

Supplementary Materials: Expedient Organocatalytic Syntheses of 4-Substituted Pyrazolidines and Isoxazolidines

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NMR spectra and chiral HPLC traces for compounds 3, 5, 8aa–8bc, 9aa–9bc, 11a–11c and 12a–12c.

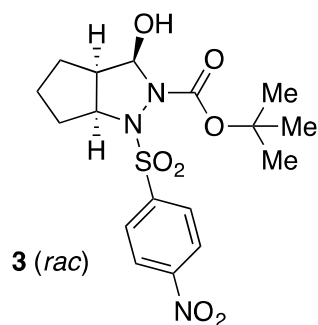


Figure S1. *tert*-Butyl (3*RS*,3*aRS*,6*aSR*)-3-Hydroxy-1-((4-nitrophenyl)sulfonyl) hexahydrocyclopenta [c] pyrazole-2(1*H*)-carboxylate, **3**.

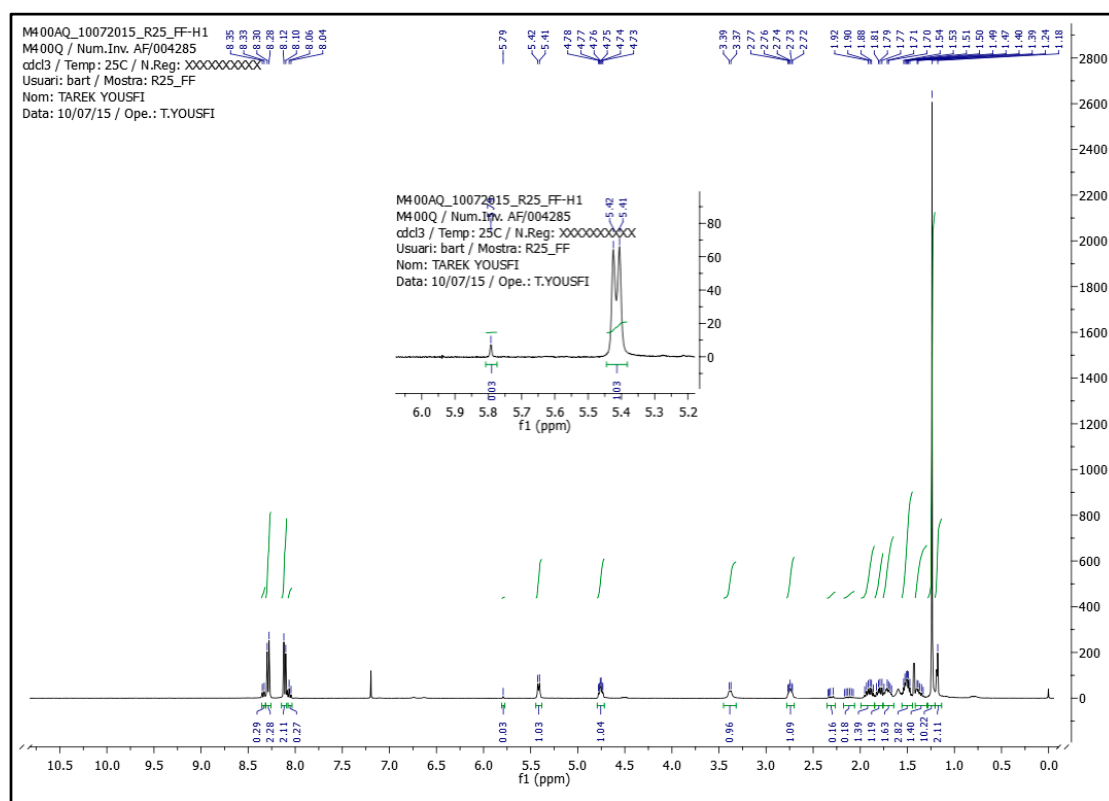


Figure S2. $^1\text{H-NMR}$ (400 MHz) of *tert*-Butyl (3*RS*,3*aRS*,6*aSR*)-3-Hydroxy-1-((4-nitrophenyl)sulfonyl) hexahydrocyclopenta [c] pyrazole-2(1*H*)-carboxylate, **3**.

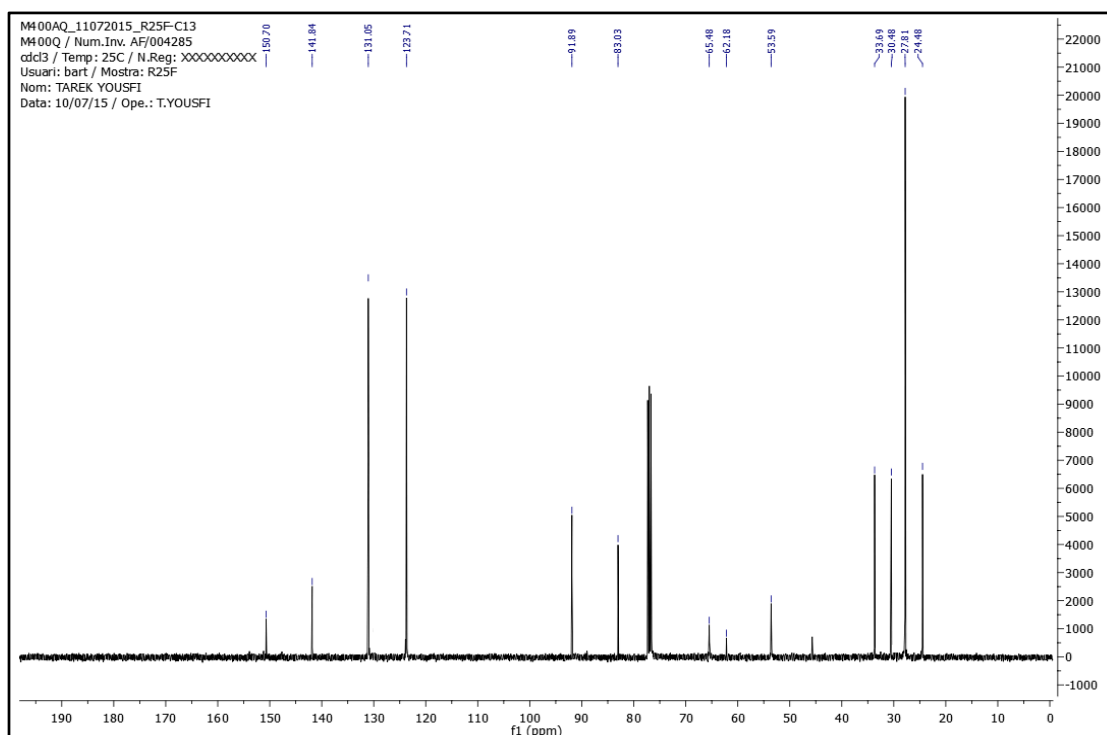


Figure S3. ^{13}C -NMR (100.6 MHz) of *tert*-Butyl (3*RS*,3*aRS*,6*aSR*)-3-Hydroxy-1-((4-nitrophenyl)sulfonyl) hexahydrocyclopenta [c] pyrazole-2(1*H*)-carboxylate, **3**.

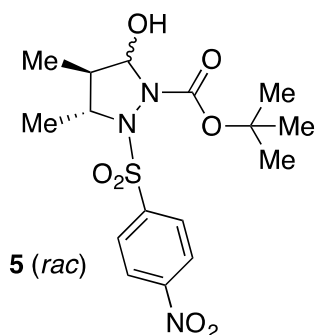


Figure S4. *tert*-Butyl 3,4-*trans*-5-Hydroxy-3,4-dimethyl-2-((4-nitrophenyl)sulfonyl)-pyrazolidine-1-carboxylate, **5**.

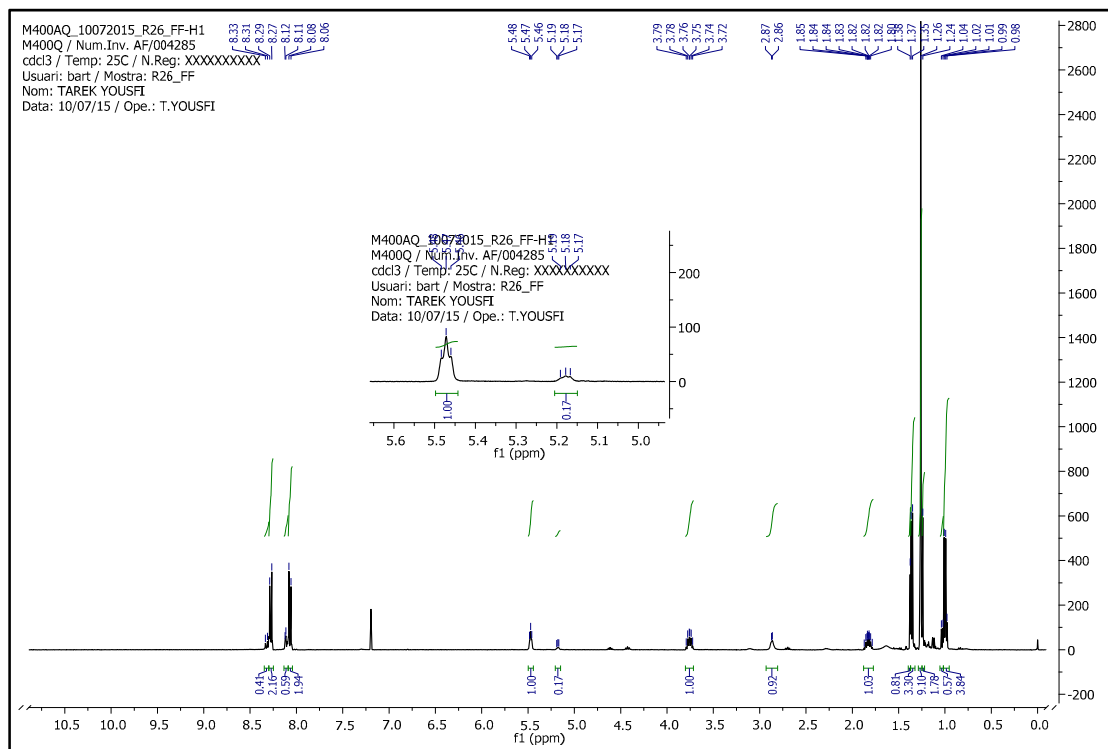


Figure S5. $^1\text{H-NMR}$ (400 MHz) of *tert*-Butyl 3,4-*trans*-5-Hydroxy-3,4-dimethyl-2-((4-nitrophenyl)sulfonyl)-pyrazolidine-1-carboxylate, 5.

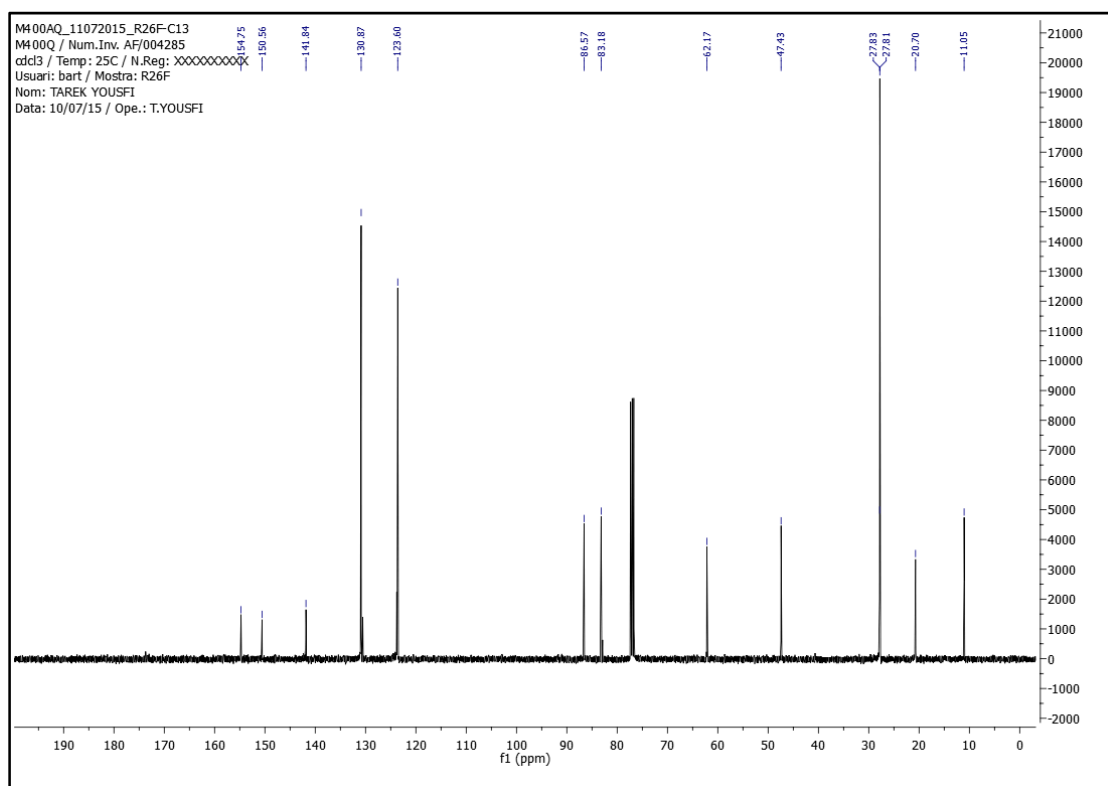


Figure S6. $^{13}\text{C-NMR}$ (100.6 MHz) of *tert*-Butyl 3,4-*trans*-5-Hydroxy-3,4-dimethyl-2-((4-nitrophenyl)sulfonyl)-pyrazolidine-1-carboxylate, 5.

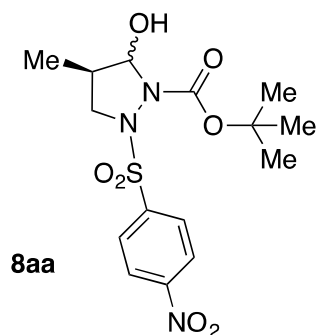


Figure S7. *tert*-Butyl 5-Hydroxy-4-methyl-2-((4-nitrophenyl)sulfonyl)-pyrazolidine-1-carboxylate, **8aa**.

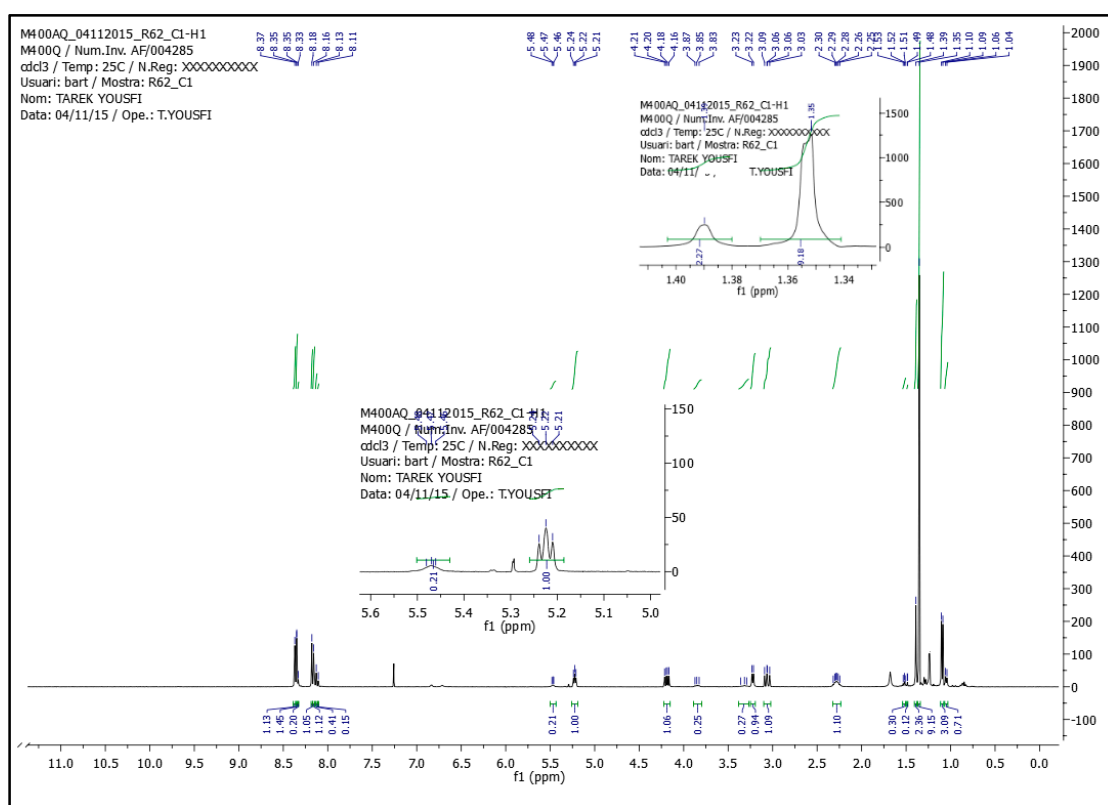


Figure S8. $^1\text{H-NMR}$ (400 MHz) of *tert*-Butyl 5-Hydroxy-4-methyl-2-((4-nitrophenyl)sulfonyl)-pyrazolidine-1-carboxylate, **8aa**.

