Supporting Information

1. General Information

The ^{1}H NMR spectra were recorded on a DPX-300 or Varian EM-360 (300 MHz). All chemical shifts (δ) were given in ppm. Data were reported as follows: chemical shift, integration, multiplicity (s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a DPX-300 (300 MHz) or DPX-400 (400 MHz). Flash column chromatography was performed using H silica gel. For thin-layer chromatography (TLC), silica gel plates (HSGF 254) were used and compounds were visualized by irradiation with UV light. Analytical high performance liquid chromatography (HPLC) was carried out on WATERS equipment using chiral columns. Melting points were determined on a SGW X-4 melting point and were uncorrected. Optical rotations were measured on a JASCO P-1010 Polarimeter at λ = 589 nm. IR spectra were recorded on a Perkin-Elmer 983G instrument. Mass spectra analysis was performed on API 200 LC/MS system (Applied Biosystems Co. Ltd.). The enantiomeric excesses of products were determined by chiral-phase HPLC analysis, using a Daicel Chiralcel OD, AD-H and AS-H column.

All ethyl 2-substitutedmethylallenoates were synthesized by reported methods and stored at 4 °C prior to use.[1,2] All α-cyanoacrylates were prepared using the standard knoevenagel condensation conditions from corresponding aldehydes. All acyl protected aminophosphines **4** were synthesized according to procedures reported previously.[3,4] All reactions were carried out employing oven-dried glassware. Unless otherwise indicated, all compounds and reagents were purchased from commercial suppliers and purified by standard techniques.

[1] X.-F. Zhu, J. Lan and O. Kwon, *J. Am. Chem. Soc.* 2003, **125**, 4716.

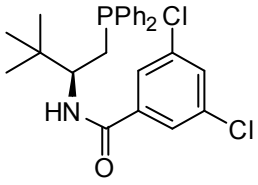
[2] R. P. Wurz and G. C. Fu, *J. Am. Chem. Soc.* 2005, **127**, 12234.

[3] H. Xiao, Z. Chai, C.-W. Zheng, Y.-Q. Yang, W. Liu, J.-K. Zhang and G. Zhao, *Angew. Chem, Int. Ed.* 2010, **49**, 4467.

[4] H. Xiao, Z. Chai, H.-F. Wang, D. Cao, W. Liu, X.-W. Wang, Y. Lu, Y.-Q. Yang and G. Zhao, *Chem. Eur. J.* 2011, **17**, 10562.

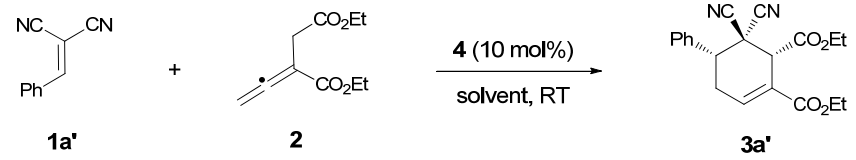
2. Characterization of catalysts 4d

(*S*)-3,5-dichloro-N-(1-(diphenylphosphino)-3,3-dimethylbutan-2-yl)benzamide (4d)

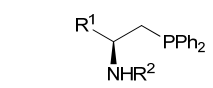


Yield: 72%; White solid. m.p. = 164-166°C; $[\alpha]_D^{26}$ 35.7 (*c* = 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50–7.42 (m, 5H), 7.36-7.30 (m, 8H), 5.73 (d, *J* = 10.1 Hz, 1H), 4.30 (m, 1H), 2.51 (dt, *J* = 13.8, 2.3 Hz, 1H), 2.30 (dd, *J* = 13.8, 12.5 Hz, 1H), 1.00 (s, 9H); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 164.4, 138.7 (d, $J_{C\text{-}P}$ = 13.9 Hz), 138.4 (d, $J_{C\text{-}P}$ = 13.9 Hz), 137.8, 135.2, 132.9, 132.7, 131.0, 129.0 (d, $J_{C\text{-}P}$ = 16.5 Hz), 128.7 (q, $J_{C\text{-}P}$ = 6.9 Hz), 128.6 (d, $J_{C\text{-}P}$ = 6.9 Hz), 125.4, 56.2 (d, $J_{C\text{-}P}$ = 14.7 Hz), 36.0 (d, $J_{C\text{-}P}$ = 7.0 Hz), 30.4 (d, $J_{C\text{-}P}$ = 13.8 Hz), 26.3; **^{31}P NMR** ($CDCl_3$, 122 MHz) δ -20.1; **IR (neat)**: 3246, 3071, 2962, 1637, 1565 1433, 1305, 1071, 1026, 805, 740, 695; **HRMS (ESI)**: calcd. for $M^+(C_{25}H_{26}NOCl_2P)$ requires 457.1129, found 457.1127.

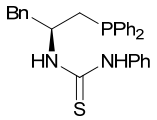
3. Table S1. Catalyst screening for [4 + 2] annulation of substituted allenoate 2 and phenylidenemalononitrile 1a'[a]



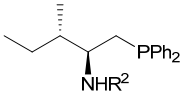
1a' **2** **3a'**



4a: R^1/R^2 = Bn/Ac
4b: R^1/R^2 = Bn/3,5-bisCF_3benzoyl
4c: R^1/R^2 = *t*-Bu/3,5-bisNO_2benzoyl
4d: R^1/R^2 = *t*-Bu/3,5-bisClbenzoyl



4e



4g: R^2 =CF_3acetyl
4j: R^2 =Boc
4l: R^2 = 3,5-bisClbenzoyl
4m: R^2 = 3,5-bisNO_2benzoyl

Entry	Catalyst	Yield[b] (%)	*D.r.*[c]	ee[d] (%)
1	**4a**	81	70:30	88/20
2	**4b**	99	73:27	95/7
3	**4c**	81	57:43	90/37
4	**4d**	54	72:28	93/19
5	**4e**	trace	-	-
6	**4g**	89	44:56	65/39
7	**4j**	75	43:57	51/2
8	**4l**	99	41:59	81/51
9	**4m**	99	66:34	84/24

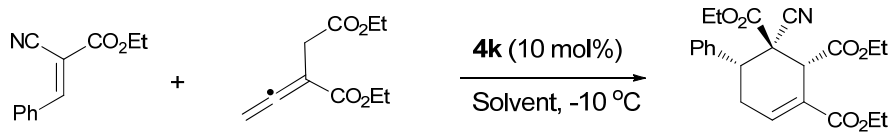
[a] All reactions were carried out with **1a'** (0.1 mmol) and α-substituted 2, 3-butadienoate **2** (0.2 mmol) in the presence of **4** (0.01 mmol) in dichloromethane (1.0 mL) at room temperature.

[b] Yields of isolated products.

[c] Determined by isolated yield.

[d] Determined by chiral HPLC analysis.

4. Table S2. Investigation on temperature and solvent effect[a]



1a **2** **3a**

Entry	solvent	Yield[b] (%)	Time/h	D.r.[c]	ee[d] (%)
1[e]	CH_2Cl_2	97	2	19:1	94
2	CH_2Cl_2	97	12	19:1	95
3[f]	CH_2Cl_2	65	24	19:1	95
4	THF	84	12	14:1	90
5	CH_3CN	91	12	14:1	76
6	o-xylene	94	24	19:1	87
7	toluene	89	24	19:1	90
8	Et_2O	66	12	15:1	91
9	CH_2ClCH_2Cl	99	4	19:1	95
10[g]	CH_2ClCH_2Cl	94	4	19:1	96

[a] All reactions were carried out with **1a** (0.08 mmol) and 2-(2-ethoxy-2-oxoethyl)-2, 3-butadienoate **2** (0.16 mmol) in the presence of **4k** (0.008 mmol) in 0.8 mL of solvent at －10 ℃.

[b] Yields of isolated products.

[c] Determined by ^{1}H NMR.

[d] Determined by chiral HPLC analysis.

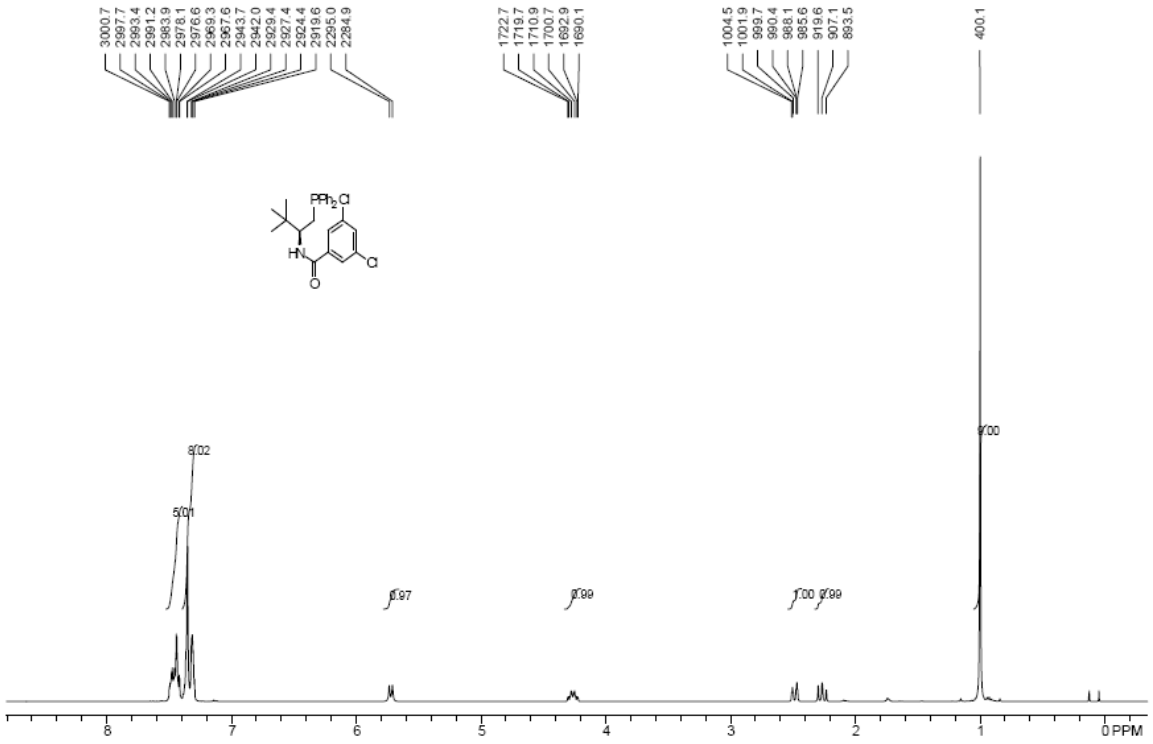
[e] The reaction temperature was 0 ℃.

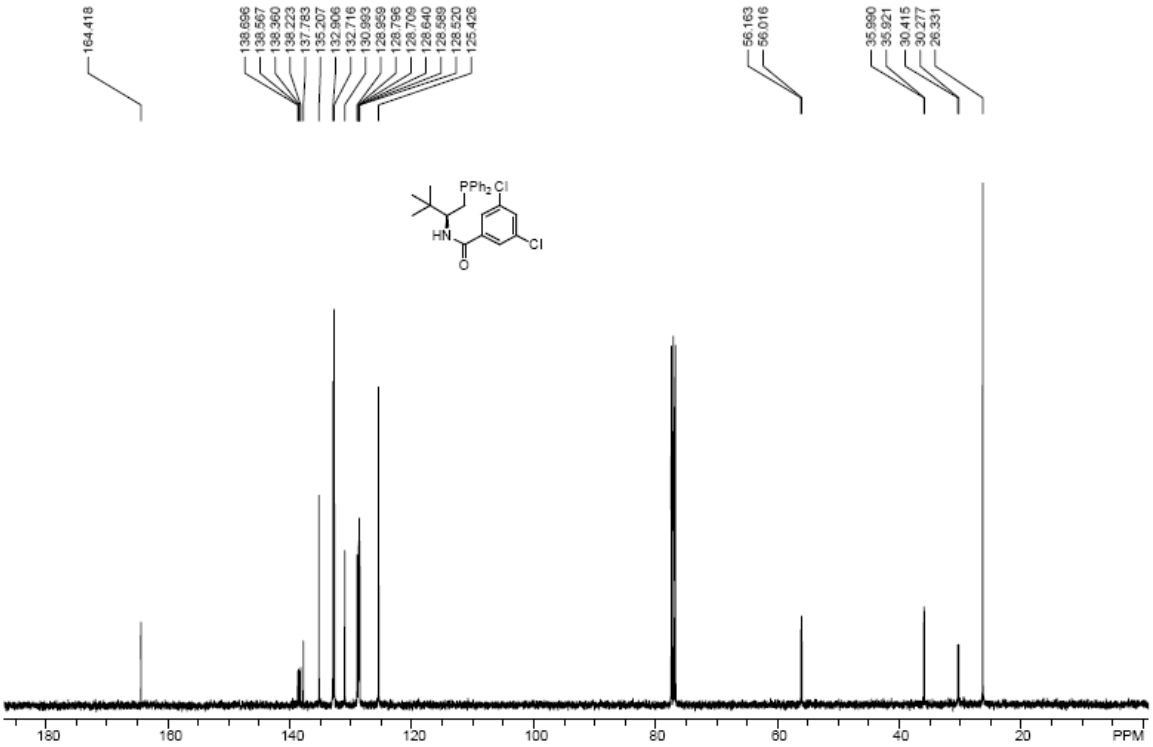
[f] The reaction temperature was －18 ℃.

[g] The reaction was conducted at －18 ℃ with 12 mol% of **4k**.

5. NMR spectra for catalyst 4d

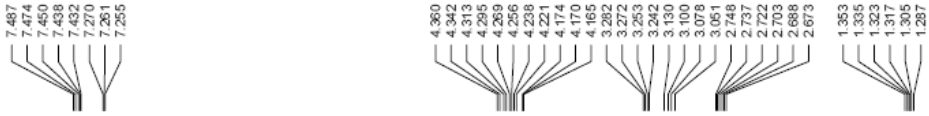
(*S*)-3,5-dichloro-N-(1-(diphenylphosphino)-3,3-dimethylbutan-2-yl)benzamide (4d)

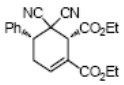


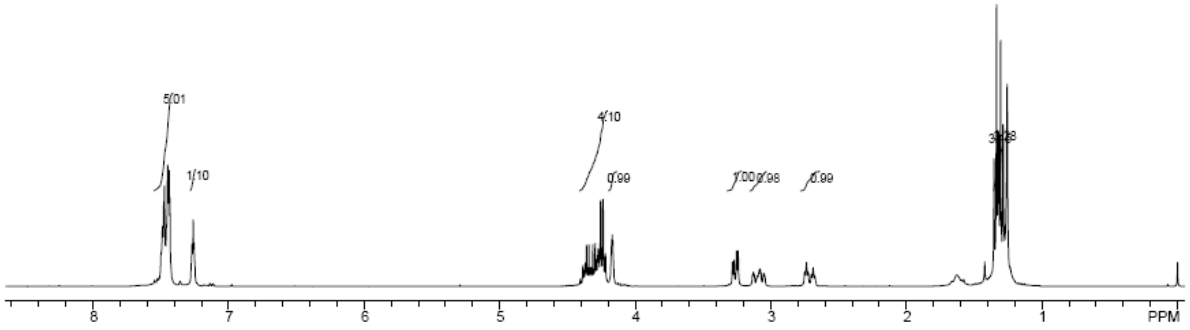


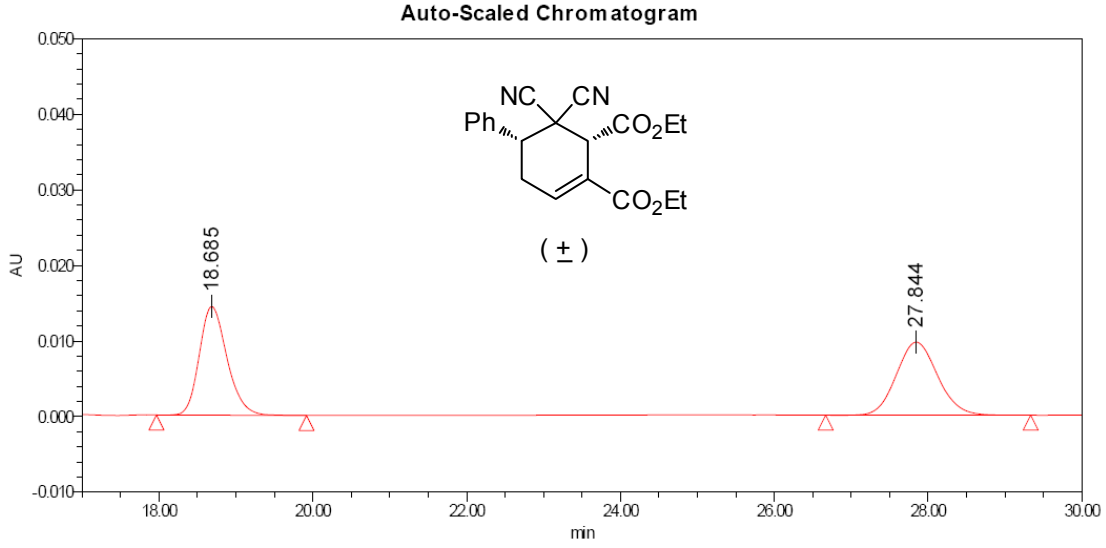
6. NMR spectra and HPLC spectra for compounds 3 and 6

(1*R*,3*S*)-diethyl 2,2-dicyano-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3,4-dicarboxylate (3a')



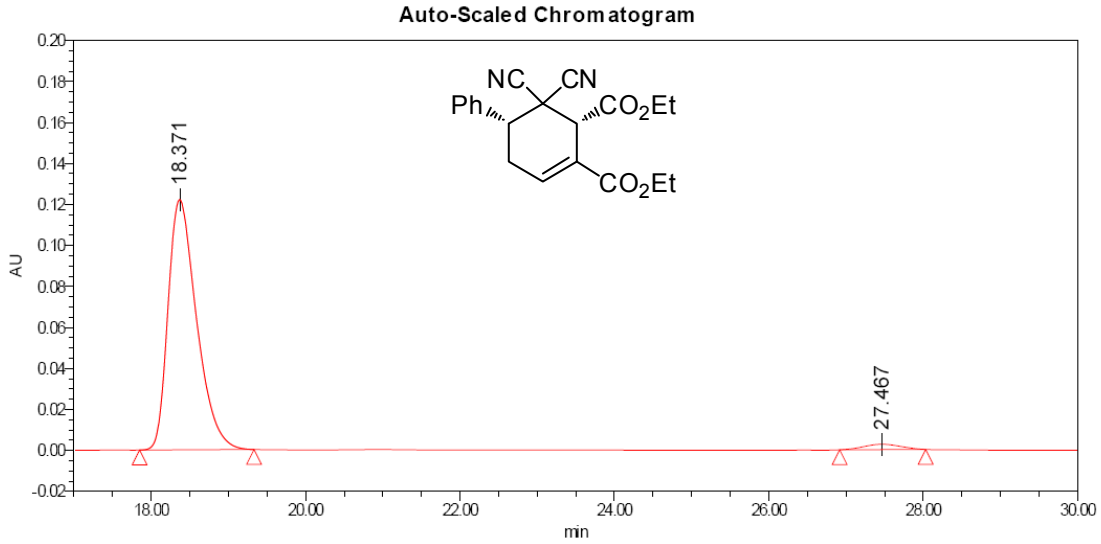






Peak Results

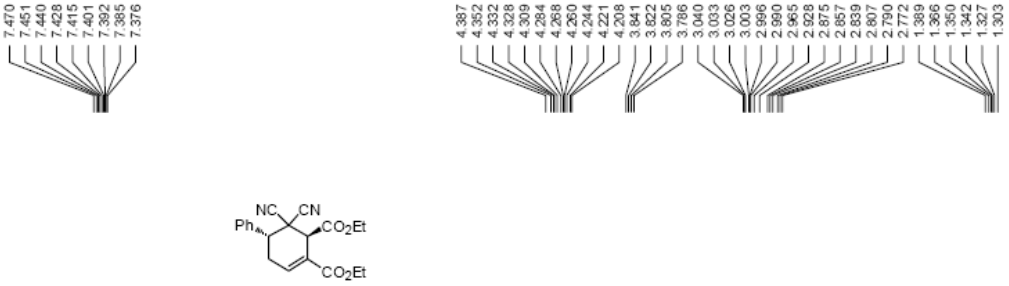
	Name	RT	Area	Height	% Height	% Area
1		18.685	361015	14390	59.80	50.05
2		27.844	360289	9672	40.20	49.95

