Electronic Supplementary Information

for

Depolymerization of PET with Ethanol by Homogeneous Iron Catalysts Applied for Exclusive Chemical Recycling of Cloth Waste

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Contents

1. Additional results for depolymerization of PET with ethanol by $FeCl_3$ and $FeBr_3$.

Table S1. Depolymerization of PET with ethanol by $FeCl_3$ and $FeBr_3$.[a]

run	catalyst (mol%)[b]	temp. / °C	time / h	conv.[c] / %	yield[d] / %	DET and EG recovery yield[e] / mg (%)
1	$FeCl_3$ (5.0)	180	18	>99	>99	740 (>99)
2	$FeCl_3$ (5.0)	180	12	>99	98	710 (96)
3	$FeCl_3$ (5.0)	160	18	>99	97	710 (96)
4	$FeCl_3$ (5.0)	160	18	>99	98	730 (99)
5	$FeCl_3$ (5.0)	160	24	>99	98	720 (97)
6	$FeCl_3$ (5.0)	120	18	>99	46	320 (43)
7	$FeCl_3$ (3.0)	180	18	>99	97	720 (97)
8	$FeCl_3$ (3.0)	180	24	>99	>99	730 (99)
9	$FeCl_3$ (3.0)	180	30	>99	>99	740 (>99)
10	$FeCl_3$ (1.0)	180	18	>99	21	150 (20)
11	$FeCl_3$ (1.0)	180	30	>99	97	700 (95)
12	$FeCl_3$ (1.0)	180	48	>99	>99	740 (>99)
13	$FeBr_3$ (5.0)	180	18	>99	>99	740 (>99)
14	$FeBr_3$ (5.0)	160	18	>99	87	700 (94)
15	$FeBr_3$ (5.0)	120	18	>99	18	170 (23)
16	$FeBr_3$ (3.0)	180	18	>99	>99	730 (99)
17	$FeBr_3$ (3.0)	180	30	>99	>99	740 (>99)
18	$FeBr_3$ (1.0)	180	18	>99	34	350 (47)
19	$FeBr_3$ (1.0)	180	30	>99	97	700 (95)
20	$FeBr_3$ (1.0)	180	48	>99	>99	740 (>99)

[a]Conditions: poly(ethylene terephthalate) (PET) prepared by cutting the bottle 500 mg, ethanol 5.0 mL. [b]Based on monomer unit in PET ($C_{10}H_8O_4$, FW 192.14). [c]Estimated by ^{13}C NMR spectra. [d]GC yield vs. internal standard (mesitylene) based on DET (diethyl terephthalate). [e]Weight of the recovered monomers.

2. GC chromatograms of the resultant mixtures for depolymerization of PET through transesterification with ethanol using $FeCl_3$ and $FeBr_3$.

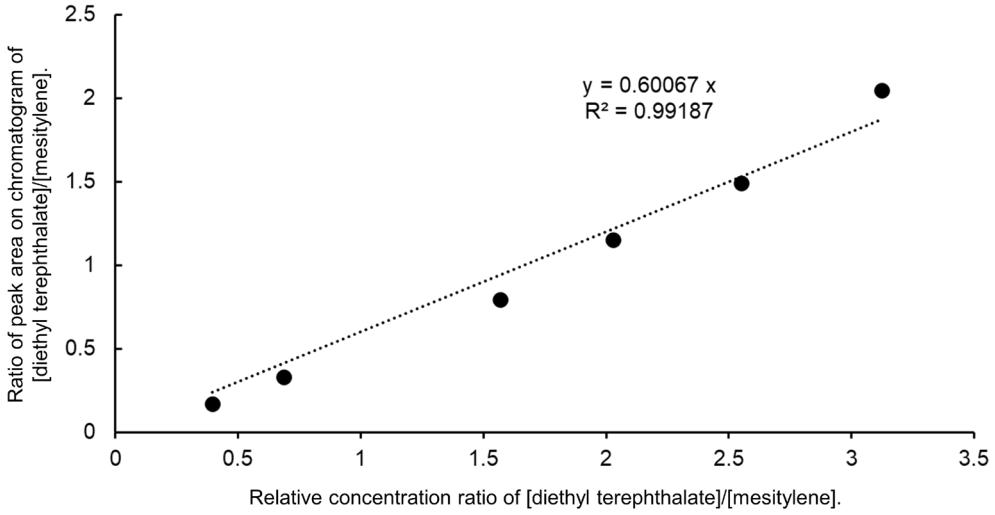


Figure S1. Calibration curve for calculations of yields of diethyl terephthalate (DET) using mesitylene as an internal standard. The retention time of the internal standard (mesitylene) at 3.69 min and for diethyl terephthalate (DET) at 10.77.

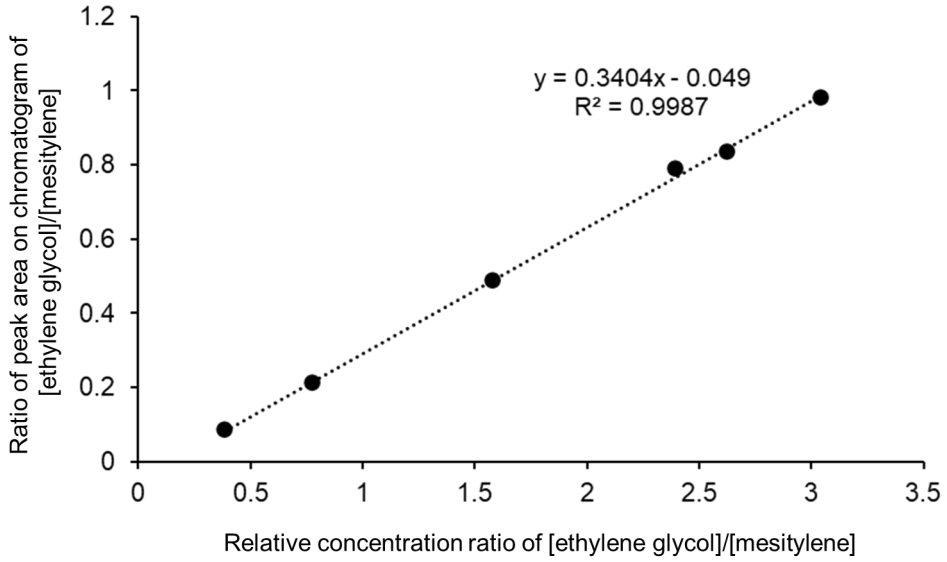


Figure S2. Calibration curve for calculations of yields of ethylene glycol (EG) using mesitylene as an internal standard. The retention time of the internal standard (mesitylene) at 3.69 min and for ethylene glycol (EG) at 1.62.

Table S2. Summary of the GC data for reaction mixtures of depolymerized PET with ethanol using $FeCl_3$.[a]

Sample	catalyst (mol%)	temp. / °C	time / h	Area under the peak (EG)[b]	Area under the peak (IS)[b]	yield[c] / %
PET-S	$FeCl_3$ (5.0)	180	18	985004	5002230	>99
PET-S	$FeBr_3$ (5.0)	180	18	1012028	5508187	>99

[a]The GC analysis used a Shimadzu gas chromatograph (GC-2014, Shimadzu Corp., Tokyo, Japan) equipped with a flame ionization detector (FID) through nitrogen as a carrier gas. Conditions are as follows (DB-1MS column, 30 m × 0.250 mm × 0.25 μm): column temp, 80 °C (4 min) followed by increasing up to 320 °C (20 °C/min) [injection 300 °C, flow (column) 1.71 mL/min]. **PET-S**: PET sheets were prepared by cutting the bottle. IS: internal standard (mesitylene). [b]At retention time 3.69 min for internal standard (mesitylene) and 1.62 min for ethylene glycol (EG).

Table S3. Summary of the GC data for reaction mixtures of depolymerized PET with ethanol using $FeCl_3$ and $FeBr_3$.[a]

Sample	catalyst (mol%)*	temp. / °C	time / h	Area under the peak (DET)[b]	Area under the peak (IS)[b]	yield[c] / %
PET-S	$FeCl_3$ (5.0)	180	18	549314	316821	>99
PET-S	$FeCl_3$ (5.0)	180	12	1924501	1188993	98
PET-S	$FeCl_3$ (5.0)	160	18	780448	433605	97
PET-S	$FeCl_3$ (5.0)	160	18	1091167	1091167	98
PET-S	$FeCl_3$ (5.0)	160	24	3005335	1764263	98
PET-S	$FeCl_3$ (5.0)	120	18	391904	500446	46
PET-S	$FeCl_3$ (3.0)	180	18	1852072	1109436	97
PET-S	$FeCl_3$ (3.0)	180	24	1630313	944651	>99
PET-S	$FeCl_3$ (3.0)	180	30	1827430	1092942	>99
PET-S	$FeCl_3$ (1.0)	180	18	1118401	3375620	21
PET-S	$FeCl_3$ (1.0)	180	30	1827430	1092942	97
PET-S	$FeCl_3$ (1.0)	180	48	2795580	1700127	>99
PET-YT	$FeCl_3$ (5.0)	180	12	392637	1014874	96
PET-YT	$FeCl_3$ (5.0)	180	16	374296	897003	>99
PET-WT	$FeCl_3$ (5.0)	180	18	1814691	991205	>99
PET-WT	$FeCl_3$ (5.0)	180	18	728770	1196060	98
PET-BT	$FeCl_3$ (5.0)	180	18	509978	710810	>99
PET-S + PE	$FeCl_3$ (5.0)	180	18	1621133	1058460	98
PET-S + Cotton	$FeCl_3$ (5.0)	180	18	1814691	991205	>99
PET-S	$FeBr_3$ (5.0)	180	18	2219355	1274960	>99
PET-S	$FeBr_3$ (5.0)	160	18	527118	420004	87
PET-S	$FeBr_3$ (5.0)	120	18	149158	533796	18
PET-S	$FeBr_3$ (3.0)	180	18	3365825	1884203	>99
PET-S	$FeBr_3$ (3.0)	180	30	1092942	1827430	>99
PET-S	$FeBr_3$ (1.0)	180	18	2038384	1120665	34
PET-S	$FeBr_3$ (1.0)	180	30	813412	449988	97
PET-S	$FeBr_3$ (1.0)	180	48	2002724	1098312	>99

[a]The GC analysis used a Shimadzu gas chromatograph (GC-2014, Shimadzu Corp., Tokyo, Japan) equipped with a flame ionization detector (FID) through nitrogen as a carrier gas. Conditions are as follows (DB-1MS column, 30 m × 0.250 mm × 0.25 μm): column temp, 80 °C (4 min) followed by increasing up to 320 °C (20 °C/min) [injection 300 °C, flow (column) 1.71 mL/min]. **PET-S**: PET sheets were prepared by cutting the bottle. **PET-YT**: Yellow textile contains 65 % PET. **PET-WT**: White textile contains 100% PET. **PET-BT**: Black textile contains 100 % PET. **IS:** internal standard (mesitylene). [b]At retention time 3.69 min for internal standard (mesitylene) and 10.77 min for diethyl terephthalate (DET). *Amount of $FeCl_3$ loaded was calculated on the basis of monomer unit in PET ($C_{10}H_8O_4$, FW 192.14) only.

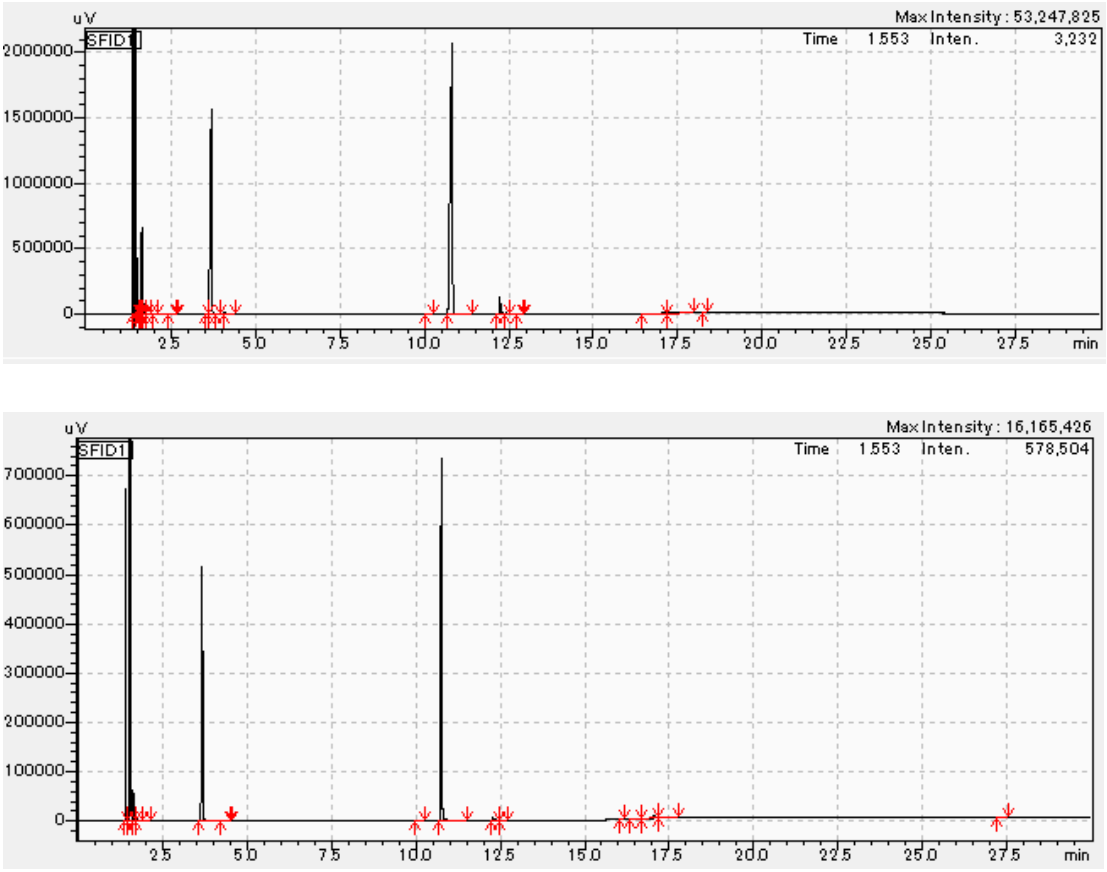


Figure S3. GC chromatograms of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 5 mol % of $FeCl_3$ at 180 °C for (top) 18 h [measured in ethanol] and (bottom) 12 h.

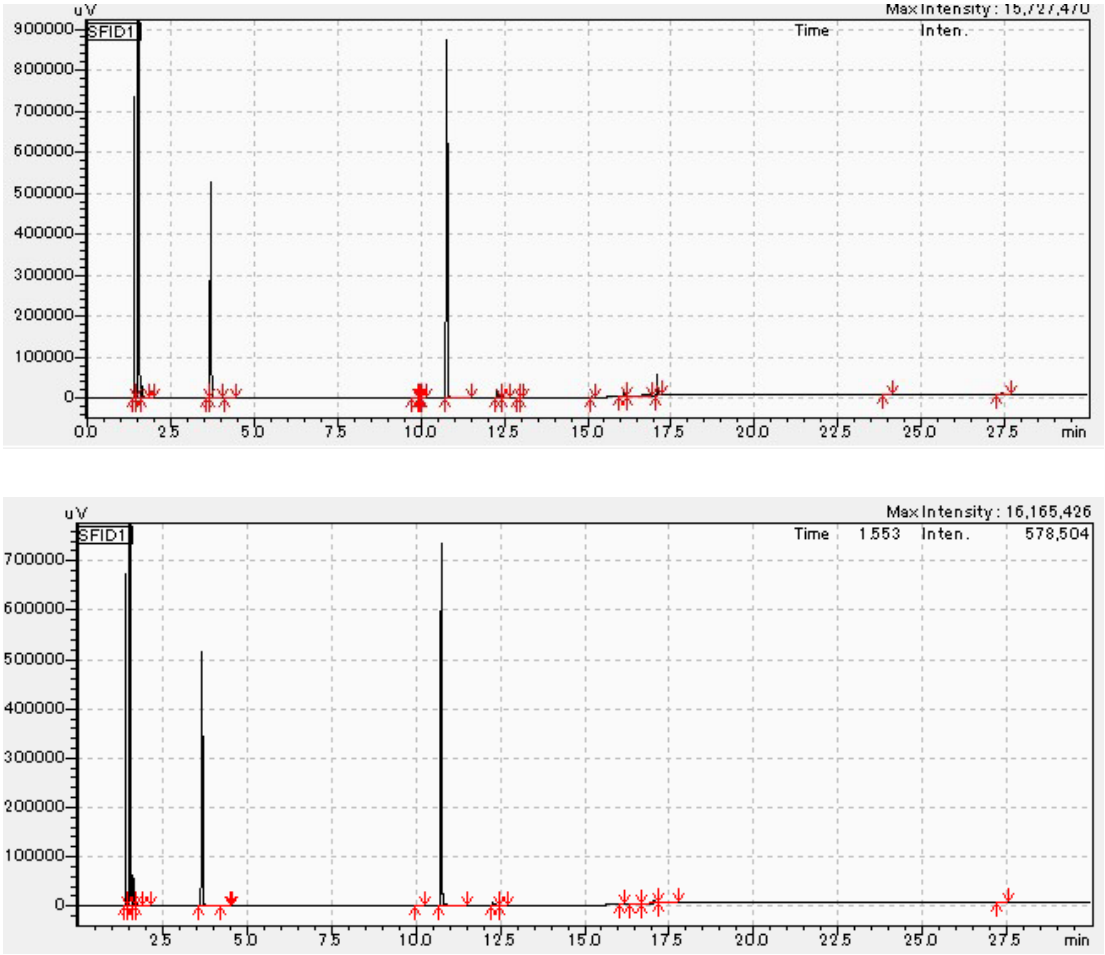


Figure S4. GC chromatograms of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 5 mol % of $FeCl_3$ at 180 °C for (top) 18 h and (bottom) 12 h.