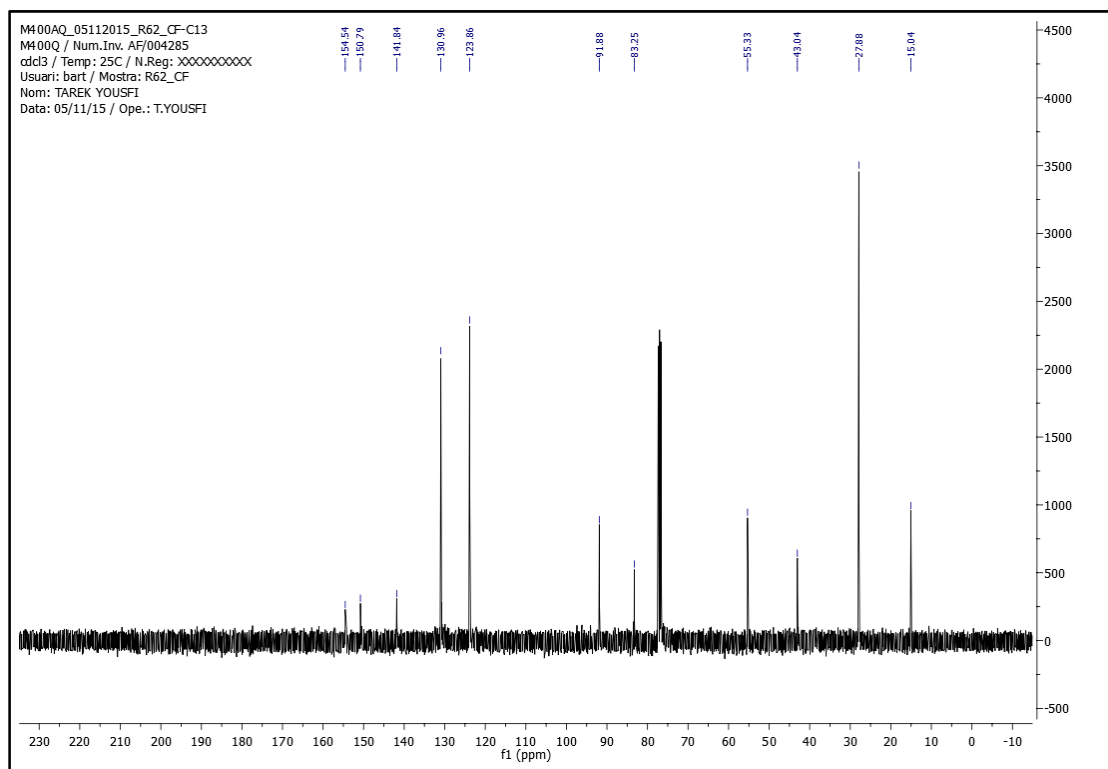


Figure S9. ¹³C-NMR (100.6 MHz) of *tert*-Butyl 5-Hydroxy-4-methyl-2-((4-nitrophenyl)sulfonyl)pyrazolidine-1-carboxylate, **8aa**.

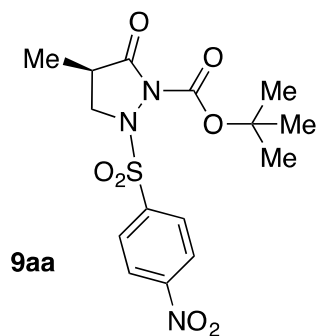


Figure S10. (-)-*tert*-Butyl 4-Methyl-2-((4-nitrophenyl)sulfonyl)pyrazolidin-5-one-1-carboxylate, **9aa**.

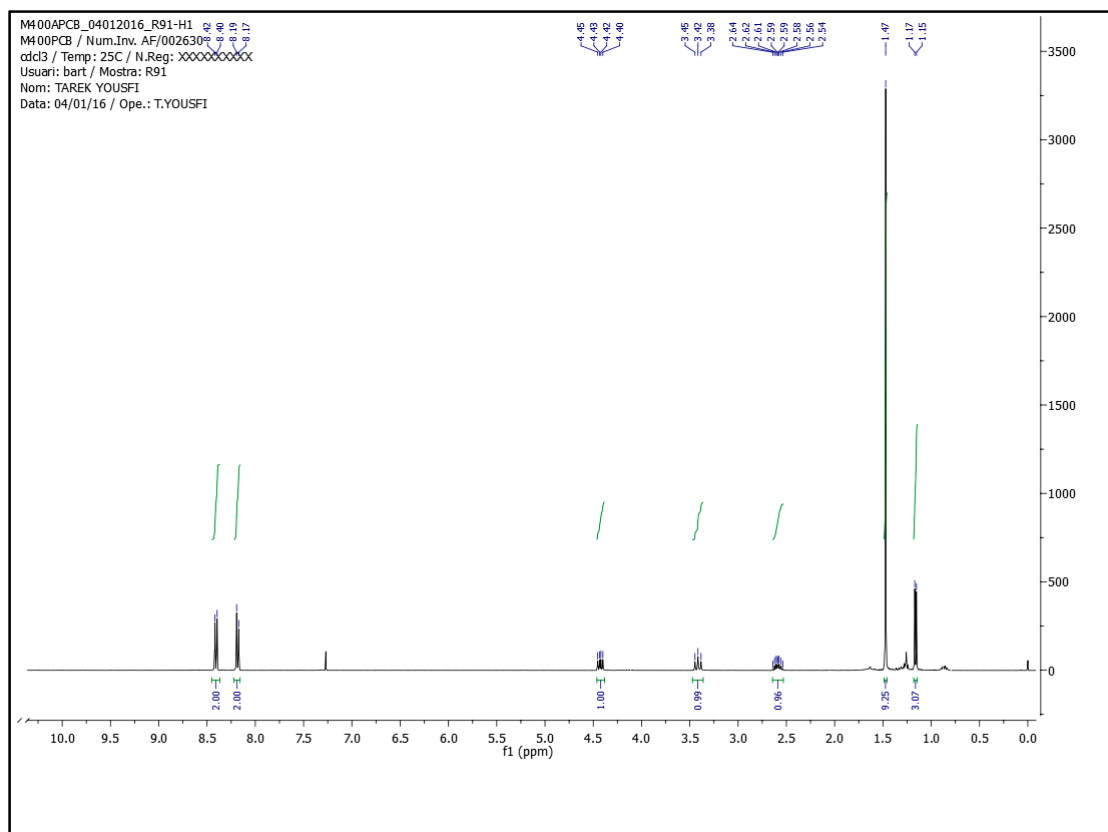


Figure S11. $^1\text{H-NMR}$ (400 MHz) of *(-)-tert*-Butyl 4-Methyl-2-((4-nitrophenyl)sulfonyl)-pyrazolidin-5-one-1-carboxylate, **9aa**.

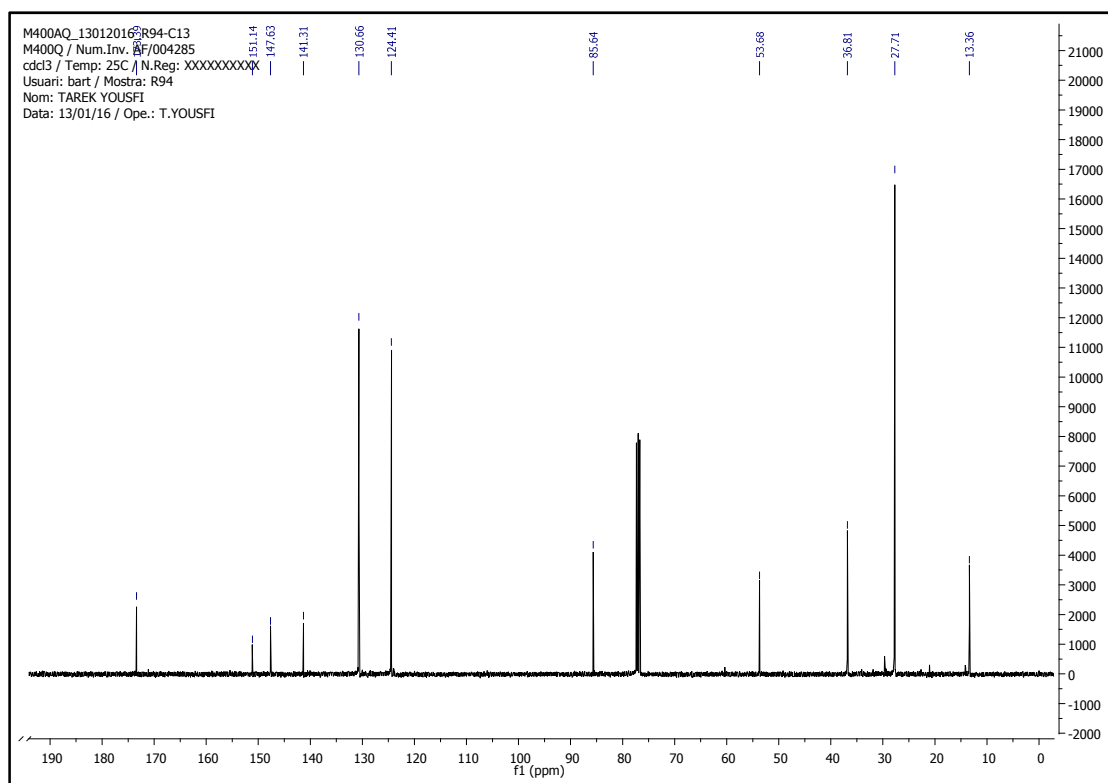


Figure S12. $^{13}\text{C-NMR}$ (100.6 MHz) of *(-)-tert*-Butyl 4-Methyl-2-((4-nitrophenyl)sulfonyl)-pyrazolidin-5-one-1-carboxylate, **9aa**.

HPLC (Chiralpak® IC column, 90:10 hexane/isopropyl alcohol, 1 µL/min, λ = 254 nm, 25 °C).

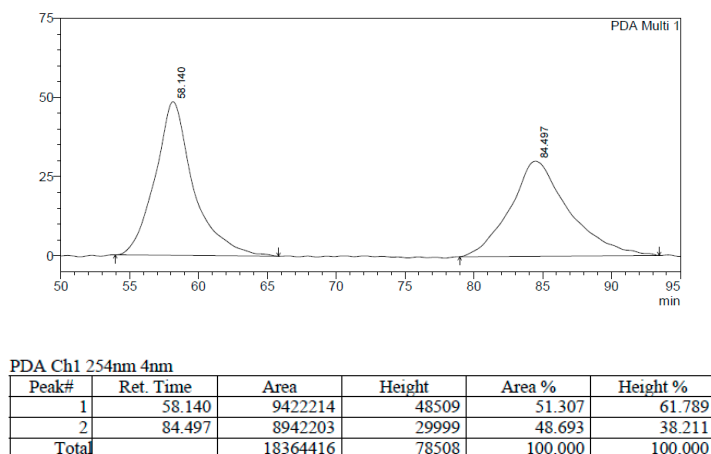


Figure S13. *rac*-9aa.

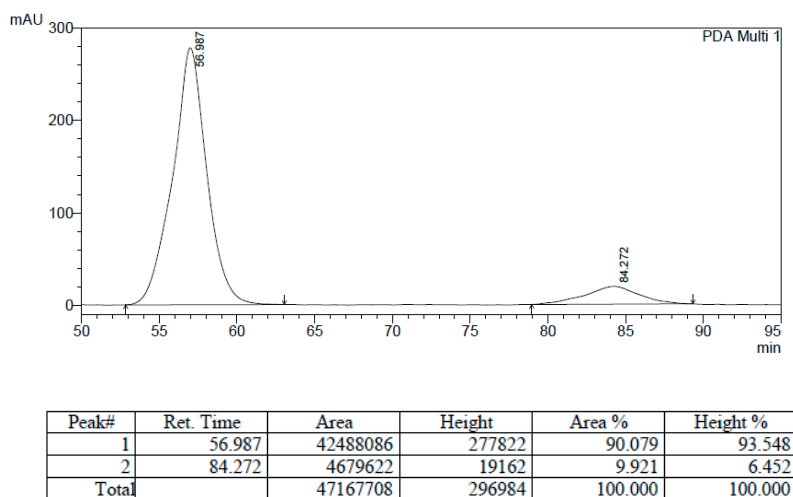


Figure S14. (-)-9aa.

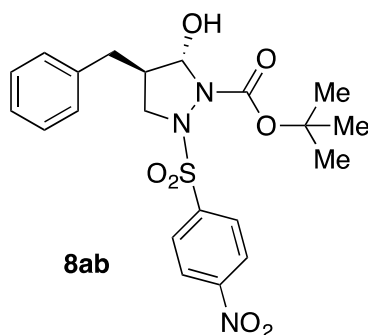


Figure S15. *tert*-Butyl 4-Benzyl-5-hydroxy-2-((4-nitrophenyl)sulfonyl)-pyrazolidine-1-carboxylate, **8ab**.

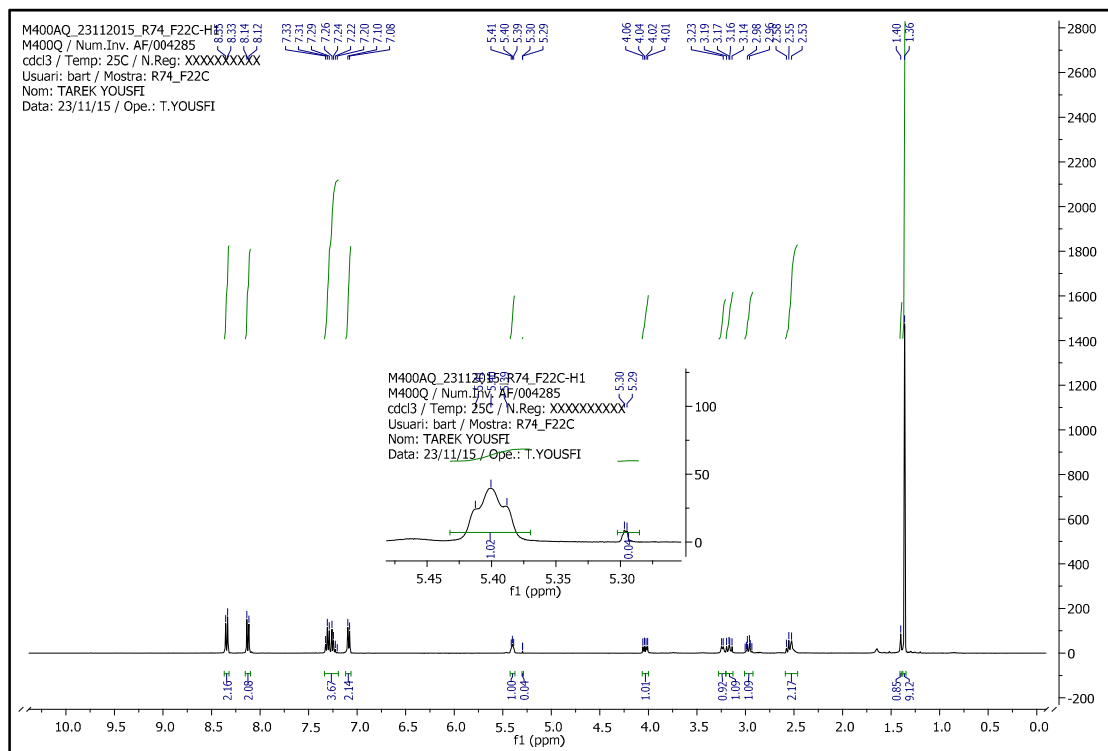


Figure S16. $^1\text{H-NMR}$ (400 MHz) of *tert*-Butyl 4-Benzyl-5-hydroxy-2-((4-nitrophenyl)sulfonyl)pyrazolidine-1-carboxylate, **8ab**.

