Supporting information

Bifunctional organocatalysts for conversion of CO_2, epoxides and aryl amines to 3-aryl-2-oxazolidinones

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1. Synthesis and Characterization for Organocatalysts

General Procedure for Synthesis of Organocatalysts

A mixture of 2,6-dibromopyridine (5 mmol), amines (10 mmol), CuI (1 mmol), *tetra*-methylethane-1,2-diamine (2 mmol) and K_2CO_3 (15 mmol) in DMSO (20 mL) was stirred for 30 min at room temperature, and then heated to 90 °C for 24 h under nitrogen atmosphere. Thereafter, 2-bromo-6-substituent-pyridine (5 mmol), amino acids (7.5 mmol), CuI (1 mmol), *N*,*N*-dimethylethylenediamine (2 mmol) and K_2CO_3 (15 mmol) in DMSO (20 mL) was allowed to react under nitrogen atmosphere. The resultant 2,6-disubstituent-pyridine (5 mmol), and alkyl halides (10 mL) was heated to the desired temperature and the reaction stirred for 8 h under air atmosphere, and affording a series of multifunctional organocatalysts **1a−g**. The solvent was concentrated under vacuum and the product of organocatalysts **1a−g** was isolated by flash chromatography.

Characterization for Organocatalysts

Data for **1a** are as follows: Purification by flash chromatography (DCM/MeOH = 20:1): a yellowish solid (1.468 g, 61%), M.P. = 159.1–159.6 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.68 (br., 1H, COOH), 10.29 (s, 1H, NCHN), 8.39 (d, J = 8.0 Hz, 1H), 8.20 (d, J = 7.2 Hz, 1H), 7.81-7.71 (m, 3H), 7.47 (d, J = 8.0 Hz, NH), 7.08 (d, J = 7.2 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 4.55 (t, J = 6.8 Hz, 2H), 4.33 (t, J = 5.6 Hz, 1H), 2.23 (sext, J = 6.8 Hz, 1H), 2.02 (sext, J = 7.2 Hz, 2H), 1.05-0.98 (m, 9H), ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 174.49, 158.93, 146.05, 142.14, 140.17, 132.09, 129.95, 127.80, 127.43, 116.44, 114.39, 103.92, 59.74, 49.04, 30.33, 22.50, 19.80, 18.85, 11.26, ppm; HRMS (MALDI) calcd for $C_{20}H_{25}N_4O_2I$ $[M\text{-}I]^+$ 353.1972, found 353.1969.

Data for **1b** are as follows: Purification by flash chromatography (DCM/MeOH = 25:1): a yellowish solid (1.227 g, 49%), M.P. = 113.2–114.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 12.66 (br., 1H, COOH), 10.27 (s, 1H, NCHN), 8.37 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 7.6 Hz, 1H), 7.80-7.70 (m, 3H), 7.62 (d, J = 8.0 Hz, NH), 7.06 (d, J = 7.2

Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 4.53 (t, *J* = 7.6 Hz, 2H), 4.41-4.35 (m, 1H), 2.02 (sext, *J* = 7.6 Hz, 2H), 1.75-1.60 (m, 2H), 1.01-0.95 (m, 6H), 0.88 (d, *J* = 6.4 Hz, 3H), ppm; ^{13}C NMR (100 MHz, DMSO-*d*$_6$): *δ* 175.72, 158.67, 146.27, 142.17, 140.25, 132.09, 130.01, 127.72, 127.43, 116.46, 114.38, 103.98, 52.65, 49.04, 24.98, 23.36, 22.47, 21.81, 11.27, ppm; HRMS (MALDI) calcd for $C_{21}H_{27}N_4O_2I$ $[M-I]^+$ 367.2129, found 367.2125.

Data for **1c** are as follows: Purification by flash chromatography (DCM/MeOH = 15:1): a yellowish solid (0.905 g, 35%), M.P. = 93.5–93.9 °C; ^{1}H NMR (400 MHz, DMSO-*d*$_6$): *δ* 12.75 (br., 1H, COOH), 10.29 (s, 1H, NCHN), 8.40 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.82-7.68 (m, 3H), 7.67 (d, *J* = 8.0 Hz, NH), 7.09 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 4.59-4.52 (m, 3H), 2.67-2.61 (m, 2H), 2.07-2.00 (m, 6H), 1.00 (t, *J* = 7.6 Hz, 3H), ppm; ^{13}C NMR (100 MHz, DMSO-*d*$_6$): *δ* 175.00, 158.65, 146.24, 142.18, 140.33, 132.09, 129.99, 127.76, 127.44, 116.55, 114.37, 104.15, 53.06, 49.05, 31.18, 30.38, 22.48, 14.97, 11.27, ppm; HRMS (MALDI) calcd for $C_{20}H_{25}N_4O_2SI$ $[M-I]^+$ 385.1693, found 385.1699.

Data for **1d** are as follows: Purification by flash chromatography (DCM/MeOH = 10:1): a yellowish solid (1.309 g, 49%), M.P. = 115.6–116.3 °C; ^{1}H NMR (400 MHz, DMSO-*d*$_6$): *δ* 12.90 (br., 1H, COOH), 10.25 (s, 1H, NCHN), 8.28 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.77-7.73 (m, 3H), 7.71 (d, *J* = 8.0 Hz, NH), 7.32-7.25 (m, 4H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 4.70-4.66 (m, 1H), 4.52 (t, *J* = 7.6 Hz, 2H), 3.22 (dd, *J* = 14.0 Hz, 4.8 Hz, 1H), 3.02 (dd, *J* = 14.0 Hz, 4.8 Hz, 1H), 2.01 (sext, *J* = 7.6 Hz, 2H), 0.99 (t, *J* = 7.6 Hz, 3H), ppm; ^{13}C NMR (100 MHz, DMSO-*d*$_6$): *δ* 174.52, 158.45, 146.08, 142.16, 140.32, 138.41, 132.07, 129.96, 129.58, 128.66, 127.78, 127.42, 126.91, 116.35, 114.39, 104.14, 55.91, 49.02, 37.53, 22.49, 11.25, ppm; HRMS (MALDI) calcd for $C_{24}H_{25}N_4O_2I$ $[M-I]^+$ 401.1972, found 401.1970.

Data for **1e** are as follows: Purification by flash chromatography (DCM/MeOH = 40:1): a yellowish solid (1.671 g, 61%), M.P. = 136.5–137.2 °C; ^{1}H NMR (400 MHz, DMSO-*d*$_6$): *δ* 12.80 (br., 1H, COOH), 10.28 (s, 1H, NCHN), 9.19 (s, 1H, OH), 8.28 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.78-7.66 (m, 3H), 7.65 (d, *J* = 8.0 Hz, NH),

7.11 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 2H), 4.61-4.52 (m, 3H), 3.09 (dd, *J* = 14.0 Hz, 4.8 Hz, 1H), 2.94-2.88 (m, 1H), 2.02 (sext, *J* = 7.6 Hz, 2H), 0.99 (t, *J* = 7.6 Hz, 3H), ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 174.94, 158.51, 156.32, 146.09, 142.04, 140.21, 132.04, 130.53, 129.91, 128.58, 127.79, 127.39, 116.46, 115.41, 114.38, 103.87, 56.55, 49.05, 36.89, 22.50, 11.25, ppm; HRMS (MALDI) calcd for $C_{24}H_{25}N_4O_3I$ $[M\text{-}I]^+$ 417.1921, found 417.1911.

Data for **1f** are as follows: Purification by flash chromatography (DCM/MeOH = 25:1): a yellowish solid (1.056 g, 50%), M.P. = 141.0–141.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.29 (s, 1H, NCHN), 9.20 (s, 1H, OH), 8.30 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.77-7.70 (m, 3H), 7.61 (d, *J* = 8.0 Hz, NH), 7.10 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 4.58-4.51 (m, 3H), 3.10 (dd, *J* = 14.0 Hz, 4.8 Hz, 1H), 2.93-2.87 (m, 1H), 2.01 (sext, *J* = 7.6 Hz, 2H), 0.99 (t, *J* = 7.6 Hz, 3H), ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 174.70, 158.51, 156.36, 146.11, 142.15, 140.21, 132.07, 130.51, 129.96, 128.51, 127.78, 127.39, 116.46, 115.40, 114.36, 103.87, 56.42, 49.00, 36.87, 22.49, 11.24, ppm; HRMS (MALDI) calcd for $C_{24}H_{25}N_4O_3Br$ $[M\text{-}Br]^+$ 417.1921, found 417.1917.

Data for **1g** are as follows: Purification by flash chromatography (DCM/MeOH = 20:1): a yellowish solid (0.972 g, 46%), M.P. = 112.3–112.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.38 (s, 1H, NCHN), 8.37 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.70-7.65 (m, 3H), 7.47 (s, NH), 7.06 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 2H), 4.52 (t, *J* = 7.6 Hz, 3H), 3.10 (dd, *J* = 14.0 Hz, 4.8 Hz, 1H), 2.89-2.82 (m, 1H), 1.98 (sext, *J* = 7.6 Hz, 2H), 0.99 (t, *J* = 7.6 Hz, 3H), ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 175.19, 158.72, 156.23, 146.13, 142.10, 139.87, 132.03, 130.50, 129.90, 129.24, 127.82, 127.26, 116.71, 115.27, 114.22, 102.97, 57.49, 48.92, 37.20, 22.51, 11.21, ppm; HRMS (MALDI) calcd for $C_{24}H_{25}N_4O_3Cl$ $[M\text{-}Cl]^+$ 417.1921, found 417.1913.

2. Synthesis of 3-Aryl-2-Oxazolidinones

General procedure for the synthesis of 3-aryl-2-oxazolidinones

Epoxides (2.0 mL), aryl amines (2.0 mmol), organocatalyst (0.05 mmol), and DBU (0.4 mmol) were introduced into a 25 mL stainless steel autoclave that was equipped with a magnetic stirrer. The reactor was pressurized with CO_2 to 0.5 MPa and then heated at 90 °C for the required time. The reactor was cooled to room temperature after the reaction. The reaction mixtures were added to brine (15 mL) and extracted three times with dichloromethane (3 × 15 mL). The solvent was removed under reduced pressure, and the products were isolated by flash chromatography.

3. NMR and IR Spectra for N-aryl-2-oxazolidinones

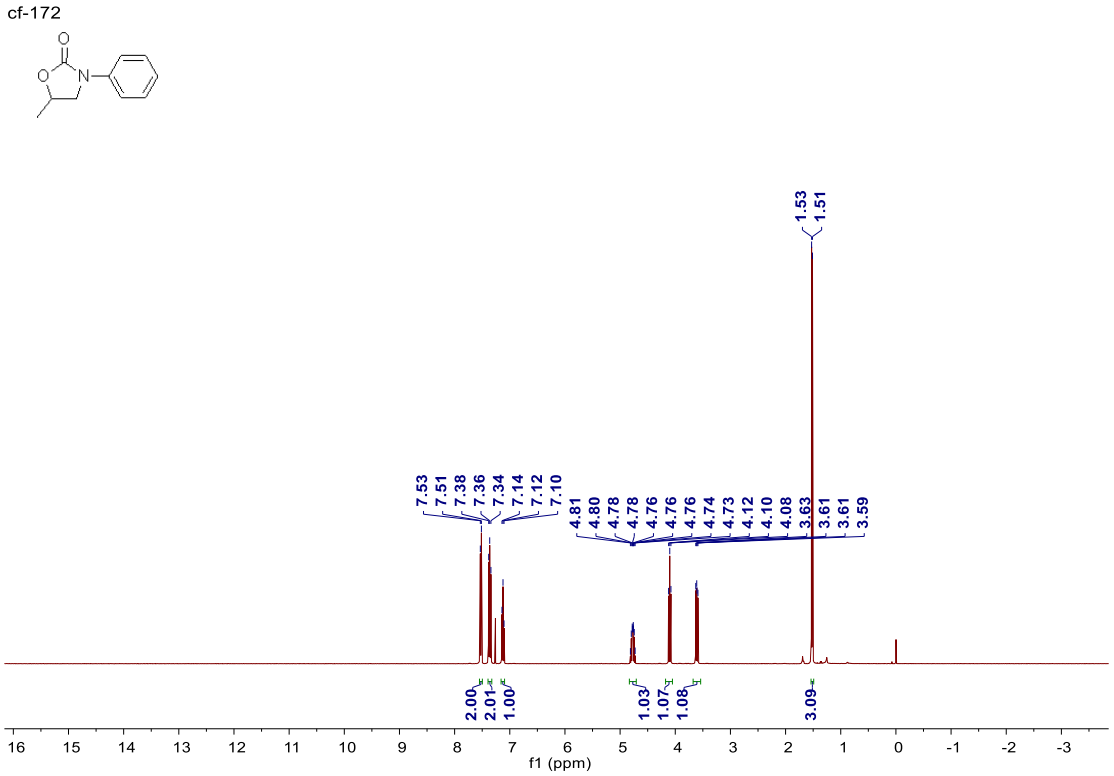

Figure S1. ^{1}H NMR spectra of oxazolidinones **4a**.

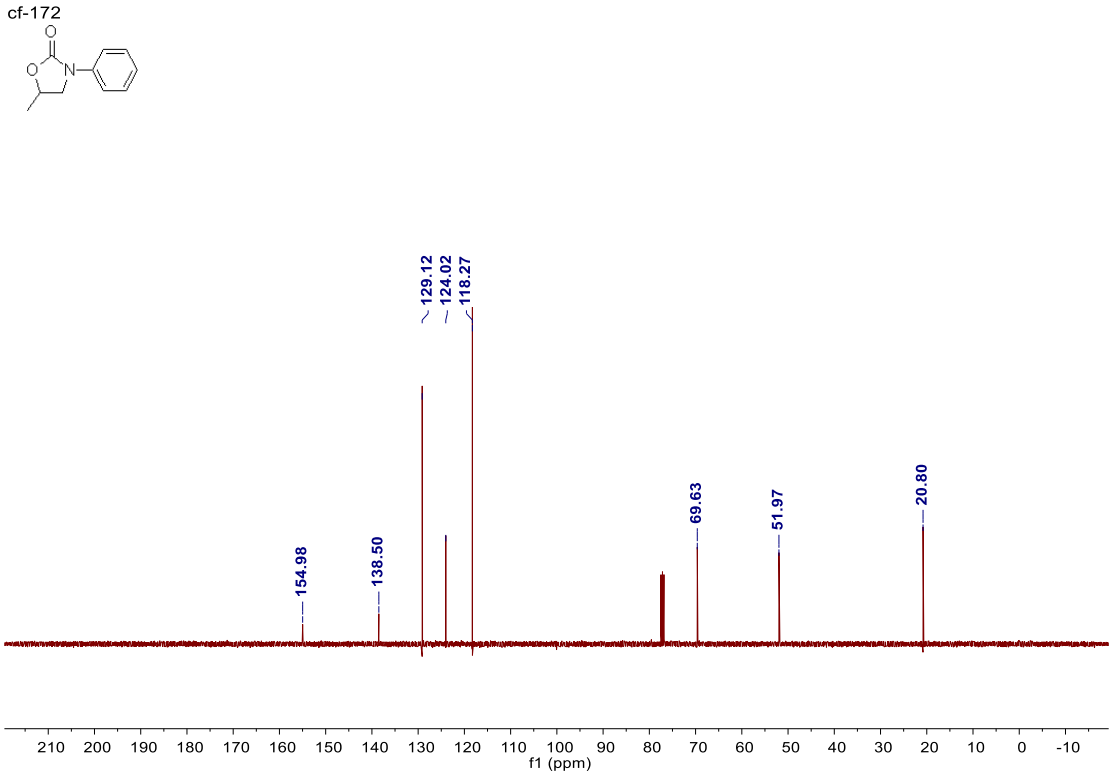

Figure S2. ^{13}C NMR spectra of oxazolidinones **4a**.

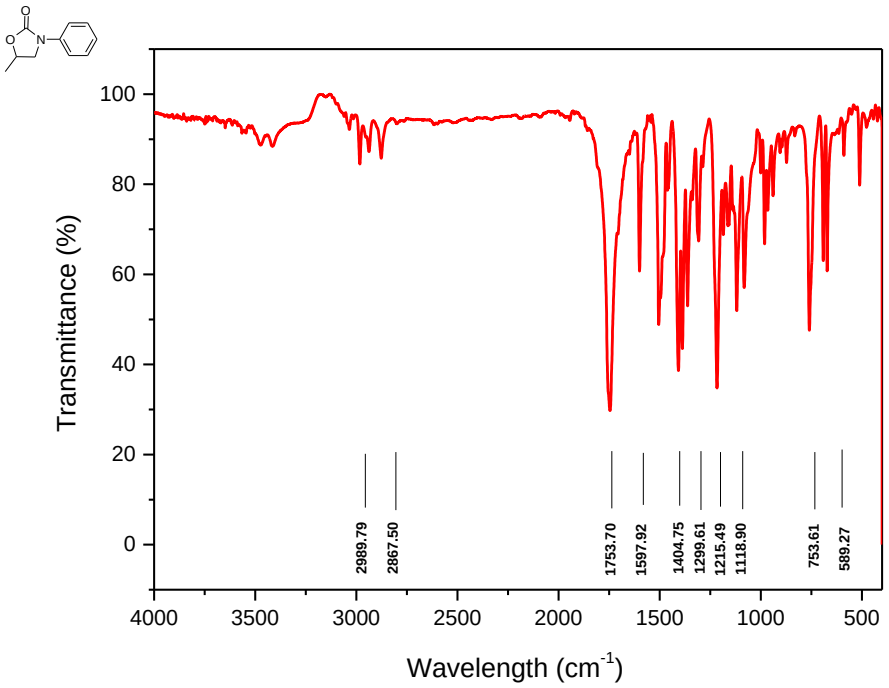

Figure S3. IR spectroscopic data of oxazolidinones **4a**.

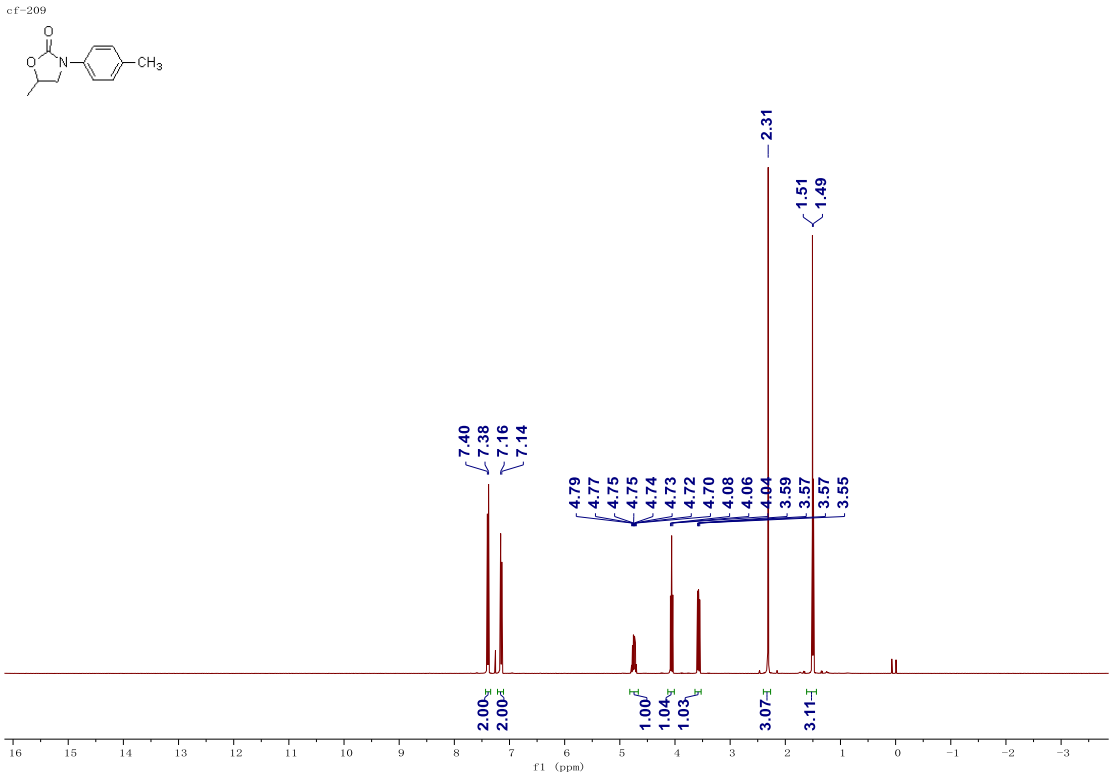

Figure S4. ^{1}H NMR spectra of oxazolidinones **4b**.

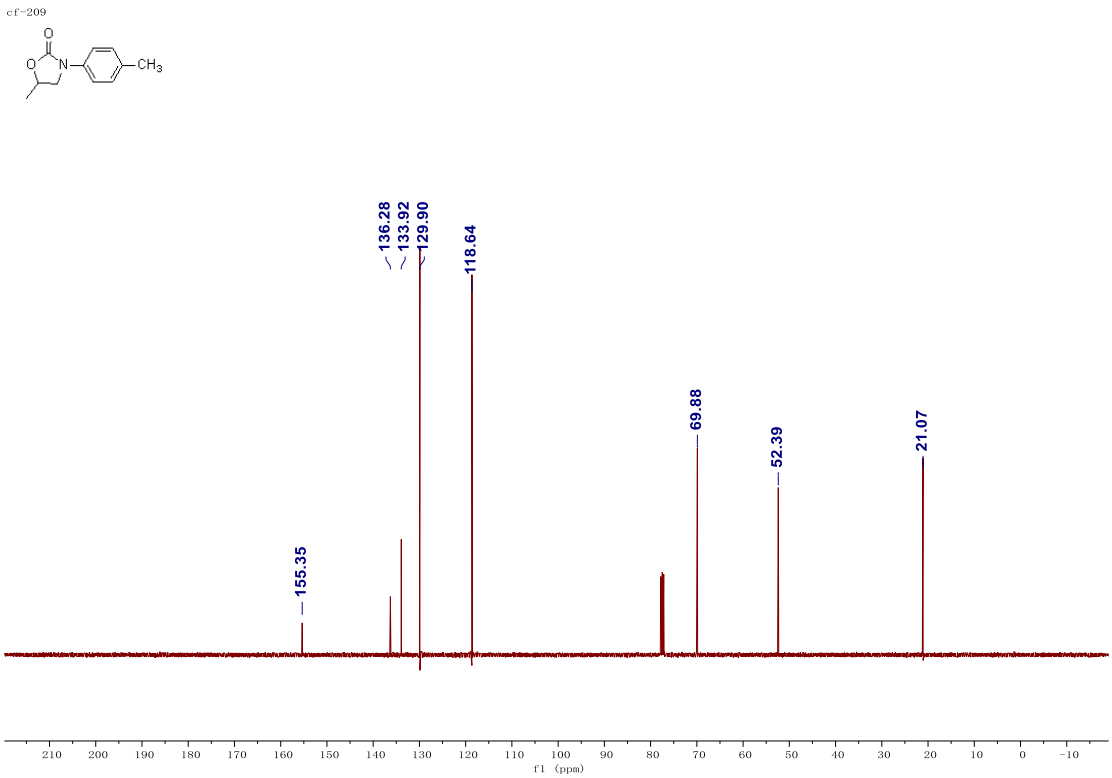

Figure S5. ^{13}C NMR spectra of oxazolidinones **4b**.

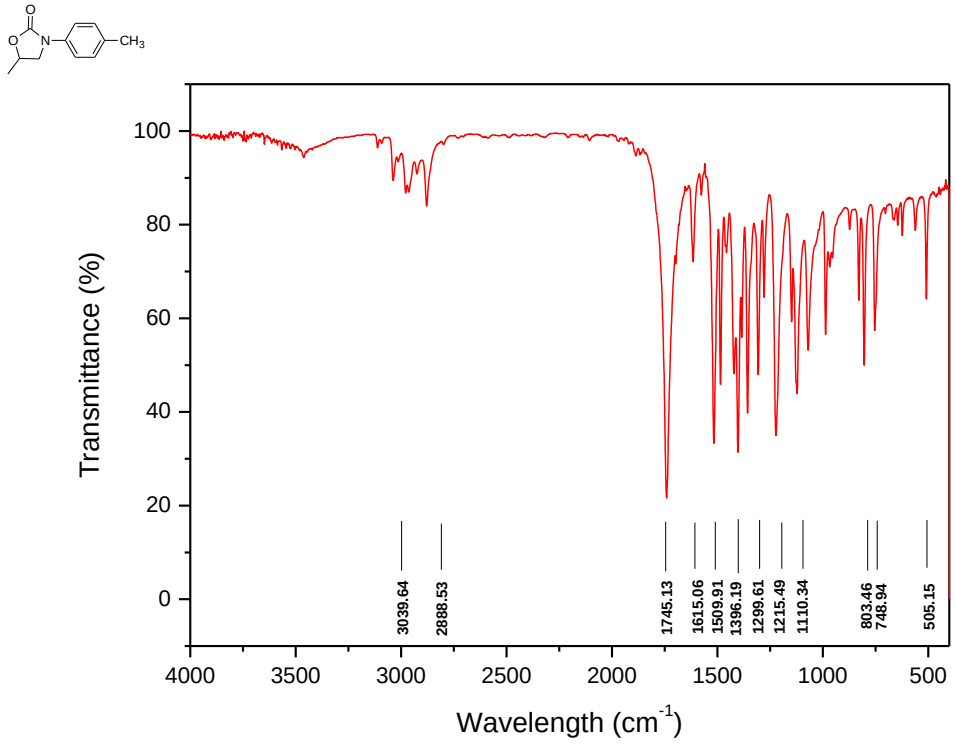

Figure S6. IR spectroscopic data of oxazolidinones **4b**.

