SUPPORTING INFORMATION

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

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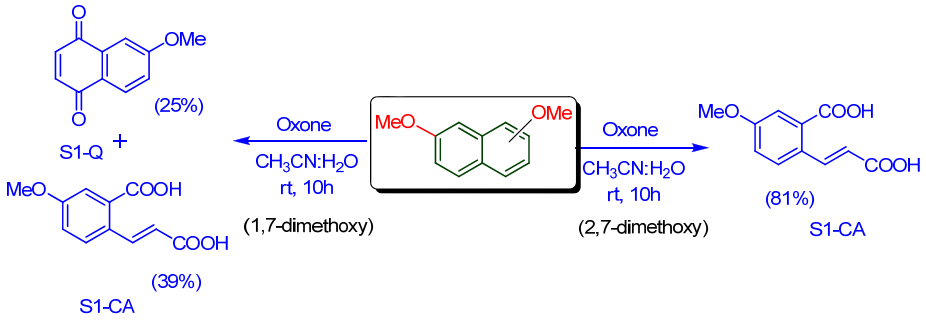
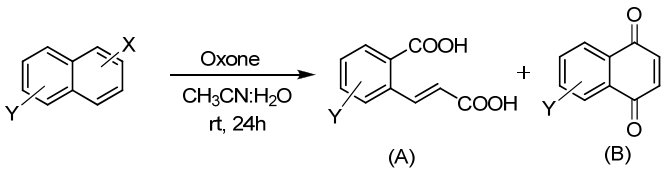
EXPERIMENTAL SECTION

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.



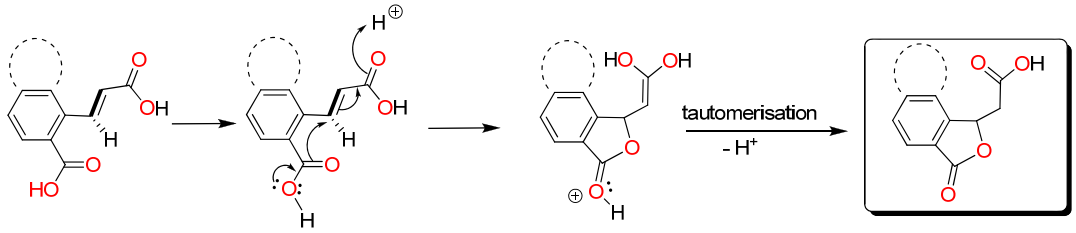
Scheme S2: Results of Oxidation of Methoxy-Naphthalenes with Oxone in $CH_3CN:H_2O$ at rt.



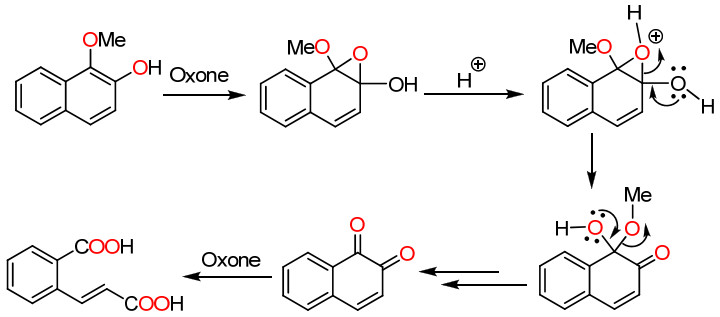
substrate		Oxone	time	yield (%)	
X	Y	(equiv.)	(h)	A	B
2-OMe	H	4	22	85	0
2-OMe	6-Br	4	24	44[a]	0
2-OMe	6-CO_2H	3	24	NR	0
1-OMe	H	4	23	64	14
1-OMe	4-CN	3	24	NR	0

[a] 50% conversion

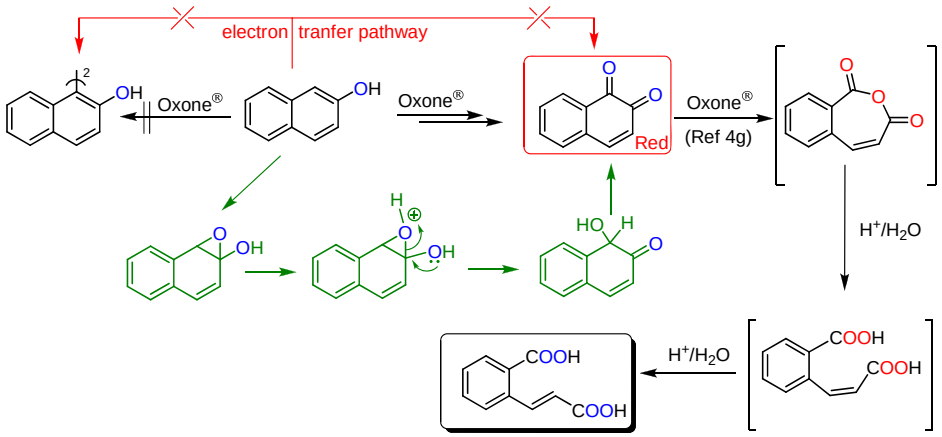
Scheme S3: Mechanism of 2-Carboxyarylacrylic Acid to Carboxymethyl Lactone.



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



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

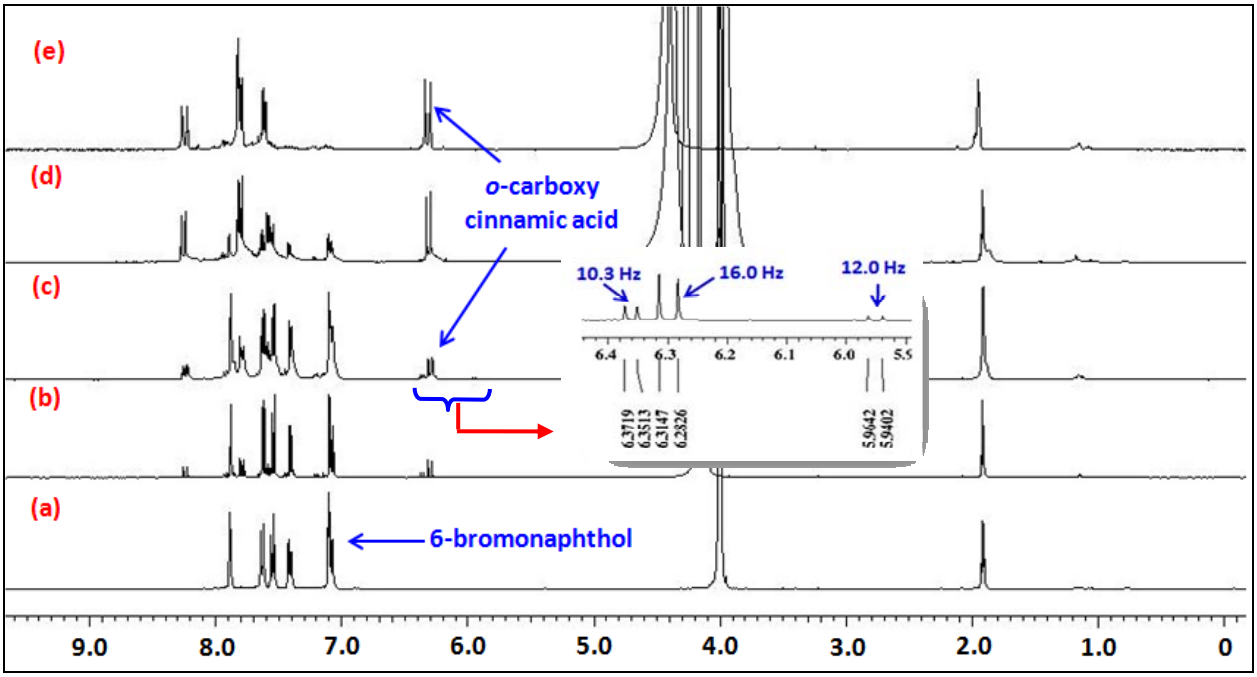


FIGURE S1. ^{1}H NMR Monitoring of oxidation of 6-bromonaphthol with Oxone (3 equiv) in CD_3CN-D_2O (1:1) at rt: (a) 0 h, before addition of Oxone, (b) after 2 h of addition of Oxone, (c) 4 h, (d) 6 h and (e) 12 h after addition of Oxone.

The doublet at δ 6.36 is attributed to *o*-quinone. The latter was isolated independently and its ^{1}H NMR spectrum recorded in a mixture of CD_3CN-D_2O (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.

^{1}H NMR Study: Influence of pH on *o*-Carboxycinnamic Acid in CD_3CN-D_2O at rt

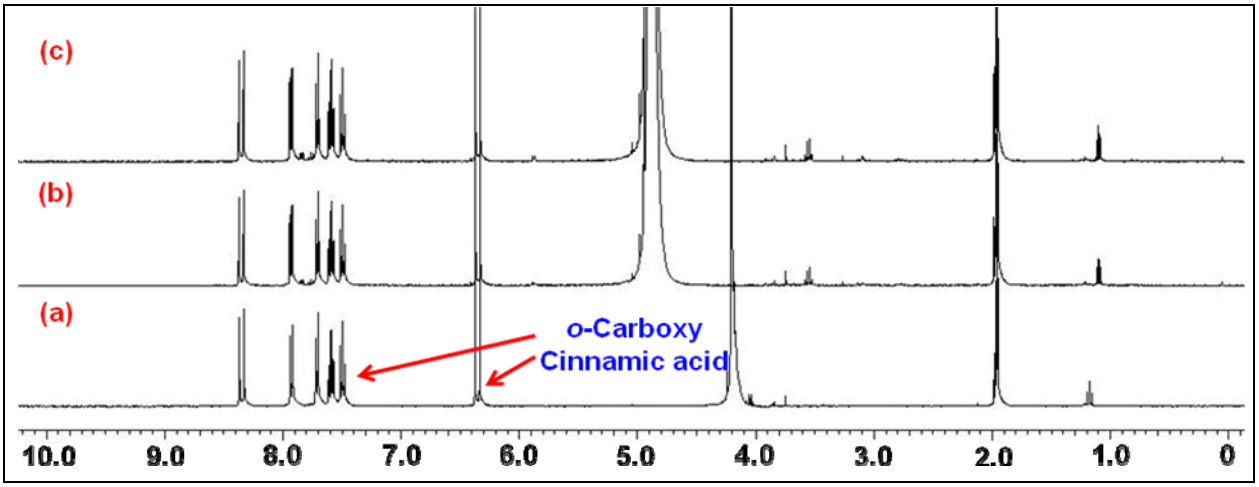
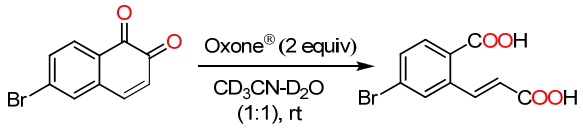


FIGURE S2. ^{1}H NMR Monitoring of oxidation of *E*-*o*-carboxycinnamic acid (5 mg, 0.026 mmol) with conc. H_2SO_4 (60 μL) in CD_3CN-D_2O (1:1)(500 μL) at rt: (a) 0 h, before addition of conc. H_2SO_4, (b) after 4 h of addition of conc. H_2SO_4, and (c) 8 h after addition of conc. H_2SO_4.

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

^{1}H NMR Monitoring of Oxidation of 6-Bromonaphthalene-1,2-dione with Oxone in CD_3CN-D_2O (1:1) at rt



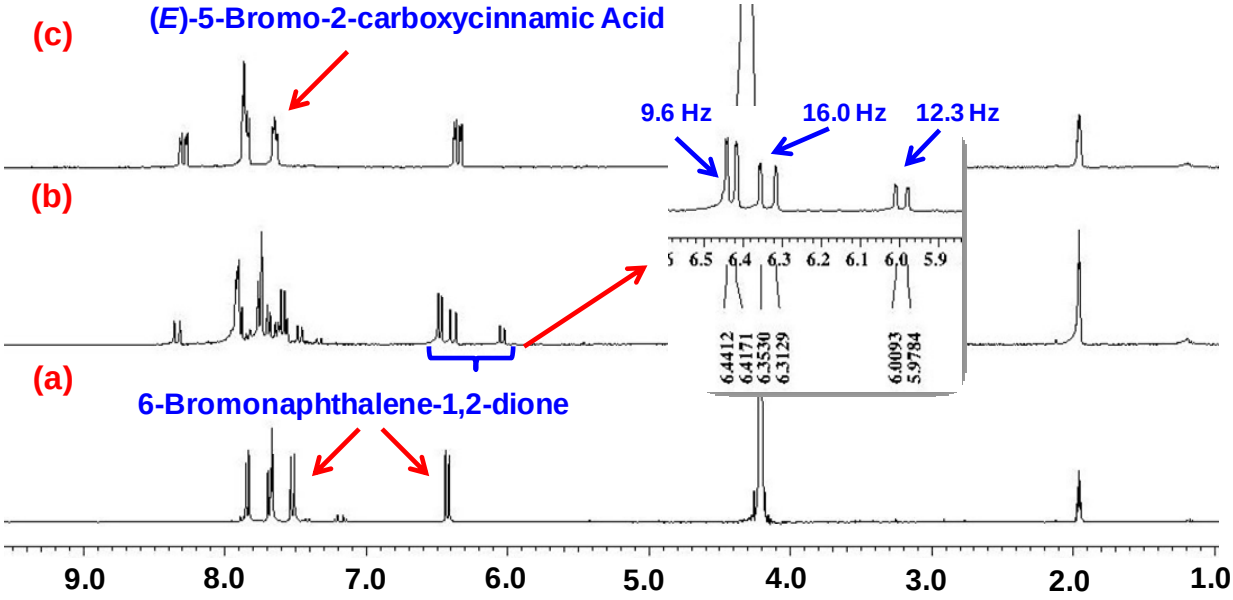


FIGURE S3. ^{1}H NMR Monitoring of the reaction of 6-bromonaphthalene-1,2-dione with Oxone in CD_3CN-D_2O (1:1). (a) Before addition of Oxone, 0 h; (b) 2 h after introduction of Oxone; (c) 8 h after introduction of Oxone.

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.

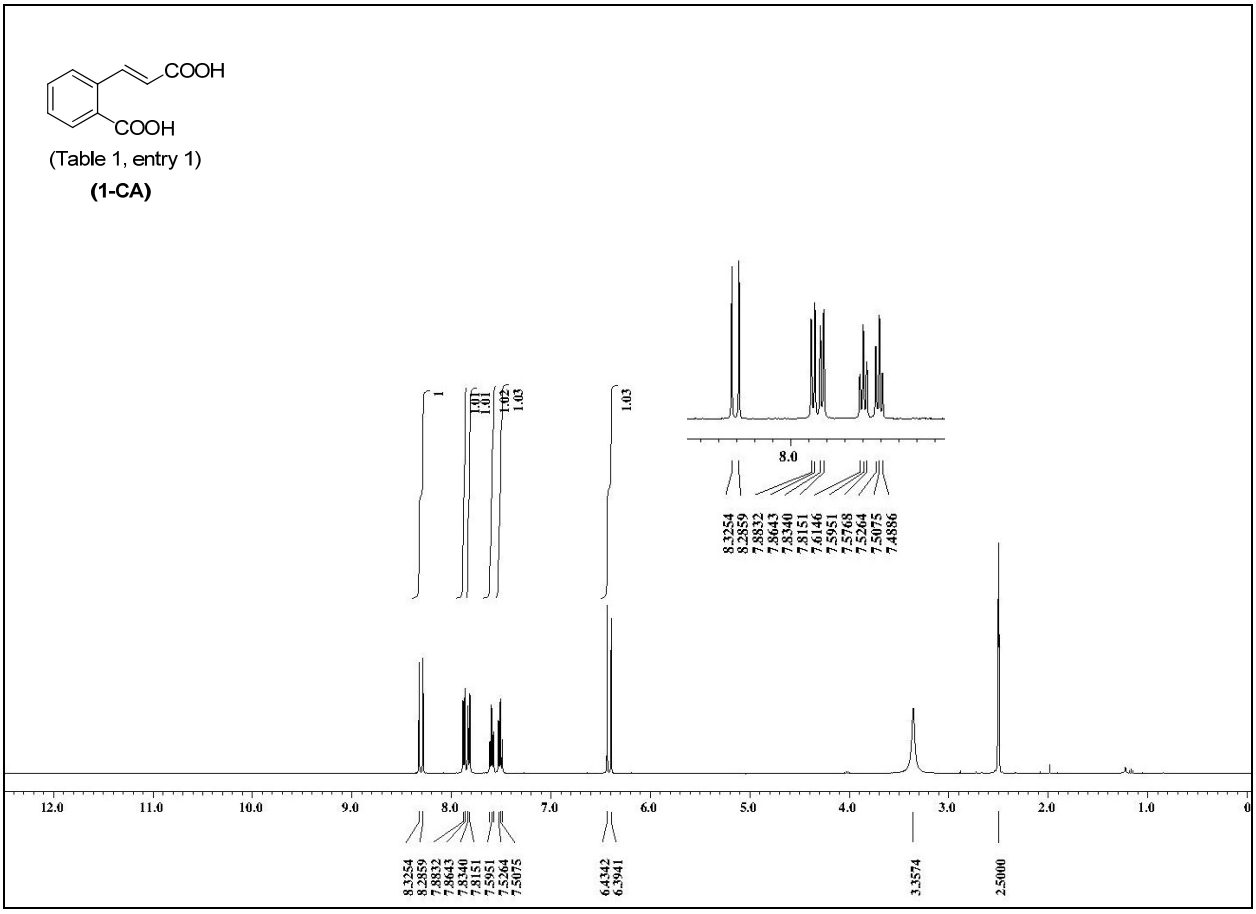


FIGURE S4. ^{1}H NMR spectrum of *(E)-o*-carboxycinnamic acid in DMSO-d_6.

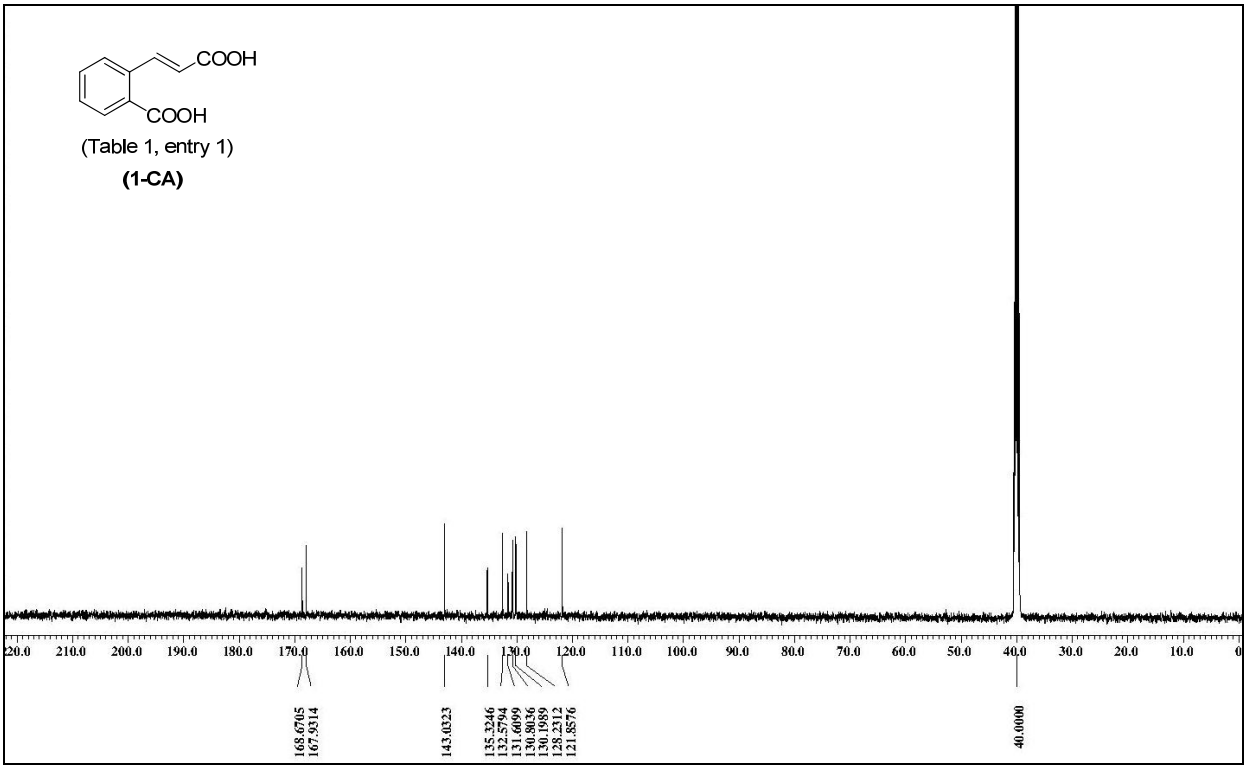


FIGURE S5. ^{13}C NMR spectrum of *(E)-o*-carboxycinnamic acid in DMSO-d_6.

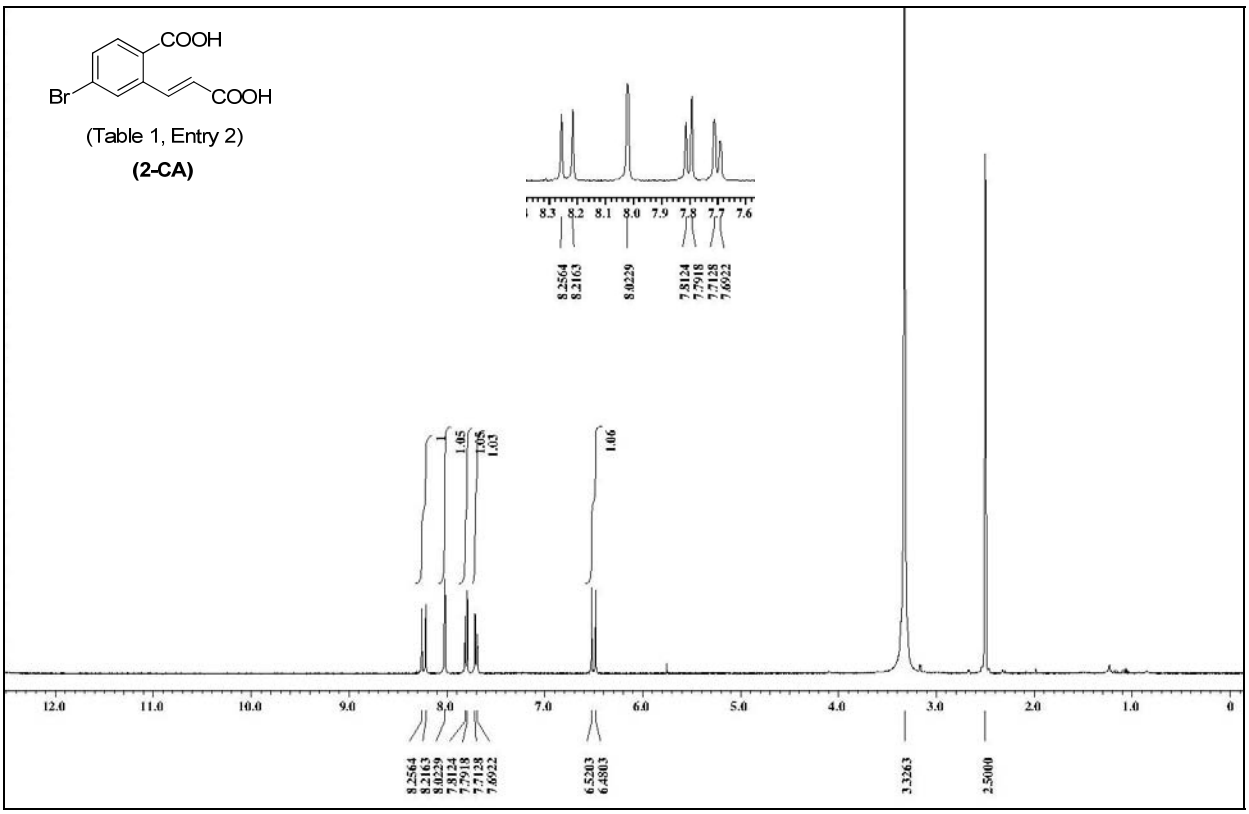


FIGURE S6. ^{1}H NMR spectrum of (*E*)-5-bromo-2-carboxycinnamic acid in DMSO-d_6.

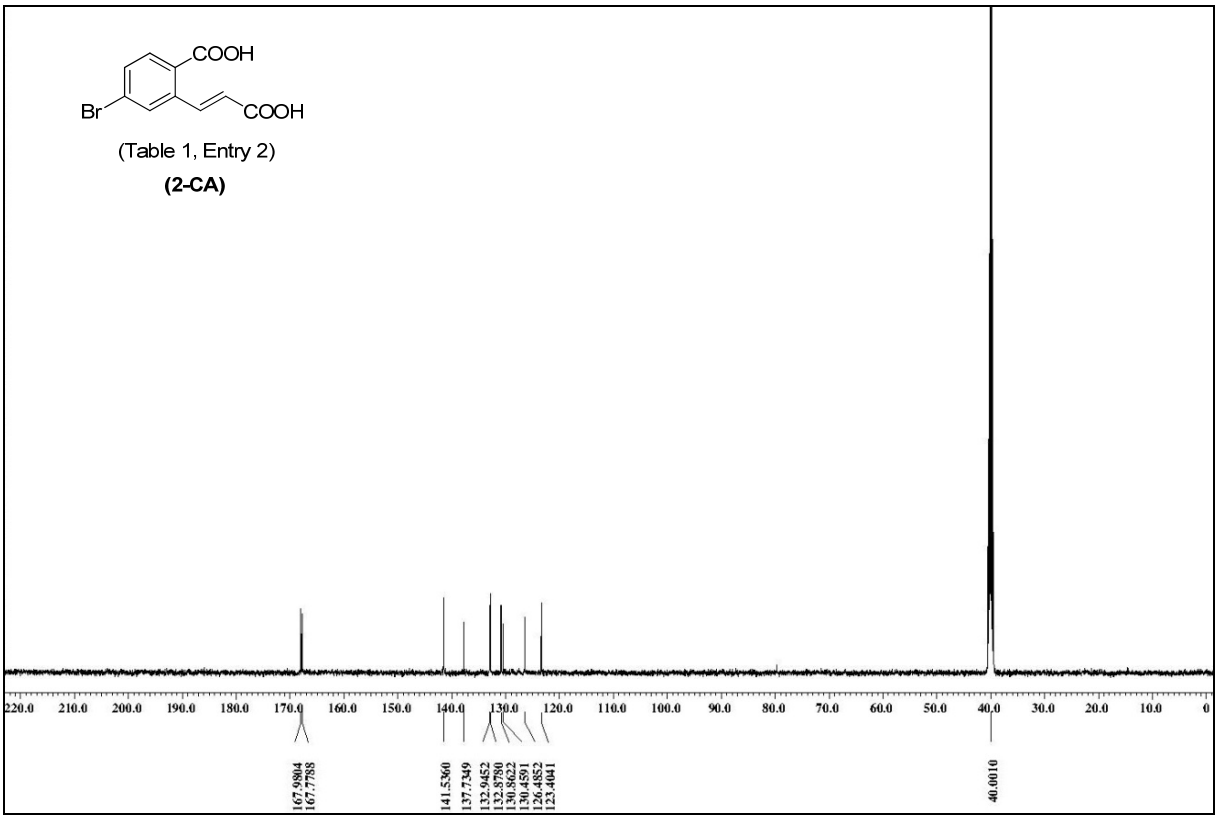


FIGURE S7. ^{13}C NMR spectrum of (*E*)-5-bromo-2-carboxycinnamic acid in DMSO-d_6.

