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of Reliable Methods
for the Preparation
of Organic Compounds

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September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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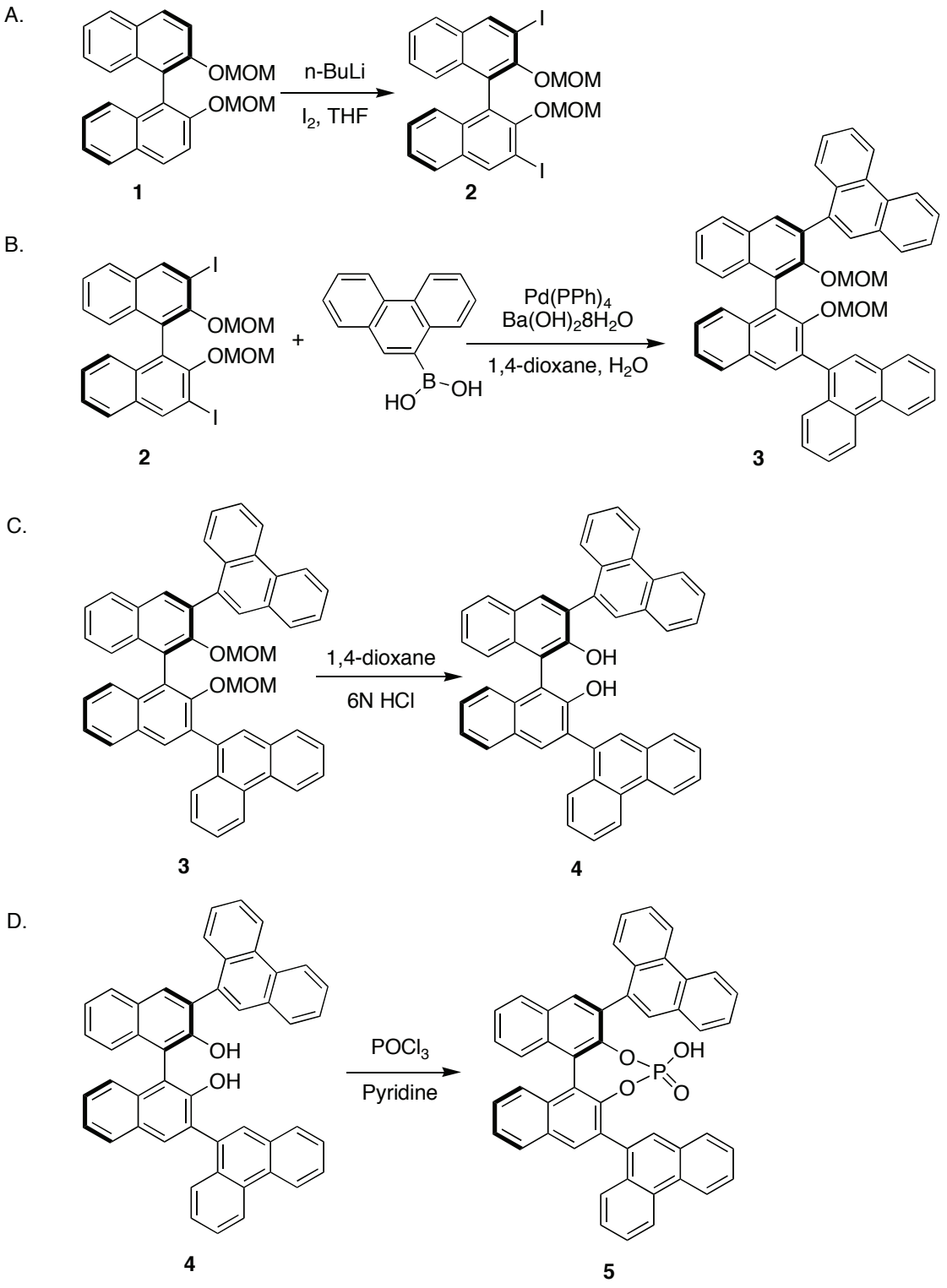
(*R*)-3,3'-BIS(9-PHENANTHRYL)-1,1'-BINAPHTHALENE-2,2'-DIYL HYDROGEN PHOSPHATE



Submitted by Wenhao Hu,*[1a] Jing Zhou,[1a] Xinfang Xu,[1a] Weijun Liu,[1b] and Liuzhu Gong.*[1b]

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1. Procedure

A. (R)-2,2'-Bis(methoxymethoxy)-3,3'-diiodo-1,1'- binaphthalene (**2**). An oven-dried, 500-mL, three-necked, round-bottomed flask is equipped with a thermometer (–50 to 50 °C) with adapter, a rubber septum, a 60-mL pressure-equalizing addition funnel fitted with a rubber septum, and a Teflon-coated magnetic stirring bar (37 mm x 16 mm). The flask is flushed with argon and charged with 3.0 g (8.0 mmol, 1 equiv) of (*R*)-(+)-2,2'-bis(methoxymethoxy)-1,1'-binaphthyl (Note 1) and 70 mL of dry tetrahydrofuran (THF) (Note 2). The resulting solution is cooled to 2–3 °C in an ice bath. Butyllithium solution (10 mL, 2.5 M, 25 mmol, 3 equiv) (Note 3) is added to the flask with a syringe pump over 30 min. After addition, the ice bath is removed, the resulting brown suspension is stirred at room temperature for 3 h. The suspension is cooled in the ice bath. A solution of 9.0 g (35 mmol, 4.4 equiv) of iodine (Note 4) in 60 mL of dry THF is charged to the addition funnel, and the solution is added to the flask over 2 min. Another 20 mL of dry THF is used to wash the addition funnel, which is also added to the flask over 1 min. After addition, the ice bath is removed. The solution is stirred at room temperature for 20 h. Progress of the reaction is monitored by TLC (Note 5). After the reaction is completed, 100 mL of saturated aqueous ammonium chloride is added (Note 6), followed with 50 g of sodium thiosulfate (Note 7). The resulting mixture is stirred vigorously until the dark color of the mixture changes into light brown, at which time the solution is transferred to a 1-L separatory funnel and extracted with ethyl acetate (2 x 300 mL) (Note 8). The combined organic solution is washed with saturated brine (200 mL) (Note 9) and dried over magnesium sulfate (40 g) (Note 10). After filtration, the solution is concentrated under reduced pressure (40 mmHg) on a rotary evaporator at 40 °C, and the residue is purified by flash chromatography on silica gel (Note 11) to give 2.0 g of **2** as a white solid (40% yield) (Note 12). The purity of **2** is determined to be 99% by HPLC (Note 13).

B. (R)-2,2'-Bis(methoxymethoxy)-3,3'-bis(9-phenanthryl)-1,1'-binaphthalene (**3**). An oven-dried, 100-mL, two-necked, round-bottomed flask is equipped with a thermometer (10 – 260 °C) with adapter, a condenser fitted with a rubber septum, and a Teflon-coated magnetic stirring bar (20 mm x 10 mm). The flask is flushed with argon and charged with (*R*)-2,2'-bis(methoxymethoxy)-3,3'-diiodo-1,1'-binaphthalene (**2**), (2.0 g, 3.2 mmol, 1.0 equiv), 9-phenanthreneboronic acid (1.42 g, 6.4 mmol, 2.0 equiv) (Note 14), barium hydroxide octahydrate (2.52 g, 8.0 mmol,

2.5 equiv) (Note 15), and *tetrakis*(triphenylphosphine)palladium(0) (0.37 g, 0.32 mmol, 10 mol%) (Note 16). Then the flask is evacuated and backfilled with argon (this sequence is repeated three times). 1,4-Dioxane (24 mL) and water (6.7 mL) are added by syringe (Notes 17 and 18). The reaction mixture is heated with an oil bath to 75-80 °C for 24 h, and the reaction progress is monitored by TLC (Note 19). After the mixture is cooled to room temperature, it is concentrated under reduced pressure (40 mmHg) on a rotary evaporator at 40 °C. The residue is extracted with dichloromethane (2 x 50 mL), and the combined organic layers are washed with 1N aqueous HCl (2 x 20 mL) and saturated brine (40 mL) and then dried over magnesium sulfate (20 g). After filtration, the residue is purified by flash chromatography on silica gel (Note 20) to give 2.1 g (91 %) of **3** as a light yellow solid (Note 21). The purity of **3** is determined to be 99% by HPLC (Note 22).

C. (R)-3,3'-Bis(9-phenanthryl)-1,1'-binaphthalene-2,2'-diol (**4**). A 100-mL, two-necked, round-bottomed flask is equipped with a thermometer (10 – 260 °C) with adapter, a water-cooled condenser, and a Teflon-coated magnetic stirring bar (20 mm x 10 mm). The flask is charged with *(R)-2,2'-bis(methoxy methoxy)-3,3'-bis(9-phenanthryl)-1,1'-binaphthalene* (**3**) (2.0 g, 2.7 mmol, 1 equiv), 1,4-dioxane (27 mL), and 6 N aqueous hydrochloric acid (3.7 mL). The reaction mixture is heated with an oil bath to 98–100 °C for 12 h, and the reaction progress is monitored by TLC (Note 23). After all of **3** is consumed, the solution is cooled to room temperature and carefully neutralized with saturated sodium bicarbonate solution (45 mL). The mixture is transferred to a 250-mL separatory funnel and extracted with dichloromethane (3 x 30 mL). The combined organic solution is concentrated under reduced pressure (40 mmHg) on a rotary evaporator at 40 °C. The residue is dissolved in dichloromethane (150 mL), and the resulting solution is washed with saturated brine (50 mL) and dried over magnesium sulfate (15 g). After filtration, the solution is concentrated under reduced pressure (40 mmHg) on a rotary evaporator at 40 °C. The residue is purified by flash chromatography on silica gel (Note 24) to give 1.74 g (99 %), of **4** as a light yellow solid (Notes 25 and 26).

D. *(R)-3,3'-Bis(9-phenanthryl)-1,1'-binaphthalene-2,2'-diyl hydrogen phosphate* (**5**). A 250-mL round-bottomed flask is equipped with a rubber septum and a Teflon-coated magnetic stirring bar (20 mm x 10 mm) and filled with argon. To the flask is charged with **4** (1.65 g, 2.58 mmol, 1 equiv). The reaction flask is placed in a room temperature water bath, and pyridine (15 mL) (Note 27) is added into the flask *via* syringe followed by

slow addition of $POCl_3$ (0.54 mL, 5.80 mmol, 2.25 equiv) (Note 28) over 15 min. After completion of the addition, the mixture is stirred for 12 h at 60 °C, and the reaction progress is monitored by TLC (Note 29). After the mixture is cooled to room temperature, H_2O (20 mL) is added, and the resulting mixture is stirred for 5 h. After that, 6 N HCl (80 mL) is added to the mixture in a water-bath, and the mixture is stirred for 30 min. The mixture is extracted with CH_2Cl_2 (2 x 500 mL). The combined organic layers are washed with 6 N HCl (100 mL), dried over sodium sulfate and solvent is evaporated to give crude product. Purification of the crude product by flash chromatography on silica gel (Note 30) affords the BINOL phosphoric acid as a white solid. The phosphoric acid can be further recrystallized in hot solvents of CH_2Cl_2 (6 mL) and petrol ether (80 mL) to give white crystals (1.65 g, 91%) (Notes 31 and 32). The product purity is >98% by ^{1}H NMR.

2. Notes

1. (*R*)-(+)-2,2'-Bis(methoxymethoxy)-1,1'-binaphthyl was purchased from Strem Chemicals, Inc. with 98% purity.

2. Tetrahydrofuran (THF) was purchased from Aldrich Chemical Company, Inc. and was distilled under argon (atmospheric pressure) from sodium benzophenone ketyl.

3. Butyllithium solution (2.5M in hexanes) was purchased from Aldrich Chemical Company, Inc. and was titrated with 1.0 M of *sec*-butanol before use.

4. Iodine was purchased from Aldrich Chemical Company, Inc. and used as received.

5. Thin layer chromatography was performed on SCRC silica gel GF 254 plates eluting with 15% ethyl acetate/petroleum ether, and the observed R_f is 0.78 for **2** and 0.62 for the mono-substituted byproduct.

6. Ammonium chloride was purchased from Aldrich Chemical Company, Inc.

7. Sodium thiosulfate was purchased from Aldrich Chemical Company, Inc.

8. Ethyl acetate was purchased from Fisher Scientific and used without further purification.

9. Sodium chloride was purchased from Aldrich Chemical Company, Inc.

10. Anhydrous magnesium sulfate was purchased from EMD Chemical Company, Inc.

11. Silica gel 60 (230 – 400 mesh) was purchased from Sorbent Technologies. Flash chromatography was performed using 170 g of silica gel 60 (6.5 x 11 cm) and 50-mL fractions were collected. The column was eluted with petroleum ether (150 mL) and then petroleum ether/ethyl acetate: 100:1 (400 mL) and 50:1 (4000 mL). Compound **2** was obtained in fractions 58-86, which were combined and concentrated under reduced pressure (40 mmHg) on a rotary evaporator at 40 °C. The resulting solid was dried at 20 mmHg for 12 h.

12. The physical properties of **2** are as follows: $[\alpha]^{20}_{D}$ –39.4 (*c* 1.22, $CHCl_3$); IR (neat): 1559, 1490, 1462, 1446, 1416, 1382, 1345, 1232, 1199, 1157, 1084, 993, 953, 903, 747, 729 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 2.61 (s, 6 H), 4.72 (d, *J* = 5.6 Hz, 2 H), 4.83 (d, *J* = 6.0 Hz, 2 H), 7.20 (d, *J* = 8.4 Hz, 2 H), 7.31 (dt, *J* = 1.2, 7.2 Hz, 2 H), 7.44 (dt, *J* = 1.2, 7.2 Hz, 2 H), 7.79 (d, *J* = 8.4 Hz, 2 H), 8.57 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 56.6, 92.7, 99.6, 126.0, 126.4, 126.7, 126.9, 127.3, 132.4, 134.0, 140.2, 152.3; HR-MS (+ESI): calcd. for $C_{24}H_{20}I_2O_4Na$ ($[M+Na^+]$): 648.9354, found: 648.9341; Anal. calcd. for $C_{24}H_{20}I_2O_4$: C, 46.03; H, 3.22. Found: C, 46.26; H, 3.10.

13. HPLC conditions: Dynamax-60A column, 0.3% isopropanol in hexanes, 1.0 mL/min, UV (226 nm) detector. The t_R of the product is 5.22 min.

14. 9-Phenanthreneboronic acid was purchased from Aldrich Chemical Company, Inc.

15. Barium hydroxide octahydrate was purchased from Fisher Scientific.

16. *Tetrakis*(triphenylphosphine)palladium(0) purchased from Aldrich Chemical Company, Inc.

17. 1,4-Dioxane was purchased from Mallinckrodt Baker, Inc. and used without further purification.

