One-pot Synthesis of Novel Functionalized Benzodiazepines via Three-component or Domino Reaction

Yue-Wei Sun Lan-Zhi Wang*

Hebei Normal University, College of Chemistry and Material Science

Shijiazhuang, 050024 (P. R. China)

Tel. 13933001162

E-mail: wanglanzhi@126.com

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Materials and Methods

Melting points were determined in open capillaries and were uncorrected. The ^{1}H NMR and ^{13}C-NMR spectral analysis were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz, respectively in DMSO-*d6* with chemical shift given in parts per million relative to tetramethylsilane (TMS) as internal standard. The signal multiplicities are represented by s (singlet), d (doublet), t (triplet), m (multiplet), and q (quartet). The IR spectra were taken on a Thermo SCIENTIFIC IR spectrophotometer in KBr pellets and reported in cm^{-1}. The elemental analysis (C, H, N) were performed with a VarioELIII Elemental Analyser. The structure of **5bac** was further determined by single-crystal X-ray diffraction on a Bruker Smart-1000 diffractometer. Low-resolution mass spectra were recorded on a Thermo DSQ II mass spectrometer. Synthetic grade chemicals were purchased from Aladdin and were used as received. The solvents were commercial products of analytical grade and dried according to the literature as necessary. The reactions were monitored by thin-layer chromatography (TLC) on pre-coated silica gel GF254 plates.

Experimental

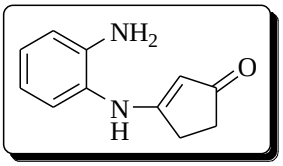
Synthesis of benzo[b][1,4]diazepine derivatives 4aaa-4dab

In a 50 mL reaction vial, the 1,2-benzenediamines **1a** (1 mmol), cyclopentane-1,3-dione **2a** (1 mmol), 2-thiazolecarboxaldehyde **3a** (1 mmol), and EtOH (2 mL) were mixed, Subsequently, the CeCl3 (0.1 mmol) was added to the reaction mixture and stirred under room temperature. Upon completion, monitored by TLC, the reaction mixture was cooled, filtered to give the crude product, which was further washed by 94% EtOH to give pure product **4aaa**.

Synthesis of benzo[b][1,4]diazepine derivatives 5aac-5daf

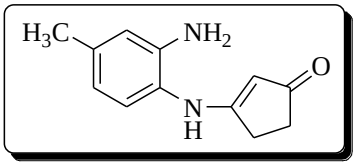
In a 50 mL reaction vial, the 1,2-benzenediamines **1a** (1 mmol), cyclopentane-1,3-dione **2a** (1 mmol) and EtOH (2 mL) were mixed and then stirred under room temperature. Subsequently, the ethyl glyoxalate **3c** (1 mmol) and γ-Fe_2O_3@SiO_2/$CeCl_3$ (0.1 mmol) were added to the reaction mixture. Upon completion, monitored by TLC, the reaction mixture was cooled, filtered to give the crude product, which was further washed by 98% EtOH to give pure product **5aac**.

Intermediate **7aa**



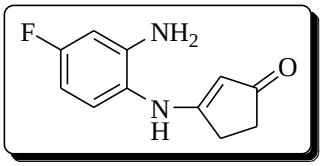
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.20 (2H, t, J=1.0 Hz), 2.67 (2H, t, J=1.0 Hz), 4.73 (1H, s), 4.97 (2H, s), 6.53-6.99 (4H, m), 8.73 (1H, s).

Intermediate **7ba**



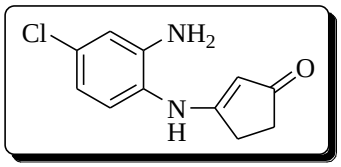
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.16 (3H, s), 2.19 (2H, t, J=1.0 Hz), 2.66 (2H, t, J=1.0 Hz), 4.67 (1H, s), 4.88 (2H, s), 6.35-6.86 (3H, m), 8.66 (1H, s).

Intermediate **7ca**



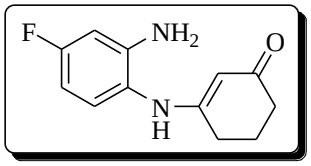
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.20 (2H, t, J=1.0 Hz), 2.67 (2H, t, J=1.0 Hz), 4.63 (1H, s), 5.31 (2H, s), 6.31-6.98 (3H, m), 8.67 (1H, s).

Intermediate **7da**



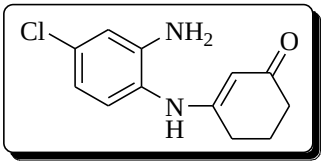
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.20 (2H, t, J=1.0 Hz), 2.67 (2H, t, J=1.0 Hz), 4.72 (1H, s), 5.32 (2H, s), 6.53-6.99 (3H, m), 8.73 (1H, s).

Intermediate **7cb**



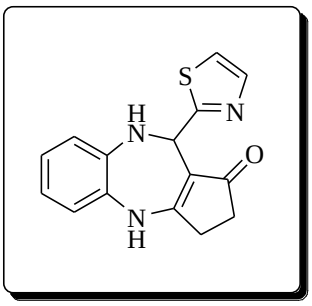
^{1}H NMR (300 MHz, DMSO-d_6): δ 1.87 (2H, m, J=1.0 Hz), 2.09 (2H, t, J=1.0 Hz), 2.47 (2H, t, J=1.0 Hz), 4.57 (1H, s), 5.24 (2H, s), 6.28-6.89 (3H, m), 8.09 (1H, s).

Intermediate **7db**



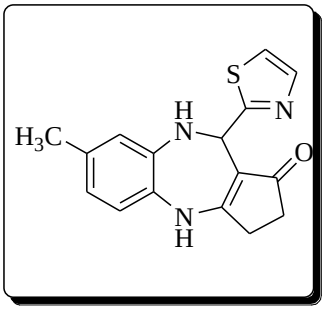
^{1}H NMR (300 MHz, DMSO-d_6): δ 1.87 (2H, m, J=1.0 Hz), 2.10 (2H, t, J=1.0 Hz), 2.48 (2H, t, J=1.0 Hz), 4.60 (1H, s), 5.25 (2H, s), 6.53-6.90 (3H, m), 8.14 (1H, s).

10-thiazolyl-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(4aaa)**



Yield: 94%;
Characteristic: Pale yellow solid;
M.p.: 277-278 °C;
IR (KBr): 3334, 3101, 1600, 1555 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.34 (2H, t), 2.74 (2H, t), 5.37 (1H, d, J=5.0 Hz), 6.28 (1H, d, J=5.0 Hz), 6.66-6.79 (4H, m), 7.39 (1H, d, J=3.0 Hz), 7.60 (1H, d, J=3.0 Hz), 9.90 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 26.98; 33.33; 54.81; 113.78; 120.15; 120.44 121.29;123.08; 123.59; 131.76; 137.80; 142.59; 167.56; 173.52; 199.48;
MS calcd for $C_{15}H_{13}N_3OS$ 283, found 284 (M+1);
Anal.calcd (%) for $C_{15}H_{13}N_3OS$: C 63.58, H 4.62, N 14.83; found: C 63.24, H 4.25, N 15.13.

7-methyl-10-thiazolyl-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(4baa)**



Yield:96%;
Characteristic: Cream colored solid;
M.p.: 264-266 °C;
IR (KBr): 3263, 3094, 1607, 1555 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.06 (3H, s), 2.33 (2H, t), 2.71 (2H, t), 5.35 (1H, d, J=5.0 Hz),

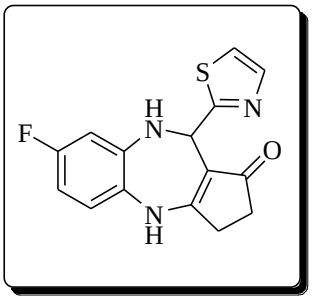
6.20 (1H, d, *J*=5.0 Hz), 6.47-6.88 (3H, m), 7.40 (1H, d, *J*=3.0 Hz), 7.61 (1H, d, *J*=3.0 Hz), 9.85 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 20.72, 26.93; 33.35; 54.71; 113.45; 120.22; 120.46 122.02;123.15; 129.25; 132.46; 137.62; 142.64; 167.41; 173.63; 199.30;

MS calcd for $C_{16}H_{15}N_3OS$ 297, found 298 (M+1);

Anal.calcd (%) for $C_{16}H_{15}N_3OS$: C 64.62, H 5.08, N 14.13; found: C 64.37, H 4.97, N 14.34.

7-fluoro-10-thiazolyl-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)- one **(4caa)**



Yield: 91%;

Characteristic: White solid;

M.p.: 265-266 °C;

IR (KBr): 3275, 3108, 1600, 1555 cm^{-1};

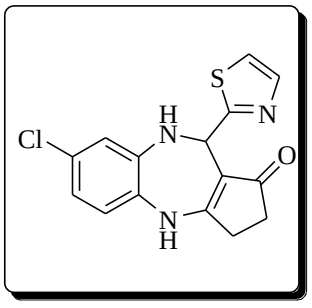
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.34 (2H, t), 2.72 (2H, t), 5.35 (1H, d, *J*=5.0 Hz), 6.57 (1H, d, *J*=5.0 Hz), 6.51-7.00 (3H, m), 7.43 (1H, d, *J*=3.0 Hz), 7.63 (1H, d, *J*=3.0 Hz), 9.95 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 26.90; 33.32; 54.62; 107.61; 107.84; 108.62; 108.86; 113.26; 120.28; 121.56; 121.65; 128.31; 139.54; 139.64; 142.72; 157.15; 159.53; 167.27; 173.13; 199.40;

MS calcd for $C_{15}H_{12}FN_3OS$ 301, found 302 (M+1);

Anal.calcd (%) for $C_{15}H_{12}FN_3OS$: C 59.79, H 4.01, N 13.94; found: C 59.58, H 3.89, N 14.11.

7-chloro-10-thiazolyl-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)- one **(4daa)**



Yield: 92%;

Characteristic: Light grey solid;

M.p.: 249-252 °C;

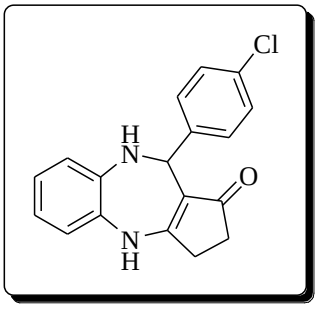
IR (KBr): 3269, 3108, 1607, 1562 cm^{-1};

^{1}H NMR (300 MHz, DMSO-d_6): δ 2.35 (2H, t), 2.73 (2H, t), 5.36 (1H, d, *J*=5.0 Hz), 6.60 (1H, d, *J*=5.0 Hz), 6.76-6.79 (4H, m), 7.44 (1H, d, *J*=3.0 Hz), 7.64 (1H, d, *J*=3.0 Hz), 10.01 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 26.94; 33.33; 54.52; 113.80; 120.33; 120.81; 121.79;126.77; 130.76; 139.33; 142.78; 167.24; 172.94; 199.59;

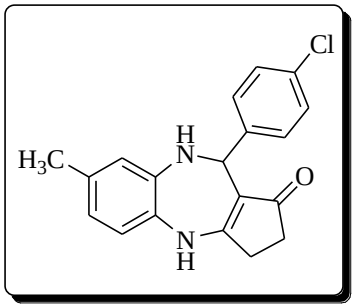
MS calcd for $C_{15}H_{12}ClN_3OS$ 317, found 318 (M+1);
Anal.calcd (%) for $C_{15}H_{12}ClN_3OS$: C 56.69, H 3.81, N 13.22; found: C 59.96, H 4.24, N 13.20.

10-(4-chlorophenyl)-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(4aab)**



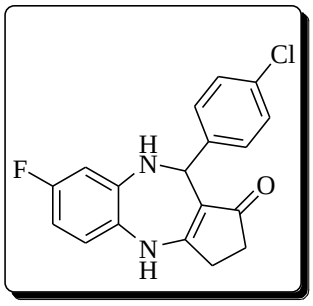
Yield: 95%;
Characteristic: Cream colored solid;
M.p.: 158-160 °C;
IR (KBr): 3308, 3062, 1600, 1562 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.33 (2H, t), 2.75 (2H, t), 5.09 (1H, d, *J*=4.5 Hz), 6.10 (1H, d, *J*=4.5 Hz), 6.56-6.97 (4H, m), 7.08 (2H, d, *J*=8.0 Hz), 7.21 (2H, d, *J*=8.0 Hz), 9.82 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 26.98; 33.39; 56.28; 114.25; 120.34; 120.90; 122.71;123.45; 128.26; 129.43; 131.26; 131.90; 138.21; 143.59; 167.67; 199.77;
MS calcd for $C_{18}H_{15}ClN_2O$ 310, found 311 (M+1);
Anal.calcd (%) for $C_{18}H_{15}ClN_2O$: C 69.57, H 4.86, N 9.01; found: C 69.34, H 4.73, N 9.17.

7-methyl-10-(4-chlorophenyl)-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(4bab)**



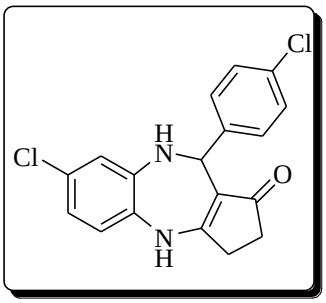
Yield: 97%;
Characteristic: Pale yellow solid;
M.p.: 168-170 °C;
IR (KBr):3275, 3049, 1620, 1555 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.04 (3H, s), 2.31 (2H, t), 2.73 (2H, t), 5.07 (1H, d, *J*=4.0 Hz), 6.03 (1H, d, *J*=4.0 Hz), 6.38-6.87 (3H, m), 7.09 (2H, d, *J*=8.0 Hz), 7.22 (2H, d, *J*=8.0 Hz), 9.79 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 20.67; 26.90; 33.38; 56.15; 113.89; 120.32; 121.56; 122.77;128.30; 129.30; 129.43; 131.23; 132.27; 137.99; 143.70; 167.45; 199.53;
MS calcd for $C_{19}H_{17}ClN_2O$ 325, found 326 (M+1);
Anal.calcd (%) for $C_{19}H_{17}ClN_2O$: C 70.26, H 5.28, N 8.62; found: C 70.43, H 5.41, N 8.36.

7-fluoro-10-(4-chlorophenyl)-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(4cab)**



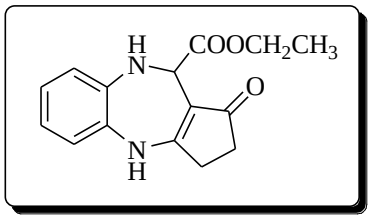
Yield: 92%;
Characteristic: White solid;
M.p.: 148-150 °C;
IR (KBr): 3301; 3088, 1620, 1562 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.33 (2H, t), 2.74 (2H, t), 5.09 (1H, d, *J*=4.0 Hz), 6.37 (1H, d, *J*=4.0 Hz), 6.42-6.99 (3H, m), 7.09 (2H, d, *J*=8.0 Hz), 7.25 (2H, d, *J*=8.0 Hz), 9.89 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 26.89; 33.38; 56.19; 107.16; 107.38; 108.23; 108.47; 113.76; 121.37; 121.48; 128.40;129.35; 131.44; 139.85; 139.95; 143.29; 157.09; 159.46; 167.28; 199.64;
MS calcd for $C_{18}H_{14}ClFN_2O$ 328, found 329 (M+1);
Anal.calcd (%) for $C_{18}H_{14}ClFN_2O$: C 65.76, H 4.29, N 8.52; found: C 65.36, H 4.49, N 8.01.

7-chloro-10-(4-chlorophenyl)-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(4dab)**



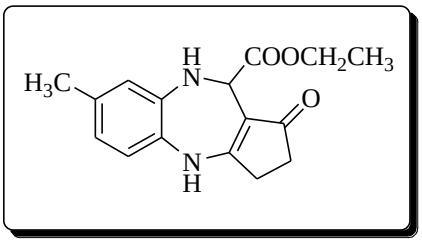
Yield: 91%;
Characteristic: Light grey solid;
M.p.:156-158 °C;
IR (KBr): 3314, 3075, 1600, 1548 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.33 (2H, t), 2.74 (2H, t), 5.08 (1H, d, *J*=4.5 Hz), 6.37 (1H, d, *J*=4.5 Hz), 6.64-6.97 (3H, m), 7.08 (2H, d, *J*=8.0 Hz), 7.26 (2H, d, *J*=8.0 Hz), 9.91 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 26.95; 33.40; 56.18; 114.33; 120.46; 121.39; 121.65;126.62; 128.49; 129.32; 130.87; 131.54; 139.63; 143.18; 167.24; 199.90;
MS calcd for $C_{18}H_{14}Cl_2N_2O$ 345, found 346 (M+1);
Anal.calcd (%) for $C_{18}H_{14}Cl_2N_2O$: C 62.62, H 4.09, N 8.11; found: C 62.41, H 4.34, N 8.36.

10-ester-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(5aac)**



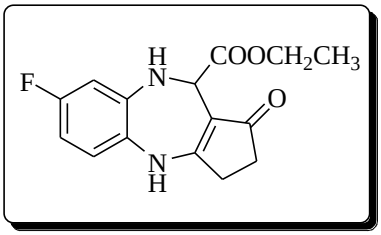
Yield: 96%;
Characteristic: Cream colored solid;
M.p.: 249-250 °C;
IR (KBr): 3301, 3153, 1717, 1626, 1562 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 0.96 (3H, t, J=7.0), 2.30 (2H, t), 2.69 (2H, t), 3.89 (2H, q, J=7.0), 4.56 (1H, d, J=5.0 Hz), 6.19 (1H, d, J=5.0 Hz), 6.78-7.01 (4H, m), 9.85 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 14.51; 26.96; 33.27; 55.92; 60.52; 110.35; 120.35; 120.87; 122.24; 123.38; 131.09; 138.17; 167.42; 171.27; 199.49;
MS calcd for $C_{15}H_{16}N_2O_3$ 272, found 273 (M+1);
Anal.calcd (%) for $C_{15}H_{16}N_2O_3$: C 66.16, H 5.92, N 10.29; found: C 66.37, H 5.79, N 10.43.

7-methyl-10-ester-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(5bac)**



Yield: 97%;
Characteristic: White solid;
M.p.: 260-262 °C;
IR (KBr): 3308, 3262, 1717, 1626, 1562 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 0.98 (3H, t, J=7.0), 2.15 (3H, s), 2.29 (2H, t), 2.67 (2H, t), 3.89 (2H, q, J=7.0), 4.55 (1H, d, J=5.0 Hz), 6.08 (1H, d, J=5.0 Hz), 6.58-6.89 (3H, m), 9.78 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 14.52; 20.73; 26.89; 33.27; 55.82; 60.47; 110.00; 120.31; 121.54; 122.49; 128.66; 132.26; 138.00; 167.29; 171.32; 199.28;
MS calcd for $C_{16}H_{18}N_2O_3$ 286, found 287 (M+1);
Anal.calcd (%) for $C_{16}H_{18}N_2O_3$: C 67.12, H 6.34, N 9.78; found: C 66.59, H 6.41, N 9.75.

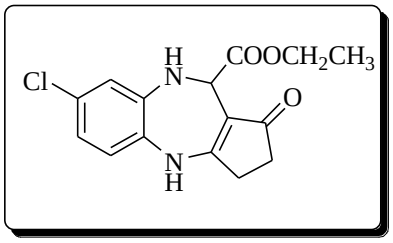
7-fluoro-10-ester-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(5cac)**



Yield: 93%;
Characteristic: White solid;

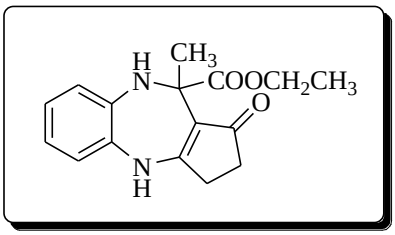
M.p.: 262-263 °C;
IR (KBr): 3308, 3256, 1717, 1607, 1569 cm^{-1};
^1H NMR (300 MHz, DMSO-d_6): δ 0.99 (3H, t, J=7.0), 2.31 (2H, t), 2.69 (2H, t), 3.92 (2H, q, J=7.0), 4.57 (1H, d, J=5.0 Hz), 6.44 (1H, d, J=5.0 Hz), 6.60-7.02 (3H, m), 9.90 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 14.50; 26.88; 33.26; 55.68; 60.68; 107.00; 107.23; 107.78; 108.02; 109.71; 121.41; 121.50; 127.51; 139.85; 139.95; 157.20; 159.57; 167.03; 171.13; 199.33;
MS calcd for $C_{15}H_{15}FN_2O_3$ 290, found 291 (M+1);
Anal.calcd (%) for $C_{15}H_{15}FN_2O_3$: C 62.06, H 5.21, N 9.65; found: C 62.10, H 5.31, N 9.58.

7-chloro-10-ester-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(5dac)**



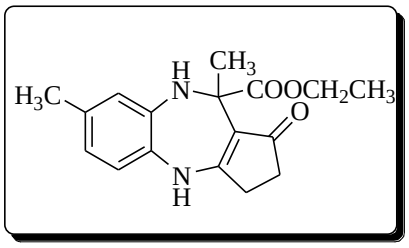
Yield: 94%;
Characteristic: White solid;
M.p.: 247-248 °C
IR (KBr): 3318, 3269, 1700, 1620, 1559 cm^{-1};
^1H NMR (300 MHz, DMSO-d_6): δ 1.00 (3H, t, J=7.0), 2.31 (2H, t), 2.69 (2H, t), 3.92 (2H, q, J=7.0), 4.56 (1H, d, J=5.0 Hz), 6.45 (1H, d, J=5.0 Hz), 6.81-7.01 (3H, m), 9.97 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 14.50; 26.93; 33.28; 55.61; 60.74; 110.26; 120.23; 121.08; 121.68; 126.67; 129.94; 139.71; 167.03; 171.07; 199.53;
MS calcd for $C_{15}H_{15}ClN_2O_3$ 307, found 308 (M+1);
Anal.calcd (%) for $C_{15}H_{15}ClN_2O_3$: C 58.73, H 4.93, N 9.13; found: C 58.47, H 5.02, N 8.98.

10-methyl-10-ester-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(5aad)**



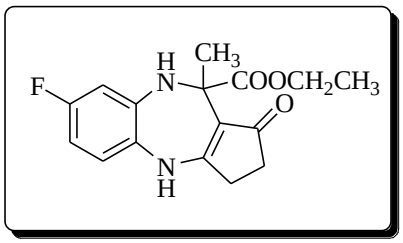
Yield: 94%;
Characteristic: Cream colored solid;
M.p.: 195-196 °C;
IR (KBr): 3308, 3203, 1704, 1600, 1562 cm^{-1};
^1H NMR (300 MHz, DMSO-d_6): δ 0.84 (3H, t, J=7.0), 1.65 (3H, s), 2.23 (2H, t), 2.64 (2H, t), 3.82 (2H, q, J=7.0), 5.40 (1H, s), 6.79-6.99 (4H, m), 9.63 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 14.40; 23.91; 27.17; 33.72; 60.41; 62.78; 113.80; 119.65; 121.50; 122.79; 123.15; 132.34; 137.25; 166.29; 172.98; 200.03;
MS calcd for $C_{16}H_{18}N_2O_3$ 286, found 287 (M+1);
Anal.calcd (%) for $C_{16}H_{18}N_2O_3$: C 67.12, H 6.34, N 9.78; found: C 67.29, H 6.51, N 9.57.

7,10-dimethyl-10-ester-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(5bad)**



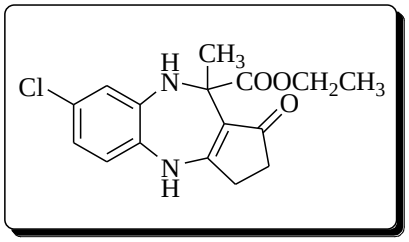
Yield: 96%;
Characteristic: Pale yellow solid;
M.p.: 244-246 °C;
IR (KBr): 3301, 3223, 1704, 1600, 1562 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 0.86 (3H, t, J=7.0), 1.64 (3H, s), 2.15(3H, s), 2.23 (2H, t), 2.64 (2H, t), 3.85 (2H, q, J=7.0), 5.34 (1H, s), 6.61-6.89 (3H, m), 9.60 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 14.41; 20.77; 23.99; 27.08; 33.68; 60.37; 62.73; 113.45; 119.59; 122.14; 123.11; 129.90; 132.01; 137.05; 166.29; 173.00; 199.86;
MS calcd for $C_{17}H_{20}N_2O_3$ 300, found 301 (M+1);
Anal.calcd (%) for $C_{17}H_{20}N_2O_3$: C 67.98, H 6.71, N 9.33; found: C 67.88, H 6.69, N 9.10.

7-fluoro-10-methyl-10-ester-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(5cad)**



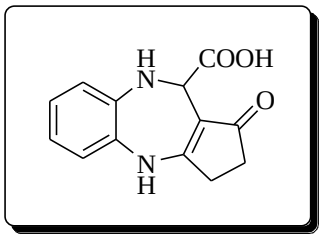
Yield: 91%;
Characteristic: Pale grey solid;
M.p.: 202-203 °C;
IR (KBr): 3334, 3282, 1724, 1607, 1562 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 0.88 (3H, t, J=7.0), 1.66 (3H, s), 2.24 (2H, t), 2.65 (2H, t), 3.87 (2H, q, J=7.0), 5.74 (1H, s), 6.63-7.02 (3H, m), 9.73 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 14.41; 23.75; 27.05; 33.69; 60.55; 62.67; 107.59; 107.81; 108.36; 108.60; 113.07; 120.66; 120.76; 128.67; 138.78; 138.88; 156.99; 159.36; 165.96; 172.75; 199.96;
MS calcd for $C_{16}H_{17}FN_2O_3$ 304, found 305 (M+1);
Anal.calcd (%) for $C_{16}H_{17}FN_2O_3$: C 63.15, H 5.63, N 9.21; found: C 62.89, H 5.47, N 9.37.

7-chloro-10-methyl-10-ester-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(5dad)**



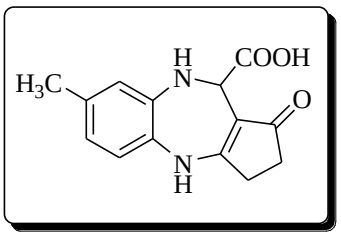
Yield: 90%;
Characteristic: Light grey solid;
M.p.: 264-266 °C;
IR (KBr): 3334, 3275, 1717, 1620, 1562 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 0.88 (3H, t, J=7.0), 1.67 (3H, s), 2.27 (2H, t), 2.66 (2H, t), 3.88 (2H, q, J=7.0), 5.76 (1H, s), 6.85-7.04 (3H, m), 9.81 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 14.41; 23.68; 27.09; 33.72; 60.59; 62.66; 113.60; 120.87; 120.98; 121.71; 126.37; 131.15; 138.70; 165.96; 172.69; 200.16;
MS calcd for $C_{16}H_{17}ClN_2O_3$ 320, found 321 (M+1);
Anal.calcd (%) for $C_{16}H_{17}ClN_2O_3$: C 59.91, H 5.34, N 8.37; found: C 59.55, H 5.60, N 8.41.

10-carboxyl-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(5aae)**



Yield: 96%;
Characteristic: Light grey solid;
M.p.: 234-236 °C;
IR (KBr): 3340, 3282, 1717, 1646, 1548 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.31 (2H, t), 2.68 (2H, t), 4.53 (1H, d, J=4.5 Hz), 6.05 (1H, d, J=4.5 Hz), 6.74-6.99 (4H, m), 9.78 (1H, s), 12.19 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 27.00; 33.30; 56.06; 110.94; 120.37; 120.61; 122.40; 123.35; 130.86; 138.52; 167.22; 172.89; 199.85;
MS calcd for $C_{13}H_{12}N_2O_3$ 244, found 245 (M+1);
Anal.calcd (%) for $C_{13}H_{12}N_2O_3$: C 63.93, H 4.95, N 11.47; found: C 63.76, H 4.71, N 11.59.

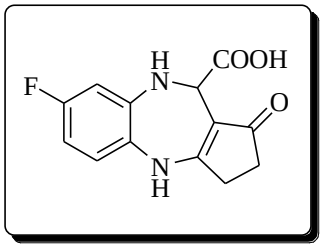
7-methyl-10-carboxyl-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(5bae)**



Yield: 97%;
Characteristic: Light grey solid;

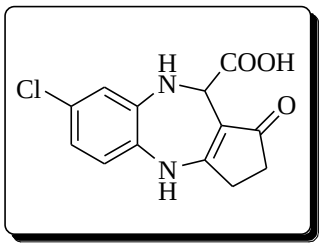
M.p.: 230-232 °C;
IR (KBr): 3372, 3314, 1762, 1646, 1517 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.15 (3H, s), 2.31 (2H, t), 2.68 (2H, t), 4.53 (1H, d, J=4.5 Hz), 6.05 (1H, d, J=4.5 Hz), 6.74-6.99 (3H, m), 9.78 (1H, s), 12.16 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 27.00; 33.30; 56.06; 110.94; 120.37; 120.61; 122.40; 123.35; 130.86; 138.52; 167.22; 172.89; 199.85;
MS calcd for $C_{13}H_{12}N_2O_3$ 258, found 259 (M+1);
Anal.calcd (%) for $C_{13}H_{12}N_2O_3$: C 65.11, H 5.46, N 10.85; found: C 65.37, H 5.71, N 10.59.

7-fluoro-10-carboxyl-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)- one **(5cae)**



Yield: 92%;
Characteristic: Cream colored solid;
M.p.: 257-258 °C;
IR (KBr): 3321, 3282, 1691, 1614, 1523 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.31 (2H, t), 2.67 (2H, t), 4.51 (1H, d, J=4.5 Hz), 6.35 (1H, d, J=4.5 Hz), 6.58-6.99 (3H, m), 9.85 (1H, s), 12.30 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 26.88; 33.37; 55.74; 106.72; 106.95; 107.82; 108.07; 110.27; 121.37; 121.47; 127.25; 140.20; 140.30; 157.18; 159.55; 166.82; 172.78; 199.65;
MS calcd for $C_{13}H_{11}FN_2O_3$ 262, found 263 (M+1);
Anal.calcd (%) for $C_{13}H_{11}FN_2O_3$: C 59.54, H 4.23, N 10.68; found: C 59.77, H 4.49, N 10.34.

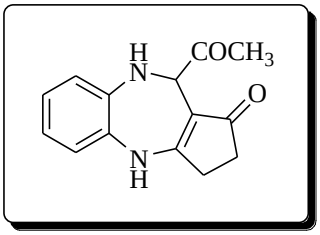
7-chloro-10-carboxyl-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)- one **(5dae)**



Yield: 91%;
Characteristic: Grey solid;
M.p.: 249-251 °C;
IR (KBr): 3289, 3217, 1710, 1607, 1555 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.32 (2H, t), 2.68 (2H, t), 4.51 (1H, d, J=4.5 Hz), 6.38 (1H, d, J=4.5 Hz), 6.79-6.99 (3H, m), 9.92 (1H, s), 12.35 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 26.92; 33.28; 55.68; 110.86; 119.45; 121.09; 121.66; 126.59; 129.72; 140.03; 166.81; 172.70; 199.82;
MS calcd for $C_{13}H_{11}ClN_2O_3$ 278, found 279 (M+1);

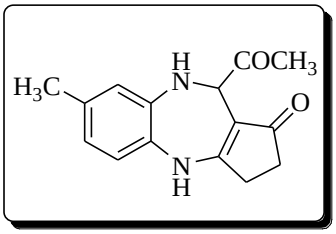
Anal.calcd (%) for $C_{13}H_{11}ClN_2O_3$: C 56.03, H 3.98, N 10.05; found: C 56.13, H 4.09, N 9.97.

10-acetyl-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(5aaf)**



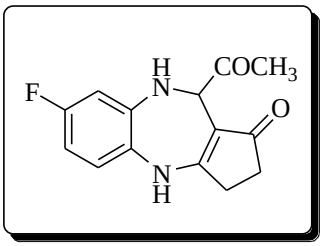
Yield: 91%;
Characteristic: Cream colored solid;
M.p.: 216-217 °C;
IR (KBr): 3359, 3269, 1704, 1626, 1562 cm^{-1};
^1H NMR (300 MHz, DMSO-d_6): δ 2.03 (3H, s), 2.34 (2H, t), 2.70 (2H, t), 4.64 (1H, d, J=4.5 Hz), 6.14 (1H, d, J=4.5 Hz), 6.71-6.99 (4H, m), 9.85 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 27.05; 28.49; 33.37; 61.80; 109.15; 120.05; 120.49; 121.86; 123.43; 129.84; 138.65; 167.13; 200.01; 206.21;
MS calcd for $C_{14}H_{14}N_2O_2S$ 242, found 243 (M+1);
Anal.calcd (%) for $C_{14}H_{14}N_2O_2$: C 69.41, H 5.82, N 11.56; found: C 69.23, H 5.59, N 11.73.

7-methyl-10-acetyl-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(5baf)**



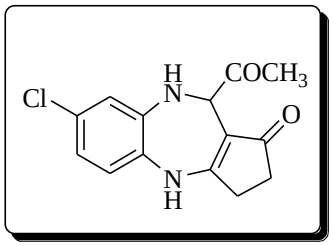
Yield: 94%;
Characteristic: Cream colored solid;
M.p.: 236-238 °C;
IR (KBr): 3327, 3275, 1704, 1620, 1548 cm^{-1};
^1H NMR (300 MHz, DMSO-d_6): δ 2.02 (3H, s), 2.16 (3H, s), 2.32 (2H, t), 2.68 (2H, t), 4.61 (1H, d, J=4.5 Hz), 6.06 (1H, d, J=4.5 Hz), 6.06-6.88 (3H, m), 9.79 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 20.76; 26.98; 28.52; 33.37; 61.70; 109.10; 120.48; 121.85; 122.02; 127.47; 132.30; 138.43; 167.00; 199.82; 206.24;
MS calcd for $C_{15}H_{16}N_2O_2$ 256, found 257 (M+1);
Anal.calcd (%) for $C_{15}H_{16}N_2O_2$: C 70.29, H 6.29, N 10.93; found: C 70.11, H 6.34, N 10.74.

7-fluoro-10-acetyl-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(5caf)**



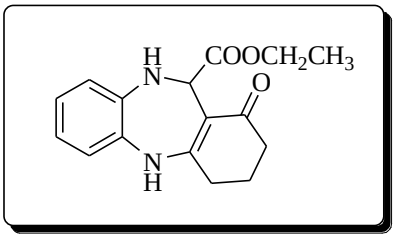
Yield: 89%;
Characteristic: Cream colored solid;
M.p.: 248-249 °C;
IR (KBr): 3346, 3269, 1717, 1626, 1548 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.05 (3H, s), 2.35 (2H, t), 2.70 (2H, t), 4.68 (1H, d, J=4.5 Hz), 6.33 (1H, d, J=4.5 Hz), 6.54-6.70 (3H, m), 9.91 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 26.99; 28.51; 33.67; 61.61; 106.17; 106.40; 107.27; 107.51; 108.64; 121.53; 121.62; 126.20; 140.57; 140.67; 157.28;159.64; 166.79; 199.87; 206.13;
MS calcd for $C_{14}H_{13}FN_2O_2$ 260, found 261 (M+1);
Anal.calcd (%) for $C_{14}H_{13}FN_2O_2$: C 64.61, H 5.03, N 10.76; found: C 64.25, H 4.87, N 10.93.

7-chloro-10-acetyl-3,4,9,10-tetrahydrobenzo[*b*]cyclopenta[*e*][1,4]diazepin-1(2*H*)-one **(5daf)**



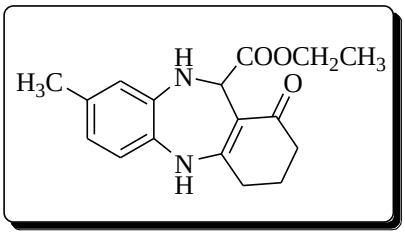
Yield: 88%;
Characteristic: Grey solid;
M.p.: 250-257 °C;
IR (KBr): 3321, 3282, 1698, 1607, 1562 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 2.05 (3H, s), 2.35 (2H, t), 2.70 (2H, t), 4.68 (1H, d, J=4.5 Hz), 6.34 (1H, d, J=4.5 Hz), 6.75-7.01 (3H, m), 9.97 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 27.04; 28.63; 33.38; 41.49; 109.19; 119.32; 120.61; 121.79; 126.72; 128.63; 140.41; 166.82; 200.10; 206.10;
MS calcd for $C_{14}H_{13}ClN_2O_2$ 277, found 278 (M+1);
Anal.calcd (%) for $C_{14}H_{13}ClN_2O_2$: C 60.77, H 4.74, N 10.12; found: C 60.68, H 5.13, N 10.01.

11-ester-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (**5abc**)



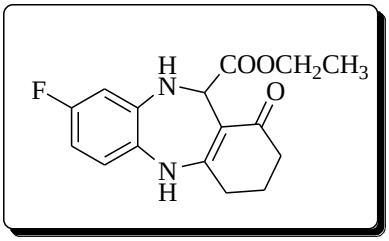
Yield: 91%;
Characteristic: Yellow solid;
M.p.: 171-173 °C;
IR (KBr): 3321, 3243, 1710, 1600, 1543 cm^{-1};
^1H NMR (300 MHz, DMSO-d_6): δ 0.91 (3H, t, J=7.0), 1.86 (2H, m), 2.21 (2H, t), 2.62 (2H, t), 3.84 (2H, q, J=7.0), 5.18 (1H, d, J=5.0 Hz), 6.17 (1H, d, J=5.0 Hz), 6.67-7.00 (4H, m), 8.88 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 14.54; 21.73; 31.12; 36.19; 56.03; 60.25; 108.20; 120.56; 120.71; 120.75; 123.23; 131.10; 138.51; 157.22; 171.54; 193.00;
MS calcd for $C_{16}H_{18}N_2O_3$ 286, found 287 (M+1);
Anal.calcd (%) for $C_{16}H_{18}N_2O_3$: C 67.12, H 6.34, N 9.78; found: C 67.30, H 6.57, N 9.49.

8-methyl-11-ester-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (**5bbc**)



Yield: 94%;
Characteristic: Pale yellow solid;
M.p.: 158-160 °C;
IR (KBr): 3327, 3230, 1710, 1607, 1529 cm^{-1};
^1H NMR (300 MHz, DMSO-d_6): δ 0.94 (3H, t, J=7.0), 1.85 (2H, m), 2.14 (3H, s), 2.19 (2H, t), 2.60 (2H, t), 3.83 (2H, q, J=7.0), 5.16 (1H, d, J=5.0 Hz), 6.04 (1H, d, J=5.0 Hz), 6.57-6.80 (3H, m), 8.80 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 14.61; 20.61; 21.75; 31.16; 36.22; 56.22; 60.20; 108.24; 120.80; 121.02; 123.96; 129.27; 131.03; 136.05; 157.15; 171.58; 193.01;
MS calcd for $C_{17}H_{20}N_2O_3$ 300, found 301 (M+1);
Anal.calcd (%) for $C_{17}H_{20}N_2O_3$: C 67.98, H 6.71, N 9.33; found: C 67.87, H 6.78, N 9.07.

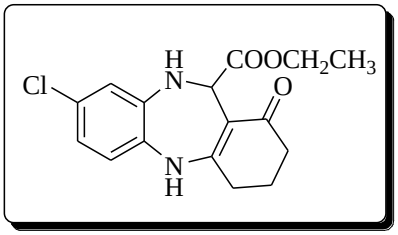
8-fluoro-11-ester-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (**5cbc**)



Yield: 88%;
Characteristic: Yellow solid;
M.p.: 240-241 °C;
IR (KBr): 3314, 3249, 1704, 1652, 1536 cm^{-1};
^1H NMR (300 MHz, DMSO-d_6): δ 0.94 (3H, t, J=7.0), 1.85 (2H, m), 2.21 (2H, t), 2.61 (2H, t), 3.87 (2H, q, J=7.0), 5.20 (1H, d, J=5.0 Hz), 6.42 (1H, d, J=5.0 Hz), 6.53-7.04 (3H, m), 8.97 (1H,

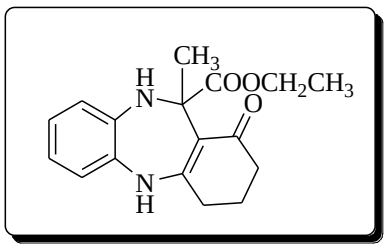
s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 14.53; 21.67; 30.99; 36.18; 55.51; 60.37; 106.27; 106.52; 106.75; 107.82; 121.84; 121.95; 127.57; 140.20; 140.30; 157.14; 157.27; 159.64; 171.42; 192.77;
MS calcd for $C_{16}H_{17}FN_2O_3$ 304, found 305 (M+1);
Anal.calcd (%) for $C_{16}H_{17}FN_2O_3$: C 63.15, H 5.63, N 9.21; found: C 63.75, H 5.57, N 9.91.

8-chloro-11-ester-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (**5dbc**)



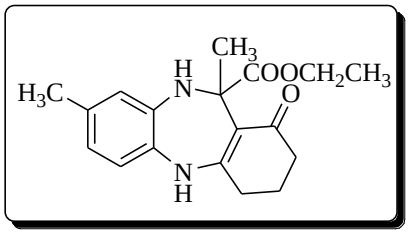
Yield: 86%;
Characteristic: Cream colored solid;
M.p.: 272-274 °C;
IR (KBr): 3321, 3237, 1717, 1639, 1529 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 0.95 (3H, t, *J*=7.0), 1.86 (2H, m), 2.23 (2H, t), 2.61 (2H, t), 3.88 (2H, q, *J*=7.0), 5.22 (1H, d, *J*=5.0 Hz), 6.44 (1H, d, *J*=5.0 Hz), 6.76-7.00 (4H, m), 8.96 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 14.51; 21.64; 31.04; 36.15; 55.43; 60.44; 108.48; 119.62; 119.86; 122.00; 126.59; 140.01; 156.93; 171.33; 192.99;
MS calcd for $C_{16}H_{17}ClN_2O_3$ 320, found 321 (M+1);
Anal.calcd (%) for $C_{16}H_{17}ClN_2O_3$: C 59.91, H 5.34, N 8.73; found: C 59.78, H 5.21, N 8.97.

11-methyl-11-ester-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (**5abd**)



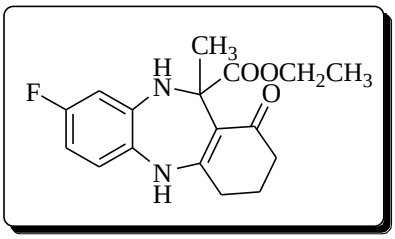
Yield: 87%;
Characteristic: Yellow solid;
M.p.: 220-221 °C;
IR (KBr): 3334, 3282, 1704, 1607, 1536 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 0.94 (3H, t, J=7.0), 1.38 (3H, s), 1.79 (2H, m), 2.11 (2H, t), 2.59 (2H, t), 3.86 (2H, q, J=7.0), 5.21 (1H, s), 6.79-7.01 (4H, m), 8.80 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 14.46; 20.66; 26.62; 31.90; 36.92; 59.92; 64.05; 113.16; 120.21; 121.63; 122.17; 123.39; 133.49; 137.79; 154.63; 173.05; 194.19;
MS calcd for $C_{17}H_{20}N_2O_3$ 300, found 301 (M+1);
Anal.calcd (%) for C17H20N2O3: C 67.98, H 6.71, N 9.33; found: C 67.54, H 6.69, N 9.18.

8,11-dimethyl-11-ester-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (**5bbd**)



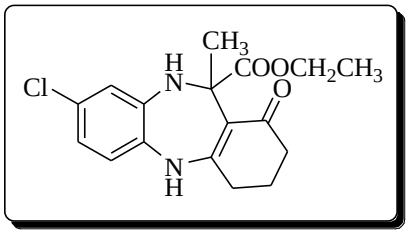
Yield: 90%;
Characteristic: Pale yellow solid;
M.p.:150-151 °C;
IR (KBr): 3334, 3282, 1704, 1607, 1543 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 0.96 (3H, t, J=7.0), 1.37 (3H, s), 1.79 (2H, m), 2.09 (2H, t), 2.15 (3H, s), 2.57 (2H, t), 3.86 (2H, q, J=7.0), 5.09 (1H, s), 6.61-6.89 (3H, m), 8.75 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 14.44; 20.69; 20.84; 26.63; 31.87; 36.90; 59.89; 64.02; 112.87; 120.16; 122.27; 122.53; 131.00; 132.32; 137.61; 154.64; 173.03; 193.95;
MS calcd for $C_{18}H_{22}N_2O_3$ 314, found 315 (M+1);
Anal.calcd (%) for $C_{18}H_{22}N_2O_3$: C 68.77, H 7.05, N 8.91; found: C 68.70, H 6.98, N 9.13.

8-fluoro-11-methyl-11-ester-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (**5cbd**)



Yield: 83%;
Characteristic: White solid;
M.p.: 226-227 °C;
IR (KBr): 3334, 3282, 1704, 1607, 1543 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 0.96 (3H, t, J=7.0), 1.39 (3H, s), 1.79 (2H, m), 2.10 (2H, t), 2.59 (2H, t), 3.89 (2H, q, J=7.0), 5.51 (1H, s), 6.62-7.02 (3H, m), 8.83 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 14.45; 20.61; 31.85; 36.88; 60.02; 64.15; 107.73; 107.96; 108.21; 112.63; 121.23; 121.33; 129.89; 139.29; 139.39; 154.44; 157.23; 159.61; 172.81; 194.18;
MS calcd for $C_{17}H_{19}FN_2O_3$ 318, found 319 (M+1);
Anal.calcd (%) for $C_{17}H_{19}FN_2O_3$: C 64.14, H 6.02, N 8.80; found: C 64.41, H 6.13, N 8.88.

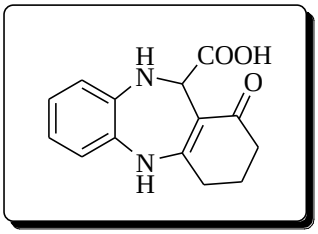
8-chloro-11-methyl-11-ester-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (**5dbd**)



Yield: 85%;
Characteristic: Grey solid;

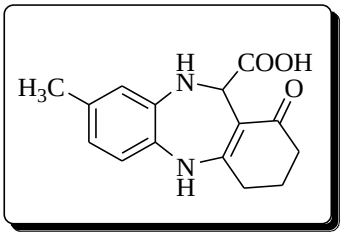
M.p.: 240-241 °C;
IR (KBr): 3337, 3281, 1706, 1608, 1540 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 0.96 (3H, t, J=7.0), 1.38 (3H, s), 1.79 (2H, m), 2.11 (2H, t), 2.58 (2H, t), 3.87 (2H, q, J=7.0), 5.43 (1H, s), 6.83-7.06 (3H, m), 8.84 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 14.50; 20.61; 26.50; 31.87; 36.88; 60.05; 63.87; 113.73; 119.43; 122.78; 123.36; 124.95; 134.71; 136.79; 154.22; 172.79; 194.54;
MS calcd for $C_{17}H_{19}ClN_2O_3$ 335, found 336 (M+1);
Anal.calcd (%) for C17H19ClN2O3: C 60.99, H 5.72, N 8.37; found: C 60.78, H 5.59, N 8.43.

11-carboxyl-2,3,4,5,10,11-hexahydro-1H-dibenzo[b,e][1,4]diazepin-1-one (**5abe**)



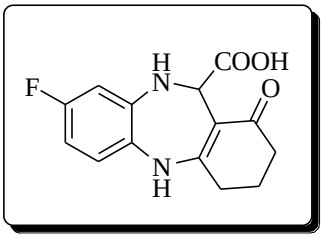
Yield: 92%;
Characteristic: Yellow solid;
M.p.: 194-196 °C;
IR (KBr): 3359, 3318, 1712, 1608, 1509 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 1.88 (2H, m), 2.22 (2H, t), 2.62 (2H, t), 5.15 (1H, s), 6.06 (1H, s), 6.68-6.99 (4H, m), 8.84 (1H, s), 12.04 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 21.72; 31.14; 36.19; 55.96; 108.82; 120.22; 120.69; 120.81; 123.18; 130.74; 138.93; 157.06; 173.17; 193.24;
MS calcd for $C_{14}H_{14}N_2O_3$ 258, found 259 (M+1);
Anal.calcd (%) for C14H14N2O3: C 65.11, H 5.46, N 10.85; found: C 64.89, H 5.21, N 10.99.

8-methyl-11-carboxyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (**5bbe**)



Yield: 94%;
Characteristic: Yellow solid;
M.p.: 210-212 °C;
IR (KBr): 3349, 3306, 1749, 1620, 1571 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 1.88 (2H, m), 2.14 (3H, s), 2.23 (2H, t), 2.62 (2H, t), 5.16 (1H, d, J=5.0), 5.99 (1H, d, J=5.0), 6.53-6.91 (3H, m), 8.83 (1H, s), 12.03 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 20.77; 21.76; 31.19; 36.21; 55.93; 108.42; 120.77; 121.04; 121.12; 128.36; 132.16; 138.80; 157.12; 173.26; 193.15;
MS calcd for $C_{15}H_{16}N_2O_3$ 272, found 273 (M+1);
Anal.calcd (%) for C15H16N2O3: C 66.16, H 5.92, N 10.29; found: C 65.97, H 5.73, N 10.41.

8-fluoro-11-carboxyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (**5cbe**)



Yield: 88%;

Characteristic: Yellow solid;

M.p.: 214-216 °C;

IR (KBr): 3337, 3300, 1706, 1620, 1534 cm^{-1};

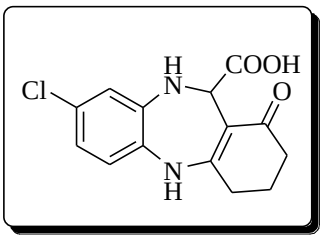
^{1}H NMR (300 MHz, DMSO-d_6): δ 1.86 (2H, m), 2.22 (2H, t), 2.60 (2H, t), 5.16 (1H, d, J=6.0), 6.34 (1H, d, J=6.0), 6.53-7.00 (3H, m), 8.89 (1H, s), 12.12 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 21.64; 31.06; 36.12; 55.47; 106.32; 106.36; 106.54; 106.60; 108.45; 121.70; 121.79; 127.17; 140.65; 140.75; 156.85; 157.29; 159.65; 173.07; 193.09;

MS calcd for $C_{14}H_{13}FN_2O_3$ 276, found 277 (M+1);

Anal.calcd (%) for $C_{14}H_{13}FN_2O_3$: C 60.87, H 4.74, N 10.14; found: C 60.38, H 4.92, N 10.01.

8-chloro-11-carboxyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (**5dbe**)



Yield: 89%;

Characteristic: Deep yellow solid;

M.p.: 224-226 °C;

IR (KBr): 3349, 3306, 1749, 1614, 1577 cm^{-1};

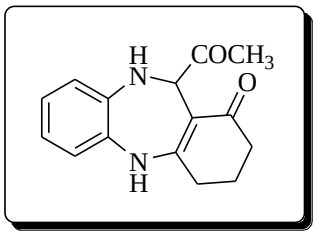
^{1}H NMR (300 MHz, DMSO-d_6): δ 1.86 (2H, m), 2.24 (2H, t), 2.61 (2H, t), 5.17 (1H, d, J=6.0), 6.35 (1H, d, J=6.0), 6.71-7.00 (3H, m), 8.93 (1H, s), 12.13 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 21.62; 31.02; 36.13; 55.40; 109.08; 119.60; 121.96; 126.55; 129.71; 140.43; 156.79; 172.99; 193.26;

MS calcd for $C_{14}H_{13}ClN_2O_3$ 292, found 293 (M+1);

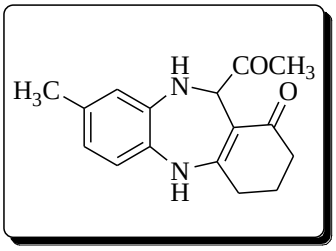
Anal.calcd (%) for C14H13ClN2O3: C 57.44, H 4.48, N 9.57; found: C 57.07, H 4.70, N 9.92.

11-acetyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (**5abf**)



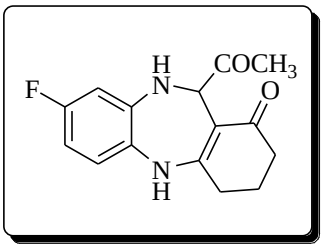
Yield: 85%;
Characteristic: Pale pink solid;
M.p.: 214-216 °C;
IR (KBr): 3324, 3239, 1706, 1601, 1534 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 1.88 (2H, m), 1.99 (3H, s), 2.23 (2H, t), 2.63 (2H, t), 5.23 (1H, d, J=5.5), 6.24 (1H, d, J=5.5), 6.66-6.98 (4H, m), 8.83 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 21.72; 28.18; 31.15; 36.24; 61.58; 108.09; 119.78; 120.04; 120.80; 123.29; 130.03; 138.64; 157.19; 193.34; 206.16;
MS calcd for $C_{15}H_{16}N_2O_2$ 256, found 257 (M+1);
Anal.calcd (%) for $C_{15}H_{16}N_2O_2$: C 70.29, H 6.29, N 10.93; found: C 70.20, H 6.18, N 11.09.

8-methyl-11-acetyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b,e*][1,4]diazepin-1-one (**5bbf**)



Yield: 87%;
Characteristic: Yellow solid;
M.p.: 219-220 °C;
IR (KBr): 3337, 3306, 1700, 1638, 1546 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 1.87 (2H, m), 1.98 (3H, s), 2.14(3H, s), 2.22 (2H, t), 2.60 (2H, t), 5.21 (1H, d, J=5.5), 6.15 (1H, d, J=5.5), 6.47-6.87 (3H, m), 8.79 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 20.75; 21.73; 28.25; 31.17; 36.26; 61.47; 107.68; 120.28; 120.56; 120.80; 127.66; 132.21; 138.48; 157.07; 193.12; 206.23;
MS calcd for $C_{16}H_{18}N_2O_2$ 270, found 271 (M+1);
Anal.calcd (%) for C16H18N2O2: C 71.09, H 6.71, N 10.36; found: C 71.08, H 6.83, N 10.26.

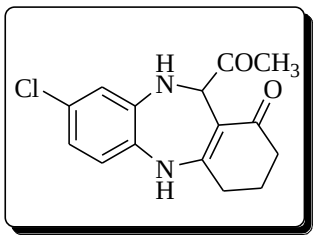
8-fluoro-11-acetyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b,e*][1,4]diazepin-1-one (**5cbf**)



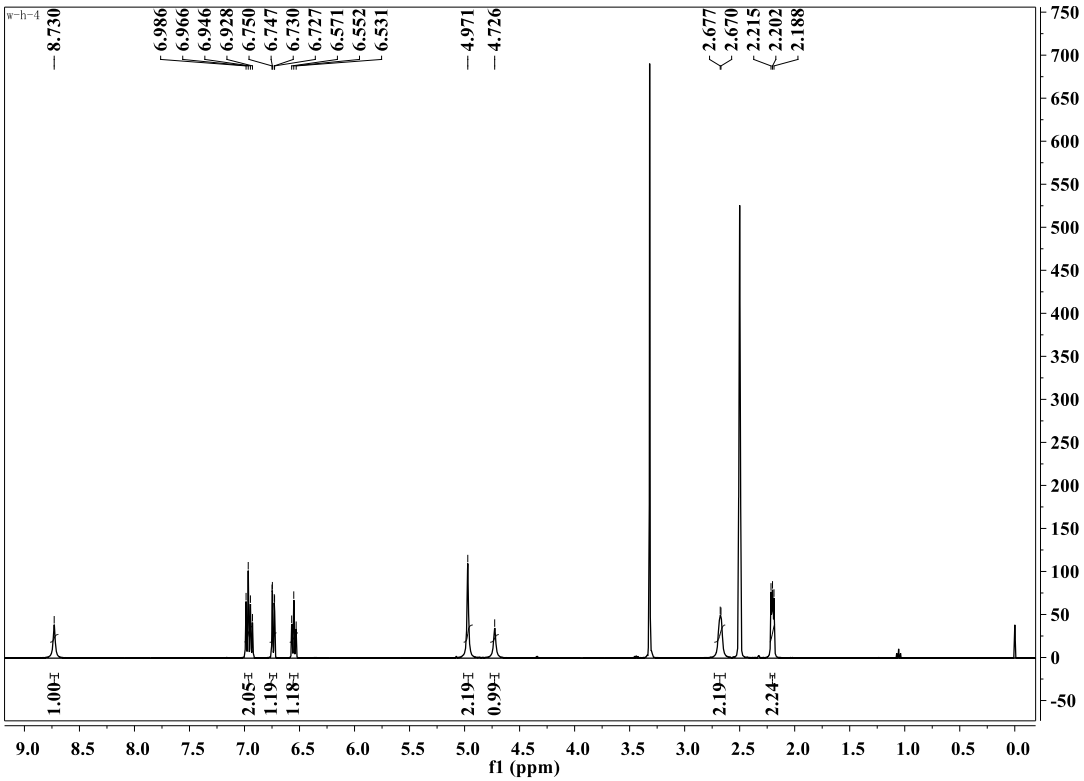
Yield: 83%;
Characteristic: Yellow solid;
M.p.: 244-246 °C;
IR (KBr): 3318, 3263,1700, 1644, 1522 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 1.87 (2H, m), 1.98 (3H, s), 2.25 (2H, t), 2.61 (2H, t), 5.26 (1H, d, J=5.5), 6.41 (1H, d, J=5.5), 6.46-6.98 (3H, m), 8.89 (1H, s);

^{13}C NMR (75 MHz, DMSO-d_6): δ 21.61; 28.16; 31.13; 36.22; 61.09; 105.48; 105.71; 105.92; 107.65; 121.78; 121.88; 126.31; 140.53; 140.63; 157.11; 157.36; 159.73; 193.19; 206.05;
MS calcd for $C_{15}H_{15}FN_2O_2$ 274, found 275 (M+1);
Anal.calcd (%) for $C_{15}H_{15}FN_2O_2$: C 65.68, H 5.51, N 10.21; found: C 65.41, H 5.91, N 10.16.