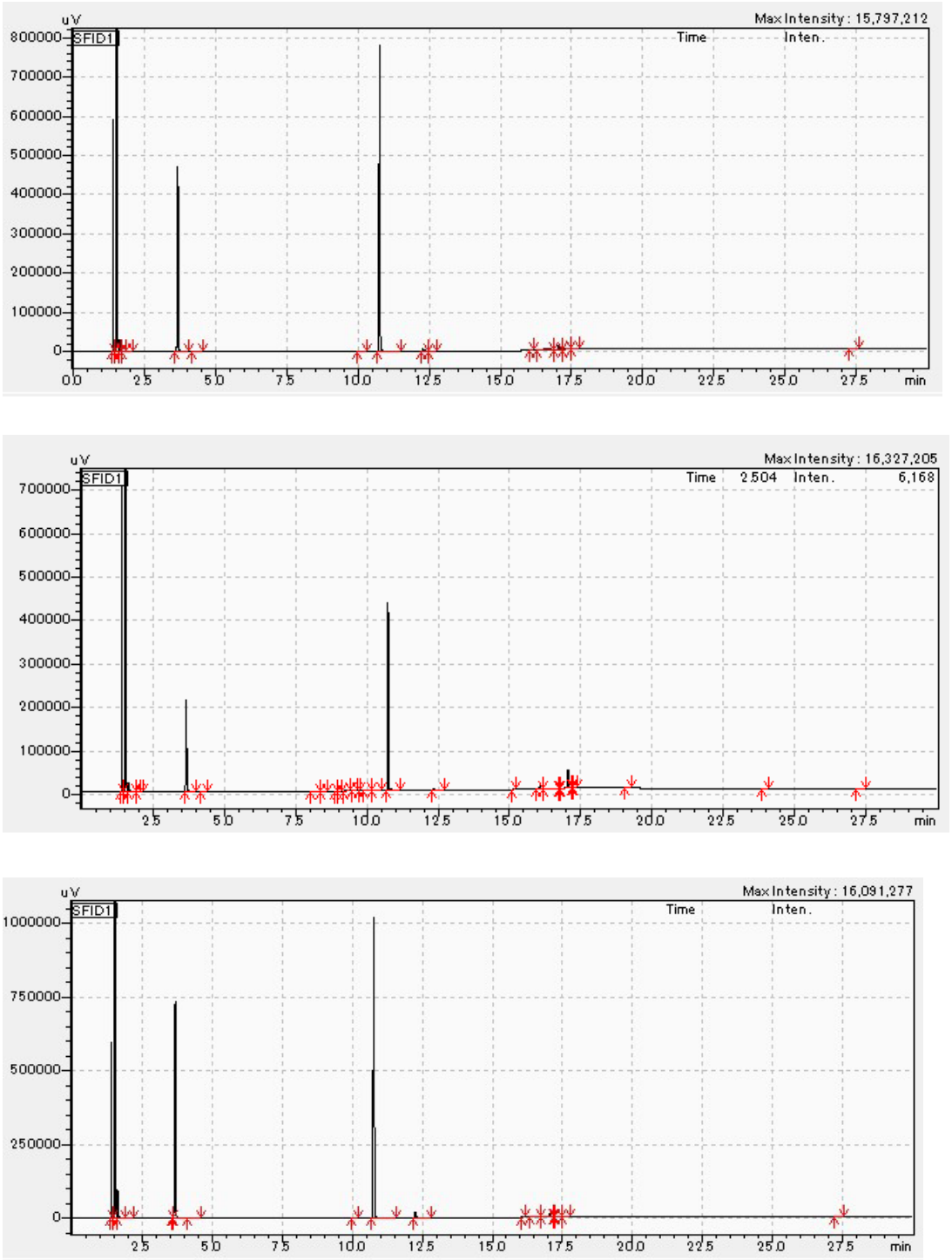


Figure S5. GC chromatograms of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 5 mol % of $FeCl_3$ at 160 °C for (top) 18 h, (middle) 18 h, and (bottom) 24 h.

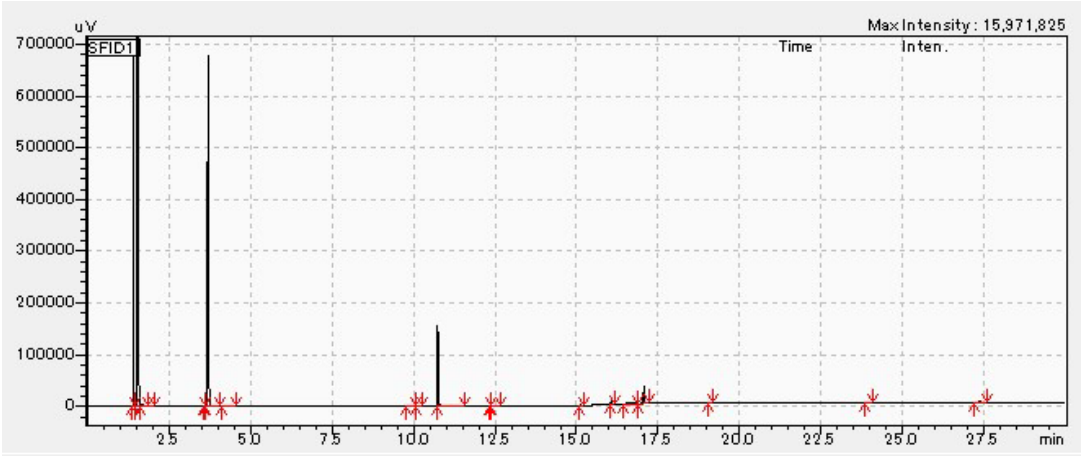


Figure S6. GC chromatogram of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 5 mol % of $FeCl_3$ at 120 °C for 18 h.

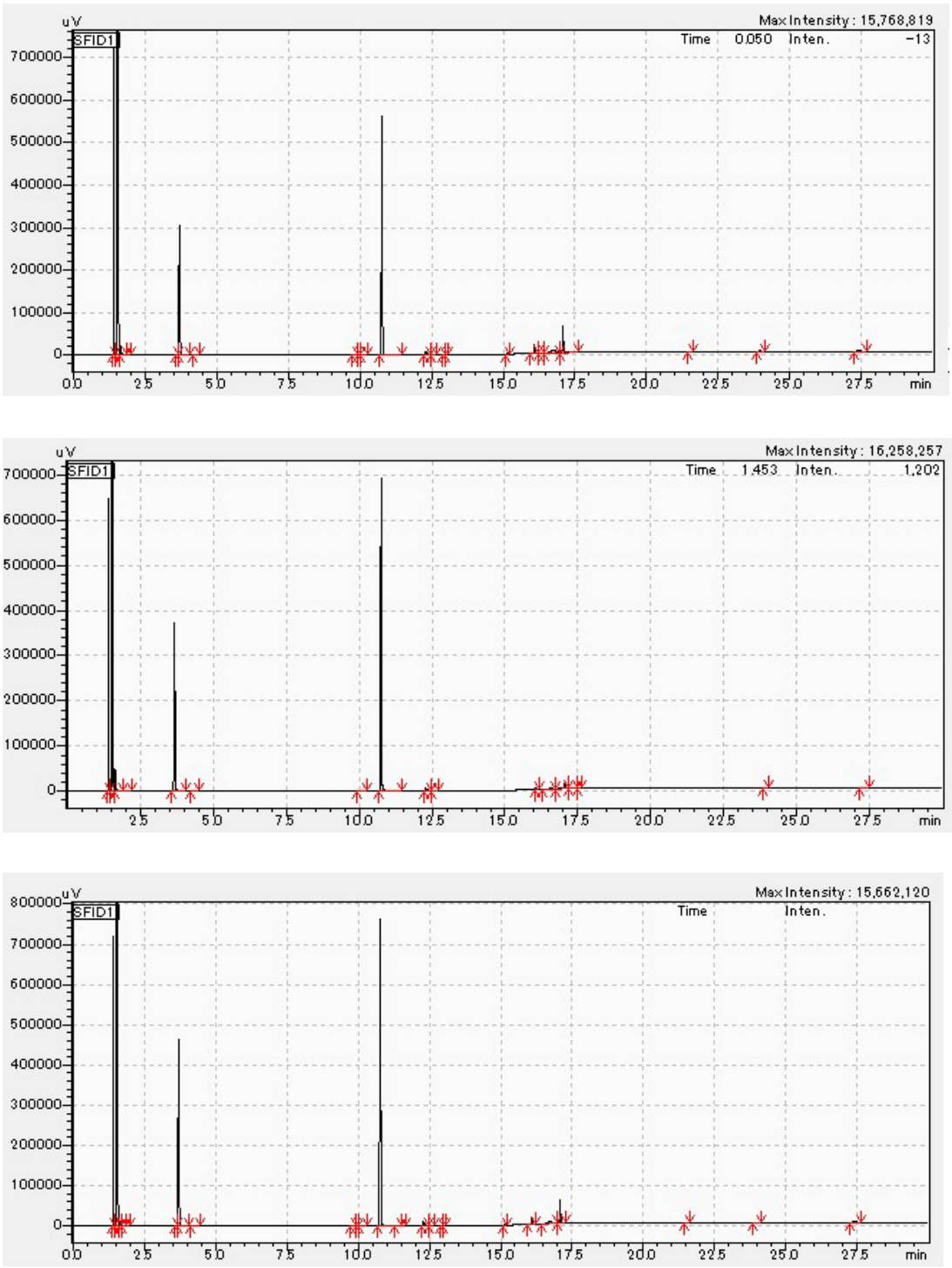


Figure S7. GC chromatograms of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 3 mol % of $FeCl_3$ at 180 °C for (top) 18 h, (middle) 24 h, and (bottom) 30 h.

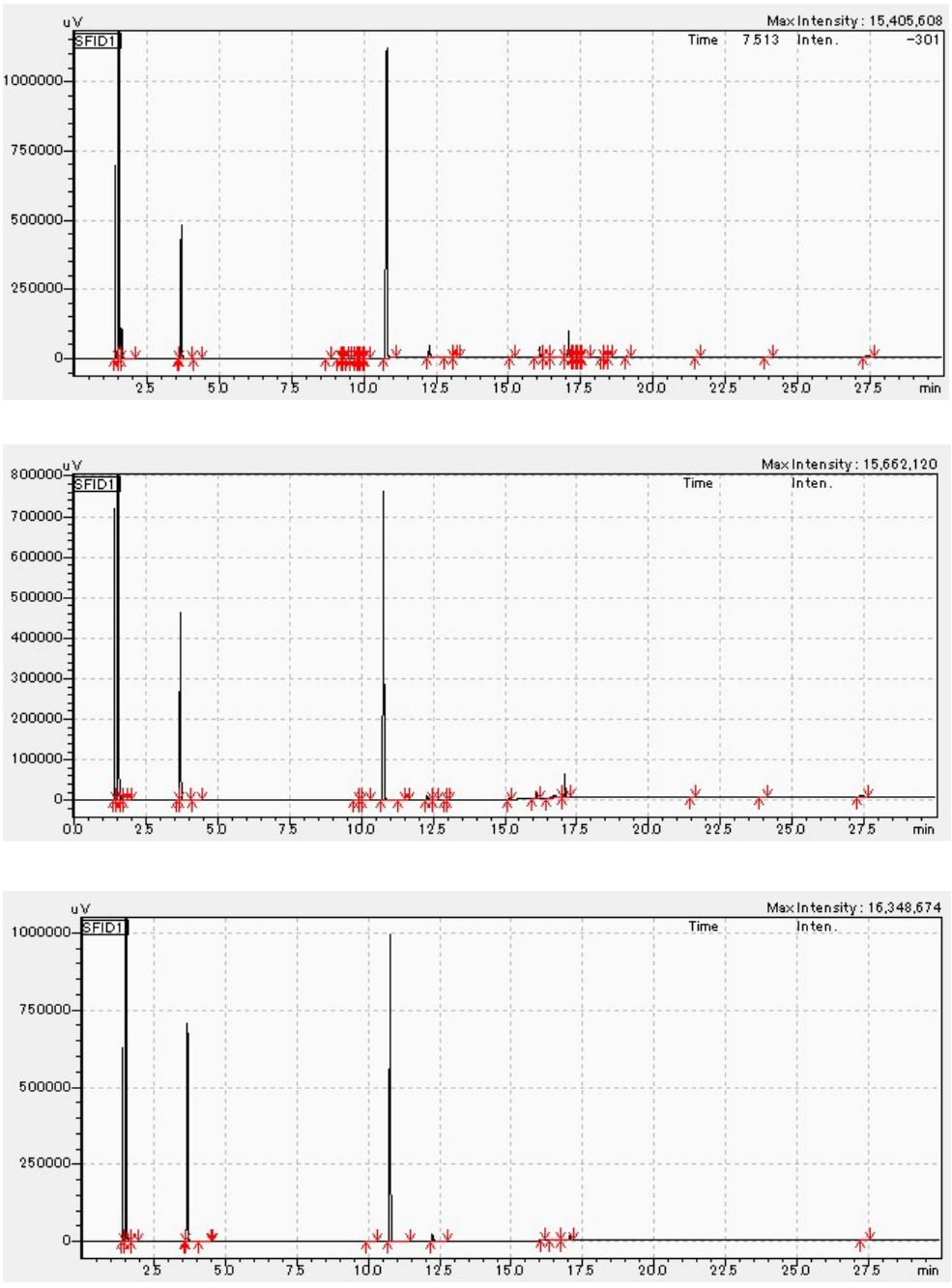


Figure S8. GC chromatograms of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 1 mol % of $FeCl_3$ at 180 °C for (top) 18 h, (middle) 30 h, and (bottom) 48 h.

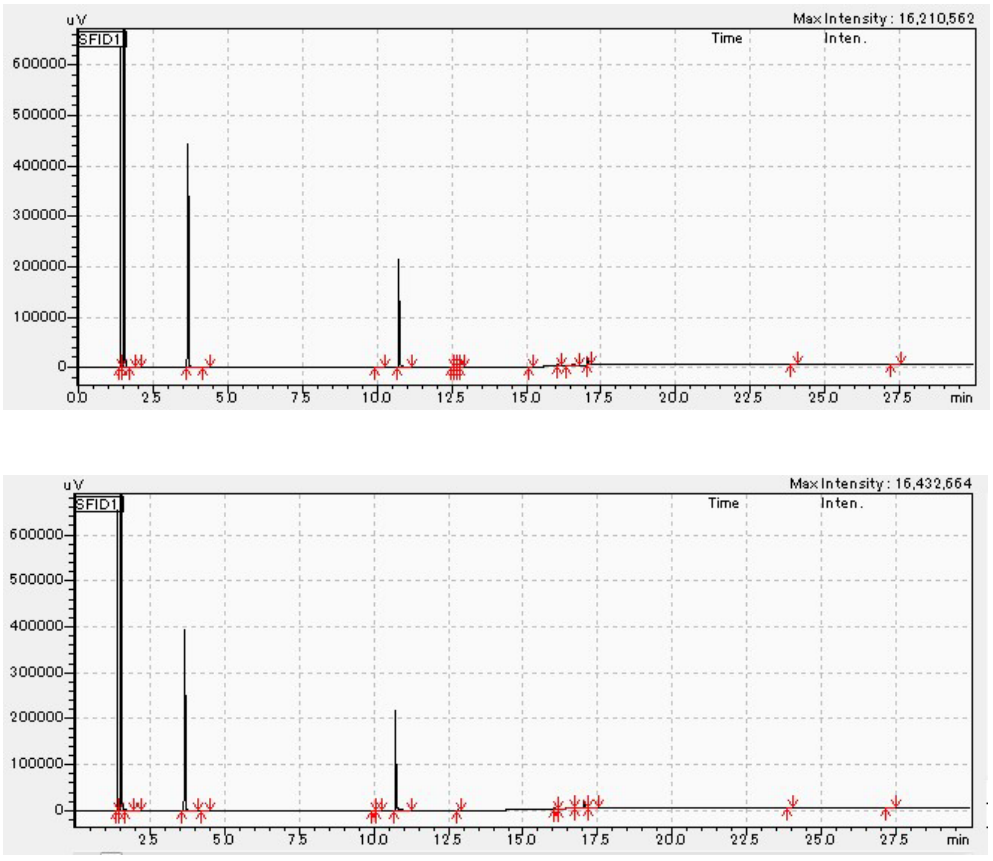


Figure S9. GC chromatograms of resultant mixtures for depolymerization of PET yellow textiles (65 % PET and 35 % cotton) through transesterification with ethanol using 5 mol% of $FeCl_3$ at 180 °C for (top) 12 h and (bottom) 16 h.