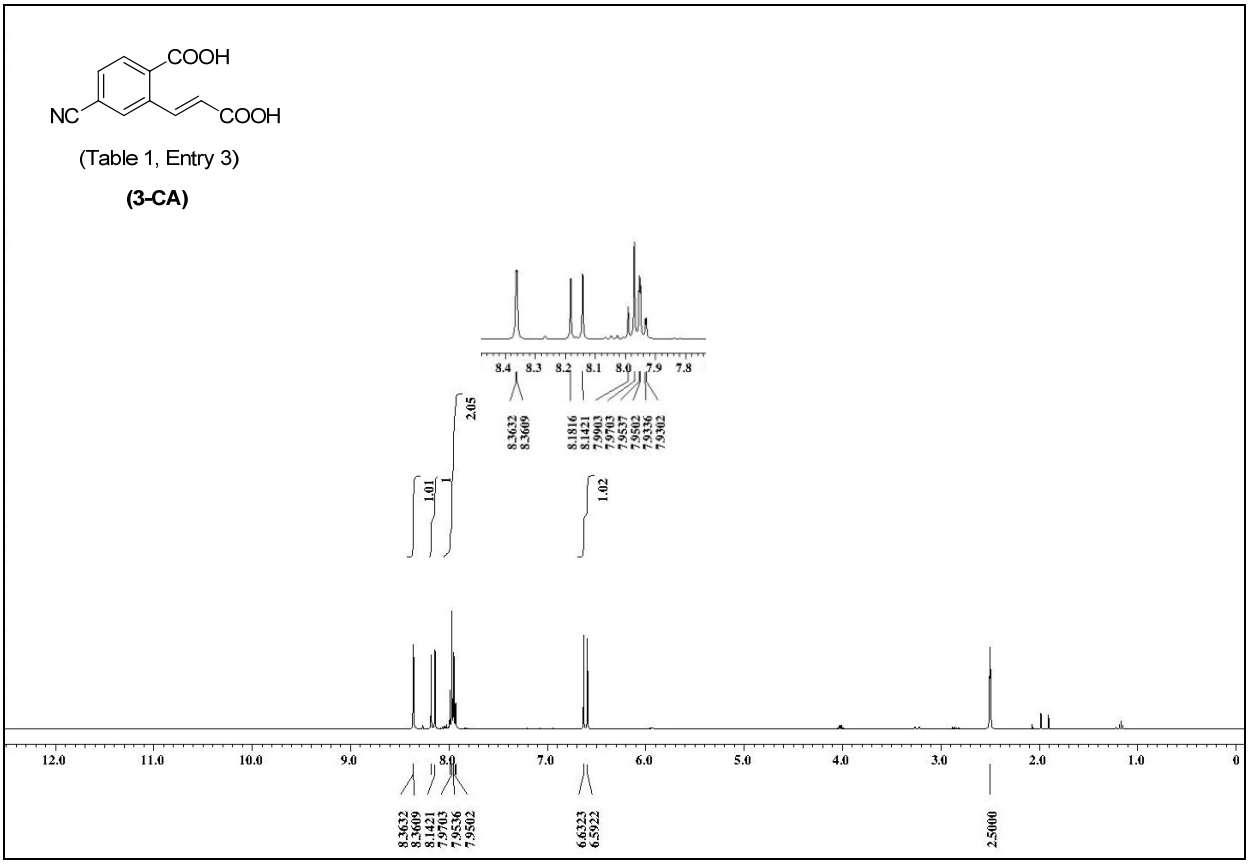


FIGURE S8. ^{1}H NMR spectrum of (*E*)-2-carboxy-5-cyanocinnamic acid in DMSO-d_6.

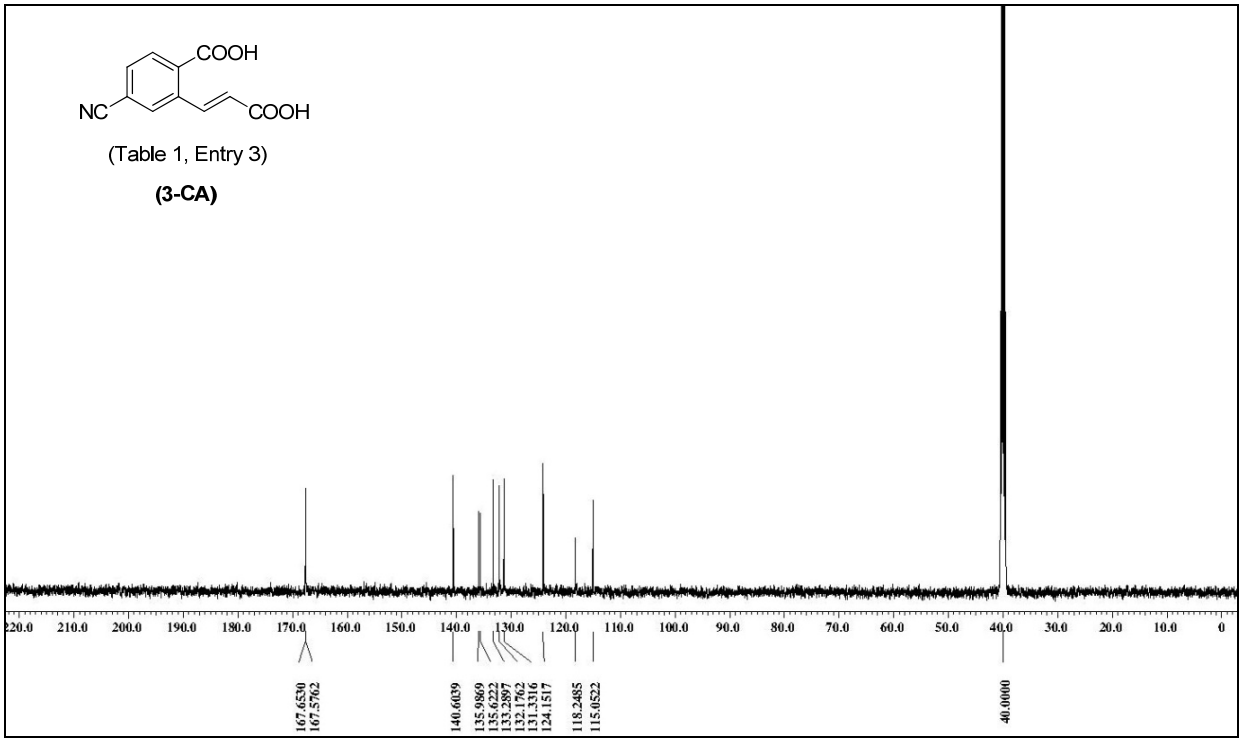


FIGURE S9. ^{13}C NMR spectrum of (*E*)-2-carboxy-5-cyanocinnamic acid in DMSO-d_6.

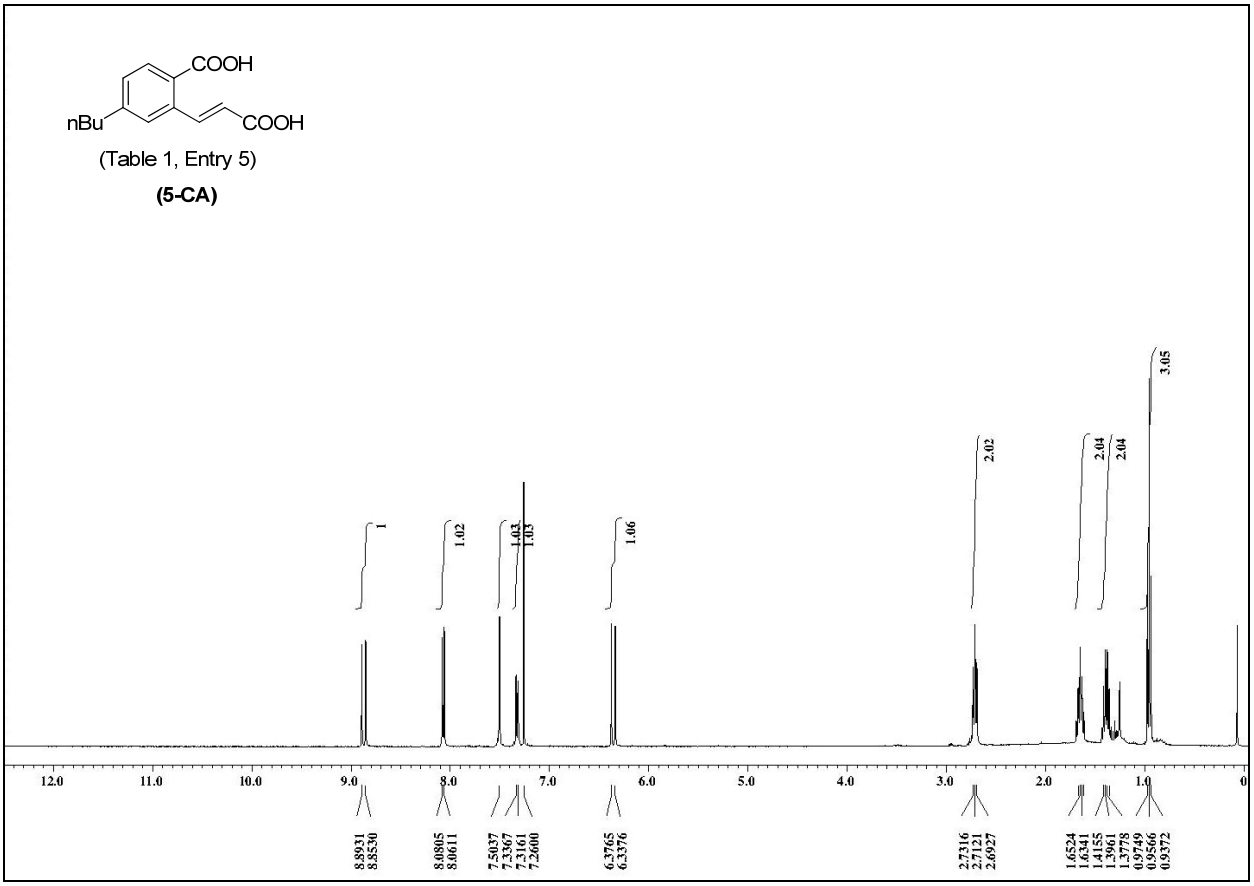


FIGURE S10. ^{1}H NMR spectrum of (*E*)-5-n-butyl-2-carboxycinnamic acid in $CDCl_3$.

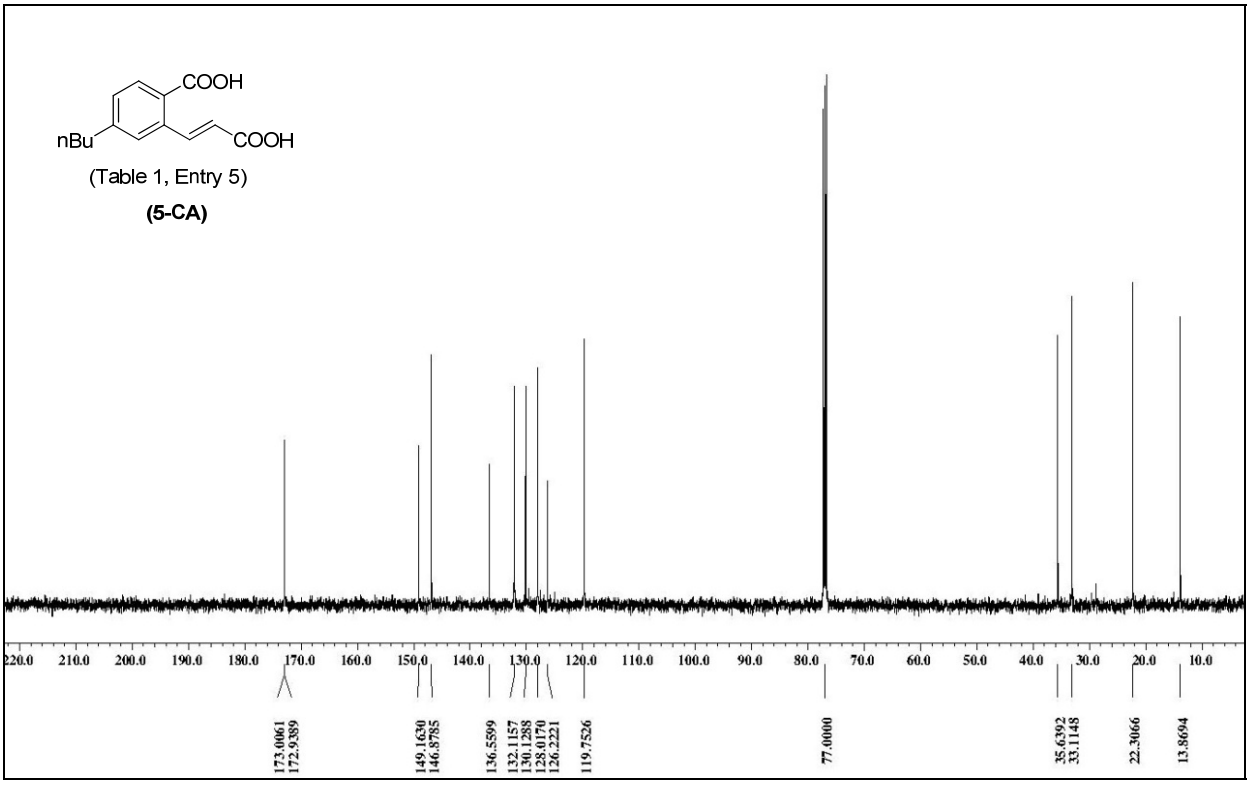


FIGURE S11. ^{13}C NMR spectrum of (*E*)-5-n-butyl-2-carboxycinnamic acid in $CDCl_3$.

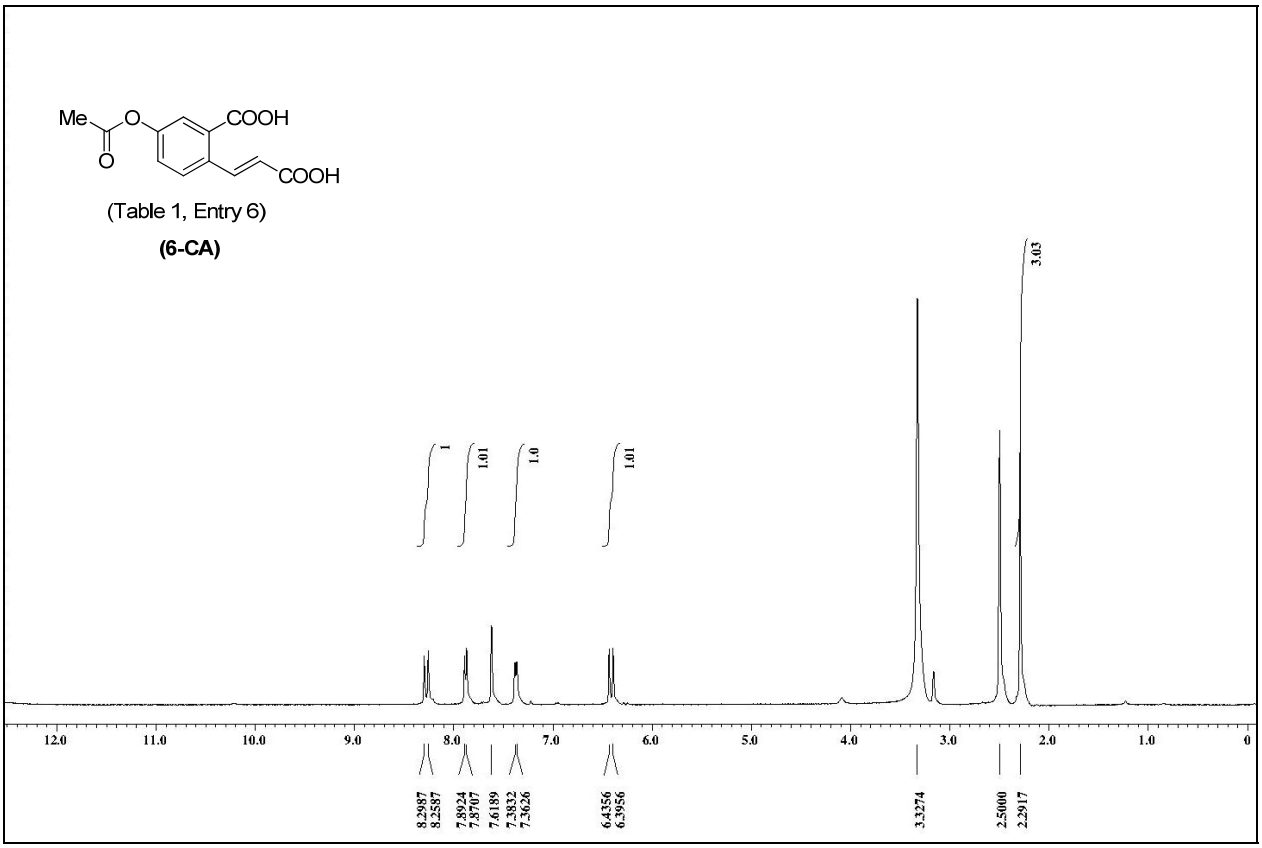


FIGURE S12. ^{1}H NMR spectrum of (*E*)-4-acetoxy-2-carboxycinnamic acid in DMSO-d_6.

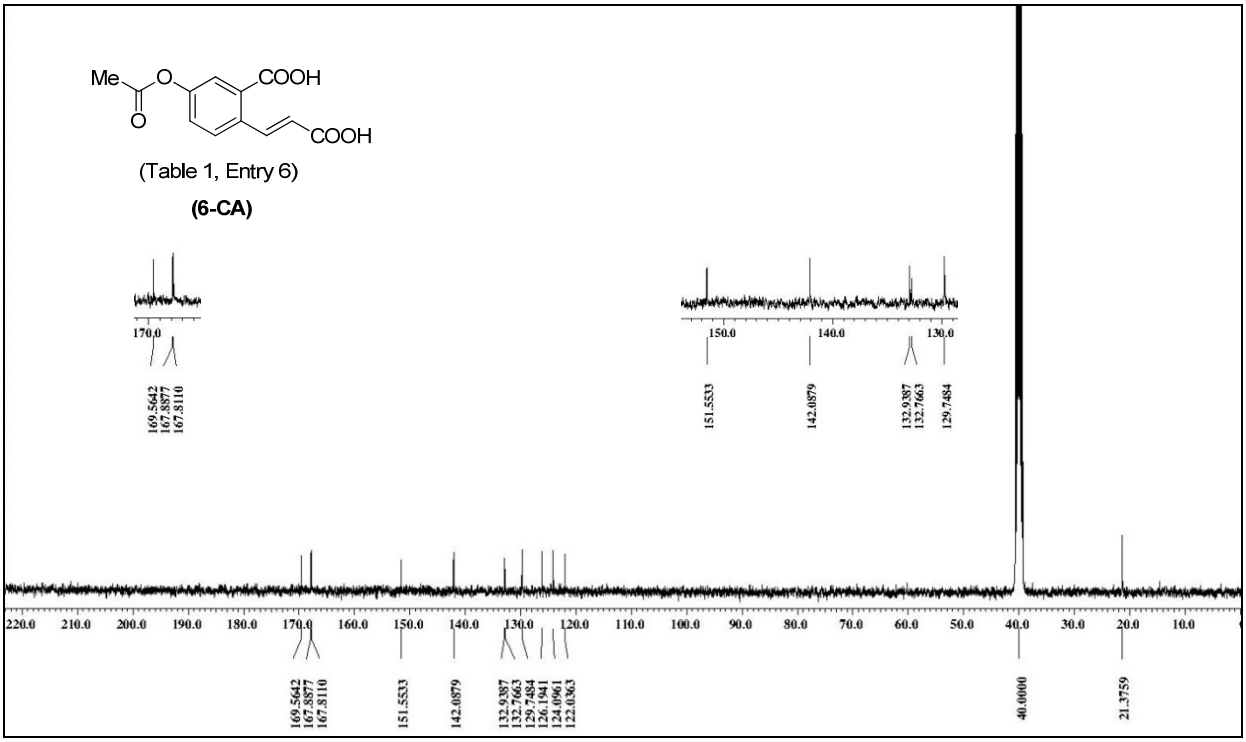


FIGURE S13. ^{13}C NMR spectrum of (*E*)-4-acetoxy-2-carboxycinnamic acid in DMSO-d_6.

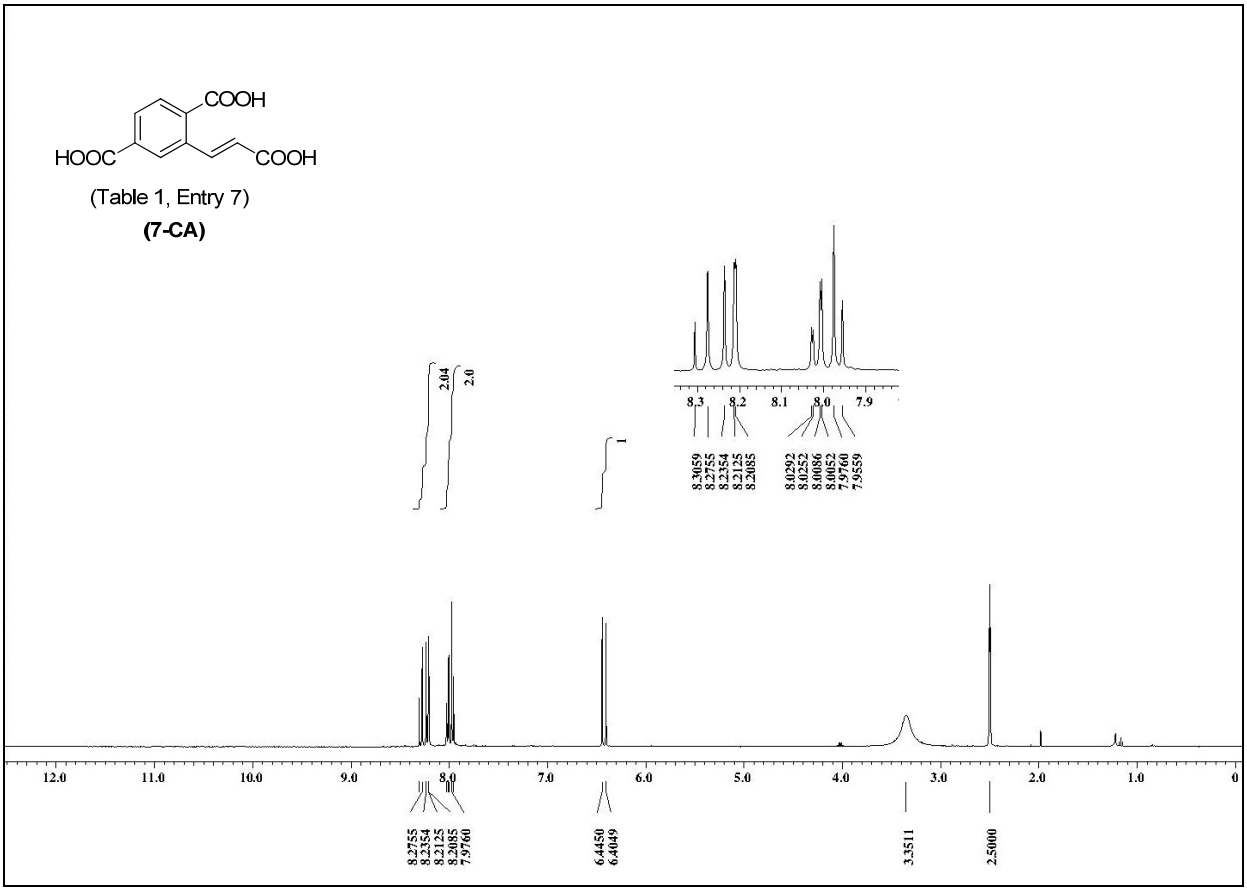


FIGURE S14. ^{1}H NMR spectrum of (*E*)-2,5-dicarboxycinamic acid in DMSO-d_6.