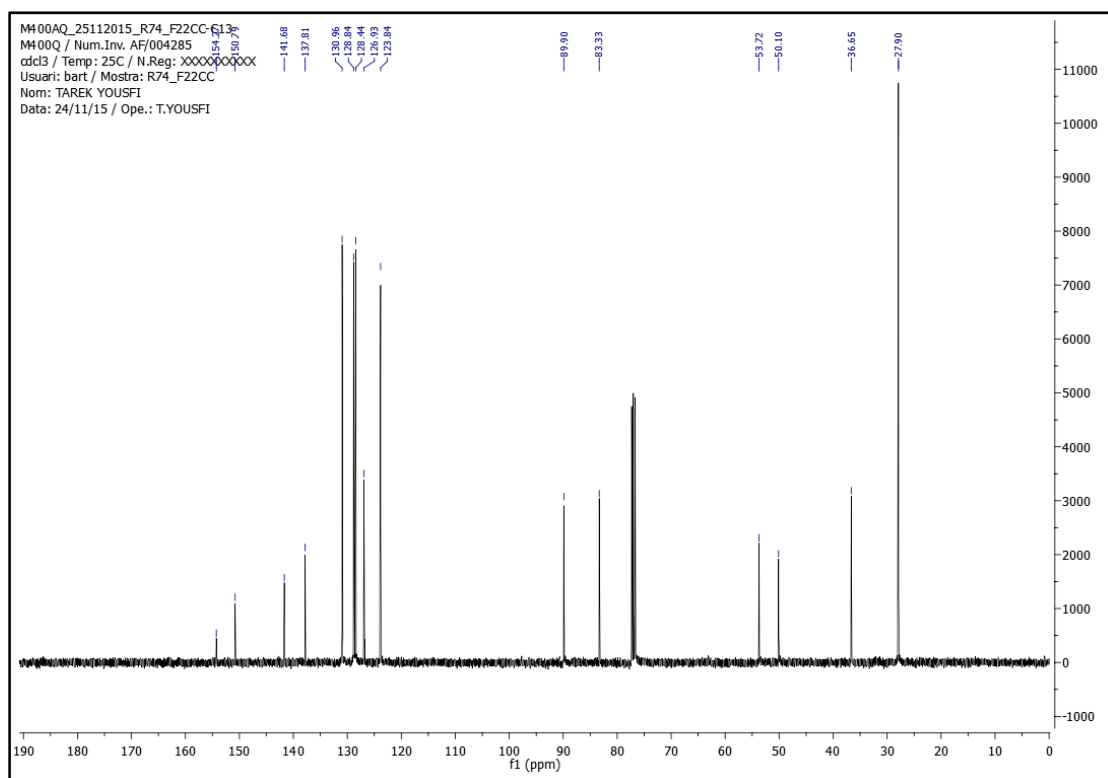


Figure S17. $^{13}\text{C-NMR}$ (100.6 MHz) of *tert*-Butyl 4-Benzyl-5-hydroxy-2-((4-nitrophenyl)sulfonyl)pyrazolidine-1-carboxylate, **8ab**.

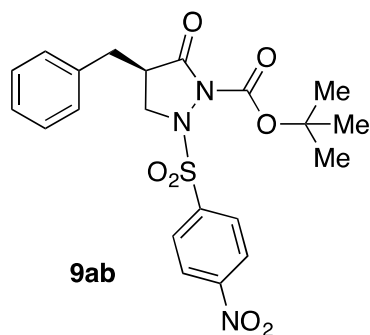


Figure S18. (-)-*tert*-Butyl 4-Benzyl-2-((4-nitrophenyl)sulfonyl)-pyrazolidin-5-one-1-carboxylate, **9ab**.

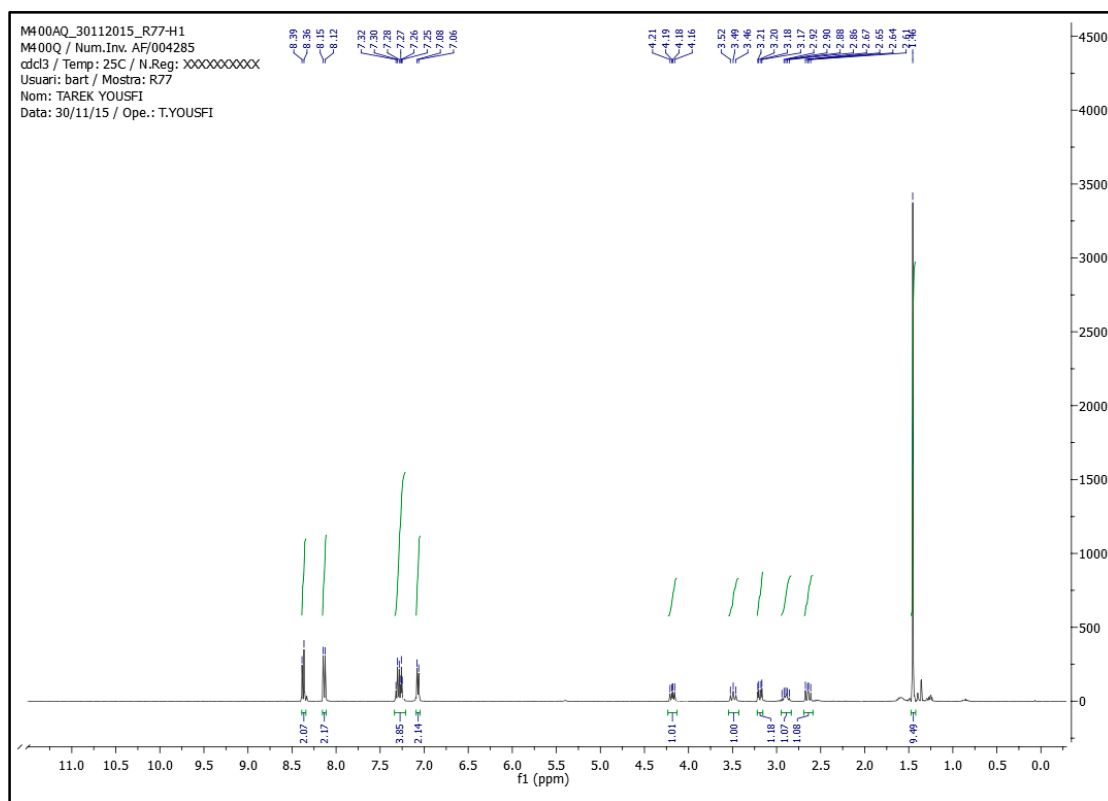


Figure S19. $^1\text{H-NMR}$ (400 MHz) of (-)-*tert*-Butyl 4-Benzyl-2-((4-nitrophenyl)sulfonyl)-pyrazolidin-5-one-1-carboxylate, **9ab**.

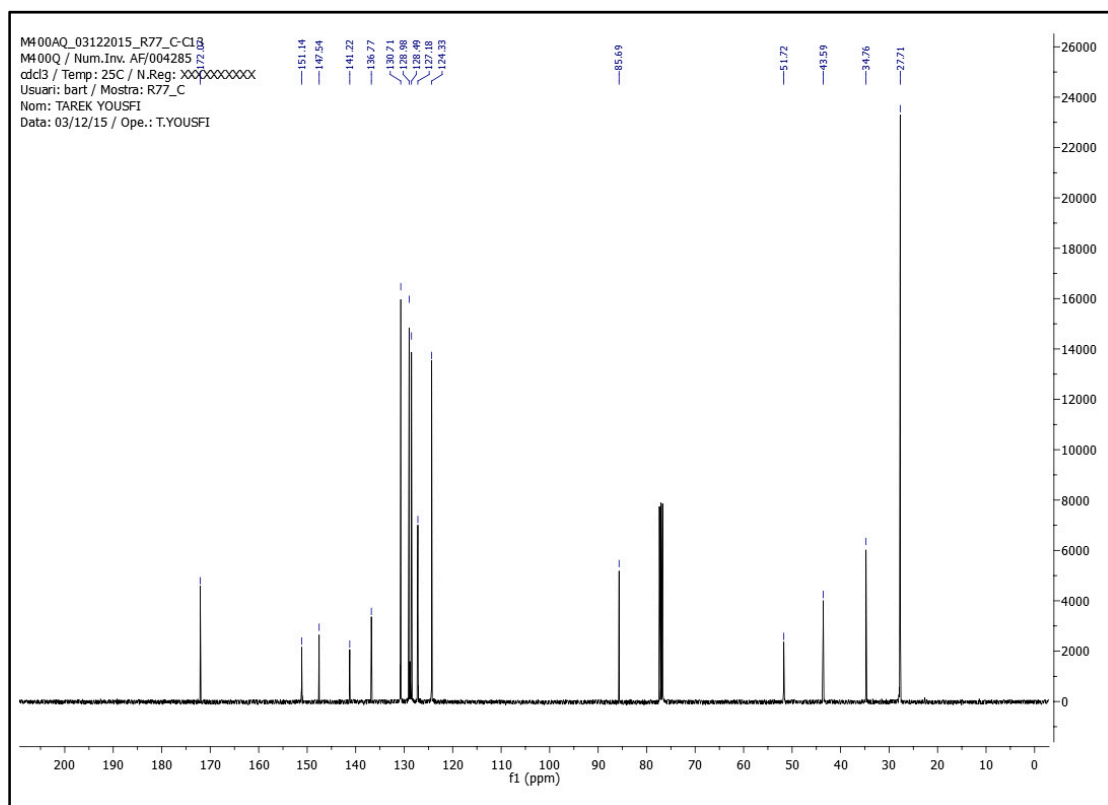
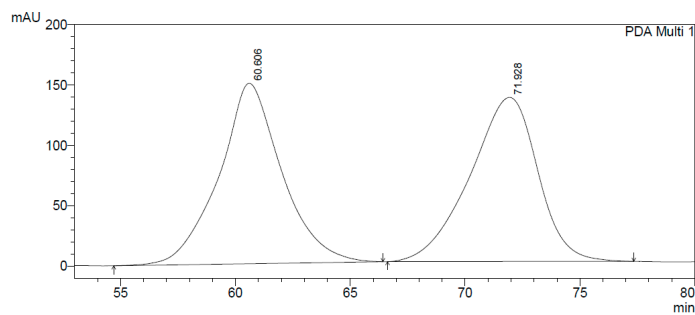


Figure S20. ^{13}C -NMR (100.6 MHz) of (-)-*tert*-Butyl 4-Benzyl-2-((4-nitrophenyl)sulfonyl)-pyrazolidin-5-one-1-carboxylate, **9ab**.

HPLC (Chiralpak[®] IC column, 90:10 hexane/isopropyl alcohol, 1 $\mu\text{L}/\text{min}$, $\lambda = 254 \text{ nm}$, 25 $^{\circ}\text{C}$).



| Peak# | Ret. Time | Area | Height | Area % | Height % |
|-------|-----------|----------|--------|---------|----------|
| 1 | 60.606 | 28447344 | 149356 | 50.513 | 52.370 |
| 2 | 71.928 | 27870083 | 135839 | 49.487 | 47.630 |
| Total | | 56317428 | 285195 | 100.000 | 100.000 |

Figure S21. *rac*-**9ab**.

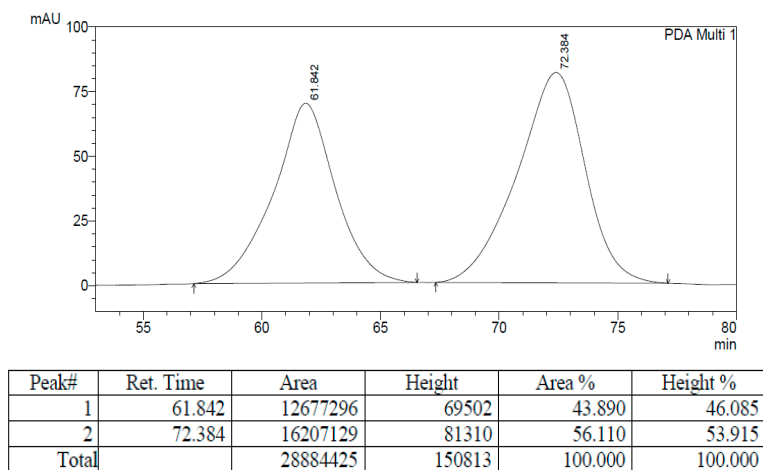


Figure S22. (-)-9ab.

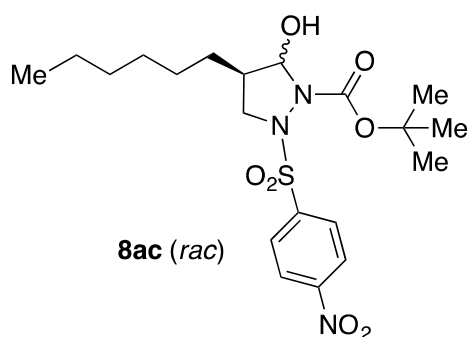
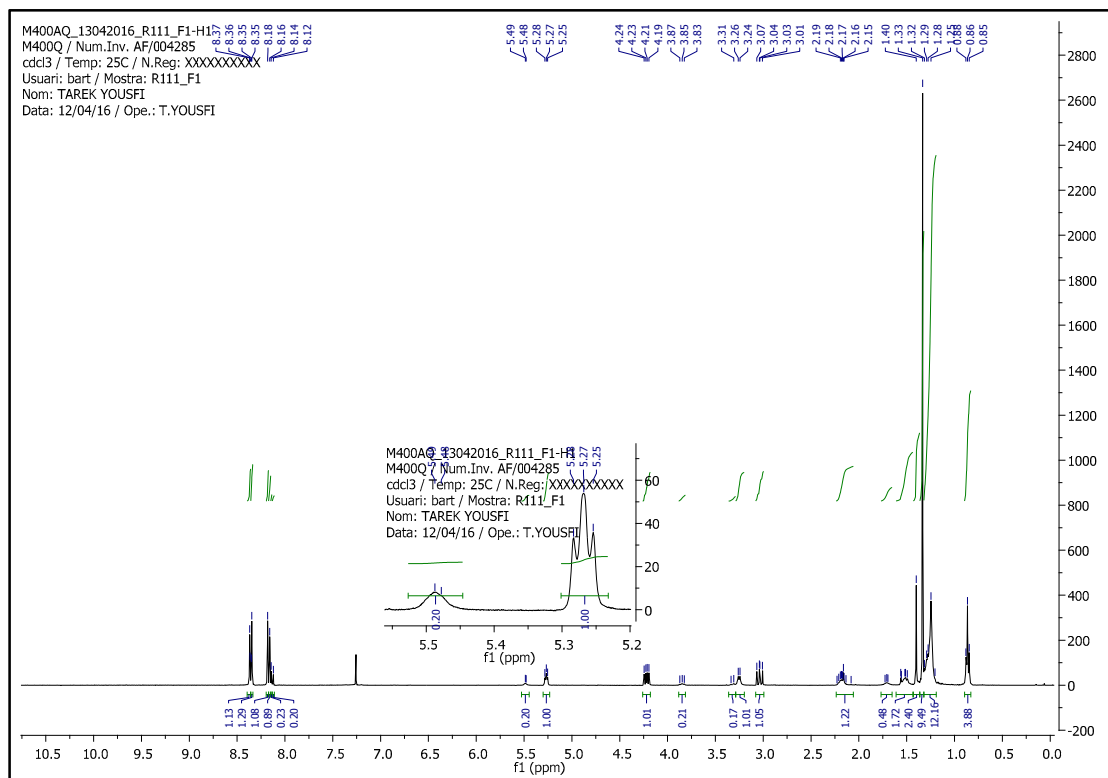
Figure S23. *tert*-Butyl 4-Hexyl-5-hydroxy-2-((4-nitrophenyl)sulfonyl)-pyrazolidine-1-carboxylate, **8ac**.

Figure S24. ¹H-NMR (400 MHz) of *tert*-Butyl 4-Hexyl-5-hydroxy-2-((4-nitrophenyl)sulfonyl)-pyrazolidine-1-carboxylate, **8ac**.

