Supporting Information

Synthesis and Application of A New Hexamethyl-1,1'-spirobiindane-based Chiral Bisphosphine (HMSI-PHOS) Ligand in Asymmetric Allylic Alkylation

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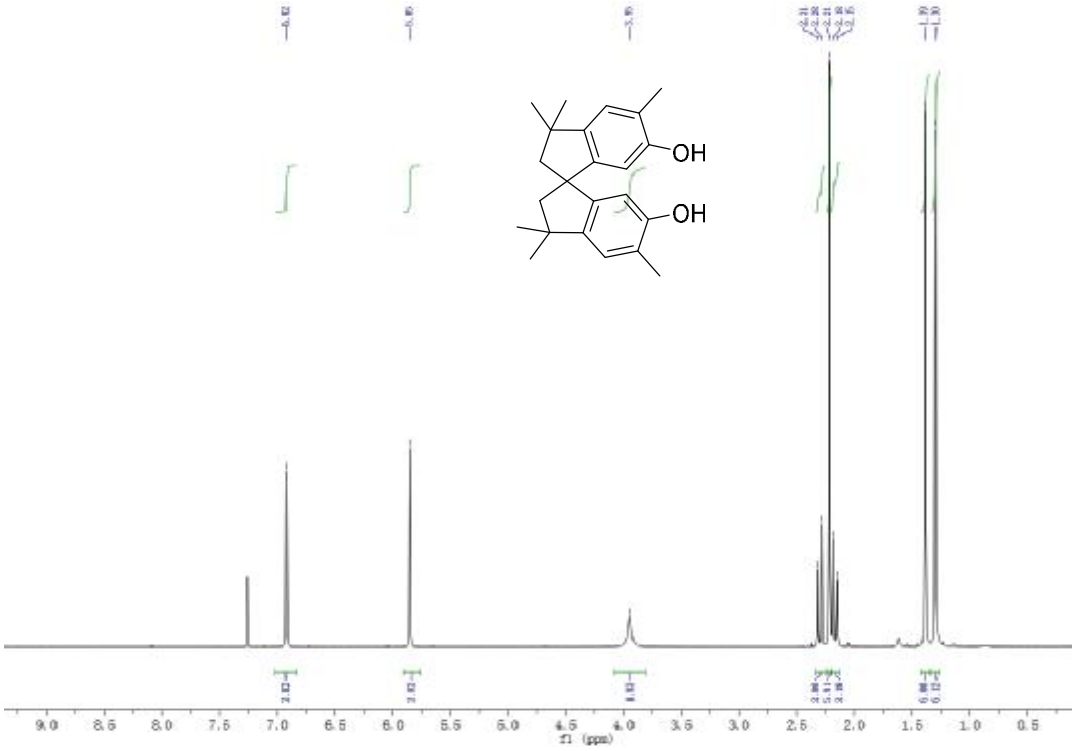
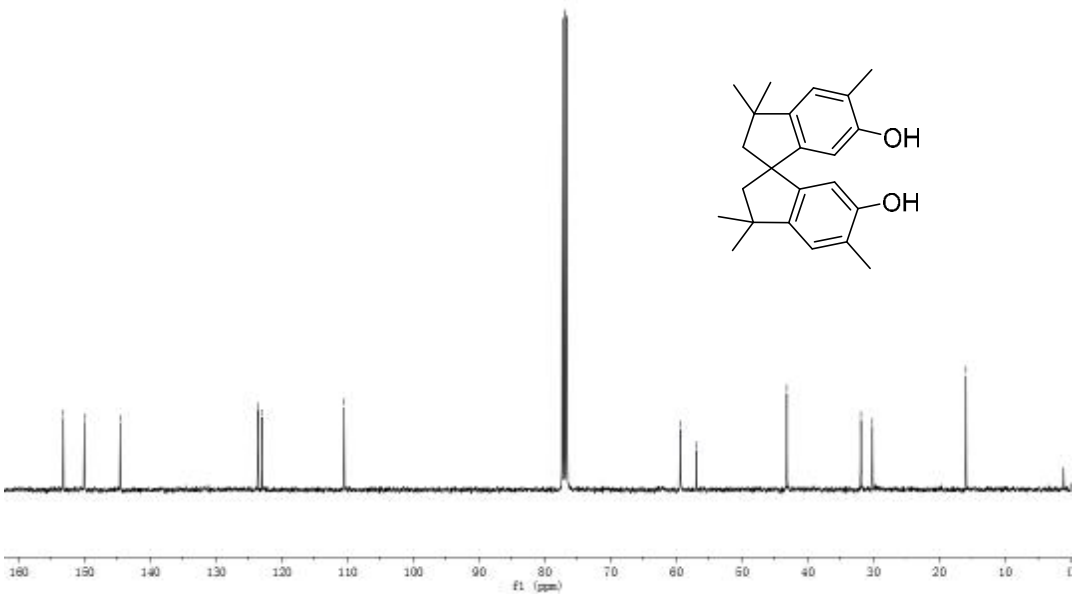
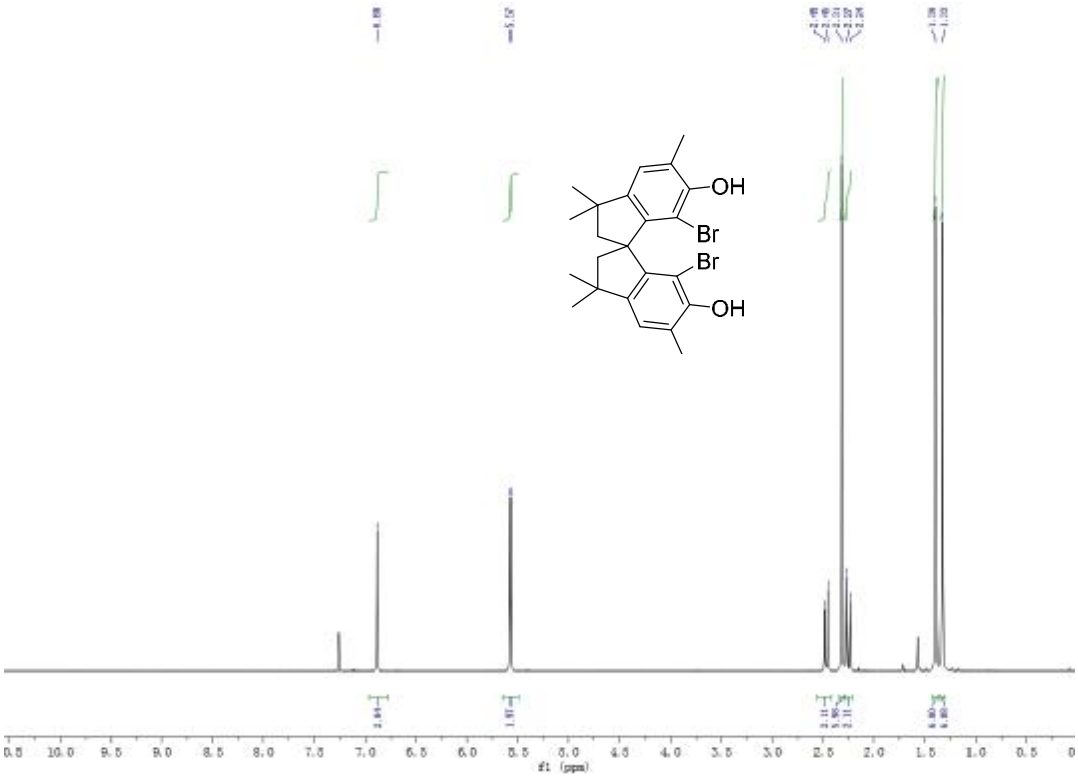
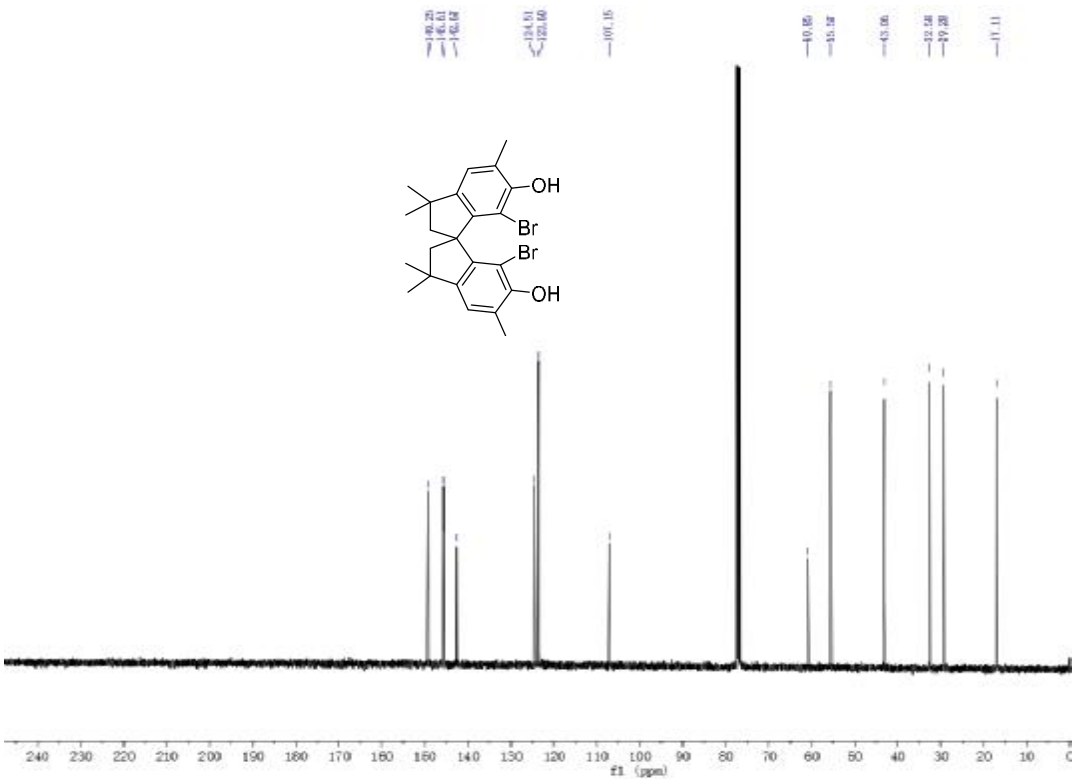
3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6,6'-diol (**5**)



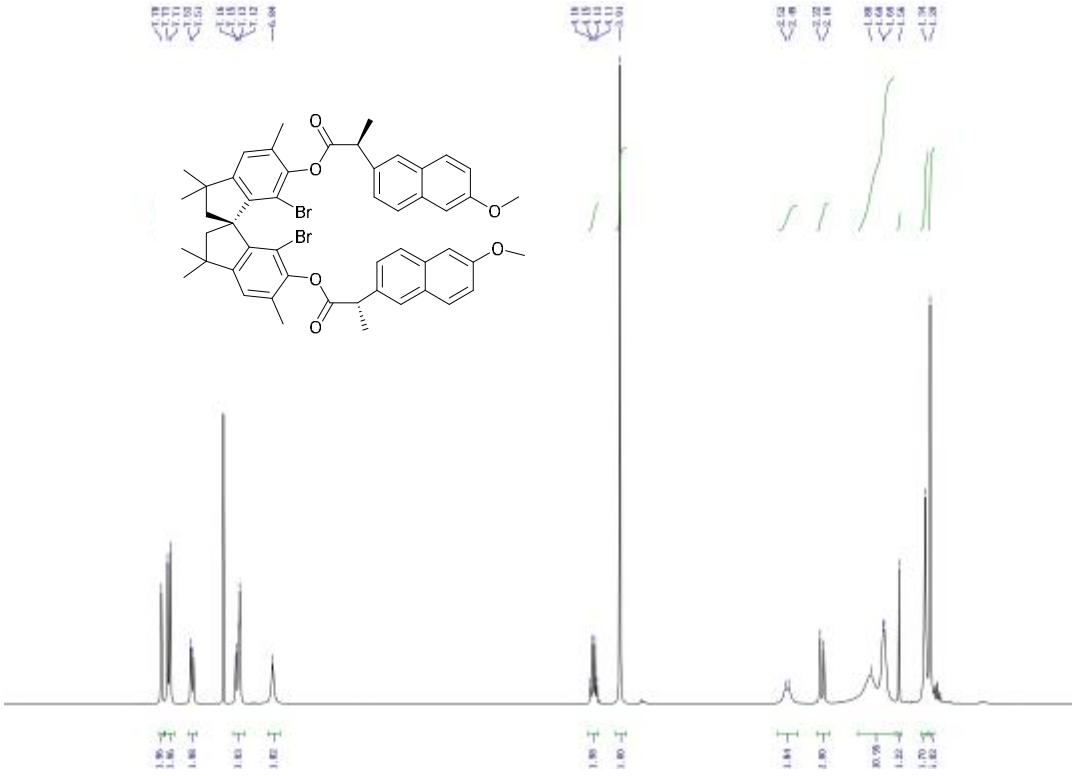


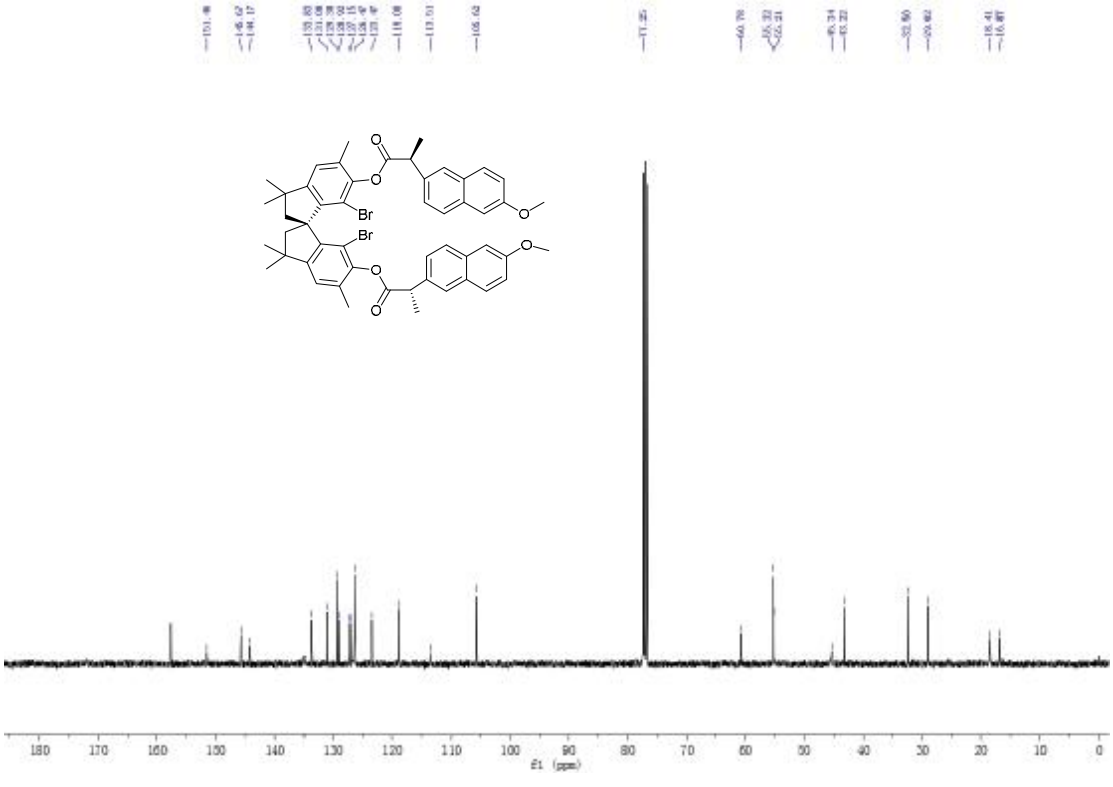
7,7'-dibromo-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6,6'-diol (**6**)



