

[3+2]-Cycloaddition of Azaoxyallyl Cations with Hexahydro-1,3,5-Triazines: Access to 4-Imidazolidinones

Danqing Ji and Jiangtao Sun*

*Jiangsu Key Laboratory of Advanced Catalytic Materials & Technology, School of
Petrochemical Engineering, Changzhou University*

Changzhou 213164, China

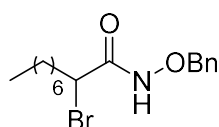
Email: jtsun@cczu.edu.cn or jtsun08@gmail.com

Table of Contents

1. General information
2. General procedure for synthesis **3**
3. Further Studies
4. X-ray structure of **3ag**
5. References
6. ¹H NMR and ¹³C NMR Spectra of compounds

General information

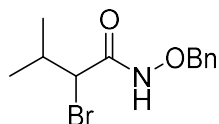
All of the reactions were carried out in flame-dried tubes under argon atmosphere. Solvents were dried prior to use. For column chromatography, 200-300 mesh silica gel was used. ^1H NMR were recorded on Bruker 300 MHz, 400 MHz or 500 MHz spectrometer and ^{13}C NMR were recorded on Bruker 75 MHz, 100 MHz or 125 MHz spectrometer in CDCl_3 . IR spectra were collected on a Nicolet IS5 FT-IR spectrometer. HRMS were performed on Agilent 6540 Q-TOF mass spectrometer (ESI). Melting points were determined on a SGW X-4B melting point apparatus. α -haloamides **1**,¹ 1,3,5-hexahydro-1,3,5-triazines² were prepared according to literature procedures.



N-(benzyloxy)-2-bromononanamide (**1f**):

This compound was prepared via general procedure as yellow oil (2.3 g, 9.38 mmol, yield: 72%).

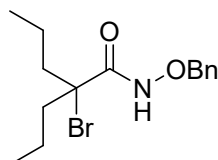
^1H NMR (400 MHz, CDCl_3) δ 8.86 (s, 1H), 7.40-7.38 (m, 5H), 4.93 (s, 2H), 4.14 (m, 1H), 2.09-1.92 (d, J = 18.7 Hz, 2H), 1.27 (m, 10H), 0.88 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.58, 134.76, 129.51, 129.03, 128.71, 78.32, 47.40, 35.38, 31.72, 29.03, 28.79, 27.12, 22.63, 14.11. IR (KBr film) 3440, 3181, 3031, 2925, 2855, 1658, 1466, 1455, 1029, 723, 590 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{16}\text{H}_{25}\text{BrNO}_2$ $[\text{M}+\text{H}]^+$: 342.1063, found: 342.1060.



N-(benzyloxy)-2-bromo-3-methylbutanamide (**1g**):

This compound was prepared via general procedure as a white solid (4.5 g, 16.57 mmol, yield: 80%), mp: 90-91 $^{\circ}\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 8.97 (s, 1H), 7.40-7.38 (m, 5H), 4.93 (s, 2H), 4.10 (d, J = 4.0 Hz, 1H), 2.38-2.34 (m, 1H), 1.01 (t, J = 4.0 Hz, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 165.76, 134.90, 129.45, 129.01, 128.71, 78.38, 56.79, 32.21, 20.36, 18.97. IR (KBr film) 3448, 2984, 1655, 1527, 1374, 1319, 1047, 999, 744, 694, 633 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{12}\text{H}_{17}\text{BrNO}_2$ $[\text{M}+\text{H}]^+$: 286.0437, found: 286.0439.

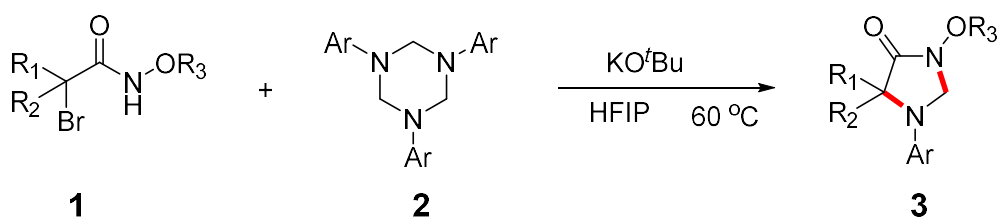


***N*-(benzyloxy)-2-bromo-2-propylpentanamide (1h):**

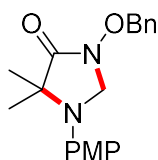
This compound was prepared via general procedure as a white solid (2.15 g, 9.38 mmol, yield: 70%), mp: 72-73 $^{\circ}\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 9.19 (s, 1H), 7.41-7.35 (m, 5H), 4.92 (s, 2H), 2.18-2.10 (m, 2H), 1.89-1.81 (m, 2H), 1.59-1.48 (m, 2H), 1.37-1.25 (m, 2H), 0.94-0.89 (m, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 167.86, 134.73, 129.42, 128.99, 128.66, 78.53, 74.02, 58.50, 45.20, 19.13, 18.46, 17.82, 13.75. IR (KBr film) 3133, 2968, 2869, 1648, 1464, 1447, 1375, 1115, 1049, 736, 692, 567 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{23}\text{BrNO}_2$ $[\text{M}+\text{H}]^+$: 328.0907, found: 328.0905.

General procedure for the preparation of compounds 3



To a solution of **2** (0.3 mmol) in HFIP (1.5mL) was added α -haloamide **1** (0.2 mmol) and t -BuOK (0.6 mmol) and stirred at 60 $^{\circ}\text{C}$ under argon atmosphere for 3 h. The reaction mixture was concentrated under vacuum, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether = 1:30-1:10) to give **3**.

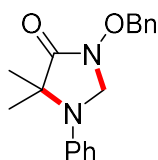


3-(benzyloxy)-1-(4-methoxyphenyl)-5,5-dimethylimidazolidin-4-one (3aa):

This compound was prepared via general procedure as yellow oil (74 mg, yield: 76%).

^1H NMR (300 MHz, CDCl_3) δ 7.48-7.46 (m, 2H), 7.40-7.38 (m, 3H), 6.81 (d, $J = 9.0$ Hz, 2H), 6.66 (d, $J = 9.0$ Hz, 2H), 5.10 (s, 2H), 4.38 (s, 2H), 3.76 (s, 3H), 1.42 (s, 6H).

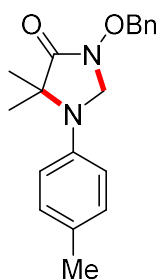
^{13}C NMR (75 MHz, CDCl_3) δ 172.98, 153.92, 137.32, 134.97, 129.62, 129.20, 128.72, 118.04, 114.69, 77.87, 63.35, 61.57, 55.61, 22.82. IR (KBr film) 3448, 2984, 1629, 1458, 1400, 1383, 1245, 1178, 817, 747, 699, 574 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 327.1709, found: 327.1707.



3-(benzyloxy)-5,5-dimethyl-1-phenylimidazolidin-4-one (3ab):

This compound was prepared via general procedure as colorless oil (68 mg, yield: 77%).

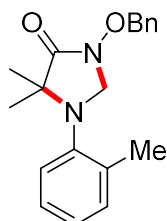
^1H NMR (400 MHz, CDCl_3) δ 7.47-7.46 (m, 2H), 7.40-7.38 (m, 3H), 7.26-7.21 (m, 2H), 6.82 (t, $J = 8.0$ Hz, 1H), 6.61 (d, $J = 8.0$ Hz, 2H), 5.11 (s, 2H), 4.41 (s, 2H), 1.56 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.19, 143.45, 134.79, 129.71, 129.37, 129.32, 128.77, 118.69, 113.82, 77.83, 62.53, 61.19, 22.93. IR (KBr film) 3448, 1637, 1400, 1384, 577 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 297.1598, found: 297.1599.



3-(benzyloxy)-5,5-dimethyl-1-(p-tolyl)imidazolidin-4-one (3ac):

This compound was prepared via general procedure as yellow oil (67 mg, yield: 72%).

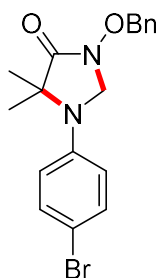
^1H NMR (400 MHz, CDCl_3) δ 7.48-7.45 (m, 2H), 7.39-7.38 (m, 3H), 7.04 (d, $J = 8.0$ Hz, 2H), 6.55 (d, $J = 8.0$ Hz, 2H), 5.11 (s, 2H), 4.39 (s, 2H), 2.25 (s, 3H), 1.51 (s, 6H). ^{13}C NMR (125 MHz, CDCl_3) δ 172.46, 141.17, 134.86, 129.85, 129.67, 129.24, 128.73, 128.48, 114.61, 77.81, 62.75, 61.25, 22.85, 20.30. IR (KBr film) 3448, 1637, 1400, 1384, 578 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 311.1754, found: 311.1753.



3-(benzyloxy)-5,5-dimethyl-1-(o-tolyl)imidazolidin-4-one (3ad):

This compound was prepared via general procedure as colorless oil (60 mg, yield: 65%).

^1H NMR (400 MHz, CDCl_3) δ 7.51 (m, 2H), 7.44-7.37 (m, 3H), 7.15 (d, $J = 8.0$ Hz, 1H), 7.06-6.98 (m, 2H), 6.74 (d, $J = 8.0$ Hz, 1H), 5.13 (s, 2H), 4.37 (s, 2H), 2.24 (s, 3H), 1.15 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 176.38, 145.10, 137.91, 135.72, 130.69, 129.55, 129.09, 128.69, 126.58, 126.27, 125.91, 77.66, 68.04, 57.60, 22.71, 18.70. IR (KBr film) 3448, 1637, 1400, 1384, 558 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 311.1754, found: 311.1753.

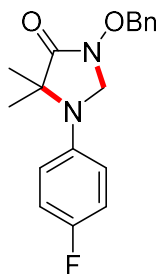


3-(benzyloxy)-1-(4-bromophenyl)-5,5-dimethylimidazolidin-4-one (3ae):

This compound was prepared via general procedure as yellow oil (90 mg, yield: 80%).

^1H NMR (400 MHz, CDCl_3) δ 7.47-7.45 (m, 2H), 7.40-7.39 (m, 3H), 7.31 (d, $J = 8.0$ Hz, 2H), 6.47 (d, $J = 8.0$ Hz, 2H), 5.11 (s, 2H), 4.36 (s, 2H), 1.53 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.86, 142.59, 134.71, 132.13, 129.72, 129.39, 128.80, 115.31,

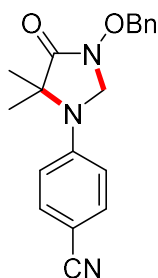
110.95, 77.90, 62.47, 61.23, 22.87. IR (KBr film) 3451, 1637, 1400, 1384, 554 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{20}\text{BrN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 375.0703, found: 375.0700.



3-(benzyloxy)-1-(4-fluorophenyl)-5,5-dimethylimidazolidin-4-one (3af):

This compound was prepared via general procedure as a white solid (79 mg, yield: 84%), mp: 125-126 $^{\circ}\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 7.48-7.46 (m, 2H), 7.40-7.39 (m, 3H), 6.94 (t, $J = 8.0$ Hz, 2H), 6.60-6.57 (m, 2H), 5.10 (s, 2H), 4.39 (s, 2H), 1.47 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.45, 158.07, 155.81, 139.92, 134.85, 129.67, 129.29, 128.77, 116.28, 116.20, 116.03, 115.80, 77.89, 63.02, 61.44, 22.88. IR (KBr film) 3448, 1637, 1400, 1384, 559 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{20}\text{FN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 315.1503, found: 315.1505.

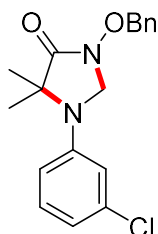


4-(3-(benzyloxy)-5,5-dimethyl-4-oxoimidazolidin-1-yl)benzonitrile (3ag):

This compound was prepared via general procedure as a white solid (84 mg, yield: 87%), mp: 135-136 $^{\circ}\text{C}$.

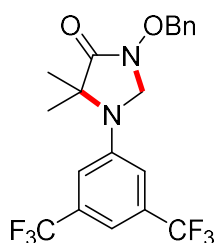
^1H NMR (400 MHz, CDCl_3) δ 7.49-7.45 (m, 4H), 7.42-7.40 (m, 3H), 6.56 (d, $J = 12.0$ Hz, 2H), 5.12 (s, 2H), 4.41 (s, 2H), 1.61 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 170.88, 146.35, 134.48, 133.86, 133.62, 129.75, 129.54, 128.87, 112.63, 100.29, 77.96, 62.08,

61.31, 22.98. IR (KBr film) 3448, 2210, 1606, 1459, 1384, 1177, 817, 713, 698, 546 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{20}\text{N}_3\text{O}_2[\text{M}+\text{H}]^+$: 322.1550, found: 322.1553.



3-(benzyloxy)-1-(3-chlorophenyl)-5,5-dimethylimidazolidin-4-one (3ah):

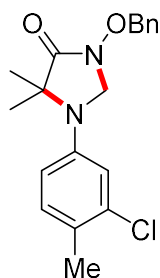
This compound was prepared via general procedure as yellow oil (77 mg, yield: 78%). ^1H NMR (400 MHz, CDCl_3) δ 7.47-7.45 (m, 2H), 7.41-7.39 (m, 3H), 7.13 (t, J = 8.0 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 6.54-6.53 (m, 1H), 6.48 (dd, J = 4.0, 4.0 Hz, 1H), 5.11 (s, 2H), 4.39 (s, 2H), 1.56 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.68, 144.52, 135.24, 134.64, 130.29, 129.72, 129.40, 128.81, 118.45, 113.39, 111.66, 77.87, 62.35, 61.25, 22.92. IR (KBr film) 3650, 3448, 1637, 1400, 1384 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{20}\text{ClN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 331.1208, found: 331.1205.



3-(benzyloxy)-1-(3,5-bis(trifluoromethyl)phenyl)-5,5-dimethylimidazolidin-4-one (3ai):

This compound was prepared via general procedure as a white solid (87 mg, yield: 67%), mp: 141-142 $^{\circ}\text{C}$.

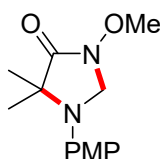
^1H NMR (400 MHz, CDCl_3) δ 7.48-7.47 (m, 2H), 7.42-7.41 (m, 3H), 6.90 (s, 2H), 5.14 (s, 2H), 4.46 (s, 2H), 1.61 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 170.89, 144.10, 134.38, 132.89, 132.45, 129.78, 129.54, 128.86, 125.12, 121.51, 112.20, 111.28, 100.00, 77.98, 62.15, 61.42, 22.95. IR (KBr film) 3448, 2360, 1637, 1400, 1384, 577 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{19}\text{F}_6\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 433.1345, found: 433.1348.



3-(benzyloxy)-1-(3-chloro-4-methylphenyl)-5,5-dimethylimidazolidin-4-one (3aj):

This compound was prepared via general procedure as yellow oil (79 mg, yield: 77%).

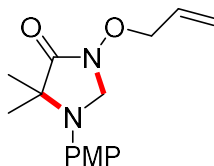
^1H NMR (400 MHz, CDCl_3) δ 7.47-7.45 (m, 2H), 7.41-7.38 (m, 3H), 7.05 (d, $J = 8.0$ Hz, 1H), 6.59 (d, $J = 4.0$ Hz, 1H), 6.45 (dd, $J = 8.0, 4.0$ Hz, 1H), 5.10 (s, 2H), 4.37 (s, 2H), 2.25 (s, 3H), 1.52 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 171.97, 142.50, 135.08, 134.70, 131.33, 129.70, 129.35, 128.78, 126.01, 114.48, 112.61, 77.85, 62.50, 61.28, 22.87, 18.87. IR (KBr film) 3676, 3448, 2923, 1654, 1637, 1400, 1384 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{22}\text{ClN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 345.1364, found: 345.1362.



3-(benzyloxy)-1-(3-chloro-4-methylphenyl)-5,5-dimethylimidazolidin-4-one (3ba):

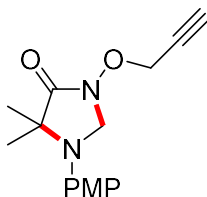
This compound was prepared via general procedure as a light yellow solid (56 mg, yield: 75%), mp: 67-68°C.

^1H NMR (400 MHz, CDCl_3) δ 6.87 (d, $J = 8.0$ Hz, 2H), 6.80 (d, $J = 12.0$ Hz, 2H), 4.69 (s, 2H), 3.92 (s, 3H), 3.78 (s, 3H), 1.44 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 172.66, 154.22, 137.23, 118.44, 114.79, 63.38, 61.88, 61.78, 55.63, 22.71. IR (KBr film) 3691, 3448, 2987, 2936, 1739, 1401, 1360, 1246, 1032, 819, 747, 581 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{13}\text{H}_{19}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 251.1390, found: 251.1393.



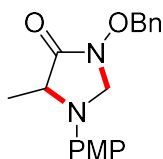
3-(allyloxy)-1-(4-methoxyphenyl)-5,5-dimethylimidazolidin-4-one (3ca):

This compound was prepared via general procedure as yellow oil (69 mg, yield: 83%). ^1H NMR (400 MHz, CDCl_3) δ 6.86 (d, J = 8.0 Hz, 2H), 6.78 (d, J = 8.0 Hz, 2H), 6.08-6.04 (m, 1H), 5.45-5.36 (m, 2H), 4.68 (s, 2H), 4.58 (d, J = 4.0 Hz, 2H), 3.78 (s, 3H), 1.44 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 172.91, 154.00, 137.33, 131.93, 121.58, 118.07, 114.75, 77.49, 63.16, 61.72, 55.62, 22.83. IR (KBr film) 3752, 3448, 1637, 1400, 1384, 577 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{21}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 277.1547, found: 277.1545.



1-(4-methoxyphenyl)-5,5-dimethyl-3-(prop-2-yn-1-yloxy)imidazolidin-4-one (3da):

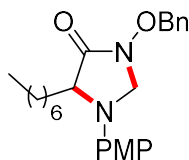
This compound was prepared via general procedure as red oil (64 mg, yield: 78%). ^1H NMR (400 MHz, CDCl_3) δ 6.87 (d, J = 8.0 Hz, 2H), 6.82 (d, J = 8.0 Hz, 2H), 4.81 (s, 2H), 4.73 (d, J = 2.4 Hz, 2H), 3.78 (s, 3H), 2.60-2.59 (m, 1H), 1.45 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 173.89, 154.26, 137.32, 118.70, 114.73, 77.94, 76.87, 63.90, 63.45, 61.56, 55.61, 22.79. IR (KBr film) 3752, 3448, 1637, 1541, 1508, 1400, 1384, 576 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 275.1390, found: 275.1392.



3-(benzyloxy)-1-(4-methoxyphenyl)-5-methylimidazolidin-4-one (3ea):

This compound was prepared via general procedure as yellow oil (64 mg, yield: 68%). ^1H NMR (400 MHz, CDCl_3) δ 7.46-7.45 (m, 2H), 7.40-7.39 (m, 3H), 6.84 (d, J = 8.0 Hz, 2H), 6.46 (d, J = 8.0 Hz, 2H), 5.09 (q, J = 12.0 Hz, 2H), 4.60 (t, J = 2.7 Hz, 1H), 4.38 (d, J = 4.0 Hz, 1H), 4.06-4.01 (m, 1H), 3.75 (s, 3H), 1.45 (d, J = 4.0 Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 169.73, 152.94, 134.81, 129.57, 129.24, 128.76, 115.13, 113.56, 111.66, 77.94, 64.92, 55.75, 54.62, 16.70. IR (KBr film) 3449, 1637, 1400,

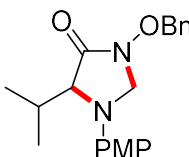
1384, 546 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 313.1547, found: 313.1550.



3-(benzyloxy)-5-heptyl-1-(4-methoxyphenyl)imidazolidin-4-one (3fa):

This compound was prepared via general procedure as yellow oil (52 mg, yield: 44%).

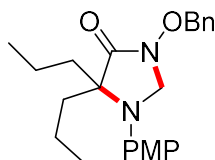
^1H NMR (400 MHz, CDCl_3) δ 7.47-7.46(m, 2H), 7.40-7.38 (m, 3H), 6.84 (d, $J = 8.0$ Hz, 2H), 6.45 (d, $J = 8.0$ Hz, 2H), 5.09 (d, $J = 4.0$ Hz, 2H), 4.60 (s, 1H), 4.41 (d, $J = 4.0$ Hz, 1H), 4.06 (s, 1H), 3.75 (s, 3H), 1.88 (s, 2H), 1.22 (s, 10H), 0.86-0.84 (m, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 169.25, 155.66, 147.52, 139.25, 129.56, 129.20, 128.71, 115.09, 113.19, 77.94, 65.33, 58.68, 56.10, 55.73, 31.76, 29.71, 29.22, 23.84, 22.62, 14.08. IR (KBr film) 3450, 1637, 1400, 1384, 581 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{33}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 397.2486, found: 397.2485.



3-(benzyloxy)-5-isopropyl-1-(4-methoxyphenyl)imidazolidin-4-one (3ga):

This compound was prepared via general procedure as colorless oil (71 mg, yield: 70%).

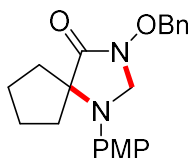
^1H NMR (400 MHz, CDCl_3) δ 7.46-7.45 (m, 2H), 7.40-7.38 (m, 3H), 6.83 (d, $J = 8.0$ Hz, 2H), 6.45 (d, $J = 8.0$ Hz, 2H), 5.07 (s, 2H), 4.65 (t, $J = 8.0$ Hz, 1H), 4.40 (d, $J = 4.0$ Hz, 1H), 3.92 (s, 1H), 3.75 (s, 3H), 2.27-2.21 (m, 1H), 1.19 (d, $J = 7.1$ Hz, 3H), 0.90 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 168.49, 152.80, 139.71, 134.98, 129.55, 129.16, 128.70, 115.05, 113.58, 78.00, 65.91, 63.29, 55.75, 30.19, 18.12, 16.96. IR (KBr film) 3691, 3448, 1654, 1637, 1400, 1384, 580 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 341.1860, found: 341.1863.



3-(benzyloxy)-1-(4-methoxyphenyl)-5,5-dipropylimidazolidin-4-one (3ha):

This compound was prepared via general procedure as colorless oil (75 mg, yield: 65%).

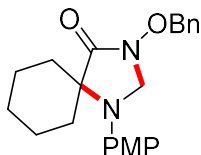
^1H NMR (400 MHz, CDCl_3) δ 7.48-7.46 (m, 2H), 7.39-7.37 (m, 3H), 6.82 (d, $J = 8.0$ Hz, 2H), 6.51 (d, $J = 8.0$ Hz, 2H), 5.10 (s, 2H), 4.47 (s, 2H), 3.75 (s, 3H), 2.05-1.98 (m, 2H), 1.87-1.79 (m, 2H), 1.13-1.03 (m, 4H), 0.79 (t, $J = 12.0$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 171.35, 152.14, 137.59, 134.90, 129.64, 129.24, 128.69, 115.07, 113.30, 78.00, 68.47, 64.03, 55.68, 38.68, 17.28, 14.00. IR (KBr film) 3651, 3448, 1654, 1637, 1400, 1384, 698, 577 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{31}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 383.2329, found: 383.2327.



3-(benzyloxy)-1-(4-methoxyphenyl)-1,3-diazaspiro[4.4]nonan-4-one (3ia):

This compound was prepared via general procedure as yellow oil (62 mg, yield: 59%).

^1H NMR (300 MHz, CDCl_3) δ 7.49-7.46 (m, 2H), 7.41-7.37 (m, 3H), 6.80 (d, $J = 12.0$ Hz, 2H), 6.58 (d, $J = 8.0$ Hz, 2H), 5.10 (s, 2H), 4.42 (s, 2H), 3.75 (s, 3H), 2.03-1.79 (m, 8H). ^{13}C NMR (75 MHz, CDCl_3) δ 175.18, 153.76, 137.25, 135.12, 129.56, 129.13, 128.71, 117.83, 114.75, 77.80, 70.66, 64.68, 55.63, 33.13, 25.68. IR (KBr film) 3691, 3448, 2924, 1654, 1648, 1637, 1629, 1400, 1384, 577 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{25}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 353.1860, found: 353.1861.

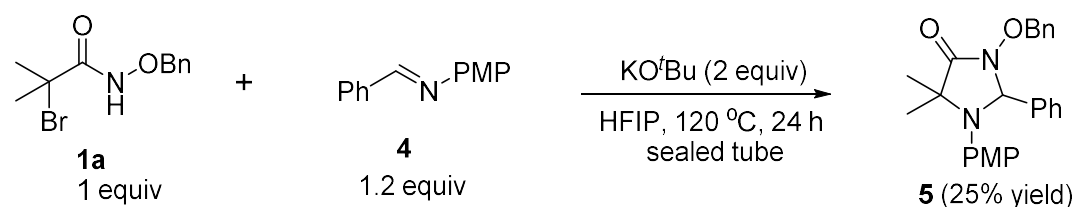


3-(benzyloxy)-1-(4-methoxyphenyl)-1,3-diazaspiro[4.5]decan-4-one (3ja):

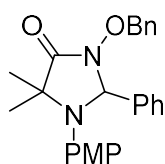
This compound was prepared via general procedure as colorless oil (62 mg, yield: 56%).

^1H NMR (400 MHz, CDCl_3) δ 7.49-7.47(m, 2H), 7.41-7.36 (m, 3H), 6.89 (d, J = 8.0 Hz, 2H), 6.76 (d, J = 8.0 Hz, 2H), 5.09 (s, 2H), 4.40 (s, 2H), 3.77 (s, 3H), 1.91-1.82 (m, 2H), 1.74-1.68 (m, 2H), 1.59-1.53 (m, 5H), 1.25-1.19 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 175.04, 156.48, 138.00, 135.50, 129.49, 129.02, 128.66, 126.00, 114.01, 77.71, 66.53, 62.98, 55.48, 31.21, 25.01, 21.59. IR (KBr film) 3670, 3448, 2921, 1648, 1637, 1571, 1440, 1384, 577 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 367.2016, found: 367.2015.

Further Studies (Scheme 3)



To a solution of **4** (0.2 mmol) in HFIP was added α -haloamide **1a** (0.24 mmol) and *t*-BuOK (0.4 mmol) and stirred at 120 °C under argon atmosphere for 24 h. The reaction mixture was concentrated under vacuum, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether = 1:20-1:5) to give the yellow oil **5**.

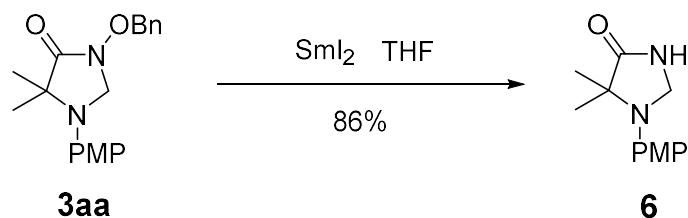


3-(benzyloxy)-1-(4-methoxyphenyl)-5,5-dimethyl-2-phenylimidazolidin-4-one (5):

This compound was prepared via general procedure as yellow oil (30 mg, yield: 25 %), mp: 150-151 °C.

