Supporting Information for

Chiral Ionic Organic Single-Crystal and Its Exfoliated Two-Dimensional Nanosheets with Boosting Enantioseparation

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1. Reagents and Apparatus

Tetraethyl orthosilicate (TEOS), polymethylhydrosiloxane (PMHS) and trifluoroacetic acid (TFA, 95%) were purchased from J&K. Sci-entific. Ltd. (Beijing, China); Polydimethylsiloxane (HO-TOS) was got form Alfa Aesar (Heysham, UK). The rest of the reagents used were analytically pure and purchased from Shanghai McLean Biochemical Technology Co. Untreated fused-silica capillary tubing (0.25 mm i.d.) was obtained from Yongnian Ruifeng Chromatogram Apparatus Co. Ltd. (Hebei, China). Commercial Abel AB-5MS capillary column (long 30 m × i.d. 0.25 mm × film thickness 0.25 μm) was obtained from Abel Ltd (America). Commercial β-DEX 120 column (long 30 m × i.d. 0.25 mm × film thickness 0.25 μm) was obtained Supelco Inc. (Bellefonte, PA, USA). The field emission scanning electron microscope (JSM-6701F, Japan) was used to characterize the morphology of materials and capillary columns; the transmission electron microscopy (Tecnai G2 TF20, FEIUSA) was used to receive the high resolution transmission electron microscope and selected area diffraction image of the 2D-NSs, the scanning probe microscope (Bruker Nano Inc, America) was used to test the thickness of 2D-NSs, the thermal gravimetric analyzer (STA449C, Germany) is used to test the thermal stability of materials; the Bruker DRX-500 NMR spectrometer (Bremen, Germany) is used for measure compound structure, Fourier transform infrared spectrometer (V70, Bruker, Germany) was used to examine the composition of materials. All the gas chromatograms were obtained by an Echrom gas chromatograph (A-90E, China) equipped with a split/splitless injector and a flame ionization detector (FID), with high-purity nitrogen (99.999%) used as the carrier gas, the injection port maintained at 250°C, the injection volume set at 1 μL, and the FID detector temperature set at 280°C.

2. Materials Preparation

Synthesis of CIL

Synthesis of CIL based on reported literature.[1-2] Firstly, L-menthol (15.63 g, 0.10 mol) was dissolved in a 250 mL round-bottom flask with 50 mL of CH_2Cl_2, and the resulting mixture was heated to 33°C to form a homogeneous transparent solution. Bromoacetyl bromide (22.43 g, 0.11 mol) was added to the above solution, and the reaction was carried out at 43°C for 3 h. The resulting product was washed three times with 40 mL of saturated Na_2SO_4 solution, and the organic phase was dried overnight with anhydrous Na_2SO_4. Finally, the filtrate was subjected to vacuum distillation, yielding a transparent orange liquid, which is identified as (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 2-bromoacetate. Then, (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 2-bromoacetat (1.86 g, 0.0254 mmol) and 4,4’-bipyridine (0.50 g, 0.0032 mmol) were dissolved in 50 mL acetonitrile then heated to 82°C for 8 h. CIL is the yellow powder solid obtained by filtration of the obtained substance, rotary evaporation to remove the solution and drying.

Synthesis of pyroglutamic acid derivative

According to literature reports, the synthesis of derivative of pyroglutamic acid was carried out as follows[3]: A solution was prepared by dissolving pyroglutamic acid (100 mg) and 1 mL of isopropanol-acetyl chloride (3:1, v/v) in a polytetrafluoroethylene-lined vessel, which was then sealed and reacted at 110°C for 1 h. The excess solvent was removed, and the resulting product was dissolved in THF (5 mL). Trifluoroacetic anhydride (1 mL) was slowly added dropwise to the solution, which was then sealed and heated at 90°C for 1 h to yield the trifluoroacetyl butyl ester derivative of pyroglutamic acid.

Fabrication of CIL, CIOC and 2D-NSs coated capillary columns

CIL, CIOC and 2D-NSs coated capillary columns (10 m × 0.25 mm i.d.) were prepared using the sol-gel method:[4-5] 100 µL of TEOS, 200 µL of HO-TOS, and 10 µL of PMHS were mixed thoroughly in a 10 mL centrifuge tube, then 2.72 mg of CIL/CIOC/2D-NSs with 500 µL of CH_2Cl_2 were added into the mixture and sonicated for 5 min. Finally, another 500 µL of CH_2Cl_2 and 150 µL TFA were added and sonicated for 5 min to obtain the gel solution. The prepared solution was then carefully pumped into a pre-treated capillary column, where it was allowed to be kept at room temperature for a period of 30 min, followed by expelling the solution from the capillary column. Subsequently, the coated capillary column was subjected to an aging process consisting of holding it at a temperature of 40°C for 30 min, gradually increasing the temperature to 200°C at a rate of 1 °C min^{-1}, and maintaining it at 200°C for 6 h, which ultimately led to the successful preparation of the CIL, CIOC or 2D-NSs coated capillary column, respectively.

3. Calculations of chromatographic parameters

The efficiency of separation was calculated by the following equations:[6]

Separation factor (α):

$$\alpha = \frac{t_{R2} - t_M}{t_{R1} - t_M} \quad (1)$$

Resolution (Rs):

$$R_S = \frac{2(t_{R2} - t_{R1})}{w_1 + w_2} \quad (2)$$

t: retention time; t_M: bed void time; *W*: the peak widths.

The enthalpy change (ΔH) and entropy change (ΔS) are calculated by the following formula:[7]

$$lnK = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} + ln\phi \quad (3)$$

T: the column temperature; ϕ: the phase ratio.

