Electronic Supplementary Information

Polystyrene-based superacidic sulfonic acid catalyst: synthesis and its application in biodiesel production

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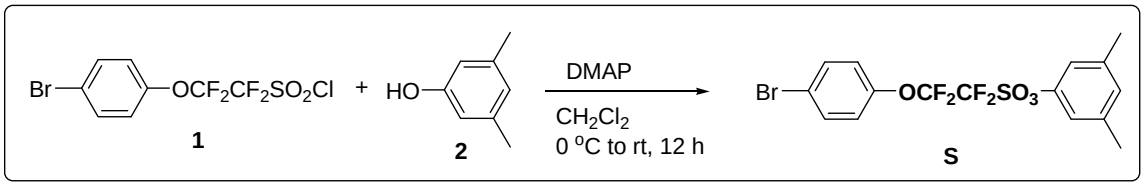
Materials and Methods

4,4'-Di-*tert*-butyl-2,2'-dipyridyl (d*t*bpy), chloro-1,5-cyclooctadiene iridium(I) dimer ($[IrCl(COD)]_2$), tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$), 4-dimethylaminopyridine (DMAP), $Na_2S_2O_4$, 3,5-dimethylphenol, and 4-bromobenzenesulfonyl chloride were reagent grade and used without further purification. Bis(pinacolato)diboron (B_2pin_2) from Frontier Scientific Co., $BrCF_2CF_2Br$ from SynQuest Labs, Inc., Chlorine gas from Praxair Inc., CFC-113 from ChemNet were used as received. Cyclooctane was dried using sodium and benzophenone, distilled under vacuum, and stored in a nitrogen-filled glove box. sPS (Mn = 48.6 kg/mol with PDI = 2.90) was obtained from LG Chemical Ltd., Daejeon, S. Korea and used as received. Anhydrous tetrahydrofuran (THF) was obtained from EMD Chemicals and collected from the container using a positive pressure of nitrogen.

^1H, ^{19}F and ^{13}C NMR spectra were obtained using a Varian NMR spectrometer (400 MHz for ^1H, 376 MHz for ^{19}F, and 100 MHz for ^{13}C) at room temperature and chemical shifts were referenced to TMS (^1H and ^{13}C) and $CFCl_3$ (^{19}F). GC/MS analysis was conducted using a Shimadzu QP2010S equipped with a 30 m × 0.25 mm SHR-XLB GC column and an EI ionization MS detector. FT-IR spectra were recorded on a Shimadzu IR Prestige-21.



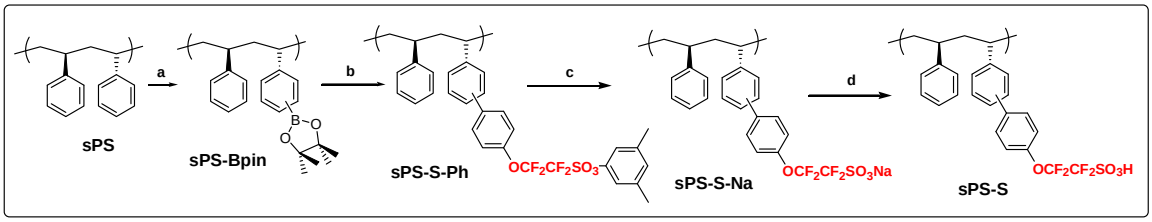
Scheme 1. Synthesis of **S**.

Synthesis of 3,5-dimethylphenyl 2-(4-bromophenoxy)tetrafluoroethanesulfonate ester (S)

Compound **1** was synthesized according to the reported procedure.[1] 3,5-Dimethylphenol (3.10 g, 25.4 mmol, 1.1 equiv) and CH_2Cl_2 (70 mL) were added to a 250 mL two-necked flask filled with nitrogen. The mixture was cooled to 0 °C. Compound **1** (8.57 g, 23.1 mmol) and DMAP (3.38 g, 27.7 mmol, 1.2 equiv) were added in sequence and the mixture was stirred at 0 °C for 2 h then room temperature for 12 h. The reaction mixture was diluted with CH_2Cl_2 (80 mL), and washed with 2 M HCl (40 mL × 3), saturated $NaHCO_3$ (40 mL), brine (30 mL), and dried over $MgSO_4$.

[1] A. E. Feiring and E. R. Wonchoba, *J. Fluorine Chem.*, 2000, **105**, 129–135.

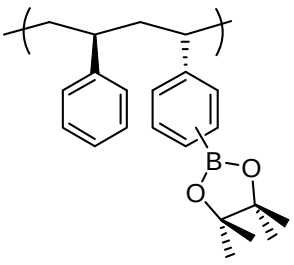
After evaporation of solvent, the resulting crude product was purified by column chromatography (hexane/ethyl acetate=10:1) to give 9.66 g of **S** as a yellowish oil (92% yield). ^{1}H NMR ($CDCl_3$): δ 7.52 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 8.8 Hz, 2H), 6.99 (s, 1H), 6.92 (s, 2H), 2.25 (s, 6H). ^{19}F NMR ($CDCl_3$): δ –81.4 (t, J = 4.3 Hz, O$\underline{CF_2}$), –112.5 (t, J = 4.3 Hz, $\underline{CF_2}SO_3$). ^{13}C NMR ($CDCl_3$): δ 150.0, 147.5, 140.4, 133.1, 129.9, 123.8, 120.7, 119.2, 115.8 (tt, $^{1}J_{CF}$ = 277.6 Hz, $^{2}J_{CF}$ = 28.6 Hz), 113.9 (tt, $^{1}J_{CF}$ = 298.1 Hz, $^{2}J_{CF}$ = 39.1 Hz), 21.4. GC/MS: 456 (M^+), 392, 192, 143, 121 (100%), 91, 77. HRMS (*m/z*) (CI, NH_3): calc. for $C_{16}H_{13}O_4BrF_4S$ $(M+NH_4)^+$ 473.9992, found 473.9996.



Reagents and conditions: (a) B_2pin_2, $[IrCl(COD)]_2$ (1.5 mol%), d*t*bpy (3 mol%), cyclooctane, 150 °C, 6 h; (b) **S** (2 equiv), $Pd(PPh_3)_4$ (4 mol%), K_3PO_4 (4.5 equiv), THF/H_2O (10/1; v/v), 80 °C, 12 h; (c) NaOH (8 equiv), dioxane/H_2O (100/1; v/v), 100 °C, 4 h; (d) 1 M H_2SO_4, reflux, 6h.

Scheme 2. Synthesis of **sPS-S**.

