Utility of silver nanoparticles embedded on covalent organic framework as a highly active catalyst for carboxylative cyclization with CO_2: a sustainable route for production of tetronic acids and oxazolidinones

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Materials

All chemicals were purchased from commercially available sources and used as received without further purification. Solvents were distilled and dried through standard methods before use.

Characterization Techniques

A D8 Advance SWAX diffractometer from Bruker-AXS utilizing a constant current (40 mA) and voltage (40 kV) was used to obtain the powder XRD pattern of the Ag@TFPNDA-COF catalyst. The XRD machine was calibrated with silicon sample utilizing Ni-filtered Cu Kα radiation (λ=0.15406 nm). On a Perkin–Elmer FTIR 783 spectrophotometer the Fourier transform infrared (FTIR) spectra of the catalysts were recorded from 400 to 4000 cm^{-1} using KBr pellets. Scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility was used to measure surface morphology of the Ag@TFPNDA-COF. BET surface area and porosity of these materials were estimated from the respective N_2 sorption isotherms at 77 K by using a Quantachrome Instruments Autosorb-1C surface area analyzer. The samples were activated at 403 K under high vacuum for 12 h before the N_2 adsorption−desorption analysis. TEM images were recorded using FEI Tecnai G2 F20 X-TWIN TEM at an accelerating voltage of 200 kV. HR-TEM, 5 mg of the AgNPs@TzTa-POP catalyst was dispersed into

absolute EtOH under the application of sonication for 30 min, followed by the sample coating on a carbon coated copper TEM grid and dried in air. All spectra were taken at 400 MHz for ^{1}H NMR. Using Bruker DPX-400 in CDCl$_3$ instrument with TMS as internal standard the products was confirmed by 1H spectroscopy.
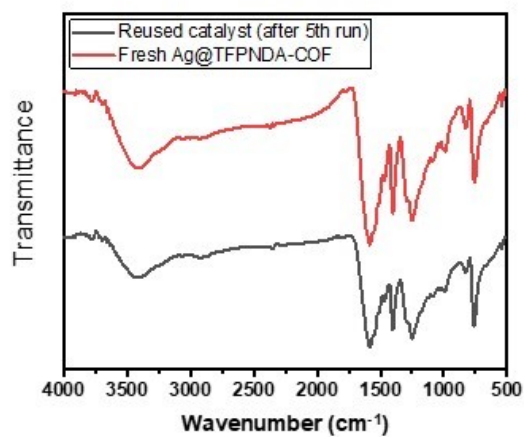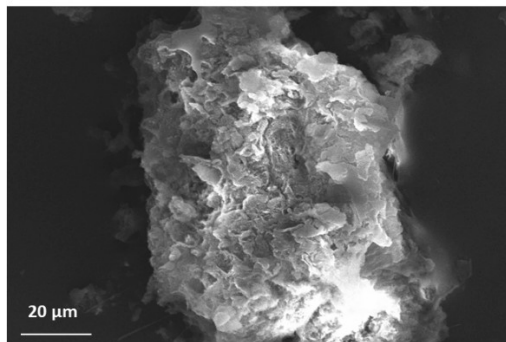

Figure S1: FT-IR spectrum of reused Ag@TFPNDA-COF

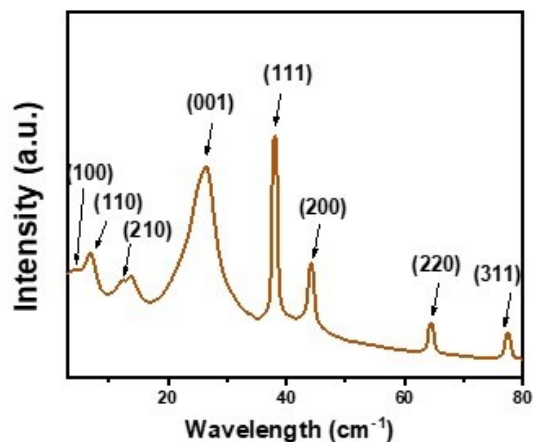Figure S2: FE-SEM picture of reused Ag@TFPNDA-COF material after 5th run.
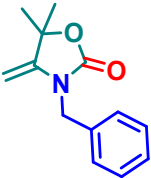
Figure S3: FE-SEM picture of reused Ag@TFPNDA-COF material after 5th run.
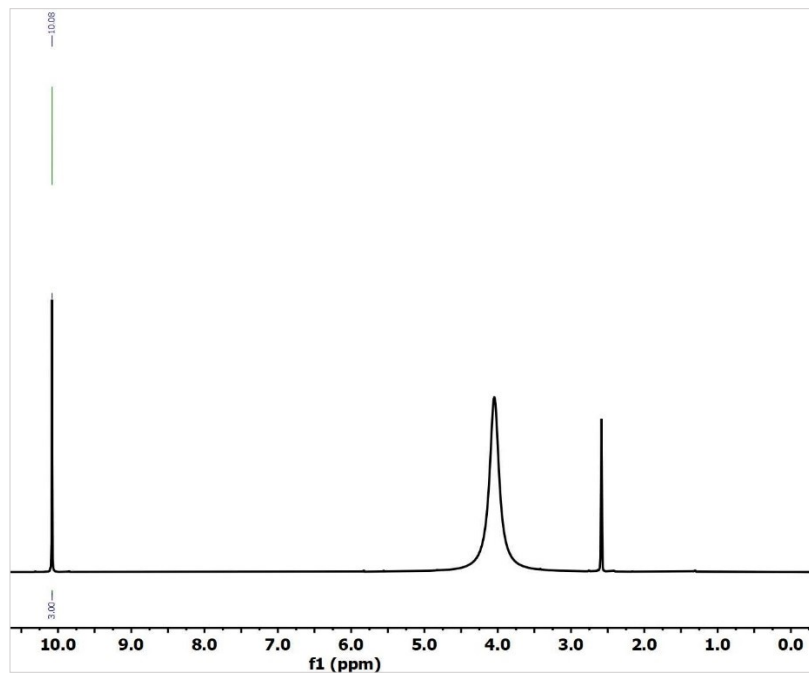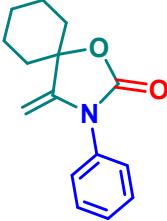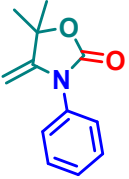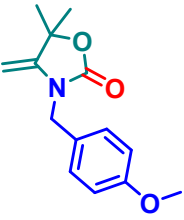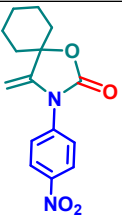

