

## SUPPORTING INFORMATION

### Highly Regioselective Isomerization-Hydroformylation of Internal Olefins to Linear Aldehyde Using Rh-Complexes with Tetrakisphosphorus Ligands

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#### Content:

1	Analytical data and synthetic methods for compounds <b>2</b> , <b>3</b> , <b>4</b> and <b>5</b>	S2
2	<sup>1</sup> H NMR and <sup>13</sup> C NMR spectra of compounds <b>2-5</b> .	S10

## General Methods/Instrument Details

All reactions and manipulations were performed in a nitrogen-filled glovebox or using standard Schlenk techniques, unless otherwise noted. Solvents were dried with standard procedures and degassed with N<sub>2</sub>. Column chromatography was performed using 200-400 mesh silica gel supplied by Sorbent technologies. Deuterated solvents were purchased from Aldrich Chemical Company. Thin layer chromatography (TLC) was performed on EM Reagents 0.25- mm silica 60-F plates. <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR spectra were recorded on Varian Mercury 400 MHz FT-NMR spectrometer or Varian Mercury 500 MHz FT-NMR spectrometer. All chemical shifts are reported in ppm. HRMS spectra were recorded on a KRATOS MS 9/50 mass spectrometer. GC analysis was carried out on a Hewlett-Packard 6890 gas chromatograph using capillary columns. Chlorodipyrrolylphosphine was prepared according to the literature procedure.<sup>1</sup> Hydroformylation reactions were repeated several times to ensure reproducibility.

3, 3', 5, 5'-Tetramethylbiphenyl-2, 2', 6, 6'-tetraol was prepared according to the literature procedures.<sup>2</sup>

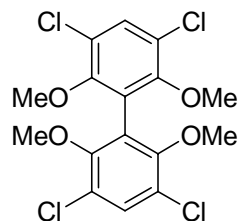
**General Procedure for Synthesis of 3, 3', 5, 5'-tetrachloro tetraol 4b.** To a 250 mL Schlenk flask was added 3, 3', 5, 5'-tetrachloro-2, 2', 6, 6'-tetramethoxybiphenyl **3b** (1.7 g, 4.1 mmol). The flask was degassed and charged with nitrogen. To the flask was added CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The resulting solution was cooled to -78 °C in a dry ice/acetone bath. To the cooled solution was added boron tribromide (1.5 mL, 18.0 mmol) dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 5 h. After cooled to 0 °C, water (50 mL) was added dropwise to quench the reaction. The organic phase was separated and the aqueous phase was extracted with ethyl acetate (3 x 25 mL). The combined organic layers was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by recrystallization from hexanes to give the titled compound **4b** (1.35 g, 92%). <sup>1</sup>H NMR (500 MHz, acetone) δ 7.38 (s, 2 H); IR (film): ν 3525, 3503, 1596, 1449, 1423, 1300, 1281, 1172, 783 cm<sup>-1</sup>; <sup>13</sup>C NMR (126 MHz, acetone) δ 152.2, 130.20, 130.18, 112.6, 110.6; IR (film): ν 3523, 1596, 1457, 1145, 1036 cm<sup>-1</sup>; HRMS (ES<sup>+</sup>) calcd for C<sub>12</sub>H<sub>5</sub>Cl<sub>4</sub>O<sub>4</sub> [M-H]<sup>+</sup> 352.8942, found 352.8965.

**General Procedure for Synthesis of Ligand 1. 3, 3', 5, 5'-Tetrachlorobiphenyl-2, 2', 6, 6'-tetrakis-(dipyrrolylphosphoramidite) (5b).** To a solution of chlorodipyrrolylphosphine (55 mmol, 10.9 g) in THF (50 mL) was added dropwise triethylamine (13 mL) and a solution of 3, 3', 5, 5'-tetrachloro tetraol (10 mmol, 3.6 g) in THF (100 mL) at room temperature. The triethylamine-HCl salts were formed immediately after the addition. The reaction mixture was stirred for 6 h at room temperature. The triethylamine-HCl salts were then filtered off, and the solvent was removed under vacuum. The crude product was purified by recrystallization from hexanes three times to afford the pure ligand **5b** (2.2 g, 22%) as an air-stable colorless solid: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.26 (s, 2 H), 6.65 (brs, 16 H), 6.21 (t, *J* = 2.2 Hz, 16 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 147.6, 131.9, 123.0, 121.40, 121.39, 121.33, 121.22, 121.15, 113.7, 113.6, 112.5, 112.4, 112.38, 112.28; <sup>31</sup>P NMR (161 MHz, CDCl<sub>3</sub>) δ 109.0; IR (film): ν 1462, 1188,

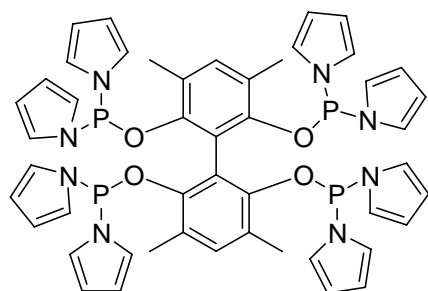
<sup>1</sup> a) R. Jackstell, H. Klein, M. Beller, K.-D. Wiese, D. Rottger, *Eur. J. Org. Chem.* **2001**, 20, 3871-3877. b) S. C. van der Slot, J. Duran, J. Luten, P. C. J. Kamer, P. W. N. M. van Leeuwen, *Organometallics* **2002**, 21, 3873-3883.

<sup>2</sup> Davis, T. L.; Walker, J. F. *J. Am. Chem. Soc.* **1930**, 52, 358-361.

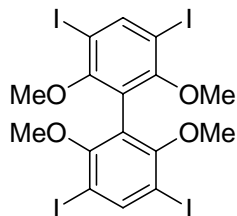
1063, 1057, 1031, 731  $\text{cm}^{-1}$ ; HRMS ( $\text{ES}^+$ ) calcd for  $\text{C}_{44}\text{H}_{35}\text{Cl}_4\text{N}_8\text{O}_4\text{P}_4$   $[\text{M}+\text{H}]^+$  1003.0486, found 1003.0463.



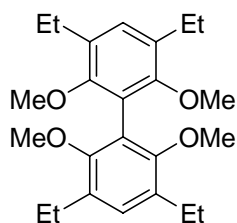
**3, 3', 5, 5'-Tetrachloro-2, 2' 6, 6'-Tetramethoxybiphenyl (3b).** A solution of 5 mL (62.5 mmol) of  $\text{SO}_2\text{Cl}_2$  in 5 mL of  $\text{CHCl}_3$  was added dropwise to a solution of 2.8 g (10 mmol) of 2, 2', 6, 6'-tetramethoxybiphenyl **1** in 20 mL of  $\text{CHCl}_3$  at room temperature. The solution was stirred and monitored by TLC plate. After 30 min, saturated NaCl solution was added carefully to the reaction mixture and the organic layer was separated. The water layer was extracted three times with chloroform (20 mL) and the organic layer was combined and dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated and the residue was passed through a short silica gel plug. The solvent was evaporated and 3.8 g of white solid was obtained in 91% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51 (s, 2 H), 3.67 (s, 12 H);  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  153.4, 130.1, 125.1, 123.5, 60.9; IR (film):  $\nu$  1467, 1419, 1284, 1102, 1017, 882  $\text{cm}^{-1}$ ; HRMS ( $\text{ES}^+$ ) calcd for  $\text{C}_{16}\text{H}_{18}\text{NCl}_4\text{O}_4$   $[\text{M}+\text{H}]^+$  427.9990, found 427.9985.



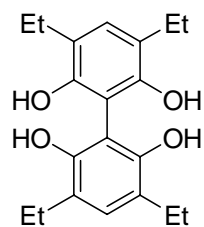
**3, 3', 5, 5'-Tetramethylbiphenyl-2, 2' 6, 6'-tetrakis-(dipyrrolylphosphoramidite) (5c).** Ligand **5c** was prepared according to the general procedure using chlorodipyrrolylphosphine (1.7 g, 8.3 mmol) and 3, 3', 5, 5'-tetramethylbiphenyl-2, 2', 6, 6'-tetraol **4c** (0.5 g, 1.9 mmol). Purification by recrystallization from hexanes gave **5c** as a white solid in 34% yield (0.6 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (brs, 16 H), 6.72 (s, 2 H), 6.20 (t,  $J = 2.2$  Hz, 16 H), 1.67 (s, 12 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.0, 134.1, 126.6, 121.31, 121.25, 121.21, 121.13, 113.2, 113.1, 112.0, 111.9, 111.8, 111.7, 16.3;  $^{31}\text{P}$  NMR (161 MHz,  $\text{CDCl}_3$ )  $\delta$  105.6; IR (film):  $\nu$  1453, 1190, 1179, 1056, 1037, 729  $\text{cm}^{-1}$ ; HRMS ( $\text{ES}^+$ ) calcd for  $\text{C}_{48}\text{H}_{47}\text{N}_8\text{O}_4\text{P}_4$   $[\text{M}+\text{H}]^+$  923.2671, found 923.2651.



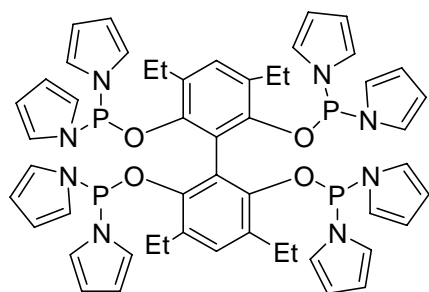
**3, 3', 5, 5'-Tetraiodo-2, 2' 6, 6'-Tetramethoxybiphenyl (2).** A 200-ml., three-necked flask is charged with 13.8 g. (50.0 mmol) of 2, 2' 6, 6'-Tetramethoxybiphenyl **1**, 9.1 g. (40.0 mmol) of periodic acid dihydrate, and 20.4 g. (80.0 mmol) of iodine. A solution of 3 mL of concentrated sulfuric acid and 20 mL of water in 100 mL of glacial acetic acid is added to this mixture. The resulting purple solution is heated at 80° with stirring for approximately 10 hours until the color of iodine disappears. The reaction mixture is diluted with approximately 250 mL of water, and the white-yellow solid that separates is collected on a Büchner funnel and washed three times with 100-mL portions of water. The product is recrystallized from boiling acetone as colorless, fine needles (31.8 g, 82%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.28 (s, 2 H), 3.59 (s, 12 H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 158.9, 147.6, 124.8, 86.7, 61.0; IR (film): ν 1641, 1450, 1397, 1250, 1154, 1059, 921 cm<sup>-1</sup>; HRMS (ES<sup>+</sup>) calcd for C<sub>16</sub>H<sub>18</sub>NI<sub>4</sub>O<sub>4</sub> [M+NH<sub>4</sub>]<sup>+</sup> 795.7415, found 795.7441.



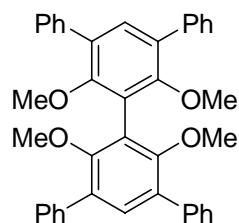
**3, 3', 5, 5'-Tetraethyl-2, 2' 6, 6'-Tetramethoxybiphenyl (3d).** 3, 3', 5, 5'-Tetraiodo-2, 2' 6, 6'-Tetramethoxybiphenyl **2** (7.8 g, 10 mmol) and ethynyltrimethylsilane (8.2 mL g, 58.0 mmol) in a mixture of triethylamine (100 mL) and piperidine (30 mL) was treated with PdCl<sub>2</sub>(PhCN)<sub>2</sub>, (0.4 mg, 1.0 mmol), triphenylphosphine (275 mg, 1.0 mmol), and CuI (80 mg). The originally yellow solution turned to green and then brown. After 3 h at room temperature it was heated at 80 °C for 24 h. The precipitate was filtered and the filtration was passed through a short silica gel plug. The obtained solution was evaporated and treated with a solution of KOH (6.0 g, 108.0 mmol) in methanol (40 mL). The reaction solution was stirred at room temperature for 2 h until TLC analysis indicated that the reaction was complete. Ether-water workup and the obtained yellow liquid was dissolved in 200 mL of mixture of ethyl acetate and methanol and combined with 5 wt% Pd/C (0.5 g) in an autoclave under a 200 psi of hydrogen atmosphere. The reaction was stirred at room temperature for 2 h until no hydrogen absorption was observed. Filtration and flash chromatography afford 2.9 g of white solid in 73% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.09 (s, 2 H), 3.53 (s, 12 H), 2.69 (q, *J* = 7.5 Hz, 8 H), 1.27 (t, *J* = 7.5 Hz, 12 H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.6, 132.2, 128.8, 123.3, 60.4, 22.9, 15.0; IR (film): ν 1468, 1425, 1058 cm<sup>-1</sup>; HRMS (ES<sup>+</sup>) calcd for C<sub>24</sub>H<sub>35</sub>O<sub>4</sub> [M+H]<sup>+</sup> 387.2535, found 387.2526.



**3, 3', 5, 5'-Tetraethylbiphenyl-2, 2' 6, 6'-tetranol (4d).** Tetranol was prepared according to the general procedure using 3, 3', 5, 5'-Tetraethyl-2, 2' 6, 6'-Tetramethoxybiphenyl **3d** (2.9 g, 7.3 mmol) and boron tribromide (3.0 mL, 36.0 mmol). Purification by recrystallization from hexanes gave **4d** as a white solid in 92% yield (2.2 g).  $^1\text{H}$  NMR (500 MHz, acetone)  $\delta$  6.92 (s, 2 H), 6.55 (s, 4 H), 2.59 (q,  $J = 7.5$  Hz, 8 H), 1.18 (t,  $J = 7.5$  Hz, 12 H);  $^{13}\text{C}$  NMR (126 MHz, acetone)  $\delta$  152.3, 130.7, 122.8, 107.0, 23.8, 15.1; IR (film):  $\nu$  3530, 3503, 1472, 1173, 1092  $\text{cm}^{-1}$ ; HRMS ( $\text{ES}^+$ ) calcd for  $\text{C}_{20}\text{H}_{27}\text{O}_4$   $[\text{M}+\text{H}]^+$  331.1909, found 331.1905.

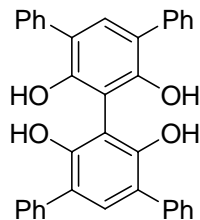


**3, 3', 5, 5'-Tetraethylbiphenyl-2, 2' 6, 6'-tetrakis-(dipyrrolylphosphoramidite) (5d).** Ligand **5d** was prepared according to the general procedure using 3, 3', 5, 5'-Tetraethylbiphenyl-2, 2' 6, 6'-tetranol **4d** (2.0 g, 6.0 mmol) and chlorodipyrrolylphosphine (5.2 g, 25.4 mmol). Purification by recrystallization from hexanes gave **5d** as a white solid in 28% yield (1.6 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.77 (brs, 18 H), 6.21 (t,  $J = 2.2$  Hz, 16 H), 2.01 (q,  $J = 7.6$  Hz, 8 H), 0.90 (t,  $J = 7.6$  Hz, 12 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.9, 132.3, 130.7, 121.1, 118.9, 111.8, 22.8, 14.3;  $^{31}\text{P}$  NMR (161 MHz,  $\text{CDCl}_3$ )  $\delta$  105.6; IR (film):  $\nu$  1453, 1174, 1083, 1044, 1025, 729  $\text{cm}^{-1}$ ; HRMS ( $\text{ES}^+$ ) calcd for  $\text{C}_{52}\text{H}_{55}\text{N}_8\text{O}_4\text{P}_4$   $[\text{M}+\text{H}]^+$  979.3297, found 979.3257.

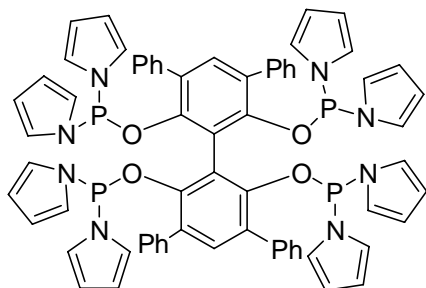


**3, 3', 5, 5'-Tetraphenyl-2, 2' 6, 6'-Tetramethoxybiphenyl (3e).** A mixture of phenylboronic acid (14.6 g, 120.0 mmol), 3, 3', 5, 5'-Tetraiodo-2, 2' 6, 6'-Tetramethoxybiphenyl **2** (7.8 g, 10 mmol), palladium tetrakis(triphenylphosphine) (1.0 g), and potassium carbonate (24 g, 160 mmol) in dry dioxane (150 mL) was stirred under nitrogen for 24 h at 85  $^\circ\text{C}$ . The resulting mixture was cooled and poured into a solution of ice with concentrated hydrochloric acid (3:1) and the organic phase was extracted twice with dichloromethane, dried over magnesium sulfate. After evaporation of the solvent, the mixture was subjected to flash chromatography to give 4.5 g (78%) of 3, 3', 5, 5'-Tetraphenyl-2, 2' 6, 6'-Tetramethoxybiphenyl **3e** as a white solid.  $^1\text{H}$  NMR

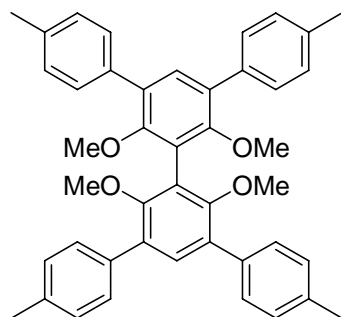
(500 MHz, CDCl<sub>3</sub>)  $\delta$  7.66 (d,  $J$  = 7.5 Hz, 8 H), 7.44 (d,  $J$  = 7.5 Hz, 8 H), 7.42 (s, 2 H), 7.36 (t,  $J$  = 7.5 Hz, 4 H), 3.42 (s, 12 H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  155.7, 138.7, 132.6, 130.4, 129.0, 128.3, 126.9, 124.1, 60.4; IR (film):  $\nu$  1459, 1410, 1215, 1068, 929, 738 cm<sup>-1</sup>; HRMS (ES<sup>+</sup>) calcd for C<sub>40</sub>H<sub>35</sub>O<sub>4</sub> [M+H]<sup>+</sup> 579.2535, found 579.2529.



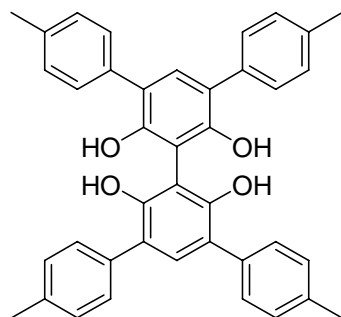
**3, 3', 5, 5'-Tetraphenylbiphenyl-2, 2' 6, 6'-tetranol(4e).** Tetranol **4e** was prepared according to the general procedure using 3, 3', 5, 5'-Tetraphenyl-2, 2' 6, 6'-Tetramethoxybiphenyl **3e** (4.5 g, 8.0 mmol) and boron tribromide (3.5 mL, 42.0 mmol). Purification by recrystallization from hexanes gave **4e** as a white solid in 89% yield (3.7 g). <sup>1</sup>H NMR (500 MHz, acetone)  $\delta$  7.69 (d,  $J$  = 7.5 Hz, 8 H), 7.52 (s, 4 H), 7.40 (t,  $J$  = 7.5 Hz, 8 H), 7.32 (s, 2 H), 7.28 (t,  $J$  = 7.5 Hz, 4 H); IR (film):  $\nu$  3523, 1456, 1154, 1033 cm<sup>-1</sup>; <sup>13</sup>C NMR (126 MHz, acetone)  $\delta$  154.1, 140.0, 133.7, 130.3, 129.0, 127.2, 122.5, 108.1; HRMS (ES<sup>+</sup>) calcd for C<sub>36</sub>H<sub>27</sub>O<sub>4</sub> [M+H]<sup>+</sup> 523.1909, found 523.1914.



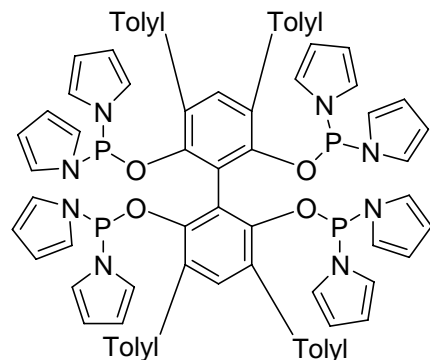
**3, 3', 5, 5'-Tetraphenylbiphenyl-2, 2' 6, 6'-tetrakis-(dipyrrolylphosphoramidite) (5e).** Ligand **5e** was prepared according to the general procedure using 3, 3', 5, 5'-Tetraphenylbiphenyl-2, 2' 6, 6'-tetranol **4e** (2.6 g, 5.0 mmol) and chlorodipyrrolylphosphine (4.8 g, 24.3 mmol). Purification by recrystallization from hexanes gave **5e** as a white solid in 26% yield (1.5 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.26 (s, 2 H), 7.24 (m, 4 H), 7.20 (m, 8 H), 7.12 (m, 8 H), 6.49 (brs, 16 H), 6.07 (t,  $J$  = 2.0 Hz, 16 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  149.42, 149.40, 136.7, 135.1, 131.2, 129.5, 128.3, 127.5, 121.0, 120.9, 118.93, 120.86, 120.79, 120.77, 120.0, 111.8; <sup>31</sup>P NMR (161 MHz, CDCl<sub>3</sub>)  $\delta$  106.5; IR (film):  $\nu$  1451, 1419, 1178, 1054, 1036, 730 cm<sup>-1</sup>; HRMS (ES<sup>+</sup>) calcd for C<sub>68</sub>H<sub>55</sub>N<sub>8</sub>O<sub>4</sub>P<sub>4</sub> [M+H]<sup>+</sup> 1171.3297, found 1171.3259.