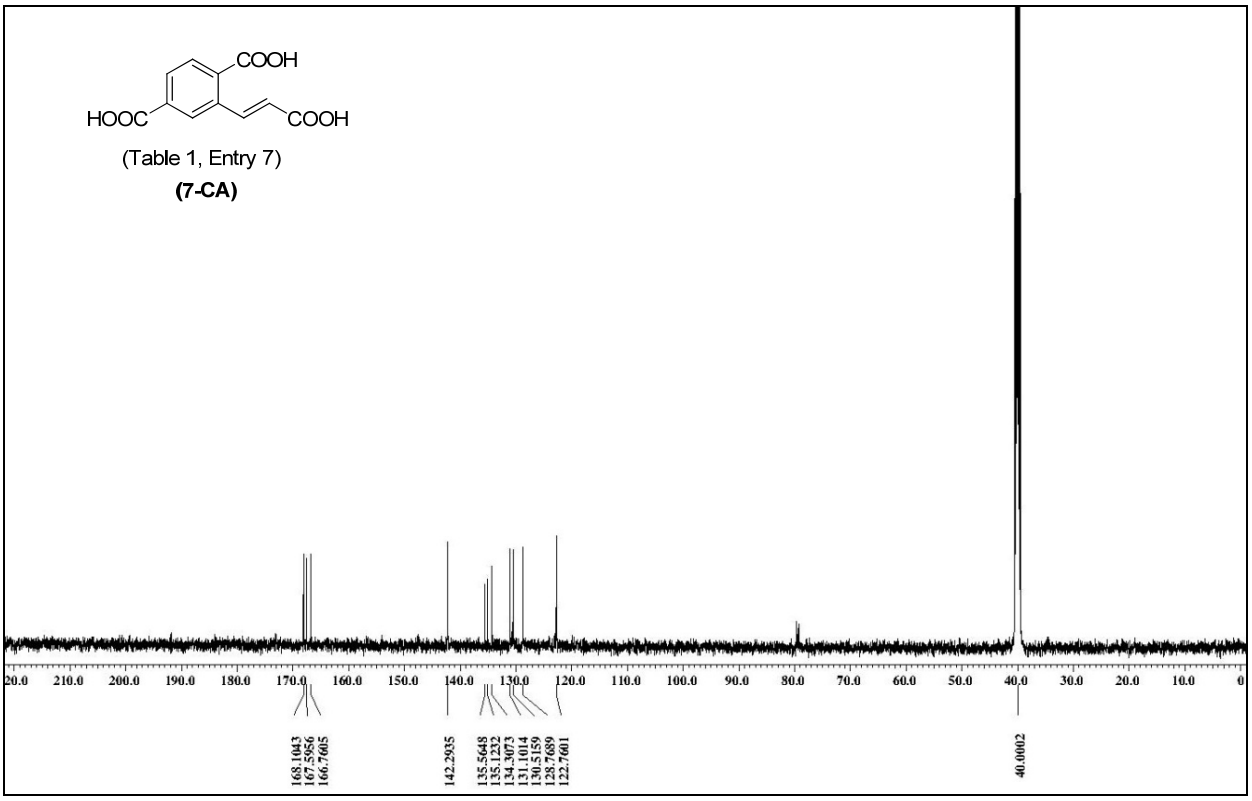


FIGURE S15. ^{13}C NMR spectrum of (*E*)-2,5-dicarboxycinamic acid in DMSO-d_6.

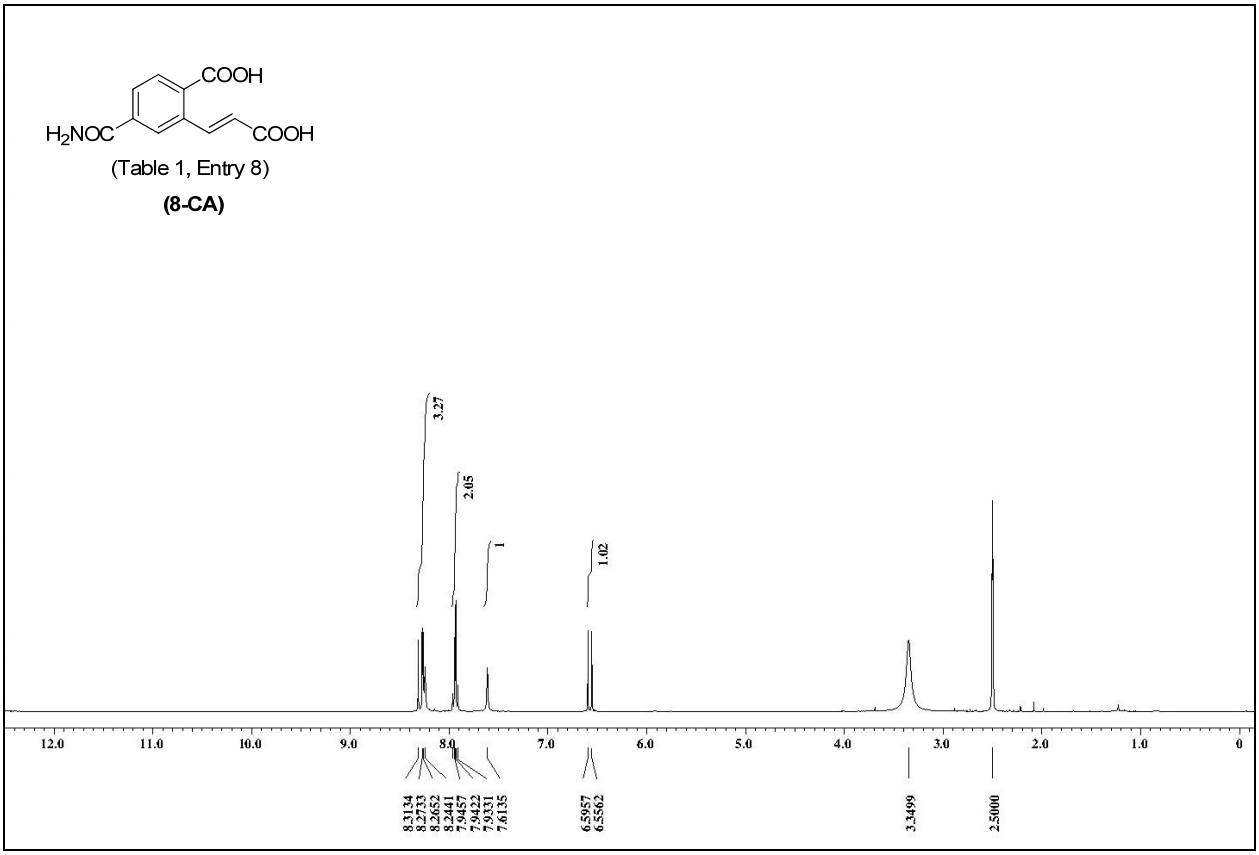


FIGURE S16. ^{1}H NMR spectrum of (*E*)-5-amido-2-carboxycinnamic acid in DMSO-d_6.

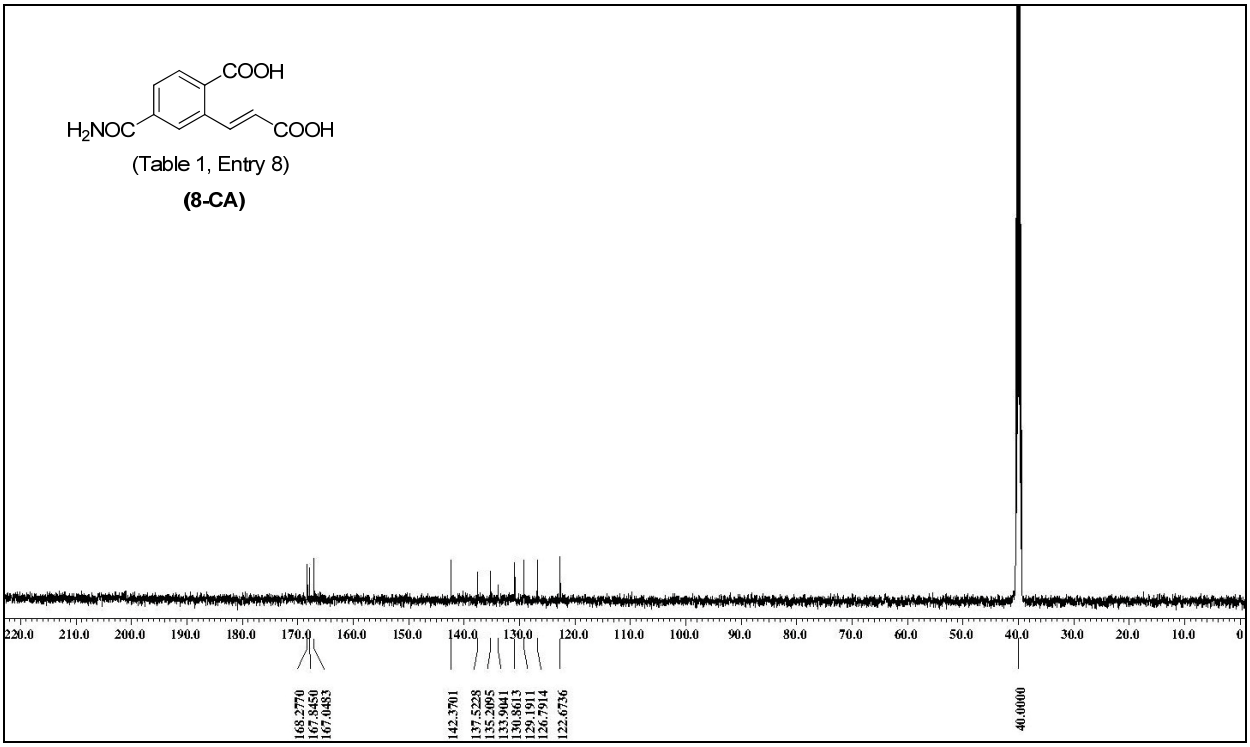


FIGURE S17. ^{13}C NMR spectrum of (*E*)-5-amido-2-carboxycinnamic acid in DMSO-d_6.

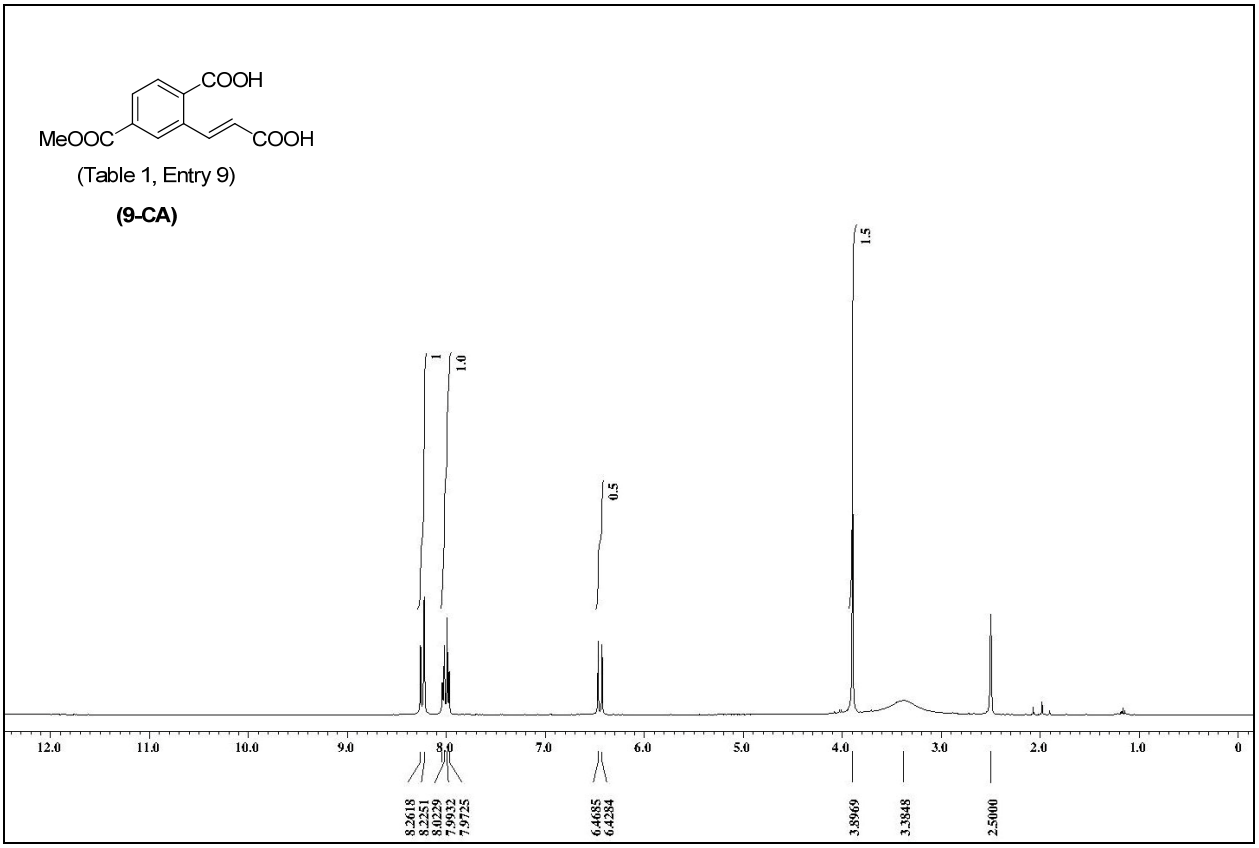


FIGURE S18. ^{1}H NMR spectrum of (*E*)-5-carbomethoxy-2-carboxycinamic acid in DMSO-d_6.

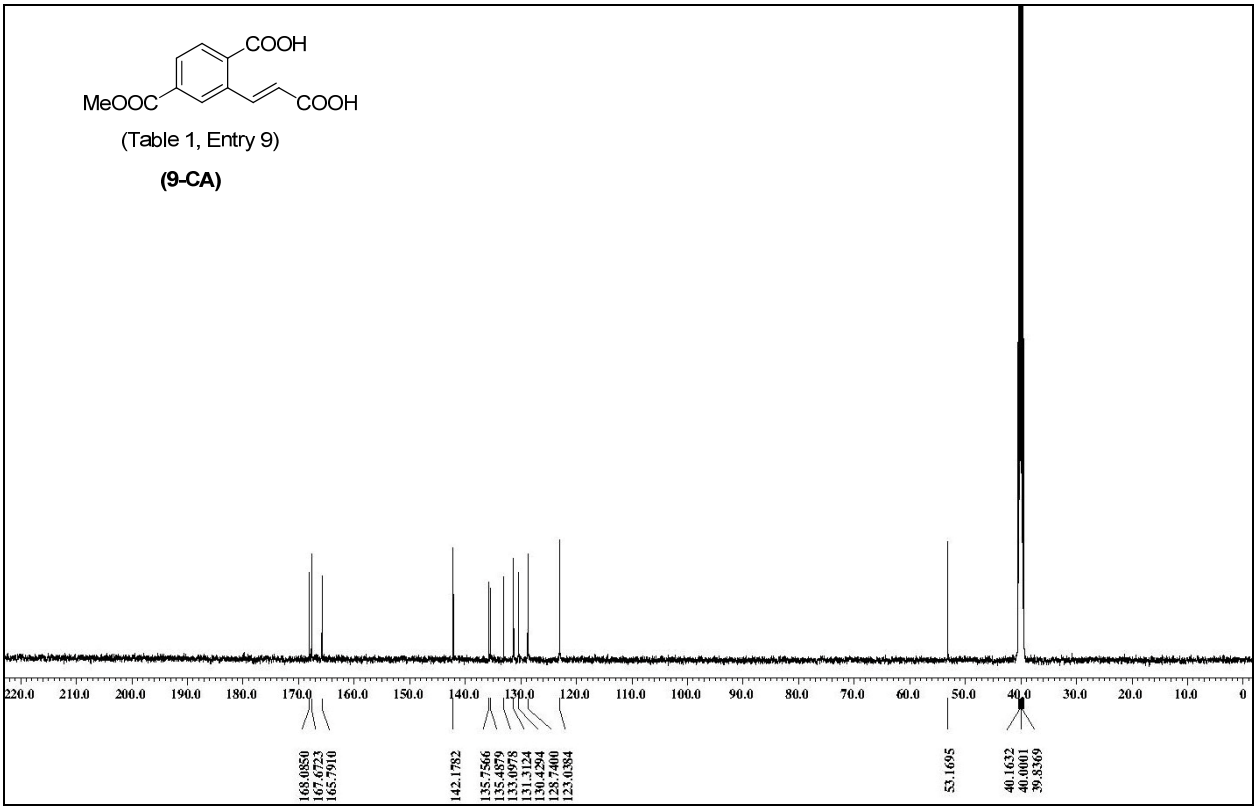


FIGURE S19. ^{13}C NMR spectrum of (*E*)-5-carbomethoxy-2-carboxycinamic acid in DMSO-d_6.

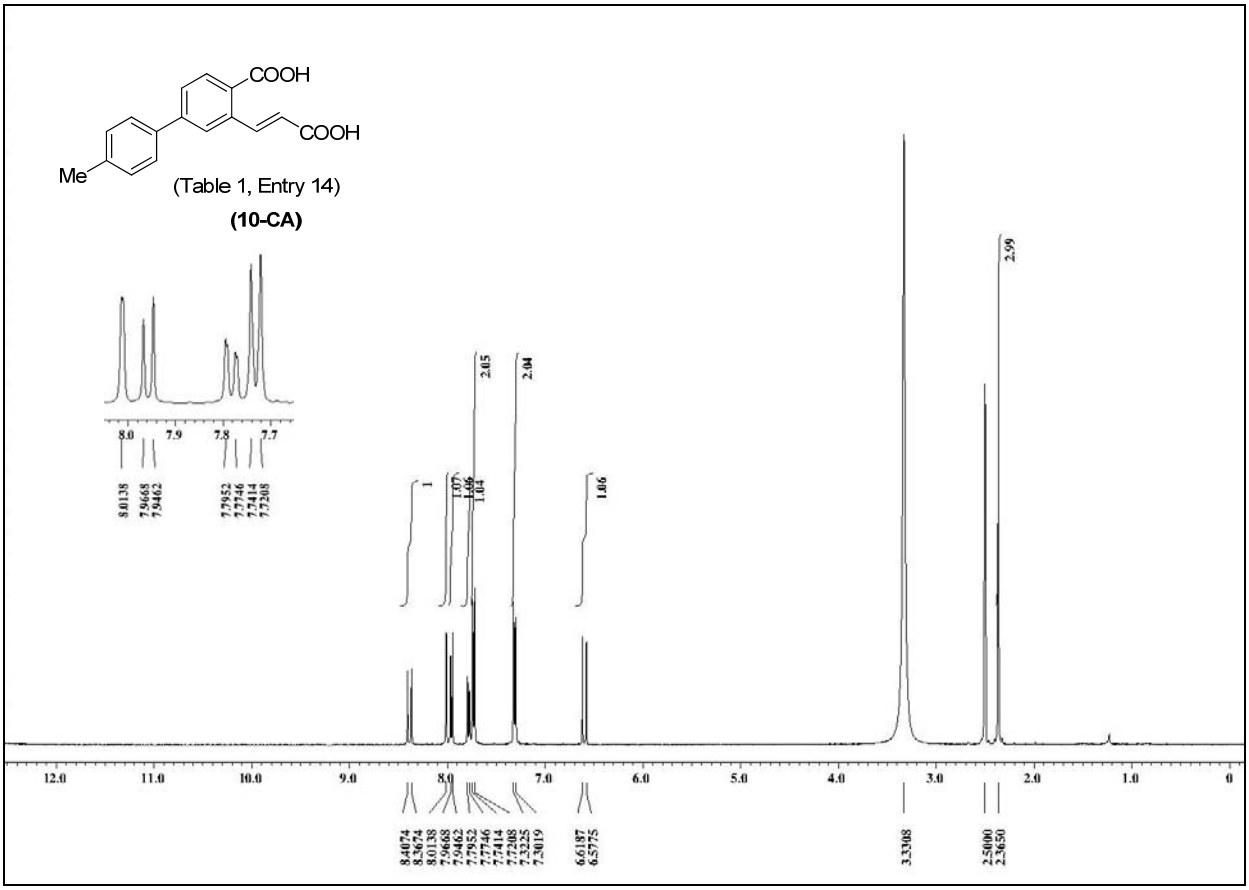


FIGURE S20. ^{1}H NMR spectrum of (*E*)-2-carboxy-5-(4-tolyl)cinnamic acid in DMSO-d_6.

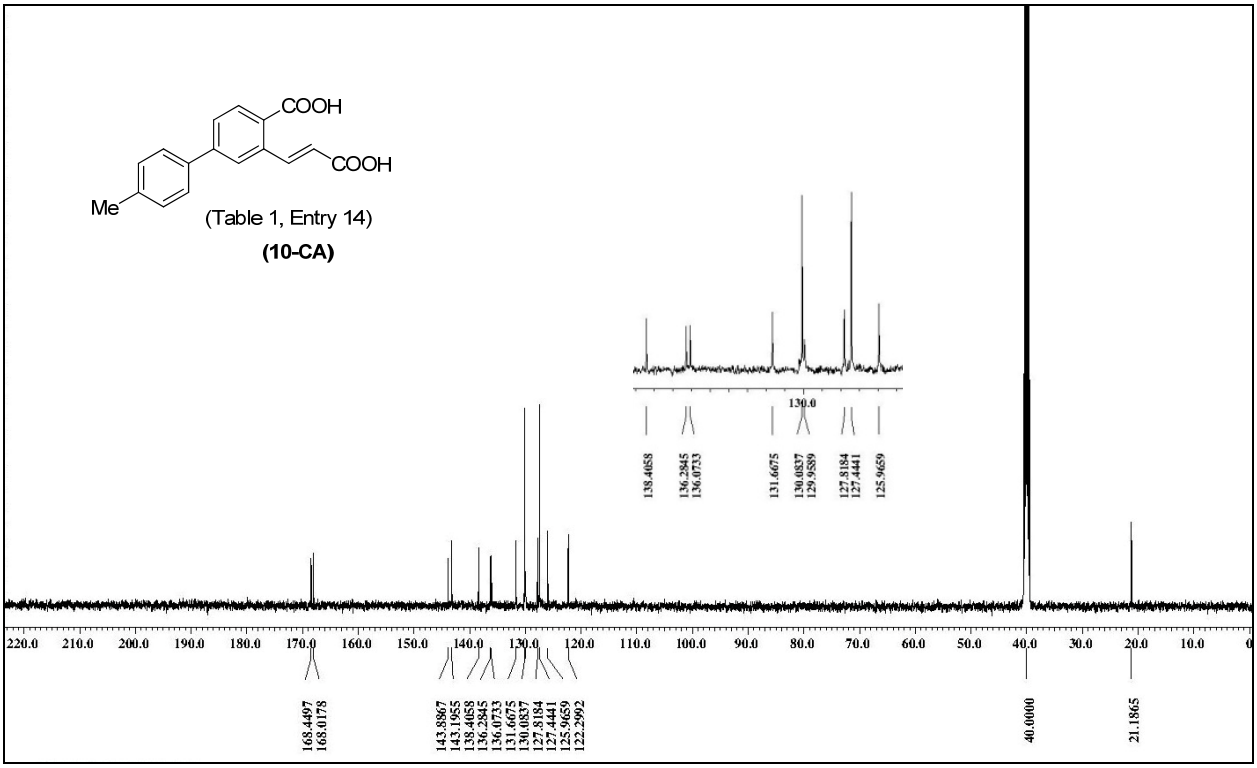


FIGURE S21. ^{13}C NMR spectrum of (*E*)-2-carboxy-5-(4-tolyl)cinnamic acid in DMSO-d_6.

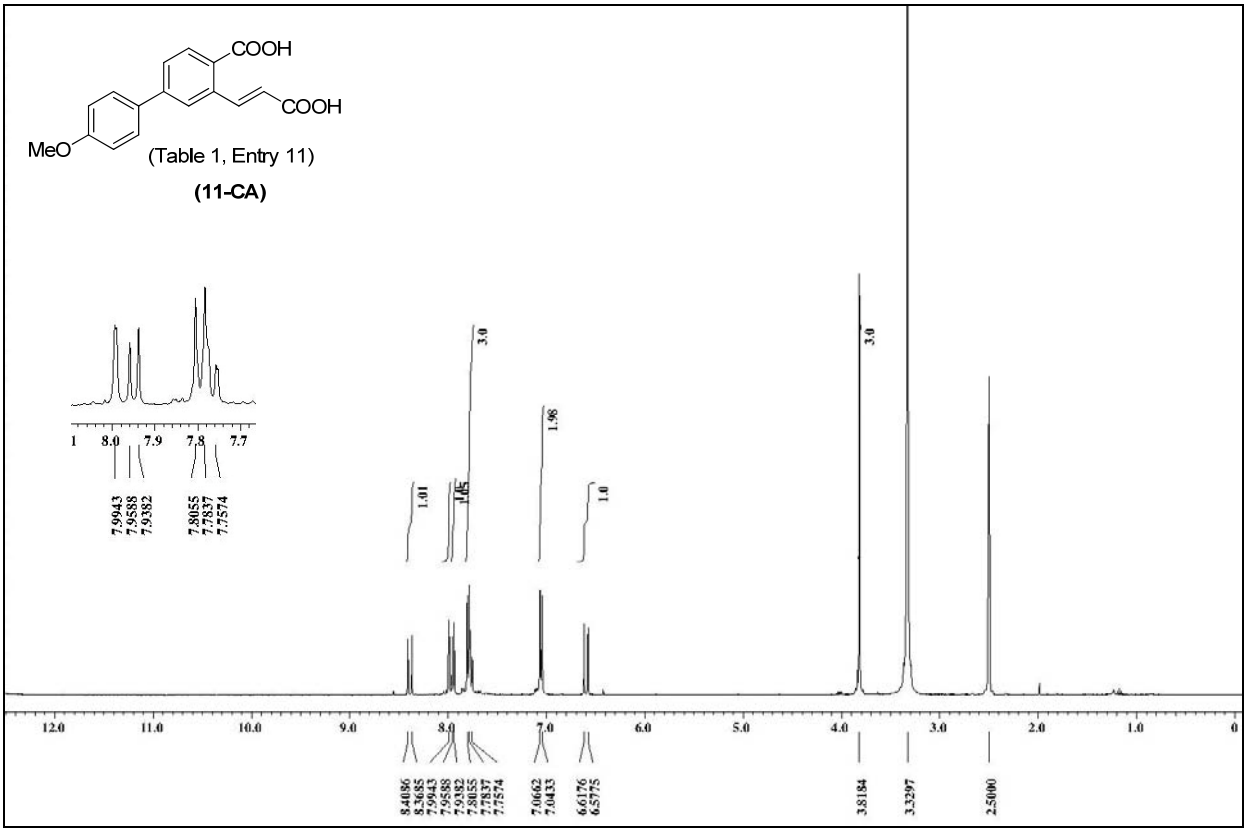


FIGURE S22. ^{1}H NMR spectrum of (*E*)-2-carboxy-5-(4-anisyl)cinnamic acid in DMSO-d_6.

