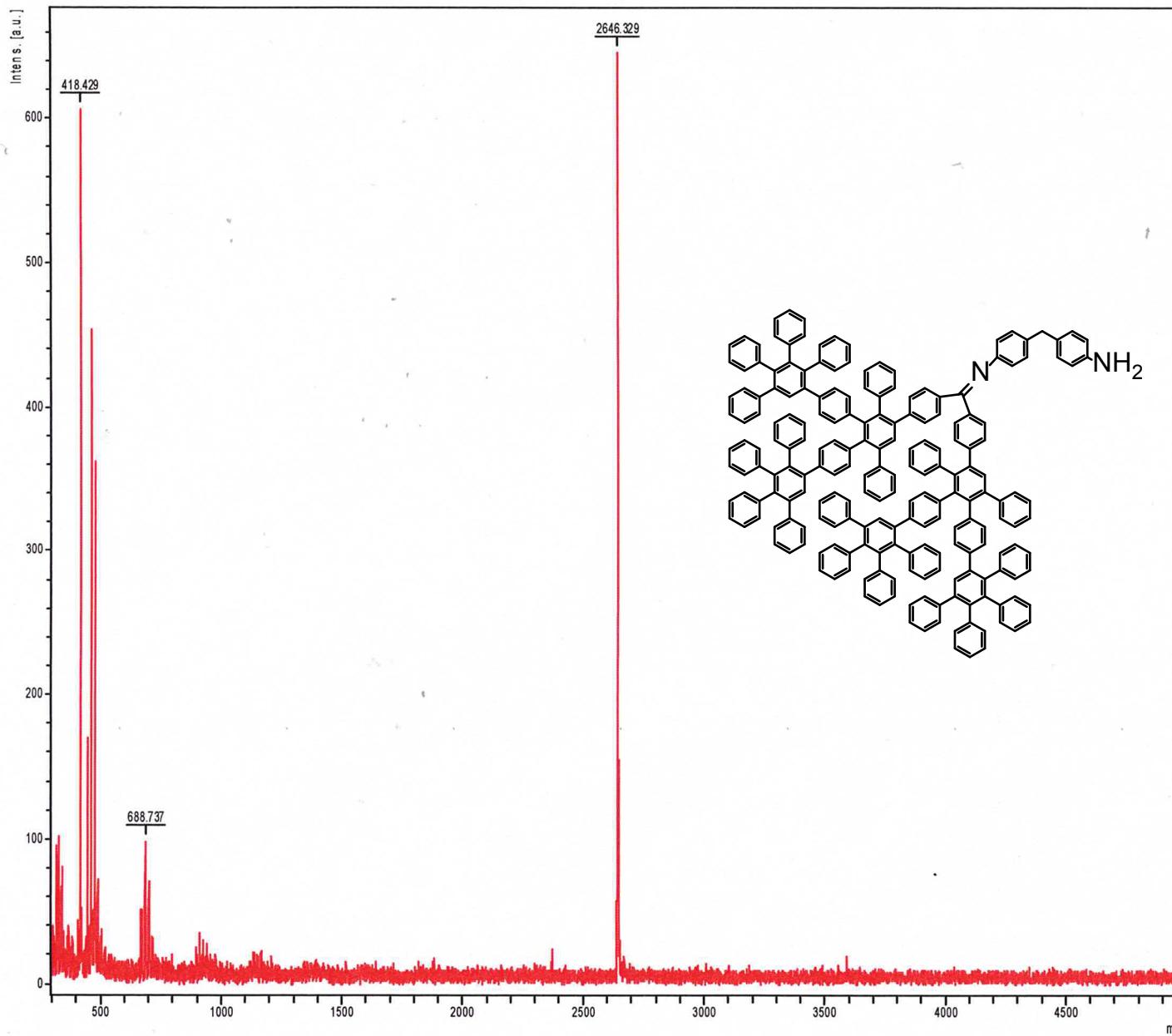
F2 - Processing parameters
SI 32768
SF 100.6127704 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Fig C60. ¹³C-NMR spectra of compound 22.

20180918 \ TM190 - preG2-2half-NH_GPC_F2_1-3kDa_60

[M+H] 2646.13 m/z

(25)



m/z	S/N	Quality Fac.	Res.	Intens.	Area
322.957	5			132	96.0 115
330.044	5			597	102 69.6
339.101	3			776	68.0 45.6
345.237	4			633	81.0 70.8
418.429	39			606	606 709
449.226	11			184	170 339
464.210	30			317	454 828
477.266	24			184	362 923
491.270	4			115	73.0 197
491.270	4			115	73.0 197
673.702	4			272	52.0 142
688.737	8			364	99.0 253
702.799	5			287	71.0 267
2646.329	76			682	646 2637

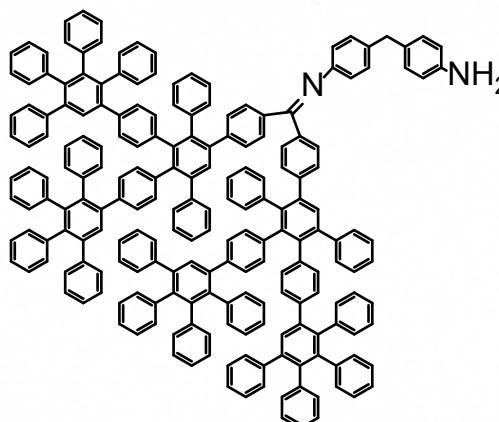


Fig C61. MALDI-TOF-MS spectra of compound 22.

pre4N 1H

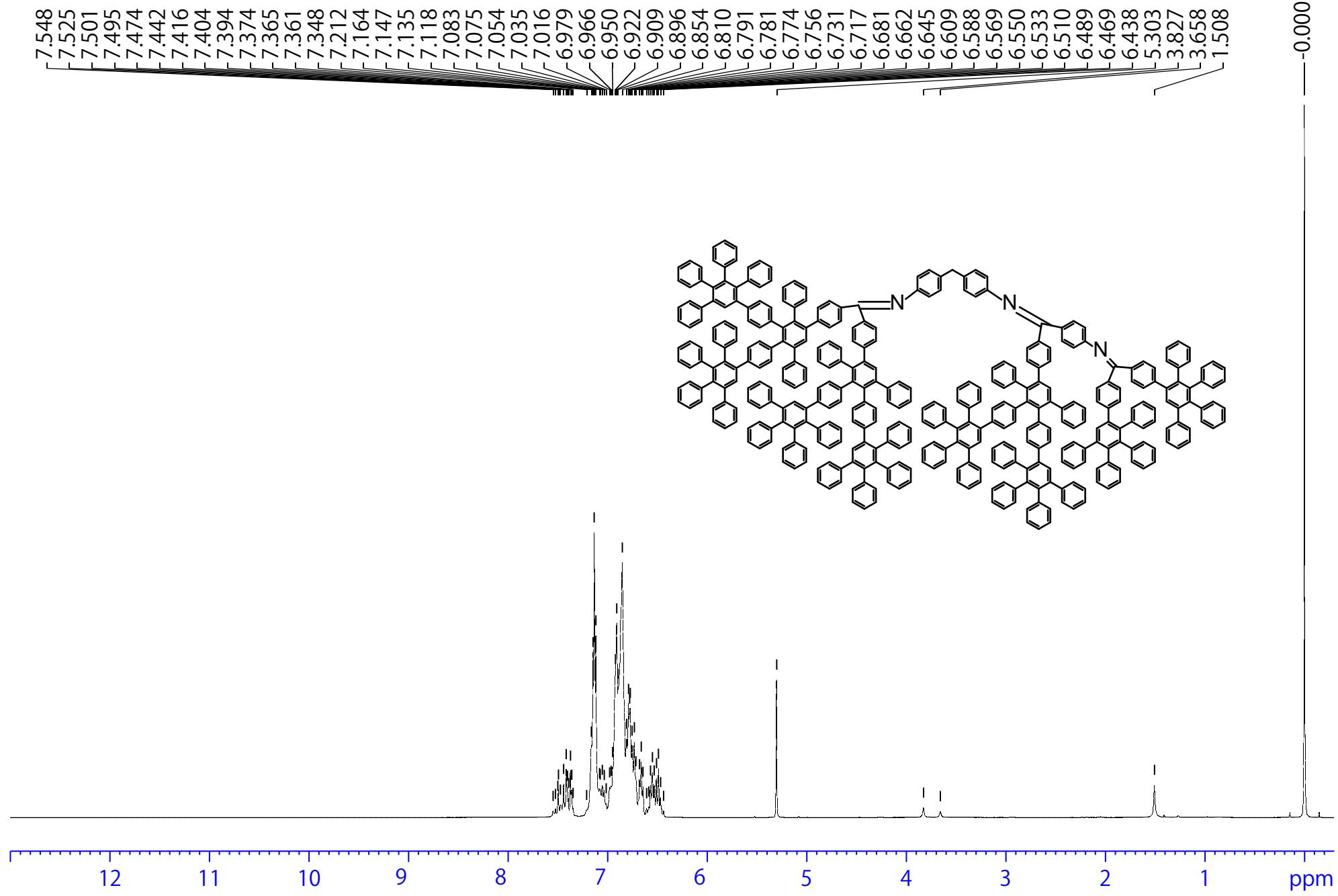
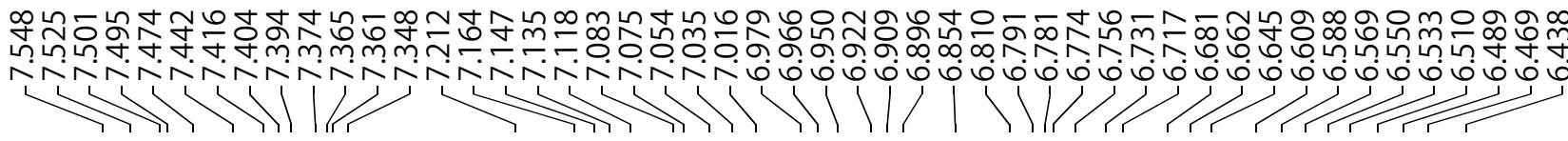