18. 1,4-Dioxane and water were all degassed with the following procedure before use: A 100-mL round-bottomed flask fitted with a adapter was charged with 50 mL of solvent. The flask was placed into a sonicator and the adapter was connected to a filtration pump. It was sonicated for 30 min under reduced pressure (approx 100 mmHg). After that, the solvent was bubbled with argon for 10 min.

19. Thin layer chromatography is eluted with 9% ethyl acetate/petrol ether, and the observed R_f is 0.38 for **3**.

20. Flash chromatography was performed using 175 g of silica gel 60 (6.5 x 11 cm) and 50-mL fractions were collected. The column was eluted

with petroleum ether (100 mL) and then petroleum ether/dichloromethane/ethyl acetate: 50:2.5:1 (250 mL), 20:1:1 (800 mL), and 15:1:1 (1800 mL). Pure **3** (1.85 g) was obtained in fractions 25-45, which were combined and concentrated under reduced pressure (40 mmHg) on a rotary evaporator at 40 °C. Fractions 46-58 were also combined and concentrated under the same conditions, and the residue was subjected to a second flash chromatography to give pure **3** (0.26 g). The combined solid was dried at 20 mmHg at 50 °C for 12 h.

21. The physical properties of **3** are as follows: $[\alpha]^{20}_{D}$ +60.1 (*c* 1.18, $CHCl_3$); IR (neat): 1492, 1448, 1424, 1392, 1351, 1246, 1198, 1155, 1068, 976, 907, 749, 725 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ: 2.10–2.15 (m, 6H), 4.27–4.60 (m, 4 H), 7.32–7.70 (m, 14 H), 7.82–8.09 (m, 10 H), 8.72–8.78 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 55.74, 55.82, 55.97, 56.11, 98.52, 98.61, 98.64, 98.81, 122.56, 122.75, 122.81, 122.93, 122.95, 125.41, 125.49, 125.53, 126.41, 126.44, 126.47, 126.51, 126.57, 126.64, 126.67, 126.74, 126.85, 126.93, 127.01, 127.40, 127.78, 128.07, 128.19, 128.40, 128.52, 128.88, 128.96, 130.27, 130.31, 130.34, 130.44, 130.52, 130.60, 130.80, 130.82, 131.14, 131.20, 131.25, 131.61, 131.64, 131.66, 131.73, 131.82, 131.86, 131.91, 131.95, 132.13, 134.10, 134.23, 134.24, 134.39, 134.46, 134.82, 134.89, 135.56, 135.58, 136.36, 136.68, 152.26, 152.29, 152.41; HR-MS (+ESI): calcd for $C_{52}H_{38}O_4Na$ ($[M+Na^+]$): 749.26623, found: 749.26691; calcd. for $C_{52}H_{42}O_4N$ [M+Na]): 749.2662, found: 749.2669; Anal. calcd. for $C_{52}H_{38}O_4$: C, 85.93; H, 5.27. Found: C, 85.63; H, 5.18.

22. HPLC conditions: Dynamax-60A column, 0.3% isopropanol in hexanes, 1.0 mL/min, UV (226 nm) detector. The t_R of **3** is 6.10 min.

23. Thin layer chromatography is eluted with 15% ethyl acetate/petroleum ether, and the observed R_f is 0.30 for **4**.

24. Column chromatography was performed using 100 g of silica gel 60 (230 – 400 mesh) (6.5 x 7.5 cm) and eluted with petroleum ether (150 mL) and then petroleum ether/dichloromethane/ethyl acetate: 50:2.5:1 (200 mL), 20:1:1 (500 mL), 20:1:2 (1000 mL), and 20:1:2.5 (300 mL). Fractions (50 mL) were collected and the desired product was obtained in fractions 23-35, which were combined and concentrated under reduced pressure (40 mmHg) on a rotary evaporator at 40 °C. The resulting solid was dried under reduced pressure (0.2 mmHg) at 50 °C for 24 h, which contains 1-2% 1,4-dioxane that could not be removed.

25. Compound **4** (50 mg) was further dried under reduced pressure (0.2 mmHg) at 100 °C for 48 h to remove the 1,4-dioxane for analysis purpose. The ^1H-NMR didn't show any decomposition comparing with the

sample before the heating. The physical properties of **4** are as follows: mp: 148–150 °C (decomposition); $[\alpha]_D^{20}$ +45.5 (*c* 1.0, $CHCl_3$); IR (neat): 3523, 3058, 1621, 1493, 1448, 1425, 1379, 1360, 1258, 1230, 1198, 1143, 905, 768, 747, 726 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ: 5.22, 5.23, 5.28, 5.33, (4 singlets, combined integration: 2H), 7.42-7.80 (m, 15H), 7.88-7.92 (m, 2H), 7.95-8.00 (m, 5H), 8.10-8.12 (m, 2H), 8.75-8.83 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 113.07, 113.17, 113.48, 122.82, 122.85, 123.10, 123.14, 123.21, 123.24, 124.50, 124.53, 124.71, 124.74, 124.93, 125.00, 126.94, 127.01, 127.05, 127.13, 127.16, 127.22, 127.28, 127.53, 127.59, 128.60, 128.71, 129.01, 129.07, 129.19, 129.41, 129.52, 129.54, 129.66, 129.67, 129.77, 130.63, 130.66, 130.69, 130.76, 130.78, 130.81, 131.29, 131.34, 131.35, 131.39, 131.66, 131.68, 131.70, 131.71, 132.26, 132.32, 133.79, 133.82, 133.92, 133.94, 133.99, 134.20, 150.80, 150.85, 150.87; HR-MS (-ESI): calcd. for $C_{48}H_{29}O_2$ ($[M-H]^-$): 637.21730, found: 637.21725.

26. HPLC conditions: Dynamax-60A column, 0.5% isopropanol in hexanes, 1.0 mL/min, UV (226 nm) detector. The t_R of **4** is 7.35 min.

27. Pyridine was distilled from KOH before use.

28. $POCl_3$ was purchased from Sinopharm Chemical Reagent Co., Ltd.

29. Thin layer chromatography is eluted with 5% methanol/ CH_2Cl_2, and the observed R_f are 0.50 for the phosphoric acid product **5** and 1.0 for **4**.

30. Column chromatography was performed using 100 g of 200–300 mesh silica gel 60 (5.5 x 11 cm) and 100-mL fractions were collected (300 mL of CH_2Cl_2, then 200 mL each of CH_2Cl_2/methanol, 100:1 and 50:1, and finally 550 mL of CH_2Cl_2/methanol, 40:1). The desired product was obtained in fractions 8-12, which were combined and concentrated by rotary evaporation under reduced pressure (40 mmHg) at 40 °C to obtain a white solid. The resulting solid was dried at 4 mmHg for 5 h.

31. The phosphoric acid product **5** exhibits the following physicochemical properties: white solid; mp: 359 – 361 °C (decomposition); $[\alpha]^{20}_D = -11.9$ (c=1, CH_2Cl_2); IR (neat): 3630, 3061, 1622, 1493, 1449, 1416, 1250, 1201, 1102, 1093, 969, 951, 907, 852, 749, 726 $cm^{-1}.cm^{-1}$; ^1H NMR (400 MHz, DMSO-d_6) δ: 7.39–7.73 (m, 16 H), 7.97–8.19 (m, 8 H), 8.88–8.93 (m, 4 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 122.43, 122.78, 123.12, 125.09, 126.23, 126.41, 126.51, 126.58, 126.79, 126.87, 128.46, 129.10, 129.40, 129.67, 130.24, 131.27, 131.43, 132.32, 133.30, 134.22, 148.10, 148.19; ^{31}P NMR (162 MHz, DMSO-d_6) δ: 2.61; HRMS (ESI): calcd. for $C_{48}H_{30}O_4P$ $(M+H)^+$ 701.1876, found: 701.1889.

32. HPLC condition: Dynamax-60A column, 7% isopropanol in hexanes, 1.0 mL/min, UV (226 nm) detector. The t_R of **5** is 21.6 min.

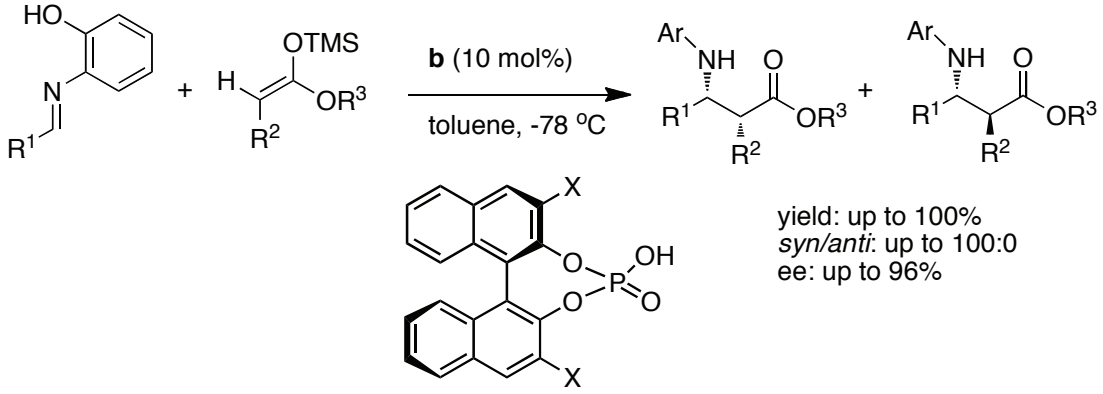
Safety and Waste Disposal Information

All hazardous materials should be handled and disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

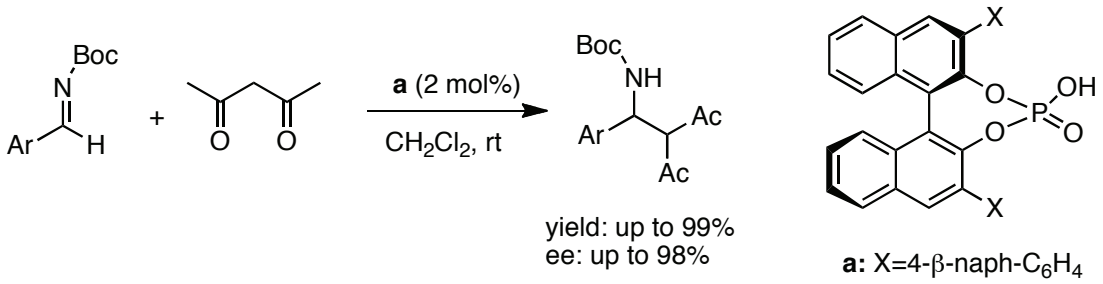
Discussion

Enantiomerically pure 3,3'-bis(9-phenanthryl)-1,1'-binaphthalene-2,2'-diyl hydrogen phosphate is used as a chiral Bronsted acid for multicomponent reactions. In 2004, the research groups of Akiyama and Terada independently reported activation of electrophiles by way of protonation with moderately strong phosphoric acids derived from chiral BINOLs.[2,3]

Scheme 1. Enantioselective Mannich-type Reaction by Akiyama, et al[2]

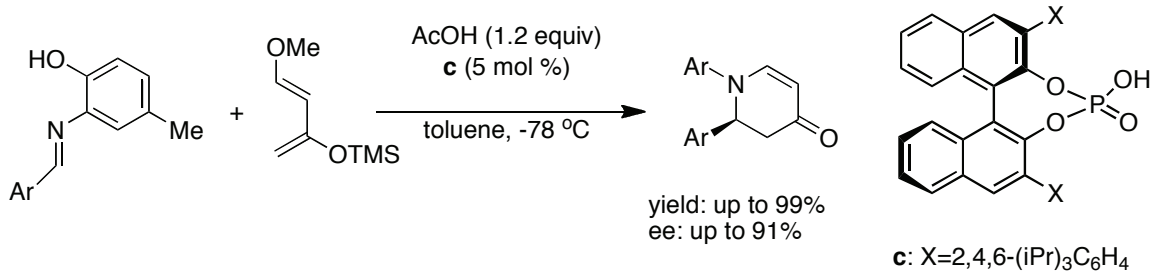


Scheme 2. Direct Mannich Reaction by Terada, et al[3]

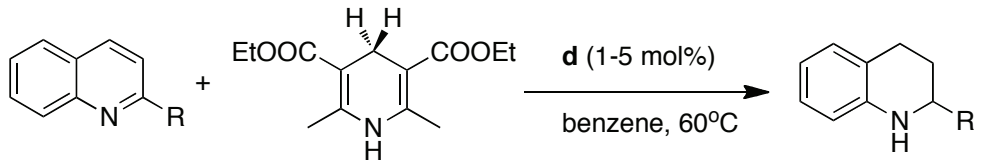


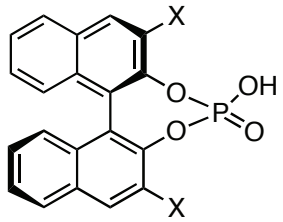
Due to the suitable acidity and cyclic structure, BINOL phosphates exhibit excellent catalytic activity as a chiral Bronsted acid for other reactions. Nucleophilic addition to aldimines, aza Diels-Alder reactions, and transfer hydrogenations can be catalyzed by BINOL phosphates to give high enantioselectivity with satisfactory yields.[4]

Scheme 3. Aza Diel-Alder Reaction by Akiyama, et al[5]



Scheme 4. Transfer Hydrogenation of Quinolines by Rueping, et al[6]





Suzuki and Grignard cross-coupling is commonly used for the coupling of BINOL and the aryl group. In 1981 Cram, et al. synthesized two optical pure 3,3'-diaryl-substituted BINOLs by a Grignard cross-coupling reaction of 3,3'-dibromo-BINOL dimethyl ether and arylmagnesium bromides employing dichlorobis(triphenylphosphine)nickel(II) as the catalyst.[7] In 1998 Jørgensen, et al. prepared 3,3'-diary BINOLs by a Suzuki cross-coupling reaction of the 3,3'-diboronic acid of BINOL with commercially available aromatic bromides.[8]

The method in this procedure can also be used to synthesize 3,3'-diphenyl or di(2-naphthyl) BINOLs.[9]

1. (a) Department of Chemistry, East China Normal University, Shanghai 200062, China; whu@chem.ecnu.edu.cn; (b) Hefei National Laboratory

for Physical Sciences at the Microscale and Department of Chemistry, University of Science and Technology of China, Hefei 230026, China; gonglz@ustc.edu.cn. Hu thanks the financial support from the National Science Foundation of China (NSFC) (20932003), and from the MOST of China (2011CB808600). Gong thanks NSFC (20732006) for the financial support.