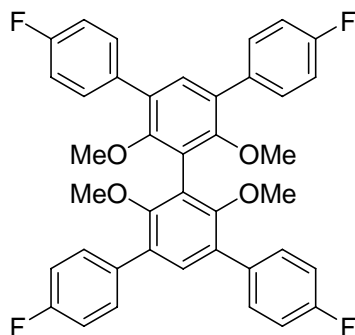
**3, 3', 5, 5'-Tetratolyl-2, 2' 6, 6'-Tetramethoxybiphenyl (3f).** 3, 3', 5, 5'-Tetratolyl-2, 2' 6, 6'-Tetramethoxybiphenyl **3f** was prepared according to the general procedure for synthesis of 3, 3', 5, 5'-tetraphenyl-2, 2' 6, 6'-tetramethoxybiphenyl **3e** by using tolylboronic acid (24.5 g, 180.0 mmol), 3, 3', 5, 5'-tetraiodo-2, 2' 6, 6'-tetramethoxybiphenyl **2** (11.9 g, 15.2 mmol). Purification by flash chromatography gave **3f** as a white solid in 72% yield (6.9 g).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (d,  $J = 7.5$  Hz, 8 H), 7.44 (s, 2 H), 7.26 (d,  $J = 7.5$  Hz, 8 H), 3.44 (s, 12 H), 2.44 (s, 12 H);  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  155.5, 136.5, 135.9, 132.3, 130.2, 128.97, 128.88, 124.2, 60.3, 21.2; IR (film):  $\nu$  1457, 1413, 1054  $\text{cm}^{-1}$ ; HRMS ( $\text{ES}^+$ ) calcd for  $\text{C}_{44}\text{H}_{43}\text{O}_4$   $[\text{M}+\text{H}]^+$  635.3161, found 635.3133.



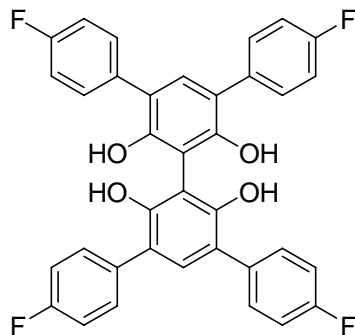
**3, 3', 5, 5'-Tetratolylbiphenyl-2, 2' 6, 6'-tetranol(4f).** Tetranol **4f** was prepared according to the general procedure using 3, 3', 5, 5'-Tetratolyl-2, 2' 6, 6'-Tetramethoxybiphenyl (5.7 g, 9.0 mmol) and boron tribromide (3.9 mL, 46.8 mmol). Purification by recrystallization from hexanes gave **4f** as a white solid in 89% yield (4.6 g).  $^1\text{H NMR}$  (500 MHz, acetone)  $\delta$  7.56 (d,  $J = 7.5$  Hz, 8 H), 7.36 (s, 4 H), 7.28 (s, 2 H), 7.21 (d,  $J = 7.5$  Hz, 8 H);  $^{13}\text{C NMR}$  (126 MHz, acetone)  $\delta$  153.8, 137.0, 136.5, 133.4, 130.2, 129.6, 122.3, 108.1, 21.2; IR (film):  $\nu$  3520, 1593, 1455, 1155, 1024  $\text{cm}^{-1}$ ; HRMS ( $\text{ES}^+$ ) calcd for  $\text{C}_{40}\text{H}_{35}\text{O}_4$   $[\text{M}+\text{H}]^+$  579.2535, found 579.2532.



**3, 3', 5, 5'-Tetratolylphenyl-2, 2' 6, 6'-tetrakis-(dipyrrolylphosphoramidite) (5f).** Ligand **5f** was prepared according to the general procedure using 3, 3', 5, 5'-Tetratolylbiphenyl-2, 2' 6, 6'-tetranol **4f** (2.8 g, 4.5 mmol) and chlorodipyrrolylphosphine (3.9 g). Purification by recrystallization from hexanes gave **5f** as a white solid in 21% yield (1.2 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.20 (s, 2 H), 7.00 (d, *J* = 2.0 Hz, 8 H), 6.95 (d, *J* = 2.0 Hz, 8 H), 6.49 (brs, 16 H), 6.05 (t, *J* = 2.0 Hz, 16 H), 2.34 (s, 12 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.3, 137.2, 134.8, 133.7, 131.1, 129.4, 129.0, 120.92, 120.88, 120.85, 120.78, 111.6, 21.2; IR (film): ν 1449, 1178, 1073, 1054, 1037, 730 cm<sup>-1</sup>; <sup>31</sup>P NMR (161 MHz, CDCl<sub>3</sub>) δ 106.8; HRMS (ES<sup>+</sup>) calcd for C<sub>72</sub>H<sub>63</sub>N<sub>8</sub>O<sub>4</sub>P<sub>4</sub> [M+H]<sup>+</sup> 1227.3923, found 1227.3933.

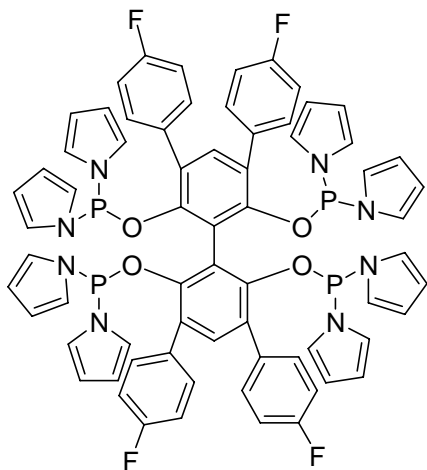


**3, 3', 5, 5'-Tetra(4-fluorophenyl)-2, 2' 6, 6'-Tetramethoxybiphenyl (3g).** 3, 3', 5, 5'-Tetra(4-fluorophenyl)-2, 2' 6, 6'-Tetramethoxybiphenyl **3g** was prepared according to the general procedure for synthesis of 3, 3', 5, 5'-tetraphenyl-2, 2' 6, 6'-tetramethoxybiphenyl **3e** by using 4-fluorophenylboronic acid (22.8 g, 163.0 mmol), 3, 3', 5, 5'-tetraiodo-2, 2' 6, 6'-tetramethoxybiphenyl **2** (10.6 g, 13.6 mmol). Purification by flash chromatography gave **3g** as a white solid in 80% yield (7.1 g). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.65-7.60 (m, 8 H), 7.38 (s, 2 H), 7.17-7.11 (m, 8 H), 3.40 (s, 12 H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ 115.9; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.3, 160.9, 155.6, 134.40, 134.38, 132.3, 130.63, 130.54, 129.6, 124.2, 115.4, 115.1, 60.3; IR (film): ν 1586, 1461, 1420, 1055 cm<sup>-1</sup>; HRMS (ES<sup>+</sup>) calcd for C<sub>40</sub>H<sub>31</sub>F<sub>4</sub>O<sub>4</sub> [M+H]<sup>+</sup> 651.2158, found 651.2186.



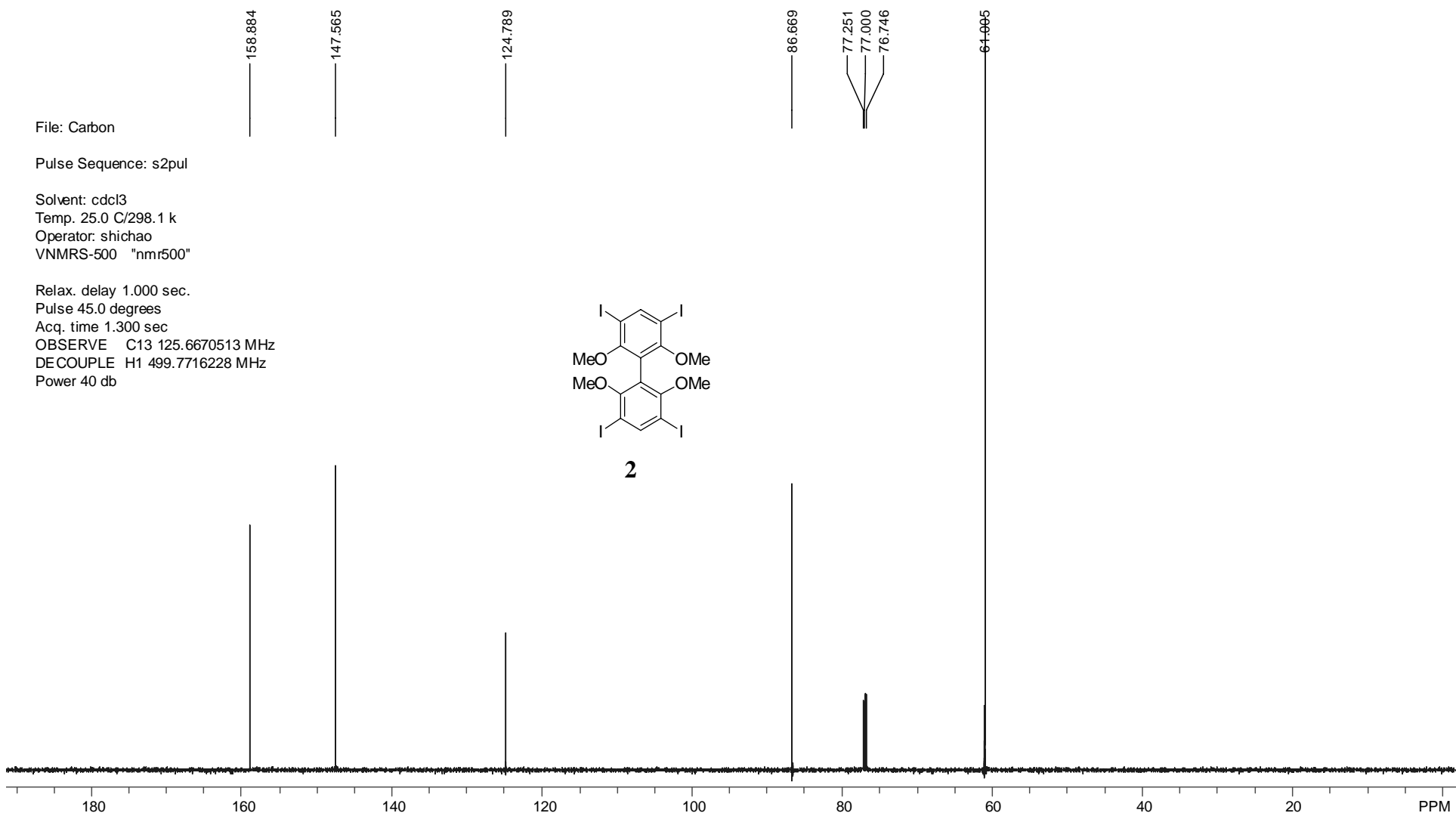
**3, 3', 5, 5'-Tetra(4-fluorophenyl)biphenyl-2, 2' 6, 6'-tetranol (4g).** Tetranol **4g** was prepared according to the general procedure using 3, 3', 5, 5'-Tetra(4-fluorophenyl)-2, 2' 6, 6'-Tetramethoxybiphenyl (6.6 g, 10.2 mmol) **3g** and boron tribromide (7.7 mL, 81.0 mmol). Purification by recrystallization from hexanes gave **4g** as a white solid in 98% yield (6.0 g). <sup>1</sup>H NMR (400 MHz, acetone) δ 7.71 (td, *J*<sub>1</sub> = 7.5 Hz, *J*<sub>2</sub> = 1.2 Hz, 8 H), 7.66 (s, 4 H), 7.31 (s, 2 H), 7.16 (td, *J*<sub>1</sub> = 7.5 Hz, *J*<sub>2</sub> = 1.2 Hz, 8 H); <sup>19</sup>F NMR (376 MHz, acetone) δ 113.5; <sup>13</sup>C NMR (100

MHz, acetone)  $\delta$  163.0, 160.6, 153.5, 135.40, 135.37, 132.85, 132.80, 131.50, 131.43, 131.41, 120.8, 114.9, 114.7, 107.2; IR (film):  $\nu$  3526, 1593, 1458, 1157, 1018  $\text{cm}^{-1}$ ; HRMS ( $\text{ES}^+$ ) calcd for  $\text{C}_{36}\text{H}_{23}\text{F}_4\text{O}_4$   $[\text{M}+\text{H}]^+$  595.1532, found 595.1545.



**3, 3', 5, 5'-Tetra(4-fluorophenyl)biphenyl-2, 2' 6, 6'-tetrakis-(dipyrrolylphosphoramidite) (5g).** Ligand **5g** was prepared according to the general procedure using 3, 3', 5, 5'-Tetra(4-fluorophenyl)biphenyl-2, 2' 6, 6'-tetranol **4g** (5.0 g, 8.4 mmol) and chlorodipyrrolylphosphine (7.5 g, 37.0 mmol). Purification by recrystallization from hexanes gave **5g** as a white solid in 31% yield (3.2 g).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.11 (s, 2 H), 7.09-6.97 (m, 8 H), 6.87-6.76 (m, 8 H), 6.54 (brs, 16 H), 6.11 (t,  $J = 1.5$  Hz, 16 H);  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  118.6;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.6, 161.2, 149.59, 149.52, 134.9, 132.17, 132.14, 131.13, 131.05, 130.7, 120.76, 120.71, 120.68, 115.2, 115.0, 112.0; IR (film):  $\nu$  1453, 1152, 1011  $\text{cm}^{-1}$ ;  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  106.6; HRMS ( $\text{ES}^+$ ) calcd for  $\text{C}_{68}\text{H}_{51}\text{F}_4\text{N}_8\text{O}_4\text{P}_4$   $[\text{M}+\text{H}]^+$  1243.2920, found 1243.2955.

**General Procedure for the Regioselective Isomerization-Hydroformylation of Internal Olefins with Ligand 5a.** A 2-mL vial with a magnetic stirring bar was charged with ligand **5a** (3  $\mu\text{mol}$ , 2.6 mg) and  $\text{Rh}(\text{acac})(\text{CO})_2$  (1  $\mu\text{mol}$ , 0.1 mL of 10 mM solution in toluene). The mixture was stirred for 5 min. 2-Octene (10 mmol, 1.56 mL) was then added, followed by decane (0.1 mL) as internal standard. The reaction mixture was transferred to an autoclave. The autoclave was purged with nitrogen three times and subsequently charged with CO (5 atm) and  $\text{H}_2$  (5 atm). The autoclave was then heated to 100  $^\circ\text{C}$  (the pressure was 11.3 atm). After 1 h, the autoclave was cooled in icy water, and the pressure (9.4 atm) was carefully released in a well-ventilated hood. The reaction mixture was immediately analyzed by GC to determine the turnover number and regioselectivity.



8.282

7.270

3.594

File: Proton

Pulse Sequence: s2pul

Solvent: CDCl3

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-500 "nmr500"

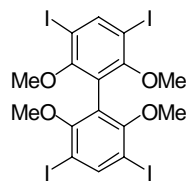
Relax. delay 1.000 sec.

Pulse 45.0 degrees

Acq. time 2.049 sec

OBSERVE H1 499.7691208 MHz

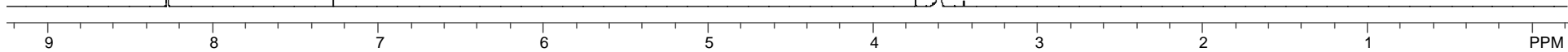
Power 40 db



**2**

12.00

1.56



7.514  
7.270

3.672

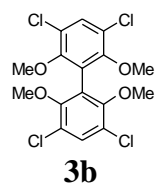
1.274

File: Proton

Pulse Sequence: s2pul

Solvent: CDCl<sub>3</sub>  
Temp. 25.0 C/298.1 k  
Operator: shichao  
VNMR5-500 "nmr500"

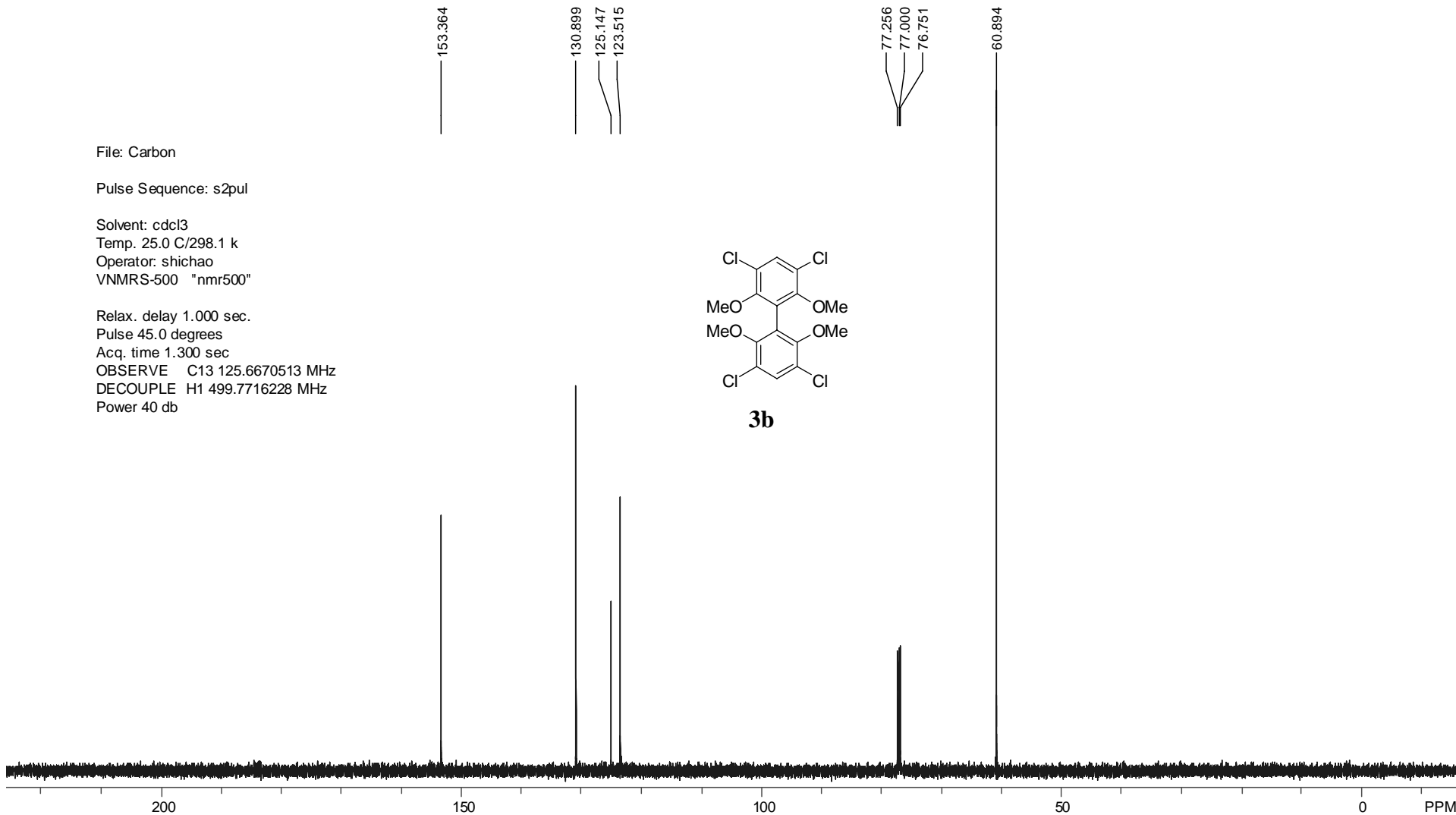
Relax. delay 1.000 sec.  
Pulse 45.0 degrees  
Acq. time 2.049 sec  
OBSERVE H1 499.7691208 MHz  
Power 40 db