Fig C62. ^1H -NMR spectra of compound 23.

pre4N 1H



— 3.827

— 3.658

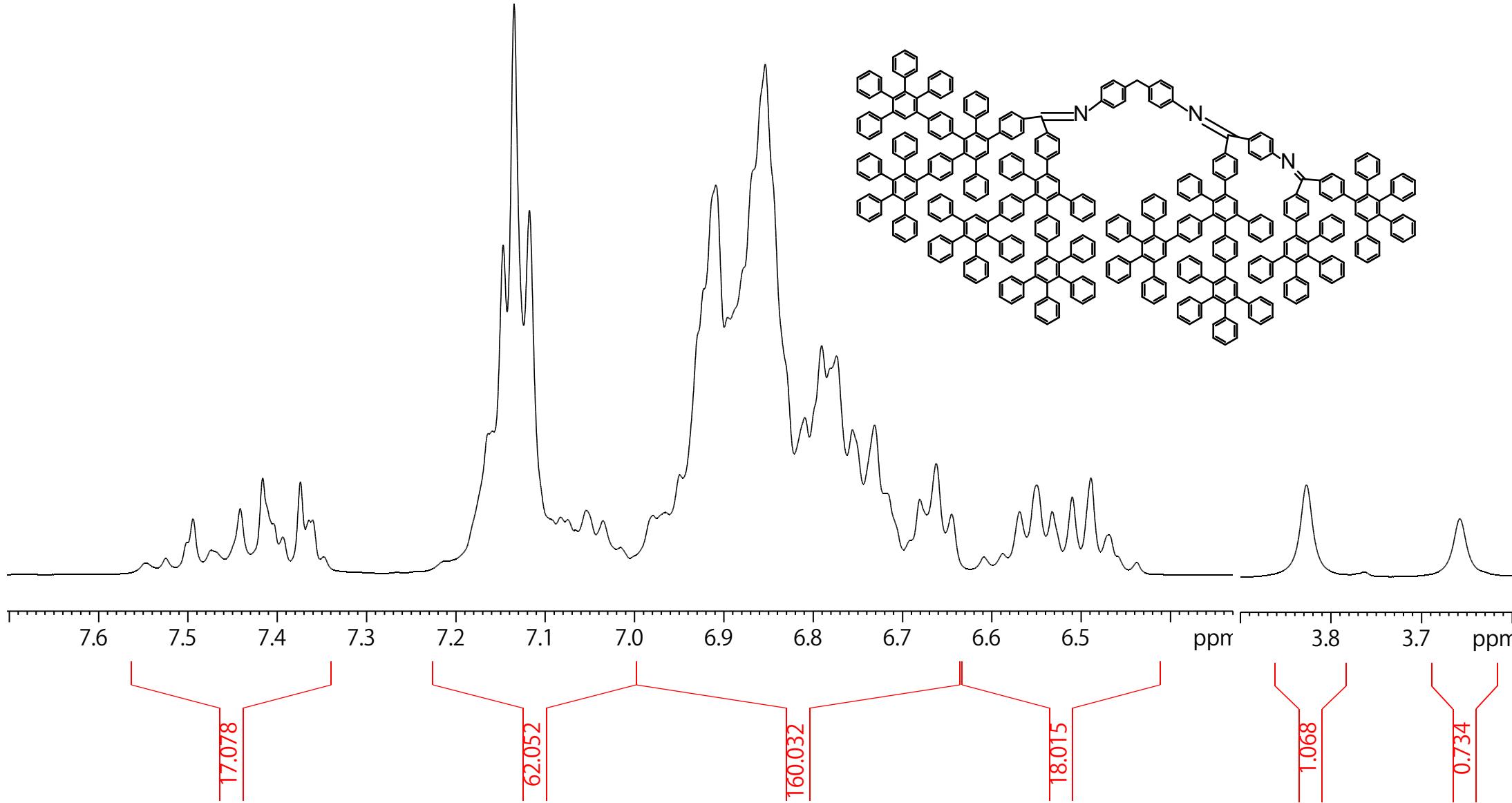


Fig C63. ^1H -NMR spectra of compound 23.

pre4N 13C

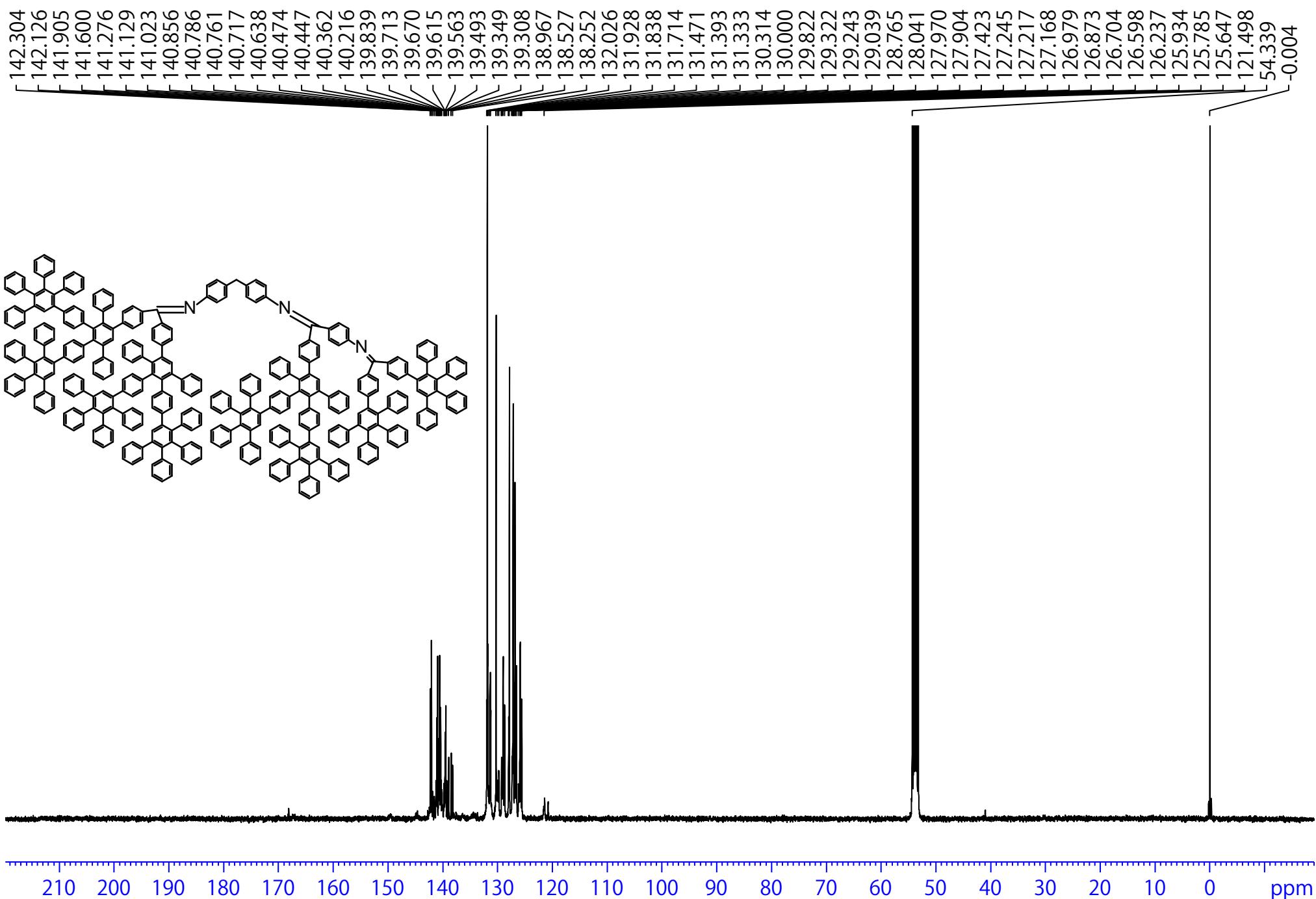


Fig C64. ¹³C-NMR spectra of compound 23.