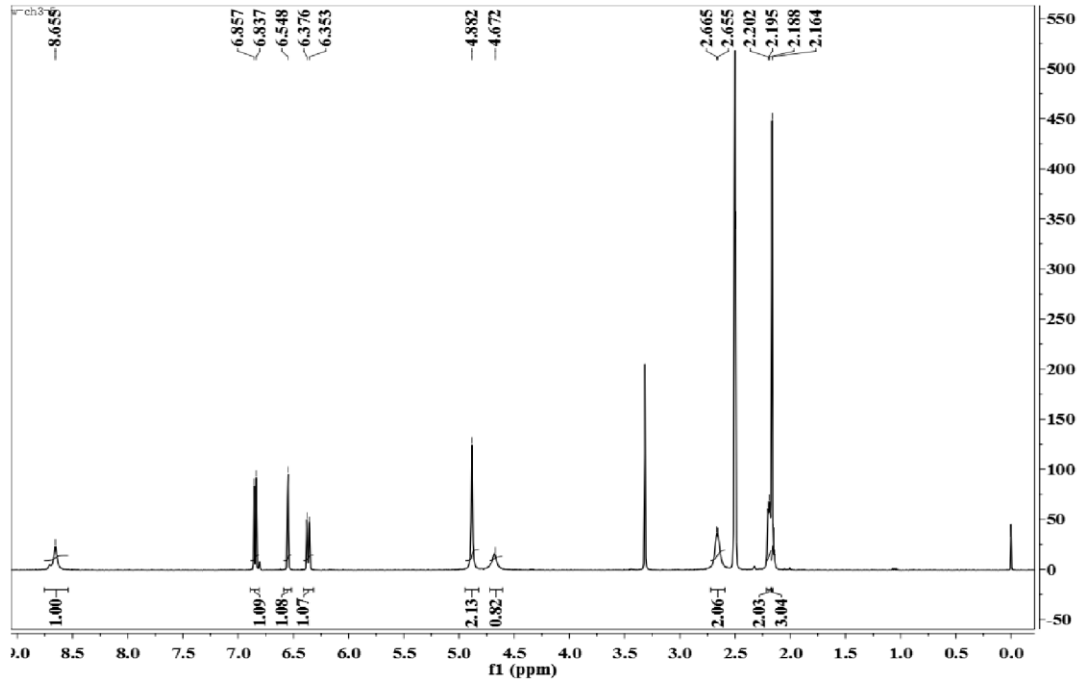
8-fluoro-11-acetyl-2,3,4,5,10,11-hexahydro-1*H*-dibenzo[*b*,*e*][1,4]diazepin-1-one (**5dbf**)



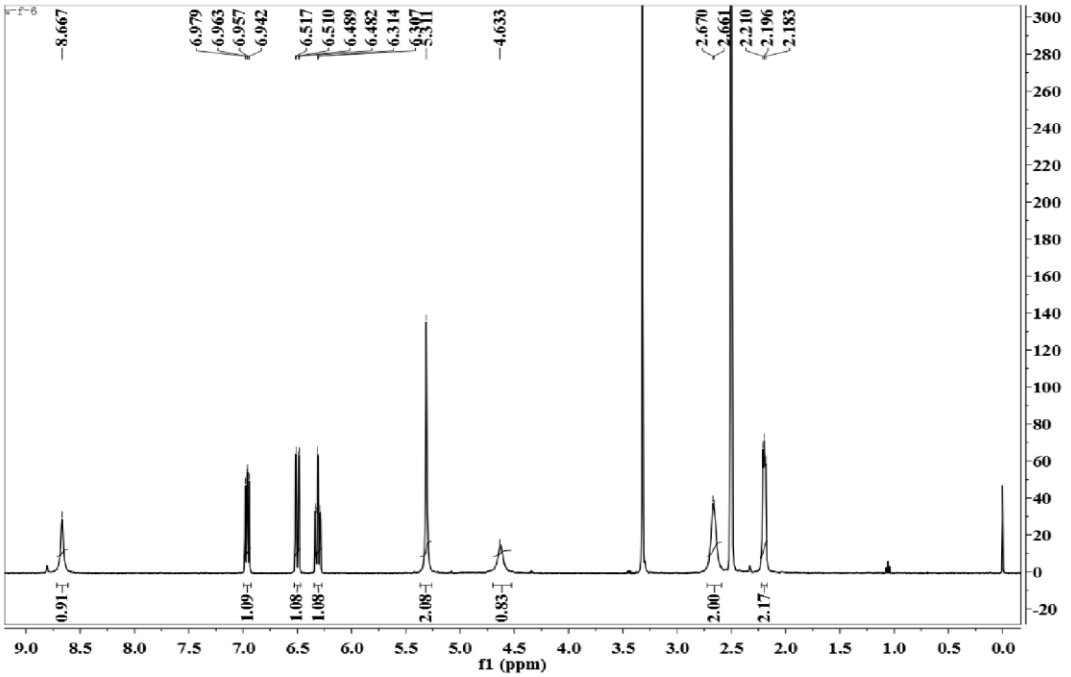
Yield: 82%;
Characteristic: Cream colored solid;
M.p.: 249-251 °C;
IR (KBr): 3324, 3239, 1706, 1600, 1540 cm^{-1};
^{1}H NMR (300 MHz, DMSO-d_6): δ 1.87 (2H, m), 1.99 (3H, s), 2.26 (2H, t), 2.62 (2H, t), 5.27 (1H, d, J=5.5), 6.42 (1H, d, J=5.5), 6.67-6.98 (3H, m), 8.95 (1H, s);
^{13}C NMR (75 MHz, DMSO-d_6): δ 21.58; 28.23; 31.10; 36.21; 60.98; 108.17; 118.75; 118.92; 122.01; 126.67; 128.76; 140.36; 157.09; 193.44; 206.01;
MS calcd for $C_{15}H_{15}ClN_2O_2$ 291, found 292 (M+1);
Anal.calcd (%) for C15H15ClN2O2: C 61.97, H 5.20, N 9.64; found: C 61.98, H 5.35, N 9.58.



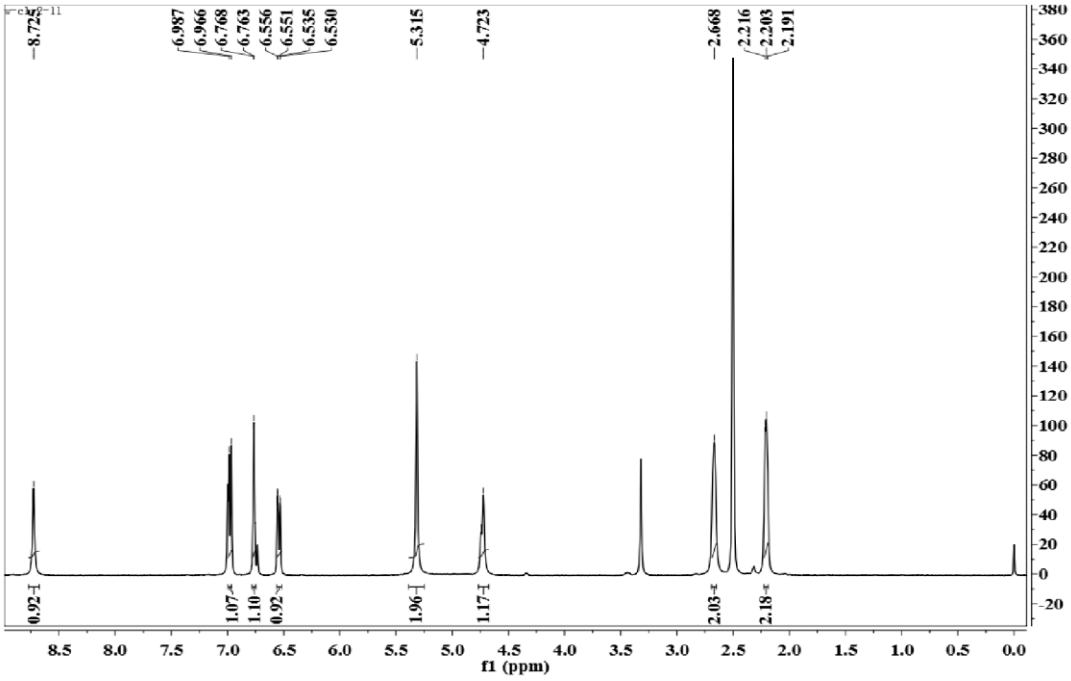
^{1}H NMR spectra of compound **7aa**



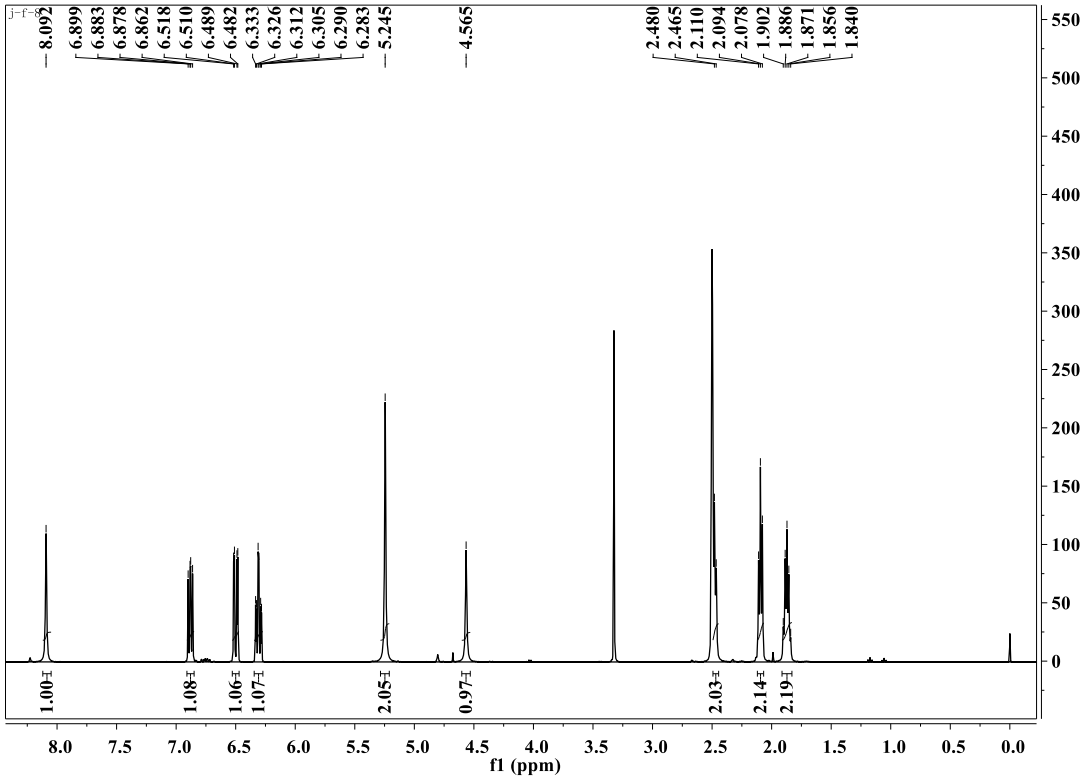
^{1}H NMR spectra of compound **7ba**



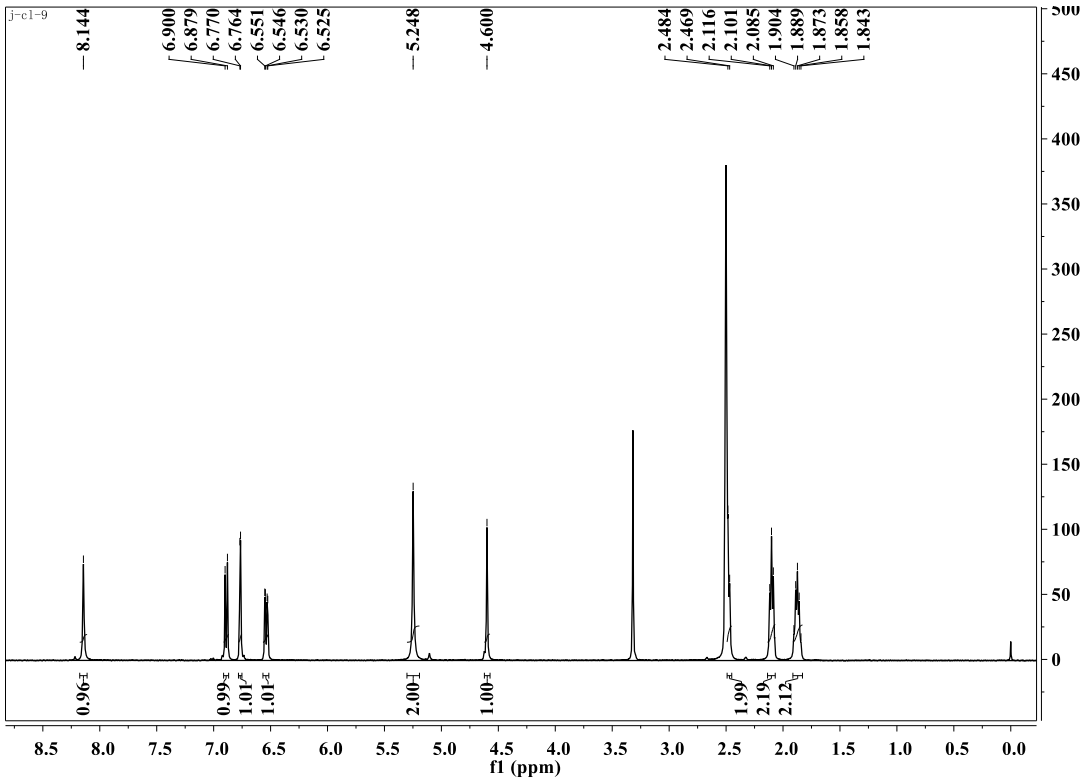
^{1}H NMR spectra of compound **7ca**



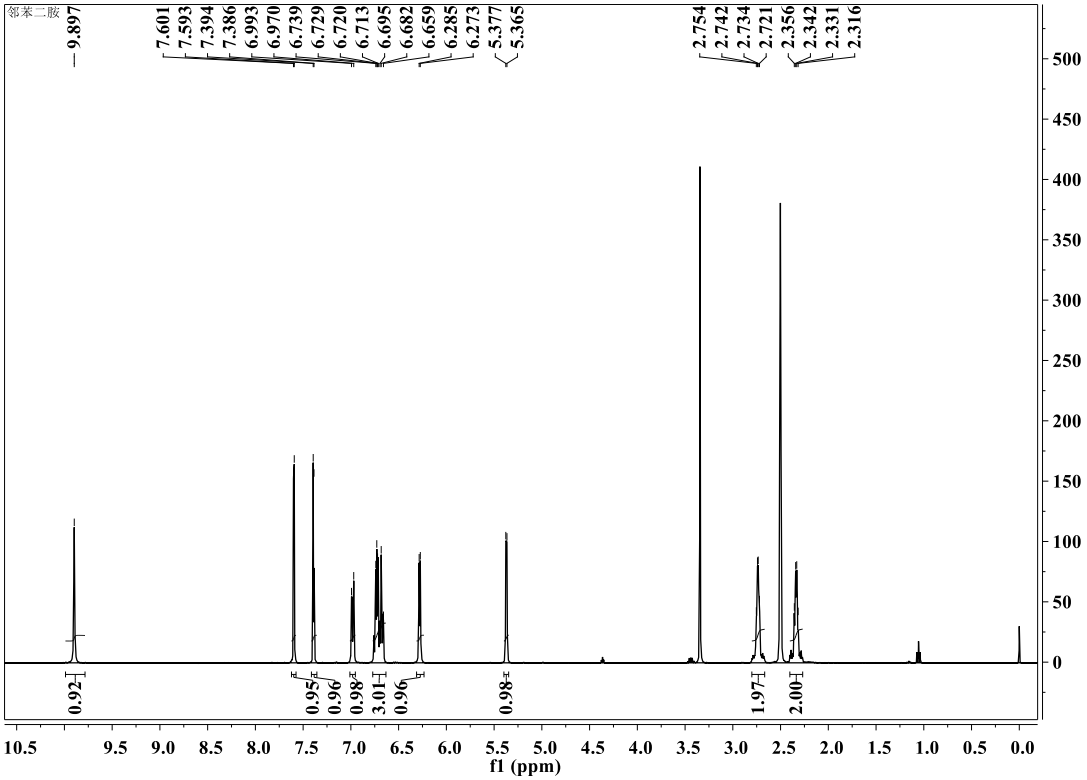
^{1}H NMR spectra of compound **7da**



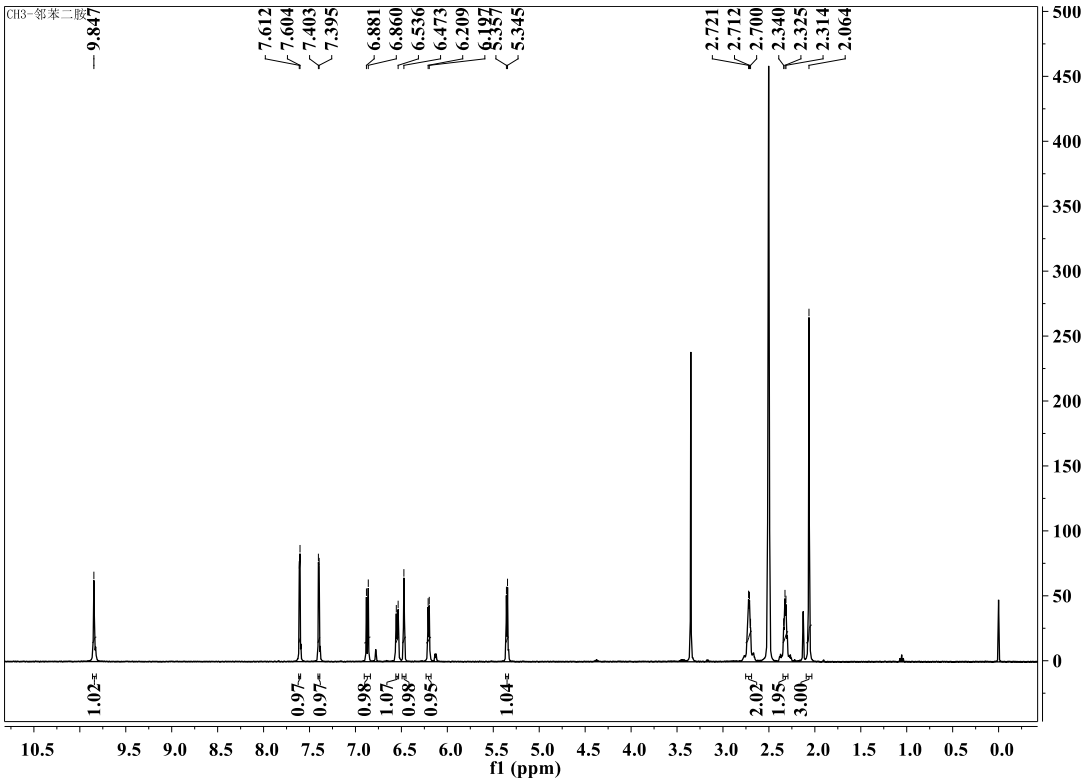
^{1}H NMR spectra of compound **7cb**



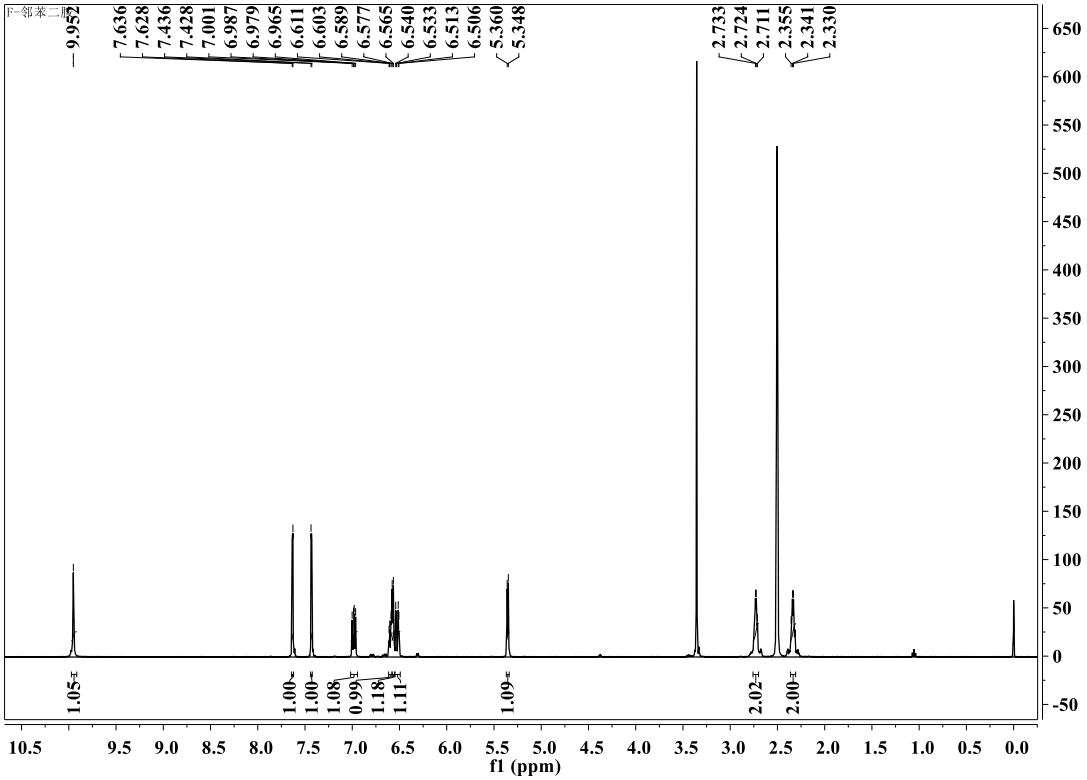
^{1}H NMR spectra of compound **7db**



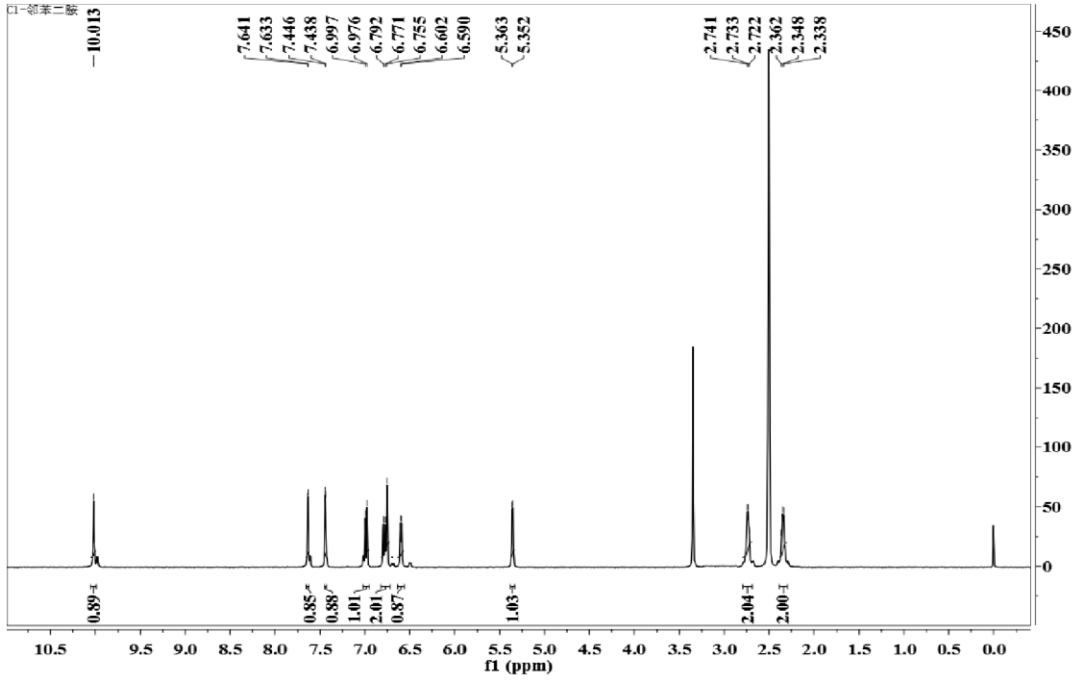
^{1}H NMR spectra of compound **4aaa**



^{1}H NMR spectra of compound **4baa**



^{1}H NMR spectra of compound **4caa**



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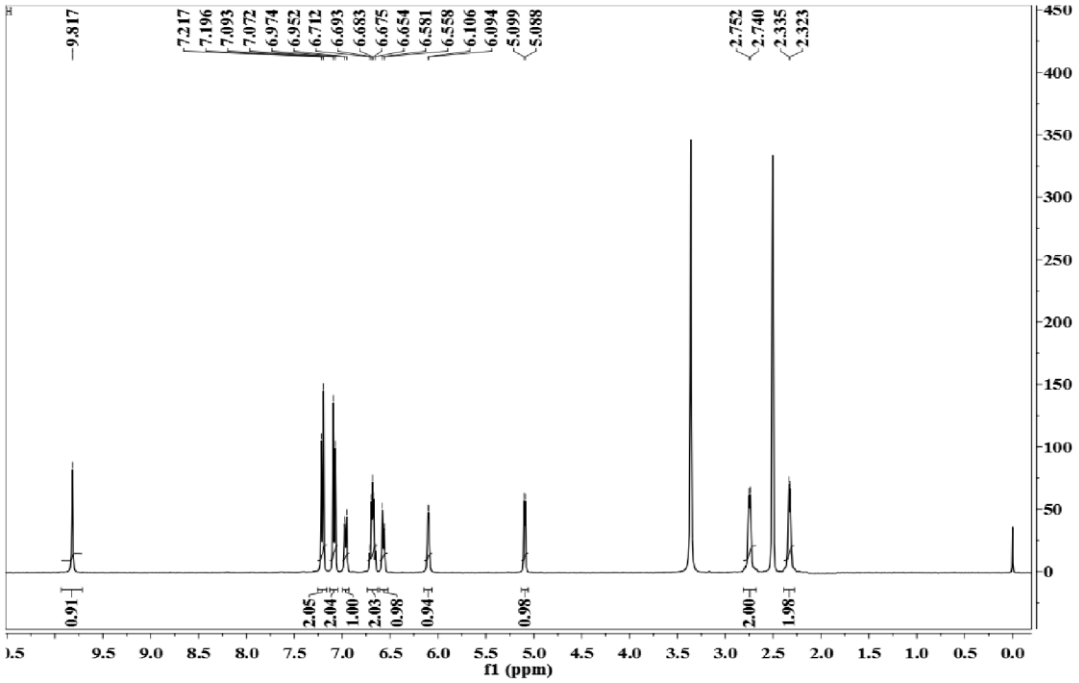
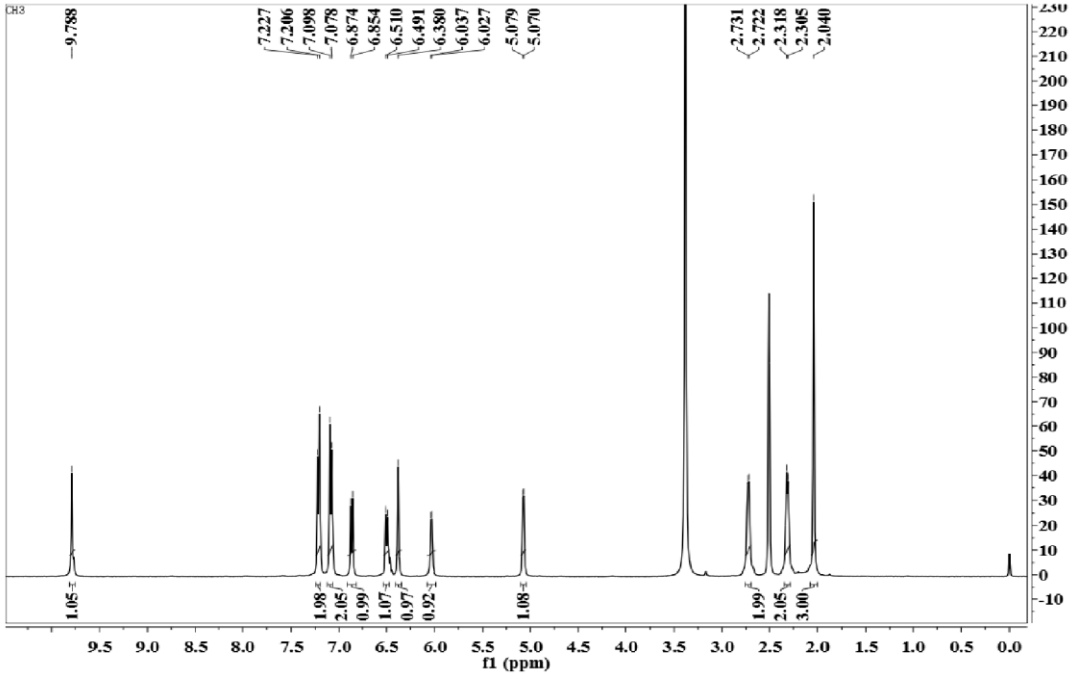
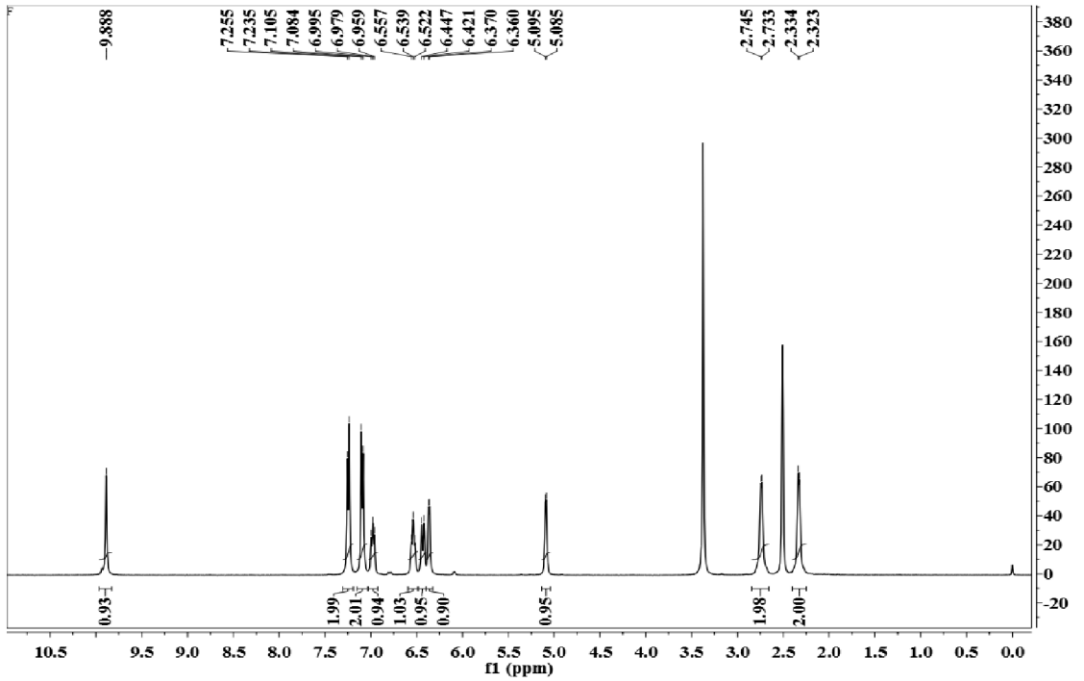


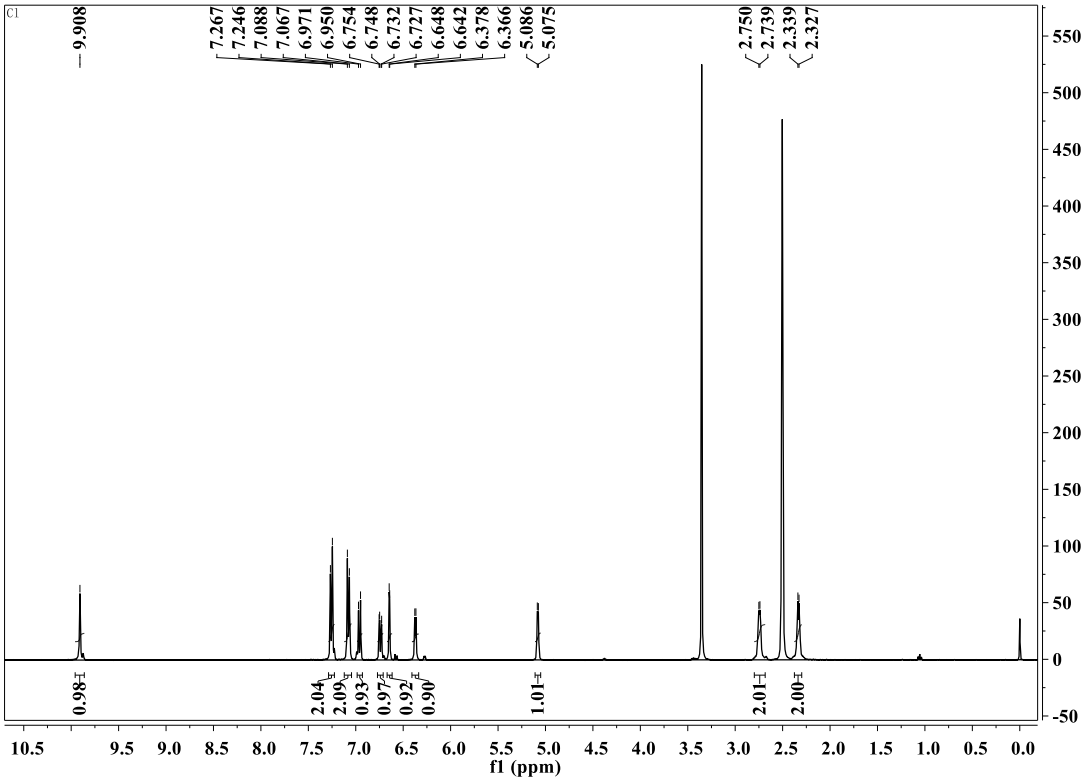
^{1}H NMR spectra of compound **4aab**



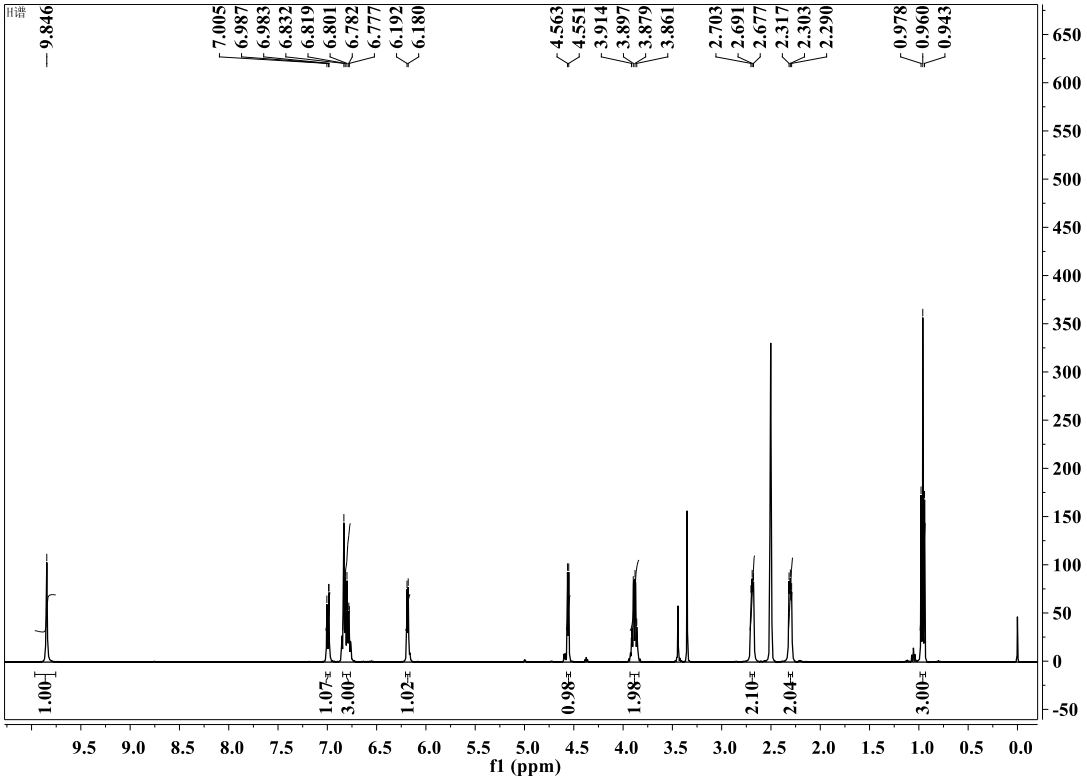
^{1}H NMR spectra of compound **4bab**



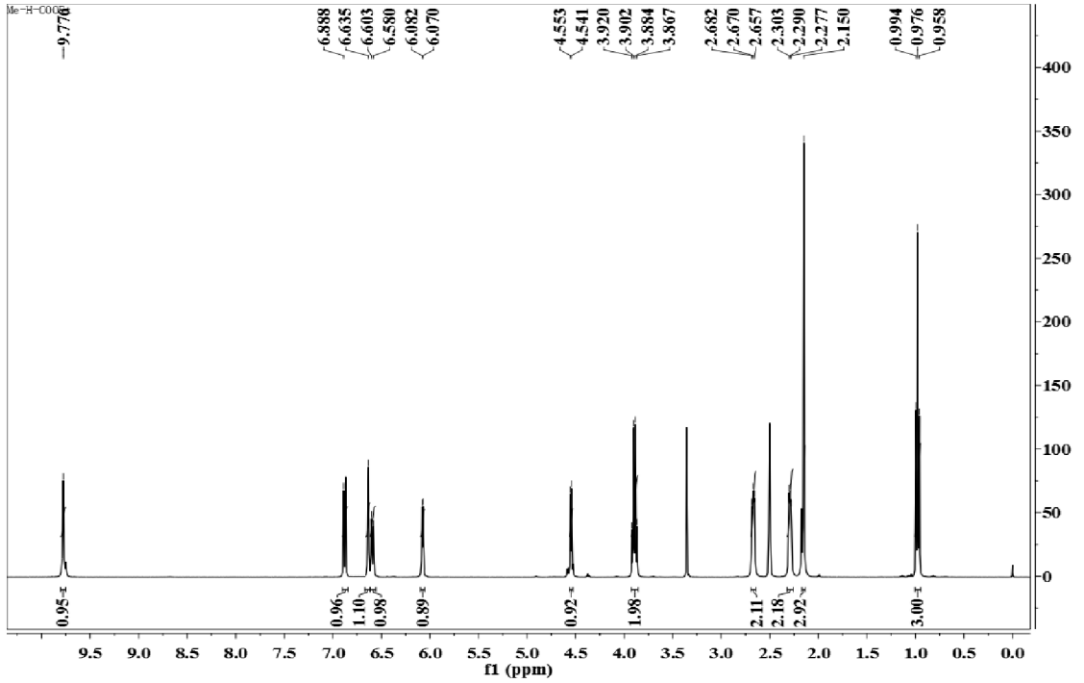
^{1}H NMR spectra of compound **4cab**



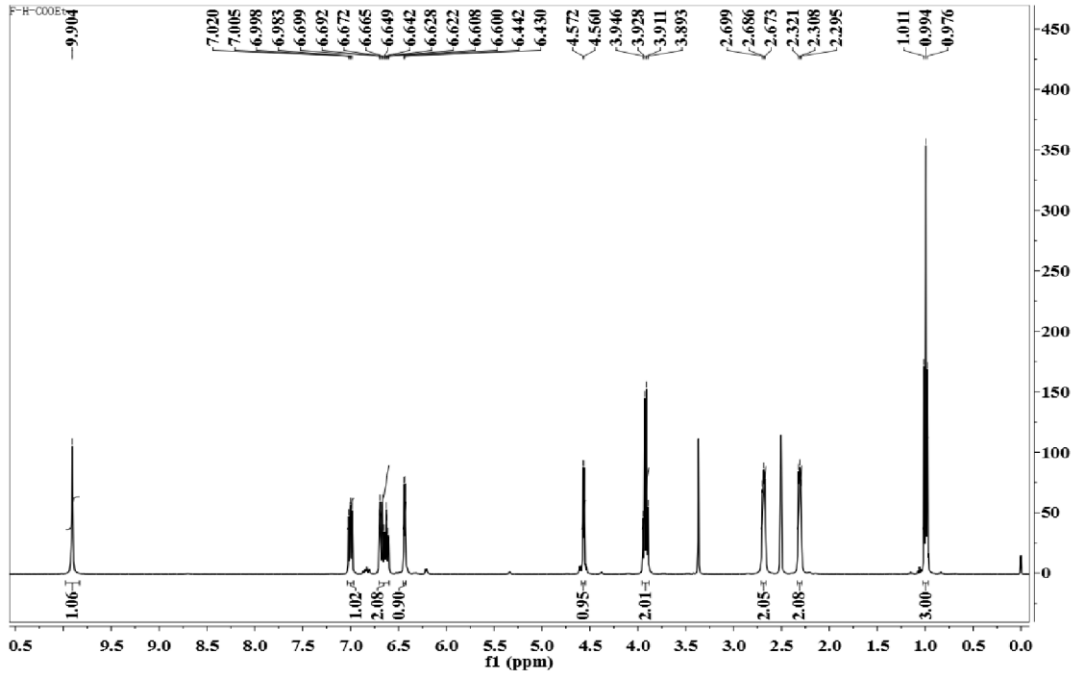
^{1}H NMR spectra of compound **4dab**



^{1}H NMR spectra of compound **5aac**



^{1}H NMR spectra of compound **5bac**



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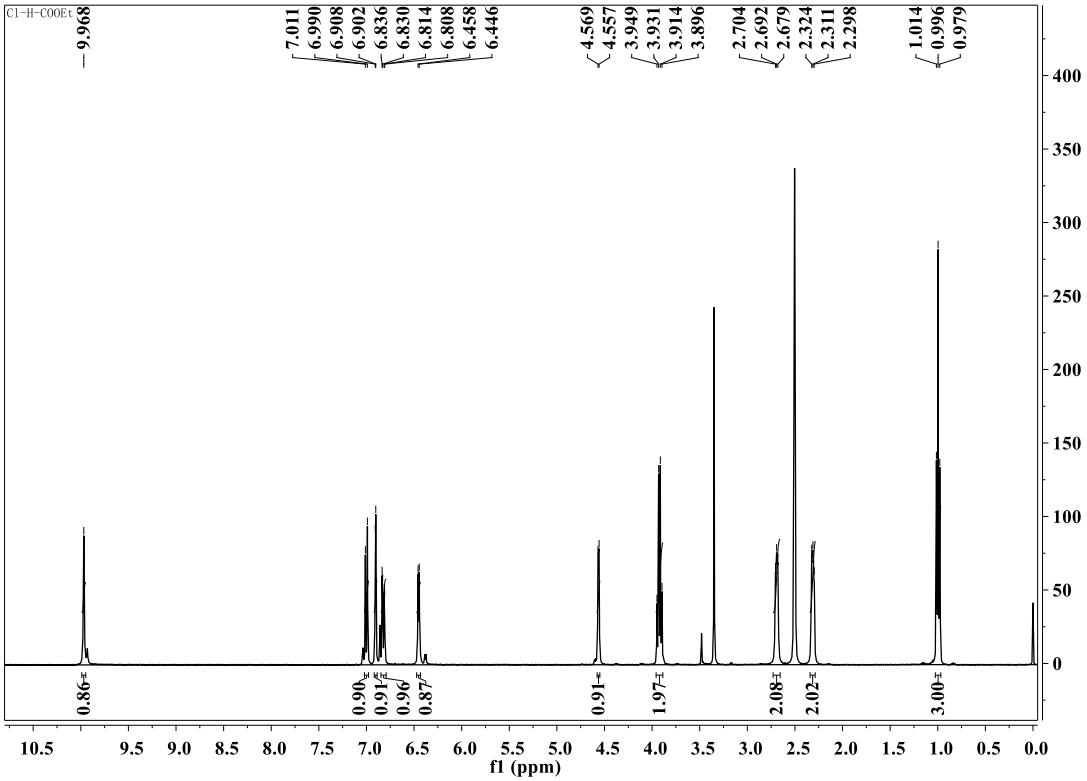

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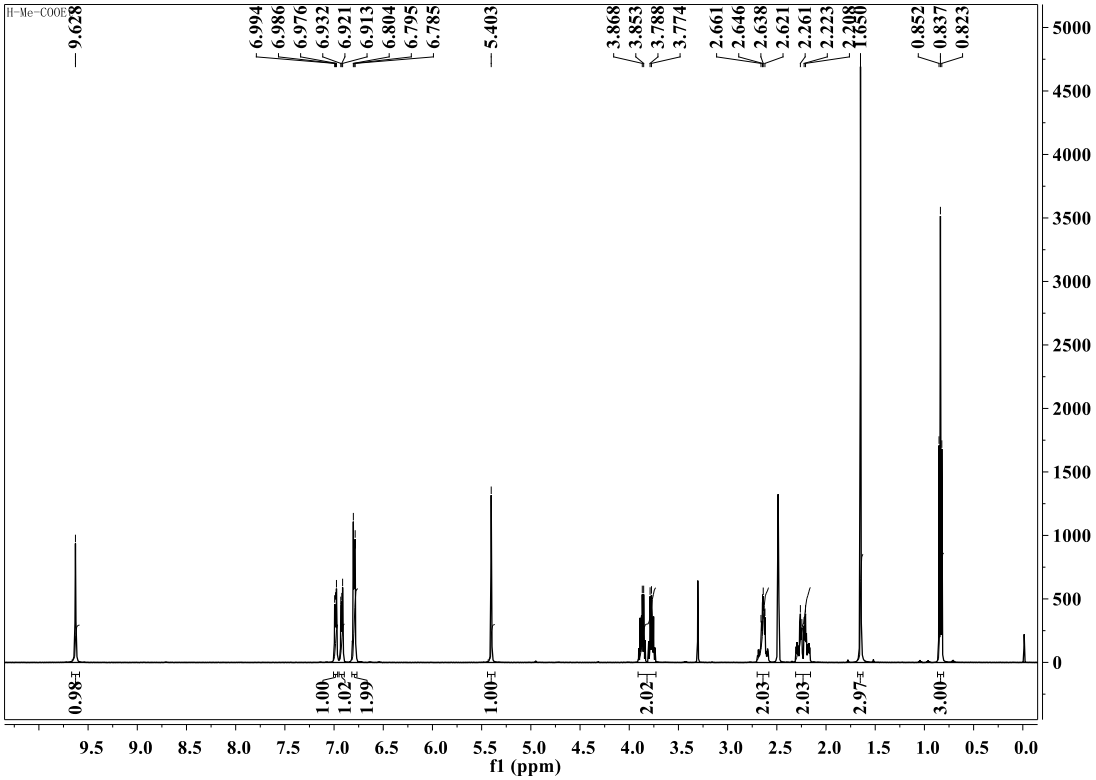
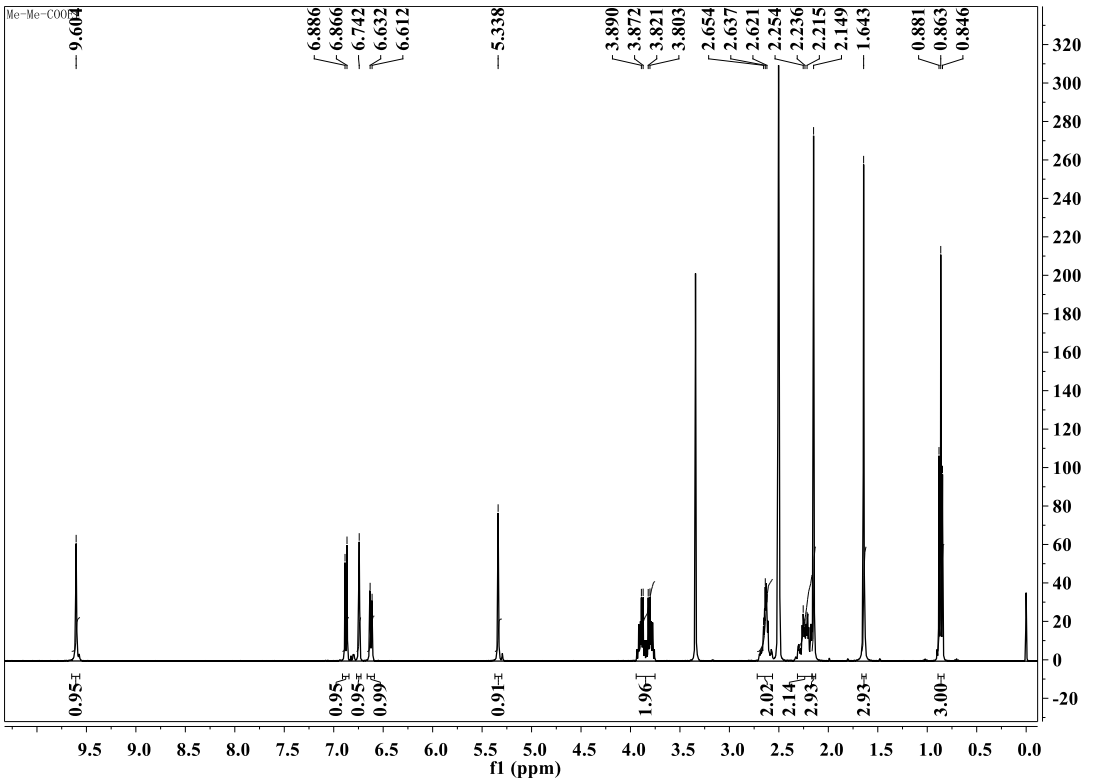
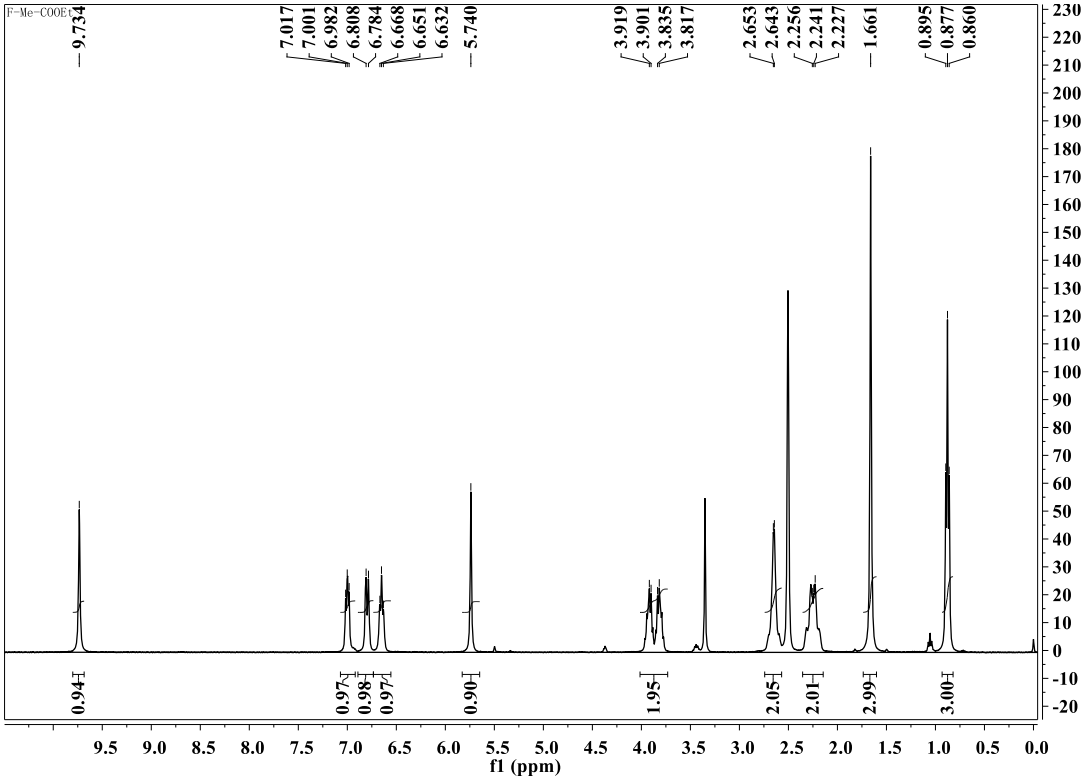


