Electronic Supporting Information (ESI) for

Soybean oil derived-process oil prepared via recyclable organocatalysis for eco-friendly styrene-butadiene rubber composites †

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(Spectral Copies of ^{1}H and ^{13}C NMR of Compounds Obtained for DMAP Salts)

I.   General Methods for Acid-Esterified Soybean Oil (ASOs)

Materials

Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Epoxidized soybean oil (ESO; average functionality ~4.0 epoxides per triglyceride) was kindly supplied by Sajo Industry (Seoul, Korea). 4-(Dimethylamino)pyridine (DMAP, 97 %) and Benzyl Bromide (99 %) was purchased from Alfa Aesar. *trans*-Cinnamic Acid (CA, Natural, ≥ 99 %), Palmitic Acid (PA, Natural, ≥ 98 %), Undecylenic Acid (UA, Natural, ≥ 97 %), Undecanoic Acid (UcA, Natural, ≥ 99 %), Valeric Acid (VA, ≥ 98 %), 4-methoxybenzoic Acid (*p*-Anisic Acid, AA, Natural, ≥ 99 %), Benzyl Chloride (99 %), Aluminum Oxide (Neutral) were purchased from Sigma-Aldrich Corp. *p*-Anisic Anhydride (AAH, ≥ 97 %), Palmitic Anhydride (PAH, Natural, ≥ 96 %), 4-Fluorobenzyl chloride (98 %), *o*-sulfobenzimide (Saccharin, > 99 %) were purchased from Tokyo Chemical Industry Co., LTD. (TCI). Silica (Ultrasil 7000 GR, Evonik Industries AG, Essen, Germany, Brunauer–Emmett–Teller (BET) surface area: 160–175 m^2/g) was used. Ethyl Acetate (Ducksan), Diethyl Ether (Ducksan), Tetrahydrofuran (J. T. Baker) for the solvent were also used as received without purification. Unless otherwise stated, all commercial reagents and solvents were used without additional purification.

Characterizations

<Nuclear Magnetic Resonance (NMR)>

^{1}H NMR was recorded on Bruker DPX-500 spectrometer (Bruker Bioscience, Billerica, USA) operating at 500 MHz. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak (CDCl$_3$, δ 7.26 ppm) or 0.0 ppm for tetramethylsilane (TMS, δ 0.00 ppm). The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, td = triplet of doublet, ddd = doublet of doublet of doublet, m = multiplet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR was recorded on Bruker DPX-500 spectrometer (Bruker Bioscience, Billerica, USA) operating at 500 MHz

and was fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of chloroform-*d*.

<Fourier Transform Infrared Spectroscopy (FT-IR)>

Fourier transform infrared spectroscopy (Cary 630 FT-IR, Agilent Technologies, USA) was performed at room temperature from 4000 to 400 cm^{-1}. The samples were mixed with KBr to prepare pellets for FT-IR analysis.

<High Resolution Mass Spectroscopy (HR-Mass)>

High resolution mass spectra were obtained from the KAIST Research Analysis Center (Daejeon) by using ESI method (XEVO G2-XS QTof, Waters Co., USA)

<Size Exclusion Chromatography (SEC)>

The molar mass average values including the number (M_n) and the weight (M_w) were obtained by size-exclusion chromatography (SEC) using tetrahydrofuran as a mobile phase at 40 °C and the calibration curve, which was fitted with 7 polystyrene standards (Shodex, Showa Denko, Tokyo, Japan) on a FUTECS GPC-6000 SEC system (FUTECS, Daejeon, Korea) equipped with a refractive index detector. The samples were passed through three consecutive Waters Styragel HR 0.5 and HR 1 columns (7.8 × 300 mm) under a constant flow rate of 1 mL min^{-1}.

<Differential Scanning Calorimetry (DSC)>

Differential scanning calorimetry (DSC) measurements were performed using a TA Q-1000 DSC (TA instrument, New Castle, USA). The samples (5-10 mg) were loaded and heated up to 200 °C, held for 10 min to remove previous thermal history, and then allowed to cool to −80 °C. The samples were

reheated up to 200 °C. The rates of heating and cooling were 10 °C min^{-1}. The values reported in this study were obtained from the second heating cycle.

< Viscosity>

Viscosity was measured using an MCR 302e rheometer (Anton Parr, Austria) under Air in 25°C.

< Biomass Carbon-Contents>

Biomass carbon ratios was measured by calculating the ratios of ^{14}C to both ^{12}C and ^{13}C using accelerator mass spectroscopy (AMS, ASTM D6866-20 Method B).

II.   Comparison Table for Epoxide Ring-Opening Reaction (Table S1)

Table S1 Comparison of representative ring opening reaction for epoxidized soybean oil and acid.

System	No catalyst	Stoichiometric metal (Mg, Li, Na)	Acid catalyst (PTSA)	Base catalyst (DMAP, Imidazole)	Recyclable organocatalyst (DMAP-BB)
(Reference)	Baltanas, M. A. et al. *Biores. Technol.* 2010, **101**, 245-254.	Sun,, X. S. et al. *J. Agric. Food Chem.* 2012, **60**, 2179-2189.	Gobin, M. et al. *Ind. Crops Prod.* 2015, **70**, 213-220.	Mija, A. et al. *Macromolecules* 2020, **53**, 2526-2538.	This study
<Raw Materials> Epoxide (Vegetable oil)	Epoxidized soybean oil	Epoxidized soybean oil	Epoxidized broccoli seed oil	Epoxidized linseed oil	Epoxidized soybean oil
Counterpart (Acid)	Dicarboxylic acid	Metal Stearate	Benzoic acid Various diacid	2,2'-Dithiodibenzoic acid	**Palmitic acid (Natural)** **Palmitic anhydride (Natural)** **Etc. (aliphatic or aromatic acid)**
Methods Conversion Selectivity	^{1}H NMR >99% N/A	^{1}H NMR >99% 95%	^{1}H NMR 41% 28%	FT-IR, ^{1}H NMR >99% Epoxy conv N/A	**^{1}H NMR, SEC(new analytical method)** **>99% Epoxy conv** **86-93% sel (Depending on substrate)**
Waste (*E*-Factor)	Remaining acid (*E*-Factor = 0.30, when assuming 100% selectivity)	Preparation residue Metal residue Remaining acid Purification residue	Remaining catalyst Side Pr.: Oligomer Remaining acid (*E*-Factor = 7.72)	Remaining catalyst Remaining diacid (Final product: Thermoset)	Side Pr.: Oligomer Remaining acid **(*E*-Factor = 0.076, applying 93% selectivity in palmitic acid esterified soybean oil)**
Biocarbon content	N/A	N/A	N/A	N/A	**100% [Vegetable Oil + Natural acid]** (except VASO [79%], AAHSO [51%])
Other Features	Excess amount of acid used Application: Lubricant	Stoichiometric reaction Extra Step for Preparation (Synthesis of Metal Stearate) Extra Step for Purification (Hydrolysis) Application: Lubricant, Thermoplastic-like material	Side Pr: Oligomer reported without data Application: Thermoset	Temperature variation during the reaction (30-180 ºC) Role: Crosslinker Application: Thermoset	**Homogeneous/Heterogeneous recyclable system (New catalyst)** **Av. 96% catalyst recovery yield** **Broad substrates (10 types of ASOs)** **Application: Rubber composite**

*Only the reaction with epoxy/acid ~1:1 ratio condition has been considered (except system with no catalyst)

Additional comparison of representative ring opening reaction conditions. (Continuing **Table S1**)

| System	Base catalyst (DMAP)	Acid catalyst (PTSA)	Ionic liquid catalyst [N_{2221}][MC])	Heterogeneous catalyst (LDH)	Recyclable organocatalyst (DMAP-BB)
(Reference)	Zeng, J.-B. et al. *Polymer testing* 2017, **57**, 281-287.	Salimon, J. et al. *Arab. J. Chem.* 2016, **9**, S1053-S1058.	Liu, R. et al. *Catal. Sci. Techno.,* 2019, **9**, 5567-5571.	Stan, R. et al. *Sustainability* 2023, **15**, 4197-4209.	This study
<Raw Materials> Epoxide (Vegetable oil)	Epoxidized soybean oil	Monoepoxide linoleic acid (MEOA)	Propylene oxide (PO)	Epoxidized linseed oil	Epoxidized soybean oil
Counterpart	Adipic acid Sebacic acid Dodecanedicarboxylic acid	Oleic acid	Methanol (MeOH)	Methacrylic acid (MA) Undecylenic acid (UA) Acetic anhydride Etc. (3 more counterpart)	**Palmitic acid (Natural) Palmitic anhydride (Natural) Etc. (aliphatic or aromatic acid)**
Methods	FT-IR	Oxirane oxygen content Iodine value	GC	FT-IR, ^{1}H NMR	**^{1}H NMR, SEC(new analytical method)**
Conversion	N/A	N/A (not full conversion)	99%	100% (MA), 30% (UA)	**>99% Epoxy conv**
Selectivity	N/A	N/A	92%	N/A	**86-93% sel (Chemoselectivity)**
Waste	Remaining catalyst Remaining acid	Used solvent (Toluene)	Excess MeOH	Used solvent (Toluene or Xylene) Remaining acid or anhydride	Side Pr.: Oligomer Remaining acid (*E*-Factor = 0.076, applying 93% selectivity in palmitic acid esterified soybean oil)
Biocarbon content	N/A	N/A	N/A	N/A	**100% [Vegetable Oil + Natural acid]** (except VASO [79%], AAHSO [51%])
Other Features	**Dicarboxylic acid used as crosslinker** Application: Thermoset **Focusing on curing behavior and mechanical properties of final products**	**Monomer used (MeOA) 20-50 wt% catalyst used based on oxirane ring** Application: Lubricant **Focusing on fitting model optimization**	**PO and MeOH used as starting material No recycling test** Application: N/A **Focusing on mechanism and selectivity with calculation (regioselectivity & polymer selectivity)**	**Acids or anhydrides are not fully bio-based No recycling test** Application: N/A **Focusing on heterogeneous catalyst and catalytic system optimization**	**Homogeneous/Heterogeneous recyclable system (New catalyst) Av. 96% catalyst recovery yield Broad substrates (10 types of ASOs)** **Application: Rubber composite** **Focusing on new selective catalytic system, fully bio-based materials, high performance rubber application**

*DMAP: 4-(Dimethylamino)pyridine, PTSA: *p*-Toluenesulfonic acid, [N2221][MC]: Triethylmethylammonium methylcarbinate, LDH: Layered double catalyst, DMAP-BB: 4-(Dimethylamino)pyridinium bromide

III. Experimental Procedure and Characterization I

### Preparation of 4-(N,N-Dimethylamino)pyridine Salt (DMAP Salt)[1]

The 70 mL vial was charged with 4-(N,N-dimethylamino)pyridine (DMAP, 4.09 mmol, 500 mg) and Benzyl Bromide (4.09 mmol, 707 mg) followed by addition of 10 mL solvent. The mixture was reacted at room temperature for overnight. After the reaction, the mixture was filtered to remove the solvent and residual DMAP and Benzyl Bromide. Solvent remaining in mixture was removed by vacuum. The crude product was then obtained. The crude product was recrystallized from ethanol/tetrahydroduran.

4-(N,N-Dimethylamino)pyridine tran-Cinnamic acid salt (DMAP-CA)
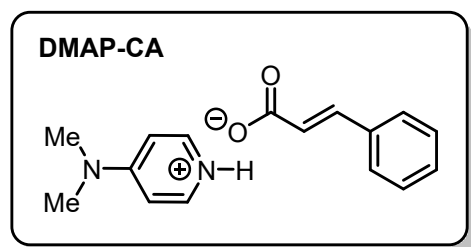
White solid; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.34-8.28 (m, 2H), 7.71-7.64 (m, 1H), 7.57-7.51 (m, 3H), 6.59-6.52 (m, 3H), 3.08(d, J = 1.5Hz, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 171.9, 155.6, 145.3, 141.8, 135.6, 129.2, 128.7, 127.8, 122.8, 106.5, 39.4; IR (KBr) ν 3411, 3377, 3021, 2948, 1642, 1555, 1165, 716, 594, 510 cm^{-1}; HRMS (EI) m/z calcd. for C$_7$H$_{11}$N$_2$ [M$^+$ - C$_9$H$_7$O$_2^-$]: 123.0917, found: 123.0920. Yield: 0.288 g, 26%

### 4-(N,N-Dimethylamino)pyridine benzyl chloride salt (DMAP-BC)
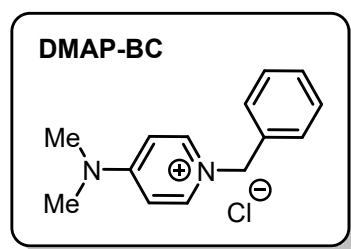
White solid; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.70 (d, J = 7.7 Hz, 2H), 7.48–7.42 (m, 2H), 7.41–7.35 (m, 3H), 6.92 (d, J = 7.8 Hz, 2H), 5.67 (s, 2H), 3.23 (s, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 156.4, 142.9,

134.3, 129.6, 129.0, 108.3, 61.2, 40.5; IR (KBr) ν 3411, 3377, 3021, 2948, 1642, 1555, 1165, 716, 594, 510 cm⁻¹; HRMS (EI) m/z calcd. for $C_{14}H_{17}N_2$ [M⁺ – Cl⁻]: 213.1387, found: 213.1387. Yield: 0.418 g, 41%