pre4N 13C

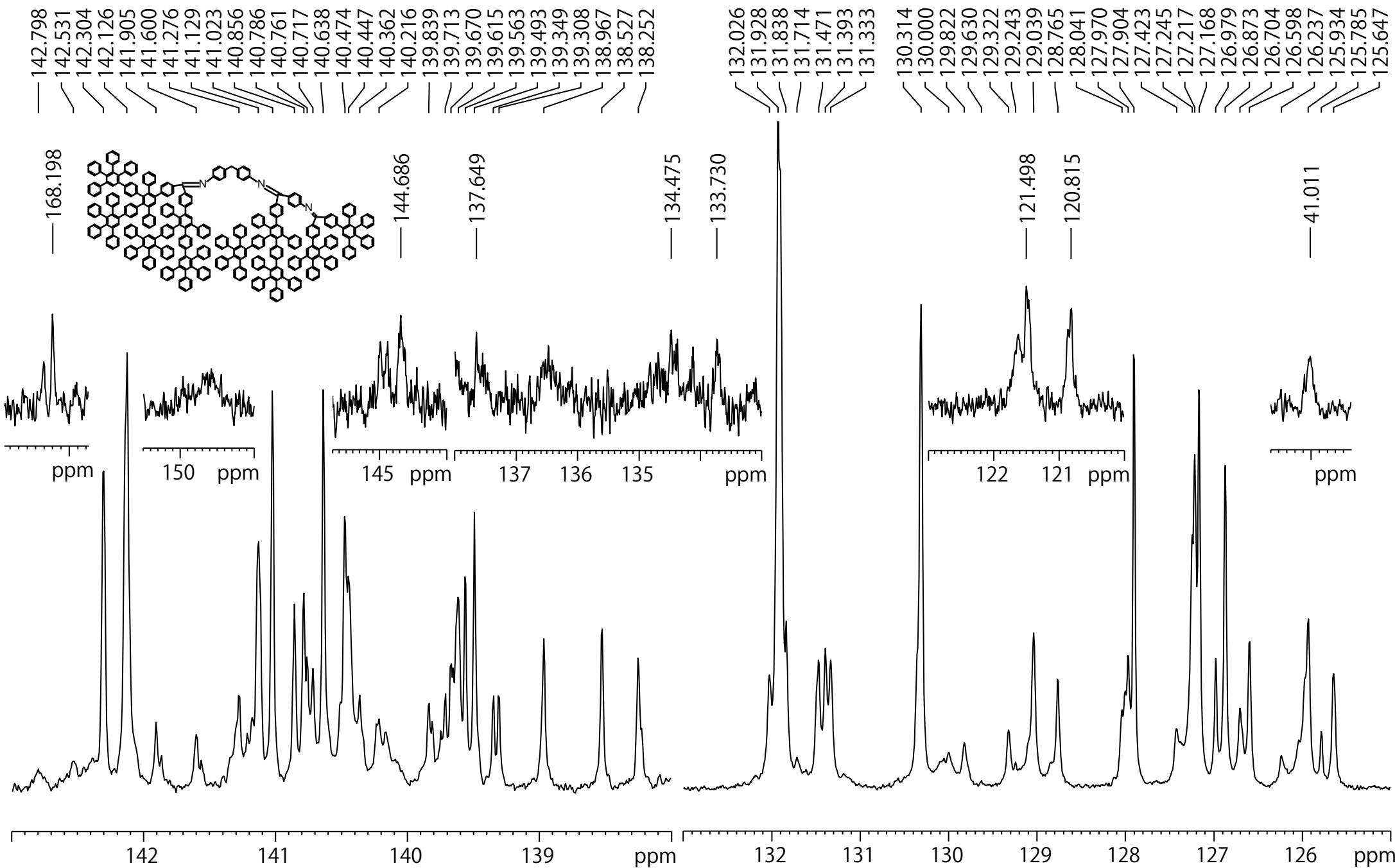


Fig C65. ¹³C-NMR spectra of compound 23.

[M+H] 4892.06

(26)