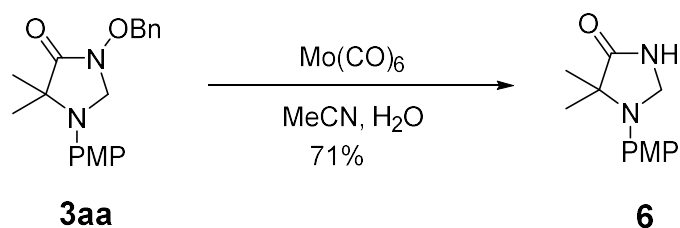
^1H NMR (400 MHz, CDCl_3) δ 6.88-6.86 (m, 2H), 6.68-6.67 (m, 3H), 6.64-6.62 (m, 3H), 6.50-6.49 (m, 2H), 6.22 (d, J = 8.0 Hz, 2H), 6.05 (d, J = 8.0 Hz, 2H), 4.95 (s, 1H), 4.26 (d, J = 8.0 Hz, 1H), 3.54 (d, J = 8.0 Hz, 1H), 3.02 (s, 3H), 1.02 (s, 3H), 0.48 (s, 3H). ^{13}C NMR (100MHz, CDCl_3) δ 172.06, 155.82, 136.72, 134.89, 134.43, 129.79, 129.64, 128.94, 128.82, 128.58, 128.43, 124.65, 114.17, 78.49, 76.14, 62.05, 55.33, 27.36,

20.05. IR (KBr film) 3439, 2952, 2931, 1735, 1511, 1379, 1351, 1250, 1033, 834, 732, 702 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{27}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 403.2016, found: 403.2012.



To a solution of 4-imidazolidinone **3aa** (0.06 g, 0.184mmol) in dry THF (0.25M) was added dry methanol (0.5 ml) and 13 ml of SmI_2 solution in THF (0.1 M). The mixture was stirred under nitrogen for 6 h at room temperature and quenched with saturated ammonium chloride solution. The mixture was extracted with ethyl acetate, washed with saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution, dried over anhydrous sodium sulfate, the solvent was removed under reduced pressure and purified by column chromatography (EtOAc: Petroleum ether = 1:5) to afford **6** a white solid (57 mg, yield: 86%, mp: 145-146 $^\circ\text{C}$).³

6: ^1H NMR (400 MHz, CDCl_3) δ 8.17 (s, 1H), 6.88 (d, $J = 8.0$ Hz, 2H), 6.77 (d, $J = 8.0$ Hz, 2H), 4.65 (s, 2H), 3.78 (s, 3H), 1.50 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3) δ 179.37, 153.14, 137.97, 116.42, 114.85, 61.21, 59.27, 55.68, 22.46. IR (KBr film) 3670, 3448, 2925, 1637, 1458, 1400, 1384, 573 cm^{-1} . HRMS (ESI) calcd. for $\text{C}_{12}\text{H}_{17}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 221.1285, found: 221.1280.

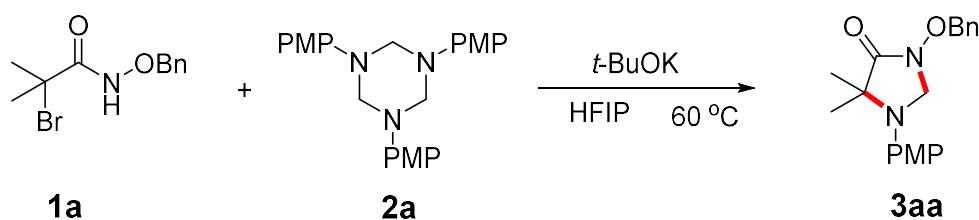


To a solution of 4-imidazolidinone **3aa** (0.06 g, 0.19 mmol) in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (9:1, degassed under nitrogen) was added Mo(CO)_6 (0.12 g, 0.46 mmol) and again degassed under nitrogen. The reaction mixture was vigorously stirred and heated to reflux for 6 hours under nitrogen. The complete consumption of **3aa** was confirmed by TLC (1:1, EtOAc: Petroleum ether). The crude reaction mixture was filtered through a celite bed and washed the celite bed with ethyl acetate (50 mL). The collected filtrates were

combined and concentrated by rotary vapor. The crude product was purified by flash column chromatography (EtOAc: Petroleum ether = 1:5) to afford product **6** (47 mg, yield: 71%, mp: 145-146 °C).⁴

6: ¹H NMR (400 MHz, CDCl₃) δ 8.17 (s, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 8.0 Hz, 2H), 4.65 (s, 2H), 3.78 (s, 3H), 1.50 (s, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 179.37, 153.14, 137.97, 116.42, 114.85, 61.21, 59.27, 55.68, 22.46. HRMS (ESI) calcd. for C₁₂H₁₇N₂O₂ [M+H]⁺: 221.1285, found: 221.1280.

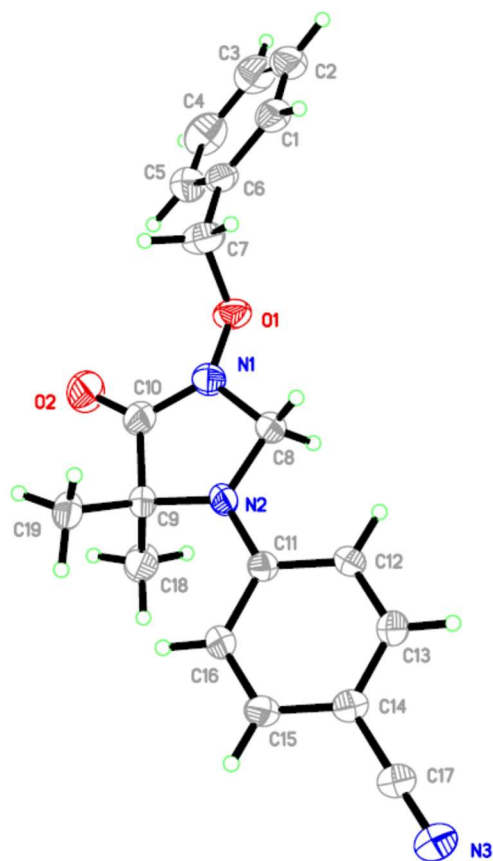
1 mmol scale for the preparation of **3aa**



To a solution of **2a** (541 mg, 1.33 mmol) in HFIP (20 mL) was added α -haloamide **1a** (544 mg, 2 mmol) and *t*-BuOK (448 mg, 4 mmol). The resulting mixture was stirred at 60 °C under argon atmosphere for 5 h. The reaction mixture was concentrated under vacuum, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether = 1:30-1:10) to give **3aa** (yellow oil, 483 mg, yield: 74%).

X-ray structure of **3ag**

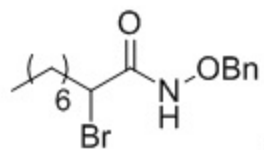
The crystal structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC 1831551, **3ag**). The data can be obtained free of charge via the internet at www.ccdc.cam.ac.uk/data_request/cif.



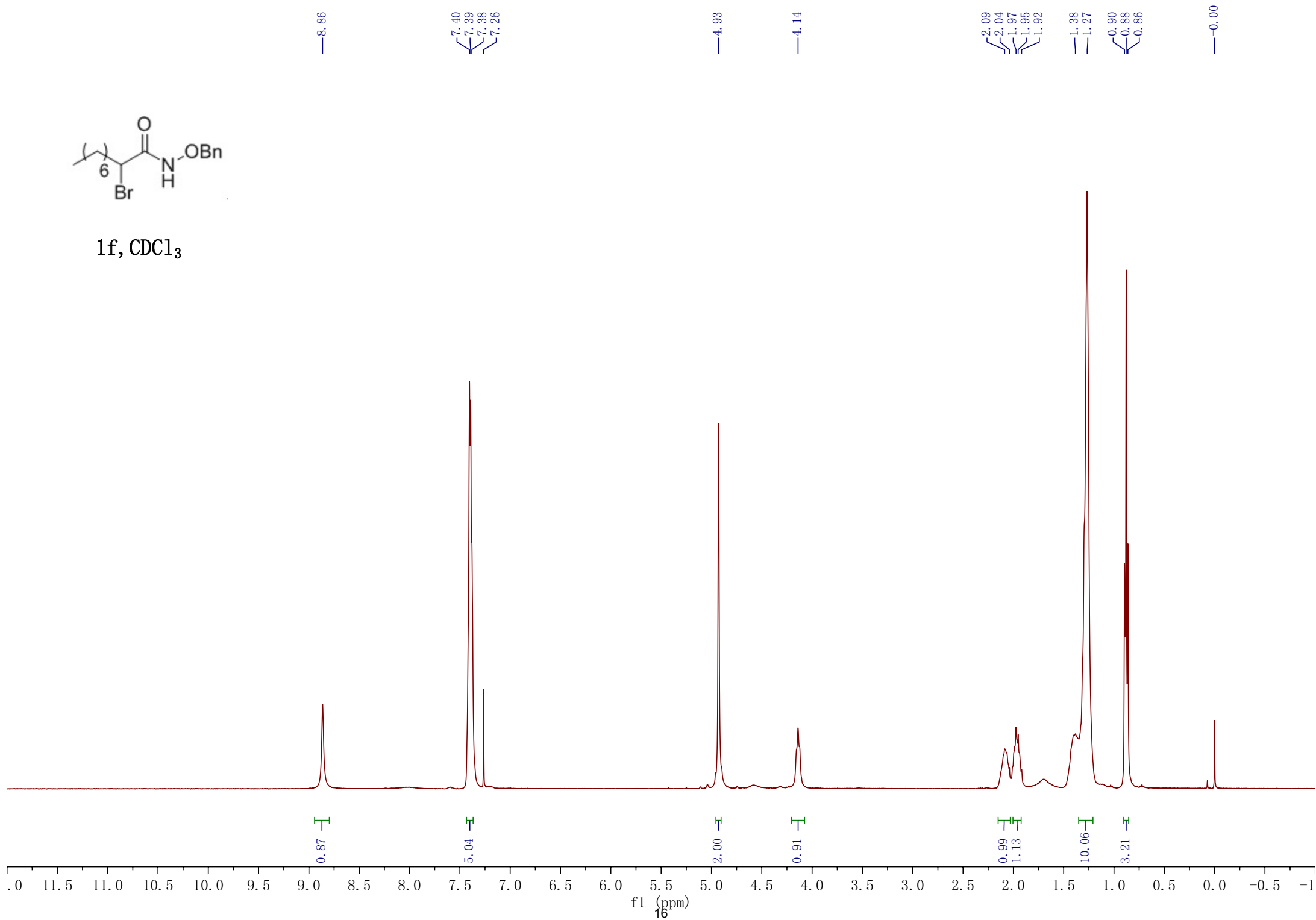
X-ray of **3ag**

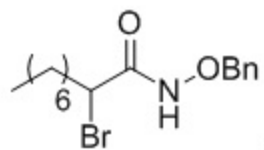
References

- [1] Jeffrey, C. S.; Barnes, K. L.; Eickhoff, J. A.; Carson, C. R. *J. Am. Chem. Soc.* **2011**, 133, 7688.
- [2] Zhu, C.; Xu, G.; Sun, J. *Angew. Chem. Int. Ed.* **2016**, 55, 11867.
- [3] Acharya, A.; Anumandla, D.; Jeffrey, C. S. *J. Am. Chem. Soc.* **2015**, 137, 14858.
- [4] Anumandla D.; Acharya, A.; Jeffrey, C. S. *Org. Lett.* **2016**, 18, 476.

