Synthesis

Reviews and Full Papers in Chemical Synthesis

Supporting Information

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One-Pot Synthesis of Bio-based Styrenes from β-(Phenyl)-β-(phenyl-thio)propionic Acids via Neutral Ionic Liquid, Microwave Irradiation Triggered Cascade Decarboxylative Dehydrosulfenylation

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1. General Experimental Section:

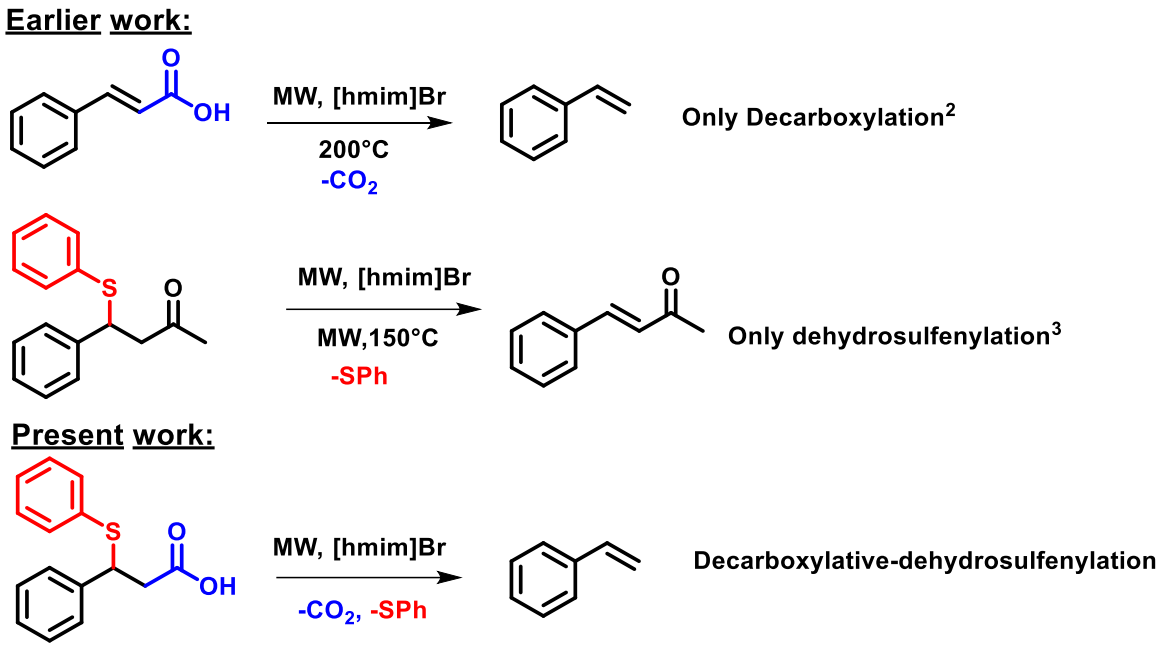
Materials:

All the substrates were obtained from commercial sources (Sigma Aldrich or Alfa-Aesar). The solvents used for isolation/purification of compound were obtained from commercial sources (Merck/S d fine) and were used without further purification. The ionic liquids used were obtained either commercially (Merck or Alfa Aesar) or synthesized according to the reported method.[1] The organic extracts were dried over anhydrous sodium sulfate (Merck grade). Evaporation of solvent was performed at reduced pressure using Buchi Rotavapor (Switzerland).

2. Analytical apparatus:

^{1}H (400 MHz/ 500 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker Avance-400 and Bruker Avance-500 spectrometer. The following abbreviations were used to designate chemical shift multiplicities: m= multiplet. The ^{13}C NMR spectra are proton decoupled. Melting points were obtained manually by capillary methods and are uncorrected. Thin layer chromatography (TLC) was performed on silica TLC plates and compounds visualized in iodine or under UV lamp. HRMS-ESI spectra were determined using Micromass Q-TOF Ultima spectrometer.

3. Schematic Representation



4. Dehydrosulfenylation-decarboxylation of β-(phenyl)-β-(phenylthio)propionic acid

We have earlier reported the dehydrosulfenylation of various thia Michael products resulting in the generation of unsaturated carbonyl/nitro compounds. In the same context we explored the synergism of microwave-[hmim]Br ionic liquid for the dehydrosulfenyltion of β-(phenyl)-β-(phenylthio)propionic acid . However we unexpectedly obtained styrene instead of the cinnamic acid.

We next screened the reaction conditions including time, temperature, addition of water to the reaction mixture inorder to improve the reaction yield and it was observed that microwave irradiating the reaction mixture at 180 °C for 45 min resulted into maximum yield of 57%.

Further among all the screened ionic liquids including acidic, basic and neutral ionic liquids, [hmim]Br was the most suitable for the reaction.

With optimized reaction condition we explored β-(phenyl)-β-(phenylthio)propionic acid with different substrates and found that substrates bearing electron donating group such as methoxy, hydroxy on phenyl ring of cinnamic acid provided the desired product (**2a-2g**, 41%-82% yield) however substrates with electron withdrawing group such as chloro did not provide the desired product. Interestingly, substrates (**1h-1p**) with thiols bearing both the electron donating and electron withdrawing group successfully yielded the desired product in 70%-84% yield .

5. NMR study for deducing the mechanism of reaction

To explore the mechanistic pathway and study the interaction of ionic liquid with substrate,[1]H NMR spectroscopy was recorded in $CDCl_3$ of standard substrate **1g**, corresponding sinnapic acid, styrene **2g** and compared with reaction mixture at0 min, 5 min, 10 min and 15 min (Figure S2-S9).