4-(*N,N*-Dimethylamino) pyridine *p*-fluorobenzyl chloride salt (DMAP-B$_f$C)
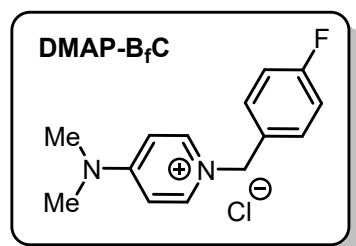
White solid; ¹H NMR (500 MHz, CDCl₃) δ 8.77 (d, *J* = 7.8 Hz, 2H), 7.55 (dd, *J* = 8.7, 5.2 Hz, 2H), 7.07 (t, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 7.8 Hz, 2H), 5.73 (s, 2H), 3.22 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 163.94, 162.0, 156.2, 142.7, 131.2, 130.7, 116.2, 108.2, 59.7, 40.3; IR (KBr) ν 3341, 2991, 1645, 1568, 1503, 1219, 1160, 855, 818, 541 cm⁻¹; HRMS (EI) m/z calcd. for $C_{14}H_{17}FN_2$ [M⁺ – Cl⁻]: 231.1293, found: 231.1307. Yield: 0.558 g, 48%

4-(*N,N*-Dimethylamino)pyridine benzyl bromide salt (DMAP-BB)
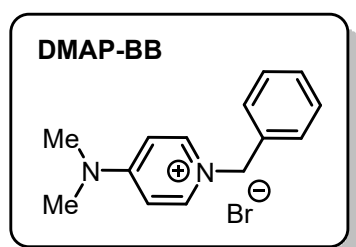
White solid; ¹H NMR (500 MHz, CDCl₃) δ 8.63-8.57 (m, 2H), 7.49-7.42 (m, 2H), 7.42-7.33 (m, 3H), 6.95-6.89 (m, 2H), 5.64 (s, 2H), 3.23 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 156.1, 142.5, 134.1, 129.2, 129.1, 128.7, 108.1, 60.5, 40.4; IR (KBr) ν 3455, 3394, 3039, 2962, 1645, 1571, 1159, 810, 726 cm⁻¹; HRMS (EI) m/z calcd. for $C_{14}H_{17}N_2$ [M⁺ – Br⁻]: 213.1387, found: 213.1387. Yield: 1.15 g, 96%

Synthesis of Acid Esterified Soybean Oil (ASO)

Epoxidized soybean oil (ESO, 2.50 g, containing 10.5 mmol of epoxy group), *trans*-Cinnamic Acid (1.60 g, 10.5 mmol), DMAP-BB (154 mg, 5.00 mol %, 0.526 mmol) were placed in 20 mL vial with stirring bar. The mixture was heated at 130 °C for 3 hours. After cooling to room temperature, tetrahydrofuran (40 mL) added to dissolve the crude oil. After 2 hours, a white solid (DMAP-BB) is precipitated at the bottom of the solution. The precipitated solid was recovered by filtration and dried in a vacuum oven at room temperature for 24 hour. The solution, from which the salt has been removed, was filtered through Al_2O_3 to remove DMAP-BB and acid residue. Tetrahydrofuran present in oil mixture is removed using a rotary evaporator under reduced pressure. Further, vacuum distillation was performed for 12 hour at 70 °C to eliminate traces of solvent.

Palmitic Acid Esterified Soybean Oil
[PASO]
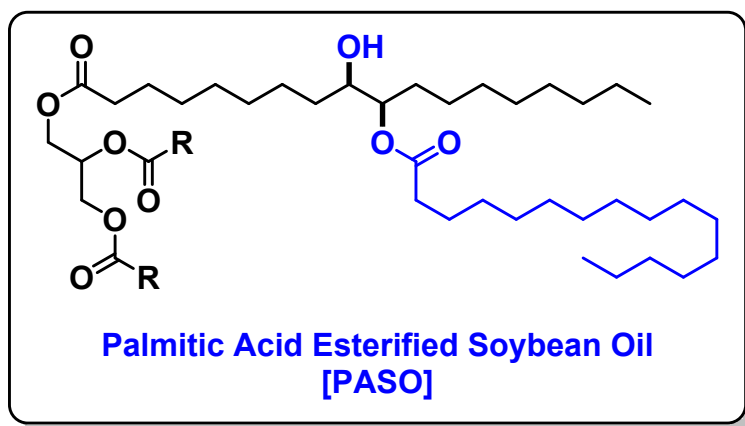
Brown Oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.31 (m, 1H), 5.29 – 5.19 (m, 1H), 4.82 (m, 1H), 4.29 (dd, *J* = 11.8, 4.3 Hz, 2H), 4.14 (dd, *J* = 11.9, 6.0 Hz, 2H), 4.01 – 3.94 (m, 1H), 3.90 (m, 1H), 3.74 (m, 1H), 3.57 (m, 1H), 3.50 – 3.43 (m, 1H), 3.39 (m, 1H), 2.31 (m, 14H), 2.02 – 1.95 (m, 1H), 1.77 – 1.06 (m, 166H), 0.92 – 0.83 (m, 21H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 178.04, 173.75, 173.28, 172.80, 81.89, 81.78, 81.35, 81.24, 80.47, 80.40, 77.25, 77.00, 76.75, 76.32, 76.15, 75.17, 75.10, 74.36, 74.29, 73.84, 72.49, 68.86, 62.07, 35.90, 35.65, 35.45, 34.51, 34.47, 34.44, 34.13, 34.03, 33.97, 33.74, 33.30, 31.91, 31.86, 31.83, 30.70, 29.68, 29.64, 29.61, 29.58, 29.50, 29.46, 29.43, 29.34, 29.29, 29.26, 29.19, 29.15, 29.10, 29.00, 28.78, 26.22, 25.87, 25.60, 25.53, 25.41, 25.27, 25.15, 25.04, 24.97, 24.84, 24.79, 24.76, 22.67, 22.64, 22.59, 22.50, 14.10, 14.04, 13.99, 13.96; IR (KBr) ν 3466, 2925, 2855, 1740, 1649, 1567, 1463, 1240, 1171, 723 cm^{-1}; SEC (THF) M_n (kg mol^{-1}) : 2.516, M_w (kg mol^{-1}) : 2.861, PDI : 1.14; Yield : 4.24 g, 85 %

Undecanoic Acid Esterified Soybean Oil
[UcASO]
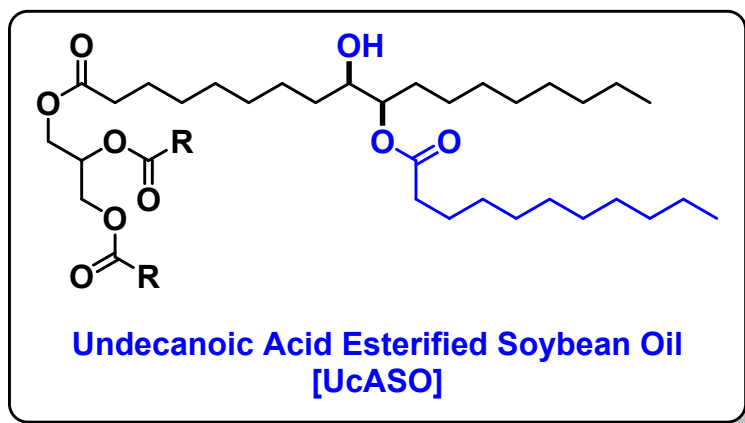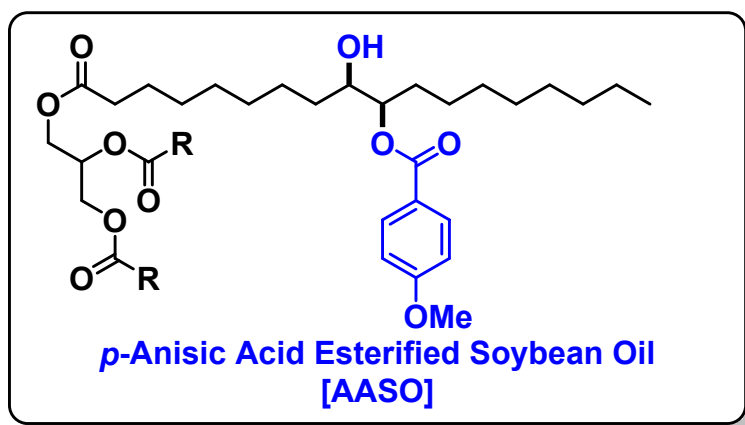
Brown Oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.30 (m, 1H), 5.27 – 5.19 (m, 1H), 4.82 (m, 1H), 4.28 (dd, J = 11.9, 4.3 Hz, 2H), 4.13 (dd, J = 12.0, 6.0 Hz, 2H), 4.00 – 3.94 (m, 1H), 3.93 – 3.87 (m, 1H), 3.77 – 3.70 (m, 1H), 3.56 (m, 1H), 3.49 – 3.42 (m, 1H), 3.39 (m, 1H), 2.36 – 2.24 (m, 14H), 2.01 – 1.96 (m, 1H), 1.76 – 1.06 (m, 123H), 0.87 (m, 21H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 178.25, 173.73, 173.27, 173.20, 172.78, 81.88, 81.77, 81.34, 81.24, 80.45, 80.40, 77.26, 77.00, 76.75, 76.30, 76.14, 75.14, 75.08, 74.33, 74.27, 73.87, 73.82, 72.51, 68.85, 65.02, 62.05, 60.37, 40.07, 35.88, 35.62, 34.64, 34.49, 34.45, 34.43, 34.28, 34.12, 34.01, 33.96, 33.94, 33.73, 33.50, 33.27, 31.89, 31.86, 31.82, 31.71, 31.60, 30.66, 30.58, 29.66, 29.62, 29.58, 29.55, 29.53, 29.48, 29.45, 29.32, 29.27, 29.23, 29.19, 29.16, 29.12, 29.08, 28.98, 28.81, 28.76, 26.19, 25.84, 25.61, 25.56, 25.39, 25.34, 25.24, 25.13, 25.08, 25.02, 24.95, 24.82, 24.78, 24.74, 22.64, 22.58, 22.56, 22.52, 22.48, 14.07, 14.01, 13.97, 13.94, 0.99; IR (KBr) ν 3461, 2923, 2854, 1736, 1649, 1566, 1460, 1237, 1163, 724 cm^{-1}; SEC (THF) M_n (kg mol^{-1}) : 2.132, M_w (kg mol^{-1}) : 2.352, PDI : 1.10; Yield : 3.74 g, 87 %

Valeric Acid Esterified Soybean Oil
[VASO]
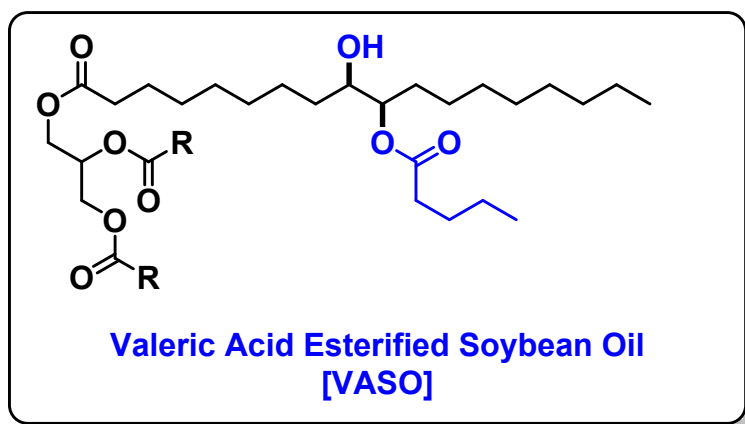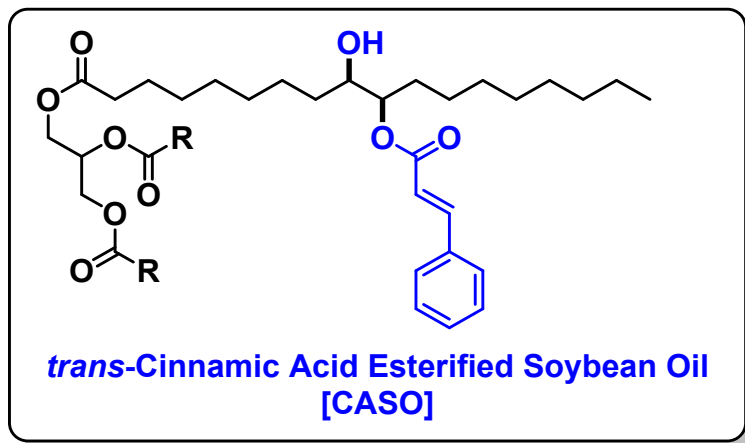
Brown Oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.30 (m, 1H), 5.24 (m, 1H), 4.82 (m, 1H), 4.28 (dd, J = 11.9, 4.4 Hz, 2H), 4.13 (dd, J = 12.0, 6.0 Hz, 2H), 3.97 (m, 1H), 3.90 (m, 1H), 3.78 – 3.69 (m, 1H), 3.59 –