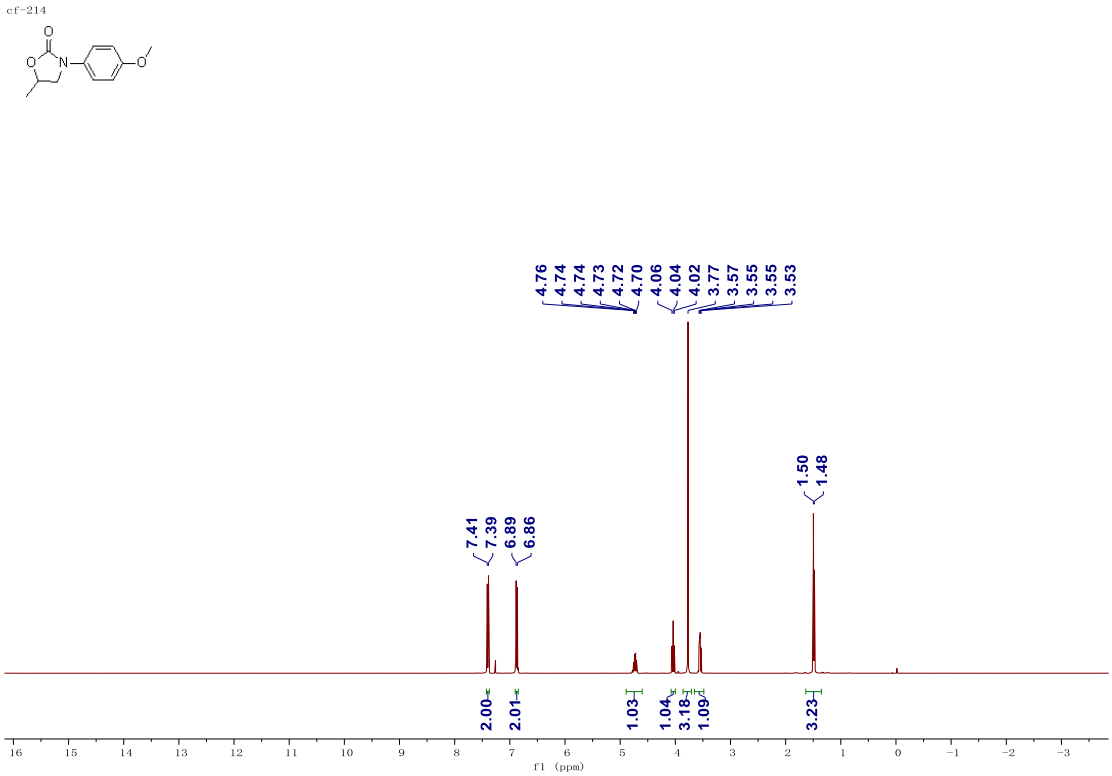

Figure S7. ^{1}H NMR spectra of oxazolidinones **4c**.

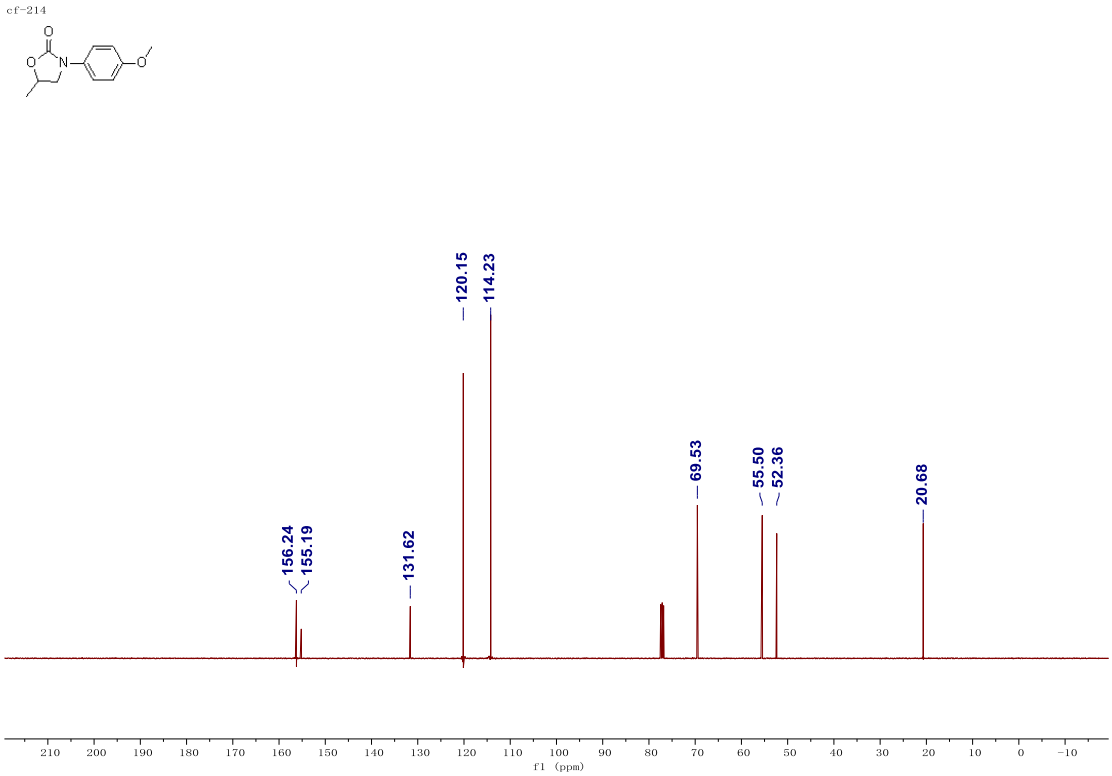

Figure S8. ^{13}C NMR spectra of oxazolidinones **4c**.

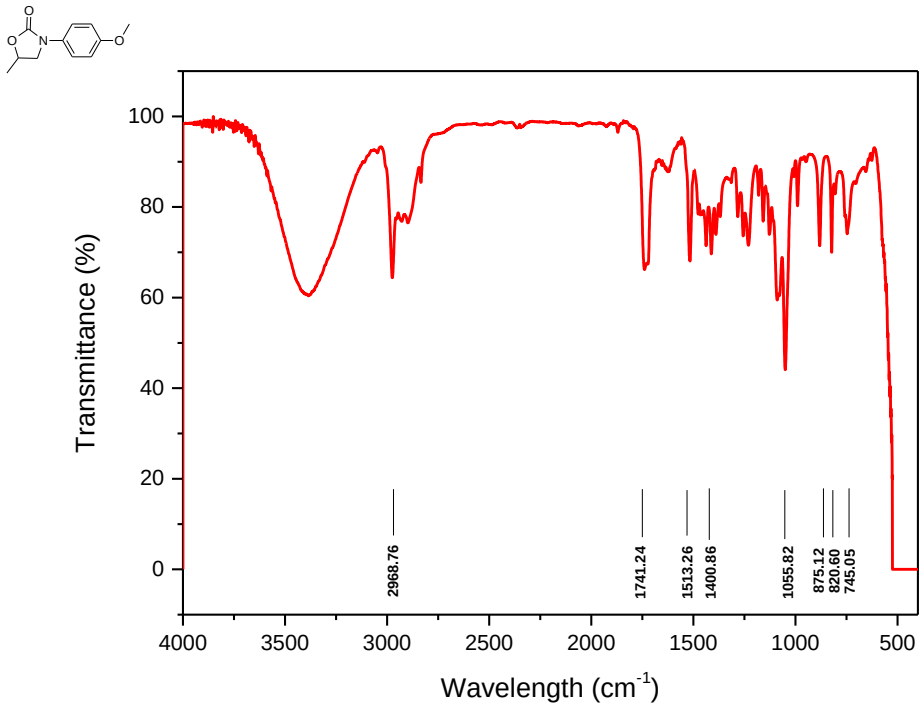

Figure S9. IR spectroscopic data of oxazolidinones **4c**.

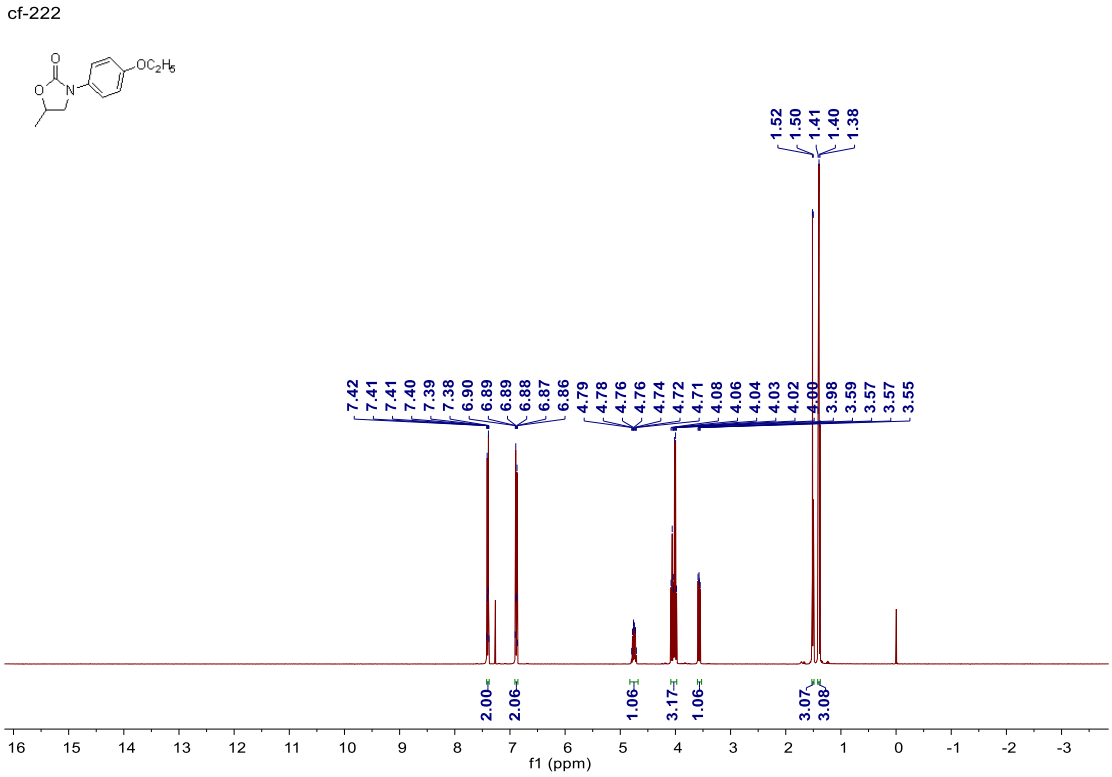

Figure S10. ^{1}H NMR spectra of oxazolidinones **4d**.

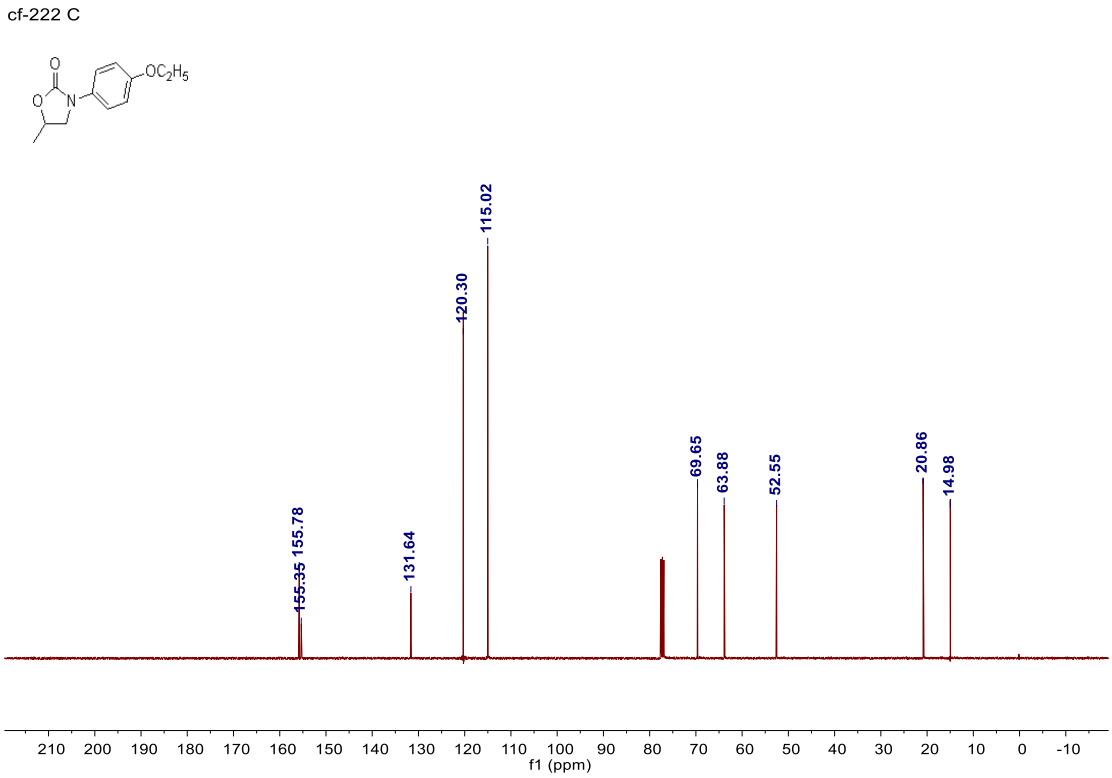

Figure S11. ^{13}C NMR spectra of oxazolidinones **4d**.

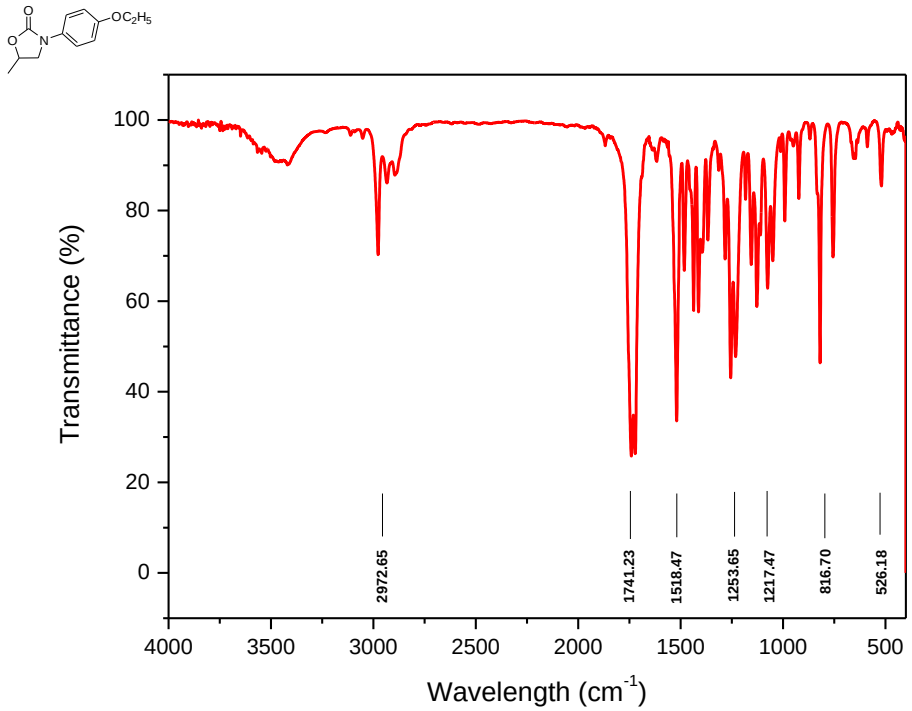

Figure S12. IR spectroscopic data of oxazolidinones **4d**.

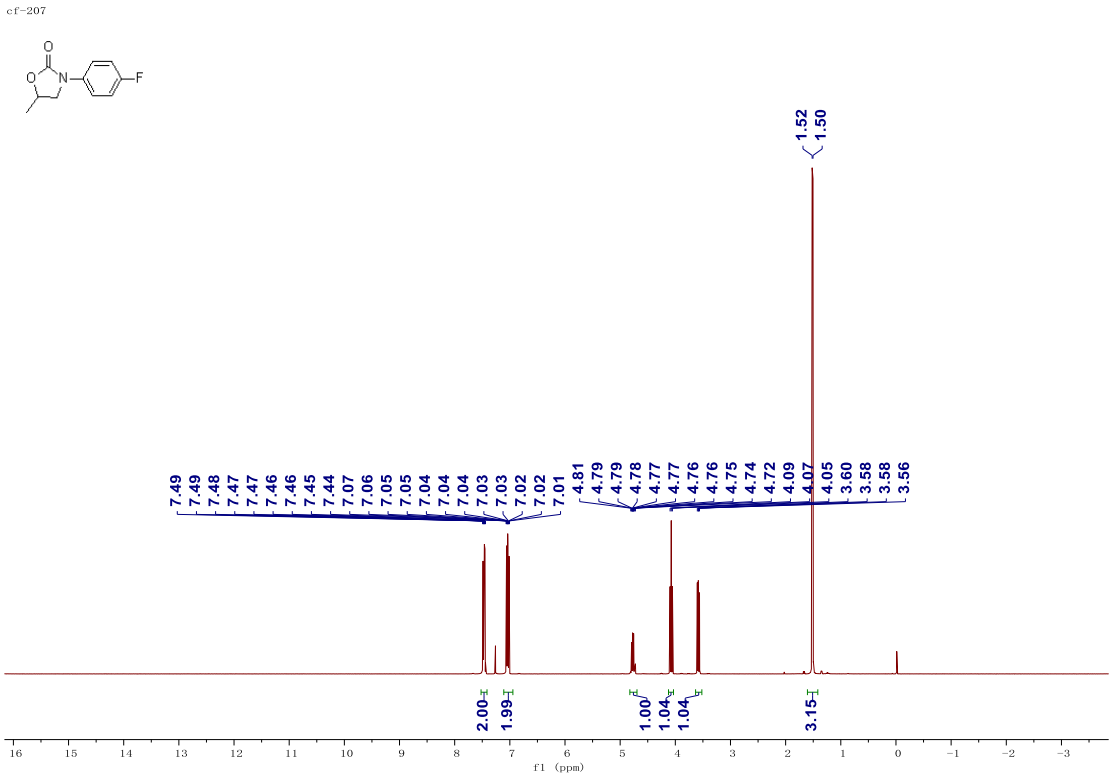

Figure S13. [1]H NMR spectra of oxazolidinones **4e**.

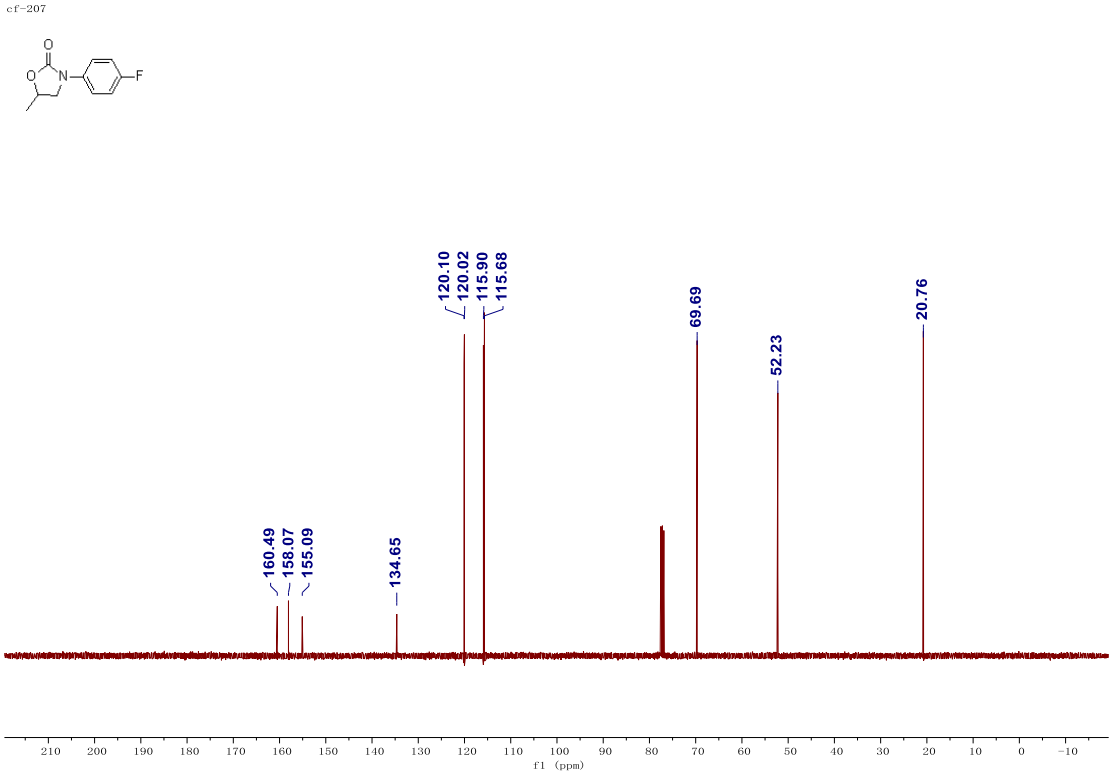

Figure S14. [13]C NMR spectra of oxazolidinones **4e**.

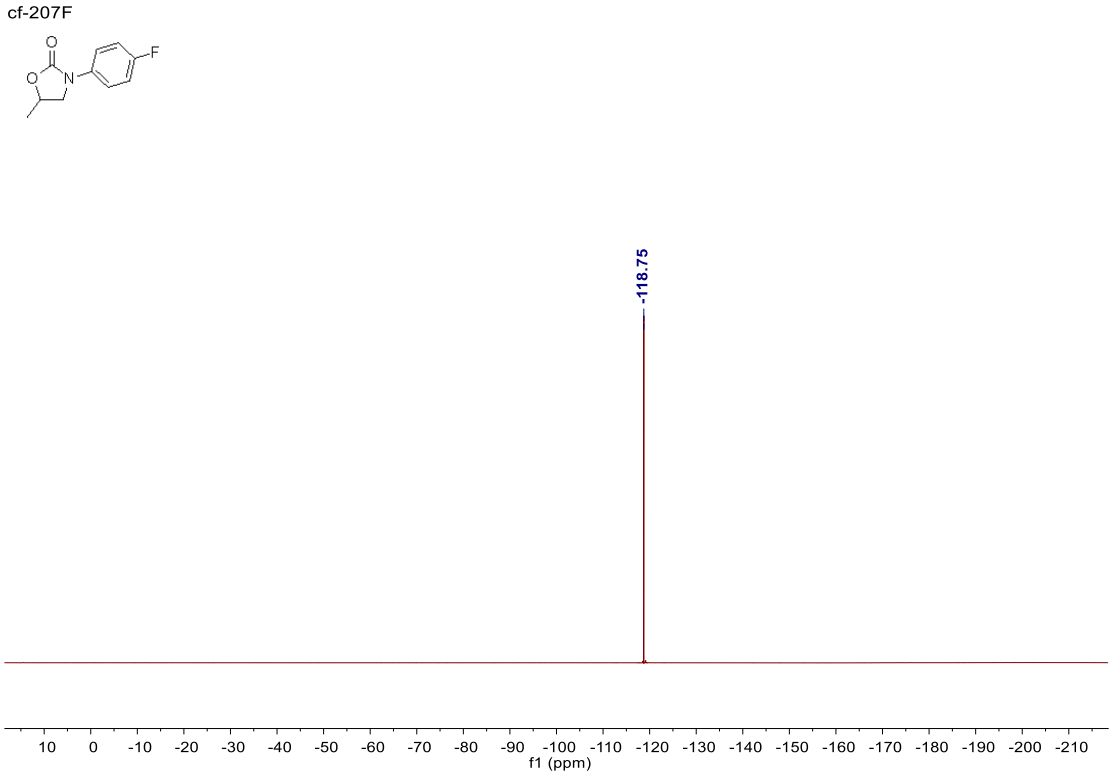

Figure S15. ^{19}F NMR spectra of oxazolidinones **4e**.

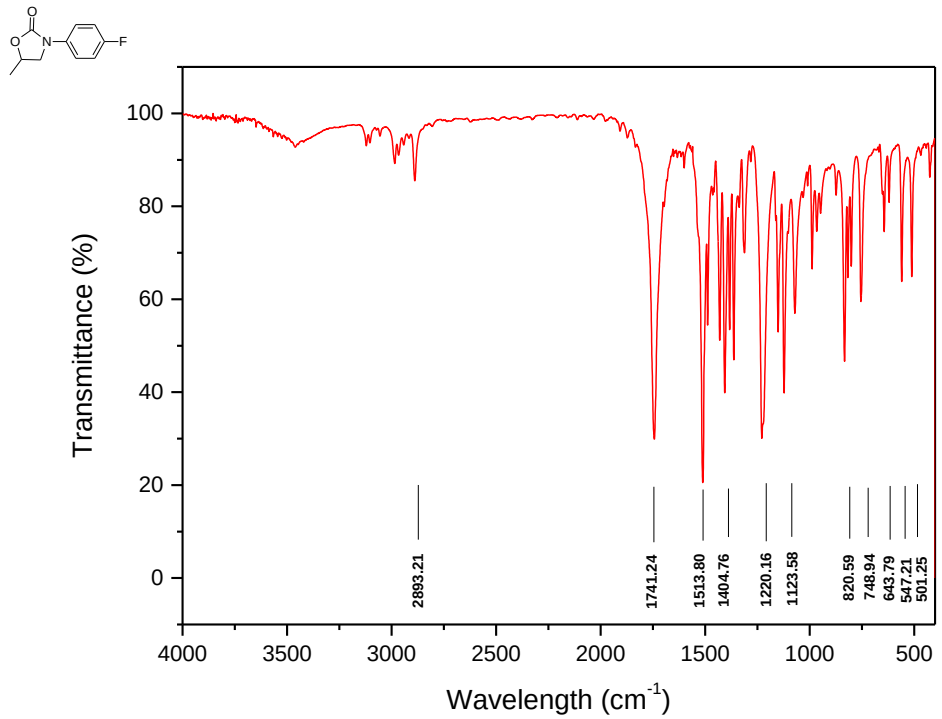

Figure S16. IR spectroscopic data of oxazolidinones **4e**.

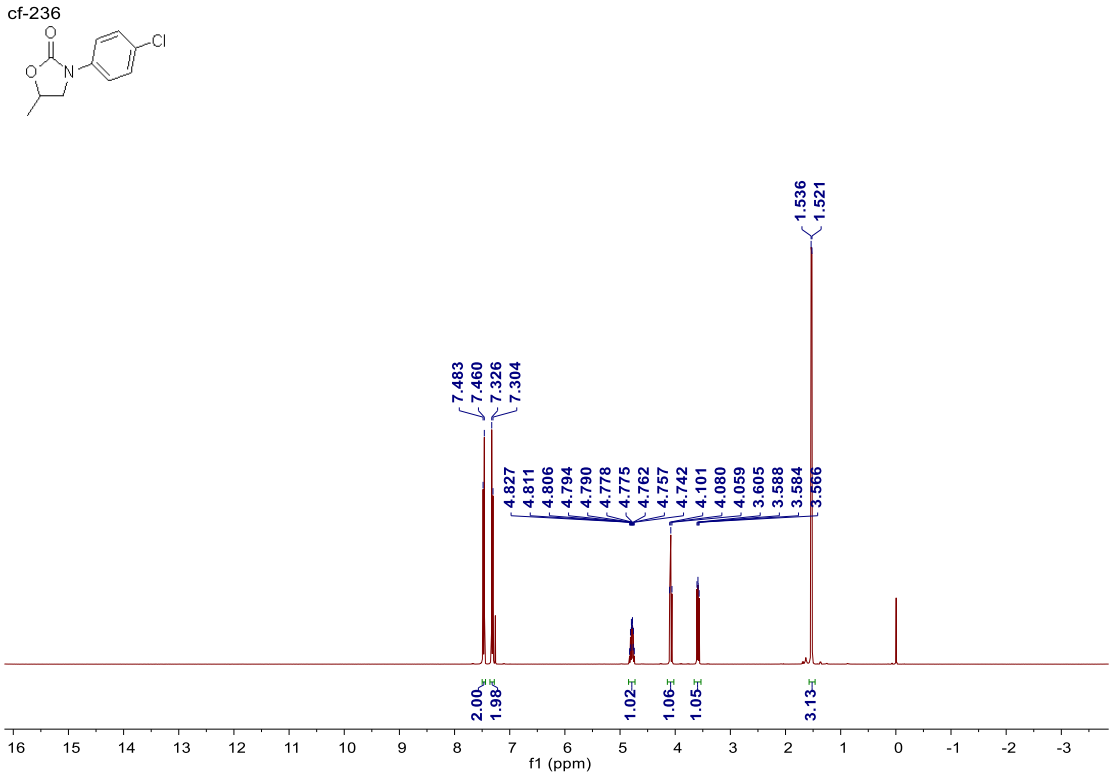

Figure S17. [1]H NMR spectra of oxazolidinones **4f**.

