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Iron-Catalyzed Intermolecular Cycloaddition of Diazo Surrogates with Hexahydro-1,3,5-Triazines

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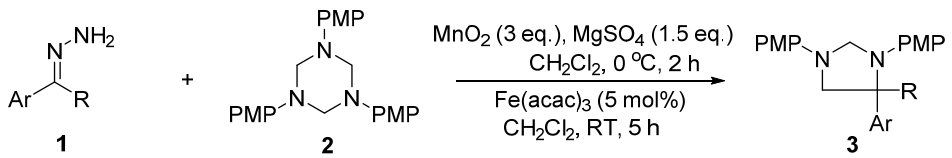
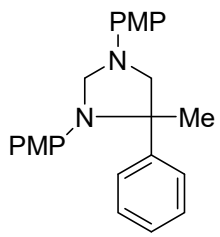
General information

All of the reactions were carried out in flame-dried tubes under argon atmosphere. Solvents were dried prior to use. For column chromatography, 200-300 mesh silica gel was used. ^{1}H NMR were recorded on Bruker 300 MHz, 400 MHz or 500 MHz spectrometer and ^{13}C NMR were recorded on Bruker 75 MHz, 100 MHz or 125MHz spectrometer in $CDCl_3$ or DMSO-d_6. HRMS were performed on Agilent 6540 Q-TOF mass spectrometer (ESI). Melting points were determined on a SGW X-4B melting point apparatus. Triazines[1], hydrazones[2] and diazo compounds[3] were known compounds and prepared according to the literature procedures.

General procedure for table 2



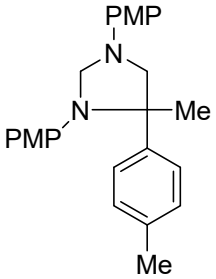
To a mixture of hydrazone **1** (0.25 mmol) and anhydrous $MgSO_4$ (0.375 mmol) in CH_2Cl_2 (5 mL) was added activated MnO_2 (0.75 mmol) at 0 ^{o}C. The reaction mixture was stirred at 0 ^{o}C for 2 h and filtered off the solid to give the solution of diazo compound which was used directly. To a tube was added triazine **2** (0.3 mmol), $Fe(acac)_3$ (5 mol%) and the above solution of diazo compound (0.25 mmol) in CH_2Cl_2 under an argon atmosphere, then the resulting solution was stirred at RT for 5 h. The reaction solution was concentrated under vacuum and the crude residue was purified by column chromatography (petroleum ether/ethyl acetate = 40:1~20:1) to afford product **3**.



1,3-bis(4-methoxyphenyl)-4-methyl-4-phenylimidazolidine (3a):

This compound was prepared via general procedure as a white solid (77 mg, yield: 82%), mp: 95-96 ^{o}C.

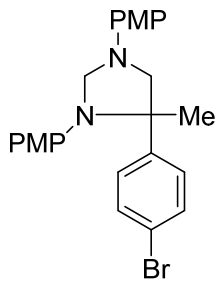
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53-7.48 (m, 2H), 7.39-7.31 (m, 2H), 7.31-7.27 (m, 1H), 6.88 (d, *J* = 9.0 Hz, 2H), 6.71 (d, *J* = 9.0 Hz, 2H), 6.60 (d, *J* = 9.0 Hz, 2H), 6.41 (d, *J* = 9.0 Hz, 2H), 4.98 (d, *J* = 3.0 Hz, 1H), 4.81 (d, *J* = 3.0 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.53 (q, *J* = 8.4 Hz, 2H), 1.82 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.79, 165.82, 159.64, 144.56, 140.67, 127.33, 126.70, 125.58, 107.70, 98.95, 82.54, 76.20, 60.27, 54.74, 50.05, 38.54, 37.15, 13.15. HRMS (ESI) calcd. for $C_{24}H_{27}N_2O_2$ $[M+H]^+$: 375.2067, found: 375.2065.



1,3-bis(4-methoxyphenyl)-4-methyl-4-(p-tolyl)imidazolidine (3b):

This compound was prepared via general procedure as a white solid (82 mg, yield: 84%), mp: 122-124 ^{o}C.

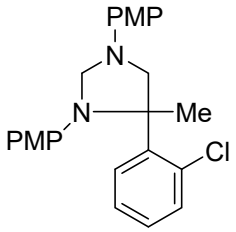
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.71 (d, *J* = 9.0 Hz, 2H), 6.59 (d, *J* = 9.0 Hz, 2H), 6.42 (d, *J* = 9.0 Hz, 2H), 4.96 (d, *J* = 3.2 Hz, 1H), 4.80 (d, *J* = 3.2 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.50 (dd, *J* = 18.0, 9.0 Hz, 2H), 2.35 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.21, 151.60, 142.00, 141.25, 138.38, 136.63, 129.45, 125.89, 115.39, 114.97, 114.37, 113.59, 65.96, 65.01, 55.87, 55.63, 21.04, 19.65. HRMS (ESI) calcd. for $C_{25}H_{29}N_2O_2$ $[M+H]^+$: 389.2224, found: 389.2222.



4-(4-bromophenyl)-4-methyl-1,3-diphenoxyimidazolidine (3c):

This compound was prepared via general procedure as a white solid (74 mg, yield: 65%), mp: 126-128 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.72 (d, *J* = 9.0 Hz, 2H), 6.59 (d, *J* = 9.0 Hz, 2H), 6.39 (d, *J* = 9.0 Hz, 2H), 4.96 (d, *J* = 3.2 Hz, 1H), 4.78 (d, *J* = 3.2 Hz, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 3.49 (dd, *J* = 20.3, 8.5 Hz, 2H), 1.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.15, 159.06, 153.53, 139.24, 132.91, 128.45, 127.76, 126.70, 125.64, 124.11, 120.90, 115.16, 114.82, 70.69, 65.05, 55.63, 55.51, 23.65. HRMS (ESI) calcd. for $C_{24}H_{26}BrN_2O_2$ $[M+H]^+$: 453.1172, found: 453.1175.

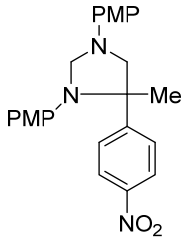


4-(2-chlorophenyl)-1,3-bis(4-methoxyphenyl)-4-methylimidazolidine (3d):

This compound was prepared via general procedure as a white solid (51 mg, yield: 50%), mp: 114-115 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.3, 2.2 Hz, 1H), 7.37 (dd, *J* = 7.1, 2.1 Hz, 1H), 7.25-7.17 (m, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.75 (d, J = 9.0 Hz, 2H), 6.65 (d, *J* = 9.0 Hz, 2H), 6.46 (d, *J* = 9.0 Hz, 2H), 4.88 (d, *J* = 3.0 Hz, 1H), 4.80 (d, *J* = 3.0 Hz, 1H), 4.07 (d, *J* = 8.8 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.52 (d, *J* = 8.8 Hz, 1H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.55, 151.62, 141.21, 137.82, 131.97, 129.76, 128.67, 126.78, 114.93, 114.84, 114.51, 114.23, 68.11, 65.69, 62.52, 55.83,

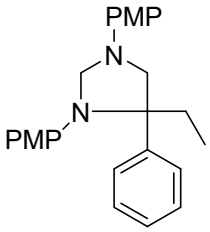
55.68, 23.42. HRMS (ESI) calcd. for $C_{24}H_{26}ClN_2O_2$ $[M+H]^+$: 409.1677, found: 409.1675.



1,3-bis(4-methoxyphenyl)-4-methyl-4-(4-nitrophenyl)imidazolidine (3e):

This compound was prepared via general procedure as a yellow solid (59 mg, yield: 71%), mp: 108-109 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 8.0 Hz, 2H), 6.37 (d, *J* = 8.0 Hz, 2H), 5.02 (s, 1H), 4.80 (s, 1H), 3.78 (s, 3H), 3.72 (s, 3H), 3.55 (s, 1H), 3.52 (s, 1H), 1.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.04, 152.70, 152.20, 147.04, 140.77, 137.44, 127.05, 124.01, 115.61, 114.98, 114.59, 114.05, 68.79, 65.55, 65.08, 55.81, 55.64, 20.46. HRMS (ESI) calcd. for $C_{23}H_{26}N_3O_4$ $[M+H]^+$: 420.1918, found: 420.1917.

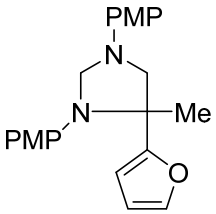


4-ethyl-1,3-bis(4-methoxyphenyl)-4-phenylimidazolidine (3f):

This compound was prepared via general procedure as a white solid (74 mg, yield: 76%), mp: 118-120 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.1 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.26 -7.21 (m, 1H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.72 (d, *J* = 9.0 Hz, 2H), 6.60 (d, *J* = 9.0 Hz, 2H), 6.42 (d, *J* = 9.0 Hz, 2H), 5.04 (d, *J* = 3.0 Hz, 1H), 4.83 (d, *J* = 3.0 Hz, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 3.61 (dd, *J* = 20.7, 8.8 Hz, 2H), 2.57 (dt, *J* = 14.8, 7.4 Hz, 1H), 2.36 (dt, *J* = 14.3, 7.1 Hz, 1H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ

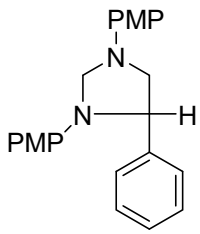
152.32, 151.53, 146.62, 141.03, 138.14, 128.64, 126.83, 125.95, 115.00, 114.54, 113.87, 69.93, 67.96, 62.72, 55.87, 55.64, 28.12, 8.31. HRMS (ESI) calcd. for $C_{25}H_{29}N_2O_2$ $[M+H]^+$: 389.2224, found: 389.2222.



4-(furan-2-yl)-1,3-bis(4-methoxyphenyl)-4-methylimidazolidine (3g):

This compound was prepared via general procedure as a yellow oil (37 mg, yield: 41%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 6.89 (d, *J* = 7.9 Hz, 2H), 6.75 (d, *J* = 7.9 Hz, 2H), 6.60 (d, *J* = 7.9 Hz, 2H), 6.54 (d, *J* = 7.9 Hz, 2H), 6.35 (s, 1H), 6.27 (s, 1H), 4.83 (s, 1H), 4.77 (s, 1H), 3.80 (s, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.50 (d, *J* = 8.2 Hz, 1H), 1.72 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.63, 152.78, 152.12, 141.98, 141.13, 138.24, 116.83, 114.98, 114.40, 113.39, 110.43, 107.11, 68.03, 61.88, 61.70, 55.86, 55.58, 19.63. HRMS (ESI) calcd. for $C_{22}H_{25}N_2O_3$ $[M+H]^+$: 365.1860, found: 365.1863.

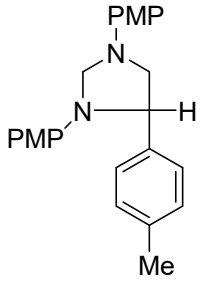


1,3-bis(4-methoxyphenyl)-4-phenylimidazolidine (3h):

This compound was prepared via general procedure as a white solid (69 mg, yield: 77%), mp: 135-136 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 -7.27 (m, 5H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 6.65 (d, *J* = 9.0 Hz, 2H), 6.53 (d, *J* = 9.0 Hz, 2H), 5.11 (d, *J* = 3.0 Hz, 1H), 4.88 (dd, *J* = 7.1, 4.8 Hz, 1H), 4.64 (d, *J* = 3.0 Hz, 1H), 3.85 (dd, *J* = 8.5, 7.3 Hz, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.44 (dd, *J* = 8.6, 4.8 Hz, 1H). ^{13}C NMR (75 MHz,

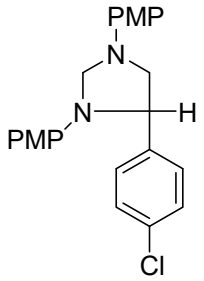
$CDCl_3$) δ 152.58, 151.96, 142.52, 141.24, 140.23, 128.81, 127.46, 126.25, 114.91, 114.80, 114.35, 113.94, 69.23, 62.54, 57.23, 55.80, 55.75. HRMS (ESI) calcd. for $C_{23}H_{25}N_2O_2$ $[M+H]^+$: 361.1911, found: 361.1909.



1,3-bis(4-methoxyphenyl)-4-(p-tolyl)imidazolidine (3i):

This compound was prepared via general procedure as a white solid (74 mg, yield: 79%), mp: 80-81 ^oC.

^1H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.9 Hz, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 8.9 Hz, 2H), 5.09 (d, *J* = 2.7 Hz, 1H), 4.88-4.83 (m, 1H), 4.63 (d, *J* = 2.7 Hz, 1H), 3.83 (d, *J* = 7.6 Hz, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.42 (dd, *J* = 8.4, 4.9 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.52, 151.91, 141.27, 140.30, 139.44, 137.04, 129.45, 126.15, 114.89, 114.77, 114.26, 113.94, 69.20, 62.29, 57.31, 55.78, 55.74, 21.11. HRMS (ESI) calcd. for $C_{24}H_{27}N_2O_2$ $[M+H]^+$: 375.2067, found: 375.2070.

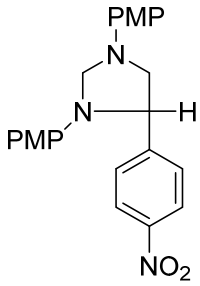


4-(4-chlorophenyl)-1,3-bis(4-methoxyphenyl)imidazolidine (3j):

This compound was prepared via general procedure as a white solid (62 mg, yield: 63%), mp: 116-118 ^oC.

^1H NMR (300 MHz, $CDCl_3$) δ 7.36-7.27 (m, 4H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 6.65 (d, *J* = 9.0 Hz, 2H), 6.51 (d, *J* = 9.0 Hz, 2H), 5.10 (d, *J* = 3.1 Hz,

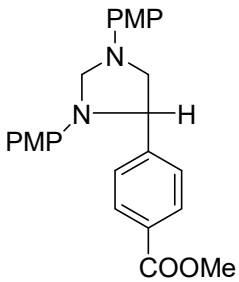
1H), 4.85 (dd, J = 7.2, 4.6 Hz, 1H), 4.61 (d, J = 3.1 Hz, 1H), 3.82 (dd, J = 8.5, 7.3 Hz, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.40 (dd, J = 8.6, 4.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.71, 152.13, 141.10, 141.07, 139.90, 133.09, 128.96, 127.66, 114.92, 114.84, 114.44, 113.93, 69.16, 61.94, 57.09, 55.78, 55.75. HRMS (ESI) calcd. for $C_{23}H_{24}ClN_2O_2$ $[M+H]^+$: 395.1521, found: 395.1525.



1,3-bis(4-methoxyphenyl)-4-(4-nitrophenyl)imidazolidine (3k):

This compound was prepared via general procedure as a yellow solid (41 mg, yield: 50%), mp: 163-164 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.5 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.8 Hz, 2H), 6.67 (d, J = 8.7 Hz, 2H), 6.49 (d, J = 8.7 Hz, 2H), 5.15 (d, J = 2.4 Hz, 1H), 5.01-4.94 (m, 1H), 4.62 (d, J = 2.4 Hz, 1H), 3.87 (t, J = 8.0 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.45 (dd, J = 8.6, 4.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.02, 152.46, 150.34, 147.48, 140.82, 139.47, 127.22, 124.16, 115.00, 114.98, 114.67, 113.88, 77.37, 77.05, 76.73, 69.17, 62.04, 56.76, 55.77, 55.76. HRMS (ESI) calcd. for $C_{23}H_{24}N_3O_4$ $[M+H]^+$: 406.1761, found: 406.1759.

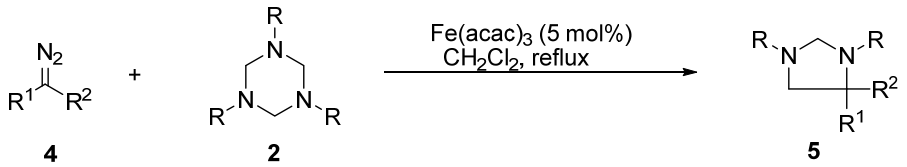


methyl 4-(1,3-bis(4-methoxyphenyl)imidazolidin-4-yl)benzoate (3l):

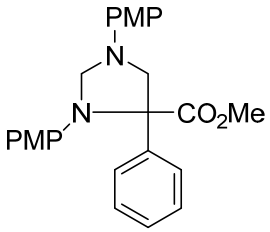
This compound was prepared via general procedure as a white solid (42 mg, yield: 50%), mp: 92-94 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 6.66 (d, *J* = 9.0 Hz, 2H), 6.50 (d, *J* = 9.0 Hz, 2H), 5.13 (d, *J* = 3.1 Hz, 1H), 4.93 (dd, *J* = 7.2, 4.7 Hz, 1H), 4.64 (s, 1H), 3.90 (s, 3H), 3.86 (dd, *J* = 5.8, 2.7 Hz, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.44 (dd, *J* = 8.6, 4.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.89, 152.83, 152.23, 147.95, 141.02, 139.88, 130.21, 129.48, 126.33, 114.96, 114.88, 114.52, 113.96, 69.26, 62.39, 56.97, 55.79, 55.76, 52.12. HRMS (ESI) calcd. for $C_{25}H_{27}N_2O_4$ $[M+H]^+$: 419.1965, found: 419.1968.

General procedure for table 3



To a tube was added triazine **2** (0.3 mmol), $Fe(acac)_3$ (5 mol%), diazo compound **4** (0.25 mmol) and CH_2Cl_2 (5 mL) under an argon atmosphere, then the resulting solution was stirred under refluxing for 6 h. The reaction solution was concentrated under vacuum and the crude residue was purified by column chromatography (petroleum ether/ethyl acetate = 30:1~10:1) to afford product **5**.

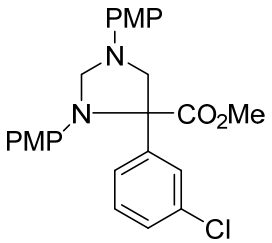


methyl 1,3-bis(4-methoxyphenyl)-4-phenylimidazolidine-4-carboxylate(5a):

This compound was prepared via general procedure as a white solid (84 mg, yield: 80%), mp: 44-46 ^{o}C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.50 (m, 2H), 7.35-7.28 (m, 3H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 8.0 Hz, 2H), 6.44 (d, *J* = 8.0 Hz, 2H), 5.03 (d, *J* = 2.6 Hz, 1H), 4.89 (d, *J* = 2.6 Hz, 1H), 4.29 (d, *J* = 8.8 Hz, 1H), 3.75 (s,

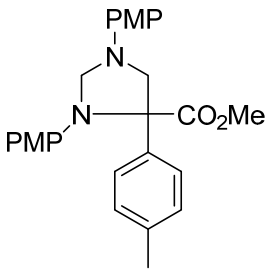
3H), 3.69 (d, J = 6.5 Hz, 6H), 3.56 (d, J = 8.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.96, 152.83, 152.10, 140.75, 138.36, 138.34, 128.46, 127.85, 127.29, 115.32, 114.95, 114.41, 114.17, 73.13, 69.30, 63.96, 55.80, 55.57, 52.64. HRMS (ESI) calcd. for $C_{25}H_{27}N_2O_4$ $[M+H]^+$: 419.1965, found: 419.1962.



Methyl 4-(3-chlorophenyl)-1,3-bis(4-methoxyphenyl)imidazolidine-4-carboxylate (5b):

This compound was prepared via general procedure as a white solid (88 mg, yield: 78%), mp: 48-50 ^{o}C.

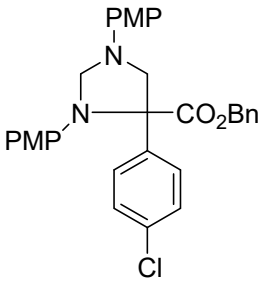
^{1}H NMR (300 MHz, DMSO-d_6) δ 7.54-7.52 (m, 1H), 7.47-7.41 (m, 1H), 7.37 (m, 2H), 6.84 (d, J = 9.0 Hz, 2H), 6.75 (d, J = 9.0 Hz, 2H), 6.72 (d, J = 9.0 Hz, 2H), 6.43 (d, J = 9.0 Hz, 2H), 5.11 (d, J = 3.0 Hz, 1H), 4.67 (d, J = 3.0 Hz, 1H), 4.11 (d, J = 9.0 Hz, 1H), 3.66 (s, 3H), 3.63 (s, 3H), 3.61 (d, J = 9.0 Hz, 1H), 3.58 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 172.46, 152.87, 152.10, 141.91, 140.78, 138.13, 133.22, 130.35, 128.10, 127.85, 126.69, 115.29, 114.99, 114.91, 114.65, 72.40, 69.37, 64.11, 55.67, 55.54, 53.23. HRMS (ESI) calcd. for $C_{25}H_{26}ClN_2O_4$ $[M+H]^+$: 453.1576, found: 453.1579.



methyl 1,3-bis(4-methoxyphenyl)-4-(p-tolyl)imidazolidine-4-carboxylate (5c):

This compound was prepared via general procedure as a white solid (75 mg, yield: 69%), mp: 47-49 ^{o}C.

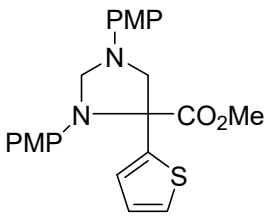
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 9.0 Hz, 2H), 7.14 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 9.0 Hz, 2H), 6.71 (d, *J* = 9.0 Hz, 2H), 6.62 (d, *J* = 9.0 Hz, 2H), 6.45 (d, *J* = 9.0 Hz, 2H), 5.02 (d, *J* = 3.0 Hz, 1H), 4.89 (d, *J* = 3.0 Hz, 1H), 4.28 (d, *J* = 9.0 Hz, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 3.69 (s, 3H), 3.54 (d, *J* = 9.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.05, 152.71, 151.94, 140.75, 138.39, 137.56, 135.19, 129.15, 127.12, 115.23, 114.87, 114.33, 114.06, 72.94, 69.23, 63.92, 55.78, 55.54, 52.62, 21.08. HRMS (ESI) calcd. for $C_{26}H_{29}N_2O_4$ $[M+H]^+$: 433.2122, found: 433.2121.



Benzyl 4-(4-chlorophenyl)-1,3-bis(4-methoxyphenyl)imidazolidine-4-carboxylate(5d):

This compound was prepared via general procedure as colorless oil (93 mg, yield: 70%).

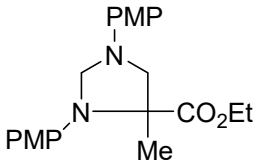
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 9.0 Hz, 2H), 7.33-7.28 (m, 1H), 7.24-7.10 (m, 4H), 6.96 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.68 (d, *J* = 9.0 Hz, 2H), 6.58 (d, *J* = 9.0 Hz, 2H), 6.40 (d, *J* = 9.0 Hz, 2H), 5.13 (d, *J* = 3.0 Hz, 1H), 5.09-5.00 (m, 2H), 4.83 (d, *J* = 3.0 Hz, 1H), 4.20 (d, *J* = 9.0 Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 3.58 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.27, 152.82, 152.37, 140.43, 138.30, 137.17, 135.11, 133.69, 129.15, 128.67, 128.15, 127.82, 115.27, 115.14, 115.00, 114.79, 114.35, 72.45, 69.41, 67.53, 63.80, 55.83, 55.38. HRMS (ESI) calcd. for $C_{31}H_{30}ClN_2O_4$ $[M+H]^+$: 529.1889, found: 529.1879.



methyl 1,3-bis(4-methoxyphenyl)-4-(thiophen-2-yl)imidazolidine-4-carboxylate (5e):

This compound was prepared via general procedure as colorless oil (55 mg, yield: 52%).

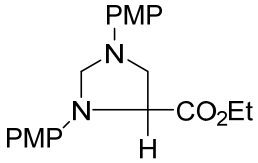
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.24 (m, 2H), 6.96 (t, *J* = 4.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 8.0 Hz, 2H), 6.50 (d, *J* = 8.0 Hz, 2H), 5.08 (s, 1H), 4.89 (s, 1H), 4.13 (d, *J* = 8.0 Hz, 1H), 3.78 (s, 3H), 3.75 (d, *J* = 8.0 Hz, 1H), 3.73 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.69, 152.79, 152.39, 142.97, 140.49, 138.18, 126.70, 126.23, 126.10, 115.23, 115.00, 114.27, 114.16, 70.23, 69.24, 64.24, 55.83, 55.54, 52.91. HRMS (ESI) calcd. for $C_{23}H_{25}N_2O_4S$ $[M+H]^+$: 425.1530, found: 425.1531.



ethyl 1,3-bis(4-methoxyphenyl)-4-methylimidazolidine-4-carboxylate(5f):

This compound was prepared via general procedure as a white solid (55 mg, yield: 62%), mp: 42-44 ^{o}C.

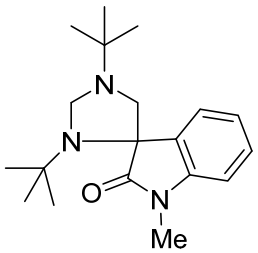
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90-6.81 (m, 4H), 6.63-6.60 (m, 4H), 4.82 (d, *J* = 4.0 Hz, 1H), 4.75 (d, *J* = 4.0 Hz, 1H), 4.19-4.12 (m, 2H), 3.80-3.77 (m, 7H), 3.51 (d, *J* = 8.0 Hz, 1H), 1.70 (s, 3H), 1.13 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.56, 152.58, 152.42, 140.82, 138.23, 115.58, 115.00, 114.65, 113.72, 69.04, 65.85, 61.47, 60.83, 55.84, 55.69, 20.71, 14.09. HRMS (ESI) calcd. for $C_{21}H_{27}N_2O_4$ $[M+H]^+$: 371.1965, found: 371.1963.



ethyl 1,3-bis(4-methoxyphenyl)imidazolidine-4-carboxylate (5g):

This compound was prepared via general procedure as a white solid (70 mg, yield: 78%), mp: 93-95 ^{o}C.

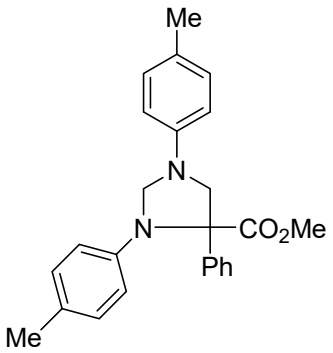
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (t, *J* = 7.3 Hz, 4H), 6.63 (d, *J* = 8.4 Hz, 2H), 6.57 (d, *J* = 8.4 Hz, 2H), 4.89 (s, 1H), 4.58 (d, *J* = 10.0 Hz, 2H), 4.23-4.12 (m, 2H), 3.77 (s, 8H), 1.20 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.45, 152.48, 152.38, 140.77, 139.47, 115.01, 114.95, 113.86, 113.25, 67.32, 61.37, 60.07, 55.81, 55.77, 51.54, 14.19. HRMS (ESI) calcd. for $C_{20}H_{25}N_2O_4$ $[M+H]^+$: 357.1809, found: 357.1811.



1,3-di-tert-butyl-1'-methylspiro[imidazolidine-4,3'-indolin]-2'-one (5h):

This compound was prepared via general procedure as colorless oil (57 mg, yield: 72%).

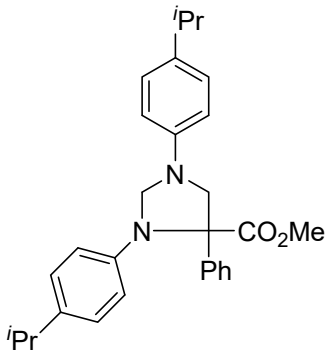
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 9.0, 3.0 Hz, 1H), 7.32-7.24 (td, *J* = 9.0, 3.0 Hz, 1H), 7.02 (td, *J* = 9.0, 3.0 Hz, 1H), 6.82 (d, *J* = 9.0 Hz, 1H), 4.17 (d, *J* = 3.0 Hz, 1H), 4.14 (d, *J* = 3.0 Hz, 1H), 3.22 (s, 3H), 3.10 (d, *J* = 9.0 Hz, 1H), 2.73 (d, *J* = 9.0 Hz, 1H), 1.11 (s, 9H), 0.93 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.82, 141.89, 133.68, 128.11, 126.35, 122.13, 107.75, 68.55, 63.57, 58.87, 54.43, 51.94, 28.20, 26.54, 26.22. HRMS (ESI) calcd. for $C_{19}H_{30}N_3O$ $[M+H]^+$: 316.2383, found: 316.2382.



methyl 4-phenyl-1,3-di-p-tolylimidazolidine-4-carboxylate(5i):

This compound was prepared via general procedure as a white solid (72 mg, yield: 75%), mp: 116-118 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59-7.49 (m, 2H), 7.37-7.24 (m, 3H), 7.08 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 6.57 (d, *J* = 9.0 Hz, 2H), 6.40 (d, *J* = 9.0 Hz, 2H), 5.08 (d, *J* = 3.0 Hz, 1H), 4.92 (d, *J* = 3.0 Hz, 1H), 4.31 (d, *J* = 9.0 Hz, 1H), 3.67 (s, 3H), 3.59 (d, *J* = 9.0 Hz, 1H), 2.26 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.99, 143.96, 141.88, 138.31, 129.88, 129.22, 128.49, 127.84, 127.80, 127.26, 127.05, 114.25, 113.25, 72.76, 68.63, 63.50, 52.75, 20.48, 20.40. HRMS (ESI) calcd. for $C_{25}H_{27}N_2O_2$ $[M+H]^+$: 387.2067, found: 387.2066.

