Supporting Information

Catalytic synthesis of renewable lubricant base oils with methyl oleate and aromatics

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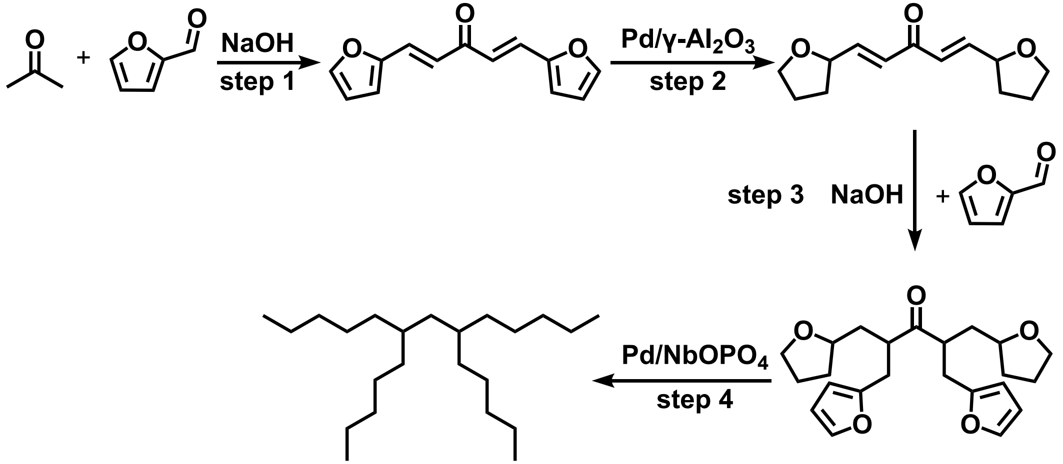
Strategy 1



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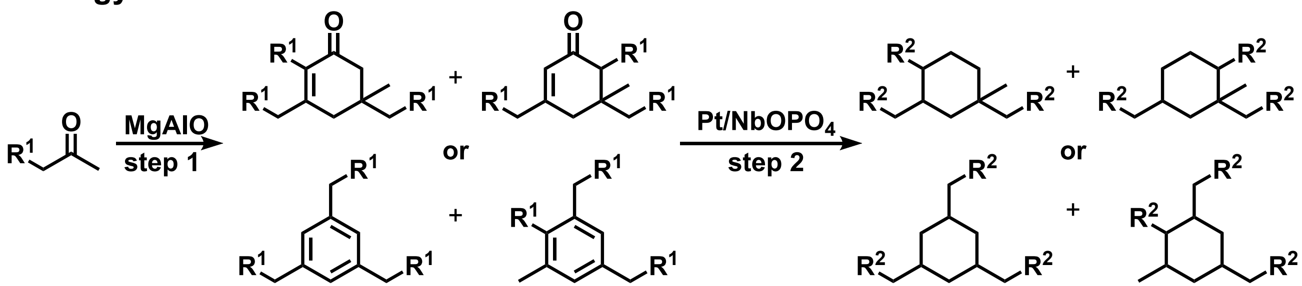

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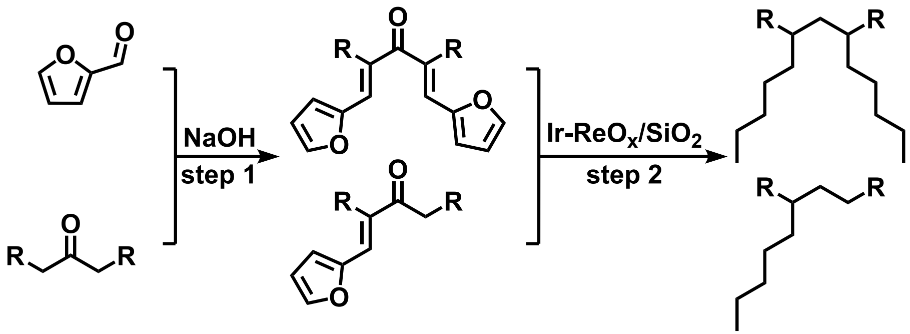

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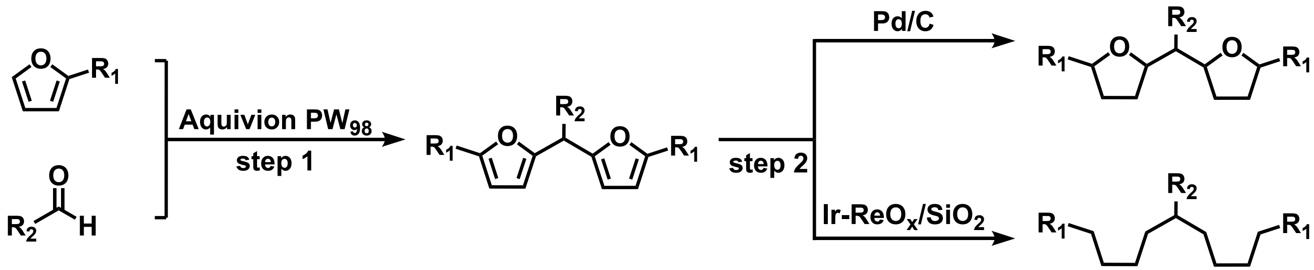

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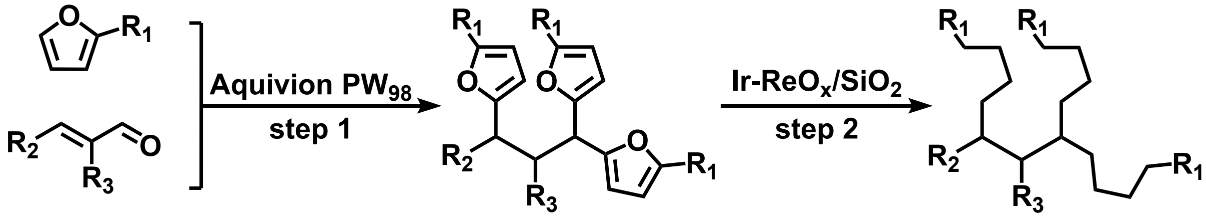

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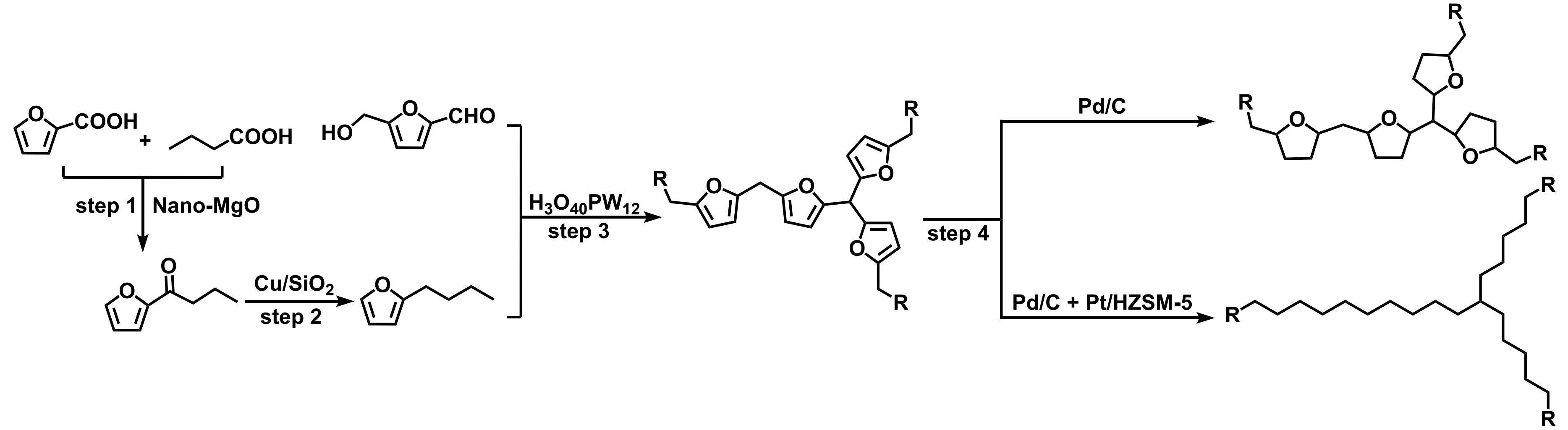

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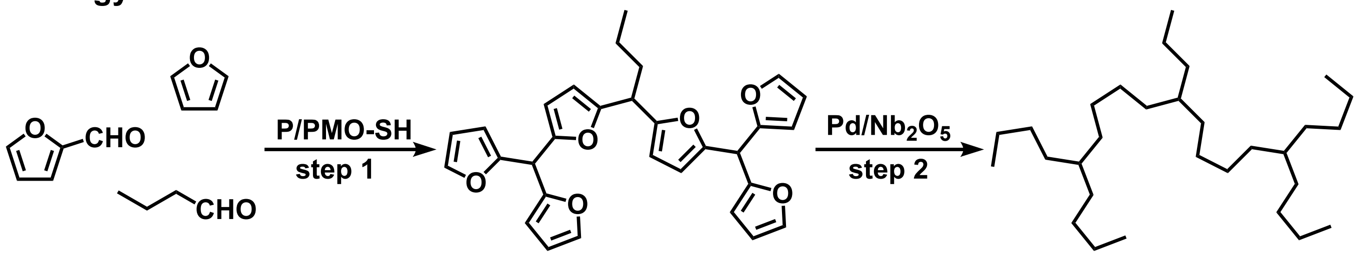

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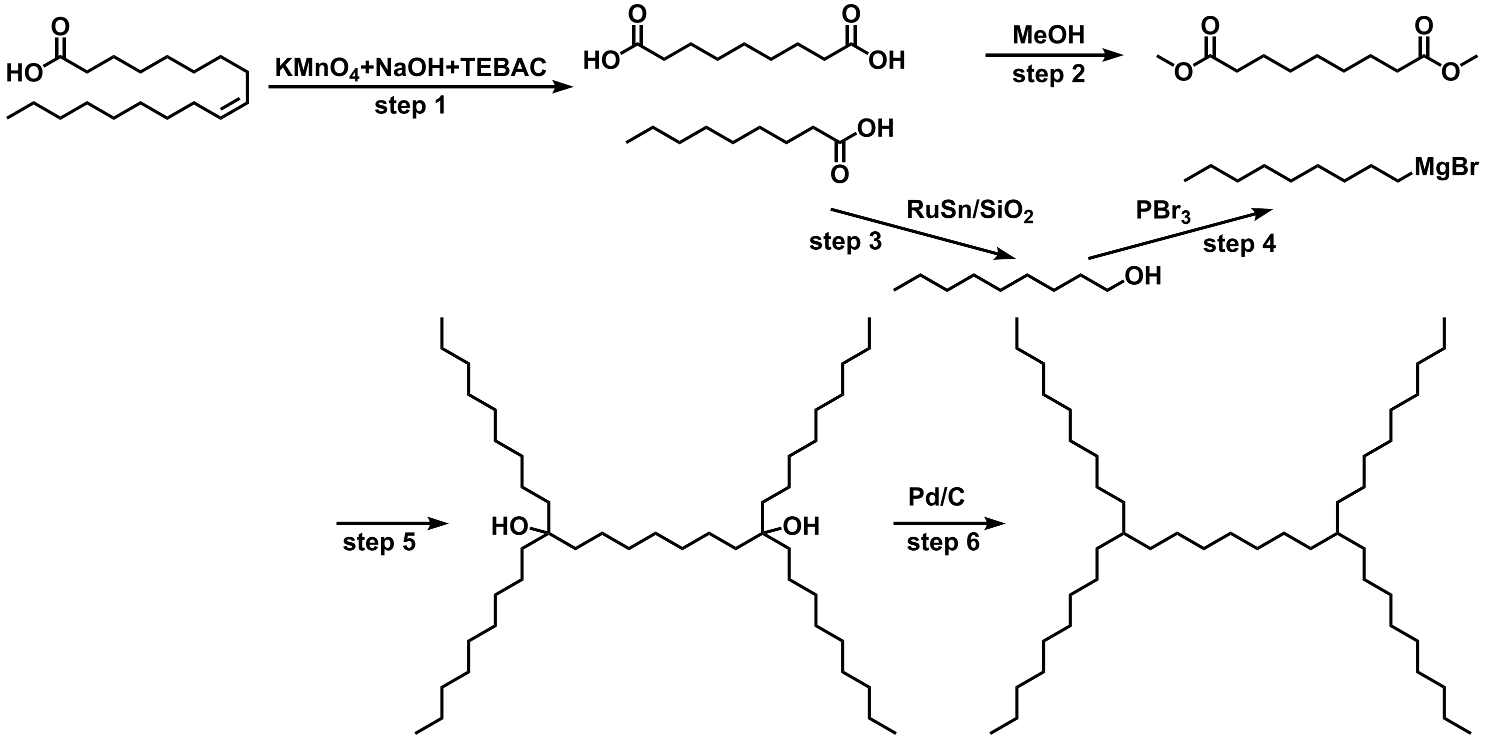

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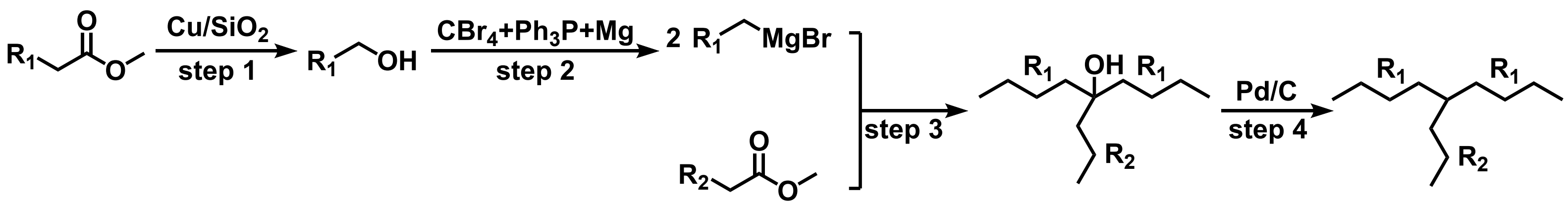

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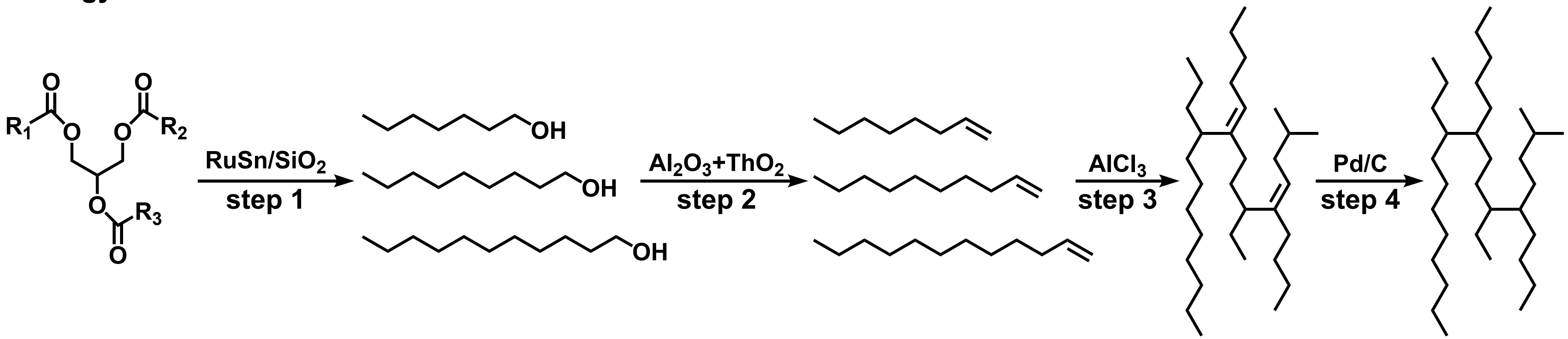

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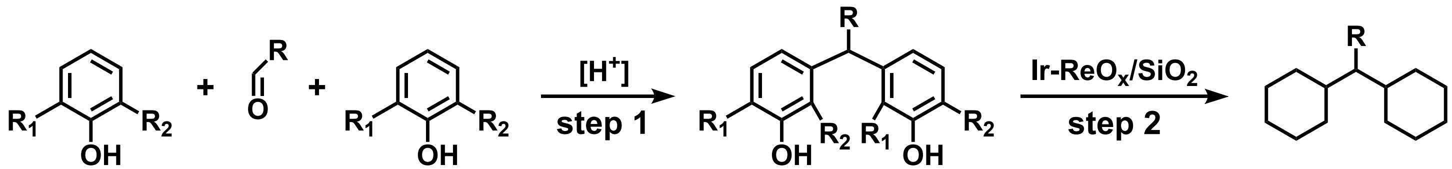
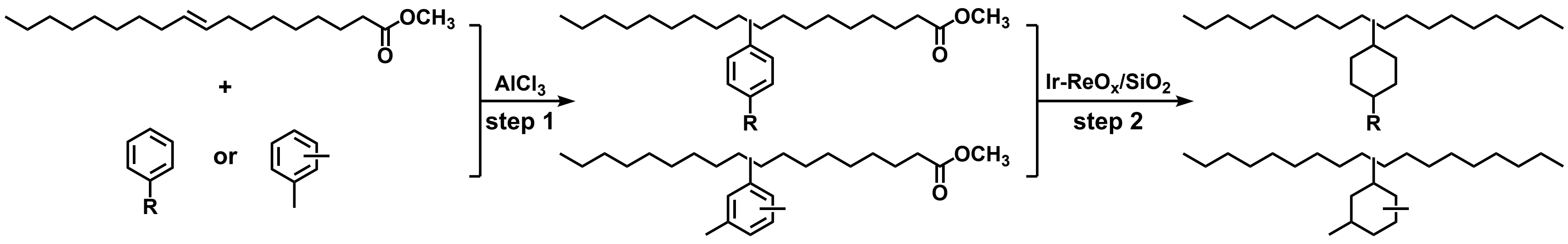


Strategy 12 (This work)

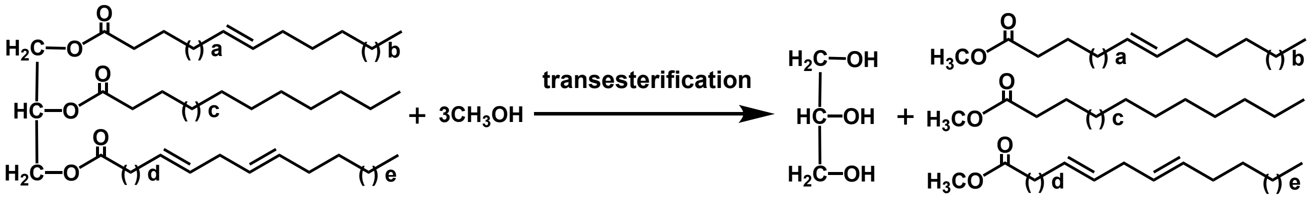


Scheme S1 The strategies for the synthesis of alkane-based lubricant base oils from biomass

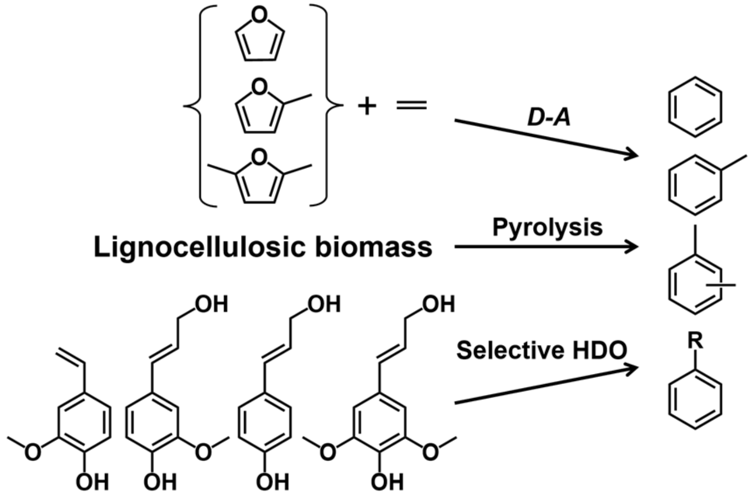
Table S1 The comparisons of the synthesis of alkane-based lubricant base oils from biomass with different strategies (Scheme S1)

Strategy	The number of steps	Reagents	Reaction conditions	Overall yield / %	References
1	4	acetone and furfural	Step 1: 40 °C, 5 h, Yield: 97%; Step 2: 130 °C, 5 h, 5 MPa H_2, Yield: 72.8%; Step 3: 50 °C, 20 h, Yield: 83.8%; Step 4: 175 °C, 24 h, 5 MPa H_2, Yield: 75.5%.	44.7	M. Gu, Q. Xia, X. Liu, Y. Guo and Y. Wang, *ChemSusChem*, 2017, **10**, 4102-4108.
2	2	methyl ketones	Step 1: 160 °C, 3 h, Yield: 98%; Step 2: 160 °C, 6 h, 3.5 MPa H_2, Yield: 98%.	96	M. Balakrishnan, G. E. Arab, O. B. Kunbargi, A. A. Gokhale, A. M. Grippo, F. D. Toste and A. T. Bell, *Green Chem.*, 2016, **18**, 3577-3581.
3	2	furfural and 12-tricosanone	Step 1: 80 °C, 8 h, Yield: 94.3%; Step 2: 180 °C, 18 h, 5 MPa H_2, Yield: 61.4%.	57.9	A. M. Norton, S. Liu, B. Saha and D. G. Vlachos, *ChemSusChem*, 2019, **12**, 4780-4785.
4	2	2-pentylfuran and lauraldehyde	Step 1: 65 °C, 6 h, Yield: 90%; Step 2: 170 °C, 12 h, 5 MPa H_2, Yield: 92%.	82.8	S. Liu, B. Saha1 and D. G. Vlachos, *Sci. Adv.*, 2019, **5**, eaav5487.
5	2	2-pentylfuran and crotanaldehyde	Step 1: 65 °C, 2 h, Yield: 72%; Step 2: 180 °C, 18 h, 5 MPa H_2 Yield: 88%.	63.4	S. Liu, B. Saha and D. G. Vlachos, *Green Chem.*, 2019, **21**, 3606-3614.
6	2	furan, furfural, and aliphatic aldehyde	Step 1: 100 °C, 12 h, Yield: 82%; Step 2: 230 °C, 3 h, Yield: 80%.	65.6	Y. Liu, S. Chen, Z. Gao, J. Tian, B. Ma and C. Zhao, *ACS Sustain. Chem. Eng.*, 2024, **12**, 3167-3174.