2. Akiyama, T.; Itoh, J.; Yokota, K.; Fuchibe, K. *Angew. Chem. Int. Ed.* **2004**, *43*, 1566–1568.
3. Uraguchi, D.; Terada, M. *J. Am. Chem. Soc.* **2004**, *126*, 5356–5357.
4. Akiyama, T. *Chem. Rev.* **2007**, *107*，5744–5758.
5. Akiyama, T.; Tamura, Y.; Itoh, J.; Morita, H.; Fuchibe, K. *Synlett.* **2006**, 141–143.
6. Rueping, M.; Antonchick, A. P.; Theissmann, T. *Angew. Chem. Int. Ed.* **2006**, *45*, 3683–3686.
7. Lingenfelter, S. D.; Helgeson, C. R.; Cram, J. D. *J. Org. Chem.* **1981**, *46*, 393–406.
8. Simonsen, B. K.; Gothelf, V. K.; Jorgensen, A. K. *J. Org. Chem.* **1998**, *63*, 7536–7538.
9. Wu, T. R.; Shen, L.-X.; Chong, J. M. *Org. Lett.* **2004**, *6*, 2701–2704.

Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

(*R*)-(+)-2,2’-Bis(methoxymethoxy)-1,1’-binaphthyl; (1738310-50-0)
n-Butyllithium; (109-72-8)
Iodine; (12190-71-5)
9-Phenanthreneboronic acid; (68572-87-2)
Tetrakis(triphenylphosphine) palladium(0); (14221-01-3)
Phosphorus oxychloride; (10025-87-3)
(*R*)-2,2'-Bis(methoxymethoxy)-3,3'-diiodo-1,1'- binaphthalene ; (189518-78-3)
(*R*)-2,2'-Bis(methoxymethoxy)-3,3'-bis(9-phenanthryl)-1,1'-binaphthalene; (1261302-60-6)
(*R*)-3,3'-Bis(9-phenanthryl)-1,1'-binaphthalene-2,2'-diol; (1058734-56-7)
(*R*)-3,3'-Bis(9-phenanthryl)-1,1'-binaphthalene-2,2'-diyl hydrogen phosphate; (864943-22-6)

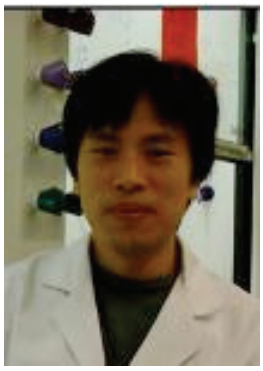
Wenhao Hu was born in 1967 in Sichuan Province, China. He received his M.S. degree in Chengdu Institute of Organic Chemistry. He obtained a Ph.D. degree from the Hong Kong Polytechnic University in 1998 under the direction of Professor Albert S. C. Chan, and was a postdoctoral fellow at the University of Arizona with Professor Michael P. Doyle. He then joined GeneSoft Pharm. Inc. at San Francisco as a Staff Scientist (2002-2003). He moved to New Jersey to join Bristol-Myers Squibb Company as a Research Investigator (2003-2006). He returned to China as a Professor in the Department of Chemistry at East China Normal University in 2006. His research interests include development of highly efficient synthetic methods and their application to biologically active compounds.

Jing Zhou was born in 1984 in Shandong Province, China. She received her bachelor's degree in Chemistry in 2007 from East China Normal University, Shanghai. She then began her graduate study in Organic Chemistry at the same university under the mentorship of Professor Wenhao Hu. She performed research on rhodium catalyzed multi-component reactions. Her current research focuses on the synthesis of immunologically active peptidyl disaccharides.

Xinfang Xu was born in 1981 in Zhejiang Province, China. He received his bachelor's degree in Chemistry from East China Normal University in 2005. He then began his graduate studies in Organic Chemistry at the same university, under the supervision of Professor Liping Yang (2005-2006) and Wenhao Hu (2006-present). His current research interest is development of novel asymmetric multi-component reactions.

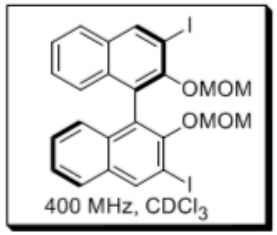
Liu-Zhu Gong was born in October 1970 in Henan, China. He graduated from Henan Normal University (1989) and received his Ph.D. (2000) from Institute of Chemistry, Chinese Academy of Sciences. He was a visiting scholar at the University of Virginia and an Alexander von Humboldt Research Fellow at the University of Munich. He became an associate professor of Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences in 2000. Since 2006 he has been a full professor at the University of Science and Technology of China. His current research interest is focused on organo- and transition metal-catalyzed asymmetric synthesis, the total synthesis of natural products, and chiral conjugated polymers.

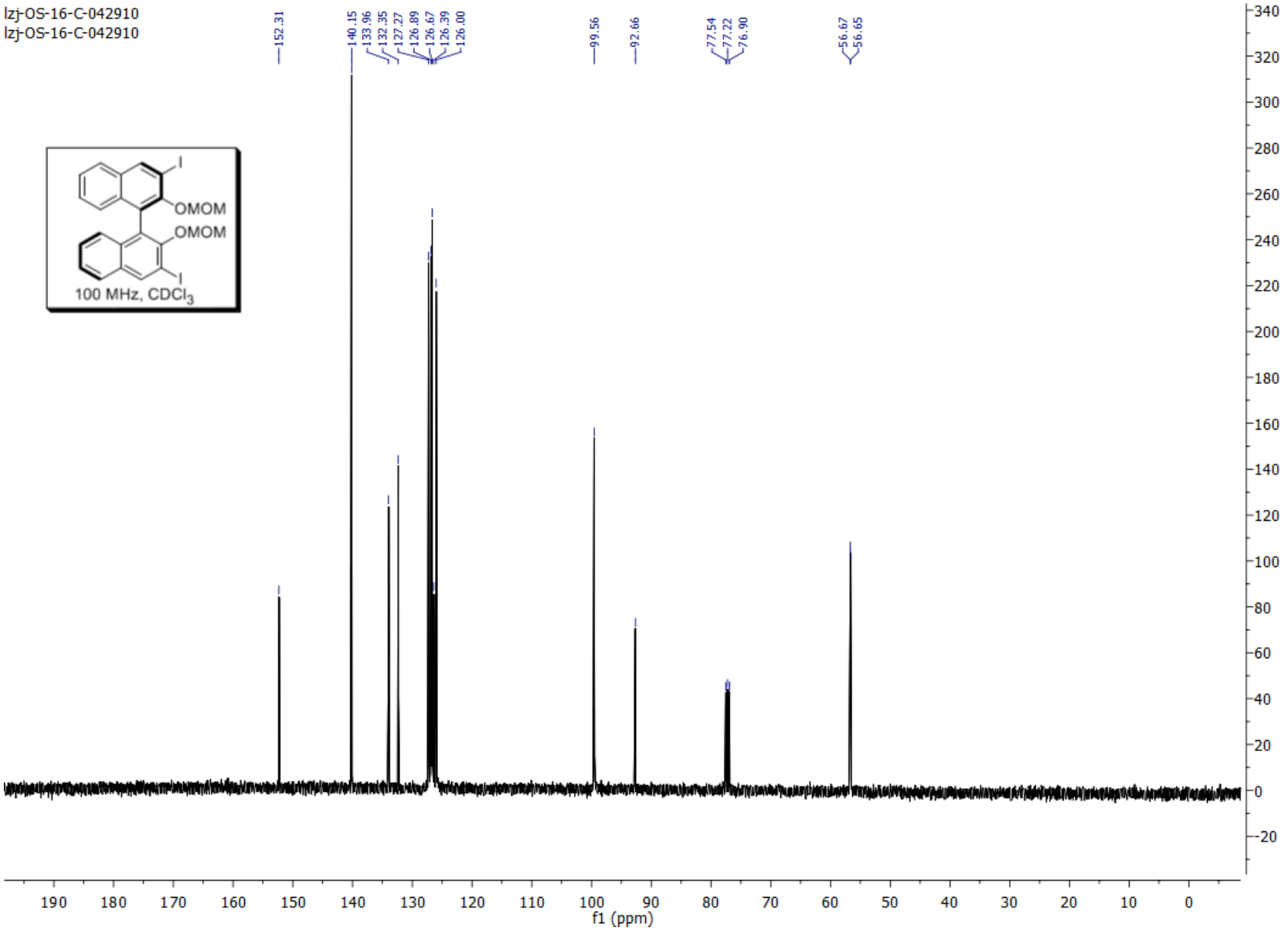
Wei-jun Liu was born in1979 in Hunan, China. He graduated from Xiangtan University (2002) and received his M.S. degree (2005) from Chengdu Institute of Organic Chemistry (Prof. Wen-Hao Hu). He joined WuXiAppTec (Shanghai) Co., Ltd. as a research chemist. He then moved to the research group of Professor Liu-Zhu Gong as a Ph.D. student at the University of Science and Technology of China. His current research interest is development of organo- and Lewis acid-catalyzed asymmetric synthesis.



Zhanjie Li was born in 1975 in Henan, China. He received his Bachelor's degree in 1996 and his Master's degree in 1999. Both were from Lanzhou University in China. After graduation in 1999, he worked at the Guangzhou Institute of Chemistry, Chinese Academy of Sciences. In 2004, he worked with Dr. Scott M. Goodman at State University of New York, College at Buffalo. In 2005 he began his PhD studies in the lab of Prof. Huw Davies at SUNY Buffalo and later on joined him at Emory University in 2008. His PhD research focuses on chiral catalyst design and Rh(II)-catalyzed asymmetric transformations of allylic and propargylic alcohols and donor/acceptor diazo compounds.

lzj-OS-16-1-041410
lzj-OS-16-1-041410

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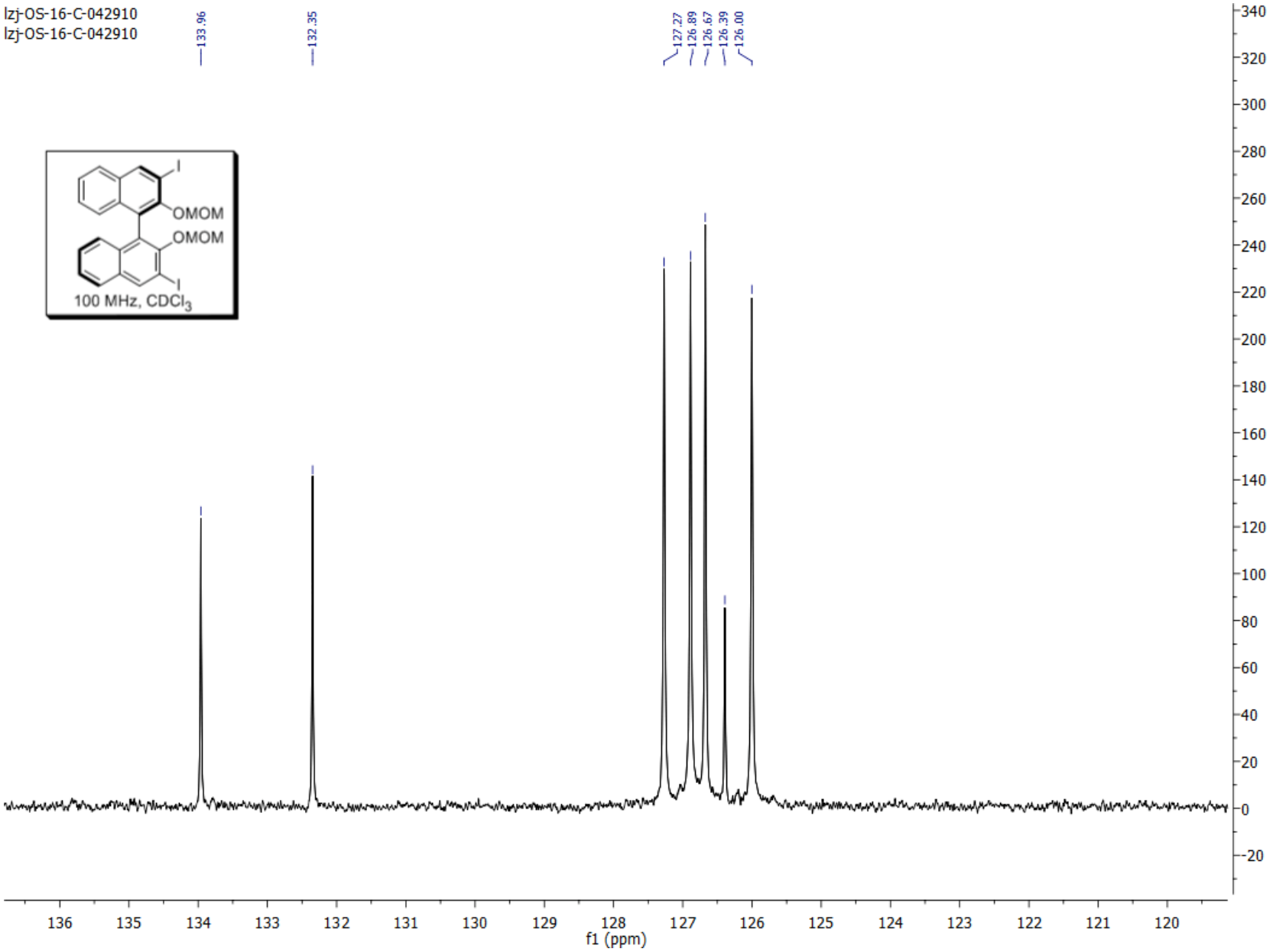
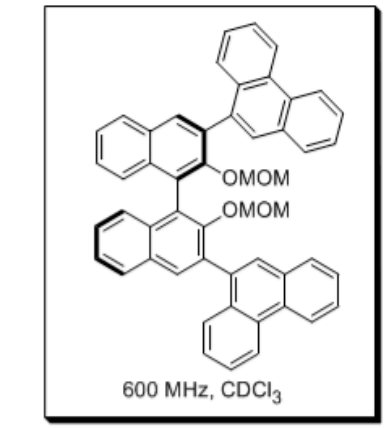
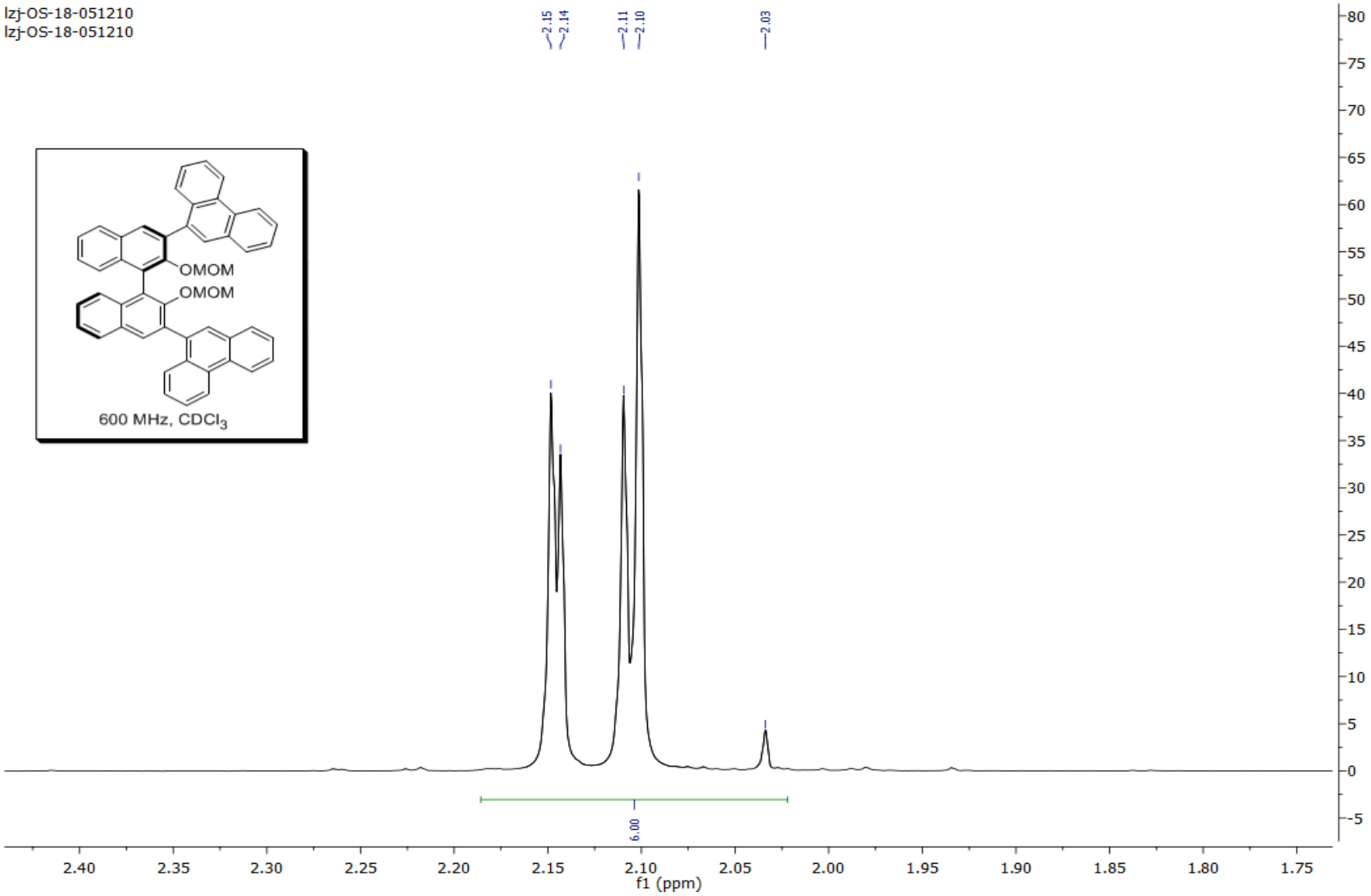
lzj-OS-16-C-042910
152.31
140.15
133.96
132.35
127.27
126.89
126.67
126.39
126.00
99.56
92.66
77.54
77.22
76.90
56.67
56.65
OMOM
OMOM
100 MHz, CDCl3
f1 (ppm)