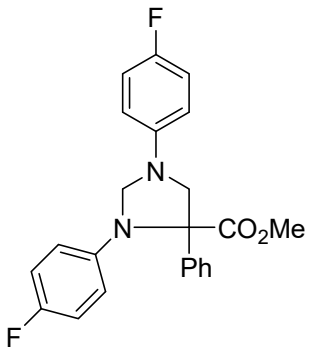


methyl 1,3-bis(4-isopropylphenyl)-4-phenylimidazolidine-4-carboxylate(5j):

This compound was prepared via general procedure as a white solid (75 mg, yield: 68%), mp: 116-118 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 9.0 Hz, 2H), 7.42-7.28 (m, 3H), 7.19 (d, *J* = 9.0 Hz, 2H), 7.01 (d, *J* = 9.0 Hz, 2H), 6.65 (d, *J* = 9.0 Hz, 2H), 6.46 (d, *J* = 9.0 Hz, 2H), 5.13 (s, 1H), 4.98 (s, 1H), 4.37 (d, *J* = 9.0 Hz, 1H), 3.72 (s, 3H), 3.63 (d, *J* = 9.0 Hz, 1H), 2.95-2.72 (m, 2H), 1.25 (d, *J* = 9.0 Hz, 6H), 1.21 (d, *J* = 9.0 Hz, 6H). ^{13}C

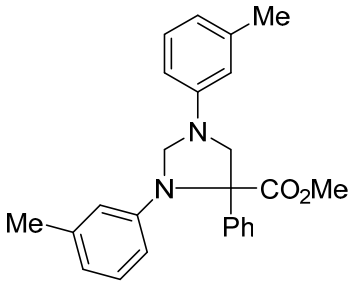
NMR (100 MHz, $CDCl_3$) δ 172.90, 144.14, 142.08, 139.02, 138.37, 138.12, 128.47, 127.81, 127.27, 127.24, 126.50, 114.18, 113.12, 72.82, 68.47, 63.37, 52.70, 33.27, 33.03, 24.27, 24.14. HRMS (ESI) calcd. for $C_{29}H_{35}N_2O_2$ $[M+H]^+$: 443.2693, found: 443.2691.



methyl 1,3-bis(4-fluorophenyl)-4-phenylimidazolidine-4-carboxylate(5k):

This compound was prepared via general procedure as a white solid (54 mg, yield: 55%), mp: 130-132 °C.

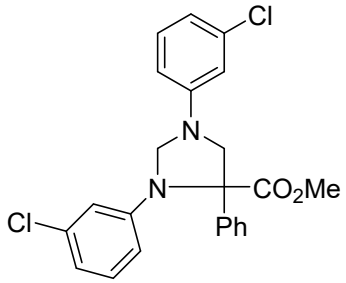
^{1}H NMR (300 MHz, DMSO-d_6) δ 7.50-7.47 (m, 2H), 7.44-7.31 (m, 3H), 7.11 (t, J = 9.0 Hz, 2H), 6.95 (t, J = 9.0 Hz, 2H), 6.84 (dd, J = 9.0, 3.0 Hz, 2H), 6.50 (dd, J = 9.0, 3.0 Hz, 2H), 5.10 (d, J = 3.0 Hz, 1H), 4.84 (d, J = 3.0 Hz, 1H), 4.33 (d, J = 9.0 Hz, 1H), 3.68 (s, 3H), 3.62 (d, J = 9.0 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 172.39, 157.80, 157.08, 154.69, 153.98, 143.22, 143.20, 140.87, 140.84, 138.34, 128.81, 128.33, 127.75, 116.14, 115.85, 115.47, 115.30, 115.20, 73.10, 69.11, 63.80, 53.20. HRMS (ESI) calcd. for $C_{23}H_{21}F_2N_2O_2$ $[M+H]^+$: 395.1566, found: 395.1565.



methyl 4-phenyl-1,3-di-m-tolylimidazolidine-4-carboxylate(5l):

This compound was prepared via general procedure as a white solid (60 mg, yield: 62%), mp: 104-106 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 6.0 Hz, 2H), 7.38-7.26 (m, 3H), 7.21-7.12 (m, 1H), 6.97 (t, *J* = 6.0 Hz, 1H), 6.66 (d, *J* = 6.0 Hz, 1H), 6.58 (d, *J* = 6.0 Hz, 1H), 6.49 (d, *J* = 6.0 Hz, 2H), 6.39 (s, 1H), 6.23 (dd, *J* = 6.0, 3.0 Hz, 1H), 5.13 (d, *J* = 3.0 Hz, 1H), 4.96 (d, *J* = 3.0 Hz, 1H), 4.33 (d, *J* = 9.0 Hz, 1H), 3.69 (s, 3H), 3.64 (d, *J* = 9.0 Hz, 1H), 2.33 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.90, 145.95, 144.11, 139.21, 138.45, 138.24, 129.23, 128.43, 128.36, 127.80, 127.21, 119.43, 118.96, 114.64, 113.85, 111.78, 110.30, 72.58, 68.19, 63.17, 52.79, 21.89, 21.79. HRMS (ESI) calcd. for $C_{25}H_{27}N_2O_2$ $[M+H]^+$: 387.2067, found: 387.2065.

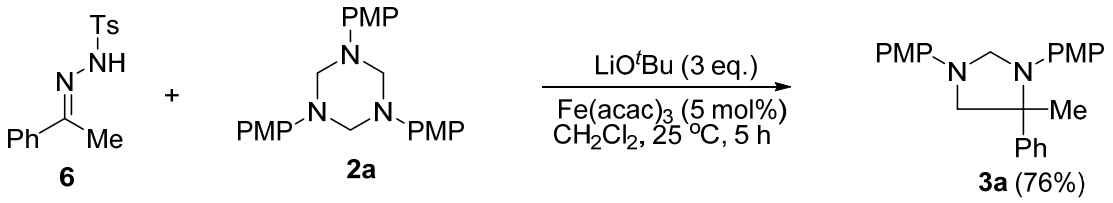


methyl 1,3-bis(3-chlorophenyl)-4-phenylimidazolidine-4-carboxylate(5m):

This compound was prepared via general procedure as a white solid (62 mg, yield: 58%), mp: 44-46 ^{o}C.

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.40-7.37 (m, 2H), 7.35-7.25 (m, 3H), 7.15 (t, *J* = 9.0 Hz, 1H), 6.96 (t, *J* = 9.0 Hz, 1H), 6.86 (t, *J* = 3.0 Hz, 1H), 6.74-6.69 (m, 2H), 6.62 (dd, *J* = 6.0, 3.0 Hz, 1H), 6.57 (t, *J* = 3.0 Hz, 1H), 6.27 (dd, *J* = 6.0, 3.0 Hz, 1H), 5.04 (d, *J* = 3.0 Hz, 1H), 4.77 (d, *J* = 3.0 Hz, 1H), 4.31 (d, *J* = 9.0 Hz, 1H), 3.61 (s, 3H), 3.59 (d, *J* = 9.0 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 171.99, 147.36, 145.44, 137.85, 134.43, 133.72, 131.00, 130.14, 128.93, 128.52, 127.68, 118.34, 117.56, 113.98, 113.66, 113.16, 112.68, 72.84, 68.09, 62.81, 53.43. HRMS (ESI) calcd. for $C_{23}H_{21}Cl_2N_2O_2$ $[M+H]^+$: 427.0975, found: 427.0977.

Cycloaddition of tosyl hydrazone with hexahydro-1,3,5-triazine for Scheme 2



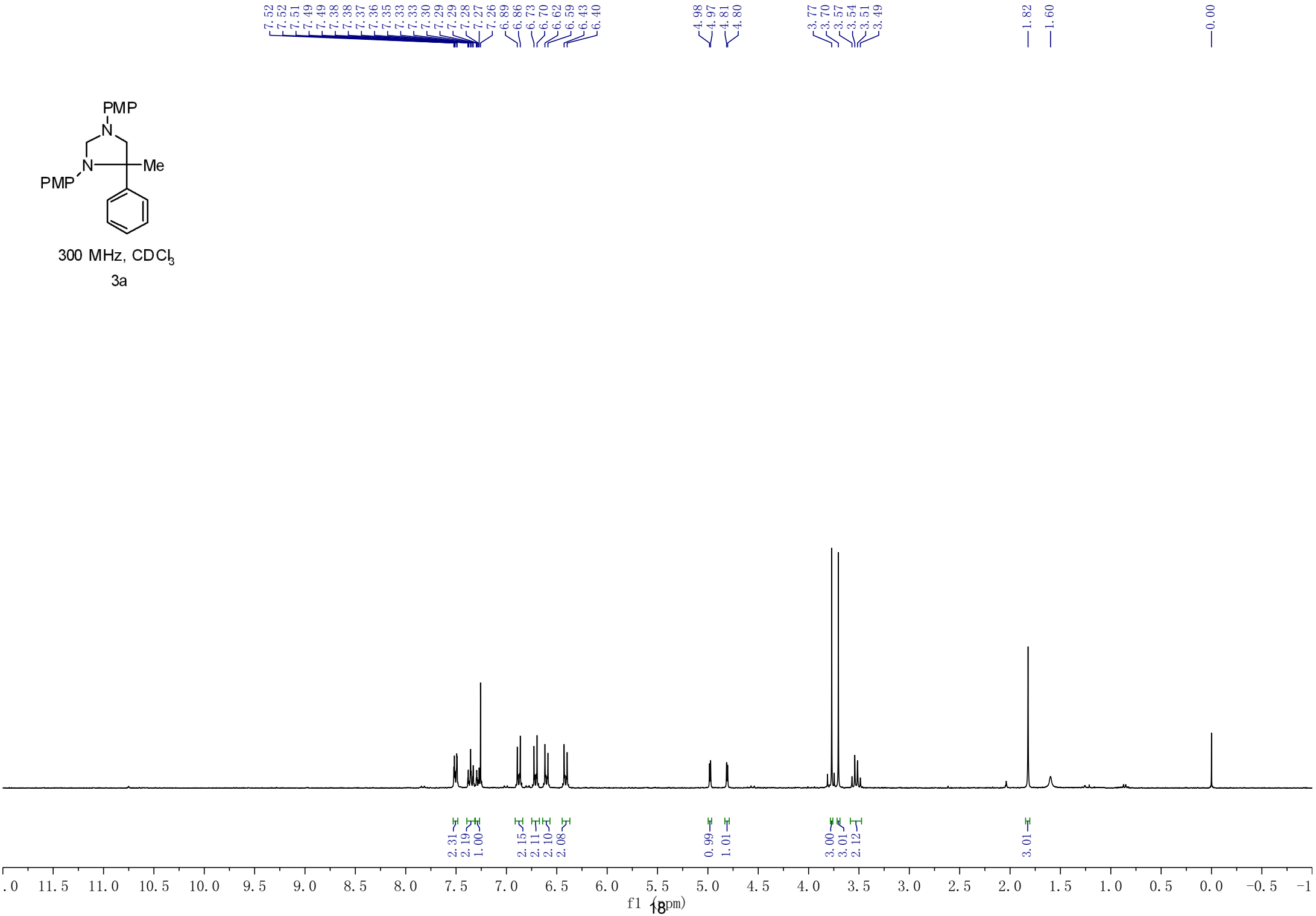
To a mixture of **6** (72 mg) and ^{t}BuOLi (60 mg) in CH_2Cl_2 (5 mL) was added riazine **2a** (121 mg, 0.3 mmol) and Fe(acac)$_3$ (4.4 mg) under an argon atmosphere, then the resulting solution was stirred at RT for 5 h. The reaction solution was concentrated under vacuum and the crude residue was purified by column chromatography (petroleum ether/ethyl acetate = 20:1) to give **3a** as a white solid (71 mg, yield: 76%), mp: 95-96°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53-7.48 (m, 2H), 7.39-7.31 (m, 2H), 7.31-7.27 (m, 1H), 6.88 (d, *J* = 9.0 Hz, 2H), 6.71 (d, *J* = 9.0 Hz, 2H), 6.60 (d, *J* = 9.0 Hz, 2H), 6.41 (d, *J* = 9.0 Hz, 2H), 4.98 (d, *J* = 3.0 Hz, 1H), 4.81 (d, *J* = 3.0 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.53 (q, *J* = 8.4 Hz, 2H), 1.82 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.79, 165.82, 159.64, 144.56, 140.67, 127.33, 126.70, 125.58, 107.70, 98.95, 82.54, 76.20, 60.27, 54.74, 50.05, 38.54, 37.15, 13.15. HRMS (ESI) calcd. for $C_{24}H_{27}N_2O_2$ $[M+H]^+$: 375.2067, found: 375.2065.

References:

[1] Zhu, C.; Xu, G.; Sun, J. *Angew. Chem. Int. Ed.* **2016**, *55*, 11867.

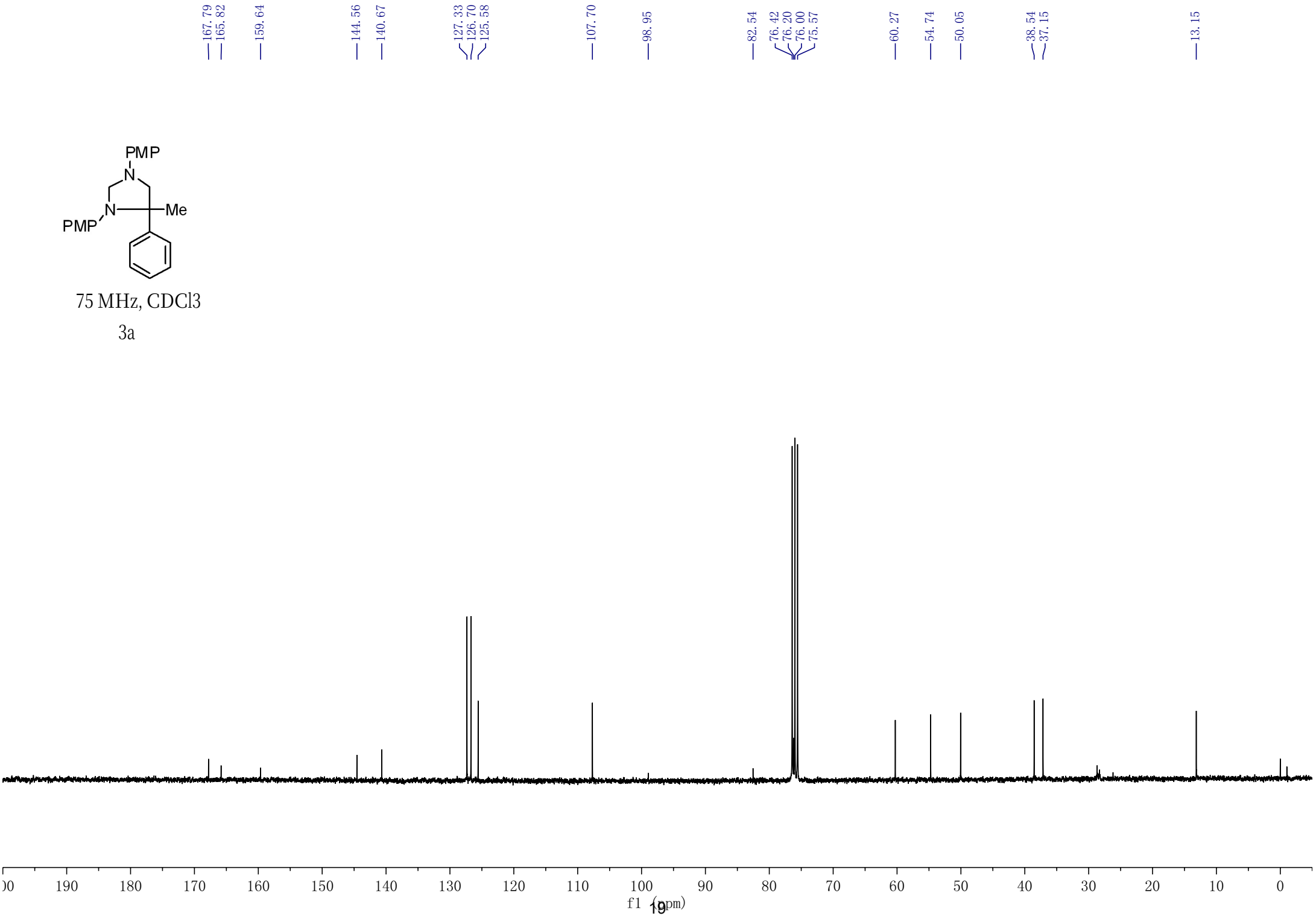
[2] Poh, J.-S.; Tran, D. N.; Battilocchio, C.; Hawkins, J. M.; Ley, S. V. *Angew. Chem. Int. Ed.* **2015**, *54*, 7920.

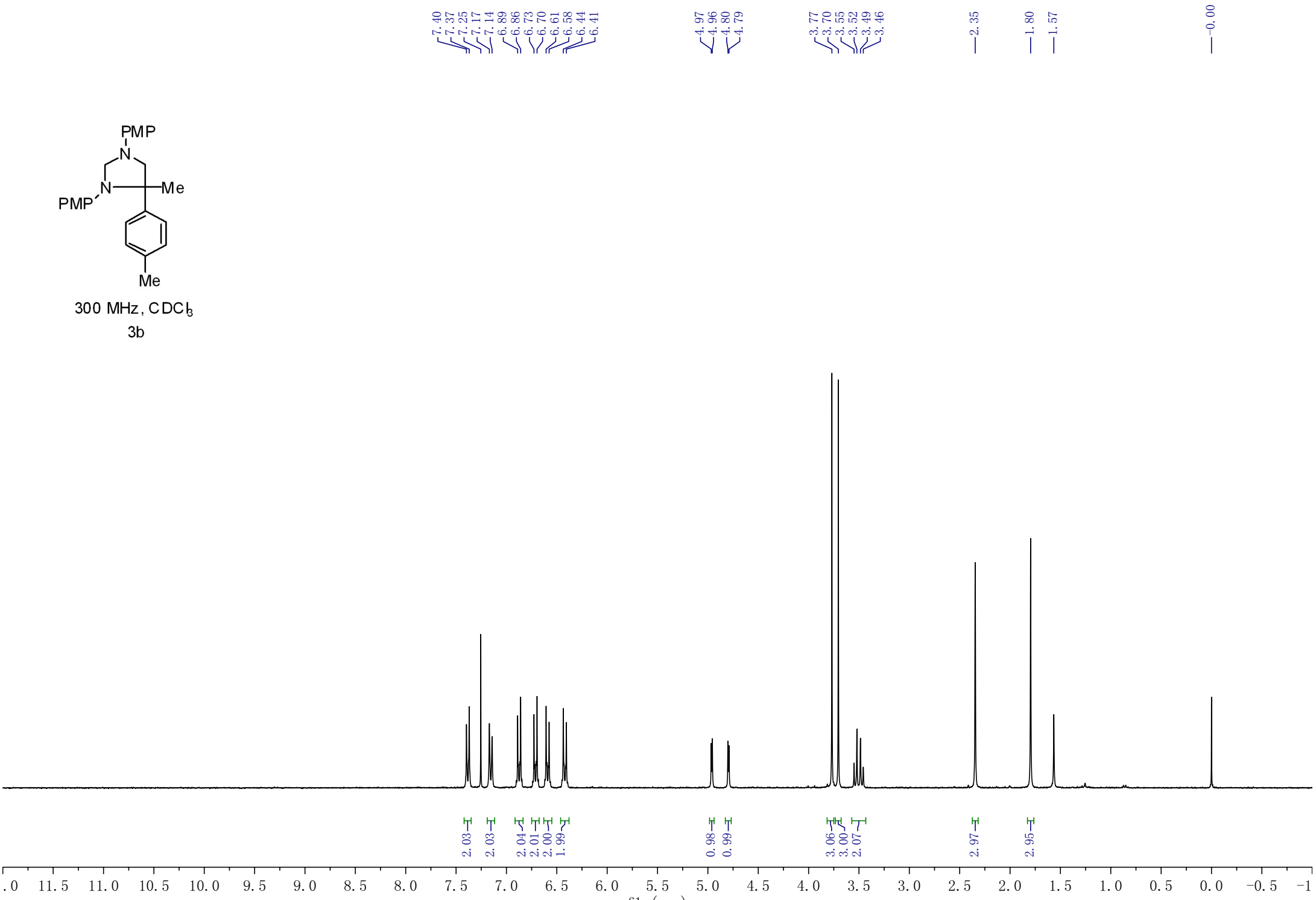
[3] Nicolle, S. M.; Moody, C. J. *Chem. Eur. J.* **2014**, 20, 4420.


7.52 7.52 7.51 7.49 7.49 7.38 7.38 7.37 7.36 7.35 7.33 7.33 7.30 7.29 7.29 7.28 7.27 7.26 6.89 6.86 6.73 6.70 6.62 6.59 6.43 6.40
4.98 4.97 4.81 4.80
3.77 3.70 3.57 3.54 3.51 3.49
1.82 1.60
0.00
PMP
N
N
Me
PMP
300 MHz, CDCl3
3a
2.31 2.19 1.00 2.15 2.11 2.10 2.08 0.99 1.01 3.00 3.01 2.12 3.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

75 MHz, CDCl3

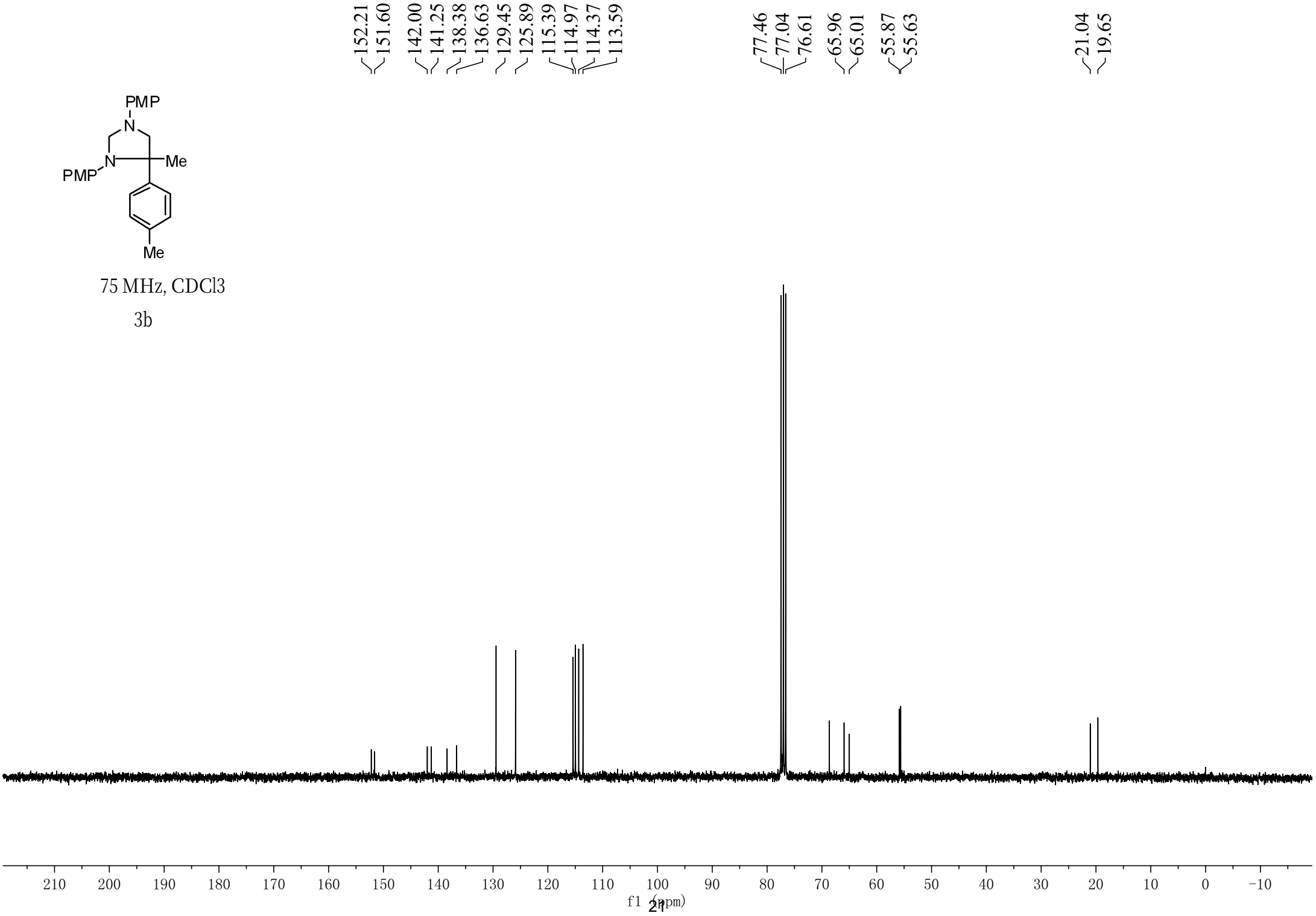
3a




PMP
N
N
Me
PMP
Me
300 MHz, CDCl3
3b
7.40
7.37
7.25
7.17
7.14
6.89
6.86
6.73
6.70
6.61
6.58
6.44
6.41
4.97
4.96
4.80
4.79
3.77
3.70
3.55
3.52
3.49
3.46
2.35
1.80
1.57
0.00
2.03
2.03
2.04
2.01
2.00
1.99
0.98
0.99
3.06
3.00
2.07
2.97
2.95
f1 (ppm)