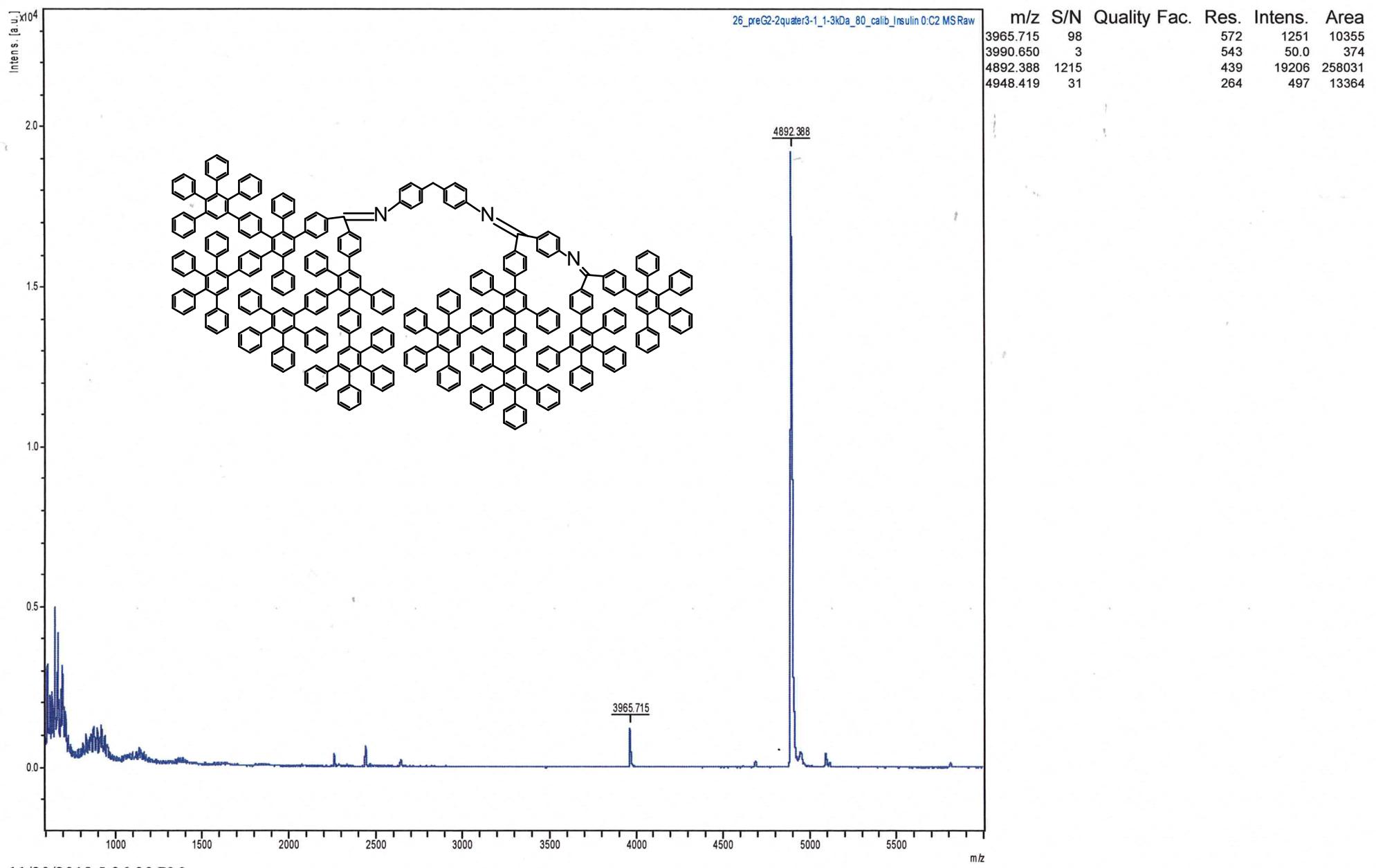
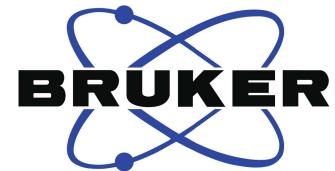
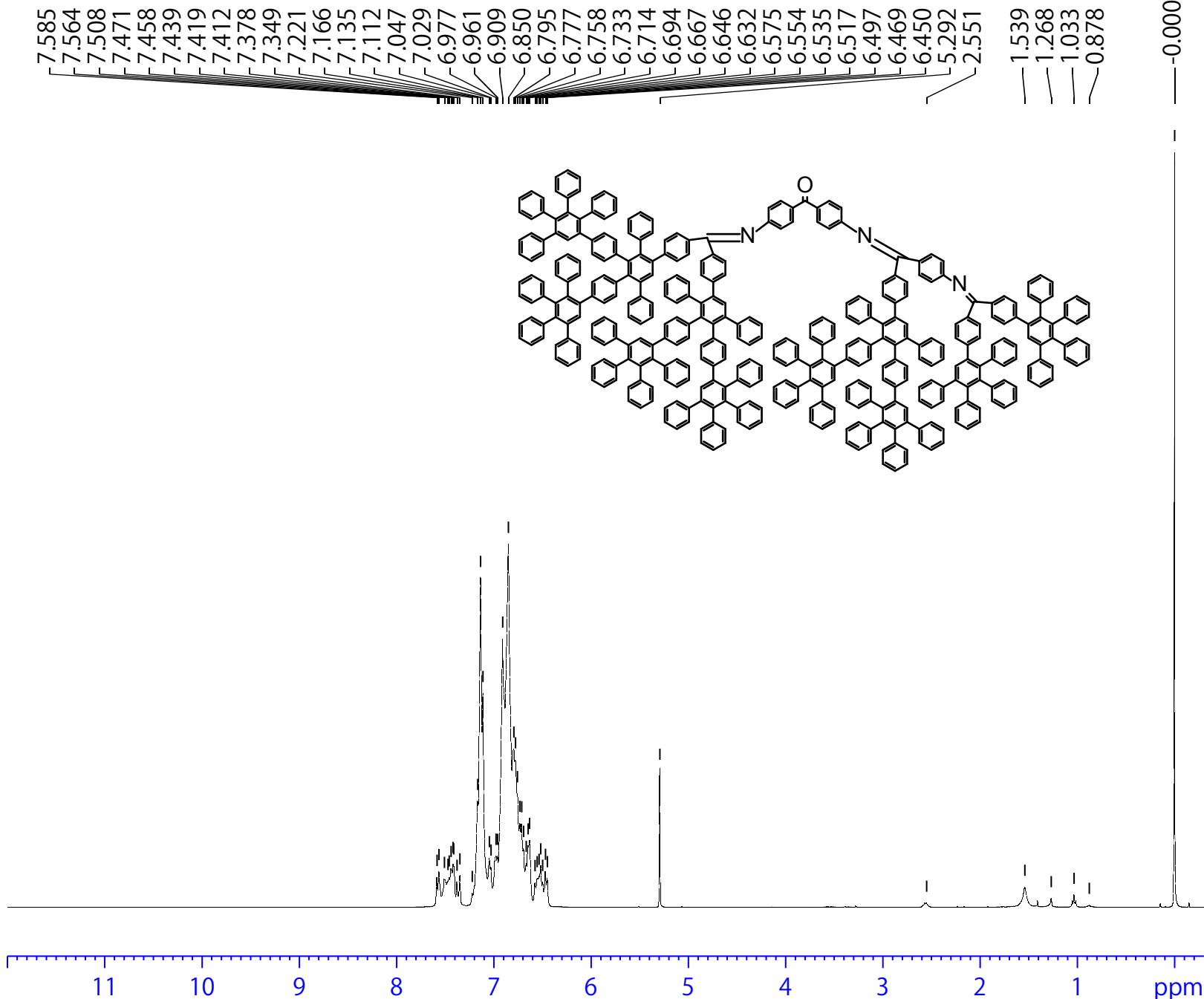


Fig C66. MALDI-TOF-MS spectra of compound 23.

4Non 1H(CD2Cl2)



Current Data Parameters
NAME NMR
EXPNO 1181
PROCNO 1

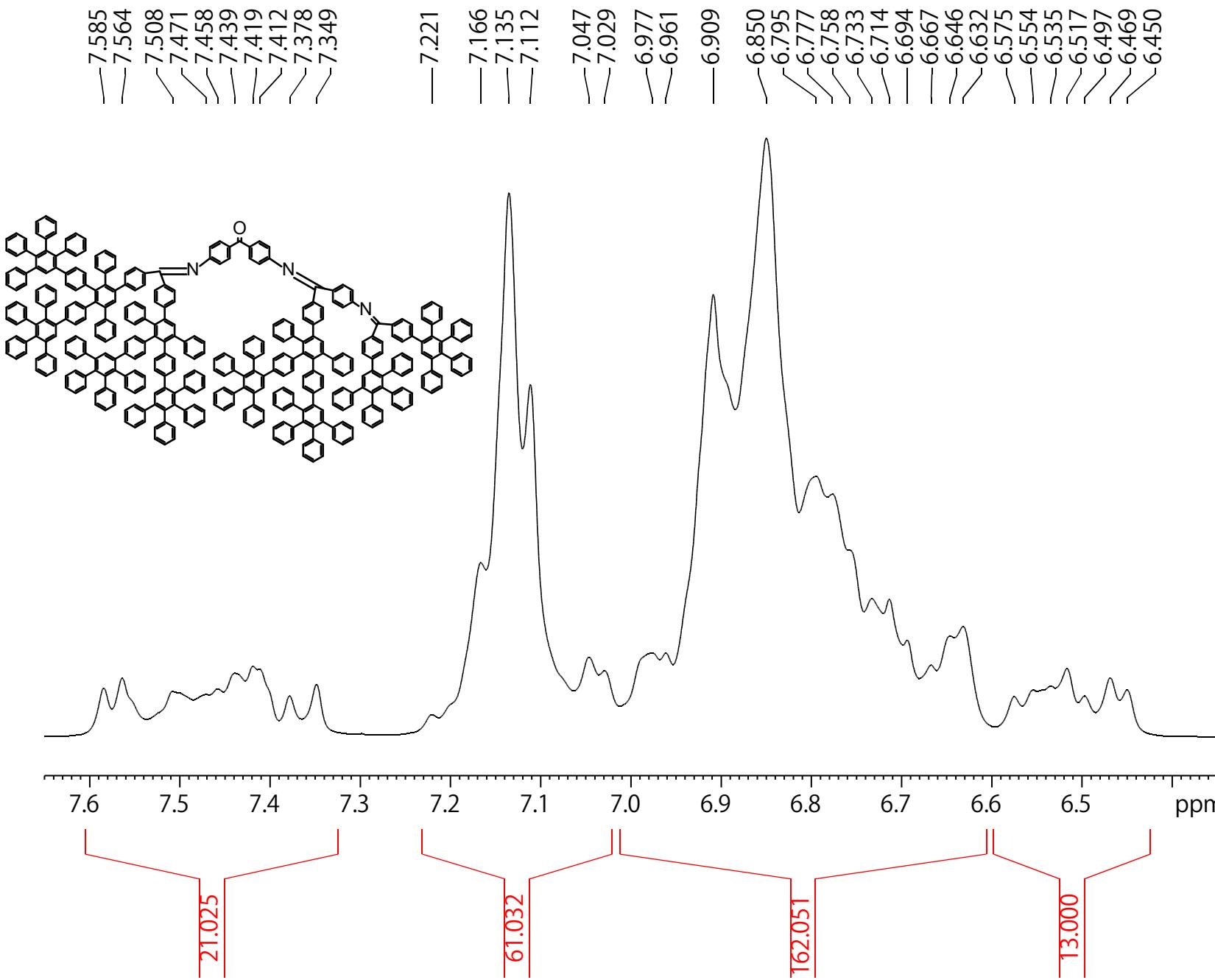
F2 - Acquisition Parameters
Date_ 20180901
Time 0.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CD2Cl2
NS 1024
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9845889 sec
RG 52.03
DW 60.800 usec
DE 6.50 usec
TE 299.0 K
D1 1.0000000 sec

===== CHANNEL f1 ======
NUC1 1H
P1 9.00 usec
PLW1 23.79999924 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300266 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig C67. ^1H -NMR spectra of compound 24.