4. Fig. S1 to S10

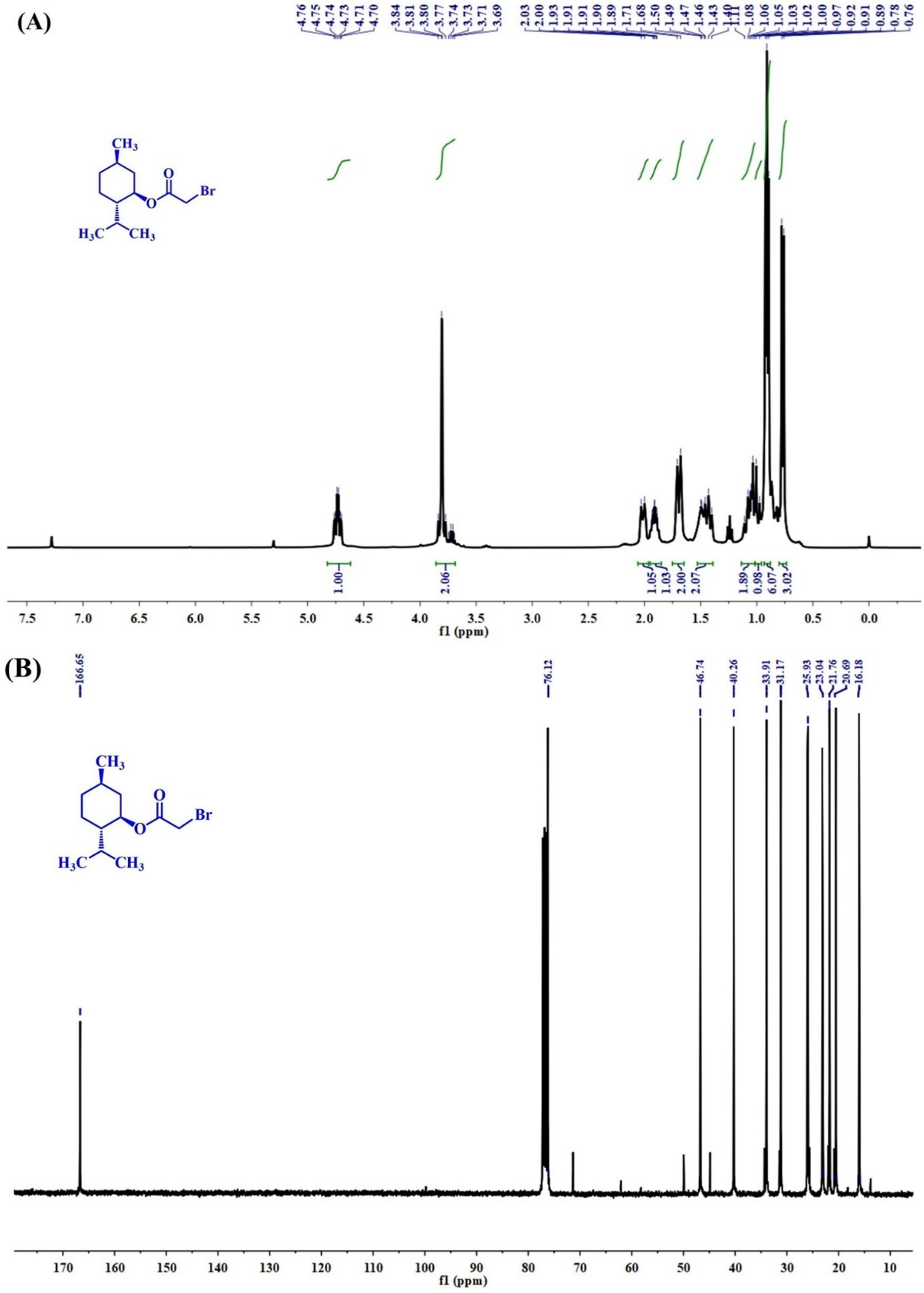

Fig. S1. NMR of (1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 2-bromoacetate. (A) ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm) δ: 0.76-0.78 (d, 3H), 0.89-0.92 (t, 6H), 0.97-1.00 (d, 1H), 1.02-1.11 (m, 2H), 1.40-1.50 (m, 2H), 1.68-1.71 (d, 2H), 1.88-1.94 (m, 1H), 2.00-2.03 (d, 1H), 3.69-3.84 (m, 2H), 4.70-4.76 (m, 1H); (B) ^{13}C NMR (DMSO, 400 MHz, δ/ppm) δ: 16.18, 20.69, 21.76, 23.04, 25.93, 31.17, 33.91, 40.26, 46.74, 76.12, 166.65.

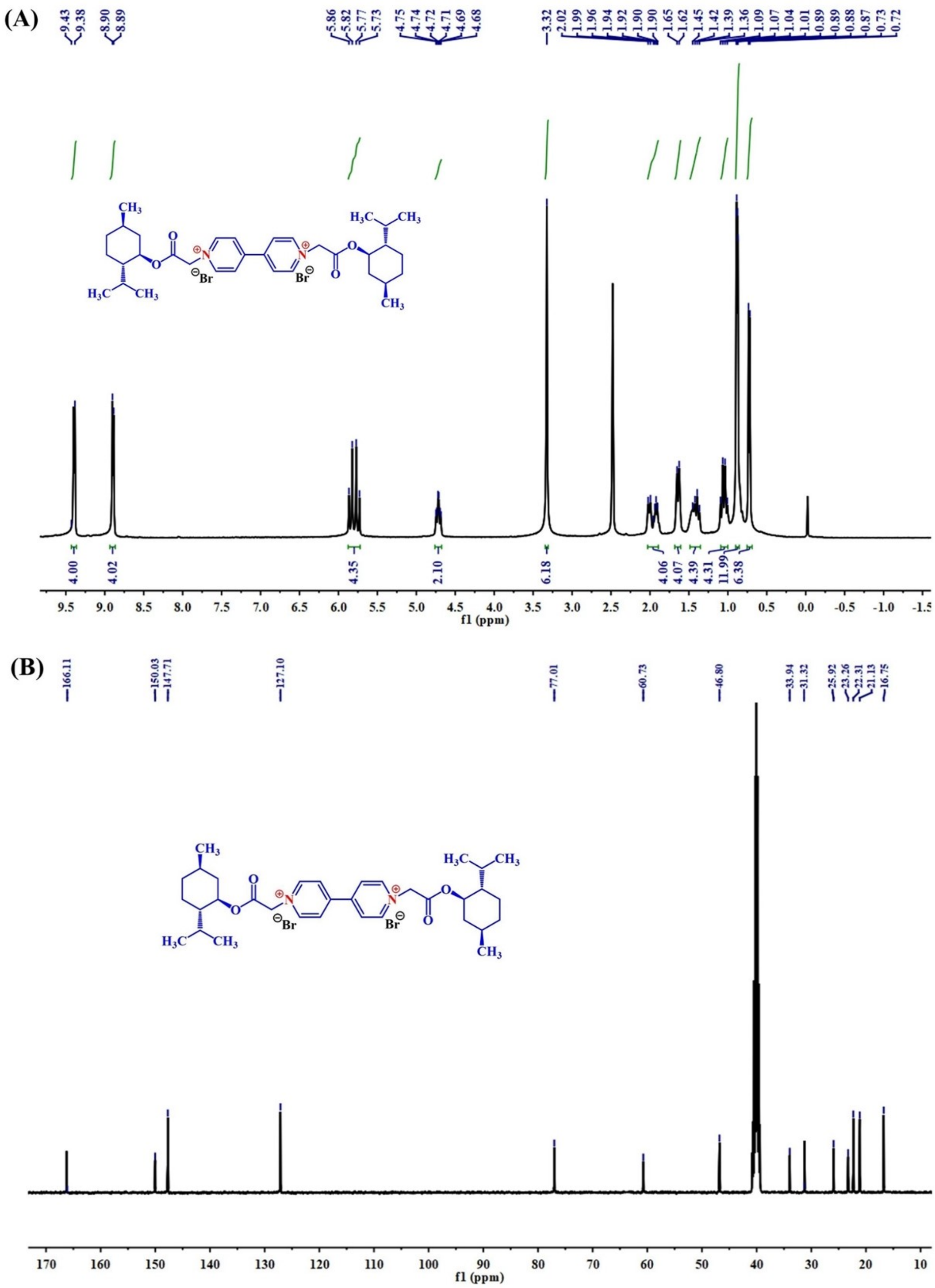

Fig. S2. NMR of CIL. (A) ^{1}H NMR ($CDCl_3$, 400 MHz, δ/ppm) δ: 0.72-0.73 (d, 6H), 0.87-0.89 (m, 12H), 1.01-1.09 (m, 4H), 1.36-1.45 (m, 4H), 1.40-1.50 (m, 2H), 1.62-1.65 (d, 4H), 1.90-2.20 (m, 4H), 3.32 (s, 6H), 4.68-4.75 (m, 2H), 5.73-5.86 (m, 4H), 8.89-8.90 (d, 4H), 9.38-9.443 (d, 4H); (B) ^{13}C NMR (DMSO, 400 MHz, δ/ppm) δ: 16.75, 21.13, 22.31, 23.26, 25.92, 31.32, 33.94, 46.80, 60.73, 77.01, 127.10, 147.71, 150.03, 166.11.