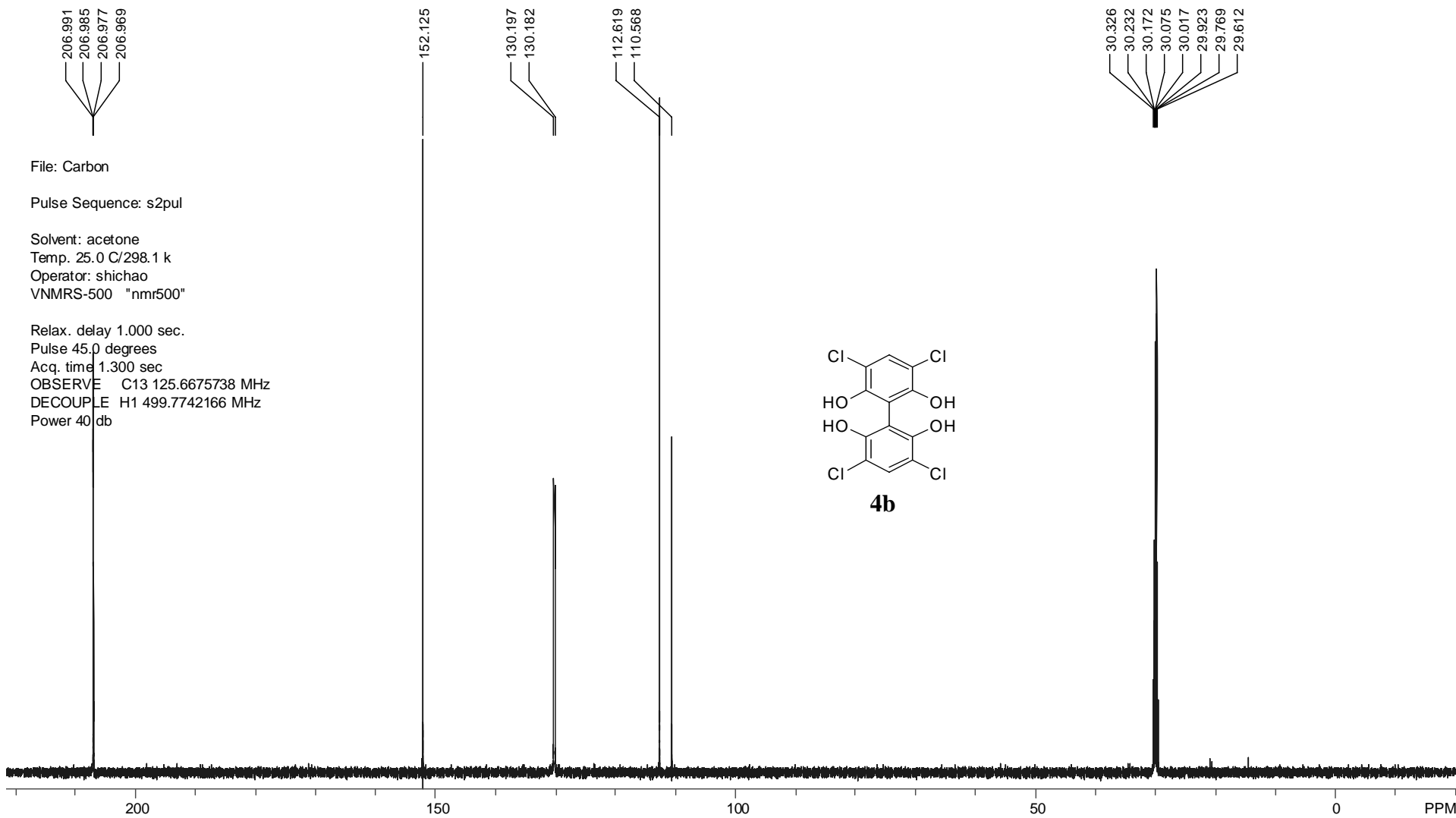


1.78

12.00

9 8 7 6 5 4 3 2 1 0 PPM





File: Proton

Pulse Sequence: s2pul

Solvent: acetone

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-500 "nmr500"

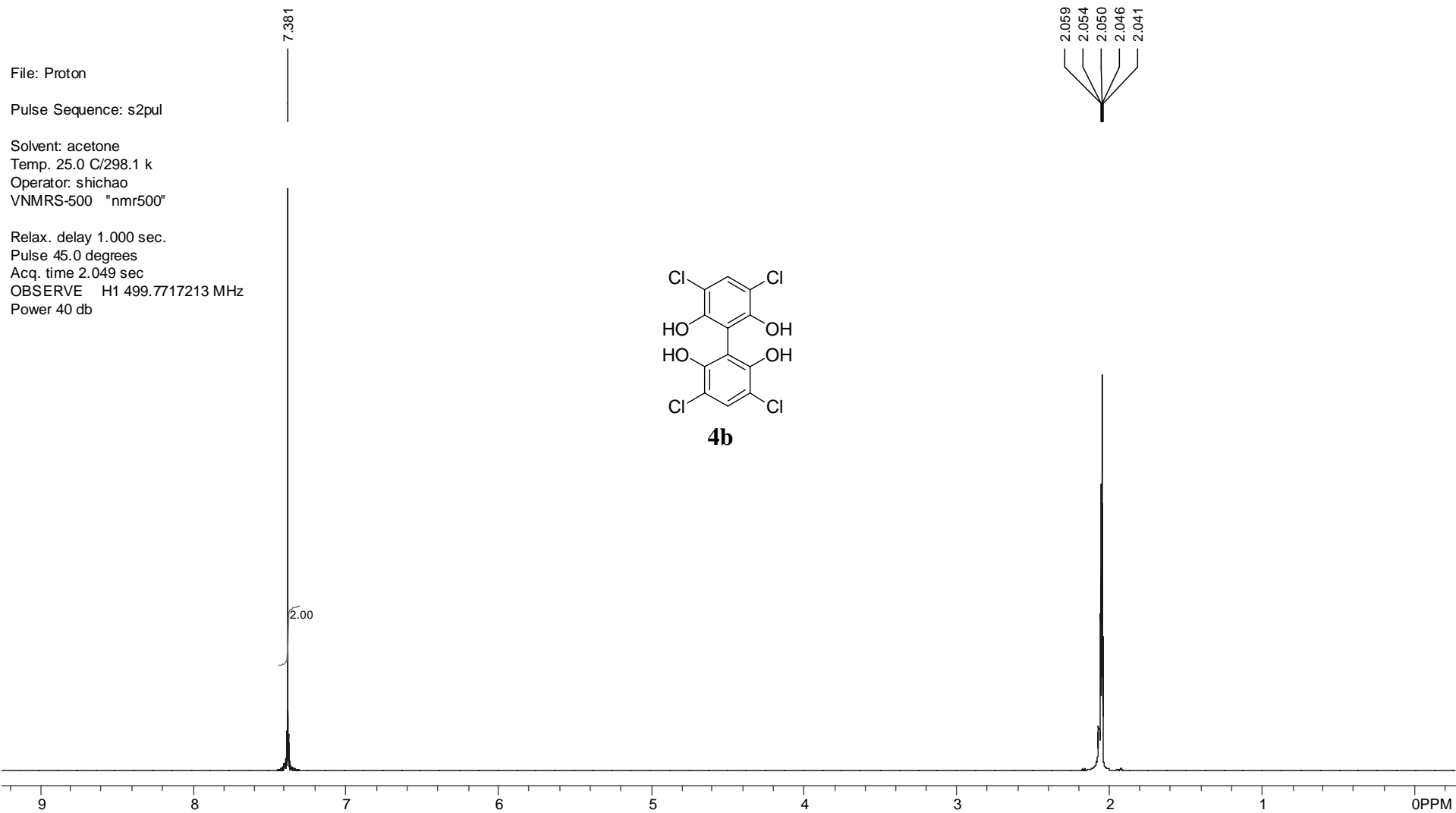
Relax. delay 1.000 sec.

Pulse 45.0 degrees

Acq. time 2.049 sec

OBSERVE H1 499.7717213 MHz

Power 40 db



147.605

131.916

122.968

121.401

121.391

121.332

121.315

121.222

121.154

113.729

113.611

112.481

112.404

112.381

112.331

112.281

77.312

77.000

76.684

File: Carbon

Pulse Sequence: s2pul

Solvent: CDCl<sub>3</sub>

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-400 "nmr400"

Relax. delay 1.000 sec.

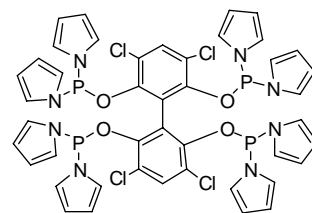
Pulse 45.0 degrees

Acq. time 1.300 sec

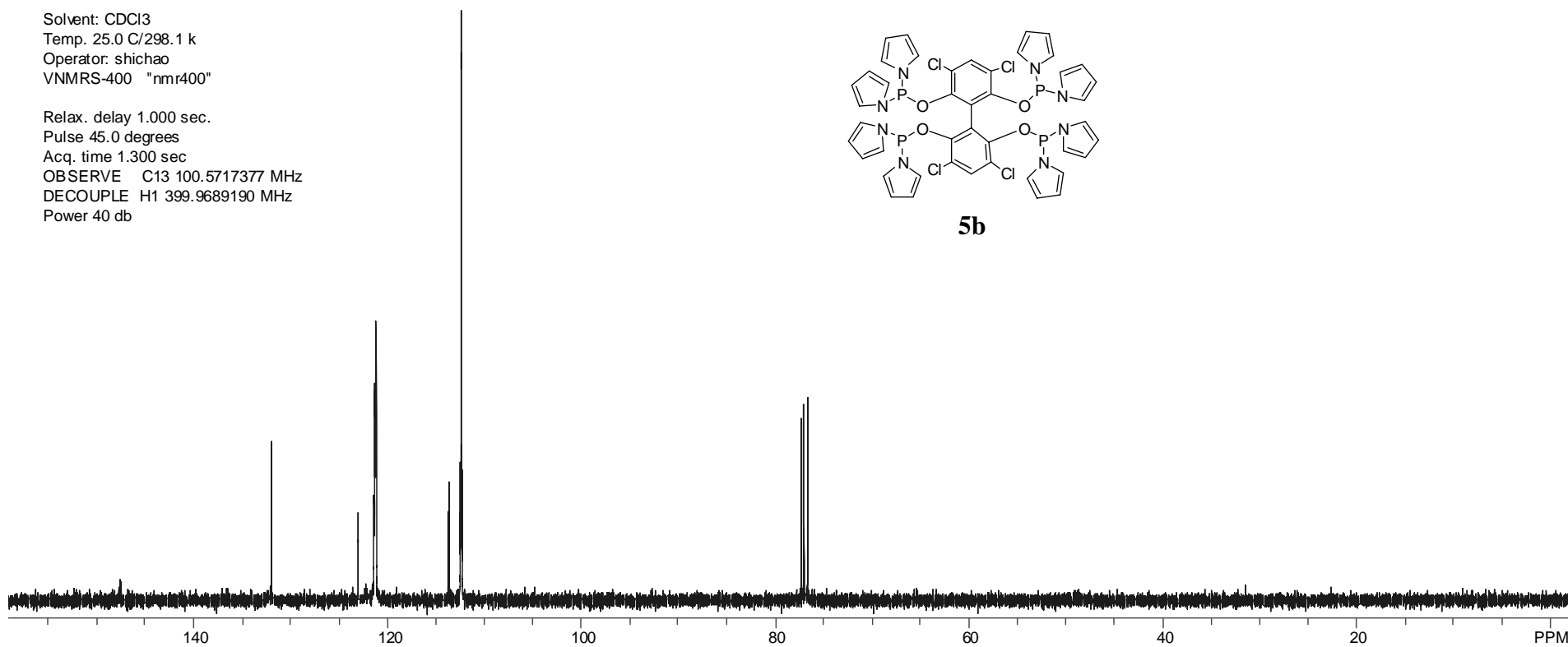
OBSERVE C13 100.5717377 MHz

DECOUPLE H1 399.9689190 MHz

Power 40 db



**5b**



File: Phosphorus

Pulse Sequence: s2pul

Solvent: CDCl<sub>3</sub>

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-400 "nmr400"

Relax. delay 1.000 sec.

Pulse 45.0 degrees

Acq. time 1.600 sec

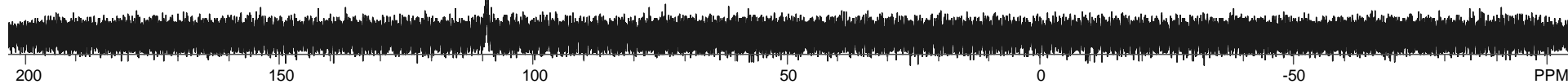
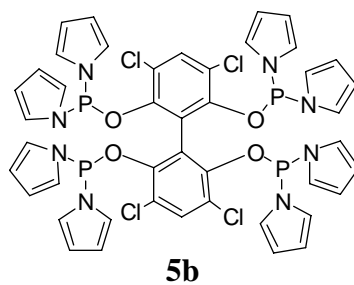
Width 37878.8 Hz

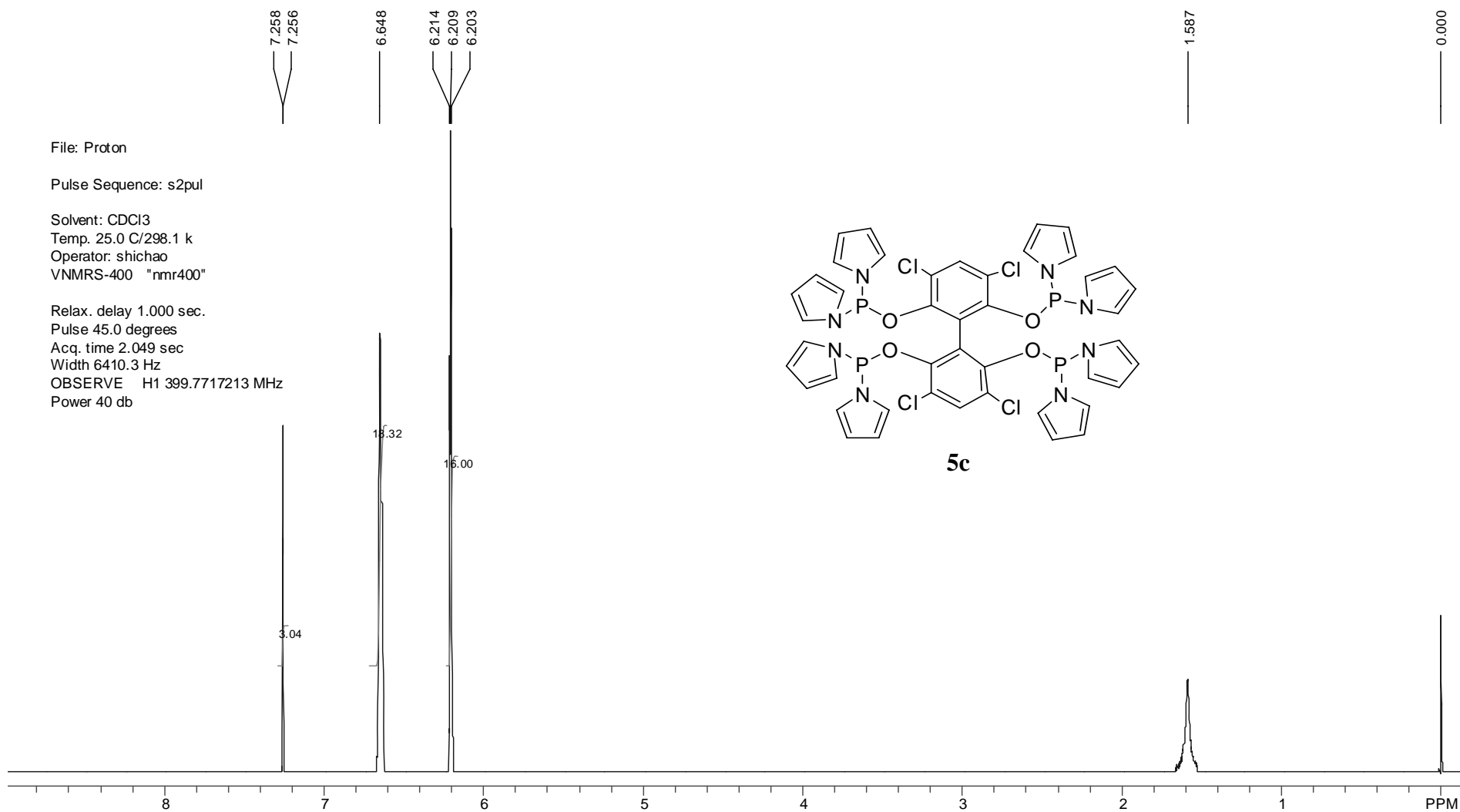
OBSERVE P31 161.9093958 MHz

DECOUPLE H1 399.9689190 MHz

Power 40 db

108.989





File: Phosphorus

Pulse Sequence: s2pul

Solvent: CDCl<sub>3</sub>

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-400 "nmr400"

Relax. delay 1.000 sec.

Pulse 45.0 degrees

Acq. time 1.600 sec

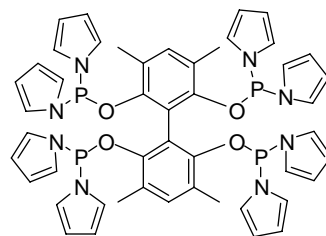
Width 37878.8 Hz

OBSERVE P31 161.9093958 MHz

DECOUPLE H1 399.9689190 MHz

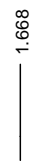
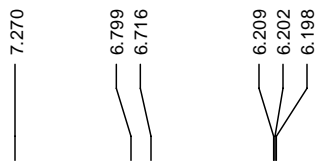
Power 40 db