Preparation of sPS-Bpin (40 mol% Bpin) [2,3]

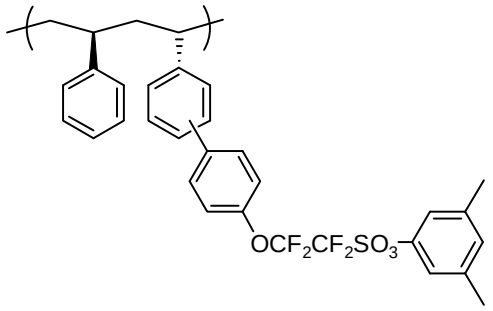


In a nitrogen-filled glove box, sPS (700 mg, 6.73 mmol polystyrene repeating unit), B_2pin_2 (1.37 g, 5.38 mmol, 0.8 equiv), $[IrCl(COD)]_2$ (54.2 mg, 1.5 mol% iridium based on the amount of B_2pin_2), d*t*bpy (43.3 mg, 3 mol% based on the amount of B_2pin_2), cyclooctane (4.30 g, 0.40 mol,

[2] J. Shin, S. M. Jensen, J. Ju, S. Lee, Z. Xue, S. K. Noh and C. Bae, *Macromolecules*, 2007, **40**, 8600–8608.
[3] Y. Chang, G. F. Brunello, J. Fuller, M. Hawley, Y. S. Kim, M. Dissabb-Miller, M. A. Hickner, S. S. Jang, C. Bae, *Macromolecules* 2011, **44**, 8458-8469.

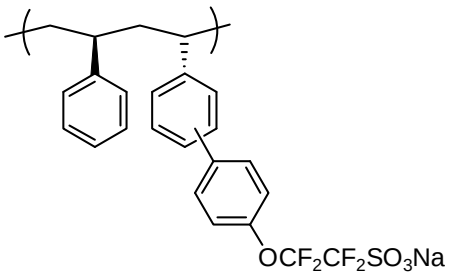
60 equiv) and a magnetic stirring bar were placed into a 30 mL vial and capped with a Teflon-lined septum. The vial was removed from the glove box and placed in an oil bath at 150 ºC for 6 h. After cooling to room temperature, the mixture was diluted with chloroform (60 mL) and filtered through a short plug of silica gel to remove the catalyst. The filtrate was concentrated by rotary evaporator to about 10 mL, and cold methanol (100 mL) was added to precipitate the polymer. The dissolution and precipitation process was repeated one more time to ensure complete removal of any small molecules trapped in the polymer. The borylated polymer was isolated as a white solid and dried under vacuum at 60 ºC (1.04 g). ^{1}H NMR (benzene-d_6): δ 8.00 (H_{arom} from C_6H_4-Bpin), 7.73 (H_{arom} from C_6H_4-Bpin), 7.08 (H_{arom}), 6.71 (H_{arom}), 2.09 (CH), 1.49 (CH_2), 1.16 (CH_3).

Preparation of sPS-Ph



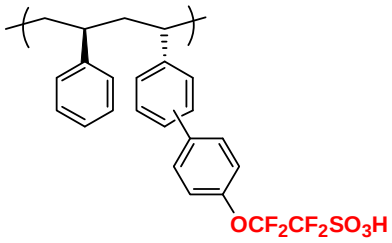
sPS-Bpin (100 mg of 40 mol% Bpin functionalized sPS, 0.250 mmol Bpin) and K_3PO_4 (0.240 g, 1.13 mmol, 4.5 equiv) were placed in a 25 mL vial and capped with a Teflon-lined septum. Tetrakis(triphenylphosphine)palladium (11.6 mg, 0.01 mmol, 4 mol%) and THF (4 mL) were added to the vial in a glove box and the vial was removed from the glove box. Compound **S** (350 mg, 0.75 mmol, 3 equiv) and water (0.4 mL) were added using syringes. The solution was stirred at 80 ^{o}C for 12 h, cooled to room temperature, diluted with chloroform (40 mL), and filtered through a short pad of silica gel. The filtrate was concentrated to about 3 mL and cold methanol (100 mL) was added to precipitate the polymer. Another cycle of dissolution in chloroform and precipitation with cold methanol provided 140 mg of **sPS-Ph** as a white solid. ^{1}H NMR (benzene-d_6): δ 7.16-7.20 (H_{arom}), 6.62-6.95 (H_{arom}), 2.18 (CH), 1.97 (CH_3), 1.59 (CH_2). ^{19}F NMR (benzene-d_6): δ –80.3 (2F, –O$\underline{CF_2}$), –111.9 (2F, $\underline{CF_2}SO_3$–). ^{13}C NMR ($CDCl_3$): δ 145.4, 140.4, 129.9, 128.1, 127.9, 125.8, 122.1, 122.0, 119.2, 44.1, 40.8, 21.5.

Preparation of sPS-S-Na



sPS-Ph (100 mg of 40 mol% sulfonated sPS; 0.158 mmol sulfonate) was dissolved in THF (4 mL) with gentle heating and NaOH (50.6 mg, 1.26 mmol, 8 equiv) and H_2O (40 μL) was added. The resulting solution was stirred at 80 °C for 4 h. After cooling to room temperature, the solvent was evaporated and the residue was dissolved in methanol, filtered through a short plug of silica gel. After evaporation of solvent, addition of H_2O (20 mL) caused precipitation of the polymer which was filtered and refluxed in the mixture of water/methanol (3/1, *v/v*) for 2 h, filtered, dried under vacuum at 110 °C for 12 h to give 87.0 mg of polymer product. ^{1}H NMR (DMSO-d_6) δ: 6.80–8.10 (H_{arom}), 1.61 (CH), 1.23 (CH_2). ^{19}F NMR (DMSO-d_6) δ: –80.4 (O$\underline{CF_2}$), –116.2($\underline{CF_2}SO_3$). ^{13}C NMR (DMSO-d_6) δ: 147.9, 145.2, 144.4, 138.8, 138.4, 136.1, 127.8, 127.2, 124.2, 122.1, 117.2 (tt, J_1 = 274.5 Hz, J_2 = 31.3 Hz), 112.8 (tt, J_1 = 285.7 Hz, J_2 = 36.4 Hz), 43.5.

Preparation of sPS-S



Acidification of the obtained sPS-S-Na was achieved by stirred the polymer in 1 M H_2SO_4 solution at 100 °C for 6 h followed by thorough rinse with deionized water. The crude polymer product was refluxed with boiling methanol for 6 h, filtered, and dried to give sPS-S. To increase surface area of solid catalyst, sPS-S was ground into fine particles before use in catalytic reactions.