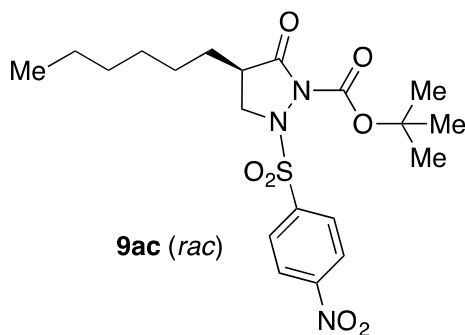


Figure S25. *tert*-Butyl 4-Hexyl-2-((4-nitrophenyl)sulfonyl)-pyrazolidin-5-one-1-carboxylate, **9ac**.

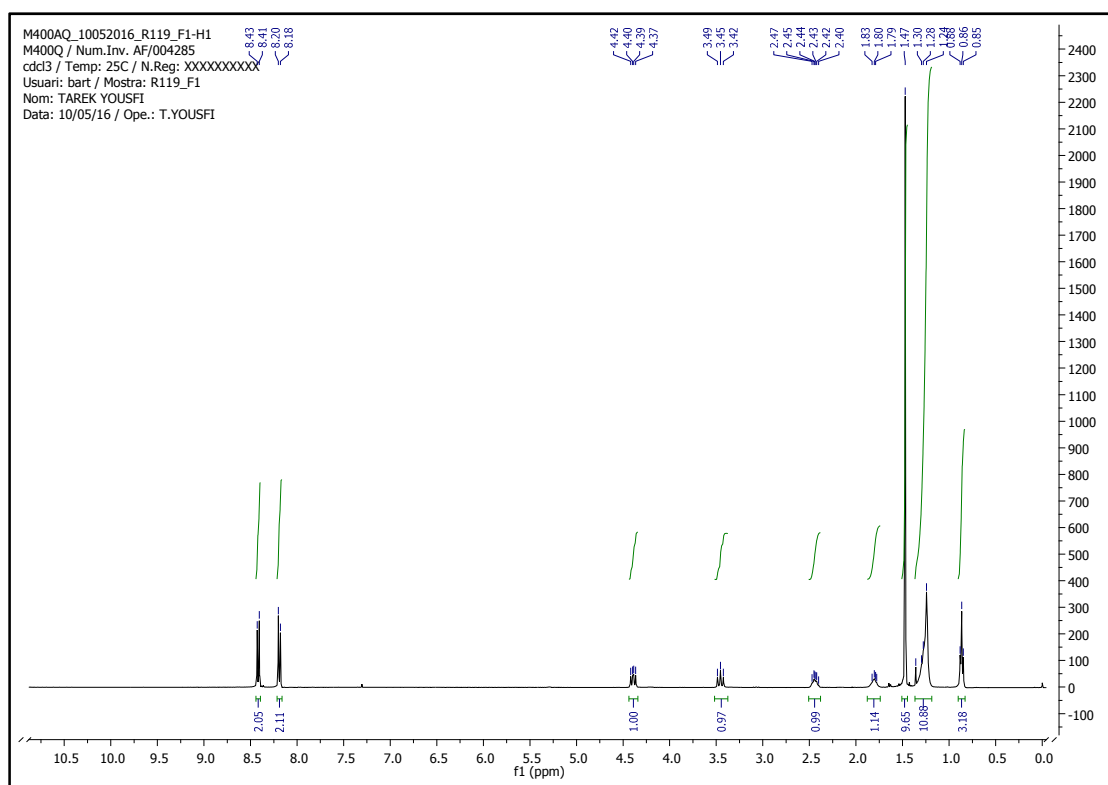


Figure S26. ¹H-NMR (400 MHz) of *tert*-Butyl 4-Hexyl-2-((4-nitrophenyl)sulfonyl)-pyrazolidin-5-one-1-carboxylate, **9ac**.

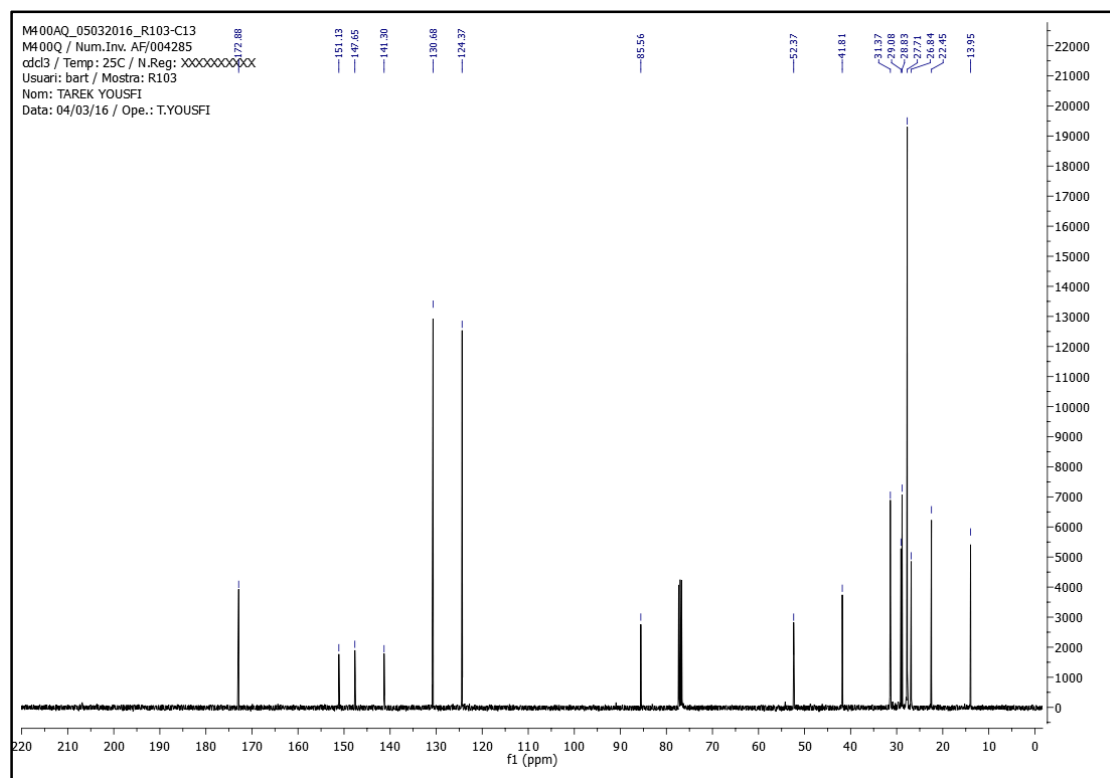


Figure S27. ^{13}C -NMR (100.6 MHz) of *tert*-Butyl 4-Hexyl-2-((4-nitrophenyl)sulfonyl)-pyrazolidin-5-one-1-carboxylate, **9ac**.

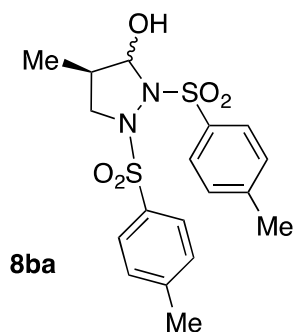


Figure S28. 4-Methyl-1,2-bis(4-toluenesulfonyl)-pyrazolidin-3-ol, **8ba**.

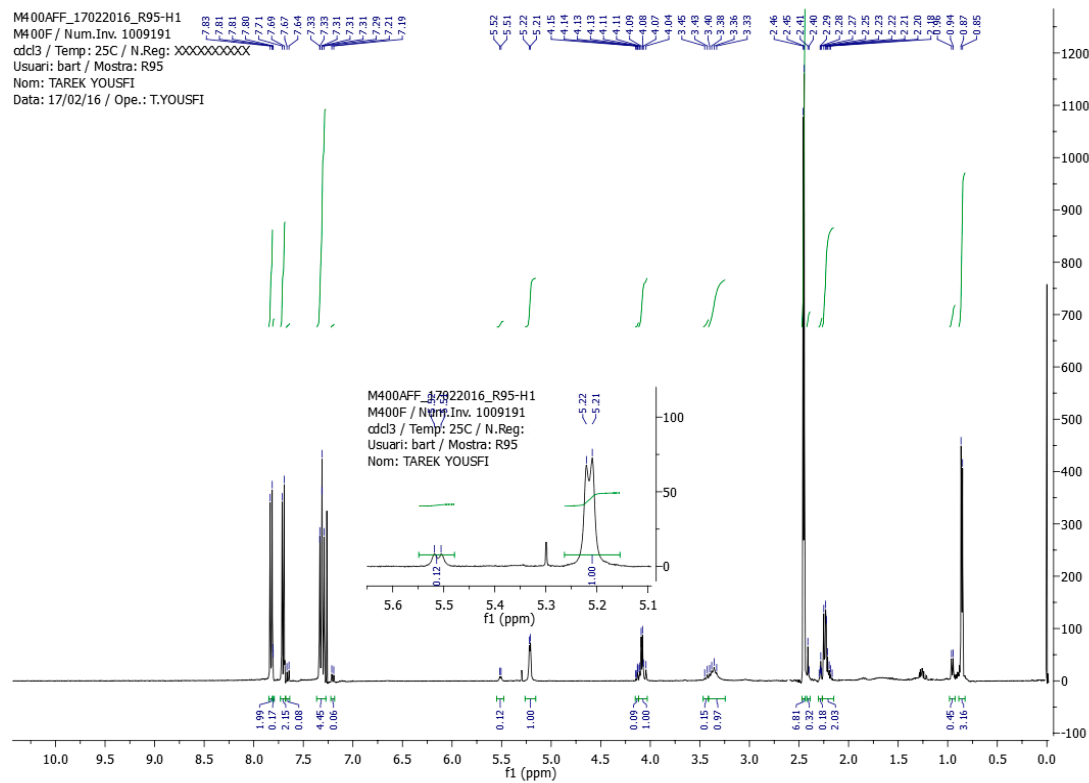


Figure S29. $^1\text{H-NMR}$ (400 MHz) of 4-Methyl-1,2-bis-(4-toluenesulfonyl)-pyrazolidin-3-ol, **8ba**.

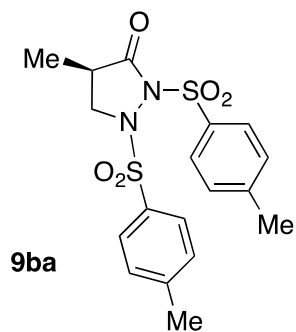


Figure S30. (-)-4-Methyl-1,2-bis-(4-toluenesulfonyl)-pyrazolidin-3-one, **9ba**.

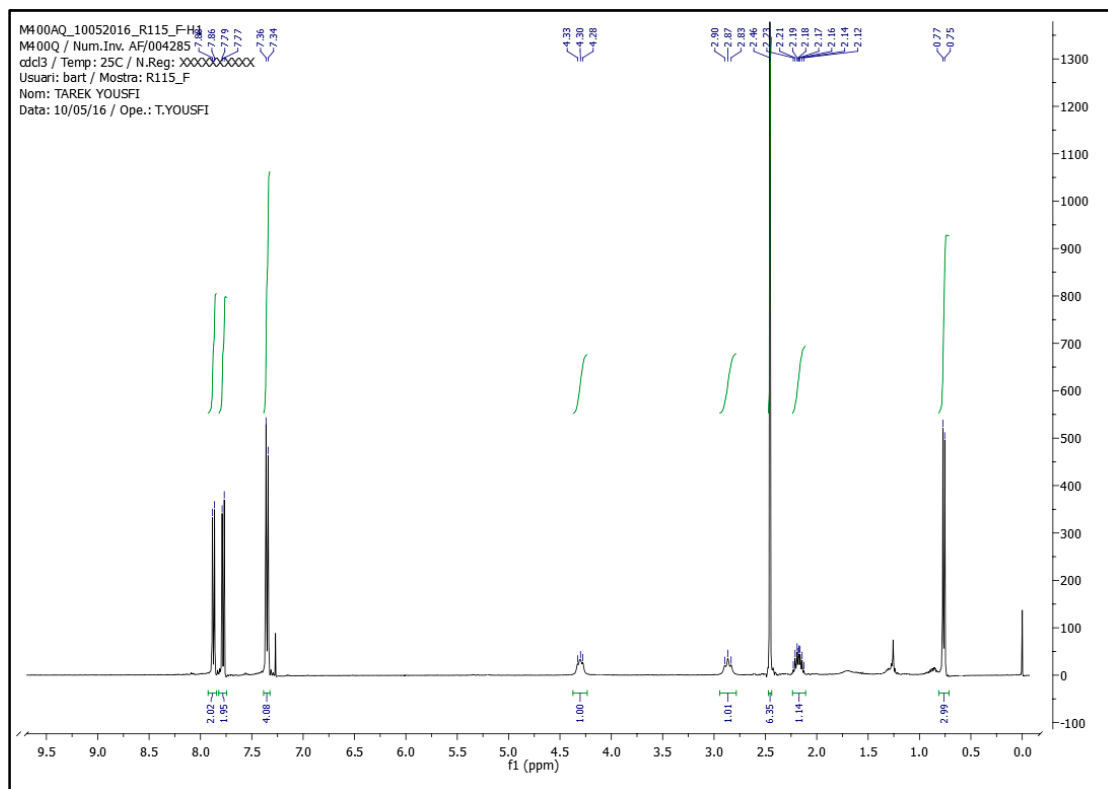


Figure S31. $^1\text{H-NMR}$ (400 MHz) of (-)-4-Methyl-1,2-bis-(4-toluenesulfonyl)-pyrazolidin-3-one, **9ba**.

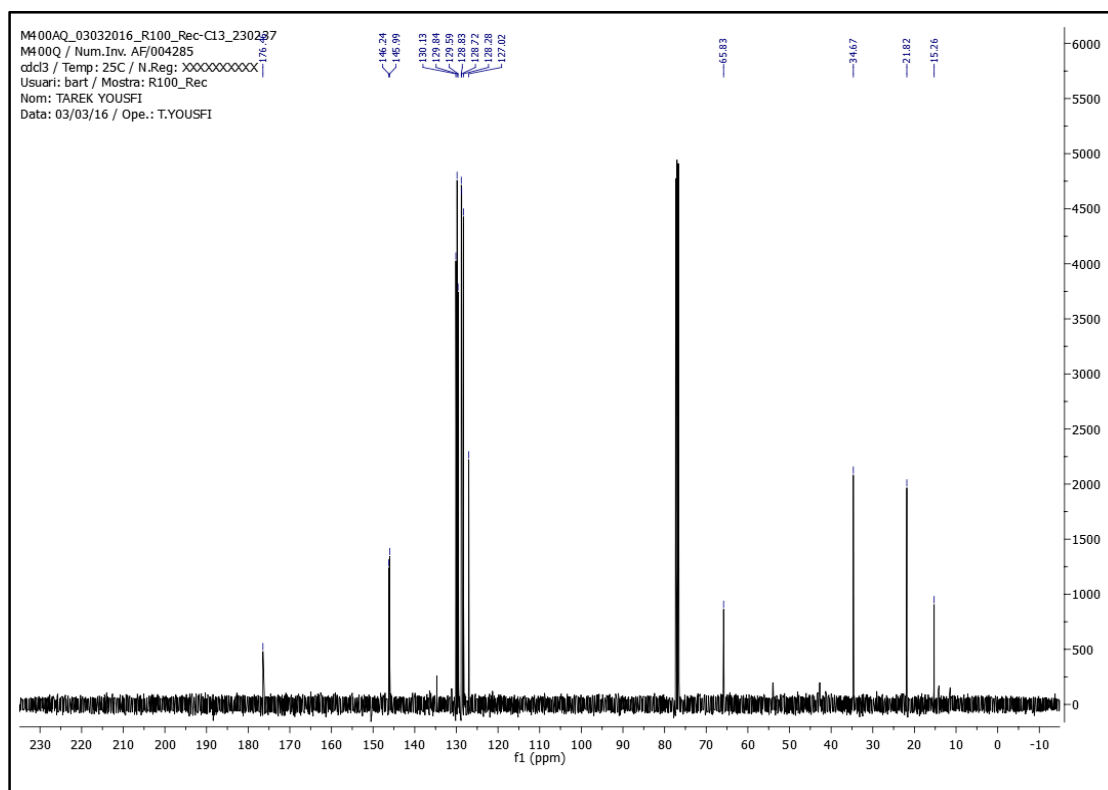
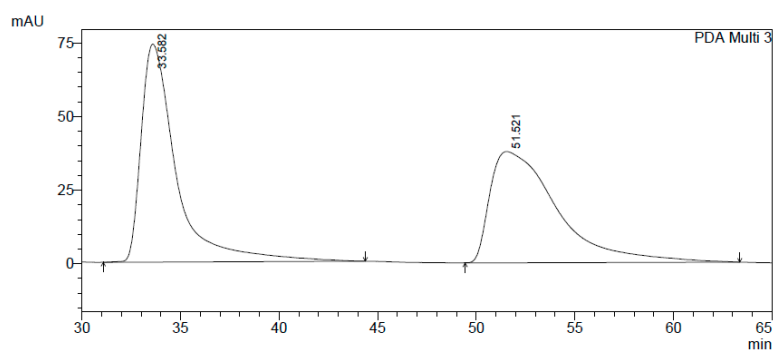


Figure S32. $^{13}\text{C-NMR}$ (100.6 MHz) of (-)-4-Methyl-1,2-bis-(4-toluenesulfonyl)-pyrazolidin-3-one, **9ba**.