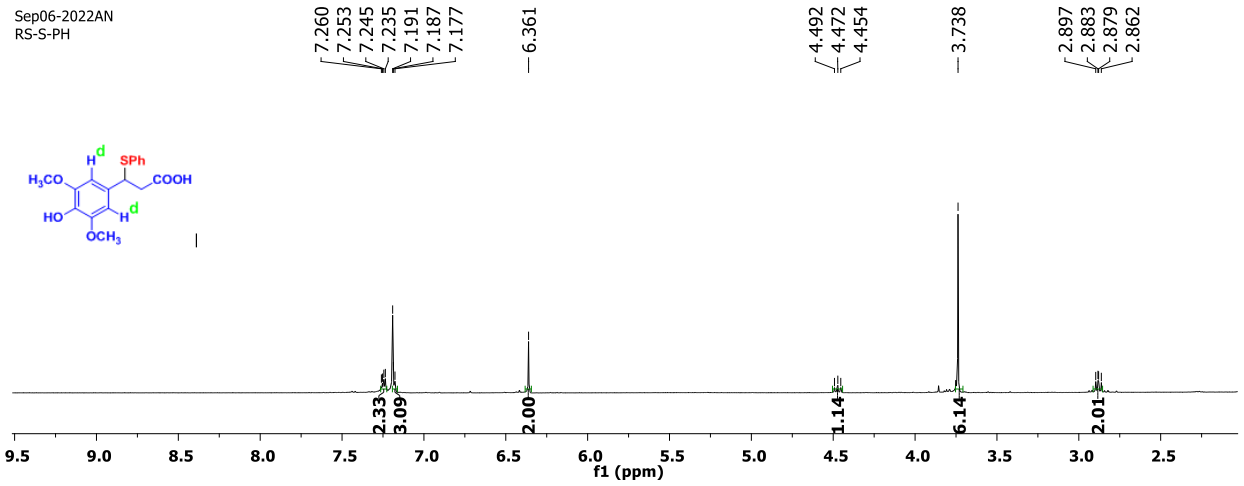


Figure S2: Full [1]H NMR spectra of **1g** in $CDCl_3$

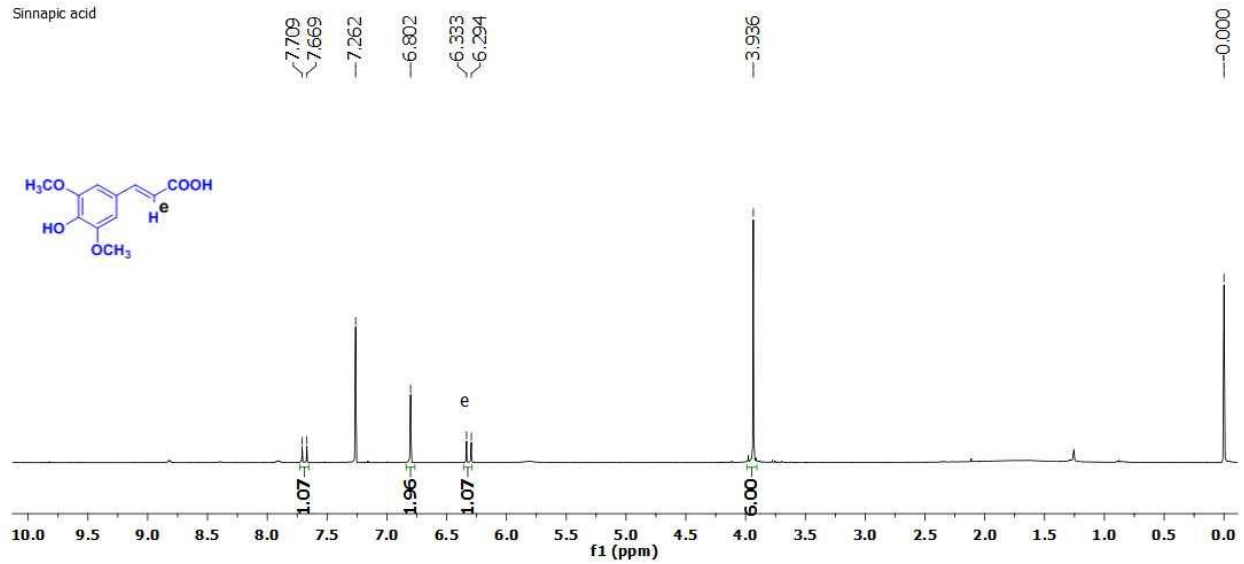


Figure S3: Full [1]H NMR spectra of **sinnapic acid** in $CDCl_3$

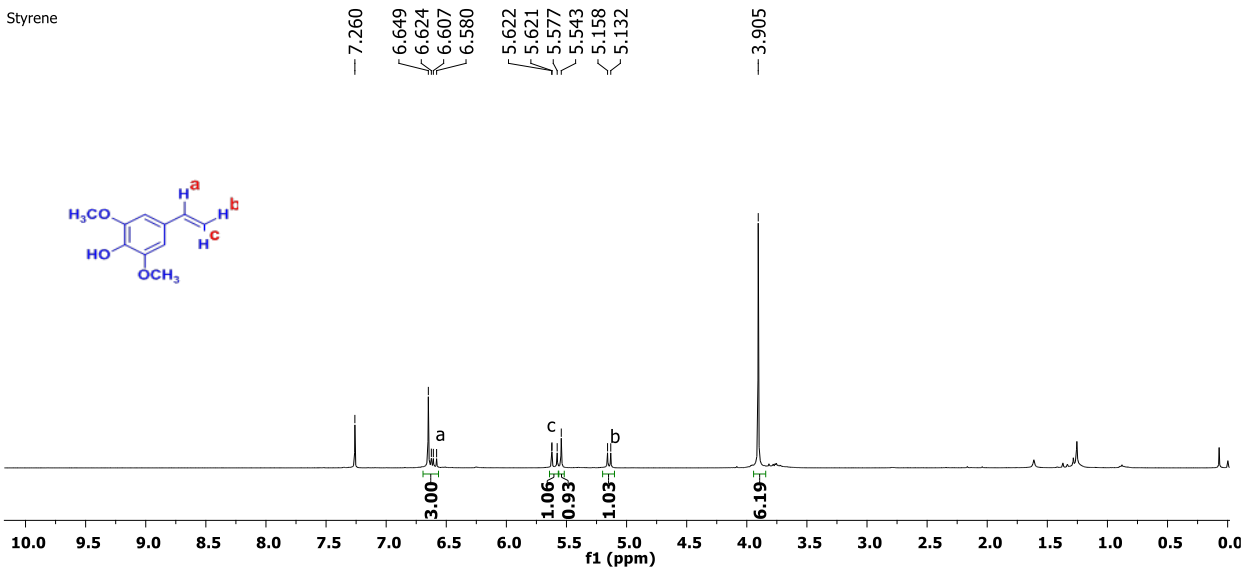


Figure S4: Full ^{1}H NMR spectra of **2g** in $CDCl_3$

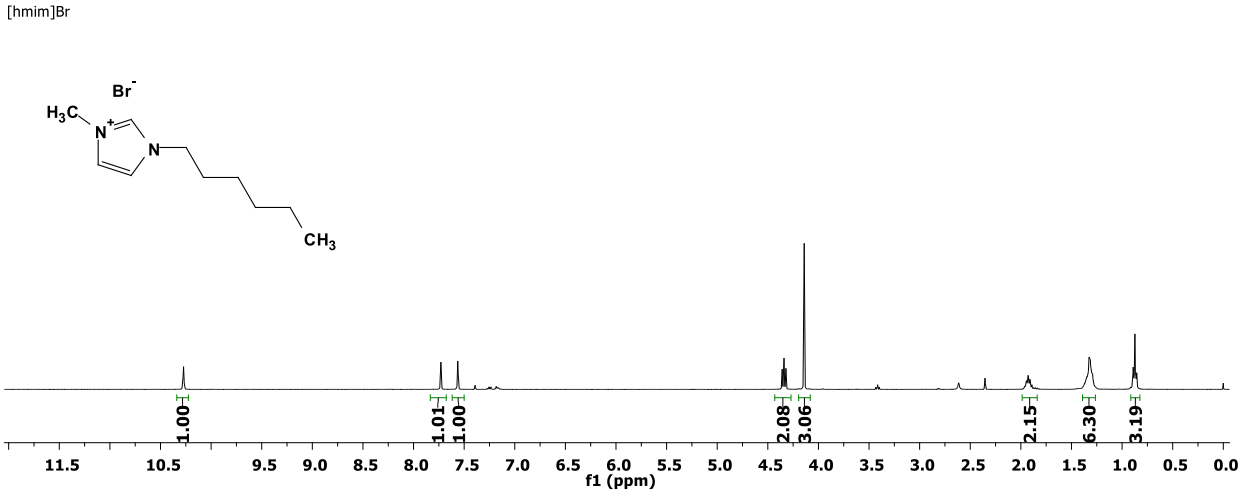


Figure S5: Full ^{1}H NMR spectra of **[hmim]Br** in $CDCl_3$

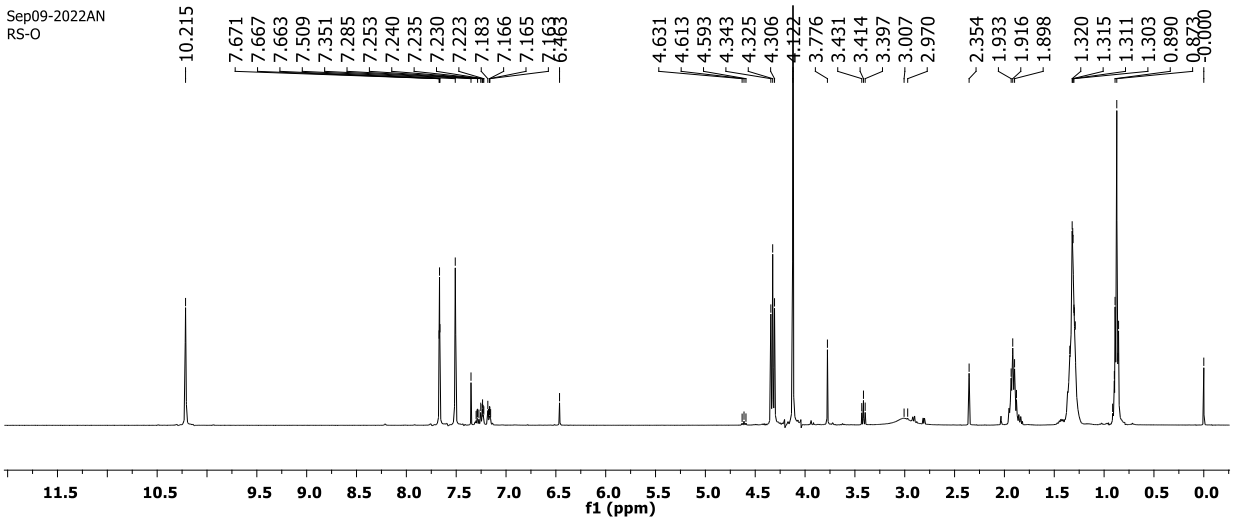


Figure S6: Full ^{1}H NMR spectra of reaction mixture (**1g+[hmim]Br]**) at **0 min** in $CDCl_3$

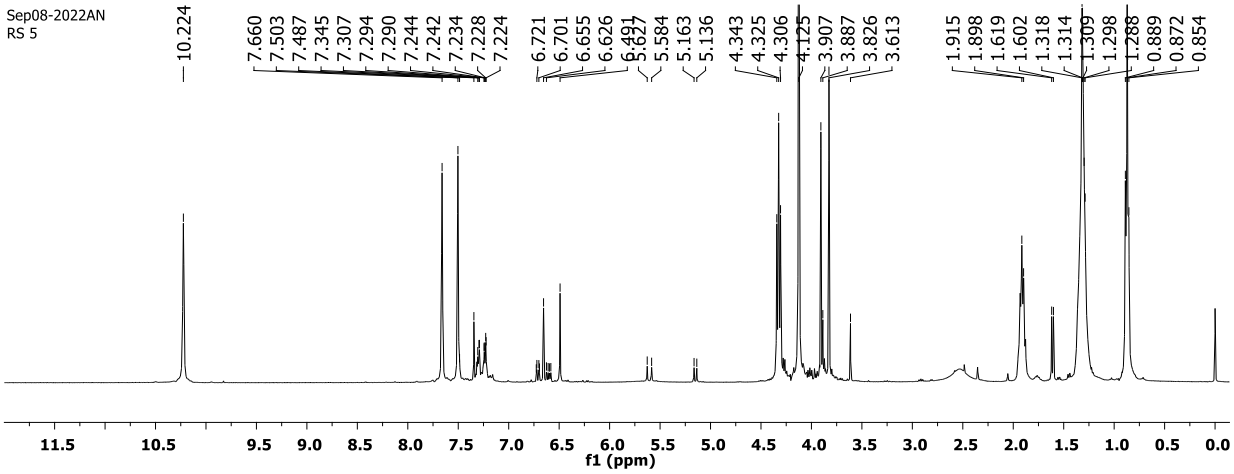


Figure S7: Full ^{1}H NMR spectra of reaction mixture (**1g+[hmim]Br]**) at **5 min** in $CDCl_3$

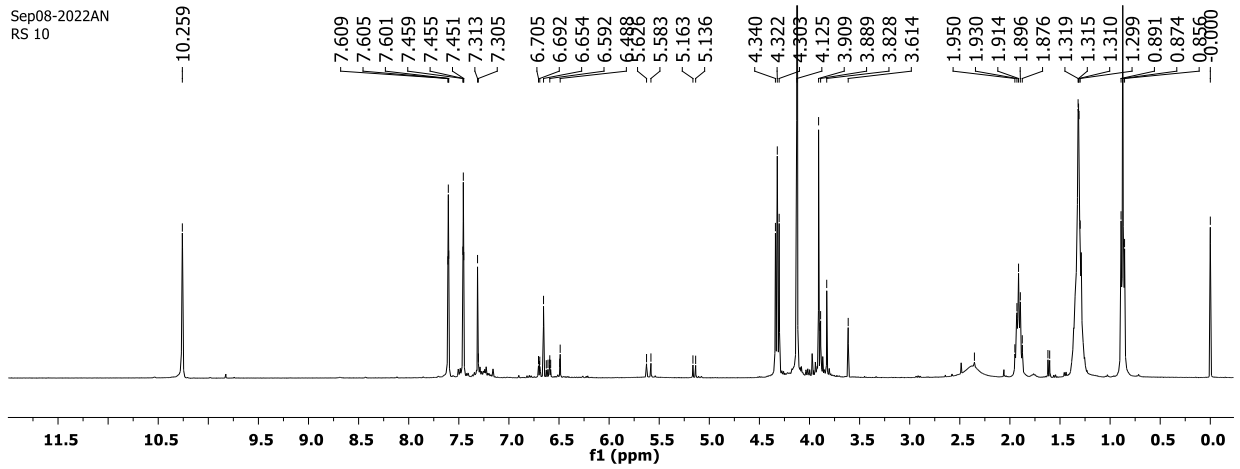