Determination of sulfonic acid amount in sPS-S by titration

The molar amount of sulfonate group in sPS-S catalyst (in mmol/g) was determined using a titration method. The sulfonated polymer in $–SO_3H$ form was equilibrated in 2 M NaCl solution at room temperature for 3 days before titration. The protons released into the aqueous solution were titrated with 0.025 M NaOH solution using phenolphthalein as an indicator. The experimental ion exchange capacity of the sPS-S was calculated according to the equation below:

$$\text{Ion exchange capacity } (\text{-}SO_3H \text{ amount in mmol/g}) = M_{NaOH} \times V_{NaOH} / W_{dry}$$

Where M_{NaOH} and V_{NaOH} are the molar concentration of volume (mL) of the aqueous NaOH solution used in titration, W_{dry} is the weight of dry membrane (g).

Characterization Data of Isolated Products

$C_{11}H_{23}CO_2CH_3$

Yield 99%, colorless oil. ^{1}H NMR ($CDCl_3$): δ 3.67 (s, 3H), 2.30 (t, *J* = 7.6 Hz, 2H), 1.62 (m, 2H), 1.26 (m, 16H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 174.53, 51.61, 34.32, 32.12, 29.80, 29.66, 29.53, 29.47, 29.36, 25.17, 22.89, 14.30. GC/MS: 214 (M^+), 171, 157, 143, 129, 101, 87, 74 (100%), 57, 43.

$C_{13}H_{27}CO_2CH_3$

Yield 92%, colorless oil. ^{1}H NMR ($CDCl_3$): δ 3.66 (s, 3H), 2.30 (t, *J* = 7.6 Hz, 2H), 1.62 (m, 2H), 1.26 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 174.45, 51.54, 34.28, 32.12, 29.87, 29.84, 29.79, 29.65, 29.55, 29.45, 29.35, 25.14, 22.88, 14.27. GC/MS: 242 (M^+), 199, 185, 157, 143, 129, 101, 87, 74 (100%), 57, 43.

$C_{15}H_{31}CO_2CH_3$

Yield 95%, white solid. ^{1}H NMR ($CDCl_3$): δ 3.67 (s, 3H), 2.30 (t, *J* = 7.6 Hz, 2H), 1.62 (m, 2H), 1.25 (m, 24H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 174.55, 51.63, 34.33, 32.14, 29.90, 29.88, 29.87, 29.81, 29.67, 29.58, 29.48, 29.38, 25.18, 22.91, 14.32. GC/MS: 270 (M^+), 227, 185, 157, 143, 129, 87, 74 (100%), 57, 43.

$C_{17}H_{35}CO_2CH_3$

Yield 97%, white solid. ^{1}H NMR ($CDCl_3$): δ 3.67 (s, 3H), 2.30 (t, *J* = 7.2 Hz, 2H), 1.62 (m, 2H), 1.25 (m, 28H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 174.56, 51.63, 34.33, 32.15, 29.88, 29.86, 29.81, 29.67, 29.58, 29.48, 29.38, 25.18, 22.91, 14.33. GC/MS: 298 (M^+), 267, 255, 241, 213, 185, 143, 129, 87, 74 (100%), 57, 43.

Supporting Figures

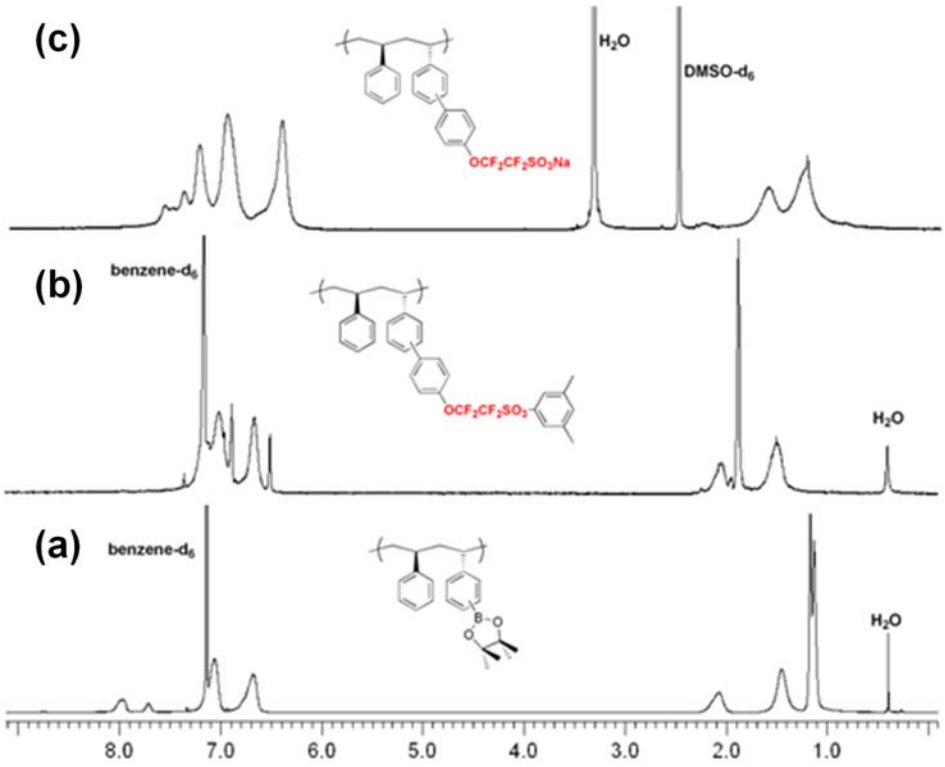


Figure S1. ^{1}H NMR spectra of (a) **sPS-Bin,** (b) **sPS-Ph** (benzene-d_6) and (c) **sPS-S-Na** (Na^+ form) (DMSO-d_6).

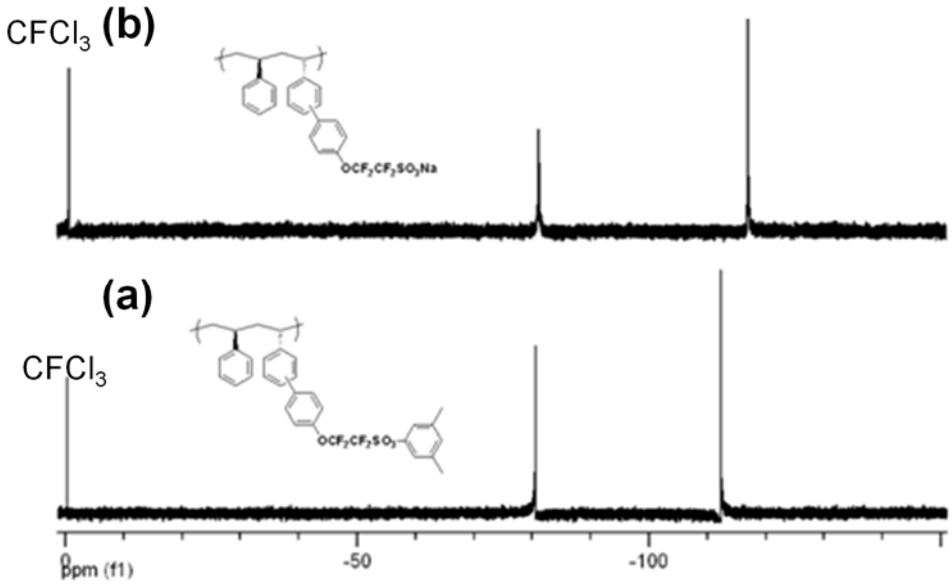


Figure S2. ^{19}F NMR of (a) **sPS-Ph** (benzene-d_6) and (b) **sPS-S-Na** (Na^+ form) (DMSO-d_6).