3.53 (m, 1H), 3.46 (m, 1H), 3.38 (m, 1H), 2.31 (m, 14H), 2.05 – 1.96 (m, 1H), 1.80 – 1.08 (m, 74H), 0.94 – 0.82 (m, 21H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 178.05, 173.70, 173.24, 172.77, 139.13, 139.08, 114.12, 114.08, 81.86, 81.76, 81.33, 81.23, 80.43, 77.25, 77.00, 76.75, 76.30, 76.14, 75.14, 75.08, 74.83, 74.62, 74.34, 74.28, 74.08, 73.82, 73.49, 72.48, 72.06, 68.84, 68.23, 65.01, 62.04, 60.36, 40.08, 35.87, 35.61, 34.66, 34.47, 34.41, 34.10, 34.00, 33.94, 33.73, 33.50, 33.26, 31.88, 31.86, 31.82, 31.80, 31.69, 31.59, 31.50, 30.65, 29.65, 29.61, 29.57, 29.55, 29.47, 29.43, 29.36, 29.31, 29.29, 29.27, 29.25, 29.22, 29.19, 29.16, 29.12, 29.08, 29.04, 29.02, 28.96, 28.86, 28.84, 28.75, 26.17, 25.83, 25.58, 25.38, 25.33, 25.23, 25.09, 25.06, 24.98, 24.92, 24.85, 24.81, 24.76, 24.73, 22.64, 22.61, 22.56, 22.51, 22.46, 21.00, 14.15, 14.08, 14.06, 14.01, 13.97, 13.93; IR (KBr) ν 3461, 2926, 2856, 1734, 1649, 1567, 1460, 1243, 1163, 726 cm^{-1}; SEC (THF) M_n (kg mol^{-1}) : 1.748, M_w (kg mol^{-1}) : 1.897, PDI : 1.08; Yield : 3.04 g, 87 %

p-Anisic Acid Esterified Soybean Oil
[AASO]

Brown Oil; ^1H NMR (500 MHz, CDCl$_3$) δ 7.98 (m, 2H), 6.95 – 6.81 (m, 2H), 5.52 (m, 1H), 5.45 (m,1H), 5.29 – 5.19 (m, 1H), 5.05 (m, 1H), 4.32 – 4.24 (m, 2H), 4.12 (m, 2H), 4.02 (m, 1H), 3.85 (m, 12H), 3.70 (m, 1H), 3.56 – 3.49 (m, 1H), 3.46 – 3.33 (m, 1H), 2.35 – 2.22 (m, 6H), 1.90 – 1.03 (m, 70H), 0.91 – 0.76 (m, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 173.29, 173.21, 172.79, 170.23, 166.17, 165.88, 165.63, 163.53, 163.41, 162.46, 132.00, 131.89, 131.77, 131.71, 131.67, 131.58, 125.79, 122.55, 122.37, 113.72, 113.67, 113.61, 113.58, 113.12, 82.15, 82.08, 81.62, 81.55, 80.63, 80.56, 77.26, 77.00, 76.75, 75.64, 74.80, 73.96, 72.72, 68.82, 65.02, 62.04, 60.36, 55.41, 55.38, 55.29, 39.87, 35.95, 35.77, 34.10, 34.00, 33.94, 33.62, 33.46, 33.32, 31.88, 31.81, 31.78, 31.64, 30.71, 29.66, 29.62, 29.58, 29.53, 29.47, 29.43, 29.39, 29.32, 29.22, 29.20, 29.17, 29.14, 29.07, 29.01, 28.94, 28.90, 26.12, 25.87, 25.65, 25.59, 25.45, 25.30, 25.27, 25.11, 24.81, 24.75, 22.65, 22.60, 22.56, 22.50, 22.43, 21.01, 14.16, 14.08, 14.05, 14.01, 13.94; IR (KBr) ν 3466, 3076, 2925, 2854, 1738, 1708, 1604, 1511,1460, 1252 , 847, 769 cm^{-1}; SEC (THF) M_n (kg mol^{-1}) : 1.799, M_w (kg mol^{-1}) : 1.990, PDI : 1.10; Yield : 3.48 g, 89 %

trans-Cinnamic Acid Esterified Soybean Oil
**[CASO]**

Brown Oil; ¹H NMR (500 MHz, CDCl₃) δ 7.69 (m, 3H), 7.52 (m, 6H), 7.41 – 7.29 (m, 9H), 6.46 (m, 3H), 5.44 (m, 1H), 5.37 (m, 1H), 5.27 – 5.20 (m, 1H), 5.05 – 4.90 (m, 1H), 4.33 – 4.20 (m, 2H), 4.18 – 4.07 (m, 2H), 4.05 (m, 1H), 3.97 (m, 1H), 3.78 (m, 1H), 3.68 – 3.62 (m, 1H), 3.51 (m, 1H), 3.42 (m, 1H), 2.35 – 2.23 (m, 7H), 1.94 – 1.11 (m, 68H), 0.87 (m, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 173.20, 172.78, 166.86, 166.60, 166.29, 145.30, 145.15, 136.47, 134.30, 134.19, 130.43, 130.32, 128.90, 128.86, 128.44, 128.12, 128.08, 127.44, 126.87, 117.93, 117.73, 82.02, 81.94, 81.48, 81.40, 80.61, 80.53, 77.26, 77.00, 76.75, 75.51, 74.71, 73.91, 73.85, 72.61, 68.82, 62.04, 40.02, 35.91, 35.65, 34.11, 34.00, 33.94, 33.67, 33.48, 33.28, 31.88, 31.84, 31.82, 31.79, 31.66, 31.63, 30.79, 29.66, 29.62, 29.58, 29.55, 29.51, 29.48, 29.43, 29.32, 29.22, 29.18, 29.13, 29.07, 29.00, 28.95, 28.92, 28.81, 26.18, 25.87, 25.63, 25.44, 25.31, 25.26, 25.10, 24.81, 24.75, 22.65, 22.61, 22.57, 22.53, 22.45, 14.09, 14.06, 14.02, 13.95; IR (KBr) ν 3464, 3061, 2924, 2854, 1739, 1708, 1637, 1573, 1164, 767, 710, 685 cm⁻¹; SEC (THF) M_n (kg mol⁻¹) : 1.852, M_w (kg mol⁻¹) : 2.033, PDI : 1.10; Yield : 3.38 g, 87 %

Undecylenic Acid Esterified Soybean Oil
[UASO]
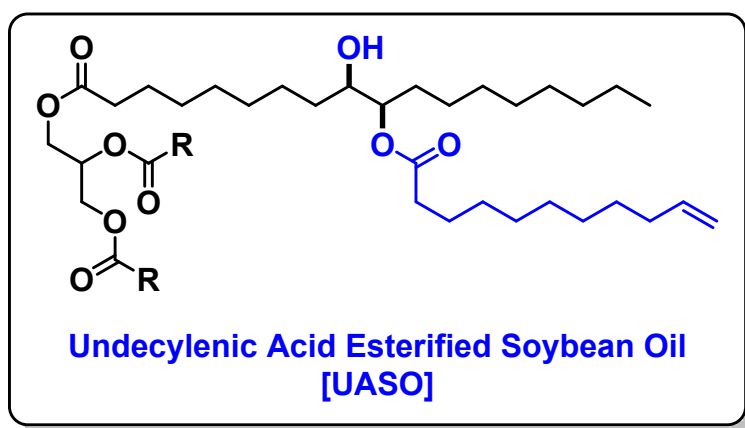
Yellow Oil; ¹H NMR (500 MHz, CDCl₃) δ 5.79 (ddt, J = 16.9, 10.2, 6.6 Hz, 3H), 5.30 (m, 1H), 5.28 – 5.19 (m, 1H), 5.02 – 4.89 (m, 6H), 4.81 (m, 1H), 4.28 (dd, J = 12.0, 4.3 Hz, 2H), 4.18 – 4.08 (m, 2H), 4.00 – 3.93 (m, 1H), 3.89 (m, 1H), 3.75 – 3.70 (m, 1H), 3.56 (m, 1H), 3.49 – 3.42 (m, 1H), 3.38 (m,

1H), 2.37 – 2.24 (m, 14H), 2.07 – 1.95 (m, 8H), 1.77 – 1.10 (m, 122H), 0.87 (m, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 178.05, 173.70, 173.24, 172.77, 139.13, 139.08, 114.12, 114.08, 81.86, 81.76, 81.33, 81.23, 80.43, 77.25, 77.00, 76.75, 76.30, 76.14, 75.14, 75.08, 74.83, 74.62, 74.34, 74.28, 74.08, 73.82, 73.49, 72.48, 72.06, 68.84, 68.23, 65.01, 62.04, 60.36, 40.08, 35.87, 35.61, 34.66, 34.47, 34.41, 34.10, 34.00, 33.94, 33.73, 33.50, 33.26, 31.88, 31.86, 31.82, 31.80, 31.69, 31.59, 31.50, 30.65, 29.65, 29.61, 29.57, 29.55, 29.47, 29. 43, 29.36, 29.31, 29.29, 29.27, 29.25, 29.22, 29.19, 29.16, 29.12, 29.08, 29.04, 29.02, 28.96, 28.86, 28.84, 28.75, 26.17, 25.83, 25.58, 25.38, 25.33, 25.23, 25.09, 25.06, 24.98, 24.92, 24.85, 24.81, 24.76, 24.73, 22.64, 22.61, 22.56, 22.51, 22.46, 21.00, 14.15, 14.08, 14.06, 14.01, 13.97, 13.93; IR (KBr) ν 3462, 3075, 2924, 2854, 1735, 1644, 1555, 1460, 1165, 909, 724 cm^{-1}; SEC (THF) M_n (kg mol^{-1}) : 1.954, M_w (kg mol^{-1}) : 2.315, PDI : 1.18; Yield : 3.42 g, 81 %

Palmitic Anhydride Esterified Soybean Oil [PAHSO]
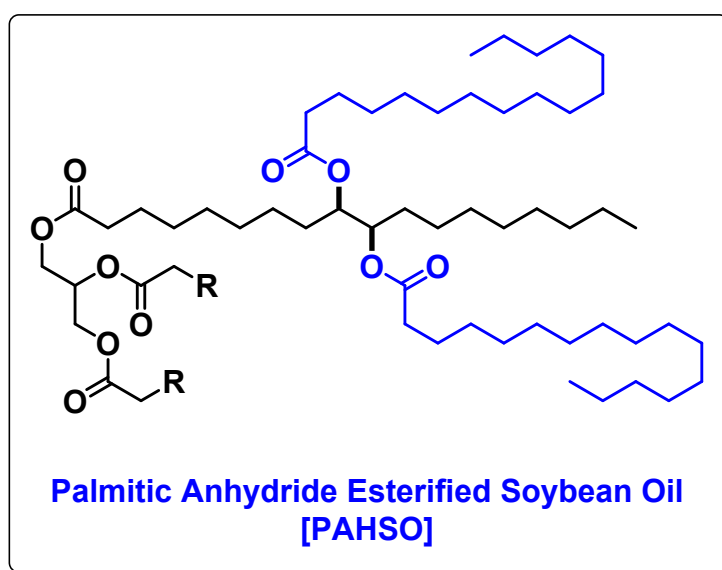
Yellow Solid; ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.27 – 5.20 (m, 1H), 5.08 – 4.96 (m, 5H), 4.96 – 4.88 (m, 2H), 4.27 (dd, J = 7.3, 3.1 Hz, 2H), 4.13 (dd, J = 5.5, 3.1 Hz, 2H), 3.88 (m, 1H), 3.69 (m, 1H), 3.56 (m, 1H), 3.27 (m, 1H), 2.30 (m, 22H), 1.78 – 1.08 (m, 282H), 0.87 (m, 33H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 177.35, 173.34, 173.30, 173.21, 173.13, 172.92, 172.73, 77.26, 77.00, 76.75, 73.91, 73.87, 73.49, 72.92, 72.87, 70.19, 68.98, 68.86, 62.04, 60.36, 34.79, 34.51, 34.40, 34.30, 34.26, 34.12, 34.01, 33.91, 32.66, 31.91, 31.82, 31.77, 31.53, 31.50, 30.79, 30.70, 30.66, 30.61, 29.70, 29.66, 29.55, 29.52, 29.46, 29.43, 29.39, 29.35, 29.32, 29.25, 29.21, 29.18, 29.10, 25.27, 25.13, 25.09, 25.06, 25.04, 24.99, 24.96, 24.83, 24.80, 24.74, 22.67, 22.64, 22.42, 14.09, 13.93; IR (KBr) ν 2917, 2851, 1737, 1648, 1464, 1163, 1112, 721 cm^{-1}; SEC (THF) M_n (kg mol^{-1}) : 4.060, M_w (kg mol^{-1}) : 4.680, PDI : 1.15; Yield : 7.27 g, 92 %

p-Anisic Anhydride Esterified Soybean Oil [AAHSO]
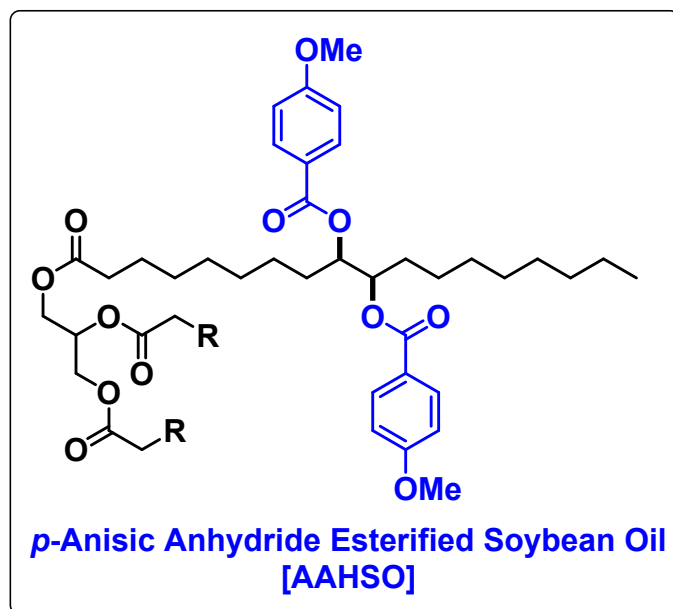
Brown Solid; ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.04 – 7.79 (m, 15H), 6.95 – 6.71 (m, 15H), 5.49 (m, 2H), 5.41 (m, 1H), 5.37 – 5.25 (m, 3H), 5.25 – 5.15 (m, 1H), 4.30 – 4.18 (m, 2H), 4.16 – 4.02 (m, 2H), 3.92 – 3.78 (m, 23H), 2.36 – 2.01 (m, 12H), 1.86 – 1.04 (m, 98H), 0.92 – 0.73 (m, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 173.26, 173.17, 172.76, 165.88, 165.67, 165.50, 165.33, 163.33, 163.30, 163.25, 131.76, 131.69, 122.56, 122.33, 122.24, 113.58, 113.54, 113.52, 113.46, 77.25, 77.00, 76.75, 74.59, 74.54, 74.28, 74.24, 73.74, 73.64, 71.20, 70.52, 70.49, 68.80, 62.02, 55.40, 55.37, 55.34, 51.84, 34.03, 33.88, 32.40, 31.90, 31.77, 31.51, 31.48, 31.01, 30.73, 29.67, 29.63, 29.43, 29.33, 29.25, 29.14, 29.08, 28.95, 25.17, 24.86, 24.80, 24.69, 22.67, 22.59, 22.46, 22.34, 14.10, 14.06, 13.97, 13.89; IR (KBr) ν 2927, 2854, 1709, 1604, 1500, 1460, 1249, 1164, 846, 766 cm^{-1}; SEC (THF) M_n (kg mol^{-1}) : 2.108, M_w (kg mol^{-1}) : 2.350, PDI : 1.11; Yield : 5.07 g, 92 %