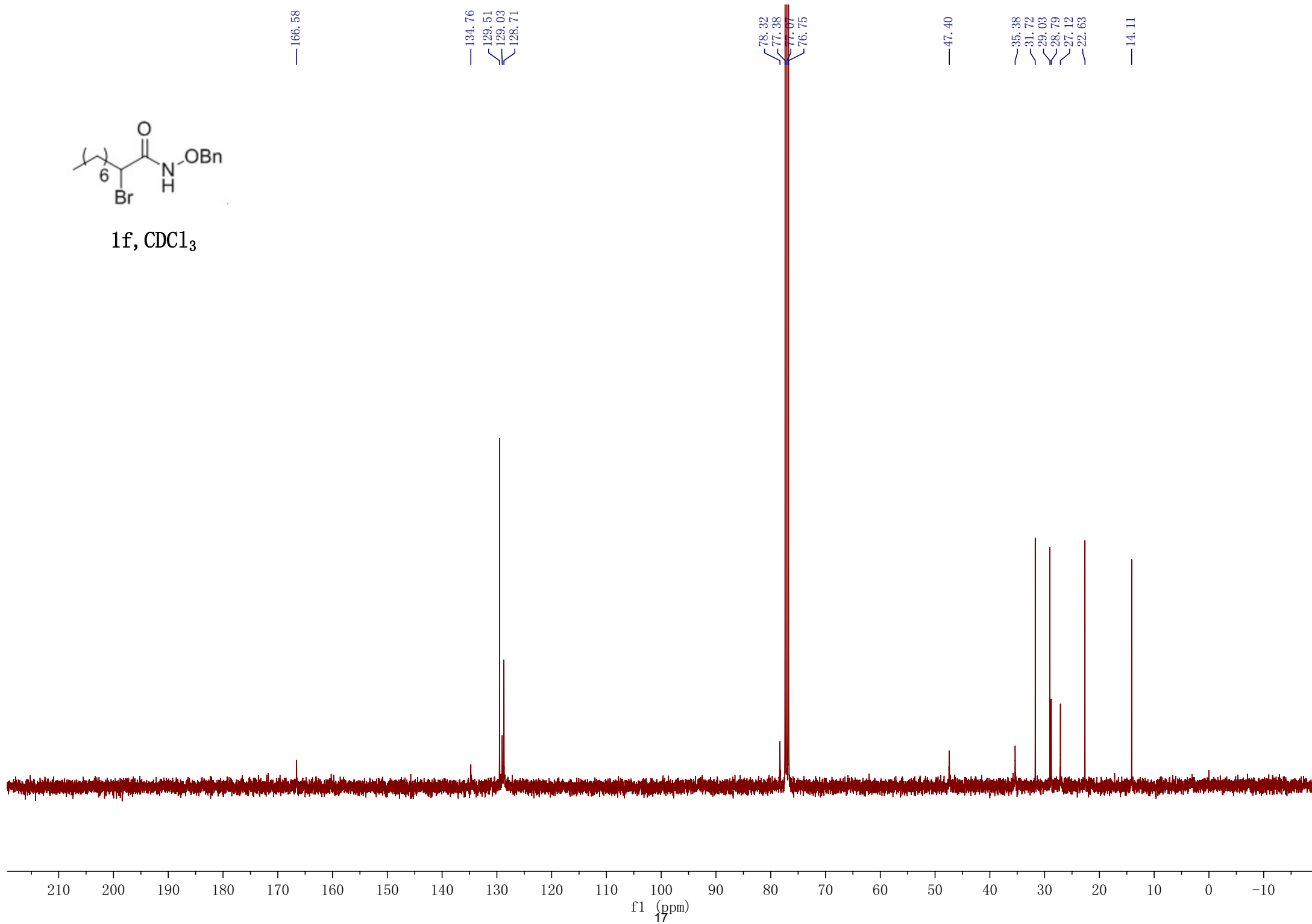


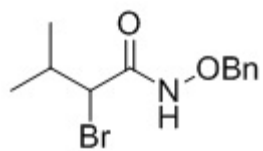
1f, CDCl₃



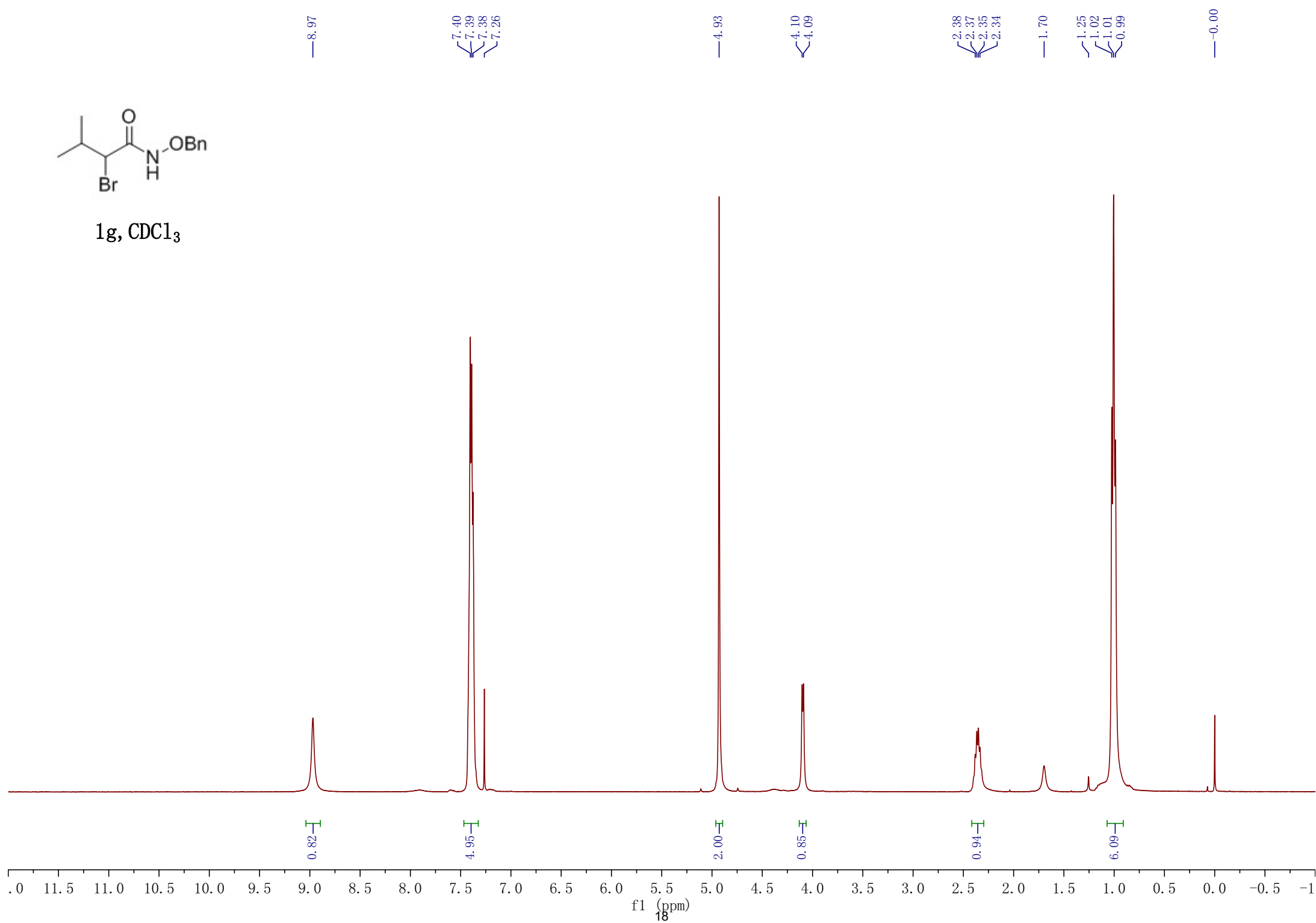


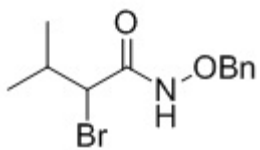
1f, CDCl₃



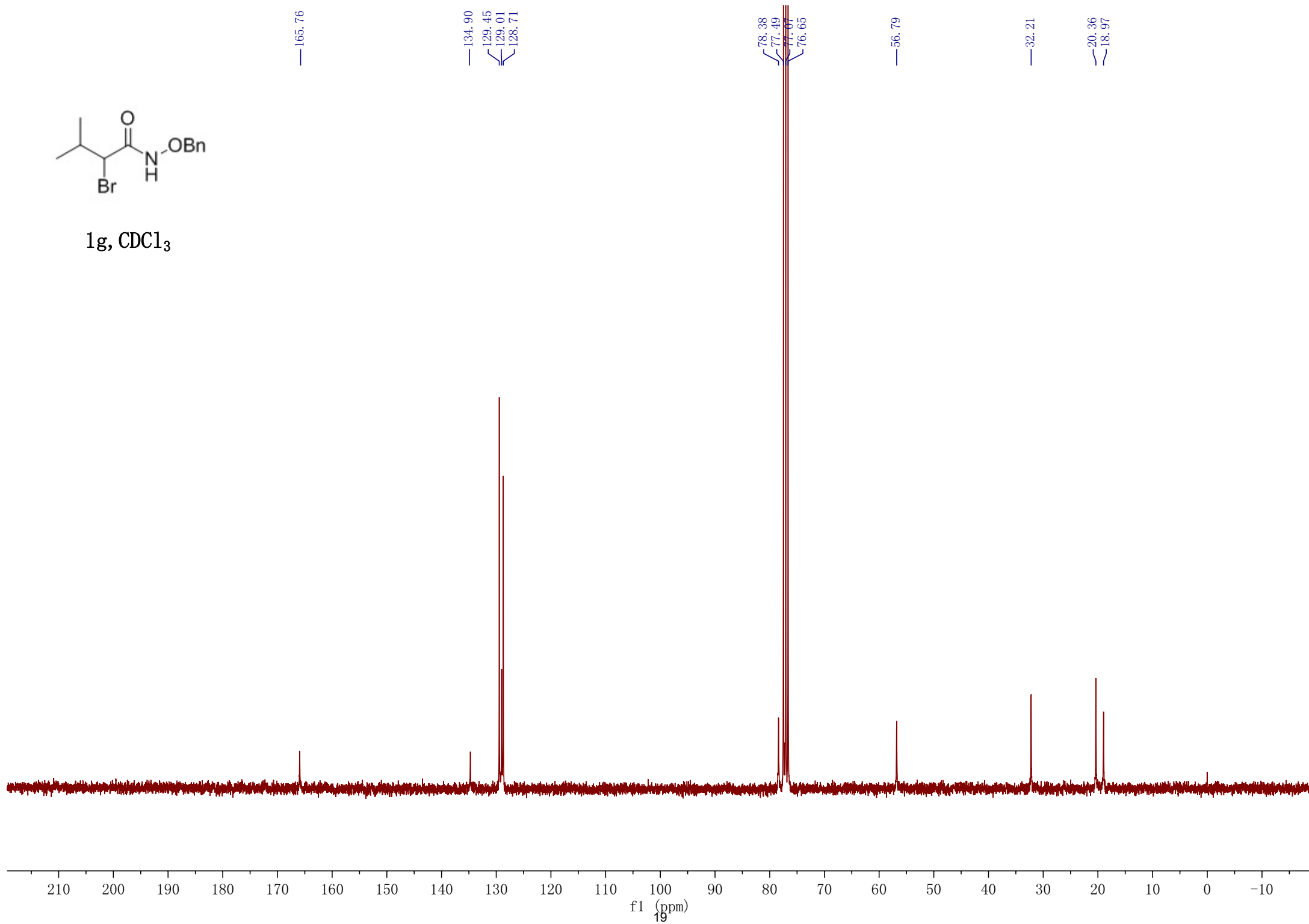


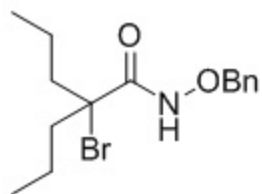
1g, CDCl₃



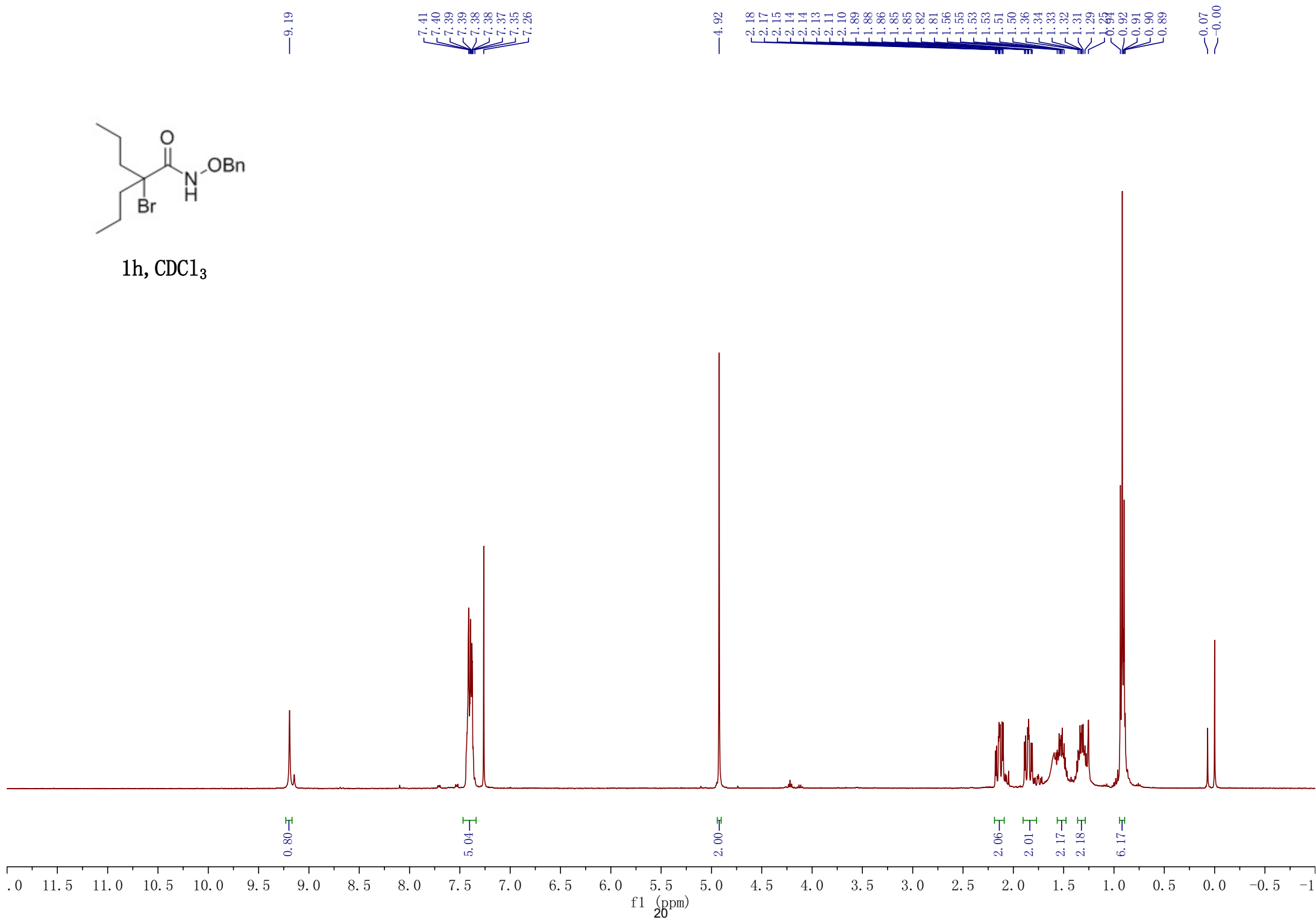


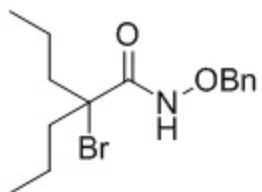
1g, CDCl₃



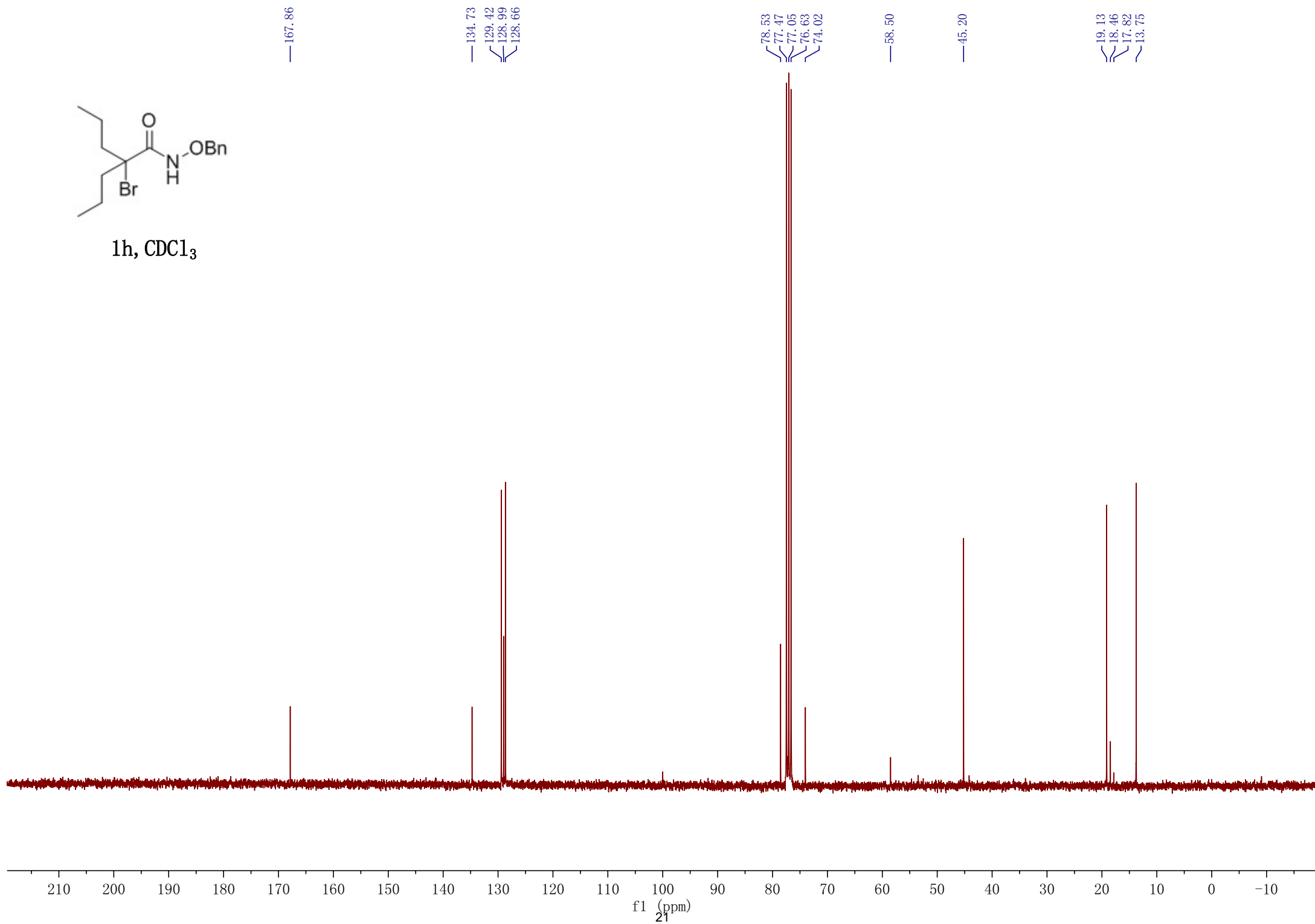


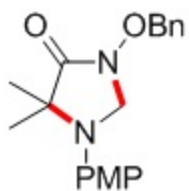
1h, CDCl₃



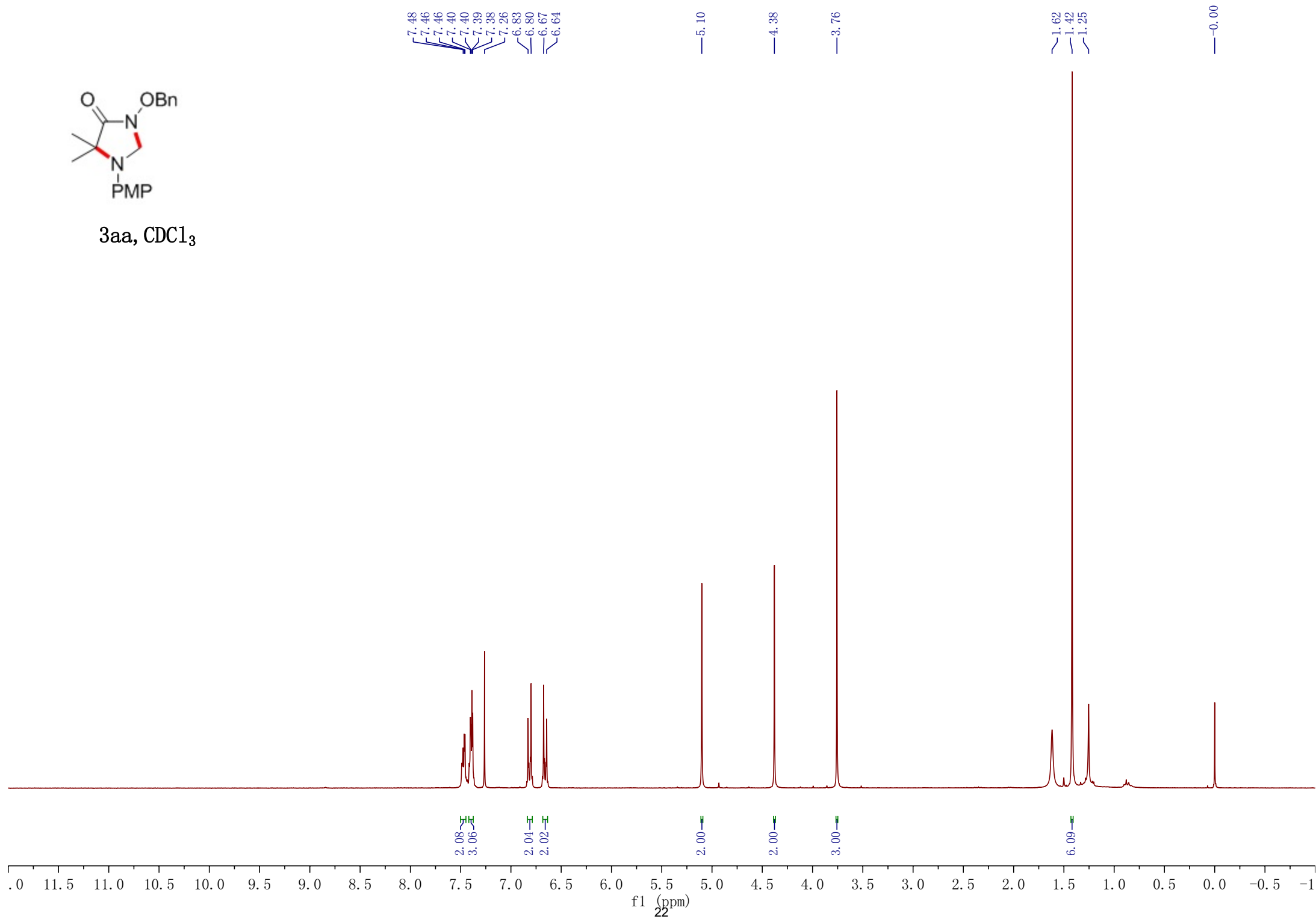


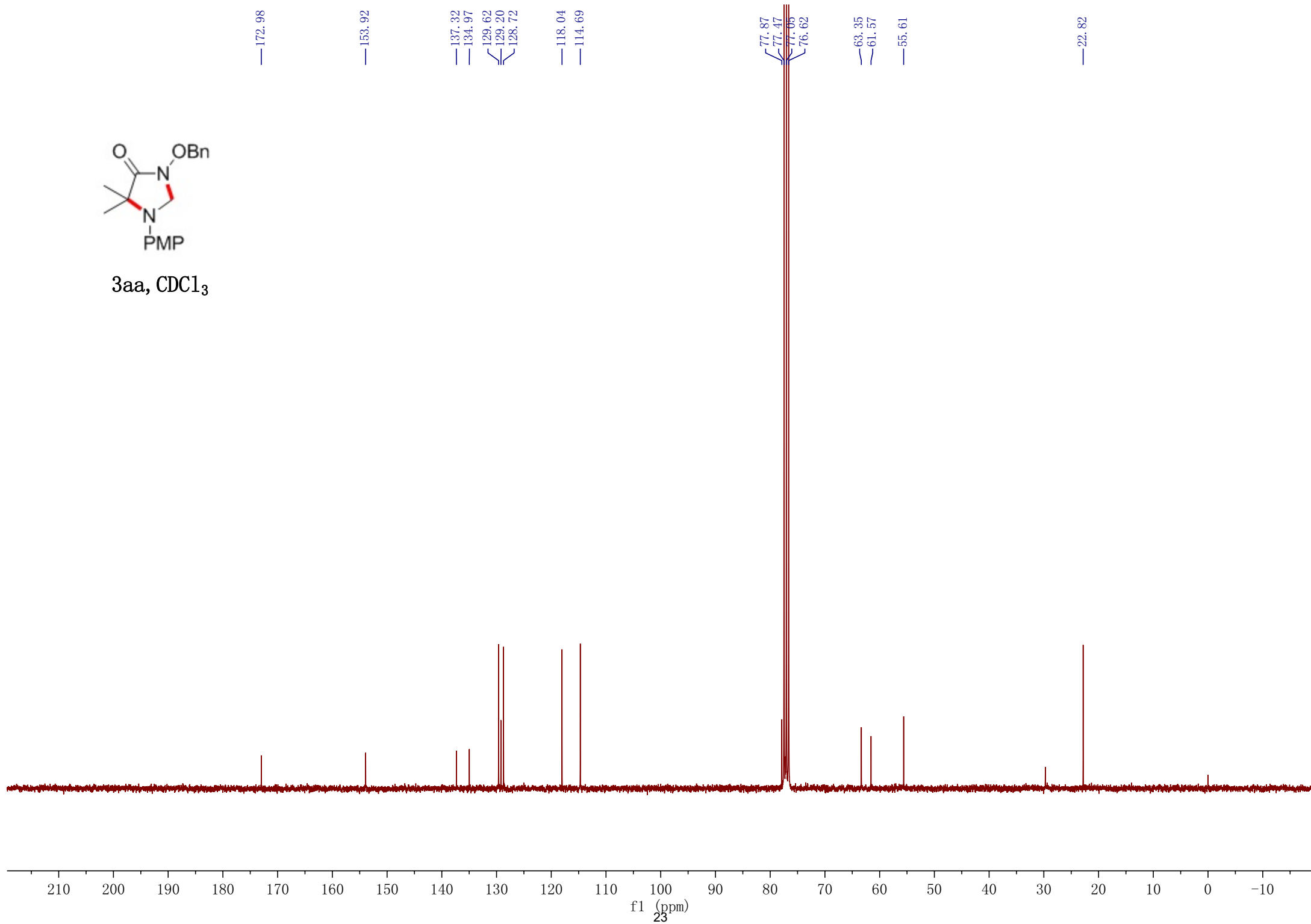
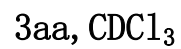
1h, CDCl₃