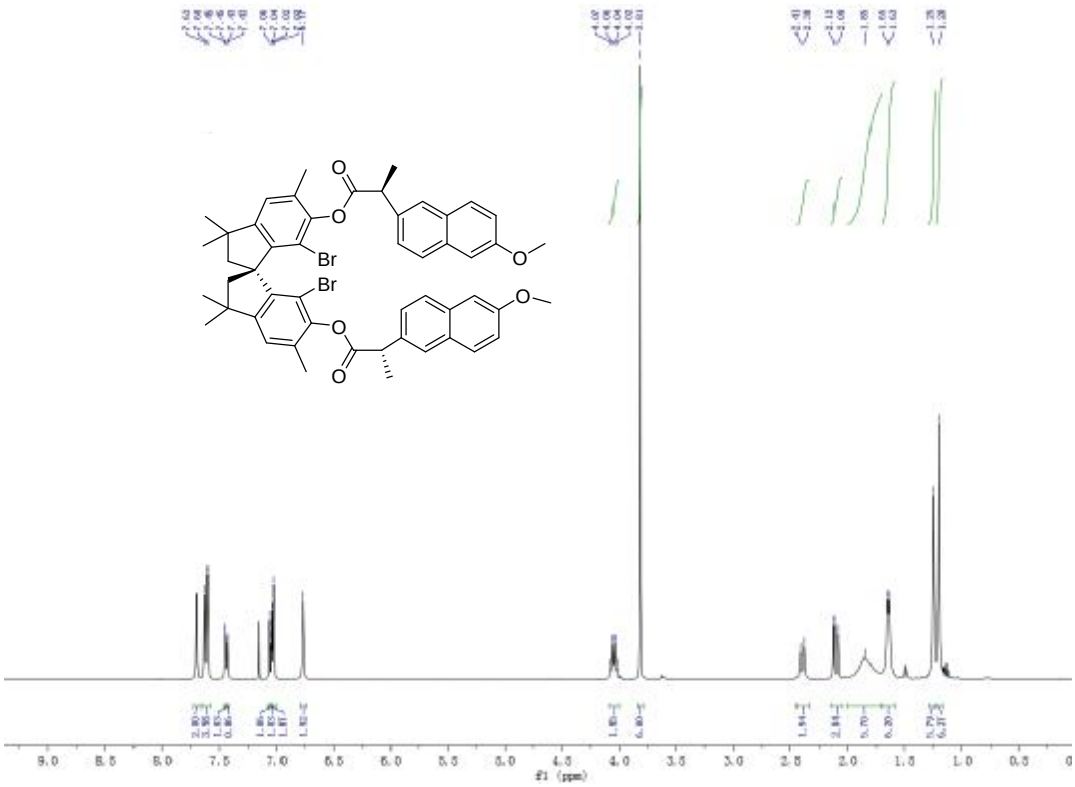


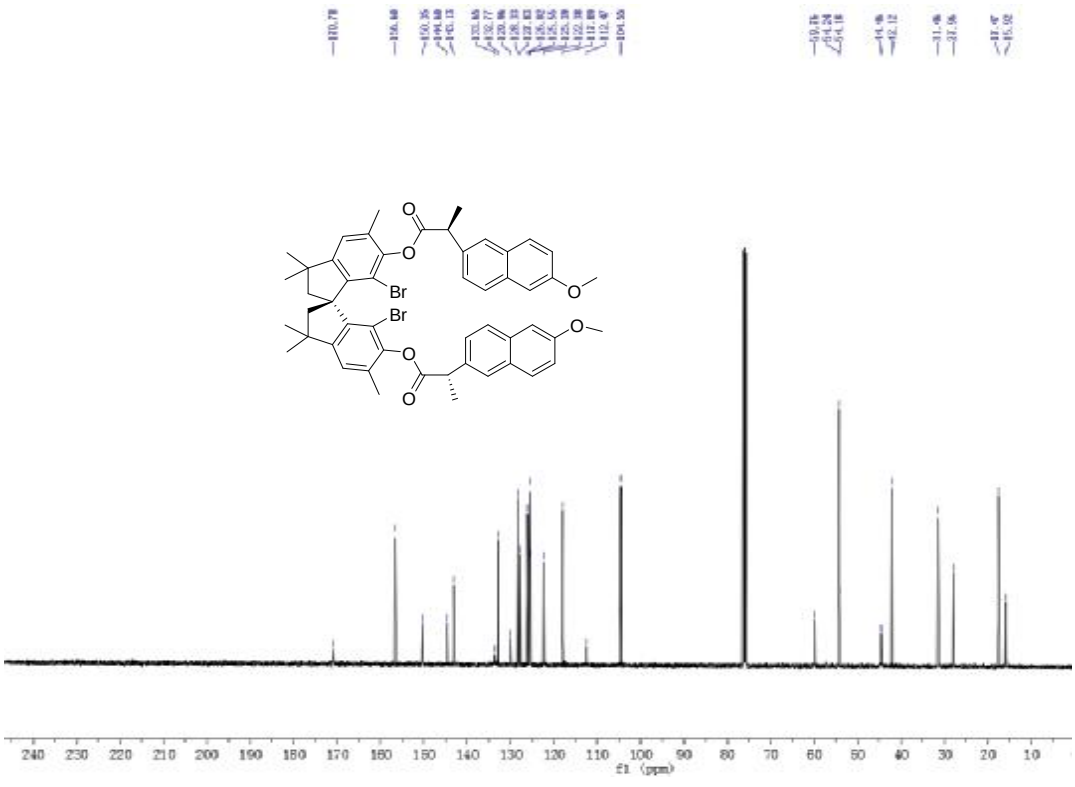
(*R*)-7,7'-dibromo-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6,6'-diyl (2S,2'S)-bis(2-(6-methoxynaphthalen-2-yl)propanoate) (*Ra,S,S*)-**7**



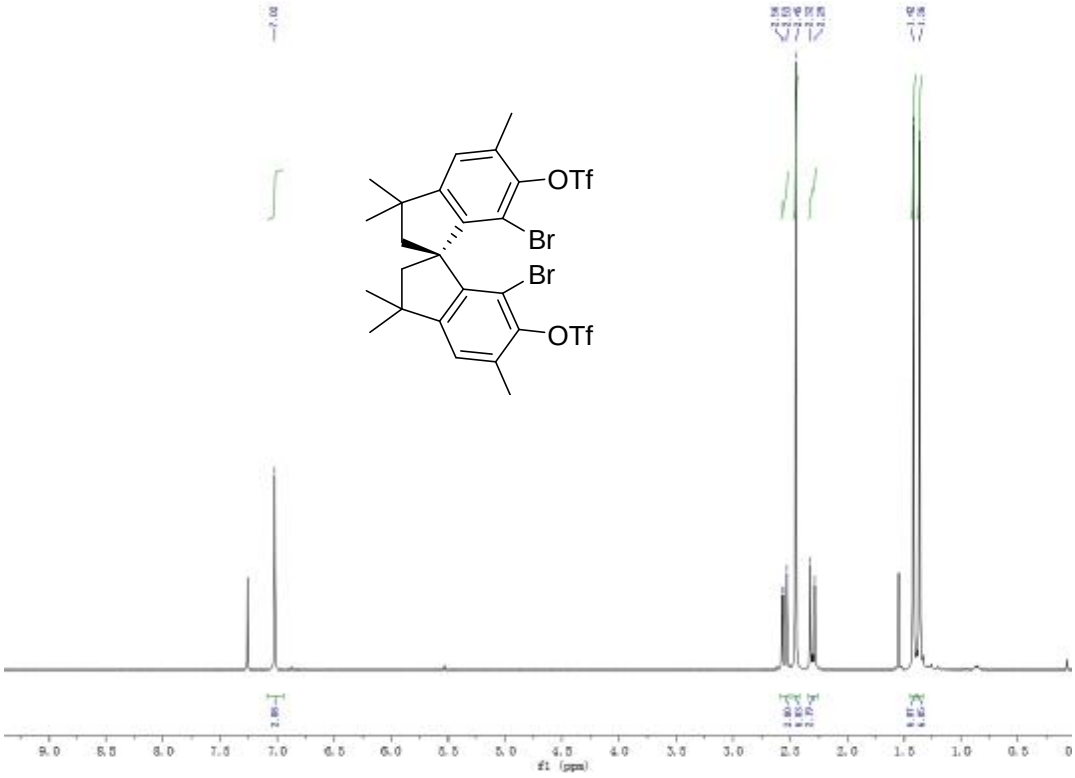


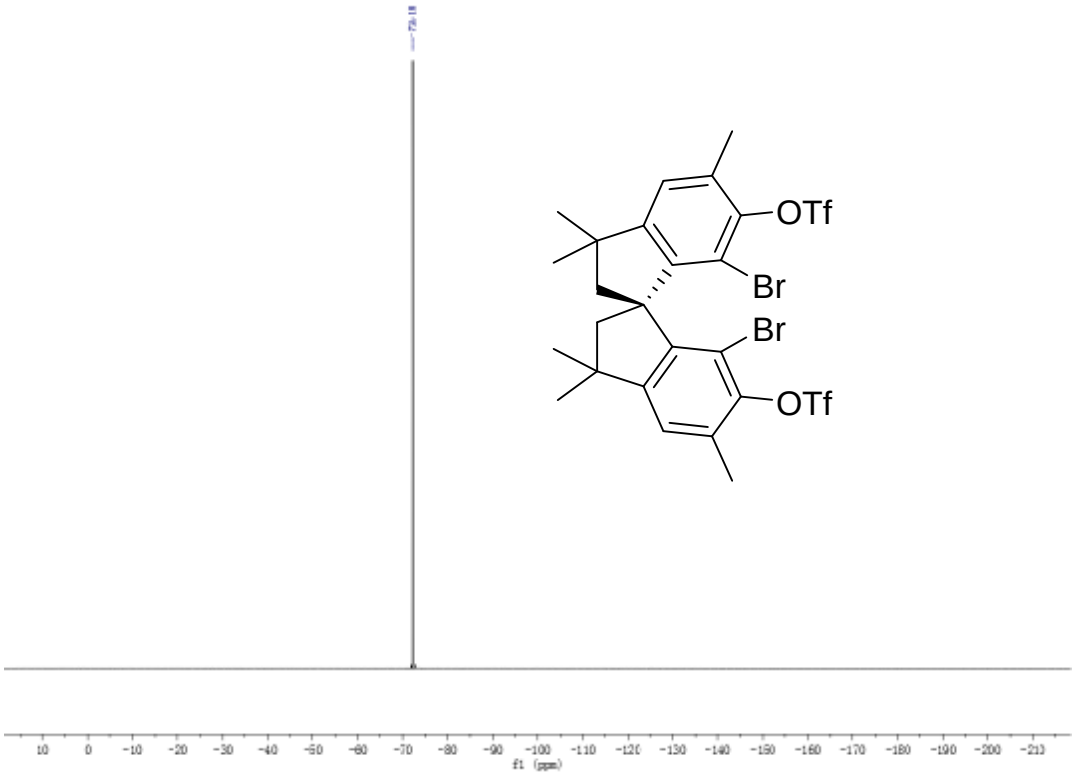
(*S*)-7,7'-dibromo-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6,6'-diyl (2S,2'S)-bis(2-(6-methoxynaphthalen-2-yl)propanoate) (*Sa*,*S*,*S*)-**7**

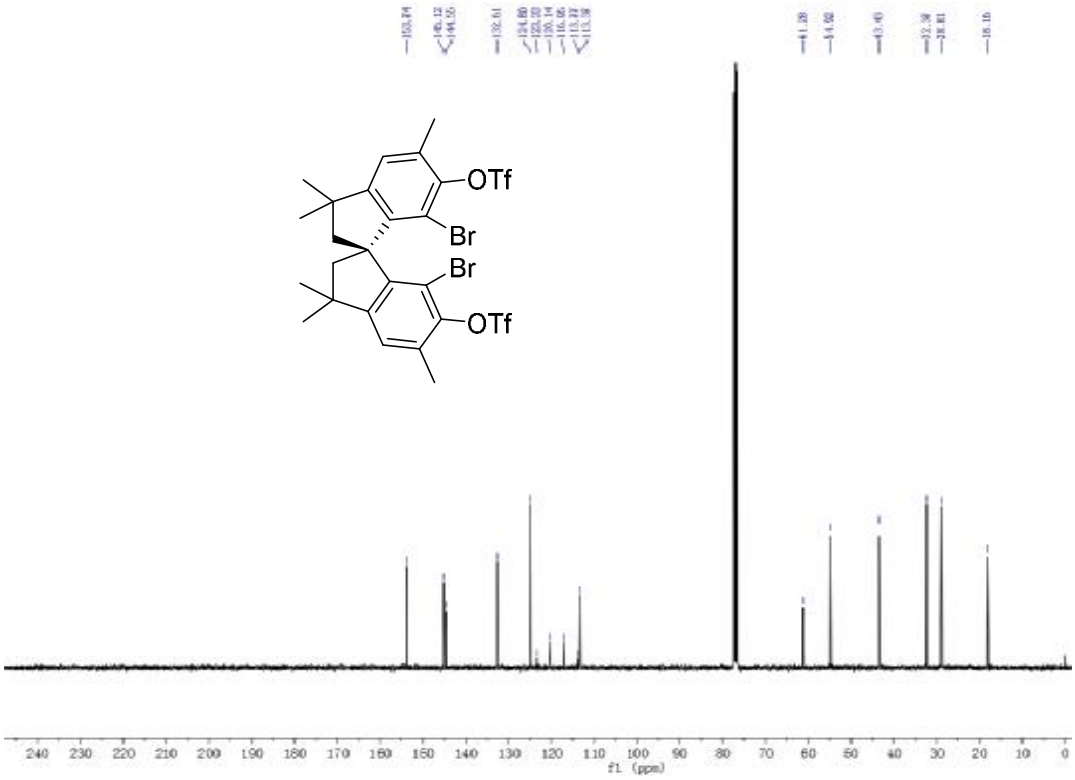




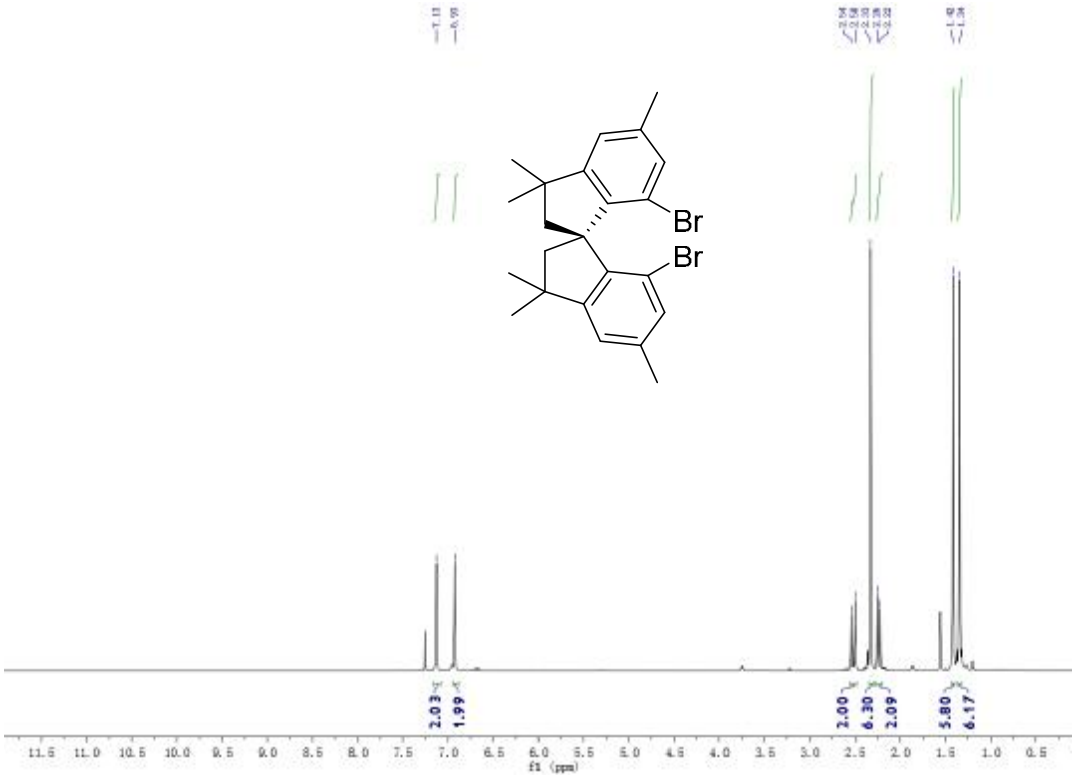
(*R*)-7,7'-dibromo-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6,6'-diyl bis(trifluoromethanesulfonate) (*R*)-**8**

