

The following information is included:

- A. Sample prep used to generate characterization data
- B. XRPD data
- C. Raman data
- D. DSC-TGA data

Numbers correlate with Tables 2 and 3 in the manuscript.

Sample prep used to generate characterization data

(1) carbamazepine:succinic acid cocrystal

Carbamazepine (1.8962 g) and succinic acid (0.4722 g) were dissolved in a mixture of 60 mL ethanol and 30 mL ethyl acetate with several minutes of sonication, followed by heating to 54 °C for approximately 45 minutes. The resulting clear solution was filtered through a 0.2 µm nylon filter into a clean glass jar and the jar was capped. White precipitate was observed after several minutes. The solution was allowed to evaporate slowly overnight, followed by fast evaporation for 2 days. The resulting dried solids were composed of blades and plates. The approximate yield was 1.9 g (80%).

(2) carbamazepine:benzoic acid cocrystal

472.3 mg of carbamazepine and 244.5 mg of benzoic acid were dissolved in 6 mL of chloroform with heating and stirring. The solution was allowed to cool and stand at room temperature for 24 hours. The solids that formed were isolated by vacuum filtration and air dried (180 mg, 25.1%yield).

(3) carbamazepine:ketoglutaric acid cocrystal (form A)

472 mg of carbamazepine and 292.4 mg of ketoglutaric acid were dissolved in 7 mL of ethyl acetate with heating and stirring. The solution was allowed to cool and stand at room temperature for 24 hours. The solids present were isolated by vacuum filtration and air dried (483 mg, 63.2%yield).

(4) carbamazepine:ketoglutaric acid cocrystal (form B)

A saturated solution of ketoglutaric acid in ethyl acetate was generated at room temperature. 5 mL of the supernatant was decanted into a clean vial. Aliquots of carbamazepine were added, with stirring at room temperature, until no additional CBZ would dissolve and solid CBZ remained in the vial. The vial was placed on a rotating wheel for 48 hours. The solid that formed was isolated by vacuum filtration, washed with cold ethyl acetate, and air dried.

(5) carbamazepine:maleic acid cocrystal

472.5 mg of carbamazepine and 116.8 mg of maleic acid were dissolved in 5 mL of acetonitrile with heating and stirring. The solution was allowed to cool to room temperature. Solids formed over the course of 4 hours. The solids were isolated by vacuum filtration and air dried (464 mg, 78.7%yield).

(6) carbamazepine:glutaric acid cocrystal

471.9 mg of carbamazepine and 132.5 mg of glutaric acid were dissolved in 5 mL of acetonitrile with heating and stirring. The solution was concentrated to ~3 mL and allowed to stand at room temperature for 24 hours. The solids that formed were isolated by vacuum filtration and air dried (486 mg, 80.4%yield).

(7) carbamazepine:malonic acid cocrystal (form A)

472.3 mg of carbamazepine and 104.1 mg of malonic acid were dissolved in 4 mL of acetonitrile with heating and stirring. The solution was allowed to cool and stand at room temperature for 24 hours. The solids present were isolated by vacuum filtration and air dried (389 mg, 67.5%yield).

(8) carbamazepine:malonic acid cocrystal (form B)

Form B of the carbamazepine:malonic acid cocrystal was prepared in bulk by slurring 1.0gm (4.23mmol) of carbamazepine in a 3.44 molal malonic acid aqueous solution for 24 hours.

(9) carbamazepine:oxalic acid cocrystal

472.6 mg of carbamazepine and 90.5 mg of oxalic acid were dissolved in 7 mL of ethyl acetate with heating and stirring. The solution was allowed to cool to room temperature and slowly evaporate to a volume of ~4 mL. The solids present were isolated by vacuum filtration and air dried (441 mg, 78.3% yield).

(12) carbamazepine:adipic acid cocrystal (form C)

472.1 mg of carbamazepine and 146.2 mg of adipic acid were dissolved in 5 mL of acetonitrile with heating and stirring. The solution was allowed to cool and stand at room temperature for 24 hours. The solids that formed were isolated by vacuum filtration and air dried (530 mg, 85.7%yield).

(14) carbamazepine:(+)-camphoric acid cocrystal (form A)

472.1 mg of carbamazepine and 400.5 mg of (+)-camphoric acid were dissolved in 5 mL of acetonitrile with heating and stirring. The solution was concentrated to ~ 1mL and sonicated for 2 seconds with a 1/8" sonicating probe at low power. The solids that formed were isolated by vacuum filtration and air dried (822 mg, 94.2%yield).

(15) carbamazepine:4-hydroxybenzoic acid cocrystal (form A)

472.4 mg of carbamazepine and 276.3 mg of 4-hydroxybenzoic acid were dissolved in 5 mL of acetonitrile with heating and stirring. The solution was concentrated to ~3 mL and allowed to stand at room temperature for 24 hours. The solids that formed were isolated by vacuum filtration and air dried (625 mg, 83.5%yield).

(16) carbamazepine:4-hydroxybenzoic acid cocrystal (form B)

472.3 mg of carbamazepine and 139.5 mg of 4-hydroxybenzoic acid were dissolved in 15 mL of a 1:1 methanol:water solution with heating and stirring. The solution was allowed to cool and stand at room temperature for 24 hours. The solids that formed were isolated by vacuum filtration and air dried (425 mg, 70%yield)

(17) carbamazepine:4-hydroxybenzoic acid cocrystal (form C)

The 1 carbamazepine:4-hydroxybenzoic acid (form C) cocrystal polymorph was obtained from experiments that were intended to form a ternary cocrystal of carbamazepine:4-hydroxybenzoic acid

and caffeine. Very good quality needle shaped crystal were formed from the ethanolic solution containing 1:10:1(CBZ:4HBA:Caffeine) molar ratio of respective components.

(18) carbamazepine:salicylic acid cocrystal

472.3 mg of carbamazepine and 276.4 mg of salicylic acid were dissolved in 6 mL of acetonitrile with heating and stirring. The solution was allowed to cool and stand at room temperature for 24 hours. The solids that formed were isolated by vacuum filtration and air dried (656 mg, 87.6%yield).

(19) carbamazepine:1-hydroxy-2-naphthoic acid cocrystal

472.2 mg of carbamazepine and 376.2 mg of 1-hydroxy-2-naphthoic acid were dissolved in 8 mL of acetonitrile with heating and stirring. The solution was allowed to cool and stand at room temperature for 24 hours. The solids that formed were isolated by vacuum filtration and air dried (705 mg, 83.1%yield).

(20) carbamazepine:DL-tartaric acid cocrystal (form A)

944.4 mg of carbamazepine and 600.4mg of DL-tartaric acid were dissolved 4 mL of methanol with heating and stirring. The volume was reduced to ~2 mL. 6 mL of acetonitrile was added and the subsequent solution was further reduced in volume to 4 mL. The solution was rapidly cooled on ice and sonicated for 10 seconds at low power with a 1/8" sonication probe, causing the formation of solids. The solids were isolated by vacuum filtration and air dried (880 mg, 57.0%yield).

(21) carbamazepine:DL-tartaric acid cocrystal (form B)

A saturated solution of L-tartaric acid in 2:1 ethanol:water was generated at 70° C. Aliquots of carbamazepine were added, with stirring at 70° C, until no additional CBZ would dissolve. The clear solution was allowed to cool to room temperature. The solid that formed after 24 hours was isolated by vacuum filtration, washed with ethanol, and air dried.

(22) carbamazepine:L-tartaric acid cocrystal

A saturated solution of L-tartaric acid in acetonitrile was generated at room temperature. 5 mL of the supernatant was decanted into a clean vial. Aliquots of carbamazepine were added, with stirring at room temperature, until no additional CBZ would dissolve and solid CBZ remained in the vial. The vial was placed on a rotating wheel for 48 hours. The solid that formed was isolated by vacuum filtration, washed with cold acetonitrile, and air dried.

(23) carbamazepine:glycolic acid cocrystal

A saturated solution of glycolic acid in acetonitrile was generated at room temperature. 5 mL of the supernatant was decanted into a clean vial. Aliquots of carbamazepine were added, with stirring at room temperature, until no additional CBZ would dissolve and solid CBZ remained in the vial. The vial was placed on a rotating wheel for 48 hours. The solid that formed was isolated by vacuum filtration, washed with cold acetonitrile, and air dried.

(24) carbamazepine:fumaric acid cocrystal (form A)

To 20ml of saturated aqueous solution of fumaric acid 100mg of CBZ was added. The slurry was stirred for 12 hours at room temperature, resulting solid was filtered and air dried.

(25) carbamazepine:fumaric acid cocrystal (form B)

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To 5ml of saturated or near saturated ethanolic solution of fumaric acid 200mg of CBZ was added. The slurry was stirred at room temperature and cocrystal was precipitated in about 15 minutes. The resulting solid was filtered and air dried.

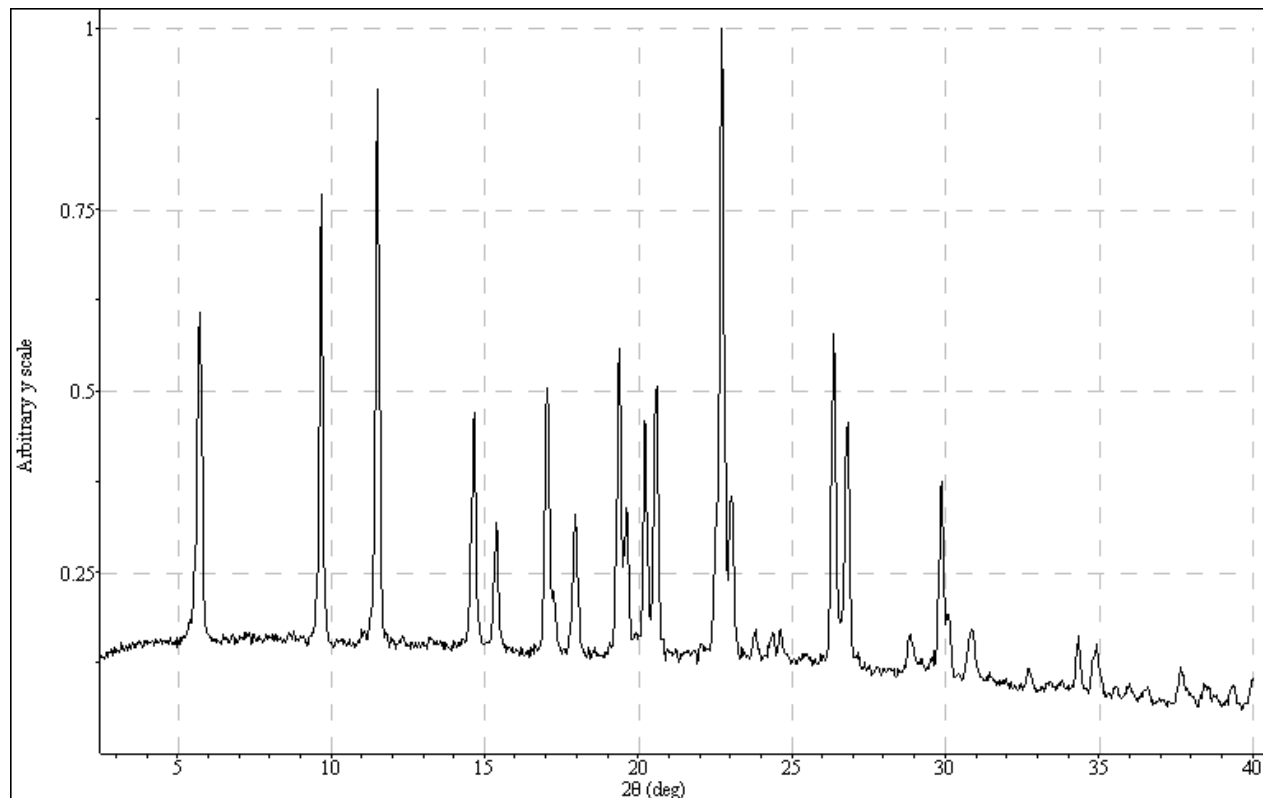
(26) carbamazepine:DL-malic acid cocrystal

A saturated solution of DL-malic acid in acetonitrile was generated at room temperature. 5 mL of the supernatant was decanted into a clean vial. Aliquots of carbamazepine were added, with stirring at room temperature, until no additional CBZ would dissolve and solid CBZ remained in the vial. The vial was placed on a rotating wheel for 48 hours. The solid that formed was isolated by vacuum filtration, washed with cold acetonitrile, and air dried.

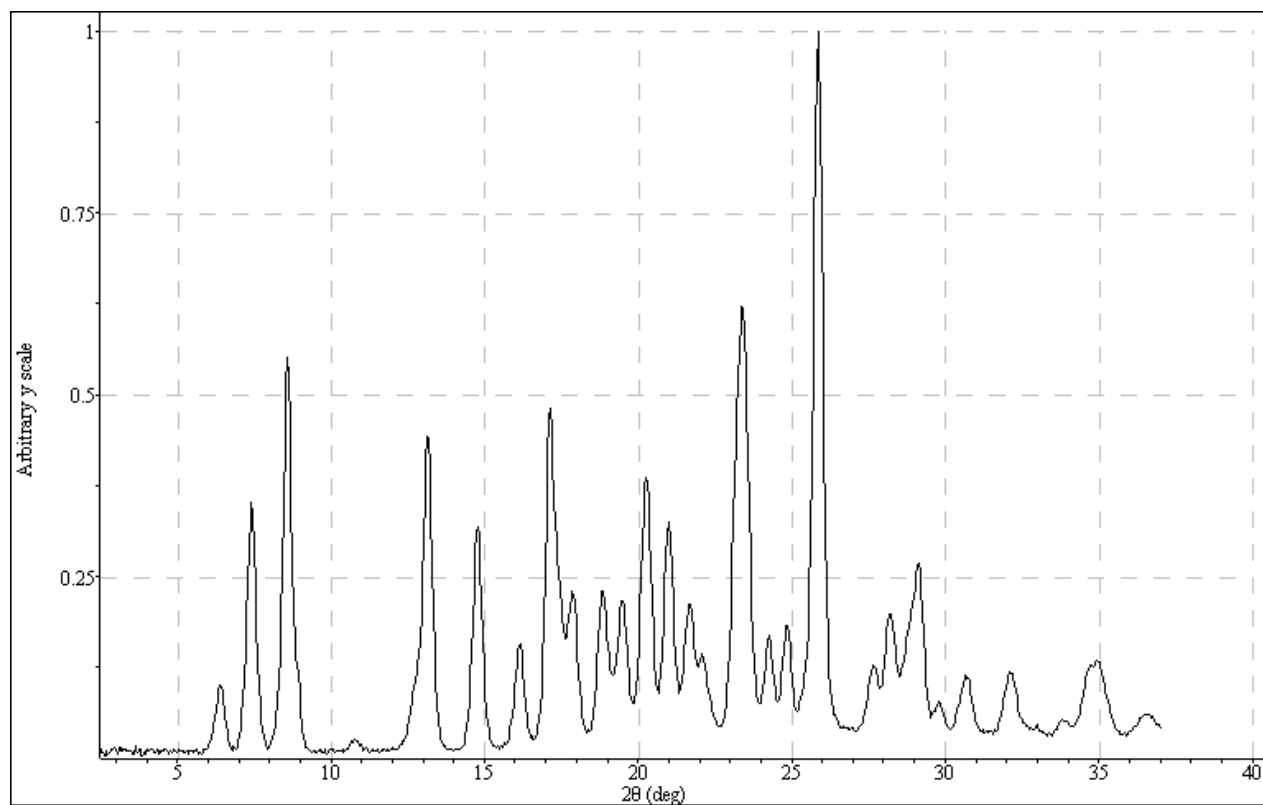
(27) carbamazepine: L-malic acid cocrystal

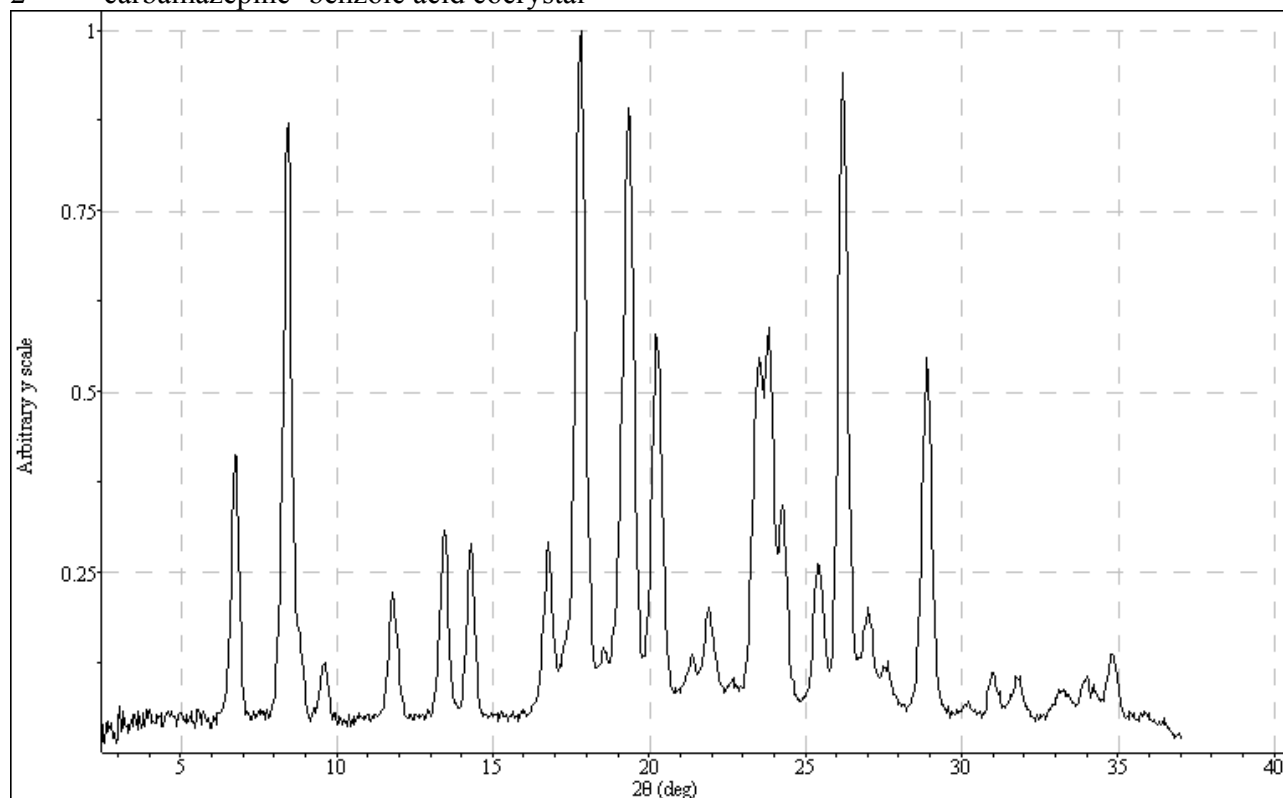
A saturated solution of L-malic acid in acetonitrile was generated at room temperature. 5 mL of the supernatant was decanted into a clean vial. Aliquots of carbamazepine were added, with stirring at room temperature, until no additional CBZ would dissolve and solid CBZ remained in the vial. The vial was placed on a rotating wheel for 48 hours. The solid that formed was isolated by vacuum filtration, washed with cold acetonitrile, and air dried.

XRPD data

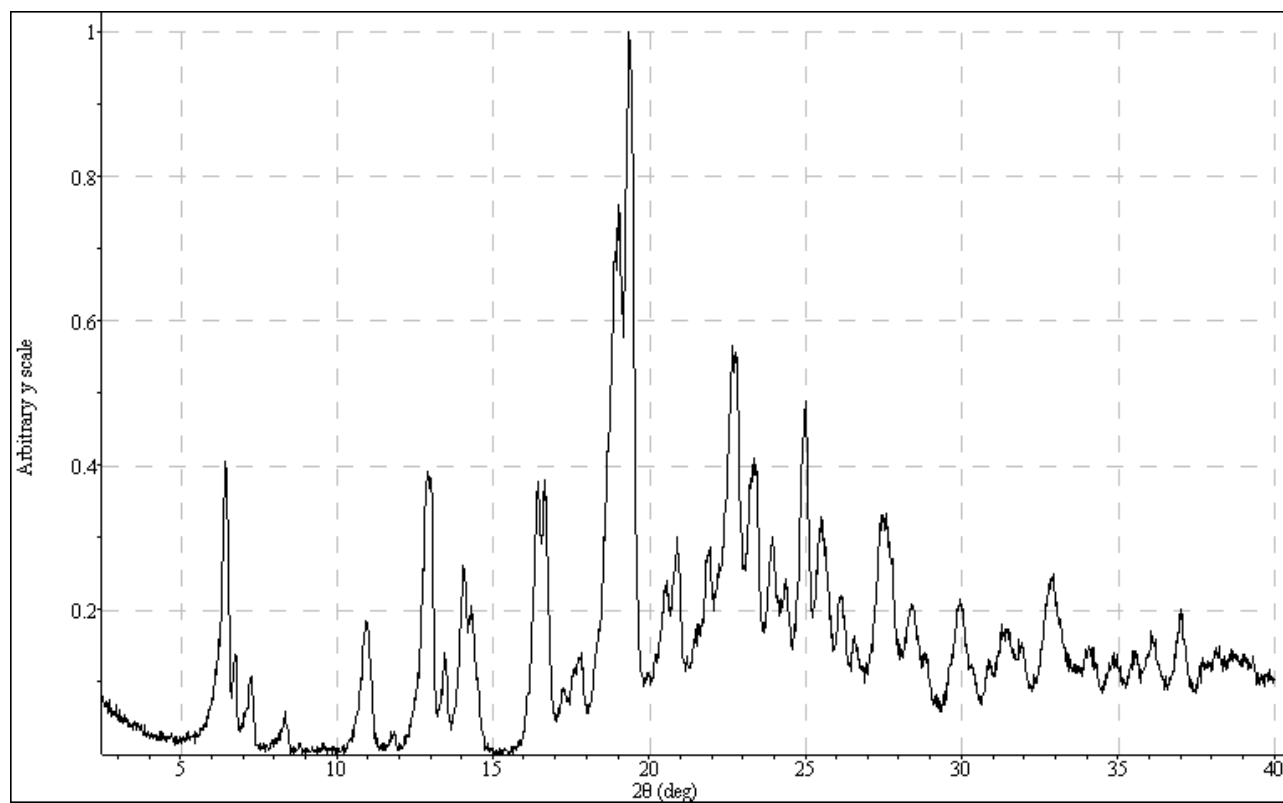


1 carbamazepine-succinic acid cocrystal

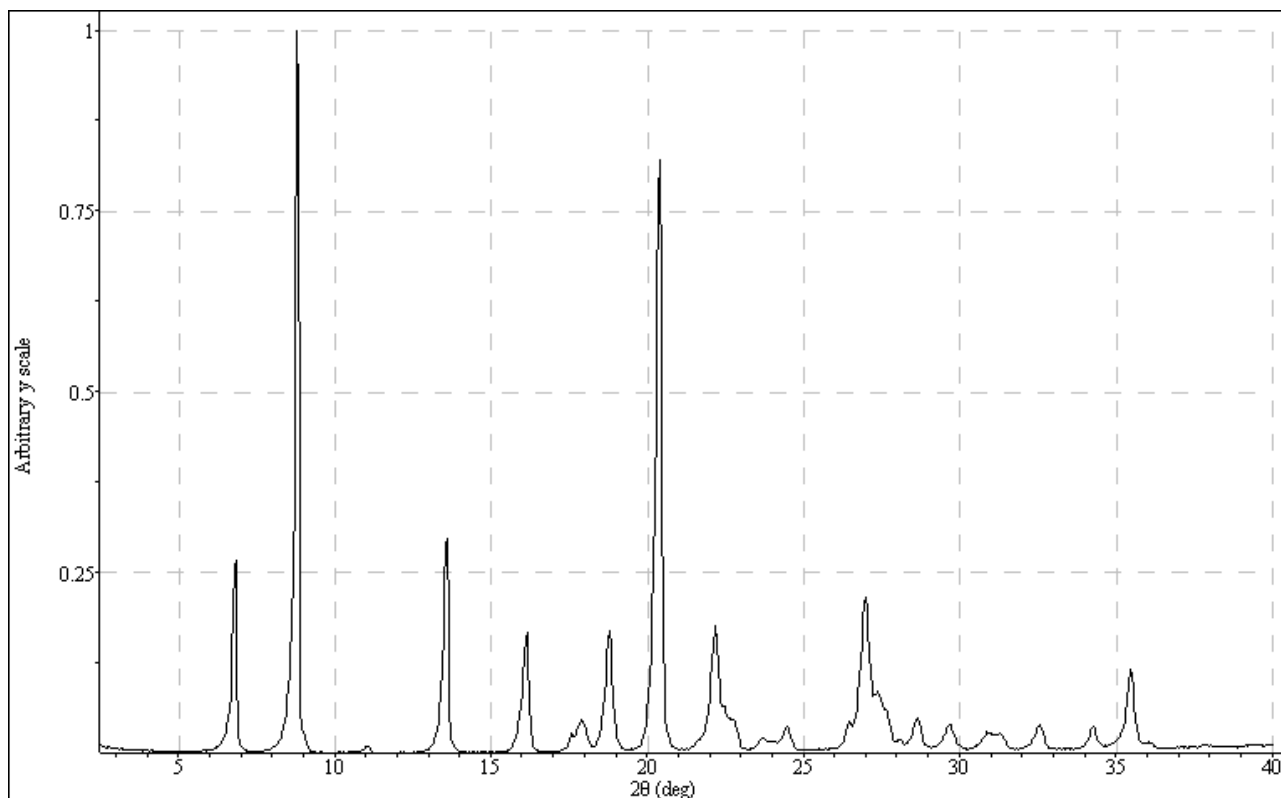




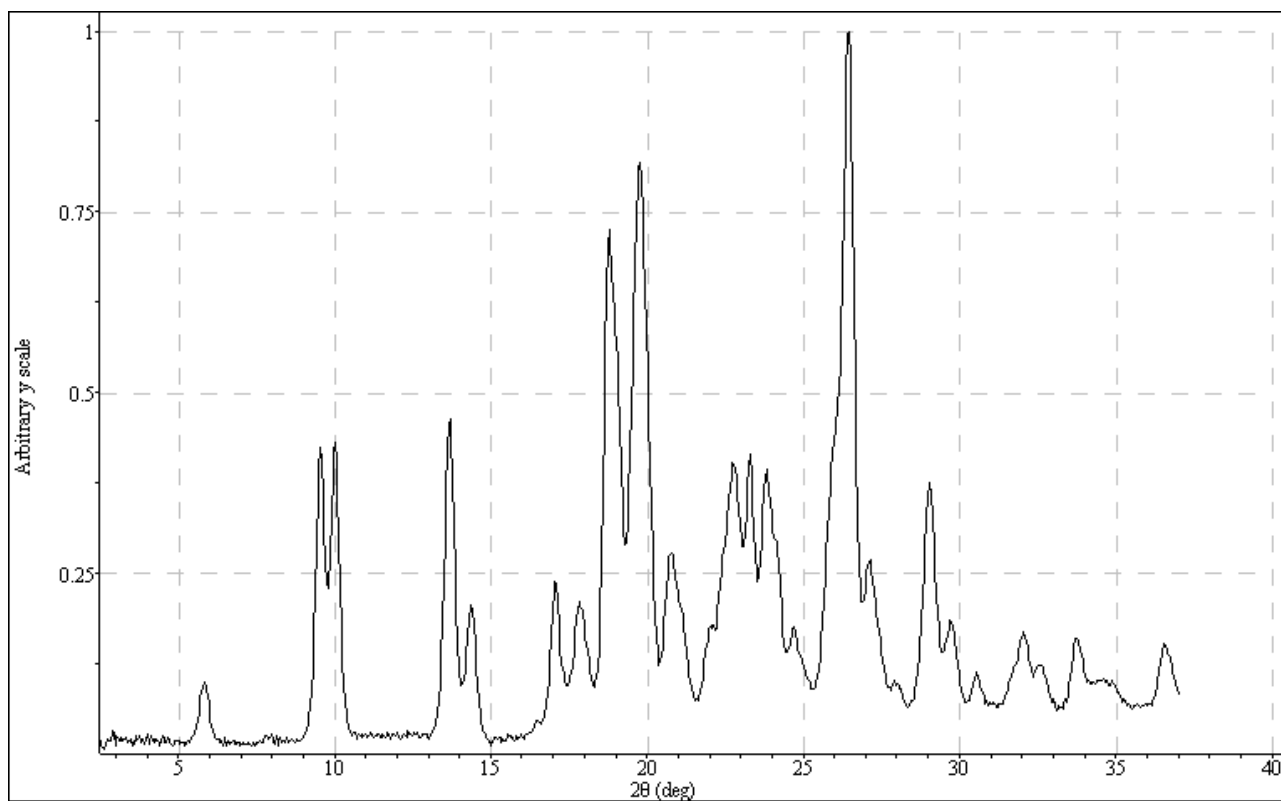
3 carbamazepine- ketoglutaric acid cocrystal, form A



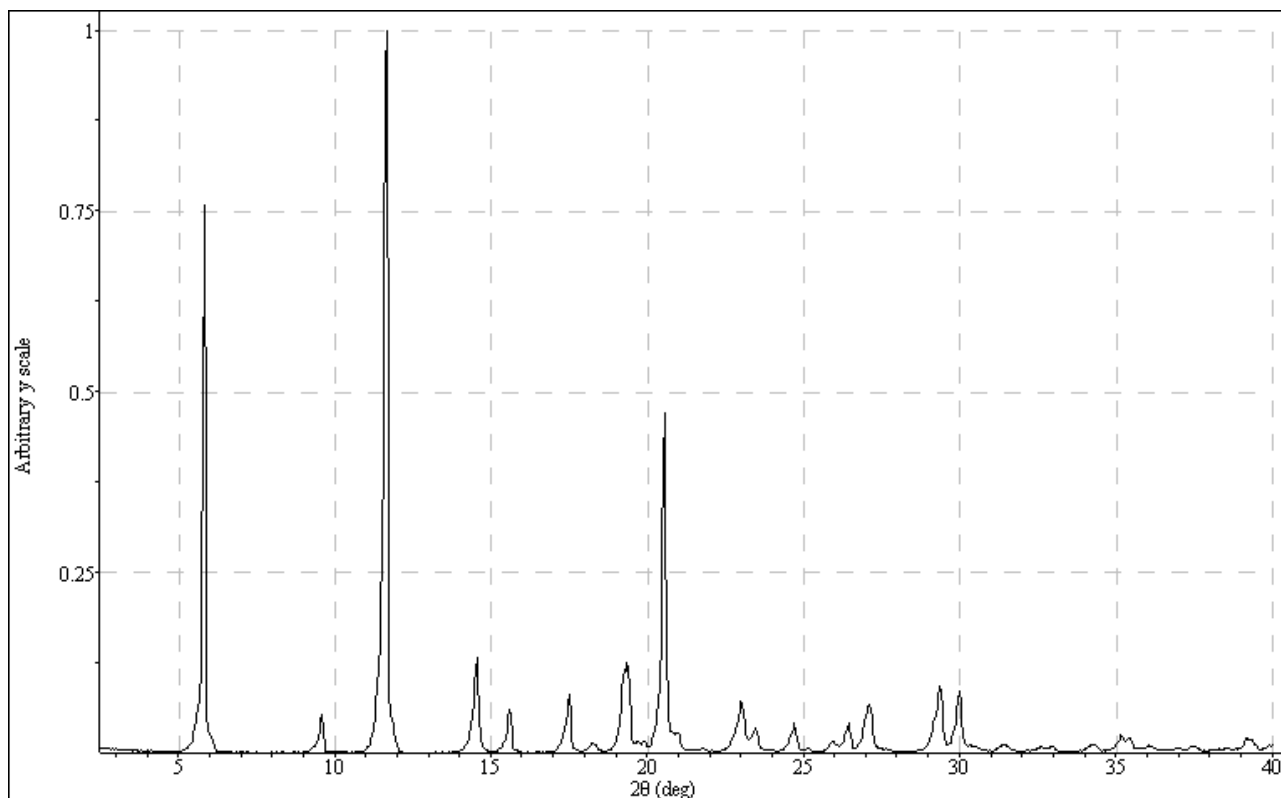
4 carbamazepine- ketoglutaric acid cocrystal, form B



