Supplementary Information for

Transforming polystyrene wastes to aromatic products near ambient temperature with aluminium chloride

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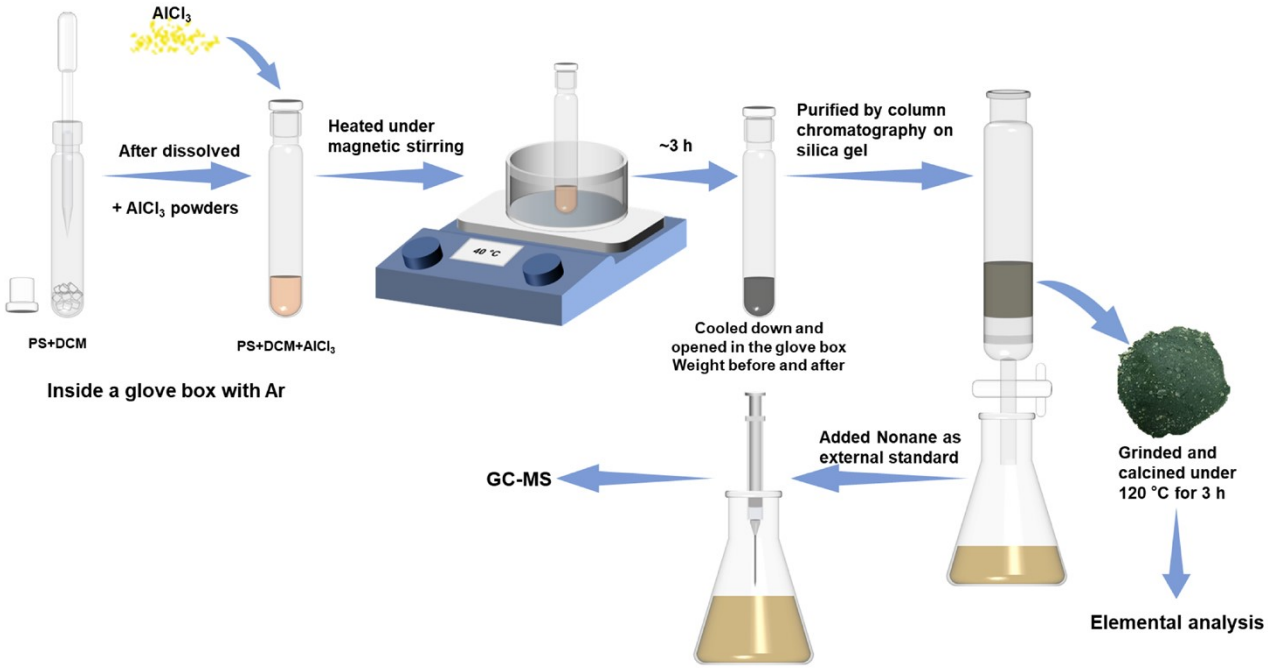


Figure S1. Schematic of the experimental process.

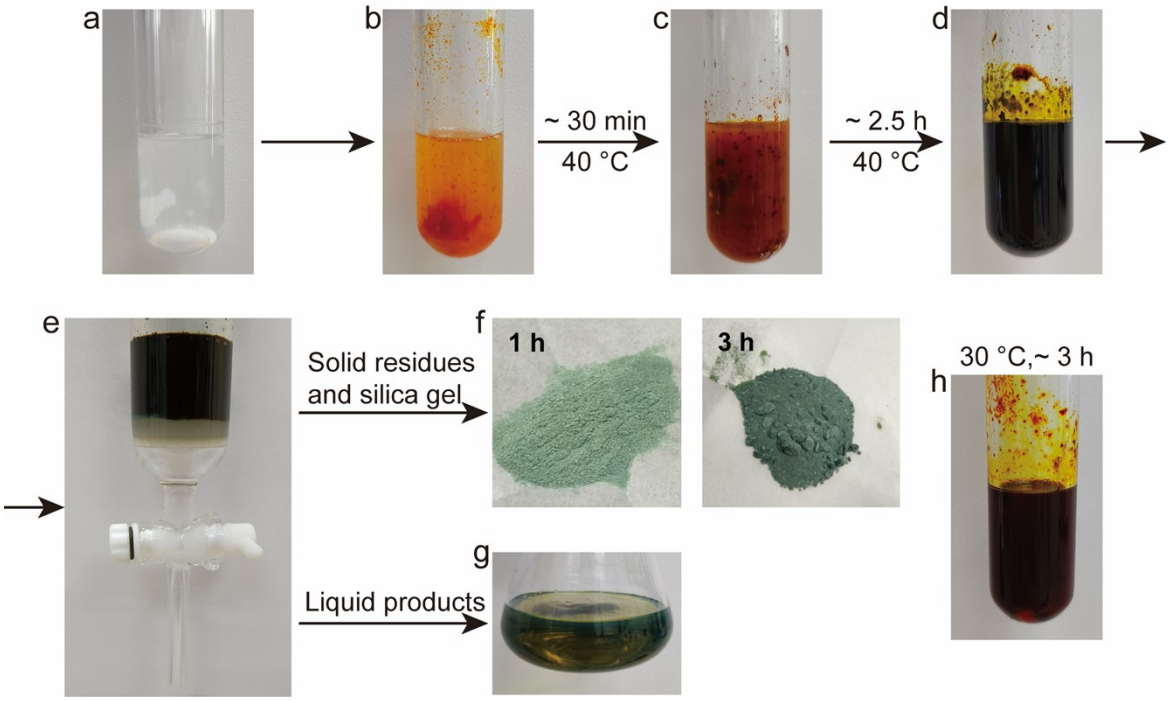
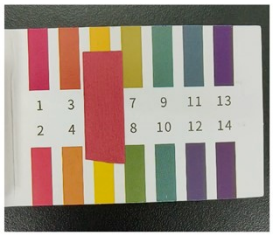
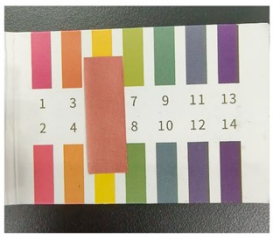
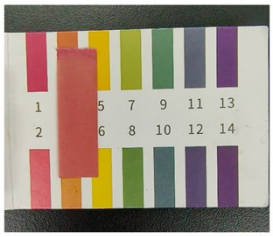


Figure S2. Experimental setup and photographs of PS degradation. (a) PS was dissolved in DCM. (b) A mixture of PS, DCM, and $AlCl_3$ in a glass tube. (c) The mixture in b after stirring for ~ 30 min at 40 °C. (d) The mixture in b after stirring for ~ 3 h at 40 °C. (e) The mixture after degradation was separated by column chromatography on silica gel with eluent of DCM. (f) Solid residues and silica gel. (g) Liquid products. (h) The mixture in b after stirring for ~ 3 h at 30 °C.