Figure S4: ^{1}H NMR (400 MHz, DMSO-d6) of 1,3,5-Triformylphloroglucinol (TFP), δ (in ppm) 10.08 (s, 3H)

1. **NMR data table of Oxazolidinone derivatives[1, 2]**

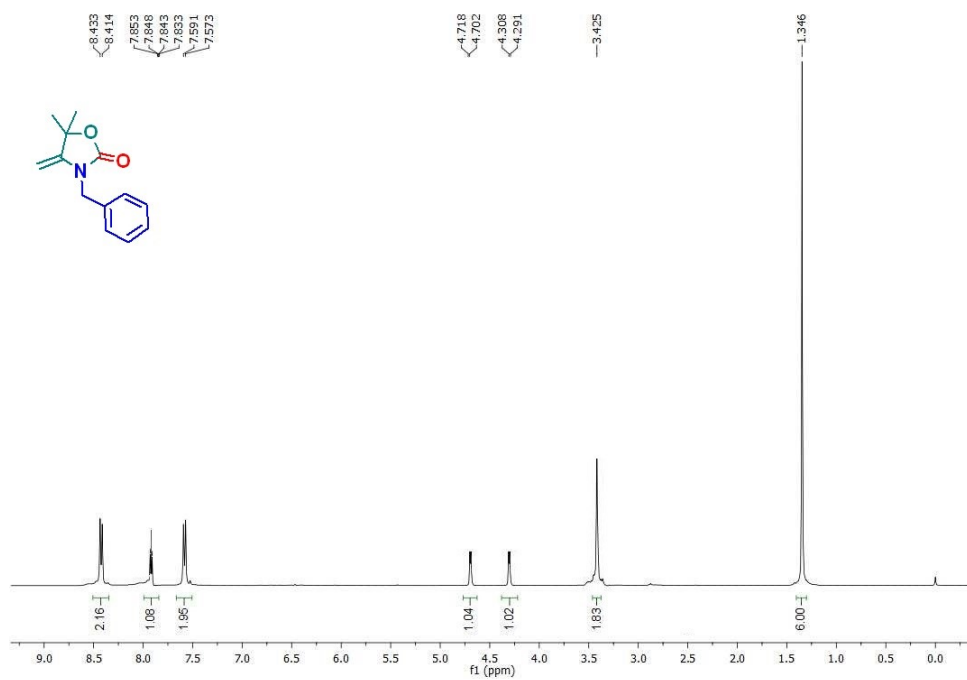| 1a		**3-benzyl-4-methylene-1-oxa-3-azaspiro[4.5]decan-2-one** ^{1}H NMR (400 MHz, CDCl$_3$): δ (in ppm) 0.871-1.625 (m, 8H), 2.095 (s, 1H), 2.125 (s, 1H), 3.225 (s, 2H), 4.255 (d, *J*= 5.6Hz, 1H), 4.617 (d, J= 5.6 Hz, 1H), 6.599 (t, *J*= 6.4 Hz, 1H), 6.678 (s, 1H), 7.7058-7.7098 (m, 3H)

