

Electronic Supplementary Information

for

Cinchona Alkaloid Derivatives modified Fe₃O₄ Nanoparticles for Enantioselective Ring Opening of *meso*- Cyclic Anhydrides

Sanjiv O. Tomer and Hemant P. Soni*

Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda,
Vadodara-390 002, Gujarat, India

*Author for Correspondence: drhpsoni@yahoo.co.in;
hemant.soni-chem@msubaroda.ac.in
Ph.+91-0265-2795552

Table of contents:

Experimental section	2-7
HPLC chromatograms and NMR spectra of the products, mQD and its intermediates	8-36

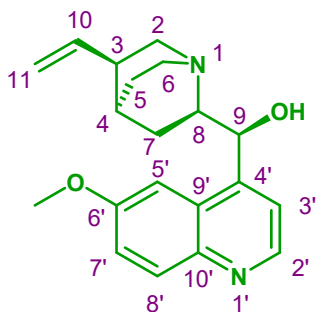


Fig. S1. Molecular frame-work of quinidine.

Table S1. BET surface characterization of as-synthesized $\text{Fe}_3\text{O}_4@\text{mQD}$ NPs.

	Parametres	Results
1	BET surface area	57.55m ² /g
2	Adsorption average pore diameter (4V/A)	115.28Å
3	Adsorption average pore width (4V/Aby BET)	129.45Å
4	Volume in pores	0.0015cm ³ /g
5	Total volume in pores	0.16 cm ³ /g

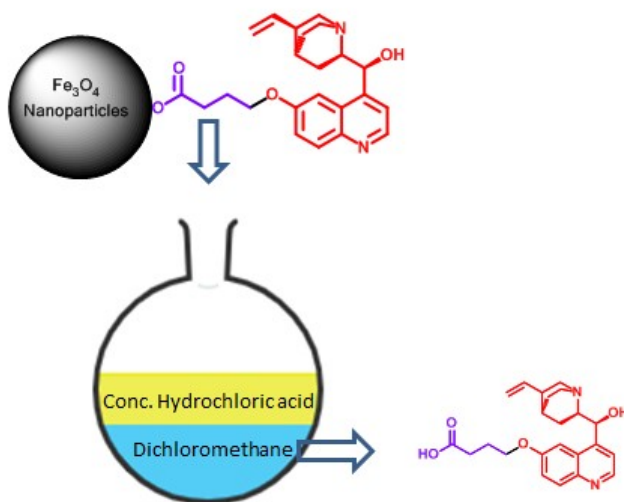


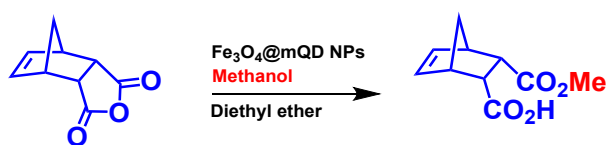
Fig. S2. Recovery process of mQD from $\text{Fe}_3\text{O}_4@\text{mQD}$ NPs.

Table S2. Specific optical rotations (SOR) of pristine and recovered mQD.

Substrate	Specific optical rotation ^a
mQD acid (pristine)	130.40°
mQD acid (recovered)	128.03°

^a [α]_D²⁵ (C=1.0 Ethanol)

Table S3. Recycling of Fe₃O₄@mQD NPs catalyst.^a



Entry	Yield (%)	ee (%)	
1	91	98	1 st reaction
2	90	97	3 rd cycle
3	93	94	5 th cycle

^a The reaction was performed by treatment of the cyclic anhydride (1.0 mmol) with methanol (10 mmol) in the presence of Fe₃O₄@mQD (100 mg) at -45°C in diethylether (5.0 mL). During the recycling of the catalyst there was no loss in the quantity of the catalyst observed so there was no requirement of top-up of additional catalyst.

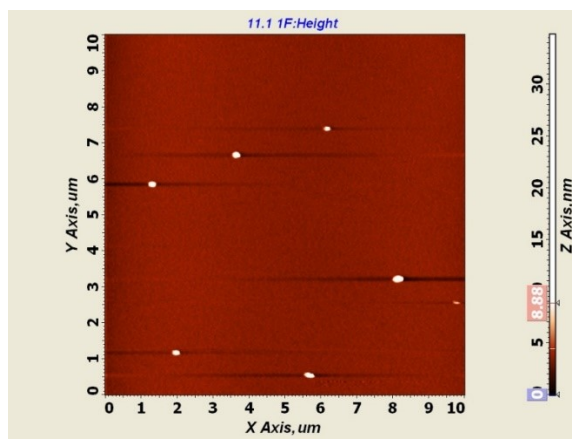
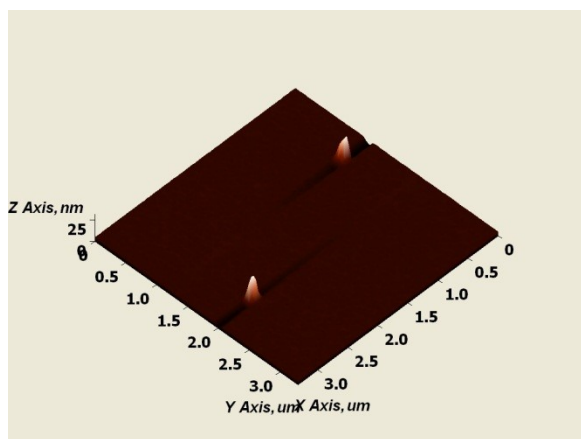
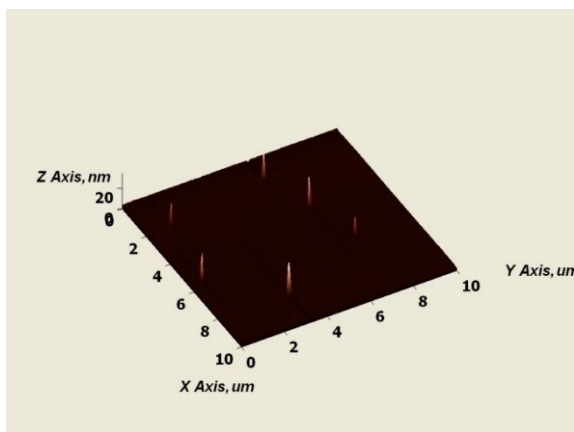
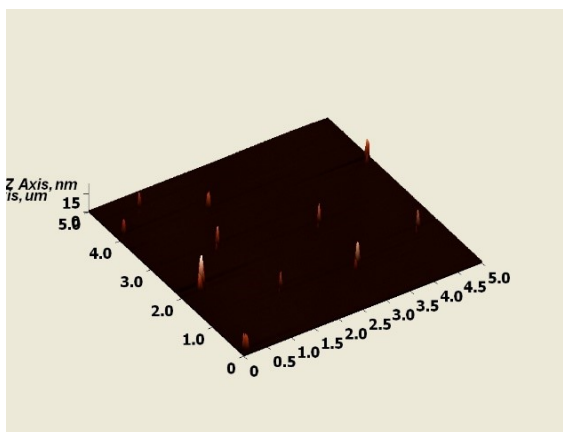


Fig. S3. AFM images of the Fe₃O₄@ester-QD NPs at various magnifications.

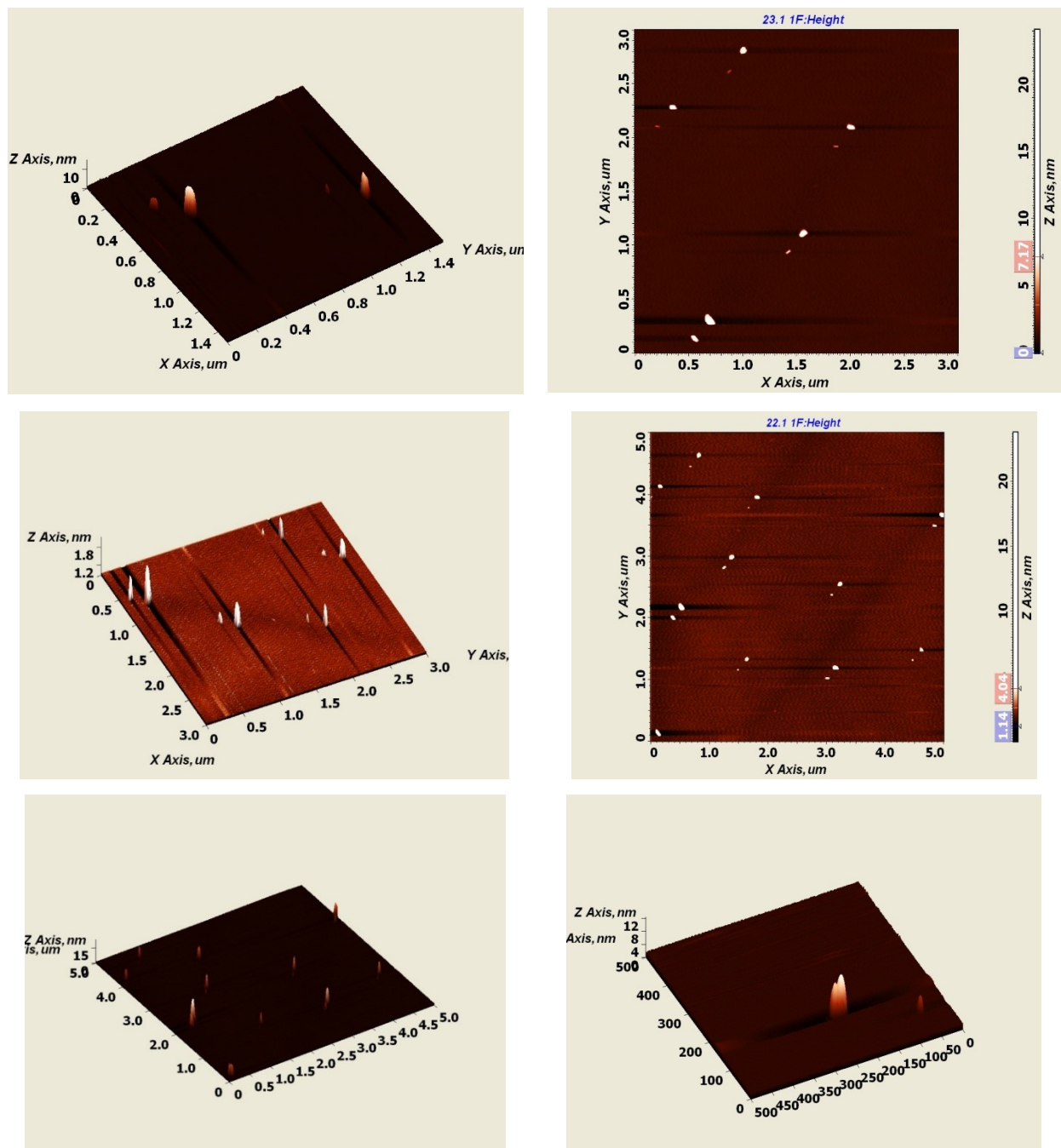


Fig. S4. AFM images of the $\text{Fe}_3\text{O}_4@\text{mQD}$ NPs at various magnifications.

Experimental section

(a)



(b)



Fig. S5. (a) Reaction mixture of Anhydride, Methanol and $\text{Fe}_3\text{O}_4@\text{mQD}$ NPs under stirring with magnetic bar (b) reaction mixture when magnetic stirring is stopped and the catalyst sticks to the magnetic needle.

NMR spectra and HPLC chromatograms of the products and mQD intermediates:

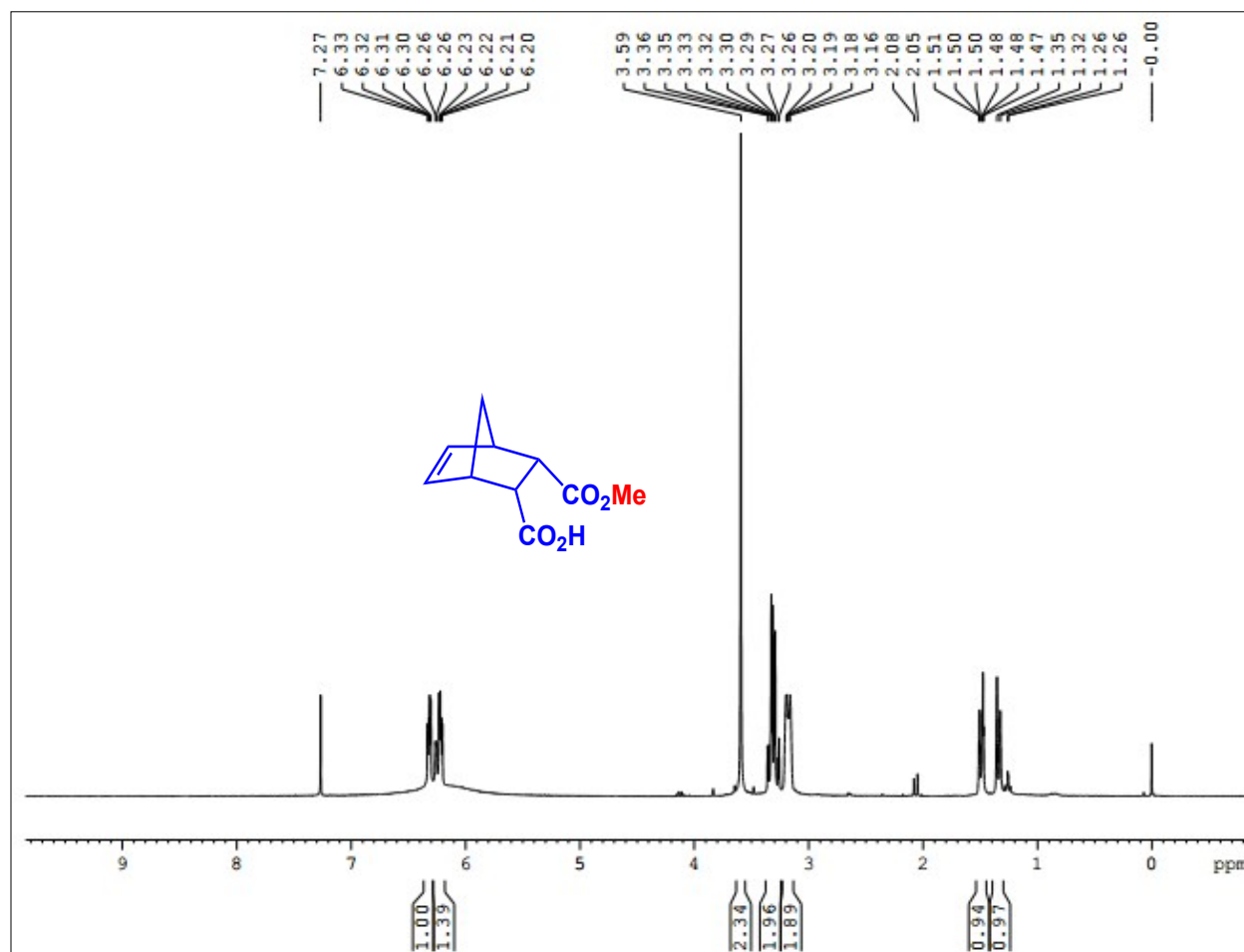


Fig. S6. ^1H NMR of (2R, 3S)-3-endo-methoxycarbonyl-bicyclo[2.2.1]hept-5-ene-2-endo-carboxylic acid (22).

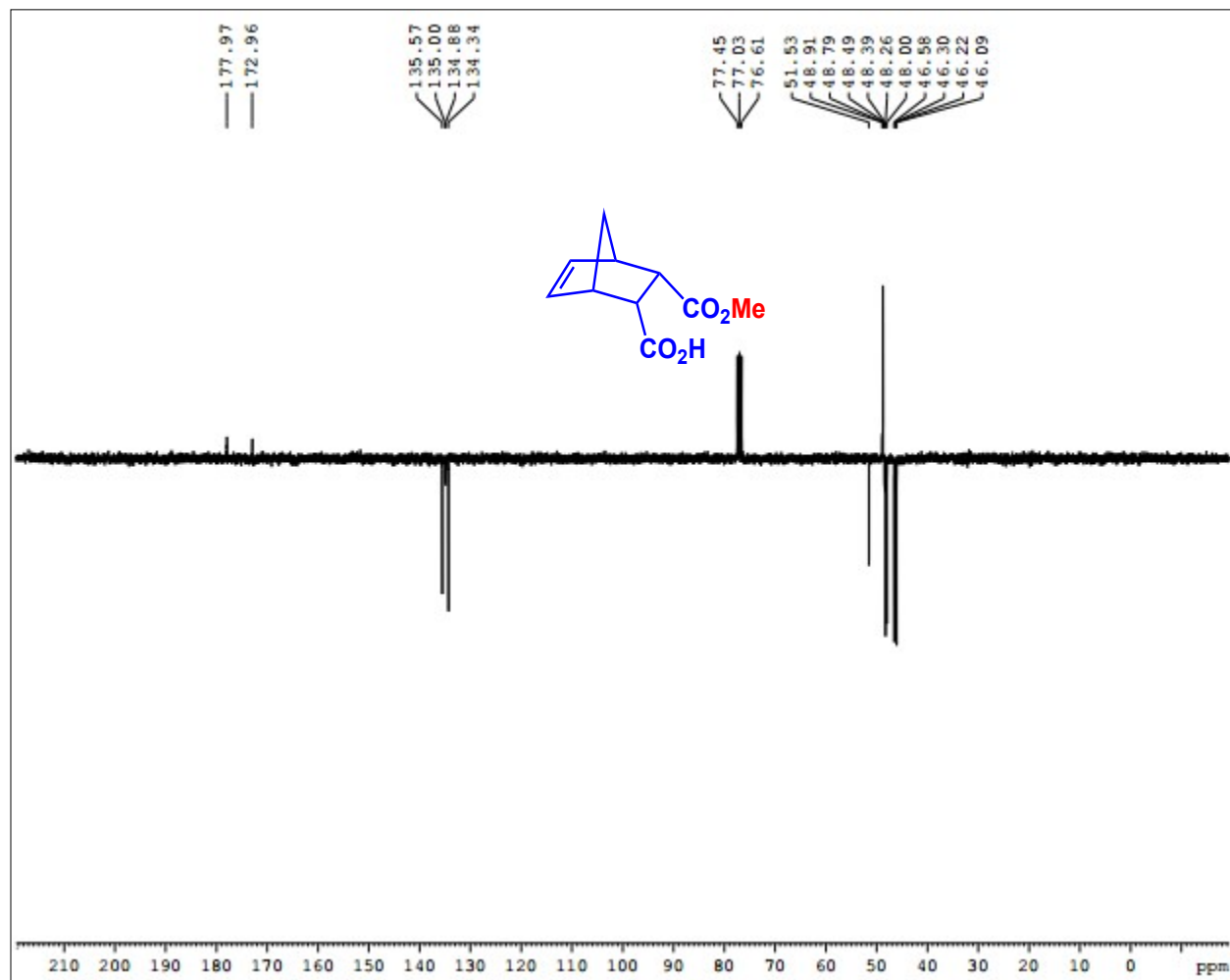


Fig. S7. ^{13}C NMR of (2R, 3S)-3-endo-methoxycarbonyl-bicyclo[2.2.1]hept-5-ene-2-endo-carboxylic acid (**22**).

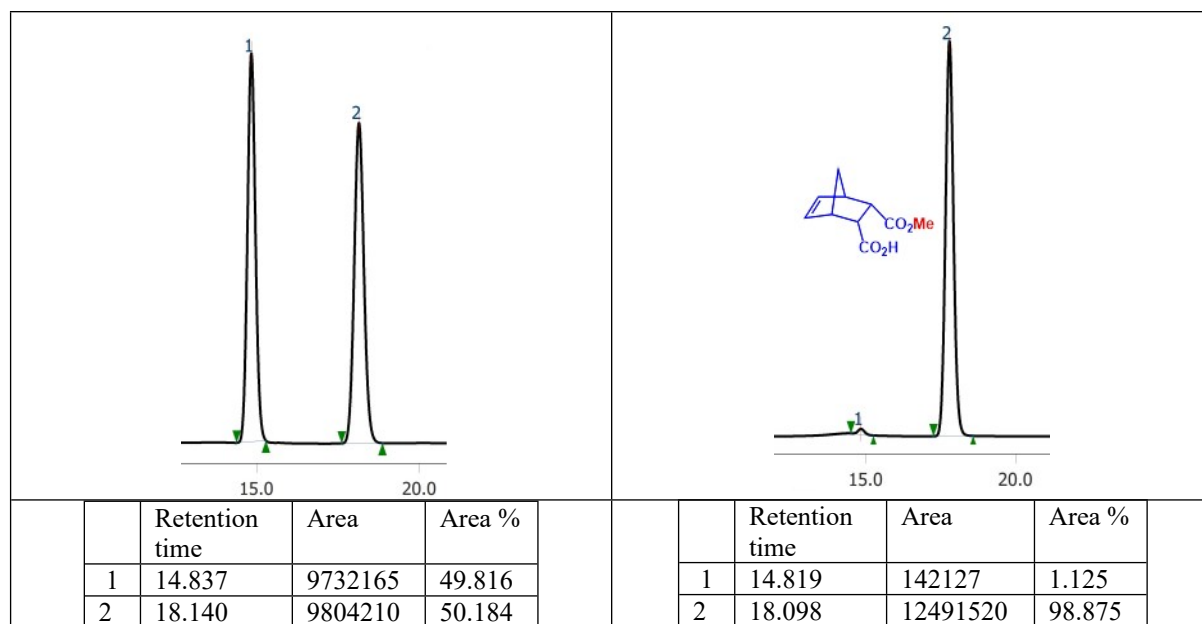


Fig. S8. HPLC chromatograms of racemic and (2*R*, 3*S*)-3-*endo*-methoxycarbonylbicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid (**22**).