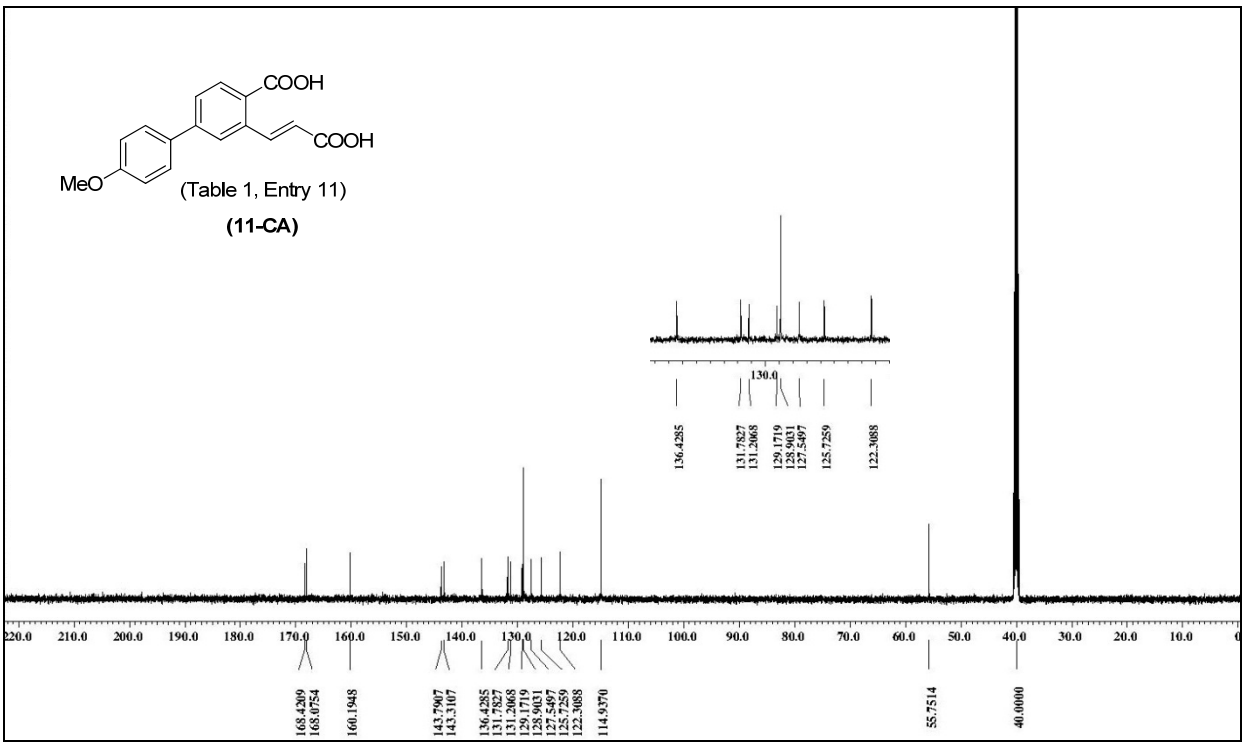


FIGURE S23. ^{13}C NMR spectrum of (*E*)-2-carboxy-5-(4-anisyl)cinnamic acid in DMSO-d_6.

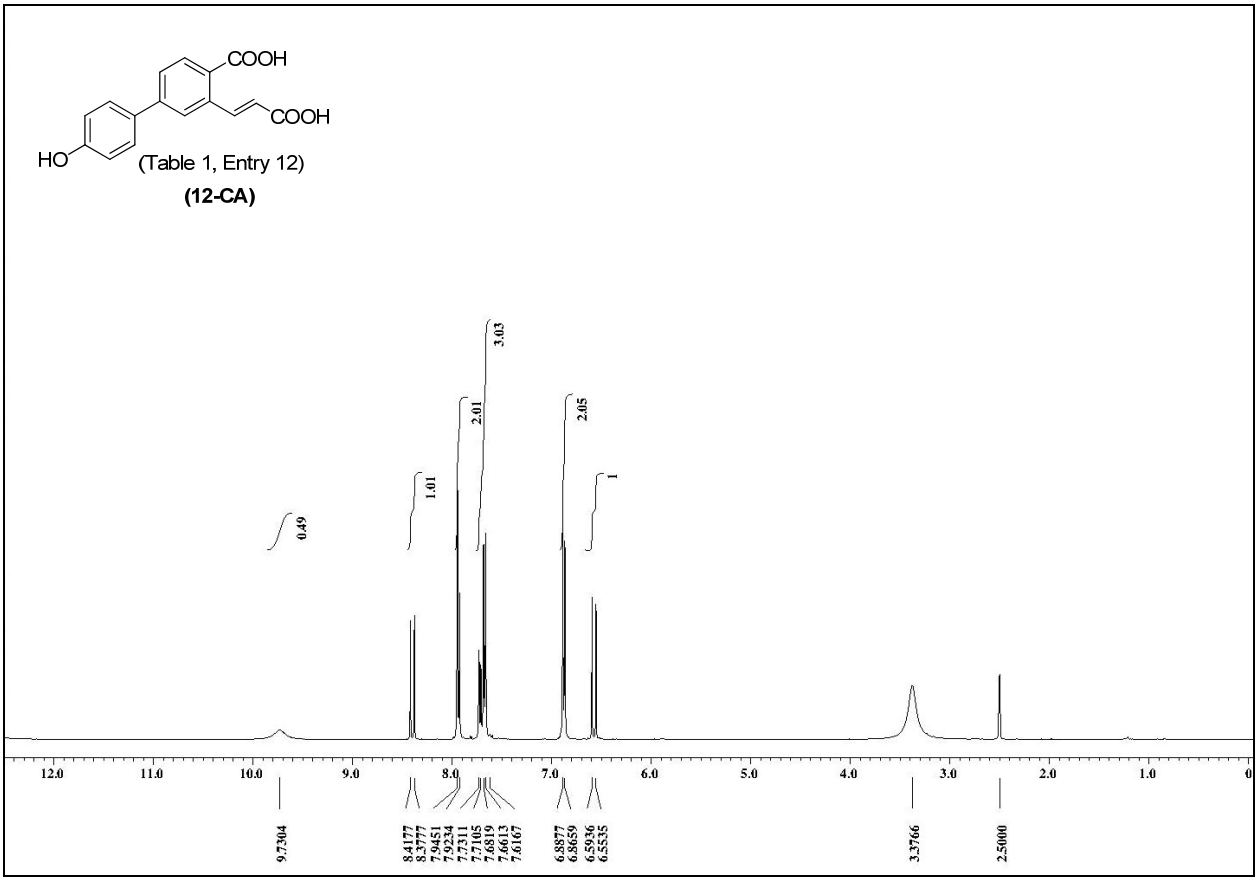


FIGURE S24. ^{1}H NMR spectrum of (*E*)-2-carboxy-5-(4-phenoxy)cinnamic acid in DMSO-d_6.

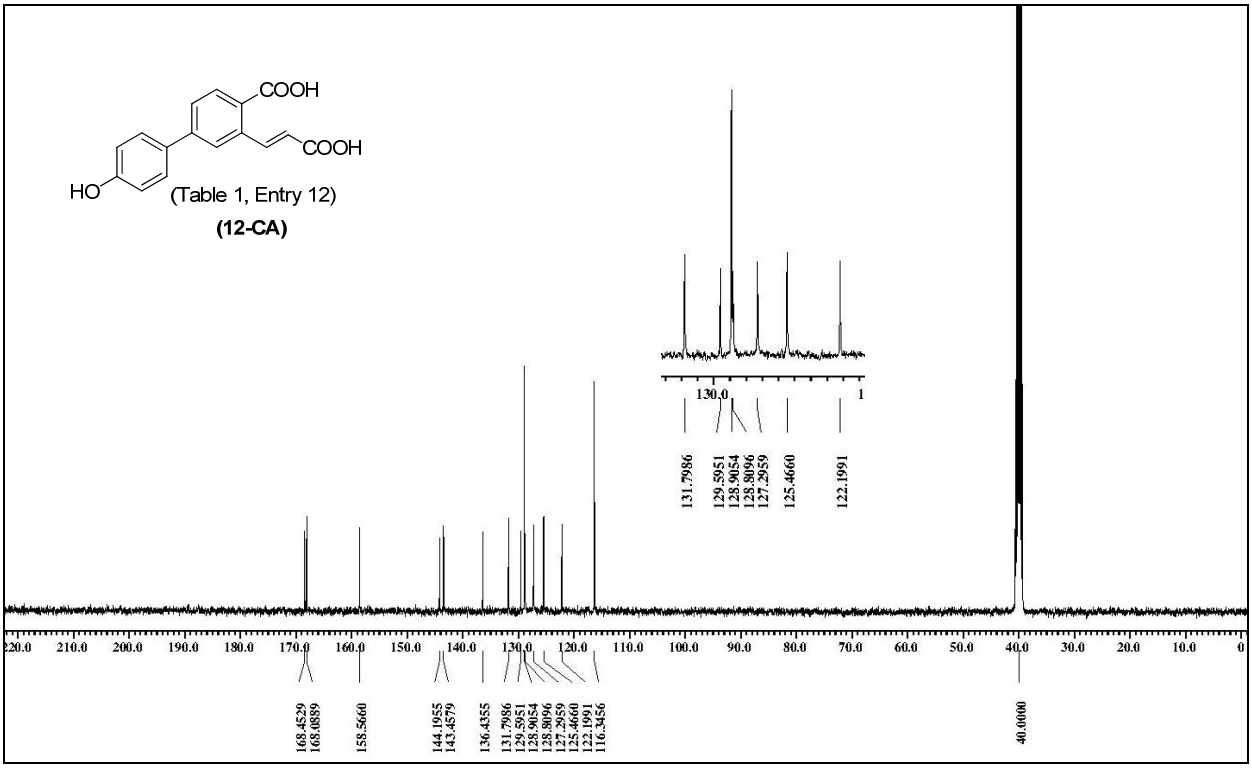


FIGURE S25. ^{13}C NMR spectrum of (*E*)-2-carboxy-5-(4-phenoxy)cinnamic acid in DMSO-d_6.

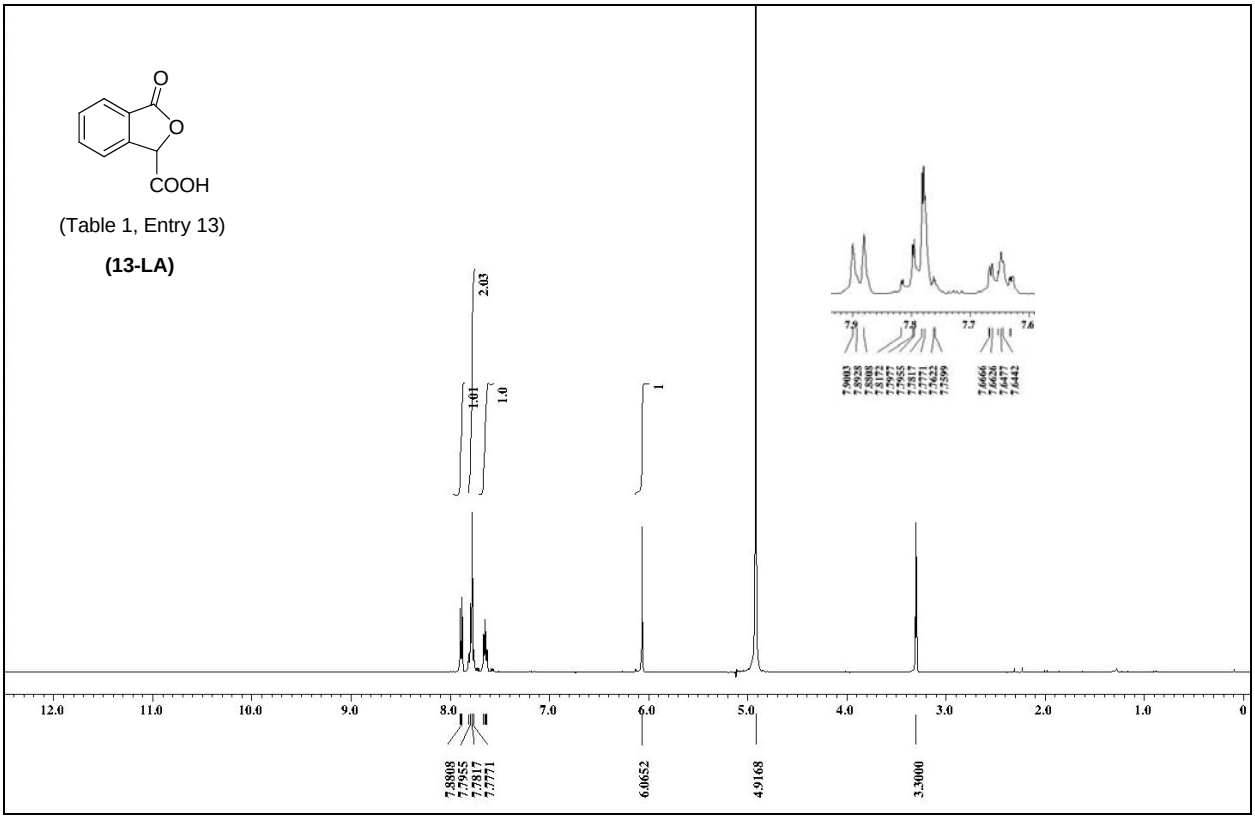


FIGURE S26. ^{1}H NMR spectrum of 3-oxo-1,3-dihydroisobenzofuran-1-carboxylic acid in CD_3OD.

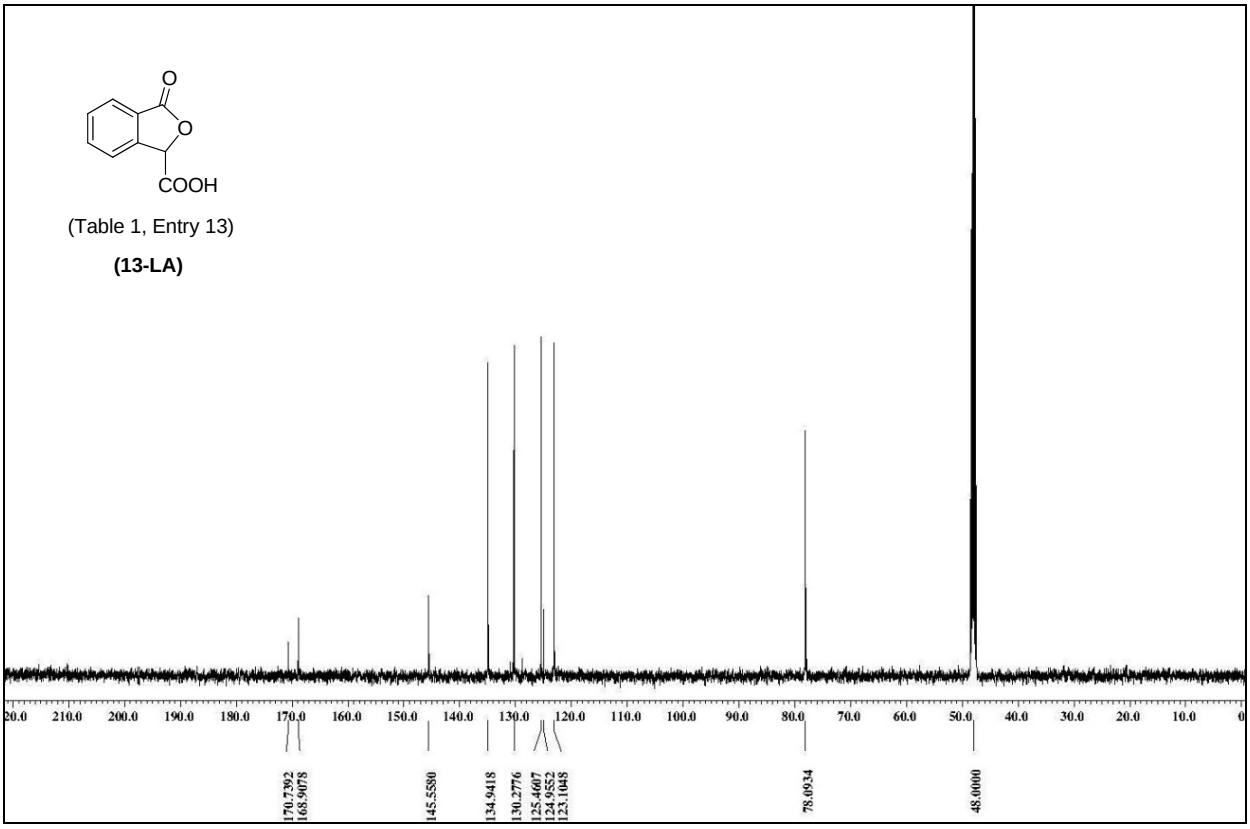


FIGURE S27. ^{13}C NMR spectrum of 3-oxo-1,3-dihydroisobenzofuran-1-carboxylic acid in CD_3OD.

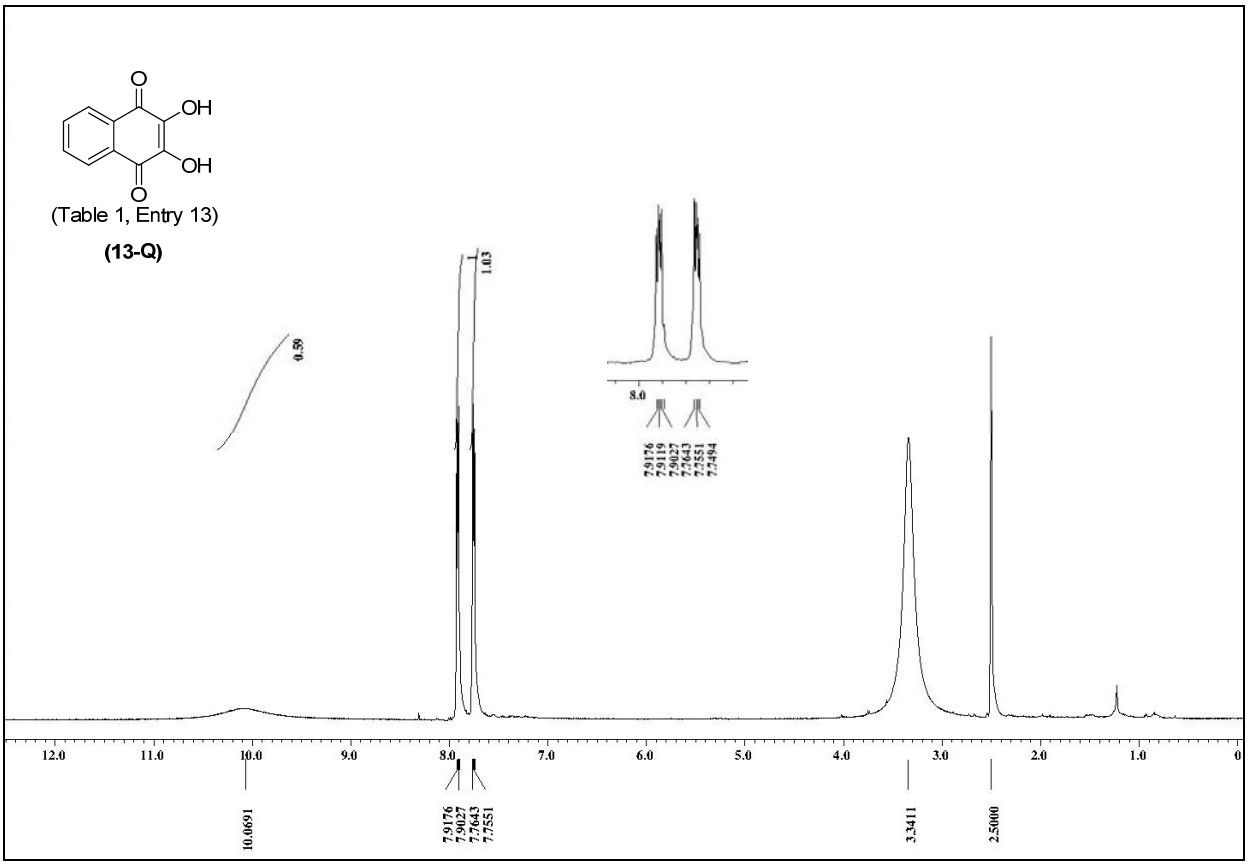


FIGURE S28. ^{1}H NMR spectrum of 2,3-dihydroxy-1,4-naphthoquinone in DMSO-d_6.

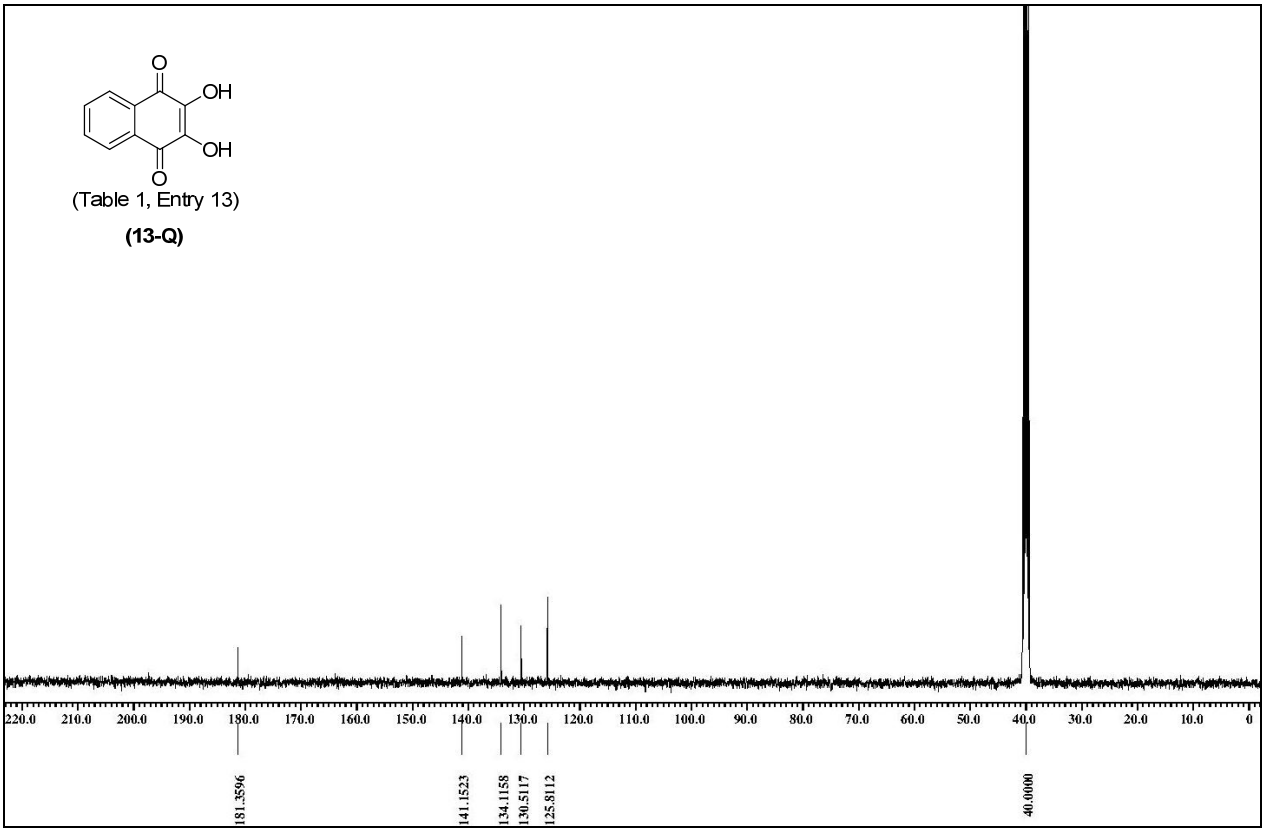


FIGURE S29. ^{13}C NMR spectrum of 2,3-dihydroxy-1,4-naphthoquinone in DMSO-d_6.

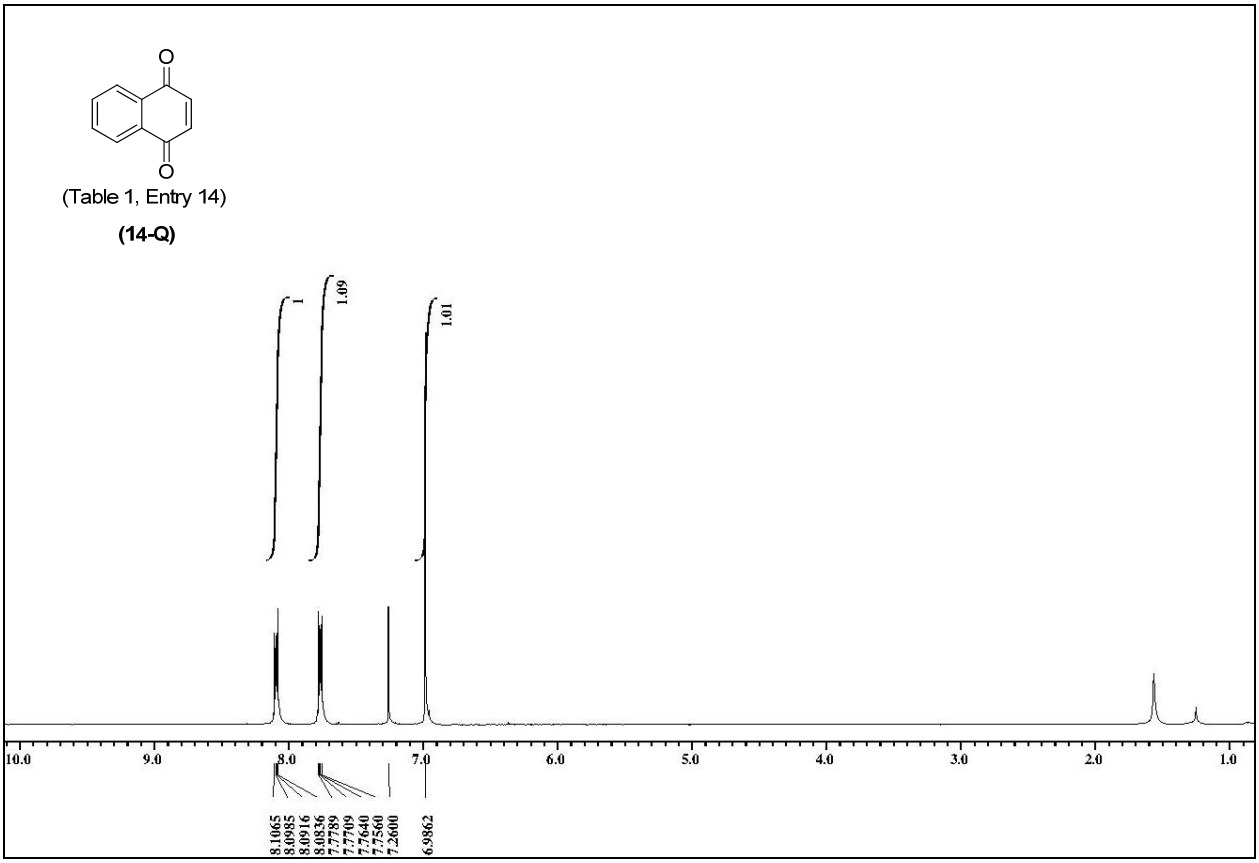


FIGURE S30. ^{1}H NMR spectrum of 1,4-naphthoquinone in $CDCl_3$.