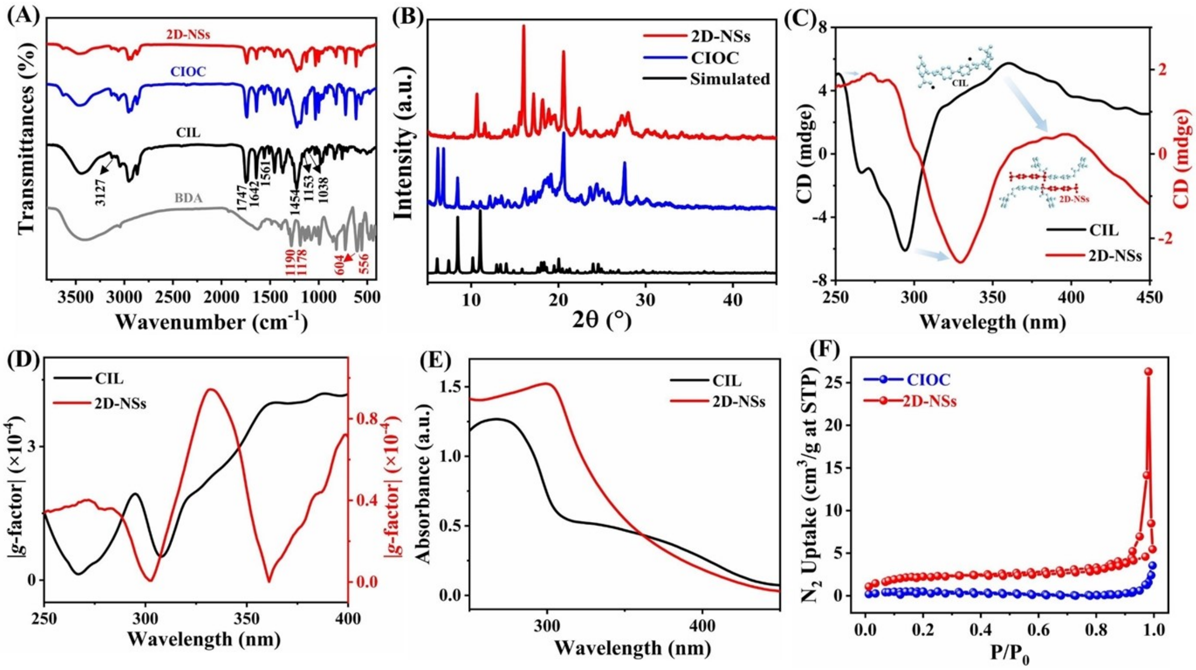

Fig. S3. FT-IR spectra of BDA, CIL, CIOC and 2D-NSs(A). XRD patterns of CIOC and 2D-NSs, simulated structure of CIOC (B). Solid CD (C), relevant *g*-factor (D) and UV-vis absorption spectra of CIL and 2D-NSs (E). N_2 sorption isotherms of CIOC and 2D-NSs (F).

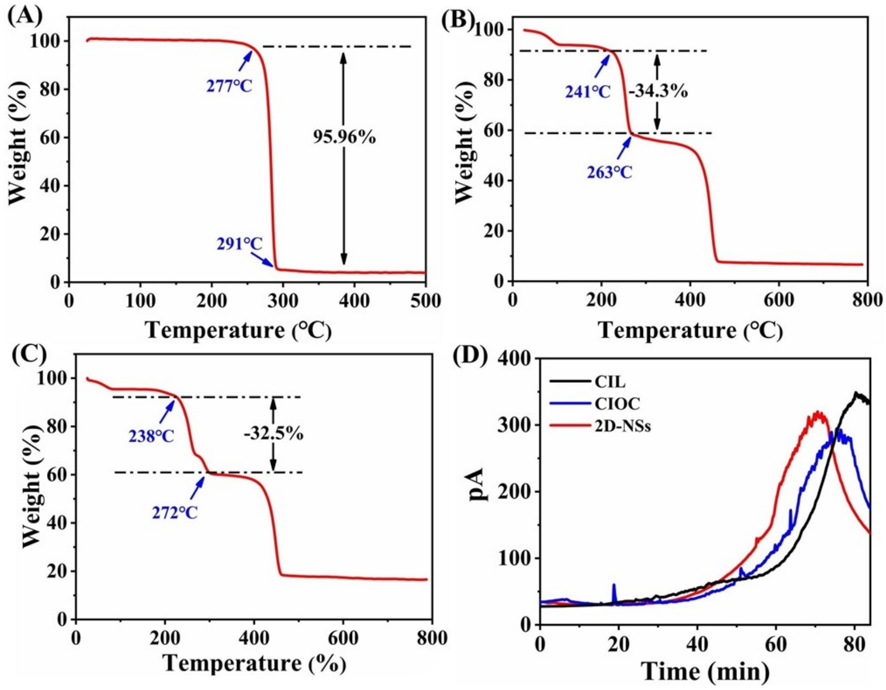

Fig. S4. Thermogravimetric curve of CIL (A), CIOC (B) and 2D-NSs (C). Bleeding curves of CIL-/CIOC-/2D-NSs coated columns (D). Oven program: 40°C to 250°C at 3 °C min^{-1}. Flow rate: 1.0 mL min^{-1}.