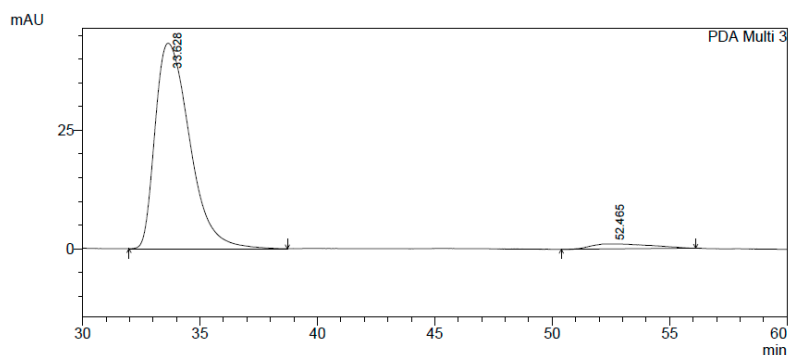
HPLC (Chiralpak® IA column, 90:10 hexane/isopropyl alcohol, 1 μ L/min, λ = 254 nm, 25 °C).



PDA Ch3 254nm 4nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|-------|-----------|----------|--------|---------|----------|
| 1 | 33.582 | 9231871 | 74031 | 50.742 | 66.222 |
| 2 | 51.521 | 8961982 | 37761 | 49.258 | 33.778 |
| Total | | 18193854 | 111792 | 100.000 | 100.000 |

Figure S33. *rac*-9ba.



PDA Ch3 254nm 4nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|-------|-----------|---------|--------|---------|----------|
| 1 | 33.628 | 4430577 | 43280 | 95.943 | 97.560 |
| 2 | 52.465 | 187341 | 1082 | 4.057 | 2.440 |
| Total | | 4617918 | 44362 | 100.000 | 100.000 |

Figure S34. (-)-9ba.

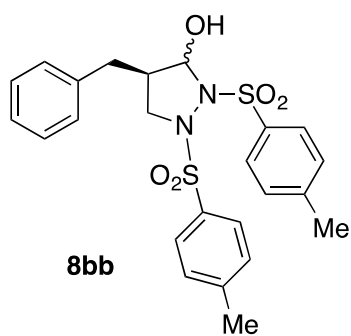


Figure S35. 4-Benzyl-1,2-bis-(4-toluenesulfonyl)-pyrazolidin-3-ol, **8bb**.

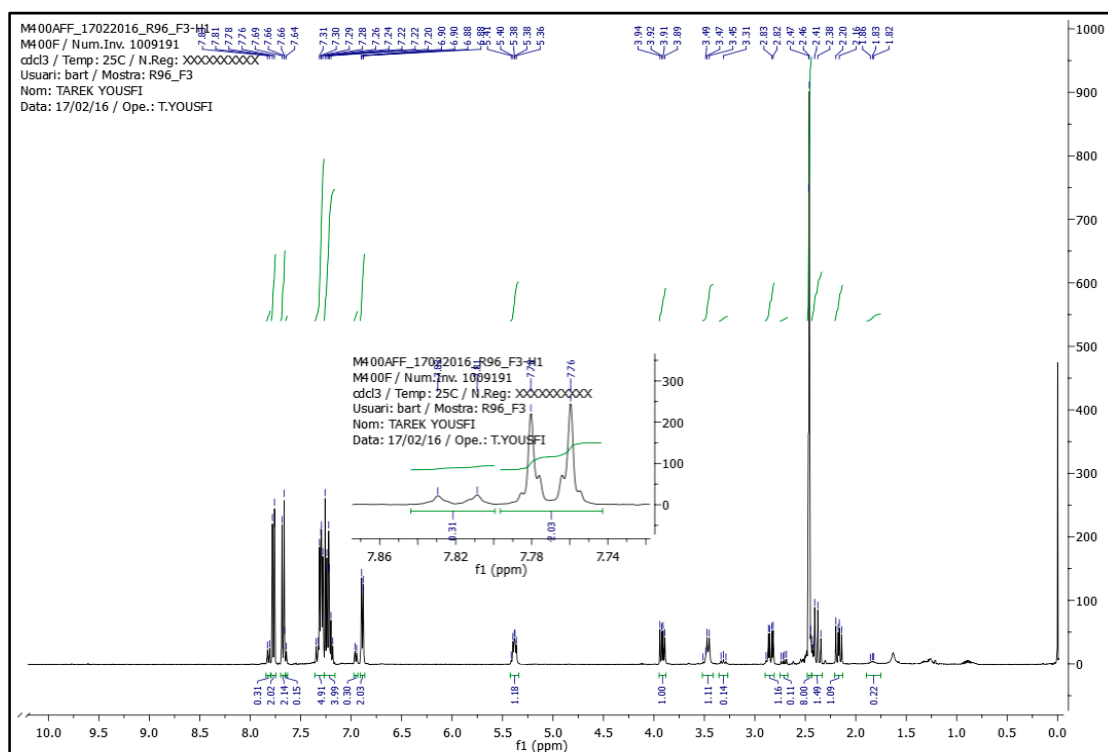


Figure S36. $^1\text{H-NMR}$ (400 MHz) of 4-Benzyl-1,2-bis(4-toluenesulfonyl)-pyrazolidin-3-ol, **8bb**.

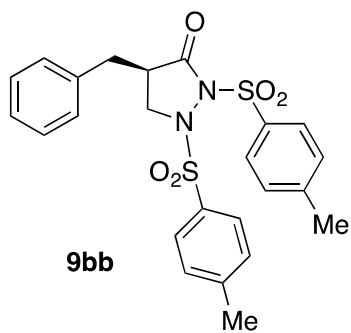


Figure S37. 4-Benzyl-1,2-bis(4-toluenesulfonyl)-pyrazolidin-3-one, **9bb**.

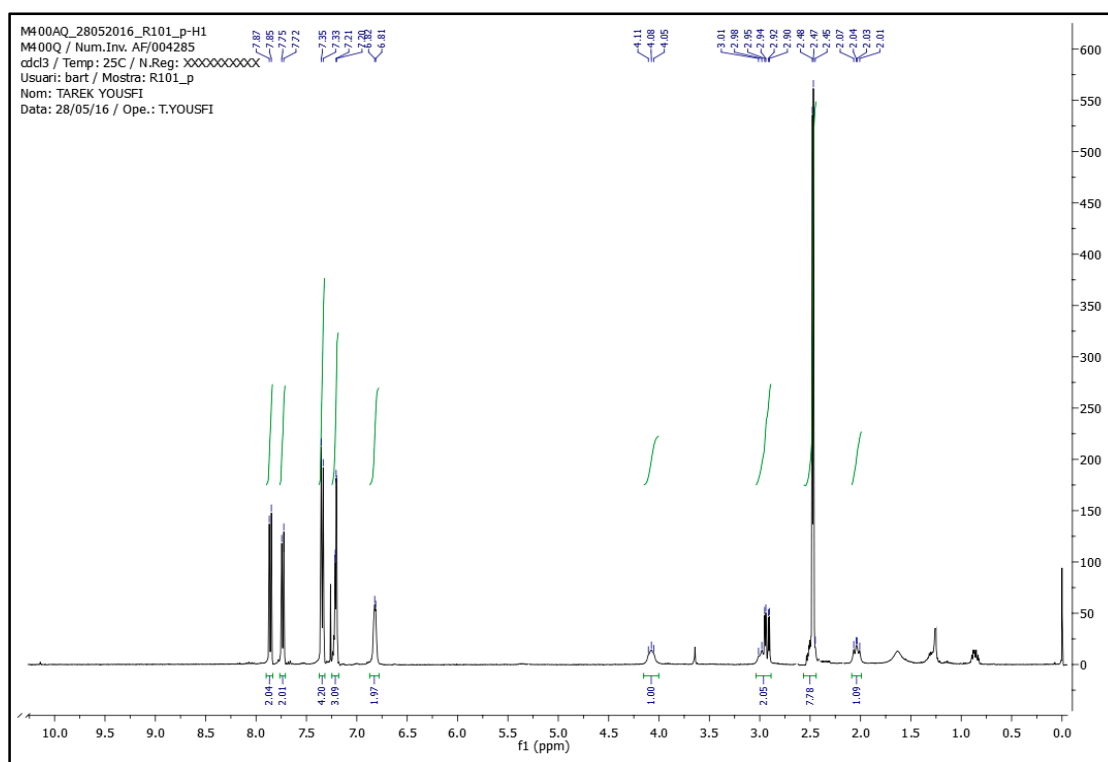


Figure S38. ¹H-NMR (400 MHz) of 4-Benzyl-1,2-bis-(4-toluenesulfonyl)-pyrazolidin-3-one, **9bb**.

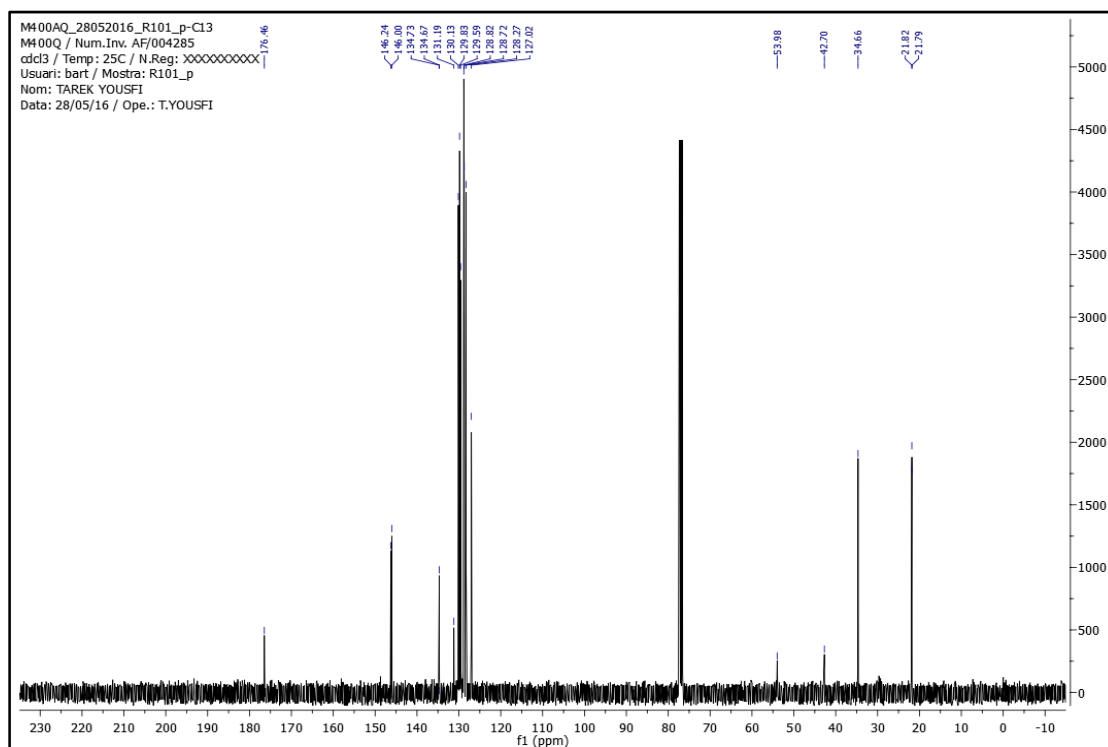
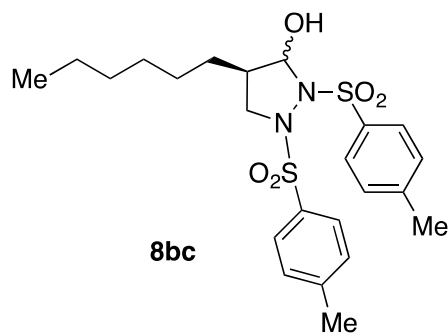
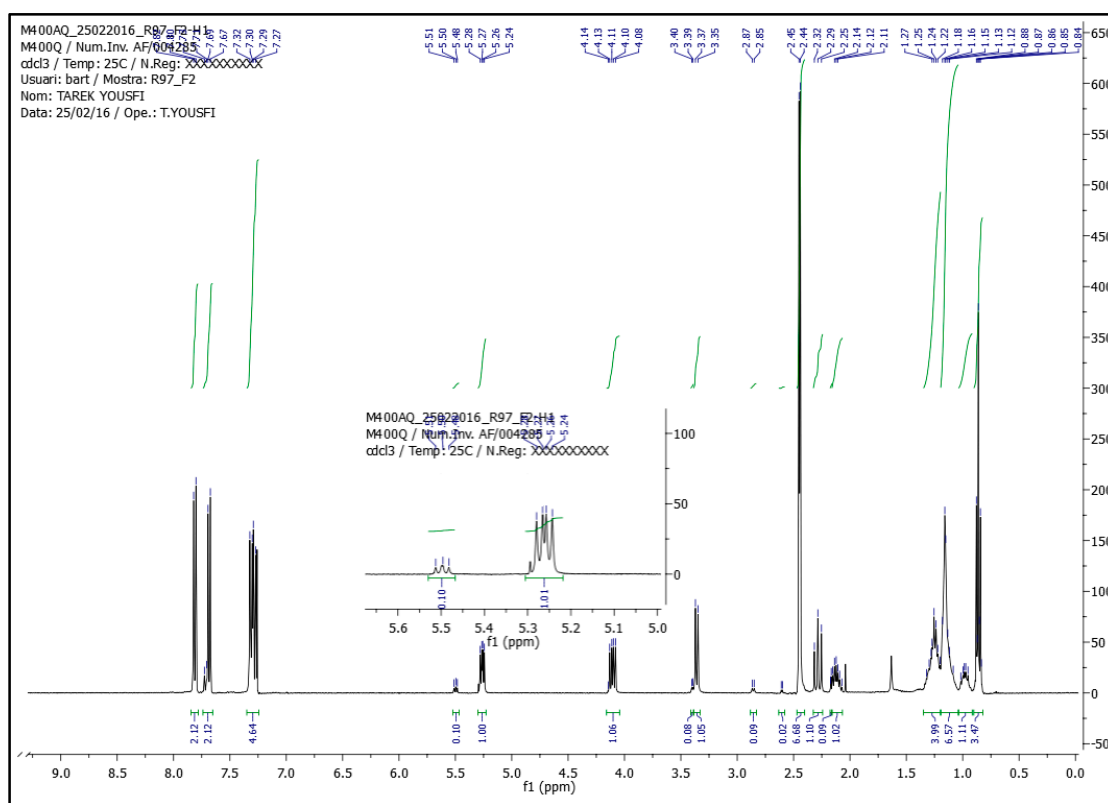
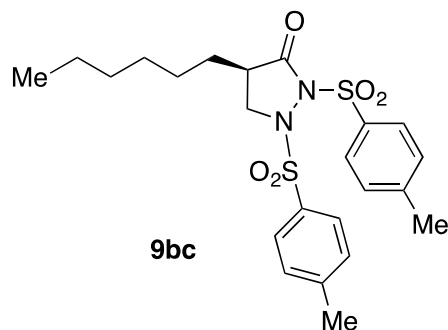


Figure S39. ¹³C-NMR (100.6 MHz) of 4-Benzyl-1,2-bis-(4-toluenesulfonyl)-pyrazolidin-3-one, **9bb**.

Figure S40. 4-Hexyl-1,2-bis-(4-toluenesulfonyl)-pyrazolidin-3-ol, **8bc**.Figure S41. ¹H-NMR (400 MHz) of 4-Hexyl-1,2-bis-(4-toluenesulfonyl)-pyrazolidin-3-ol, **8bc**.Figure S42. (-)-4-Hexyl-1,2-bis-(4-toluenesulfonyl)-pyrazolidin-3-one, **9bc**.

