Supporting information

Metal-free Bi-functional Cooperative catalysis: Amine and quaternary amine-functionalized dendritic fibrous nanosilica as heterogeneous catalysts for Henry reaction and CO_2 conversion†

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Contents

1. Materials & Methods

Tetrphenylphosphonium bromide (TPPB), Urea, p-Xylene, Propanol, TEOS, Benzaldehyde (99%) 2,4,6-trihydroxy benzaldehyde (98%), Vanillin (>98%), Furfural (>98%), Styrene oxide (97%) 5-Methylfurfural (>98%) and 3-APTES were obtained from Merck (Sigma-Aldrich) & TCI India Pvt. Ltd.; p-hydroxybenzaldehyde (95%), ammonium nitrate, and Nitromethane (98%) were obtained from SRL Pvt. Ltd.; 2-Nitrobenzaldehyde (99%), Salicylaldehyde (98%), Nitroethane (98%), Dry toluene, and Dry acetonitrile were obtained from Spectrochem Pvt. Ltd. All chemicals and dry solvents were used without further purification.

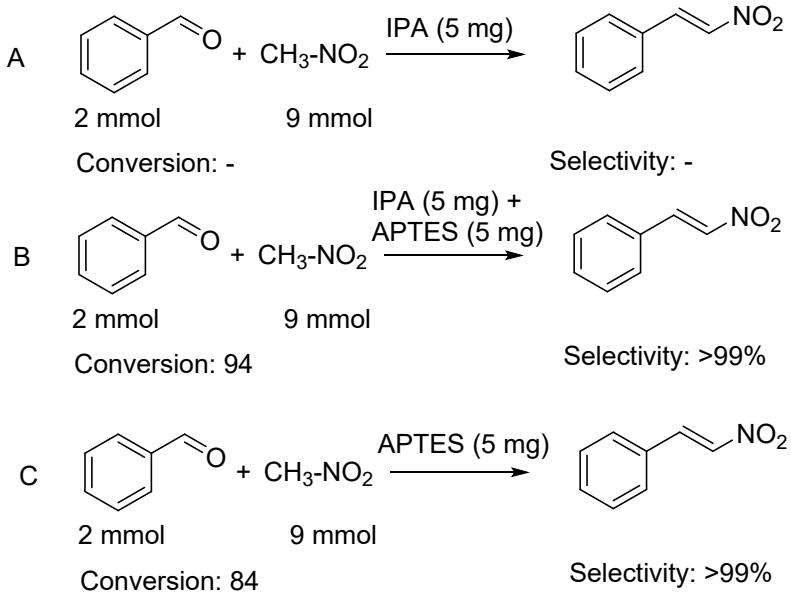
2. Instrumentation

For structural characterization, FTIR spectra were measured with a Perkin-Elmer GX spectrophotometer (manufactured in the USA) using KBr pellets. Surface area measurements were conducted with the Micromeritics 3 FLEX instrument, activating the sample at 65 °C for 50 minutes before analysis. Scanning electron microscopy (SEM-Leo series 1420 VP) equipped with INCA, and transmission electron microscopy (TEM) using a JEOL JEM 2100 microscope with Lacey carbon-coated grids, were employed to determine surface morphology. X-ray photoelectron spectroscopy (XPS) was conducted for chemical and surface state analysis using a Thermo Fisher Nexsa spectrophotometer with monochromated Al Kα radiation (energy of 1486.6 eV). Powder X-ray diffraction profiles were recorded using a MiniFlex-II (FD 41521) powder diffractometer from Rigaku, Japan, with a scan rate of 1° per minute. Thermal stability investigation involved TGA analysis using a Mettler-Toledo (TGA/SDTA 851E) instrument in the presence of air, with a heating rate of 10 °C/min. Thermal stability was investigated using TGA analysis on a Mettler-Toledo (TGA/SDTA 851E) instrument in an air

atmosphere, with a heating rate of 10 °C/min. 1H and 13C NMR spectra were recorded on a Bruker Advance 500 MHz NMR. Thermal stability was investigated using TGA analysis on a Mettler-Toledo (TGA/SDTA 851E) instrument in an air atmosphere, with a heating rate of 10 °C/min. The conversion and selectivity were analysed using a gas chromatography system equipped with an FID detector (GC-7890B-Agilent) with HP-5 column, consisting of 5% diphenyl and 95 % dimethyl polysiloxane capillary stationary phase and nitrogen as the carrier gas. The product was confirmed by GC-MS (equipped with FID as a detector (GC-MS Shimadzu, QP-2010, Japan) with HP-5 column which consists of 5 % diphenyl and 95 % dimethyl polysiloxane capillary phase with helium as the carrier gas and NMR analysis.

3. Controlled Experiments

IPA (-OH) and APTMS (-NH_2) were taken as model compounds for the amine and hydroxyl functionality of DFNS@NH_2 (**Scheme S1**). The presence of Si-OH and –NH_2 from DFNS@NH_2 was confirmed by FT-IR.



(Scheme S1): Reaction Conditions: Benzaldehyde: 2 mmol, Nitromethane: 11.2 mmol, Temperature; 50 °C, 6 h, Catalyst; 5 mg, A-IPA (5 mg), B-IPA+APTES (5+5 mg), and C-IPA (5 mg).

Table S1. Studies on the variation of catalysts for the nitroaldol condensation between benzaldehyde and nitromethane

Entry	**Catalyst**	**Conv. (%)**	**Selectivity (%)**	
			B	**C**
1	blank	-	-	-
2	$Si(OH)_4$	-	-	-
3	SiO_2	-	-	-
4	$SiO_2@NH_2$	3	100	-
5	$Ba(OH)_2$	-	-	-
6	$DFNS@NH_2$	>87	>99	-
7	MgO	51	>99	-
8	$MgO\text{-}NH_2$	>99	89	11

[a]**Reaction condition:** Benzaldehyde: 2 mmol (0.2 ml), Nitromethane: 9 mmol (0.6 ml), Temperature; 50 ˚C, 6 h