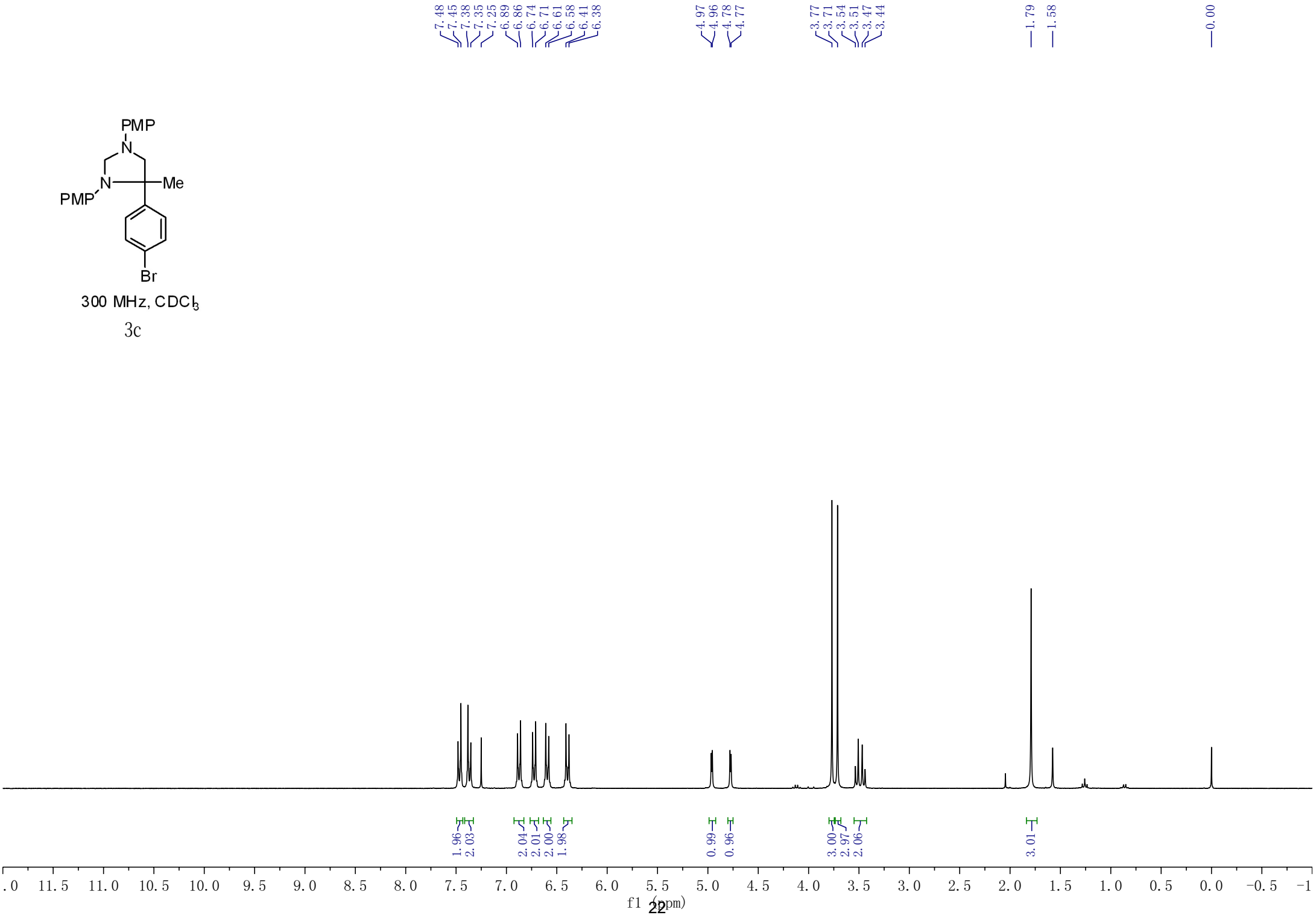
75 MHz, CDCl3

3b



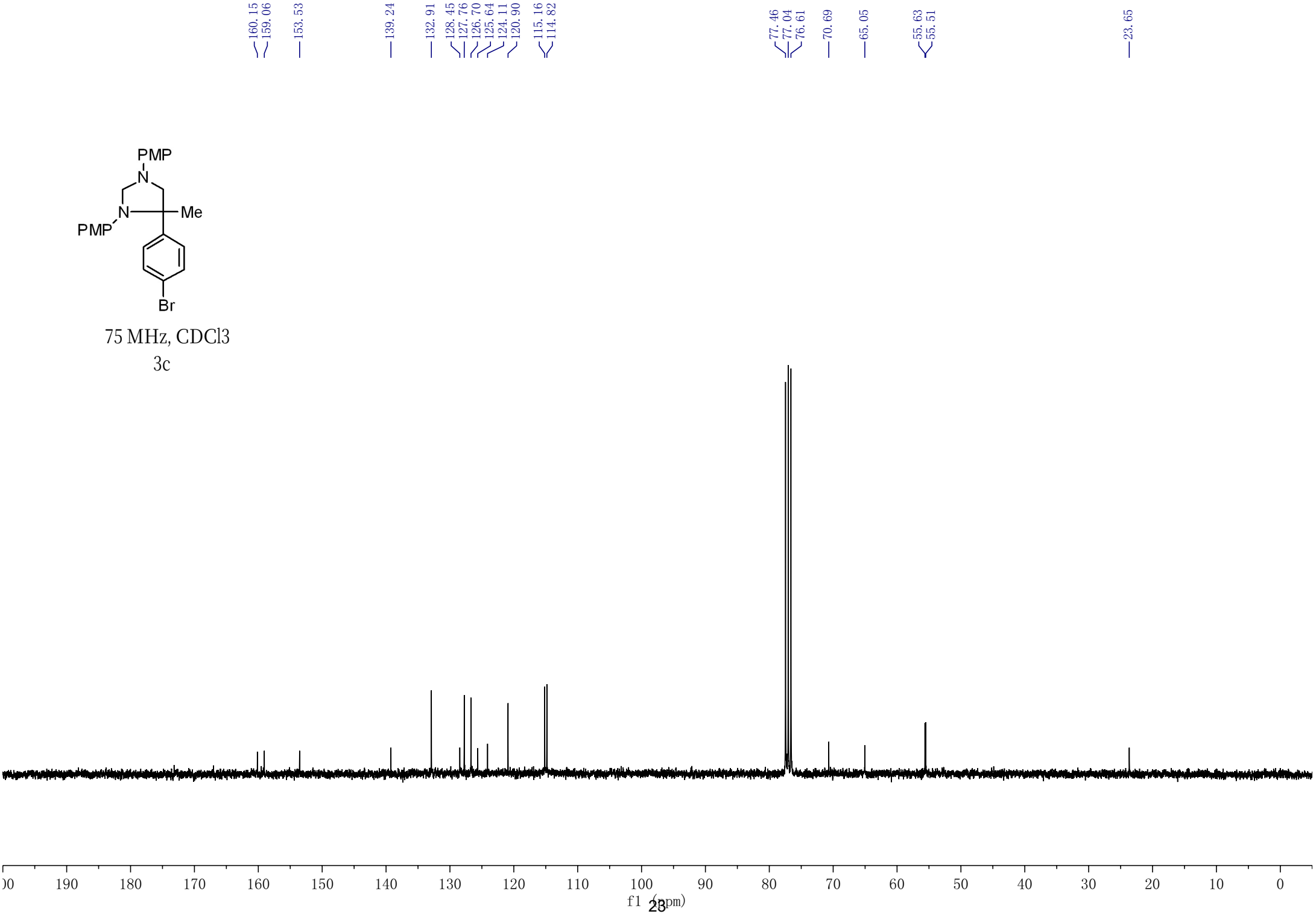
300 MHz, $CDCl_3$

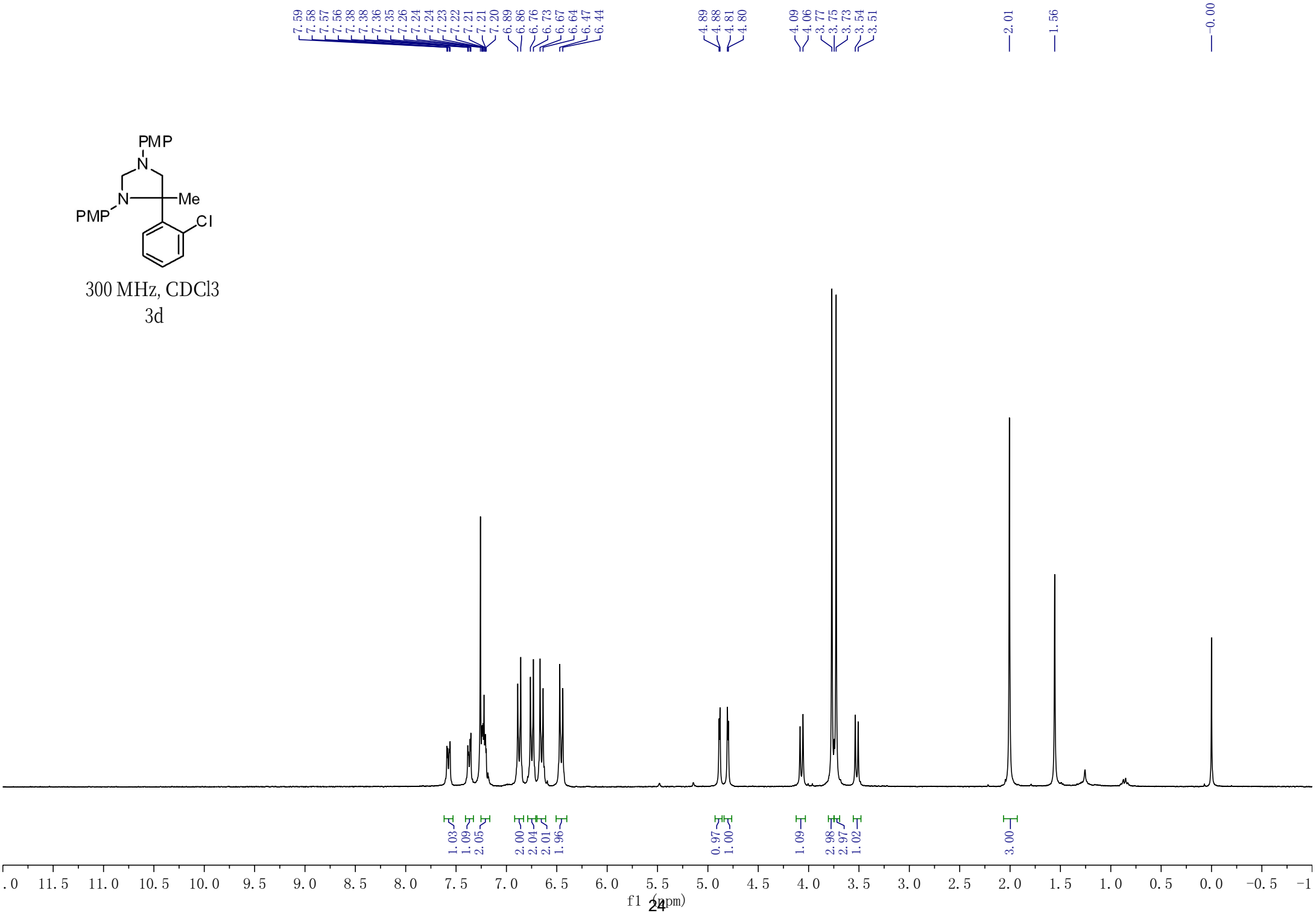
3c



75 MHz, CDCl3

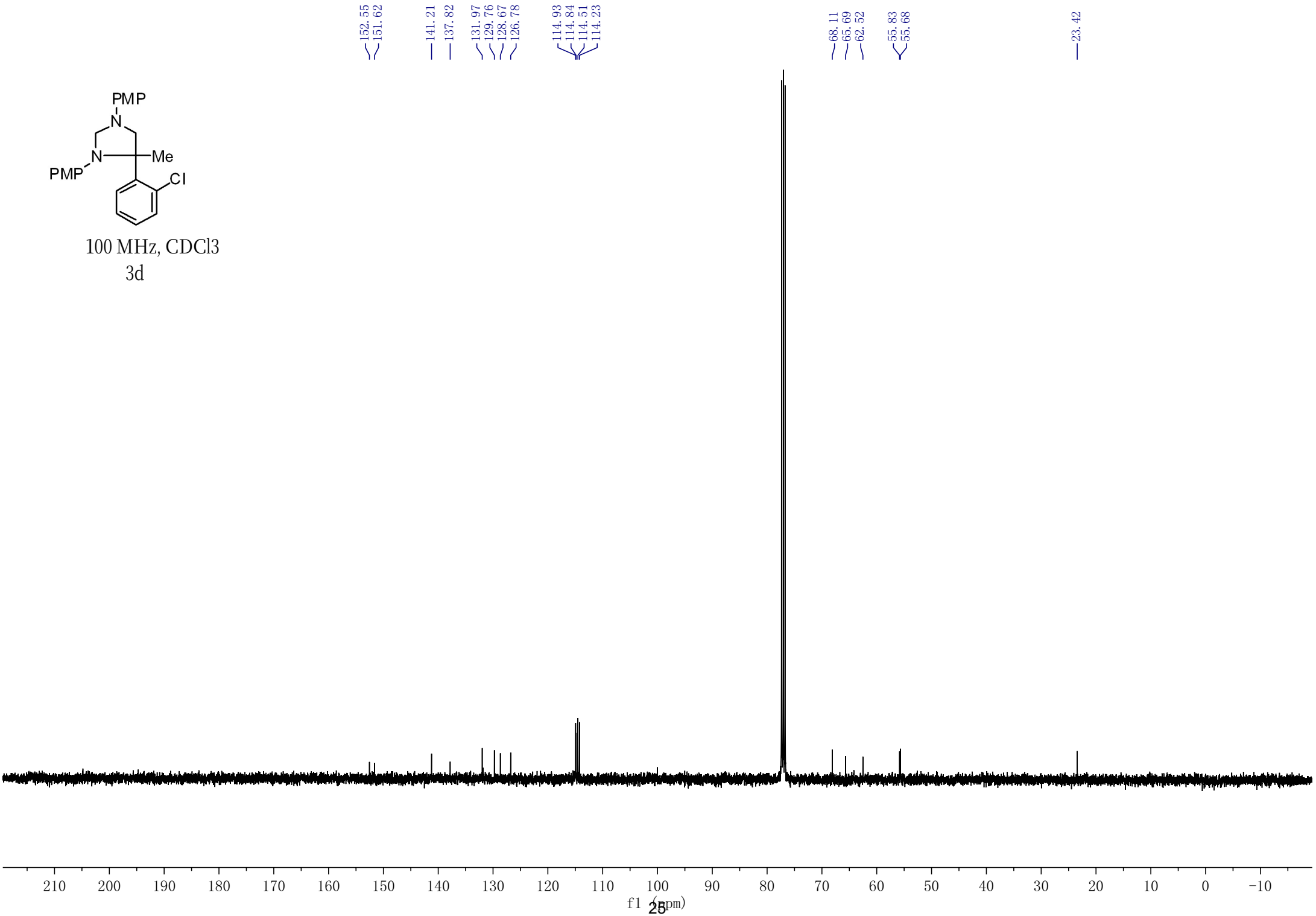
3c



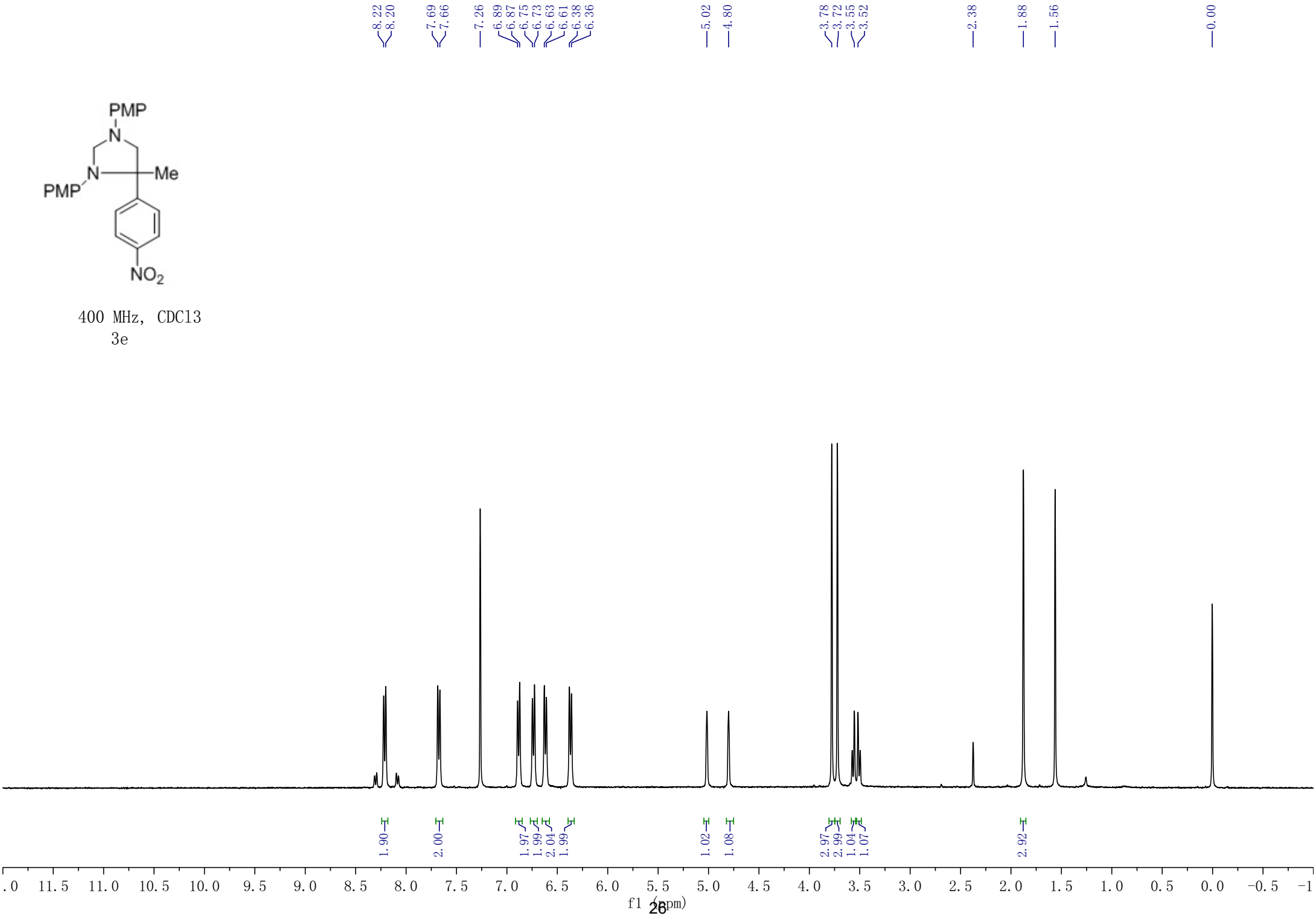

PMP
N
N
Me
PMP
Cl
300 MHz, CDCl3
3d
7.59
7.58
7.57
7.56
7.38
7.38
7.36
7.35
7.26
7.24
7.24
7.23
7.22
7.21
7.21
7.20
6.89
6.86
6.76
6.73
6.67
6.64
6.47
6.44
4.89
4.88
4.81
4.80
4.09
4.06
3.77
3.75
3.73
3.54
3.51
2.01
1.56
0.00
1.03
1.09
2.05
2.00
2.04
2.01
1.96
0.97
1.00
1.09
2.98
2.97
1.02
3.00
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

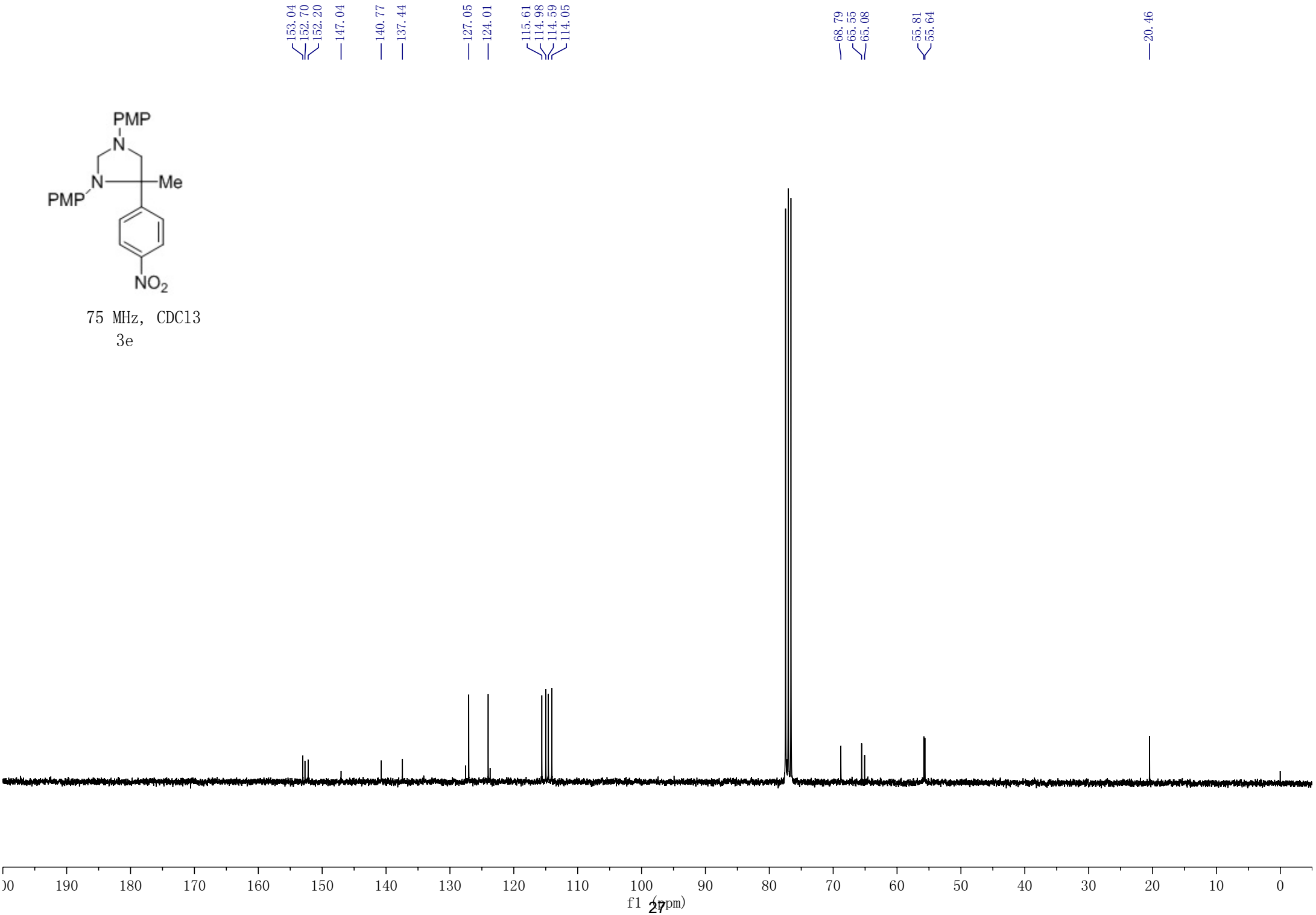
100 MHz, CDCl3

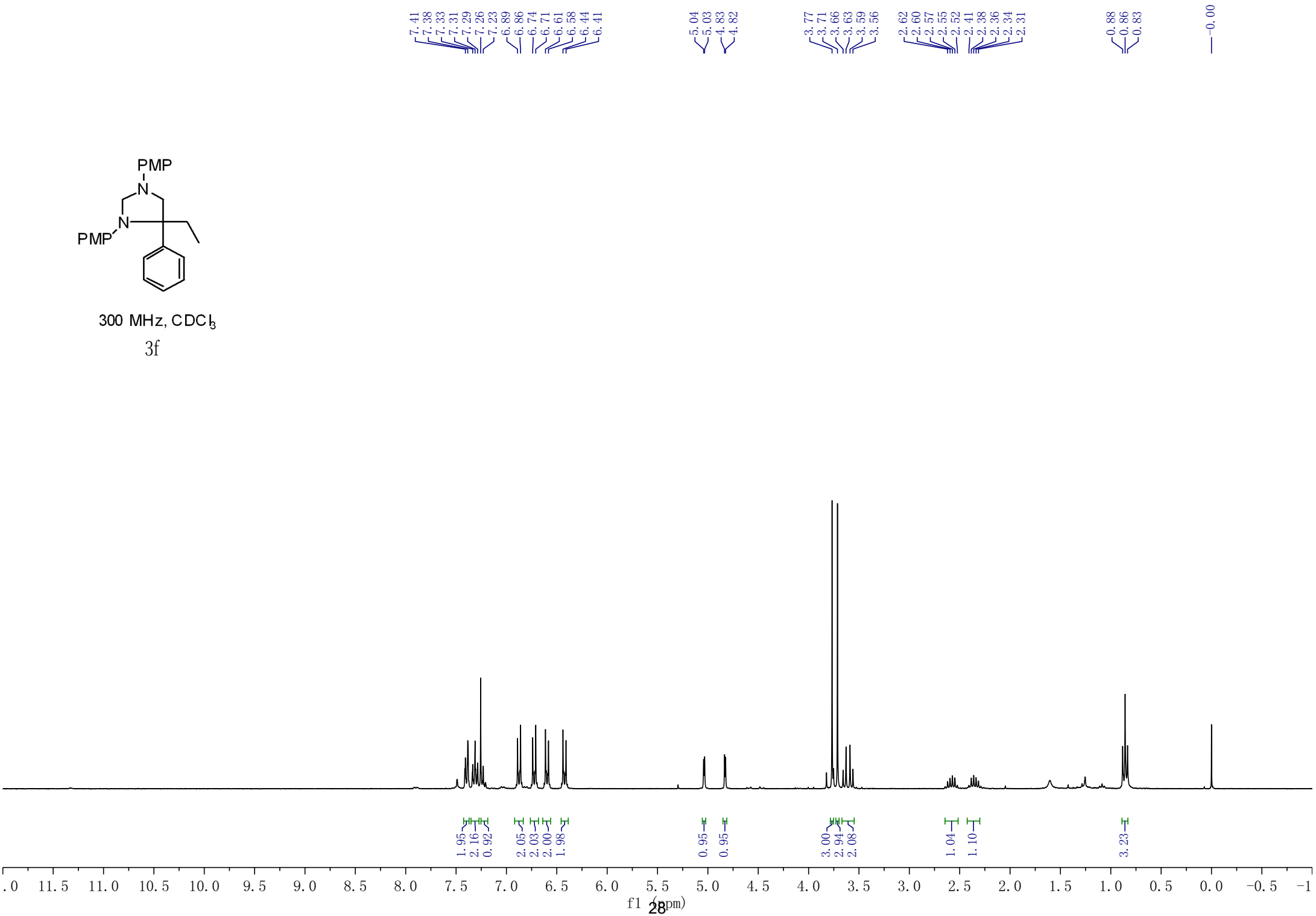
3d



400 MHz, CDCl3
3e

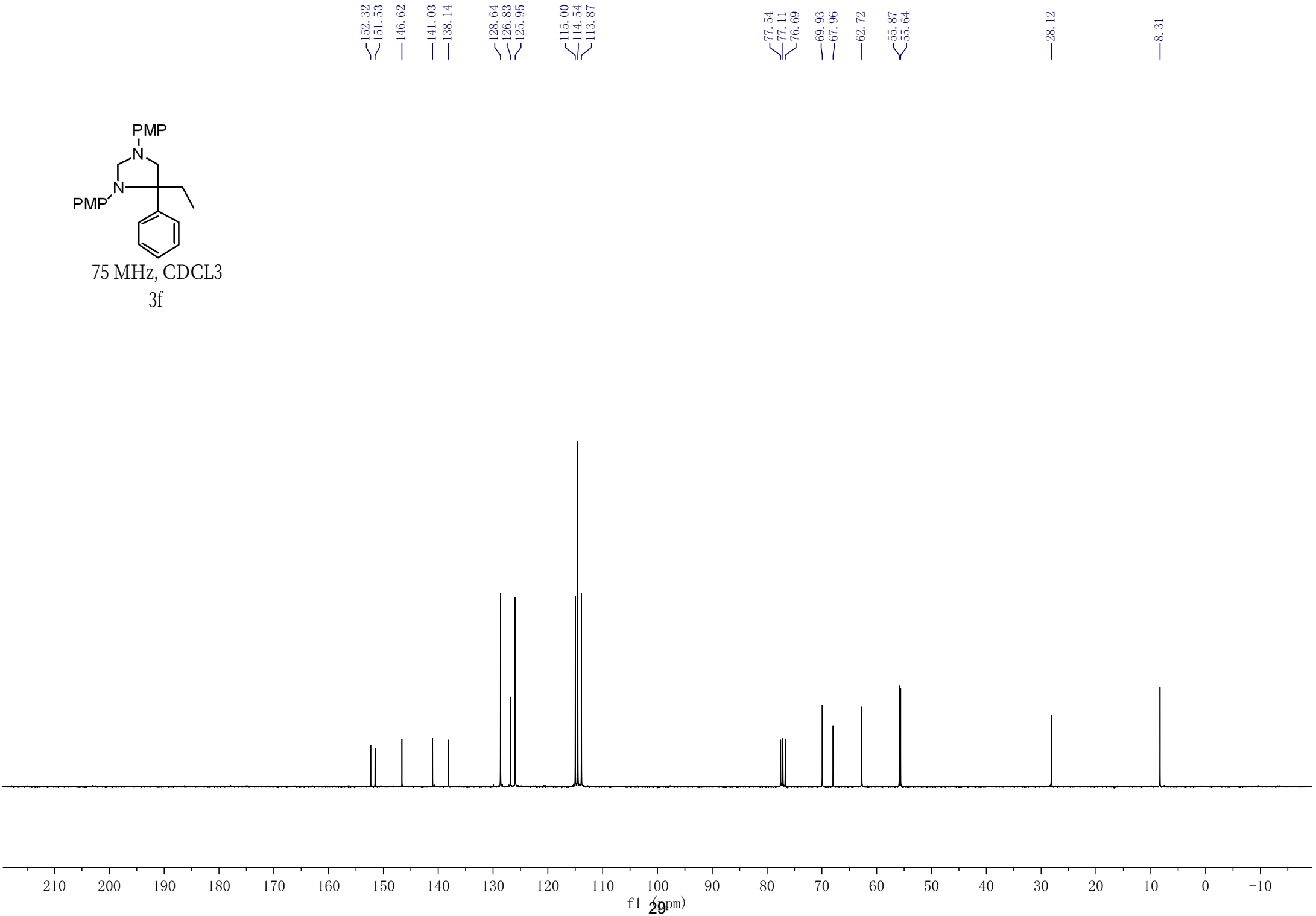



153.04
152.70
152.20
147.04
140.77
137.44
127.05
124.01
115.61
114.98
114.59
114.05
68.79
65.55
65.08
55.81
55.64
20.46
PMP
N
N
Me
PMP
NO2
75 MHz, CDCl3
3e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.41
7.38
7.33
7.31
7.29
7.26
7.23
6.89
6.86
6.74
6.71
6.61
6.58
6.44
6.41
5.04
5.03
4.83
4.82
3.77
3.71
3.66
3.63
3.59
3.56
2.62
2.60
2.57
2.55
2.52
2.41
2.38
2.36
2.34
2.31
0.88
0.86
0.83
0.00
PMP
N
N
PMP
300 MHz, CDCl3
3f
1.95
2.16
0.92
2.05
2.03
2.00
1.98
0.95
0.95
3.00
2.94
2.08
1.04
1.10
3.23
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