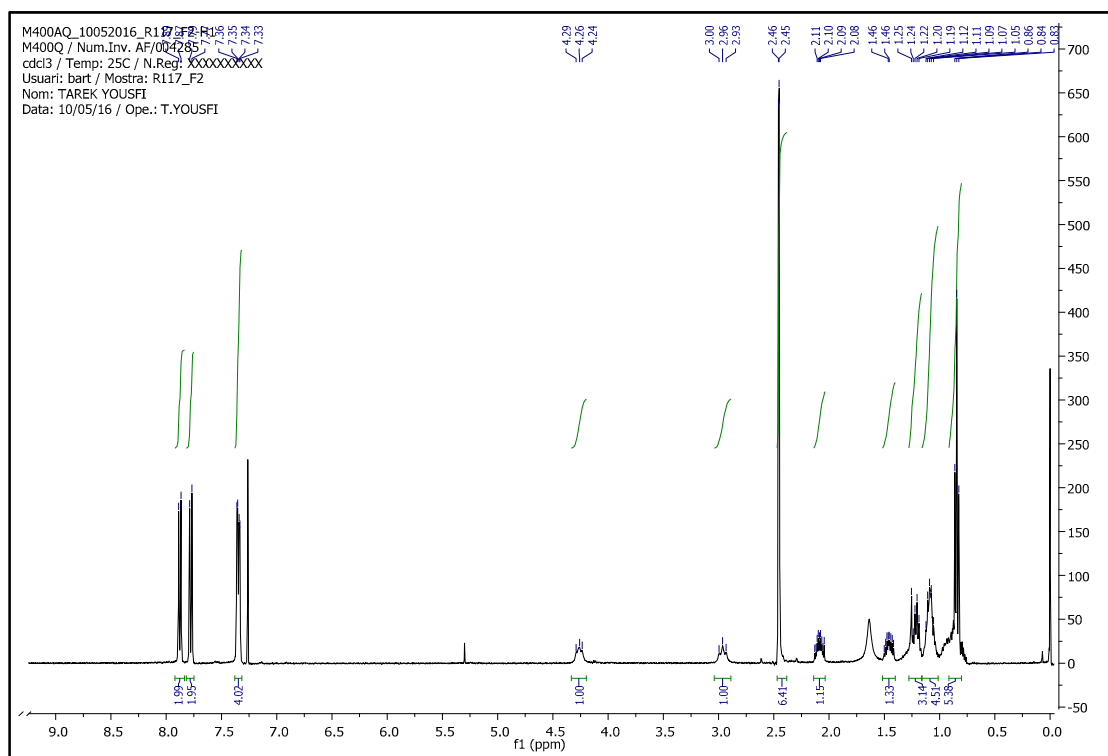


Figure S43. $^1\text{H-NMR}$ (400 MHz) of (-)-4-Hexyl-1,2-bis-(4-toluenesulfonyl)-pyrazolidin-3-one, **9bc**.

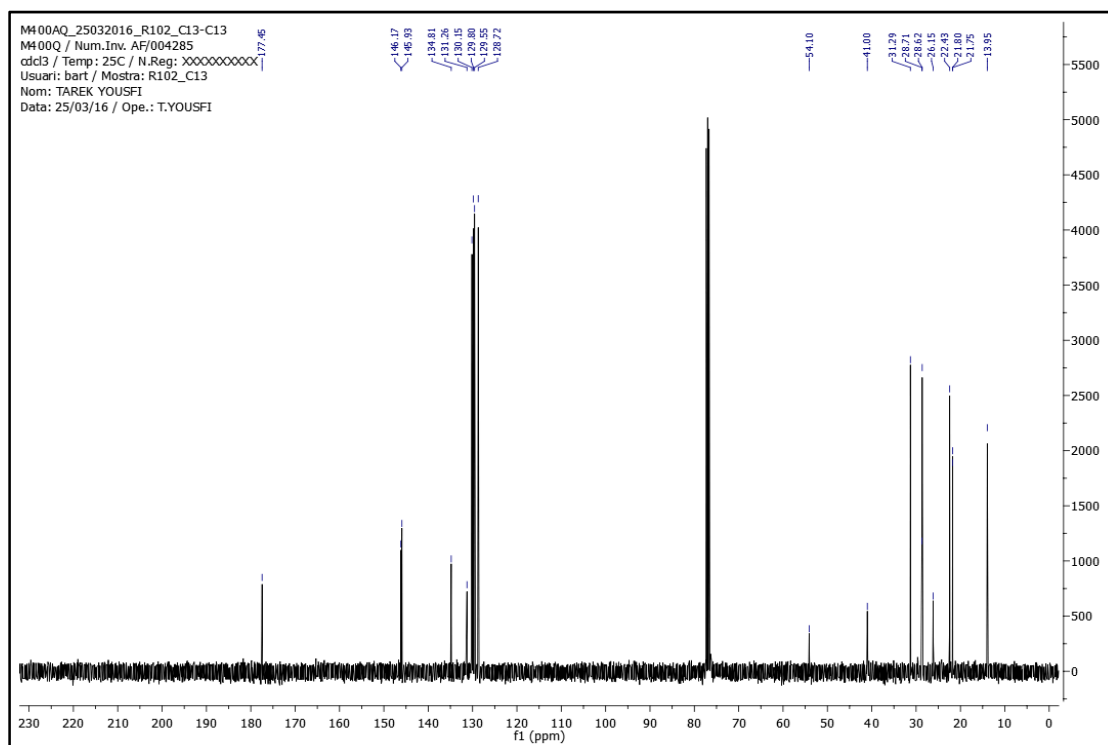
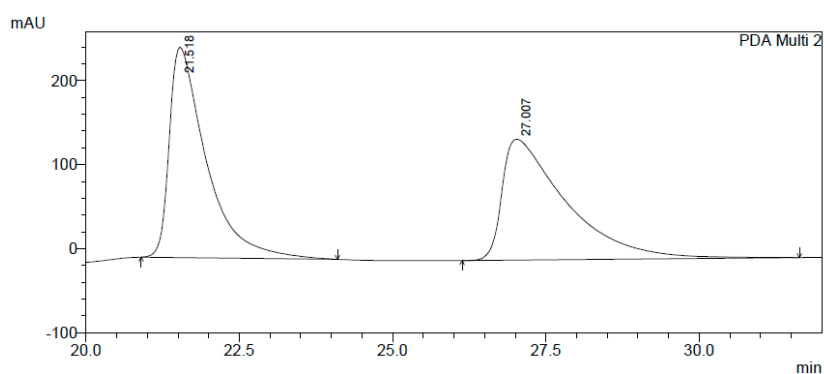


Figure S44. $^{13}\text{C-NMR}$ (100.6 MHz) of (-)-4-Hexyl-1,2-bis-(4-toluenesulfonyl)-pyrazolidin-3-one, **9bc**.

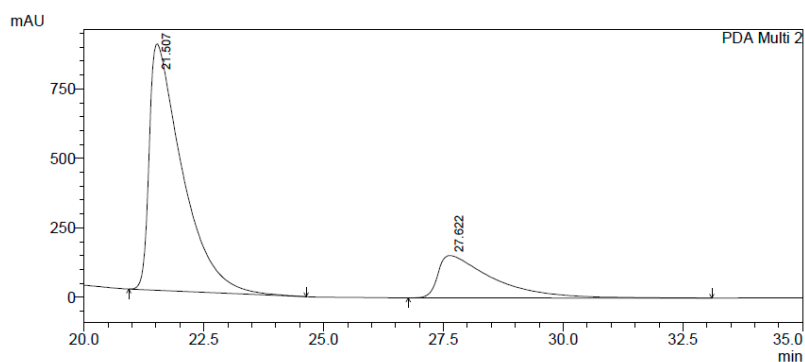
HPLC (Chiralpak® IB column, 93:7 hexane/isopropyl alcohol, 1 μ L/min, λ = 220 nm, 25 °C).



PDA Ch2 220nm 4nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|-------|-----------|----------|--------|---------|----------|
| 1 | 21.518 | 10499107 | 250442 | 50.153 | 63.528 |
| 2 | 27.007 | 10435081 | 143784 | 49.847 | 36.472 |
| Total | | 20934189 | 394226 | 100.000 | 100.000 |

Figure S45. *rac*-9bc.



PDA Ch2 220nm 4nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|-------|-----------|----------|---------|---------|----------|
| 1 | 21.507 | 42470297 | 886214 | 77.915 | 85.333 |
| 2 | 27.622 | 12038479 | 152324 | 22.085 | 14.667 |
| Total | | 54508775 | 1038538 | 100.000 | 100.000 |

Figure S46. (-)-9bc.

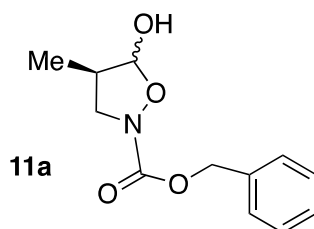


Figure S47. Benzyl 5-Hydroxy-4-methyl-isoxazolidine-2-carboxylate, **11a**.

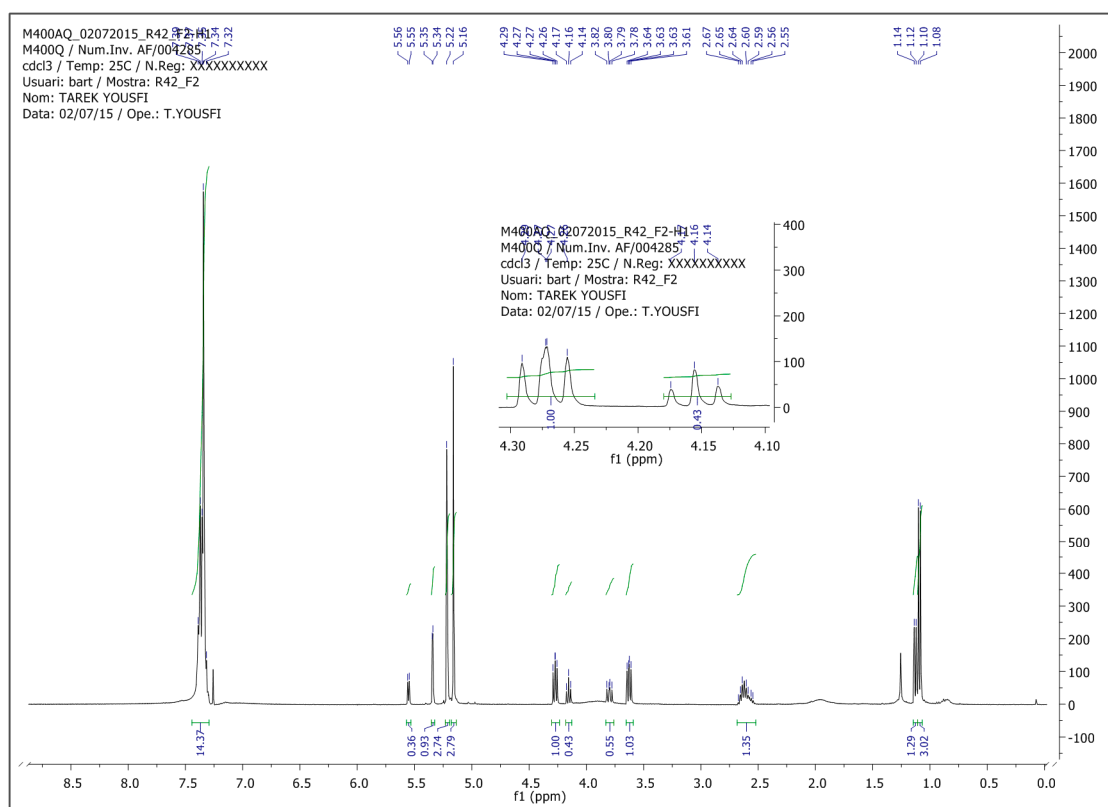


Figure S48. $^1\text{H-NMR}$ (400 MHz) of Benzyl 5-Hydroxy-4-methyl-isoxazolidine-2-carboxylate, **11a**.

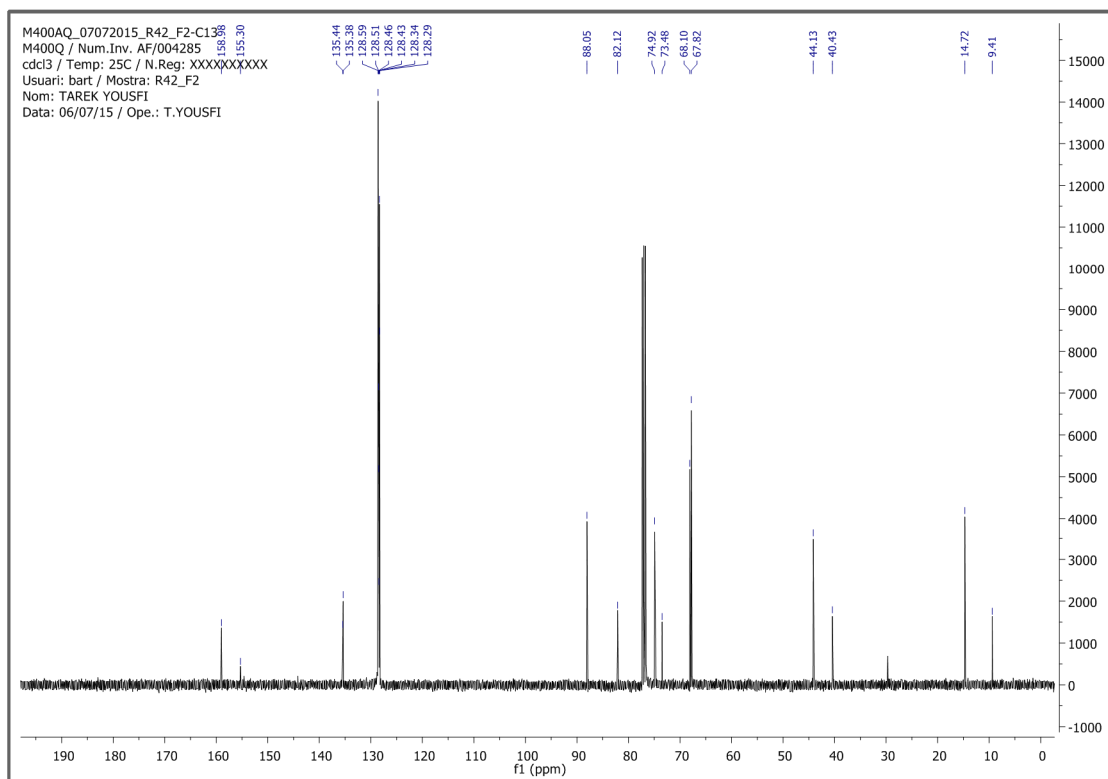


Figure S49. $^{13}\text{C-NMR}$ (100.6 MHz) of Benzyl 5-Hydroxy-4-methyl-isoxazolidine-2-carboxylate, **11a**.

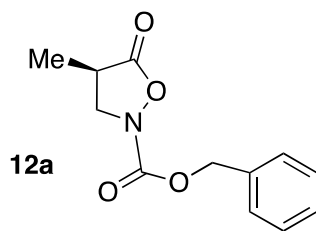


Figure S50. Benzyl 4-Methyl-5-oxo-isoxazolidine-2-carboxylate, **12a**.

