

Deep Hydrogenation of Coal Tar over Ni/ZSM-5 Catalyst

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Supporting Information

Reagents and Materials

Cyclohexane (99.5% purity) and naphthalene (99% purity) were purchased from Suyi Chemical Reagent Co., Ltd., Shanghai, China. Anthracene (Alfa Aesar Co., Tianjin, 98% purity), phenanthrene (Aladdin Reagent Co., Shanghai, China; 97% purity), 9,10-diphenylanthracene (Aladdin Reagent Co., Shanghai, China; 98% purity), and ZSM-5 zeolite (Qilu Huaxin Co., Ltd., Shandong, China; Si: Al=38) were also commercially purchased. ZSM-5 zeolite were sieved through a 80-mesh sieve (particle size < 178 μm) and dried in vacuum at 80 °C over night before use. Coal tar was provided by Shanxi Coal and Chemical Technology Institute Co., Ltd.

Preparation of catalyst

According to the method we previously reported, the ZSM-5 supported Ni catalysts was prepared as follows. Diethyl ether (25 mL), ZSM-5 (8 g, particle size < 178 μm), and Ni(CO)₄ (2 mL) were put into the autoclave. After replacing air inside the autoclave with N₂, the mixture in the autoclave was slowly stirred (70 rpm) for 1 h at room temperature to sufficiently impregnate Ni(CO)₄ onto the support. Then the autoclave was heated to 100 °C and kept at the temperature for 1 h with rapid agitation (150 rpm) to allow in situ decomposition of Ni(CO)₄ onto the support. After cooling the autoclave, CO in the autoclave was released followed by subsequent heating and cooling mentioned above to decompose Ni(CO)₄ as exhaustively as possible. Then the reaction mixture was taken out from the autoclave and filtrated under N₂ protection to obtain the supported Ni catalyst.

Mass Spectra for Deep Hydrogenation Products of anthracene and phenanthrene

Qualitatively analyzed by GC/MS, the deep hydrogenation products of anthracene and phenanthrene are matched and compared with standard mass spectra, which are demonstrated from Fig. S1 to S7. The blue parts in the figures indicate the standard mass spectra, and the black lines indicate the actual ones.

All of the matching degrees surpass 95%, especially for the 1,2,3,4,5,6,7,8-octahydroanthracene (99%), 1,2,3,4,4,9,10,10-octahydrophenanthrene (99%), perhydrophenanthrene (97%) and anthracene perhydride (97%).

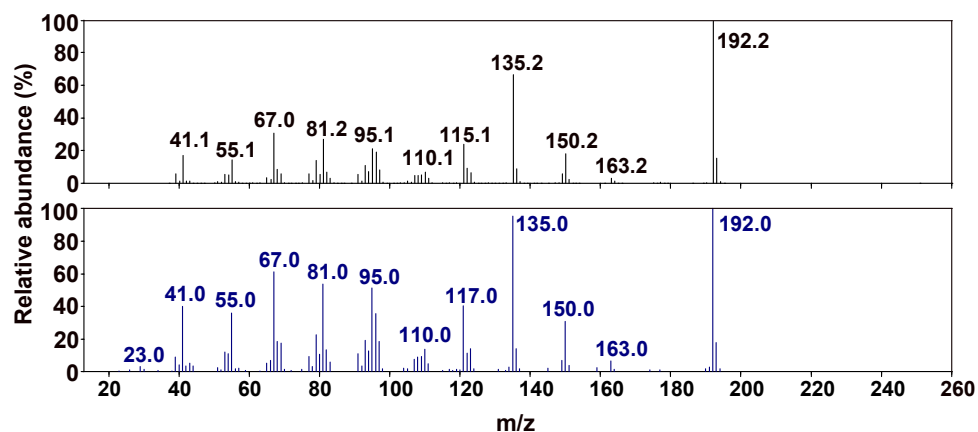


Fig. S1 Mass spectra of anthracene perhydride (Matching 97%).

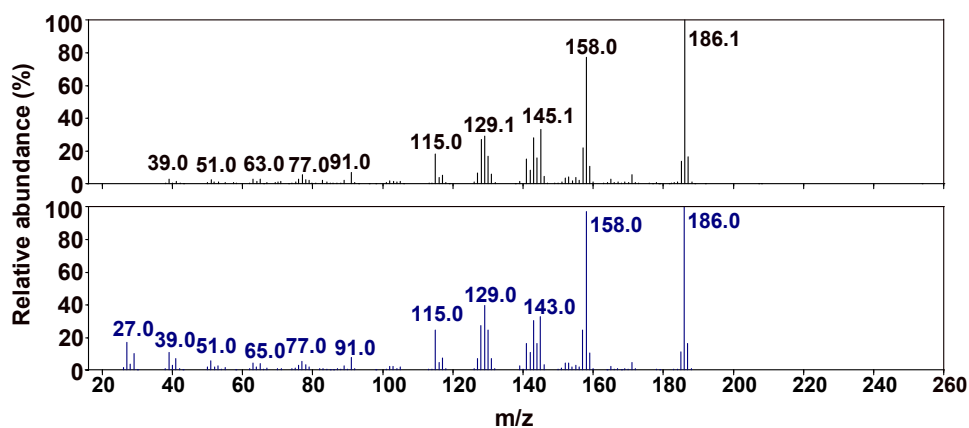


Fig. S2 Mass spectra of 1,2,3,4,5,6,7,8-octahydroanthracene (Matching 99%).