¹H NMR Analysis after Reaction (Calculation of Conversion & Selectivity, Fig. S1)[2]
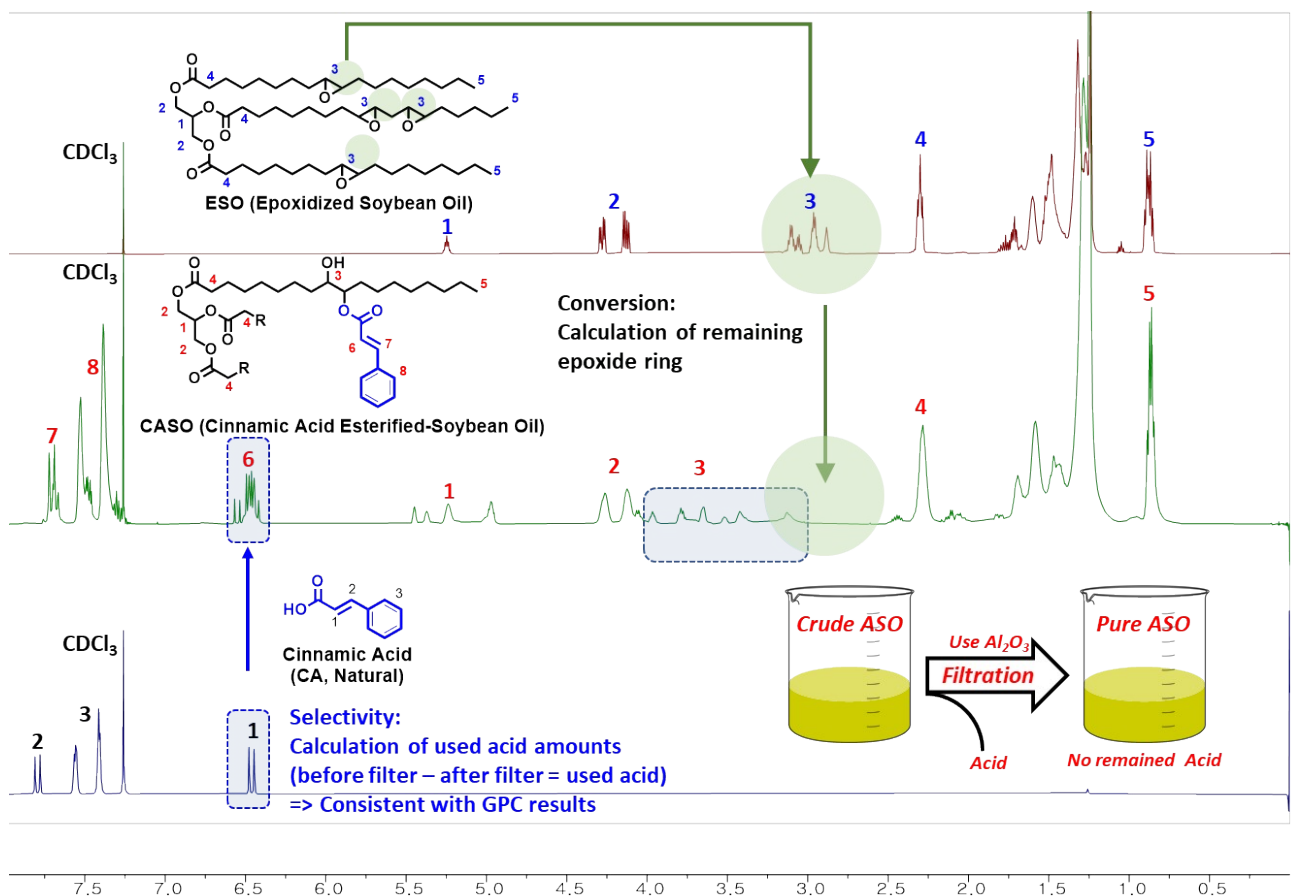
Fig. S1 ¹H NMR Analysis after Epoxide Ring Opening Reaction of ESO.

Calculation of Conversion:

The disappearance of $I_{3.2\text{-}2.8}$ of ESO in CASO can be employed to infer the conversion of ESO

$$Conversion\ (\%) = \left(1 - \frac{I_{3.2-2.8}\ of\ ASO}{I_{3.2-2.8}\ of\ ESO}\right) \times\ 100\ (\%)$$

$I_{3.2\text{-}2.8}$: Integral ratio of 3.2 – 2.8 Peak in ESO ¹H NMR

Calculation of Selectivity:

$$Selectivity_{NMR}\ (\%) = \left(\frac{I_{6.4}\ of\ Filtered\ CASO}{I_{6.4}\ of\ Crude\ CASO\ \times\ \dfrac{Calculated\ Epoxide\ value}{Assumed\ Epoxide\ value}}\right) \times\ 100\ (\%)$$

SEC Analysis after Reaction (Calculation of Selectivity, Fig. S2)[3]
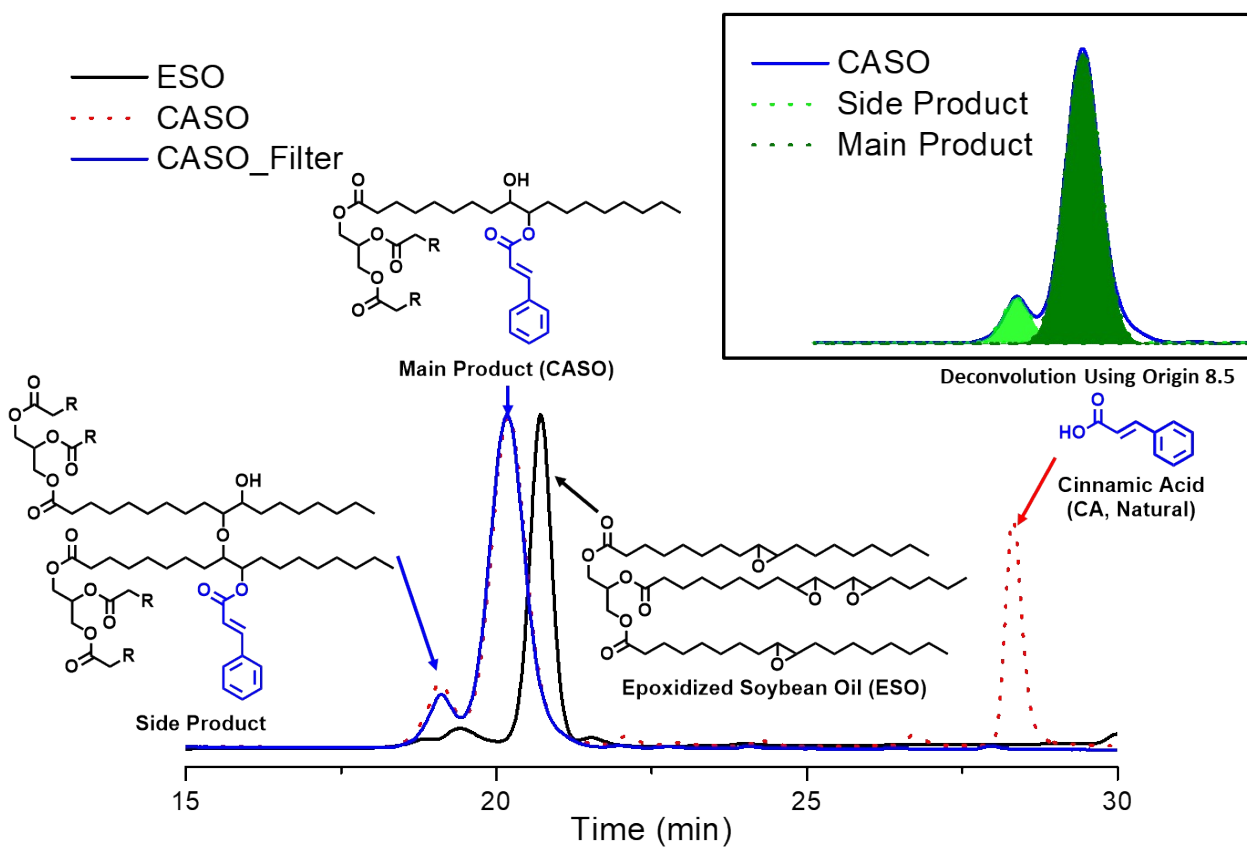
Fig. S2 SEC Analysis after Epoxide Ring Opening Reaction of ESO.

Calculation of Selectivity:

We utilized deconvolution method of Origin 8.5 to determine selectivity by analyzing the relative areas

of individual peaks.

Substrate Scope (DMAP and DMAP-BB system, Scheme S1)

Epoxidized Soybean Oil (ESO)

Catalyst (5 mol %)
Acid or Anhydride
(1.0 equiv.)

130 °C, 3 hour
Solvent-Free Reaction

R^2
R^1

R^1 = Aliphatic or Aromatic
R^2 = OH or CO_2R^1

a)

Acid Esterified Soybean Oil [ASO]
(Conversion, Selectivity [Main:Side])

DMAP System: PASO99 (99%, 99:1) [b,c]
DMAP-BB System: PASO93 (99%, 93:7)

DMAP System: UcASO90 (99%, 90:10)
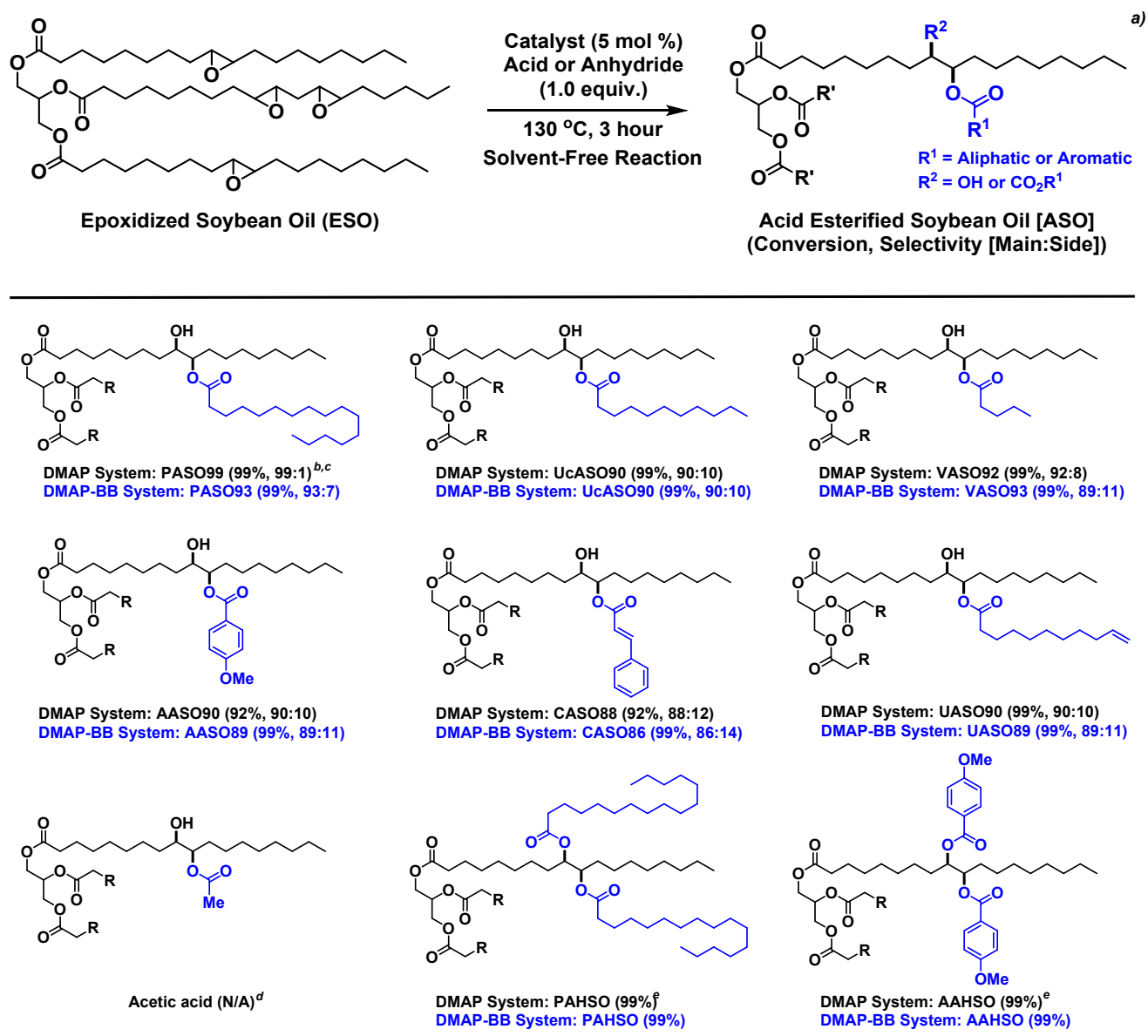**DMAP-BB System: UcASO90 (99%, 90:10)**