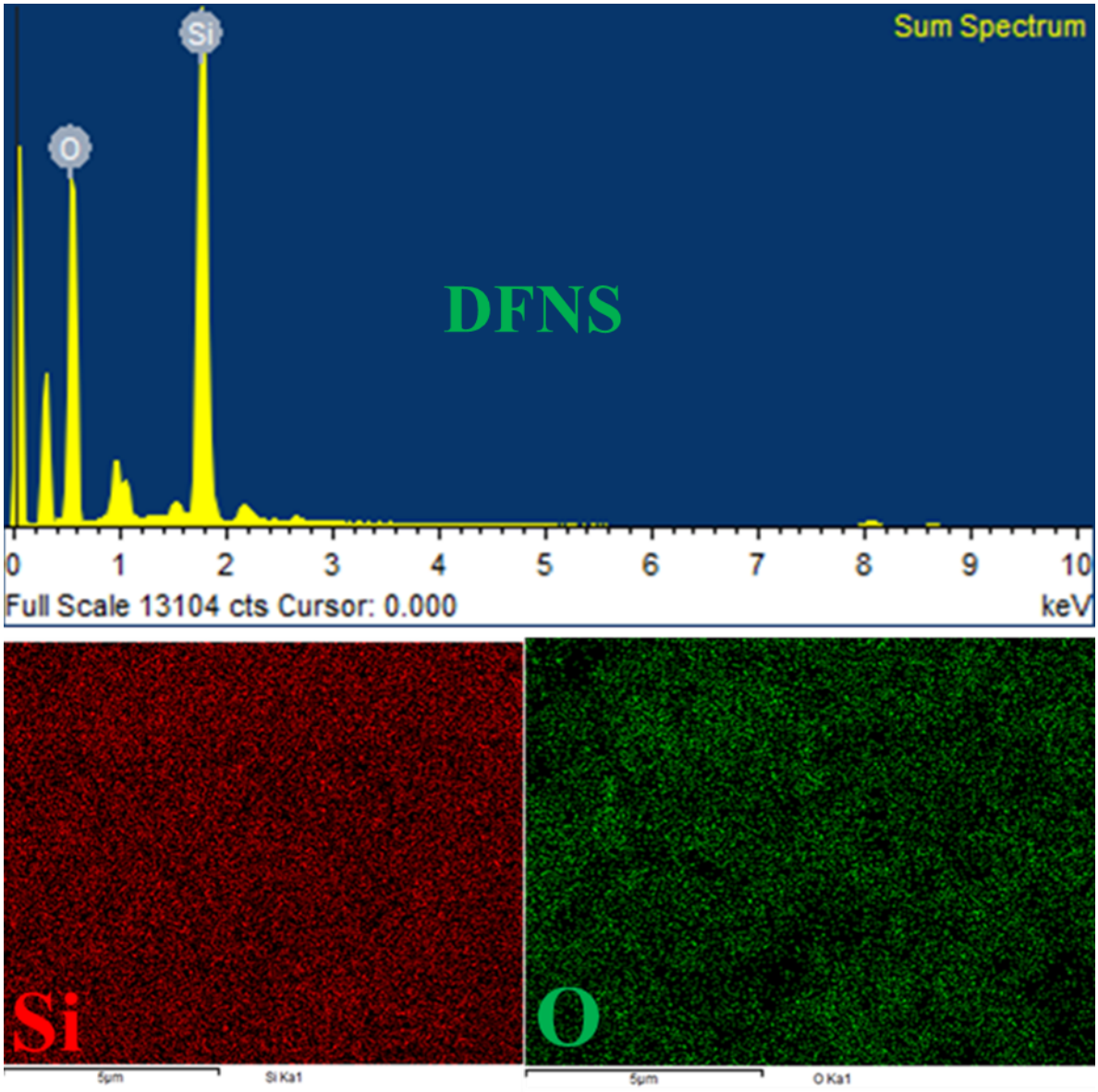


Fig. S1 The EDX analysis spectrum and mapping of the synthesized DFNS material.

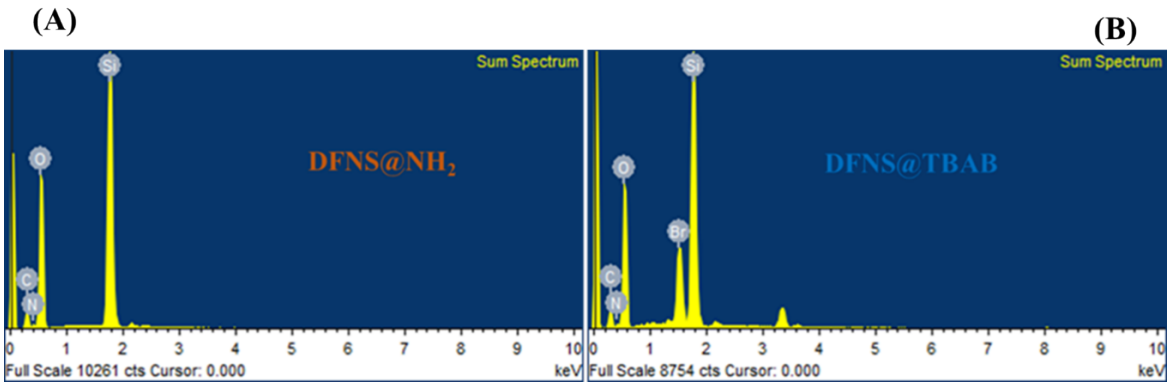


Fig. S2 (A) The EDX analysis spectrum of the synthesized DFNS@NH_2 & the final Material DFNS@TBAB (B).

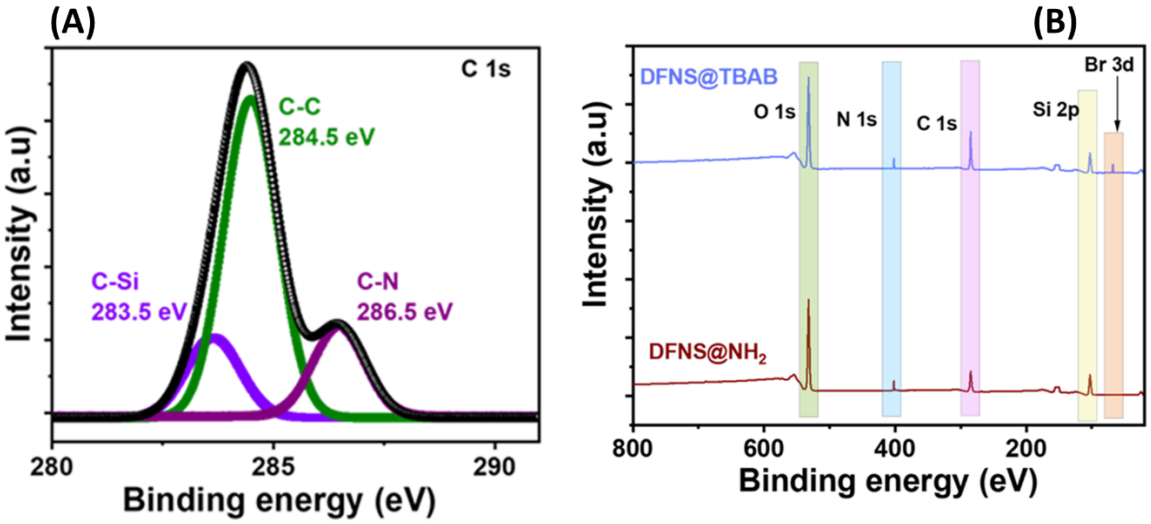


Fig. S3 (A, B) The comparison of the XPS spectrum of the synthesized DFNS@NH_2 & the final material DFNS@TBAB.

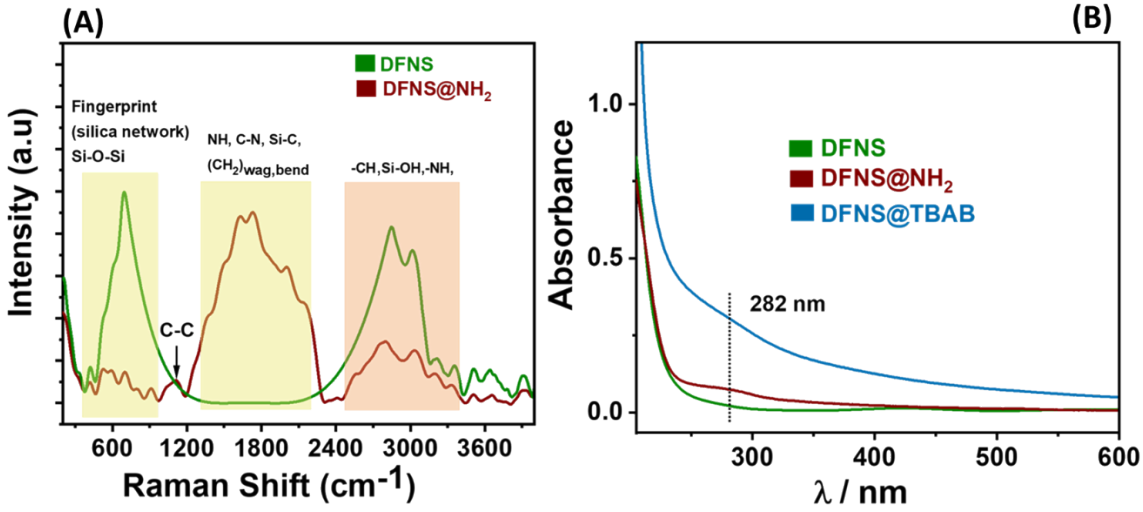


Fig. S4 (A) The comparison of the Raman spectra of the synthesized DFNS and aminated DFNS@NH_2 materials; (B) The UV-Vis profile of the DFNS, DFNS@NH_2 & DFNS@TBAB materials

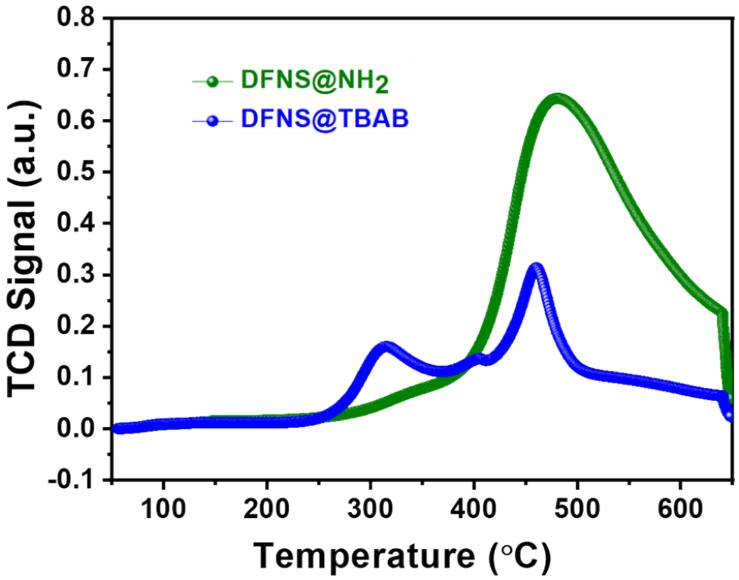


Fig. S5 The CO_2-TPD of DFNS@NH_2 and DFNS@TBAB.