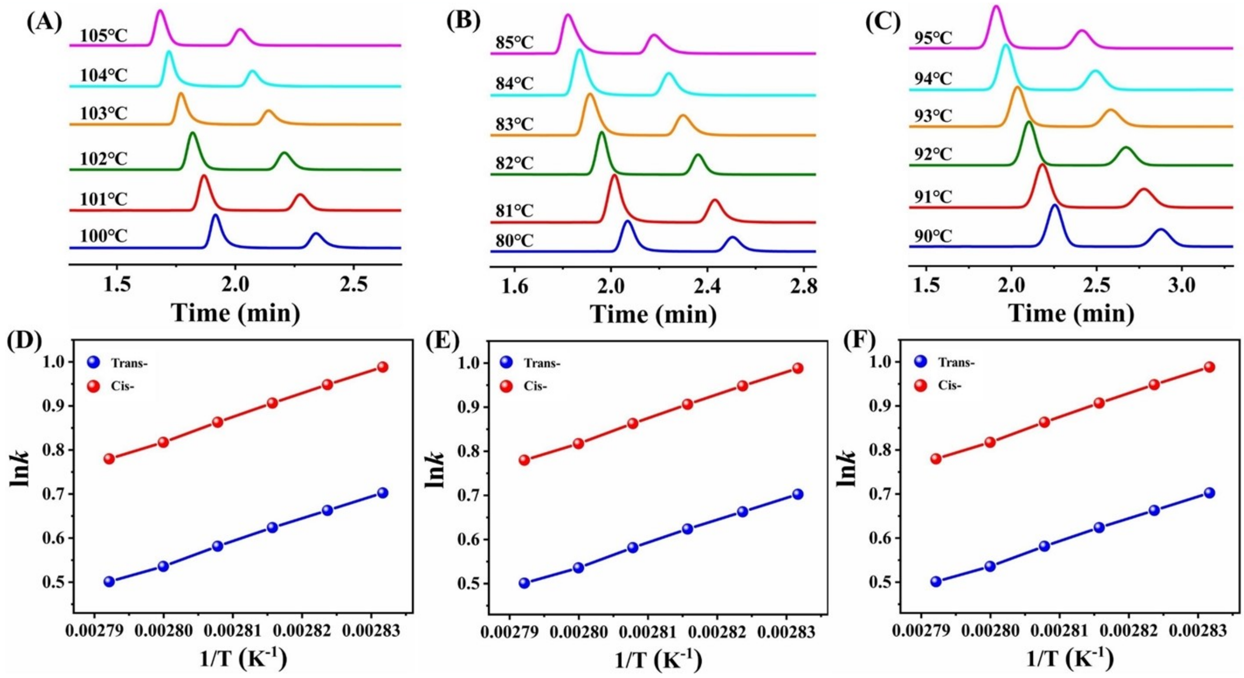

Fig. S5. Chromatograms of decahydronaphthalene isomers at varying temperature (100-105°C) on CIL coated columns (A), Van't Hoff plot of trans-/cis-decahydronaphthalene (D). Chromatograms of decahydronaphthalene isomer at varying temperature (80-85°C) on CIOC coated columns (B), Van't Hoff plot of trans-/cis-decahydronaphthalene (E). Chromatograms of decahydronaphthalene isomers at varying temperature (90-95°C) on 2D-NSs coated columns (C), Van't Hoff plot of trans-/cis-decahydronaphthalene (F).

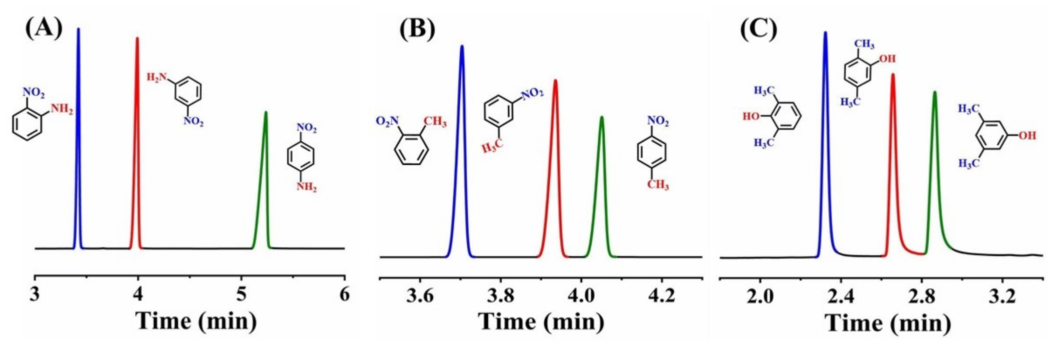

Fig. S6. Gas chromatograms of positional isomers on AB-5MS column (long 30 m): nitroaniline (A), nitrotoluene (B), dimethylphenol (C). Oven program: 100°C to 170°C at 30 °C min^{-1} for (A), 50°C to 150°C at 30 °C min^{-1} for (B), 70°C to 150°C at 20 °C min^{-1} for (C). Flow rate: 3.0 mL min^{-1} for (A); 2.0 mL min^{-1} for (B, C).