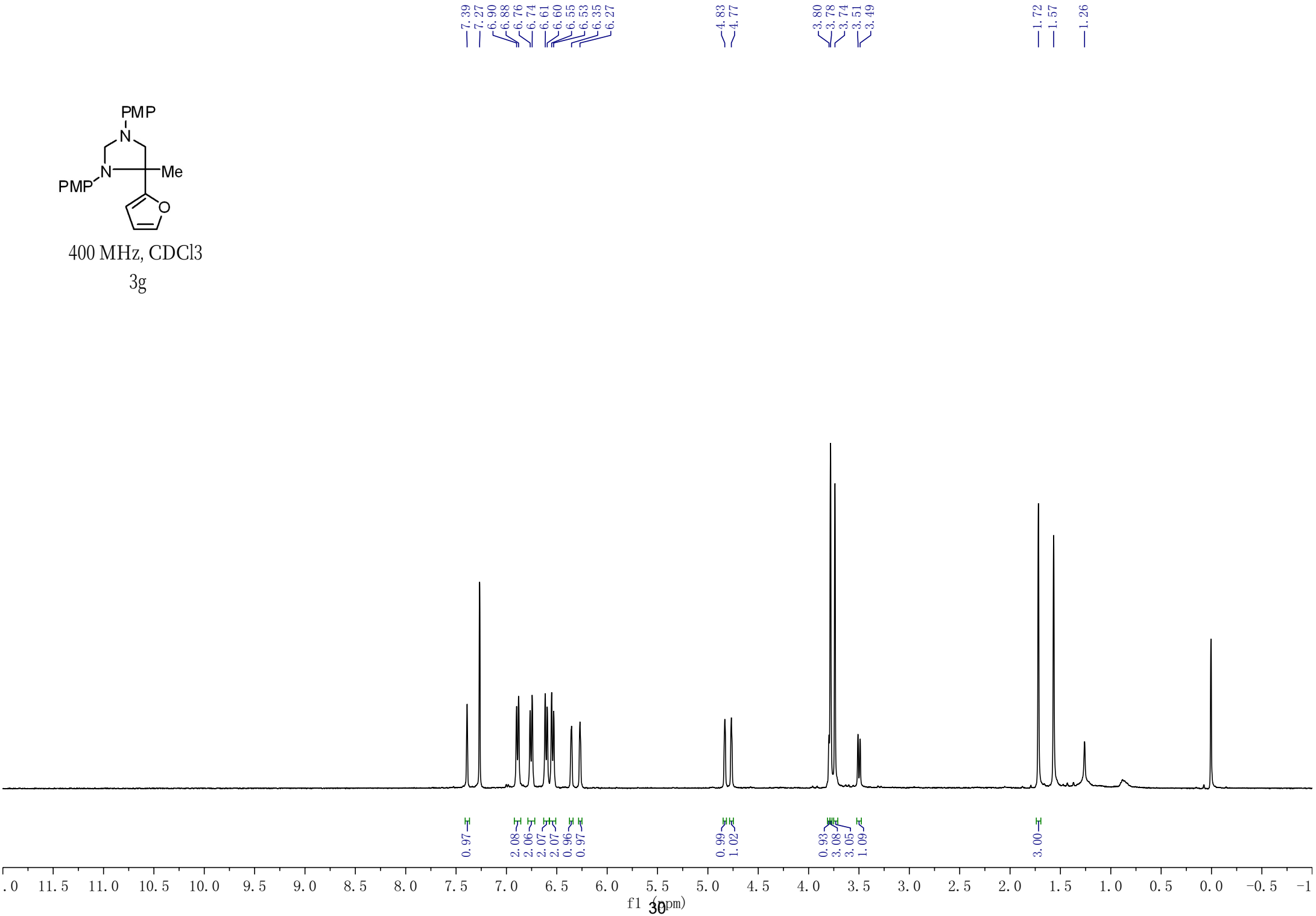
75 MHz, CDCL3

3f



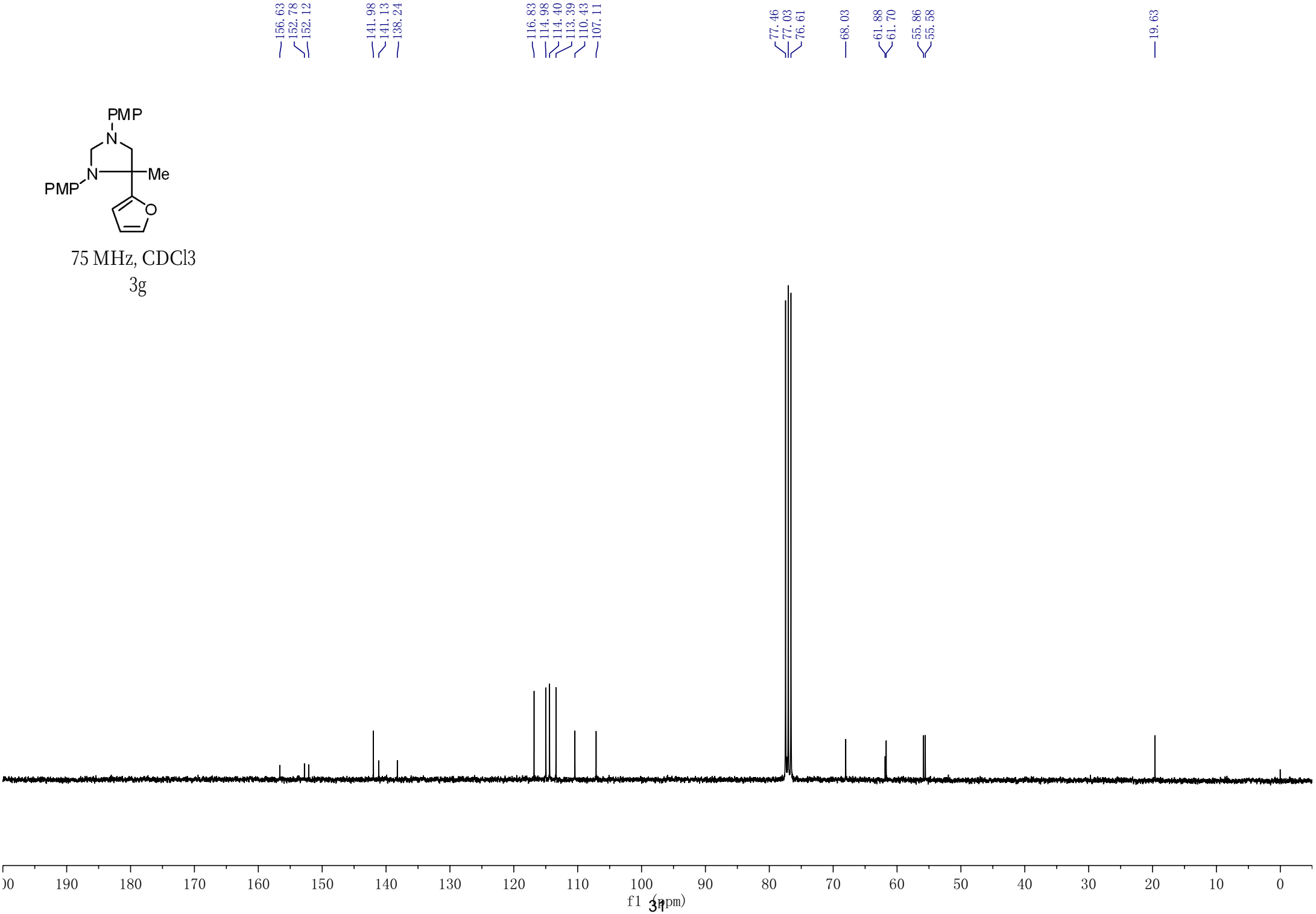
400 MHz, CDCl3

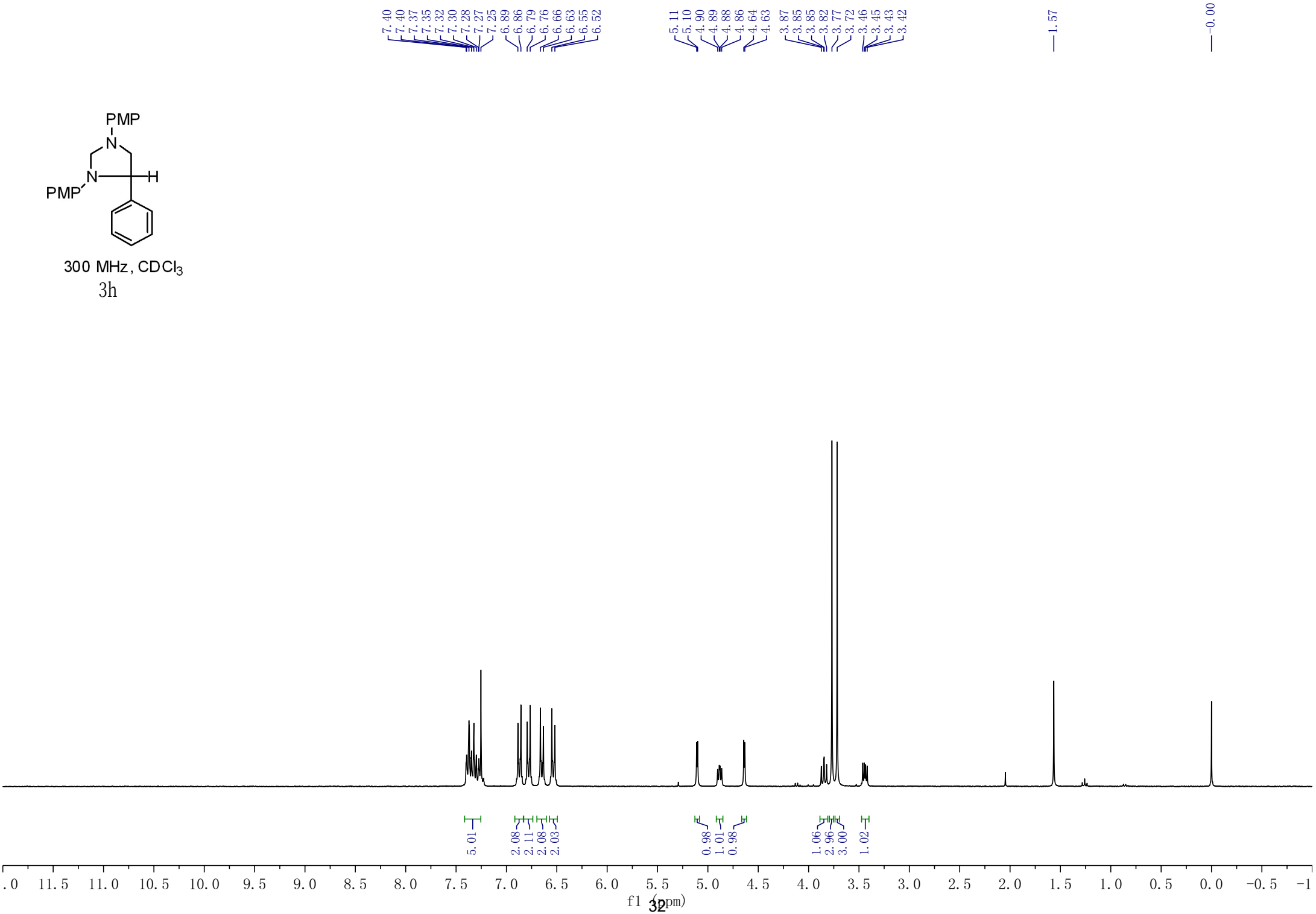
3g

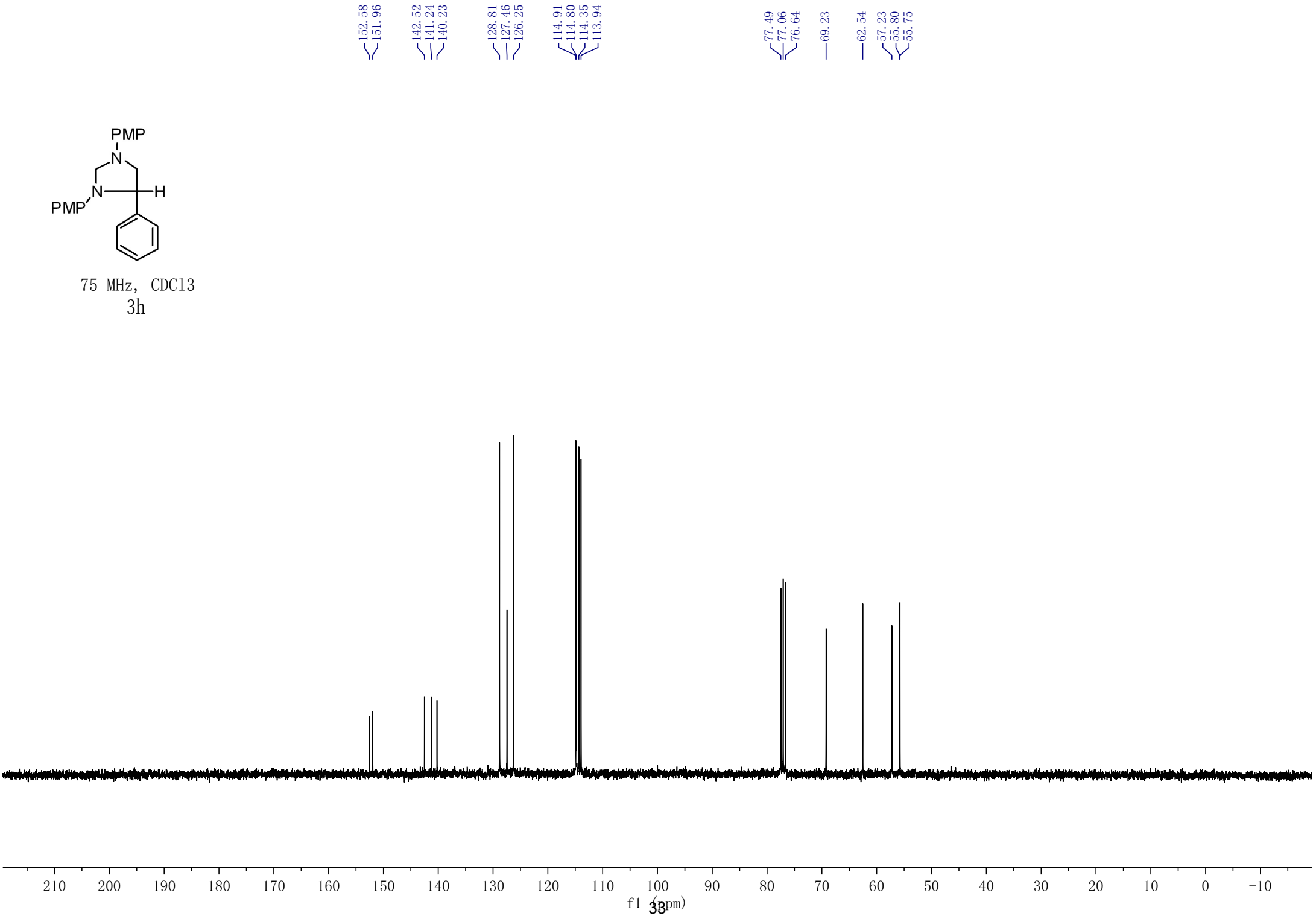


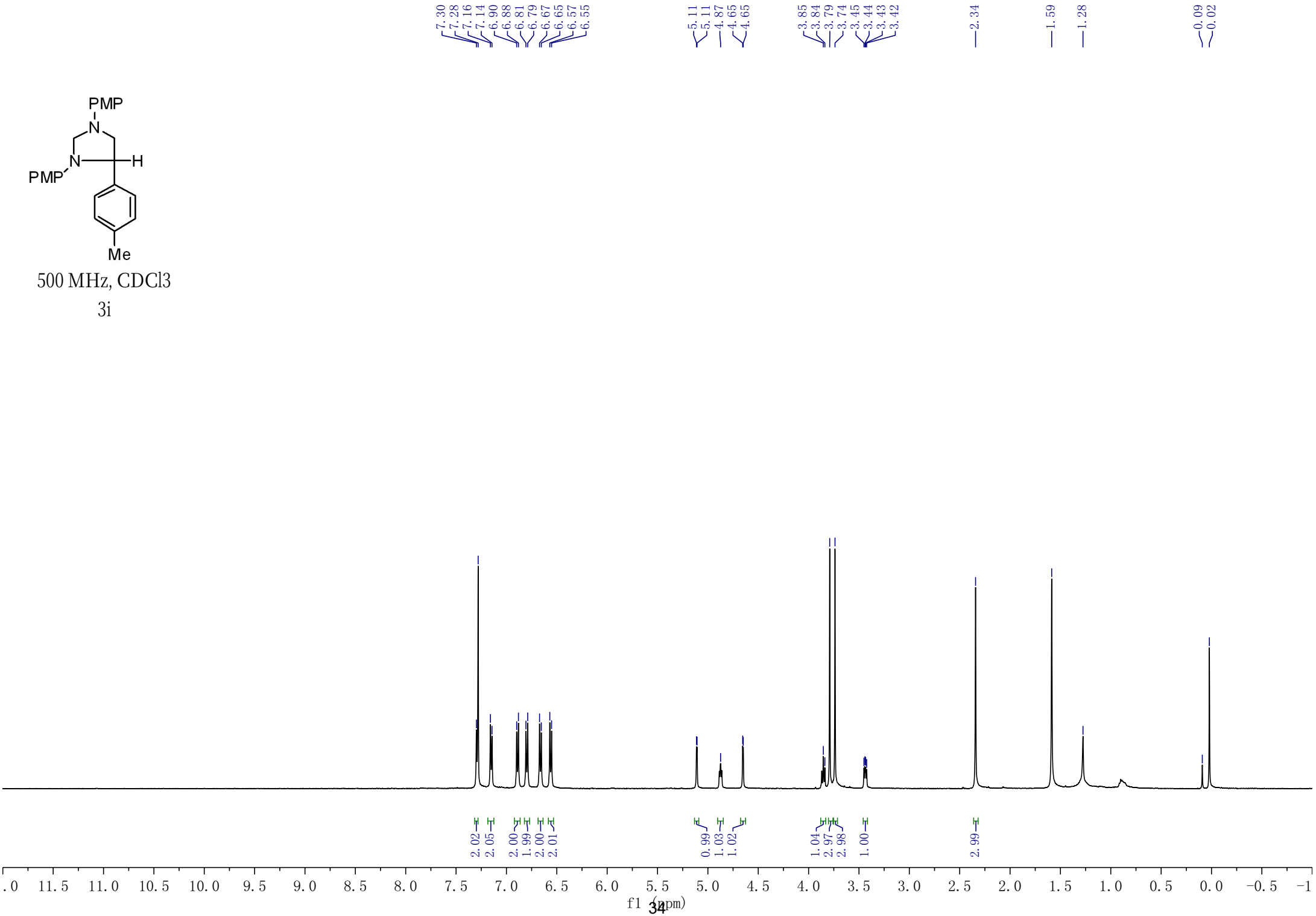
75 MHz, CDCl3

3g



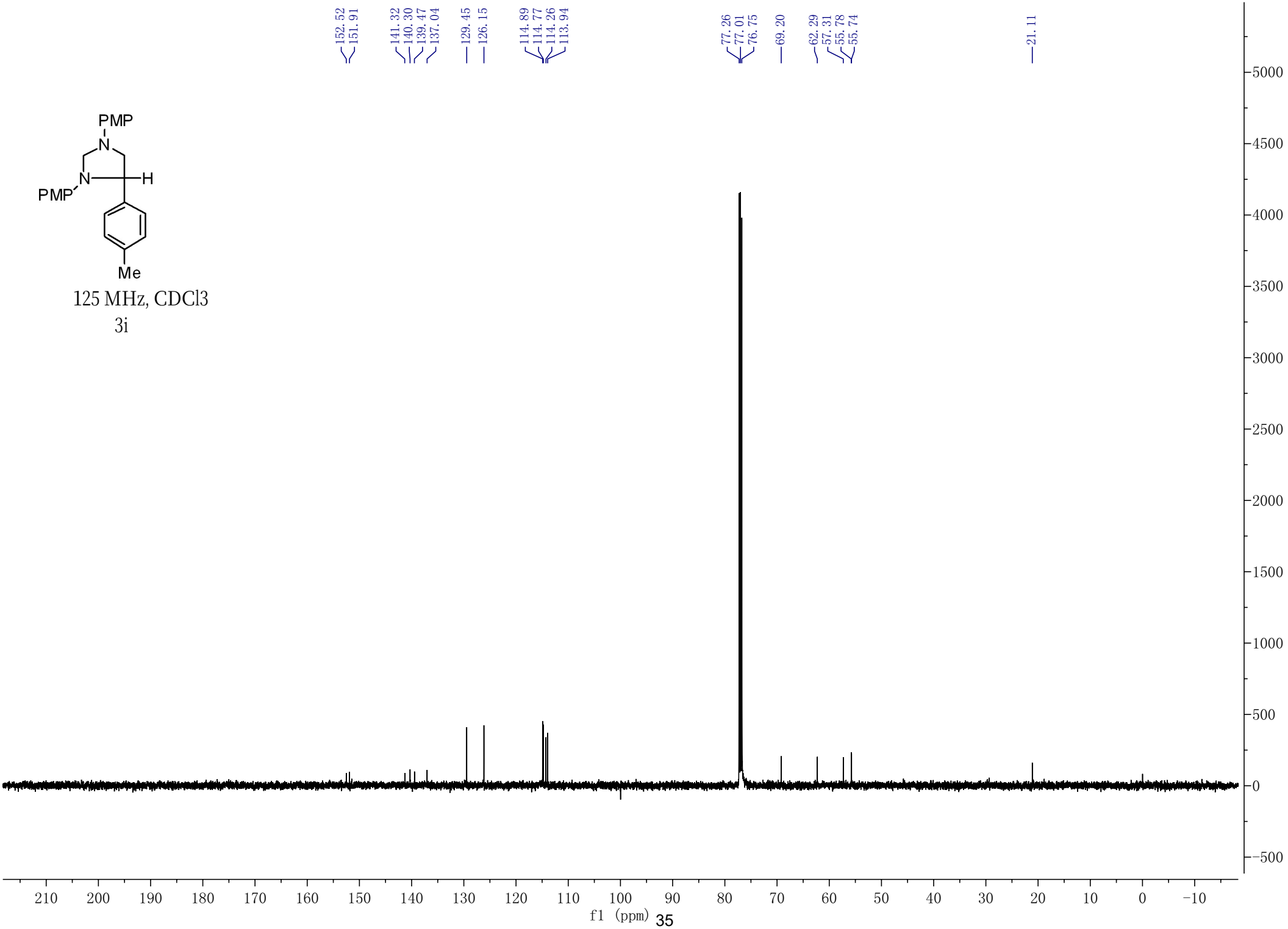

7.40
7.40
7.37
7.35
7.32
7.30
7.28
7.27
7.25
6.89
6.86
6.79
6.76
6.66
6.63
6.55
6.52
5.11
5.10
4.90
4.89
4.88
4.86
4.64
4.63
3.87
3.85
3.85
3.82
3.77
3.72
3.46
3.45
3.43
3.42
1.57
0.00
PMP
N
N
H
PMP
300 MHz, CDCl3
3h
5.01
2.08
2.11
2.08
2.03
0.98
1.01
0.98
1.06
2.96
3.00
1.02
.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


152.58
151.96
142.52
141.24
140.23
128.81
127.46
126.25
114.91
114.80
114.35
113.94
77.49
77.06
76.64
69.23
62.54
57.23
55.80
55.75
PMP
N
N
H
PMP
75 MHz, CDC13
3h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.30
7.28
7.16
7.14
6.90
6.88
6.81
6.79
6.67
6.65
6.57
6.55
5.11
5.11
4.87
4.65
4.65
3.85
3.84
3.79
3.74
3.45
3.44
3.43
3.42
2.34
1.59
1.28
0.09
0.02
PMP
N
N
H
PMP
Me
500 MHz, CDCl3
3i
2.02
2.05
2.00
1.99
2.00
2.01
0.99
1.03
1.02
1.04
2.97
2.98
1.00
2.99
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