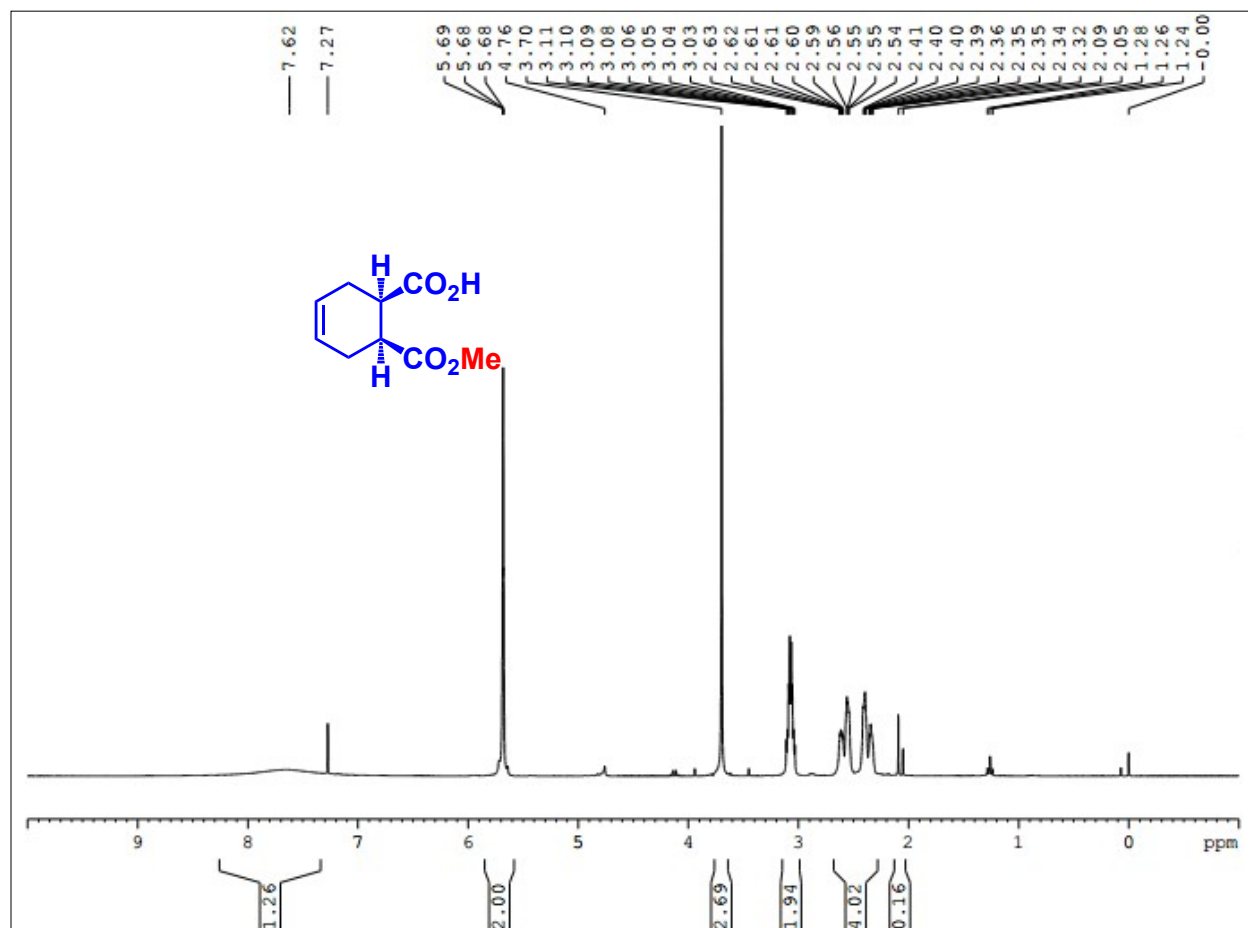


Fig. S9. ¹H NMR of (1R,2S)-*cis*-2-methoxycarbonyl-cyclohex-4-ene-1-carboxylic acid (**24**).

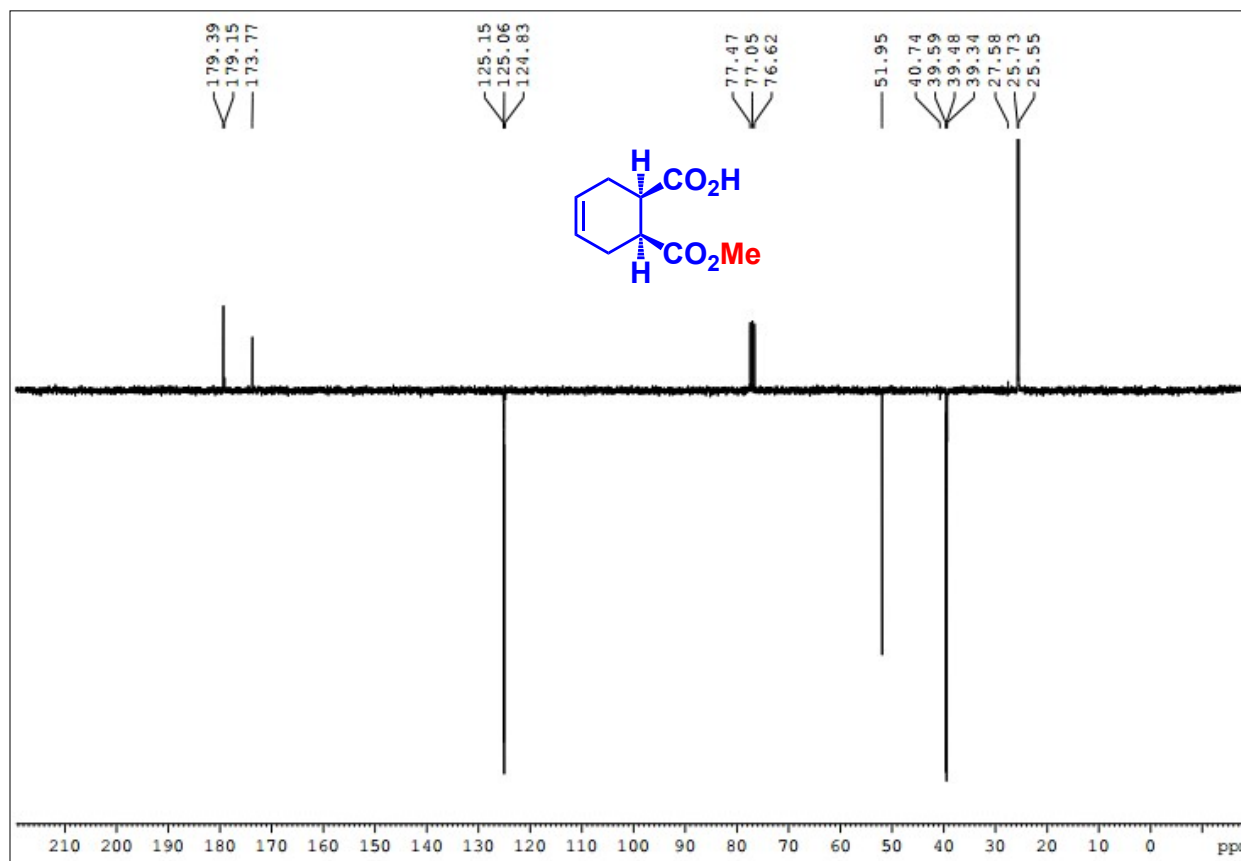


Fig. S10. ^{13}C NMR of (1*R*, 2*S*)-*cis*-2-methoxycarbonyl-cyclohex-4-ene-1-carboxylic acid (**24**).

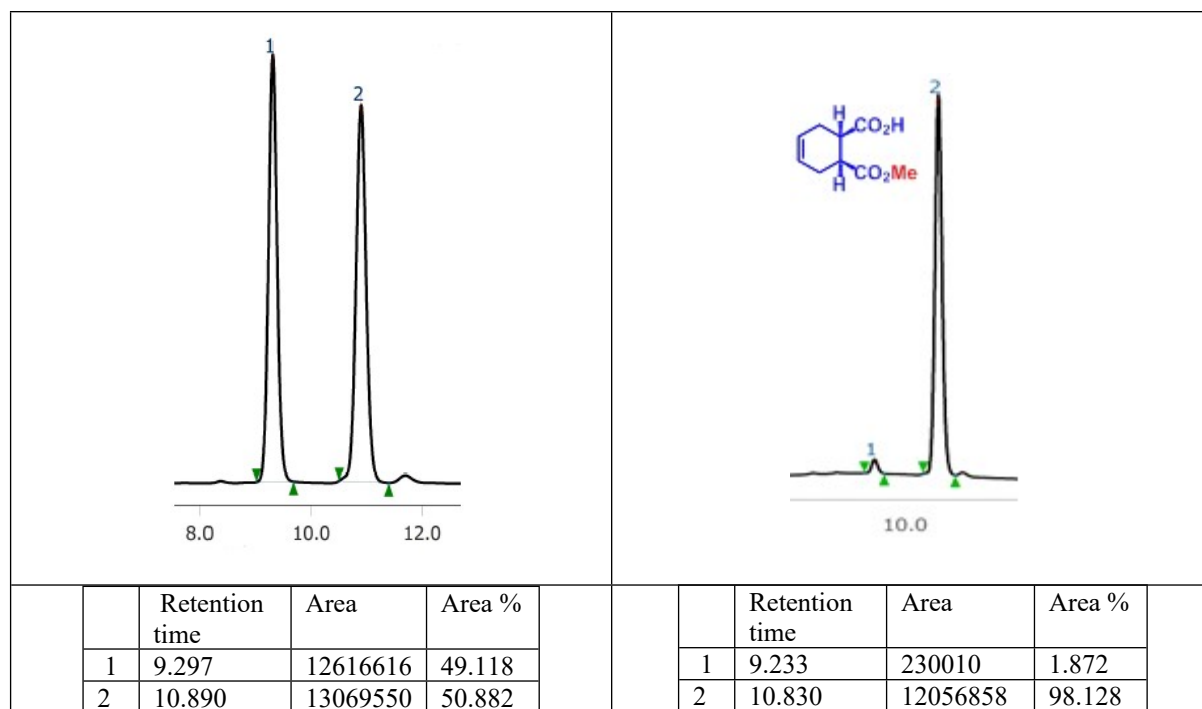


Fig. S11. HPLC chromatographs of racemic and (1*R*, 2*S*) *cis*-2-methoxycarbonyl-cyclohex-4-ene-1-carboxylic acid (**24**).

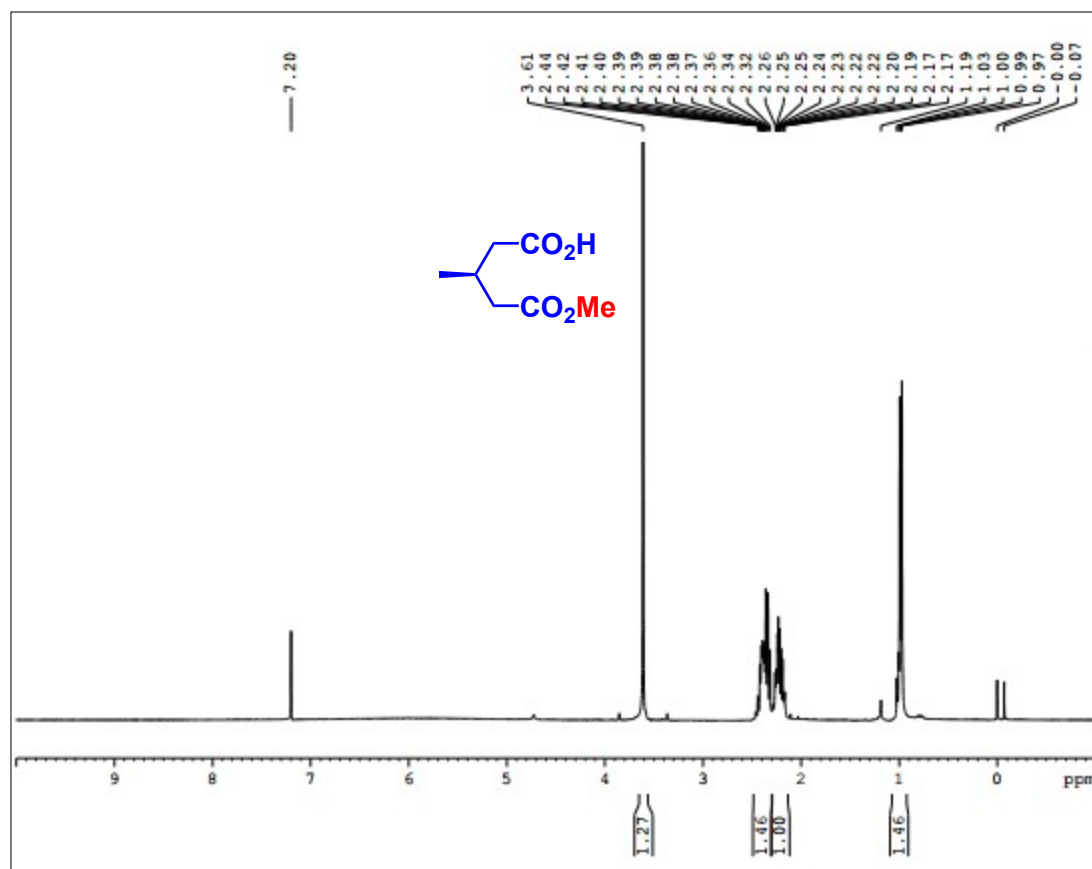


Fig. S12. ¹H NMR of (3R)-5-methoxy-3-methyl-5-oxopentanoic acid (**26**).

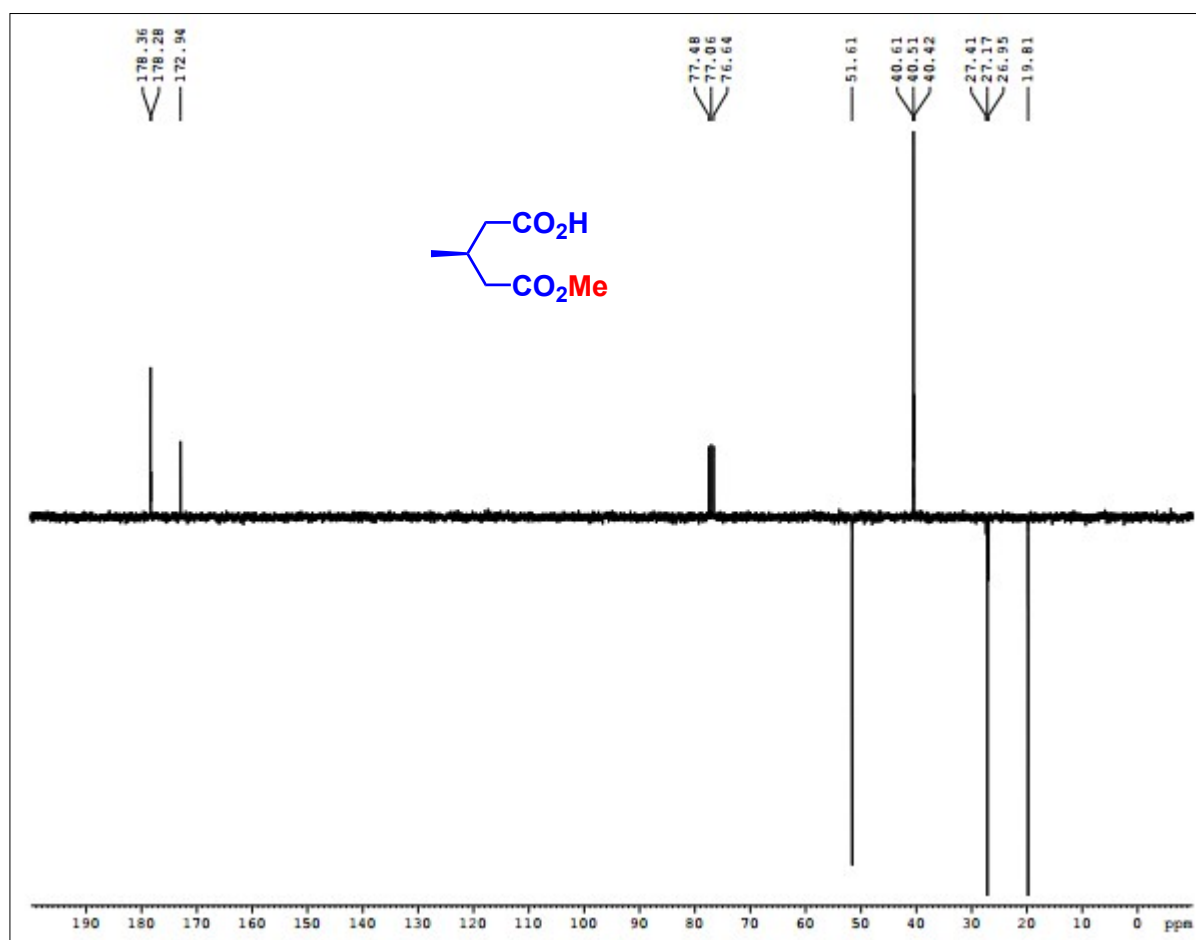


Fig. S13. ¹³C NMR of (3R)-5-methoxy-3-methyl-5-oxopentanoic acid (**26**).

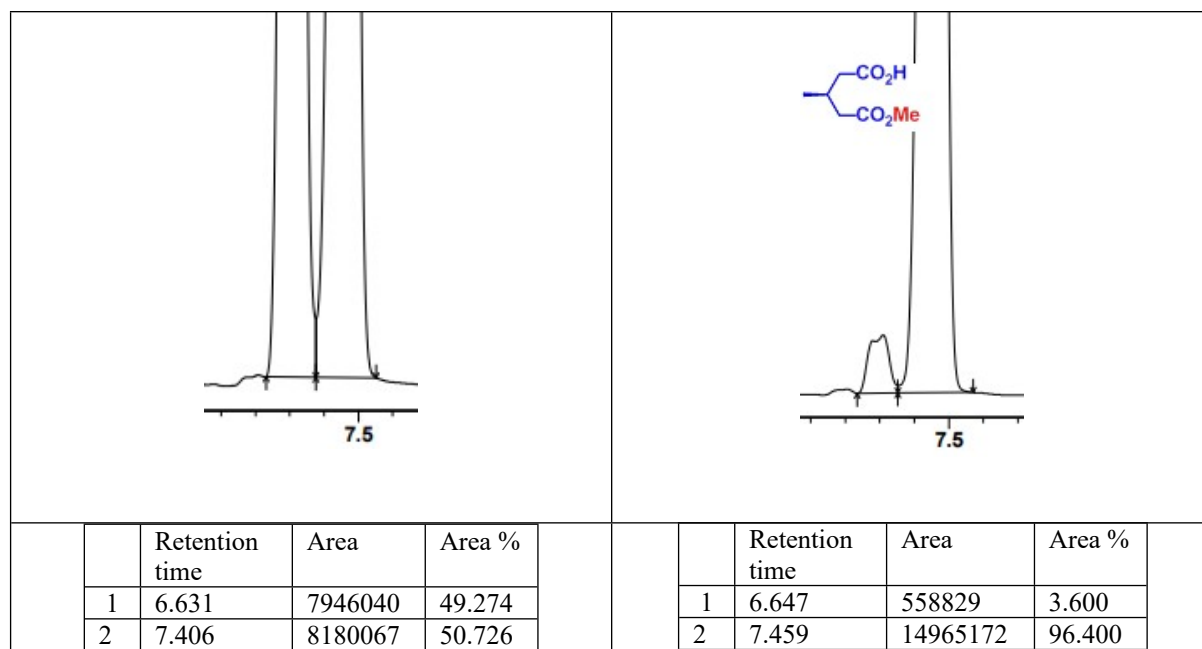


Fig. S14. HPLC chromatograms of racemic and (3R)-5-methoxy-3-methyl-5-oxopentanoic acid (26).