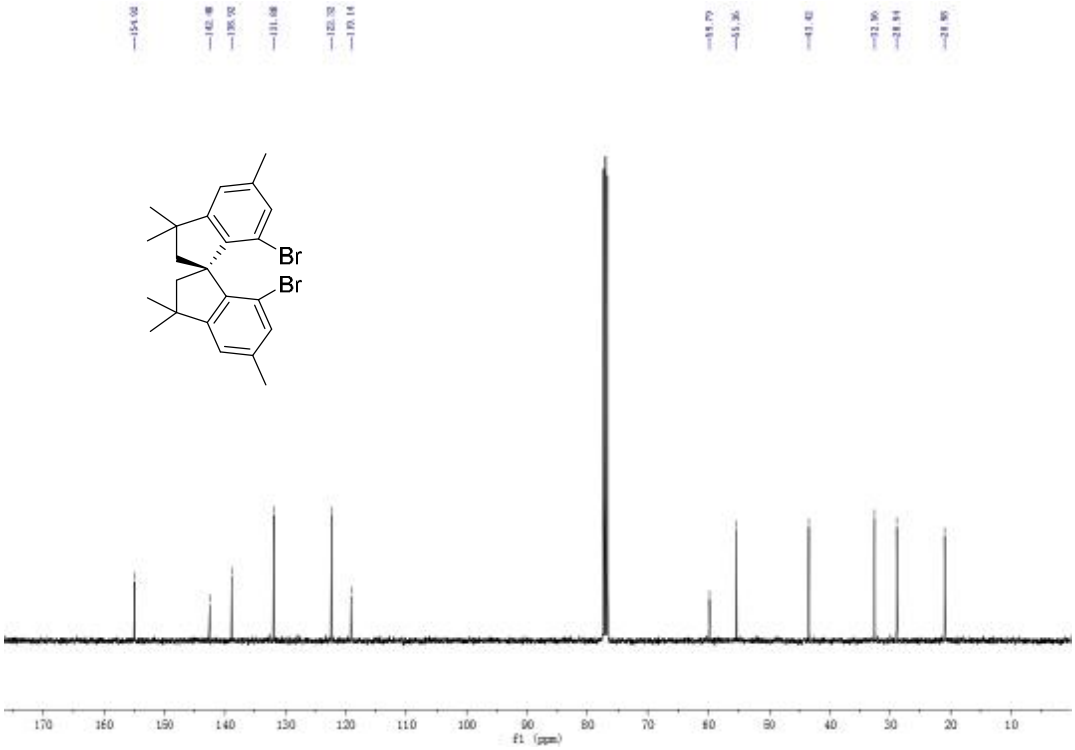




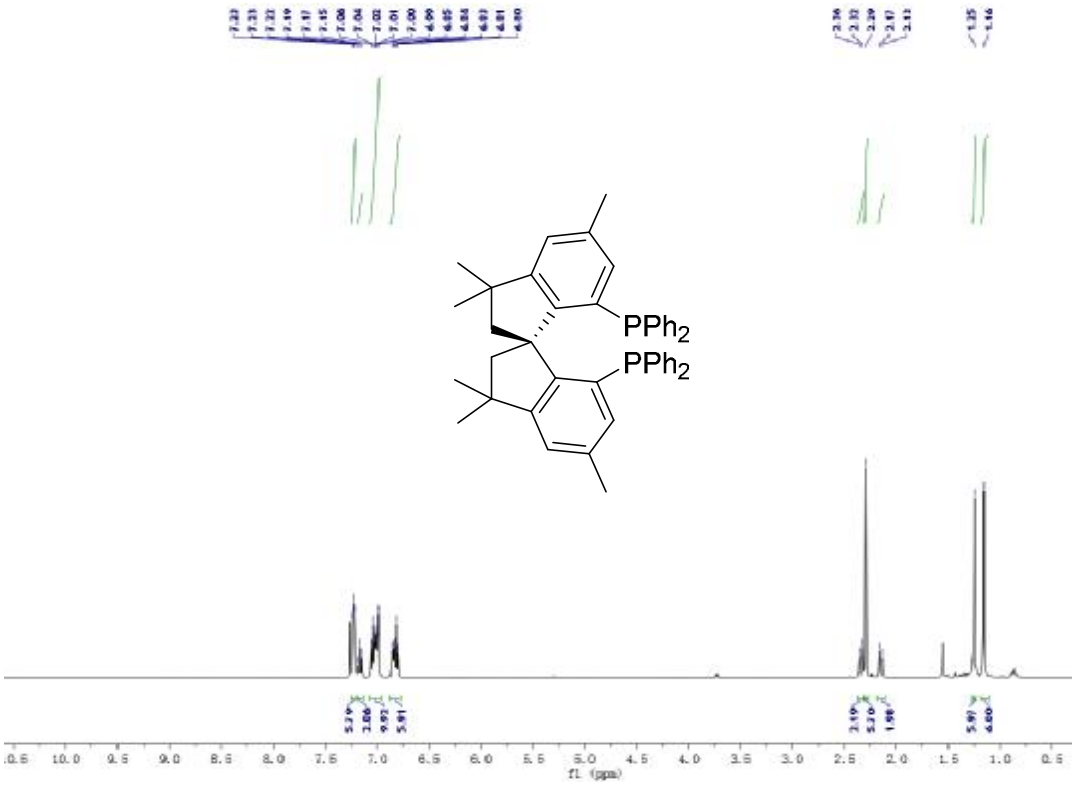


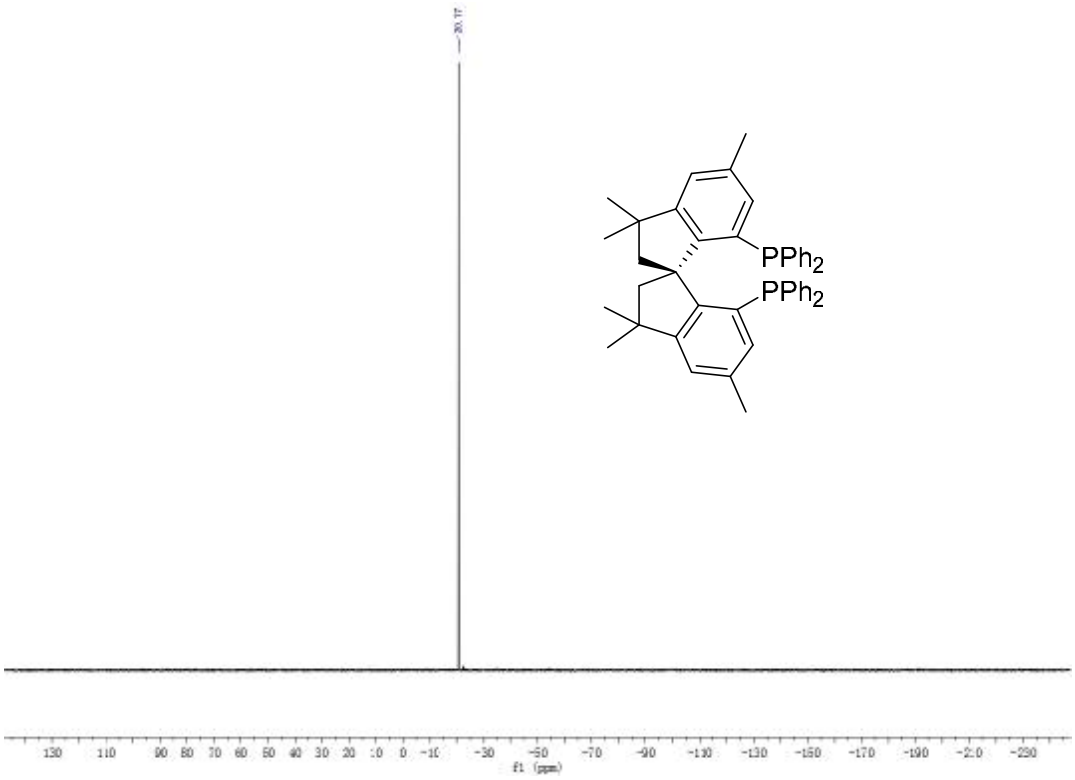
(*R*)-7,7'-dibromo-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene] (*R*)-**9**

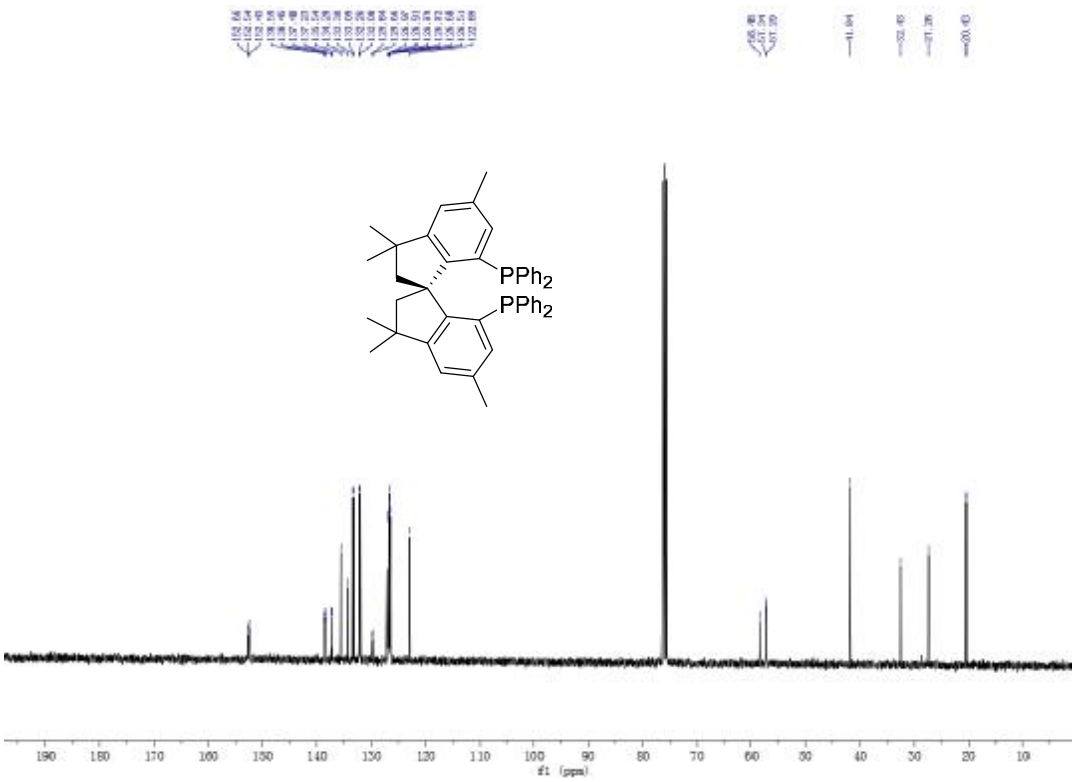




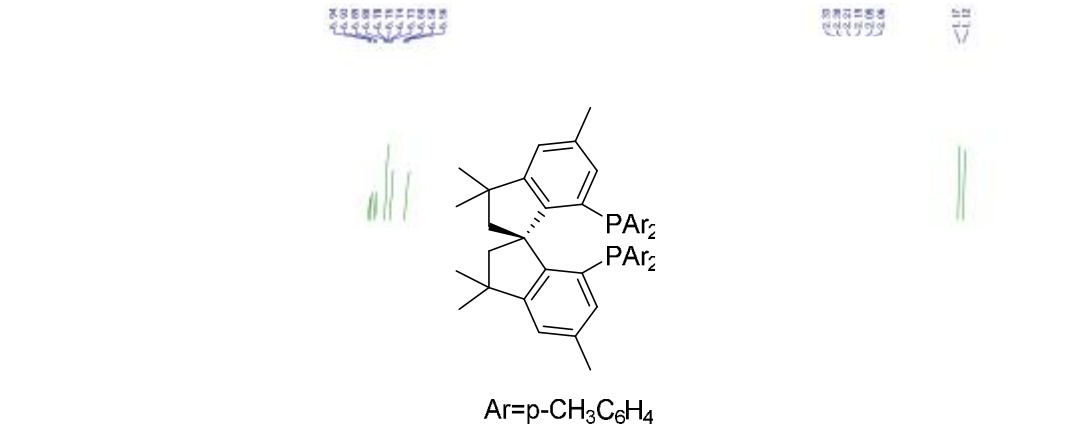
(*R*)-(3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(diphenylphosphane) (*R*)-**1a**

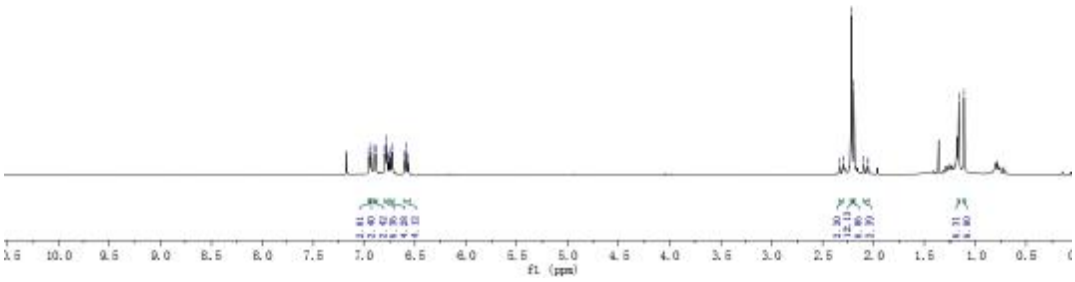


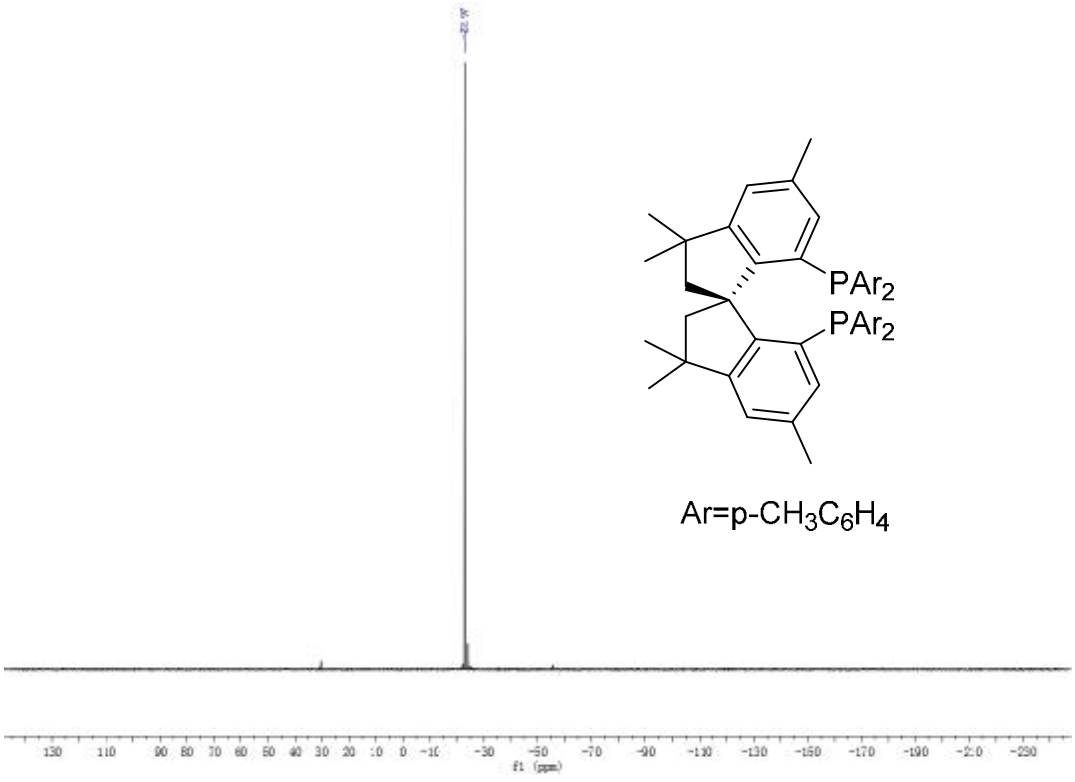

PPh2
PPh2
f1 (ppm)

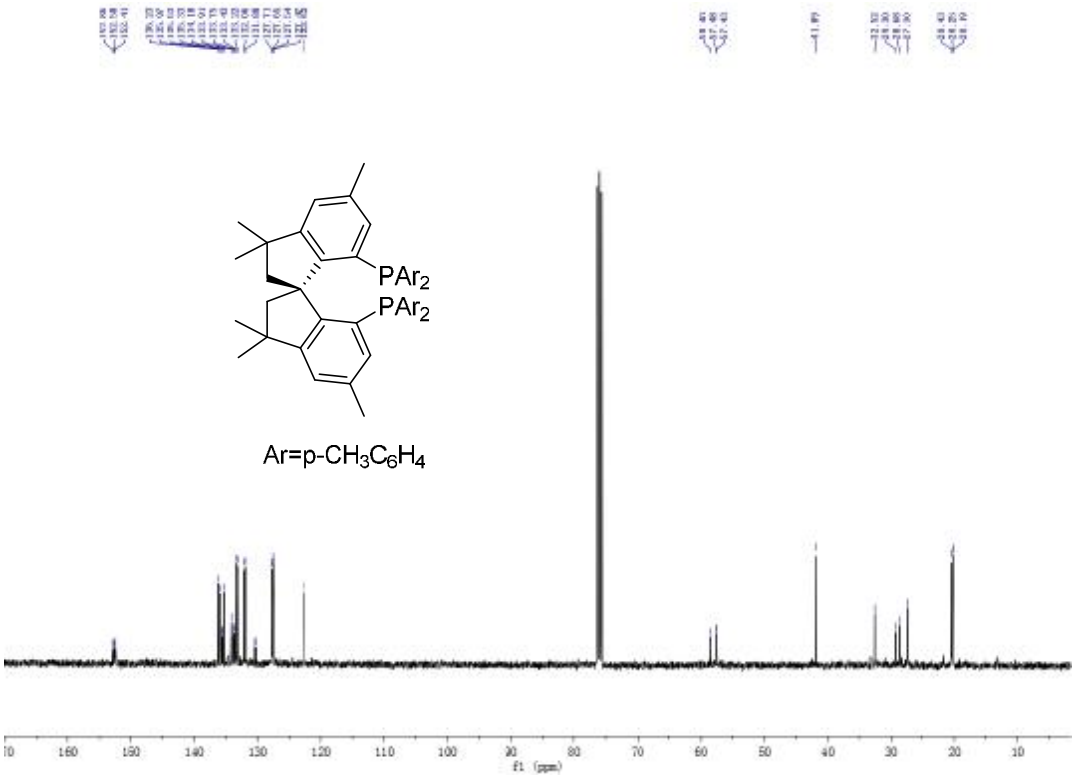

PPh2
PPh2
f1 (ppm)

(*R*)-(3,3,3',3',7,7'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-5,5'-diyl)bis(di-p-tolylphosphane) (*R*)-**1b**