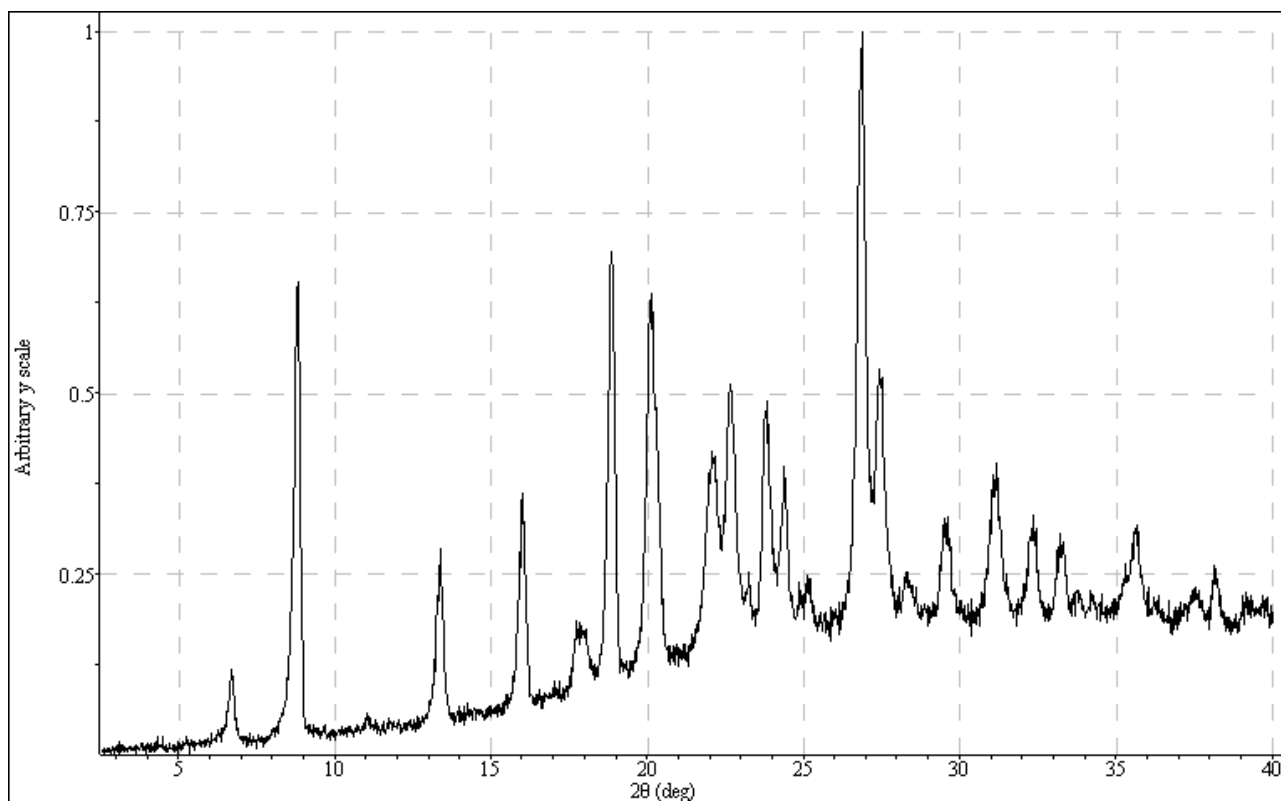
5 carbamazepine- maleic acid cocrystal



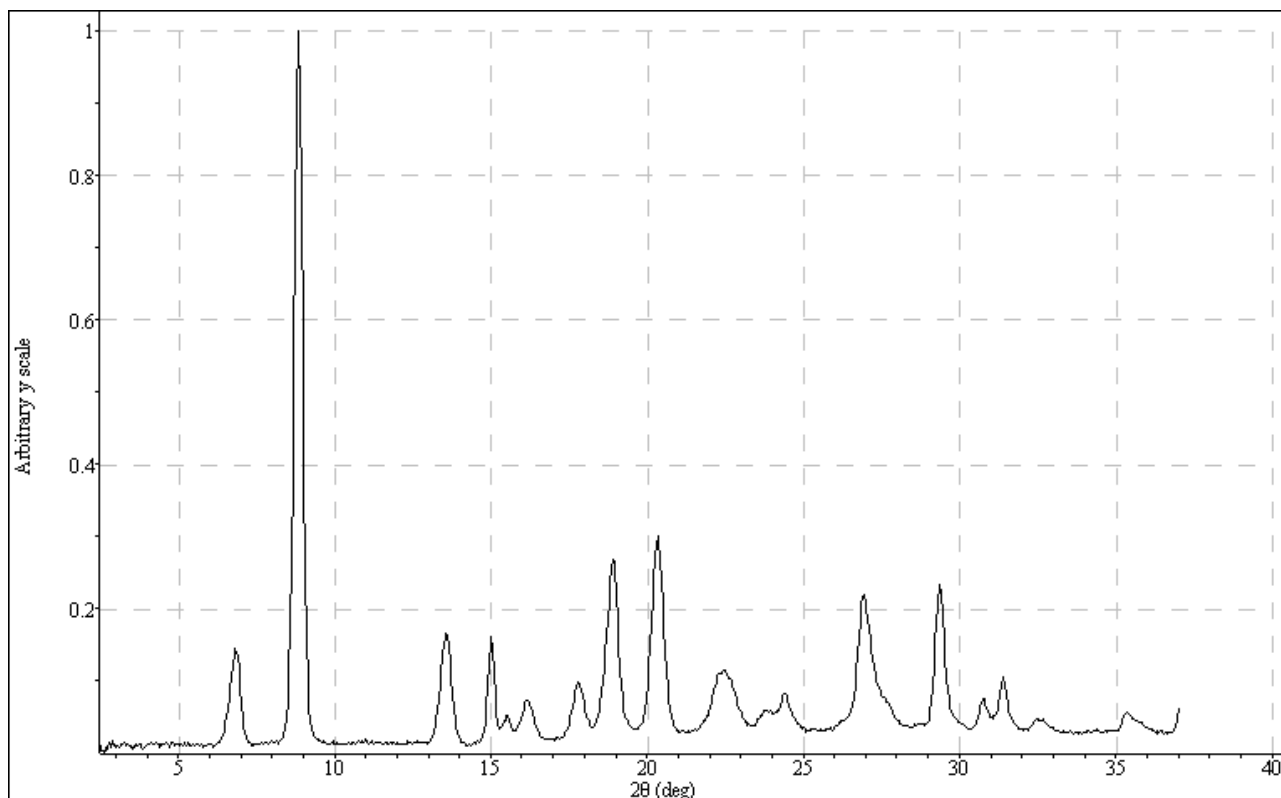
6 carbamazepine- glutaric acid cocrystal



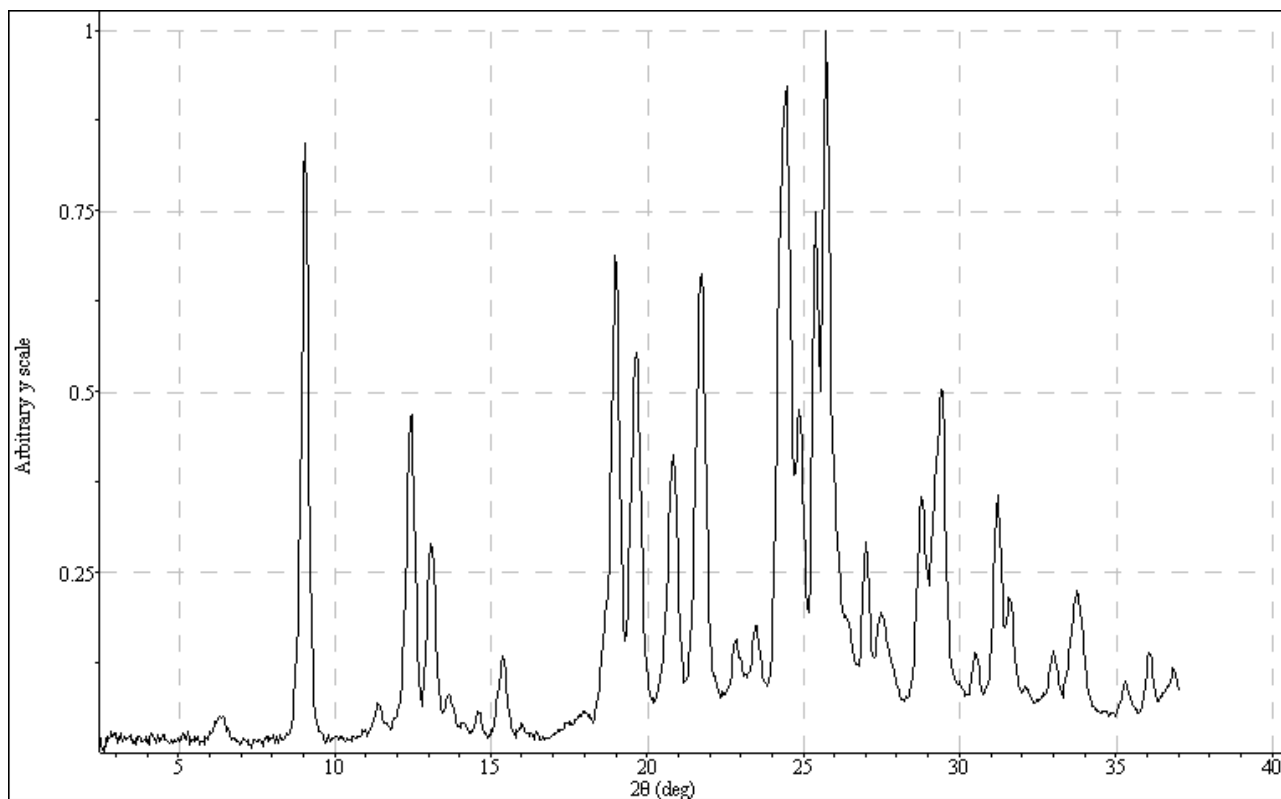
7 carbamazepine- malonic acid cocrystal, form A



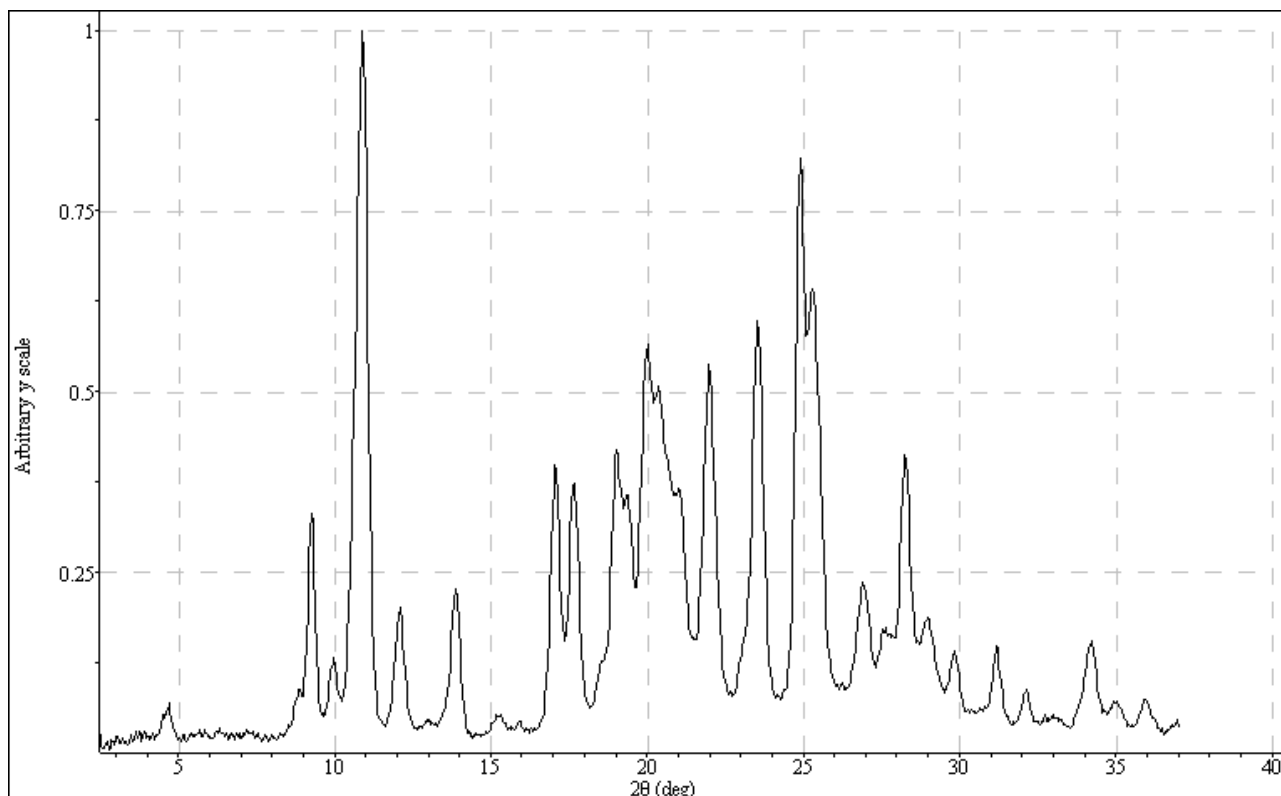
8 carbamazepine- malonic acid cocrystal, form B



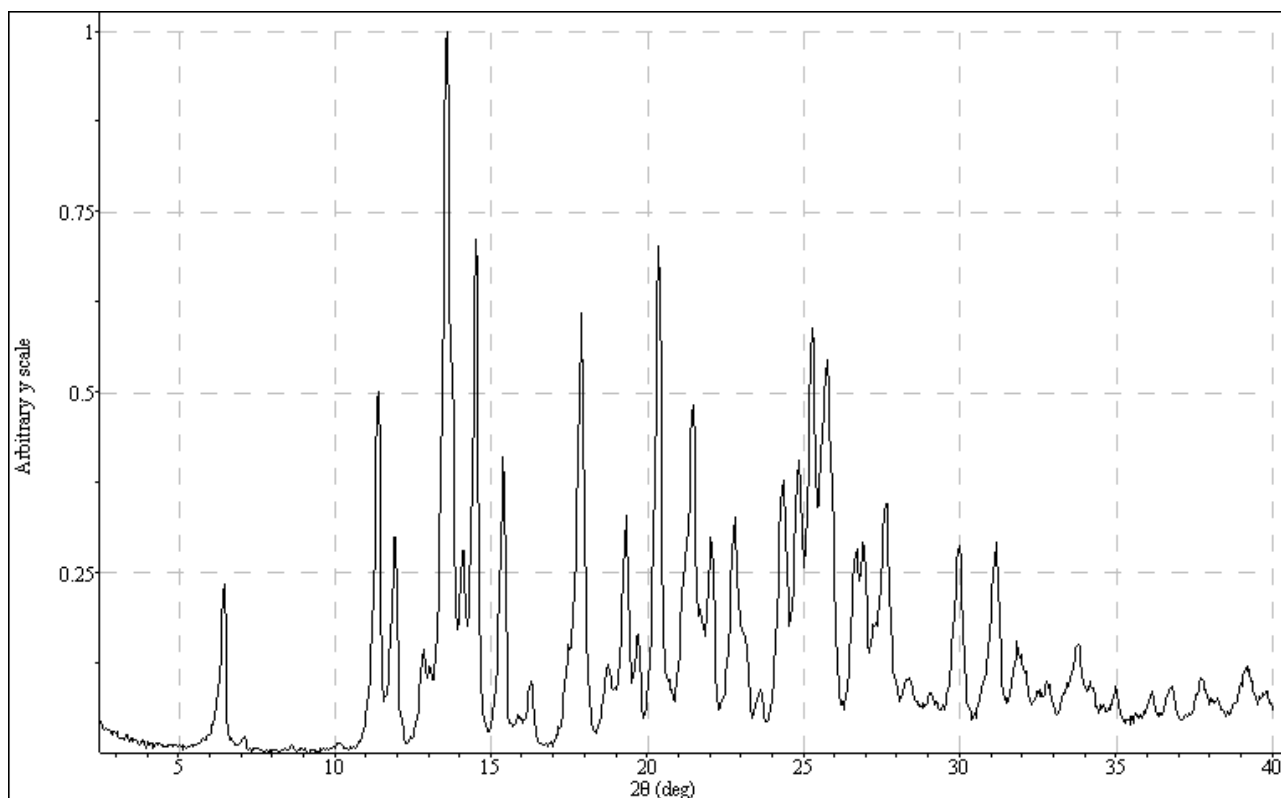
9 carbamazepine- oxalic acid cocrystal



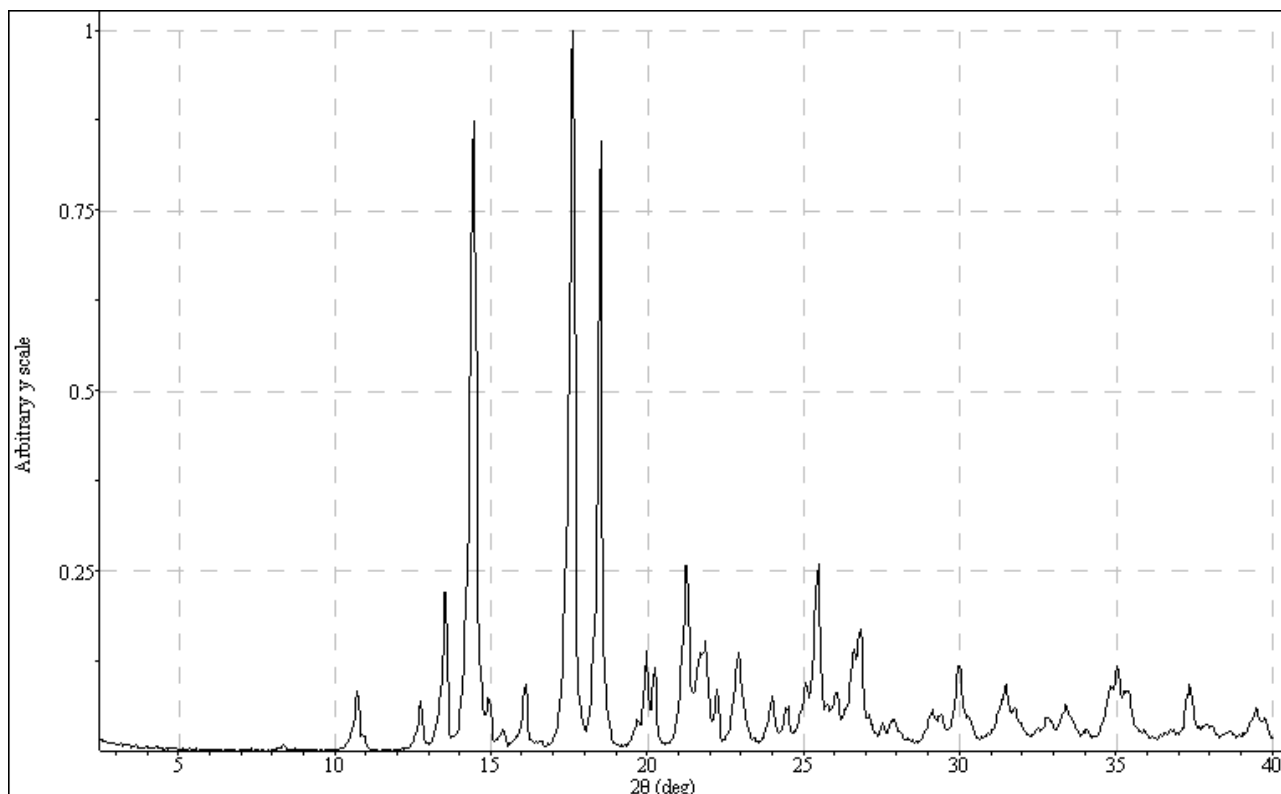
10 carbamazepine- adipic acid cocrystal, form A



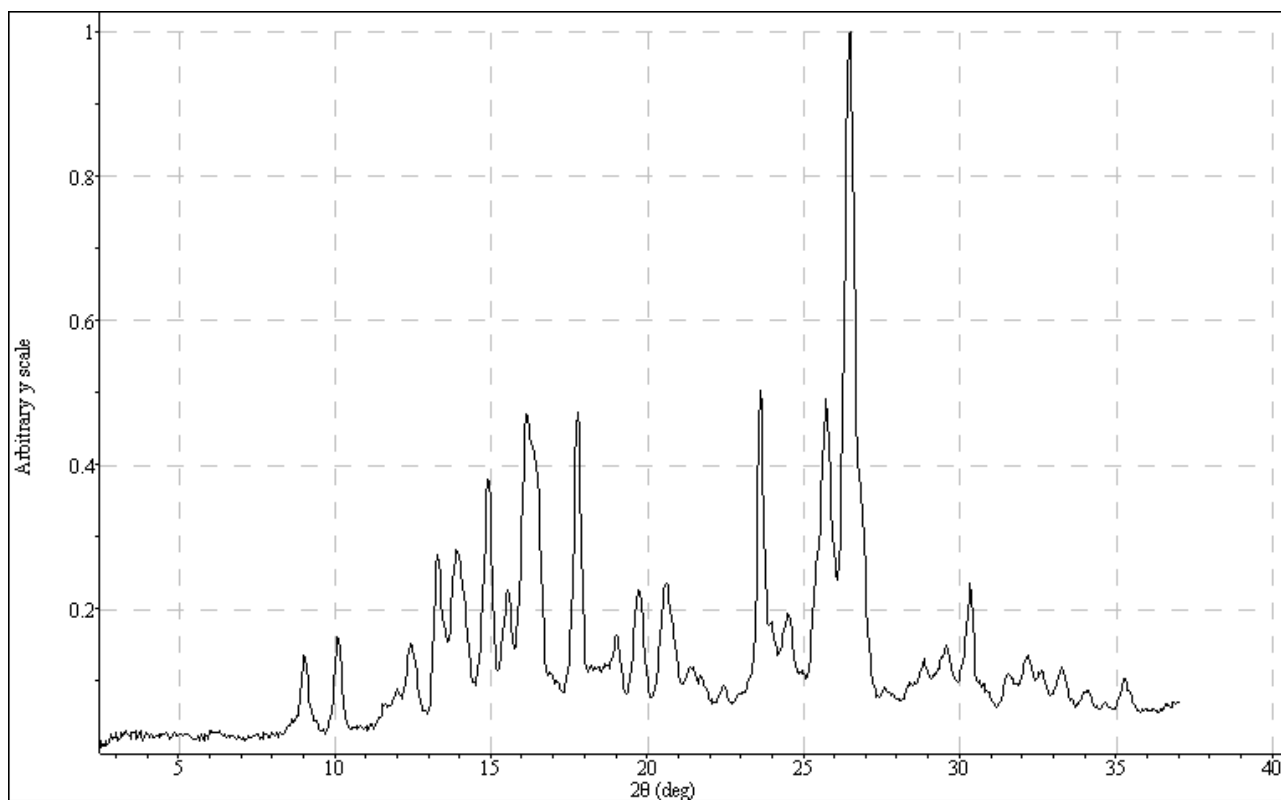
11 carbamazepine- adipic acid cocrystal, form B



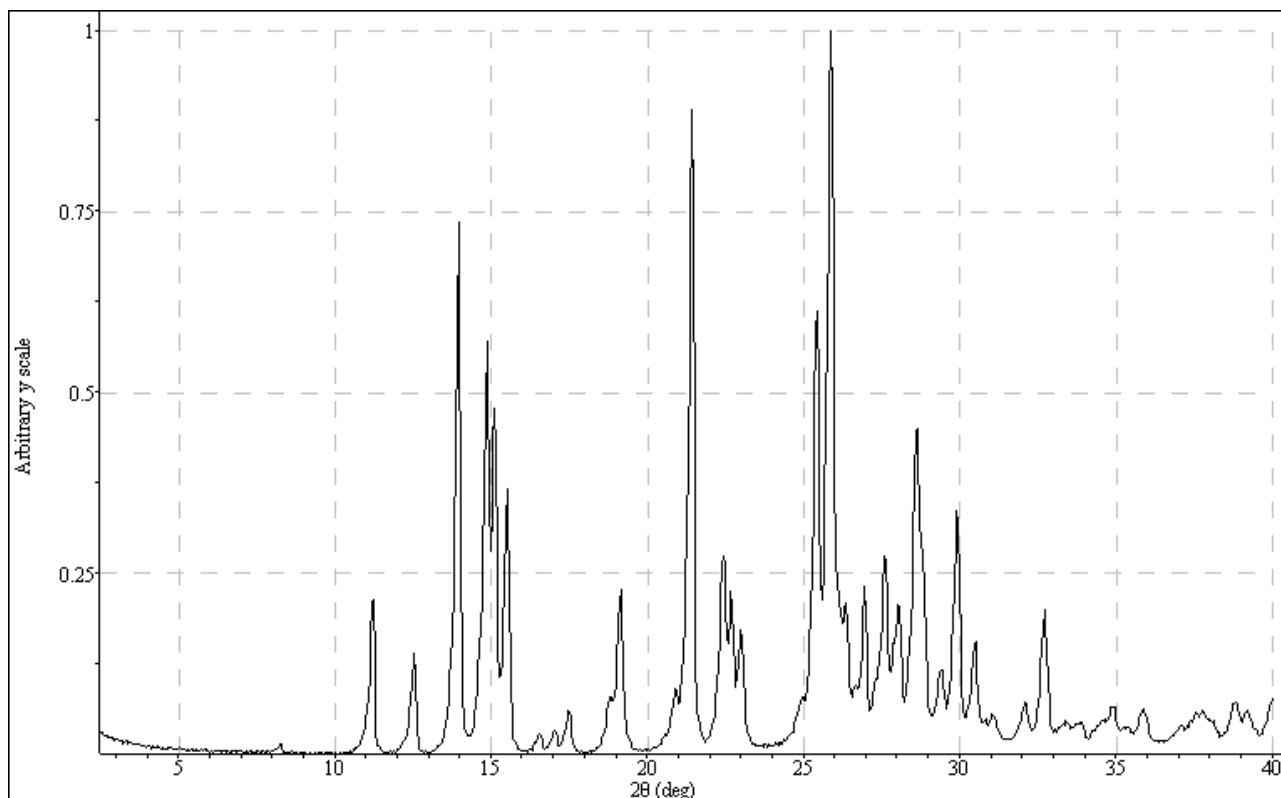
12 carbamazepine- adipic acid cocrystal, form C



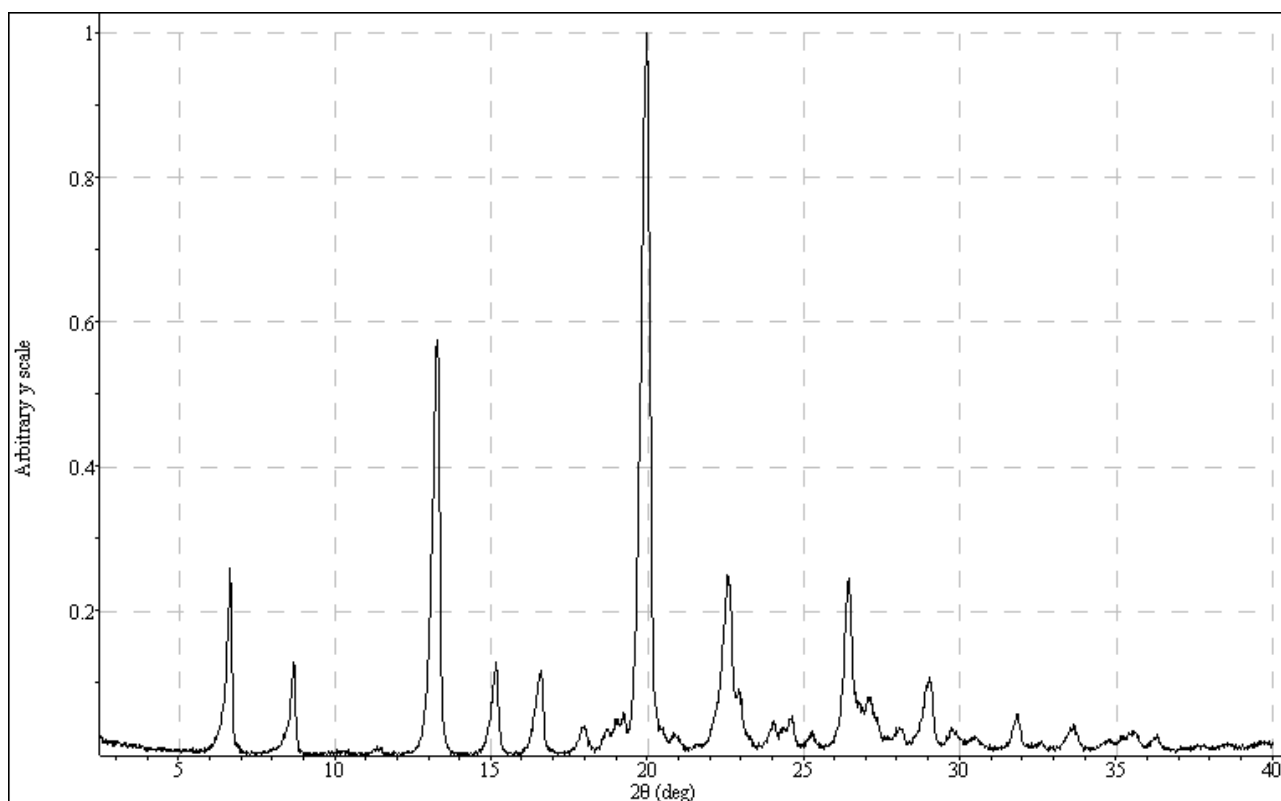
13 carbamazepine-(+)-camphoric acid cocrystal, form B



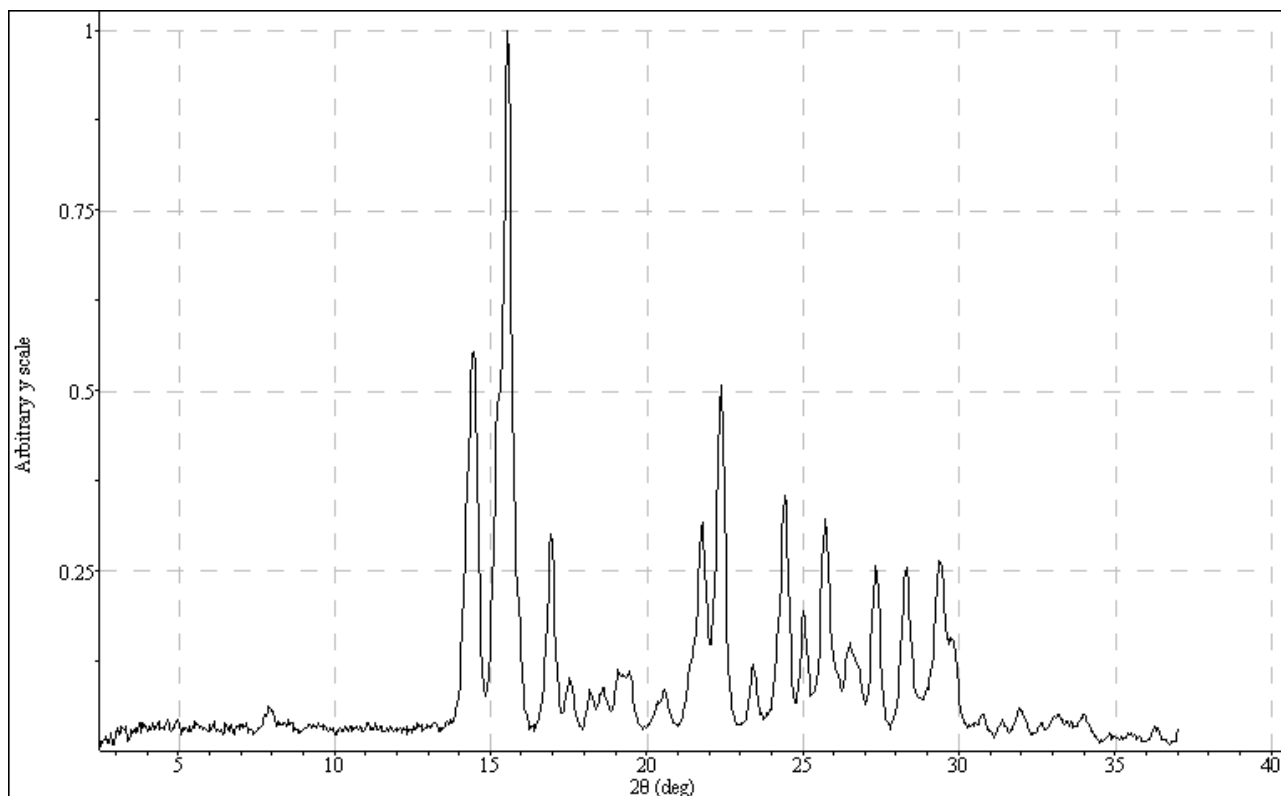
14 carbamazepine-(+)-camphoric acid cocrystal, form A



