Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Synthesis and characterization of 5-amino-1,3,6-trinitro-1*H*-benzo[*d*]imidazol-2(3*H*)-one as the energetic material

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Part A: Experimental

Caution

The titled compound is energetic material and tends explode under certain conditions. Proper protective measures (safety glasses, face shields, leather coat, ear plugs and earthening equipment and person) should be taken during the synthesis, test and measurement processes, especially when these compounds are prepared on a larger scale.

Materials and instruments: The starting materials used in the present study were of AR grade and purchased from the trade without further purification. Melting point was measured on a X-4 melting point apparatus and was uncorrected. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were recorded on Bruker Avance Spectrometer (TMS as an internal standard). Chemical shifts (δ) are reported in part per million (ppm). The coupling constants (J) are reported in hertz (Hz). High-resolution mass spectra were recorded on a Finnigan TSQ Quantum ultra AM mass spectrometer. Elemental analysis was carried out on Perkin-Elmer instrument.

5-amino-1,3,6-trinitro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (2)

a. From **1**:5-amino-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**1**) (3.0 g, 20.1 mmol) was added slowly to a solution of fuming nitric acid (6 mL) and acetic anhydride (50 mL) which was stirred at the ice bath. The reaction mixture was kept stirring for 30 min, and poured into crushed ice, and then filtered, washed with water and dried to give 5-amino-1,3,6-trinitro-1*H*-benzo[*d*]imidazol-2(3*H*) -one (**2**) as a yellow solid (0.6 g, 11%); IR: 3073, 2246, 1732, 1603, 1560, 1510, 1440, 1370, 1324, 1238, 1210, 1116, 983, 824 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 12.59 (s, 2H), 8.55 (s, 1H), 8.14 (s, 1H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 154.59, 141.55, 138.60, 132.65, 112.70, 107.45, 98.65; Anal. Calcd. for $C_7H_4N_6O_7$: C, 29.59; H, 1.42; N, 29.58; found: C, 29.51; H, 1.35; N, 29.50%.

b. From **11**: 1-acetyl-5-amino-6-nitro-1*H*-benzo [*d*]imidazol-2(3*H*)-one (**11**) (0.20 g, 0.8 mmol) was added very slowly to a solution of 20%N_2O_5/HNO_3 (1g) and 2 mL of trifluoromethanesulfonic acid (TFMSAA) which was stirred at the ice bath. The reaction mixture was maintained stirring for 20 min, and poured into crushed ice, then filtered, washed with water and dried to give 5-amino-1,3,6-trinitro-1*H*-benzo[*d*]imidazol -2(3*H*)-one (**2**) as a yellow solid (0.18 g, 75%), whose ^{1}H NMR was identified with an authentic sample.

Tert-butyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-ylcarbamate (3)

To a stirred solution of 5-amino-1*H*-benzo[*d*] imidazol-2(3*H*)-one (**1**) (1.0 g, 6.7 mmol) in methanol (30 mL), dibutyldicarbonate (2.5 mL) was added dropwise at room temperature. The reaction mixture was evaporated after 30 min, and crystallized in methanol to give tert-butyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-ylcarbamate (**3**) as a pale pink solid (1.9 g, 96%), m.p. 245-247 ^{o}C (dec.); IR: 3344, 3125, 2984, 1694, 1643, 1512, 1474, 1388, 1291, 1235, 1211, 1163, 1053, 1024, 852 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 10.49 (s, 1H), 10.40 (s, 1H), 9.15(s, 1H), 7.23(s, 1H), 6.93 (d, J=8.20 Hz, 1H), 6.77 (d, J=8.20 Hz, 1H), 1.46 (s, 9H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 155.00, 152.39, 132.59, 129.24, 124.24, 110.42, 107.63, 99.21, 78.10, 27.66; Anal. Calcd. for $C_{12}H_{15}N_3O_3$: C, 57.82; H, 6.07; N, 16.86; found: C, 57.70; H, 6.16; N, 16.80%; MS (ESI) m/z: 250.02 (M+H).

2-chloro-*N*-(2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (4)

To a stirred solution of 5-amino-1*H*-benzo[*d*] imidazol-2(3*H*)-one (**1**) (1.0 g, 6.7 mmol) in acetonitrile (30 mL), was added dropwise chloroacetyl chloride (1.5mL) at room temperature, and maintained for 40 min. The reaction mixture was then filtered, washed with water, and dried to give 2-chloro-*N*-(2-oxo-2,3 -dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**4**) as a pale pink solid (1.36 g, 90%), m.p. >300 ^{o}C; IR: 3289, 2997, 1729, 1675, 1653, 1539, 1505, 1473, 1203, 1027, 845 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 10.60 (s, 1H), 10.55(s, 1H), 10.18(s, 1H), 7.45(s, 1H), 7.02 (d, J=8.30 Hz, 1H), 6.86 (d, J=8.30 Hz, 1H), 4.22 (s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 163.57, 154.97, 131.54, 129.18, 125.55, 111.51, 107.81, 100.28, 43.10; Anal. Calcd. for $C_9H_8ClN_3O_2$: C, 47.91; H, 3.57; N, 18.62; found: C, 47.85; H, 3.48; N, 18.68%; MS (ESI) m/z: 225.96:227.97=3:1 (M+H).

***N*-(1,3-diacetyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (5)**

5-amino-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**1**) (6.0 g, 40.3 mmol) was dissolved in 60 mL of acetic anhydride, the reaction mixture was heated to 120 ^{o}C and maintained three hours at this temperature, then the precipitate was cooled to 0 ^{o}C, filtered off, thoroughly washed with

dichloromethane, then water, and dried to give *N*-(1,3-diacetyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*] imidazol-5-yl)acetamide (**5**) as a white solid (10.5 g, 95%), m.p. 248-250 °C (dec.); IR: 1762, 1703, 1485, 1431, 1360, 1313, 1243, 1179, 1011, 823 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ 10.10 (s, 1H), 8.43 (s, 1H), 8.00 (d, *J*=8.85 Hz, 1H), 7.56 (d, *J*=8.85 Hz, 1H), 2.64 (s, 3H), 2.63 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 169.72, 169.46, 167.71, 150.39, 135.91, 126.18, 121.41, 114.67, 113.97, 105.47, 25.45, 25.27, 23.45; Anal. Calcd. for $C_{13}H_{13}N_3O_4$: C, 56.72; H, 4.76; N, 15.27; found: C, 56.65; H, 4.71; N, 15.35%; MS (ESI) m/z: 297.95 (M+Na).

***N*-(2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (6)**

5-amino-1*H*-benzo[*d*]imidazol-2(3*H*)-one (**1**) (5.0 g, 33.56 mmol) was dissolved in 50 mL of acetic anhydride, the reaction mixture was heated to 40 °C and maintained four hours at this temperature, then the precipitate was cooled to 0 °C, filtered off, washed with dichloromethane, and then water, and dried to give *N*-(2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**6**) as a white solid (6.3 g, 98%), m.p. >300 °C; IR: 2989, 1719, 1651, 1621, 1539, 1501, 1364, 1273, 1254, 1203, 1157, 1029, 885 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ 10.51 (s, 1H), 10.45 (s, 1H), 9.77 (s, 1H), 7.45 (s, 1H), 6.83 (d, J=7.9 Hz, 1H), 6.81 (d, *J*=7.9 Hz, 1H), 2.00 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 167.18, 154.98, 132.52, 129.08, 124.86, 111.06, 107.65, 100.05, 23.40; Anal. Calcd. for $C_9H_9N_3O_2$: C, 56.54; H, 4.74; N, 21.98; found: C, 56.48; H, 4.67; N, 22.05%; MS (ESI) m/z: 214.02 (M+Na).

2-chloro-*N*-(4,6-dinitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (7)

2-chloro-*N*-(2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**4**) (3.0 g, 13.3 mmol) was added slowly to a solution of fuming nitric acid (4 mL) and concentrated sulfuric acid (50 mL) which was stirred at the ice bath. The reaction mixture was kept stirring for 40 min, and poured into crushed ice, and then filtered, washed with water and dried to give 2-chloro-*N*-(4,6- dinitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**7**) as a pale yellow solid (2.5 g, 60%); m.p. 300-302 °C (dec.); IR: 3332, 3231, 2989, 1742, 1688, 1614, 1514, 1403, 1352, 1293, 1187, 993 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ 12.03 (s, 1H), 11.83 (s, 1H), 10.31 (s, 1H), 7.37 (s, 1H) , 4.31 (s, 2H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 165.78, 154.86, 133.73, 132.36, 124.95, 123.66, 122.76, 109.99, 42.14; Anal. Calcd. for $C_9H_6ClN_5O_6$: C, 34.25; H, 1.92; N, 22.19; found: C, 34.30; H, 1.85; N, 22.12%; MS (ESI) m/z: 313.84: 315.83=3:1 (M-H).

***N*-(1,3-diacetyl-6-nitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (8)**

N-(1,3-diacetyl-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**5**) (3.0 g, 10.9 mmol) was added slowly to a solution of fuming nitric acid (5 mL) and concentrated sulfuric acid (50 mL) which was stirred at the ice bath. The reaction mixture was kept stirring for 40 min, and poured into crushed ice, and then filtered, washed with water and dried to give *N*-(1,3-diacetyl- 6-nitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**8**) as a yellow solid (2.88 g, 83%), m.p. 208-210 °C; IR: 3356, 3304, 1733, 1712, 1671, 1608, 1494, 1367, 1317, 1278, 1165, 1100, 1067, 1003 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ 10.41 (s, 1H), 8.59 (s, 1H), 8.42 (s, 1H), 2.67 (s, 3H), 2.66 (s, 3H), 2.08(s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 169.74, 169.54, 167.98, 150.04, 137.65, 129.97, 128.89, 122.44, 110.08, 25.30, 25.07, 22.93; Anal. Calcd. for $C_{13}H_{12}N_4O_6$: C, 48.75; H, 3.78; N, 17.49; found: C, 48.69; H, 3.70; N, 17.41%; MS (ESI) m/z: 342.94 (M+Na).

***N*-(4,6-dinitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (9)**

N-(2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**6**) (2.0 g, 10.5 mmol) was added slowly to a solution of fuming nitric acid (3 mL) and concentrated sulfuric acid (40 mL) which was stirred at the ice bath. The reaction mixture was kept stirring for 30 min, and poured into crushed ice, and then filtered, washed with water and dried to give *N*-(4,6-dinitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**9**) as a yellow solid (2.45 g, 83%), m.p. >300 °C; IR: 3346, 3242, 2989, 1738, 1678, 1604, 1547, 1510, 1476, 1410, 1296, 1246, 1176, 993 cm^{-1}; ^1H NMR (DMSO-d_6, 500 MHz): δ 11.97 (s, 1H), 11.77 (s, 1H), 9.96 (s, 1H), 7.33 (s, 1H), 2.03 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 169.02, 154.88, 133.50, 132.22, 124.54, 122.76, 110.30, 22.39; Anal. Calcd. for $C_9H_7N_5O_6$: C, 38.44; H, 2.51; N, 24.91; found: C, 38.38; H, 2.45; N, 24.99%; MS (ESI) m/z: 279.90(M-H).

1-acetyl-5-amino-6-nitro-1*H*-benzo[*d*]imidazol-2(3*H*)-one (11)

N-(1,3-diacetyl-6-nitro-2-oxo-2,3-dihydro-1*H*-benzo[*d*]imidazol-5-yl)acetamide (**8**) (0.5 g, 1.56 mmol) was dissolved in 20 mL of acetonitrile, and then 0.5 mL of 1,8-diazabicyclo[5.4.0]undec-7-ene was added dropwise, the reaction mixture gradually turned into red. After 30 min, the reaction mixture was evaporated, and added 10 mL of water, the yellow solid was precipitated after standing for 25 min. the mixture was filtered, washed with water, and dried to give 1-acetyl-5-amino-6-nitro- 1*H*-benzo[*d*]imidazol-2(3*H*)-one (**11**) (0.3 g, 81%); m.p.