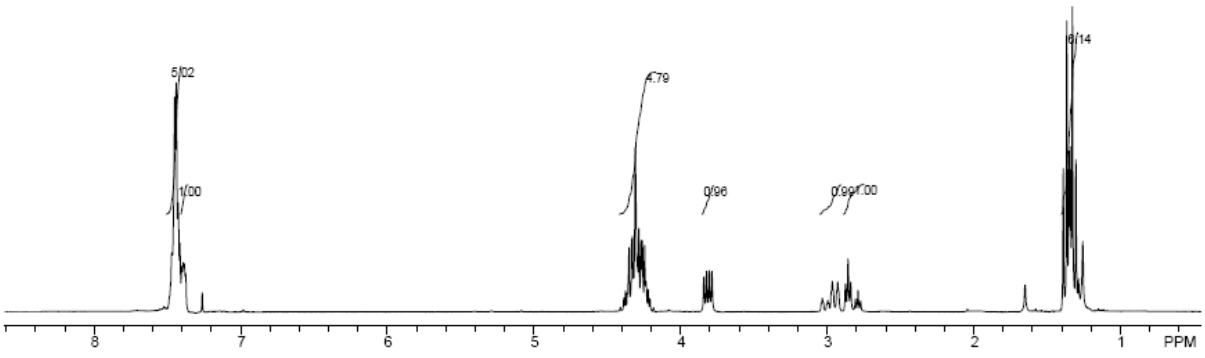


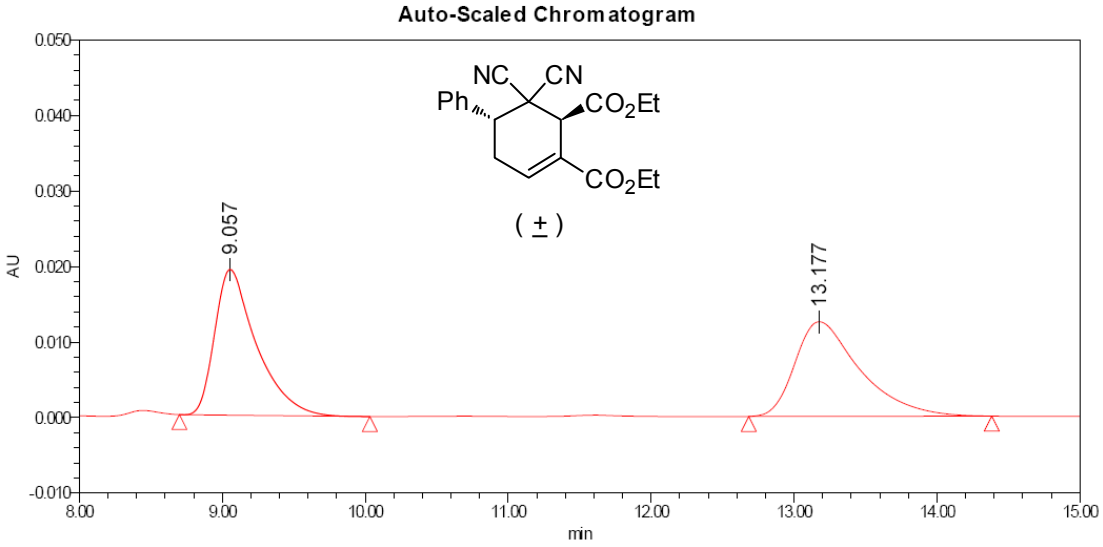
Peak Results

	Name	RT	Area	Height	% Height	% Area
1		18.371	3132376	122125	97.90	97.33
2		27.467	86014	2619	2.10	2.67

(1*R*,3*R*)-diethyl 2,2-dicyano-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3,4-dicarboxylate (S3a')

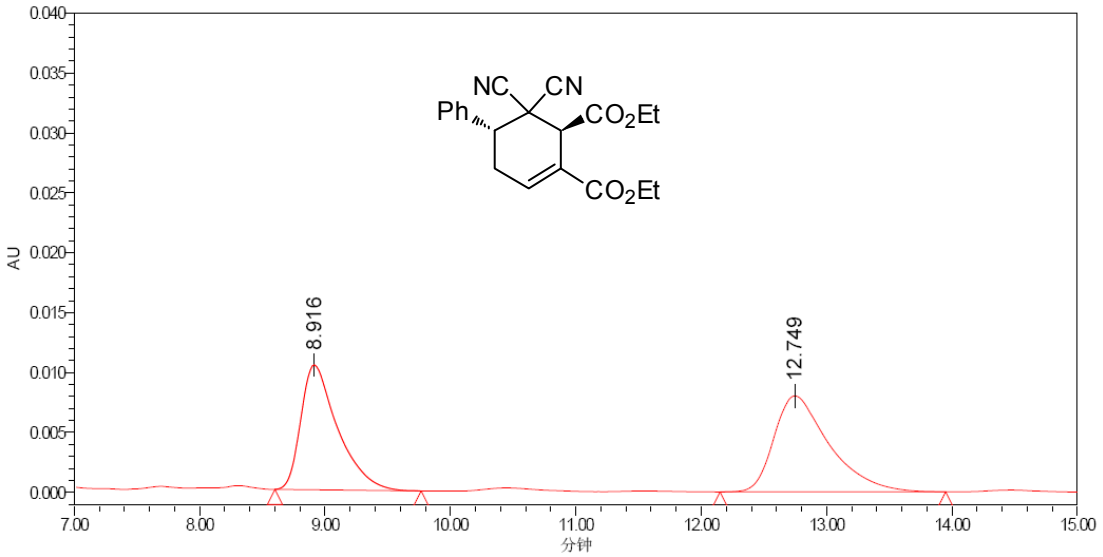






Peak Results

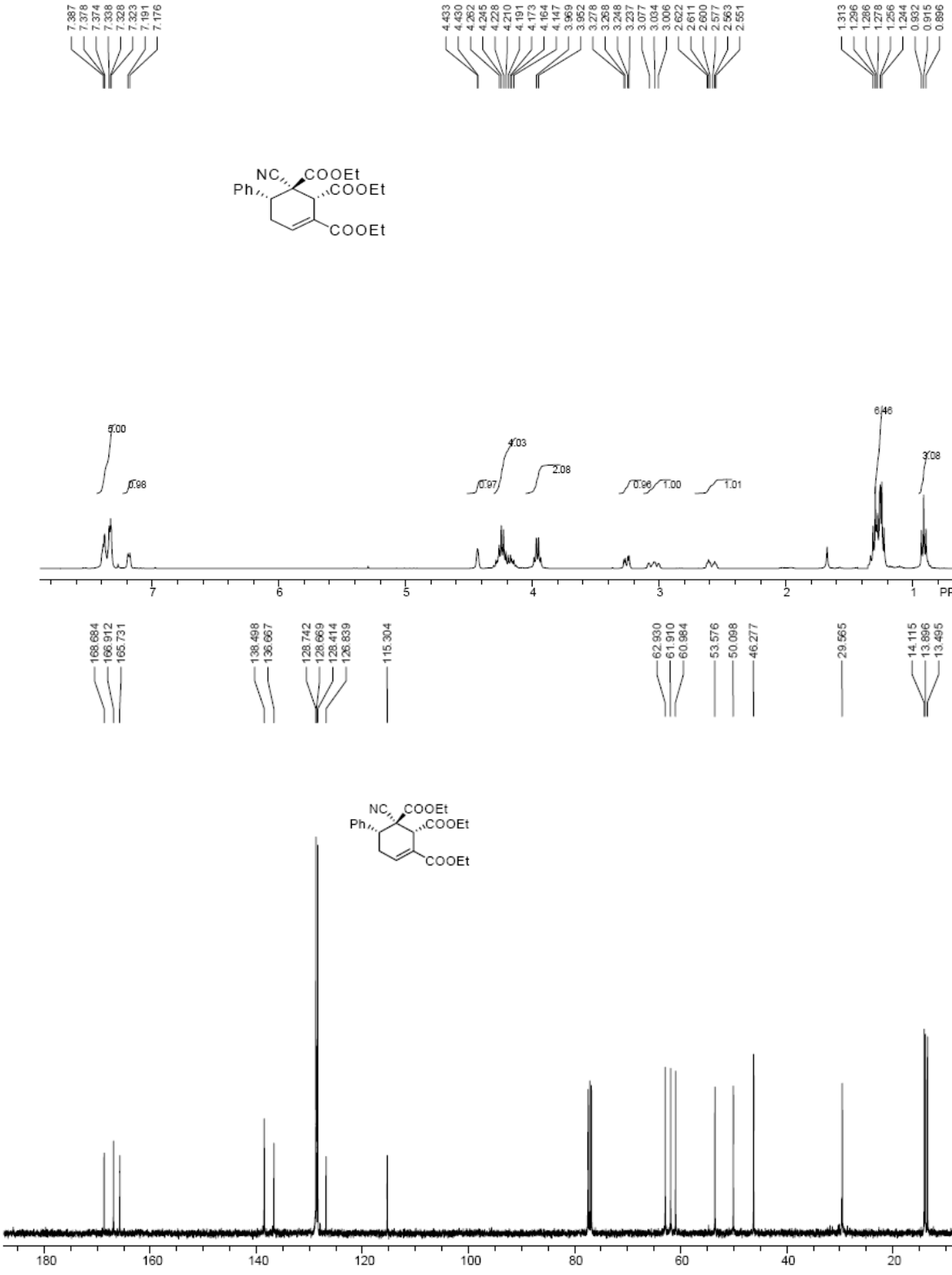
	Name	RT	Area	Height	% Height	% Area
1		9.057	391481	19335	60.68	49.76
2		13.177	395188	12526	39.32	50.24

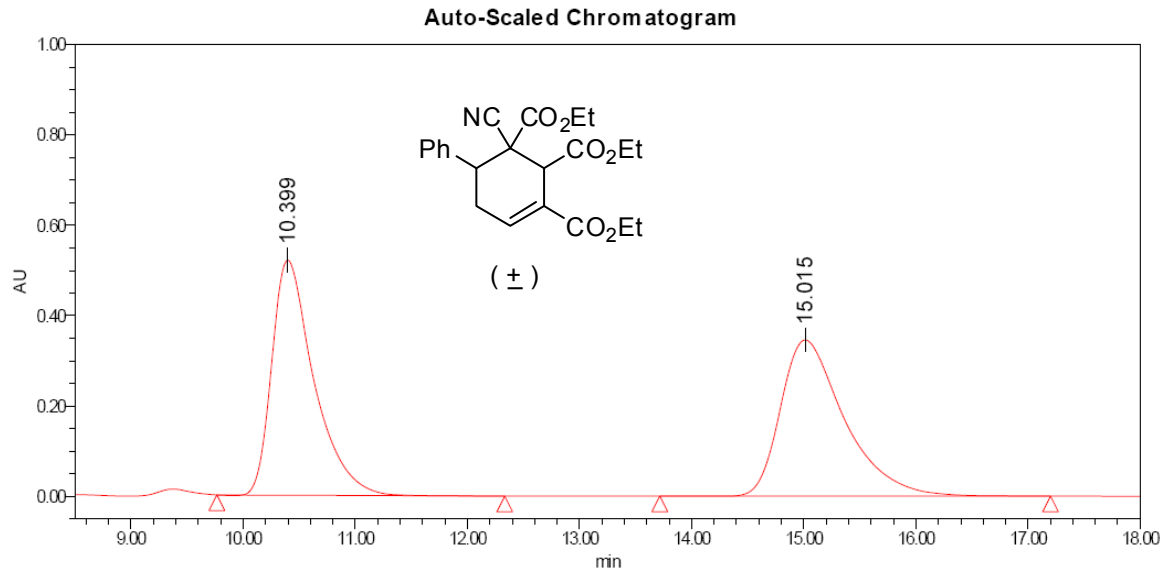


色谱峰结果

	名字	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		8.916	212822	10419	46.50
2		12.749	244881	8017	53.50

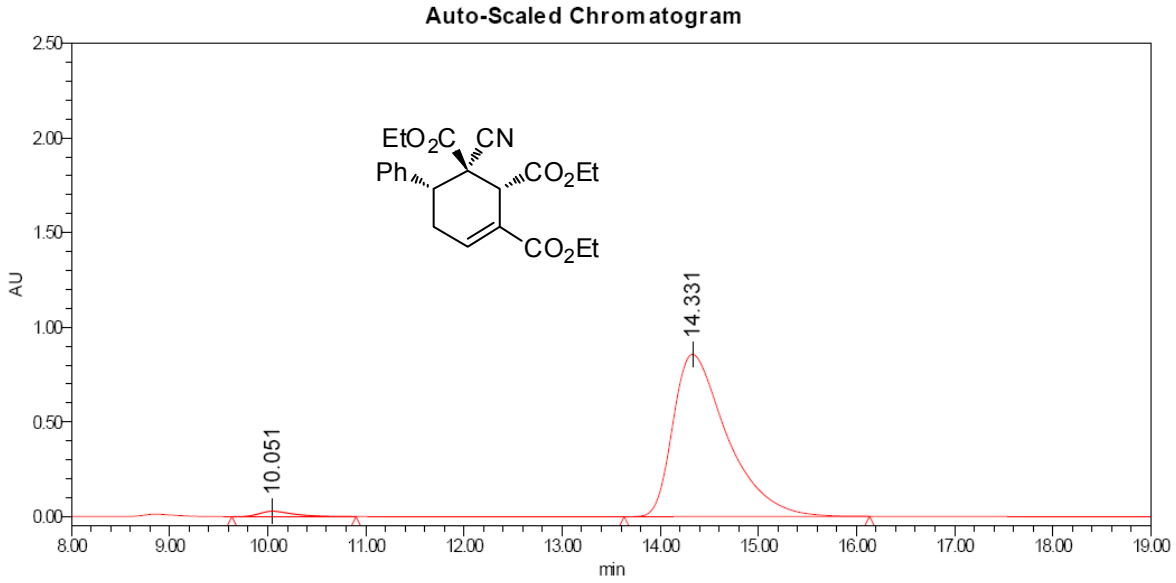
(1*R*,2*R*,3*R*)-triethyl 2-cyano-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2,3,4-tricarboxylate (3a)





Peak Results

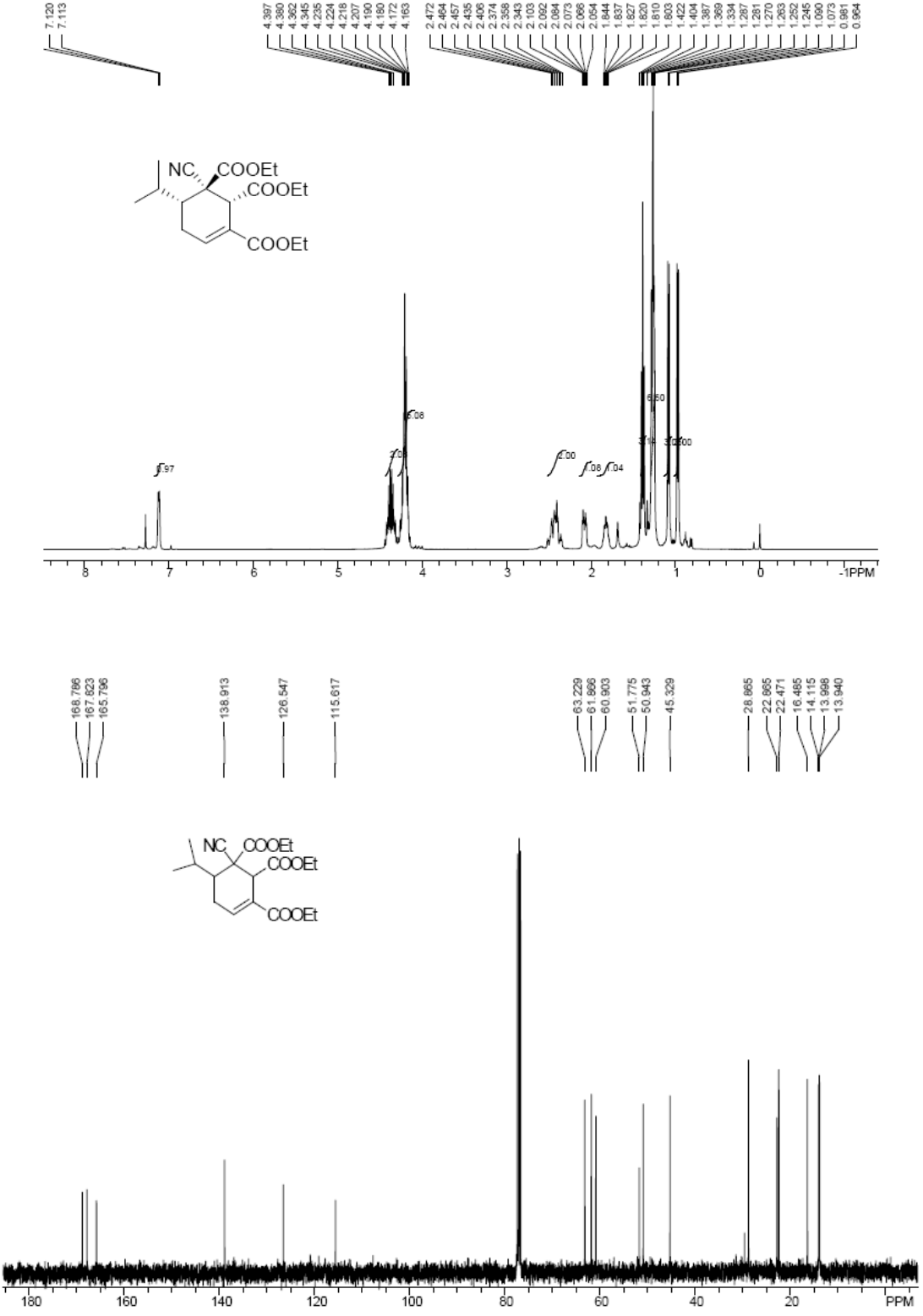
	Name	RT	Area	Height	% Height	% Area
1		10.399	13602097	520362	60.11	49.91
2		15.015	13649203	345274	39.89	50.09

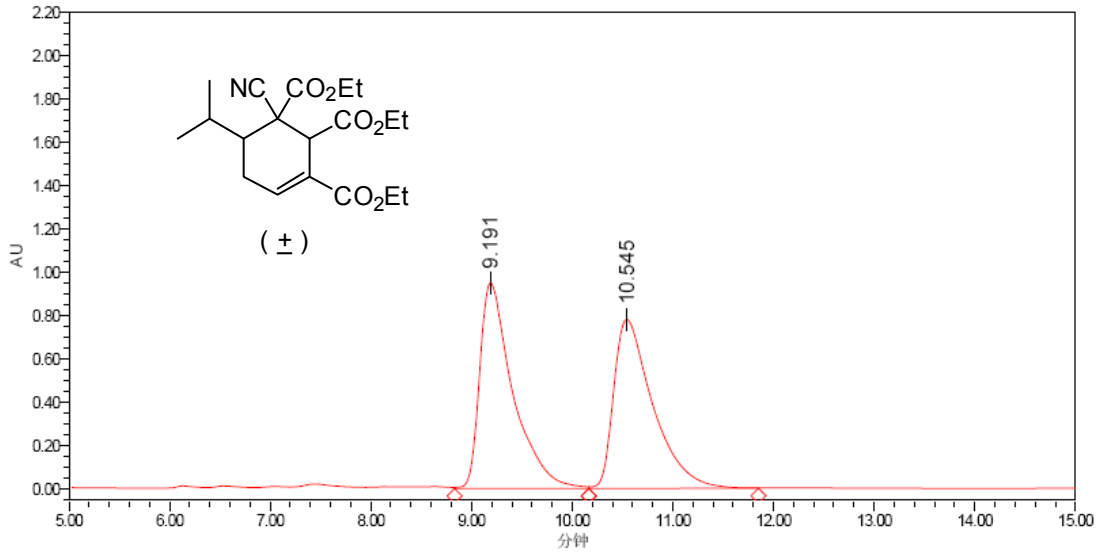


Peak Results

	Name	RT	Area	Height	% Height	% Area
1		10.051	689564	28782	3.25	2.06
2		14.331	32859855	856482	96.75	97.94

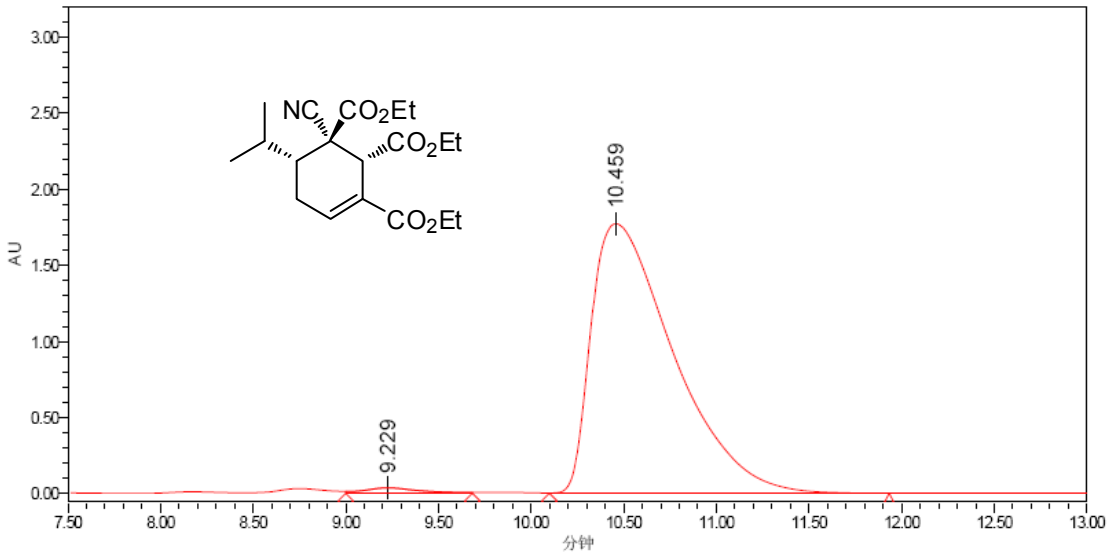
(1*R*,2*R*,6*R*)-triethyl 1-cyano-6-isopropylcyclohex-3-ene-1,2,3-tricarboxylate (3b)