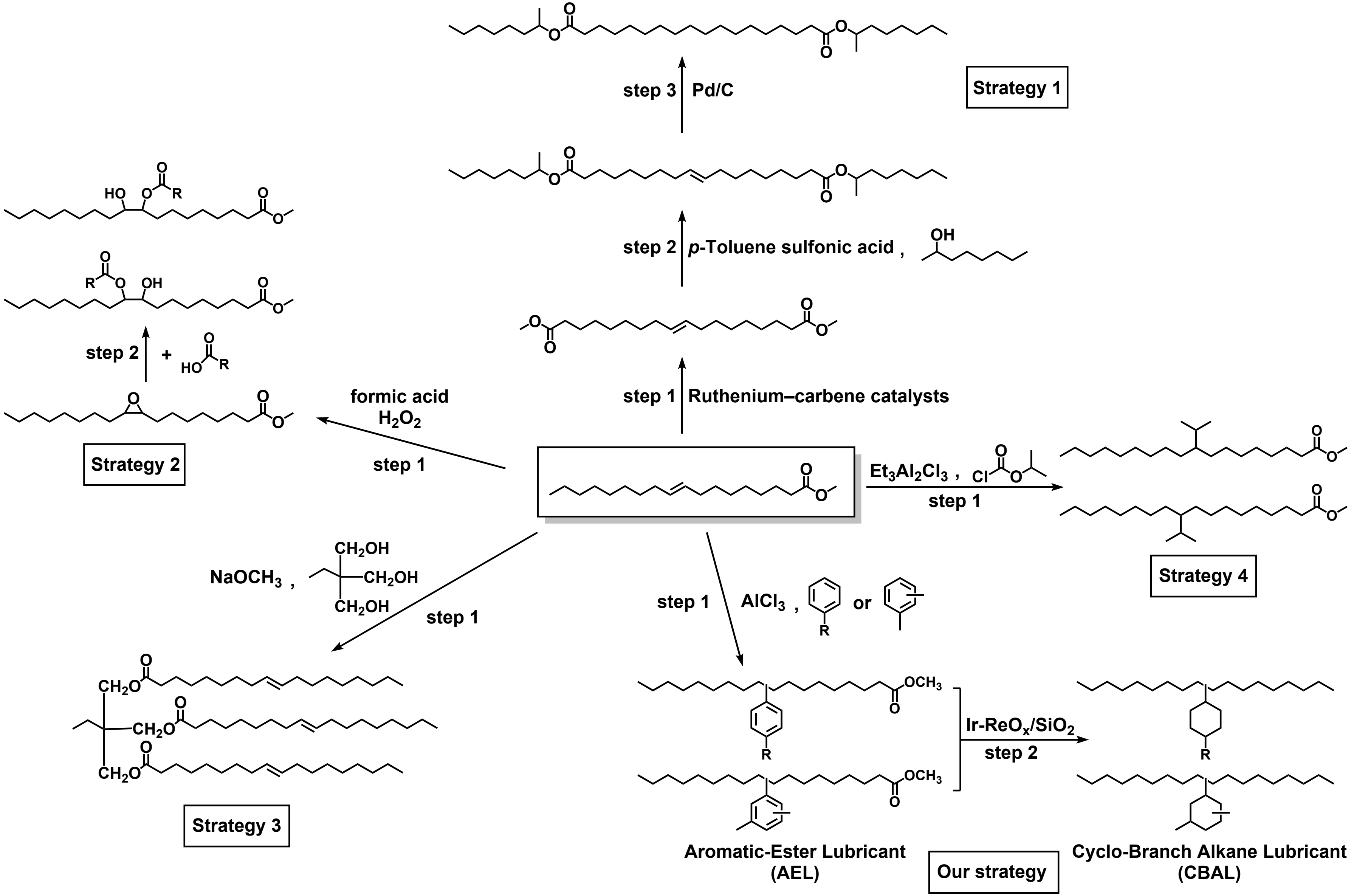
7	4	hexanoic acid, furoic acid and HMF	Step 1: 260 °C, 6 h, Yield: 82.2%; Step 2: 220 °C, 3 h, 2 MPa H_2, Yield: 96.5%; Step 3: 60 °C, 12 h, Yield: 91-93%; Step 4: 260 °C, 10 h, 5 MPa H_2, Yield: 98%.	70.7	S. Chen and C. Zhao, *ACS Sustain. Chem. Eng.*, 2021, **9**, 10818-10826.
8	6	oleic acid	Step 1: 50 °C, 8 h, $Yield_{nonanoic\ acid}$: 81%, $Yield_{azelaic\ acid}$: 96%; Step 2: 120 °C, 3 h, Yield: 100%; Step 3: 250 °C, 3 h, 4 MPa H_2, Yield: 96.9%; Step 4: 0 °C, 2h, 25 °C, 4h, Yield: 75.3%; Step 5: 250 °C, 3 h, 4 MPa H_2, Yield: 85%; Step 6: 250 °C, 3 h, 4 MPa H_2, Yield: 75%.	37.7	S. Chen, T. Wu and C. Zhao, *ChemSusChem*, 2020, **13**, 5516-5522.
9	4	fatty acid methyl esters	Step 1: 240 °C, 4 h, Yield: 82%; Step 2: 50 °C, 3 h, Yield: 99%; Step 3: 0 °C, 5 h, Yield: 82.1%; Step 4: 250 °C, 3 h, 1 MPa H_2, Yield: 100%.	67.3	S. Chen, T. Wu, Y. Fang and C. Zhao, *Renew. Energy*, 2022, **186**, 280-287.
10	4	lipids	Step 1: 300 °C, 6 h, 5 MPa H_2, Yield: 99%; Step 2: 300 °C, 6 h, Yield: 90%; Step 3: 120 °C, 4 h, Yield: 95%; Step 4: 250 °C, 3 h, 4 MPa H_2, Yield: 100%.	84.6	S. Chen, T. Wu and C. Zhao, *Green Chem.*, 2020, **22**, 7348-7354.
11	2	guaiacol and lauryl aldehyde	Step 1: 150 °C, 12 h, Yield: 76%; Step 2: 200 °C, 12 h, 5MPa H_2, Yield: 82%.	62.3	E. O. Ebikade, S. Sadula, S. Liu and D. G. Vlachos, *Green Chem.*, 2021, **23**, 10090-10100.
12	**2**	**methyl oleate and bio-aromatics**	**Step 1: 60 °C, 1 h, Yield: 99%;** **Step 2: 180 °C, 12 h, 4 MPa H_2, Yield: 96.3%.**	**96.3**	**This Work**



Scheme S2 Approaches to the synthesis of methyl oleate via transesterification of lipids with methanol.



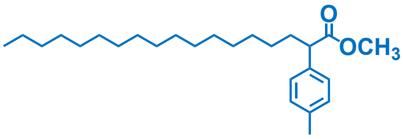
Scheme S3 Approaches to the synthesis of bio-aromatics from lignocellulosic, furan compounds and lignin monomer.



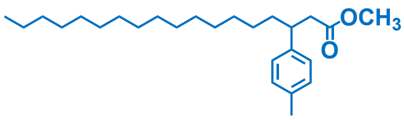
Scheme S4 Strategies for the synthesis of bio-lubricants with methyl oleate.

Table S2 The comparisons of the synthesis of bio-lubricant base oils from methyl oleate with different strategies (Scheme S4)

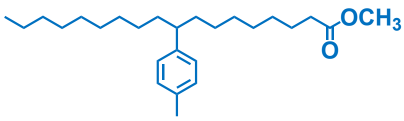
Strategy	**The number of steps**	**Reagents**	**Reaction conditions**	**Overall yield / %**	**References**
1	3	methyl oleate and 2-octanol	Step 1: 110 °C, 2h; Step 2: 100 °C, 2-12 h; Step 3: room temperature, overnight, 2-12 h.	68.4	J.-L. Dubois, J.-L. Couturier, S. J. Asadauskas, L. Labanauskas, D. Bražinskienė and R. Blaauw, *RSC Adv.*, 2021, **11**, 31030-31041.
2	2	methyl oleate and organic acids	Step 1: room temperature, 5 h; Step 2: 100 °C, 7 h.	80.0	K. M. Doll, B. K. Sharma and S. Z. Erhan, *Ind. Eng. Chem. Res.*, 2007, **46**, 3513-3519.
3	1	methyl oleate and trimethylolpropane	Step 1: 2 h, 130 °C.	79.7	M. S. Elmelawy, A. El-Meligy, H. A. Mawgoud, A. S. Morshedy, S. A. Hanafy and I. E.-t. El-sayed, *Biomass Convers. Biorefinery*, 2021, **13**, 1645-1657.
4	1	methyl oleate and isopropyl chloroformate	Step 1: 1 h, 15 °C.	71	U. Biermann and J. O. Metzger, *J. Am. Chem. Soc.*, 2004, **126**, 10319-10330.
5	**1**	**methyl oleate and bio-aromatics**	**Step 1: 60 °C, 1 h.**	**99**	**This Work**
6	**2**	**methyl oleate and bio-aromatics**	**Step 1: 60 °C, 1 h;** **Step 2: 180 °C, 12 h, 4 MPa H_2.**	**91.1**	**This Work**



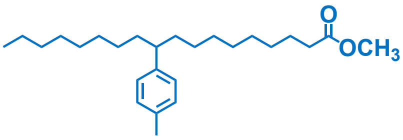
2-MMPO



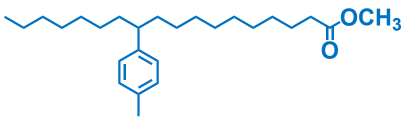
3-MMPO



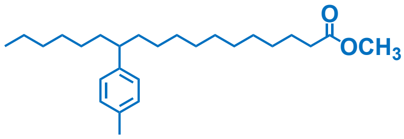
9-MMPO



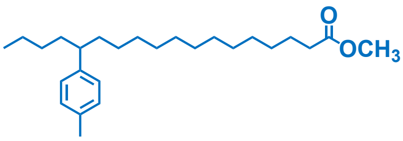
10-MMPO



11-MMPO



12-MMPO



14-MMPO

Fig. S1 The observed isomers of methyl (methylphenyl) octadecanoate (MMPO) in the alkylation step

Table S3 Effects of reaction time on the alkylation of methyl oleate over $AlCl_3$.

Entry	Time / h	Con. / %	Yield / %	C.B. / %
1	0.25	99.9	97.4	98.4
2	1	99.9	99.0	99.9
3	2	99.9	96.2	97.2
4	3	99.9	98.7	99.7
5	4	99.9	99.9	99.9

Reaction condition: $AlCl_3$ (3.75 mmol), methyl oleate (3 mmol), toluene (48 mmol), 60 °C.

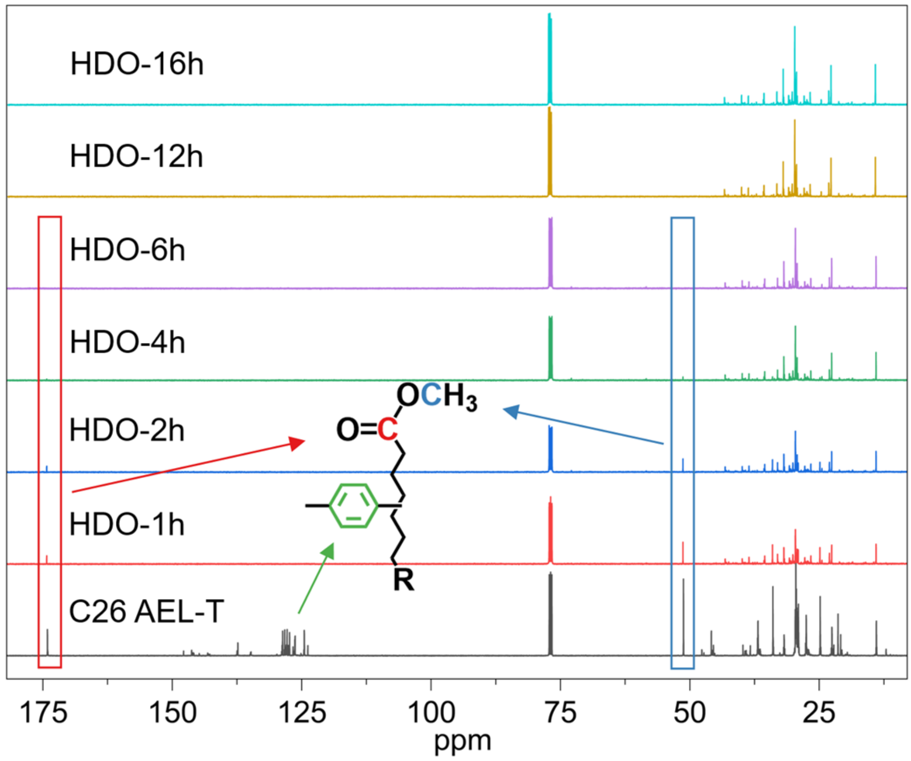


Fig. S2 The measurement of ^{13}C-NMR of the products from time dependent experiments.

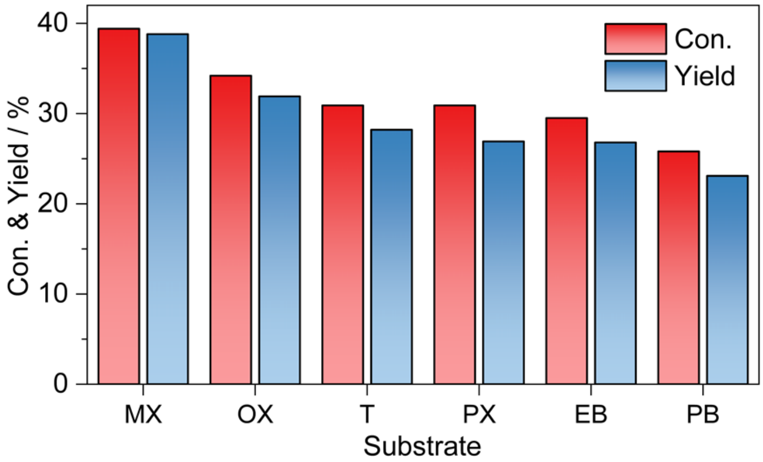


Fig. S3 Alkylation of methyl oleate with diverse aromatics at low conversion. Reaction conditions: $AlCl_3$ (1.5 mmol), methyl oleate (3 mmol), aromatic (48 mmol), T (60 °C), t (1 h).

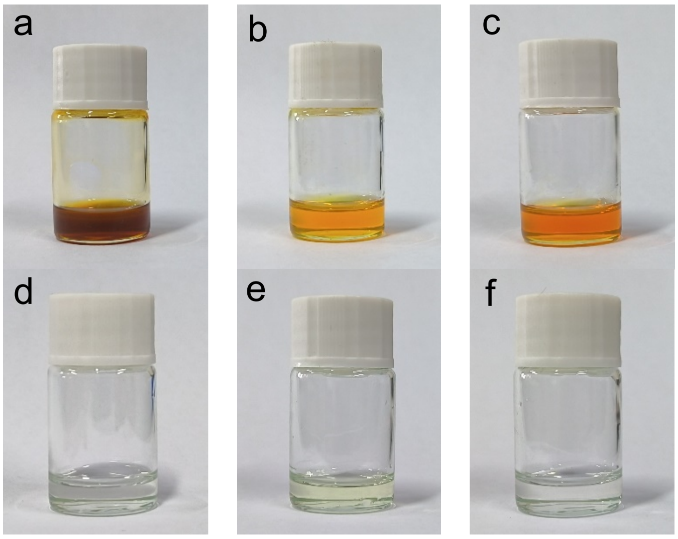
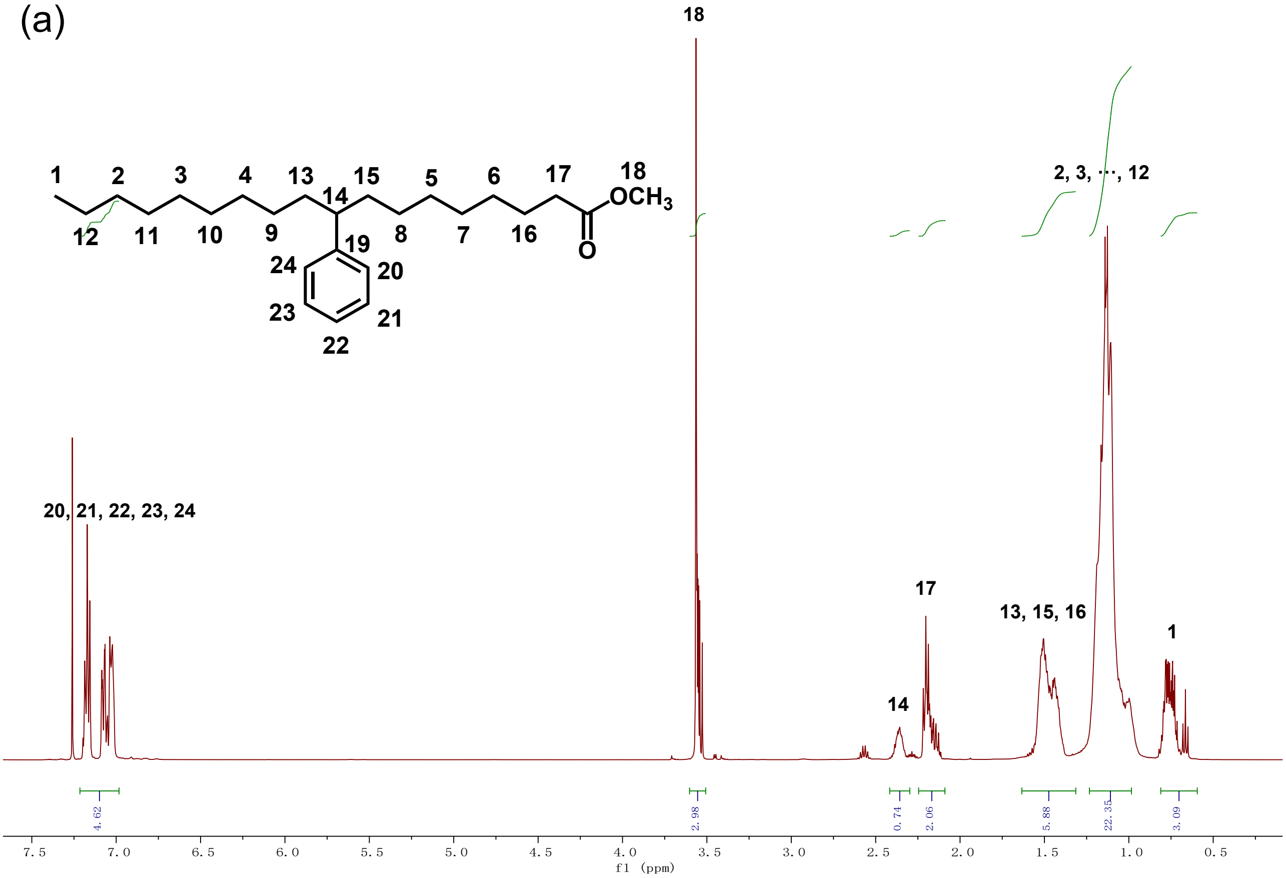


Fig. S4 The appearance of C_{26} AEL-T (a), C_{27} AEL-PX (b), C_{28} AEL-PB (c), C_{25} CBAL-T (d), C_{26} CBAL-PX (e), C_{27} CBAL-PB (f).