4Non 1H(CD2Cl2)



Current Data Parameters
NAME NMR
EXPNO 1181
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180901
Time 0.48
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CD2Cl2
NS 1024
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9845889 sec
RG 52.03
DW 60.800 usec
DE 6.50 usec
TE 299.0 K
D1 1.0000000 sec

===== CHANNEL f1 =====
NUC1 1H
P1 9.00 usec
PLW1 23.79999924 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 65536
SF 400.1300266 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Fig C68. ¹H-NMR spectra of compound 24.

examdata 1182 1 C:\Bruker\TopSpin4.1.1

4Non 13C(CD2Cl2)

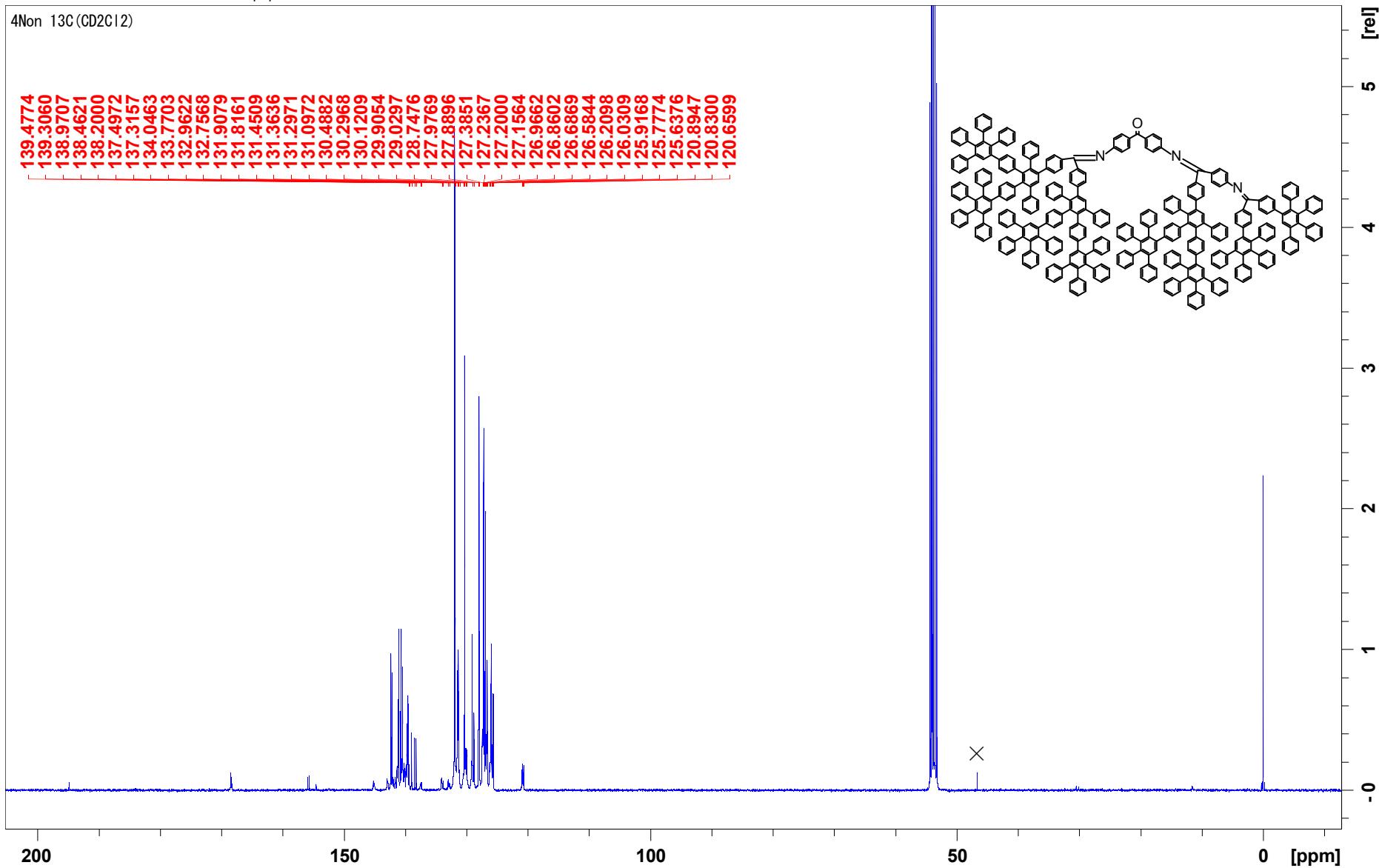


Fig C69. ¹³C-NMR spectra of compound 24.

4Non 13C (CD2Cl2)

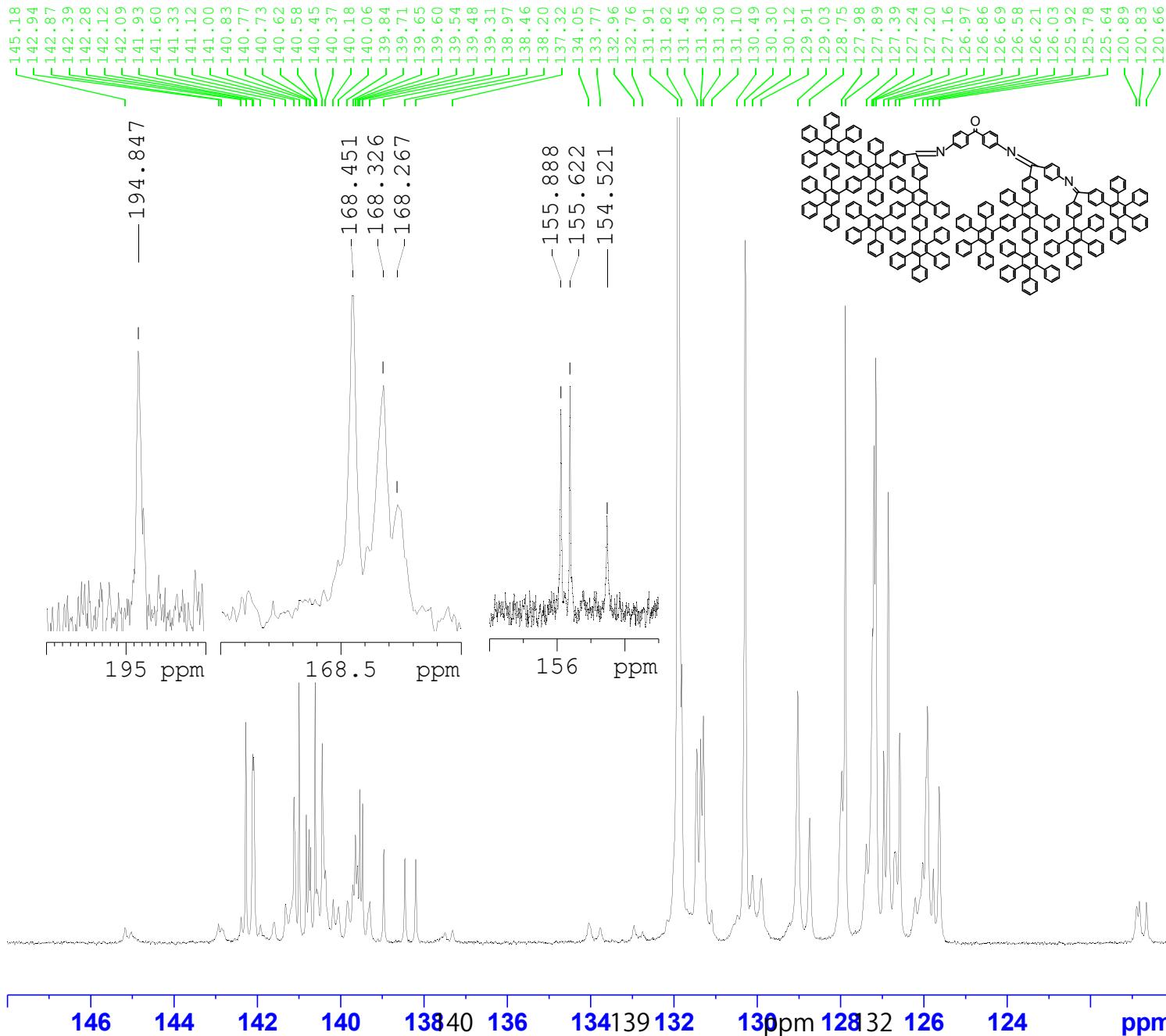
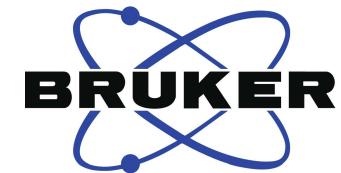


Fig C70. 13C-NMR spectra of compound 24.