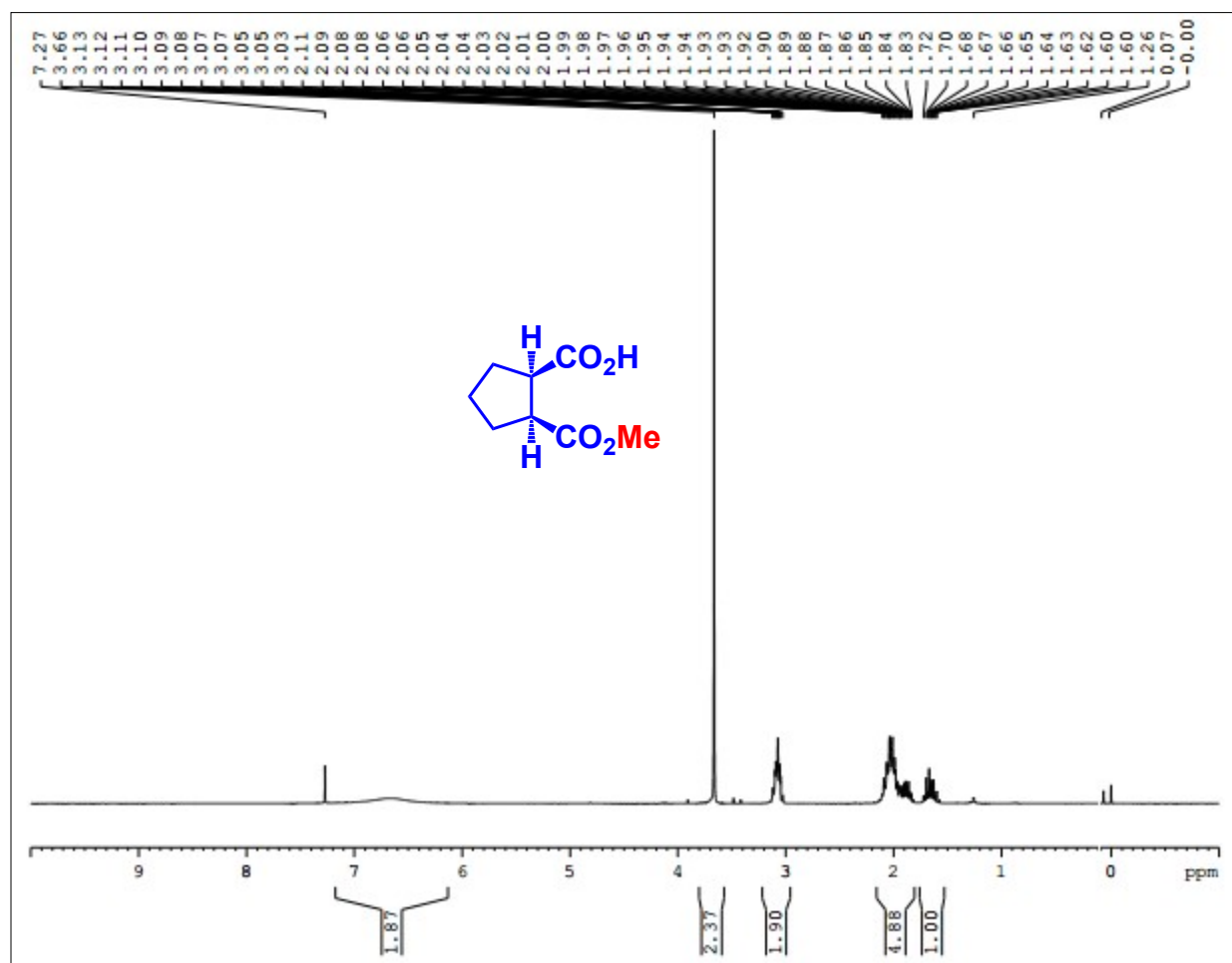


Fig. S15. ¹H NMR of (1*R*,2*S*)-*cis*-2-Methoxycarbonyl-cyclopentane-1-carboxylic acid (**28**).

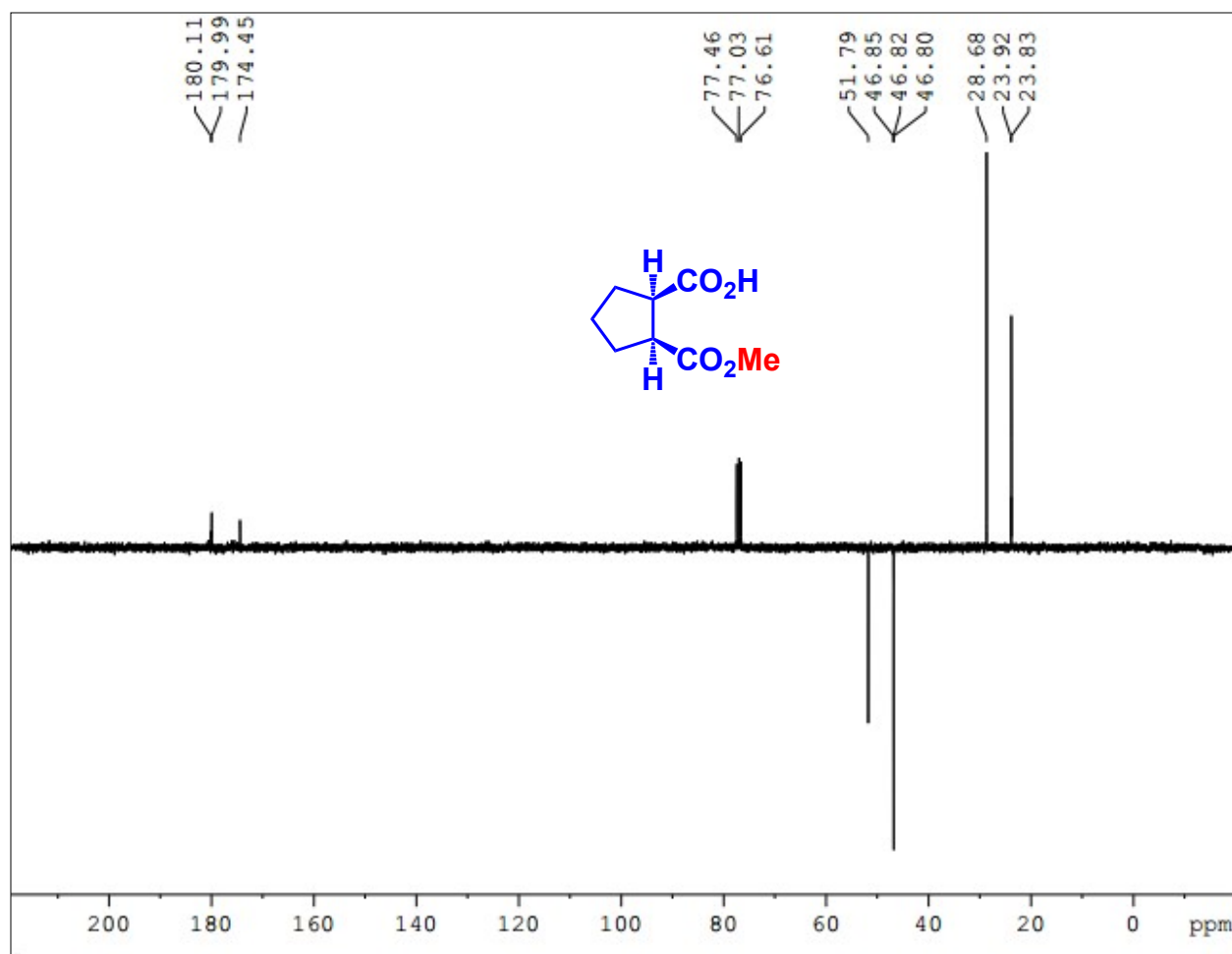


Fig. S16. ^{13}C NMR of (1*R*, 2*S*)-*cis*-2-Methoxycarbonyl-cyclopentane-1-carboxylic acid (28).

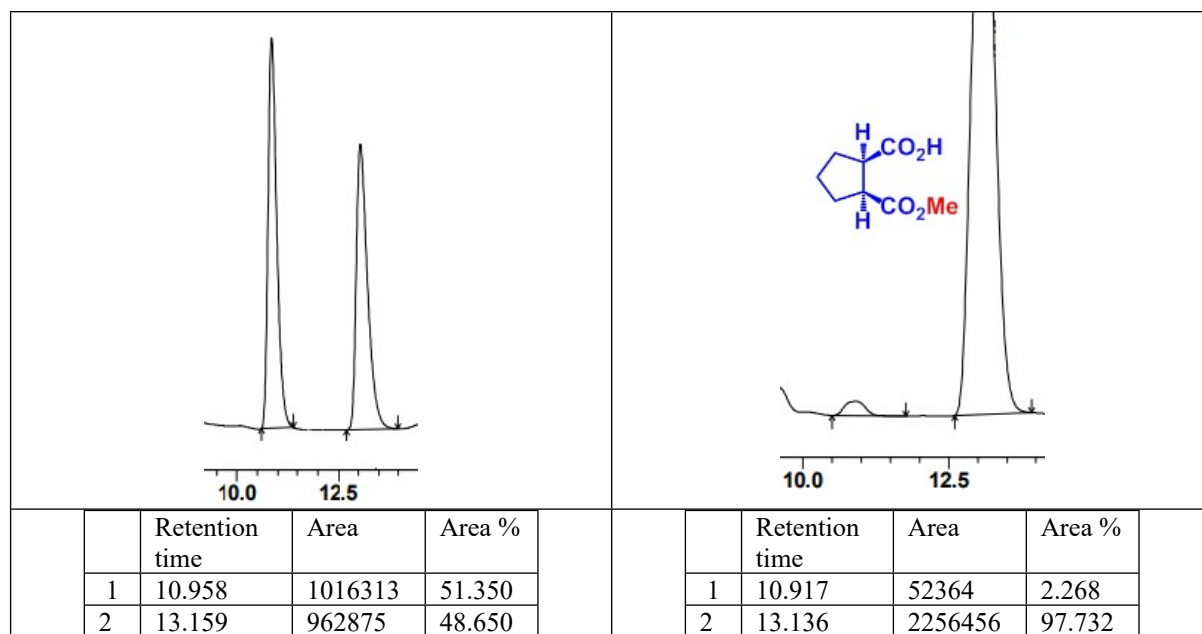


Fig. S17. HPLC chromatograms of racemic and (1*R*, 2*S*)-*cis*-2-Methoxycarbonyl-cyclopentane-1-carboxylic acid (**28**).

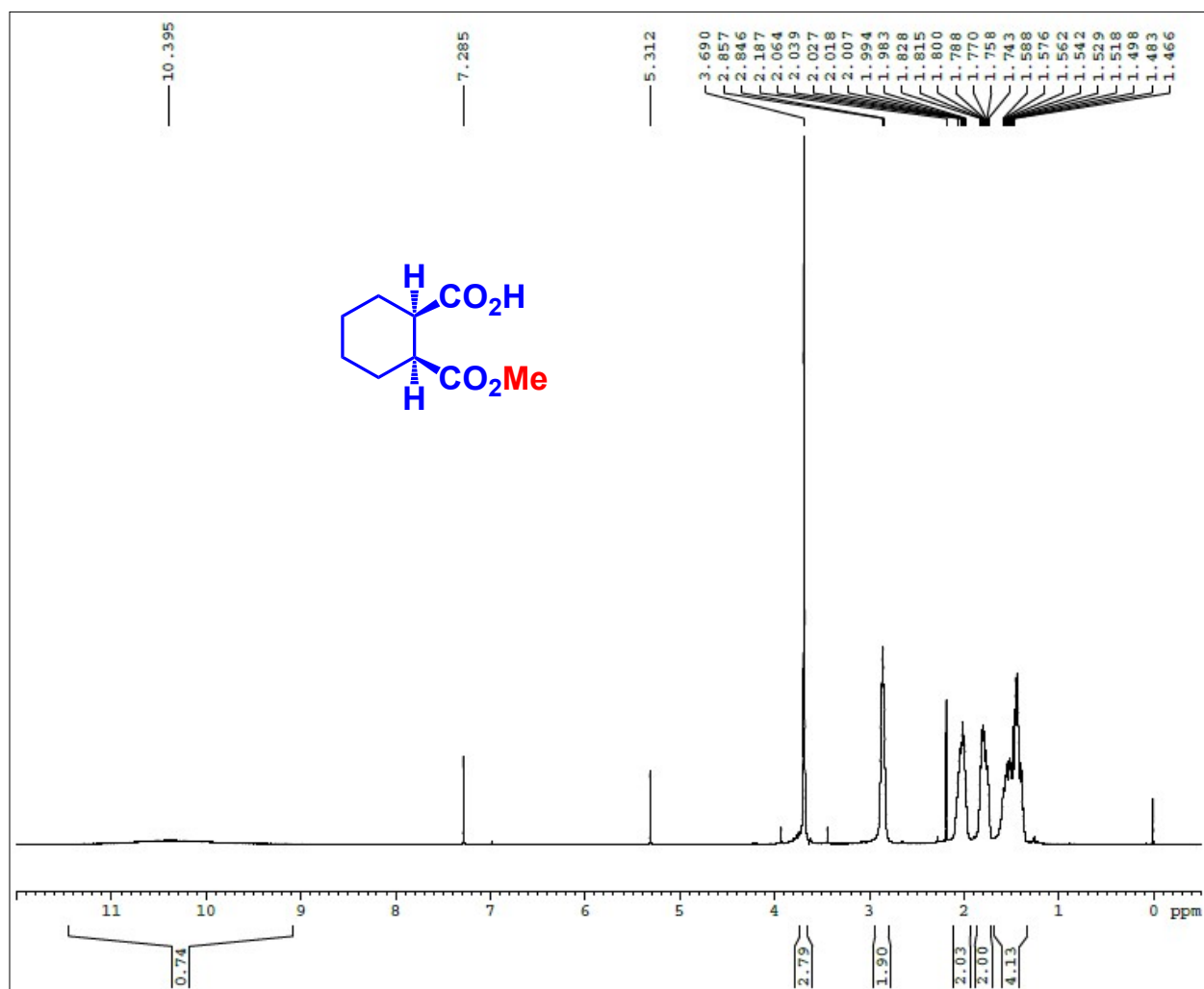


Fig. S18. ¹H NMR of (1R, 2S)-2-(methoxycarbonyl)-cyclohexane-1-carboxylic acid (**30**).

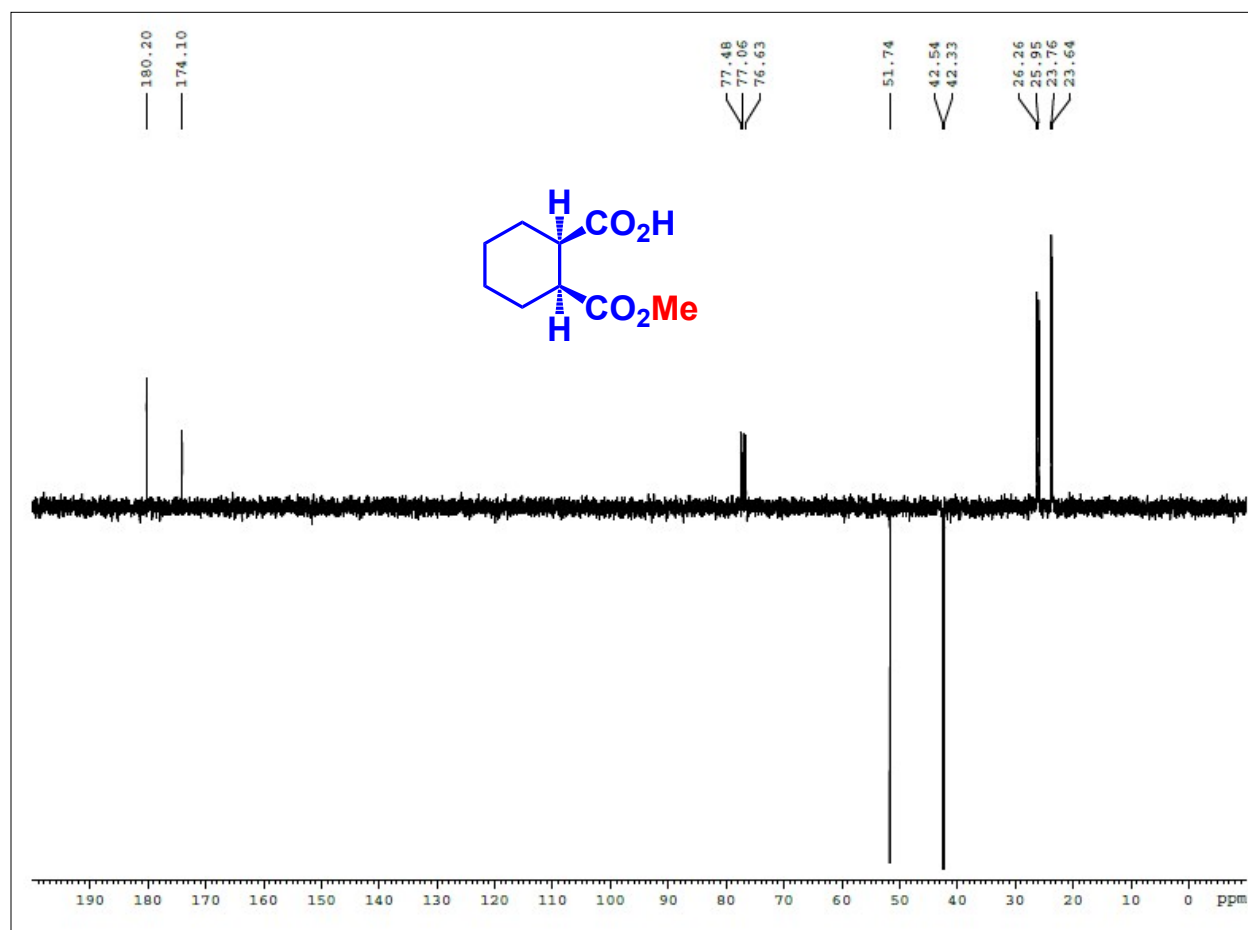


Fig. S19. ^{13}C NMR of (1R, 2S)-2-(methoxycarbonyl)-cyclohexane-1-carboxylic acid (**30**).

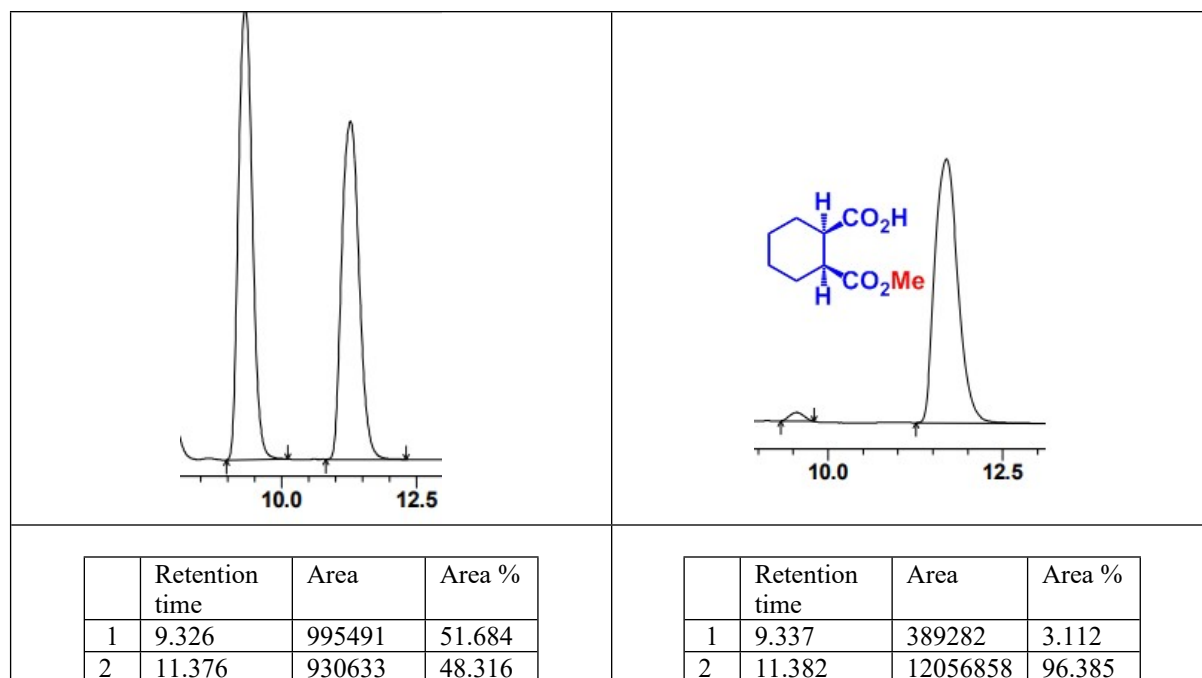


Fig. S20. HPLC chromatograms of racemic and (1R, 2S)-2-(methoxycarbonyl)cyclohexane-1-carboxylic acid (**30**).

