Experimental Section

Materials.

All reagents were used as received without any further purification unless stated otherwise. Glycidyl methacrylate (GM, Acros 97%) and 4-vinylbenzyl chloride (VBC, Aldrich 90%) were distilled before use. Dichloromethane (DCM) and N,N-dimethylformamide (DMF) were distilled from calcium hydride. 2,2-Azoisobutyronitrile (AIBN) and N-isopropylacrylamide (NIPAAM) were purified by recrystallization from methanol and hexane, respectively. S-1-Dodecyl-S'-(α,α'-dimethyl-α"-acetic acid)trithiocarbonate (TC)[1], 2-cyanoprop-2-yl-4-cyanodithiobenzoate (CPD)[2], 4-(3-butenyl)styrene (BS)[3], phenyl 4-vinylbenzene sulfonate (PVBS)[4], 1-(2-(prop-2-yn-1-yloxy)ethyl)-1H-imidazole (PEI)[5] were synthesized according to literature procedures.

Measurements.

All ^{1}H NMR spectra were recorded on a Bruker AVANCEIII^{TM} 500 spectrometer (500 MHz) by using $CDCl_3$ or DMSO-d_6 as a solvent. GPC data were obtained from Waters GPC system equipped with a Waters 2414 refractive index (RI) detector, a 1515 isocratic HPLC pump, and two Waters HPLC columns. THF (HPLC grade) was used as the solvent for polymers and eluent for GPC with a flow rate of 1 ml/min at 30 ^{o}C. FTIR analyzed were carried out using Thermo NICOLET is50. TEM images were obtained using a JEM-2100F TEM instrument. Samples were prepared by dip-coating a 400 mesh carbon-coated copper grid from the dilute sample solution allowing the solvent to evaporate. GC analyzed were recorded on an Agilent 6890 Series GC System with a Hewlett-Packard 5973 Mass Selective Detector (70 eV) using a HP-5MS fused silica capillary column and N_2 as a carrier gas (1 mL/min). The split ratio was 1:50. The injector temperature was 280 ^{o}C and detector was 280 ^{o}C. The column temperature was kept at 60 ^{o}C for 3 min, increased to 280 ^{o}C at a rate of 25 ^{o}C/min, and then held at 280 ^{o}C for 3 min. The fluorescence data was obtained by Hitachi F-7000 Fluorescence Spectrophotometer with a λ_{exc} = 515 nm.

Synthesis

The synthesis of P(GM-g-LA-g-VBC/BS) core-shell bottlebrush copolymer precursors is as described in the literature[6].

1. Synthesis of P(GM-g-LA-g-VBC/BS-g-PVBS/NIPAAM)

Poly (GM-g-LA-g-VBC/BS) (50 mg), NIPAAM (1.2 g), AIBN (0.08 mg), PVBS (70 mg) and 1,4-dioxane (2 ml) were mixed in a reaction vessel and degassed by 3 freeze-pump-thaw cycles. The polymerization was conducted at 60 ^{o}C for 6 h. The resulting mixture was precipitated from DCM into ethyl ether 3 times and dried under vacuum at room temperature for 24 h. Yield = 125 mg (5.9%). ^{1}H NMR: n (NIPAAM) = 300, n (PVBS = 20).

2. Intramolecular shell-cross-linking

Bottlebrush copolymers of P(GM-g-LA-g-VBC/BS-g-PVBS\NIPAAM) (125 mg) were dissolved in 50 ml of DCM under nitrogen. Grubbs' first generation catalyst (13 mg) was added into the reaction solution and stirred at room temperature under nitrogen for 12 h. At the end of the reaction, 0.05 ml of ethyl vinyl ether was injected

to the solution to quench the catalyst. Then most of the solvent was evaporated and shell-cross-linked polymers were precipitated into ethyl ether and precipitated from DCM into ethyl ether 2 more times.

3. Core etching

Cross-linked bottlebrush copolymers (125 mg) were dissolved in 50 ml MeOH, 0.1 ml 50% NaOH was added at room temperature and then heating to 50 ^{o}C for 24 h. The solvent was evaporated and precipitated into ethyl ether 3 times.

4. The azidation of organic nanotube (N_3-Nanotube)

To a solution of PLA removed organic nanotube (100 mg) in 10 ml DMF was added NaN_3 (65 mg, 1 mmol) and the mixture was heated to 50 ^{o}C for 19 h and then dialyzed against nanopure water for three days to remove residuals.