DMAP System: VASO92 (99%, 92:8)
DMAP-BB System: VASO93 (99%, 89:11)

DMAP System: AASO90 (92%, 90:10)
DMAP-BB System: AASO89 (99%, 89:11)

DMAP System: CASO88 (92%, 88:12)
DMAP-BB System: CASO86 (99%, 86:14)

DMAP System: UASO90 (99%, 90:10)
DMAP-BB System: UASO89 (99%, 89:11)

Acetic acid (N/A) [d]

DMAP System: PAHSO (99%) [f]
DMAP-BB System: PAHSO (99%)

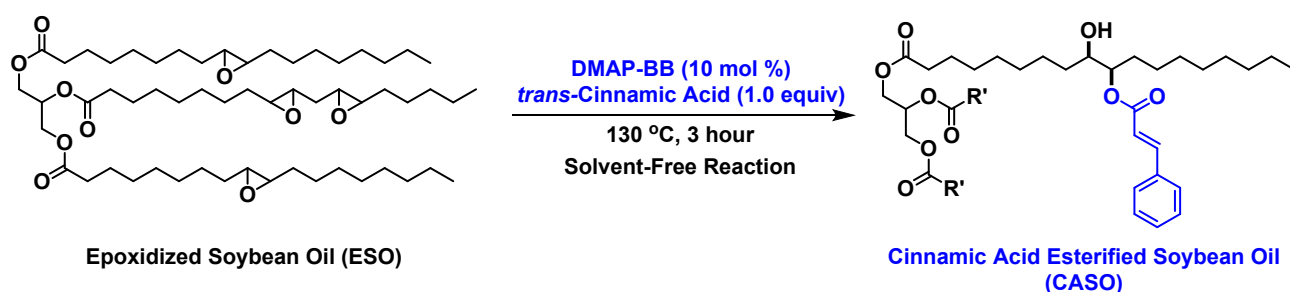**DMAP System: AAHSO (99%)** [e]
DMAP-BB System: AAHSO (99%)

Scheme S1 Scope of acid esterified soybean oil (ASO) using 4-(*N,N*-Dimethylamino)pyridine (DMAP, Homogeneous System) and 4-(*N,N*-Dimethylamino)pyridine benzyl bromide Salt (DMAP-BB, Homogeneous/Heterogeneous Hybrid System). Conversion (%) and selectivity (main product [β-hydroxyl ester]:side product [hydroxyl ether ester]) were analyzed by ^{1}H NMR spectroscopy and SEC data, respectively. Reaction condition: [a] 2.50 g of ESO (2.63 mmol = 10.5 mmol of epoxide ring [1.0 equiv]), 5.0 mol % catalyst, 1.0 equiv. acid, 130 °C, 3 hour, solvent-free [b] 1.0 mol % DMAP-BB (Conv: 99%, Sel: 80:20), [c] No catalyst (Conv: 99%, Sel: 60:40), [d] Decomposition occurs, [e] 1.0 equiv. anhydride.

Recycling Test (DMAP-BB, Table S2, Fig. S3)

Epoxidized soybean oil (ESO, 2.5 g, containing, 10.5 mmol of epoxy group), *trans*-Cinnamic Acid (CA, 1.6 g, 10.5 mmol), DMAP-BB (308 mg, 10.0 mol %, 1.05 mmol) were placed in 20 mL vial with stirring bar. The mixture was heated at 130 °C for 3 hours. After cooling to room temperature, tetrahydrofuran (40 mL) added to dissolve the crude oil. After 2 hours, a white solid (DMAP-BB) is precipitated at the bottom of the solution. The precipitated solid was recovered by filtration and dried in a vacuum oven at room temperature for 24 hours. The experiment was repeated using recovered salt.

Table S2. Solvent screening of DMAP-BB catalyst for precipitation after the ring-opening reaction[a]

Epoxidized Soybean Oil (ESO) → Cinnamic Acid Esterified Soybean Oil (CASO)

DMAP-BB (10 mol %)
trans-Cinnamic Acid (1.0 equiv)
130 °C, 3 hour
Solvent-Free Reaction

Precipitating Solvent	Ethyl Acetate (EA)	Methylethyl Ketone (MEK)	2-Methyl tetrahydrofuran (2-MeTHF)	Tetrahydrofuran (THF)
Greeness Evaluation[b]	Recommended	Recommended	Problematic (Recommended)[f]	Problematic
Conversion (%)[c]	99	99	99	99
Selectivity (M_n, Main:Side)[d]	1612-4075 (89:11)	1620-4148 (89:11)	1600-4032 (89:11)	1587-3946 (88:12)
Recovery yield of catalyst (%)[e]	95	71	97	99

[a]See ESI for the detailed recycle procedure for the acid-esterified soybean oil. [b]Determined by solvent selection guide [Prat, D. et al. CHEM21 selection guide of classical- and less classical-solvents. *Green Chem.* 2016, **18**, 288−296]. [c]Determined by relative integrations for the corresponding methine protons of the glycerol unit and protons on the oxirane ring in the ^{1}H NMR analysis of the acid-esterified soybean oil. [d]Calculated from the respective ratios for the low-molecular-weight region and the high-molecular-weight region in SEC after precipitation. [e]Calculated from the mass of the remaining catalyst after precipitation followed by filtration on 1st cycle. [f]2-Methyltetrahydrofuran (2-MeTHF): Biomass-derived solvent, considered as green solvent in [Alcántara, A. R. et al. 2-Methyltetrahydrofuran as a suitable green solvent for phthalimide functionalization promoted by supported KF. *Green Chem.* 2010, **12**, 1380−1382].
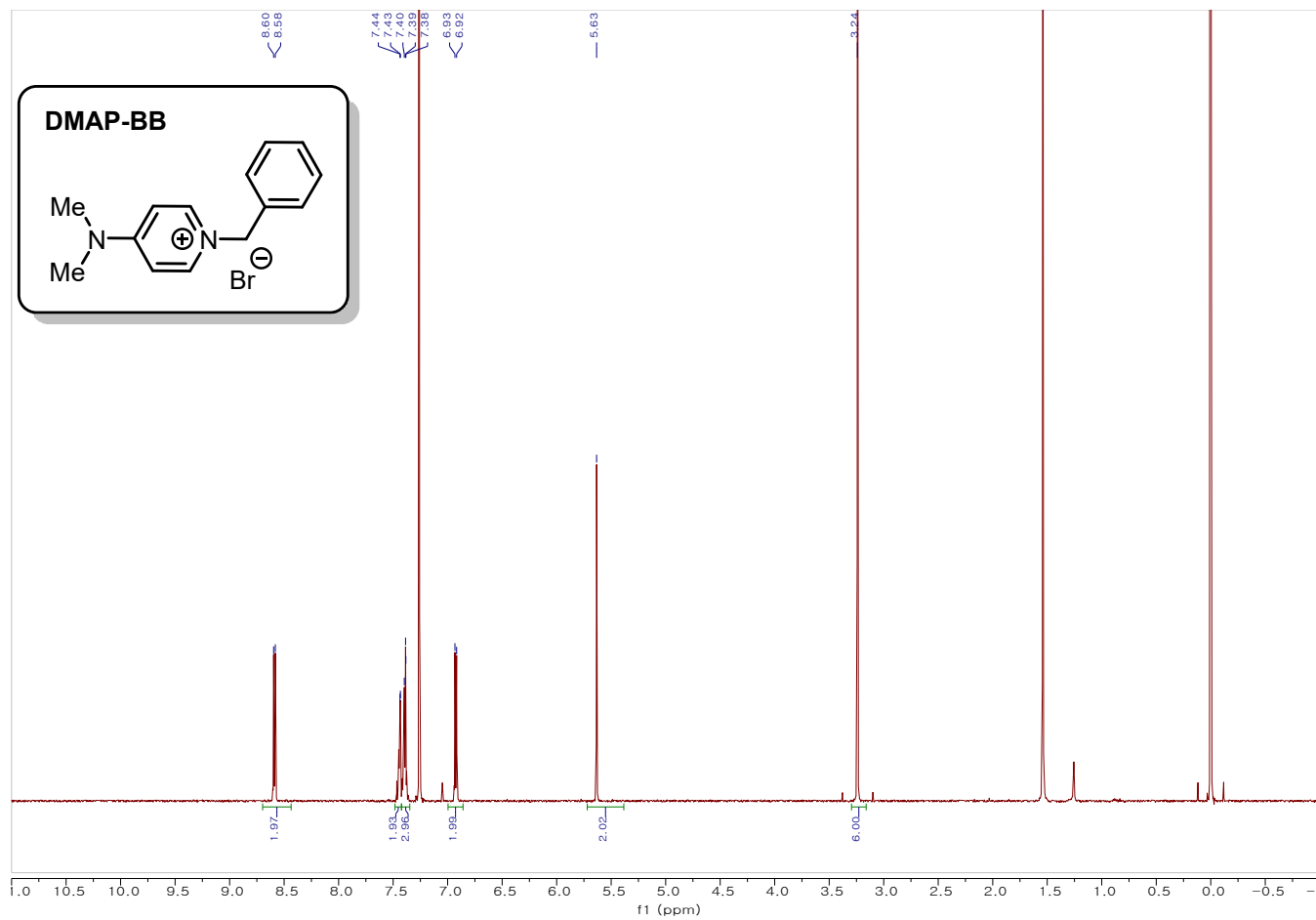
Fig. S3 ^{1}H NMR analysis of isolated DMAP-BB after reaction (recycled DMAP-BB).

Physical & Chemical Properties of ASOs (Table S3)

Table S3 Physical and chemical properties of acid esterified soybean oils (ASOs)

| Substrate	M_n (kg mol^{-1})^a	M_w (kg mol^{-1})^a	PDI^a	T_g (°C)^b	Viscosity at 25 °C (Pa · s)^c	Biocarbon Contents (%)^d
ESO	1.316	1.360	1.03	-63.2	0.3	>99
TDAE	-	-	-	-51.3	3.3	-
PASO99	2.516	2.861	1.14	-38.1	4.0	>99
PASO80	2.559	3.002	1.17	-39.4	2.9	>99
PASO60	2.555	3.374	1.32	-39.6	2.4	>99
UASO90	1.954	2.315	1.18	-52.6	3.3	>99
UcASO90	2.132	2.352	1.10	-45.6	3.7	>99
VASO92	1.748	1.897	1.08	-45.7	4.3	79
CASO88	1.852	2.033	1.10	-7.8	2180.6	>99
AASO90	1.799	1.990	1.10	-15.1	3274.2	>99
PAHSO	4.060	4.680	1.15	2.5	-^{e}	>99
AAHSO	2.108	2.350	1.11	5.8	-^{e}	51

^{a}Calculated from their respective ratios for low molecular weight region and high molecular weight region in SEC. ^{b}Observed by differential scanning calorimetry (DSC, second heating cycle) at 10 °C min^{-1} under N_2. ^{c}Viscosity was measured using an MCR 302e rheometer under Air in 25°C. ^{d}Comparison of biocarbon contents for the ALO series were theoretically calculated using structural compositions or experimentally determined by accelerator mass spectrometer (AMS). ^{e}Cannot be measured as it is in the solid state

Synthesis of Process Oil Treated Silica Particle (Fig. S4)

Tetrahydrofuran (10 g), silica (1.0 g), ASO (0.1 g) were placed in 20 mL vial with stirring bar. The mixture was stirred at room temperature for 2 hours. Then the suspensions were centrifuged to get the precipitates. The precipitates were dried at 70 °C for 24 hours. The samples were mixed with KBr to prepare pallets for FT-IR analysis
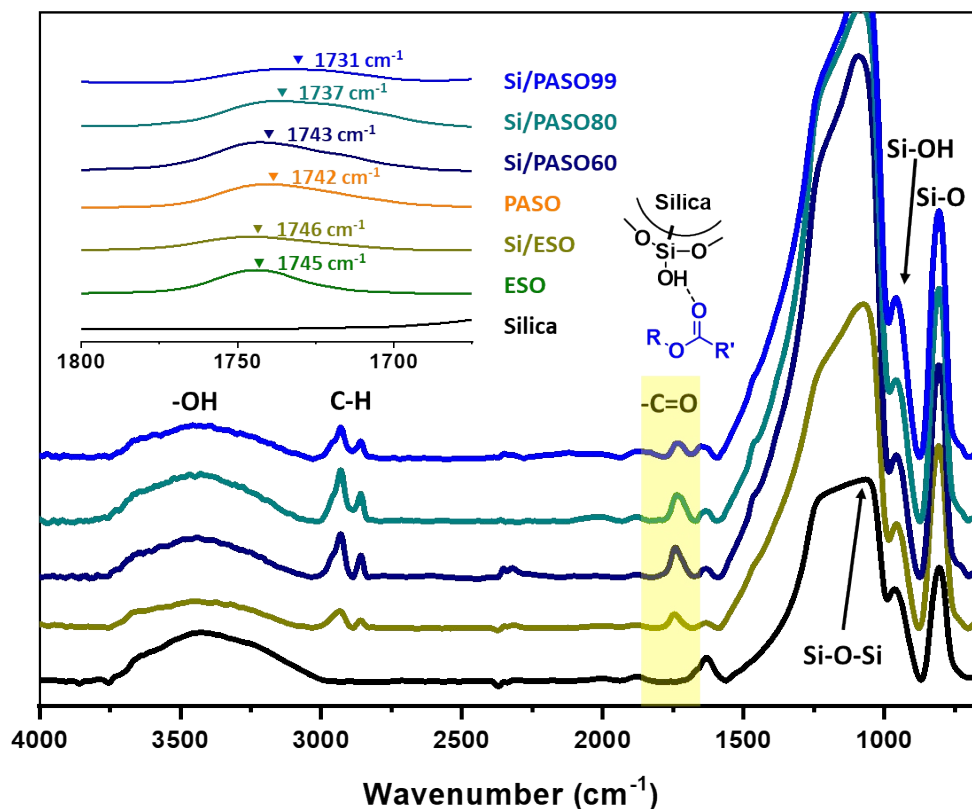
Fig. S4 FT-IR spectra of ESO and PASO series (PASO90, PASO80, and PASO 60) treated silica and ESO, PASO.