105.648



5c

180 160 140 120 100 80 60 40 20 PPM

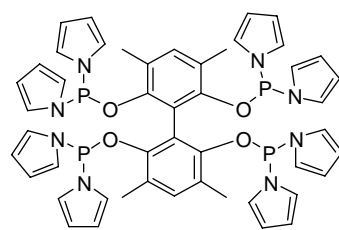


File: Proton

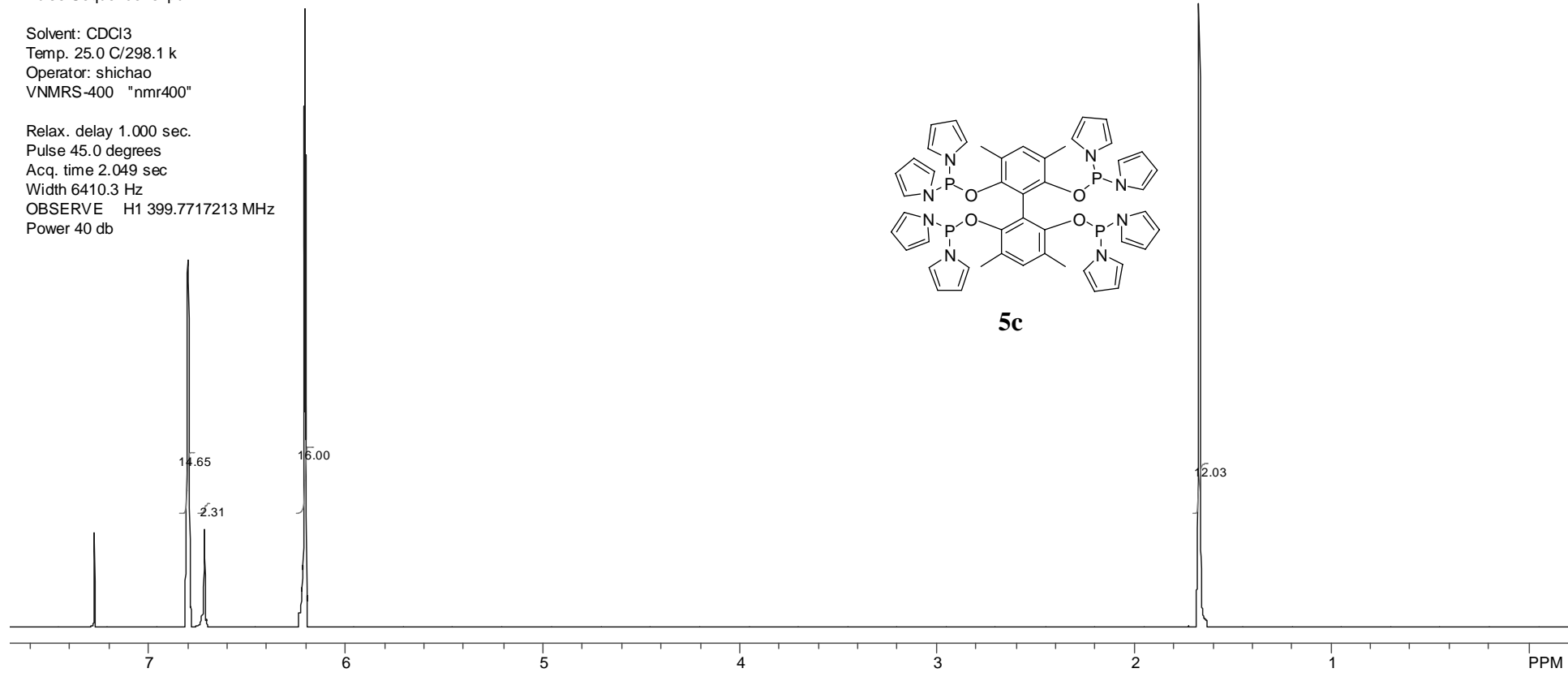
Pulse Sequence: s2pul

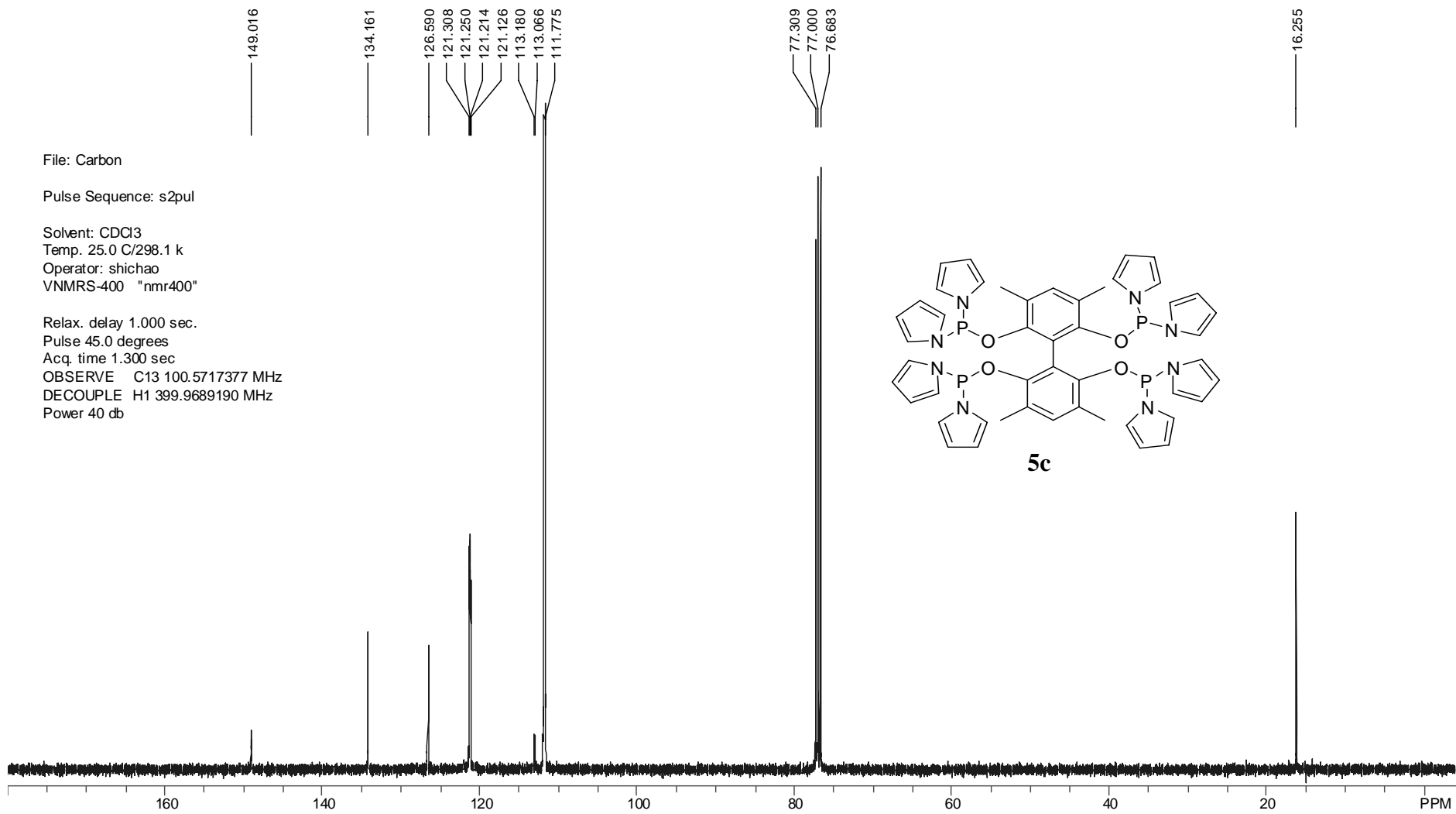
Solvent: CDCl3  
 Temp. 25.0 C/298.1 k  
 Operator: shichao  
 VNMRS-400 "nmr400"

Relax. delay 1.000 sec.  
 Pulse 45.0 degrees  
 Acq. time 2.049 sec  
 Width 6410.3 Hz  
 OBSERVE H1 399.7717213 MHz  
 Power 40 db



**5c**





File: Carbon

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-500 "nmr500"

Relax. delay 1.000 sec.

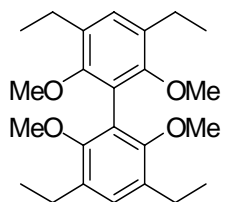
Pulse 45.0 degrees

Acq. time 1.300 sec

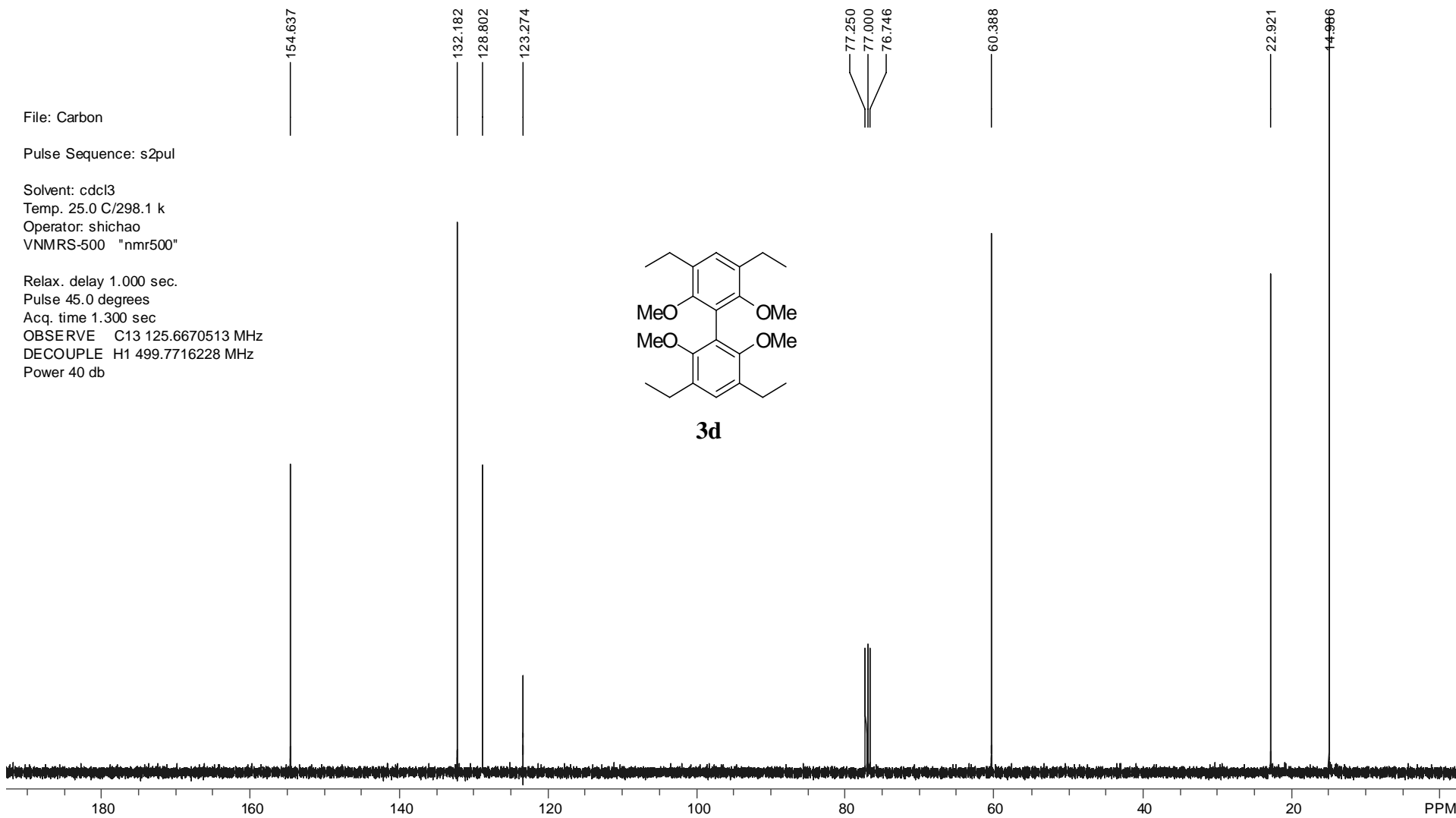
OBSERVE C13 125.6670513 MHz

DECOUPLE H1 499.7716228 MHz

Power 40 db



3d



7.270  
7.086

File: Carbon

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-500 "nmr500"

Relax. delay 1.000 sec.

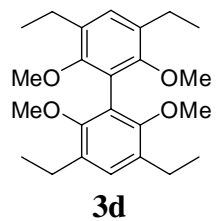
Pulse 45.0 degrees

Acq. time 1.300 sec

OBSERVE C13 125.6670513 MHz

DECOUPLE H1 499.7716228 MHz

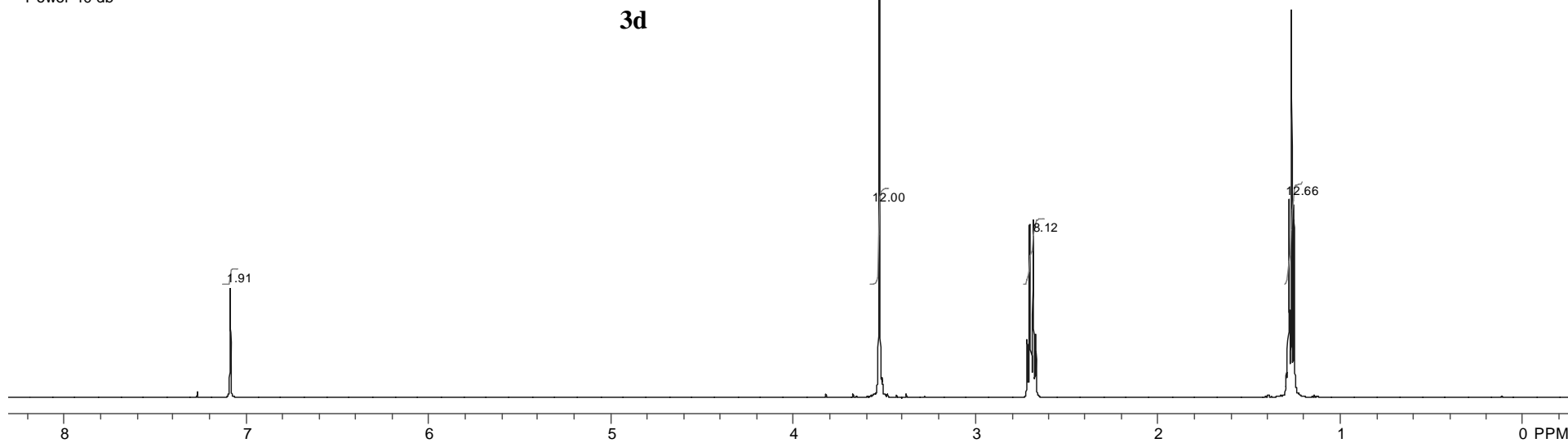
Power 40 db

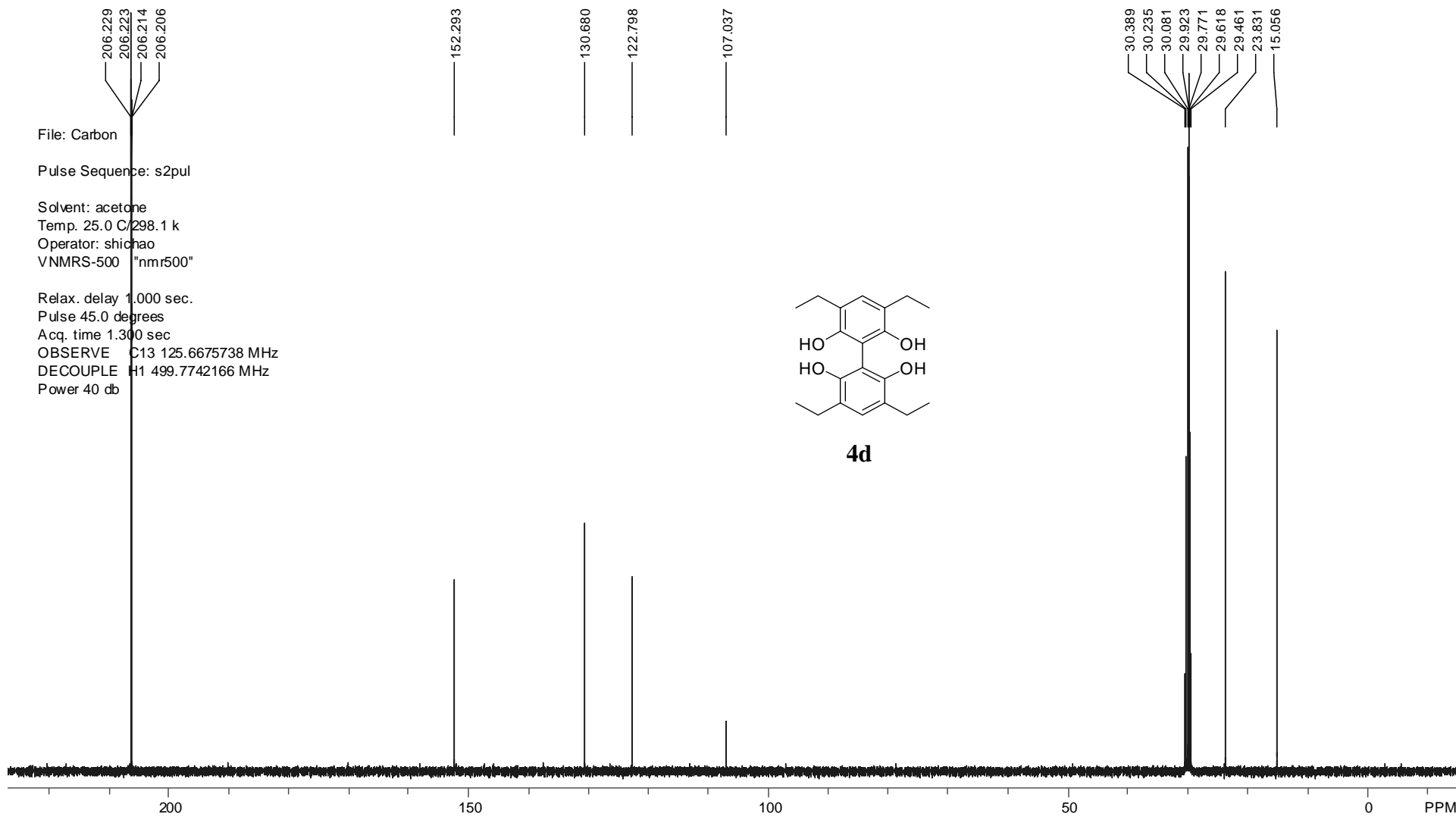


3.529

2.717  
2.702  
2.687  
2.672

1.284  
1.269  
1.254





6.919  
6.548

2.611  
2.597  
2.582  
2.566  
2.059  
2.054  
2.050  
2.046  
2.041

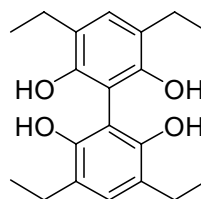
1.195  
1.180  
1.165

File: Proton

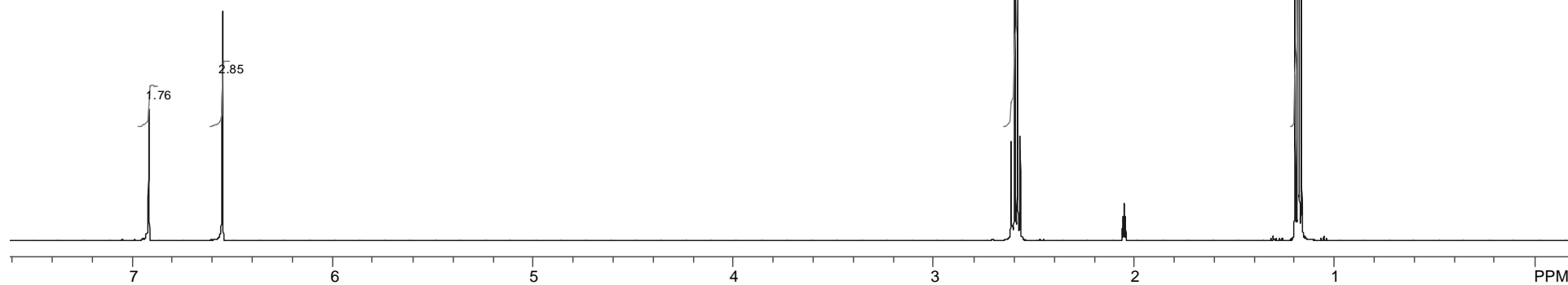
Pulse Sequence: s2pul

Solvent: acetone  
Temp. 25.0 C/298.1 k  
Operator: shichao  
VNMRS-500 "nmr500"

Relax. delay 1.000 sec.  
Pulse 45.0 degrees  
Acq. time 2.049 sec  
OBSERVE H1 499.7717213 MHz  
Power 40 db



4d



File: Phosphorus

Pulse Sequence: s2pul

Solvent: CDCl<sub>3</sub>

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-400 "nmr400"

Relax. delay 1.000 sec.

Pulse 45.0 degrees

Acq. time 1.600 sec

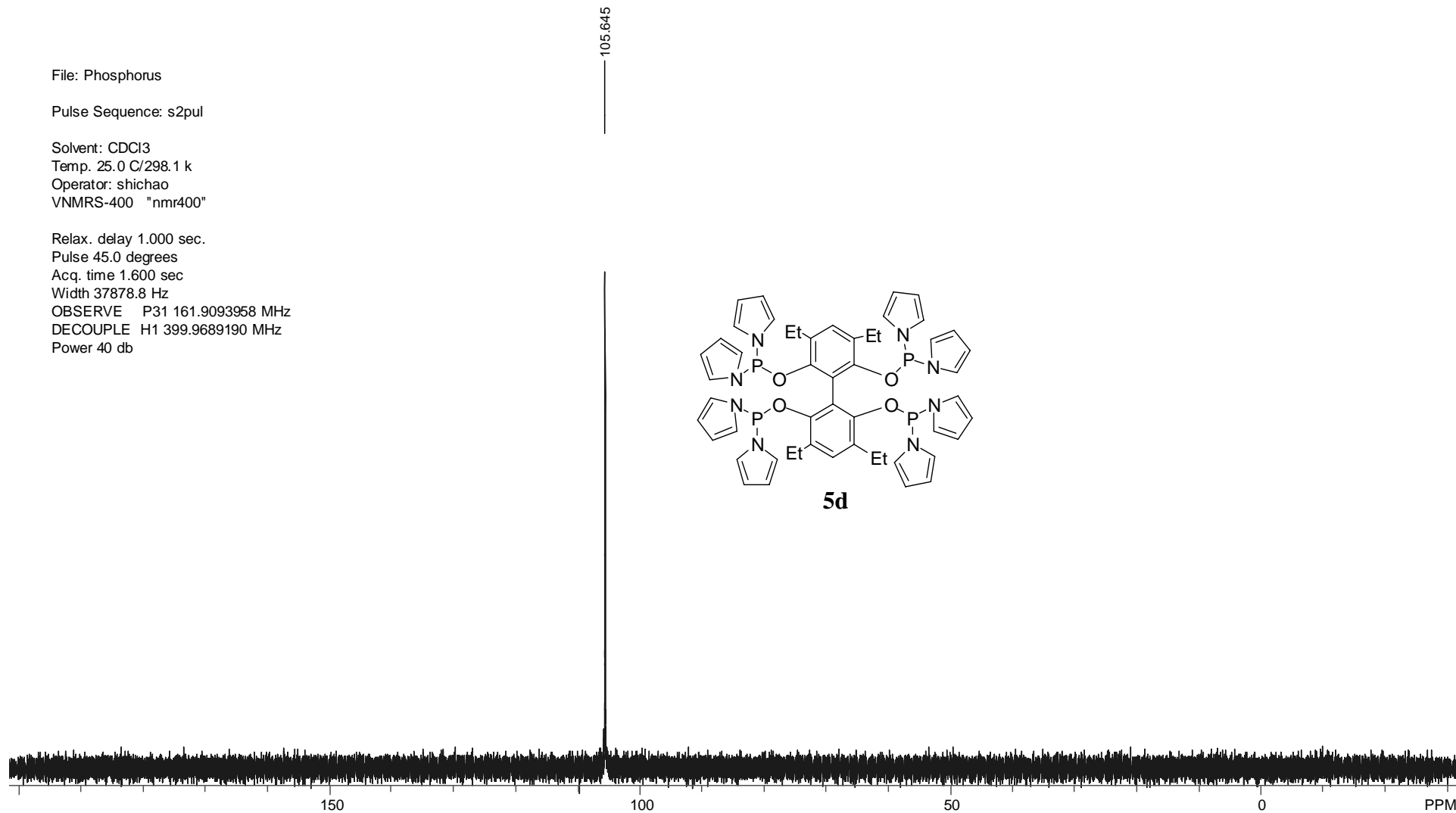
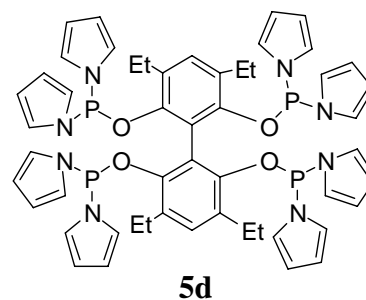
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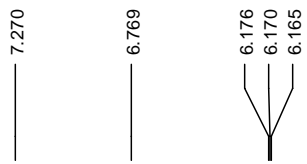
OBSERVE P31 161.9093958 MHz

