

SUPPORTING INFORMATION

Synthesis of *o*-Carboxyarylacrylic Acids by Room Temperature Oxidative Cleavage of Hydroxynaphthalenes and Higher Aromatics with Oxone[®]

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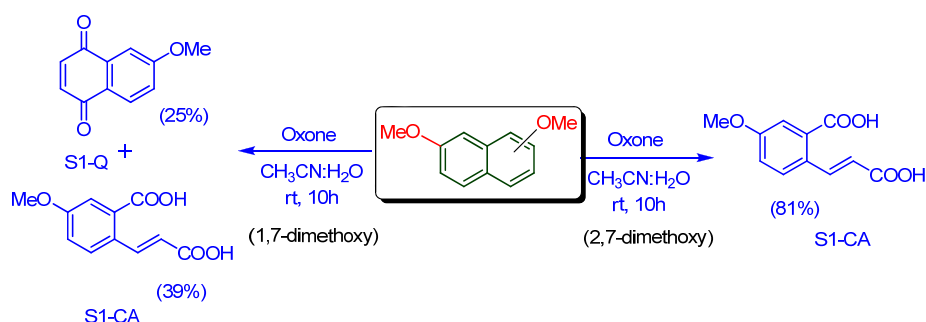
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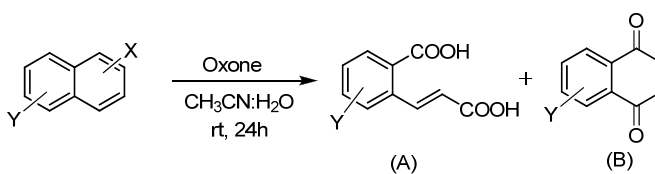
EXPERIMENTAL SECTION

General Aspects. Column chromatography was conducted with silica gel of 100-200 μ particle size. NMR spectra were recorded with 400 MHz and 500 MHz spectrometers. IR spectra were recorded on an FT-IR spectrophotometer. Mass spectral analyses were carried out with ESI-Q^{TOF} instrument. Melting point was measured in Guna melting point apparatus, India are uncorrected.

Scheme S1: Results of Oxidation of 1,7 and 2,7-Dimethoxy Naphthalene with Oxone at rt.



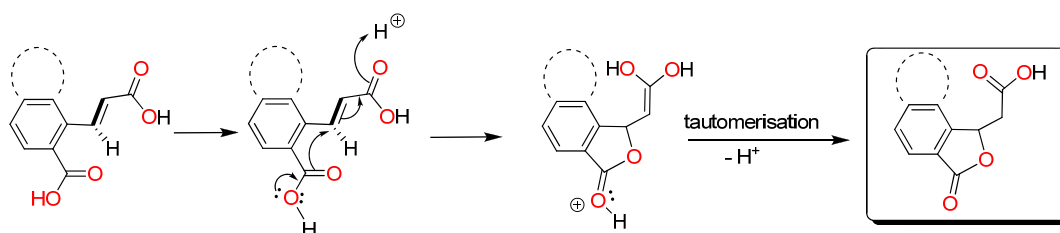
Scheme S2: Results of Oxidation of Methoxy-Naphthalenes with Oxone in $\text{CH}_3\text{CN}:\text{H}_2\text{O}$ at rt.



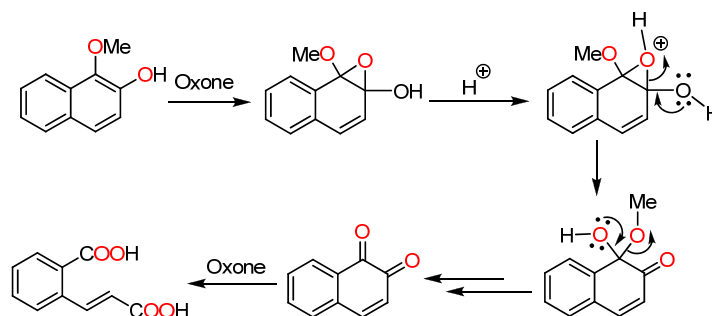
substrate		Oxone (equiv.)	time (h)	yield (%)	
X	Y			A	B
2-OMe	H	4	22	85	0
2-OMe	6-Br	4	24	44 ^a	0
2-OMe	6-CO ₂ H	3	24	NR	0
1-OMe	H	4	23	64	14
1-OMe	4-CN	3	24	NR	0

^a 50% conversion

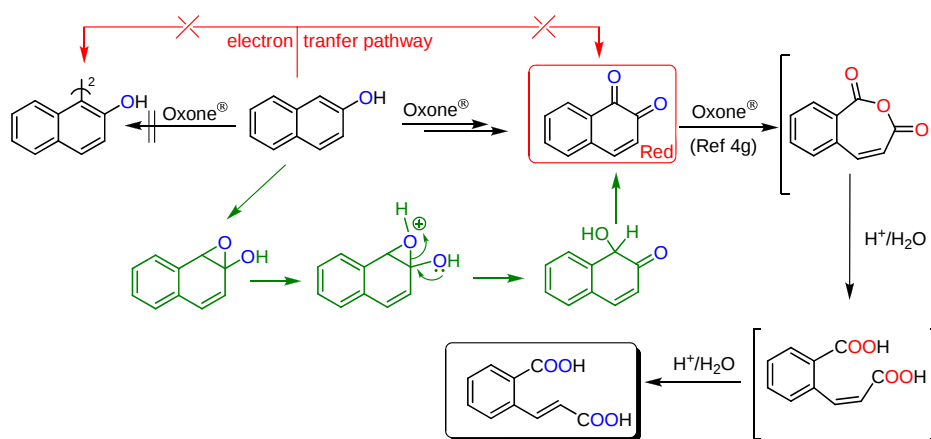
Scheme S3: Mechanism of 2-Carboxyarylacrylic Acid to Carboxymethyl Lactone.



Scheme S4: Mechanism of Oxidation of 1-Methoxy-2-naphthol to *o*-Carboxycinnamic Acid.



Scheme S5: Mechanism of Oxidation of Naphthol with Oxone[®] to *o*-Carboxycinnamic Acid



¹H NMR Monitoring of Oxidation of 6-Bromonaphthol with Oxone at rt

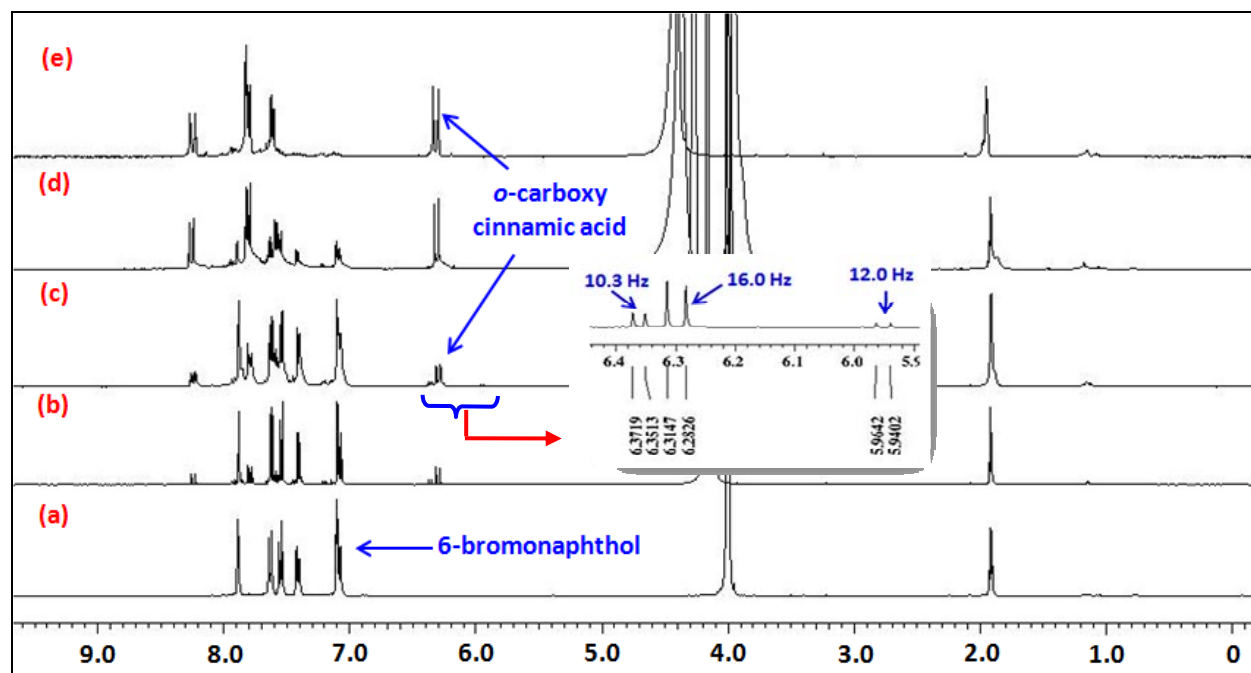


FIGURE S1. ¹H NMR Monitoring of oxidation of 6-bromonaphthol with Oxone (3 equiv) in CD₃CN-D₂O (1:1) at rt: (a) 0 h, before addition of Oxone, (b) after 2 h of addition of Oxone, (c) 4 h, (d) 6 h and (e) 12 h after addition of Oxone.

The doublet at δ 6.36 is attributed to *o*-quinone. The latter was isolated independently and its ¹H NMR spectrum recorded in a mixture of CD₃CN-D₂O (1:1, v/v) in the presence of Oxone, see Figure S3. The diagnostic doublet for the *o*-quinone was observed at δ 6.43. We believe that a small difference in the chemical shift is due to presumably to the difference in the effective concentrations of Oxone, which is acidic to influence the chemical shifts. It should also be noted that the evidence for the formation of *o*-quinone comes from the fact that the reaction mixture turns red color subsequent to introduction of Oxone.

¹H NMR Study: Influence of pH on *o*-Carboxycinnamic Acid in CD₃CN-D₂O at rt

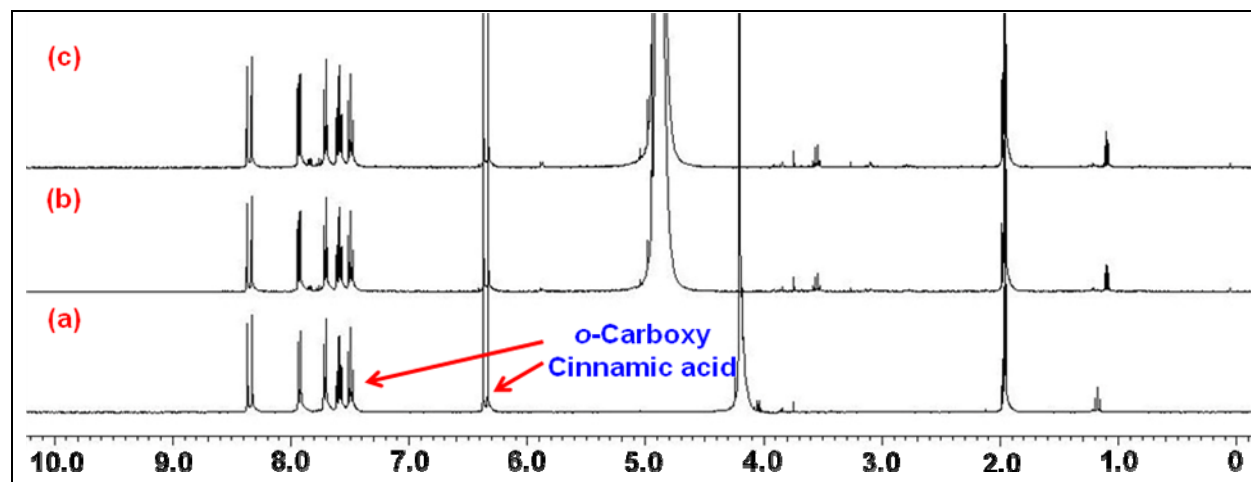


FIGURE S2. ¹H NMR Monitoring of oxidation of *E*-*o*-carboxycinnamic acid (5 mg, 0.026 mmol) with conc. H₂SO₄ (60 μL) in CD₃CN-D₂O (1:1)(500 μL) at rt: (a) 0 h, before addition of conc. H₂SO₄, (b) after 4 h of addition of conc. H₂SO₄, and (c) 8 h after addition of conc. H₂SO₄.

Conclusion: No evidence for formation of carboxymethyl-lactone, derived by intramolecular Michael addition, was observed.

^1H NMR Monitoring of Oxidation of 6-Bromonaphthalene-1,2-dione with Oxone in $\text{CD}_3\text{CN-D}_2\text{O}$ (1:1) at rt

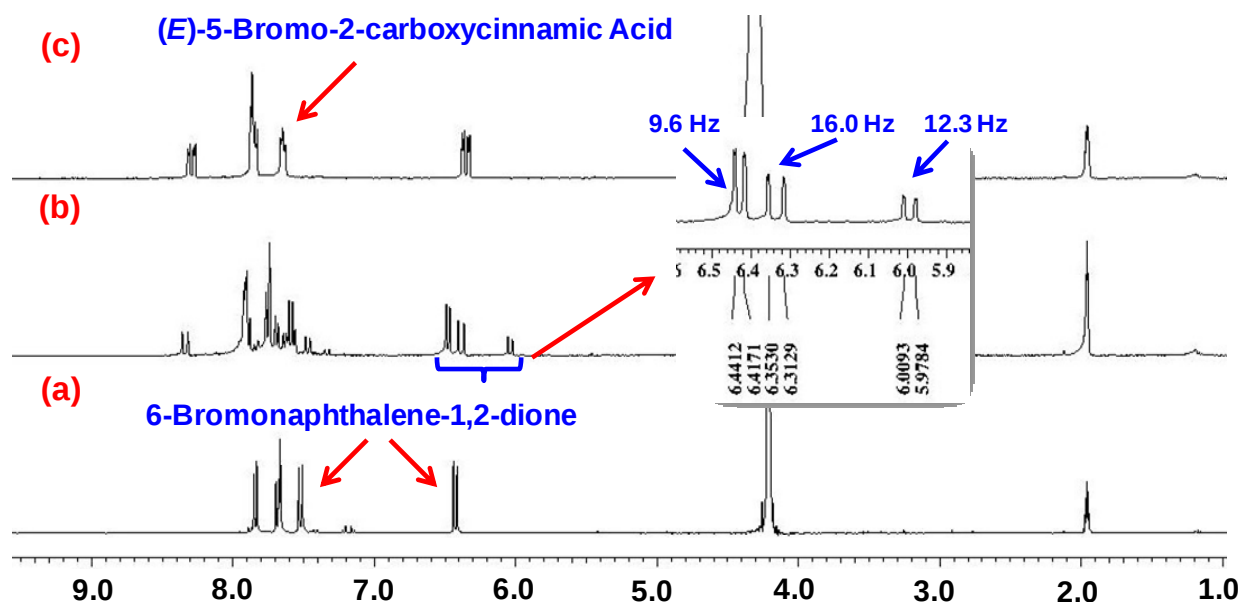
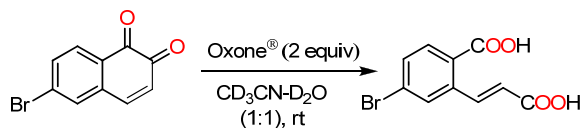


FIGURE S3. ^1H NMR Monitoring of the reaction of 6-bromonaphthalene-1,2-dione with Oxone in $\text{CD}_3\text{CN-D}_2\text{O}$ (1:1). (a) Before addition of Oxone, 0 h; (b) 2 h after introduction of Oxone; (c) 8 h after introduction of Oxone.

Conclusion: The *o*-quinone converts to *E*- and *Z*-cinnamic acids. Also noteworthy is the fact that under the conditions of the reactions, the *Z*-cinnamic acid is eventually converted to the *E*-isomer entirely.

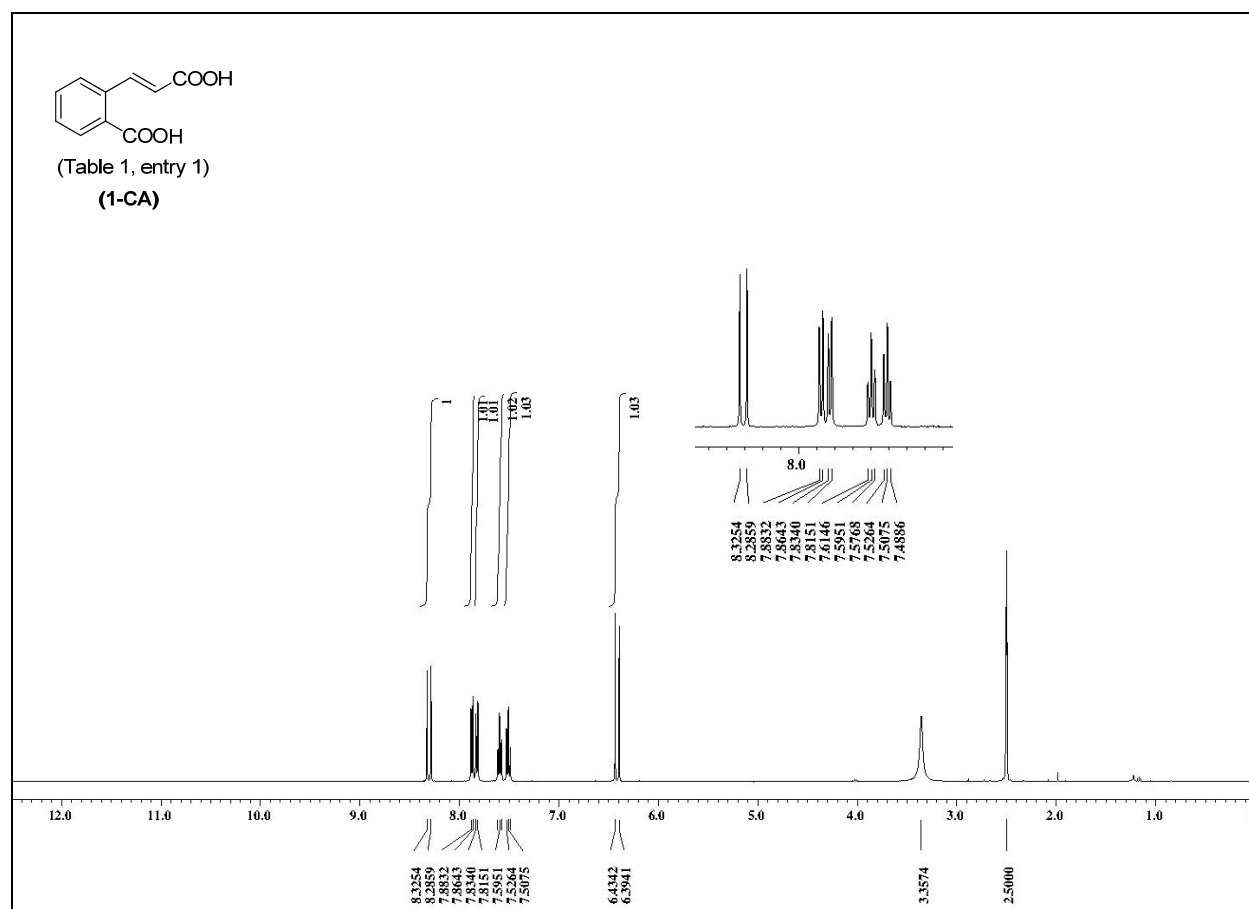


FIGURE S4. ¹H NMR spectrum of *(E)*-*o*-carboxycinnamic acid in DMSO-*d*₆.

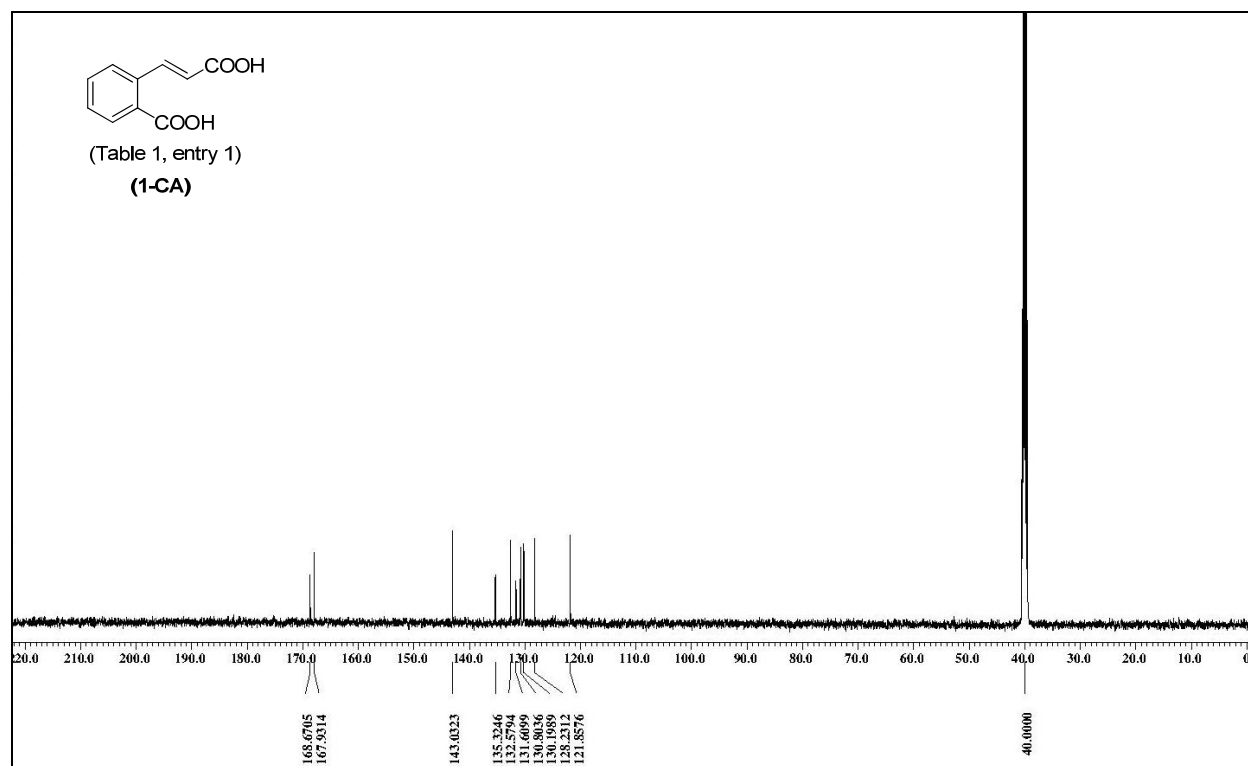


FIGURE S5. ^{13}C NMR spectrum of (*E*)-*o*-carboxycinnamic acid in $\text{DMSO-}d_6$.

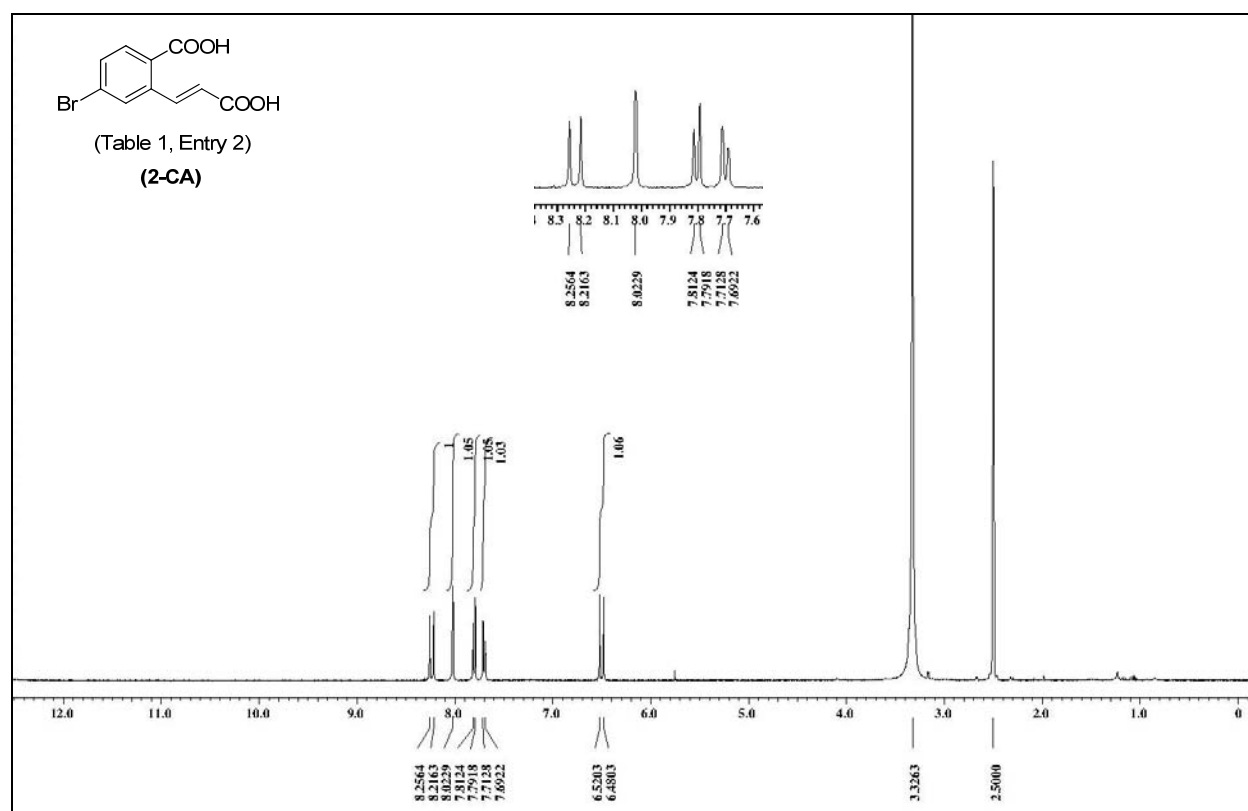


FIGURE S6. ^1H NMR spectrum of (*E*)-5-bromo-2-carboxycinnamic acid in DMSO- d_6 .