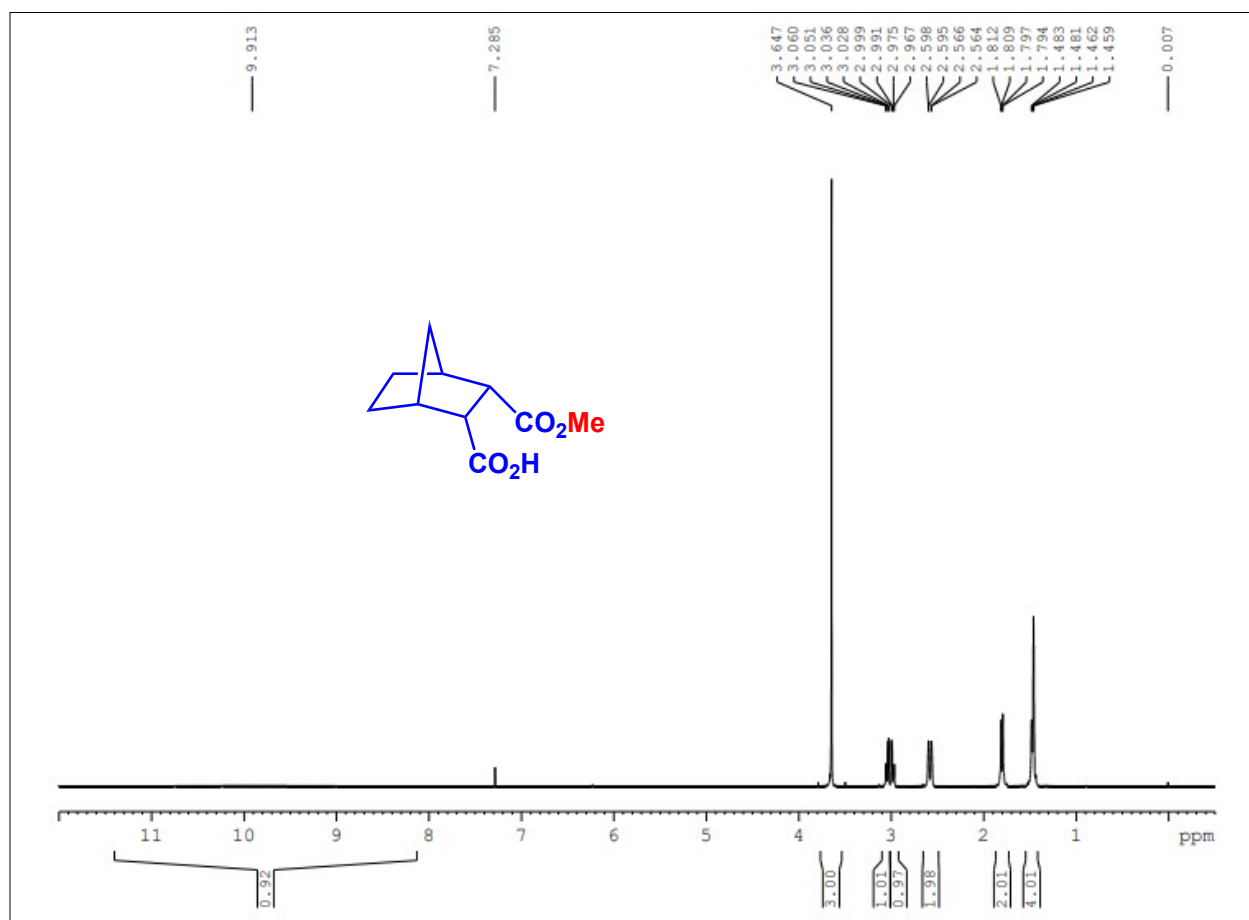


Fig. S21. ¹H NMR of (1R,2R,3S,4S)-3-(methoxycarbonyl)bicyclo[2.2.1]heptane-2-carboxylic acid (32).

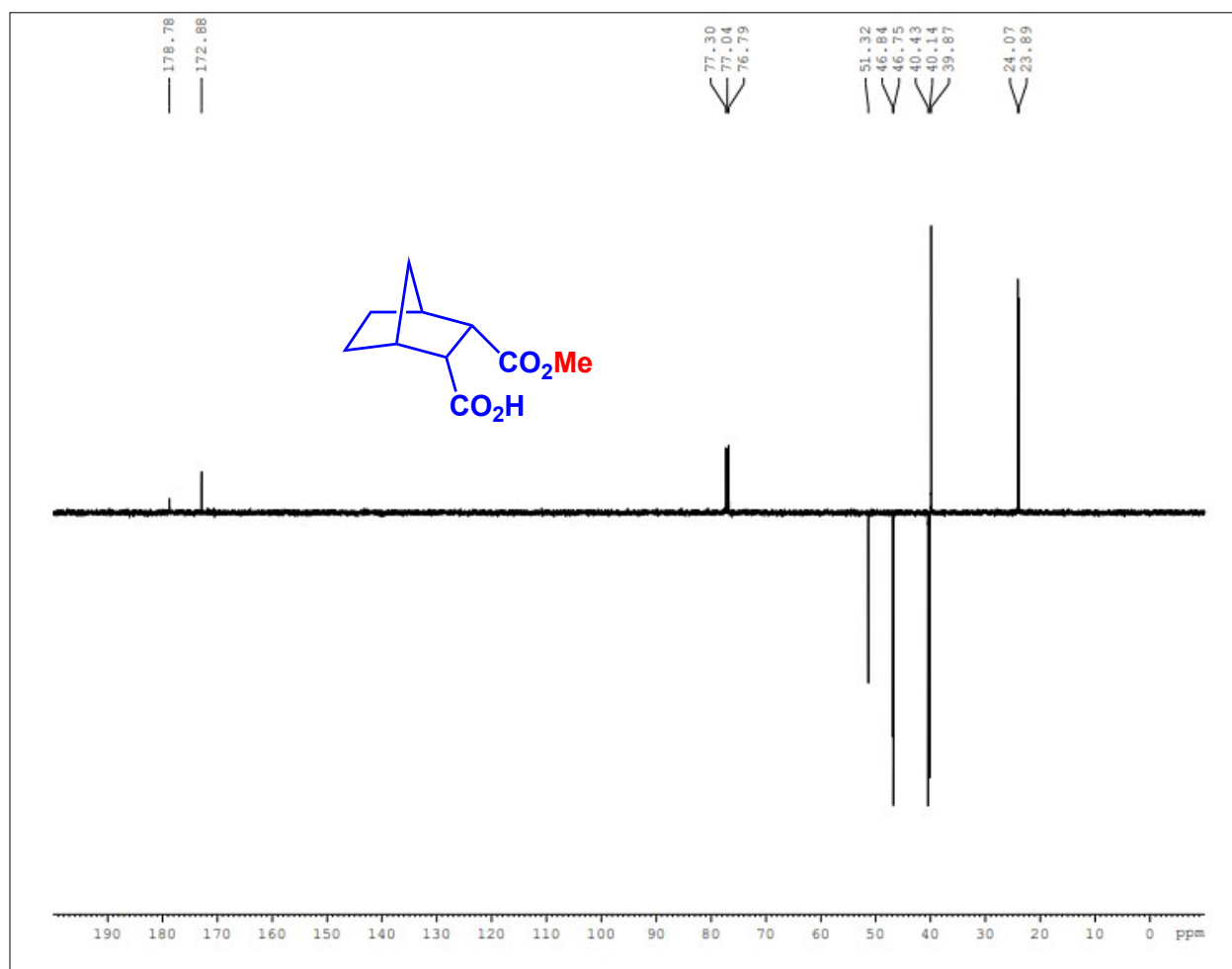


Fig. S22. ^{13}C NMR of (1R,2R,3S,4S)-3-(methoxycarbonyl)bicyclo[2.2.1]heptane-2-carboxylic acid (32).

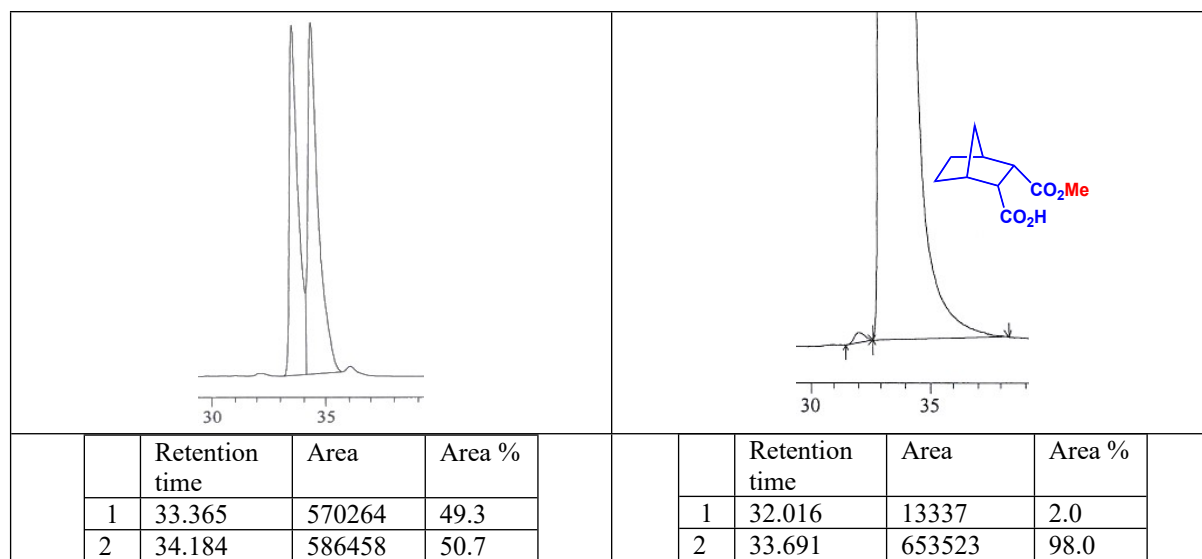


Fig. S23. HPLC chromatograms of racemic and (1R,2R,3S,4S)-3(methoxycarbonyl)bicyclo[2.2.1]heptane-2-carboxylic acid (32).

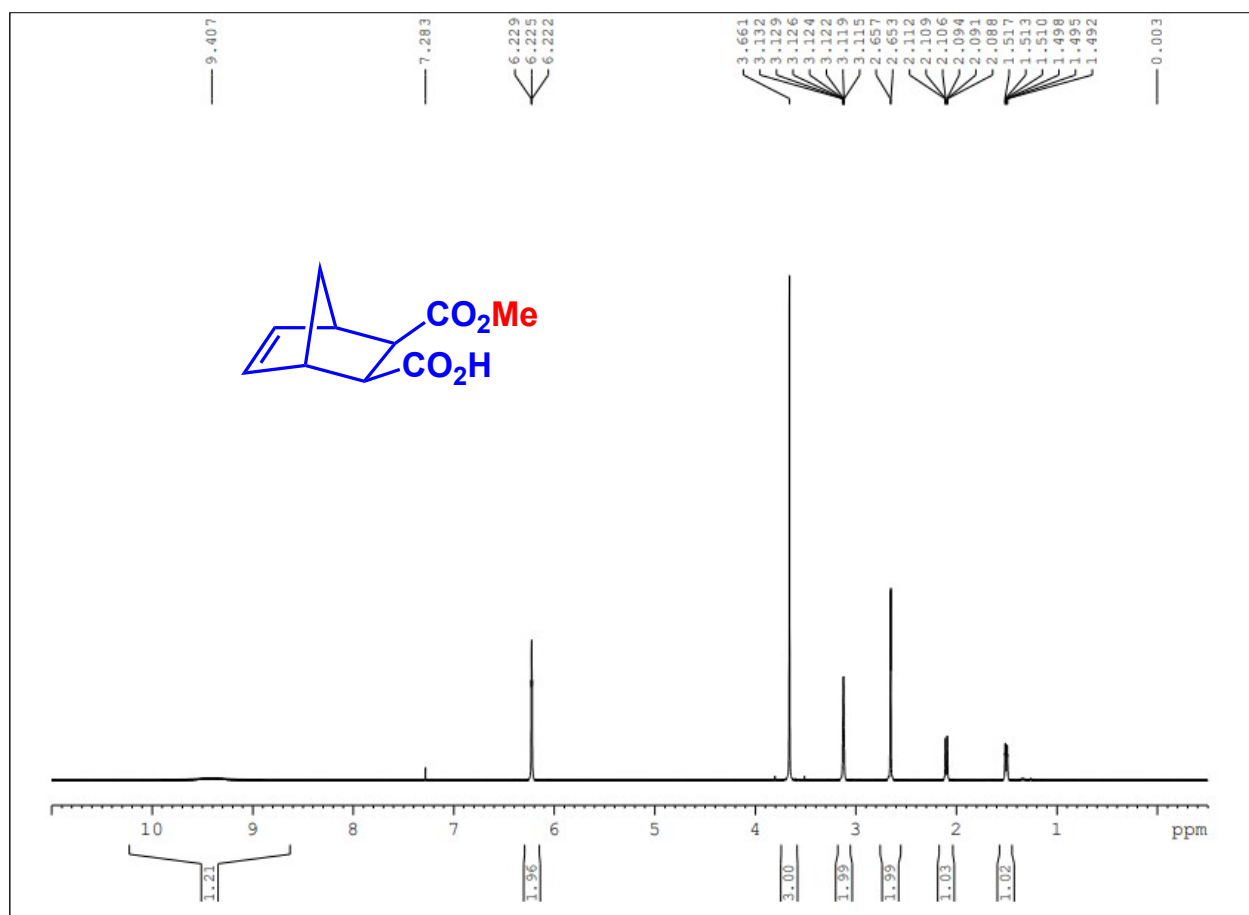


Fig. S24. ¹H NMR of (1R,2R,3S,4S)-3-(methoxycarbonyl)bicyclo[2.2.1]heptane-2-carboxylic acid (34).

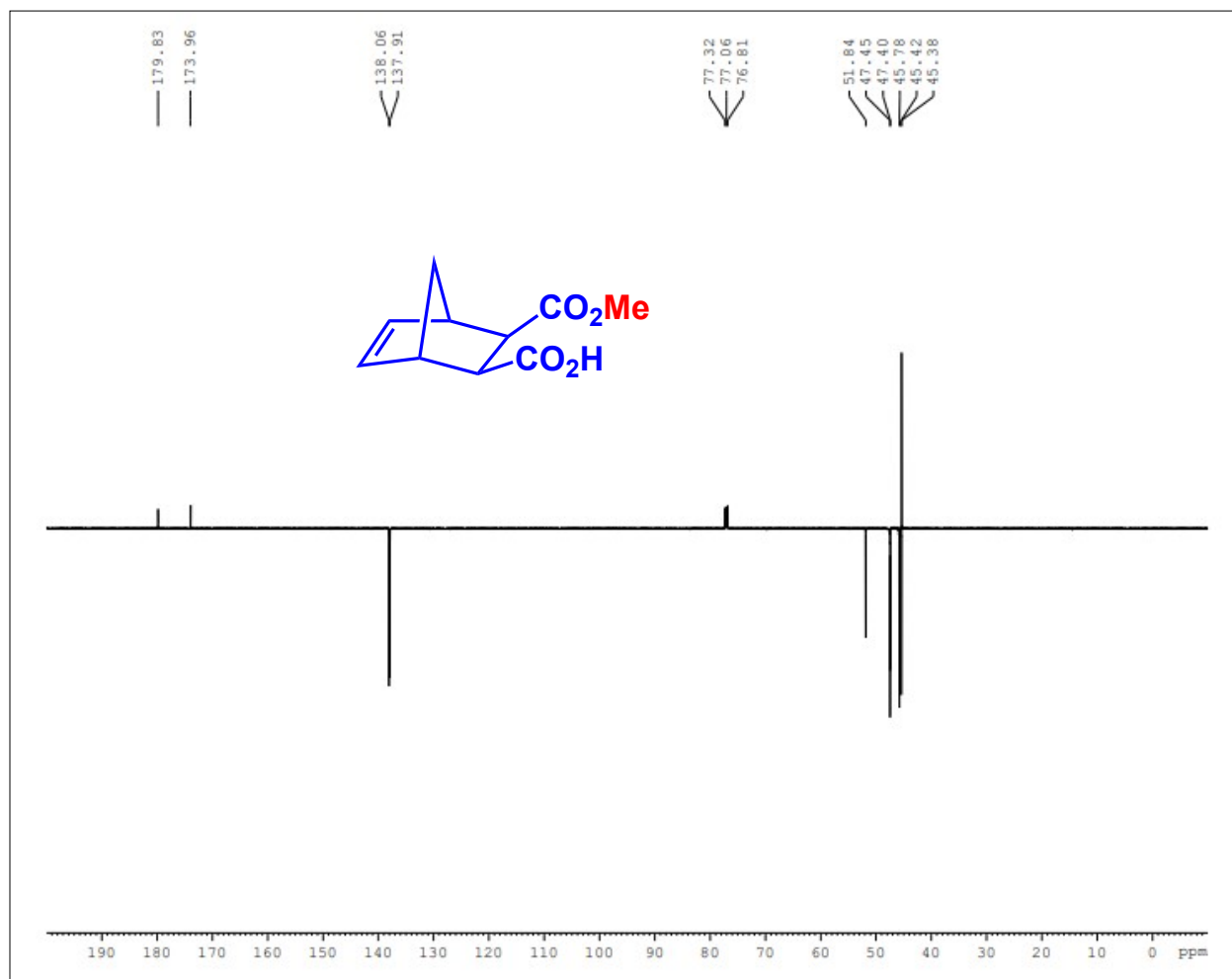


Fig. S25. ^{13}C NMR of (1R,2R,3S,4S)-3-(methoxycarbonyl)bicyclo[2.2.1]heptane-2-carboxylic acid (34).

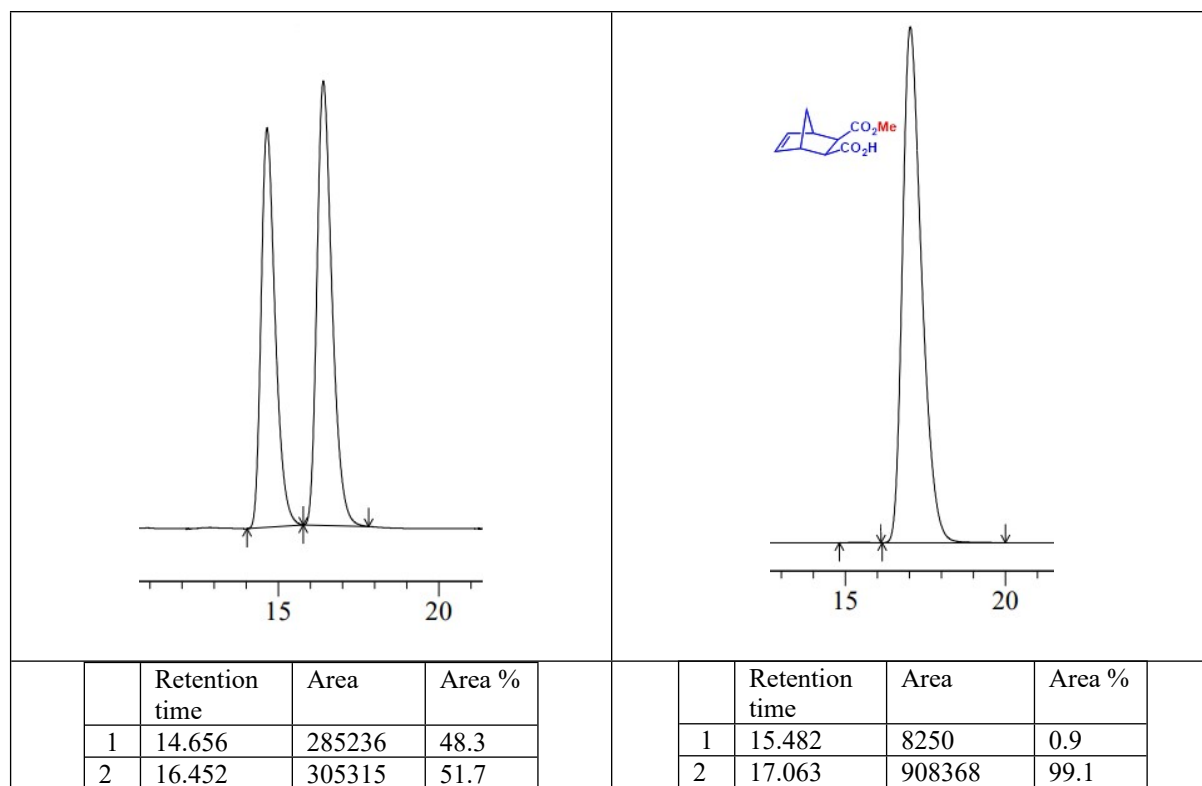


Fig. S26. HPLC chromatograms of racemic and (1R,2R,3S,4S)-3-(methoxycarbonyl)bicyclo- [2.2.1]heptane-2-carboxylic acid (34).