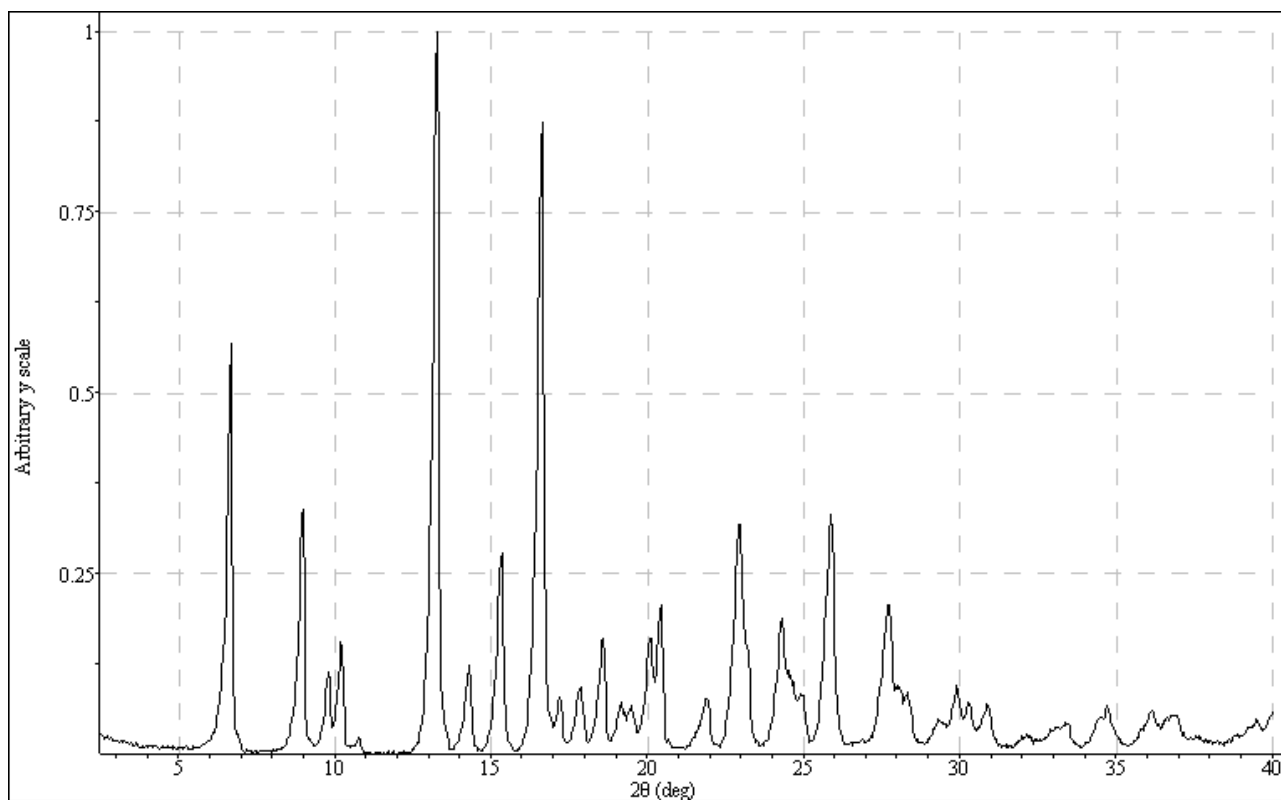
15 carbamazepine- 4-hydroxybenzoic acid cocrystal, form A



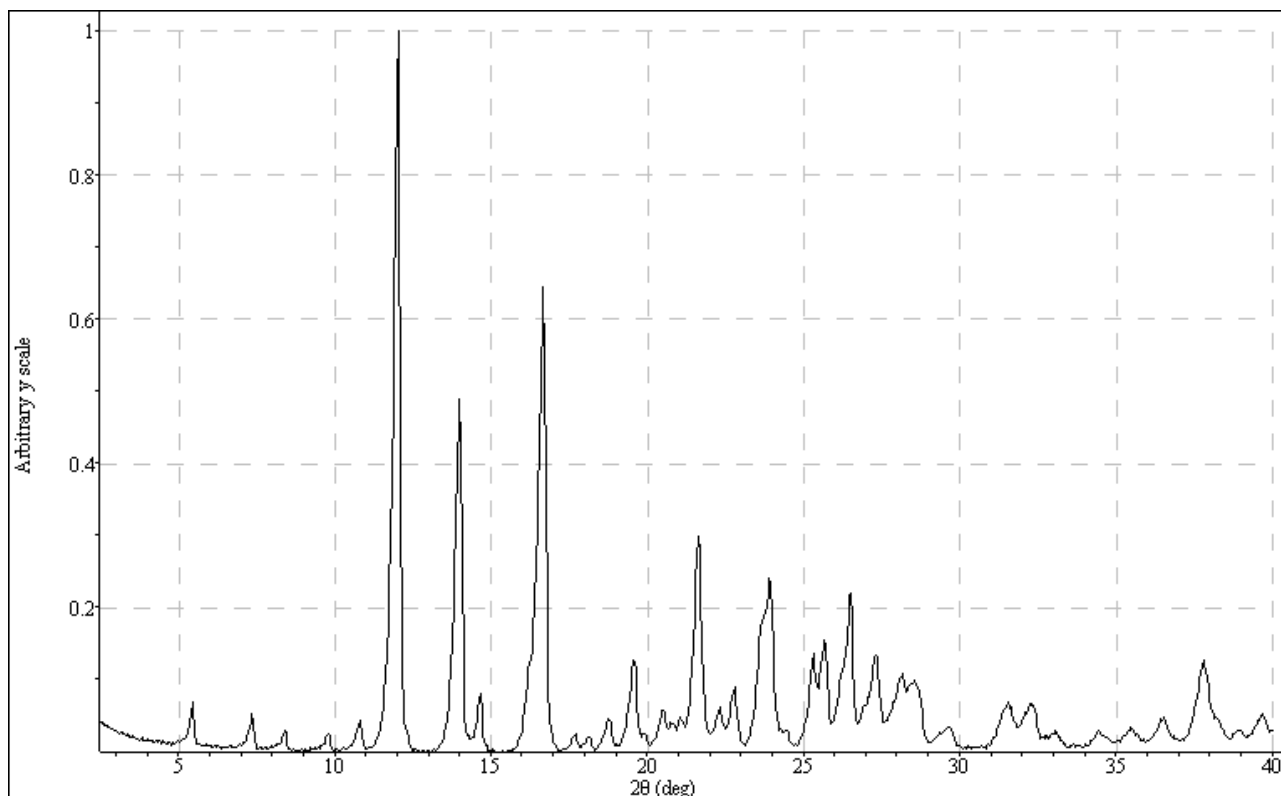
16 carbamazepine- 4-hydroxybenzoic acid cocrystal, form B



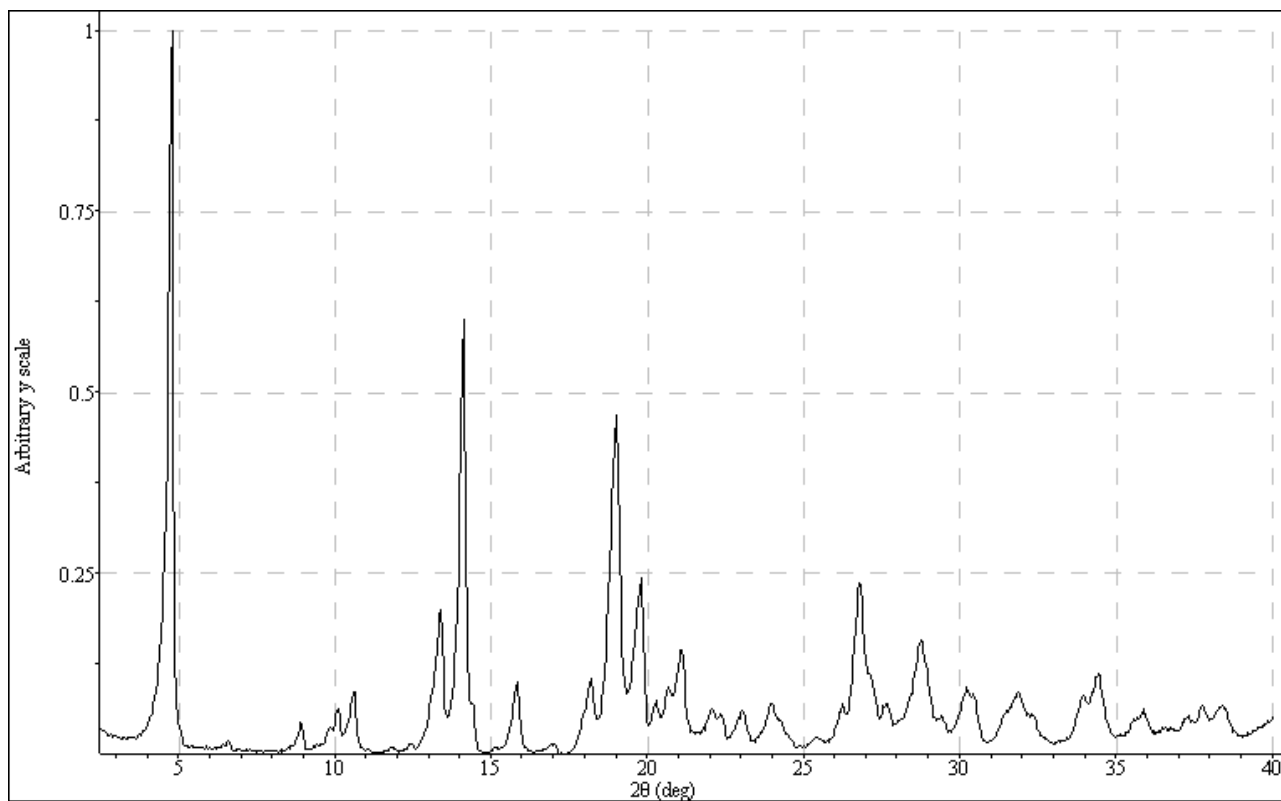
17 carbamazepine- 4-hydroxybenzoic acid cocrystal, form C



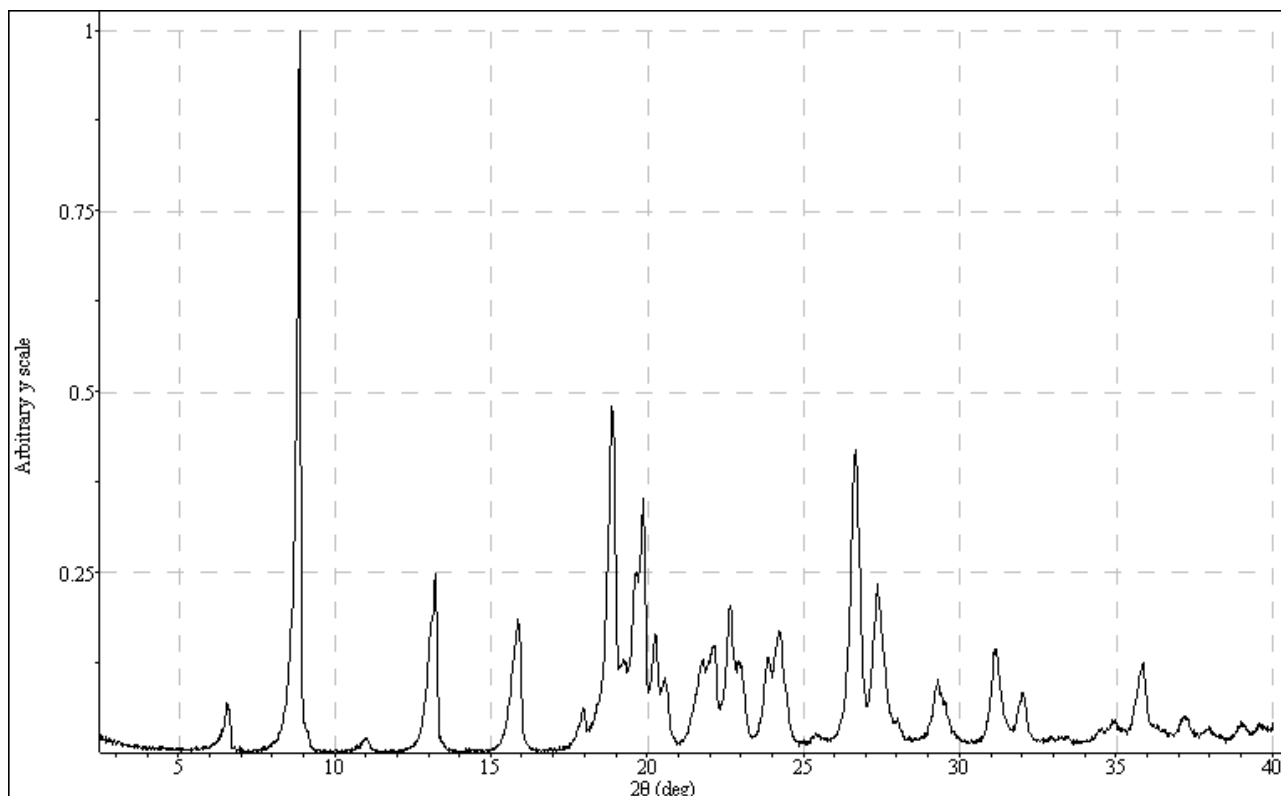
18 carbamazepine salicylic - acid cocrystal



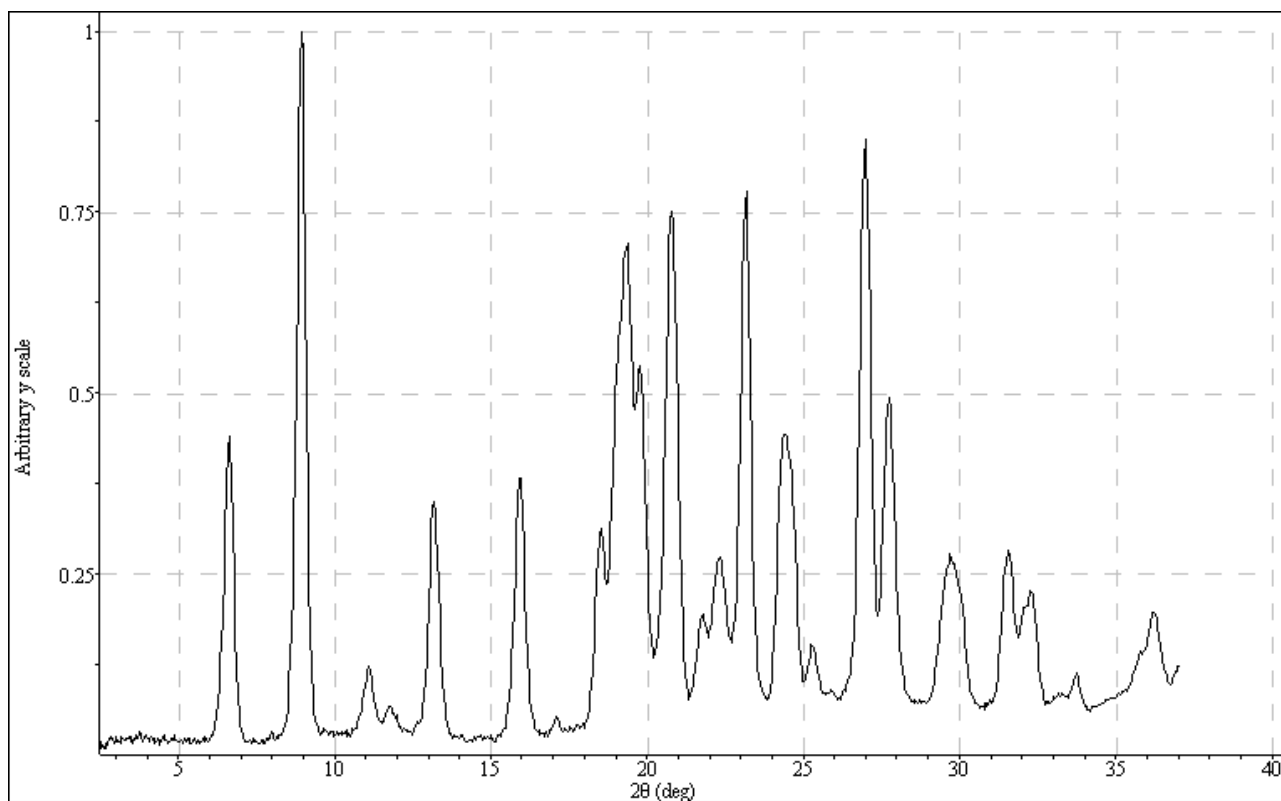
19 carbamazepine- 1-hydroxy-2-naphthoic acid cocrystal



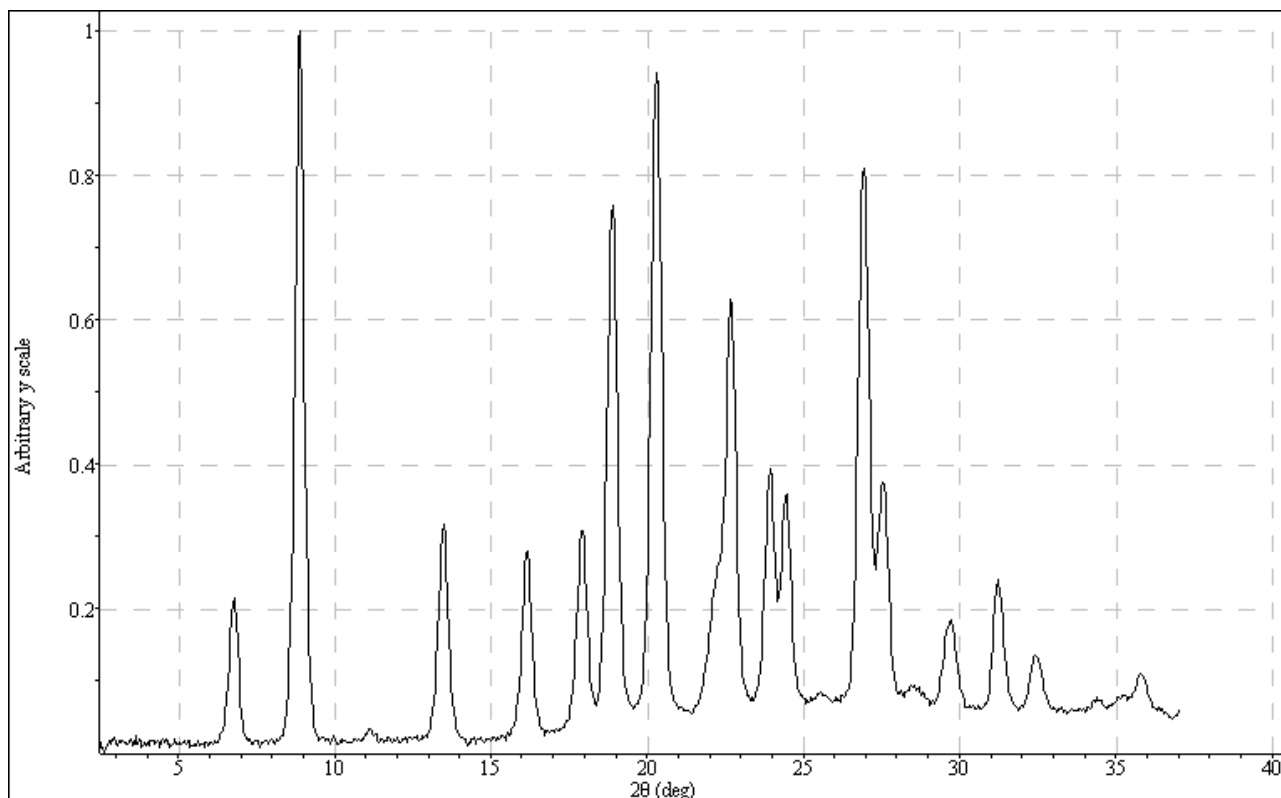
20 carbamazepine- DL-tartaric acid cocrystal, form A



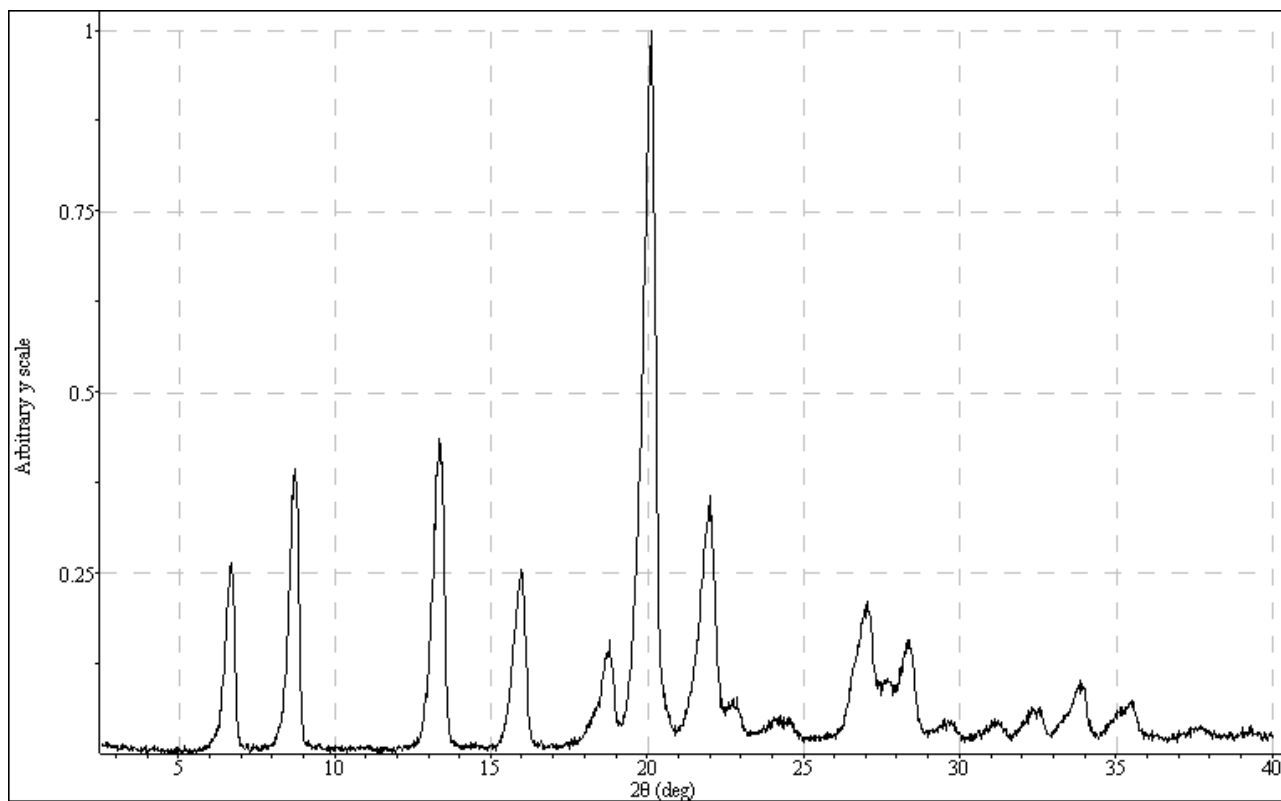
21 carbamazepine- DL-tartaric acid cocrystal, form B



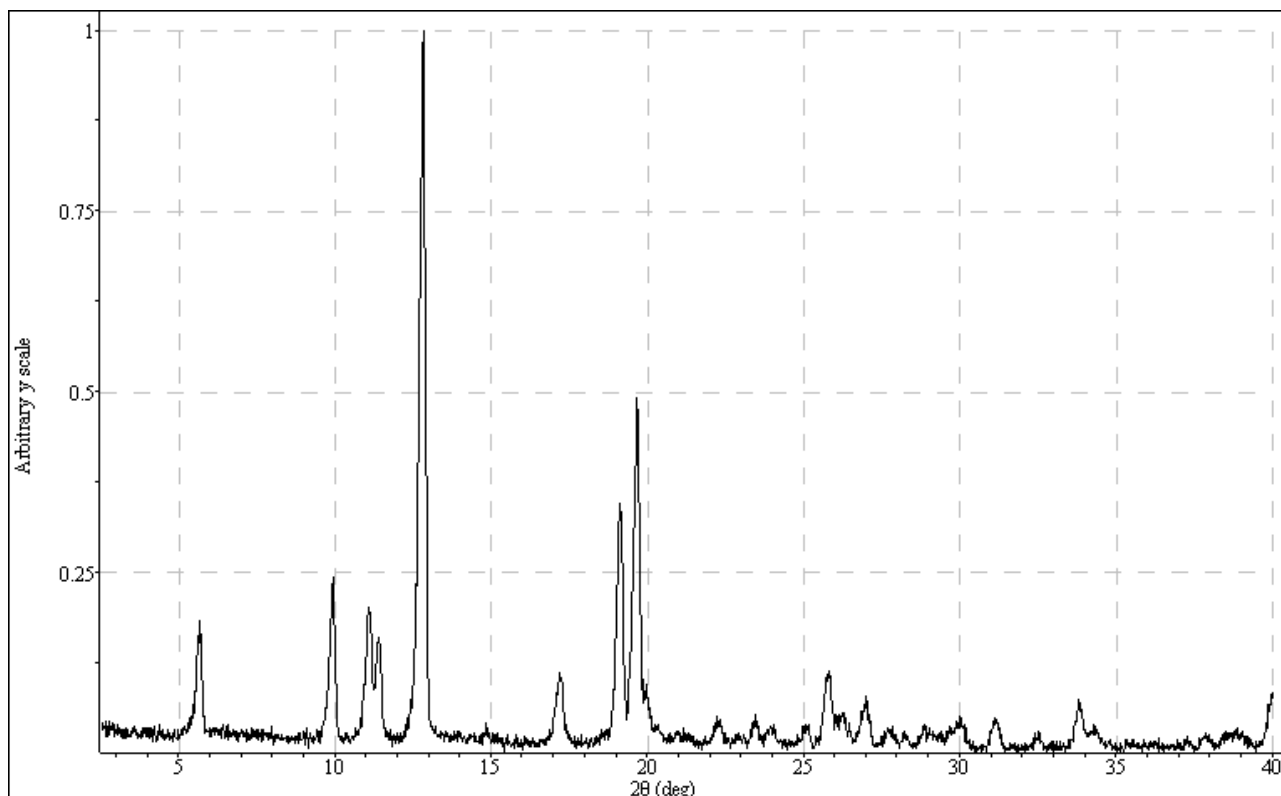
22 carbamazepine- L-tartaric acid cocrystal



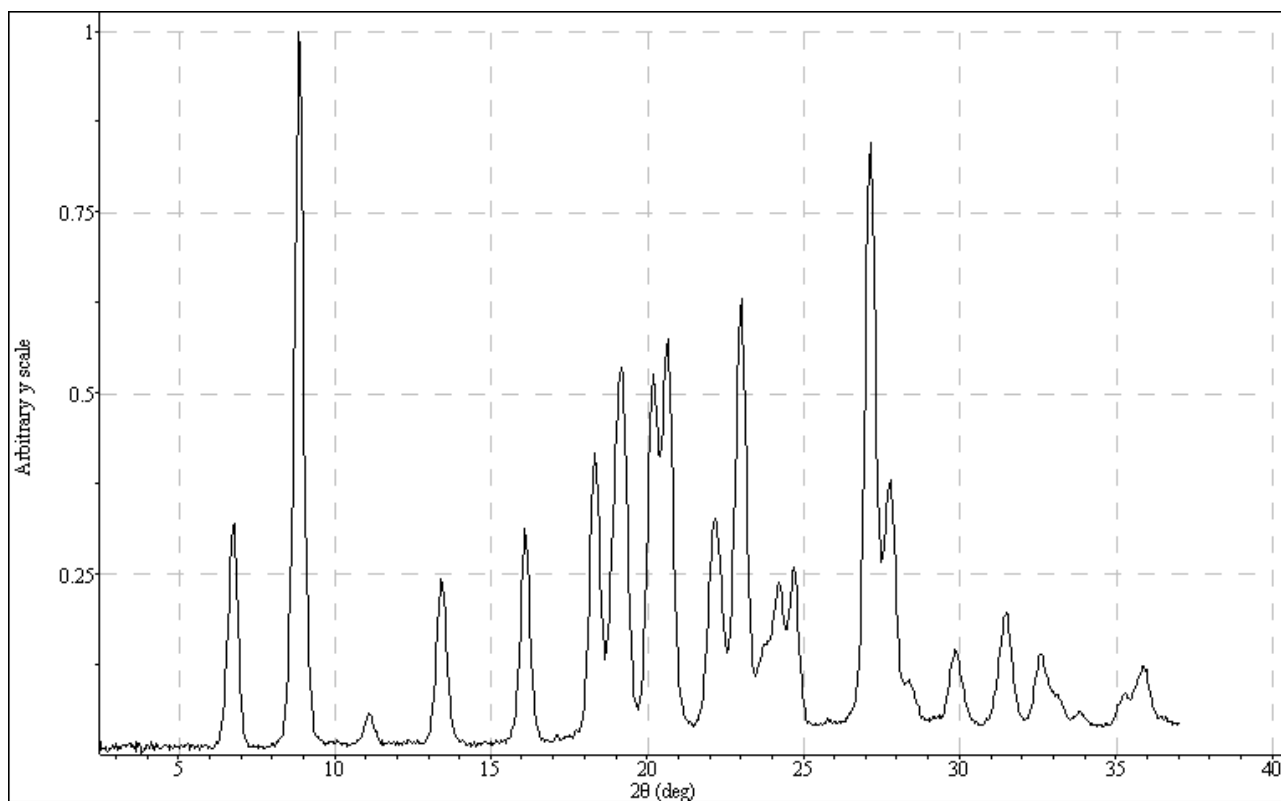
23 carbamazepine- glycolic acid cocrystal