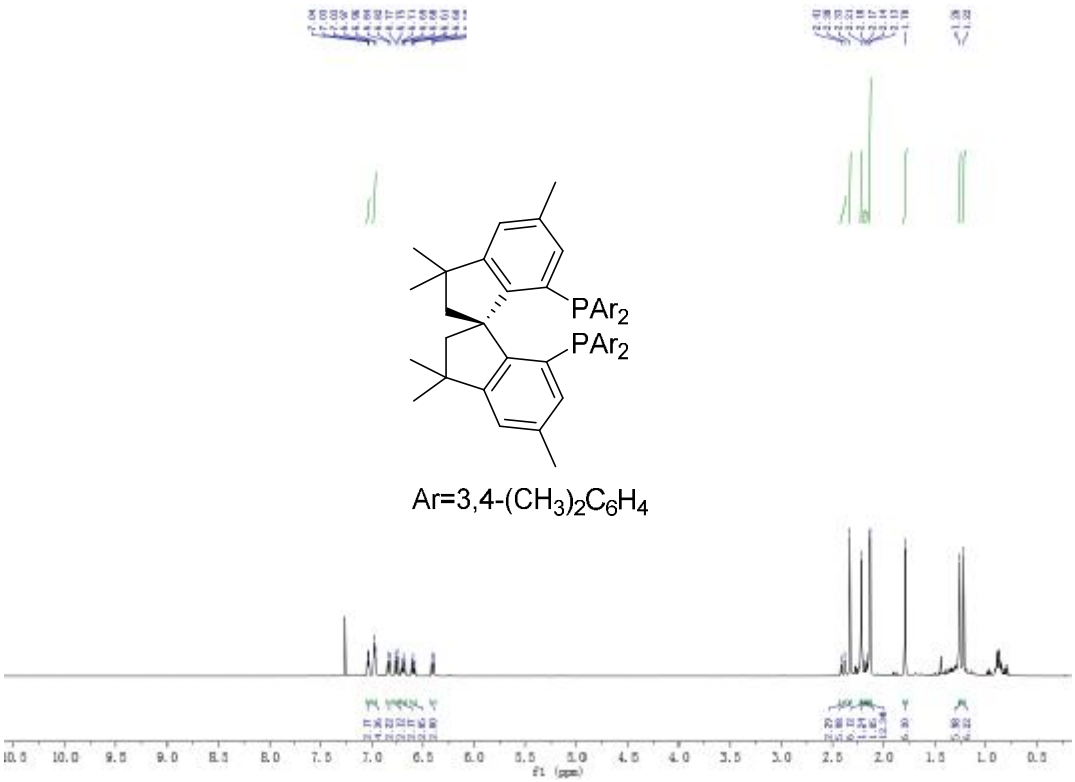


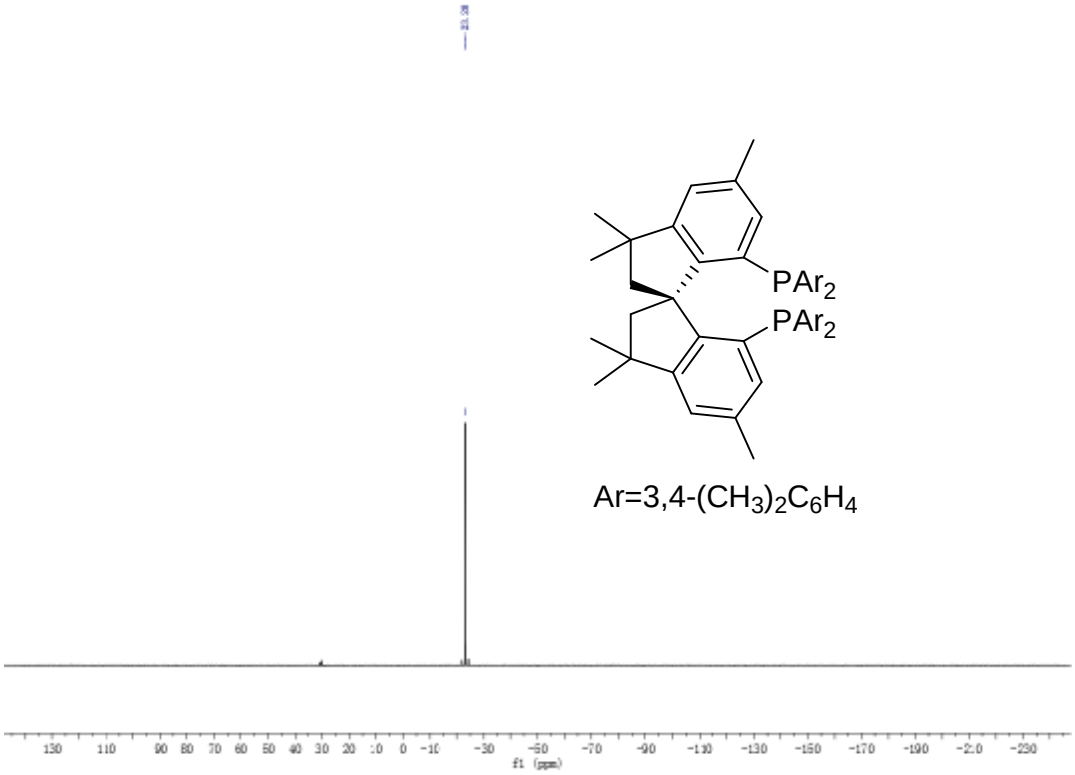


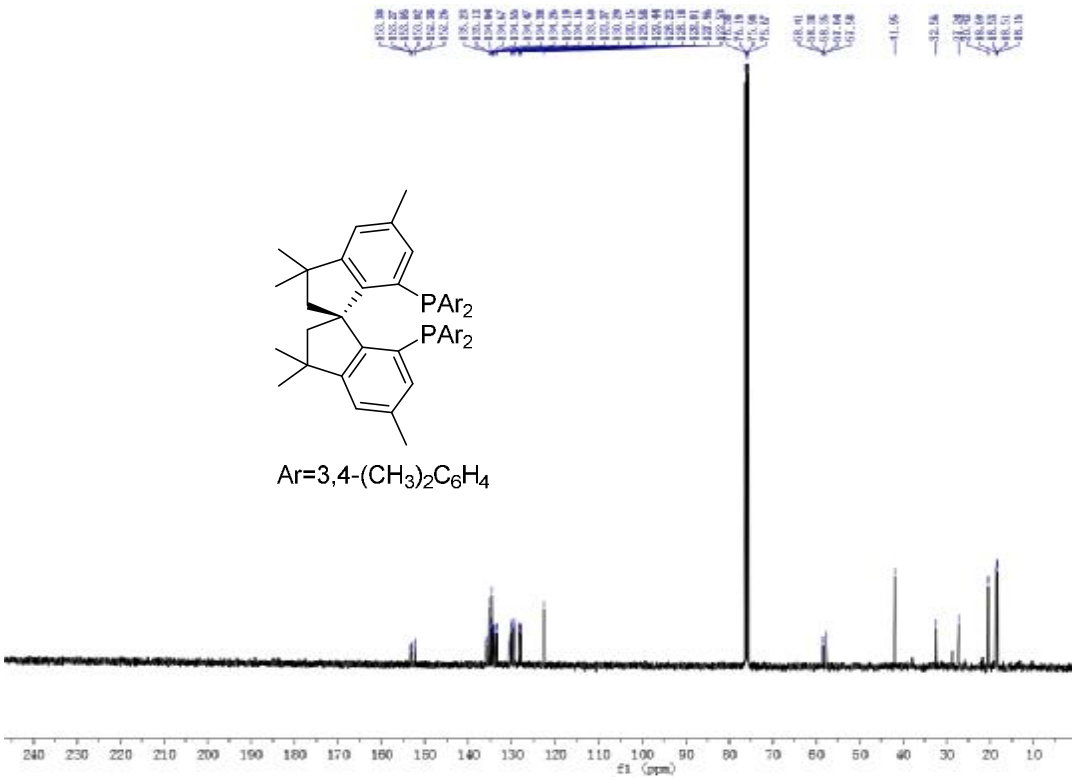




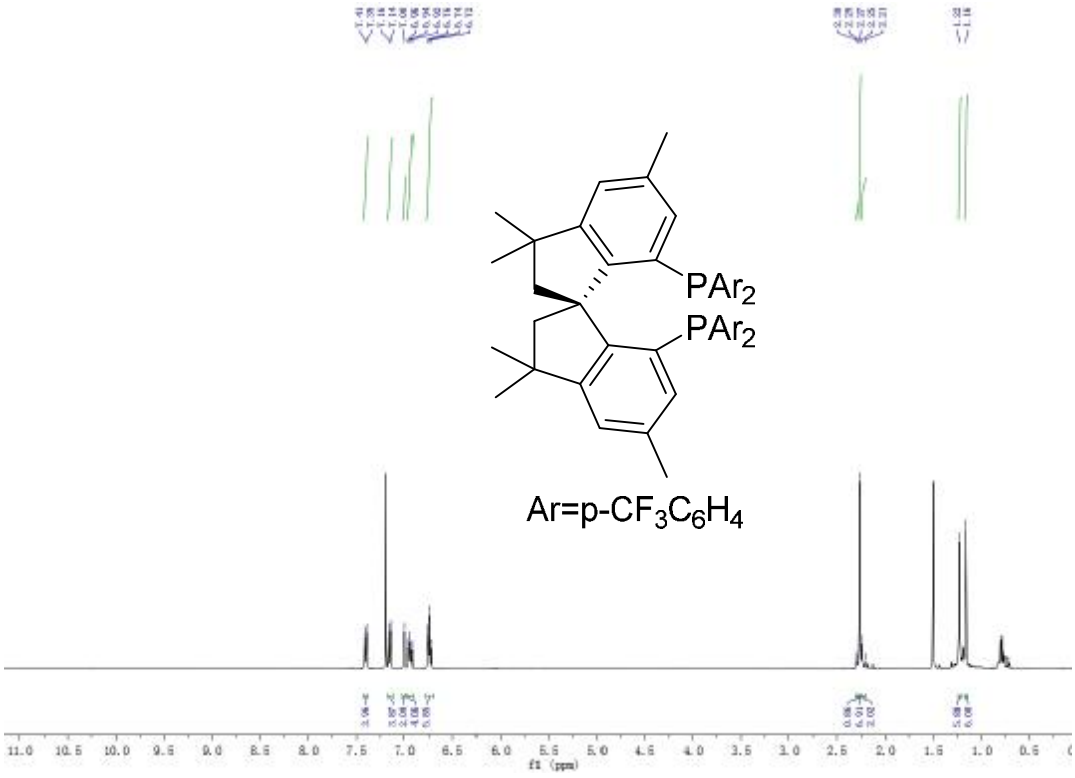
(*R*)-(3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(bis(3,4-dimethylphenyl)phosphane) (*R*)-**1c**

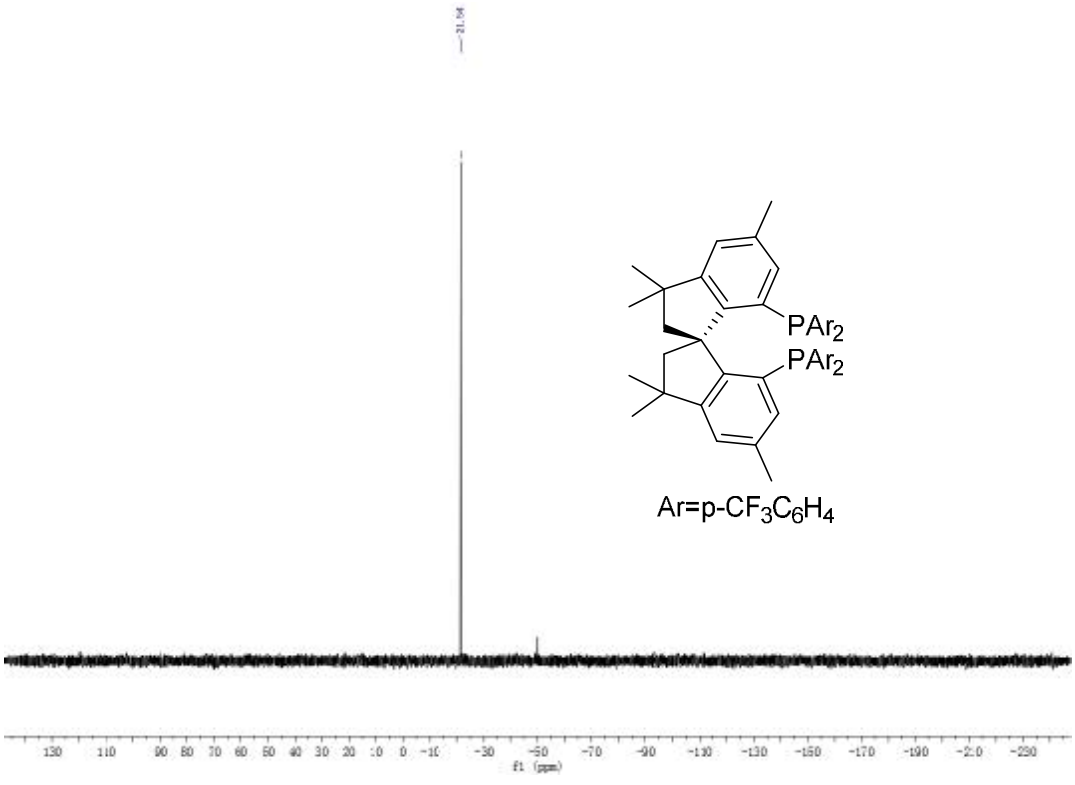


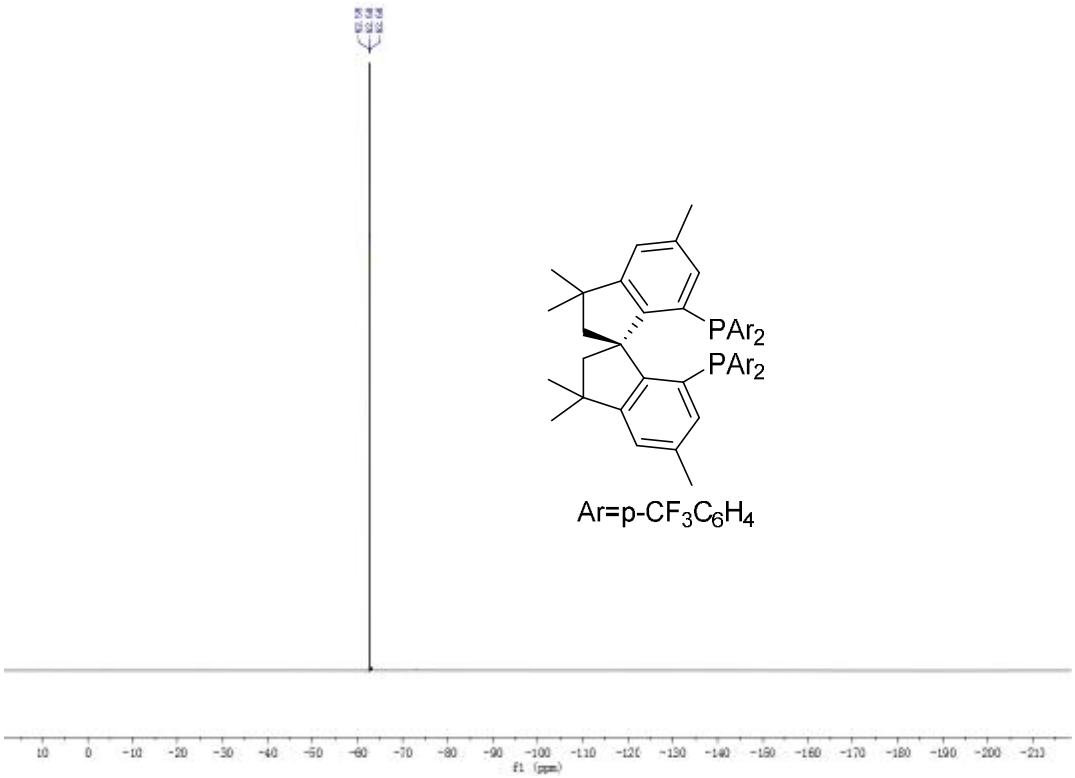

PAr2
PAr2
Ar=3,4-(CH3)2C6H4
f1 (ppm)

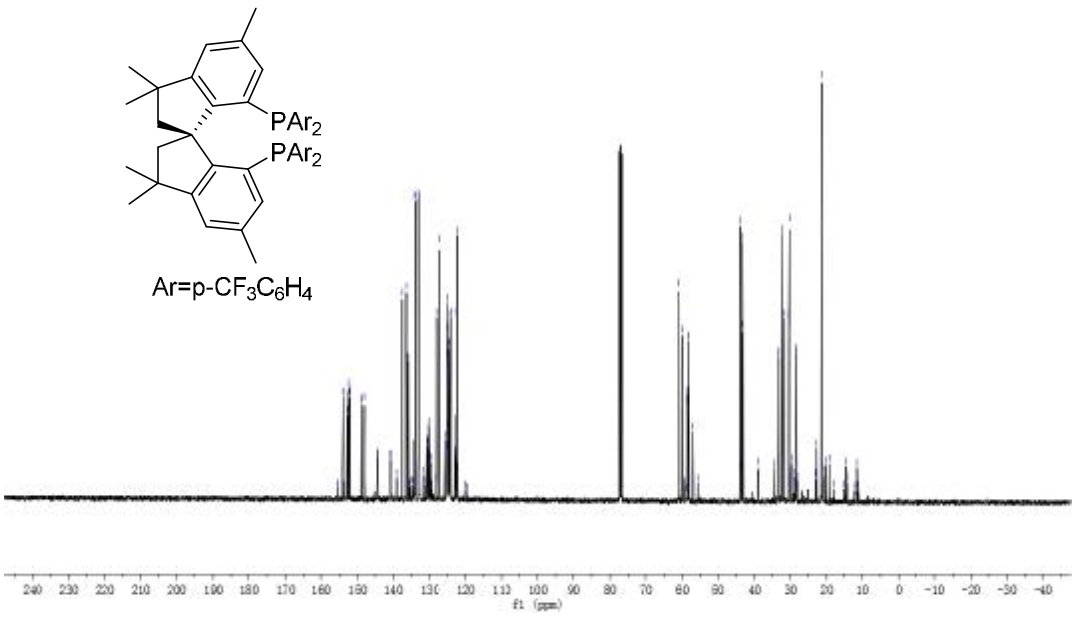

PAr2
PAr2
Ar=3,4-(CH3)2C6H4
f1 (ppm)

(*R*)-(3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diyl)bis(bis(4-(trifluoro methyl)phenyl)phosphane) (*R*)-**1d**

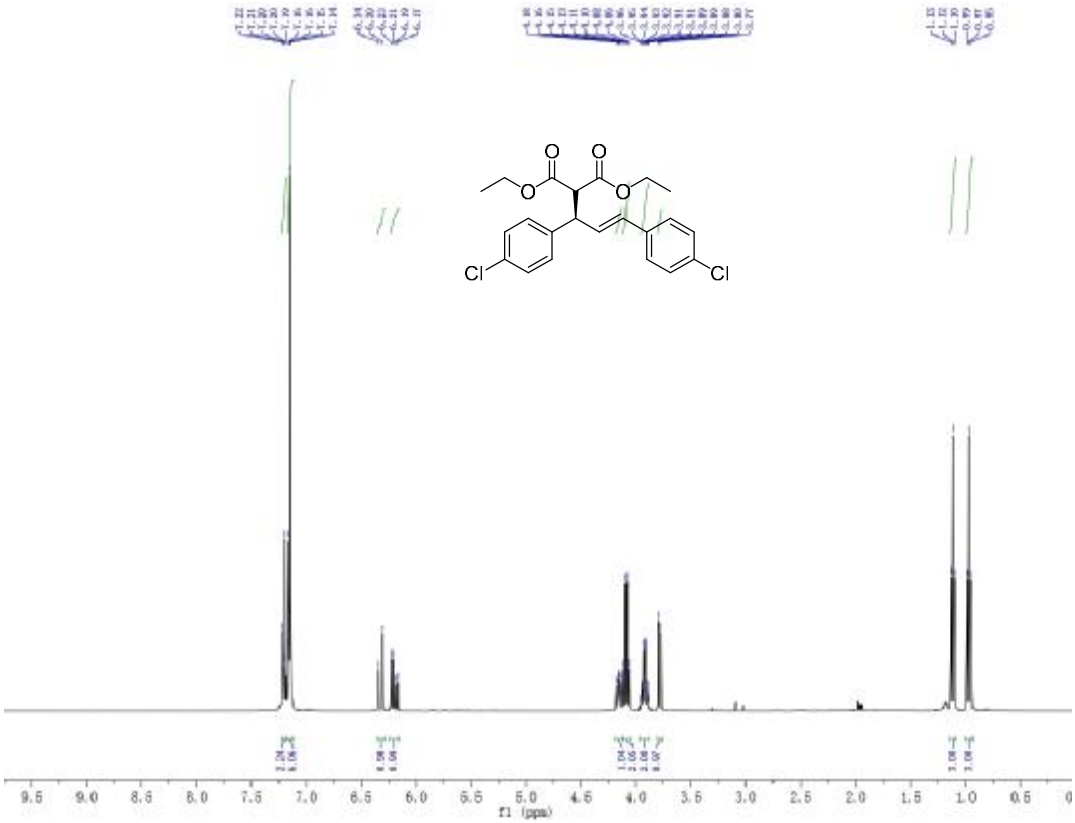


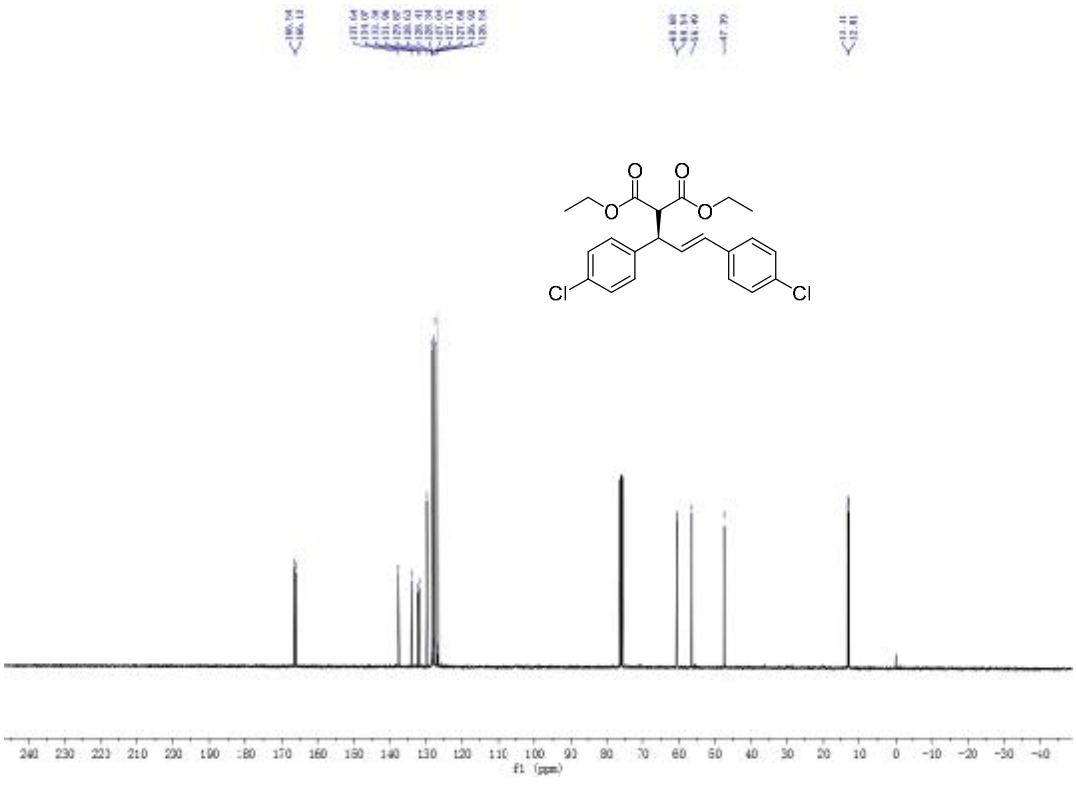



PAr2
PAr2
Ar=p-CF3C6H4
f1 (ppm)