(a)


18
1
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18
OCH3
14
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11
10
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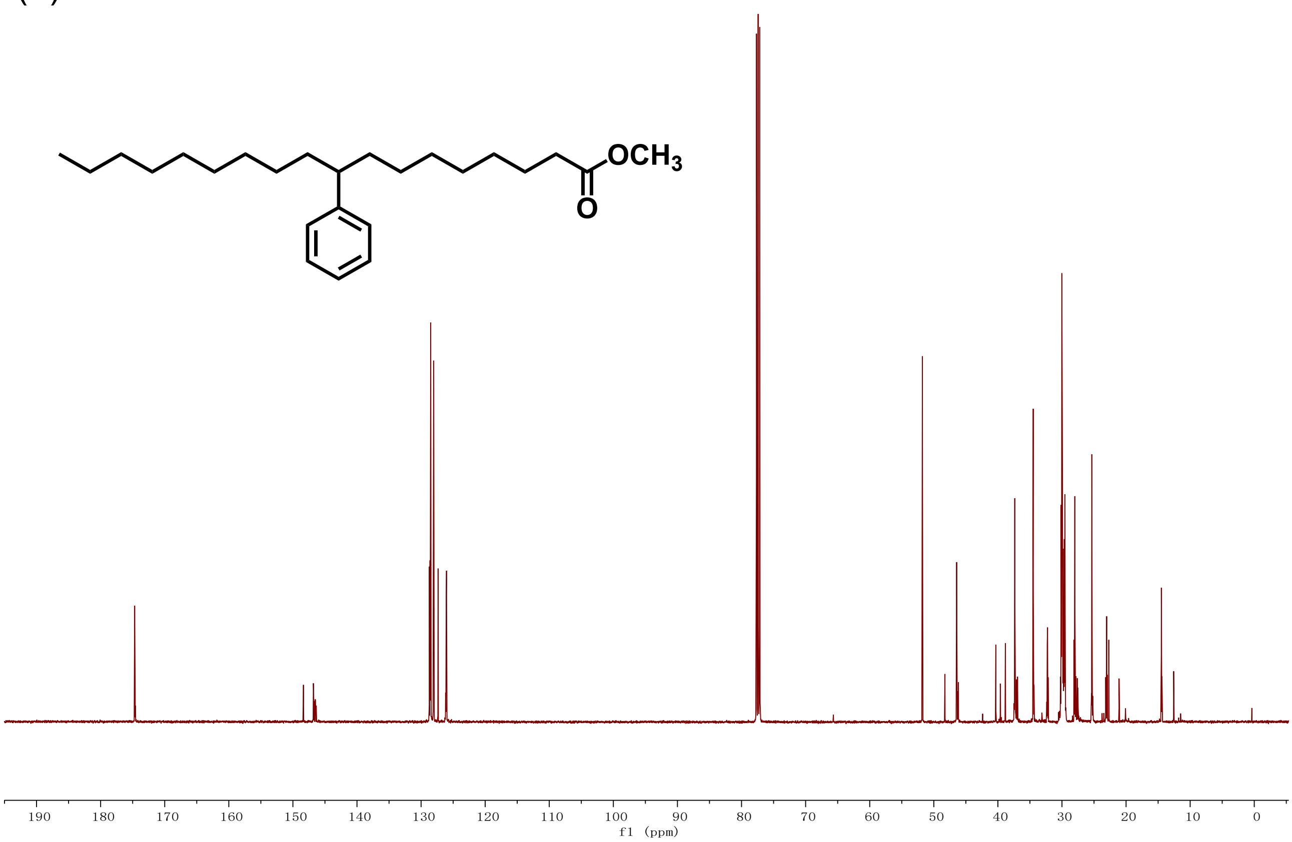
8
7
16
O
24
20
23
21
22
2, 3, ···, 12
20, 21, 22, 23, 24
17
13, 15, 16
1
14
4.62
2.98
0.74
2.06
5.88
22.35
3.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

(b)


OCH3
O
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170
160
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130
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110
100
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80
70
60
50
40
30
20
10
0
f1 (ppm)

(c)

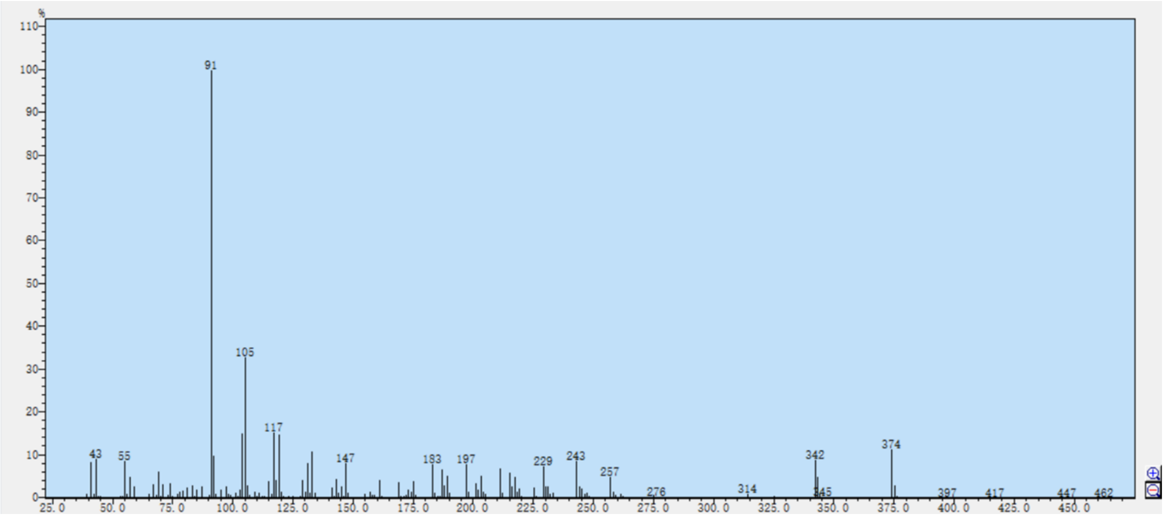
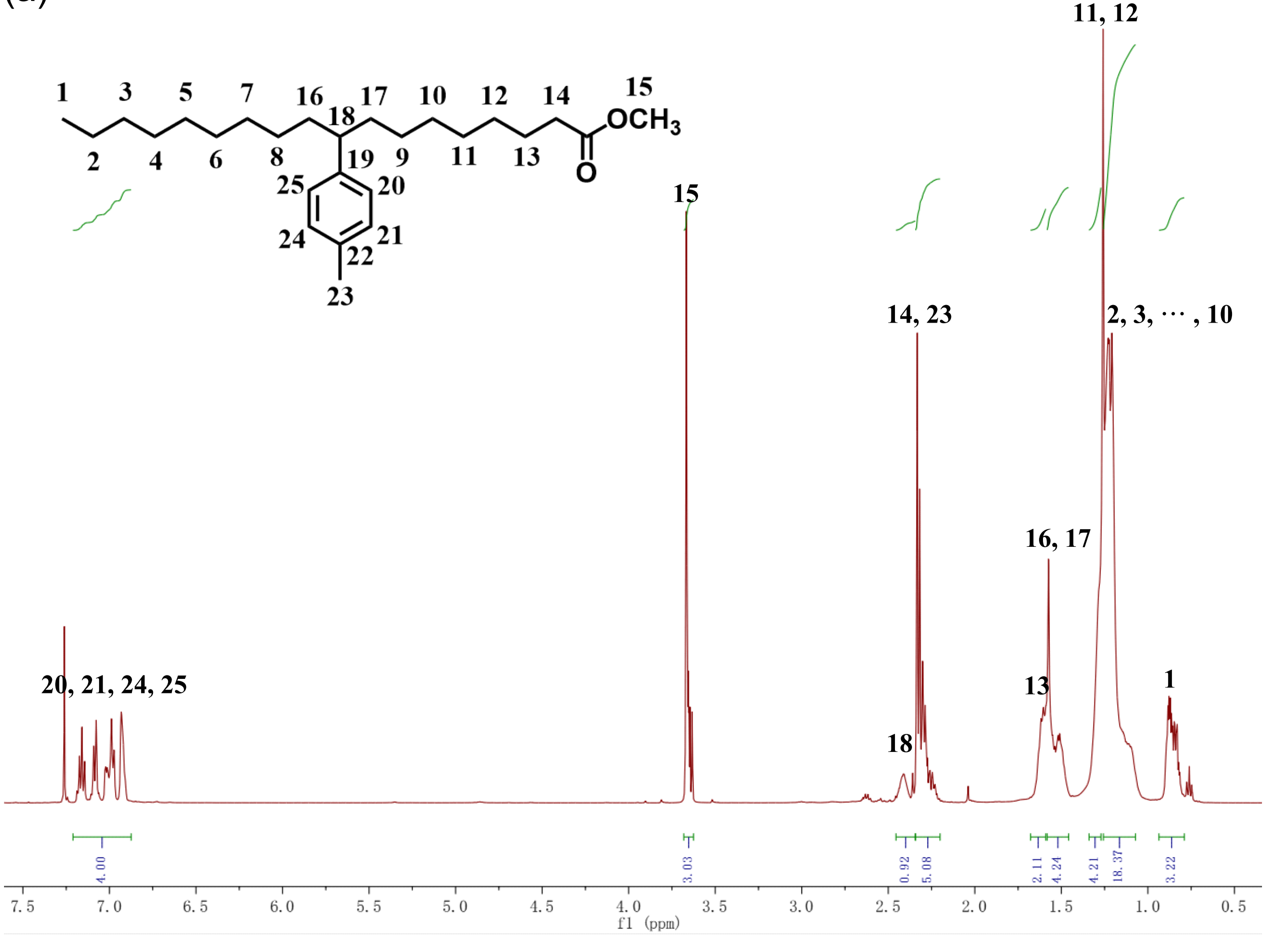


Fig. S5 (a) ^{1}H-NMR, (b) ^{13}C-NMR, and (c) Mass spectra of C_{25} AEL-B.

(a)



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OCH3
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25
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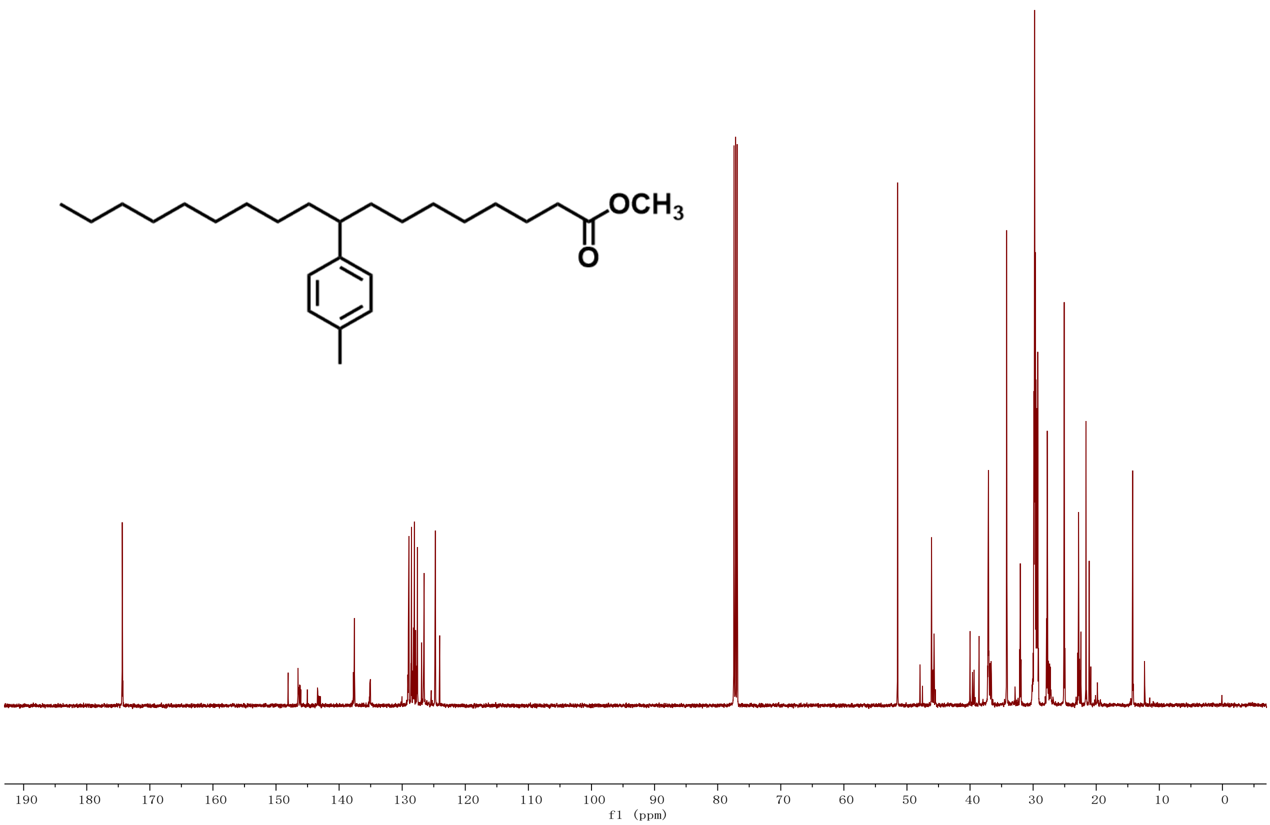
24
21
22
23
15
14, 23
11, 12
2, 3, ⋯ , 10
16, 17
13
1
18
20, 21, 24, 25
4.00
3.03
0.92
5.08
2.11
4.24
4.21
18.37
3.22
f1 (ppm)

(b)



OCH3
O
f1 (ppm)

(c)

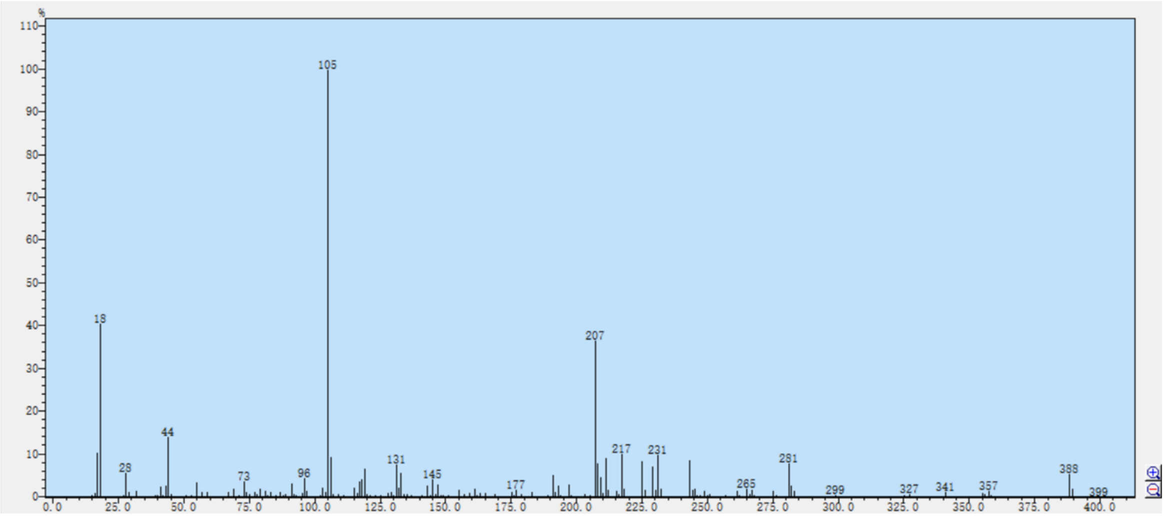
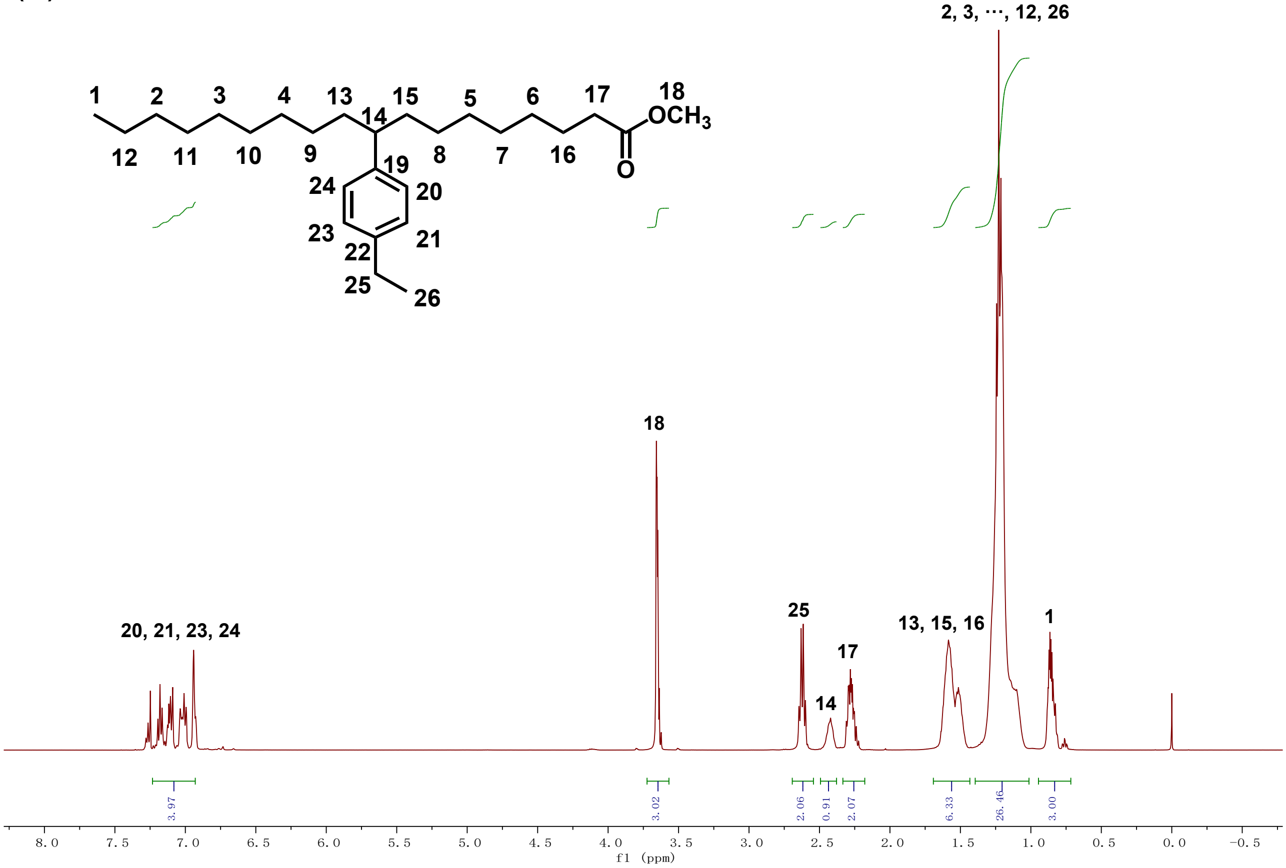


Fig. S6 (a) [1]H-NMR, (b) [13]C-NMR, and (c) Mass spectra of C_{26} AEL-T.