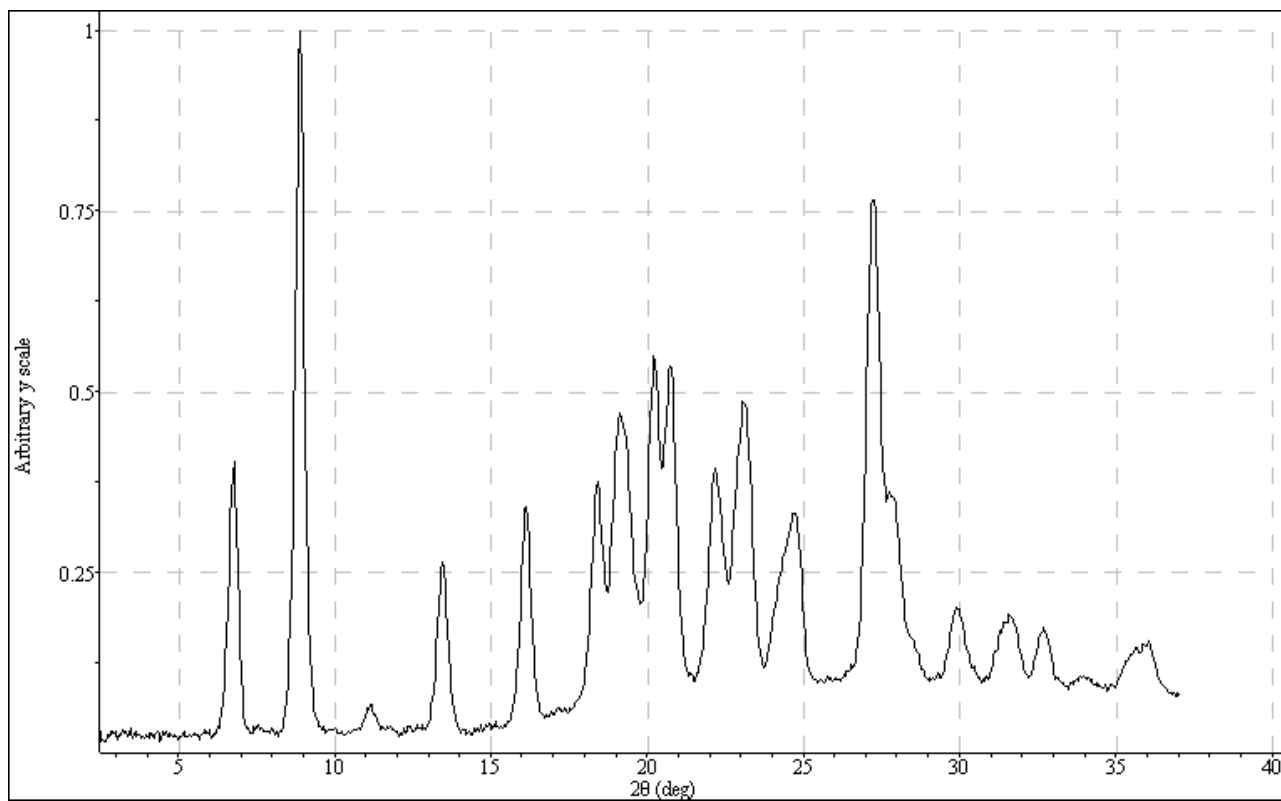
24 carbamazepine- fumaric acid cocrystal, form A



25 carbamazepine- fumaric acid cocrystal, form B

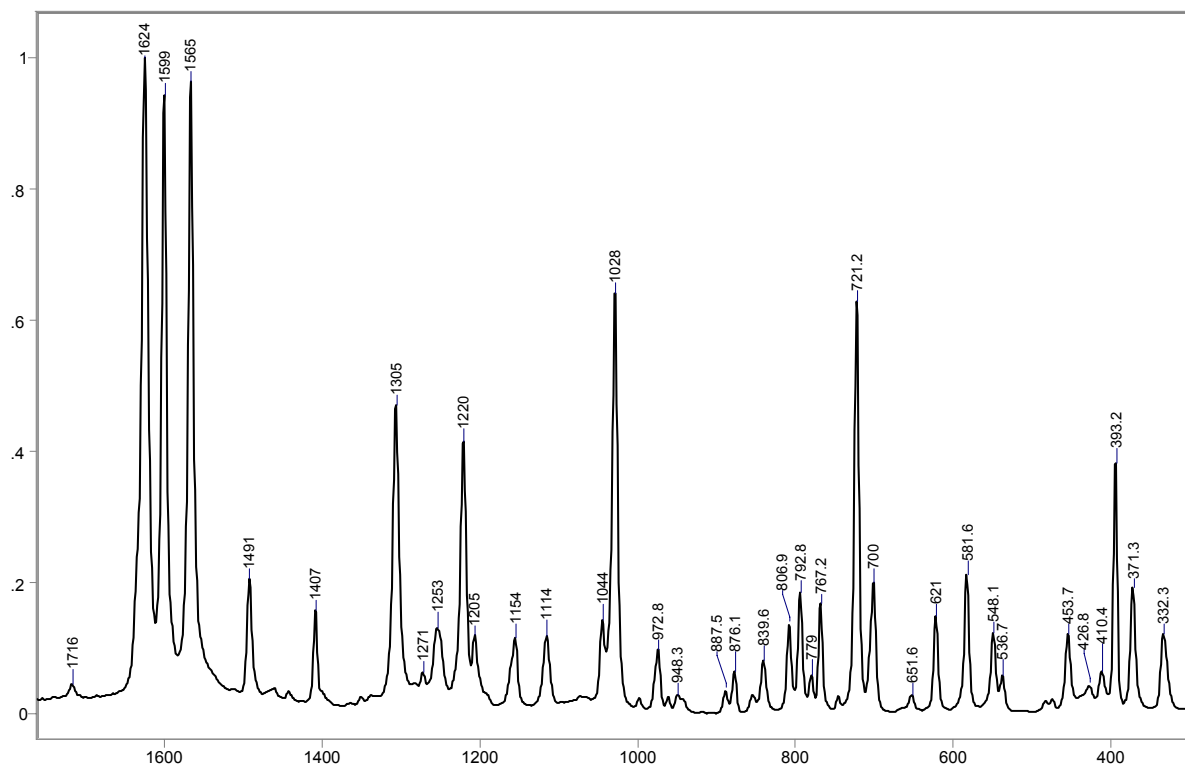


26 carbamazepine- DL-malic acid cocrystal

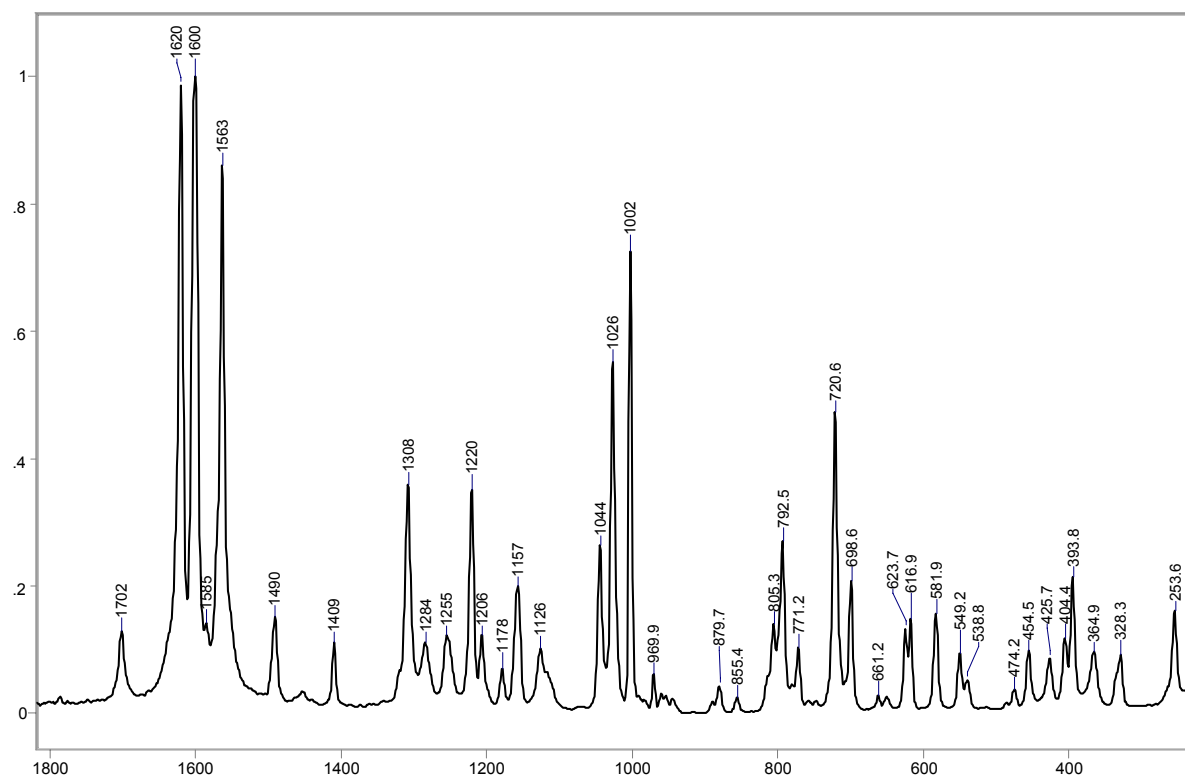


27 carbamazepine- L-malic acid cocrystal

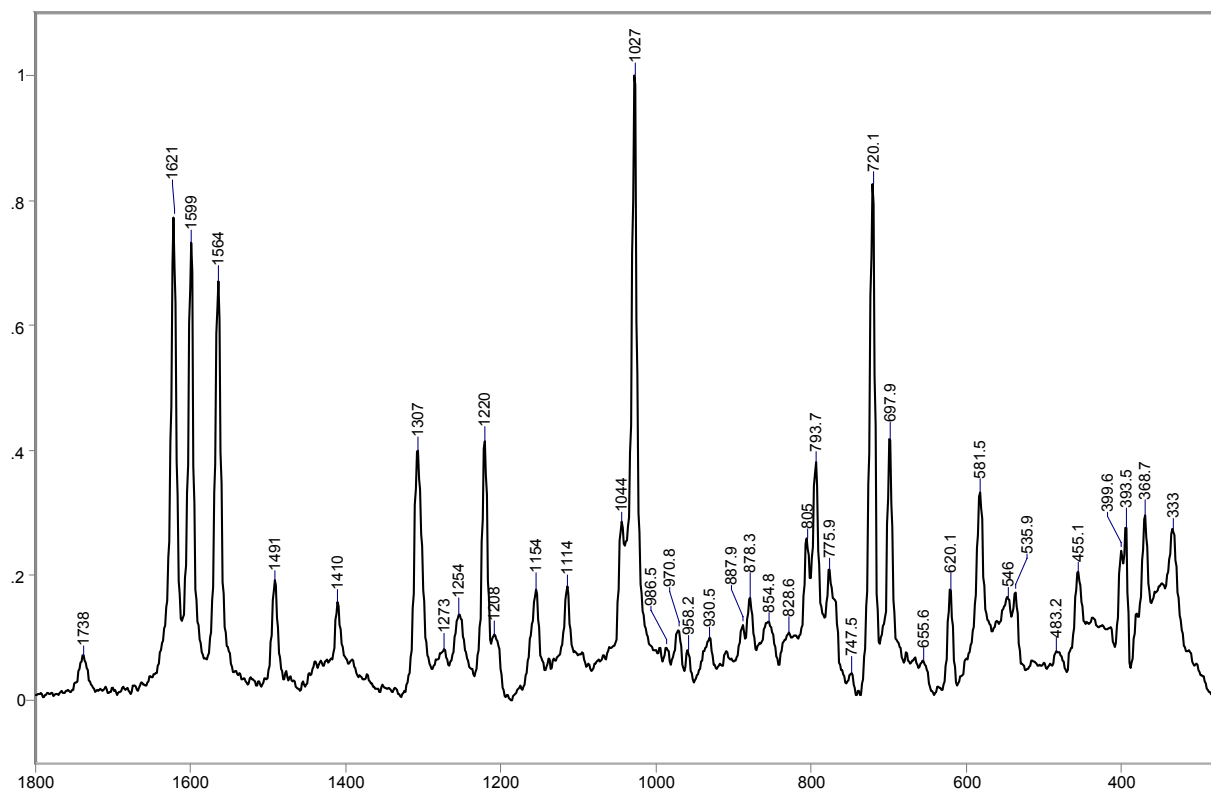
Raman data



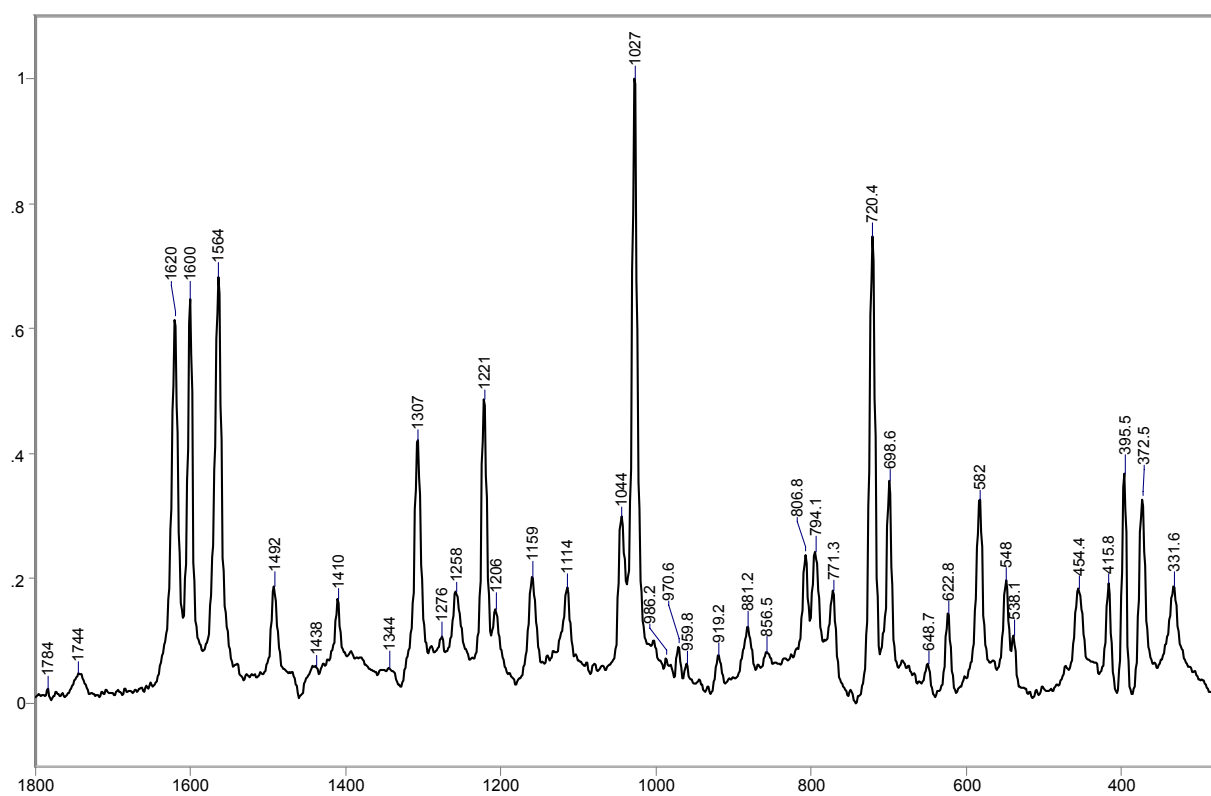
1 carbamazepine-succinic acid cocrystal

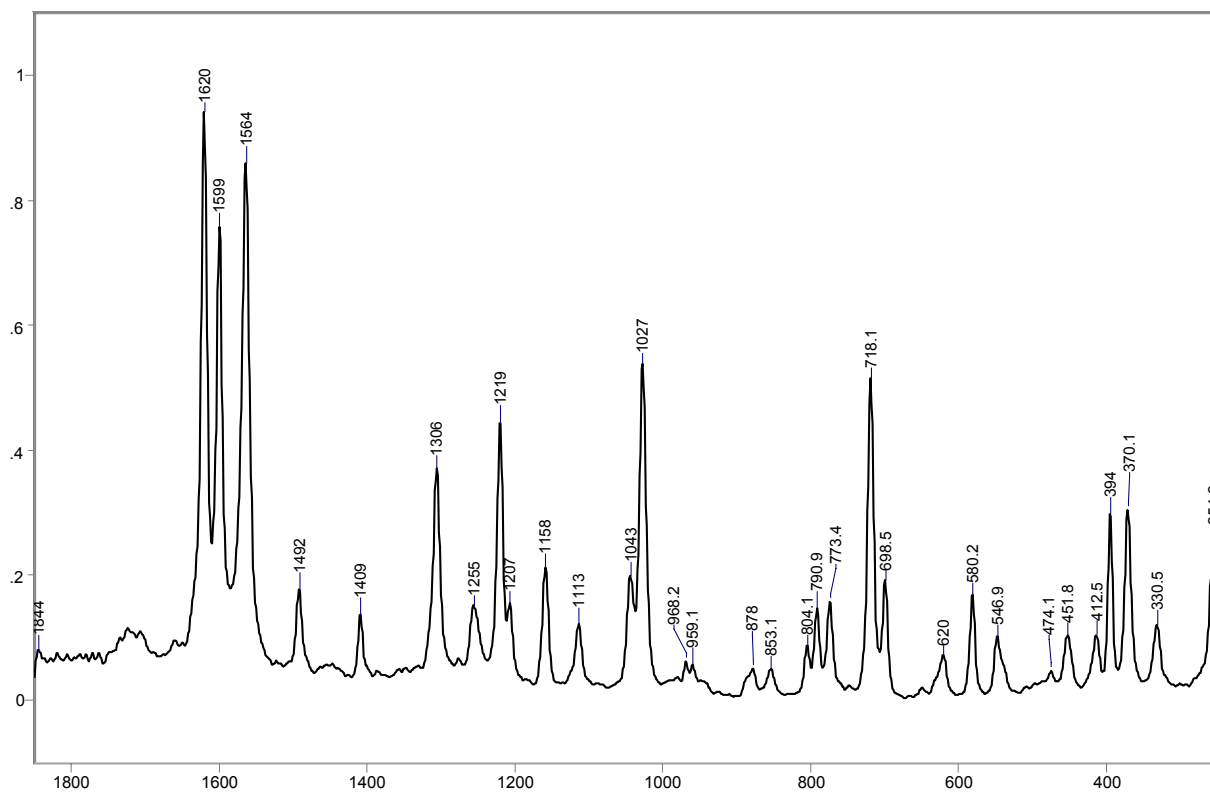


2 carbamazepine-benzoic acid cocrystal

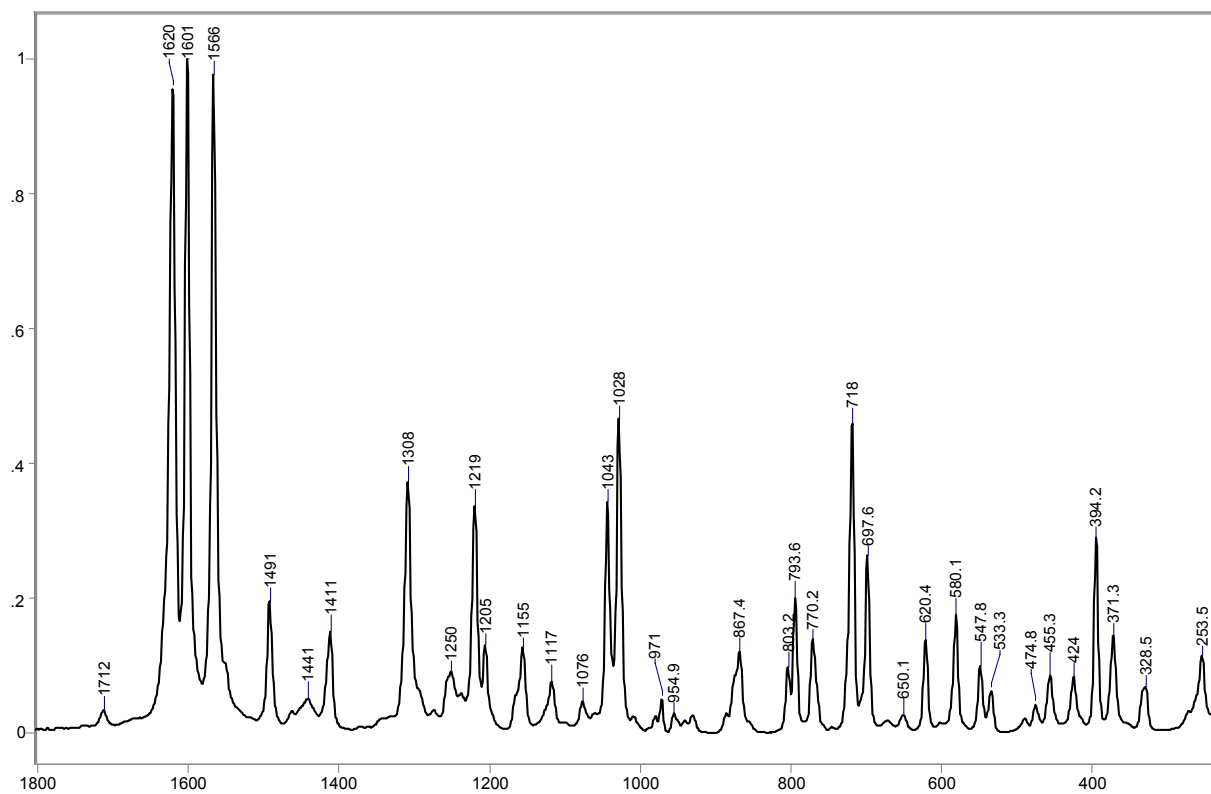


3 carbamazepine- ketoglutaric acid cocrystal, form A

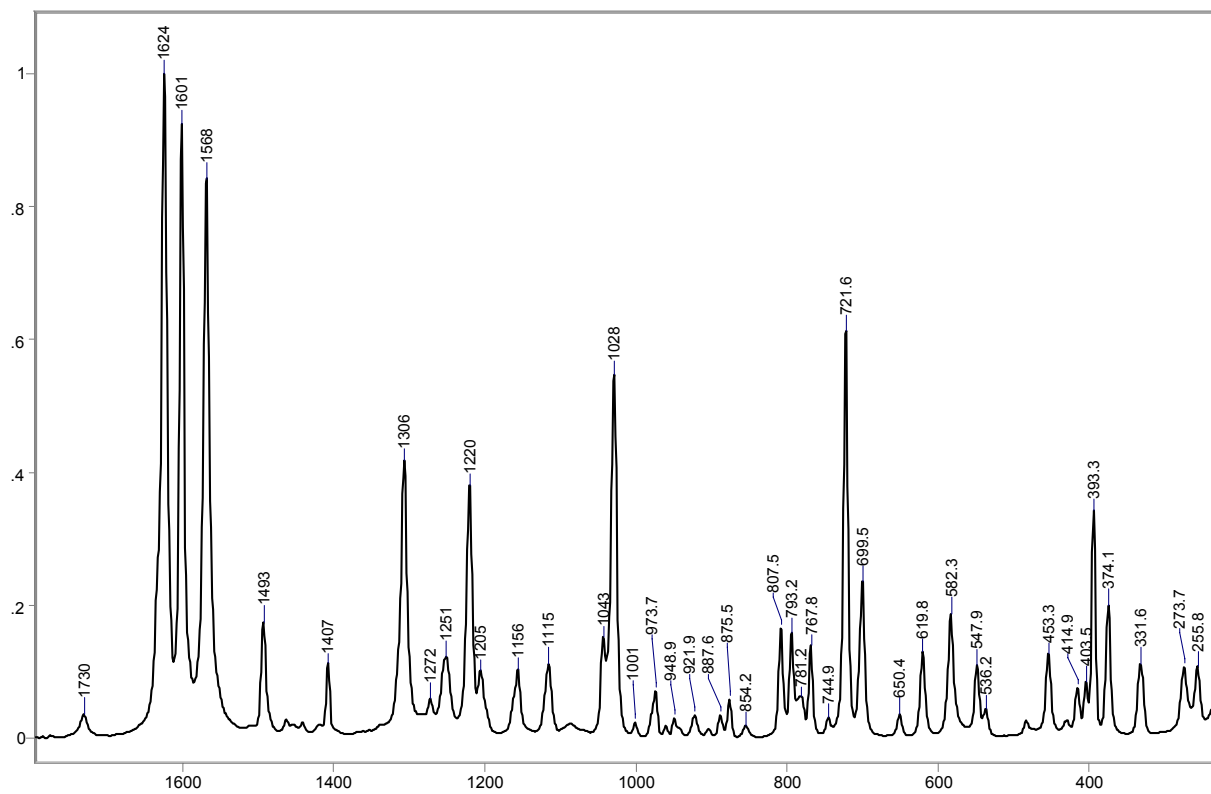




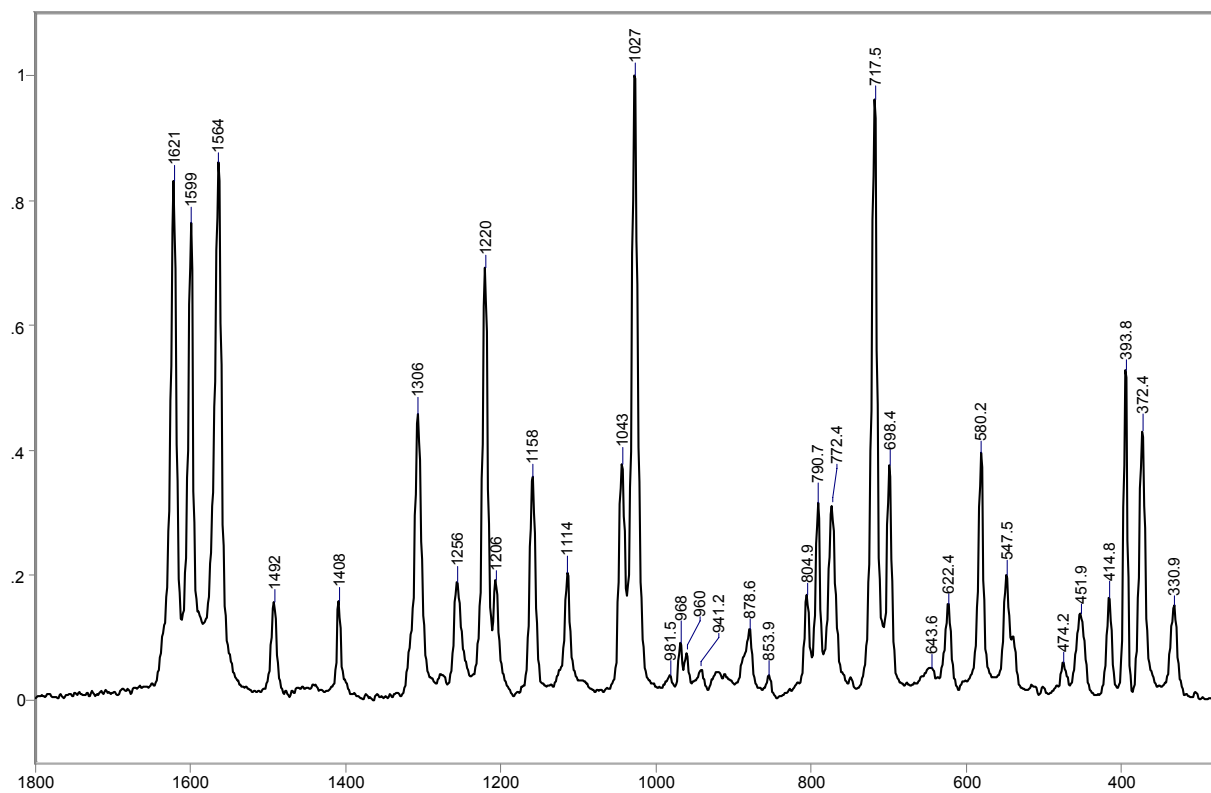
5 carbamazepine- maleic acid cocrystal



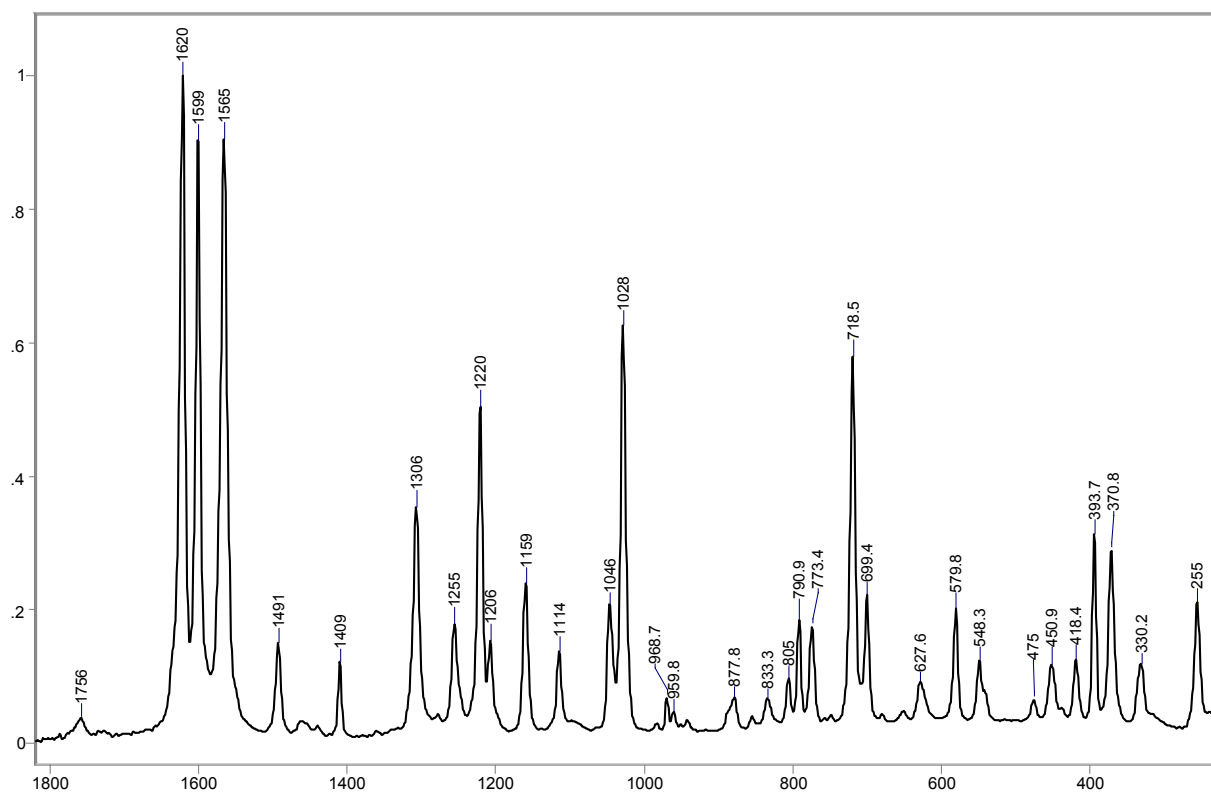
6 carbamazepine- glutaric acid cocrystal