Synthesis of ASO 100 gram Scale

Epoxidized soybean oil (ESO, 100 g, containing 422 mmol of epoxy group), Palmitic Acid (110 g, 422 mmol), DMAP-BB (6.19 g, 5 mol %, 21.1 mmol) were placed in 500 mL Round bottom flask with stirring bar. The mixture was heated at 130 °C for 24 hours. After cooling to room temperature, tetrahydrofuran (500 mL) added to dissolve the crude oil. After 2 hours, a white solid (DMAP-BB) is precipitated at the bottom of the solution. The precipitated solid was recovered by filtration and dried in a vacuum oven at room temperature for 24 hours. The solution, from which the salt has been removed, was filtered through Al_2O_3 to remove DMAP-BB and acid residue. Tetrahydrofuran present in oil mixture is removed using a rotary evaporator under reduced pressure. Further, vacuum distillation was performed for 12 hours at 70 °C to eliminate traces of solvent. (Yield : 144 g, 71%)

IV.   General Methods for SBR/ASO Composites

Materials

SSBR (SOL-5220M, Kumho Petrochemical Co. Daejeon, Korea, styrene content: 26.5 wt%, vinyl content: 26 wt%, non-oil extended) was used as the base polymer. Silica (Ultrasil 7000 GR, Evonik Industries AG, Essen, Germany, Brunauer–Emmett–Teller (BET) surface area: 160–175 m^2/g) was used as a filler; and bis-[3-(triethoxysilyl)propyl]tetrasulfide (TESPT, Si-69, Evonik Korea Ltd., Seoul, Korea) was used as a silane coupling agent. Moreover, TDAE oil (Kukdong Oil & Chemicals Co., Yangsan, Korea) was used as a processing aid for mixing. ZnO and stearic acid (both from Sigma-Aldrich Corp., Seoul, Korea) were used as activators, and N-(1,3-dimethylbutyl)-N-phenyl-p-phenylenediamine (6PPD, Kumho Petrochemical Co., Daejeon, Korea) was used as an antioxidant in the compound. Additionally, sulfur (Daejung Chemicals & Metals Co., Siheung, Korea) was used as a crosslinking agent. N-cyclohexyl benzothiazole-2-sulfenamide (CBS, 98%, Tokyo Chemical Industry Co. Ltd., Tokyo, Japan) and 1,3-diphenylguanidine (DPG, 98%, Tokyo Chemical Industry Co. Ltd., Tokyo, Japan) were used as cure accelerators.®

Characterizations

< Payne Effect>

The rubber processing analyzer RPA 2000 made by Alpha Technologies was used to evaluate the silica dispersion and filler-filler interaction of a compound based on the ASTM D8059 standard. The storage modulus (G') of the uncured compound was measured at a temperature of 60 °C in the range of 0.20 %–100 % strain (frequency 1 Hz). The G' value is large in the low-strain region because the silica agglomerates are not destroyed, whereas the G' value decreased in the high-strain region as the agglomerates are destroyed. Therefore, the change in G', i.e., $\Delta G'$ (G' at 0.20% - G' at 100%) is called the Payne effect, which indicates the degree of filler–filler interaction.

< Cure Characteristics>

For measuring the cure characteristics of the compound, a RPA 2000 made by Alpha Technologies was operated for 20 min, maintaining a vibration angle of ±1 °C and temperature of 160 °C while the minimum torque (T_{min}), maximum torque (T_{max}), scorch time (t_{10}), and optimal cure time (t_{90}) were measured.

< Crosslink Density, Gel Fraction, and Bound Rubber Content>

A swelling test was performed on the SBR/silica compounding prepared with the synthesized process oil. For this purpose, the sample was swollen to maximum at room temperature. After, excess solvent was removed with a filter paper, and the weight was measured, followed by vacuum drying at 60 °C. The crosslinking density was calculated by applying the Flory-Rehner equation[4].

$$v_r = \frac{m_r}{m_r + m_s(\rho_r \div \rho_s)}$$

$$V_e = \frac{v_r + \chi v_r^2 + \ln(1 - v_r)}{v_s(0.5v_r - v_r^{\frac{1}{3}})}$$

where v_r represents the volume fraction, m_r represents rubber mass (g) and m_s represents the weight of the solvent in the swollen gel rubber. ρ_r is the density of the rubber before the experiment, and ρ_s is the density of the solvent (toluene = 0.867 g cm^{-3}). V_e represents the apparent cross-link density (g cm^{-3}), χ is the Flory-Huggins parameter, the degree of interaction between the gel and the solvent, and the value of SBR/toluene in the literature is 0.446. v_s represents the solvent molar volume (toluene = 106.29 cm^3 mol^{-1}).

Soxhlet extraction was used to determine the gel fraction of SBR/silica compounding with different ASO additions. First, samples were extracted with acetone for 24 hours to quantify ASO. Afterwards,

the samples were extracted for 48 hours using toluene to separate the lower weight soluble fraction. Then, the sample was vacuum-dried at 60°C for 24 h and the mass was measured until the weight did not change. The gel fraction is the ratio of highly crosslinked rubber residue, and the gel fraction data was obtained using the equation:

$$Gel\ Fraction\ (\%) = \frac{mass\ of\ dried\ residue}{sample\ mass} \times 100$$

The SBR/silica compounding were stored for at least 3 weeks before measuring the bound rubber content and dried under conditions similar to the experiments described above. The bound rubber content data was obtained by calculating the following equation.

$$Bound\ rubber\ content\ (\%) = \frac{m_g - (m_e \times C_f)}{m_e \times (1 - C_f)} \times 100$$

where C_f represents filler mass of the sample, and m_g represents the mass for rubber-filler gel whereas, m_e represents the mass after acetone extraction.

< Mechanical Properties >

A 100 mm (length) x 25 mm (width) dumbbell-shaped specimen that was prepared according to ATSM D 412 was measured at a speed of 500 mm/min using a universal testing machine (UTM, KSU-05M-C, KSU Co., Ansan, Korea) to measure the mechanical properties (tensile strength, modulus, and elongation at break) of vulcanizates.

< Abrasion Resistance >

The abrasion resistance was measured according to DIN 53516 using a Deutsche Industrie Normen (DIN) abrasion tester (Withlab Co., Gunpo, Korea). The specimen was prepared in a cylindrical shape with a diameter of 16 mm and thickness of 8 mm. The mass reduction after moving the specimen 40 m across the surface of an abrasive sheet mounted on a cylindrical drum revolving at 40 ± 1 rpm was measured by applying a load of 5 N.

< **Dynamic Viscoelastic Properties** >

For the dynamic viscoelastic properties of the compound, the storage modulus (G'), loss modulus (G"), and tan δ were measured from -70 to 70 °C under a 10 Hz frequency at 0.5% strain using a strain-controlled rheometer (ARES-G2, TA Instrument, USA).

V. Experimental Procedure and Characterization II

Preparation of SBR/ASO Composites (Compounding Procedure, Scheme S2)

◉ **Compounding Procedure**

Mixing Parameters		
Stage	Time (sec)	Condition
Masterbatch Stage (SMB) (Initial Temp: 110 °C)	0:00	Charge Rubber (SBR)
	0:40	Charge Silica, TESPT, Processing Aid
	6:00	Charge ZnO, Stearic Acid, 6PPD
	8:00	Drop Based on Max Temperature (140 °C)
Final Masterbatch Stage (FMB) (Roll Setting Temp: 60 °C)	0:00	Charge Masterbatch (SMB)
	0:40	Charge Sulfur, DPG, CBS
	5:00	Drop

*SBR: Styrene-Butadiene Rubber
*TESPT (Coulping Reagent): Bis(3-Triethoxysilyl)-propyl)tetrasulfide
*ZnO: Zinc Oxide
*6PPD (Anti-Oxidant):N-(1,3-Dimethylbutyl)-N'-phenylbenzenediamine
*DPG (Vulcanization Accelerator): Diphenylguanidine
*CBS (Vulcanization Accelerator): N-Cyclohexyl-2-benzothiazyl sulfenamide

	SBR (Rubber)	Silica (Filler)	Process Oil (Plasticizer)	TESPT (Si Coupling)	6-PPD (Anti-Oxidant)	Vulcanization Reagent (Crosslinking)
SBR/Oil (phr)	100	70	20	5.6	2	8.5

*SBR: Styrene-Butadiene Rubber, TESPT: Bis(3-Triethoxysilyl)-propyl)tetrasulfide.
6PPD:N-(1,3-Dimethylbutyl)-N'-phenylbenzenediamine
*Vulcanization Reagent: Sulfur (1.5 phr), ZnO(Activator, 3 phr), Stearic Acid (Activator, 1 phr),
DPG (Accelerator, 1.5 phr): Diphenylguanidine, CBS (Accelerator, 1.5 phr): N-Cyclohexyl-2-benzothiazyl sulfenamide
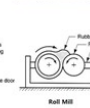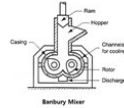
Scheme S2 Compounding procedure of SBR/ASO composites

Curing Properties (Table S4)

Table S4 Curing properties of various SBR/ASO composites[a]

Composites	t_{10} (min)	t_{90} (min)	Δt (t_{90}-t_{10}) (min)	M_L (Nm)	M_H (Nm)	ΔM (M_H-M_L) (Nm)
SBR/TDAE	3.26	14.19	10.93	0.55	2.76	2.22
SBR/ESO	3.90	15.98	12.08	0.38	2.13	1.75
SBR/PASO99	3.68	13.21	9.53	0.37	2.74	2.37
SBR/PASO60	4.32	12.59	8.27	0.43	2.39	1.96
SBR/UASO90	4.59	13.14	8.55	0.36	3.22	2.85
SBR/VASO90	4.48	12.07	7.59	0.39	2.80	2.42
SBR/AASO90	3.69	13.12	9.43	0.48	2.66	2.18

[a]Condition: RPA 160 ºC, 20 min

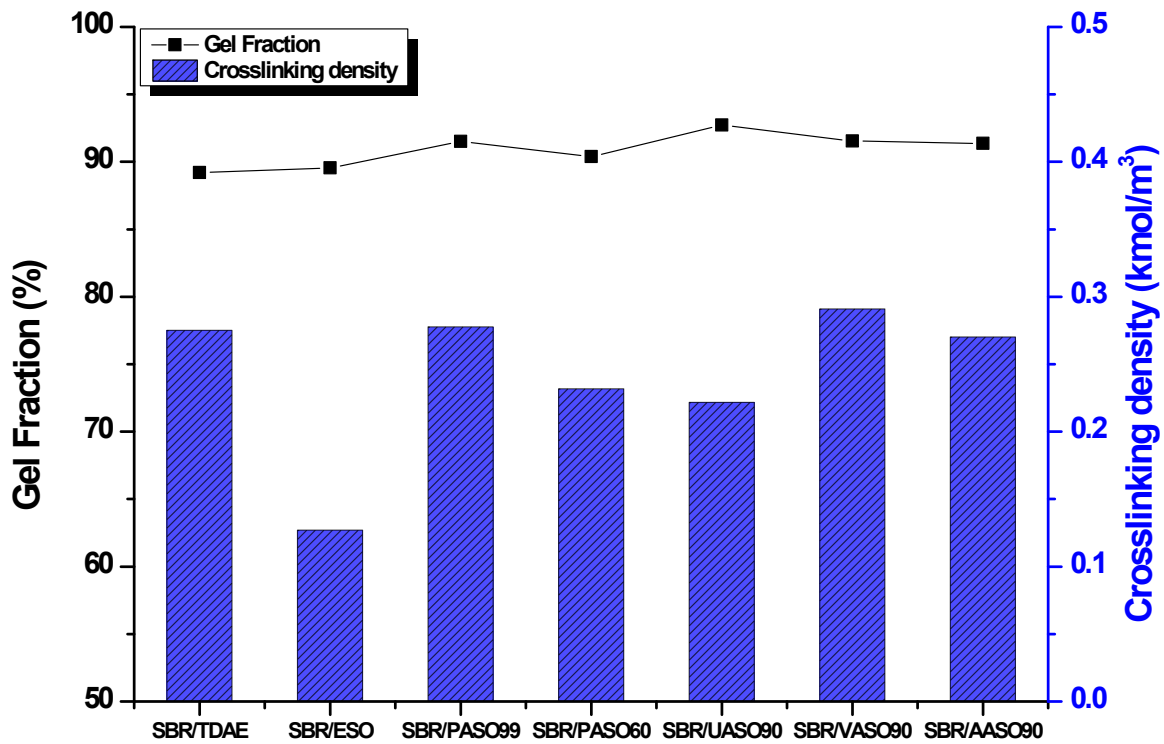**Crosslink Density, Gel Fraction, and Bound Rubber Contents (Fig. S5, Fig. S6)**