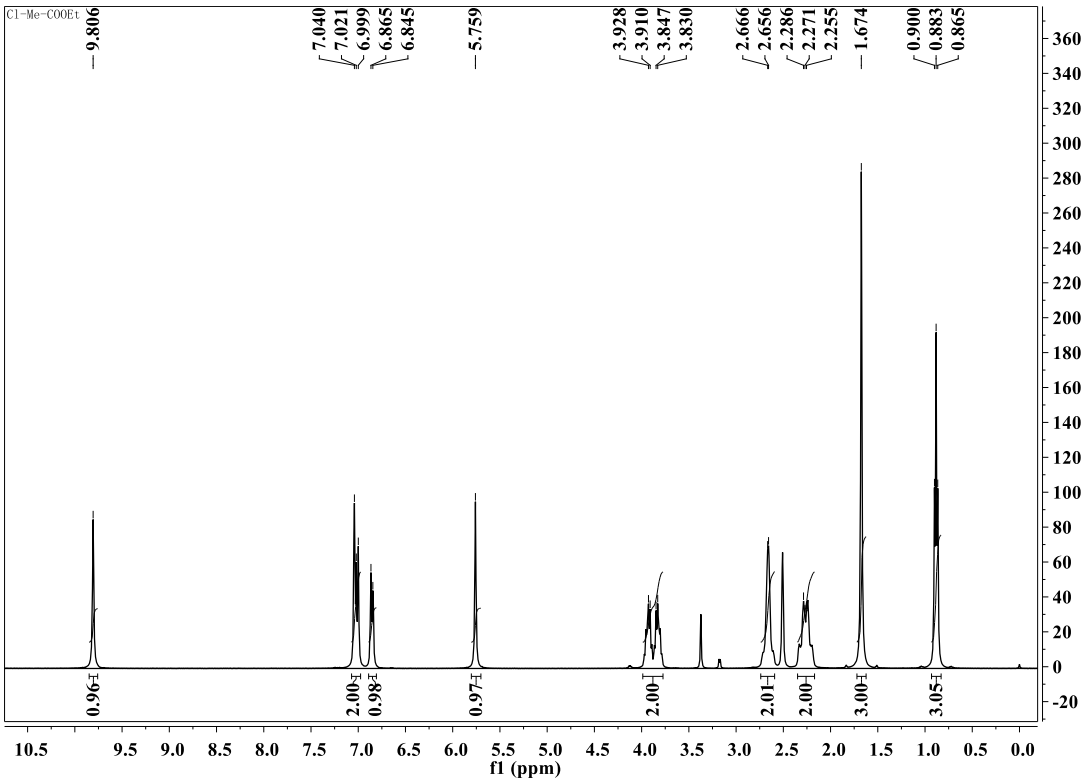
^{1}H NMR spectra of compound **5aad**



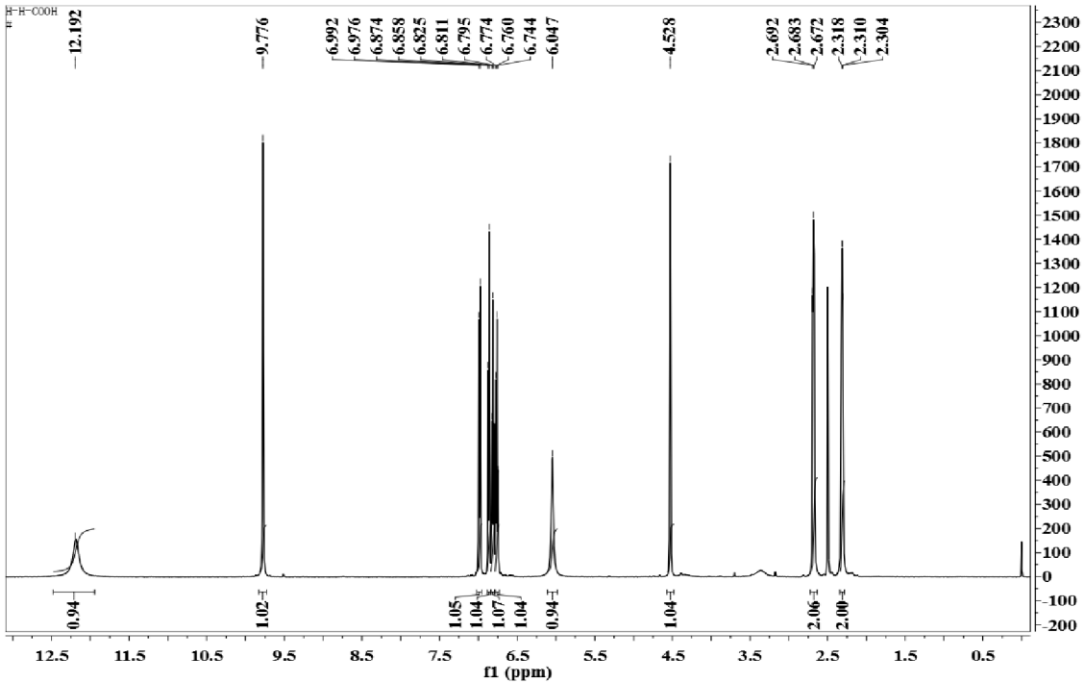
^{1}H NMR spectra of compound **5bad**



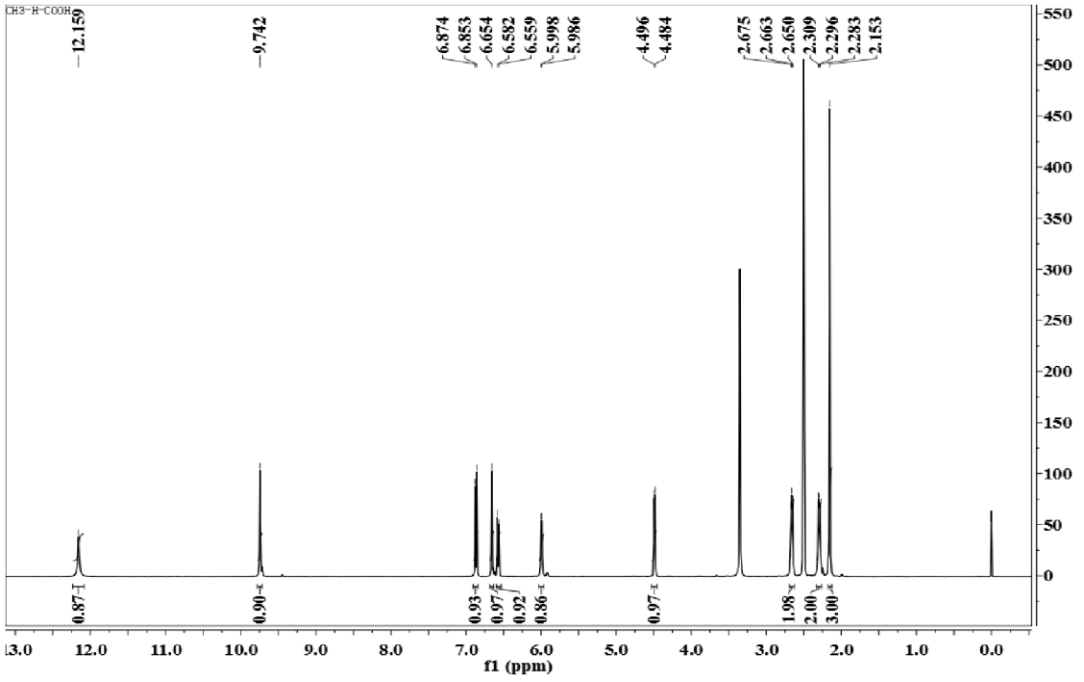
^{1}H NMR spectra of compound **5cad**



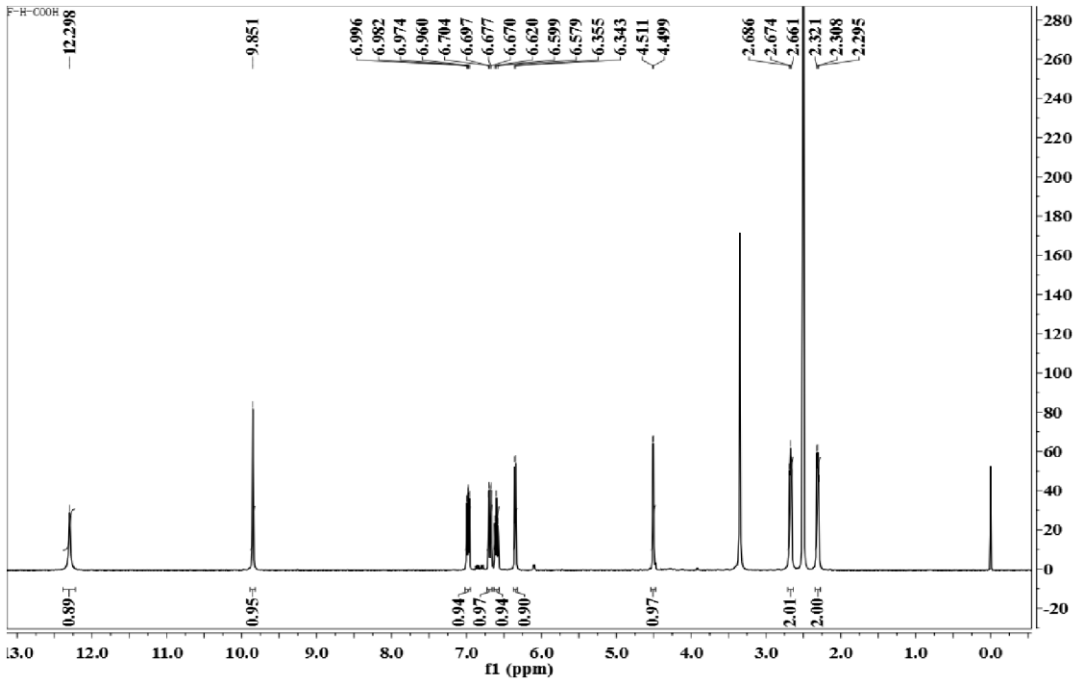
^{1}H NMR spectra of compound **5dad**



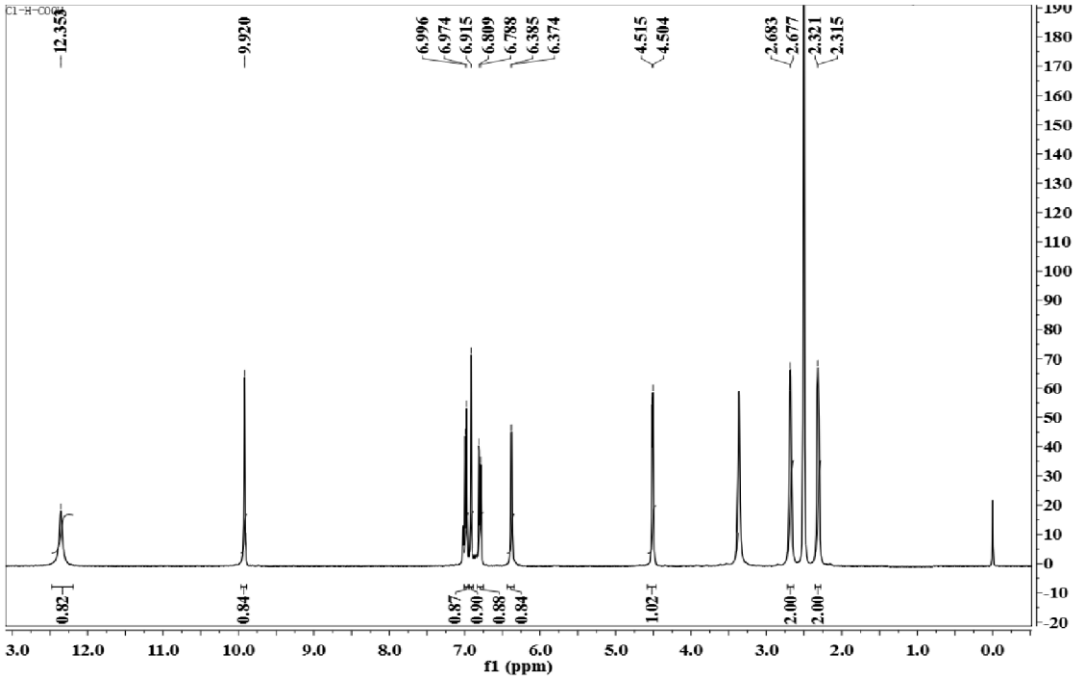
^{1}H NMR spectra of compound **5aae**



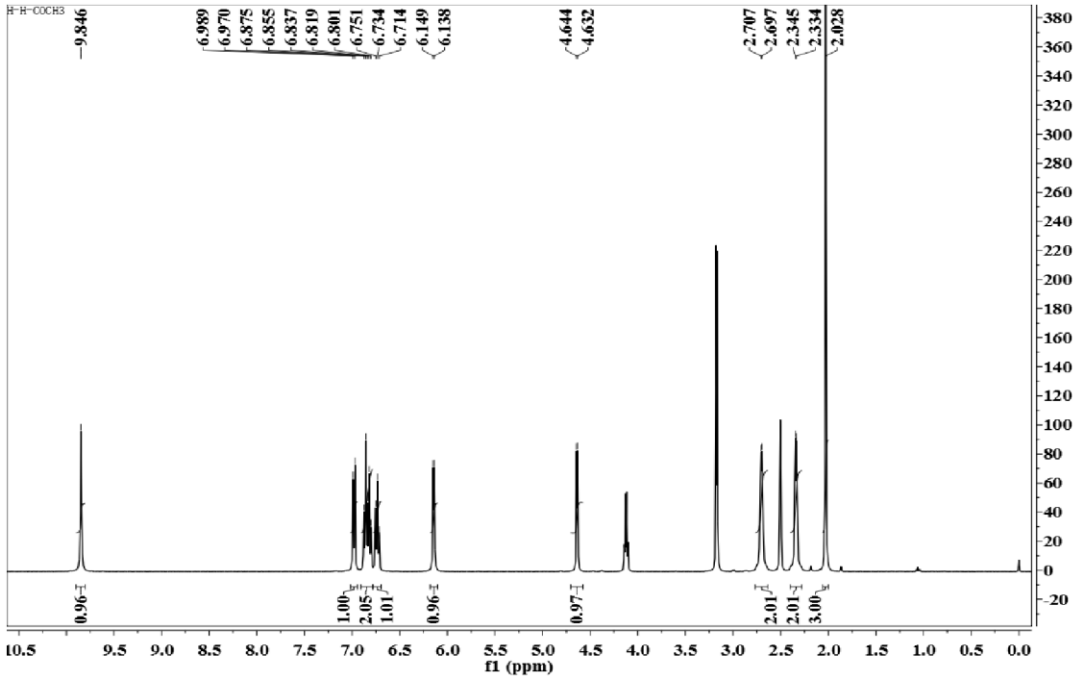
^{1}H NMR spectra of compound **5bae**



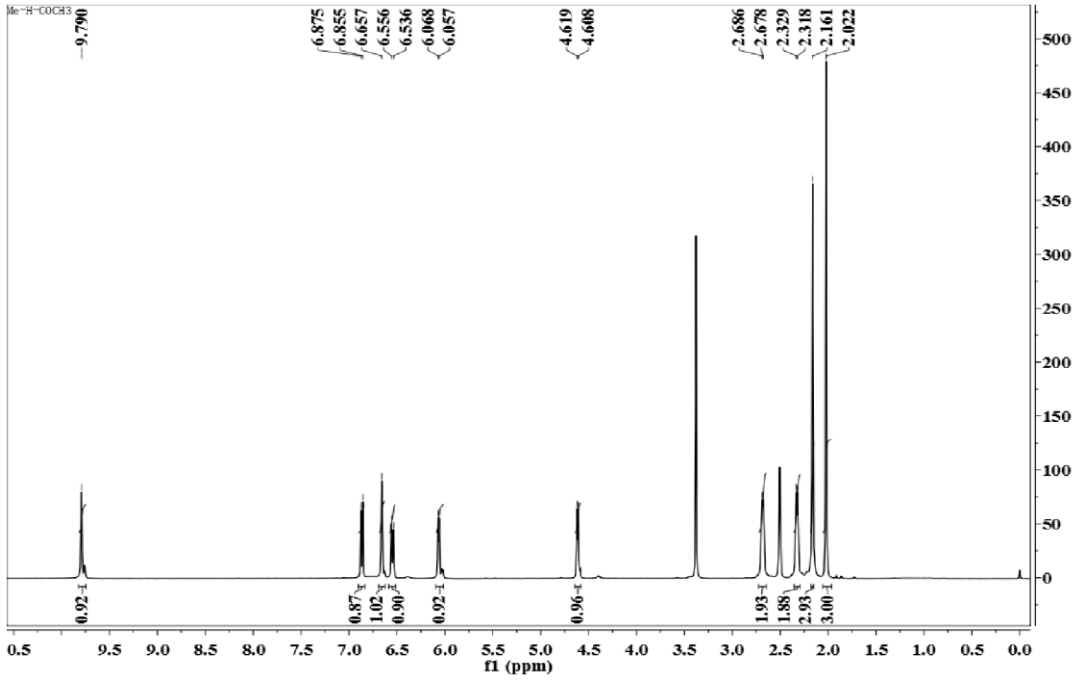
^{1}H NMR spectra of compound **5cae**



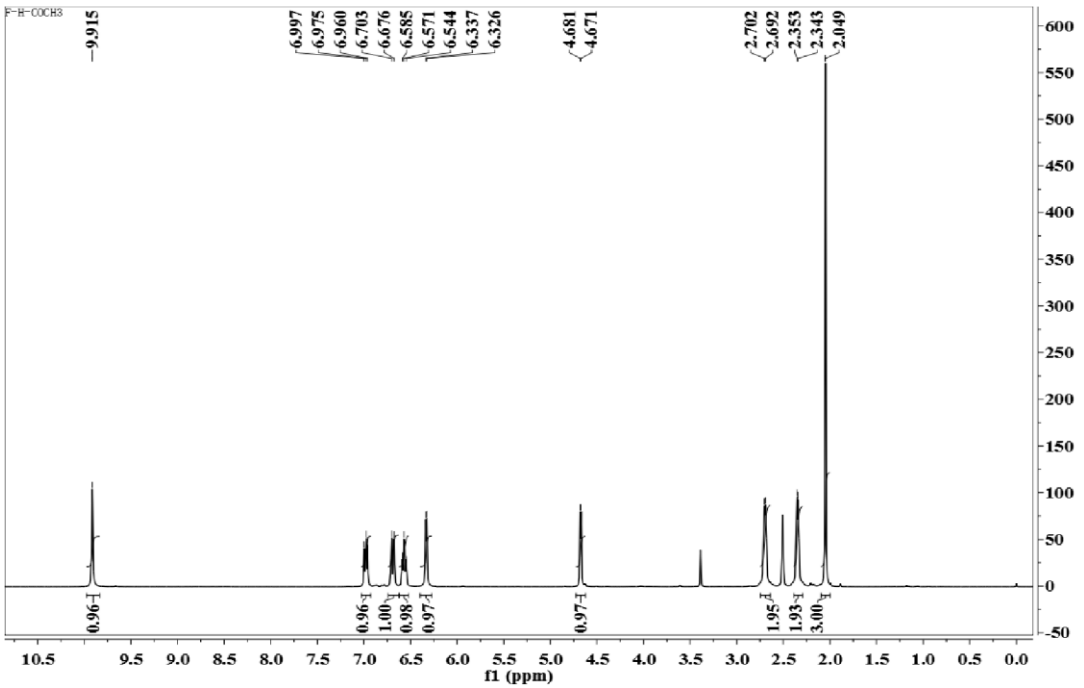
^{1}H NMR spectra of compound **5dae**



^{1}H NMR spectra of compound **5aaf**



^{1}H NMR spectra of compound **5baf**



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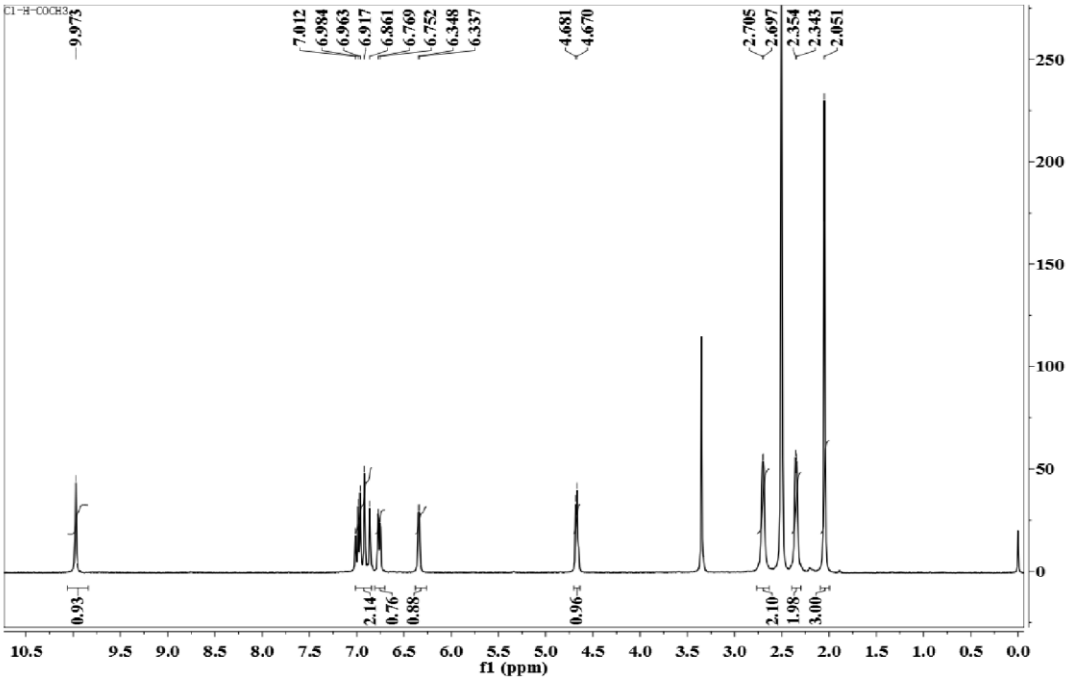
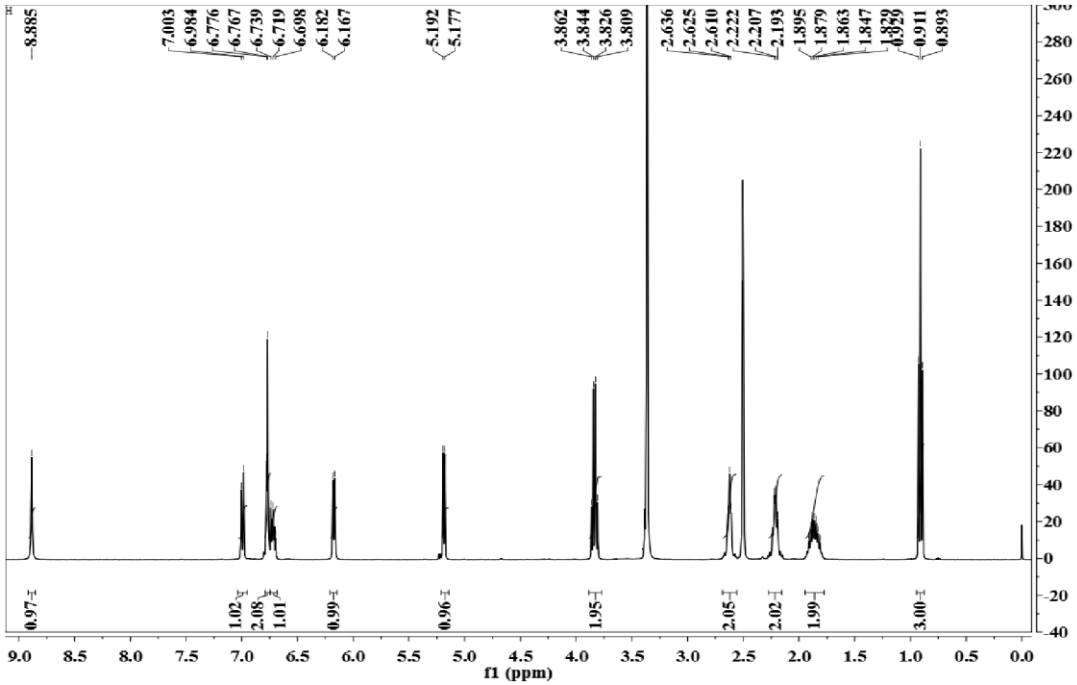
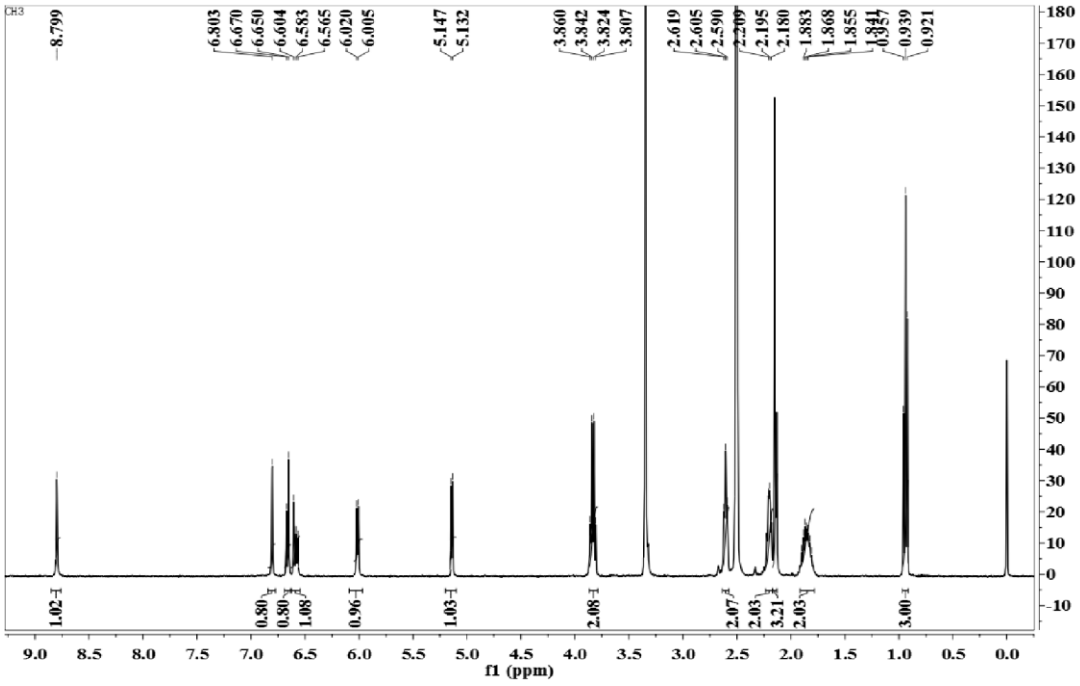


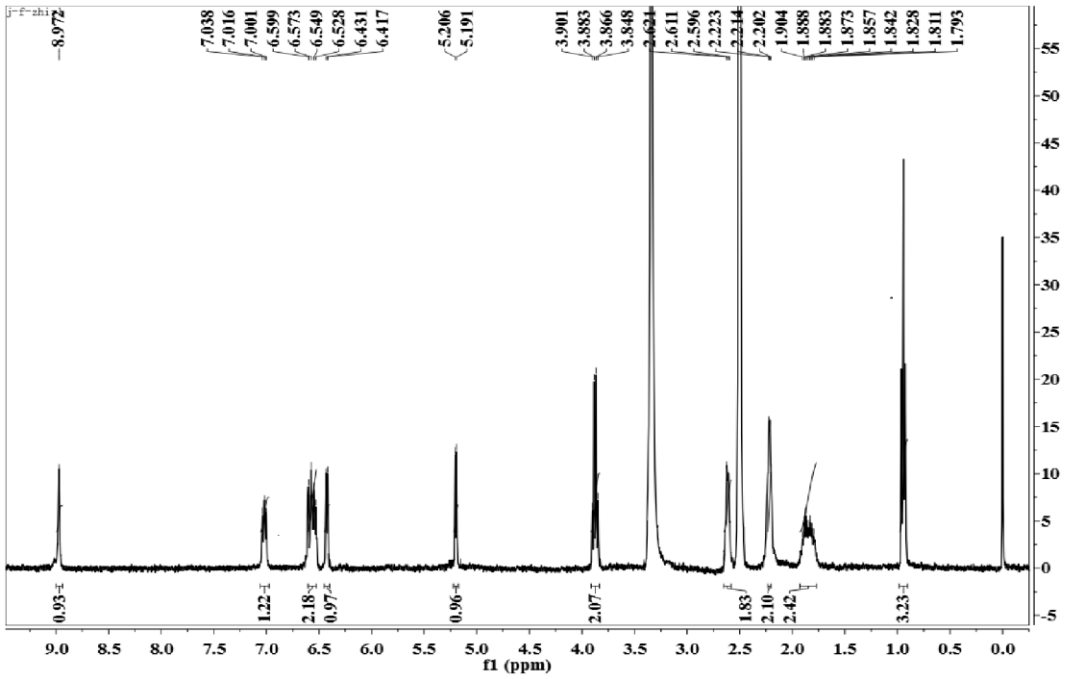
^{1}H NMR spectra of compound **5daf**



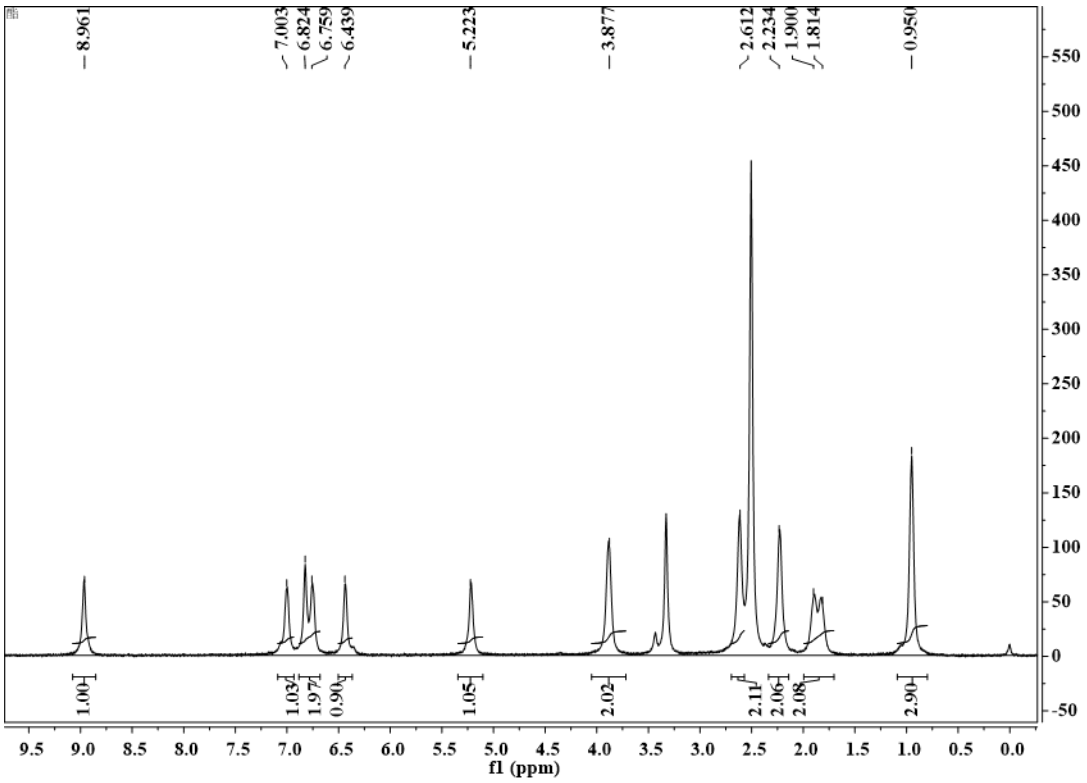
^{1}H NMR spectra of compound **5abc**



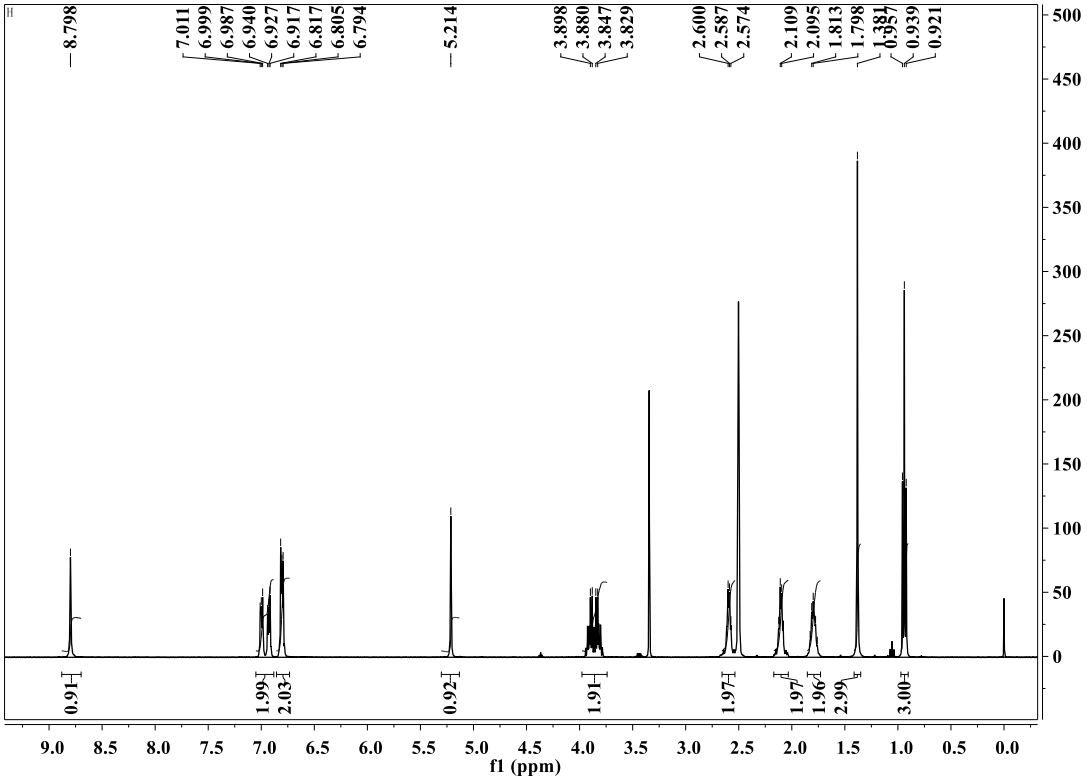
^{1}H NMR spectra of compound **5bbc**



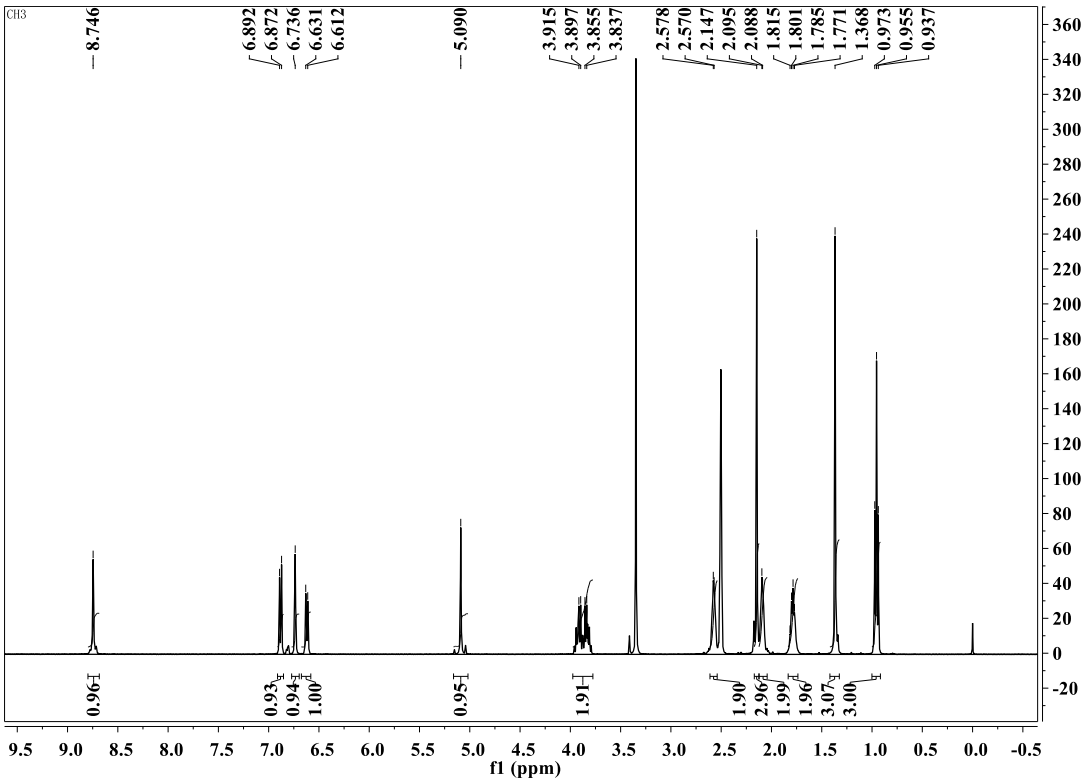
^{1}H NMR spectra of compound **5cbc**



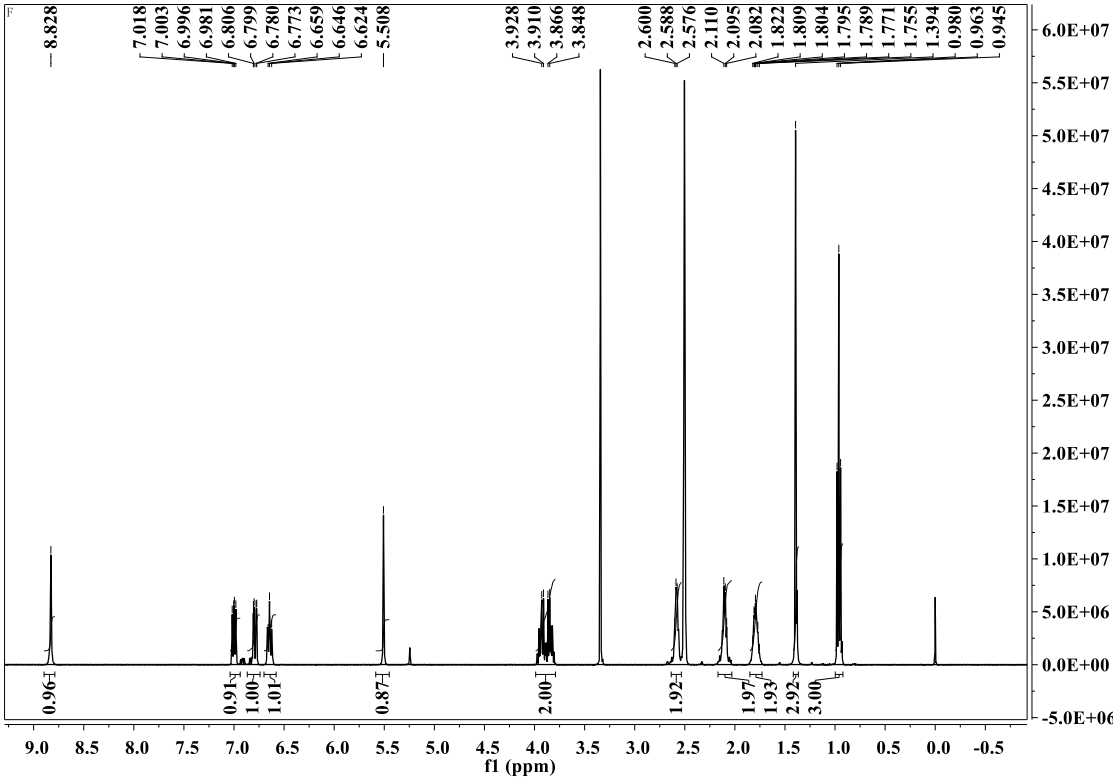
^{1}H NMR spectra of compound **5dbc**



^{1}H NMR spectra of compound **5abd**



^{1}H NMR spectra of compound **5bbd**



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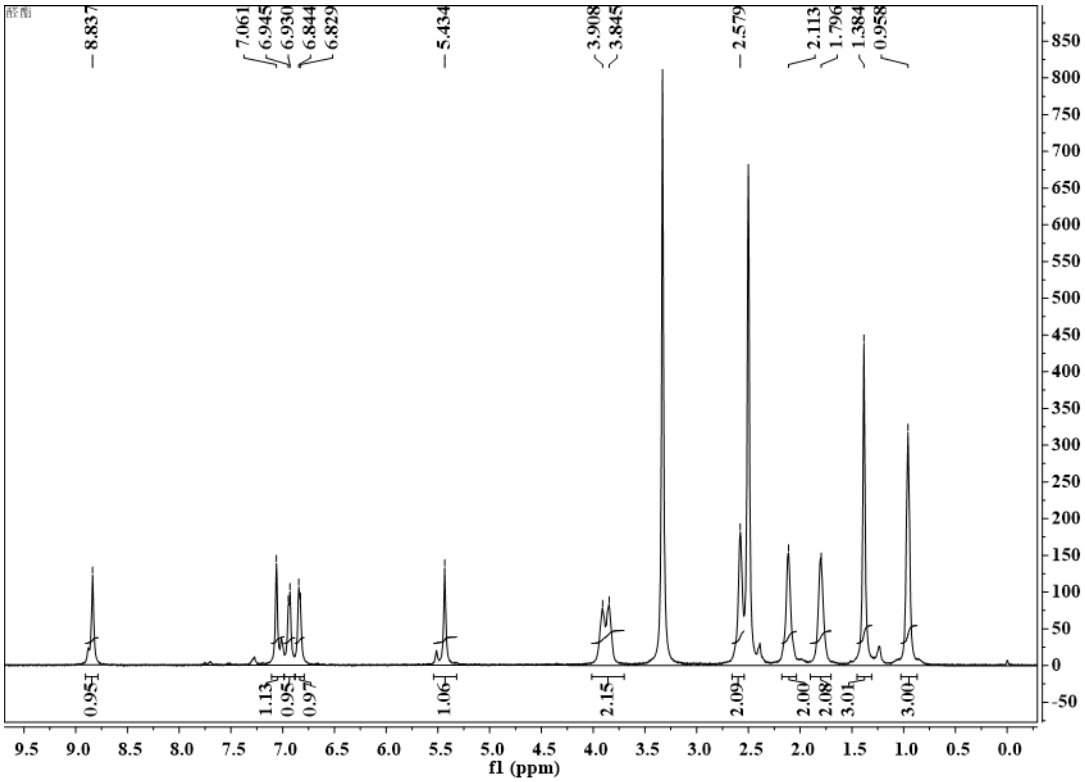

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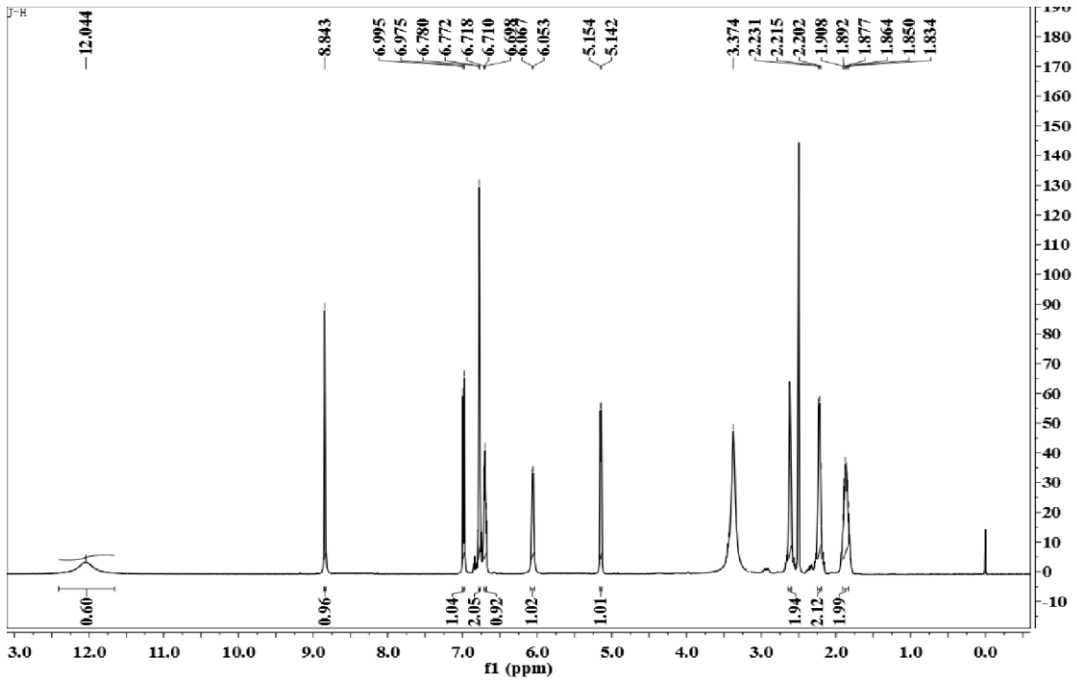
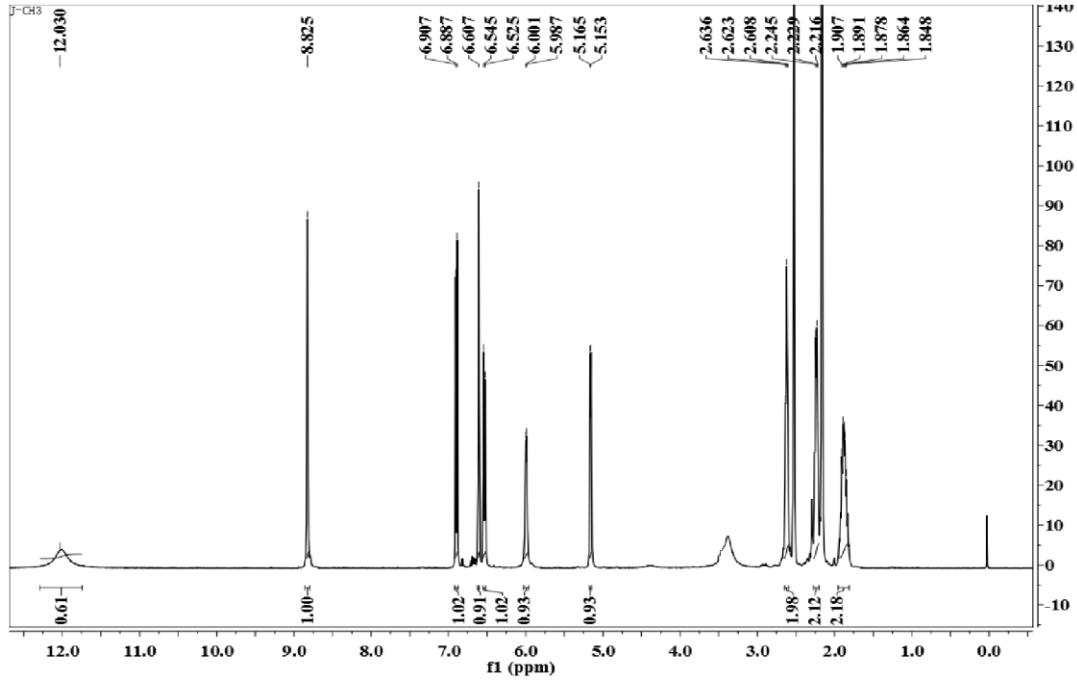
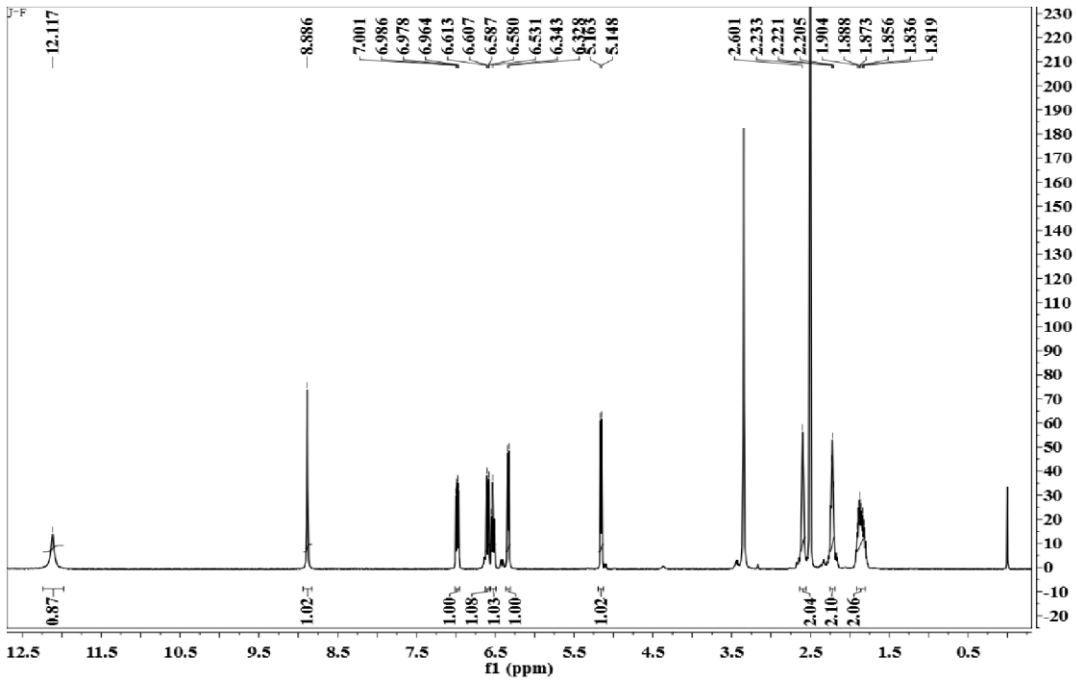


^{1}H NMR spectra of compound **5abe**



^{1}H NMR spectra of compound **5bbe**



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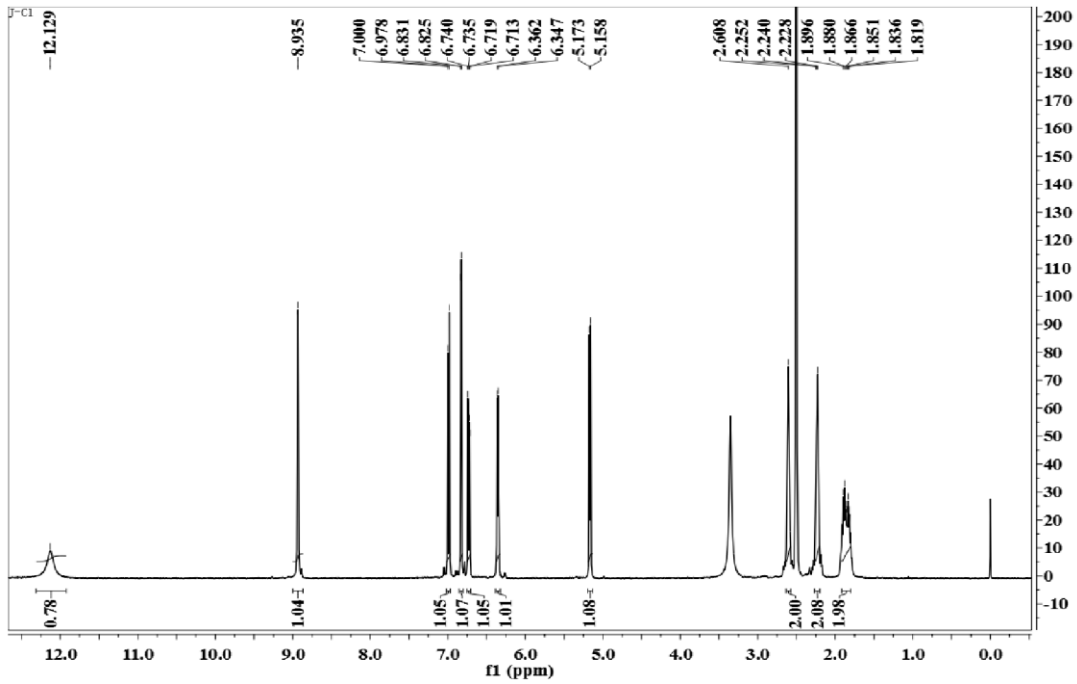
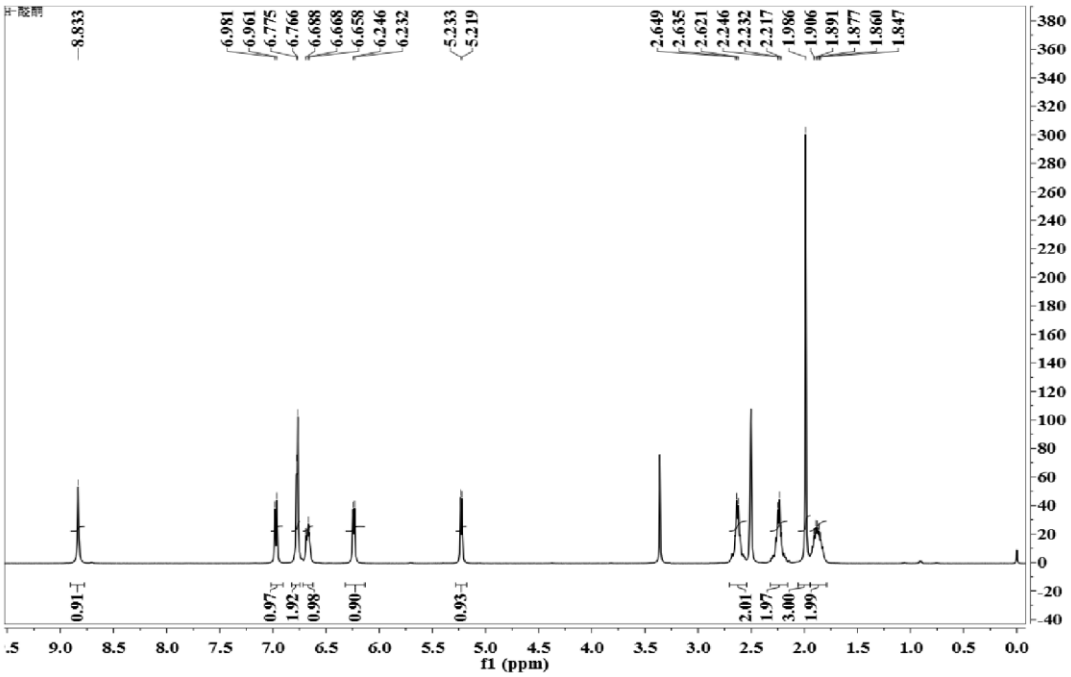


^{1}H NMR spectra of compound **5dbe**



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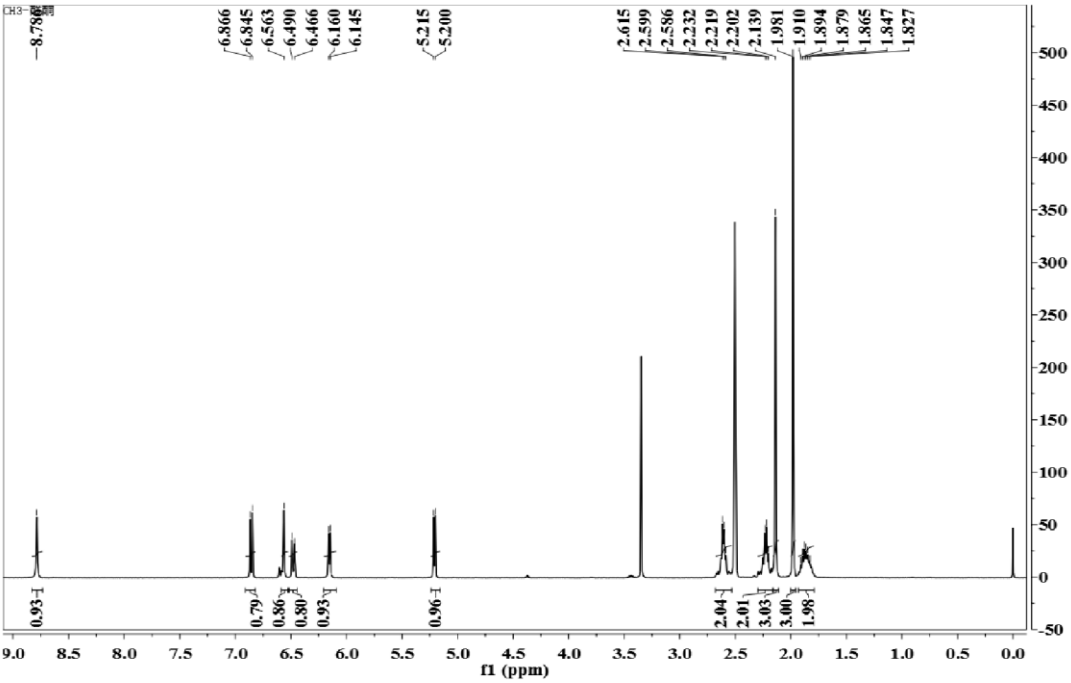
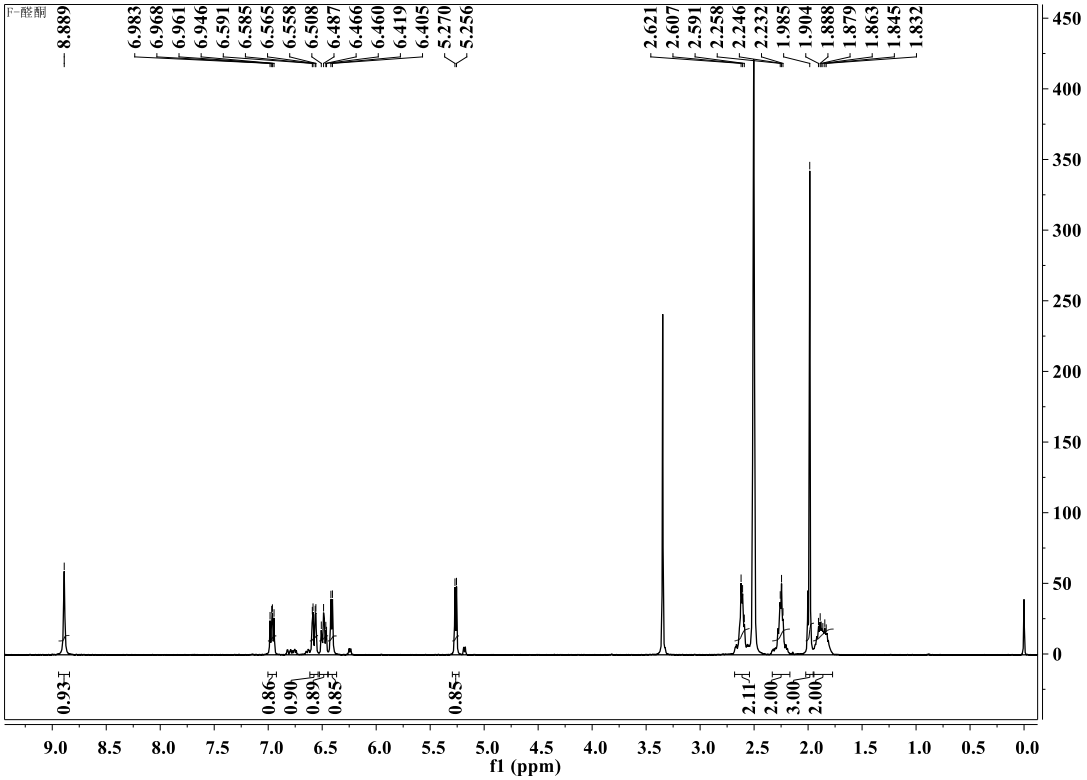
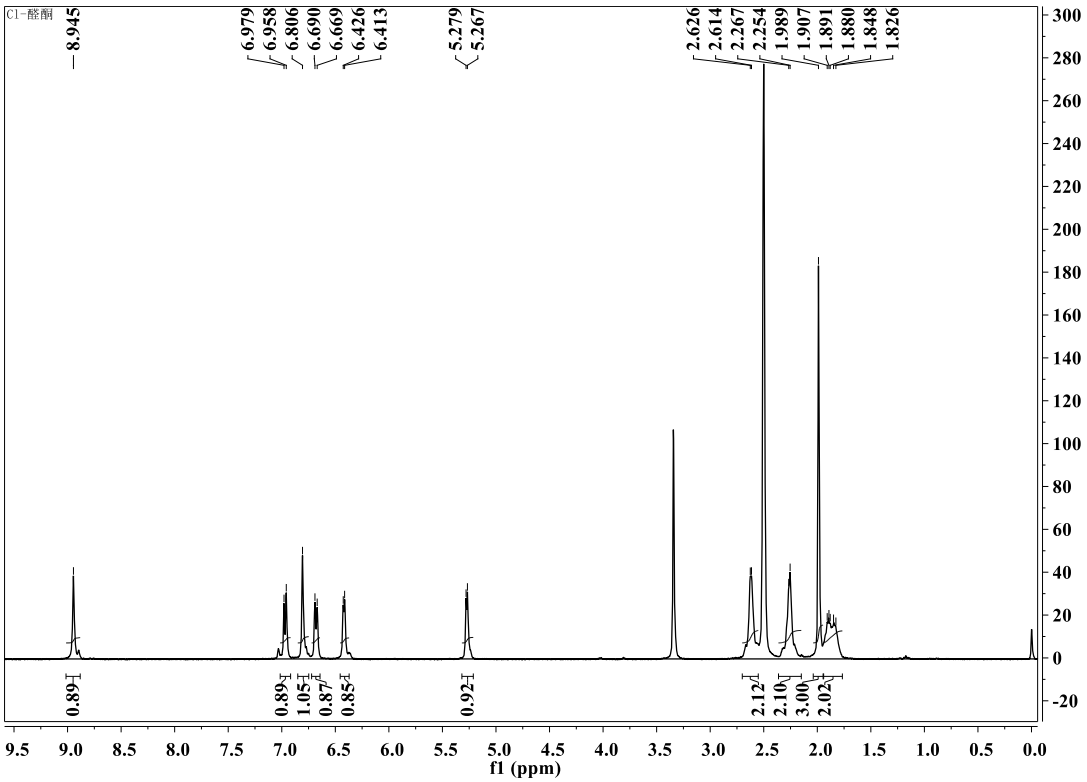