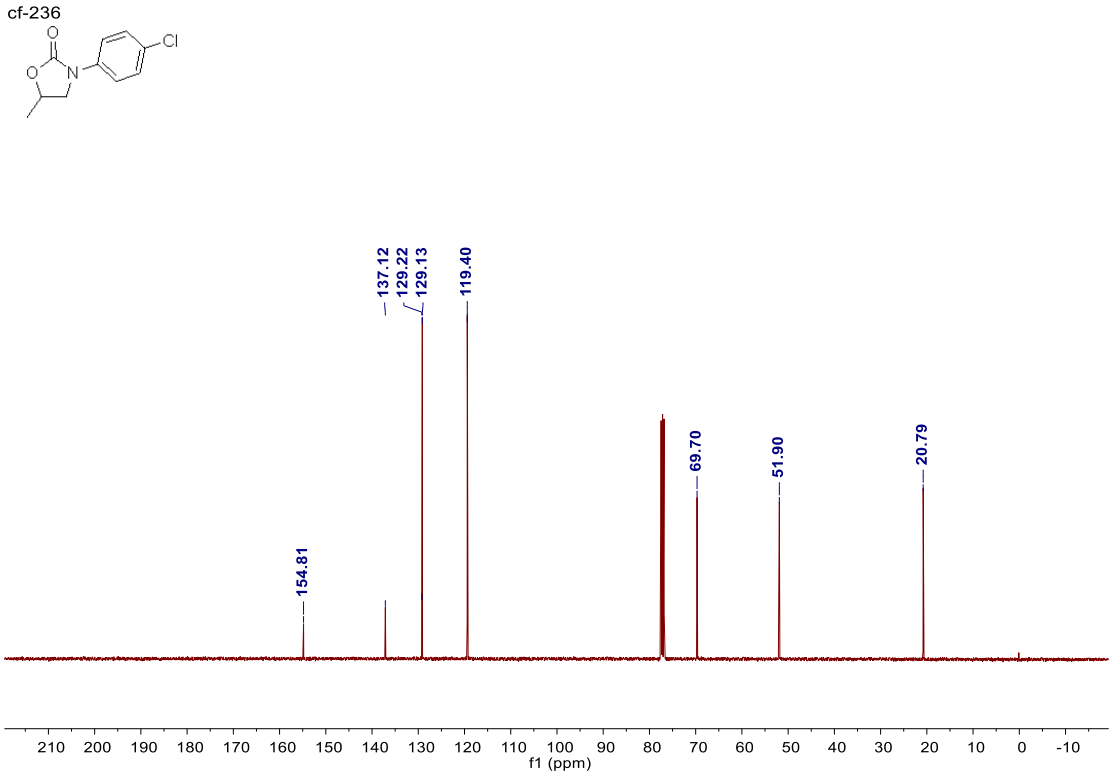

Figure S18. [13]C NMR spectra of oxazolidinones **4f**.

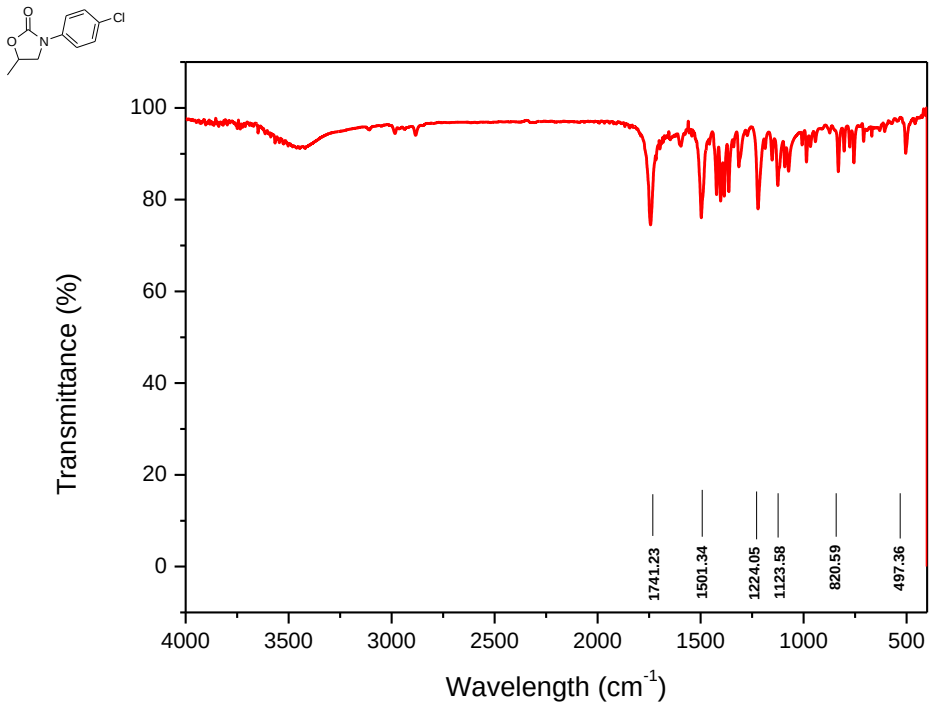

Figure S19. IR spectroscopic data of oxazolidinones **4f**.

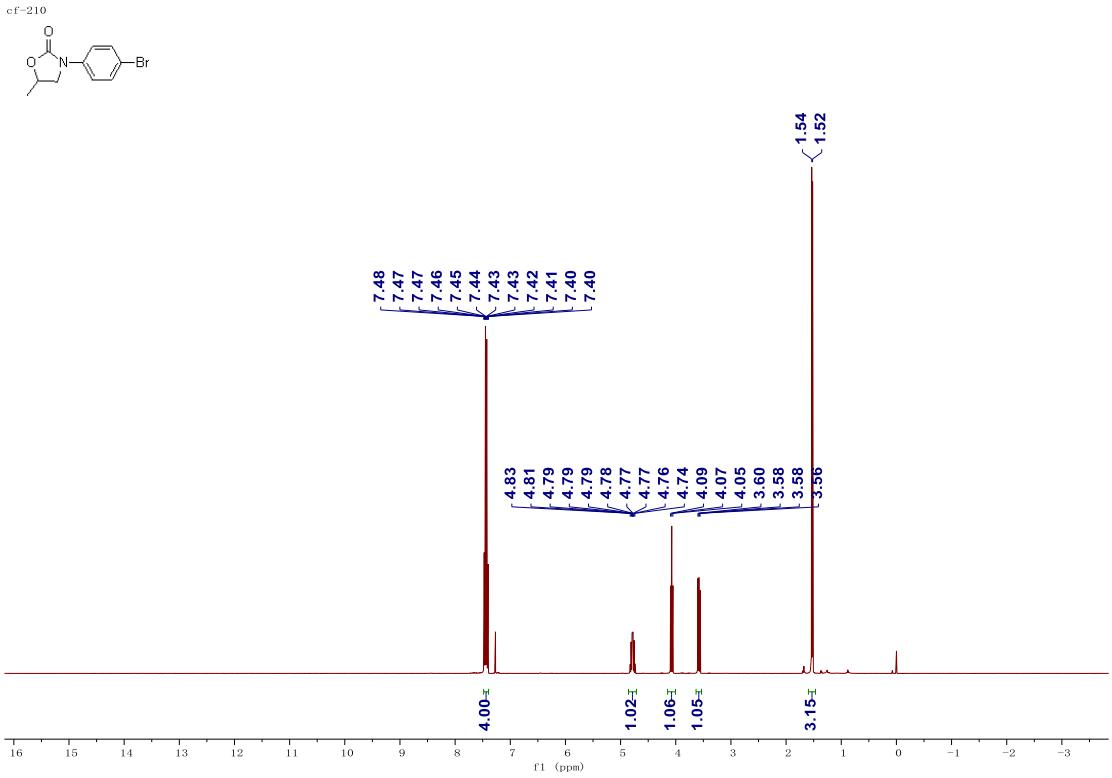

Figure S20. ^{1}H NMR spectra of oxazolidinones **4g**.

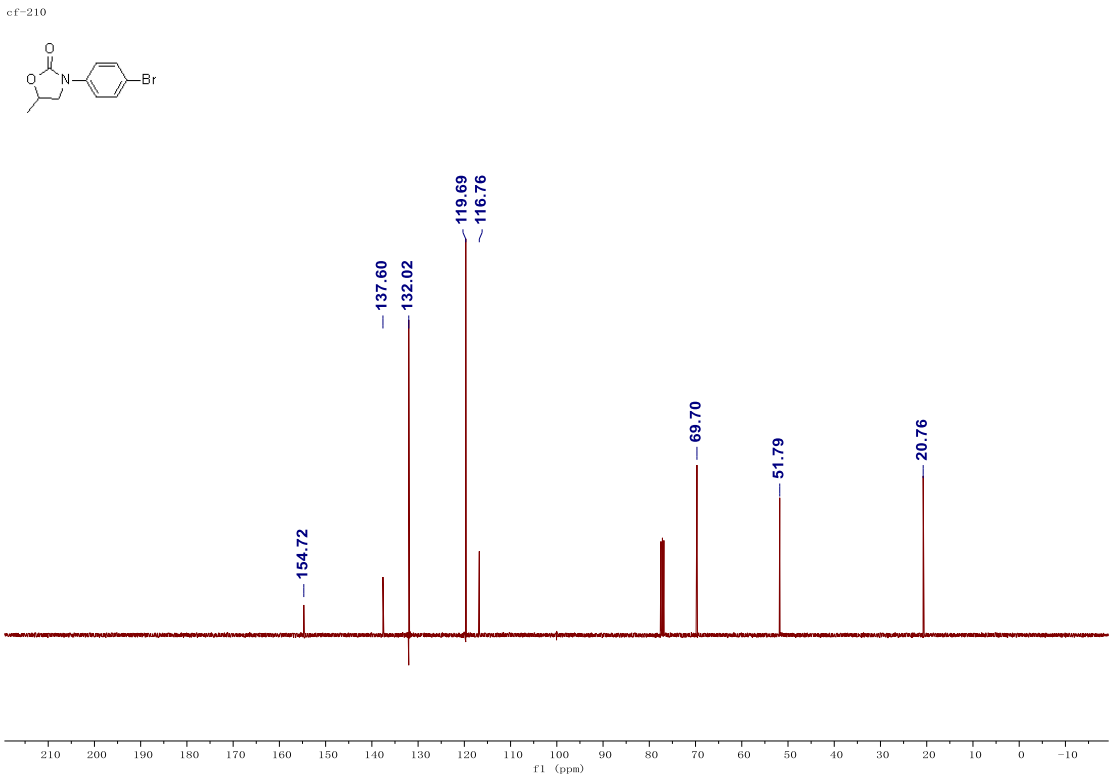

Figure S21. ^{13}C NMR spectra of oxazolidinones **4g**.

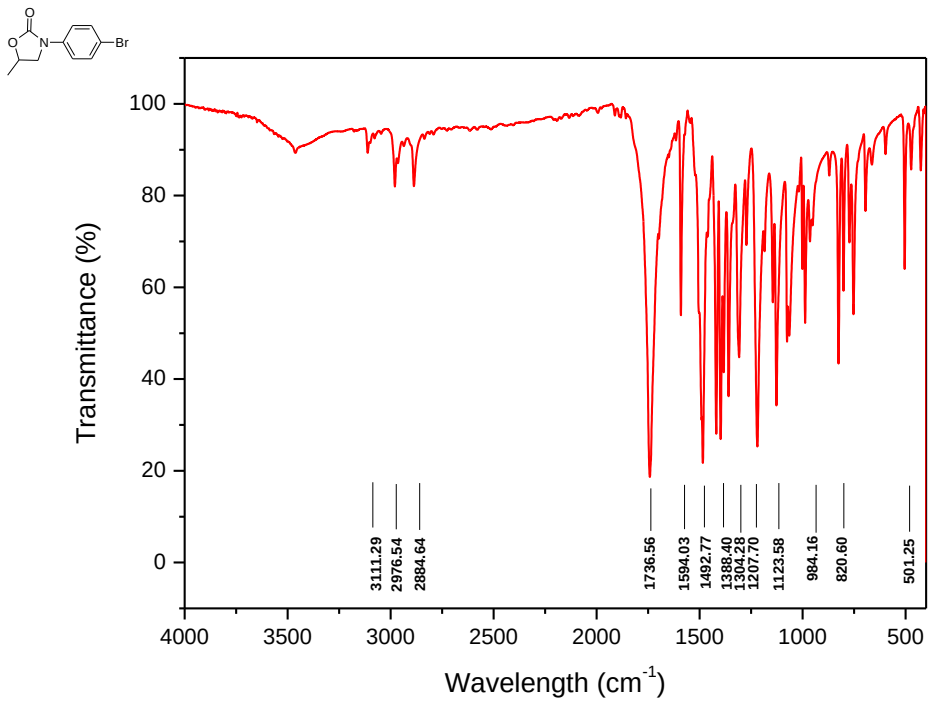

Figure S22. IR spectroscopic data of oxazolidinones **4g**.

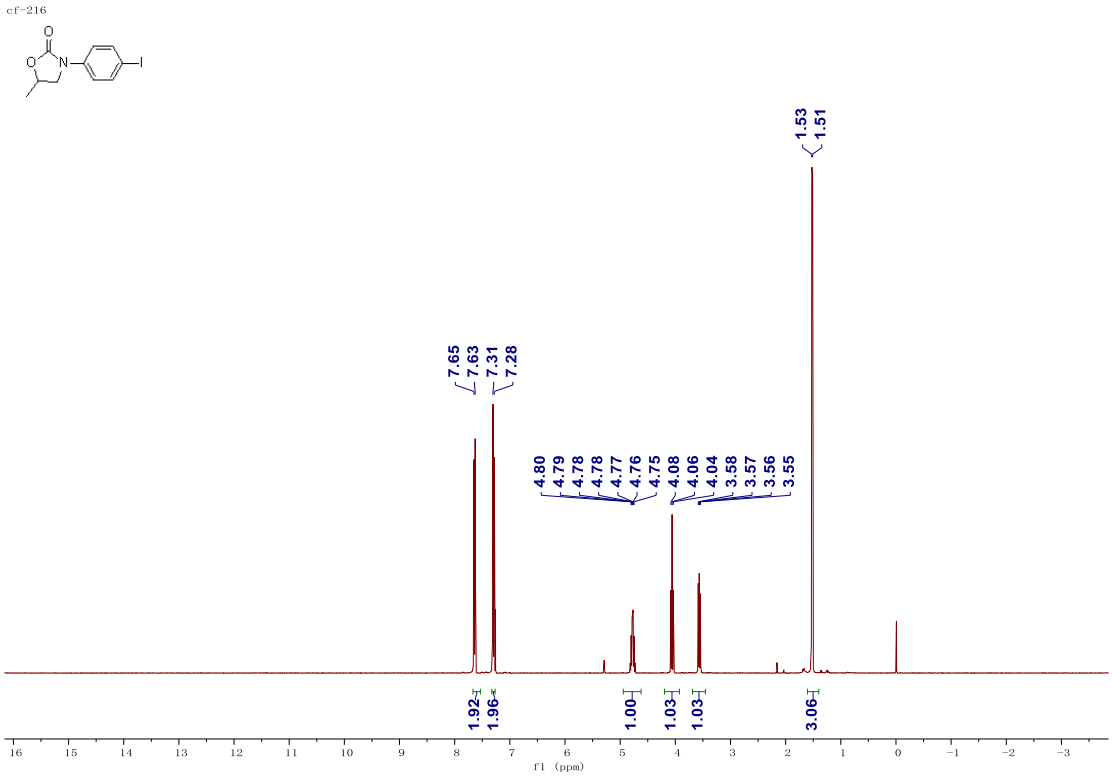

Figure S23. ^{1}H NMR spectra of oxazolidinones **4h**.

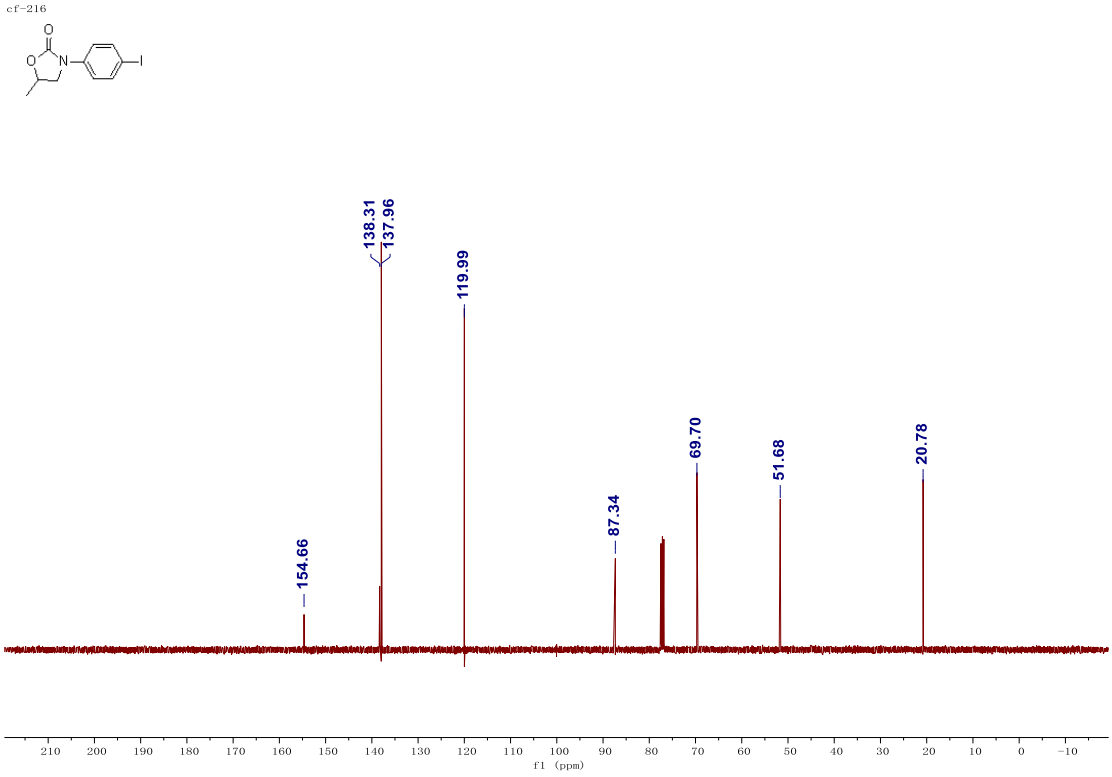

Figure S24. ^{13}C NMR spectra of oxazolidinones **4h**.

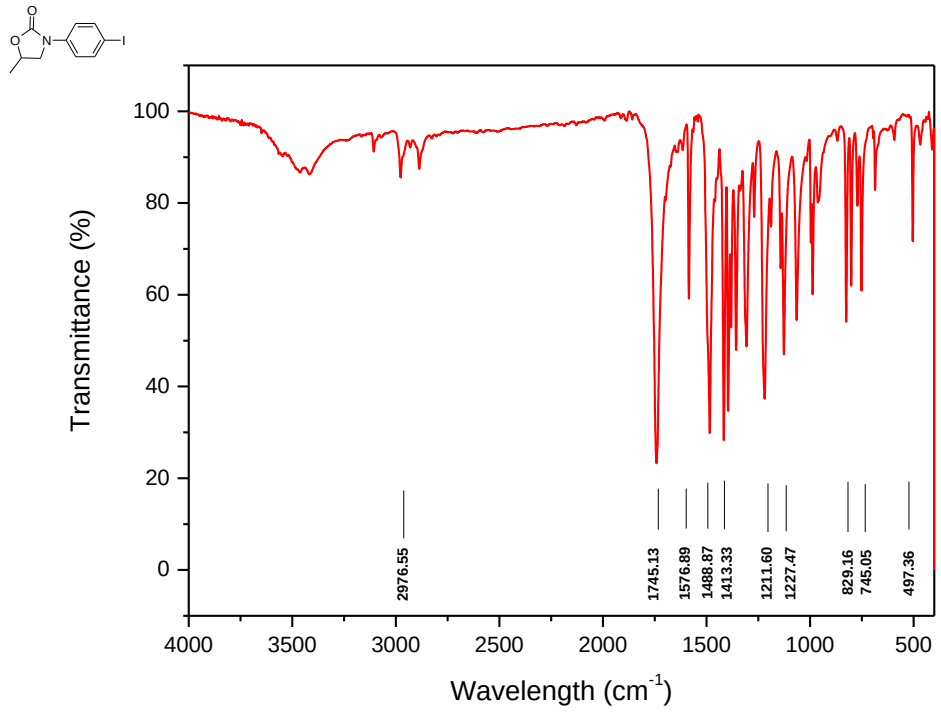

Figure S25. IR spectroscopic data of oxazolidinones **4h**.

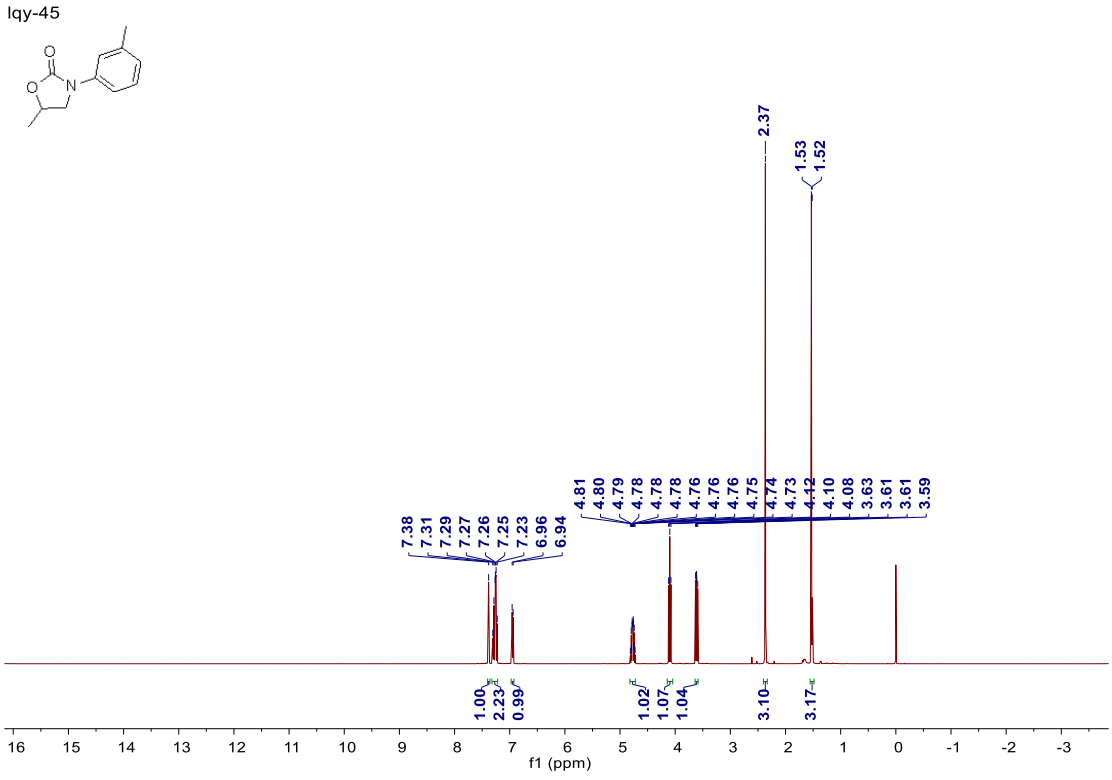

Figure S26. ^{1}H NMR spectra of oxazolidinones **4i**.

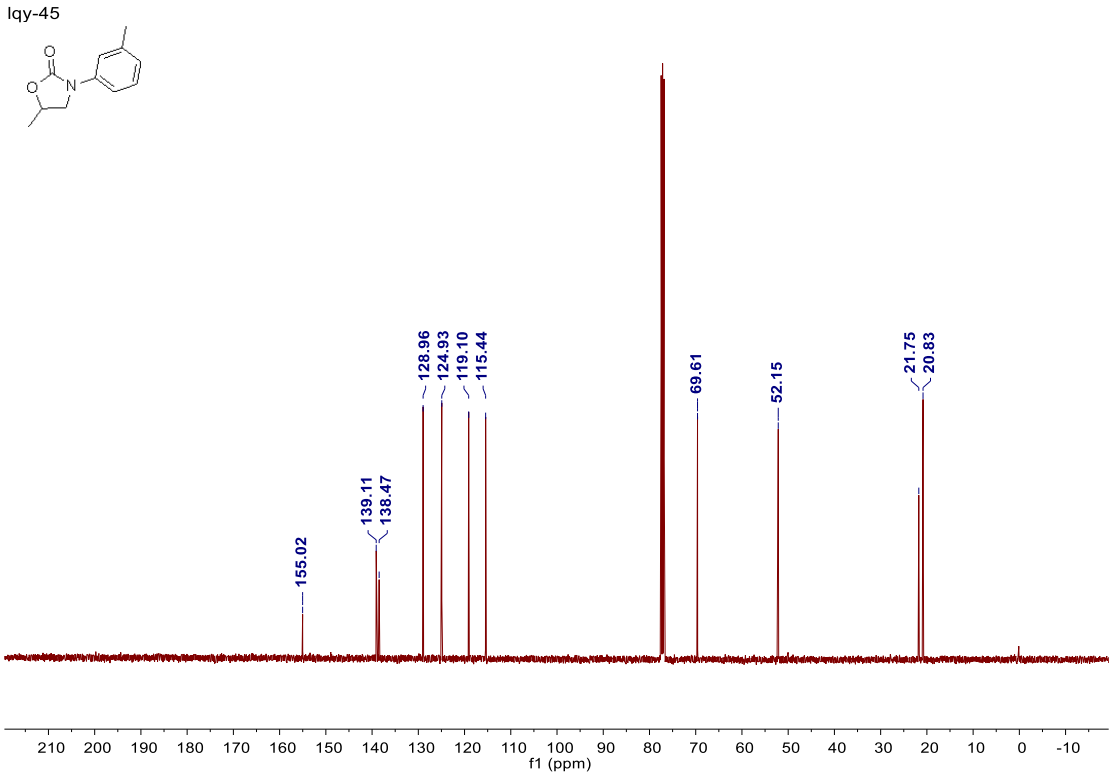

Figure S27. ^{13}C NMR spectra of oxazolidinones **4i**.