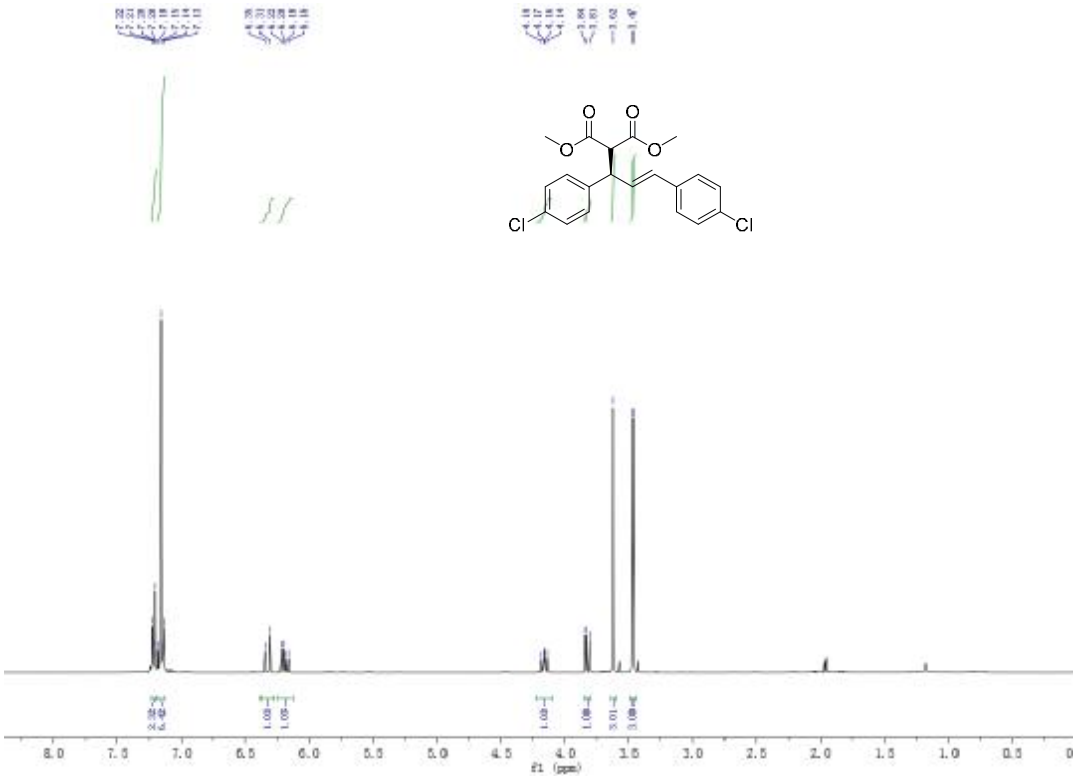

PAr2
PAr2
Ar=p-CF3C6H4
f1 (ppm)

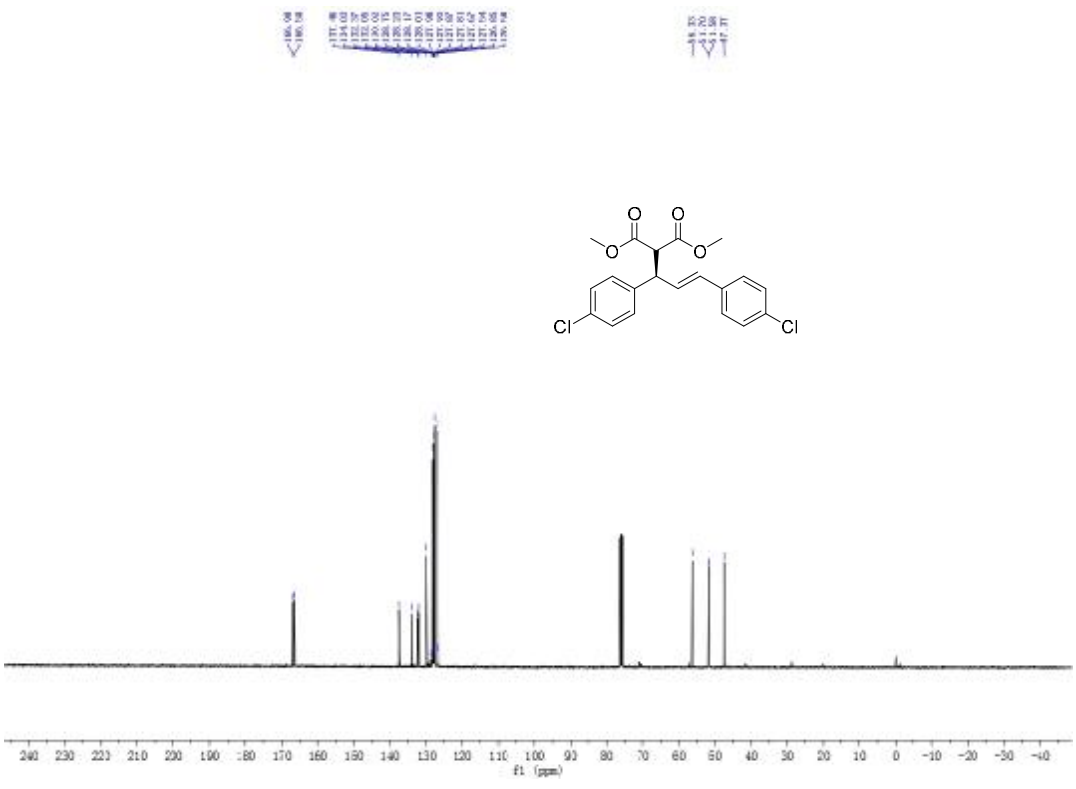
Diethyl (*R*,*E*)-2-(1,3-bis(4-chlorophenyl)allyl)malonate (**4a**)





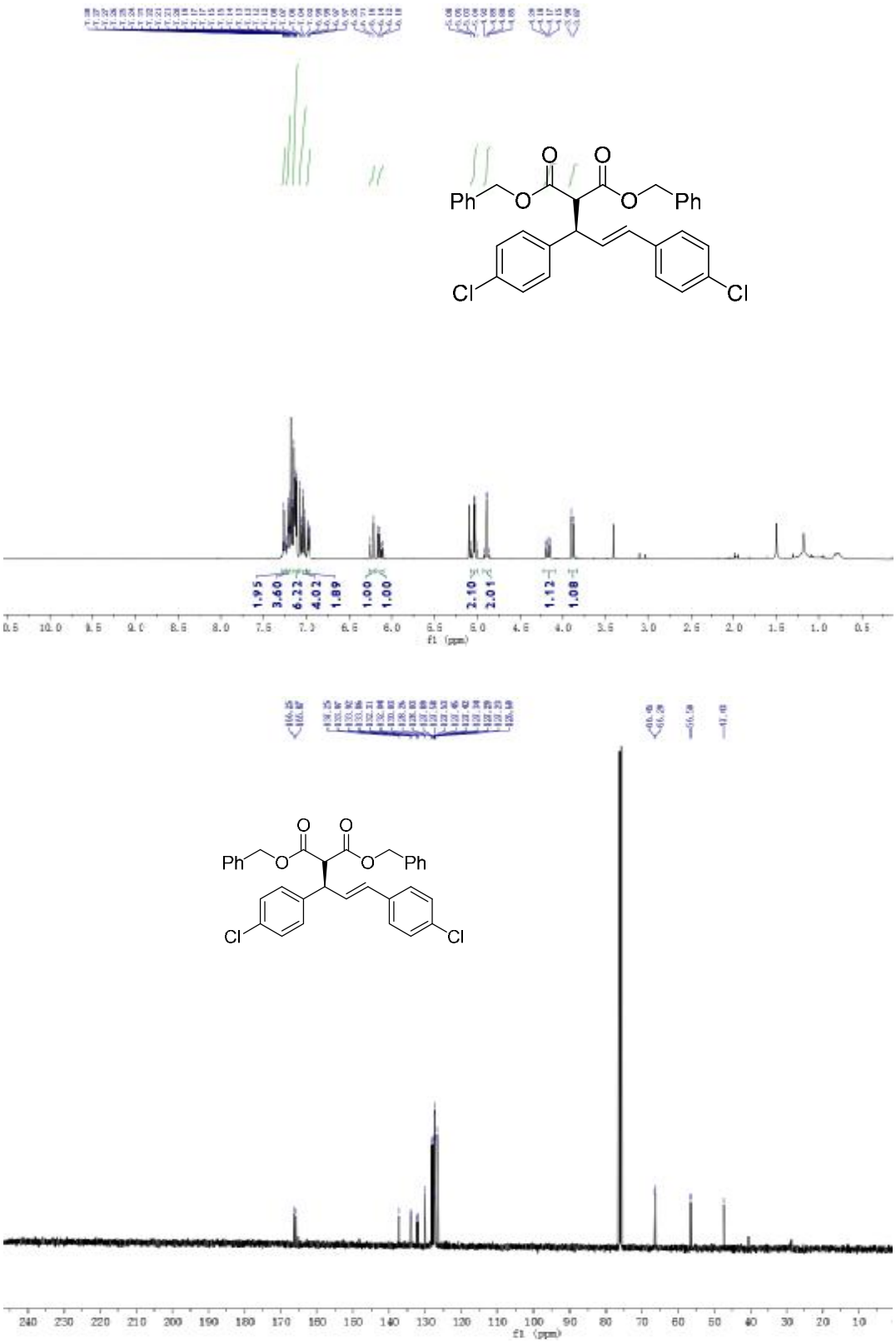
Dimethyl (*R*,*E*)-2-(1,3-bis(4-chlorophenyl)allyl)malonate (**4b**)



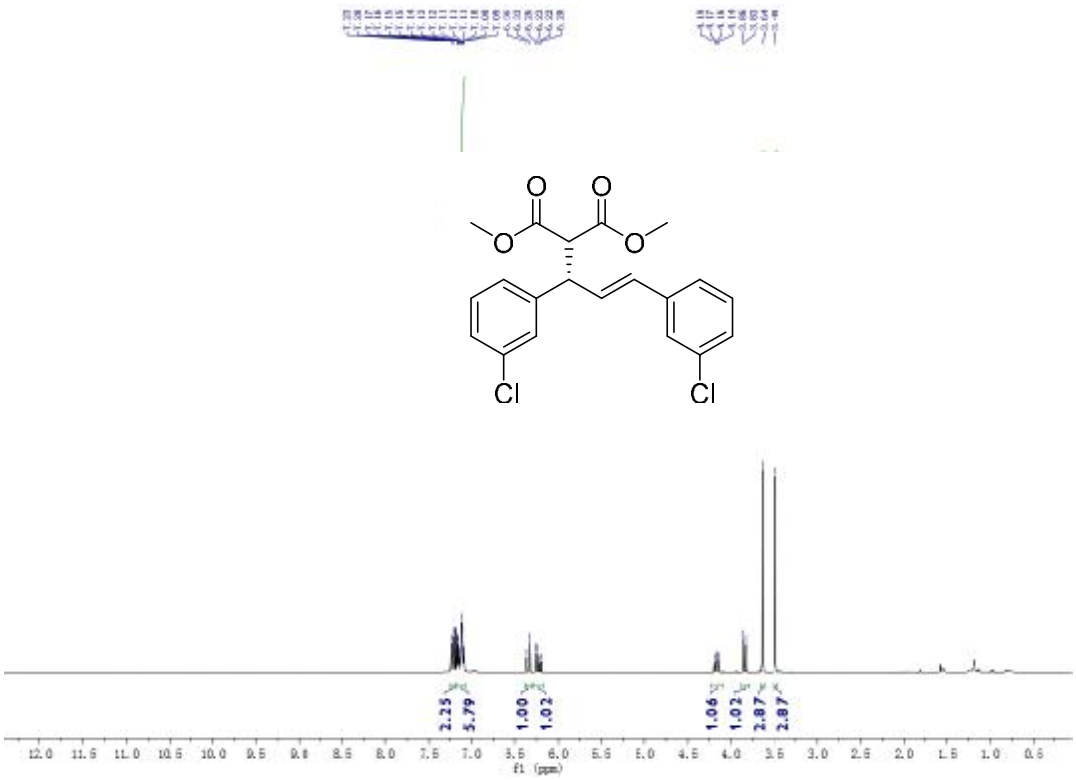


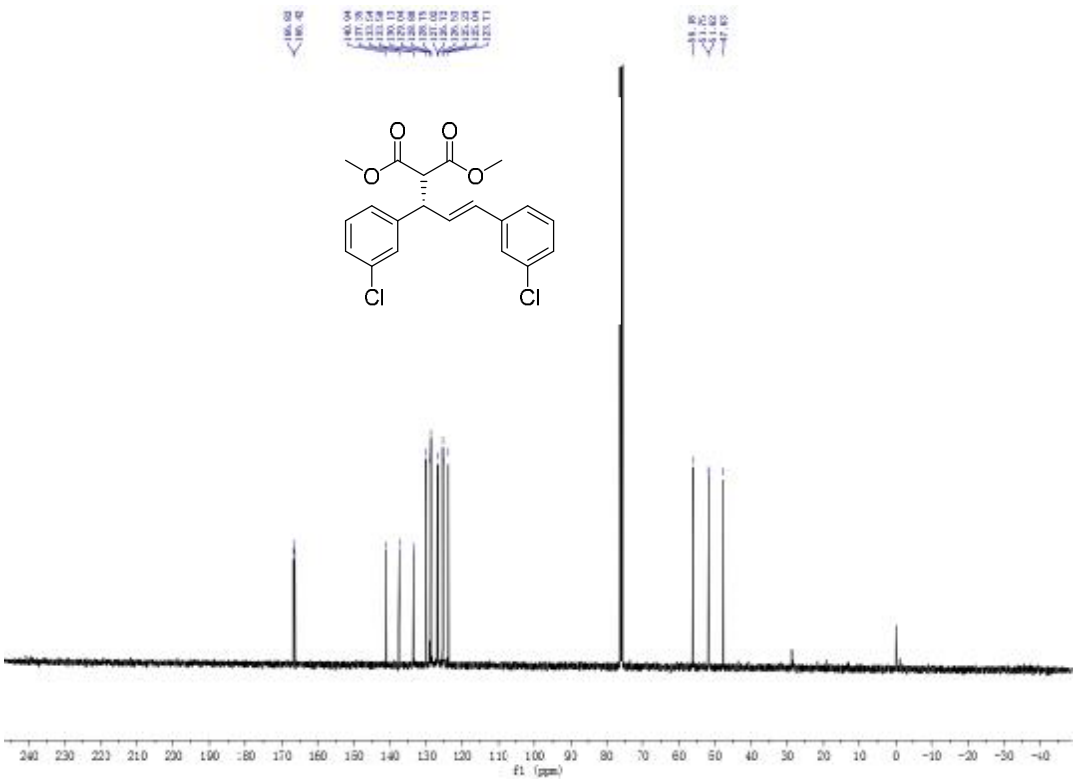
Diisopropyl (*R*,*E*)-2-(1,3-bis(4-chlorophenyl)allyl)malonate (**4c**)

Dibenzyl (*R*,*E*)-2-(1,3-bis(4-chlorophenyl)allyl)malonate (**4d**)