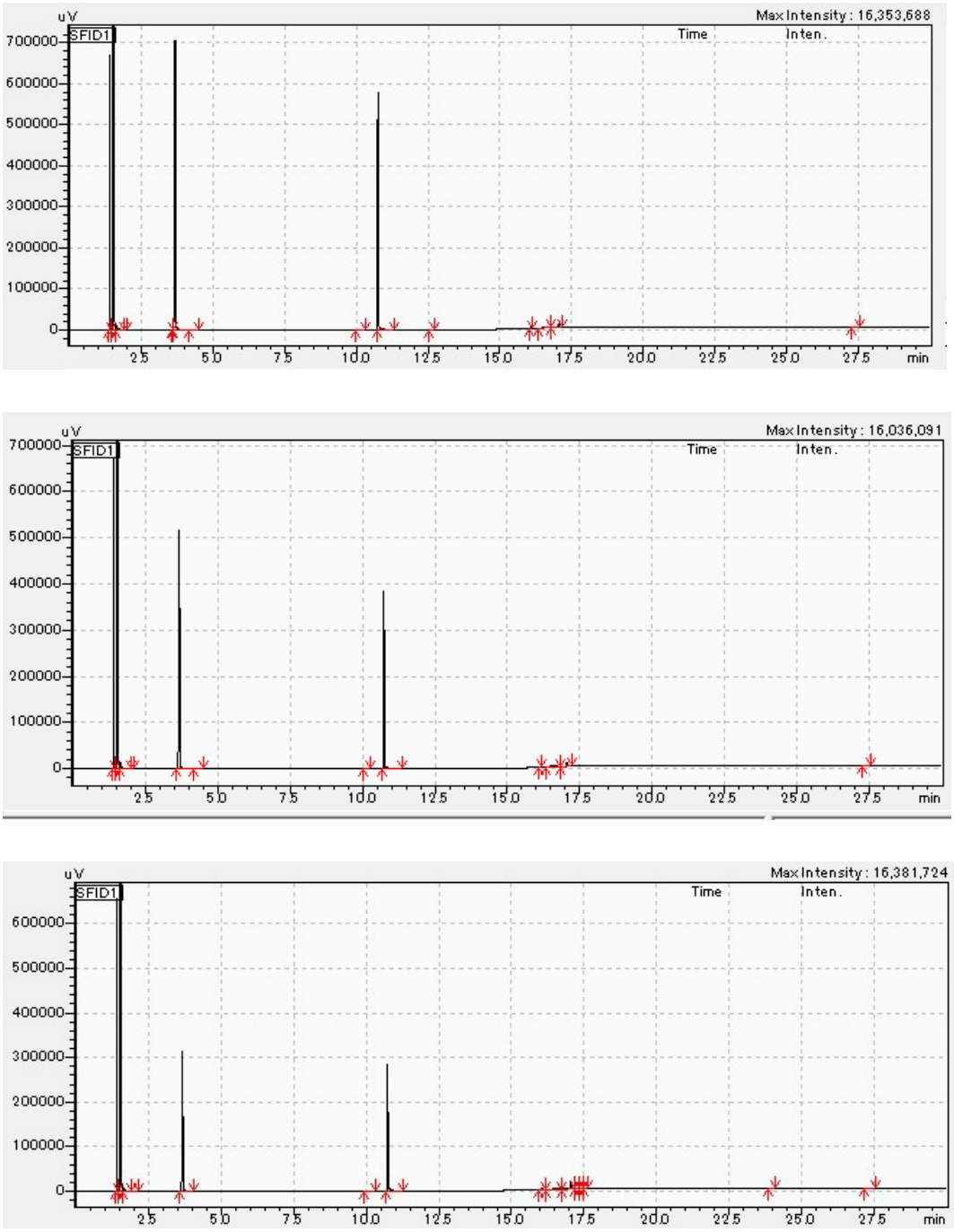


Figure S10. GC chromatograms of resultant mixtures for depolymerization of PET yellow textiles through transesterification with ethanol using 5 mol% of $FeCl_3$ at 180 °C for 18 h (top) white textile (100 % PET), (middle) white textile (100 % PET), and (bottom) black textile (100 % PET).

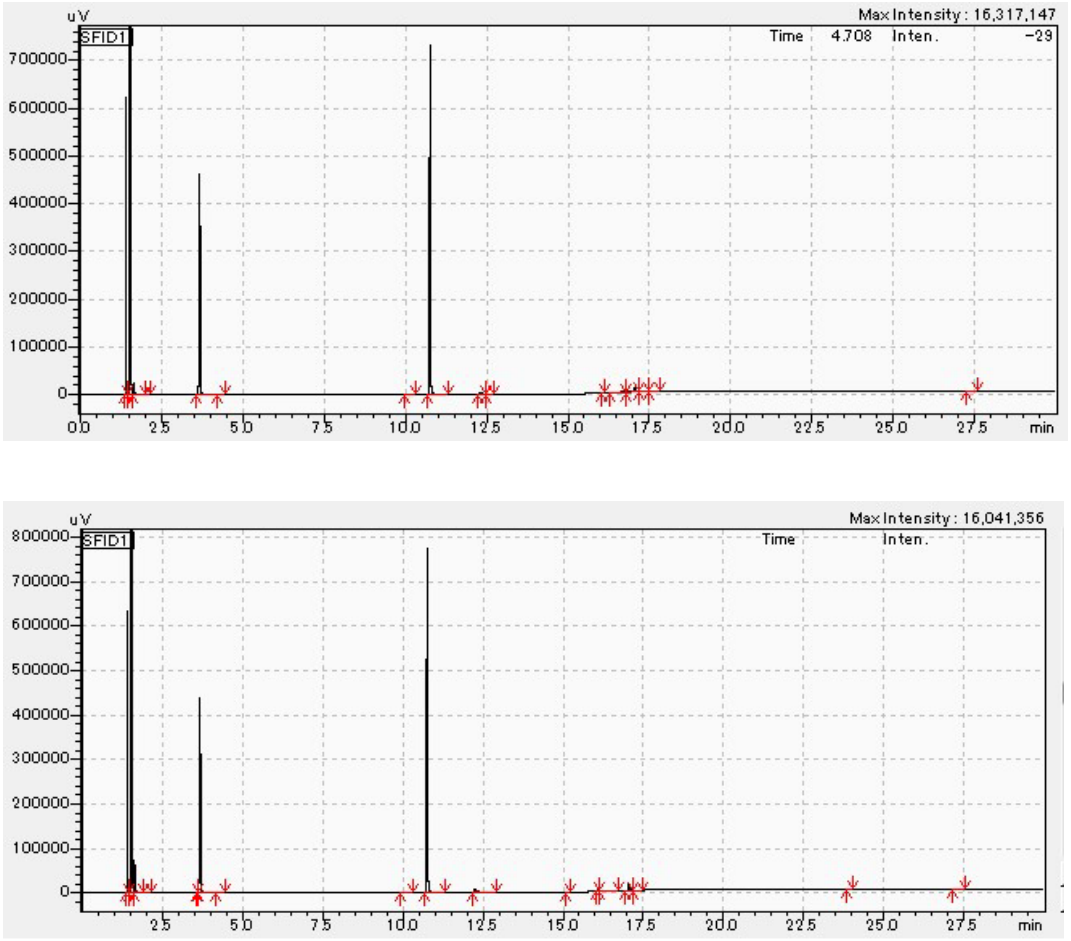


Figure S11. GC chromatograms of resultant mixtures for selective depolymerization of PET sheets through transesterification with ethanol from its mixture with (top) Polyethylene and (bottom) cotton using 5 mol% of $FeCl_3$ at 180 °C for 18 h.

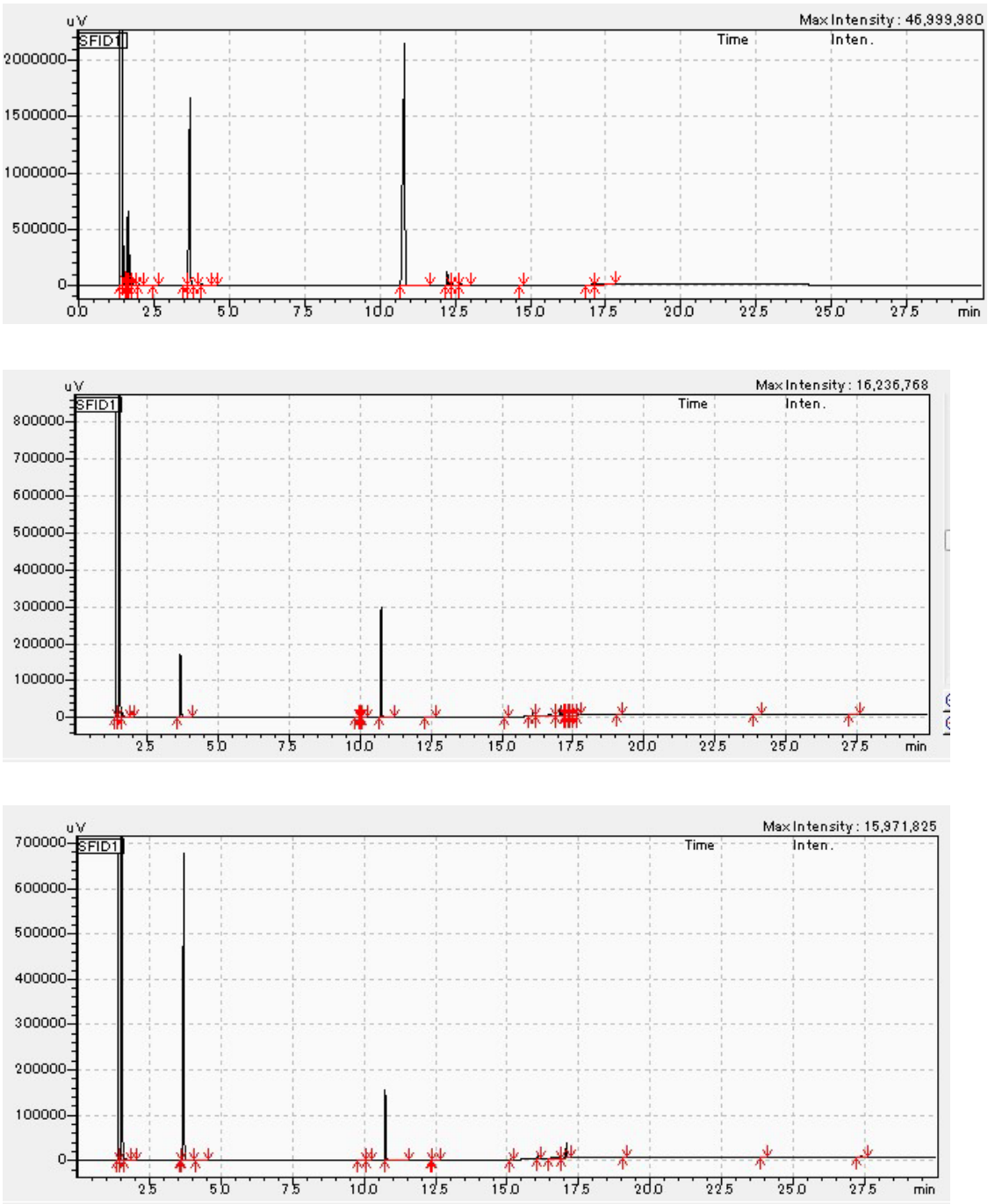


Figure S12. GC chromatograms of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 5 mol % of $FeBr_3$ for 18 h at (top) 180 °C, (middle) 160 °C, and (bottom) 120 °C.

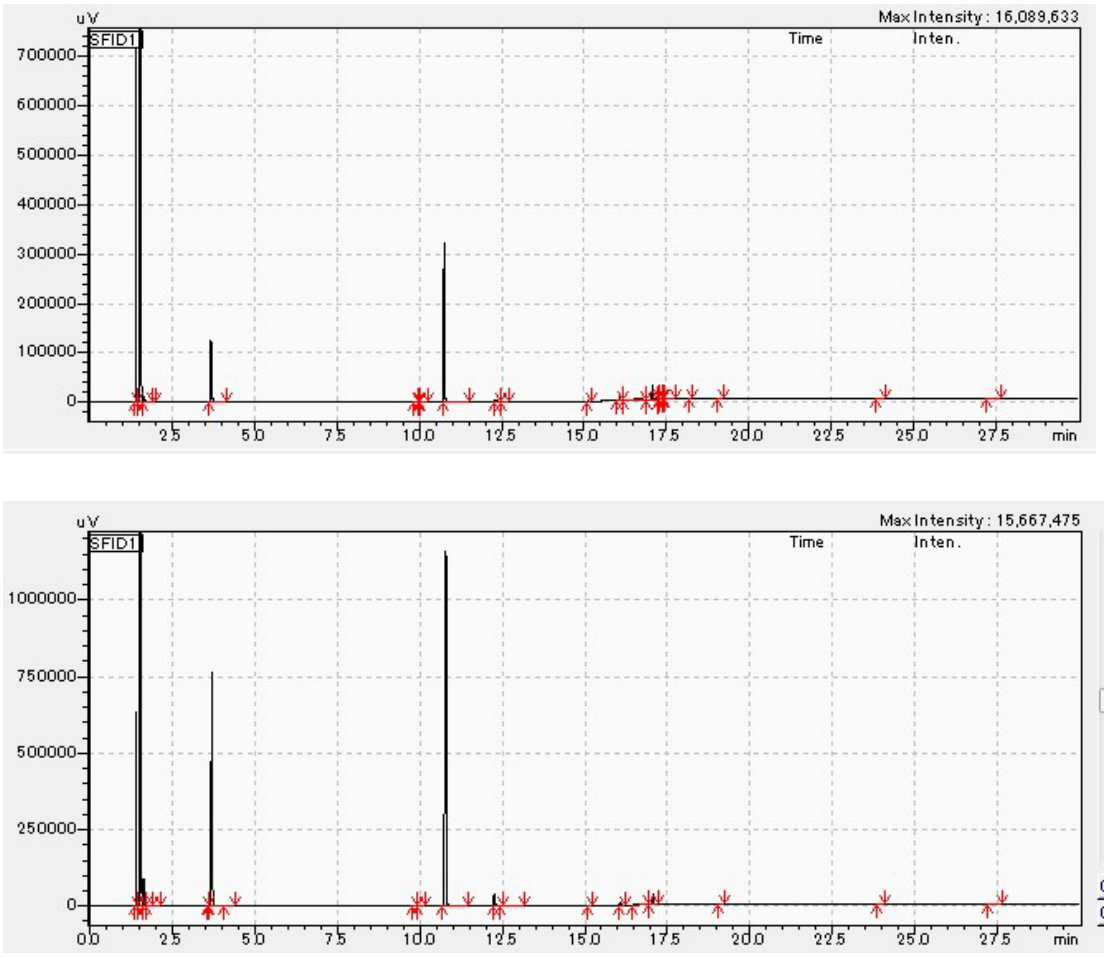
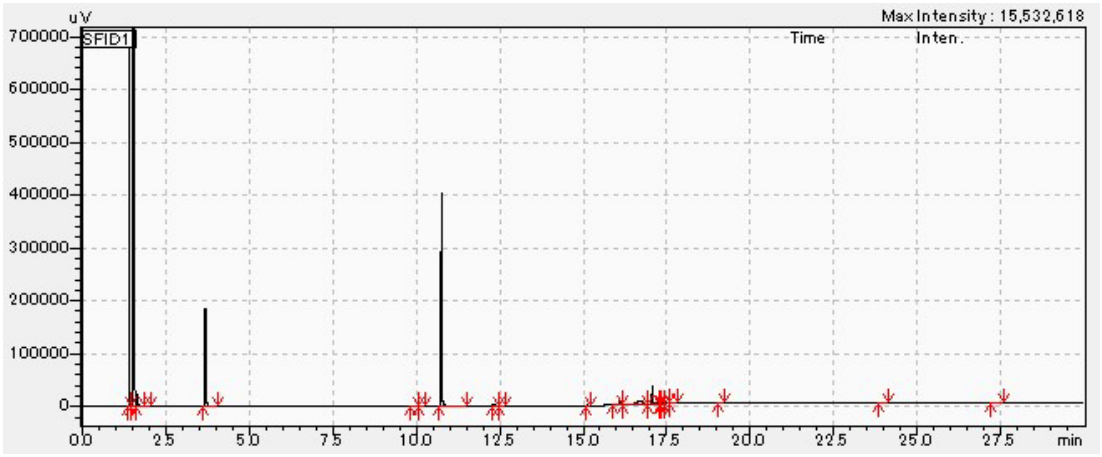
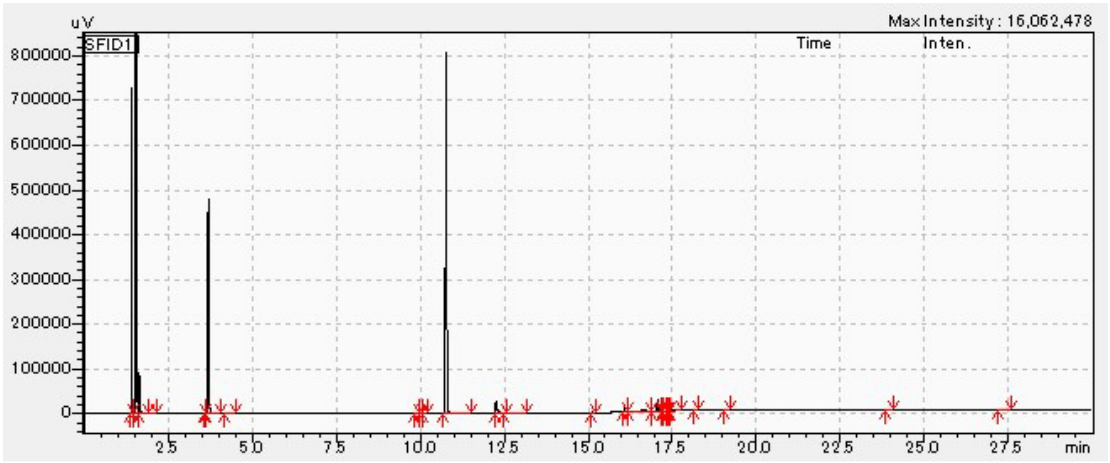


Figure S13. GC chromatograms of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 3 mol % of $FeBr_3$ at 180 °C for (top) 18 h and (bottom) 30 h.





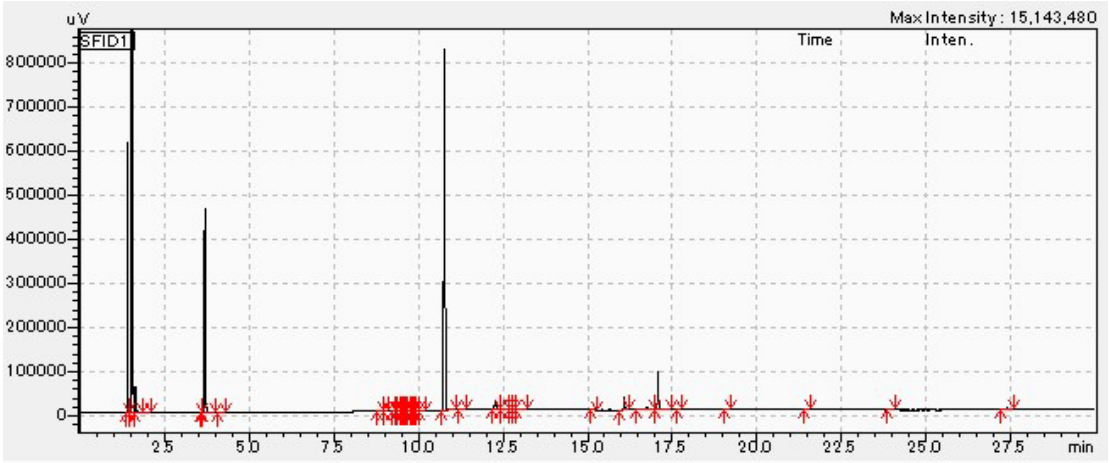


Figure S14. GC chromatograms of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 1 mol % of $FeBr_3$ at 180 °C for (top) 18 h, (middle) 30 h, and (bottom) 48 h.