5. Synthesis of organic nanotube supported imidazole catalyst (Base-Nanotube)

A mixture of $CuSO_4{\cdot}5H_2O$ (40 mg, 0.16 mmol), Sodium Ascorbate (80 mg, 0.4 mmol), 1-(2-(prop-2-yn-1-yloxy)ethyl)-1H-imidazole(PEI) (12 mg, 0.16 mmol), N_3-Nanotube (100 mg), 15 ml H_2O and 15ml DMF were placed in a reaction flask. The mixture was stirred at 60 ^{o}C for 24 h under N_2. The solvent was evaporated under vacuum and precipitated into ethyl ether. Then precipitated from DMF into ethyl ether 2 times and then dialyzed against nanopure water for three days to remove residuals.

6. Synthesis of organic nanotube supported sulfonic acid and imidazole catalyst (Acid-Base-Nanotube)

The Acid-Base-Nanotube was obtained through Base-Nanotube acidified in acetic acid aqueous by ion exchange. Base Nanotube (10 mg) was dissolved in 1 ml H_2O, acetic acid (6 mg) was added. The solution was stirred at RT for 10 min. Then the solution was dialyzed against nanopure water for three days to remove residuals.

7. Synthesis of organic nanotube supported sulfonic acid catalyst (Acid-Nanotube)

The Acid-Nanotube was obtained through core etched bottlebrush copolymers acidified in acetic acid aqueous by ion exchange. Core etched bottlebrush copolymers (10 mg) was dissolved in 1 ml H_2O, acetic acid (7 mg) was added. The solution was stirred at RT for 10 min. Then the solution was dialyzed against nanopure water for three days to remove residuals.

8. Synthesis of poly(PVBS)

Phenyl 4-vinylbenzene sulfonate (PVBS 500 mg), TC (14 mg), AIBN (0.63 mg) and 1,4-dioxane (0.5 ml) were mixed in a reaction vessel and degassed by 3 freeze-pump-thaw cycles. The polymerization was conducted at 60 ^{o}C for 20 h. The mixture was diluted with DCM, precipitated into methanol 3 times and dried under vacuum at room temperature for 24 h. Yield = 83 mg (17 %). GPC (PS standards): Mn = 2,900 g/mol, Mw/Mn = 1.13. ^{1}H NMR: n (PVBS) = 15.

9. Synthesis of P(PVBS-co-NIPAAM)

Poly (PVBS) (20 mg), NIPAAM (695 mg), AIBN (0.08 mg), 1,4-dioxane (4.2 ml) were mixed in a reaction vessel and degassed by 3 freeze-pump-thaw cycles. The polymerization was conducted at 60 ^{o}C for 5 h. The resulting mixture was precipitated from DCM into ethyl ether 3 times and dried under vacuum at room temperature for 24 h. Yield = 180 mg (23 %). ^{1}H NMR: n (NIPAAM) = 300.

10. Synthesis of P(PTSA-co-NIPAAM)

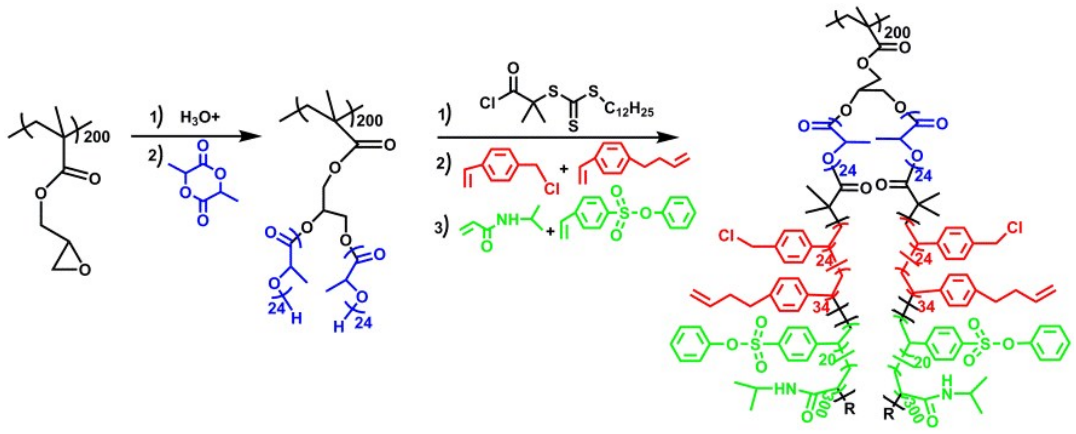
P(PVBS-co-NIPAAM) (100 mg) was dissolved in 10 ml MeOH and 0.5 ml 5 M NaOH aquous solution was added. The solution was heated to 50 ^{o}C for 16 h. After the reaction was finished, 1 ml 5 M H_2SO_4 was added to acidize the product for 5 h at room temperature. The P(PTSA-co-NIPAAM) was obtained after the solution was dialyzed against nanopure water for three days to remove residuals.