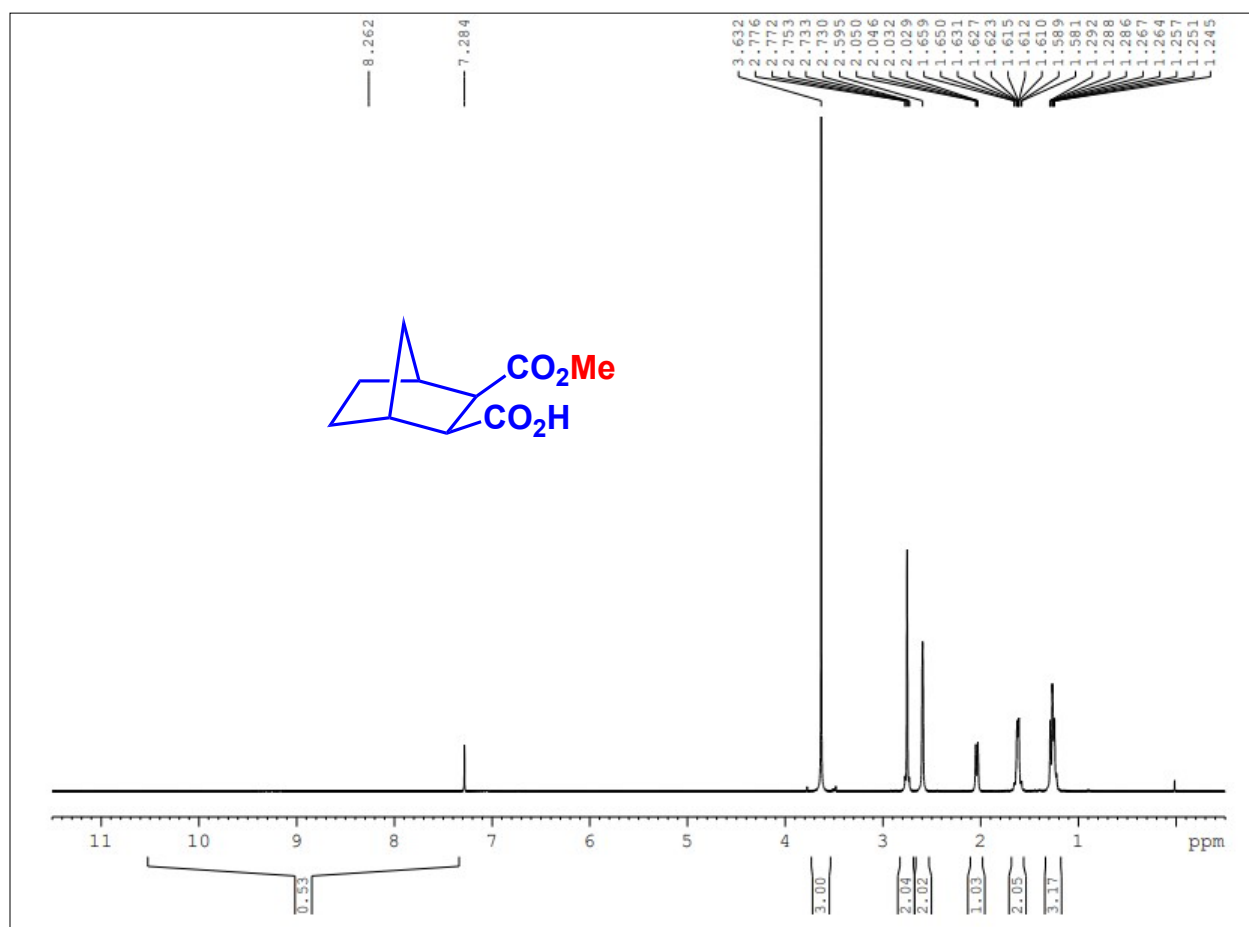


Fig. S27. ¹H NMR of (1R,2R,3S,4S)-3-(methoxycarbonyl)bicyclo[2.2.1]heptane-2-carboxylic acid (36).

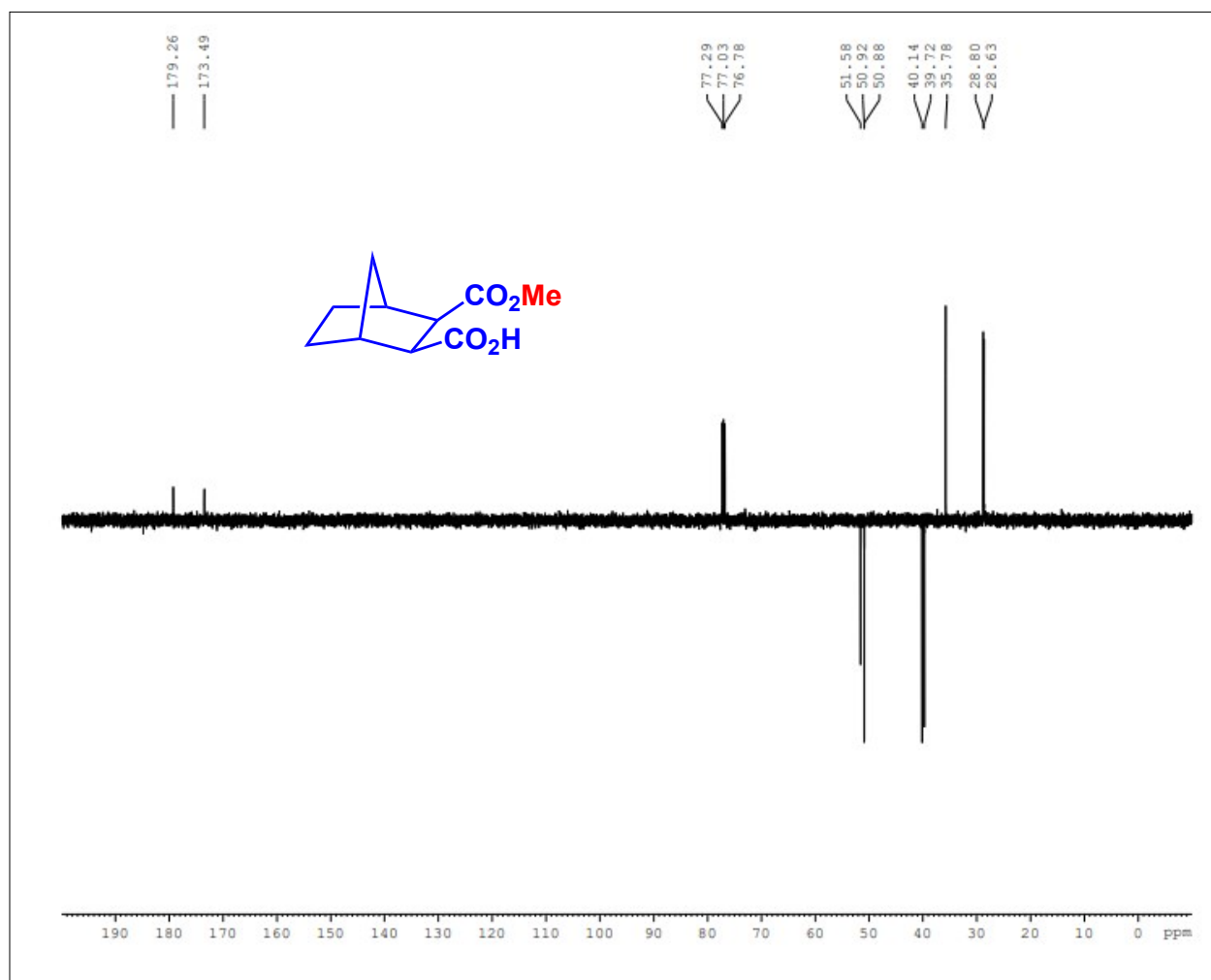


Fig. S28. ¹³C NMR of (1R,2R,3S,4S)-3-(methoxycarbonyl)bicyclo[2.2.1]heptane-2-carboxylic acid (36).

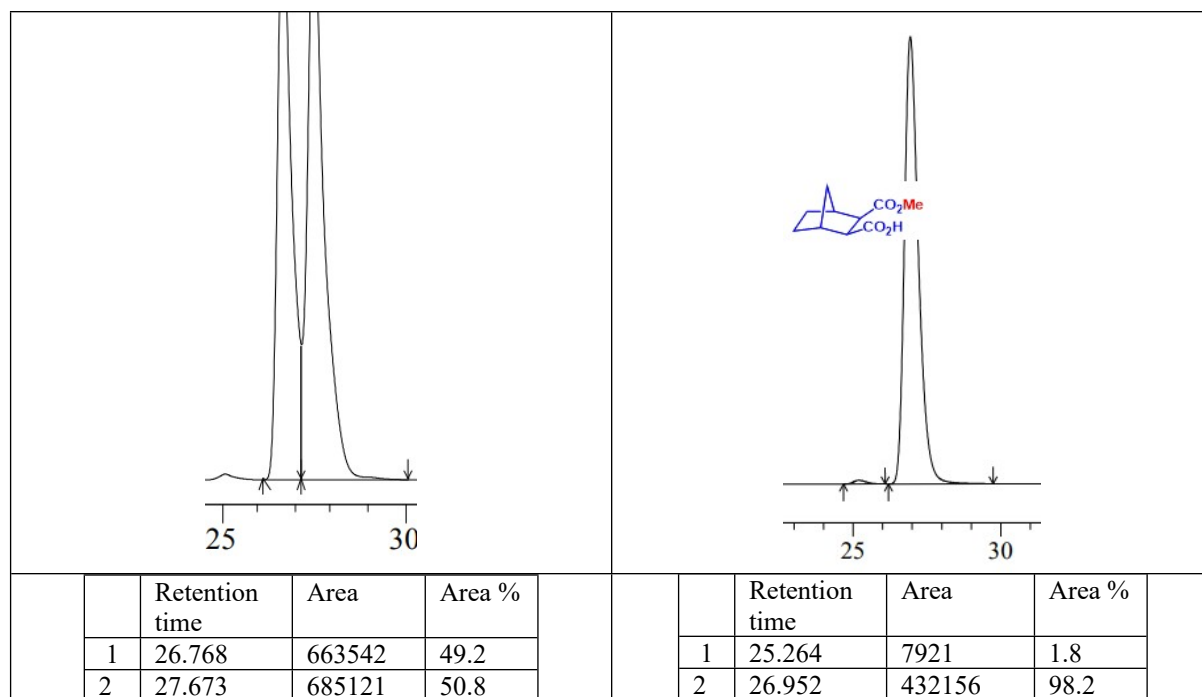


Fig. S29. HPLC chromatograms of racemic and (1R,2R,3S,4S)-3-(methoxycarbonyl)bicyclo[2.2.1]heptane-2-carboxylic acid (36).

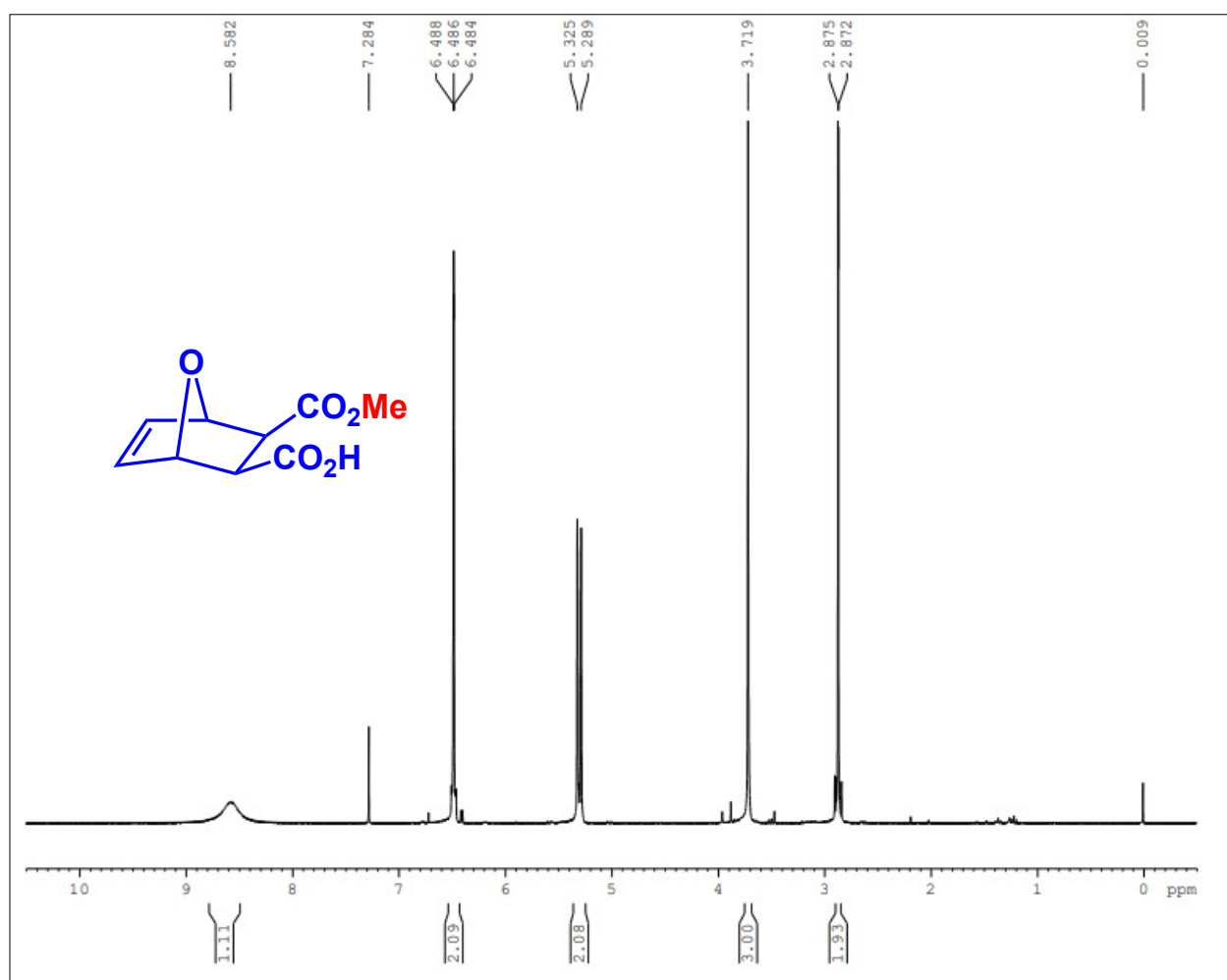


Fig. S30. ^1H NMR of (1S,2R,4R)-3-(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid (38).

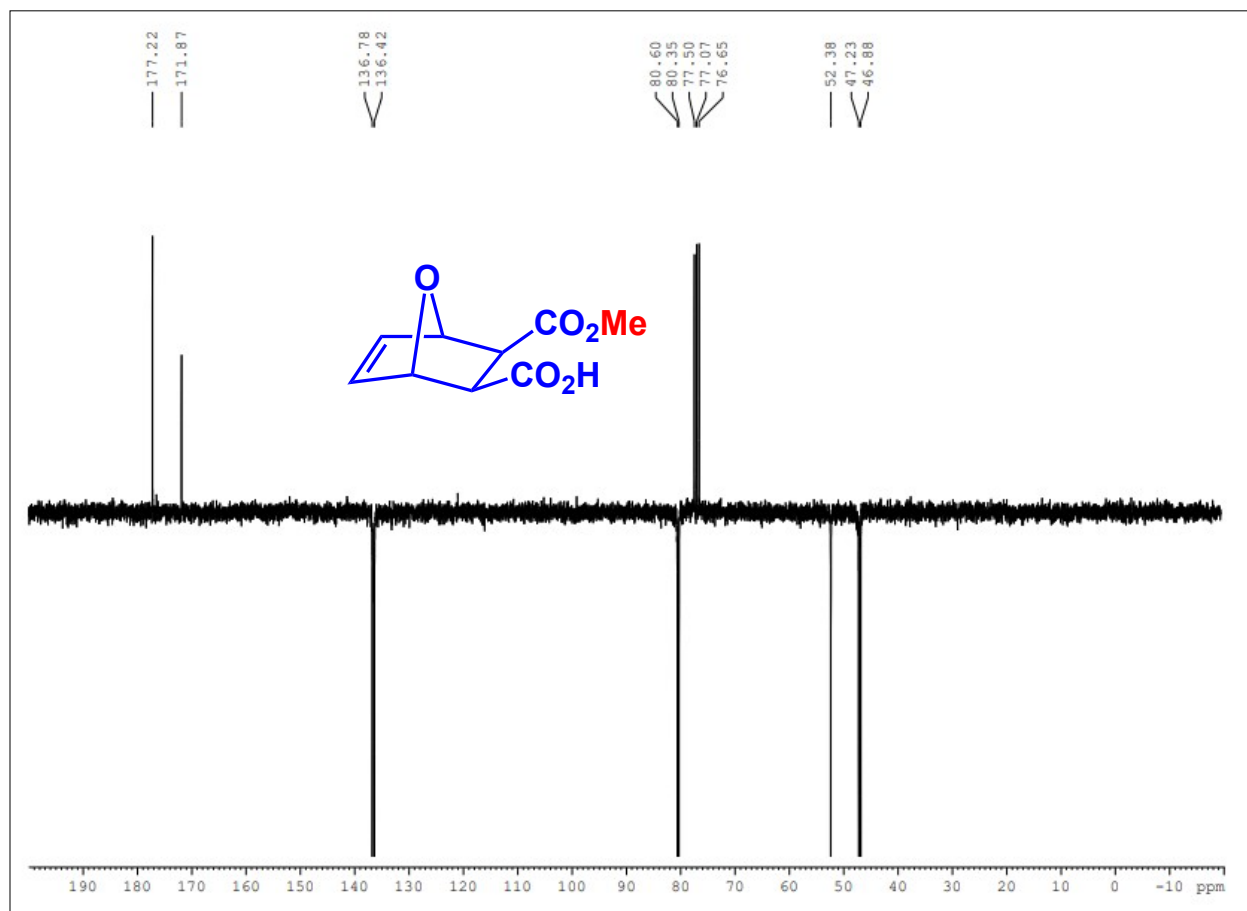


Fig. S31. ^{13}C NMR of (1S,2R,4R)-3-(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid (38).

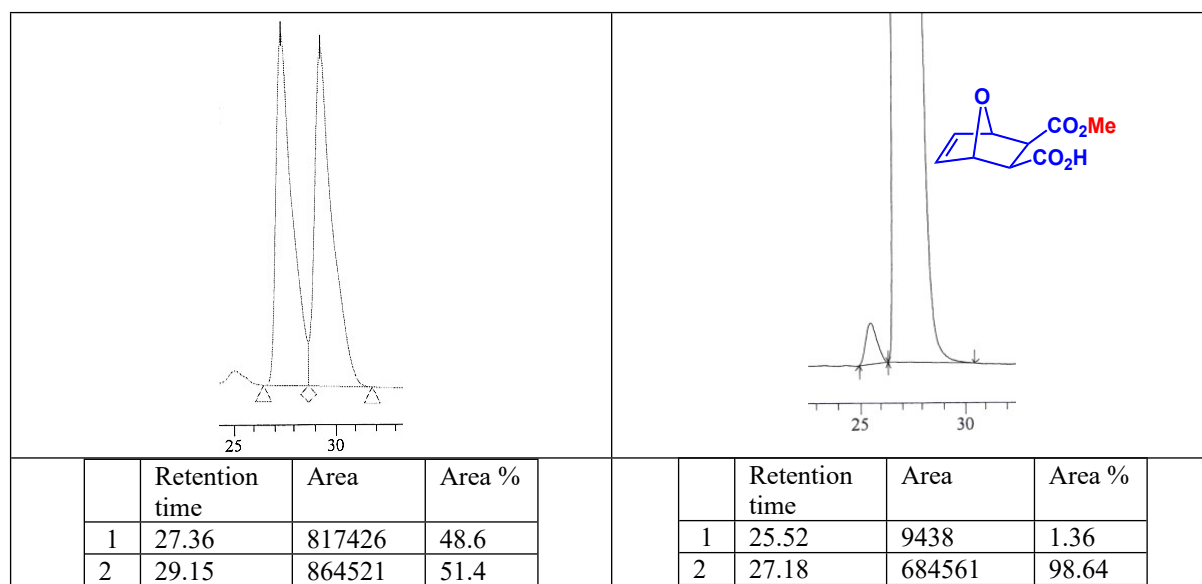


Fig. S32. HPLC chromatograms of racemic and (1S,2R,4R)-3-(methoxycarbonyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid (38).