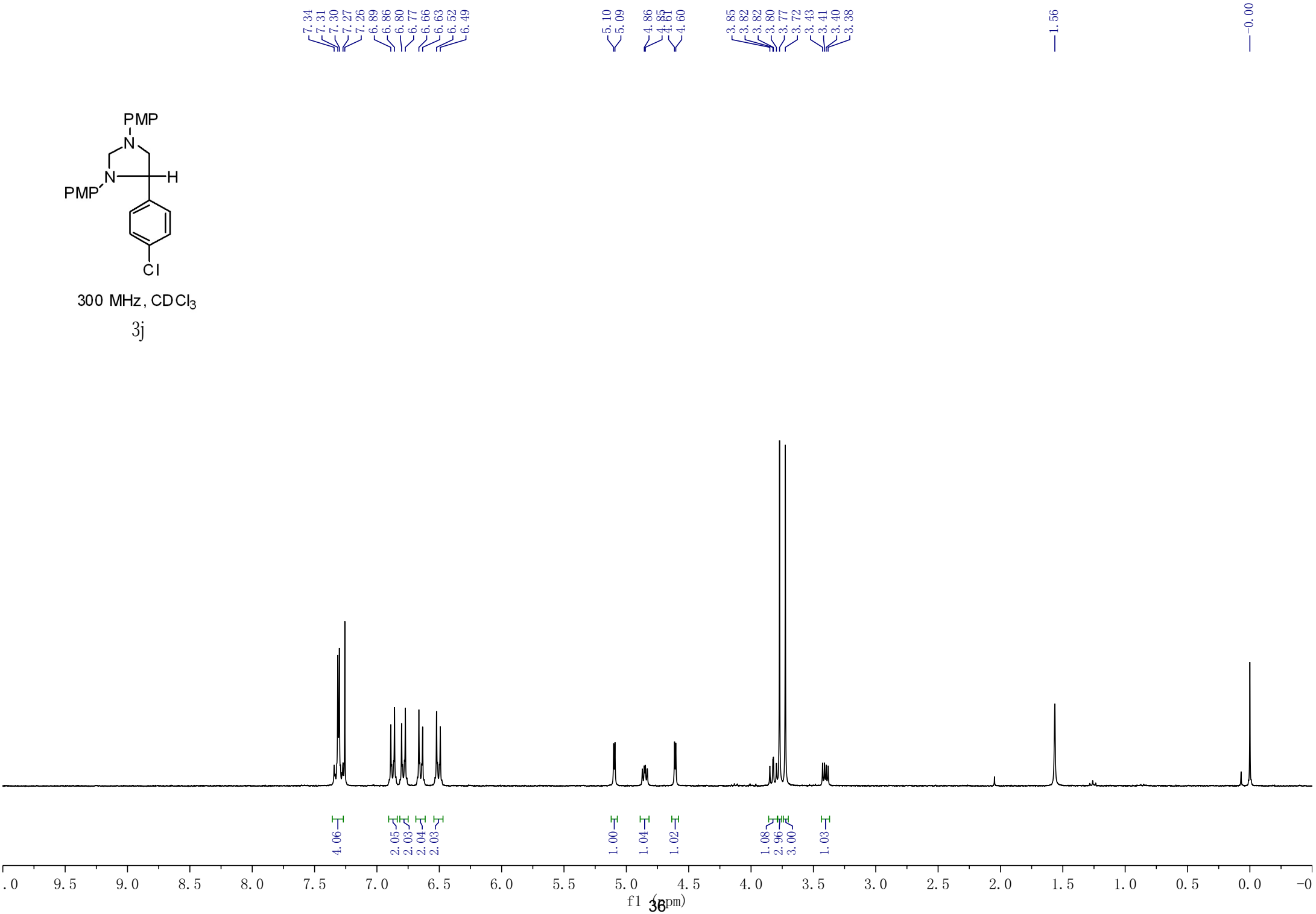
125 MHz, CDCl3

3i



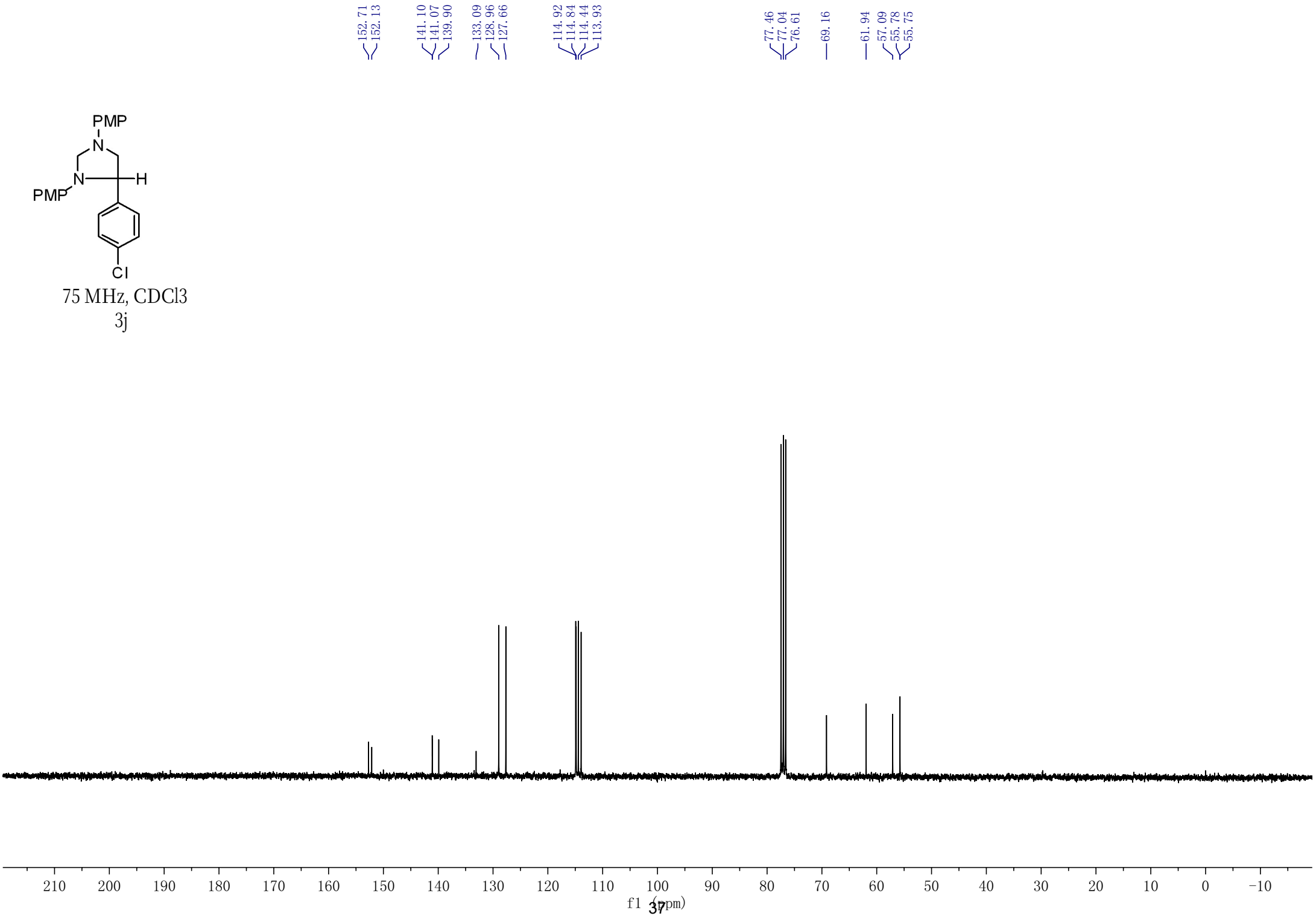
300 MHz, $CDCl_3$

3j



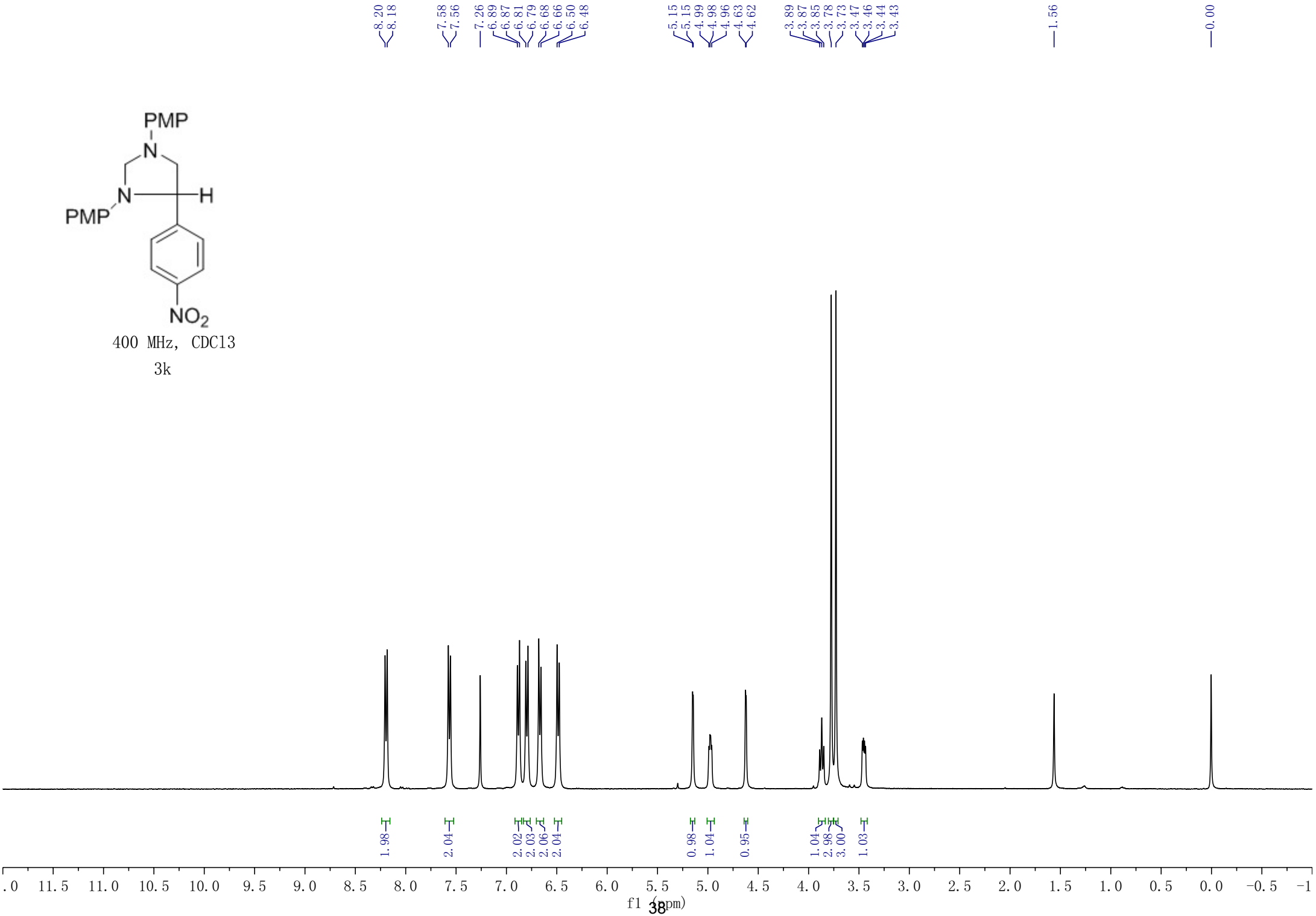
75 MHz, CDCl3

3j

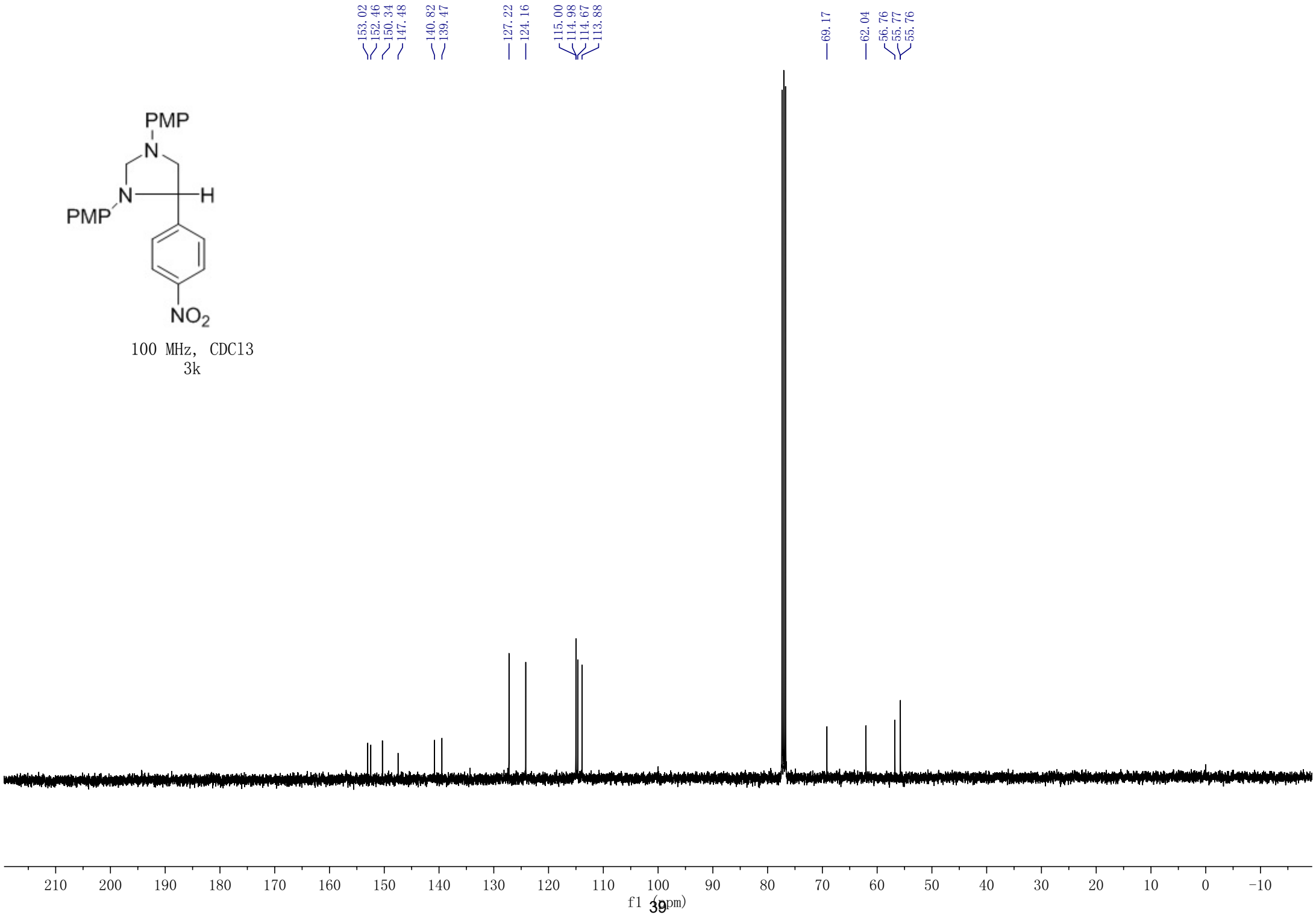


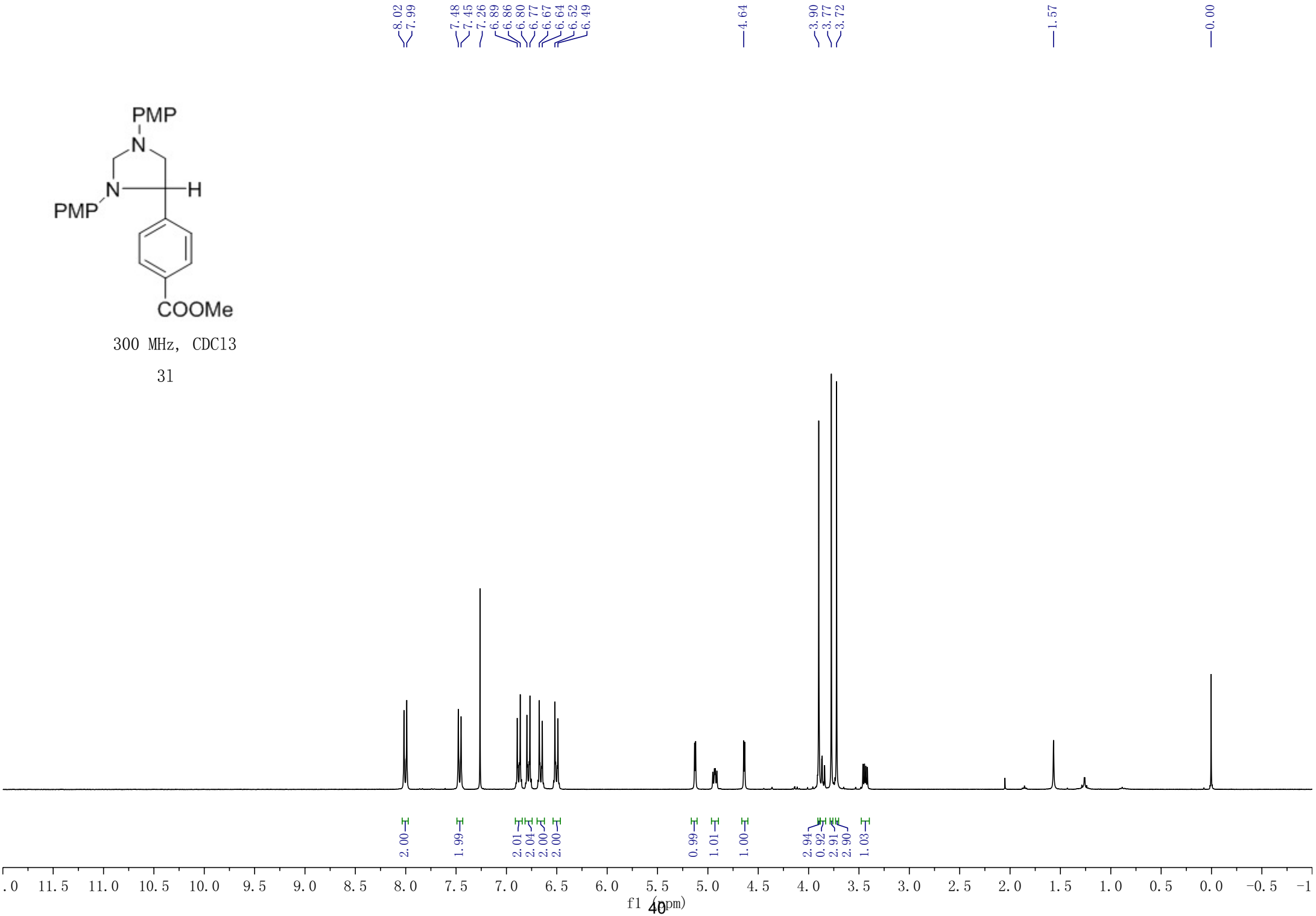
400 MHz, CDCl3

3k



100 MHz, CDCl3
3k



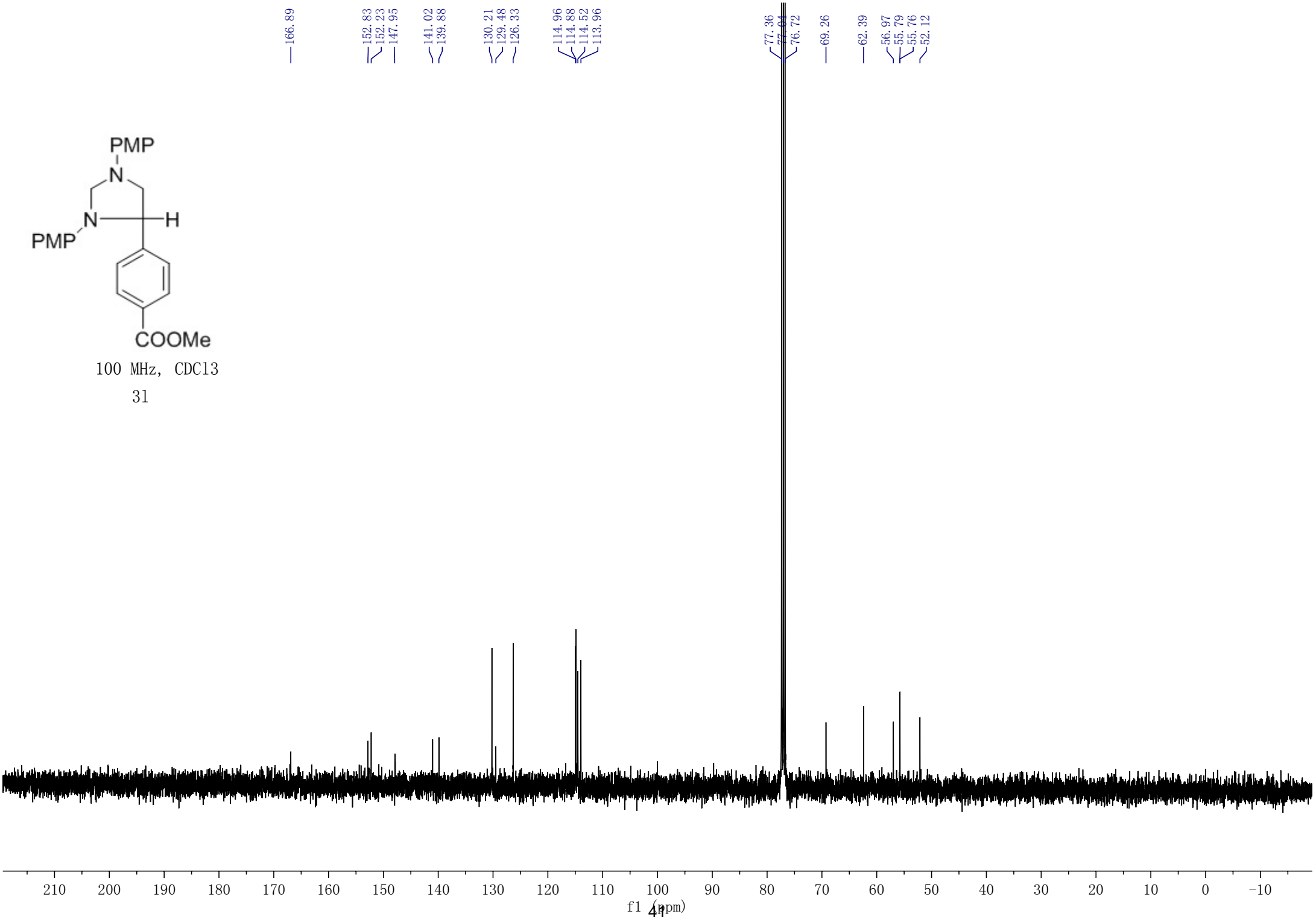


300 MHz, CDCl3

31

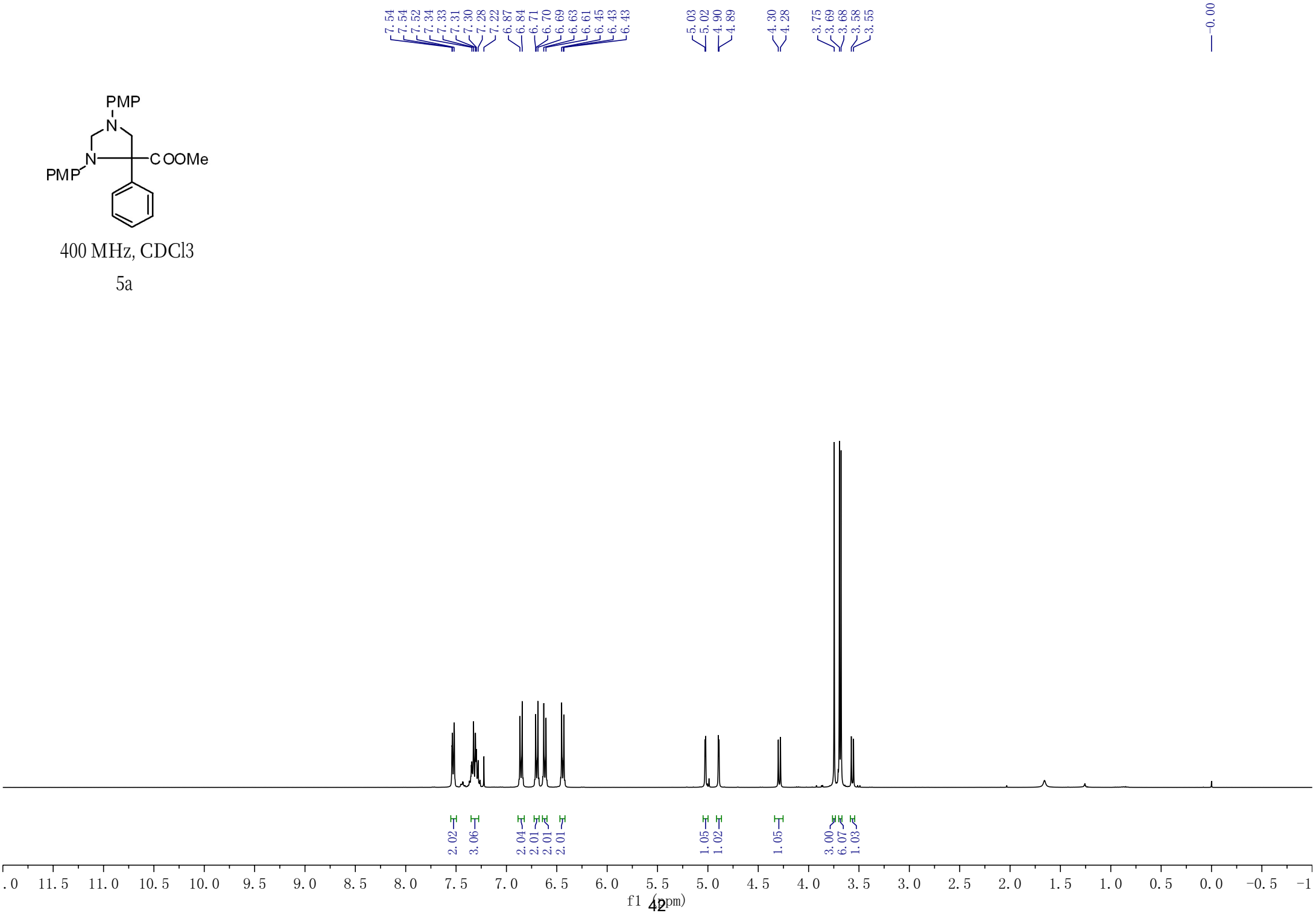
100 MHz, CDCl3

31



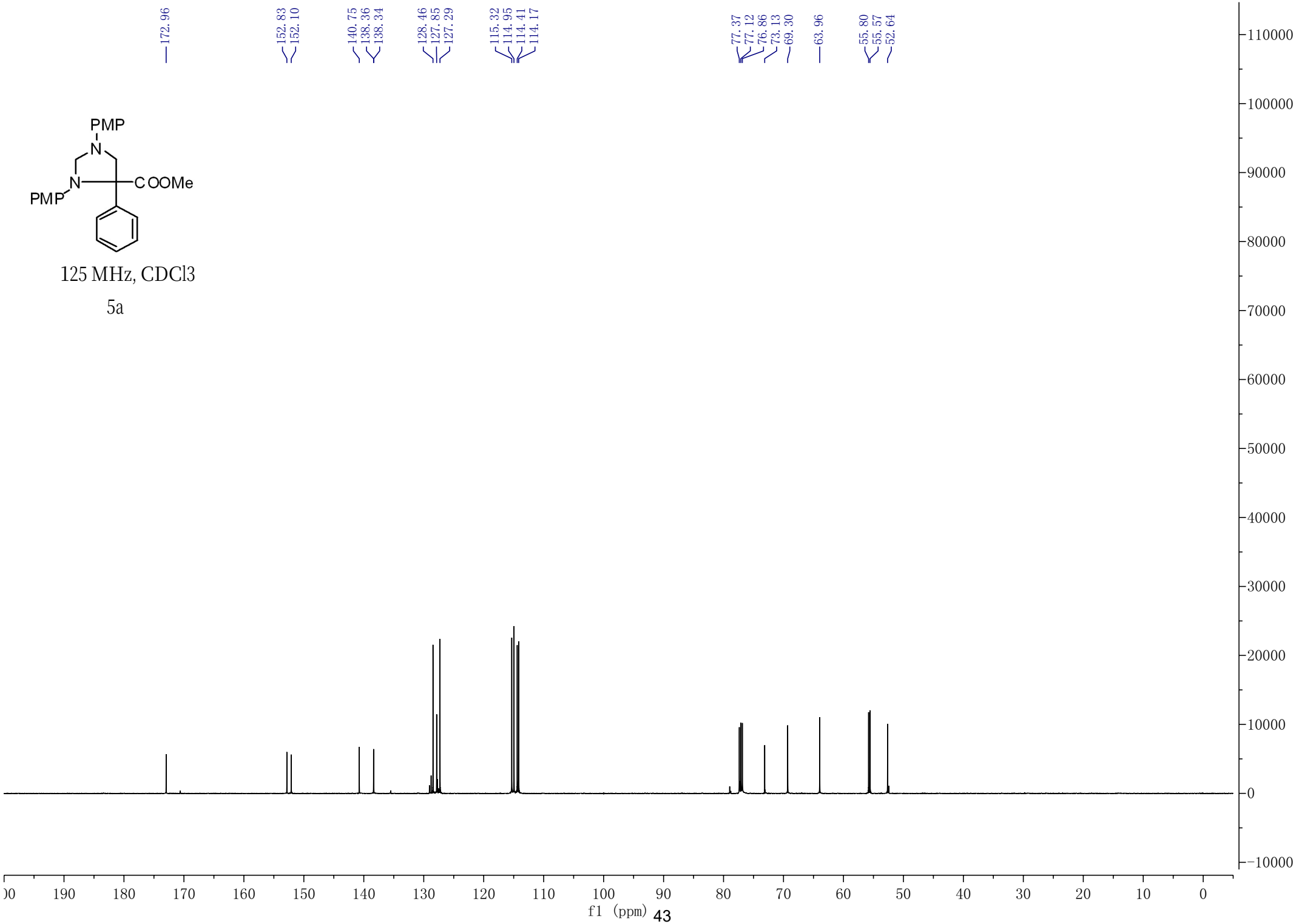
400 MHz, CDCl3

5a



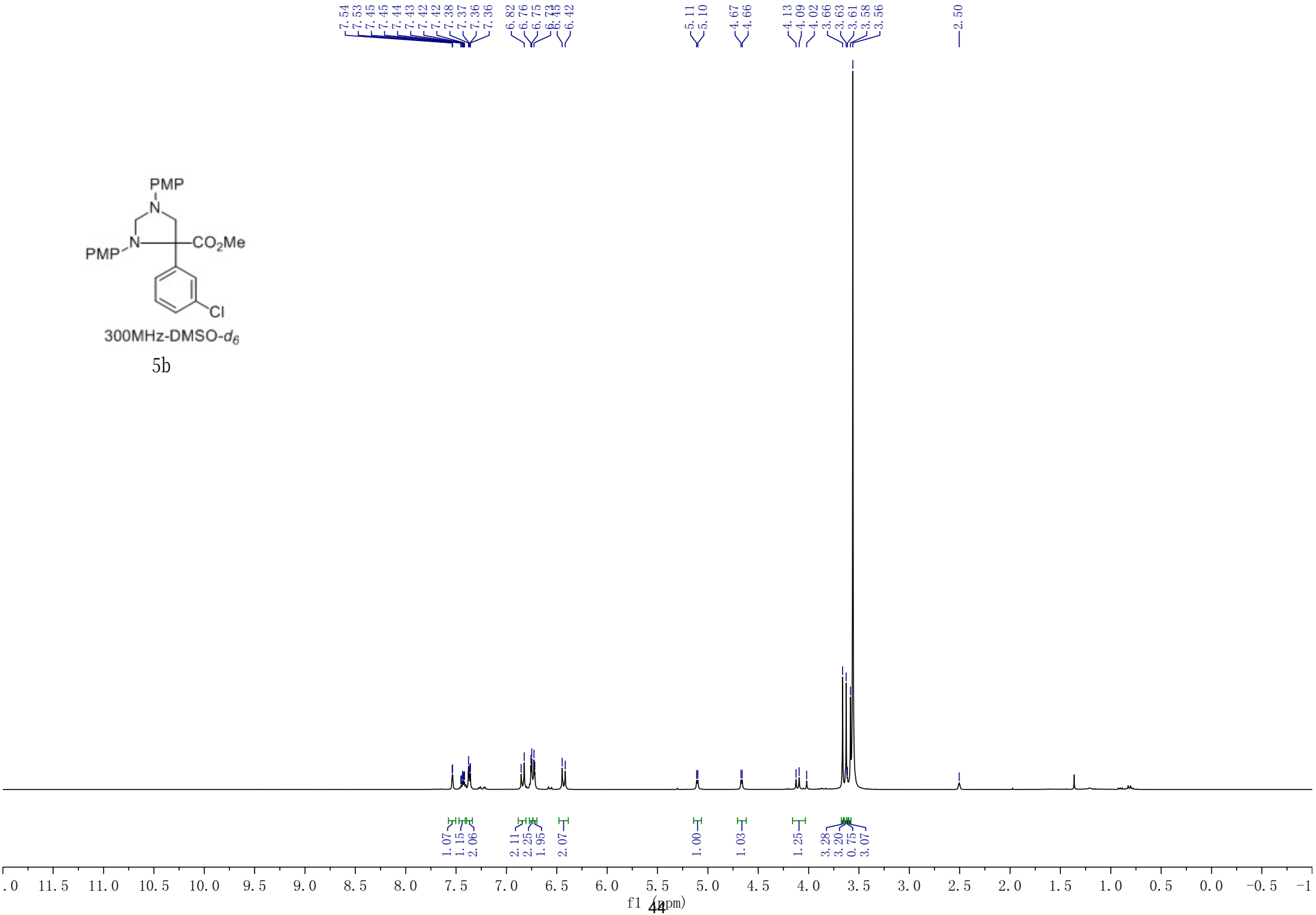
125 MHz, CDCl3

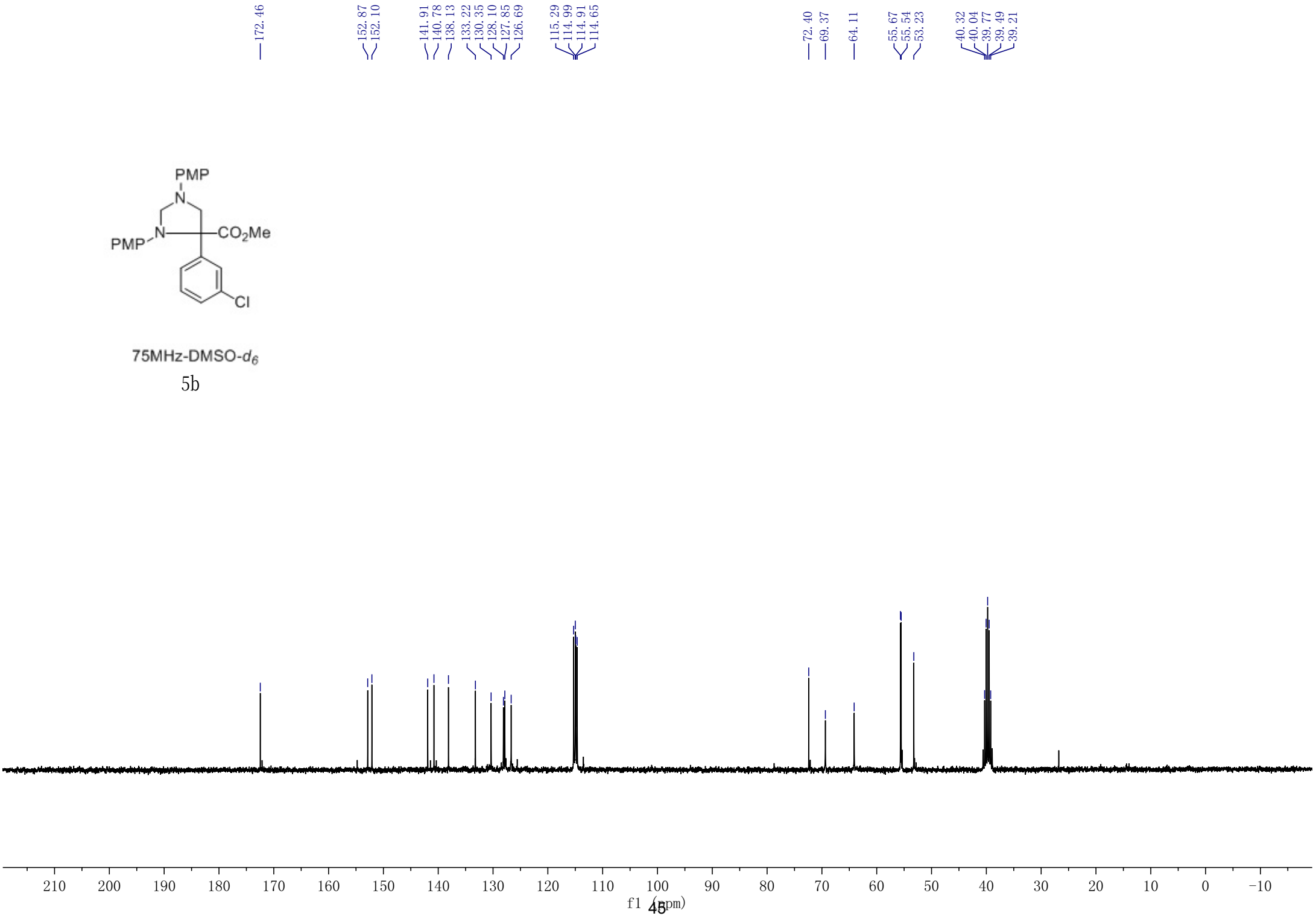
5a

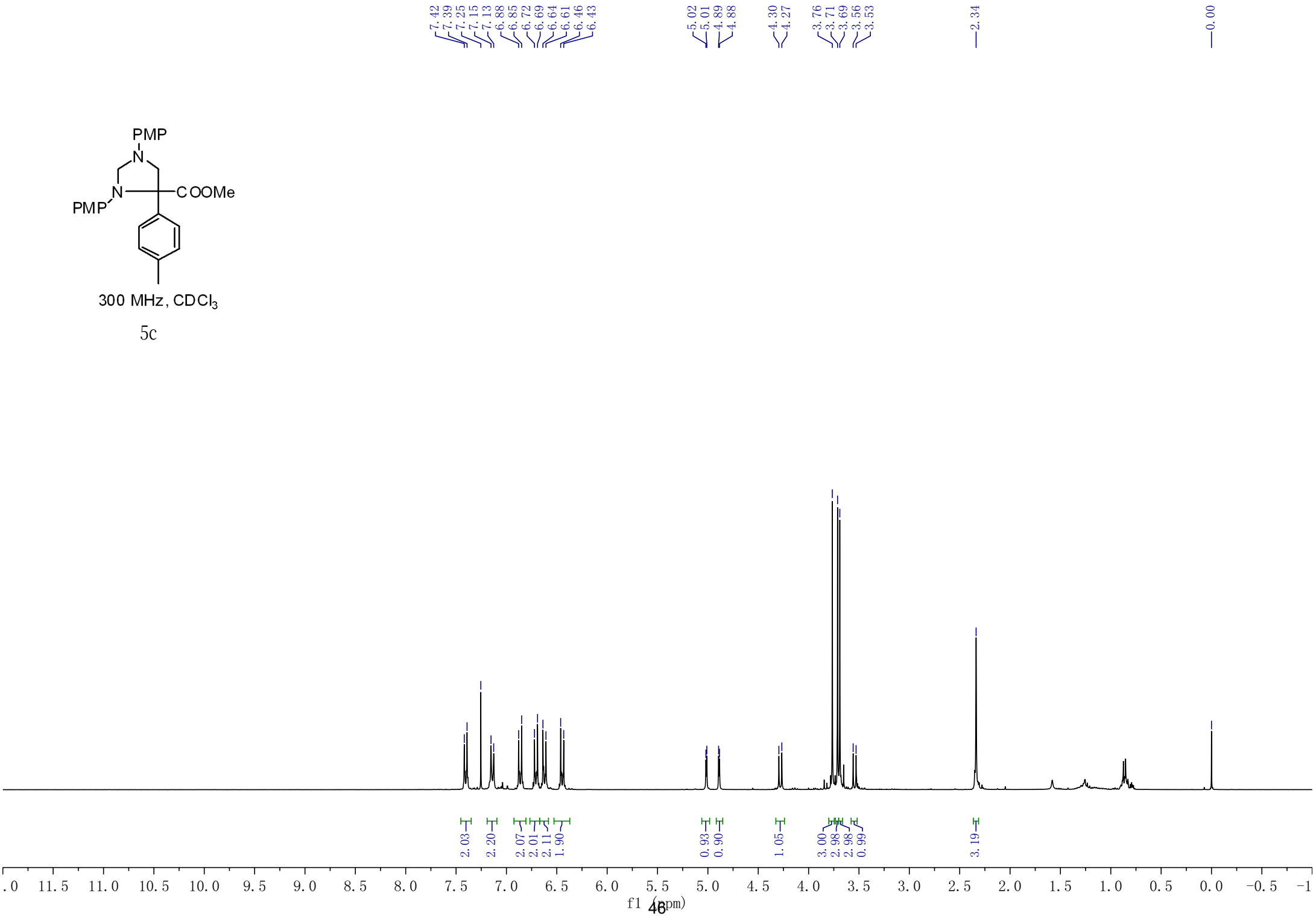


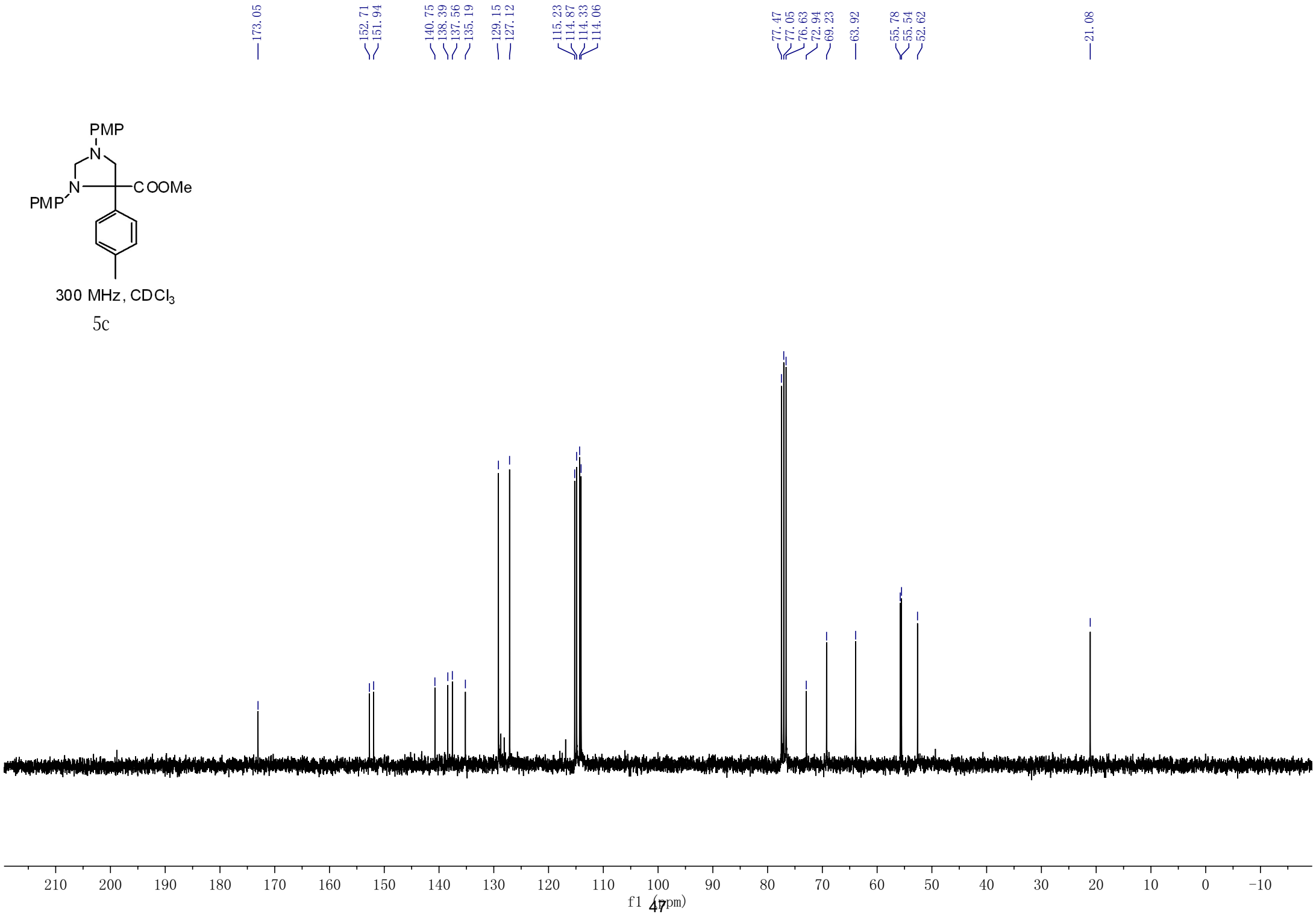
300MHz-DMSO-d_6

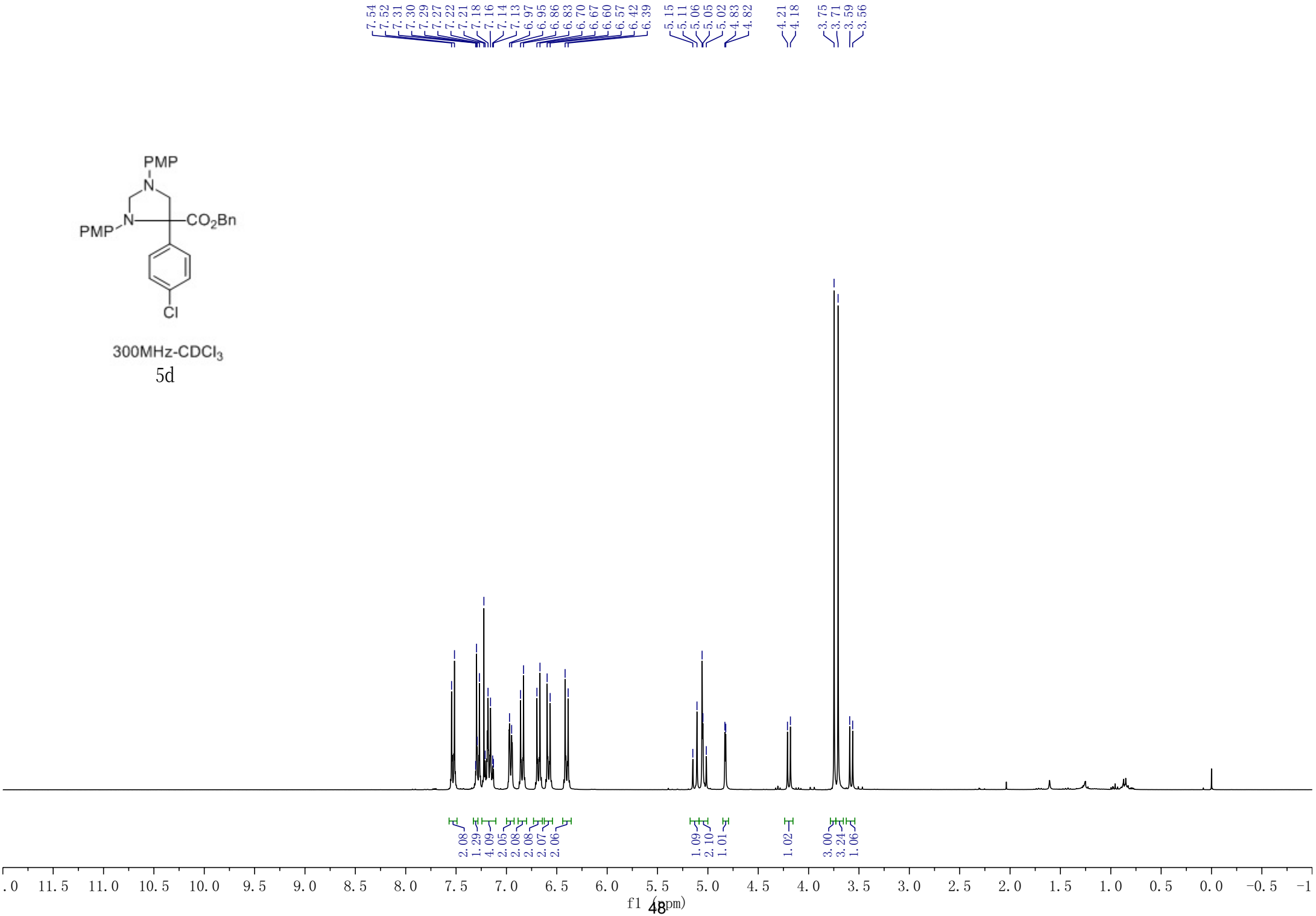
5b




172.46
152.87
152.10
141.91
140.78
138.13
133.22
130.35
128.10
127.85
126.69
115.29
114.99
114.91
114.65
72.40
69.37
64.11
55.67
55.54
53.23
40.32
40.04
39.77
39.49
39.21
PMP
N
N
PMP
CO2Me
Cl
75MHz-DMSO-d6
5b
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

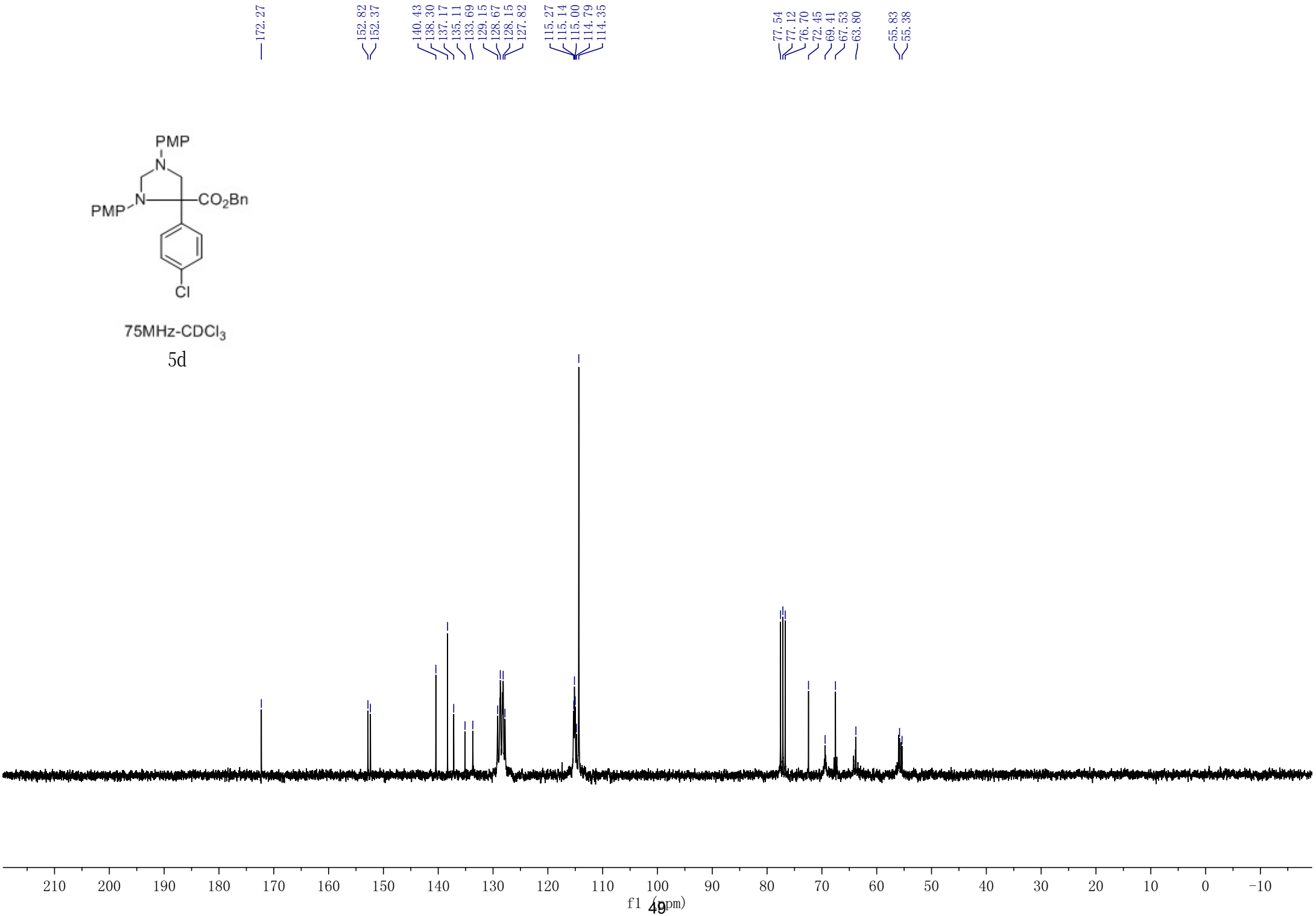

7.42
7.39
7.25
7.15
7.13
6.88
6.85
6.72
6.69
6.64
6.61
6.46
6.43