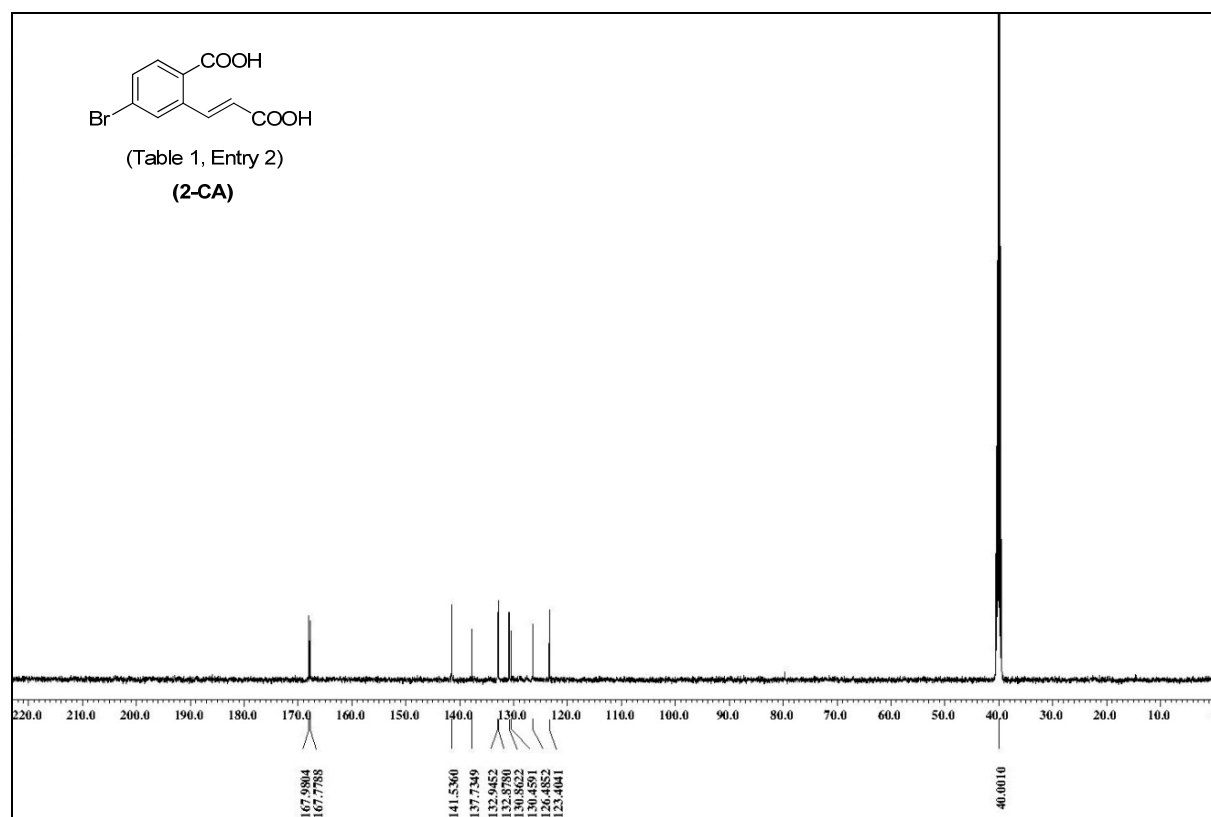


FIGURE S7. ^{13}C NMR spectrum of (*E*)-5-bromo-2-carboxycinnamic acid in $\text{DMSO-}d_6$.

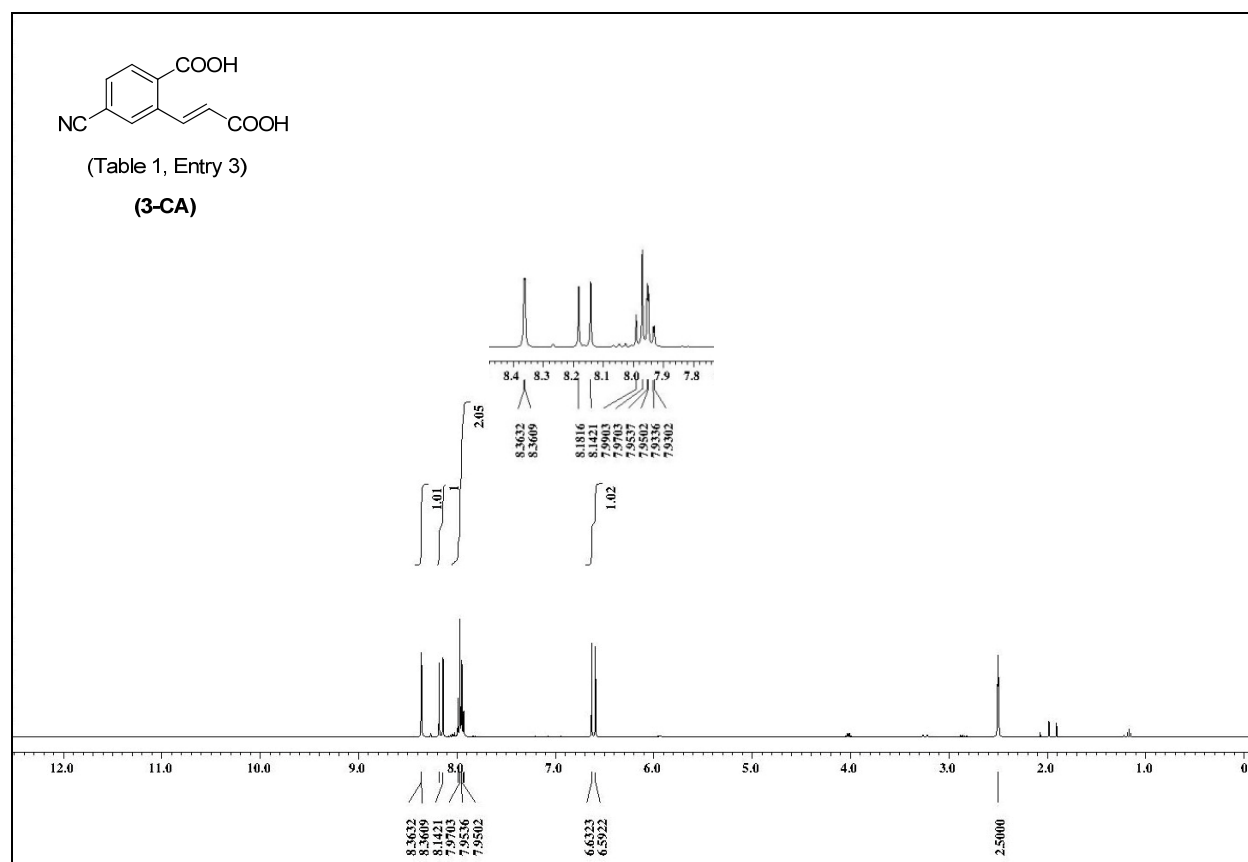


FIGURE S8. ¹H NMR spectrum of (*E*)-2-carboxy-5-cyanocinnamic acid in DMSO-*d*₆.

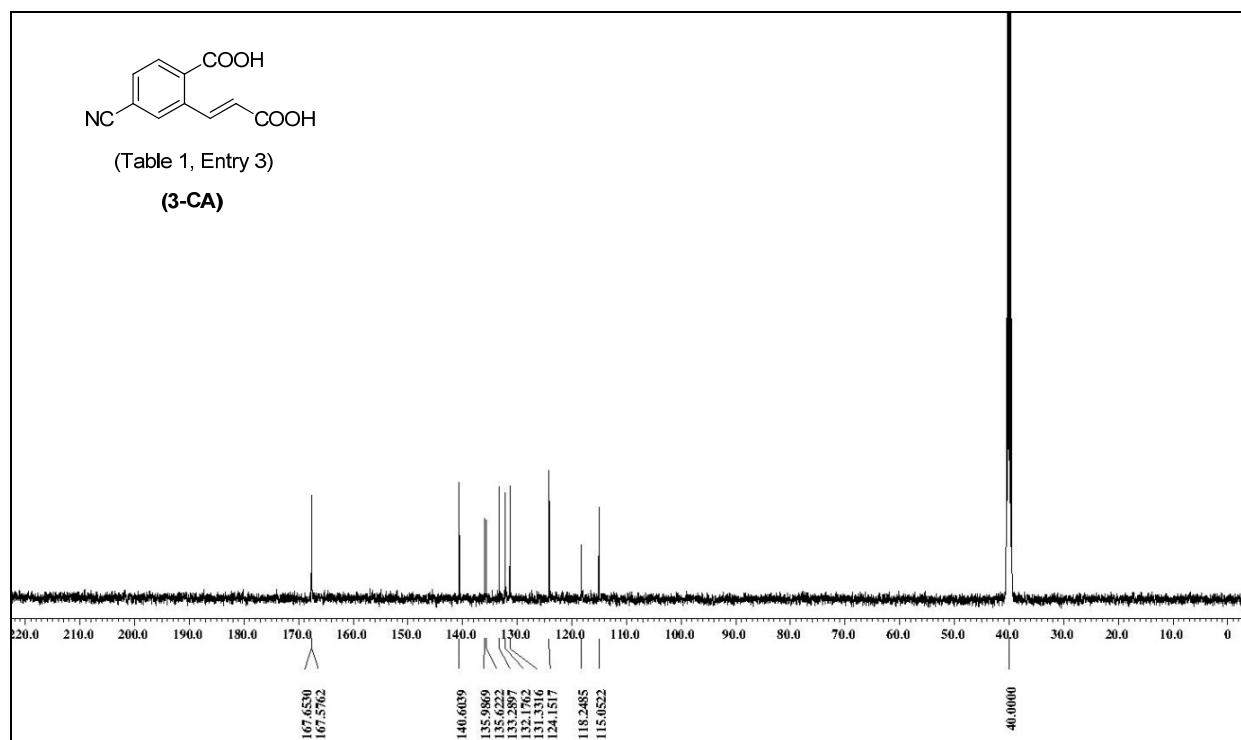


FIGURE S9. ^{13}C NMR spectrum of (*E*)-2-carboxy-5-cyanocinnamic acid in $\text{DMSO-}d_6$.

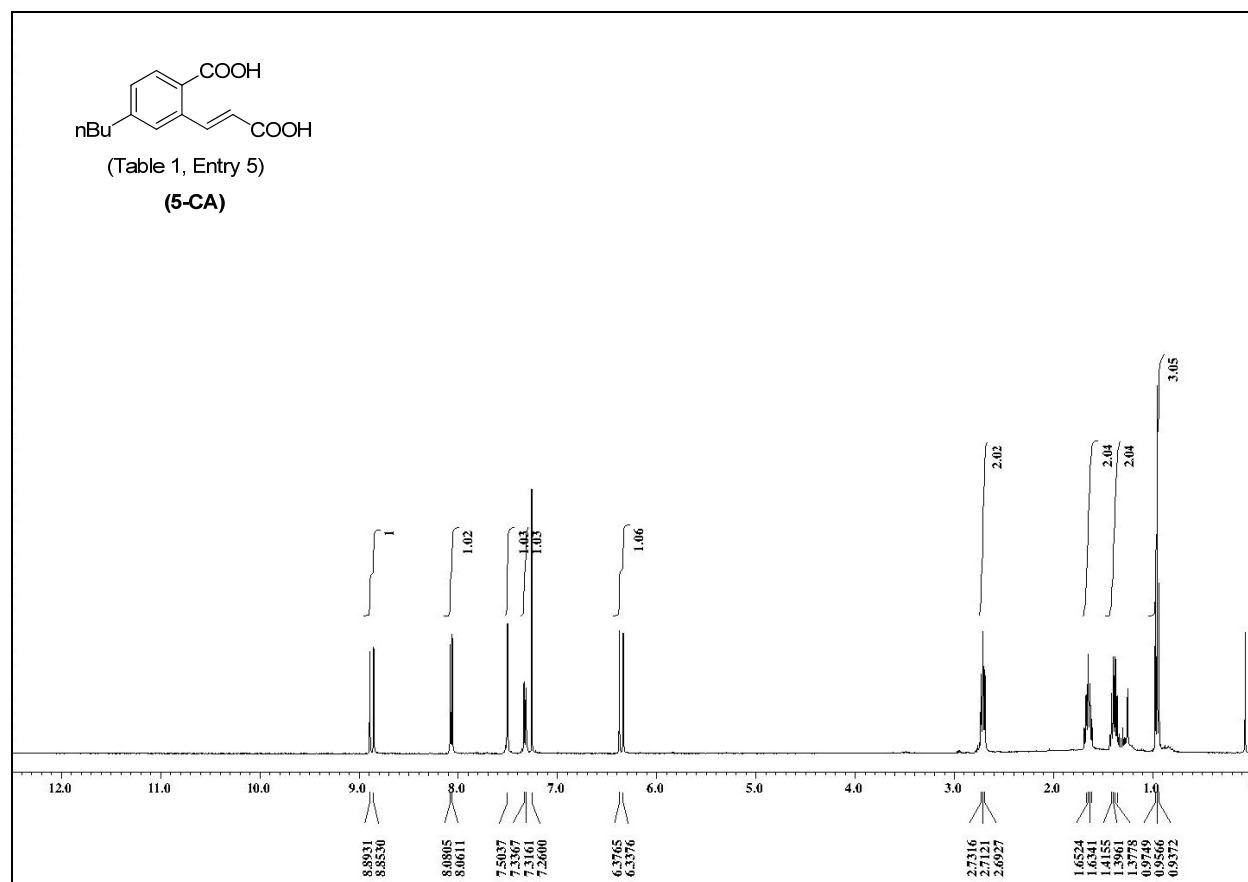


FIGURE S10. ^1H NMR spectrum of (*E*)-5-*n*-butyl-2-carboxycinnamic acid in CDCl_3 .

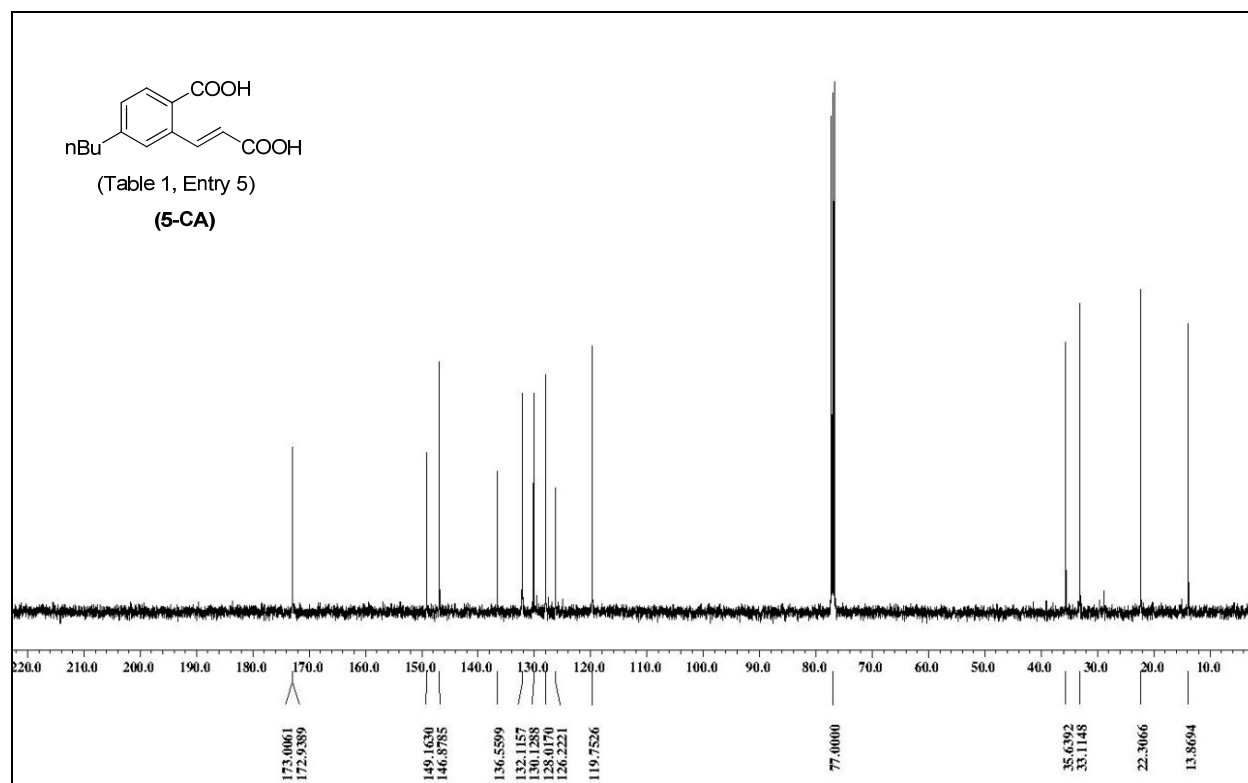


FIGURE S11. ^{13}C NMR spectrum of (*E*)-5-n-butyl-2-carboxycinnamic acid in CDCl_3 .

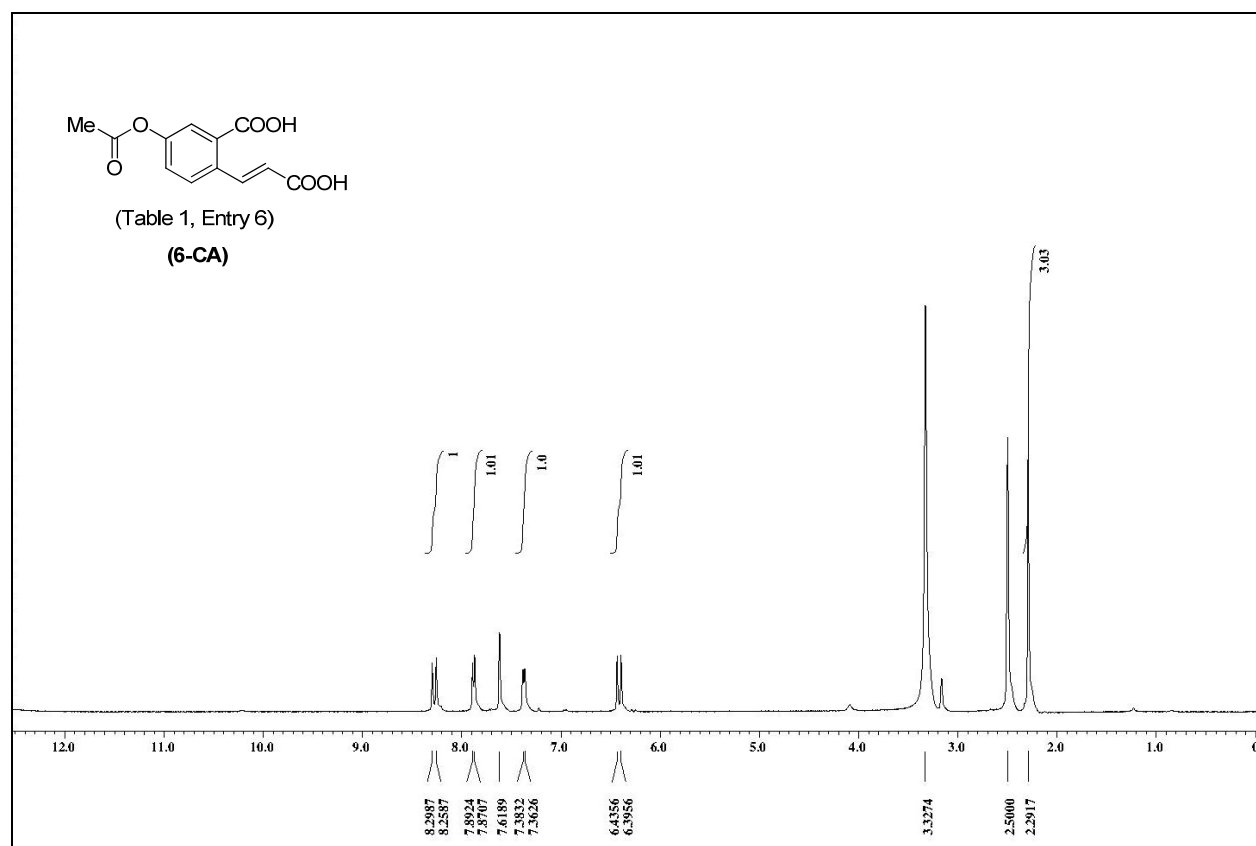


FIGURE S12. ^1H NMR spectrum of (*E*)-4-acetoxy-2-carboxycinnamic acid in $\text{DMSO}-d_6$.

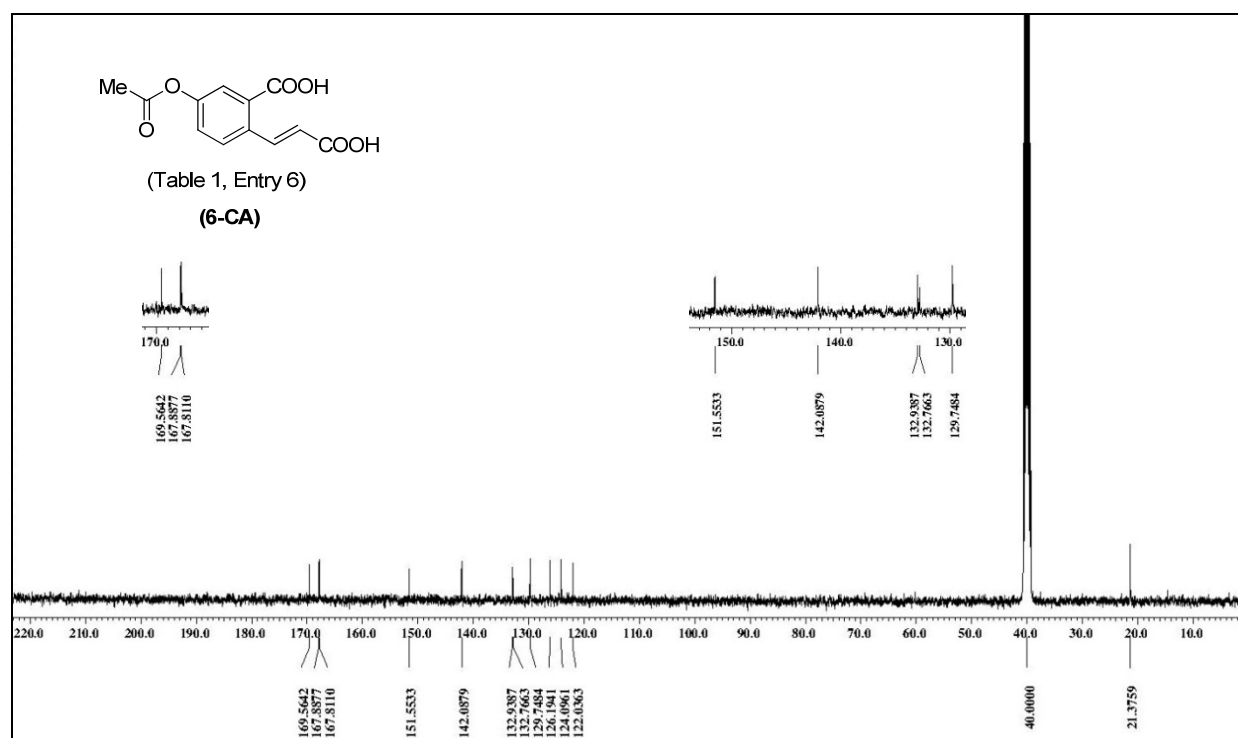


FIGURE S13. ^{13}C NMR spectrum of (*E*)-4-acetoxy-2-carboxycinnamic acid in $\text{DMSO}-d_6$.

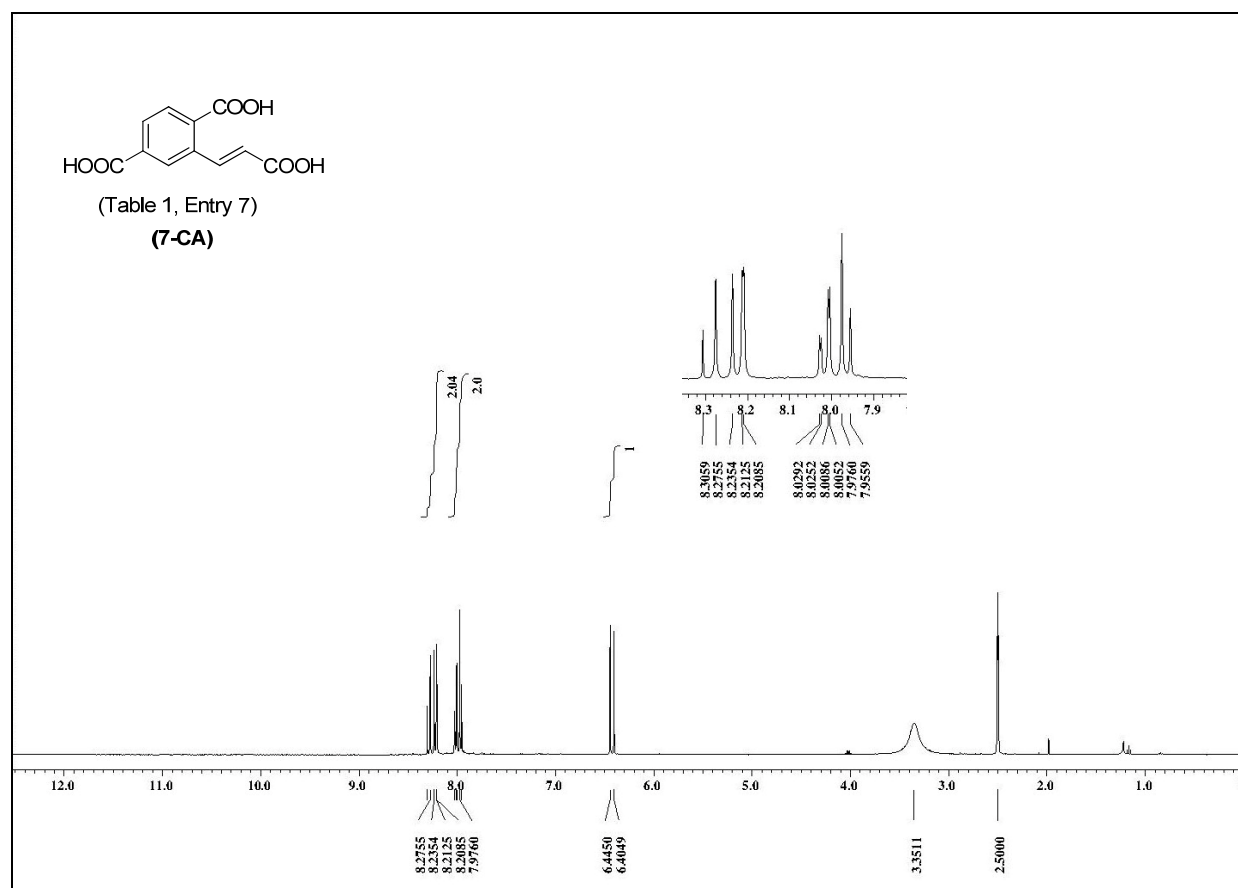


FIGURE S14. ¹H NMR spectrum of (*E*)-2,5-dicarboxycinamic acid in DMSO-*d*₆.