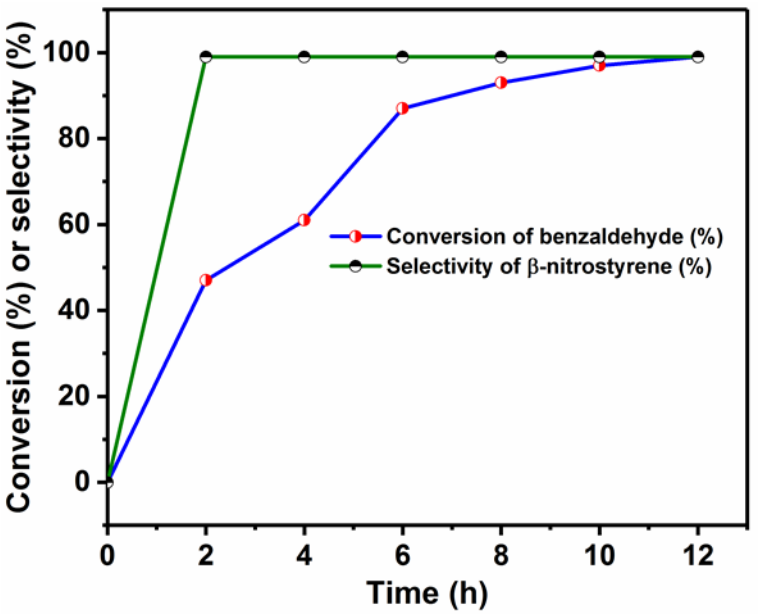


Fig. S6 Effect of time, Reaction condition: Benzaldehyde; 2 mmol, Nitromethane; 11.2 mmol, Catalyst; 20 mg, Temperature; 50 °C.

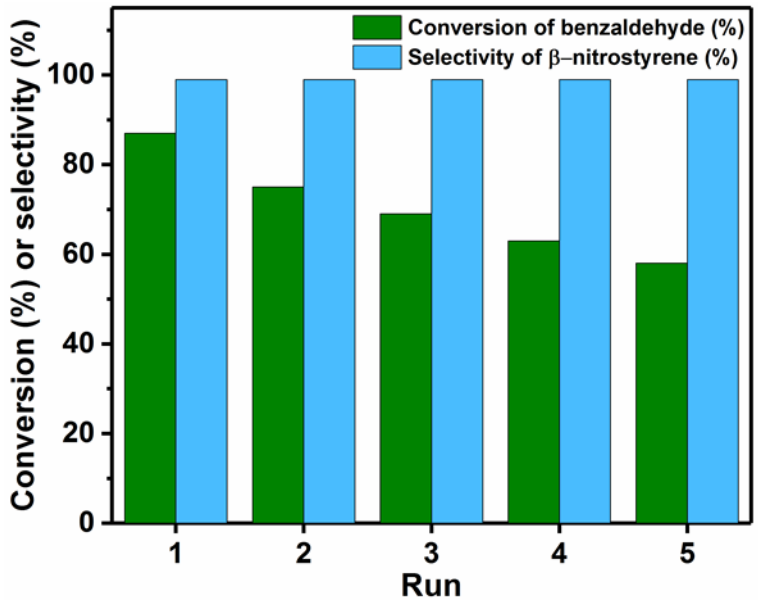


Fig. S7 Recyclability studies of DFNS@NH_2[a]Reaction condition: Benzaldehyde: 2 mmol, Nitroethane: 11.2 mmol, Catalyst 20 mg, Temperature; 50°C, Time: 6 h.

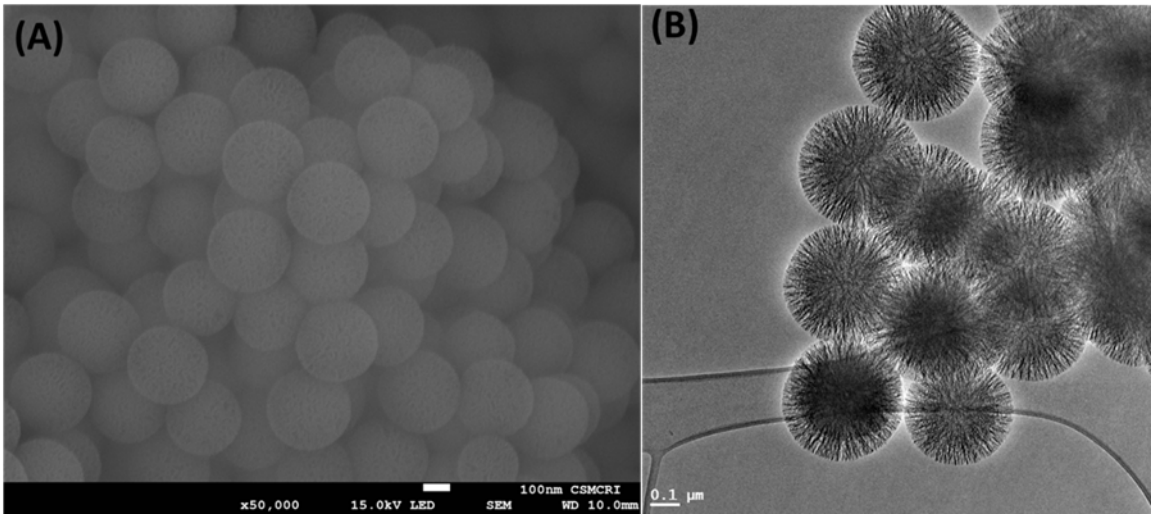


Fig. S8 (A, B) The FeSEM and TEM images of the recycled catalyst after 5 cycles having retained dendritic morphology.

4. GC-MS profile of the selected products

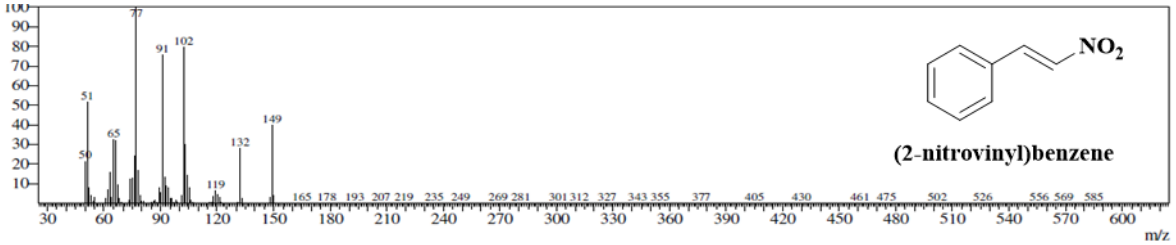


Fig. S9 GC-MS profile for (2-nitrovinyl)benzene.

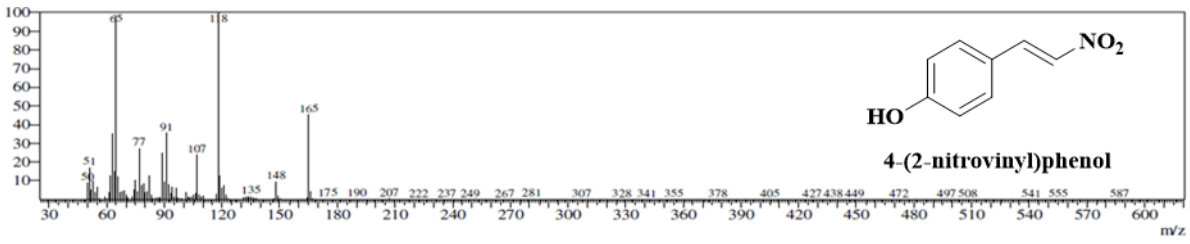


Fig. S10 GC-MS profile for 4-(2-nitrovinyl)phenol.