Figure S8: Full ^{1}H NMR spectra of reaction mixture (**1g+[hmim]Br]**) at **10 min** in $CDCl_3$

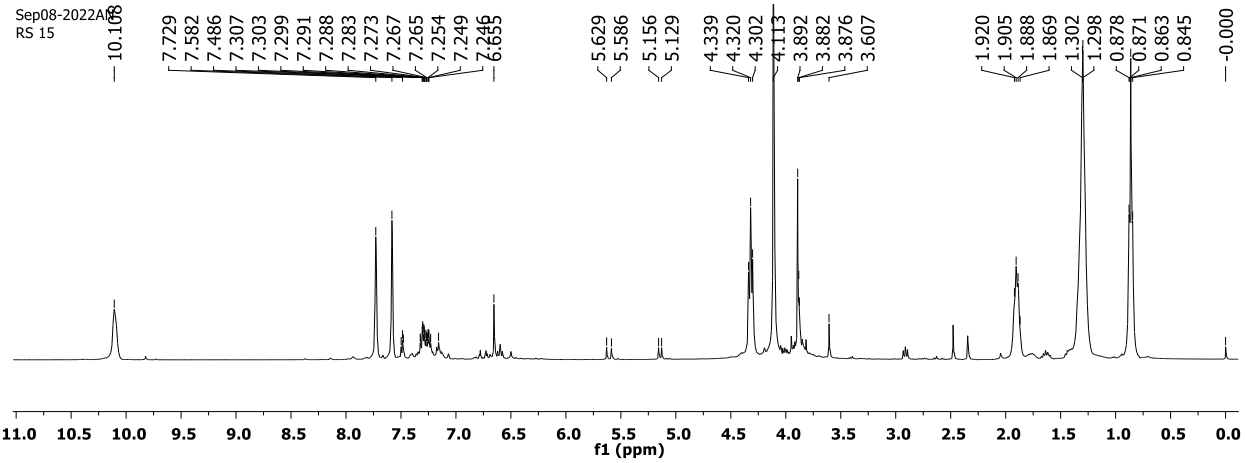
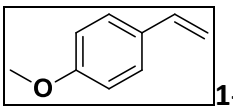


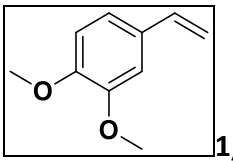
Figure S9: Full ^{1}H NMR spectra of reaction mixture (**1g+[hmim]Br]**) at **15 min** in $CDCl_3$

6.Characterization data of compounds 2a-2g



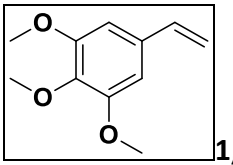
1-Methoxy-4-vinylbenzene [2a][5]

57% yield, Oil, ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42– 7.39 (m, 2H), 6.93 – 6.90 (m, 2H), 6.67 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.67 (d, *J* = 17.6 Hz, 1H), 5.12 (d, *J* = 10.8 Hz, 1H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.58, 136.60, 130.30, 127.85, 114.46, 112.20, 55.58.