	In Ar glove box	Heated 40 °C for 3 h	pH indicator strips after 3 h
A **PS+DCM**			
B **$AlCl_3$**			
C **$AlCl_3$ + PS**			
D **$AlCl_3$ + DCM**			

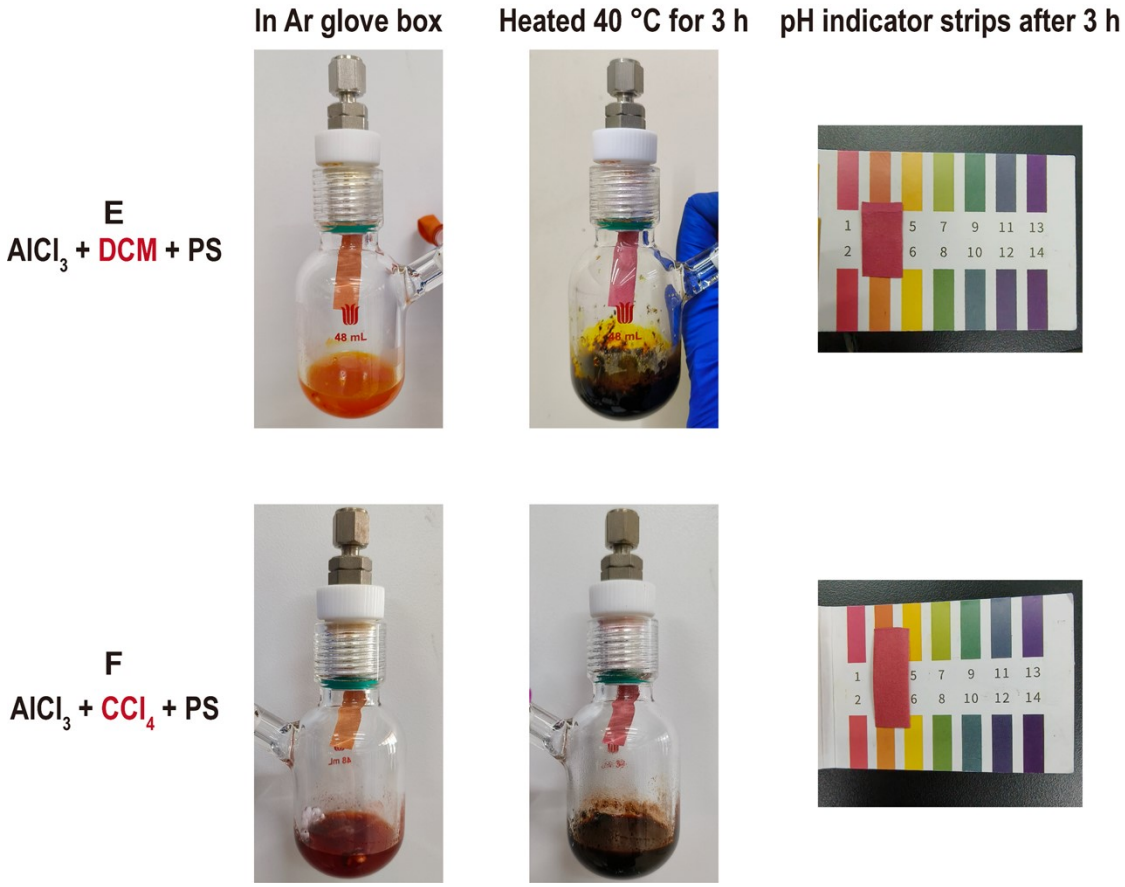


Figure S3. Experiments on HCl generation at 40 °C. (A) PS and DCM. (B) $AlCl_3$. (C) $AlCl_3$ and PS. (D) $AlCl_3$ and DCM. (E) $AlCl_3$, DCM, and PS. (F) $AlCl_3$, CCl_4, and PS. DCM (99.9%, water ≤ 30 ppm) and CCl_4 (99.5%, water ≤ 50 ppm) were extra dry solvents. $AlCl_3$ and PS were mixed and sealed under an argon atmosphere in a glovebox, with yellow pH indicator strips fixed in the Schlenk flask, which was equipped with an open-top screw cap and a silicone liner. After syringe transfer of DCM and CCl_4 into the flask, the mixture was heated at 40 °C for 3 h. Reaction conditions: 40 °C, 3 h, 1.00 g PS, $m_{PS}/m_{AlCl_3} = 4$ (0.25 g $AlCl_3$), 10.00 g extra dry DCM or CCl_4.

The origin of HCl generation was elucidated through comparative analysis of pH indicator strips color variations in Fig. S3A-F. PS and DCM exhibited no detectable HCl production under reaction conditions (Fig. S3A). Notably, the pH strips transitioned from yellow (pH 5-6) to orange (pH 3-4) before thermal treatment, indicating HCl production from hydrolysis of $AlCl_3$ [equation (1)] with trace moisture (< 20 ppm) from the glovebox atmosphere (Fig. S3B-F, left panels). Post-reaction at 40 °C for 3 h, all strips progressed to red (pH 1-2; Fig. S3B-F, middle/right panels), demonstrating that HCl generation predominantly arises from continuous hydrolysis with trace water in both atmosphere and solvents (DCM: ≤ 30 ppm, CCl_4: ≤ 50 ppm), rather than through hydrogen abstraction by $AlCl_3$ from solvent molecules (Fig. S3F, no H in CCl_4).