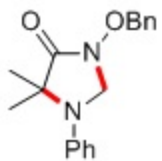




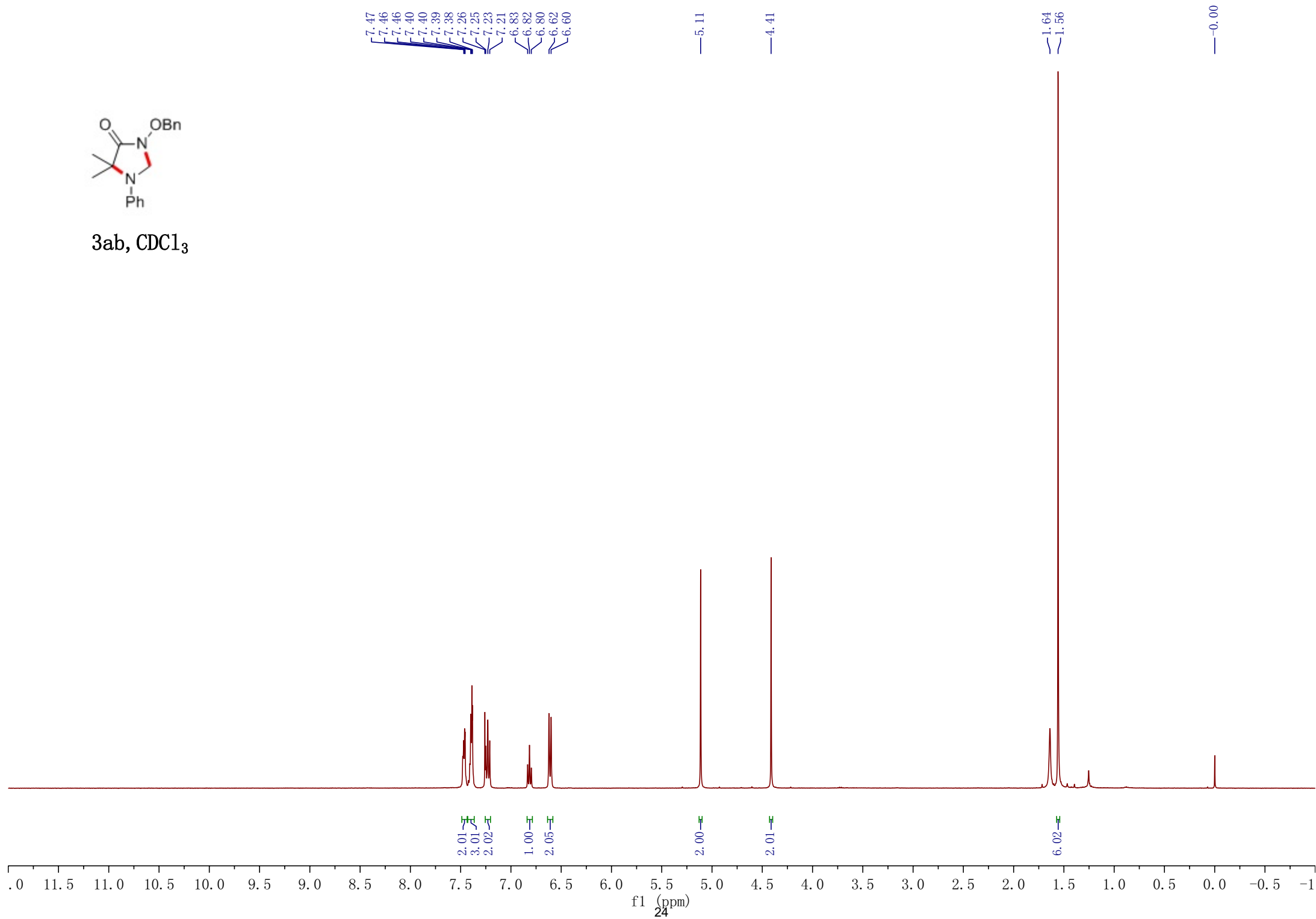
3aa, CDCl_3

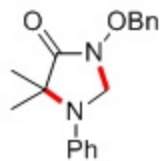




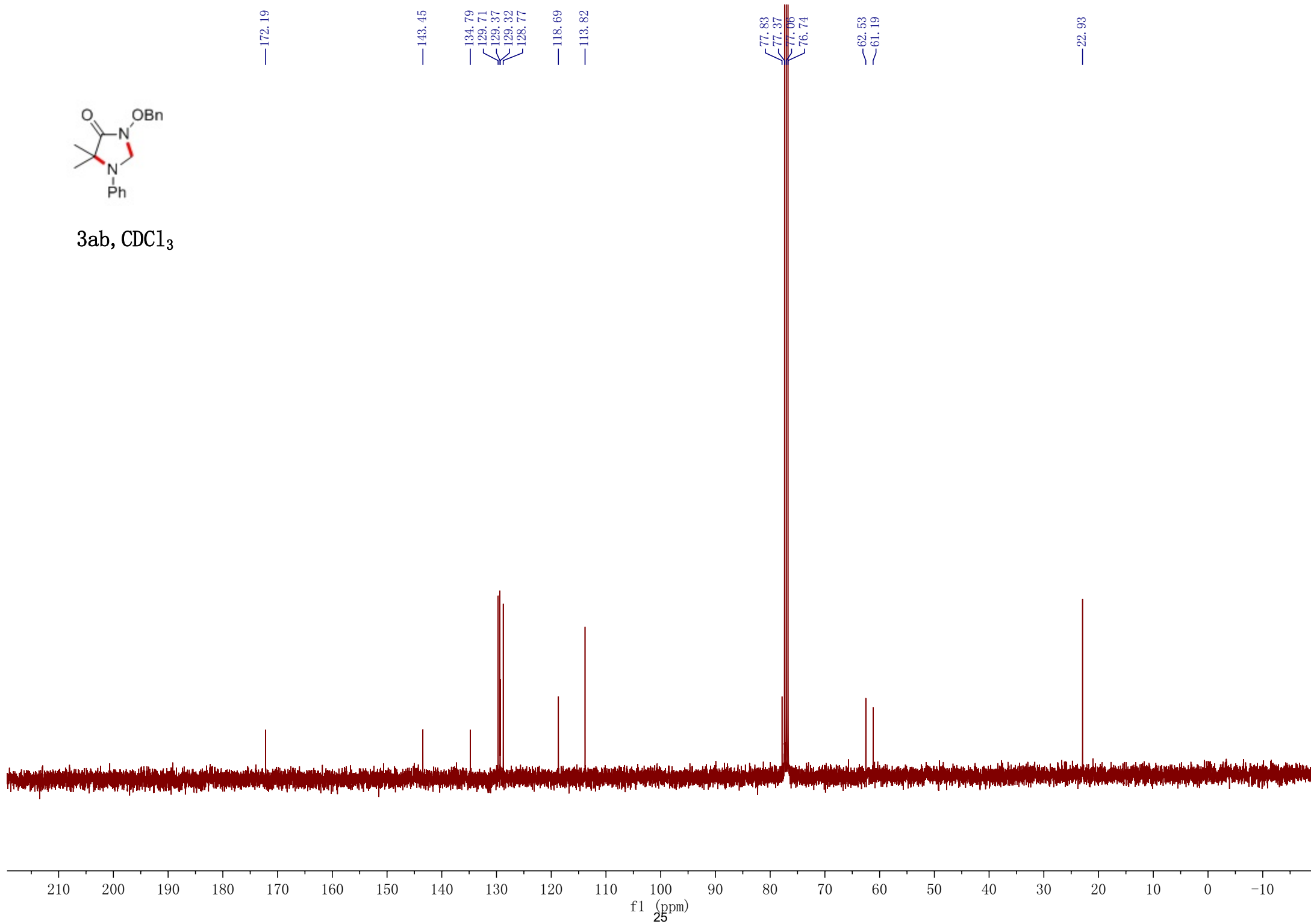


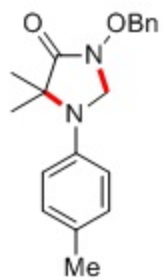
3ab, CDCl_3



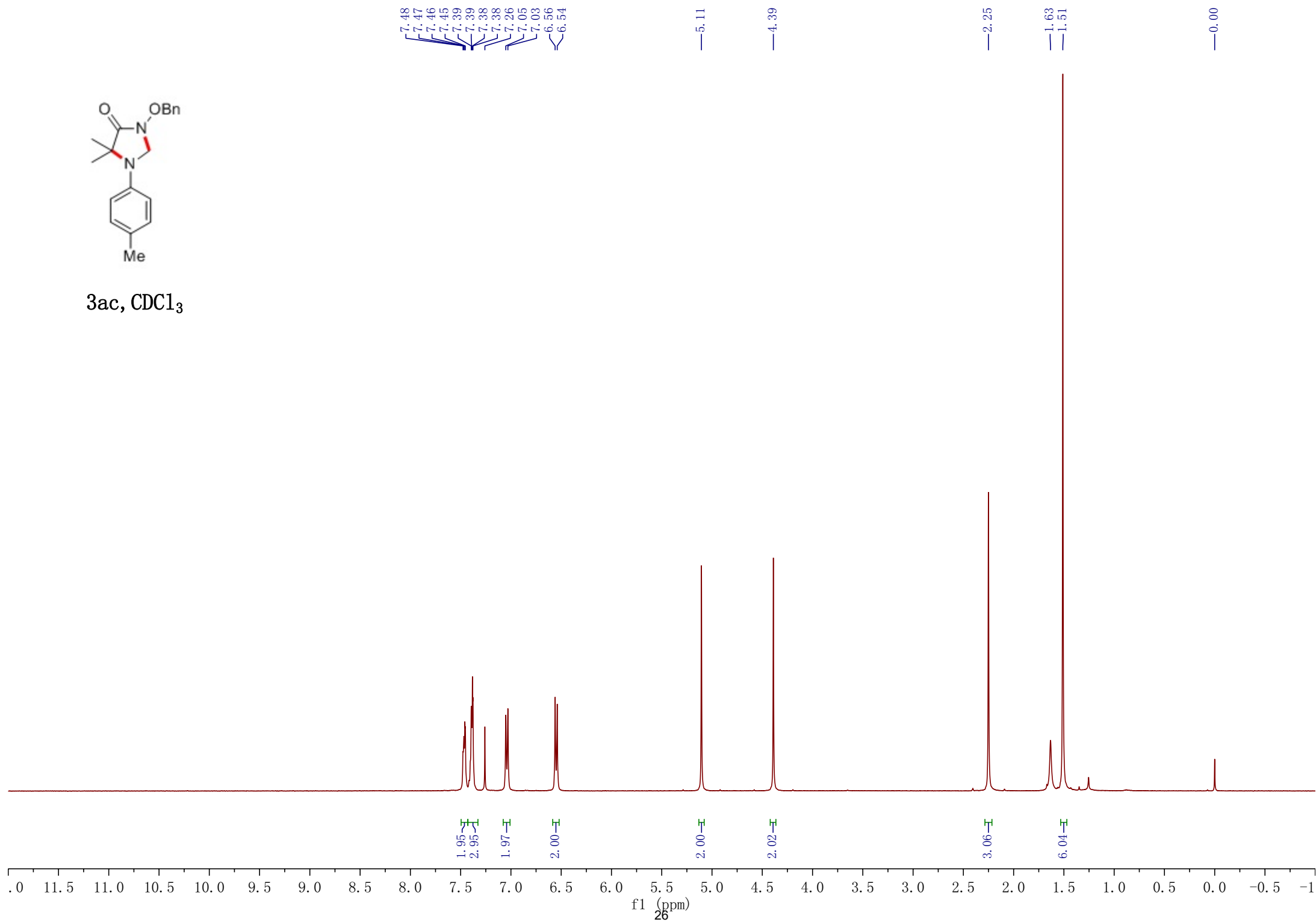


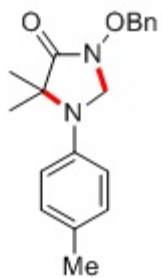
3ab, CDCl₃



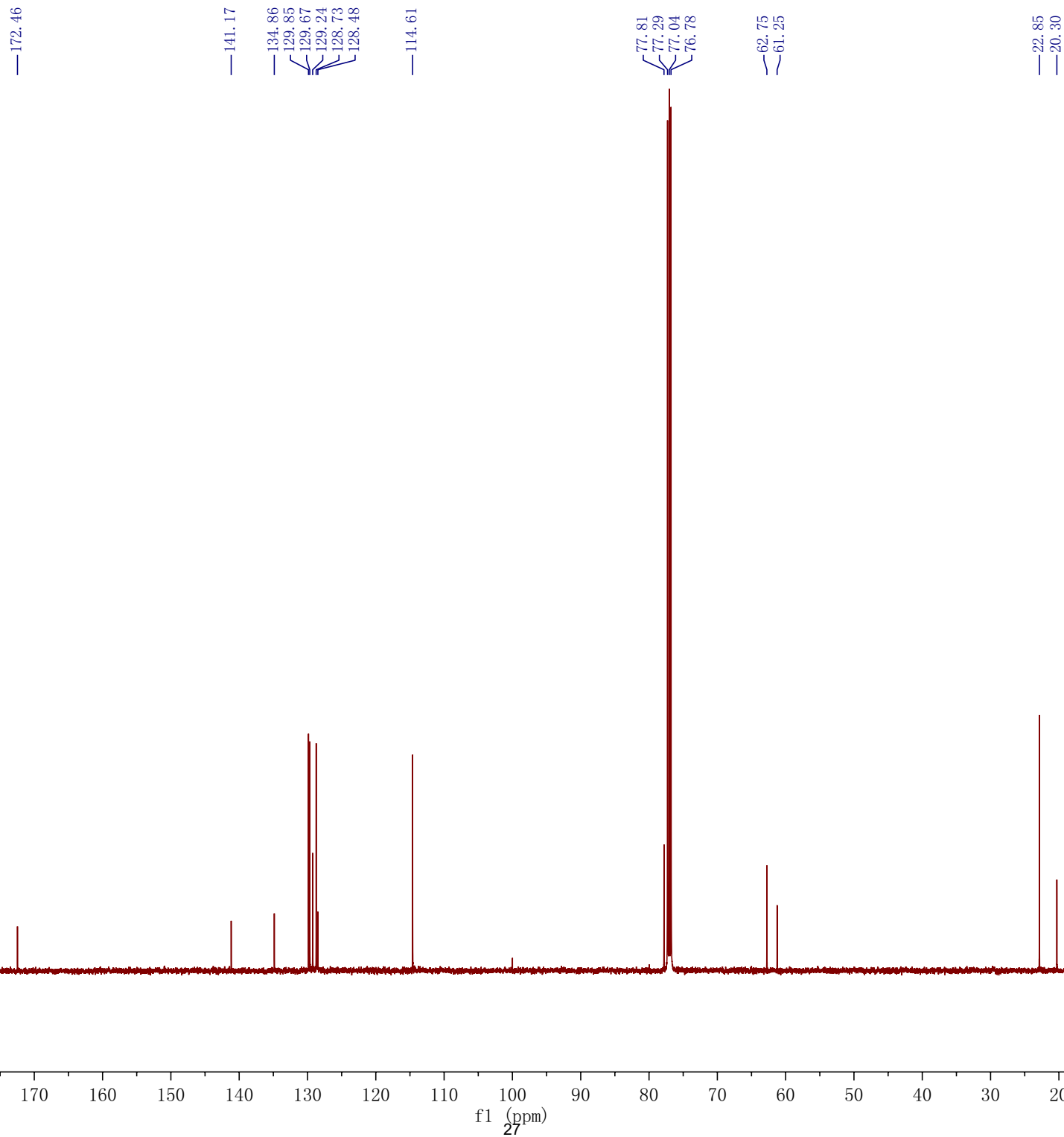


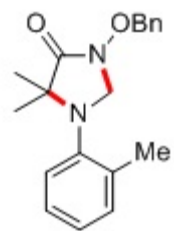
3ac, CDCl_3



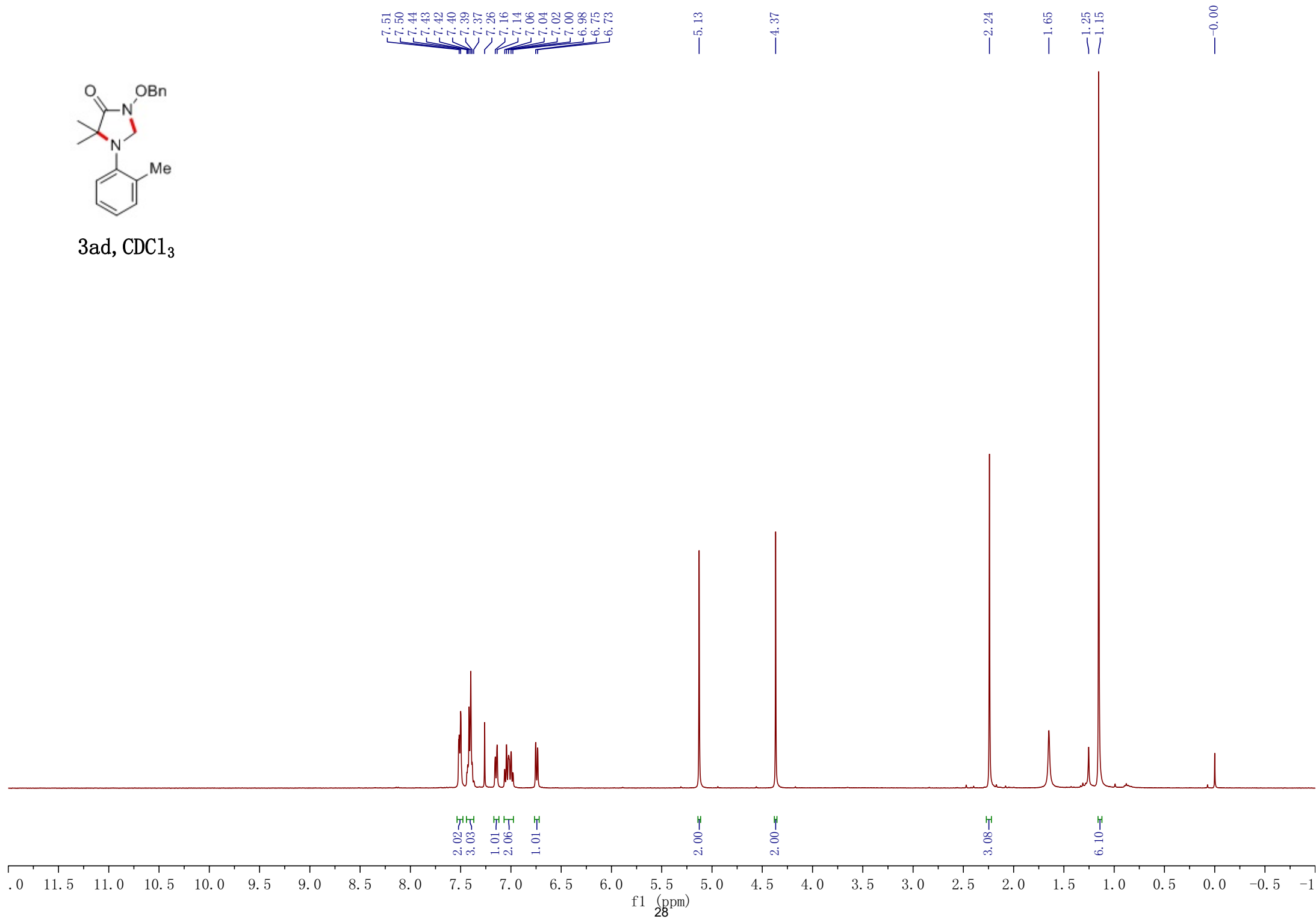


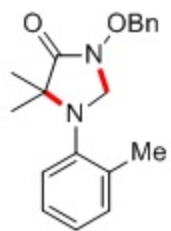
3ac, CDCl₃



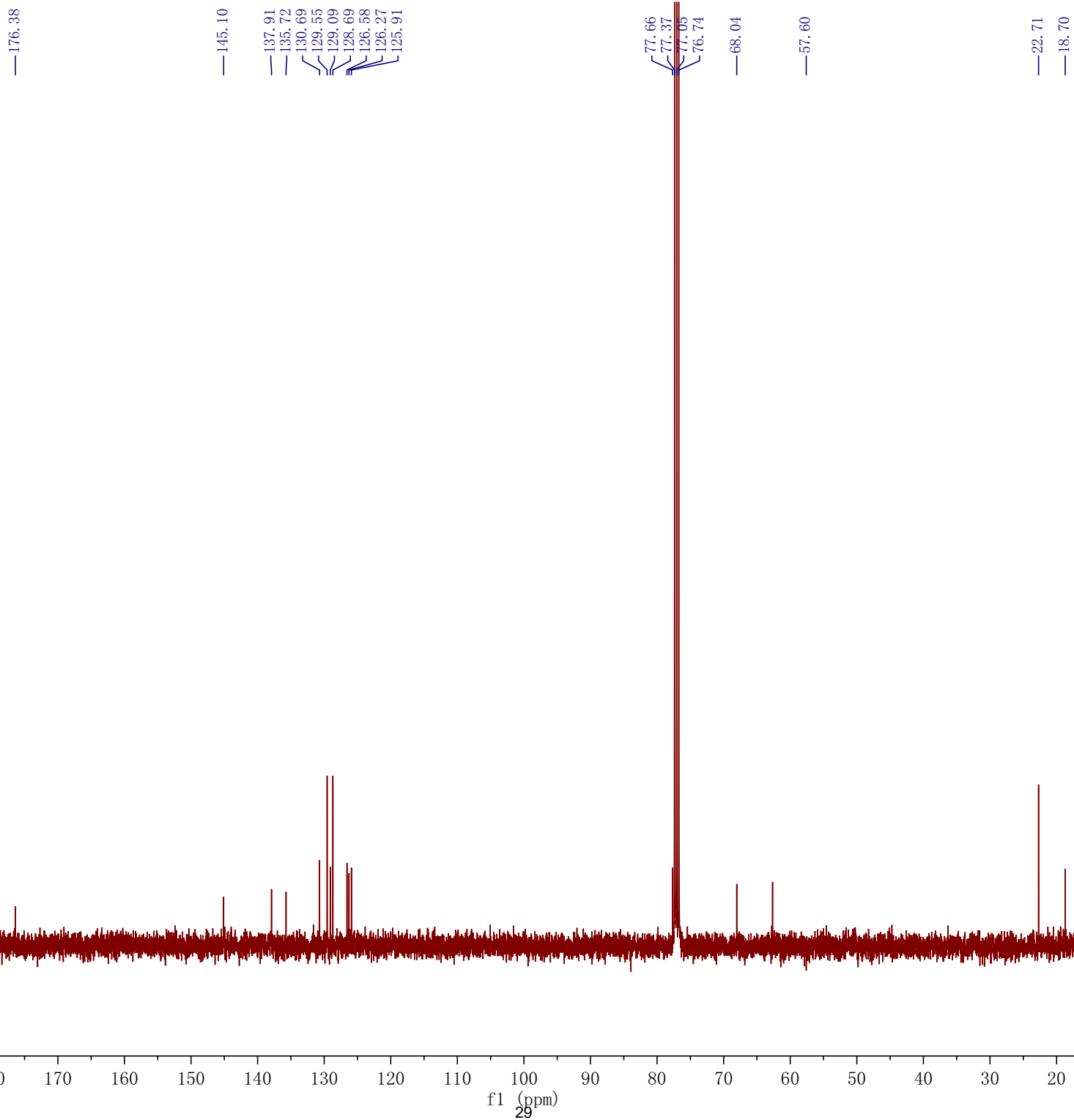


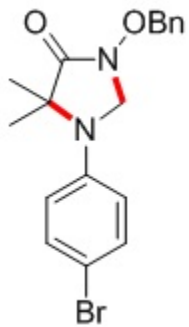
3ad, CDCl₃



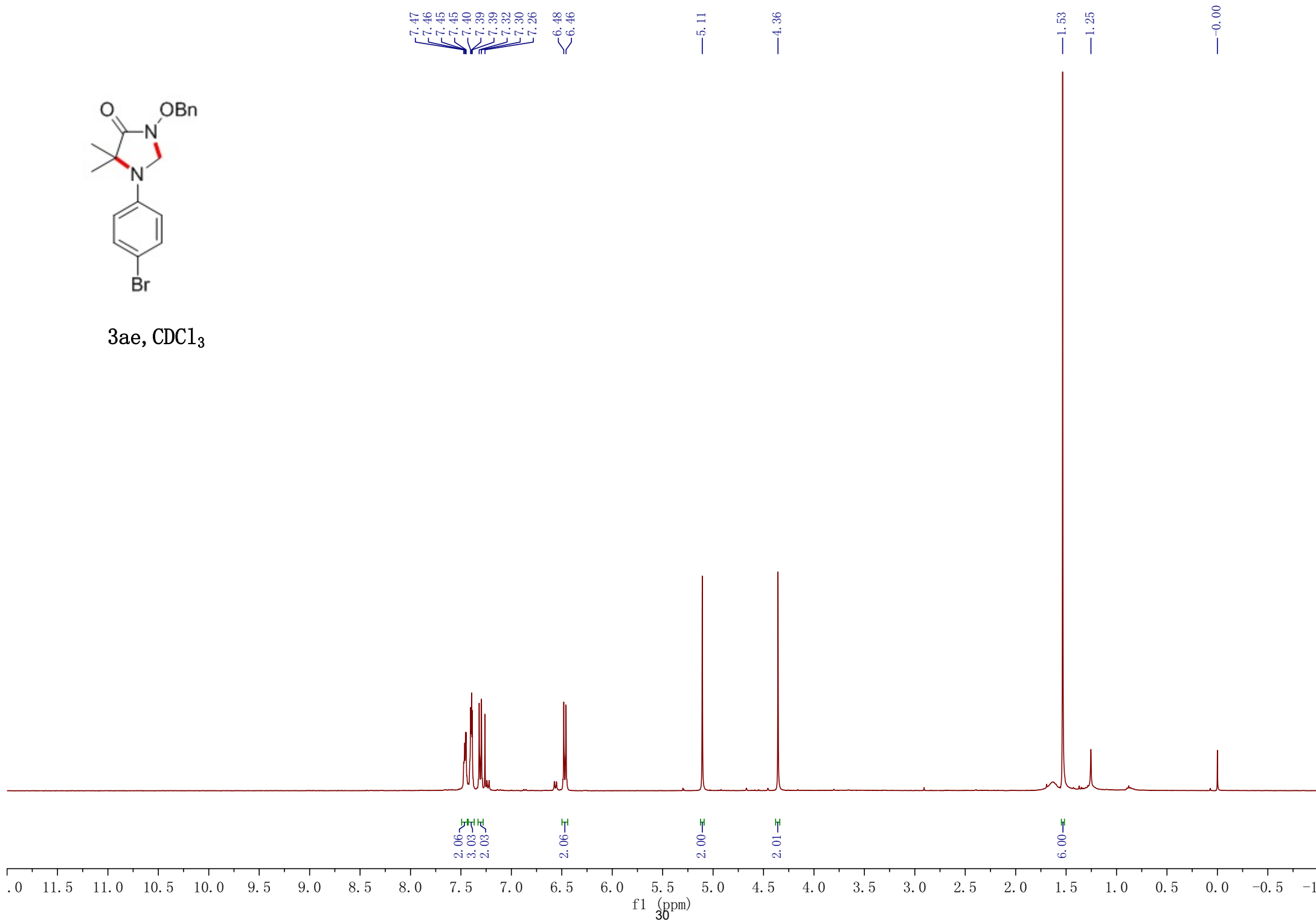


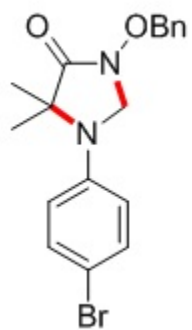
3ad, CDCl_3



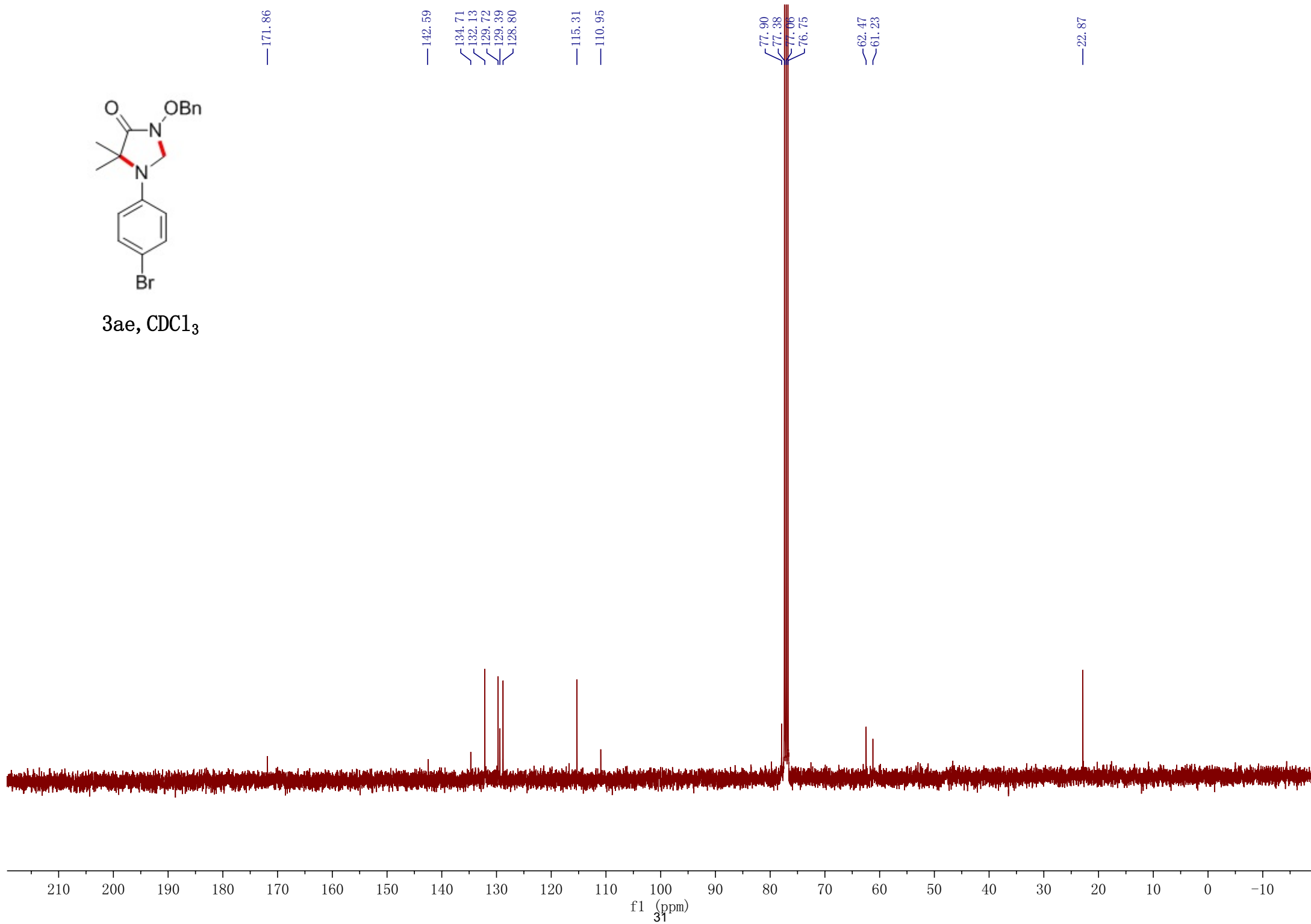