|		
1b		**4-methylene-3-phenyl-1-oxa-3-azaspiro[4.5]decan-2-one** ^{1}H NMR (400 MHz, CDCl$_3$): δ (in ppm) 1.171-1.598 (m, 10H), 4.423 (t, J=6.8Hz, 2H), 6.577 (d, J= 6.4Hz, 2H), 6.657 (d, J= 7.2 Hz, 1H), 7.029 (t, J= 7.2Hz, 2H)
1c		**5,5-dimethyl-4-methylene-3-phenyloxazolidin-2-one** ^{1}H NMR (400 MHz, CDCl$_3$): δ (in ppm) 1.972 (s, 6H), 4.370 (d, J= 6Hz, 1H), 4.769 (d, J= 6Hz, 1H), 7.240 (d, J= 7.6Hz, 2H), 7.295-7.330 (m, 2H), 7.414 (s, 1H)
1d		**3-benzyl-5,5-dimethyl-4-methyleneoxazolidin-2-one** ^{1}H NMR (400 MHz, CDCl$_3$): δ (in ppm) 1.346 (s, 6H), 3.425 (s, 2H), 4.291 (d, J= 6.8Hz, 1H), 4.702 (d, J= 6.4Hz, 1H), 7.573 (d, J= 7.2Hz, 2H), 7.833-7.853 (m, 1H), 8.414 (d, J= 7.6Hz, 2H)
1e		**3-(4-methoxybenzyl)-5,5-dimethyl-4-methyleneoxazolidin-2-one** ^{1}H NMR (400 MHz, CDCl$_3$): δ (in ppm) 1.688 (s, 6H), 3.244 (s, 2H), 3.684 (s, 3H), 4.494 (d, J= 4.4Hz, 2H), 6.864 (d, J= 7.6Hz, 2H), 7.704 (d, J= 8Hz, 2H)
1f		**4-methylene-3-(4-nitrophenyl)-1-oxa-3-azaspiro[4.5]decan-2-one** ^{1}H NMR (400 MHz, CDCl$_3$): δ (in ppm): 0.792-1.546 (m, 10H), 4.219 (m, 2H), 6.545 (d, J= 9.2Hz, 2H), 7.993 (d, J= 9.2Hz, 2H)
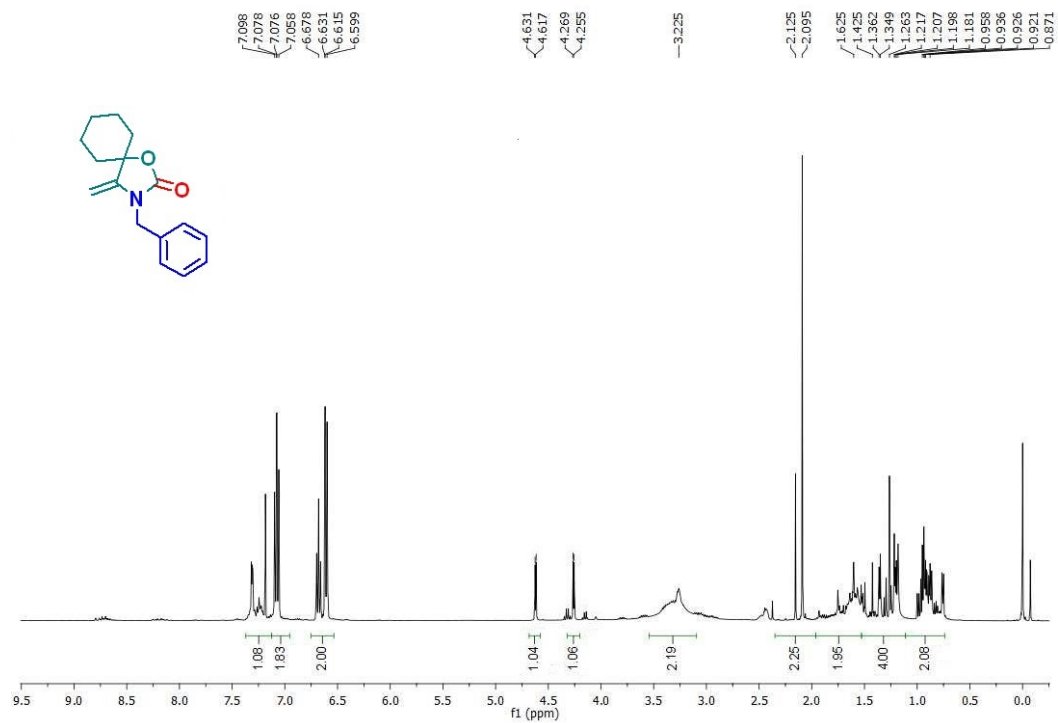
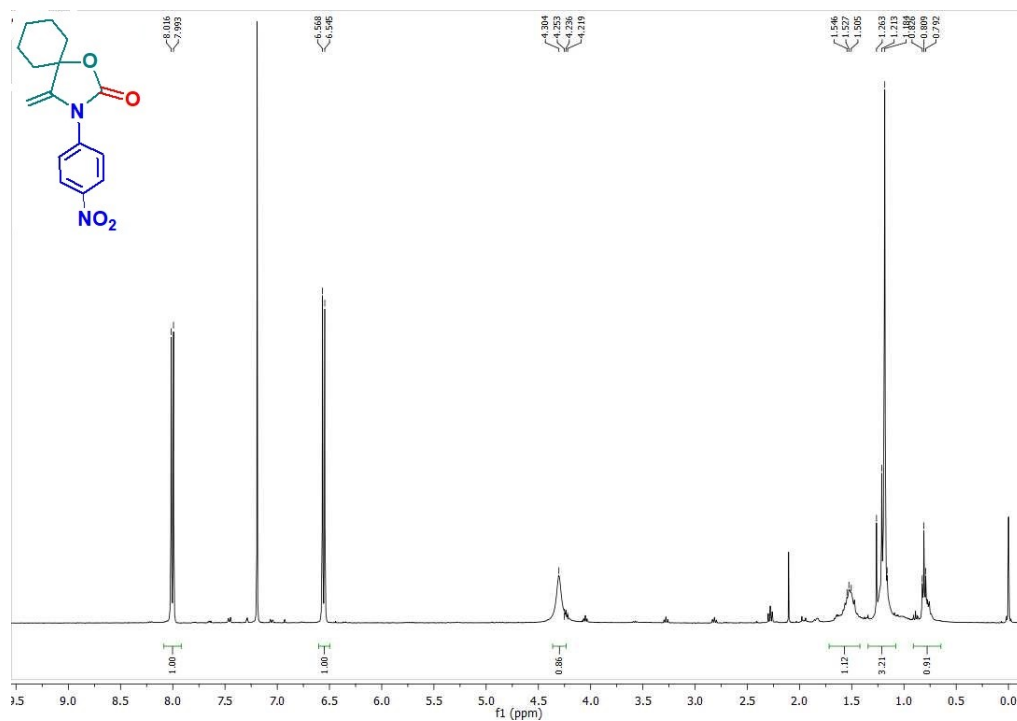1a: ^{1}H NMR data of 3-benzyl-4-methylene-1-oxa-3-azaspiro[4.5]decan-2-one
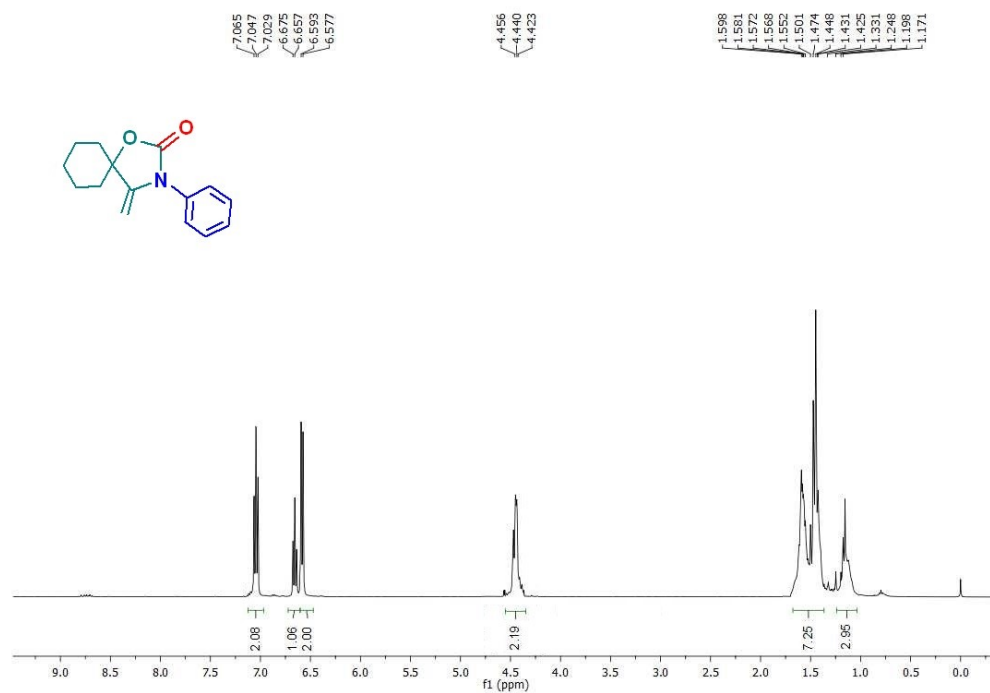
1b: ^{1}H NMR data of 4-methylene-3-phenyl-1-oxa-3-azaspiro[4.5]decan-2-one
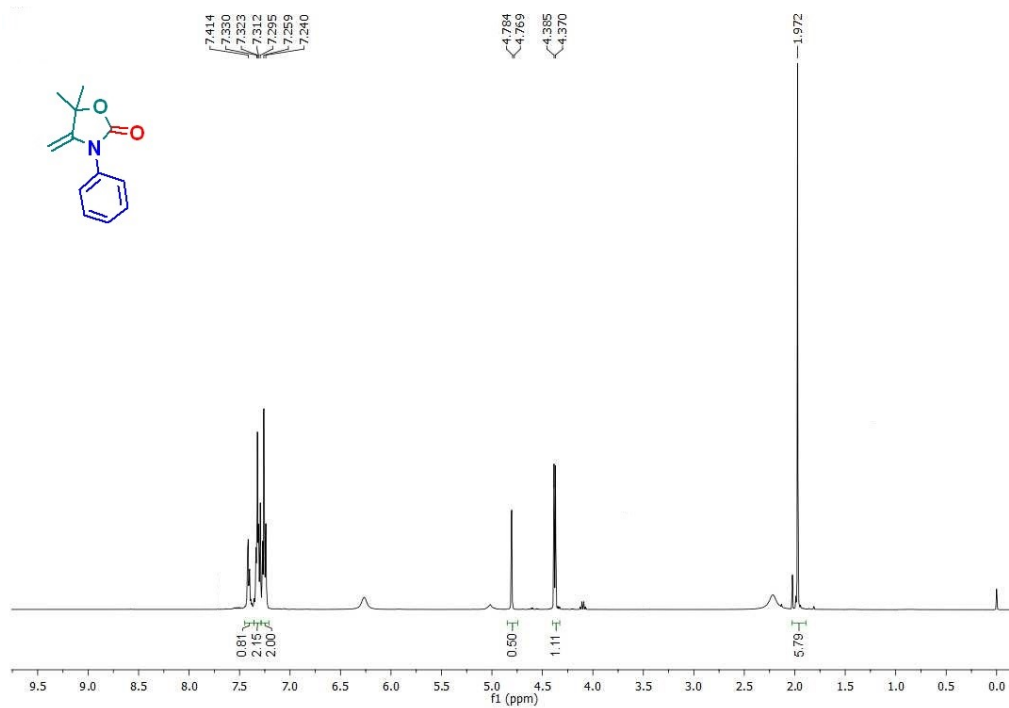
1c: ^{1}H NMR data of 5,5-dimethyl-4-methylene-3-phenyloxazolidin-2-one