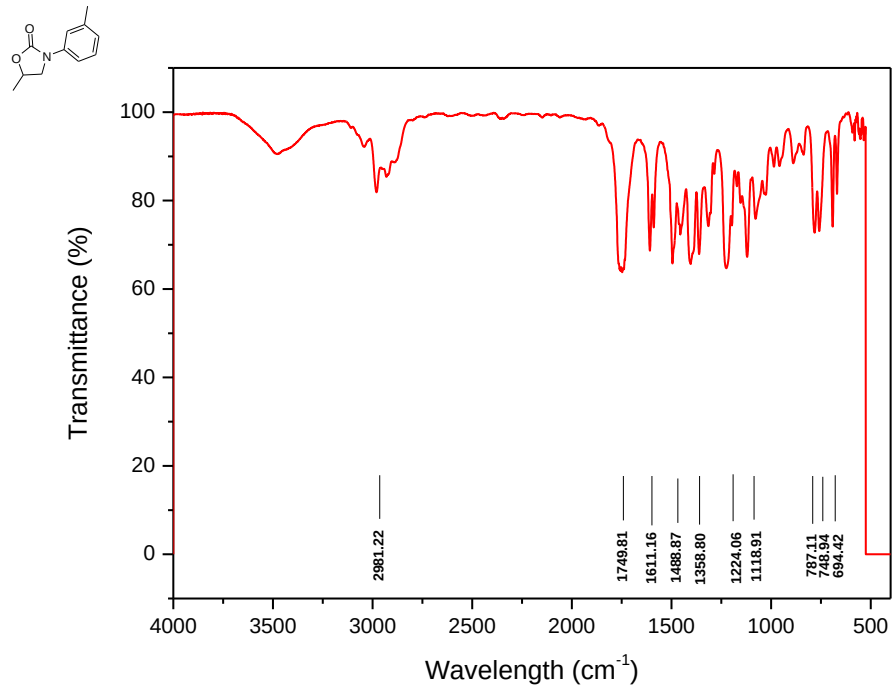

Figure S28. IR spectroscopic data of oxazolidinones **4i**.

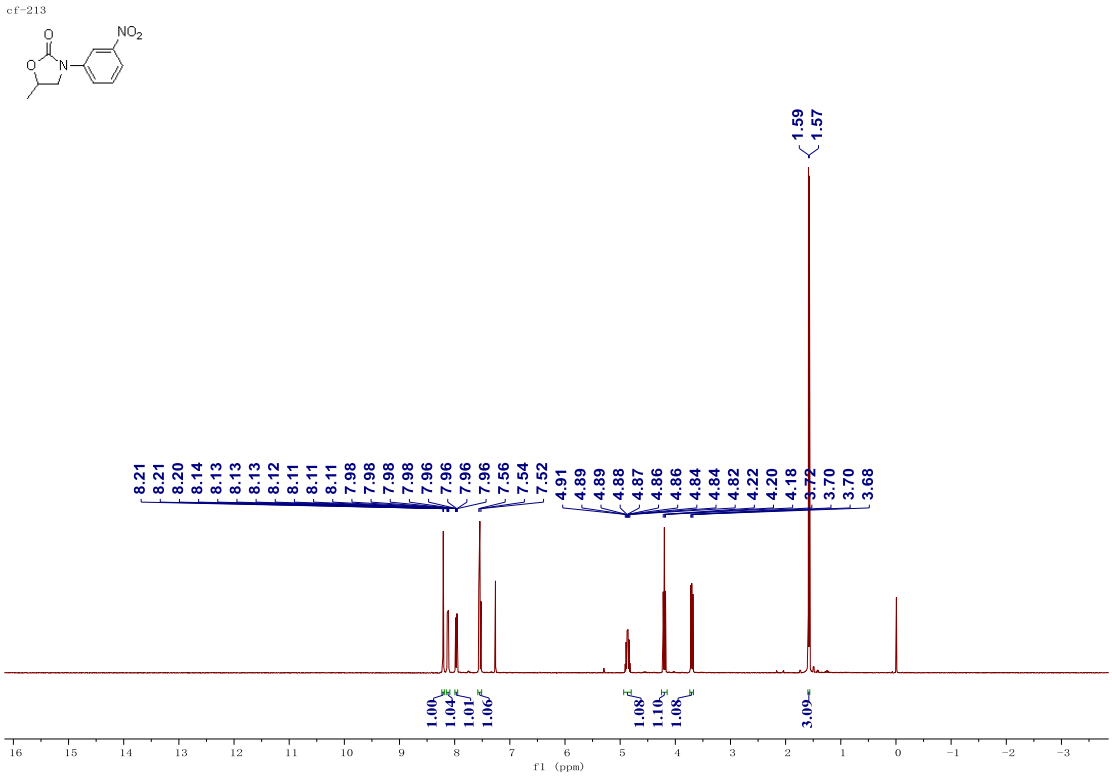

Figure S29. ^{1}H NMR spectra of oxazolidinones **4j**.

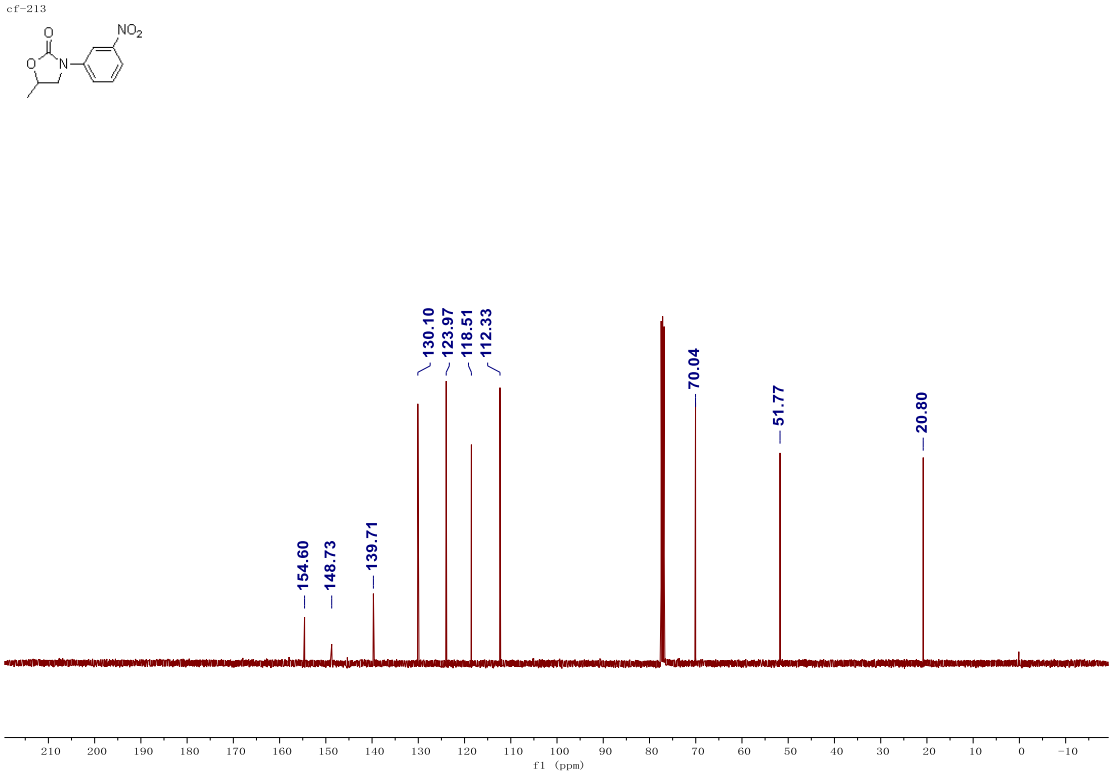

Figure S30. ^{13}C NMR spectra of oxazolidinones **4j**.

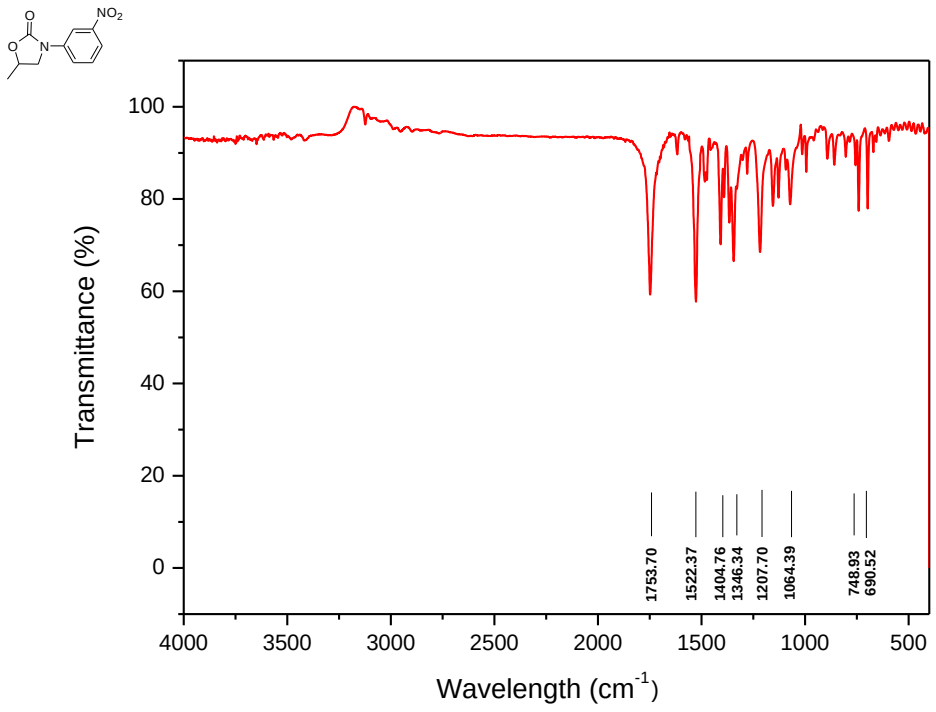

Figure S31. IR spectroscopic data of oxazolidinones **4j**.

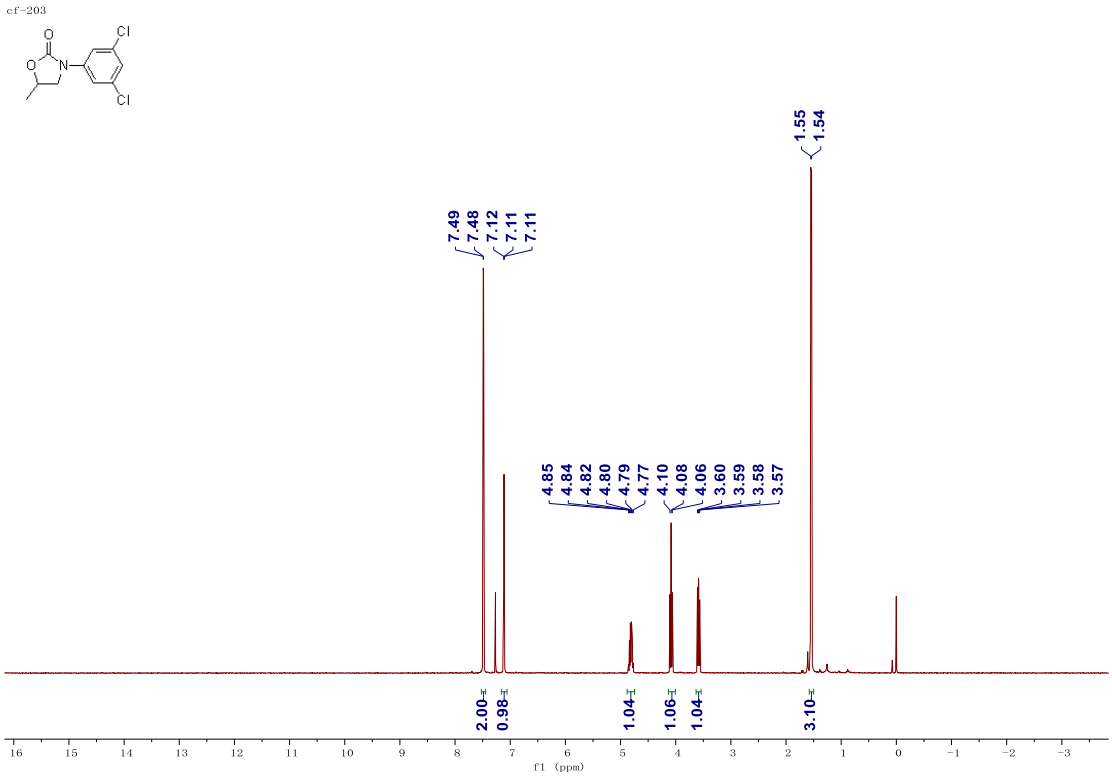

Figure S32. ^{1}H NMR spectra of oxazolidinones **4k**.

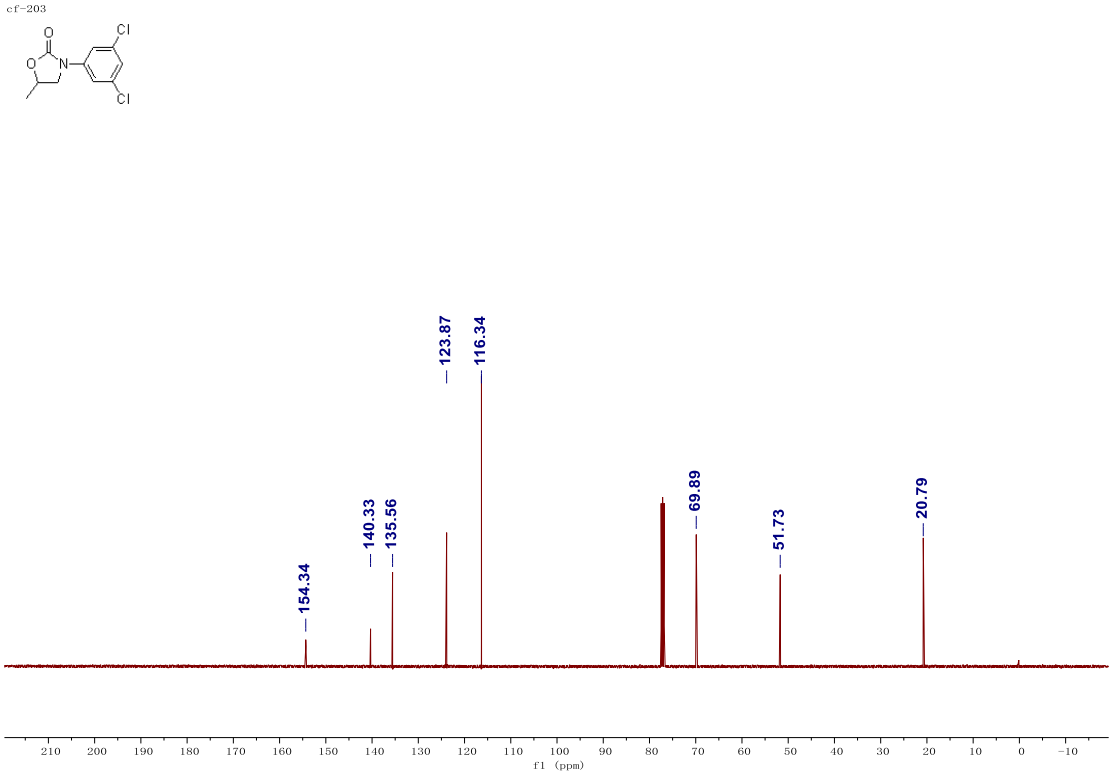

Figure S33. ^{13}C NMR spectra of oxazolidinones **4k**.

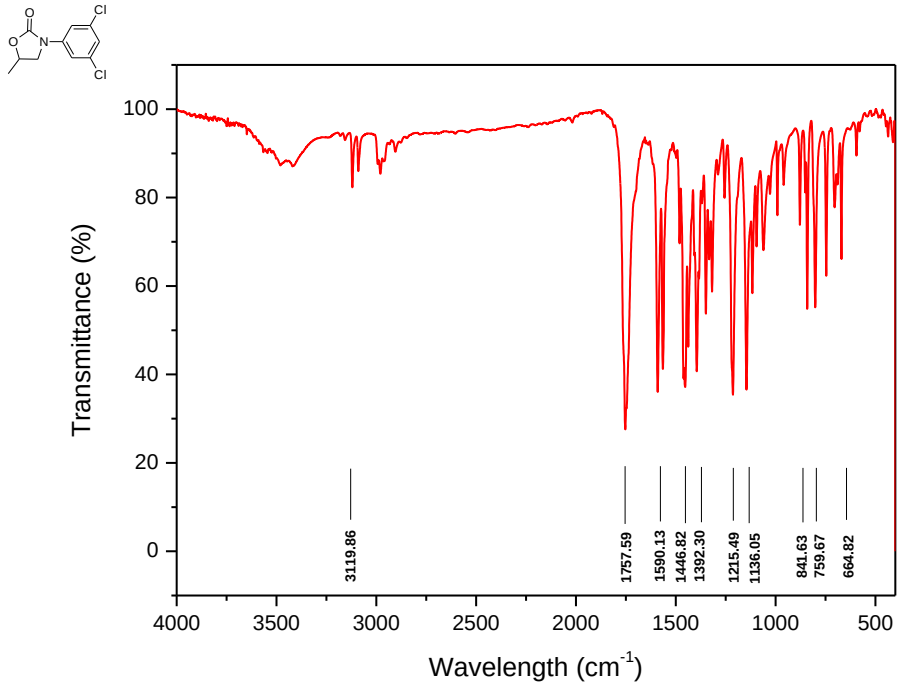

Figure S34. IR spectroscopic data of oxazolidinones **4k**.

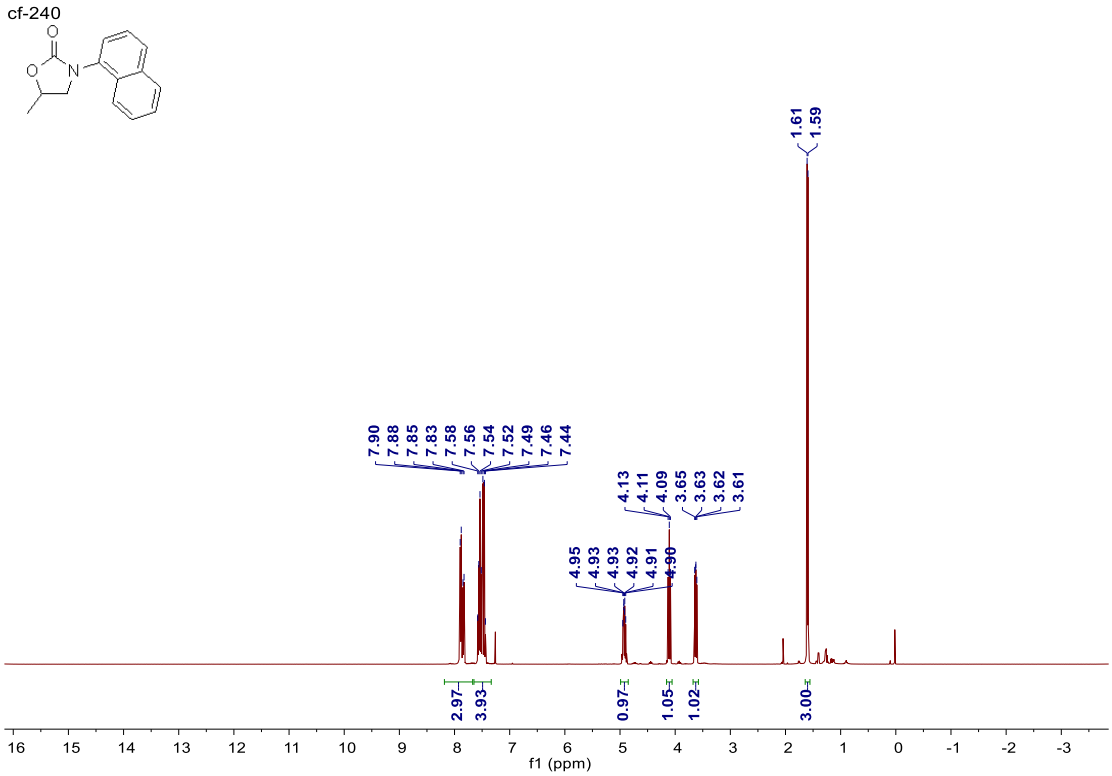

Figure S35. [1]H NMR spectra of oxazolidinones **4l**.

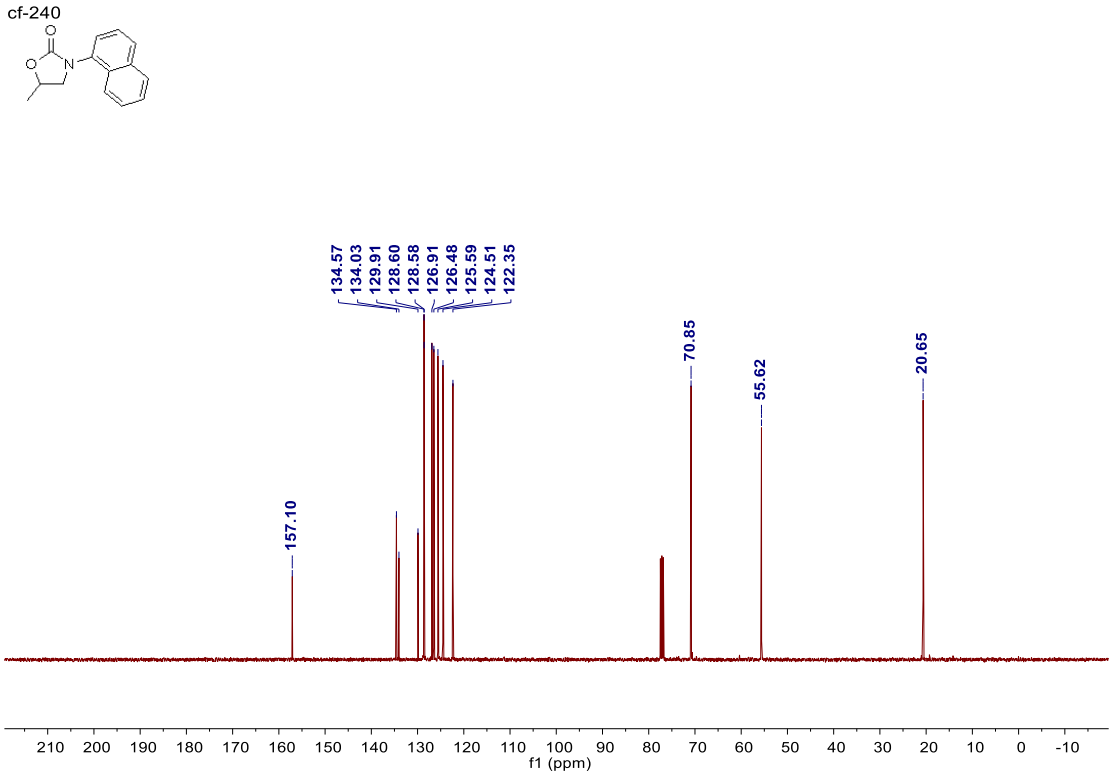

Figure S36. [13]C NMR spectra of oxazolidinones **4l**.

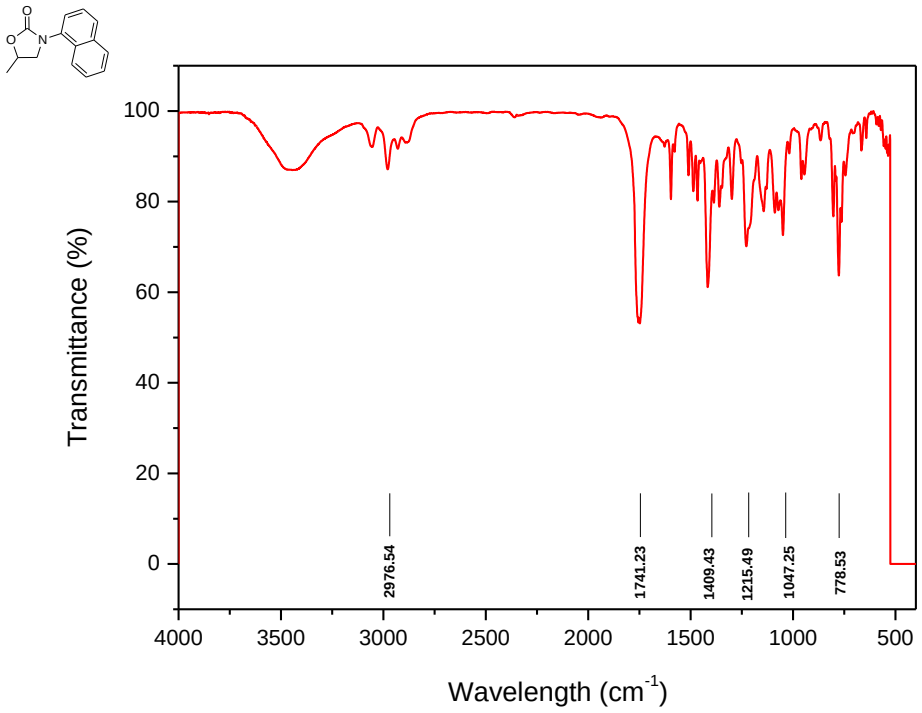

Figure S37. IR spectroscopic data of oxazolidinones **4l**.

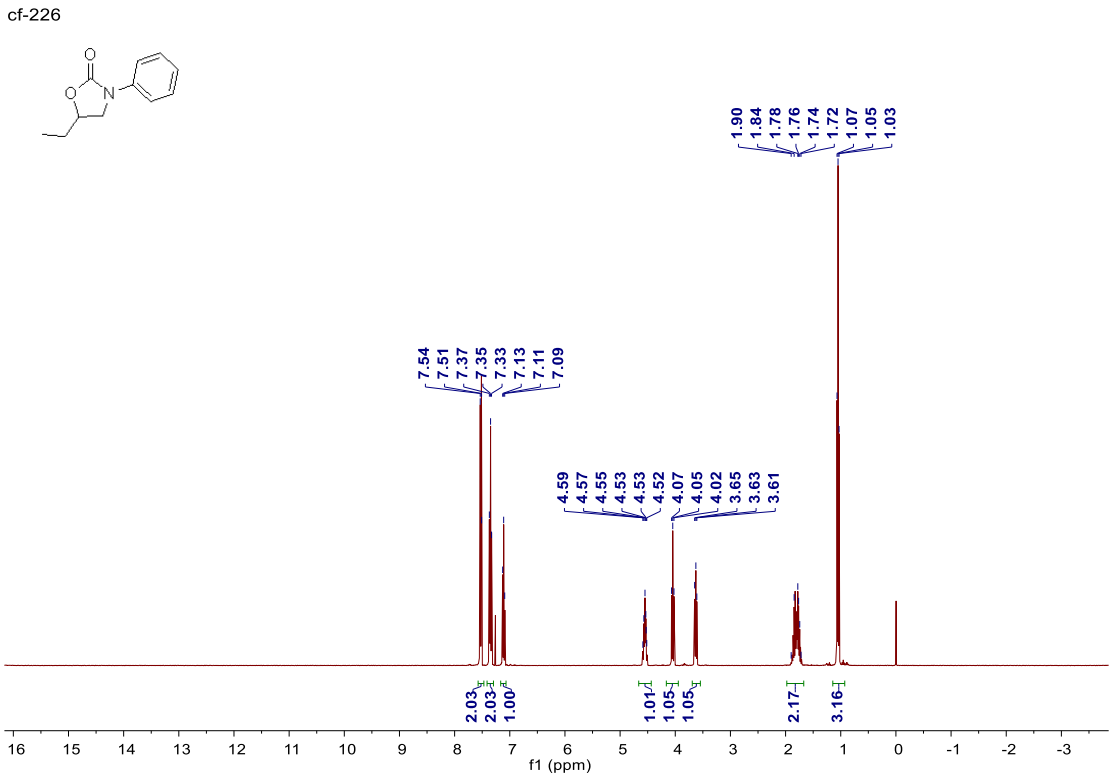

Figure S38. ^{1}H NMR spectra of oxazolidinones **4m**.