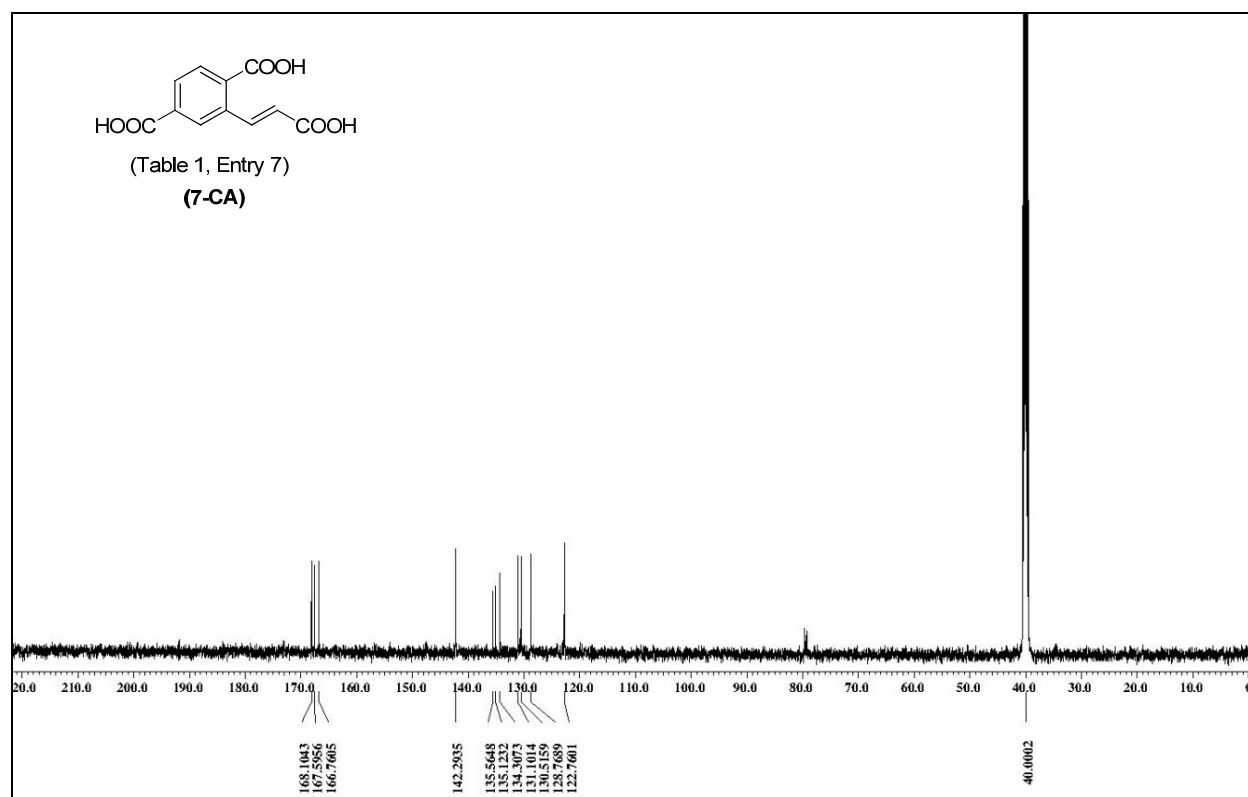


FIGURE S15. ^{13}C NMR spectrum of (*E*)-2,5-dicarboxycinnamic acid in $\text{DMSO-}d_6$.

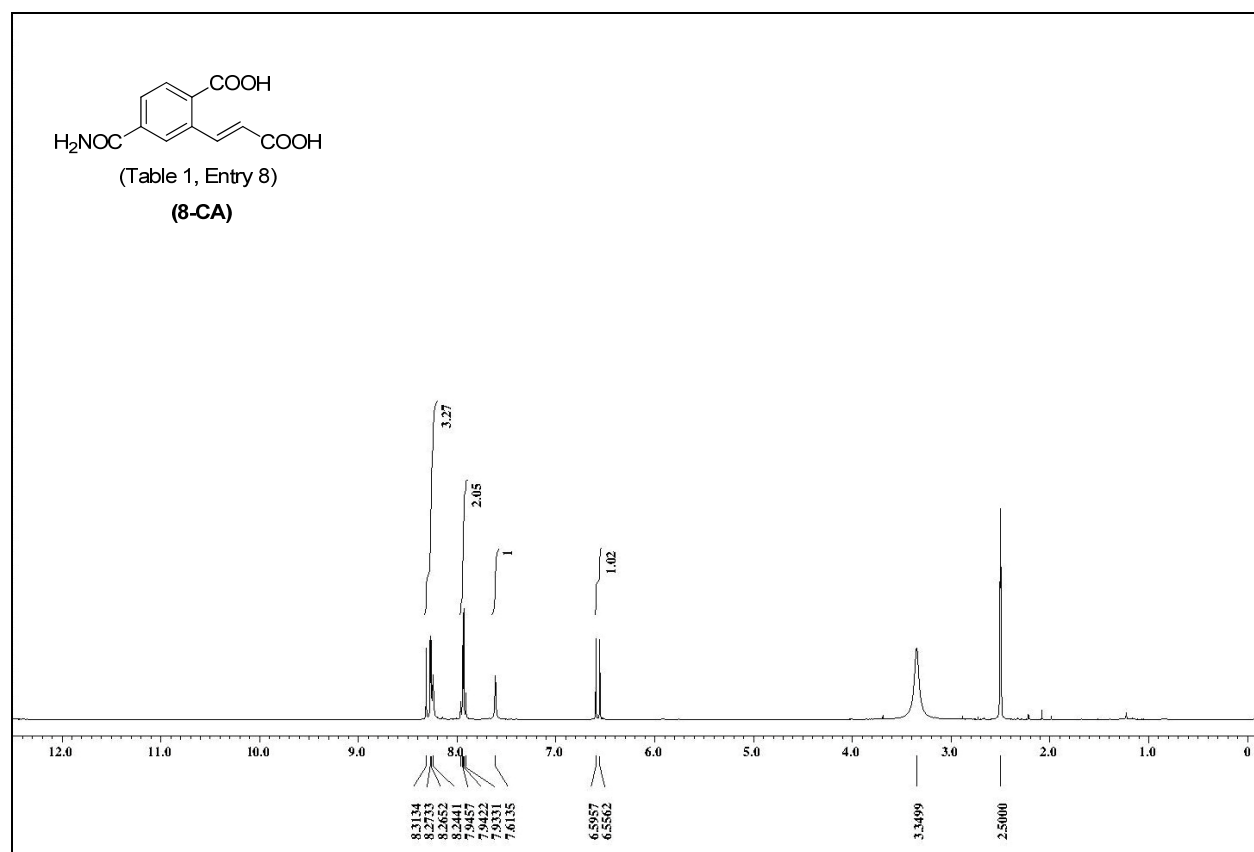


FIGURE S16. ^1H NMR spectrum of (*E*)-5-amido-2-carboxycinnamic acid in $\text{DMSO-}d_6$.

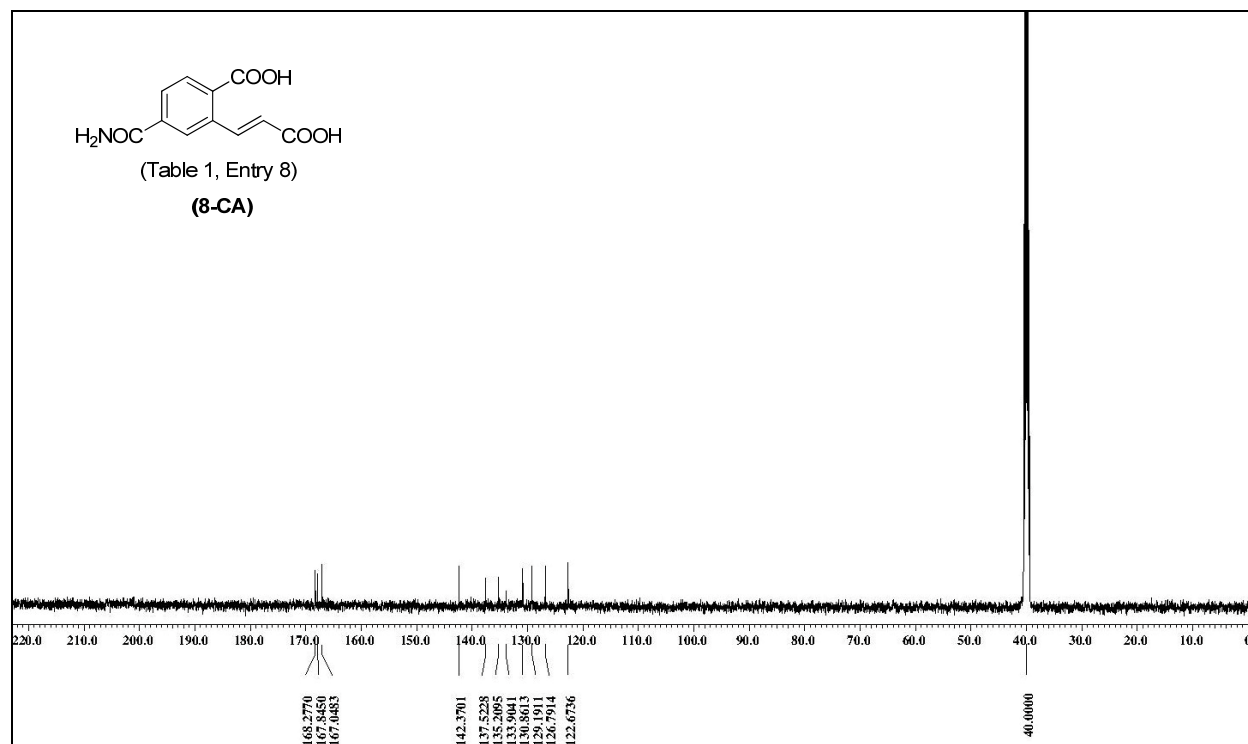


FIGURE S17. ^{13}C NMR spectrum of (*E*)-5-amido-2-carboxycinnamic acid in $\text{DMSO-}d_6$.

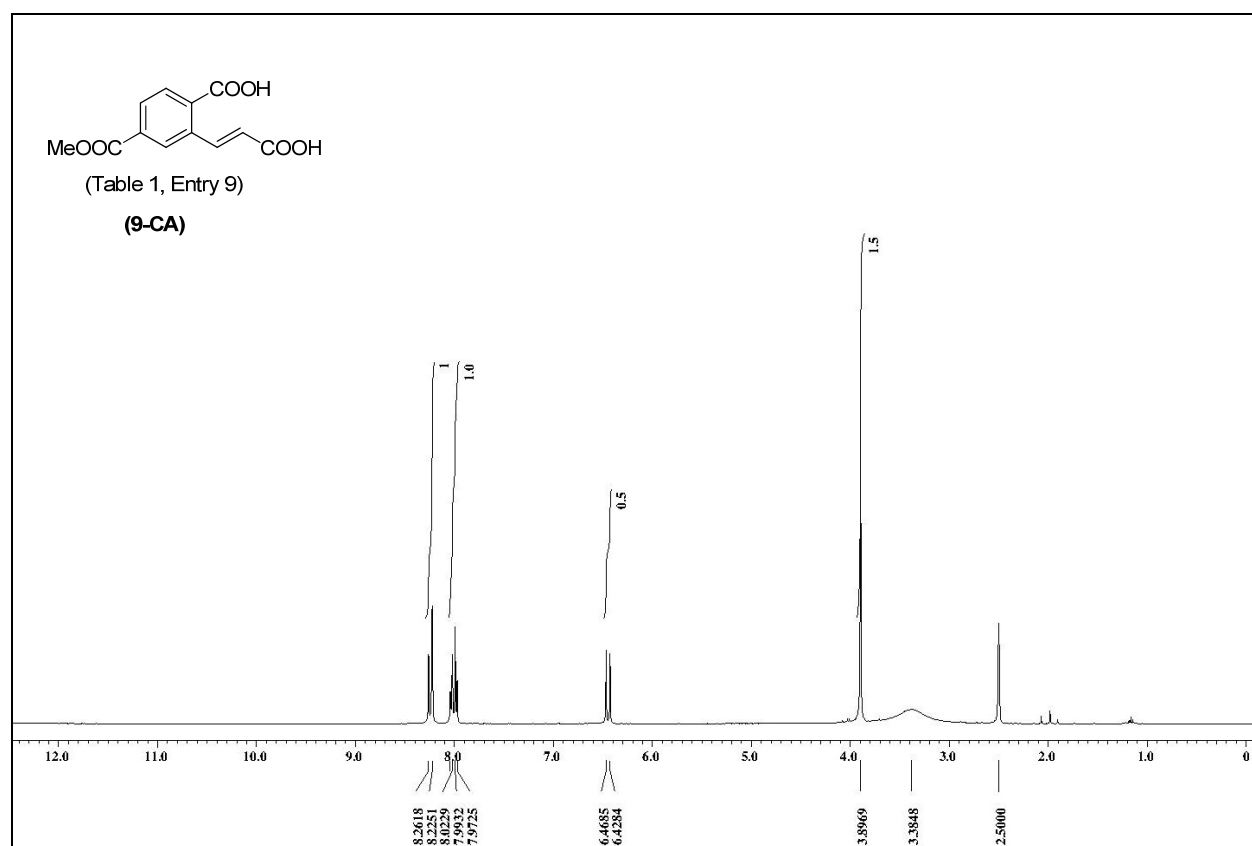


FIGURE S18. ¹H NMR spectrum of (*E*)-5-carbomethoxy-2-carboxycinnamic acid in DMSO-*d*₆.

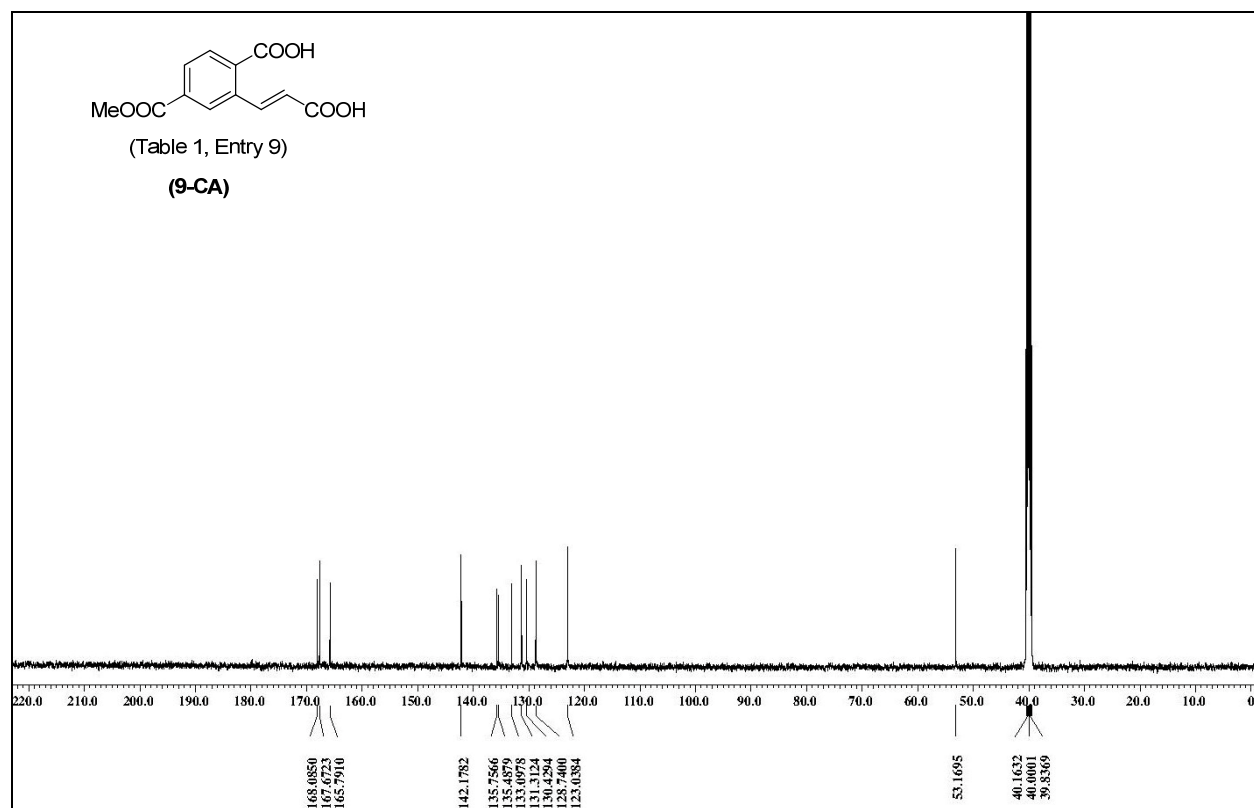


FIGURE S19. ^{13}C NMR spectrum of (*E*)-5-carbomethoxy-2-carboxycinnamic acid in $\text{DMSO-}d_6$.

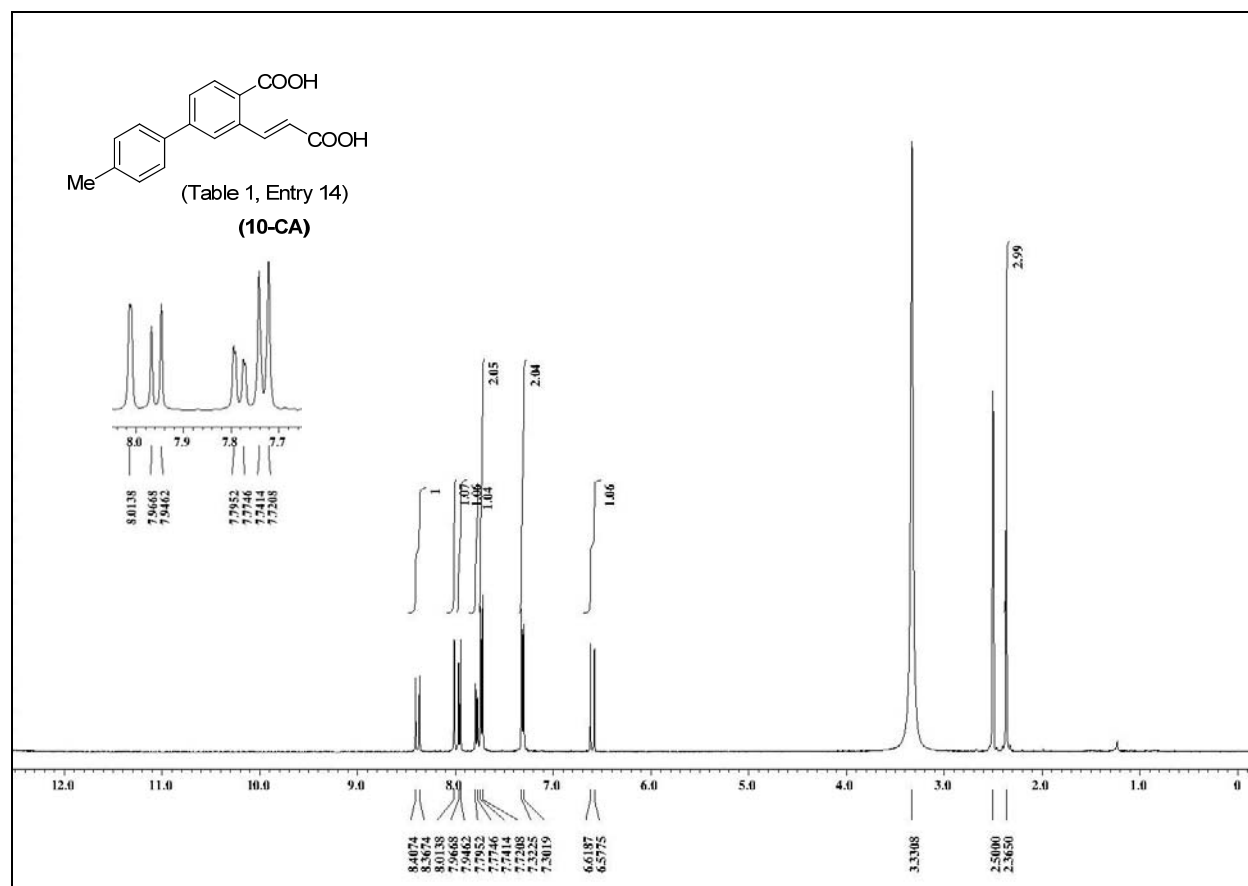


FIGURE S20. ^1H NMR spectrum of (E)-2-carboxy-5-(4-tolyl)cinnamic acid in $\text{DMSO}-d_6$.

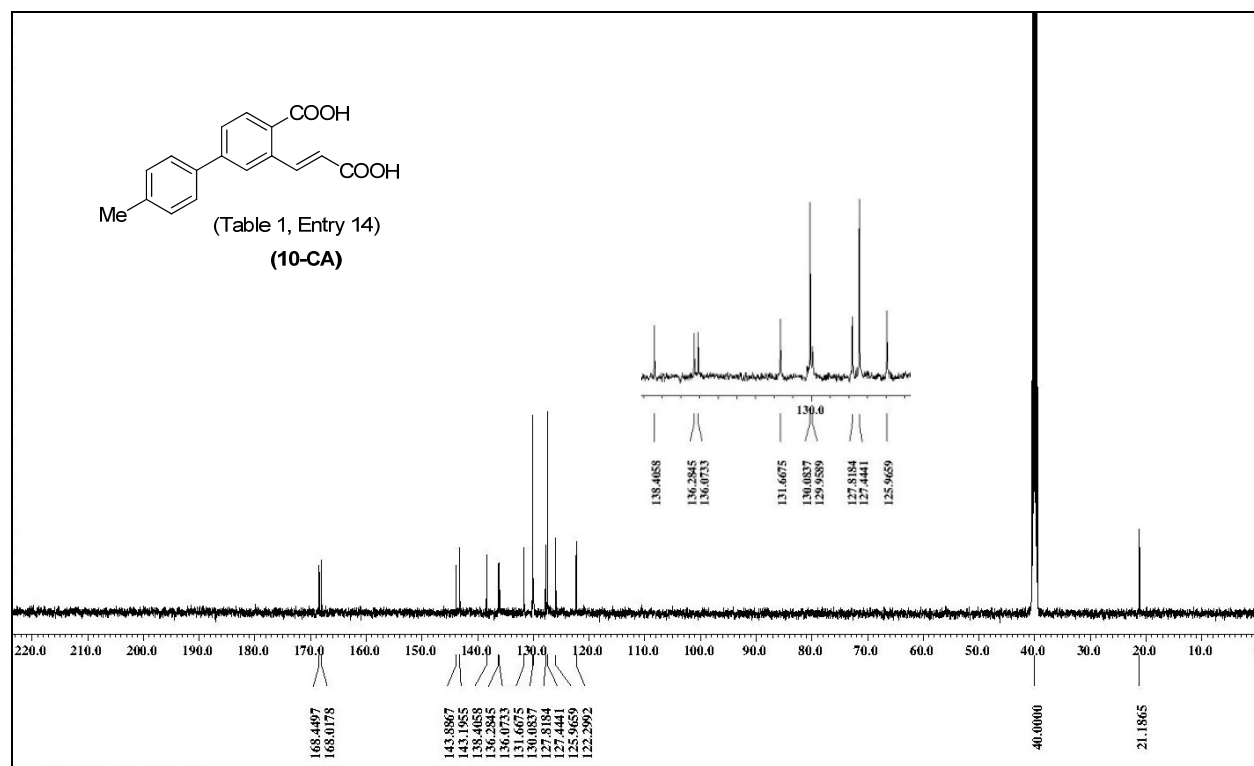


FIGURE S21. ^{13}C NMR spectrum of (E)-2-carboxy-5-(4-tolyl)cinnamic acid in $\text{DMSO}-d_6$.

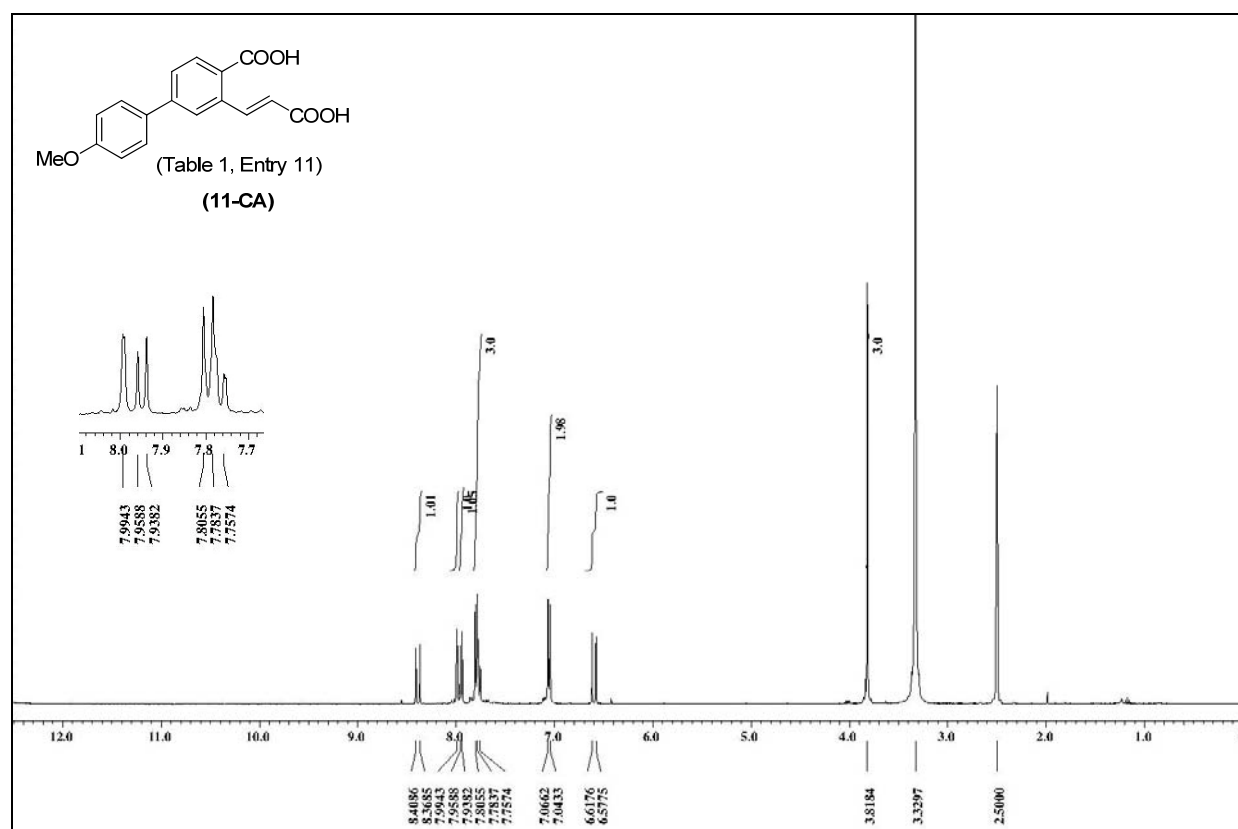


FIGURE S22. ¹H NMR spectrum of (*E*)-2-carboxy-5-(4-anisyl)cinnamic acid in DMSO-*d*₆.