$$AlCl_3 + 3\,H_2O \rightarrow Al(OH)_3 + 3\,HCl \quad (1)$$

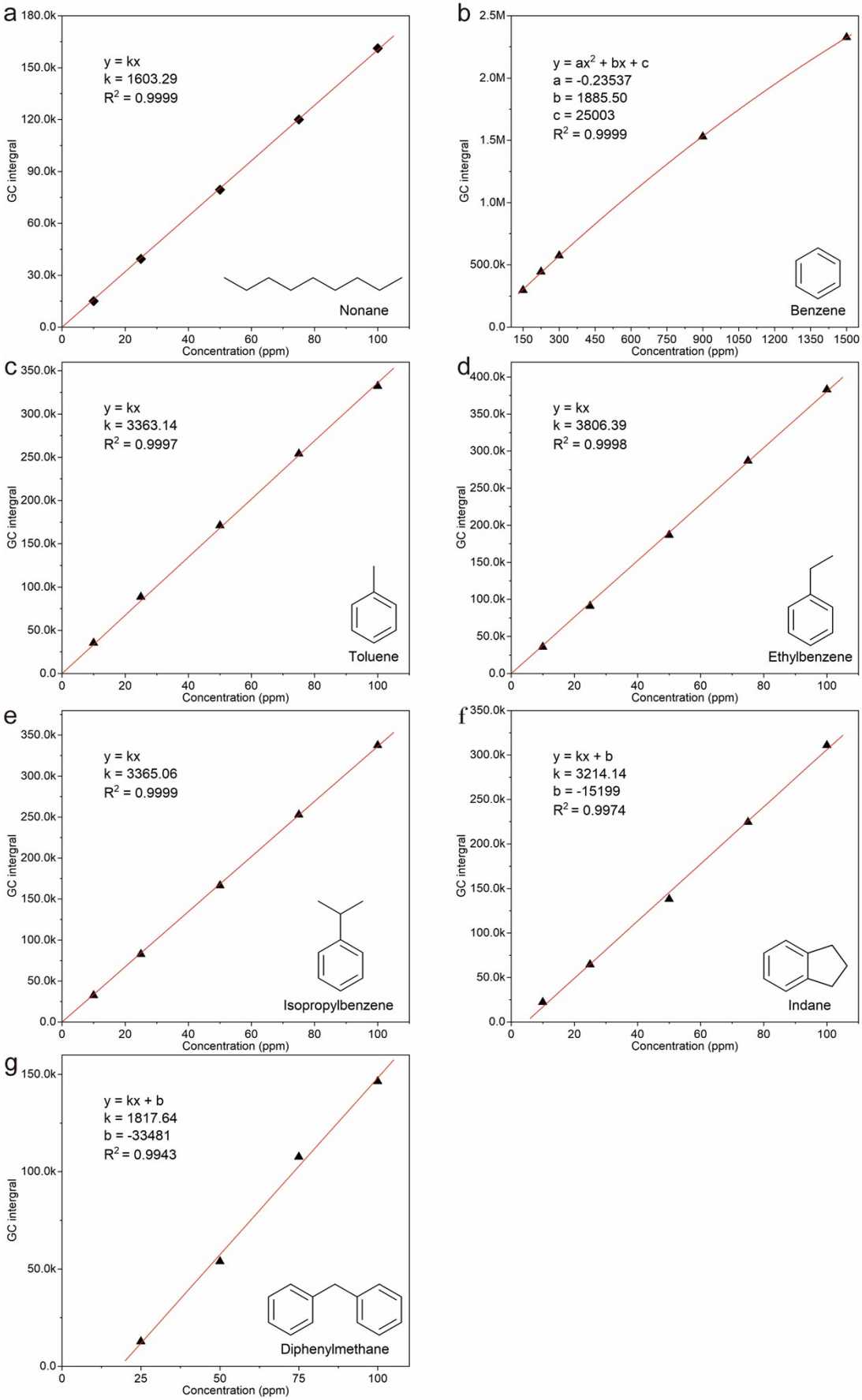
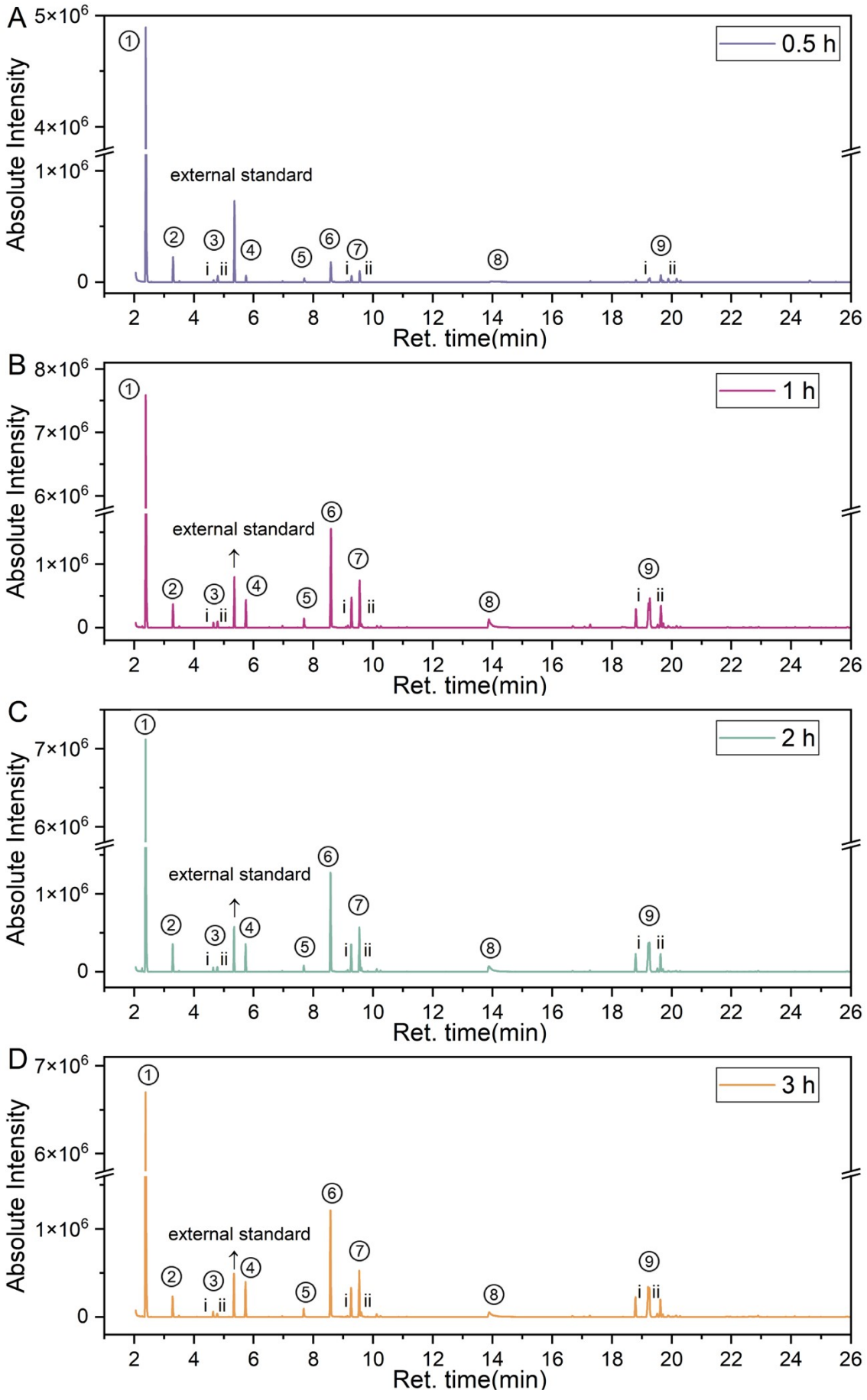


Figure S4. GC-MS calibration curves of (a) nonane (external standard), (b) benzene, (c) toluene, (d) ethylbenzene, (e) isopropylbenzene, (f) indane, (g) diphenylmethane (DPM).


A
B
C
D
Absolute Intensity
Ret. time(min)
0.5 h
1 h
2 h
3 h
external standard
①
②
③
④
⑤
⑥
⑦
⑧
⑨
i
ii