lzj-OS-16-C-042910
lzj-OS-16-C-042910
133.96
132.35
127.27
126.89
126.67
126.39
126.00
OMOM
OMOM
I
I
100 MHz, CDCl3
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
136
135
134
133
132
131
130
129
128
127
126
125
124
123
122
121
120
f1 (ppm)

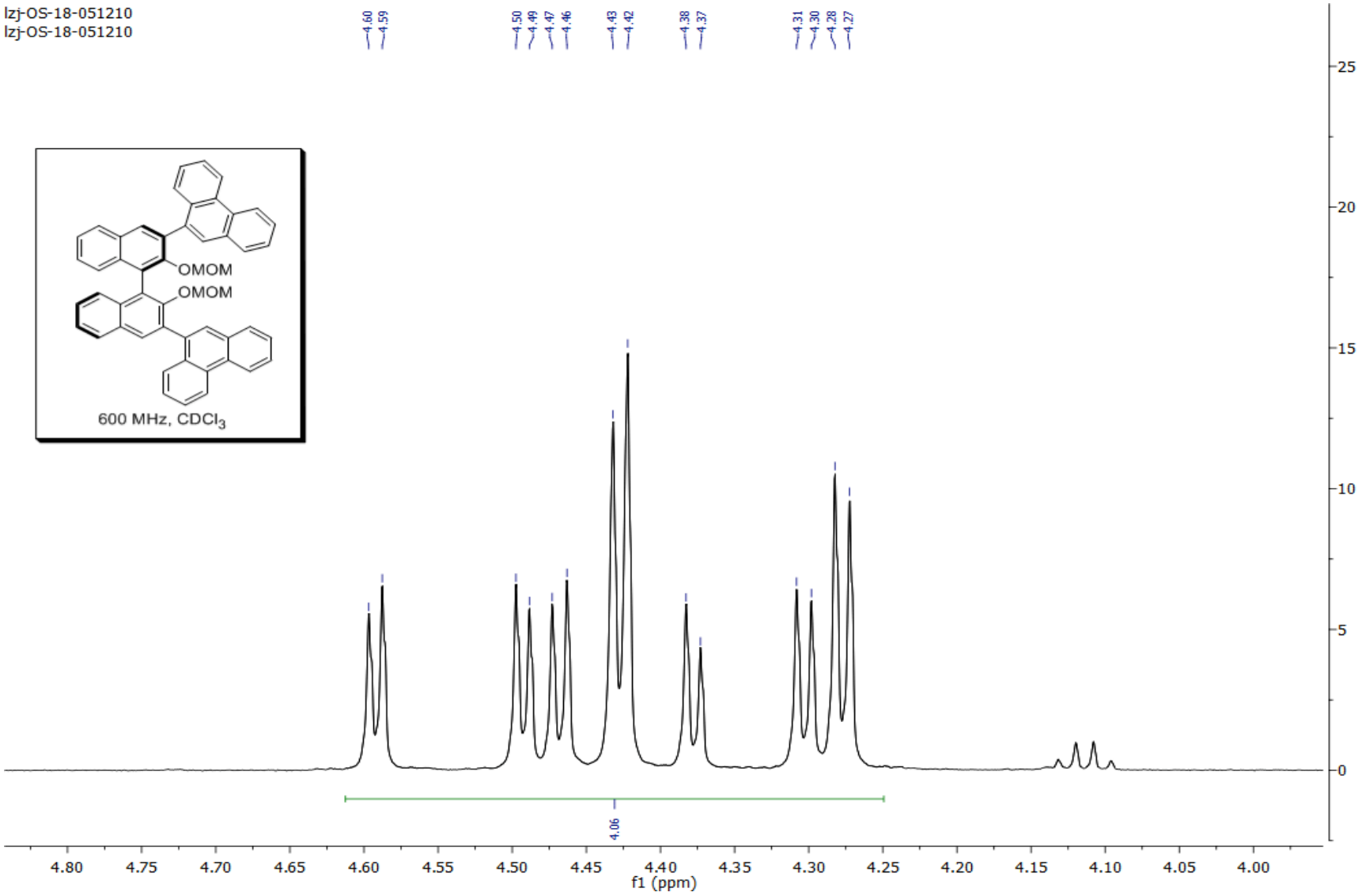
lzj-OS-18-051210
lzj-OS-18-051210

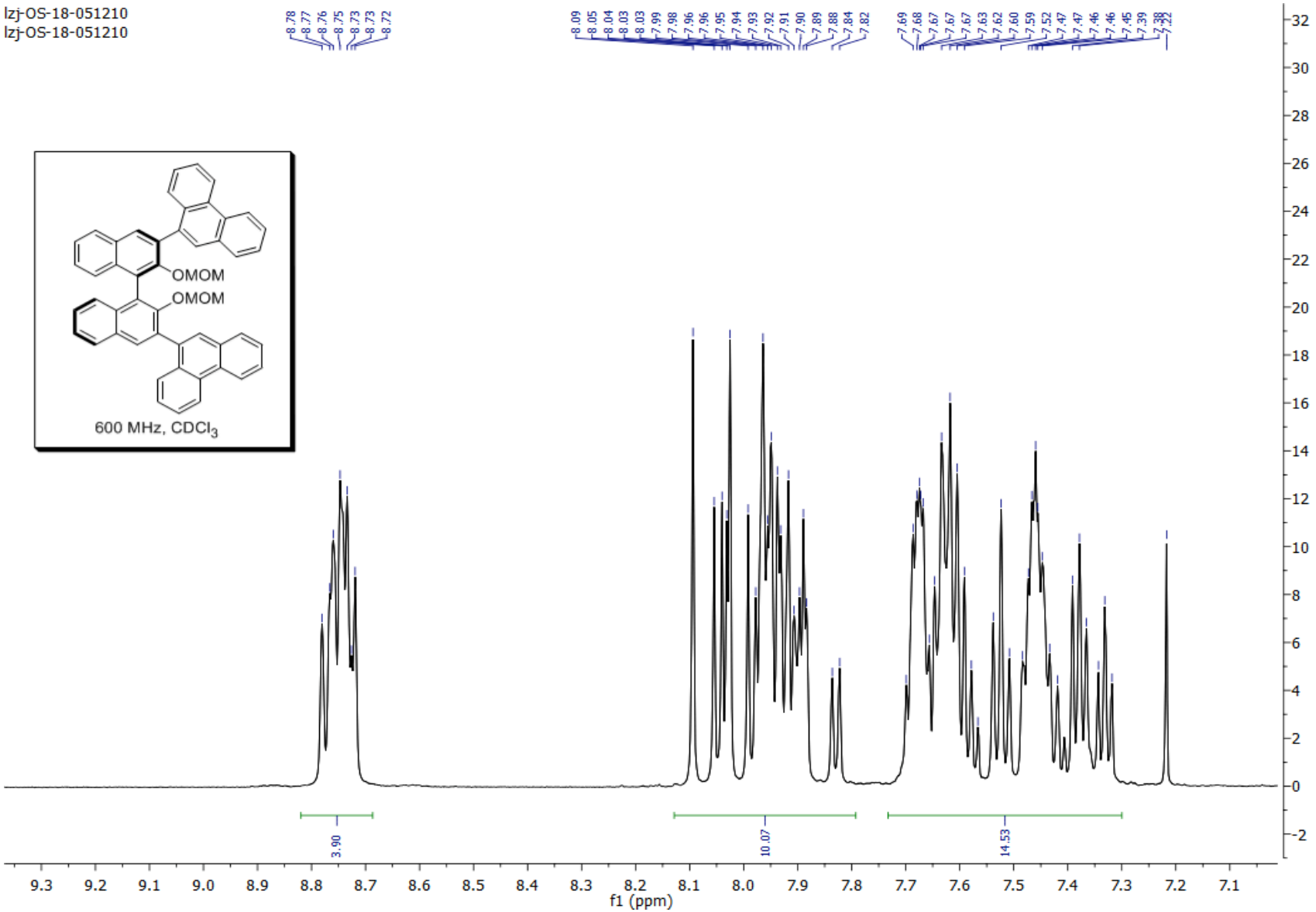


f1 (ppm)

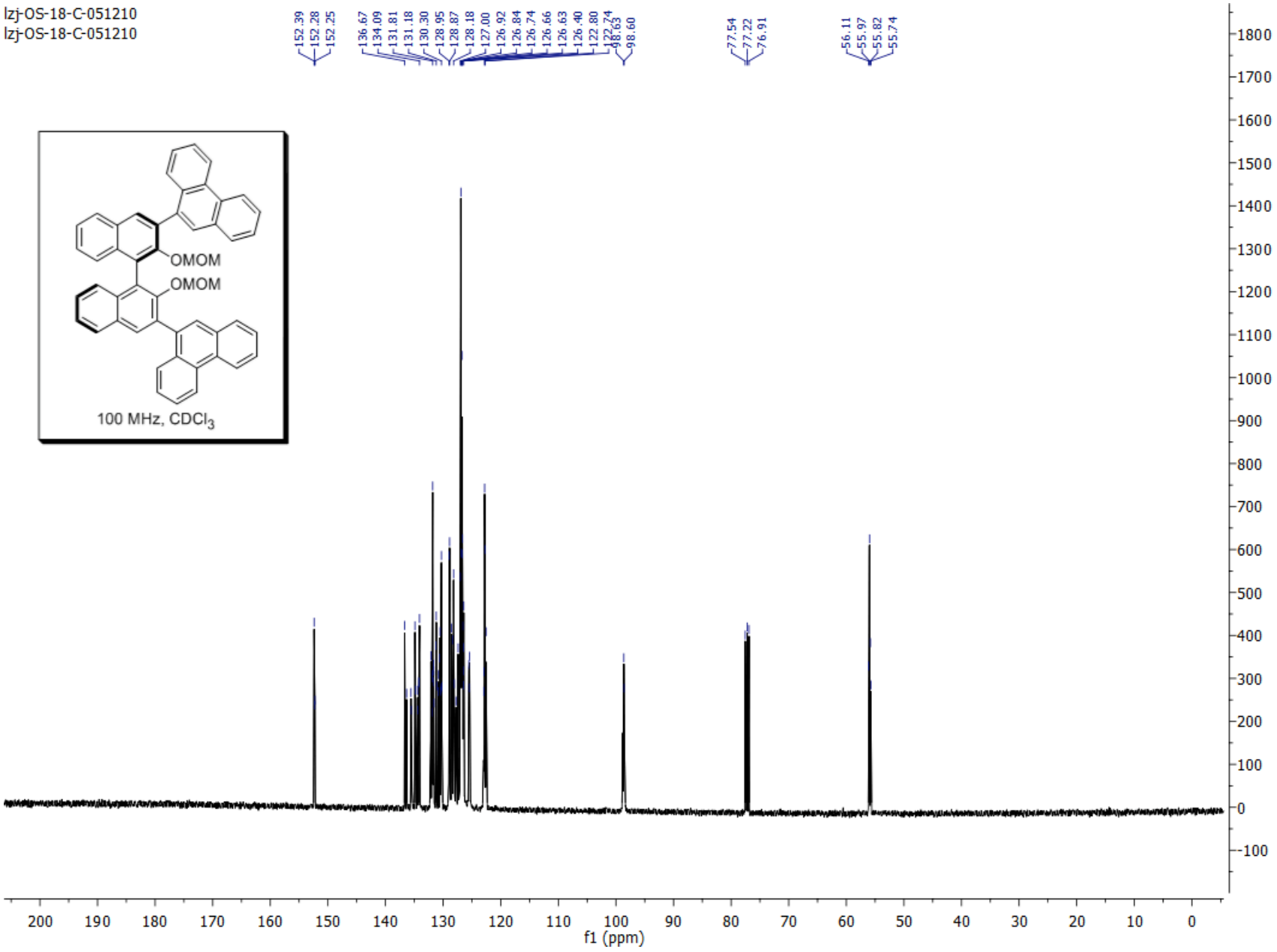

lzj-OS-18-051210
lzj-OS-18-051210
2.15
2.14
2.11
2.10
2.03
OMOM
OMOM
600 MHz, CDCl3
6.00
f1 (ppm)