>300 ºC; IR: 3463, 3332, 3066, 1719, 1698, 1646, 1614, 1557, 1488, 1369, 1316, 1274, 1173, 1065, 1018, 917 cm^{-1}; ^{1}H NMR (DMSO-d_6, 500 MHz): δ 11.15 (s, 2H), 10.19 (s, 1H), 7.54 (s, 1H), 7.50 (s, 1H), 2.10 (s, 3H); ^{13}C NMR (DMSO-d_6, 125 MHz): δ 168.09, 155.12, 134.78, 133.81, 127.71, 125.67, 104.11, 103.04, 23.44; Anal. Calcd. for $C_9H_8N_4O_4$: C, 45.77; H, 3.41; N, 23.72; found: C, 45.70; H, 3.35; N, 23.81%; MS (ESI) m/z: 234.92 (M-H).

Part B: Copies of ^{1}H-NMR, ^{13}C NMR, IR and MS

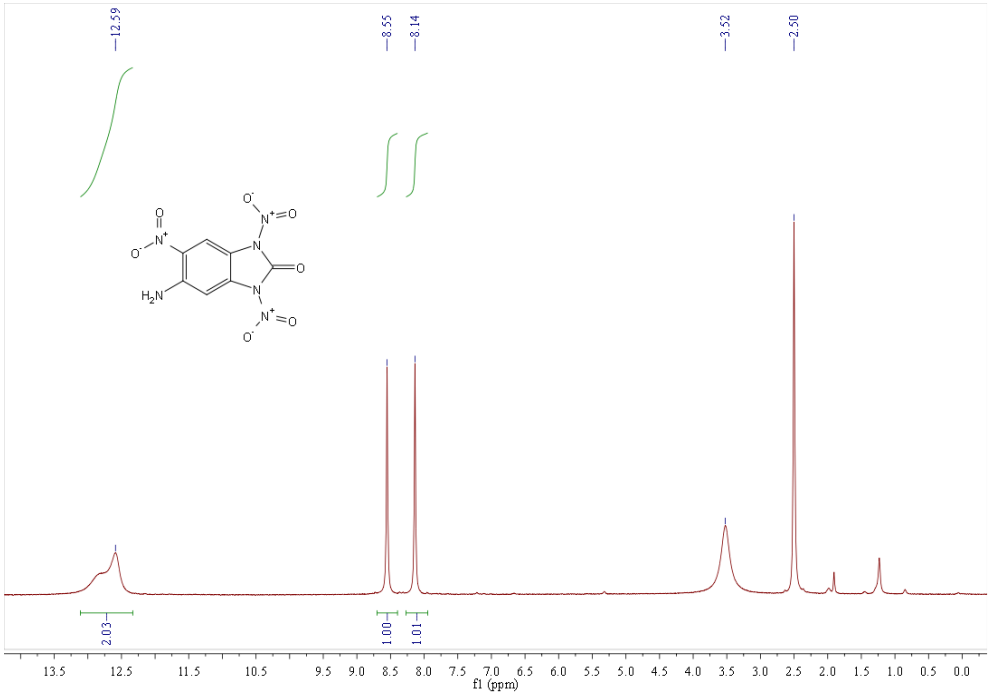


Fig.1-1 ^{1}H NMR spectrum of **2** in DMSO-d_6, 500MHz

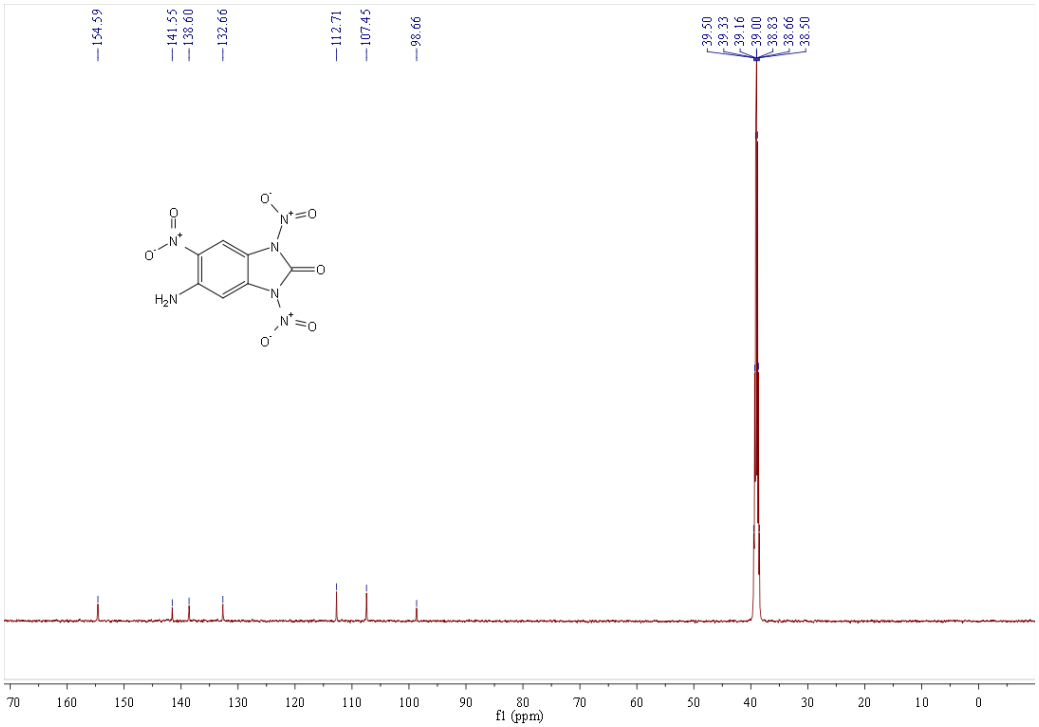


Fig.1-2 ^{13}C NMR spectrum of **2** in DMSO-d_6, 500MHz

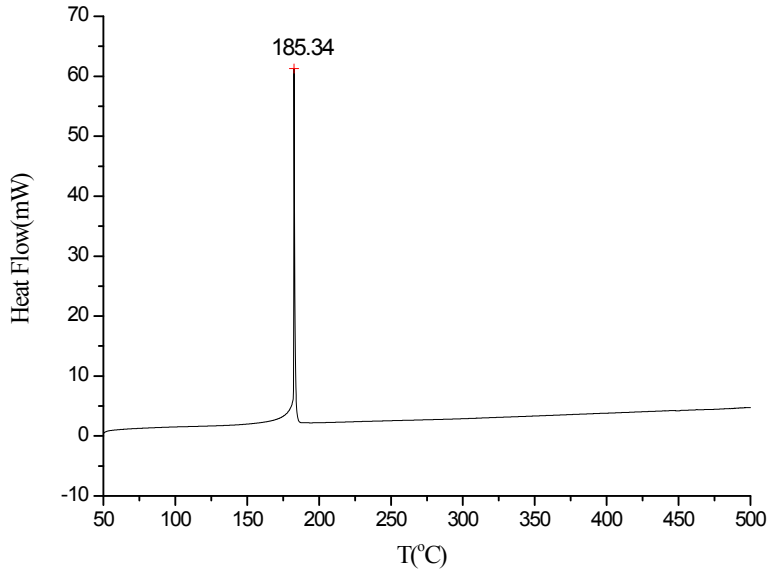


Fig.1-3 DSC curve of **2**

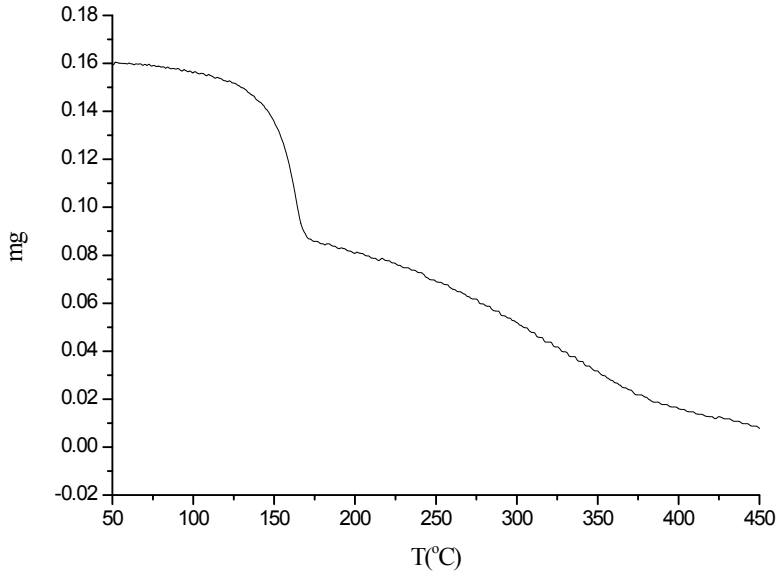


Fig.1-4 TG curve of **2**

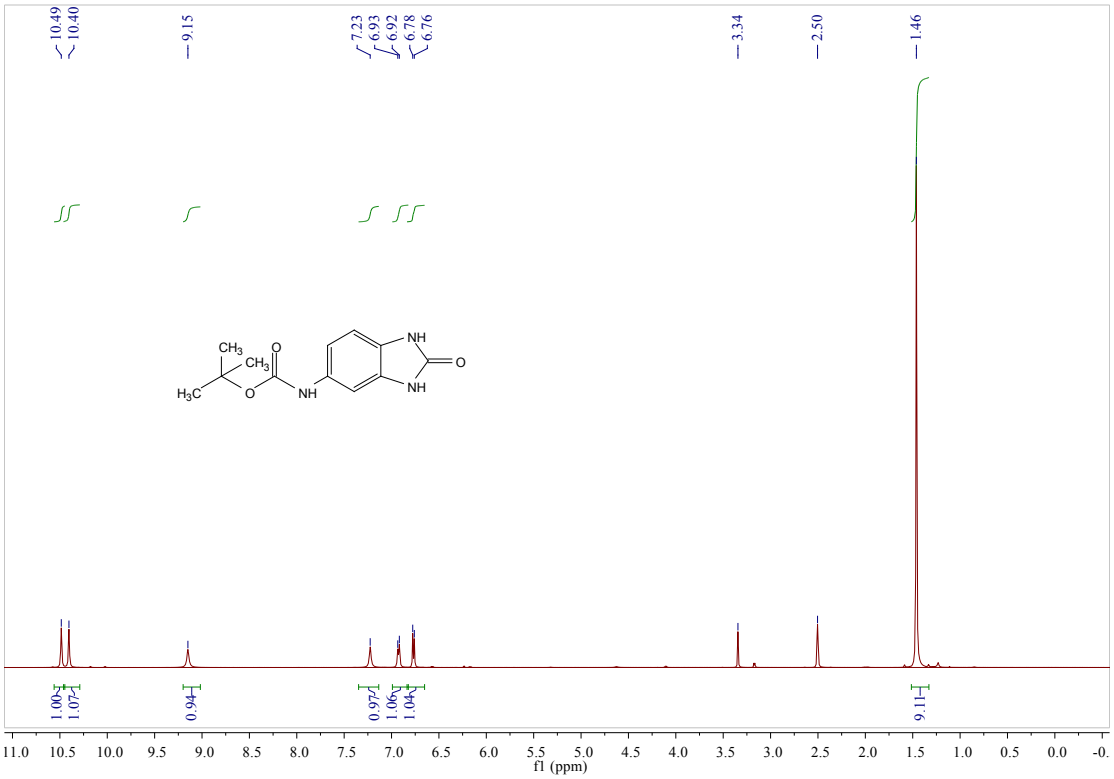


Fig. 2-1 ^{1}H NMR spectrum of **3** in DMSO-d_6, 500MHz