11. Catalysis Experiment

Catalysis experiments were conducted in a reaction bottle at room temperature. A mixture of benzaldehyde dimethylacetal (20 μL), ethyl cyanoacetate (145 μL), and H_2O (2 mL) were added to a reaction bottle. The Acid-Base-Nanotube (30 mg) was added into the reactor and reacted at room temperature for 24 h. Then the product was extracted by ethyl ether 3 times and analyzed by GC. The Acid-Base-Nanotube catalyst was still dissolved in H_2O and used for the next experiment.

To investigate the recyclability of the Acid-Base-Nanotube catalyst, a six recycle test was performed. The Acid-Base-Nanotube catalyst was still dissolved in H_2O in the reaction bottle after the first reaction. Benzaldehyde dimethylacetal (20 μL) and ethyl cyanoacetate (145 μL) were added in the bottle and reacted at room temperature for 24 h. Then the product was extracted by ethyl ether 3 times and analyzed by GC.

Controlled experiments were designed to demonstrate the superiority of the Acid-Base-Nanotube catalyst. In five same reaction bottles, a mixture of benzaldehyde dimethylacetal (20 μL), ethyl cyanoacetate (145μL), and H_2O (2 mL) was added. No catalyst, Acid-Nanotube, Base-Nanotube, either free acid or base catalyst with relative Acid-Base-Nanotube catalyst were used for the controlled experiments. The mixture was reacted at room temperature with a constant stirring for 24 h. Then the product was extracted by ethyl ether 3 times and analyzed by GC.