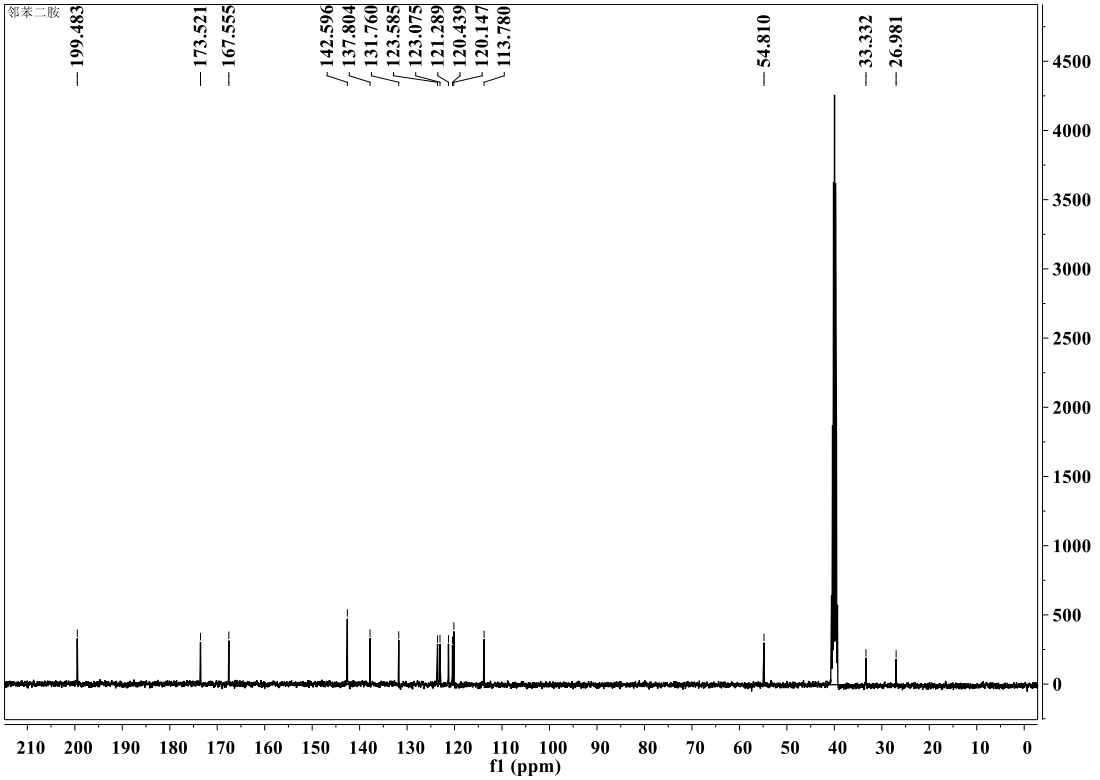
^{1}H NMR spectra of compound **5bbf**



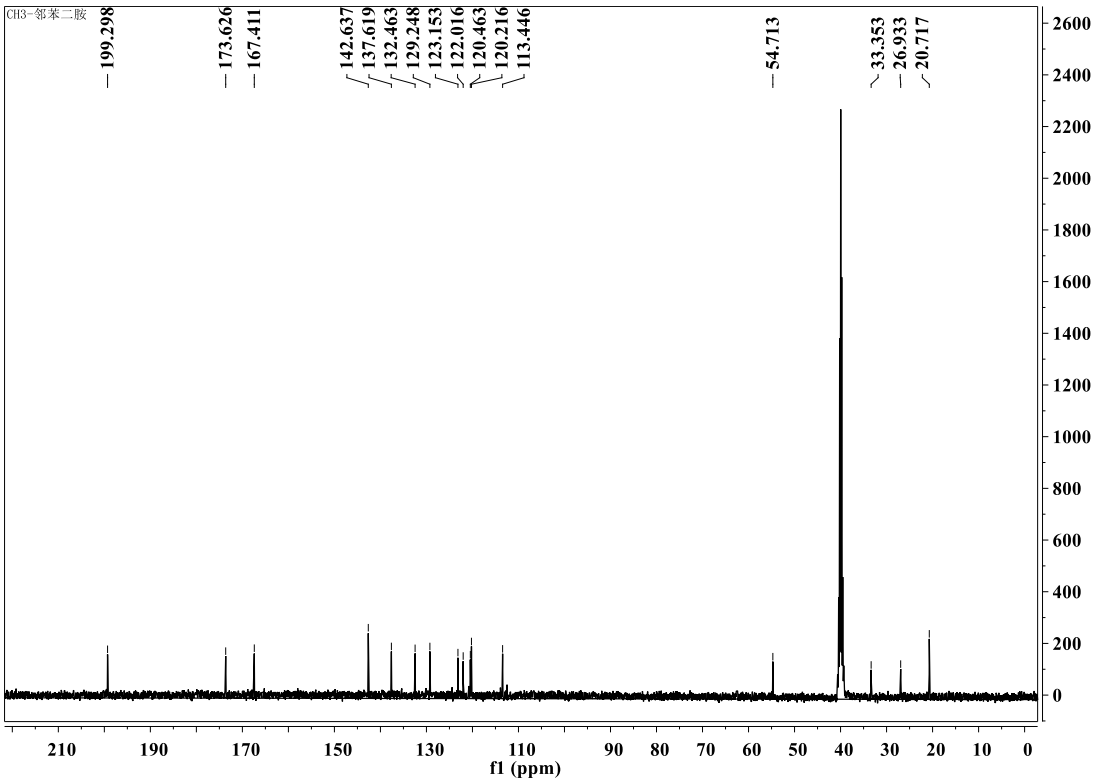
^{1}H NMR spectra of compound **5cbf**



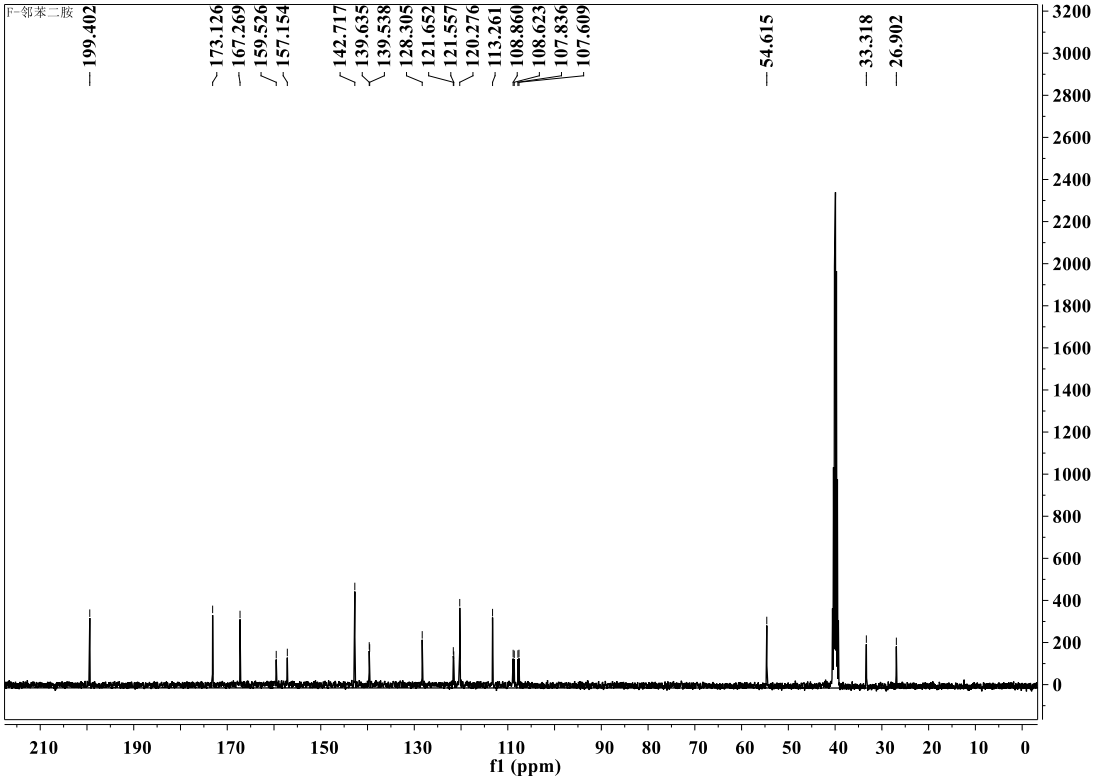
^{1}H NMR spectra of compound **5dbf**



^{13}C NMR spectra of compound **4aaa**



^{13}C NMR spectra of compound **4baa**



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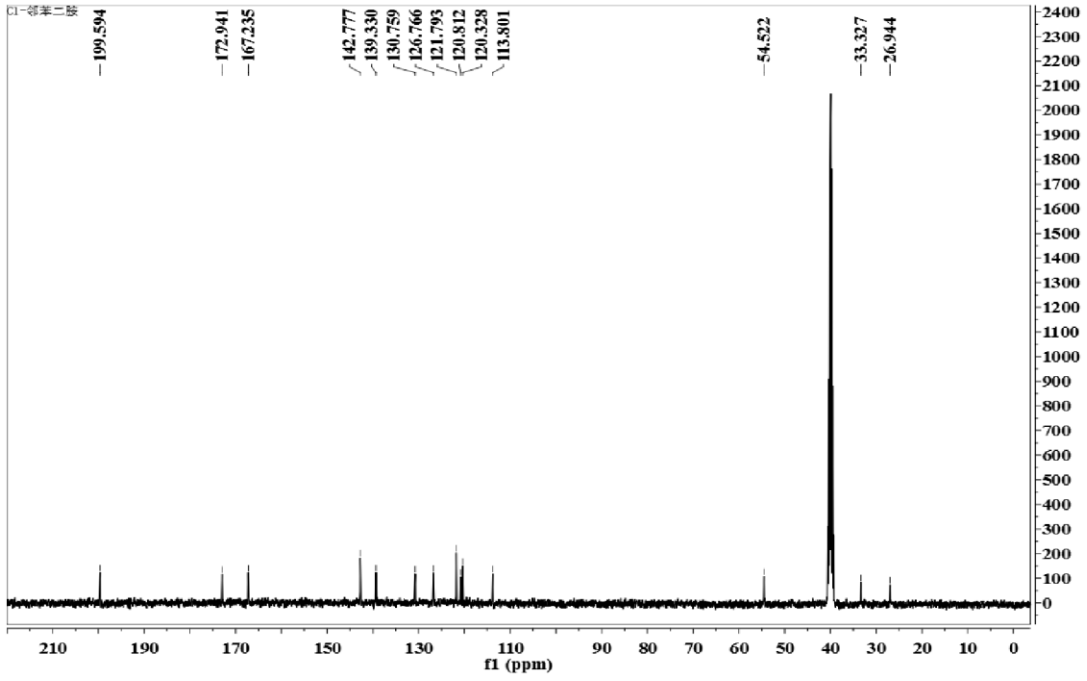
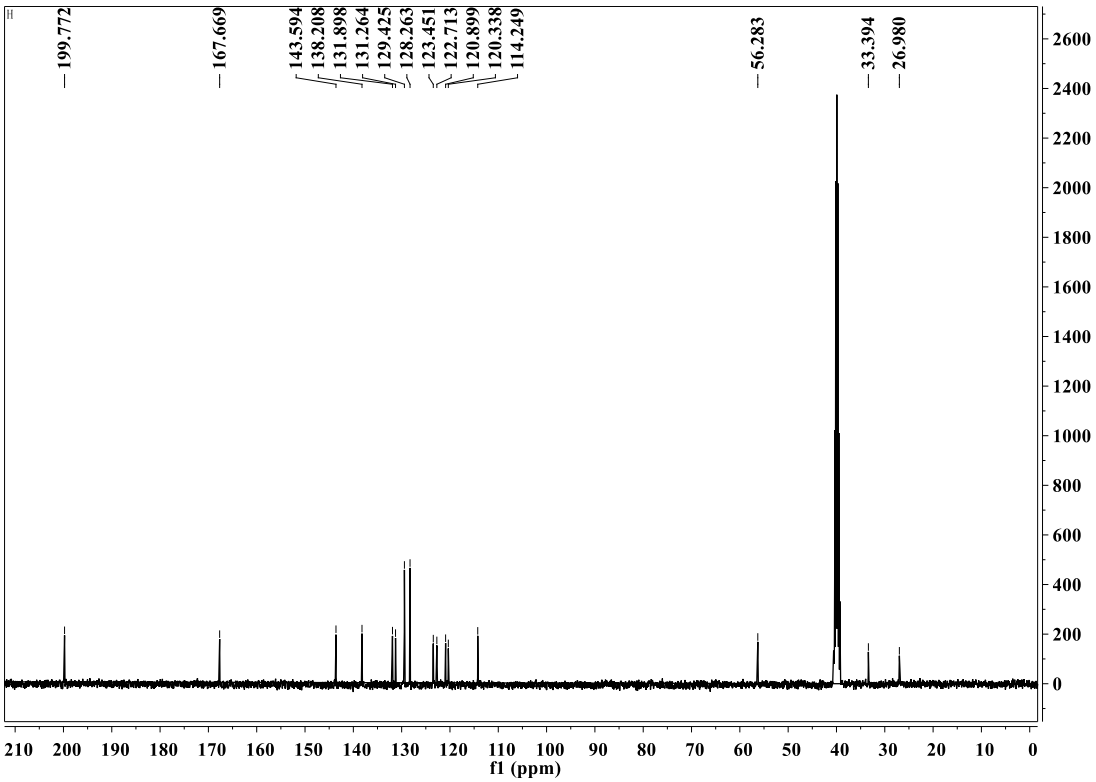


^{13}C NMR spectra of compound **4daa**



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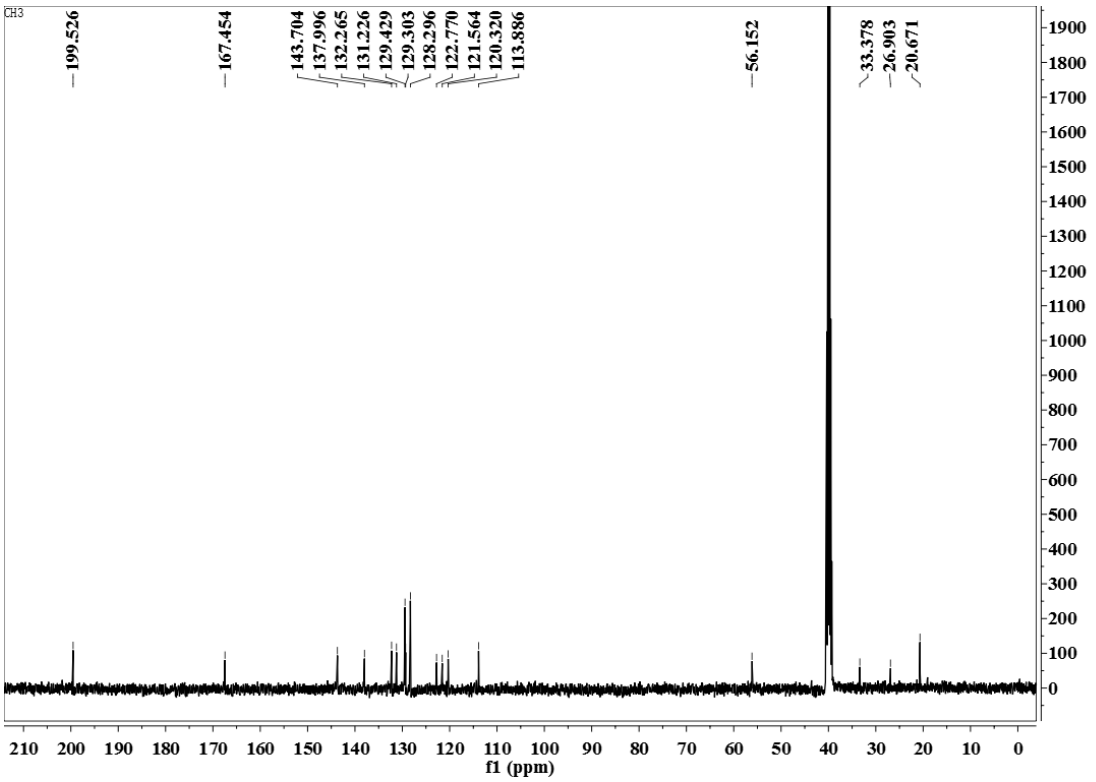

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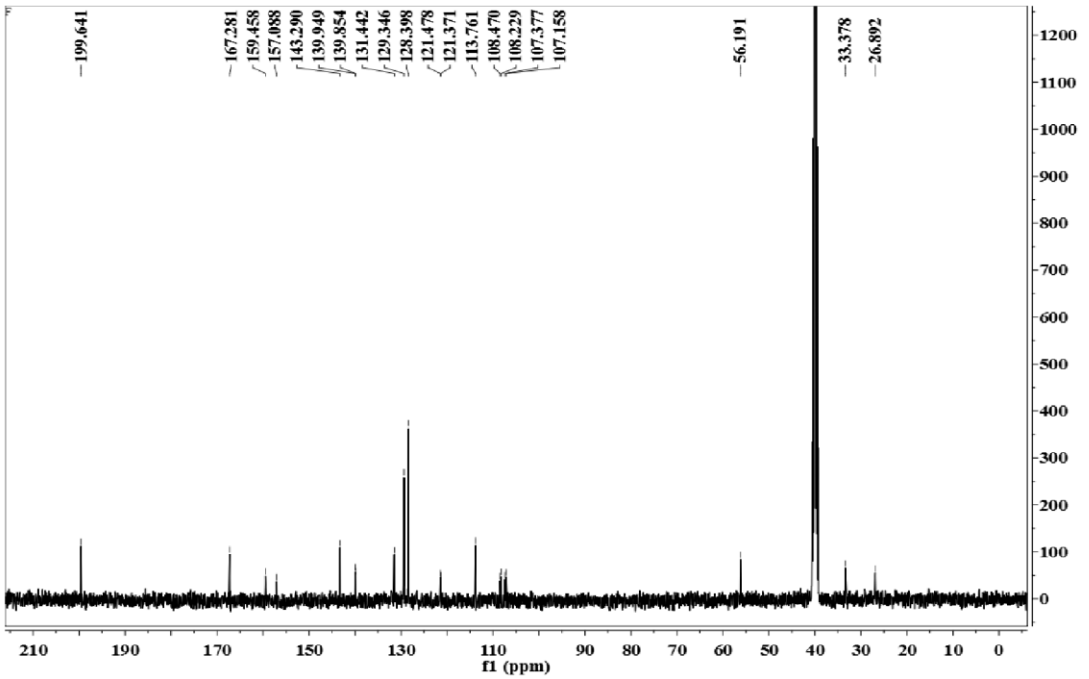

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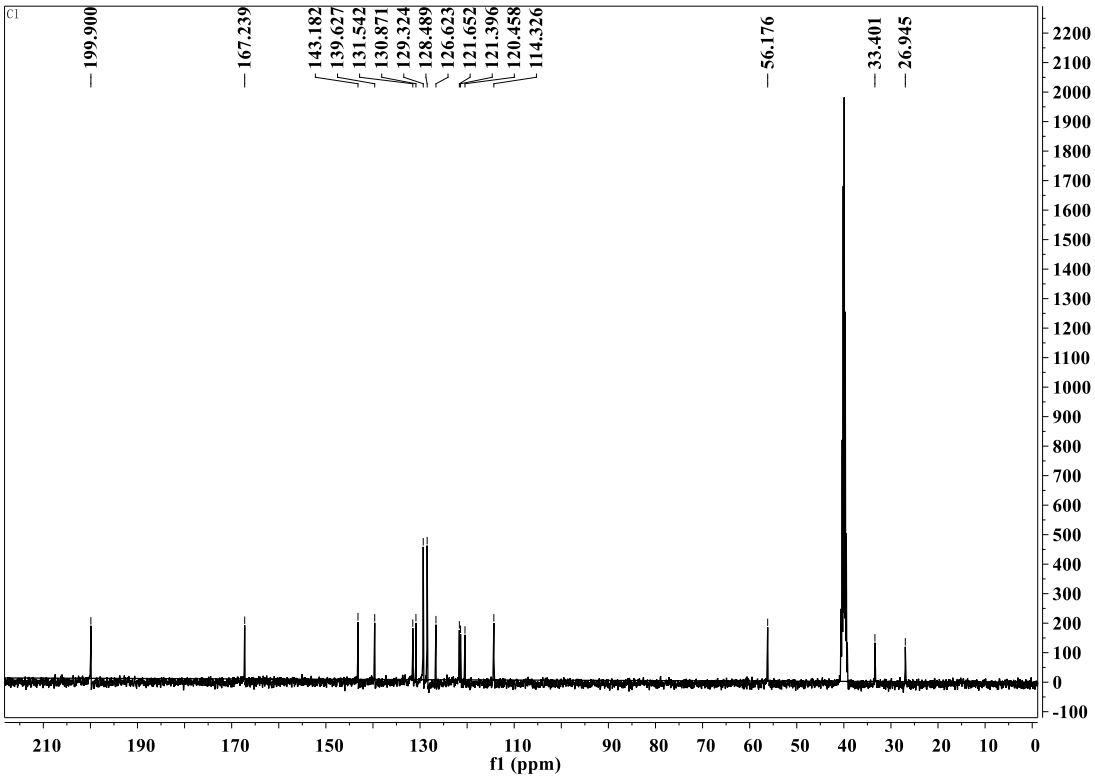

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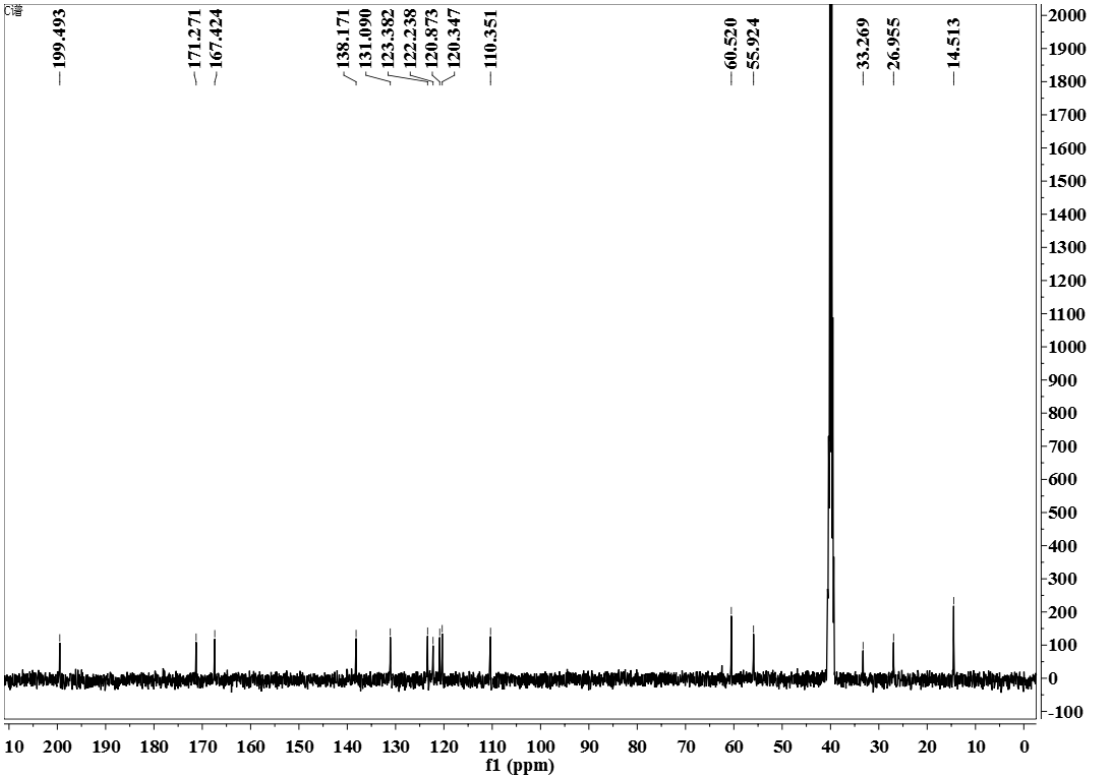
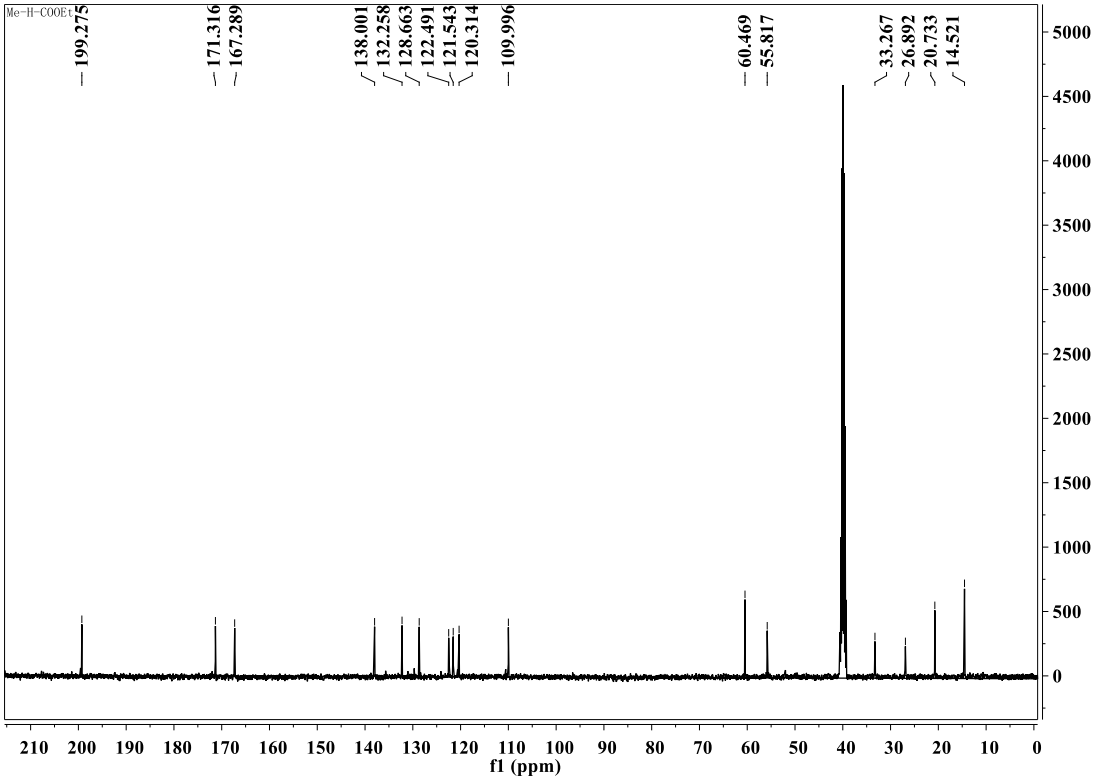
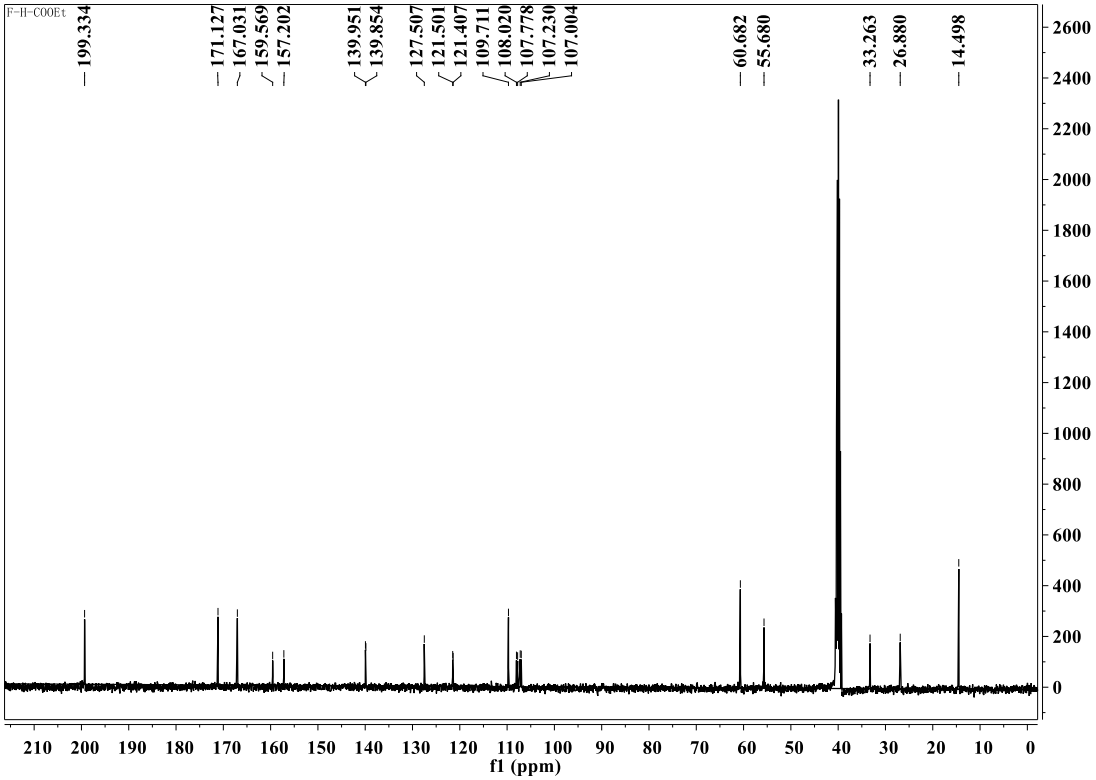


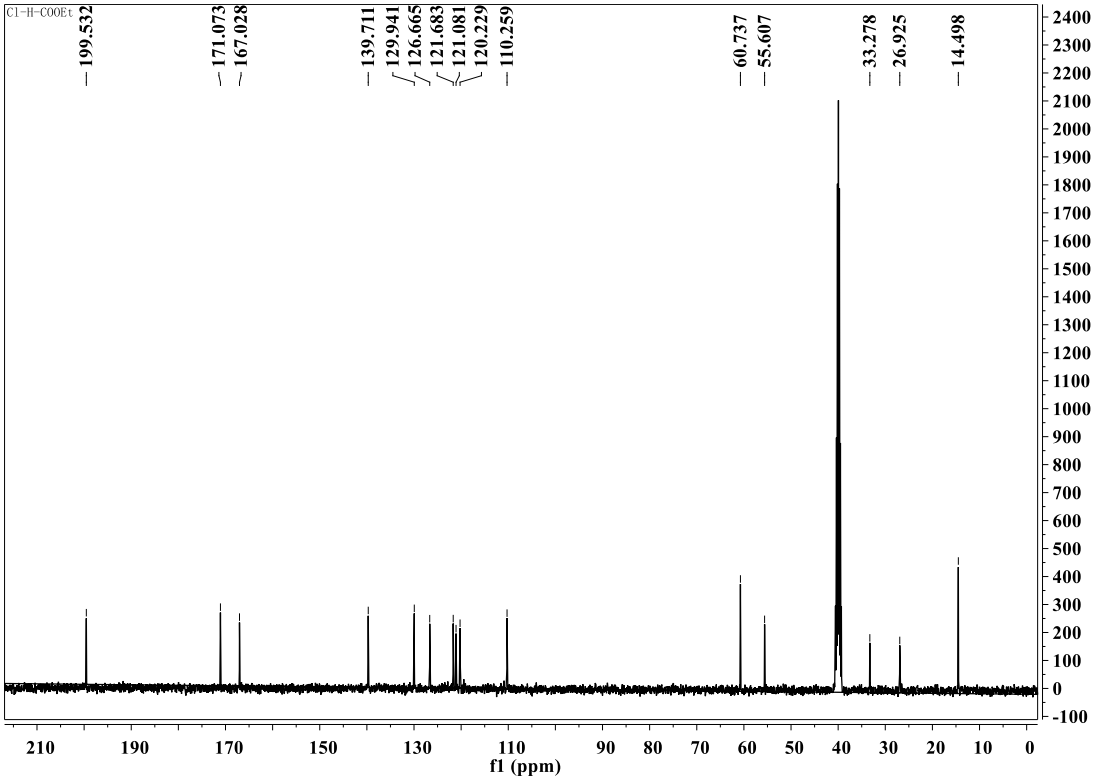
^{13}C NMR spectra of compound **5aac**



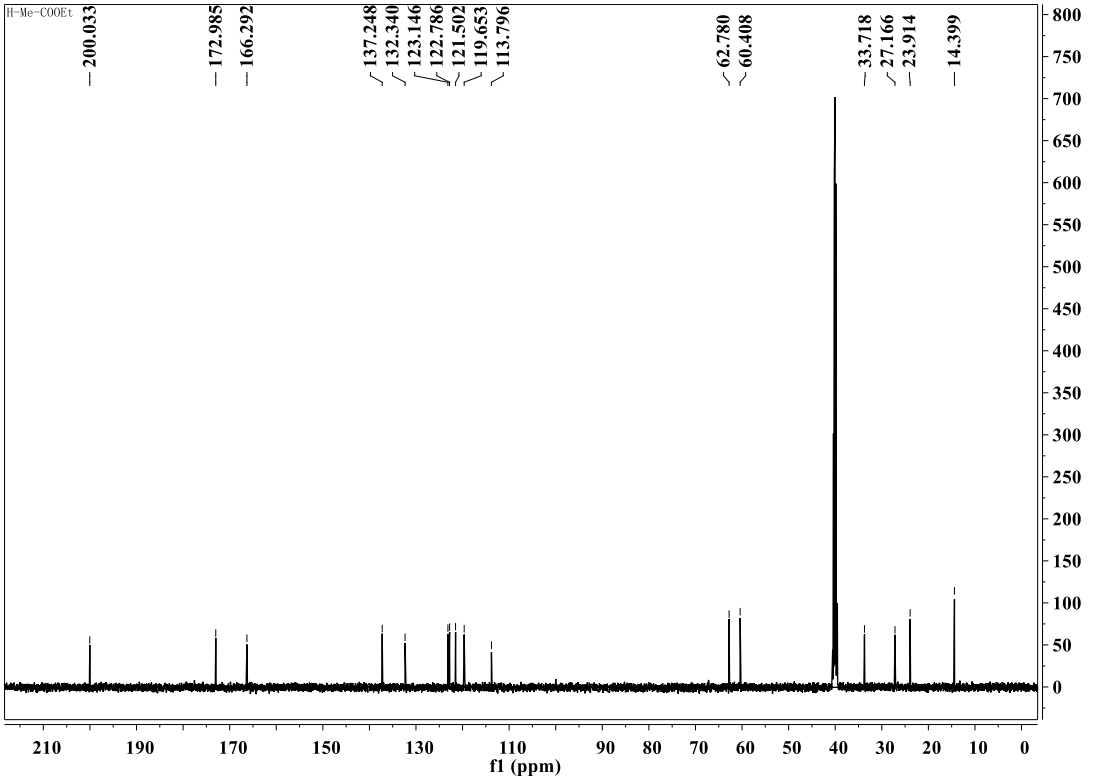
^{13}C NMR spectra of compound **5bac**



^{13}C NMR spectra of compound **5cac**



^{13}C NMR spectra of compound **5dac**



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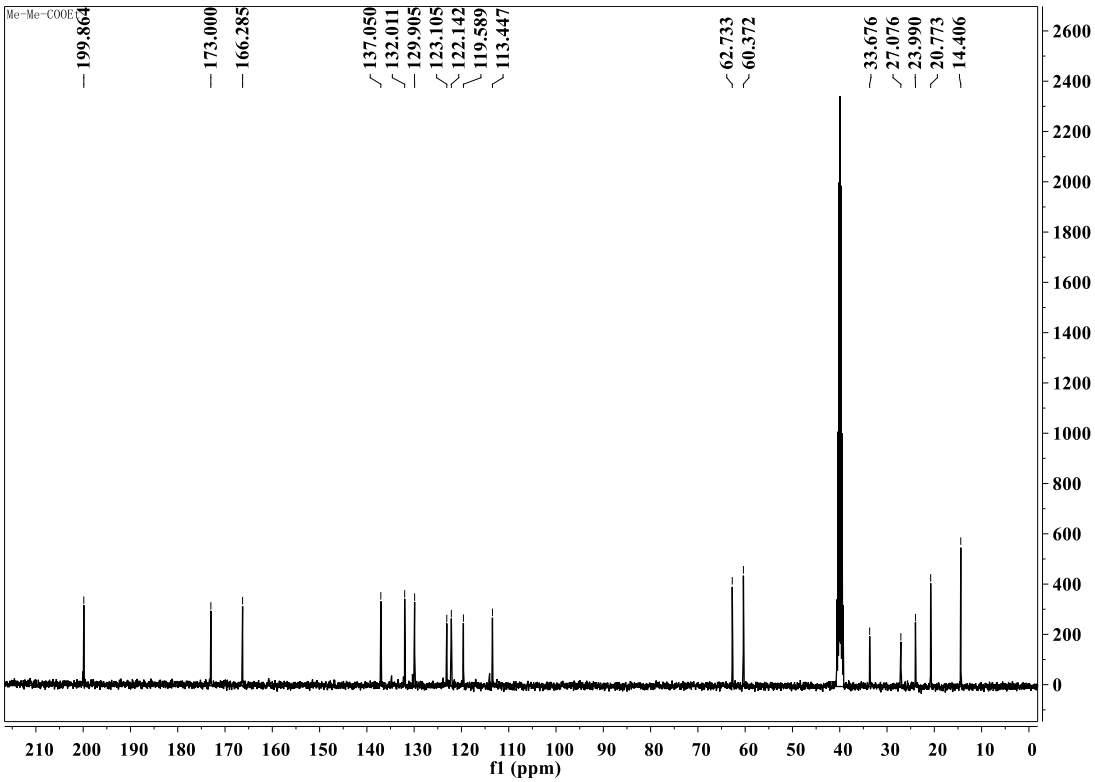
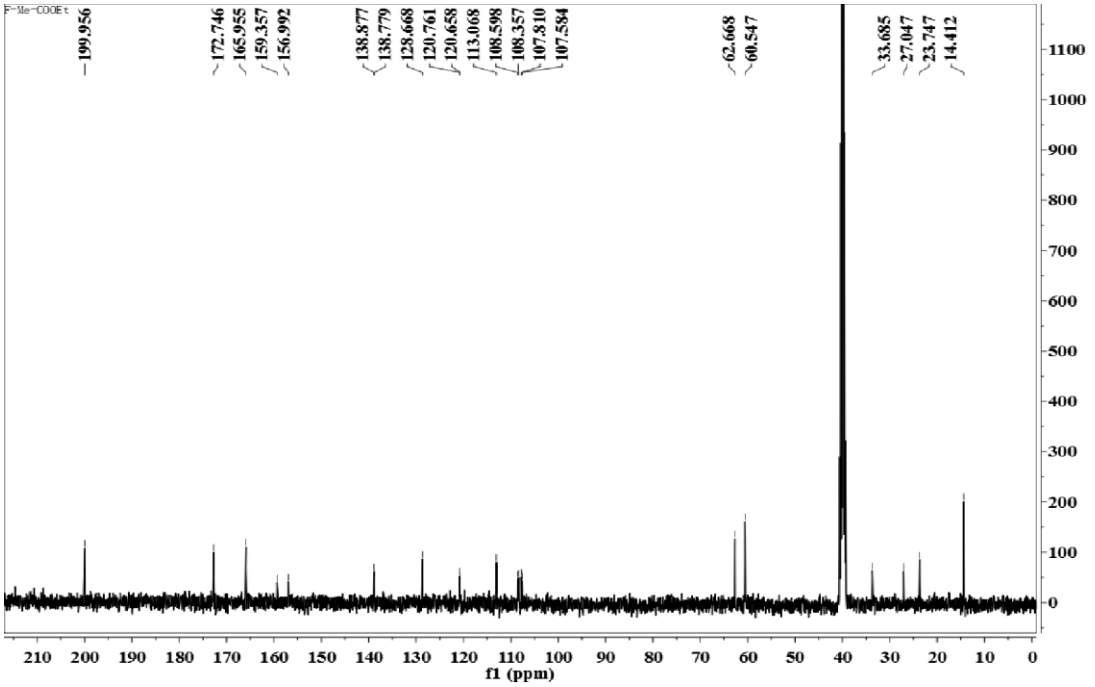
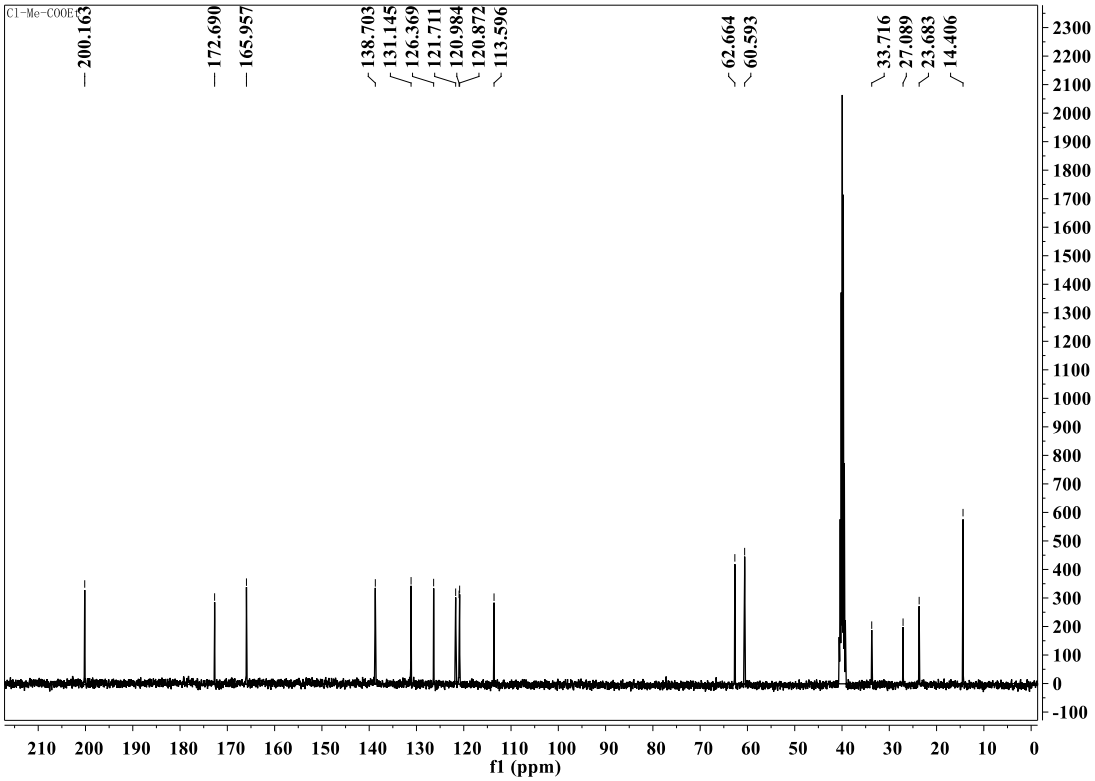


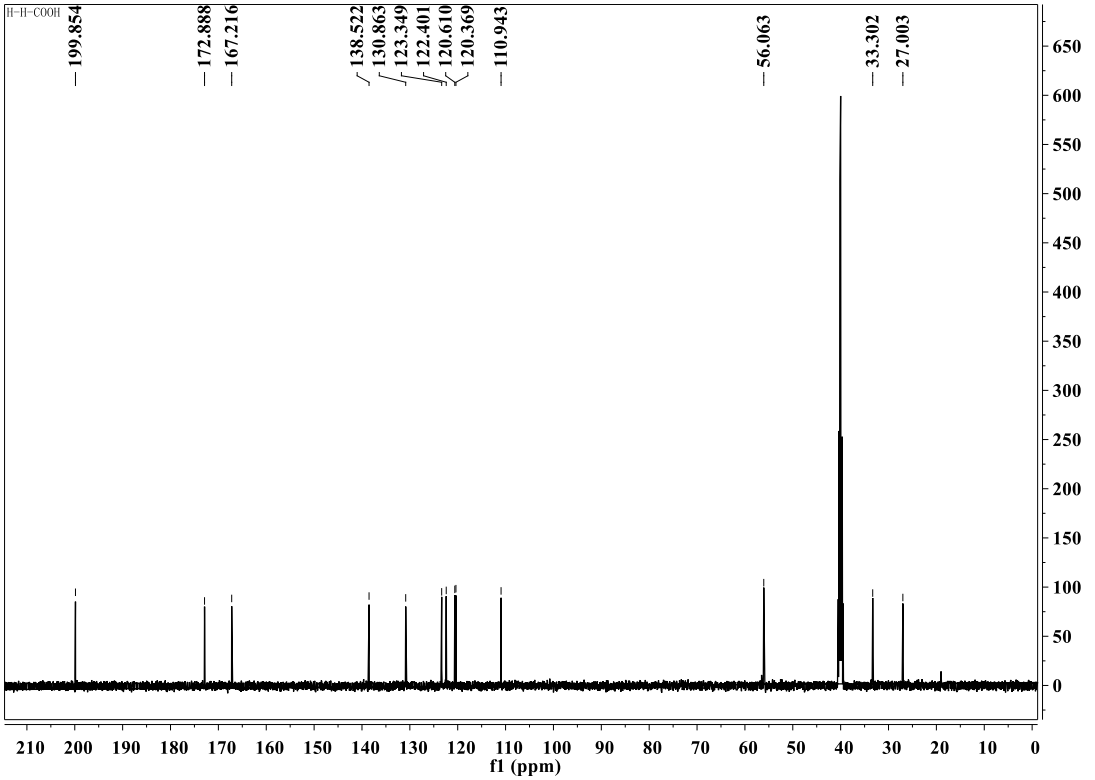
^{13}C NMR spectra of compound **5bad**



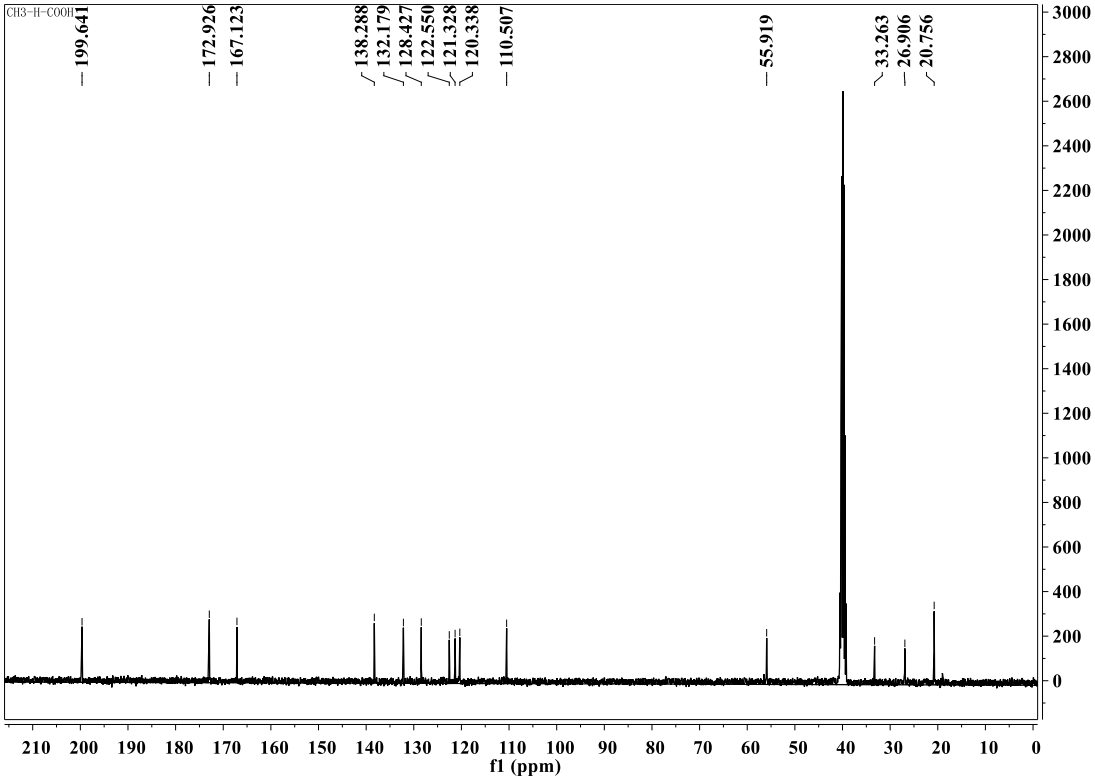
^{13}C NMR spectra of compound **5cad**



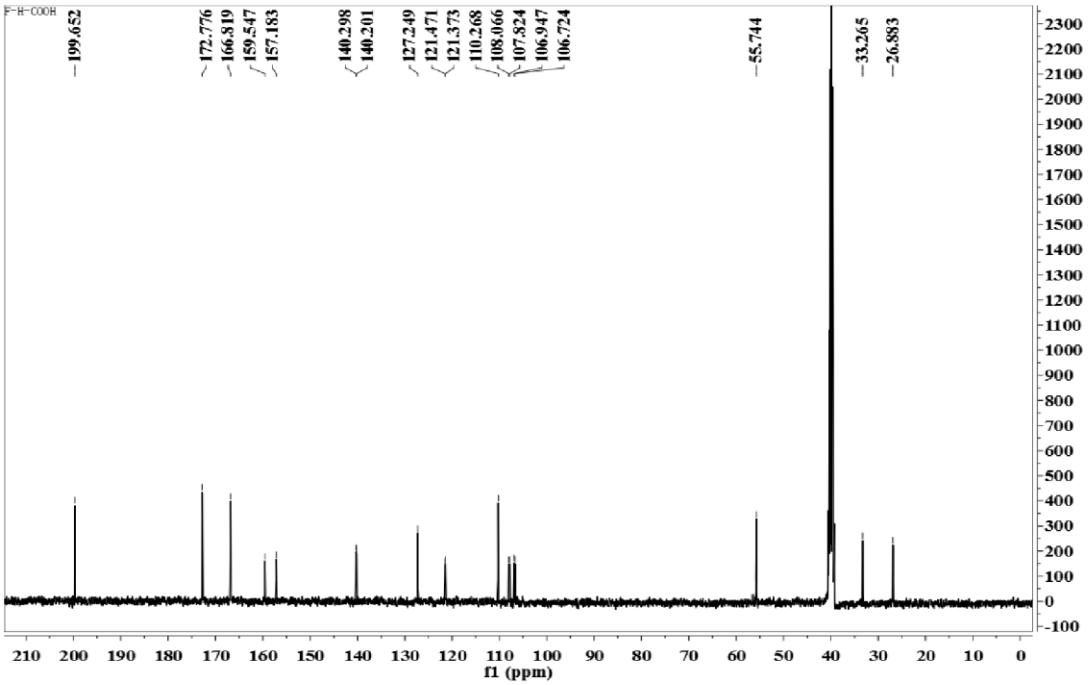
^{13}C NMR spectra of compound **5dad**



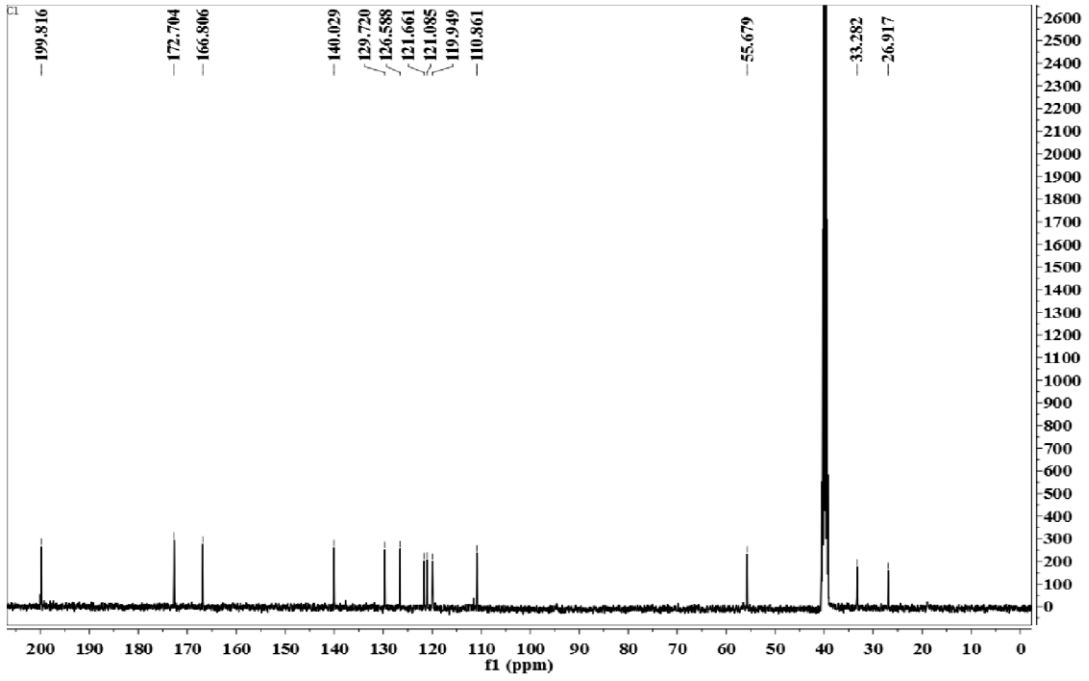
^{13}C NMR spectra of compound **5aae**



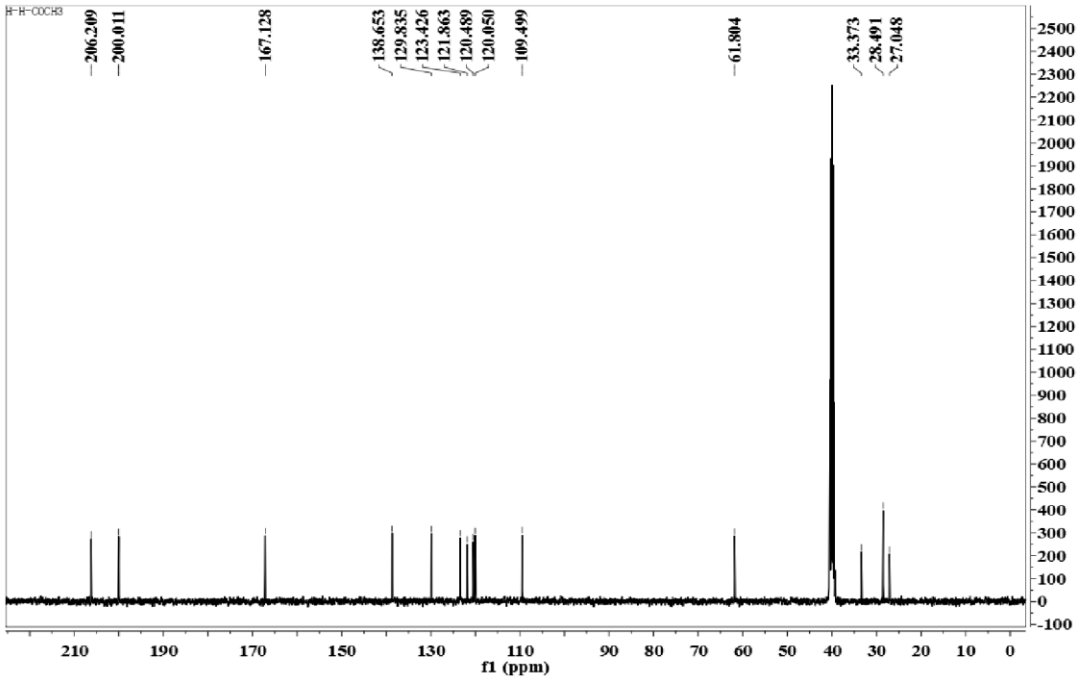
^{13}C NMR spectra of compound **5bae**



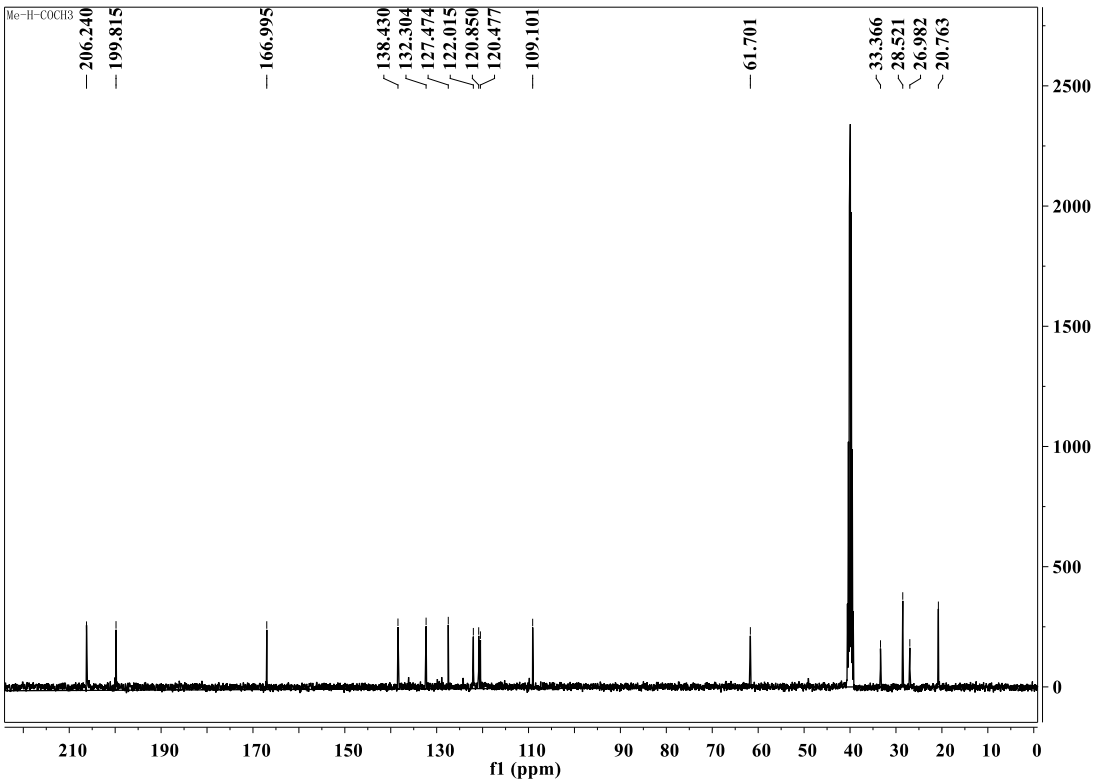
^{13}C NMR spectra of compound **5cae**



^{13}C NMR spectra of compound **5dae**



^{13}C NMR spectra of compound **5aaf**



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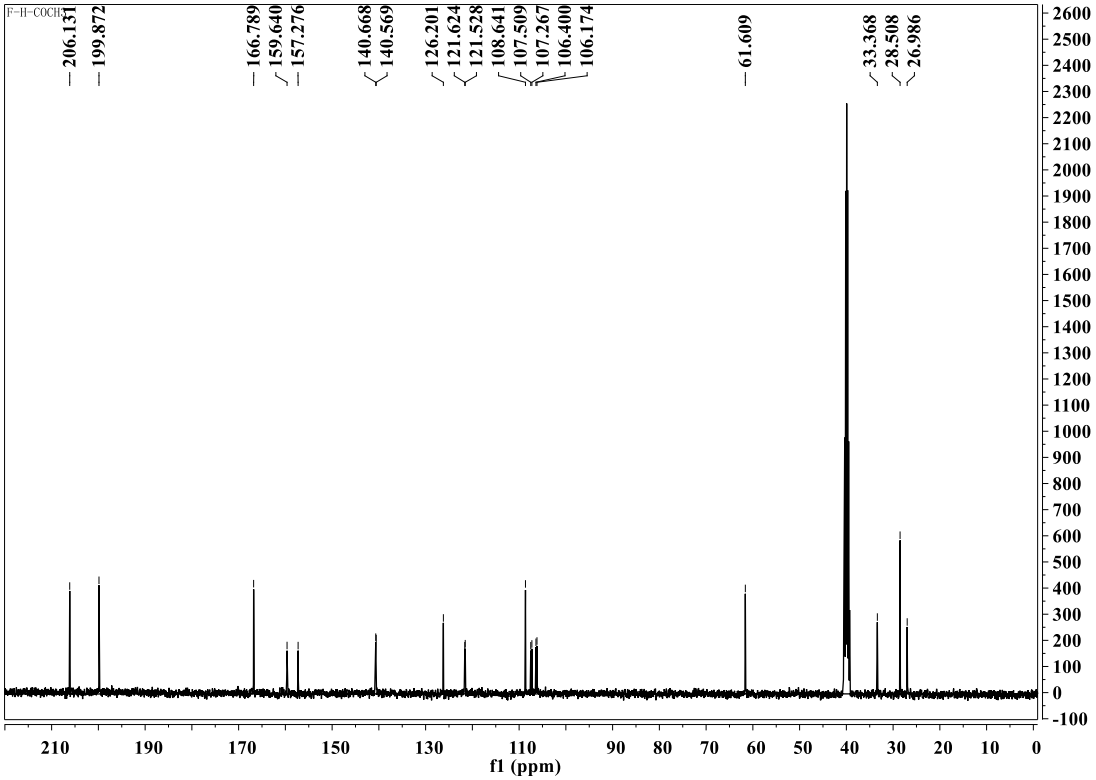