(a)


2, 3, ⋯, 12, 26
1 2 3 4 13 15 5 6 17 18
OCH3
14
12 11 10 9 8 7 16
O
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24 20
23 21
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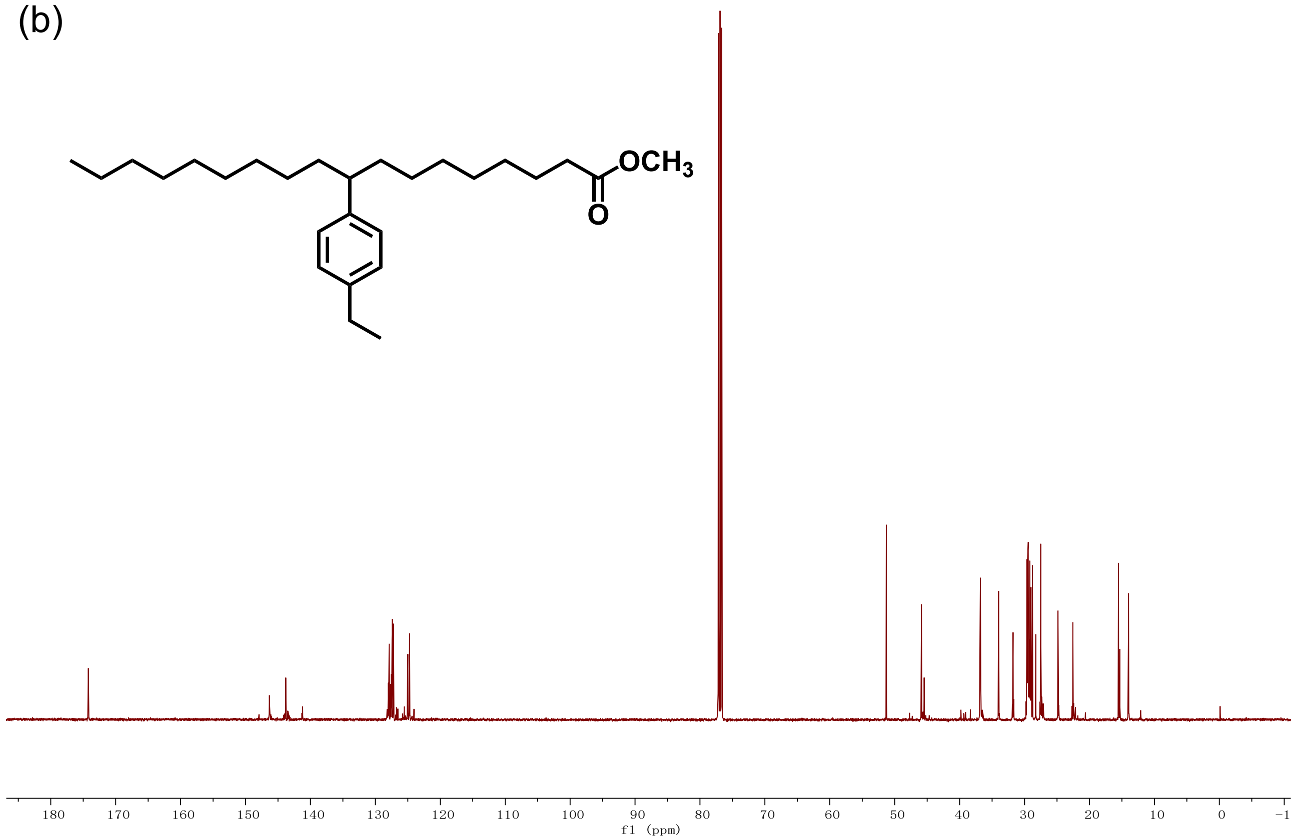
25 26
18
25
14
17
20, 21, 23, 24
13, 15, 16
1
3.97
3.02
2.06
0.91
2.07
6.33
26.46
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

(b)


OCH3
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180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

(c)

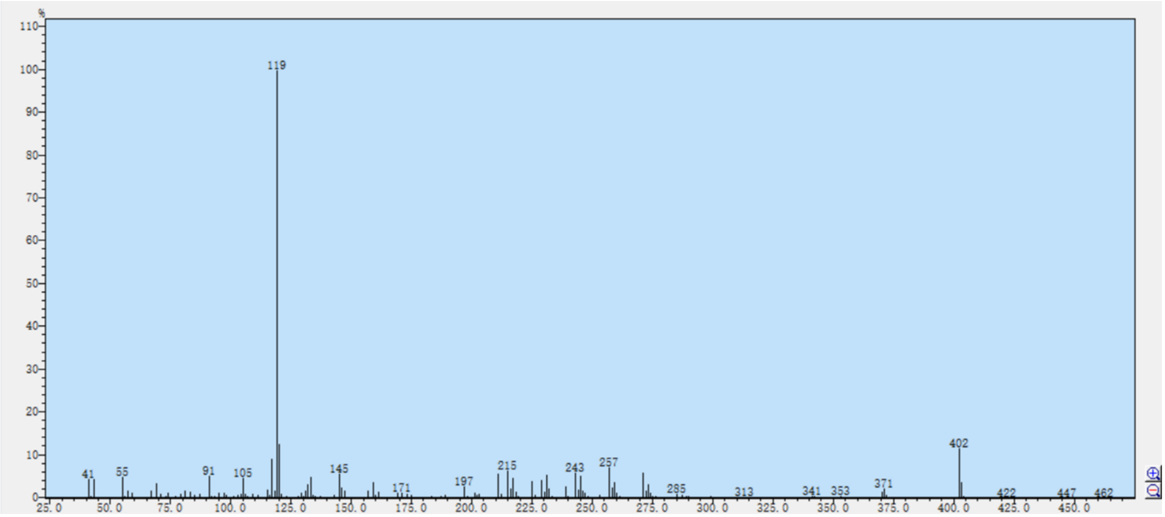
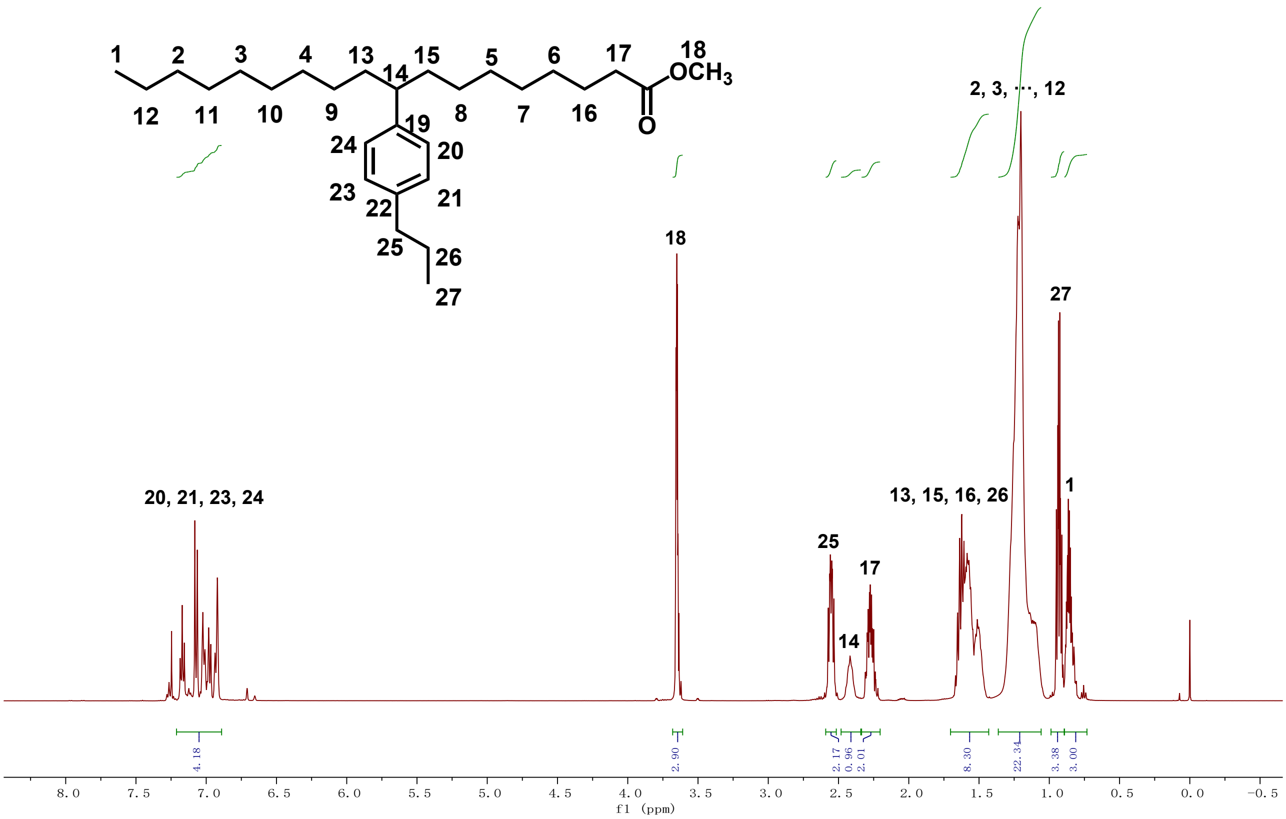


Fig. S7 (a) [1]H-NMR, (b) [13]C-NMR, and (c) Mass spectra of C_{27} AEL-EB.

(a)



OCH3
O
18
20, 21, 23, 24
2, 3, ···, 12
27
1
25
14
17
13, 15, 16, 26
4.18
2.90
2.17
0.96
2.01
8.30
22.34
3.38
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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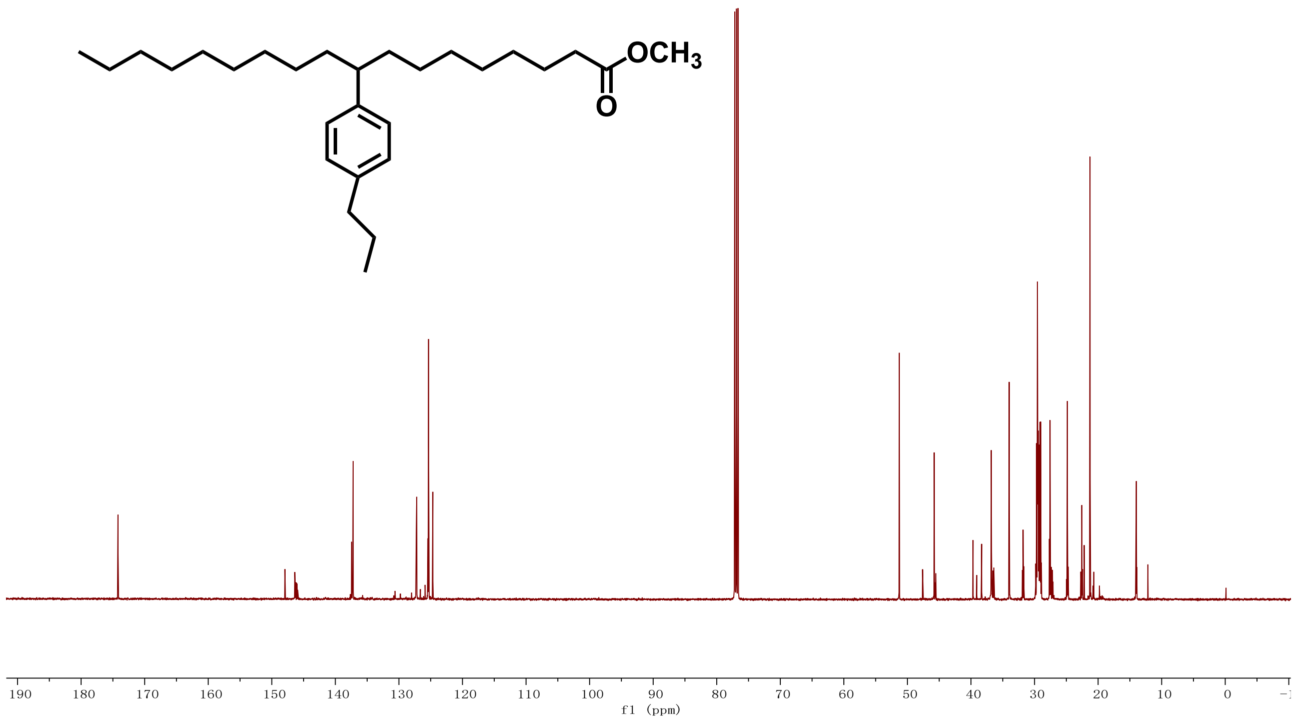
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

(b)



OCH3
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f1 (ppm)

(c)

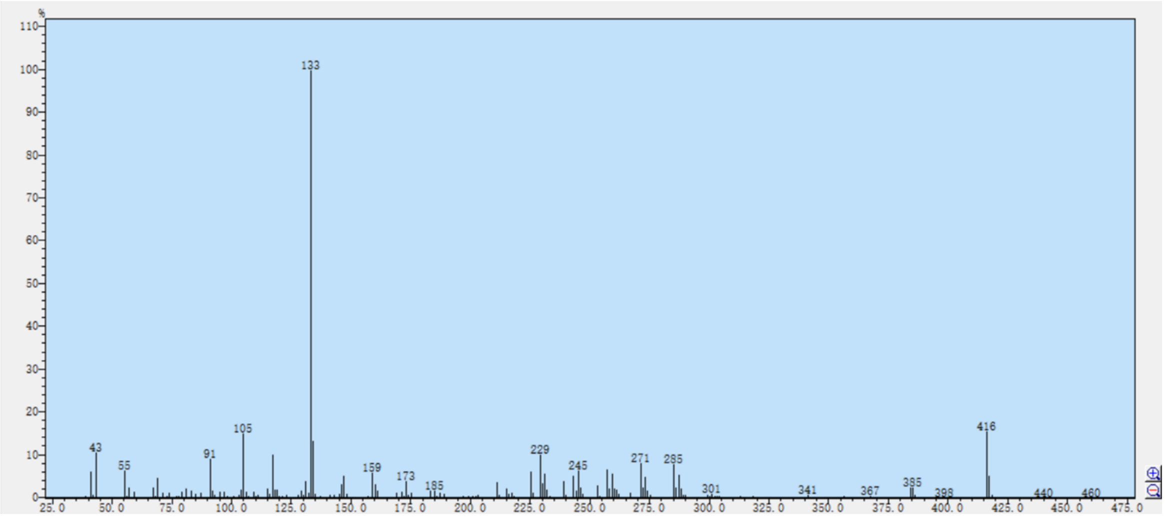
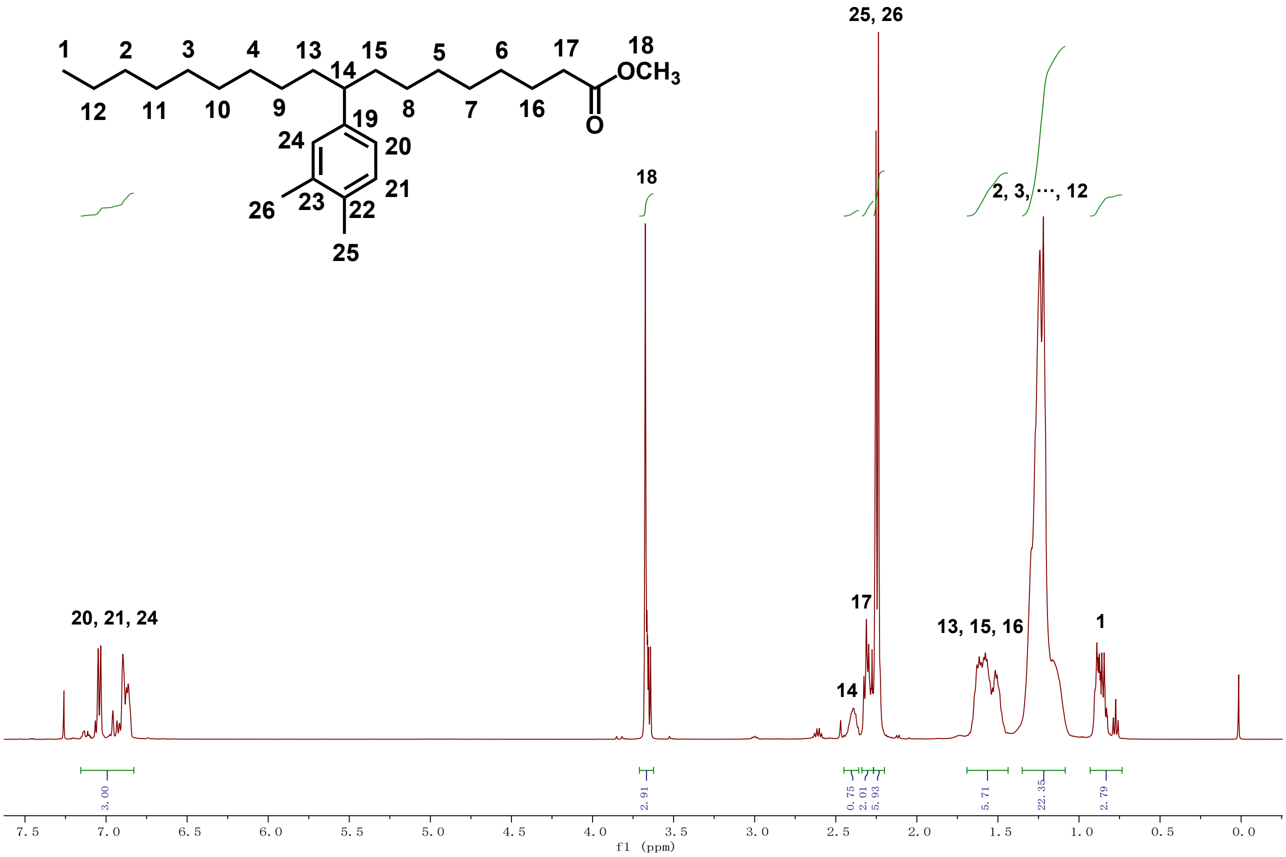


Fig. S8 (a) ^{1}H-NMR, (b) ^{13}C-NMR, and (c) Mass spectra of C_{28} AEL-PB.

(a)



1
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OCH3
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21
22
23
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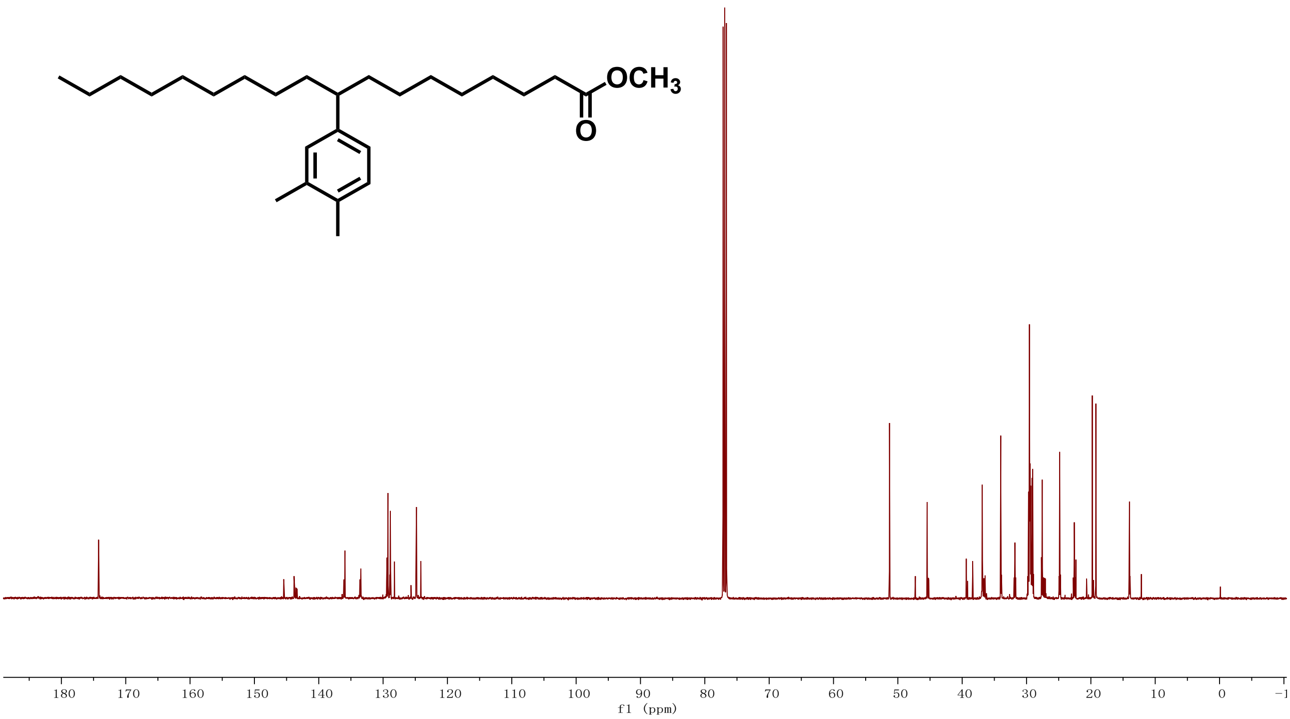
25
26
25, 26
18
20, 21, 24
17
14
13, 15, 16
2, 3, ···, 12
1
3.00
2.91
0.75
2.01
5.93
5.71
22.35
2.79
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

(b)



OCH3
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

(c)

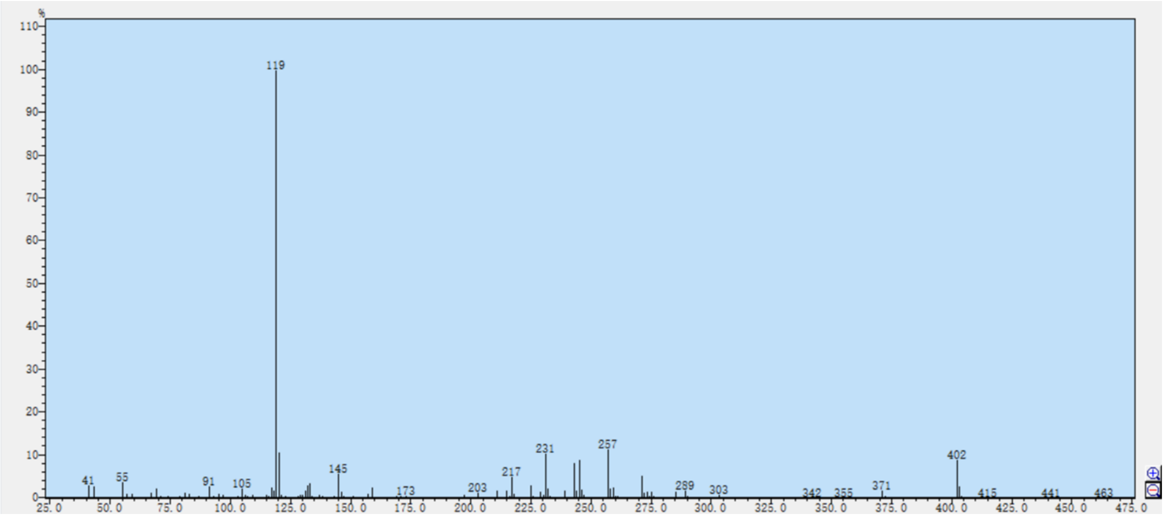
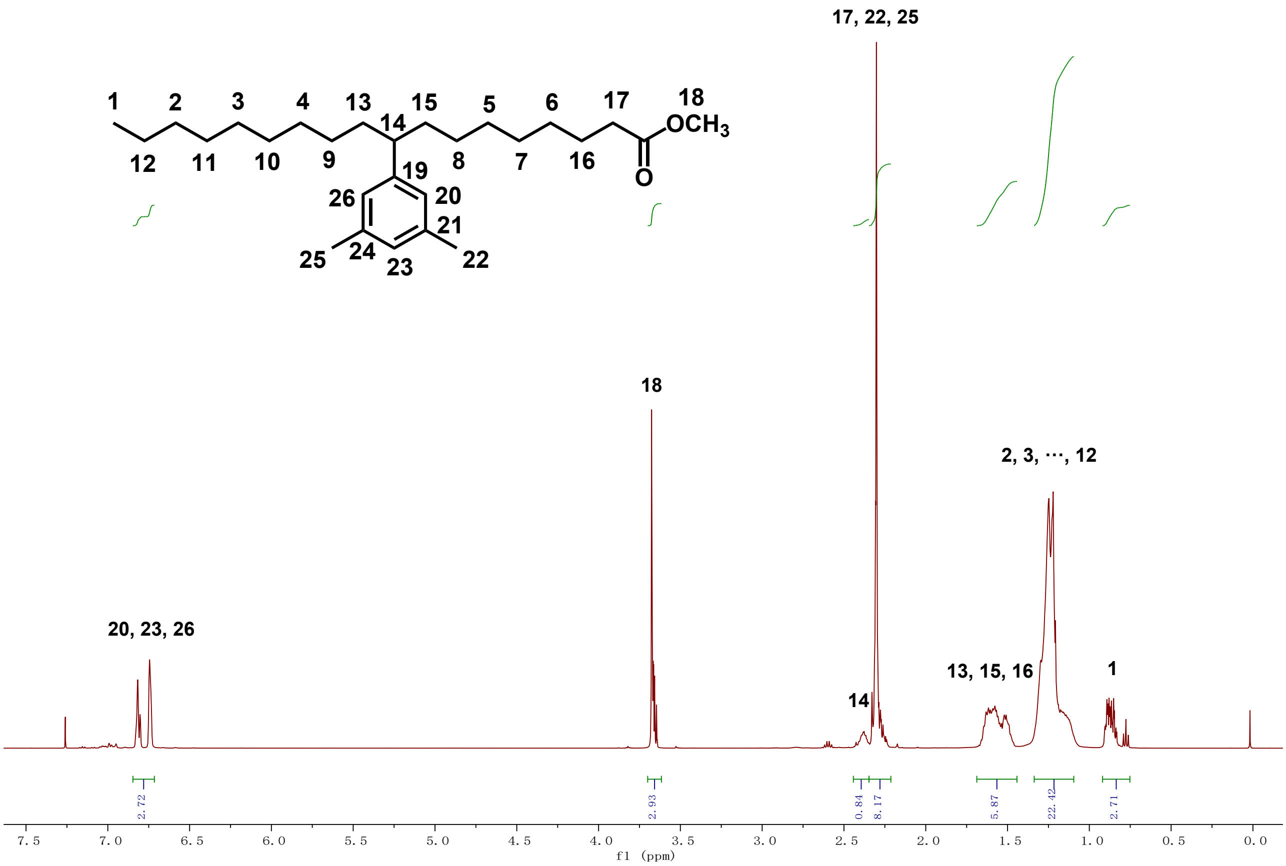