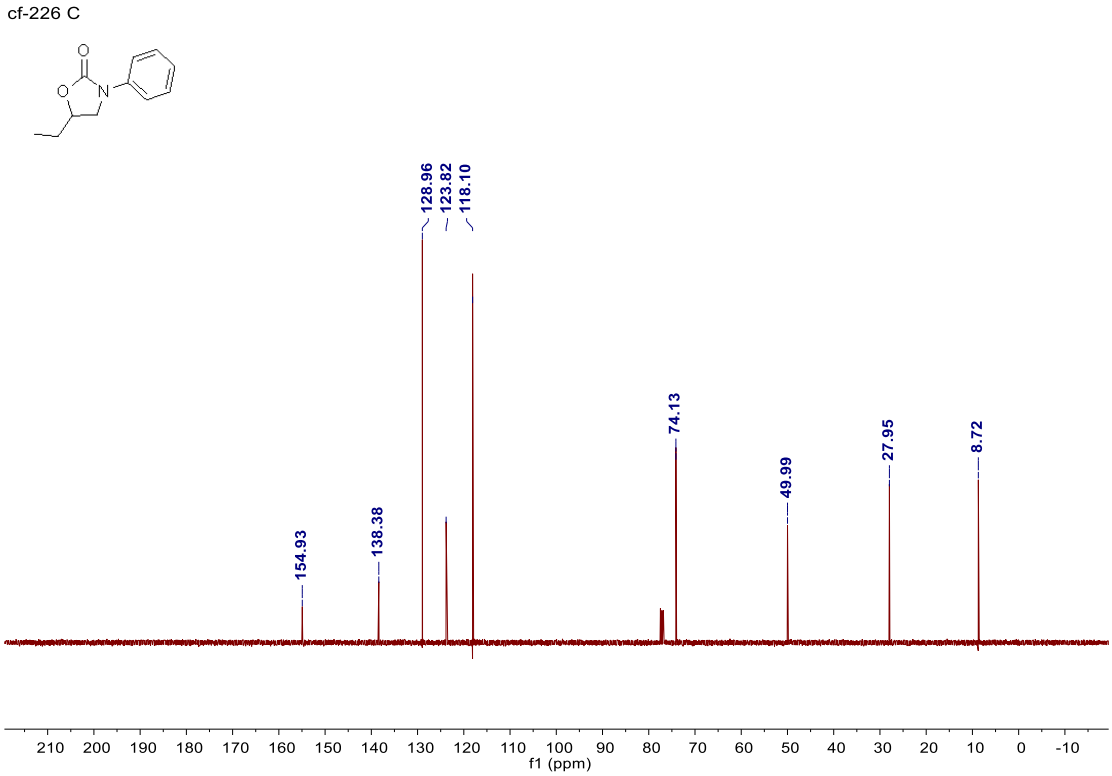

Figure S39. ^{13}C NMR spectra of oxazolidinones **4m**.

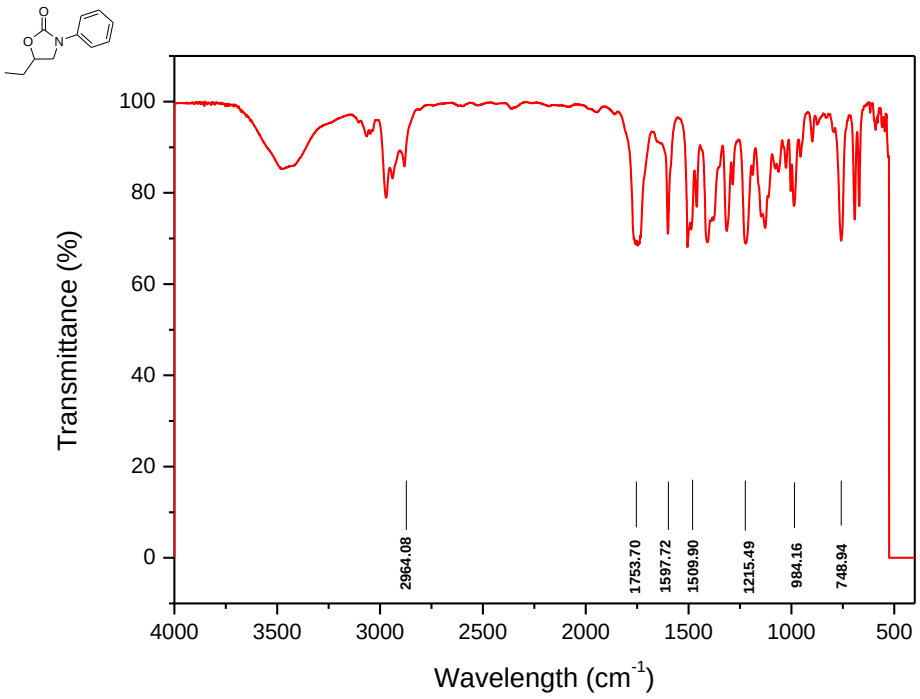

Figure S40. IR spectroscopic data of oxazolidinones **4m**.

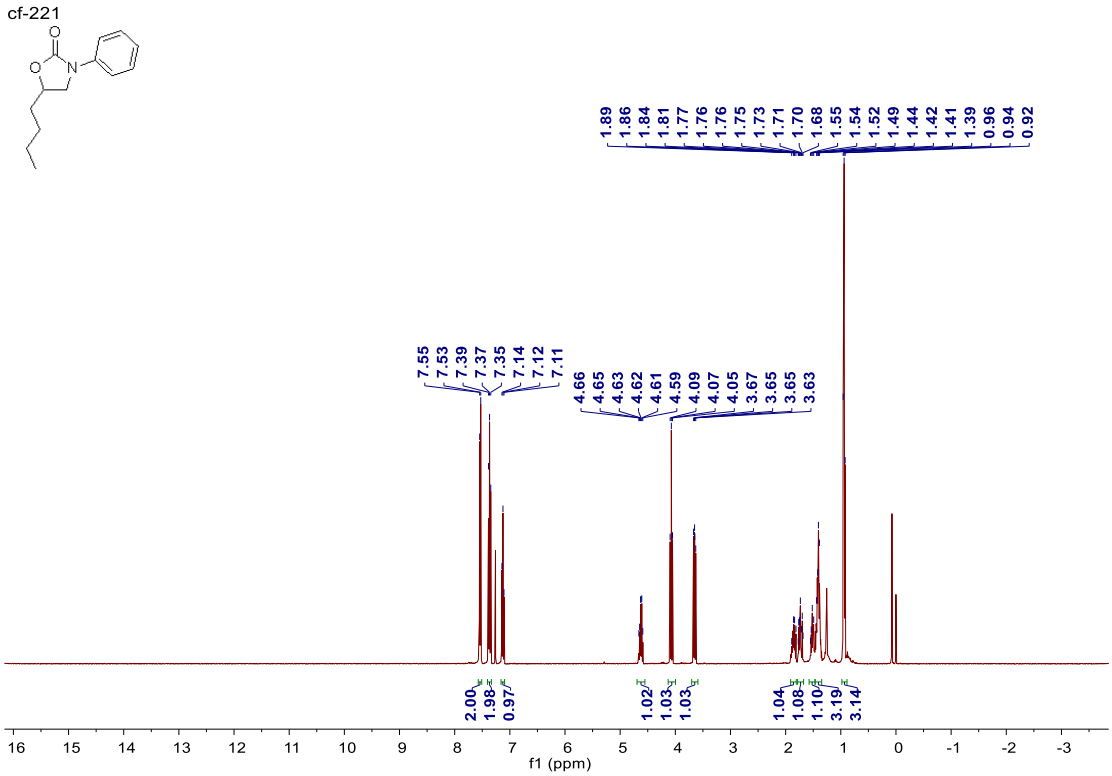

Figure S41. ^{1}H NMR spectra of oxazolidinones **4n**.

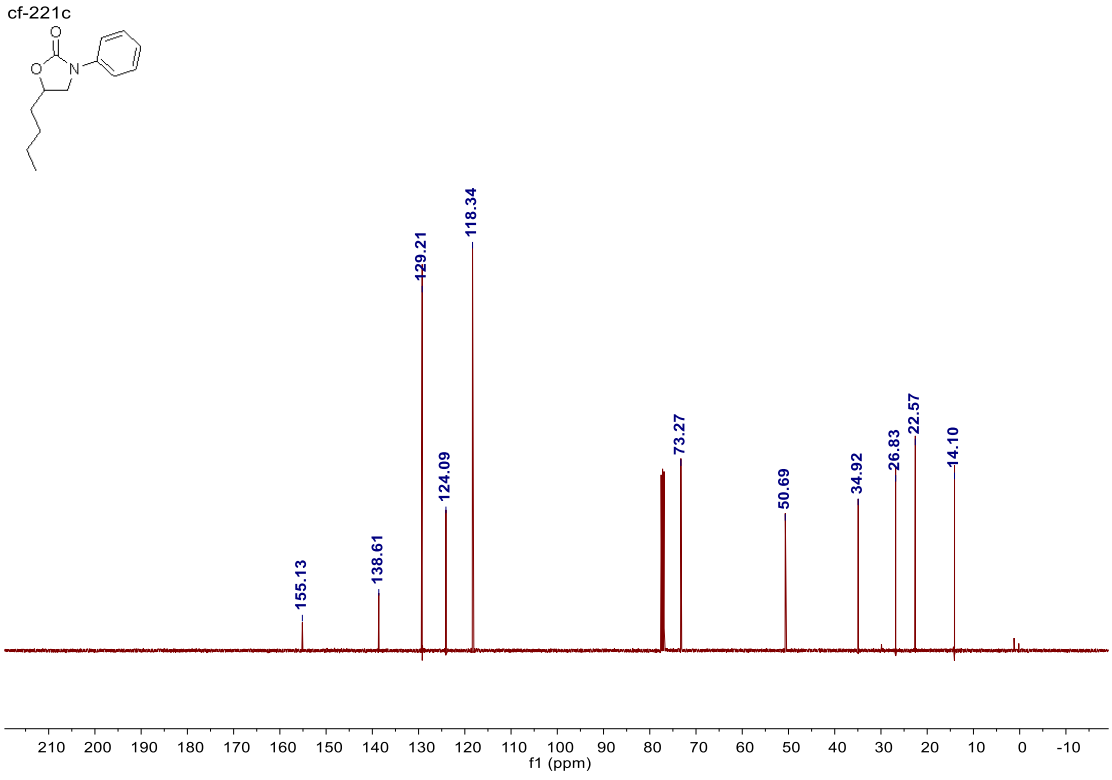

Figure S42. ^{13}C NMR spectra of oxazolidinones **4n**.

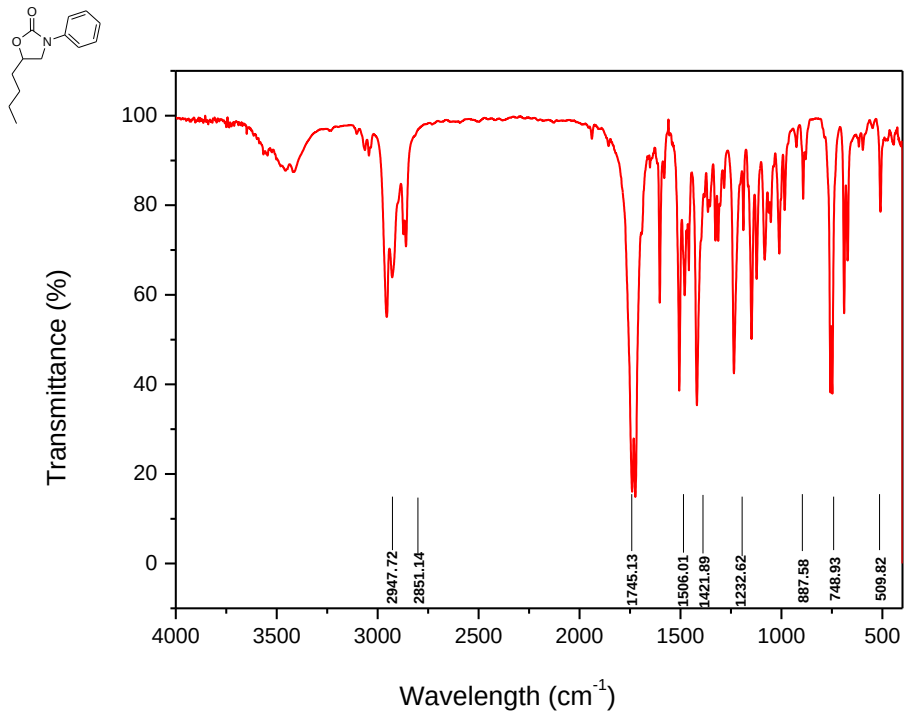

Figure S43. IR spectroscopic data of oxazolidinones **4n**.

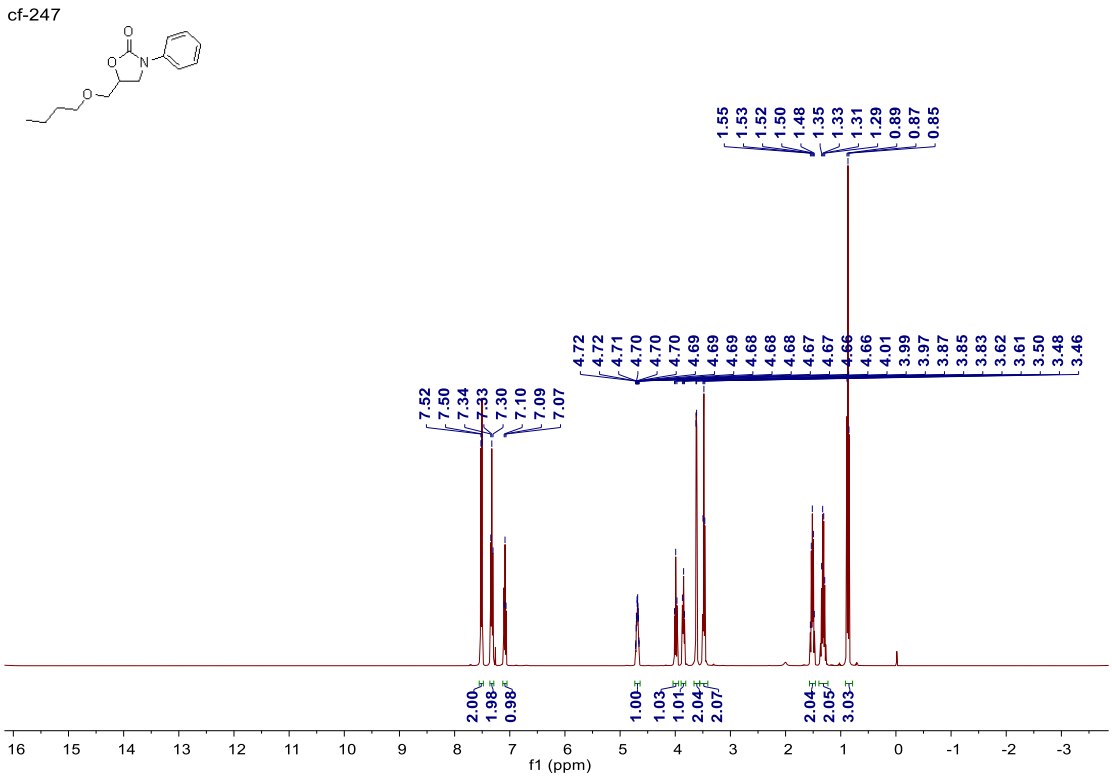

Figure S44. ^{1}H NMR spectra of oxazolidinones **4o**.

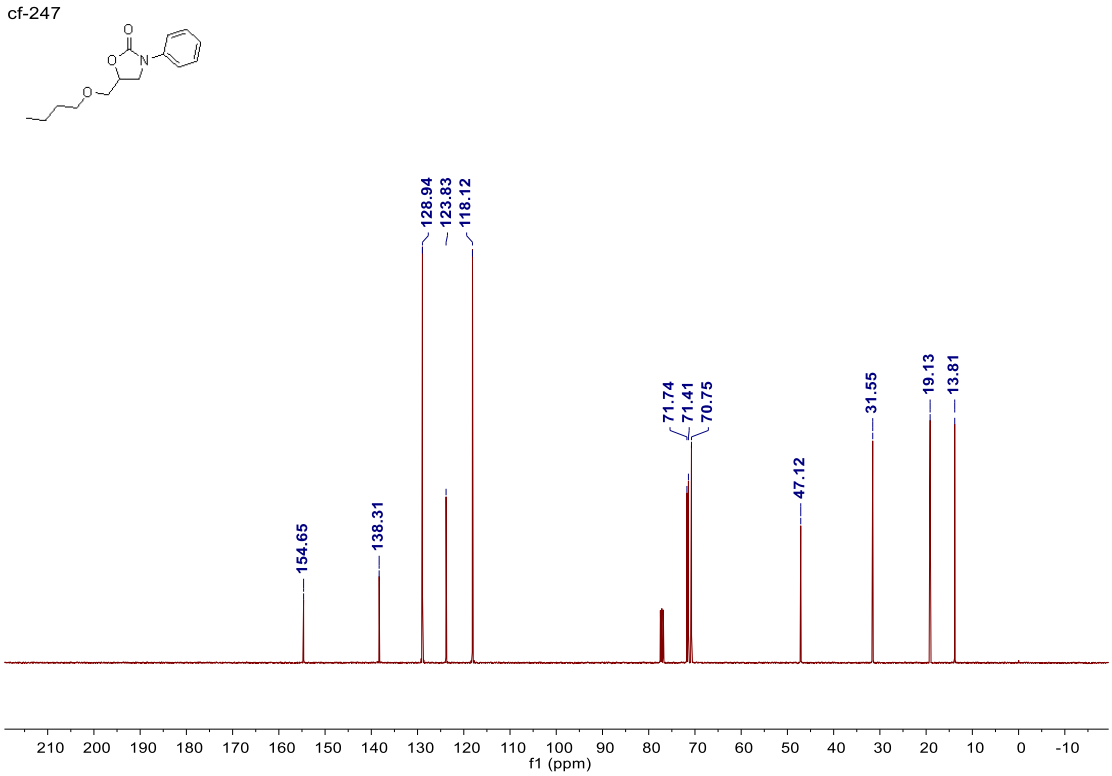

Figure S45. ^{13}C NMR spectra of oxazolidinones **4o**.

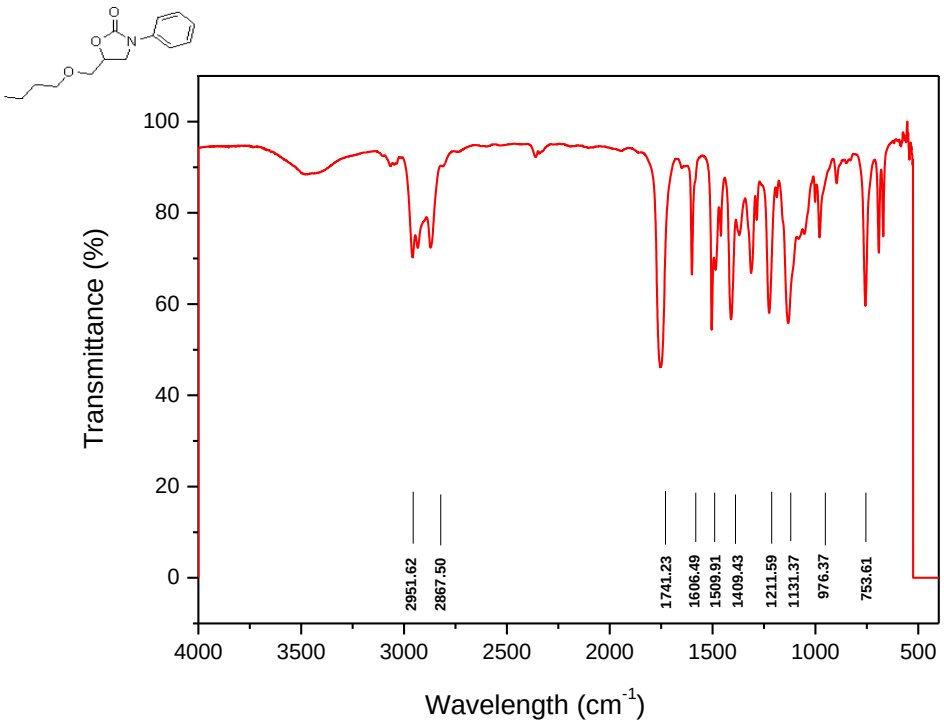

Figure S46. IR spectroscopic data of oxazolidinones **4o**.

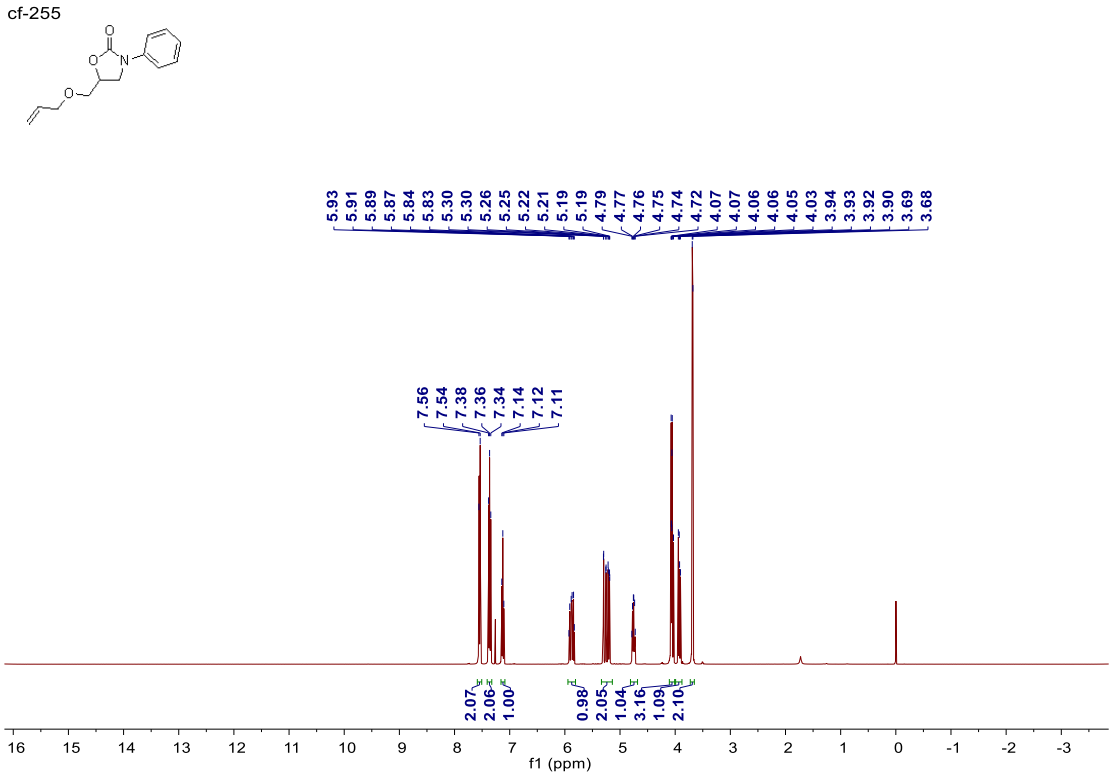

Figure S47. [1]H NMR spectra of oxazolidinones **4p**.

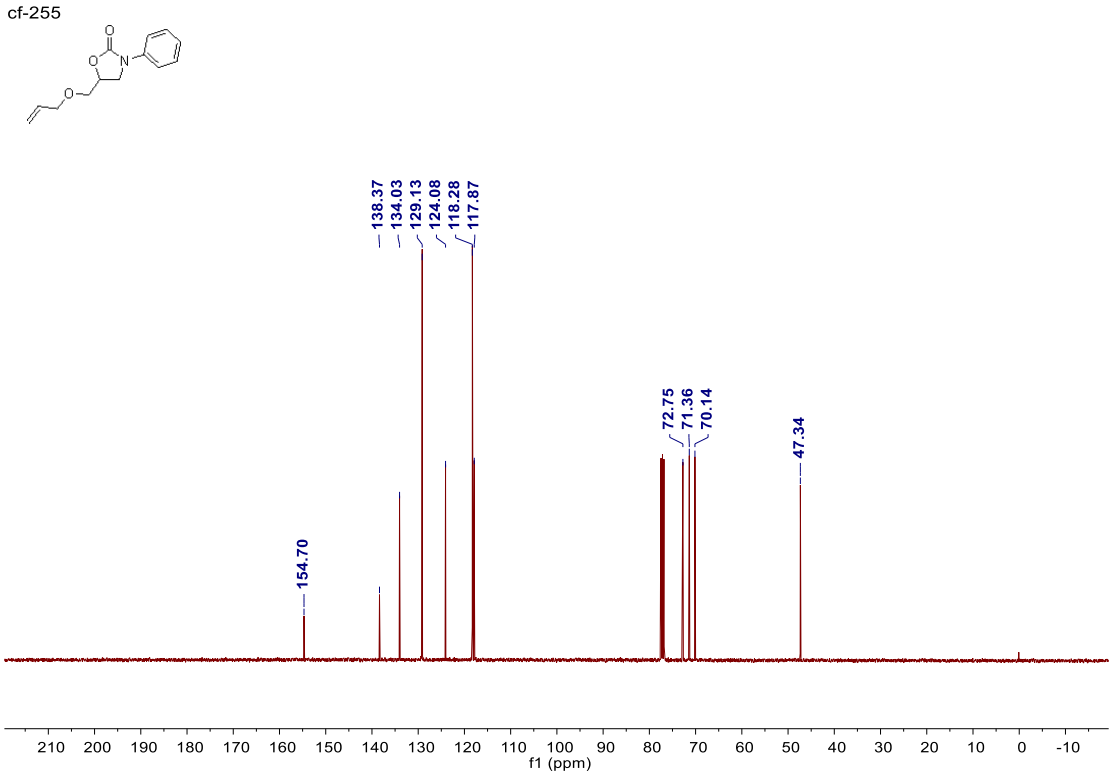

Figure S48. [13]C NMR spectra of oxazolidinones **4p**.