lzj-OS-18-051210
lzj-OS-18-051210




lzj-OS-18-051210
lzj-OS-18-051210
8.78
8.77
8.76
8.75
8.73
8.73
8.72
8.09
8.05
8.04
8.03
8.03
7.99
7.98
7.96
7.96
7.95
7.94
7.93
7.92
7.91
7.90
7.89
7.88
7.84
7.82
7.69
7.68
7.67
7.67
7.67
7.63
7.62
7.60
7.59
7.52
7.47
7.47
7.46
7.46
7.45
7.39
7.38
7.22
OMOM
OMOM
600 MHz, CDCl3
3.90
10.07
14.53
f1 (ppm)

lzj-OS-18-C-051210
lzj-OS-18-C-051210



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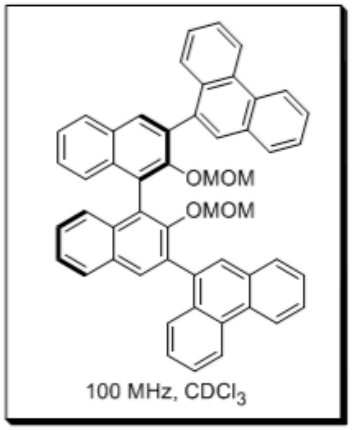
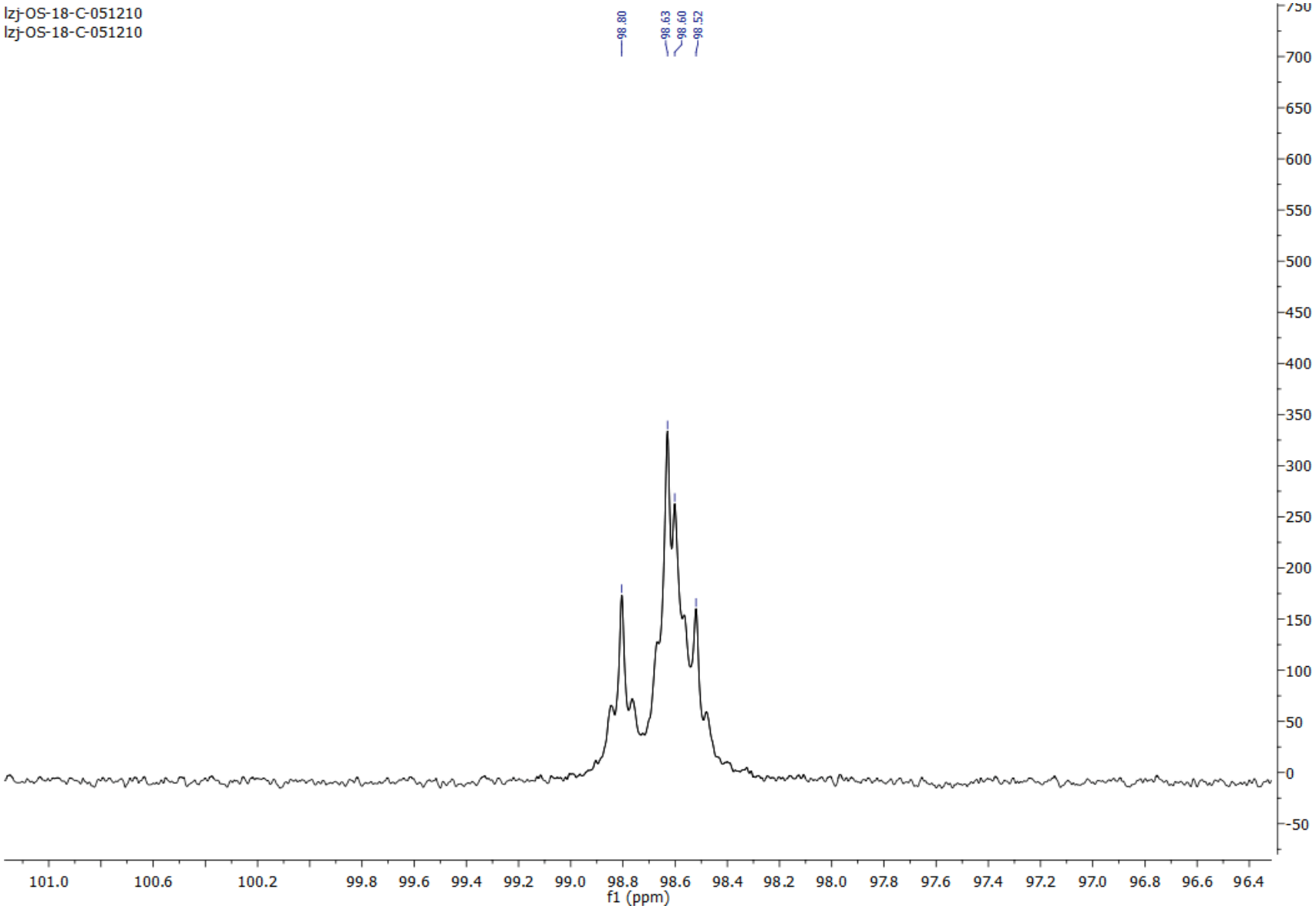
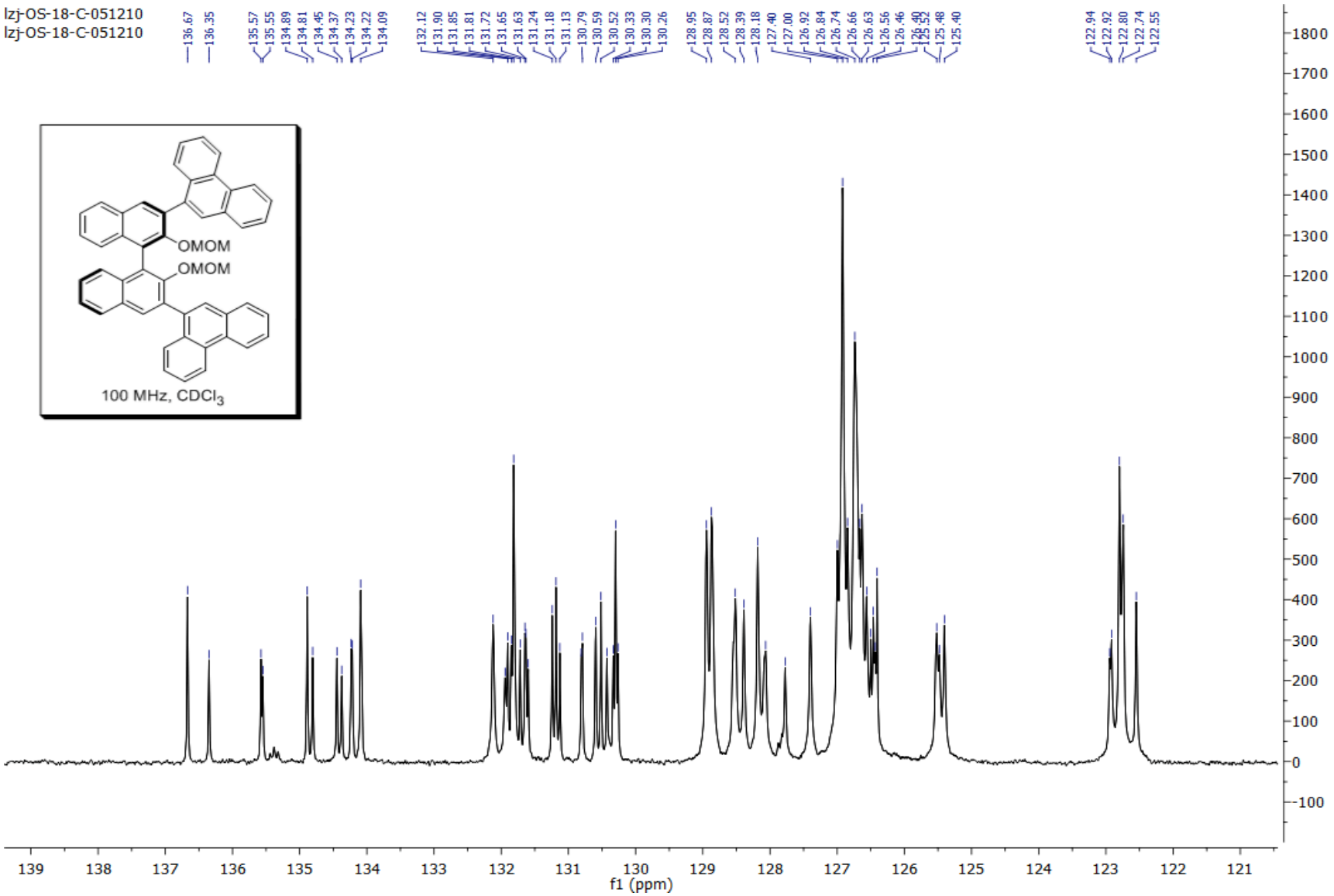
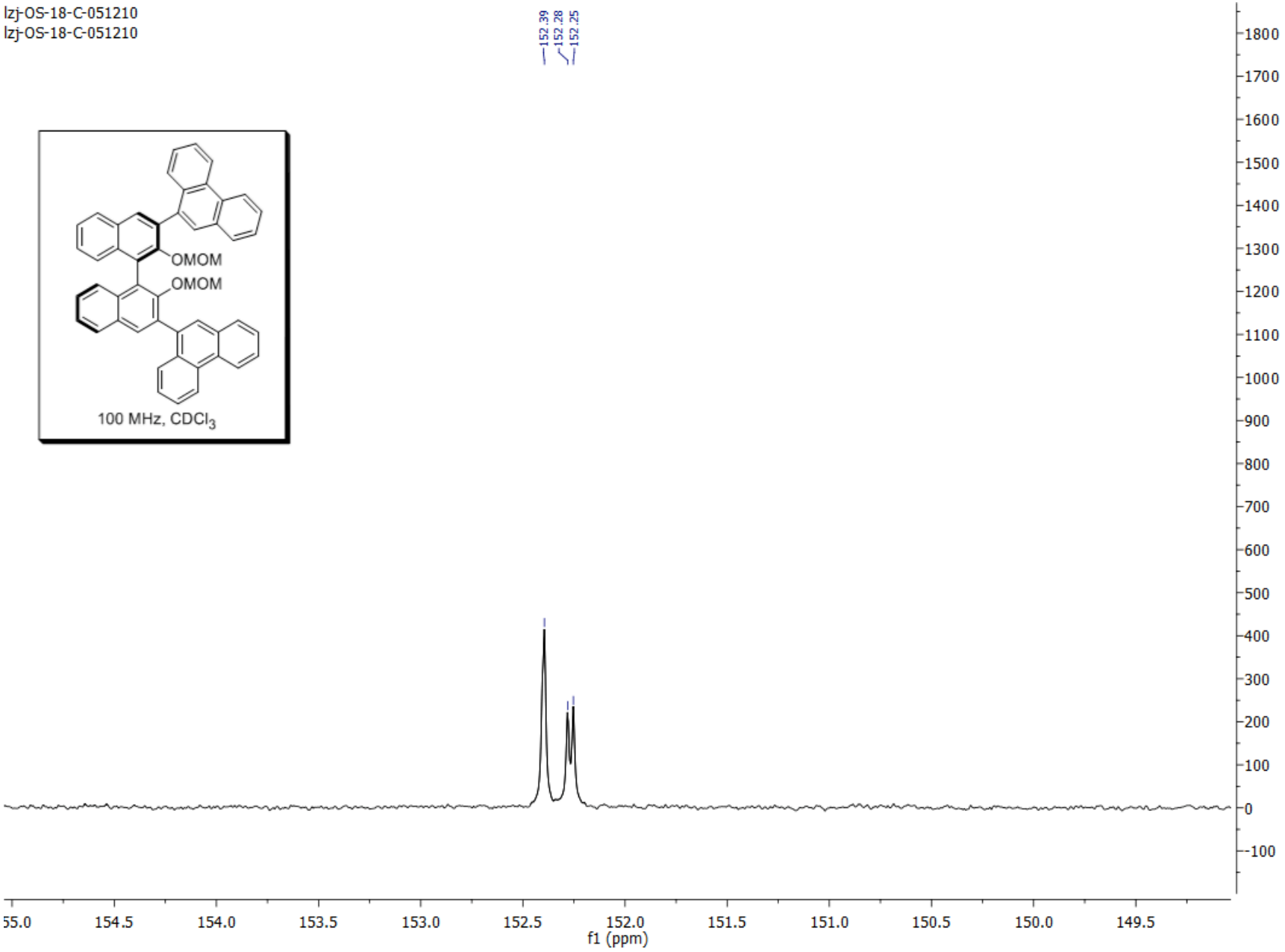
lzj-OS-18-C-051210

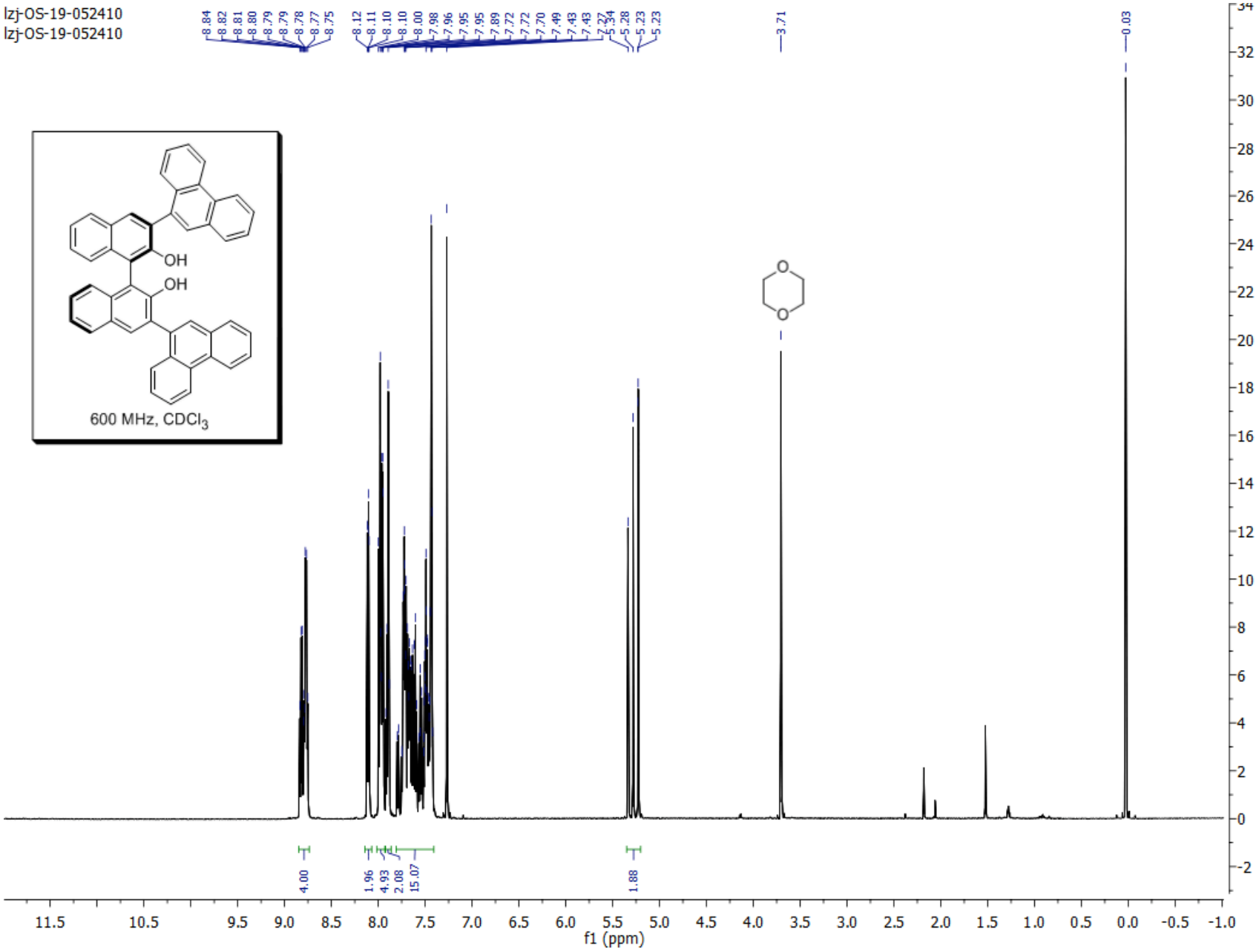



lzj-OS-18-C-051210
lzj-OS-18-C-051210
98.80
98.63
98.60
98.52
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
101.0
100.6
100.2
99.8
99.6
99.4
99.2
99.0
98.8
98.6
98.4
98.2
98.0
97.8
97.6
97.4
97.2
97.0
96.8
96.6
96.4
f1 (ppm)

