What is claimed is:

1. A salt, which is 4,4'-(((((2,2'-dichloro-[1,1'-biphenyl]-3,3'-diyl)bis(azanediyl))bis(carbonyl))bis(1-methyl-1,4,6,7-tetrahydro-5H-imidazo[4,5-c]pyridine-2,5-diyl))bis(ethane-2,1-diyl))bis(bicyclo[2.2.1]heptane-1-carboxylic acid) di-hydrochloric acid salt.

2. The salt of claim 1, having Form I, wherein Form I has at least one X-ray powder diffraction (XRPD) peak, in terms of 2-theta (± 0.2 degrees), selected from 5.7, 8.5, 9.6, 9.9, 11.8, 12.3, 13.1, 13.4, 13.8, 14.2, 14.5, 15.4, 15.8, 16.8, 17.3 and 17.6 degrees.

3. The salt of claim 2, having an X-ray powder diffraction pattern as substantially shown in Figure 7.

4. The salt of claim 2, having a first endothermic peak with an onset temperature at 31.1 ^{o}C and a maximum at 91.4 ^{o}C, and a second endothermic peak with an onset temperature at 231.0 ^{o}C and a maximum at 236.4 ^{o}C in a differential scanning calorimetry (DSC) thermogram.

5. The salt of claim 1, having Form II, wherein Form II has at least one X-ray powder diffraction (XRPD) peak, in terms of 2-theta (± 0.2 degrees), selected from 4.6, 6.9, 8.9, 11.2, 11.7, 13.2, 13.9, 14.3, 14.8, 16.0, 16.7, 17.2, 17.9, 25.3 and 25.6 degrees.

6. The salt of claim 5, having an X-ray powder diffraction pattern as substantially shown in Figure 11.

7. The salt of claim 5, having a first endothermic peak with an onset temperature at 22.2 ^{o}C and a maximum at 89.7 ^{o}C, and a second endothermic peak with an onset temperature at 251.7 ^{o}C and a maximum at 258.3 ^{o}C in a differential scanning calorimetry (DSC) thermogram.

8. The salt of claim 1, having Form III, wherein Form III has at least one X-ray powder diffraction (XRPD) peak, in terms of 2-theta (± 0.2 degrees), selected from 9.2, 11.2, 14.9, 17.0, 17.8, 19.7, 24.4 and 25.9 degrees.

9. The salt of claim 8, having an X-ray powder diffraction pattern as substantially shown in Figure 14.

10. The salt of claim 8, having an endothermic peak with an onset temperature of 247 ± 3 ^{o}C and a maximum at 258 ± 3 ^{o}C in a differential scanning calorimetry (DSC) thermogram.

11. The salt of claim 1, having Form IV, wherein Form IV has at least one X-ray powder diffraction (XRPD) peak, in terms of 2-theta (± 0.2 degrees), selected from 5.4, 8.8, 10.9, 13.0, 15.1, 16.2, 17.5, 21.9 and 26.3 degrees.

12. The salt of claim 11, having an X-ray powder diffraction pattern as substantially shown in Figure 17.

13. The salt of claim 11, having an endothermic peak with an onset temperature of 268 ± 3 ºC and a maximum at 273 ± 3 ºC in a differential scanning calorimetry (DSC) thermogram.

14. The salt of claim 1, having Form V, wherein Form V has at least one X-ray powder diffraction (XRPD) peak, in terms of 2-theta (± 0.2 degrees), selected from 5.8, 9.1, 13.4, 14.8, 16.6, 17.1, 18.1 and 19.3 degrees.

15. The salt of claim 14, having an X-ray powder diffraction pattern as substantially shown in Figure 21.

16. The salt of claim 14, having an endothermic peak with an onset temperature of 241 ± 3 ºC and a maximum at 249 ± 3 ºC in a differential scanning calorimetry (DSC) thermogram.

17. The salt of claim 1, having Form VII, wherein Form VII has at least one X-ray powder diffraction (XRPD) peak, in terms of 2-theta (± 0.2 degrees), selected from 5.7, 9.9, 11.5, 14.1, 14.9, 17.0 and 24.4 degrees.