DECOUPLE H1 399.9689190 MHz

Power 40 db

105.645



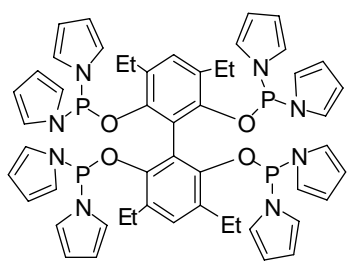


File: Proton

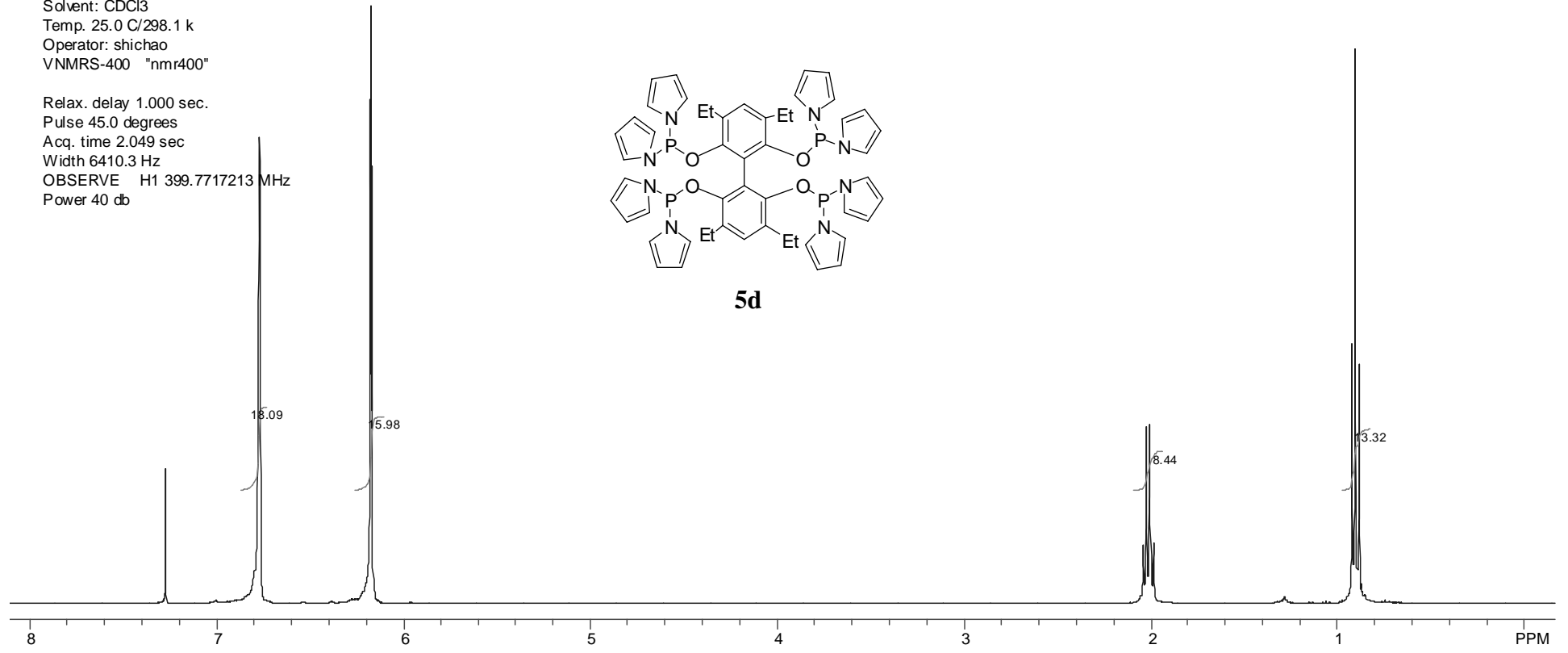
Pulse Sequence: s2pul

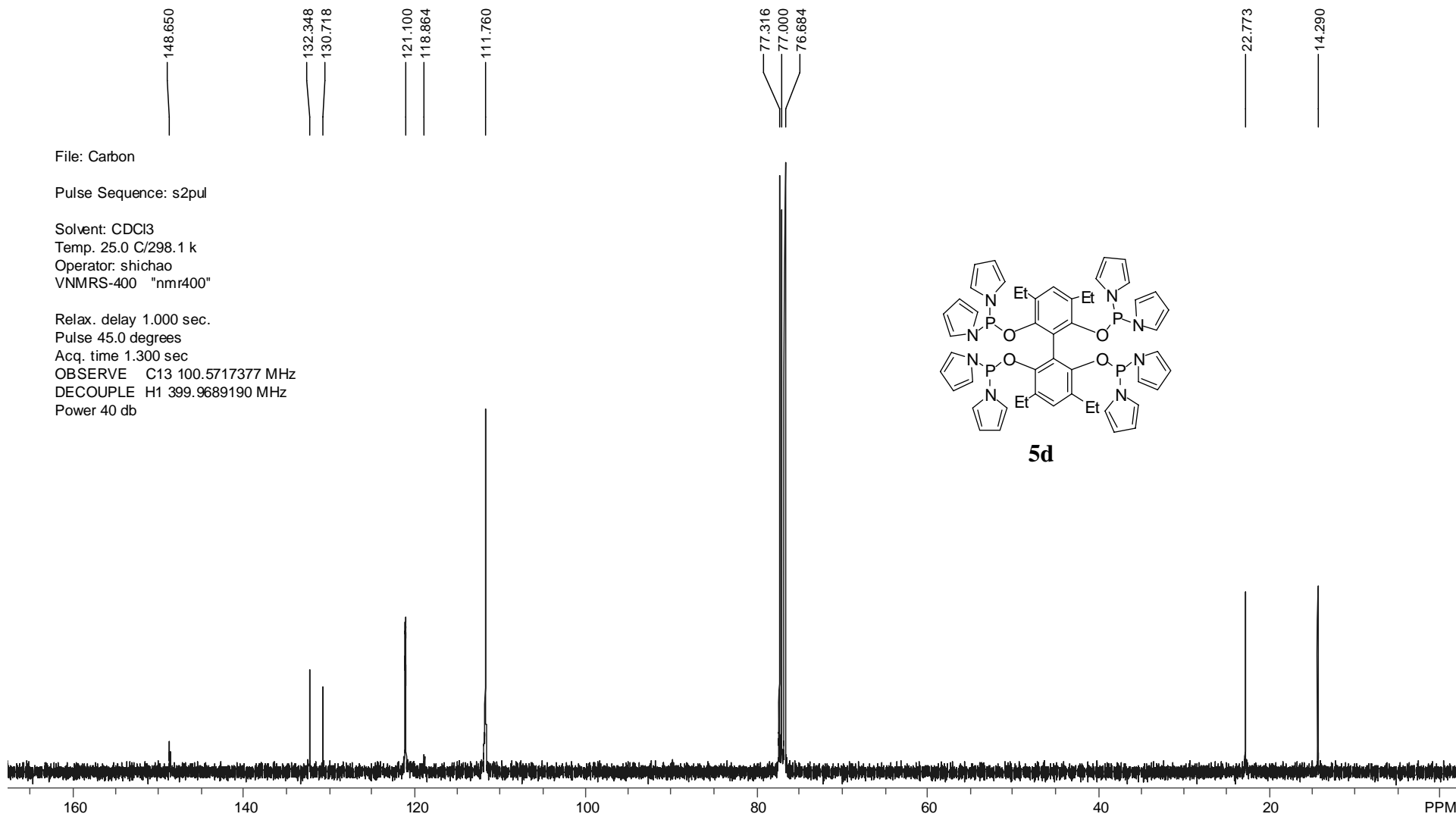
Solvent: CDCl3  
Temp. 25.0 C/298.1 k  
Operator: shichao  
VNMR5-400 "nmr400"

Relax. delay 1.000 sec.  
Pulse 45.0 degrees  
Acq. time 2.049 sec  
Width 6410.3 Hz  
OBSERVE H1 399.7717213 MHz  
Power 40 db



5d







File: Carbon

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-500 "nmr500"

Relax. delay 1.000 sec.

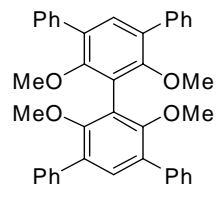
Pulse 45.0 degrees

Acq. time 1.300 sec

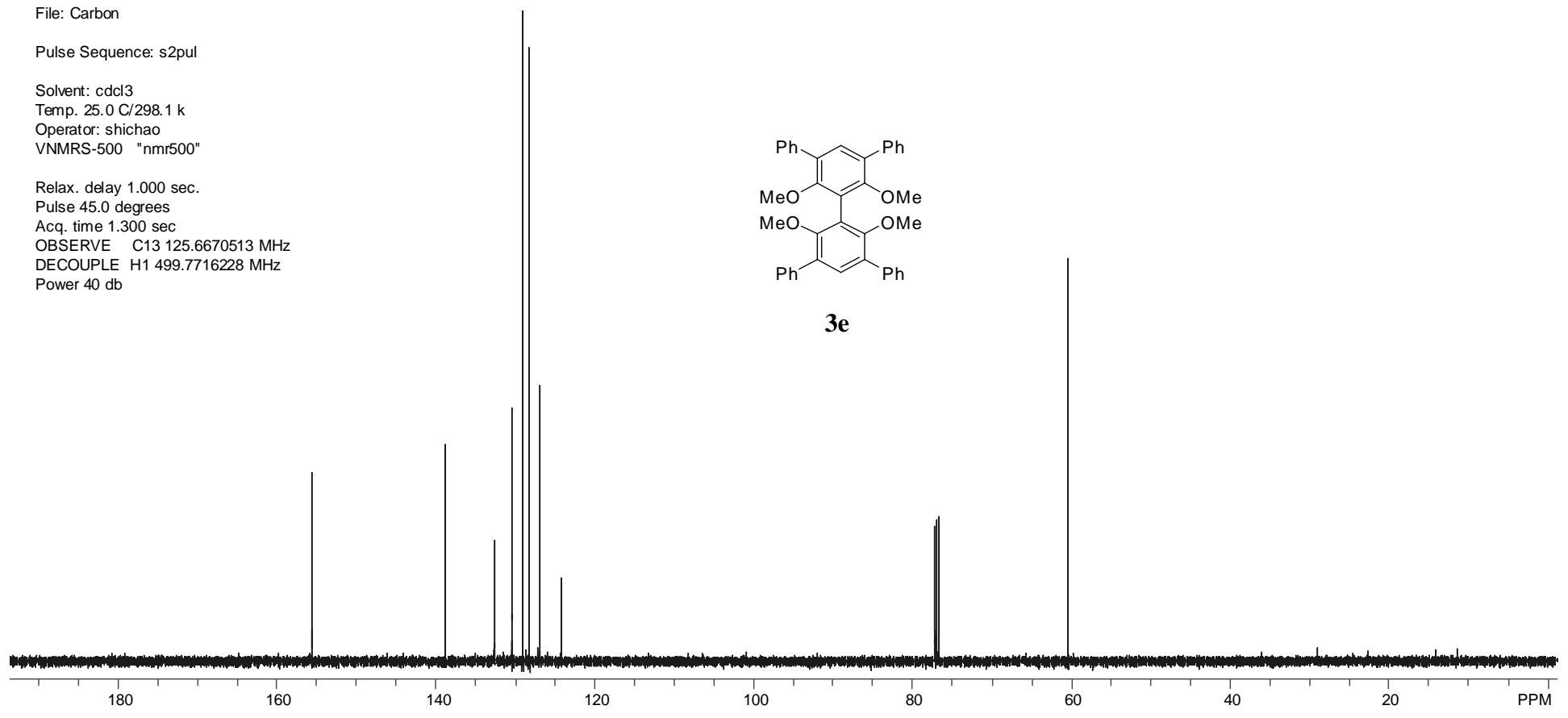
OBSERVE C13 125.6670513 MHz

DECOUPLE H1 499.7716228 MHz

Power 40 db



**3e**



7.675  
7.672  
7.659  
7.656  
7.452  
7.440  
7.424  
7.372  
7.370  
7.367  
7.358  
7.355  
7.340  
7.270

File: Proton

Pulse Sequence: s2pul

Solvent: CDCl3

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-500 "nmr500"

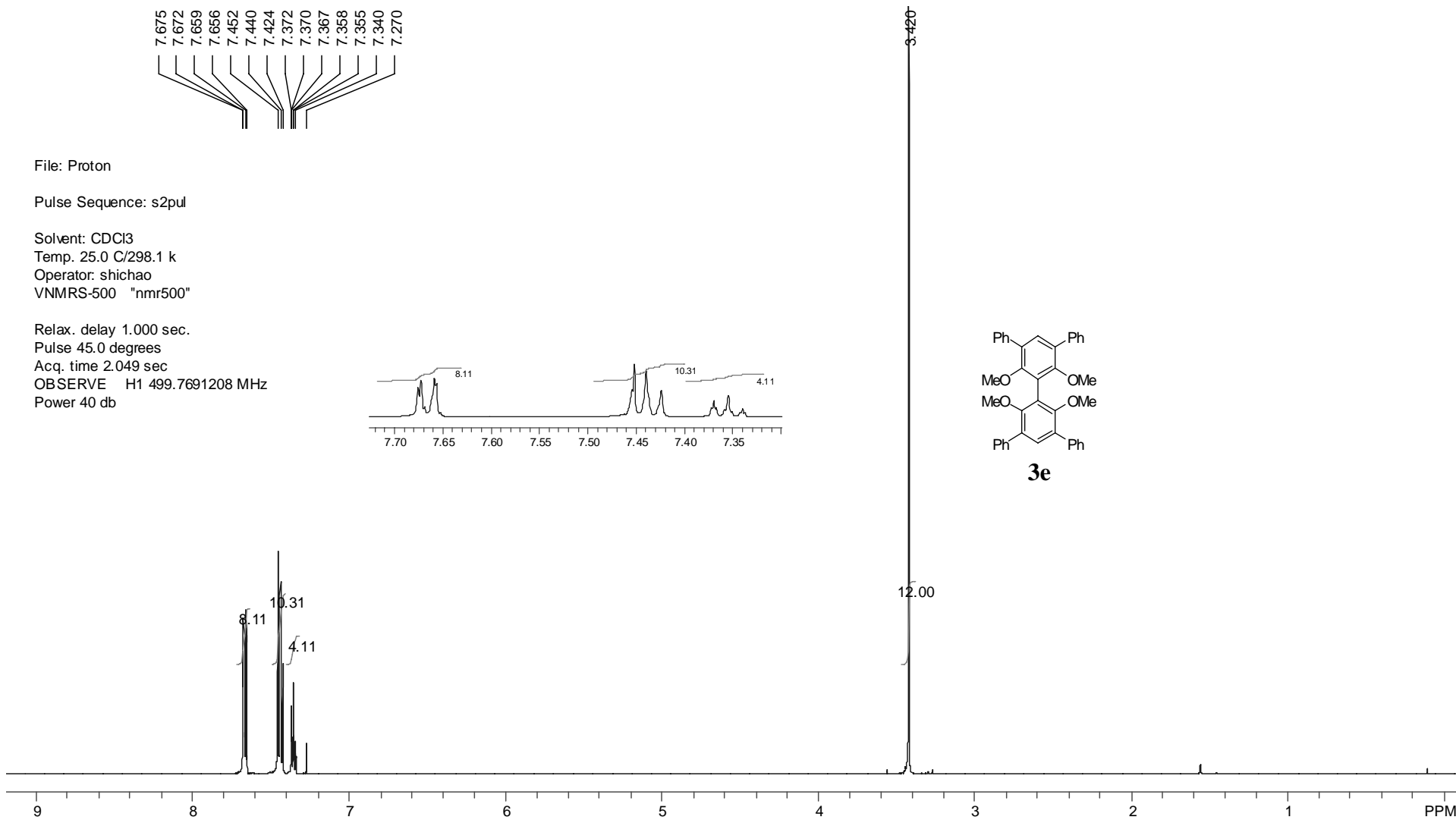
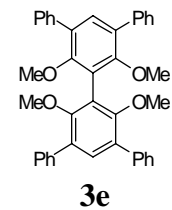
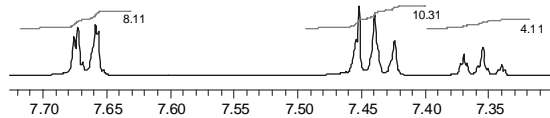
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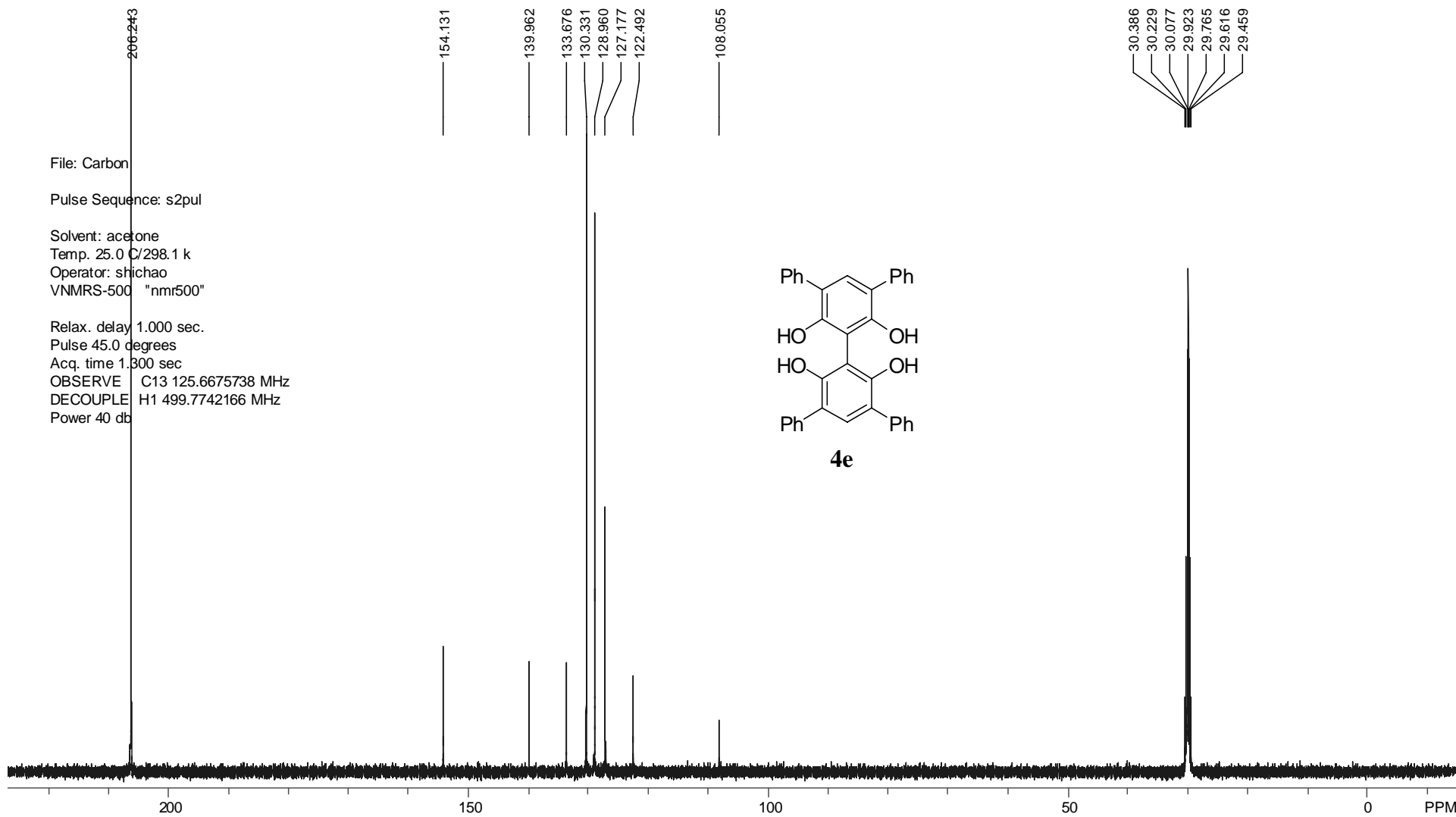
Pulse 45.0 degrees

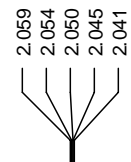
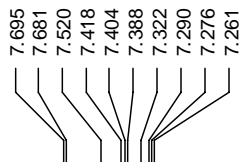
Acq. time 2.049 sec