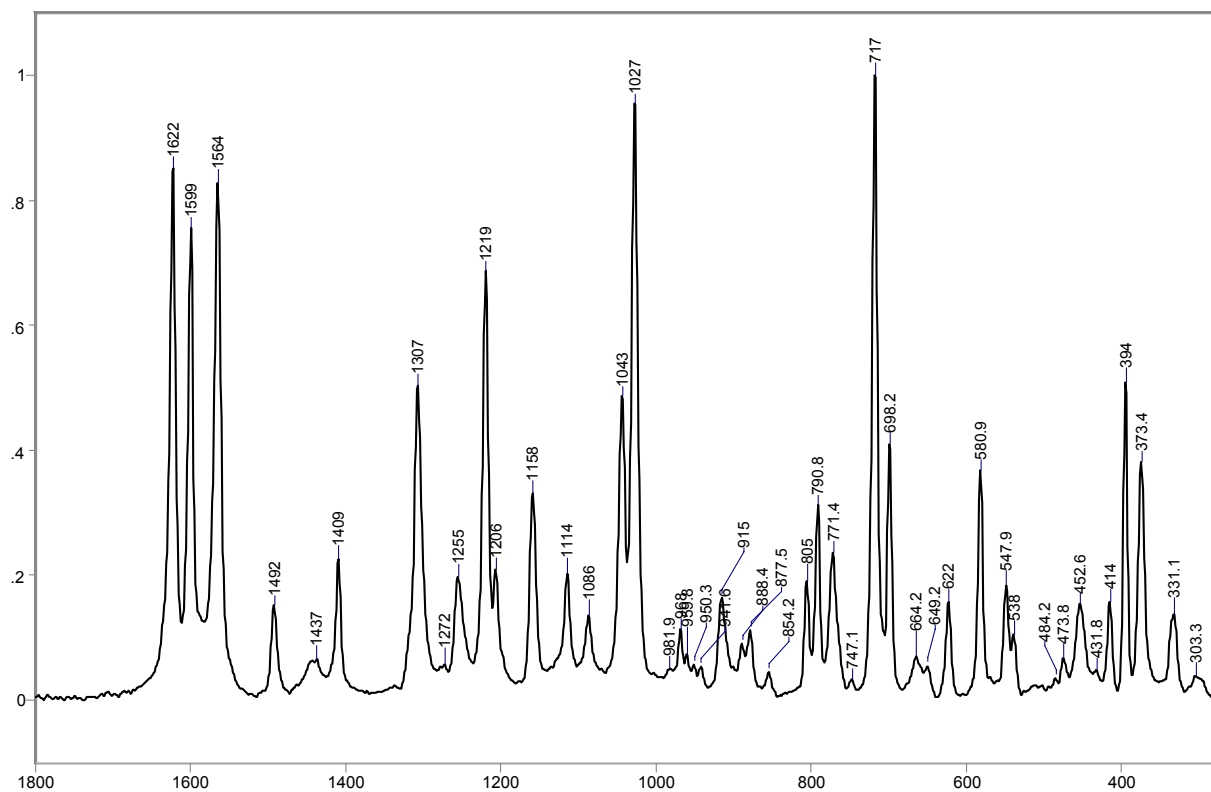


7 carbamazepine- malonic acid cocrystal, form A

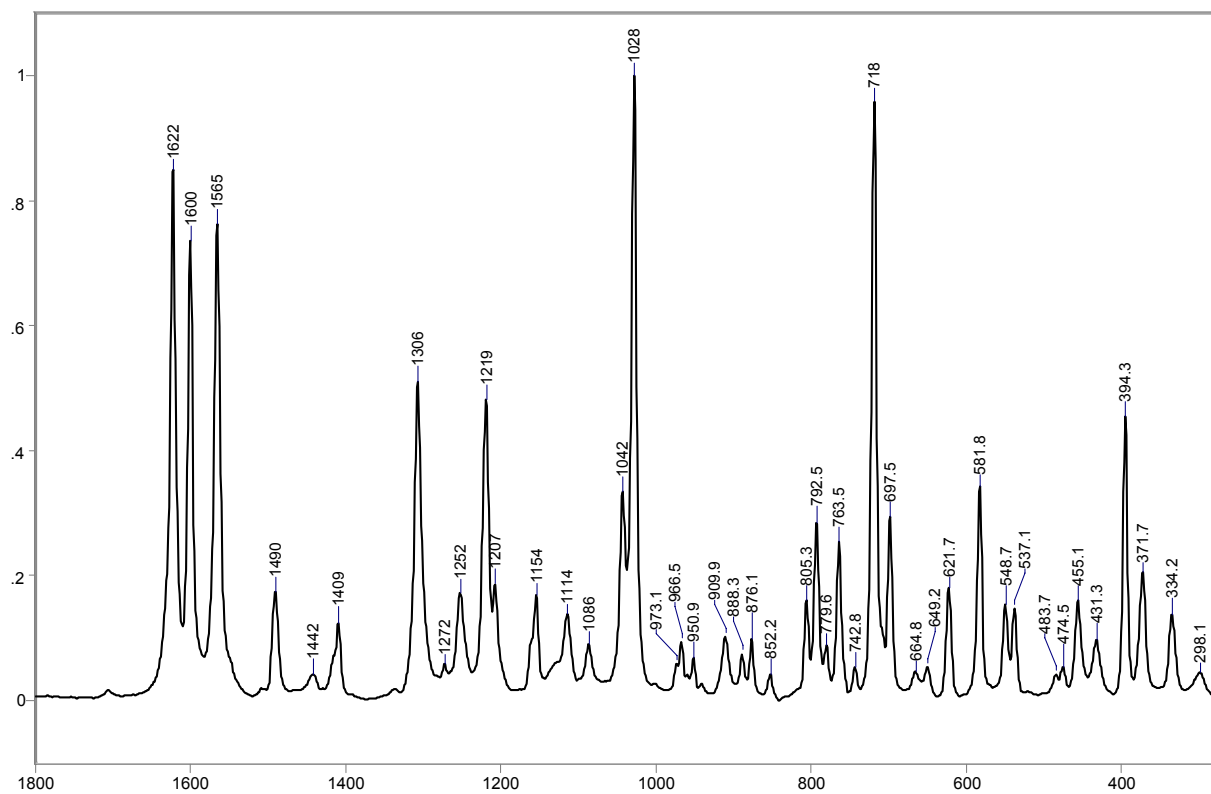


8 carbamazepine- malonic acid cocrystal, form B

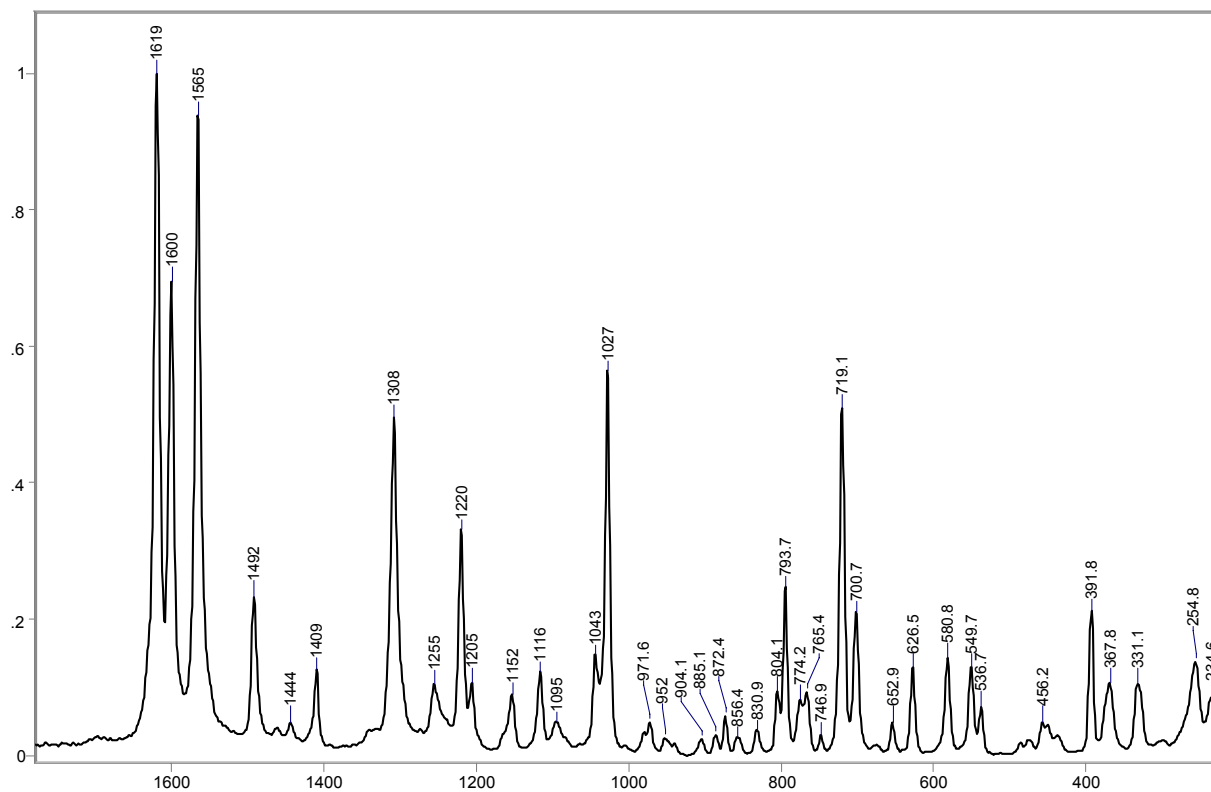




10 carbamazepine- adipic acid cocrystal, form A

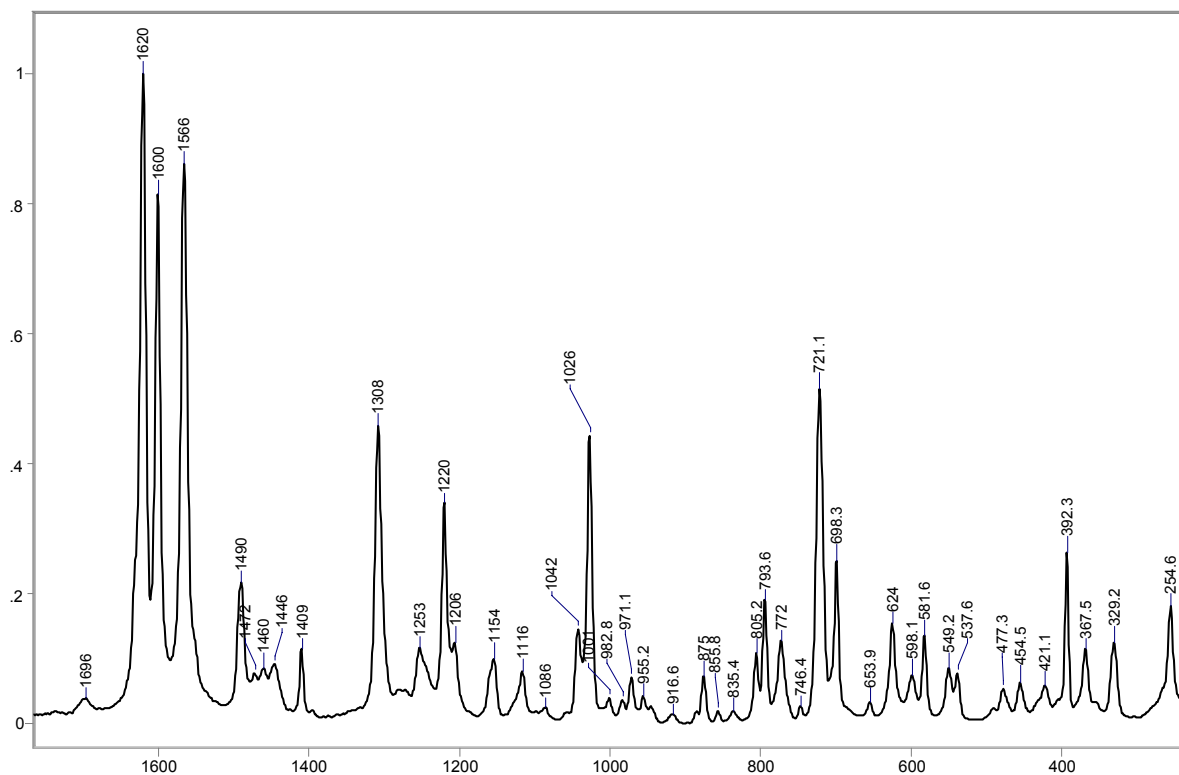


11 carbamazepine- adipic acid cocrystal, form B

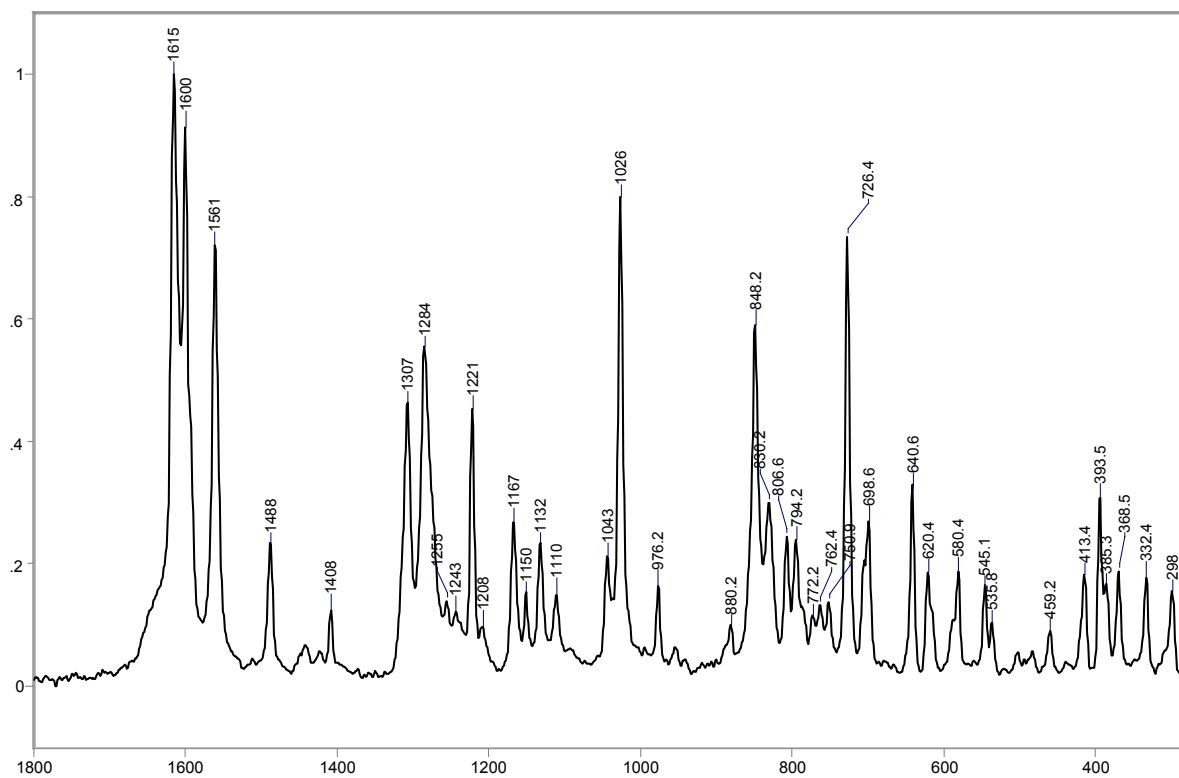


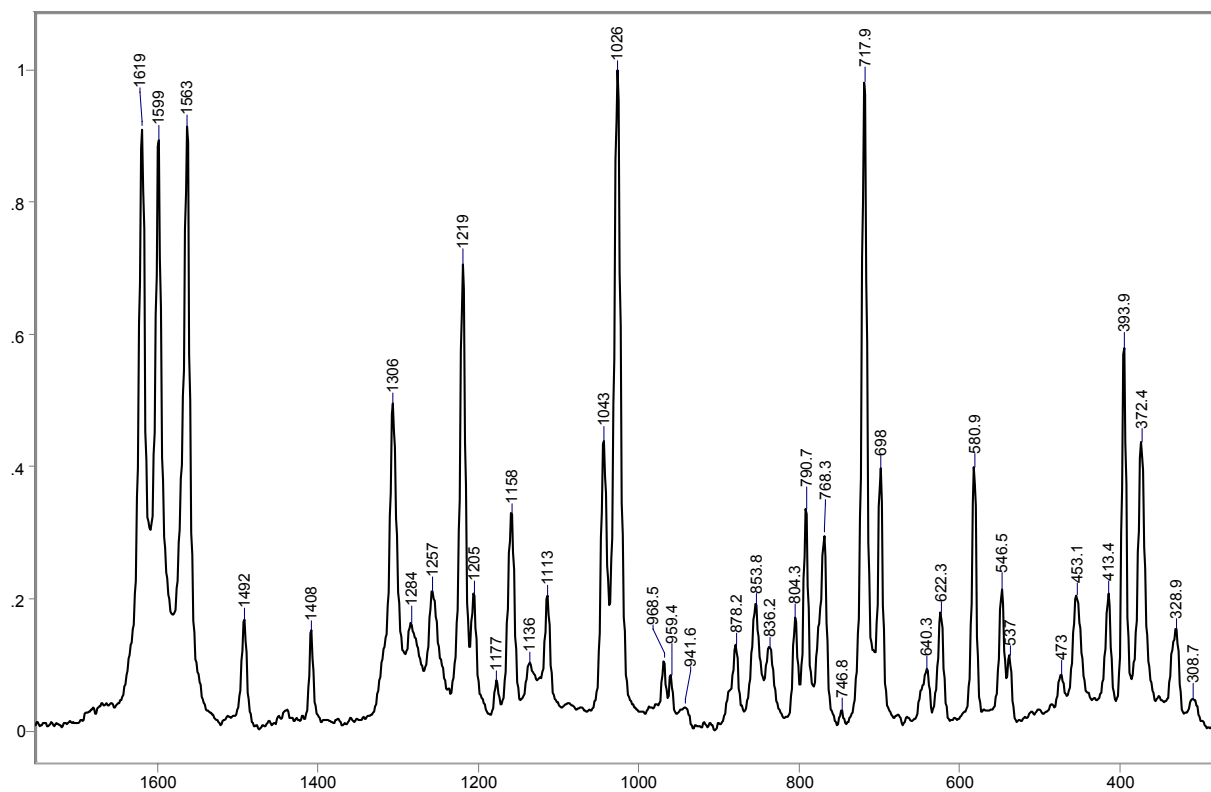
12 carbamazepine- adipic acid cocrystal, form C

13 carbamazepine- (+)-camphoric acid cocrystal, form B [not available – XRPD only]

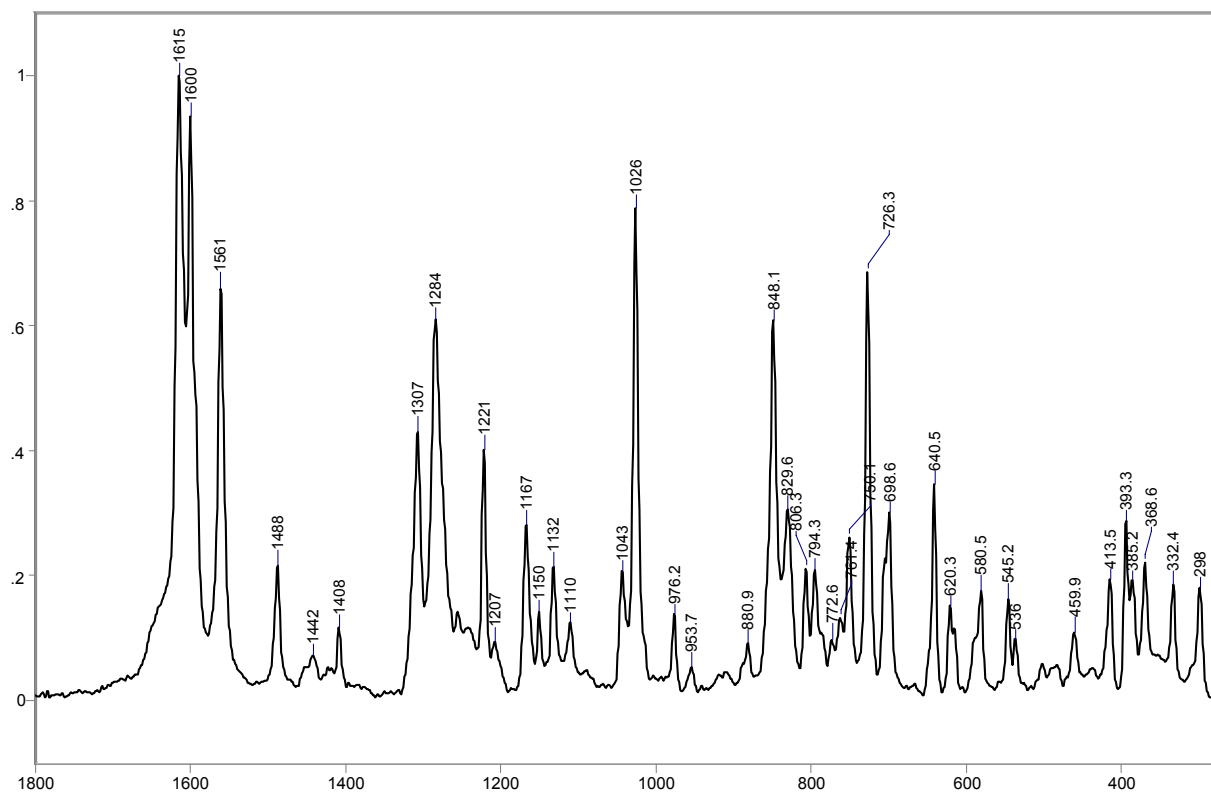


14 carbamazepine- (+)-camphoric acid cocrystal, form A

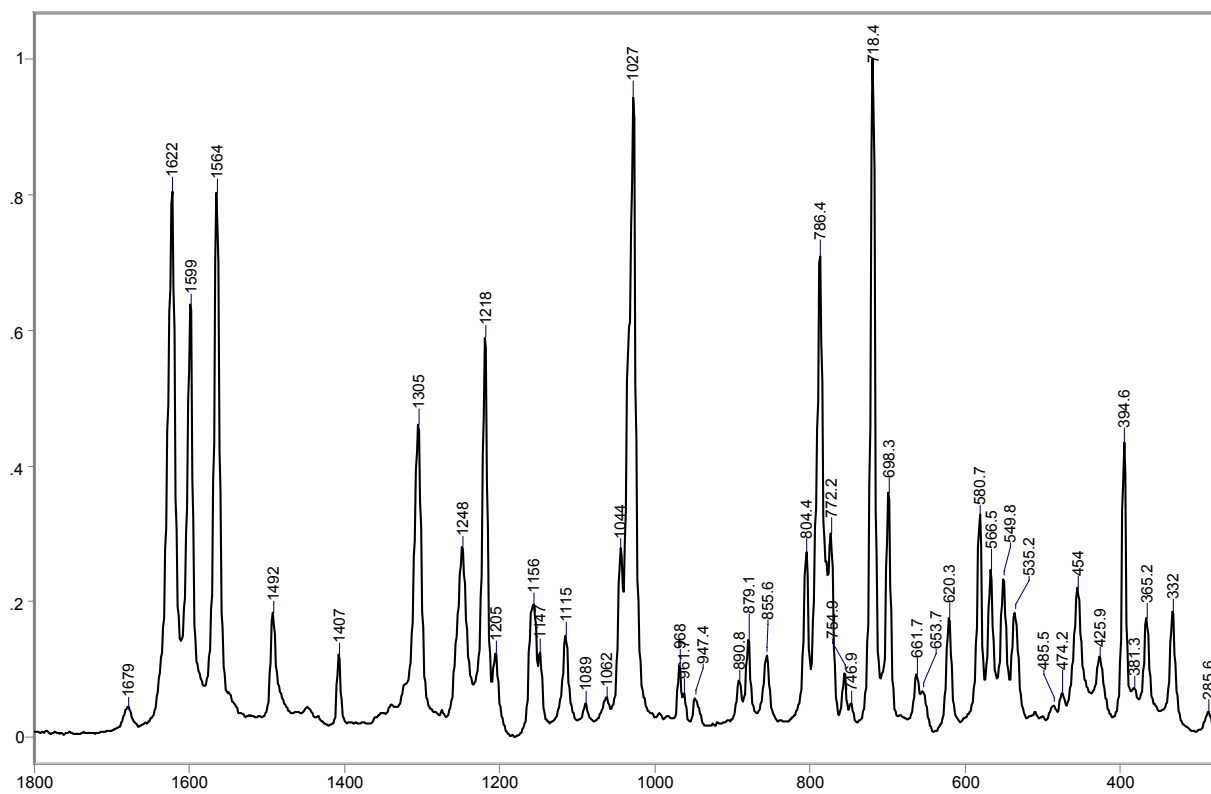




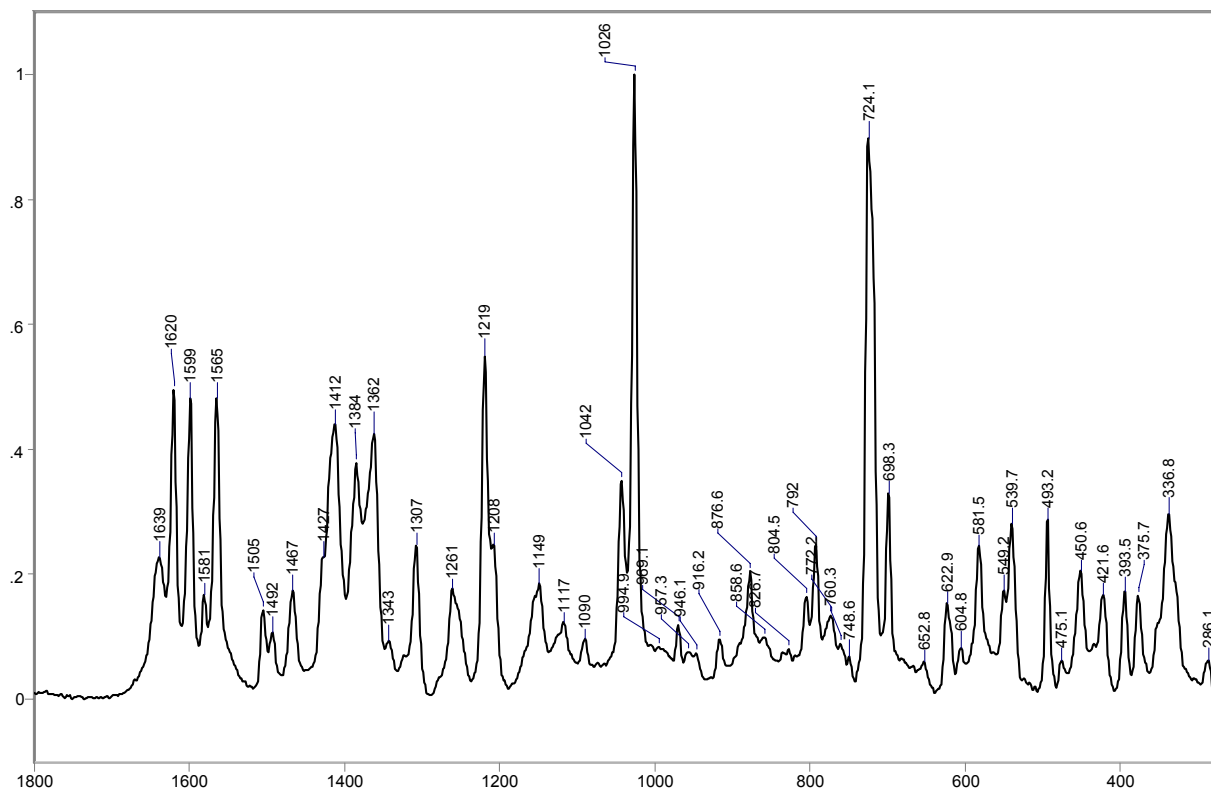
16 carbamazepine- 4-hydroxybenzoic acid cocrystal, form B



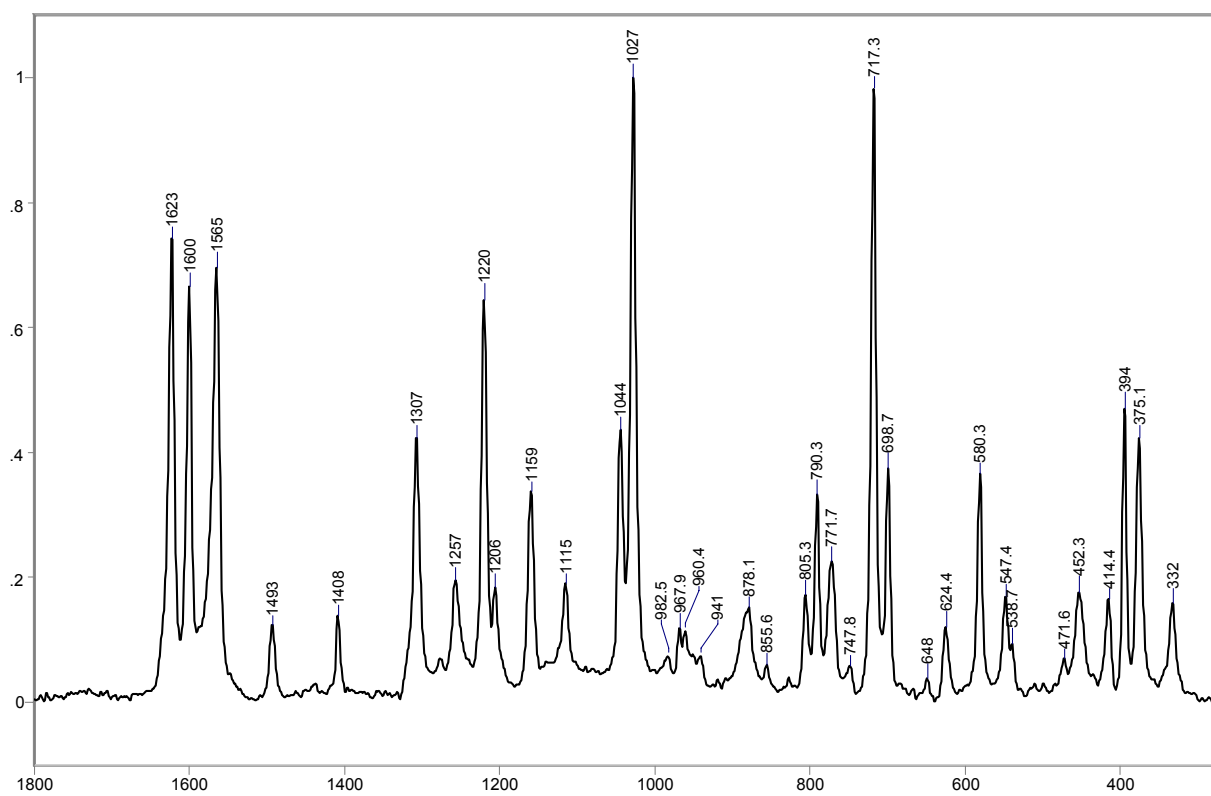
17 carbamazepine-4-hydroxybenzoic acid cocrystal, form C