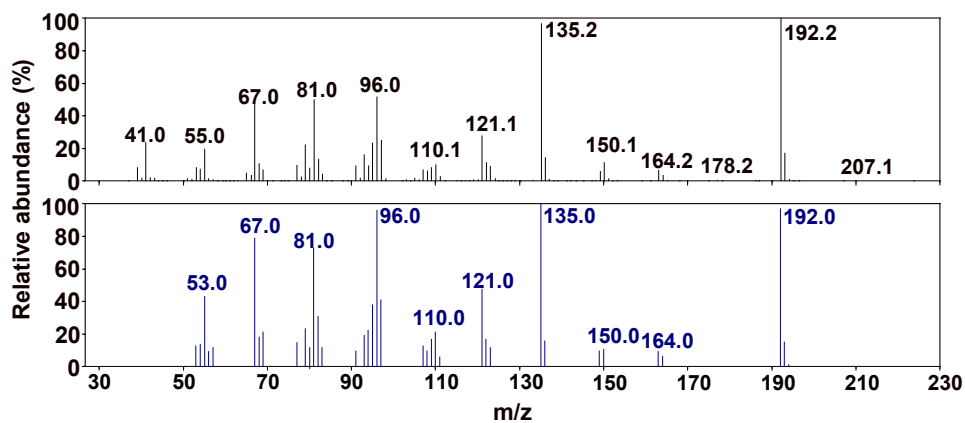


Fig. S3 Mass spectra of perhydrophenanthrene (Matching 97%).

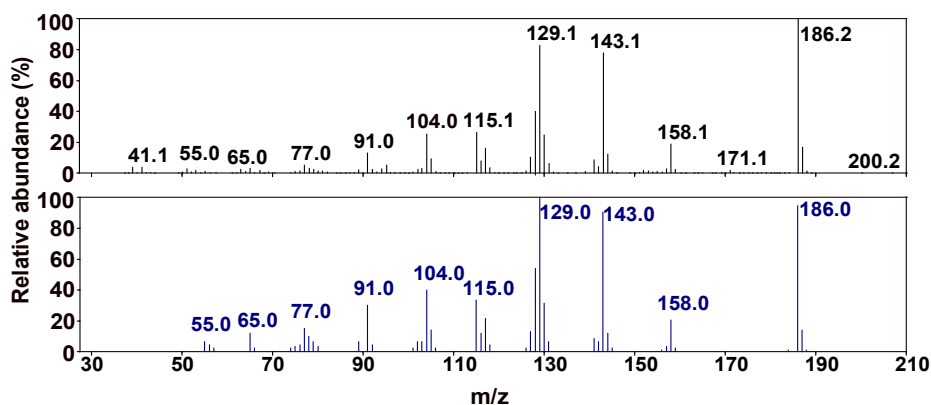


Fig. S4 Mass spectra of 1,2,3,4,4,9,10,10-octahydrophenanthrene (Matching 99%).

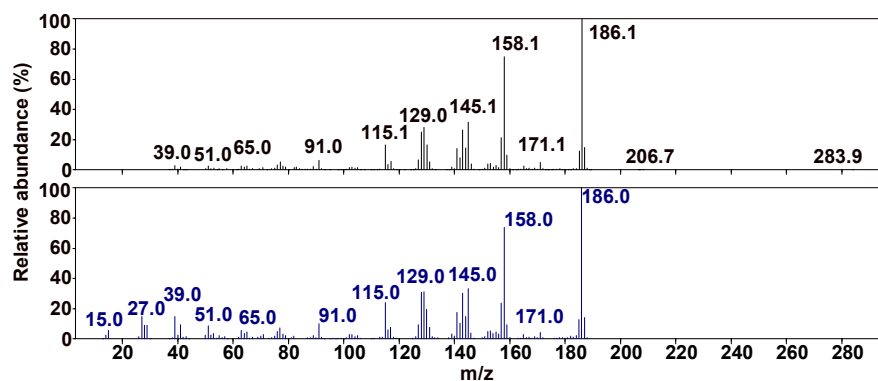


Fig. S5 Mass spectra of 1,2,3,4,5,6,7,8-octahydrophenanthrene (Matching 96%).

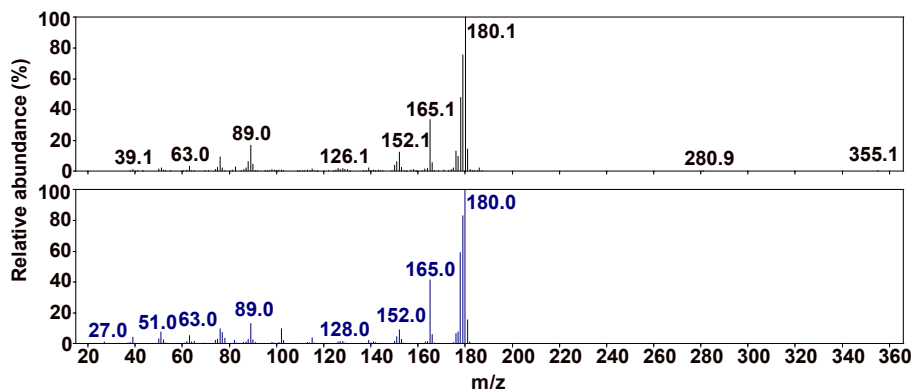


Fig. S6 Mass spectra of 9,10-dihydrophenanthrene (Matching 96%).