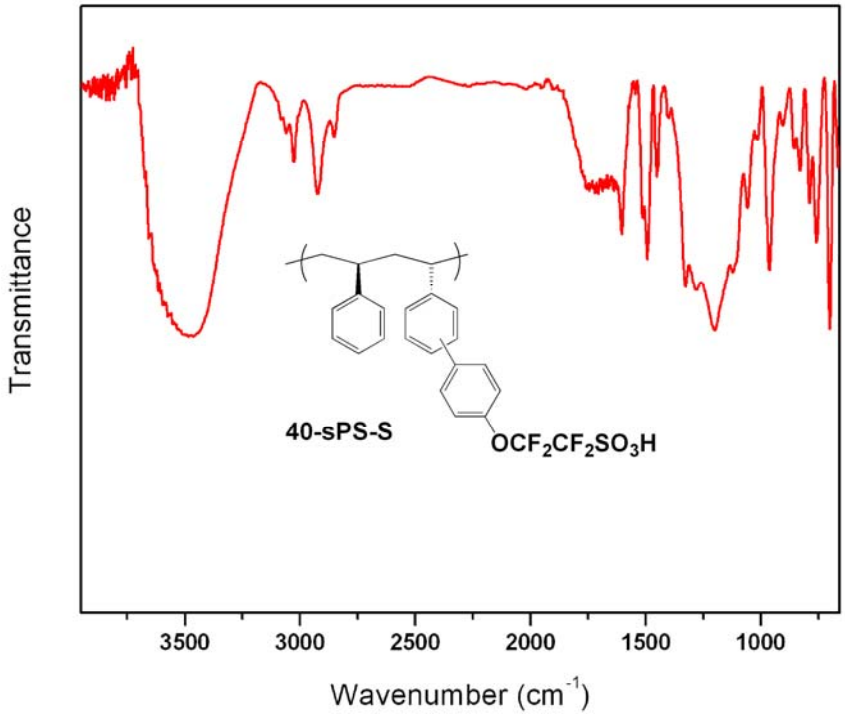


Figure S3. FT-IR spectrum of **sPS-S.**

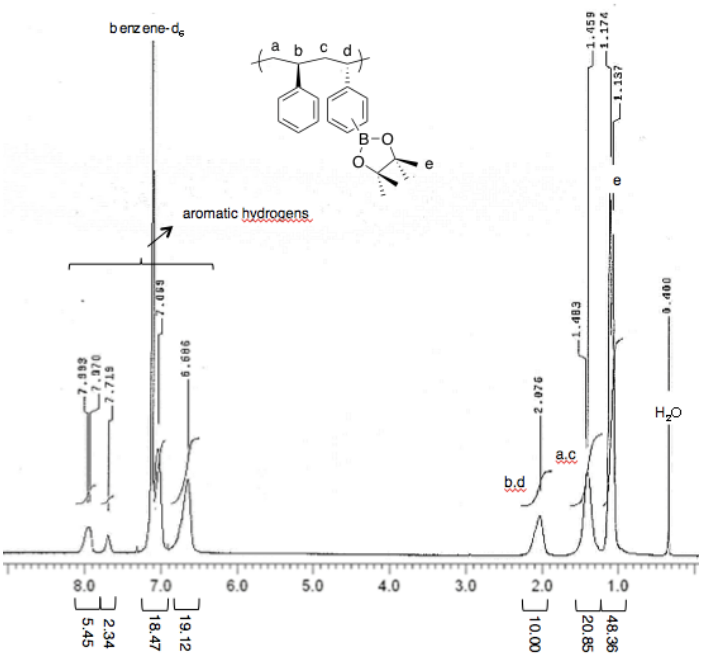


Figure S4. ^{1}H NMR (benzene-d_6) spectrum of **sPS-Bpin**.

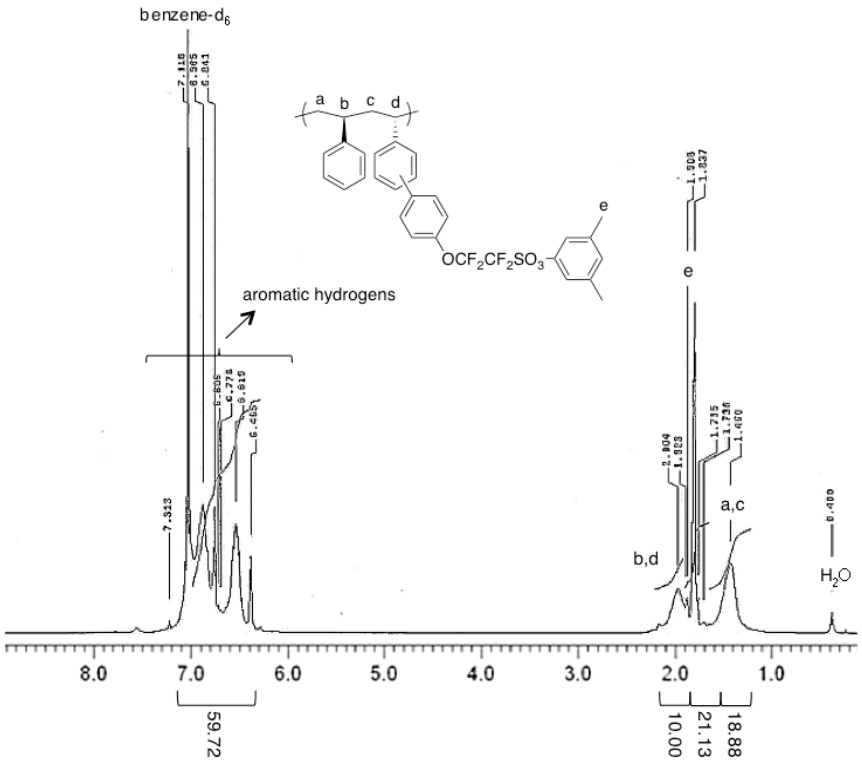


Figure S5. ^{1}H NMR (benzene-d_6) spectrum of **sPS-Ph**.