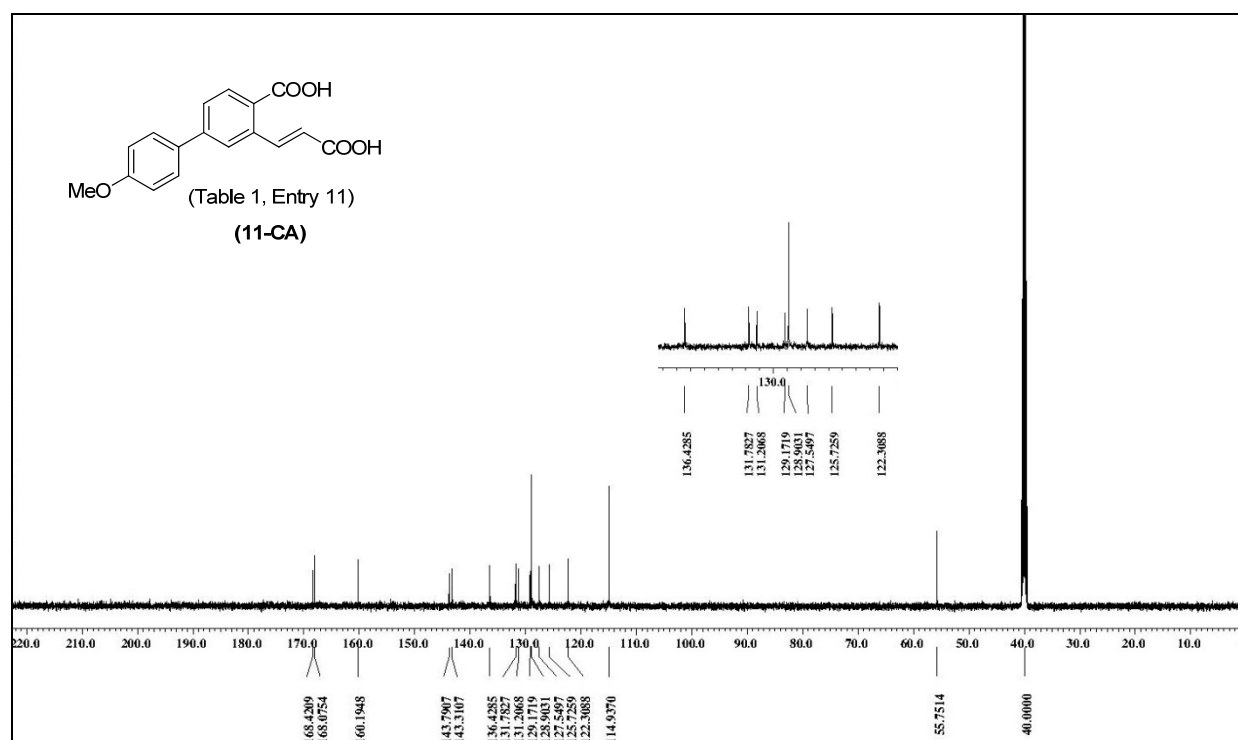


FIGURE S23. ^{13}C NMR spectrum of (*E*)-2-carboxy-5-(4-anisyl)cinnamic acid in $\text{DMSO-}d_6$.

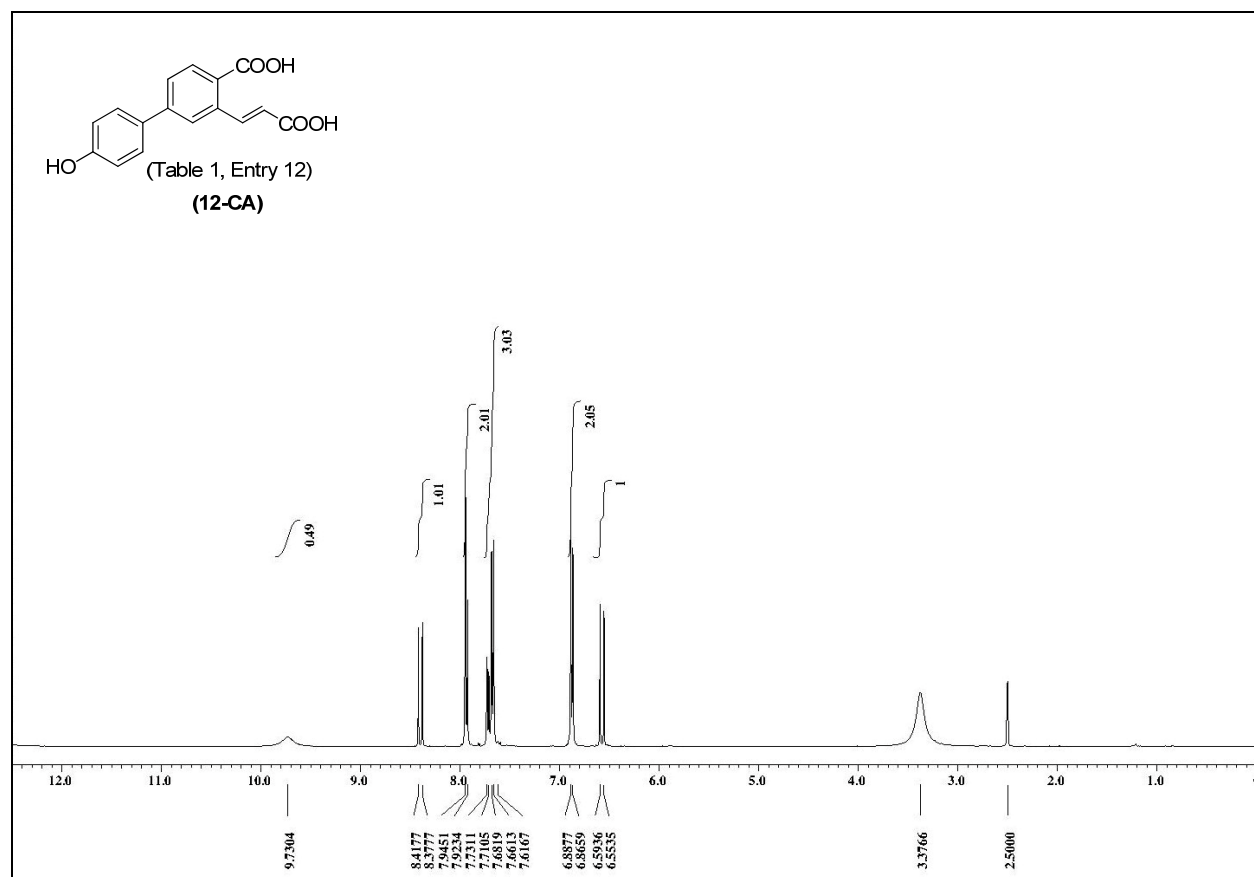


FIGURE S24. ¹H NMR spectrum of (E)-2-carboxy-5-(4-phenoxy)cinnamic acid in DMSO-d₆.

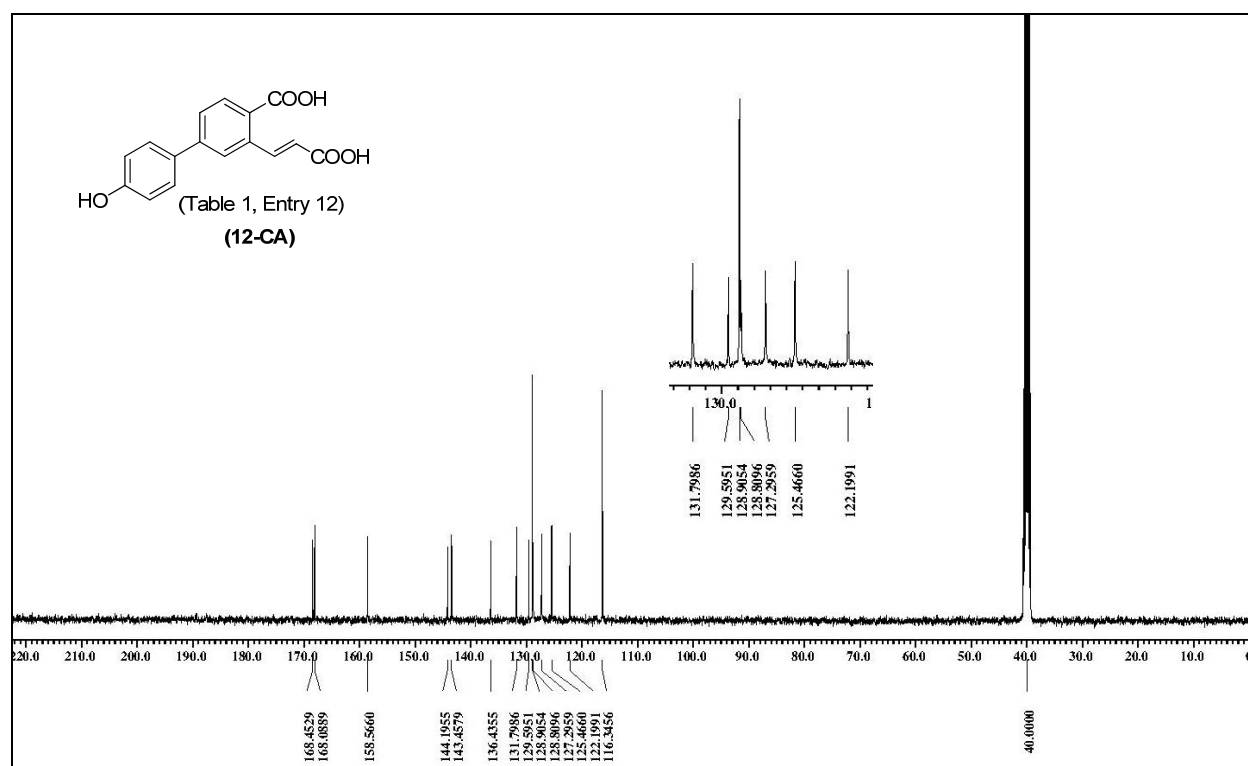


FIGURE S25. ¹³C NMR spectrum of (*E*)-2-carboxy-5-(4-phenoxy)cinnamic acid in DMSO-*d*₆.

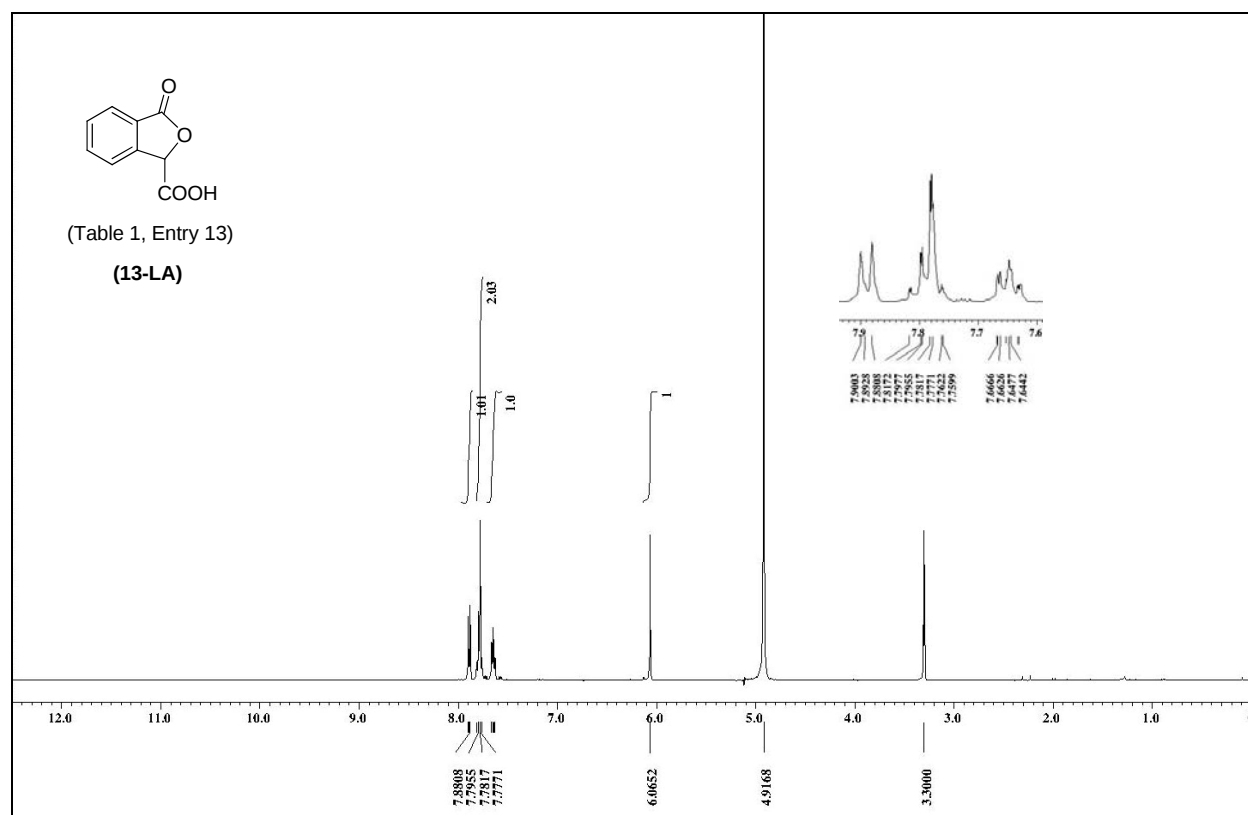


FIGURE S26. ^1H NMR spectrum of 3-oxo-1,3-dihydroisobenzofuran-1-carboxylic acid in CD_3OD .

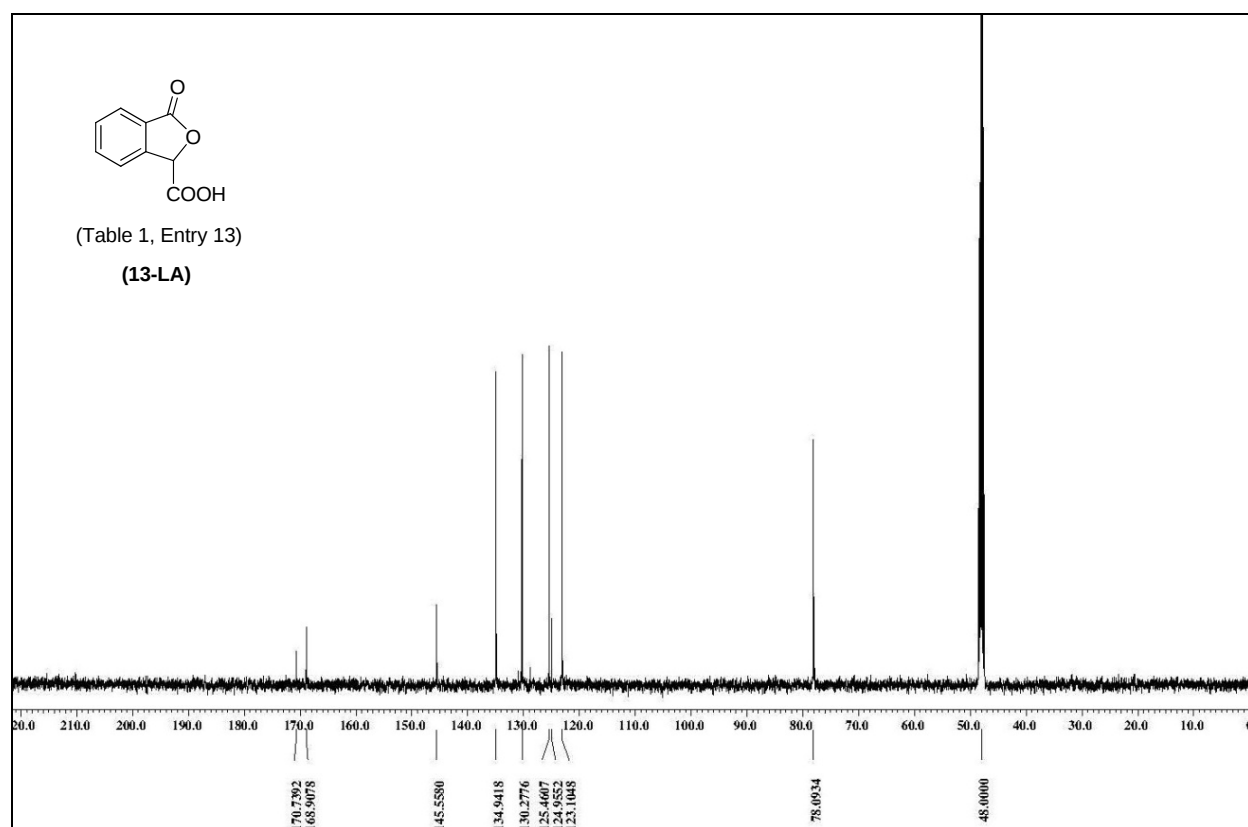


FIGURE S27. ^{13}C NMR spectrum of 3-oxo-1,3-dihydroisobenzofuran-1-carboxylic acid in CD_3OD .

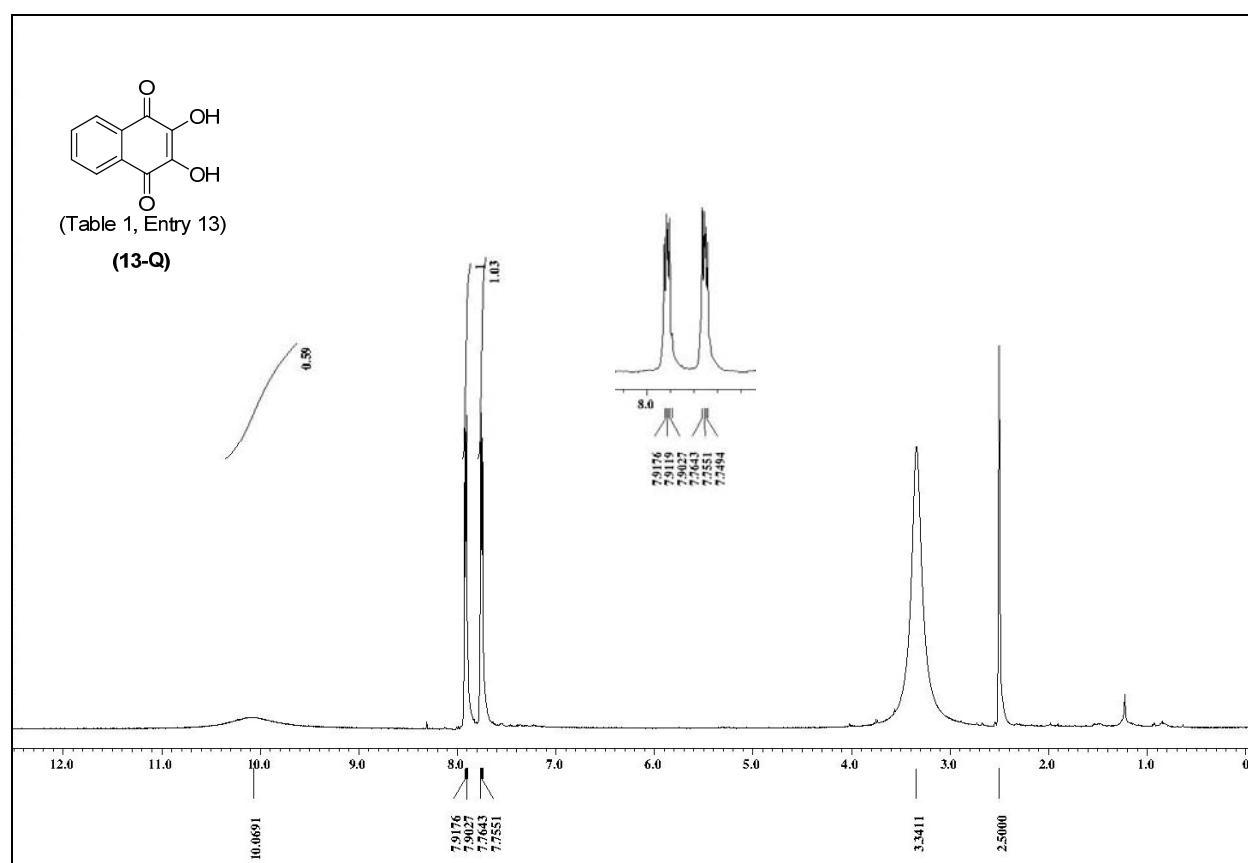


FIGURE S28. ^1H NMR spectrum of 2,3-dihydroxy-1,4-naphthoquinone in $\text{DMSO-}d_6$.

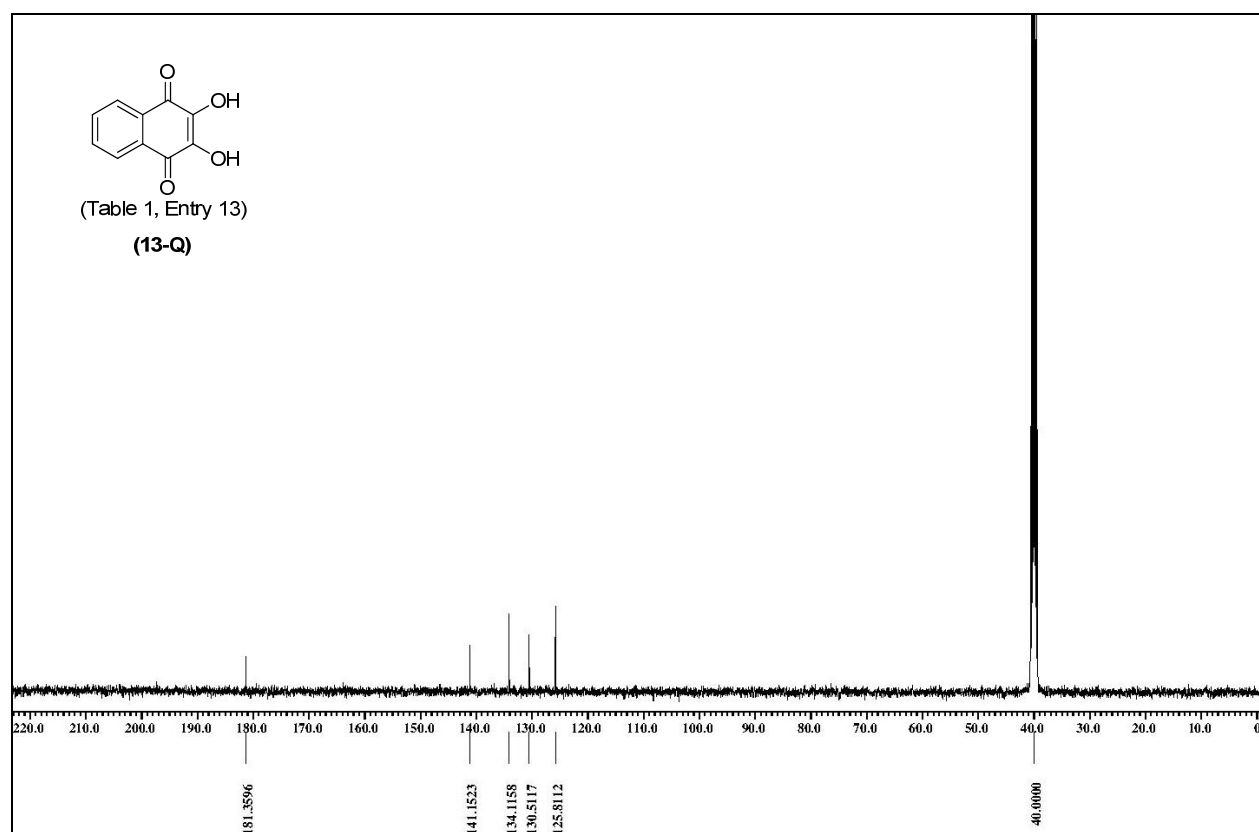


FIGURE S29. ^{13}C NMR spectrum of 2,3-dihydroxy-1,4-naphthoquinone in $\text{DMSO-}d_6$.