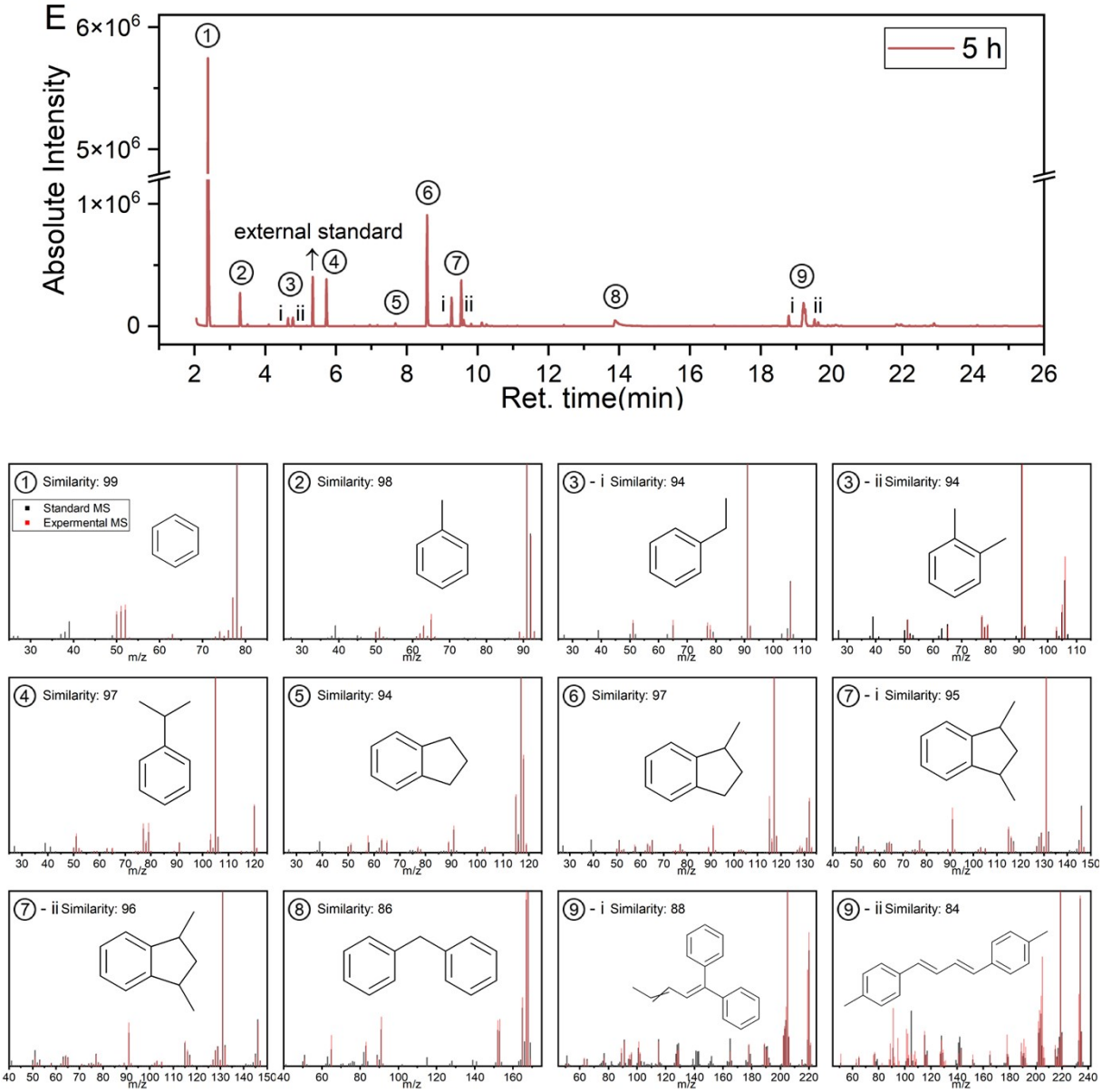
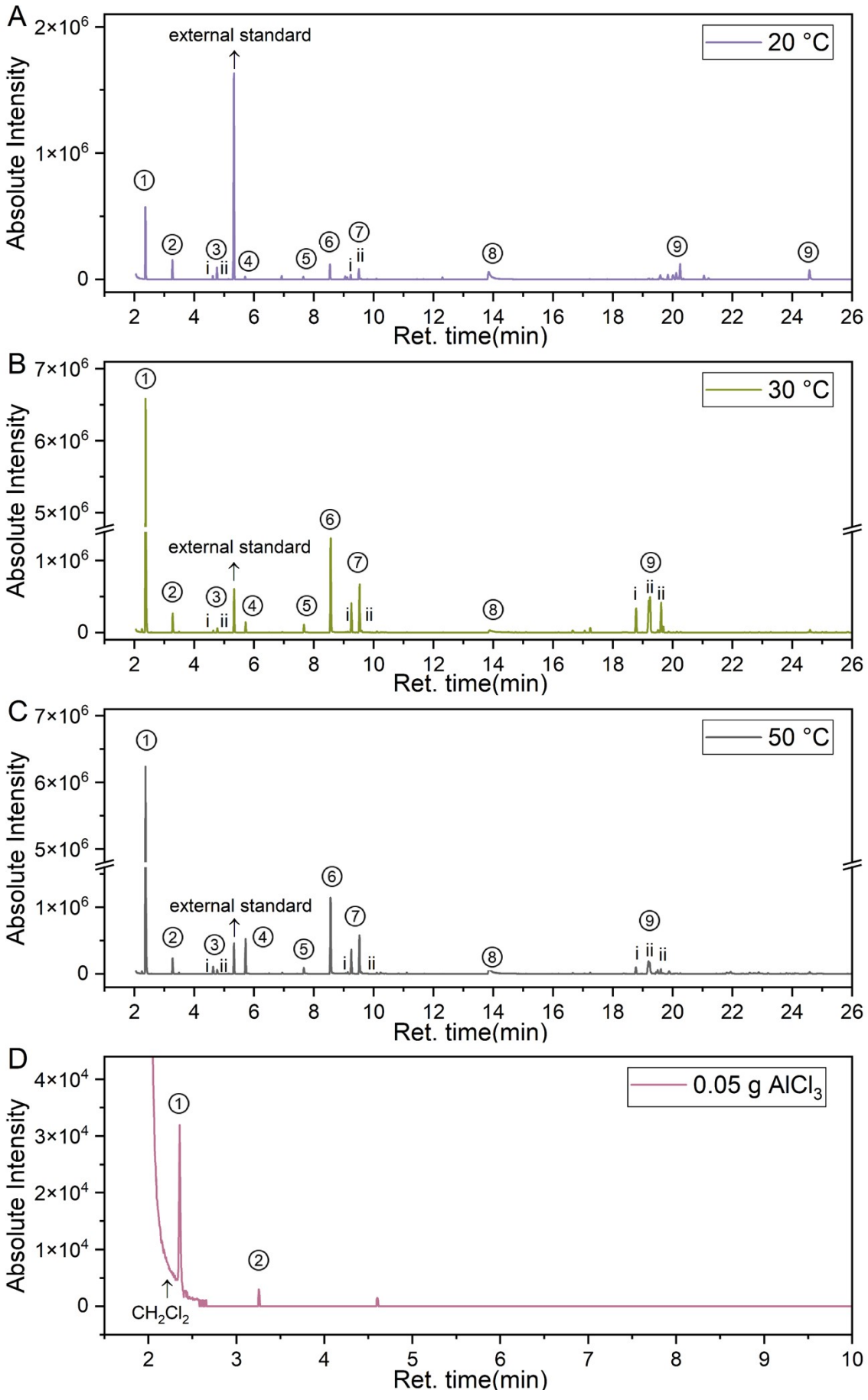


Figure S5. Time-resolved GC traces and mass spectra of liquid products after degradation. The standard mass spectra of the products were obtained from the NIST library. Reaction conditions: 40 °C, 1.00 g PS, $m_{PS}/m_{AlCl_3} = 4$ (0.25 g $AlCl_3$), 10.00 g DCM. (A-E) Magnification of GC traces in Fig. 2C 30 μL nonane was added as an external standard. The fractions of products were evaluated by GC peak areas.

The relative response factors for each structurally similar species were assumed to be 1.0.[1] The xylene (3-ii) is quantified by calibration curves of ethylbenzene (3-i) in Fig. S4 (d); 1-methylindan (6) and 1,3-dimethylindan (7-i & ii) are quantified by calibration curves of indane (5) in Fig. S4 (f); the others with two benzene rings (9-i & ii) are quantified by calibration curves of DPM (8) in Fig. S4 (g).


A
B
C
D
Absolute Intensity
Ret. time(min)
external standard
20 °C
30 °C
50 °C
0.05 g AlCl3
CH2Cl2