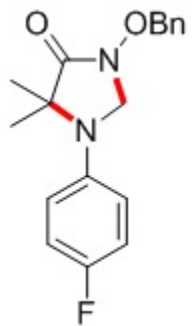
3ae, CDCl₃



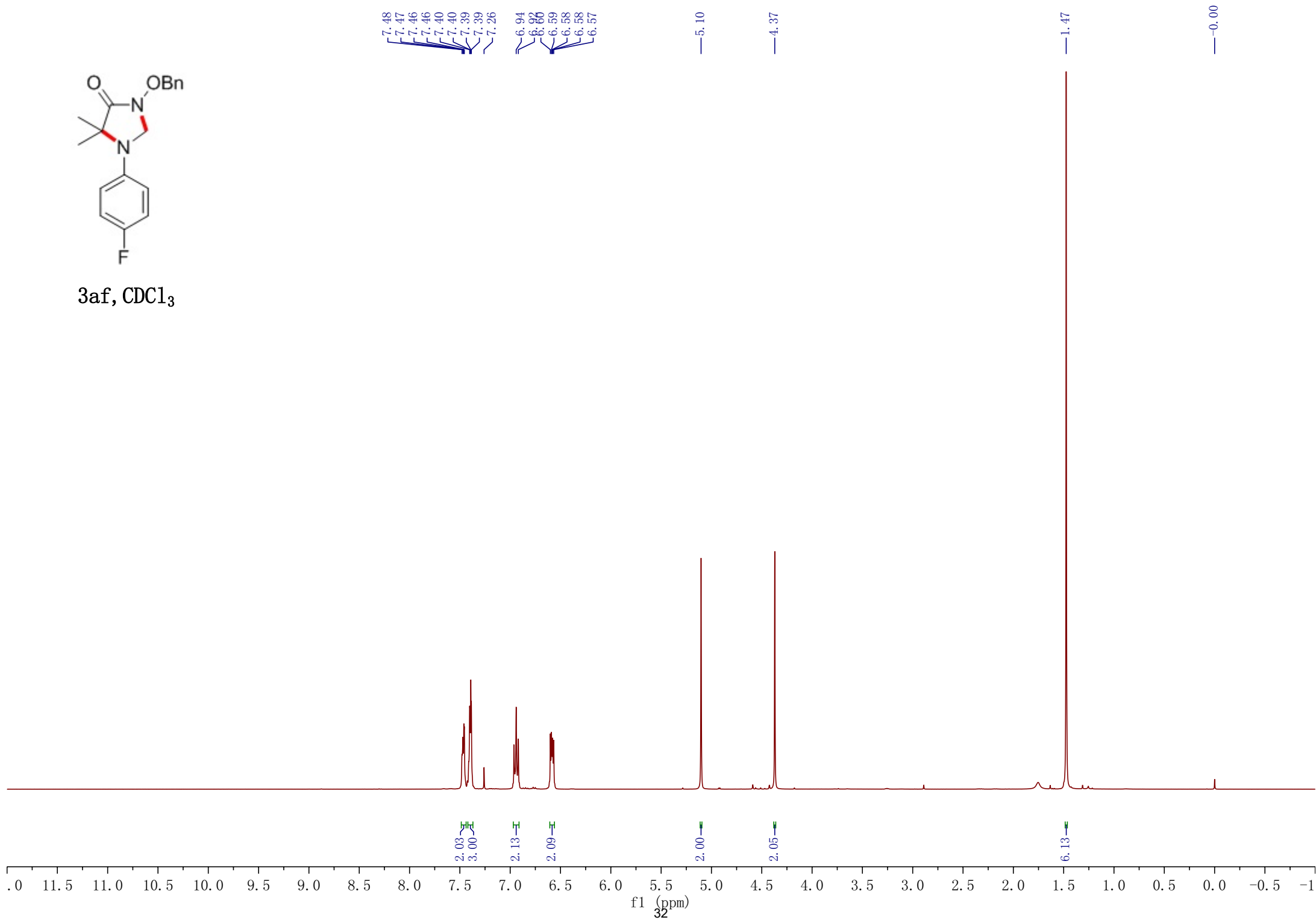


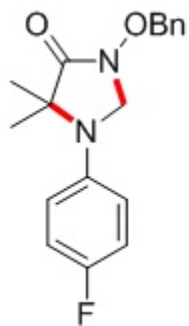
3ae, CDCl_3



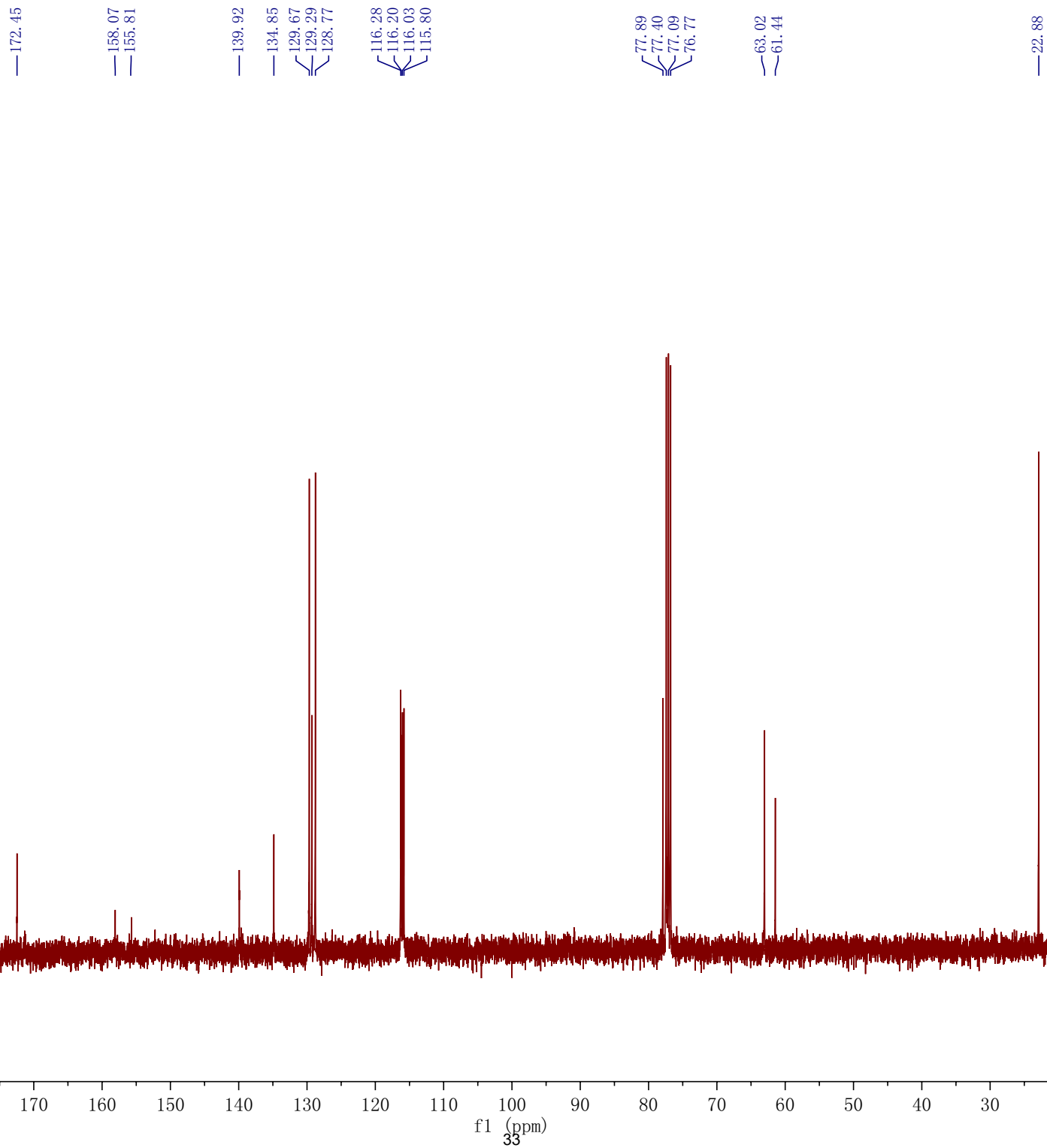


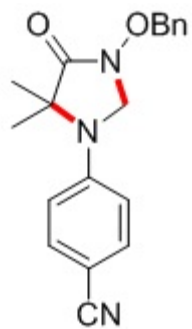
3af, CDCl₃



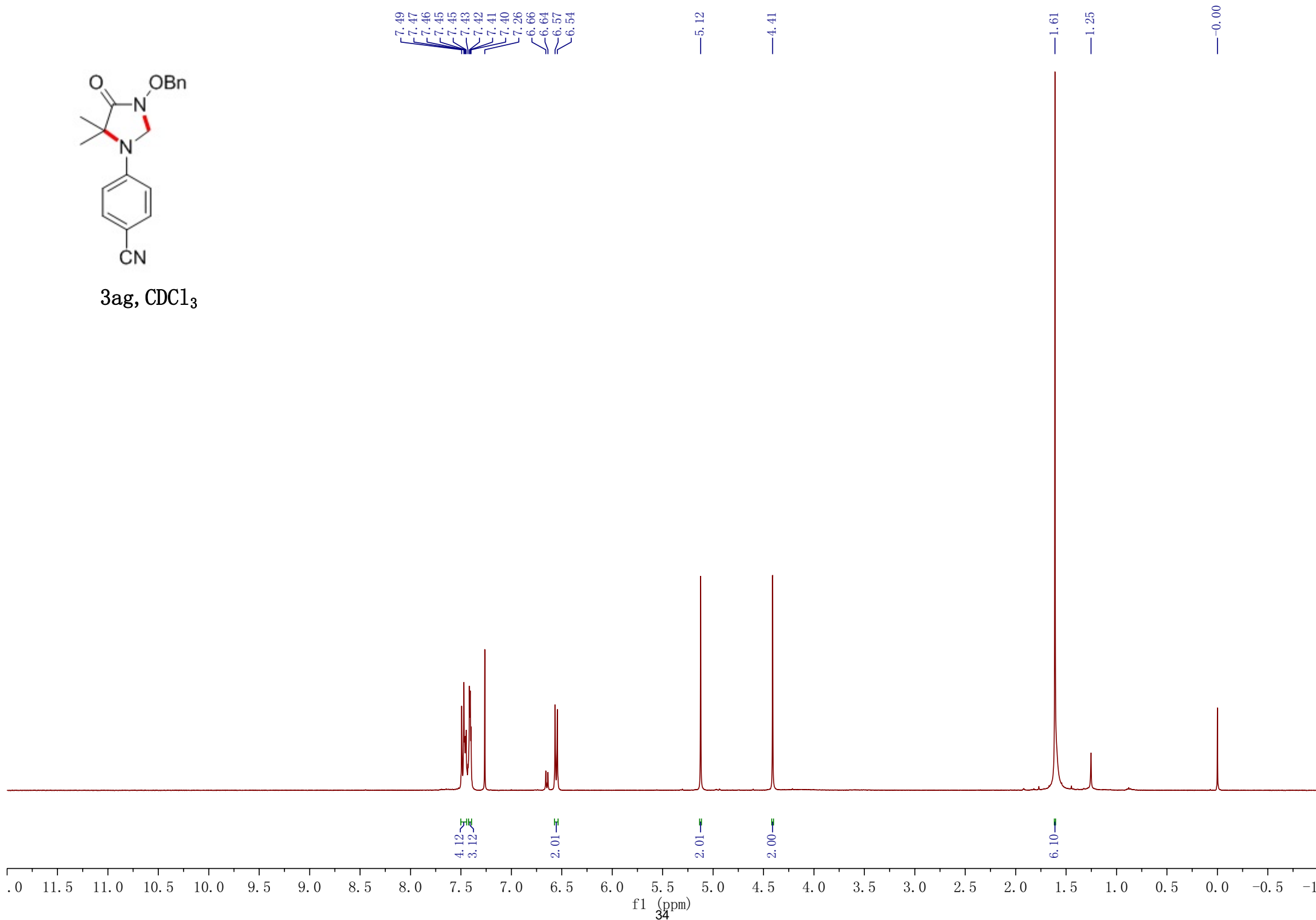


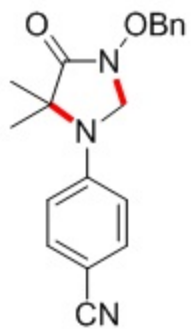
3af, CDCl₃



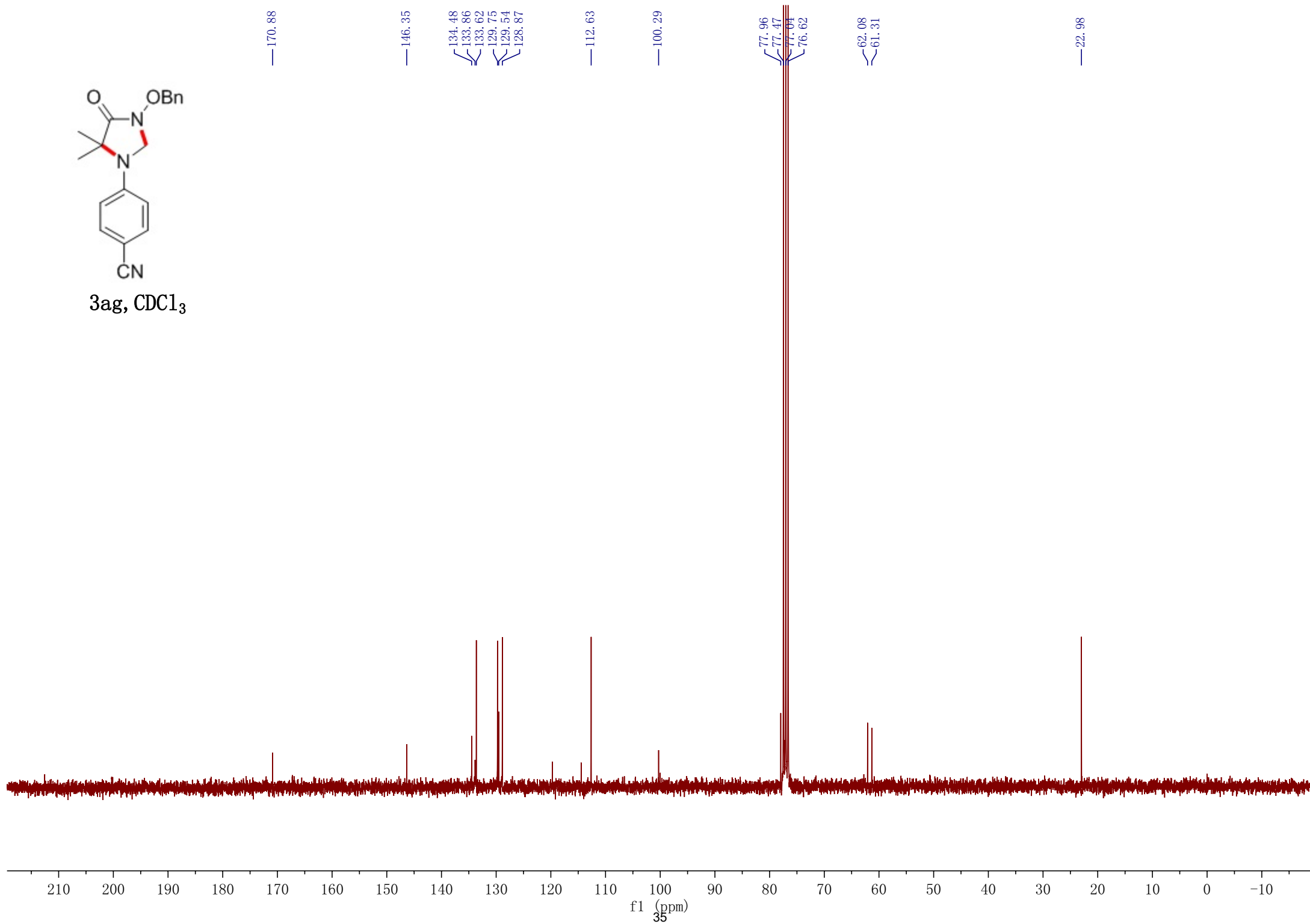


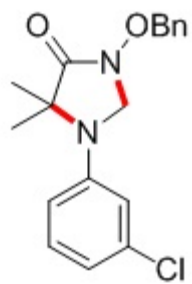
3ag, CDCl₃



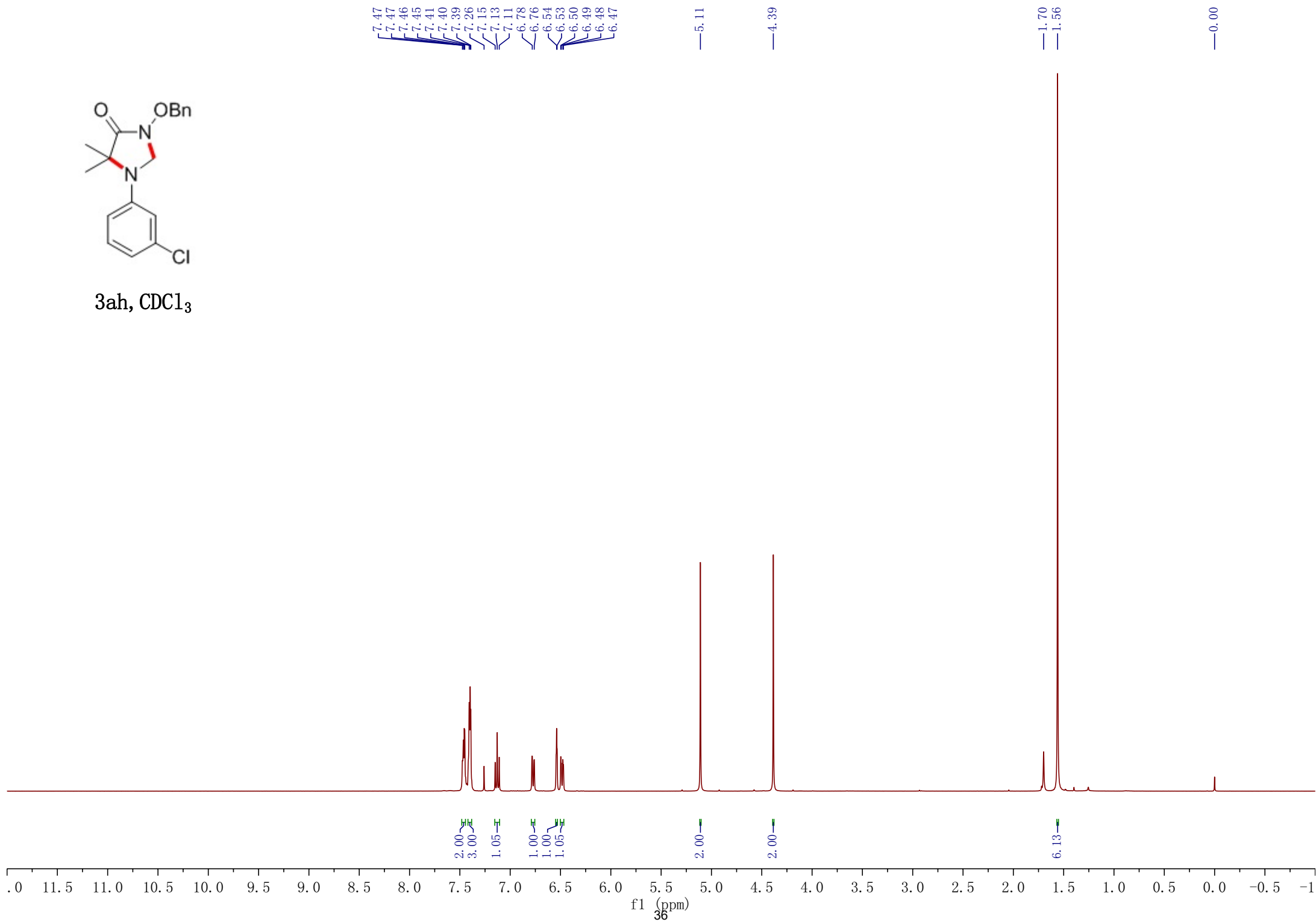


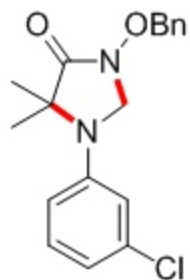
3ag, CDCl₃



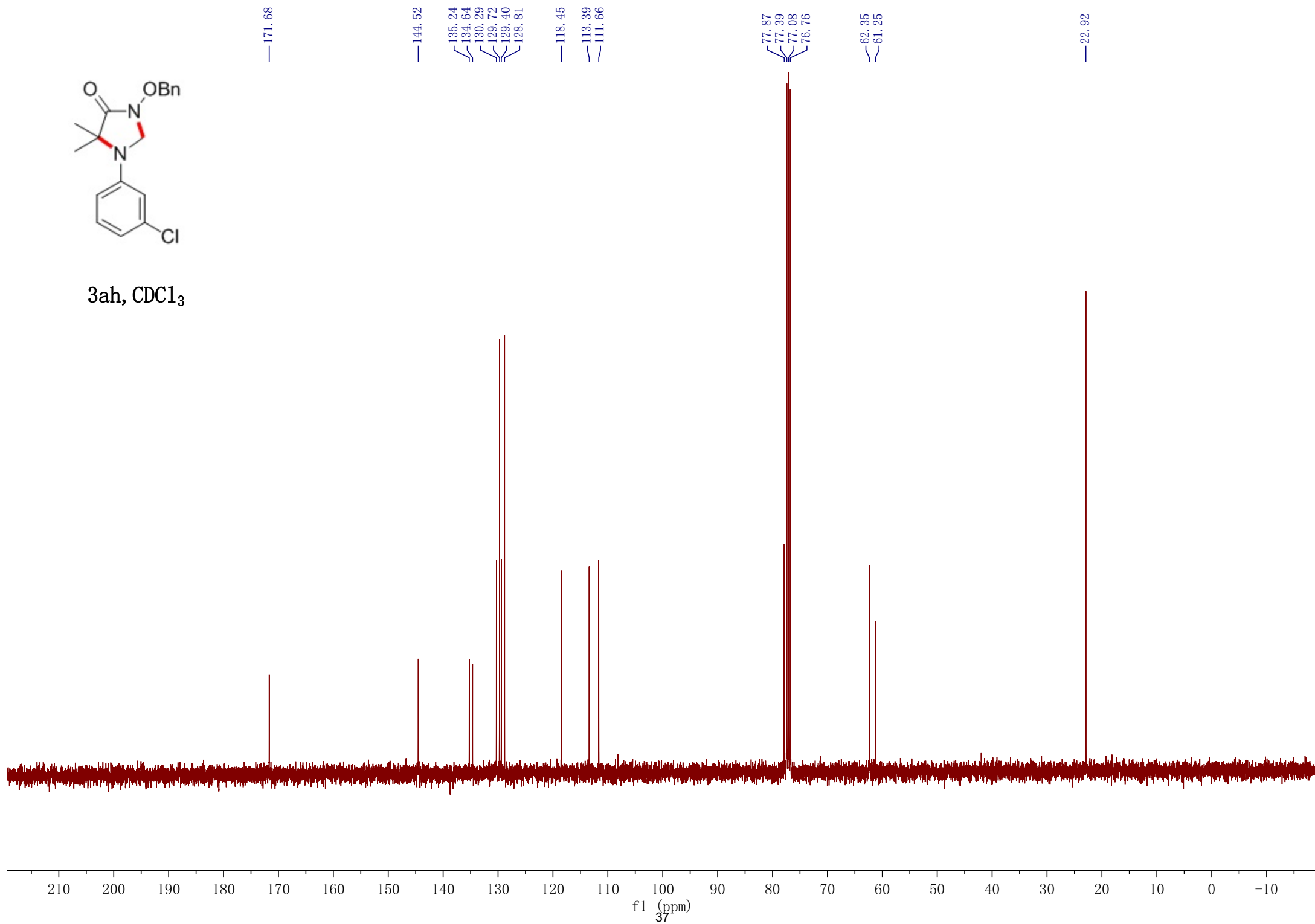


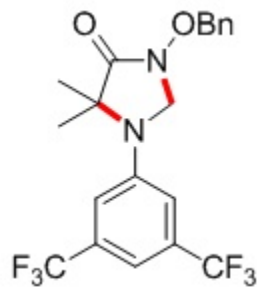
3ah, CDCl_3



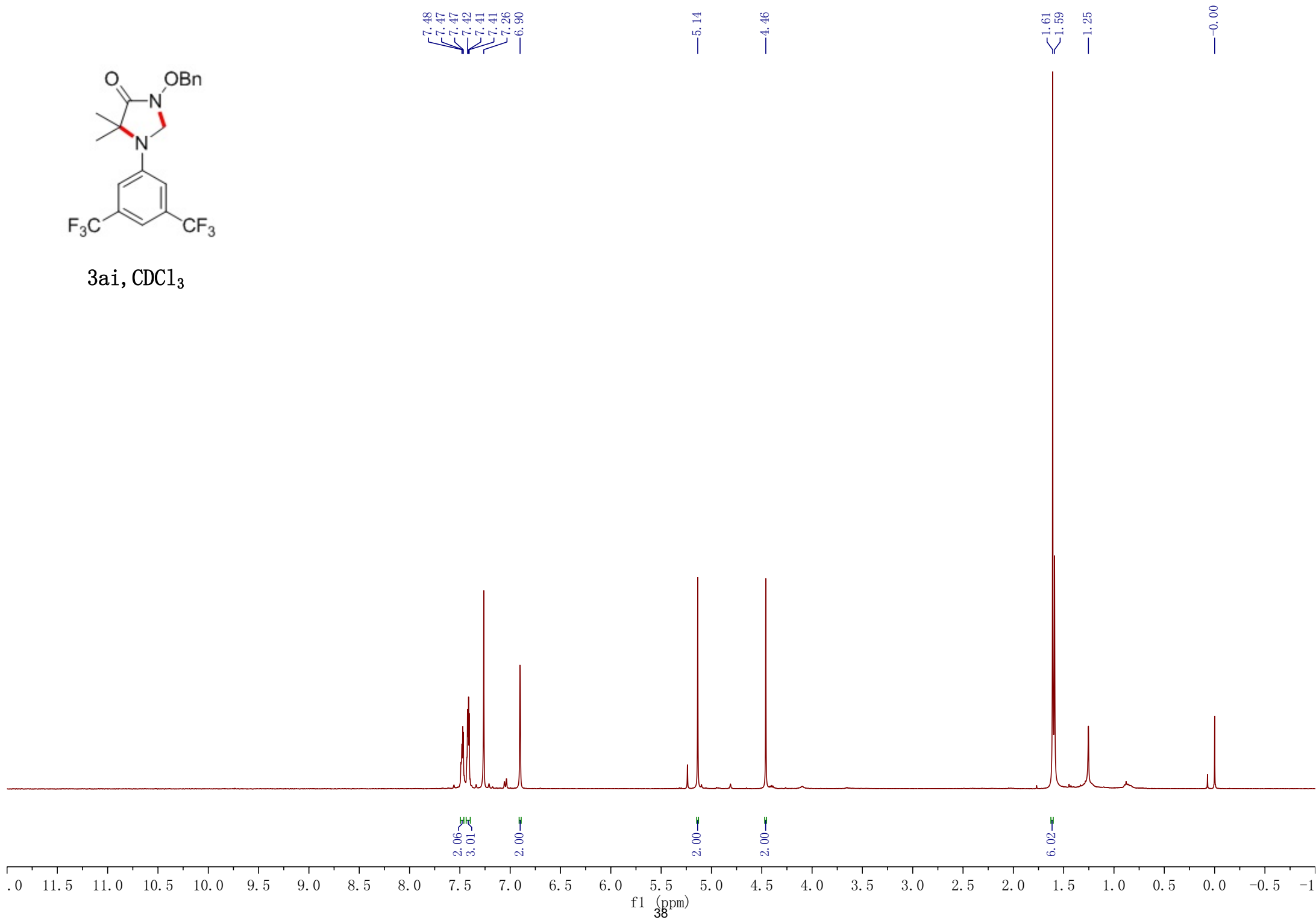


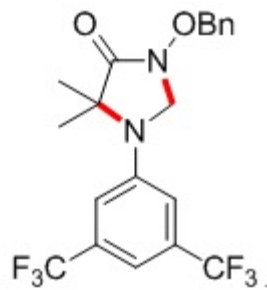
3ah, CDCl_3



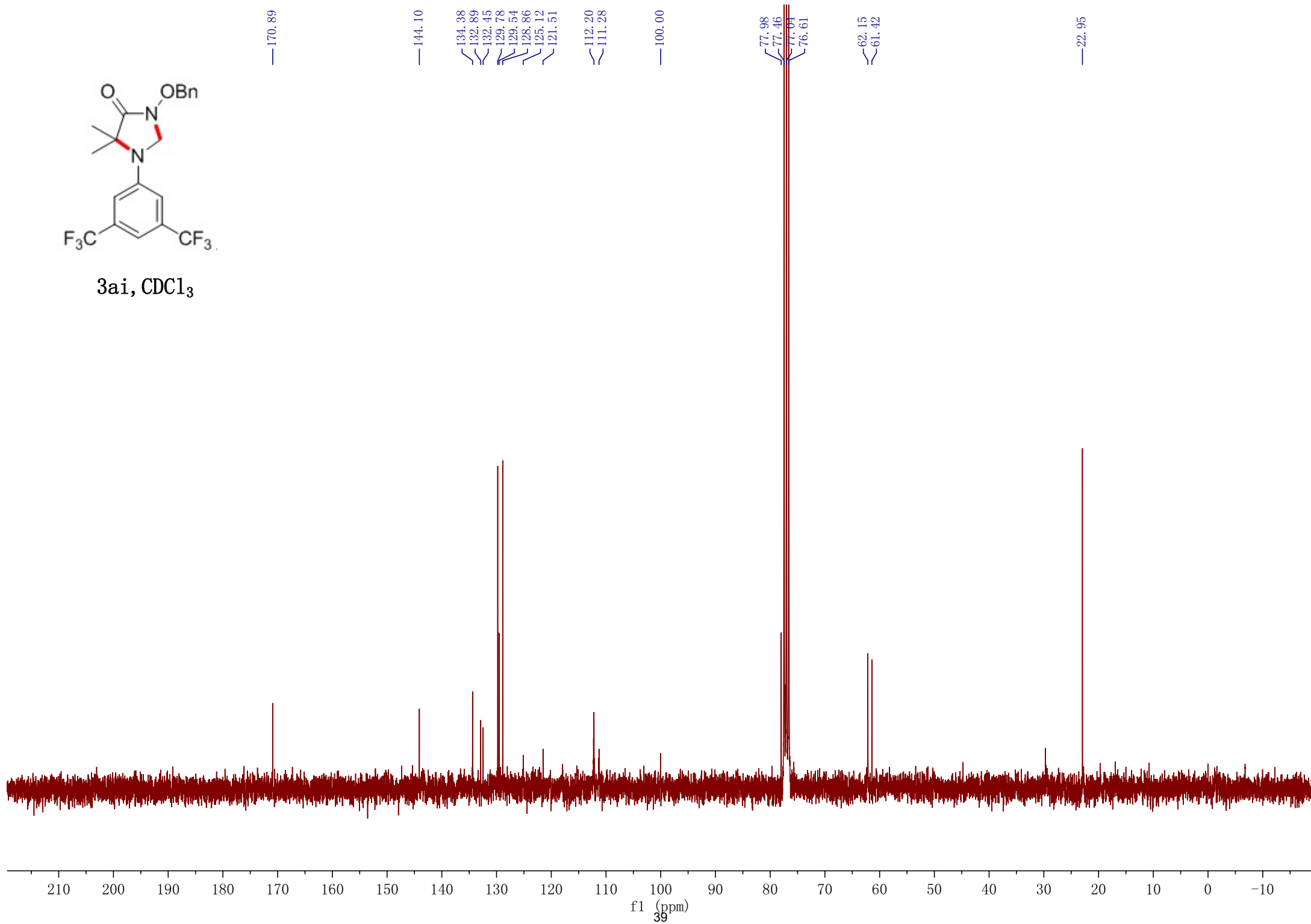