1d: ^{1}H NMR data of 3-benzyl-5,5-dimethyl-4-methyleneoxazolidin-2-one
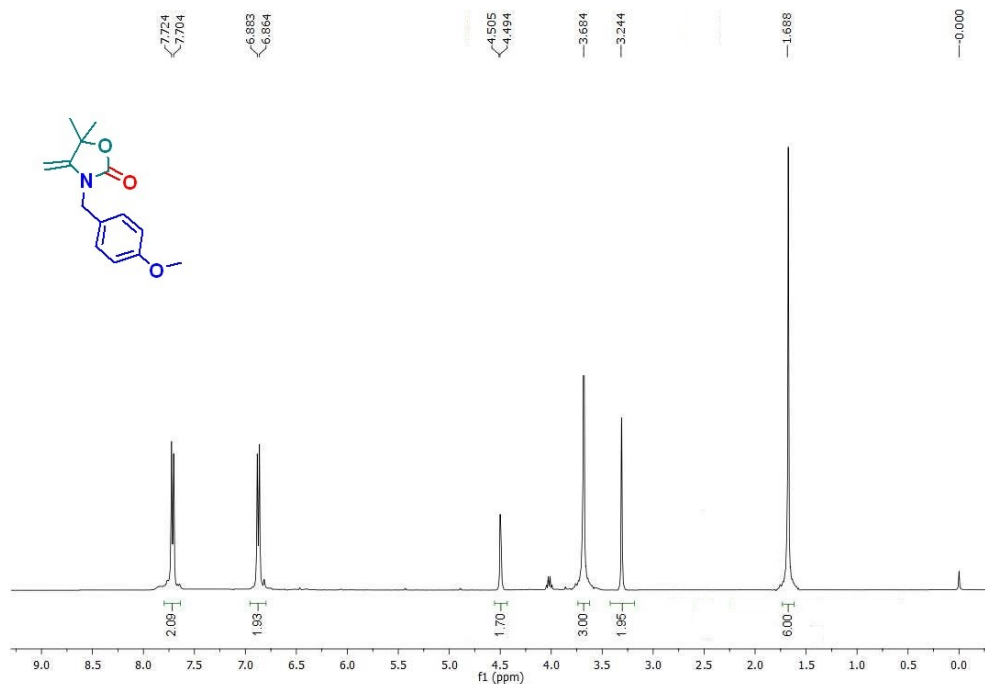
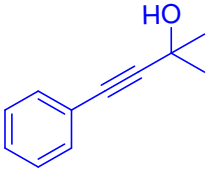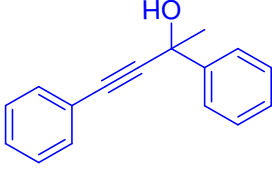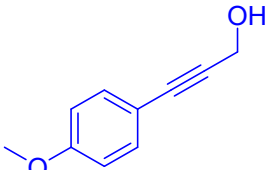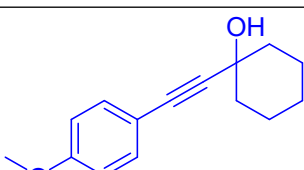1e: ^{1}H NMR data of 3-(4-methoxybenzyl)-5,5-dimethyl-4-methyleneoxazolidin-2-one


1f: ^{1}H NMR data of 4-methylene-3-(4-nitrophenyl)-1-oxa-3-azaspiro[4.5]decan-2-one