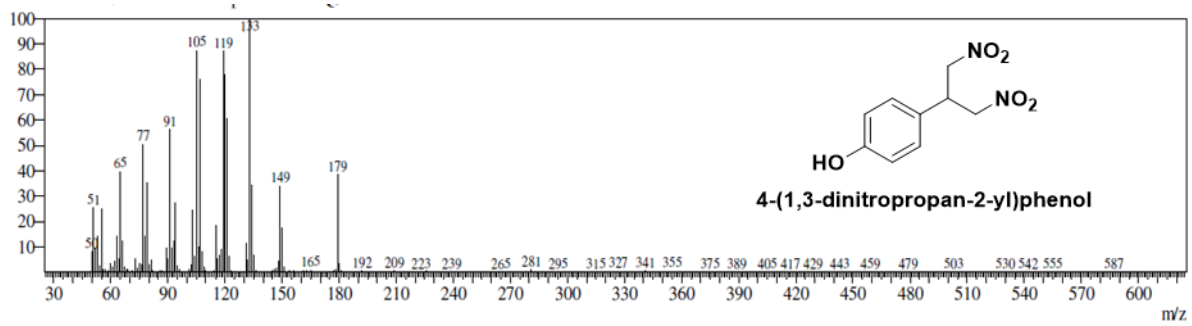


Fig. S11 GC-MS profile for 4-(1,3-dinitropropan-2-yl)phenol.

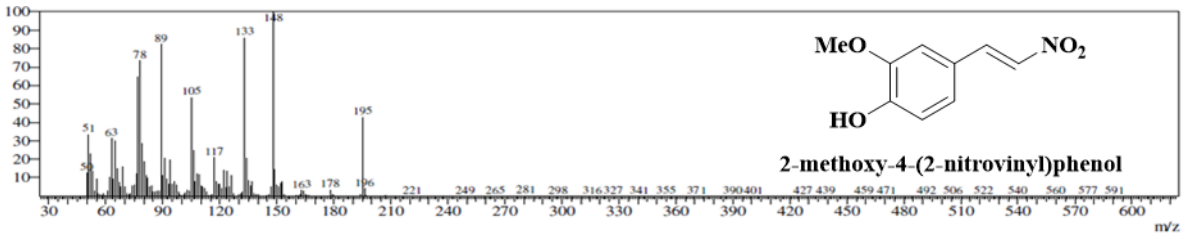


Fig. S12 GC-MS profile for 2-methoxy-4-(2-nitrovinyl)phenol.

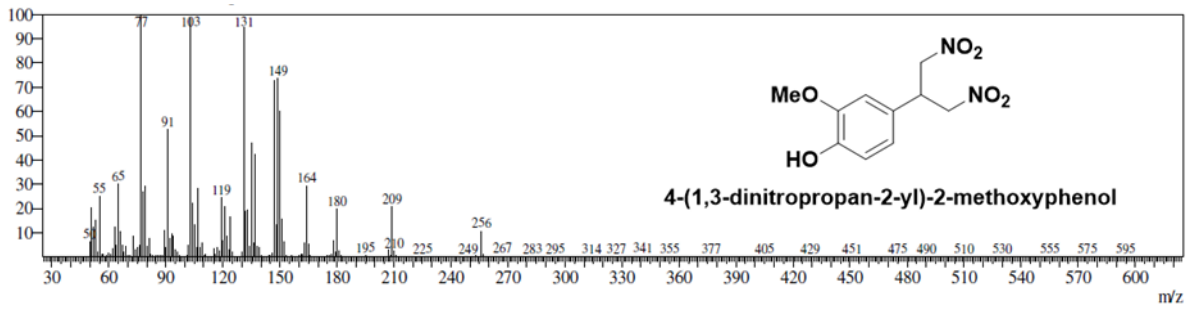


Fig. S13 GC-MS profile for 4-(1,3-dinitropropan-2-yl)-2-methoxyphenol.

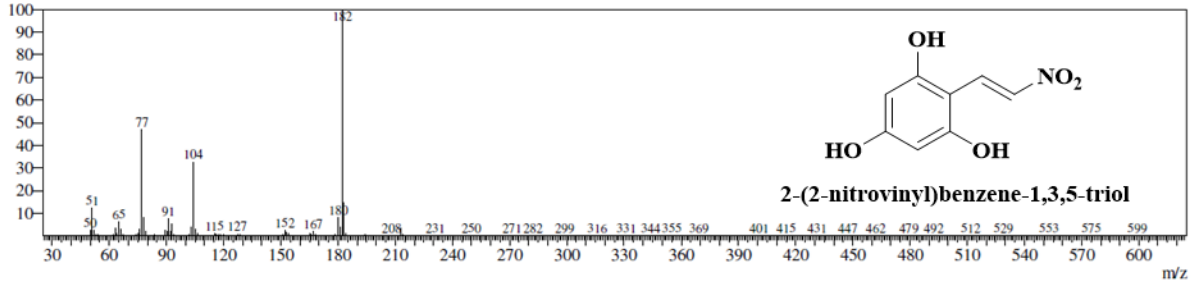


Fig. S14 GC-MS profile for 2-(2-nitrovinyl)benzene-1,3,5-triol.

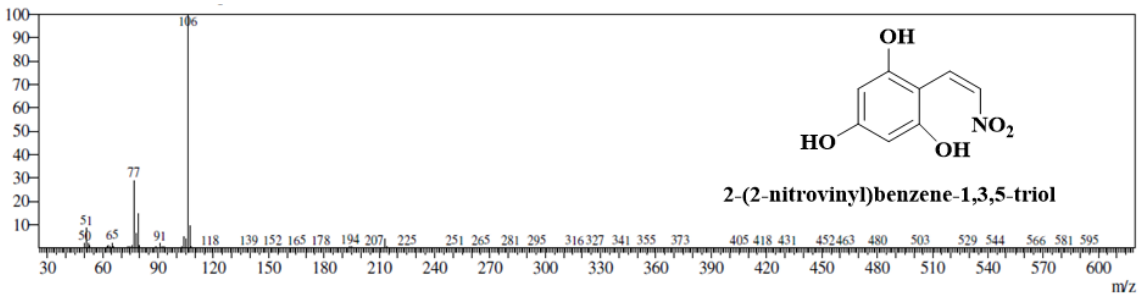


Fig. S15 GC-MS profile for 2-(2-nitrovinyl)benzene-1,3,5-triol.

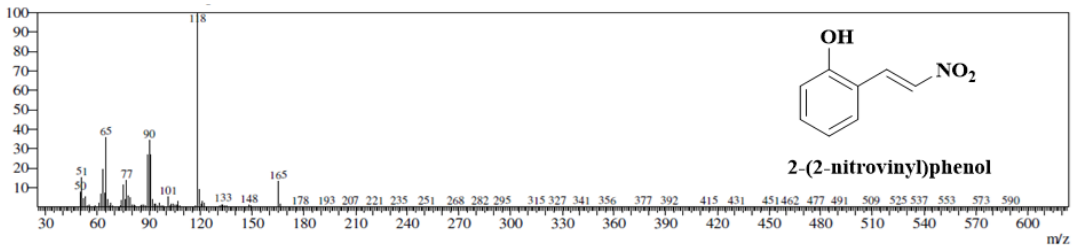


Fig. S16 GC-MS profile for 2-(2-nitrovinyl)phenol.