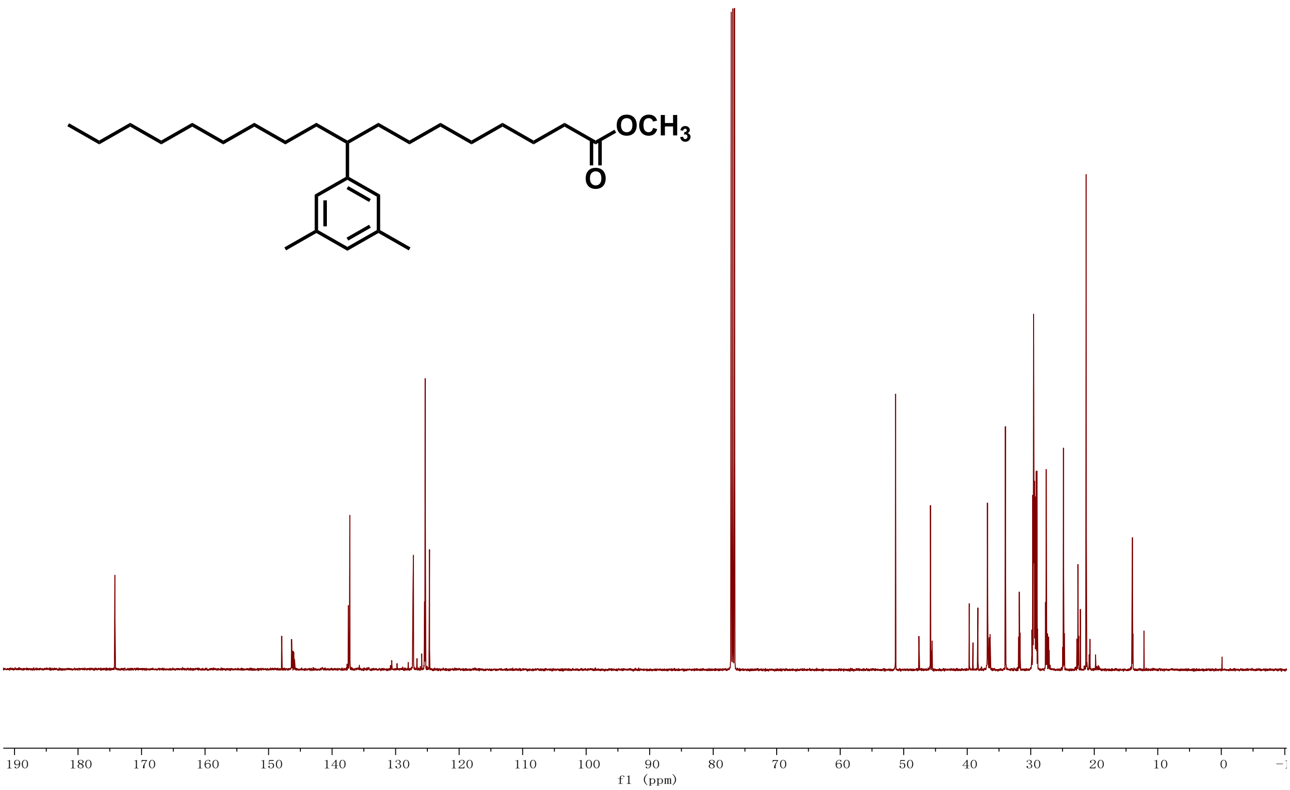
Fig. S9 (a) ^{1}H-NMR, (b) ^{13}C-NMR, and (c) Mass spectra of C_{27} AEL-OX.

(a)



17, 22, 25
1
2
3
4
13
15
5
6
17
18
OCH3
14
12
11
10
9
8
7
16
O
19
26
20
21
25
24
23
22
18
2, 3, ···, 12
20, 23, 26
14
13, 15, 16
1
2.72
2.93
0.84
8.17
5.87
22.42
2.71
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

(b)



OCH3
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

(c)

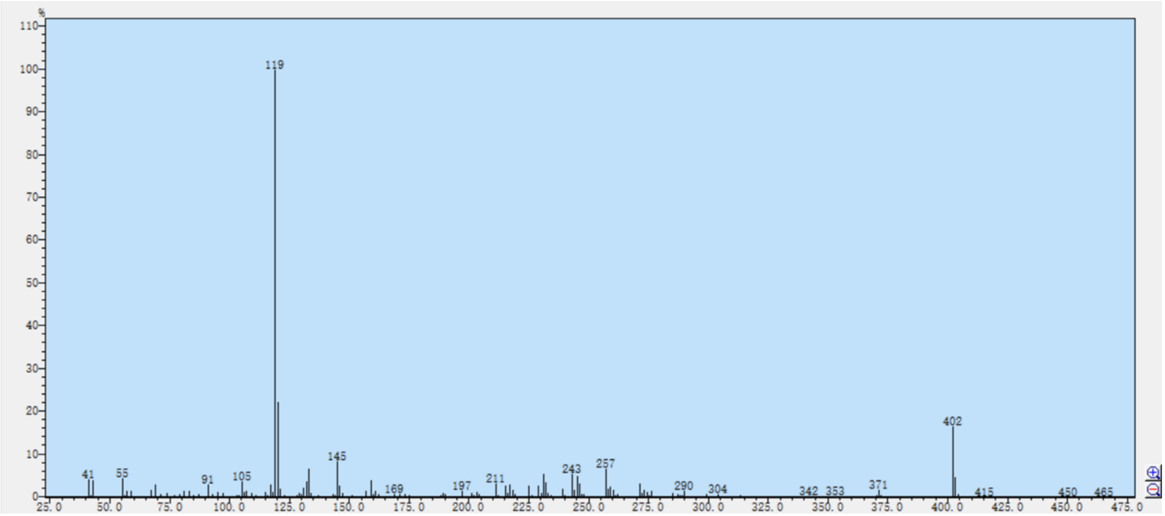
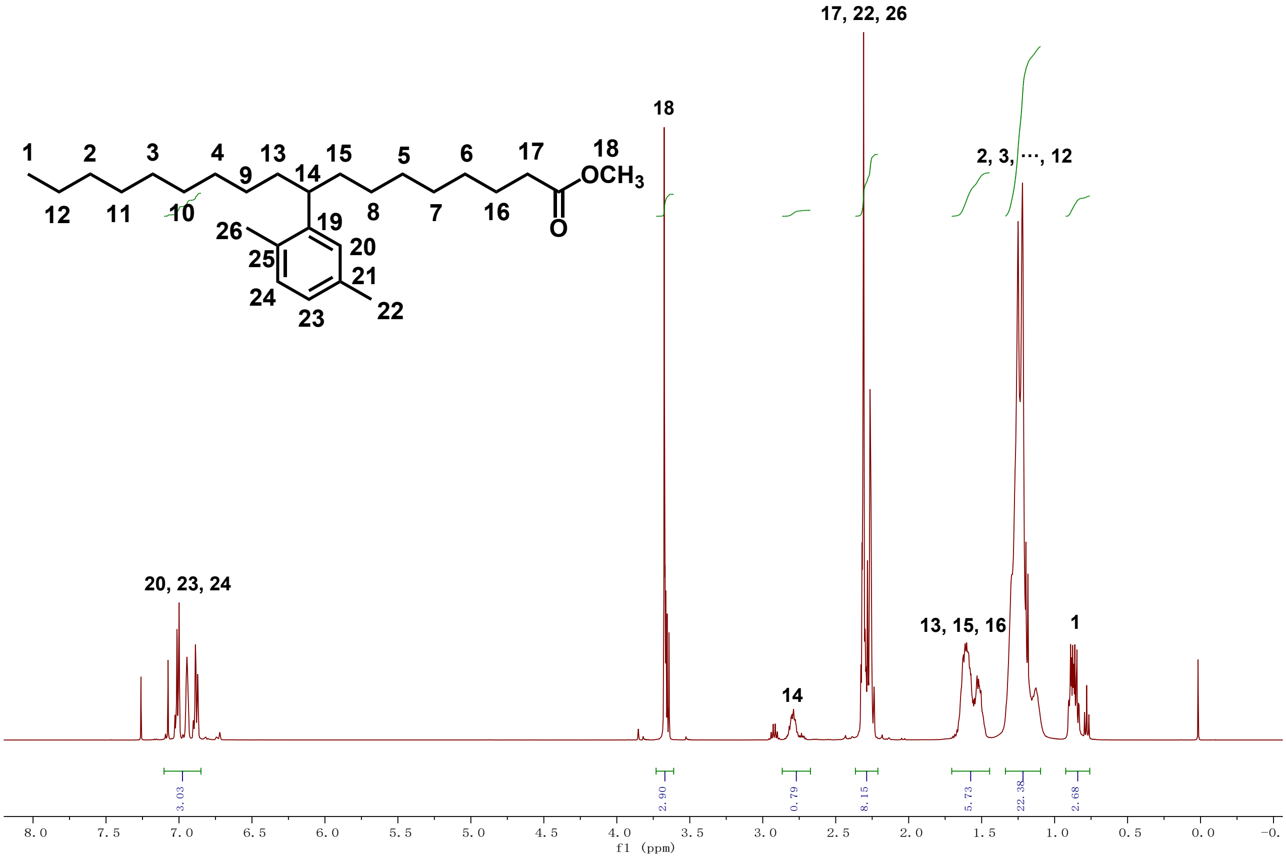


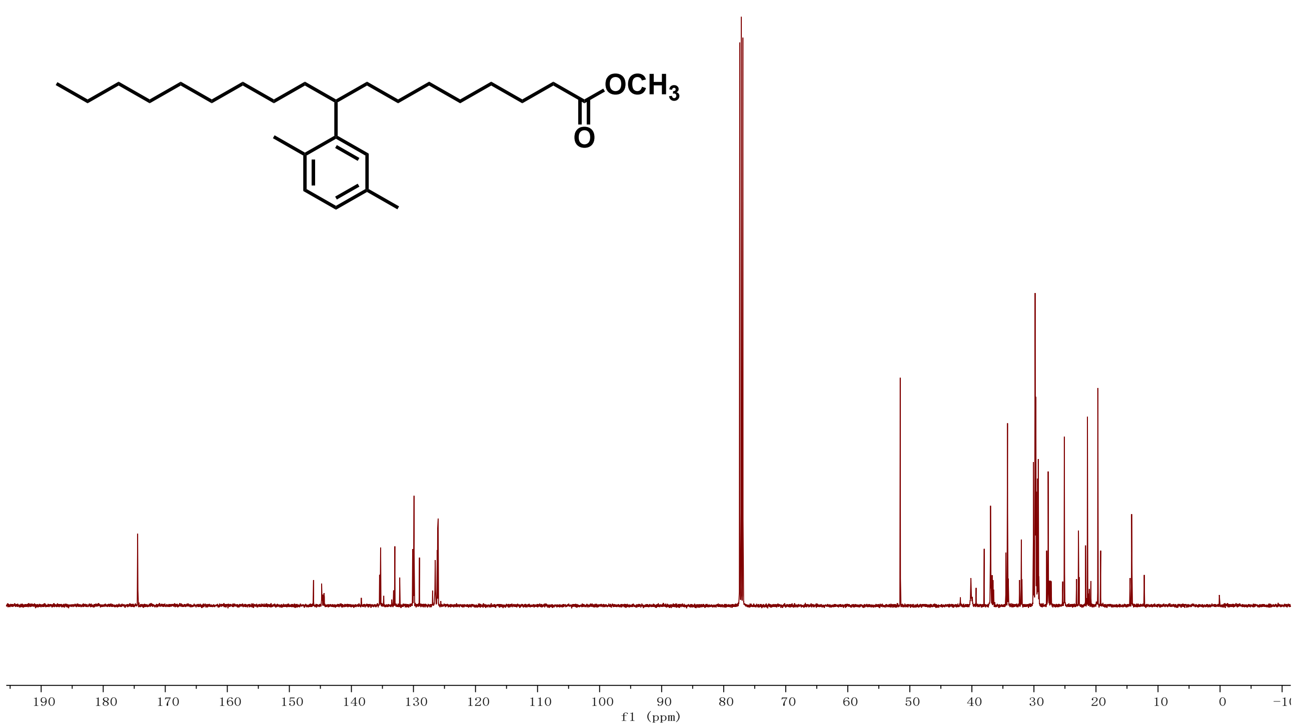
Fig. S10 (a) ^{1}H-NMR, (b) ^{13}C-NMR, and (c) Mass spectra of C_{27} AEL-MX.

(a)



1
2
3
4
13
14
15
5
6
17
18
OCH3
O
12
11
10
9
8
7
16
19
20
21
22
23
24
25
26
18
17, 22, 26
2, 3, ···, 12
20, 23, 24
14
13, 15, 16
1
3.03
2.90
0.79
8.15
5.73
22.38
2.68
f1 (ppm)

(b)



OCH3
O
f1 (ppm)

(c)

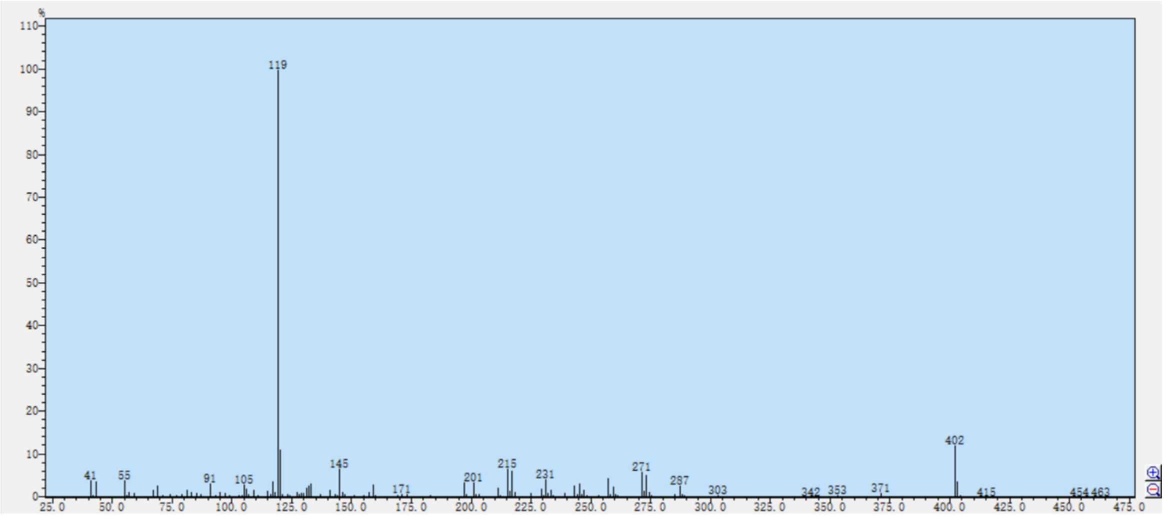
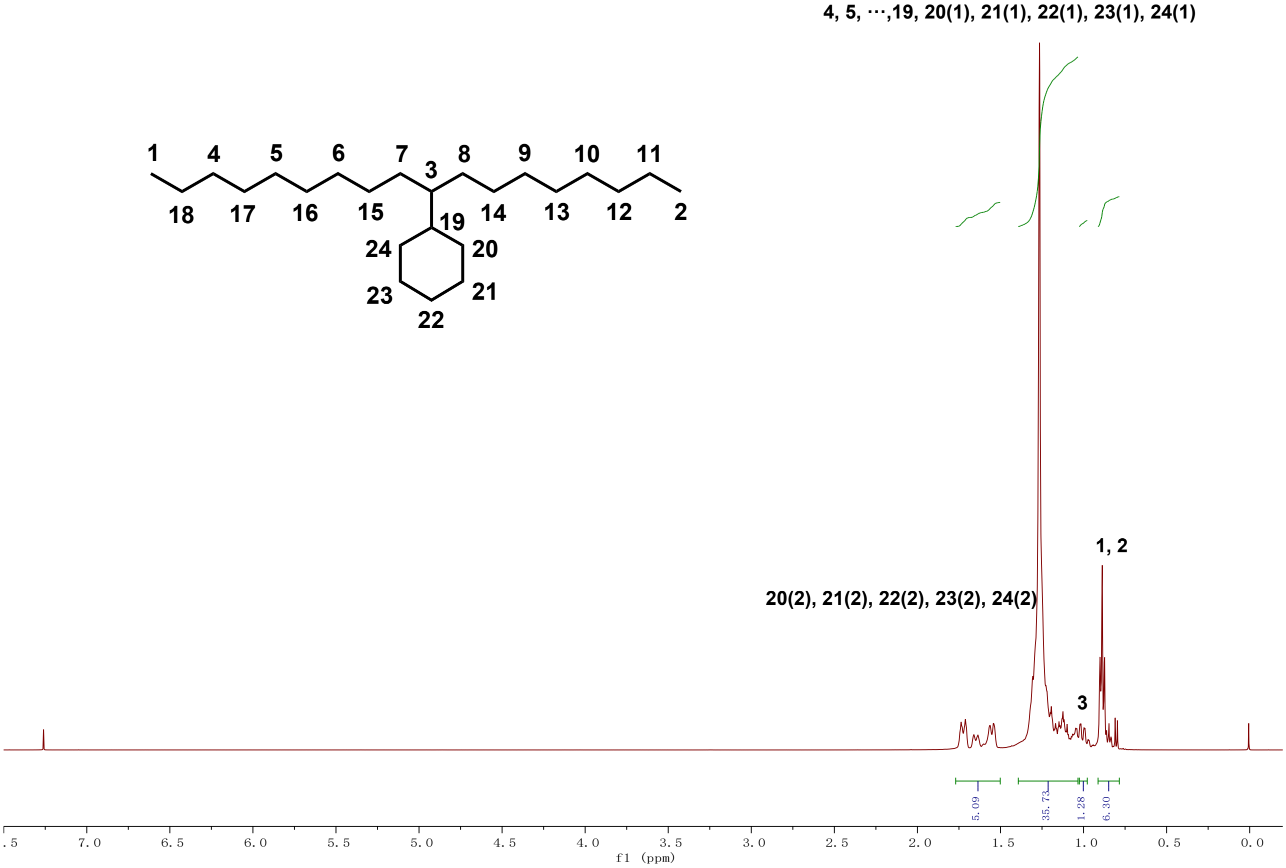
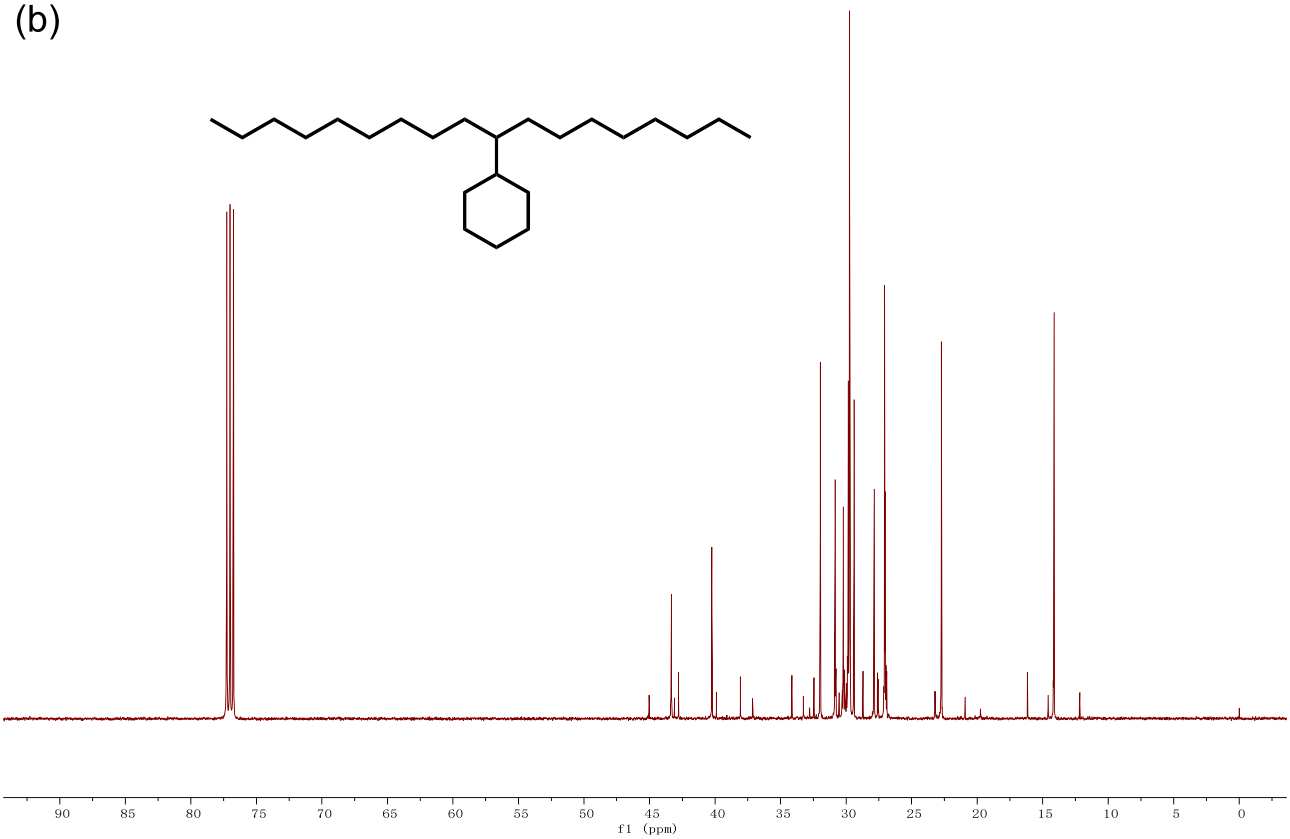


Fig. S11 (a) [1]H-NMR, (b) [13]C-NMR, and (c) Mass spectra of C_{27} AEL-PX.