OBSERVE H1 499.7691208 MHz

Power 40 db





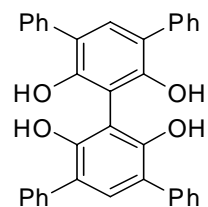
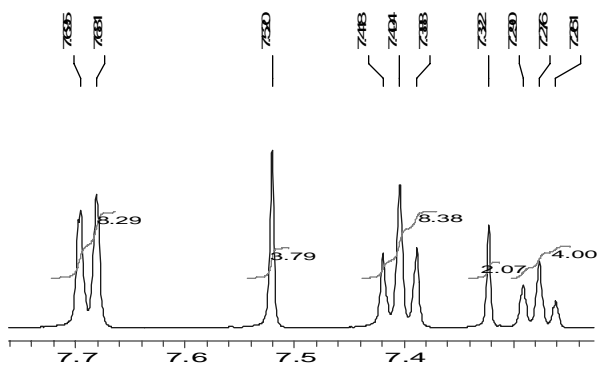


File: Proton

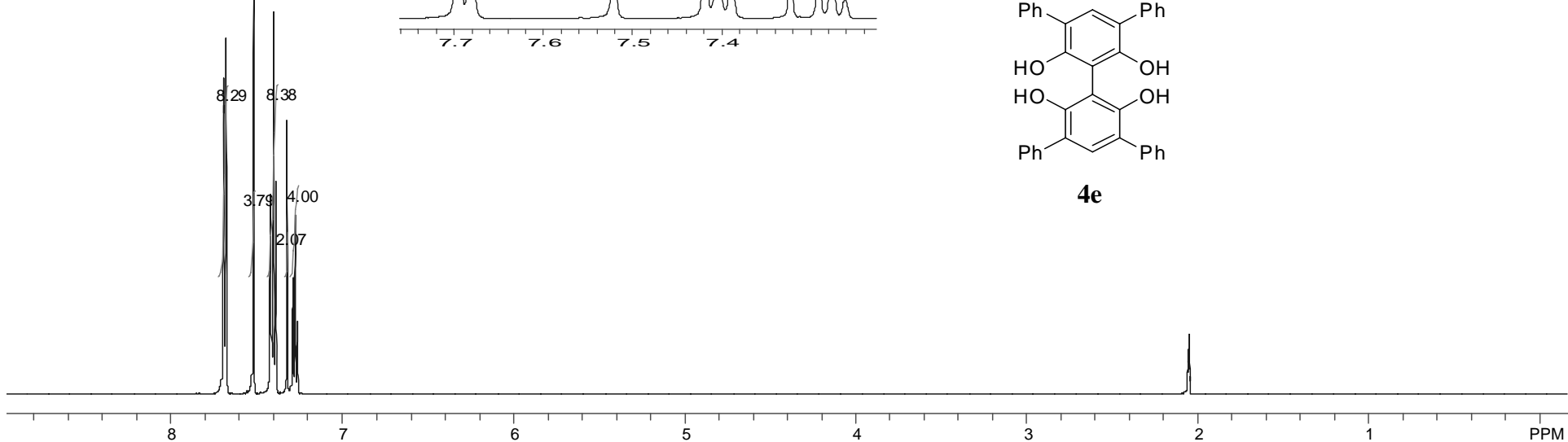
Pulse Sequence: s2pul

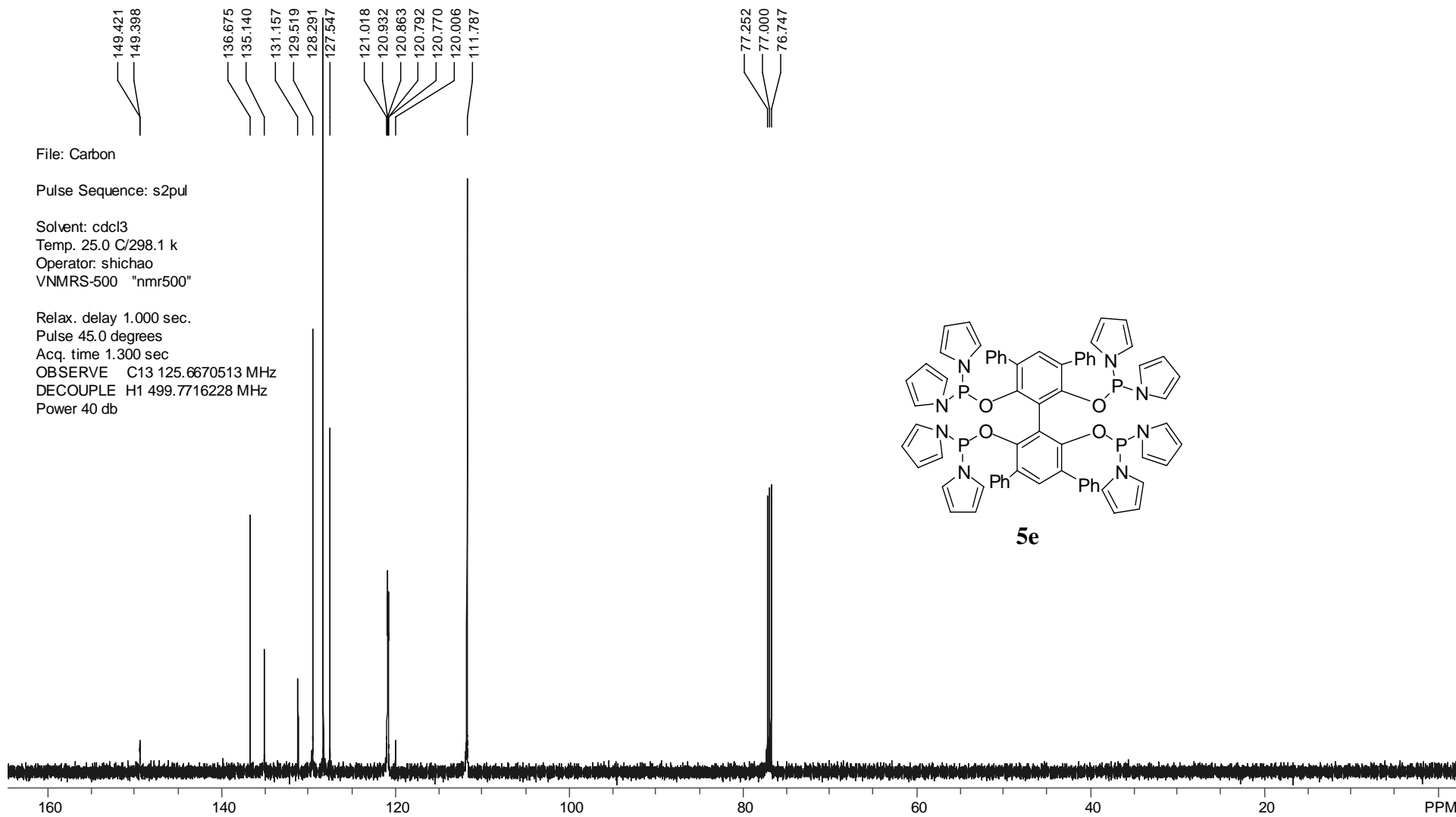
Solvent: acetone  
Temp. 25.0 C/298.1 k  
Operator: shichao  
VNMRS-500 "nmr500"

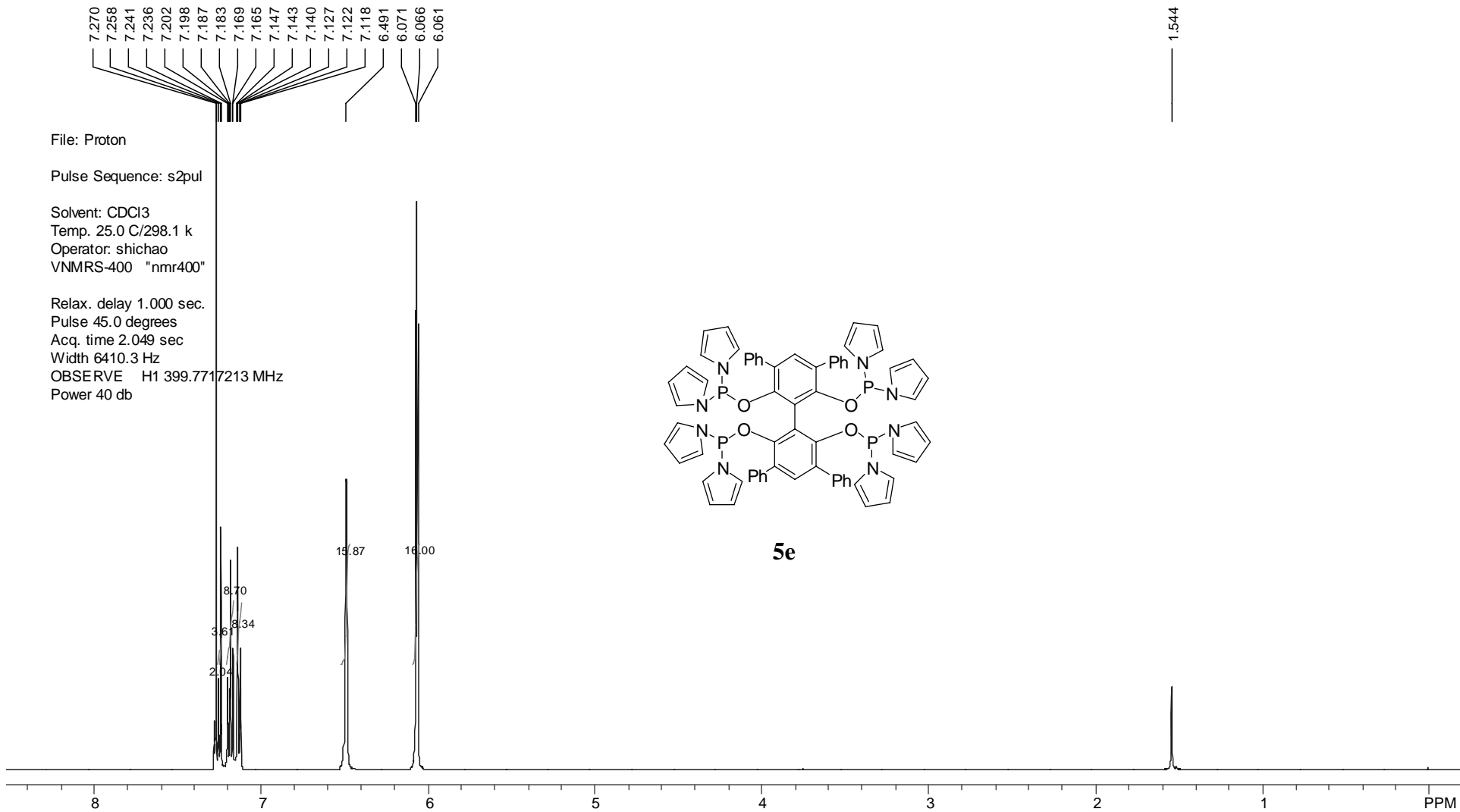
Relax. delay 1.000 sec.  
Pulse 45.0 degrees  
Acq. time 2.049 sec  
OBSERVE H1 499.7717213 MHz  
Power 40 db



**4e**







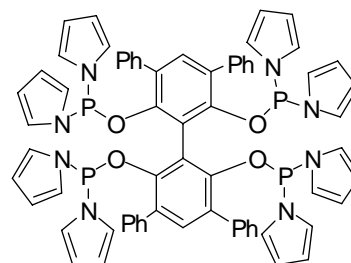
106.502

File: Phosphorus

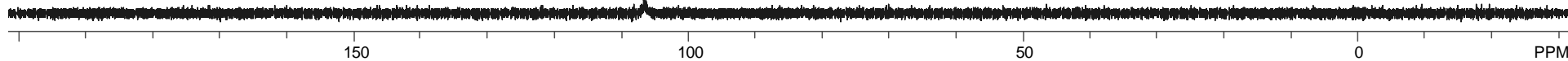
Pulse Sequence: s2pul

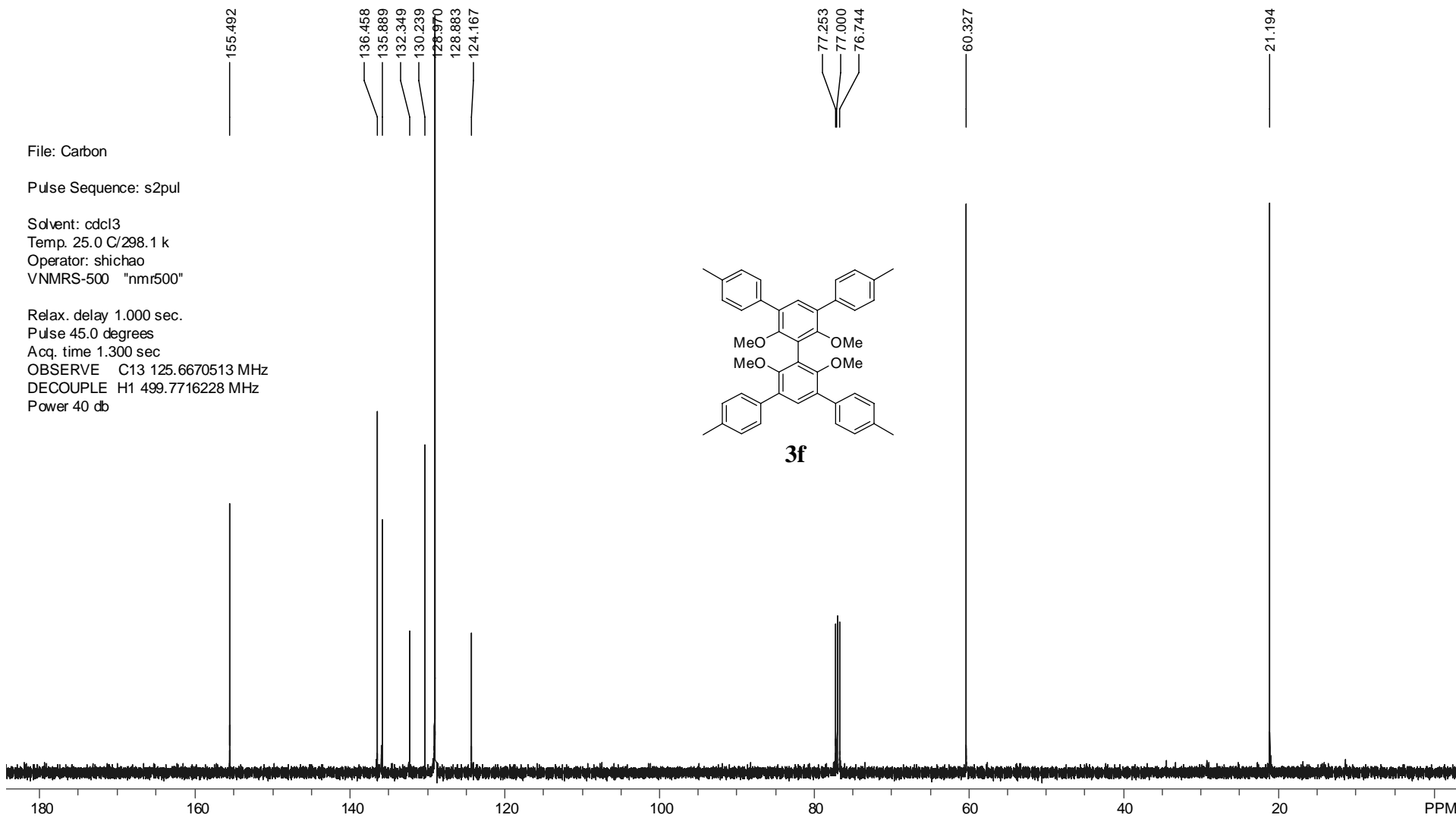
Solvent: CDCl<sub>3</sub>  
Temp. 25.0 C/298.1 k  
Operator: shichao  
VNMRS-400 "nmr400"

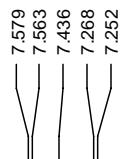
Relax. delay 1.000 sec.  
Pulse 45.0 degrees  
Acq. time 1.600 sec  
Width 37878.8 Hz  
OBSERVE P31 161.9093958 MHz  
DECOUPLE H1 399.9689190 MHz  
Power 40 db



5e







File: Proton

Pulse Sequence: s2pul

Solvent: CDCl3

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-500 "nmr500"

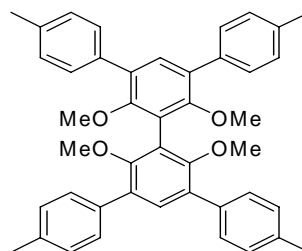
Relax. delay 1.000 sec.

Pulse 45.0 degrees

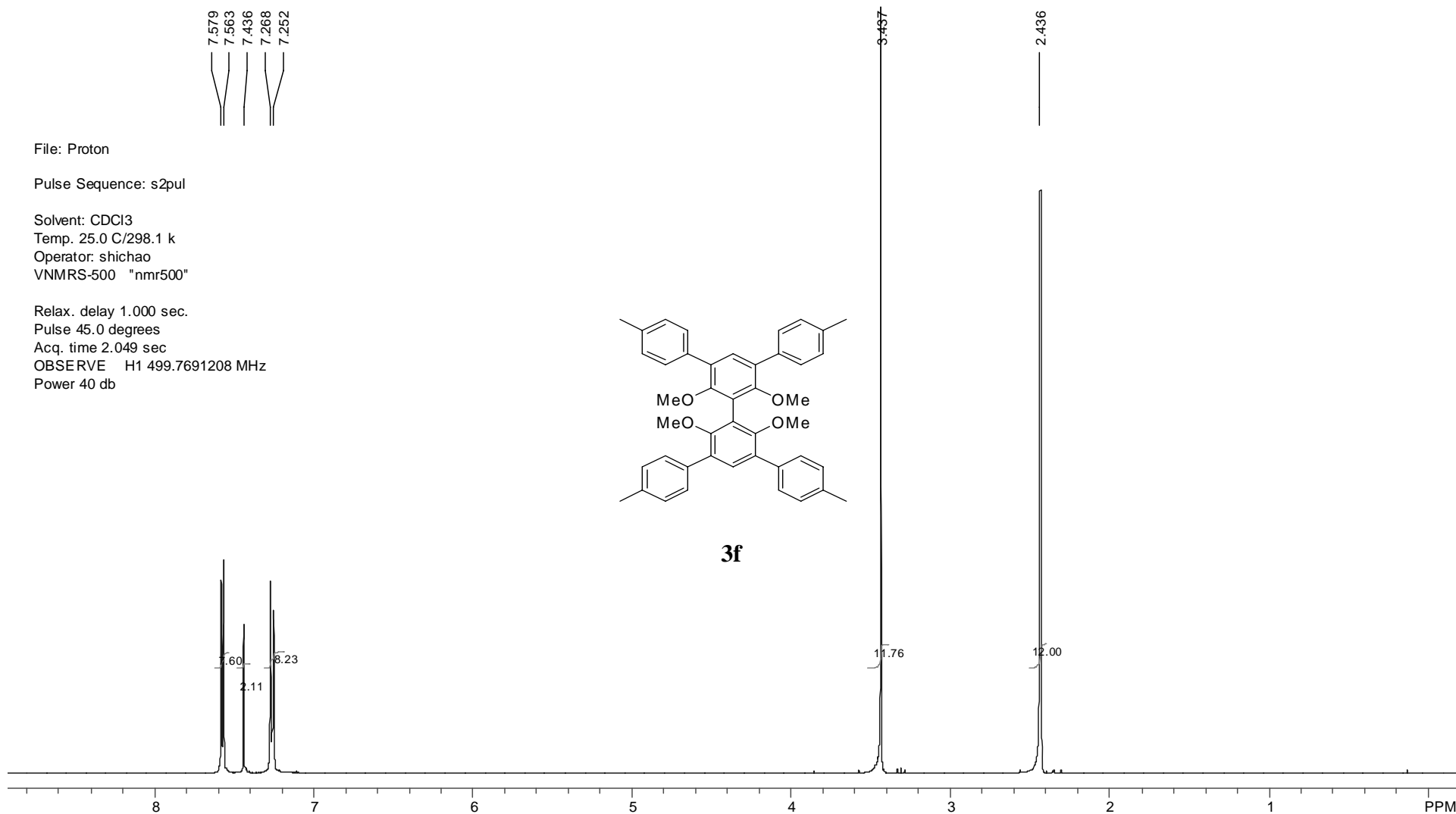
Acq. time 2.049 sec

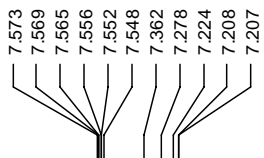
OBSERVE H1 499.7691208 MHz

Power 40 db



3f





File: Proton

Pulse Sequence: s2pul

Solvent: acetone

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-500 "nmr500"

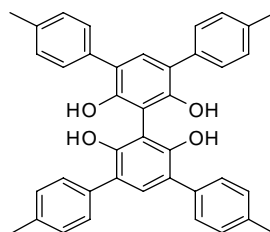
Relax. delay 1.000 sec.