色谱峰结果

	名字	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		9.191	21676381	949686	50.68
2		10.545	21092376	779402	49.32



色谱峰结果

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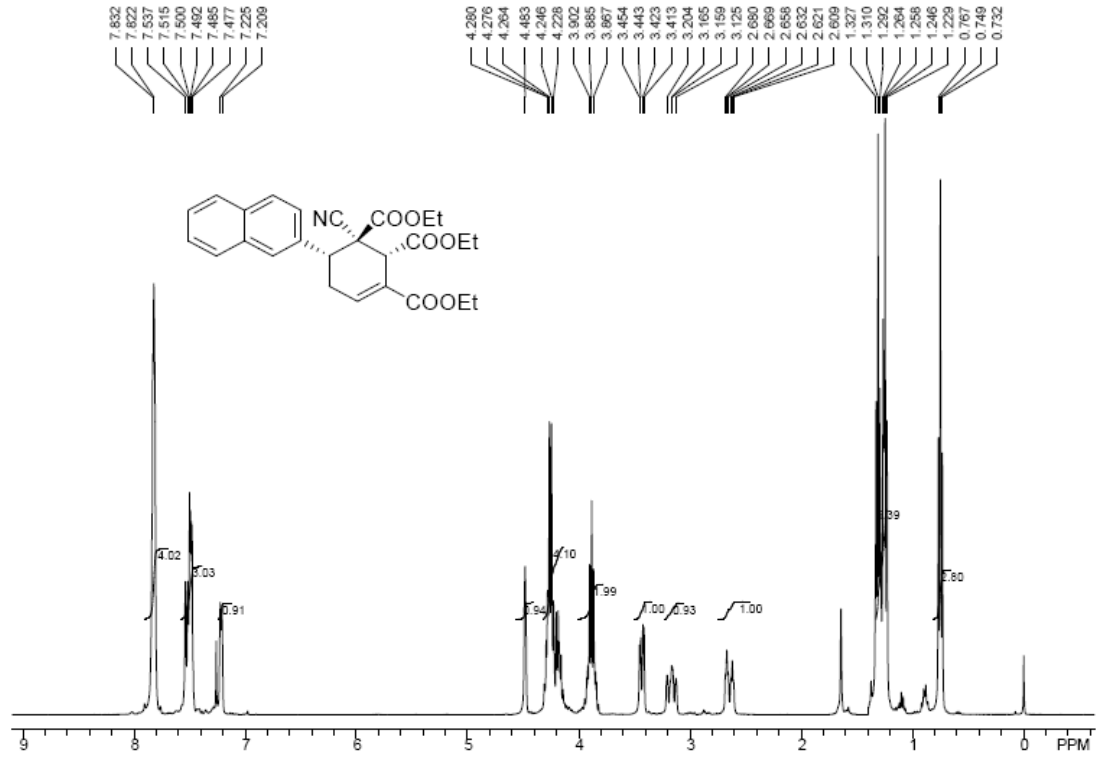
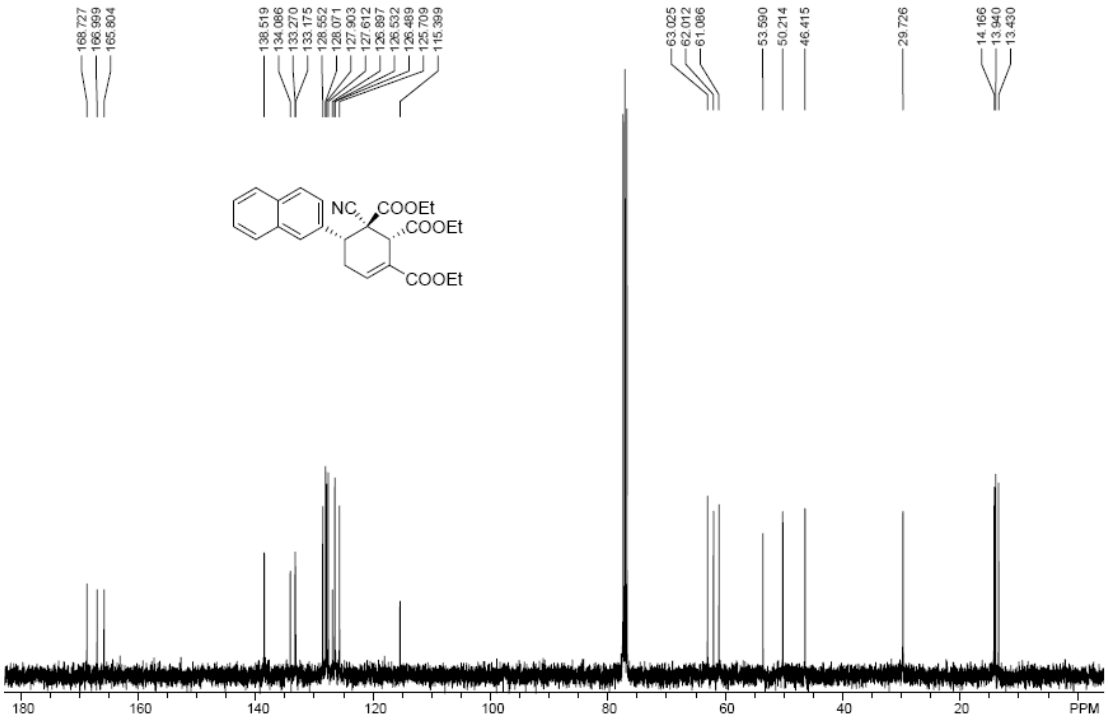
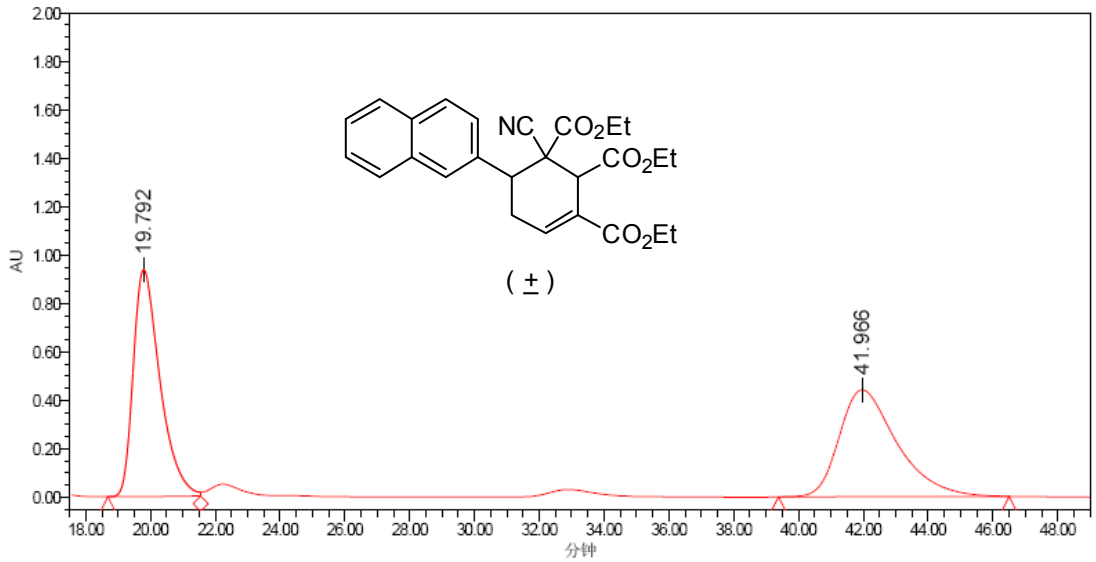
1		9.229	747530	35658	1.35
2		10.459	54583924	1772413	98.65

(1*R*,2*R*,6*R*)-triethyl 1-cyano-6-(naphthalen-2-yl)cyclohex-3-ene-1,2,3-tricarboxylate (3c)

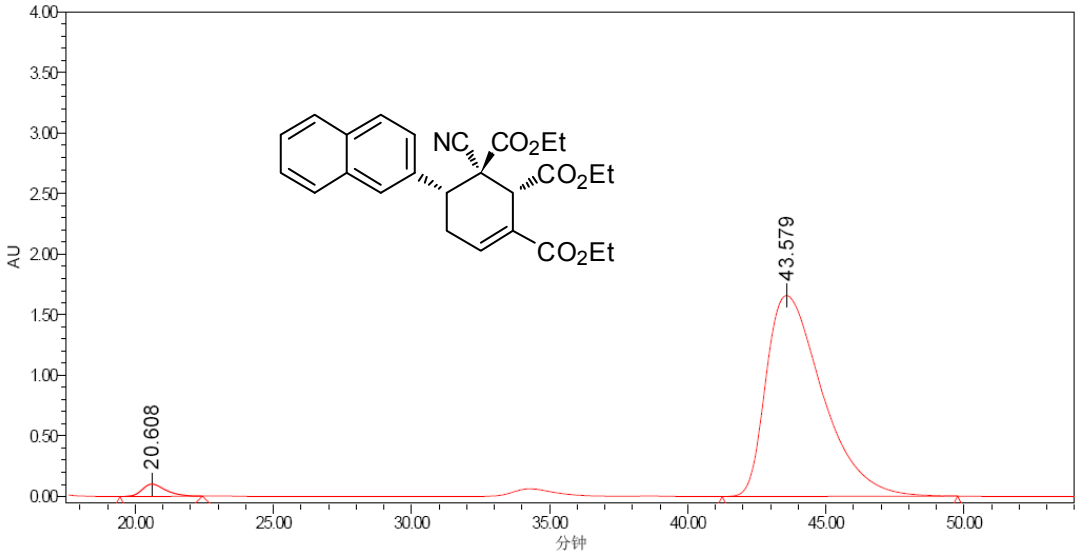






色谱峰结果

	名字	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		19.792	53767881	937386	49.60
2		41.966	54645810	441481	50.40



色谱峰结果

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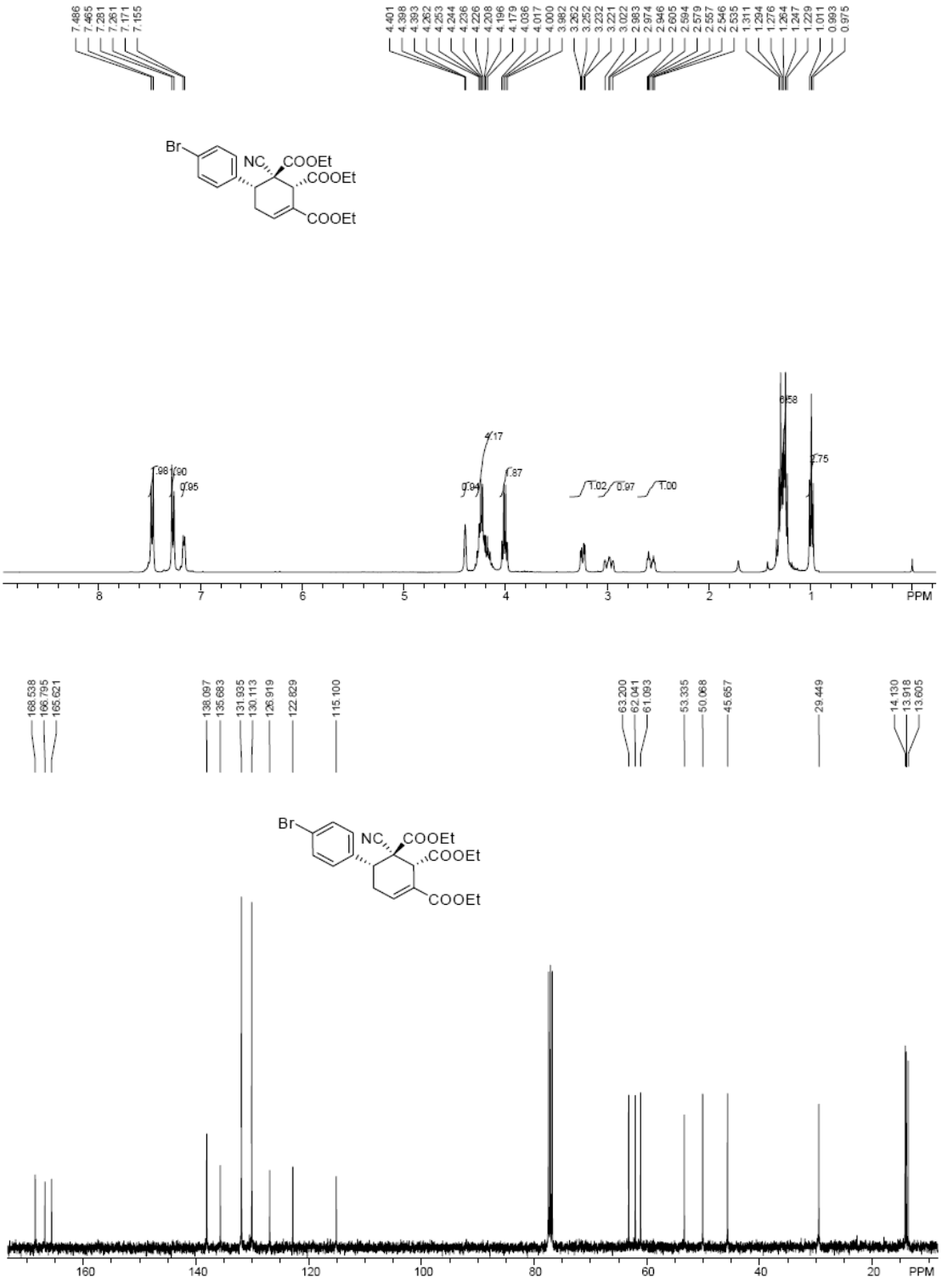
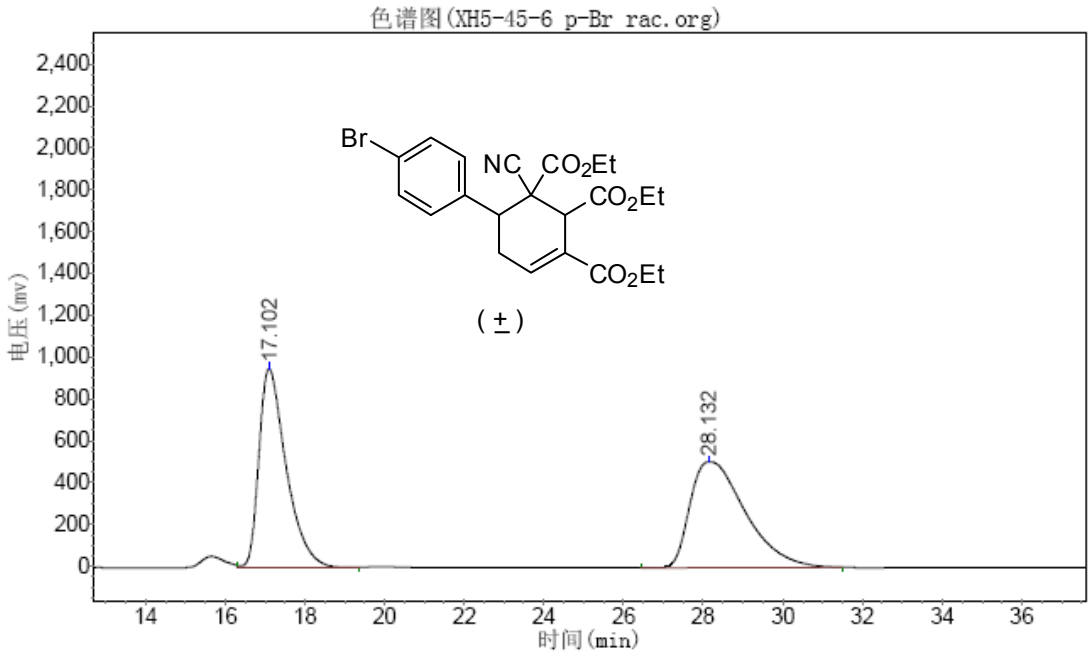
1		20.608	5943755	100432	2.47
2		43.579	234701653	1658442	97.53

(1*R*,2*R*,3*R*)-triethyl 4'-bromo-2-cyano-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2,3,4-tricarboxylate (3d)





峰号	峰名	保留时间	峰高	峰面积	含量
1		17.102	951761.688	45519812.000	48.1816
2		28.132	505564.406	48955760.000	51.8184
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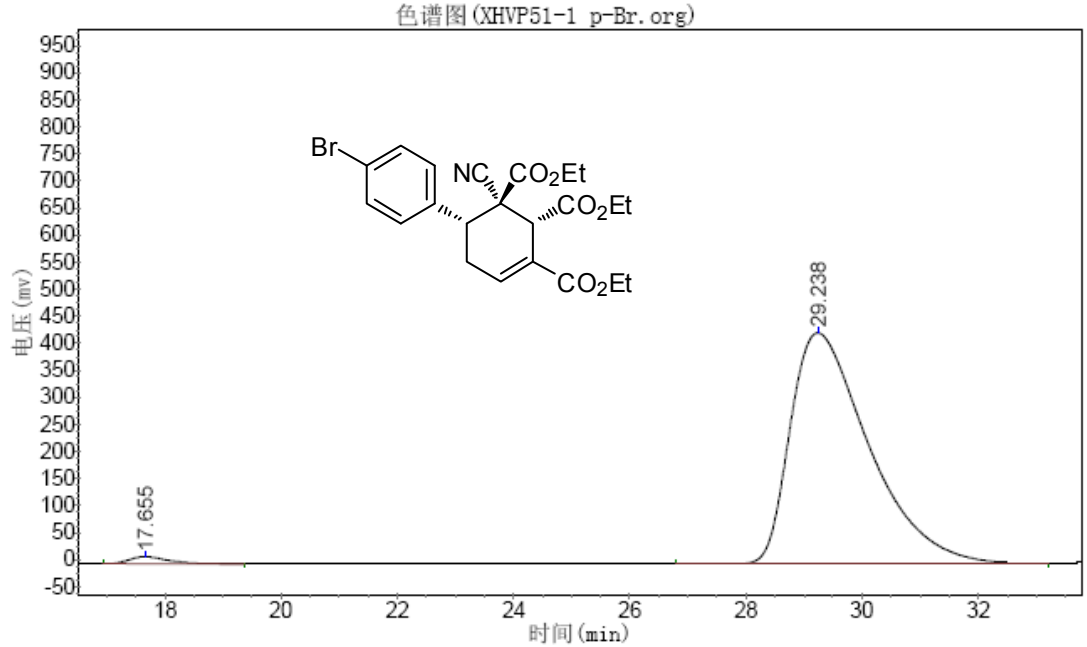

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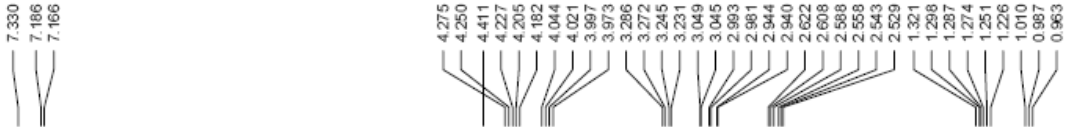
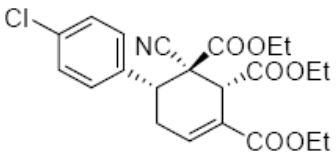
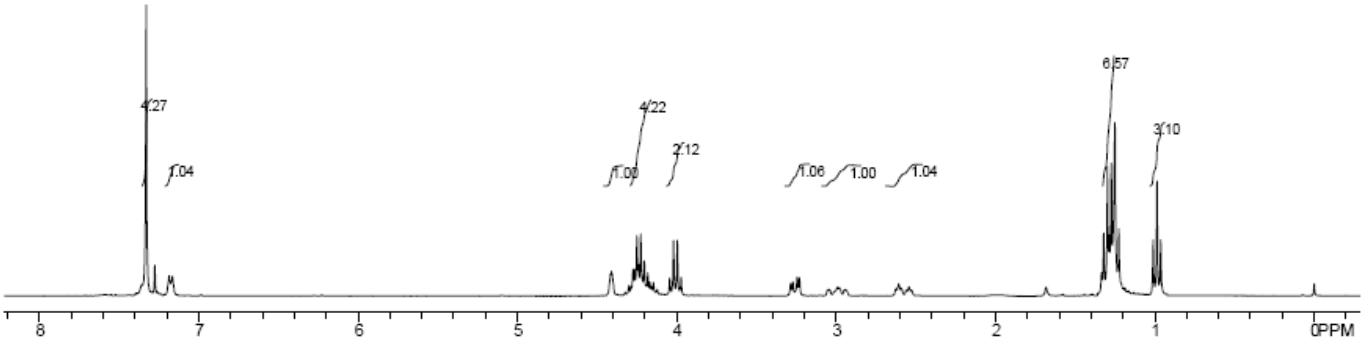
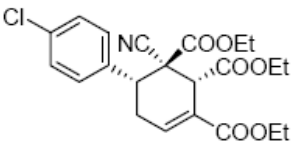
2		29.238	427727.406	40362740.000	98.5989
总计			440331.355	40936304.438	100.0000