(a)


4, 5, ⋯,19, 20(1), 21(1), 22(1), 23(1), 24(1)
1 4 5 6 7 3 8 9 10 11
18 17 16 15 19 14 13 12 2
24 20
23 21
22
20(2), 21(2), 22(2), 23(2), 24(2)
1, 2
3
5.09
35.73
1.28
6.30
f1 (ppm)

(b)


f1 (ppm)

(c)

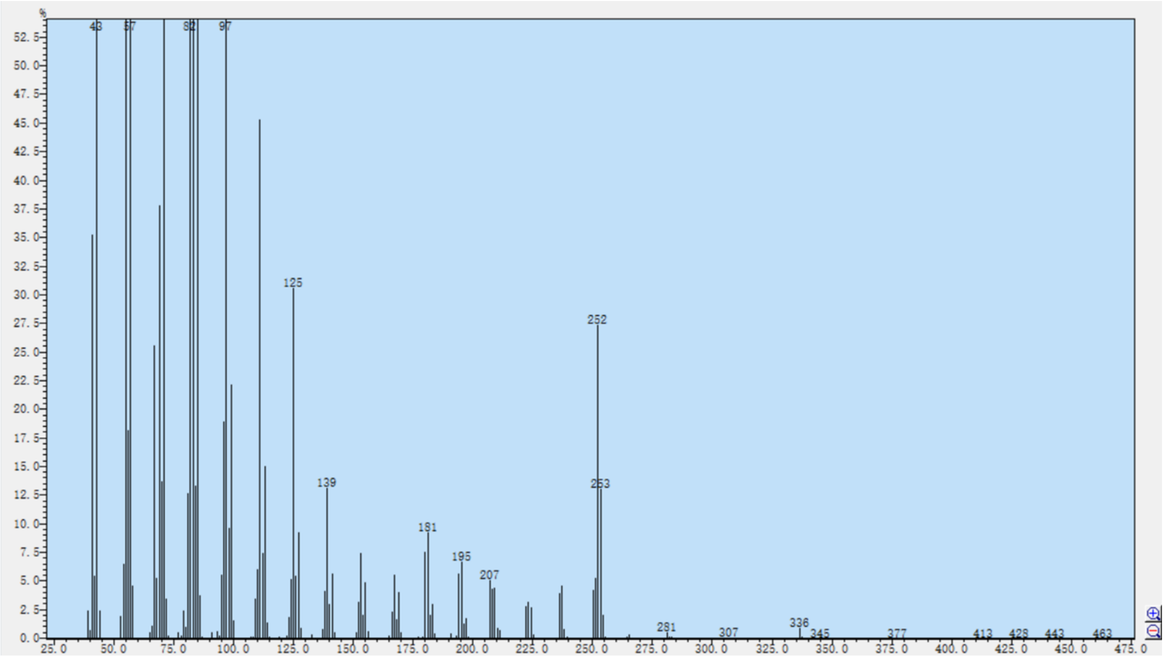
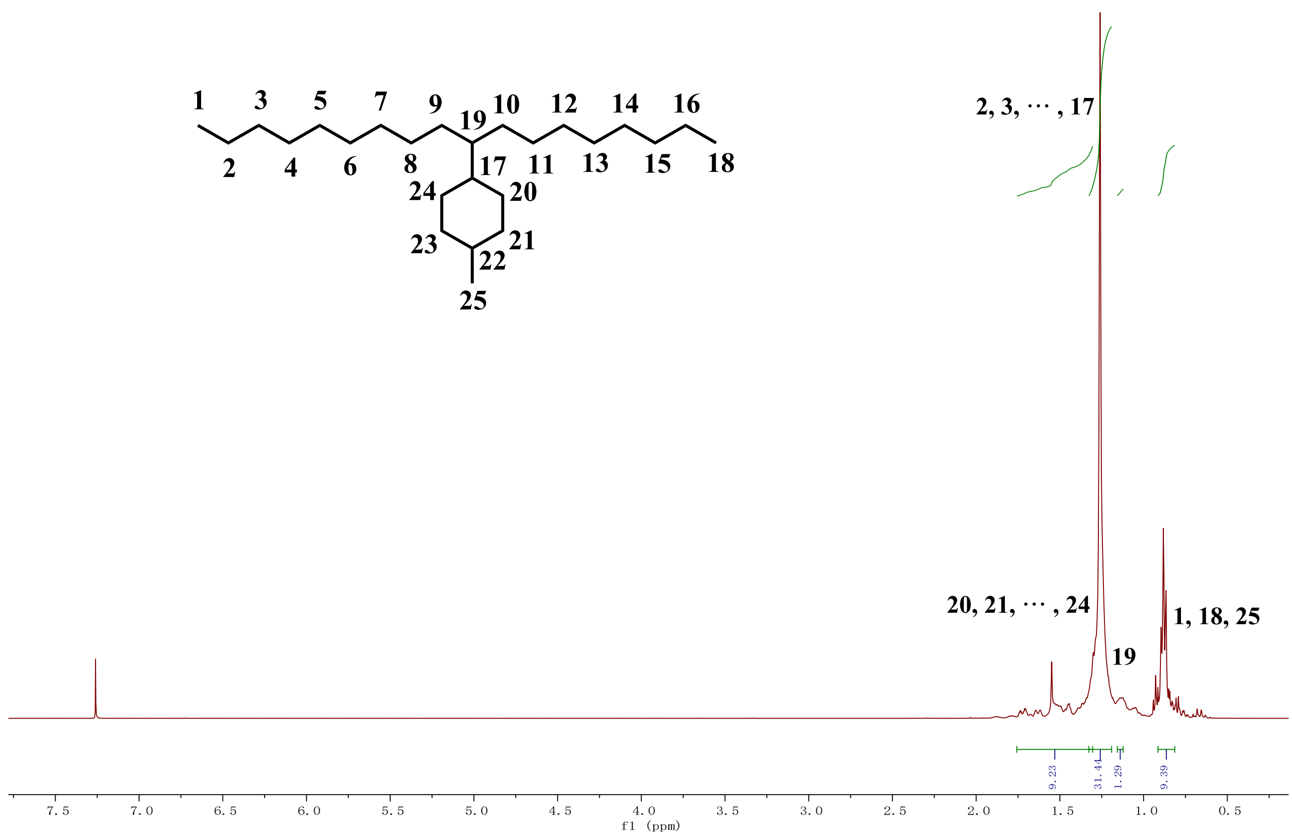
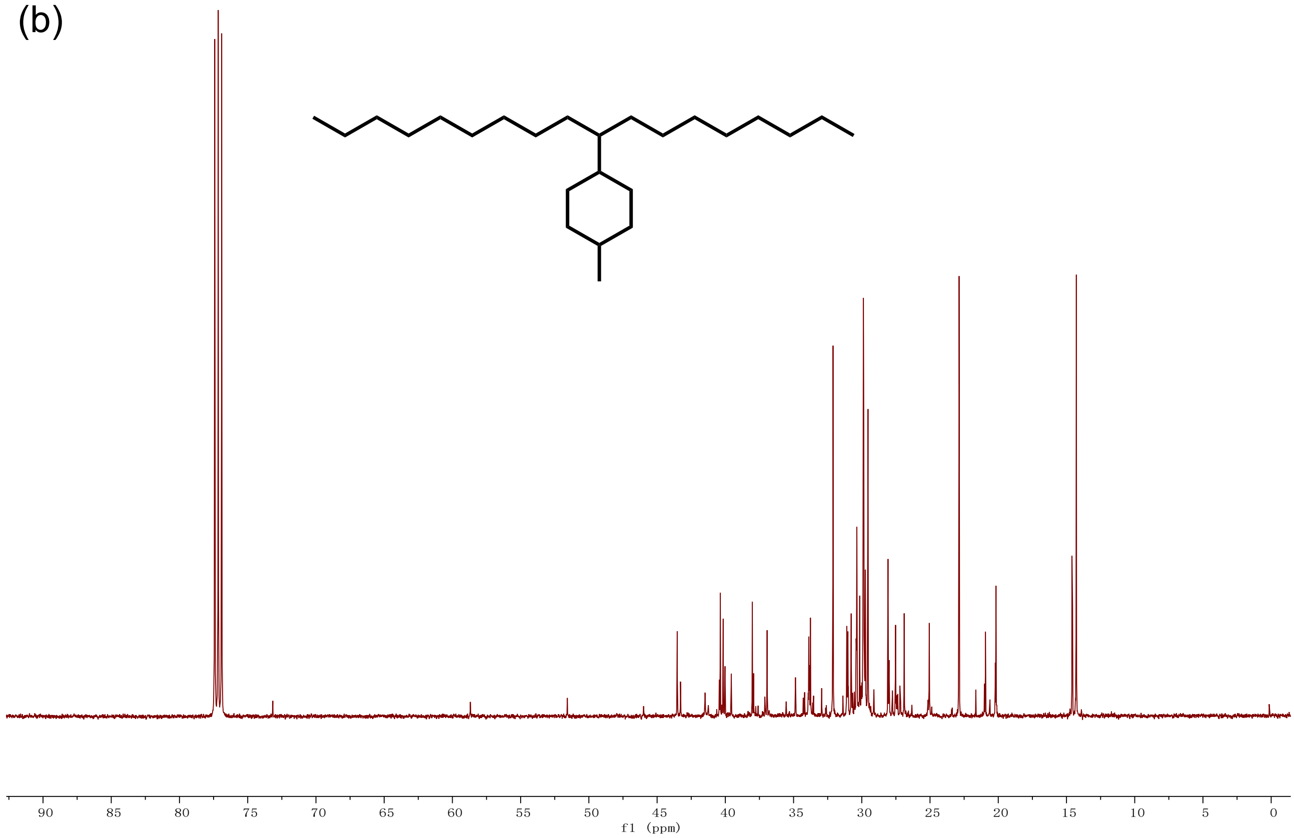


Fig. S12 (a) ^{1}H-NMR, (b) ^{13}C-NMR, and (c) Mass spectra of C_{24} CBAL-B.

(a)


1 3 5 7 9 19 10 12 14 16
2 4 6 8 17 11 13 15 18
24 20
23 21
22
25
2, 3, ⋯ , 17
20, 21, ⋯ , 24
19
1, 18, 25
9.23
31.44
1.29
9.39
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

(b)


90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

(c)

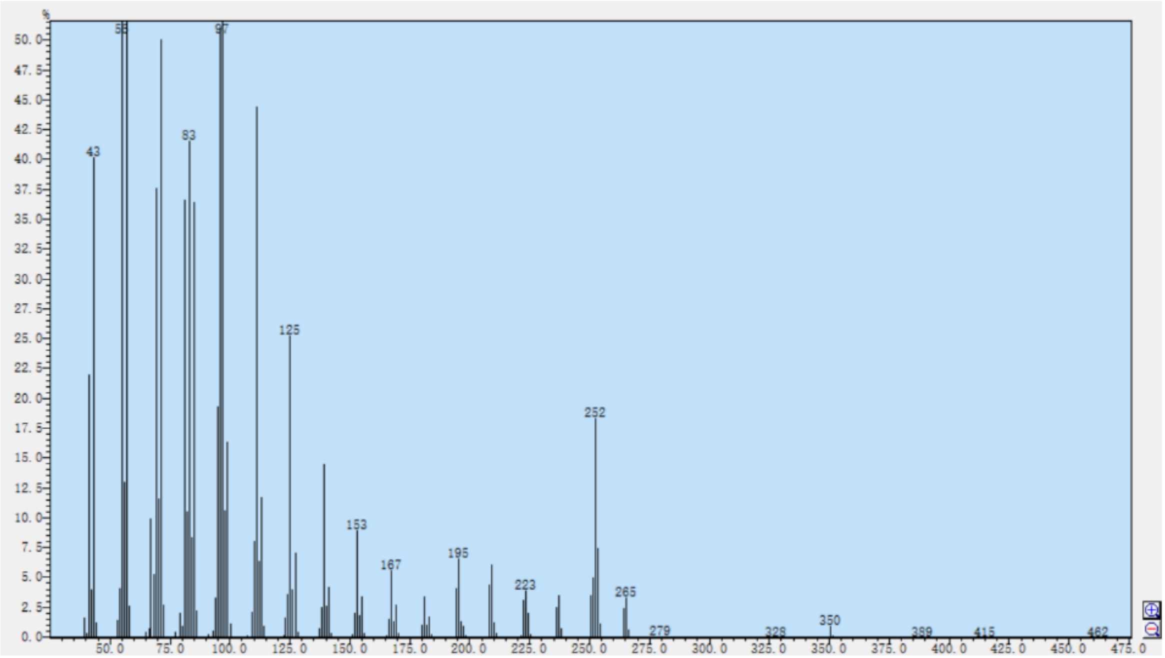
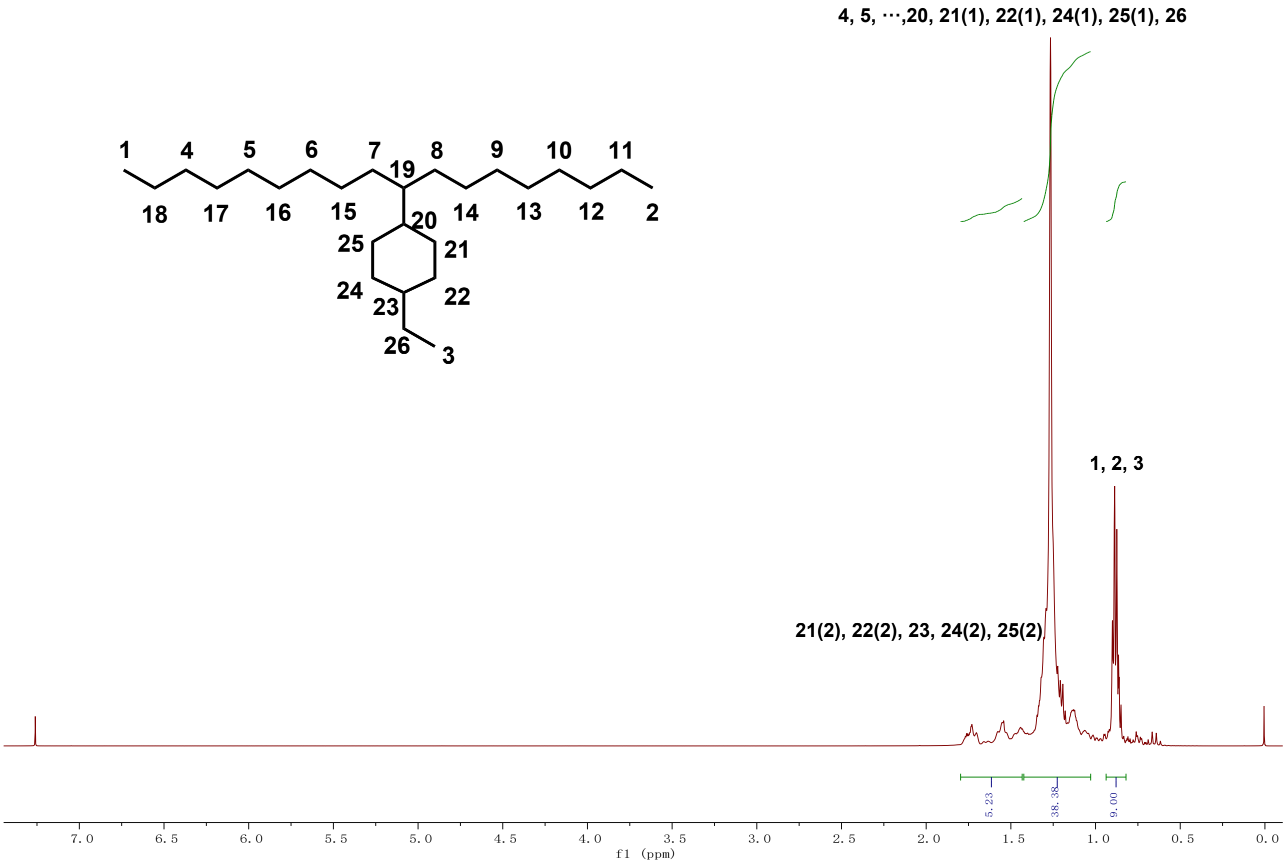
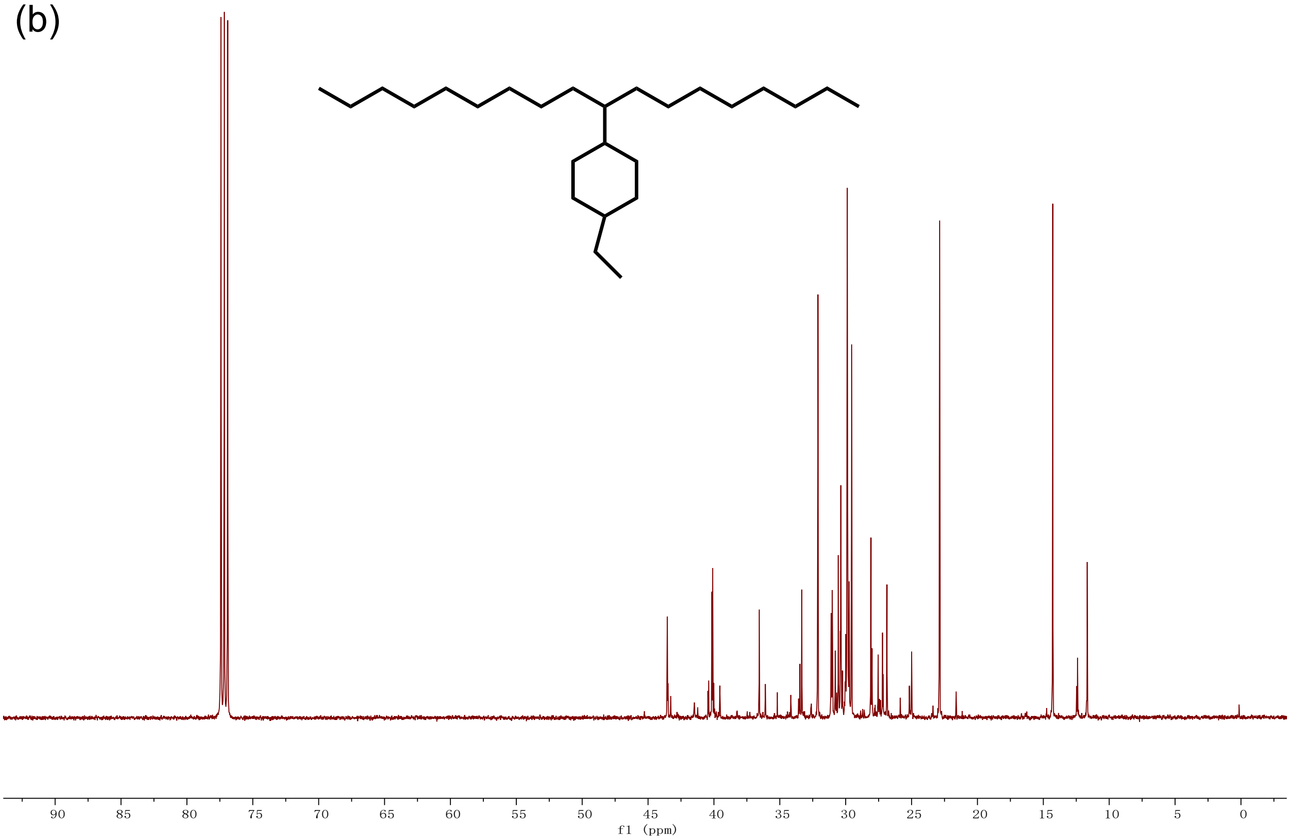


Fig. S13 (a) ^{1}H-NMR, (b) ^{13}C-NMR, and (c) Mass spectra of C_{25} CBAL-T.