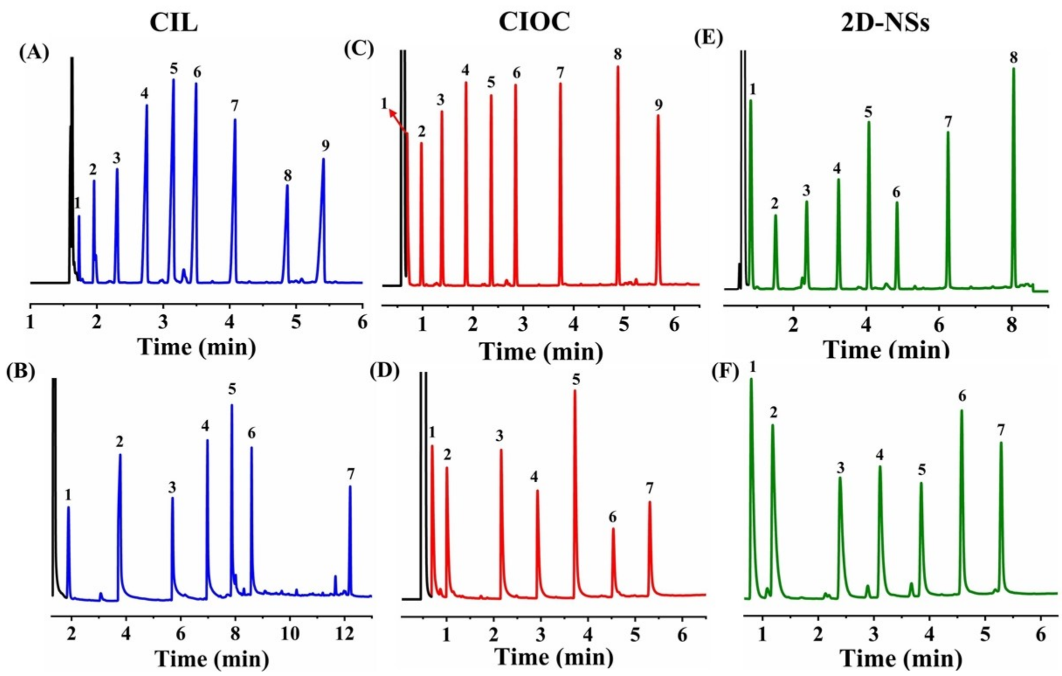

Fig. S7. Separation of n-alkanes and n-alkanols on CIL, CIOC and 2D-NSs columns. Gas chromatograms on CIL coated column of n-alkanes (A): (1) n-hexane, (2) n-heptane, (3) n-octane, (4) n-nonane, (5) n-decane, (6) n-undecane, (7) n-tridecane, (8) n-hexadecane, (9) n-octadecane; n-alkanols (B): (1) n-butanol, (2) n-hexanol, (3) n-heptanol, (4) n-octanol, (5) n-nonanol, (6) n-decanol, (7) n-undecanol. Gas chromatograms on CIOC coated column n-alkanes (C): (1) n-hexane, (2) n-heptane, (3) n-octane, (4) n-nonane, (5) n-decane, (6) n-undecane, (7) n-tridecane, (8) n-hexadecane, (9) n-octadecane; n-alkanols (D): (1) n-propanol, (2) n-butanol, (3) n-hexanol, (4) n-heptanol, (5) n-octanol, (6) n-nonanol, (7) n-decanol. Gas chromatograms on 2D-NSs coated column of n-alkanes (E): (1) n-hexane, (2) n-heptane, (3) n-octane, (4) n-nonane, (5) n-decane, (6) n-undecane, (7) n-tridecane, (8) n-hexadecane; n-alkanols (F): (1) n-butanol, (2) n-hexanol, (3) n-heptanol, (4) n-octanol, (5) n-nonanol, (6) n-decanol, (7) n-undecanol. Oven program: 30°C (for 1 min) to 60°C at 20 °C min^{-1}, to 180°C at 40 °C min^{-1} for (A); 35°C (for 2 min) to 100°C at 20 °C min^{-1} for (B); 32°C to 180°C at 30 °C min^{-1} for (C); 50°C to 130°C at 15 °C min^{-1} for (D); 40°C (for 1 min) to 180°C at 20 °C min^{-1} for (E); 50°C to 180°C at 20 °C min^{-1} for (F). Flow rate: 3.0 mL min^{-1} for (A); 0.5 mL min^{-1} (for 2 min) to 3.0 mL min^{-1} at 2 min min^{-2} for (B); 2.0 mL min^{-1} for (C, D, E); 1.5 mL min^{-1} for (F).

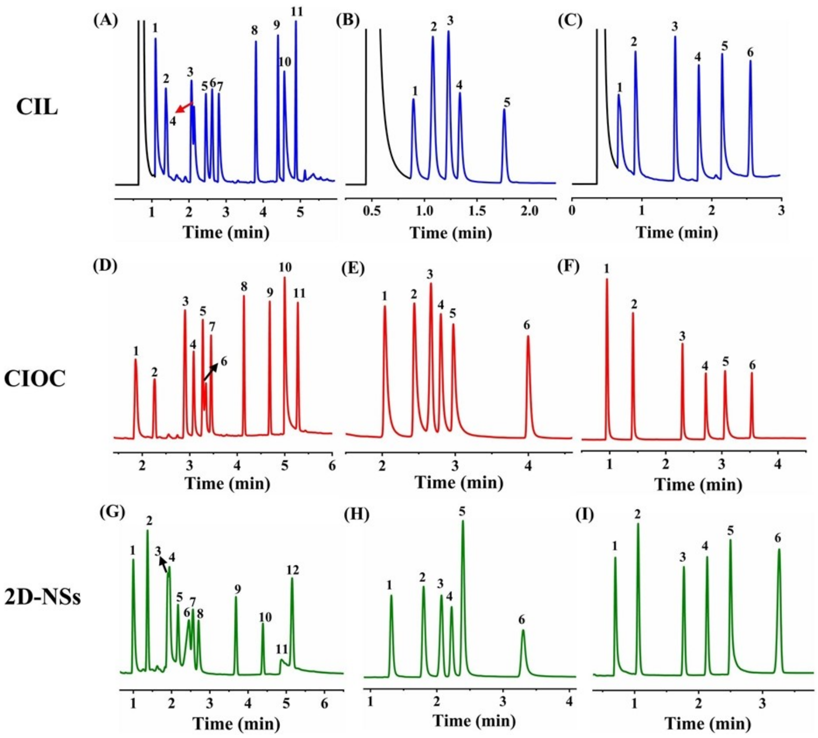

Fig. S8. Separation of Grob, phenols and anilines mixtures on CIL, CIOC and 2D-NSs coated columns. Gas chromatographs on CIL coated column of Grob mixture (A): (1) 2,3-butanediol, (2) decane, (3) n-octanol + nonanal, (4), 2,6-dimethylphenol (5) dodecane, (6) 2,6-dimethylaniline, (7) 2-ethylhexanoic acid, (8) dicyclohexyl amine, (9) methyl undecanoate, (10) dicyclohexyl amine, (11) methyl dodecanoate; phenols mixtures (B): (1) phenol, (2) 4-methylphenol, (3) 2,5-dimethylphenol, (4) p-dimethylphenol, (5) 4-tert-butylphenol; anilines mixtures (C): (1) aniline, (2) 2-chloroaniline, (3) 2,4-dichloroaniline, (4) 2-nitroaniline, (5) 3-nitroaniline, (6) tribromoaniline. Gas chromatographs on CIOC coated column of Grob mixture (D): (1) 2,3-butanediol, (2) decane, (3) n-octanol + nonanal, (4) 2,6-dimethylphenol, (5) dodecane, (6) 2,6-dimethylaniline, (7) 2-ethylhexanoic acid, (8) methyl decanoate, (9) methyl undecanoate, (10) dicyclohexyl amine, (11) methyl dodecanoate; phenols mixtures (E): (1) phenol, (2) 4-methylphenol, (3) 2-nitrophenol, (4) 2,5-dimethylphenol, (5) 3-ethylphenol (6) 4-tert-butylphenol; anilines mixtures (F): (1) aniline, (2) 2-chloroaniline, (3) 2,4-dichloroaniline, (4) 2-nitroaniline, (5) 3-nitroaniline, (6) tribromoaniline. Gas chromatographs on 2D-NSs column of Grob mixture (G): (1) 2,3-butanediol, (2) decane, (3) n-octanol, (4) nonanal, (5) 2,6-dimethylphenol, (6) dodecane, (7) 2,6-dimethylaniline, (8) 2-ethylhexanoic acid, (9) methyl decanoate, (10) methyl undecanoate, (11) dicyclohexyl amine, (12) methyl dodecanoate; phenols mixtures (H): (1) phenol, (2) 4-methylphenol, (3) 2-nitrophenol, (4) 2,5-dimethylphenol, (5) 3-ethylphenol (6) 4-tert-butylphenol; anilines mixtures (I): (1) aniline, (2) 2-chloroaniline, (3) 2,4-dichloroaniline, (4) 2-nitroaniline, (5) 3-nitroaniline, (6) 1,3,5-tribromoaniline. Oven program: 80°C to 110°C at 10 °C min^{-1}, to 180°C at 30 °C min^{-1} for (A); 90°C to 190°C at 25 °C min^{-1} for (B); 100°C to 190°C at 30 °C min^{-1} for (C); 90°C to 180°C at 25 °C min^{-1} for (D); 110°C to 150°C at 20 °C min^{-1} for (E); 100°C to 150°C at 20 °C min^{-1}, to 190°C at 40 °C min^{-1} for (F); 100°C to 130°C (for 1 min) at 20 °C min^{-1}, to 170°C at 20 °C min^{-1} for (G); 110°C to 130°C at 10 °C min^{-1}, to 150°C at 25 °C min^{-1} for (H); 110°C to 190°C at 30 °C min^{-1} for (I). Flow rate: 1.0 mL min^{-1} for (A, D, G); 1.5 mL min^{-1} for (B, H); 2.0 mL min^{-1} for (C, F, I); 0.5 mL min^{-1} for (E).