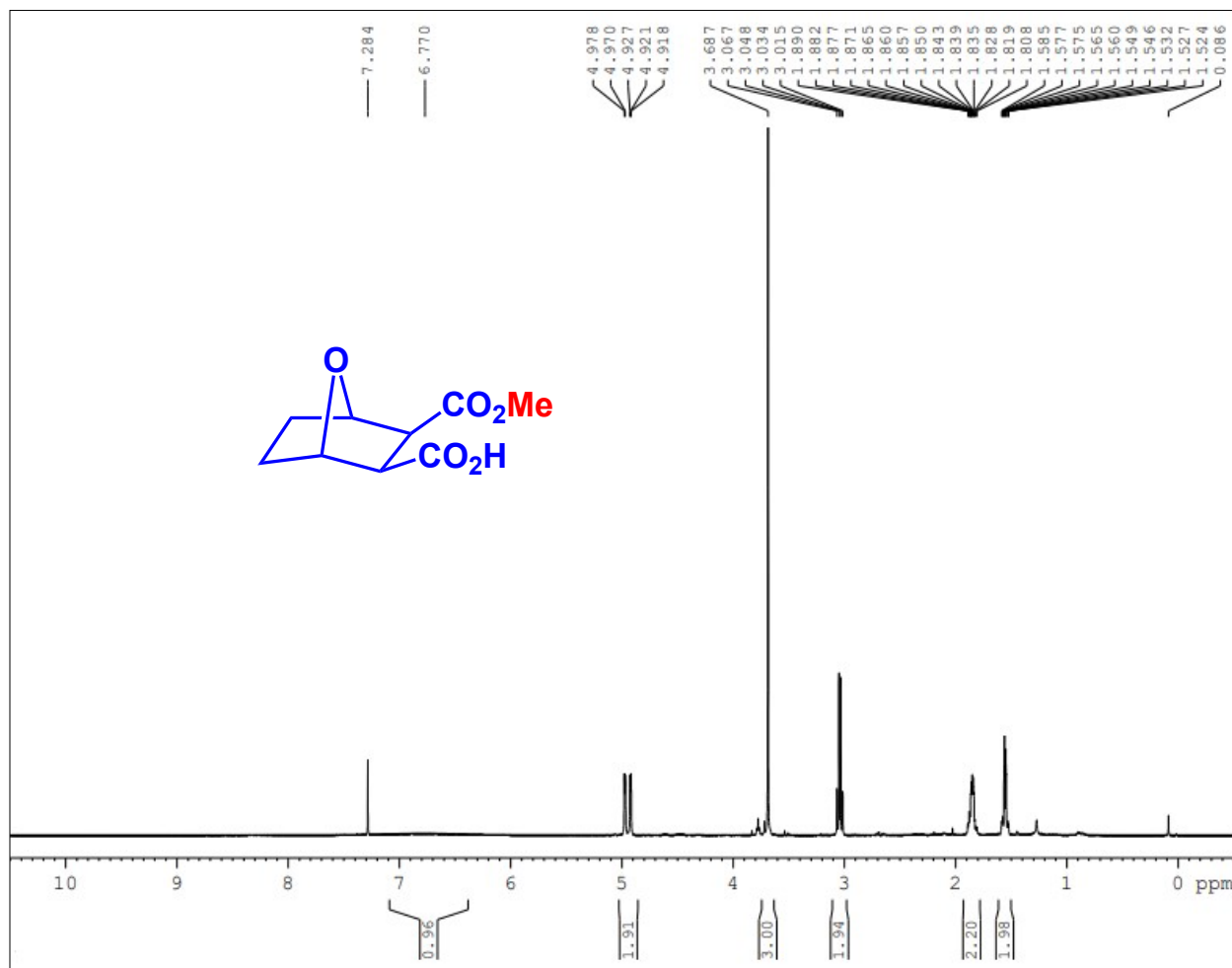


Fig. S33. ¹H NMR of (1S,2R,4R)-3-(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptane-2-carboxylic acid (40).

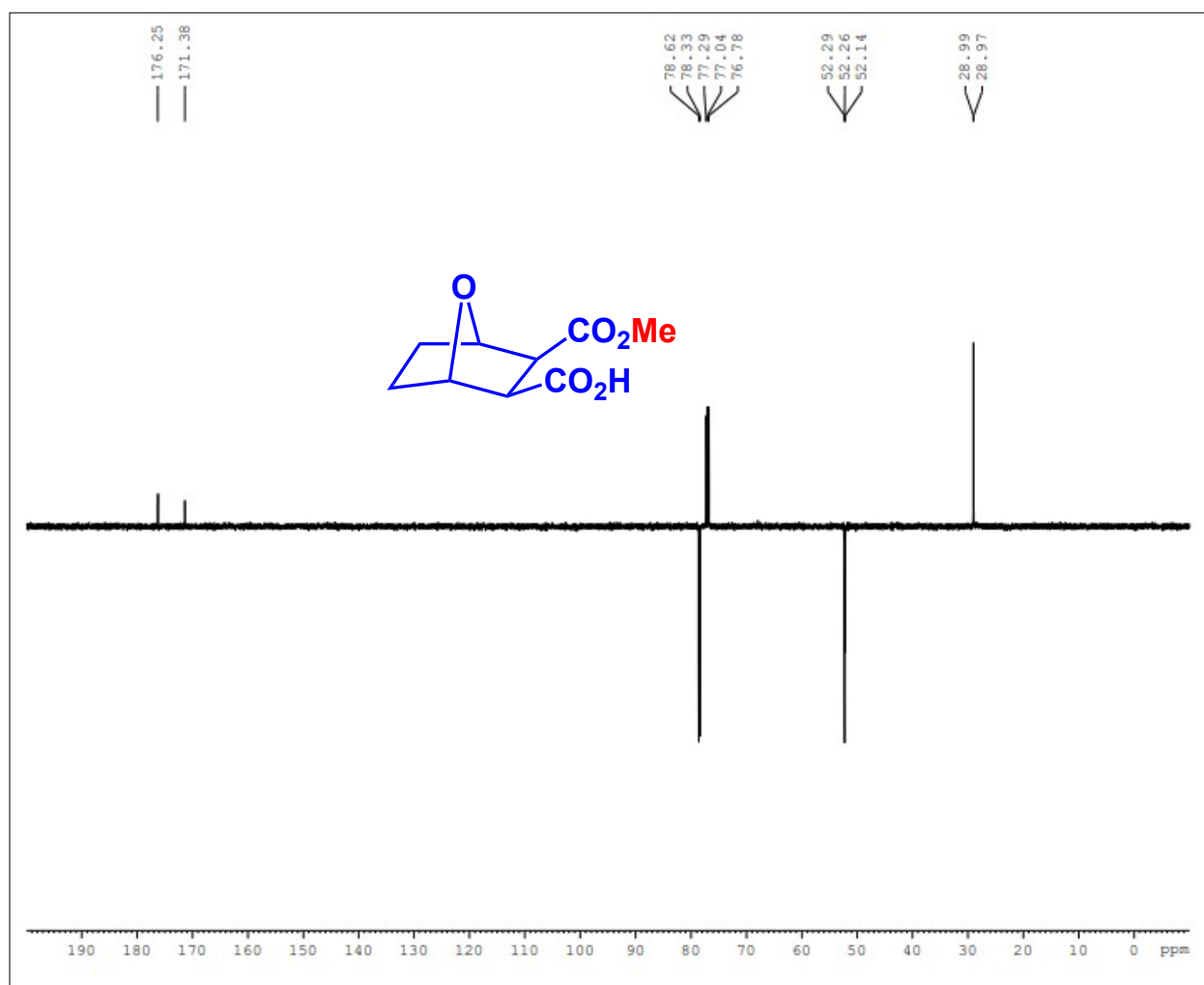


Fig. S34. ^{13}C NMR of (1S,2R,4R)-3-(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptane-2-carboxylic acid (40).

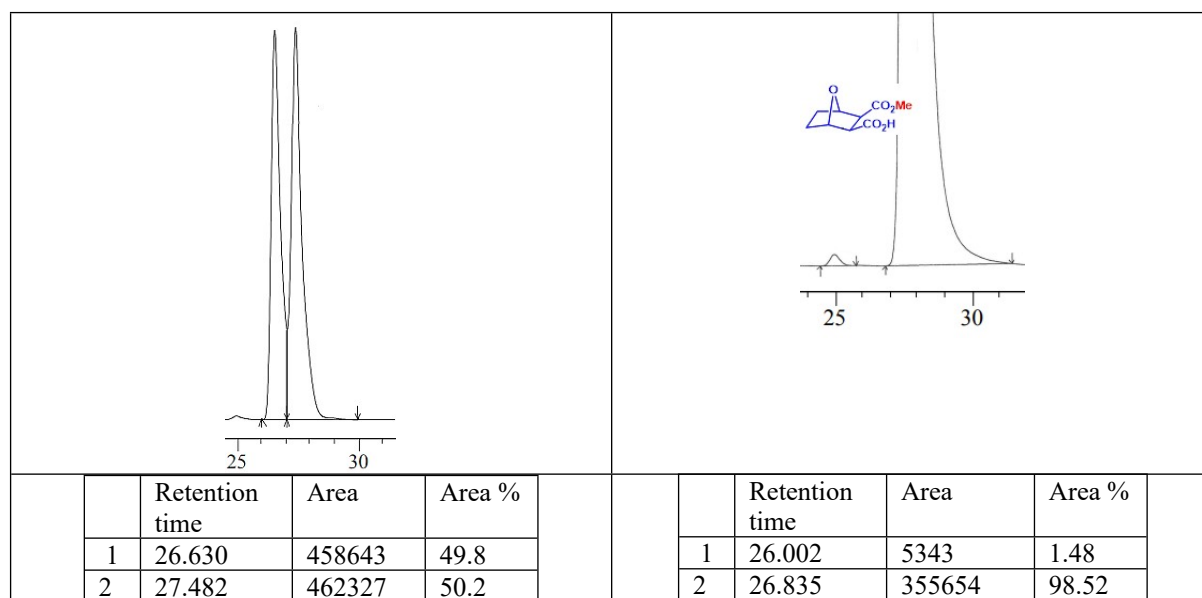


Fig. S35. HPLC chromatograms of racemic and (1S,2R,4R)-3-(methoxycarbonyl)-7-oxabicyclo[2.2.1]heptane-2-carboxylic acid (40).

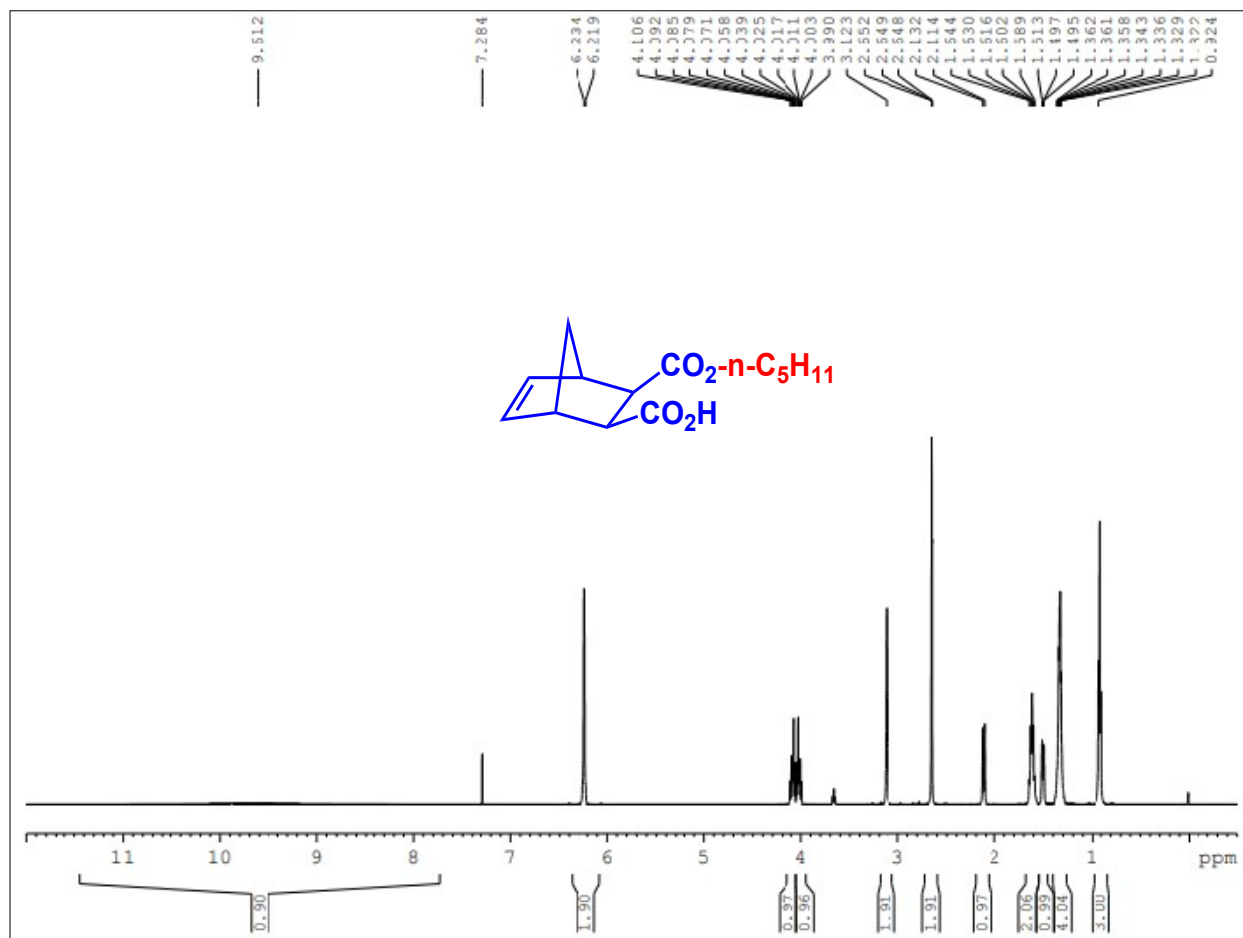


Fig. S36. ¹H NMR of (1S, 2S, 4R)-3-((pentyloxy)carbonyl)bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (41).

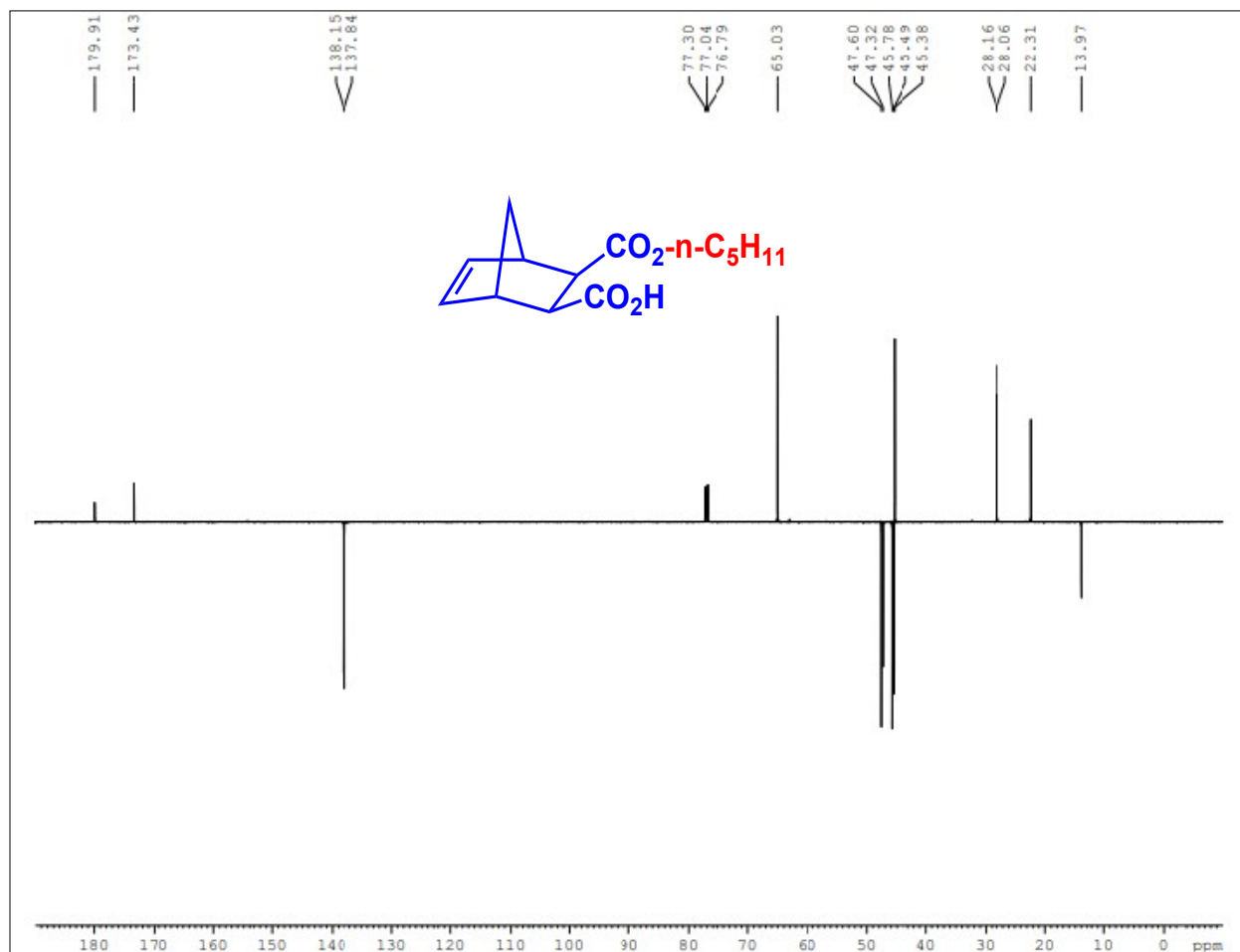


Fig. S37. ^{13}C NMR of (1S, 2S, 4R)-3-((pentyloxy)carbonyl)bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (41).

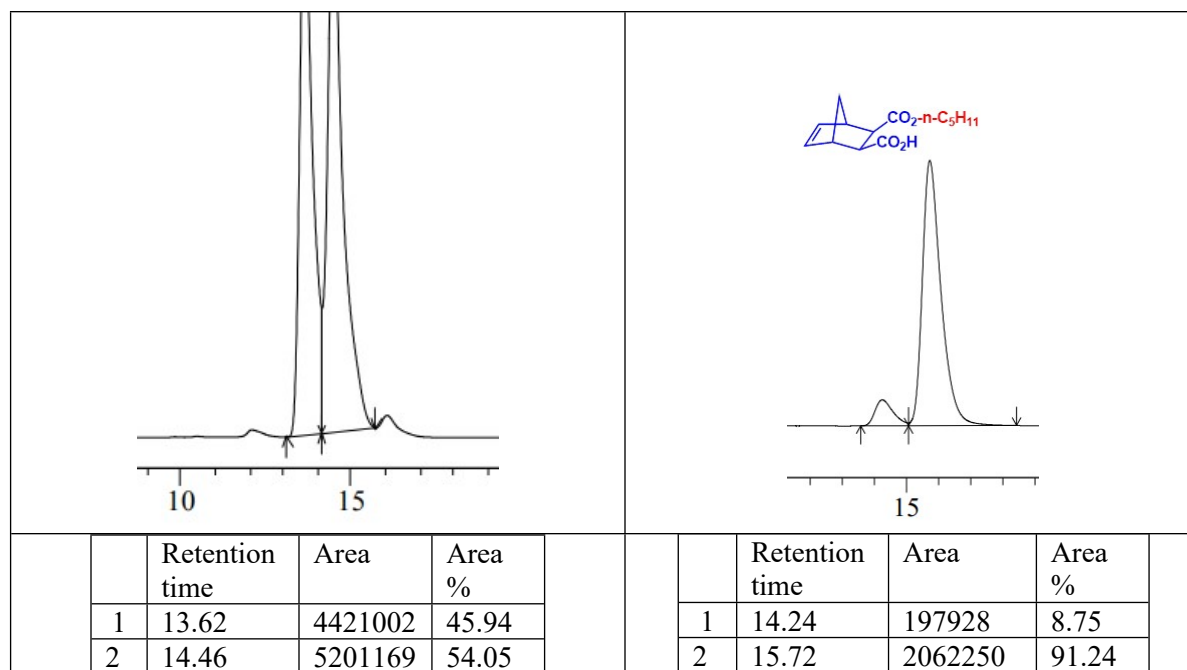


Fig. S38. HPLC chromatographs of racemic and (1S, 2S, 4R)-3-((pentyloxy) carbonyl) bicyclo [2.2.1]hept-5-ene-2-carboxylic acid (41).