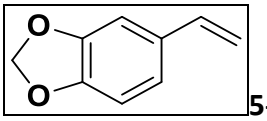
1,2-Dimethoxy-5-vinylbenzene [2b][6]

60% yield, Yellow liquid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 – 6.94 (m, 2H), 6.83 (d, *J* = 6.8 Hz, 1H), 6.65 (dd, *J* = 14.0, 8.4 Hz, 1H), 5.61 (d, *J* = 14 Hz, 1H), 5.15 (d, *J* = 8.8 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.04, 149.00, 136.50, 130.76, 119.45, 111.80, 111.08, 108.59, 55.93, 55.82.



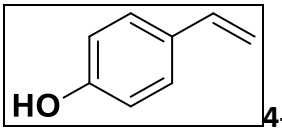
1,2,3-Trimethoxy-5-vinylbenzene [2c]

53% yield, oil, ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.78 (s, 2H), 6.72 – 6.56 (m, 1H), 5.80 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.21 (dd, *J* = 10.8, 0.8 Hz, 1H), 3.80 (s, 6H), 3.66 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.47, 137.17, 133.34, 114.08 , 104.08, 60.512, 56.36.



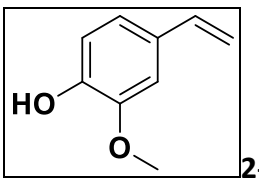
5-Vinylbenzo[d][1,3]dioxole [2d]

41% yield, oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 1H), 6.86 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 1H), 6.65 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.98 (s, 2H), 5.60 (d, *J* = 17.6 Hz, 1H), 5.15 (d, *J* = 10.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.00, 147.36, 136.37, 132.16, 120.99, 111.96, 108.19, 105.42, 101.04.



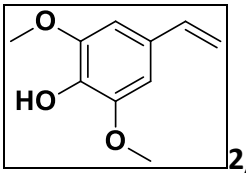
4-Vinylphenol [2e][7]

75% yield, colourless oil, ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.50 (s, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 6.61 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.58 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.04 (dd, *J* = 10.8, 0.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.84, 136.90, 128.75, 127.88, 115.81, 111.07.



2-Methoxy-4-vinylphenol [2f][6]

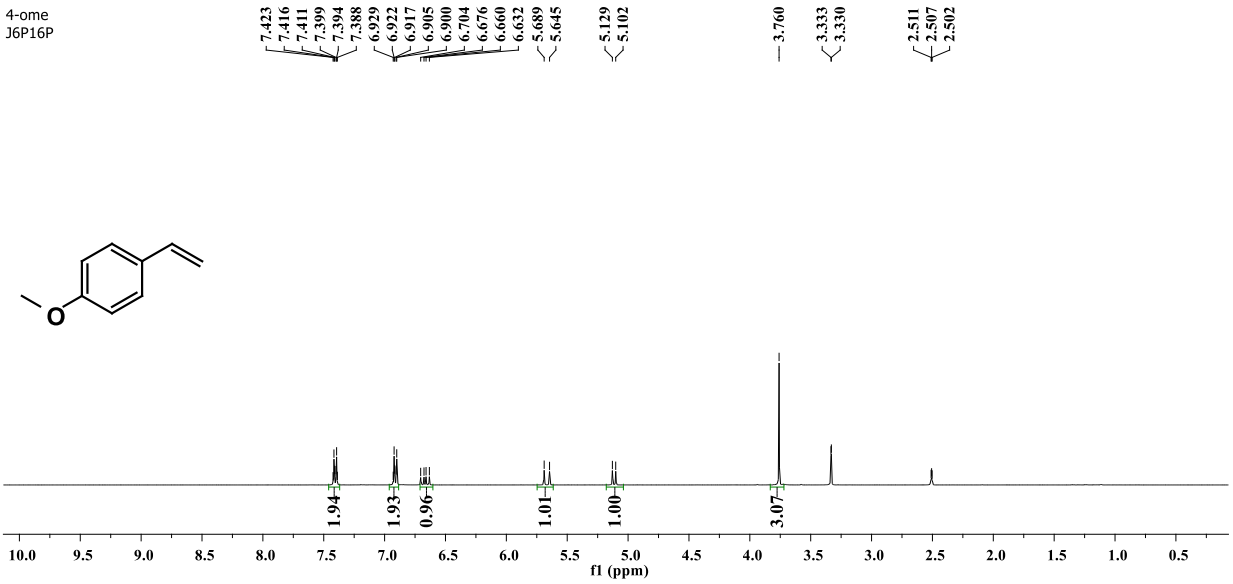
80% yield, colourless oil, ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.07 (s, 1H), 7.04 (d, *J* = 2.0 Hz, 1H), 6.85 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.61 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.63 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.06 (dd, *J* = 10.8, 0.8 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.15, 147.16, 137.15, 129.27, 119.98, 115.83, 111.41, 110.08, 56.04.



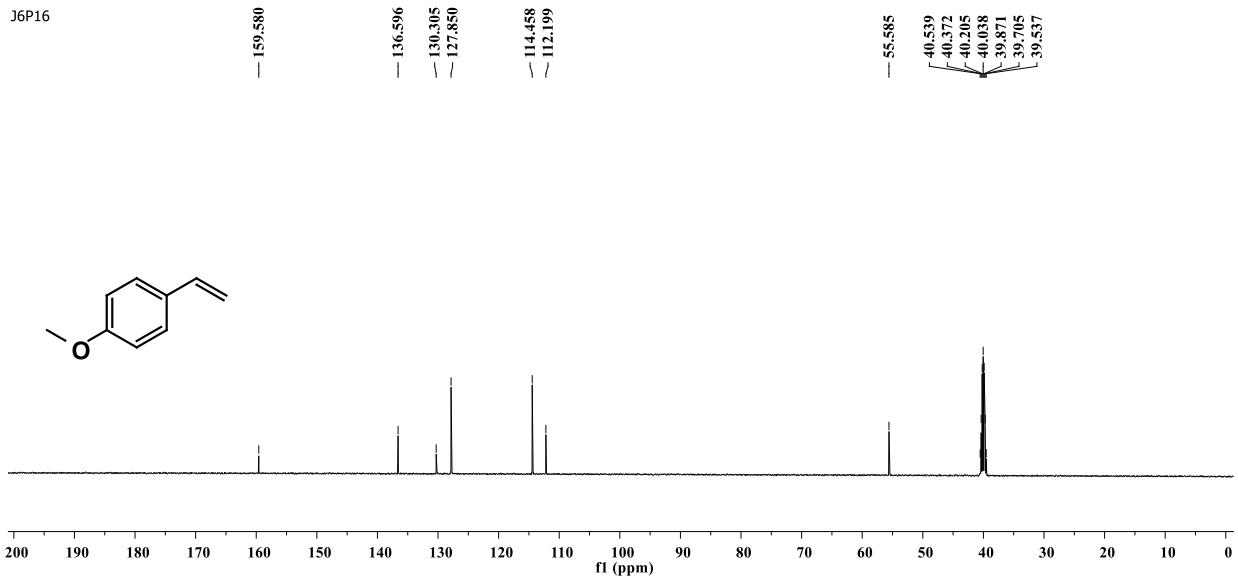
2,6-Dimethoxy-4-vinylphenol [2g][5]

82% yield, colourless oil, ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.44 (s, 1H), 6.74 (s, 2H), 6.60 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.68 (dd, *J* = 17.2, 0.8 Hz, 1H), 5.09 (dd, *J* = 10.8, 0.8 Hz, 1H), 3.78 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.52, 137.45, 136.31, 128.20, 111.82, 104.36, 56.47.