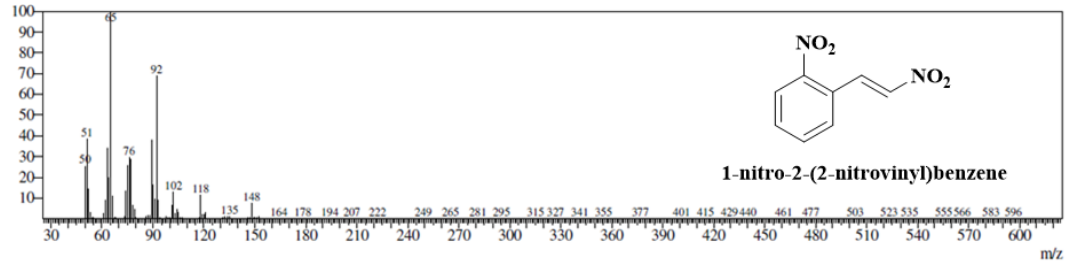


Fig. S17 GC-MS profile for 1-nitro-2-(2-nitrovinyl)benzene.

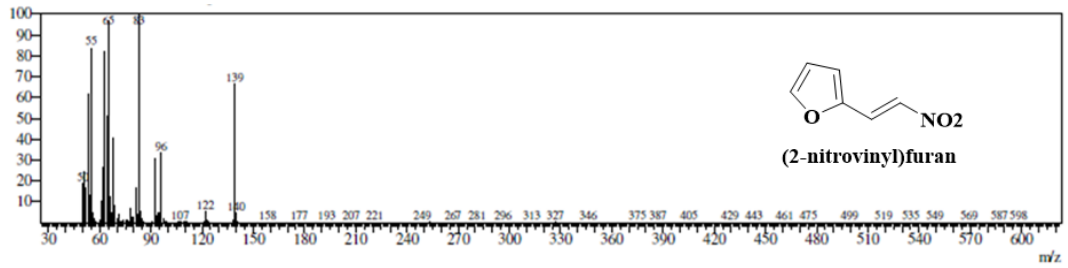


Fig. S18 GC-MS profile for 2-(2-nitrovinyl)furan.

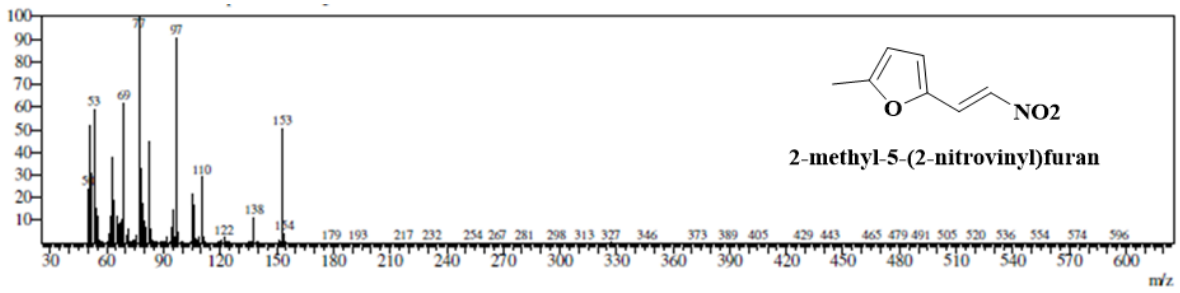


Fig. S19 GC-MS profile for 2-methyl-5-(2-nitrovinyl)furan.

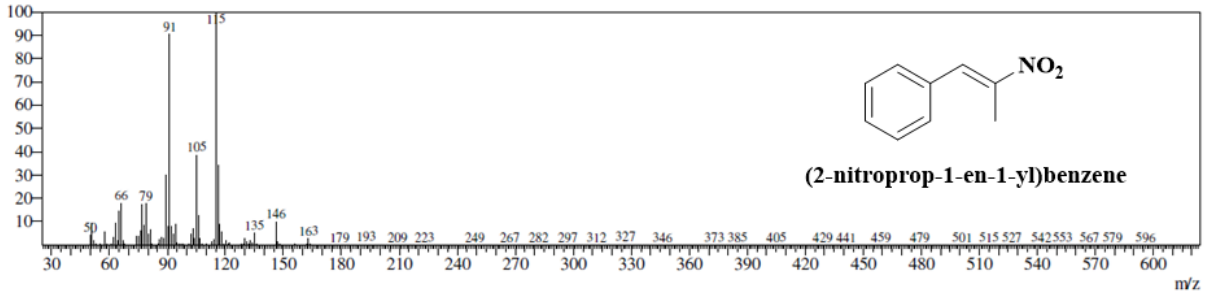


Fig. S20 GC-MS profile for (2-nitroprop-1-en-1-yl)benzene.

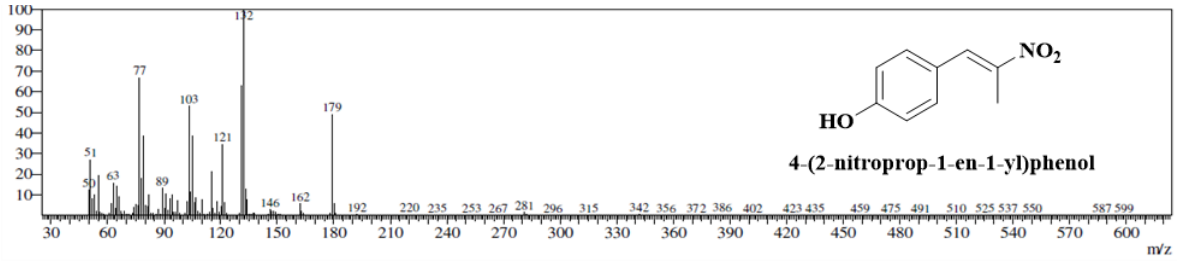


Fig. S21 GC-MS profile for 4-(2-nitroprop-1-en-1-yl)phenol.

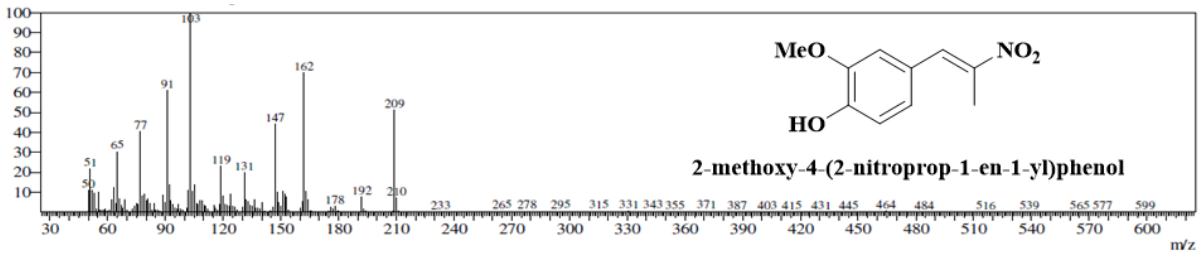


Fig. S22 GC-MS profile for 2-methoxy-4-(2-nitroprop-1-en-1-yl)phenol.

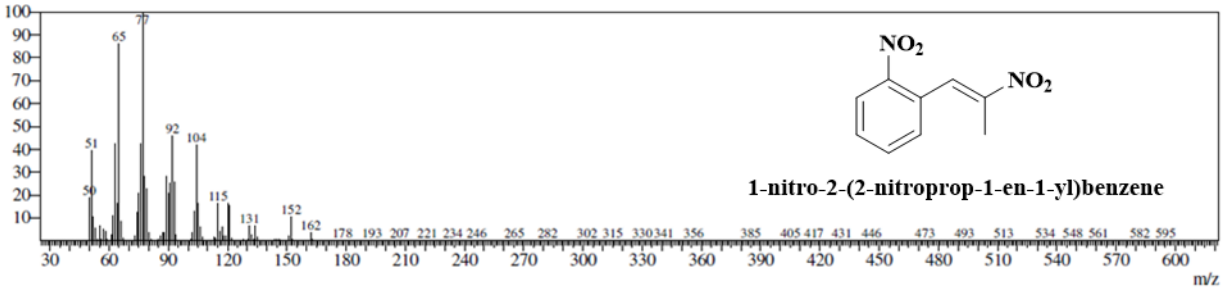


Fig. S23 GC-MS profile for 1-nitro-2-(2-nitroprop-1-en-1-yl)benzene.