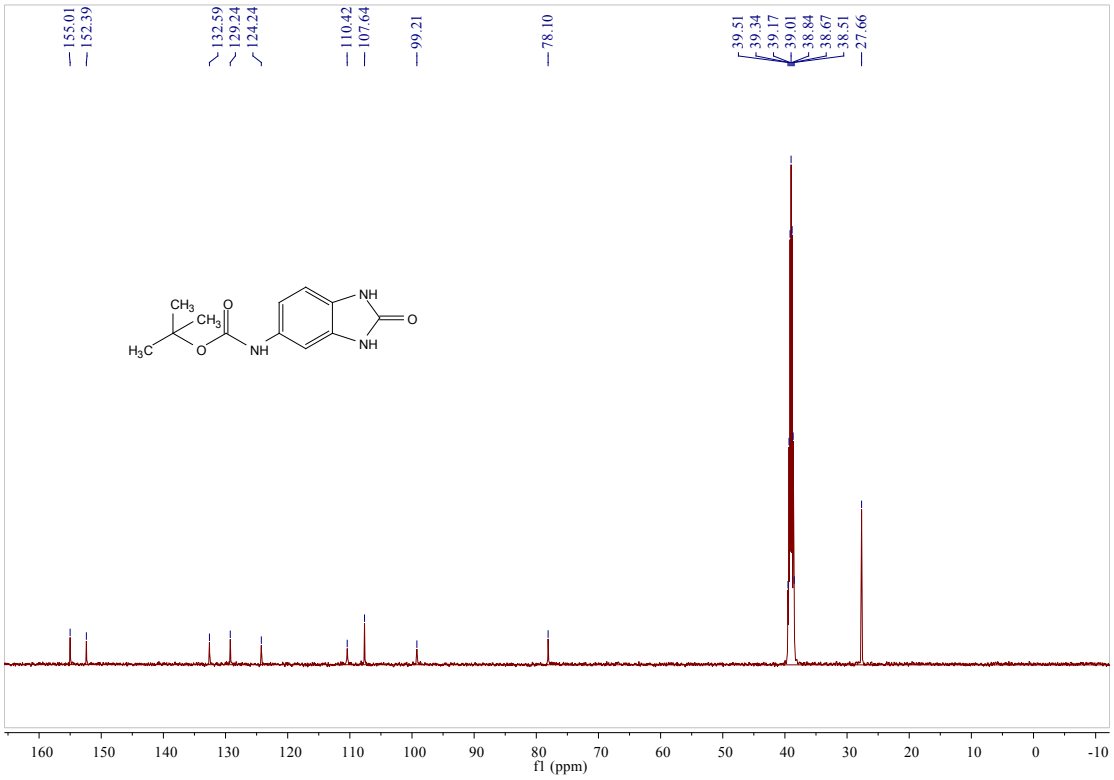


Fig. 2-2 ^{13}C NMR spectrum of **3** in DMSO-d_6, 500MHz

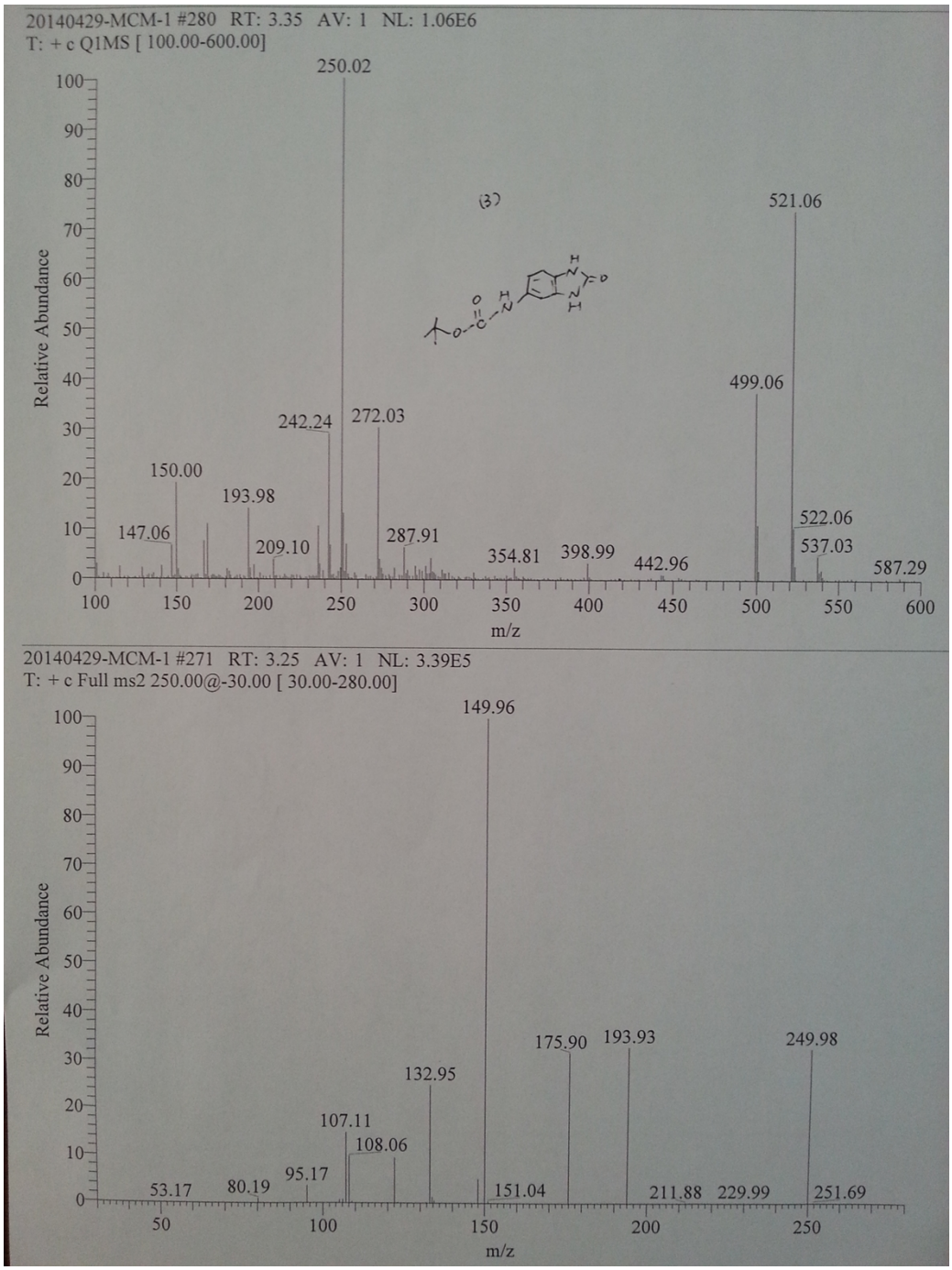


Fig.2-3 MS(ESI) spectrum of **3**

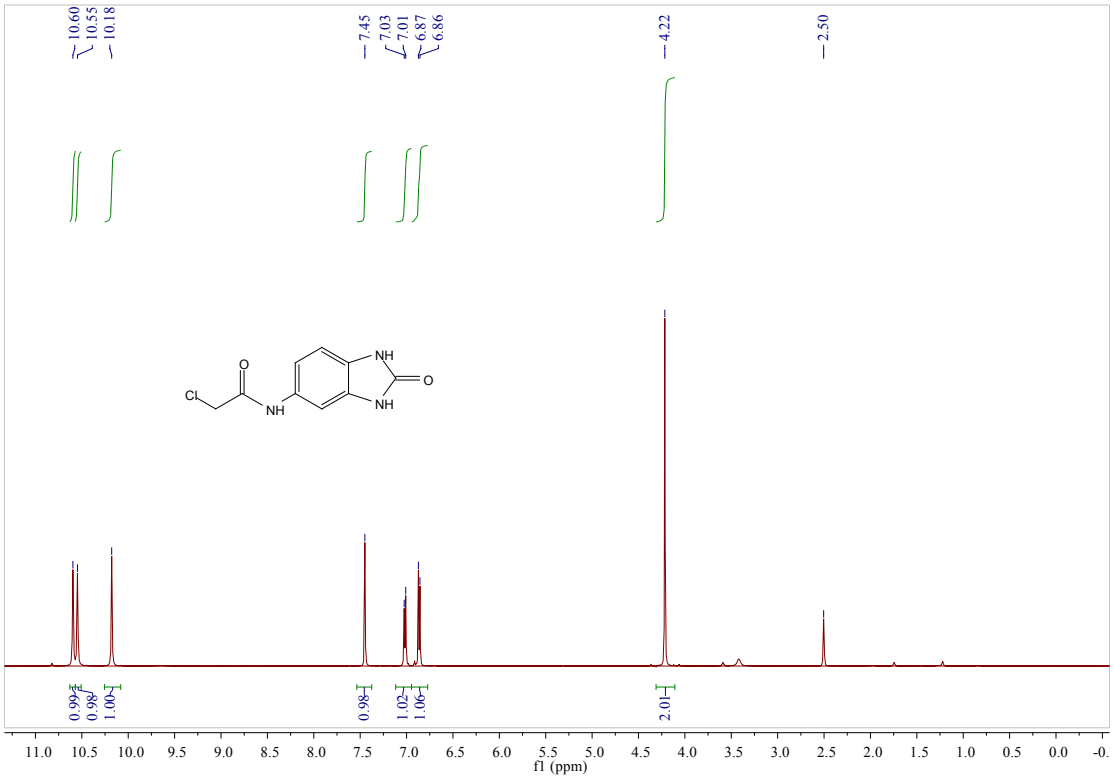


Fig. 3-1 ^{1}H NMR spectrum of **4** in DMSO-$d_{6,}$ 500MHz

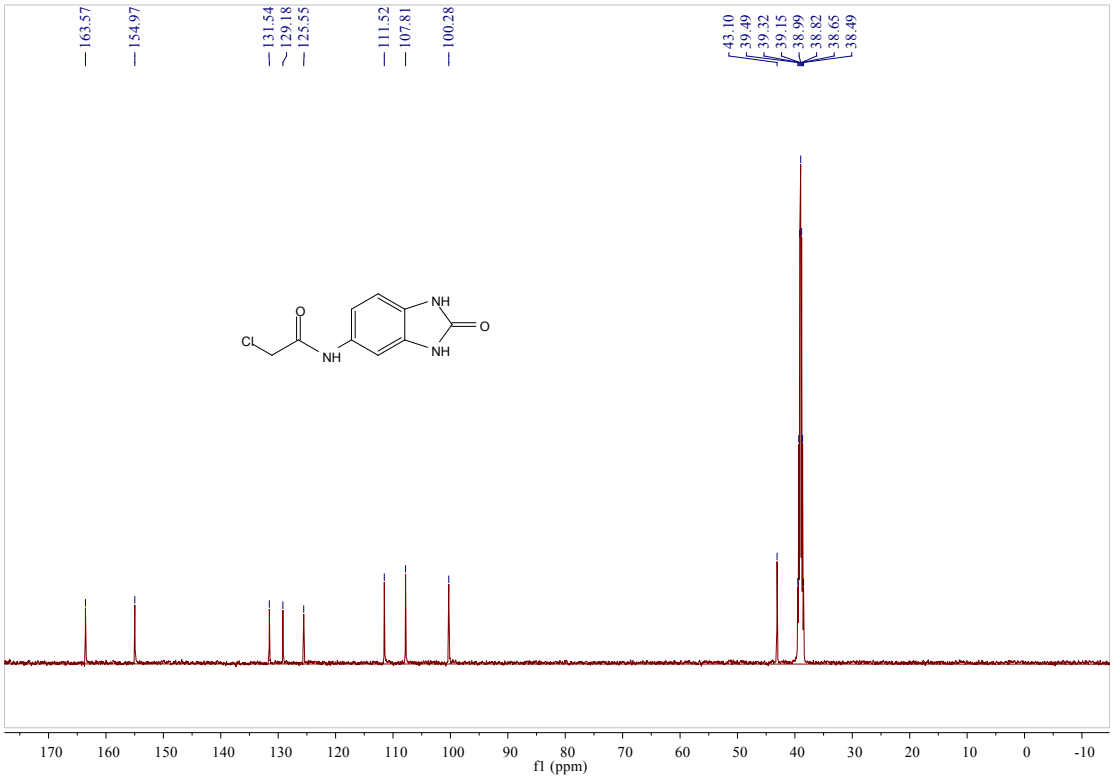


Fig. 3-2 ^{13}C NMR spectrum of **4** in DMSO-$d_{6,}$ 500MHz

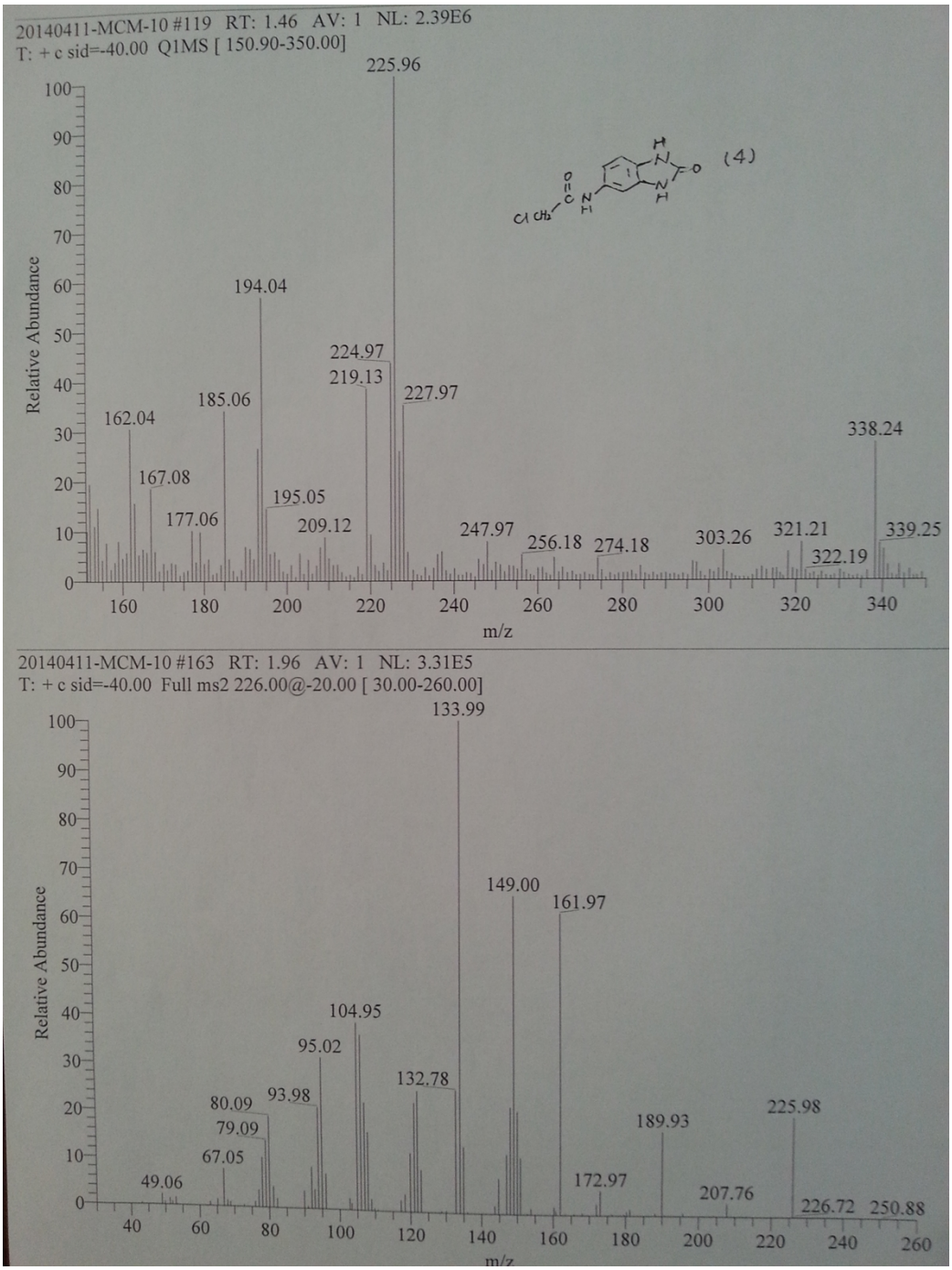


Fig. 3-3 MS(ESI) spectrum of **4**