18. The salt of claim 17, having an X-ray powder diffraction pattern as substantially shown in Figure 29.

19. The salt of claim 17, having a first endothermic peak with an onset temperature at 44 ± 3 ºC and a maximum at 85 ± 3 ºC, and a second endothermic peak with an onset temperature at 260 ± 3 ºC and a maximum at 274 ± 3 ºC in a differential scanning calorimetry (DSC) thermogram.

20. The salt of claim 1, having Form VIII, wherein Form VIII has at least one X-ray powder diffraction (XRPD) peak, in terms of 2-theta (± 0.2 degrees), selected from 6.6, 11.2, 13.1, 14.7, 16.7, 19.0 and 24.1 degrees.

21. The salt of claim 20, having an X-ray powder diffraction pattern as substantially shown in Figure 33.

22. The salt of claim 20, having a first endothermic peak with an onset temperature at 44 ± 3 ºC and a maximum at 78 ± 3 ºC, and a second endothermic peak with an onset

temperature at 246 ± 3 ºC and a maximum at 253 ± 3 ºC in a differential scanning calorimetry (DSC) thermogram.

23. The salt of claim 1, having Form IX, wherein Form IX has at least one X-ray powder diffraction (XRPD) peak, in terms of 2-theta (± 0.2 degrees), selected from 3.8, 6.6, 10.7, 13.1, 15.3, 16.3, 17.5 and 19.1 degrees.

24. The salt of claim 23, having an X-ray powder diffraction pattern as substantially shown in Figure 37.

25. The salt of claim 23, having a first endothermic peak with an onset temperature at 43 ± 3 ºC and a maximum at 64 ± 3 ºC, and a second endothermic peak at 116 ± 3 ºC and a maximum at 132 ± 3 ºC, and a third endothermic peak at 266 ± 3 ºC and a maximum at 276 ± 3 ºC in a differential scanning calorimetry (DSC) thermogram.

26. A salt, which is 4,4'-(((((2,2'-dichloro-[1,1'-biphenyl]-3,3'-diyl)bis(azanediyl))bis(carbonyl))bis(1-methyl-1,4,6,7-tetrahydro-5H-imidazo[4,5-c]pyridine-2,5-diyl))bis(ethane-2,1-diyl))bis(bicyclo[2.2.1]heptane-1-carboxylic acid) mono-hydrochloric acid salt.

27. The salt of claim 26, having Form VI, wherein Form VI has at least one X-ray powder diffraction (XRPD) peak, in terms of 2-theta (± 0.2 degrees), selected from 6.4, 11.1, 12.6, 13.8, 14.6, 15.7, 16.9, 17.6, 19.0 and 19.5 degrees.

28. The salt of claim 27, having an X-ray powder diffraction pattern as substantially shown in Figure 25.

29. The salt of claim 27, having a first endothermic peak with an onset temperature at 44 ± 3 ºC and a maximum at 77 ± 3 ºC, and a second endothermic peak with an onset temperature at 244 ± 3 ºC and a maximum at 251 ± 3 ºC in a differential scanning calorimetry (DSC) thermogram.

30. A salt, which is 4,4'-(((((2,2'-dichloro-[1,1'-biphenyl]-3,3'-diyl)bis(azanediyl))bis(carbonyl))bis(1-methyl-1,4,6,7-tetrahydro-5H-imidazo[4,5-c]pyridine-2,5-diyl))bis(ethane-2,1-diyl))bis(bicyclo[2.2.1]heptane-1-carboxylic acid) di-sodium salt.

31. The salt of claim 30, having an X-ray powder diffraction pattern as substantially shown in Figure 4.

32. The salt of claim 30, having at least one X-ray powder diffraction (XRPD) peak, in terms of 2-theta (± 0.2 degrees), selected from 5.3, 7.1, 10.6, 13.9, 14.3, 16.1 and 17.4 degrees.