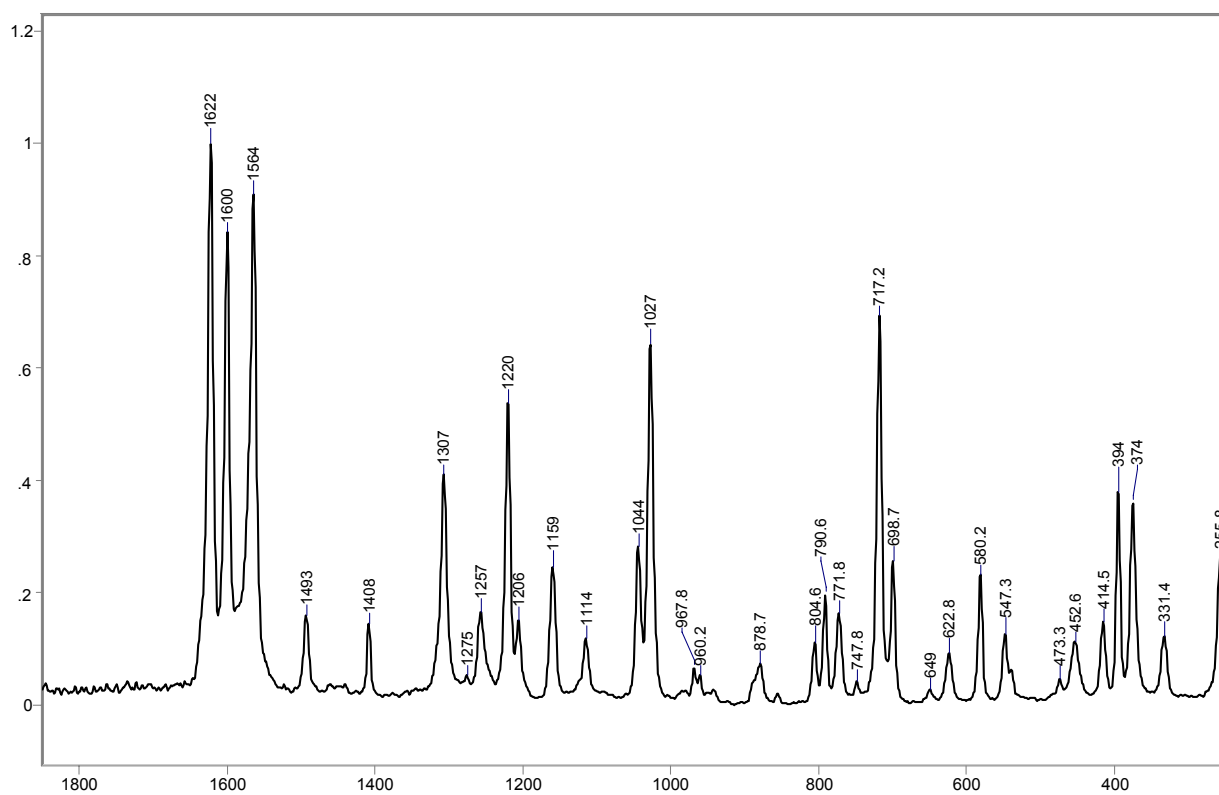


18 carbamazepine salicylic acid cocrystal

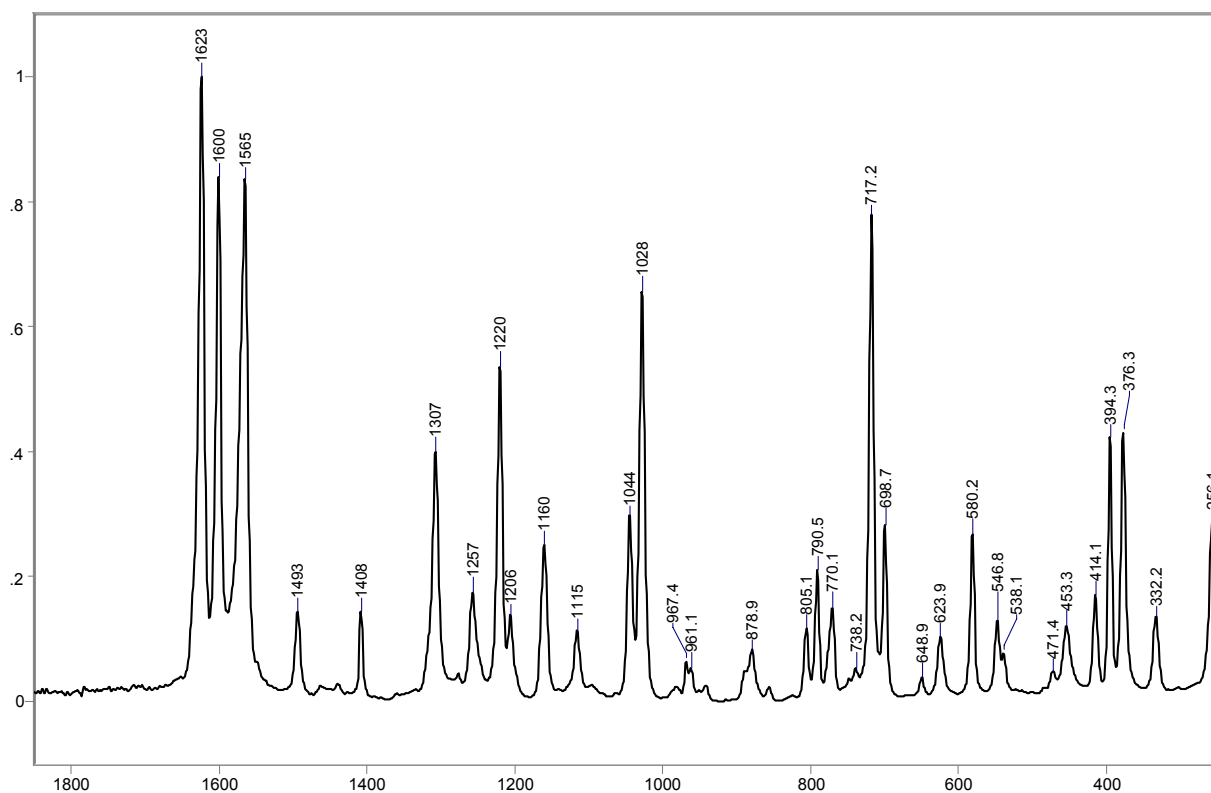


19 carbamazepine- 1-hydroxy-2-naphthoic acid cocrystal

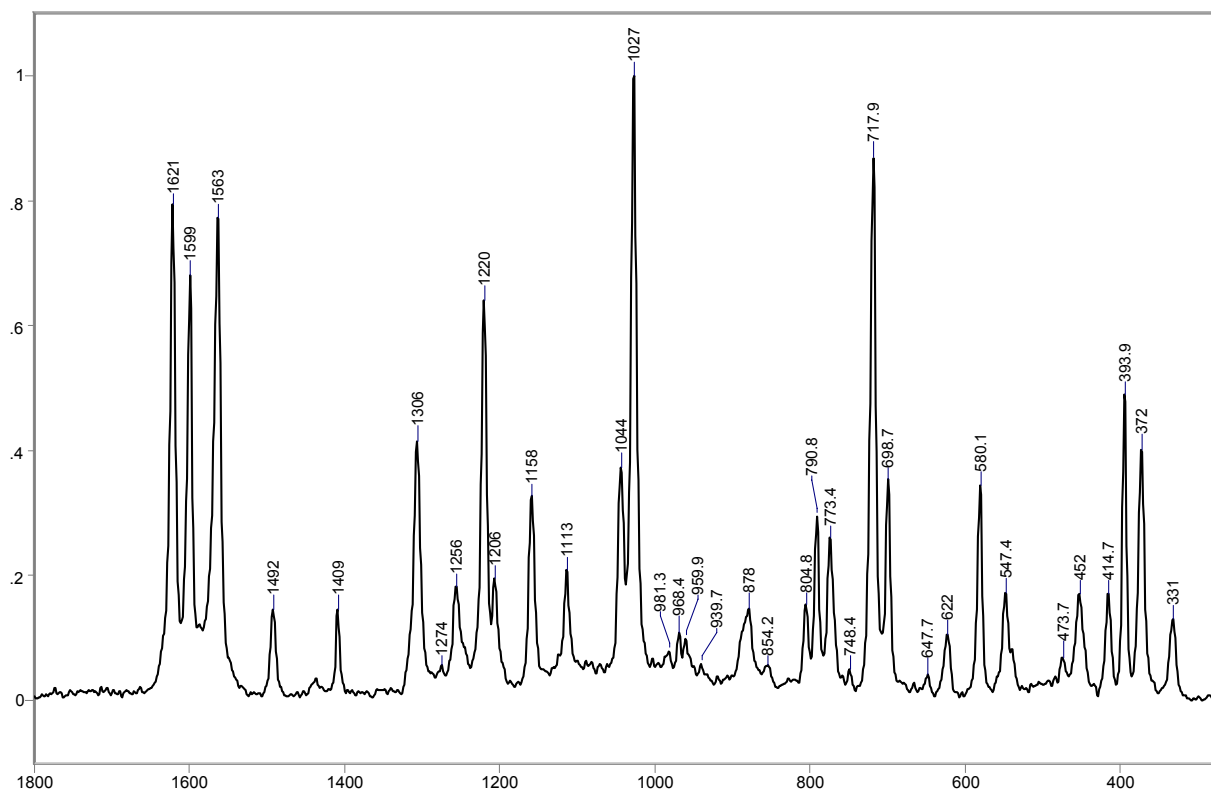




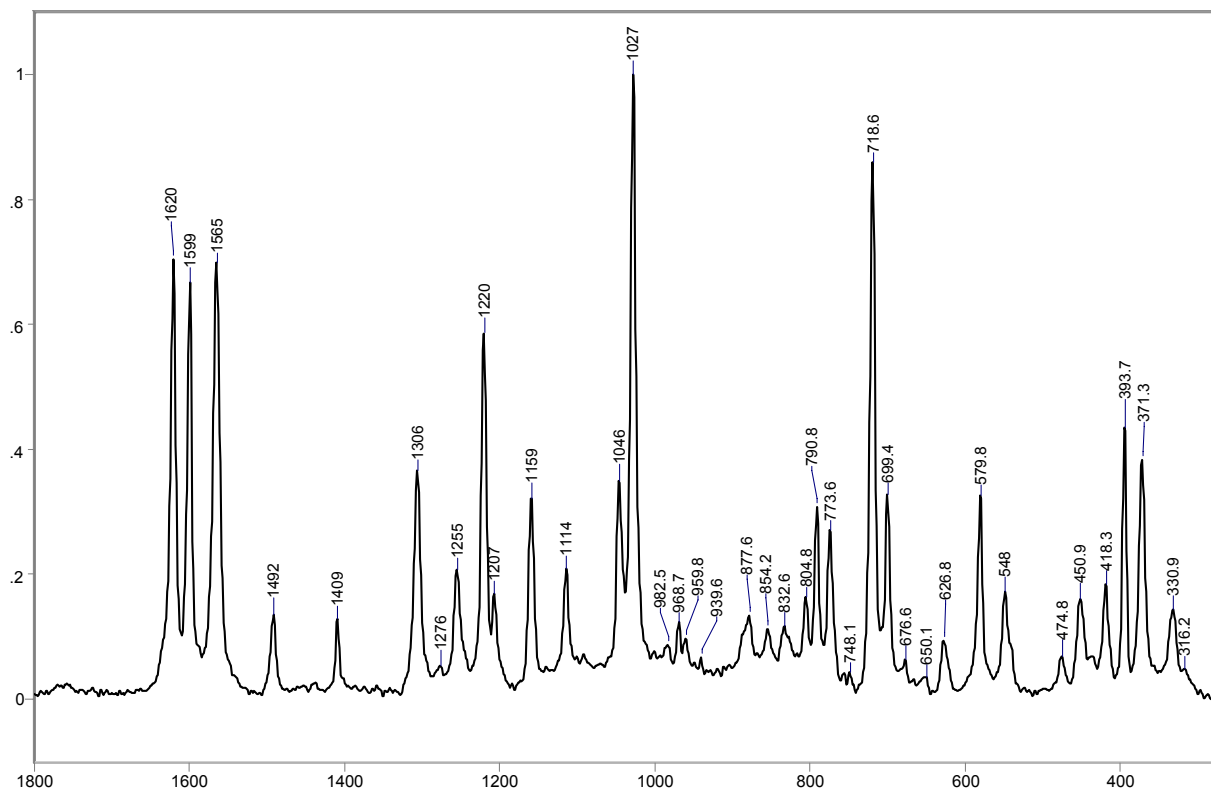
21 carbamazepine- DL-tartaric acid cocrystal, form B



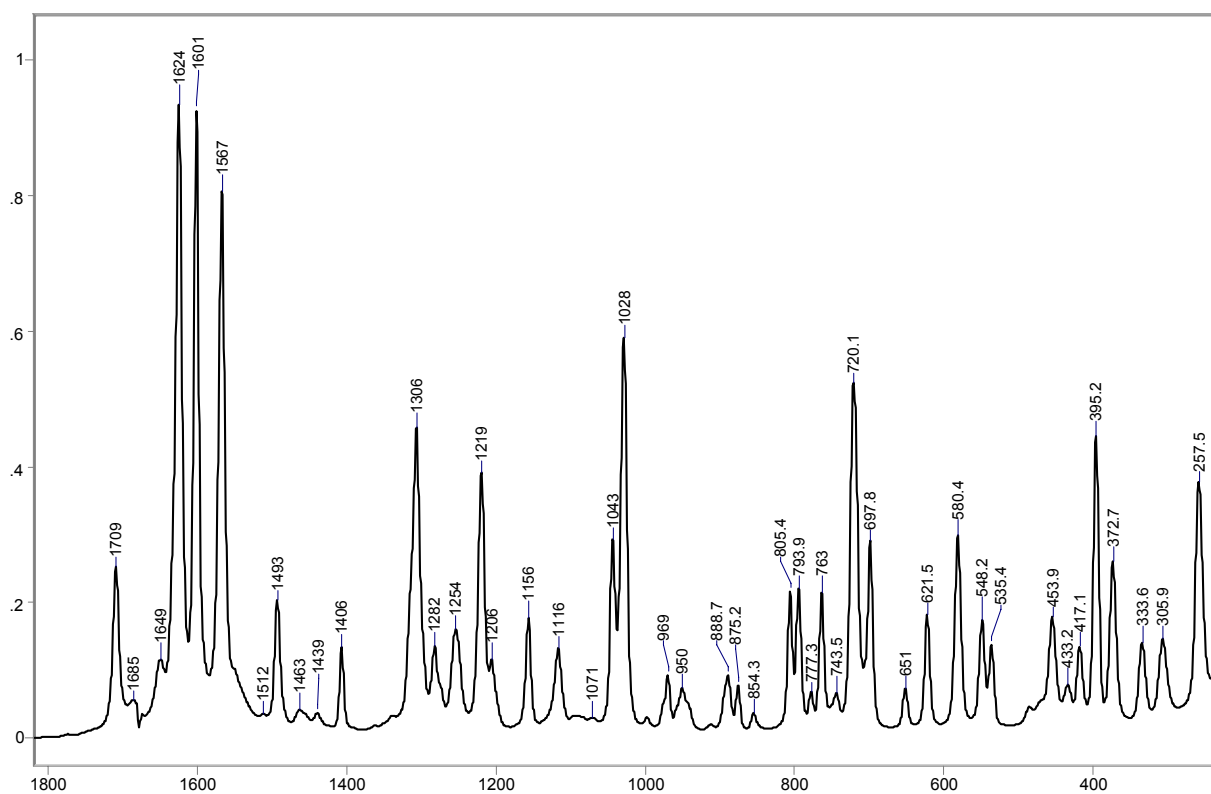
22 carbamazepine- L-tartaric acid cocrystal