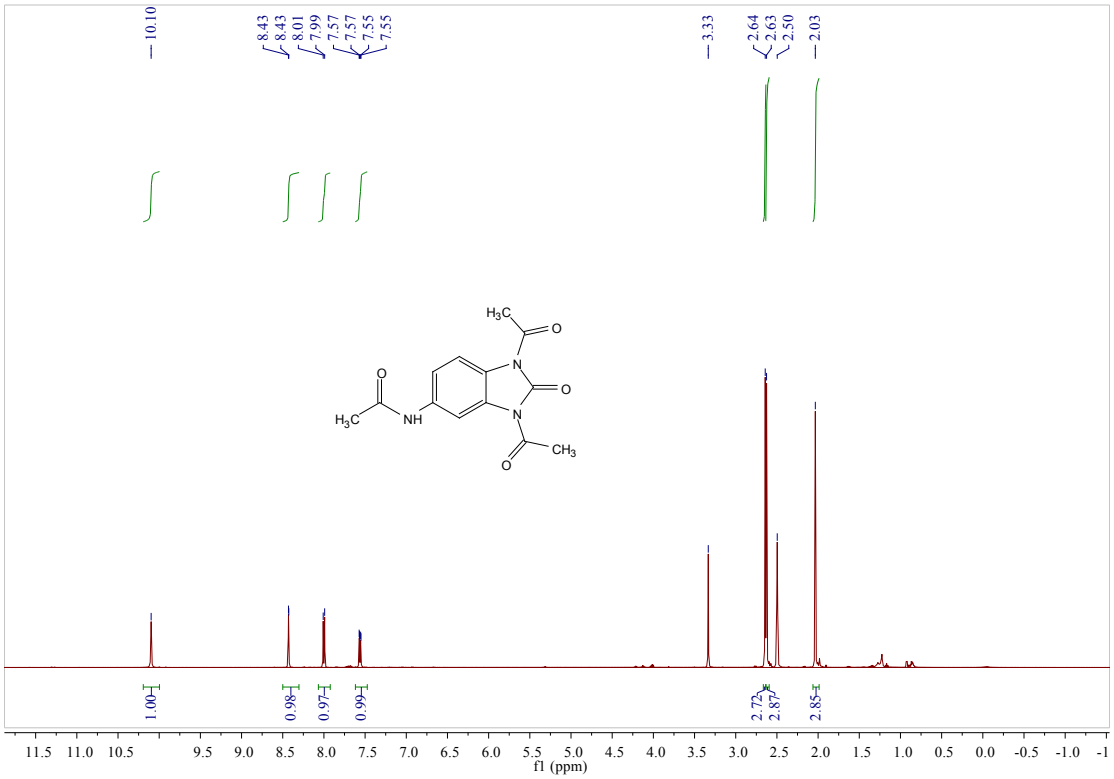


Fig. 4-1 ^{1}H NMR spectrum of **5** in DMSO-$d_{6,}$ 500MHz

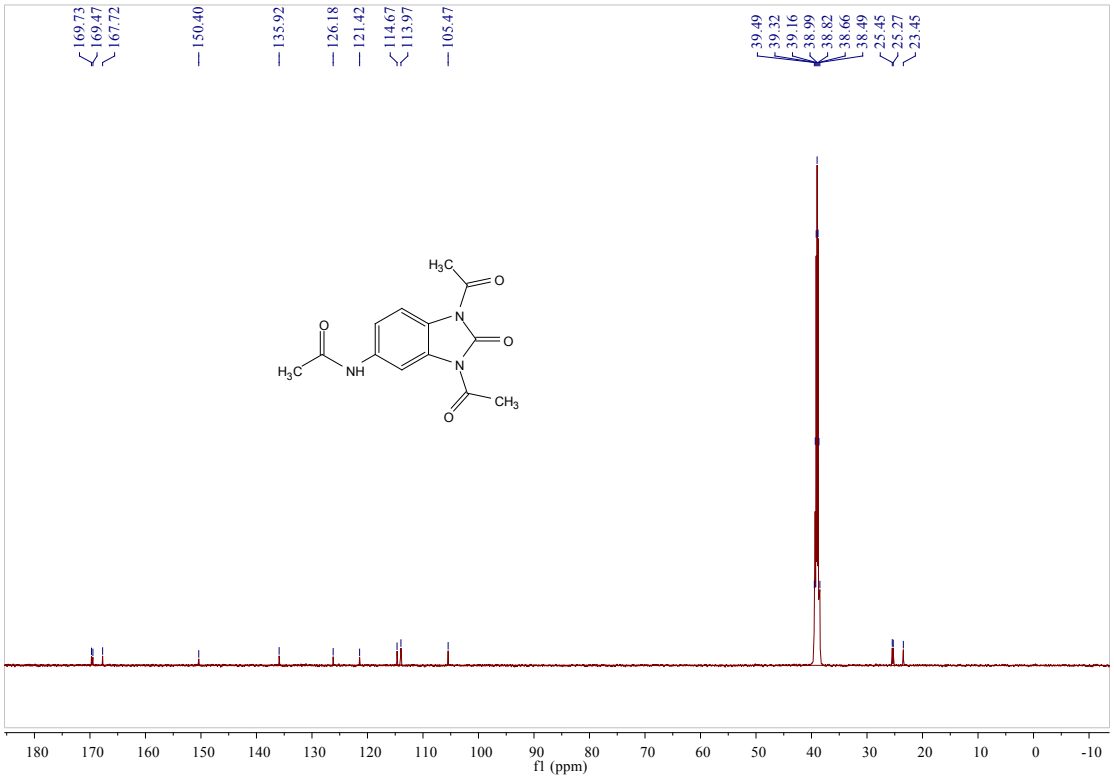


Fig. 4-2 ^{13}C NMR spectrum of **5** in DMSO-$d_{6,}$ 500MHz

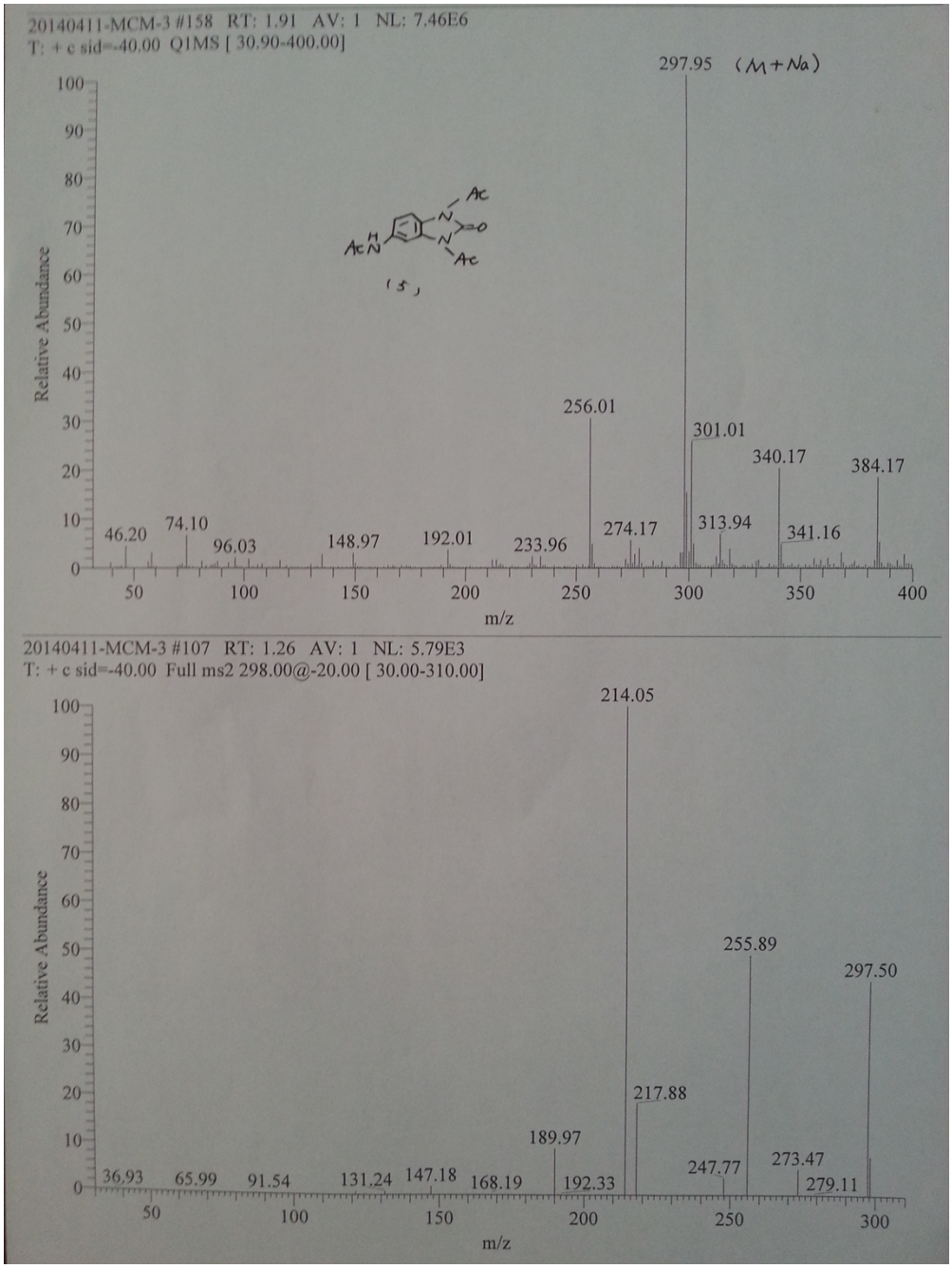


Fig. 4-3 MS(ESI) spectrum of **5**

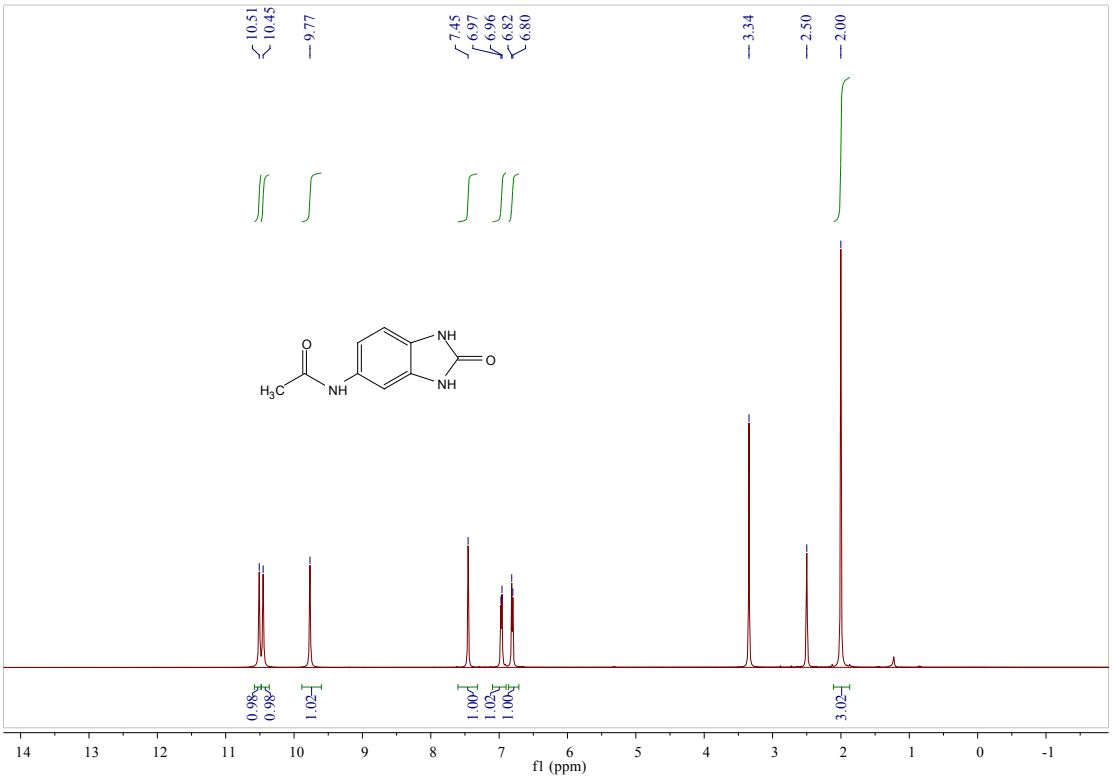


Fig. 5-1 ^{1}H NMR spectrum of **6** in DMSO-$d_{6,}$ 500MHz

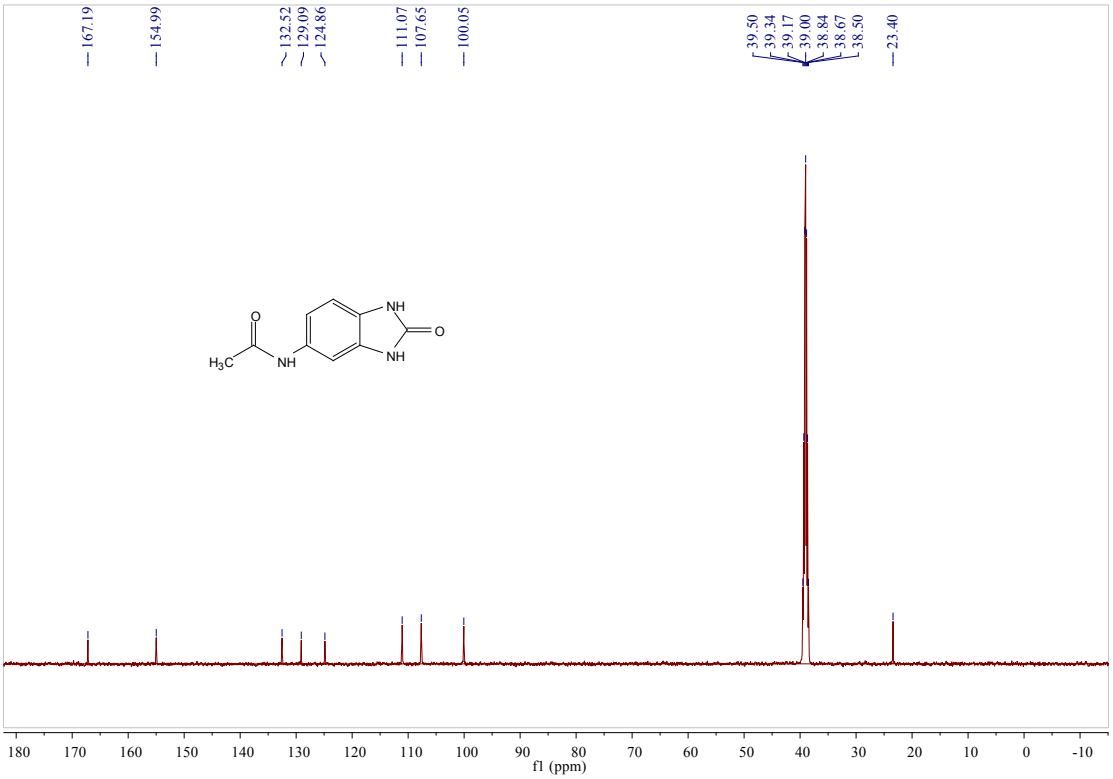