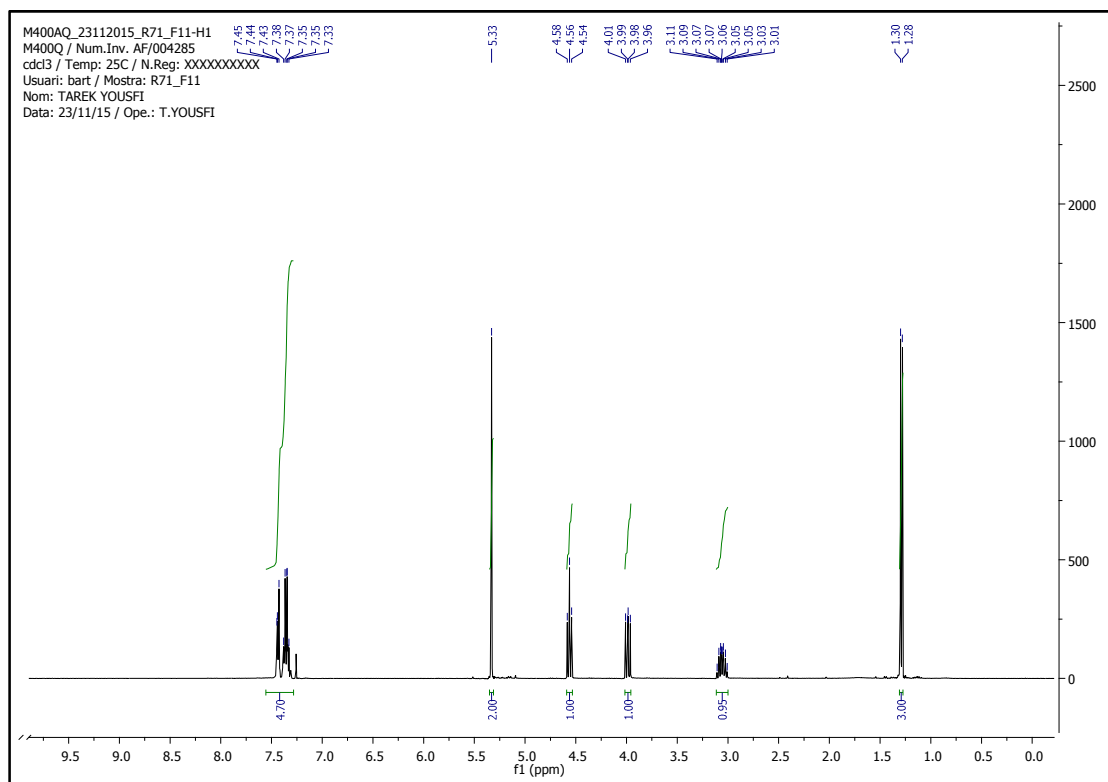


Figure S51. $^1\text{H-NMR}$ (400 MHz) of Benzyl 4-Methyl-5-oxo-isoxazolidine-2-carboxylate, **12a**.

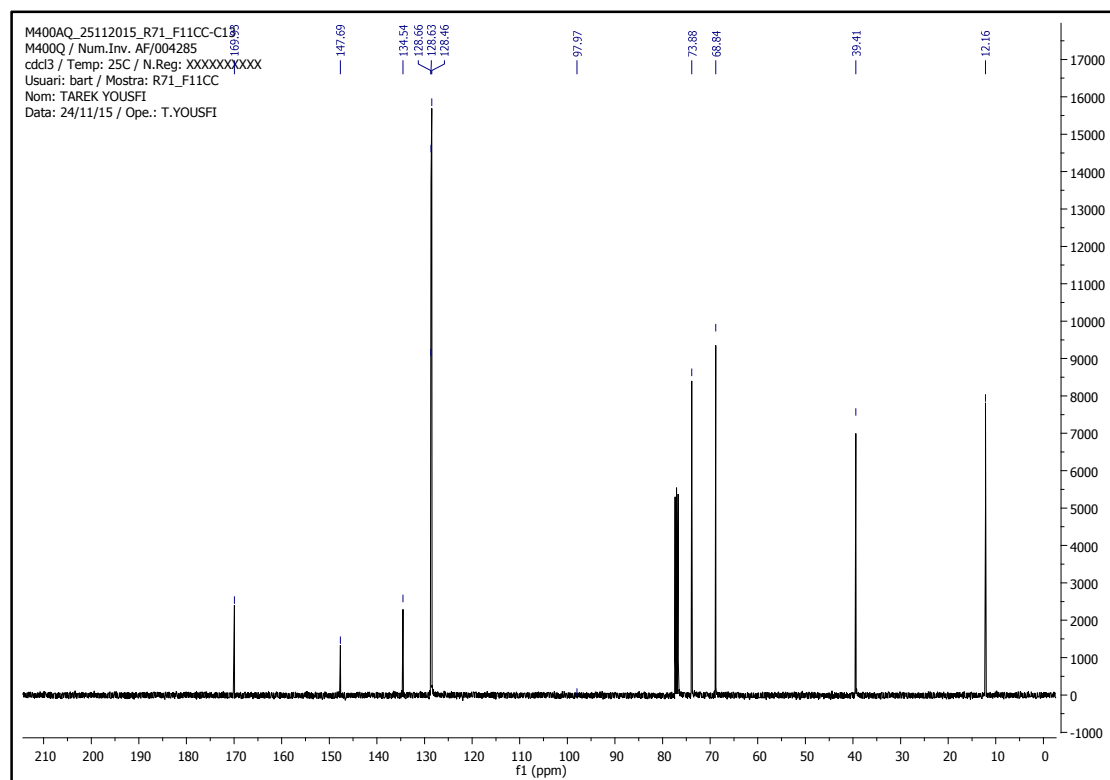


Figure S52. ^{13}C -NMR (100.6 MHz) of Benzyl 4-Methyl-5-oxo-isoxazolidine-2-carboxylate, **12a**.

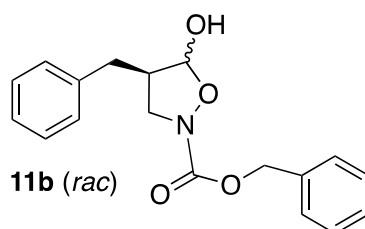
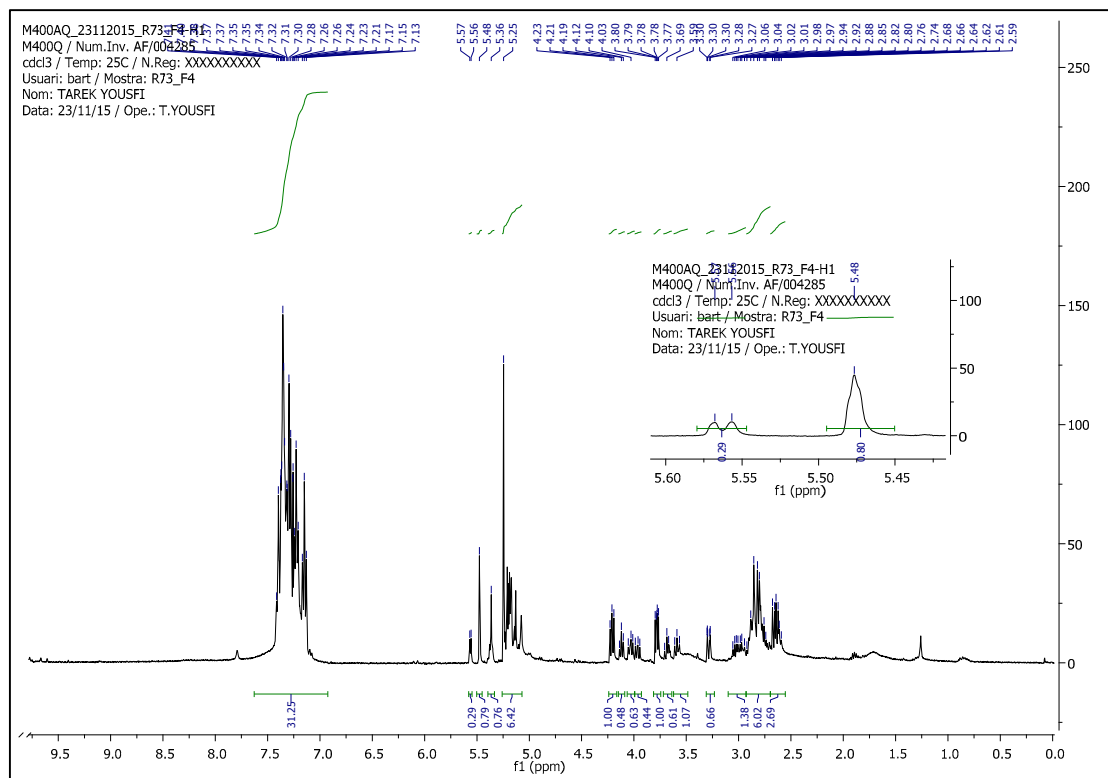
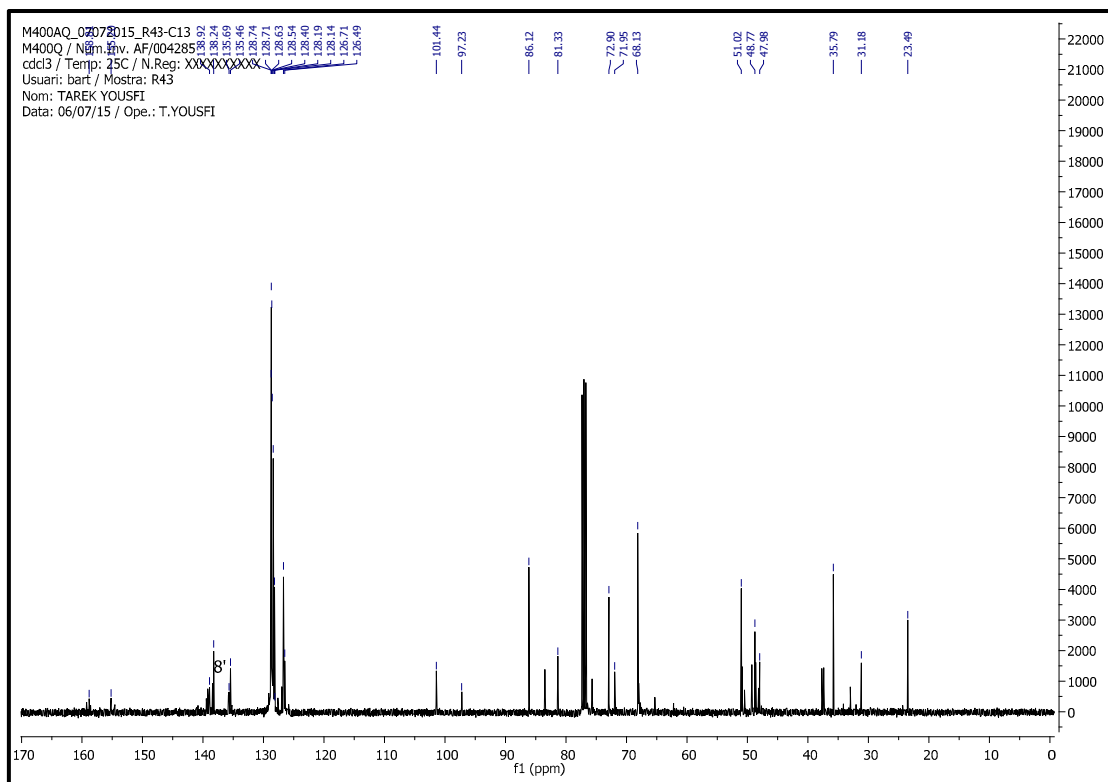


Figure S53. Benzyl 4-Benzyl-5-Hydroxy-isoxazolidine-2-carboxylate, **11b**.

Figure S54. ¹H-NMR (400 MHz) of Benzyl 4-Benzyl-5-Hydroxy-isoxazolidine-2-carboxylate, **11b**.Figure S55. ¹³C-NMR (100.6 MHz) of Benzyl 4-Benzyl-5-Hydroxy-isoxazolidine-2-carboxylate, **11b**.

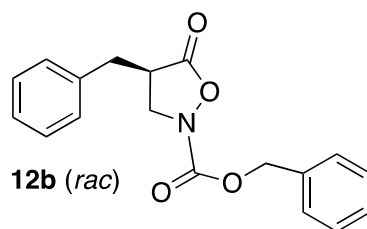


Figure S56. Benzyl 4-Benzyl-5-oxo-isoxazolidine-2-carboxylate, **12b**.

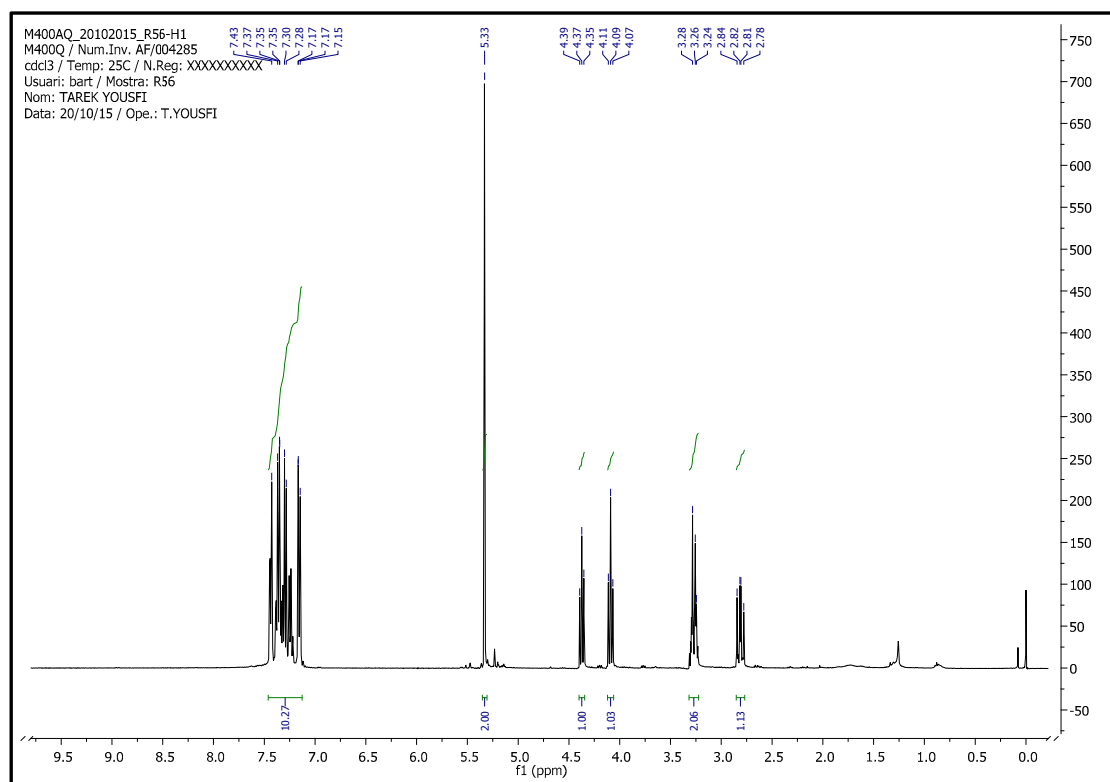


Figure S57. $^1\text{H-NMR}$ (400 MHz) of Benzyl 4-Benzyl-5-oxo-isoxazolidine-2-carboxylate, **12b**.

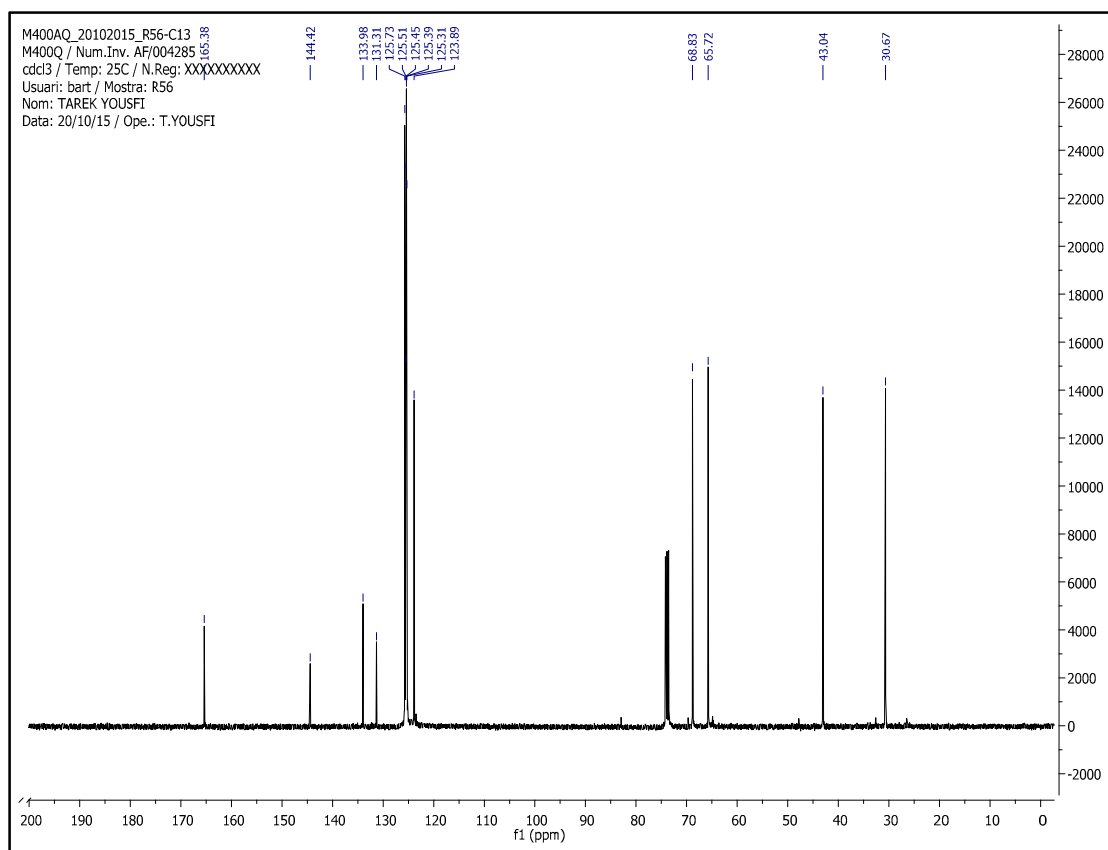


Figure S58. ^{13}C -NMR (100.6 MHz) of Benzyl 4-Benzyl-5-oxo-isoxazolidine-2-carboxylate, **12b**.