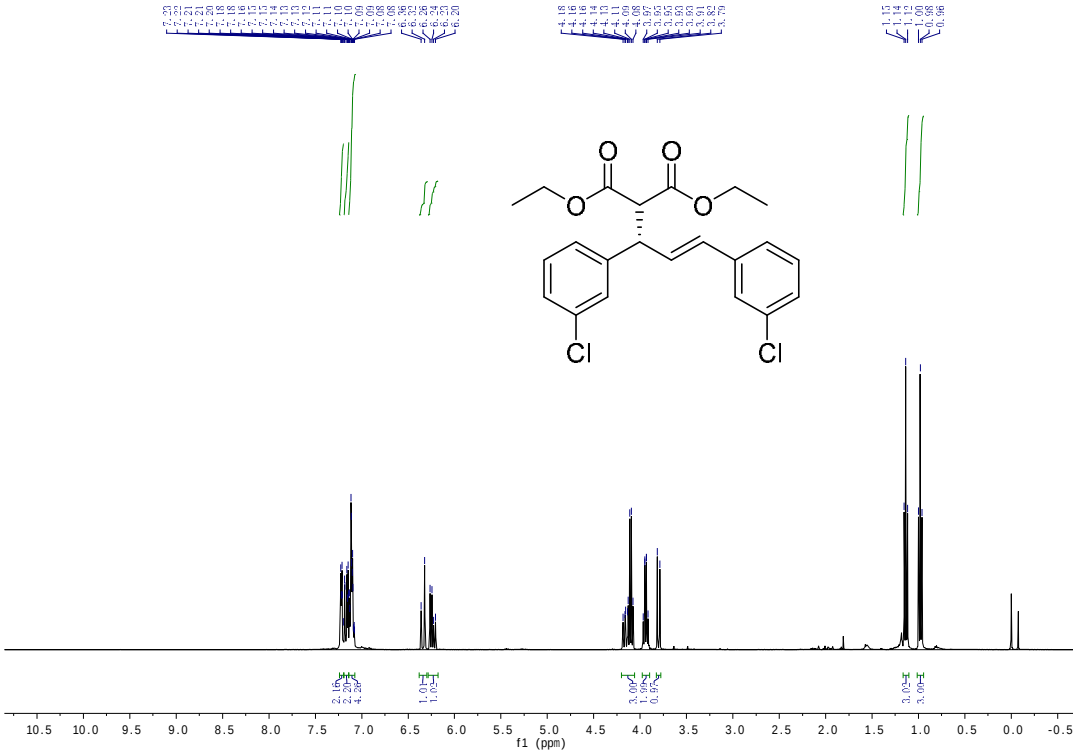


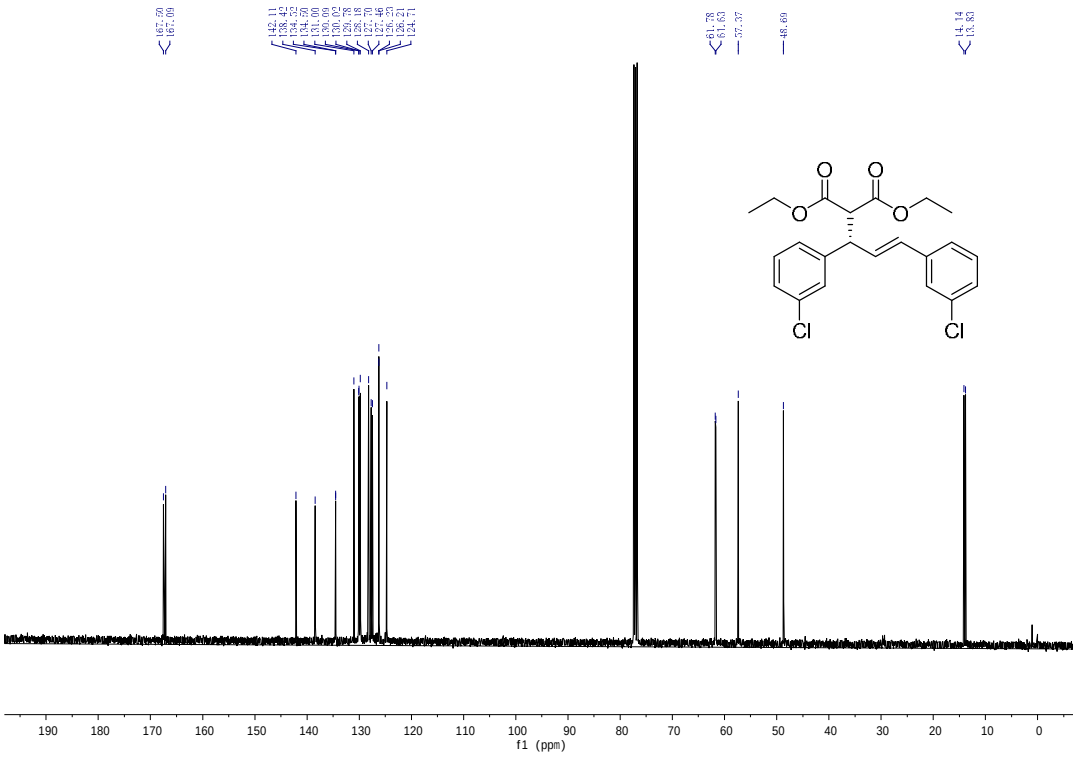
Dimethyl (*S*,*E*)-2-(1,3-bis(3-chlorophenyl)allyl)malonate (**4e**)





Diethyl (*S*,*E*)-2-(1,3-bis(3-chlorophenyl)allyl)malonate (**4f**)





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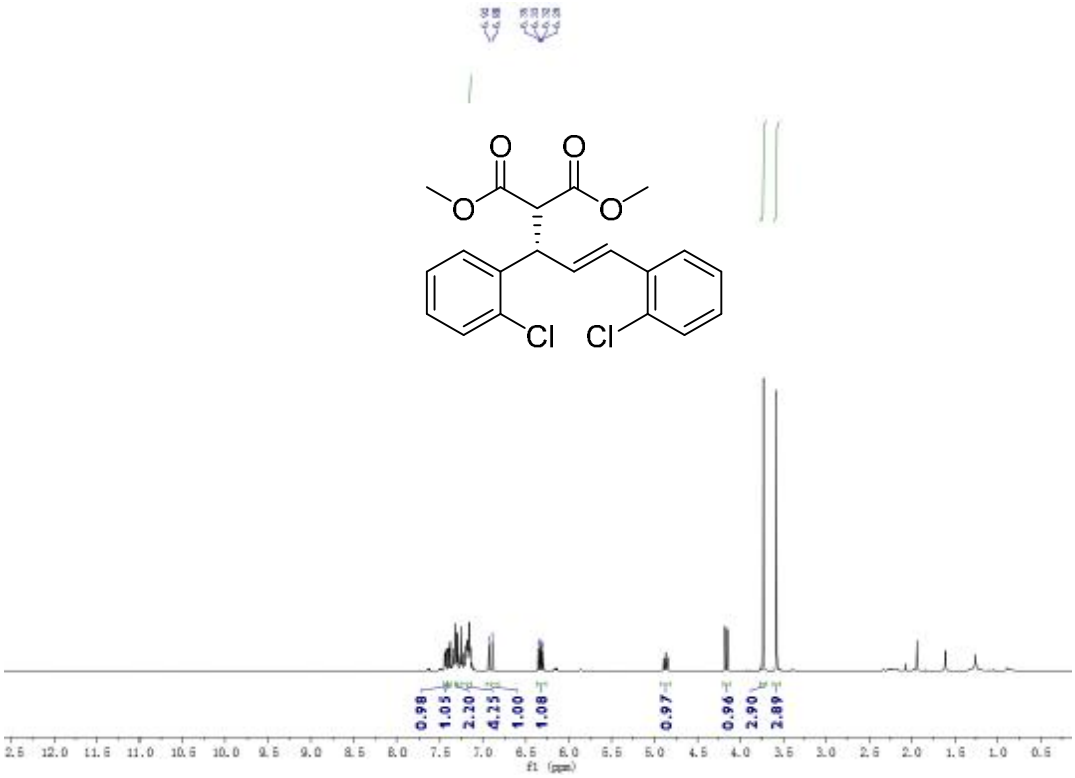
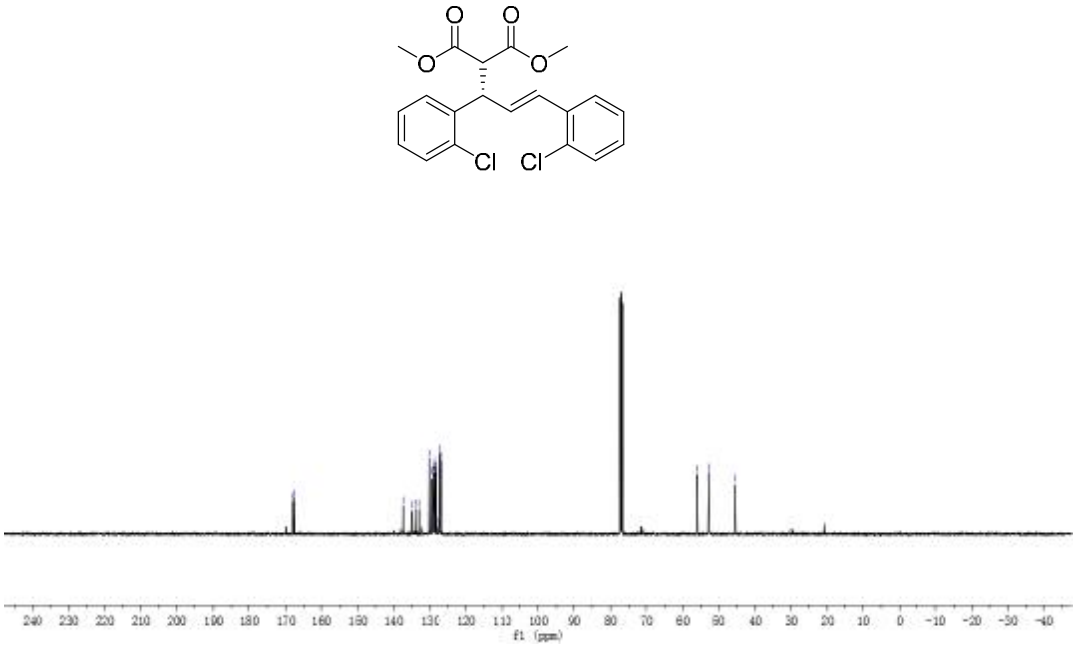
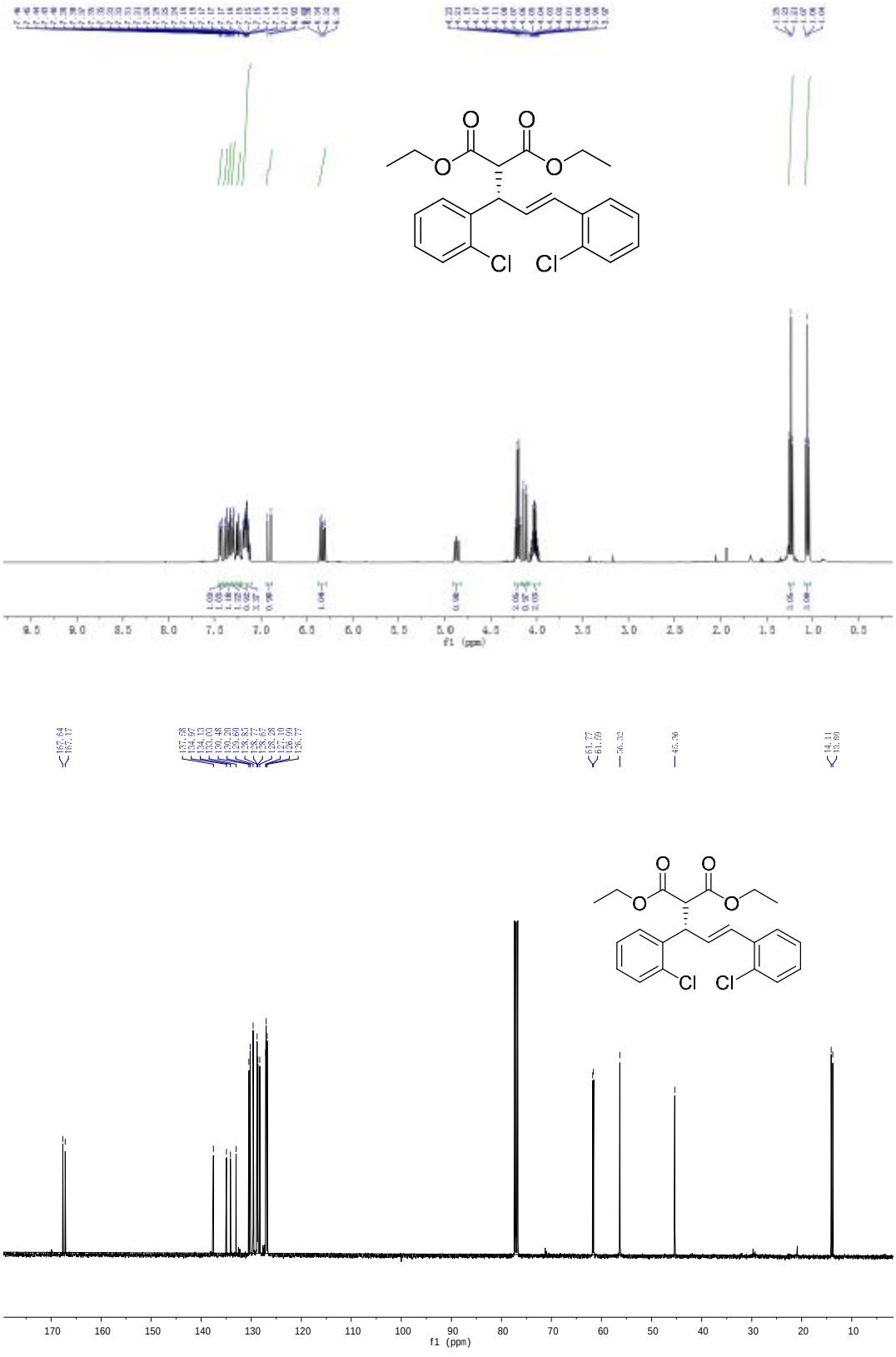
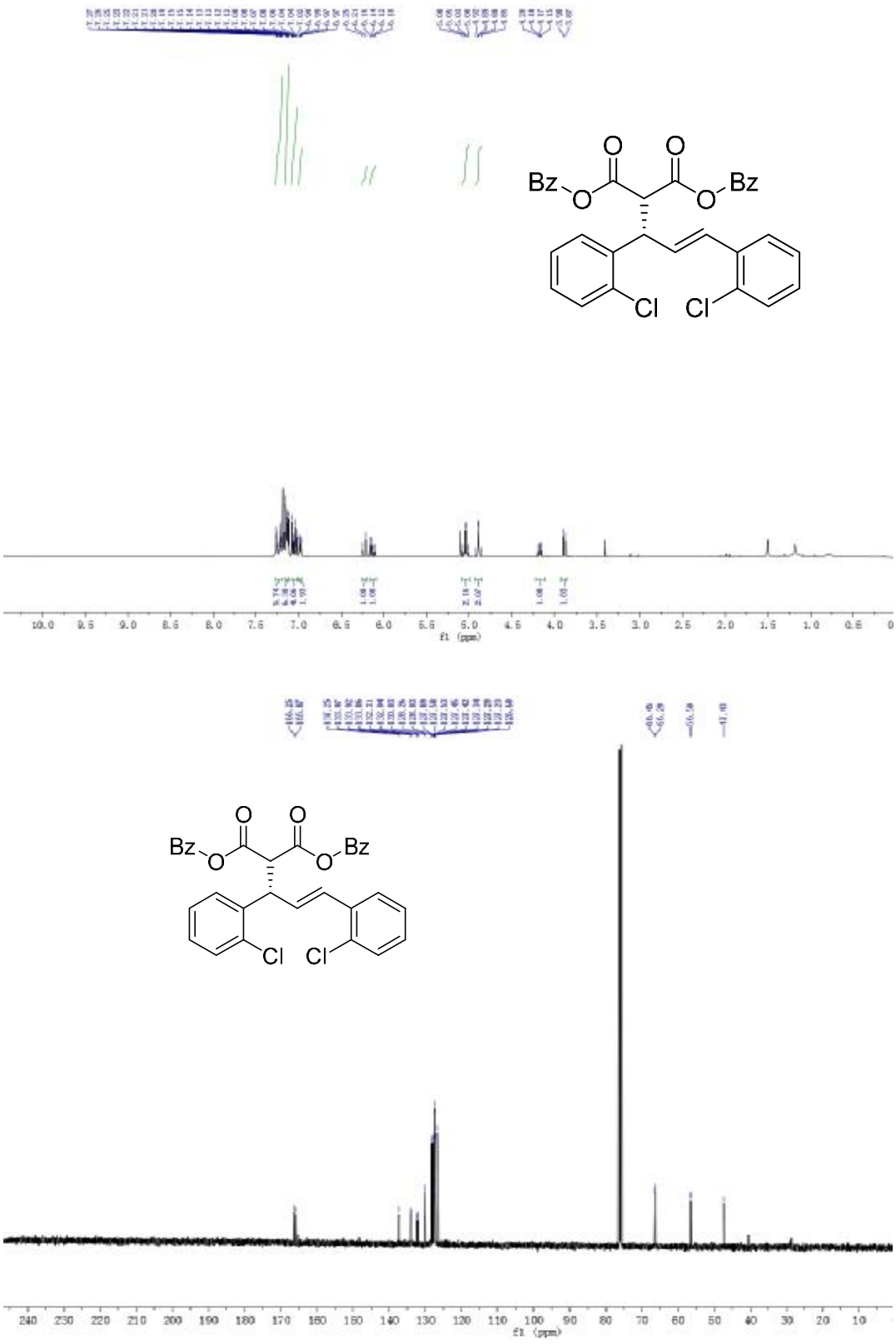




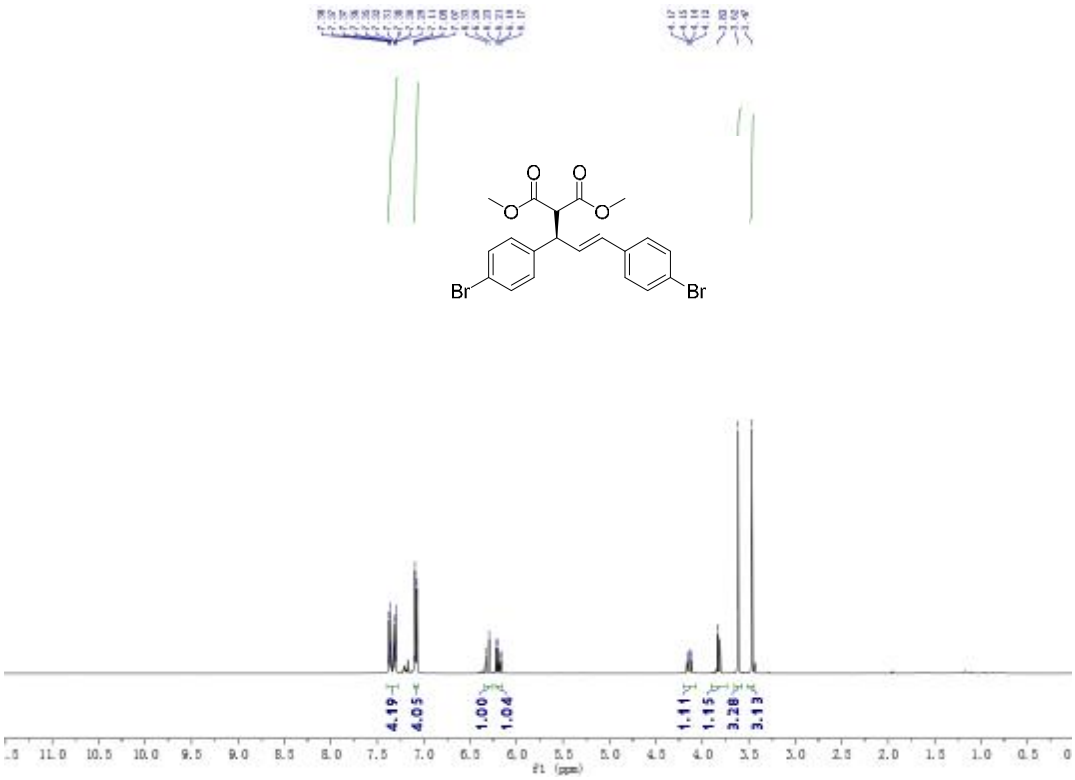
Diethyl (*S*,*E*)-2-(1,3-bis(2-chlorophenyl)allyl)malonate (**4h**)