3. Selected ^{13}C NMR spectra of the resultant depolymerization mixtures.

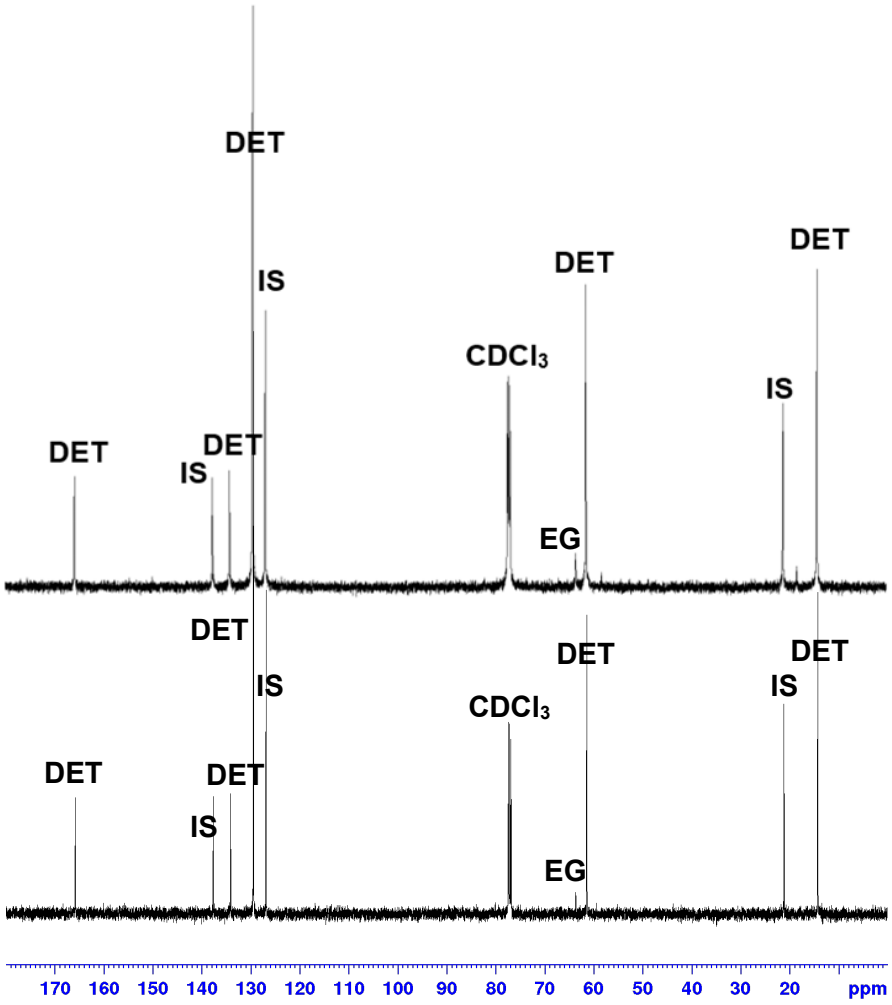


Figure S15. ^{13}C NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 5 mol % of $FeCl_3$ at 180 °C for (top) 18 h and (bottom) 12 h. [Reaction mixtures after removal of volatiles]

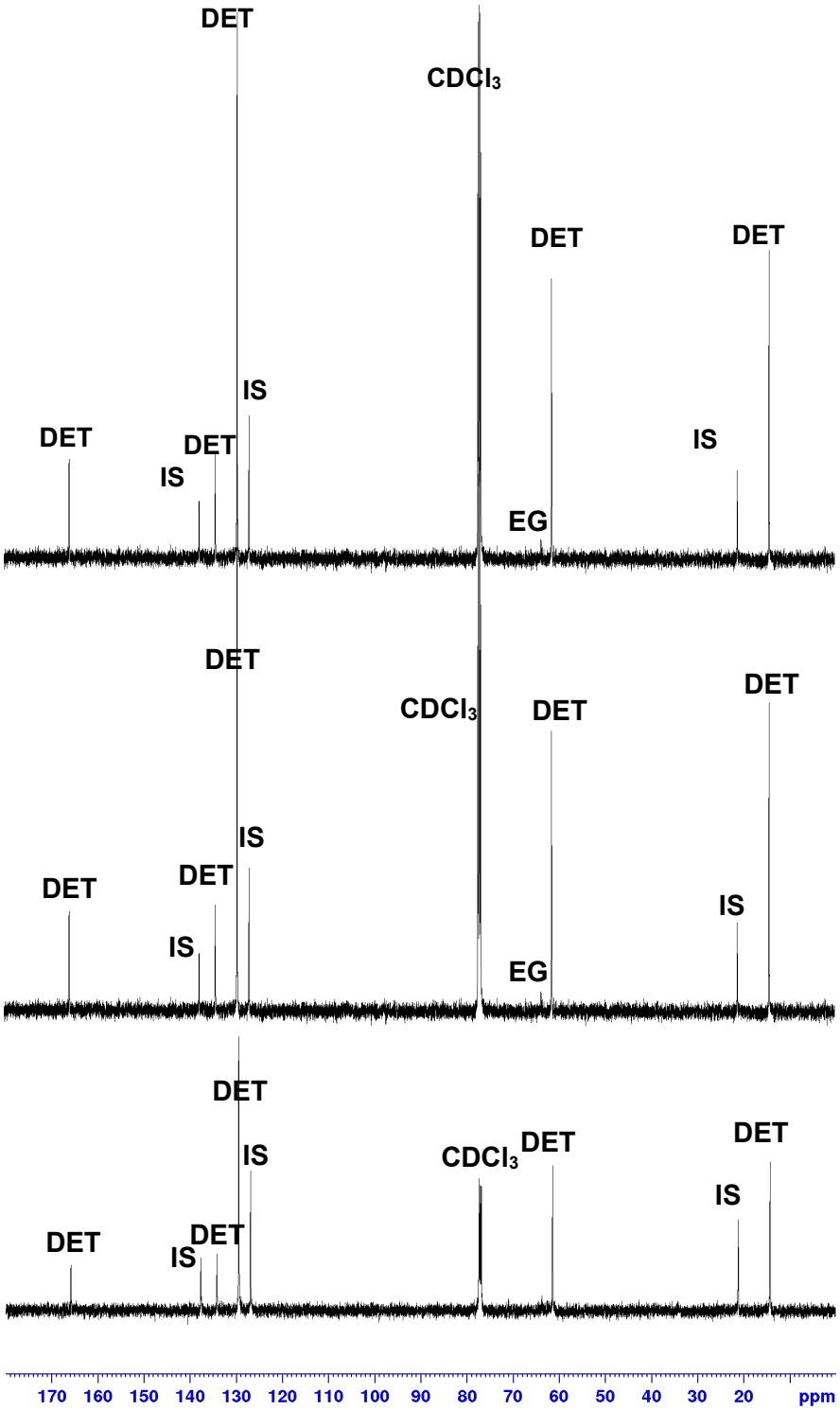


Figure S16. ^{13}C NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 5 mol % of $FeCl_3$ at 160 °C for (top) 18 h, (middle) 18 h, and (bottom) 24 h. [Reaction mixtures after removal of volatiles]

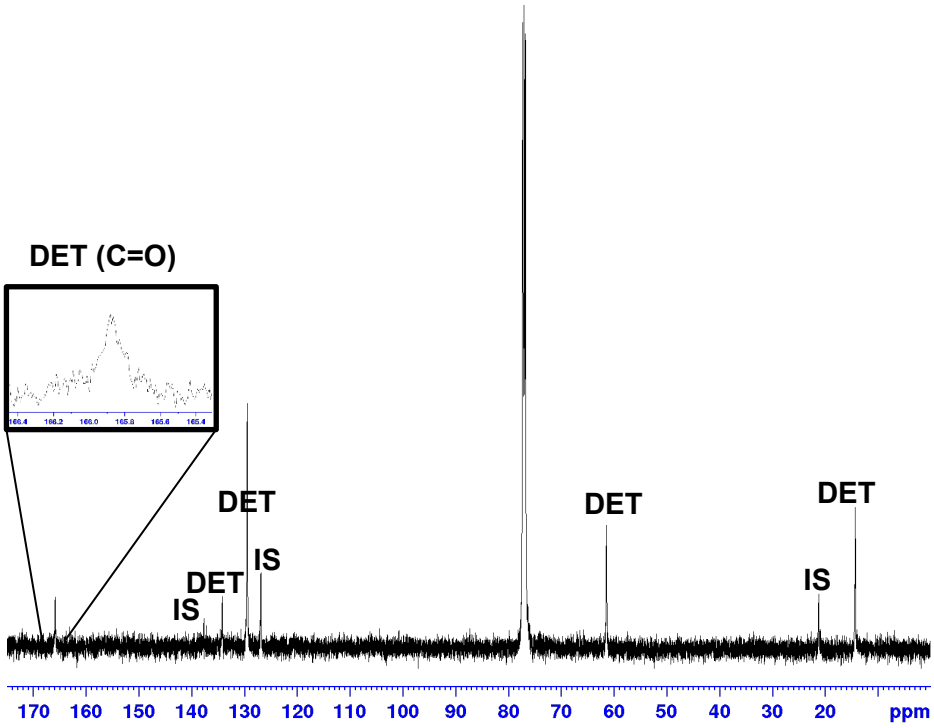


Figure S17. ^{13}C NMR spectrum (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 5 mol % of $FeCl_3$ at 120 °C for 18 h. [Reaction mixtures after removal of volatiles]

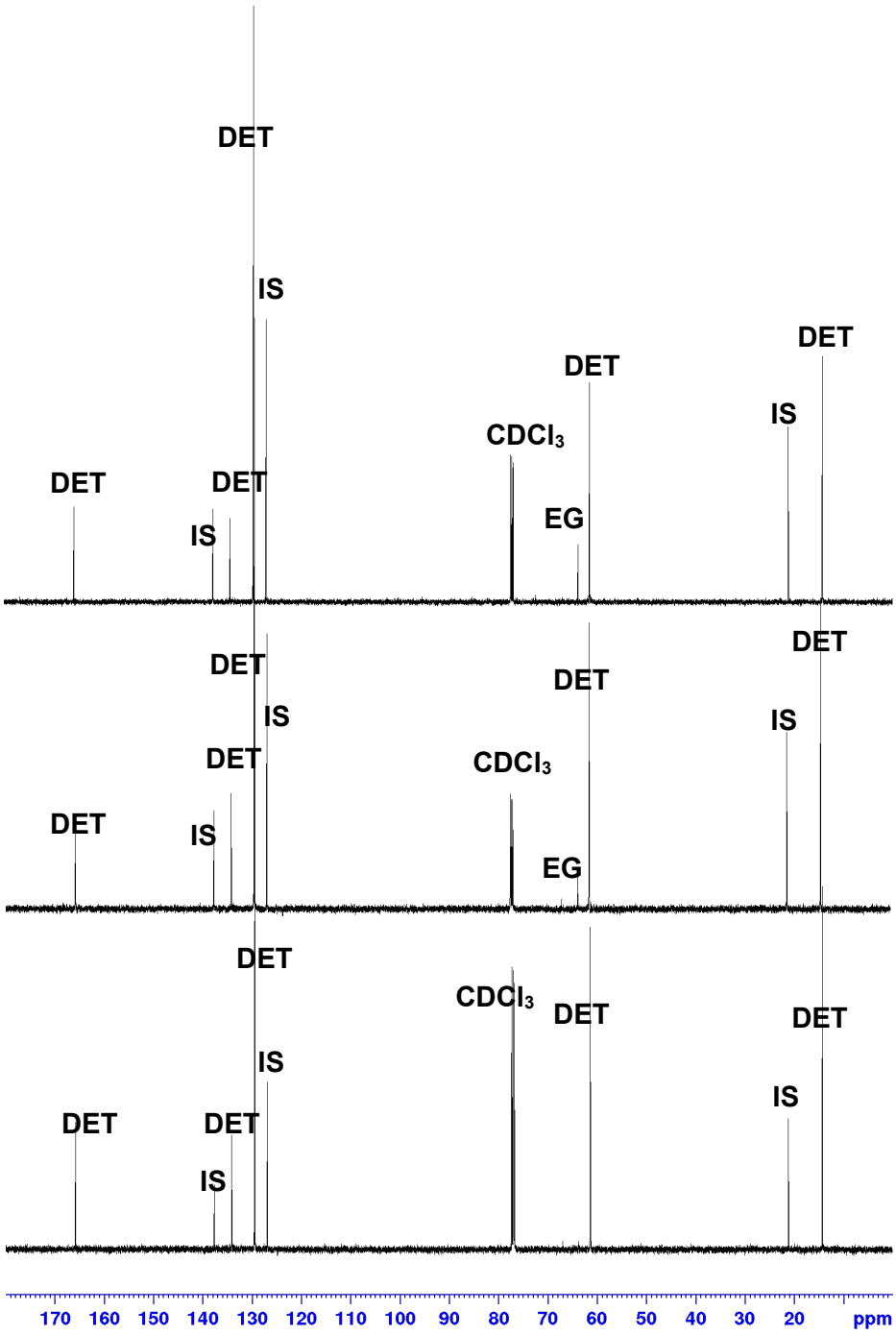


Figure S18. ^{13}C NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 3 mol % of $FeCl_3$ at 180 °C for (top) 18 h, (middle) 24 h, and (bottom) 30 h. [Reaction mixtures after removal of volatiles]

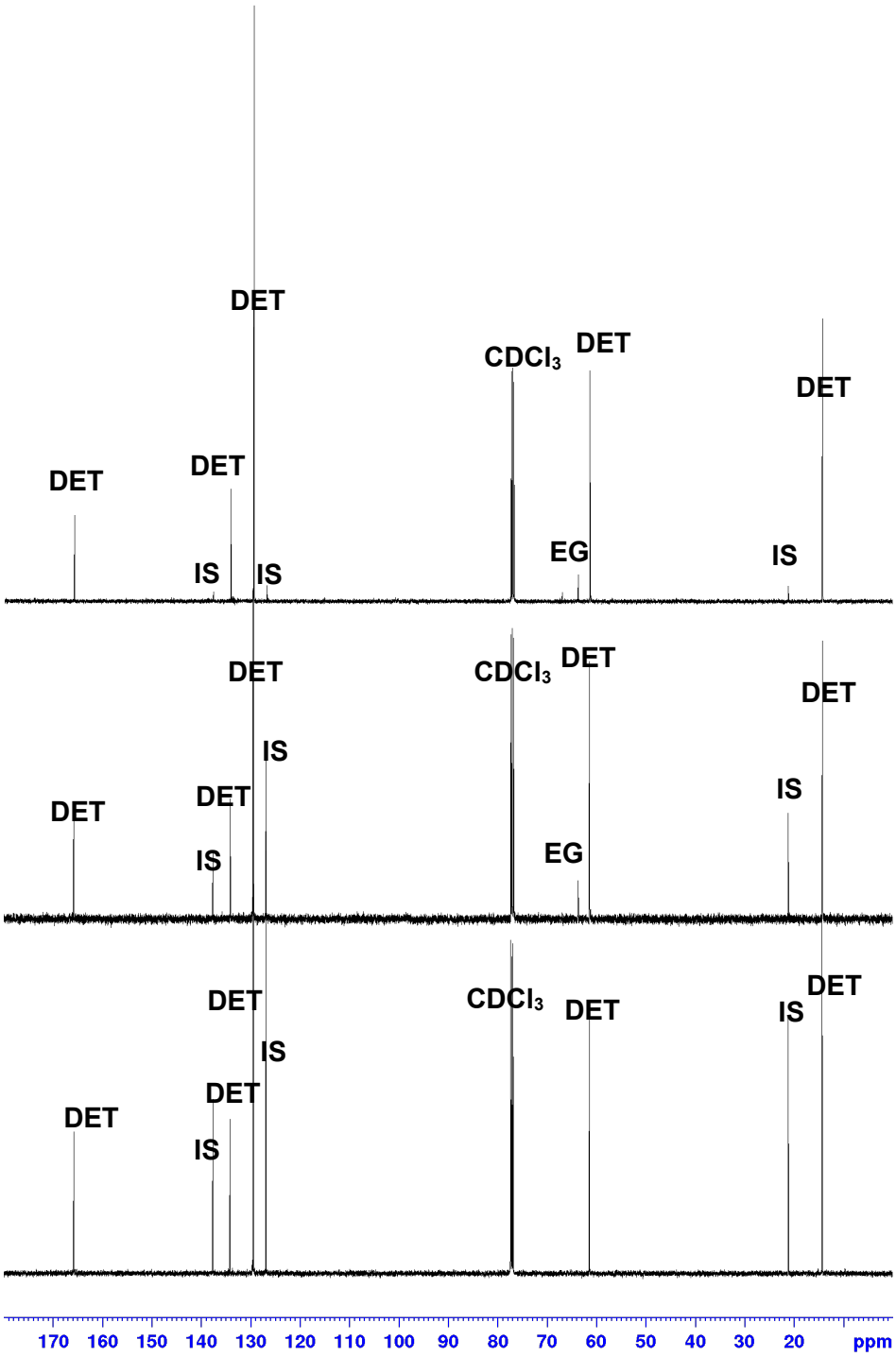


Figure S19. ^{13}C NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 1 mol % of $FeCl_3$ at 180 °C for (top) 18 h, (middle) 30 h, and (bottom) 48 h. [Reaction mixtures after removal of volatiles]