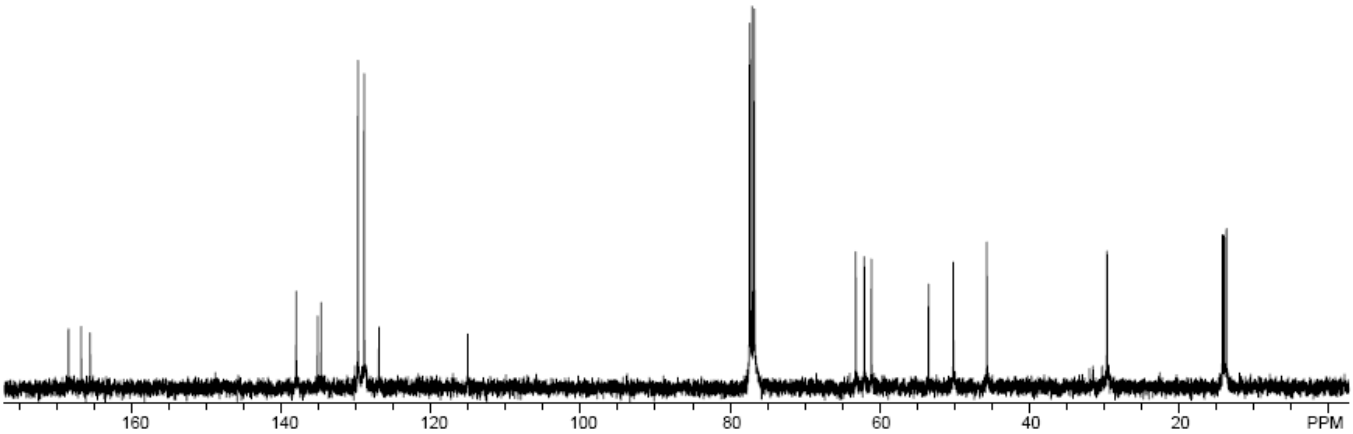
(1*R*,2*R*,3*R*)-triethyl 4'-chloro-2-cyano-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2,3,4-tricarboxylate (3e)

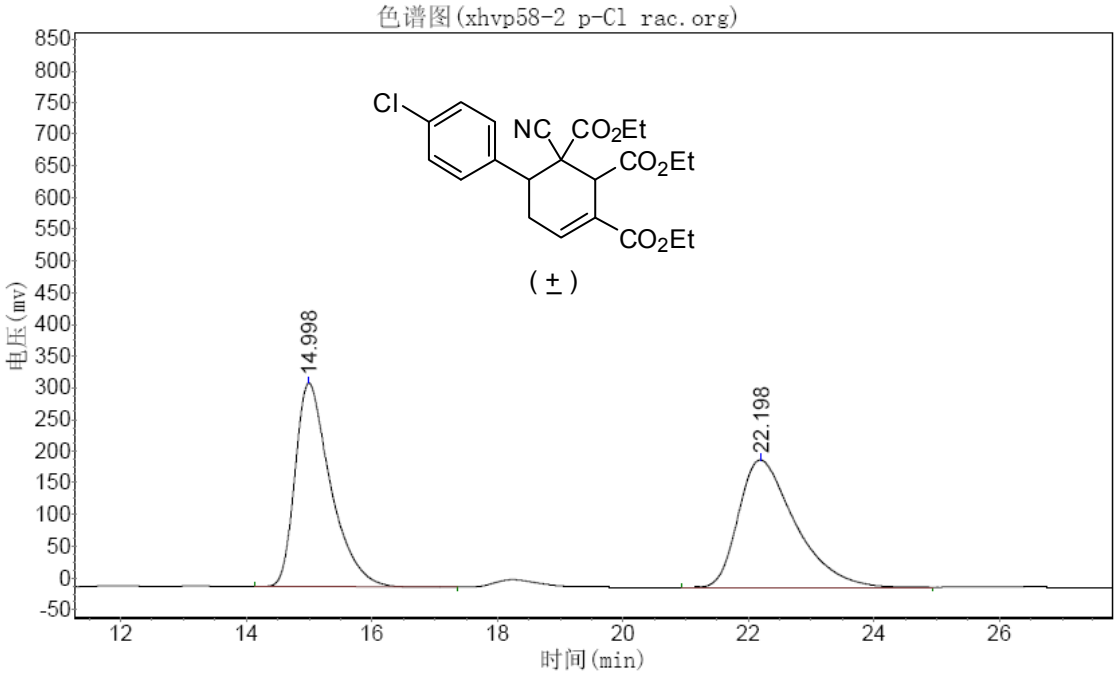






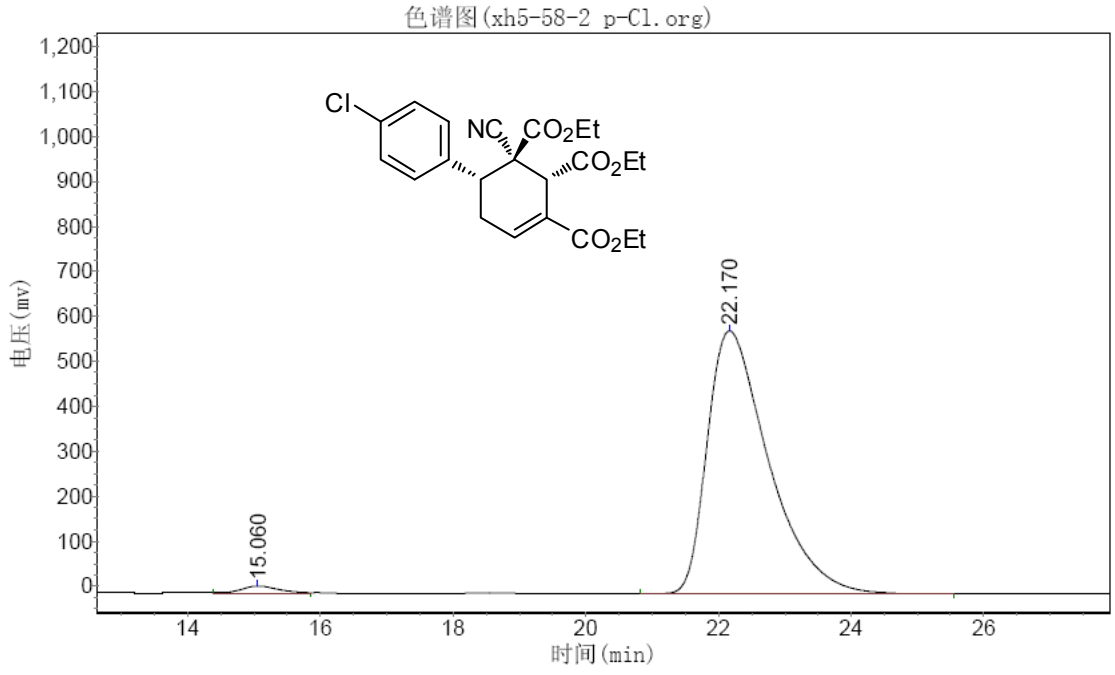






分析结果表

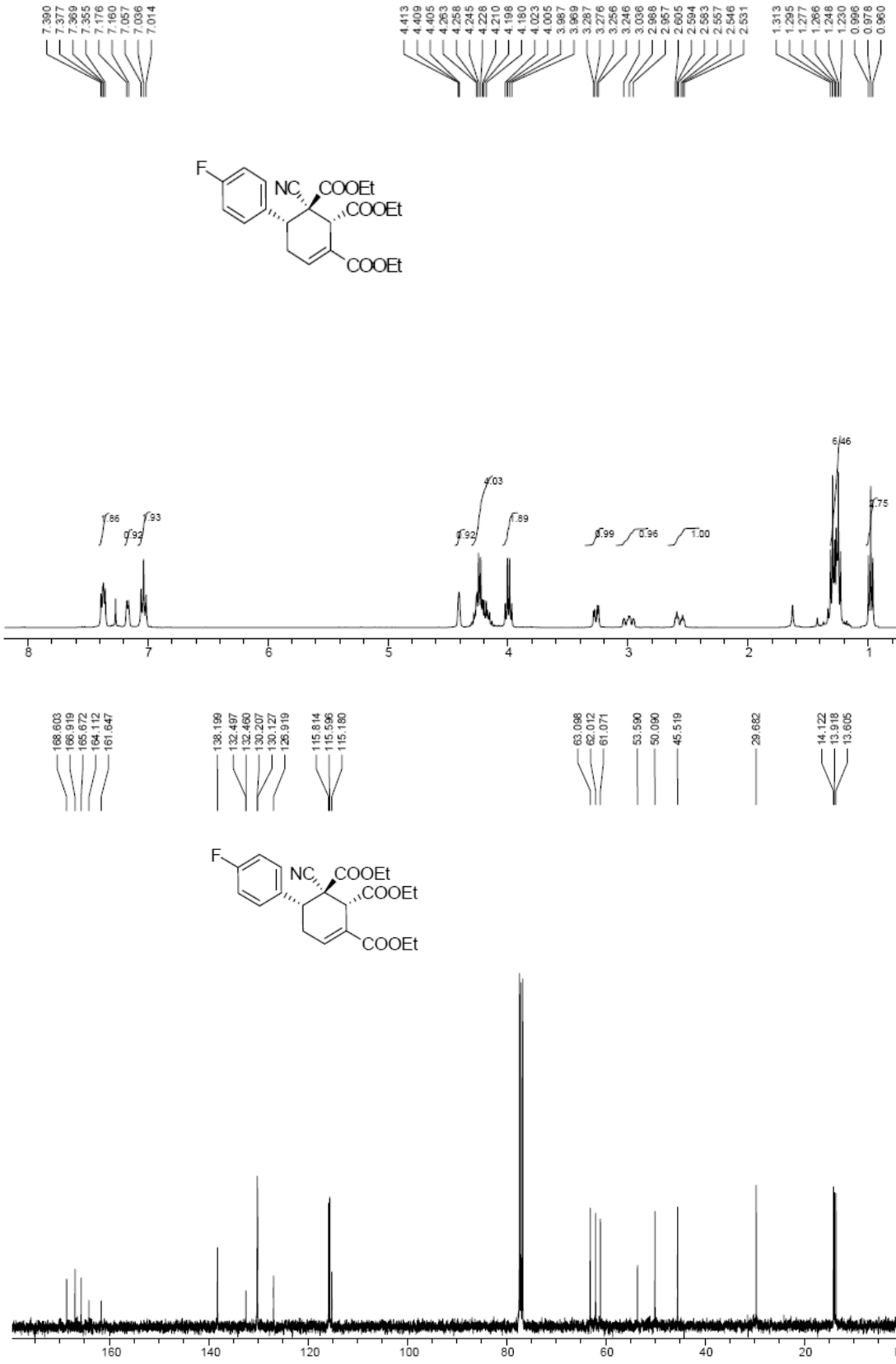
峰号	峰名	保留时间	峰高	峰面积	含量
1		14.998	321086.063	12732046.000	50.0474
2		22.198	200522.141	12707942.000	49.9526
总计			521608.203	25439988.000	100.0000

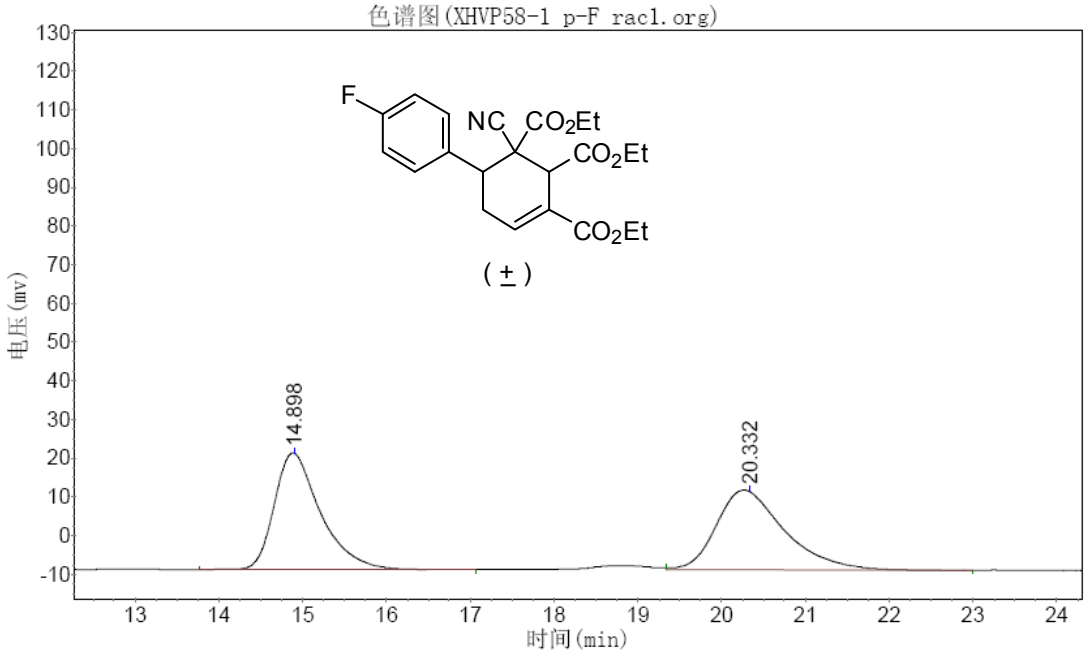


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		15.060	15891.893	603689.250	1.5862
2		22.170	584415.375	37454872.000	98.4138
总计			600307.268	38058561.250	100.0000

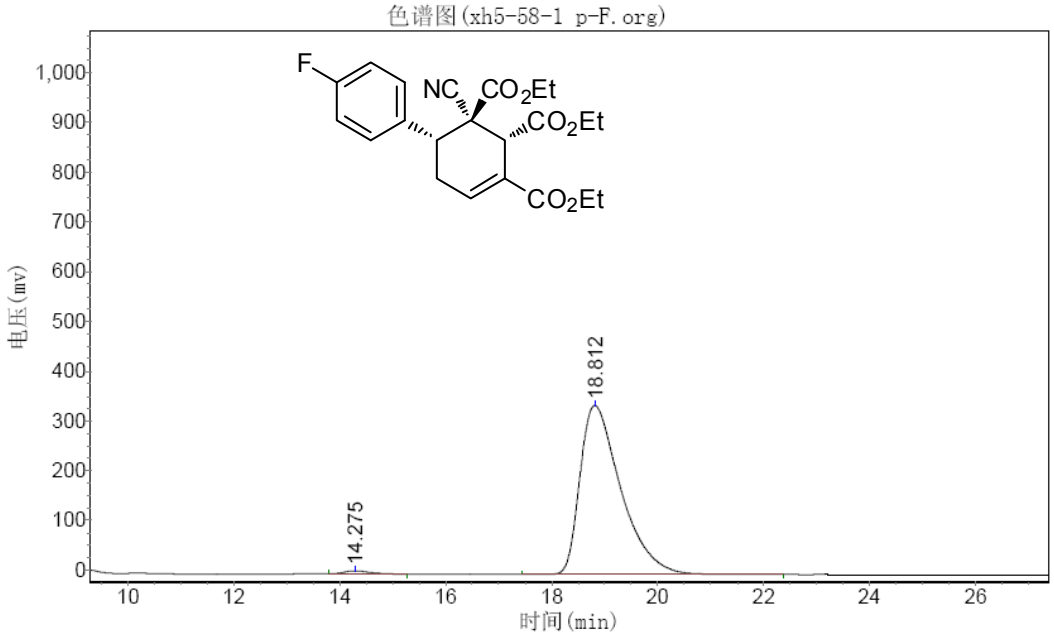
(1*R*,2*R*,3*R*)-triethyl 2-cyano-4'-fluoro-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2,3,4-tricarboxylate (3f)





分析结果表

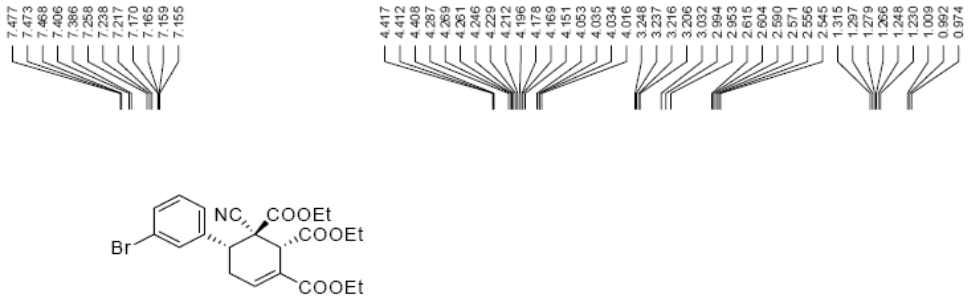
峰号	峰名	保留时间	峰高	峰面积	含量
1		14.898	30169.730	1168469.250	49.6863
2		20.332	20596.578	1183223.125	50.3137
总计			50766.309	2351692.375	100.0000

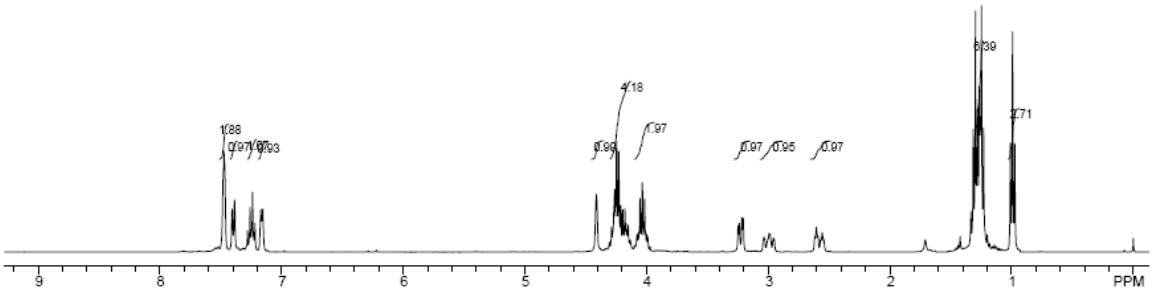


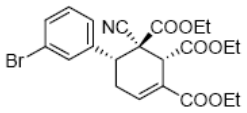
分析结果表

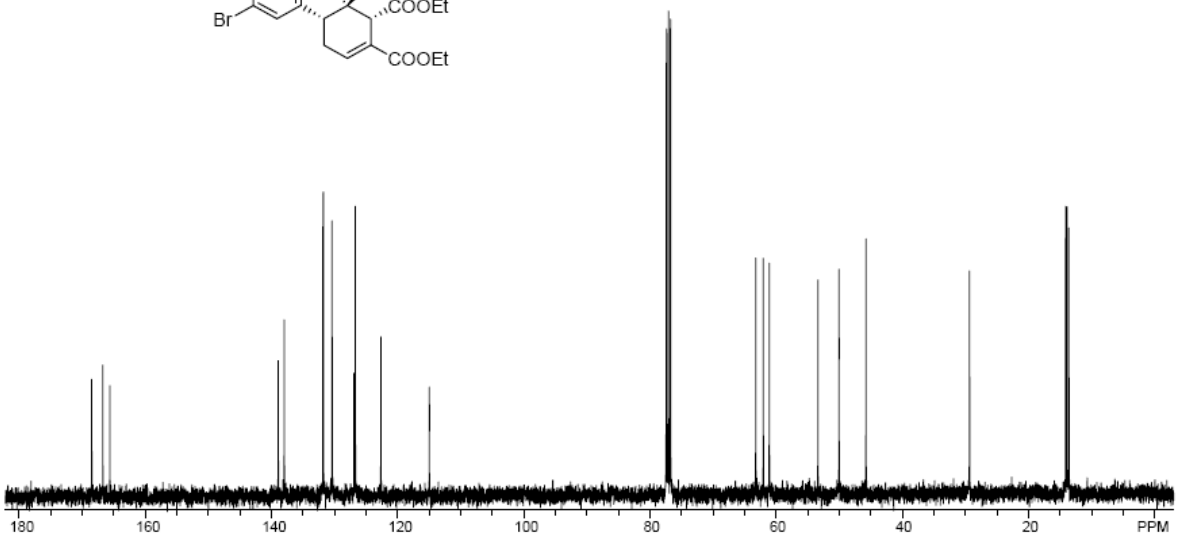
峰号	峰名	保留时间	峰高	峰面积	含量
1		14.275	6682.639	234408.281	1.2745
2		18.812	339601.813	18157046.000	98.7254
总计			346284.452	18391454.281	100.0000

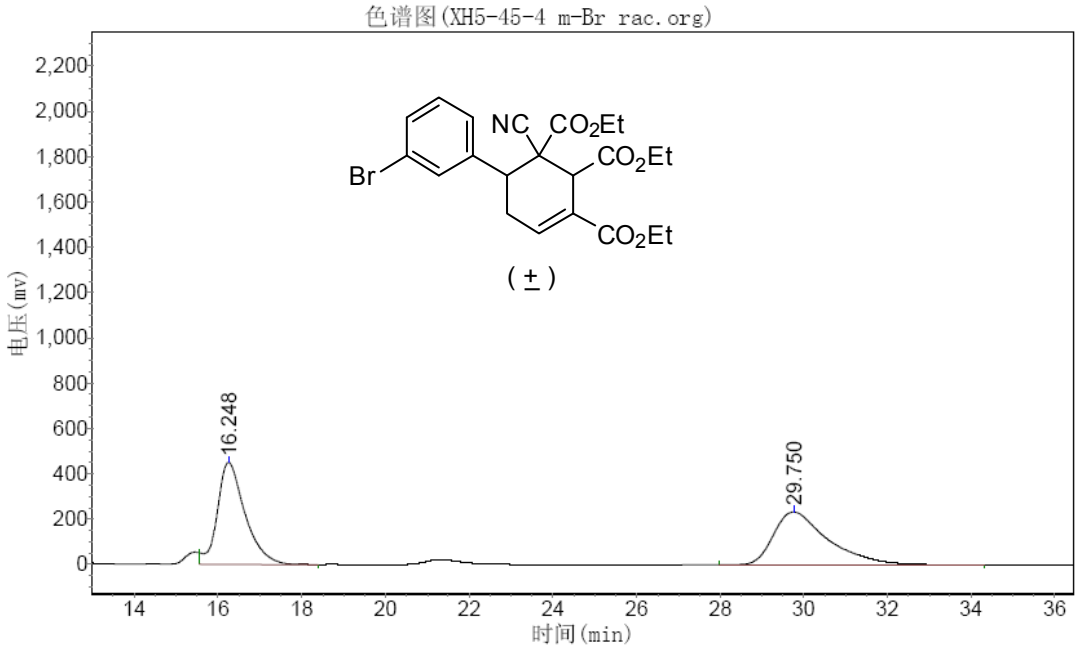
(1*R*,2*R*,3*R*)-triethyl 3'-bromo-2-cyano-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2,3,4-tricarboxylate (3g)