Pulse 45.0 degrees

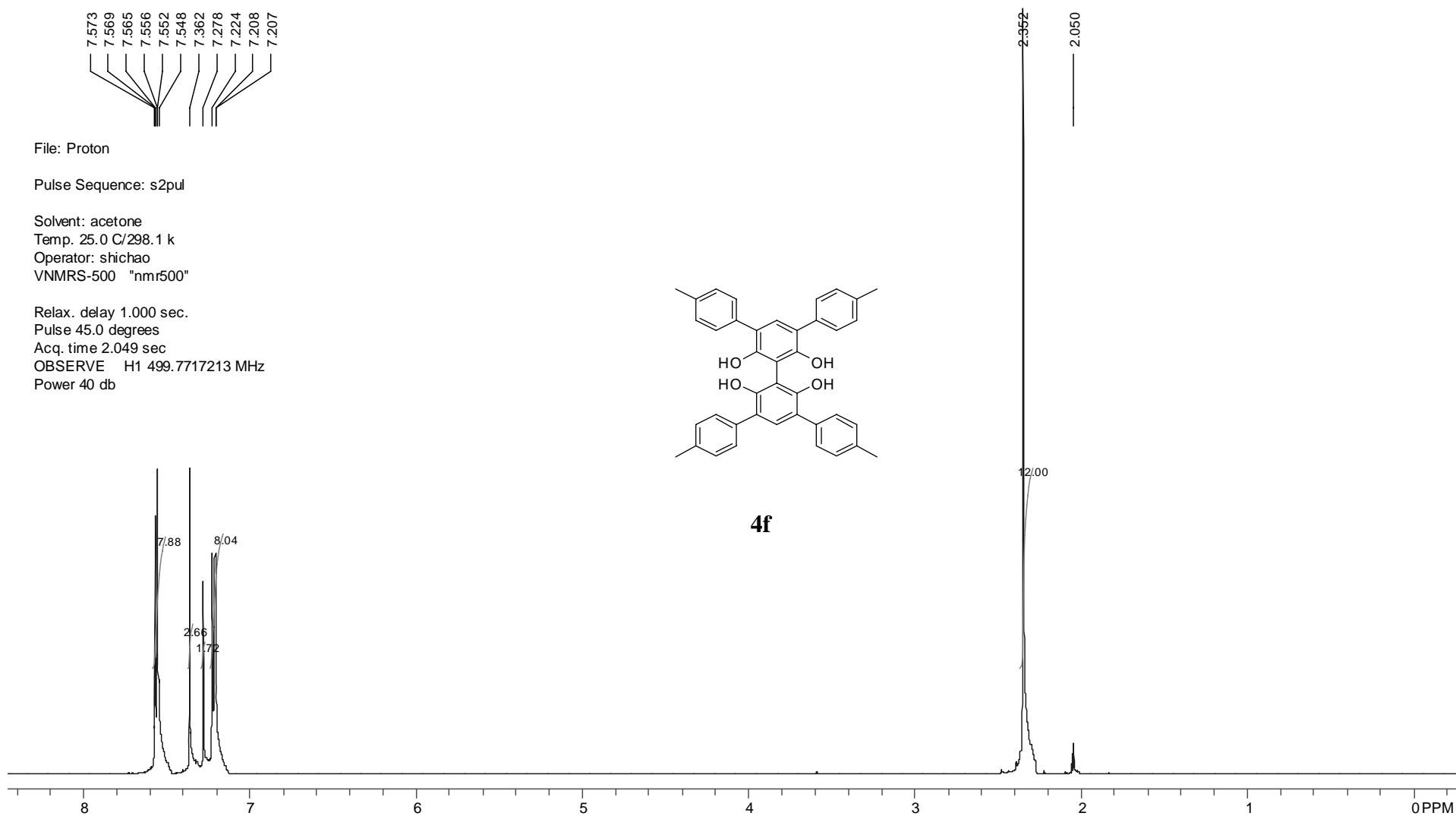
Acq. time 2.049 sec

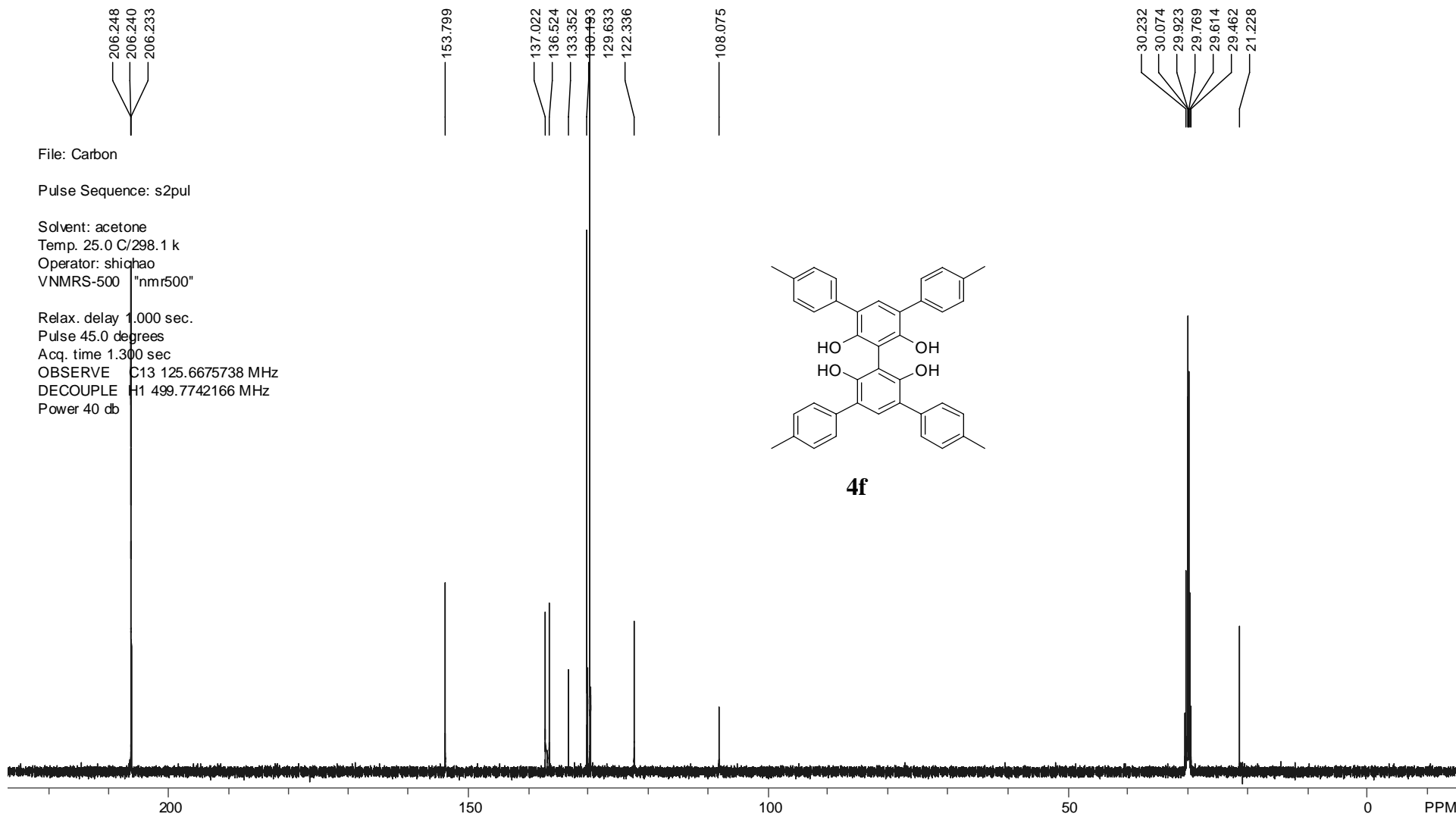
OBSERVE H1 499.7717213 MHz

Power 40 db



**4f**





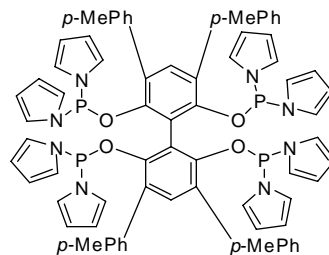
File: Phosphorus

Pulse Sequence: s2pul

Solvent: CDCl3  
Temp. 25.0 C/298.1 k  
Operator: shichao  
VNMRS-500 "nmr500"

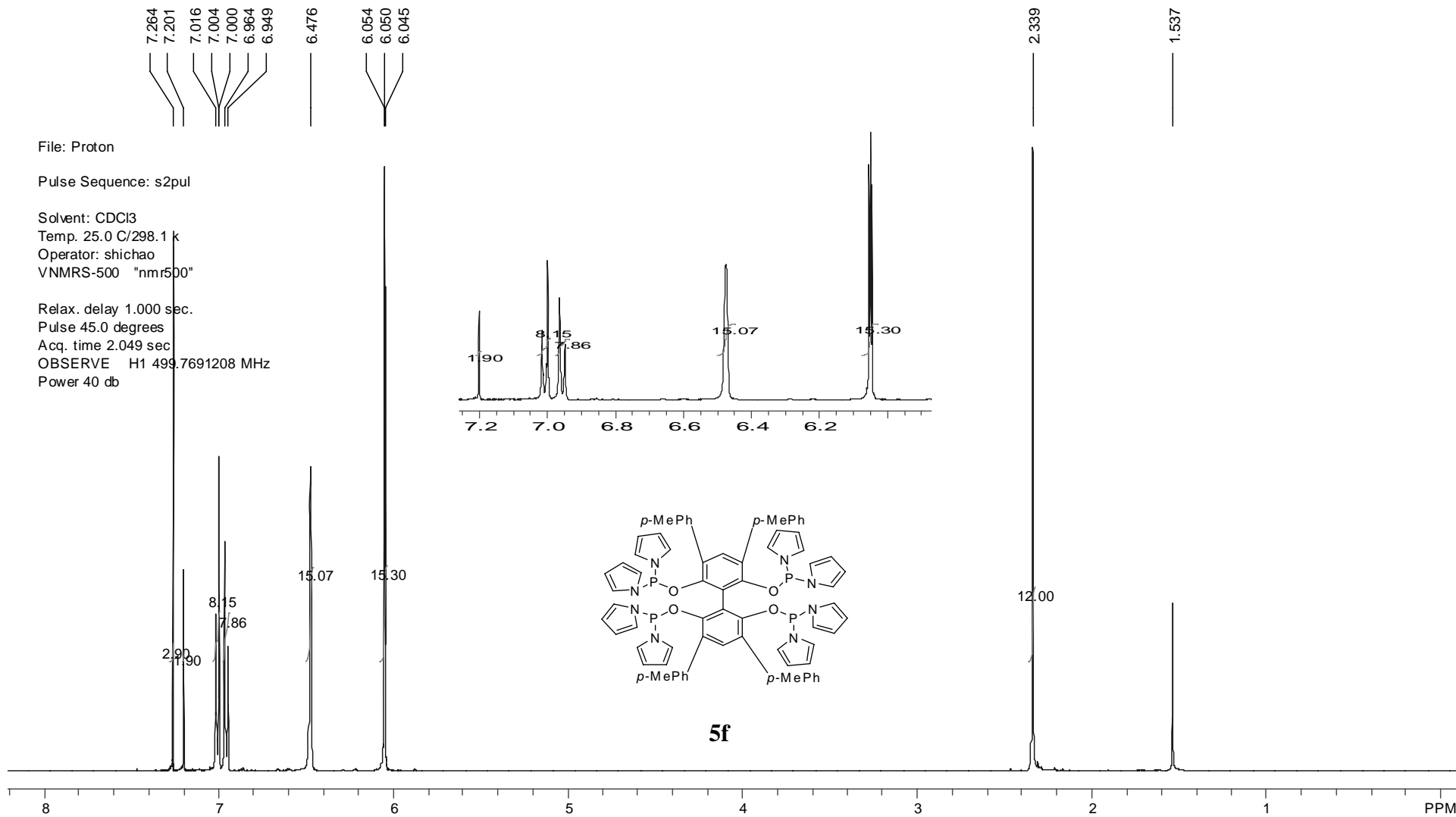
Relax. delay 1.000 sec.  
Pulse 45.0 degrees  
Acq. time 1.600 sec  
Width 52083.3 Hz  
OBSERVE P31 202.3105438 MHz  
DECOUPLE H1 499.7729072 MHz  
Power 40 db

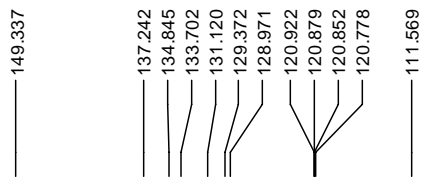
106.759



5f







File: Carbon

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-500 "nmr500"

Relax. delay 1.000 sec.

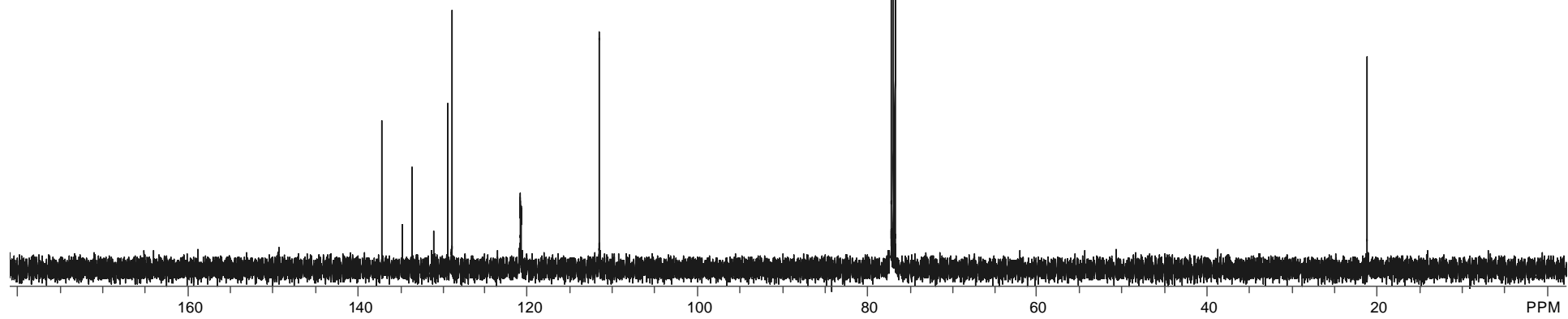
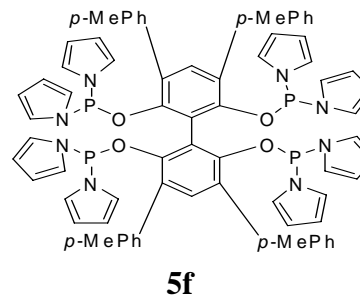
Pulse 45.0 degrees

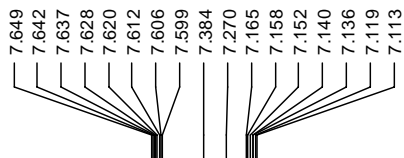
Acq. time 1.300 sec

OBSERVE C13 125.6670513 MHz

DECOUPLE H1 499.7716228 MHz

Power 40 db





File: Proton

Pulse Sequence: s2pul

Solvent: CDCl3

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-400 "nmr400"

Relax. delay 1.000 sec.

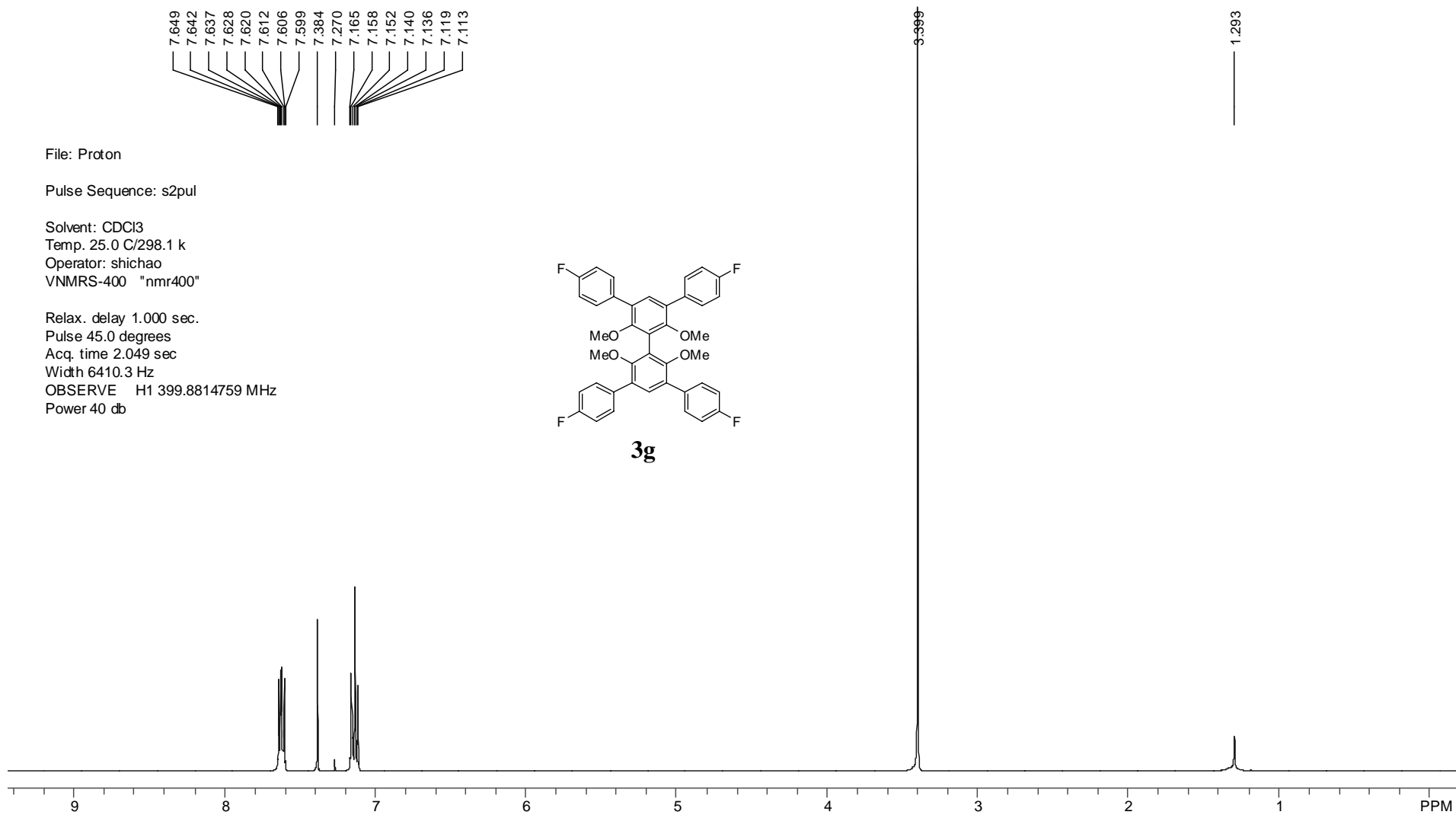
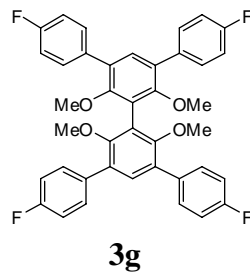
Pulse 45.0 degrees

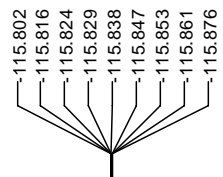
Acq. time 2.049 sec

Width 6410.3 Hz

OBSERVE H1 399.8814759 MHz

Power 40 db





File: Fluorine

Pulse Sequence: s2pul

Solvent: CDCl3

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-400 "nmr400"

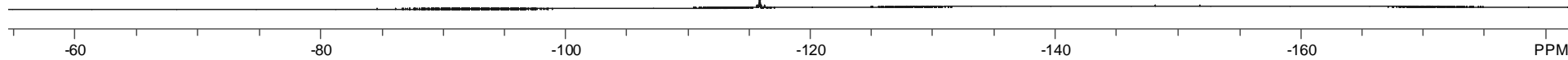
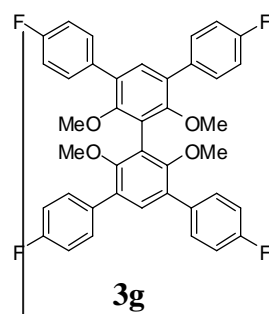
Relax. delay 1.000 sec.

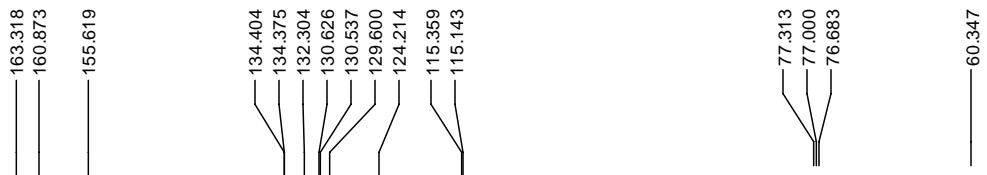
Pulse 30.0 degrees

Acq. time 1.133 sec

Width 78125.0 Hz

OBSERVE F19 376.2646829 MHz





File: Carbon

Pulse Sequence: s2pul

Solvent: CDCl3

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-400 "nmr400"

Relax. delay 1.000 sec.