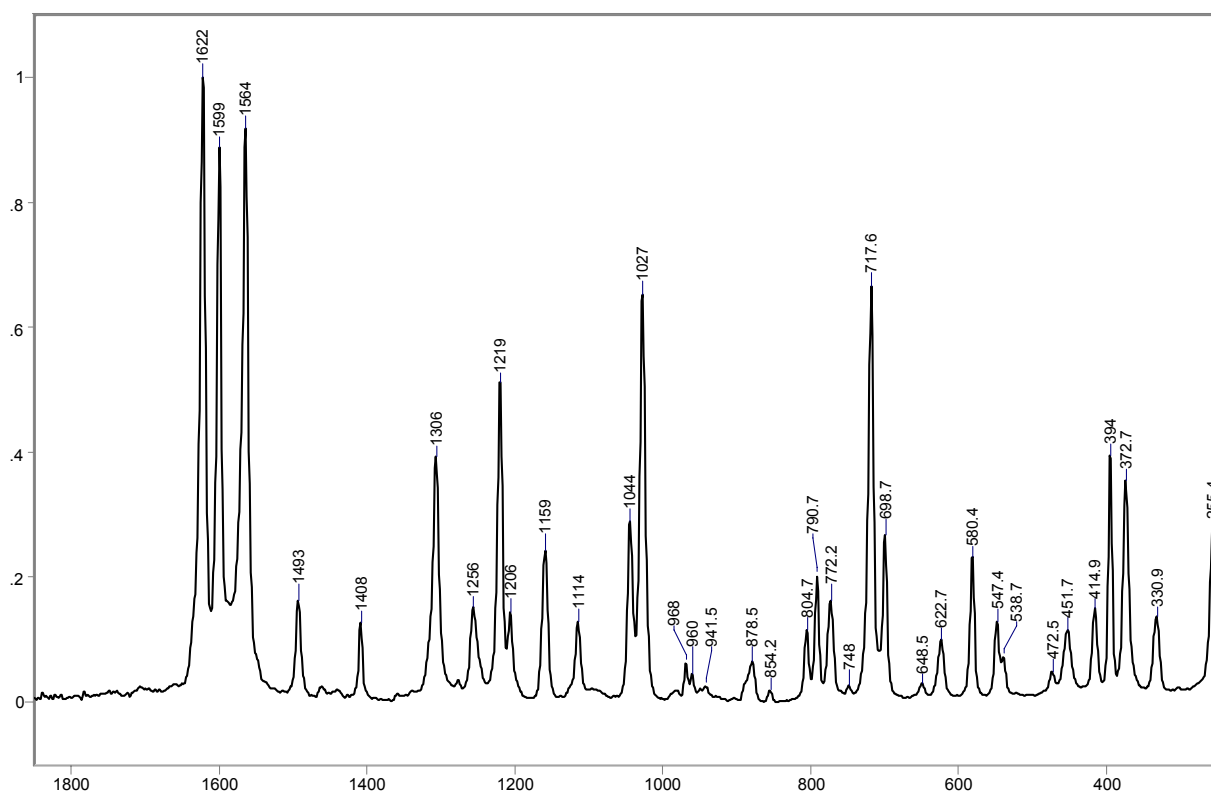


23 carbamazepine- glycolic acid cocrystal

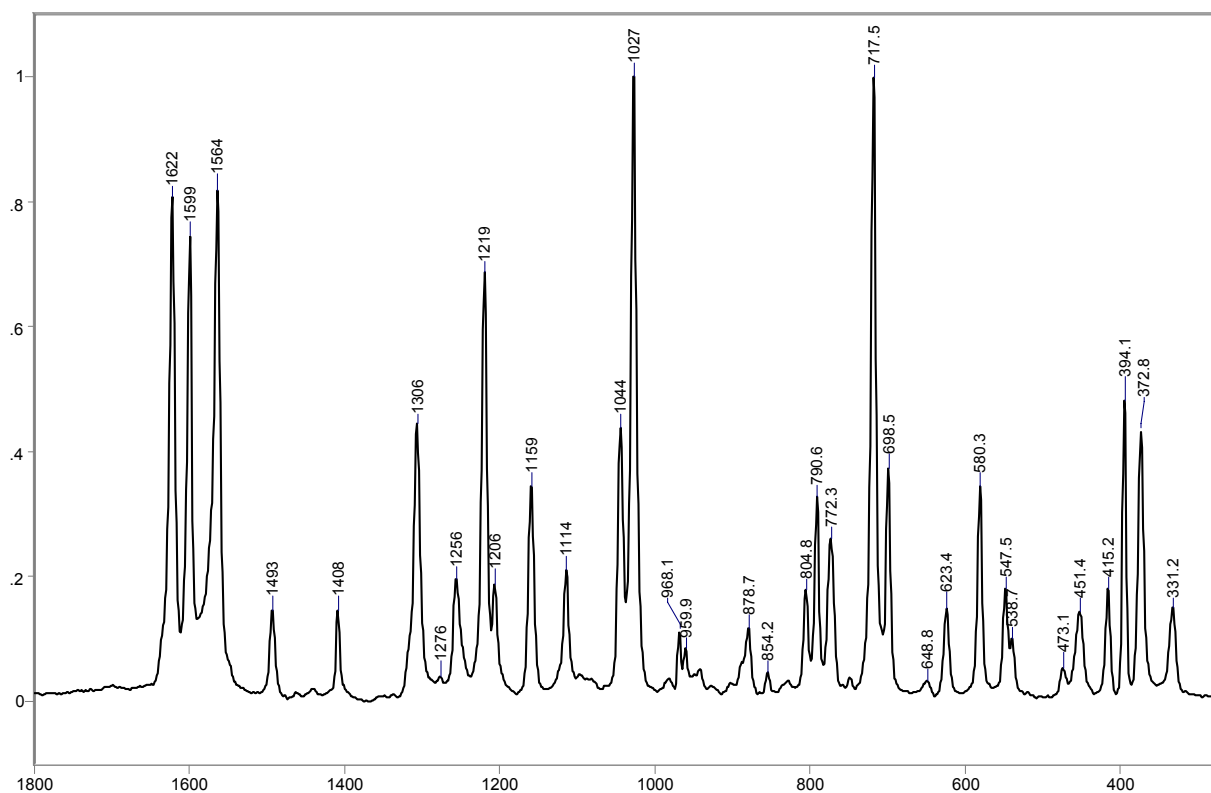


24 carbamazepine- fumaric acid cocrystal, form A



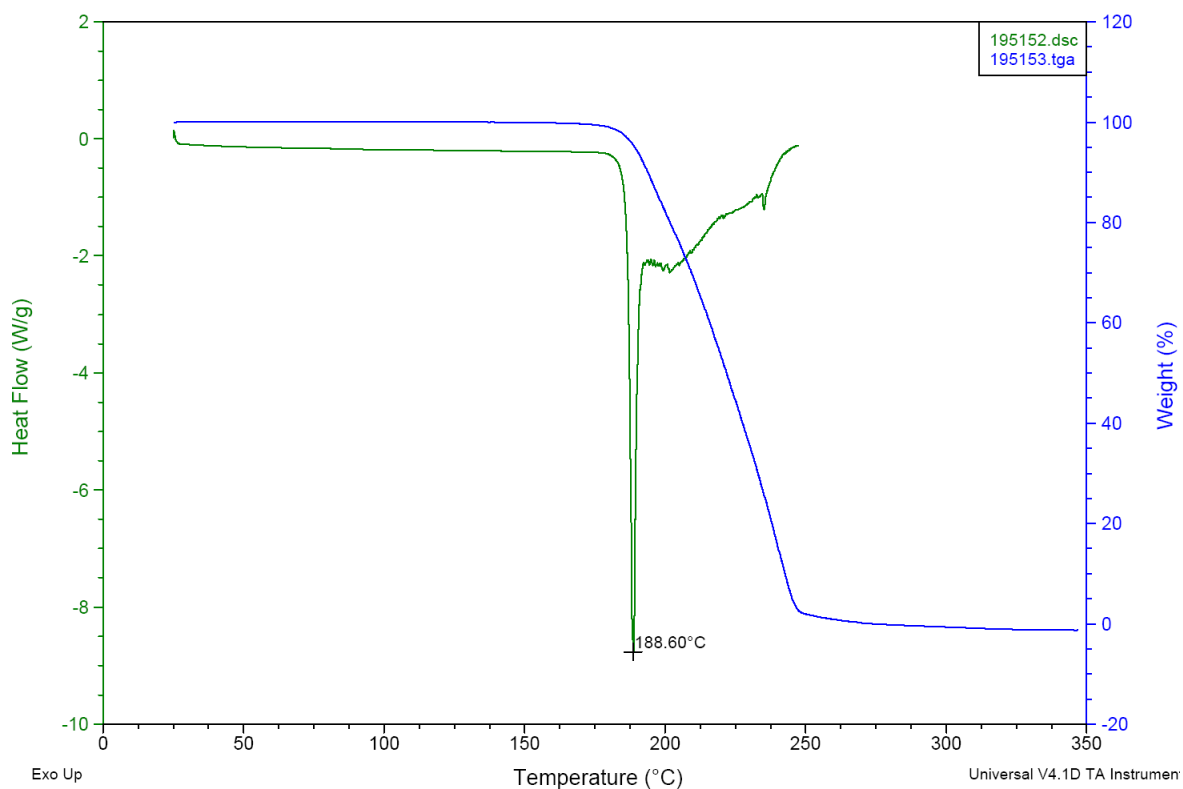


26 carbamazepine- DL-malic acid cocrystal

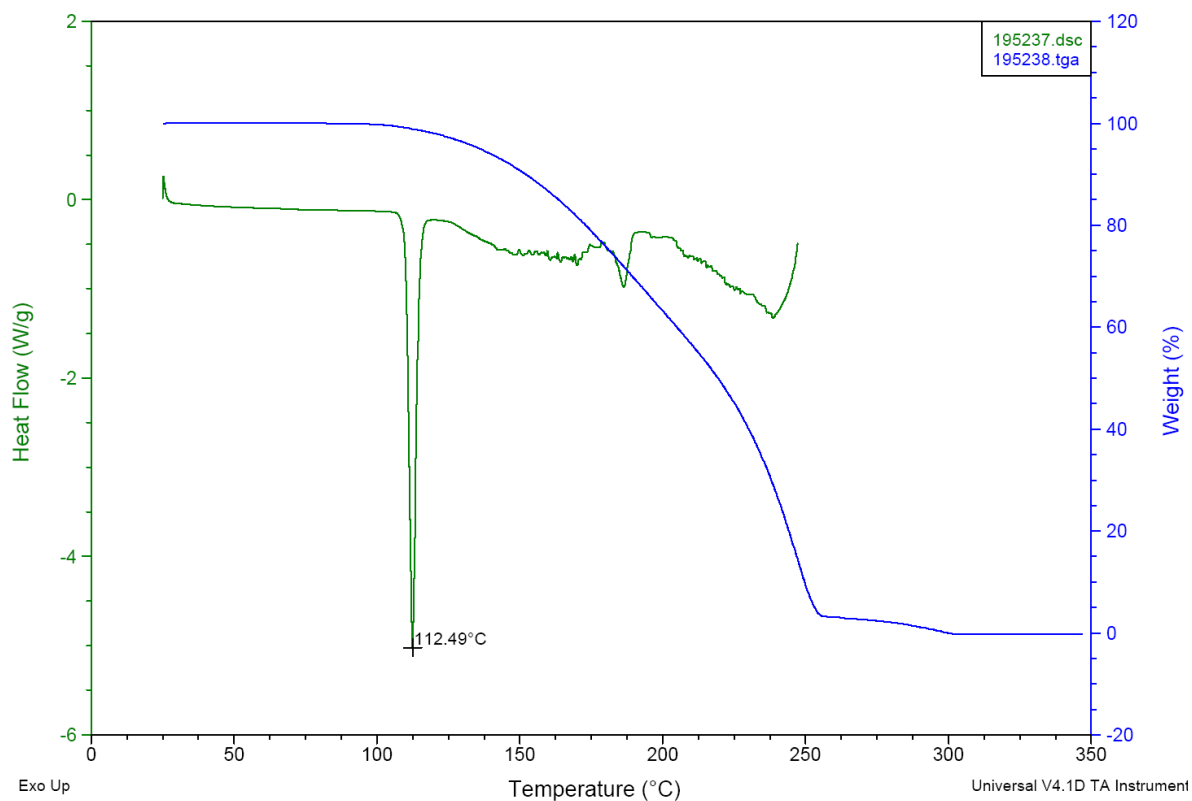


27 carbamazepine- L-malic acid cocrystal

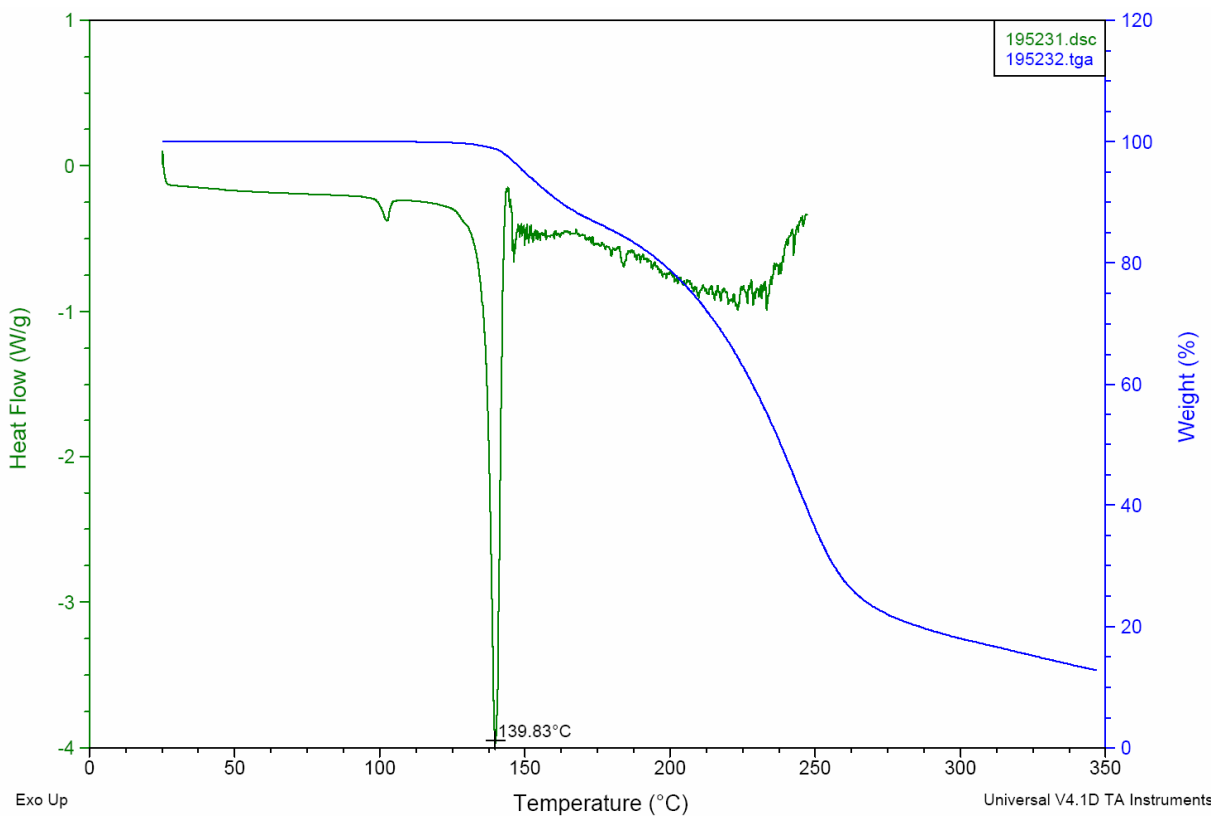
DSC-TGA data

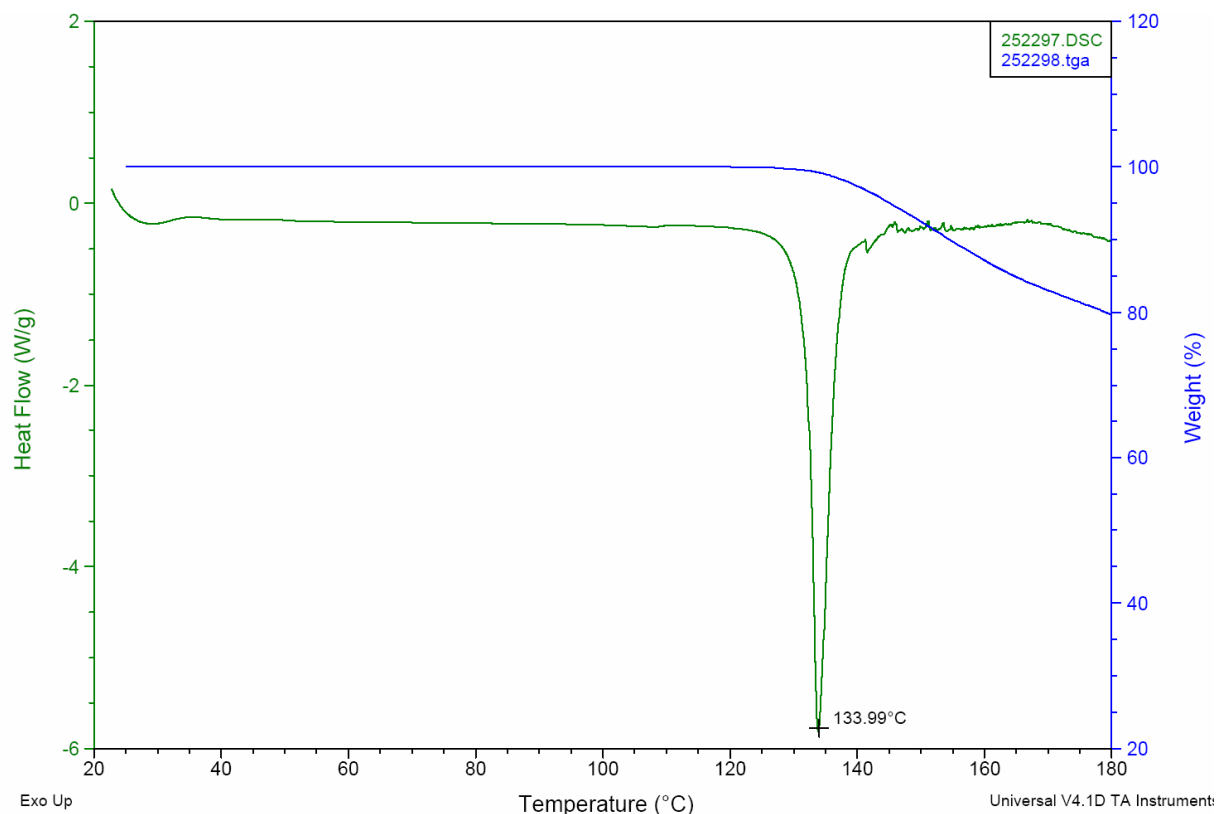


1 carbamazepine-succinic acid cocrystal

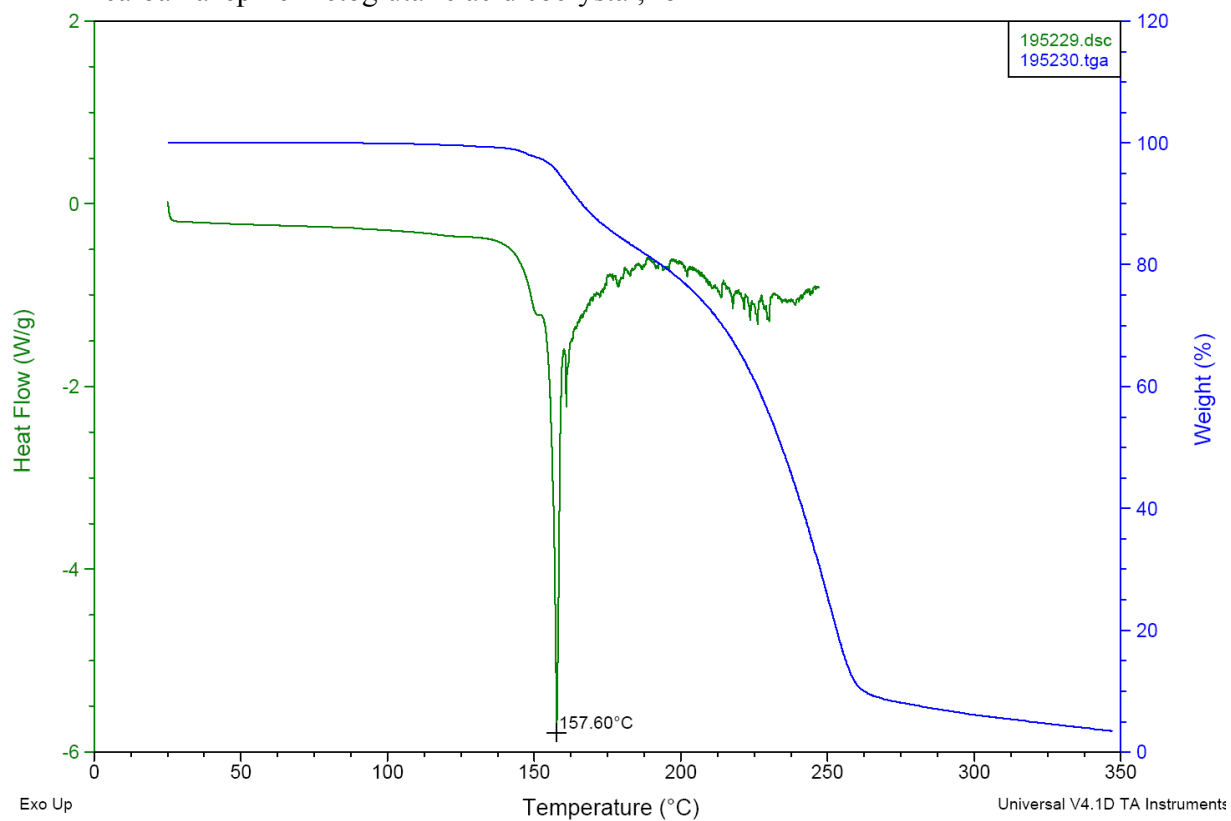


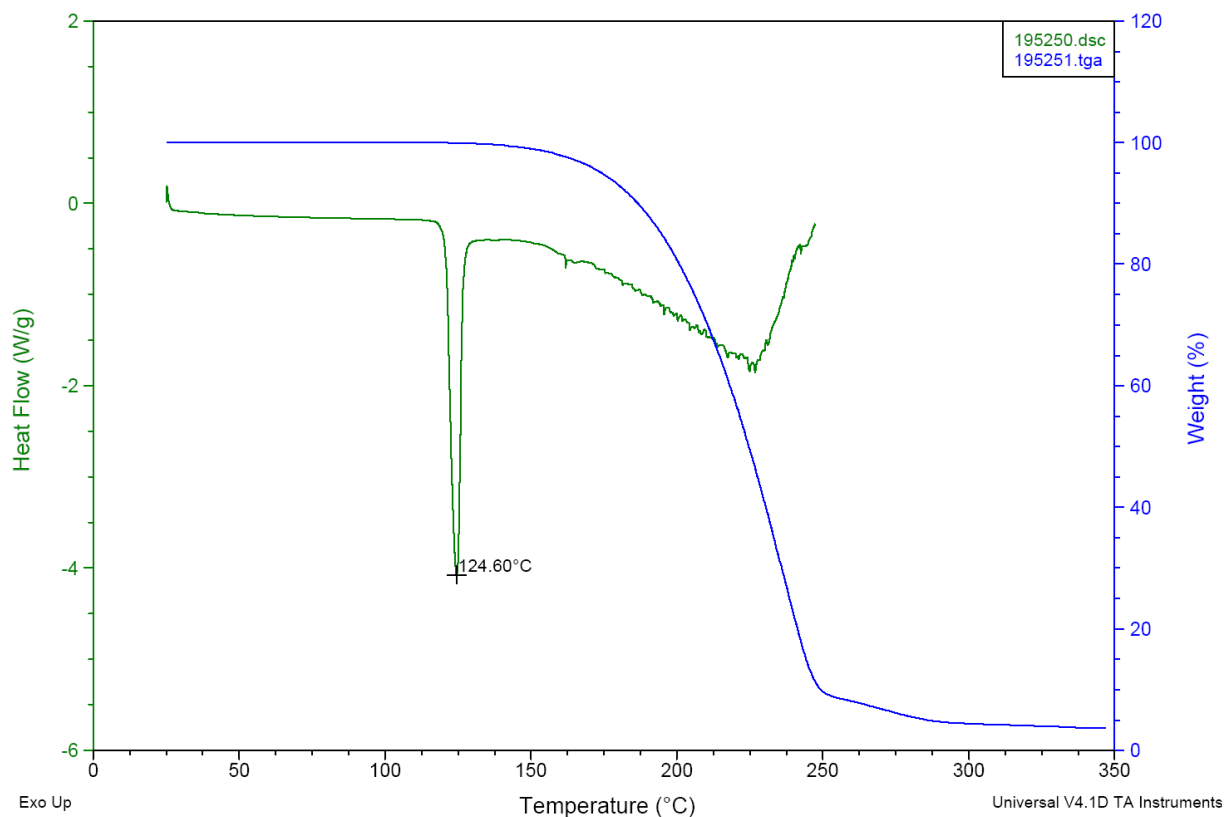
2 carbamazepine- benzoic acid cocrystal



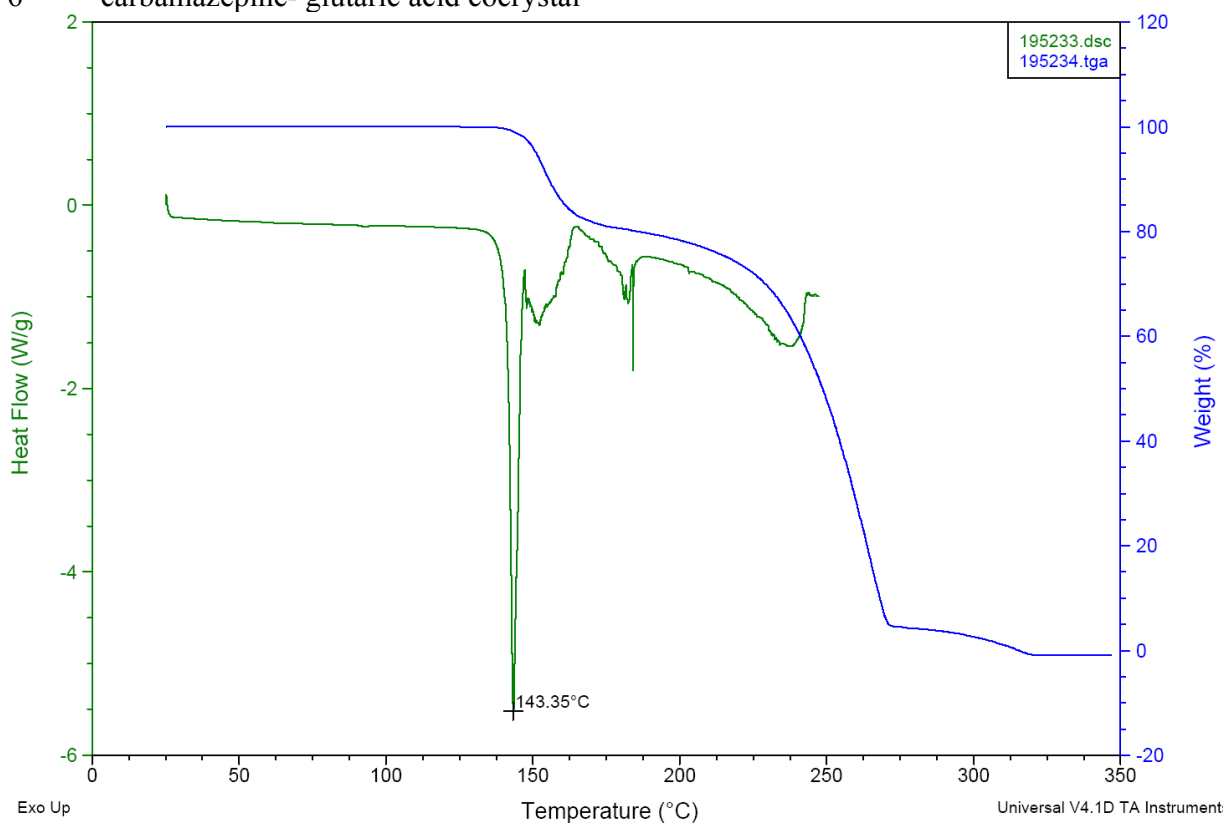


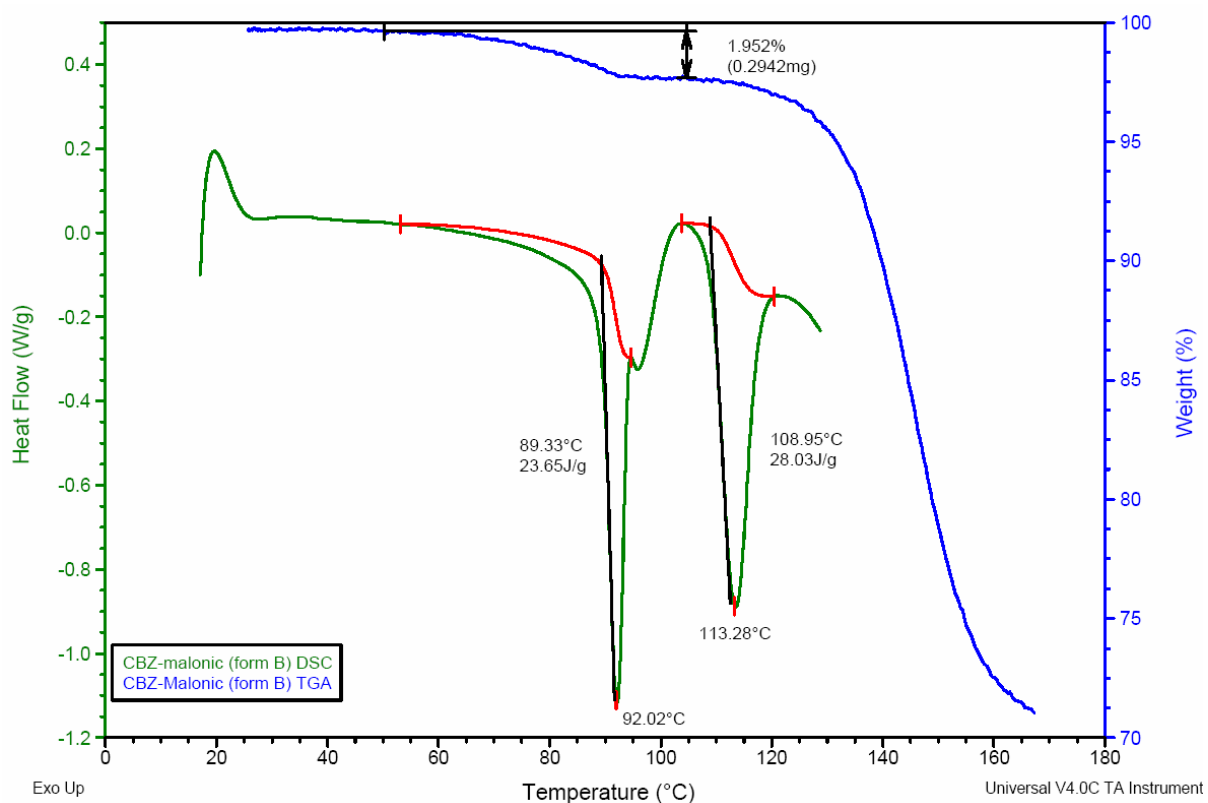
4 carbamazepine- ketoglutaric acid cocrystal, form B



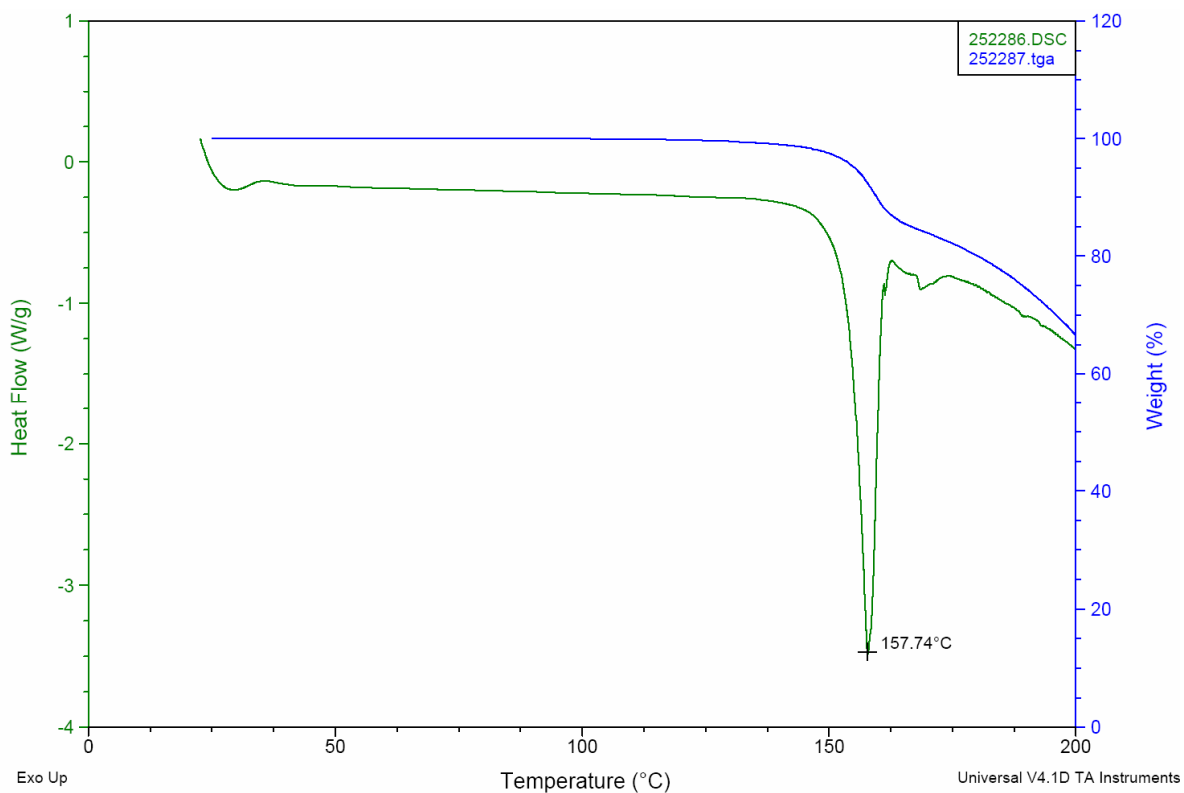


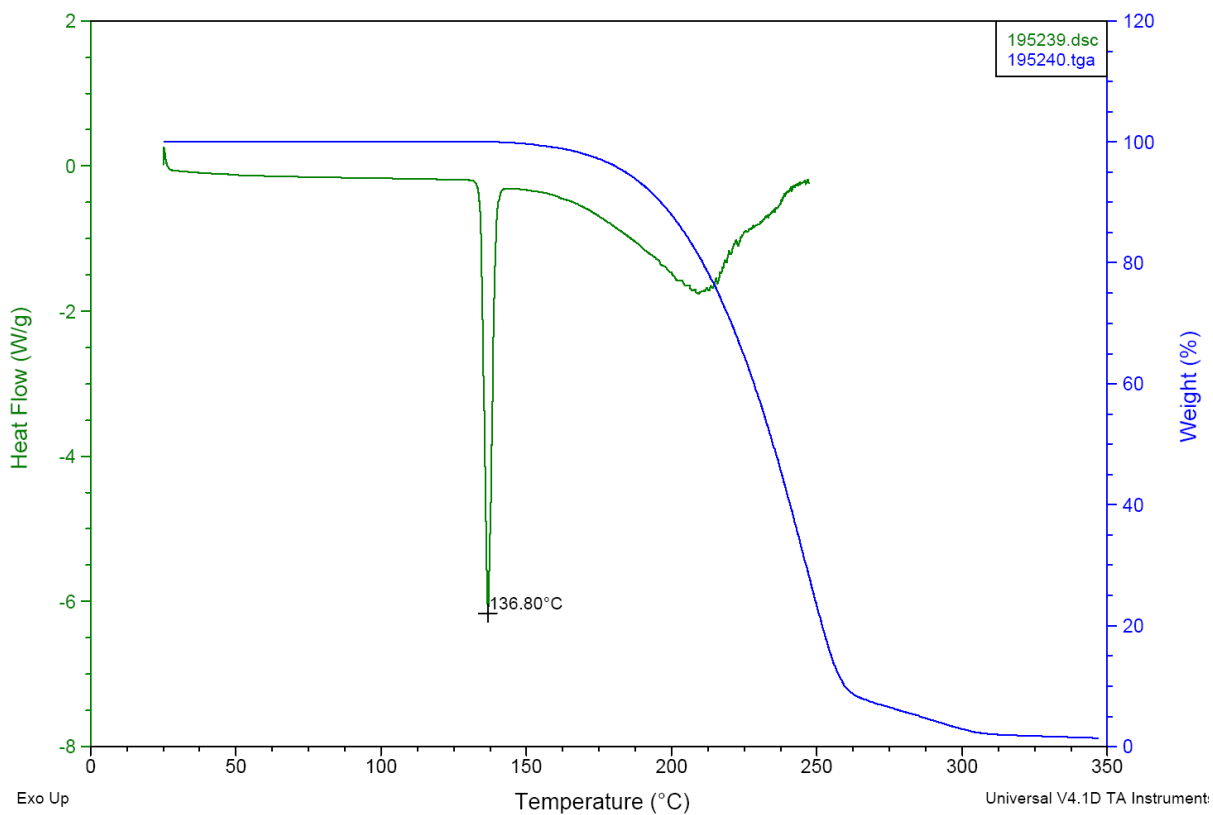
6 carbamazepine- glutaric acid cocrystal

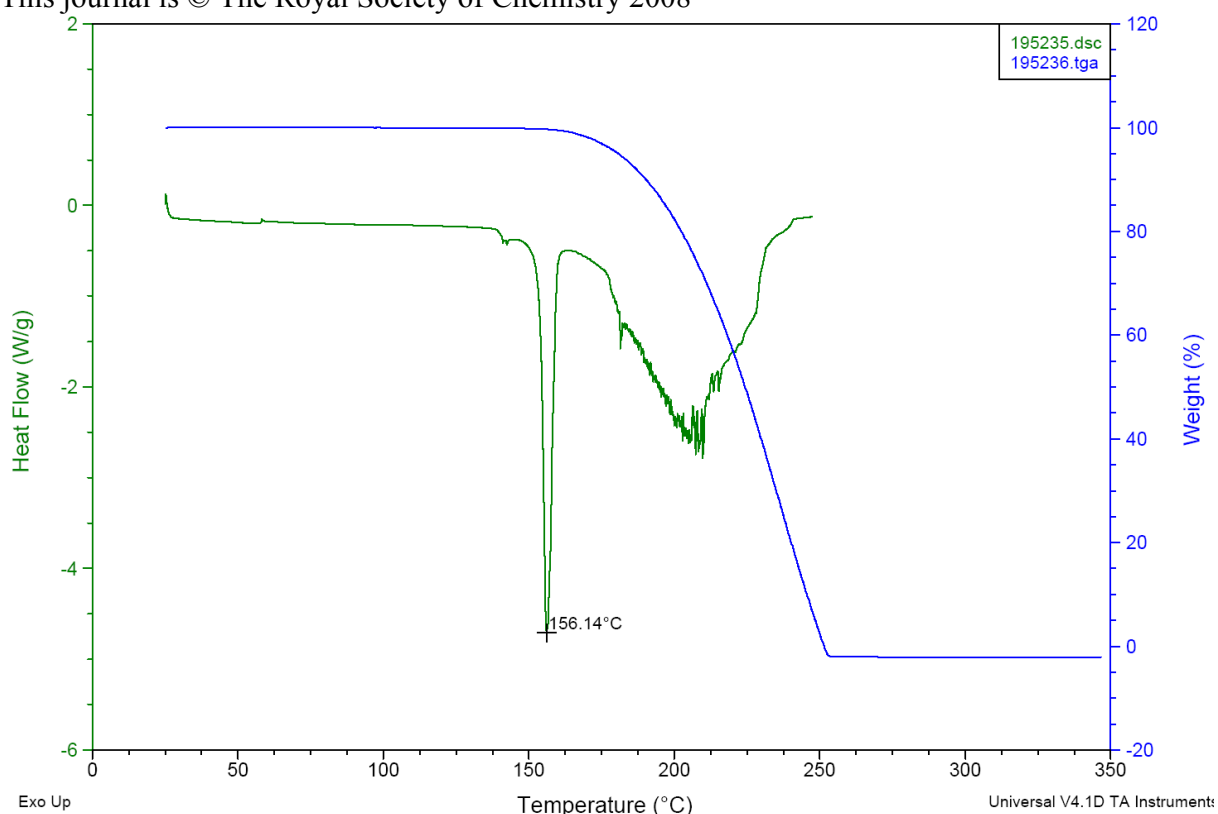




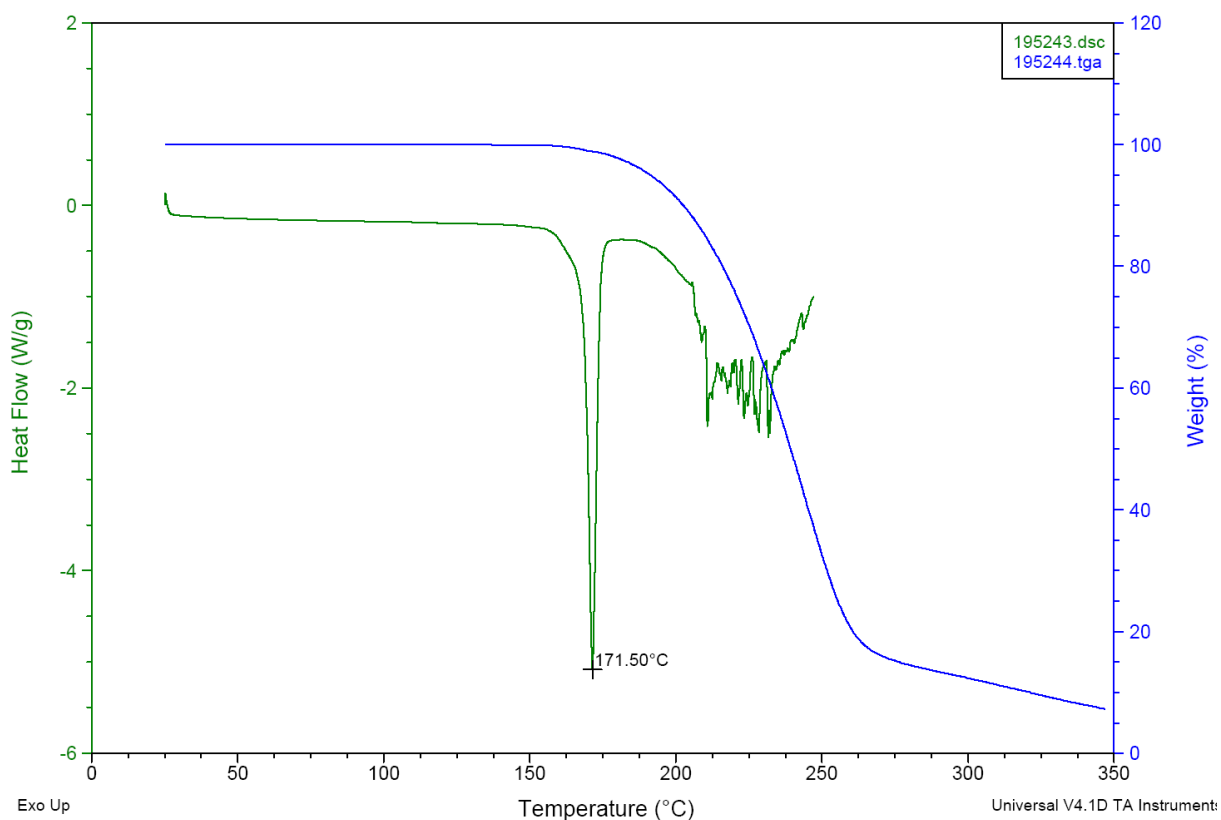
8 carbamazepine- malonic acid cocrystal, form B



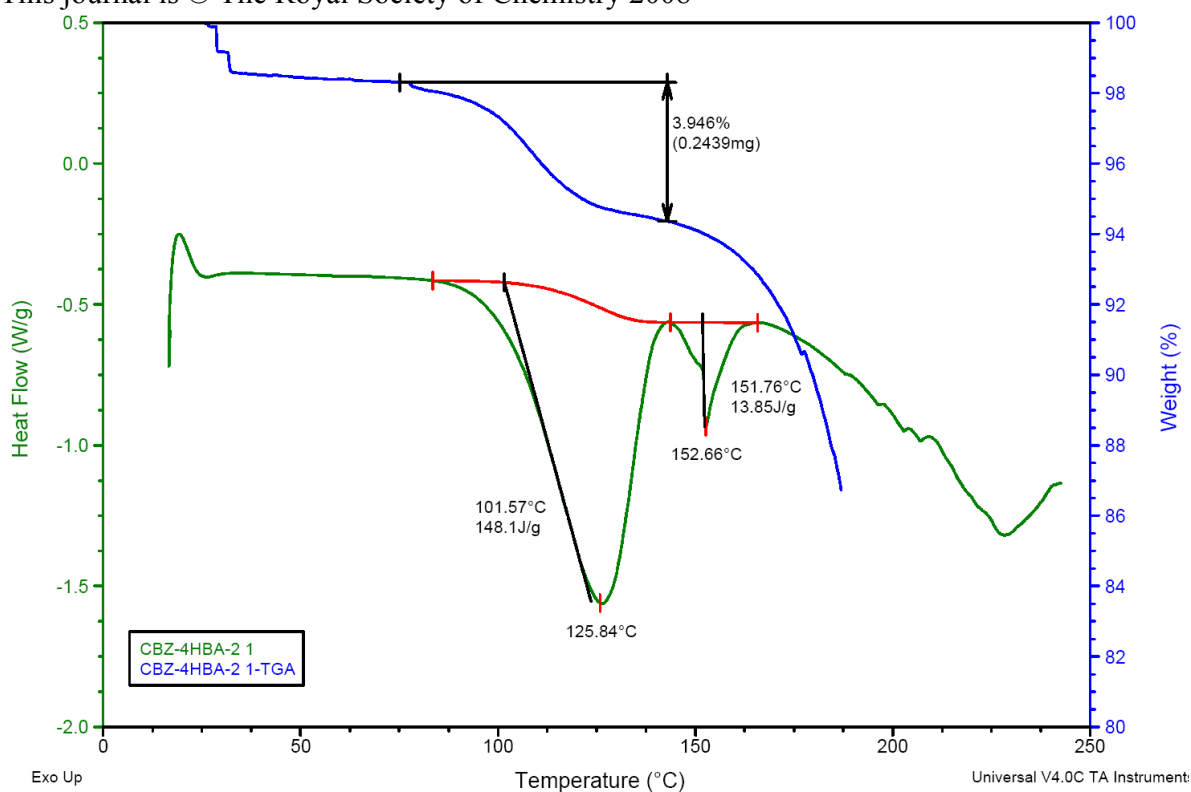




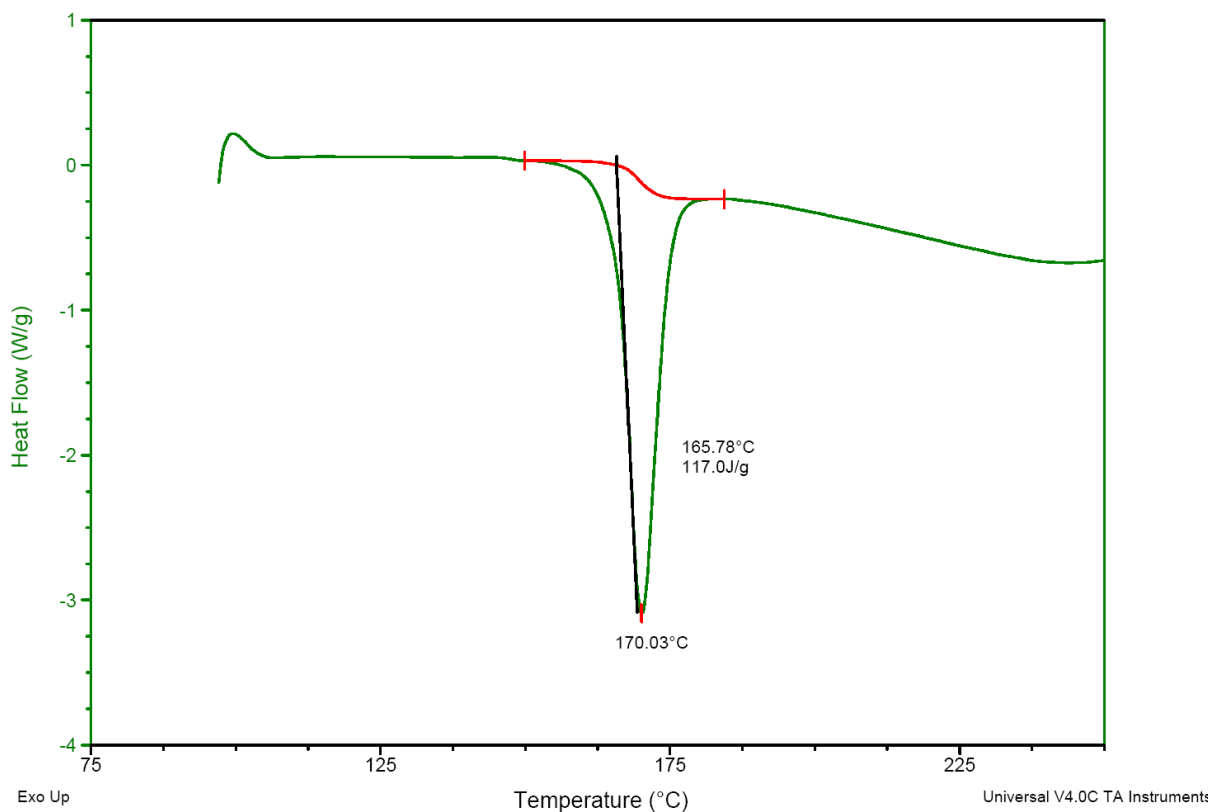
14 carbamazepine- (+)-camphoric acid cocrystal, form A