33. The salt of claim 30, having a first endothermic peak with an onset temperature of 47 ± 3 ºC and a maximum at 108 ± 3 ºC and a second endothermic peak with an onset temperature of 258 ± 3 ºC and a maximum at 280 ± 3 ºC in a differential scanning calorimetry (DSC) thermogram.

34. A solid form of 4,4'-(((((2,2'-dichloro-[1,1'-biphenyl]-3,3'-diyl)bis(azanediyl))bis(carbonyl))bis(1-methyl-1,4,6,7-tetrahydro-5H-imidazo[4,5-c]pyridine-2,5-diyl))bis(ethane-2,1-diyl))bis(bicyclo[2.2.1]heptane-1-carboxylic acid), wherein the solid form is crystalline.

35. The solid form of claim 34, having an X-ray powder diffraction pattern as substantially shown in Figure 1.

36. The solid form of claim 34, having at least one X-ray powder diffraction (XRPD) peak, in terms of 2-theta (± 0.2 degrees), selected from 6.2, 10.9, 11.3, 12.4, 13.7, 14.5, 15.5, 17.5, and 18.8 degrees.

37. The solid form of claim 34, having a first endothermic peak with an onset temperature of 33 ± 3 ºC and a maximum at 70 ± 3 ºC and a second endothermic peak with an onset temperature of 244 ± 3 ºC and a maximum at 250 ± 3 ºC in a differential scanning calorimetry (DSC) thermogram.

38. A pharmaceutical composition comprising a salt of any one of claims 1-33 or a solid form of any one of claims 34-37, and a pharmaceutically acceptable carrier or excipient.

39. A solid oral dosage form comprising the pharmaceutical composition of claim 38.

40. Use of a salt of any one of claims 1-33 or a solid form of any one of claims 34-37, in the manufacture of a medicament for inhibiting PD-1/PD-L1 interaction.

41. Use of a salt of any one of claims 1-33 or a solid form of any one of claims 34-37, in the manufacture of a medicament for treating a disease or disorder associated with inhibition of PD-1/PD-L1 interaction.

42. The use according to claim 41, wherein the disease or disorder is cancer or an infection.

43. The use according to claim 42, wherein the disease or disorder is cancer, and the cancer is a metastatic cancer that expresses PD-L1, lung cancer, non-small cell lung cancer, hepatic cancer, melanoma, cancer of the bladder, cancer of the urethra, renal cancer, or clear cell carcinoma.

44. Use of a salt of any one of claims 1-33 or a solid form of any one of claims 34-37, in the manufacture of a medicament for enhancing, stimulating and/or increasing the immune response in a patient.

45. A process of preparing the salt of claim 1, comprising reacting said Compound 1 with at least two equivalents of hydrochloric acid.

46. A process of preparing the salt of any one of claims 2-4, comprising:

a) preparing a suspension of Compound 1 and at least 2 equivalents of hydrochloric acid in a solvent comprising acetone;

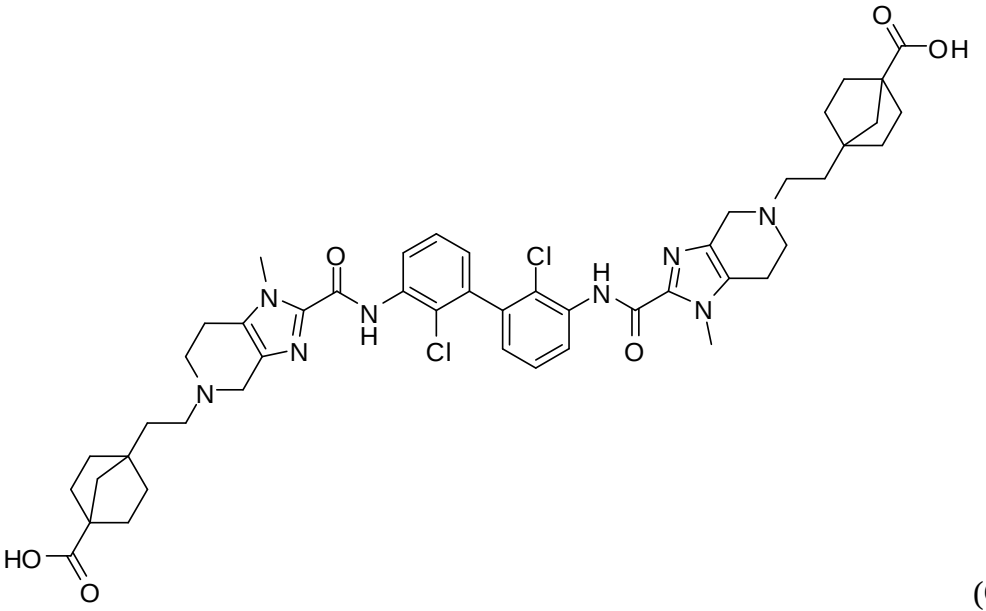
b) heating the suspension of a) to above room temperature to form a clear solution;