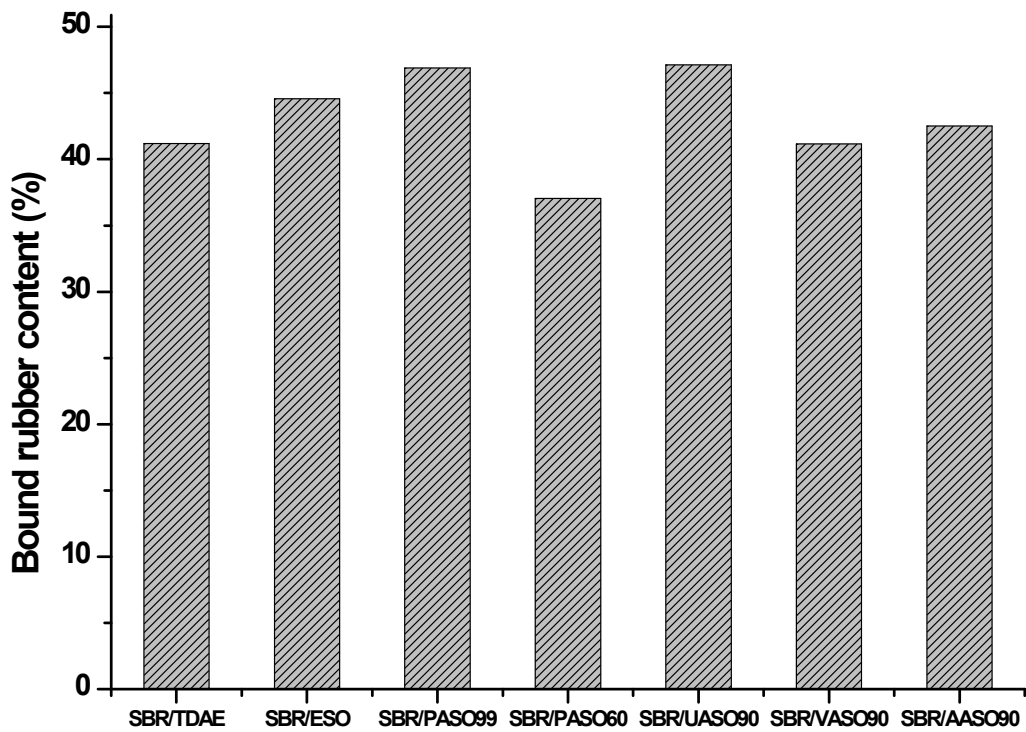**Fig. S5** Crosslink density and Gel fraction of SBR/ASO vulcanizates.

Fig. S6 Bound rubber content of SBR/ASO vulcanizates.

Viscoelastic Properties (Table S5)

Table S5 Viscoelastic properties of various SBR/ASO vulcanizates

| Composites	T_g (ºC)	Rolling Resistance (L) tan δ at 60 ºC	Wet Traction (H) G'' at 0 ºC	Snow Traction (L) tan δ at -10 ºC (G' at -30 ºC)
SBR/TDAE	-33.5	0.120	2.57	0.251 (71.7)
SBR/ESO	-35.9	0.158	2.46	0.236 (56.1)
SBR/PASO99	-32.4	0.116	2.31	0.246 (84.4)
SBR/PASO60	-33.5	0.127	2.33	0.242 (81.7)
SBR/UASO90	-33.6	0.112	2.09	0.250 (56.9)
SBR/VASO90	-32.4	0.110	2.49	0.258 (78.7)
SBR/AASO90	-33.6	0.130	7.76	0.181 (144.4)

Morphology Studies (Fig. S7)
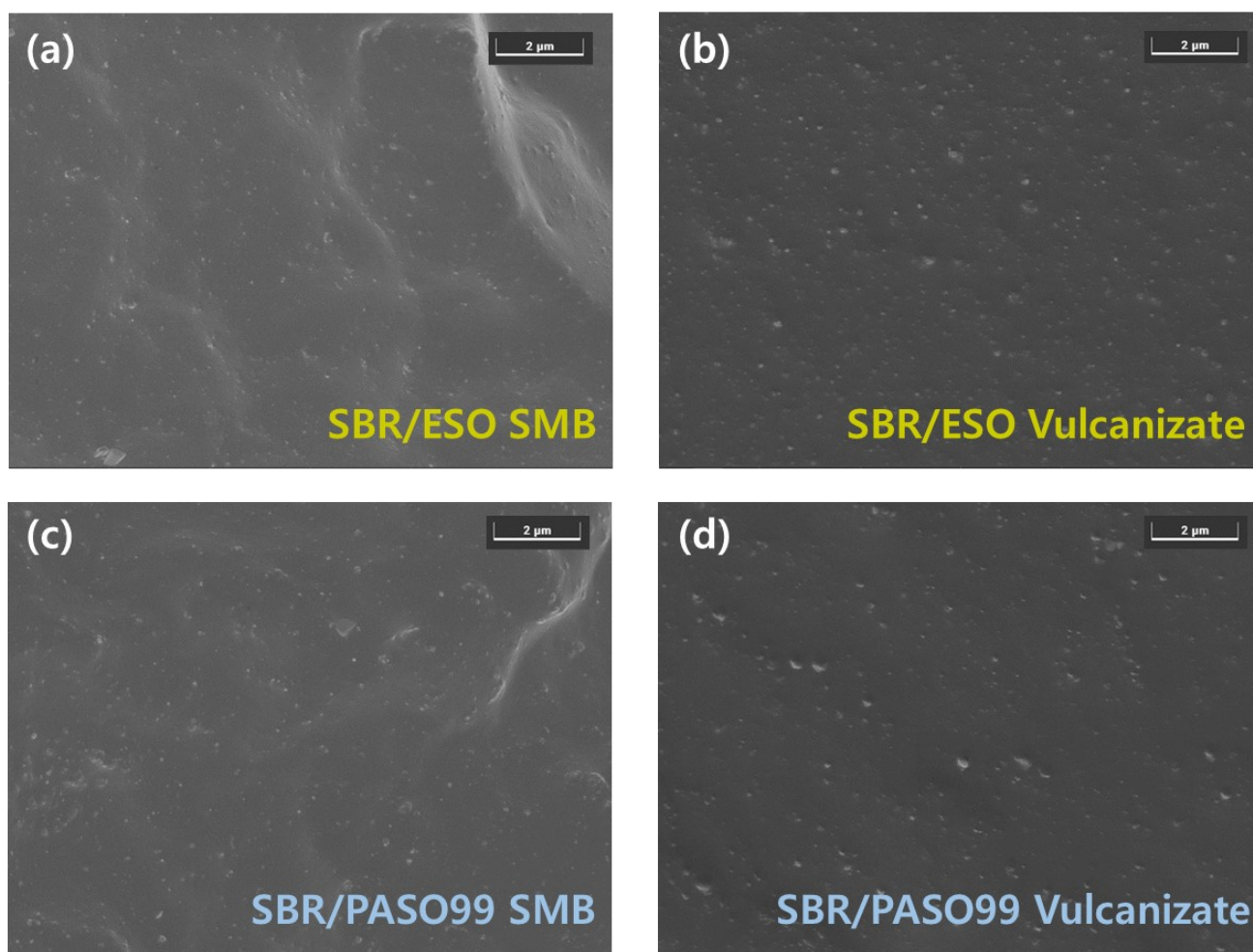
Fig. S7 Morphology observation by scanning electron microscope (SEM) analysis.

The SEM analysis in Fig. S7 presents images of silica master batch (SMB) and vulcanizate samples. White dots in the micrographs signify the presence of silica particles, and the grey area corresponds to the SBR matrix. Notably, in the SMB of the SBR/ESO composite, spherical silica particles ranging from 50 to 100 nm demonstrate excellent dispersion within the SBR matrix. Interestingly, there is no significant difference in silica dispersion in the SMB of the SBR/PASO99 composite.

Thermal Properties (Fig. S8)

(a)

(b)
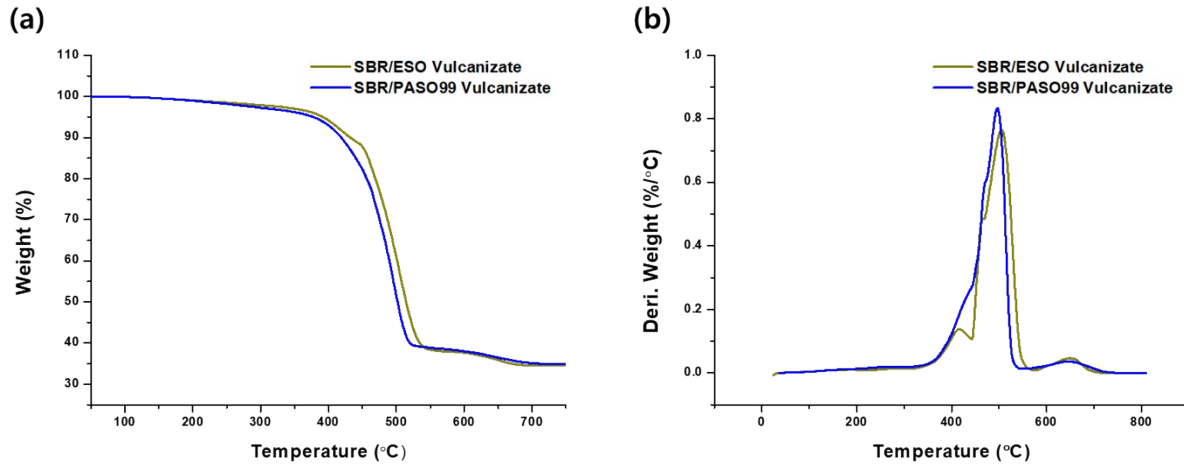
Fig. S8 Thermal property observation by thermogravimetric analysis (TGA) analysis. (a) Thermogravimetric curves of SBR/ESO Vulcanizate and SBR/PASO99 Vulcanizate, (b) Derivative of thermogravimetric curve of SBR/ESO Vulcanizate and SBR/PASO99 Vulcanizate.

Thermal stability of SBR/ESO vulcanizate and SBR/PASO99 were observed by TGA. In Fig. S8, the weight loss curves of SBR/ESO and SBR/PASO99 rubber composites have been observed. The initial transition in the range of 320-440 °C results from the decomposition of ESO and PASO99 which starts from 324 °C and 334 °C, respectively. The complete decomposition of the rubber matrix was observed after 500 °C. In addition, the T_{max} value of composites are found to be comparable with 505 °C for SBR/ESO vulcanizate and 497 °C for SBR/PASO99 vulcanizate, respectively. Final amounts of residue was found to show 35 wt% which is consistent value with silica contents in compounding process. Both vulcanizates, SBR/ESO and SBR/PASO99, revealed to be exist as stable composite before 300 °C. It is important to highlight that the thermal stability of the materials is adequately maintained at 130 °C, a temperature which reaches during tire tread operation.