Scheme S1. Synthesis procedure of bottlebrush copolymer precursors

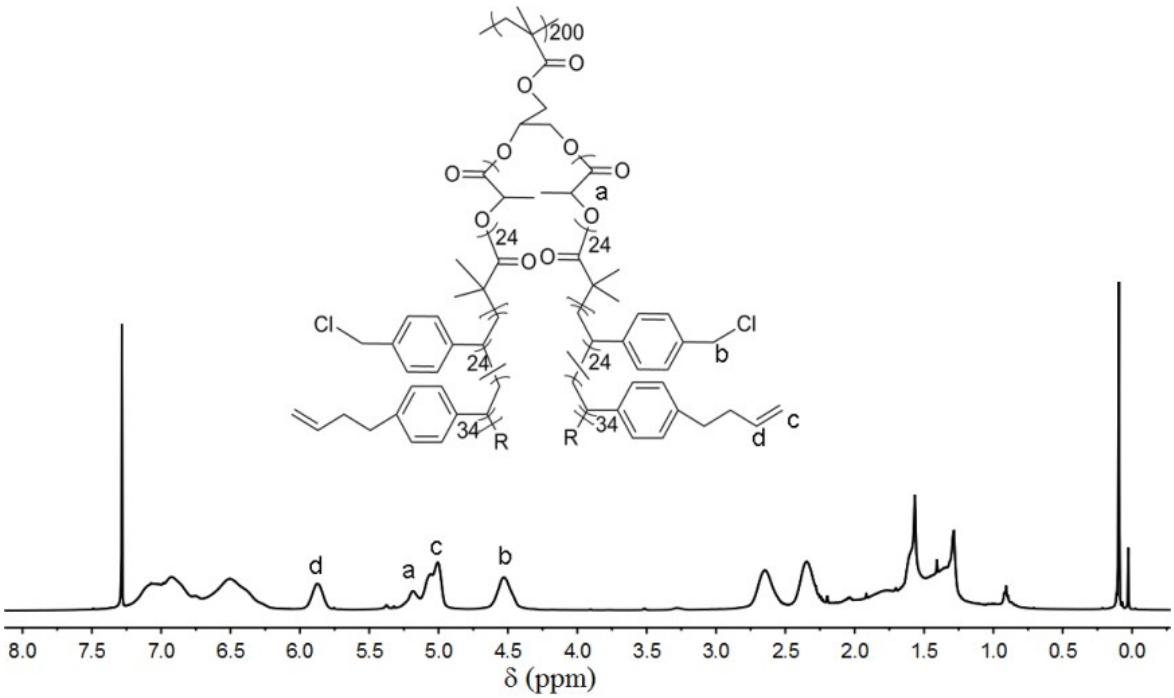


Fig S1. ^{1}H NMR of P(GM-g-LA-g-VBC/BS) in $CDCl_3$

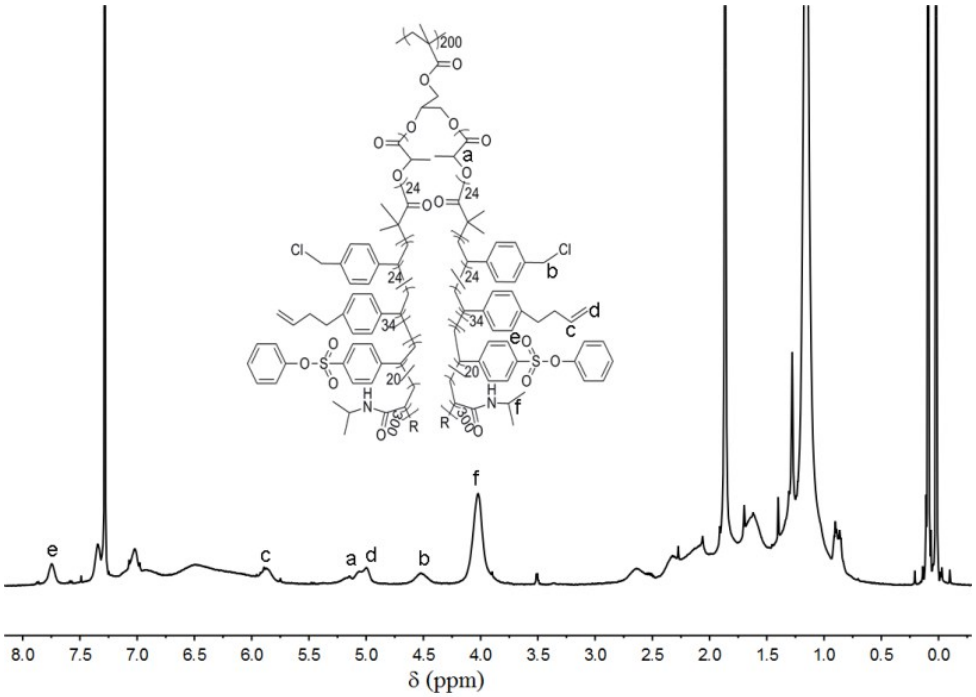


Fig S2. ^{1}H NMR of P(GM-g-LA-g-VBC/BS-g-PVBS/NIPAAM) in $CDCl_3$

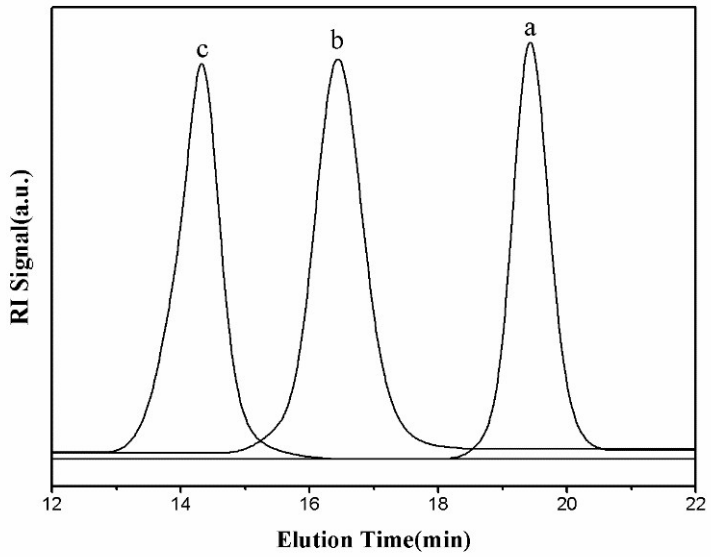


Fig S3. SEC traces of (a) PGM, (b) P(GM-g-LA), (c) P(GM-g-LA-g-VBC/BS)