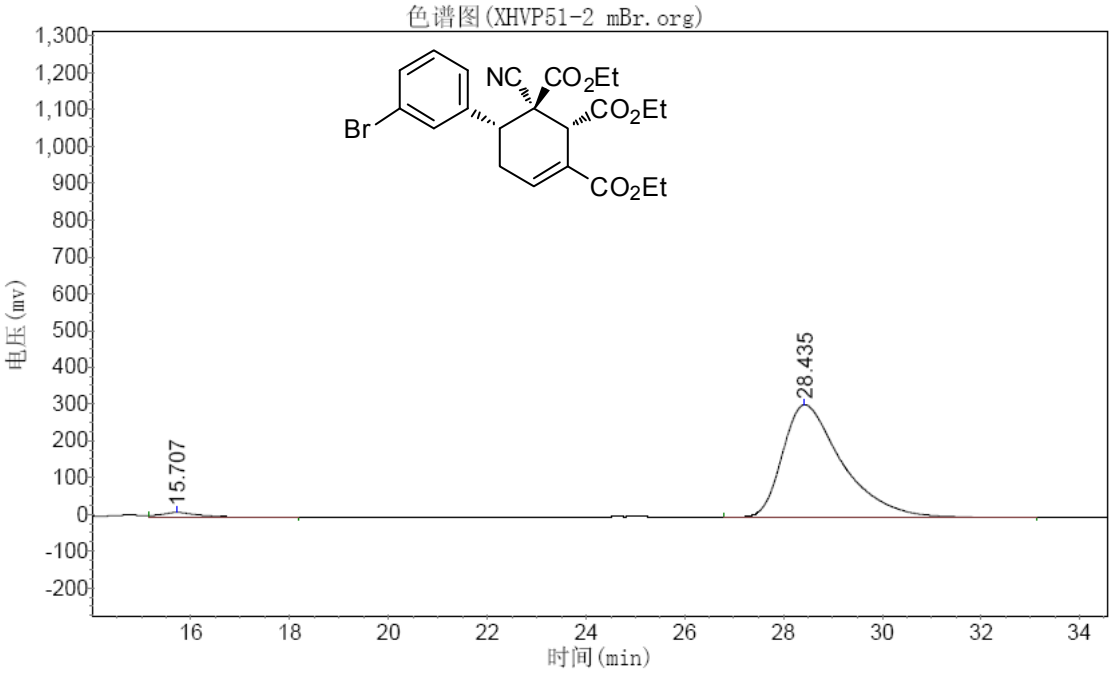






分析结果表

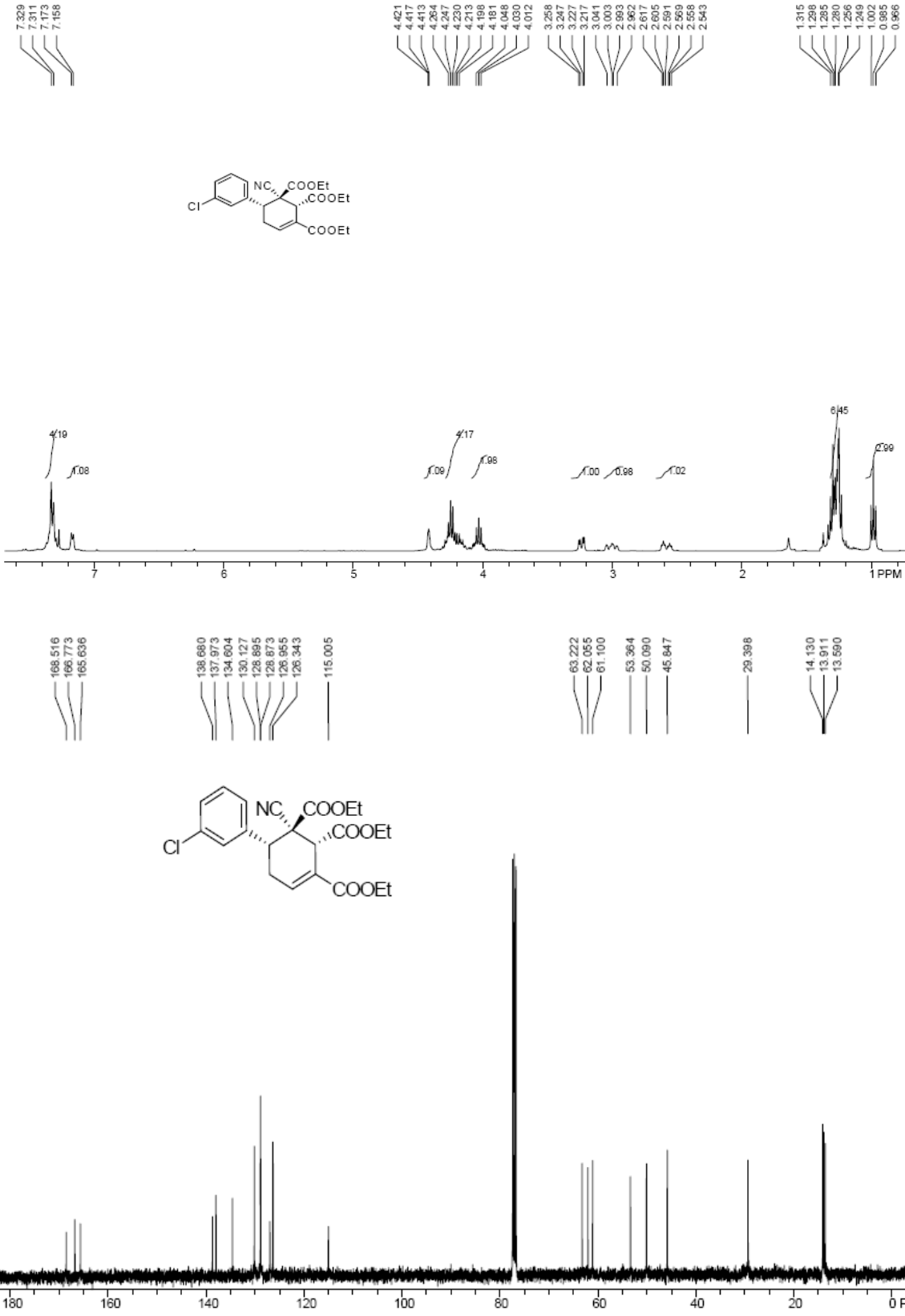
峰号	峰名	保留时间	峰高	峰面积	含量
1		16.248	449646.125	20645268.000	49.3775
2		29.750	234298.875	21165786.000	50.6225
总计			683945.000	41811054.000	100.0000

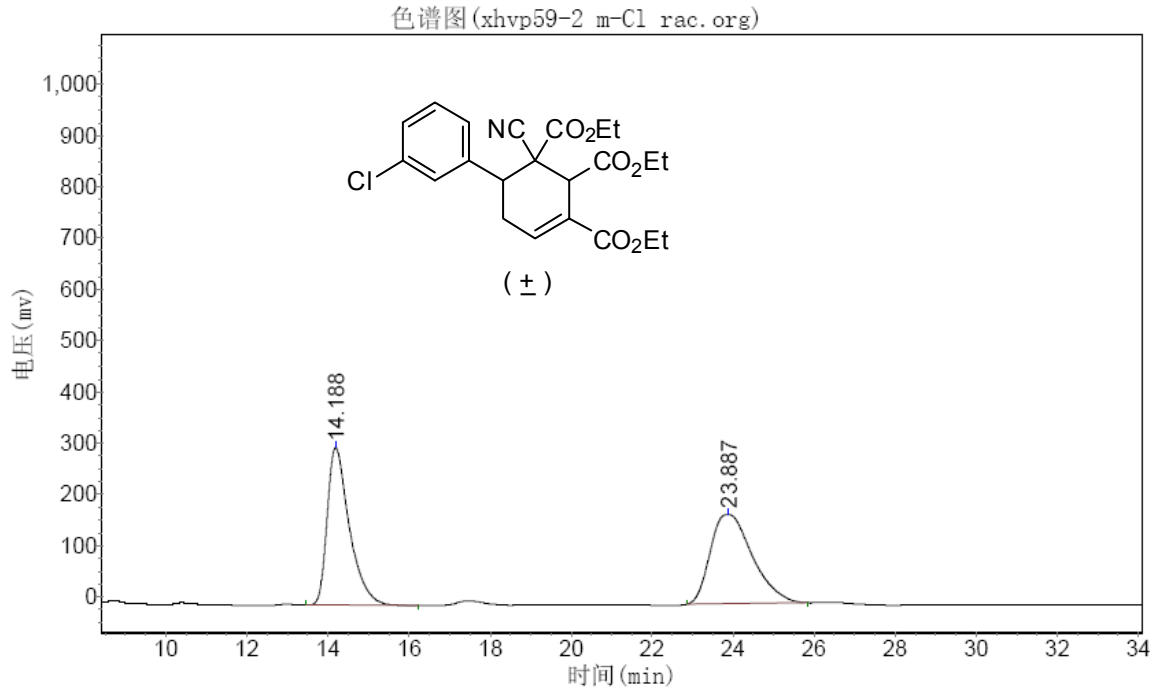


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		15.707	12830.537	659997.938	2.5324
2		28.435	304714.406	25402404.000	97.4676
总计			317544.943	26062401.938	100.0000

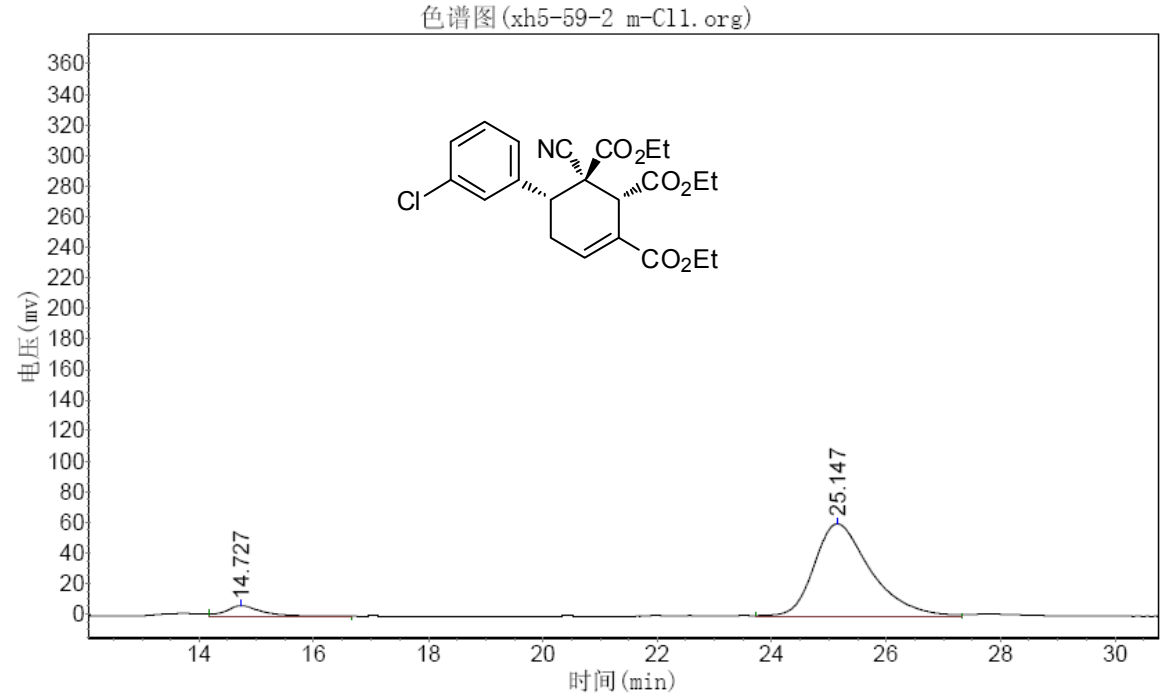
(1*R*,2*R*,3*R*)-triethyl 3'-chloro-2-cyano-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2,3,4-tricarboxylate (3h)





分析结果表

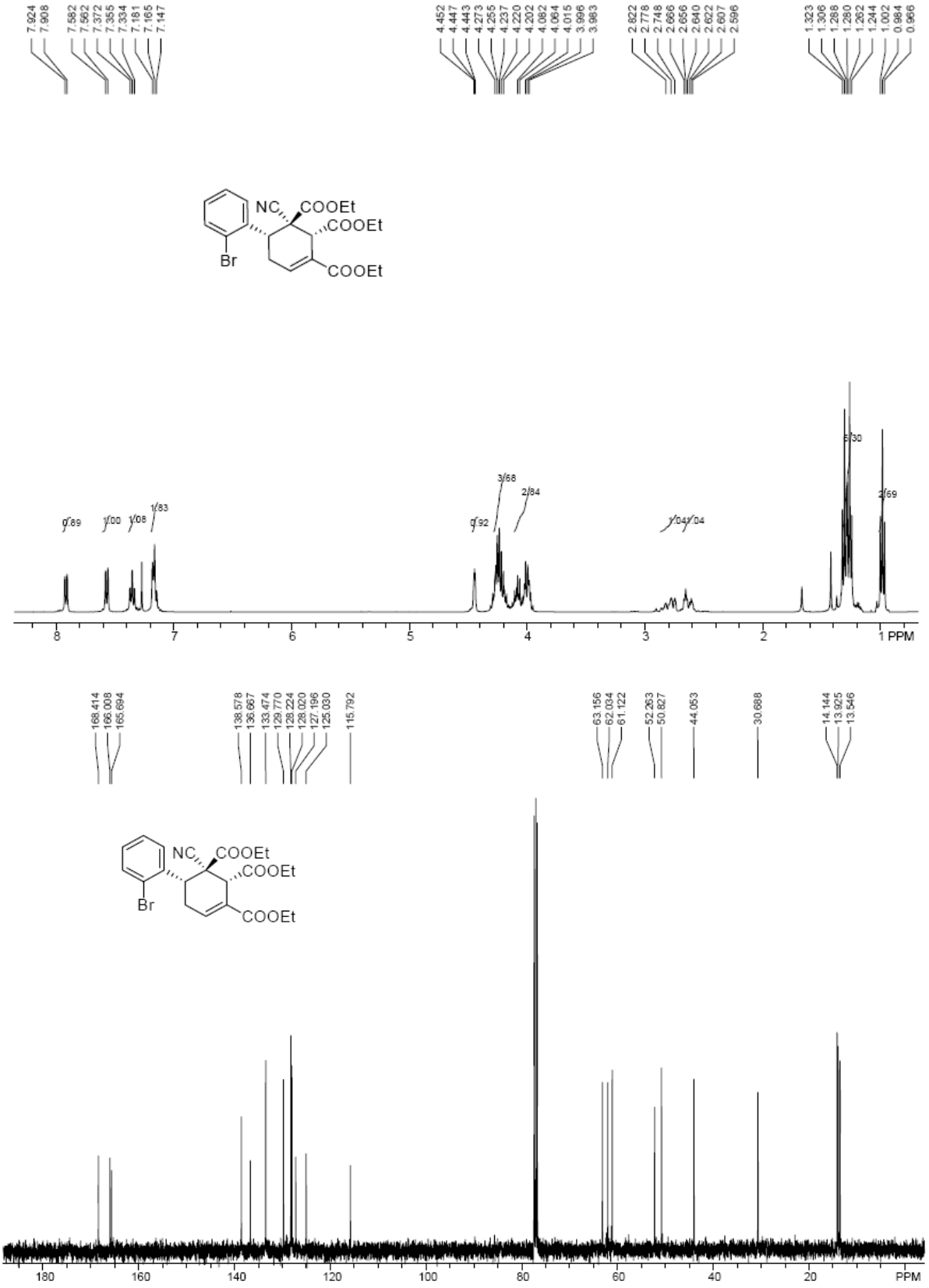
峰号	峰名	保留时间	峰高	峰面积	含量
1		14.188	307867.063	11684887.000	48.1897
2		23.887	174418.469	12562817.000	51.8103
总计			482285.531	24247704.000	100.0000

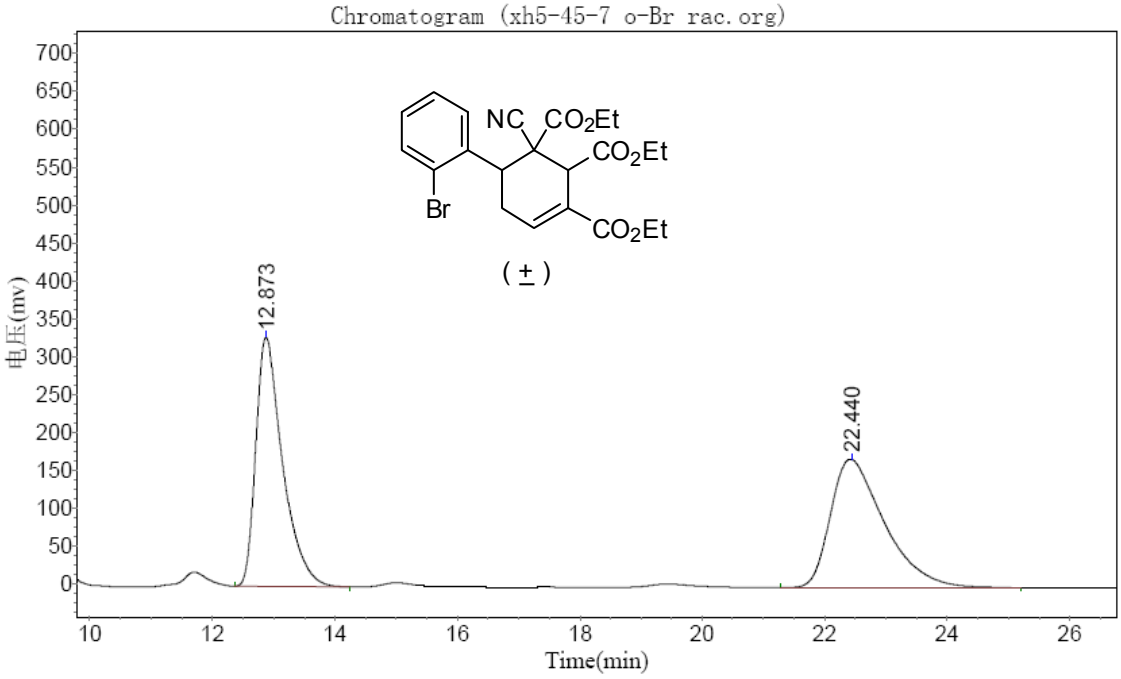


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		14.727	6751.718	292922.406	6.6639
2		25.147	60242.348	4102736.250	93.3361
总计			66994.066	4395658.656	100.0000

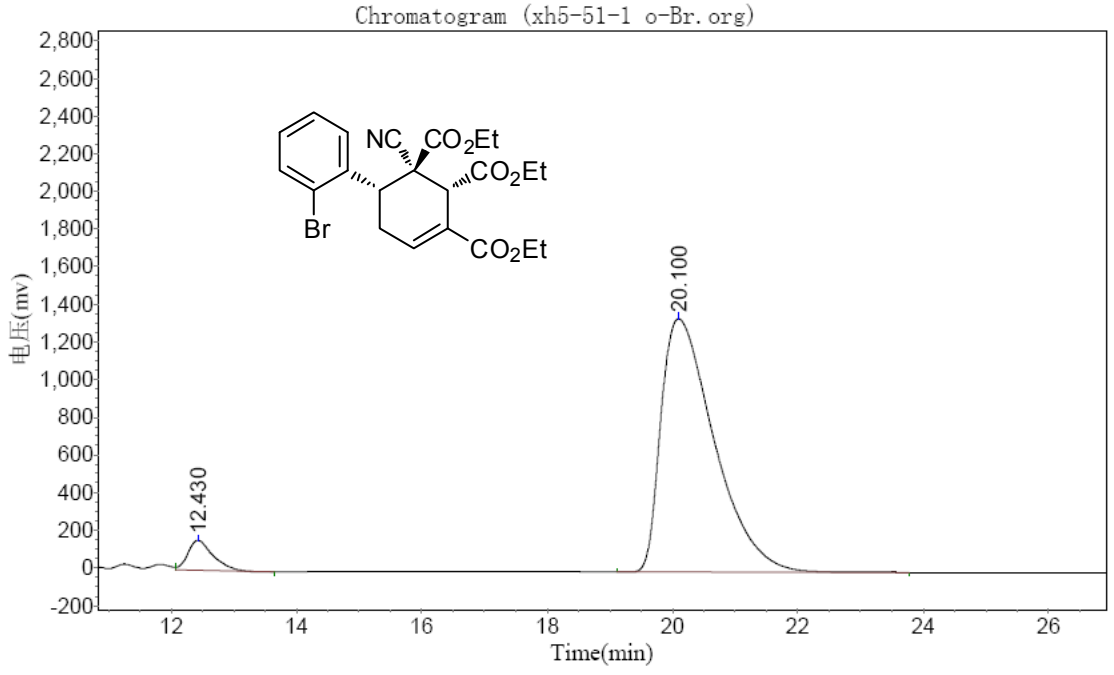
(1*S*,2*R*,3*R*)-triethyl 2'-bromo-2-cyano-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2,3,4-tricarboxylate (3i)