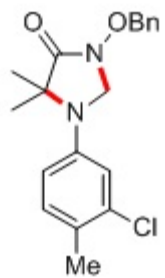
3ai, CDCl₃



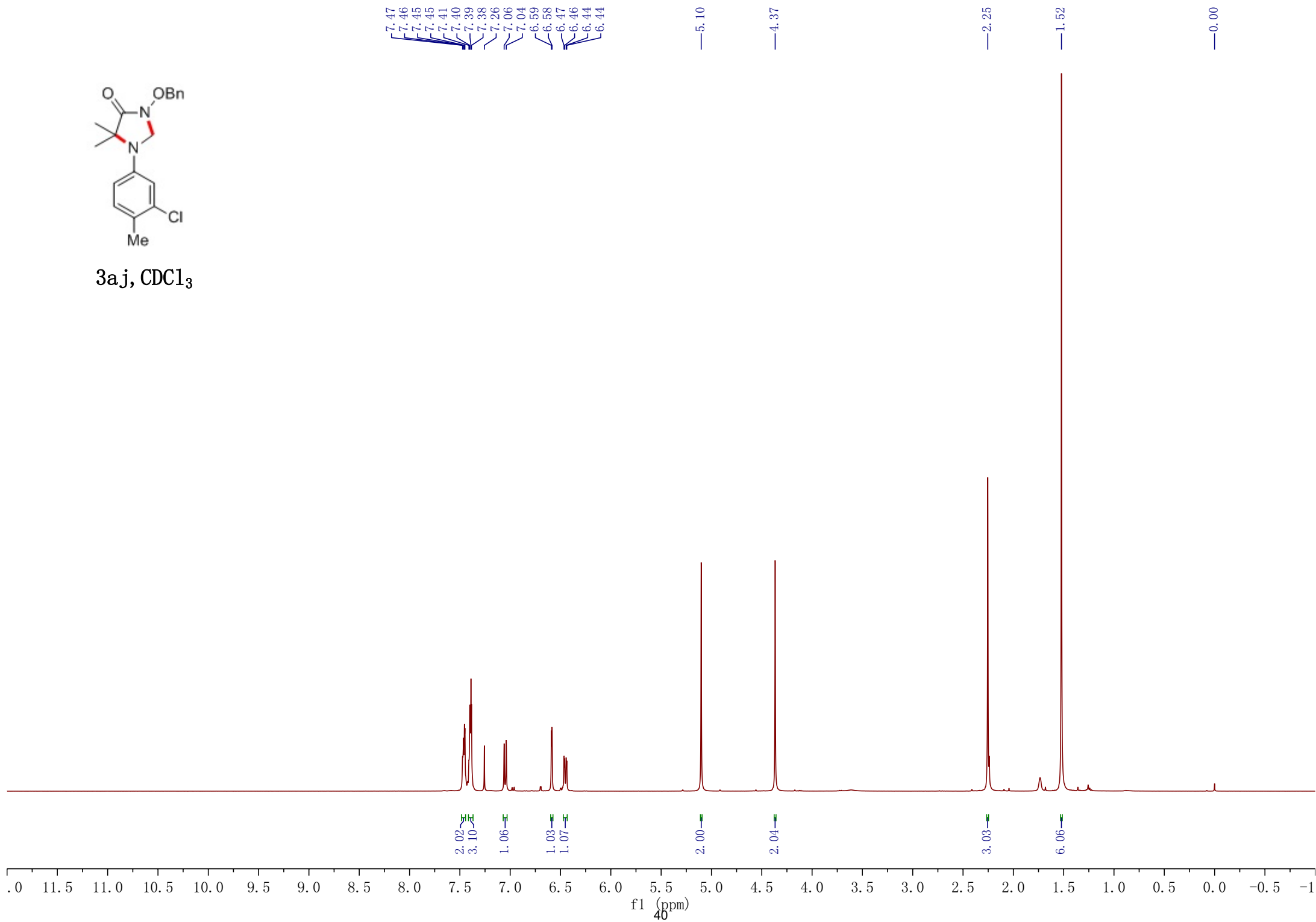


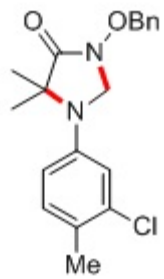
3ai, CDCl₃



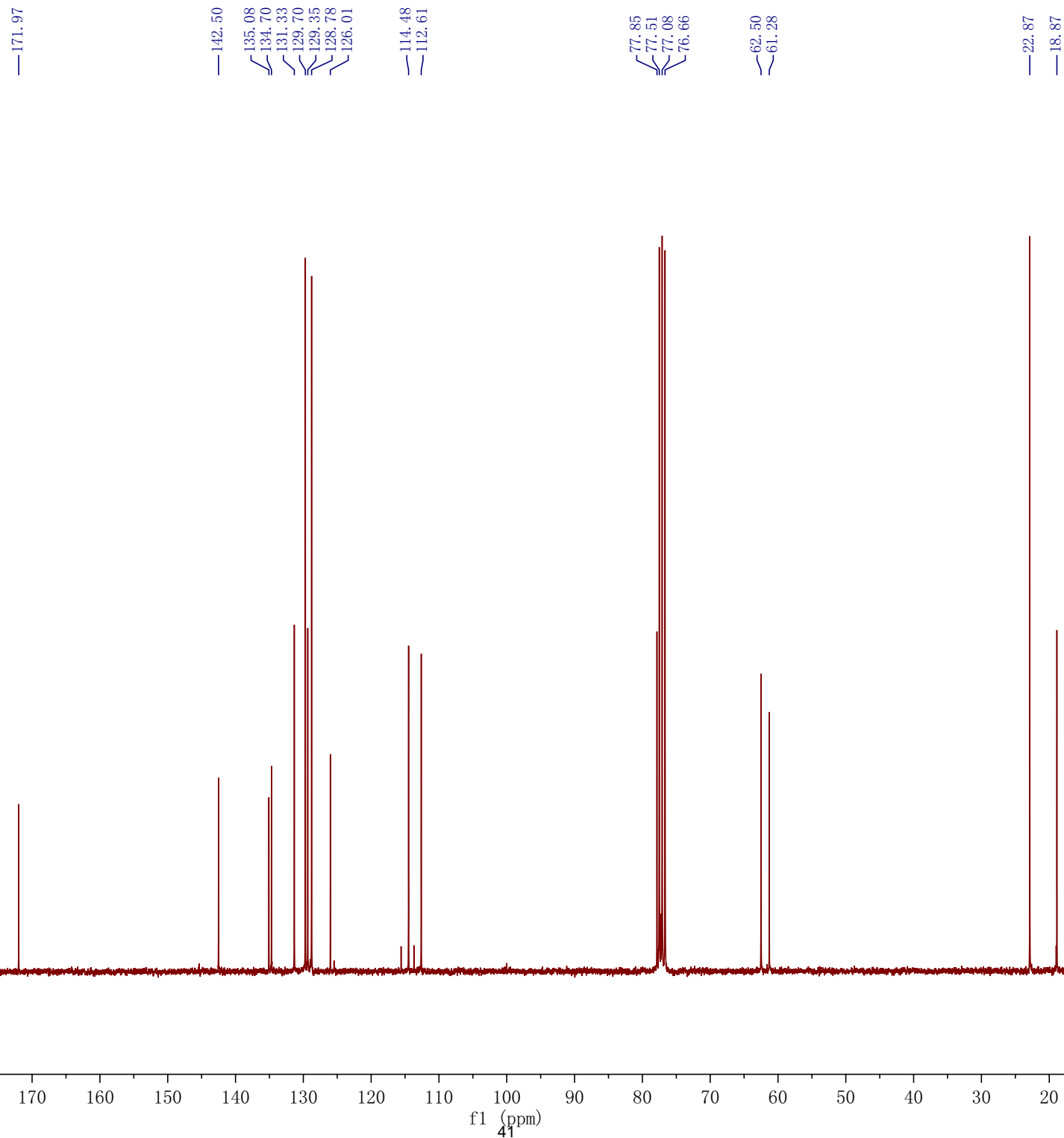


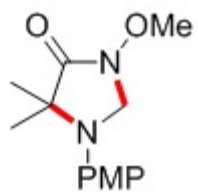
3aj, CDCl₃



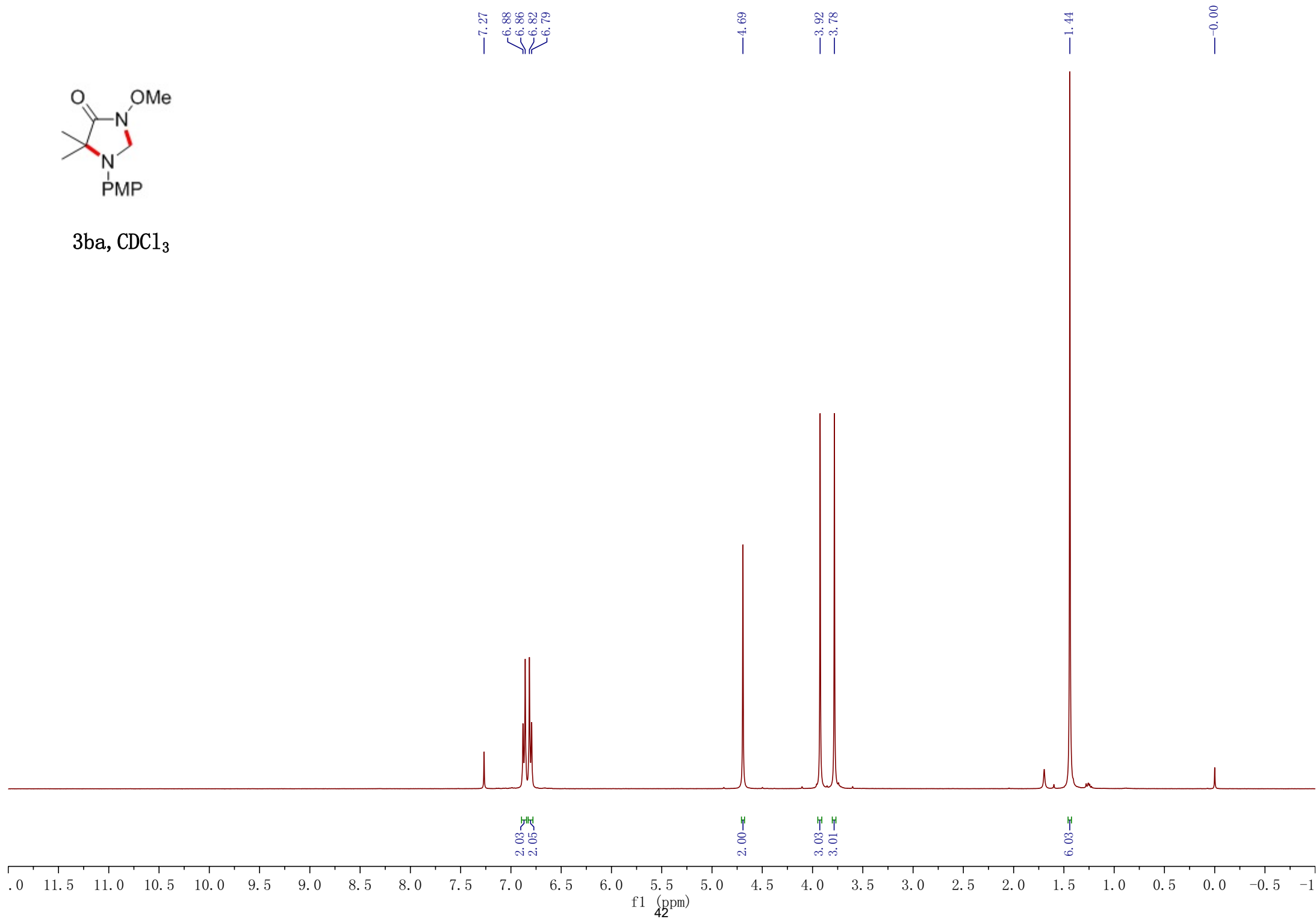


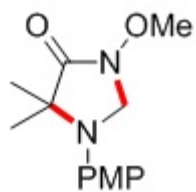
3aj, CDCl₃



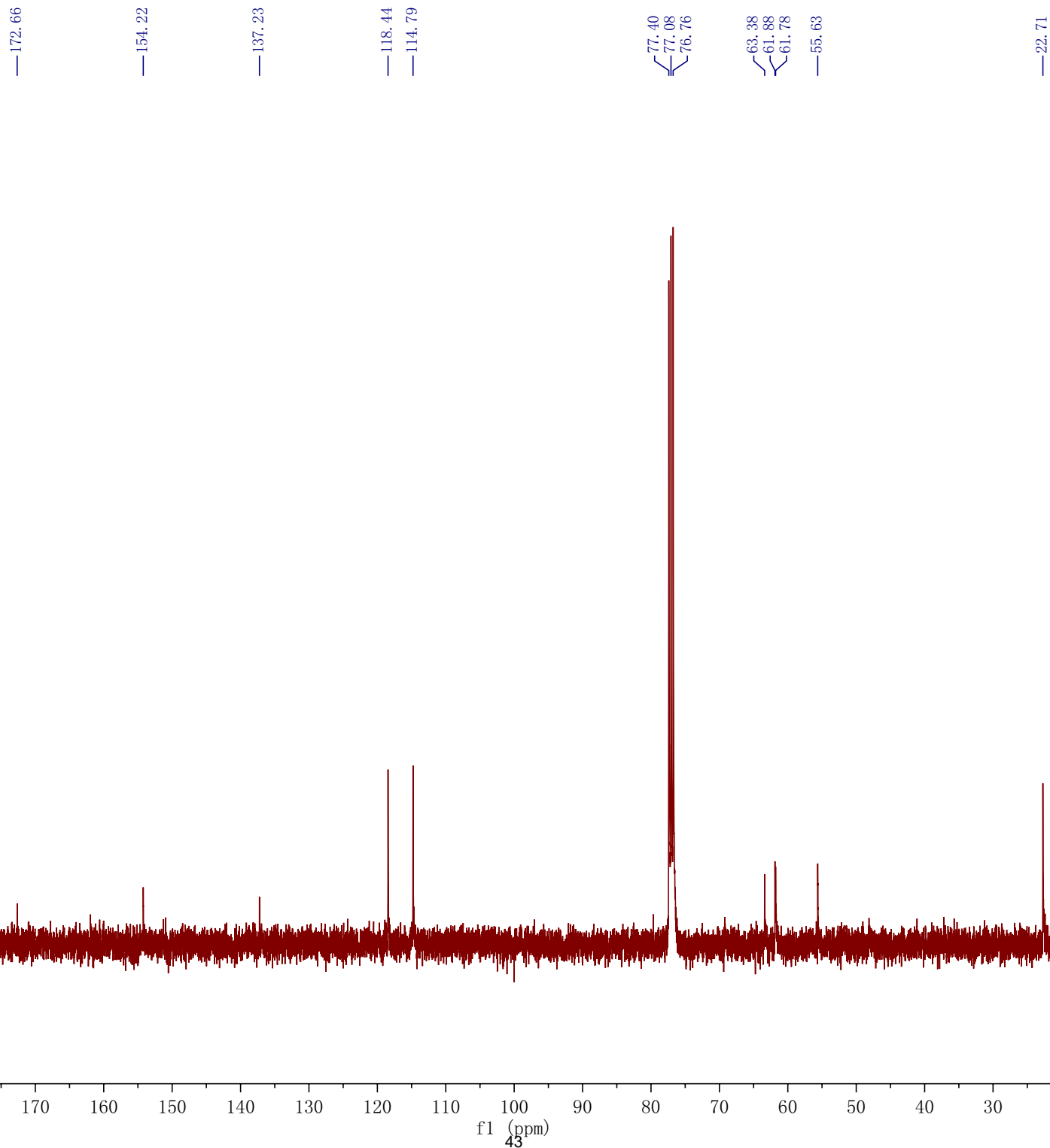


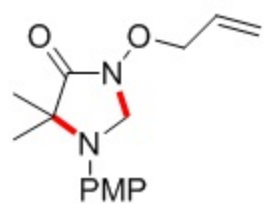
3ba, CDCl_3



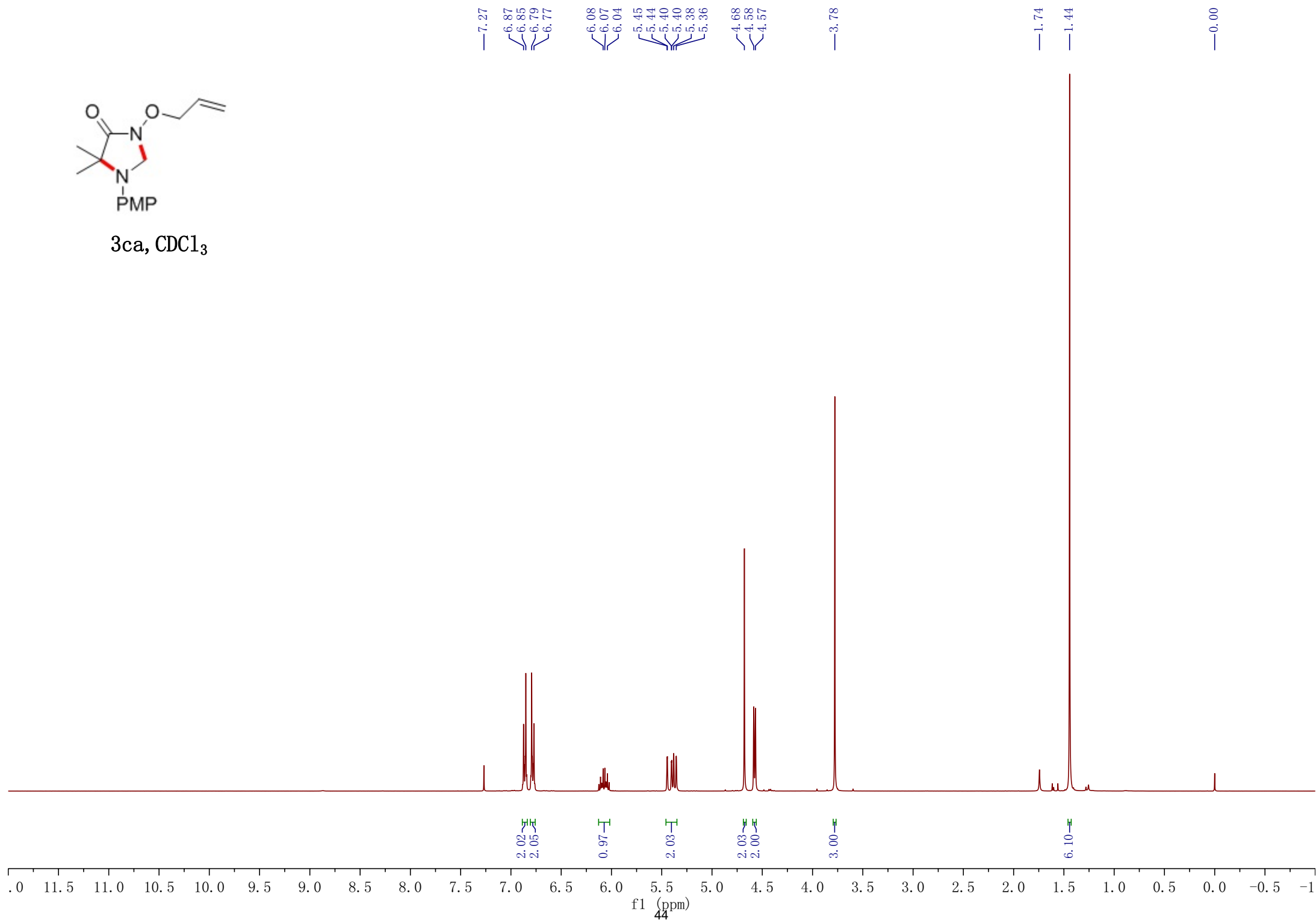


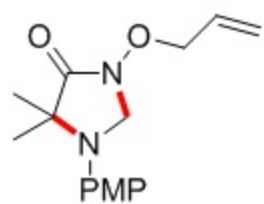
3ba, CDCl₃



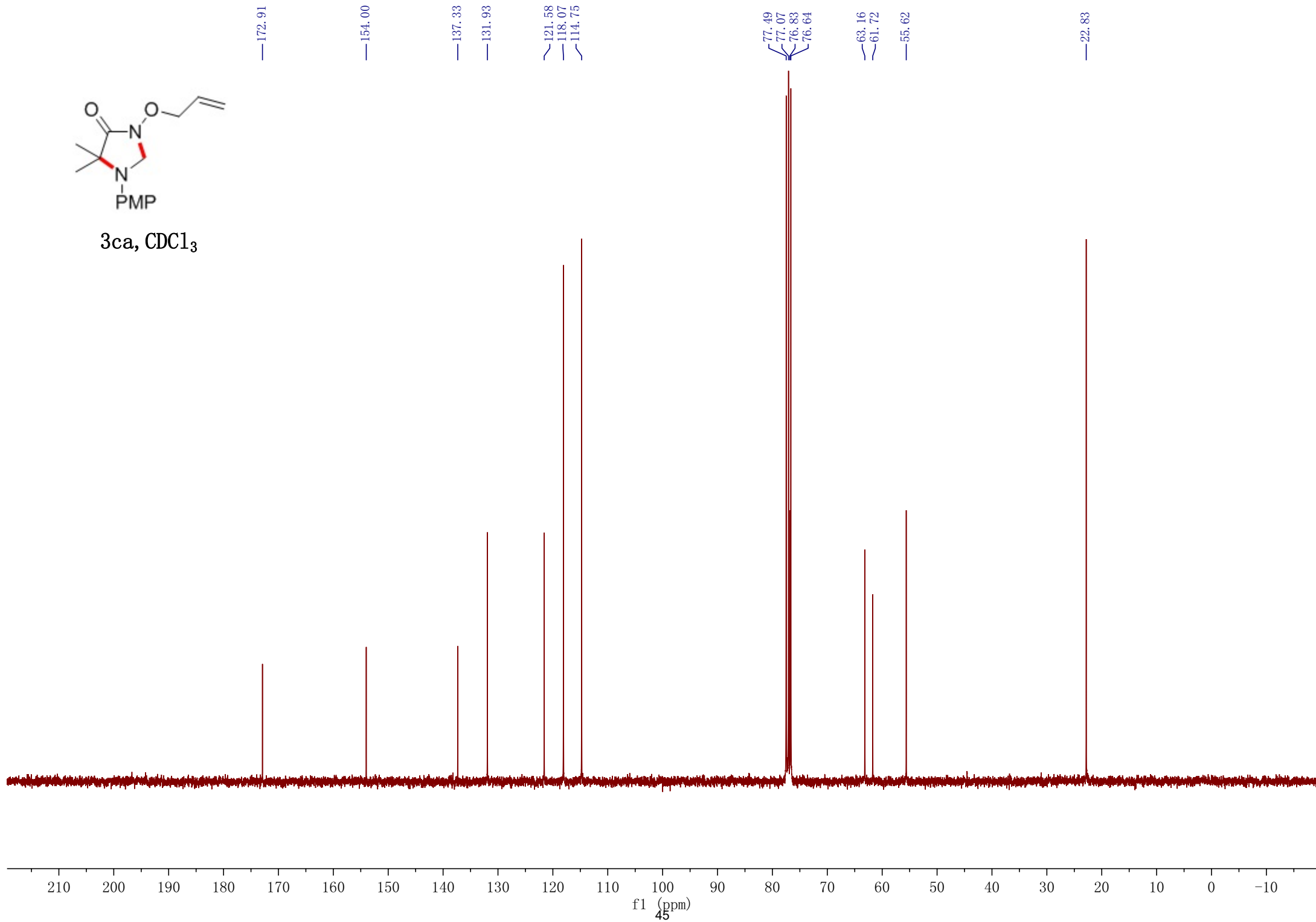


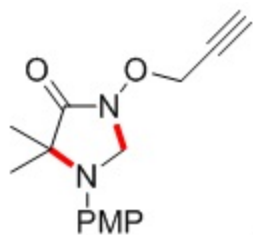
3ca, CDCl_3



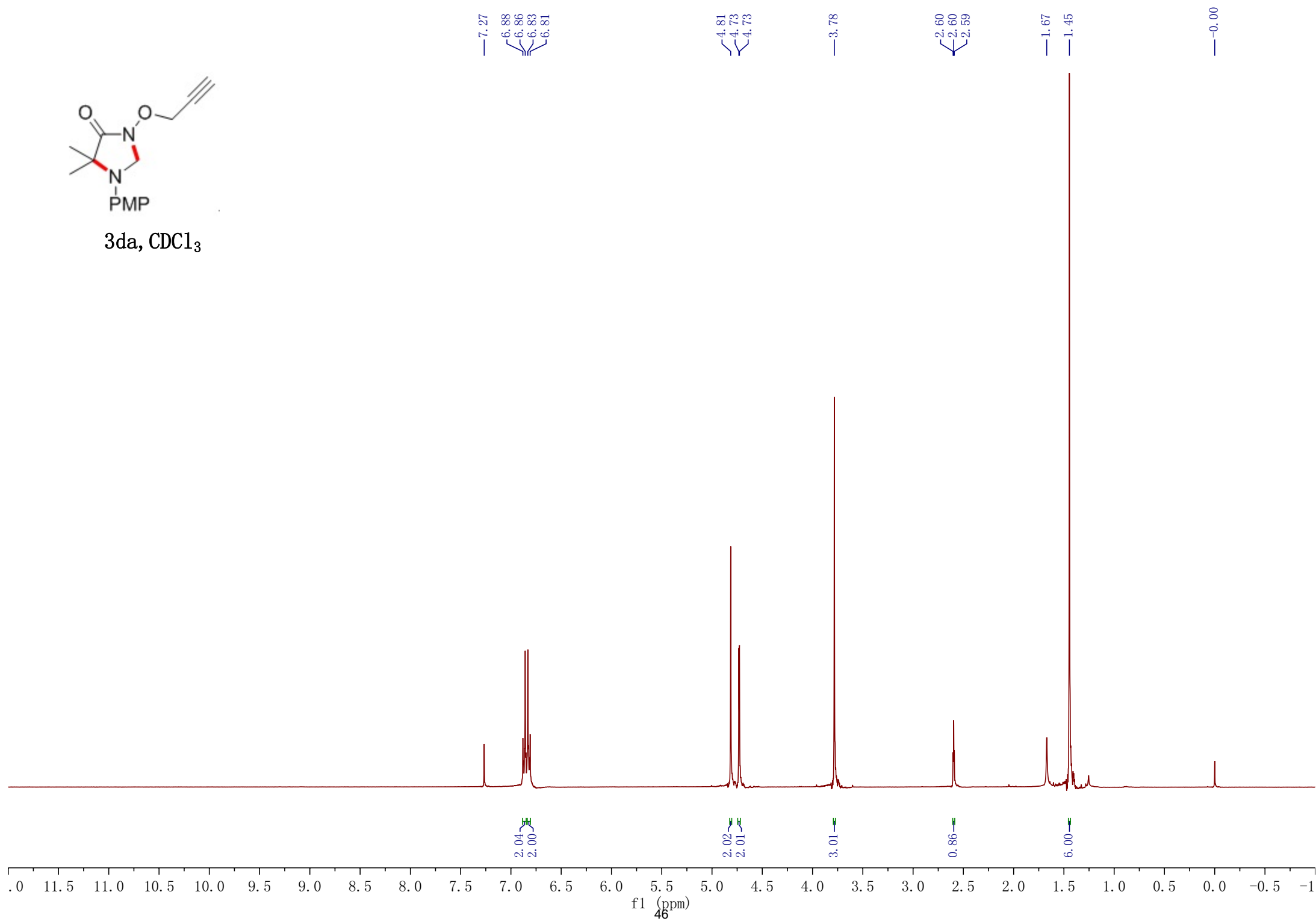


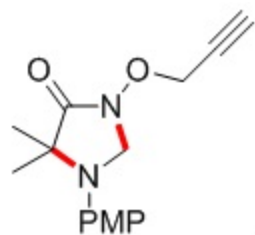
3ca, CDCl₃



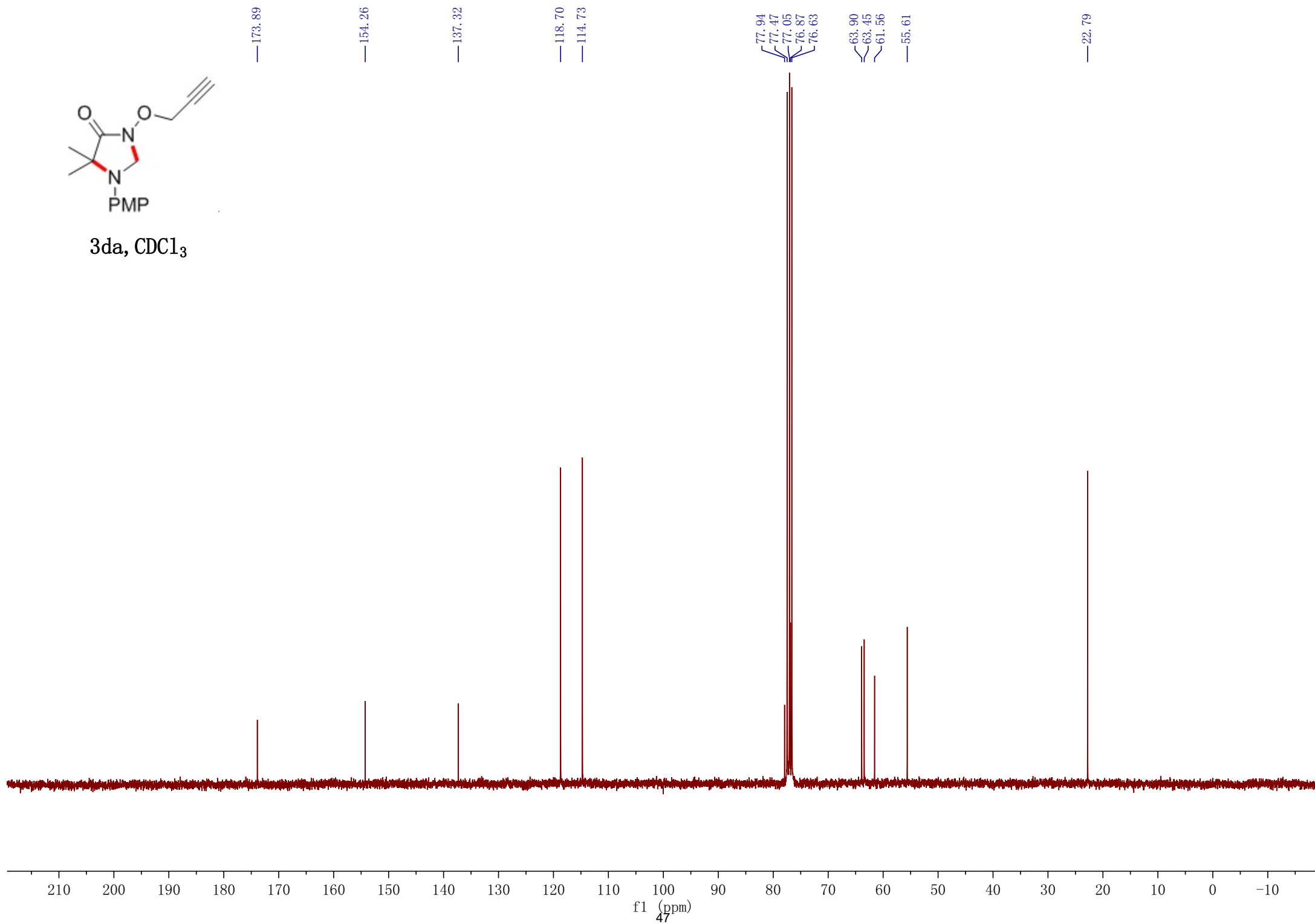