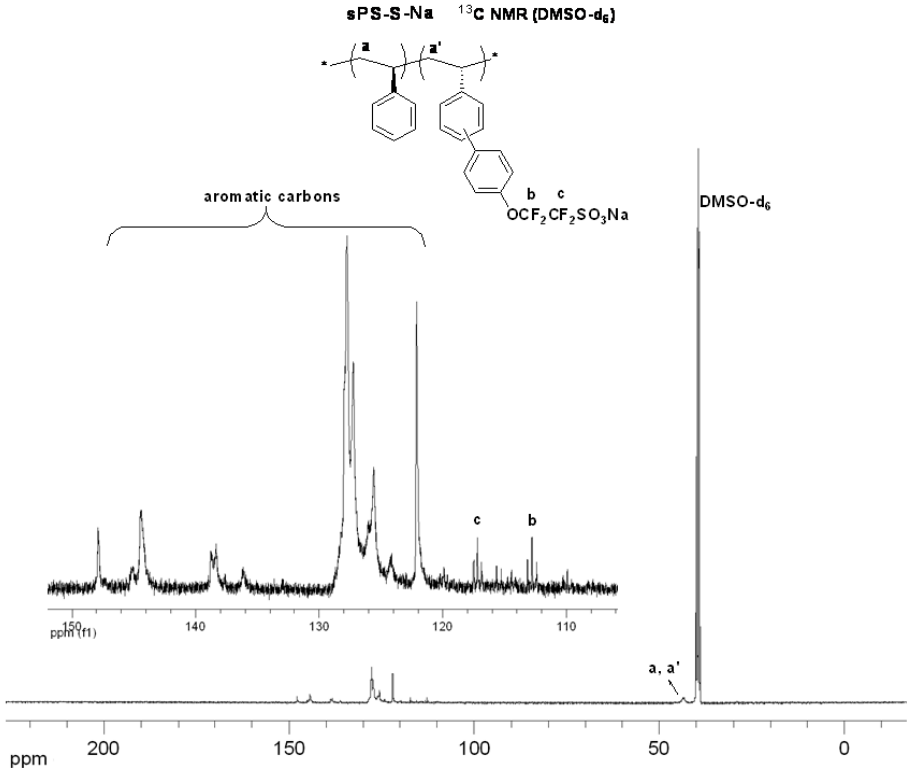


Figure S6. ^{13}C NMR (DMSO-d_6) spectrum of **sPS-S-Na**.

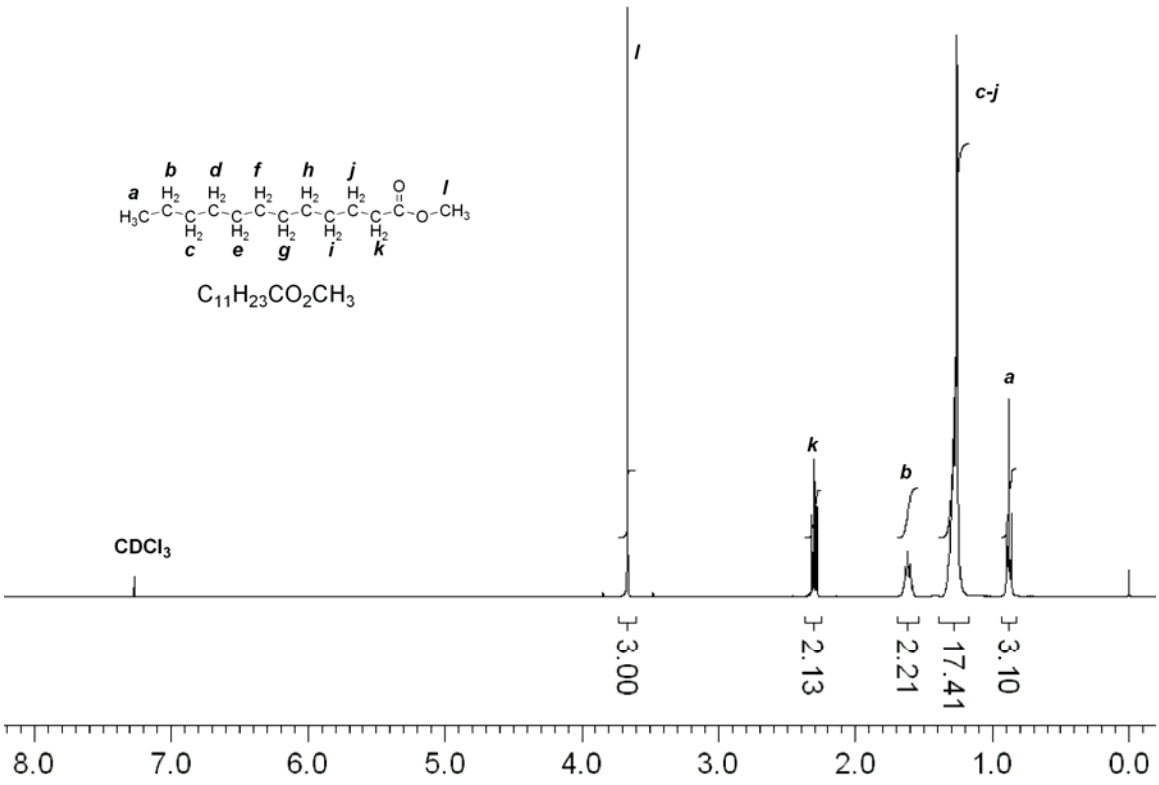


Figure S7. ^{1}H NMR ($CDCl_3$) spectrum of $C_{11}H_{23}CO_2CH_3$.