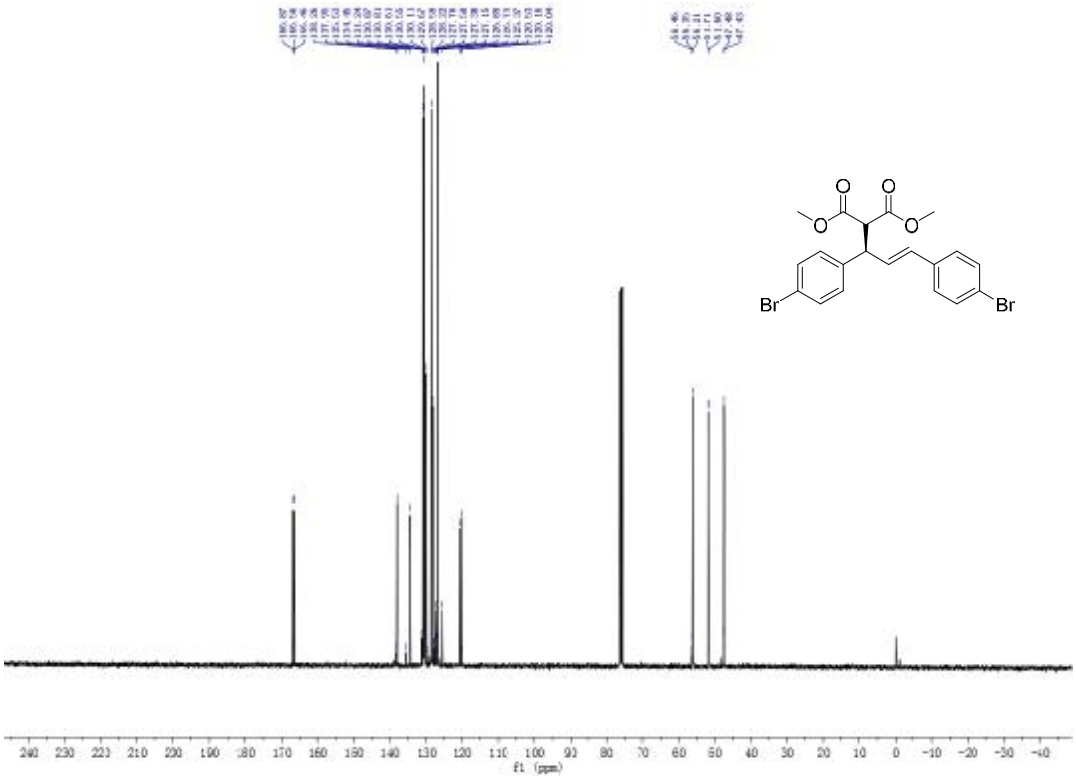


Dibenzyl (*S*,*E*)-2-(1,3-bis(2-chlorophenyl)allyl)malonate (**4i**)

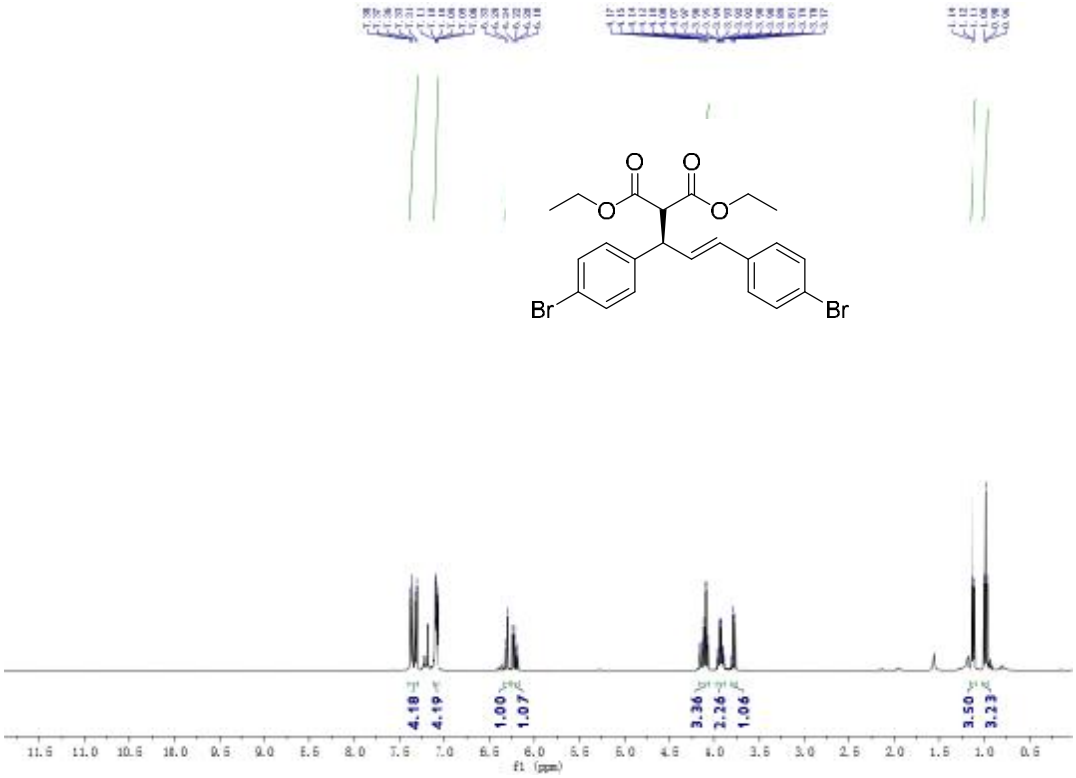


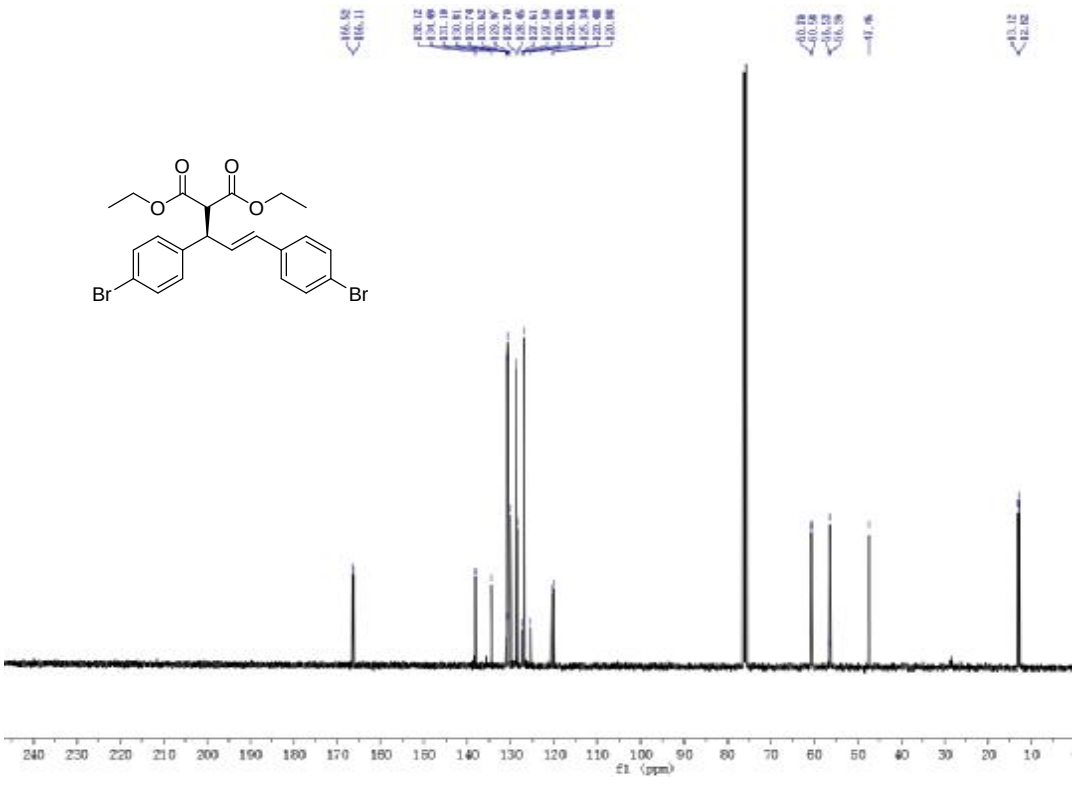
Dimethyl (*R*,*E*)-2-(1,3-bis(4-bromophenyl)allyl)malonate (**4j**)



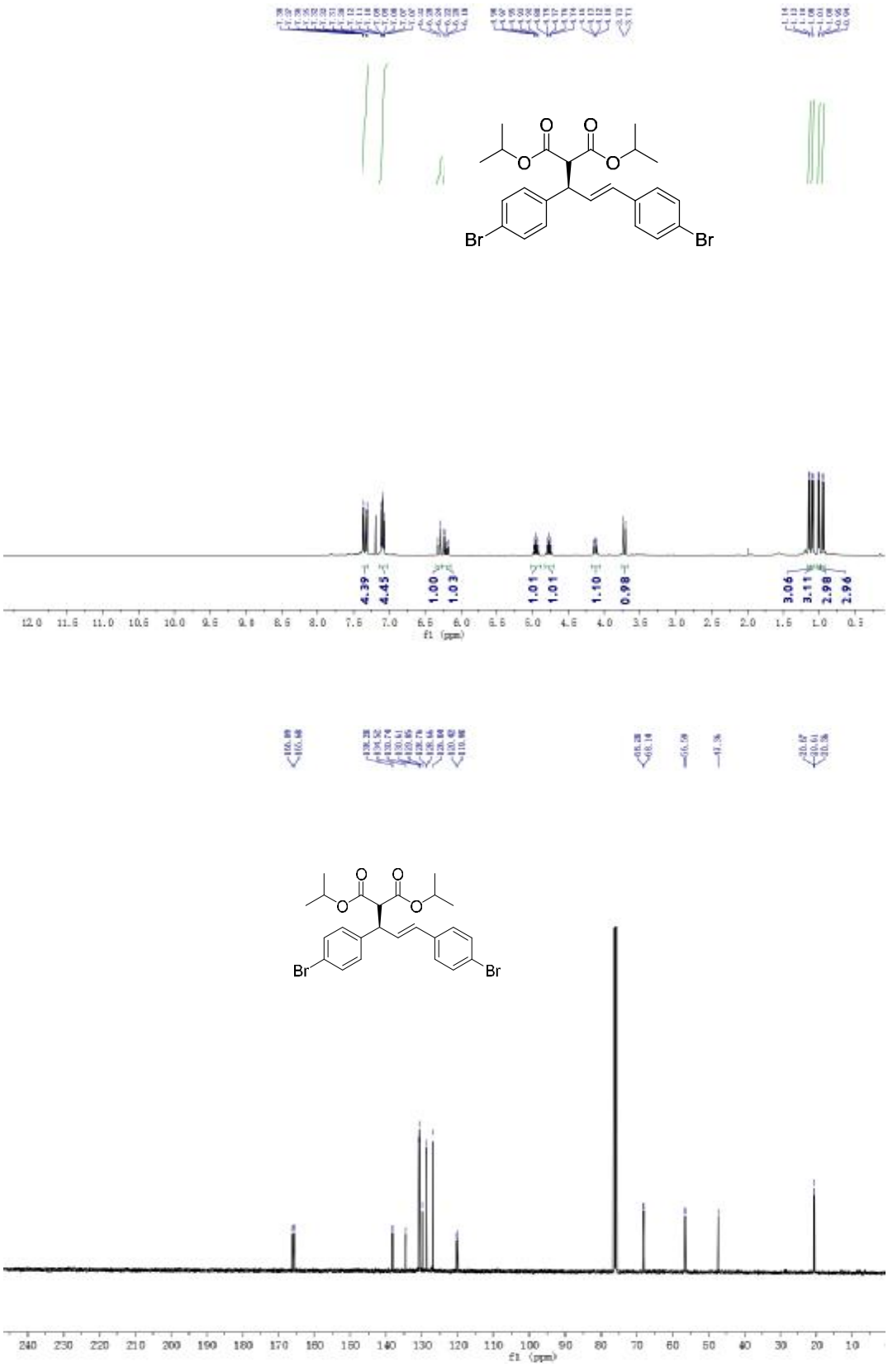


Diethyl (*R*,*E*)-2-(1,3-bis(4-bromophenyl)allyl)malonate (**4k**)

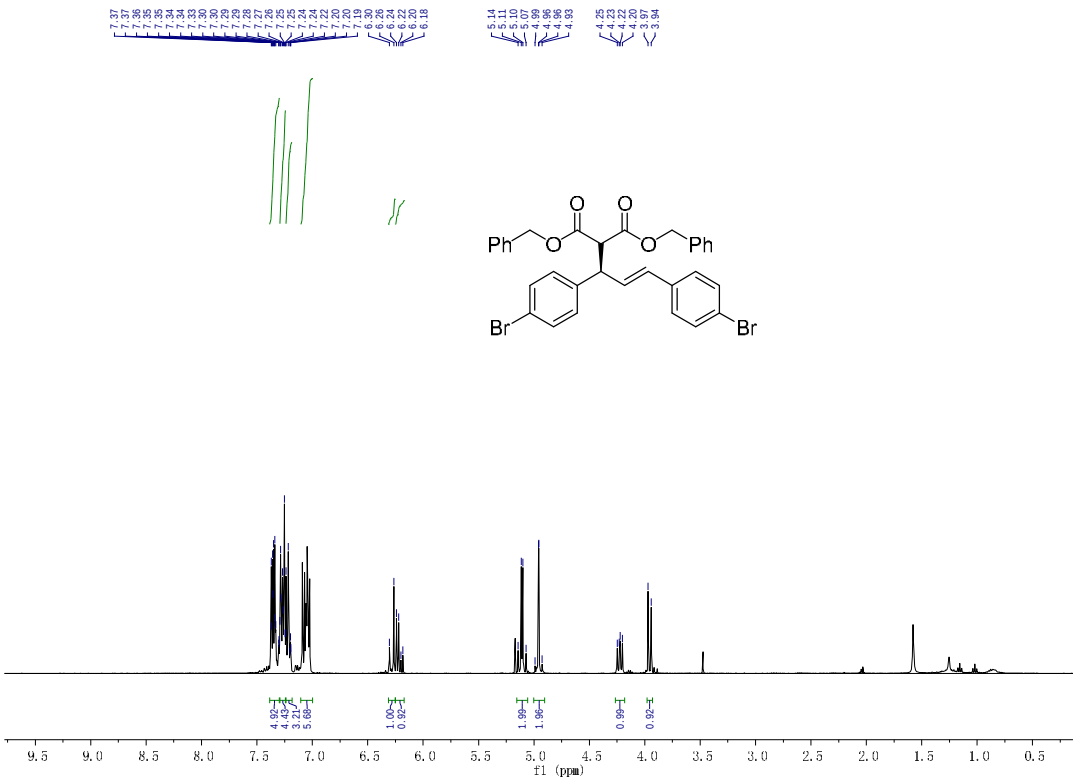


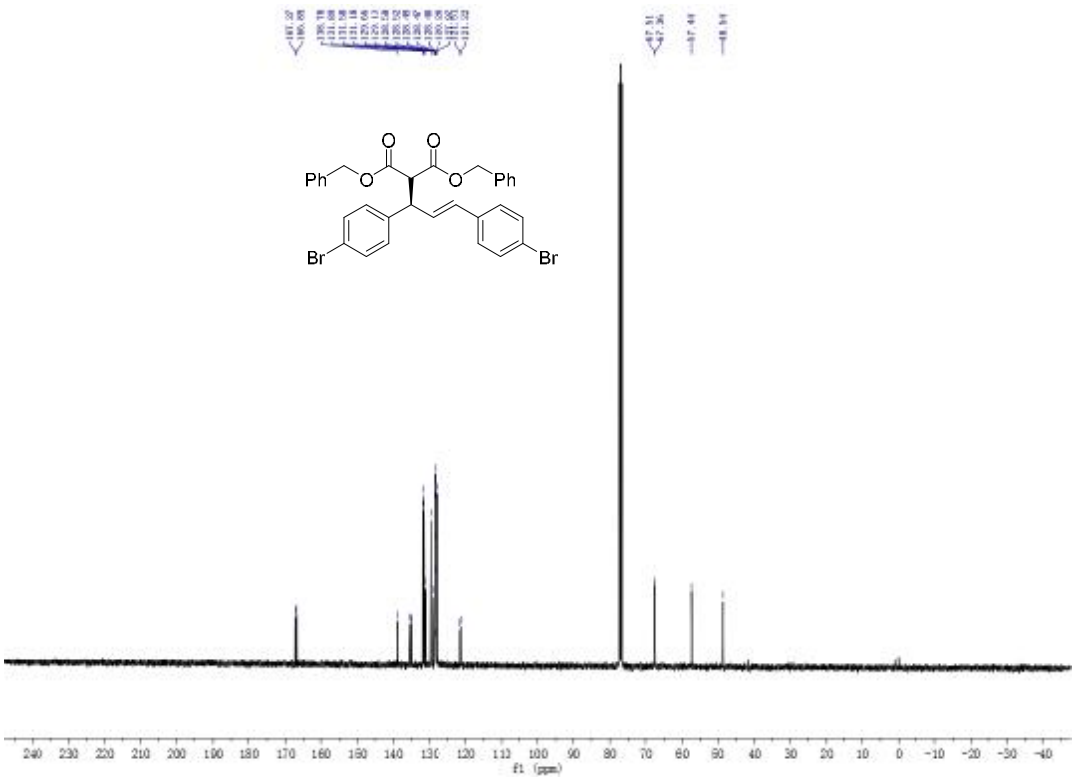


Diisopropyl (*R*,*E*)-2-(1,3-bis(4-bromophenyl)allyl)malonate (**4l**)