Fig. 5-2 ^{13}C NMR spectrum of **6** in DMSO-$d_{6,}$ 500MHz

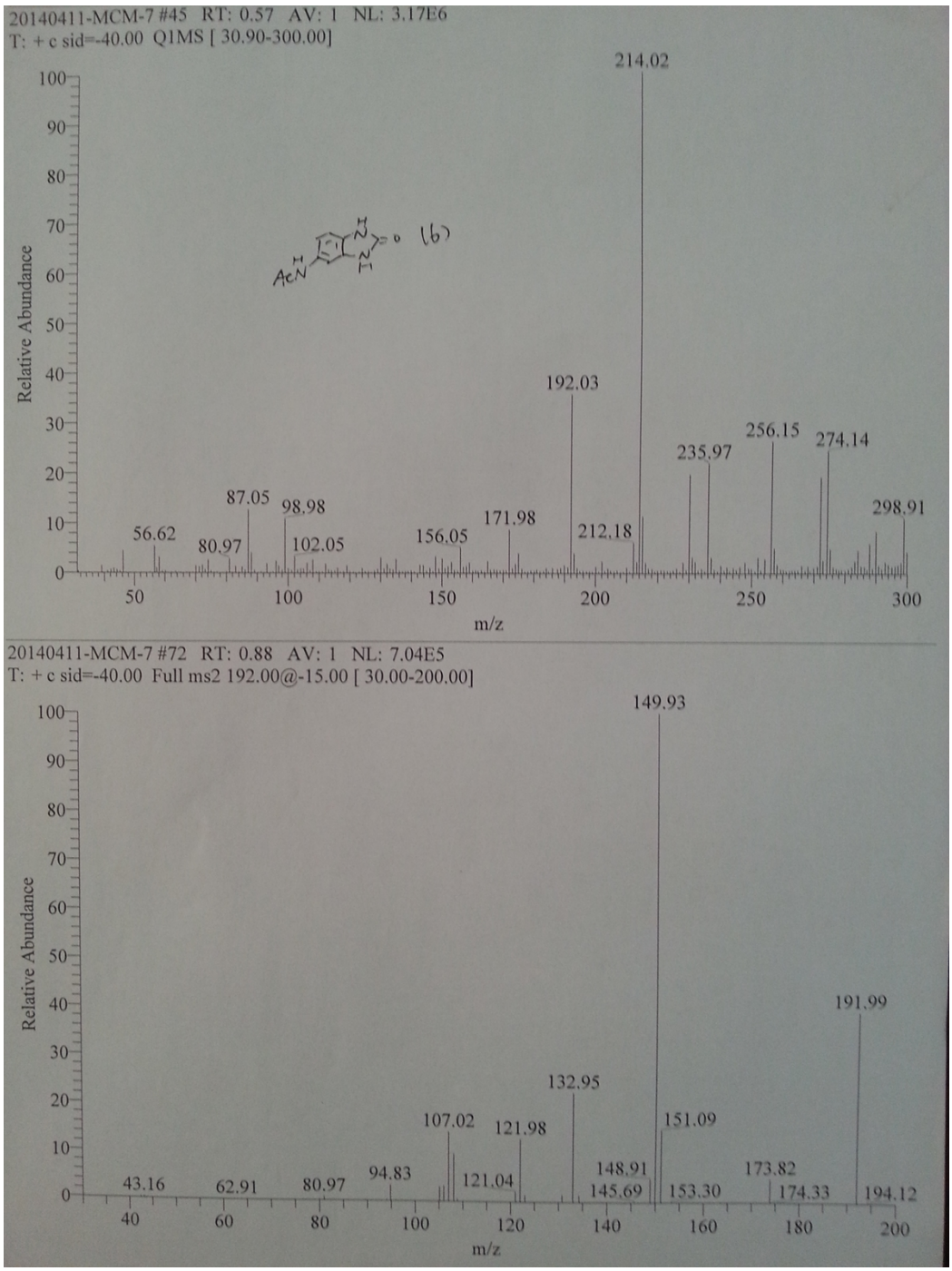


Fig. 5-3 MS(ESI) spectrum of **6**

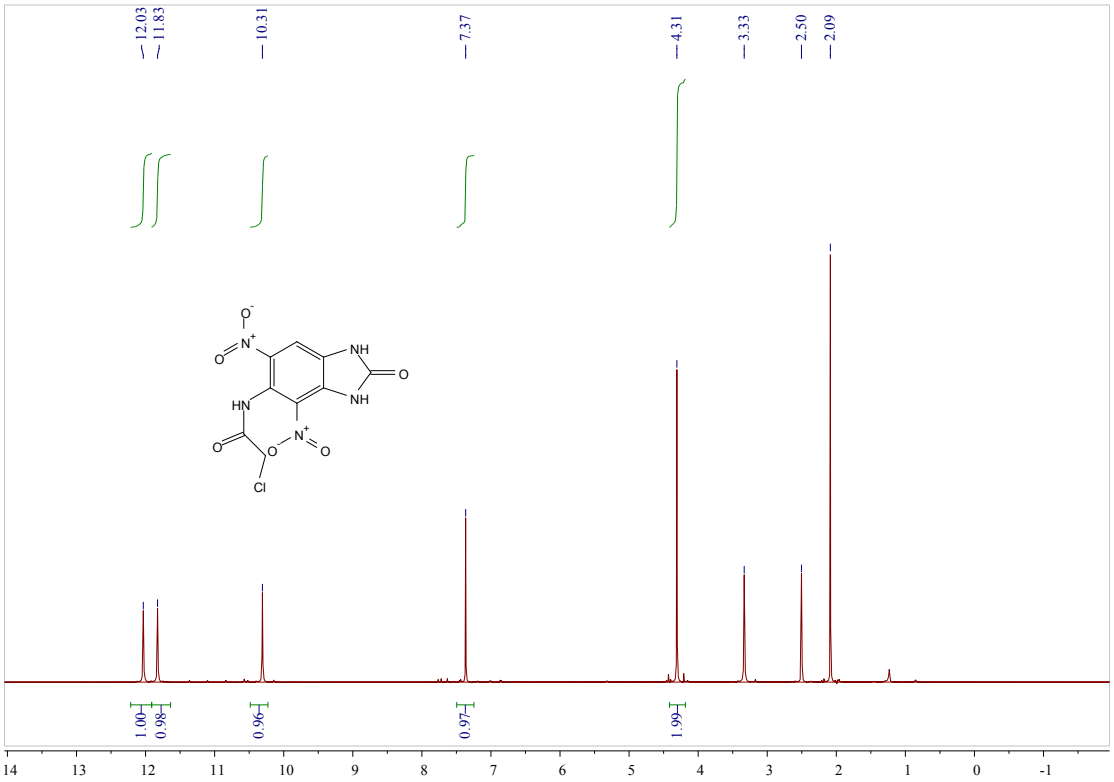


Fig. 6-1 ^{1}H NMR spectrum of **7** in DMSO-$d_{6,}$ 500MHz

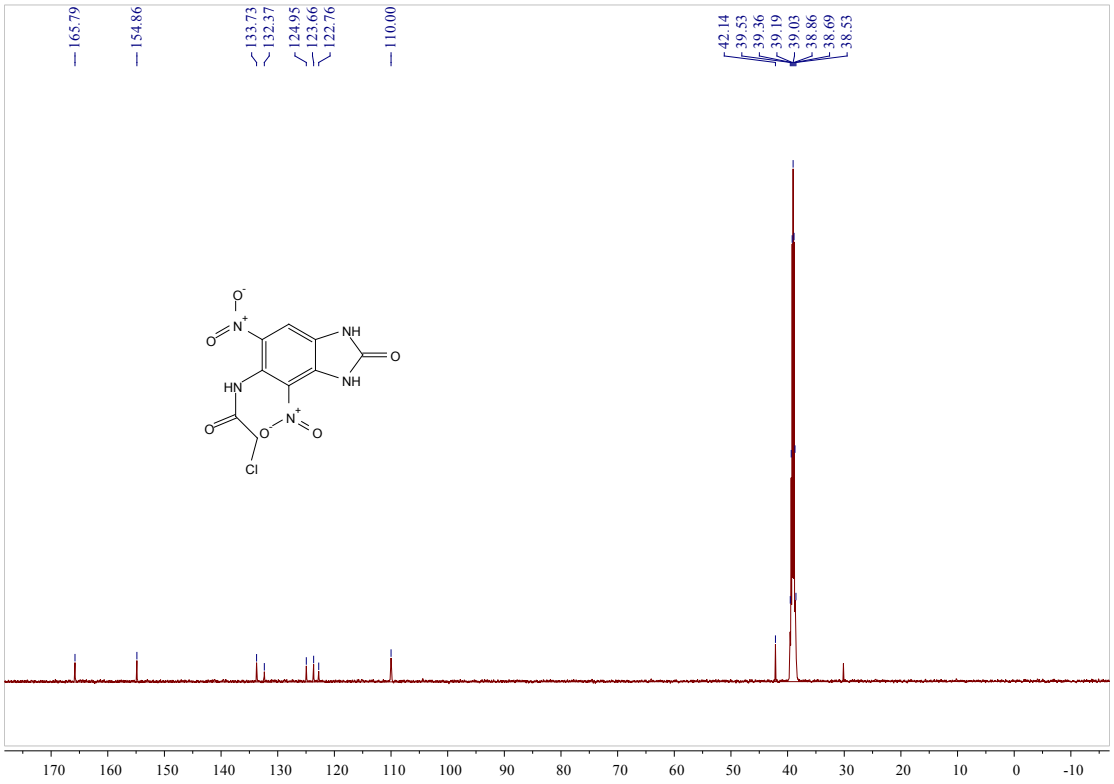


Fig. 6-2 ^{13}C NMR spectrum of **7** in DMSO-$d_{6,}$ 500MHz

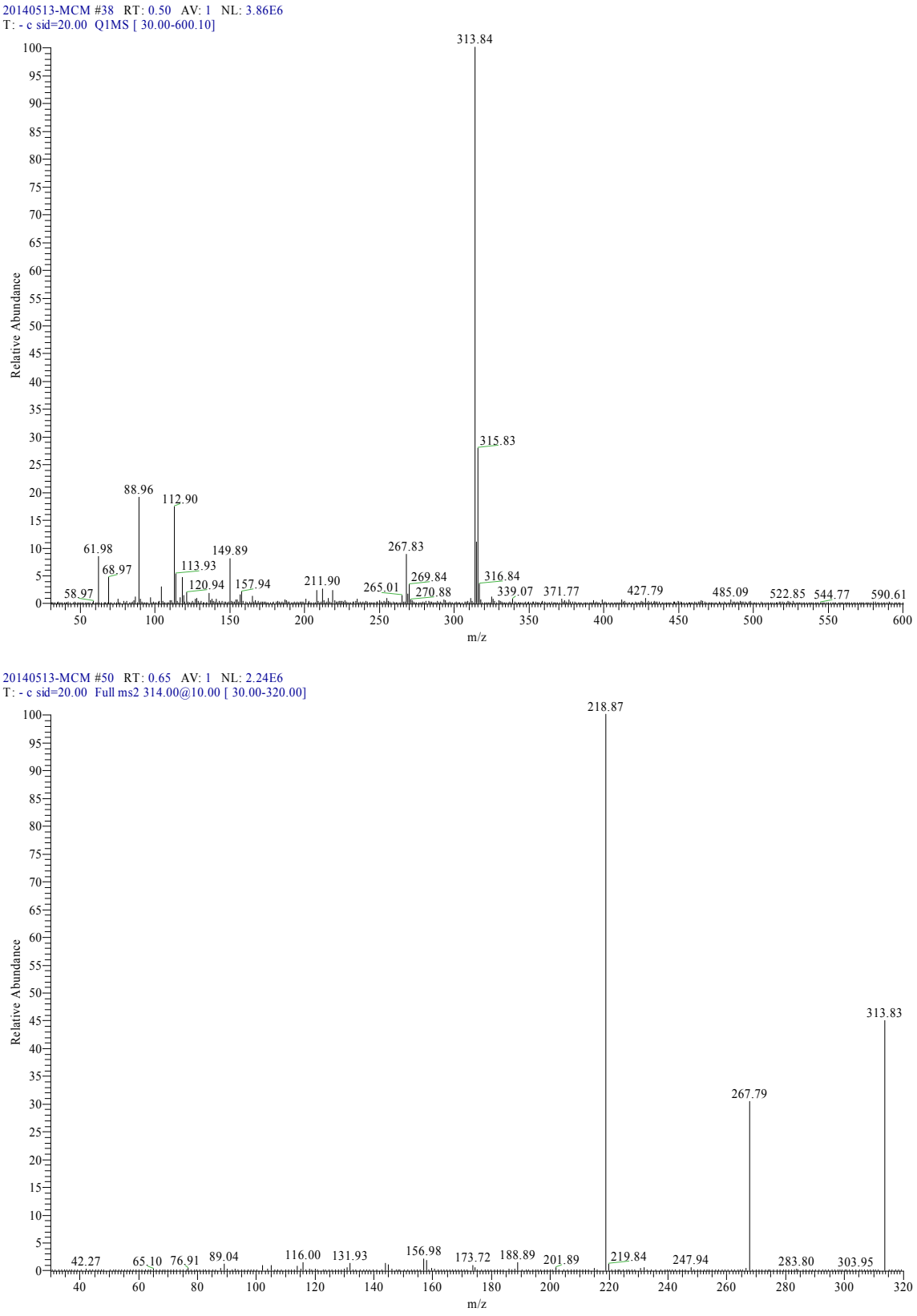


Fig. 6-3 MS(ESI) spectrum of **7**

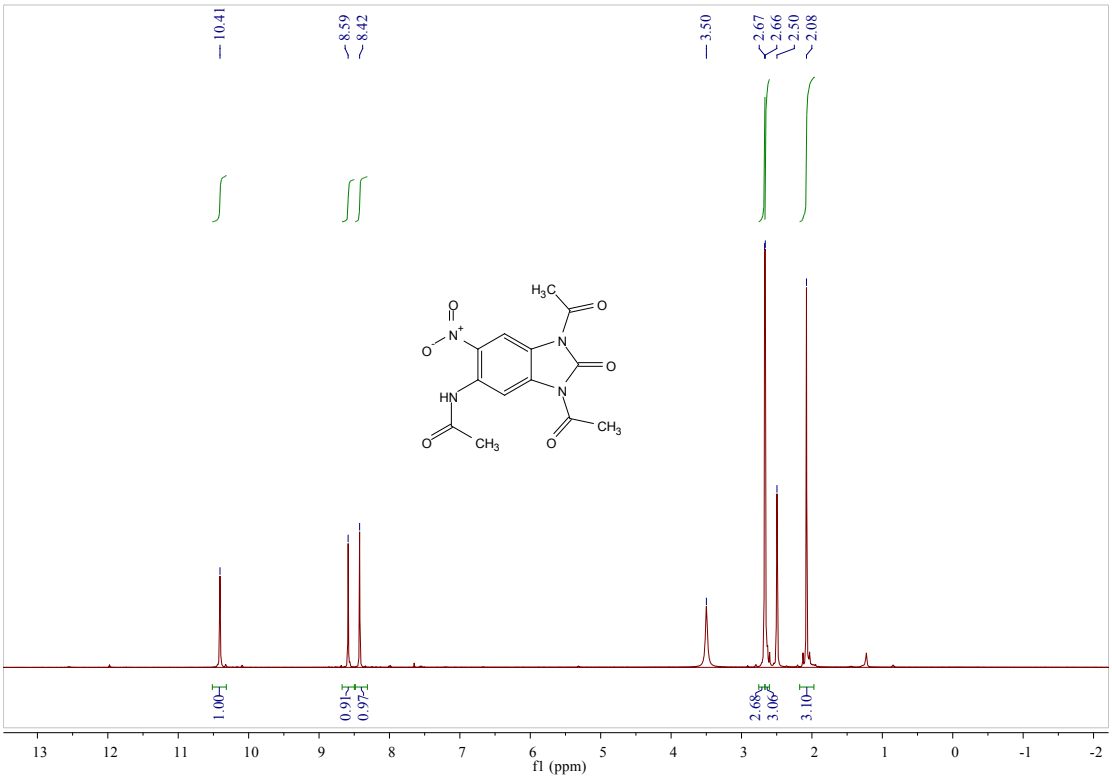