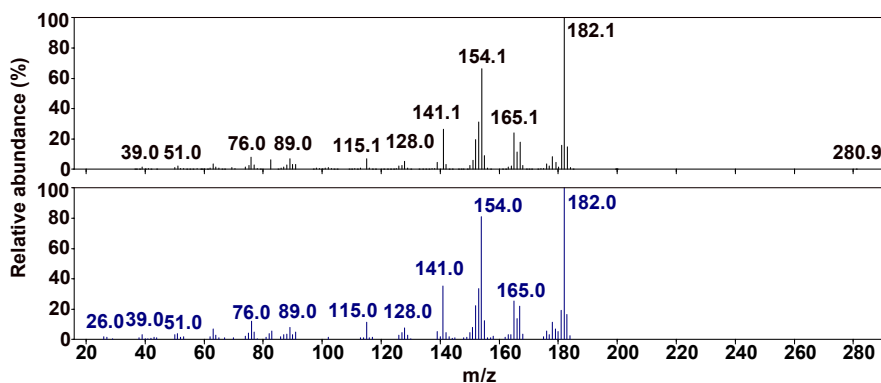


Fig. S7 Mass spectra of 1,2,3,4-tetrahydrophenanthrene (Matching 96%).

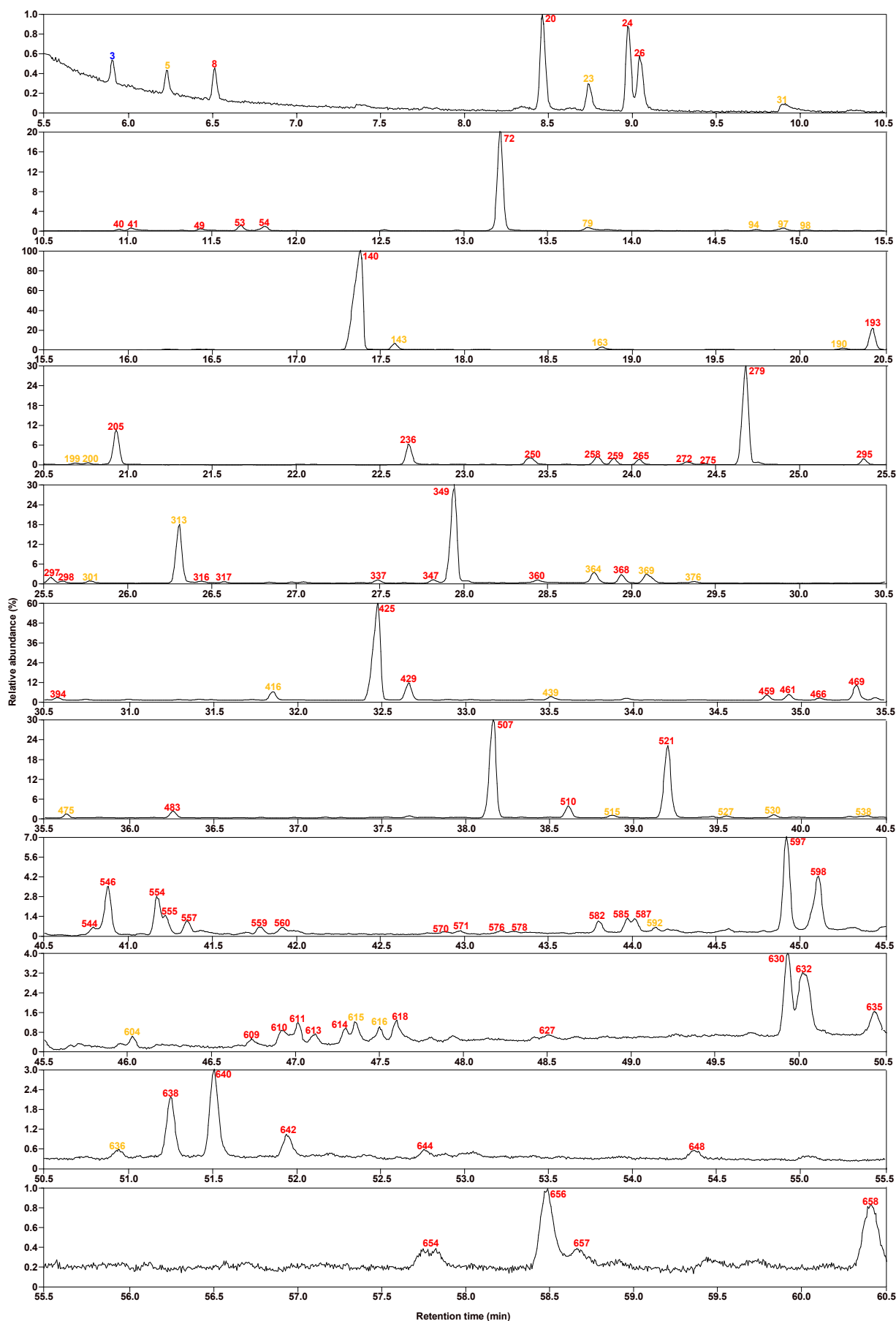


Fig. S8 Total chromatogram of HTCT (the numbers in blue, red and yellow color denote alkanes, arenes and heteroatomic compounds respectively).