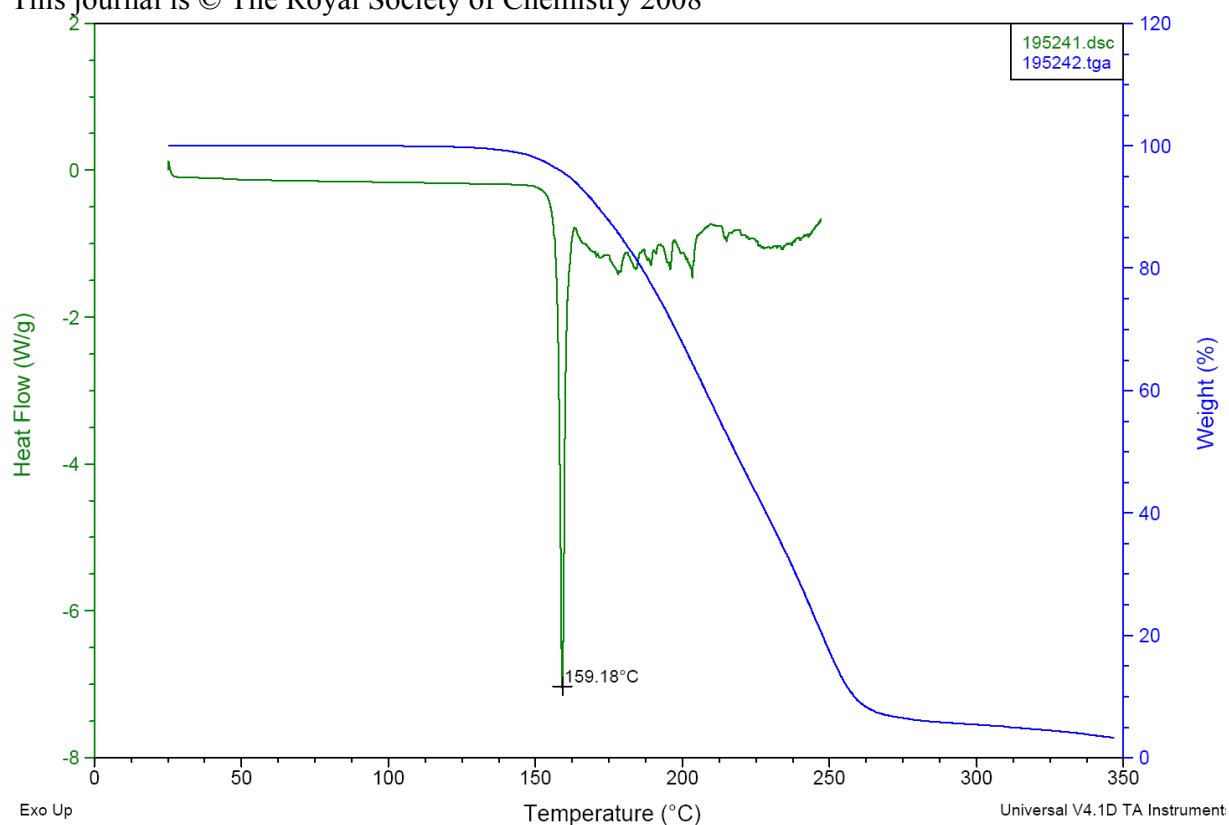
15 carbamazepine- 4-hydroxybenzoic acid cocrystal, form A



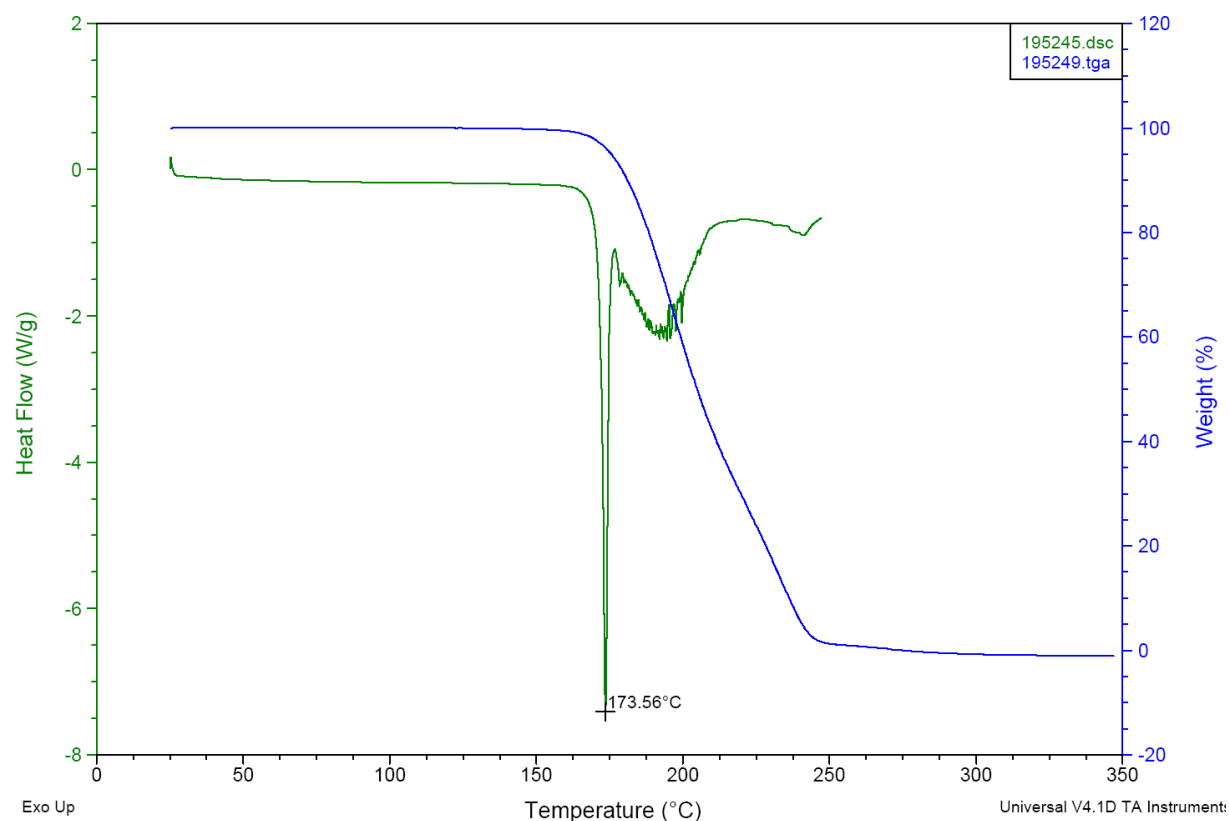
16 carbamazepine- 4-hydroxybenzoic acid cocrystal, form B



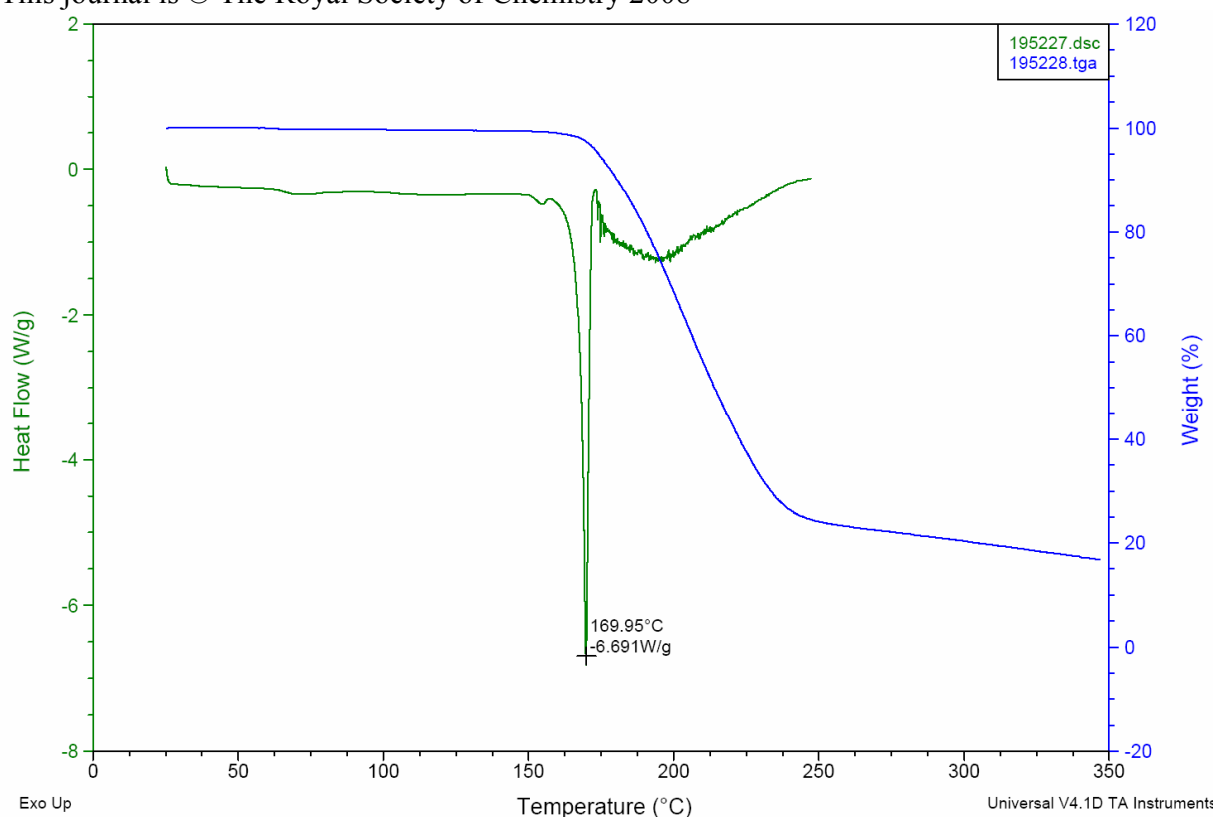
17 carbamazepine- 4-hydroxybenzoic acid cocrystal, form C



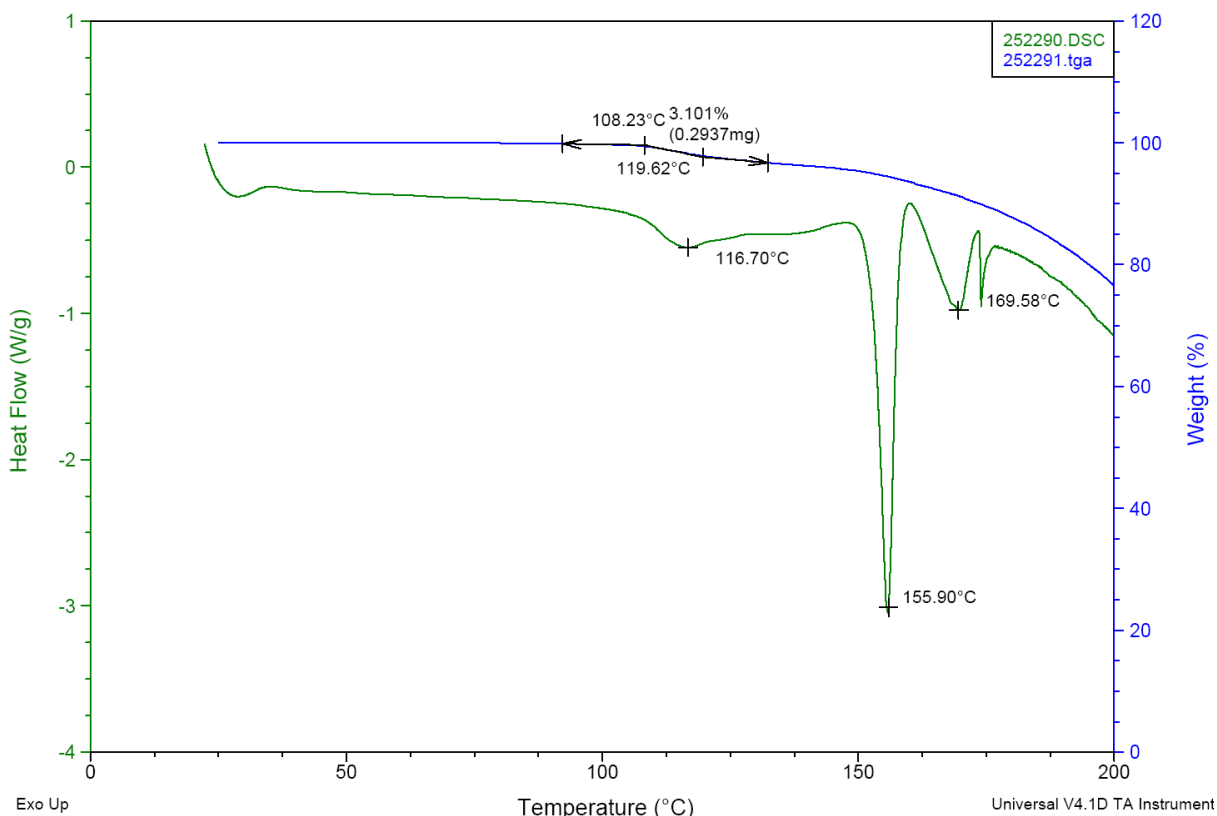
18 carbamazepine salicylic - acid cocrystal



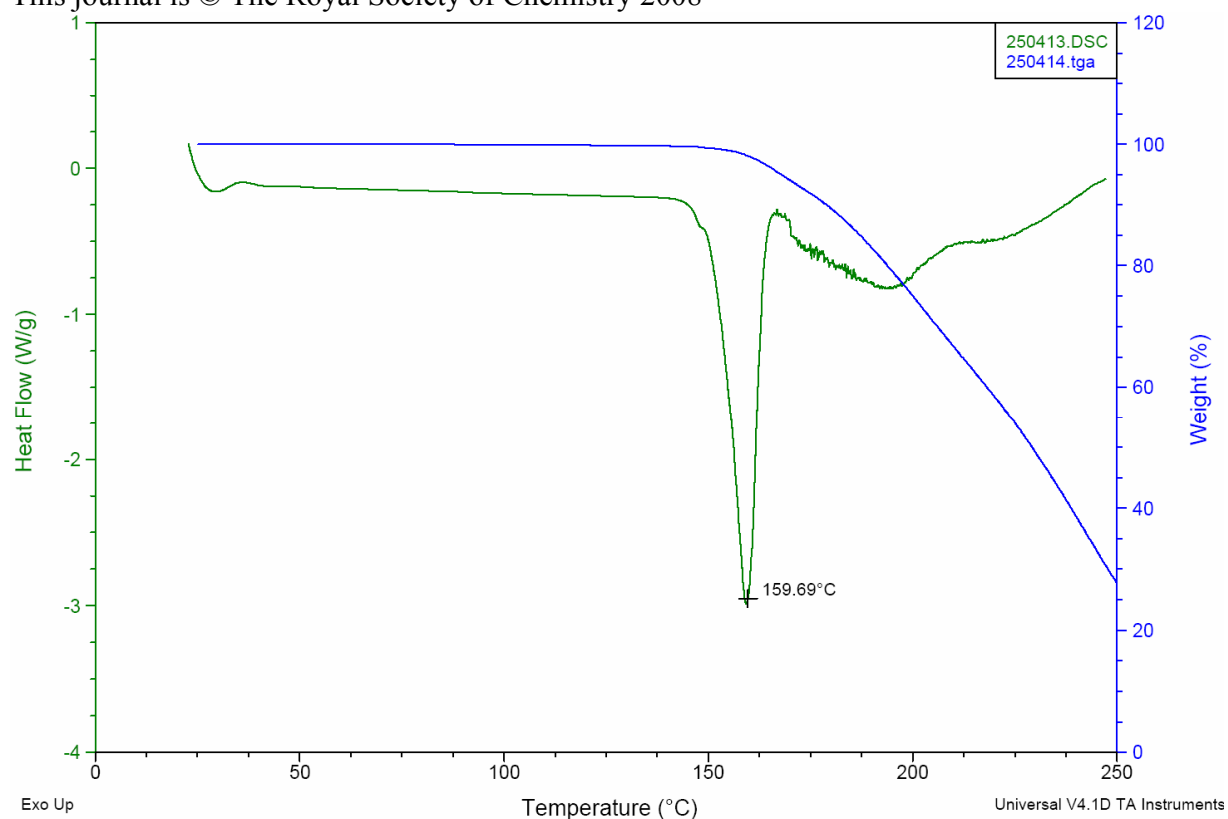
19 carbamazepine- 1-hydroxy-2-naphthoic acid cocrystal



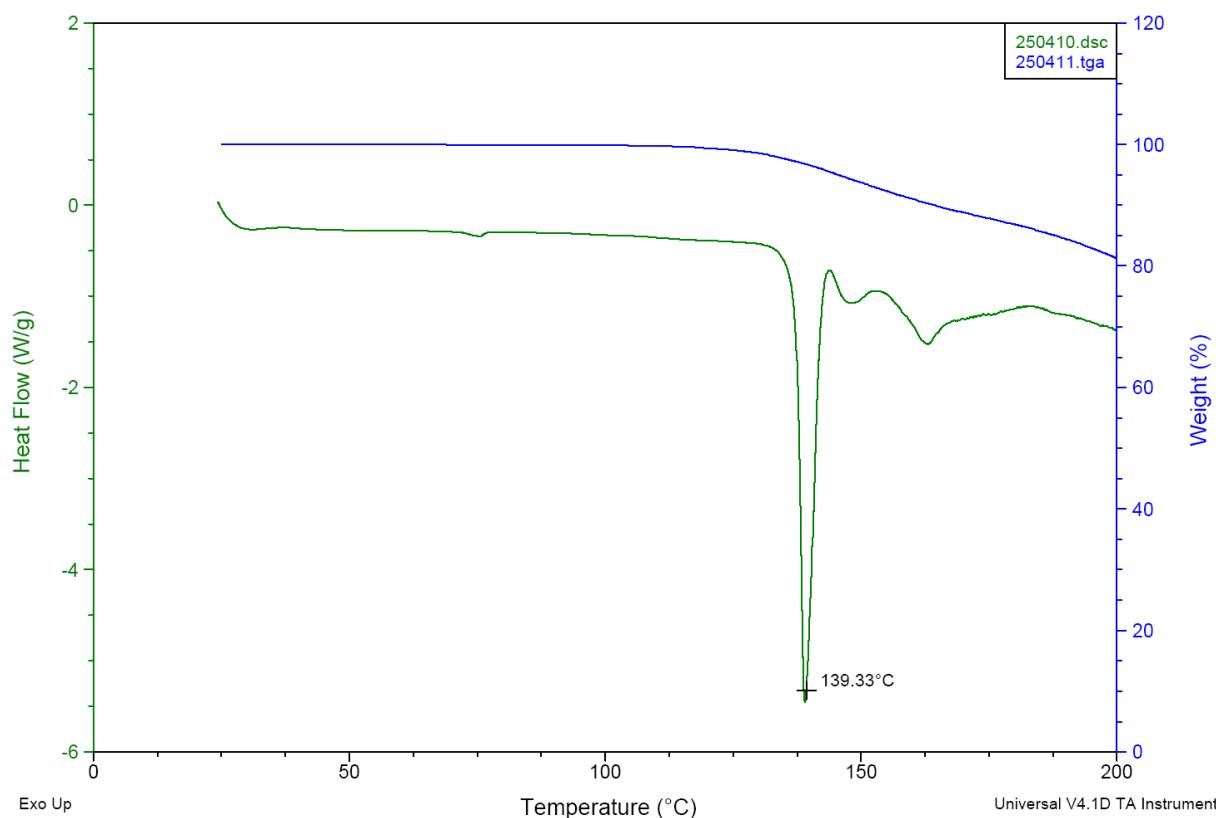
20 carbamazepine- DL-tartaric acid cocystal, form A



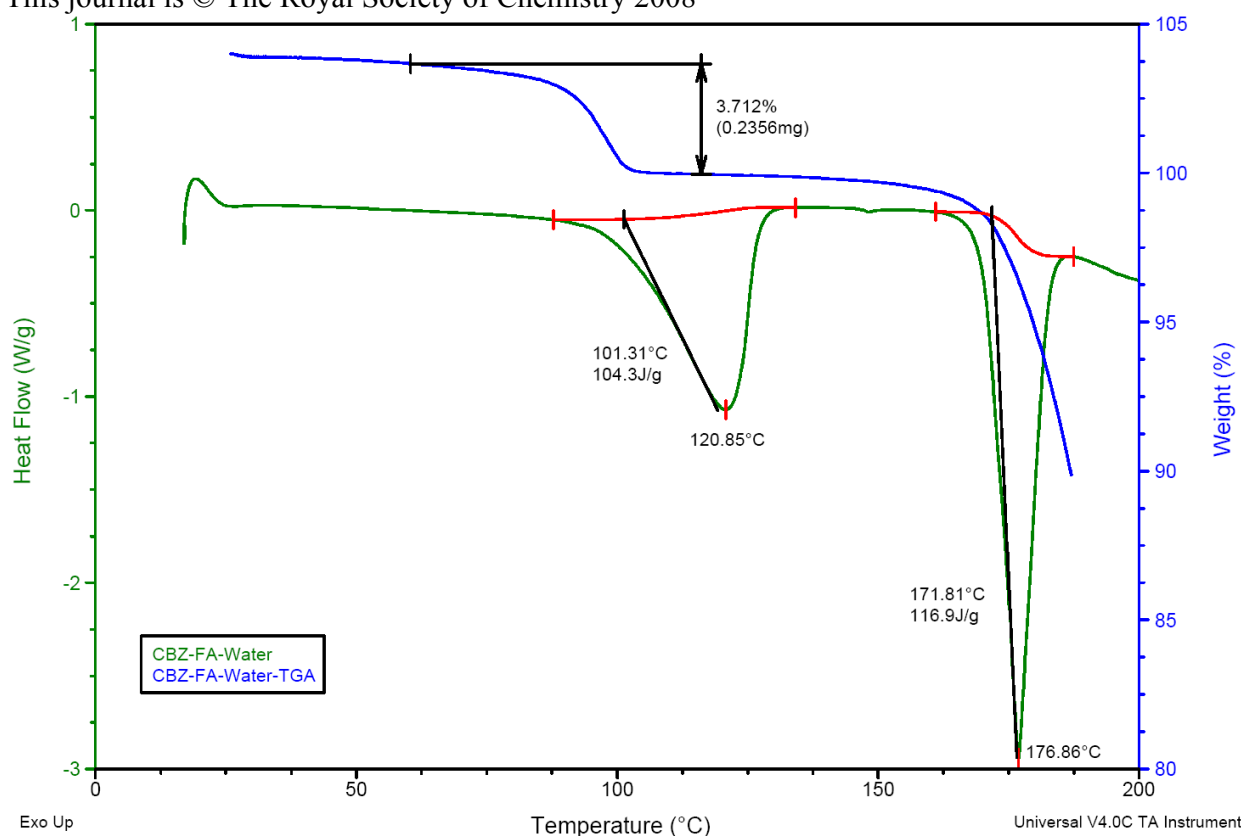
21 carbamazepine- DL-tartaric acid cocystal, form B



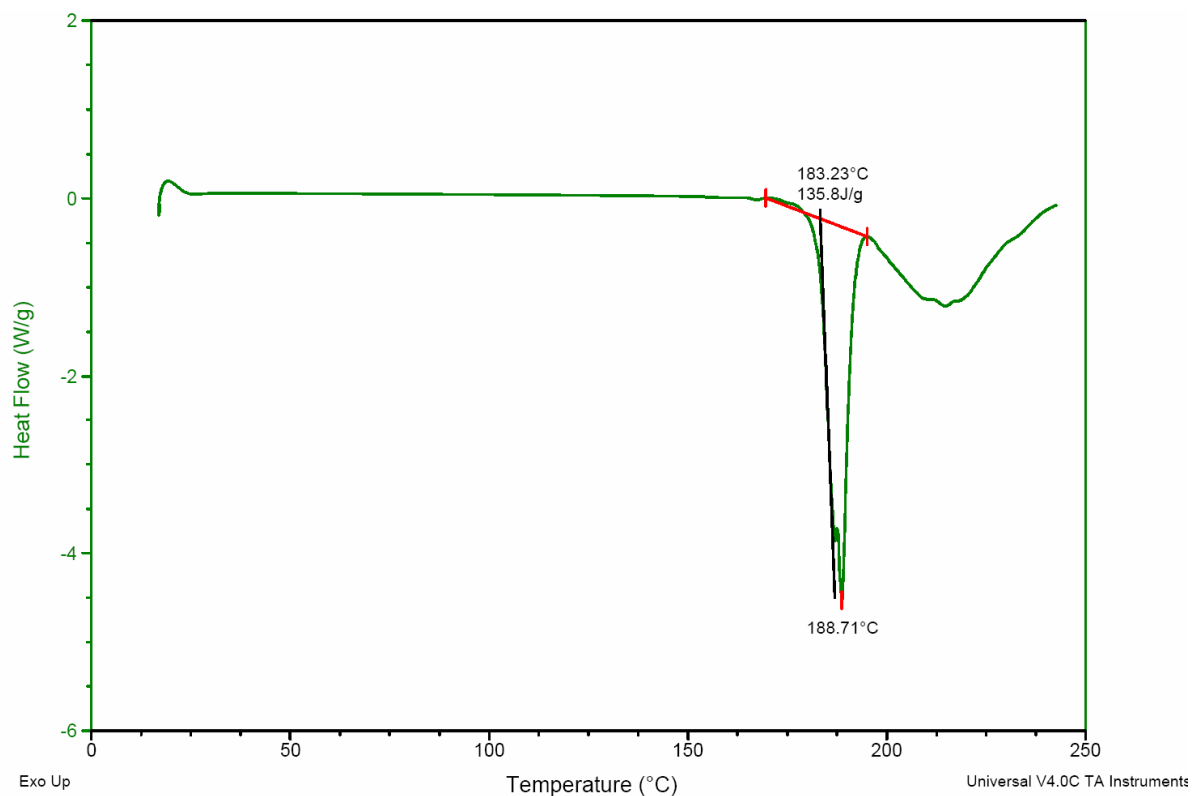
22 carbamazepine- L-tartaric acid cocrystal



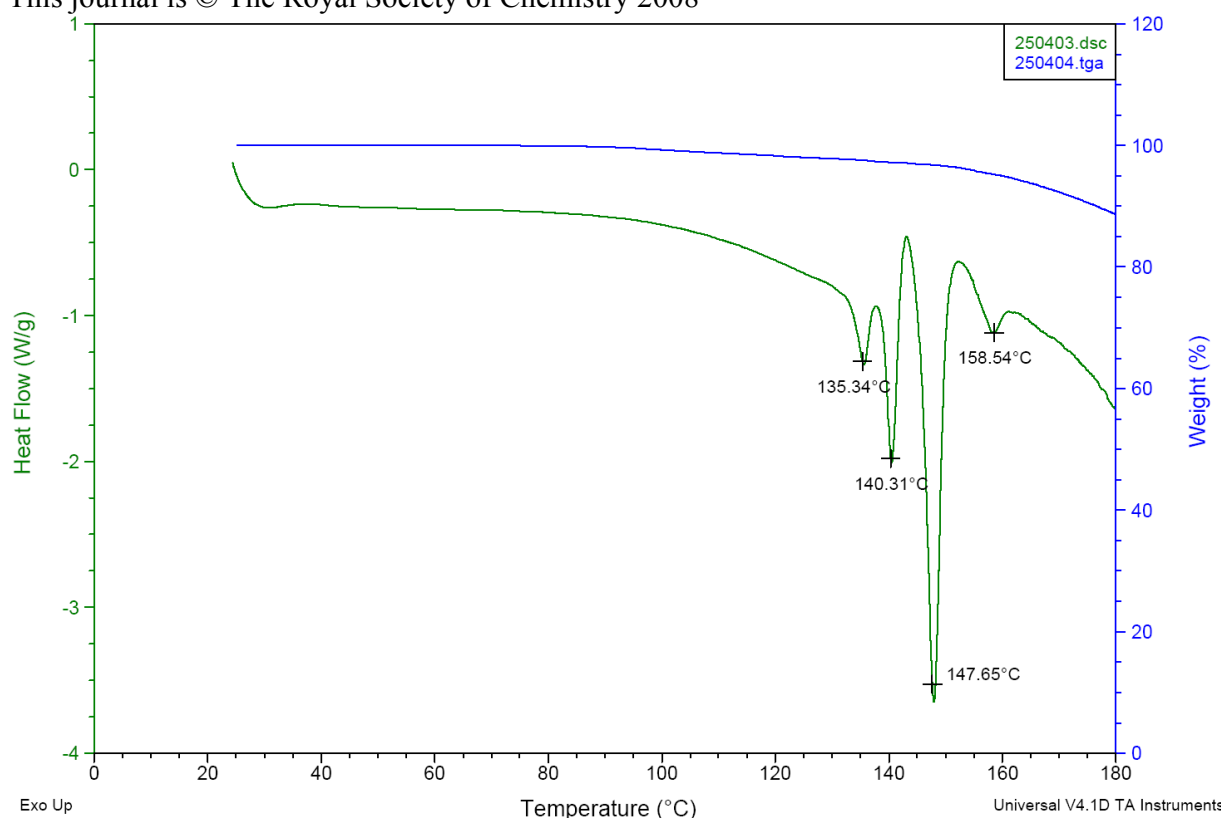
23 carbamazepine- glycolic acid cocrystal



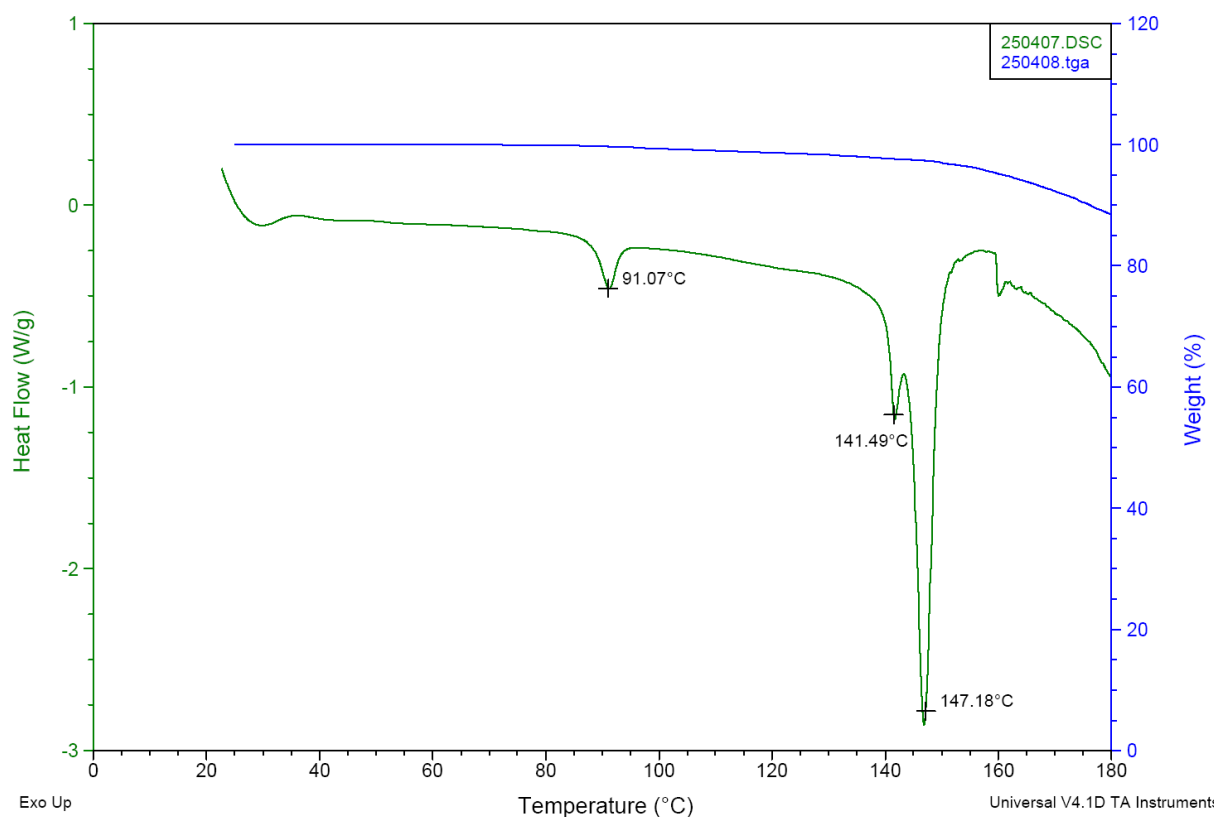
24 carbamazepine- fumaric acid cocrystal, form A



25 carbamazepine- fumaric acid cocrystal, form B



26 carbamazepine- DL-malic acid cocrystal



27 carbamazepine- L-malic acid cocrystal

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