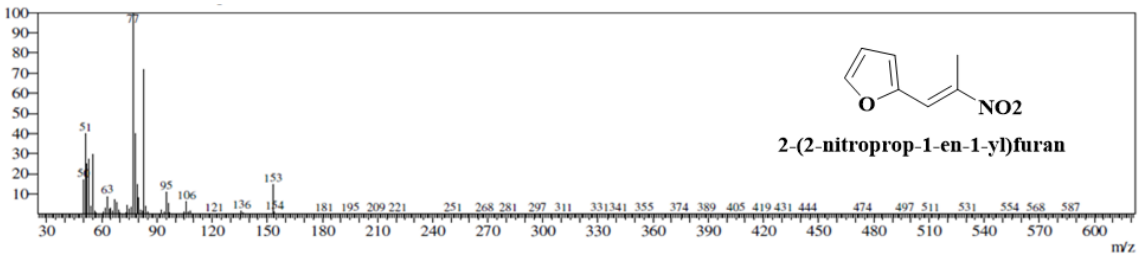


Fig. S24 GC-MS profile for 2-(2-nitroprop-1-en-1-yl)furan.

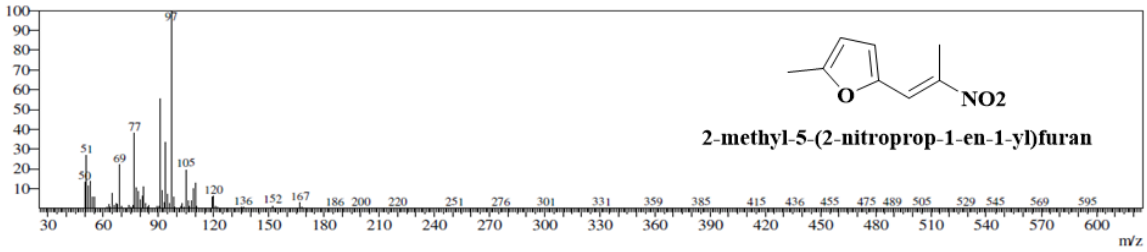


Fig. S25 GC-MS profile for 2-methyl-5-(2-nitroprop-1-en-1-yl)furan.