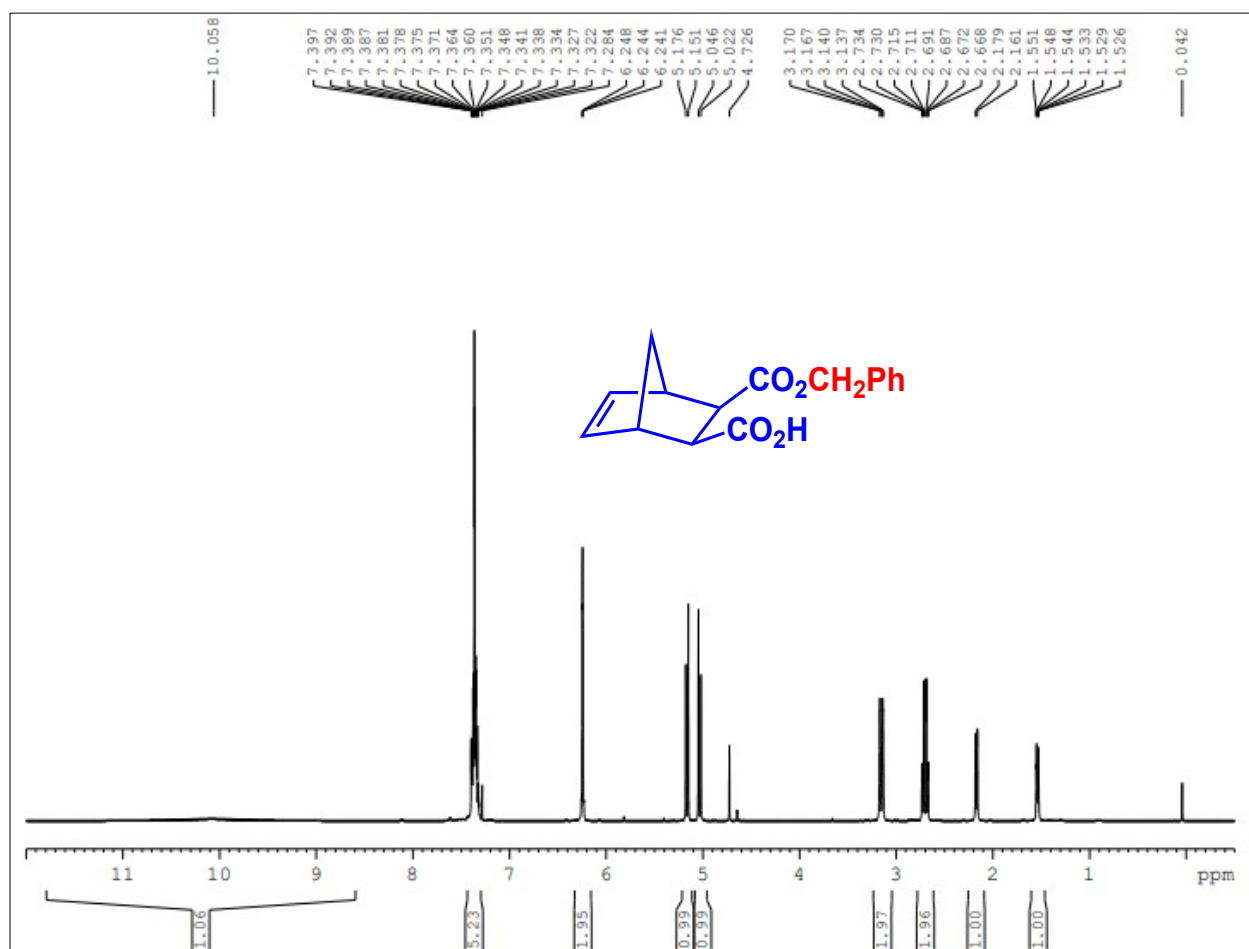


Fig. S39. ¹H NMR of (1S, 2S, 4R)-3-((benzyloxy)carbonyl)bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (43).

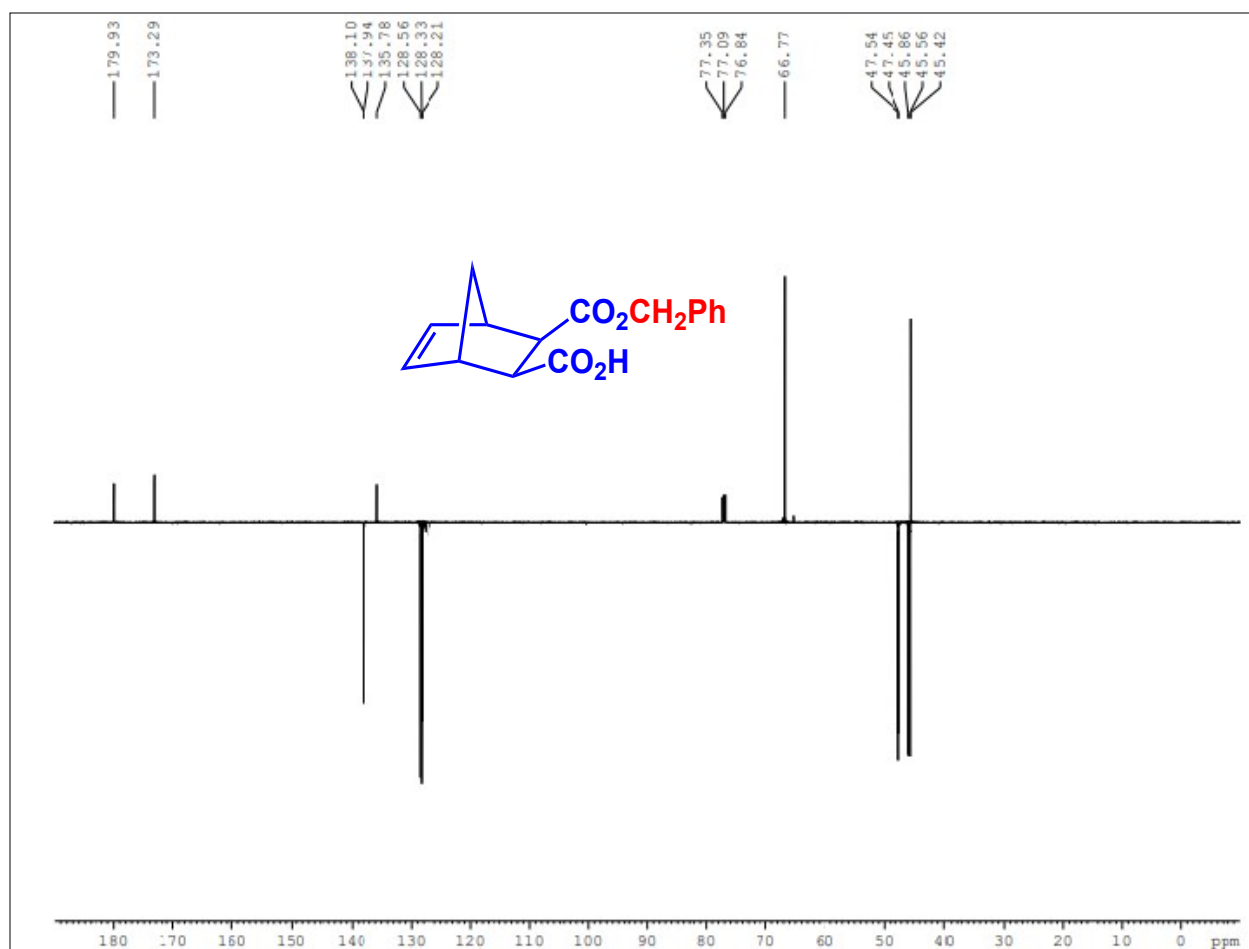


Fig. S40. ^{13}C NMR of (1S, 2S, 4R)-3-((benzyloxy)carbonyl)bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (43).

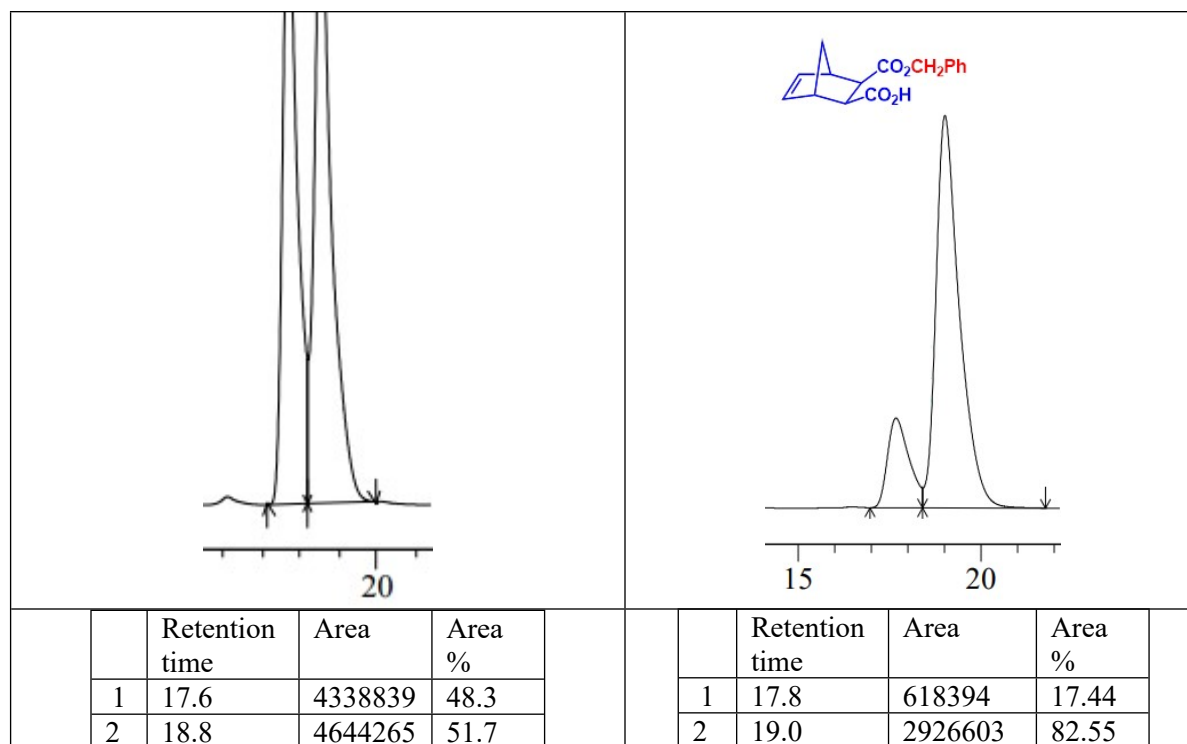


Fig. S41. HPLC chromatographs of racemic and (1S, 2S, 4R)-3-((benzyloxy)carbonyl)bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (43).

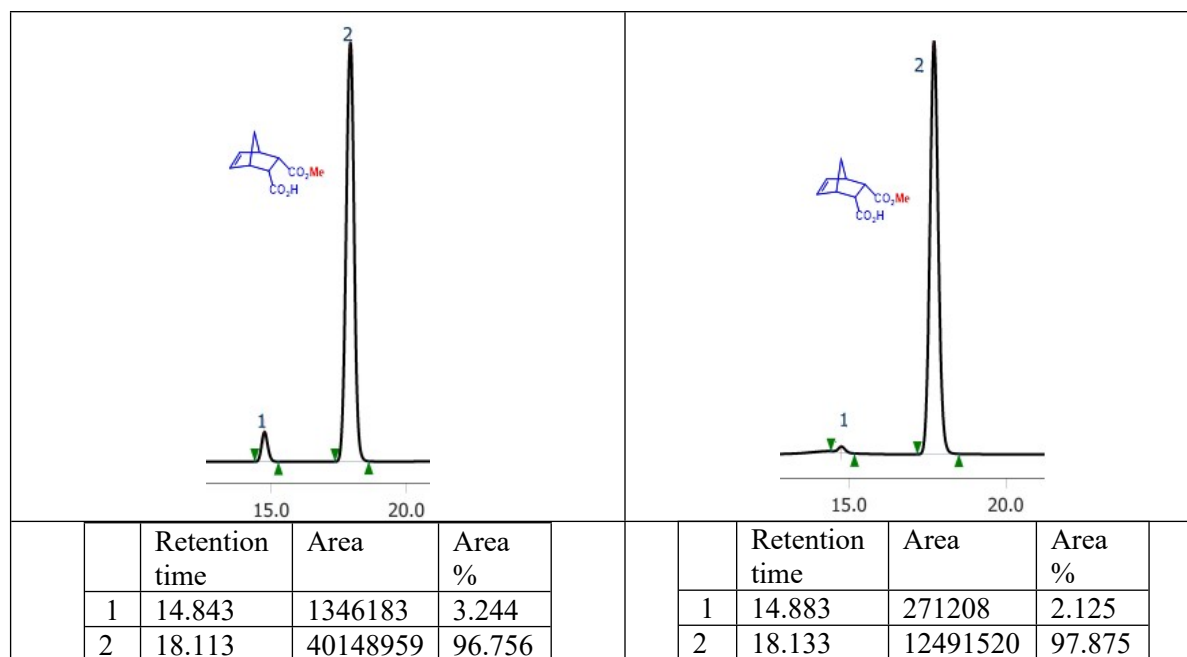


Fig. S42. HPLC chromatograms of racemic and (2*R*, 3*S*)-3-*endo*-Methoxycarbonyl-bicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid synthesized at 25 and 0°C.

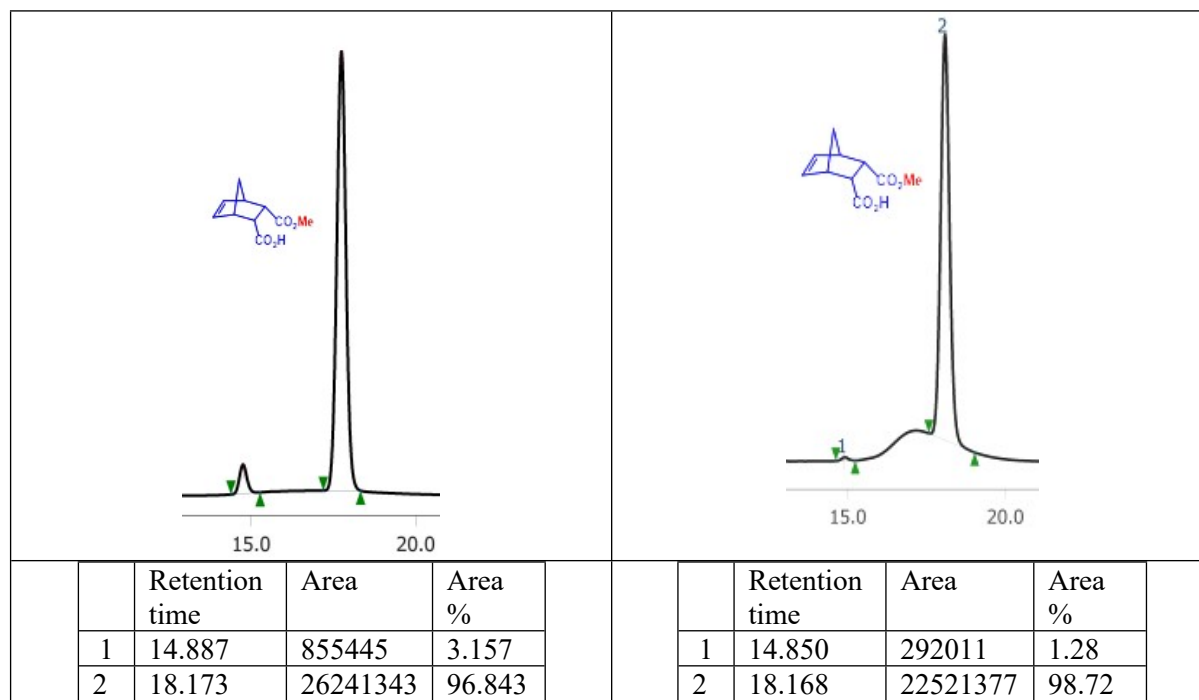


Fig. S43. HPLC chromatograms of racemic and (2*R*, 3*S*)-3-*endo*-Methoxycarbonyl-bicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid synthesized after using the catalyst 10 and 5 cycles.

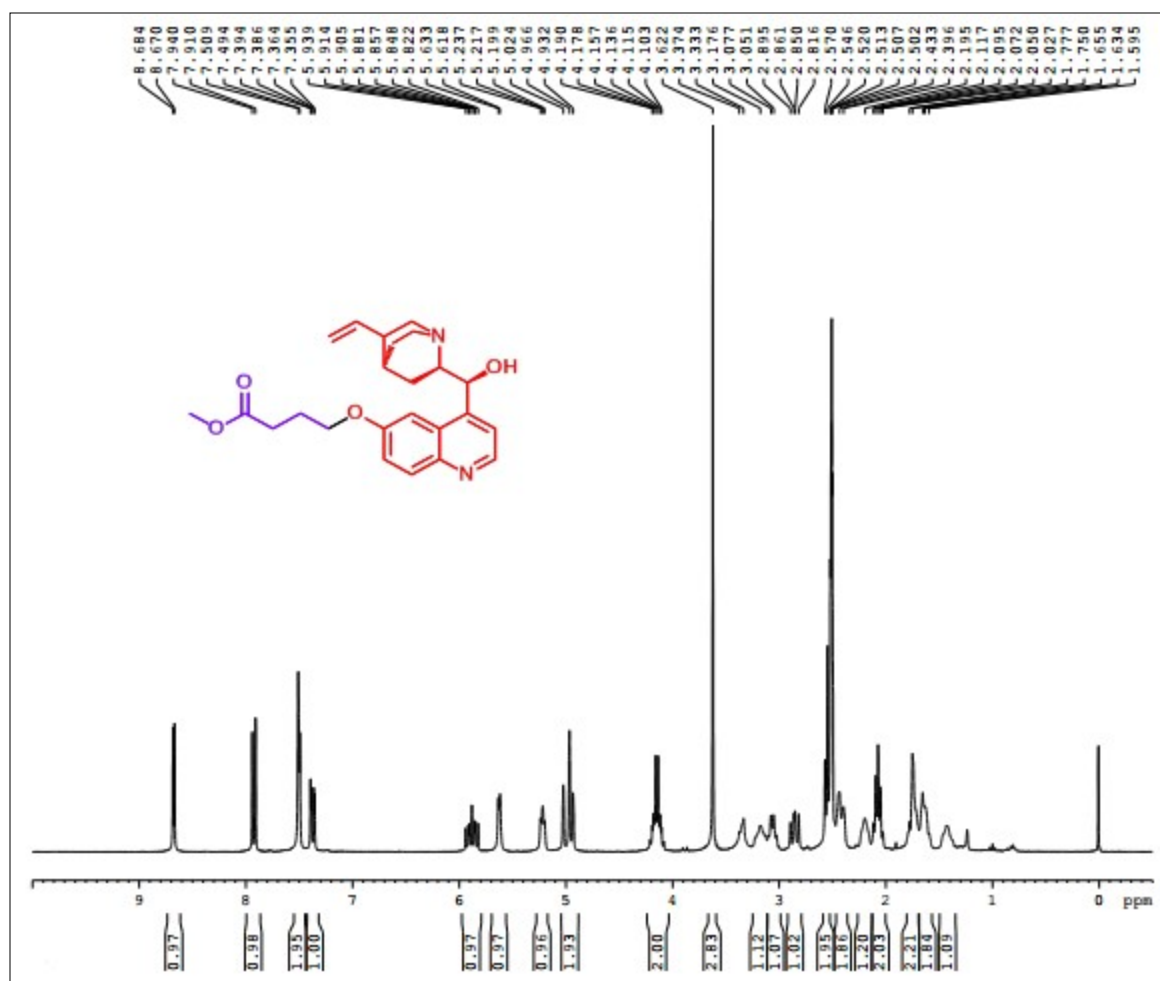


Fig. S44. ^1H NMR of 4-((4-((1S)-hydroxy((2R,4S,5R)-5-vinylquinuclidin-2-yl)methyl)quinolin-6-yl)oxy) butanoic acid methyl ester (18).