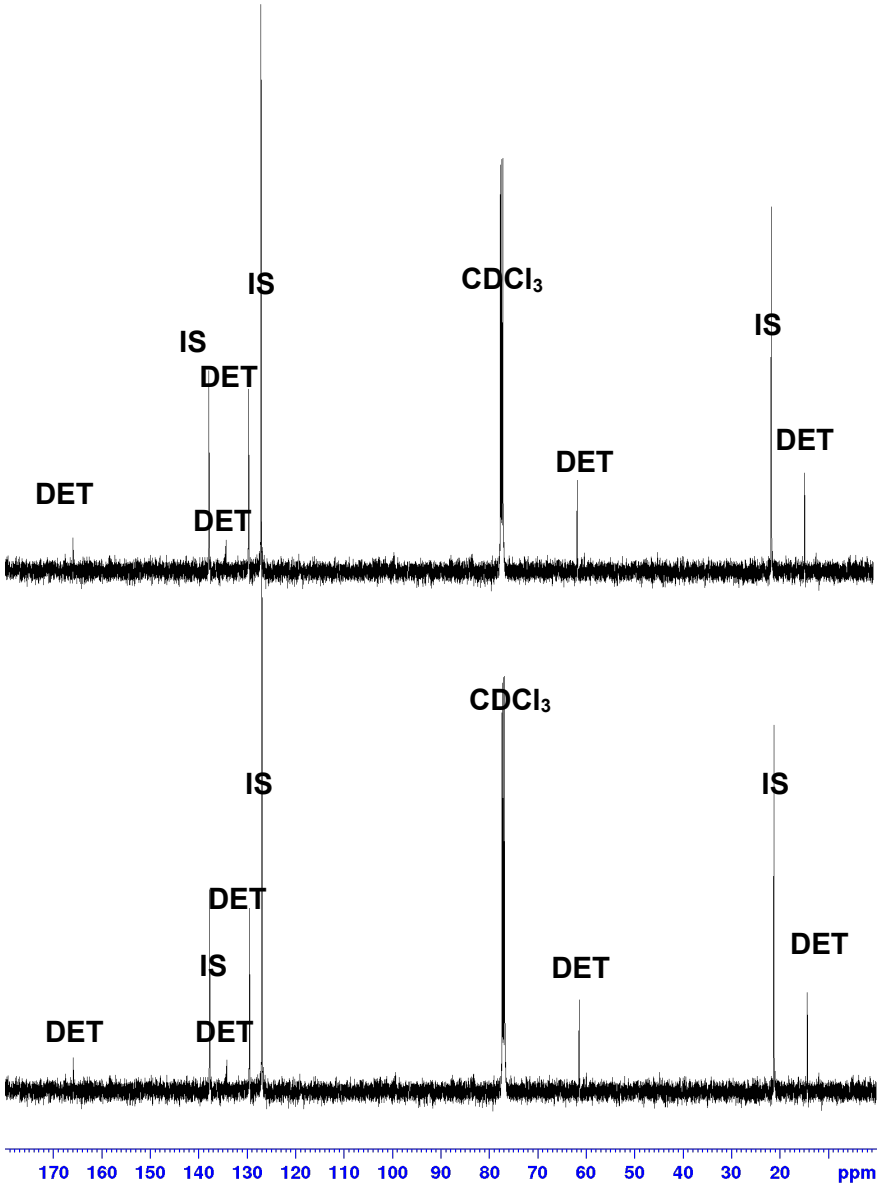


Figure S20. ^{13}C NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET yellow textiles (65 % PET and 35 % cotton) through transesterification with ethanol using 5 mol% of $FeCl_3$ at 180 °C for (top) 12 h and (bottom) 16 h. [Reaction mixtures after removal of volatiles]

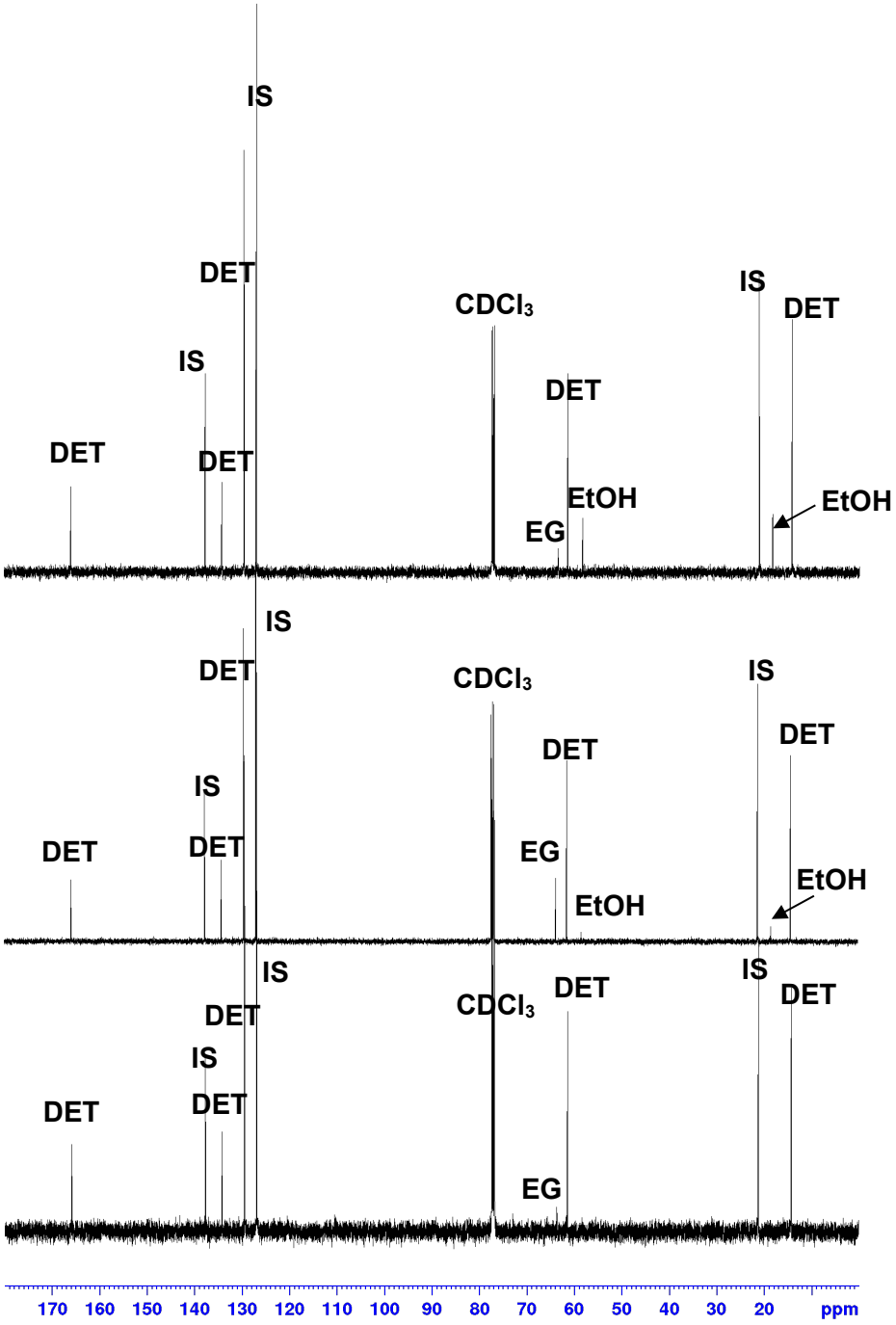


Figure S21. ^{13}C NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET yellow textiles through transesterification with ethanol using 5 mol% of $FeCl_3$ at 180 °C for 18 h (top) white textile (100 % PET), (middle) white textile (100 % PET), and (bottom) black textile (100 % PET). [Reaction mixtures after removal of volatiles]

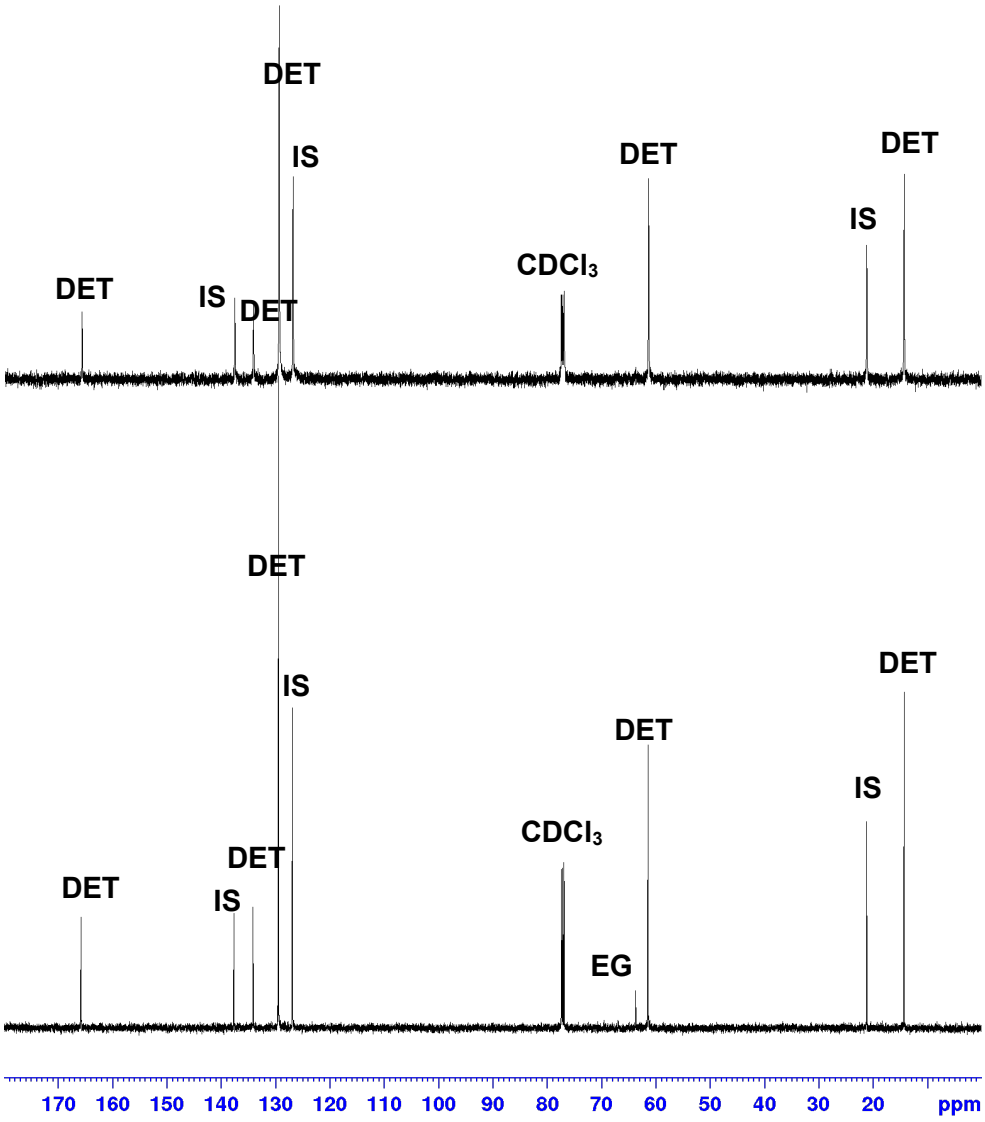


Figure S22. ^{13}C NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for selective depolymerization of PET sheets through transesterification with ethanol using 5 mol% of $FeCl_3$ at 180 °C for 18 h from its mixture with (top) Polyethylene and (bottom) cotton. [Reaction mixtures after removal of volatiles]

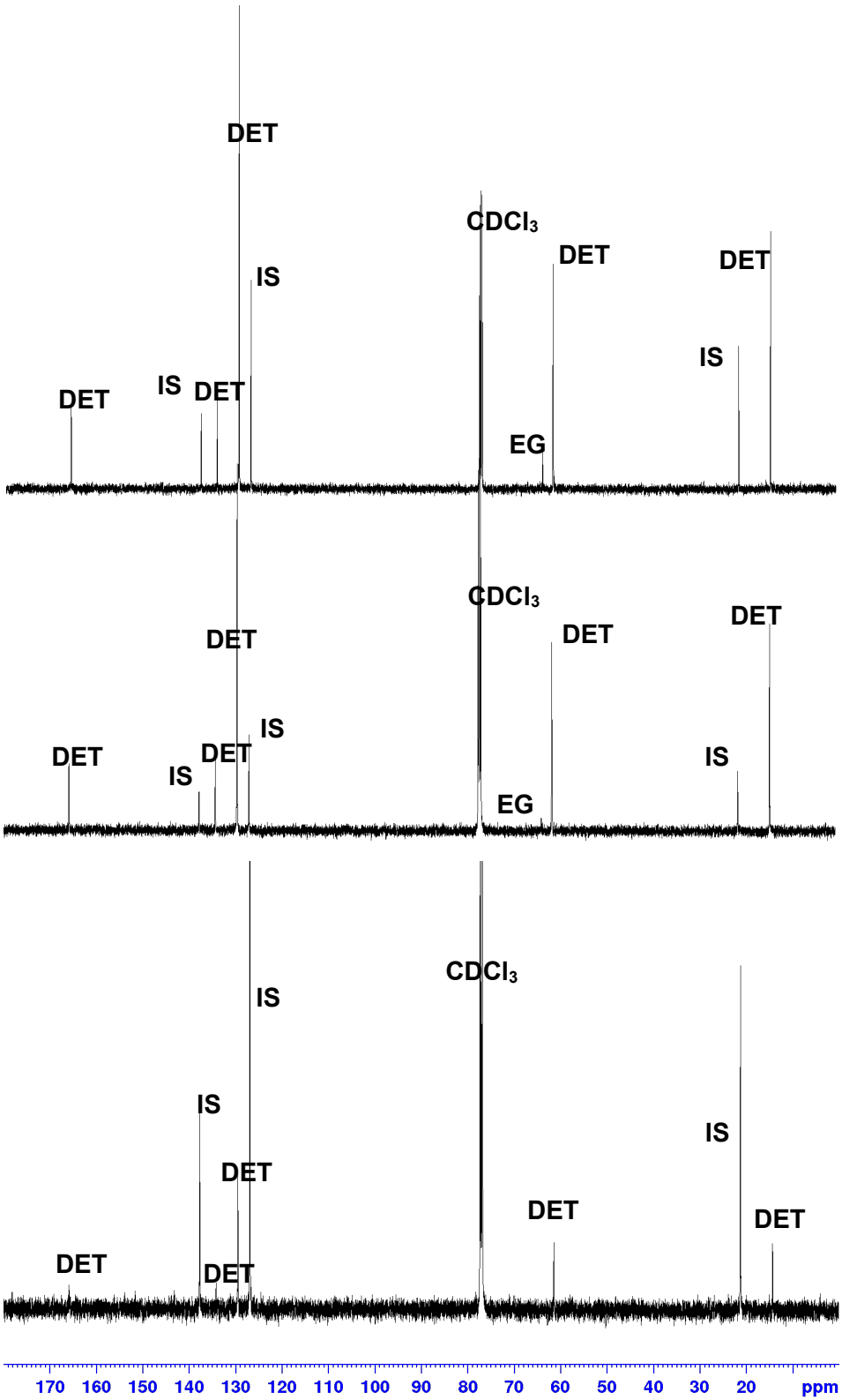


Figure S23. ^{13}C NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 5 mol % of $FeBr_3$ for 18 h at (top) 180 °C, (middle) 160 °C, and (bottom) 120 °C. [Reaction mixtures after removal of volatiles]

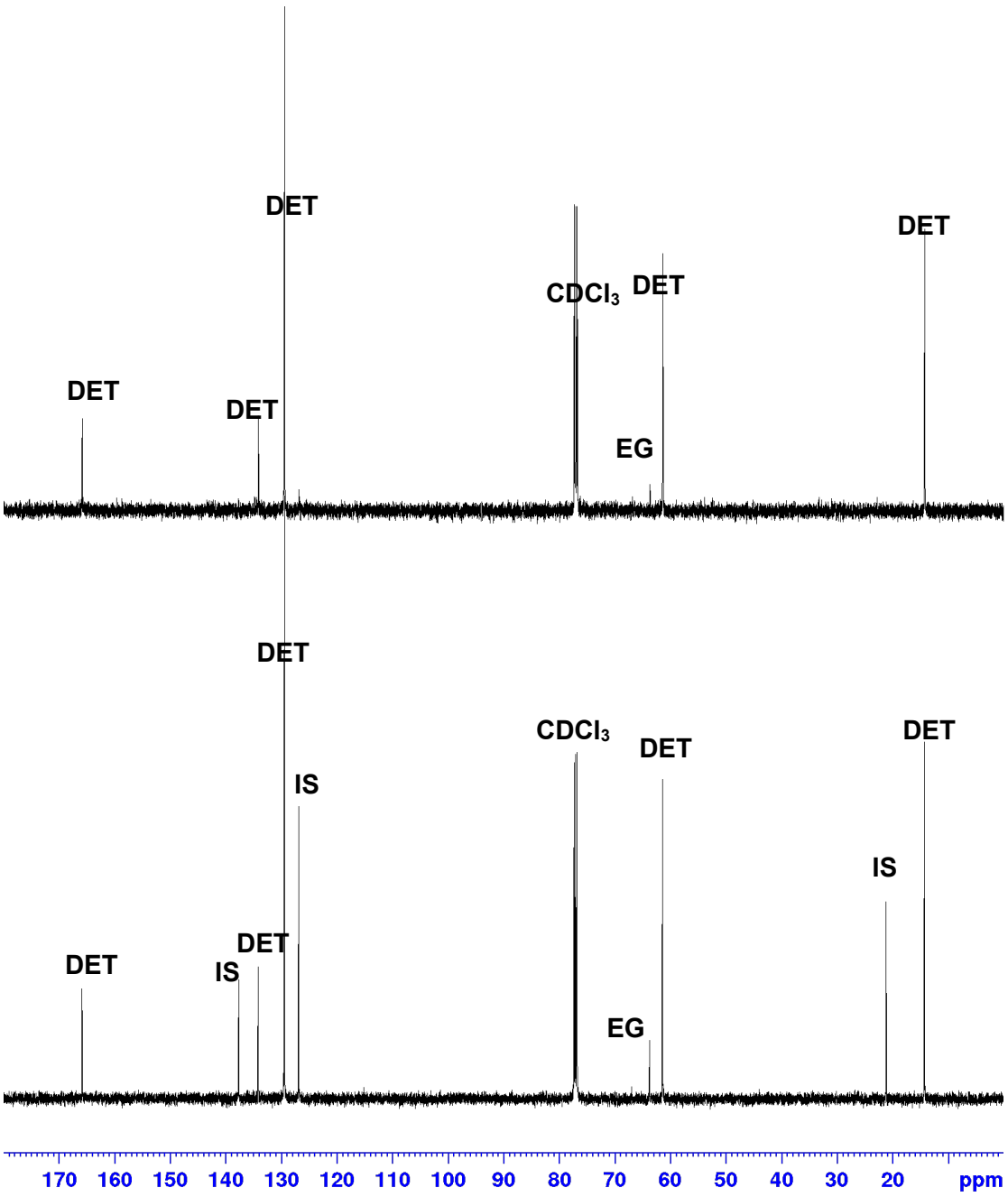


Figure S24. ^{13}C NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 3 mol % of $FeBr_3$ at 180 °C for (top) 18 h and (bottom) 30 h. [Reaction mixtures after removal of volatiles]