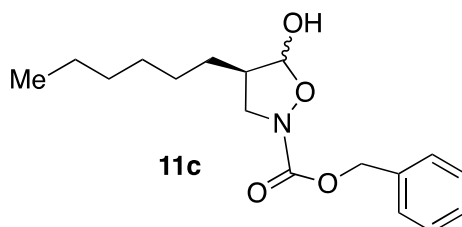


Figure S59. Benzyl 4-Hexyl-5-hydroxy-isoxazolidine-2-carboxylate, **11c**.

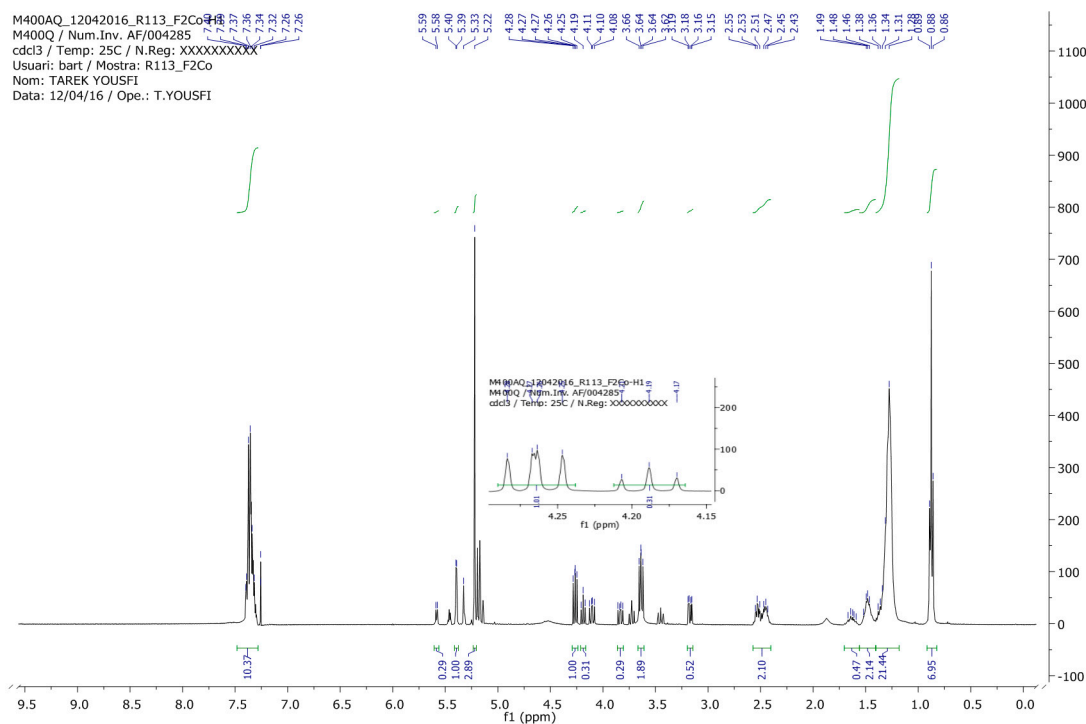


Figure S60. ^1H -NMR (400 MHz) of Benzyl 4-Hexyl-5-hydroxy-isoxazolidine-2-carboxylate, **11c**.

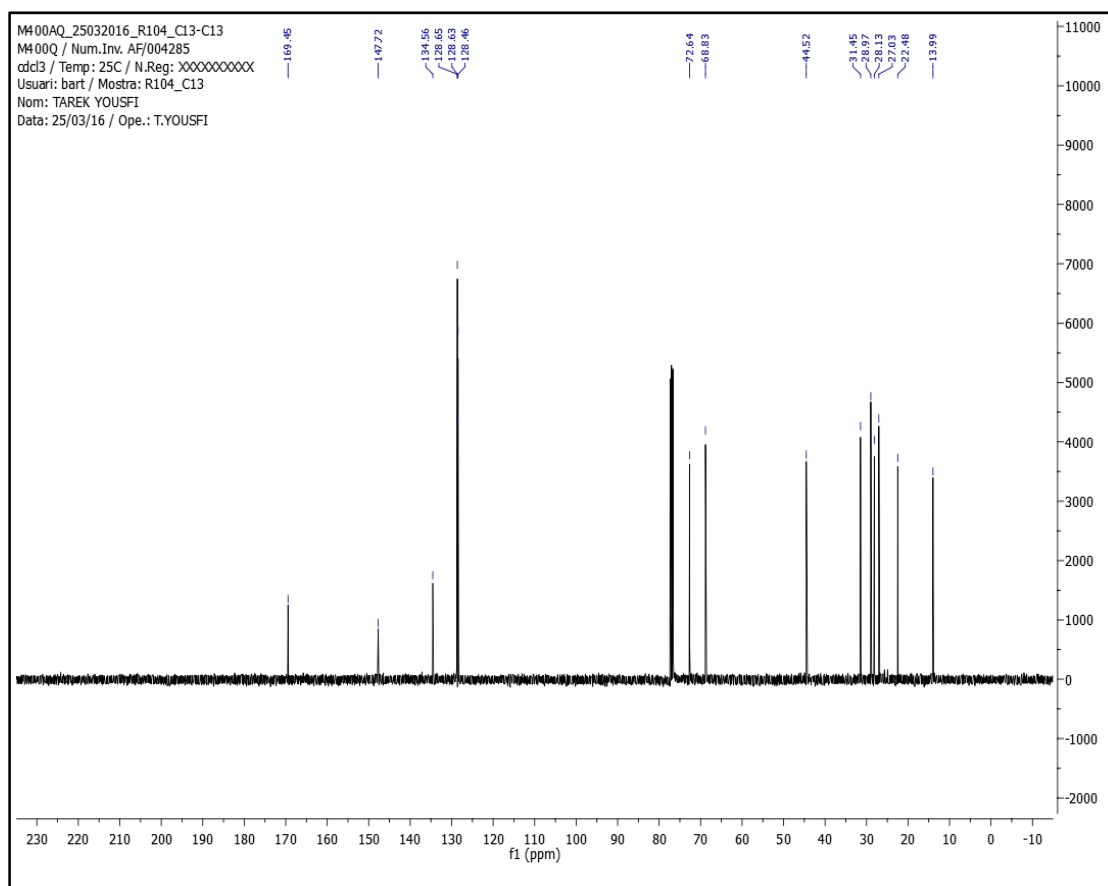


Figure S61. ^{13}C -NMR (100.6 MHz) of Benzyl 4-Hexyl-5-hydroxy-isoxazolidine-2-carboxylate, **11c**.

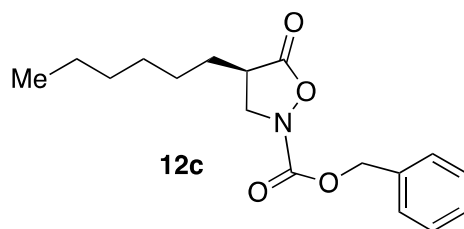


Figure S62. (-)-Benzyl 4-Hexyl-5-oxo-isoxazolidine-2-carboxylate, **12c**.

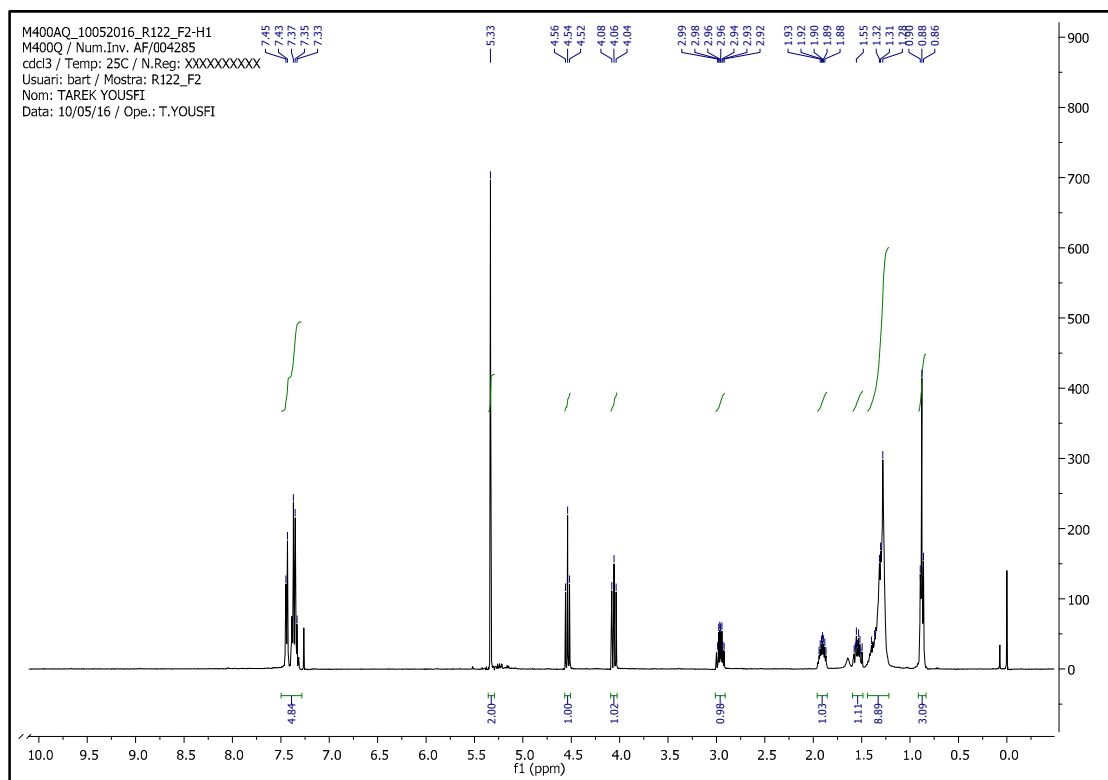


Figure S63. $^1\text{H-NMR}$ (400 MHz) of (-)-Benzyl 4-Hexyl-5-oxo-isoxazolidine-2-carboxylate, **12c**.

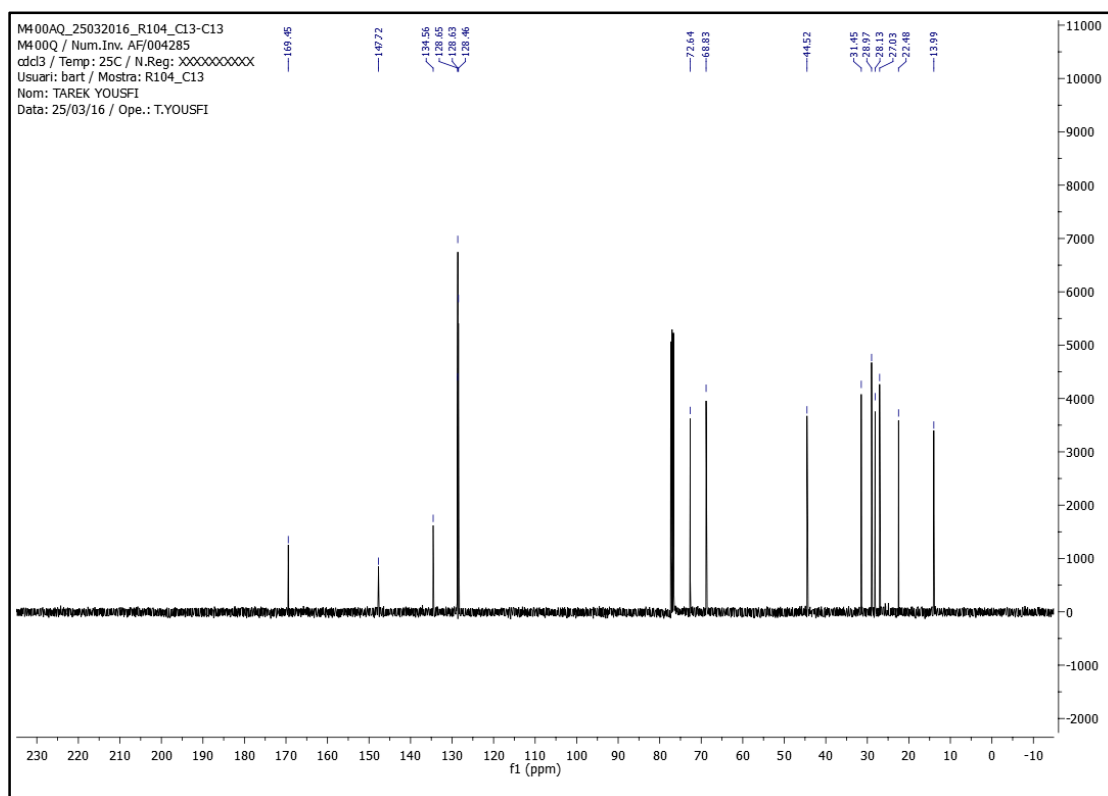
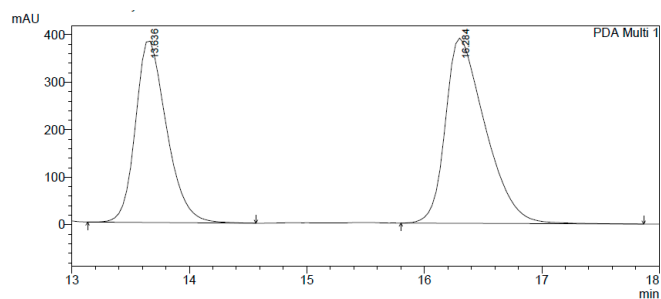


Figure S64. ^{13}C -NMR (100.6 MHz) of (-)-Benzyl 4-Hexyl-5-oxo-isoxazolidine-2-carboxylate, **12c**.

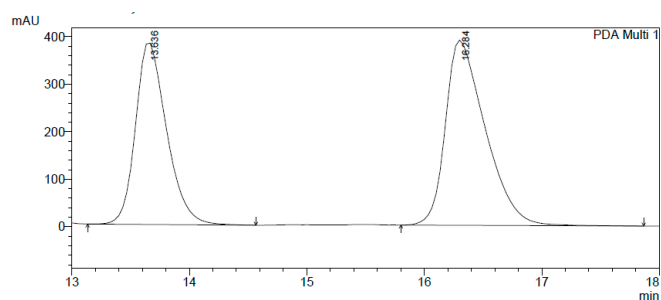
HPLC (Chiralpak[®] IB column, 90:10 hexane/isopropyl alcohol, 1 $\mu\text{L}/\text{min}$, $\lambda = 254 \text{ nm}$, 25 $^{\circ}\text{C}$).



Peak table

| PDA Ch3 254nm 4nm | | | | | | |
|-------------------|-----------|---------|--------|---------|----------|--|
| Peak# | Ret. Time | Area | Height | Area % | Height % | |
| 1 | 13.636 | 1272551 | 69970 | 43.403 | 49.555 | |
| 2 | 16.284 | 1659359 | 71226 | 56.597 | 50.445 | |
| Total | | 2931910 | 141196 | 100.000 | 100.000 | |

Figure S65. *rac*-**12c**.



PeakTable

PDA Ch3 254nm 4nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|-------|-----------|---------|--------|---------|----------|
| 1 | 13.636 | 1272551 | 69970 | 43.403 | 49.555 |
| 2 | 16.284 | 1659359 | 71226 | 56.597 | 50.445 |
| Total | | 2931910 | 141196 | 100.000 | 100.000 |

Figure S66. (-)-12c.