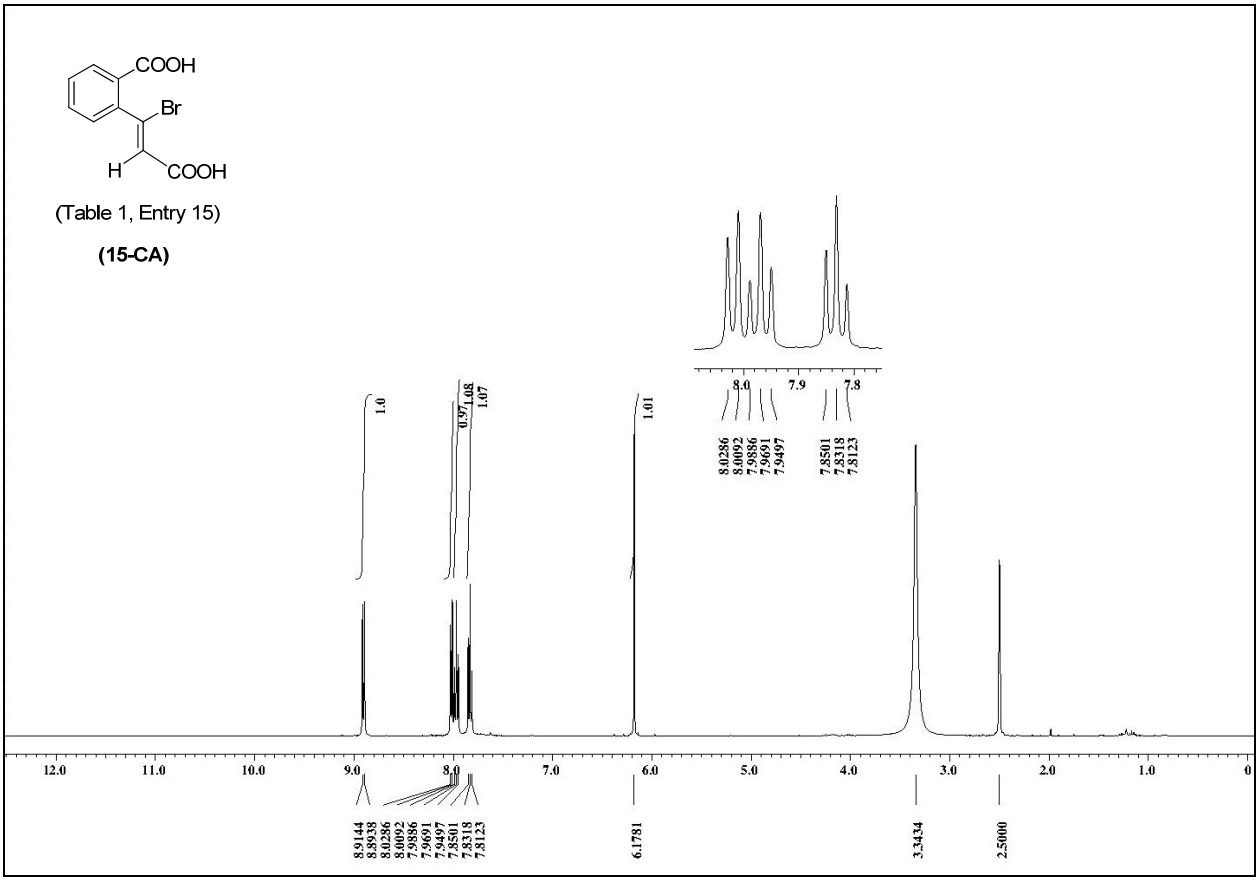


FIGURE S31. ^{1}H NMR spectrum of β-bromo-2-carboxycinnamic acid in DMSO-d_6.

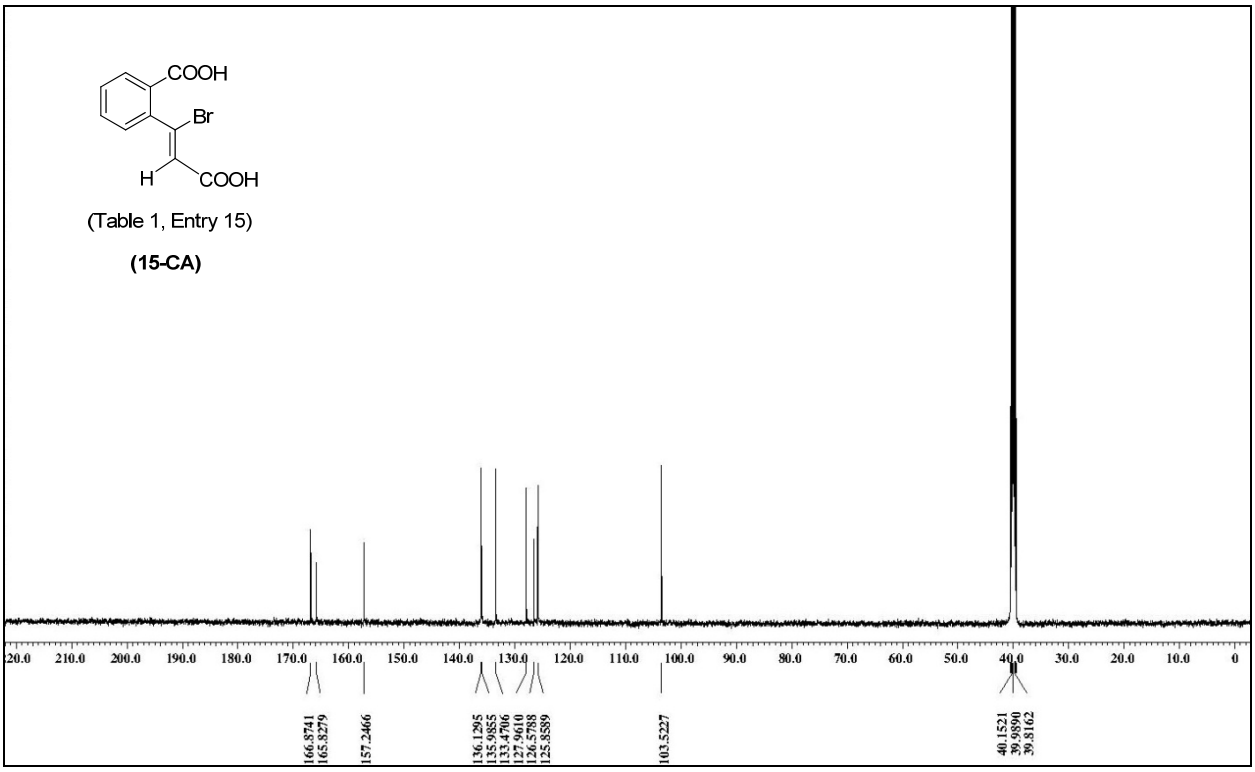


FIGURE S32. ^{13}C NMR spectrum of β-bromo-2-carboxycinnamic acid in DMSO-d_6.

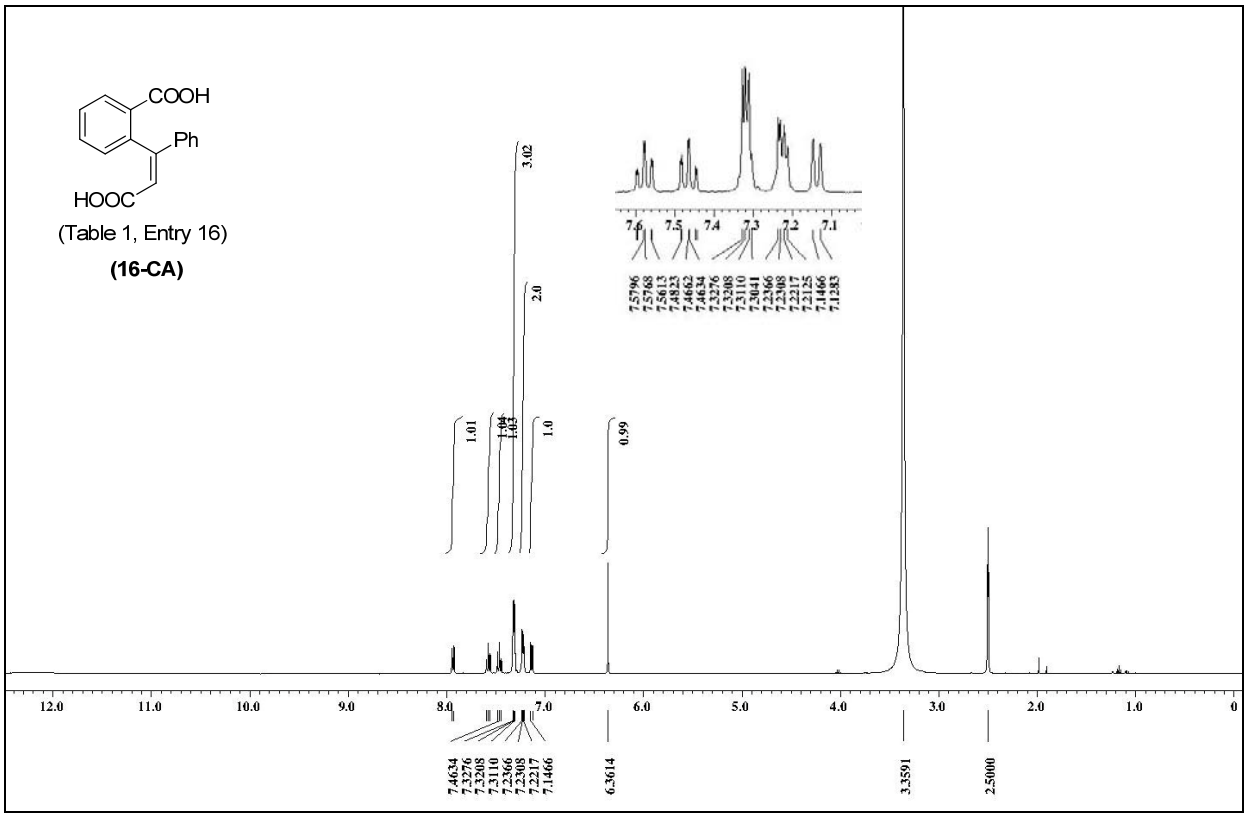


FIGURE S33. ^{1}H NMR spectrum of β-phenyl-2-carboxycinnamic acid in DMSO-d_6.

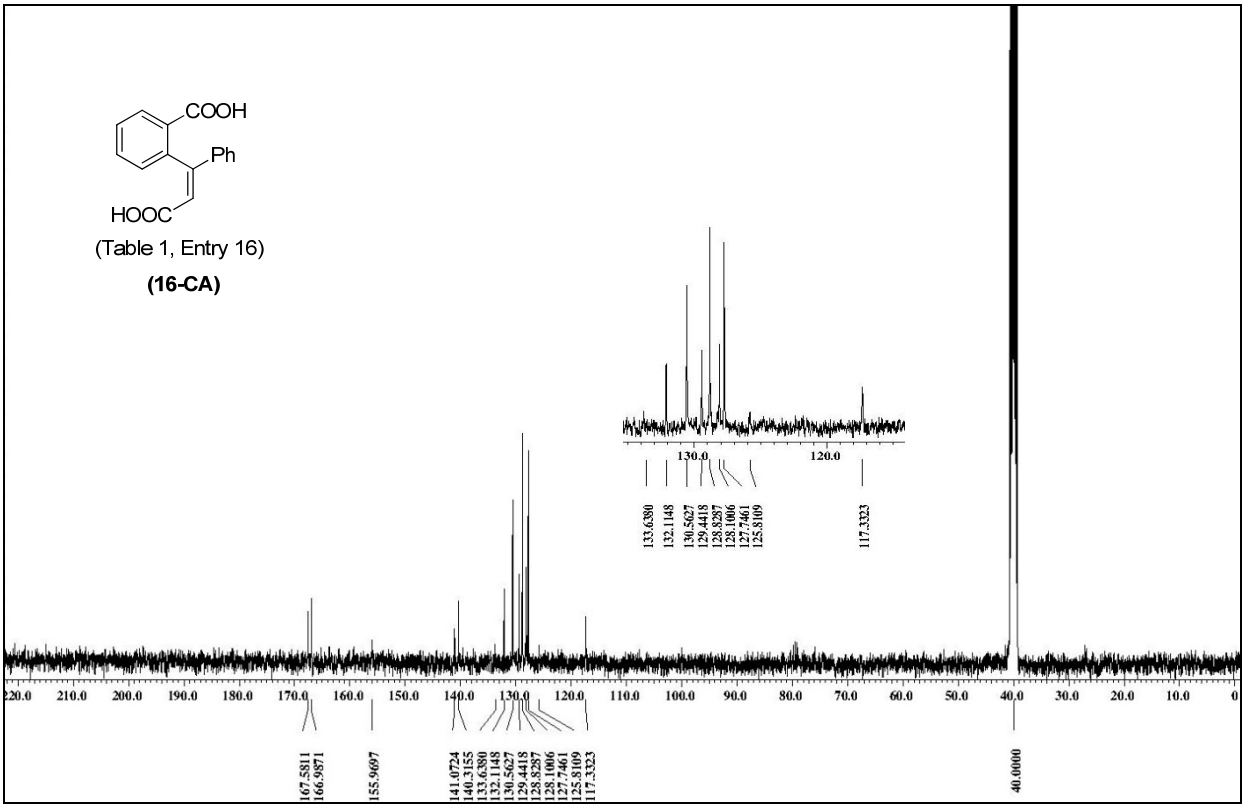


FIGURE S34. ^{13}C NMR spectrum of β-phenyl-2-carboxycinnamic acid in DMSO-d_6.

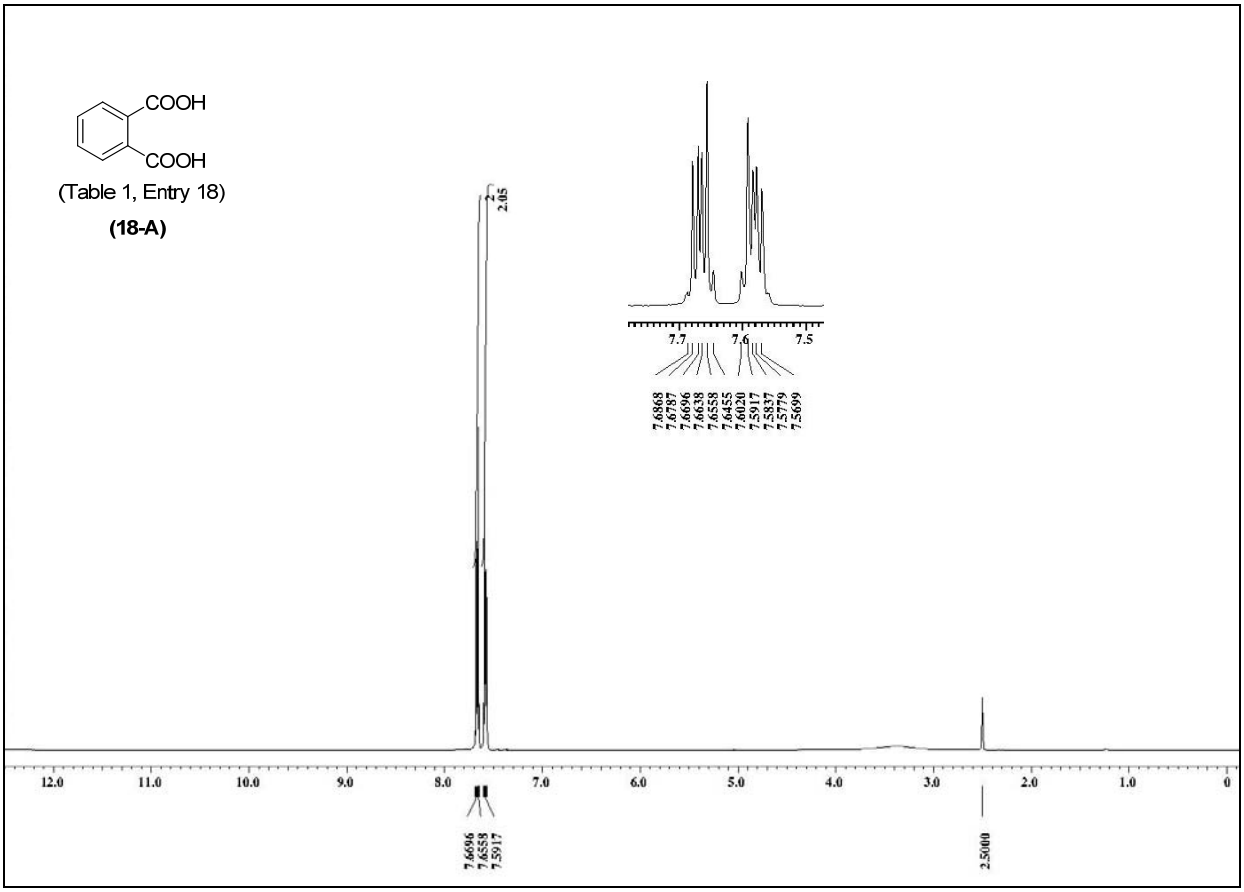


FIGURE S35. ^{1}H NMR spectrum of *o*-phthalic acid in DMSO-d_6.

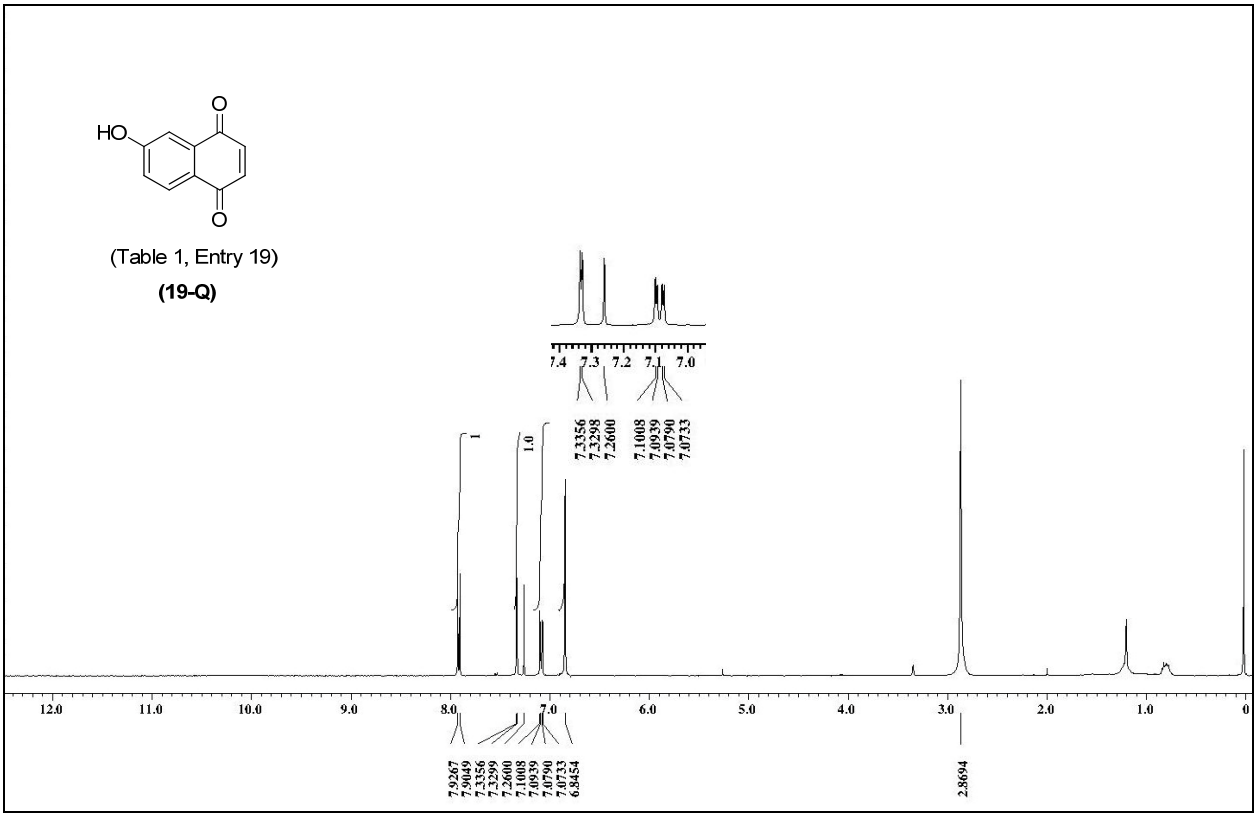


FIGURE S36. ^{1}H NMR spectrum of 6-hydroxy-1,4-naphthoquinone in $CDCl_3$+CD_3OD.

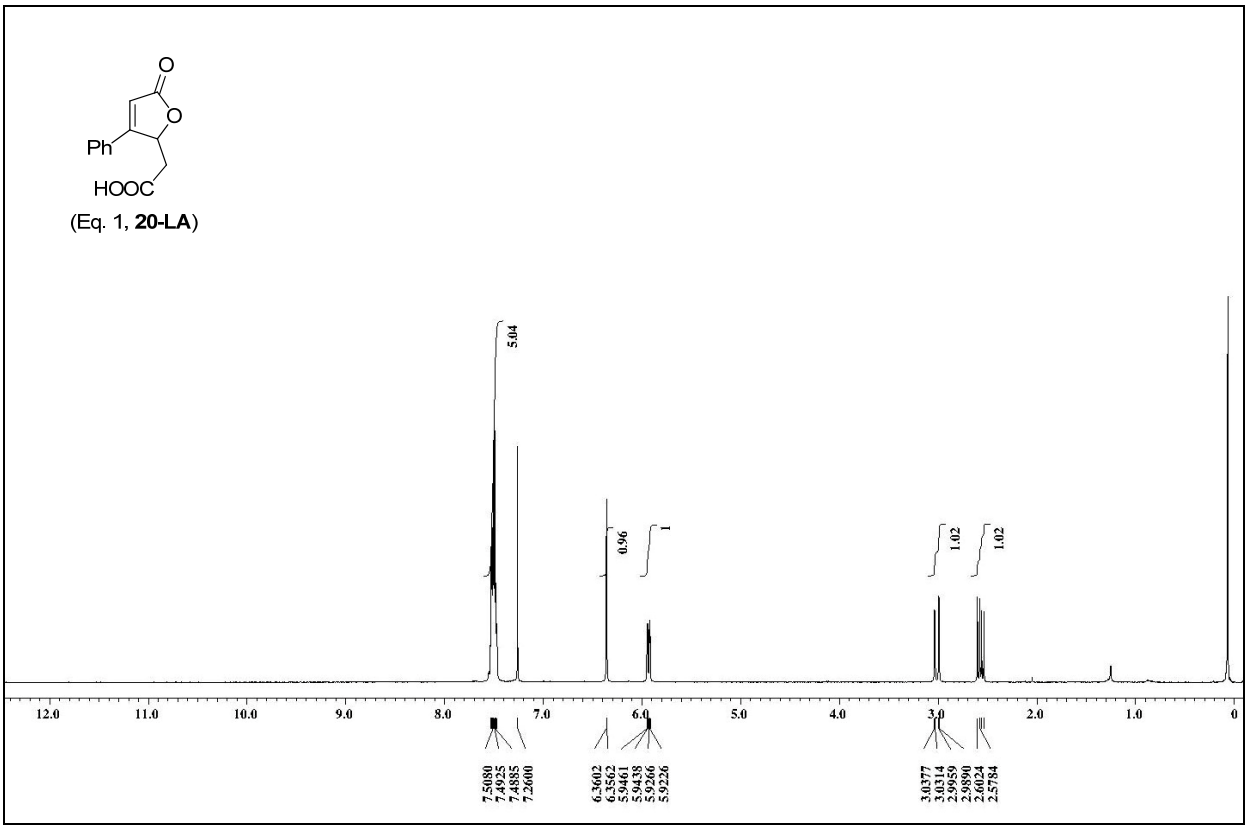


FIGURE S37. ^{1}H NMR spectrum of 5-oxo-3-phenyl-2,5-dihydro-2-furanacetic acid in $CDCl_3$.

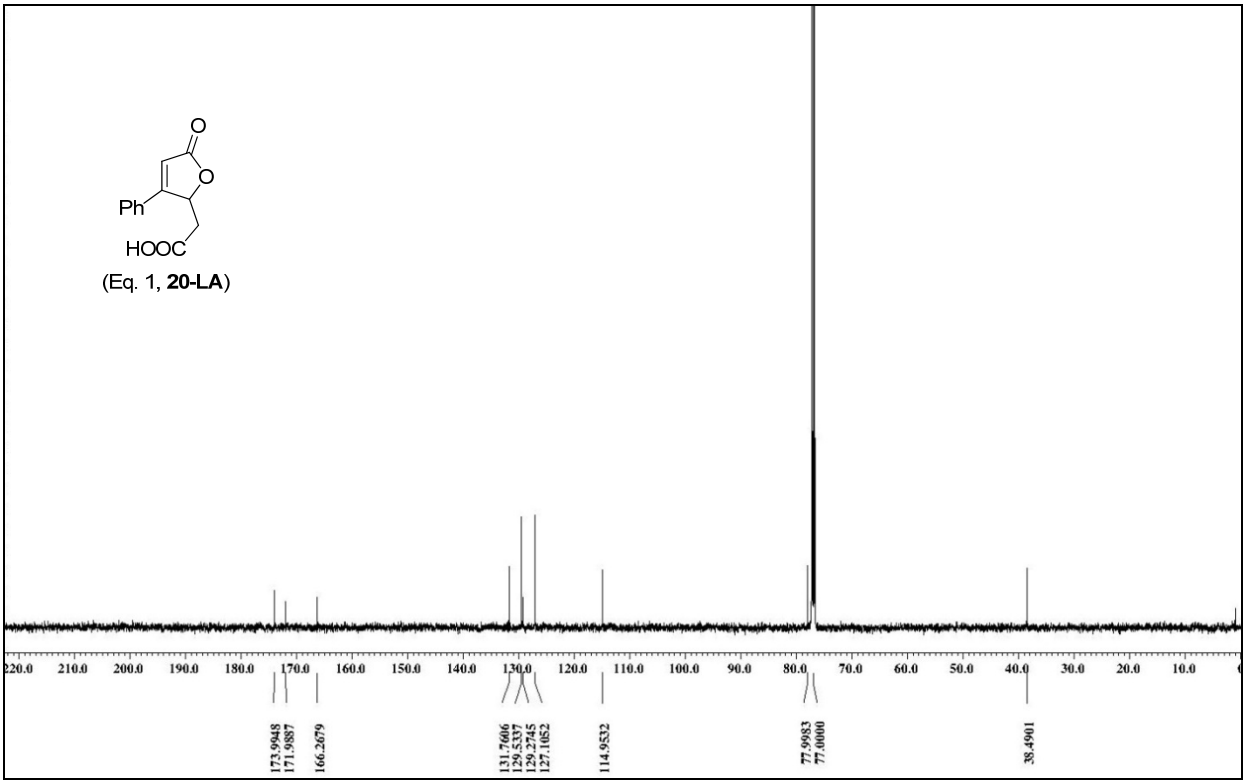


FIGURE S38. ^{13}C NMR spectrum of 5-oxo-3-phenyl-2,5-dihydro-2-furanacetic acid in $CDCl_3$.