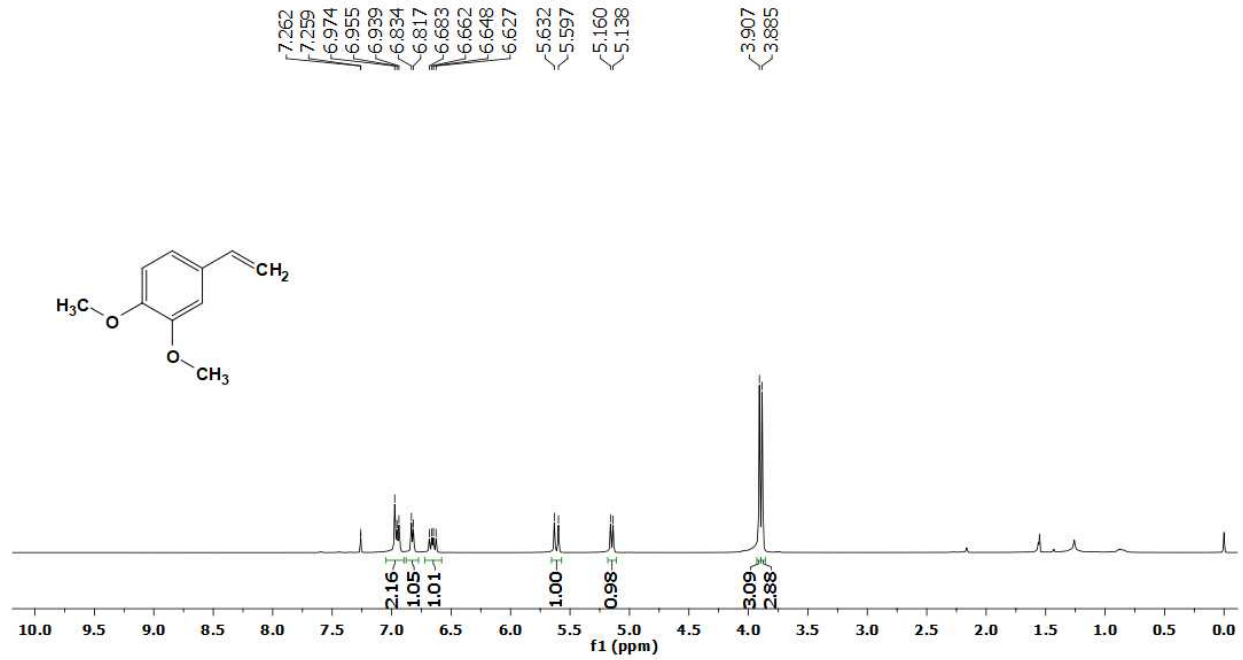
7. Spectroscopic data



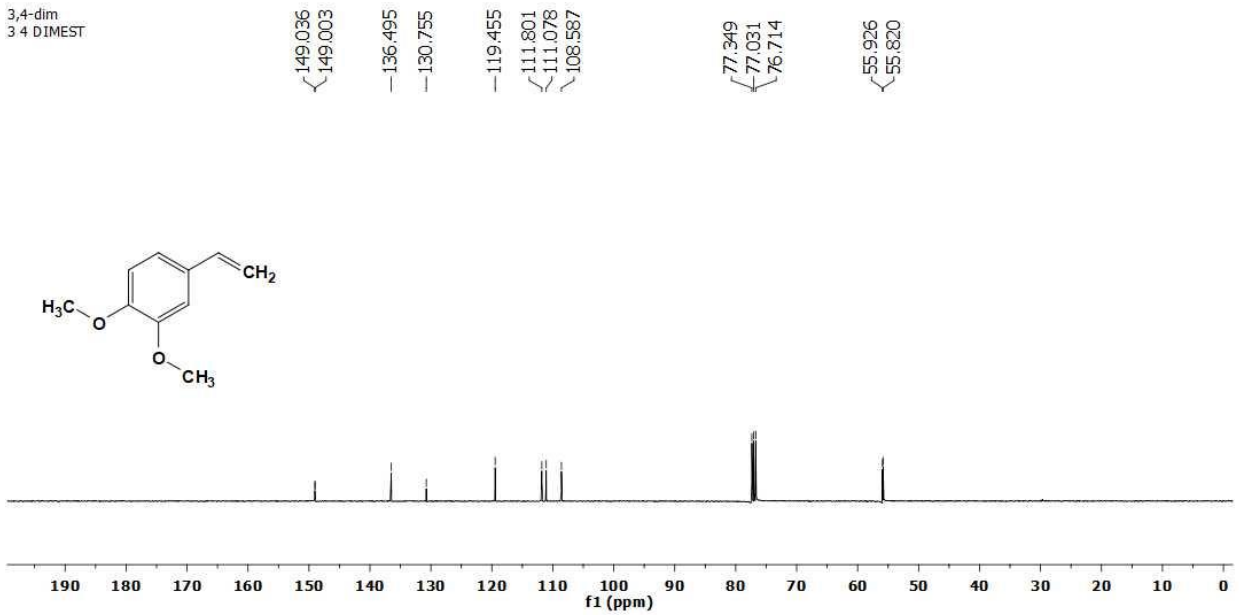
^{1}H NMR of**2a** in DMSO-d_6



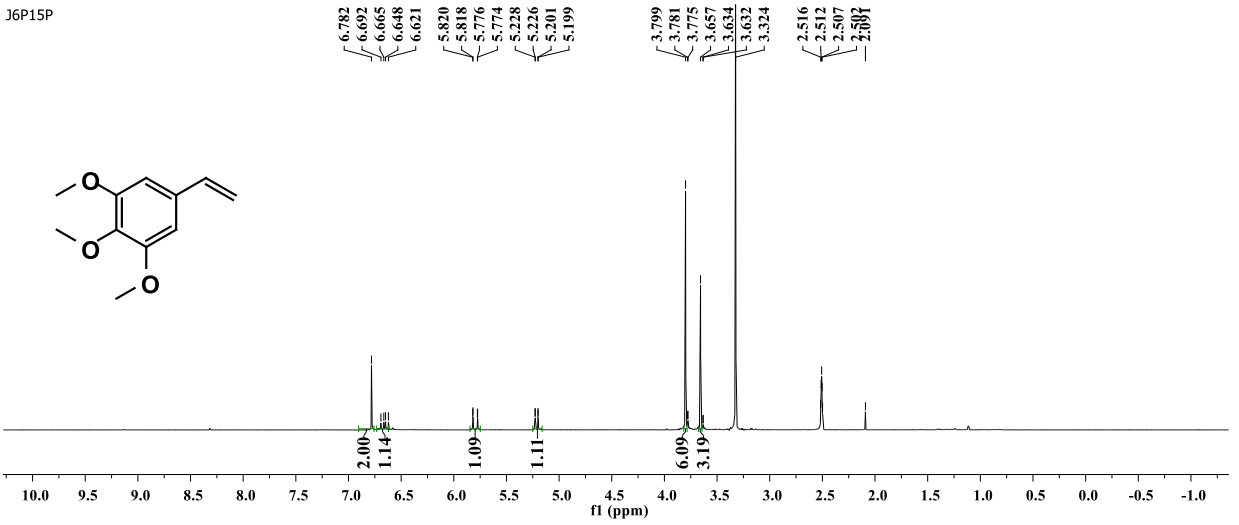
^{13}C NMR of **2a** in DMSO-d_6