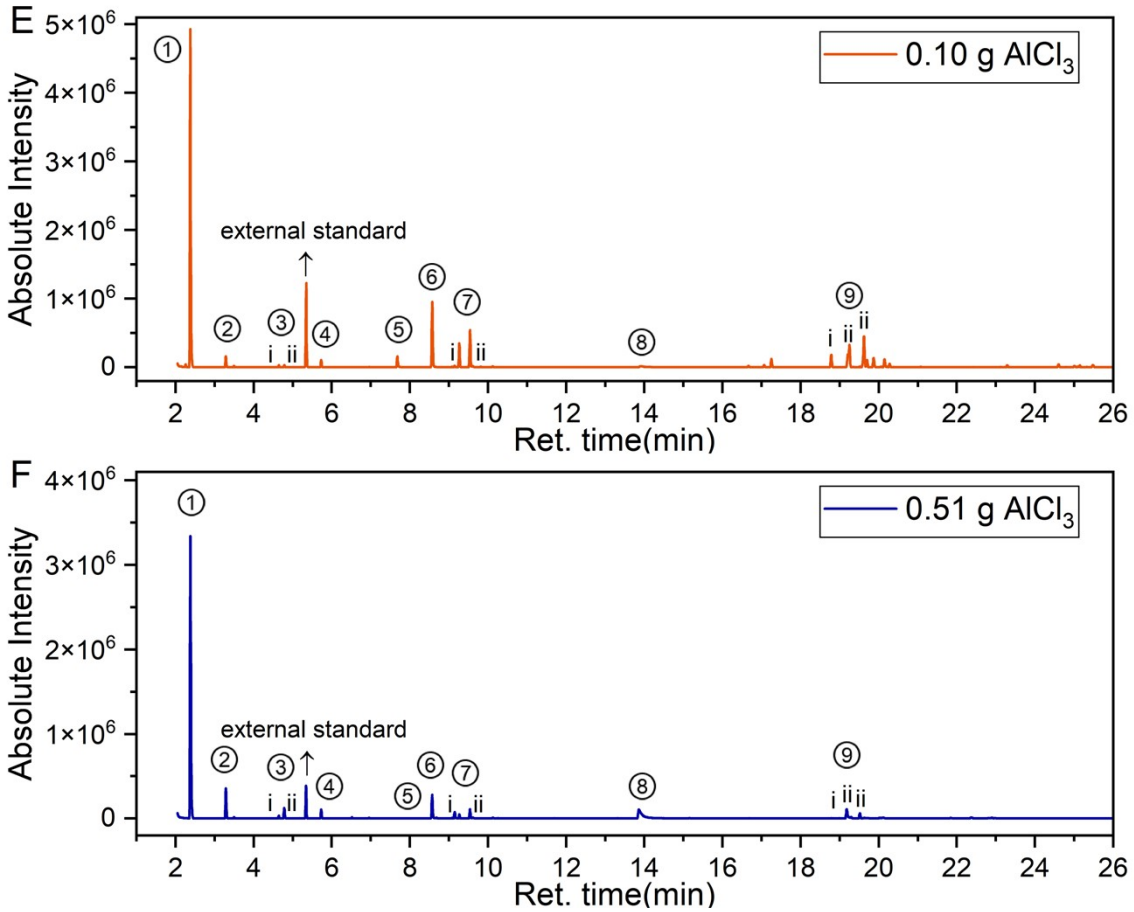


Figure S6. GC traces of liquid products after degradation under varying temperatures and $AlCl_3$ weights. (A) 20 °C, (B) 30 °C, (C) 50 °C, other reaction conditions: 1.00 g PS, $m_{PS}/m_{AlCl_3} = 4$ (0.27 g $AlCl_3$), 10.00 g DCM. (D) 0.05 g $AlCl_3$, (E) 0.10 g $AlCl_3$, (F) 0.51 g $AlCl_3$, other reaction conditions: 40 °C, 1.00 g PS, 10.00 g DCM. 30 μL nonane was added as an external standard (10 μL nonane for the sample reacted at 20 °C). The MS spectra and corresponding chemical structures of the products are shown in Fig. S5.

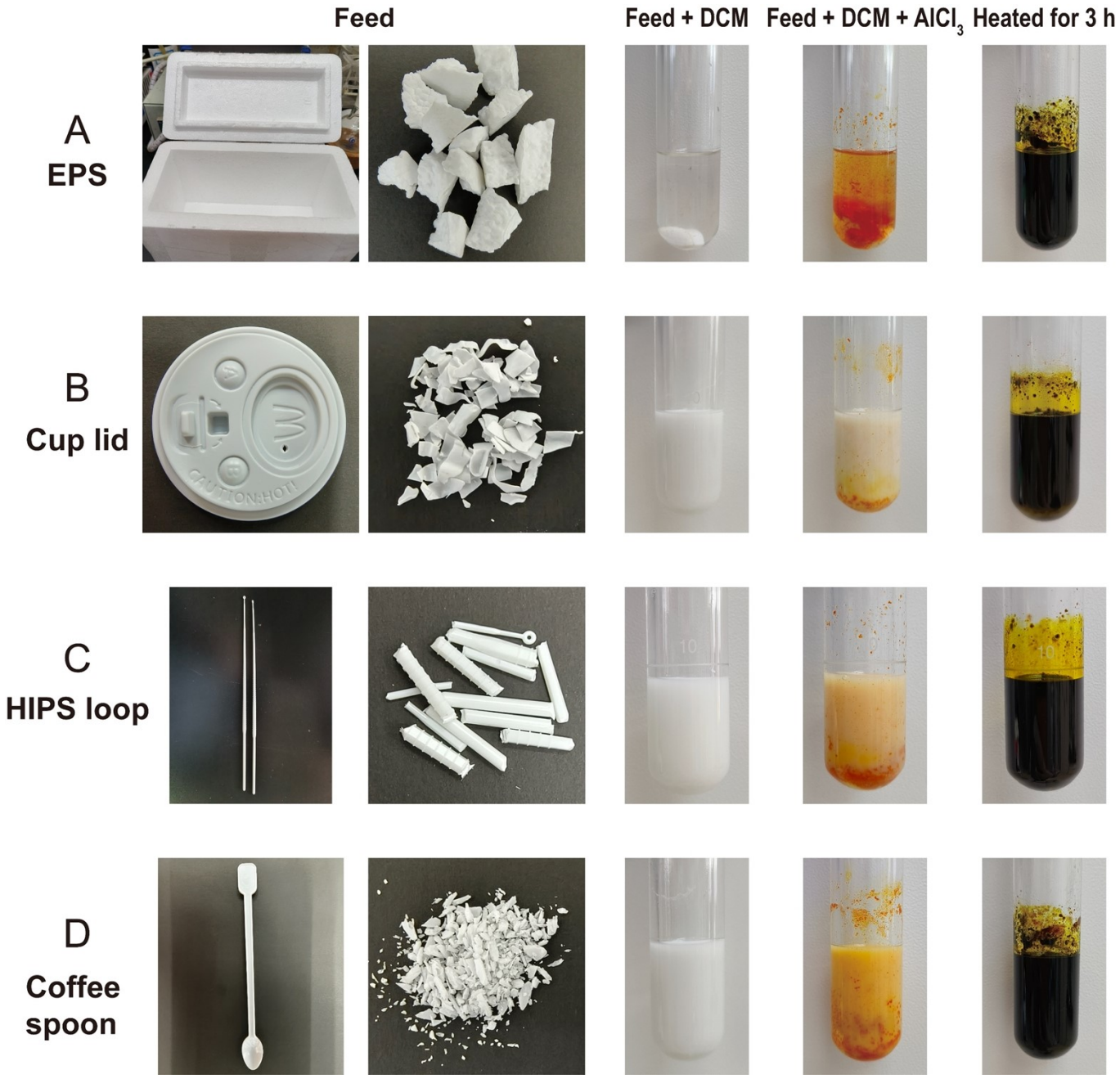


Figure S7. Photographs depicting the degradation of 1-gram postconsumer PS wastes, (A) EPS, (B) cup lid, (C) HIPS disposable inoculating loop (HIPS loop), and (D) coffee spoon. Reaction conditions: 1.00 g PS wastes, $^{m_{PS}}/_{m_{AlCl_3}} = 4$ (0.27 g $AlCl_3$), 10.00 g DCM.