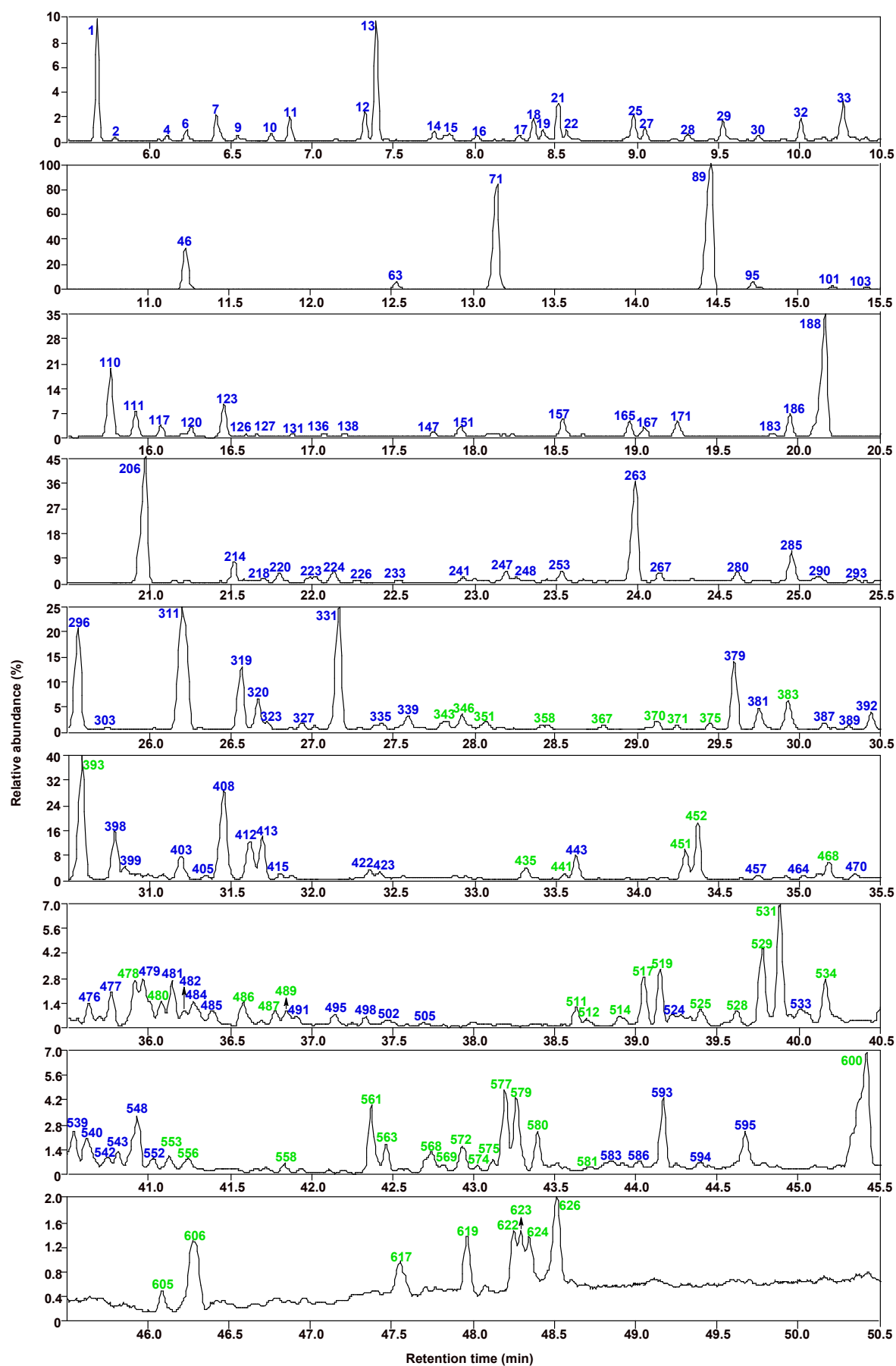


Fig. S9. Total chromatogram of HHTCT (the numbers in blue and green color denote alkanes and deep hydrogenated products respectively).

Table S1 Compounds detected in HTCT and their contents (wt%).

Peak	Compound	Content	Peak	Compound	Content
3	Methylcyclohexane	0.022	469	Cyclopentaphenanthrene	1.820
5	2-Methoxytetrahydrofuran	0.020	475	Dibutylphthalate	0.194
8	Toluene	0.027	483	2-Phenylnaphthalene	0.413
20 and 26	Xylene	0.198	507 and 510	Fluoranthene	7.019
23	Cyclohexanol	0.024	515	1,8-Anthracenediamine	0.232
24	Styrene	0.084	521	Pyrene	4.814
31	Dimethylpyridine	0.018	527, 530	Benzonaphthofuran	0.456
40, 41, 49, 53	Trimethylbenzene	0.684	and 538		
and 54			544, 557, 559	Methylpyrene	0.462
72	Indene	3.357	and 560		
79	Methylphenol	0.131	546, 554	Benzofluorene	1.411
94, 97 and 98	2-Methylbenzofuran	0.177	and 555		
140	Naphthalene	25.484	570, 571, 576	Dimethylpyrene	0.133
143	Benzothiophene	1.057	and 578		
163	Quinoline	0.548	582	Benzonaphthothiophene	0.519
190 and 200	Methylquinoline	0.452	585	Benzophenanthrene	0.163
193 and 205	Methylnaphthalene	5.459	587	Cyclopentapyrene	0.162
199	5-Methylbenzothiophene	0.093	592	Benzacridine	0.037
236	Biphenyl	1.039	597 and 598	Triphenylene	2.237
250, 258, 259, 265	Dimethylnaphthalene	1.837	604	Naphthoxanthene	0.096
272 and 275			609 and 610	7-Methylbenzanthracene	0.252
279	Acenaphthylene	5.044	611 and 614	Dinaphthylmethane	0.344
295 and 298	Methylbiphenyl	0.390	613	2-Methyltriphenylene	0.100
297	Acenaphthene	0.307	615 and 616	Alizarin	0.321
301	Naphthalenecarbonitrile	0.134	618	Hexaethylidenecyclohexane	0.195
313	Dibenzofuran	3.088	627	9-Phenylanthracene	0.053
316 and 317	Trimethylnaphthalene	0.170	630, 632, 638	Benzopyrene	2.513
337	Phenalene	0.204	and 640		
347, 349, 360	Fluorene	6.266	635	Benzacephenanthrylene	0.225
and 368			636	Dinaphthofuran	0.022
364, 369 and 376	Methyldibenzofuran	1.514	642	Perylene	0.186
394	2-Methylfluorene	0.301	644 and 648	Dibenzofluorene	0.043
416	Dibenzothiophene	1.022	654	Benzonaphthacene	0.084
425	Phenanthrene	12.850	656 and 658	Benzoperylene	0.506
429	Anthracene	1.999	657	Benzotriphenylene	0.065
439	Carbazole	0.516			
459, 461 and 466	Methylphenanthrene	1.588			