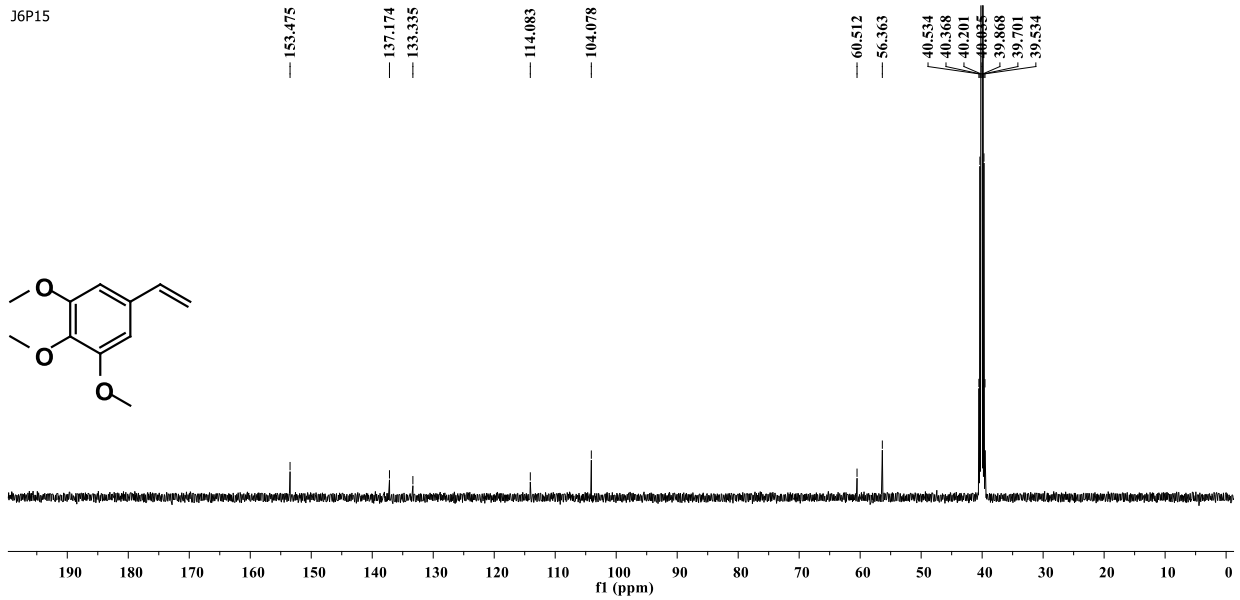
^{1}H NMR of **2b** in DMSO-d_6



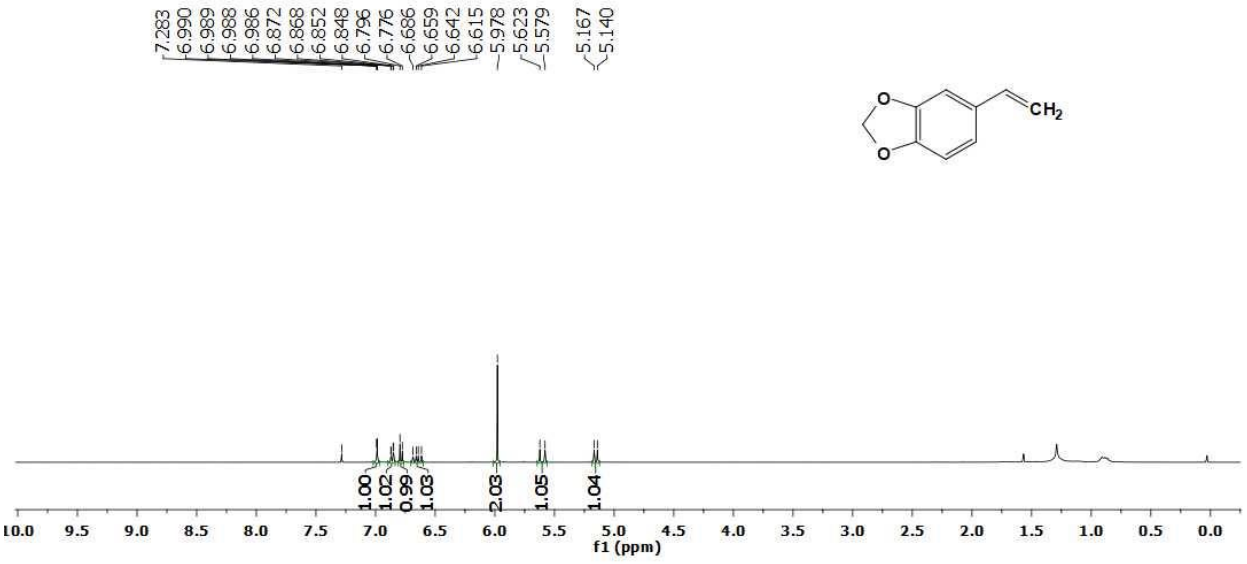
^{13}C NMR of **2b** in DMSO-d_6



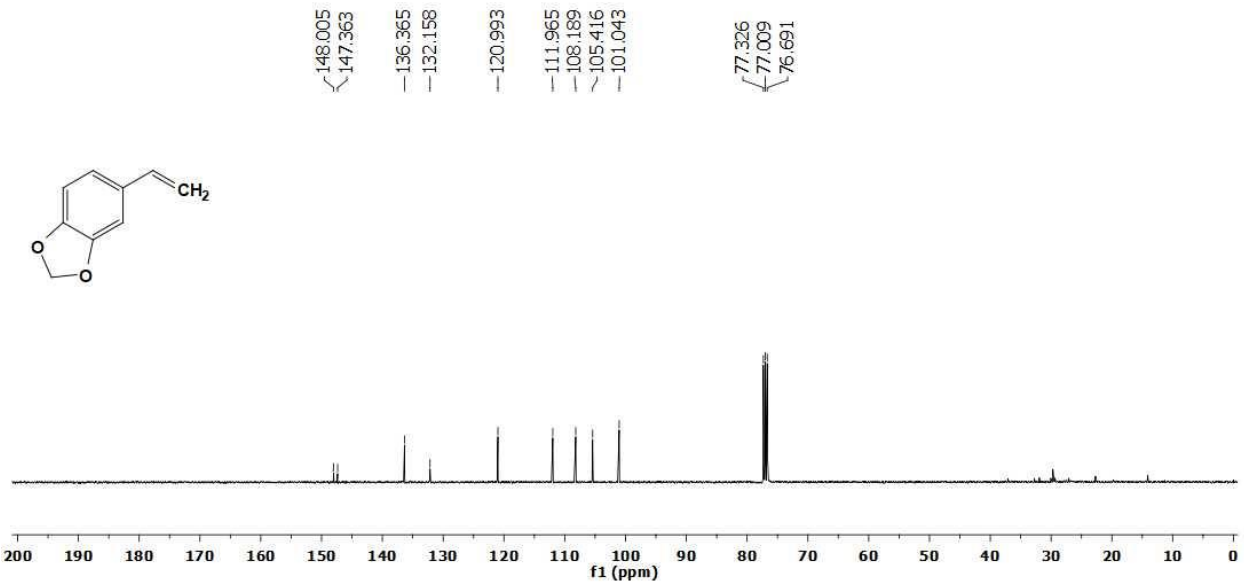
^{1}H NMR of **2c** in DMSO-d_6