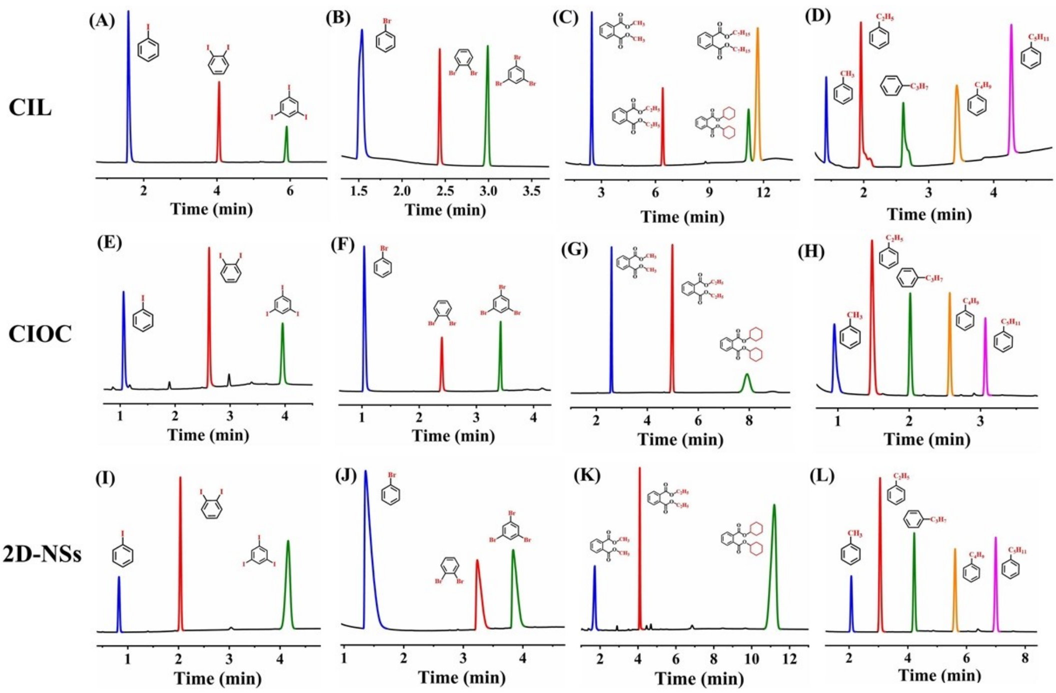

Fig. S9. Separation of benzene series on CIL, CIOC and 2D-NSs coated columns. Gas chromatographs of CIL coated columns of polyiodobenzene (A), polybromobenzene (B), PAE (C) and alkylbenzenes (D). Gas chromatographs of CIOC coated column of polyiodobenzene (E), polybromobenzene (F), PAE (G), alkylbenzenes (H). Gas chromatographs of 2D-NSs coated column of polyiodobenzene (I), polybromobenzene (J), PAE (K), alkylbenzenes (L). Oven program: 50°C to 180°C at 20 °C min^{-1} for (A); 70°C to 150°C at 30 °C min^{-1} for (B); 110°C to 200°C at 10 °C min^{-1} for (C); 50°C (for 1 min) to 70°C at 30 °C min^{-1}, to 140°C at 15 °C min^{-1} for (D); 80°C to 180°C at 30 °C min^{-1} for (E); 80°C to 140°C at 20 °C min^{-1}, to 180°C at 50 °C min^{-1} for (F); 110°C to 190°C at 20 °C min^{-1} for (G); 50°C (for 0.8 min) to 120°C at 30 °C min^{-1} for (H); 110°C to 180°C at 35 °C min^{-1} for (I); 50°C to 160°C at 35 °C min^{-1} for (J); 100°C to 180°C at 20 °C min^{-1} for (K); 50°C to 120°C at 10 °C min^{-1} for (L). Flow rate: 2.0 mL min^{-1} for (A, C, F, G, I); 3.0 mL min^{-1} for (B, E, H); 1.0 mL min^{-1} for (D, K, L); 1.5 mL min^{-1} for (J).