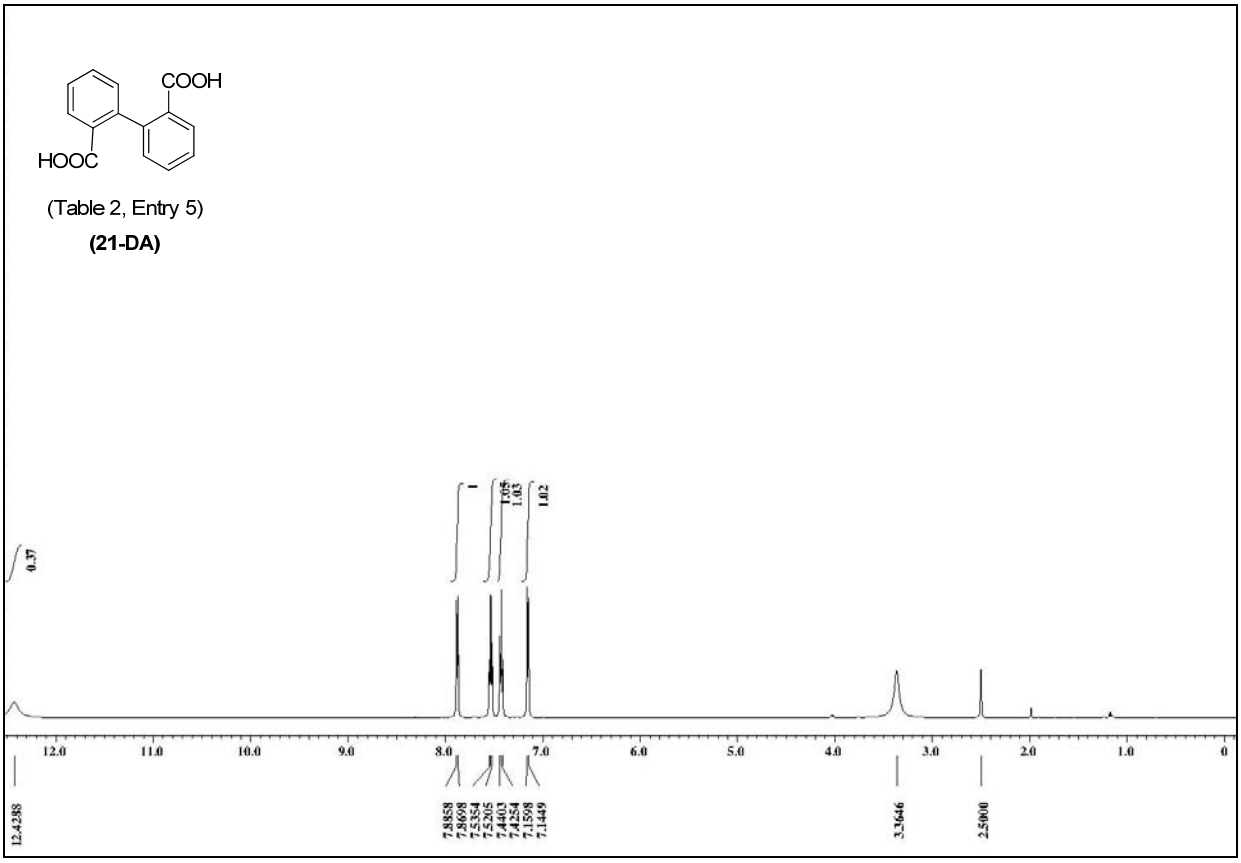


FIGURE S39. ^{1}H NMR spectrum of diphenic acid in DMSO-d_6.

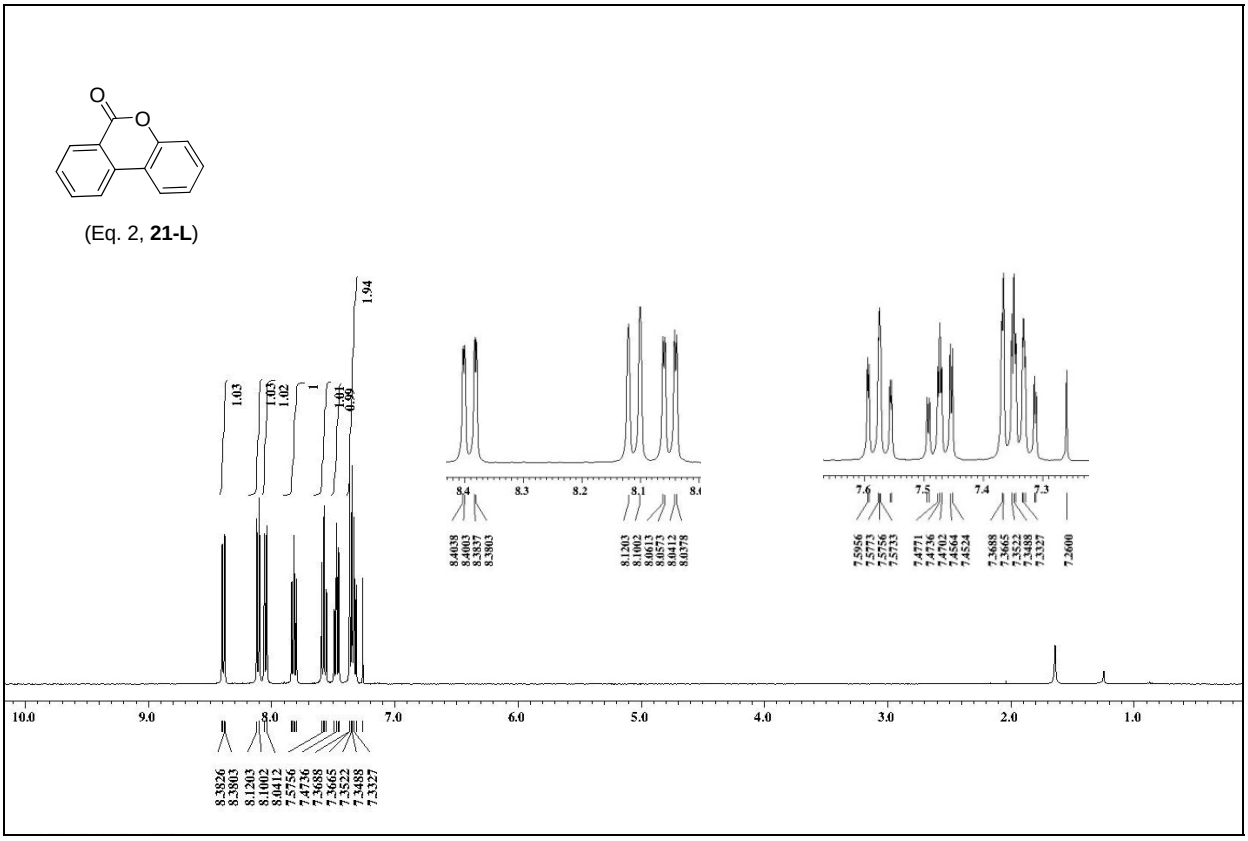


FIGURE S40. ^{1}H NMR spectrum of dibenzo[b,d]pyrone in $CDCl_3$.

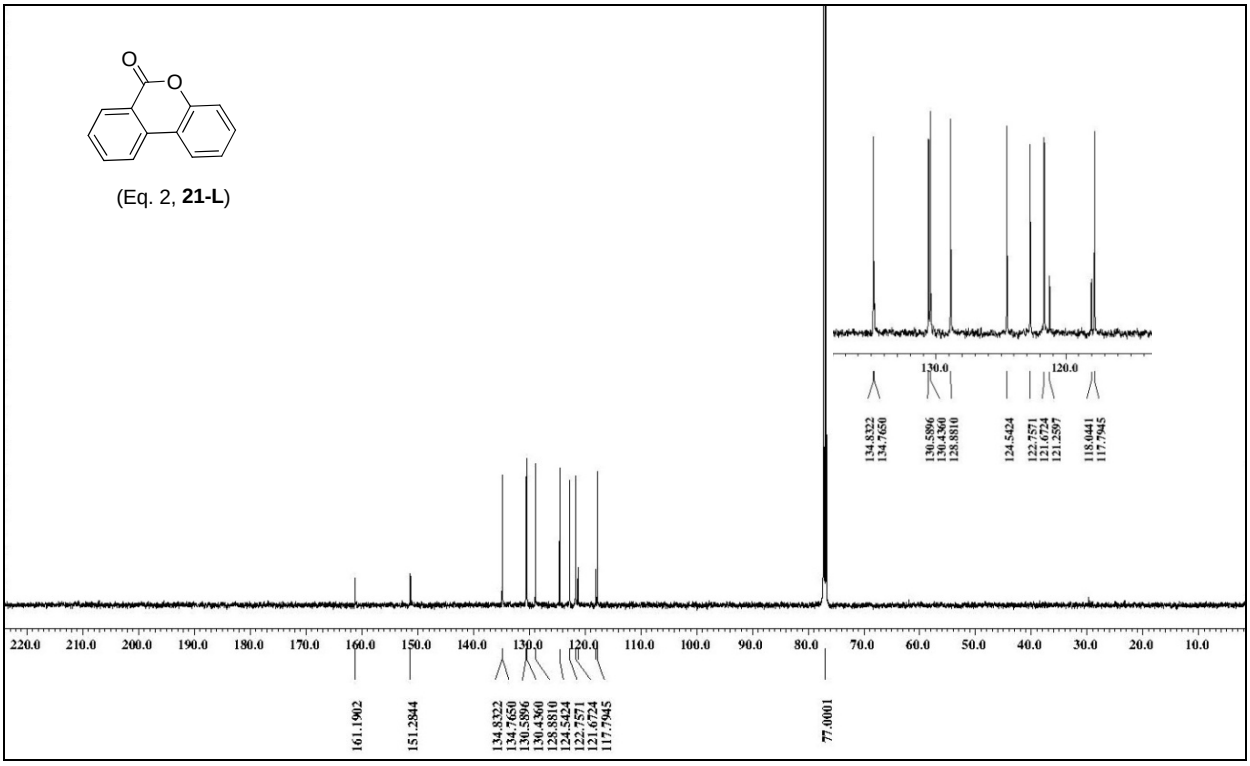


FIGURE S41. ^{13}C NMR spectrum of dibenzo[b,d]pyrone in $CDCl_3$.

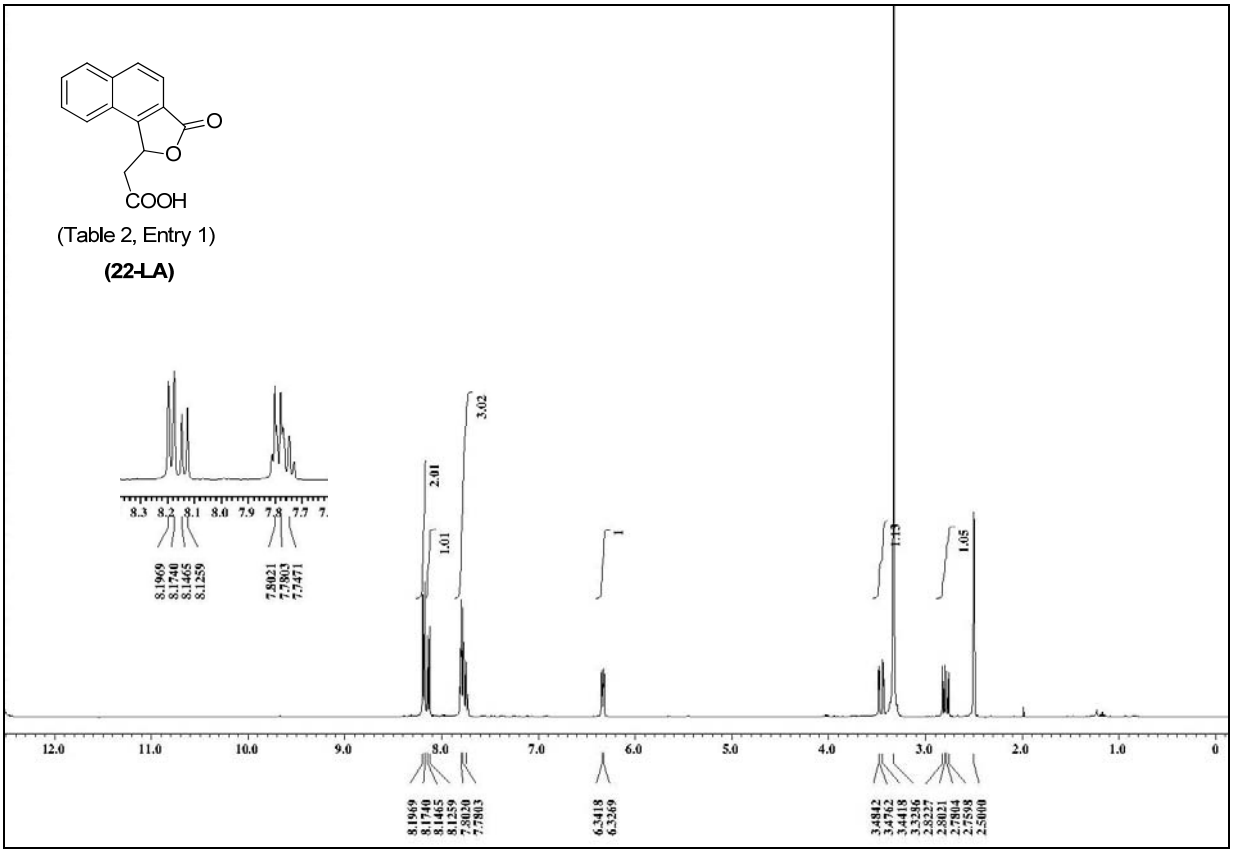


FIGURE S45. ^{1}H NMR spectrum of 2-(3-oxo-1,3-dihydronaphtho[2,1-c]furan-1-yl)acetic acid in DMSO-d_6.

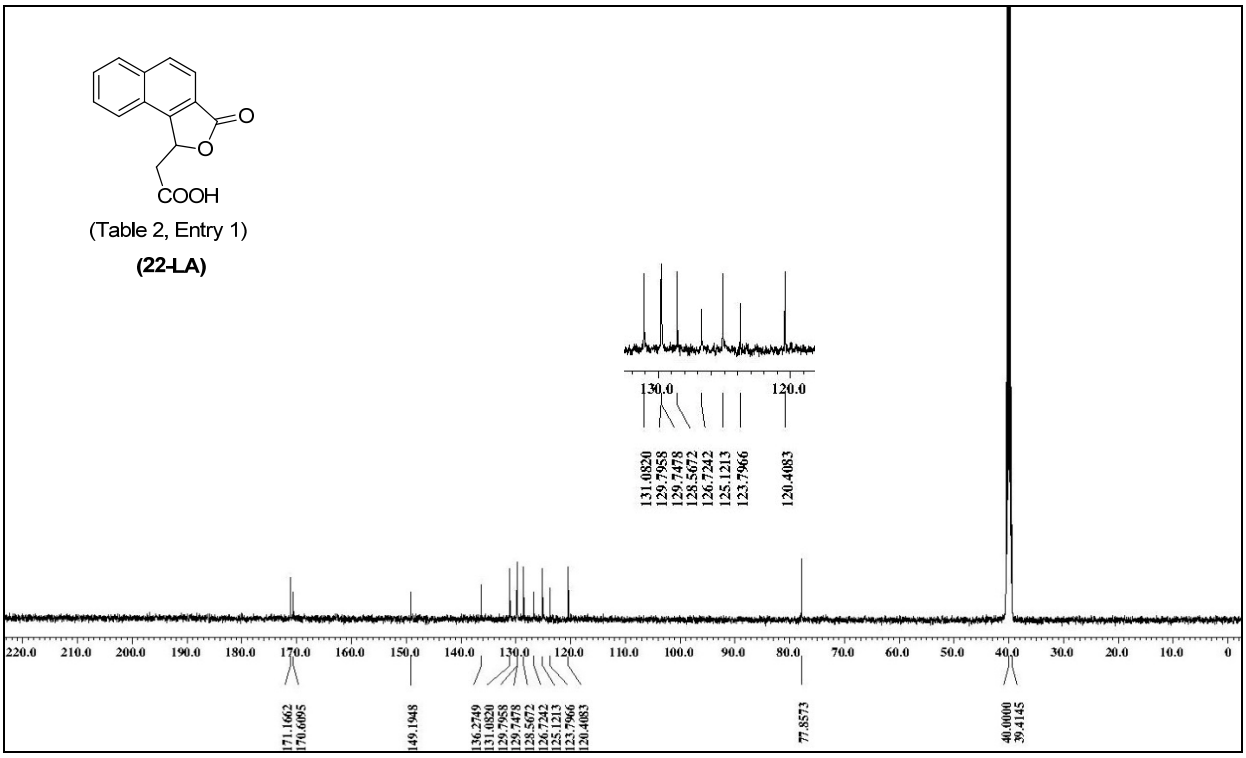


FIGURE S46. ^{13}C NMR spectrum of 2-(3-oxo-1,3-dihydronaphtho[2,1-c]furan-1-yl)acetic acid in DMSO-d_6.

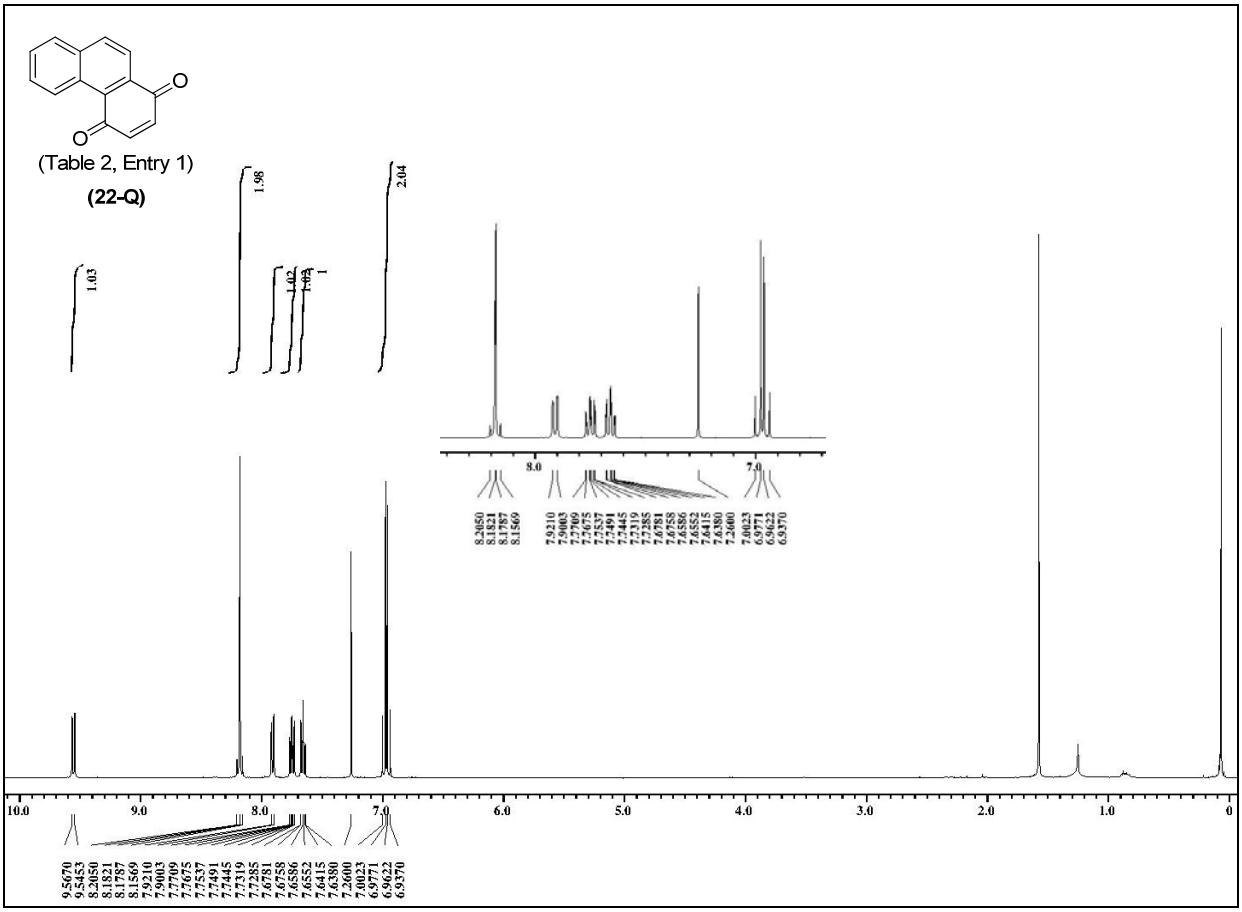


FIGURE S42. ^{1}H NMR spectrum of 1,4-phenanthroquinone in $CDCl_3$.

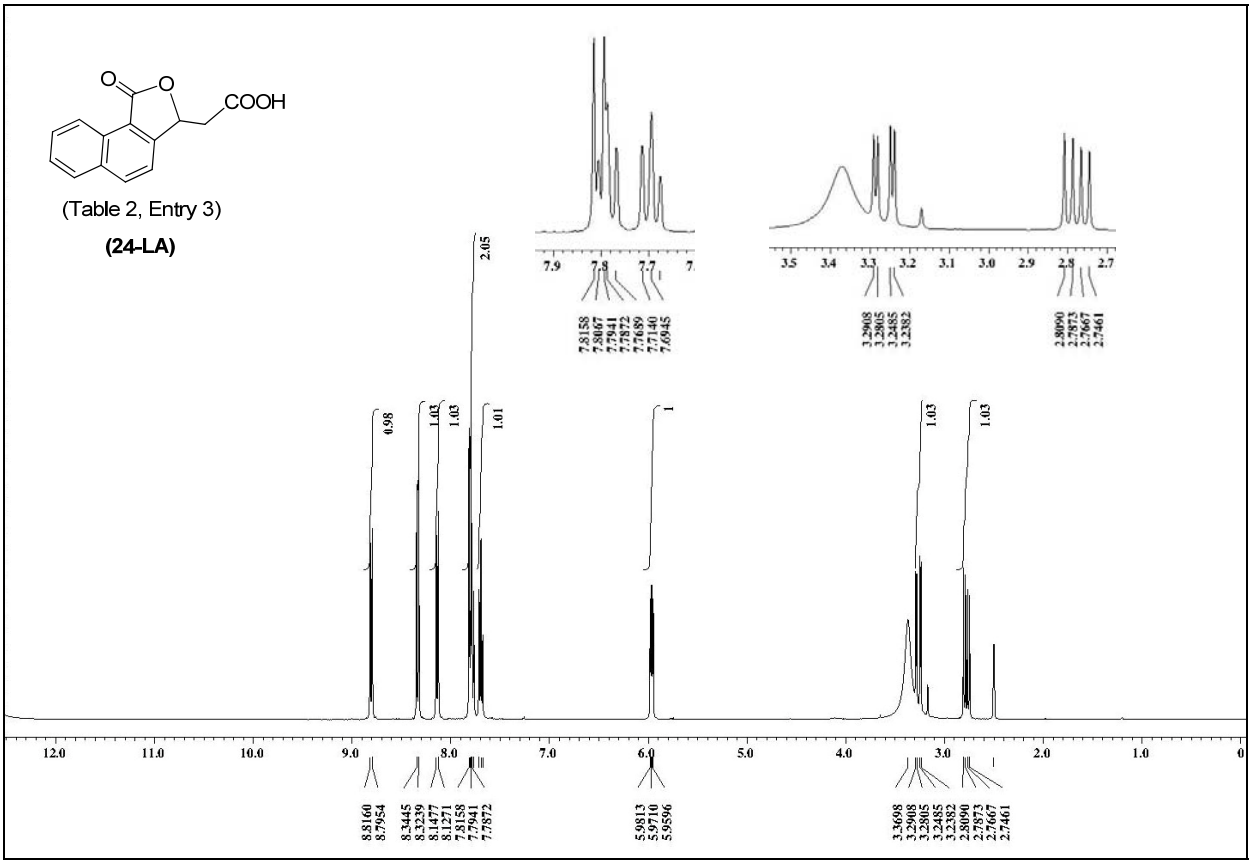


FIGURE S43. ^{1}H NMR spectrum of 2-(1-oxo-1,3-dihydronaphtho[2,1-c]furan-3-yl)acetic acid in DMSO-d_6.