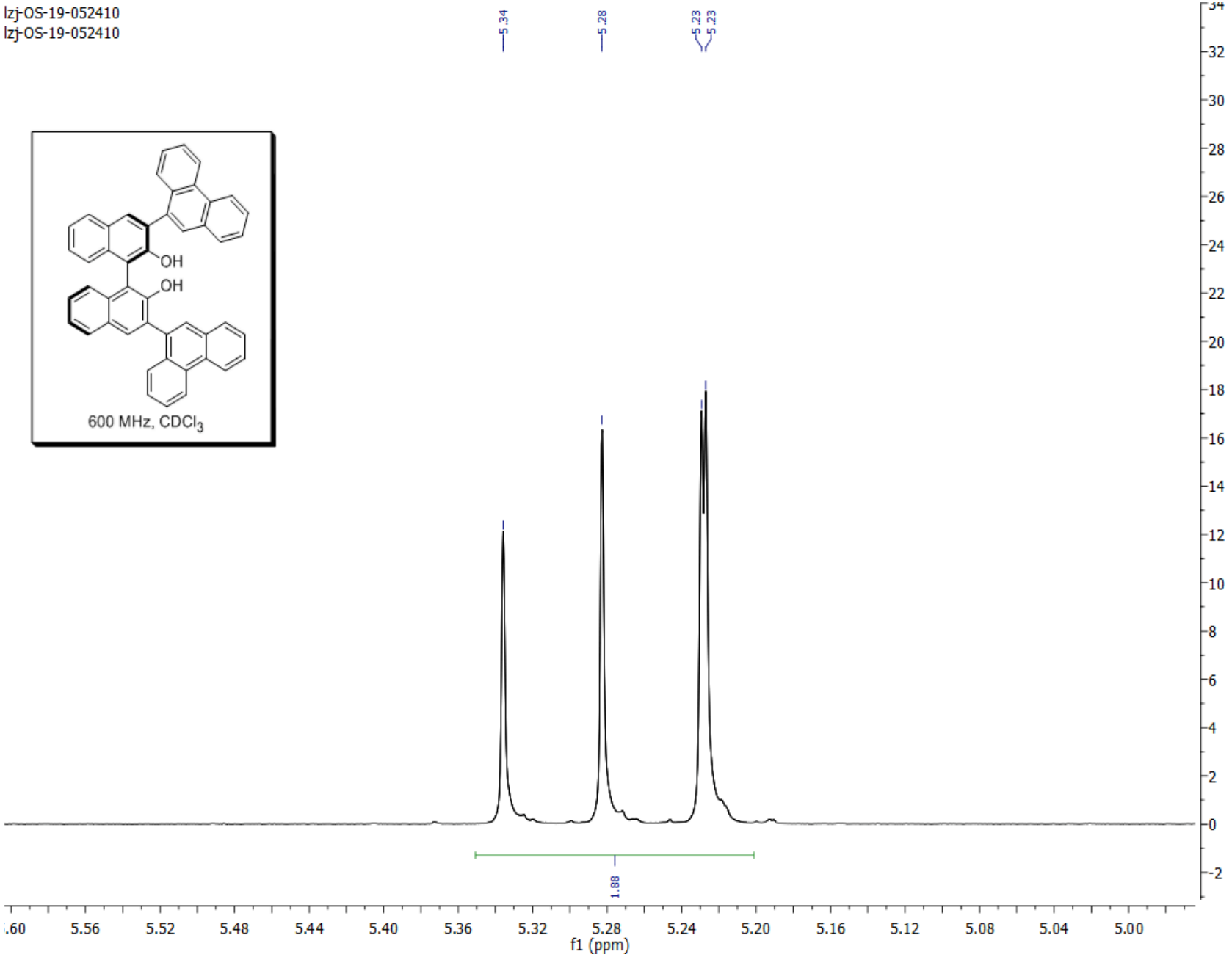

lzj-OS-18-C-051210
lzj-OS-18-C-051210
136.67
136.35
135.57
135.55
134.89
134.81
134.45
134.37
134.23
134.22
134.09
132.12
131.90
131.85
131.81
131.72
131.65
131.63
131.24
131.18
131.13
130.79
130.59
130.52
130.33
130.30
130.26
128.95
128.87
128.52
128.39
128.18
127.40
127.00
126.92
126.84
126.74
126.66
126.63
126.56
126.46
125.48
125.40
122.94
122.92
122.80
122.74
122.55
OMOM
OMOM
100 MHz, CDCl3
f1 (ppm)

lzj-OS-18-C-051210
lzj-OS-18-C-051210

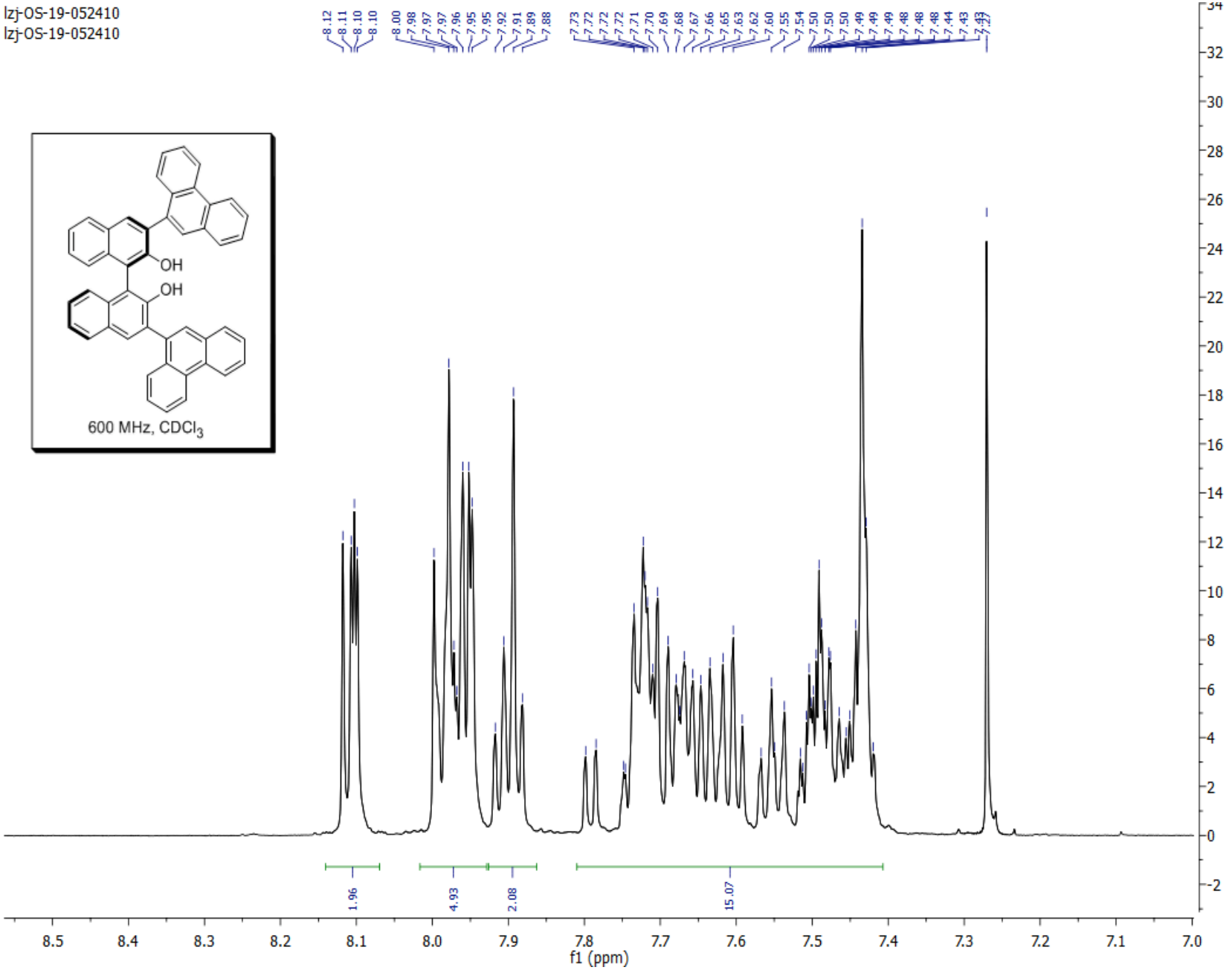



lzj-OS-19-052410
lzj-OS-19-052410
8.84
8.82
8.81
8.80
8.79
8.79
8.78
8.77
8.75
8.12
8.11
8.10
8.10
8.00
7.98
7.96
7.95
7.95
7.89
7.72
7.72
7.70
7.49
7.43
7.43
7.27
5.34
5.28
5.23
5.23
3.71
0.03
OH
OH
600 MHz, CDCl3
4.00
1.96
4.93
2.08
15.07
1.88
f1 (ppm)