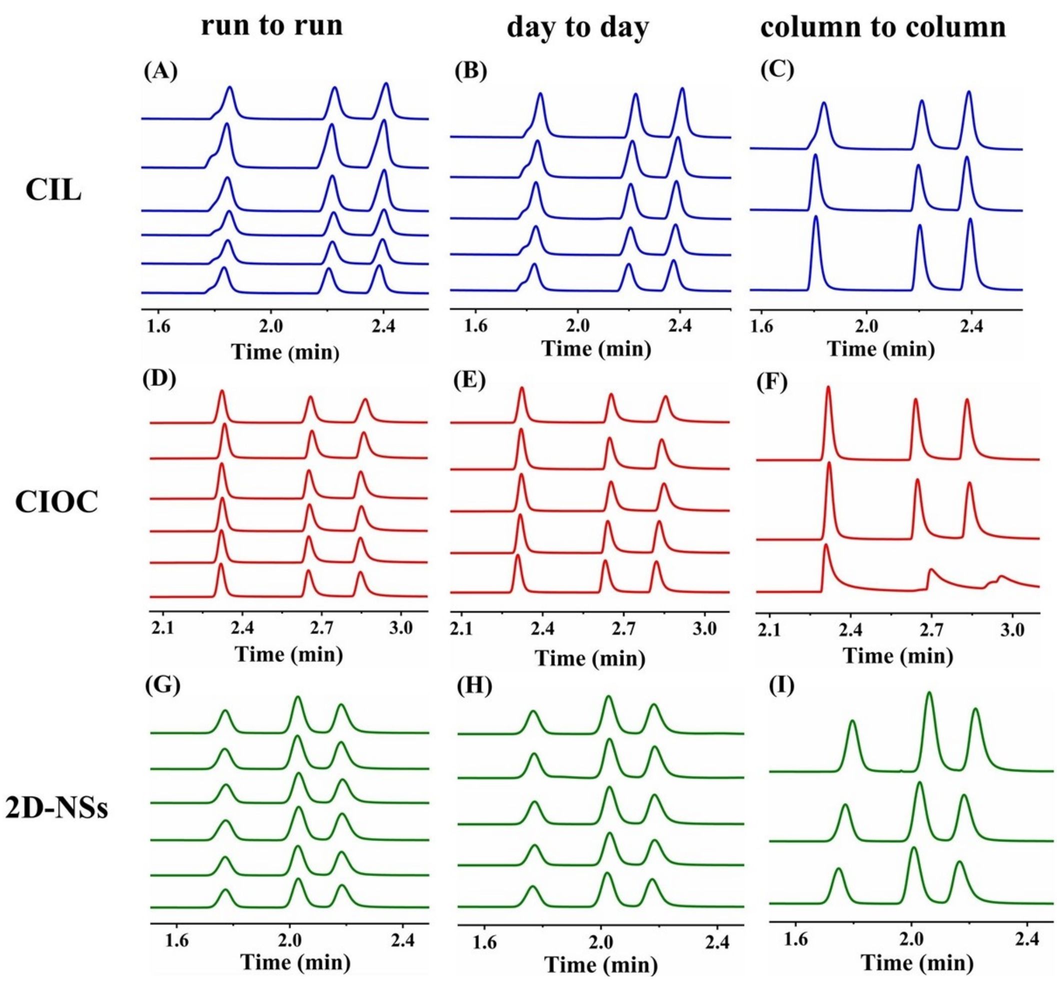

Fig. S10. Gas chromatographs of xylenol isomers by six consecutive injects on CIL coated column (A), CIOC coated column (D) and 2D-NSs coated column (G). Gas chromatographs of xylenol isomers by five consecutive days on CIL coated column (B), CIOC coated column (E) and 2D-NSs coated column (H). Gas chromatographs of xylenol isomers by three different columns of CIL (C), CIOC (G) and 2D-NSs (I).

5. Table S1 to S10

Table S1. Crystallographic data and parameters for CIOC.

Name	CIOC
Empirical formula	$C_{46}H_{58}N_2O_{10}S_2$
Formula weight	863.06
Temperature/K	296.15
Crystal system	Orthorhombic
Space group	$C222_1$
a/Å	9.0954(14)
b/Å	28.981(4)
c/Å	20.898(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5508.5(14)
Z	4
ρ_{calc} (g/cm^3)	1.041
μ/mm^{-1}	0.145
***F* (000)**	1840.0
Crystal size/mm^3	0.3 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	2.81 to 62.672
Index ranges	-11 ≤ h ≤ 13, -29 ≤ k ≤ 42, -30 ≤ l ≤ 28
Reflections collected	19100
Independent reflections	8118 [Rint = 0.0297, Rsigma = 0.0447]
Data/restraints/parameters	8118/0/274
Goodness-of-fit on F^2	0.999
Final R indexes(I>=2σ (*I*)]	R1 = 0.0517, wR2 = 0.1295
Final R indexes [all data]	R1 = 0.0929, wR2 = 0.1414
Largest diff. peak/hole/e Å^{-3}	0.20/-0.17
CCDC number	2361107

Table S2. Anisotropic Displacement Parameters (Å2×103) for CIOC.

Atom	x	y	z	U (eq)
C1	52.2(16)	60.8(14)	57.4(13)	-3.0(11)
C2	41.0(14)	66.2(16)	68.2(16)	1.9(12)
C3	39.4(13)	63.2(16)	67.9(16)	7.2(12)
C4	41.5(16)	55.0(14)	62.4(14)	0.5(11)
C5	49.7(16)	72.4(17)	61.6(16)	-4.2(12)
C6	55.8(17)	75.0(18)	58.6(15)	-6.6(12)
C7	50.0(16)	73.2(18)	54.2(14)	-0.2(12)
C8	43.9(14)	78.9(18)	49.5(13)	5.3(12)
C9	38.0(14)	51.8(13)	47.2(11)	-0.2(9)
C10	39.0(13)	69.2(16)	50.3(13)	0.4(11)
C11	50.8(15)	64.6(16)	49.7(13)	4.0(11)
C12	73.7(17)	57.6(14)	40.2(11)	2.7(10)
C13	74.8(18)	56.2(14)	50.0(13)	1.3(11)
C14	81(2)	47.4(14)	62.1(15)	0.0(11)
C15	86(3)	70(2)	95(2)	-8.1(17)
C16	82(2)	67.9(19)	120(3)	0.1(19)
C17	136(4)	72(2)	98(3)	-15.4(18)
C18	123(3)	64.1(18)	77.4(18)	-15.5(16)
C19	112(3)	56.6(16)	65.8(17)	-5.7(13)
C20	112(4)	57(2)	147(4)	-21(2)
C21	175(5)	97(3)	228(6)	4(3)
C22	100(4)	117(4)	312(9)	-36(4)
C23	85(3)	144(4)	169(5)	-35(4)
N1	55.1(12)	59.1(11)	39.4(9)	0.7(8)
O1	132(2)	78.6(14)	69.7(13)	-8.7(10)
O2	121(2)	80.2(15)	73.1(13)	12.4(10)
O3	67.1(16)	328(5)	70.5(15)	11(2)
O4	170(3)	58.8(11)	53.4(10)	10.0(9)
O5	91.5(14)	52.0(9)	48.4(9)	-4.1(7)
S1	63.4(4)	87.9(5)	56.6(4)	1.8(4)

Table S3. McReynolds constants of CIL, CIOC and 2D-NSs columns.

Stationary phases	X’	Y’	Z’	U’	S’	average polarity
CIL	1078	670	738	819	810	179
CIOC	602	725	721	808	880	103
2D-NSs	105	206	168	175	164	164

Temperature, 120°C; flow rate: 1.0 mL/min.

Table S4. Chromatographic conditions, Rs and α of racemates on CIL coated column.

enantiomers	Temperature (°C)	v (mL min^{-1})	Rs	α
trans-stilbene oxide	180	1.0	3.71	1.06
decahydronaphthalene	85	2.0	2.64	1.19
mandelonitrile	80	2.0	6.85	1.55
pyroglutamic acid*	180	1.0	4.89	1.14
mandelic acid	100	2.0	20.21	3.80
diflubenzuron	100	2.0	5.86	1.38
furoin	190	1.0	6.43	1.11
propiconazole	180	1.0	0.98	1.15

*Trifluoroacetyl butyl ester derivatives.

Table S5. Chromatographic conditions, Rs and α of racemates on CIOC coated column.

enantiomers	Temperature (°C)	v (mL min^{-1})	Rs	α
decahydronaphthalene	105	1.0	2.99	1.19
mandelonitrile	80	2.0	11.00	1.49
epichlorohydrin	110	1.0	17.92	1.76
pyroglutamic acid*	180	1.0	9.08	1.38
trans-stilbene oxide	180	1.0	2.09	1.09
diflubenzuron	140	2.	13.48	2.18
triflumuron	100	2.0	1.92	1.28
hexaflumuron	150	2.0	6.28	1.14
benzoin ethyl ether	170	1.0	7.28	1.47
2-phenyloxolane	150	1.0	1.04	1.05

*Trifluoroacetyl butyl ester derivatives.