2. NMR data table of Propargyl Alcohols[3, 4]

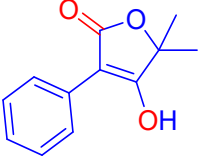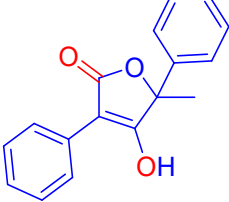| 2a		**2-methyl-4-phenylbut-3-yn-2-ol** ^{1}H NMR (400 MHz, CDCl$_3$): δ (in ppm) 1.537 (s, 6H), 7.200 (t, J = 4Hz, 3H), 7.319 (d, J = 4Hz, 2H).
2b		**2,4-diphenylbut-3-yn-2-ol** ^{1}H NMR (400 MHz, CDCl$_3$): δ (in ppm) 1.869 (s, 3H), 7.251-7.333 (m, 5H, Ar-H), 7.370 (d, J = 7.6 Hz, 2H), 7.470-7.494 (m, 1H), 7.721 (d, J = 7.6 Hz, 2H).
2c		**3-(4-methoxyphenyl)prop-2-yn-1-ol** ^{1}H NMR (400 MHz, CDCl$_3$): δ (in ppm) 3.766 (s, 3H), 4.528 (s, 2H), 6.668 (d, J= 7.2 Hz, 2H), 7.536 (d, J= 7.2Hz, 2H).
2d		**1-((4-methoxyphenyl)ethynyl)cyclohexan-1-ol** ^{1}H NMR (400 MHz, CDCl$_3$): δ (in ppm) 1.237- 2.044 (m, 10 H), 3.801 (s, 3H), 6.814 (d, J= 9.2 Hz, 2H), 7.350 (d, J= 8.8 Hz, 2H).
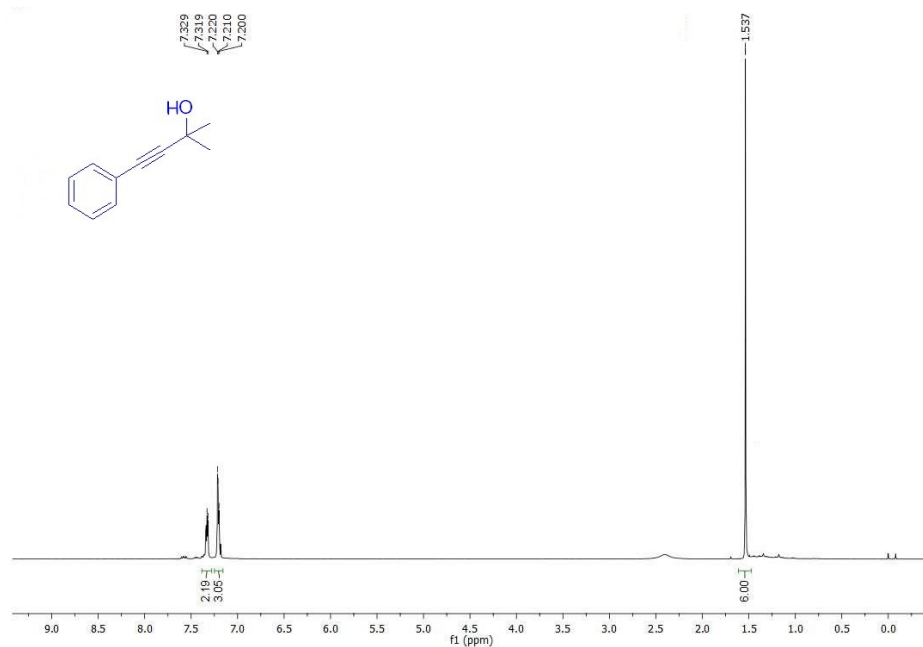
2a: ^{1}H NMR data of 2-methyl-4-phenylbut-3-yn-2-ol
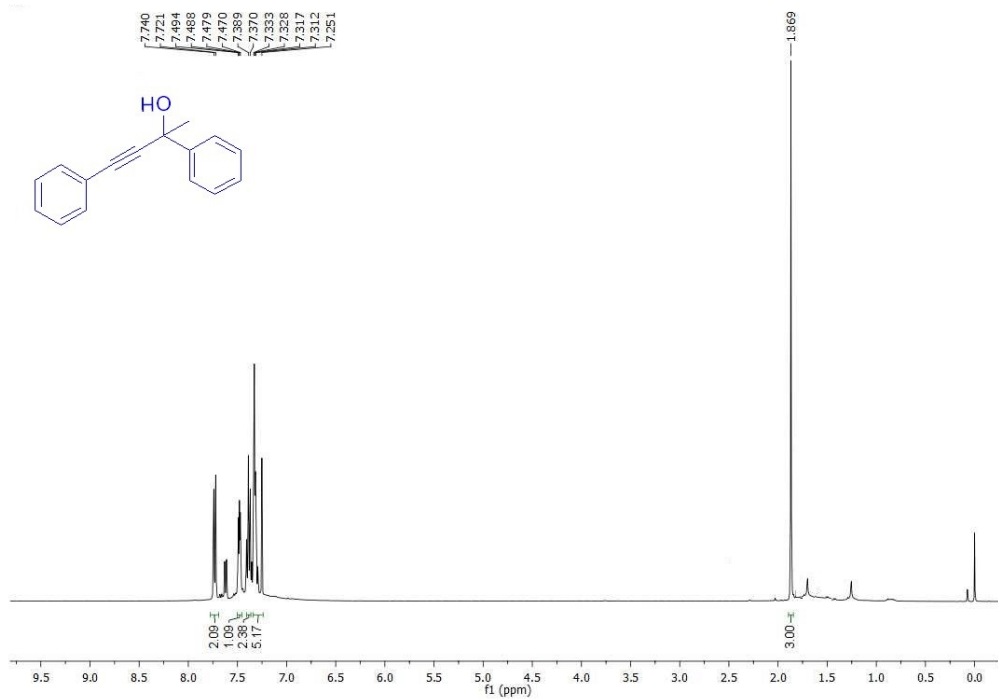
2b: ¹H NMR data of 2,4-diphenylbut-3-yn-2-ol
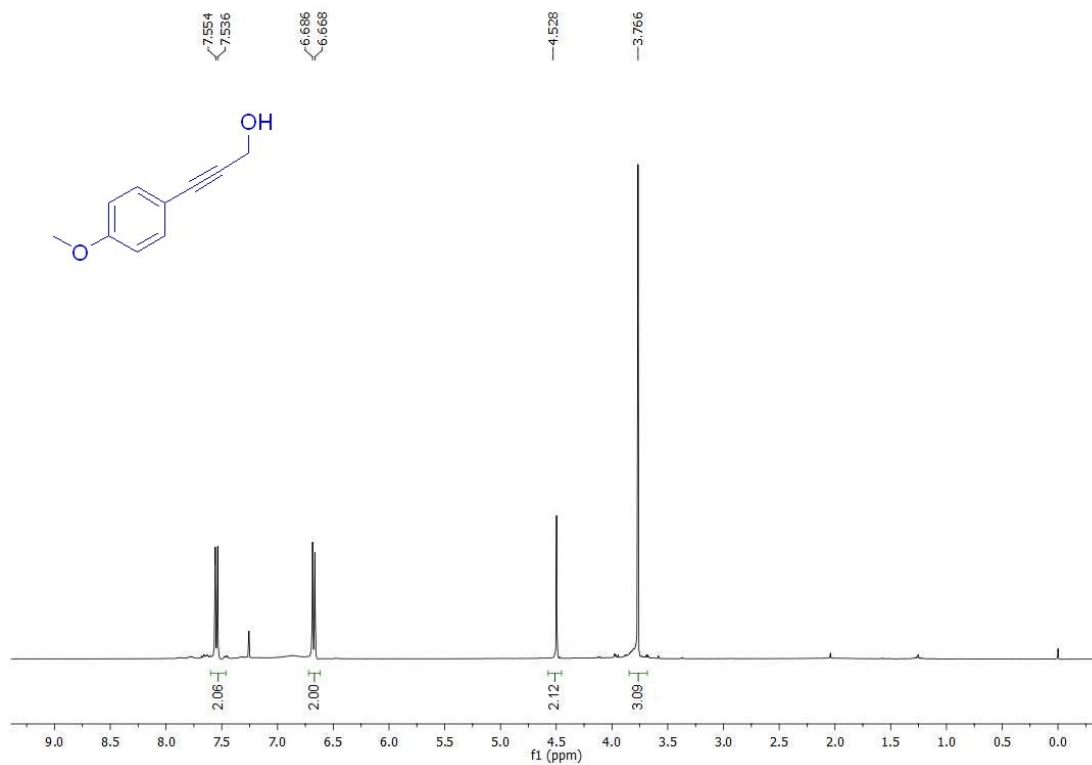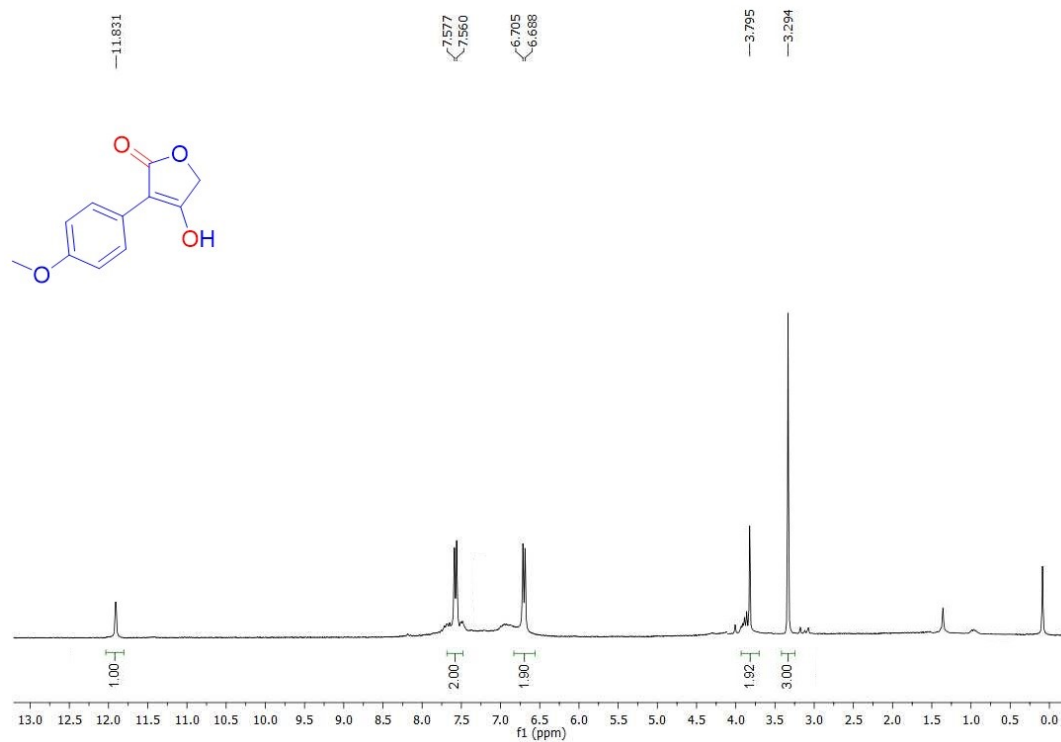