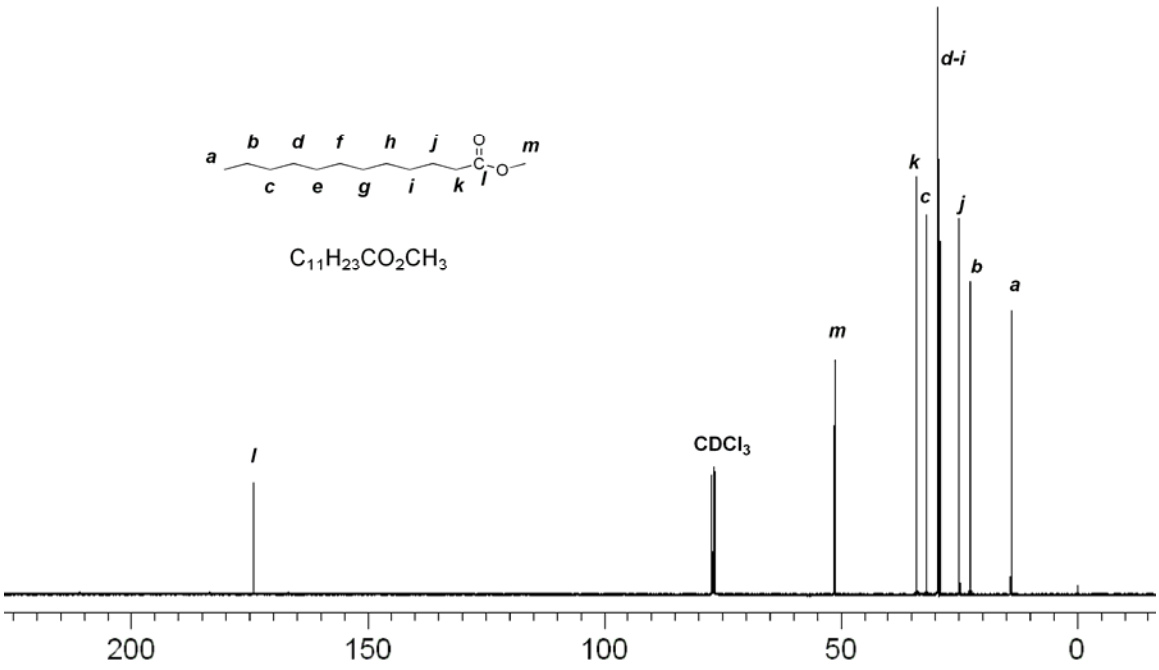


Figure S8. ^{13}C NMR ($CDCl_3$) spectrum of $C_{11}H_{23}CO_2CH_3$.

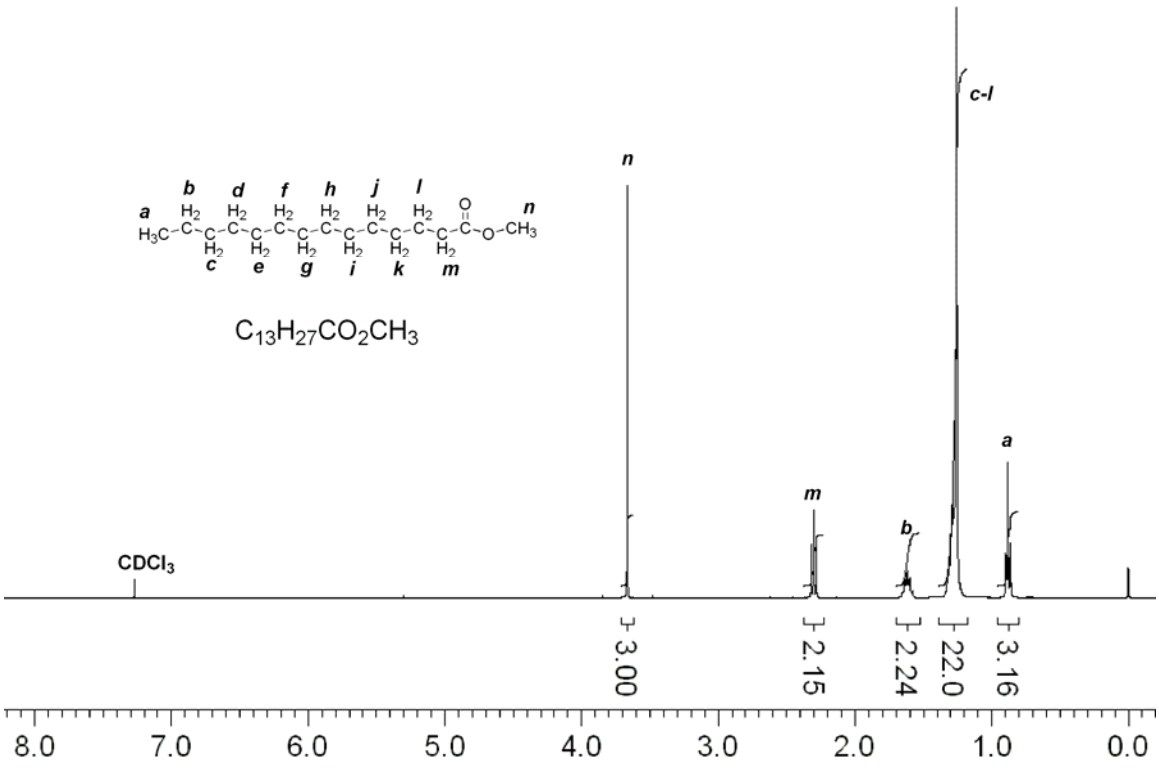


Figure S9. ^{1}H NMR ($CDCl_3$) spectrum of $C_{13}H_{27}CO_2CH_3$.