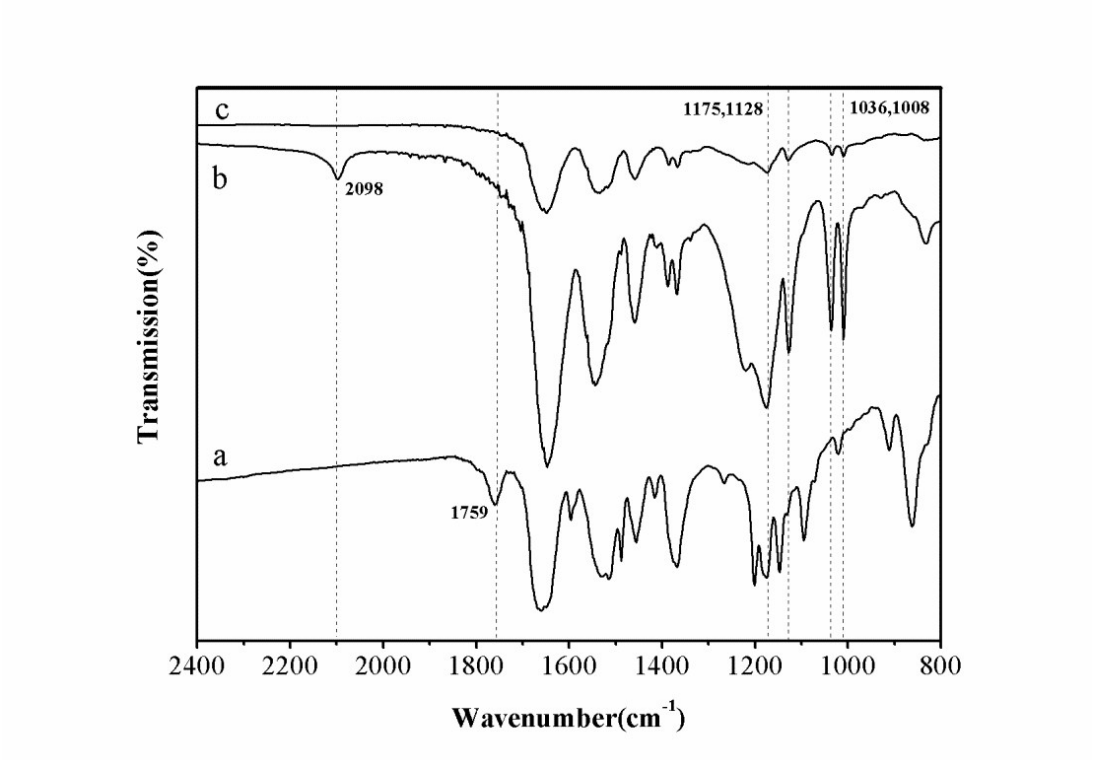


Fig S4. FTIR of (a) intramolecular cross-linked nanotubes, (b) N3-Nanotubes, and (c) Acid-Base Nanotubes