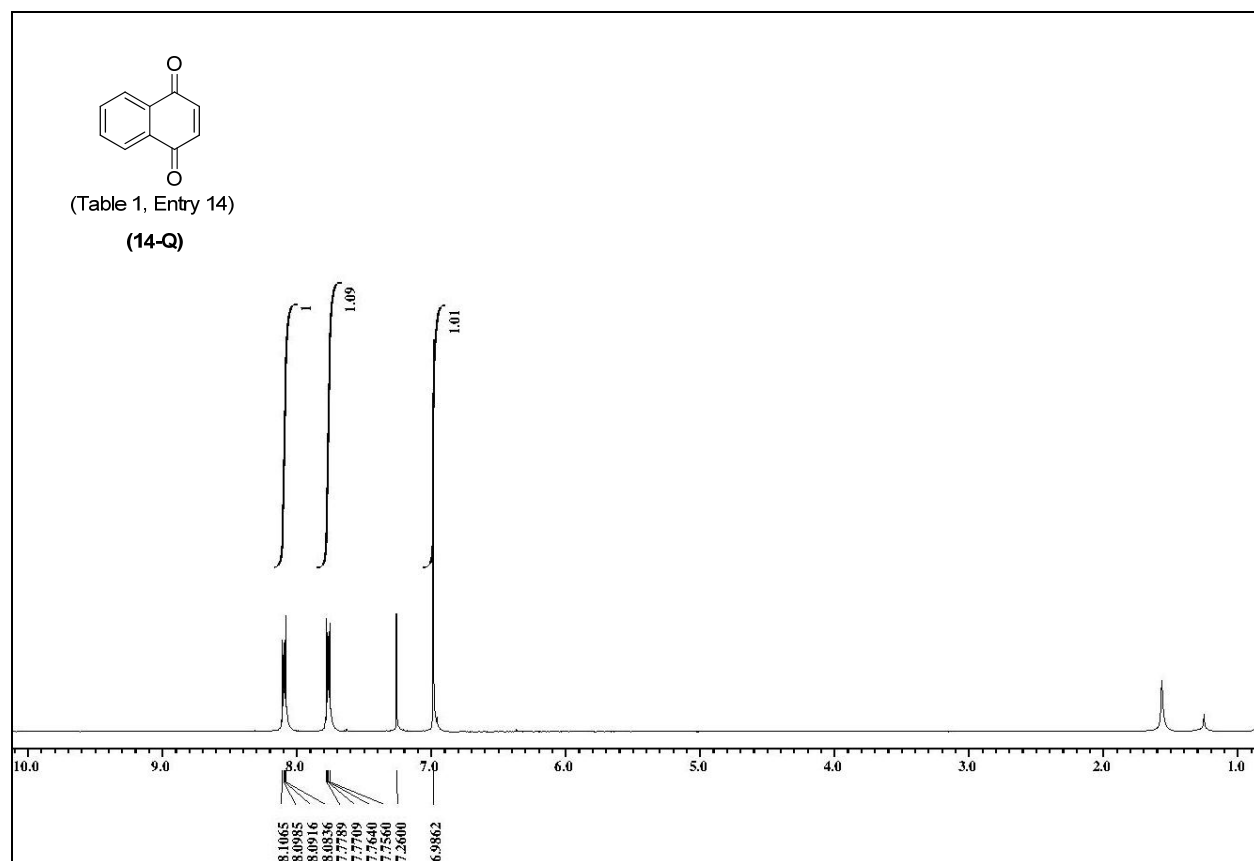


FIGURE S30. ^1H NMR spectrum of 1,4-naphthoquinone in CDCl_3 .

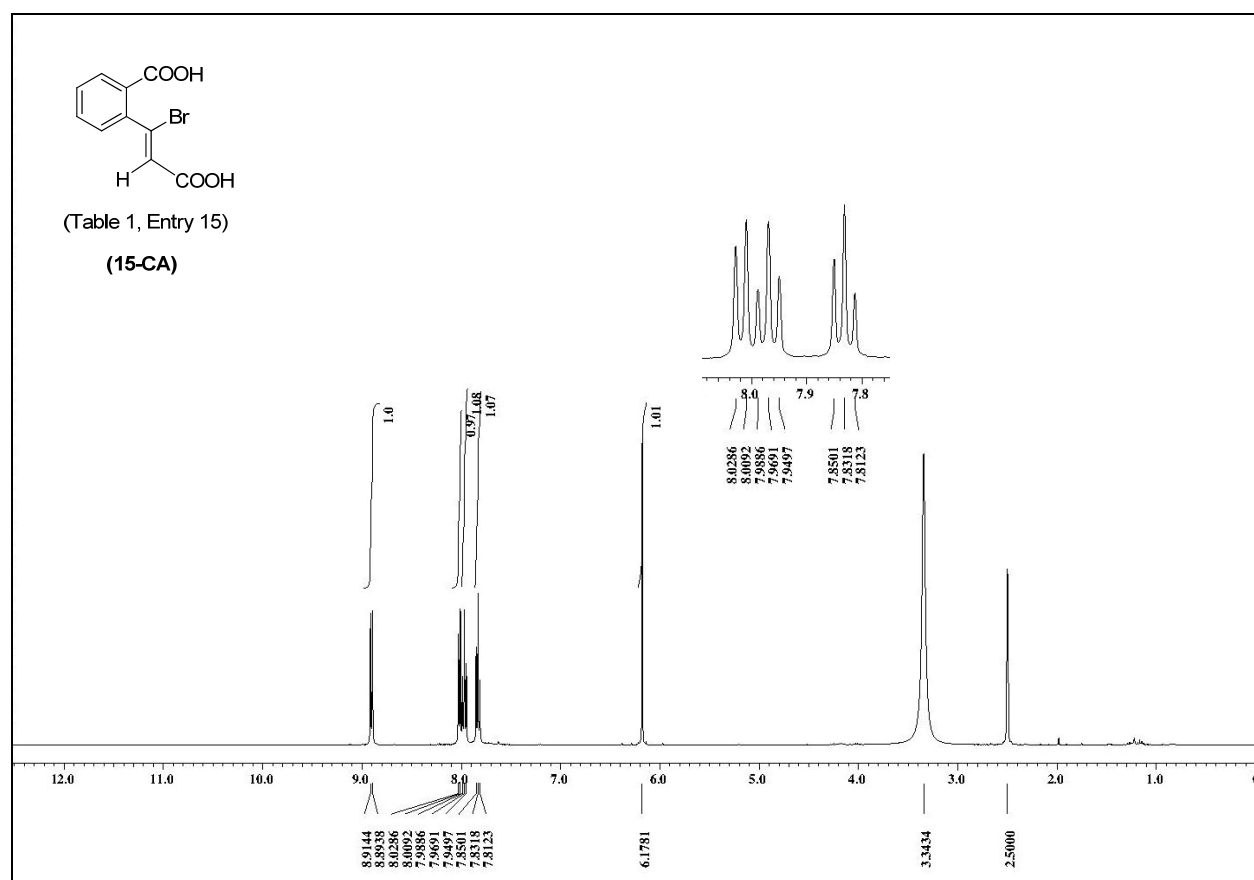


FIGURE S31. ^1H NMR spectrum of β -bromo-2-carboxycinnamic acid in $\text{DMSO-}d_6$.

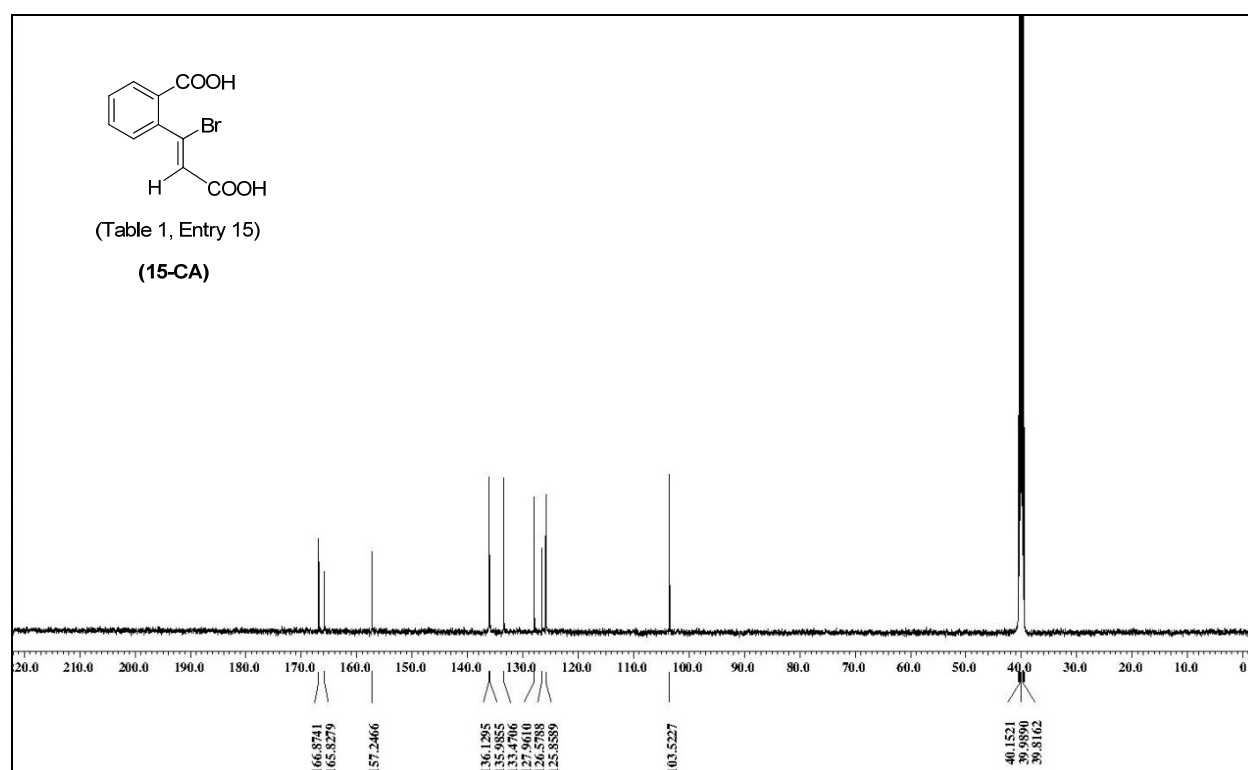


FIGURE S32. ^{13}C NMR spectrum of β -bromo-2-carboxycinnamic acid in $\text{DMSO-}d_6$.

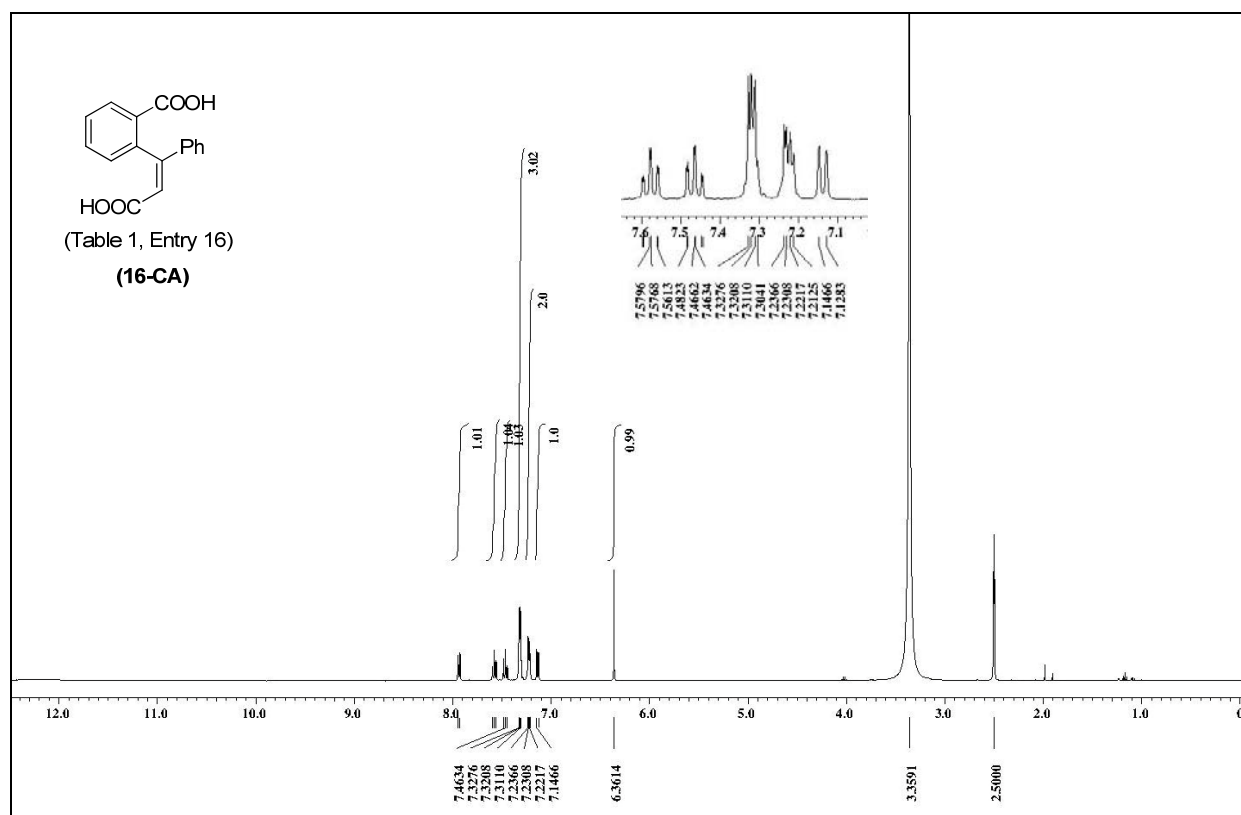


FIGURE S33. ^1H NMR spectrum of β -phenyl-2-carboxycinnamic acid in DMSO- d_6 .

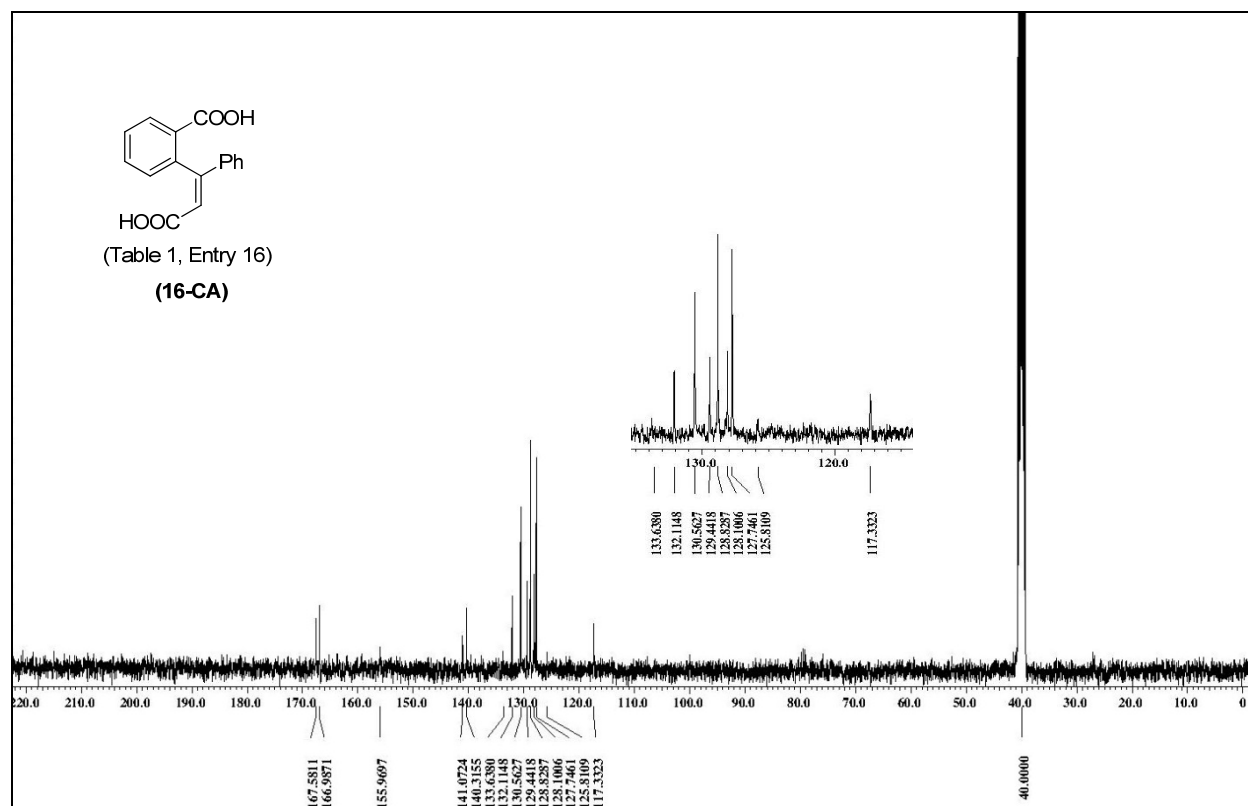


FIGURE S34. ^{13}C NMR spectrum of β -phenyl-2-carboxycinnamic acid in $\text{DMSO-}d_6$.

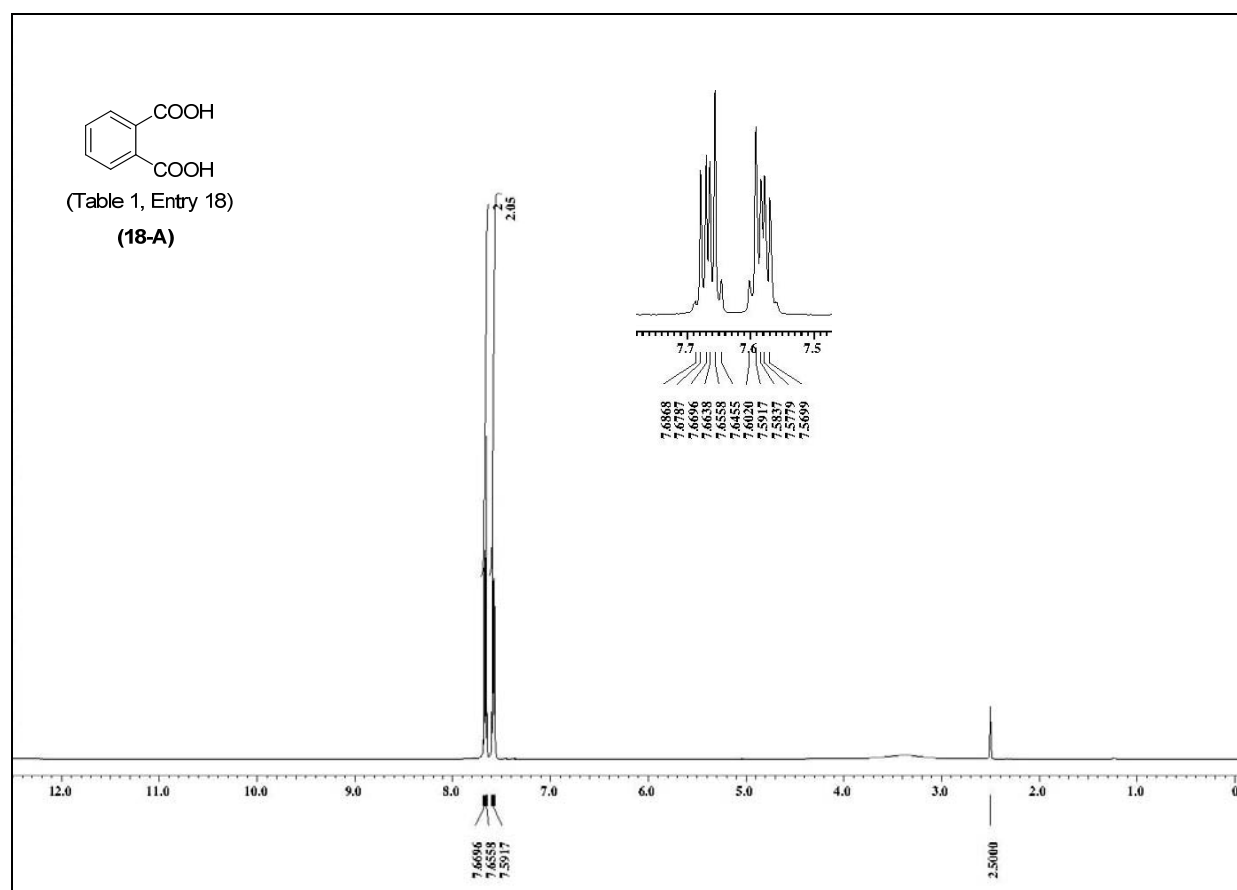


FIGURE S35. ^1H NMR spectrum of *o*-phthalic acid in $\text{DMSO}-d_6$.

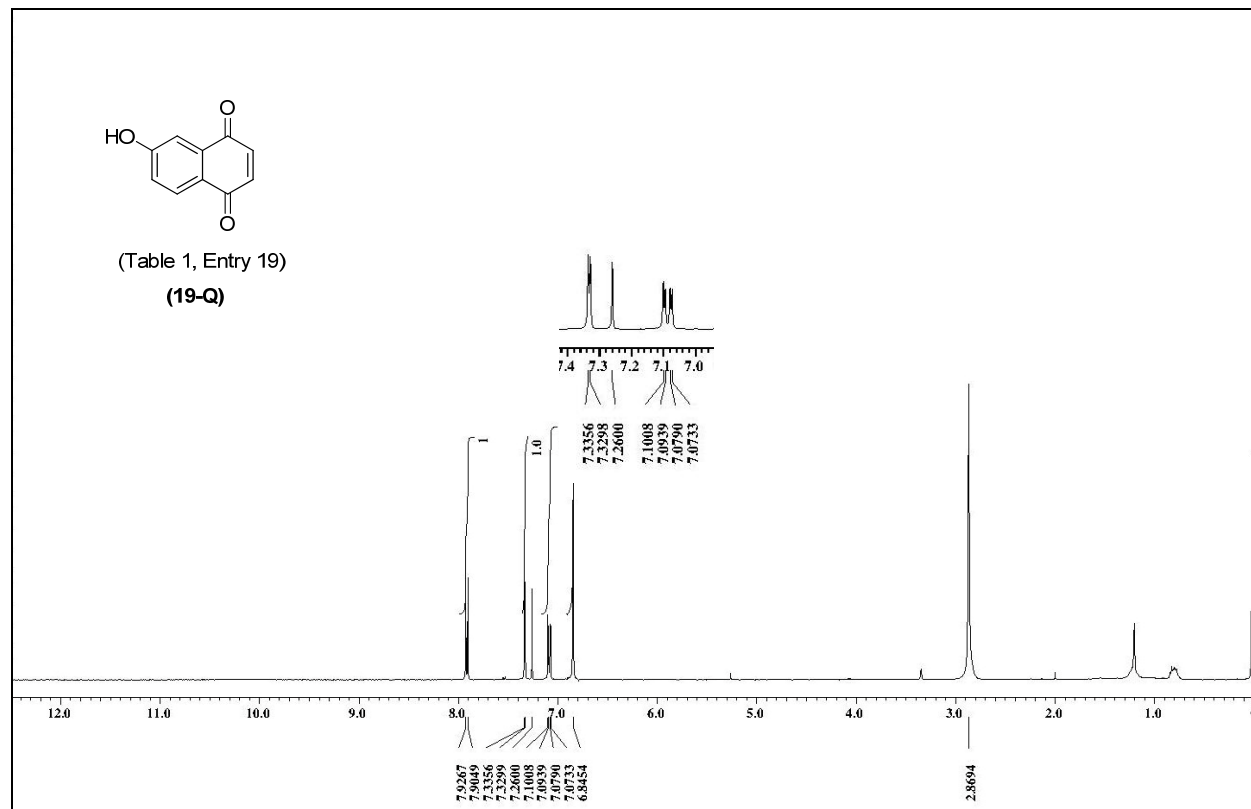


FIGURE S36. ¹H NMR spectrum of 6-hydroxy-1,4-naphthoquinone in CDCl₃+CD₃OD.

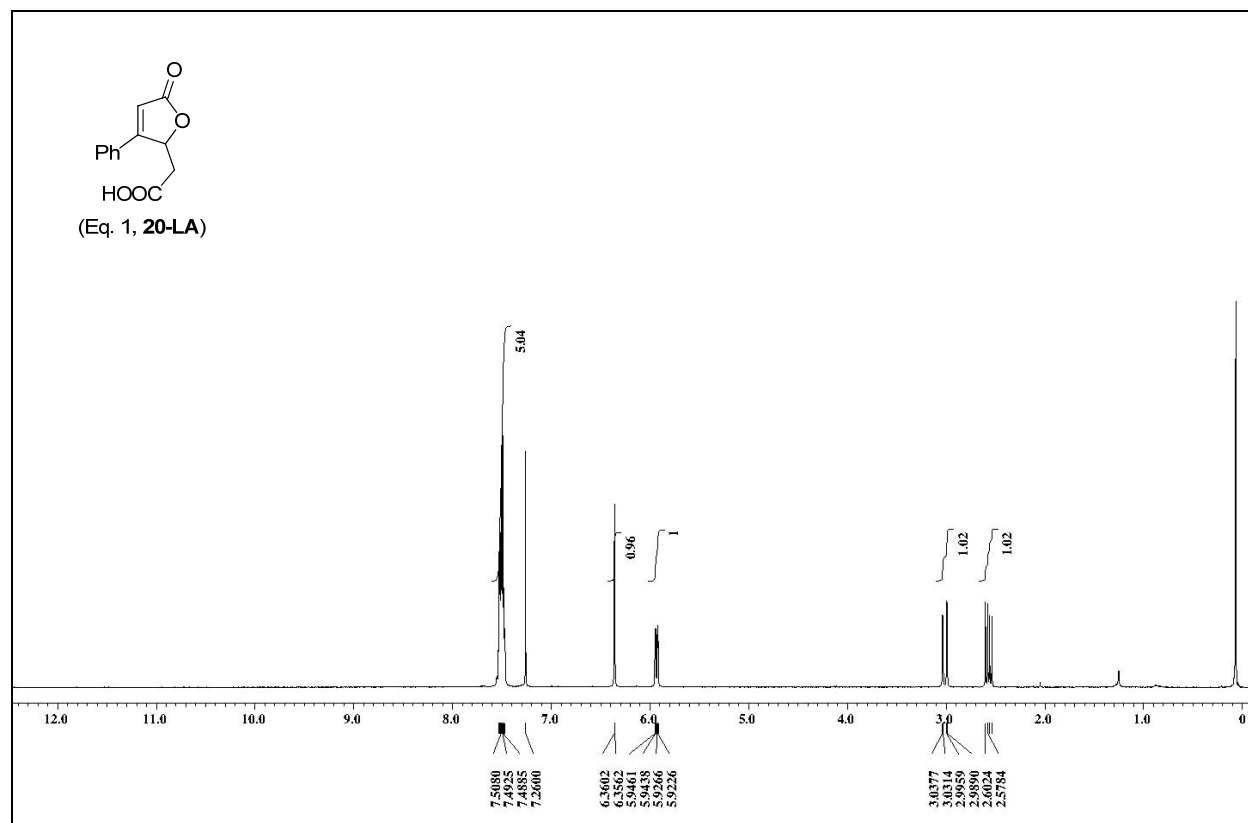


FIGURE S37. ¹H NMR spectrum of 5-oxo-3-phenyl-2,5-dihydro-2-furanacetic acid in CDCl₃.