Table S2 Compounds detected in HHTCT and their yields (wt%).

Peak	Compound	Yield	Peak	Compound	Yield
1	Methylcyclohexane	0.515	379, 398	Hexadecahdropyrene	3.014
2	Ethylcyclopentane	0.023	and 423		
4 and 6	Methylheptane	0.077	381, 403, 408		
7 and 10-12	Dimethylcyclohexane	0.433	412, 413	Hexadecahydrofluoranthene	8.143
9	Methylethylcyclopentane	0.018	and 443		
13	Ethylcyclohexane	0.113	387, 389, 392	Ethane-1,1-diylbis-	1.212
14, 17-19 and 30	Trimethylcyclohexane	0.295	399 and 405	decahydronaphthalene	
15	Dimethylheptane	0.067	415	Octahydromethylphenanthrene	0.181
16	Methyloctane	0.031	422	Hexadecahydroindenoindene	0.325
21, 22, 25 and 27	Methylethylcyclohexane	0.486	435	Octahydromethylanthracene	0.444
28	Isopropylcyclohexane	0.038	441, 451, 452	Decahdropyrene	3.203
29	Propylcyclohexane	0.125	and 468		
32	Tetramethylcyclohexane	0.123	457, 464	Octadecahydronaphthacene	0.538
33 and 46	Octahydroindene	2.777	and 470		
63	Butylcyclohexane	0.088	476, 477, 479		
71 and 89	Decalin	20.896	481, 482, 484	Octadecahydrochrysene	1.318
95, 101, 103			485 and 491		
110, 111, 117	Methyldecalin	4.647	478 and 480	Decahydrobenzofluorene	0.385
120 and 123			486, 487, 489		
126, 127, 131	Dimethyldecalin	0.470	511, 512, 514	Dodecahydrochrysene	1.933
136, 138 and 147			517, 519, 525		
151, 165 and 167	Ethyldecalin	0.859	531 and 534		
157, 171 and 206	Dodecahydroacenaphthylene	5.165	495, 498, 502	Octadecahydrotriphenylene	0.313
183 and 186	Tricyclododecane	0.600	and 505		
188	Bicyclohexyl	3.205	524, 533, 539		
214, 224, 226			540, 542, 543	Eicosahdroperylene	1.694
241, 247, 248	Dodecahydrofluorene	5.288	548 and 552		
and 263			528 and 529	Dodecahydronaphthacene	0.566
218, 220, 223	Methylbicyclohexyl	1.010	553 and 556	Octahydrophenylanthracene	0.305
233 and 253			558, 574, 575	Tetradecahdroperylene	0.378
267, 280, 285	Tetradecahydroanthracene	5.046	580 and 581		
296, 319 and 327			561 and 563	Dodecahydrotriphenylene	0.447
290,293,303,311	Perhydrophenanthrene	7.051	568, 569, 572	Tetradecahydro-	2.002
320, 323 and 331			577, 579	benzo[b]fluoranthene	
335 and 339	Perhydromethylphenanthrene	0.625	and 600		
343	Octahydrophenanthrene	0.271	583, 586	Tetradecahydrobenzo[a]pyren	0.666
346, 351, 358	Dodecahydro-	0.783	and 593-595	e	
and 367	cyclopentaphenanthrene		605, 606, 617		
370, 371 and 375	Octahydrodimethyl-	0.452	619, 622-624	Hexadecahydrobenzoperylene	0.802
	(1-methylethenyl)naphthalene		and 626		