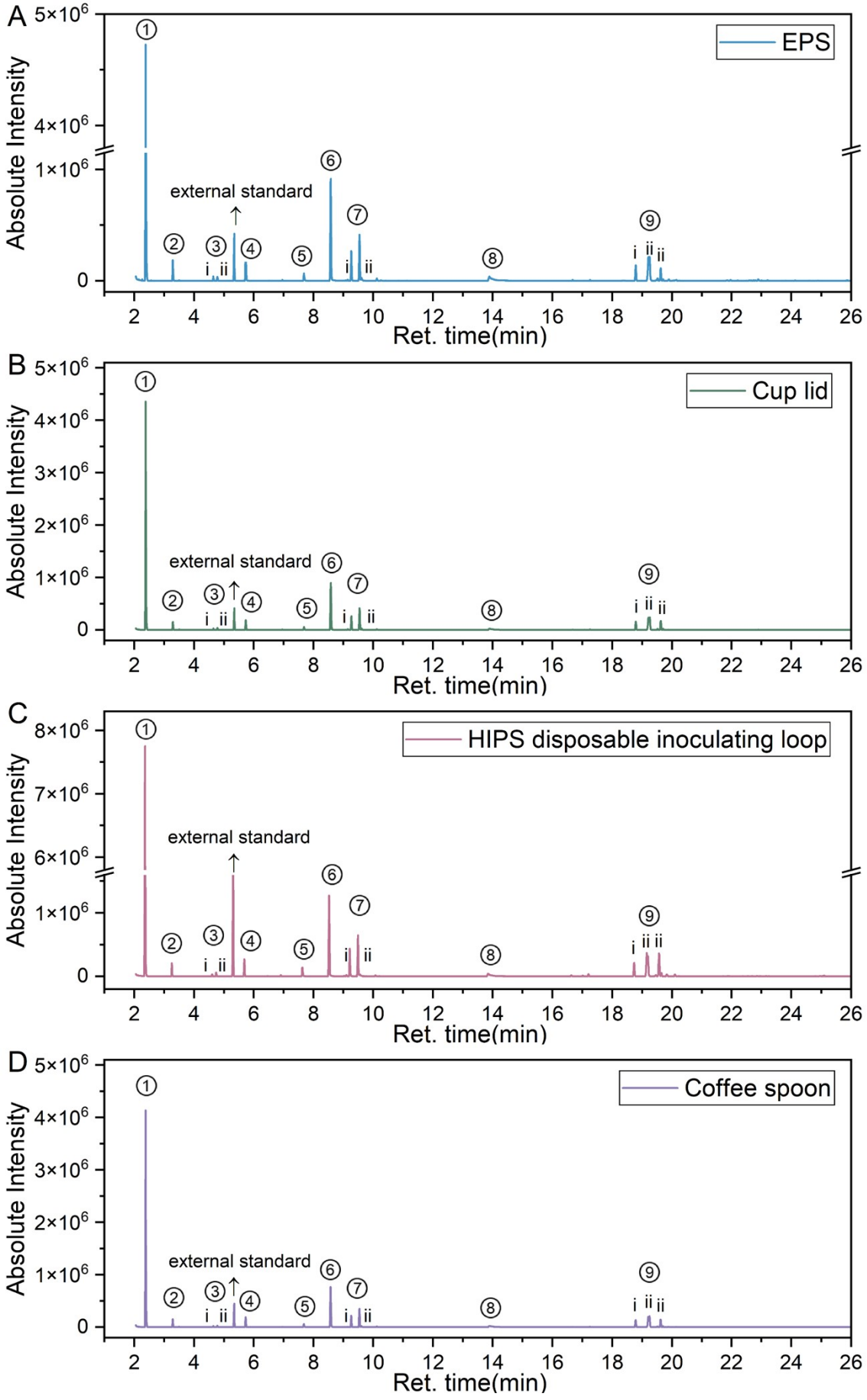


Figure S8. GC traces of liquid products of postconsumer PS wastes, (A) EPS, (B) cup lid, (C) HIPS

disposable inoculating loop, and (D) coffee spoon. 40 μL of nonane was added as an external standard (80 μL of nonane for the HIPS disposable inoculating loop). The MS spectra and corresponding chemical structures of the products are shown in Fig. S5.

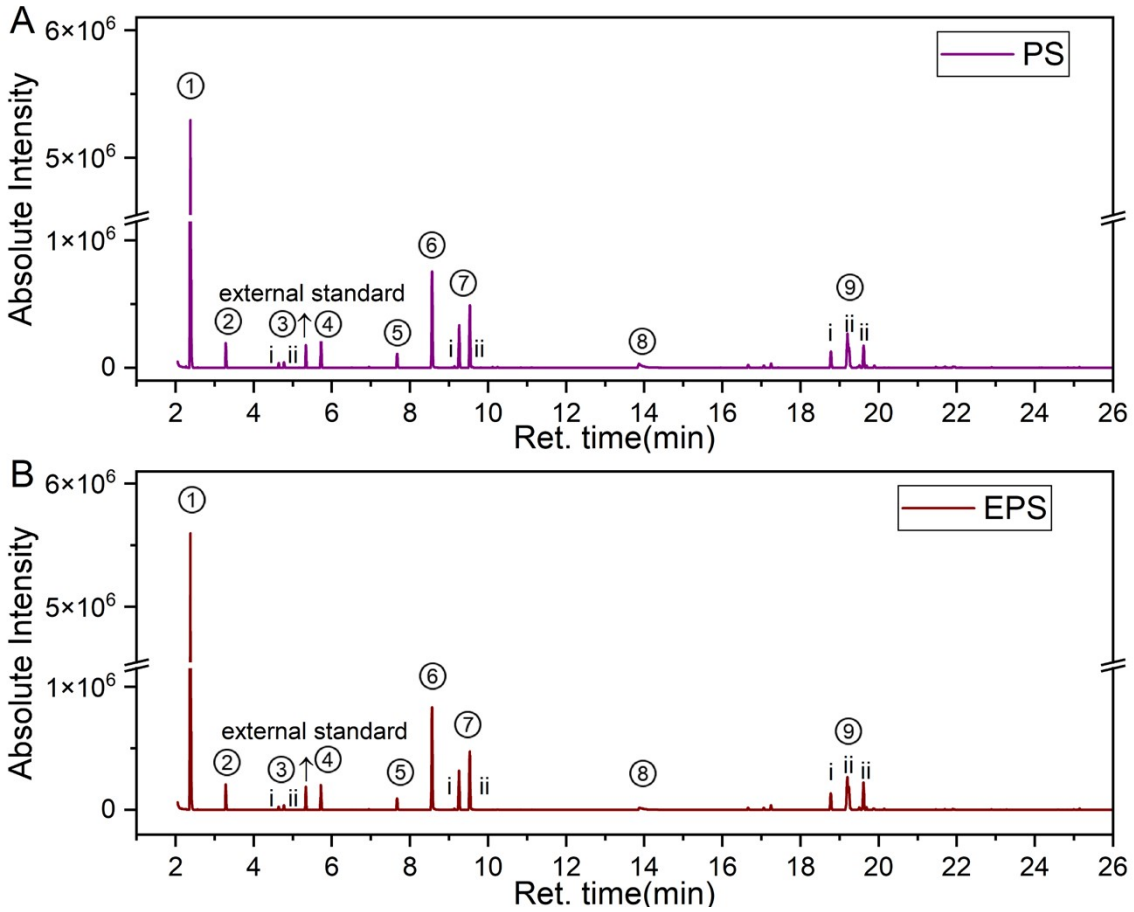
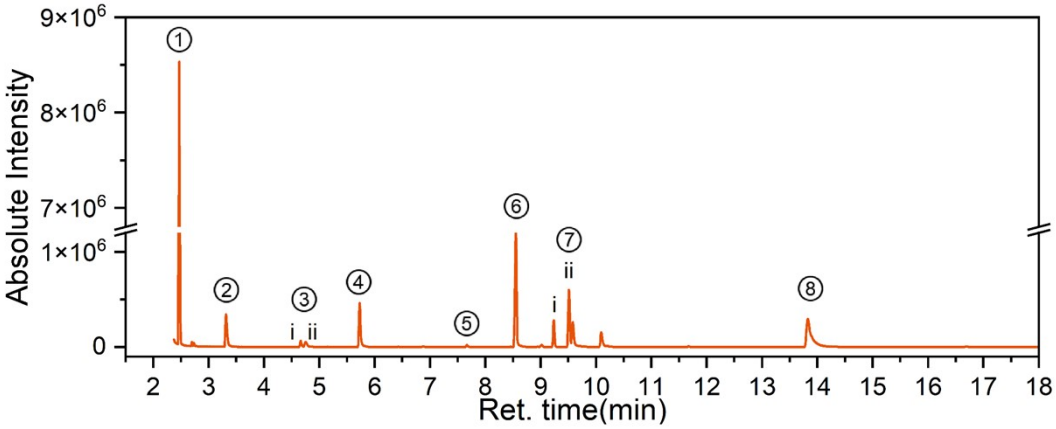
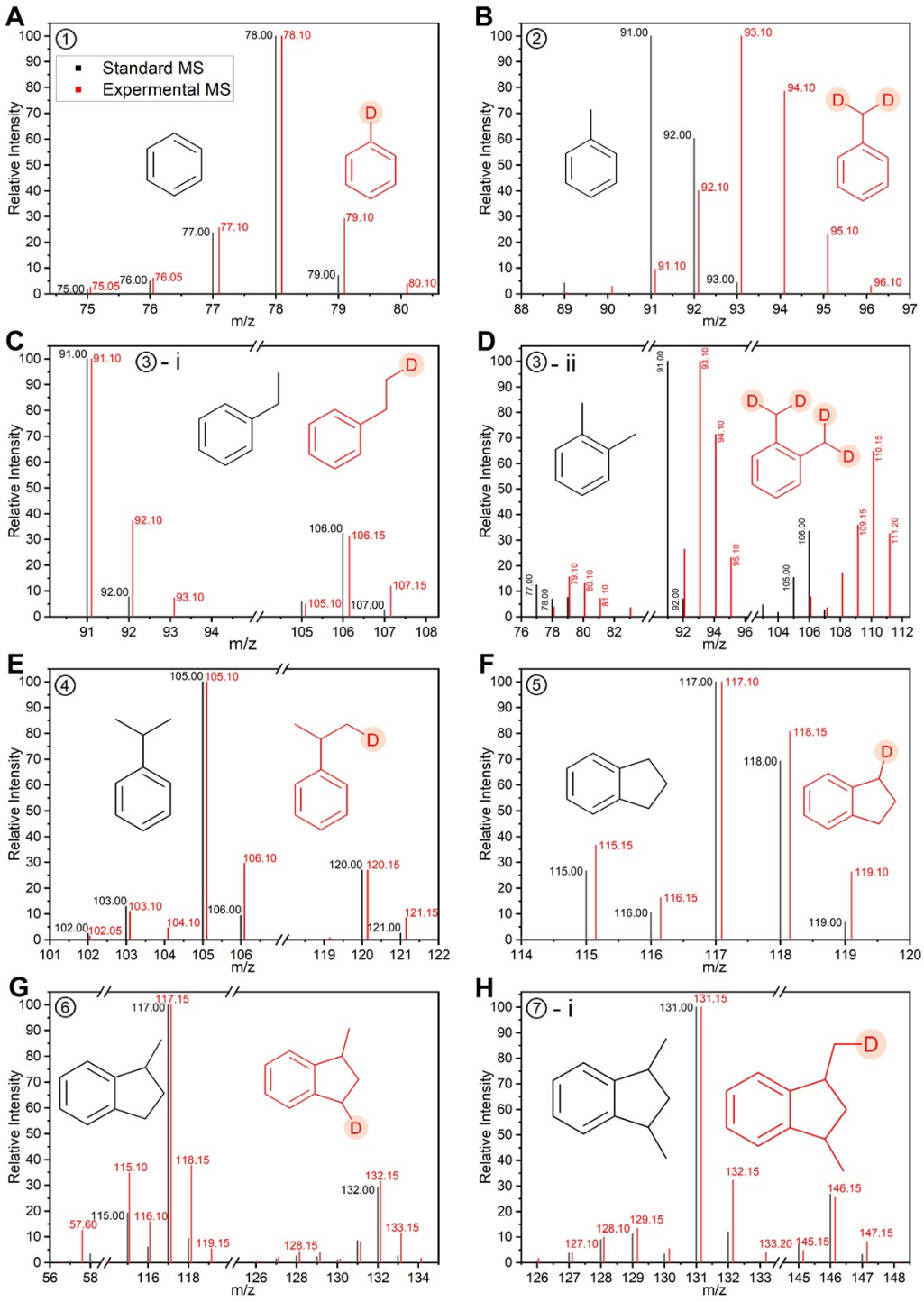