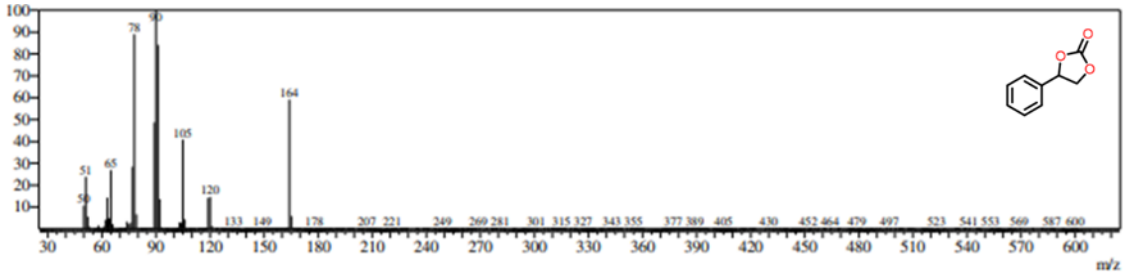


Fig. S26 GC-MS profile for 4-phenyl-1,3-dioxolan-2-one

5. ^{1}H and ^{13}C NMR analysis

^{1}H and ^{13}C NMR analysis

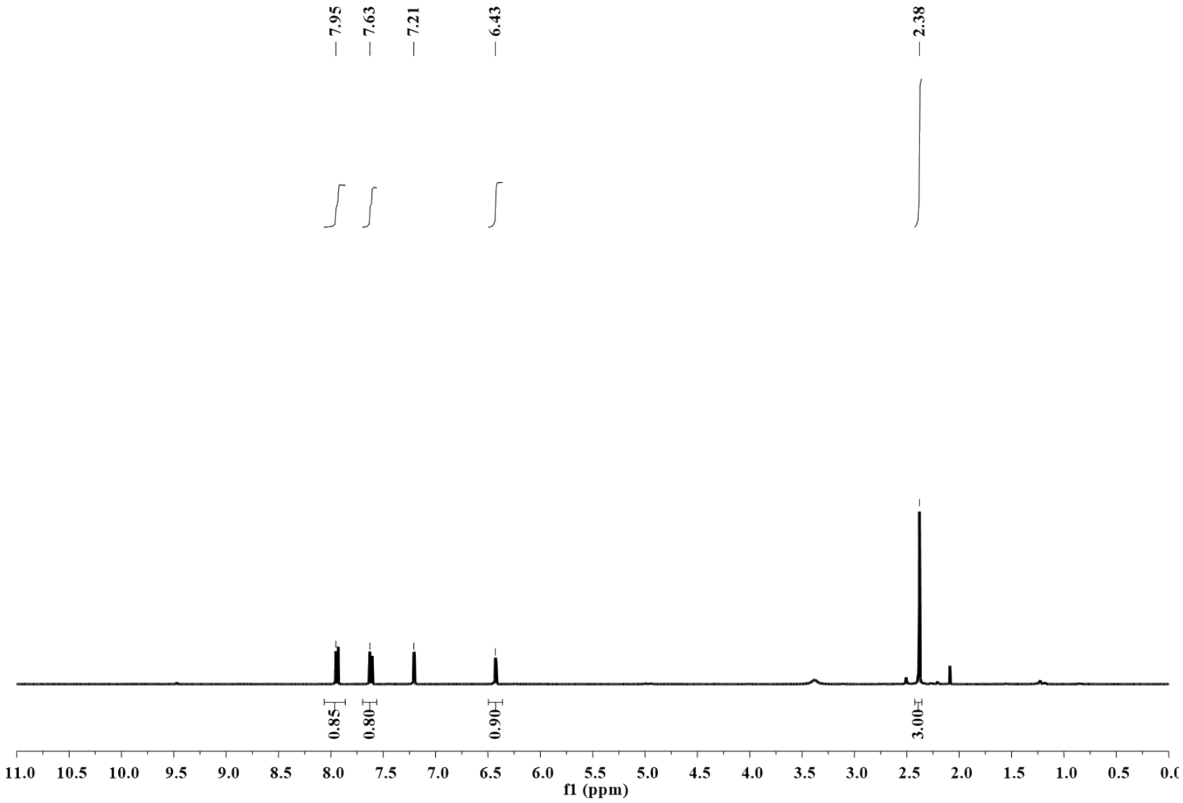


Fig. S27 ^{1}H NMR spectrum of 2-methyl-5-(2-nitrovinyl)furan

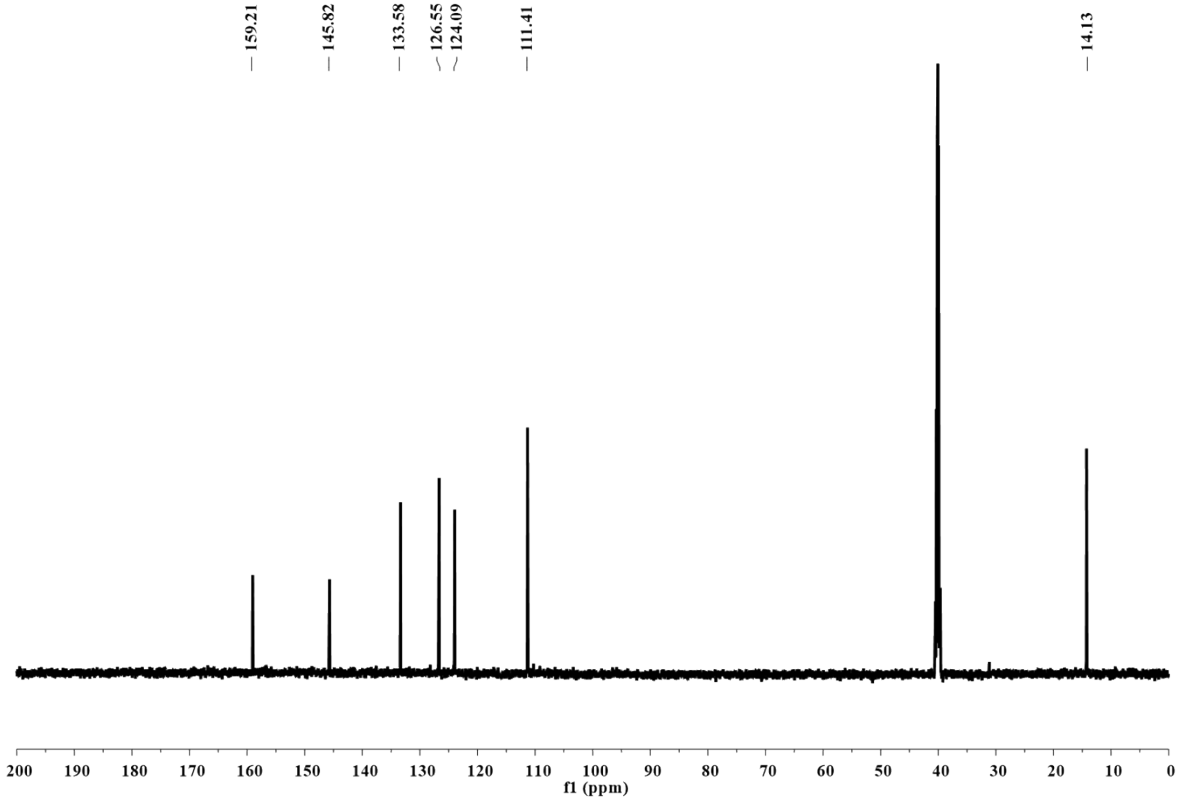


Fig. S28 ^{13}C NMR spectrum of 2-methyl-5-(2-nitrovinyl)furan

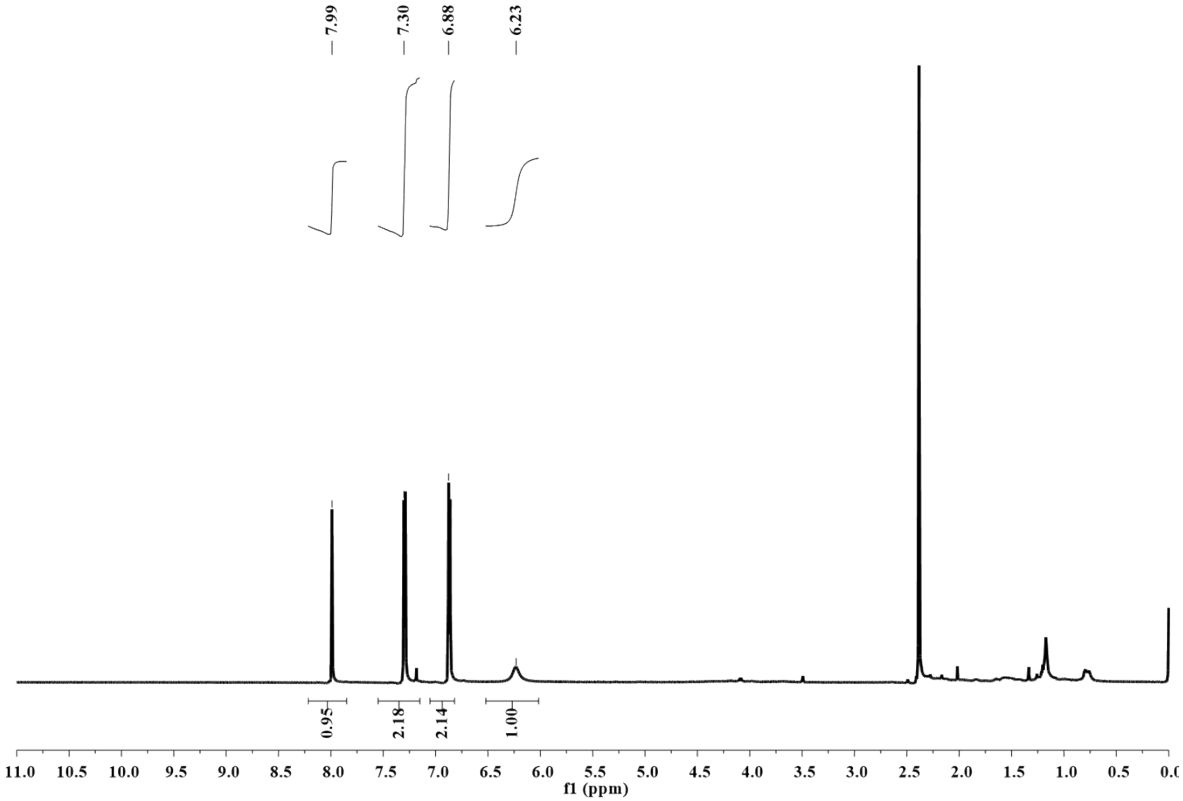


Fig. S29 ^{1}H NMR spectrum of 4-(2-nitrovinyl)phenol

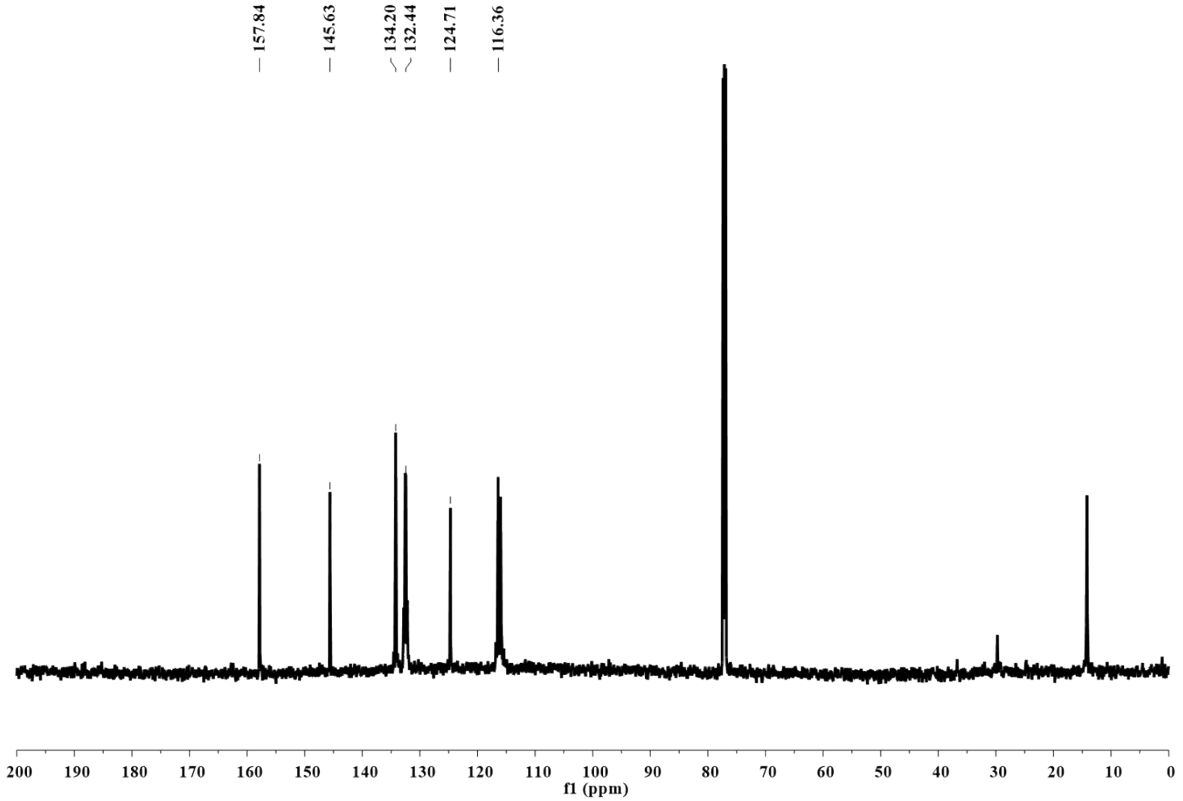


Fig. S30 ^{13}C NMR spectrum of 4-(2-nitrovinyl)phenol

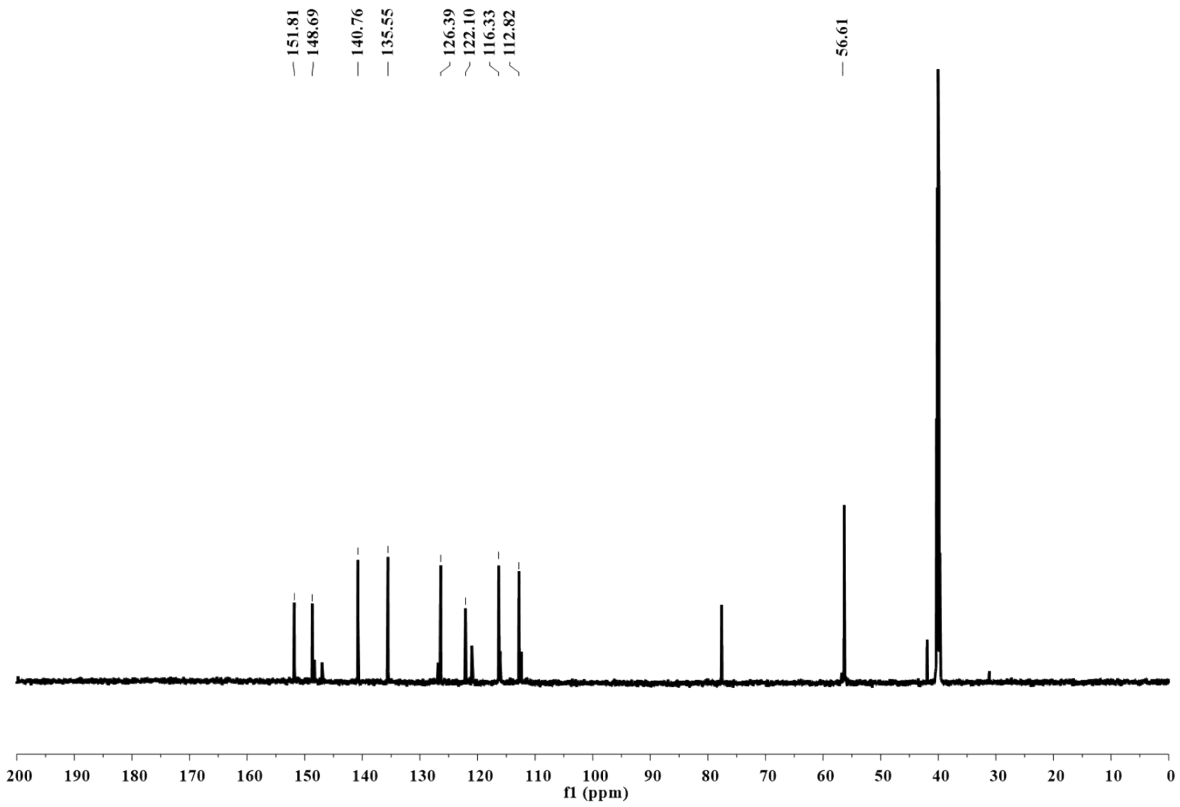


Fig. S31 ^{13}C NMR spectrum of 2-methoxy-4-(2-nitrovinyl)phenol

Table S2. Optimization studies cycloaddition of styrene oxide with CO_2 using DFNS@TBAB

Entry	Catalyst	Catalyst amount	Temp (°C)	Time (h)	Conv. (%)	Sel. (%)
1	-	-	100	12	-	-
2	DFNS@NH_2	25	100	12	-	-
3[a]	DFNS@NH_2 + CTAB	25	100	12	96	90
4[b]	DFNS@NH_2 + KI	25	100	12	90	88
5[c]	DFNS@NH_2 + n-BB	25	100	12	46	94
6[d]	n-BB	25	100	12	16	90
7	DFNS@TBAB	25	100	12	34	90
8	DFNS@TBAB	12.5	100	12	14	93
9	DFNS@TBAB	50	100	12	58	98
10	DFNS@TBAB	50	100	12	72	98
11	DFNS@TBAB	100	100	12	100	98

12	DFNS@TBAB	25	60	12	-	-
13	DFNS@TBAB	25	80	12	10	98
14	DFNS@TBAB	25	100	12	36	98
15	DFNS@TBAB	25	120	12	88	98
16	DFNS@TBAB	25	120	3	10	98
17	DFNS@TBAB	25	120	6	34	98
18	DFNS@TBAB	25	120	9	66	98
19	DFNS@TBAB	25	120	12	88	98
20	DFNS@TBAB	25	120	15	94	98

Reaction conditions: Styrene oxide: 2.08 mmol and balloon CO_2 pressure, [(a)]CTAB (5 mg), [(a)]KI (5 mg), [(c)]n-BB (5 mg), and [(d)]25 mg. n-BB: n-butyl bromide

Table S3. Comparison of metal-free catalyst for Henry reaction between benzaldehyde and nitromethane

Sr. No.	**Catalyst**	**Reaction condition**	**Yield (%)**	**Reference**
1	μ-Chlorotris(tetrahydrofuran)[tris[1,1,1-trimethyl-*N*-(trimethylsilyl)silanaminat	Catalyst: 2 mol%, BA: 1 equivalent, NM: 1 equivalent, THF, 66 °C, 24 h	10	S1
2	Ammonium acetate	Catalyst: 0.3 mmol, BA: 1 mmol, NM: 3 mL, microwave, 90 °C, 1 h	95	S2