Results

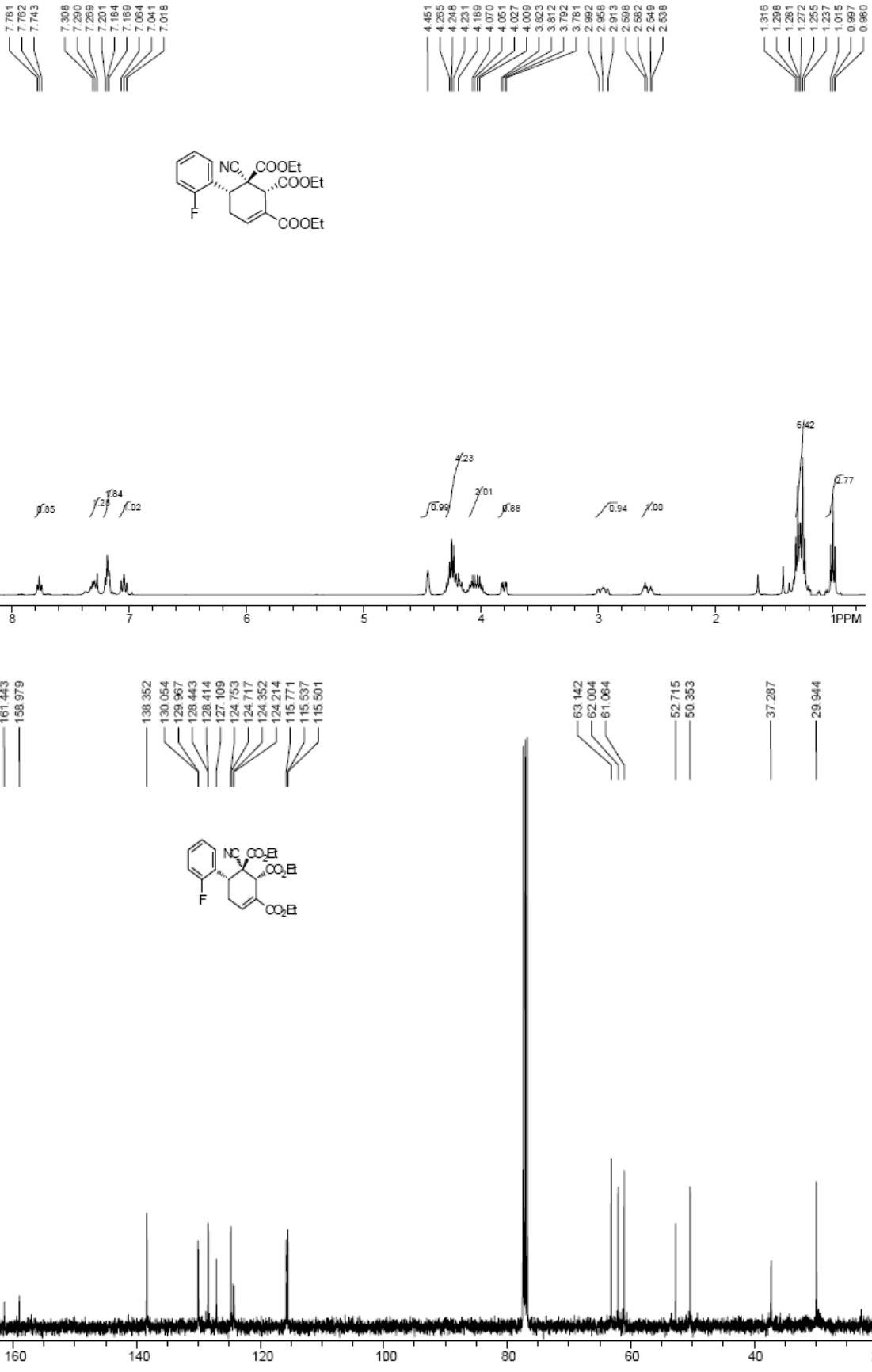
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.873	328444.938	10127977.000	49.4888
2		22.440	169349.109	10337229.000	50.5112
Total			497794.047	20465206.000	100.0000

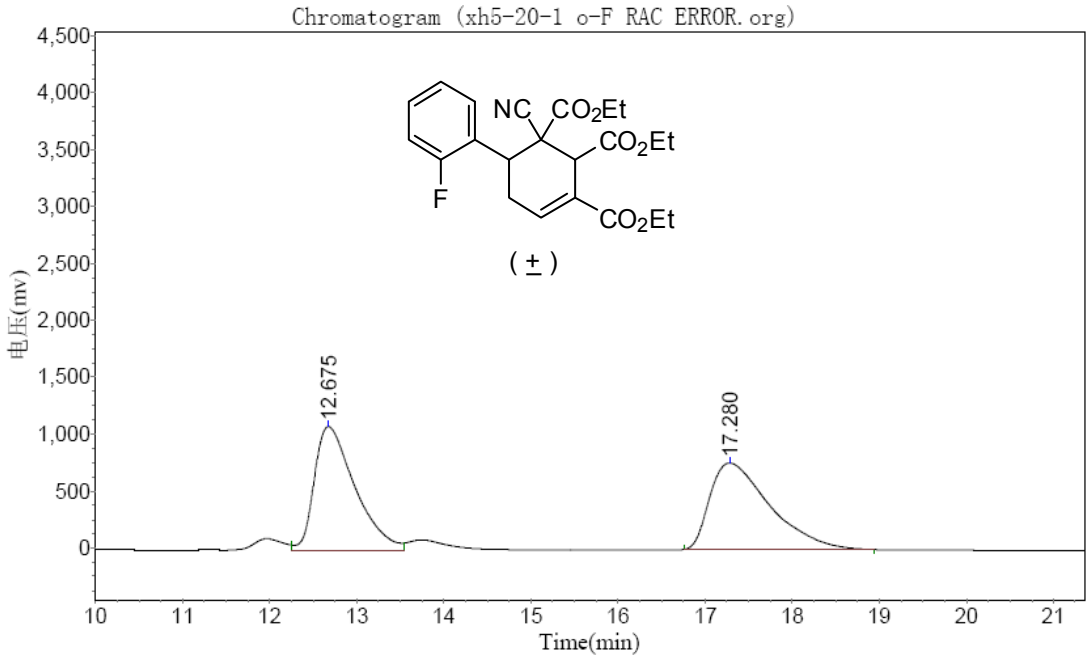


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.430	159640.094	4497643.500	5.3562
2		20.100	1346783.625	79473272.000	94.6438
Total			1506423.719	83970915.500	100.0000

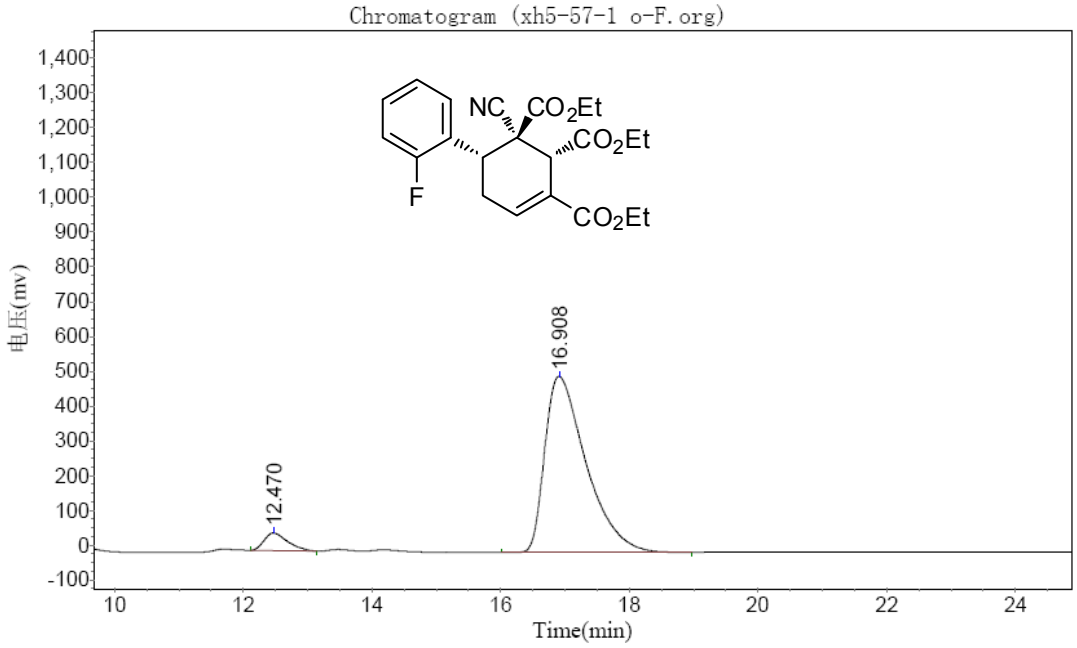
(1*S*,2*R*,3R)-triethyl 2-cyano-2'-fluoro-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2,3,4-tricarboxylate (3j)





Results

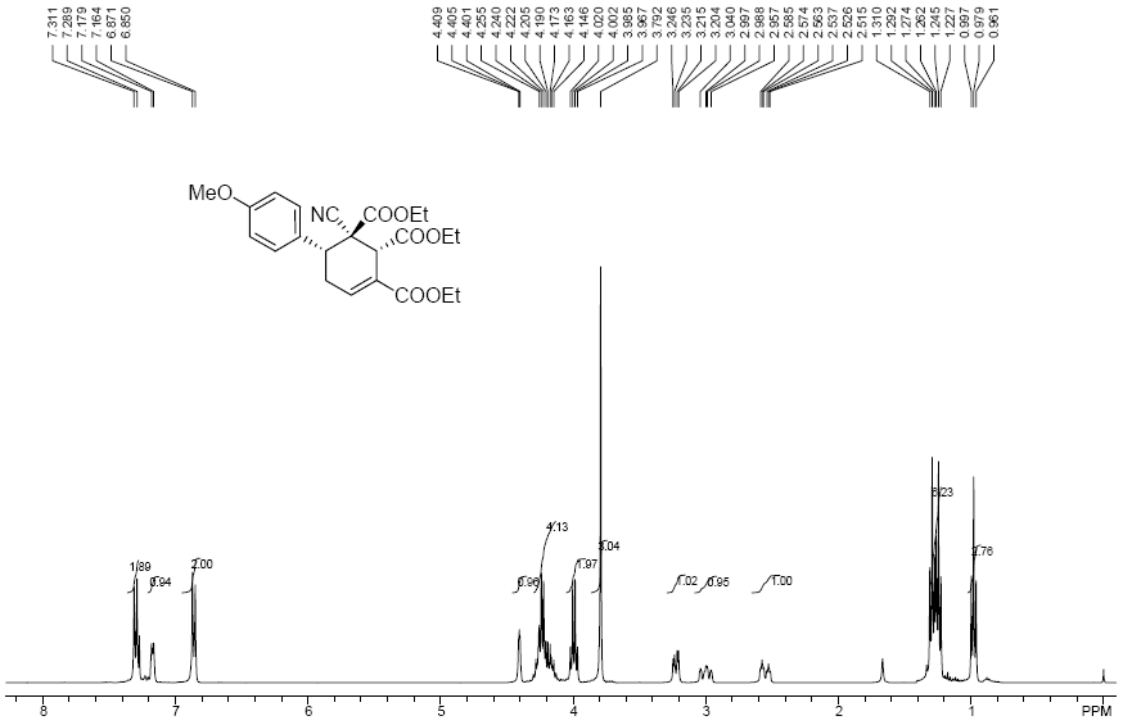
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.675	1082474.875	34906236.000	49.0885
2		17.280	758087.063	36202608.000	50.9115
Total			1840561.938	71108844.000	100.0000

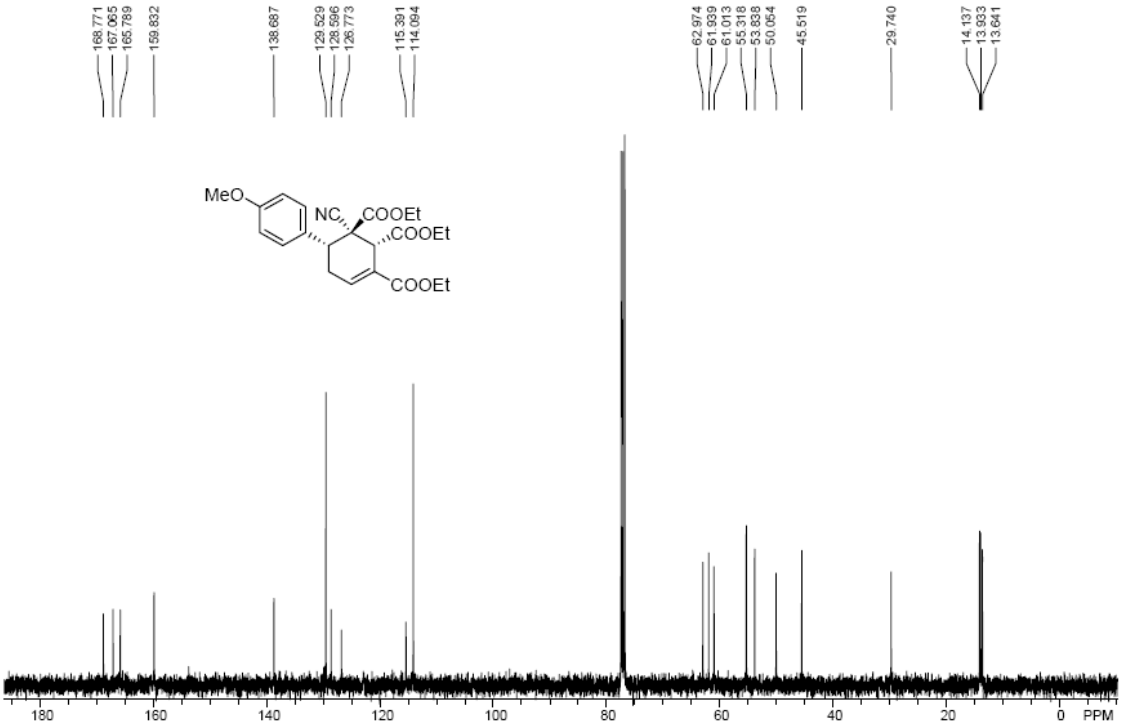


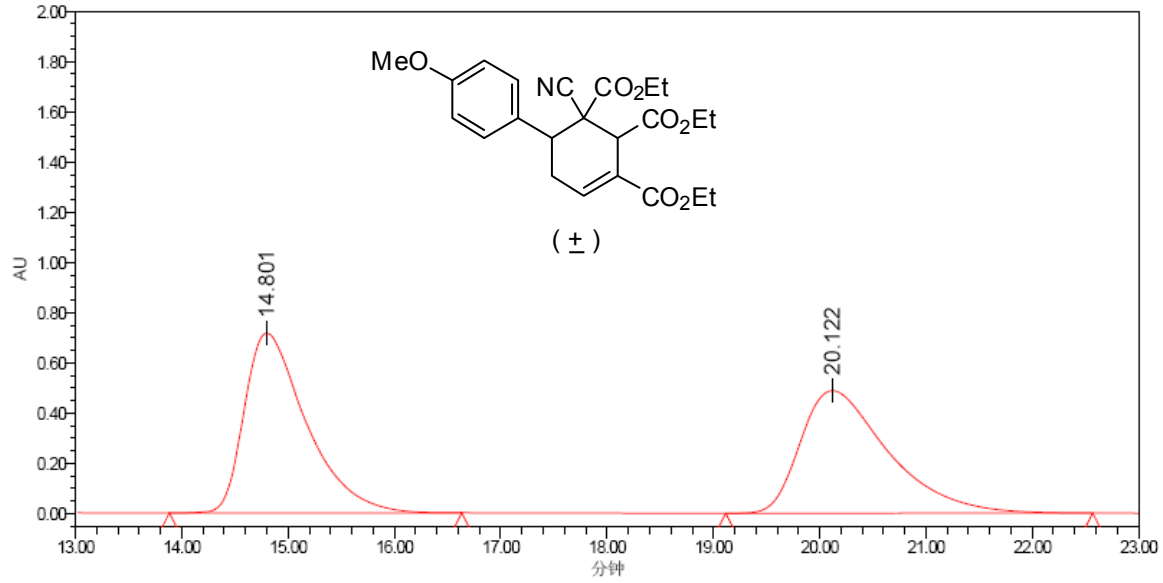
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.470	50949.445	1286587.625	5.3925
2		16.908	506791.063	22572376.000	94.6075
Total			557740.508	23858963.625	100.0000

(1*R*,2*R*,3*R*)-triethyl 2-cyano-4'-methoxy-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2,3,4-tricarboxylate (3k)

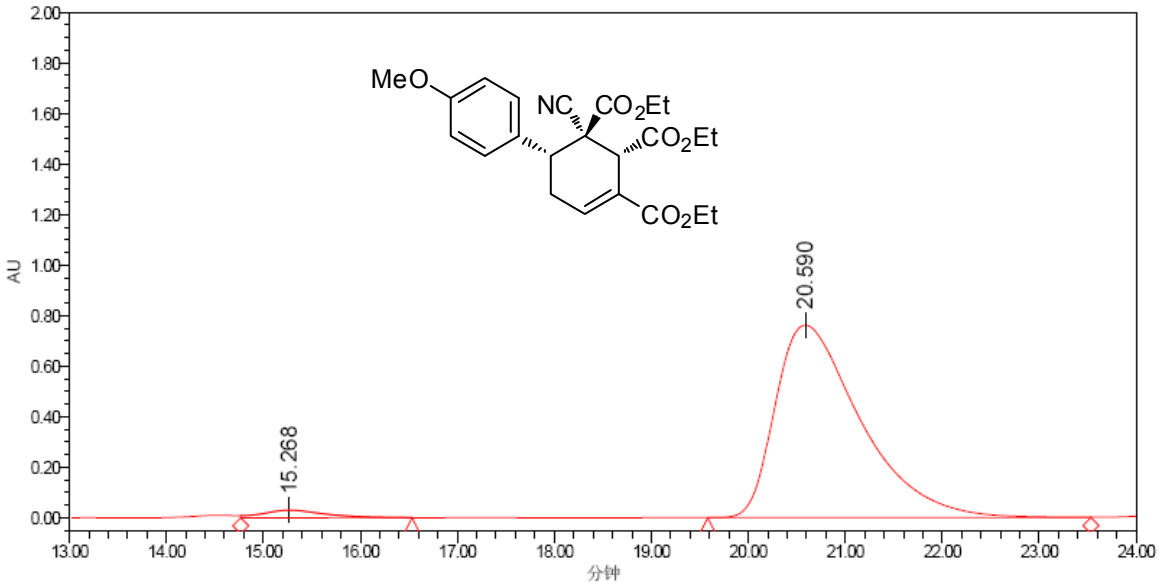






色谱峰结果

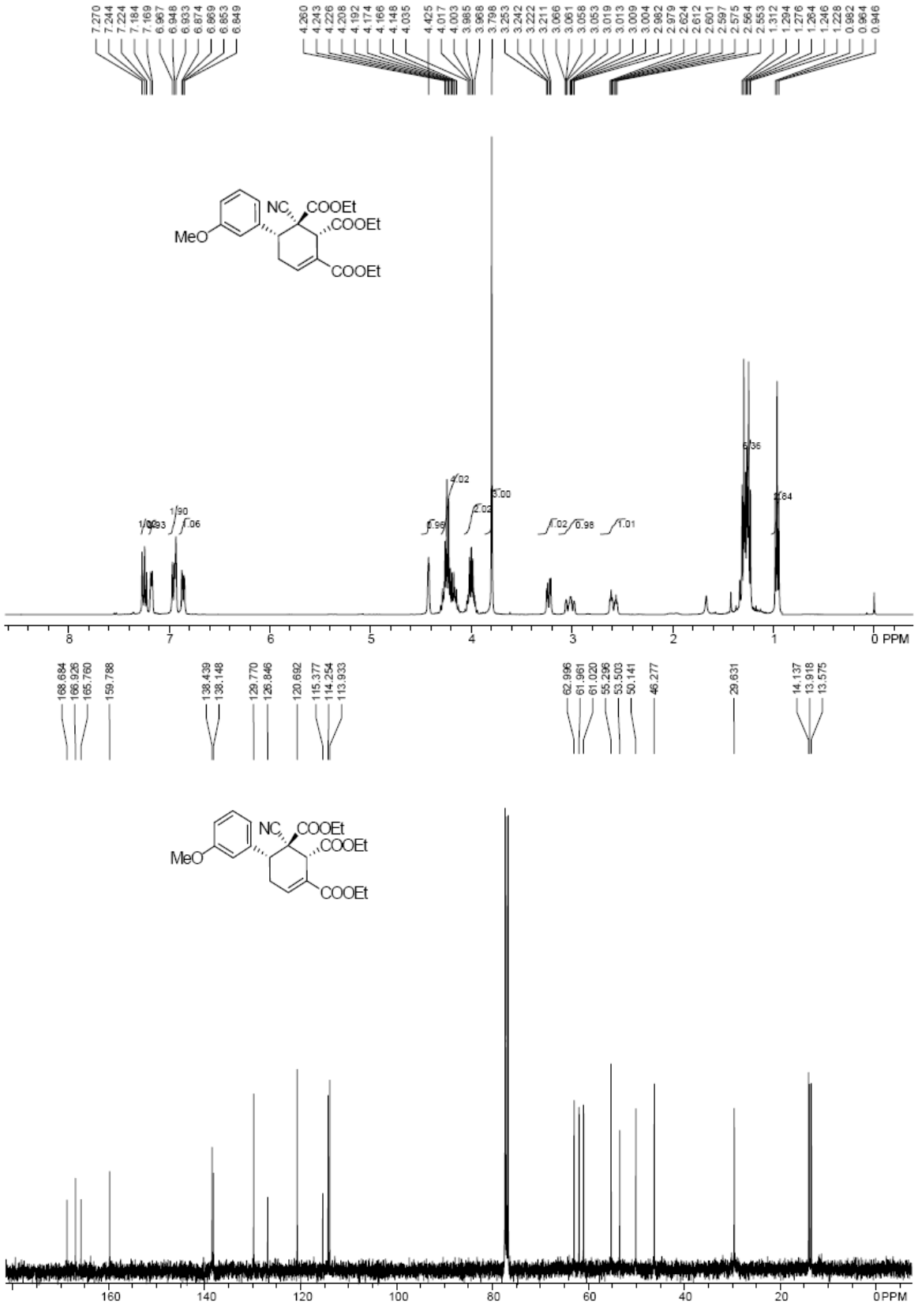
	名字	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		14.801	29029711	715967	50.93
2		20.122	27973465	487896	49.07