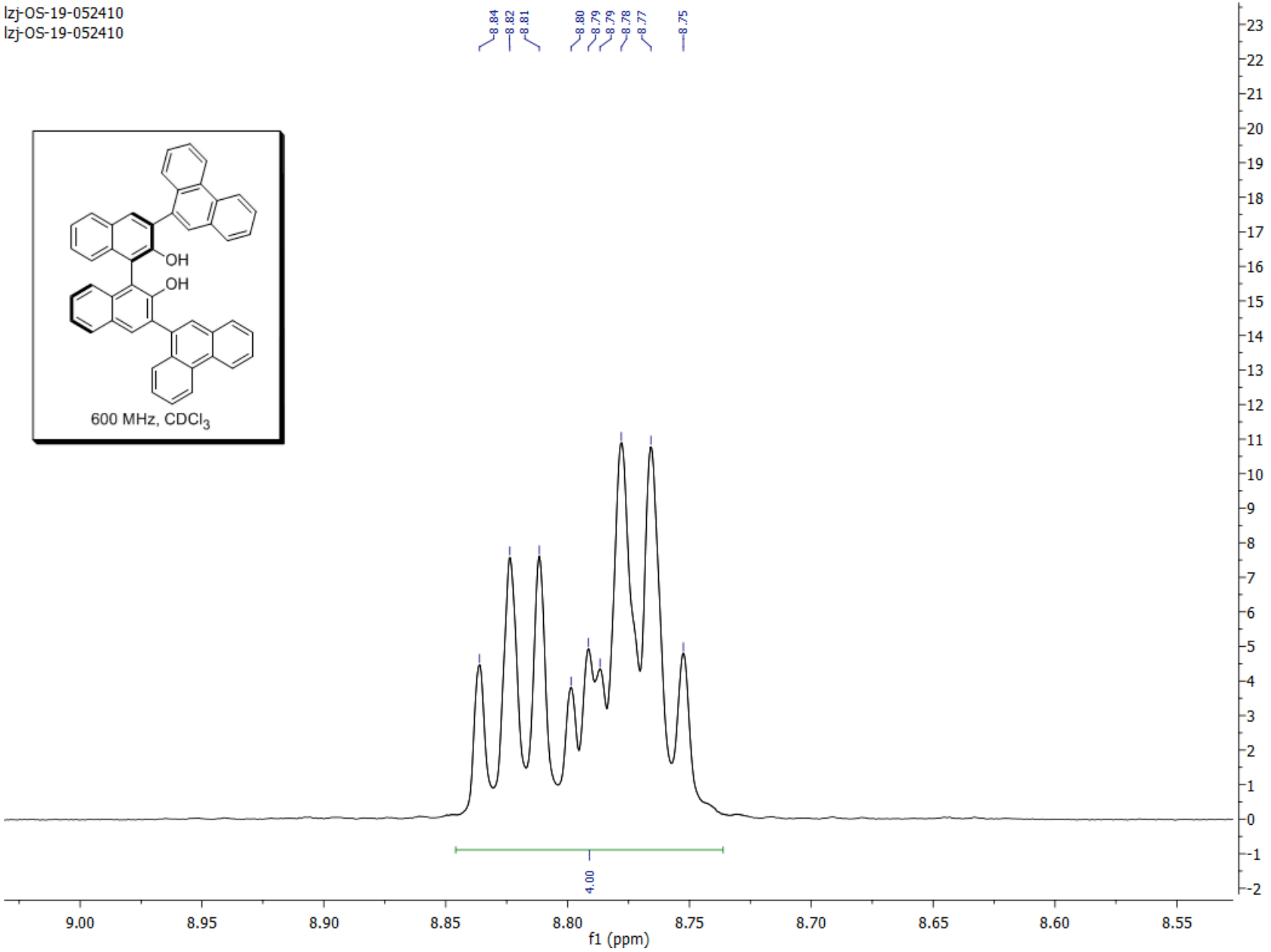
lzj-OS-19-052410
lzj-OS-19-052410

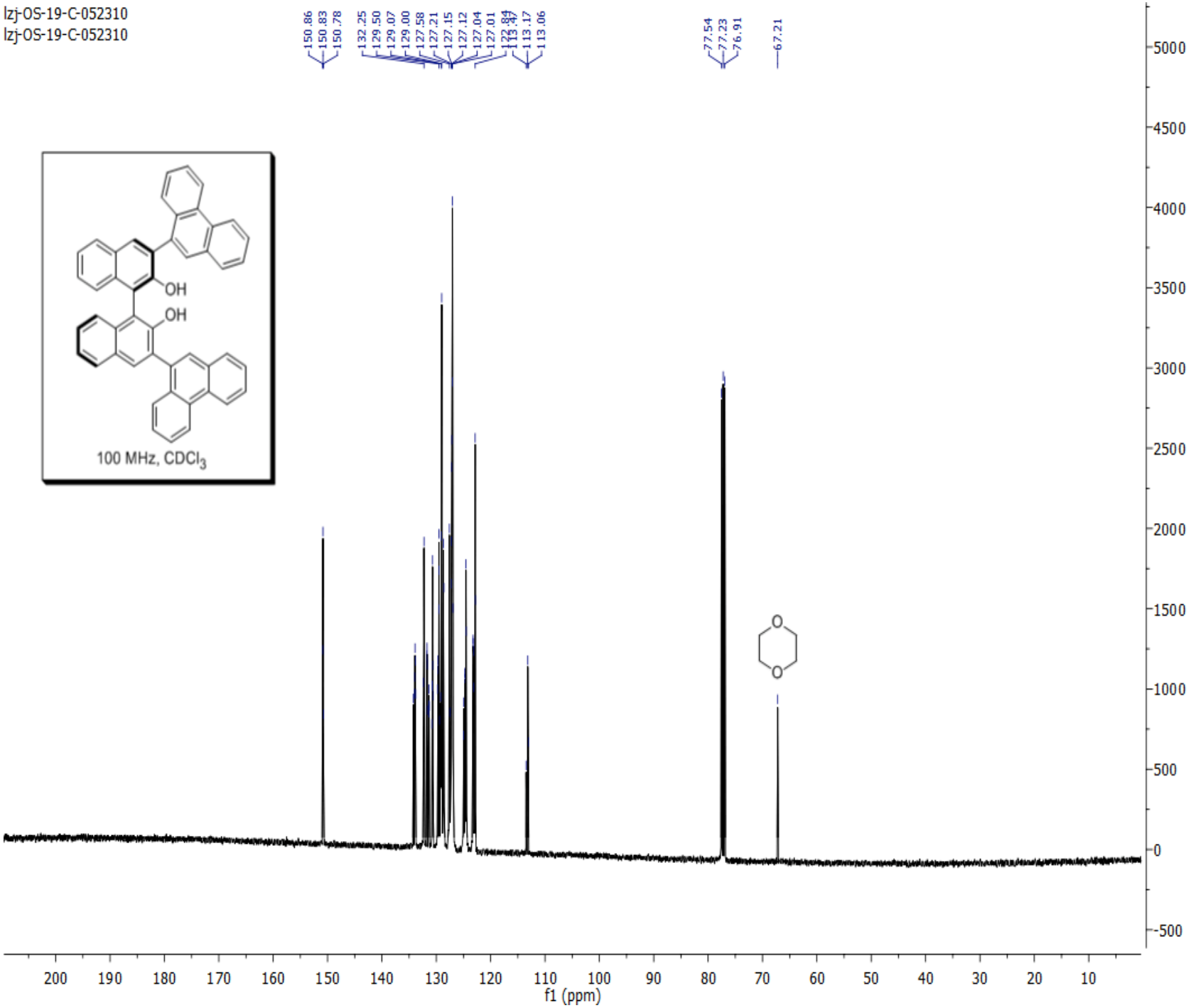


lzj-OS-19-052410
lzj-OS-19-052410

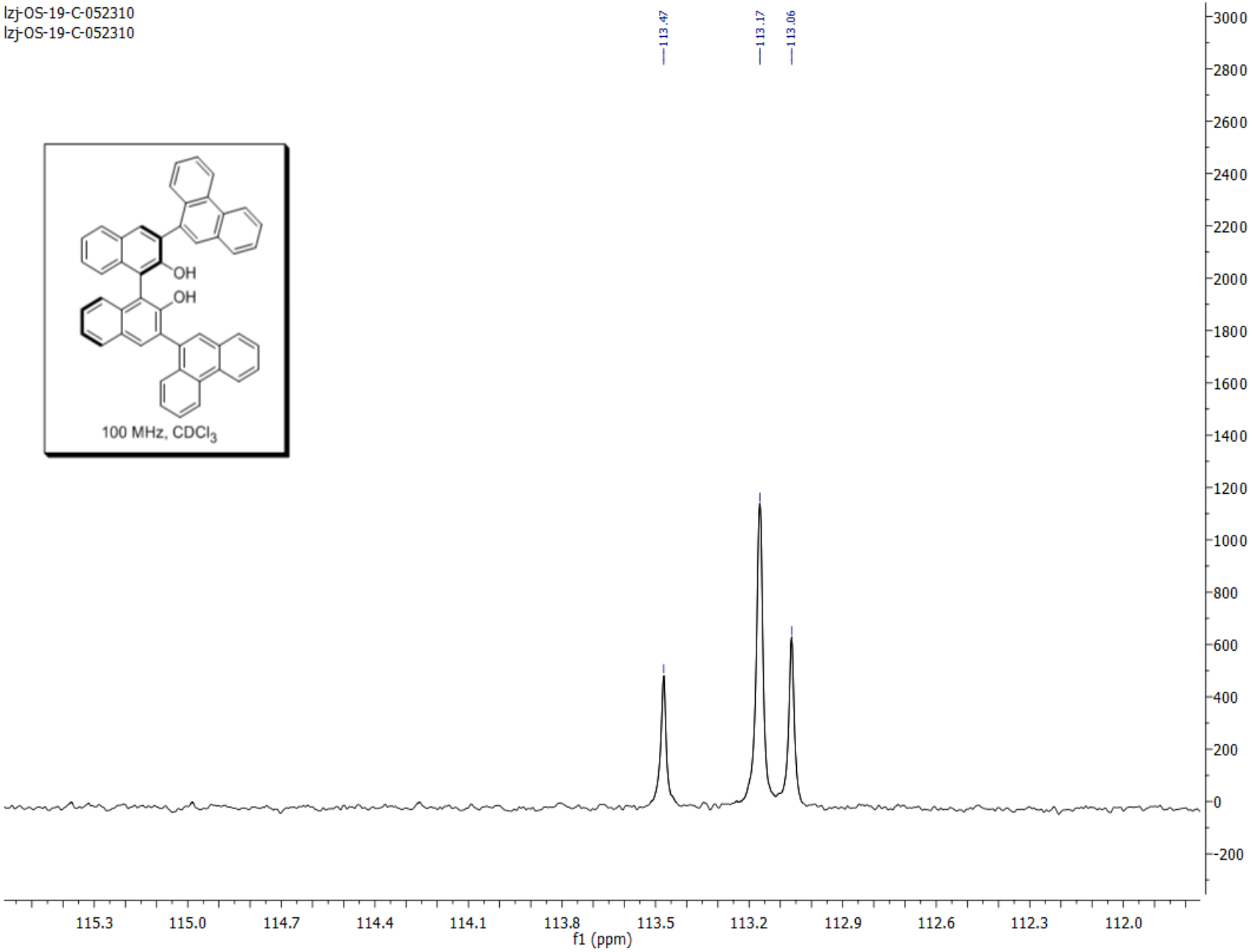


lzj-OS-19-052410
lzj-OS-19-052410




lzj-OS-19-C-052310
lzj-OS-19-C-052310
150.86
150.83
150.78
132.25
129.50
129.07
129.00
127.58
127.21
127.15
127.12
127.04
127.01
113.17
113.06
77.54
77.23
76.91
67.21
OH
OH
100 MHz, CDCl3
O
O
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

lzj-OS-19-C-052310
lzj-OS-19-C-052310



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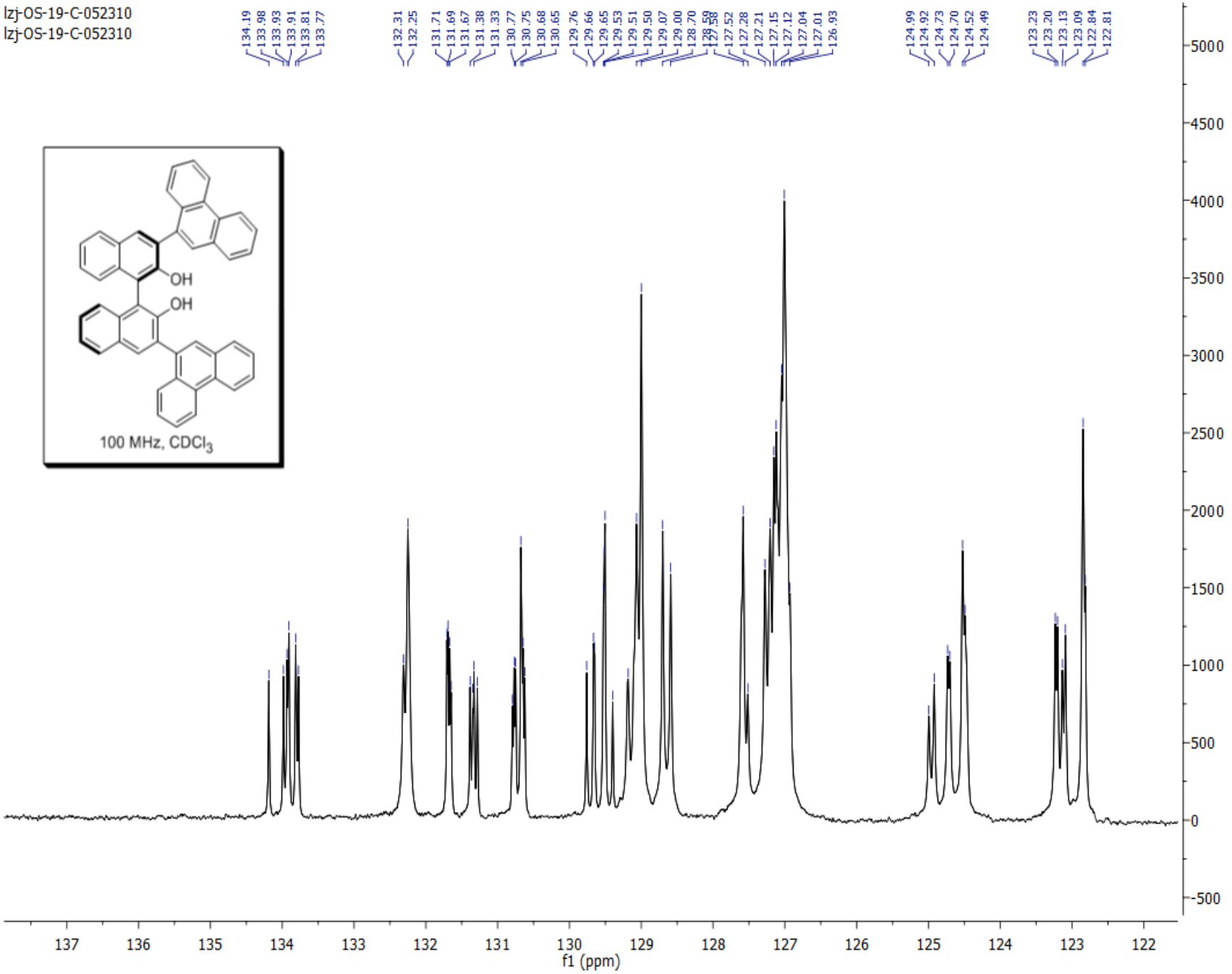
lzj-OS-19-C-052310