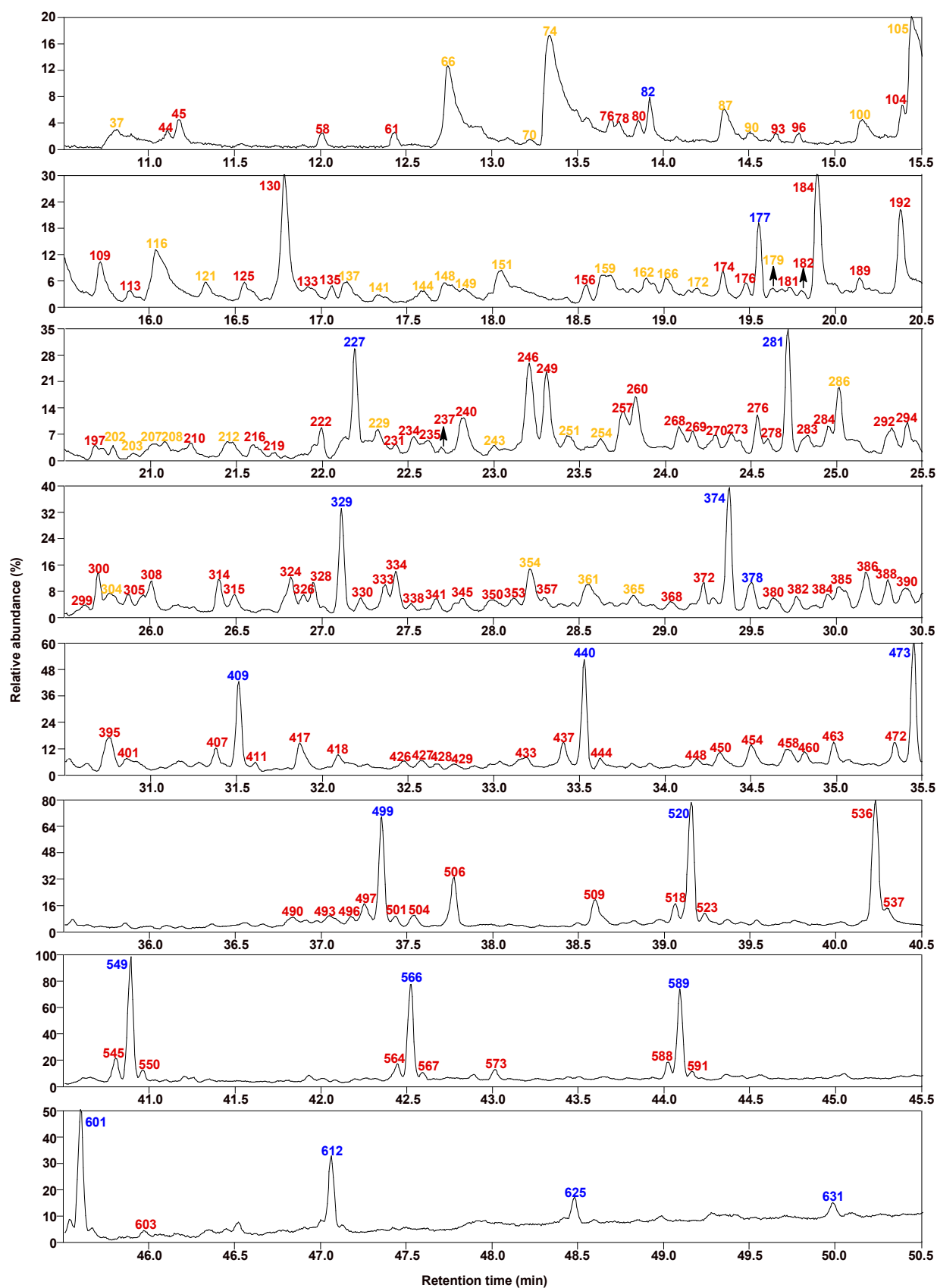


Fig. S10 Total chromatogram of LTCT (the numbers in blue, red and yellow color denote alkanes, unsaturated hydrocarbons including olefins and arenes, and heteroatomic compounds respectively).