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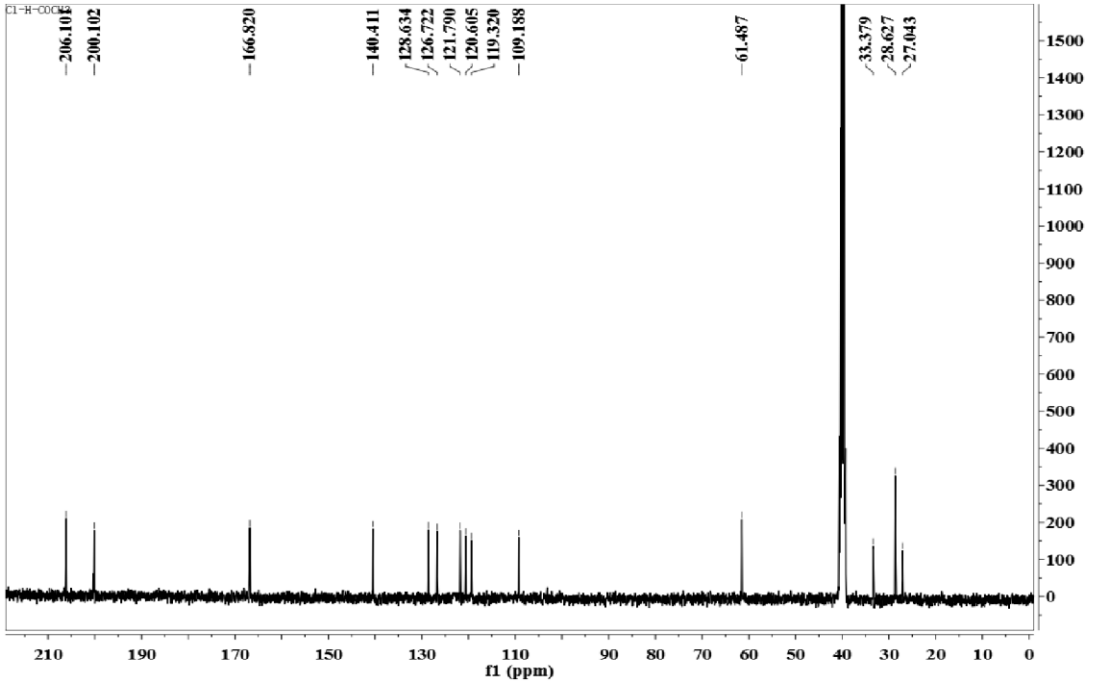
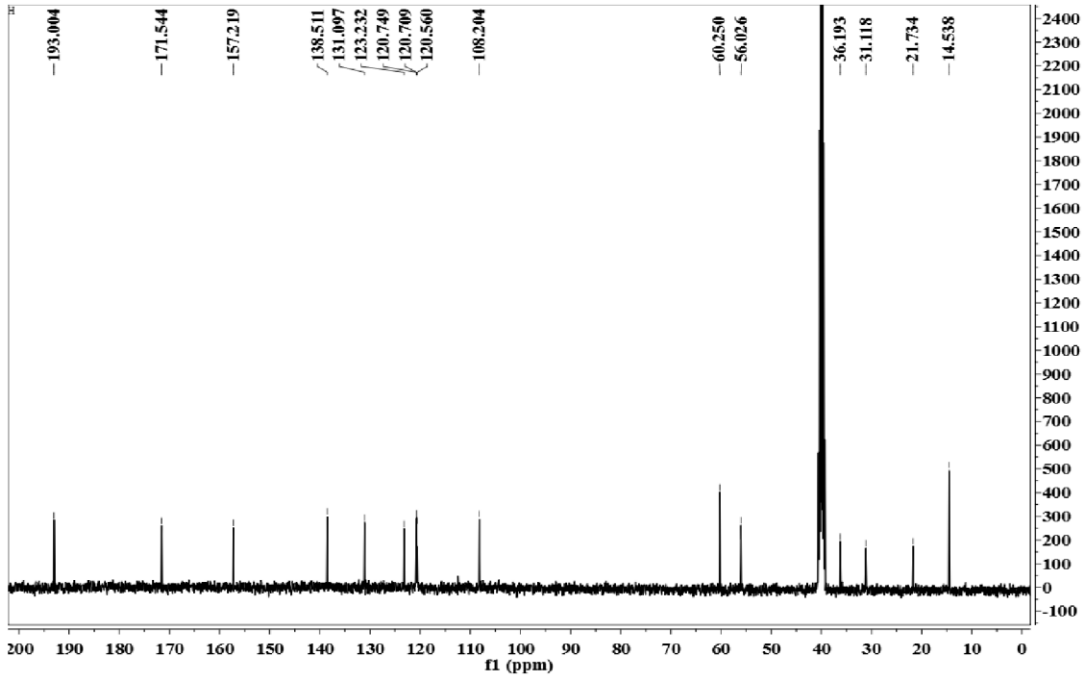
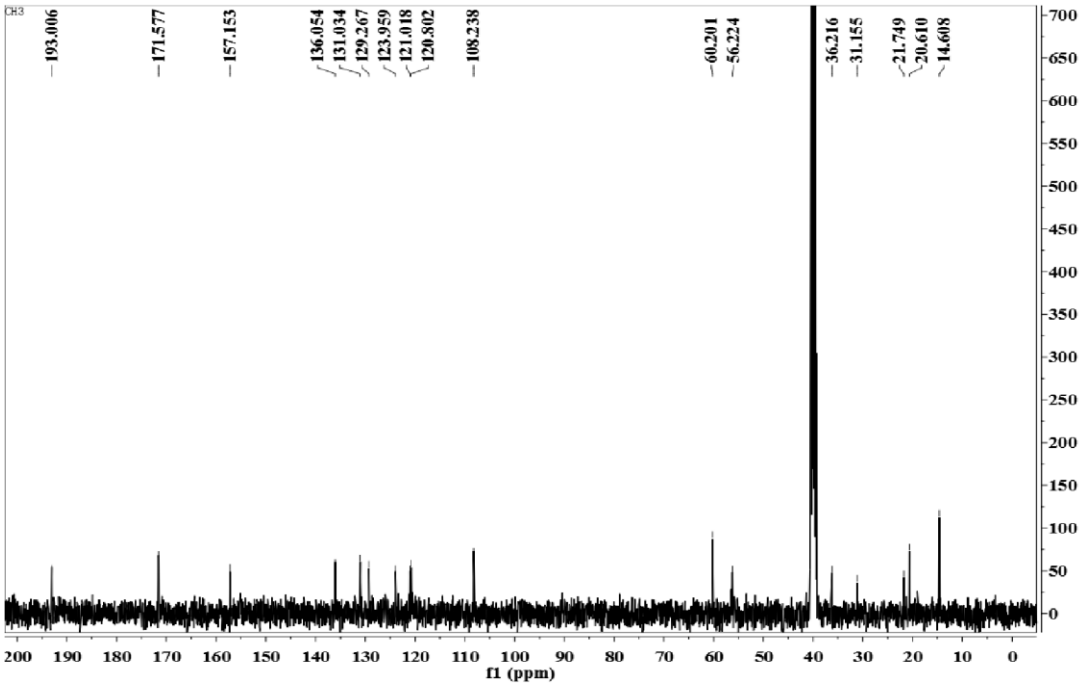


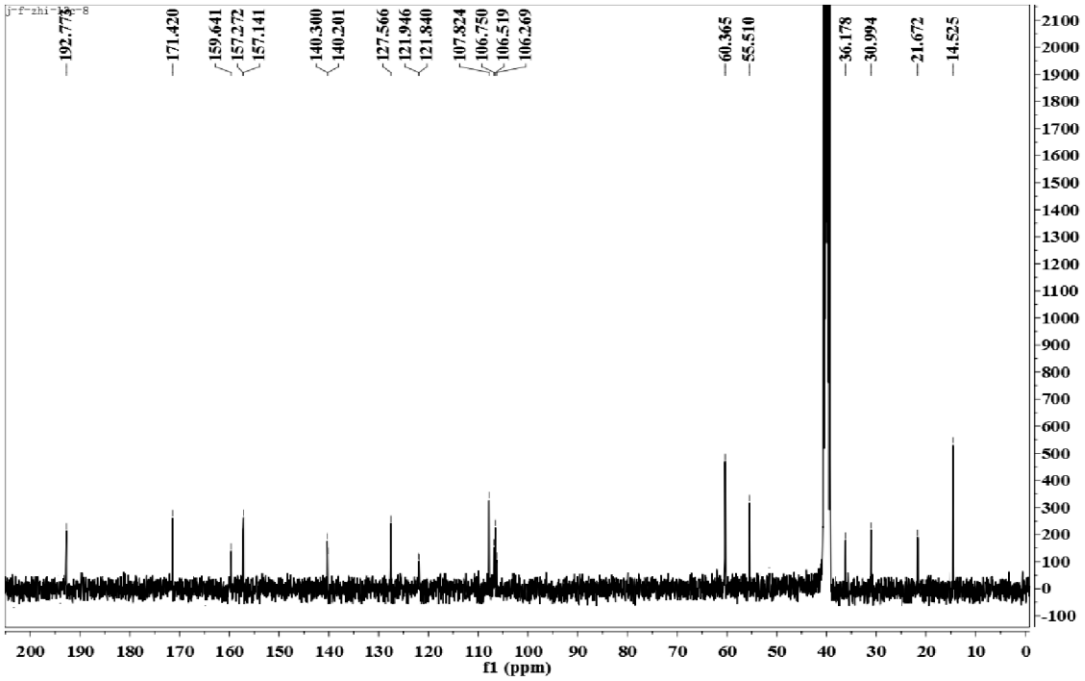
^{13}C NMR spectra of compound **5daf**



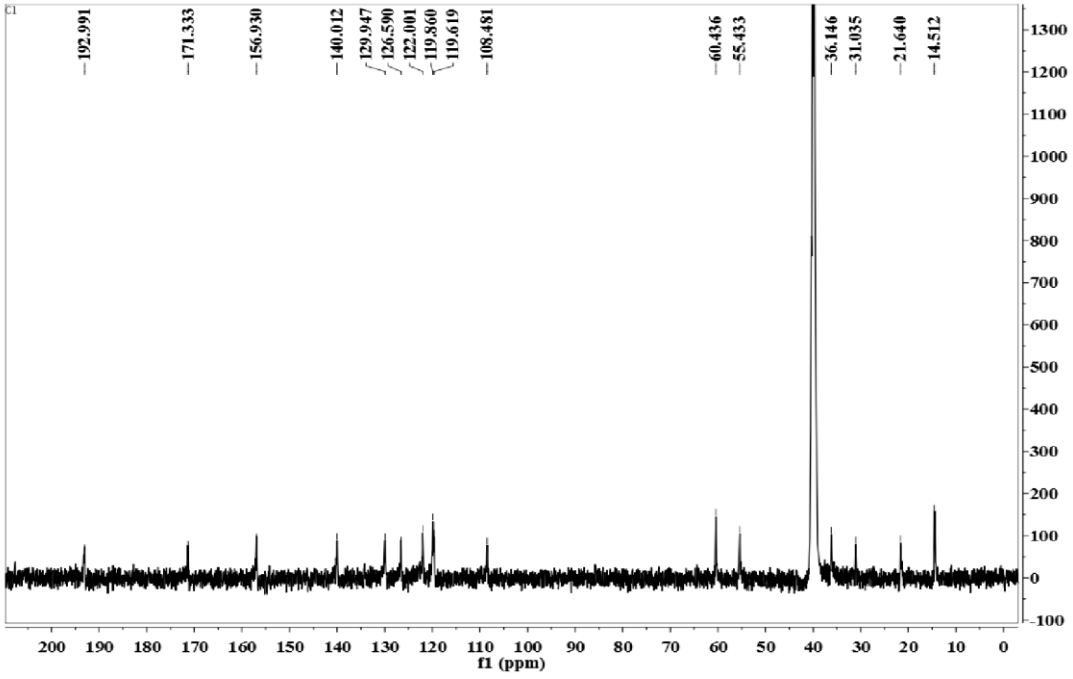
^{13}C NMR spectra of compound **5abc**



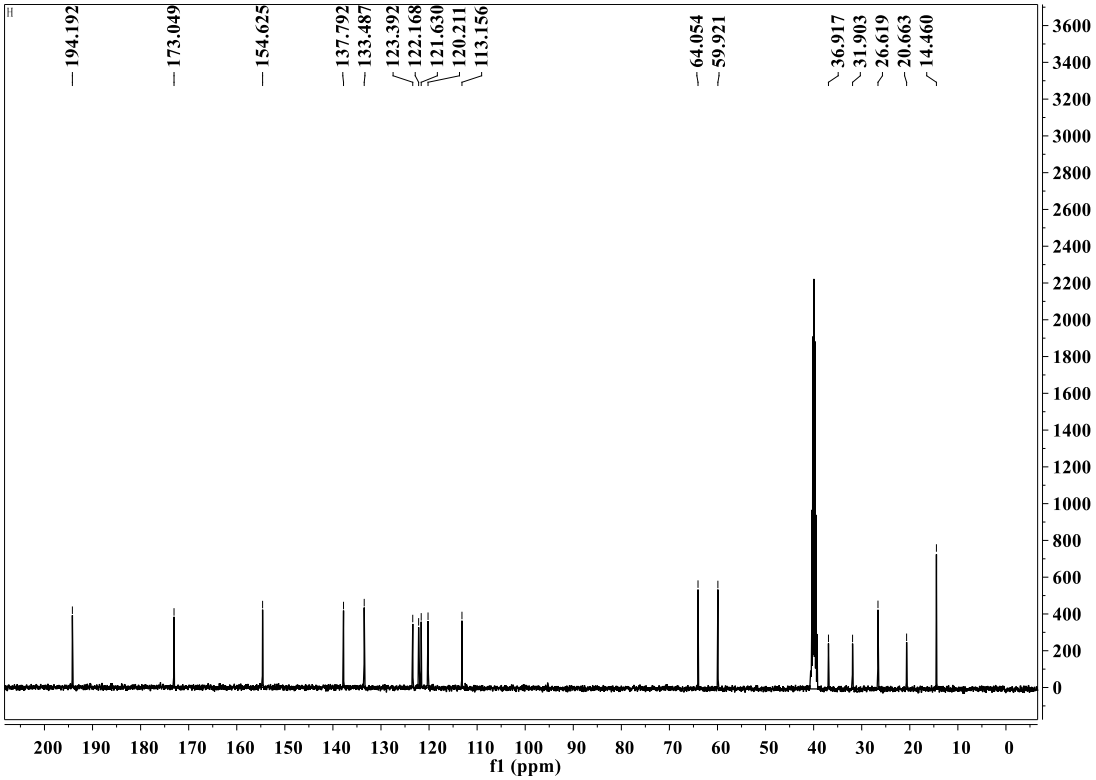
^{13}C NMR spectra of compound **5bbc**



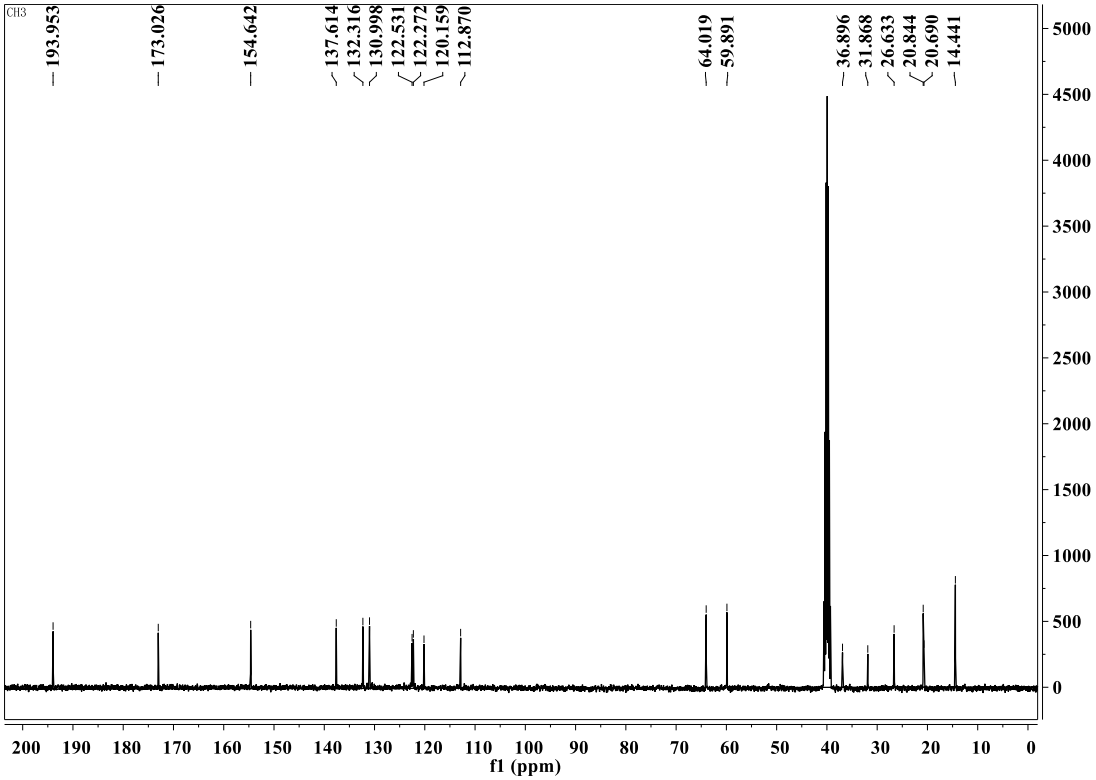
^{13}C NMR spectra of compound **5cbc**



^{13}C NMR spectra of compound **5dbc**



^{13}C NMR spectra of compound **5abd**



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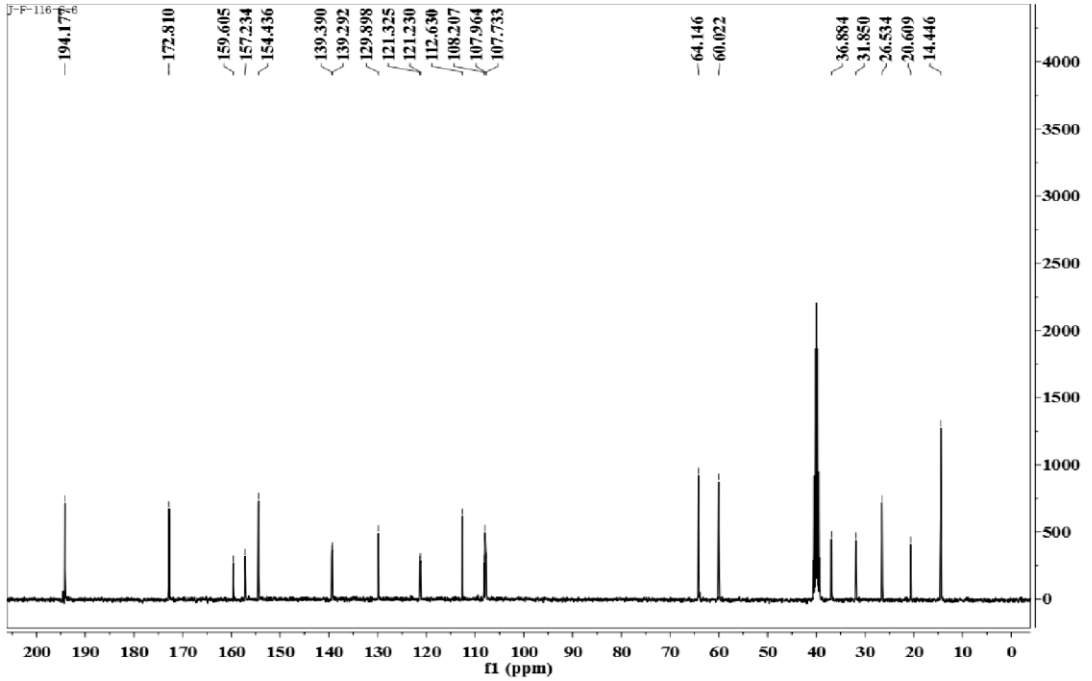
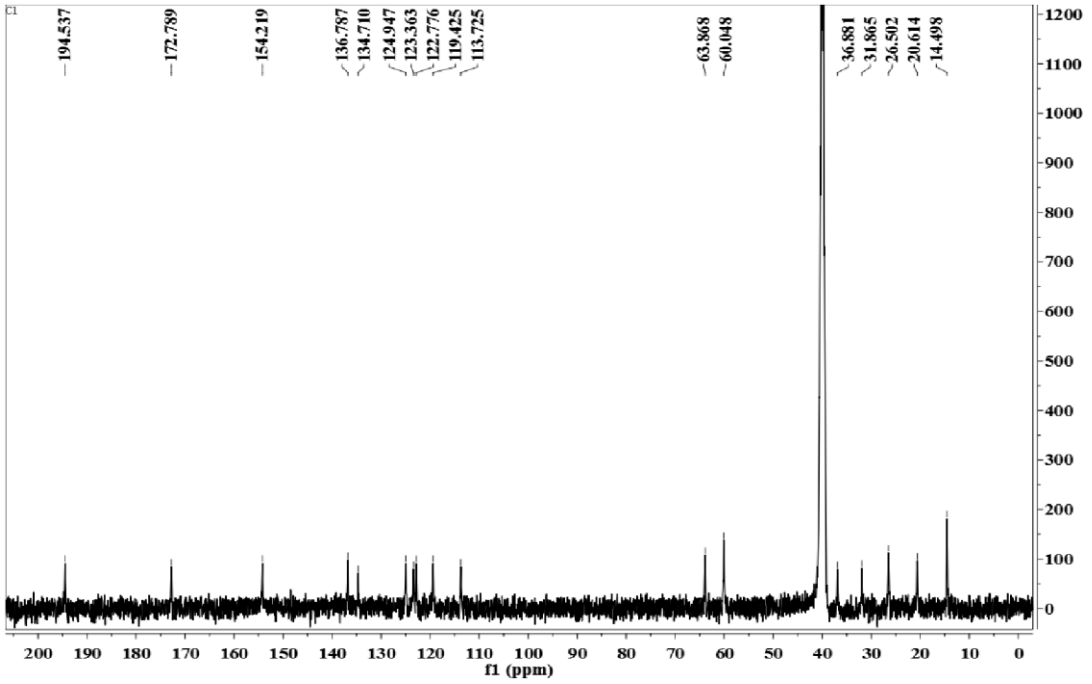
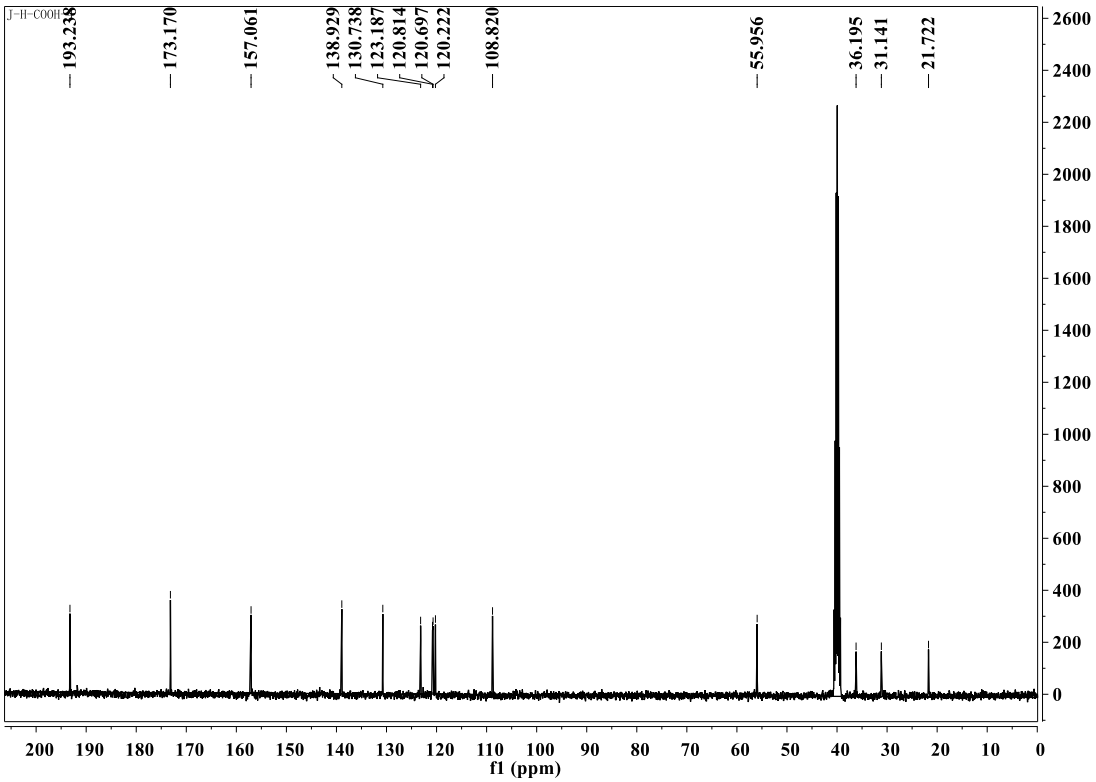


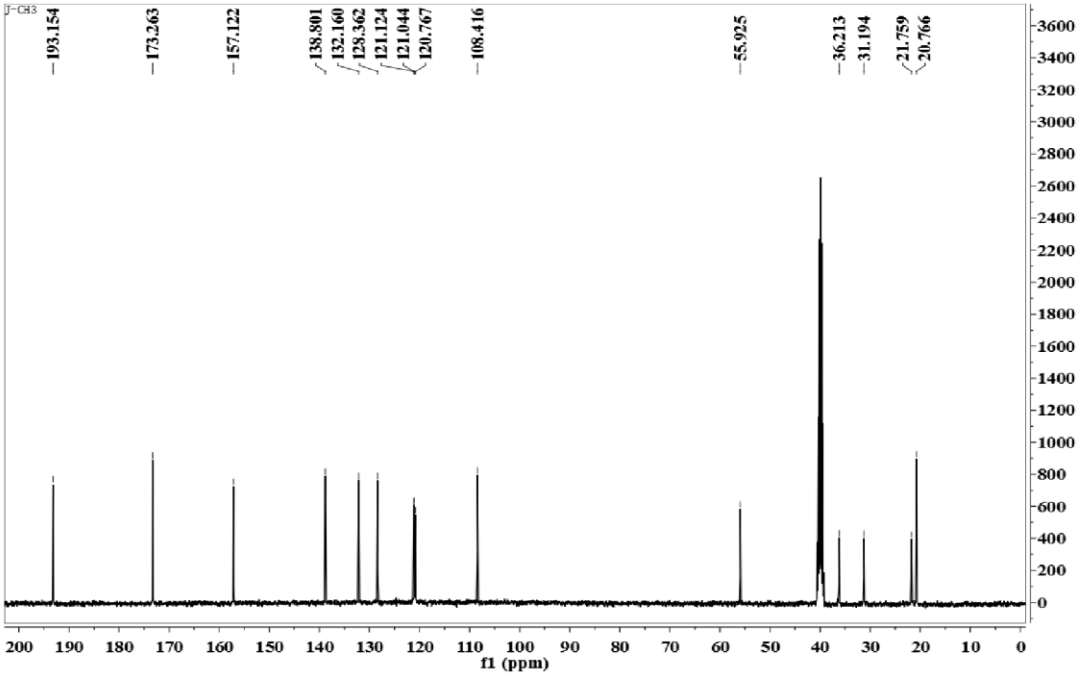
^{13}C NMR spectra of compound **5cbd**



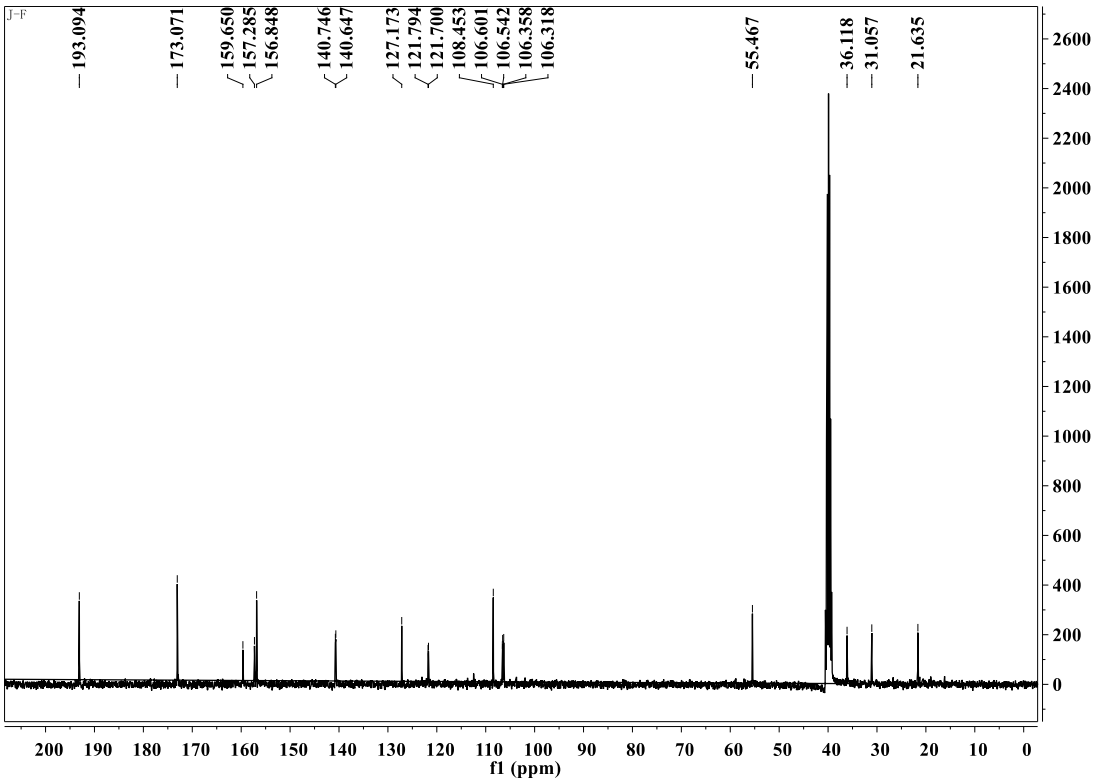
^{13}C NMR spectra of compound **5dbd**



^{13}C NMR spectra of compound **5abe**



^{13}C NMR spectra of compound **5bbe**



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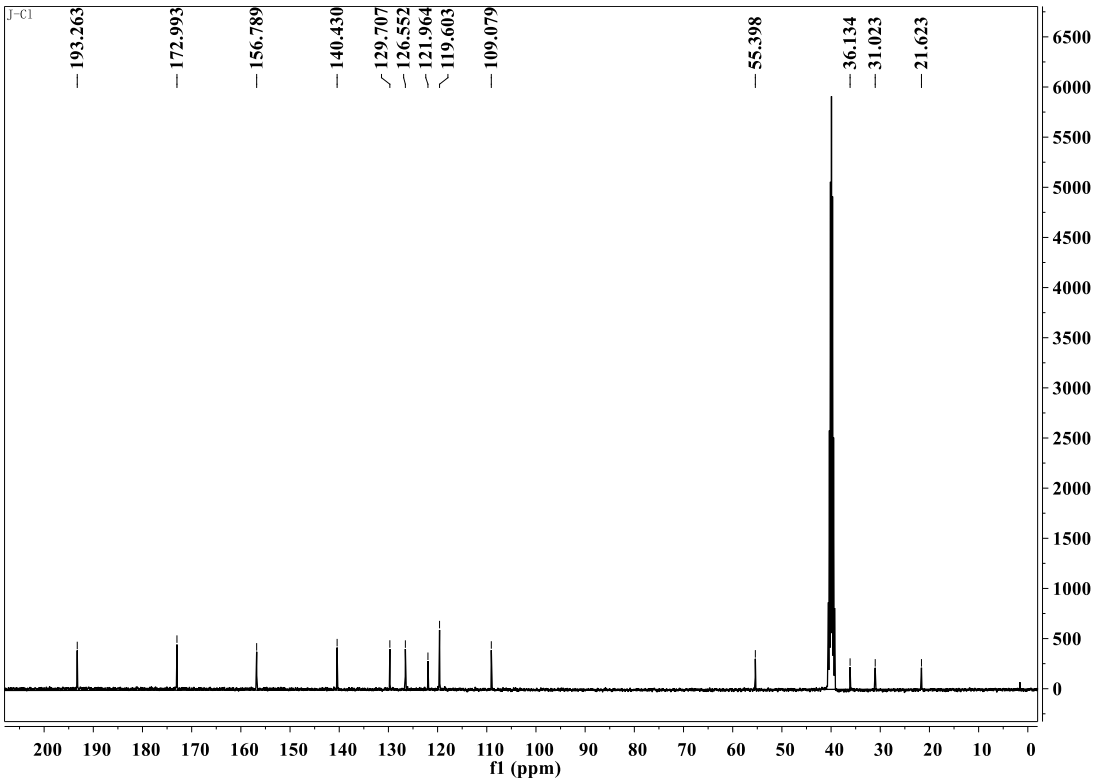
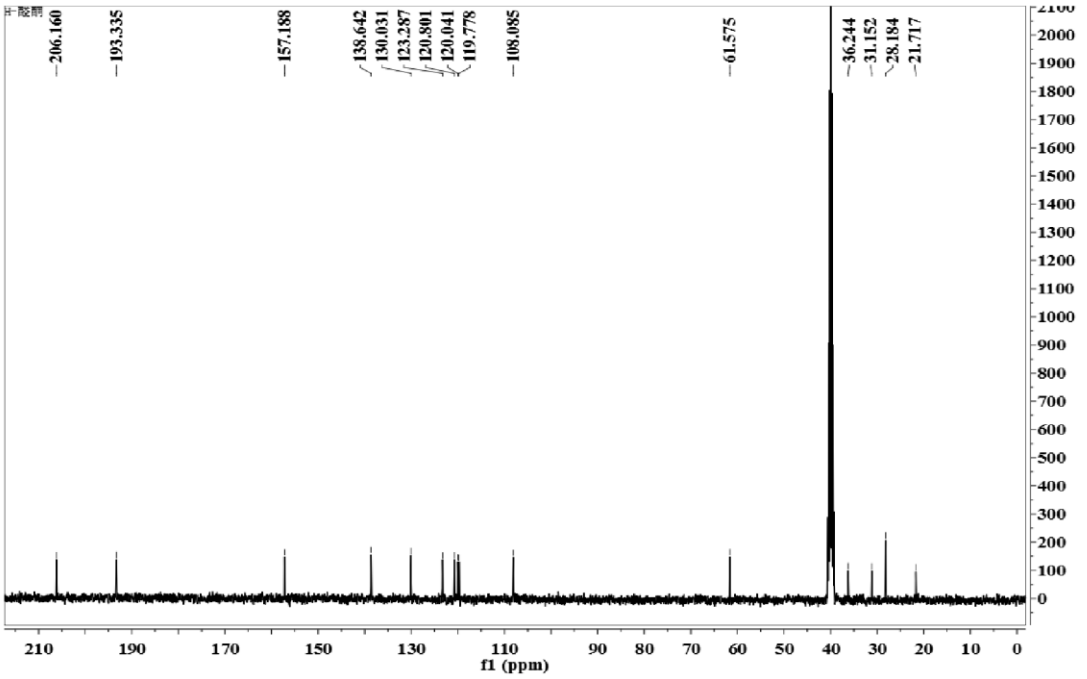
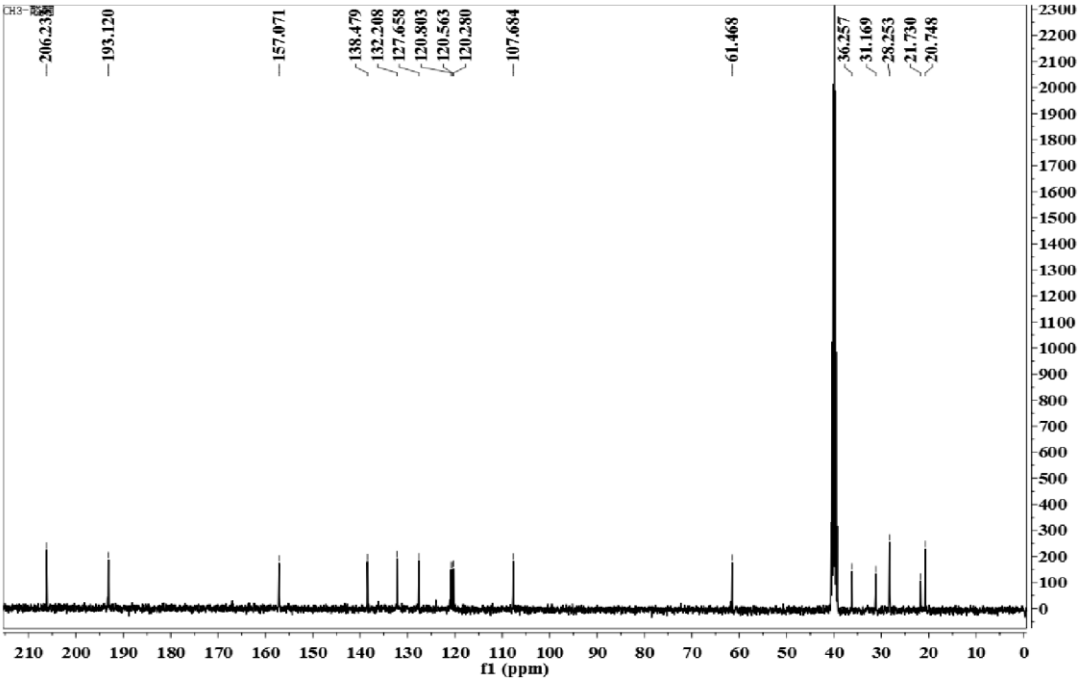


^{13}C NMR spectra of compound **5dbe**



^{13}C NMR spectra of compound **5abf**



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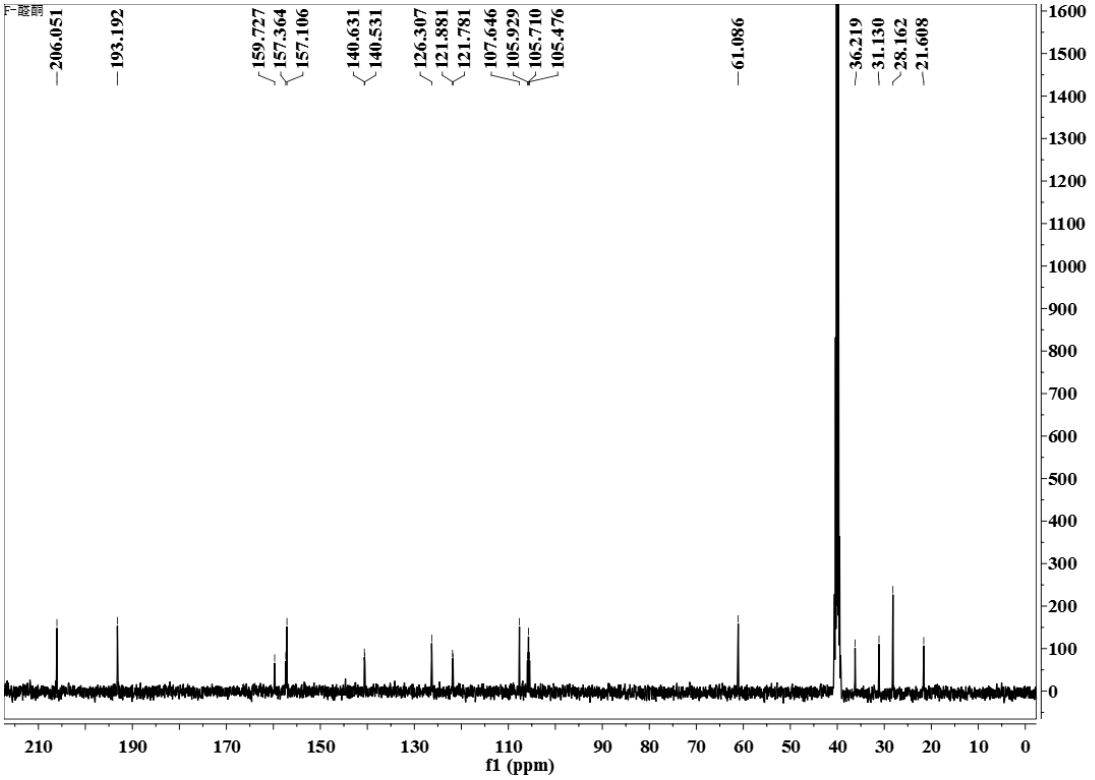

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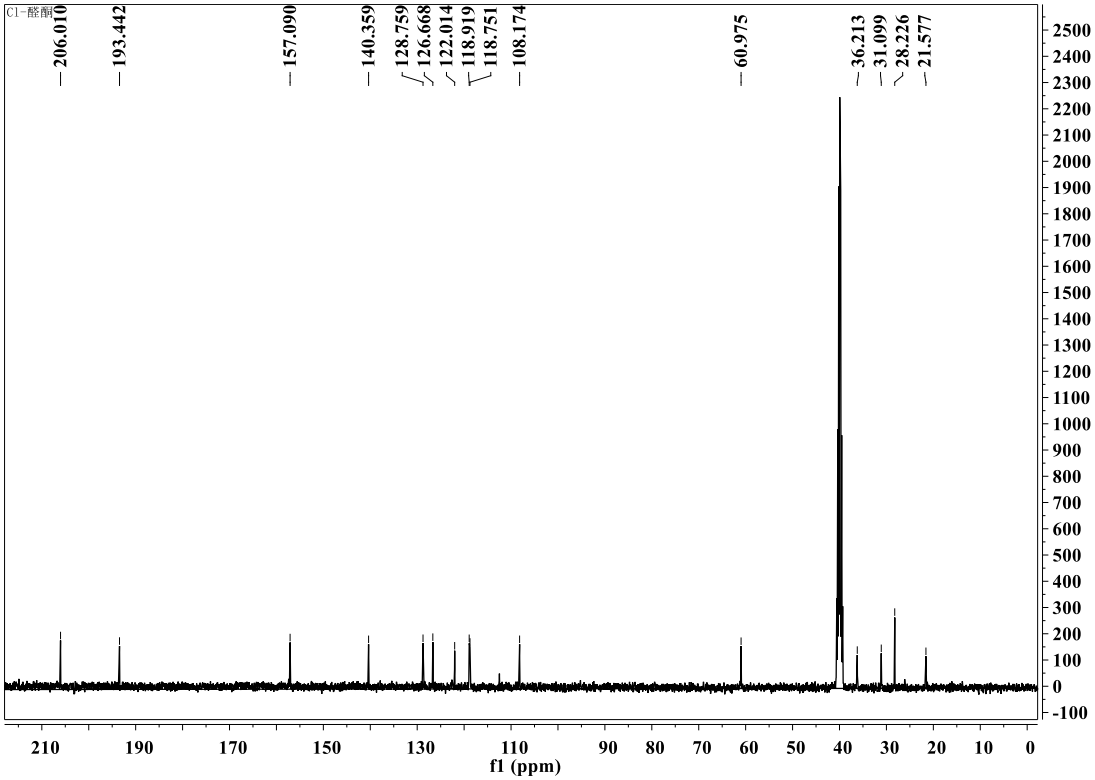
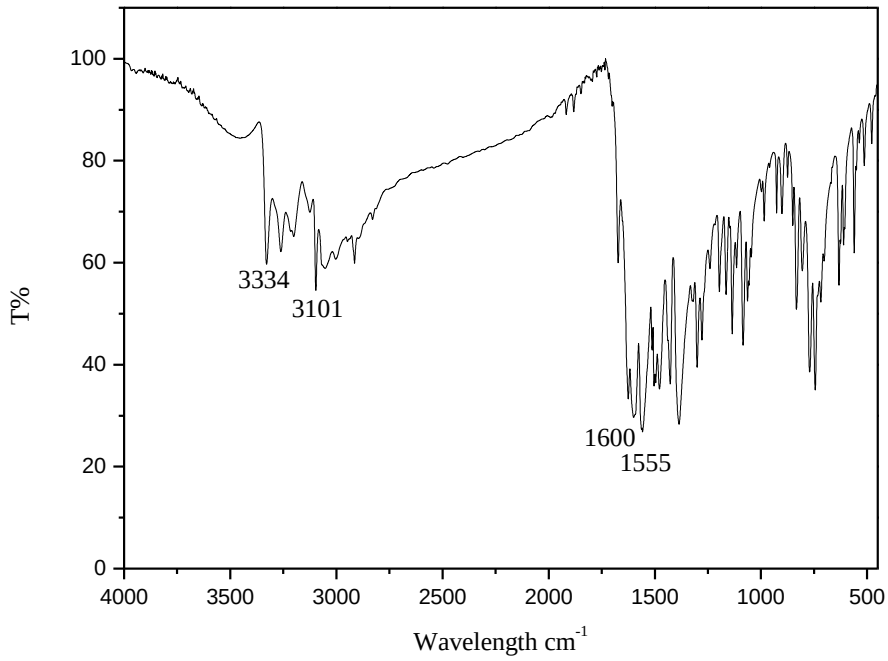
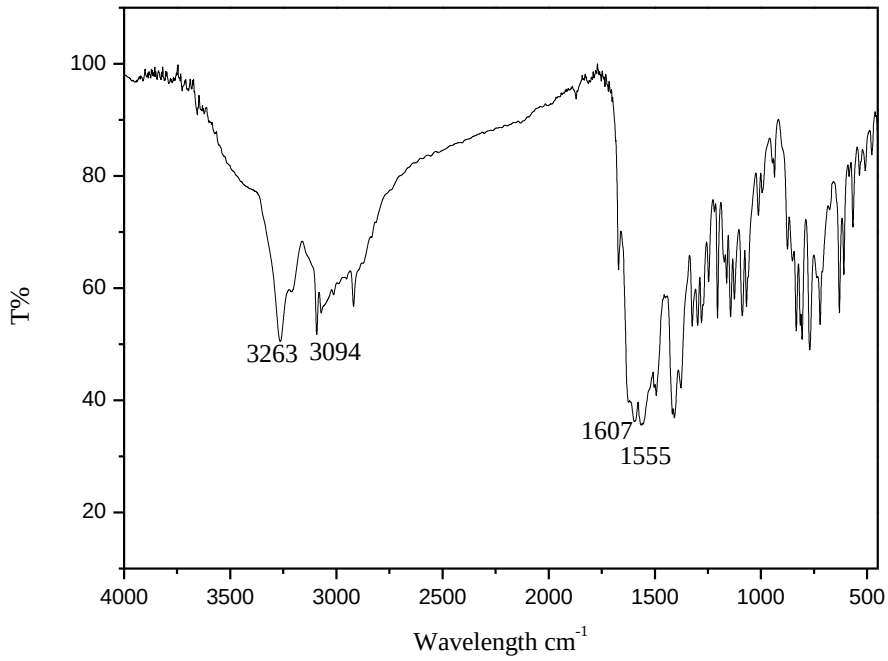