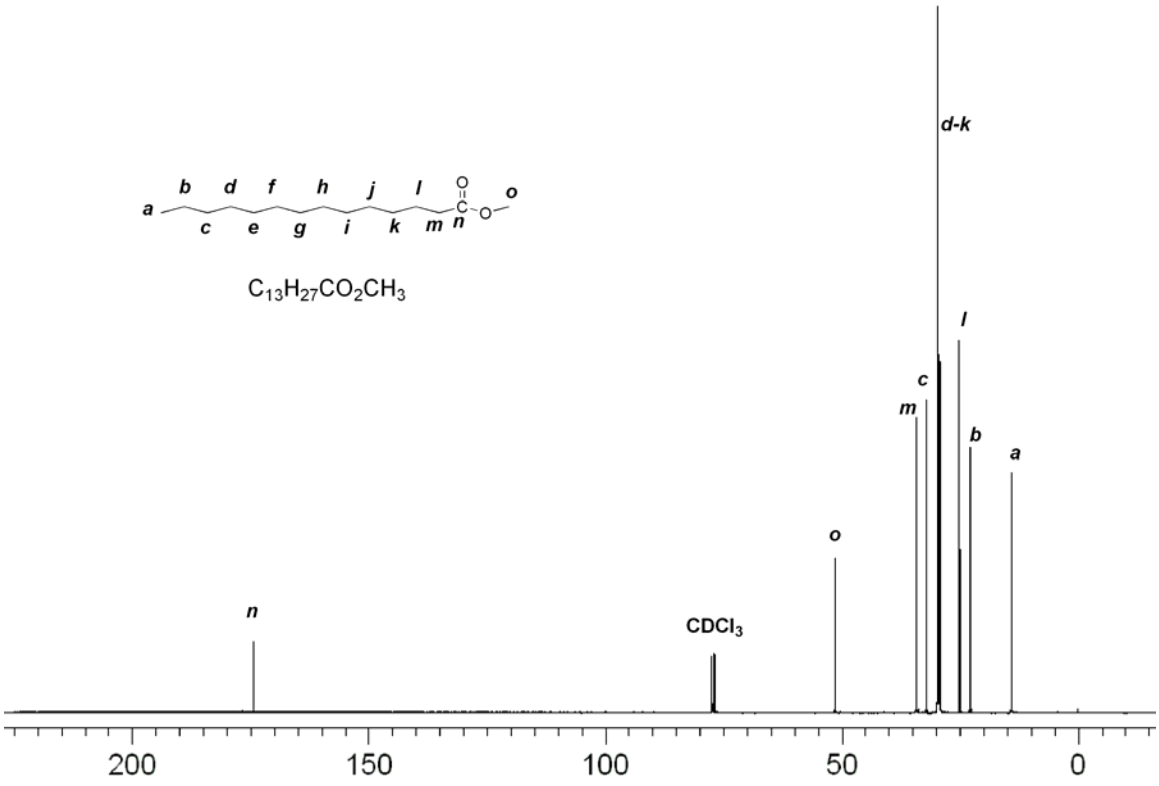


Figure S10. ^{13}C NMR ($CDCl_3$) spectrum of $C_{13}H_{27}CO_2CH_3$.

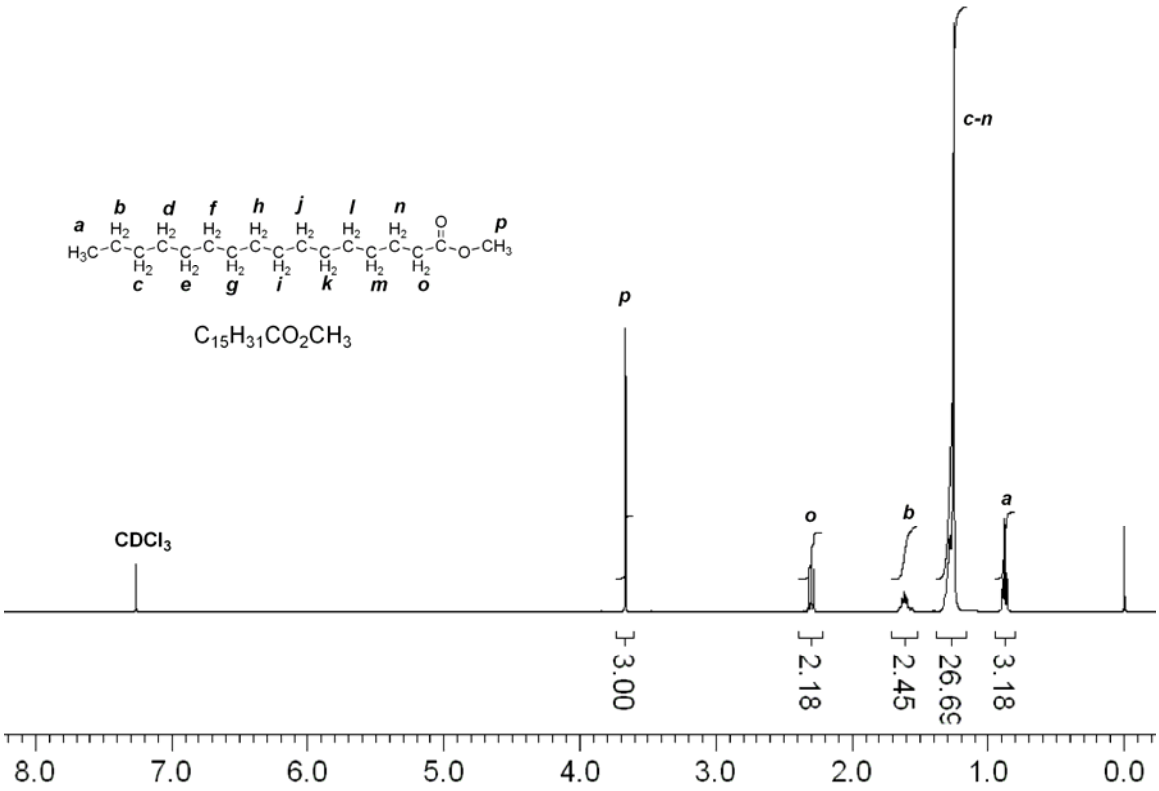


Figure S11. ^{1}H NMR ($CDCl_3$) spectrum of $C_{15}H_{31}CO_2CH_3$.

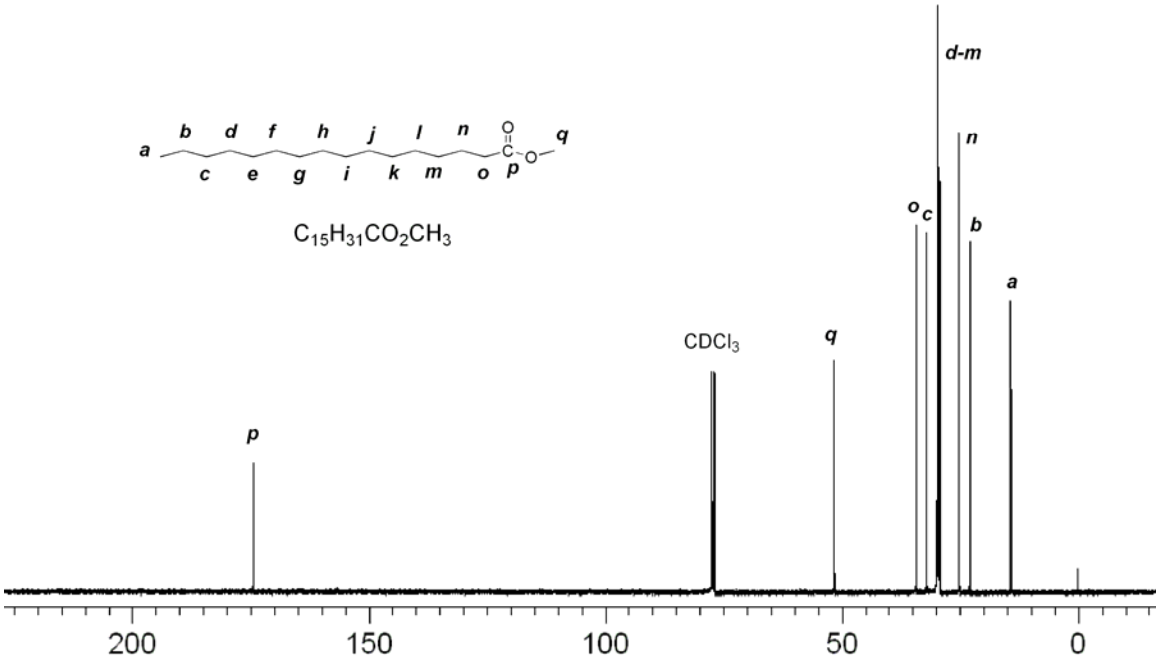


Figure S12. ^{13}C NMR ($CDCl_3$) spectrum of $C_{15}H_{31}CO_2CH_3$.