c) cooling the clear solution of b) to about room temperature;

d) adding a solvent comprising acetone to the mixture of c) to form a cloudy solution; and

e) filtering the cloudy solution of d) to provide said Form I as a solid.

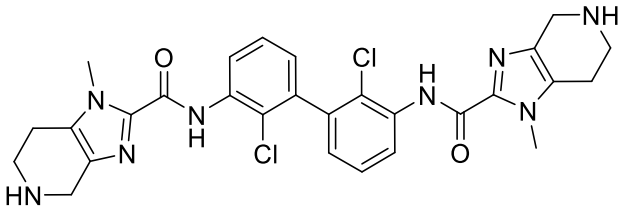
47. A process of preparing Compound 1:



(Compound 1)

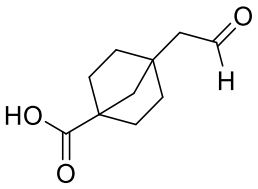
or a salt thereof, comprising:

reacting Compound 5-6:



(Compound 5-6)

with 4-(2-oxoethyl)bicyclo[2.2.1]heptane-1-carboxylic acid (Compound 5-4):

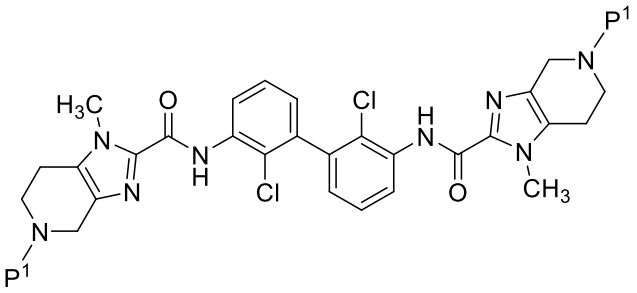


(Compound 5-4)

in the presence of a reducing agent to form said Compound 1, or a salt thereof.

48. The process of claim 47, wherein said Compound 5-6 is prepared by a process comprising:

deprotecting Compound 5-3a:

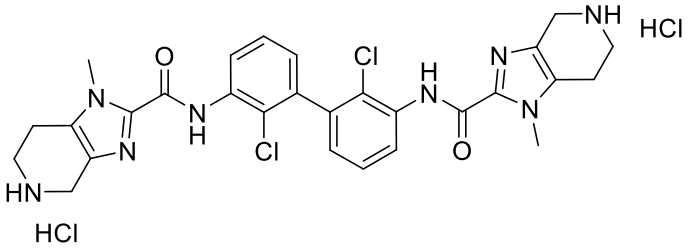


(Compound 5-3a)

to form said Compound 5-6, wherein P^1 is an amine protecting group.

49. The process of claim 48, wherein the deprotecting comprises:

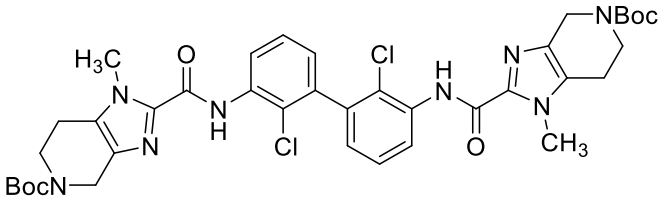
reacting said Compound 5-3a with hydrochloric acid in a solvent to form Compound 5-5:



(Compound 5-5); and

neutralizing said Compound 5-5 with base to form said Compound 5-6.