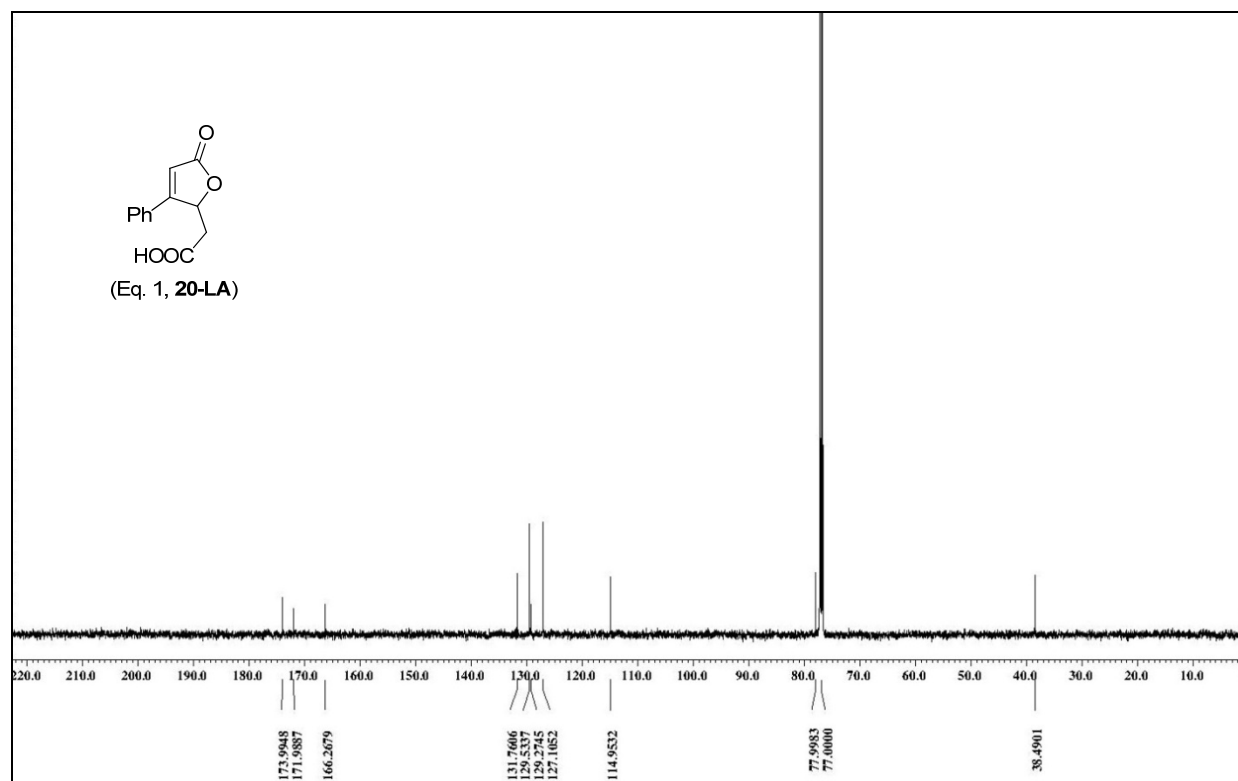


FIGURE S38. ^{13}C NMR spectrum of 5-oxo-3-phenyl-2,5-dihydro-2-furanacetic acid in CDCl_3 .

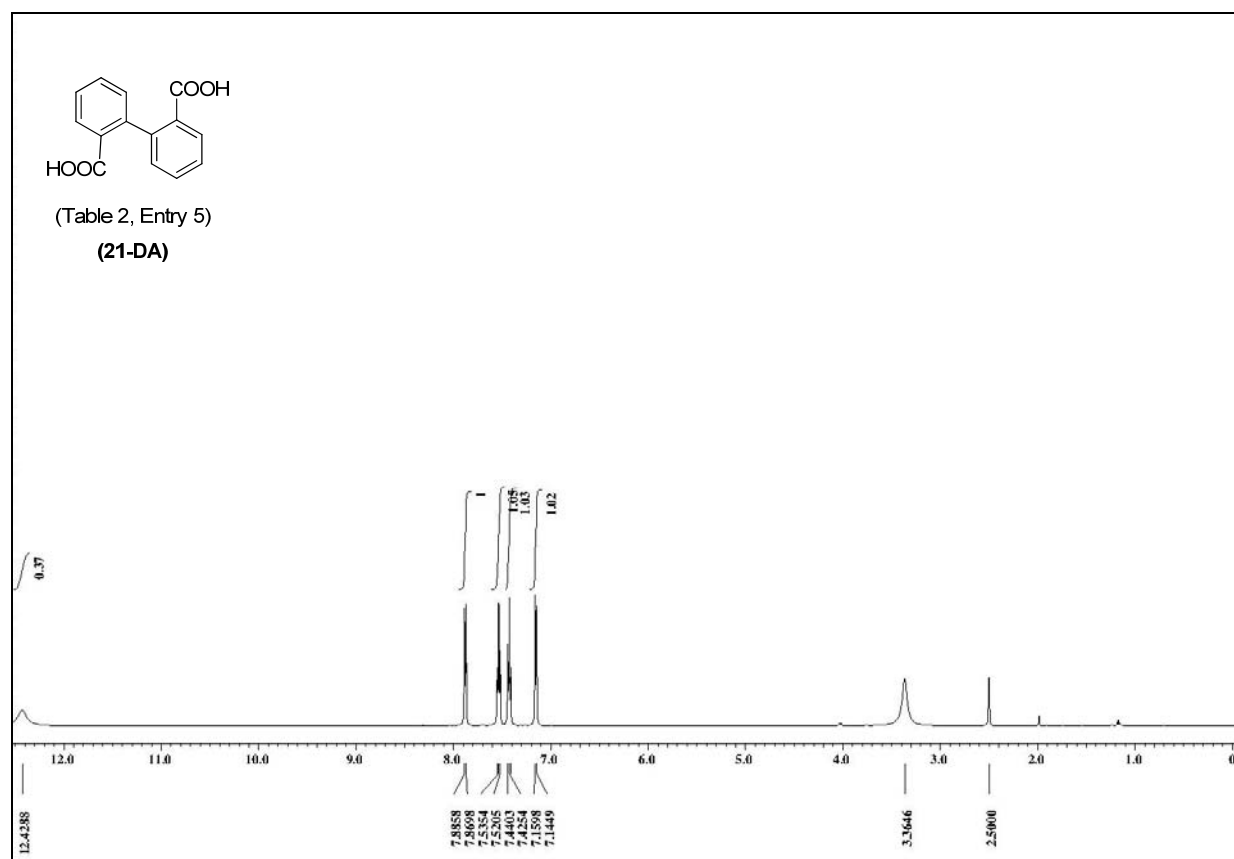


FIGURE S39. ^1H NMR spectrum of diphenic acid in $\text{DMSO-}d_6$.

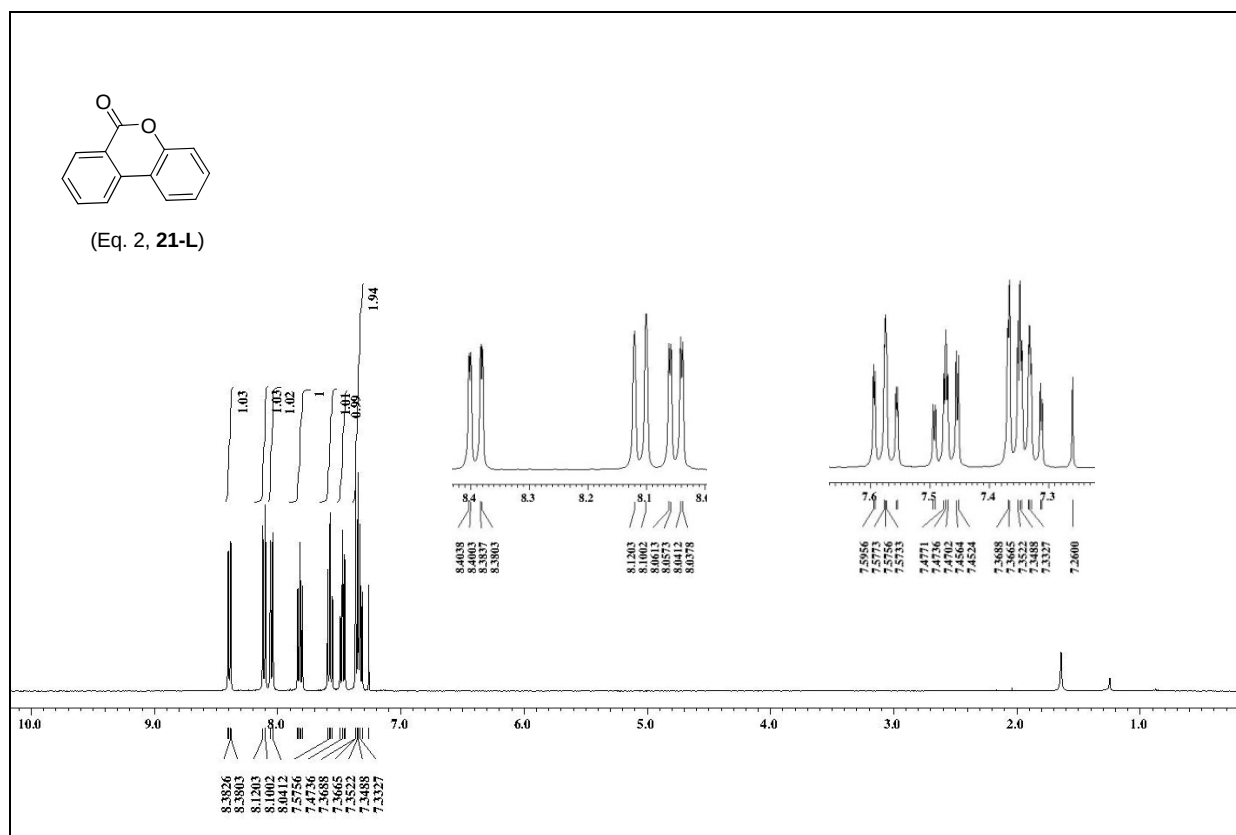


FIGURE S40. ¹H NMR spectrum of dibenzo[b,d]pyrone in CDCl₃.

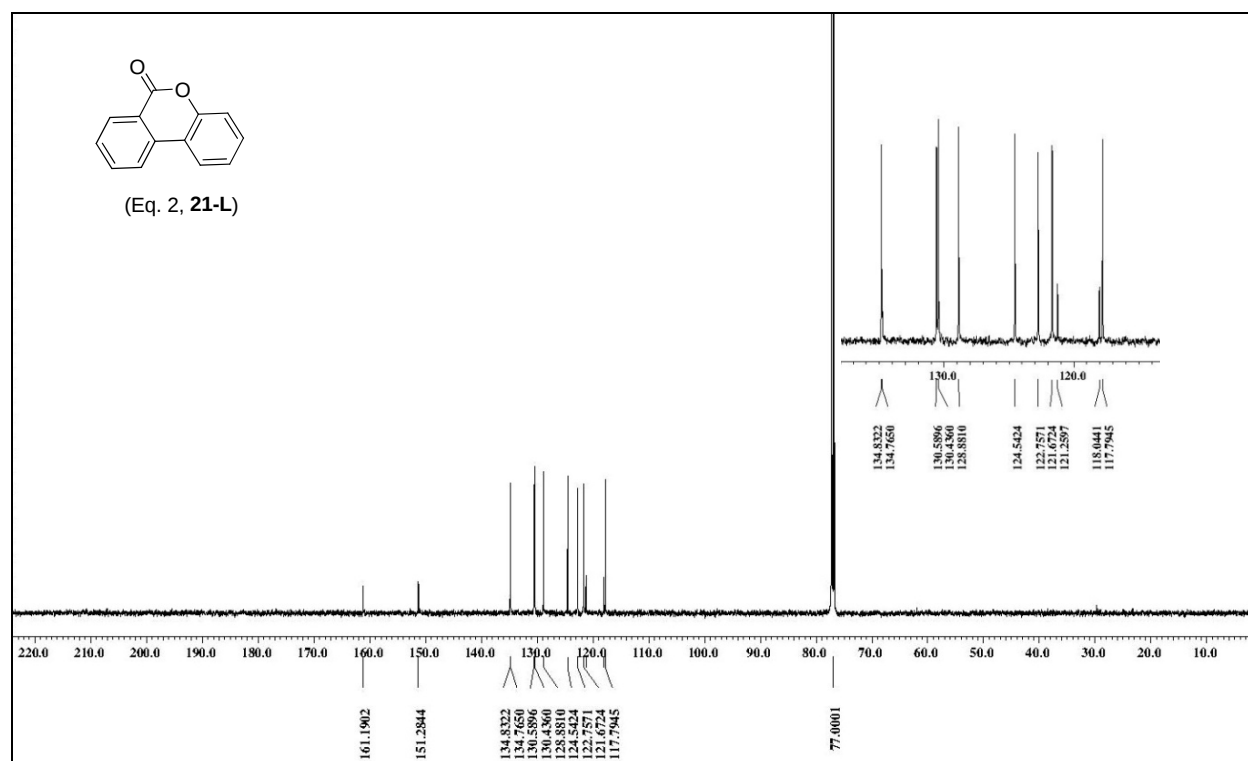


FIGURE S41. ^{13}C NMR spectrum of dibenzo[b,d]pyrone in CDCl_3 .

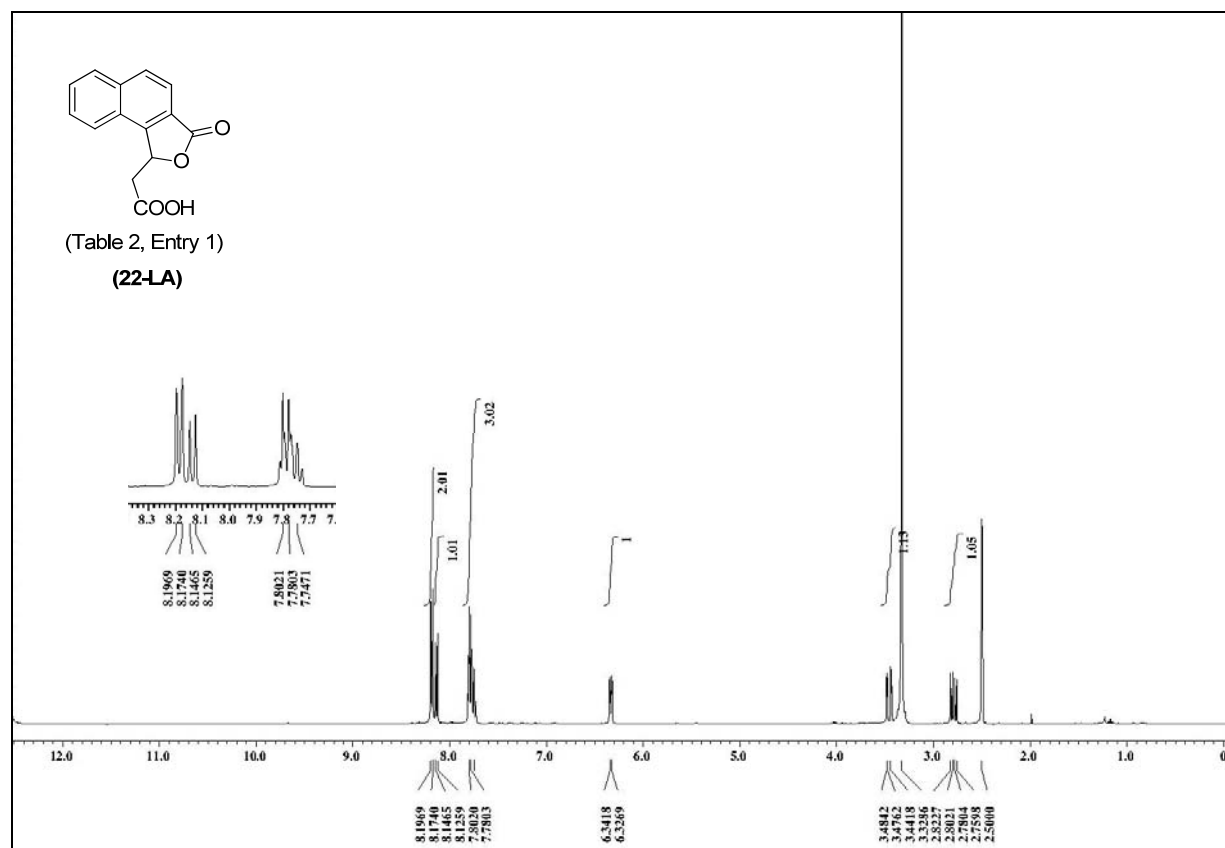


FIGURE S45. ¹H NMR spectrum of 2-(3-oxo-1,3-dihydronaphtho[2,1-c]furan-1-yl)acetic acid in DMSO-*d*₆.

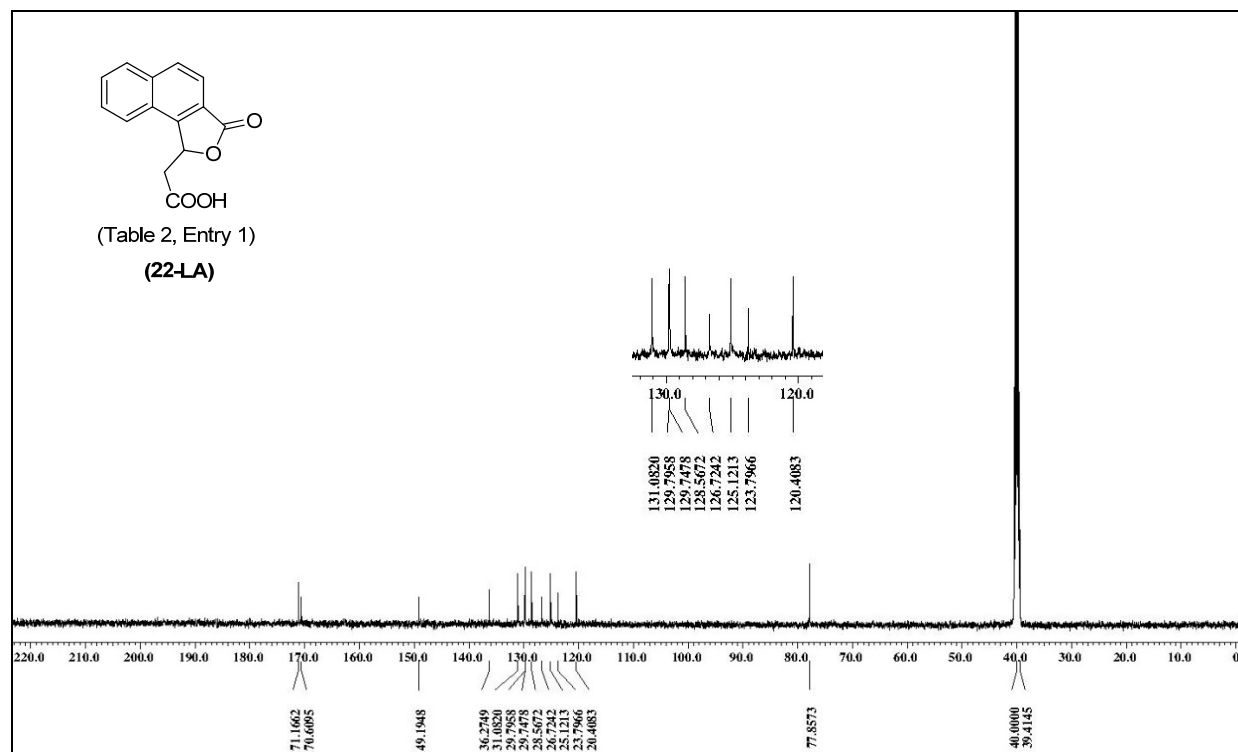


FIGURE S46. ¹³C NMR spectrum of 2-(3-oxo-1,3-dihydronaphtho[2,1-c]furan-1-yl)acetic acid in DMSO-*d*₆.

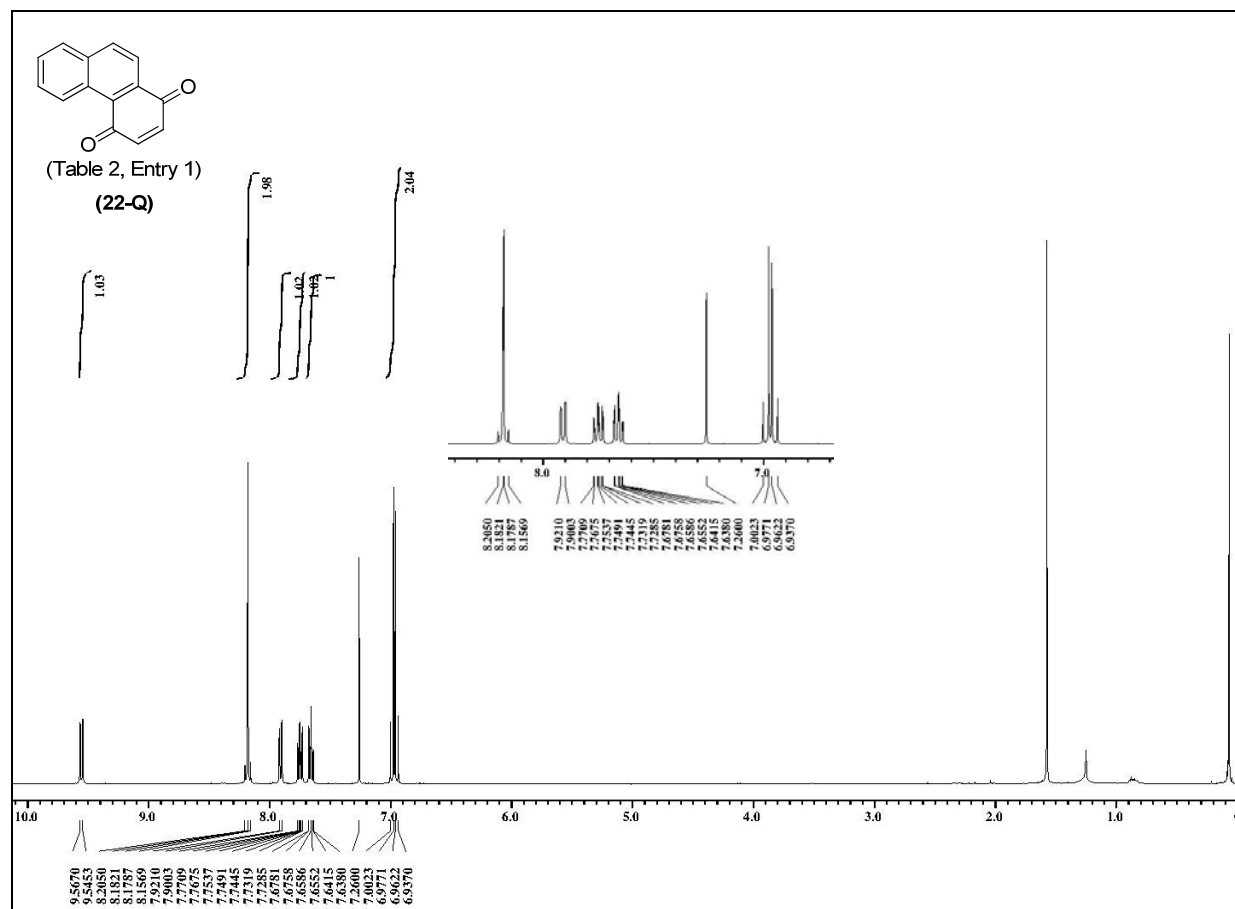


FIGURE S42. ¹H NMR spectrum of 1,4-phenanthroquinone in CDCl₃.

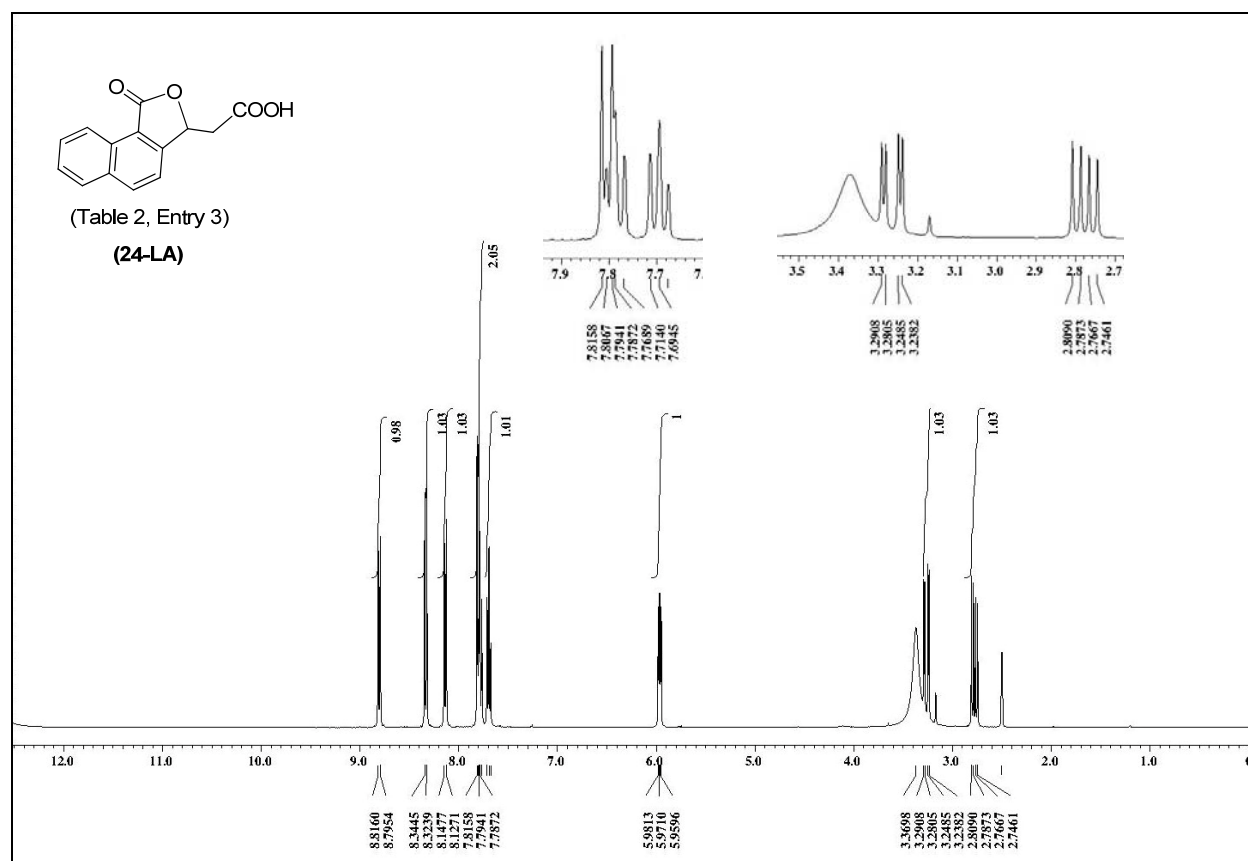


FIGURE S43. ¹H NMR spectrum of 2-(1-oxo-1,3-dihydronaphtho[2,1-c]furan-3-yl)acetic acid in DMSO-*d*₆.