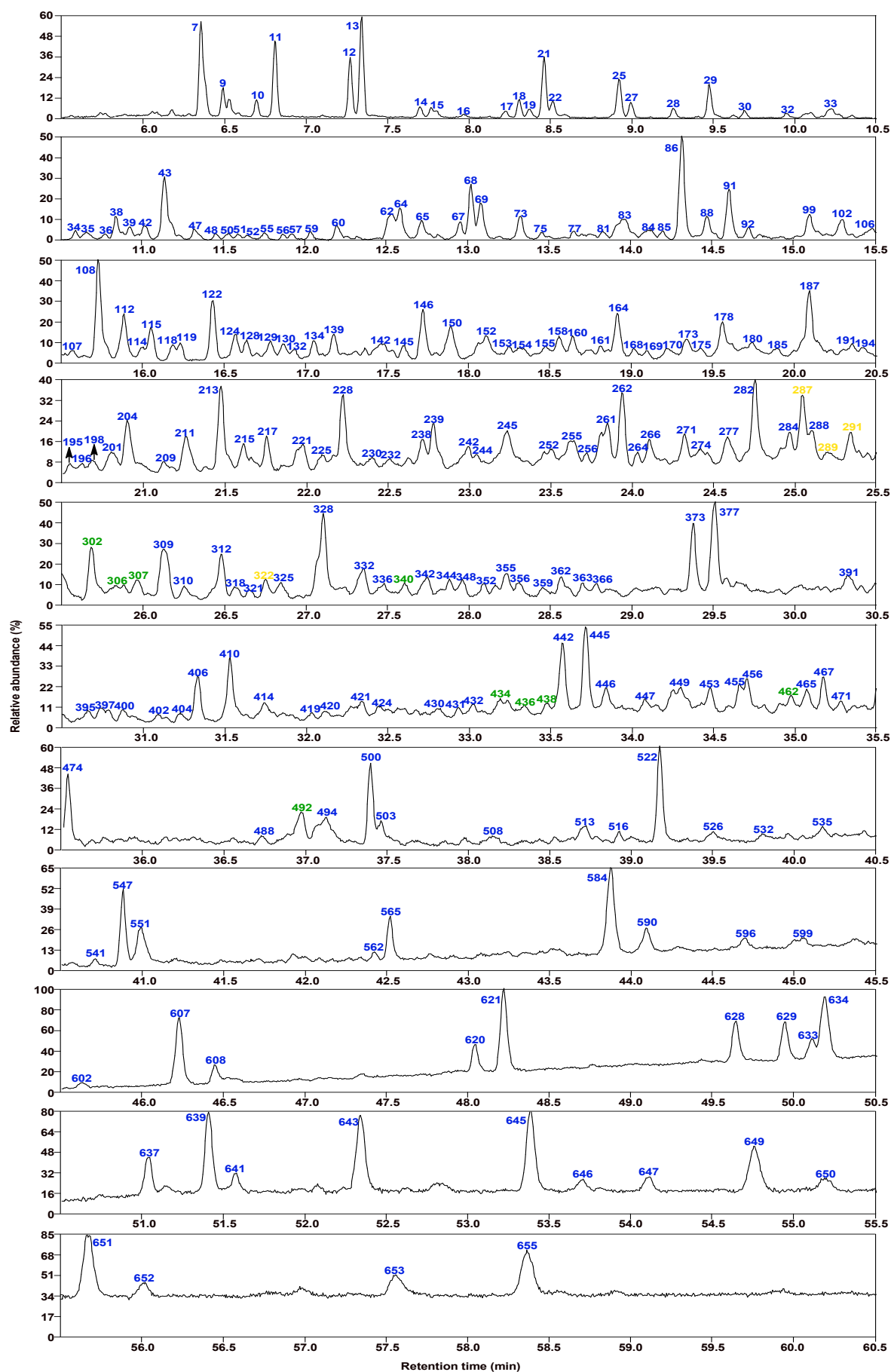


Fig. S11 Total chromatogram of HLTCT (the numbers in blue, green and yellow color denote alkanes, deep hydrogenated products and heteroatomic compounds respectively).

Table S3 Compounds detected in LTCL and their contents (wt%).

Peak	Compound	Content	Peak	Compound	Content
37	Phenol	0.356	284	Acenaphthene	0.185
44, 45 and 58	Trimethylbenzene	0.318	286	Ditertbutylphenol	0.567
61	Indane	0.095	292, 294, 299	Trimethylnaphthalene	5.652
66, 70 and 74	Methylphenol	2.051	305, 308, 314		
76 and 78	Ethyl dimethylbenzene	0.095	315, 324, 326		
80, 104 and 109	Methylindan	0.968	and 334		
82	Undecane	0.221	300	Tertbutyltetralin	0.628
87, 105, 116	Dimethylphenol	3.707	304	Dibenzofuran	0.664
and 121			328, 330	Hexadecene	1.070
90	2-Methylbenzofuran	0.057	and 338		
93 and 96	Durene	0.107	329	Hexadecane	1.474
100	Ethylphenol	0.237	341	Isopropenylnaphthalene	0.304
113	Butynylbenzene	0.145	345 and 350	Methylbiphenyl	1.029
125	Dodecene	0.296	353	Tertbutylnaphthalene	0.211
130	Naphthalene	1.645	354, 361	Methyldibenzofuran	2.217
133, 135, 156	Dimethylindan	0.804	and 365		
and 176			357, 382, 395	Tetramethylnaphthalene	2.133
137, 149, 162	Trimethylphenol	0.826	and 401		
and 166			368	Ethylbiphenyl	0.148
141 and 144	Dimethylbenzofuran	0.506	372	Heptadecene	0.644
148, 151 and 159	Ethylmethylphenol	1.522	374	Heptadecane	1.814
172 and 179	Thymol	0.206	378	Dimethylheptadecane	0.635
174	Tridecene	0.283	380	Dimethylisopropylnaphthalene	0.301
177	Tridecane	0.660	384, 385, 386	Methylfluorene	2.508
181, 182, 189	Dimethyltetralin	0.495	and 390		
and 231			388	Methylundecene	0.573
184 and 192	Methylnaphthalene	2.767	407 and 411	Octadecene	0.759
197	Trimethylindan	0.125	409	Octadecane	1.805
202 and 203	Naphthalenemethanol	0.192	417	Anthracene	0.890
207 and 208	Indanol	0.209	418	Phenanthrene	0.506
210	Diethylmethylbenzene	0.099	426 and 427	Dimethylfluorene	0.533
212	Tetramethylphenol	0.473	428 and 429	Methylstilbene	0.260
216 and 219	Trimethylindene	0.512	433	Tetrahydrodimethylantracene	0.400
222	Tetradecene	0.500	437 and 444	Nonadecene	1.108
227	Tetradecane	1.162	440	Nonadecane	2.269
229, 243, 251	Methylindanol	0.995	448, 450	Methylantracene	1.686
and 254			and 454		
234 and 269	Ethyl naphthalene	0.482	458, 460	Methylphenanthrene	1.856
235 and 237	Trimethyltetralin	0.209	and 463		
240, 246, 249, 257	Dimethylnaphthalene	4.710	472	Eicosene	0.617
260 and 268			473	Eicosane	2.488
270, 273, 276, 278	Pentadecene	1.536	490, 493	Dimethylphenanthrene	1.691
and 283			and 496		
281	Pentadecane	1.159	497 and 501	Heneicosene	1.348

Table S3 Compounds detected in LTCL and their contents (wt%) (Continued).