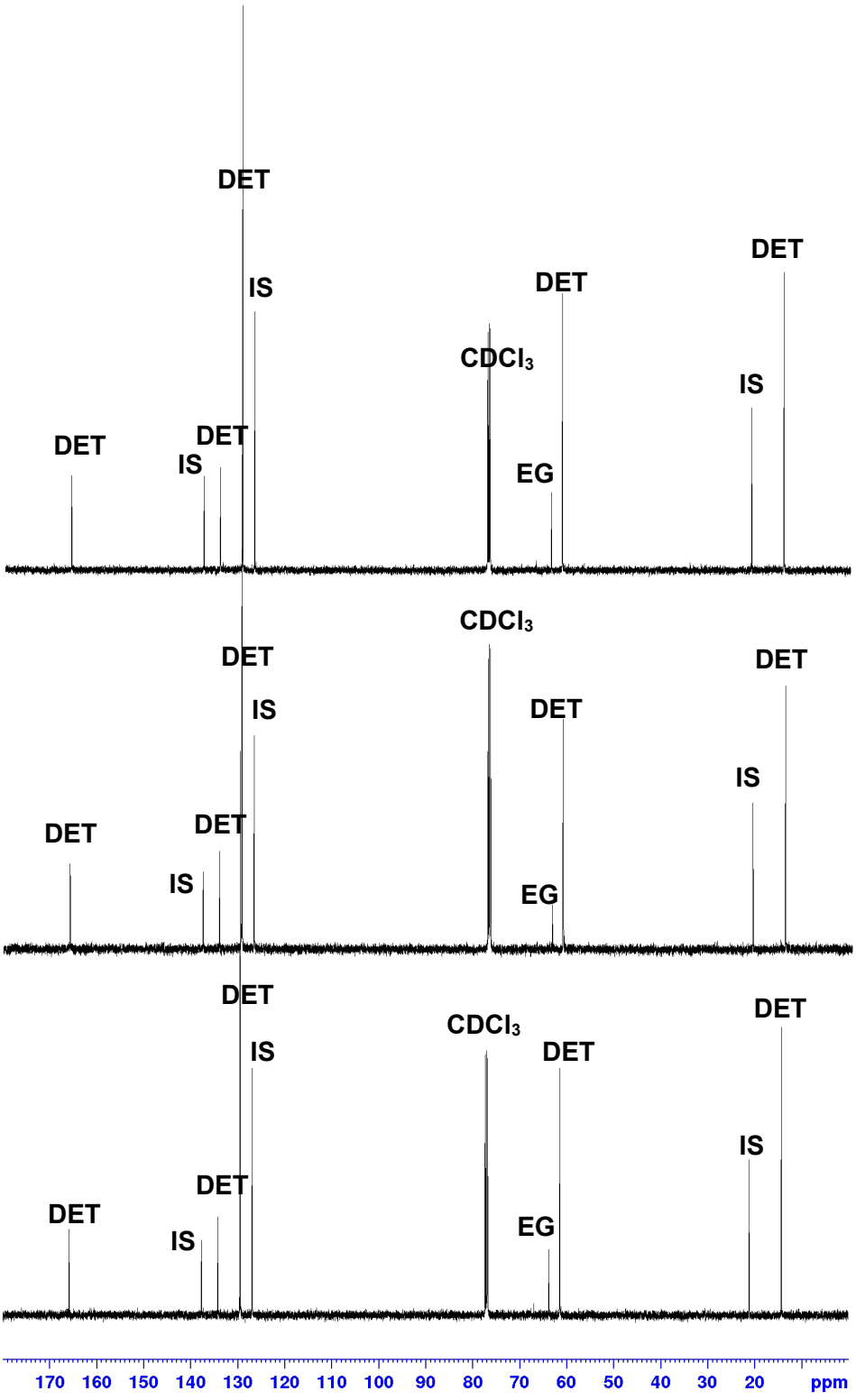


Figure S25. ^{13}C NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 1 mol % of $FeBr_3$ at 180 °C for (top) 18 h, (middle) 30 h, and (bottom) 48 h.

4. Selected ^{1}H NMR spectra of the resultant depolymerization mixtures

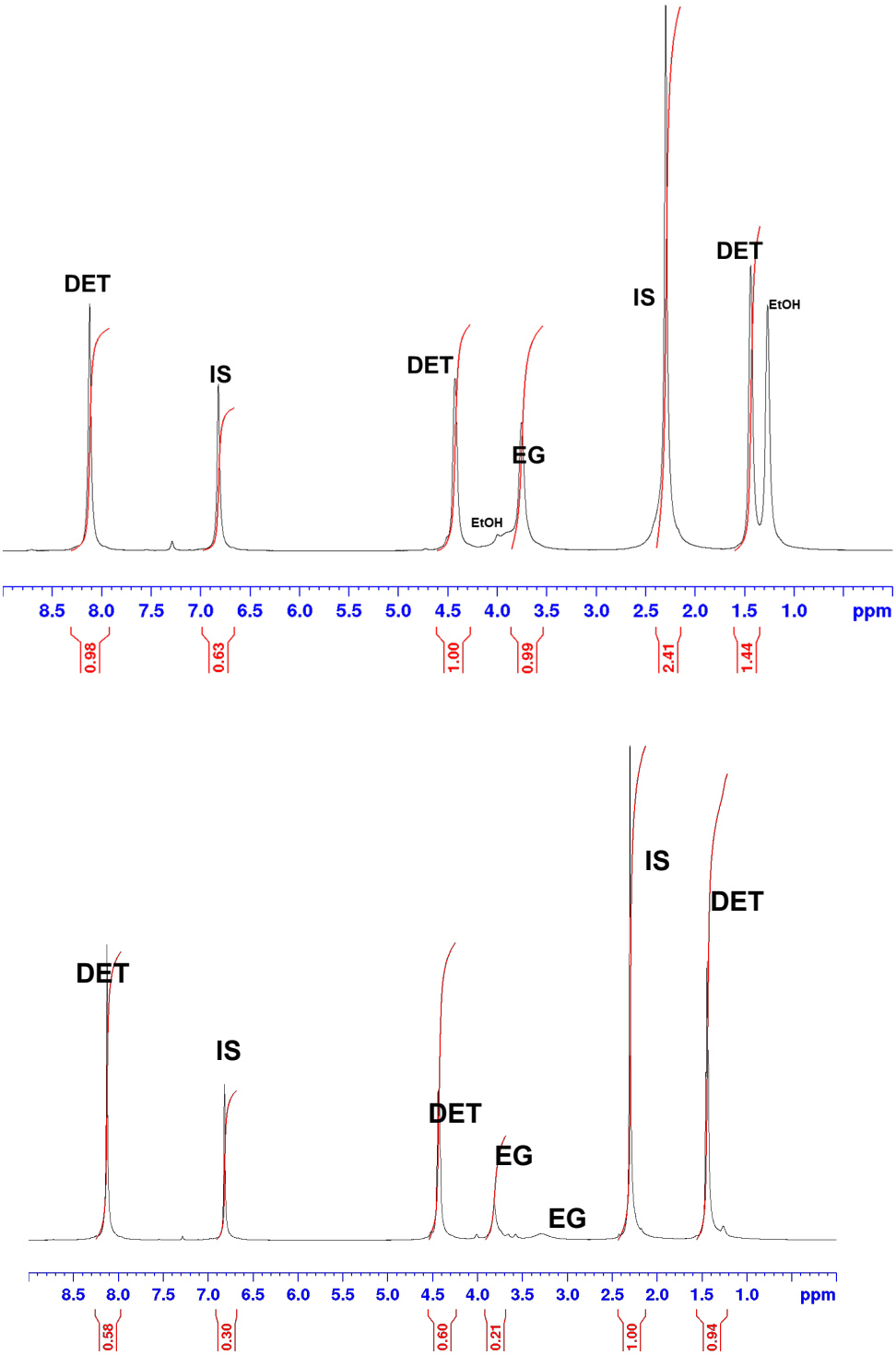


Figure S26. ^{1}H NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 5 mol % of $FeCl_3$ at 180 °C for (top) 18 h and (bottom) 12 h. [Reaction mixtures after removal of volatiles]

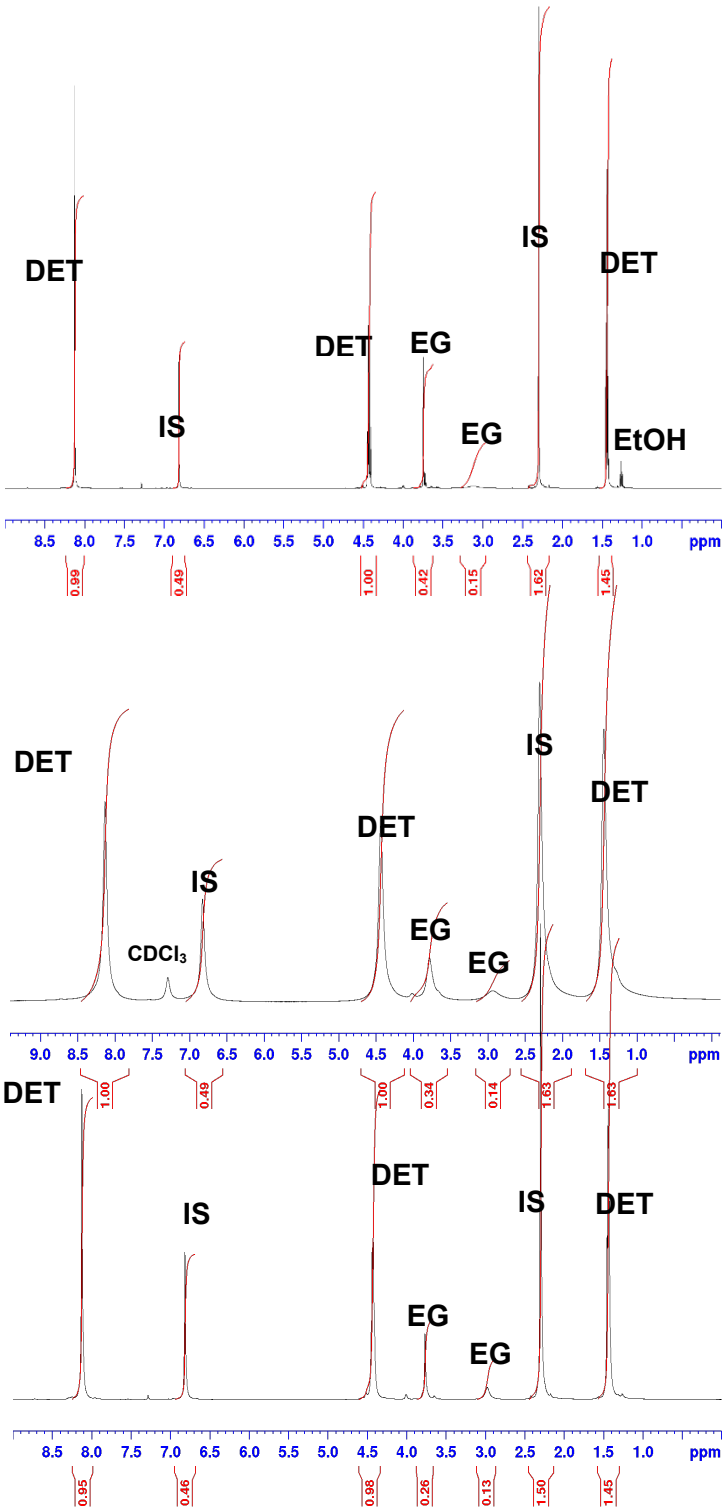


Figure S27. ^{1}H NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 5 mol % of $FeCl_3$ at 160 °C for (top) 18 h, (middle) 18 h, and (bottom) 24 h. [Reaction mixtures after removal of volatiles]

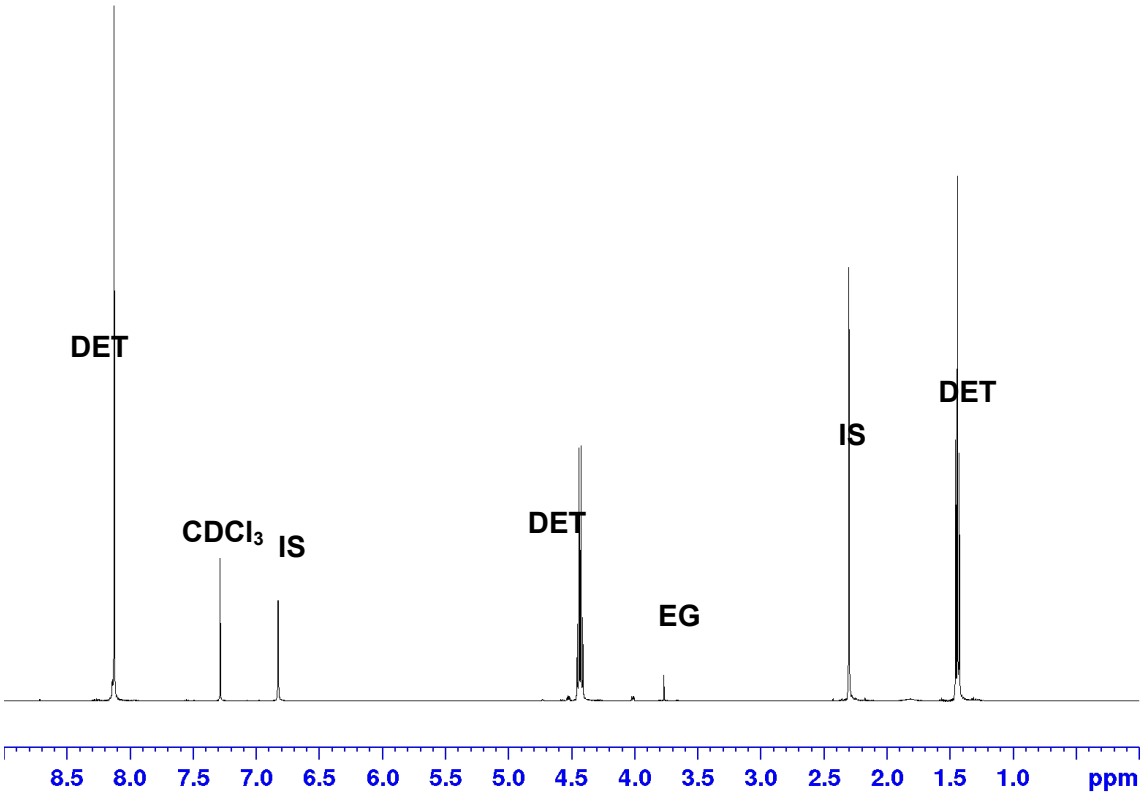


Figure S28. ^{1}H NMR spectrum (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 5 mol % of $FeCl_3$ at 120 °C for 18 h. [Reaction mixtures after removal of volatiles]

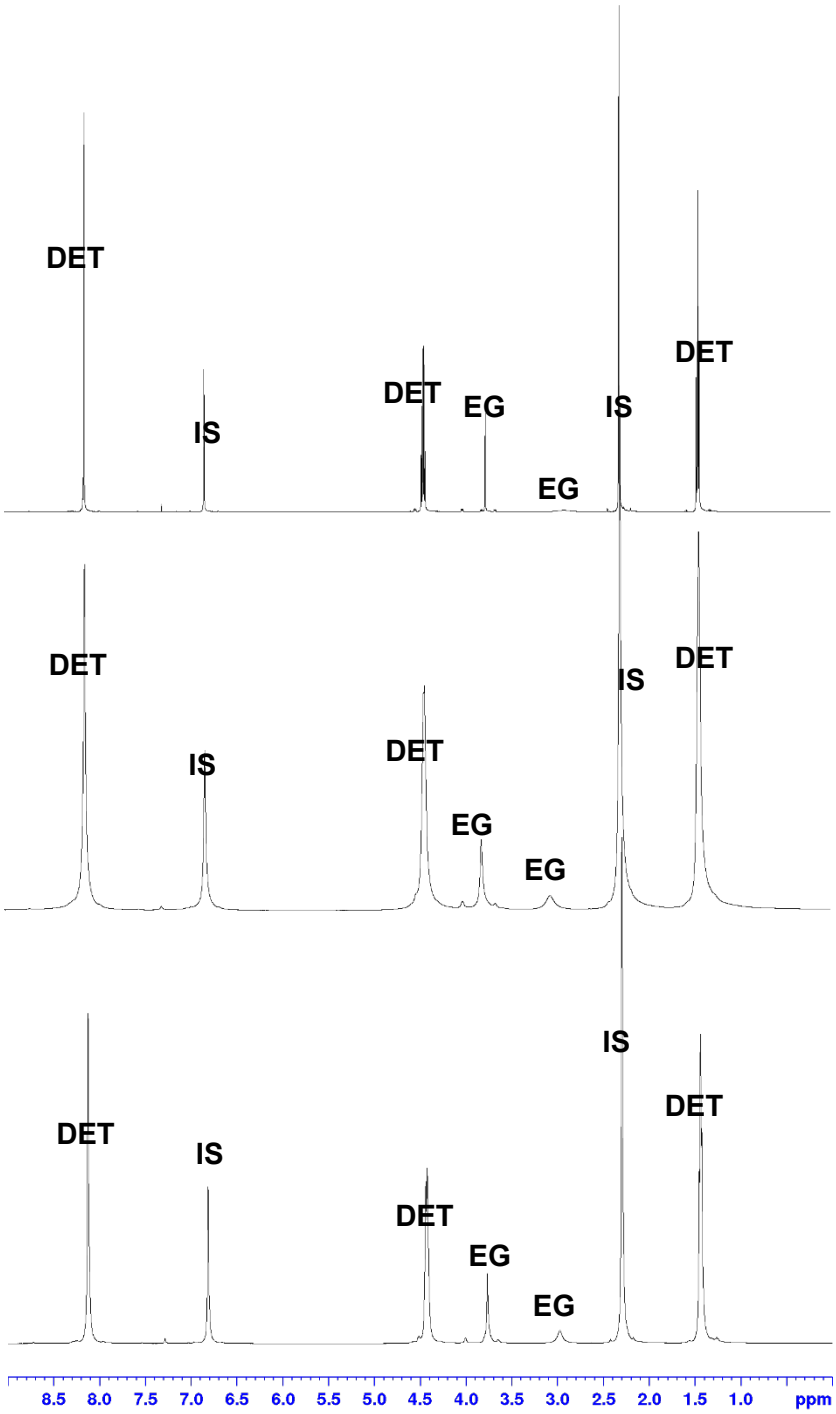


Figure S29. ^{1}H NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 3 mol % of $FeCl_3$ at 180 °C for (top) 18 h, (middle) 24 h, and (bottom) 30 h. [Reaction mixtures after removal of volatiles]