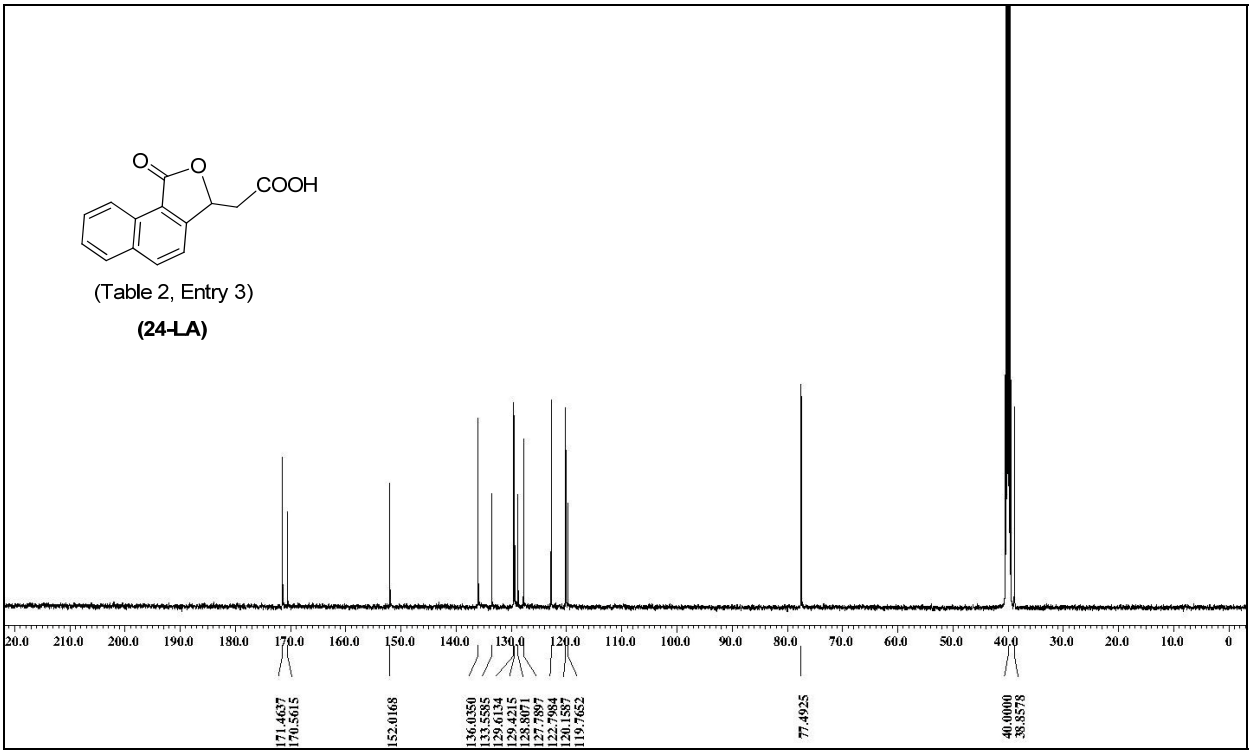


FIGURE S44. ^{13}C NMR spectrum of 2-(1-oxo-1,3-dihydronaphtho[2,1-c]furan-3-yl)acetic acid in DMSO-d_6.

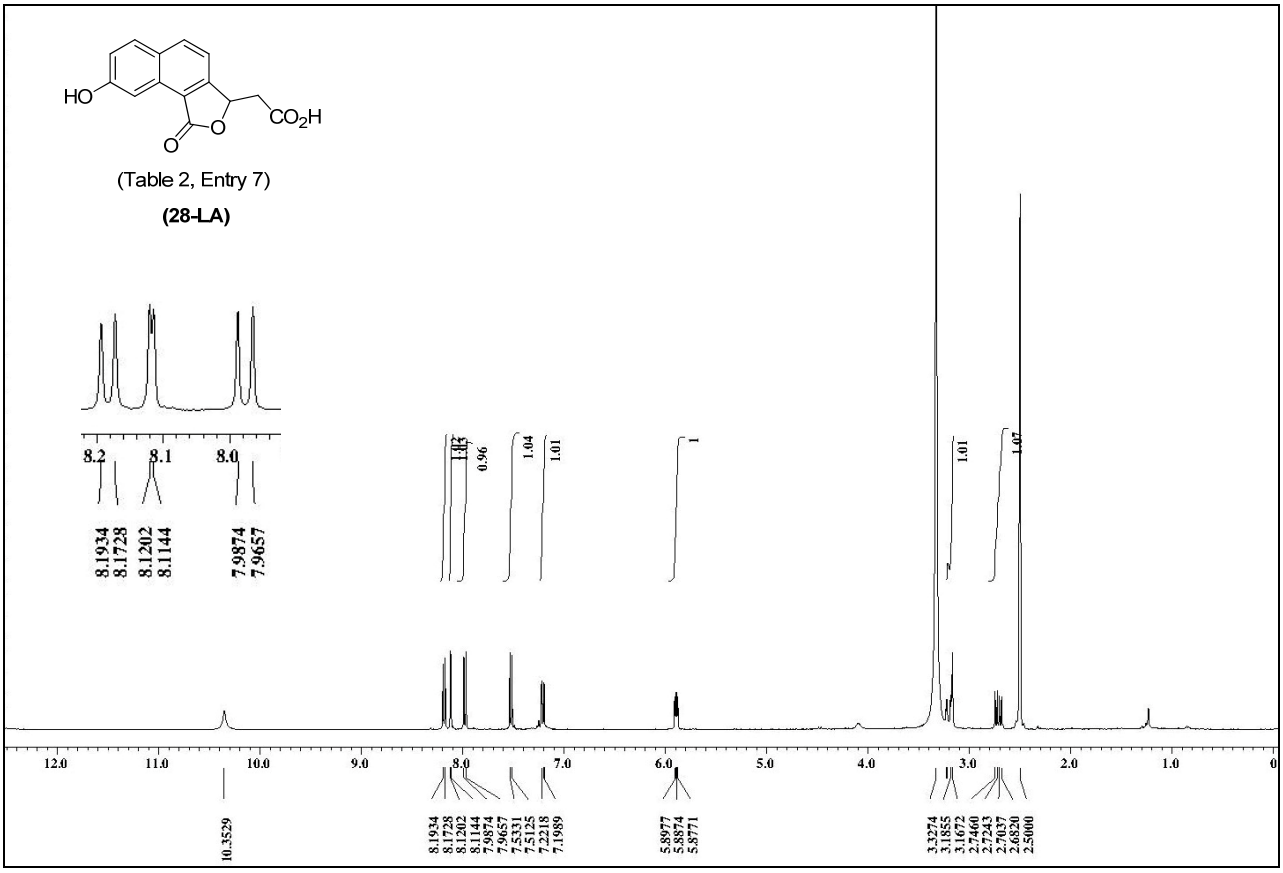


FIGURE S47. ^{1}H NMR spectrum of 2-(8-hydroxy-1-oxo-1,3-dihydronaphtho[2,1-c]furan-3-yl)acetic acid in DMSO-d_6.

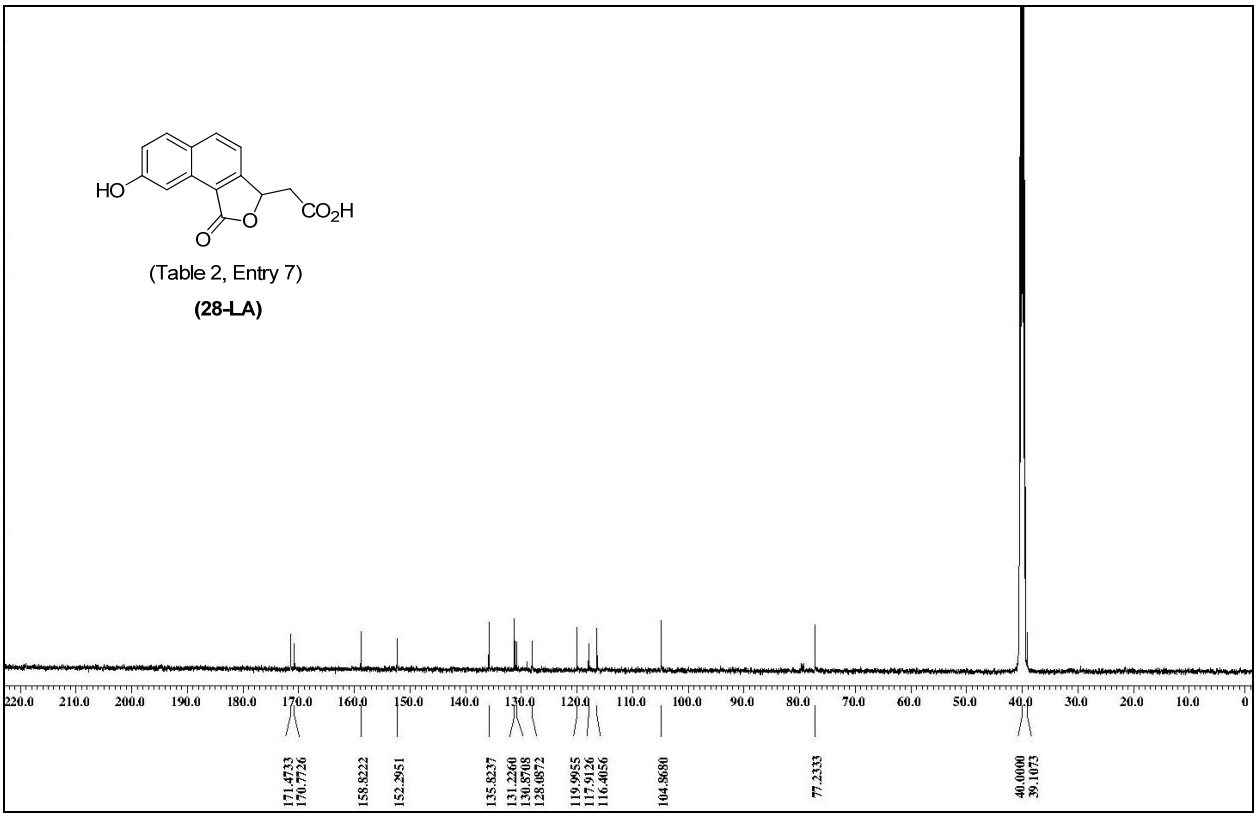


FIGURE S48. ^{13}C NMR spectrum of 2-(8-hydroxy-1-oxo-1,3-dihydronaphtho[2,1-c]furan-3-yl)acetic acid in DMSO-d_6.

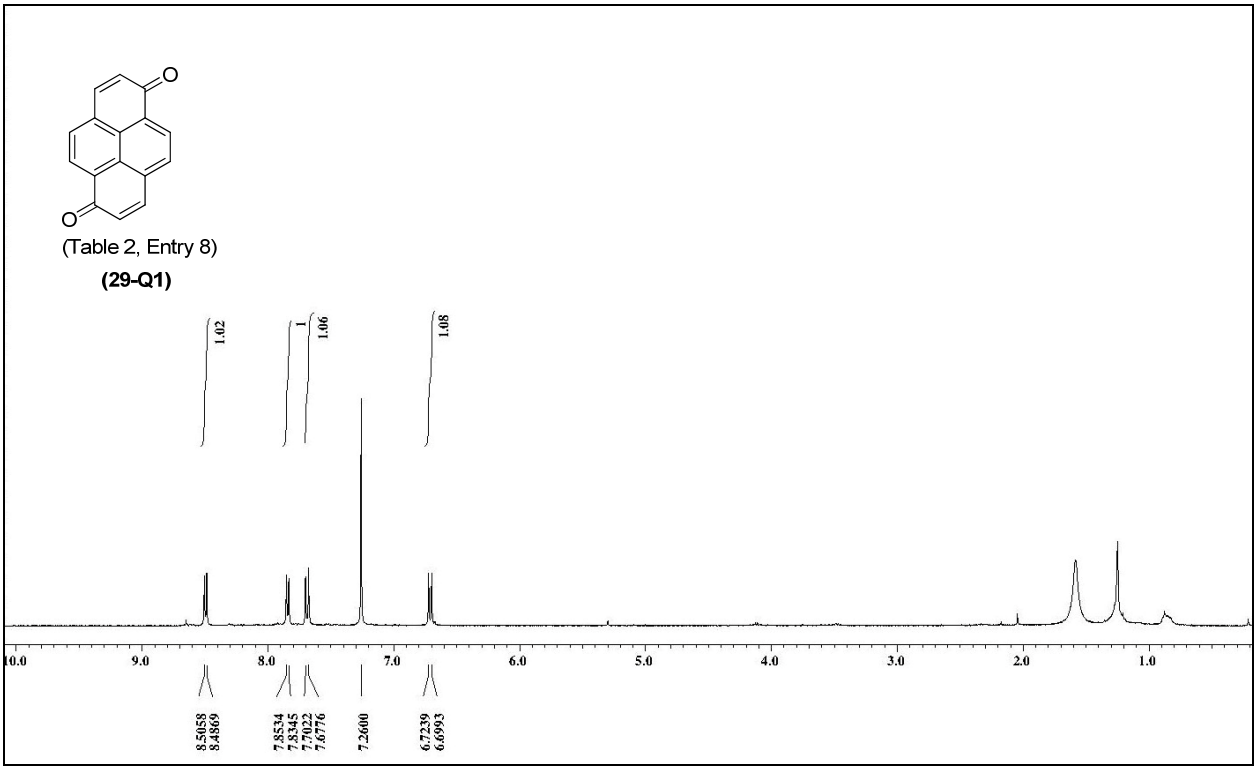


FIGURE S49. ^{1}H NMR spectrum of 1,6-diketopyrene in $CDCl_3$.

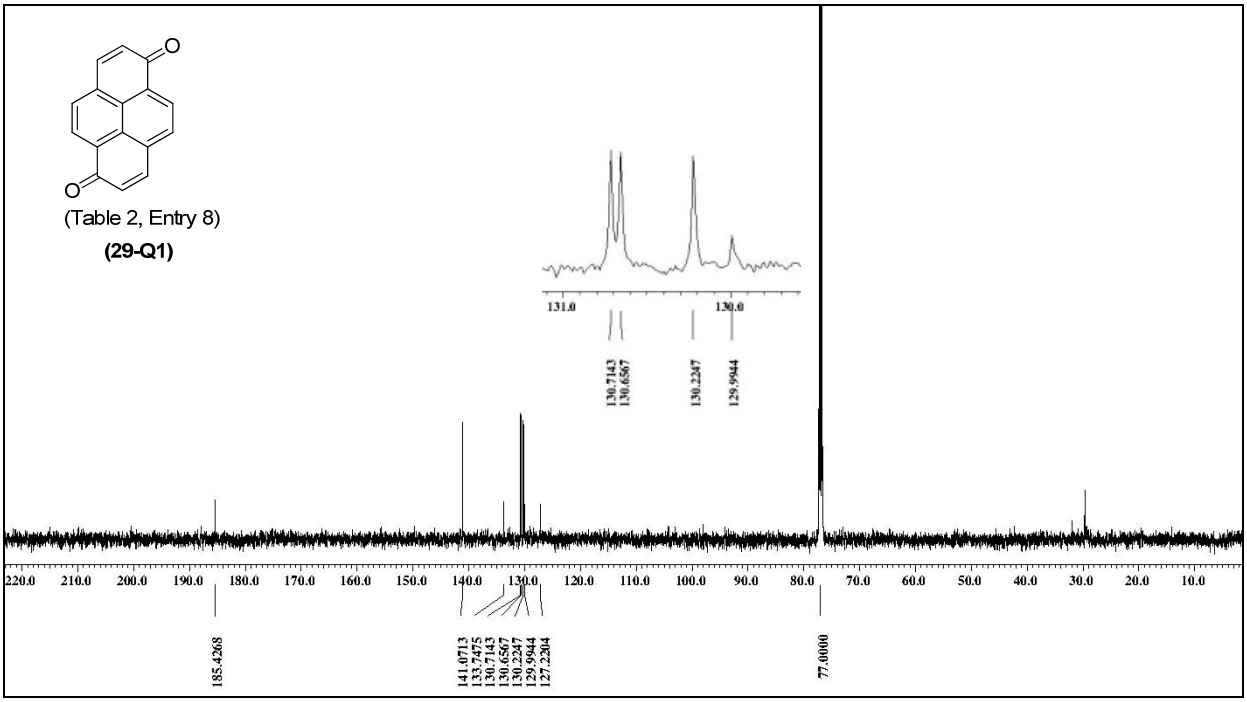


FIGURE S50. ^{13}C NMR spectrum of 1,6-diketopyrene in $CDCl_3$.

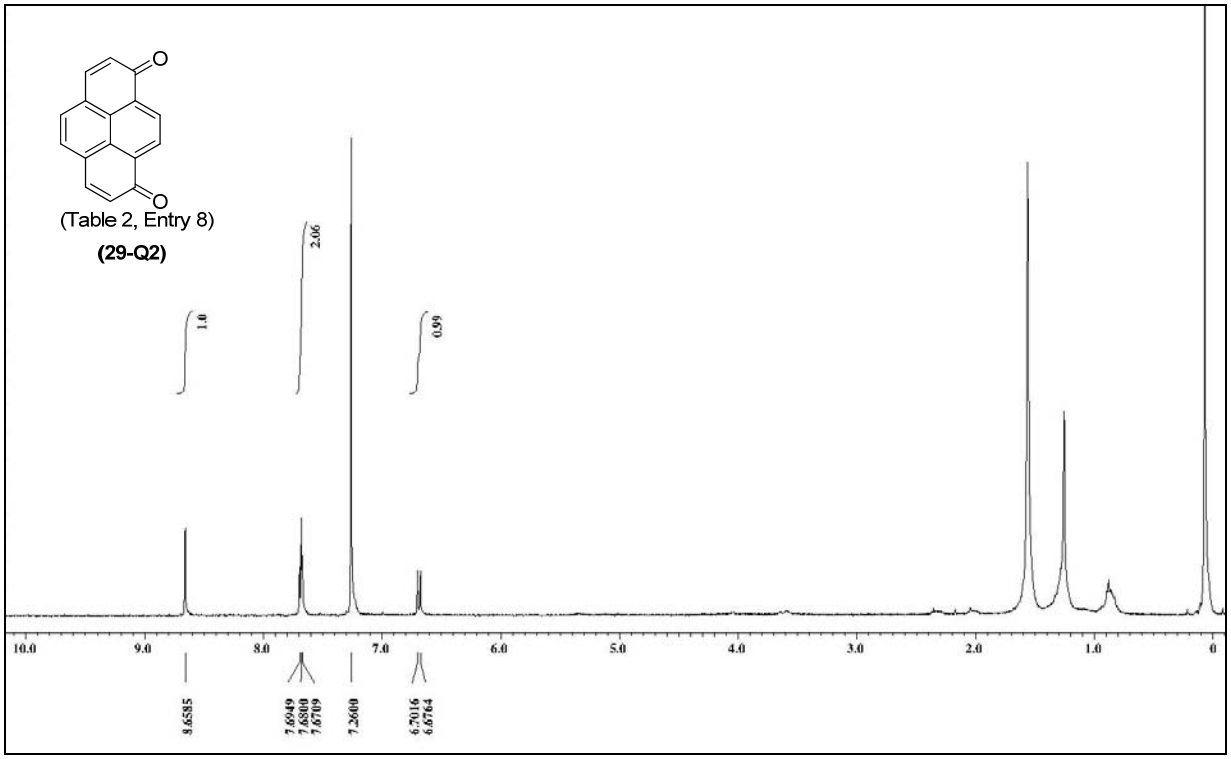


FIGURE S51. ^{1}H NMR spectrum of 1,8-diketopyrene in $CDCl_3$.

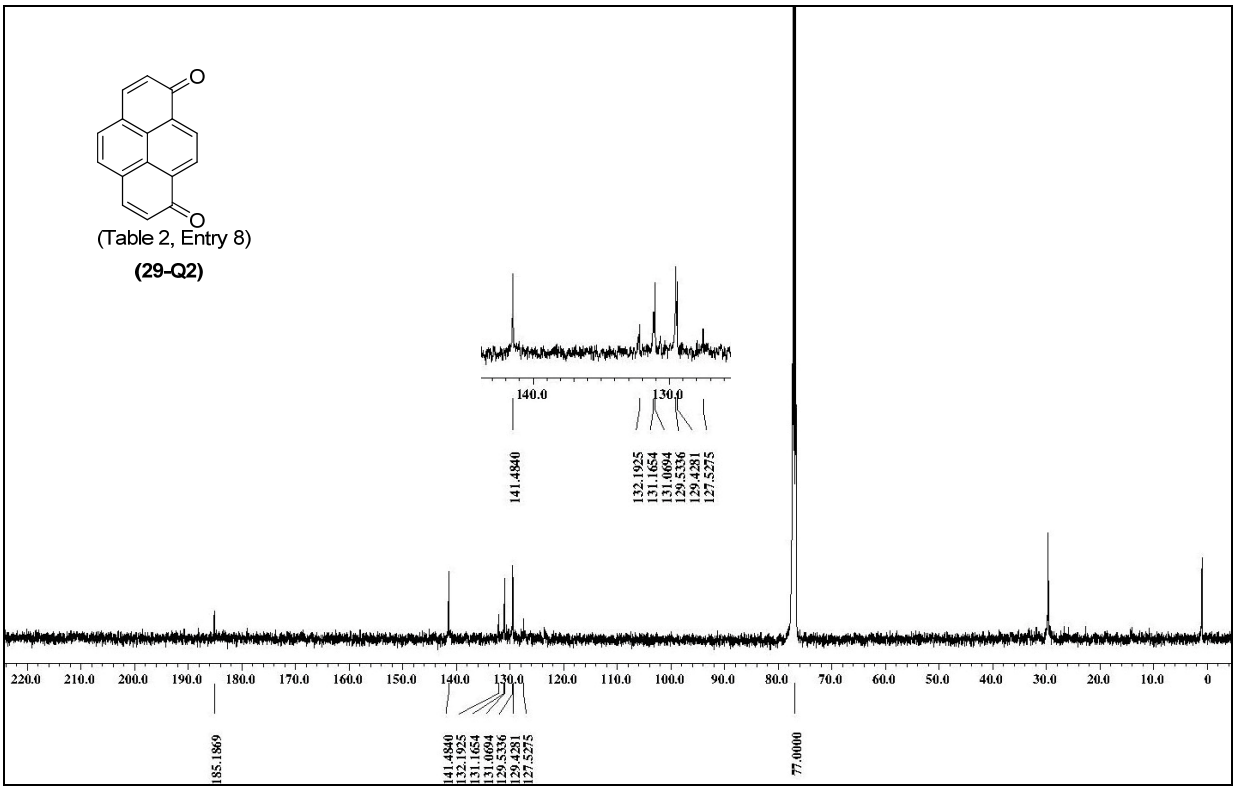


FIGURE S52. ^{13}C NMR spectrum of 1,8-diketopyrene in $CDCl_3$.

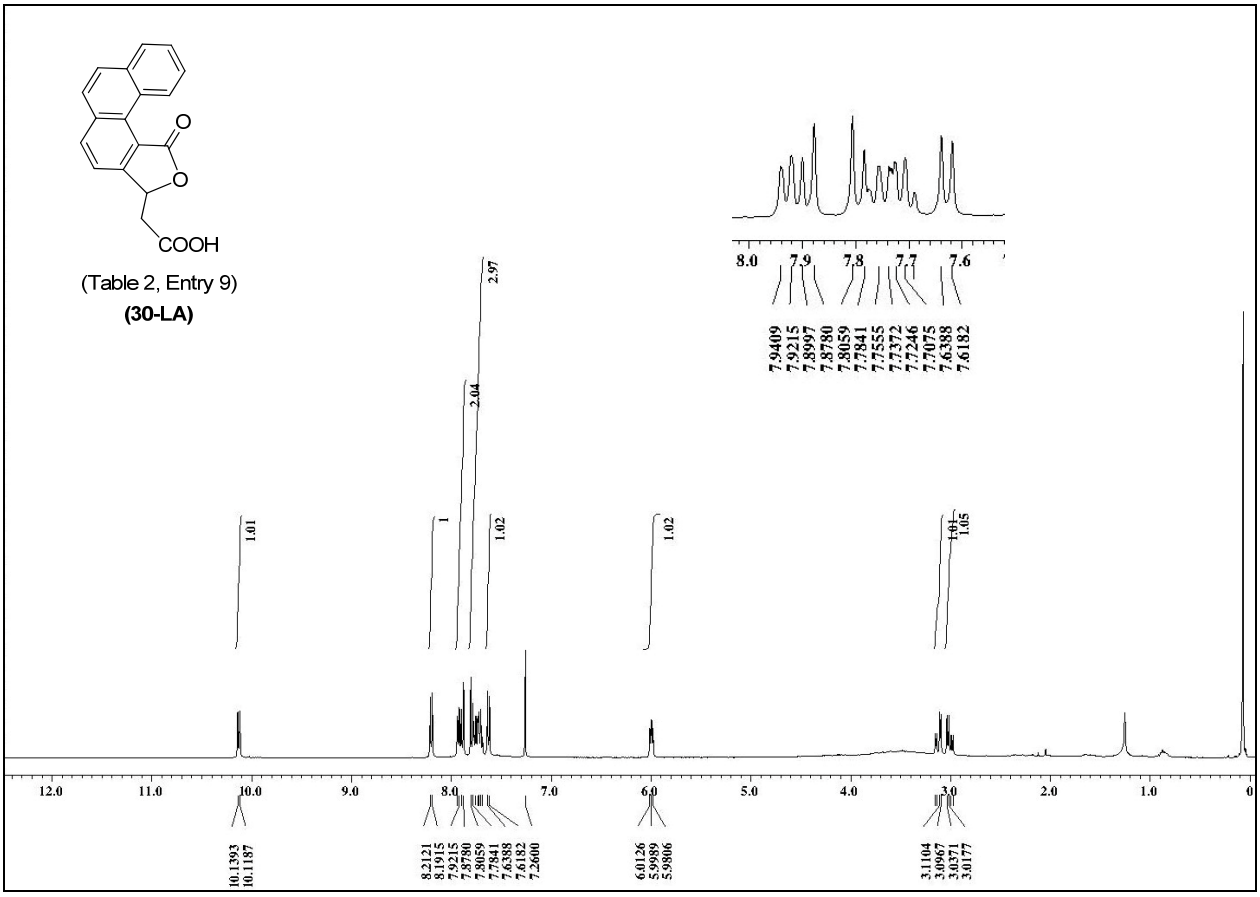


FIGURE S53. ^{1}H NMR spectrum of 2-(1-oxo-1,3-dihydrophenanthro[2,1-c]furan-3-yl)acetic acid in $CDCl_3$.