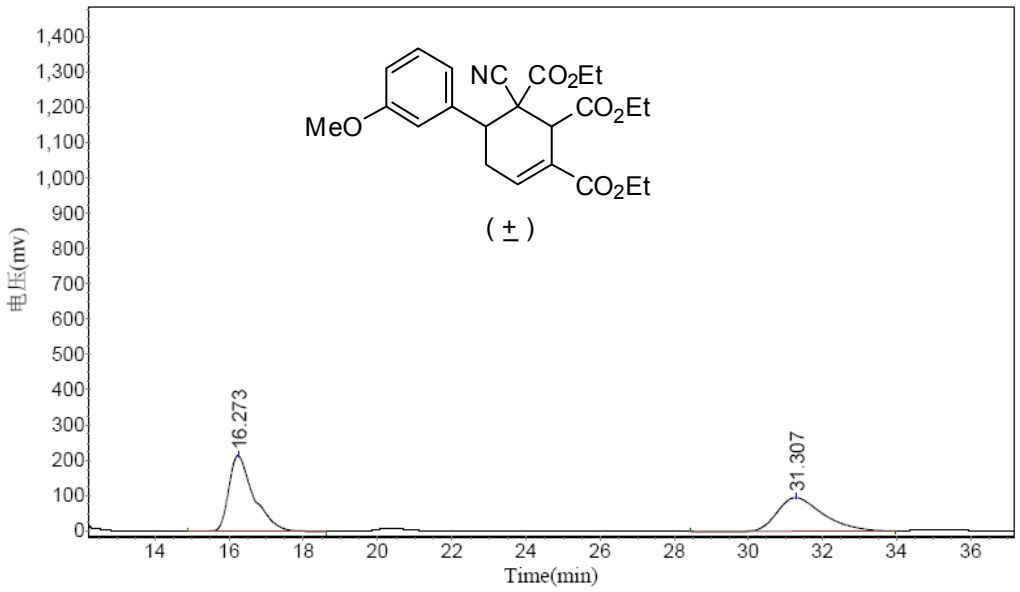


色谱峰结果

	名字	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		15.268	1297114	29793	2.71
2		20.590	46628737	761789	97.29

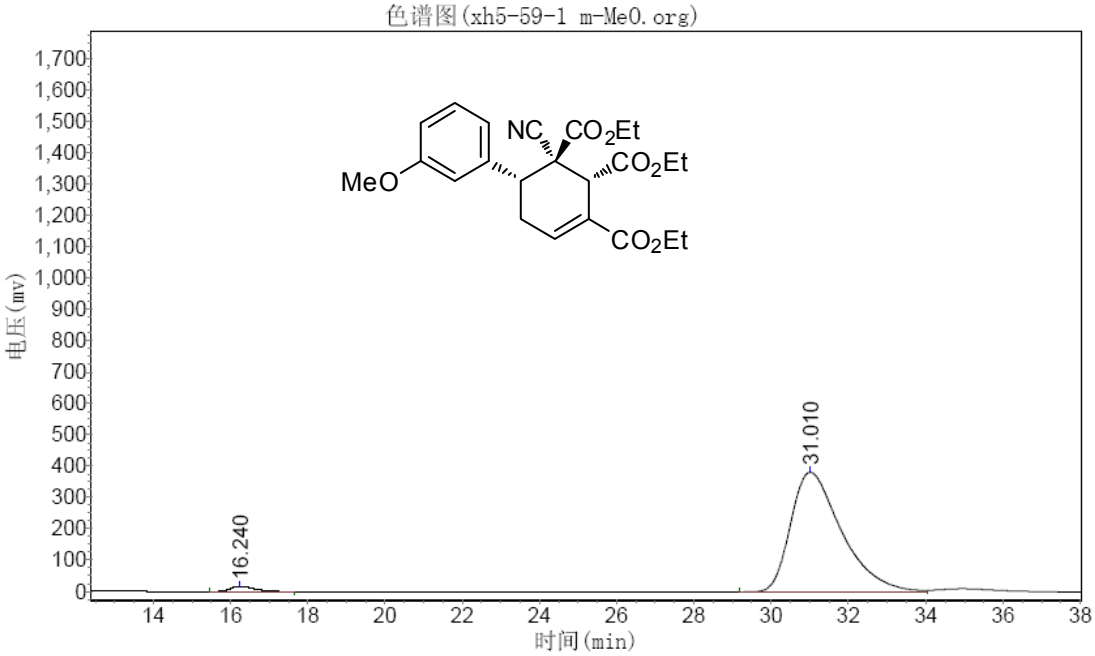
(1*R*,2*R*,3*R*)-triethyl 2-cyano-3'-methoxy-1,2,3,6-tetrahydro-[1,1'-biphenyl]-2,3,4-tricarboxylate (3l)





Results

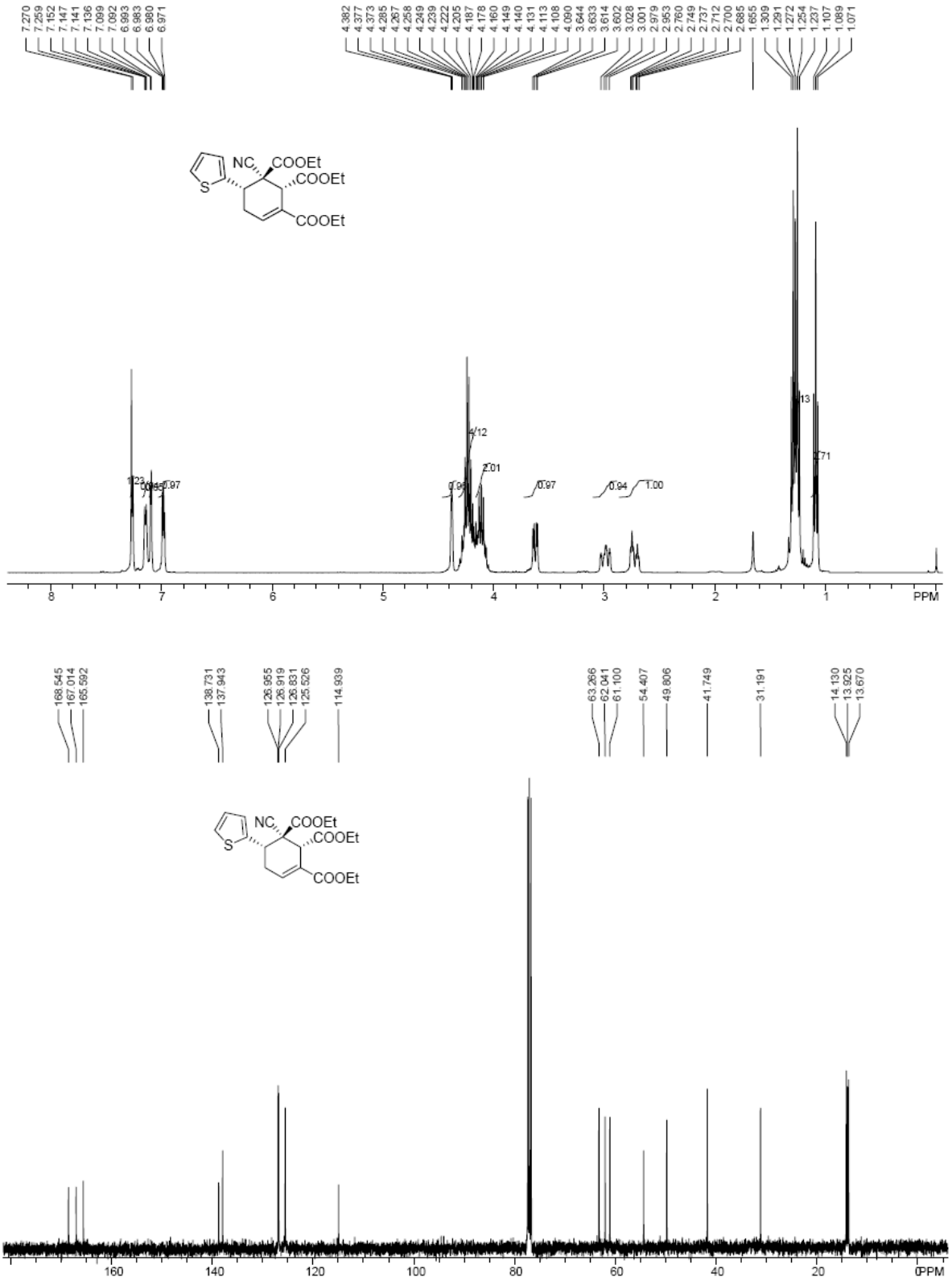
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.273	214201.203	10110994.000	54.5046
2		31.307	95763.148	8439740.000	45.4954
Total			309964.352	18550734.000	100.0000

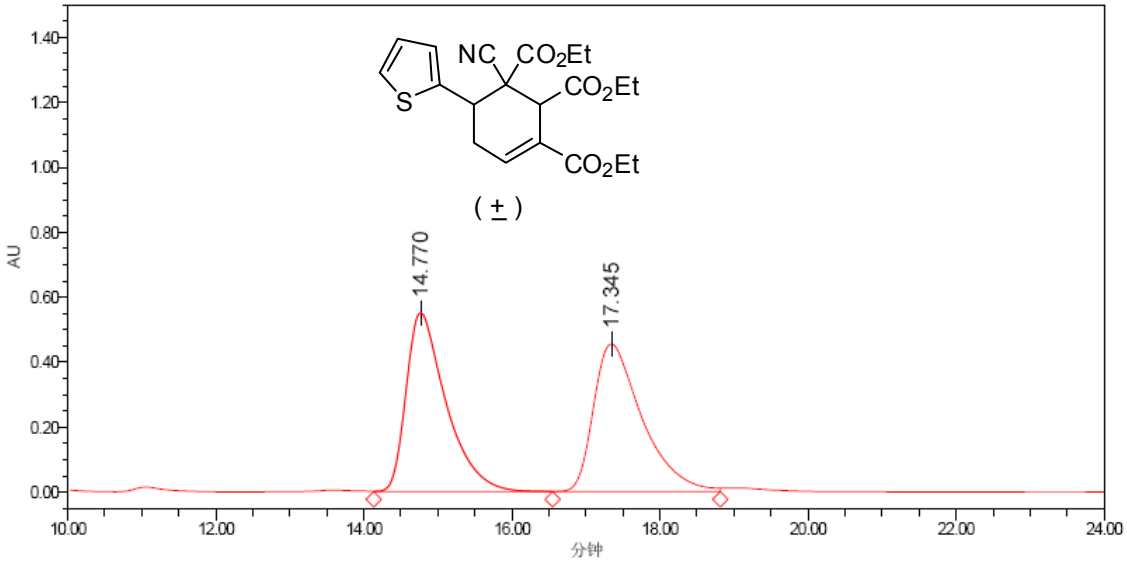


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		16.240	17859.225	789455.750	2.2045
2		31.010	381625.188	35021992.000	97.7955
总计			399484.412	35811447.750	100.0000

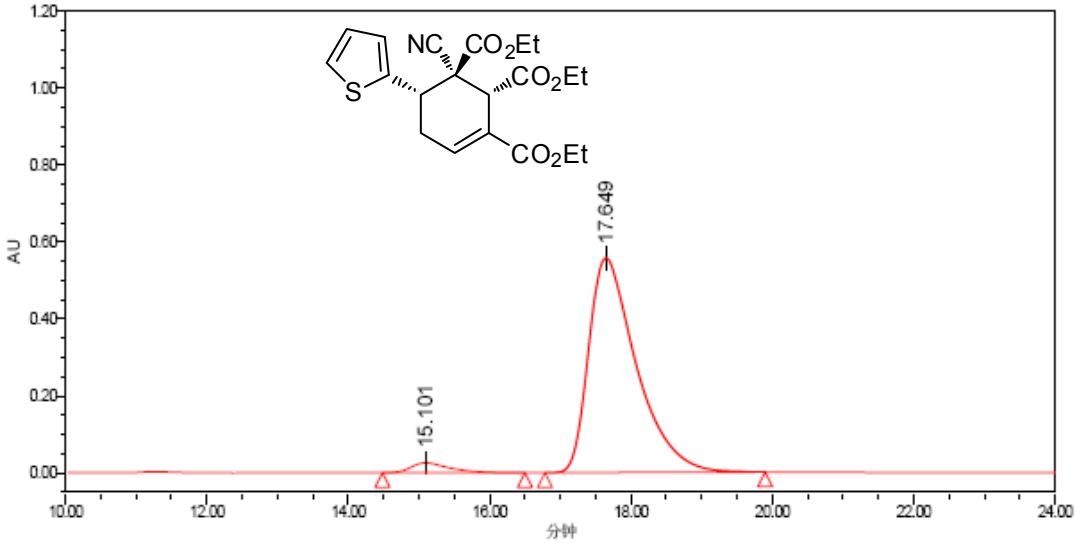
(1*S*,2*R*,6*S*)-triethyl 1-cyano-6-(thiophen-2-yl)cyclohex-3-ene-1,2,3-tricarboxylate (3m)





色谱峰结果

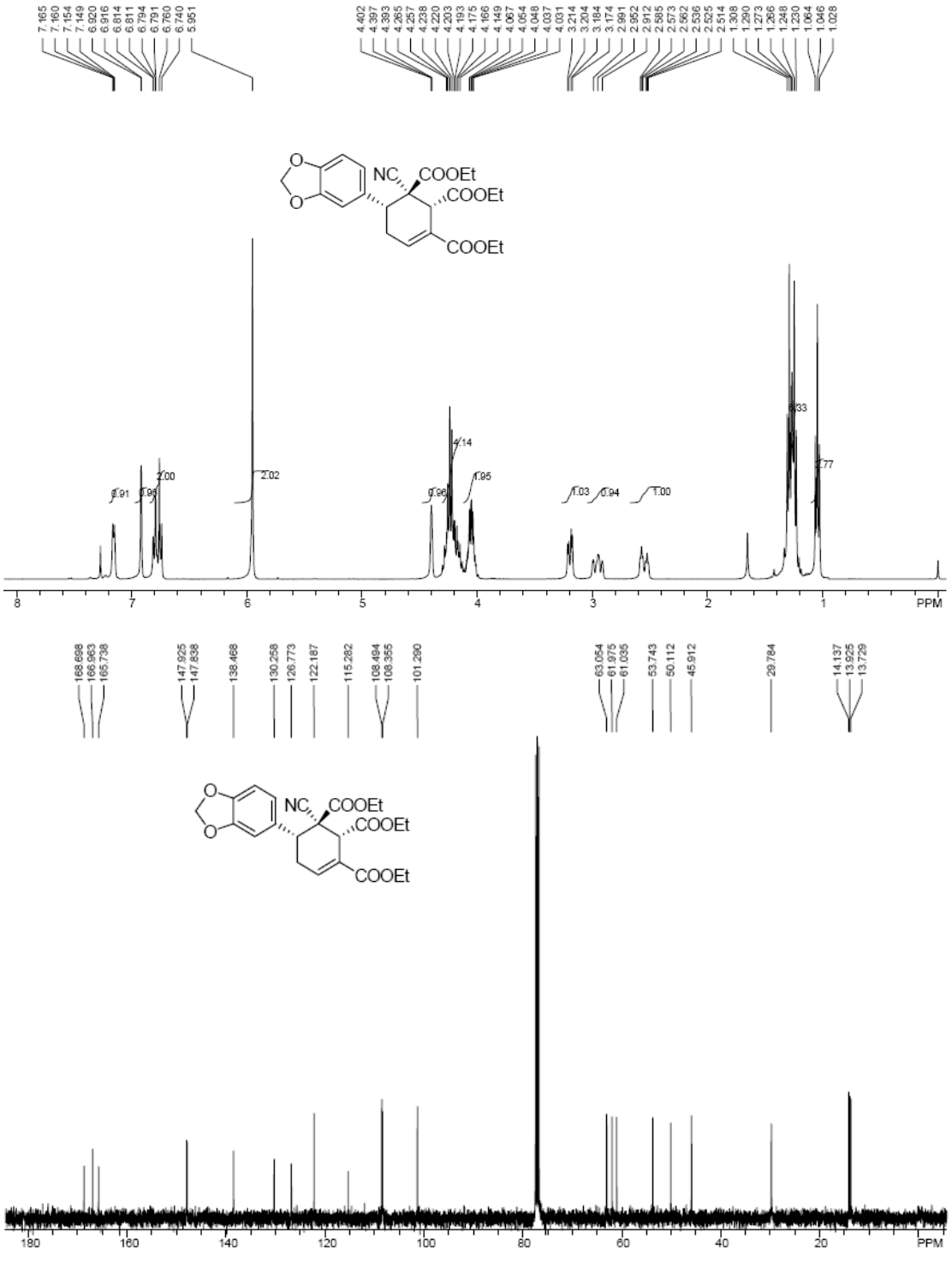
	名字	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		14.770	20731822	550741	50.00
2		17.345	20729663	454610	50.00

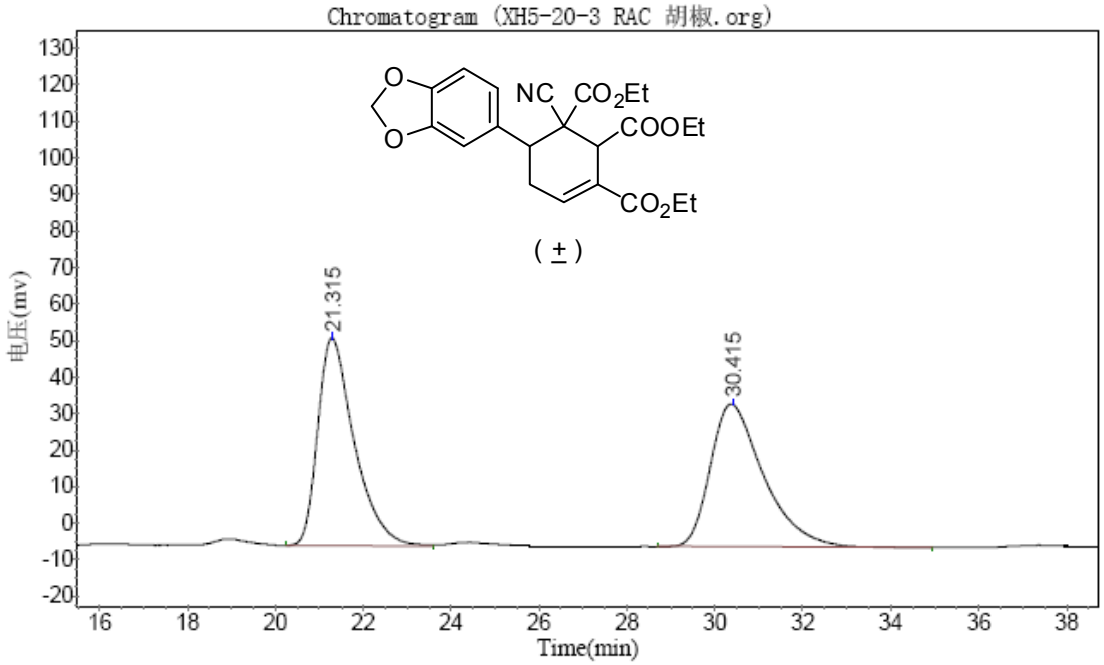


色谱峰结果

	名字	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		15.101	966420	25762	3.57
2		17.649	26131458	557055	96.43