lzj-OS-19-C-052310
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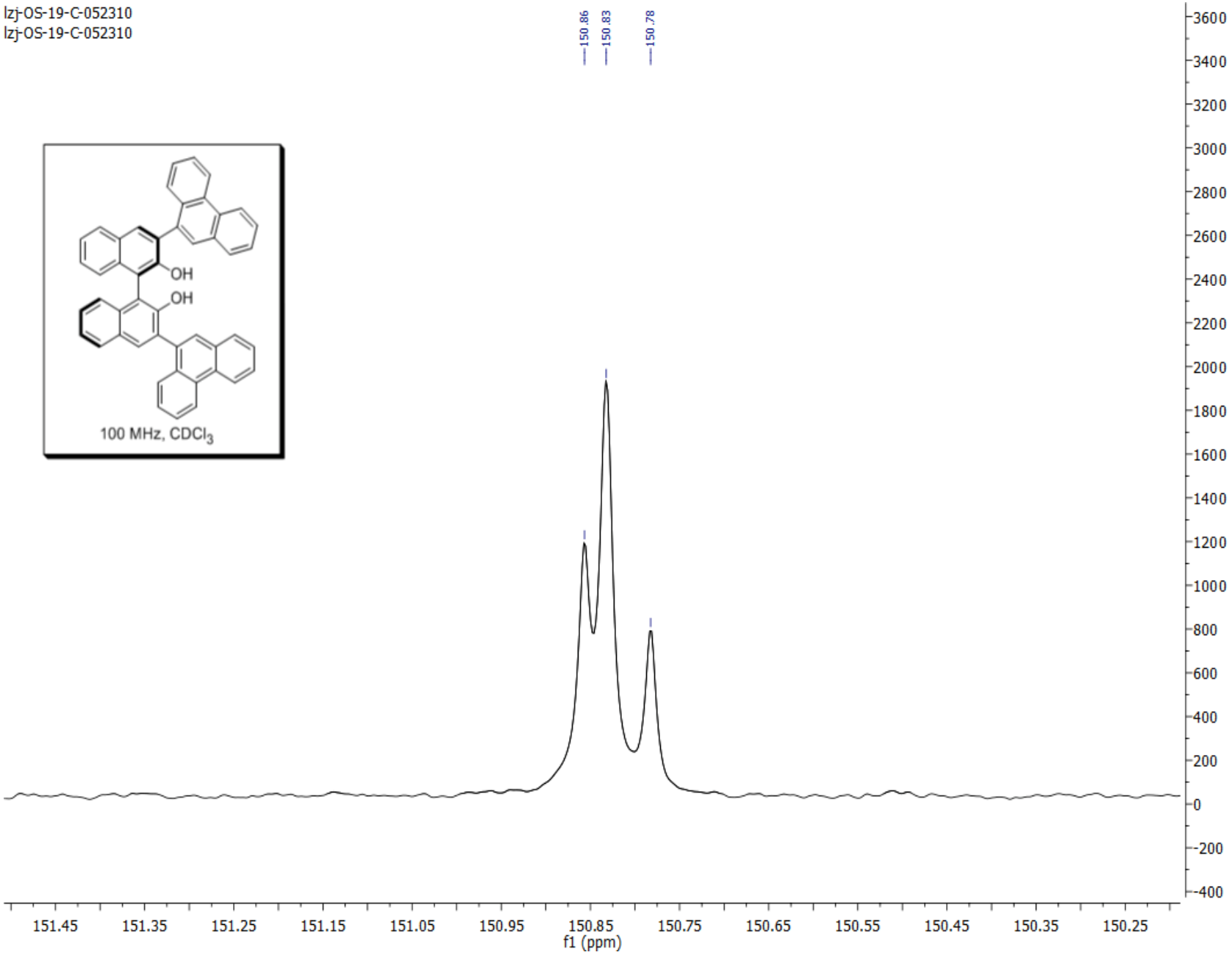
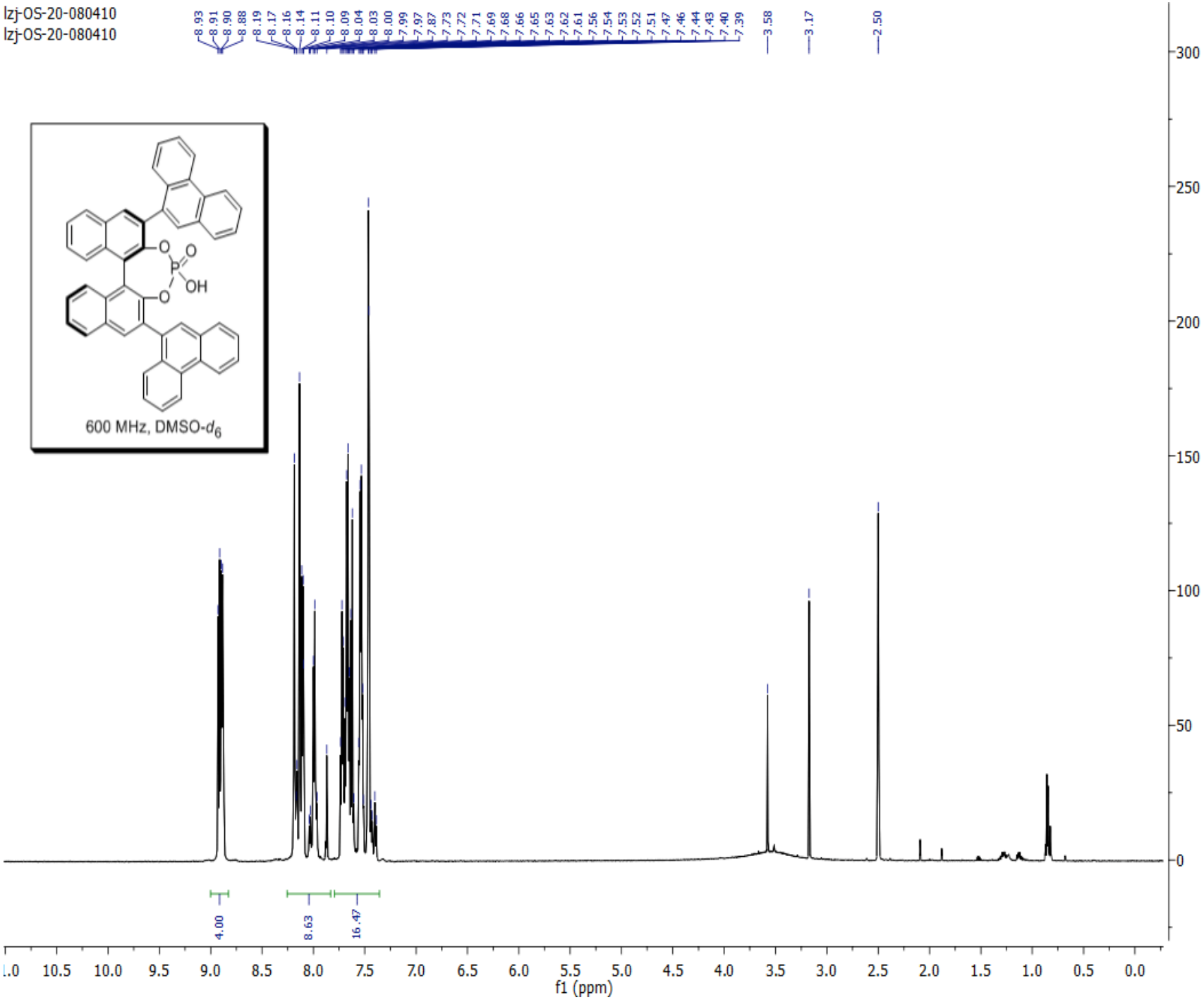
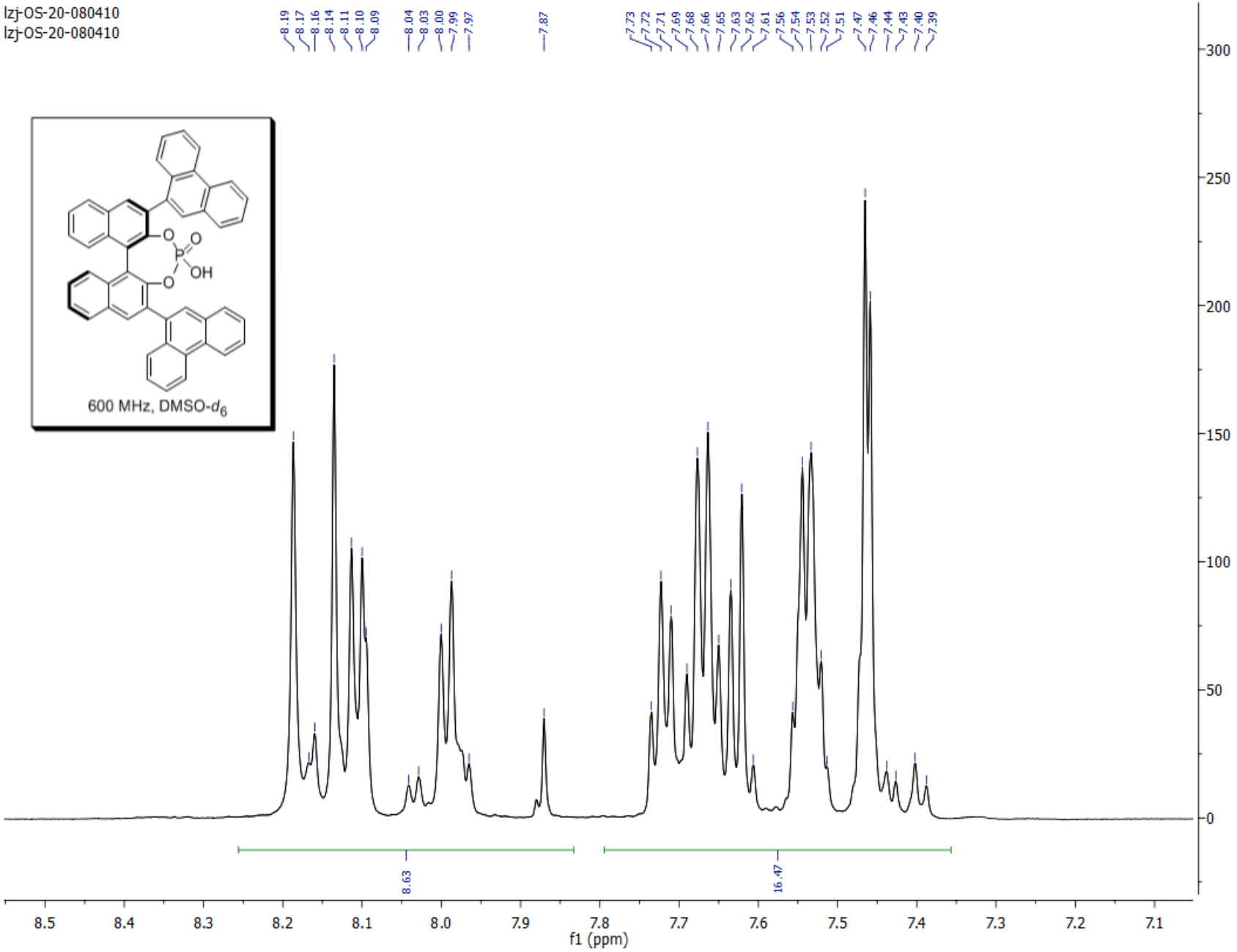
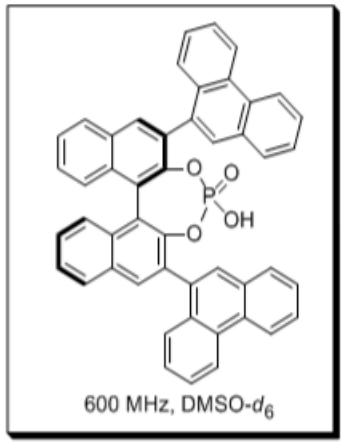


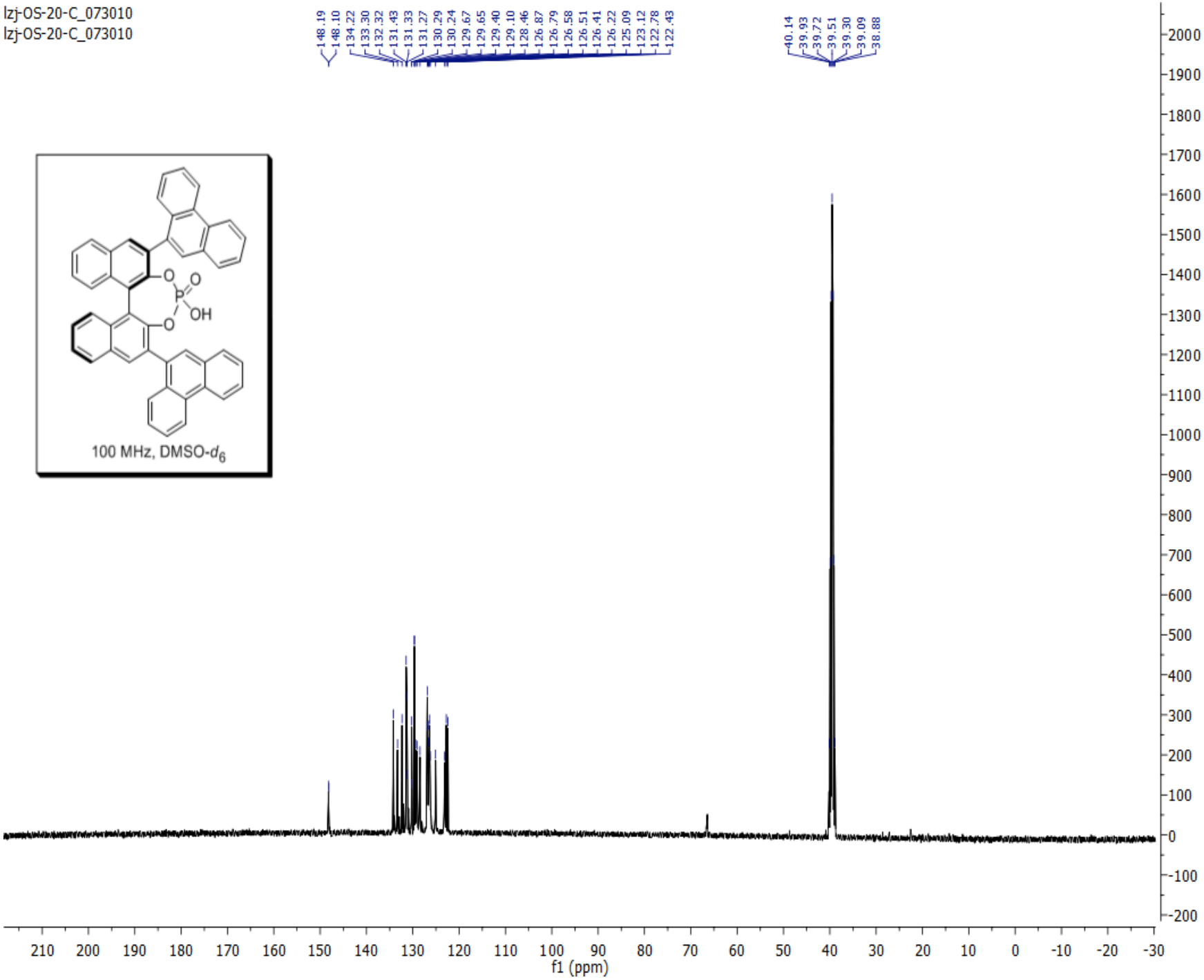

lzj-OS-20-080410
lzj-OS-20-080410
8.93
8.91
8.90
8.88
8.19
8.17
8.16
8.14
8.11
8.10
8.09
8.04
8.03
8.00
7.99
7.97
7.87
7.73
7.72
7.71
7.69
7.68
7.66
7.65
7.63
7.62
7.61
7.56
7.54
7.53
7.52
7.51
7.47
7.46
7.44
7.43
7.40
7.39
3.58
3.17
2.50
O
O
P
OH
O
600 MHz, DMSO-d_6
4.00
8.63
16.47
f1 (ppm)


lzj-OS-20-080410
lzj-OS-20-080410
8.19
8.17
8.16
8.14
8.11
8.10
8.09
8.04
8.03
8.00
7.99
7.97
7.87
7.73
7.72
7.71
7.69
7.68
7.66
7.65
7.63
7.62
7.61
7.56
7.54
7.53
7.52
7.51
7.47
7.46
7.44
7.43
7.40
7.39
O
O
P
OH
O
600 MHz, DMSO-d_6
300
250
200
150
100
50
0
8.63
16.47
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)

lzj-OS-20-080410
lzj-OS-20-080410

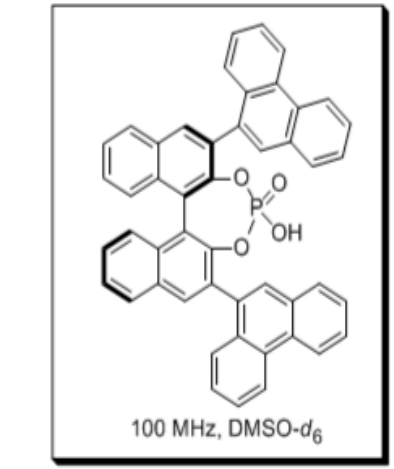


lzj-OS-20-C_073010
lzj-OS-20-C_073010



lzj-OS-20-C_073010

lzj-OS-20-C_073010



100 MHz, DMSO-d_6

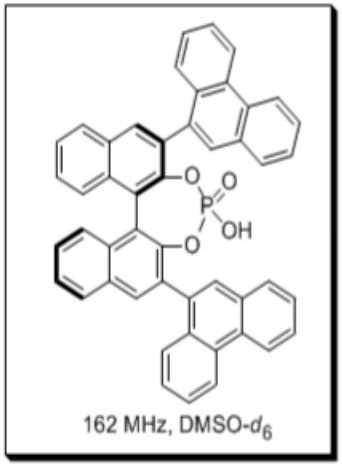
148.19
148.10
134.22
133.30
132.32
131.43
131.33
131.27
130.29
130.24
129.67
129.65
129.40
129.10
128.46
126.87
126.79
126.58
126.51
123.12
122.78
122.43

650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

154 152 150 148 146 144 142 140 138 136 134 132 130 128 126 124 122 120

f1 (ppm)

lzj-OS-20-P-073110
lzj-OS-20-P-073110



162 MHz, DMSO-d_6

2.61

900 850 800 750 700 650 600 550 500 450 400 350 300 250 200 150 100 50 0 -50

40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40

f1 (ppm)