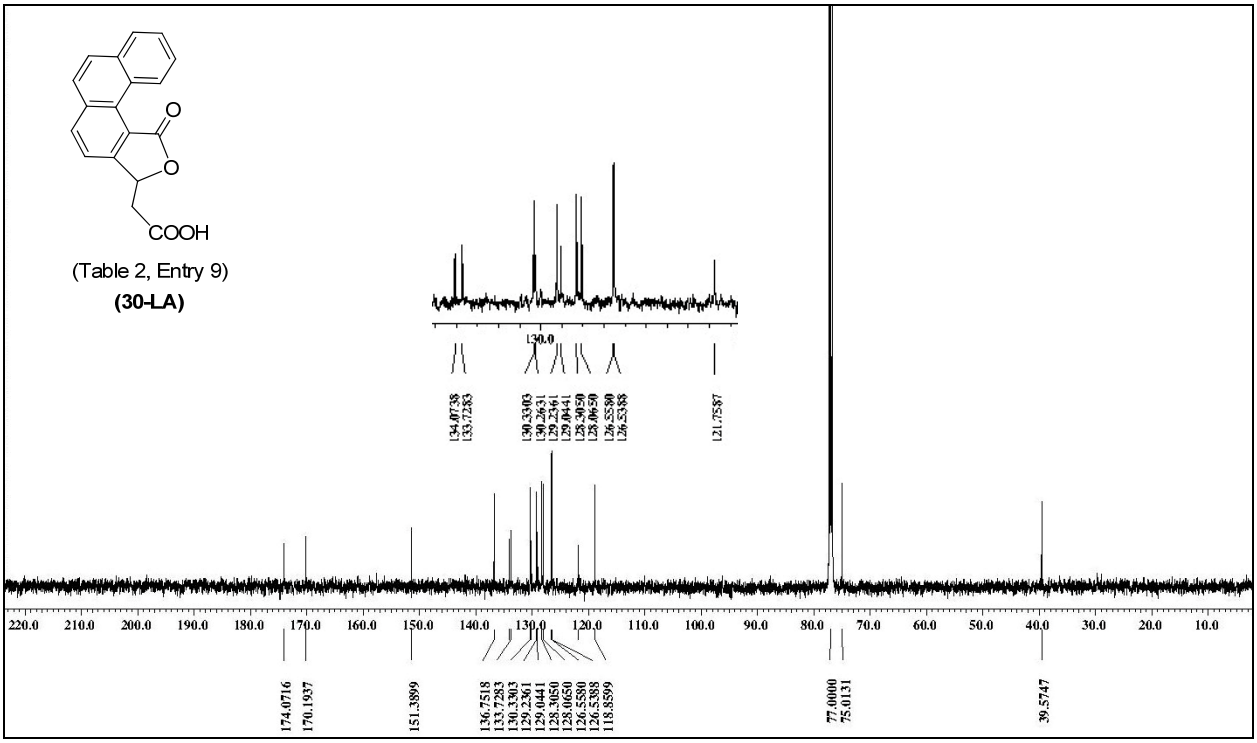


FIGURE S54. ^{13}C NMR spectrum of 2-(1-oxo-1,3-dihydrophenanthro[2,1-c]furan-3-yl)acetic acid in $CDCl_3$.

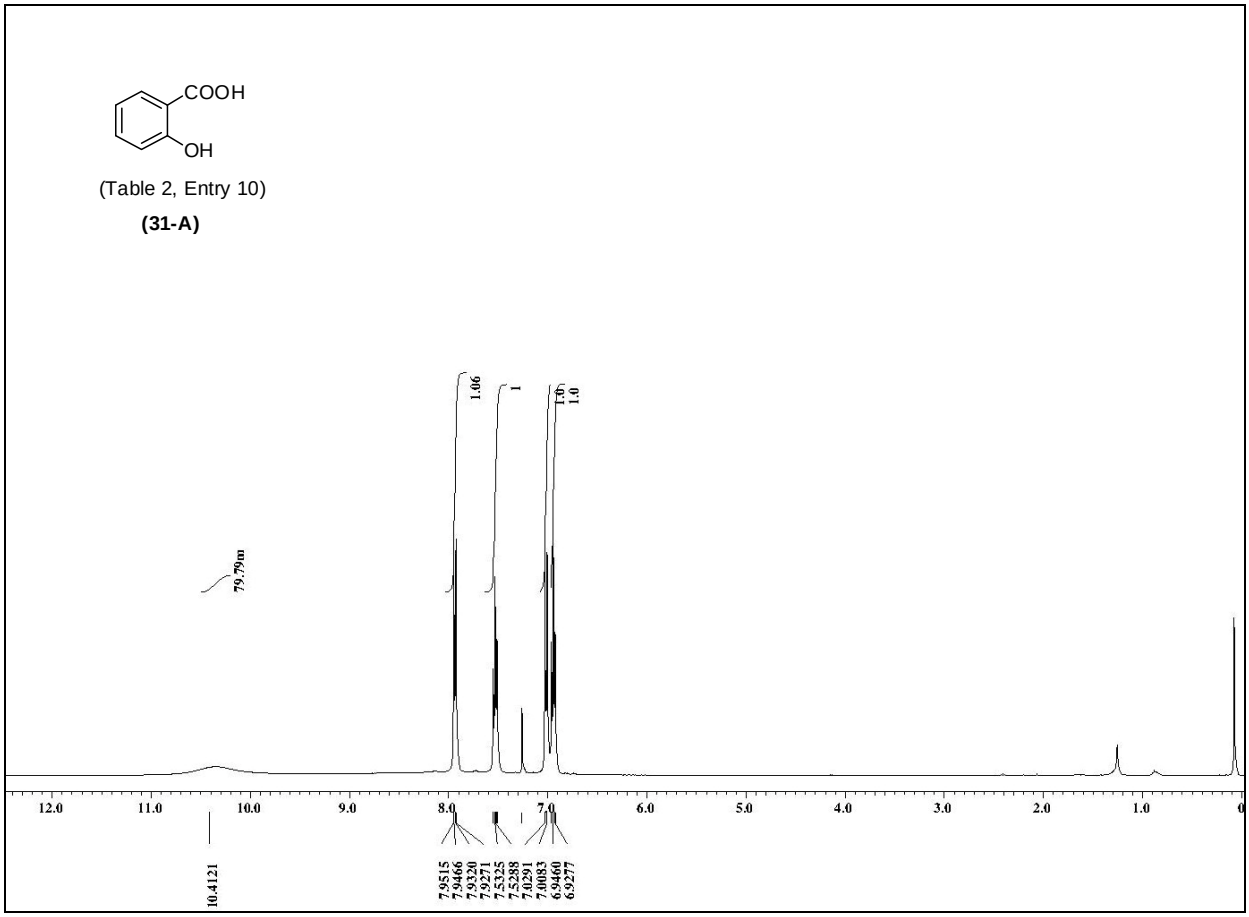


FIGURE S55. ^{1}H NMR spectrum of 2-hydroxybenzoic acid in $CDCl_3$.

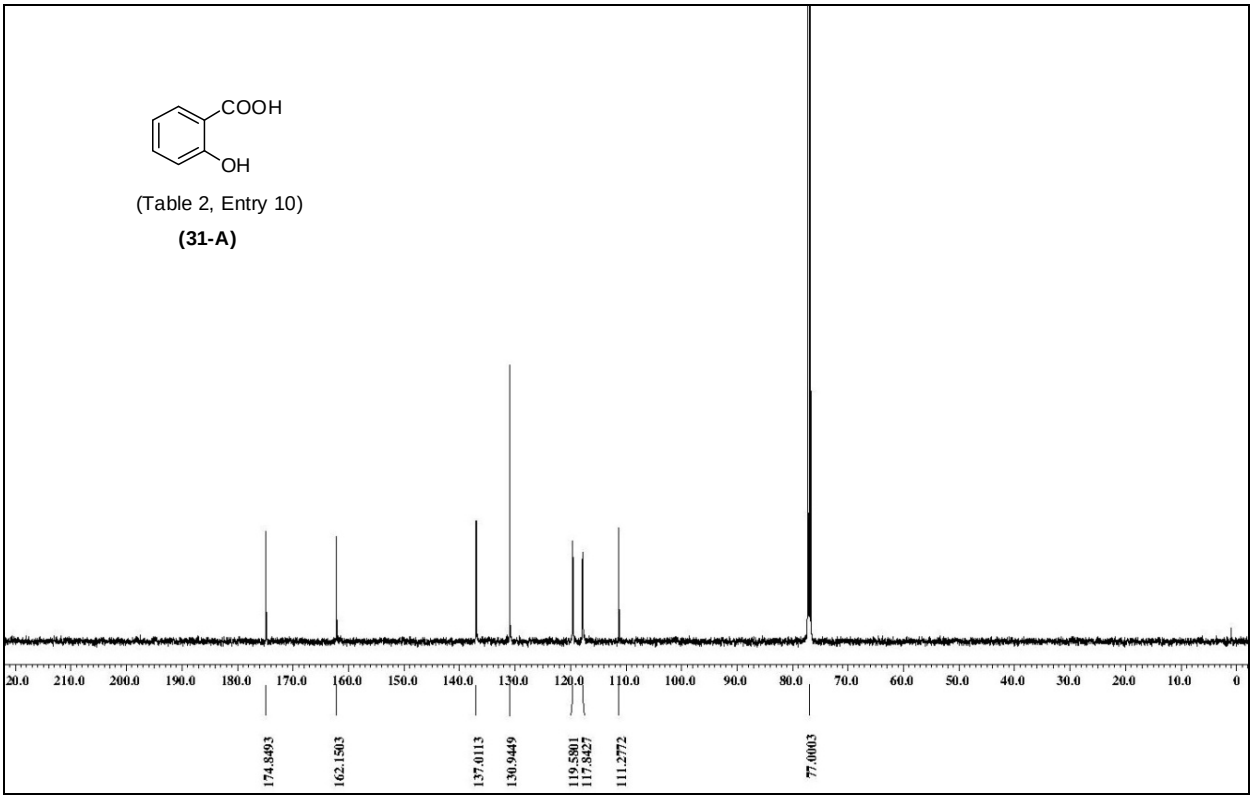


FIGURE S56. ^{13}C NMR spectrum of 2-hydroxybenzoic acid in $CDCl_3$.

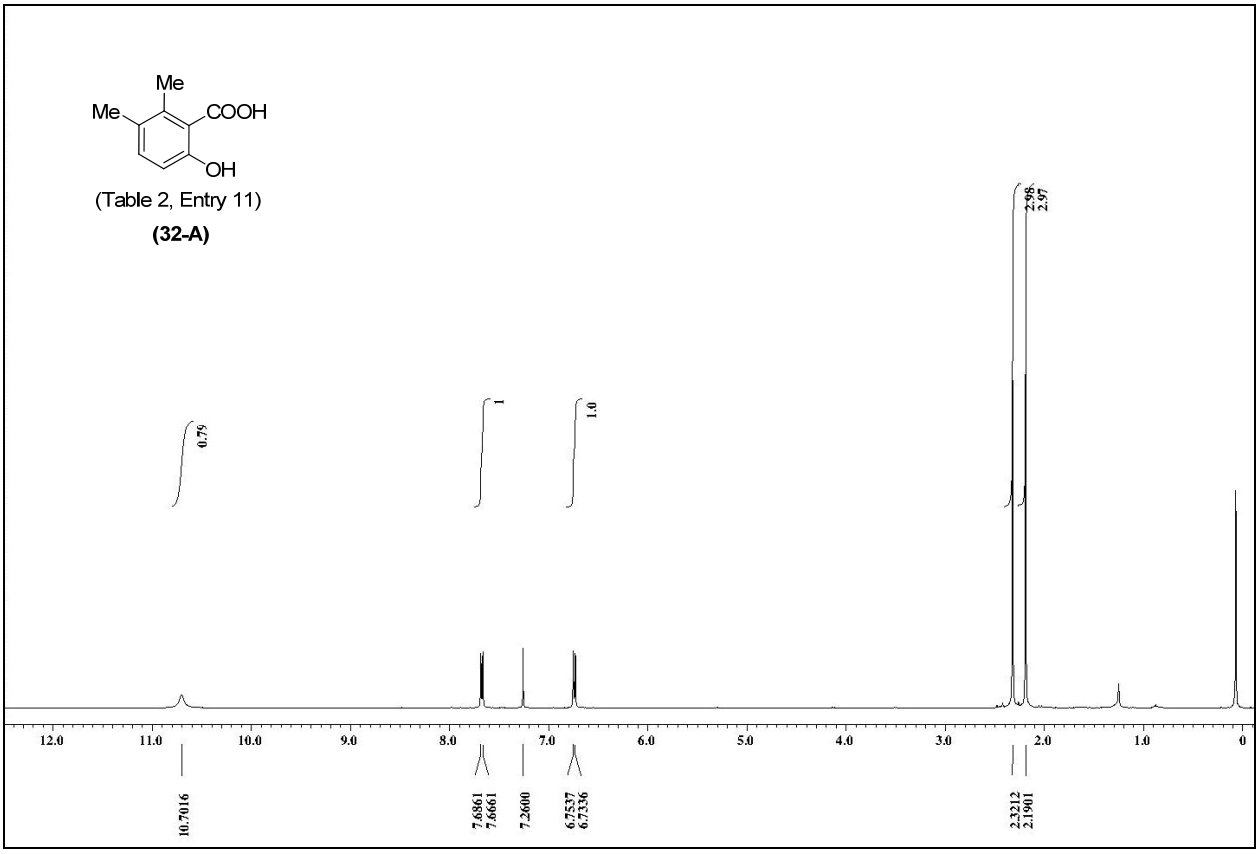


FIGURE S57. ^{1}H NMR spectrum of 5,6-dimethyl-2-hydroxybenzoic acid in $CDCl_3$.

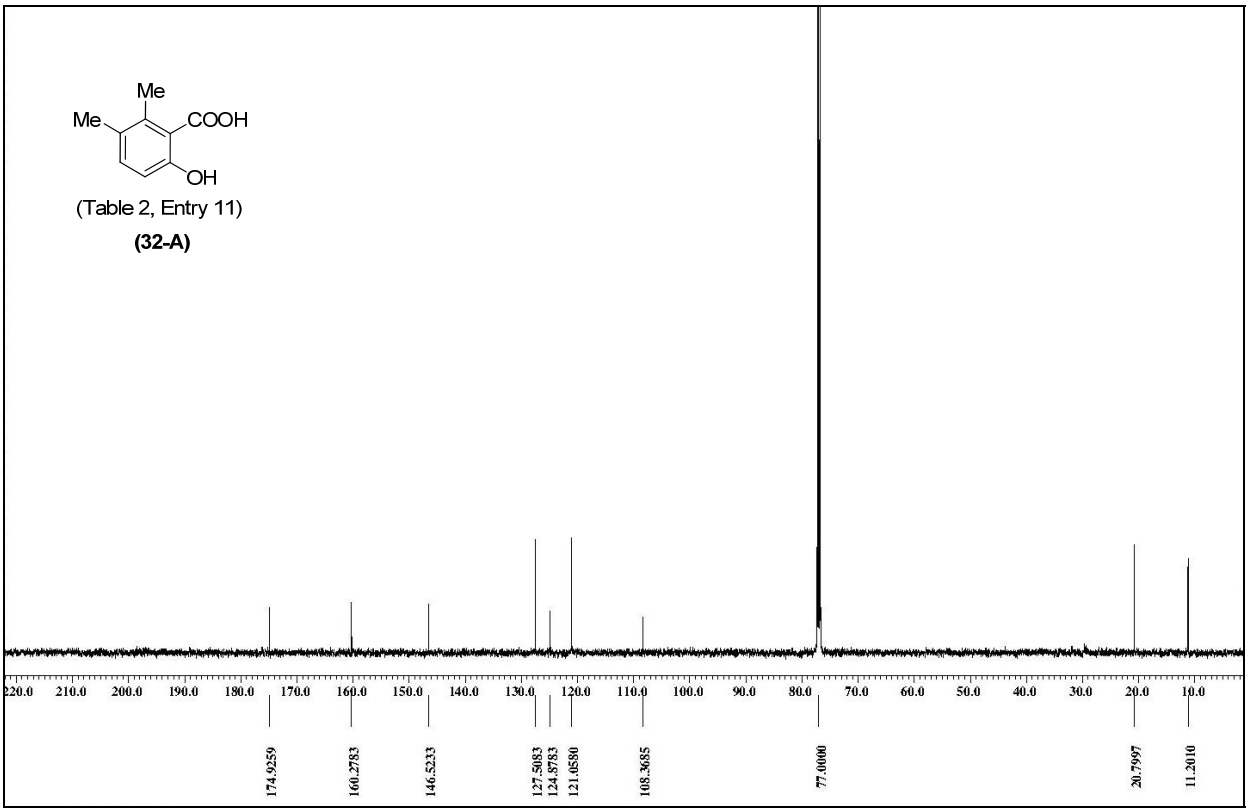


FIGURE S58. ^{13}C NMR spectrum of 5,6-dimethyl-2-hydroxybenzoic acid in $CDCl_3$.

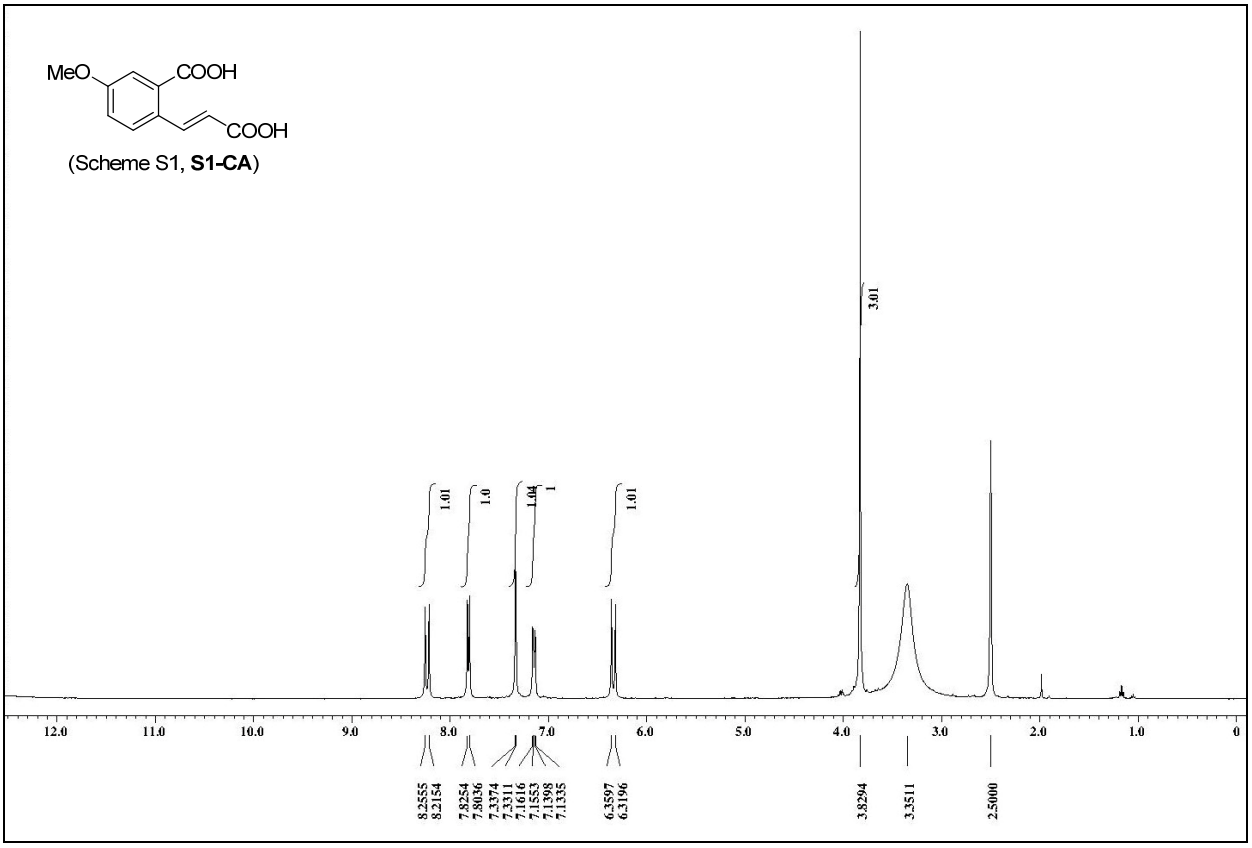


FIGURE S59. ^{1}H NMR spectrum of (*E*)-2-carboxy-4-methoxycinnamic acid in DMSO-d_6.

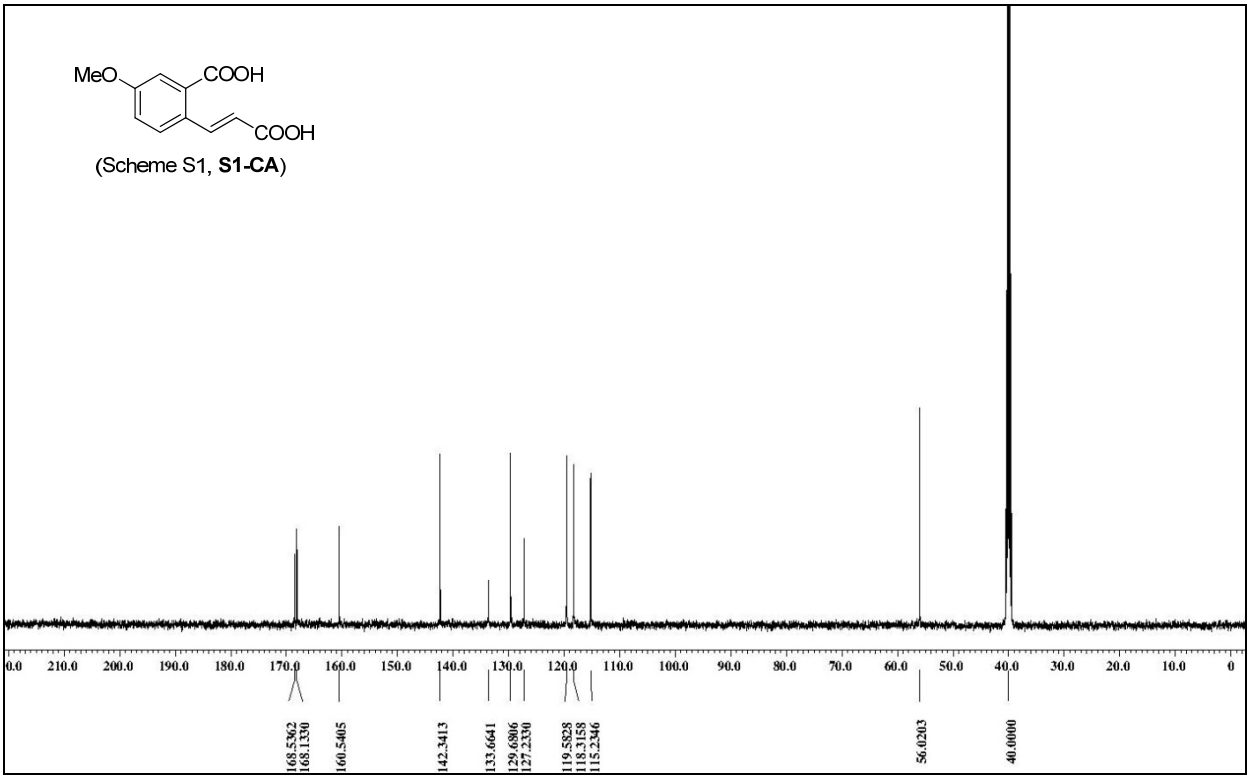


FIGURE S60. ^{13}C NMR spectrum of (*E*)-2-carboxy-4-methoxycinnamic acid in DMSO-d_6.

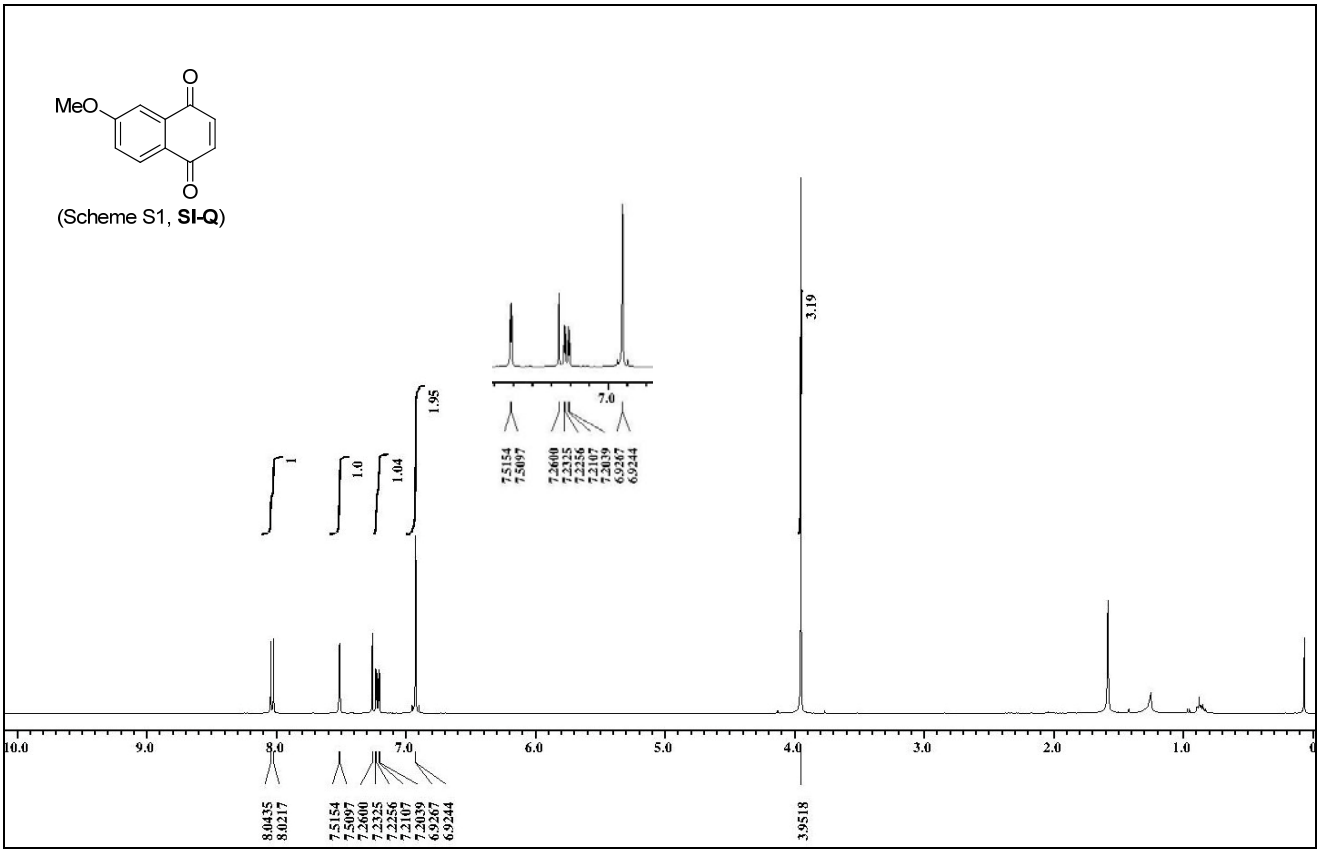


FIGURE 61. ^{1}H NMR spectrum of 6-methoxy-1,4-naphthoquinone in $CDCl_3$.