2c: ¹H NMR data of 3-(4-methoxyphenyl)prop-2-yn-1-ol
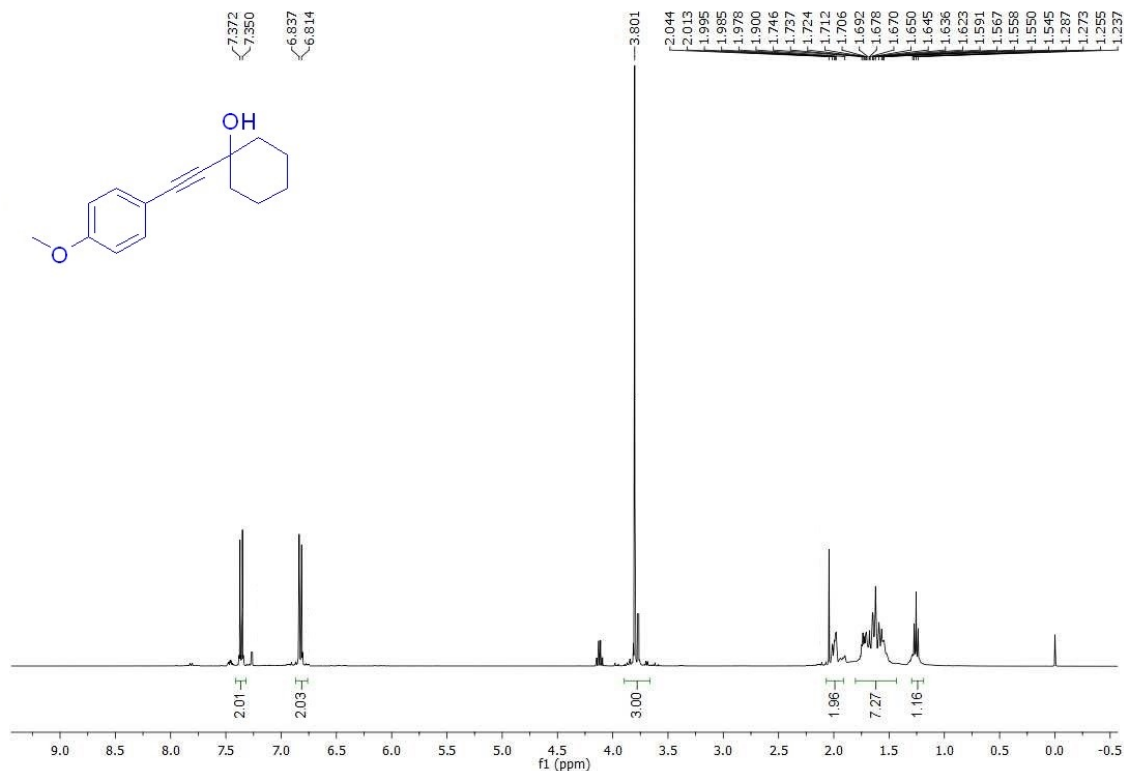
2d: ¹H NMR data of 1-((4-methoxyphenyl)ethynyl)cyclohexan-1-ol