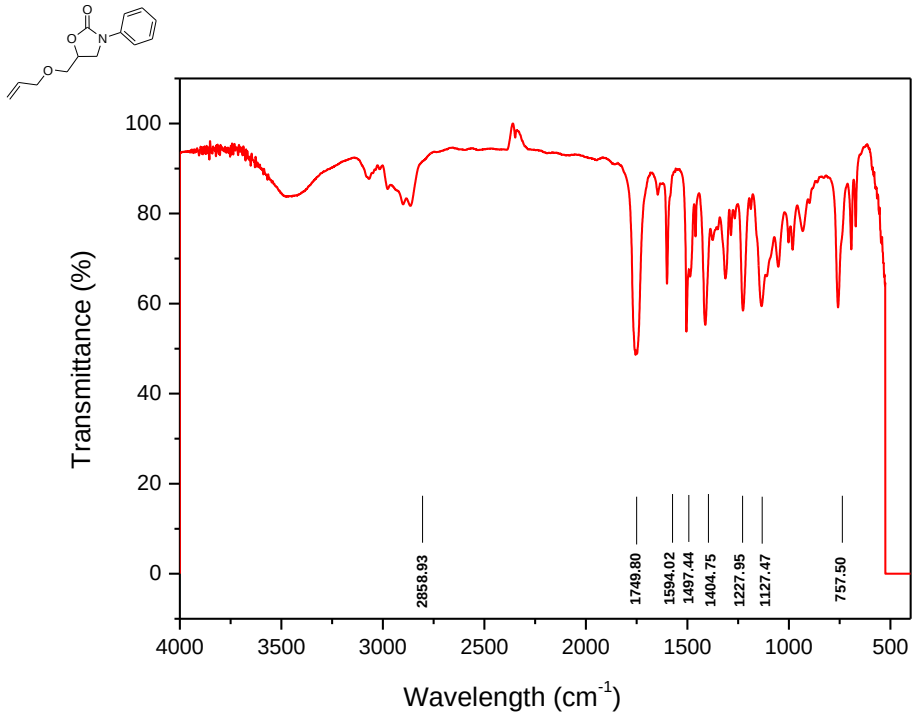

Figure S49. IR spectroscopic data of oxazolidinones **4p**.

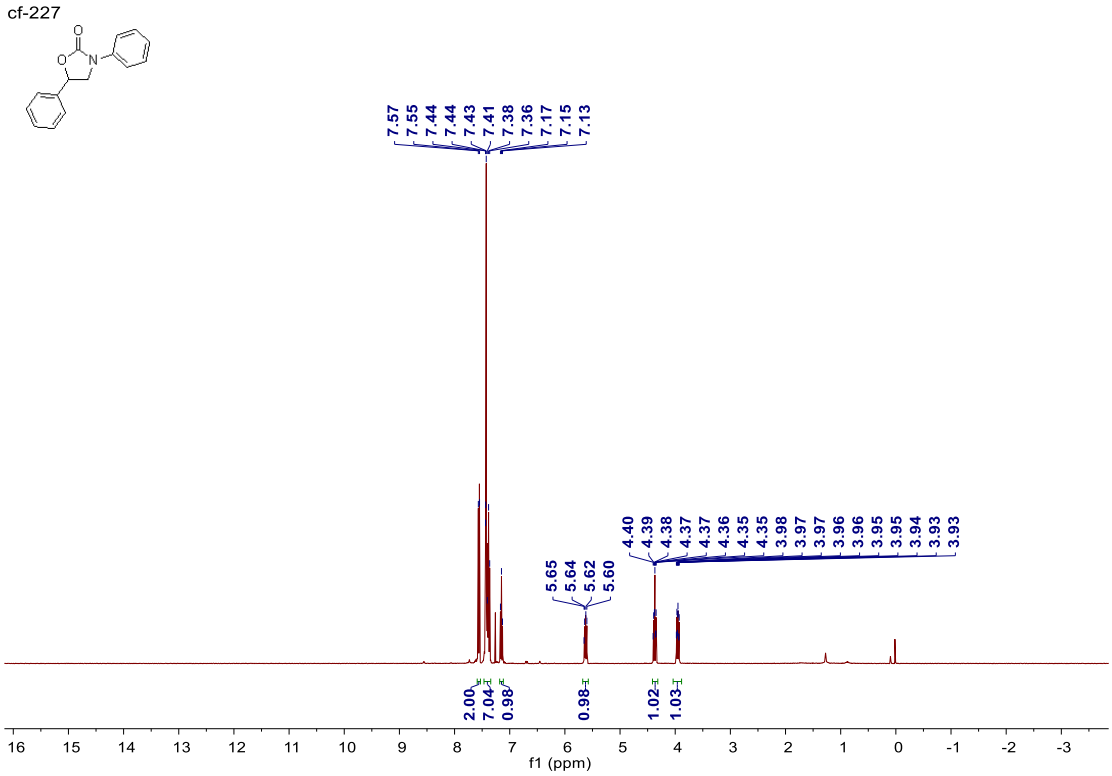

Figure S50. ^{1}H NMR spectra of oxazolidinones **4q**.

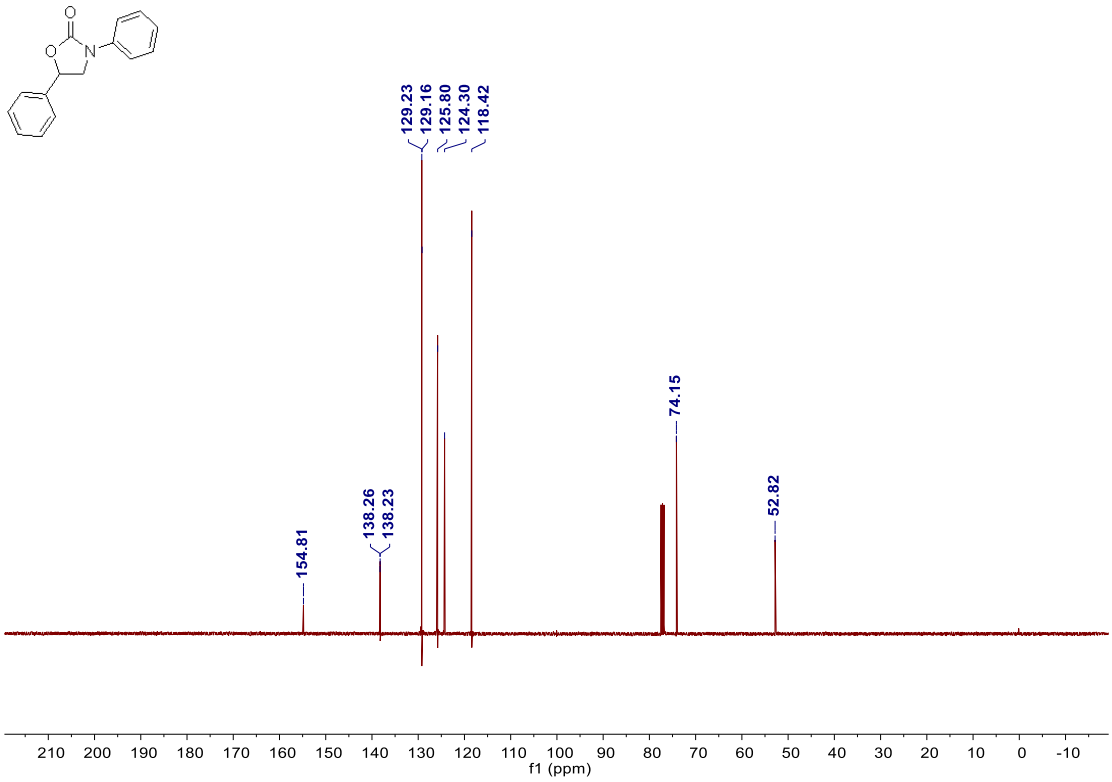

Figure S51. ^{13}C NMR spectra of oxazolidinones **4q**.

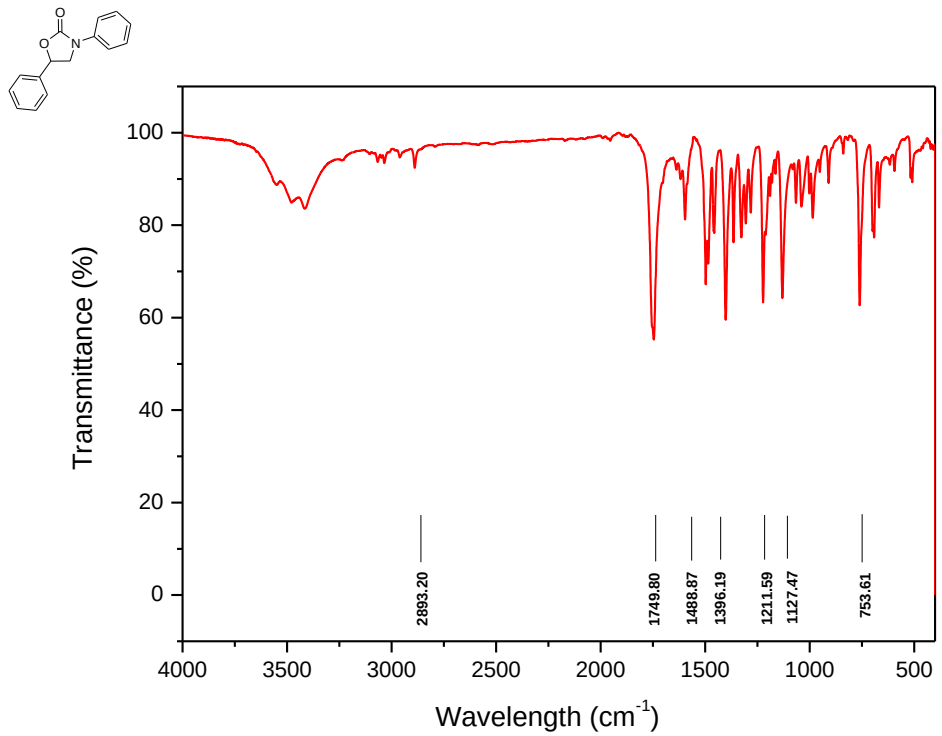

Figure S52. IR spectroscopic data of oxazolidinones **4q**.

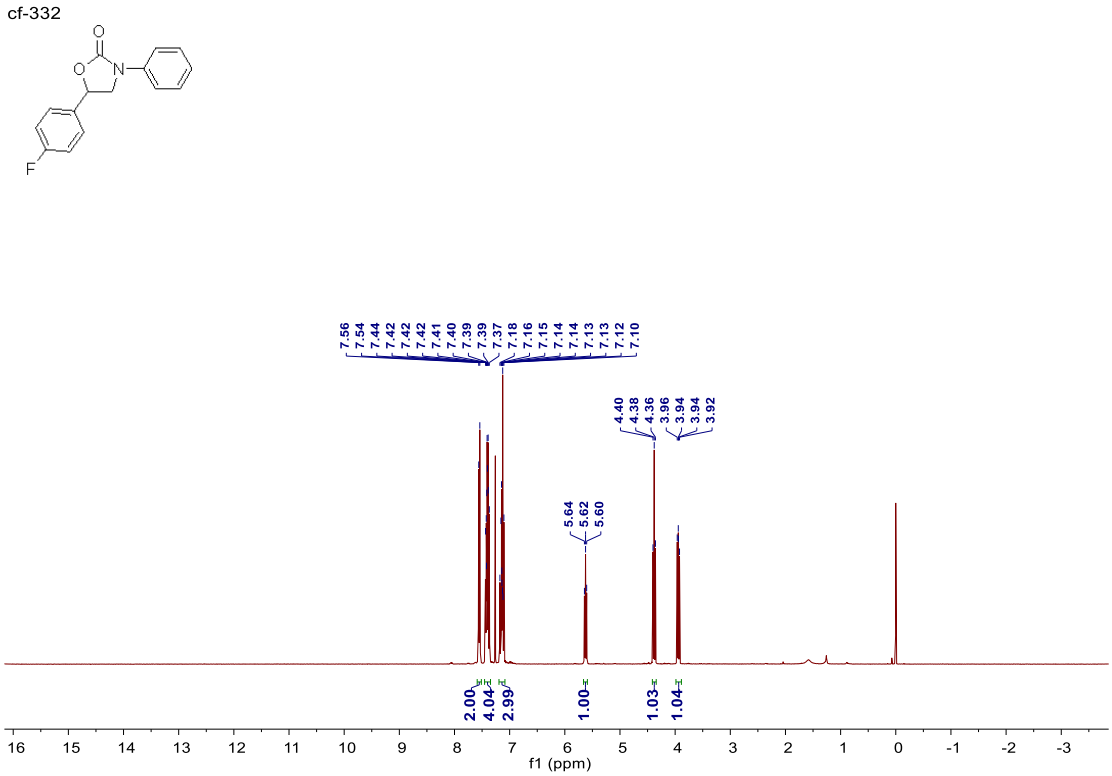

Figure S53. [1]H NMR spectra of oxazolidinones **4r**.

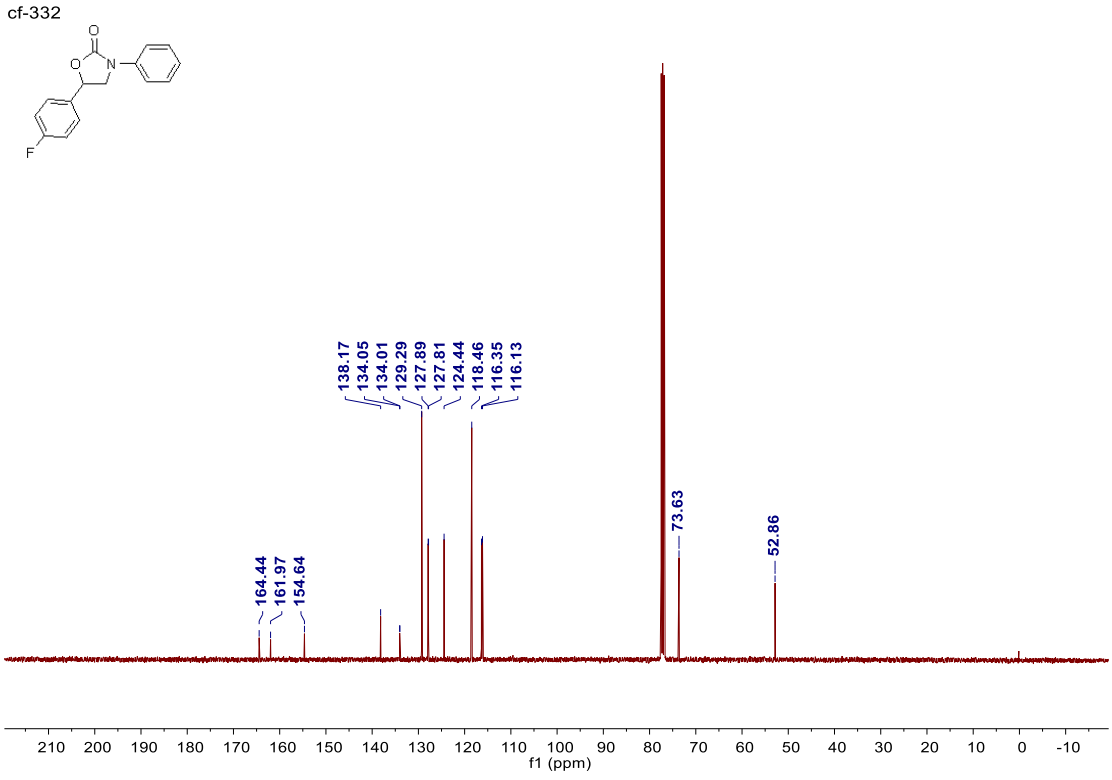

Figure S54. [13]C NMR spectra of oxazolidinones **4r**.

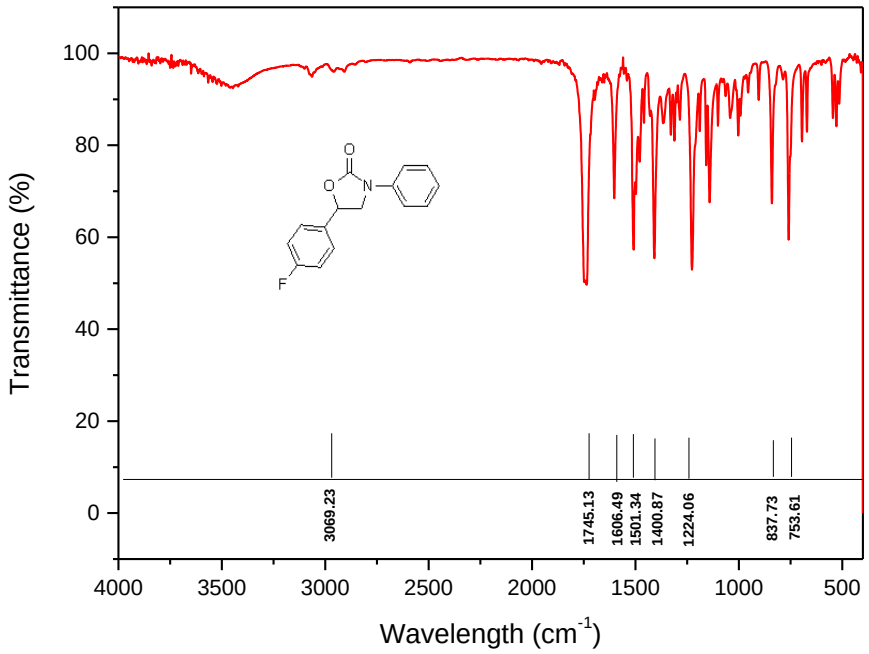

Figure S55. IR spectroscopic data of oxazolidinones **4r**.

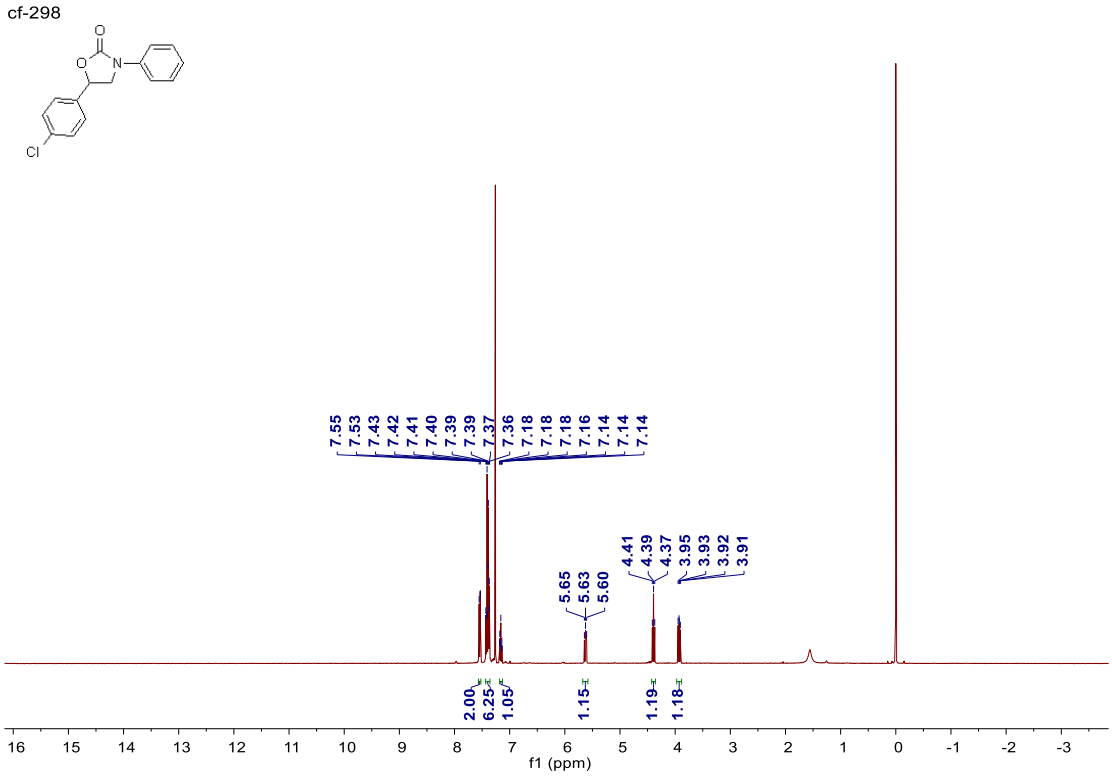

Figure S56. ^{1}H NMR spectra of oxazolidinones **4s**.

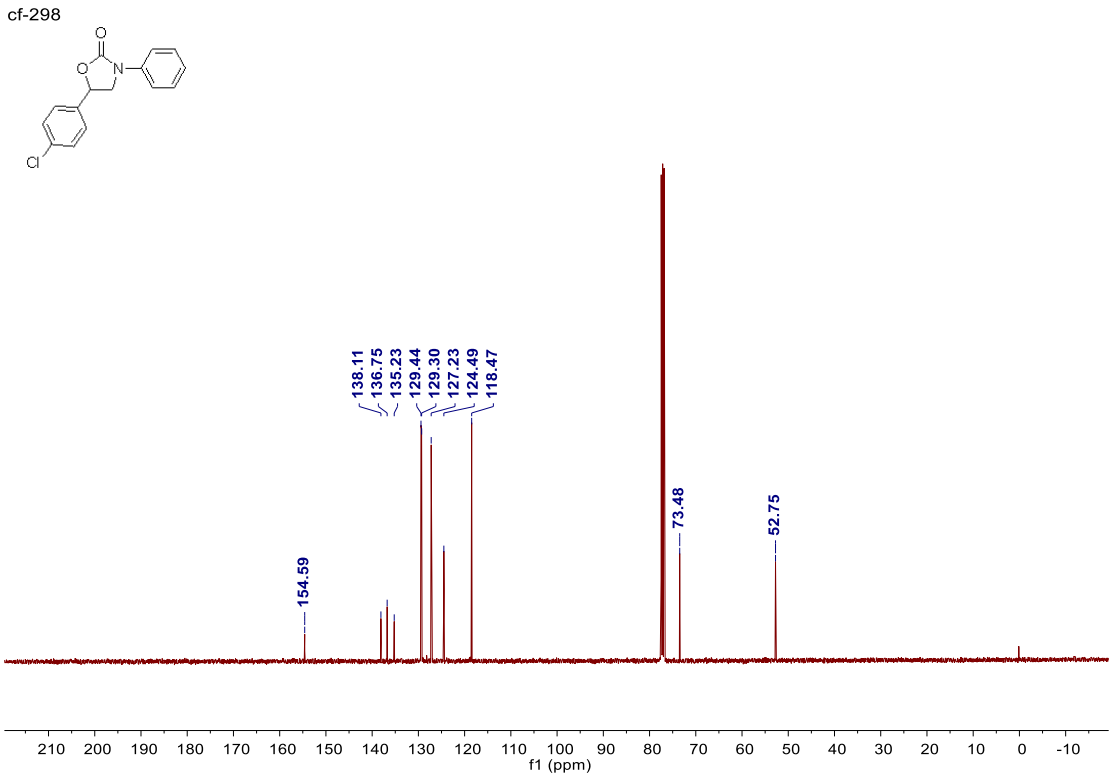

Figure S57. ^{13}C NMR spectra of oxazolidinones **4s**.

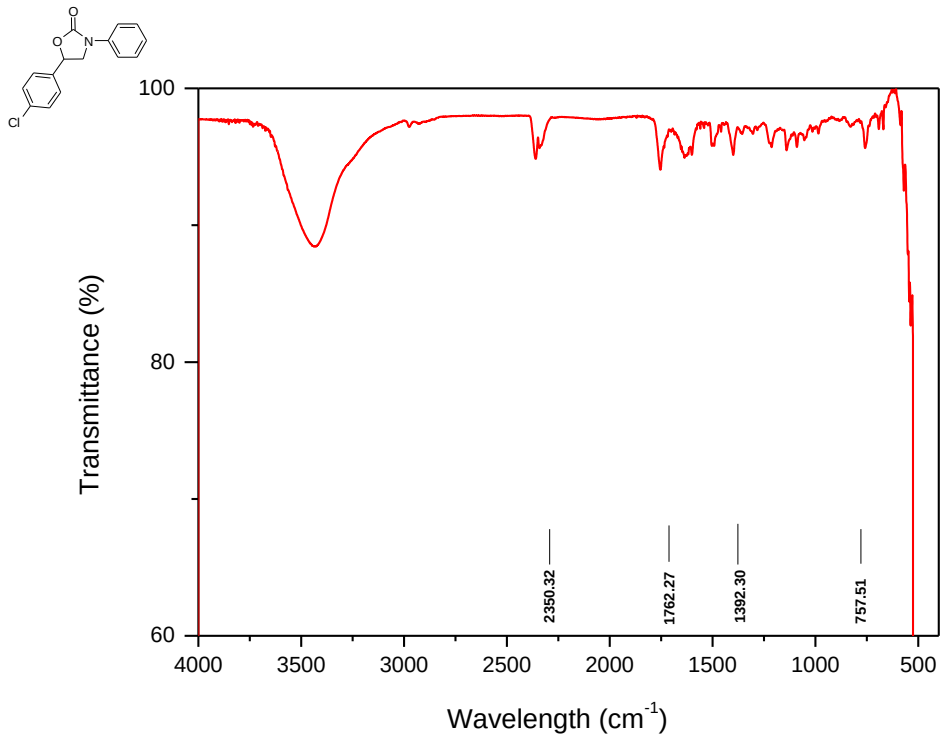

Figure S58. IR spectroscopic data of oxazolidinones **4s**.