^{13}C NMR of **2c** in DMSO-d_6



^{1}H NMR of **2d** in DMSO-d_6



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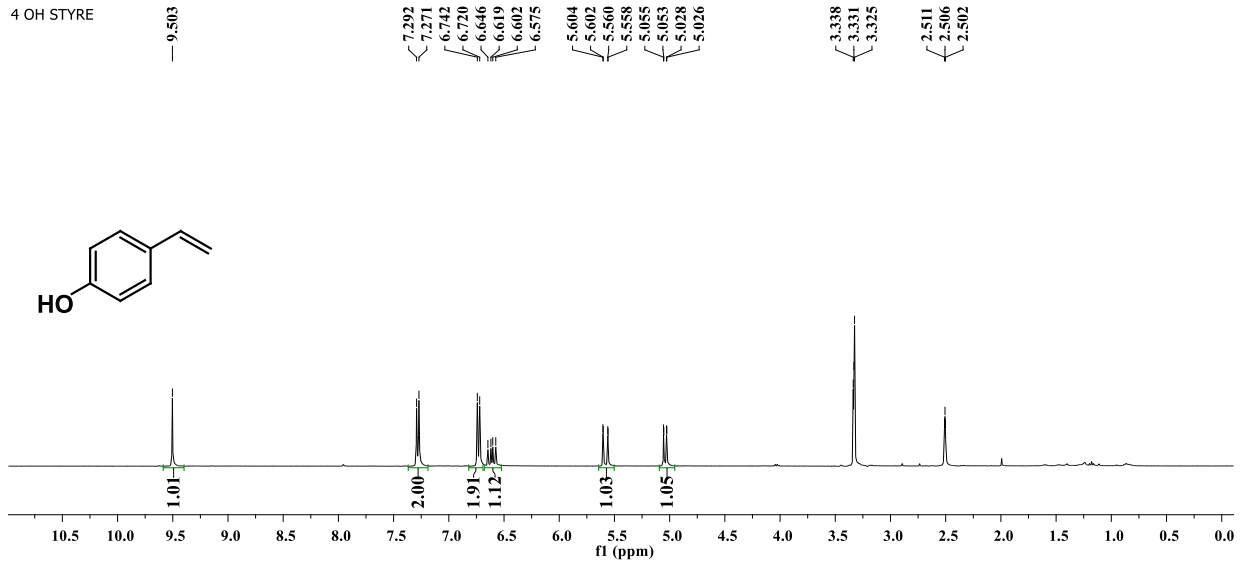
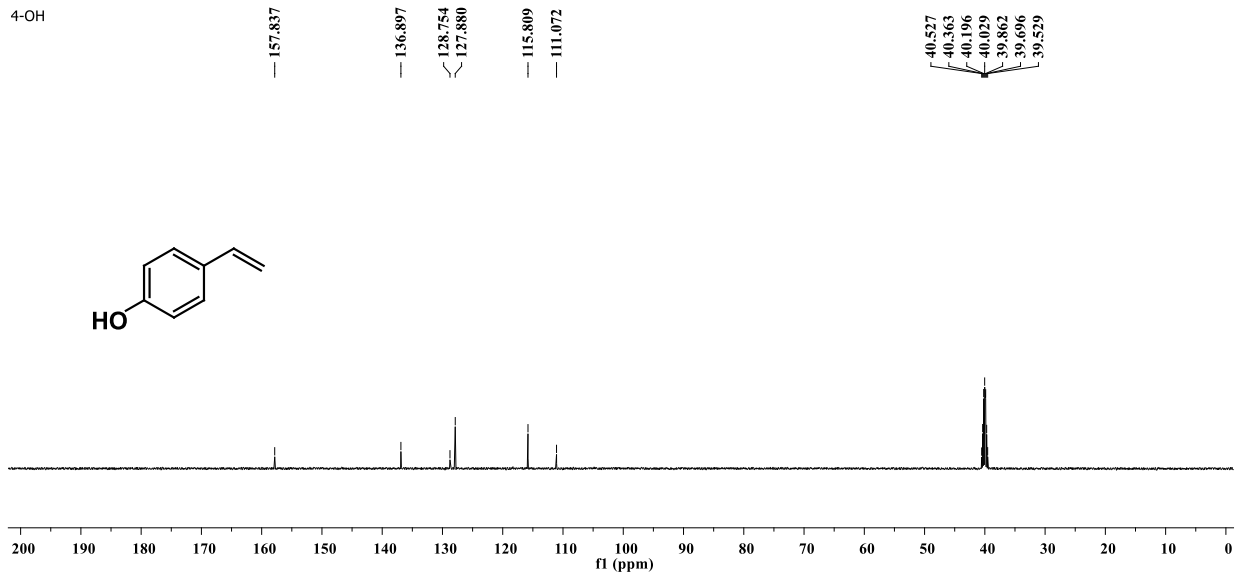
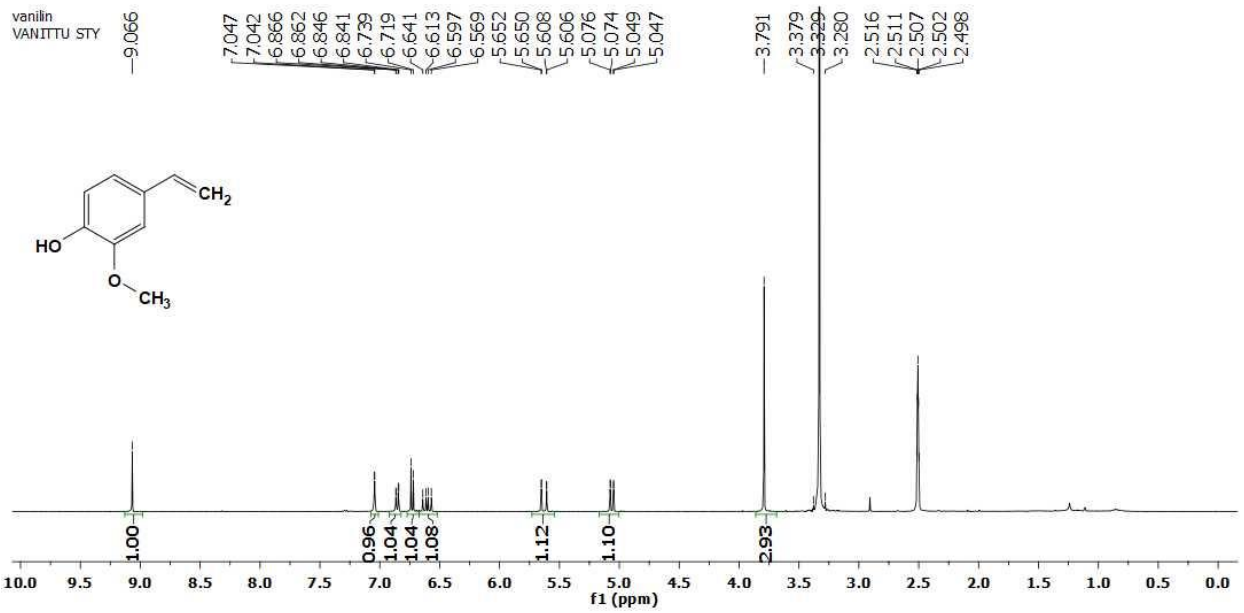