Fig. 7-1 ^{1}H NMR spectrum of **8** in DMSO-d_6, 500MHz

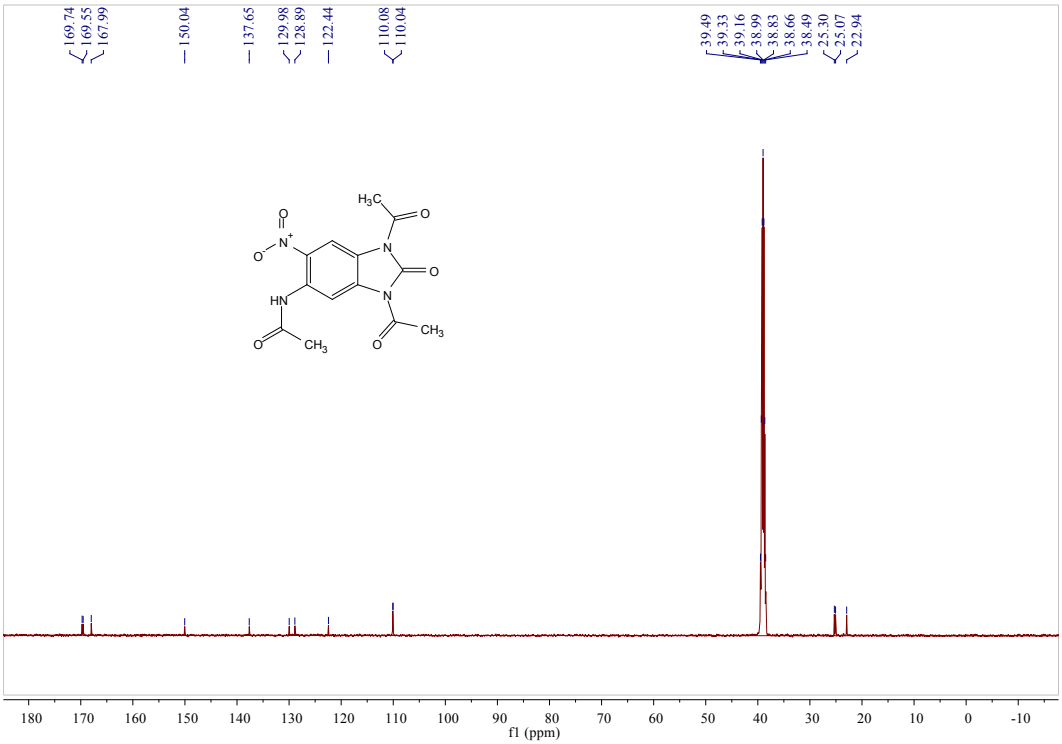


Fig. 7-2 ^{13}C NMR spectrum of **8** in DMSO-d_6, 500MHz

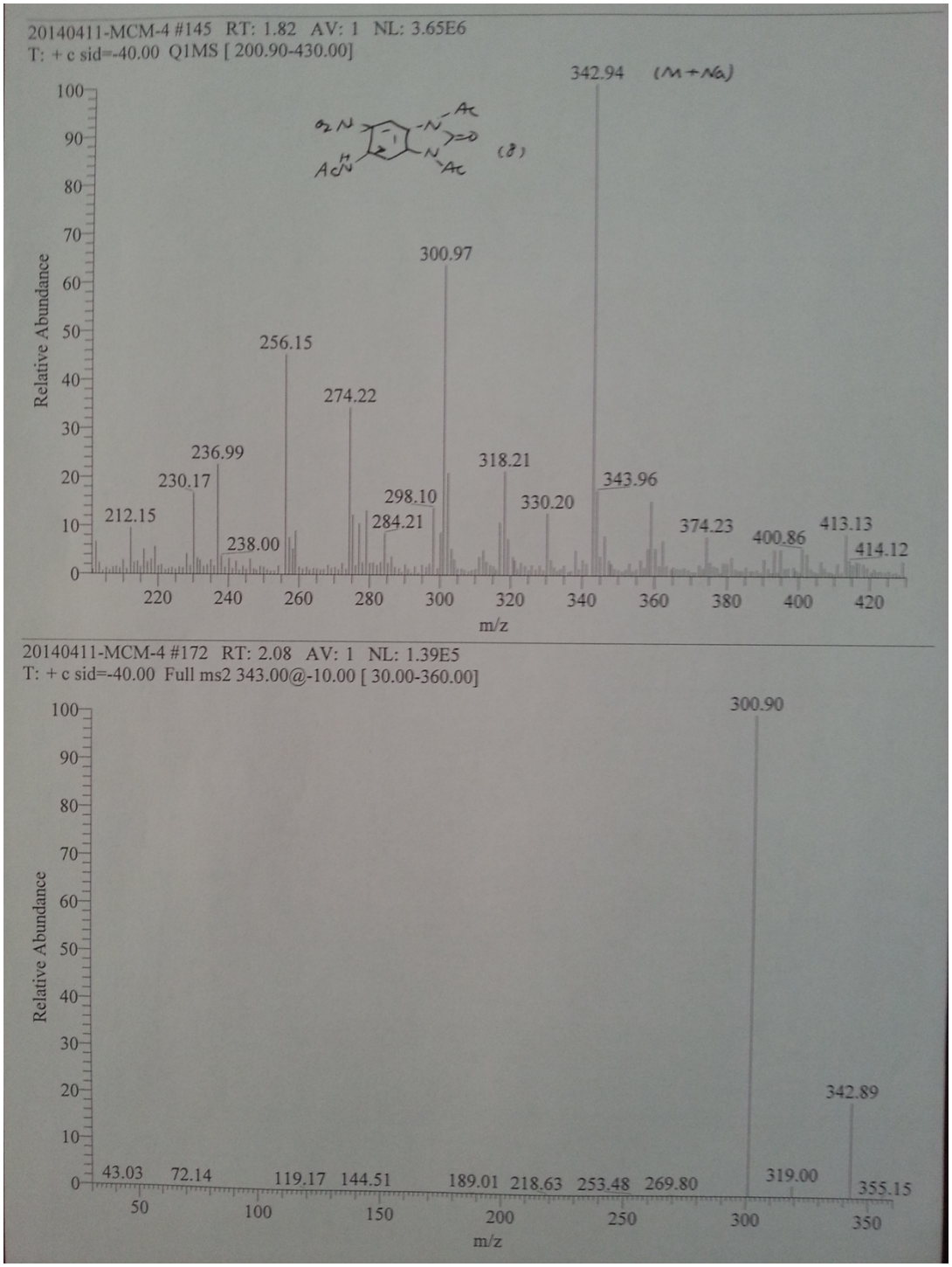


Fig. 7-3 MS(ESI) spectrum of **8**

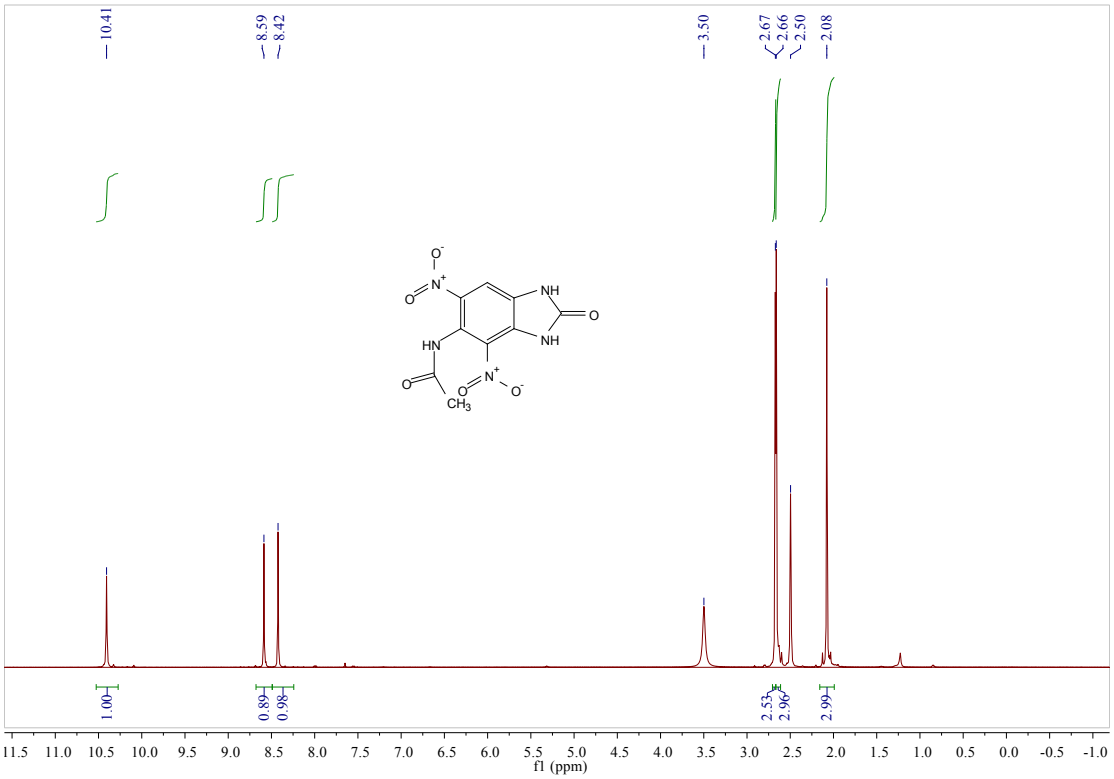


Fig. 8-1 ^{1}H NMR spectrum of **9** in DMSO-d_6, 500MHz

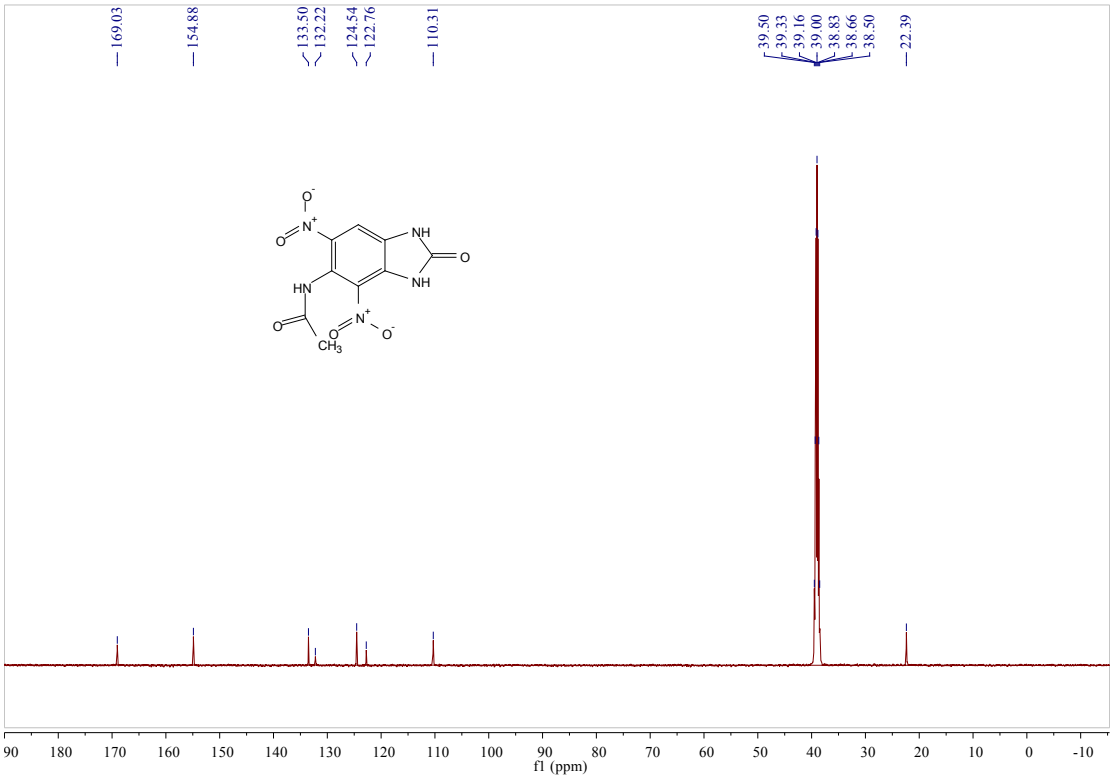


Fig. 8-2 ^{13}C NMR spectrum of **9** in DMSO-d_6, 500MHz

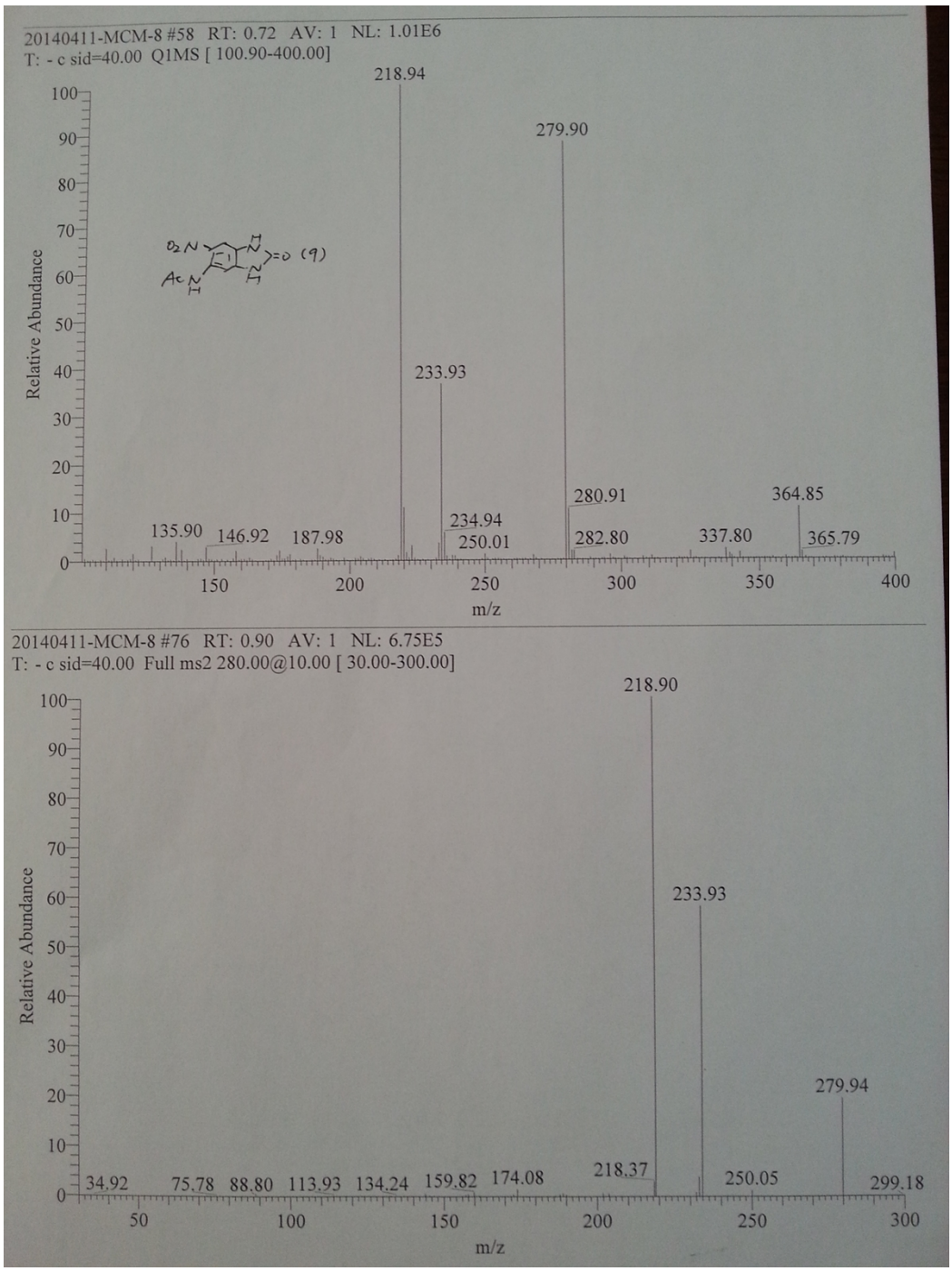