VI. References

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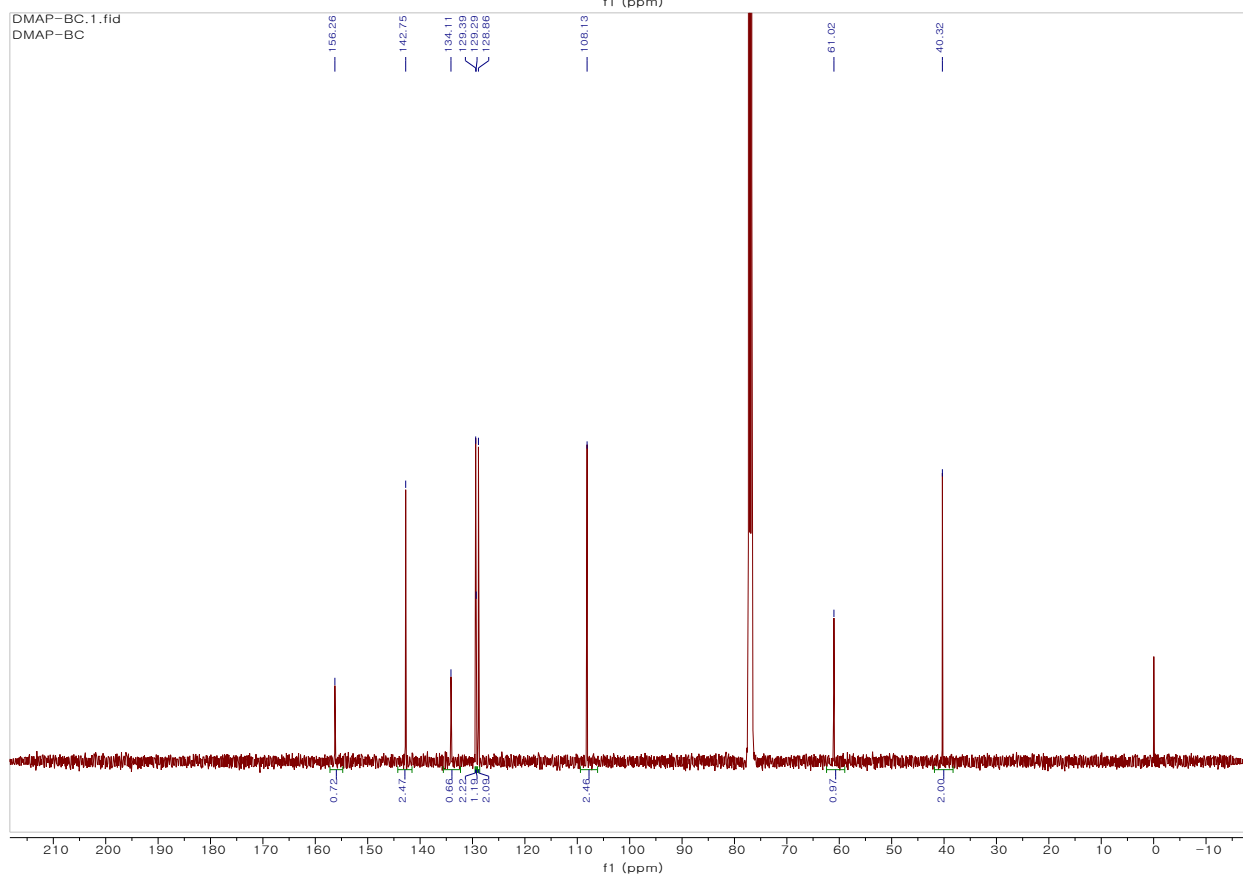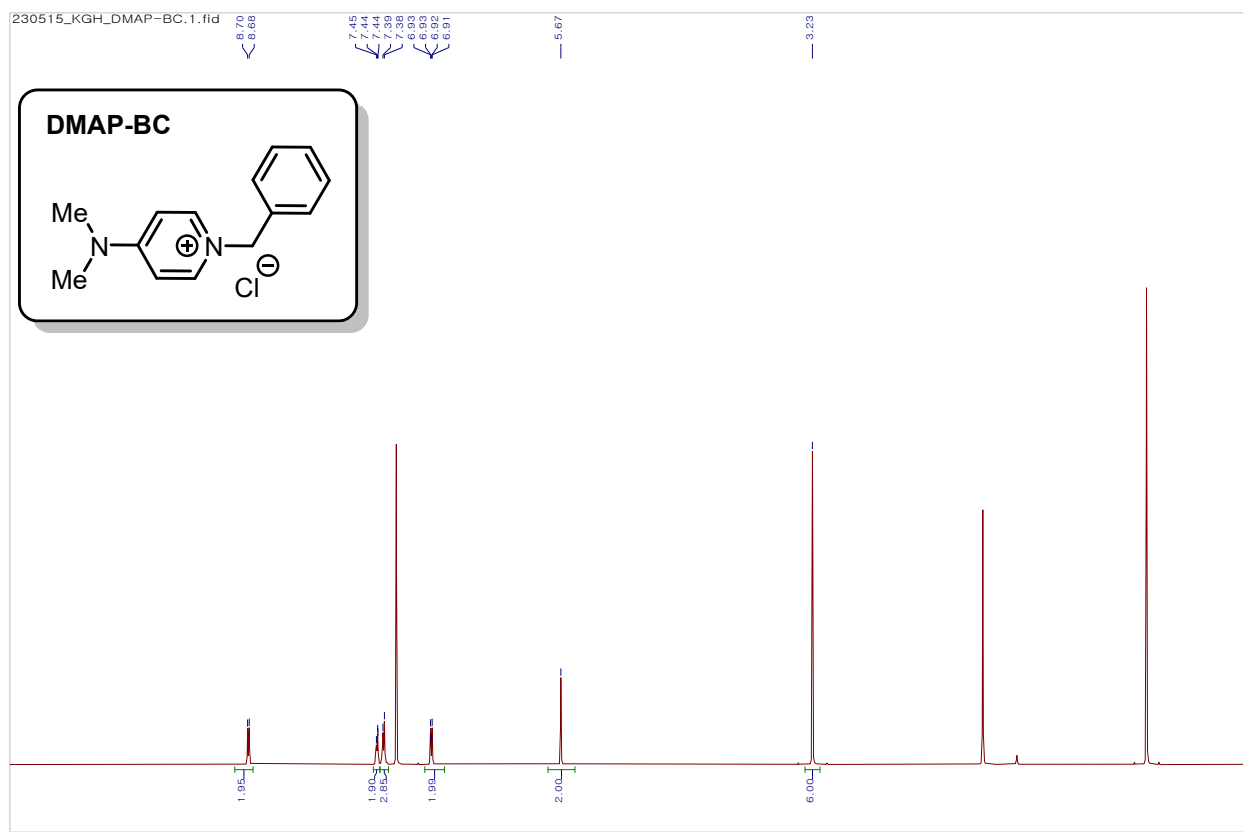
Appendix I

Spectral Copies of ^{1}H and ^{13}C NMR of
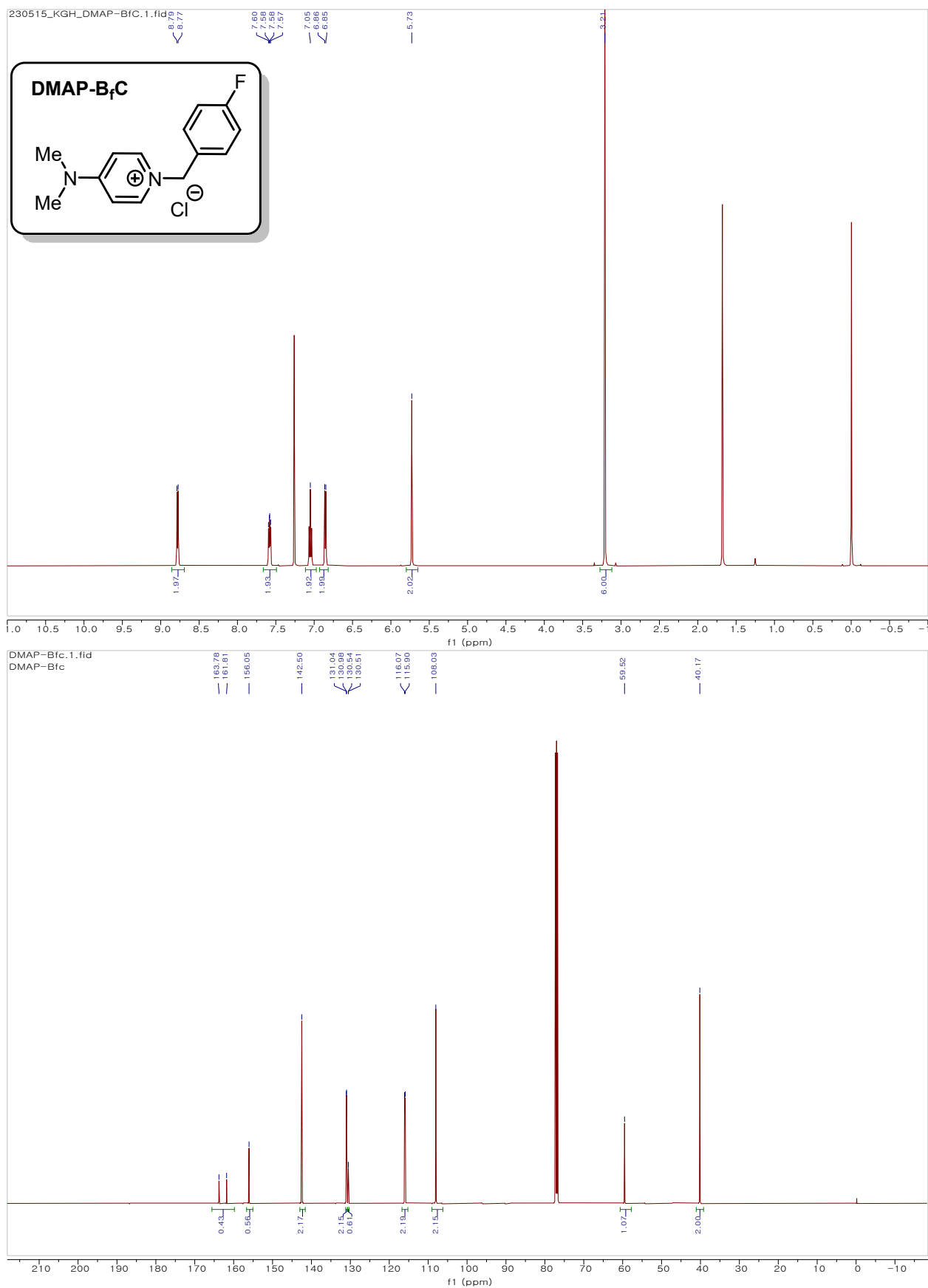
Compounds Obtained for DMAP Salt

4-(*N,N*-Dimethylamino)pyridine *tran*-Cinnamic acid salt (DMAP-CA) :
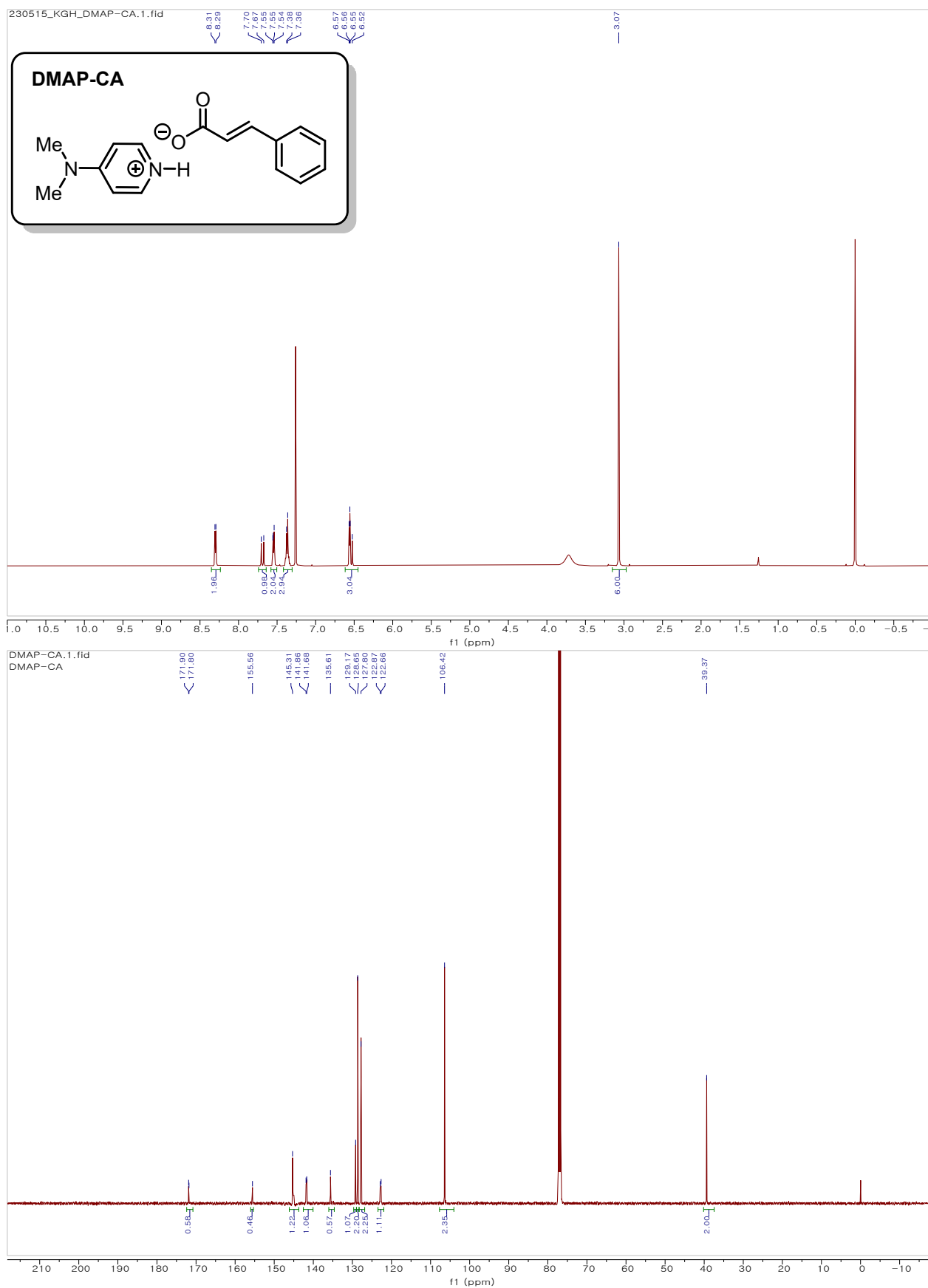
4-(*N,N*-Dimethylamino)pyridine benzyl chloride salt (DMAP-BC) :

4-(*N,N*-Dimethylamino) pyridine *p*-fluorobenzyl chloride salt (DMAP-B_fC) :

4-(*N*,*N*-Dimethylamino)pyridine benzyl bromide salt (DMAP-BB)