Peak	Compound	Content	Peak	Compound	Content
499	Heneicosane	3.207	564 and 567	Tetracosene	1.072
504	Fluoranthene	0.484	566	Tetracosane	3.487
506	Butylhexylnaphthalene	1.680	573	Isopropyldimethylphenanthrene	0.516
509	Pyrene	1.151	588 and 591	Pentacosene	0.982
518 and 523	Docosene	1.048	589	Pentacosane	3.197
520	Docosane	3.877	601	Hexacosane	1.663
536	Isopropylmethylphenanthrene	4.413	603	Hexacosene	0.231
537	Methylpyrene	0.818	612	Heptacosane	1.044
545 and 550	Tricosene	1.413	625	Octacosane	0.403
549	Tricosane	4.250	631	Nonacosane	0.278

Table S4 Compounds detected in HLTCL and their yields (wt%).

Peak	Compound	Yield	Peak	Compound	Yield
7 and 10-12	Dimethylcyclohexane	4.148	204	Dodecahydroacenaphthylene	1.033
9	Methylethylcyclopentane	0.342	209, 211, 213		
13	Ethylcyclohexane	1.585	230, 232, 242	Dimethylbicyclohexyl	2.795
14, 17-19 and 30	Trimethylcyclohexane	0.430	and 244		
15	Dimethylheptane	0.231	215	Methyltridecane	0.231
16	Methyloctane	0.040	221 and 245	Perhydrophenalene	1.309
21, 22, 25, 27 and 28	Methylethylcyclohexane	2.411	225	Decahydroisopropyl- dimethylnaphthalene	0.157
29	Propylcyclohexane	0.640	228	Tetradecane	1.458
32	Tetramethylcyclohexane	0.063	238 and 239	Ethylbicyclohexyl	1.469
33, 43 and 56	Octahydroindene	1.744	252	Perhydroanthracene	0.147
34, 38, 39, 47 and 48	Isopropylmethyl- cyclohexane	1.316	255 and 256	Octylcyclohexane	0.548
35, 36 and 42	Ethyl dimethylcyclohexane	0.791	261	Methyltetradecane	0.725
50, 51 and 55	Diethylcyclohexane	0.652	262, 266, 271 and 284	Dodecahydrofluorene	2.286
52	Bicyclopentyl	0.233	264, 274 and 277	Methylpentadecane	0.627
57	Methylpropylcyclohexane	0.251	282	Pentadecane	1.522
59 and 60	Butylcyclohexane	0.273	287, 289 and 291	Ditertbutylphenol	1.012
62, 64, 65, 67 69, 73 and 85	Octahydromethylindene	3.533	288, 309, 312 and 325	Perhydrophenanthrene	2.870
68 and 86	Decalin	2.912	302, 306 and 307	Tetramethyltetralin	1.496
75, 77, 81 and 84	Isopropyl dimethyl- cyclopentane	1.053	310, 321 and 328	Hexadecane	2.323
83	Undecane	0.541	318, 332, 336 342, 344, 348 and 352	Perhydromethylphenanthrene	1.658
88	Octahydroethylindene	0.573	322	Dihydrotetramethylindenone	0.253
91, 92, 99, 102			340	Isopropylmethyltetralin	0.210
108, 112, 115 119 and 122	Methyldecalin	8.006	355 and 356 359, 363 and 366	Methylpentadecane	0.347
106, 107, 114, 124 128, 130, 132, 134 139, 142, 145, 146 150, 152, 155, 158 160, 169 and 170 118, 164, 168	Dimethyldecalin	9.872	362	Decylcyclohexane	0.211
173, 175, 180 and 185	Ethyldecalin	3.348	373	Heptadecane	1.272
129	Dodecane	0.540	377 and 391	Dimethylheptadecane	1.727
153, 154 and 178	Tridecane	1.893	395, 397, 400 and 406	Hexadecahydropyrene	1.232
161	Dimethyldodecane	0.438	402 and 404	Hexadecahydrofluoranthene	0.257
187	Bicyclohexyl	1.834	410	Octadecane	1.221
191, 194, 195, 196 198, 201 and 217	Methylbicyclohexyl	1.562	414 and 419	Eicosane	0.316

Table S4 Compounds detected in HLTCL and their yields (wt%) (Continued).

Peak	Compound	Yield	Peak	Compound	Yield
420, 421, 424 430 and 431 432 434, 436 and 438 442, 445, 446 447, 449 and 456 453 455 462 and 492 465, 467 and 471 474, 488 and 494 500, 503, 508 and 513 516	Cyclohexylperhydro- anthracene Propnediylbiscyclohexane Octahydromethylanthracene Nonadecane Longipinane Diethyldecahydro- methanonaphthalene Octahydroisopropyl- methylphenanthrene Octadecahydrochrysene Eicosane Heneicosane Dodecylcyclohexane	0.671 0.153 0.573 4.750 0.410 0.459 1.264 1.094 2.701 1.274 0.142	522, 526, 532 and 535 541 547 551 and 565 562 584 and 590 596 and 599 607 and 608 620 621 628 and 629 633 and 634 637, 639 and 643 641 645, 649 and 655 646 647 and 650 651 and 653 652	Docosane Butanediylbiscyclohexane Methyleicosane Tetracosane Heptadecyclohexane Pentacosane Hexacosane Heptacosane Octacosane Nonacosane Triacontane Methyltriacontane Hentriacontane Dodecylperhydroanthracene Tetratriacontane Stigmastane Hopane Hexatriacontane Isobutylisocopalane	2.183 0.131 1.579 2.215 0.136 3.466 0.443 3.887 1.203 3.592 3.478 4.336 6.049 0.433 5.958 0.437 1.021 3.255 0.637