Fig. 8-3 MS(ESI) spectrum of **9**

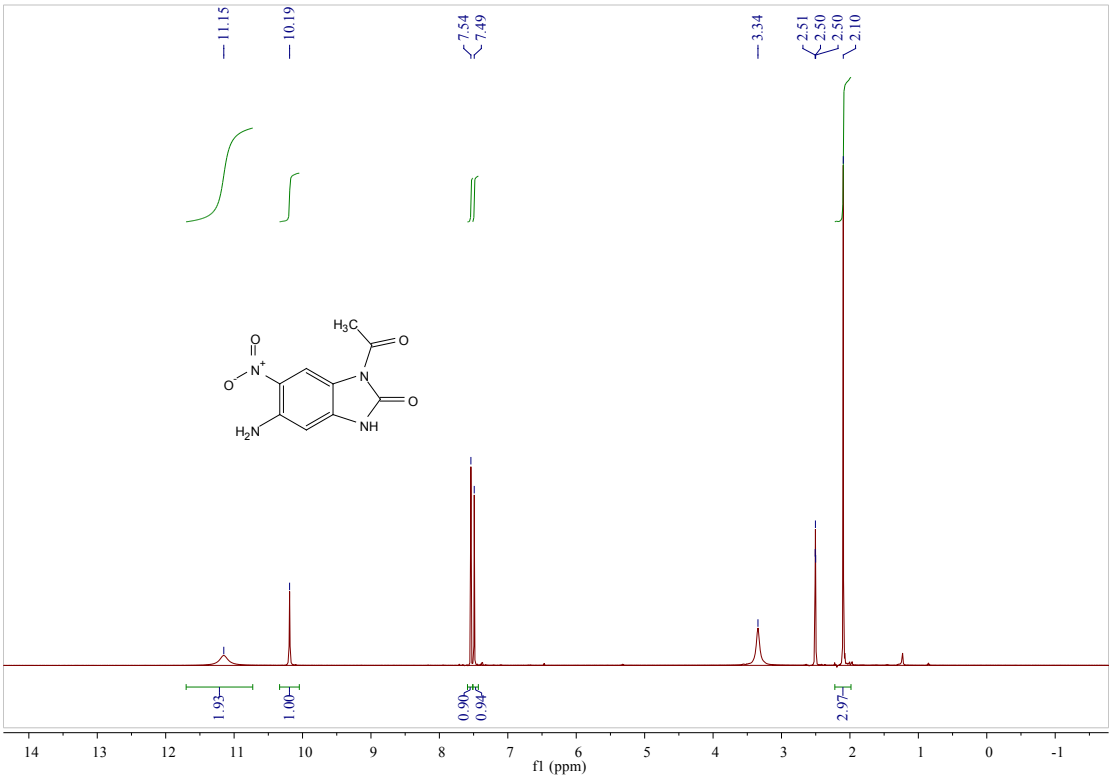


Fig. 9-1 ^{1}H NMR spectrum of **11** in DMSO-$d_{6,}$ 500MHz

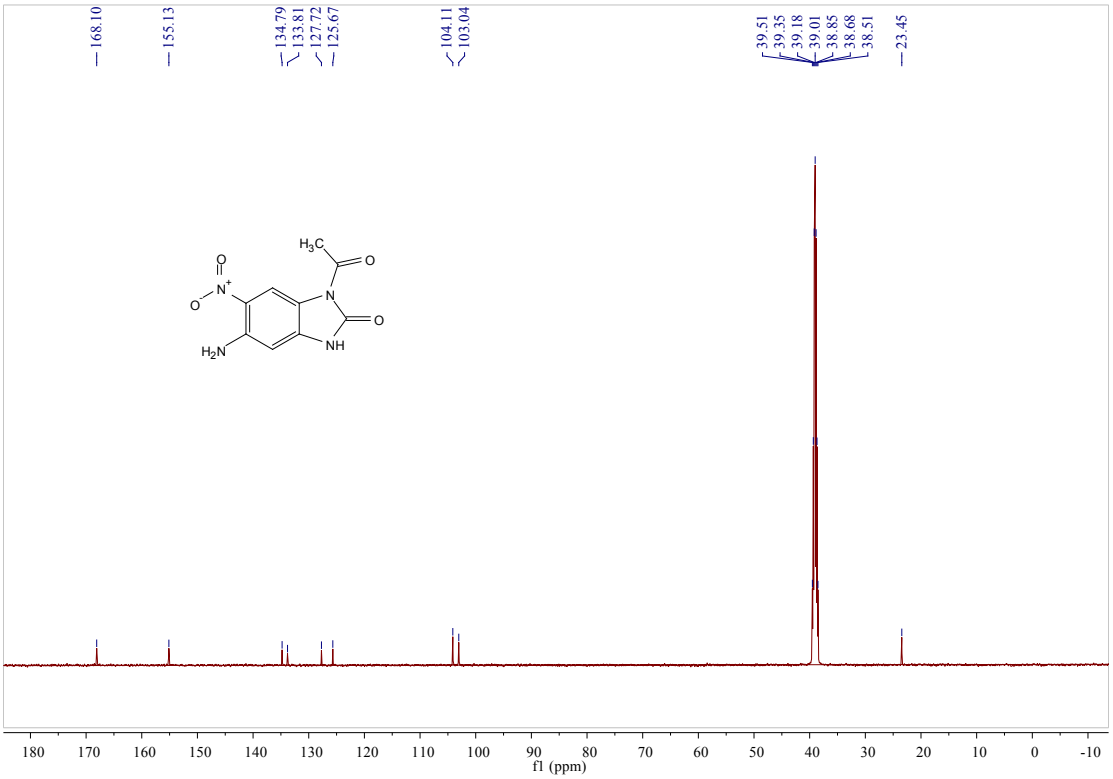


Fig. 9-2 ^{13}C NMR spectrum of **11** in DMSO-$d_{6,}$ 500MHz

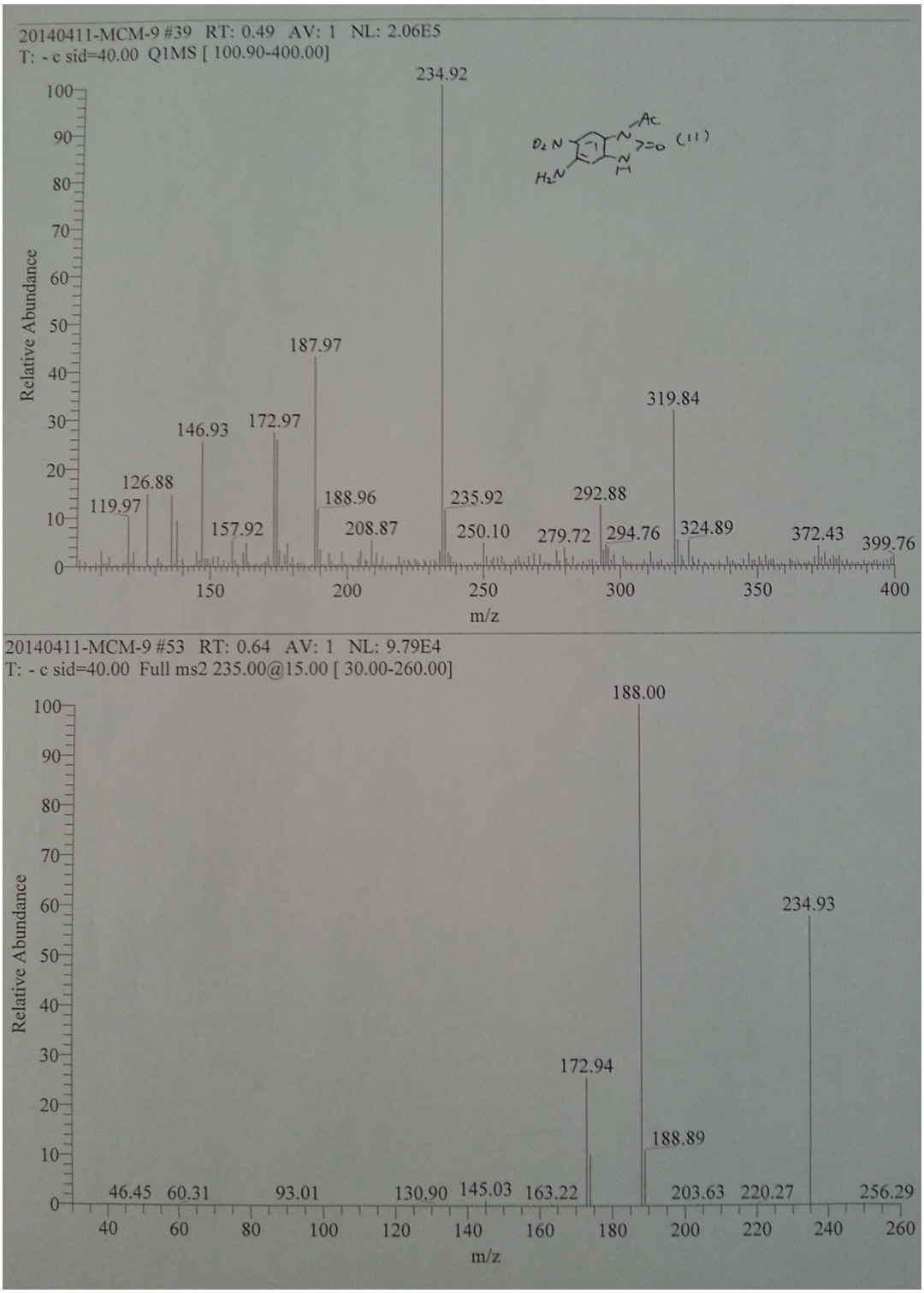
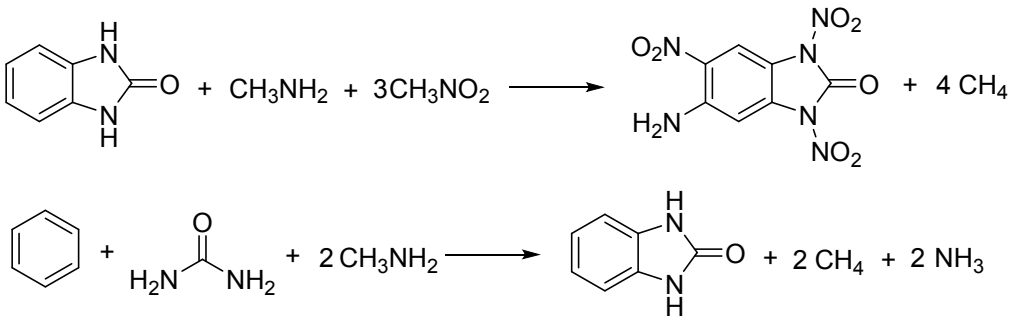


Fig. 9-3 MS(ESI) spectrum of **11**

Part C: Designed isodesmic reactions



Scheme 1 The designed isodesmic reactions for the prediction of (ΔH^o_f gas)