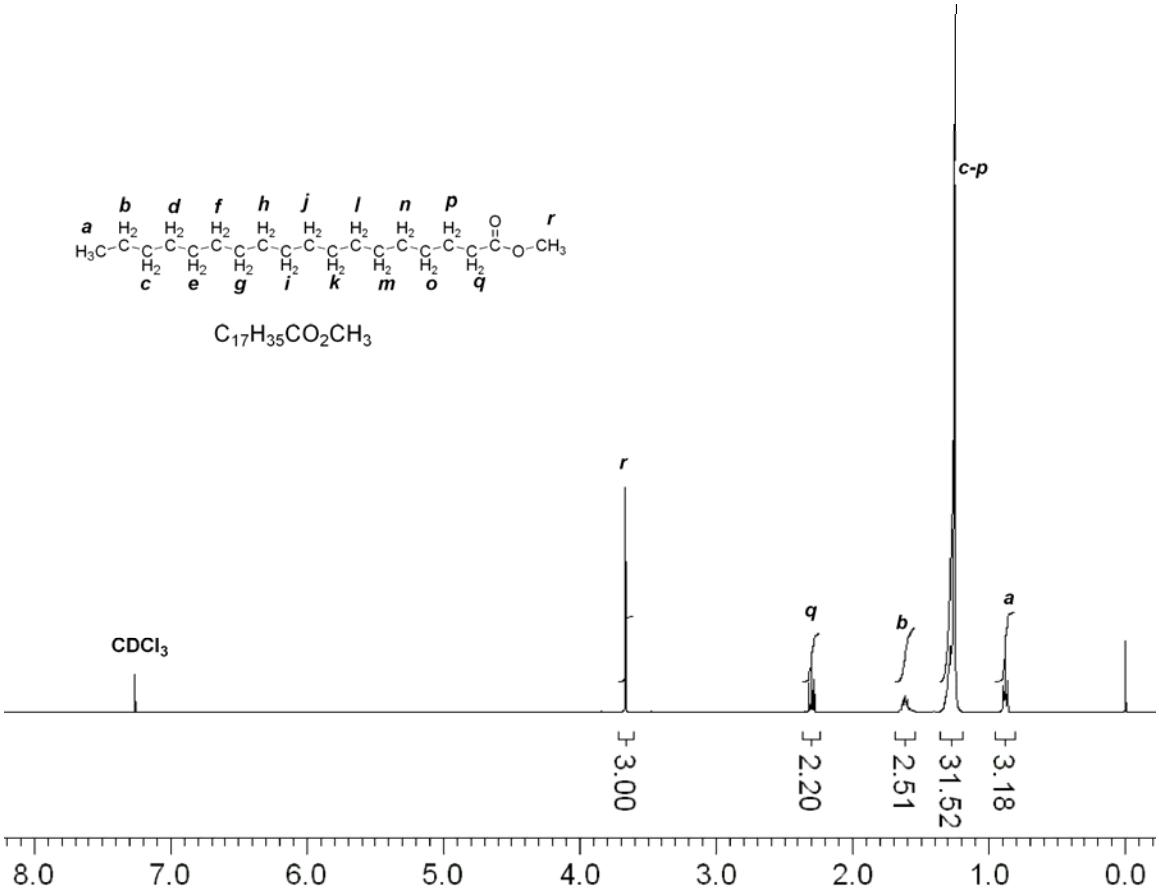


Figure S13. ^{1}H NMR ($CDCl_3$) spectrum of $C_{17}H_{35}CO_2CH_3$.

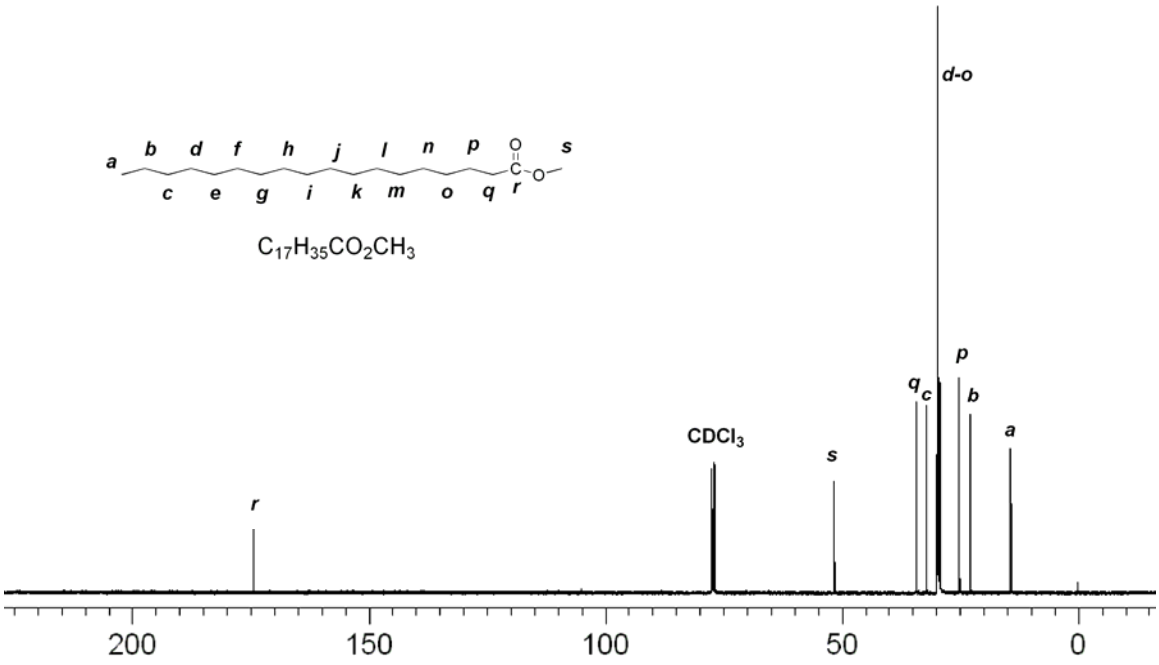


Figure S14. ^{13}C NMR ($CDCl_3$) spectrum of $C_{17}H_{35}CO_2CH_3$.