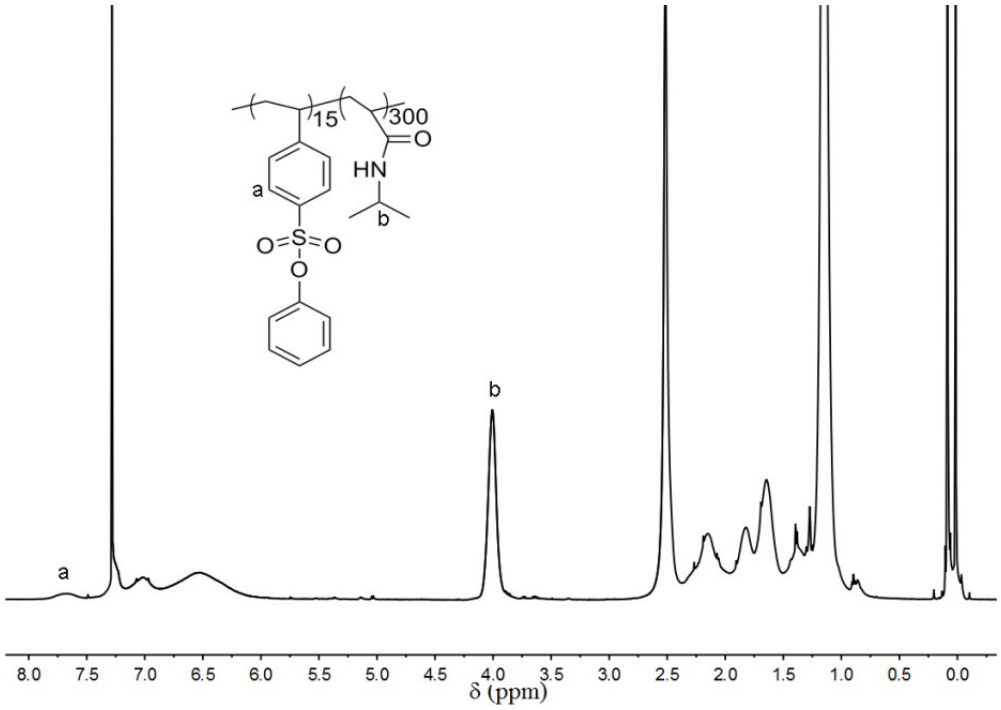
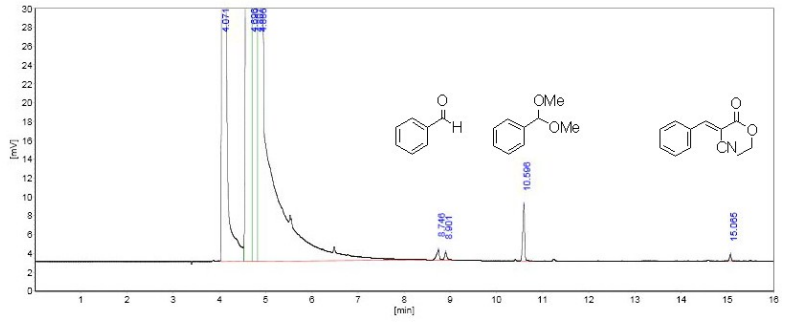


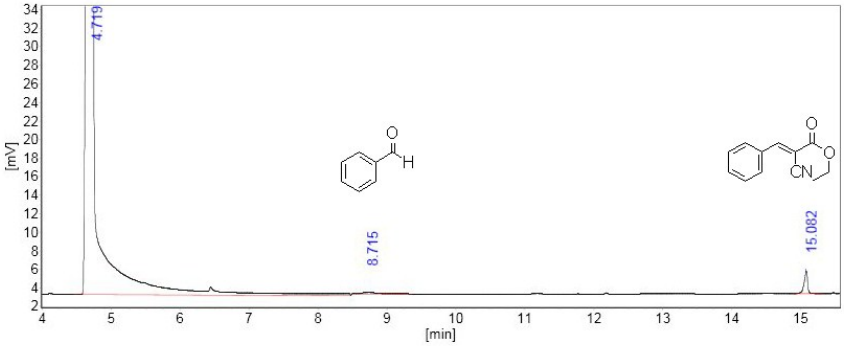
Fig S5. ^{1}H NMR of the P(PVBS-co-NIPAAM) precursors in $CDCl_3$



Analysis Result

Entry	Compound Name	Time [min]	Height [uV]	Area [uV*s]
1		4.071	177382	726179
2		4.696	175588	1219928
3		4.807	197748	1291021
4		4.886	196307	1739863
5		8.746	1057	964
6		8.901	819	646
7		10.596	6013	17357
8		15.065	661	708

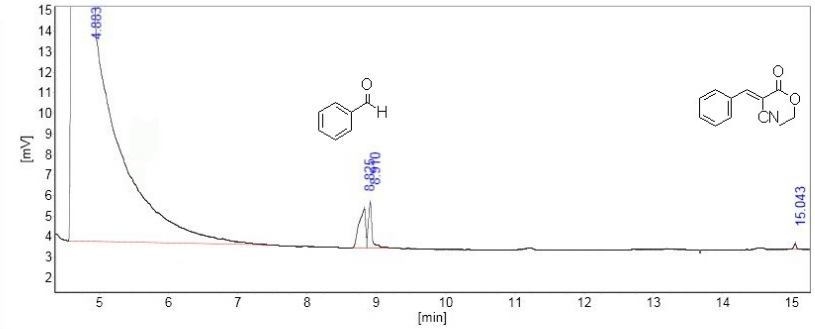
Fig S6. GC data for entry 1 in Table 1



Analysis Result

Entry	Compound Name	Time [min]	Height [uV]	Area [uV*s]
1		4.719	151695	936996
2		8.715	24	11
3		15.082	2410	8569