Figure S9. GC traces of liquid products after 10-gram scale-up degradation, (A) PS and (B) EPS. 140 μL of nonane was added as an external standard. The MS spectra and corresponding chemical structures of the products are shown in Fig. S5.


Absolute Intensity
Ret. time(min)
①
②
③
i ii
④
⑤
⑥
⑦
i
ii
⑧


A
① Standard MS
Expermental MS
B
②
C
③ - i
D
③ - ii
E
④
F
⑤
G
⑥
H
⑦ - i
Relative Intensity
m/z

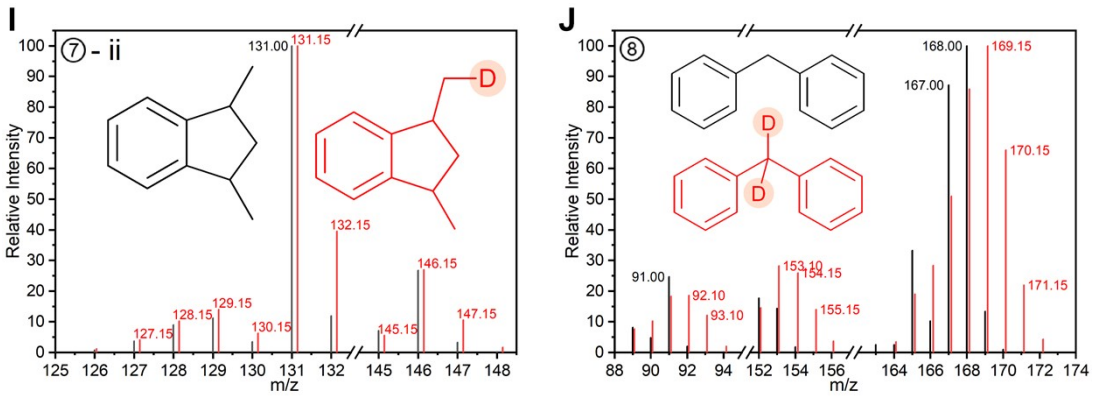


Figure S10. GC trace and mass spectra of liquid products after reaction with CD_2Cl_2 in the presence of $AlCl_3$ for 3 h (from GC-MS analysis). Reaction conditions: 0.10 g PS, $m_{PS}/m_{AlCl_3} = 2.5$ (0.04 g $AlCl_3$), 0.4 g CD_2Cl_2 (0.25 mL).

The standard mass spectra (black, from NIST library), experimental mass spectra (red), and proposed molecular formula (red) are shown in (A-J): (A) Benzene (C_6H_6) and benzene-d_1 (C_6H_5D). (B) Toluene (C_7H_8) and toluene-d_2 ($C_7H_6D_2$). (C) Ethylbenzene (C_8H_{10}) and ethylbenzene-d_1 (C_8H_9D). (D) xylene (C_8H_{10}) and xylene-d_4 ($C_8H_6D_4$). (E) Isopropylbenzene (C_9H_{12}) and isopropylbenzene-d_1 ($C_9H_{11}D$). (F) Indane (C_9H_{10}) and indane-d_1 (C_9H_9D). (G) 1-methylindan ($C_{10}H_{12}$) and 1-methylindan-d_1 ($C_{10}H_{11}D$). (H & I) 1,3-dimethylindan ($C_{11}H_{14}$) and 1,3-dimethylindan-d_1 ($C_{11}H_{13}D$). (J) diphenylmethane (DPM, $C_{13}H_{12}$) and diphenylmethane-d_2 ($C_{13}H_{11}D_2$).

M refers to the relative molecular mass of the compounds. As shown in Fig. S10A, C, E, and F-I, the increasing relative intensity of the (M+1) peak in the mass spectra indicates the incorporation of one deuterium atom in the compounds.[2] The incorporations were probably formed by β-hydride abstraction followed by H/D transfer.[3] In Fig. S10B and J, the relative molecular mass of toluene and DPM are 92 and 168, respectively; the appearance of (M+2) peaks confirms the additional incorporation of two deuterium atoms in the molecule. The results demonstrate that toluene and DPM were obtained via the Friedel-Crafts reaction of benzene with DCM. The appearance of (M+4) peaks (m/z 110) in Fig. S10D confirms the additional incorporation of two deuterium atoms in the xylene molecule, indicating xylene was generated by two successive Friedel-Crafts reactions of benzene with DCM.

Table S1. The feed and product phases after reactions.