Current Data Parameters
NAME examdata
EXPNO 1182
PROCNO 1

F2 - Acquisition Parameters
Date 20180903
Time 11.19
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CD2Cl2
NS 61440
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 192.24
DW 20.800 usec
DE 6.50 usec
TE 300.0 K
D1 2.00000000 sec
D11 0.03000000 sec

===== CHANNEL f1 ======
NUC1 13C
P1 9.00 usec
PLW1 113.00000000 W
SFO1 100.6228293 MHz

===== CHANNEL f2 ======
CPDPRG[2] waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 12.00000000 W
PLW12 0.33333001 W
PLW13 0.27000001 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127298 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

[M+H] 4906.04

27

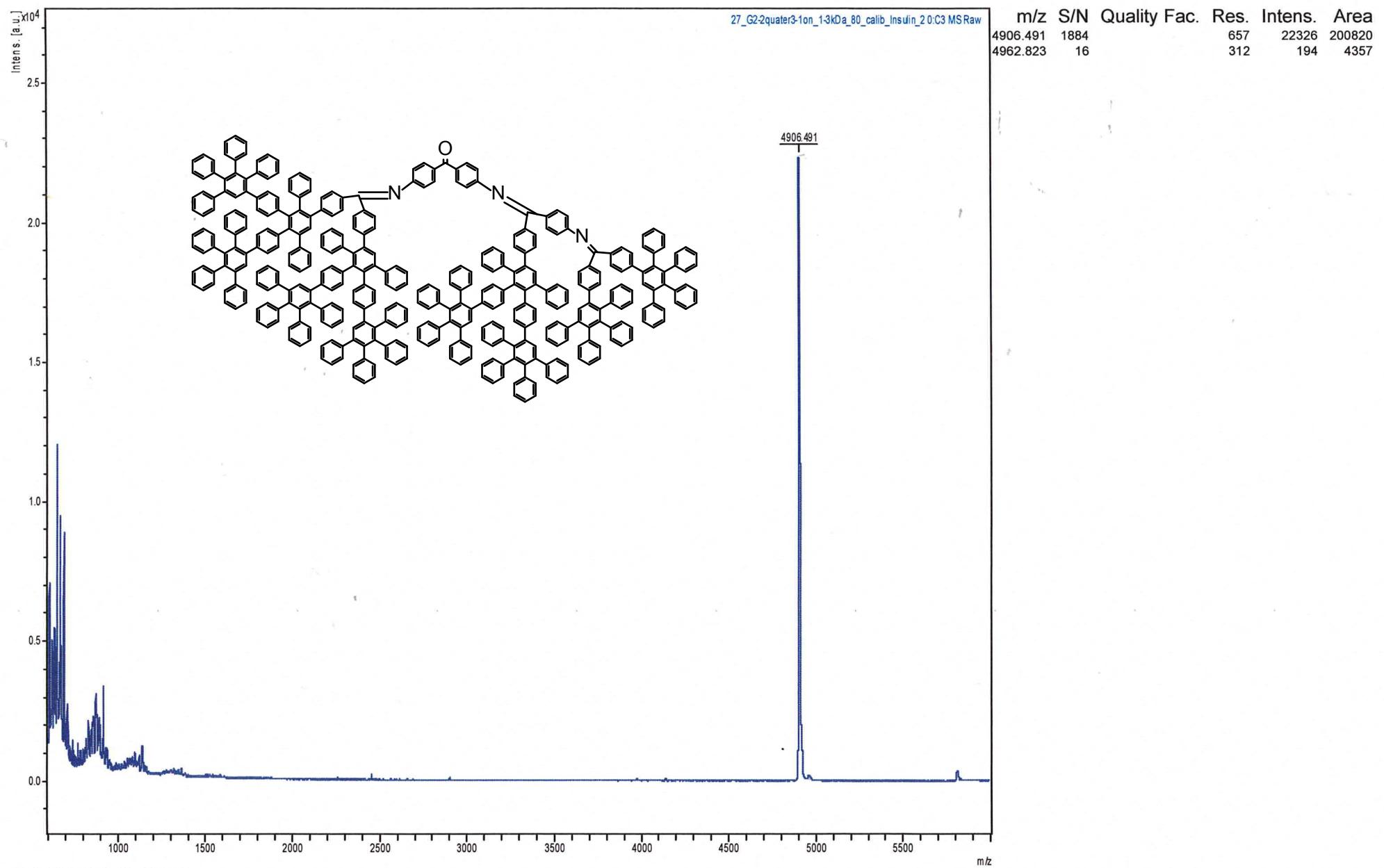
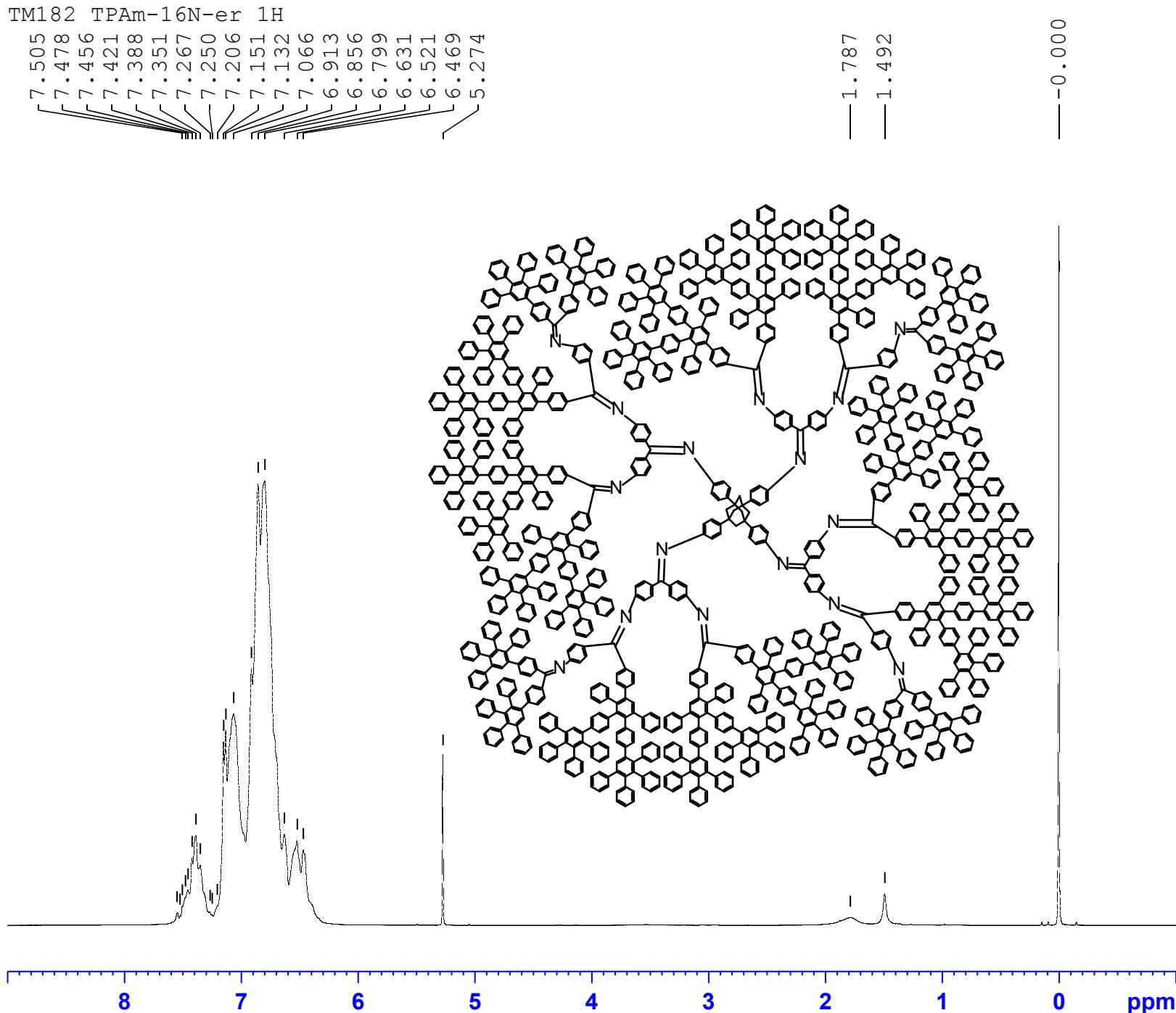


Fig C71. MALDI-TOF-MS spectra of compound 24.