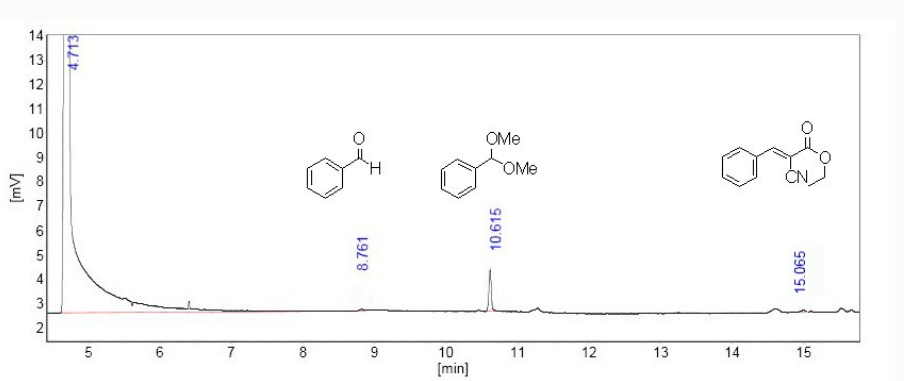
Fig S7. GC data for entry 2 in Table 1



Analysis Result

Entry	Compound Name	Time [min]	Height [uV]	Area [uV*s]
1		4.003	36	89
2		4.091	34951	86878
3		4.155	12322	45435
4		4.883	322703	4261977
5		8.825	1902	8281
6		8.910	2215	1442
7		15.043	256	717

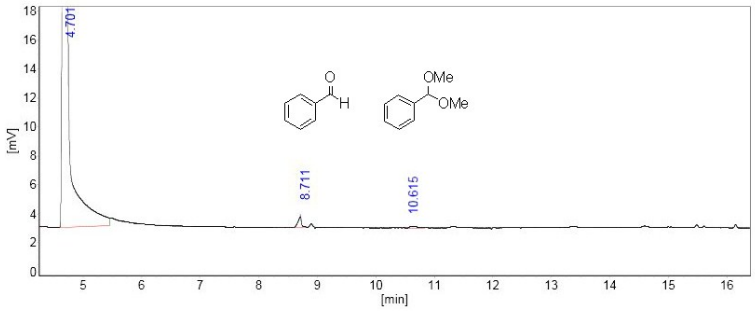
Fig S8. GC data for entry 3 in Table 1



Analysis Result

Entry	Compound Name	Time [min]	Height [uV]	Area [uV*s]
1		4.713	93172	389126
2		8.761	4	97
3		10.615	1680	3872
4		15.065	44	480

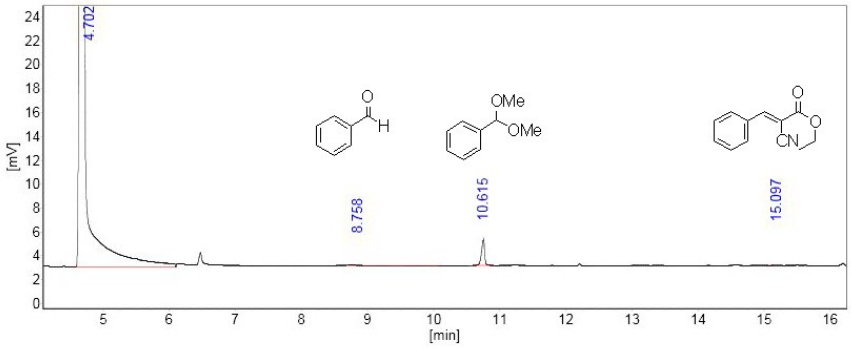
Fig S9. GC data for entry 4 in Table 1



Analysis Result

Entry	Compound Name	Time [min]	Height [uV]	Area [uV*s]
1		3.953	29	49
2		4.127	1527	5751
3		4.701	97016	434226
4		8.711	721	961
5		10.615	51	52

Fig S10. GC data for entry 5 in Table 1



Analysis Result

Entry	Compound Name	Time [min]	Height [uV]	Area [uV*s]
1		4.120	45	111
2		4.702	106587	487247
3		8.758	16	17
4		10.615	2126	7222
5		15.097	11	23

Fig S11. GC data for entry 6 in Table 1

Reference:

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