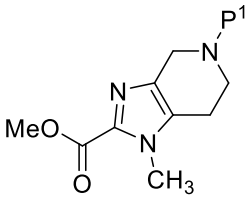
50. The process of claim 48 or 49, wherein said Compound 5-3a is Compound 5-3:



(Compound 5-3)

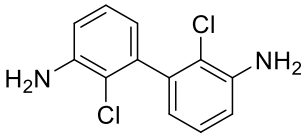
51. The process of claim 48 or 49, wherein said Compound 5-3a is prepared by a process comprising:

reacting Compound 5-2a:



(Compound 5-2a)

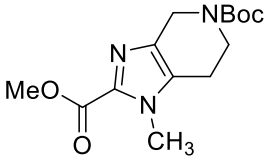
with Compound 5-1:



(Compound 5-1)

in the presence of a base in a solvent to form said Compound 5-3a, wherein P^1 is an amine protecting group.

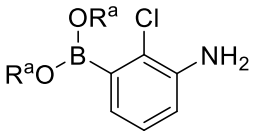
52. The process of claim 51, wherein said Compound 5-2a is Compound 5-2:



(Compound 5-2).

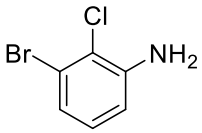
53. The process of claim 51 or 52, wherein said Compound 5-1 is prepared by a process comprising:

reacting Compound 6-1a:



(Compound 6-1a)

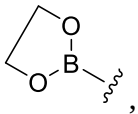
with Compound 2-3:



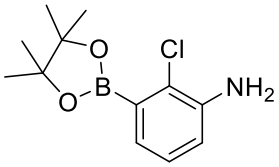
(Compound 2-3)

in the presence of a Suzuki catalyst and a base in a solvent to form said Compound 5-1, wherein:

each R^a is independently selected from H and C_{1-6} alkyl; or

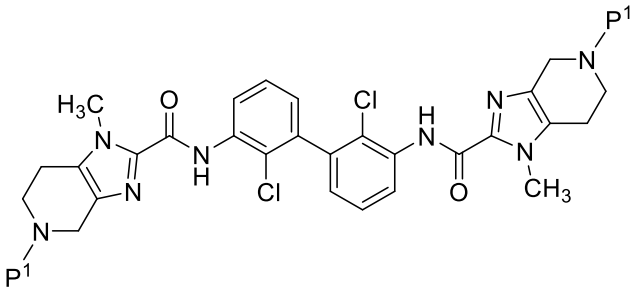
each R^a, together with the oxygen atoms to which they are attached and the boron atom to which the oxygen atoms are attached, form a ring of formula , which is optionally substituted with 1, 2, 3, or 4 C_{1-4} alkyl groups.

54. The process of claim 53, wherein said Compound 6-1a is Compound 6-1:

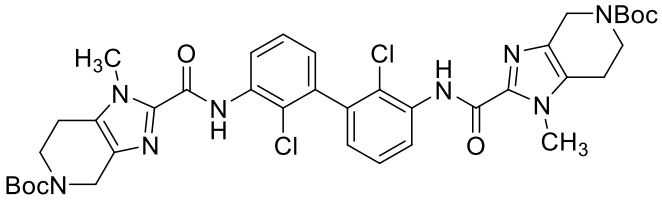


(Compound 6-1).

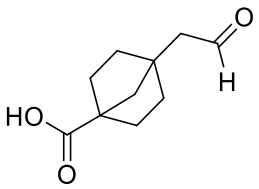
55. A compound selected from Compound 5-3a, Compound 5-3, Compound 5-4, and Compound 5-1:



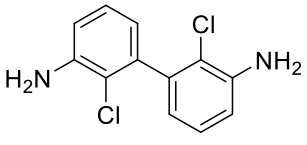
(Compound 5-3a)



(Compound 5-3)



(Compound 5-4)



(Compound 5-1)

or a salt thereof.