3. NMR data table of Tetronic acids[5, 6]

3a		**4-hydroxy 3-(4-methoxyphenyl)-1-oxaspiro[4.5]dec-3-en-2-one** ¹H NMR (400 MHz, CDCl₃): δ (in ppm) 1.067- 1.824 (m, 10H), 3.578 (s, 3H), 7.083 (d, J= 7.2 Hz, 2H), 7.550 (d, J= 8.8Hz, 2H), 11.539 (s, 1H)
3b		**4-hydroxy-3-(4-methoxyphenyl)furan-2(5H)-one** ¹H NMR (400 MHz, CDCl₃): δ (in ppm) 3.294 (s, 3H), 3.795 (s, 2H), 6.688 (d, J= 6.8 Hz, 2H), 7.560 (d, J= 6.8 Hz, 2H), 11.831 (s, 1H)
3c		**4-hydroxy-5,5-dimethylfuran-2(5H)-one** ¹H NMR (400 MHz, CDCl₃): δ (in ppm) 2.057 (s, 6H), 5.430 (s, 1H), 11.294 (s, 1H)

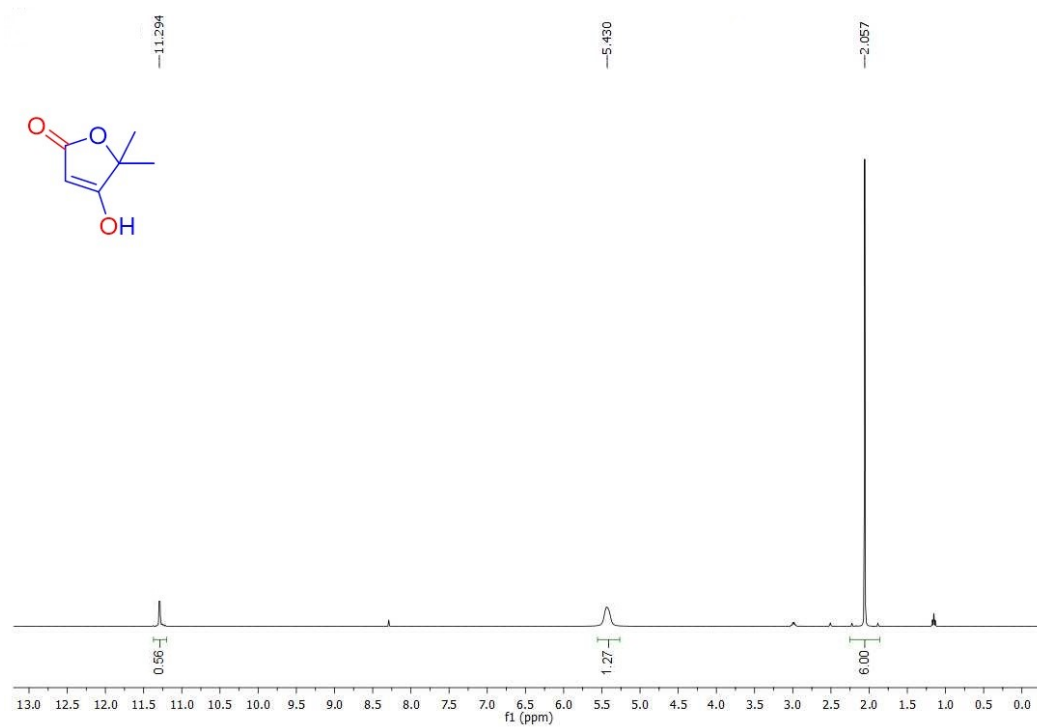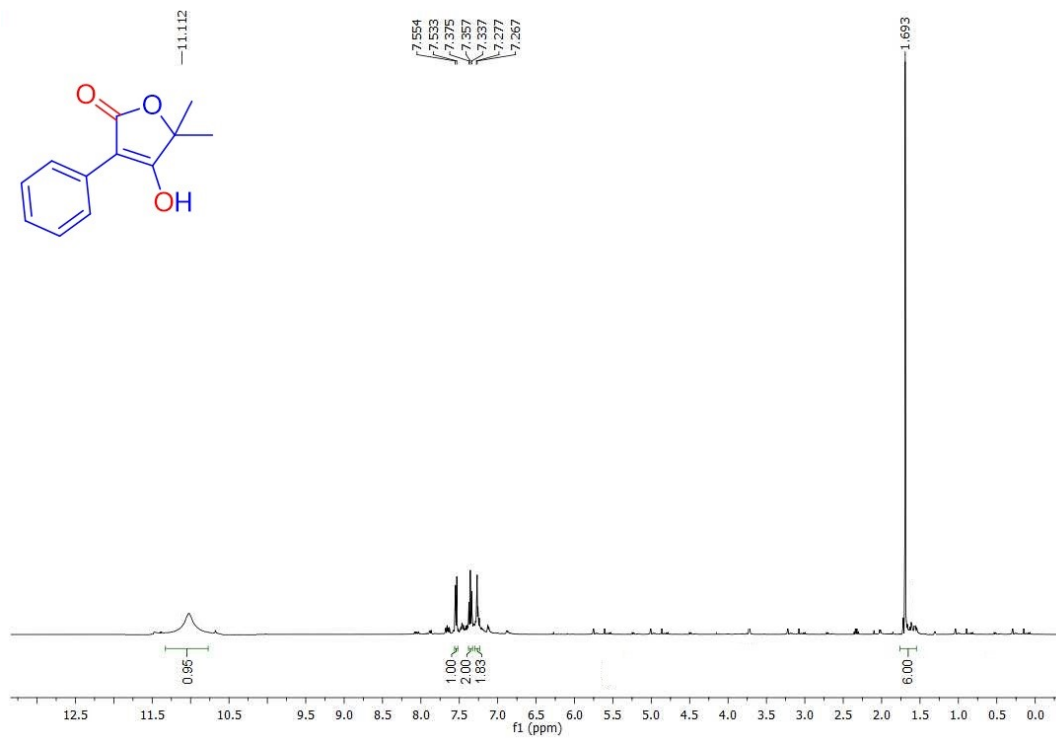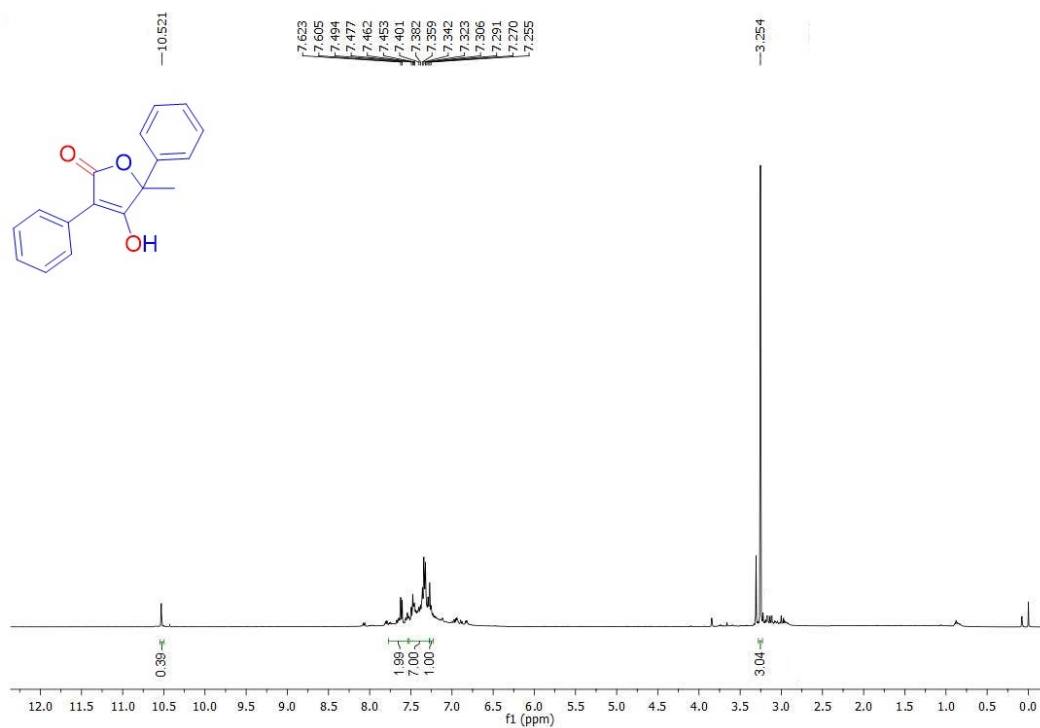| 3d		**4-hydroxy-5,5-dimethyl-3-phenylfuran-2(5H)-one** ^{1}H NMR (400 MHz, CDCl$_3$): δ (in ppm) 1.693 (s, 6H), 7.267 (d, J= 4Hz, 2H), 7.337 (t, J= 8Hz, 2H), 7.533 (d, J= 8.4Hz, 1H), 11.112 (s, 1H)