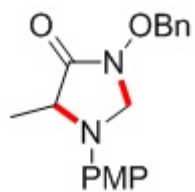
3da, CDCl₃



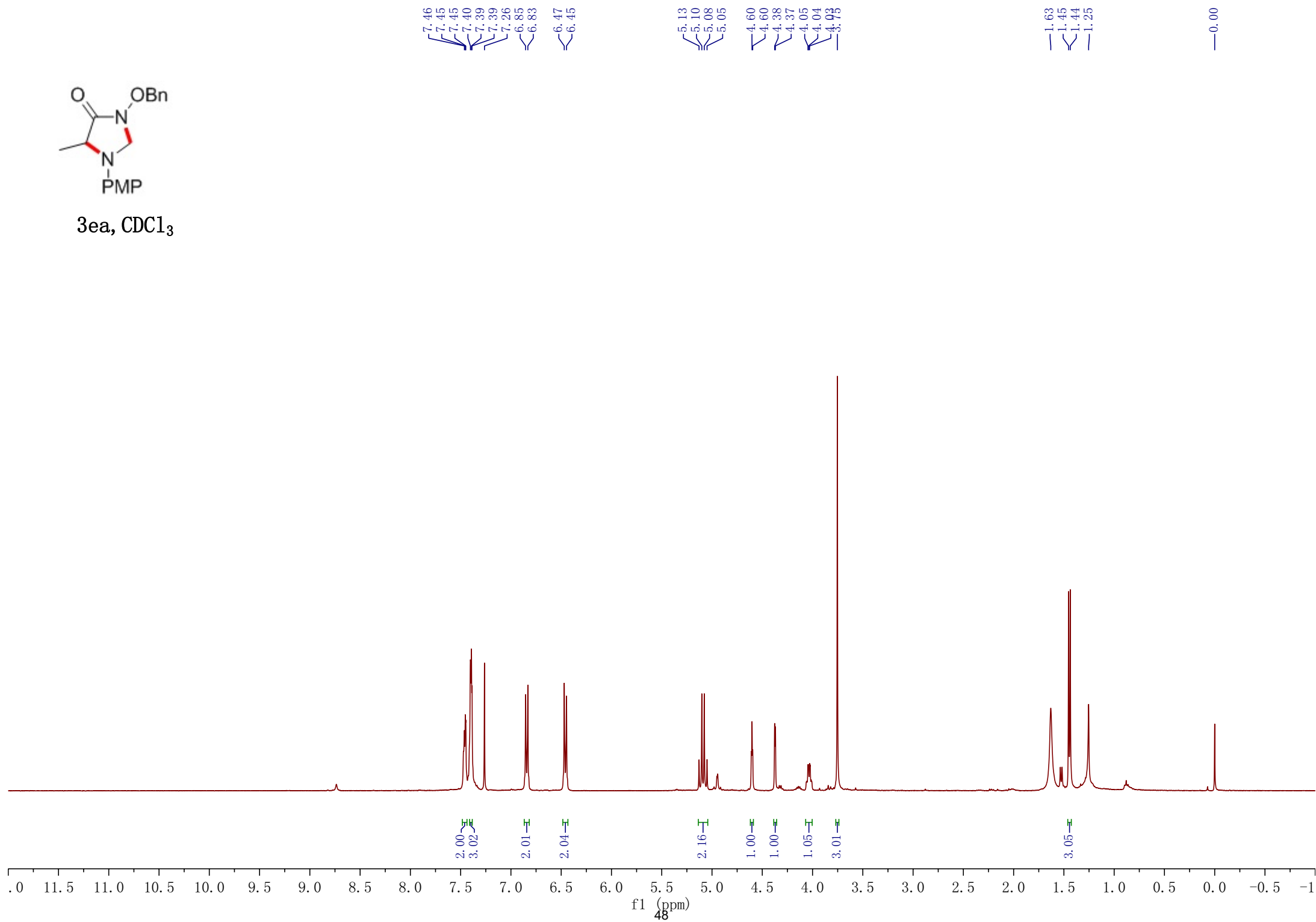


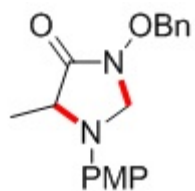
3da, CDCl₃



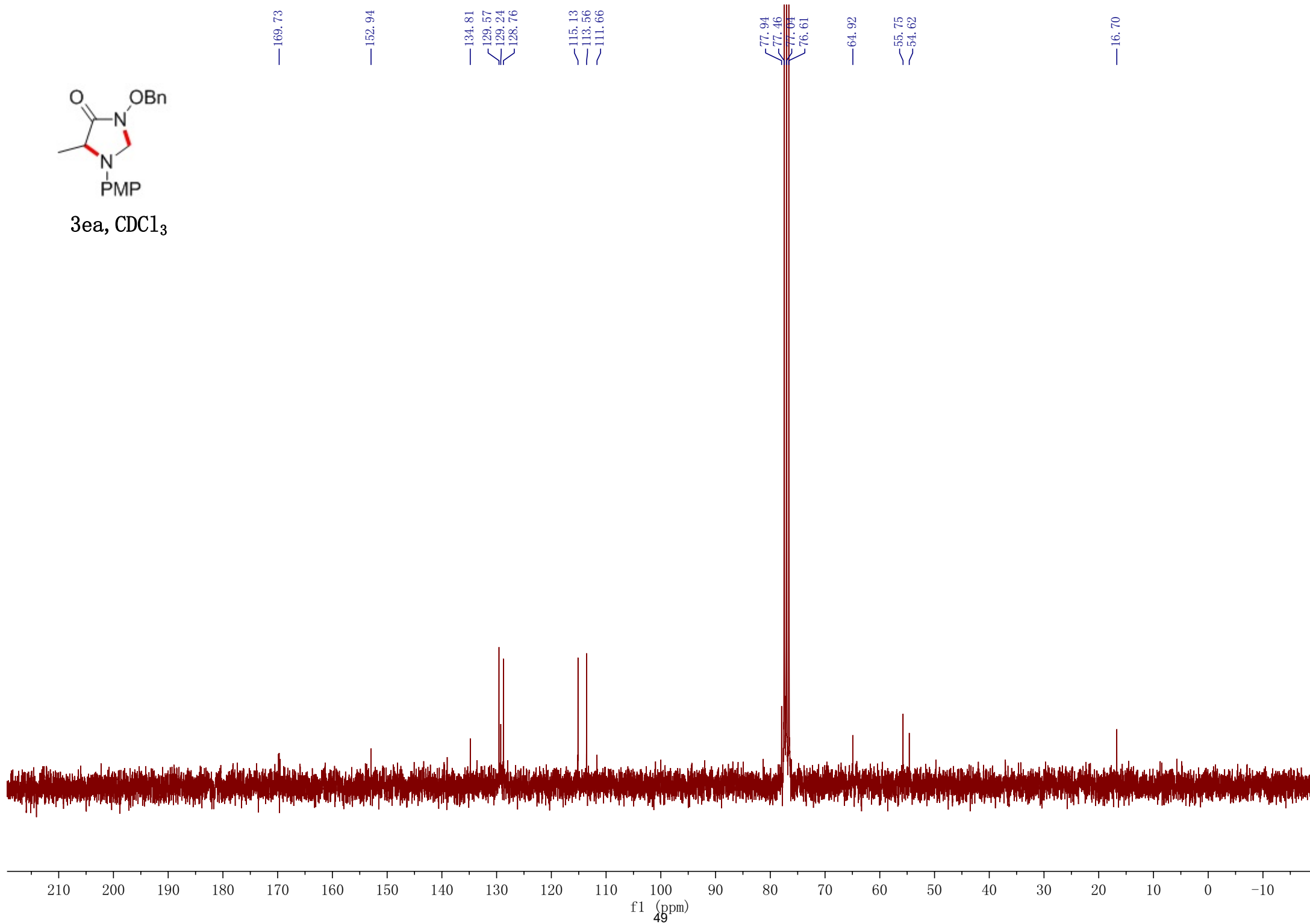


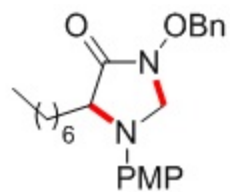
3ea, CDCl₃



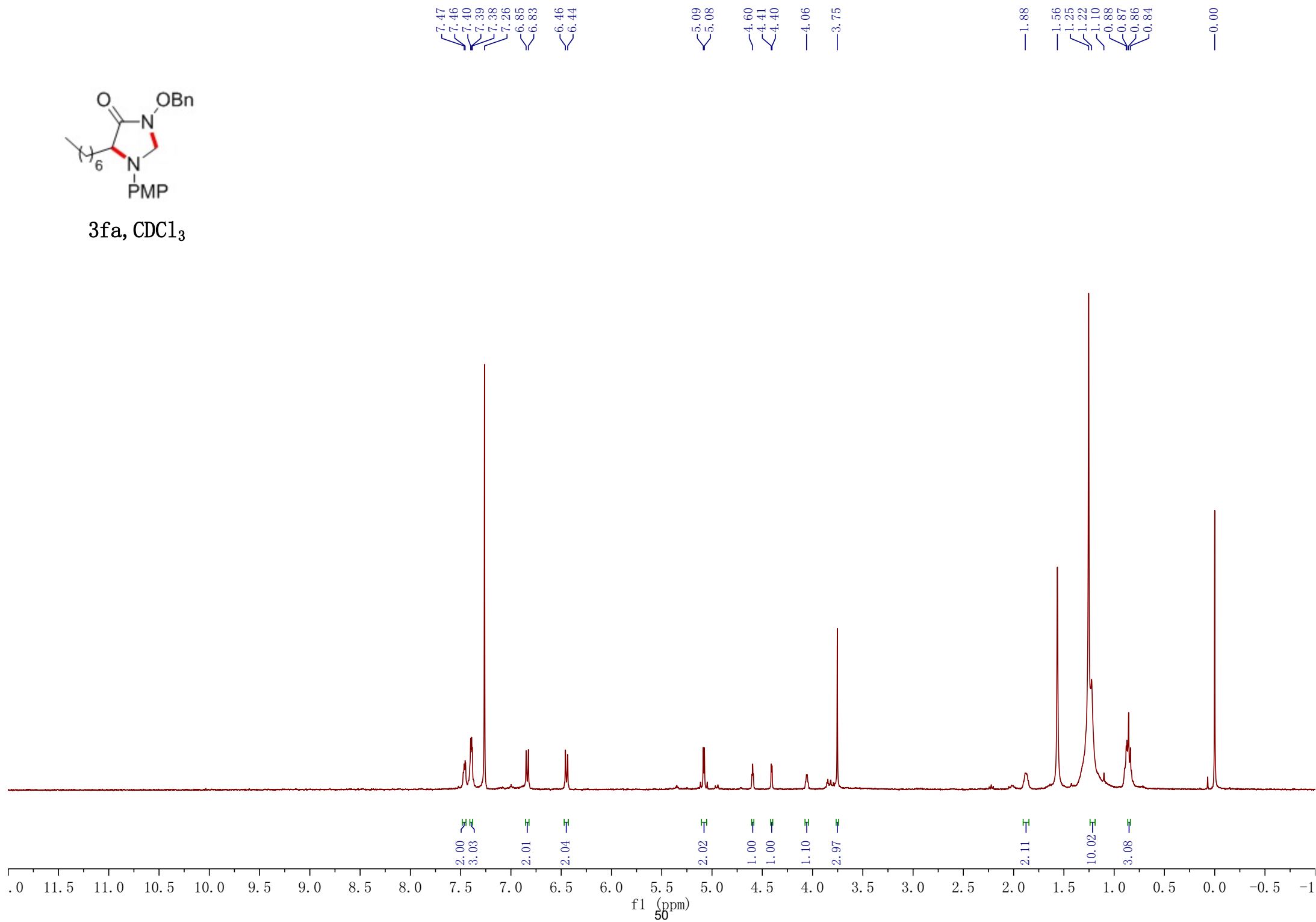


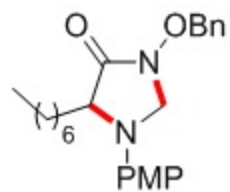
3ea, CDCl₃



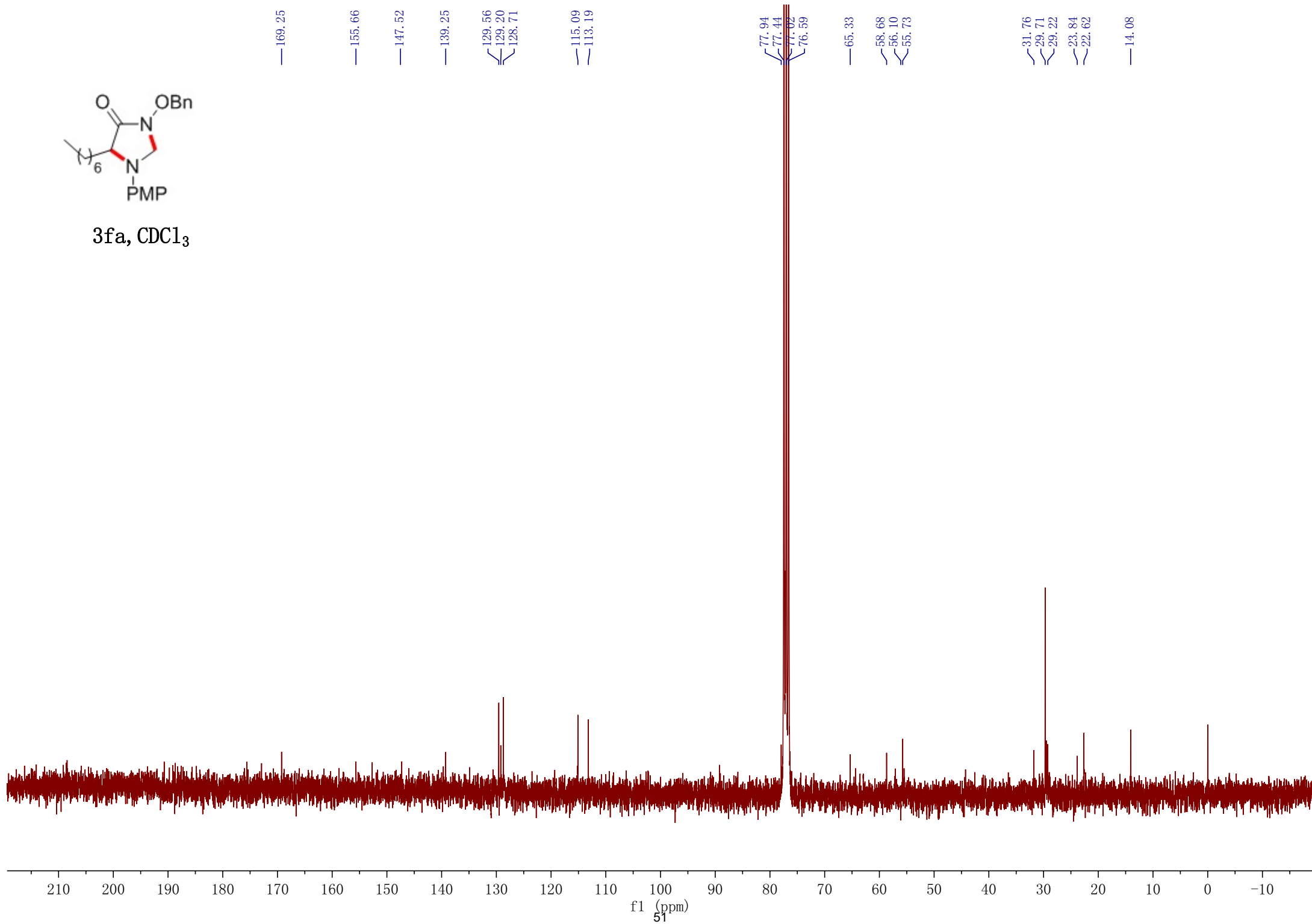


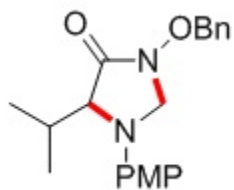
3fa, CDCl₃



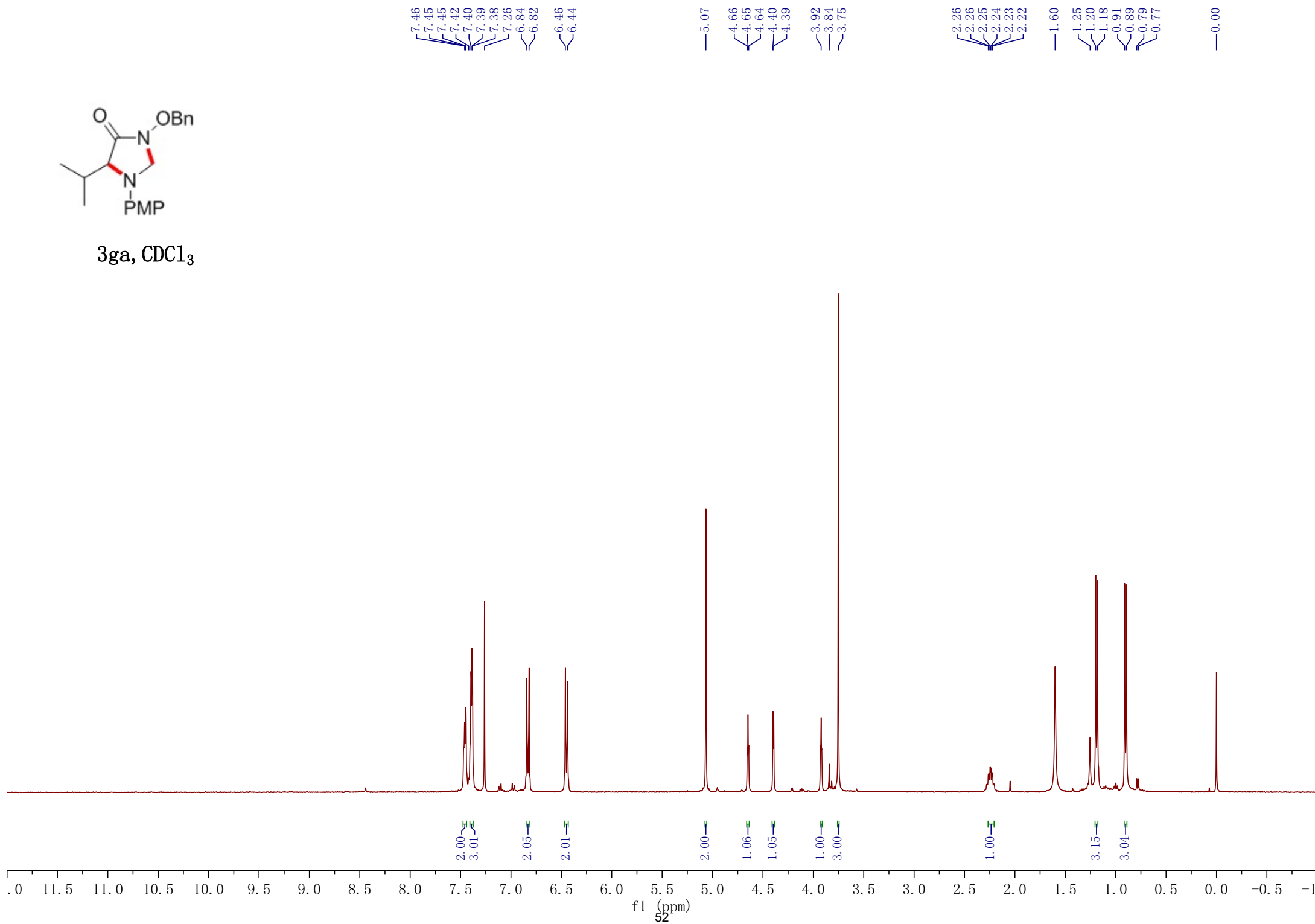


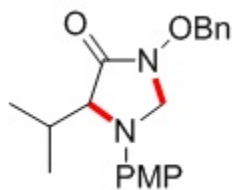
3fa, CDCl_3



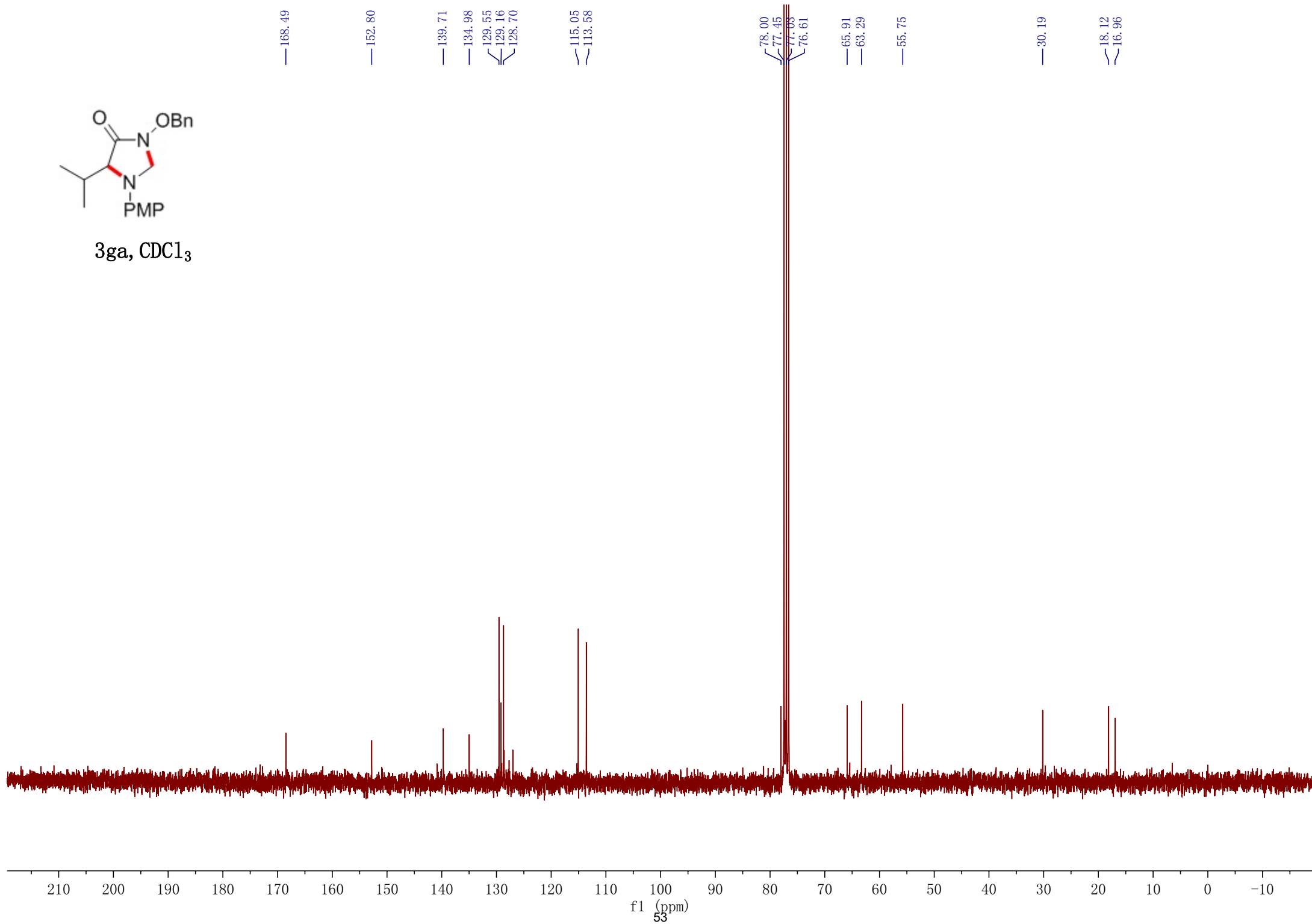


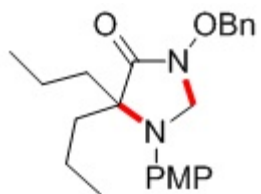
3ga, CDCl_3



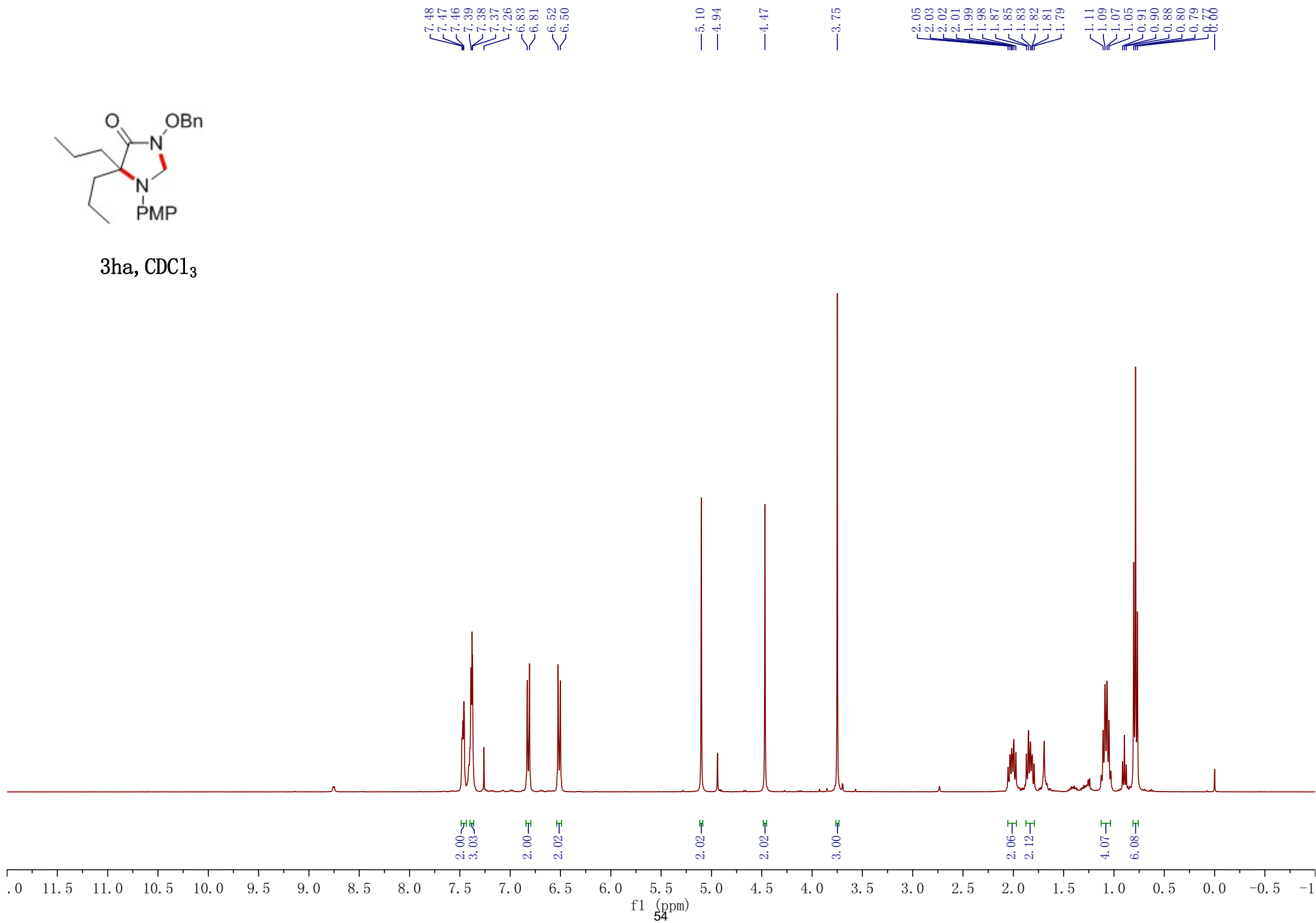


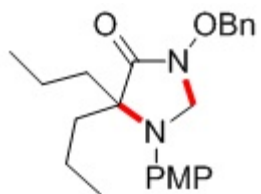
3ga, CDCl₃



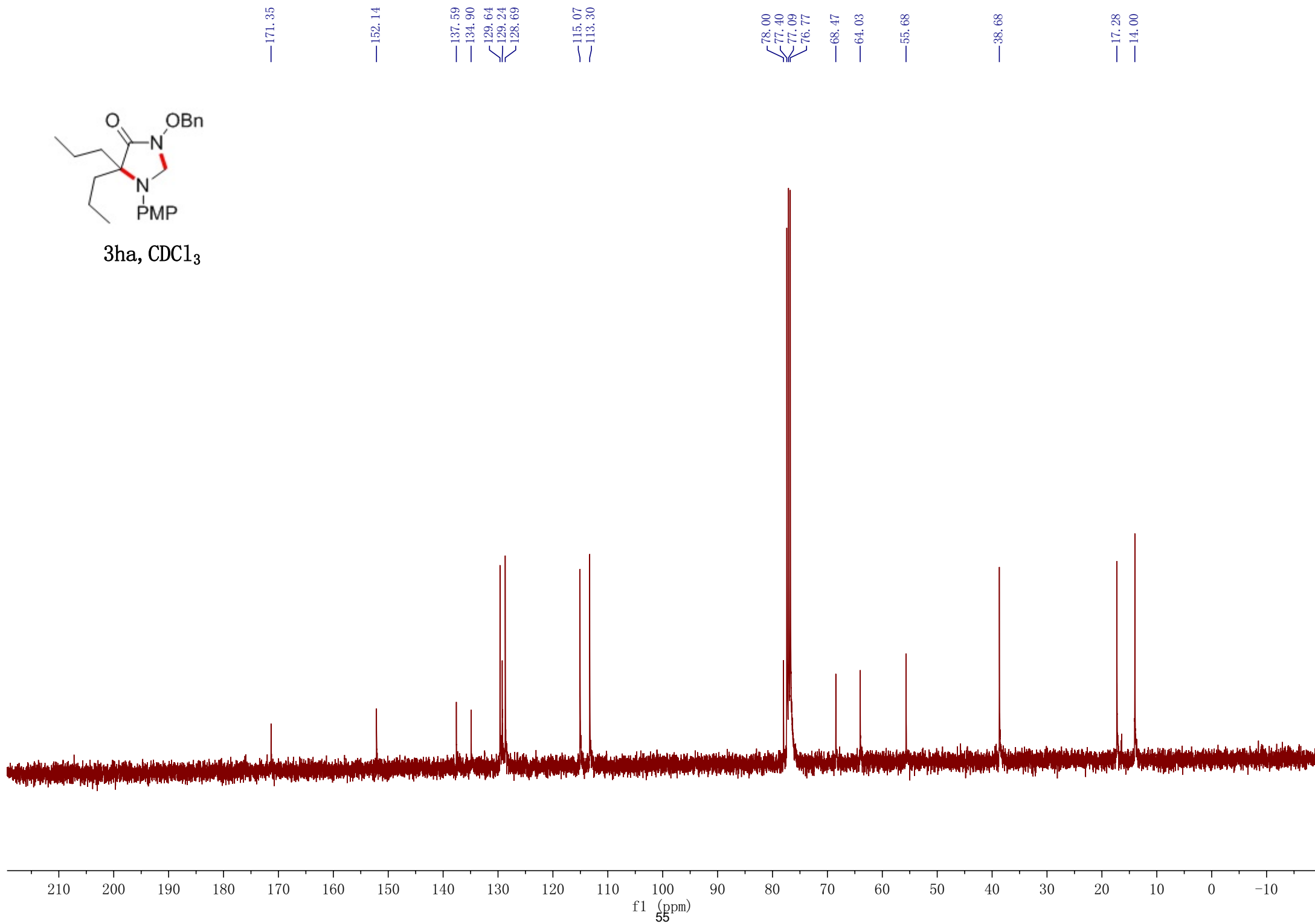