5.02
5.01
4.89
4.88
4.30
4.27
3.76
3.71
3.69
3.56
3.53
2.34
0.00
PMP
N
N
COOMe
PMP
300 MHz, CDCl3
5c
2.03
2.20
2.07
2.01
2.11
1.90
0.93
0.90
1.05
3.00
2.98
2.98
0.99
3.19
f1 (ppm)


173.05
152.71
151.94
140.75
138.39
137.56
135.19
129.15
127.12
115.23
114.87
114.33
114.06
77.47
77.05
76.63
72.94
69.23
63.92
55.78
55.54
52.62
21.08
PMP
N
N
COOMe
PMP
300 MHz, CDCl3
5c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


PMP
N
N
PMP
CO2Bn
Cl
300MHz-CDCl3
5d
7.54
7.52
7.31
7.30
7.29
7.27
7.22
7.21
7.18
7.16
7.14
7.13
6.97
6.95
6.86
6.83
6.70
6.67
6.60
6.57
6.42
6.39
5.15
5.11
5.06
5.05
5.02
4.83
4.82
4.21
4.18
3.75
3.71
3.59
3.56
2.08
1.29
4.09
2.05
2.08
2.08
2.07
2.06
1.09
2.10
1.01
1.02
3.00
3.24
1.06
f1 (ppm)

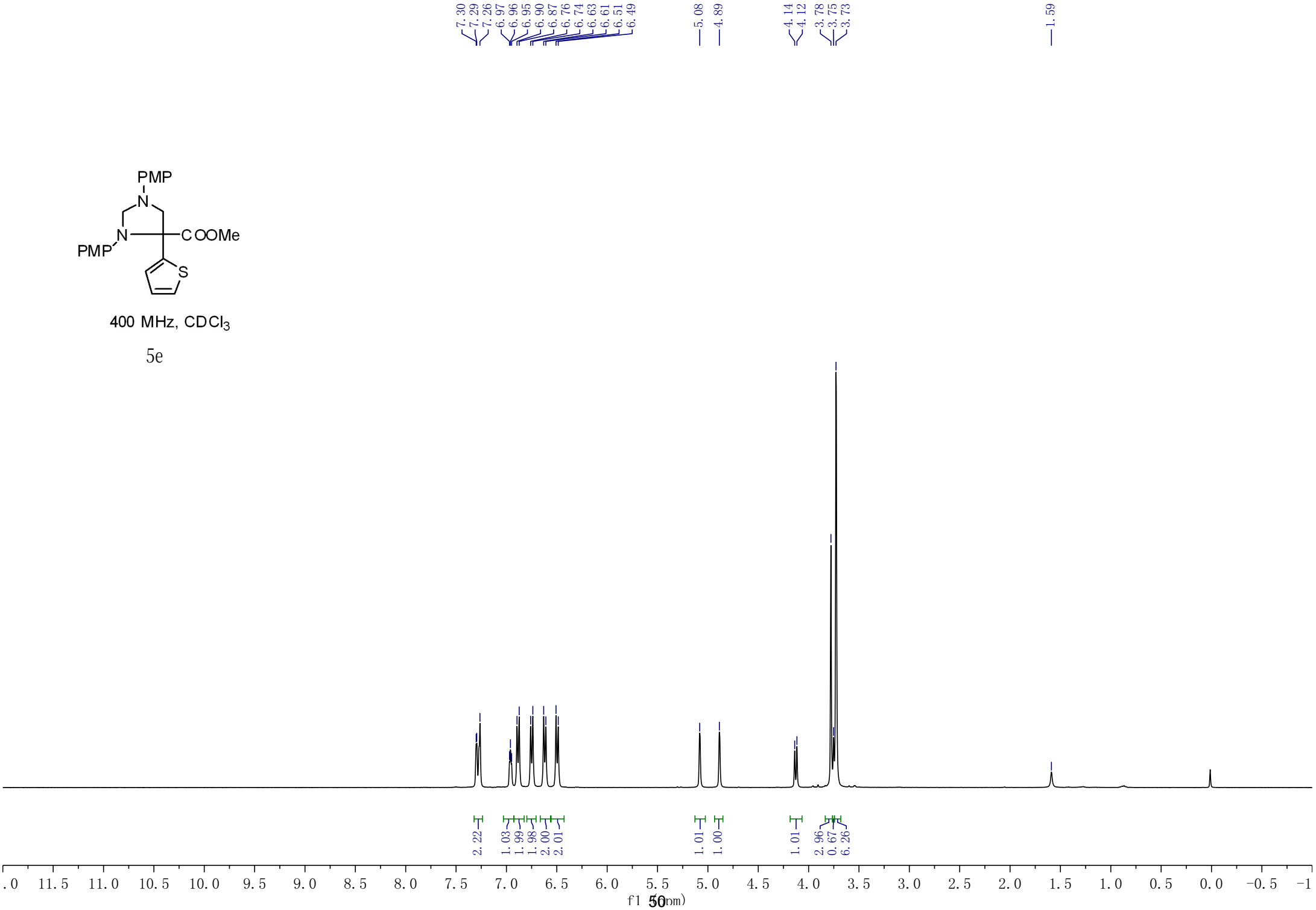
75MHz-$CDCl_3$

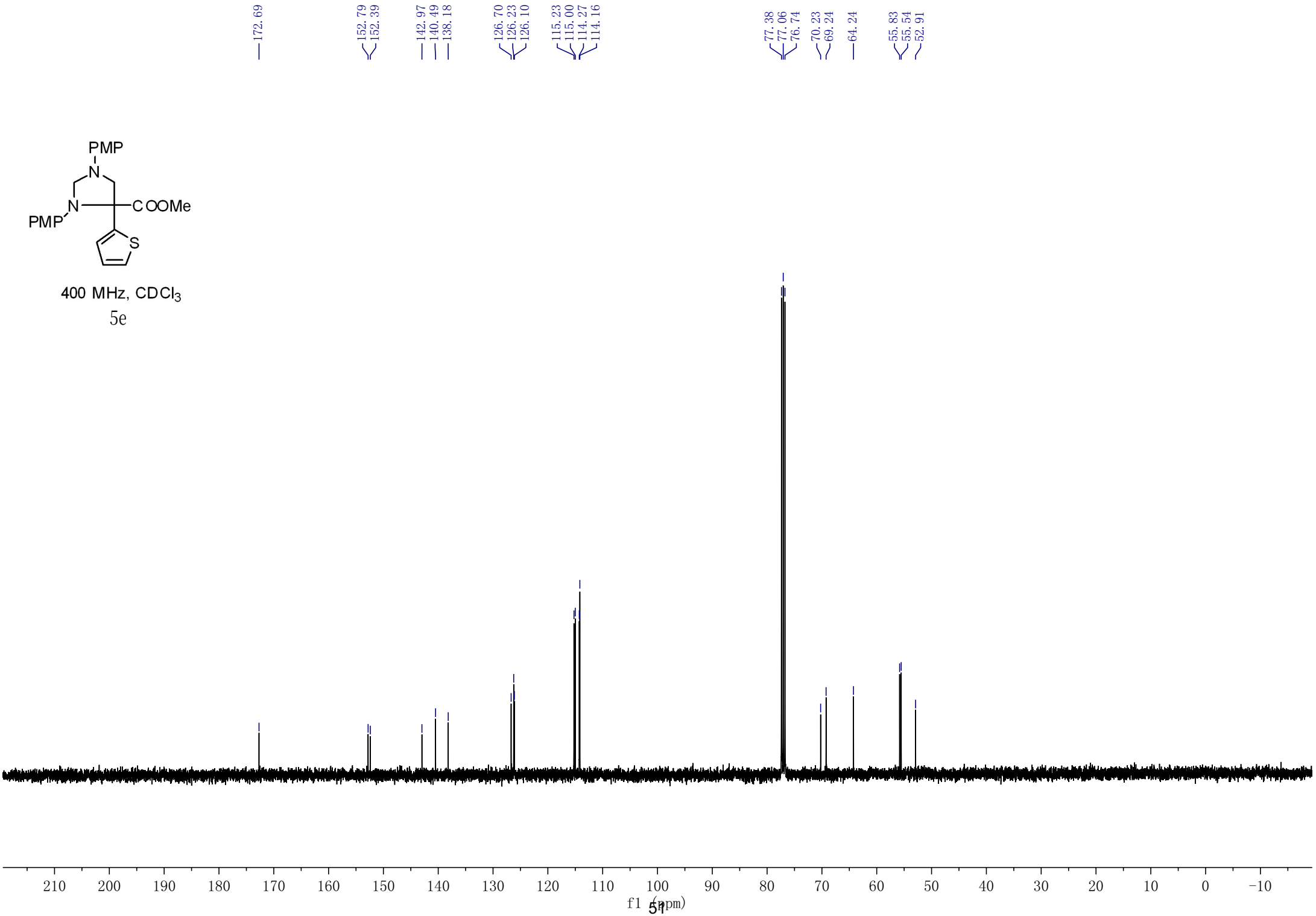
5d



400 MHz, $CDCl_3$

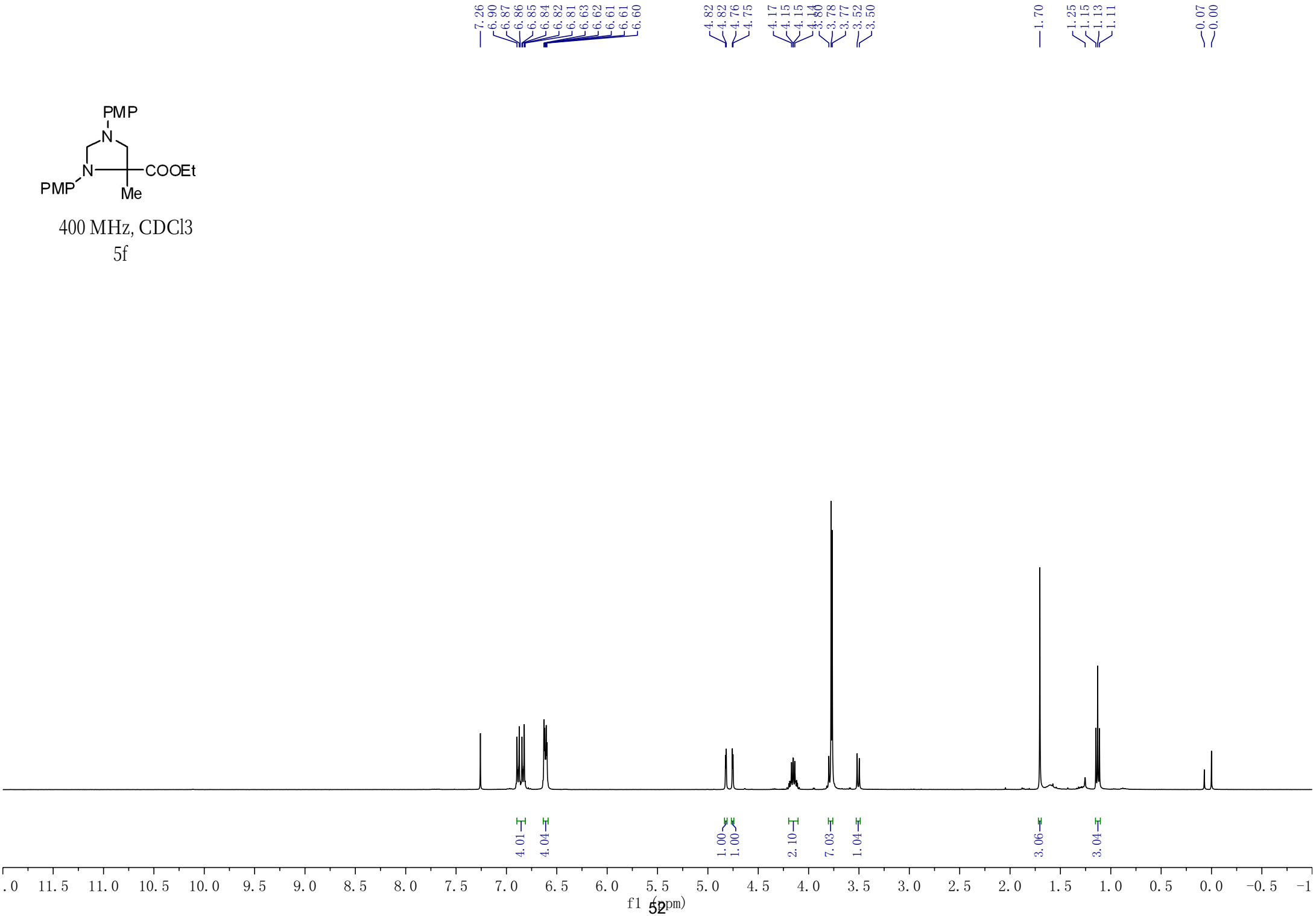
5e




172.69
152.79
152.39
142.97
140.49
138.18
126.70
126.23
126.10
115.23
115.00
114.27
114.16
77.38
77.06
76.74
70.23
69.24
64.24
55.83
55.54
52.91
PMP
N
N
COOMe
PMP
S
400 MHz, CDCl3
5e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