3e		**4-hydroxy-5-methyl-3,5-diphenylfuran-2(5H)-one** ^{1}H NMR (400 MHz, CDCl$_3$): δ (in ppm) 3.254 (s, 3H), 7.255-7.342 (m, 1H), 7.359-7.462 (m, 7H), 7.477-7.623 (m, 2H), 10.521 (s, 1H)
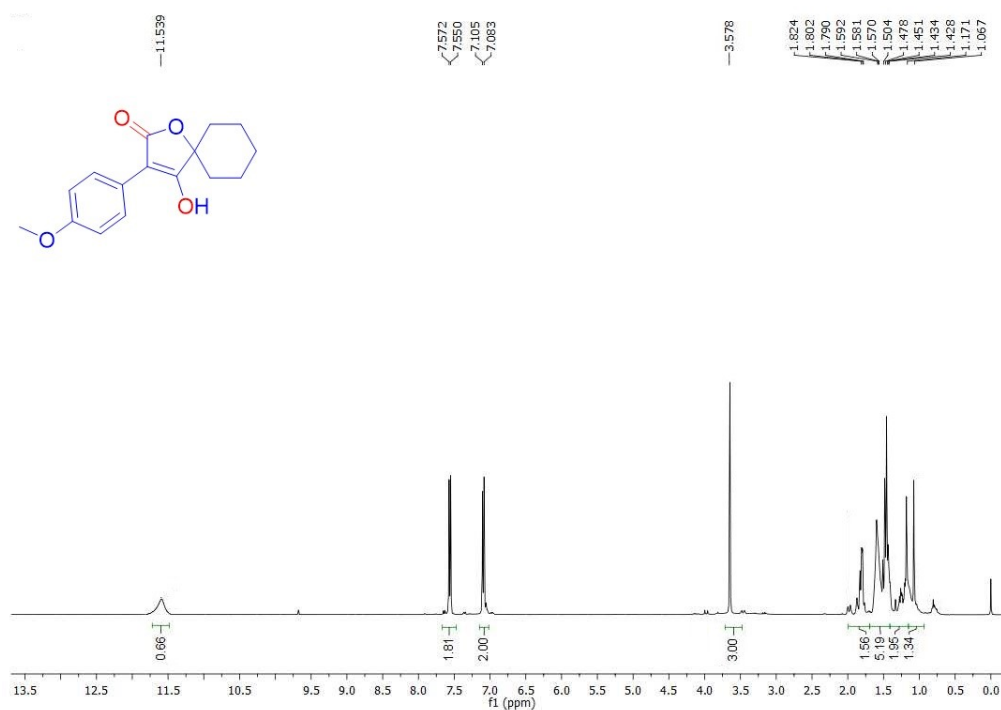
3a: ^{1}H NMR data of 4-hydroxy 3-(4-methoxyphenyl)-1-oxaspiro[4.5]dec-3-en-2-one

3b: ^{1}H NMR data of 4-hydroxy-3-(4-methoxyphenyl)furan-2(5H)-one

3c: ^{1}H NMR data of 4-hydroxy-5,5-dimethylfuran-2(5H)-one

3d: ¹H NMR data of 4-hydroxy-5,5-dimethyl-3-phenylfuran-2(5H)-one

3e: ¹H NMR data of 4-hydroxy-5-methyl-3,5-diphenylfuran-2(5H)-one

References

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6. A. Manchoju and S. V. Pansare, *Organic Letters*, 2016, **18**, 5952-5955.