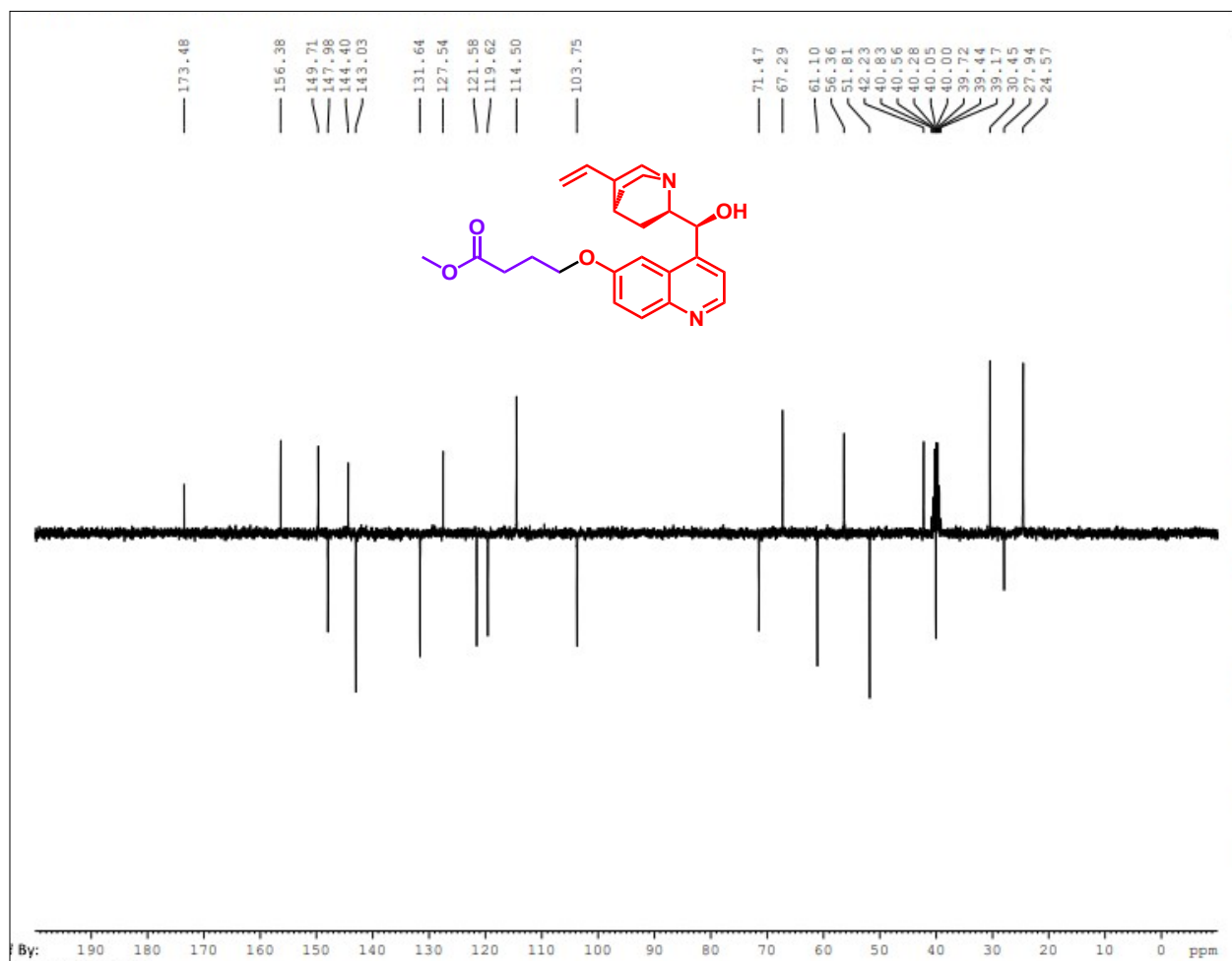


Fig. S45. ¹³C NMR of 4-((4-((1S)-hydroxy((2R,4S,5R)-5-vinylquinuclidin-2-yl)methyl)quinolin-6-yl)oxy)butanoic acid methyl ester (18).

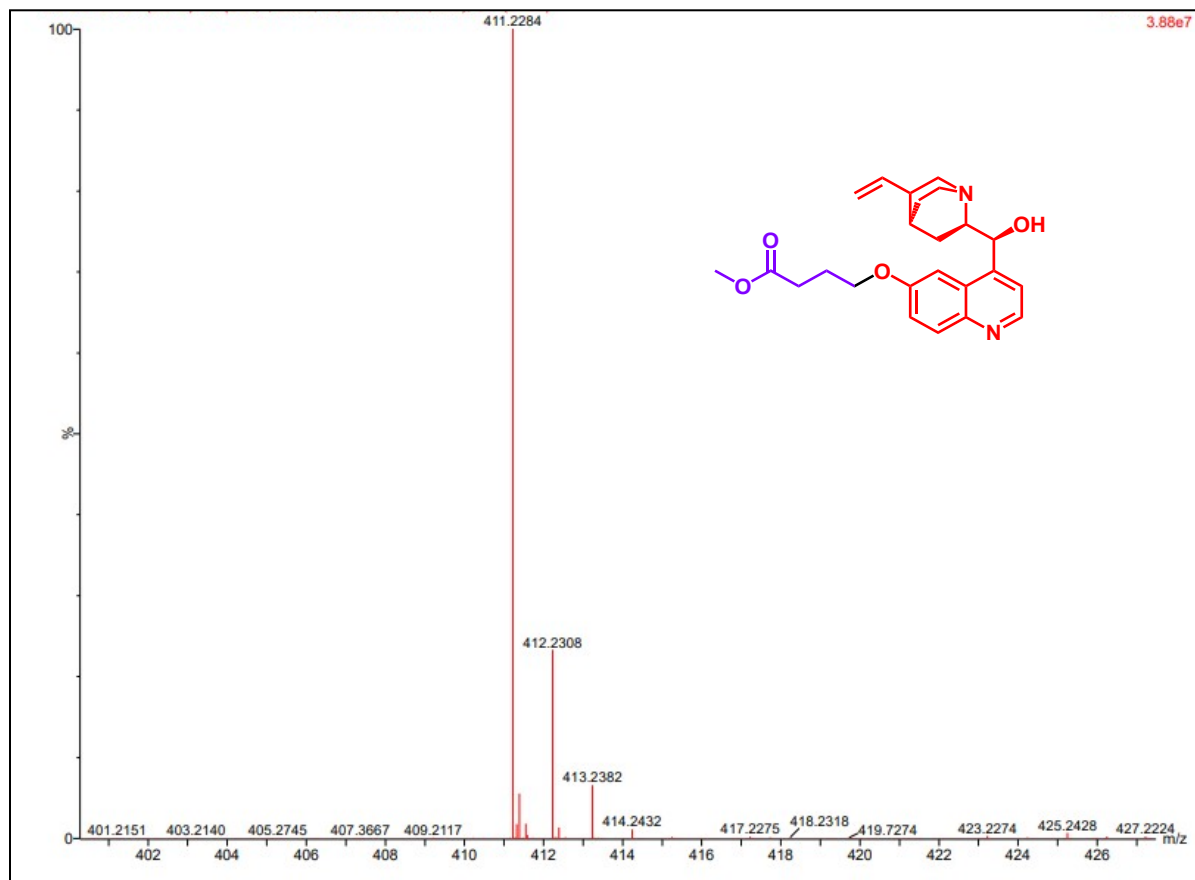


Fig. S46. HRMS of 4-((4-((1S)-hydroxy((2R,4S,5R)-5-vinylquinuclidin-2-yl)methyl)quinolin-6-yl)oxy)butanoic acid methyl ester (18).

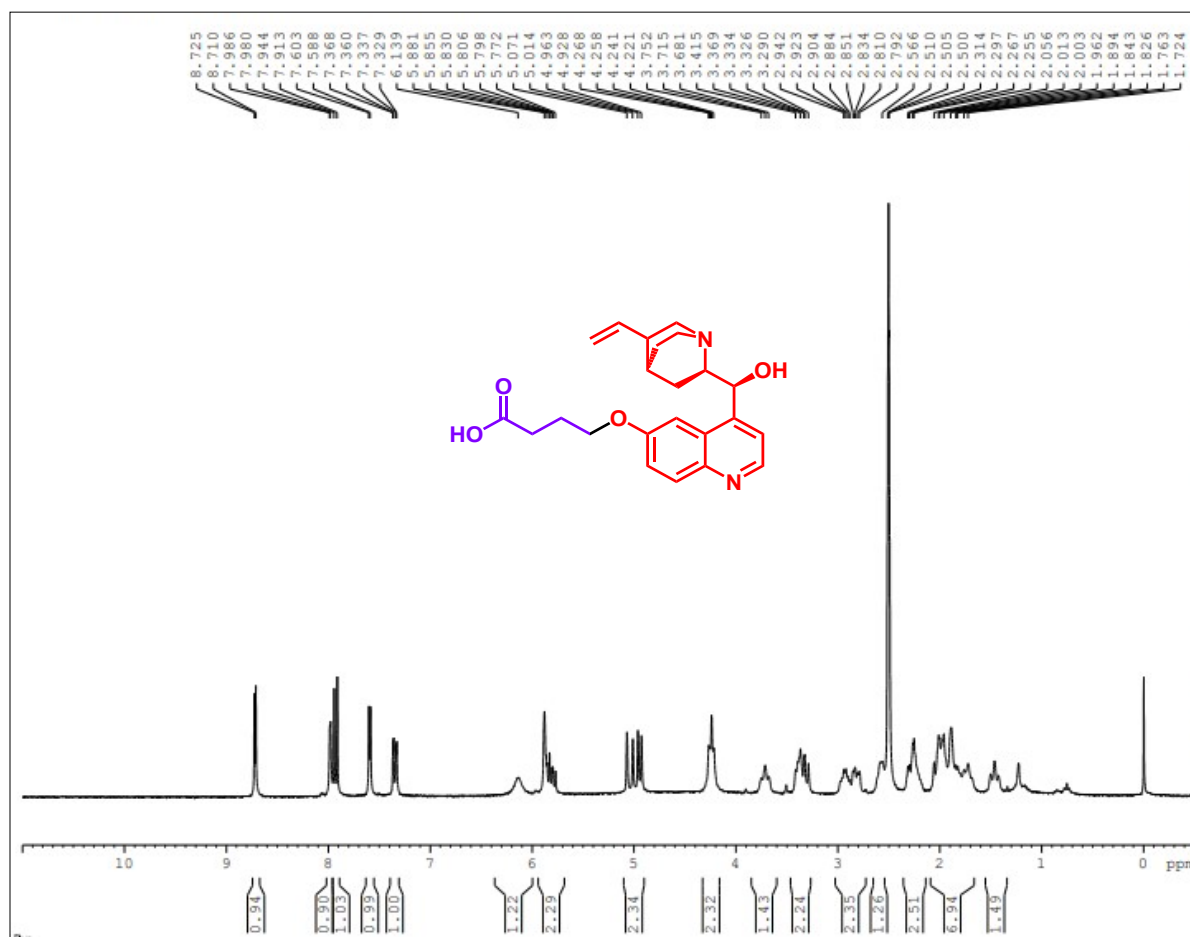


Fig. S47. ¹H NMR of 4-((4-((1S)-hydroxy((2R,4S,5R)-5-vinylquinuclidin-2-yl)methyl)quinolin-6-yl)oxy)butanoic acid (19).

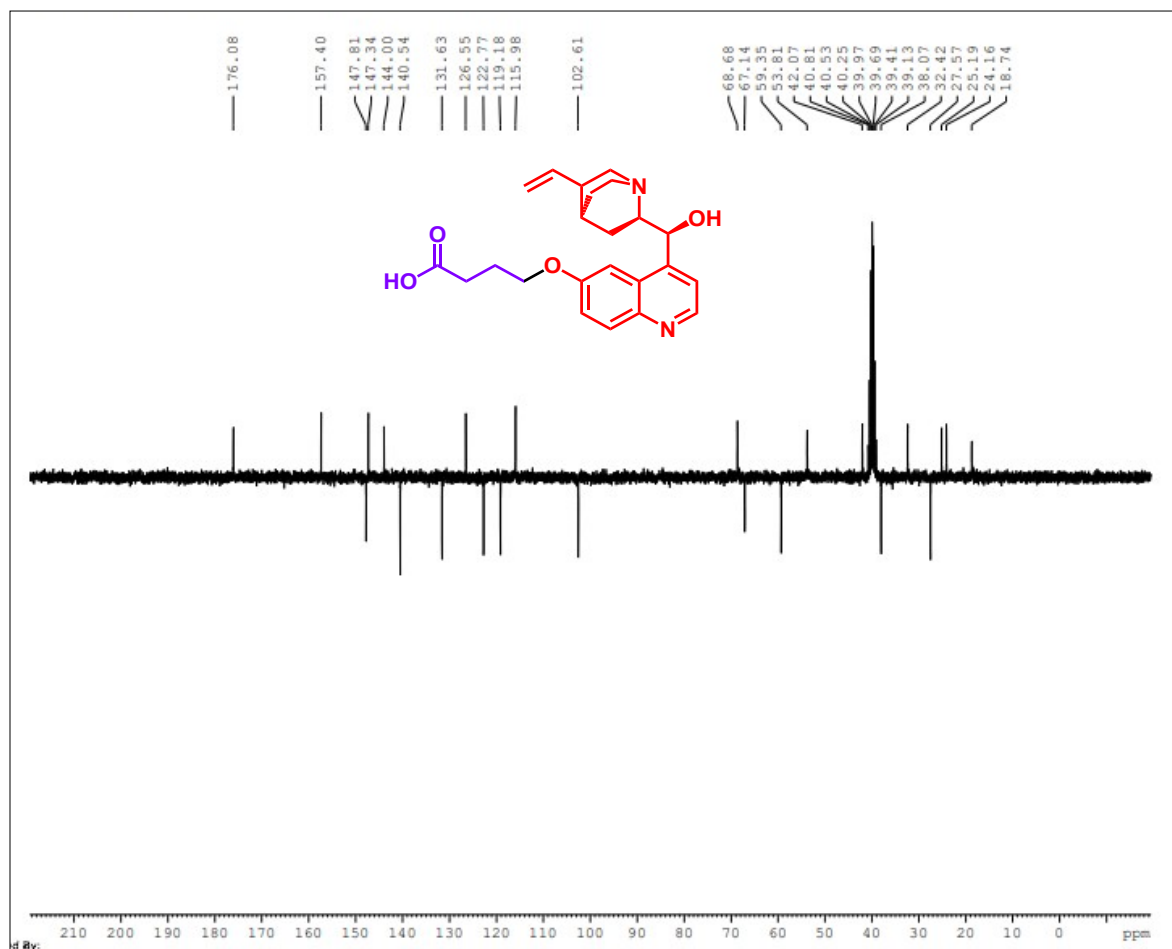


Fig. S48. ¹³C NMR of 4-((4-(((1S)-hydroxy((2R,4S,5R)-5-vinylquinuclidin-2-yl)methyl)quinolin-6-yl)oxy)butanoic acid (19).

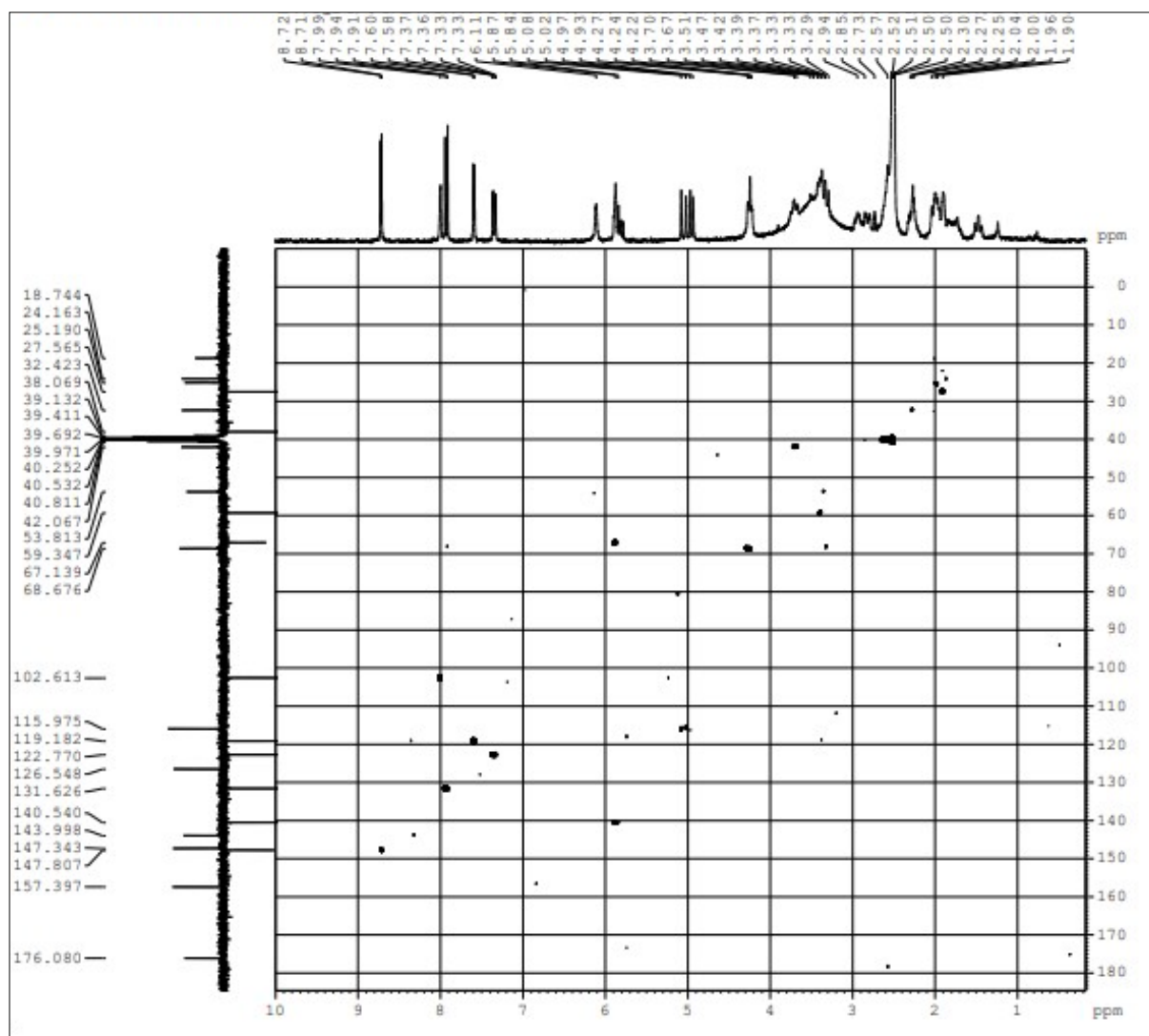


Fig. S49. HSQC of 4-((4-((1S)-hydroxy((2R,4S,5R)-5-vinylquinuclidin-2-yl)methyl)quinolin-6-yl)oxy)butanoic acid (19).

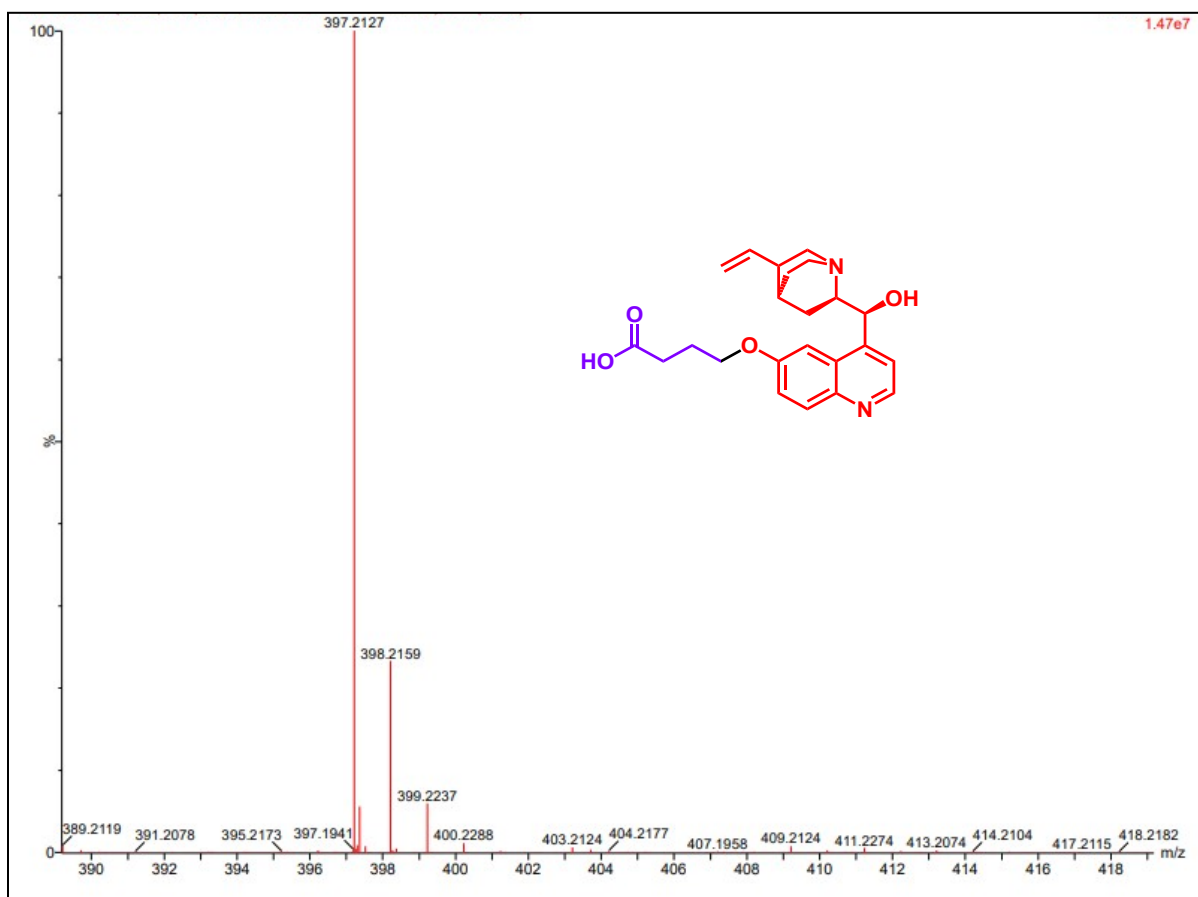


Fig. S50. HRMS of 4-((4-((1S)-hydroxy((2R,4S,5R)-5-vinylquinuclidin-2-yl)methyl)quinolin-6-yl)oxy)butanoic acid (19).