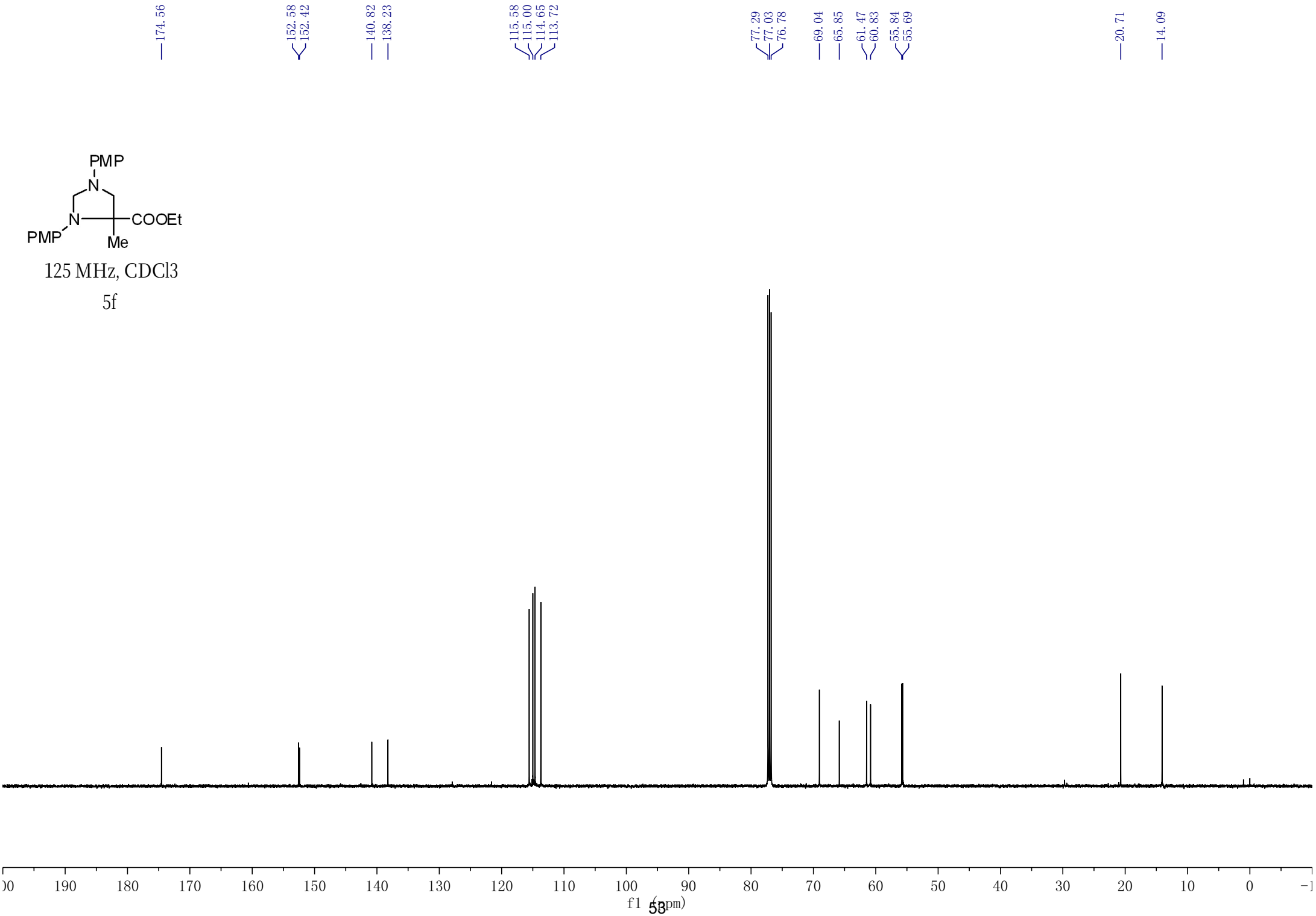
400 MHz, CDCl3

5f



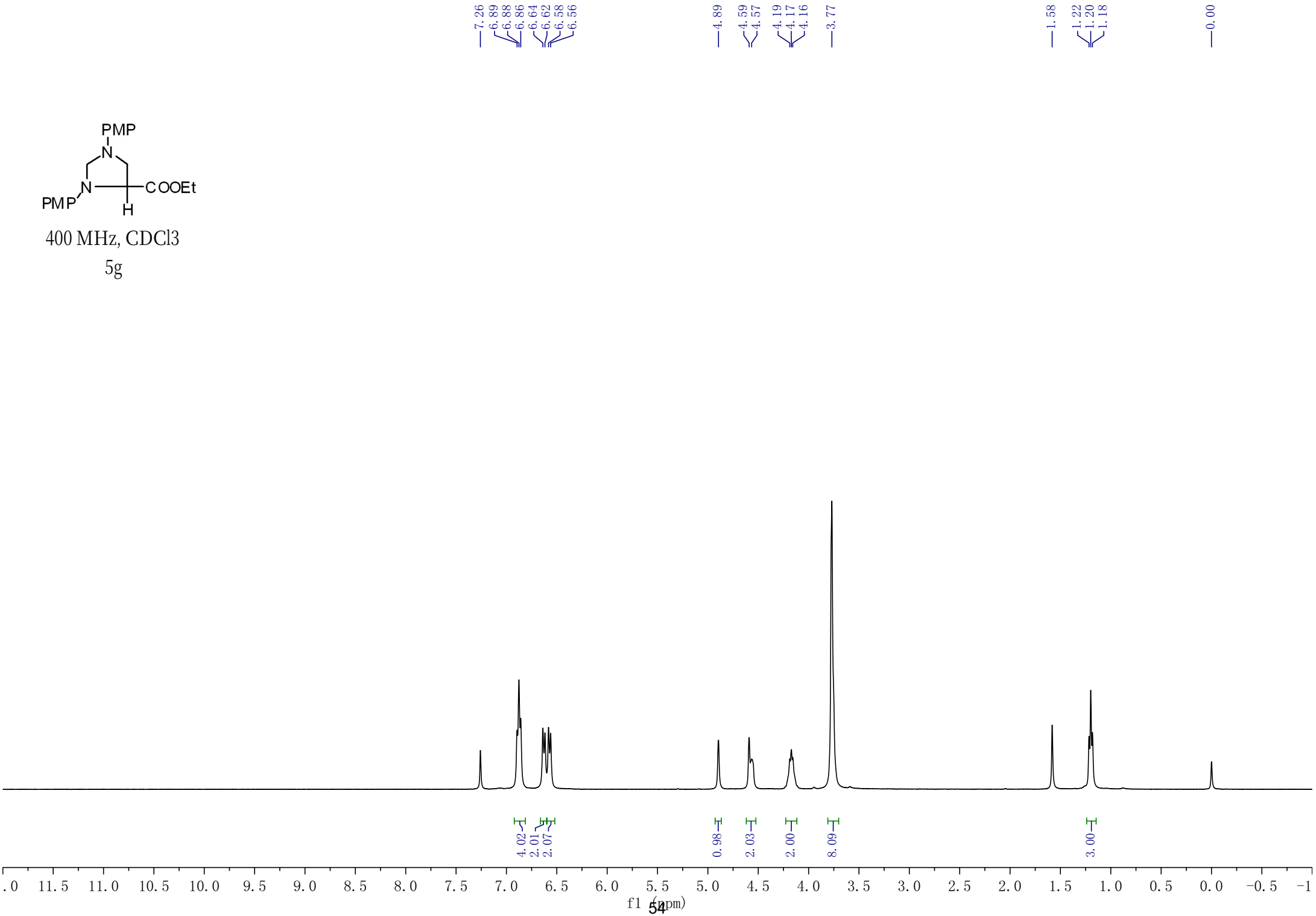
125 MHz, CDCl3

5f



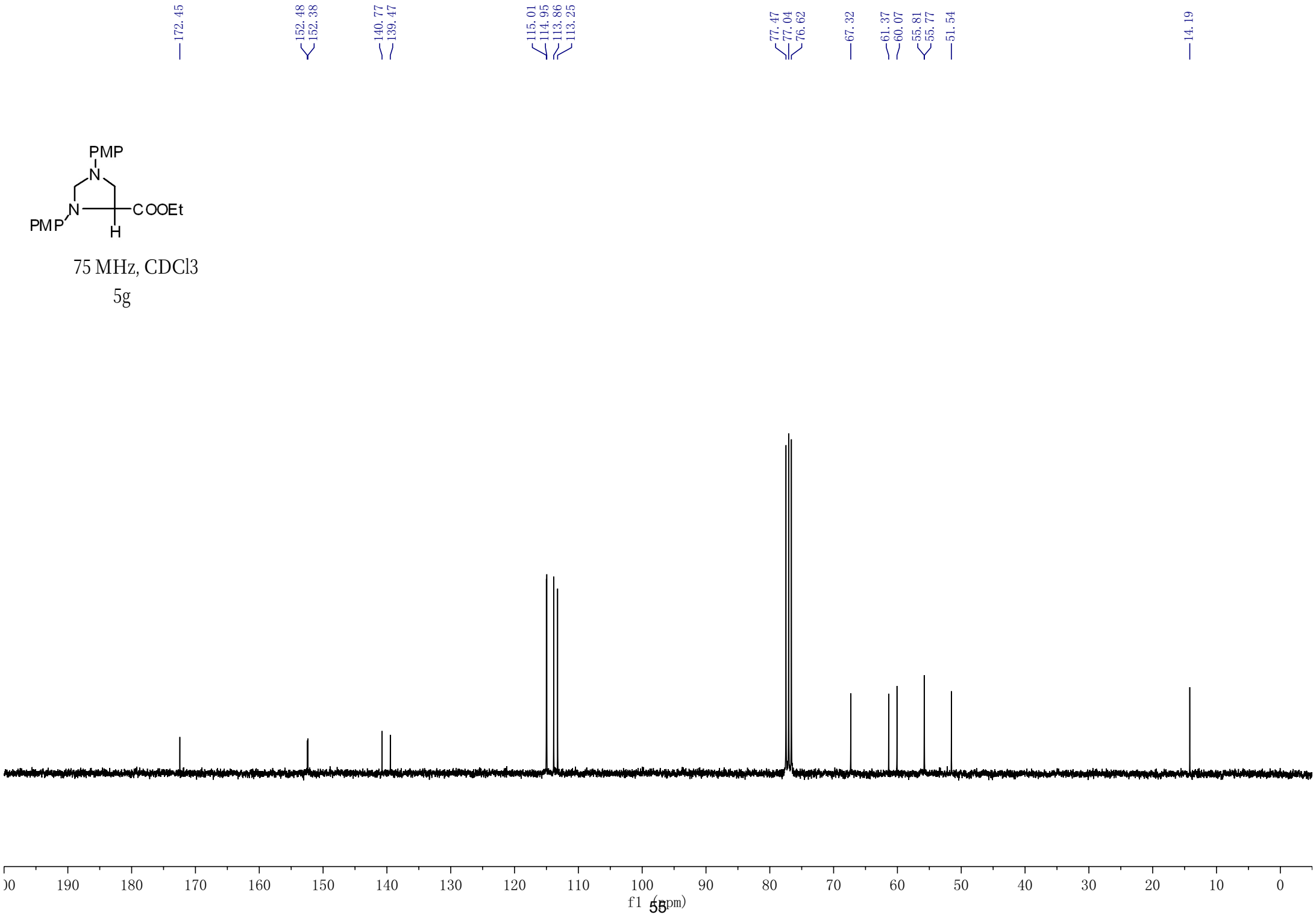
400 MHz, CDCl3

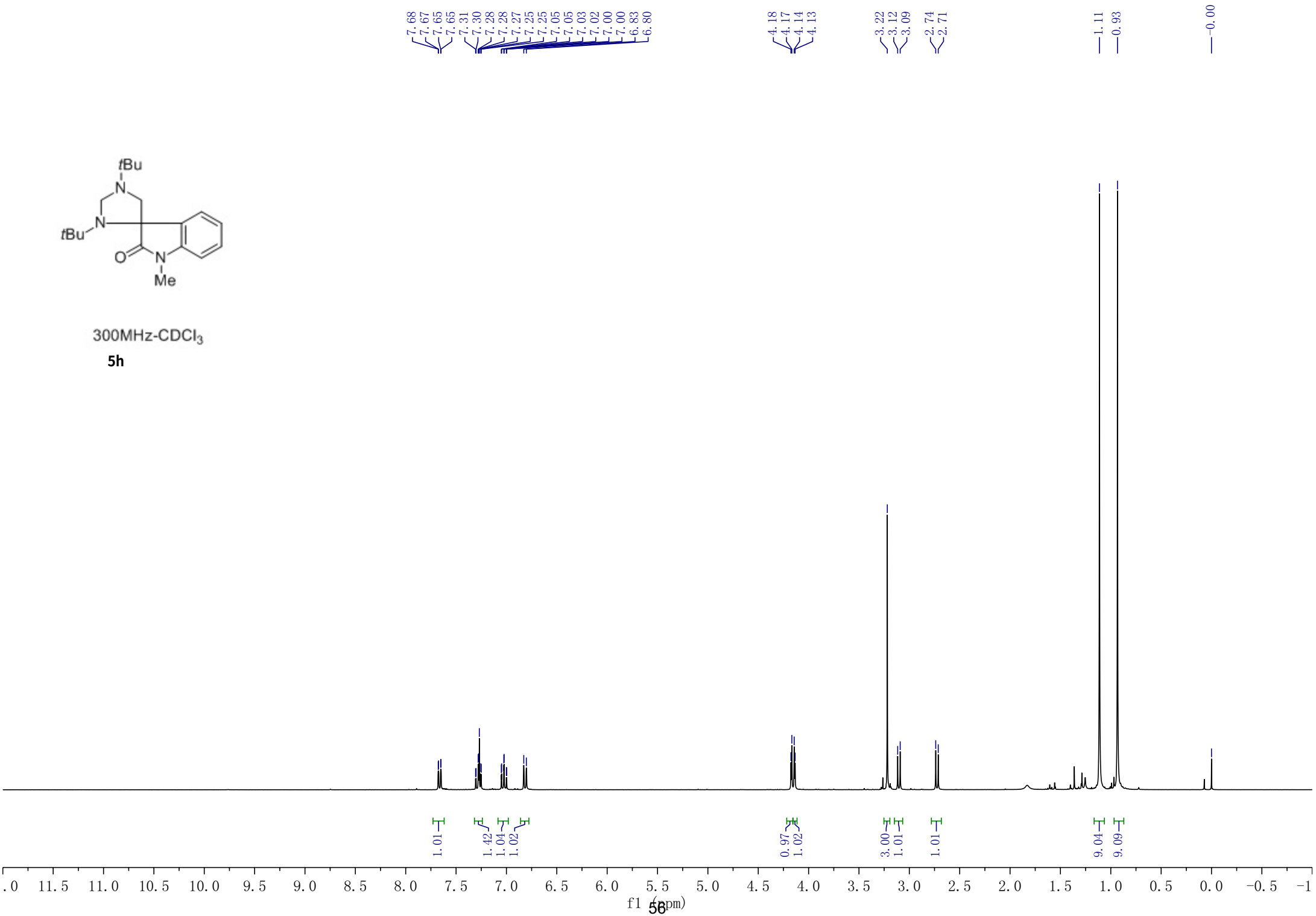
5g

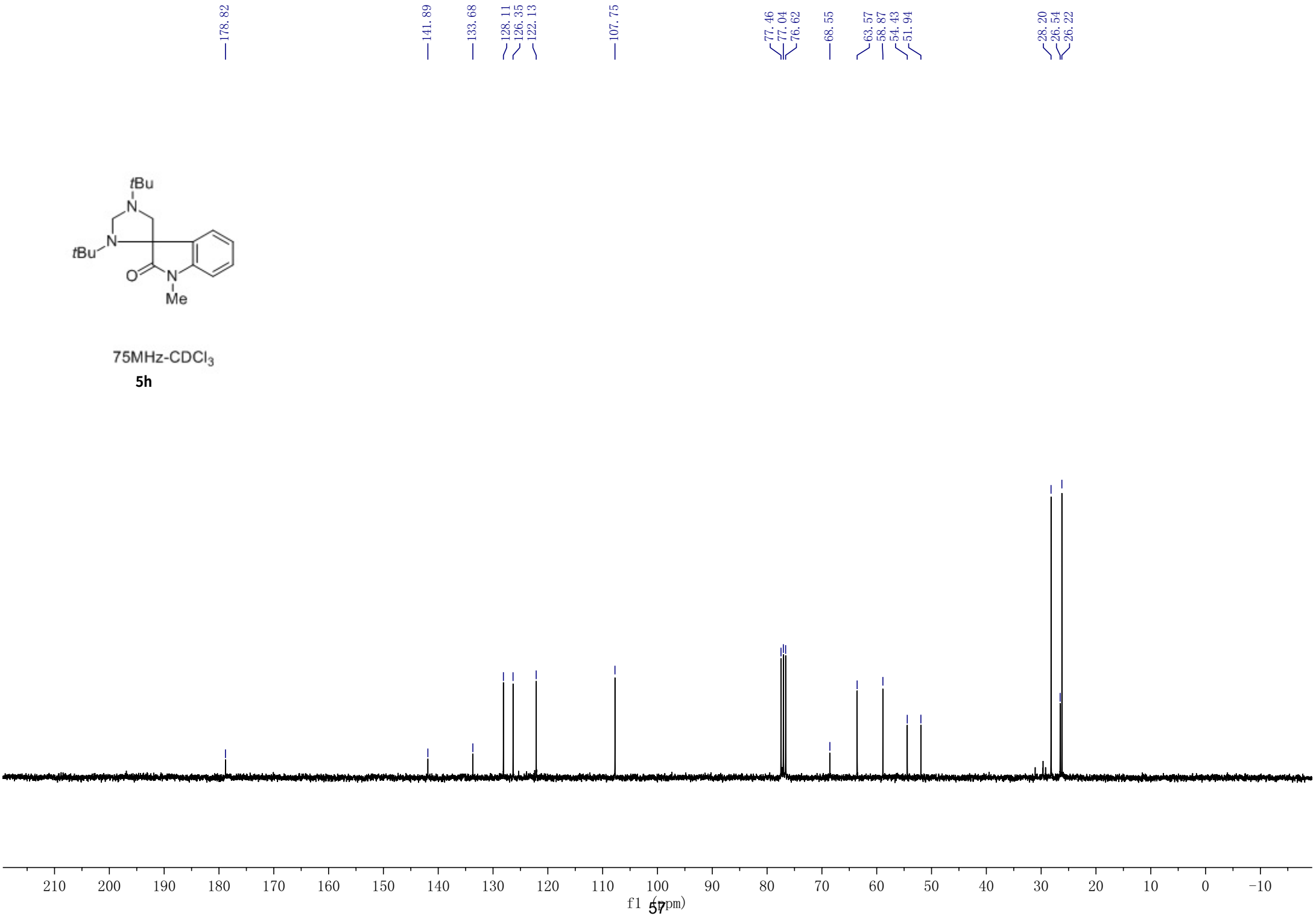


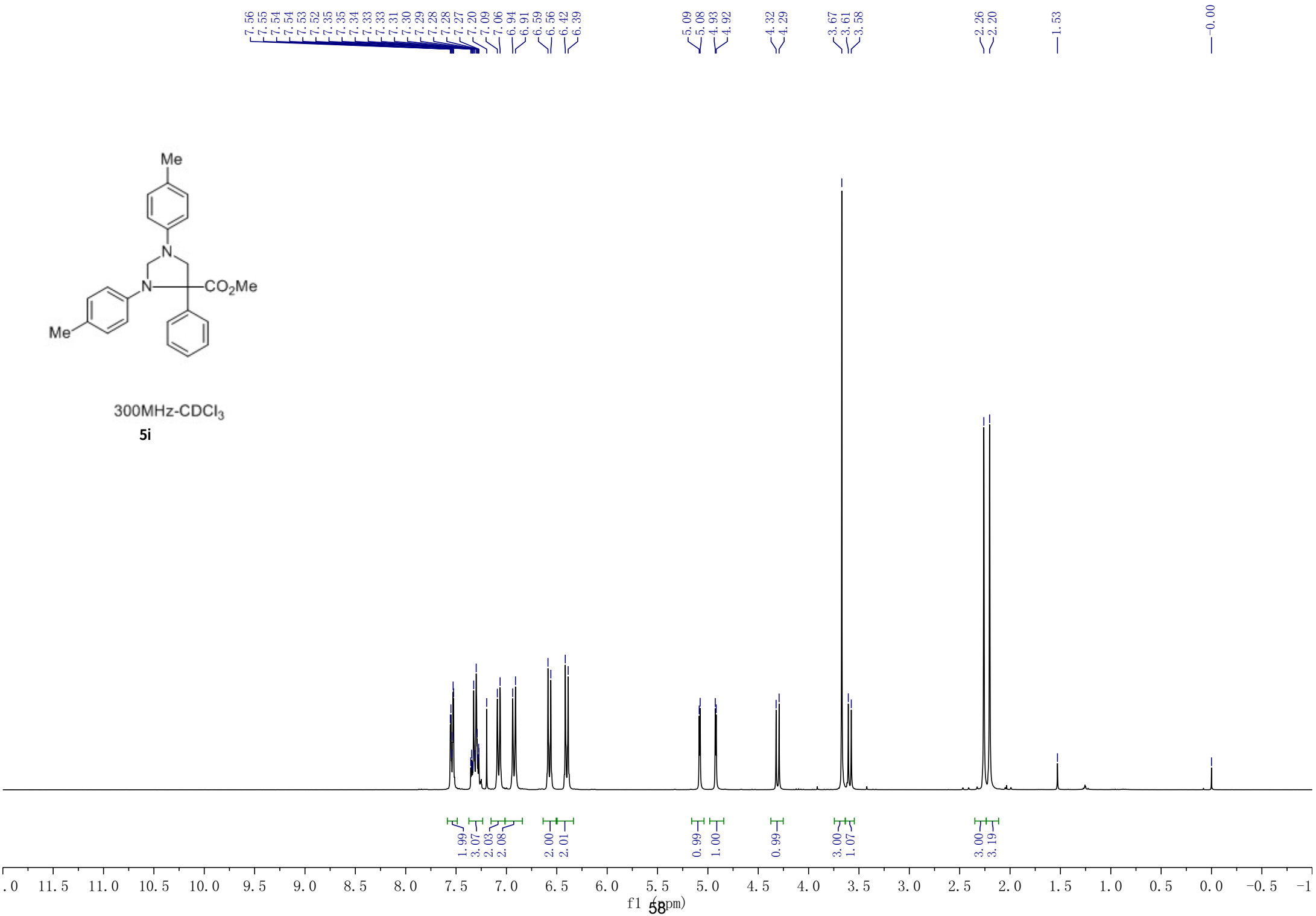
75 MHz, CDCl3

5g



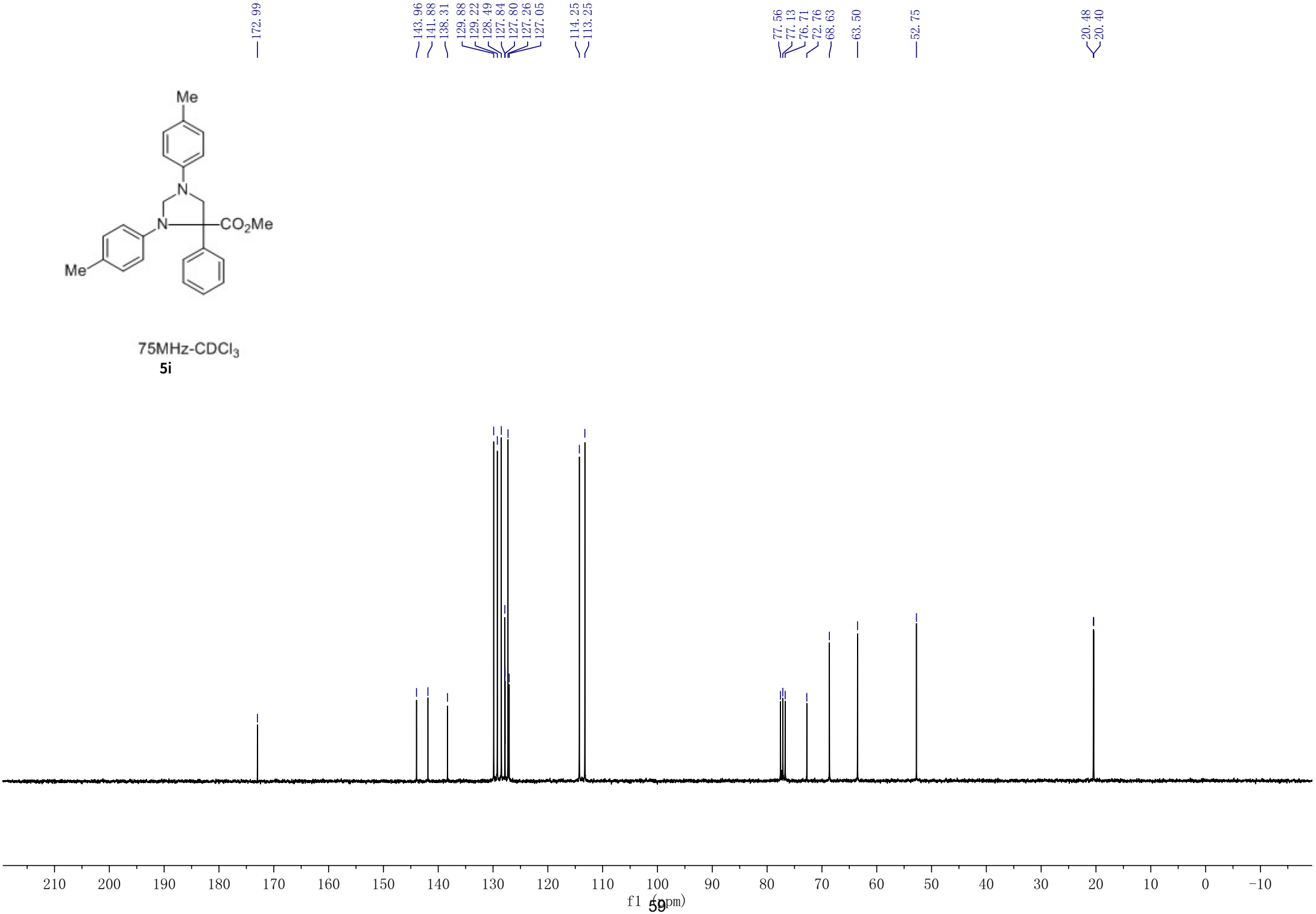

7.68
7.67
7.65
7.65
7.31
7.30
7.28
7.28
7.27
7.25
7.25
7.05
7.05
7.03
7.02
7.00
7.00
6.83
6.80
4.18
4.17
4.14
4.13
3.22
3.12
3.09
2.74
2.71
1.11
0.93
-0.00
tBu
N
N
tBu
O
N
Me
300MHz-CDCl3
5h
1.01
1.42
1.04
1.02
0.97
1.02
3.00
1.01
1.01
9.04
9.09
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

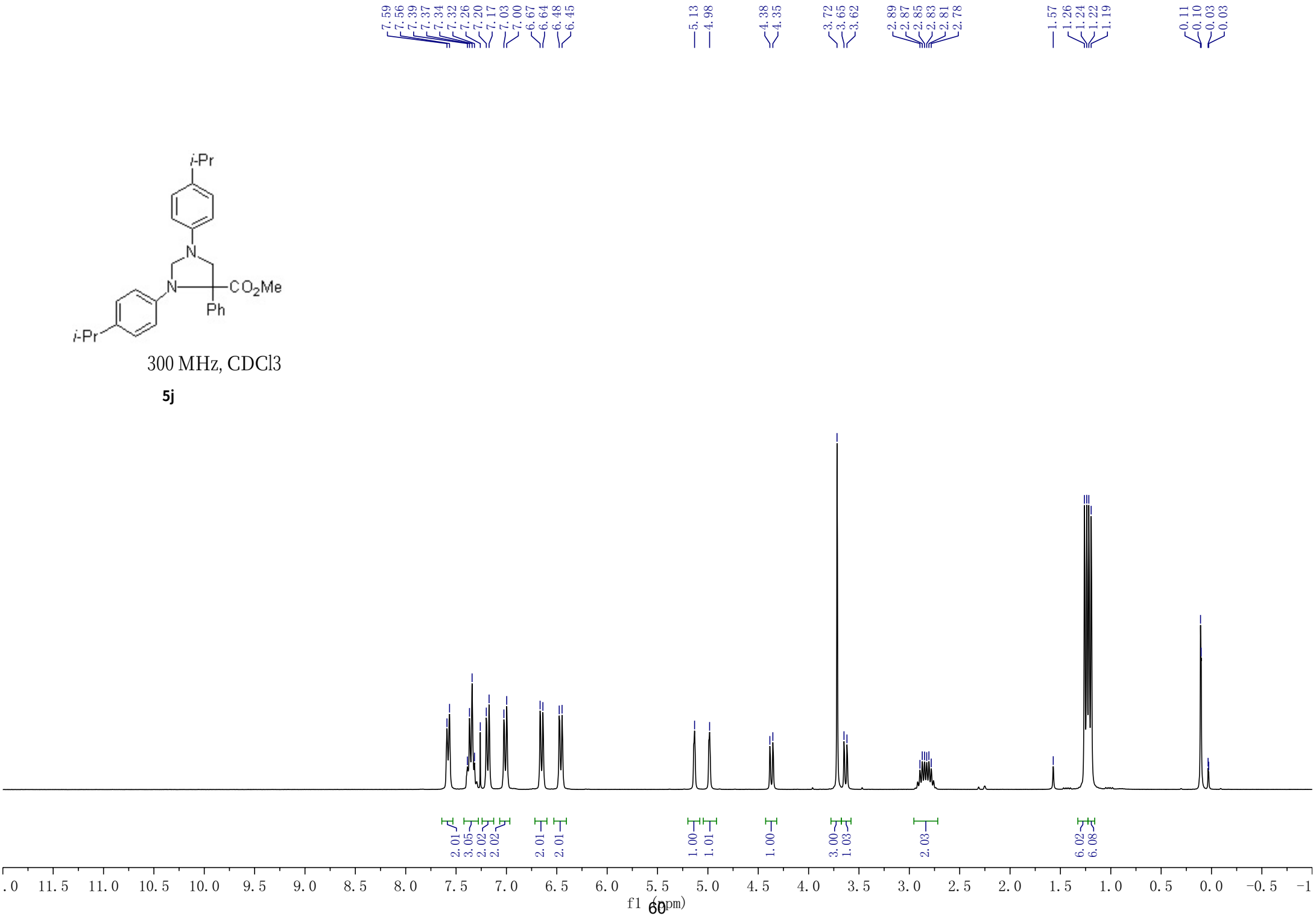

178.82
141.89
133.68
128.11
126.35
122.13
107.75
77.46
77.04
76.62
68.55
63.57
58.87
54.43
51.94
28.20
26.54
26.22
tBu
N
N
tBu
O
N
Me
75MHz-CDCl3
5h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.56
7.55
7.54
7.54
7.53
7.52
7.35
7.35
7.34
7.33
7.33
7.31
7.30
7.29
7.28
7.28
7.27
7.20
7.09
7.06
6.94
6.91
6.59
6.56
6.42
6.39
5.09
5.08
4.93
4.92
4.32
4.29
3.67
3.61
3.58
2.26
2.20
1.53
0.00
Me
N
N
CO2Me
Me
300MHz-CDCl3
5i
1.99
3.07
2.03
2.08
2.00
2.01
0.99
1.00
0.99
3.00
1.07
3.00
3.19
f1 (ppm)