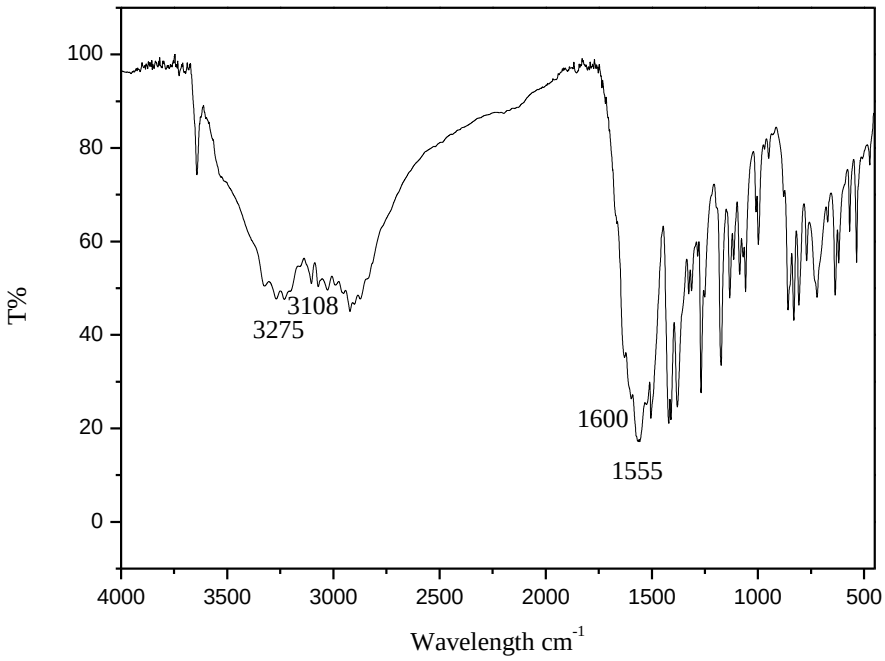
^{13}C NMR spectra of compound **5dbf**



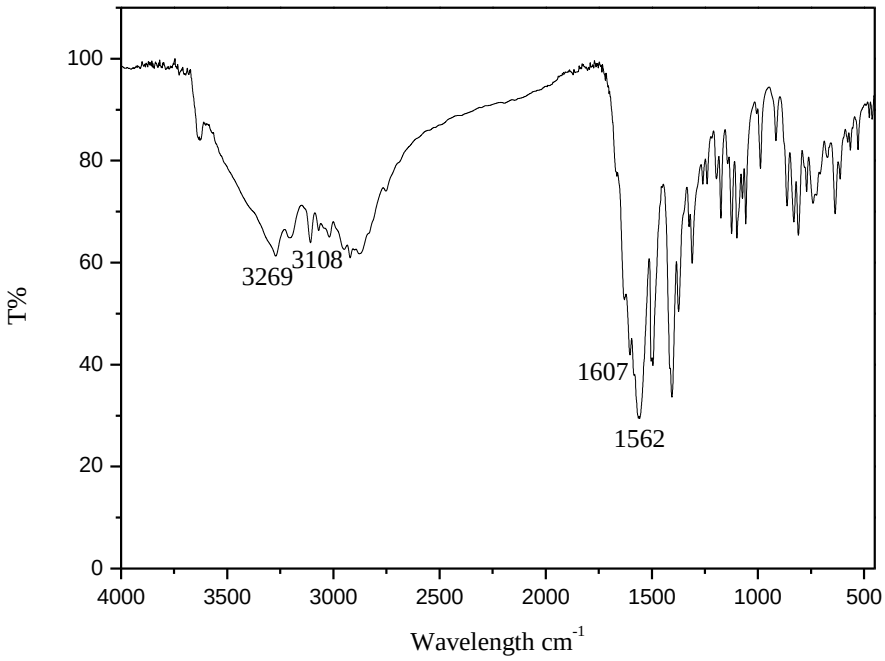
IR spectra of compound **4aaa**



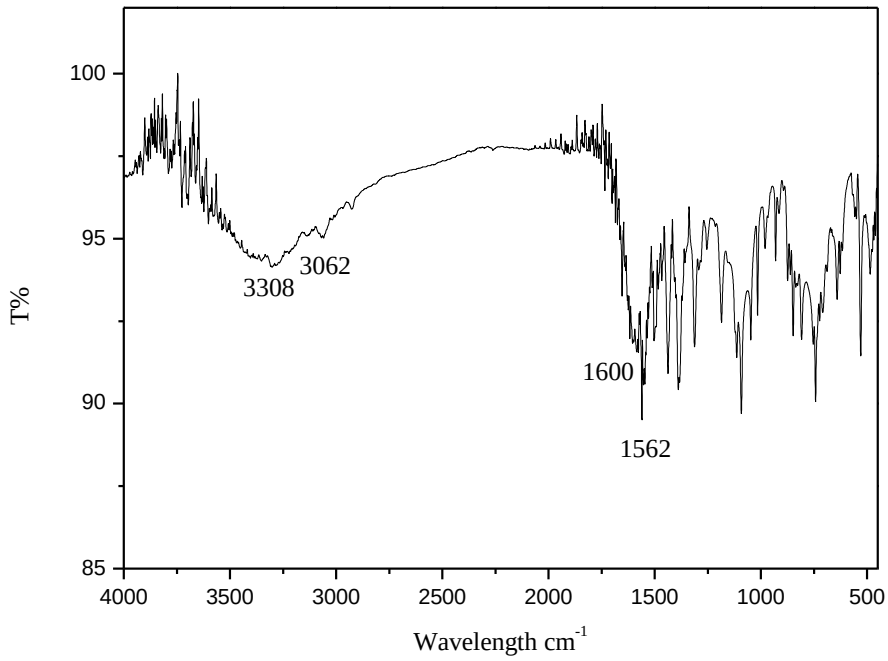
IR spectra of compound **4baa**



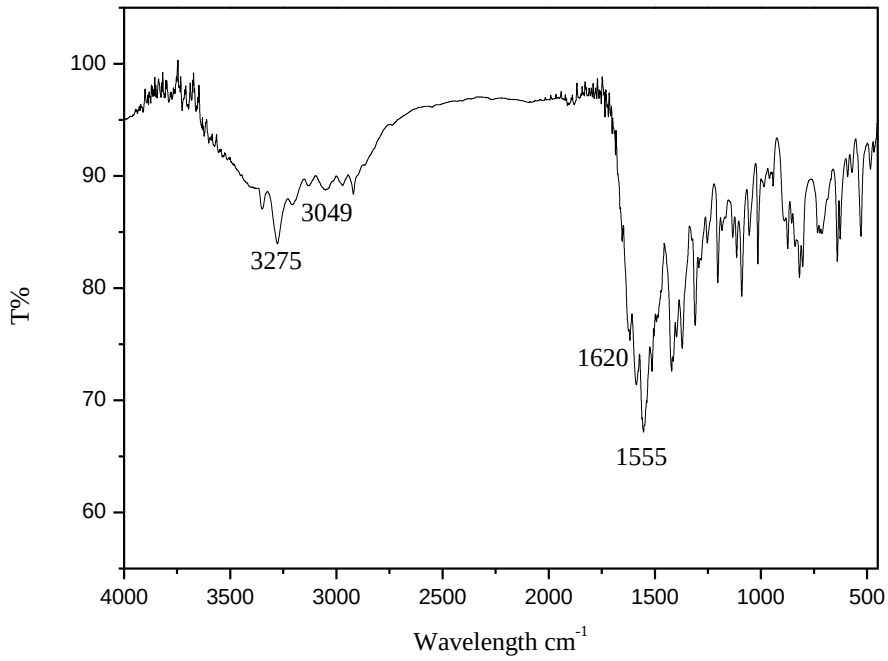
IR spectra of compound **4caa**



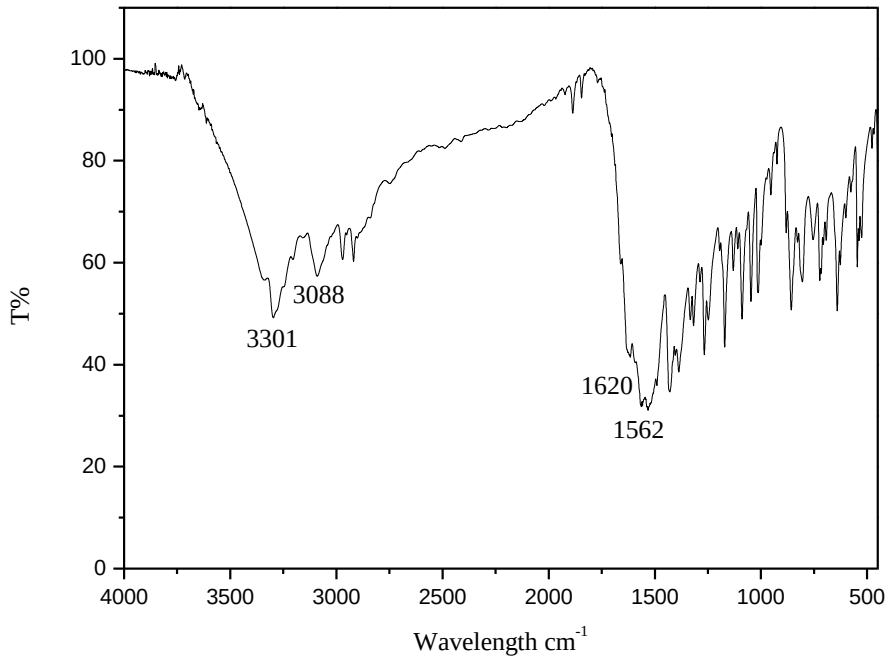
IR spectra of compound **4daa**



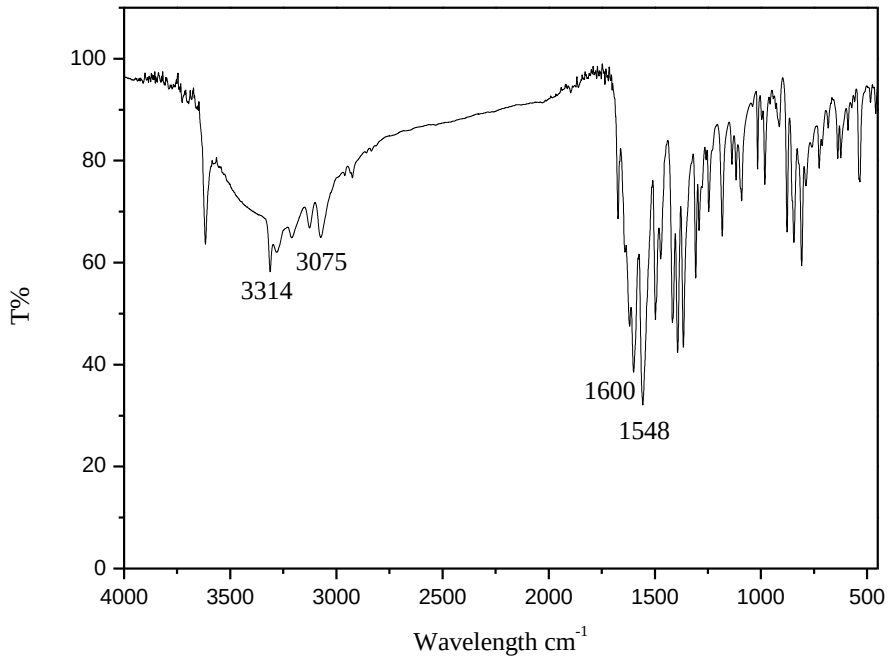
IR spectra of compound **4aab**



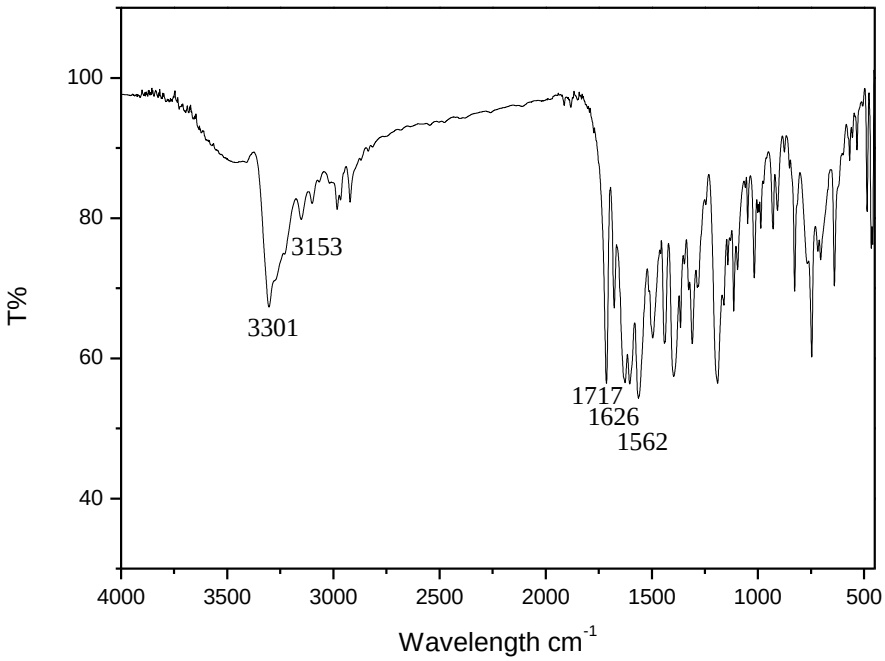
IR spectra of compound **4bab**



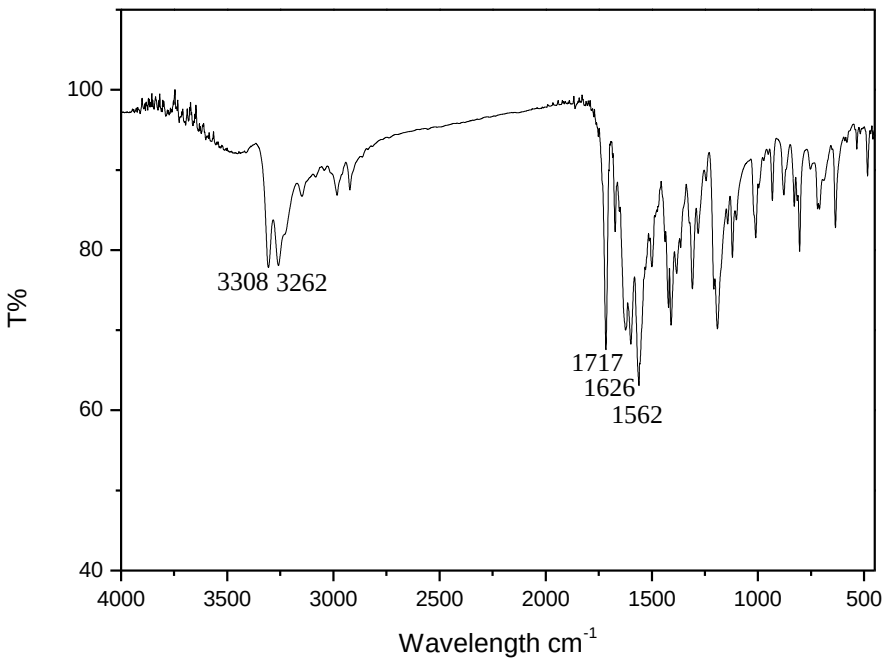
IR spectra of compound **4cab**



IR spectra of compound **4dab**



IR spectra of compound **5aac**



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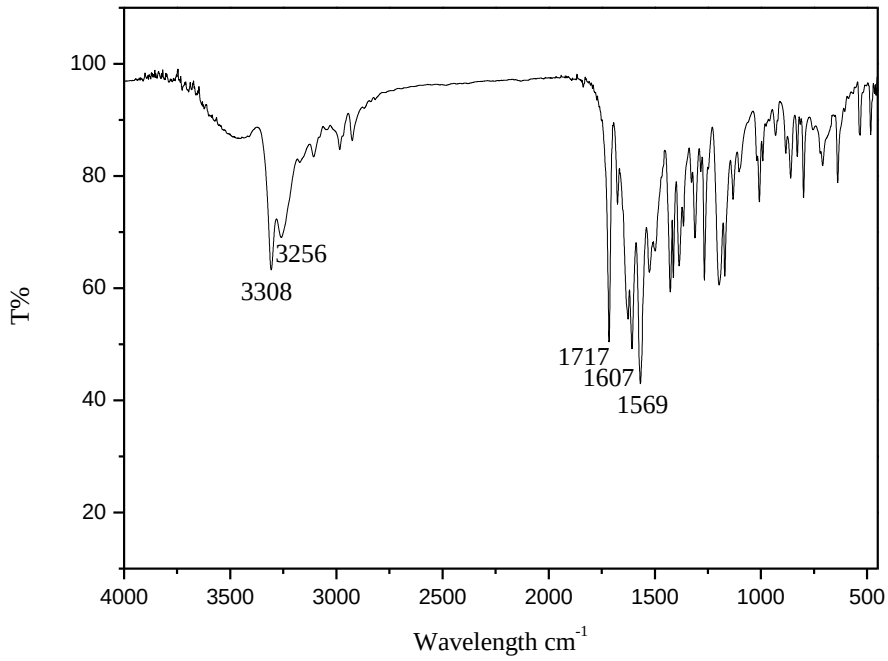

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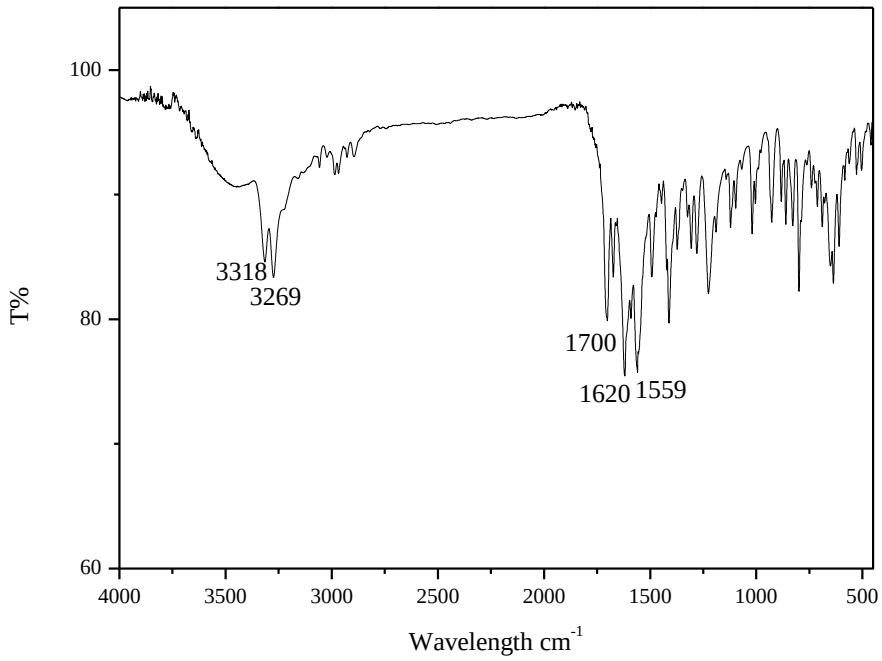

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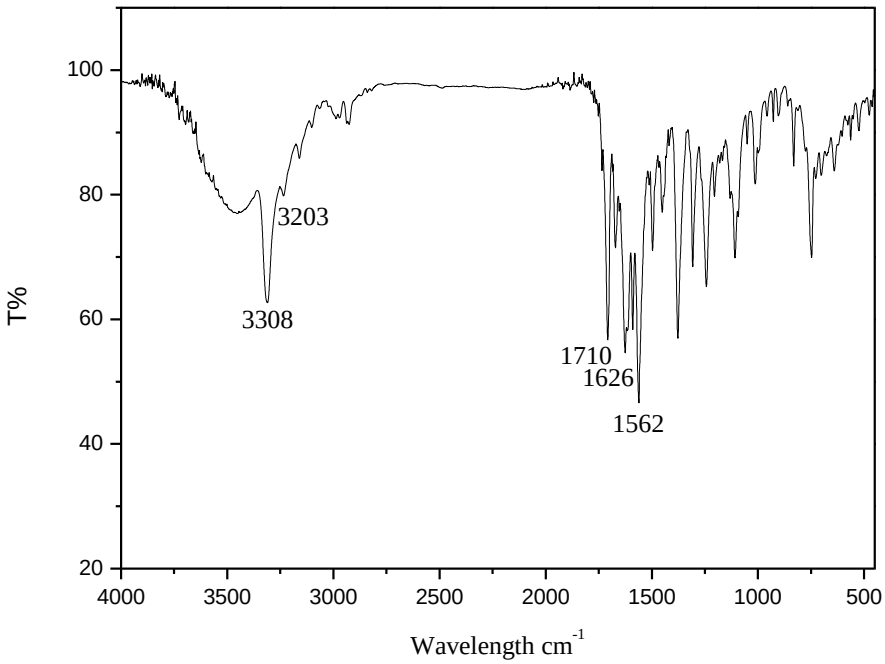
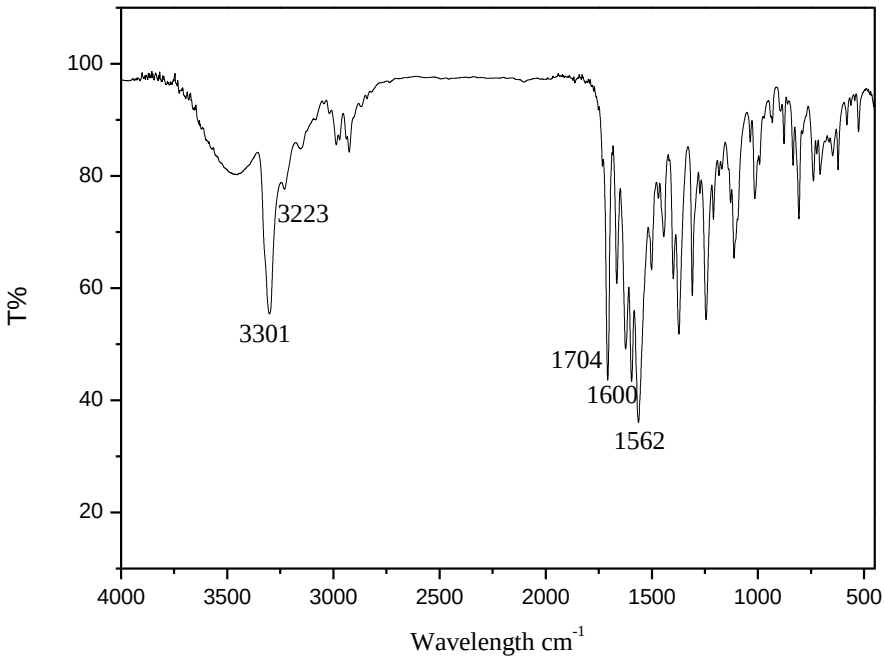
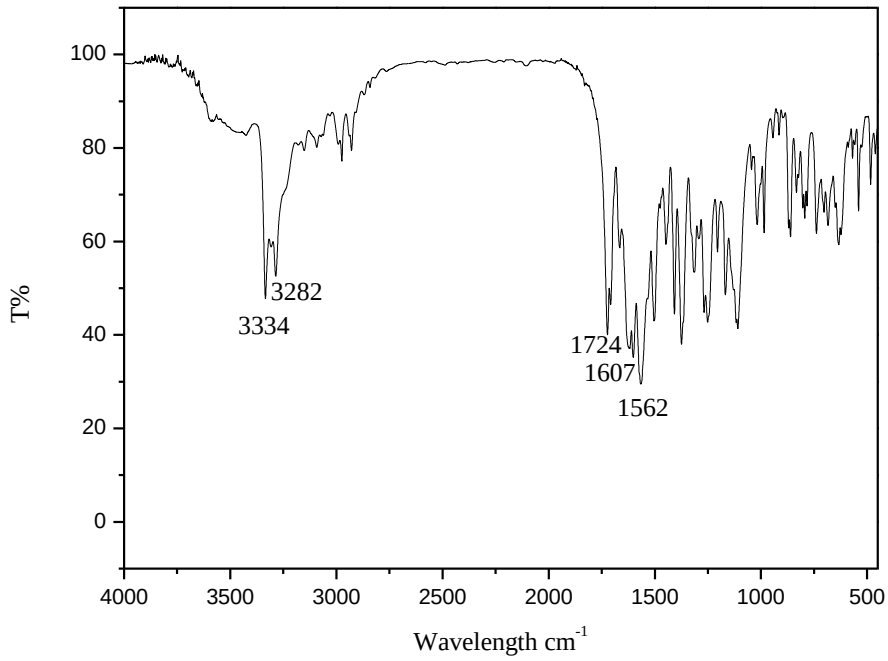


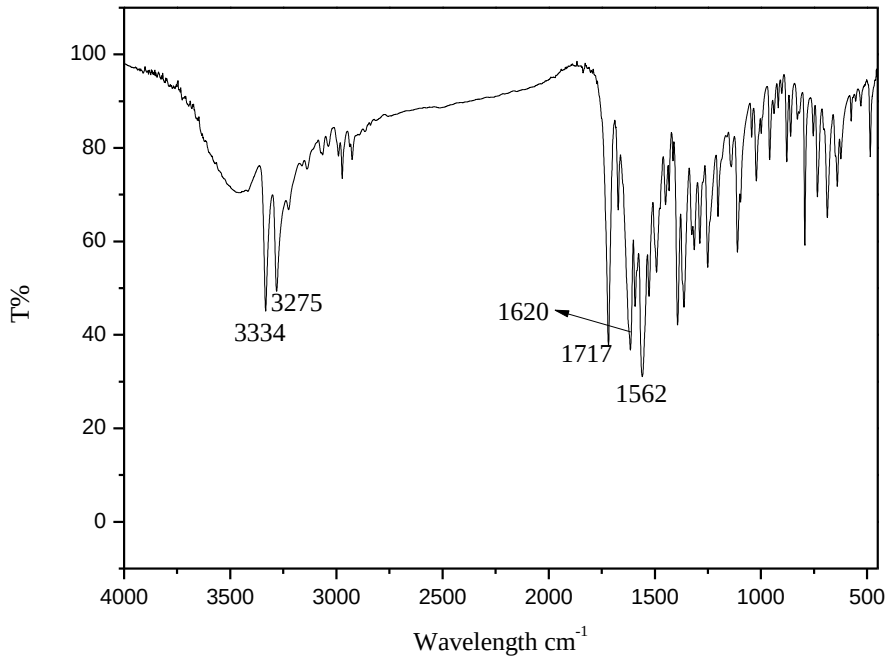
IR spectra of compound **5aad**



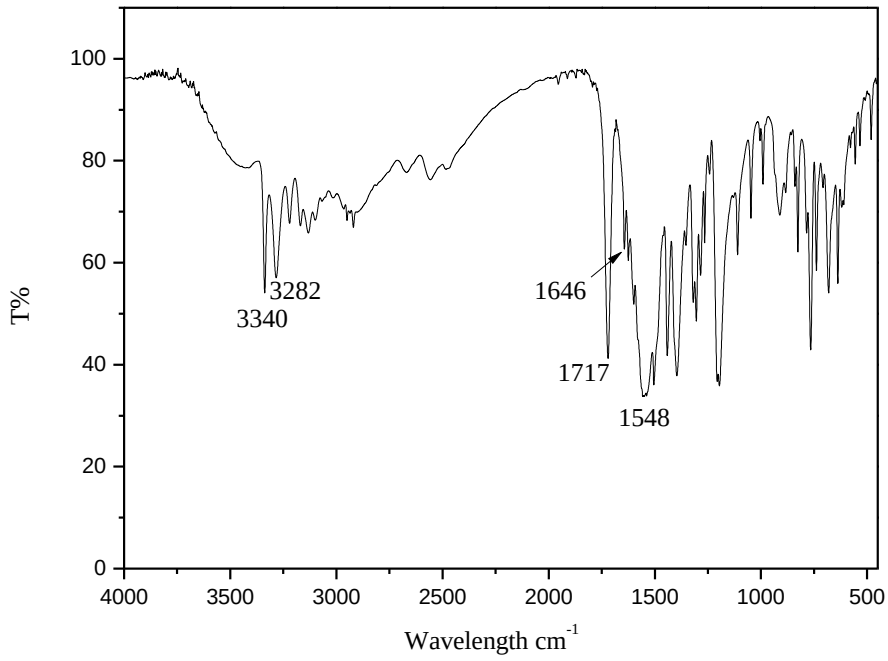
IR spectra of compound **5bad**



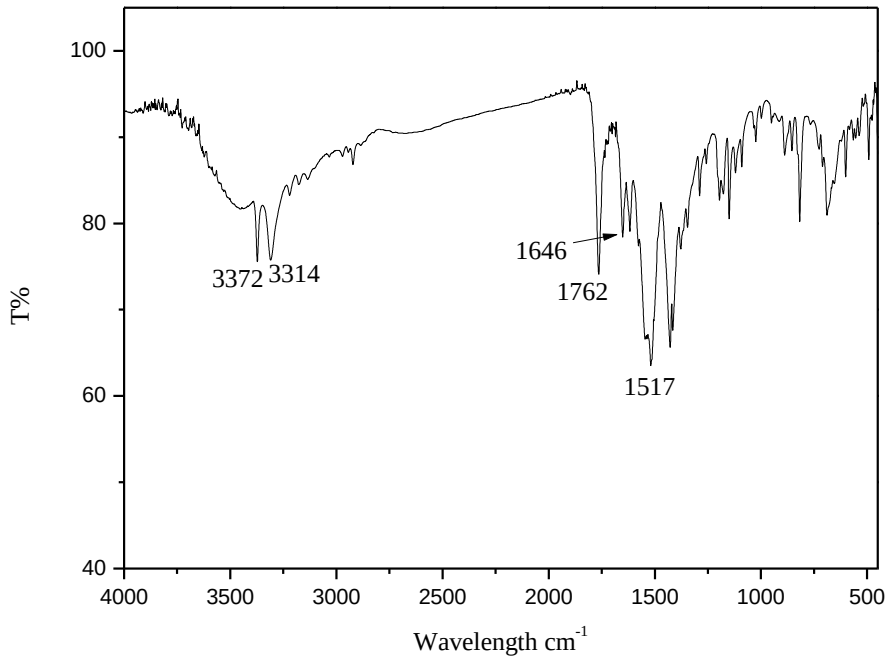
IR spectra of compound **5cad**



IR spectra of compound **5dad**



IR spectra of compound **5aae**



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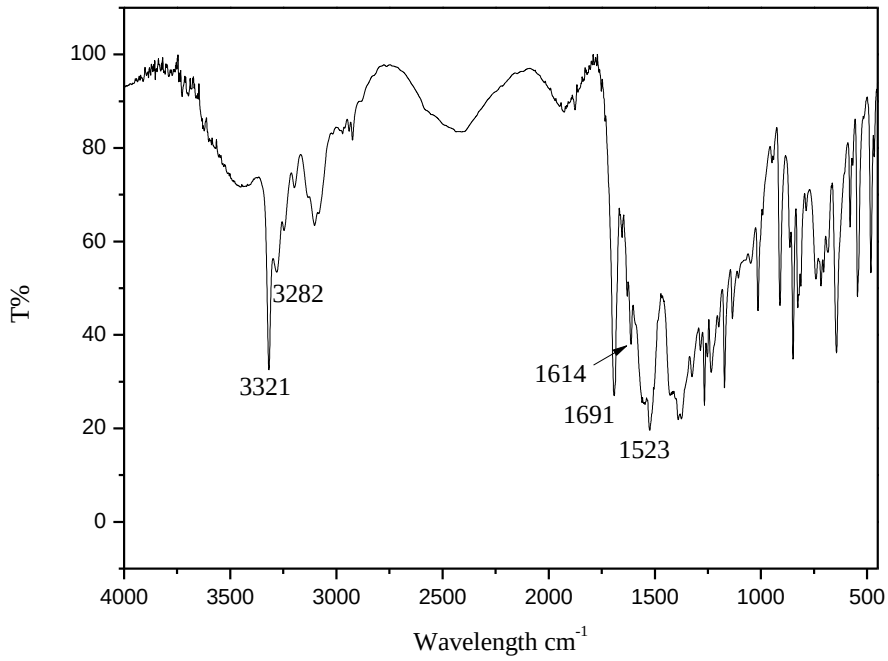
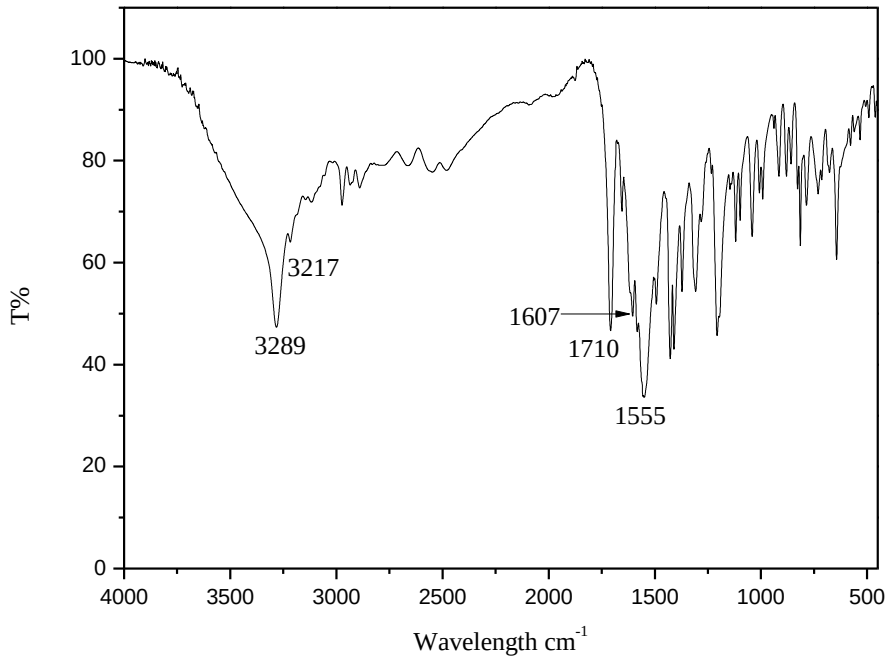
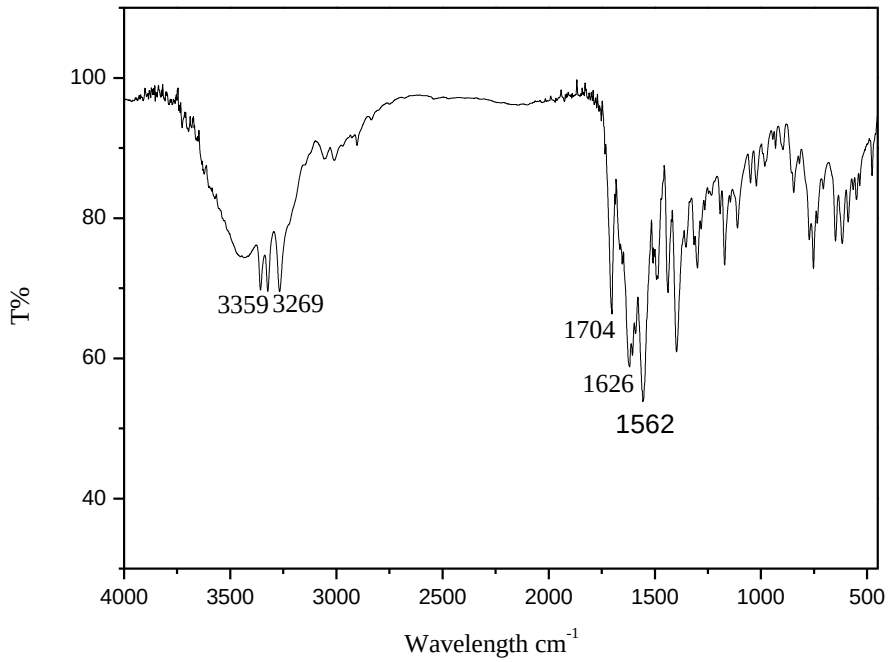


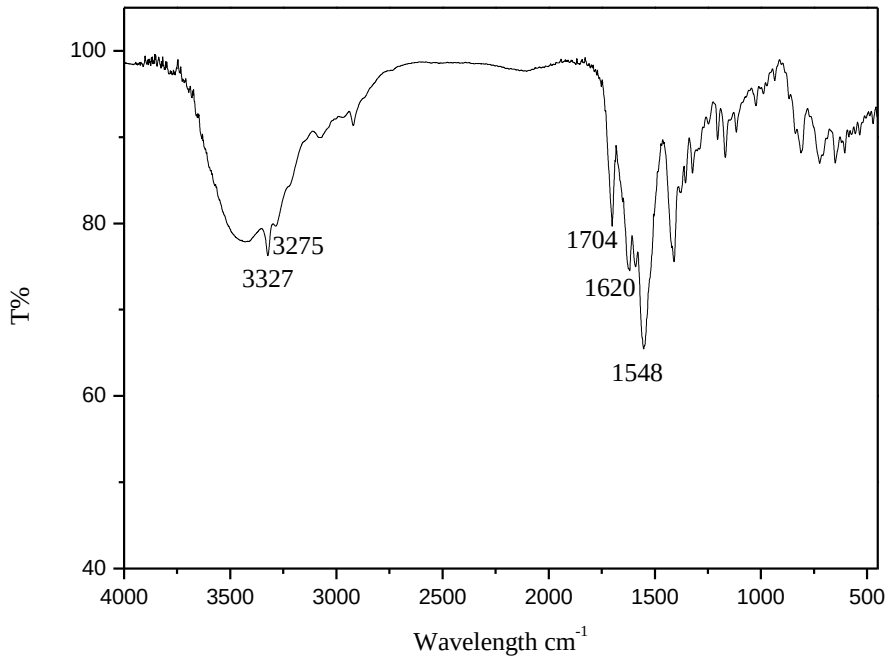
IR spectra of compound **5cae**



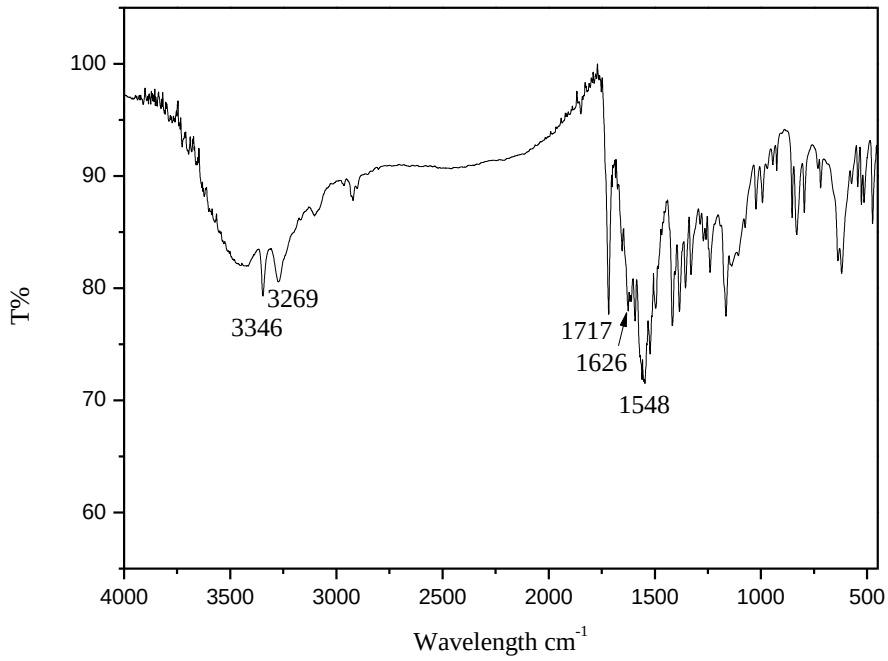
IR spectra of compound **5dae**



IR spectra of compound **5aaf**



IR spectra of compound **5baf**



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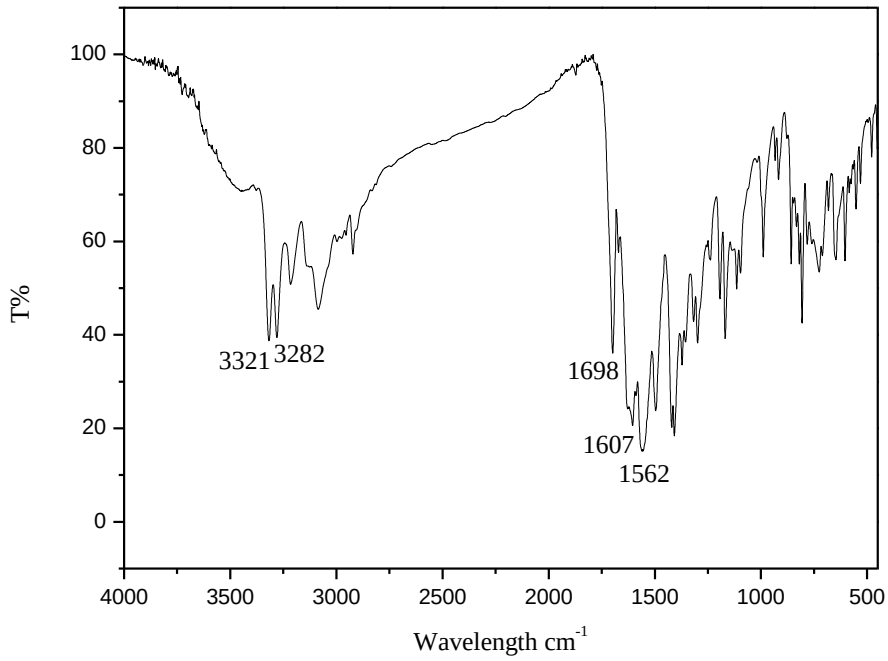

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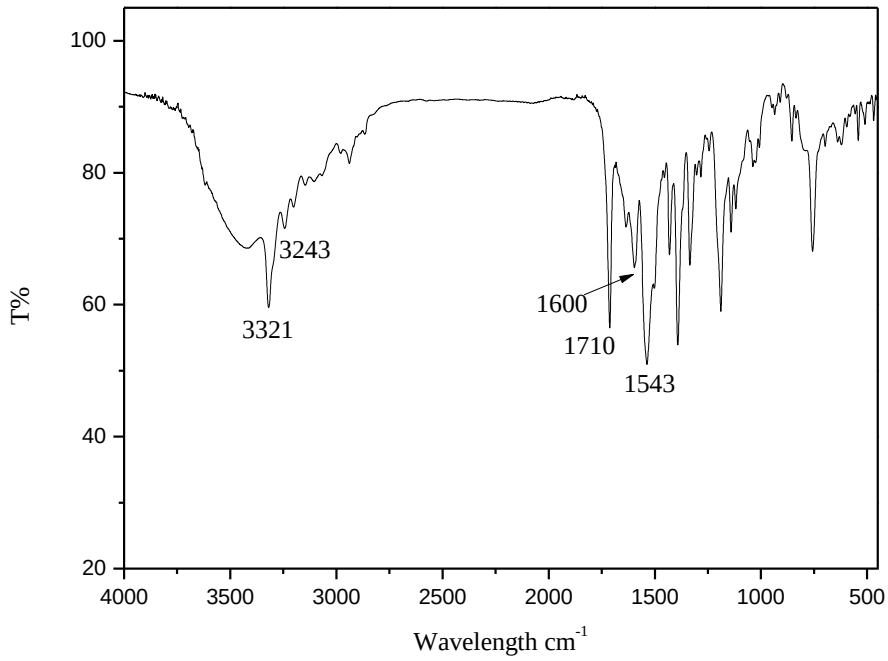
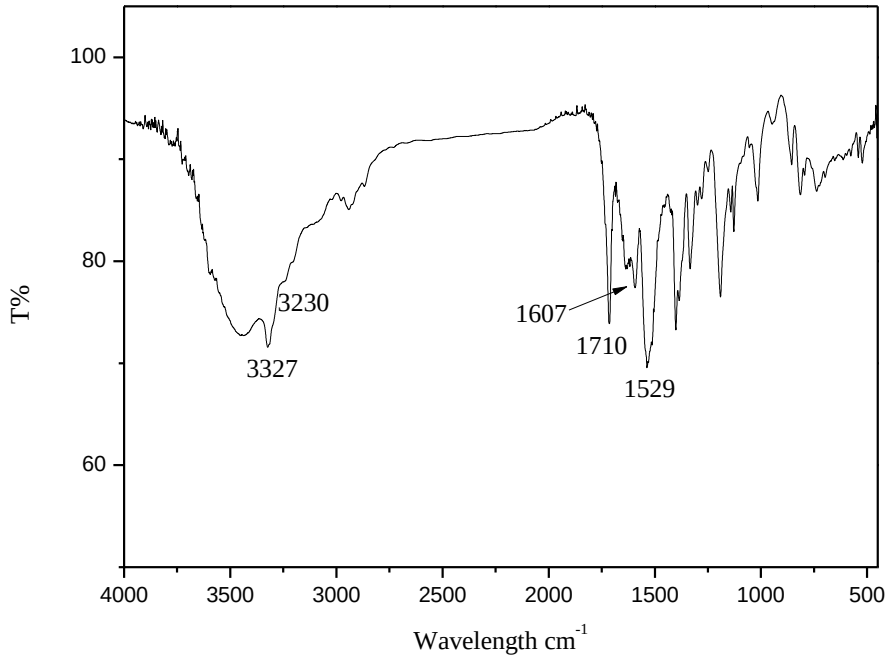
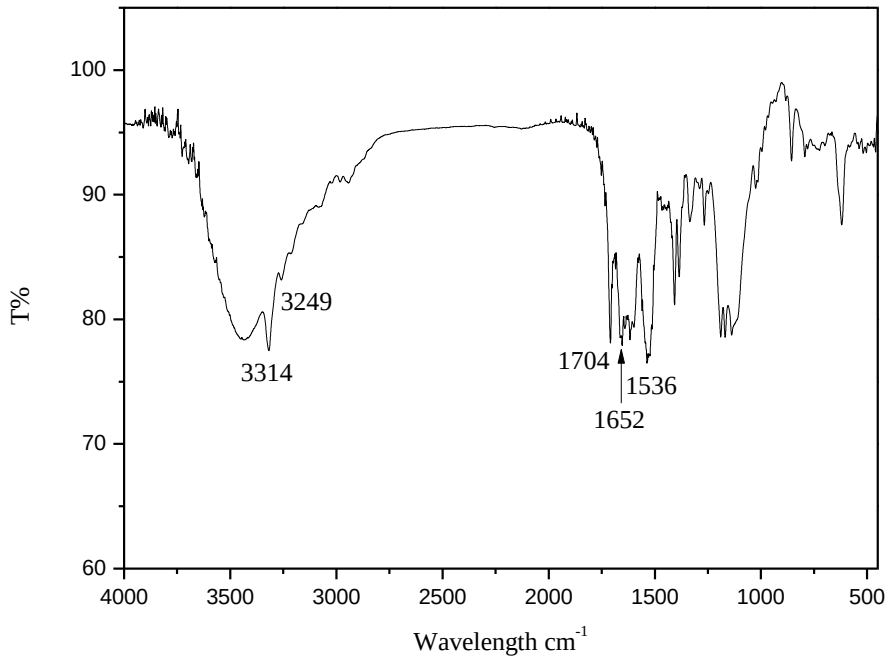