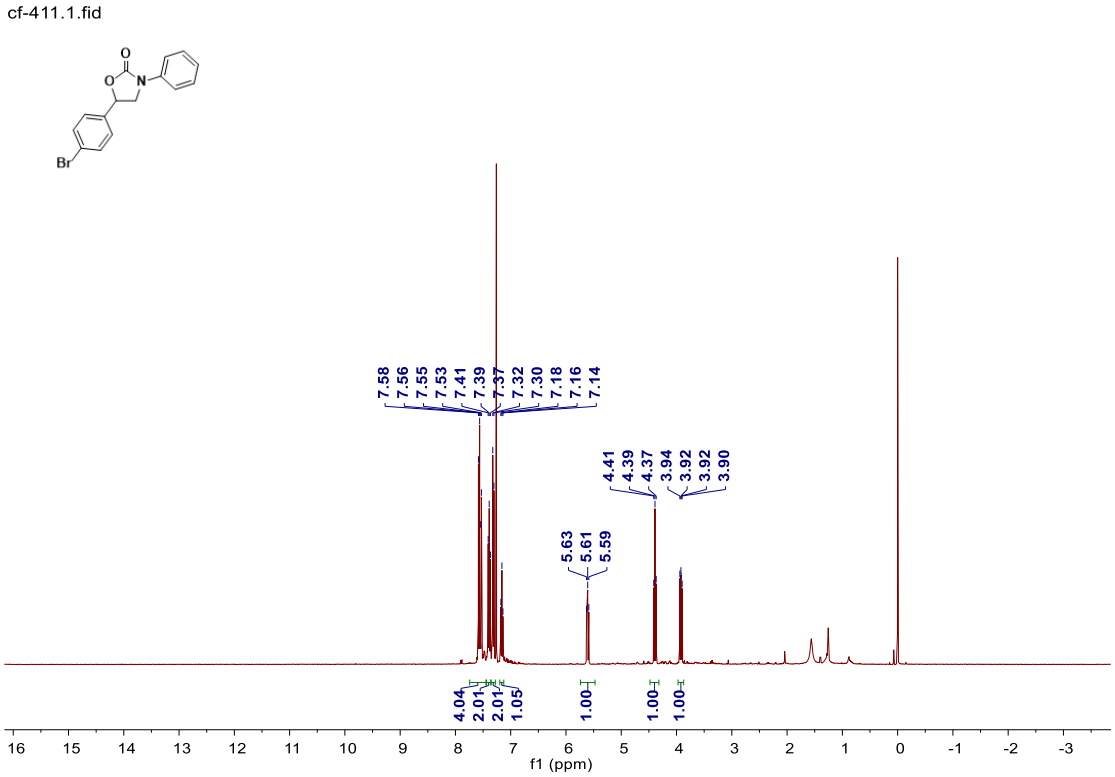

Figure S59. [1]H NMR spectra of oxazolidinones **4t**.

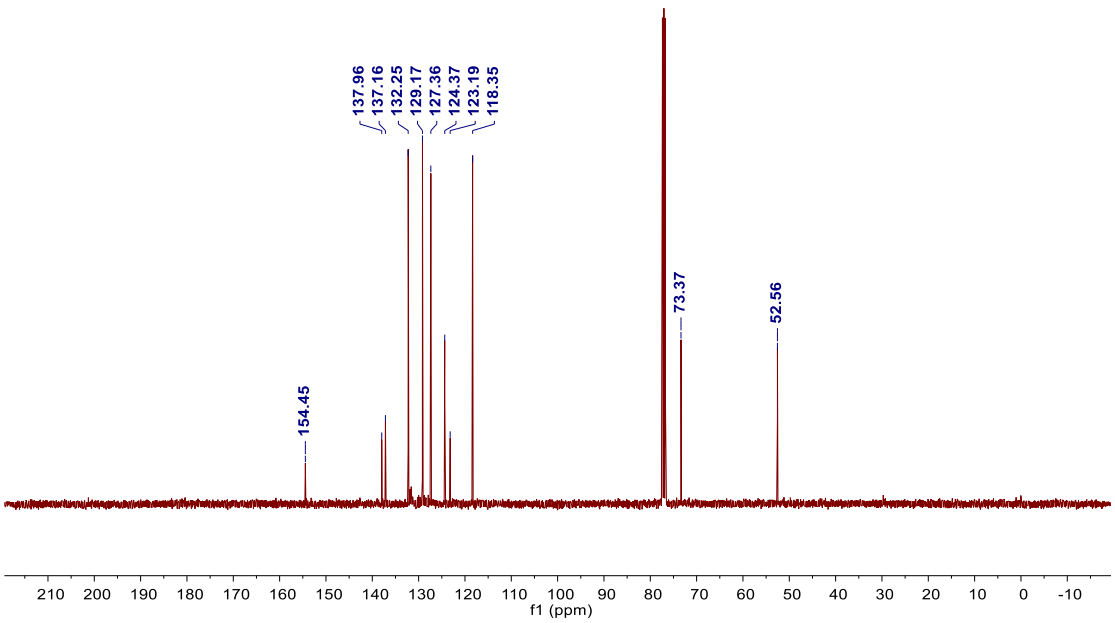

Figure S60. [13]C NMR spectra of oxazolidinones **4t**.

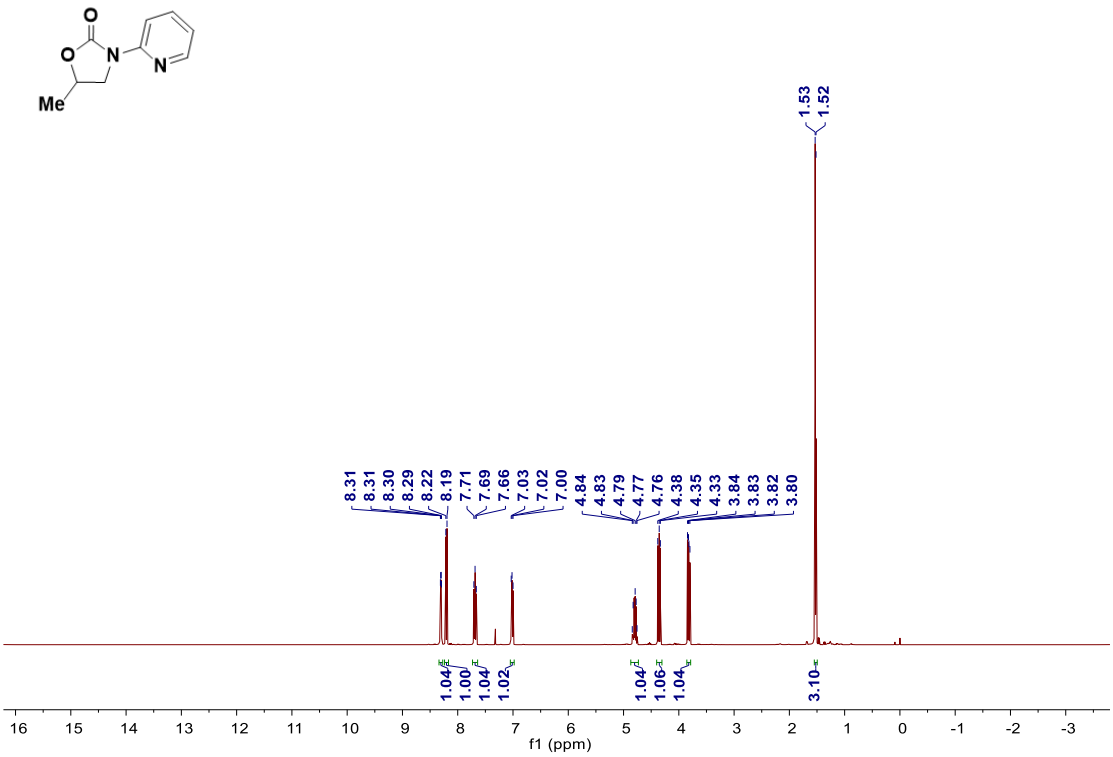

Figure S61. [1]H NMR spectra of oxazolidinones **4u**.

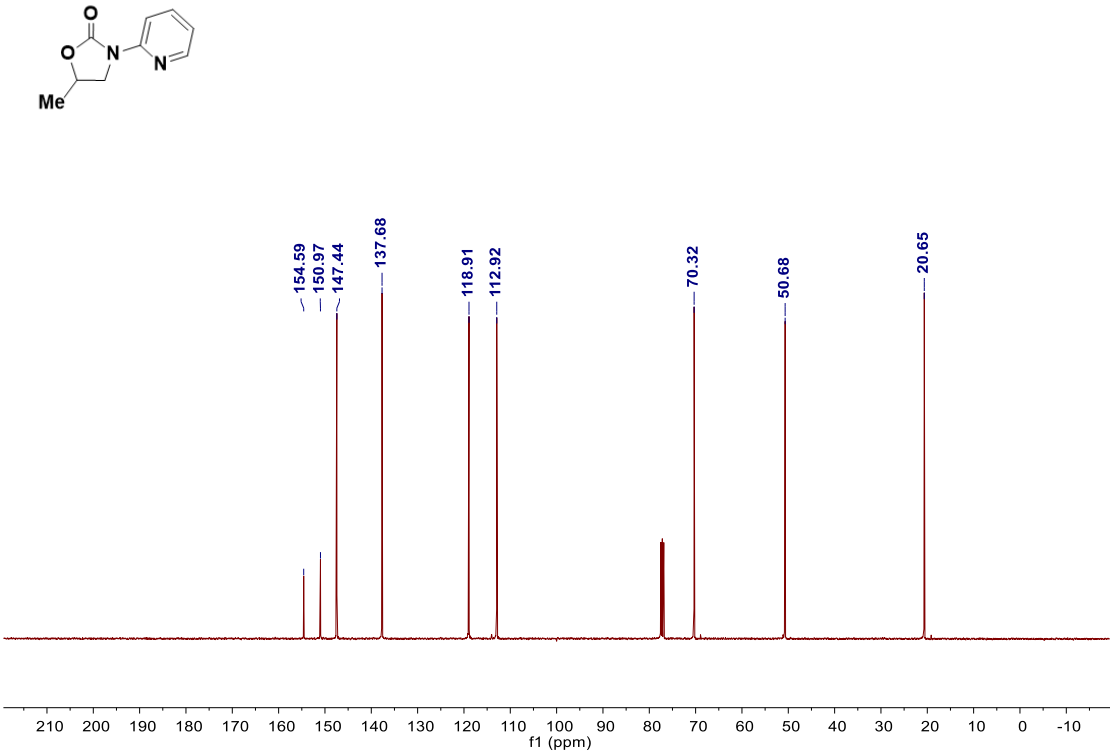

Figure S62. [13]C NMR spectra of oxazolidinones **4u**.

4. NMR Spectra for Organocatalysts

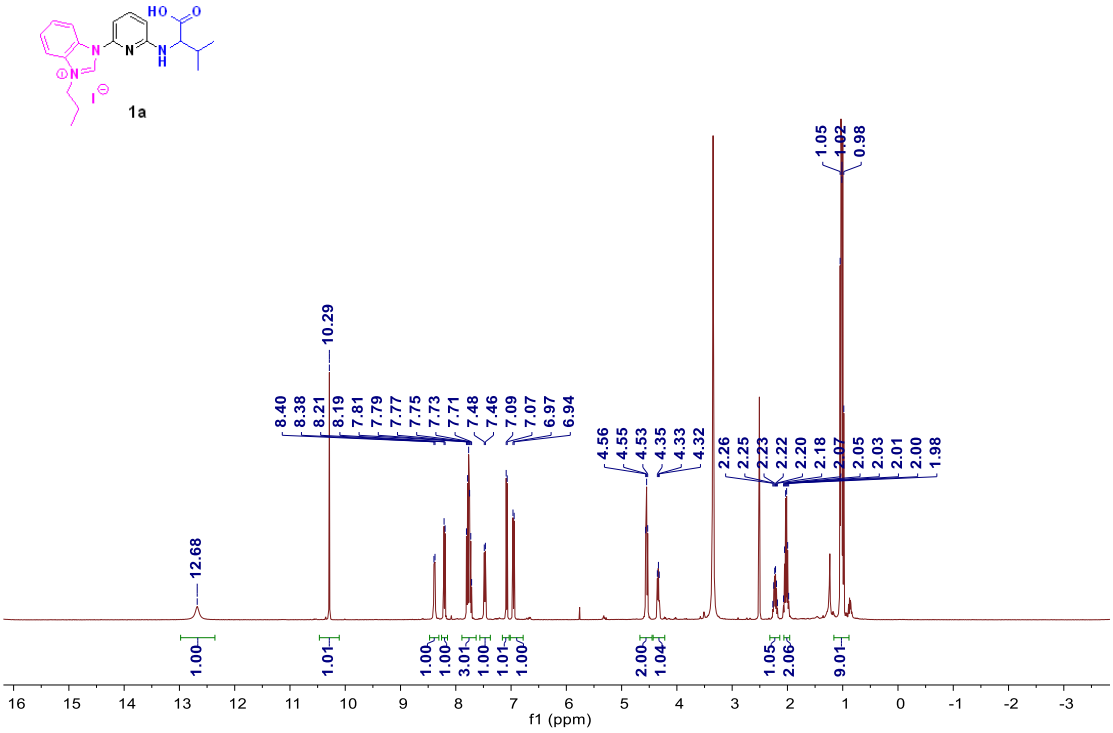

Figure S63. ^{1}H NMR spectra of organocatalyst **1a**.

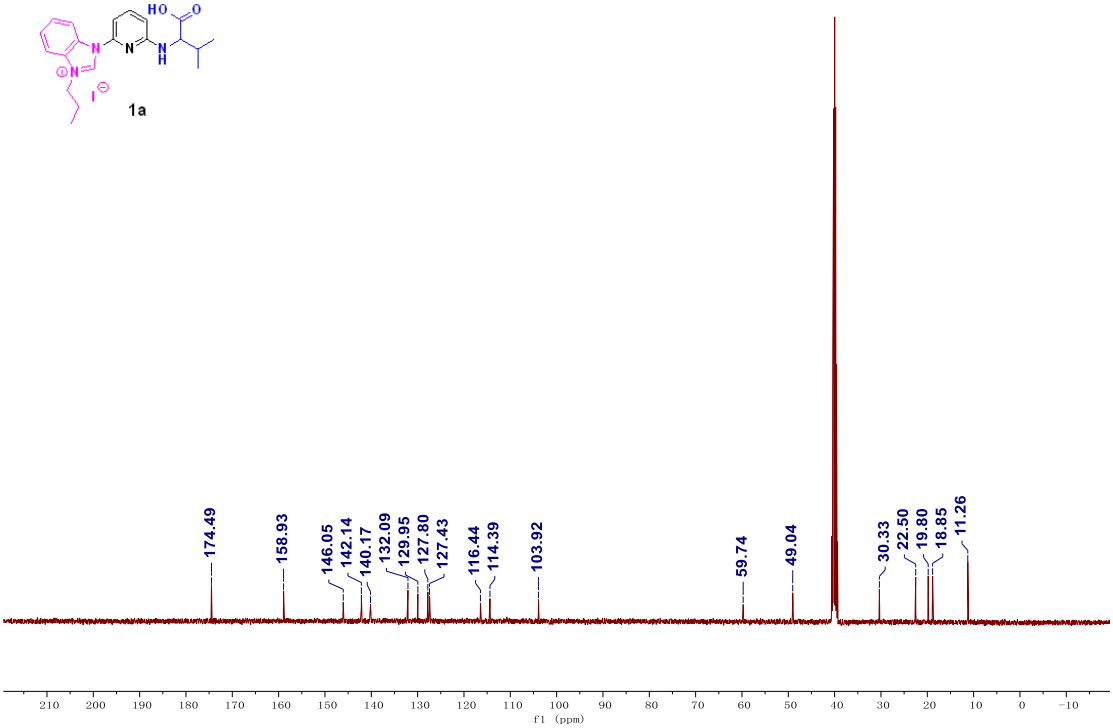

Figure S64. ^{13}C NMR spectra of organocatalyst **1a**.

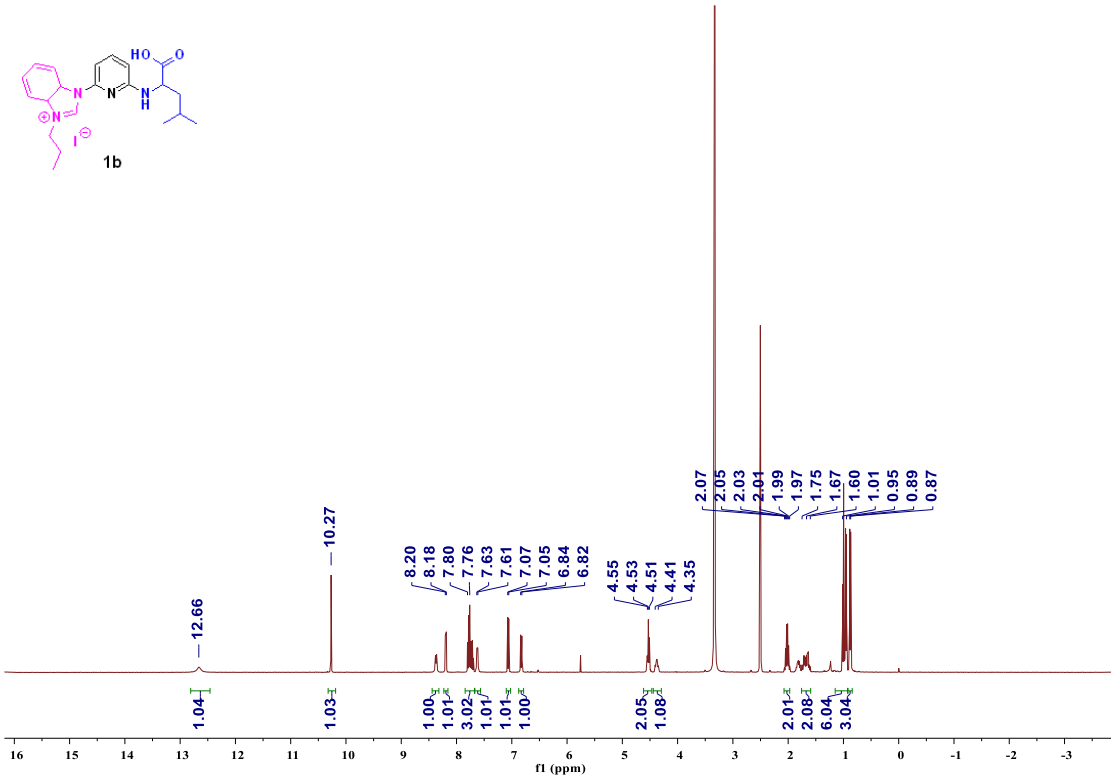

Figure S65. [1]H NMR spectra of organocatalyst **1b**.

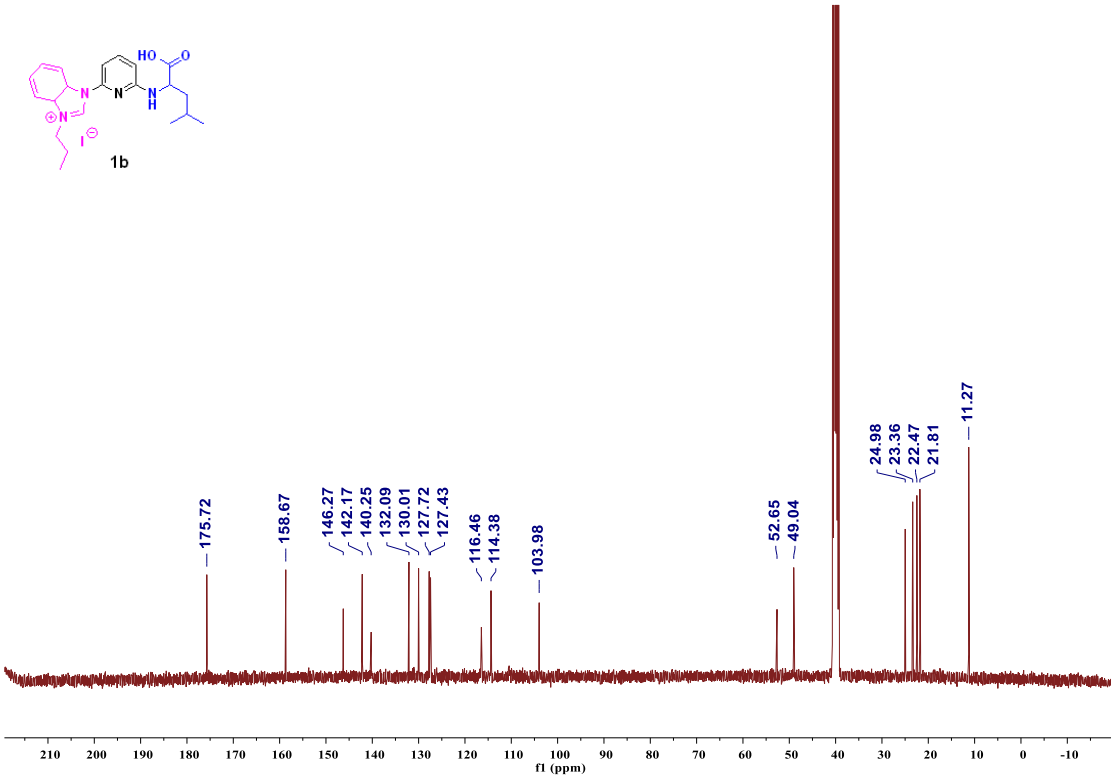

Figure S66. [13]C NMR spectra of organocatalyst **1b**.

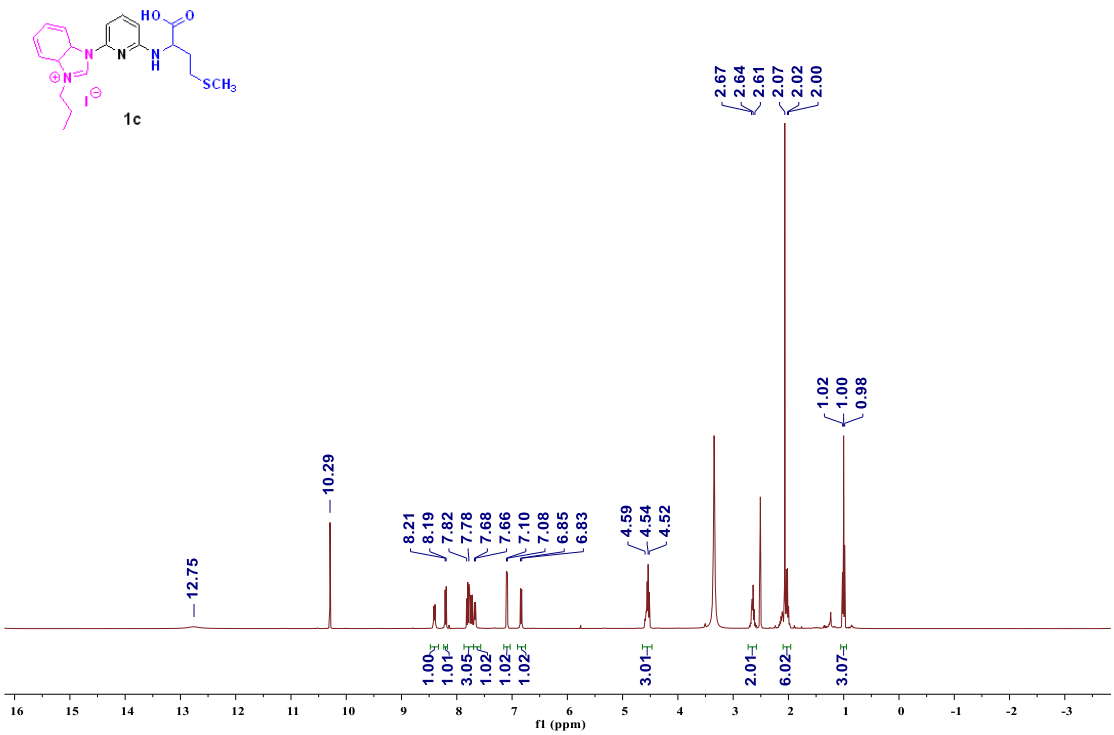

Figure S67. ^{1}H NMR spectra of organocatalyst **1c**.

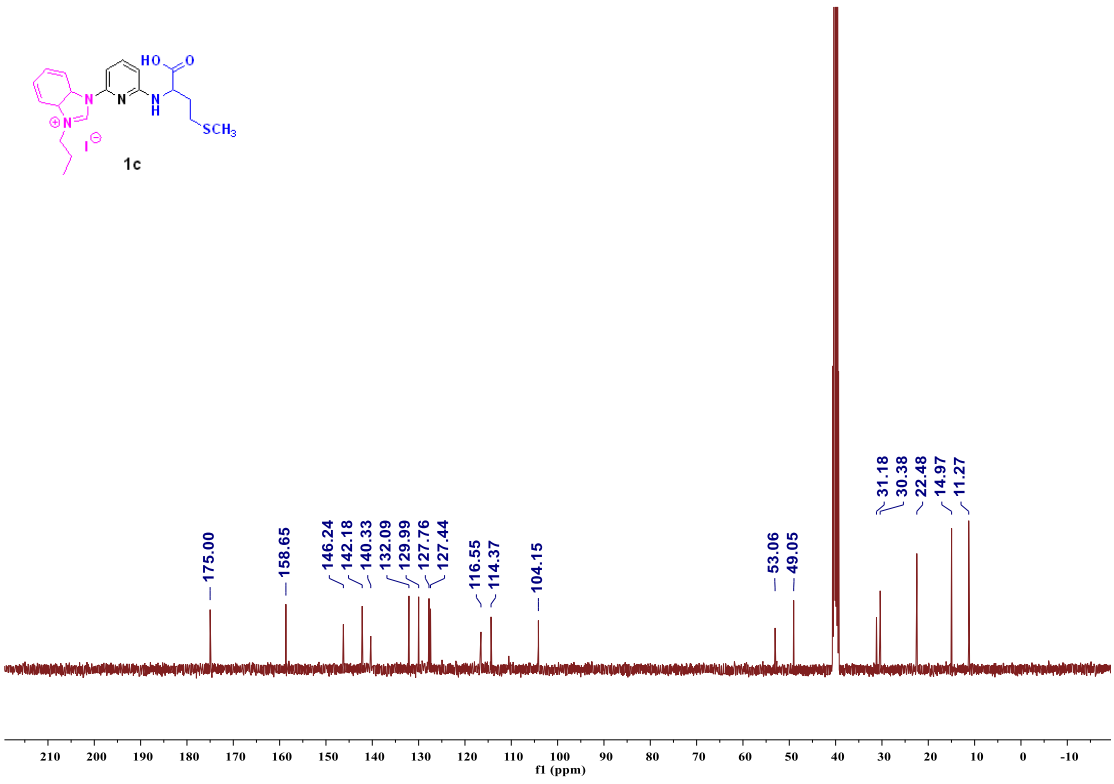

Figure S68. ^{13}C NMR spectra of organocatalyst **1c**.