Current Data Parameters
 NAME NMR
 EXPNO 1091
 PROCNO 1

F2 - Acquisition Parameters
 Date 20180429
 Time 2.29
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zg30
 TD 65536
 SOLVENT CD2C12
 NS 1024
 DS 2
 SWH 8223.685 Hz
 FIDRES 0.125483 Hz
 AQ 3.9845889 sec
 RG 31.33
 DW 60.800 usec
 DE 6.50 usec
 TE 300.2 K
 D1 1.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 9.00 usec
 PLW1 23.79999924 W
 SFO1 400.1324710 MHz

F2 - Processing parameters
 SI 65536
 SF 400.1300336 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

Fig C72. ¹H-NMR spectra of PPDPA16.

TM182 TPAm-16N-er 1H

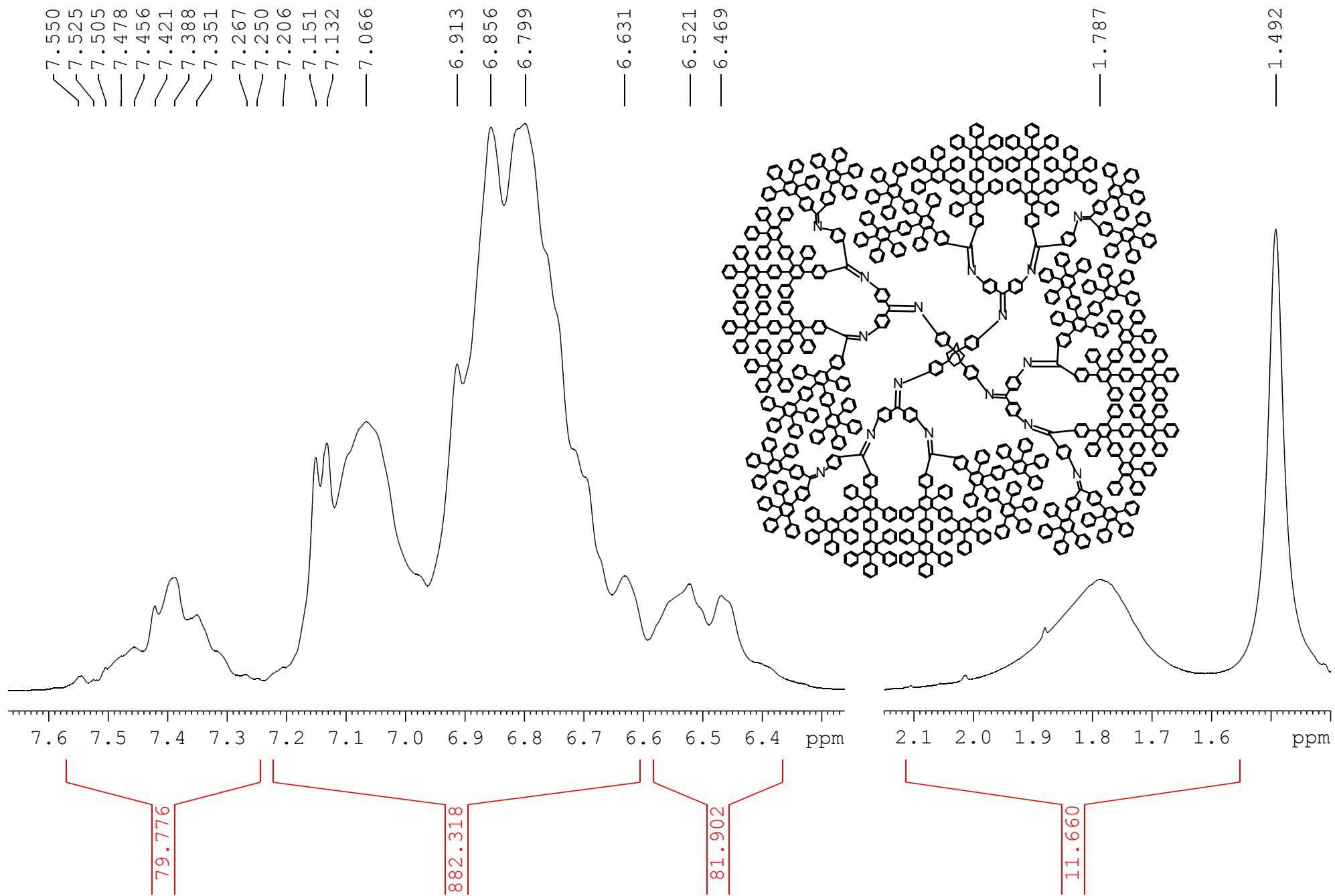
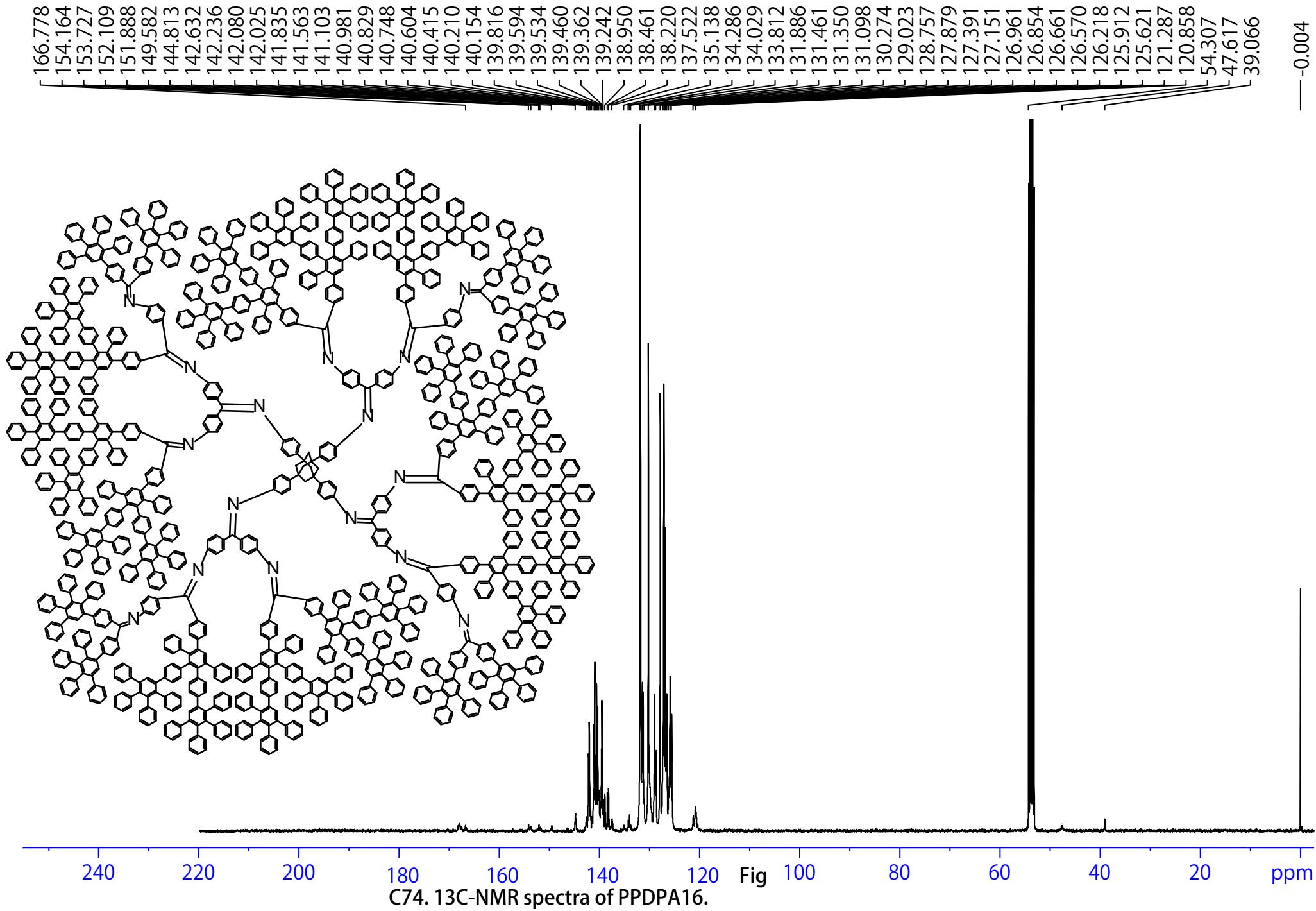


Fig C73. ¹H-NMR spectra of PPDPA16.