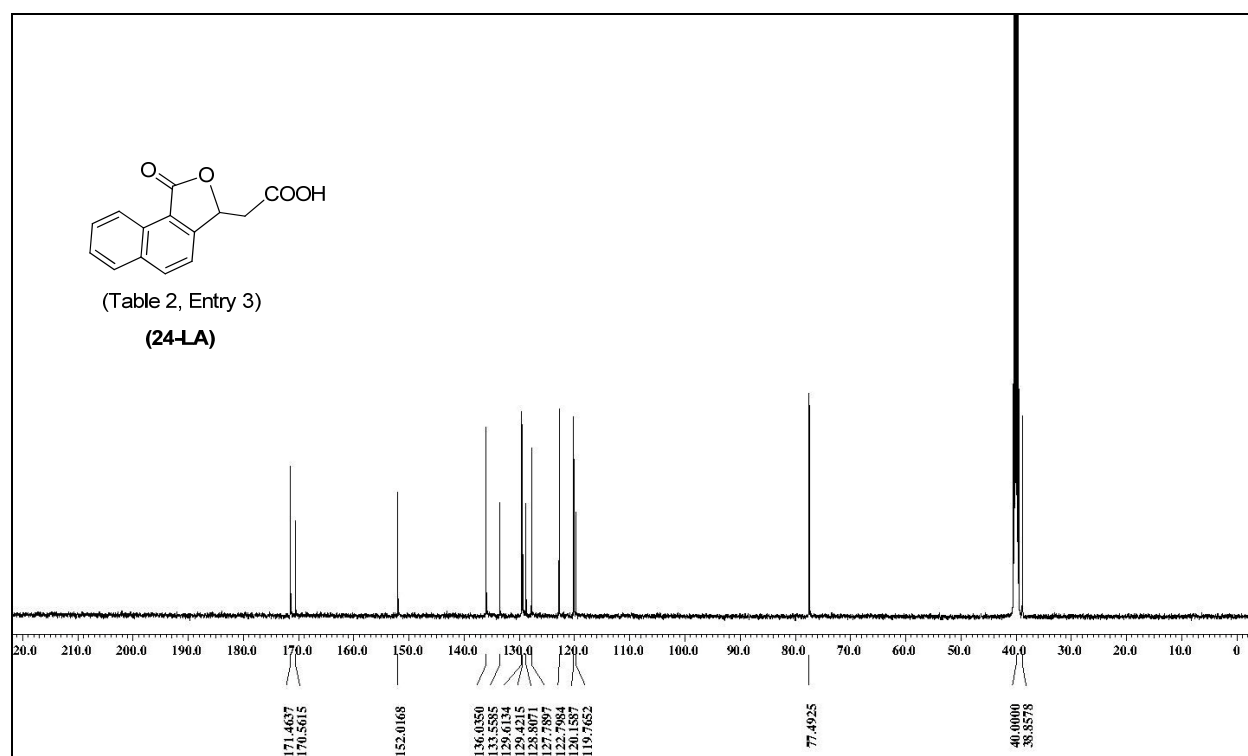


FIGURE S44. ^{13}C NMR spectrum of 2-(1-oxo-1,3-dihydronaphtho[2,1-c]furan-3-yl)acetic acid in $\text{DMSO-}d_6$.

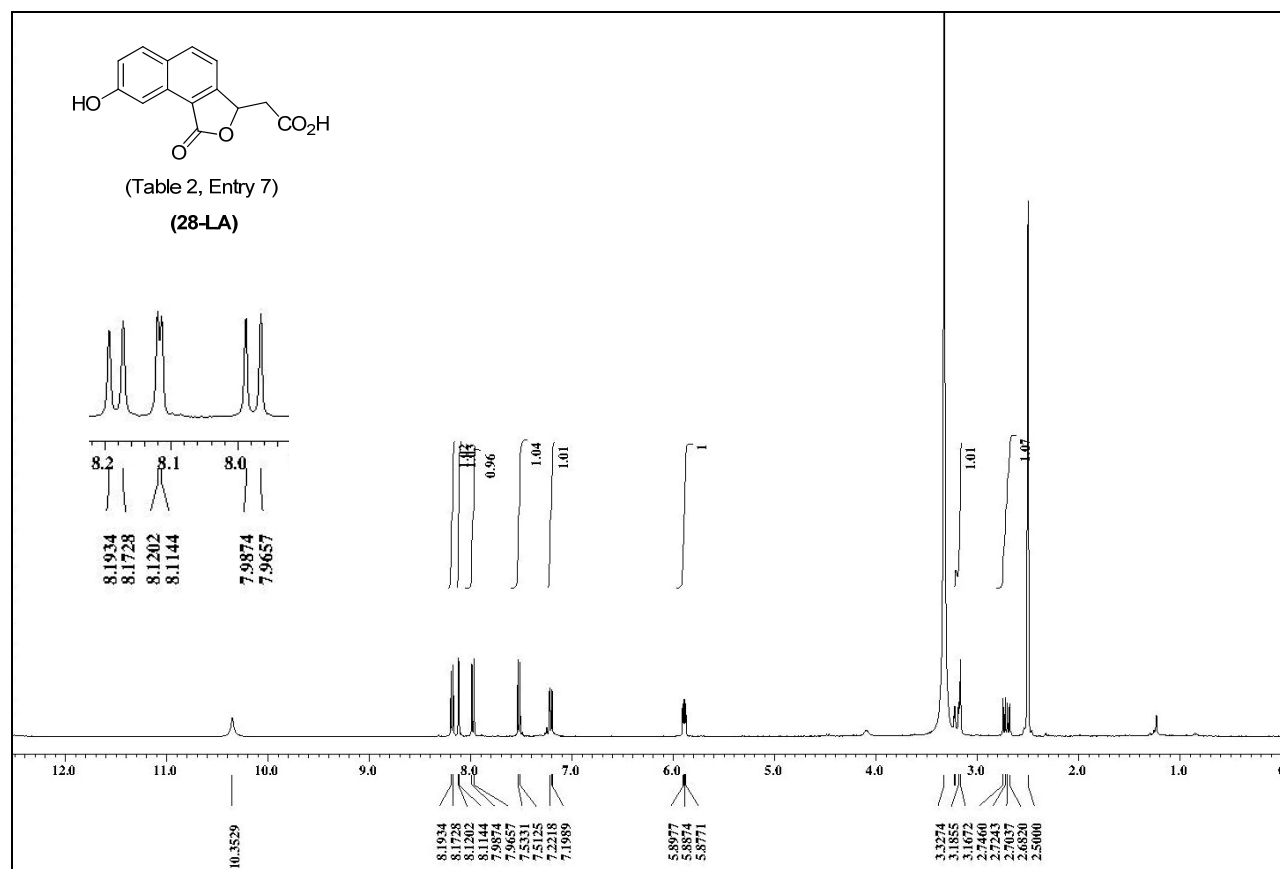


FIGURE S47. ¹H NMR spectrum of 2-(8-hydroxy-1-oxo-1,3-dihydronaphtho[2,1-c]furan-3-yl)acetic acid in DMSO-*d*₆.

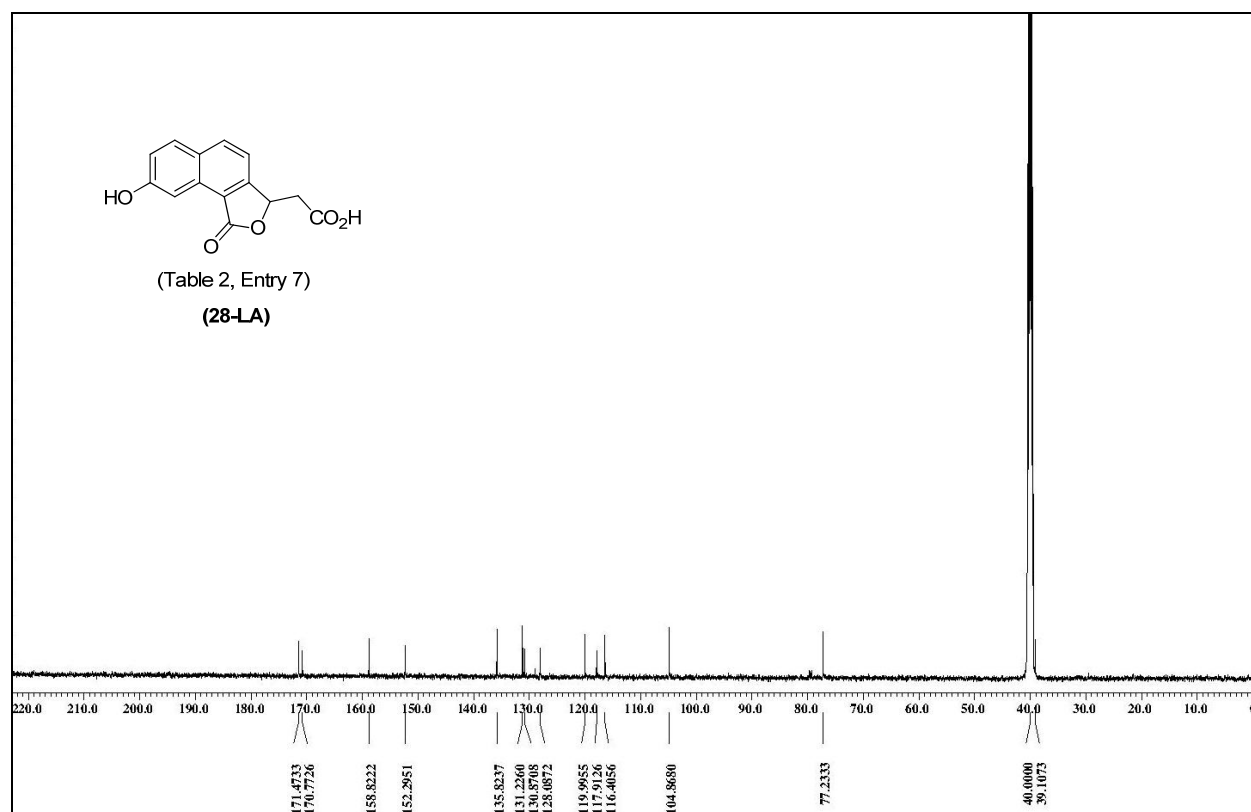


FIGURE S48. ¹³C NMR spectrum of 2-(8-hydroxy-1-oxo-1,3-dihydronaphtho[2,1-c]furan-3-yl)acetic acid in DMSO-*d*₆.

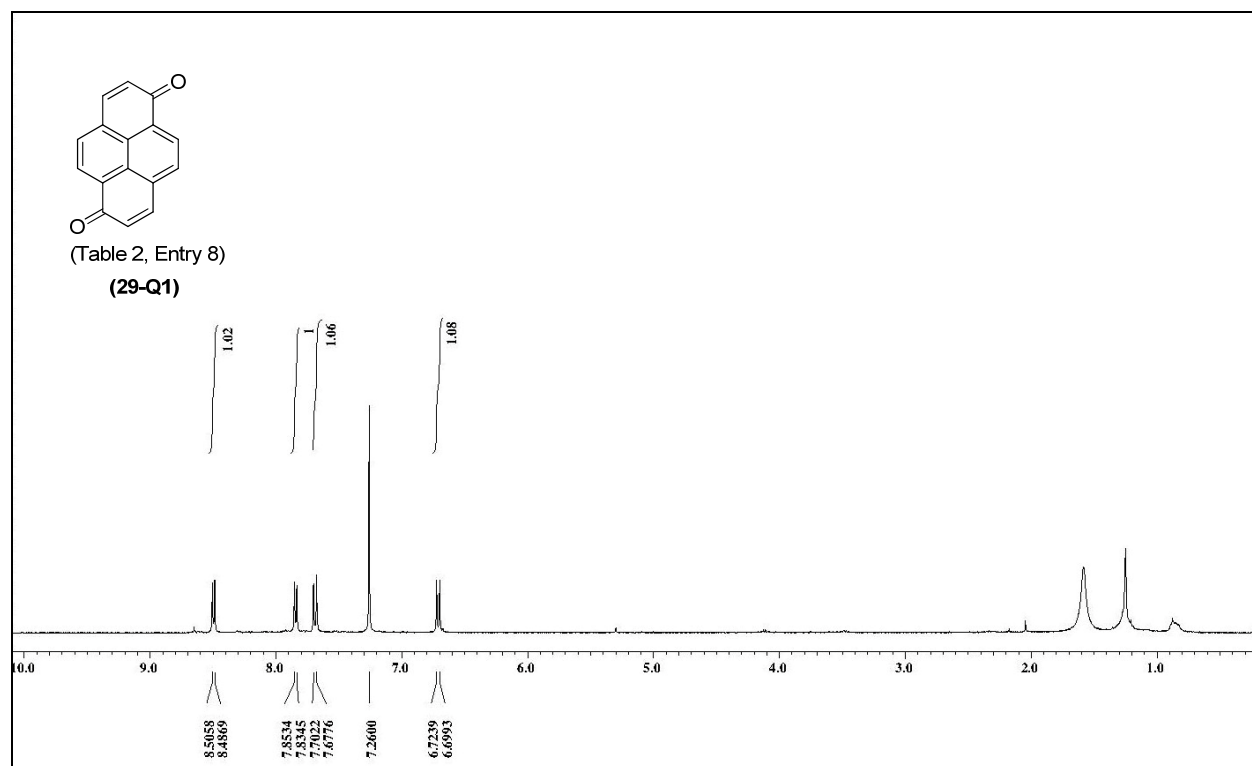


FIGURE S49. ^1H NMR spectrum of 1,6-diketopyrene in CDCl₃.

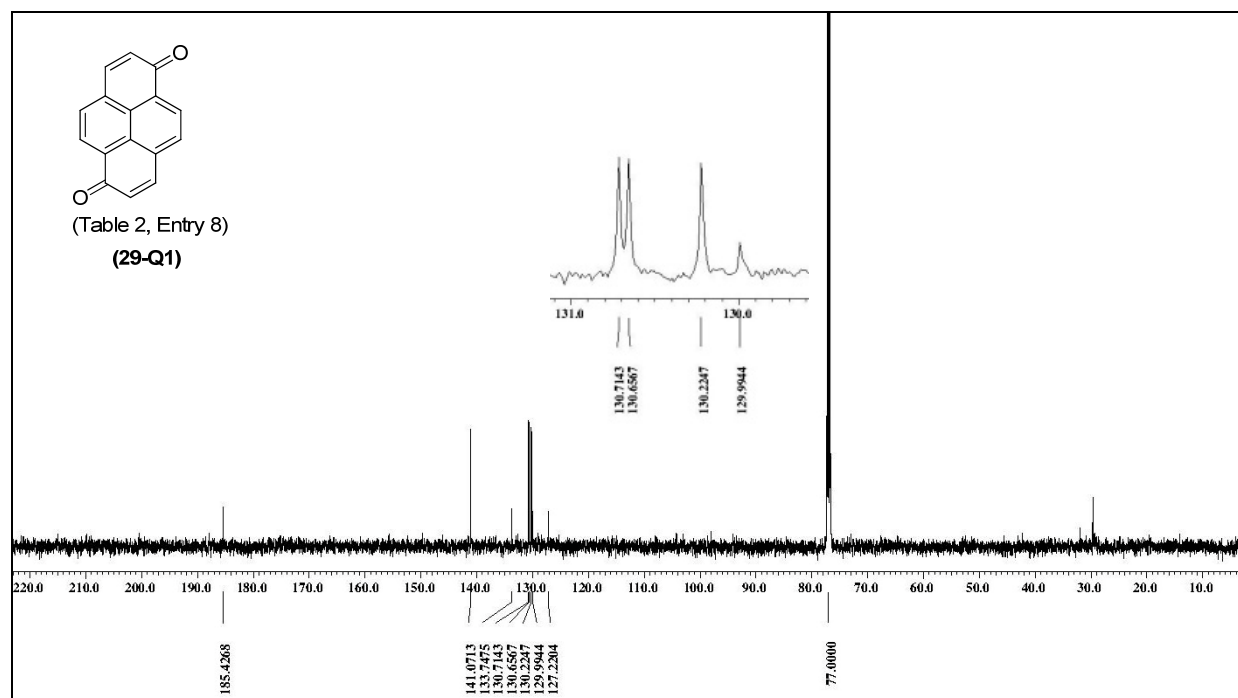


FIGURE S50. ^{13}C NMR spectrum of 1,6-diketopyrene in CDCl_3 .

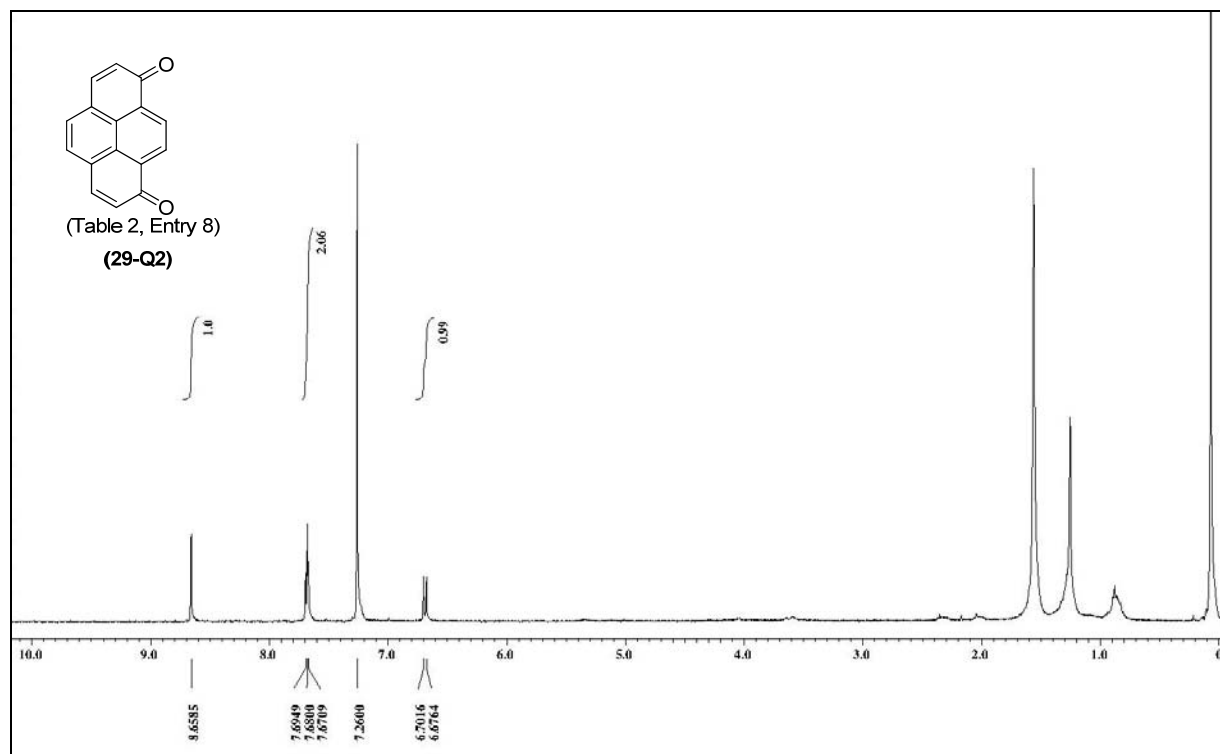


FIGURE S51. ^1H NMR spectrum of 1,8-diketopyrene in CDCl_3 .

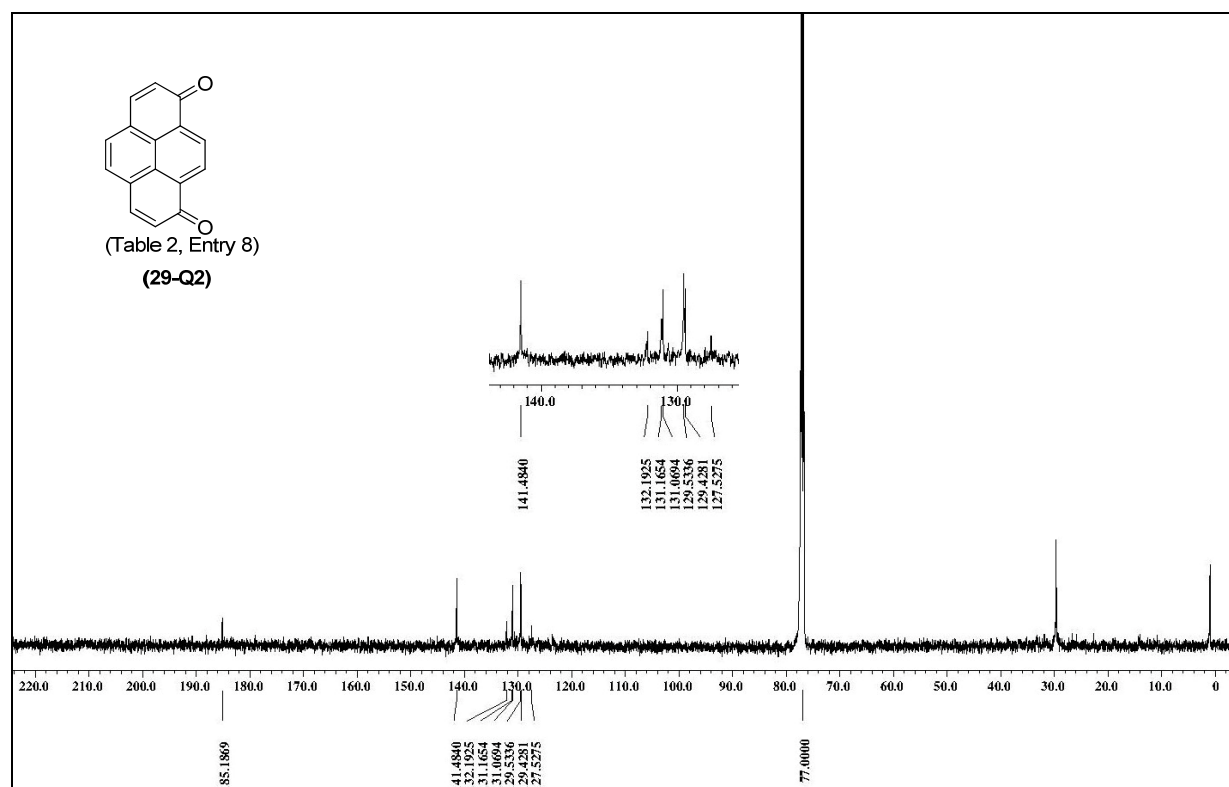


FIGURE S52. ^{13}C NMR spectrum of 1,8-diketopyrene in CDCl_3 .

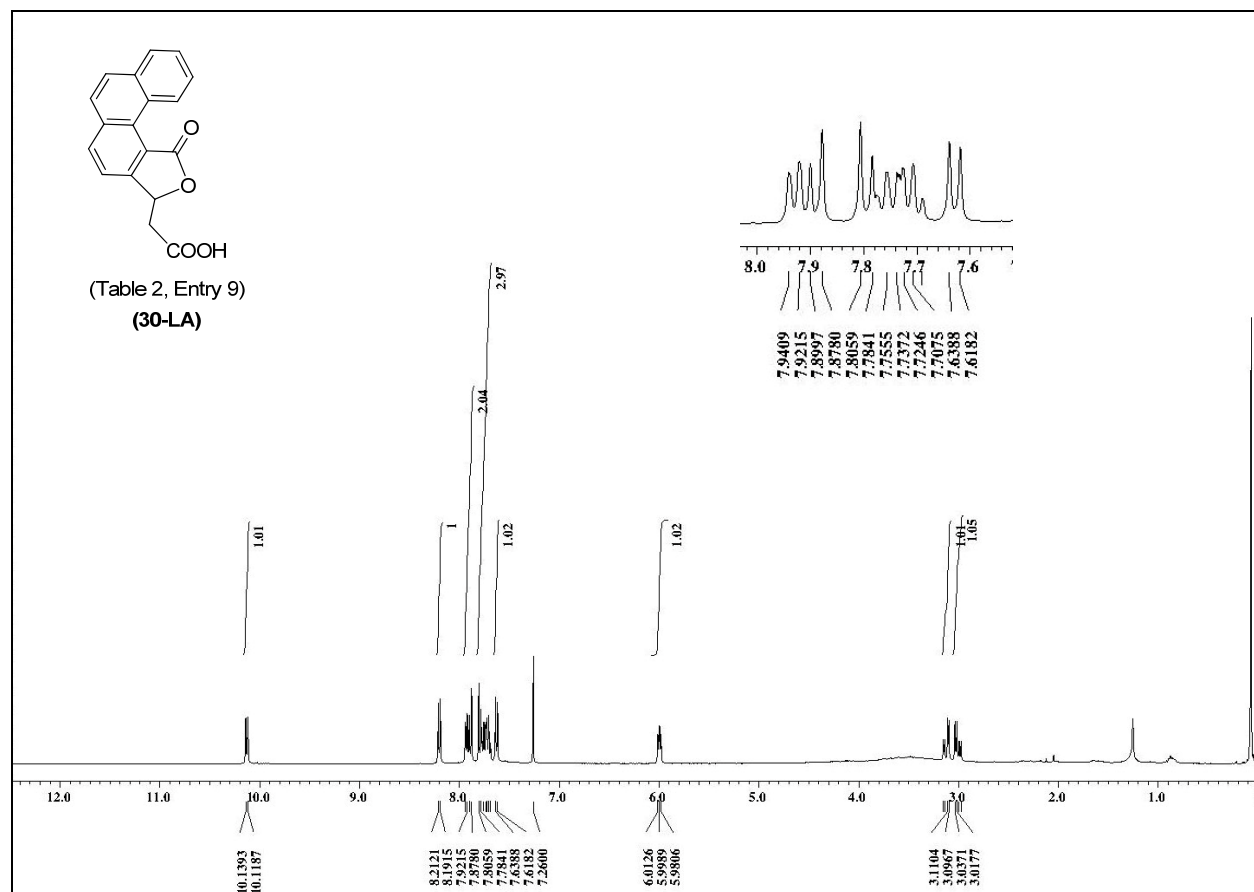
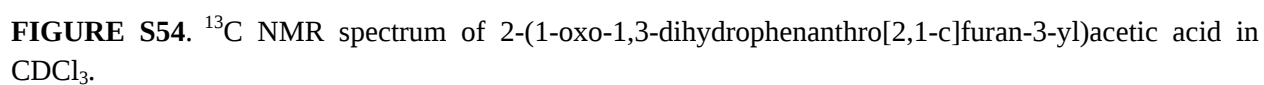


FIGURE S53. ¹H NMR spectrum of 2-(1-oxo-1,3-dihydrophenanthro[2,1-c]furan-3-yl)acetic acid in CDCl₃.