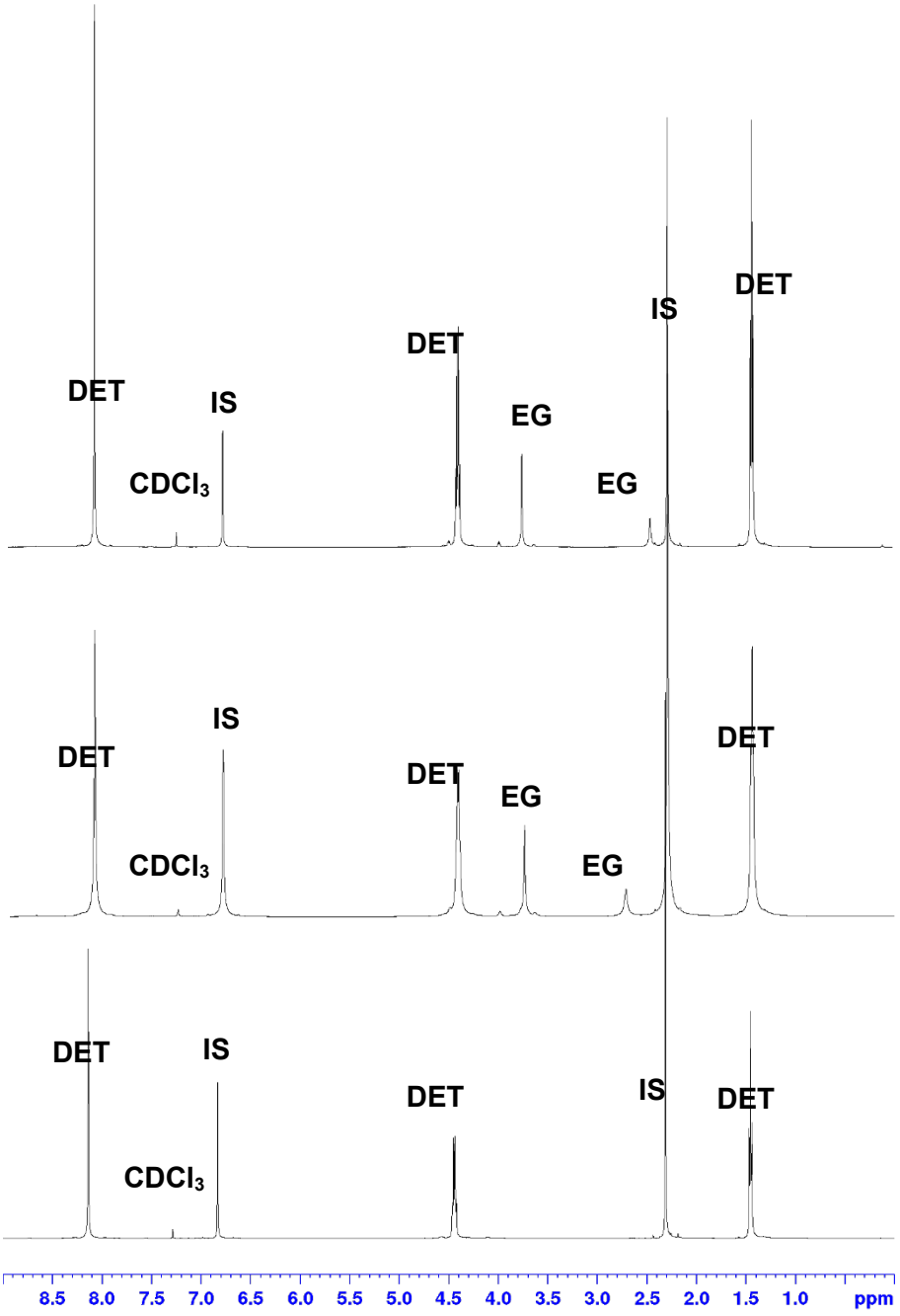


Figure S30. ^{1}H NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 1 mol % of $FeCl_3$ at 180 °C for (top) 18 h, (middle) 30 h, and (bottom) 48 h. [Reaction mixtures after removal of volatiles]

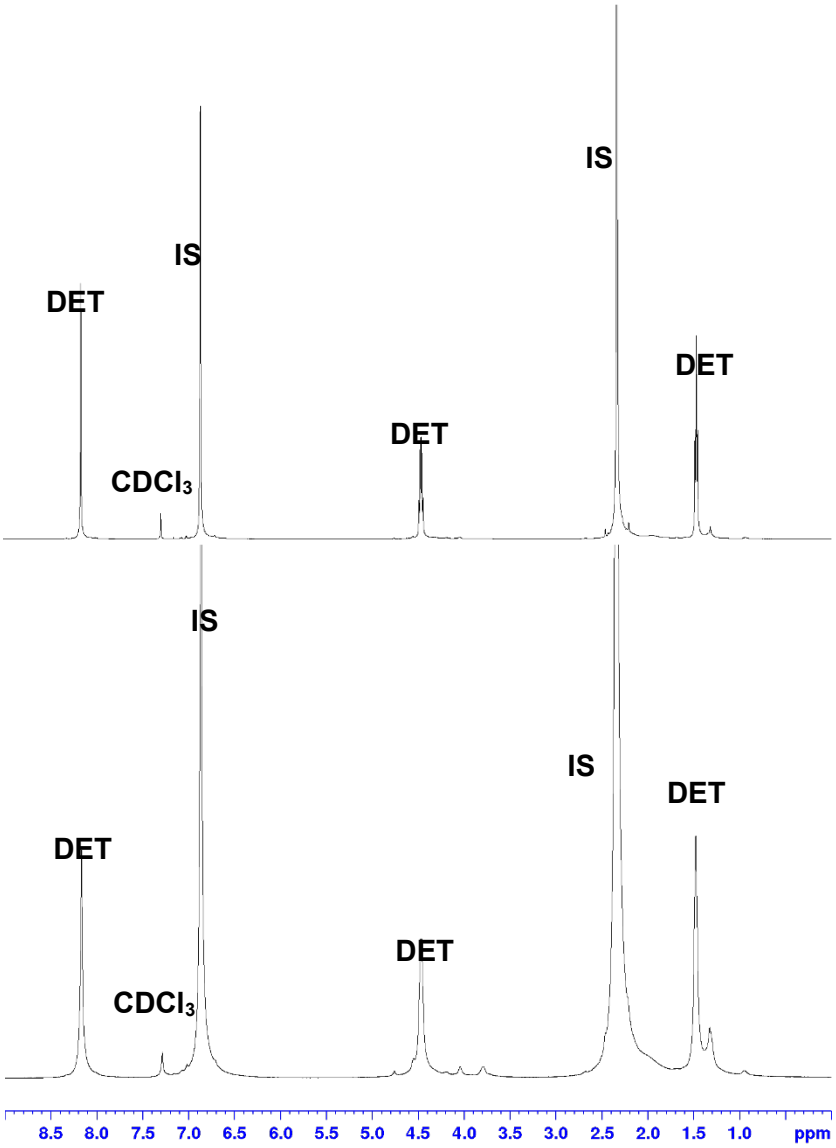


Figure S31. ^{1}H NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET yellow textiles (65 % PET and 35 % cotton) through transesterification with ethanol using 5 mol% of $FeCl_3$ at 180 °C for (top) 12 h and (bottom) 16 h. [Reaction mixtures after removal of volatiles and ethylene glycol]

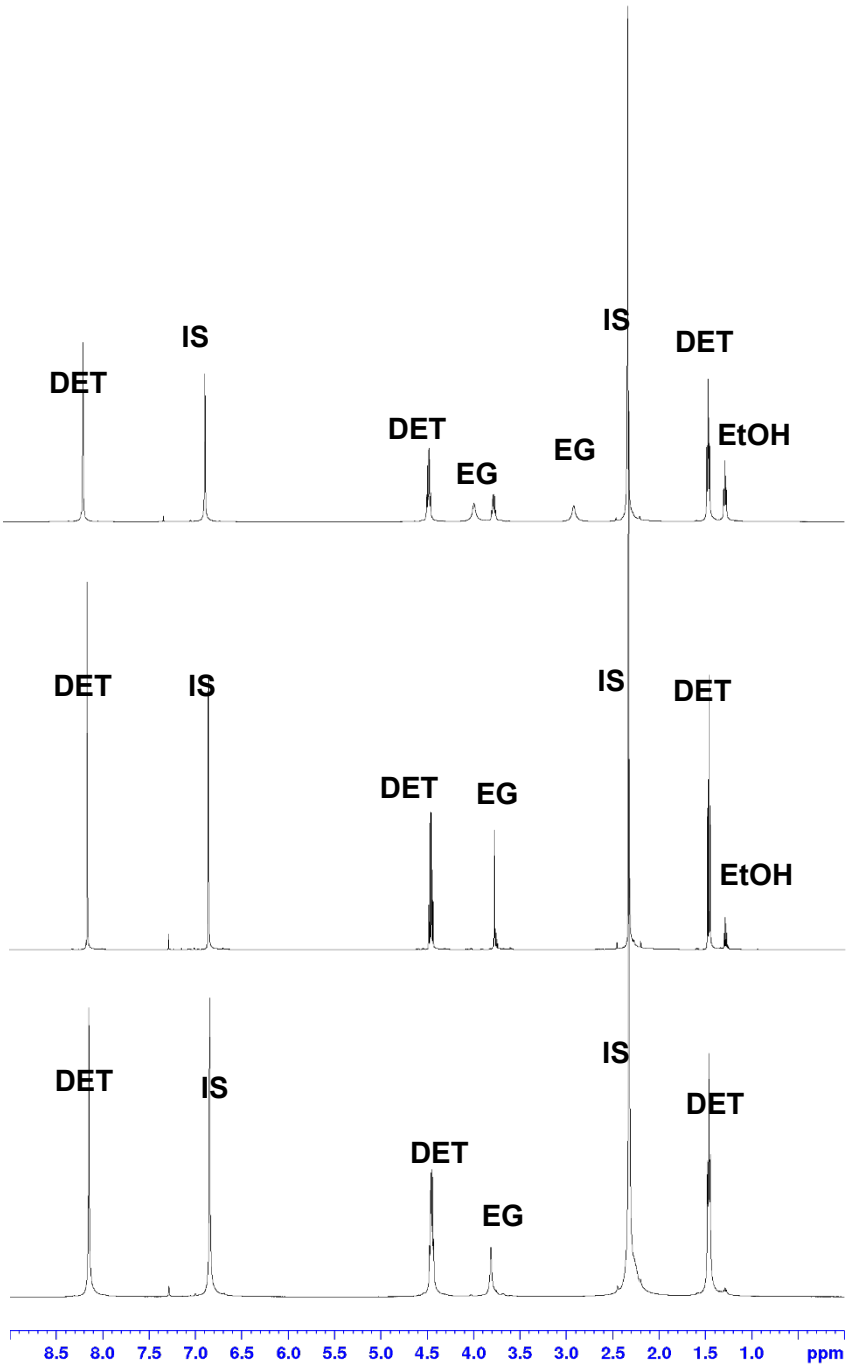


Figure S32. ^{1}H NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET yellow textiles through transesterification with ethanol using 5 mol% of $FeCl_3$ at 180 °C for 18 h (top) white textile (100 % PET), (middle) white textile (100 % PET), and (bottom) black textile (100 % PET). [Reaction mixtures after removal of volatiles]

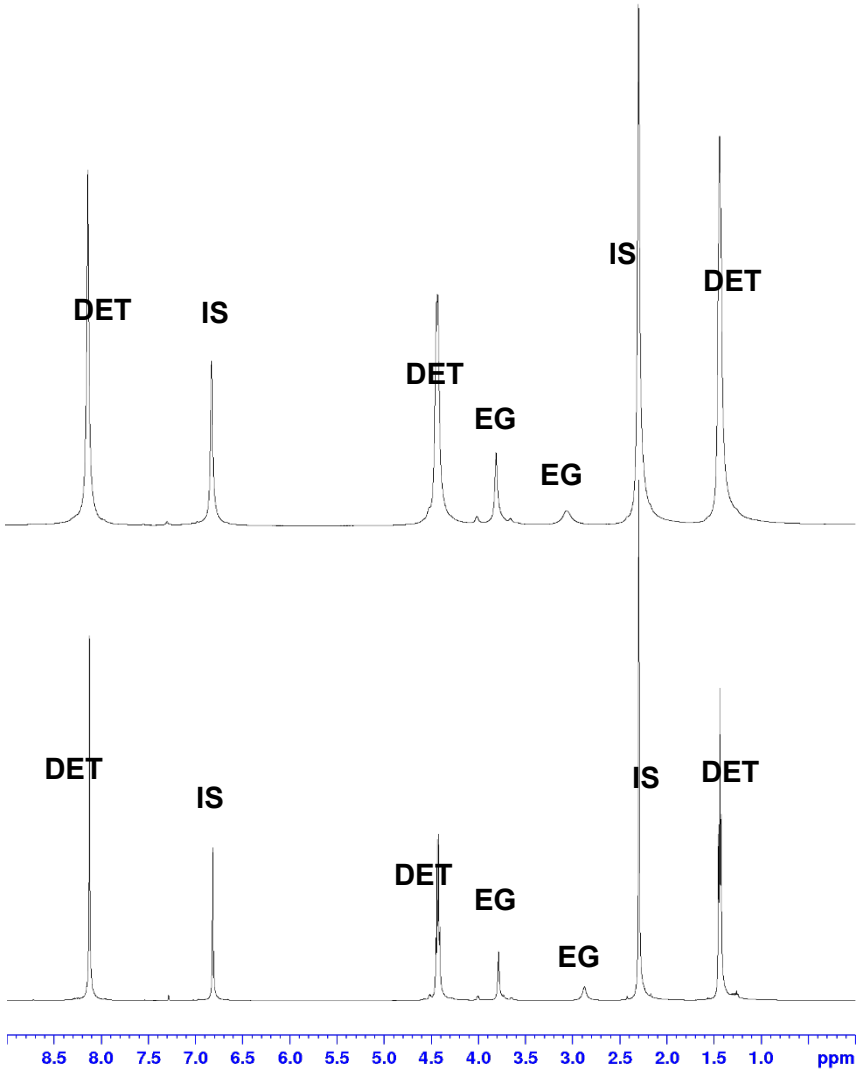


Figure S33. ^{1}H NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for selective depolymerization of PET sheets through transesterification with ethanol using 5 mol% of $FeCl_3$ at 180 °C for 18 h from its mixture with (top) Polyethylene and (bottom) cotton. [Reaction mixtures after removal of volatiles]

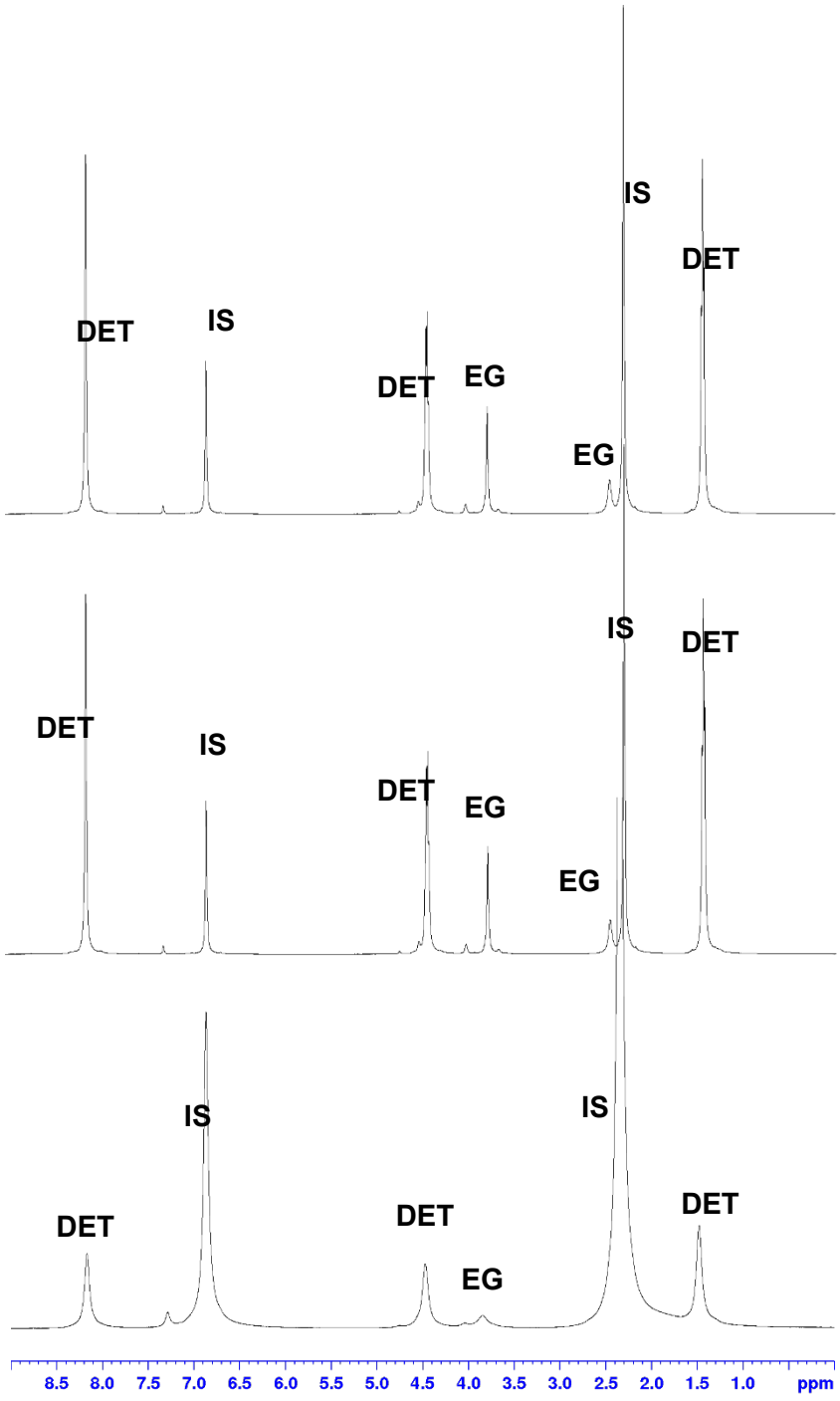


Figure S34. ^{1}H NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 5 mol % of $FeBr_3$ for 18 h at (top) 180 °C, (middle) 160 °C, and (bottom) 120 °C. [Reaction mixtures after removal of volatiles]