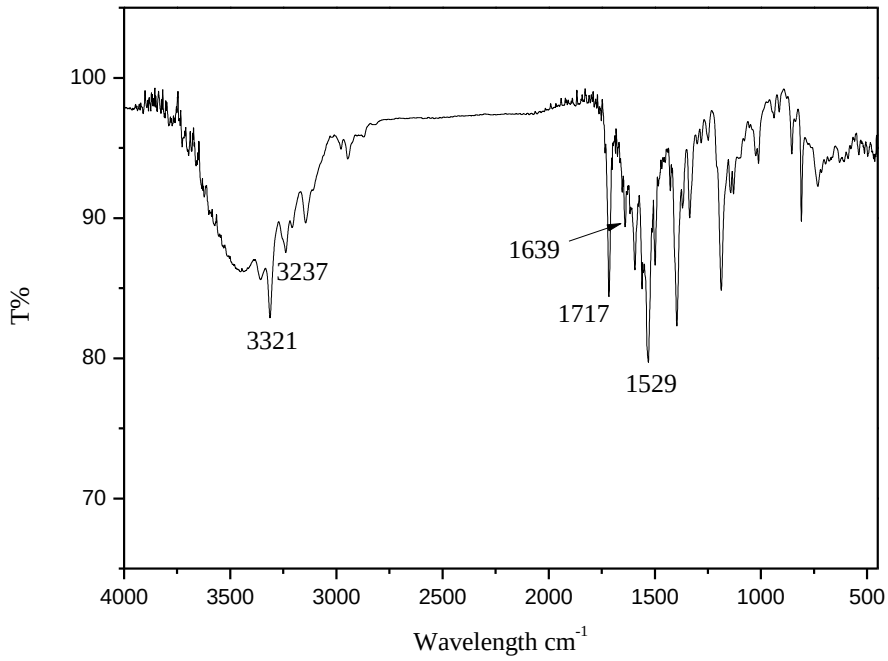
IR spectra of compound **5abc**



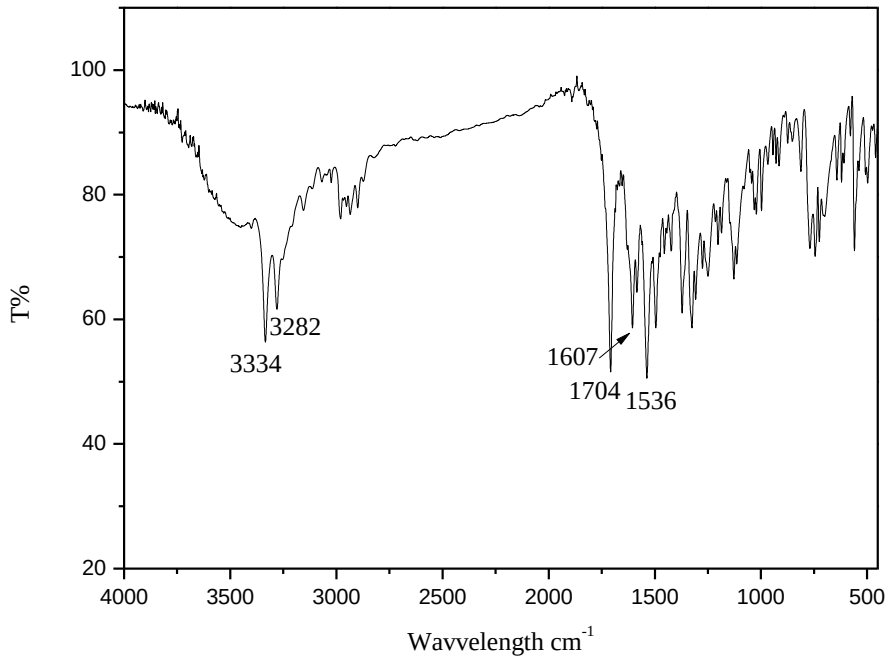
IR spectra of compound **5bbc**



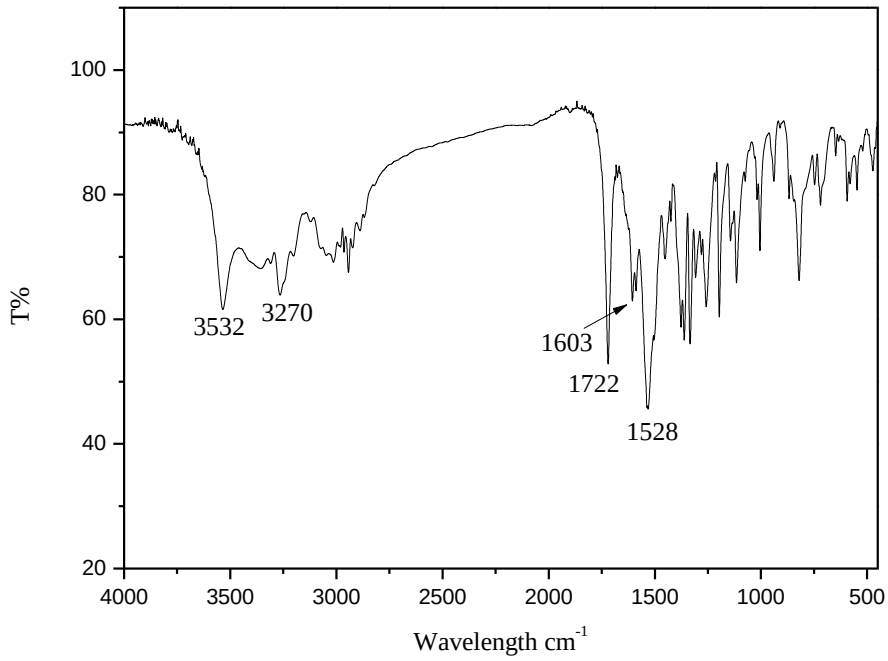
IR spectra of compound **5cbc**



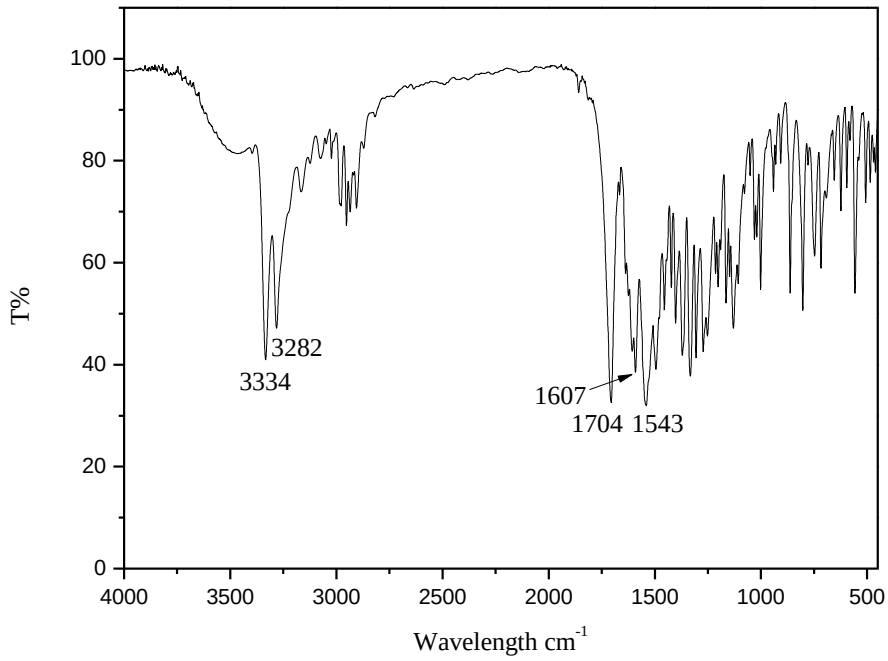
IR spectra of compound **5dbc**



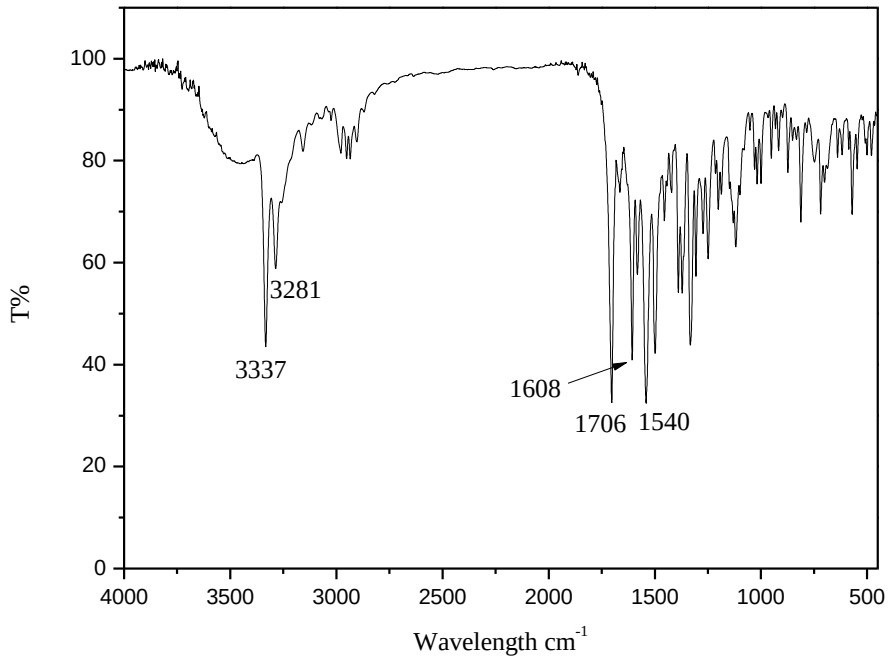
IR spectra of compound **5abd**



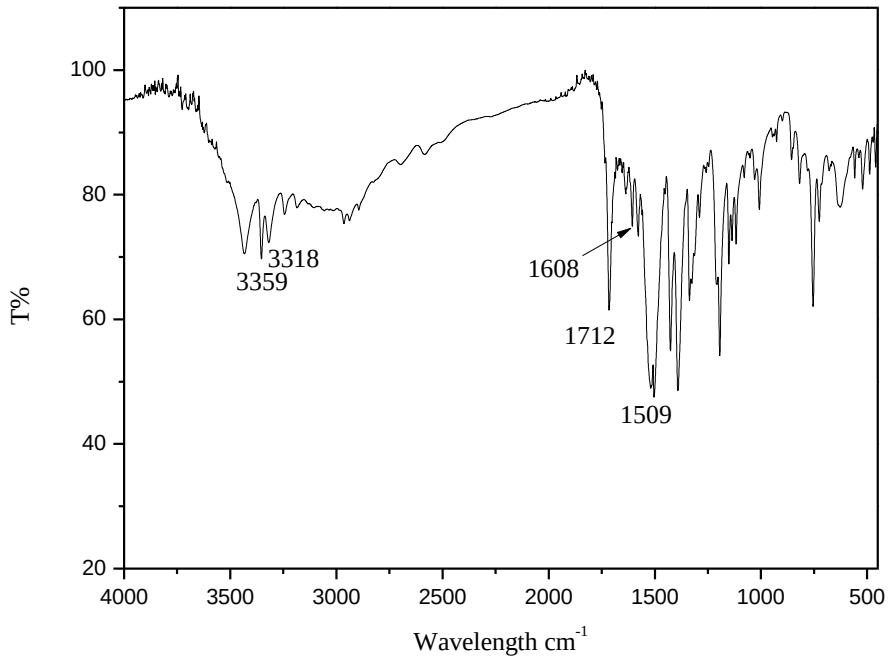
IR spectra of compound **5bbd**



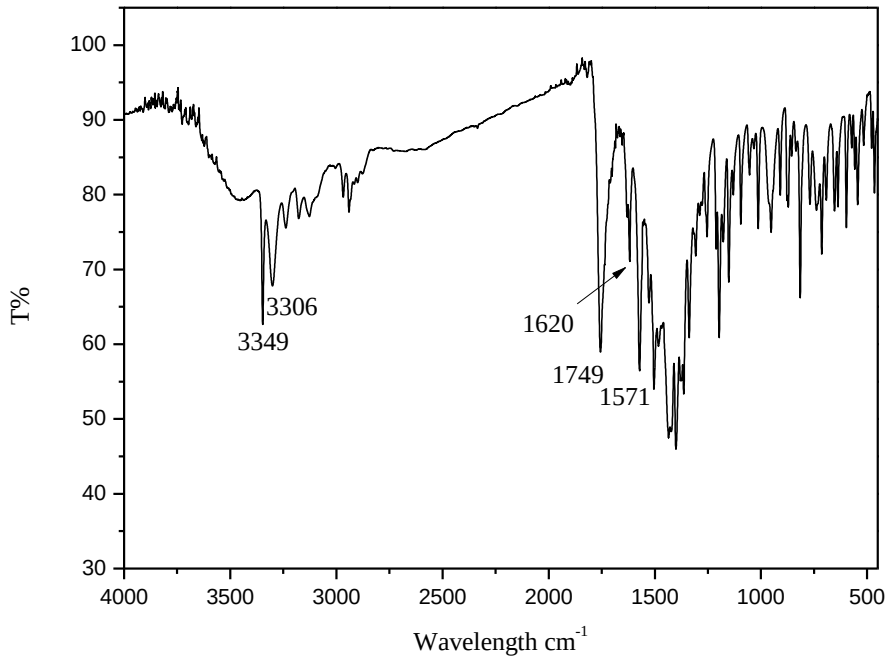
IR spectra of compound **5cbd**



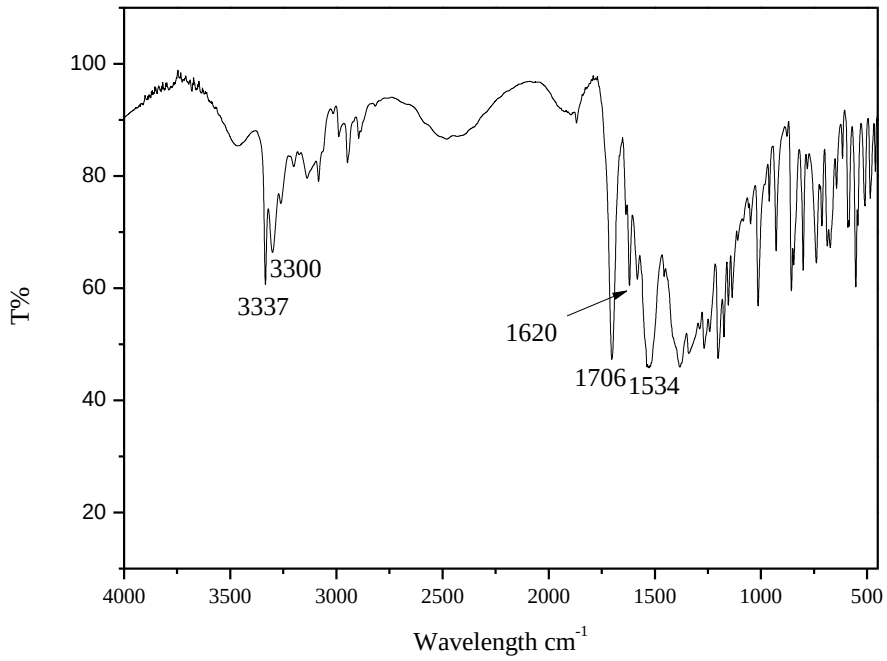
IR spectra of compound **5dbd**



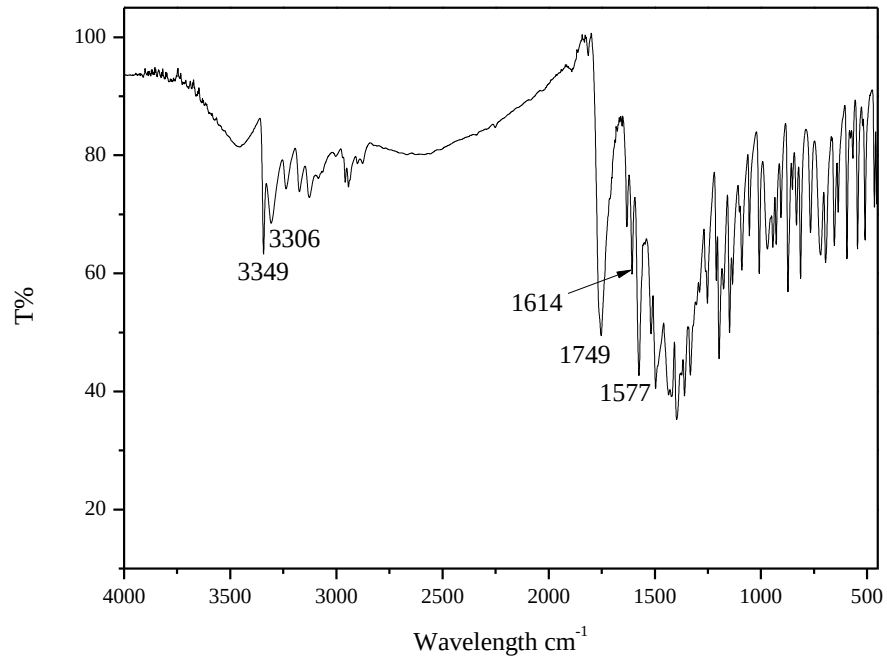
IR spectra of compound **5abe**



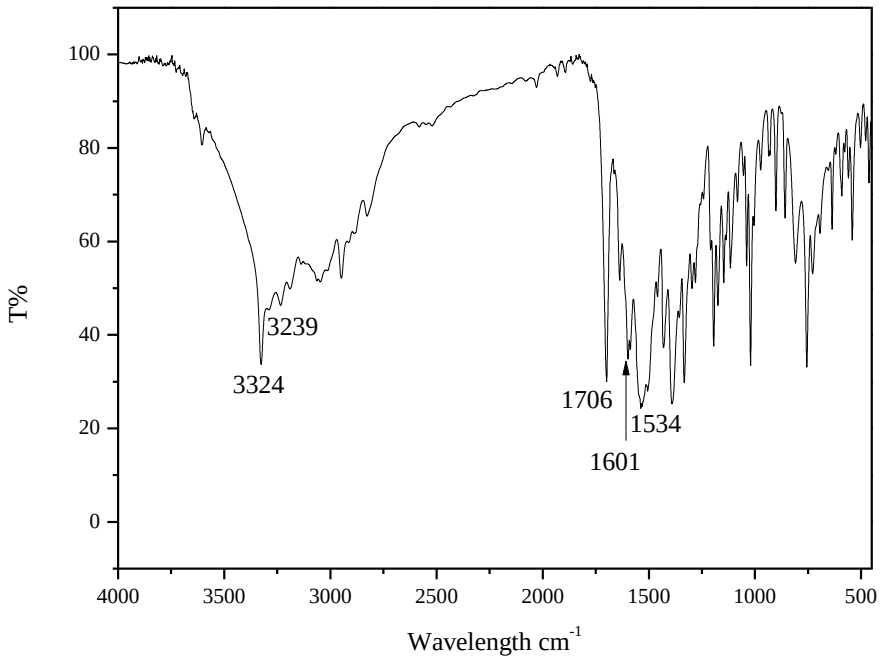
IR spectra of compound **5bbe**



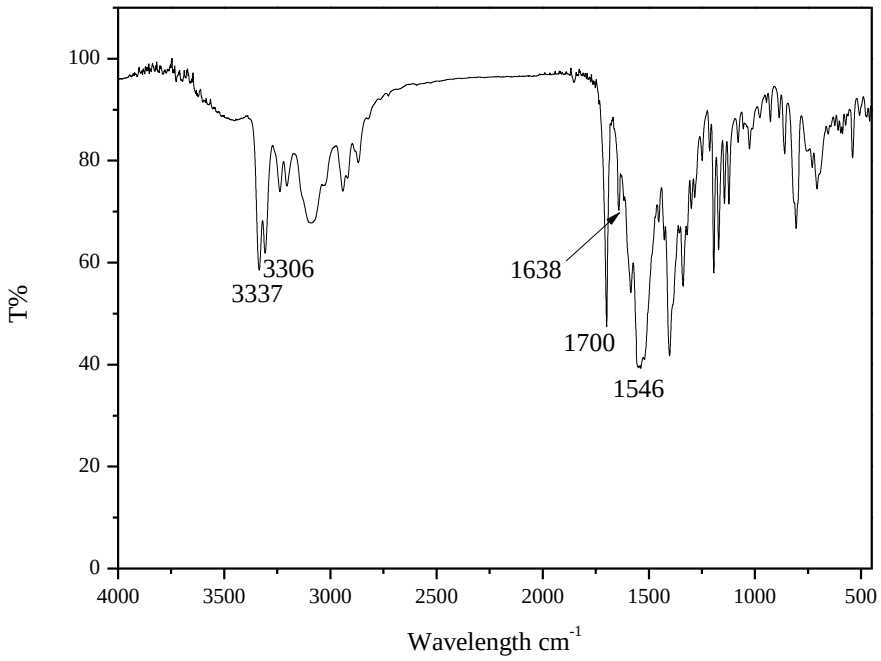
IR spectra of compound **5cbe**



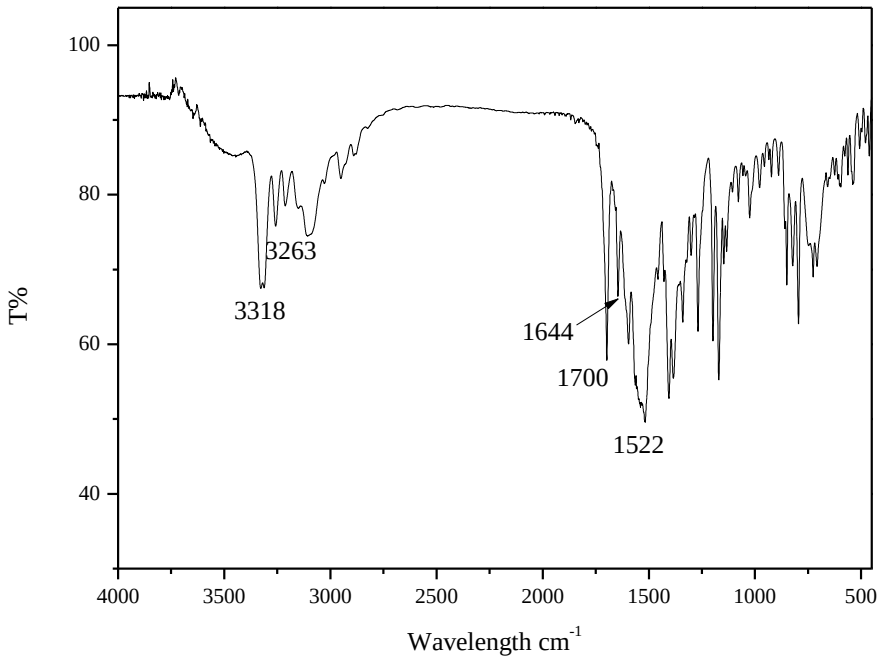
IR spectra of compound **5dbe**



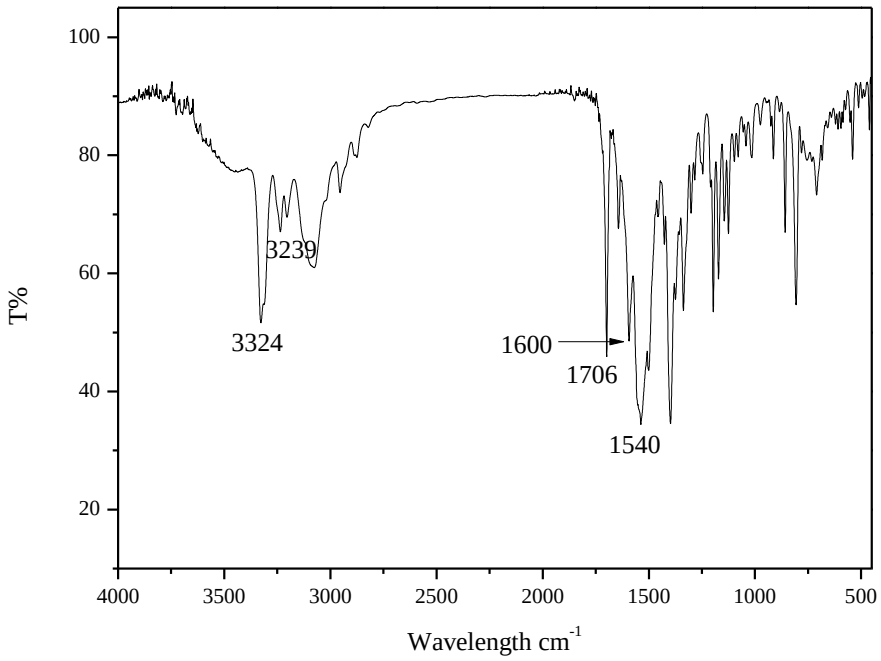
IR spectra of compound **5abf**



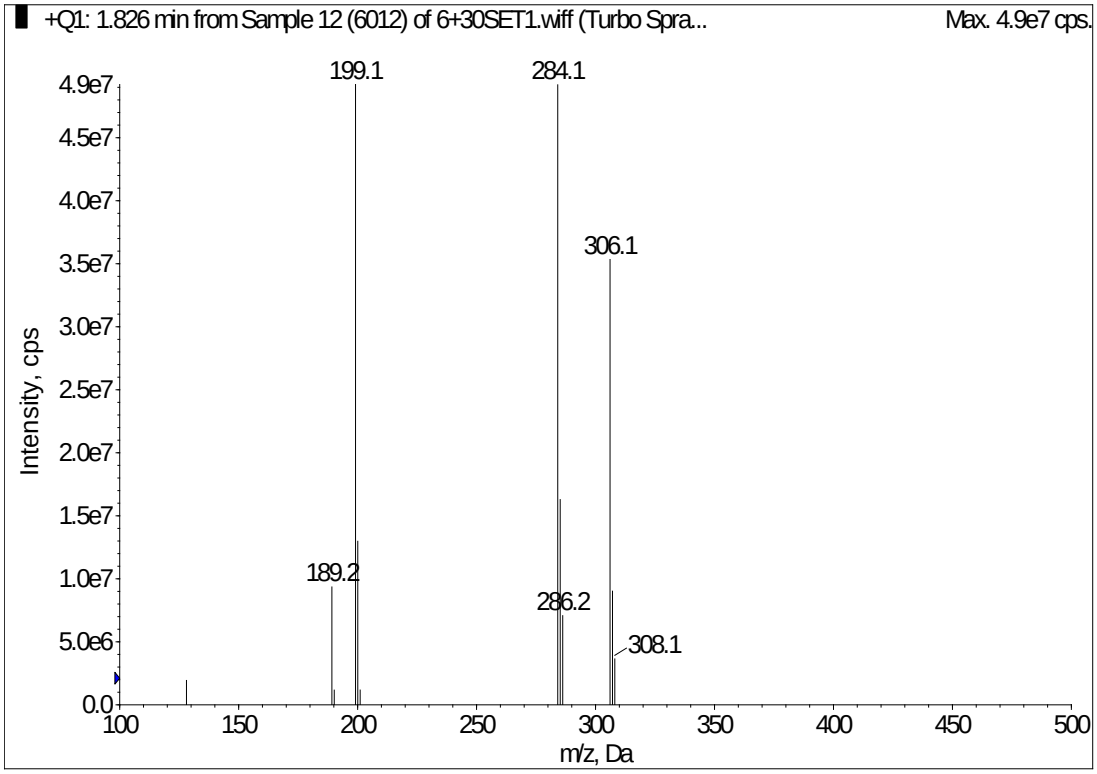
IR spectra of compound **5bbf**



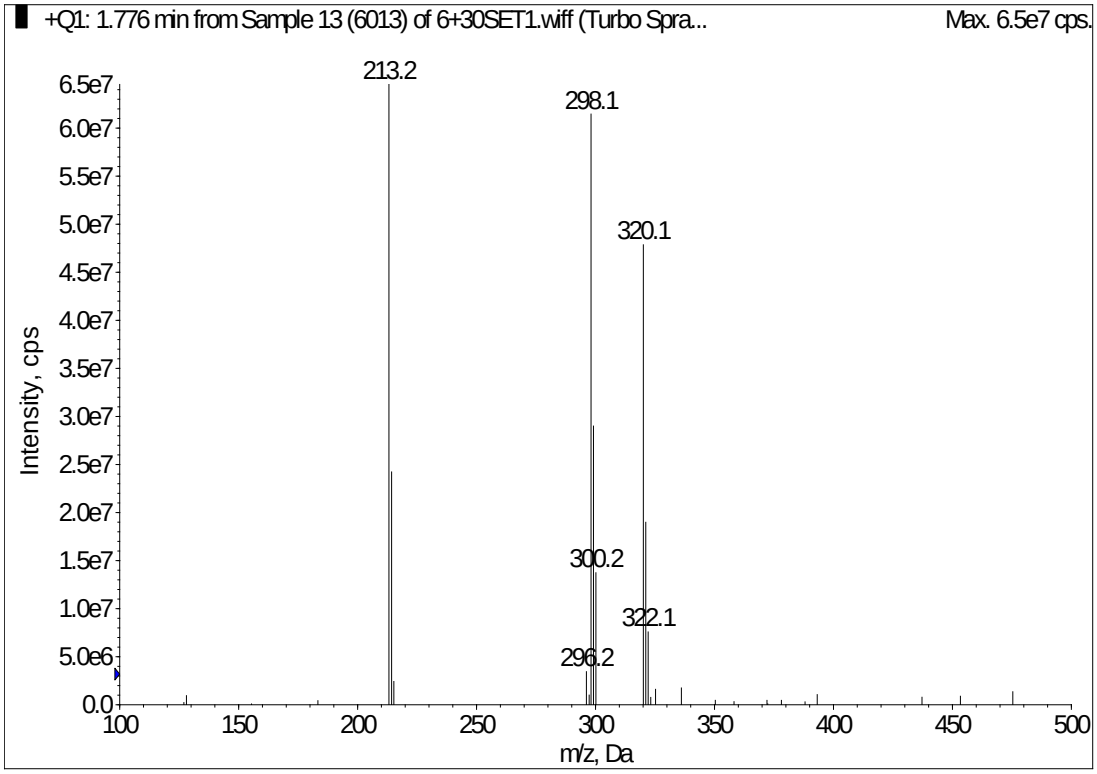
IR spectra of compound **5cbf**



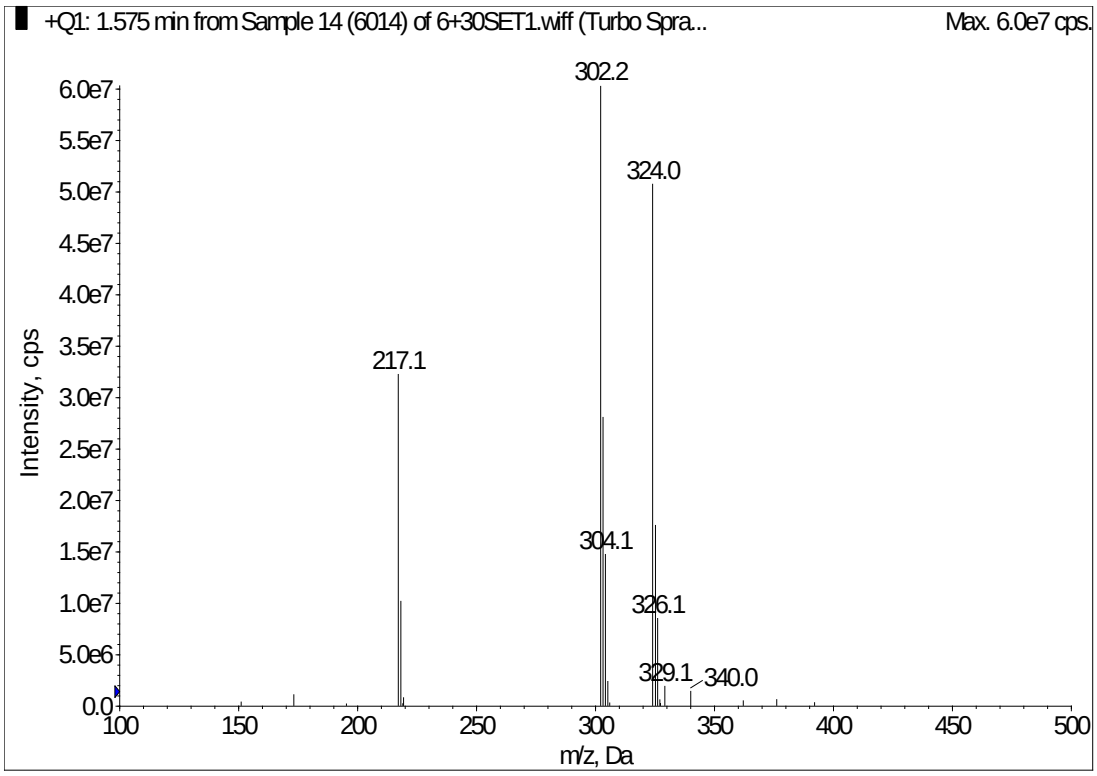
IR spectra of compound **5dbf**



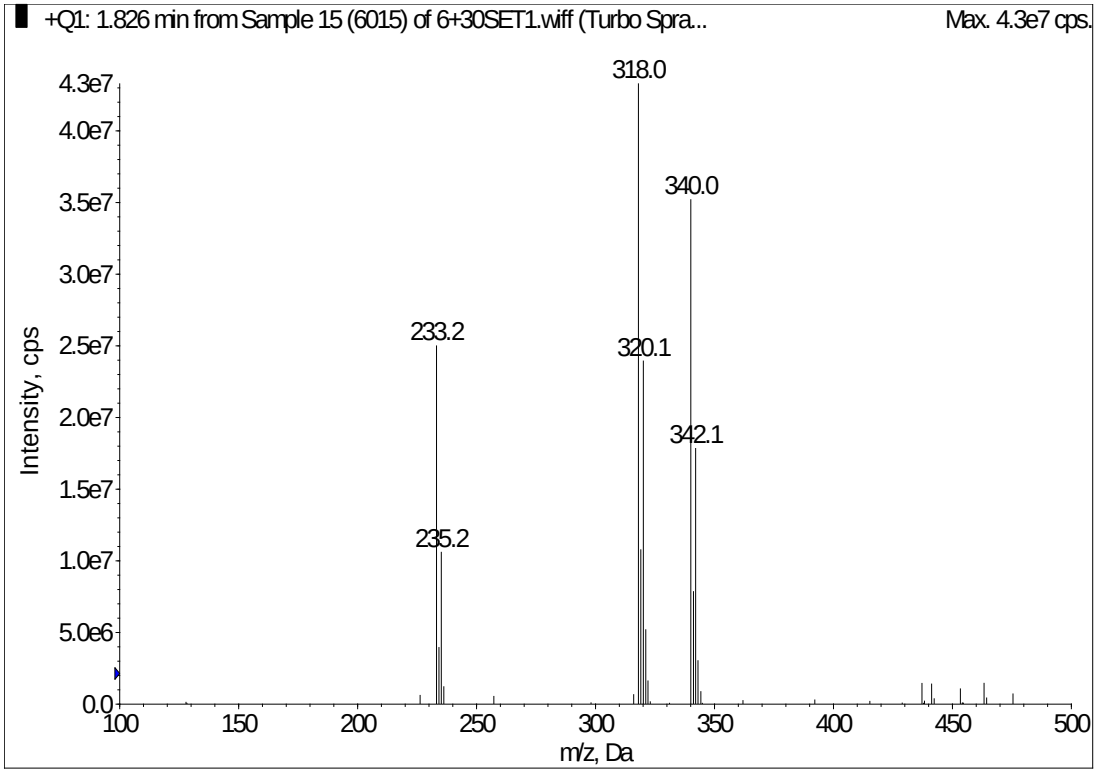
MS of compound **4aaa**



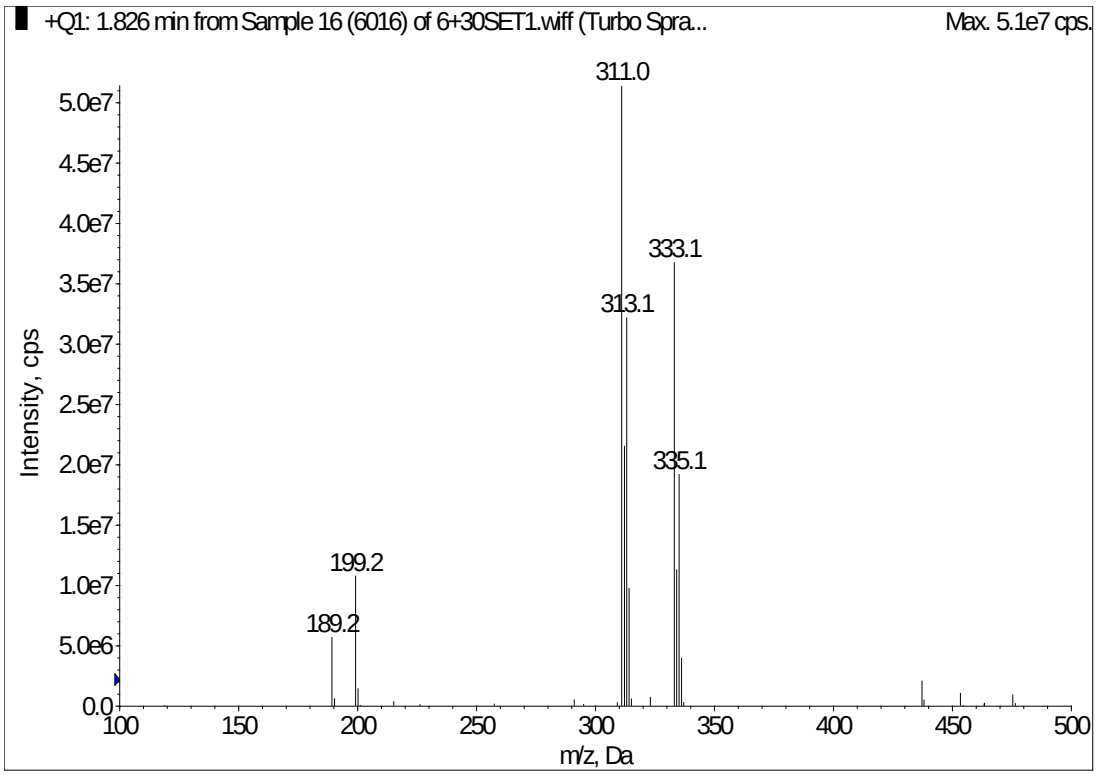
MS of compound **4baa**



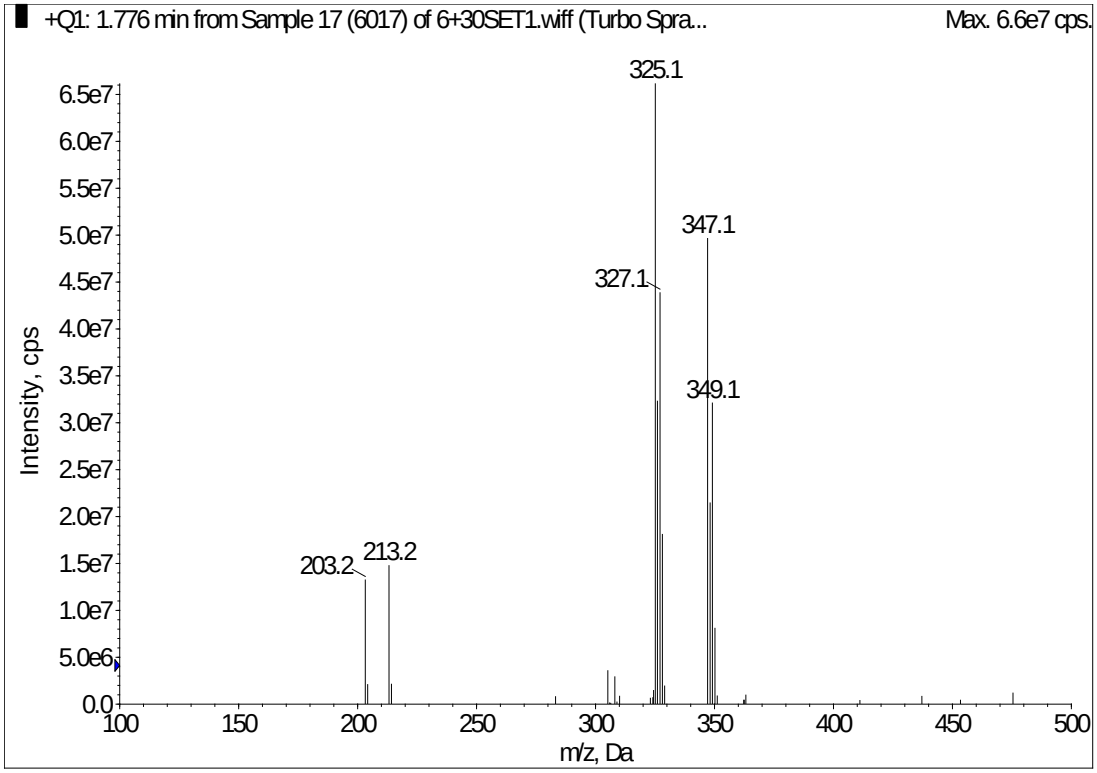
MS of compound **4caa**



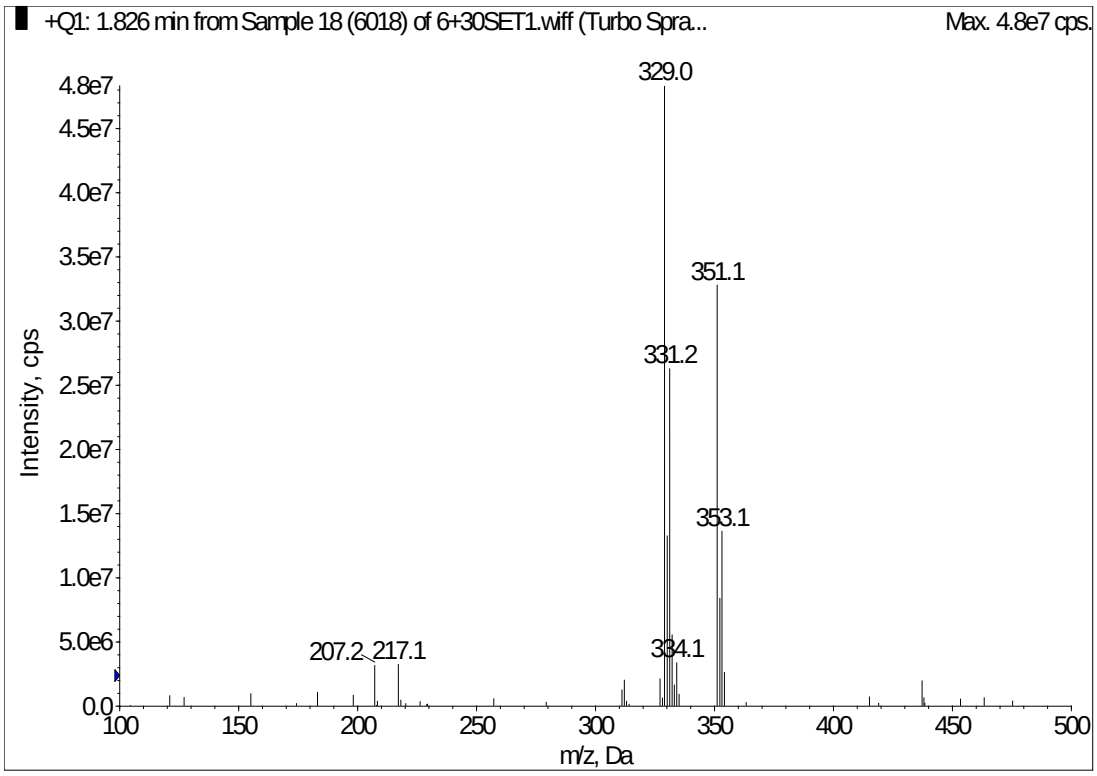
MS of compound **4daa**



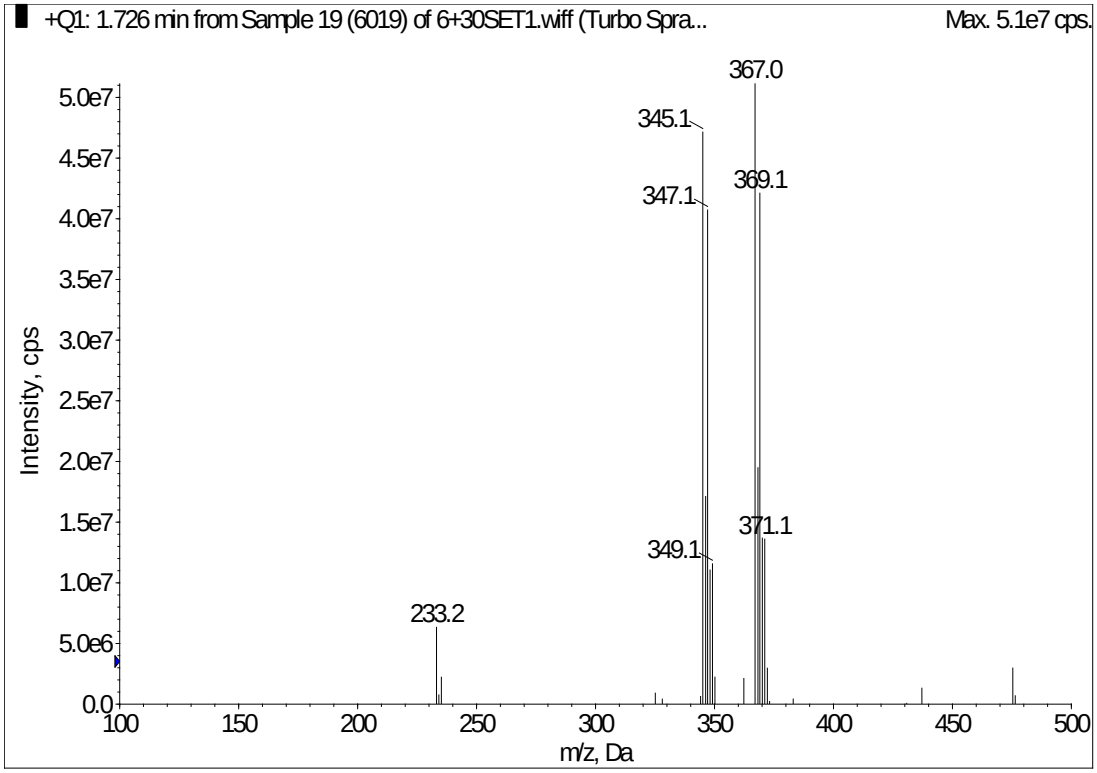
MS of compound **4aab**



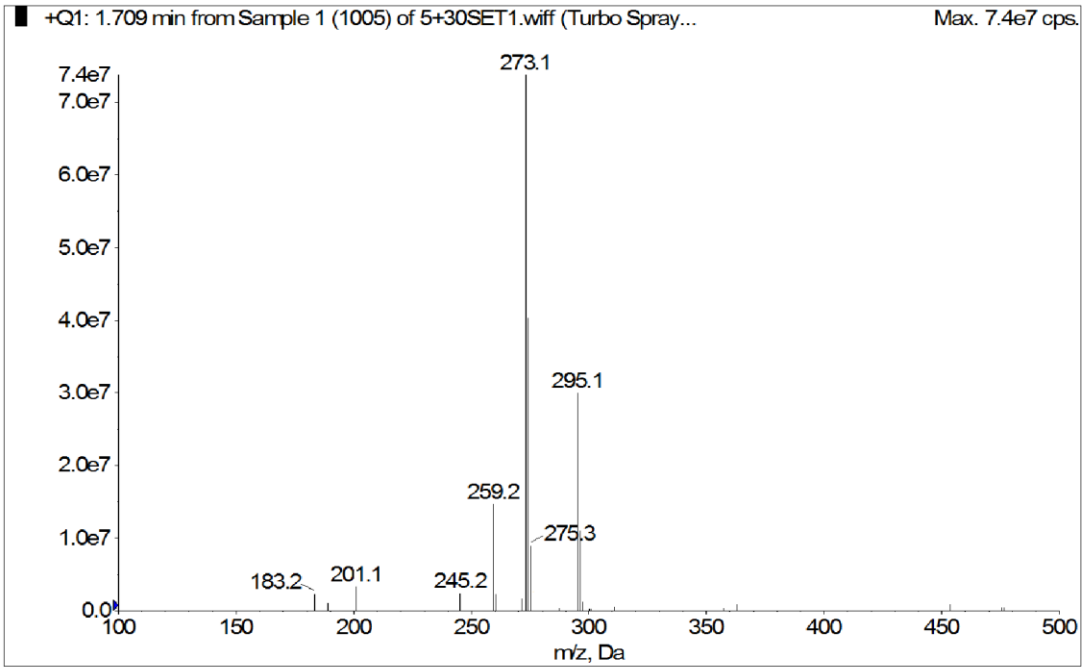
MS of compound **4bab**



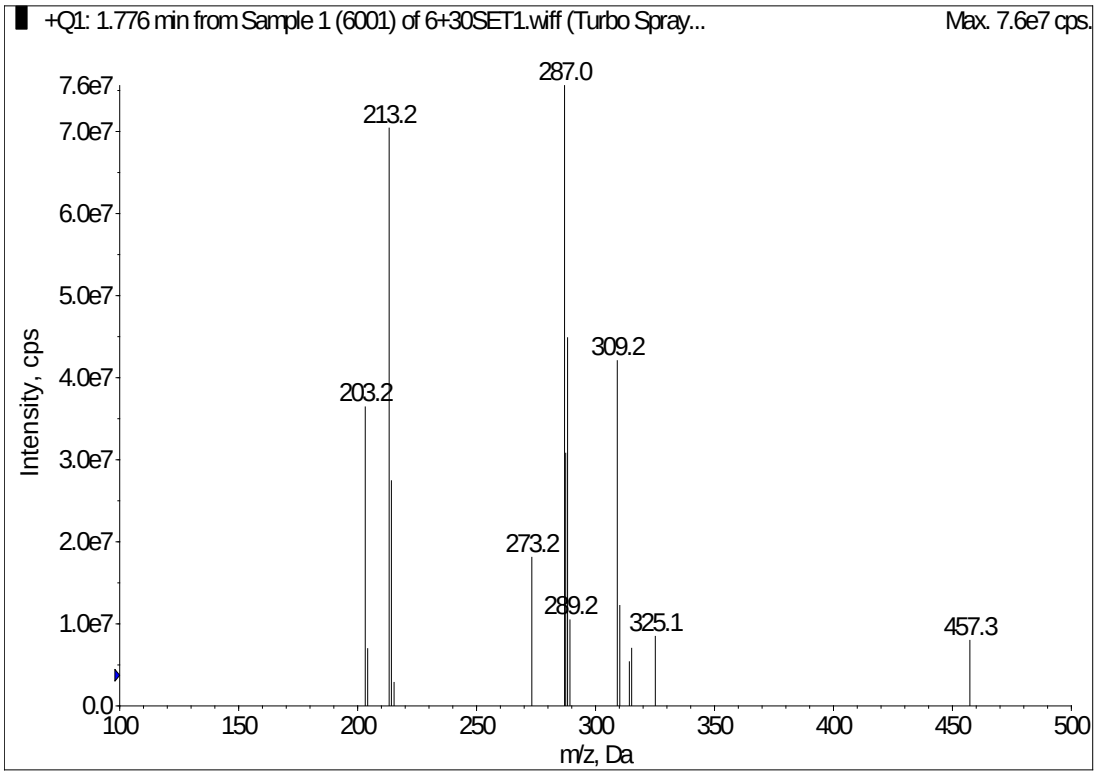
MS of compound **4cab**



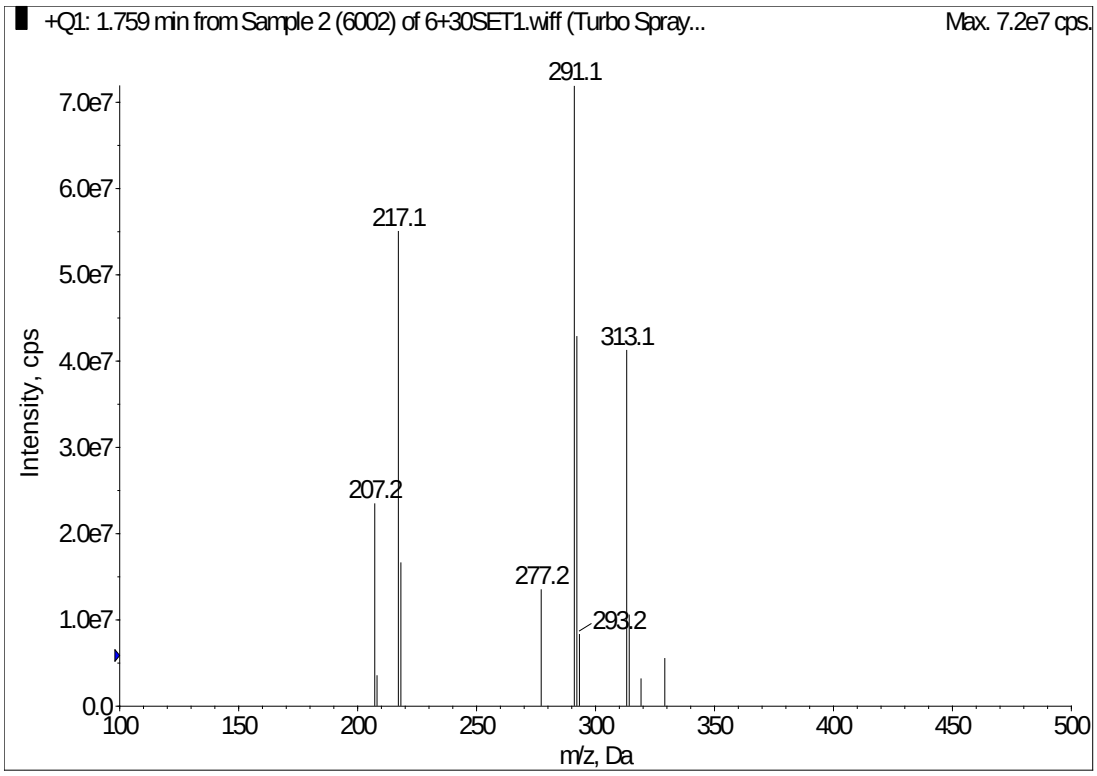
MS of compound **4dab**



MS of compound **5aac**



MS of compound **5bac**



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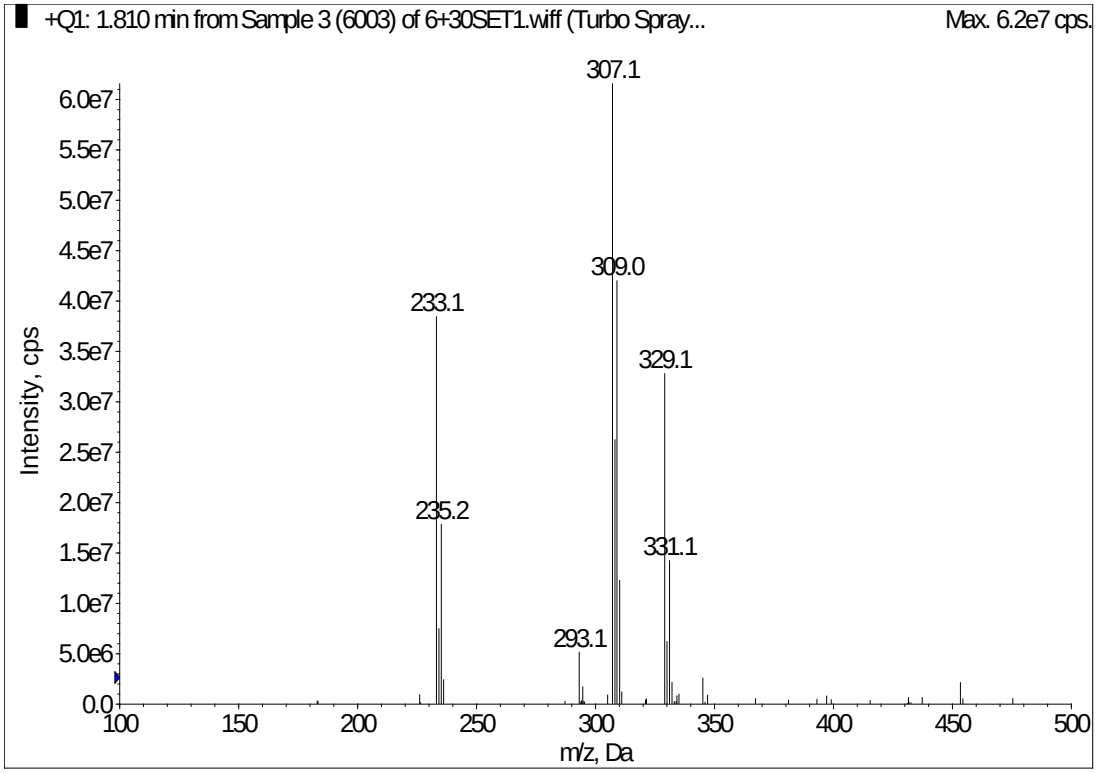

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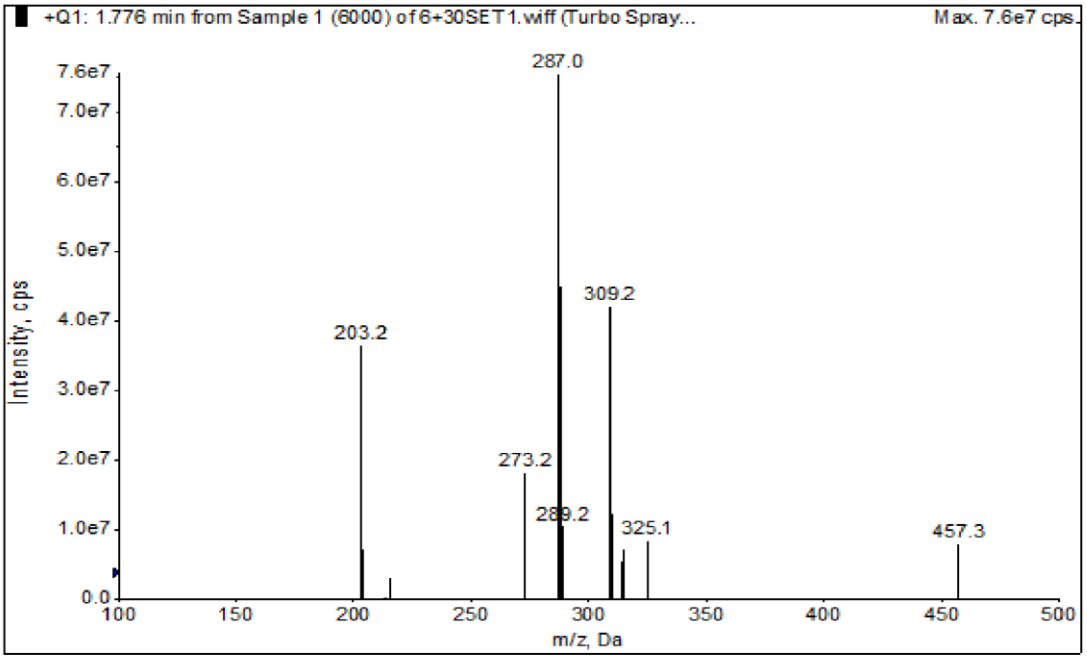
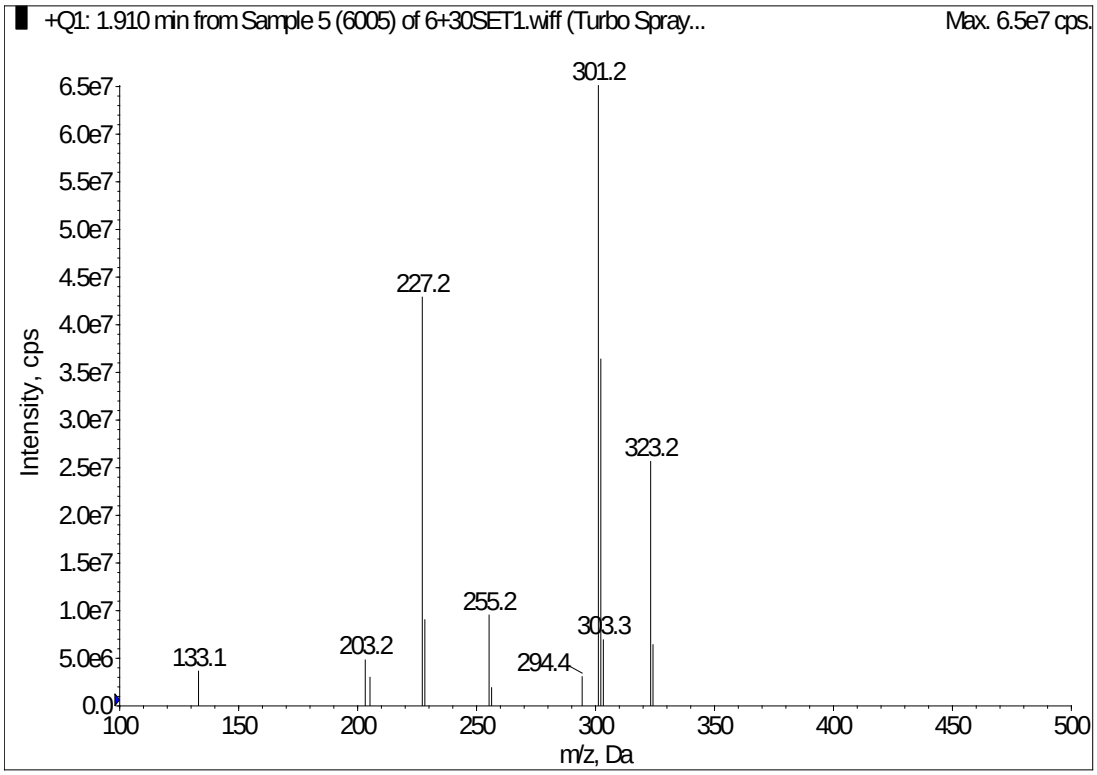
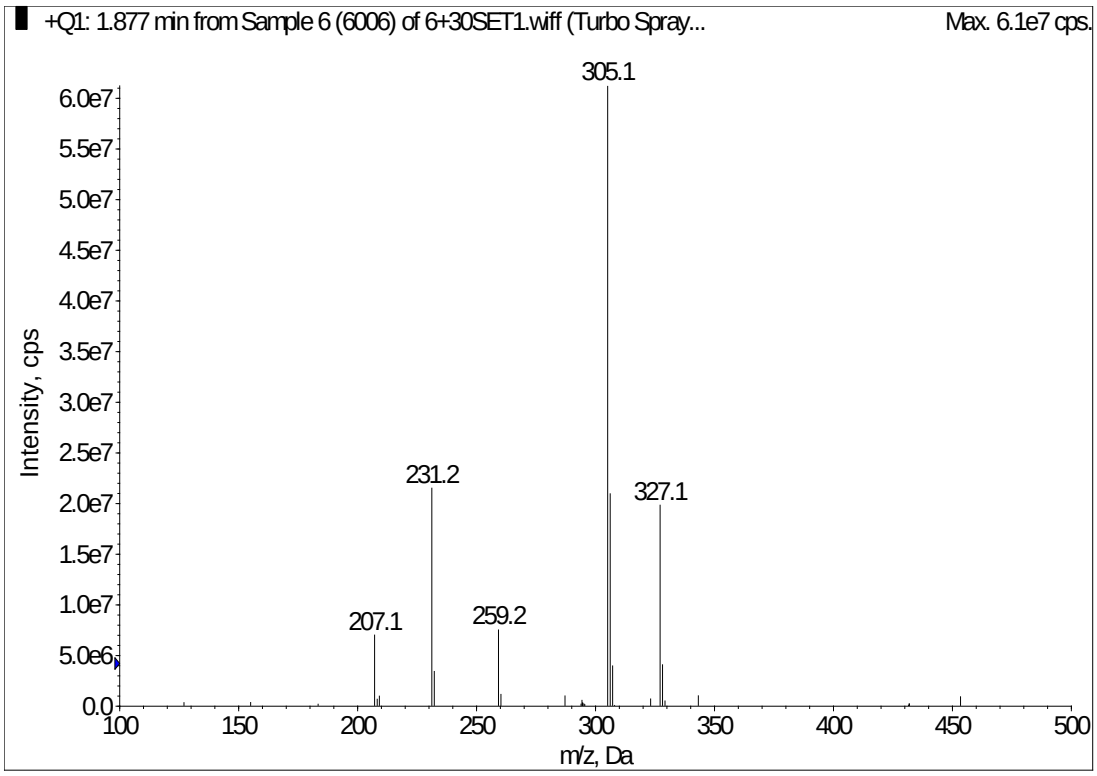