3	Amine functionalized Yolk–shell-structured mesoporous silica	Catalyst: 5 mol%, BA: 1.0 mmol, NM: 1.0 mL, 90 °C, 3 h	99	S3
4	SiO_2 and triethylamine	Catalyst: 200 mg, Triethylamine: 0.2 mmol, BA: 2.0 mmol, NM: 2 mL, 50 °C, 17 h	18	S4
5	AFB	Catalyst: 26.5 mg, BA: 2.5 mmol, NM: 2 mL, 90 °C, 6 h	92	S5

6	AP-GO	Catalyst containing 0.075 mmol nitrogen species, BA: 0.306 mL (3.0 mmol), NM: 6.0 mL, 100 °C, 6.0 h	90	S6
7	DFNS@NH_2	Catalyst: 20 mg, BA: 2 mmol, NM: 11.2 mmol, , 60 °C, 6 h,	>99	**This work**

BA: Benzaldehyde, NM: Nitromethane, AP-GO: Graphene oxide-supported primary amine, AFB: Amine functionalized bagasse

Table S4. Comparison of metal-free catalysts for the synthesis of styrene carbonate from styrene oxide and CO_2

Catalyst	**Co-catalyst**	**Reaction conditions**	**Conv. (%)**	**Sel. (%)**	**Ref.**
SB	KI	2 MPA CO_2, 120 °C, 6 h	87	99	S7
COP-222	-	0.1 MPA CO_2, 100 °C, 24 h	99	99	S8
Amb-OH-I-910	-	3.0 MPa of CO_2, 120 °C, 24 h	-	99	S9
PQPBrCOOH	-	0.1 MPA CO_2, 120 °C, 12 h	-	98.2	S10
CSGOArg aerogels	THAB	100 °C, 8 h	-	65.39[a]	S11
[CMPy]Br/MA (1:1)	-	CO_2 balloon pressure, 90 °C, 1 h	100	100	S12
[TMGVBr]10@COF	-	0.1 MPA CO_2, acetonitrile (2 mL), 100 °C, 10 h	-	41.7[a]	S13
Ketimine derivatives	TBAI	1 MPA CO_2, RT, 24 h	-	94 [a]	S14
QAFB	-	0.1 MPA CO_2, 120 °C, 12 h	61	99	S5
DFNS@T	**-**	**CO_2 (balloon pressure),**	**94**	**98**	**This**

BAB	**120 °C, 15 h**	**work**

Abbreviations: SO: Styrene oxide, C_3N_4: Graphitic carbon nitride, u-g-C_3N_4: Urea derived graphitic carbon nitride, p-TBIB: metal-free microporous polymeric spheres catalyst, P-g-C_3N_4: Phosphorus doped graphitic carbon nitride, Amb-OH-I-910: Ion-exchange step into their iodide counterparts, OX-BC: Oxidised biochar, SB: sugarcane bagasse, QAFB: Quaternary ammonium salt functionalized sugarcane bagasse, tetrabutylammonium bromide (TBAB), [CMPy]Br: 1-(carboxymethyl)pyridinium bromide, KI: Potassium iodide.[a]Yield

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