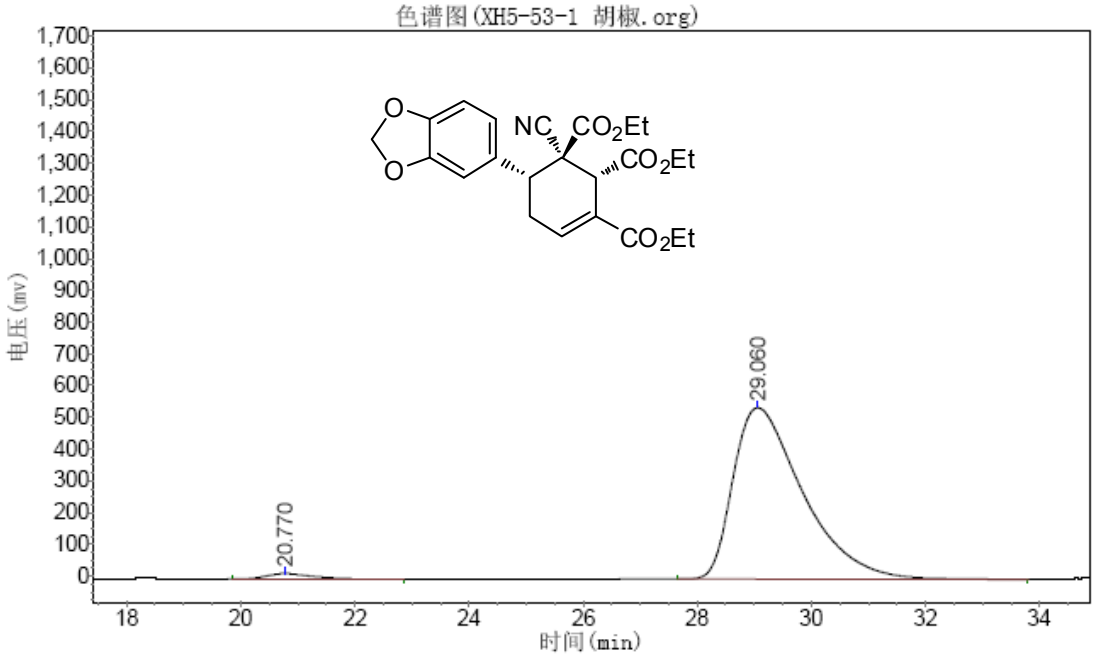
(1*R*,2*R*,6*R*)-triethyl 6-(benzo[d][1,3]dioxol-5-yl)-1-cyanocyclohex-3-ene-1,2,3-tricarboxylate (3n)





Results

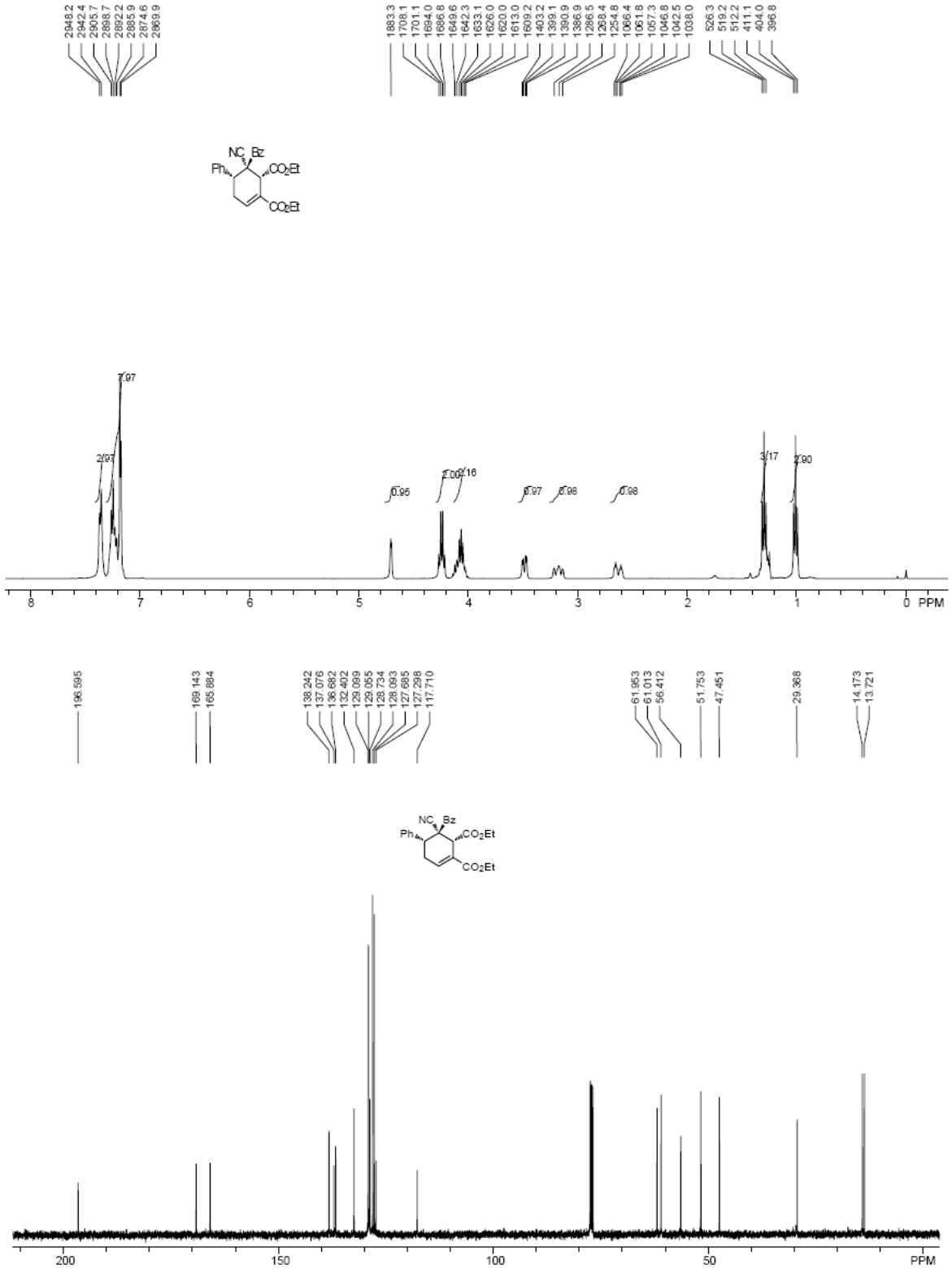
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.315	57020.715	3316651.750	49.8726
2		30.415	39188.531	3333597.250	50.1274
Total			96209.246	6650249.000	100.0000

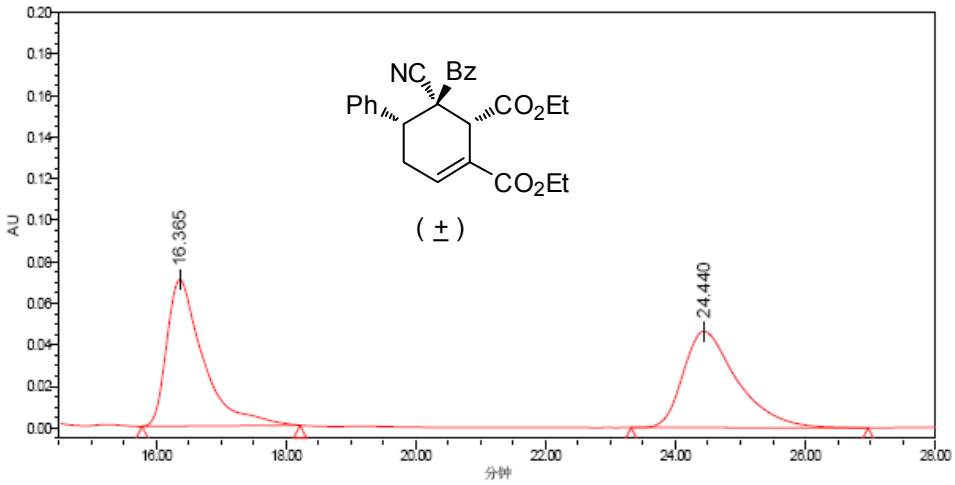


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		20.770	16548.156	926244.625	1.9790
2		29.060	539854.188	45876372.000	98.0210
总计			556402.344	46802616.625	100.0000

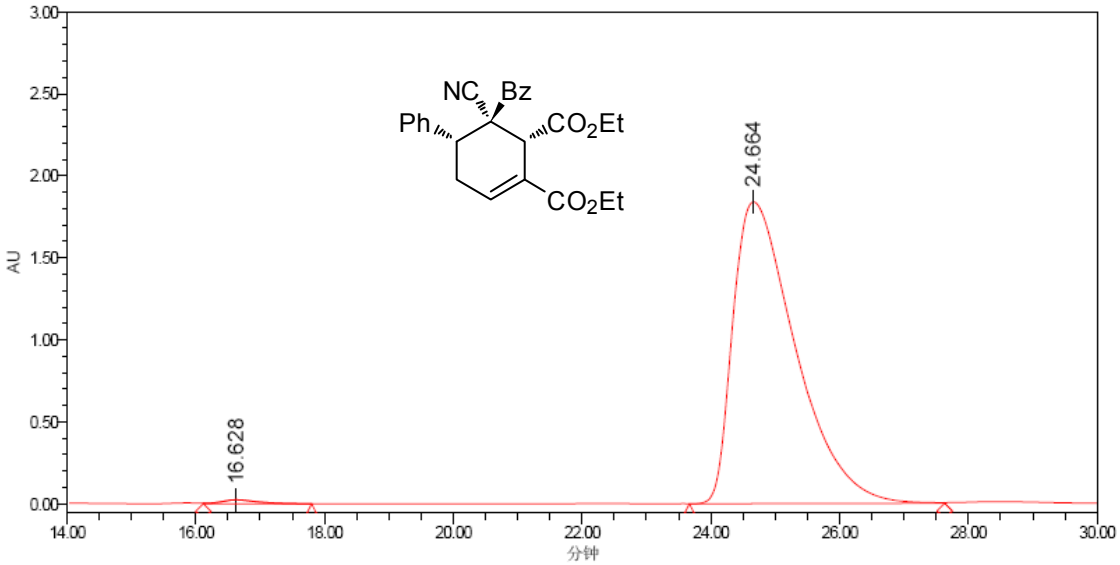
(1*R*,2*R*,3*S*)-diethyl 2-benzoyl-2-cyano-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3,4-dicarboxylate (6)





色谱峰结果

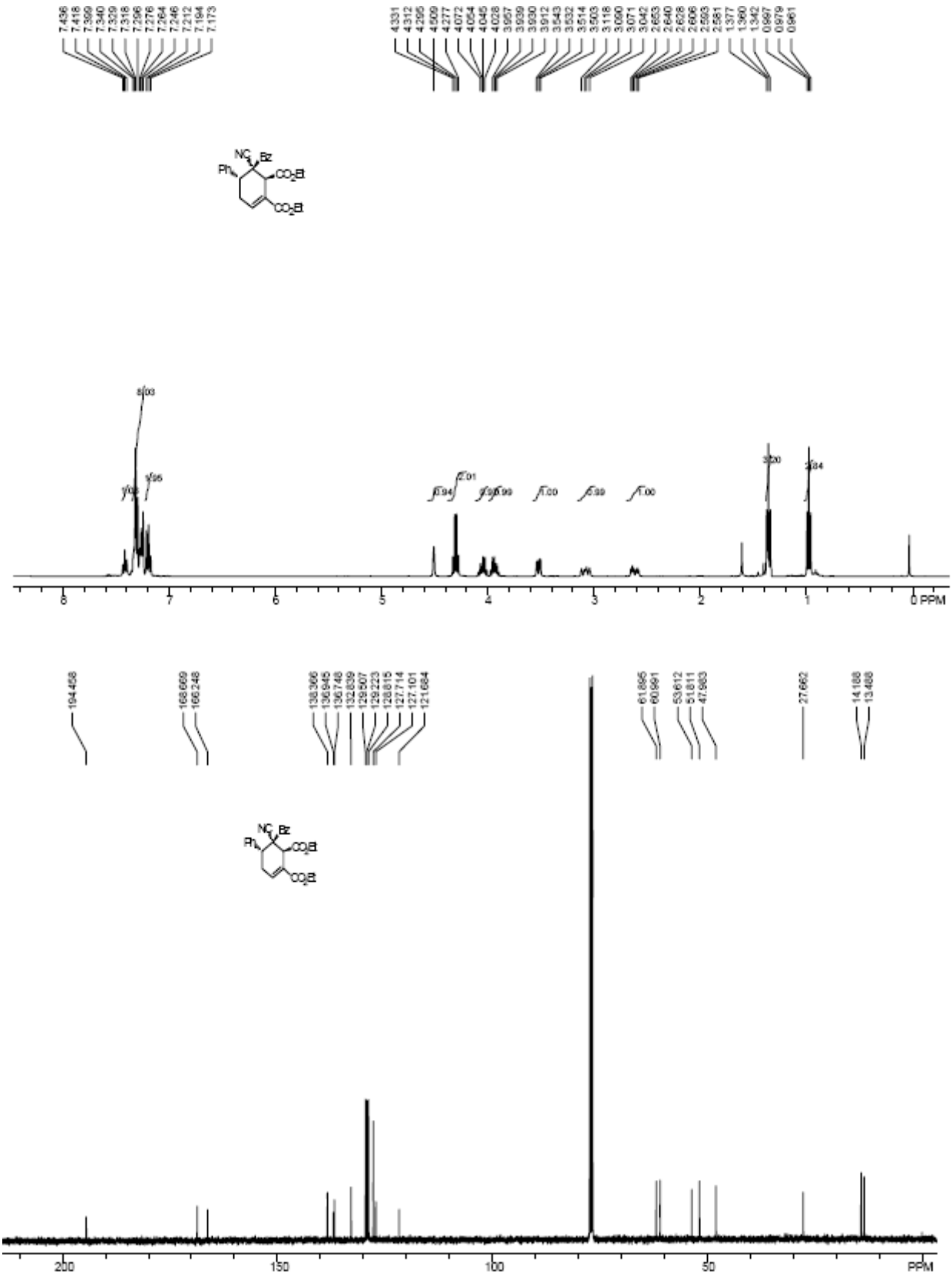
	名字	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		16.385	2751200	70596	50.69
2		24.440	2676810	46442	49.31

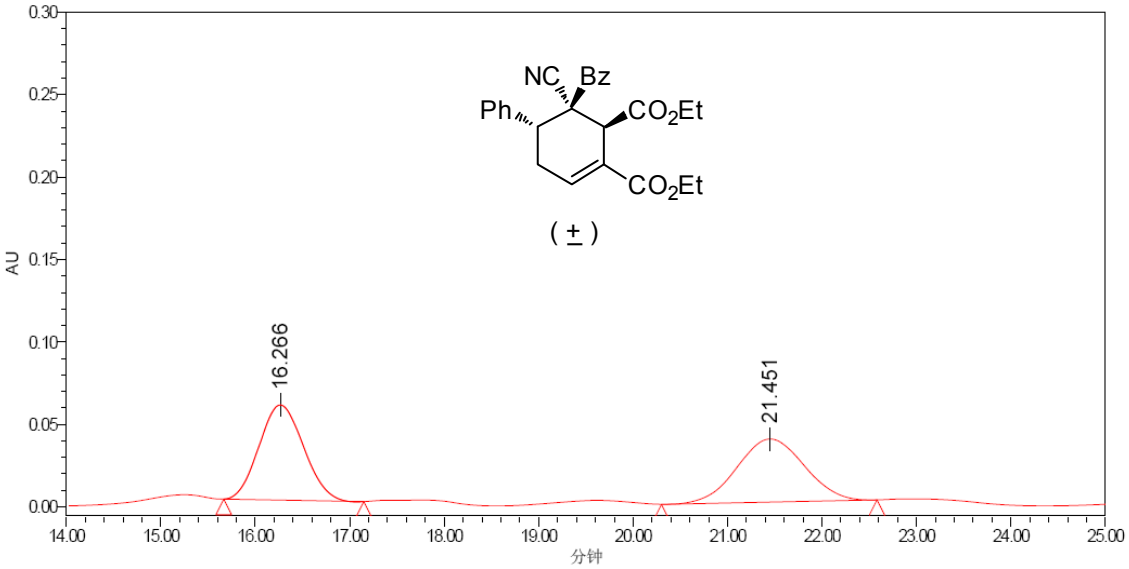


色谱峰结果

	名字	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		16.628	925692	24354	0.74
2		24.664	124373113	1839996	99.26

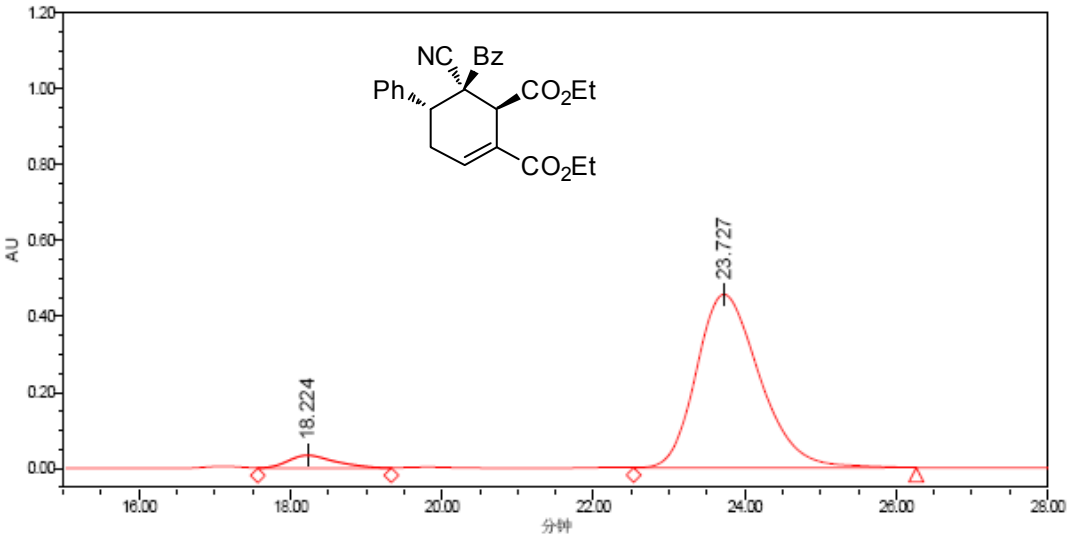
(1*R*,2*R*,3*R*)-diethyl 2-benzoyl-2-cyano-1,2,3,6-tetrahydro-[1,1'-biphenyl]-3,4-dicarboxylate (S6)





色谱峰结果

	名字	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		16.266	1887453	57729	49.92
2		21.451	1893377	38294	50.08



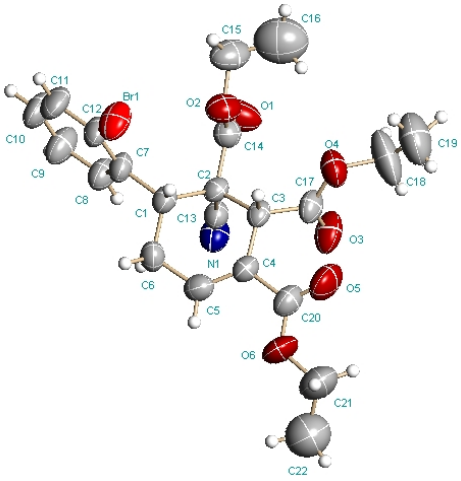
色谱峰结果

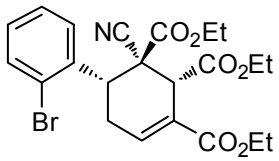
	名字	保留时间 (分钟)	面积 (微伏*秒)	高度 (微伏)	% 面积
1		18.224	1465277	33808	5.23
2		23.727	26540097	456670	94.77

7. Determination of Configurations for Compounds 3 and 6

The absolute configuration of the product **3i** was assigned by X-ray crystallographic analysis to be (1*S*,2*R*,3*R*) (Figure S1). The configurations of other products derived from α-cyanoacrylates were assigned by analogy. The configuration of the product **6** derived from oxo-diene **5** was determined by NOESY spectrum. The configuration of the known compound **3a'** derived from arylidenemalononitriles were assigned by comparison with literature NMR data.[5]

CCDC 860051 (**3i**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.





3i

Figure S1. X-ray structure of **3i**

Identification code	cd201394
Empirical formula	C22 H24 Br N O6
Formula weight	478.33
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	P2(1)
Unit cell dimensions	a = 8.1070(11) Å α = 90 deg.
	b = 12.1050(16) Å β = 101.055(2) deg.
	c = 11.6138(16) Å γ = 90 deg.
Volume	1118.6(3) $Å^3$
Z, Calculated density	2, 1.420 Mg/m^3
Absorption coefficient	1.874 mm^{-1}
F(000)	492
Crystal size	0.357 x 0.128 x 0.124 mm^3
Theta range for data collection	1.79 to 26.00 deg.
Limiting indices	-9<=h<=9, -14<=k<=14, -14<=l<=11
Reflections collected / unique	6158 / 4065 [R(int) = 0.0667]
Completeness to theta = 26.00	99.6 %
Absorption correction	Empirical

Max. and min. transmission	1.0000 and 0.0946
Refinement method	Full-matrix least-squares on F^2
Data /restraints / parameters	4065 / 29 / 285
Goodness-of-fit on F^2	0.920
Final R indices [I>2sigma(I)]	R1 = 0.0553, wR2 = 0.1301
R indices (all data)	R1 = 0.0745, wR2 = 0.1386
Absolute structure parameter	0.017(13)
Extinction coefficient	0.014(3)
Largest diff. peak and hole	0.529 and -0.313 $e.A^{-3}$

NOSEY Spectra of 6