TM182 TPAm-16N-er 13C



TM182 TPAm-16N-er 13C

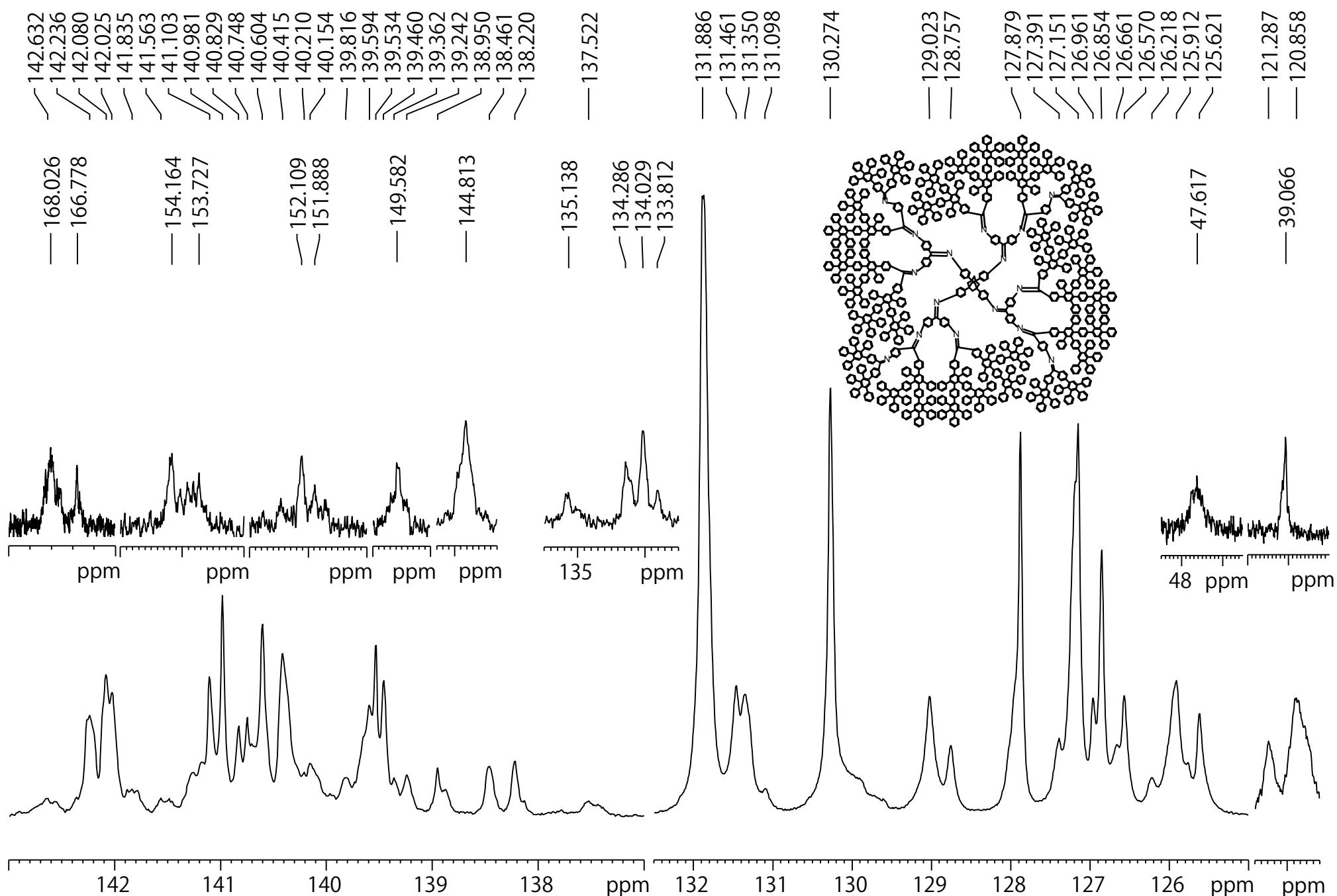
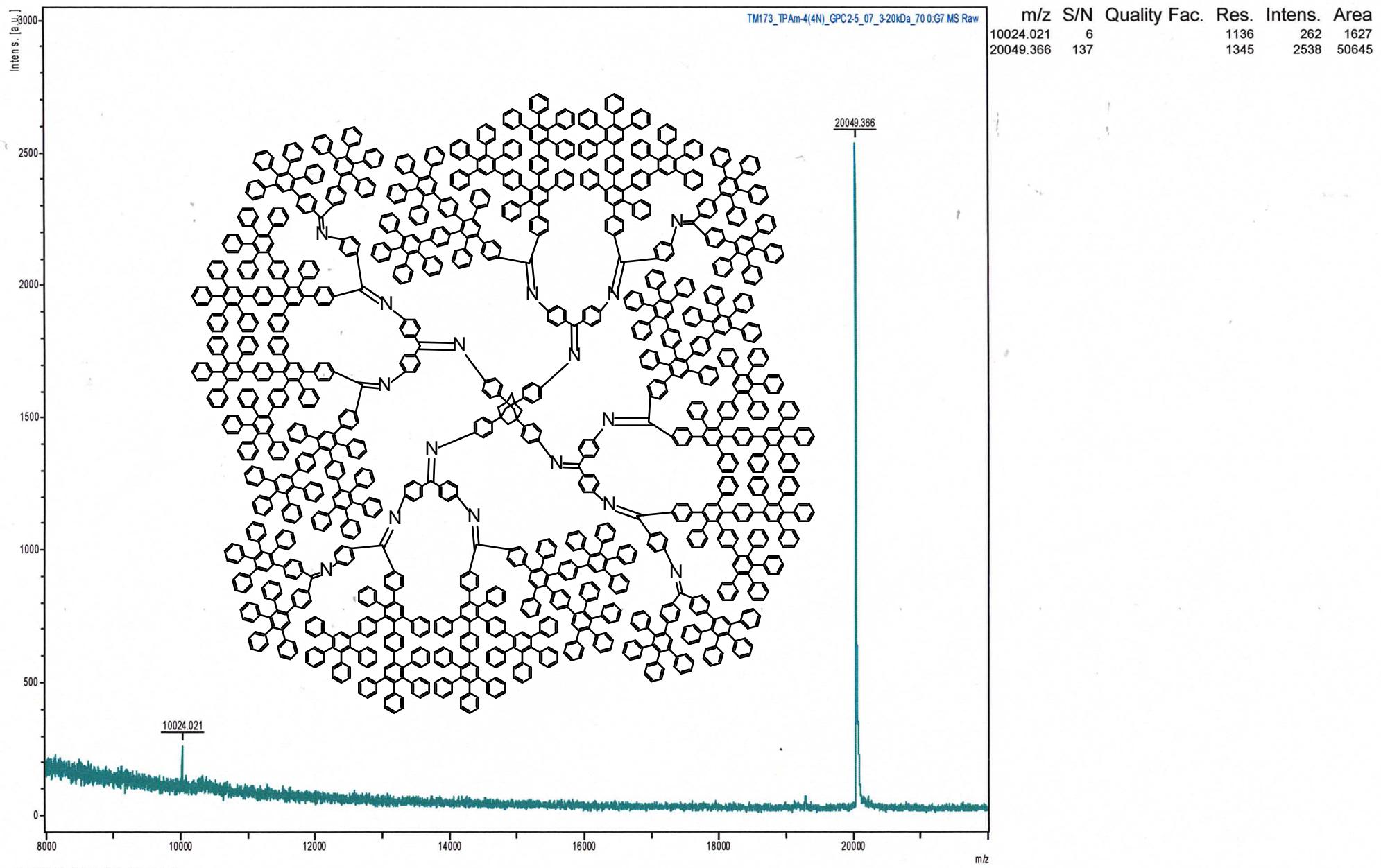


Fig C75. ¹³C-NMR spectra of PPDPA16.

20171117\TPAm-4(4N)_GPC2-5_07

[M+H] 20049.37

(34)



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Fig C76. MALDI-TOF-MS spectra of PPDPA16.