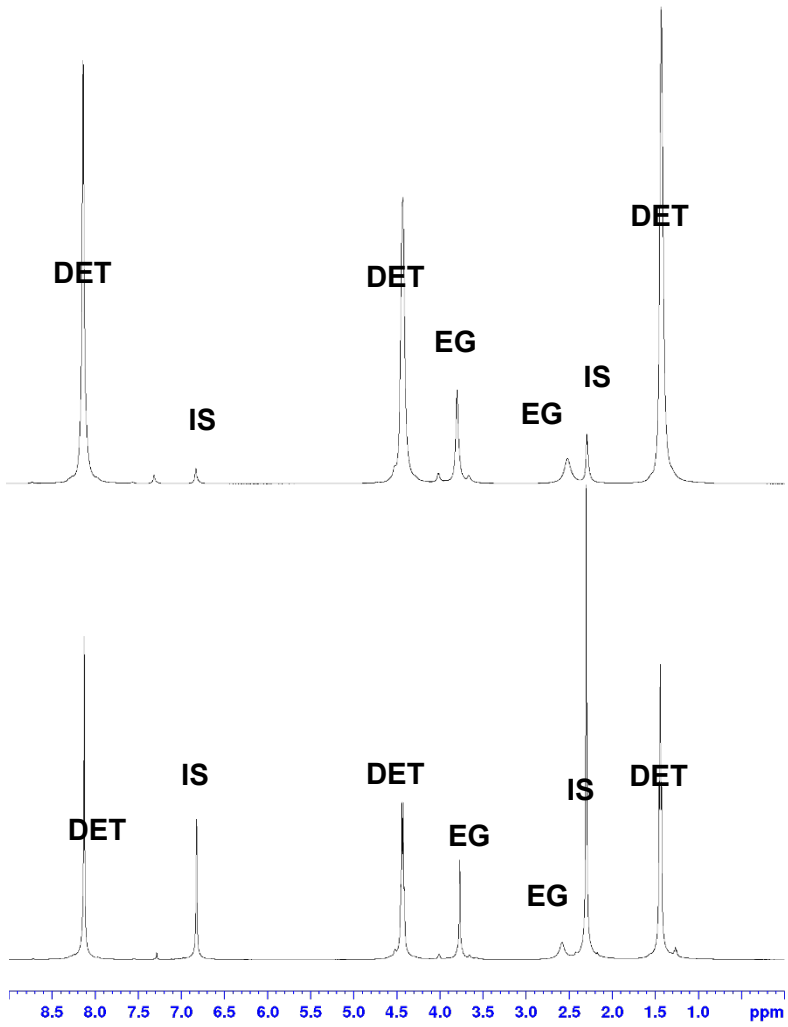


Figure S35. ^{1}H NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 3 mol % of $FeBr_3$ at 180 °C for (top) 18 h and (bottom) 30 h. [Reaction mixtures after removal of volatiles]

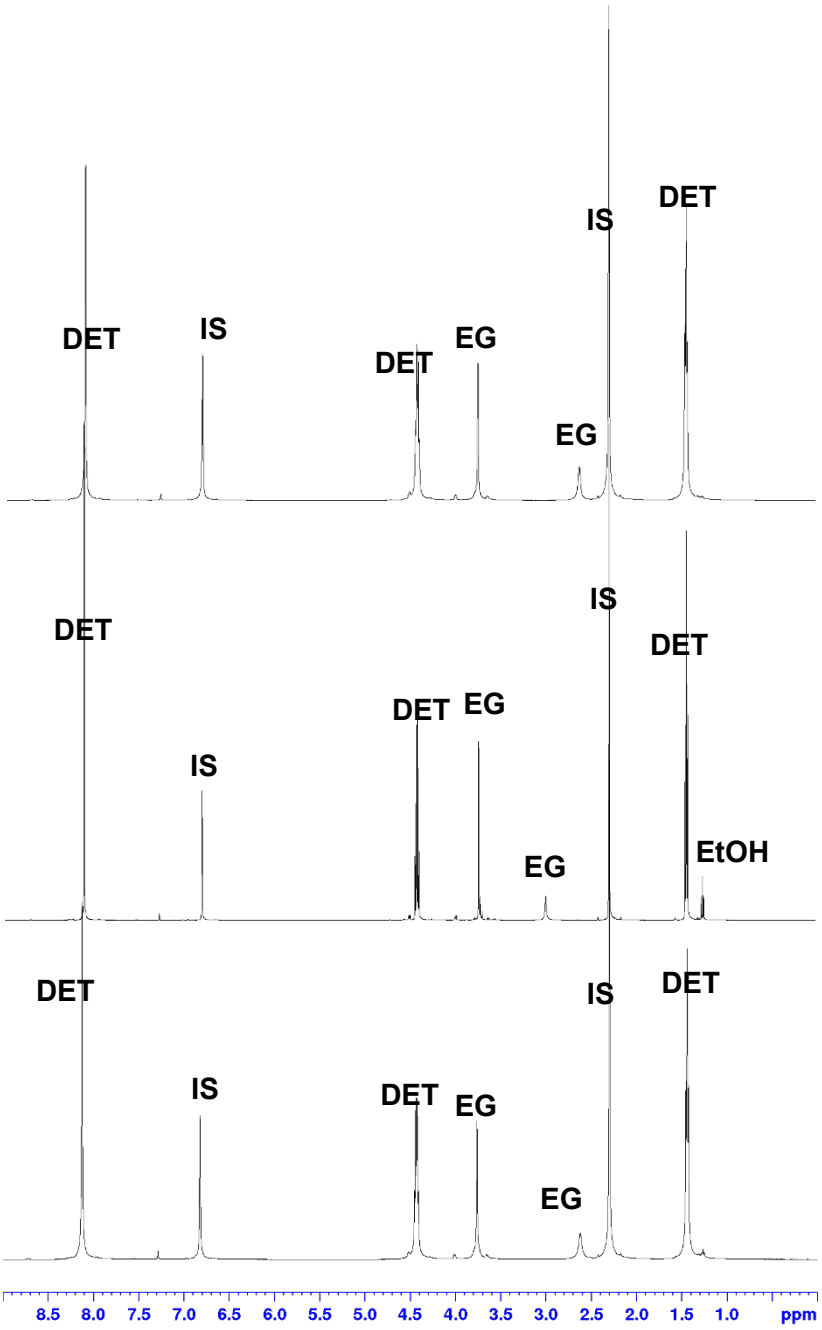


Figure S36. ^{1}H NMR spectra (in $CDCl_3$ at 25 °C) of resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using 1 mol % of $FeBr_3$ for 18 h at 180 °C for (top) 18 h, (middle) 30 h, and (bottom) 48 h. [Reaction mixtures after removal of volatiles]

5. Photos for selected experimental trials

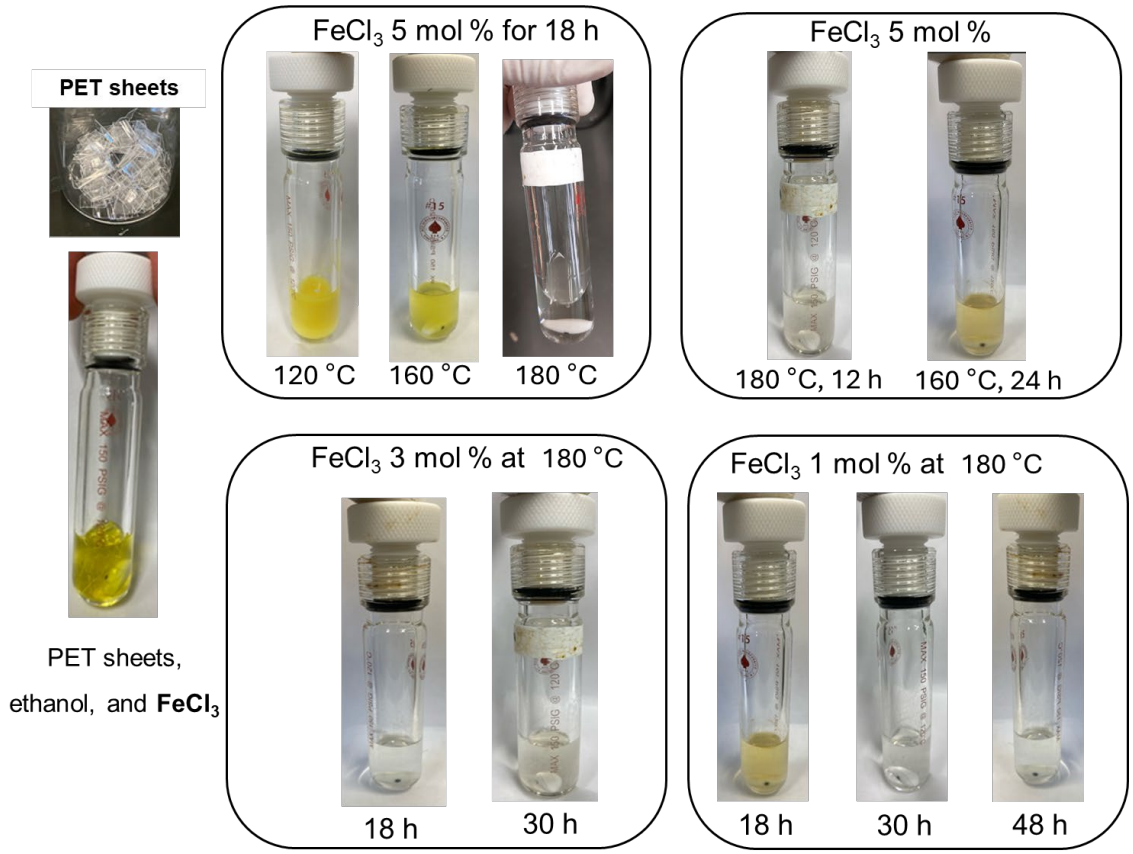


Figure S37. Photos for resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using $FeCl_3$ at different catalyst loadings, times, and temperatures.

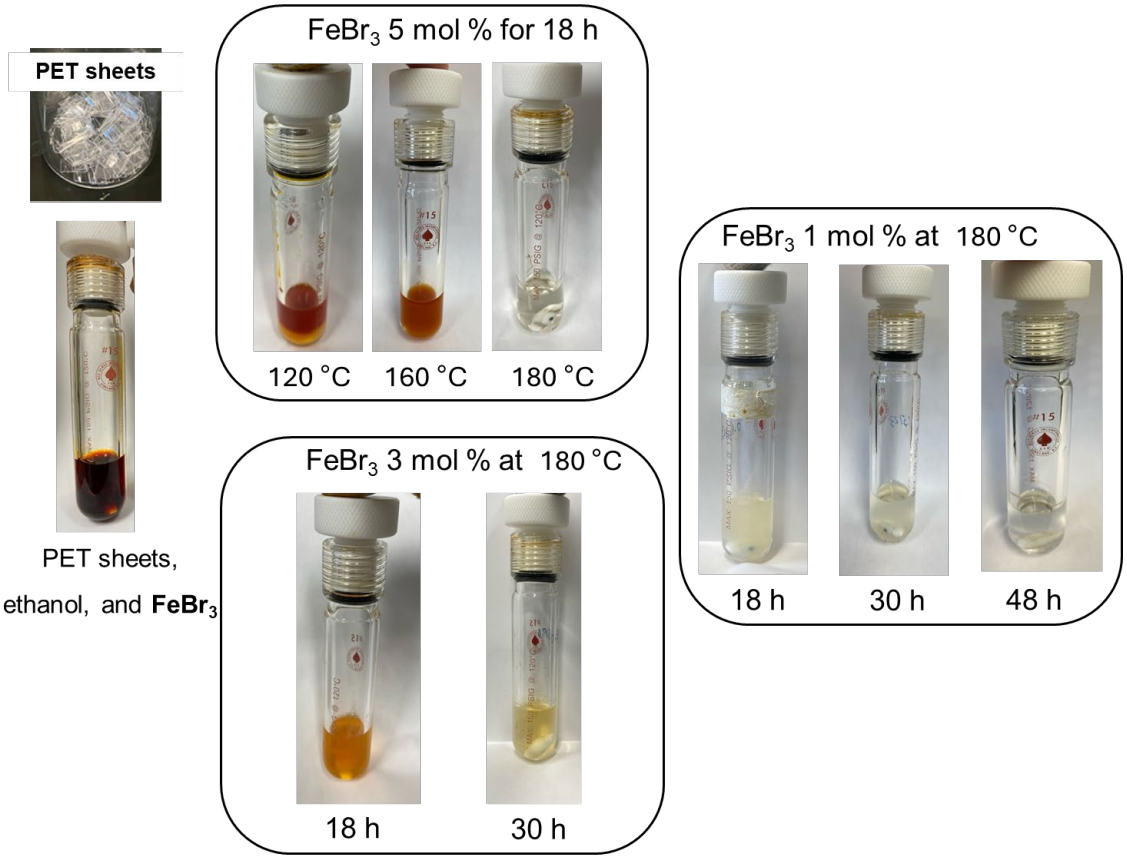


Figure S38. Photos for resultant mixtures for depolymerization of PET sheets through transesterification with ethanol using $FeBr_3$ at different catalyst loadings, times, and temperatures.

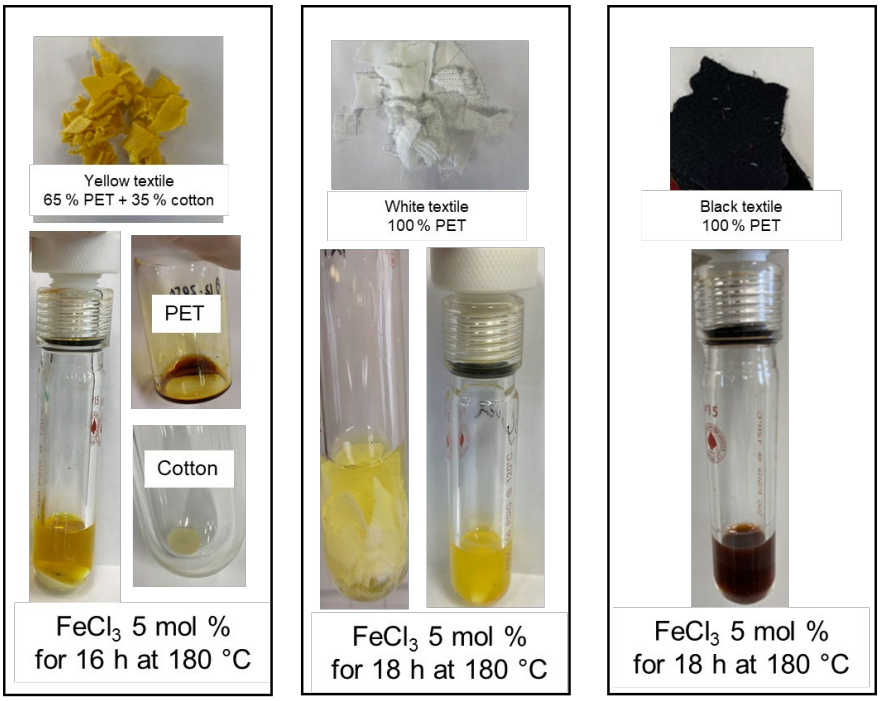


Figure S39. Photos for resultant mixtures for depolymerization of PET textiles through transesterification with ethanol using $FeCl_3$.

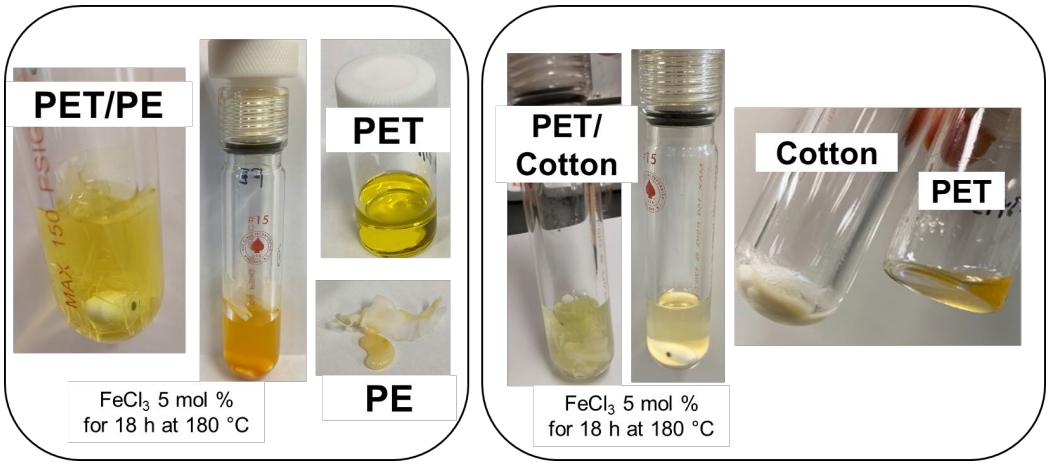


Figure S40. Photos for resultant mixtures for selective depolymerization of PET sheets from its mixture with PE or cotton through transesterification with ethanol using $FeCl_3$.