Reaction time (h)	Feed (g)			Gas phase		Solid phase		Liquid phase	
	PS	$AlCl_3$	DCM	g	wt. %	g	wt. %	g	wt. %
0.5 (40 °C)	1.0076	0.25	9.98	0.04	0.36	0.6747	6.00	10.5229	93.64
1 (40 °C)	1.0024	0.25	10.16	0.03	0.26	0.8519	7.47	10.5305	92.27
2 (40 °C)	1.0104	0.24	10.10	0.06	0.53	0.5307	4.68	10.7597	94.79
3 (40 °C)	1.0037	0.25	9.93	0.05	0.45	0.6723	6.01	10.4614	93.54
5 (40 °C)	1.0012	0.25	9.70	0.05	0.46	0.5972	5.45	10.3040	94.09
3 (40 °C, 0.05 g $AlCl_3$)	1.0058	0.05	9.80	0	0	0.9244	8.52	9.9314	91.48
3 (40 °C, 0.1 g $AlCl_3$)	1.0048	0.10	10.87	0.01	0.09	0.3719	3.39	10.5929	96.52
3 (40 °C, 0.5 g $AlCl_3$)	1.0010	0.51	9.94	0.26	2.27	0.8672	7.57	10.3238	90.16
3 (20 °C)	1.0046	0.25	9.71	0.02	0.18	1.2005	10.95	9.7441	88.87
3 (30 °C)	1.0004	0.28	10.07	0.04	0.35	0.5328	4.69	10.7776	94.96
3 (50 °C)	1.0063	0.27	10.19	0.06	0.52	0.5669	4.94	10.8394	94.54

Table S2. Elemental analysis results of PS feed and solid residues.

	Substrates	m_{Sample} (g)	Elemental analysis (wt. %)		C/H	[b] $m_{C\ \&\ H}$ (g)	[c] Conversion (wt. %)
			C	H			
Feed	PS	-	92.12	7.88	11.69	-	-
[a] Solid residues	0.5 h (40 °C)	3.6422	6.06	3.7722	1.61	0.3583	64.4
	1 h (40 °C)	3.8186	5.64	2.7181	2.07	0.3192	68.2
	2 h (40 °C)	3.5176	6.08	2.3619	2.57	0.2968	70.6
	3 h (40 °C)	3.6246	5.67	2.3166	2.45	0.2893	71.2
	5 h (40 °C)	3.5662	6.09	2.5161	2.42	0.3069	69.3
	3 h (40 °C, 0.05 g $AlCl_3$)	3.8931	20.66	2.8491	7.25	0.9152	9.0
	3 h (40 °C, 0.1 g $AlCl_3$)	3.3326	9.23	3.3120	2.79	0.4180	58.4
	3 h (40 °C, 0.5 g $AlCl_3$)	3.8238	6.14	2.4976	2.46	0.3303	67.0
	3 h (20 °C)	4.1677	18.54	3.3087	5.60	0.9106	9.4
	3 h (30 °C)	3.4954	6.15	2.5724	2.39	0.3047	69.5
	3 h (50 °C)	3.5202	5.46	2.4103	2.27	0.2772	72.5

[a] Solid residues mean the residual solid after reaction containing catalyst and silica gel (3 g) for column chromatography.

[b] Calculation equation: $m_{Sample} \times [C\ (wt.\ \%) + H\ (wt.\ \%)]$, where m_{Sample} is the mass of solid residues after heating at 120 °C for 3 h.

[c] Calculation equation: $(m_{Feed} - m_{C\ \&\ H})/m_{Feed} \times 100\%$, where m_{Feed} is the mass of PS feeds from Table S1.

Table S3. GPC analysis of PS molecular weight during degradation (40 °C).

Reaction time (h)	M_n	M_w	DPI (M_w/M_n)
0	14561	139540	9.58
0.5	5035	107551	21.36
1	932	20280	21.75
3	246	2198	8.93

Table S4. The postconsumer polystyrene wastes feed and product phases after reactions.

Substrates	Feed (g)			Gas phase		Solid phase		Liquid phase	
	PS wastes	$AlCl_3$	DCM	g	wt. %	g	wt. %	g	wt. %
EPS	1.0023	0.28	10.48	0.07	0.59	0.3291	2.80	11.3632	96.61
Cup lid	1.0053	0.28	10.81	0.05	0.41	0.3506	2.90	11.6947	96.69
[a] HIPS loop	1.0030	0.24	9.76	0.09	0.82	0.3907	3.55	10.5223	95.63
Coffee spoon	1.0021	0.28	10.44	0.04	0.34	0.3062	2.61	11.3759	97.05

[a] HIPS loop: disposable inoculating loop made of HIPS (high impact polystyrene) material.

Table S5. Elemental analysis results of postconsumer polystyrene wastes and solid residues.

Substrates		m_{Sample} (g)	Elemental analysis (wt. %)		C/H	[b] $m_{C\ \&\ H}$ (g)	[c] Conversion (wt. %)
			C	H			
EPS	Feed	1.0023	90.45	8.6327	10.48	0.9931	72.2
	[a] Solid residues	3.3110	5.93	2.4083	2.46	0.2759	
Cup lid	Feed	1.0053	90.92	8.4058	10.82	0.9985	78.0
	[a] Solid residues	3.2794	4.49	2.1948	2.05	0.2192	
[d] HIPS loop	Feed	1.0030	91.10	8.4484	10.78	0.9985	71.1
	[a] Solid residues	3.3692	6.02	2.5426	2.37	0.2885	
Coffee spoon	Feed	1.0021	91.59	8.1243	11.27	0.9992	77.7
	[a] Solid residues	3.2618	4.64	2.1997	2.11	0.2233	

[a] Solid residues mean the residual solid after reaction containing catalyst and silica gel (3 g) for column chromatography.

[b] Calculation equation: $m_{Sample} \times [C\ (wt.\ \%) + H\ (wt.\ \%)]$, where m_{Sample} is the mass of solid residues after heating at 120 °C for 3 h.

[c] Calculation equation: $\left(1 - m_{C\ \&\ H}\ of\ solid\ residues / m_{C\ \&\ H}\ of\ feed\right) \times 100\%$.

[d] HIPS loop: disposable inoculating loop made of HIPS (high impact polystyrene) material.

Table S6. The feed and product phases after 10 g scale-up reactions.

Substrates	Feed (g)			Gas phase		Solid phase		Liquid phase	
	PS wastes	$AlCl_3$	DCM	g	wt. %	g	wt. %	g	wt. %
PS	10.0072	2.01	46.62	0.14	0.24	4.2428	7.24	54.2544	92.52
EPS	10.0238	1.87	33.48	0.16	0.35	1.6693	3.68	43.5445	95.97

Table S7. Elemental analysis results of solid residues after 10 g scale-up reactions.

Substrates		m_{Sample} (g)	Elemental analysis (wt. %)		C/H	[b] $m_{C \& H}$ (g)	[c] Conversion (wt. %)
			C	H			
PS	Feed	10.0072	92.12	7.88	11.69	10.0072	77.2
	[a] Solid residues	9.2632	16.30	4.1459	3.93	1.8935	
EPS	Feed	10.0238	90.45	8.6327	10.48	9.9952	88.9
	[a] Solid residues	6.6772	10.33	3.1801	3.25	0.9021	

[a] Solid residues mean the residual solid after reaction containing catalyst and silica gel (5 g) for column chromatography.

[b] Calculation equation: $m_{Sample} \times [C\ (wt.\ \%) + H\ (wt.\ \%)]$, where m_{Sample} is the mass of solid residues after heating at 120 °C for 3 h.

[c] Calculation equation: $\left(1 - m_{C \& H \text{ of solid residues}} / m_{C \& H \text{ of feed}}\right) \times 100\%$.

Refences

1. W. Zhang, S. Kim, L. Wahl, R. Khare, L. Hale, J. Hu, D. M. Camaioni, O. Y. Gutiérrez, Y. Liu and J. A. Lercher, *Science*, 2023, **379**, 807-811.
2. Q. Wang, Y. Zhao, Y. Zhang, T. Zhang, S. He and Y. Wei, *Energy & Fuels*, 2020, **34**, 5485-5496.
3. L. Qiu, F. Polo-Garzon, L. L. Daemen, M.-J. Kim, J. Guo, B. G. Sumpter, M. R. Koehler, C. A. Steren, T. Wang, L. T. Kearney, T. Saito, Z. Yang and S. Dai, *Journal of the American Chemical Society*, 2025, DOI: 10.1021/jacs.5c01107.