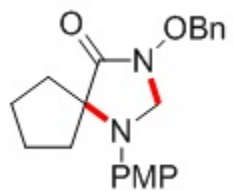
3ha, CDCl_3



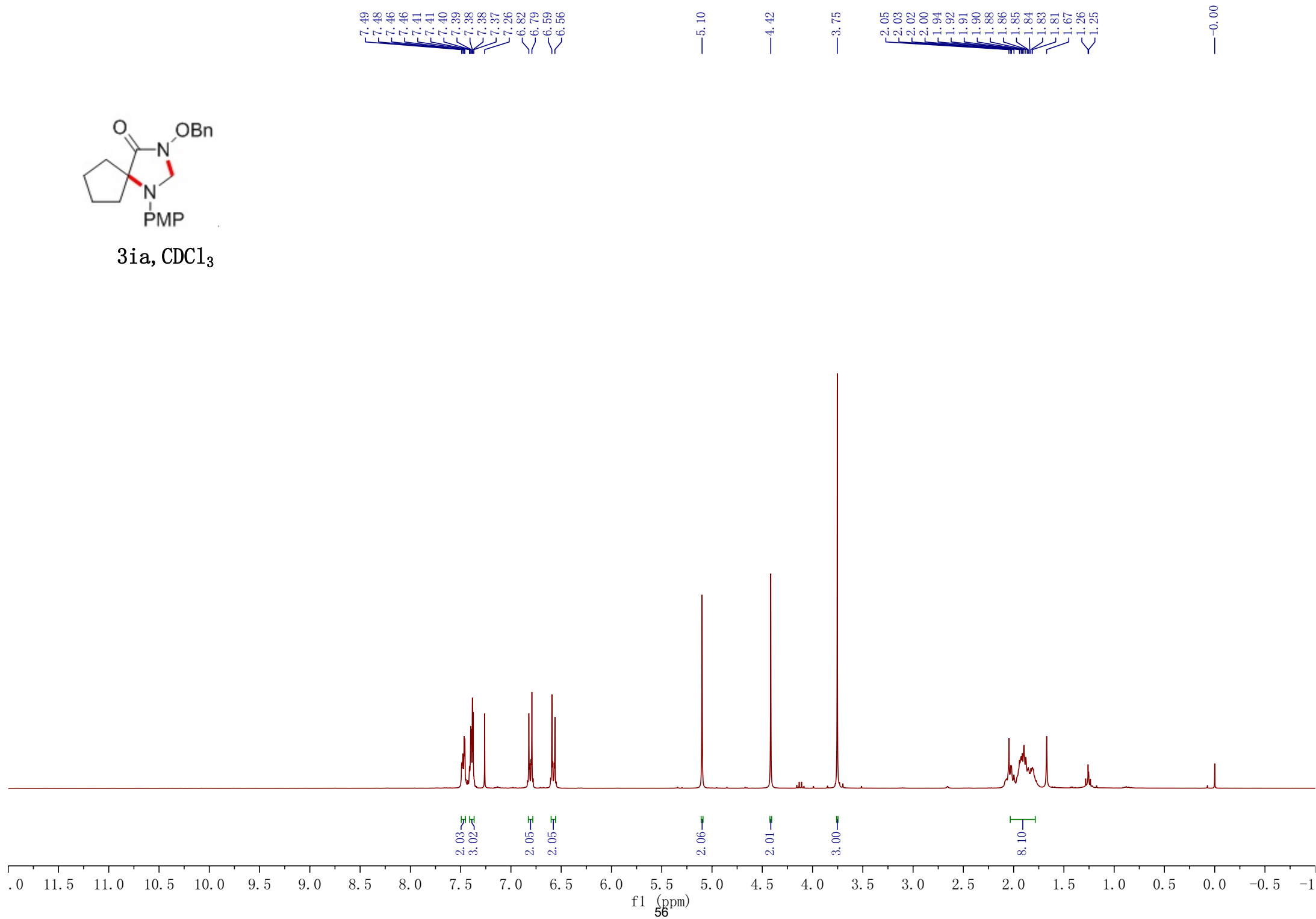


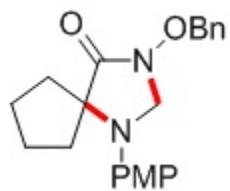
3ha, CDCl₃



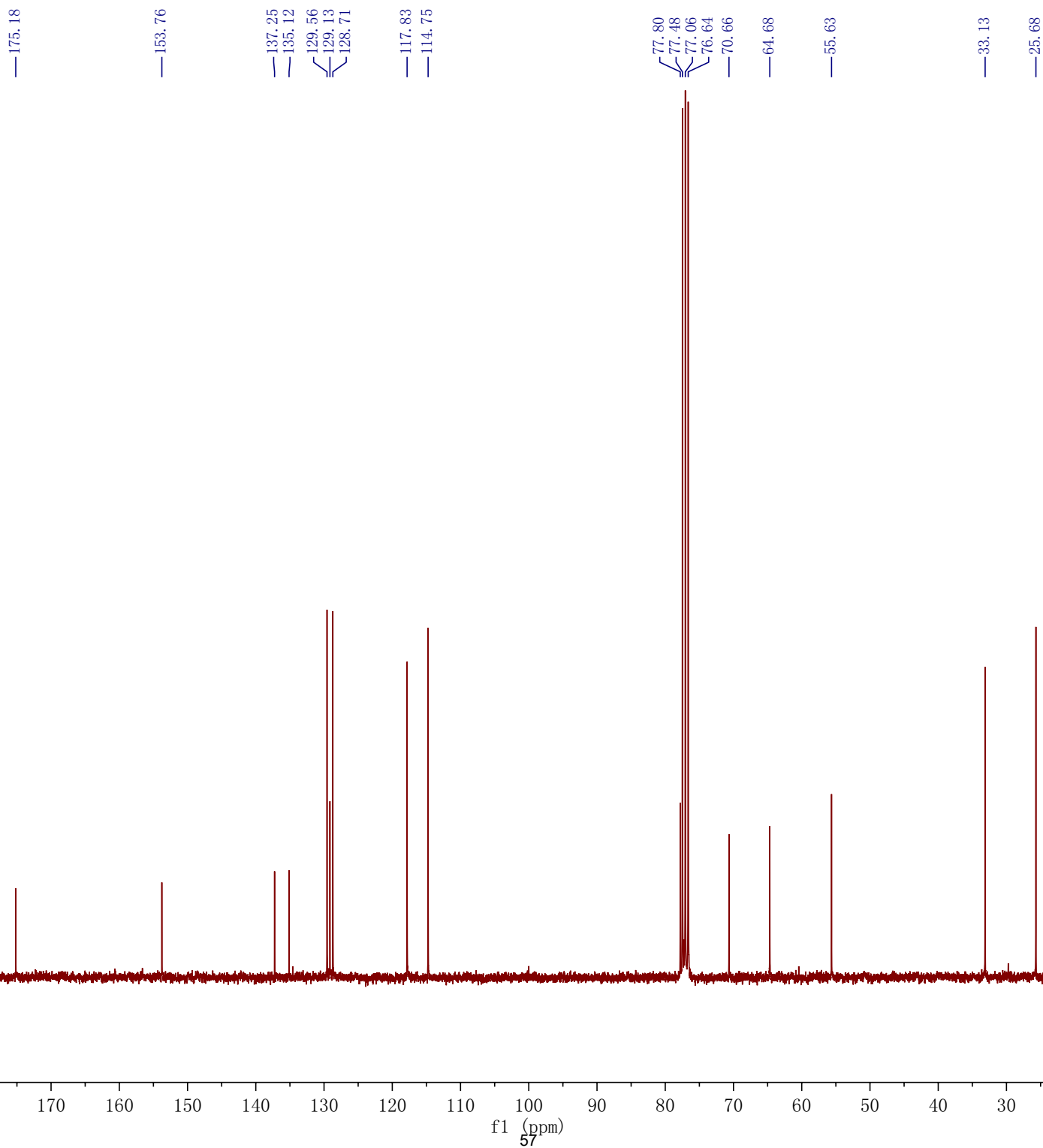


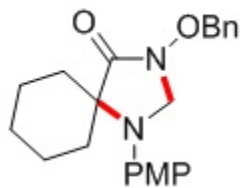
3ia, CDCl₃



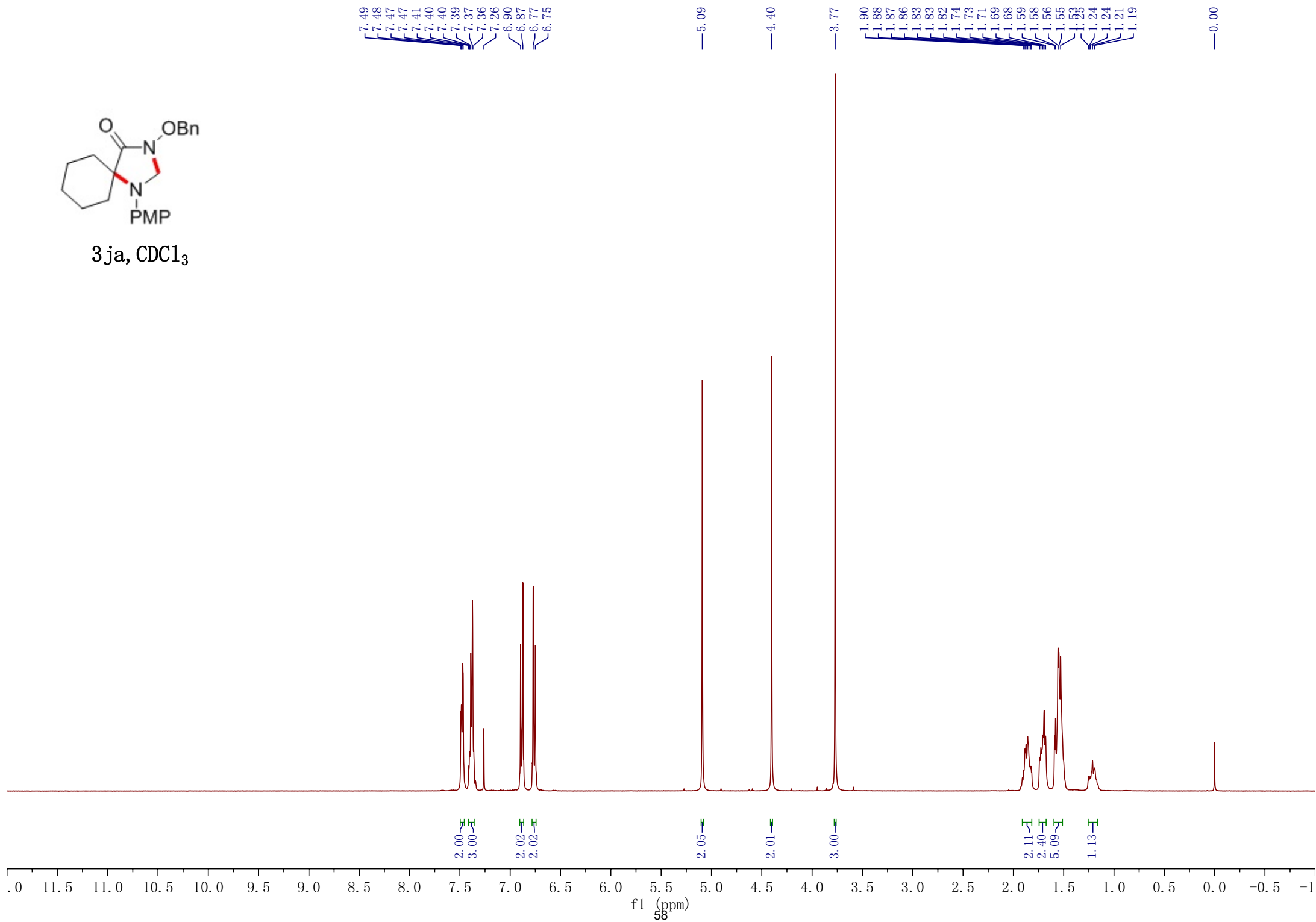


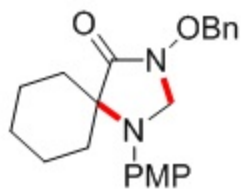
3ia, CDCl_3



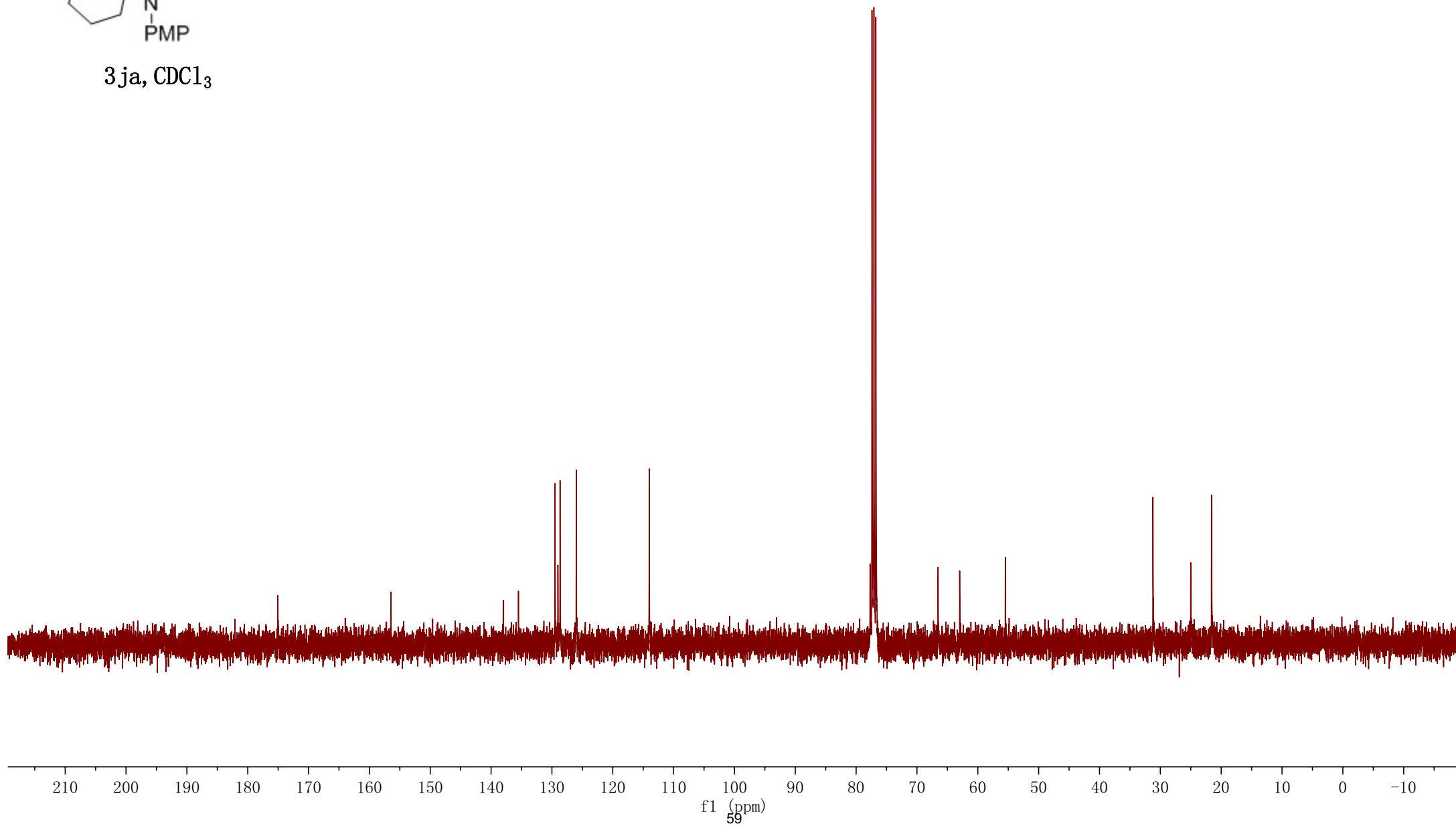


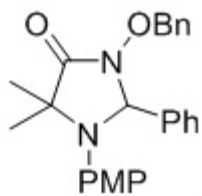
3ja, CDCl_3



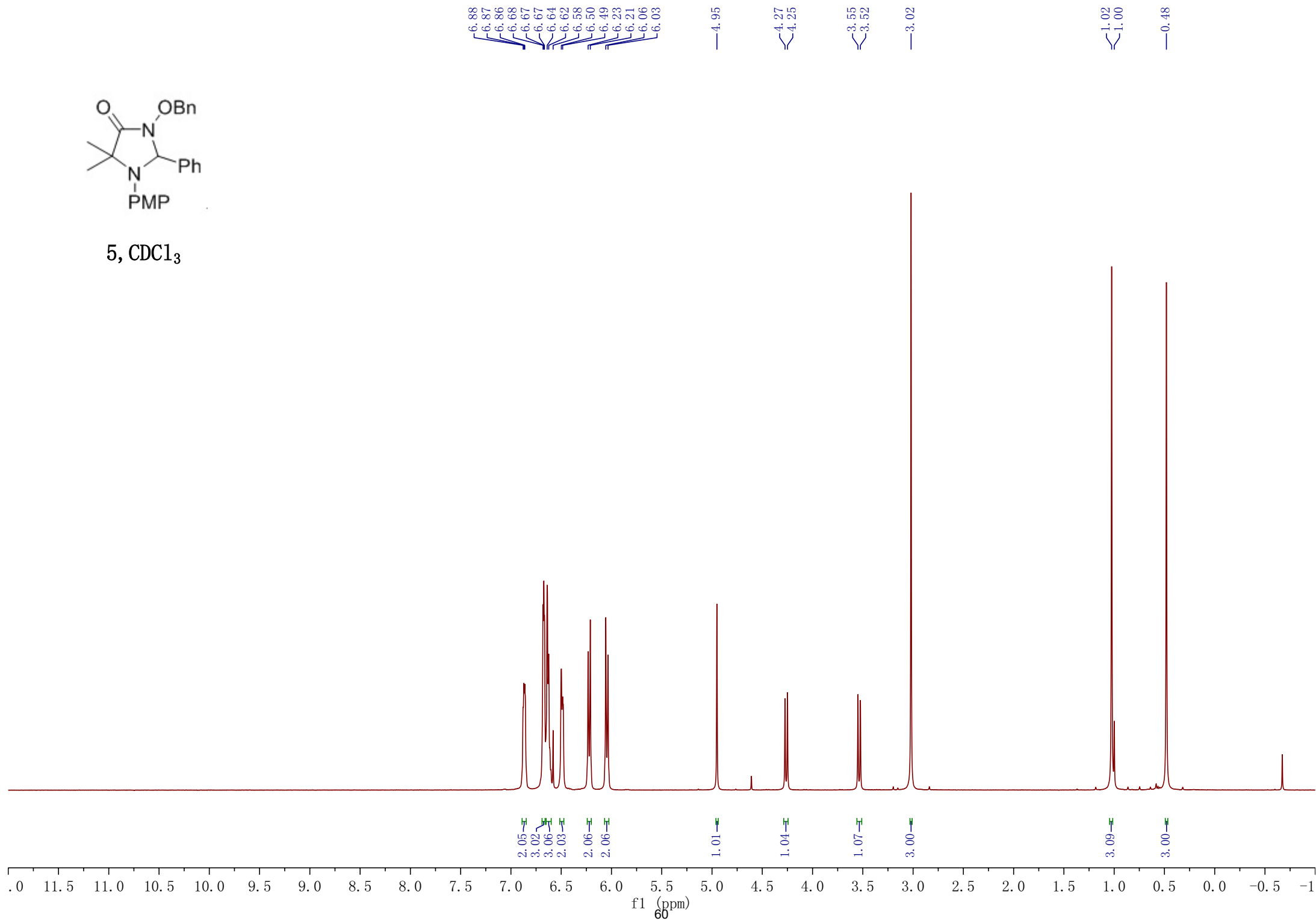


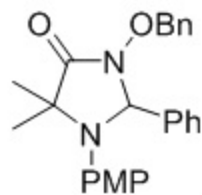
3ja, CDCl₃



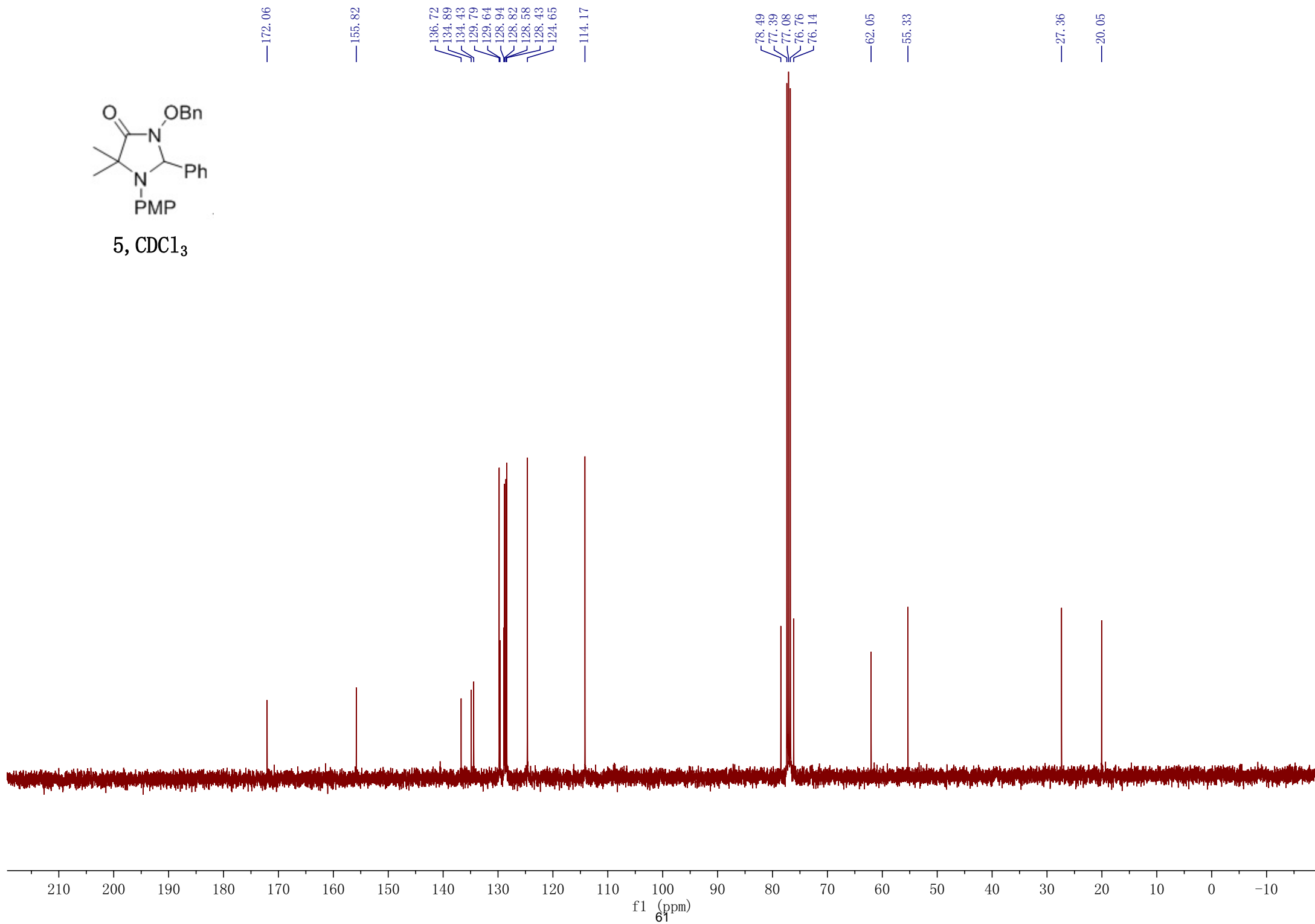


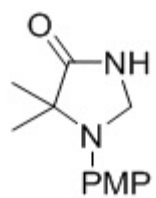
5, CDCl_3



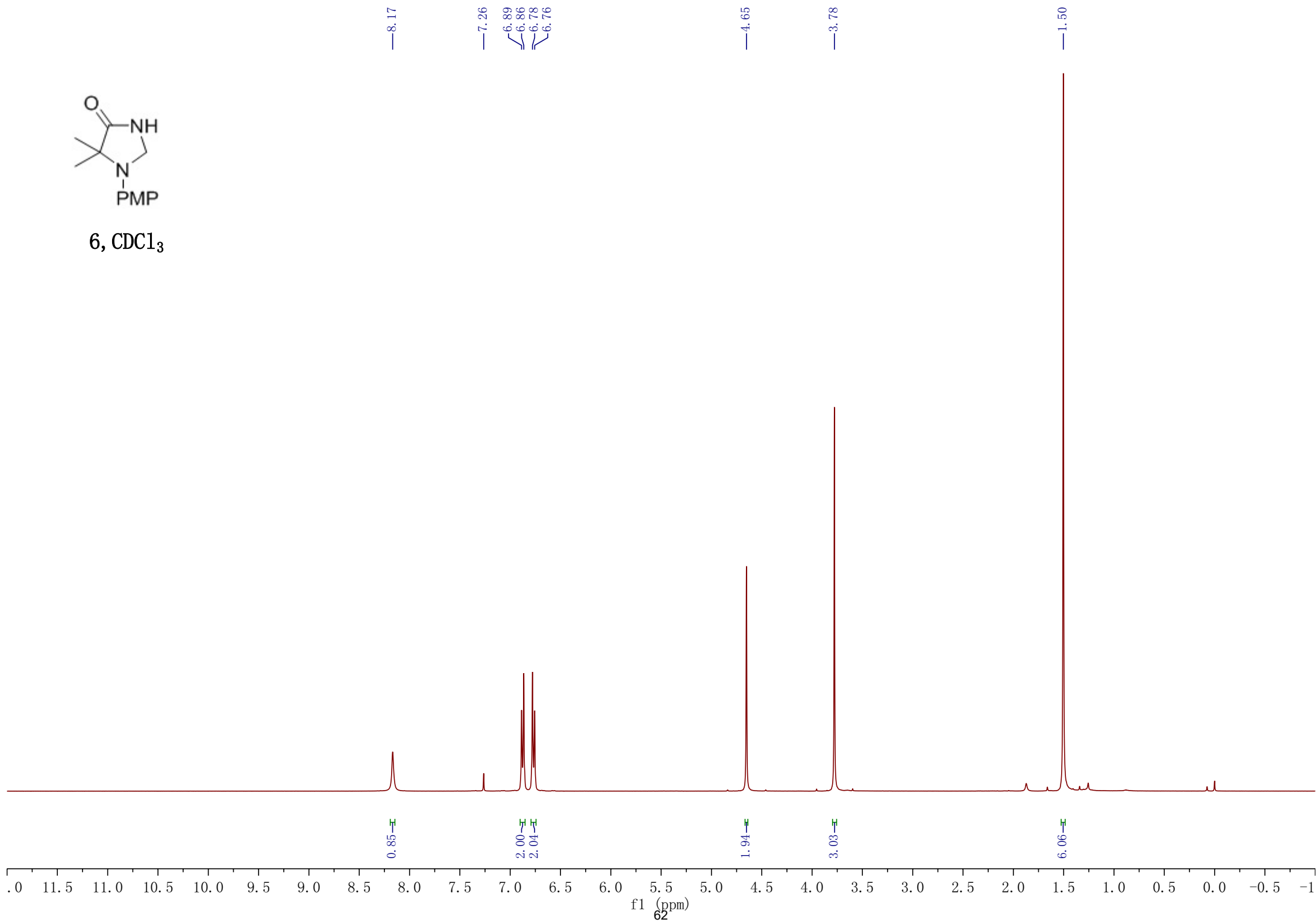


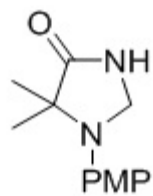
5, CDCl_3





6, CDCl_3





6, CDCl₃