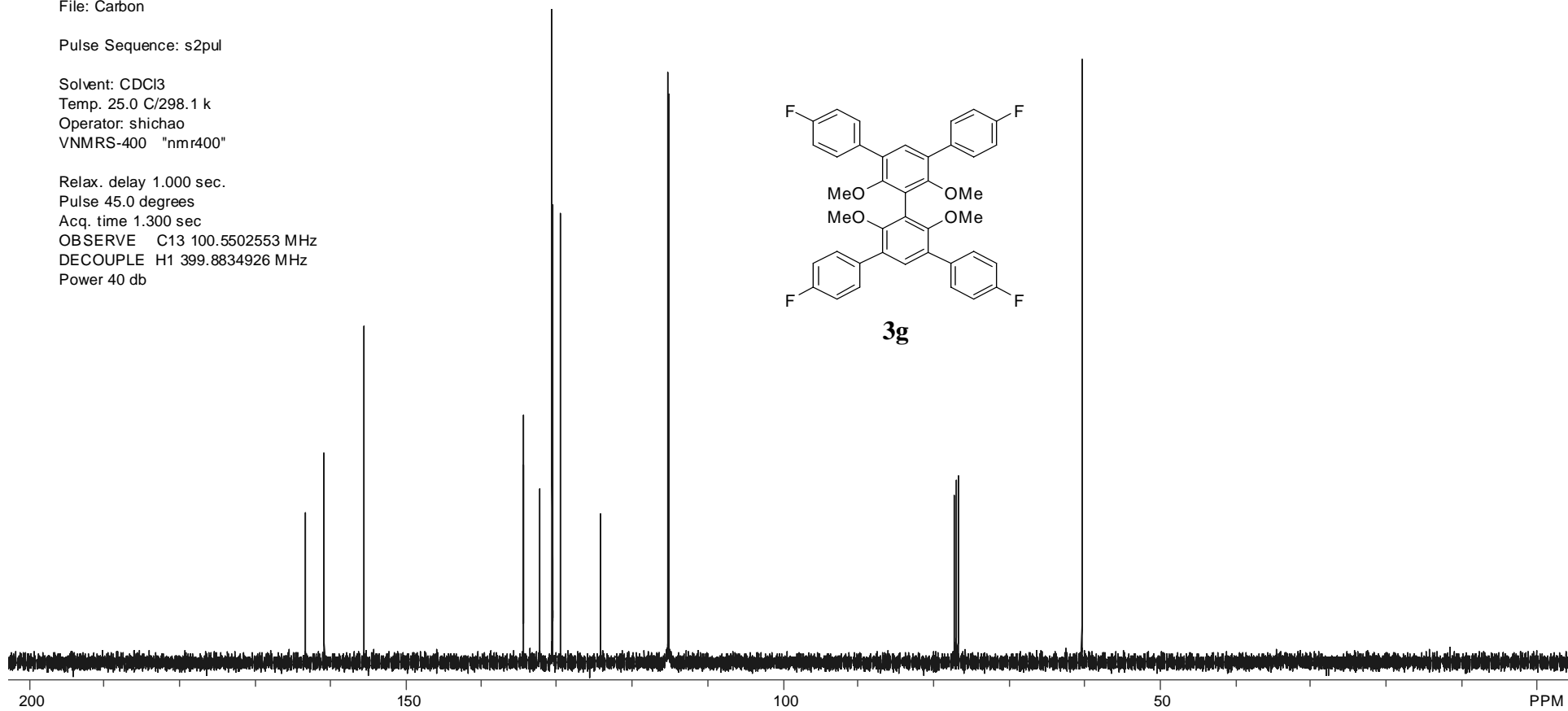
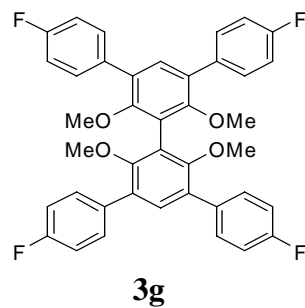
Pulse 45.0 degrees

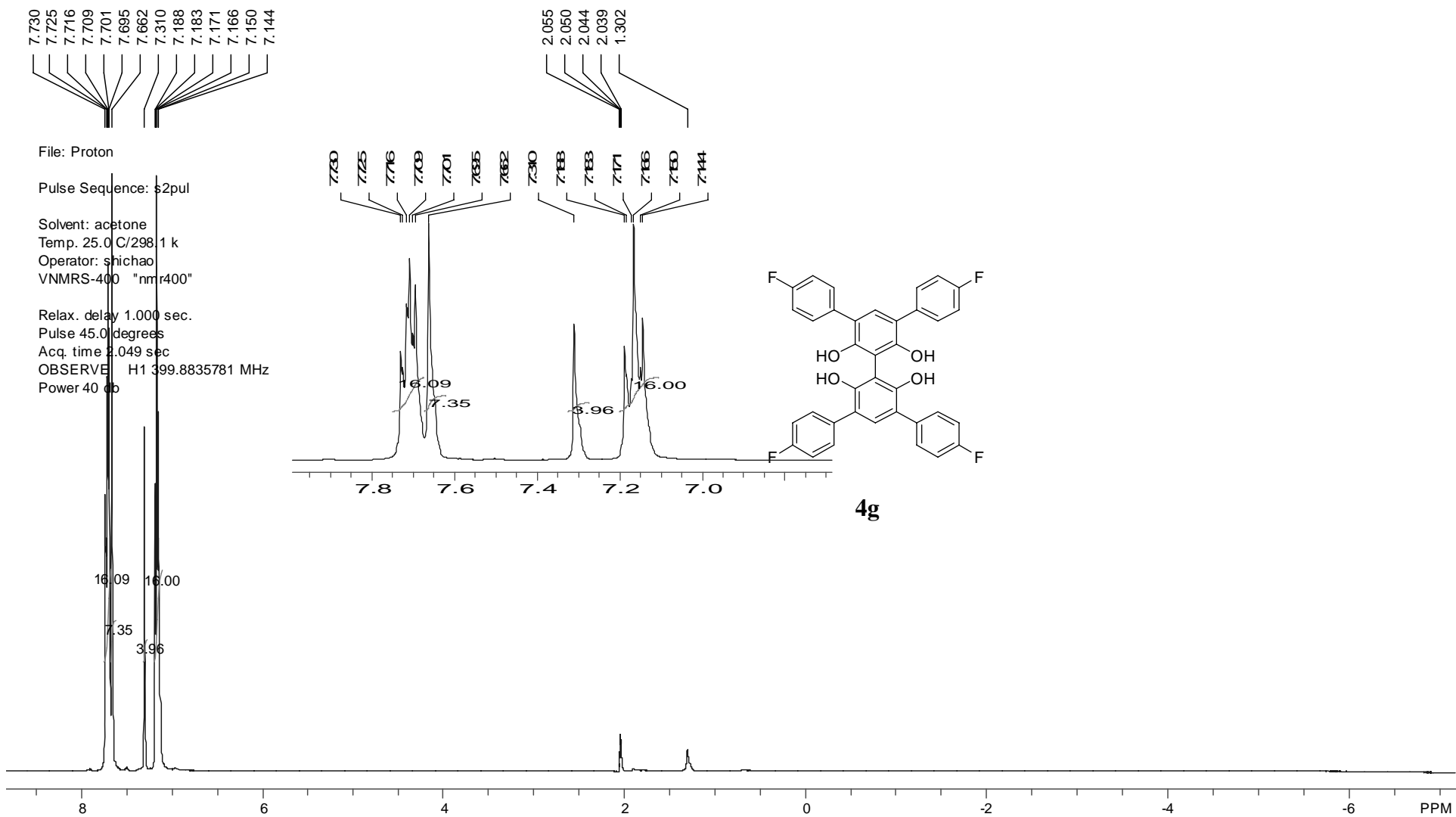
Acq. time 1.300 sec

OBSERVE C13 100.5502553 MHz

DECOUPLE H1 399.8834926 MHz

Power 40 db





-113.454  
-113.468  
-113.477  
-113.483  
-113.492  
-113.501  
-113.508  
-113.516  
-113.532

File: Fluorine

Pulse Sequence: s2pul

Solvent: acetone

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-400 "nmr400"

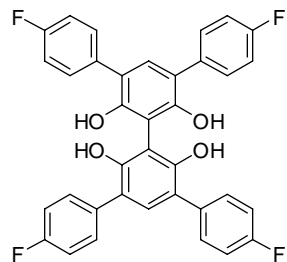
Relax. delay 1.000 sec.

Pulse 30.0 degrees

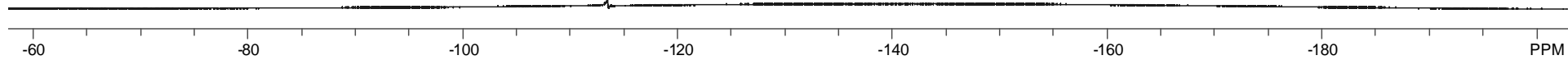
Acq. time 1.133 sec

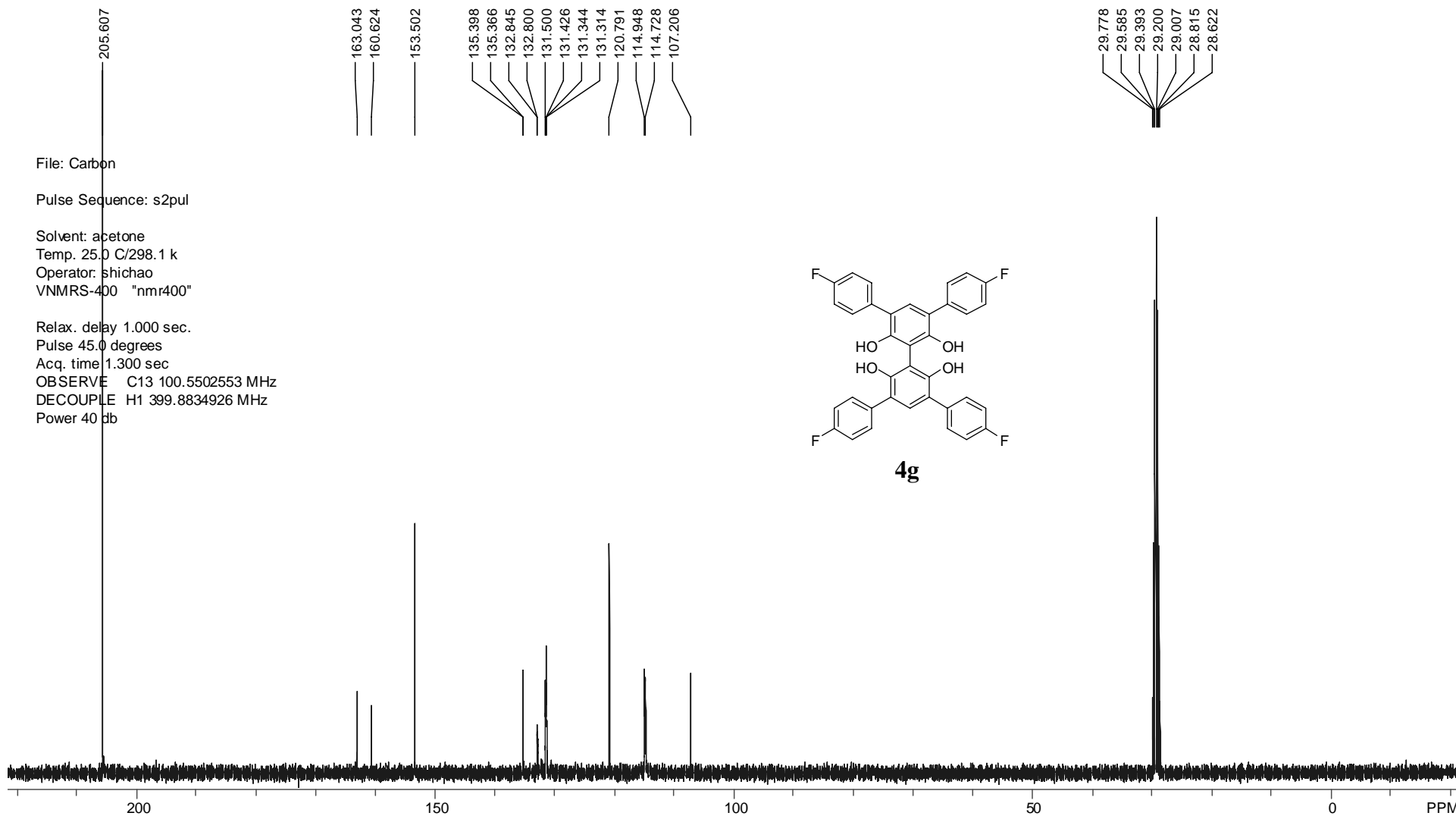
Width 78125.0 Hz

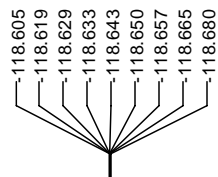
OBSERVE F19 376.2646829 MHz



**4g**







File: Fluorine

Pulse Sequence: s2pul

Solvent: CDCl3

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-400 "nmr400"

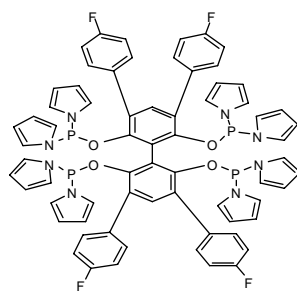
Relax. delay 1.000 sec.

Pulse 30.0 degrees

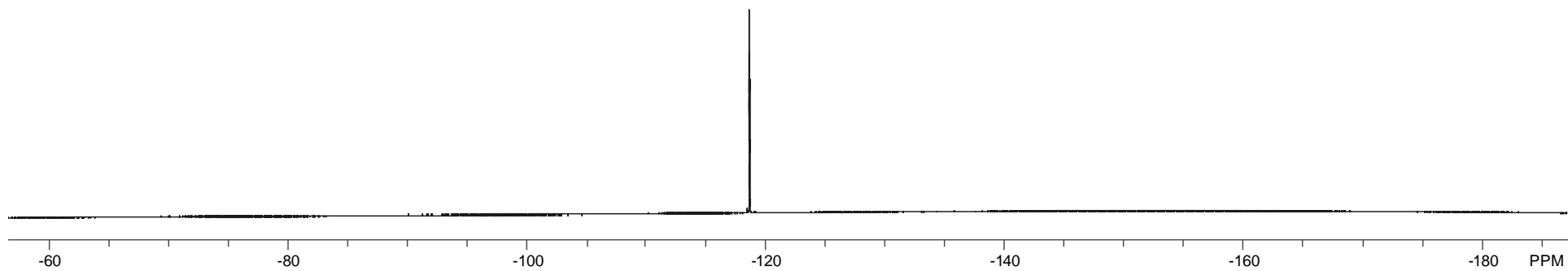
Acq. time 1.133 sec

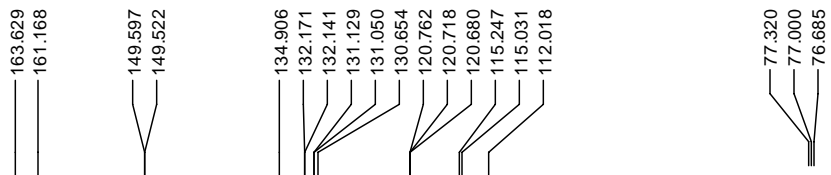
Width 78125.0 Hz

OBSERVE F19 376.2656499 MH



5g





File: Carbon

Pulse Sequence: s2pul

Solvent: CDCl3

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-400 "nmr400"

Relax. delay 1.000 sec.

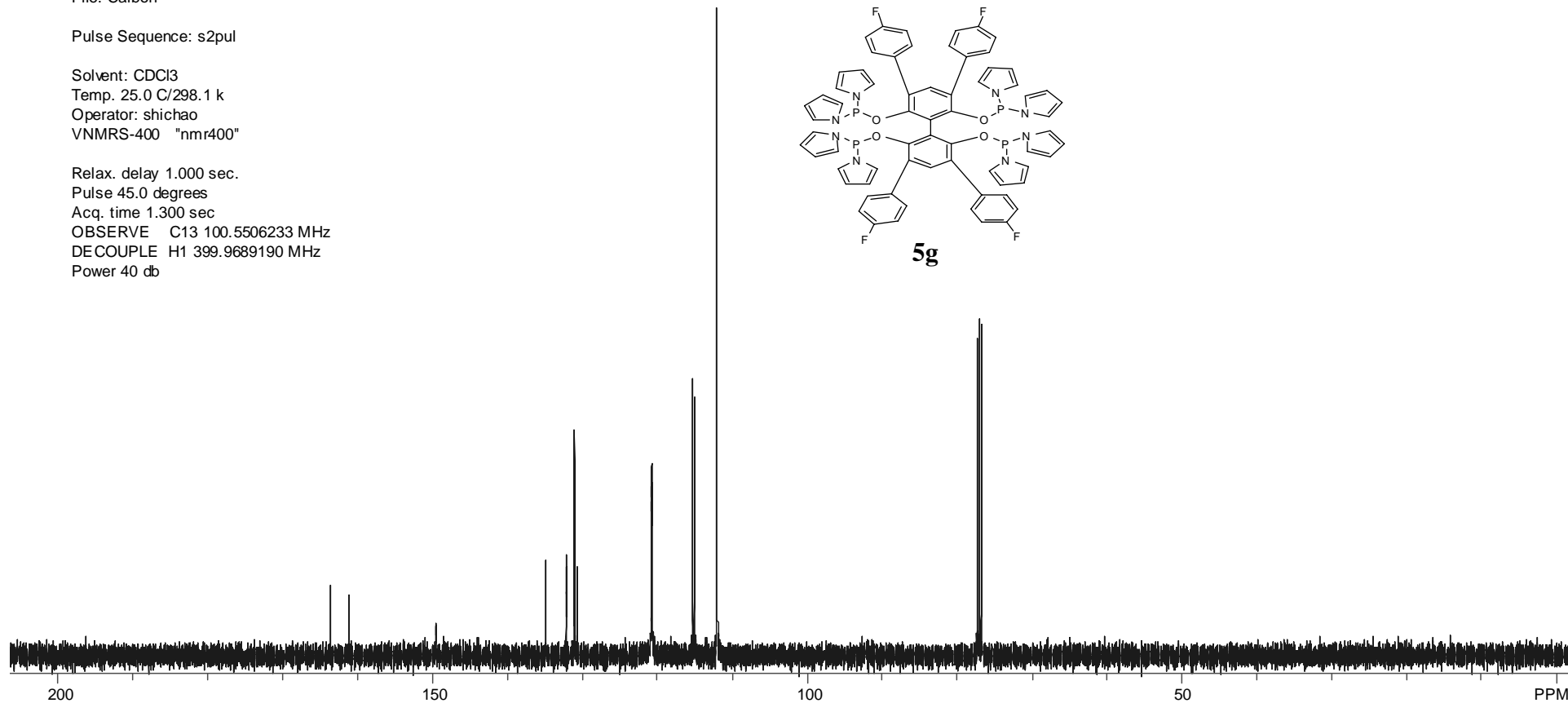
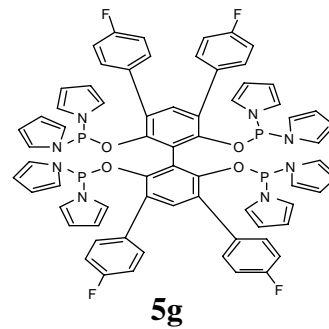
Pulse 45.0 degrees

Acq. time 1.300 sec

OBSERVE C13 100.5506233 MHz

DECOUPLE H1 399.9689190 MHz

Power 40 db



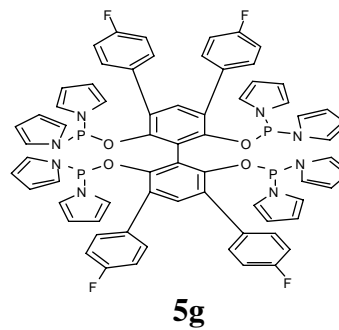
File: Phosphorus

Pulse Sequence: s2pul

Solvent: CDCl<sub>3</sub>  
Temp. 25.0 C/298.1 k  
Operator: shichao  
VNMRS-400 "nmr400"

Relax. delay 1.000 sec.  
Pulse 45.0 degrees  
Acq. time 1.600 sec  
Width 37878.8 Hz  
OBSERVE P31 161.8748148 MHz  
DECOUPLE H1 399.8834926 MHz  
Power 40 db

106.593



200 150 100 50 PPM

7.270  
7.111  
7.092  
7.045  
7.015  
7.008  
7.003  
6.994  
6.986  
6.979  
6.972  
6.868  
6.850  
6.842  
6.837  
6.821  
6.804  
6.799  
6.771  
6.762  
6.544  
6.118  
6.112  
6.108

1.558

File: Proton

Pulse Sequence: s2pul

Solvent: CDCl3

Temp. 25.0 C/298.1 k

Operator: shichao

VNMRS-400 "nmr400"

Relax. delay 1.000 sec.

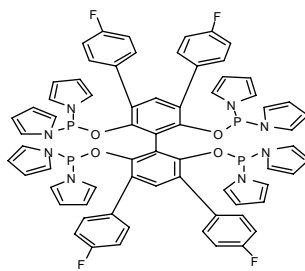
Pulse 45.0 degrees

Acq. time 2.049 sec

Width 6410.3 Hz

OBSERVE H1 399.8814928 MHz

Power 40 db



5g