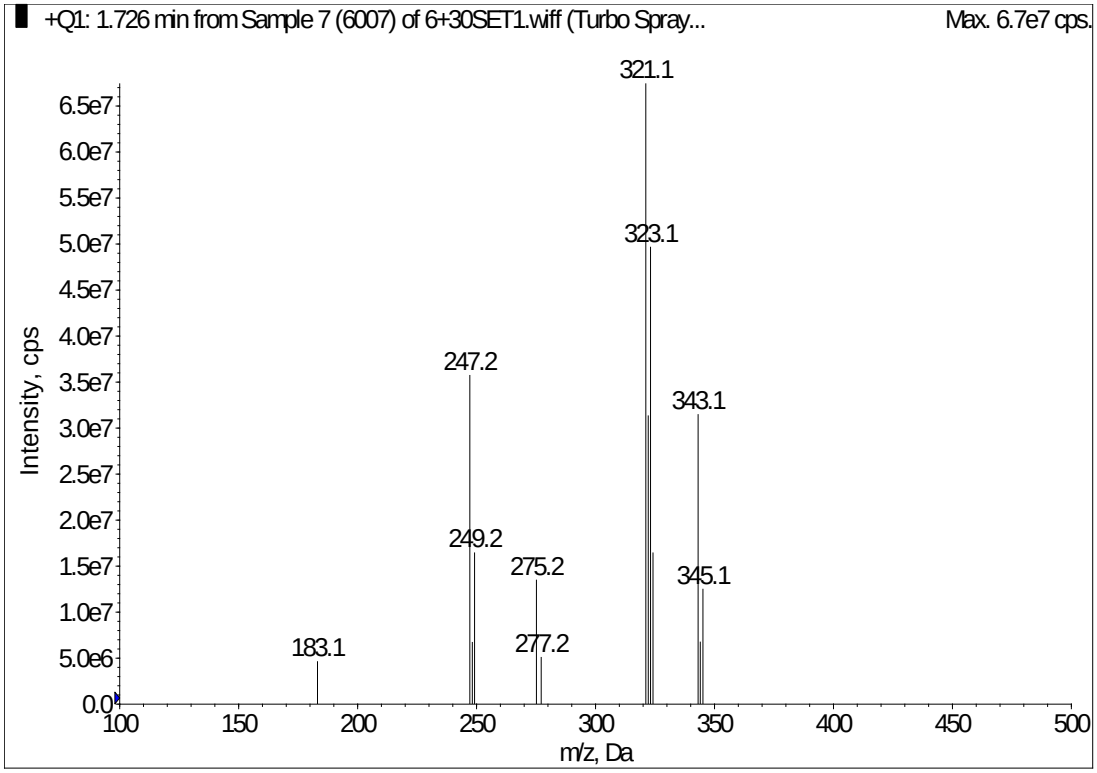
MS of compound **5aad**



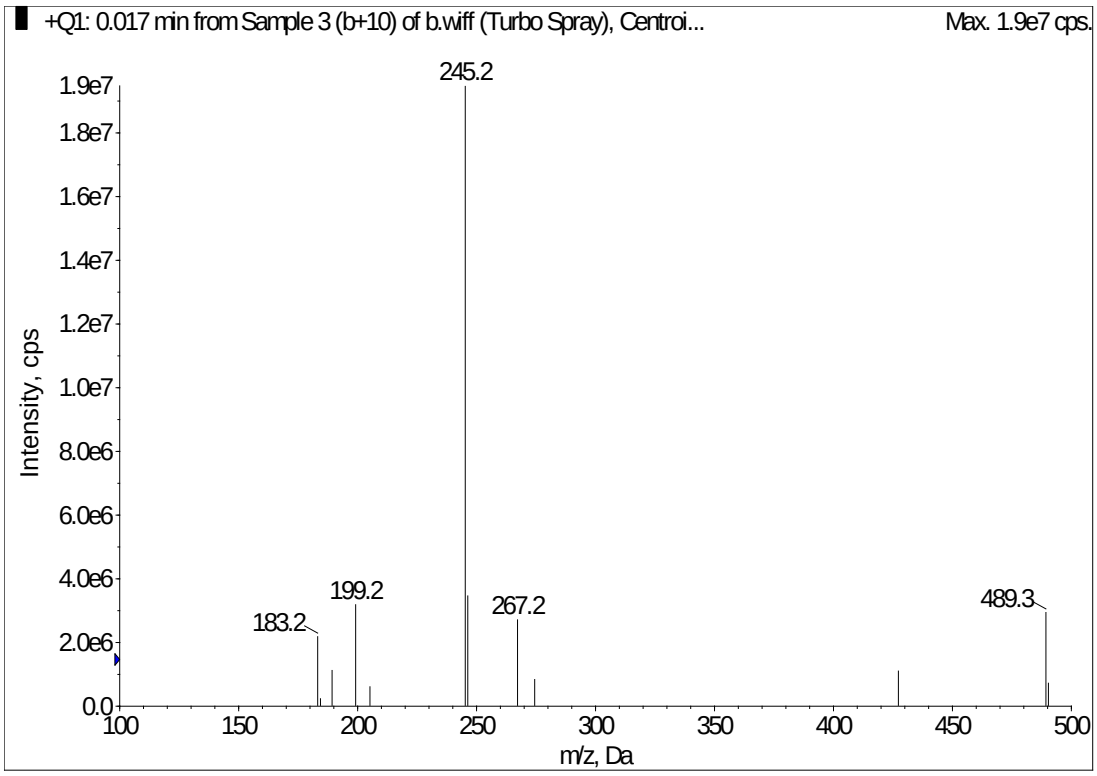
MS of compound **5bad**



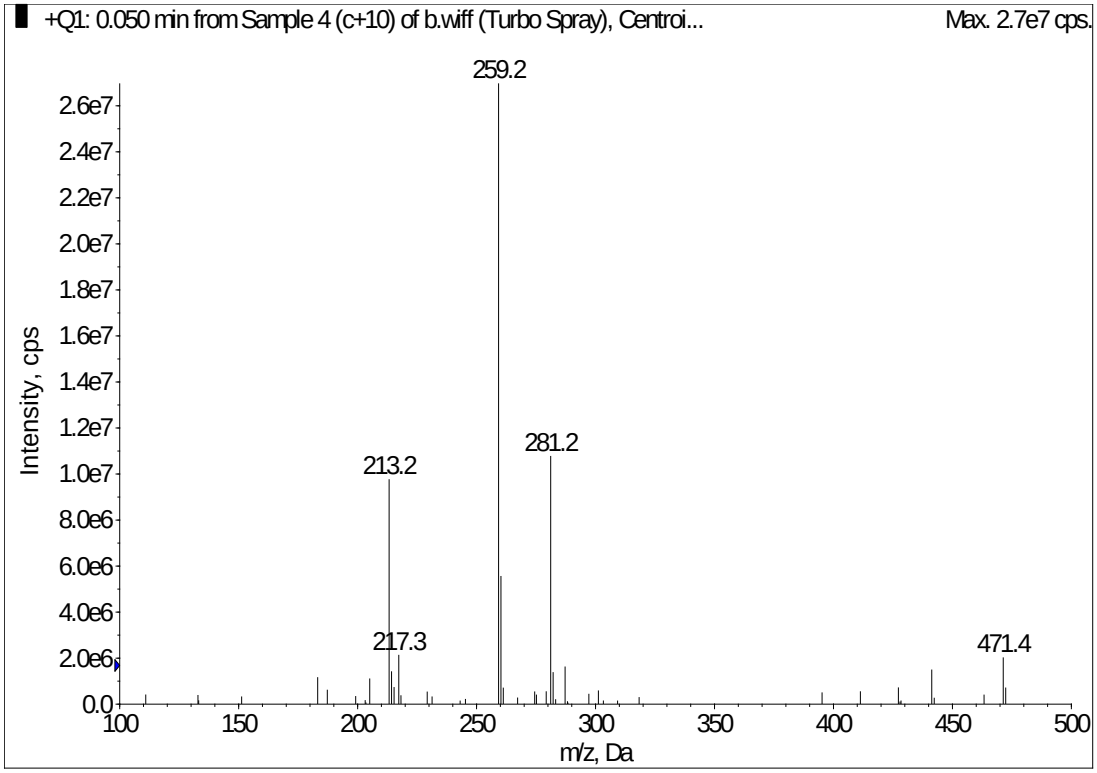
MS of compound **5cad**



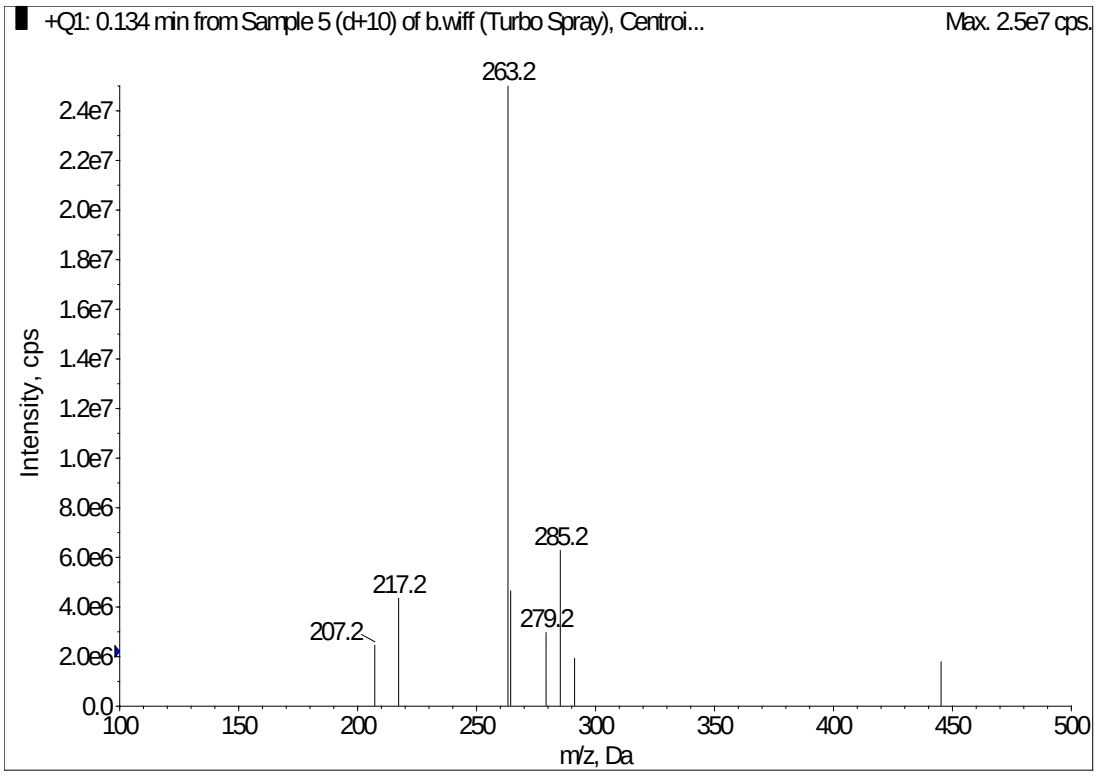
MS of compound **5dad**



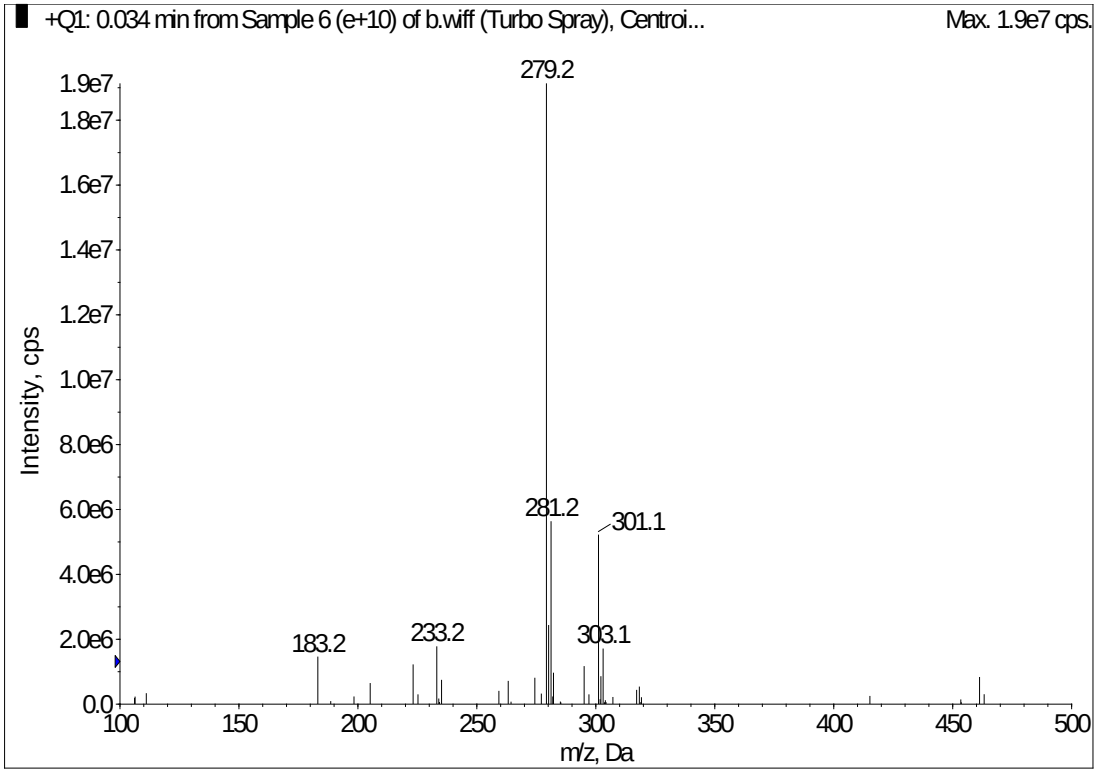
MS of compound **5aae**



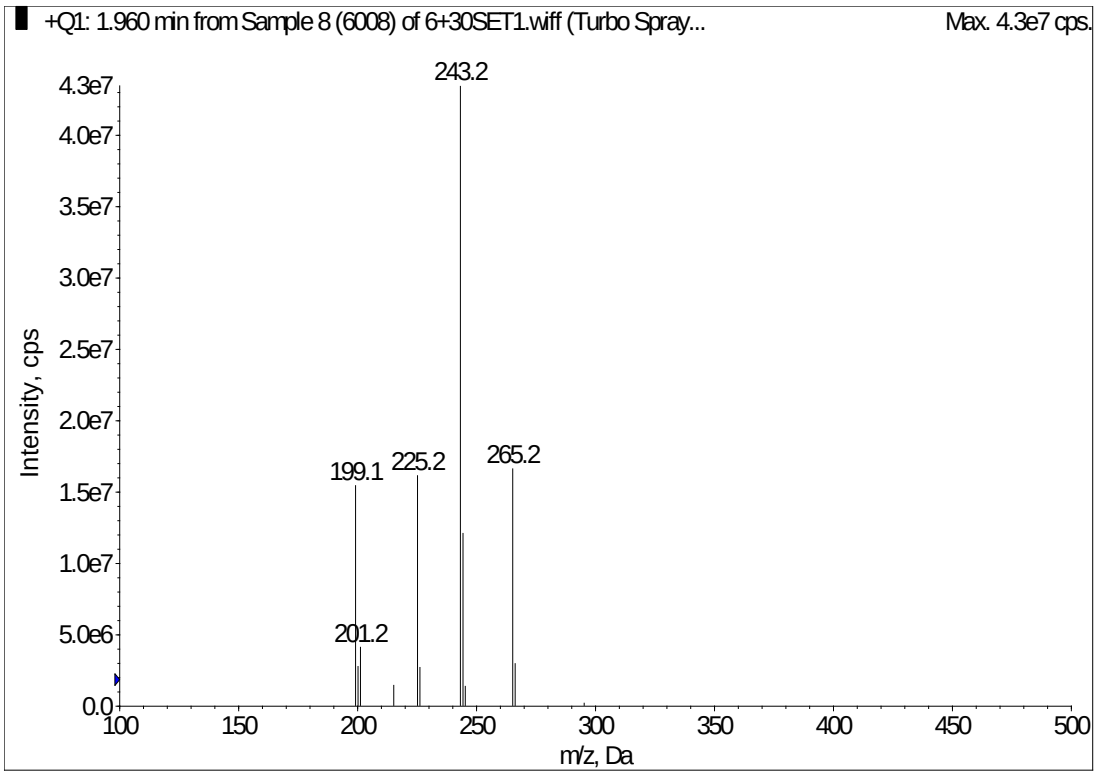
MS of compound **5bae**



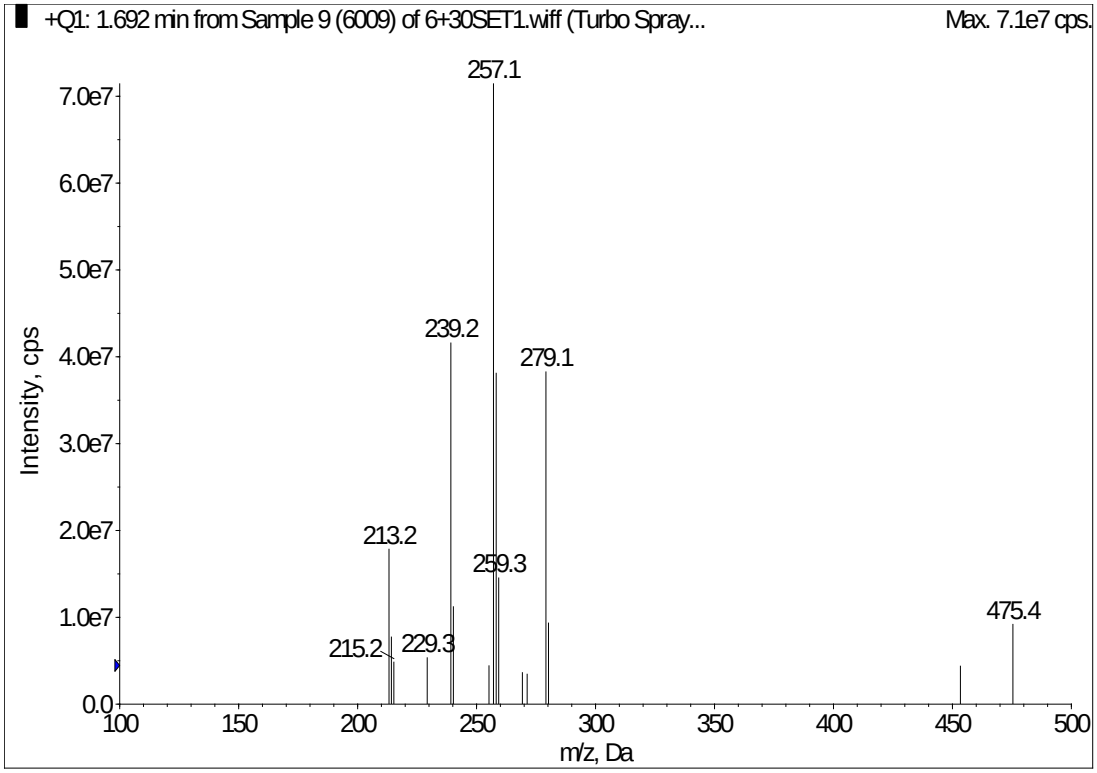
MS of compound **5cae**



MS of compound **5dae**



MS of compound **5aaf**



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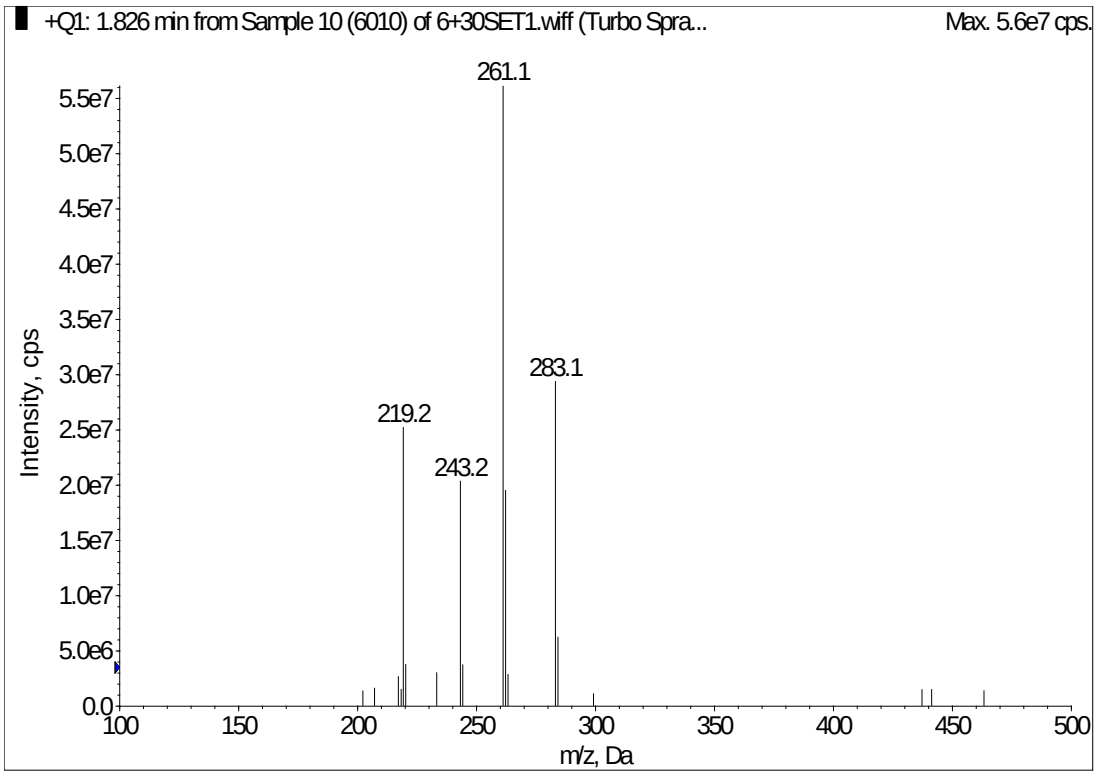
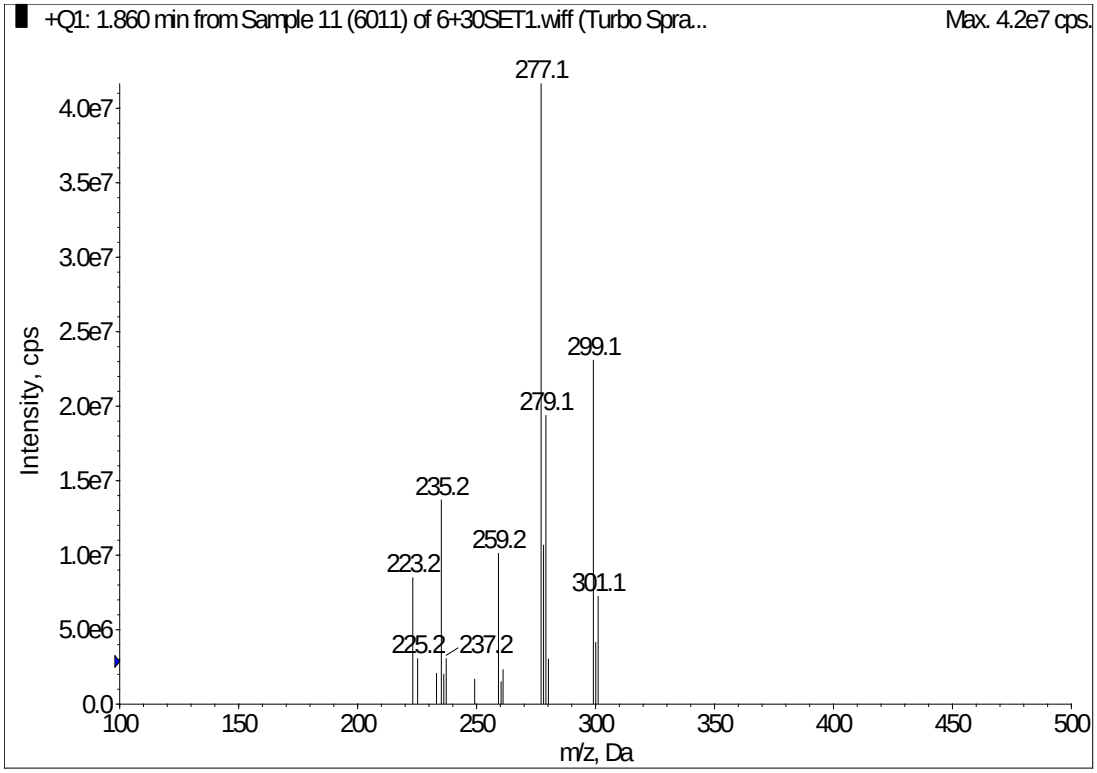
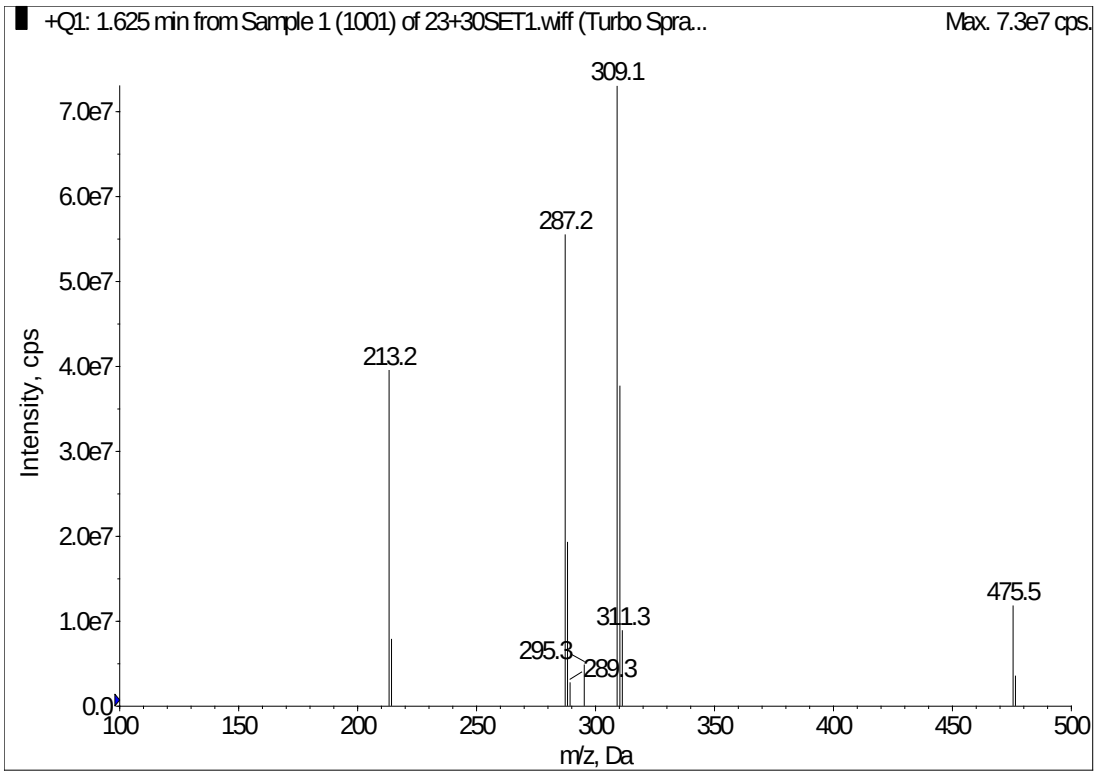


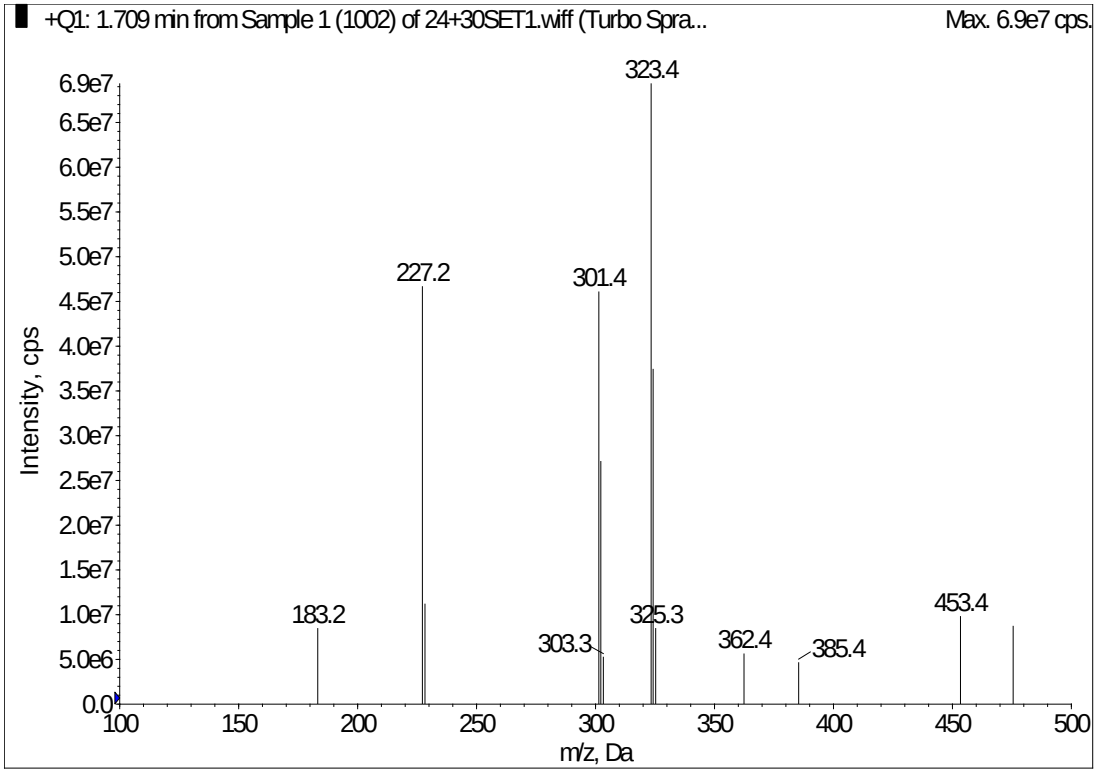
MS of compound **5caf**



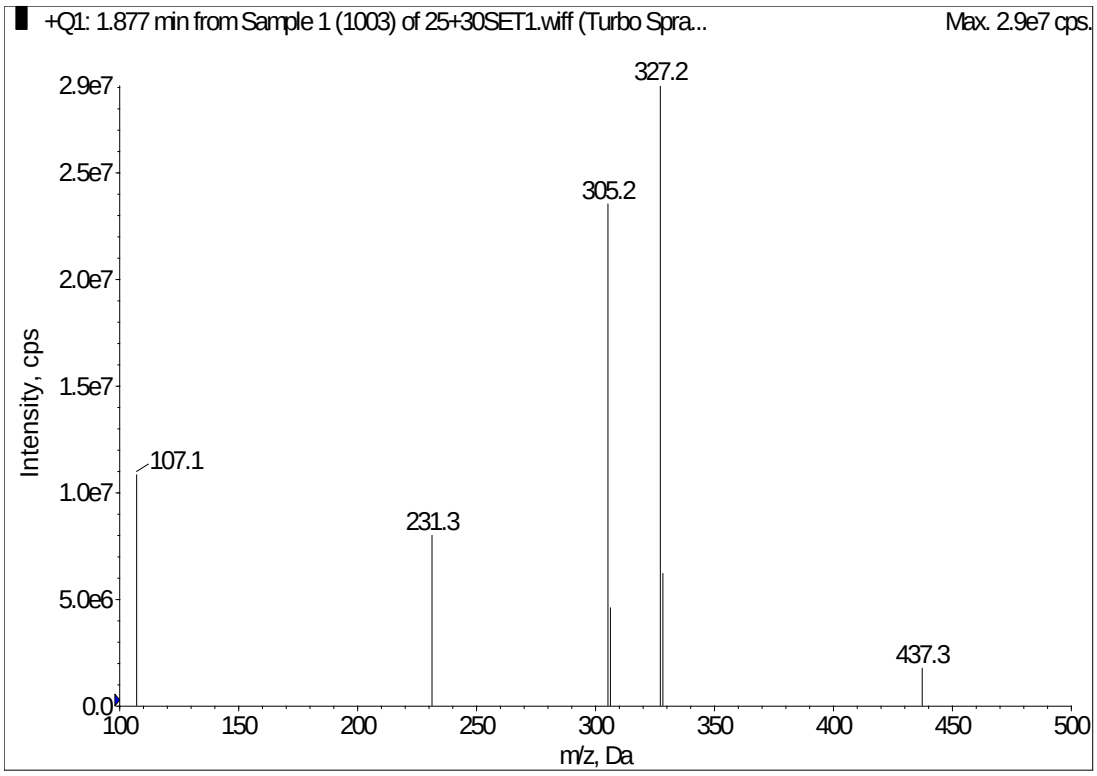
MS of compound **5daf**



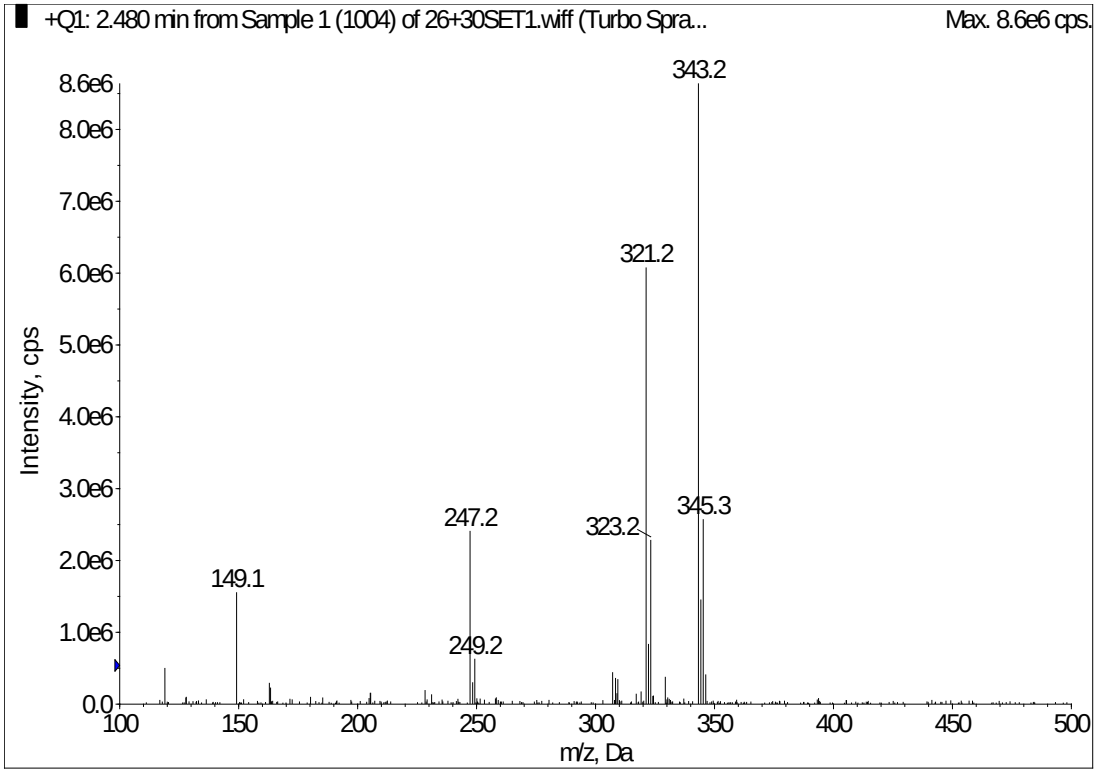
MS of compound **5abc**



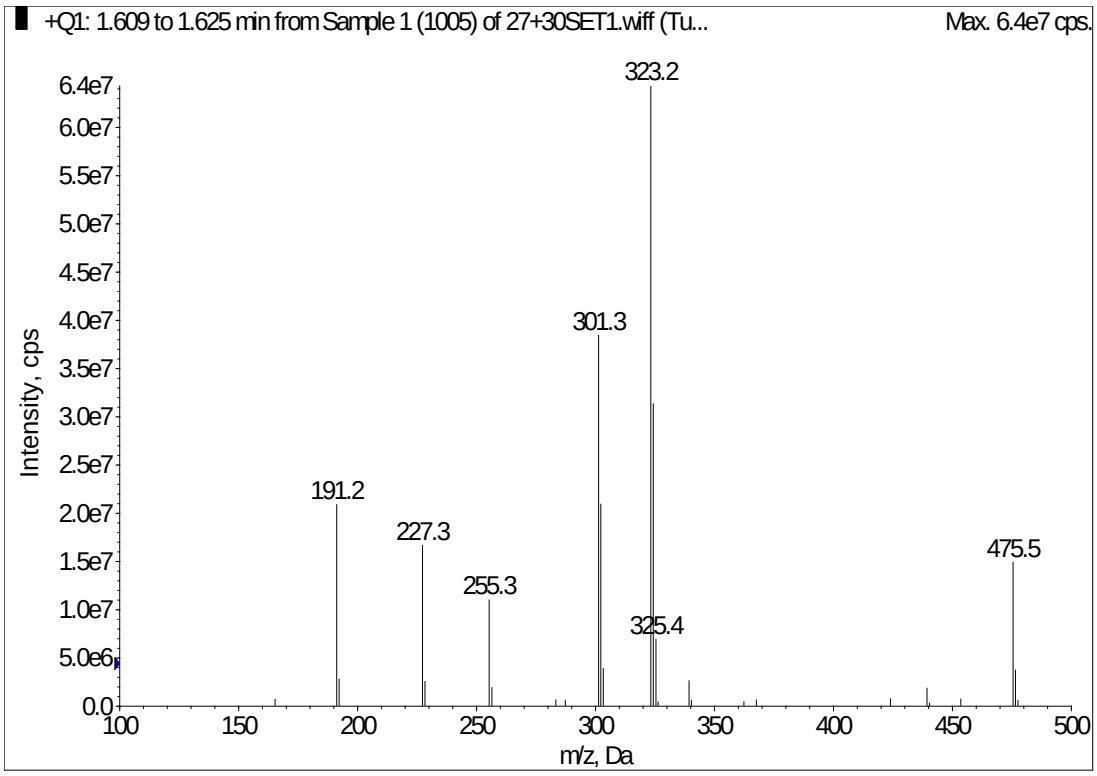
MS of compound **5bbc**



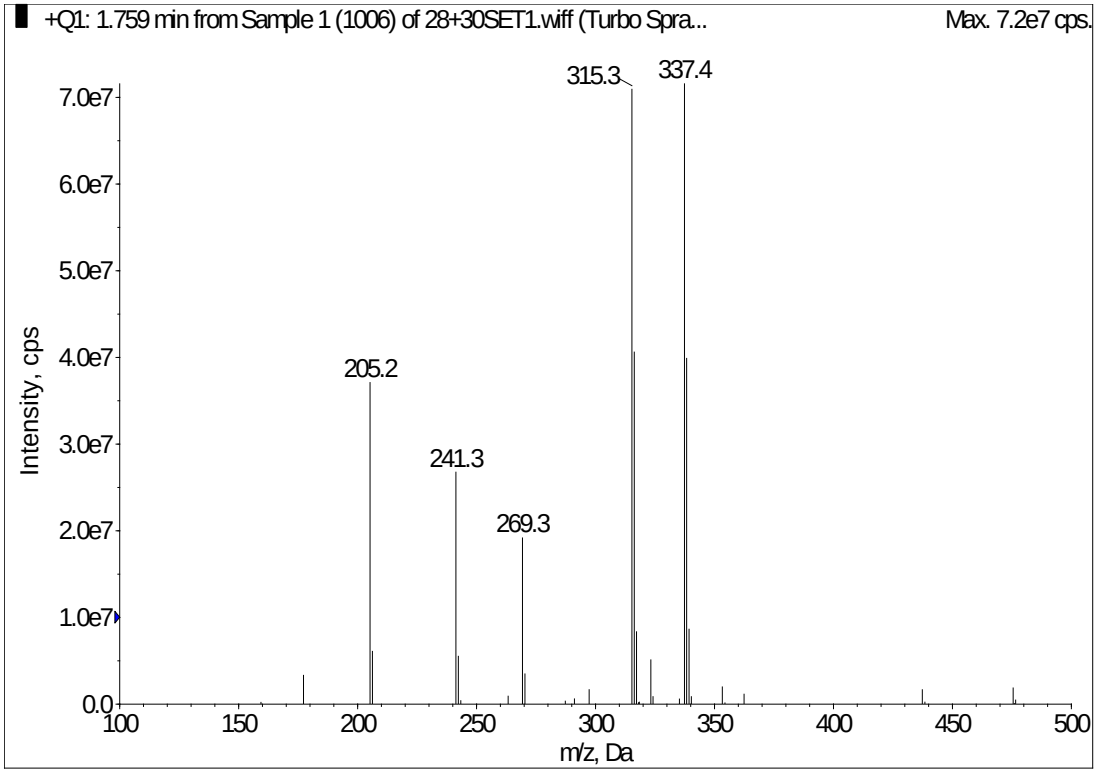
MS of compound **5cbc**



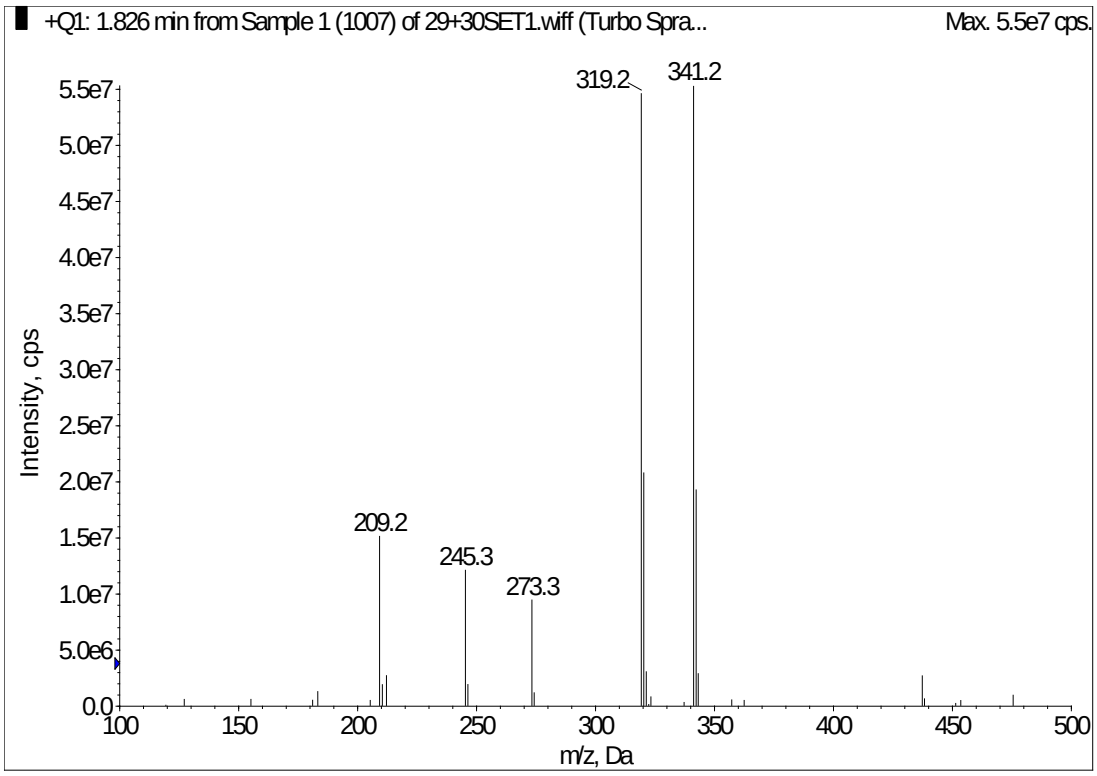
MS of compound **5dbc**



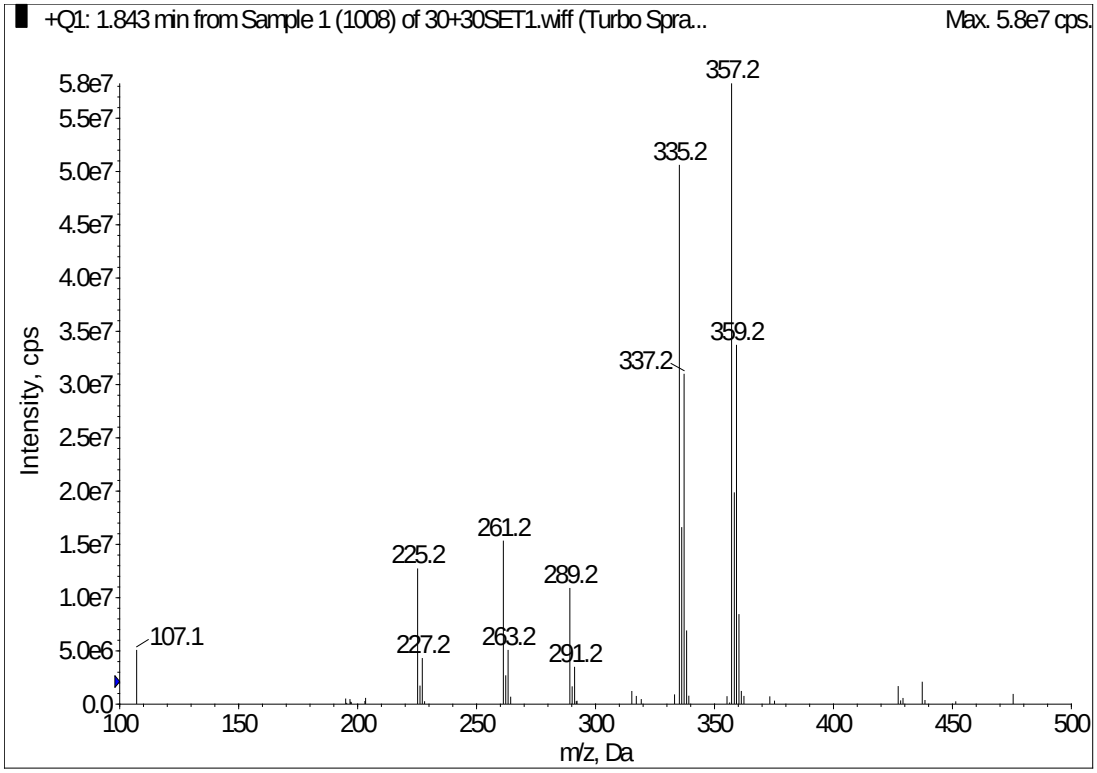
MS of compound **5abd**



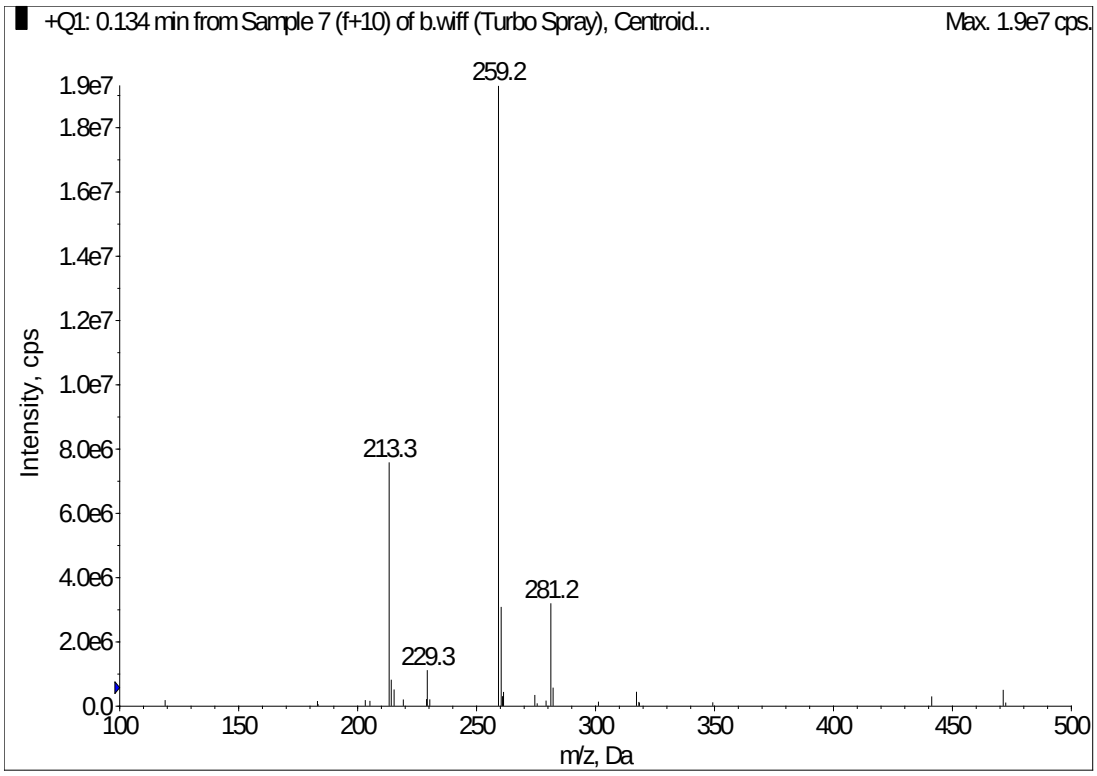
MS of compound **5bdb**



MS of compound **5cbd**



MS of compound **5dbd**



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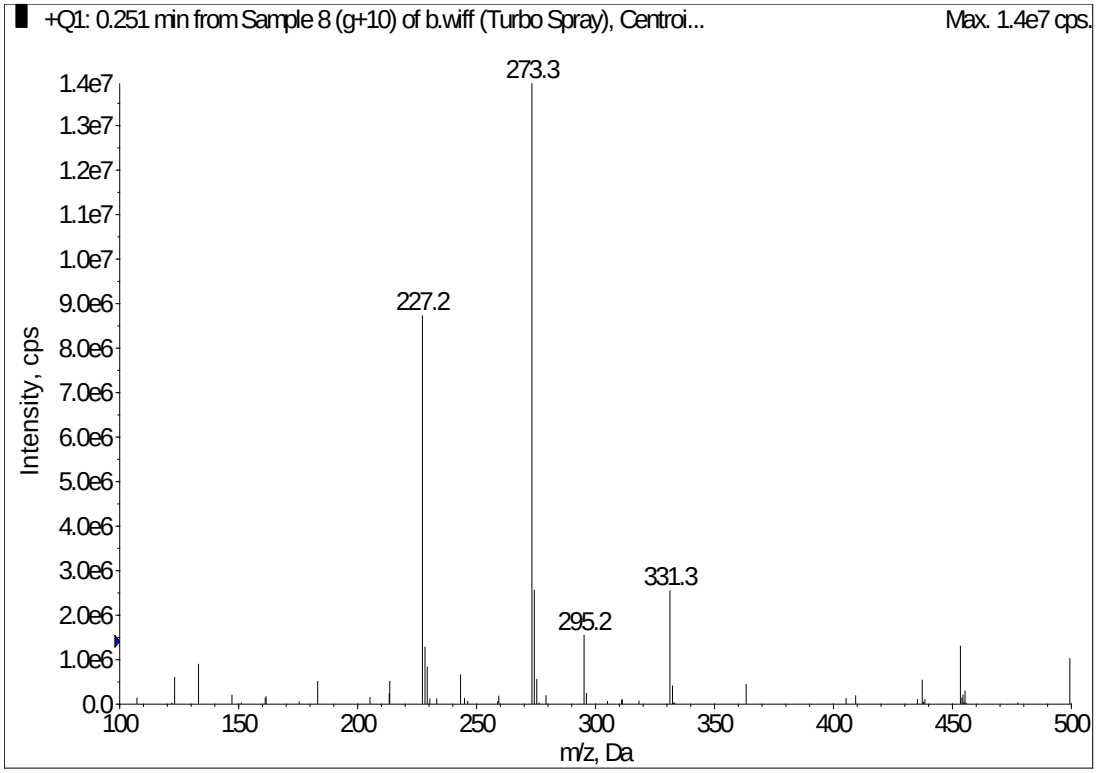

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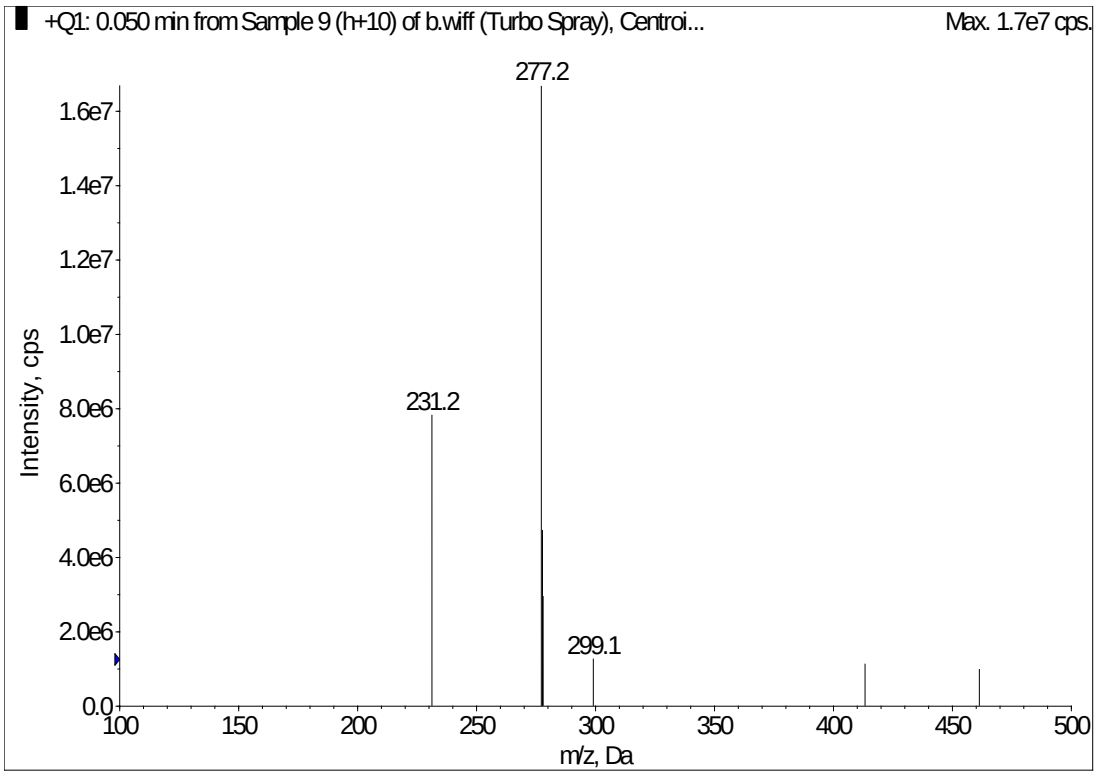
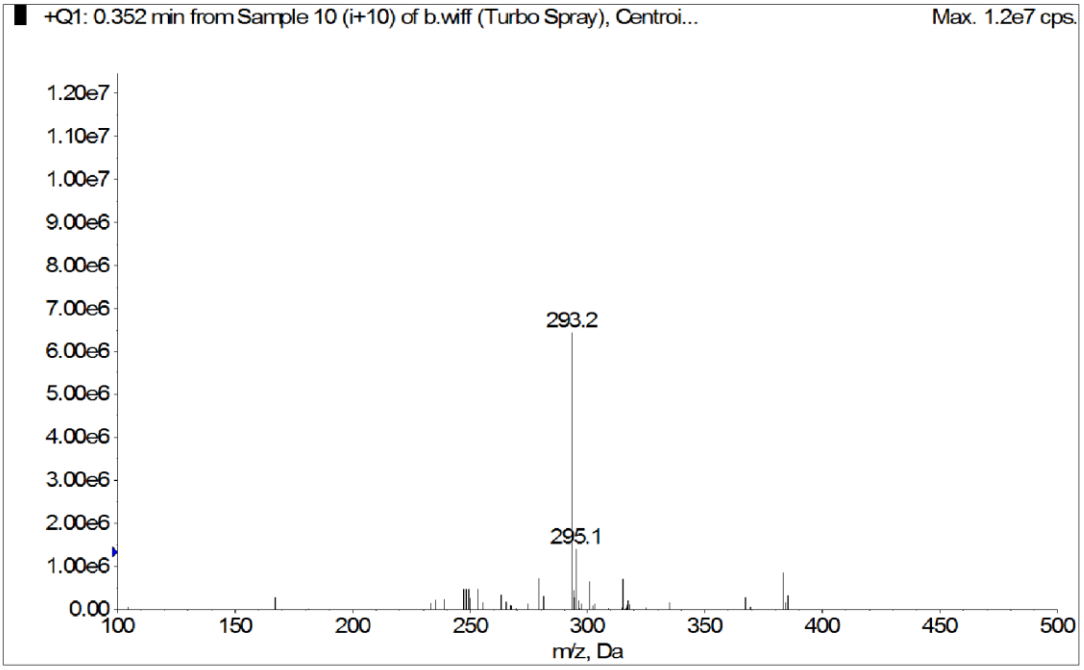


MS of compound **5cbe**



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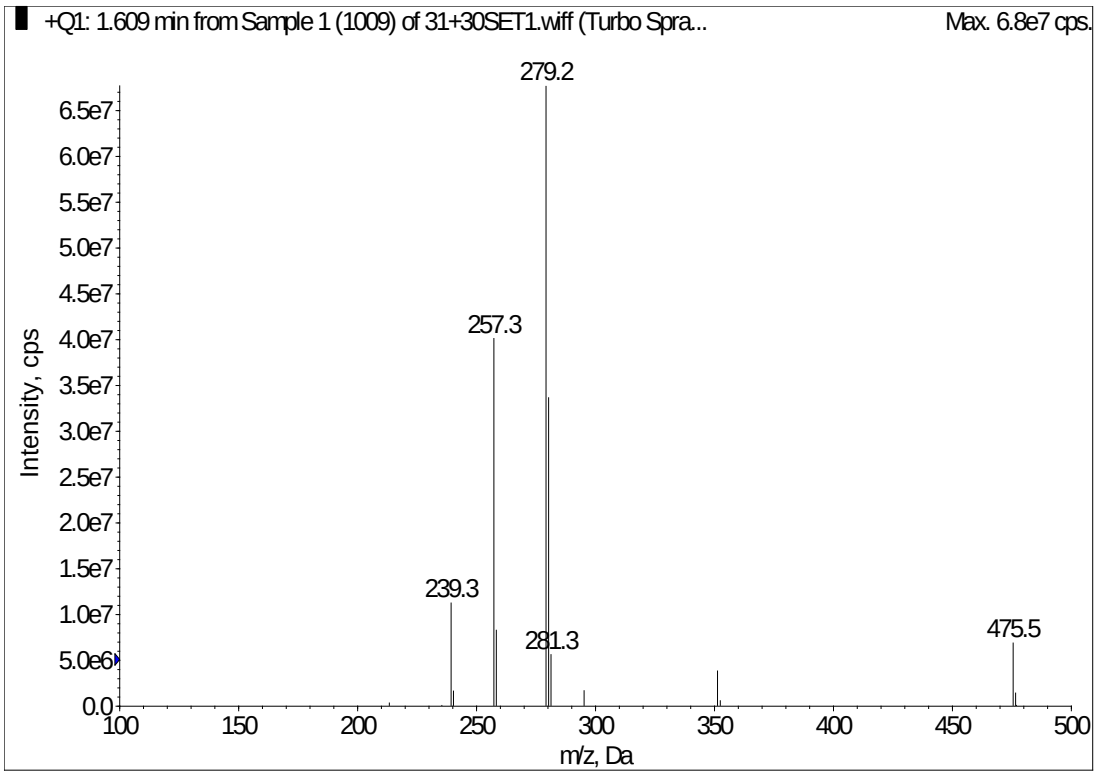

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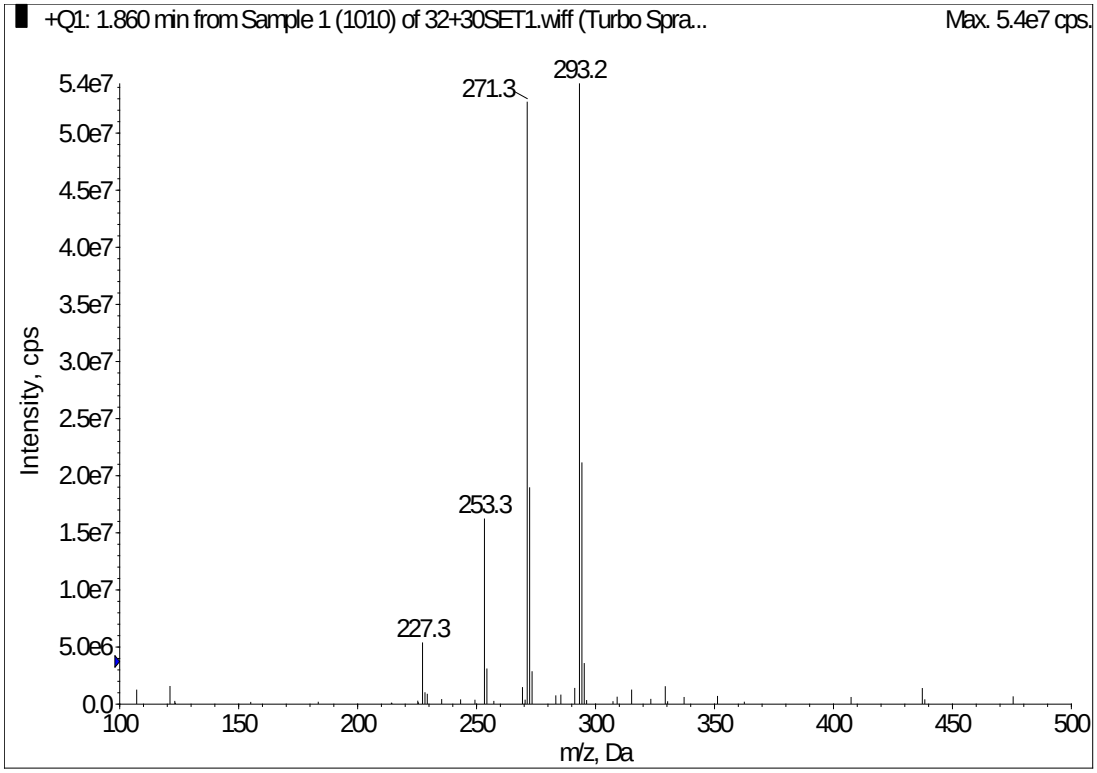

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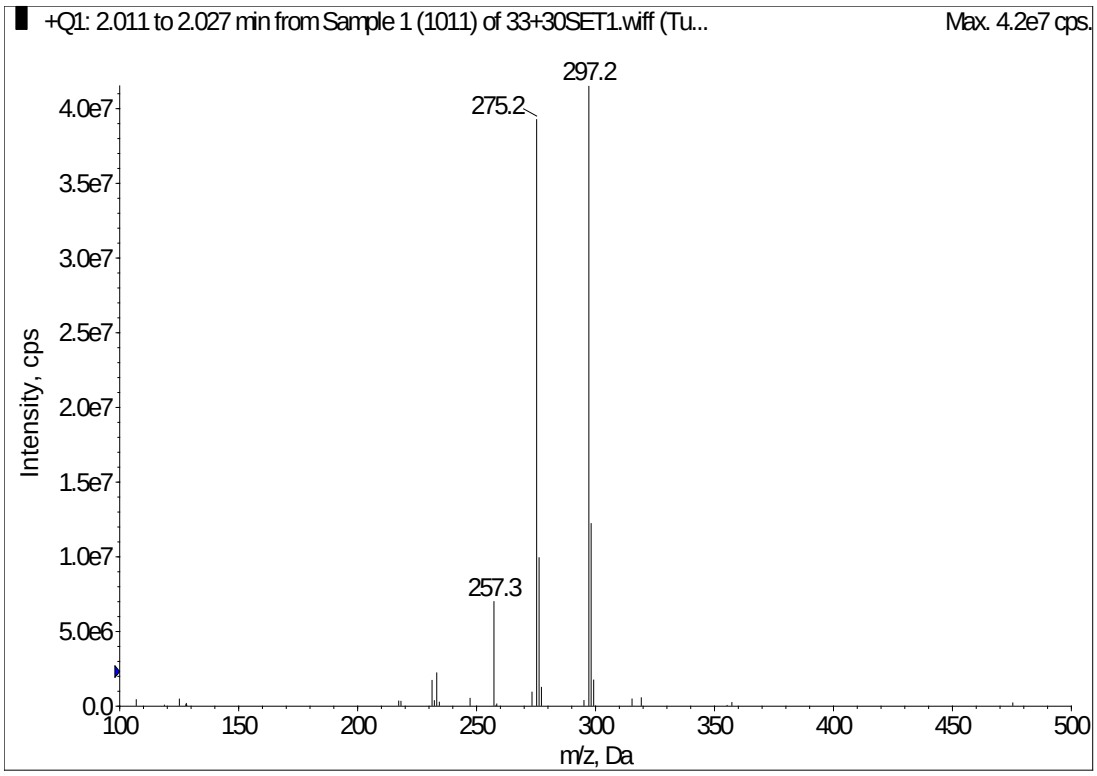

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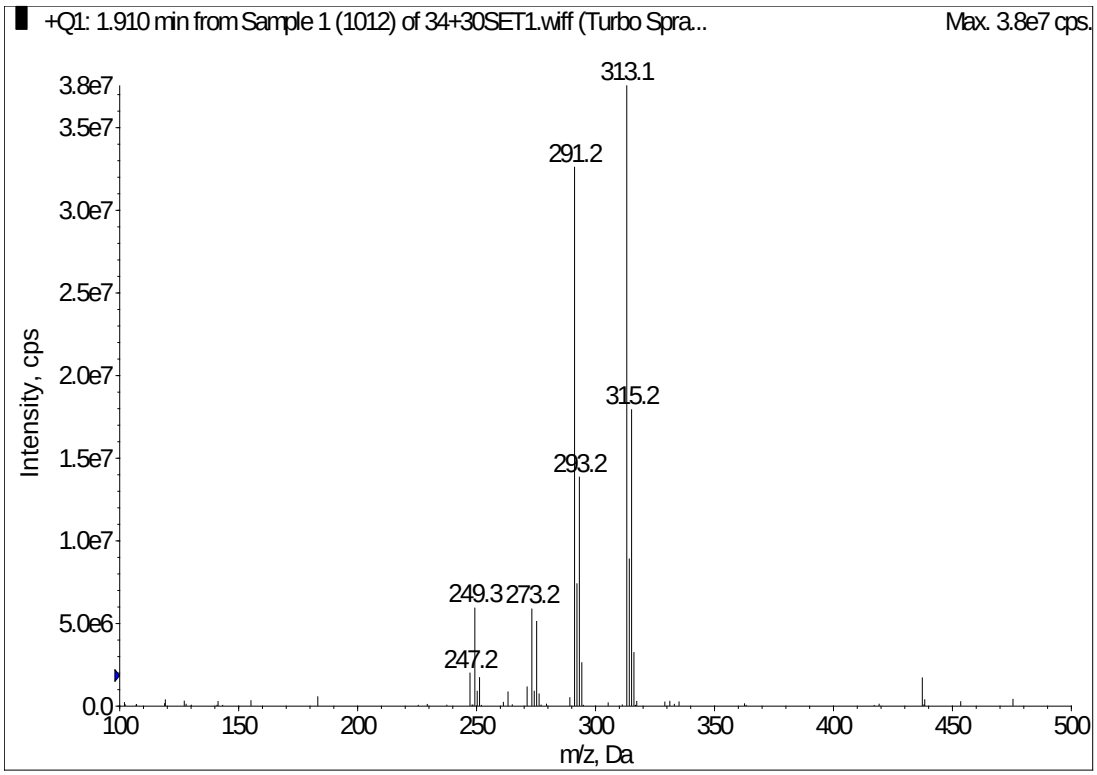

MS of compound **5dbf**