Table S6. Chromatographic conditions, Rs and α of isomers on 2D-NSs coated column.

enantiomers	Temperature (°C)	v (mL min^{-1})	Rs	α
decahydronaphthalene	45	1.5	4.68	1.27
mandelonitrile	150	1.0	14.85	11.33
epichlorohydrin	70	1.0	13.29	1.92
benzoin	150	1.0	5.26	1.31
pyroglutamic acid*	180	1.0	2.81	1.14
trans-stilbene oxide	150	1.5	17.97	1.57
diflubenzuron	140	2.0	15.99	2.11
triflumuron	115	1.0	2.80	1.23
hexaflumuron	140	1.0	4.09	1.48
epibromohydrin	50	2.	3.62	1.29
ibuprofen	150	1.5	5.26	1.31
benzoin methyl ether	60	1.3	10.91	1.77
furoin	180	1.0	5.35	1.30

*Trifluoroacetyl butyl ester derivatives.

Table S7. Comparison of enantioseparation performance of enantiomers by 2D-NSs coated GC columns and β-DEX 120 commercial columns.

enantiomers	2D-NSs				β-DEX 120			
	T (°C)	v (mL min^{-1})	Rs	α	T (°C)	v (mL min^{-1})	Rs	α
decahydronaphthalene	45	1.5	4.68	1.27	150	1.0	7.42	1.18
mandelonitrile	150	1.0	14.85	11.33	150	1.0	-	1.00
epichlorohydrin	70	1.0	13.29	1.92	100	1.0	-	1.00
benzoin	150	1.0	5.26	1.31	220	1.0	6.74	1.14
pyroglutamic acid*	180	1.0	2.81	1.14	140	2.0	3.40	1.52
trans-stilbene oxide	150	1.5	17.97	1.57	210	1.0	-	1.00
diflubenzuron	140	2.0	15.99	2.11	200	2.0	10.77	1.48
triflumuron	115	1.0	2.80	1.23	200	1.0	4.00	1.13
hexaflumuron	140	1.0	4.09	1.48	220	10	2.13	1.06
epibromohydrin	50	2.0	3.62	1.29	130	1.0	-	1.00
ibuprofen	150	1.5	5.26	1.31	210	1.0	1.04	1.02`
benzoin methyl ether	60	1.3	10.91	1.77	180	1.0	1.13	1.01
furoin	100	1.0	5.35	1.30	180	1.0	1.25	1.03

*Trifluoroacetyl butyl ester derivatives.

Table S8. The thermodynamic parameters of (+/–)-decahydronaphthalene on CIL, CIOC and 2D-NSs coated columns.

Columns	Analytes	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} k^{-1})	ΔG (kJ mol^{-1})	R^2
CIL	(+)-decahydronaphthalene	-44.56	-148.01	-8.13±0.26	0.9990
	(–)-decahydronaphthalene	-43.14	-146.37	-7.30±0.25	0.9994
CIOC	(+)-decahydronaphthalene	-44.83	-144.21	-7.51±0.25	0.9997
	(–)-decahydronaphthalene	-44.38	-145.20	-6.69±0.25	0.9998
2D-NSs	(+)-decahydronaphthalene	-48.28	-147.54	-15.25±0.23	0.9995
	(–)-decahydronaphthalene	-48.68	-151.12	-14.35±0.23	0.9998

Table S9. Rs and α of positional isomers on CIL, CIOC, 2D-NSs and AB-5MS columns.

Analytes	**CIL**		**CIOC**		**2D-NSs**		**AB-5MS**	
	Rs	**α**	**Rs**	**α**	**Rs**	**α**	**Rs**	**α**
***o*-/*m*-nitroaniline**	4.46	1.20	3.98	1.19	3.61	1.36	1.11	1.17
***m*-/*p*-nitroaniline**	8.26	1.26	3.22	1.31	3.59	1.46	14.49	1.31
***o*-/*m*-nitrotoluene**	2.71	1.08	3.92	1.08	2.06	1.17	6.33	1.06
***m*-/*p*-nitrotoluene**	1.63	1.04	2.25	1.04	1.90	1.16	2.97	1.03
***o*-/*m*-dimethylphenol**	5.58	1.20	6.42	1.14	3.37	1.14	4.60	1.07
***m*-/*p*-dimethylphenol**	2.75	1.08	3.41	1.08	1.93	1.08	6.54	1.04

Table S10. Rs and α of benzene series on CIL, CIOC and 2D-NSs coated columns.

Analytes	CIL		CIOC		2D-NSs	
	Rs	α	Rs	α	Rs	α
iodobenzene/1,2-diiodobenzene	30.12	2.57	27.84	2.47	22.31	2.46
1,2-diiodobenzene/1,3,5-triiodobenzene	20.87	1.45	21.49	1.51	20.08	2.04
bromobenzene/1,2-dibromobenzene	13.29	1.59	23.79	2.31	10.59	2.38
1,2-dibromobenzene/1,3,5-tribromobenzene	13.31	1.23	20.75	1.43	3.85	1.18
dimethyl-/diethyl-phthalate	5.74	2.60	28.35	1.92	24.82	2.92
diethyl-/dicyclohexyl-phthalate	25.72	1.74	11.46	1.59	20.30	2.38
dicyclohexyl-/diheptyl-phthalate	1.95	1.05	-	-	-	-
toluene/ethylbenzene	11.89	1.38	7.30	1.56	10.12	1.42
ethylbenzene/propylbenzene	11.51	1.33	8.66	1.36	10.92	1.38
propylbenzene/butylbenzene	9.51	1.32	11.04	1.28	12.43	1.33
butylbenzene/phenylbenzene	9.42	1.24	10.73	1.19	12.12	1.25

Table S11. Repeatability and reproducibility for the retention time of xylenol isomers on CIL, CIOC and 2D-NSs coated columns.

Column			***2,6-*** **dimethyl phenol**	***2,5-*** **dimethylp henol**	***3,5-*** **dimethyl phenol**
CIL	**run to run (n=6)**	**t_R (min)**	1.846	2.218	2.340
		RSD (%)	0.393	0.335	0.336
	day to day (n=5)	**t_R (min)**	1.839	2.210	2.389
		RSD (%)	0.473	0.476	0.531
	column to column (n=3)	**t_R (min)**	1.819	2.186	2.373
		RSD (%)	1.222	1.998	1.843
CIOC	**run to run (n=6)**	**t_R (min)**	2.322	2.652	2.848
		RSD (%)	0.099	0.060	0.064
	day to day (n=5)	**t_R (min)**	2.320	2.645	2.839
		RSD (%)	0.103	0.336	0.476
	column to column (n=3)	**t_R (min)**	2.310	2.662	2.877
		RSD (%)	0.523	1.168	2.452
2D-NSs	**run to run (n=6)**	**t_R (min)**	1.772	2.029	2.184
		RSD (%)	0.077	0.097	0.089
	day to day (n=5)	**t_R (min)**	1.770	2.028	2.182
		RSD (%)	0.185	0.161	0.139
	column to column (n=3)	**t_R (min)**	1.772	2.033	2.190
		RSD (%)	1.354	1.343	1.311

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