75MHz-$CDCl_3$

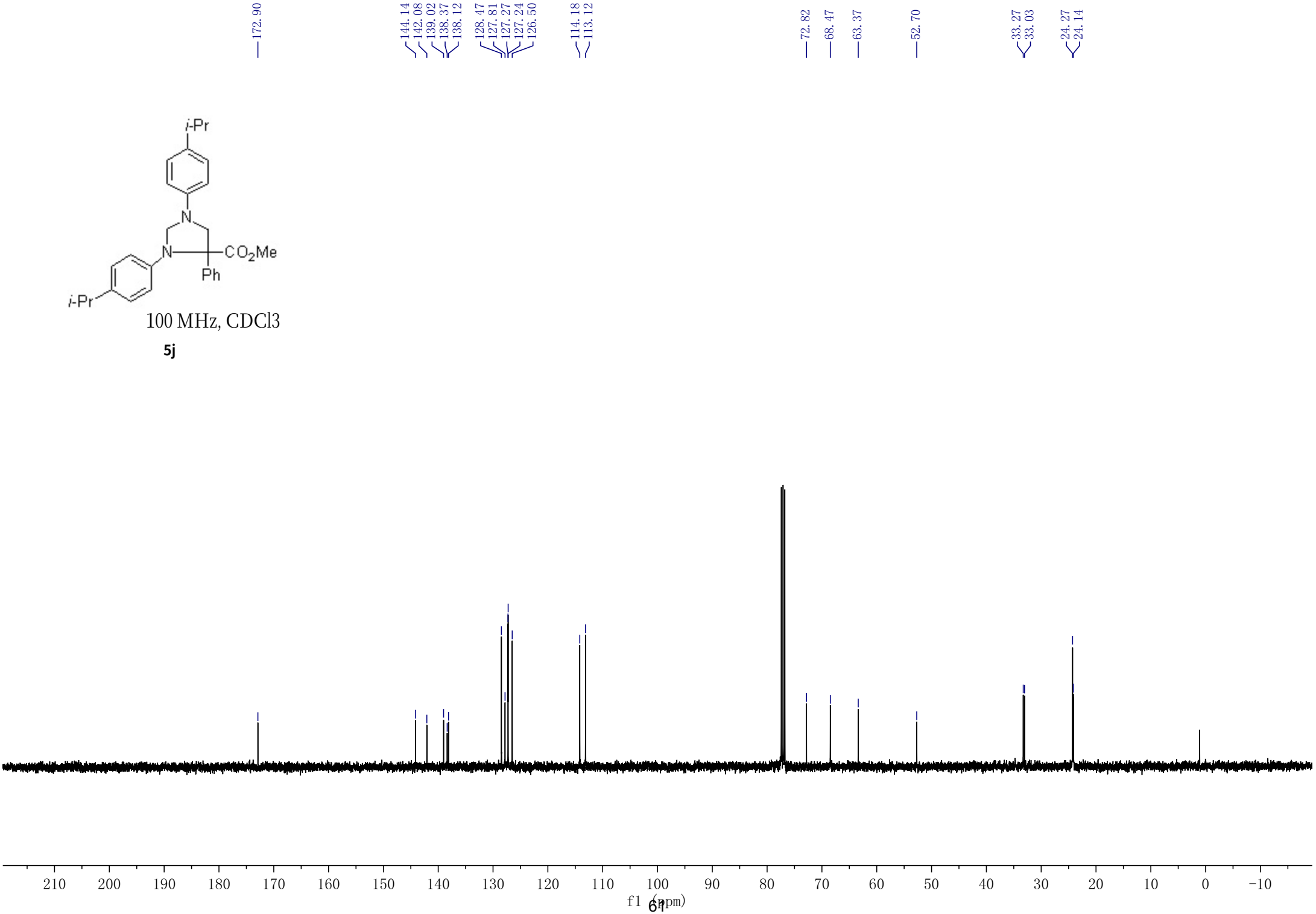
5i

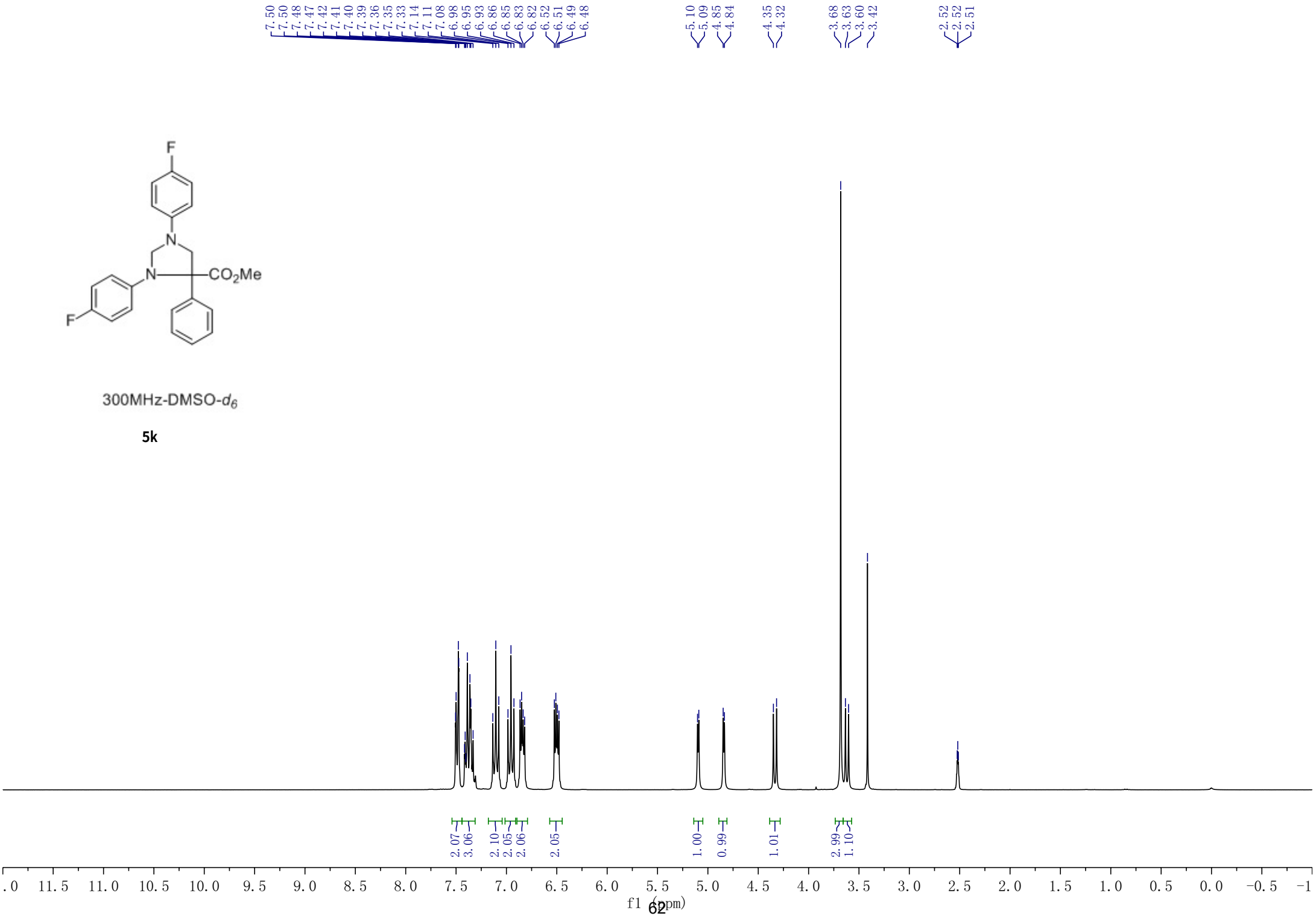


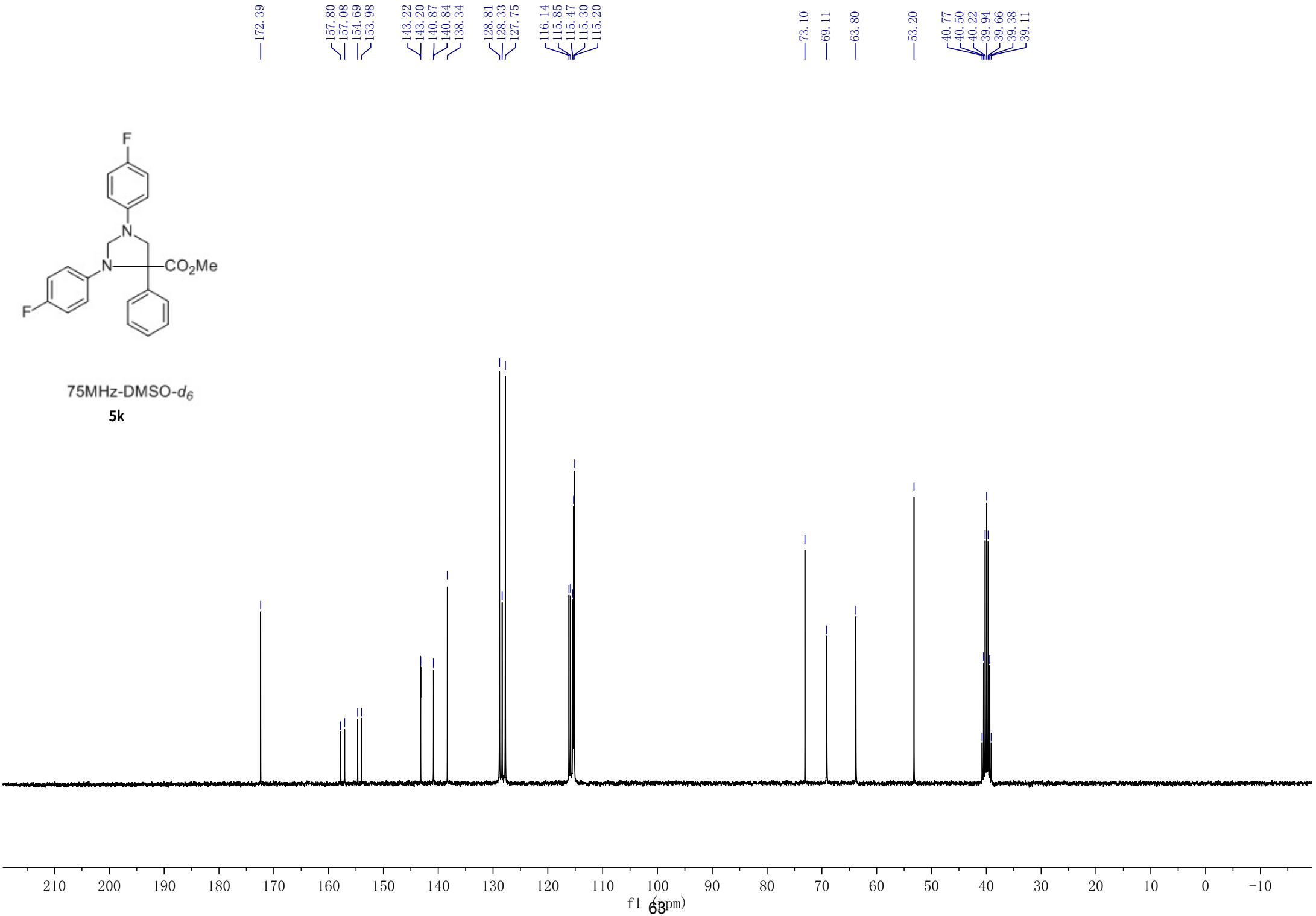

7.59
7.56
7.39
7.37
7.34
7.32
7.26
7.20
7.17
7.03
7.00
6.67
6.64
6.48
6.45
5.13
4.98
4.38
4.35
3.72
3.65
3.62
2.89
2.87
2.85
2.83
2.81
2.78
1.57
1.26
1.24
1.22
1.19
0.11
0.10
0.03
0.03
i-Pr
N
N
CO2Me
Ph
i-Pr
300 MHz, CDCl3
5j
2.01
3.05
2.02
2.02
2.01
2.01
1.00
1.01
1.00
3.00
1.03
2.03
6.02
6.08
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

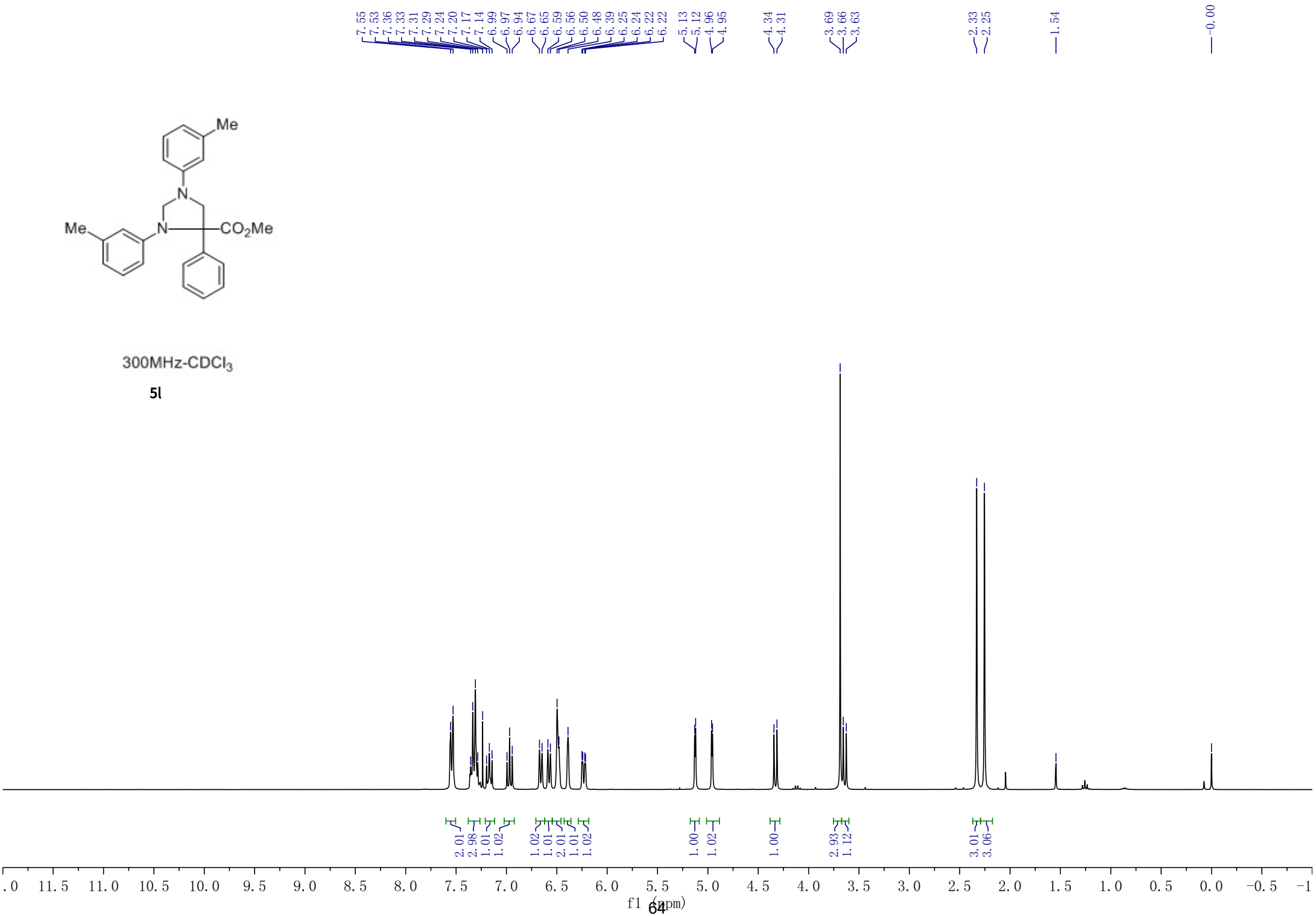
100 MHz, CDCl3

5j



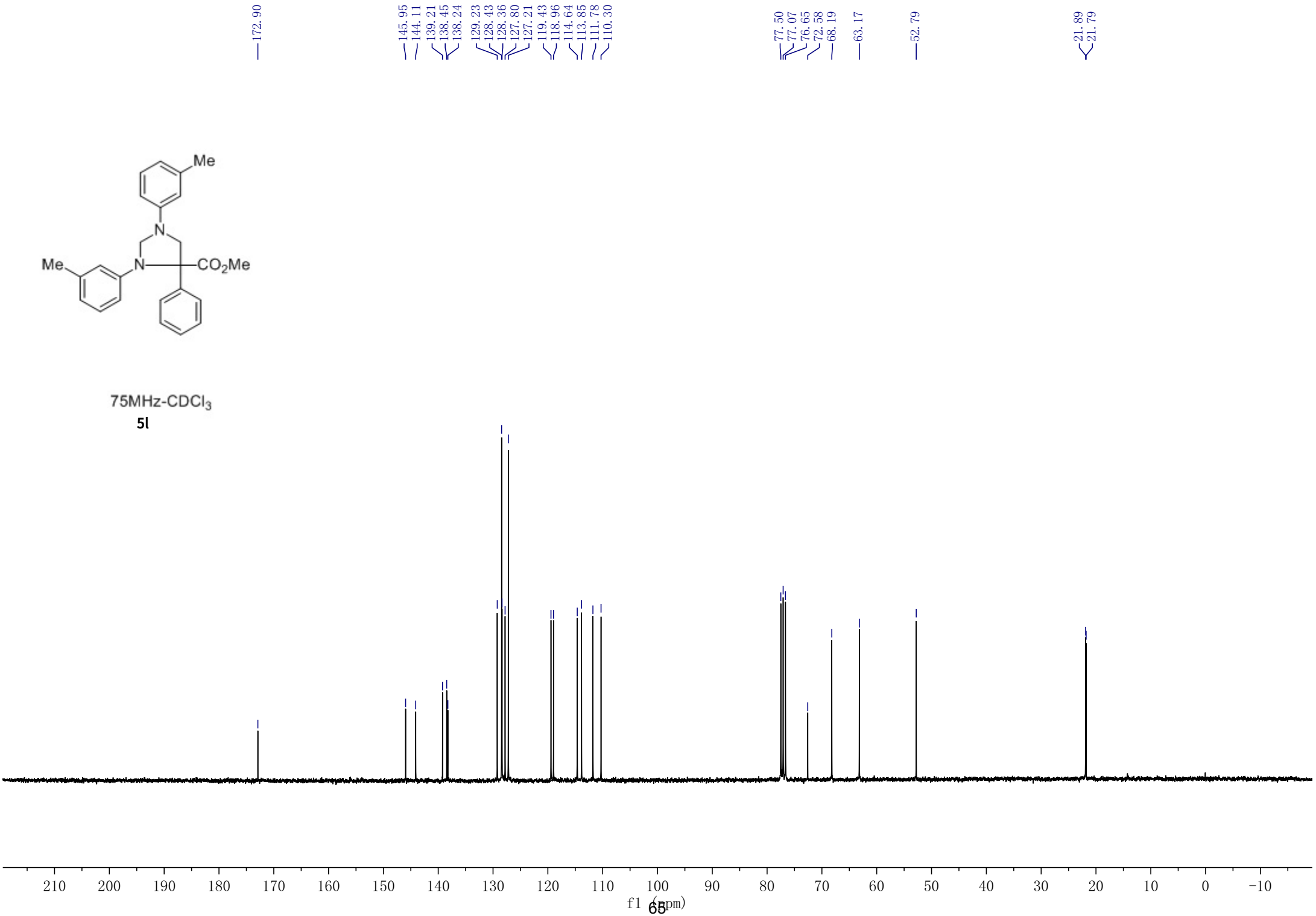

7.50
7.50
7.48
7.47
7.42
7.41
7.40
7.39
7.36
7.35
7.33
7.14
7.11
7.08
6.98
6.95
6.93
6.86
6.85
6.83
6.82
6.52
6.51
6.49
6.48
5.10
5.09
4.85
4.84
4.35
4.32
3.68
3.63
3.60
3.42
2.52
2.52
2.51
F
N
N
CO2Me
F
300MHz-DMSO-d6
5k
2.07
3.06
2.10
2.05
2.06
2.05
1.00
0.99
1.01
2.99
1.10
.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

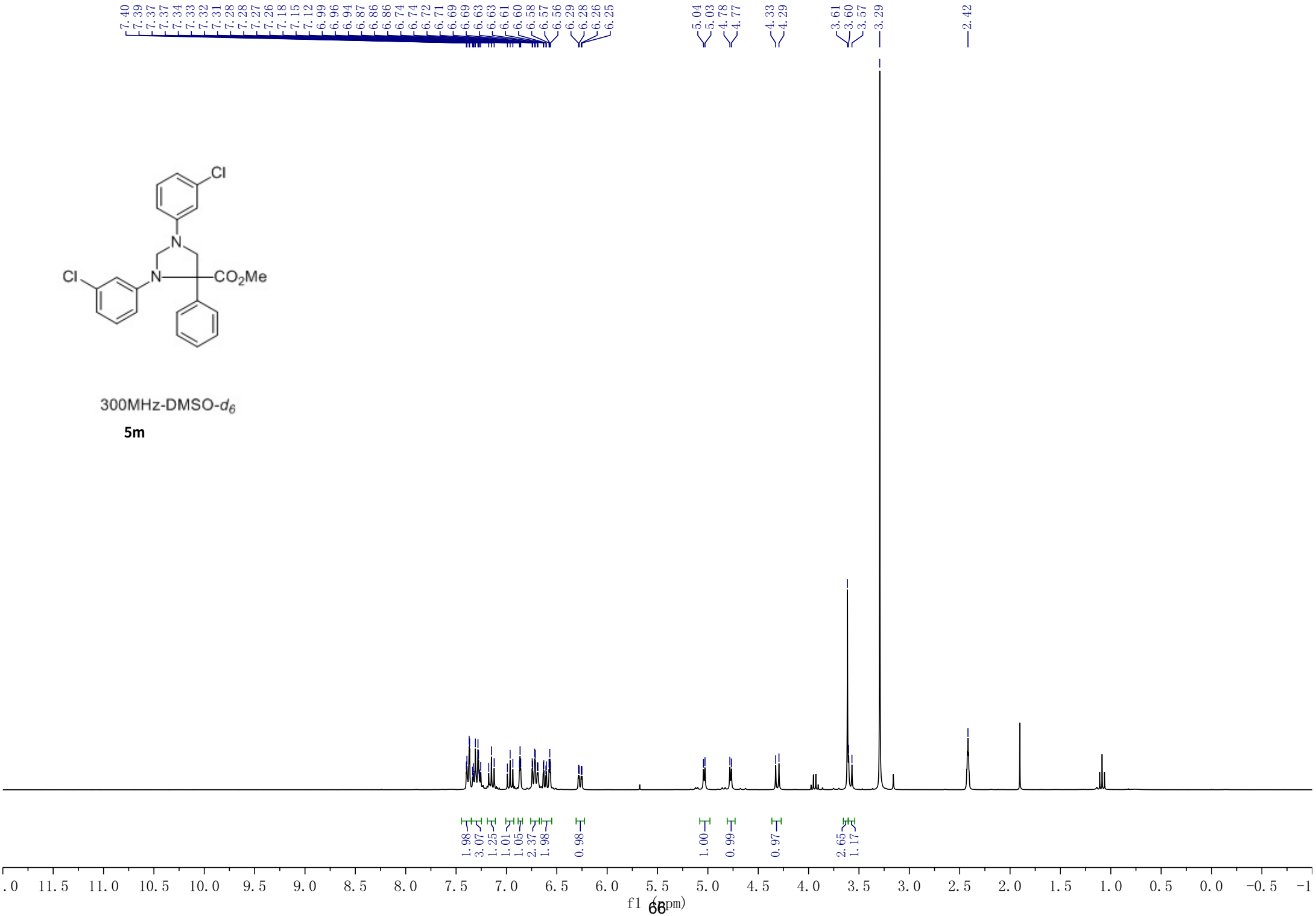

172.39
157.80
157.08
154.69
153.98
143.22
143.20
140.87
140.84
138.34
128.81
128.33
127.75
116.14
115.85
115.47
115.30
115.20
73.10
69.11
63.80
53.20
40.77
40.50
40.22
39.94
39.66
39.38
39.11
F
N
N
CO2Me
F
75MHz-DMSO-d6
5k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

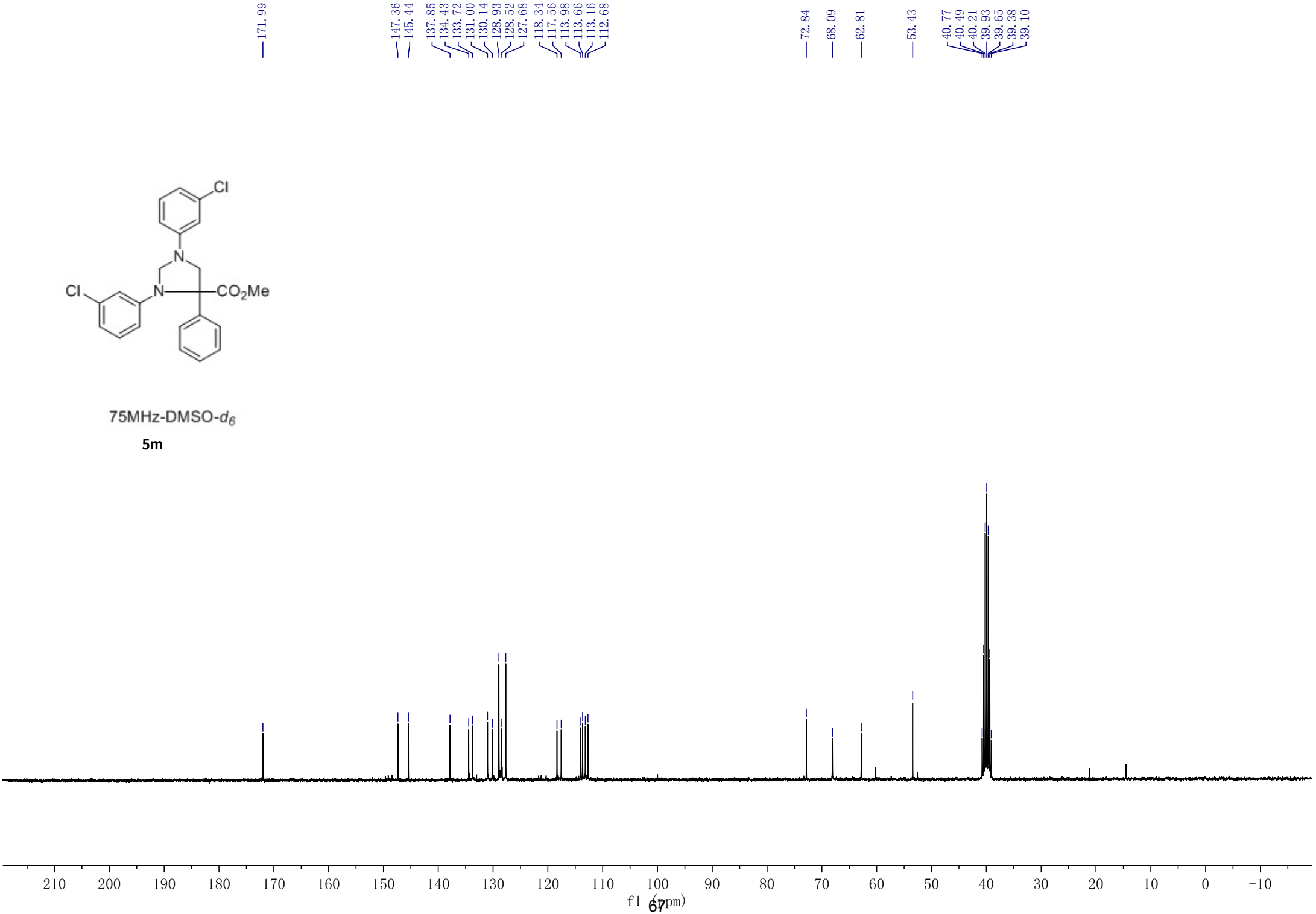

7.55
7.53
7.36
7.33
7.31
7.29
7.24
7.20
7.17
7.14
6.99
6.97
6.94
6.67
6.65
6.59
6.56
6.50
6.48
6.39
6.25
6.24
6.22
6.22
5.13
5.12
4.96
4.95
4.34
4.31
3.69
3.66
3.63
2.33
2.25
1.54
0.00
Me
N
N
Me
CO2Me
300MHz-CDCl3
5l
2.01
2.98
1.01
1.02
1.02
1.01
2.01
1.01
1.02
1.00
1.02
1.00
2.93
1.12
3.01
3.06
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

75MHz-$CDCl_3$

5l




7.40 7.39 7.37 7.37 7.34 7.33 7.32 7.31 7.28 7.28 7.27 7.26 7.18 7.15 7.12 6.99 6.96 6.94 6.87 6.86 6.86 6.74 6.74 6.72 6.71 6.69 6.69 6.63 6.63 6.61 6.60 6.58 6.57 6.56 6.29 6.28 6.26 6.25
5.04 5.03 4.78 4.77
4.33 4.29
3.61 3.60 3.57
3.29
2.42
Cl
N
N
Cl
CO2Me
300MHz-DMSO-d6
5m
1.98 3.07 1.25 1.01 1.05 2.37 1.98 0.98 1.00 0.99 0.97 2.65 1.17
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

75MHz-DMSO-d_6

5m