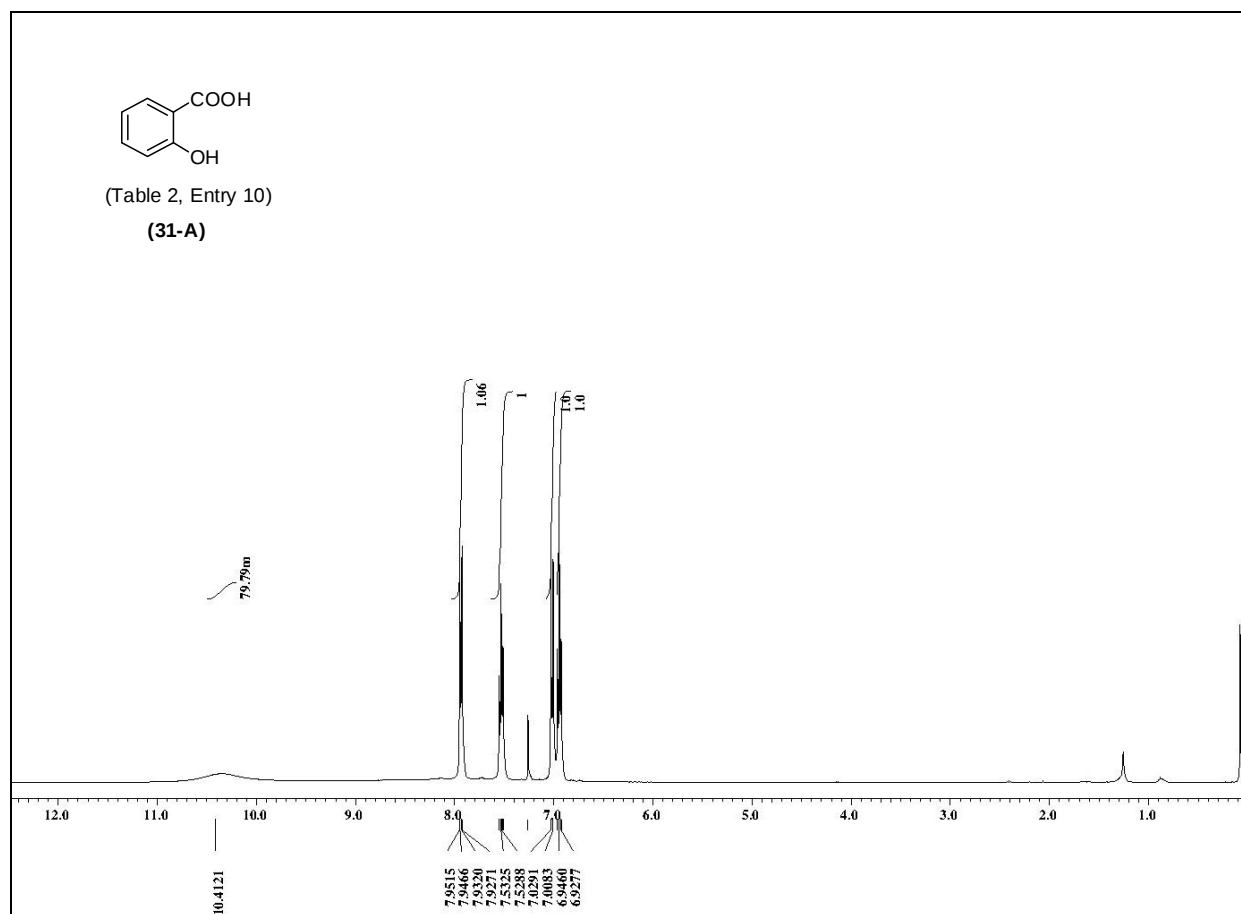


FIGURE S55. ^1H NMR spectrum of 2-hydroxybenzoic acid in CDCl_3 .

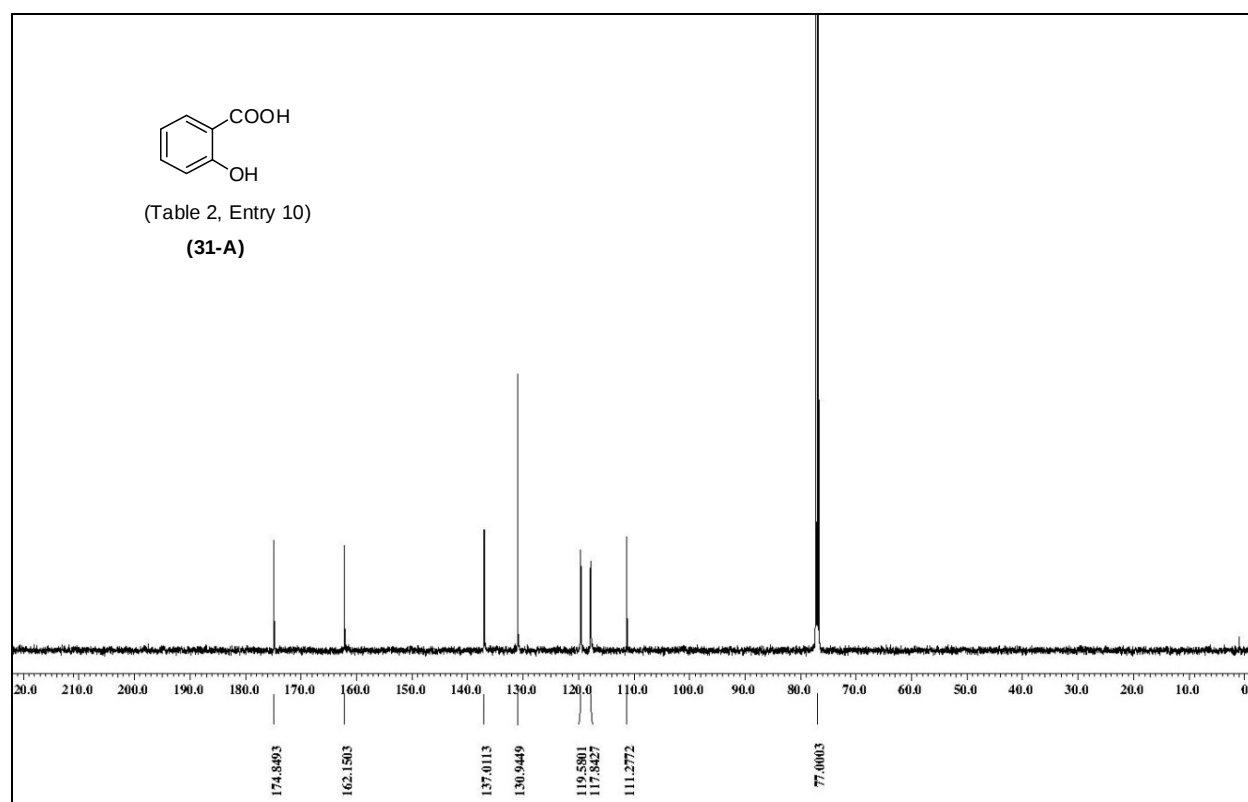


FIGURE S56. ¹³C NMR spectrum of 2-hydroxybenzoic acid in CDCl₃.

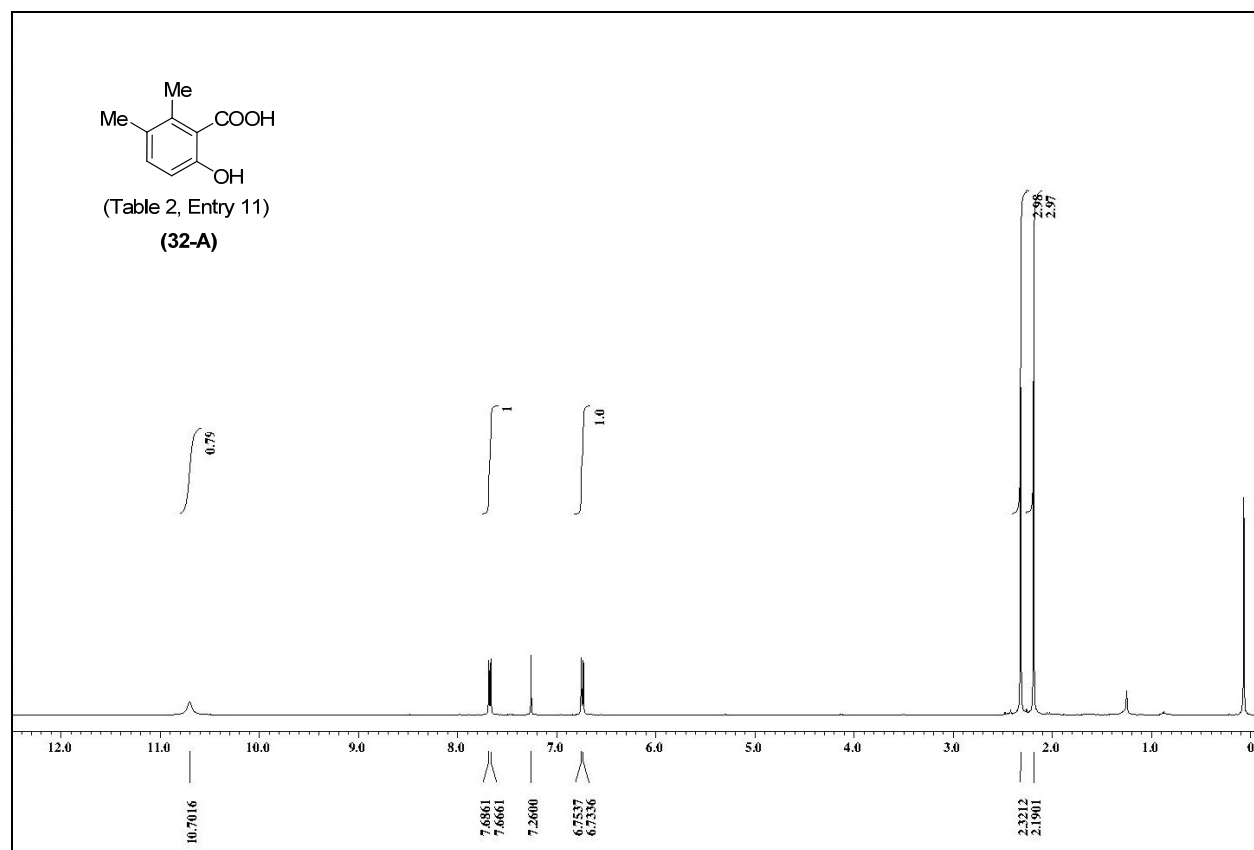


FIGURE S57. ^1H NMR spectrum of 5,6-dimethyl-2-hydroxybenzoic acid in CDCl_3 .

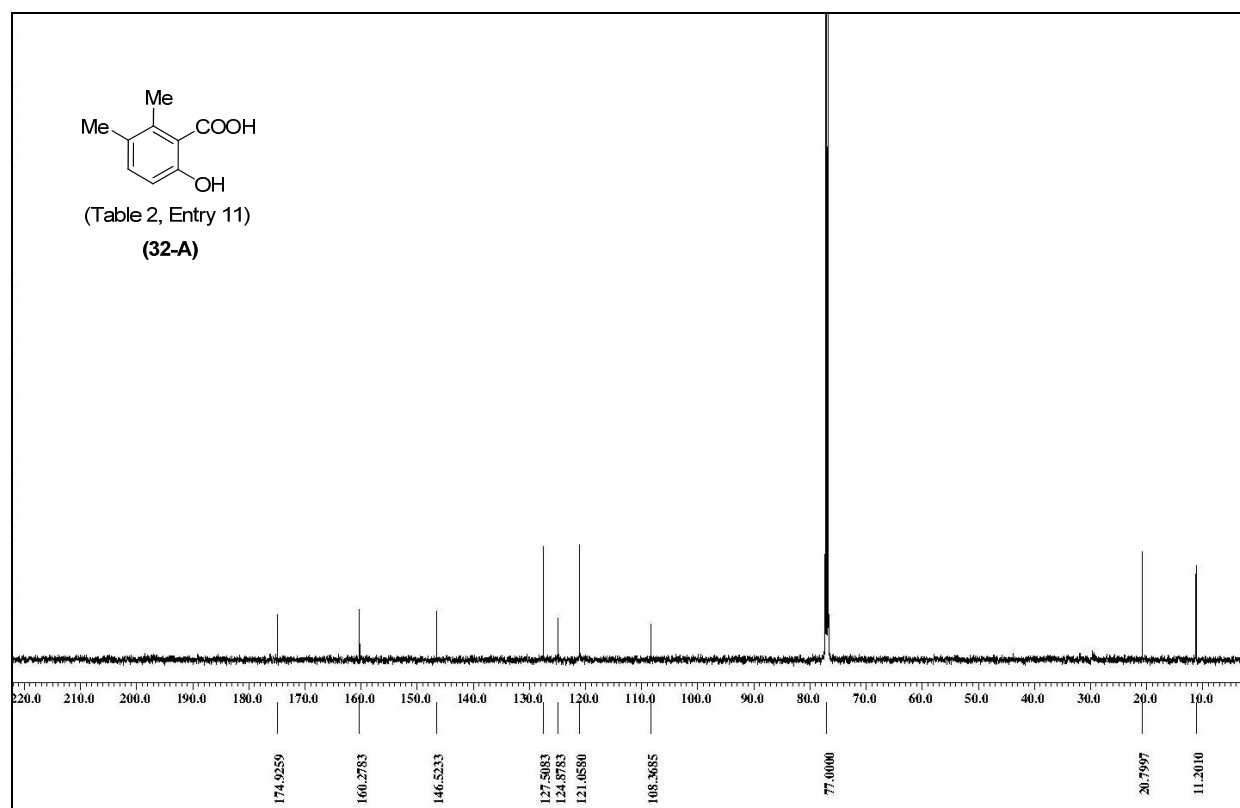


FIGURE S58. ^{13}C NMR spectrum of 5,6-dimethyl-2-hydroxybenzoic acid in CDCl_3 .

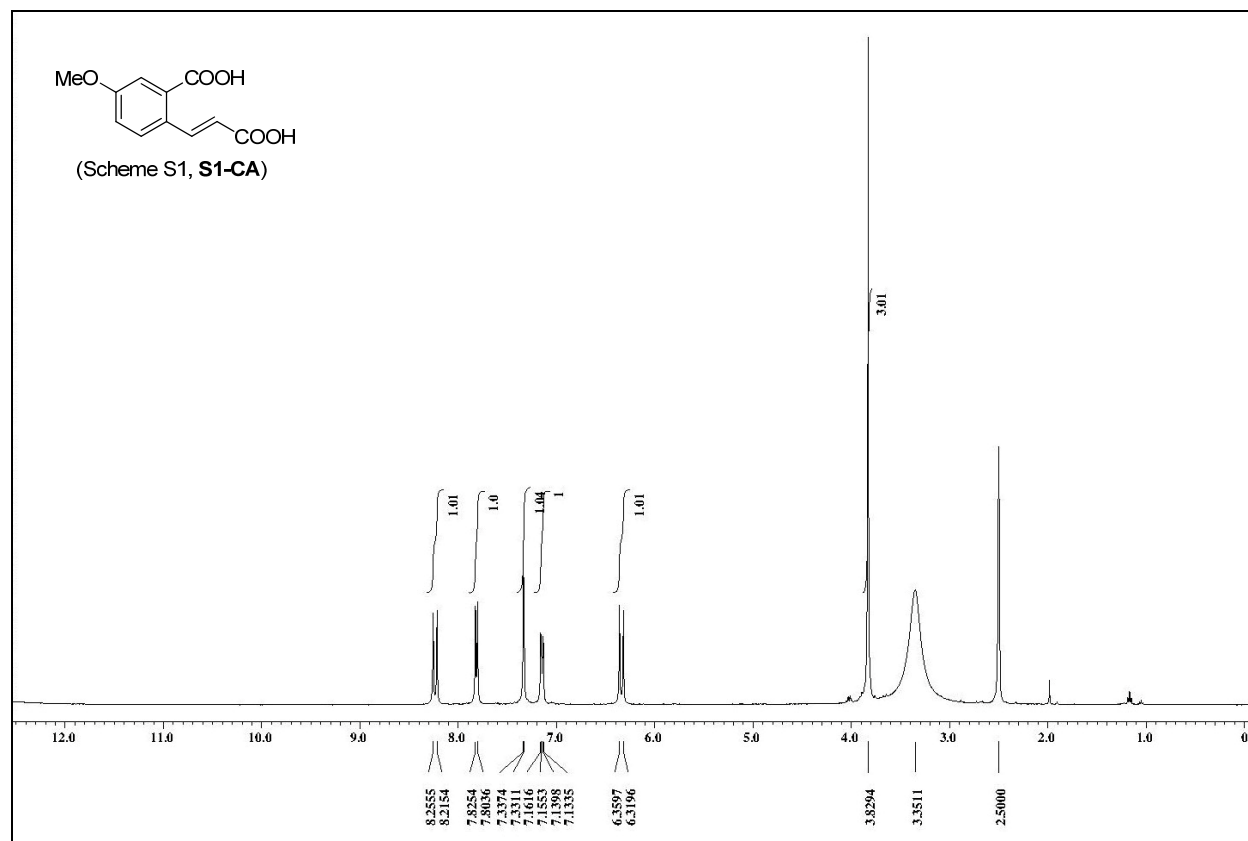


FIGURE S59. ¹H NMR spectrum of (*E*)-2-carboxy-4-methoxycinnamic acid in DMSO-*d*₆.

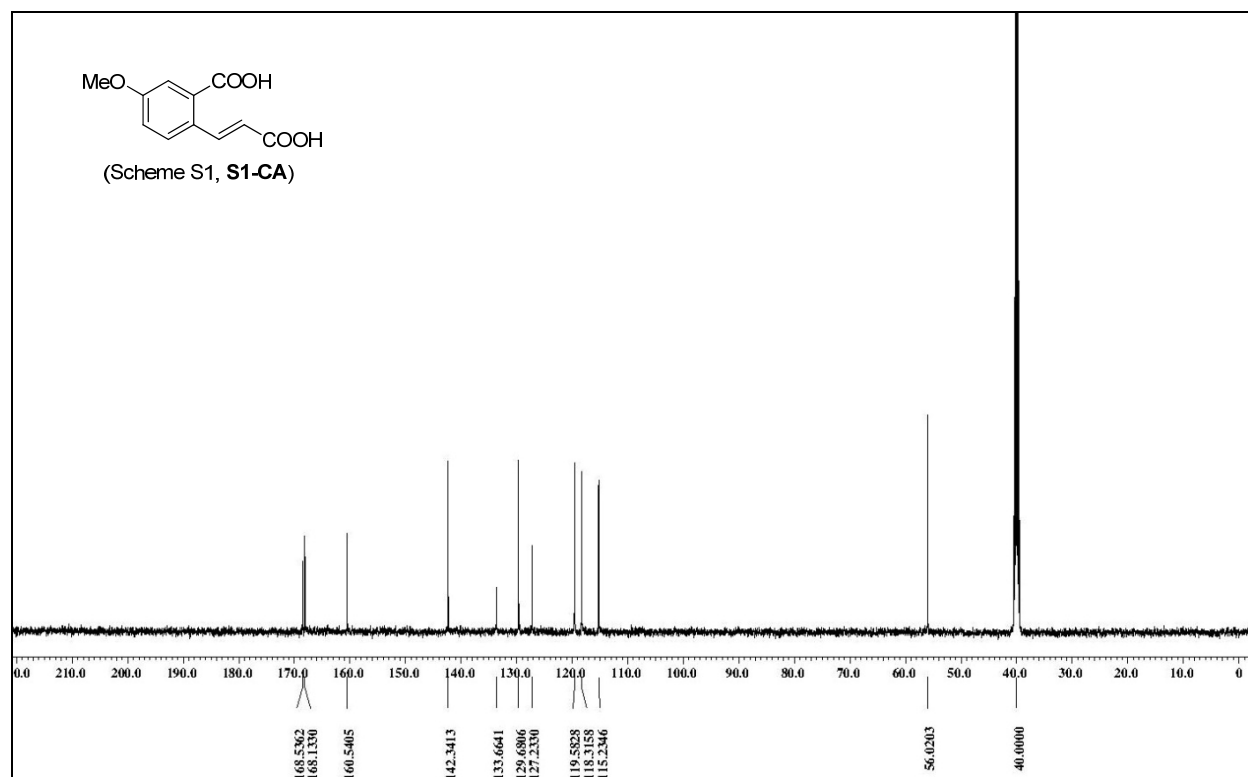


FIGURE S60. ¹³C NMR spectrum of (*E*)-2-carboxy-4-methoxycinnamic acid in DMSO-*d*₆.

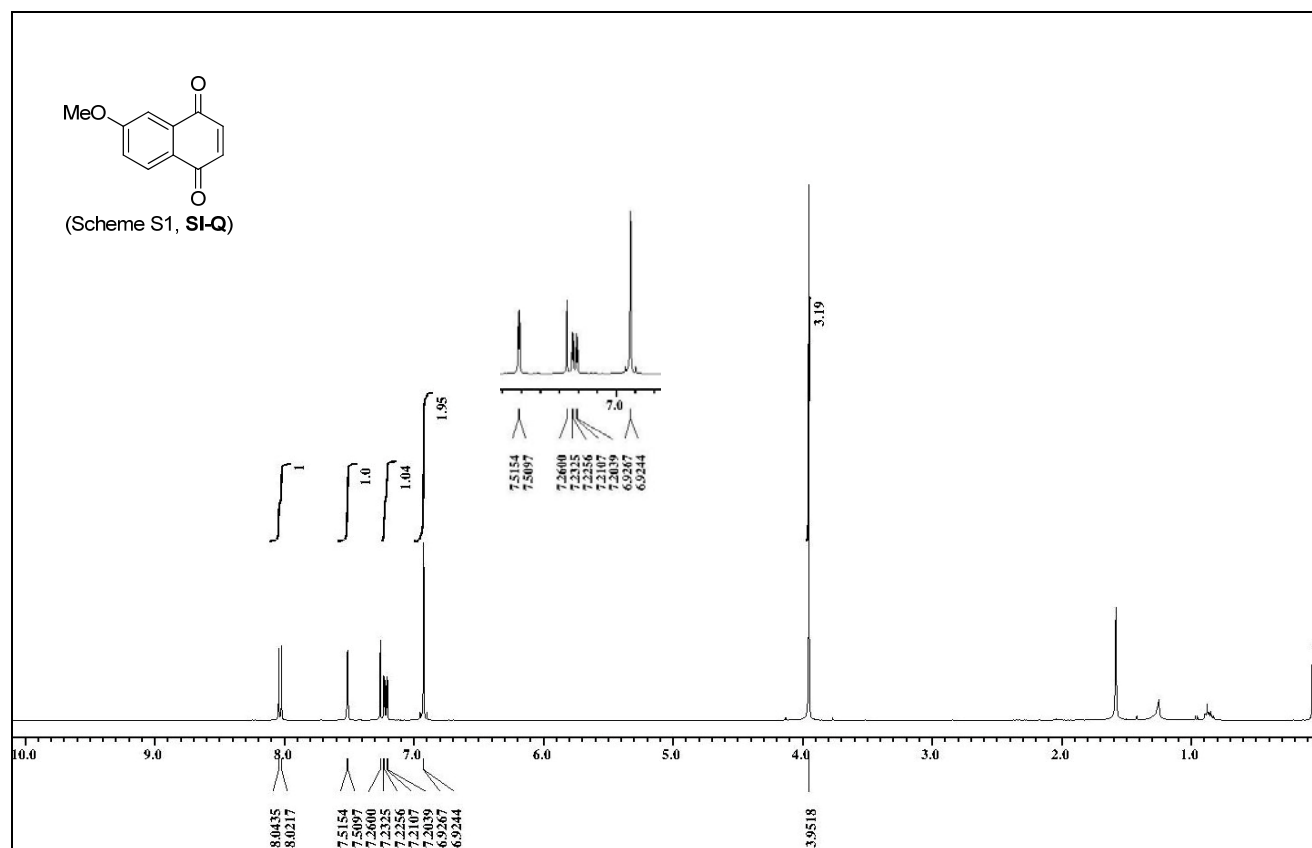


FIGURE 61. ^1H NMR spectrum of 6-methoxy-1,4-naphthoquinone in CDCl_3 .