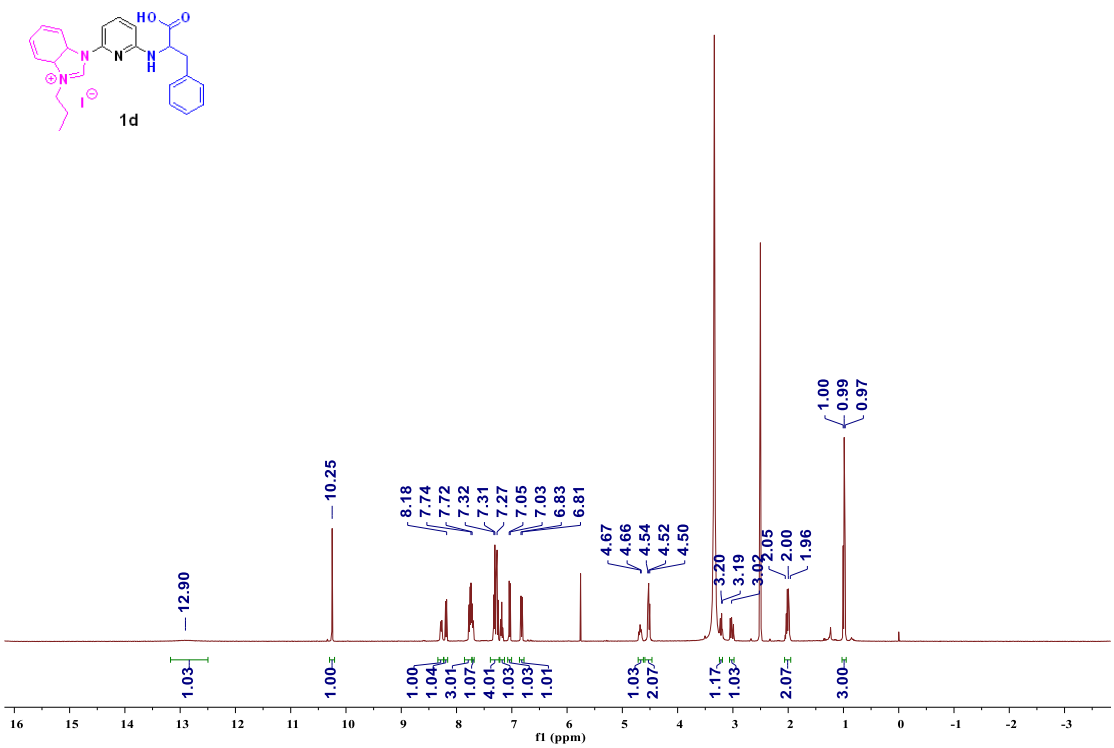

Figure S69. [1]H NMR spectra of organocatalyst **1d**.

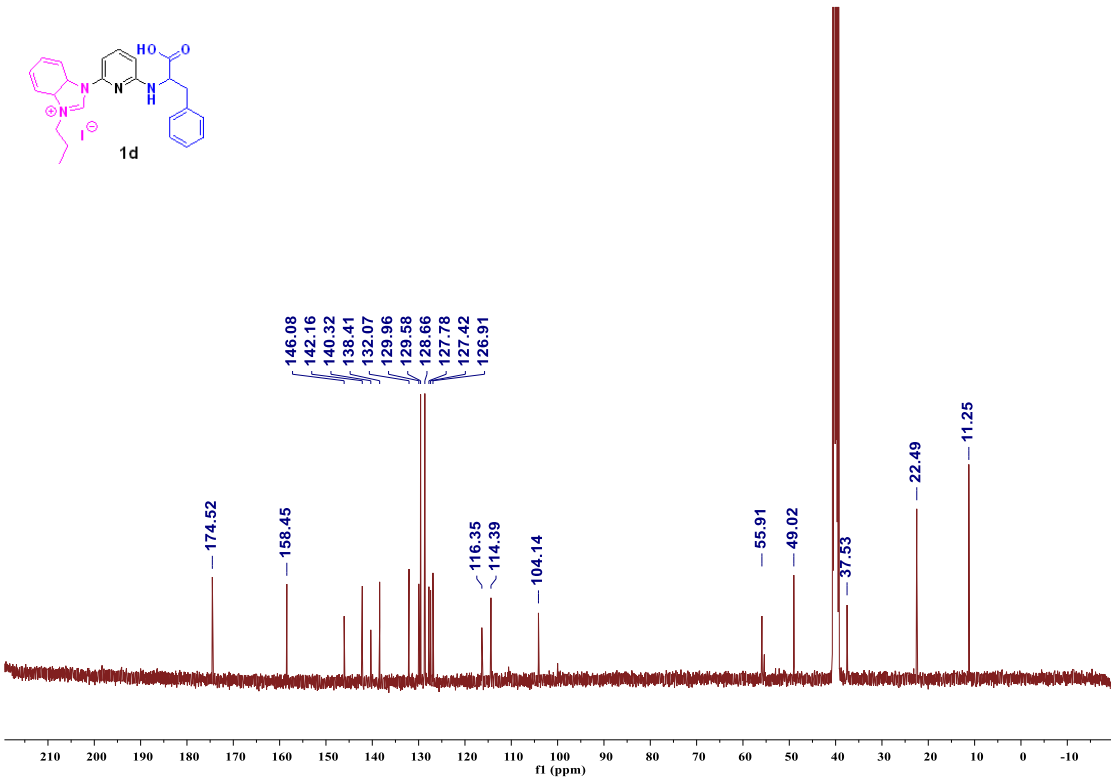

Figure S70. [13]C NMR spectra of organocatalyst **1d**.

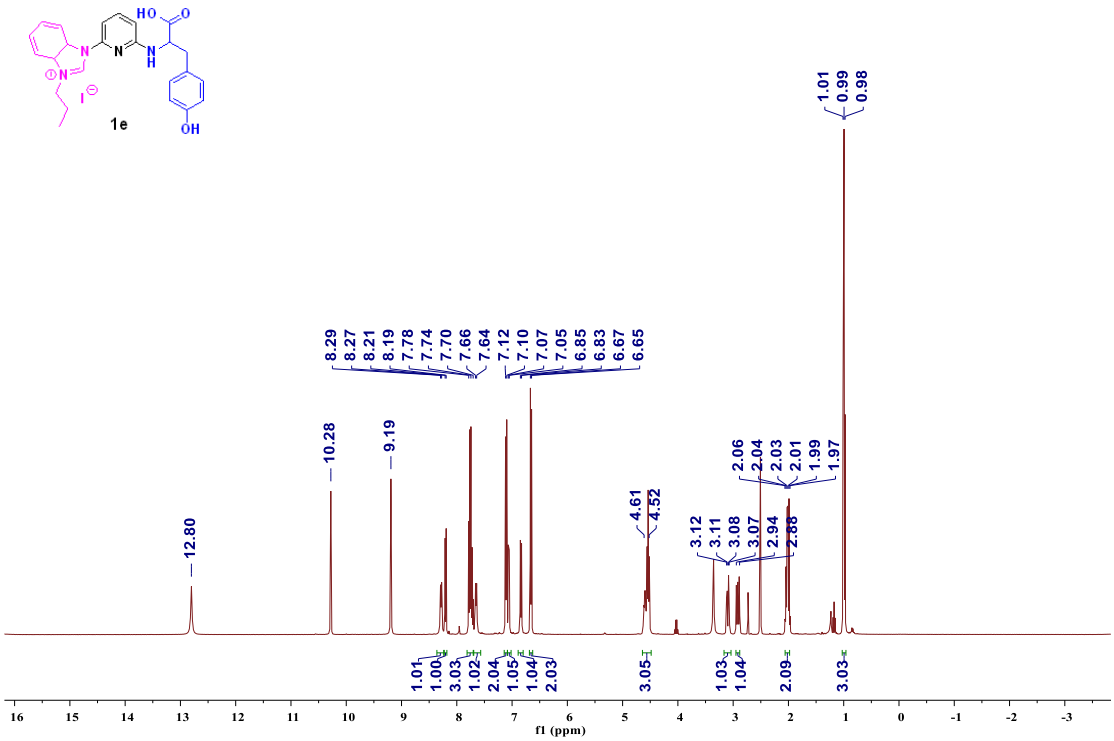

Figure S71. [1]H NMR spectra of organocatalyst **1e**.

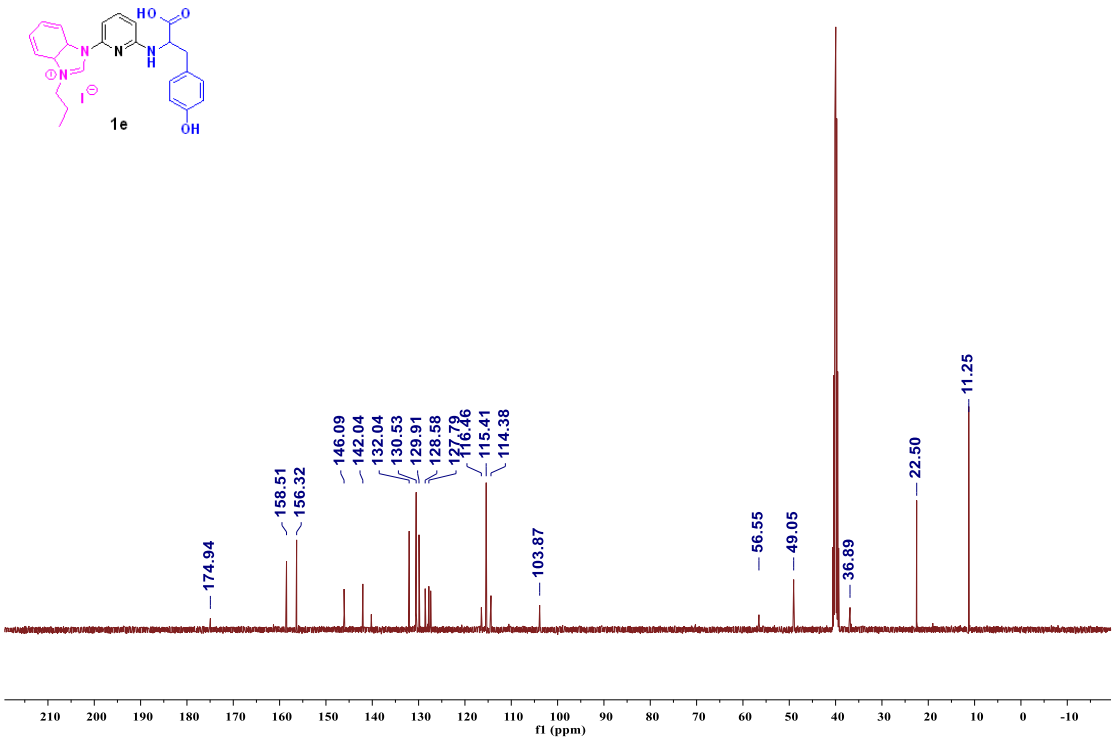

Figure S72. [13]C NMR spectra of organocatalyst **1e**.

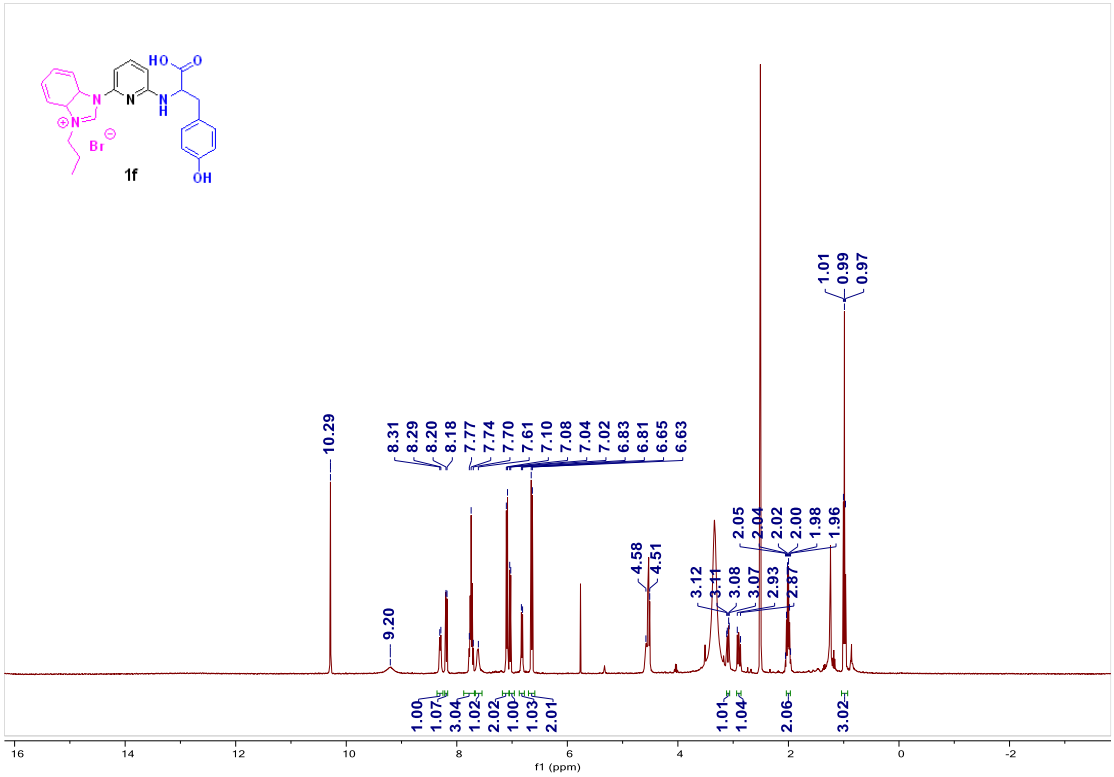

Figure S73. [1]H NMR spectra of organocatalyst **1f**.

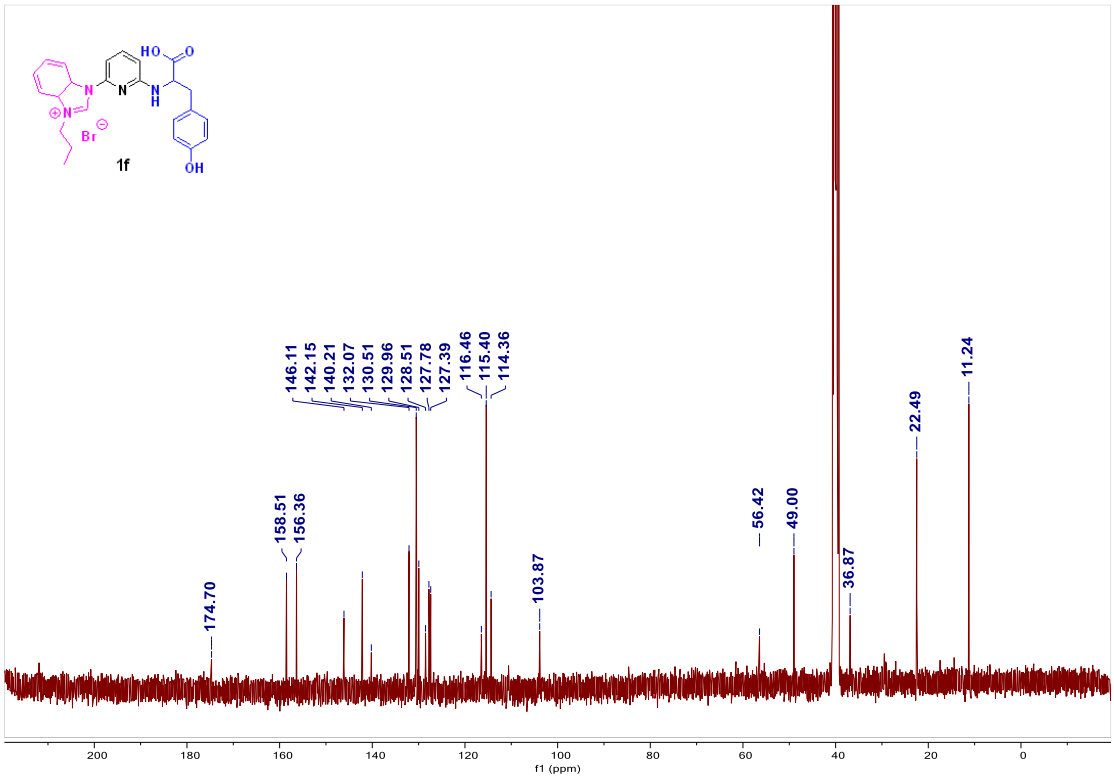

Figure S74. [13]C NMR spectra of organocatalyst **1f**.

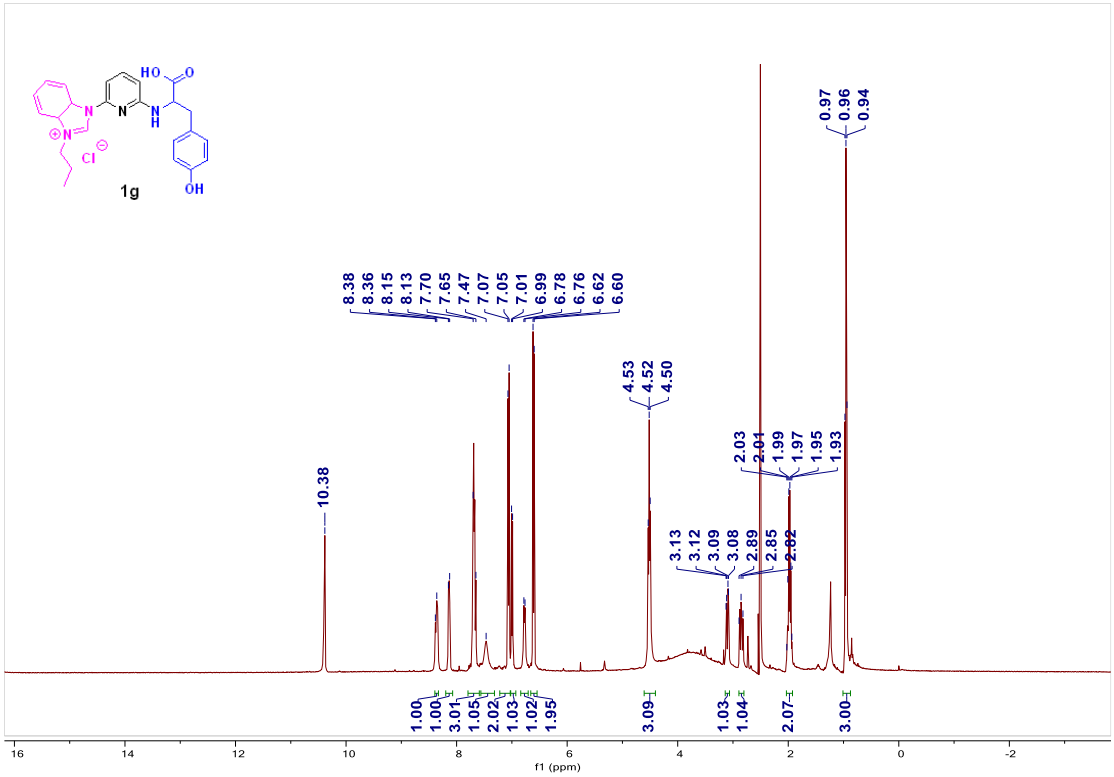

Figure S75. ^{1}H NMR spectra of organocatalyst **1g**.

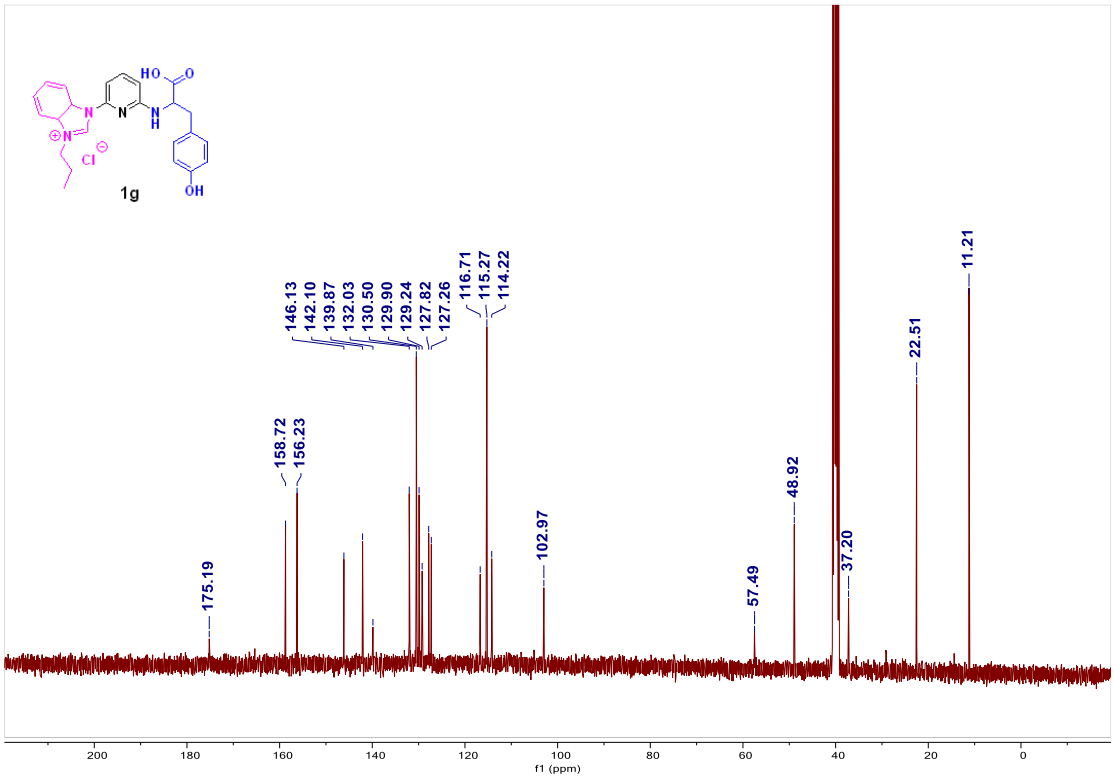

Figure S76. ^{13}C NMR spectra of organocatalyst **1g**.

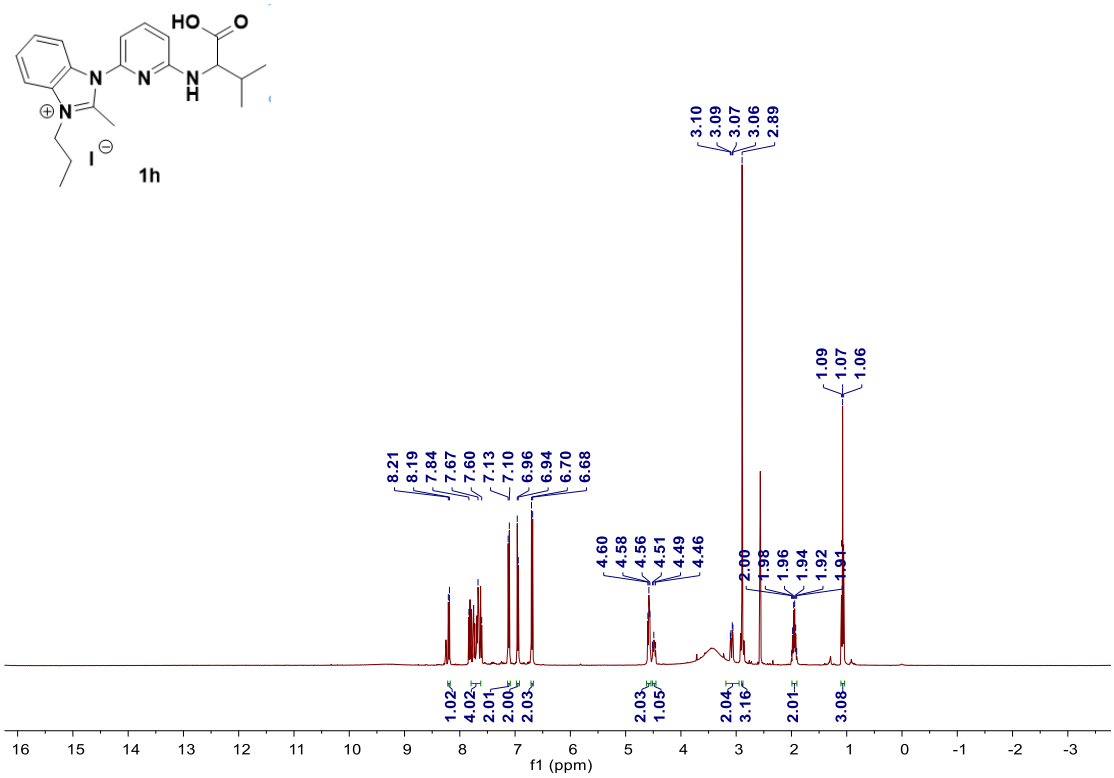

Figure S77. ^{1}H NMR spectra of organocatalyst **1h**.

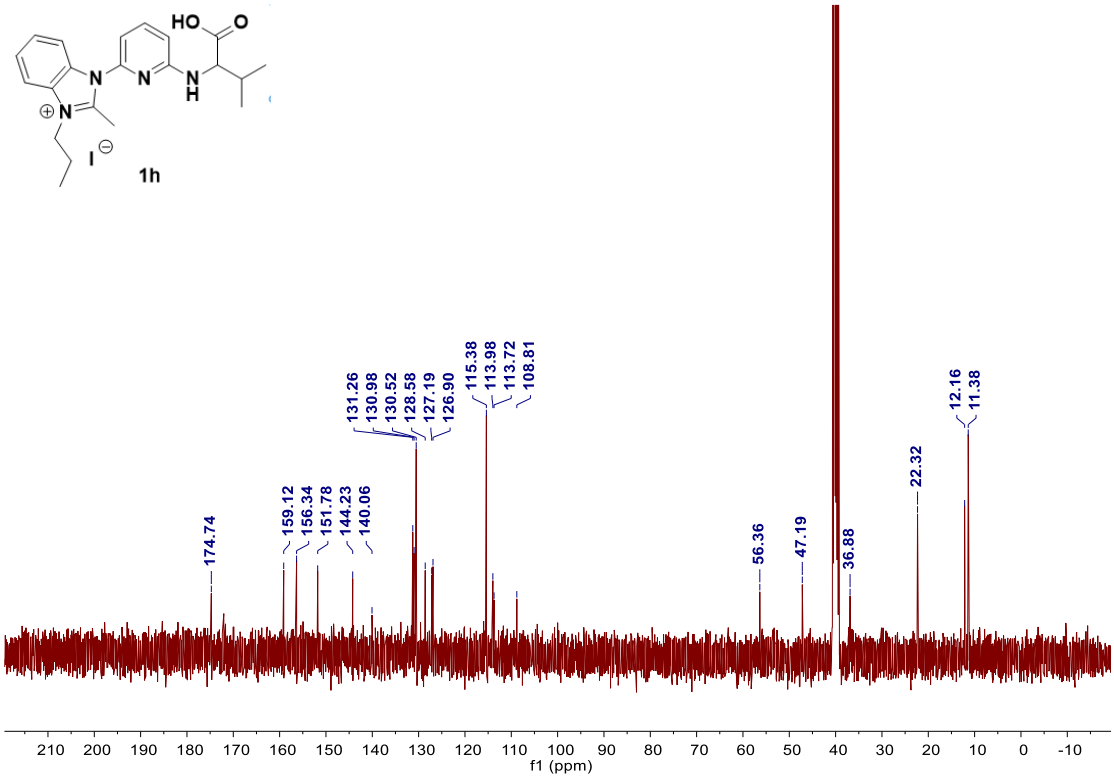

Figure S78. ^{13}C NMR spectra of organocatalyst **1h**.