(a)


4, 5, ⋯,20, 21(1), 22(1), 24(1), 25(1), 26
1 4 5 6 7 19 8 9 10 11
18 17 16 15 20 14 13 12 2
25 21
24 23 22
26 3
1, 2, 3
21(2), 22(2), 23, 24(2), 25(2)
5.23
38.38
9.00
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

(b)


90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

(c)

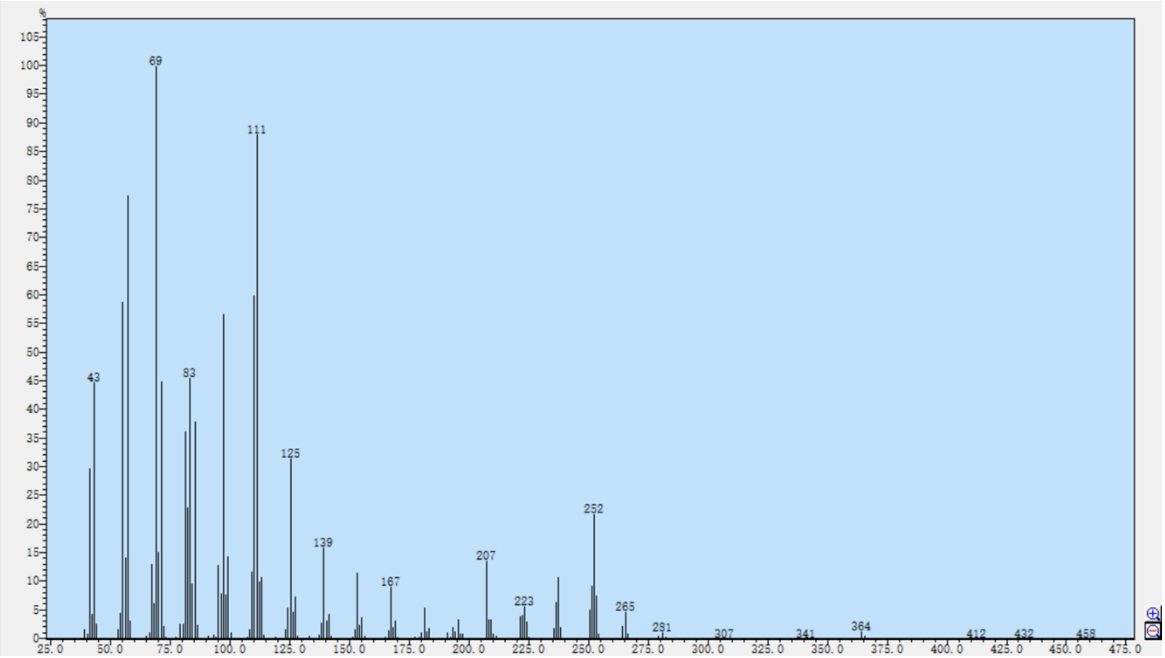
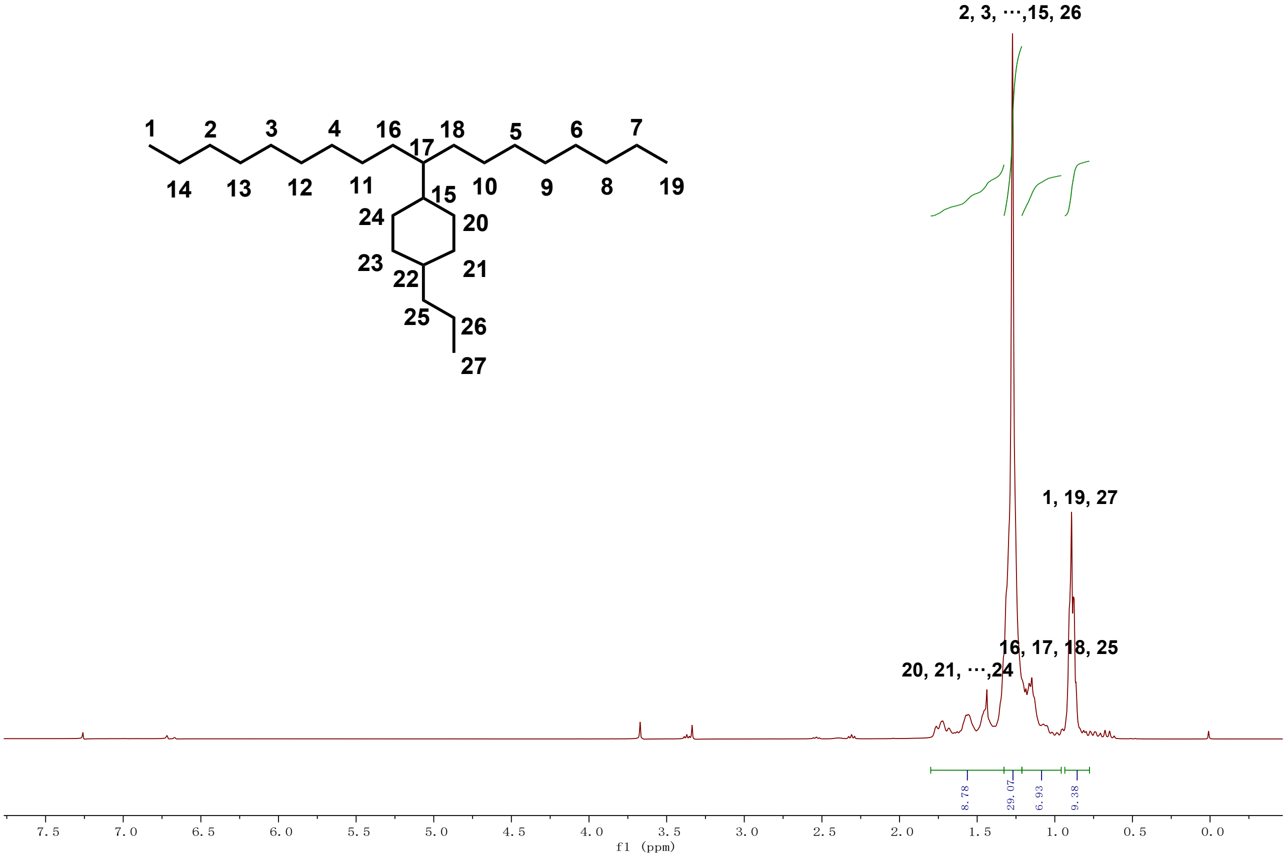
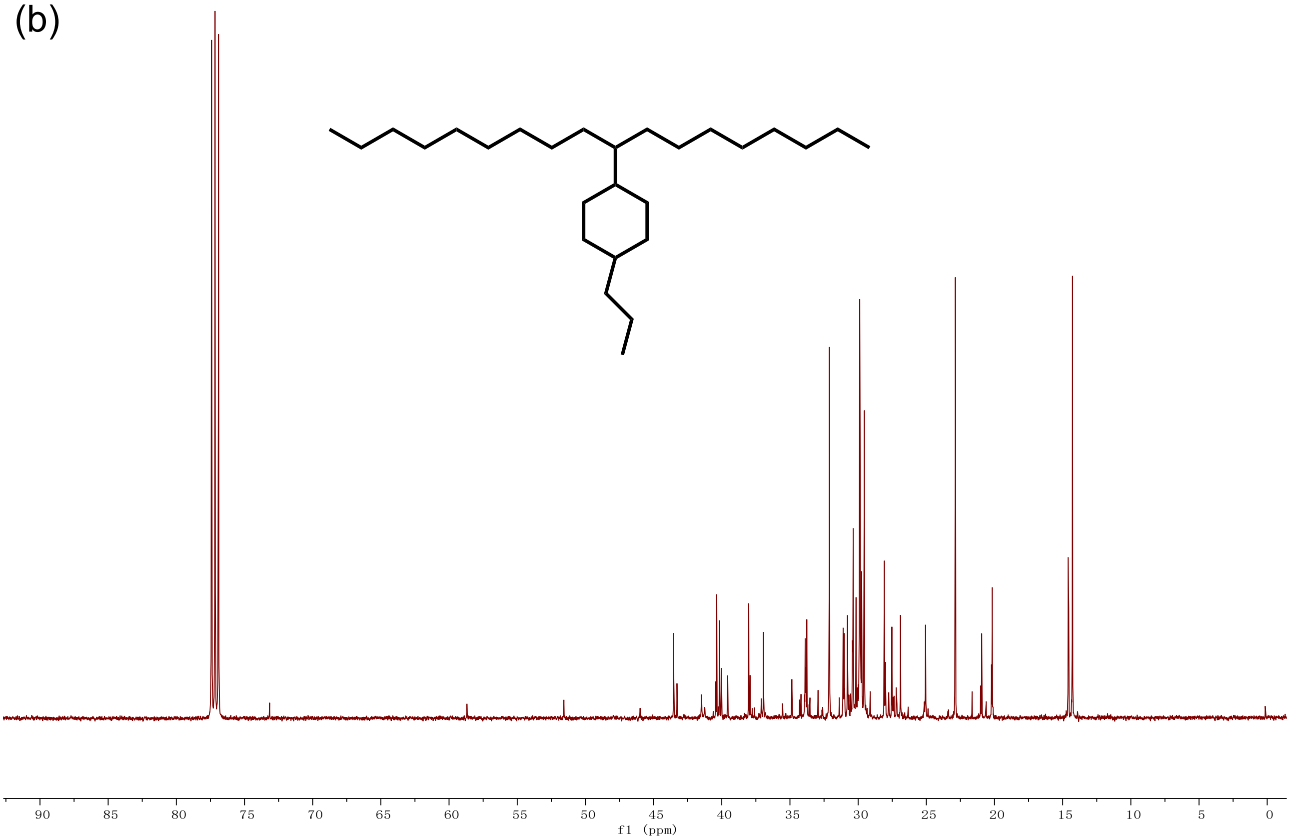


Fig. S14 (a) [1]H-NMR, (b) [13]C-NMR, and (c) Mass spectra of C_{26} CBAL-EB.

(a)


2, 3, ···,15, 26
1, 19, 27
16, 17, 18, 25
20, 21, ···,24
8.78
29.07
6.93
9.38
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

(b)


90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

(c)

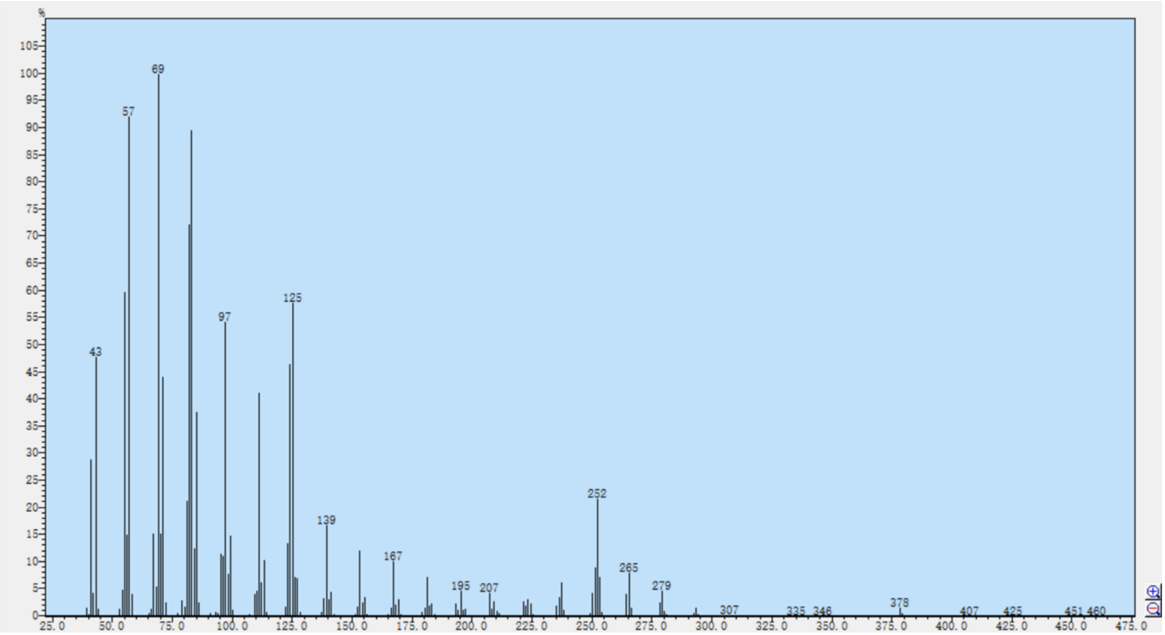
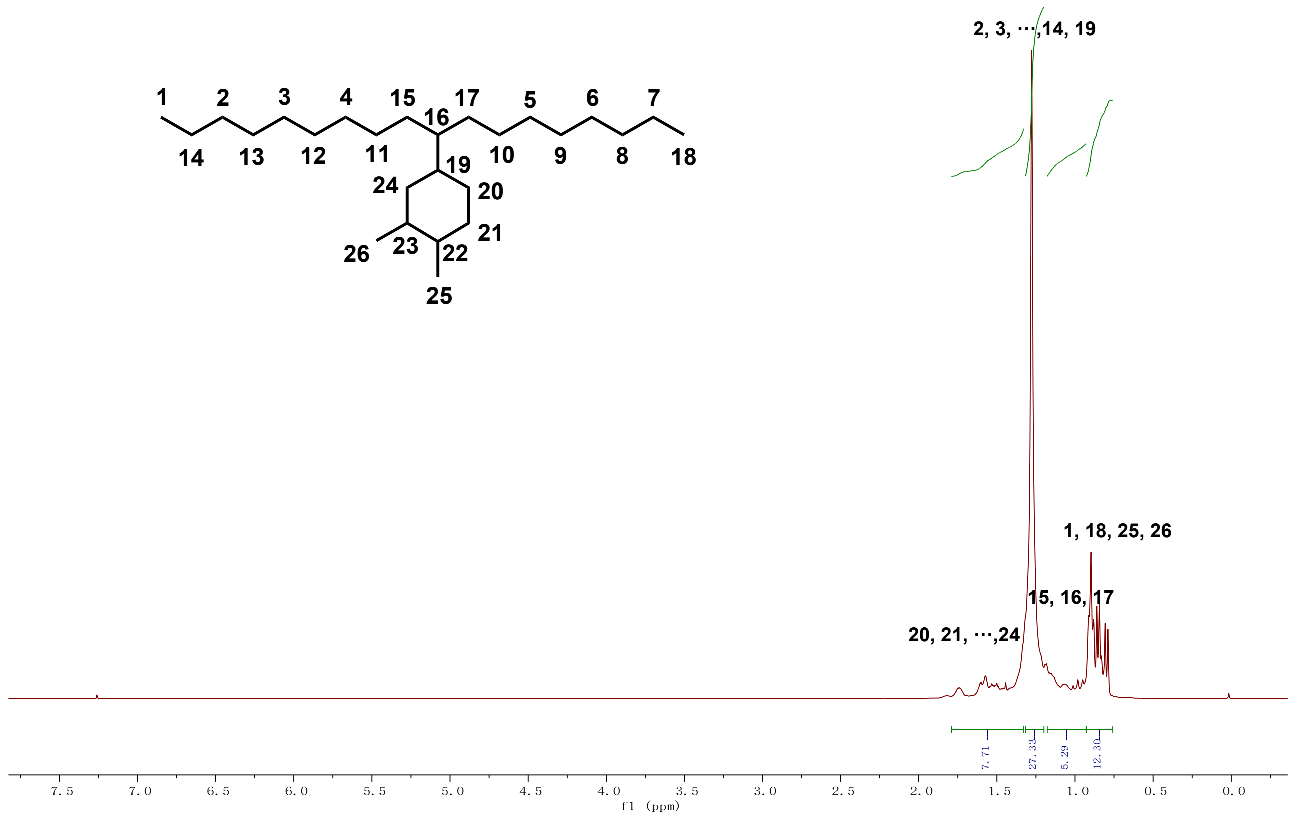


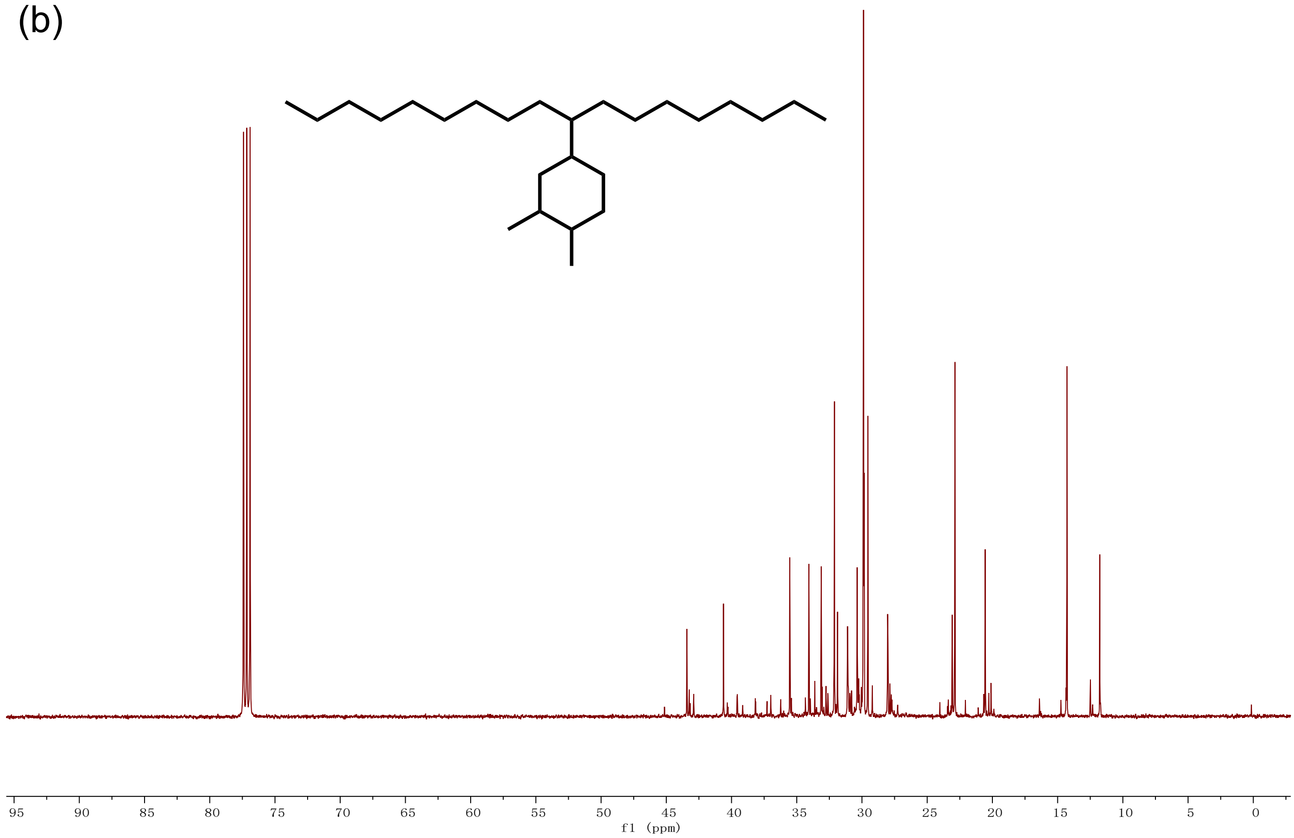
Fig. S15 (a) [1]H-NMR, (b) [13]C-NMR, and (c) Mass spectra of C_{27} CBAL-PB.