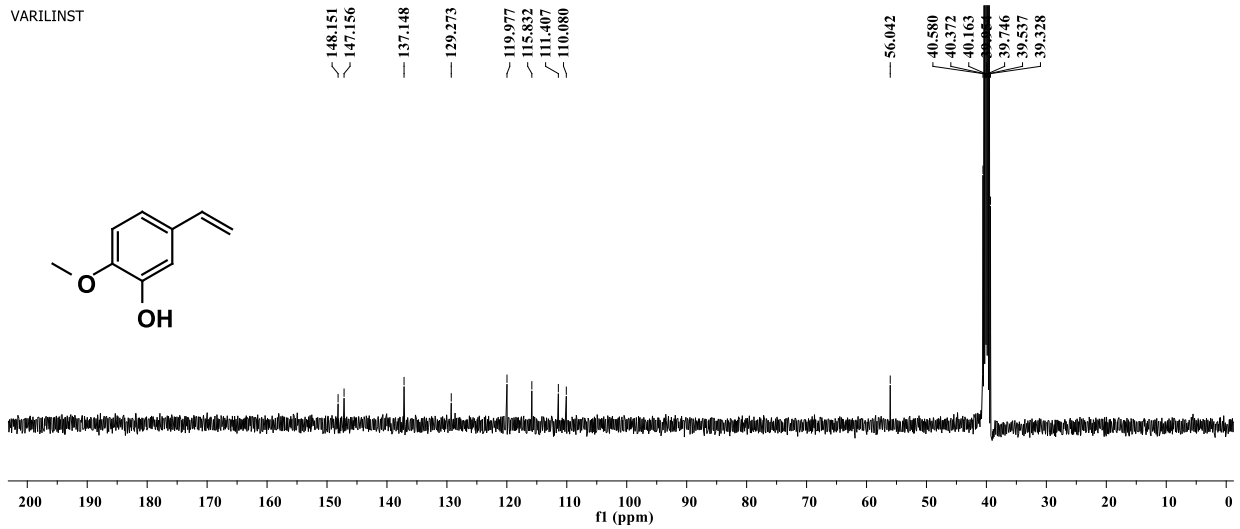
^{1}H NMR of **2e** in DMSO-d_6



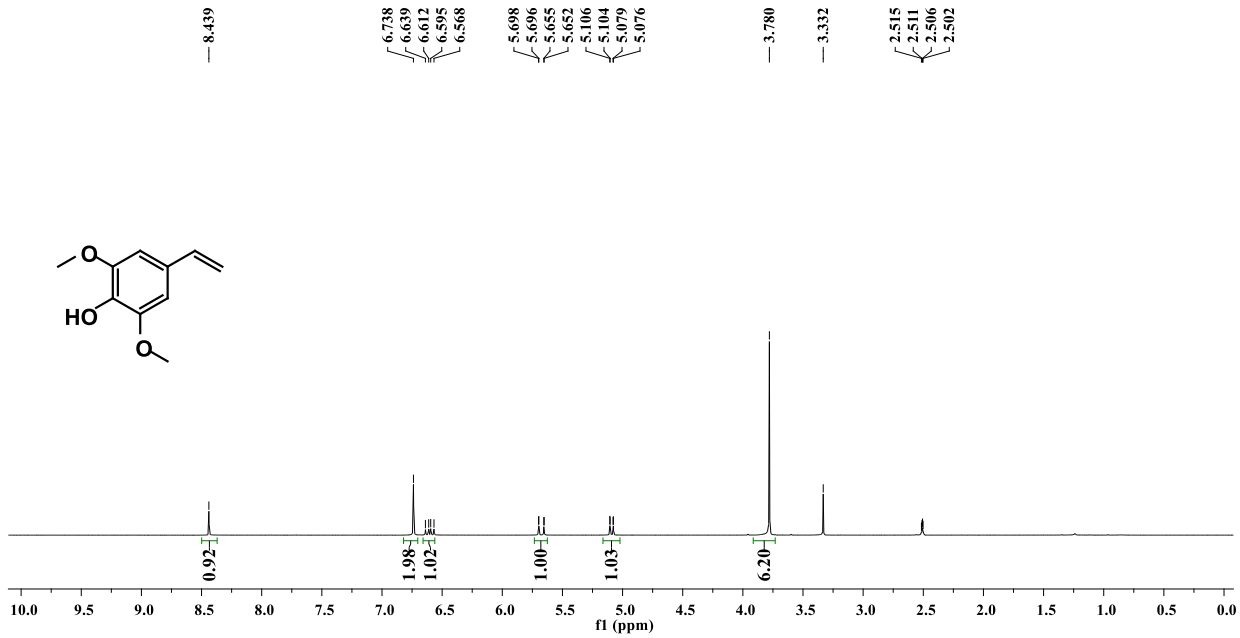
^{13}C NMR of **2e** in DMSO-d_6



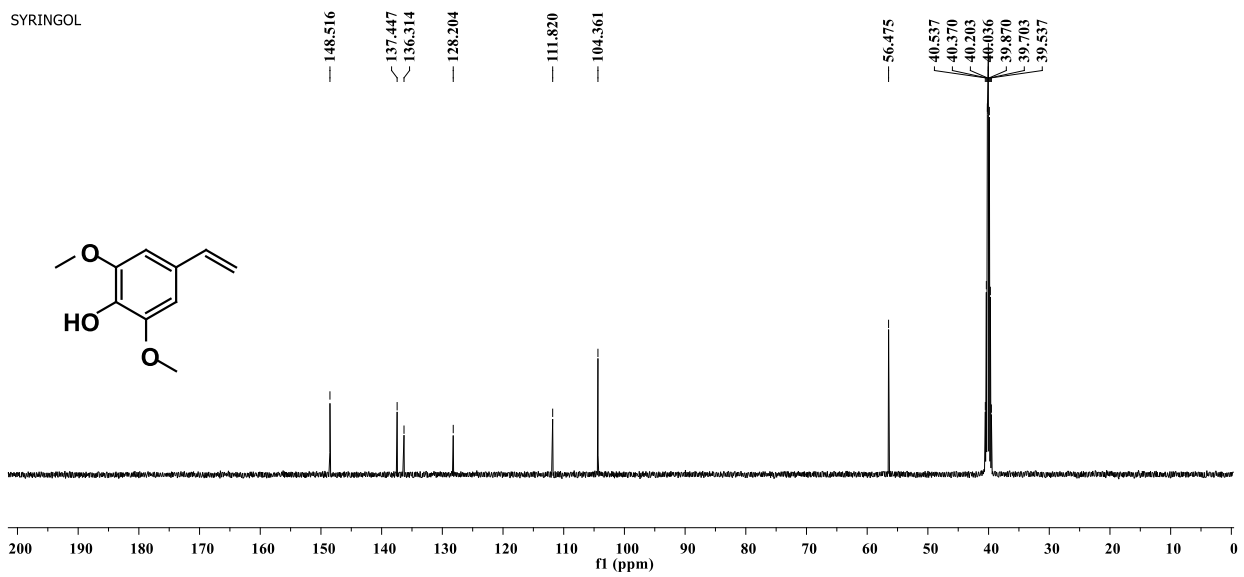
^{1}H NMR of **2f** in DMSO-d_6



^{13}C NMR of **2f** in DMSO-d_6



^{1}H NMR of **2g** in DMSO-d_6



^{13}C NMR of **2g** in DMSO-d_6

8. Reference

1. a) Law, M. C.; Wong, K. Y.; Chan, T. H. *Green Chem*. **2002**, *4*, 328–330; b) Nockemann, P.; Binnemans, K.; Driesen, K. *Chem. Phys. Lett*. **2005**, *415*, 131–136; c) Handy, S. T.; Okello, M. *J. Org. Chem.* **2005**, *70*, 1915-1918.
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