(a)



1
2
3
4
15
16
17
5
6
7
14
13
12
11
19
10
9
8
18
24
20
21
26
23
22
25
2, 3, ⋯,14, 19
1, 18, 25, 26
15, 16, 17
20, 21, ⋯,24
7.71
27.33
5.29
12.30
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

(b)



95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

(c)

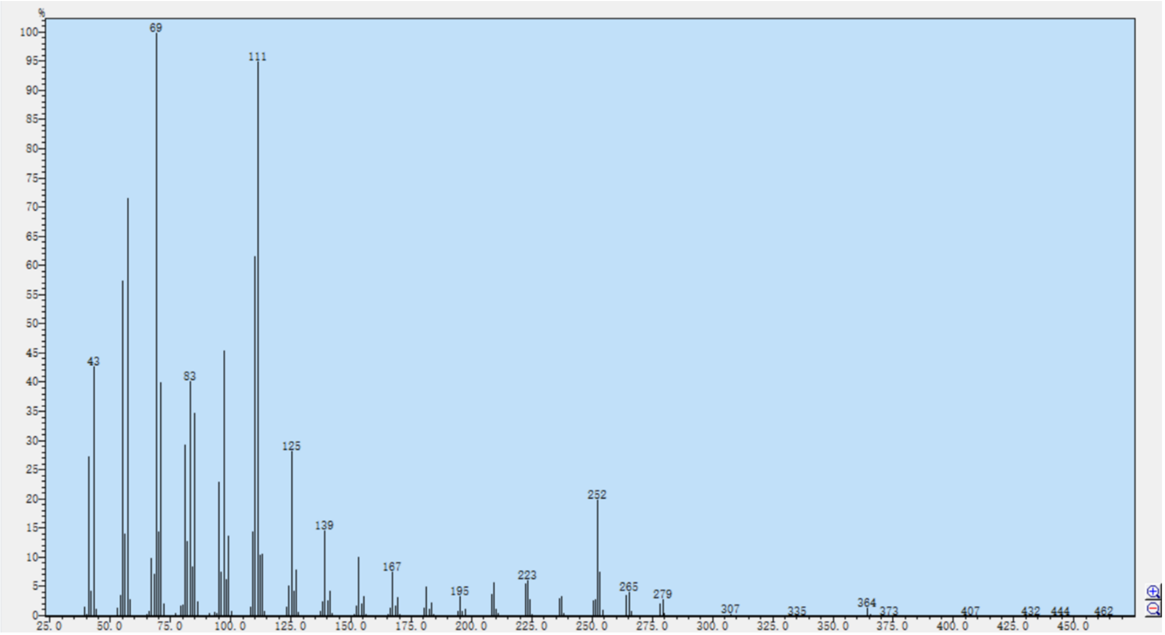
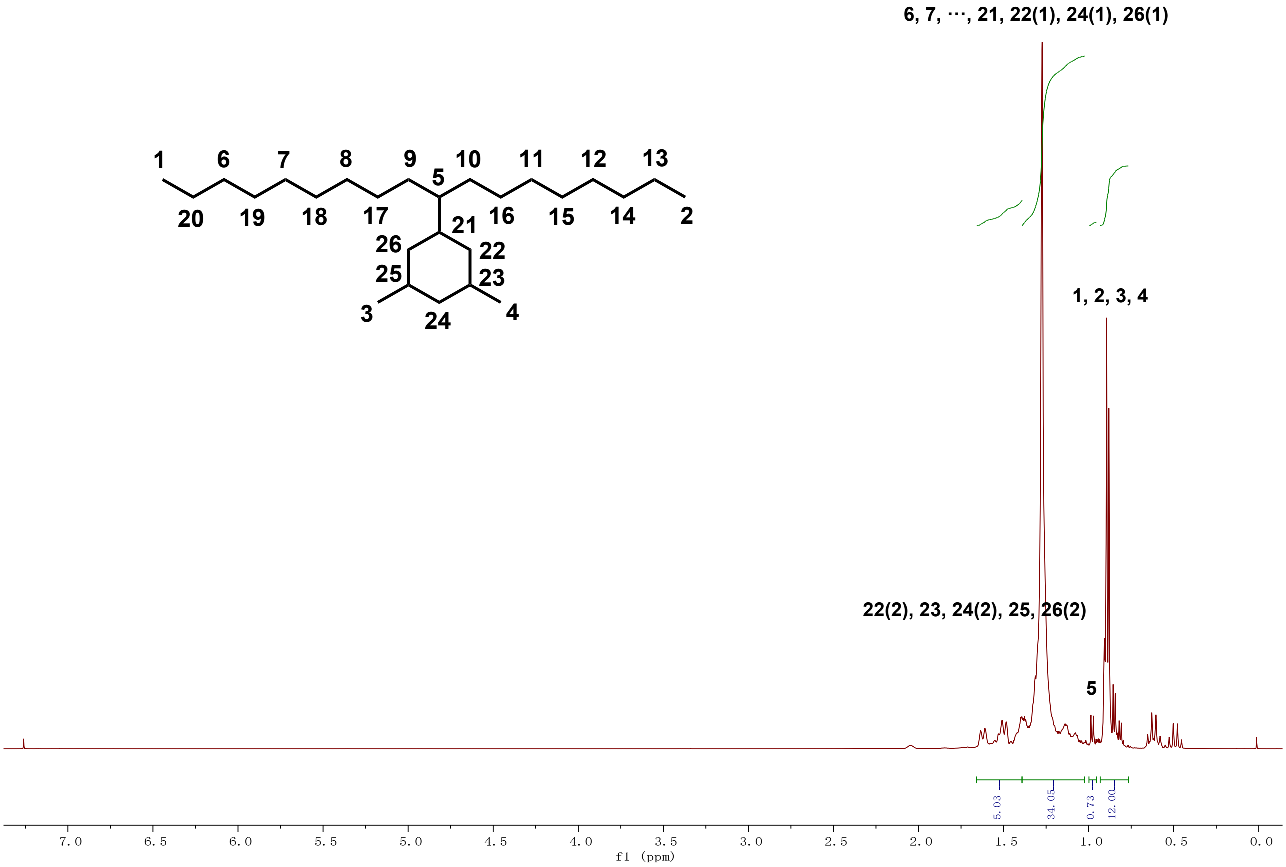
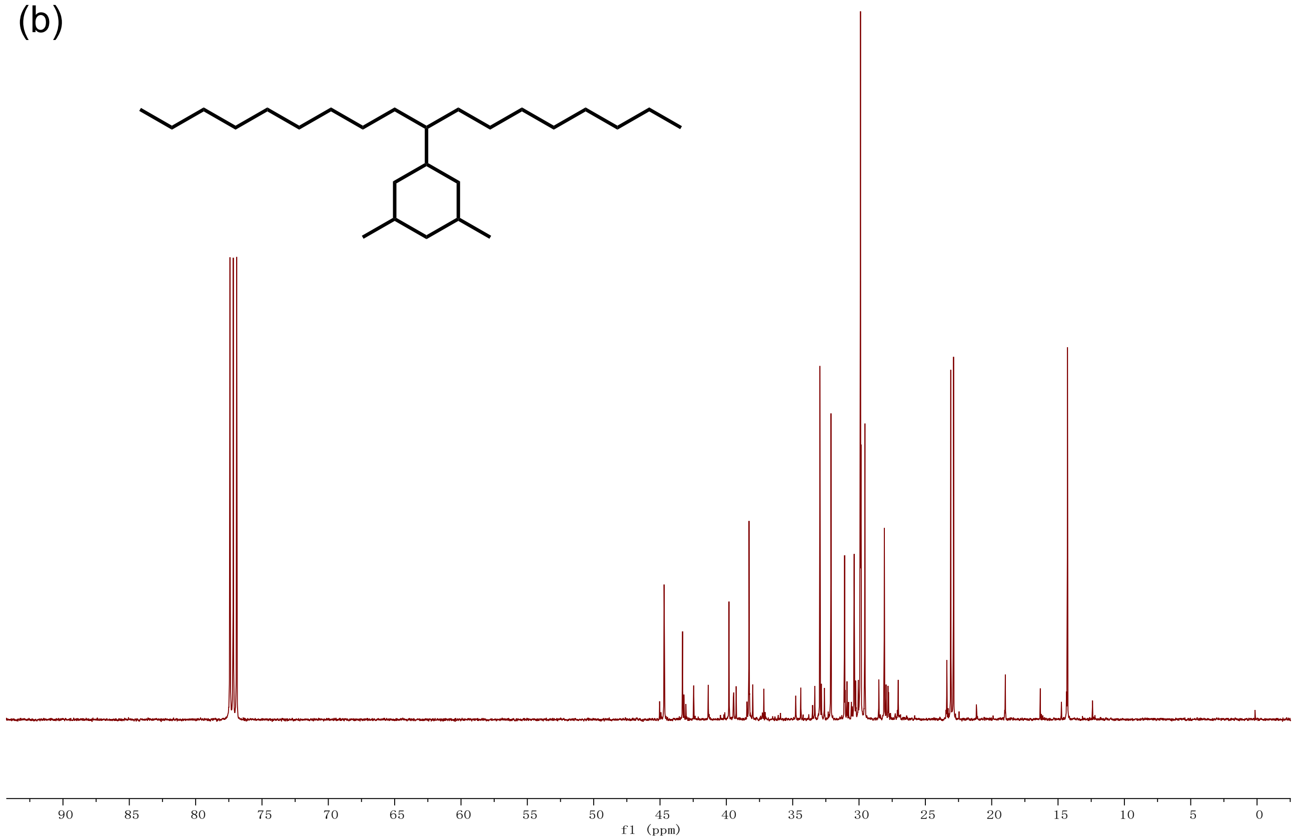


Fig. S16 (a) ^{1}H-NMR, (b) ^{13}C-NMR, and (c) Mass spectra of C_{26} CBAL-OX.

(a)


6, 7, ···, 21, 22(1), 24(1), 26(1)
1, 2, 3, 4
22(2), 23, 24(2), 25, 26(2)
5
1
6
7
8
9
5
10
11
12
13
20
19
18
17
21
16
15
14
2
26
22
25
23
3
24
4
5.03
34.05
0.73
12.00
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

(b)


90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)

(c)

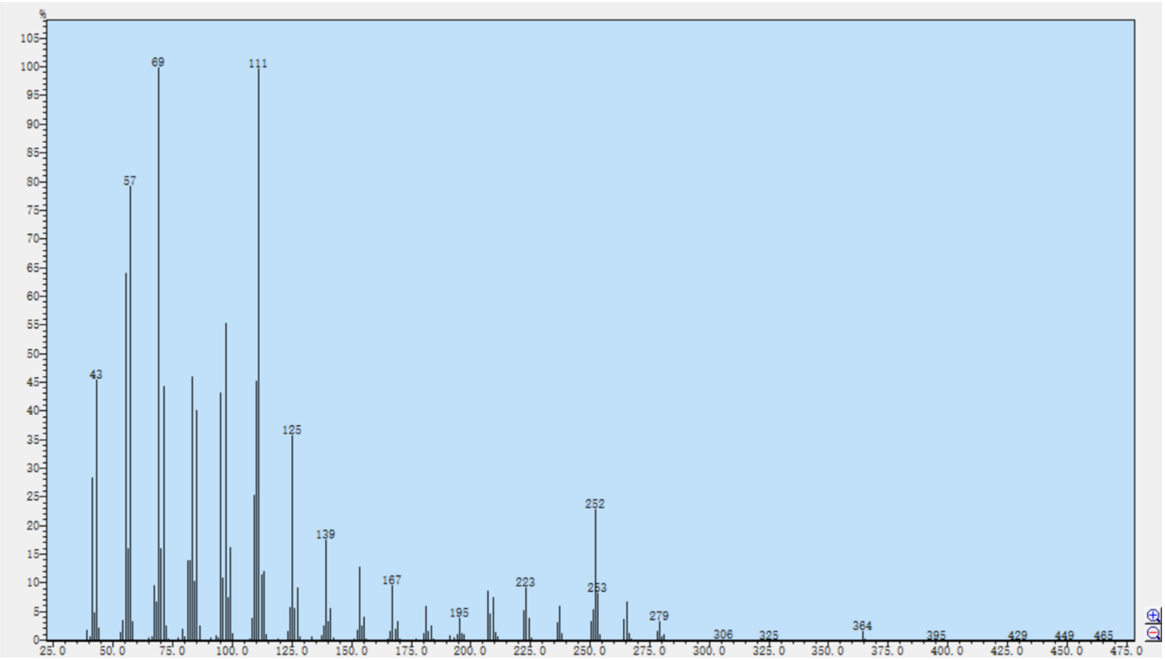
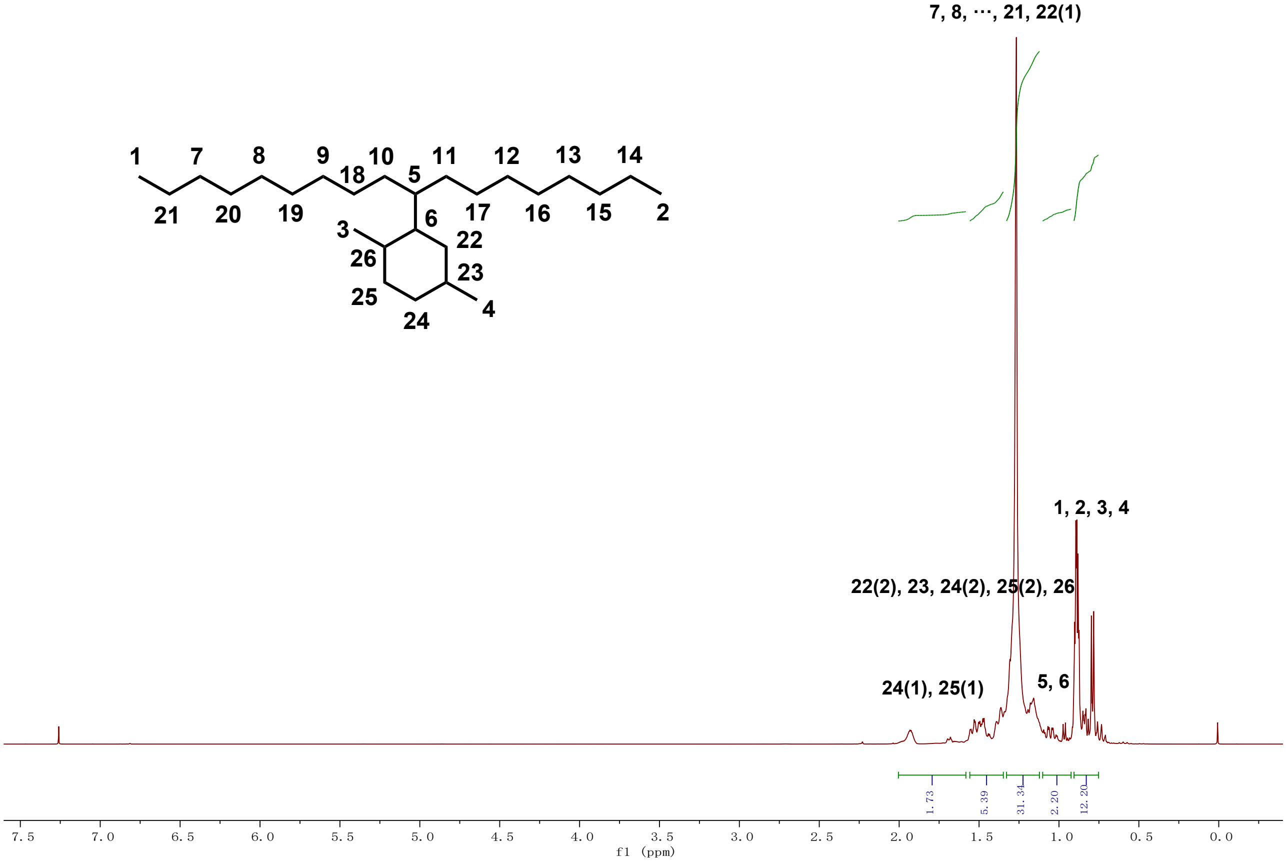
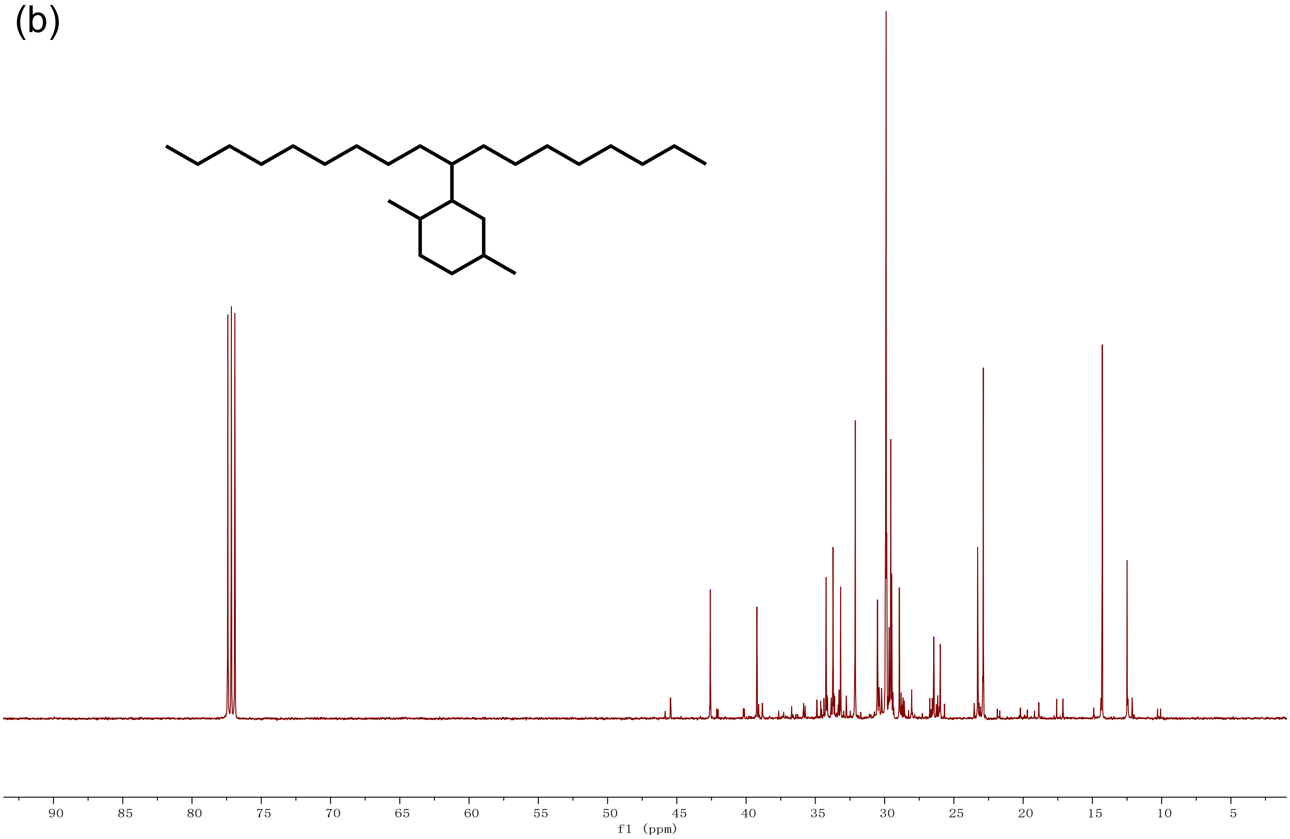


Fig. S17 (a) [1]H-NMR, (b) [13]C-NMR, and (c) Mass spectra of C_{26} CBAL-MX.

(a)


7, 8, ···, 21, 22(1)
1 7 8 9 18 10 5 11 12 13 14
21 20 19 6 17 16 15 2
3 26 22
23
25 24 4
1, 2, 3, 4
22(2), 23, 24(2), 25(2), 26
24(1), 25(1)
5, 6
1.73
5.39
31.34
2.20
12.20
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

(b)


90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

(c)

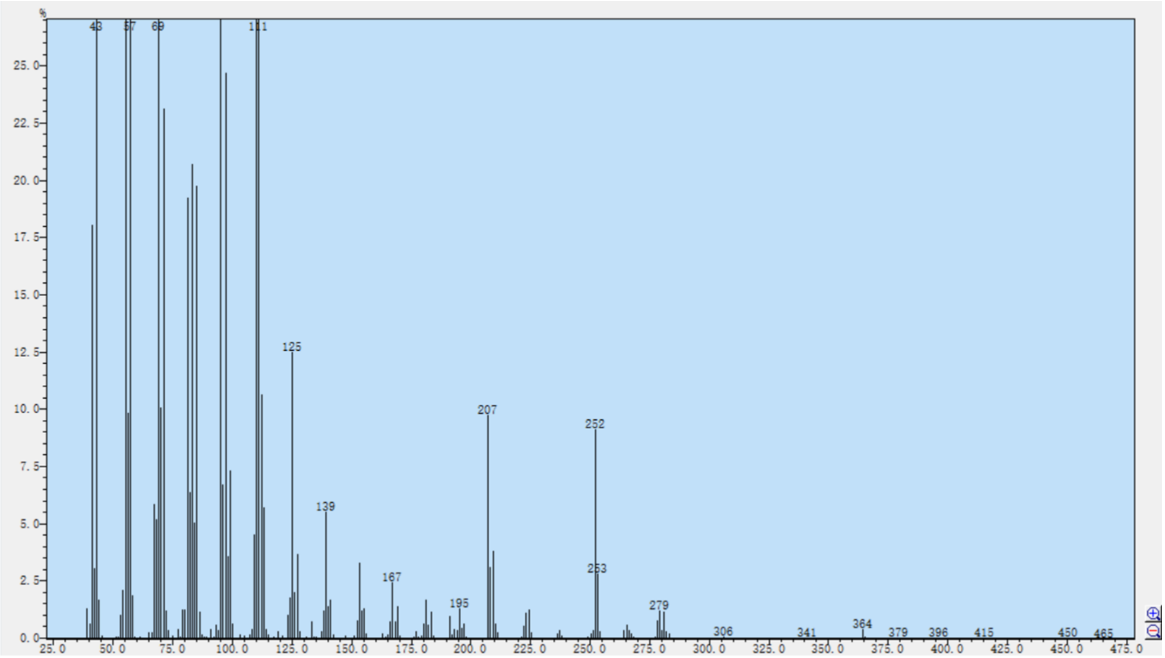


Fig. S18 (a) ^{1}H-NMR, (b) ^{13}C-NMR, and (c) Mass spectra of C_{26} CBAL-PX.