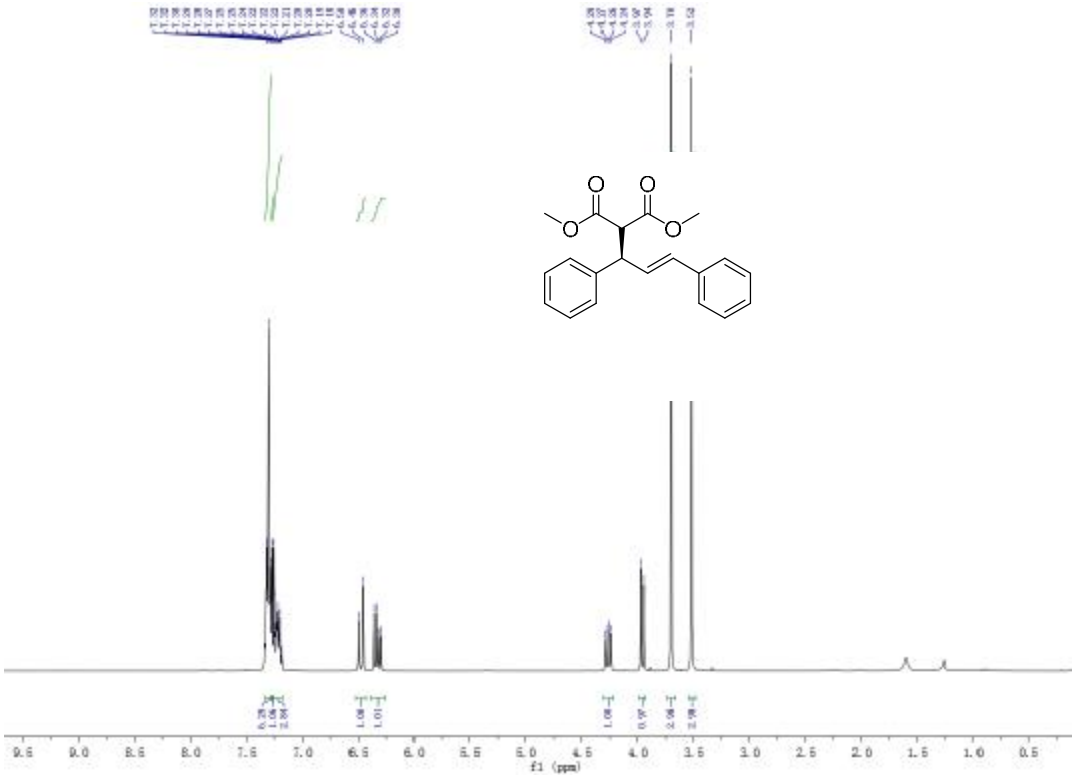


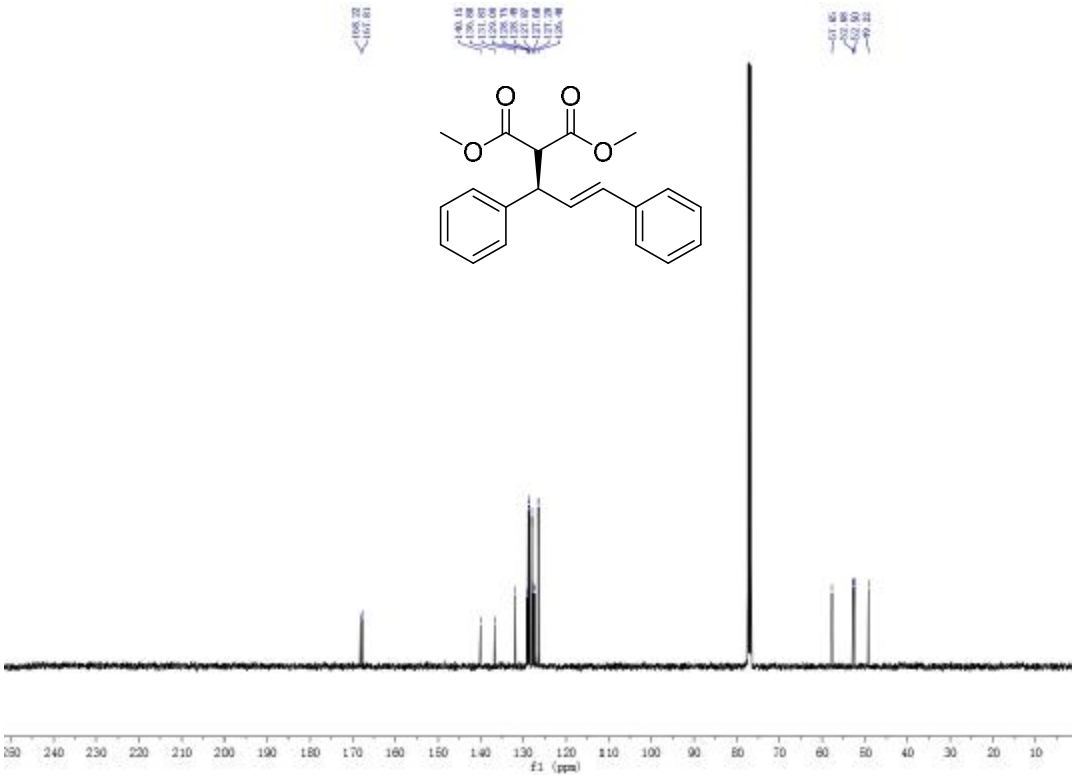
Dibenzyl (*R*,*E*)-2-(1,3-bis(4-bromophenyl)allyl)malonate (**4m**)



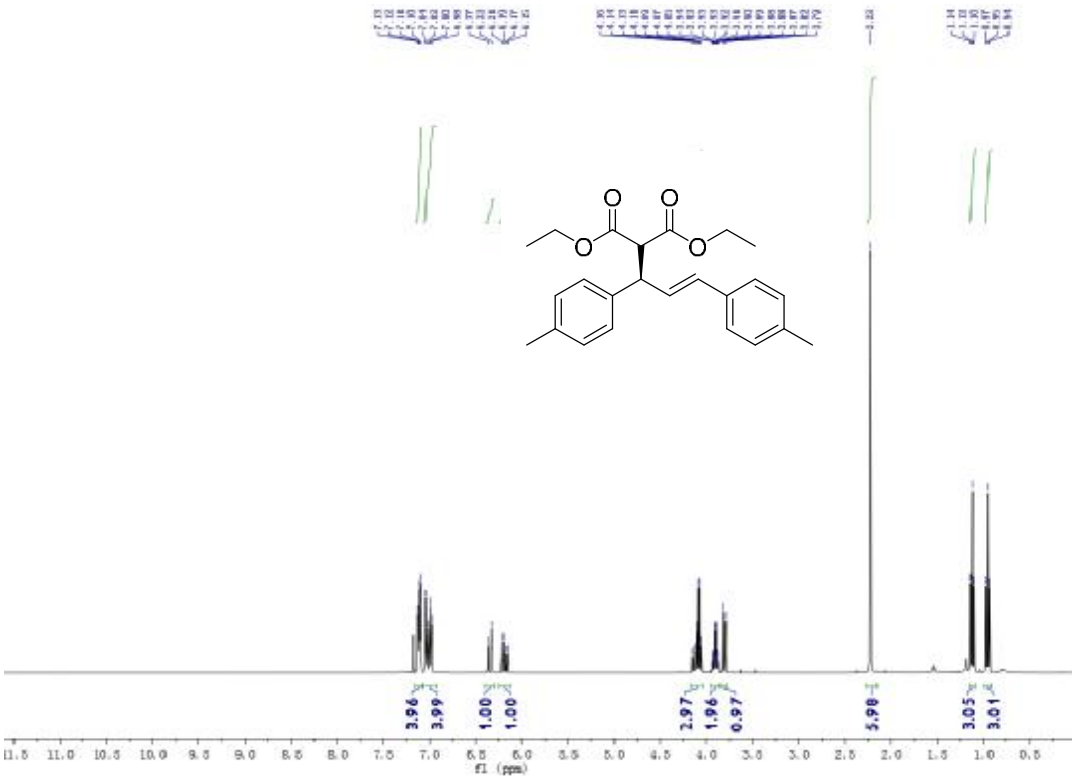


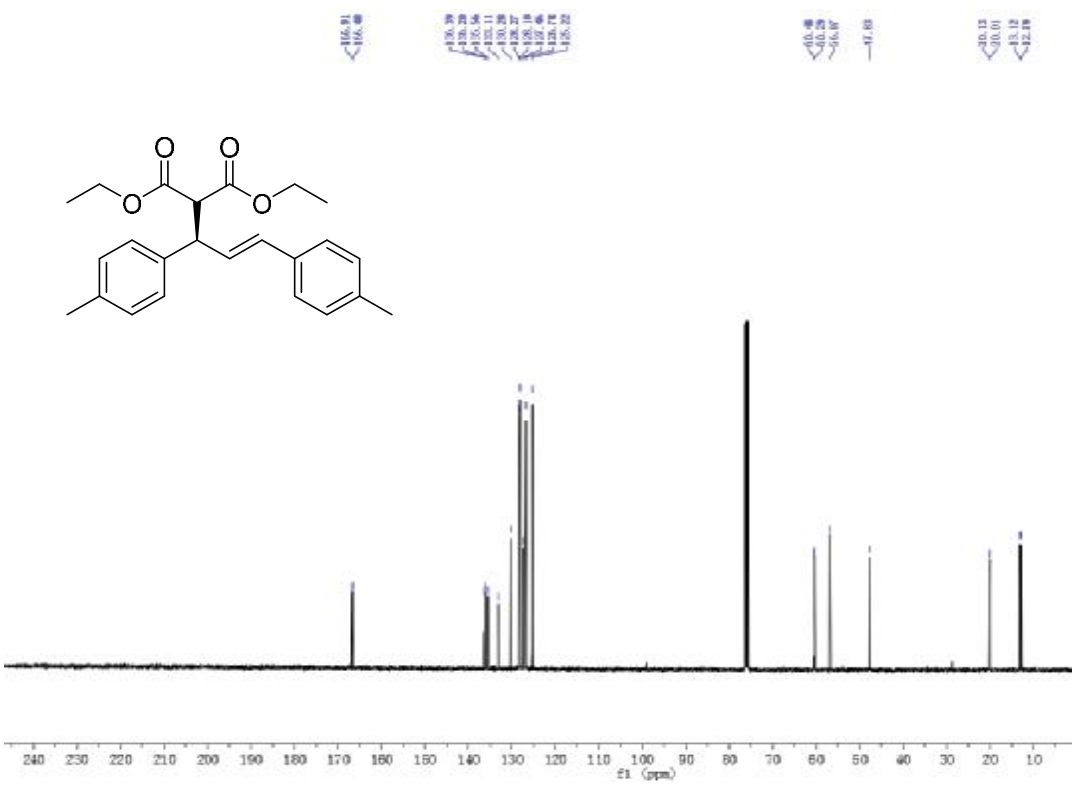
Dimethyl (*R*,*E*)-2-(1,3-diphenylallyl)malonate (**4n**)





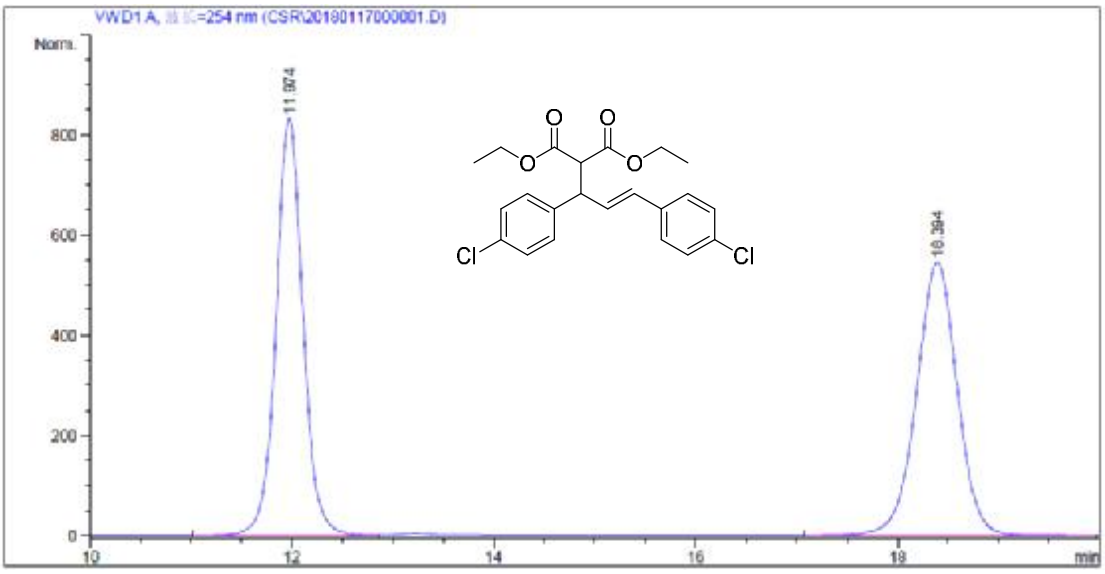
Diethyl (*R*,*E*)-2-(1,3-di-p-tolylallyl)malonate (**4o**)



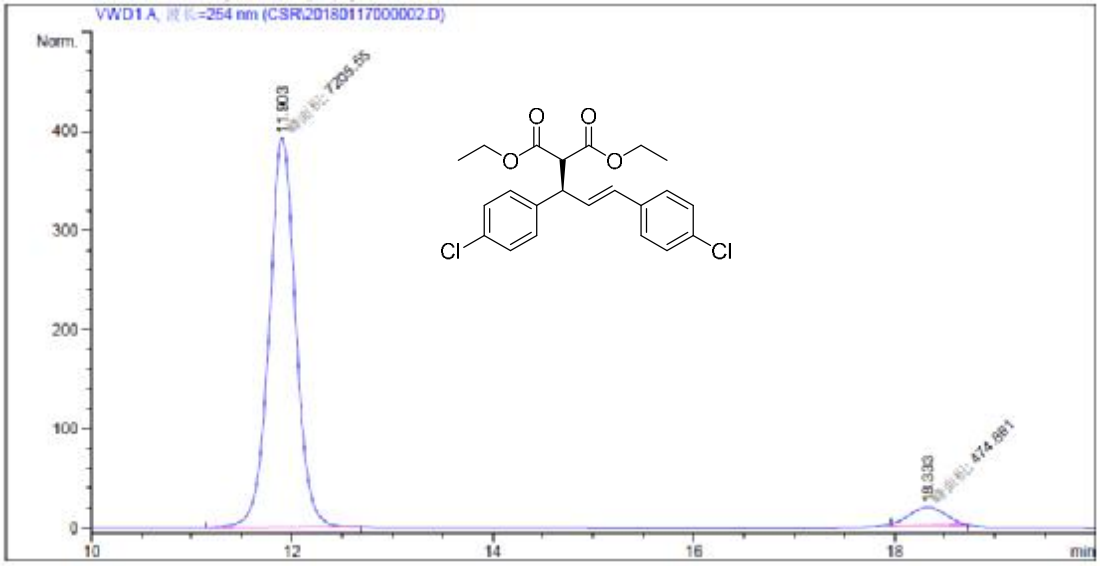


Copies of HPLC trace

Diethyl (*R*,*E*)-2-(1,3-bis(4-chlorophenyl)allyl)malonate (**4a**)

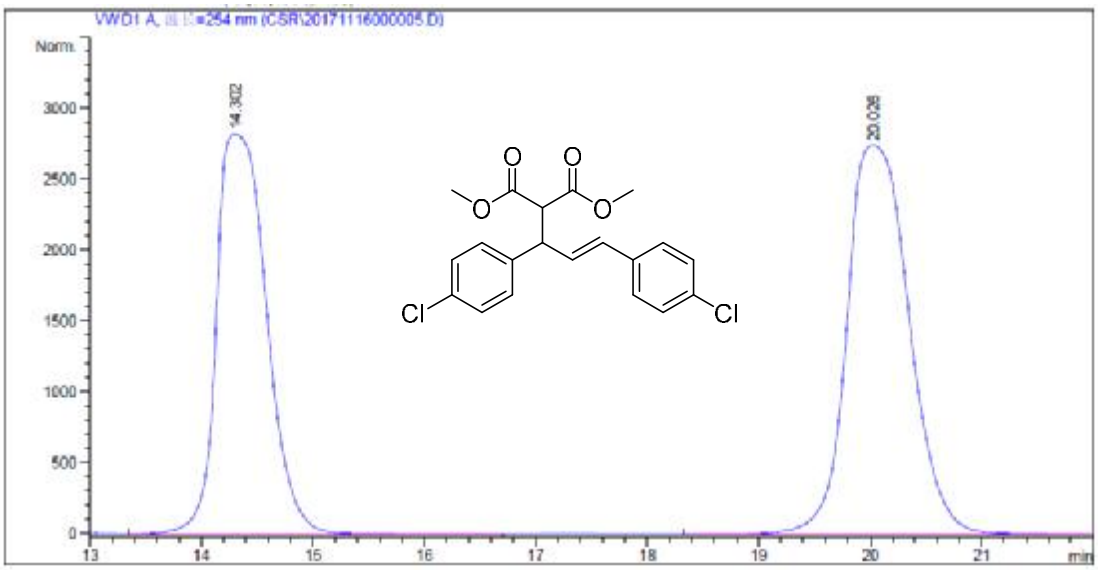


#	[min]		[min]	mAU	*s	[mAU]	%
1	11.974	VV	0.2837	1.54483e4		831.66119	50.2498
2	18.394	VB	0.4316	1.52947e4		546.02551	49.7502

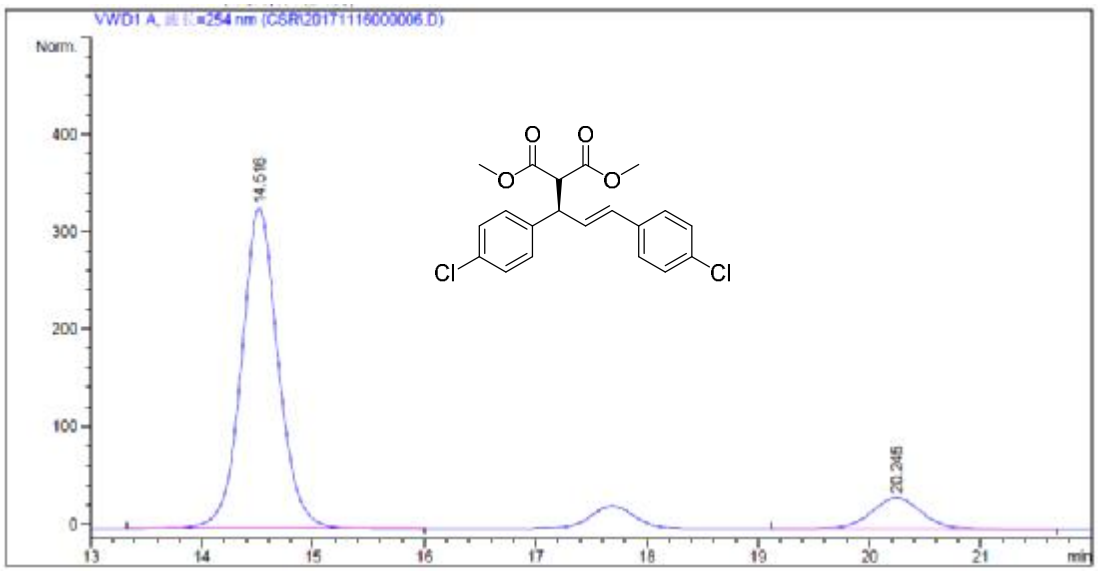


#	[min]		[min]	mAU	*s	[mAU]	%
1	11.903	MM	0.3058	7205.55127		392.70865	93.8172
2	18.333	MM	0.4192	474.86130		18.87784	6.1828

Dimethyl (*R*,*E*)-2-(1,3-bis(4-chlorophenyl)allyl)malonate (**4b**)

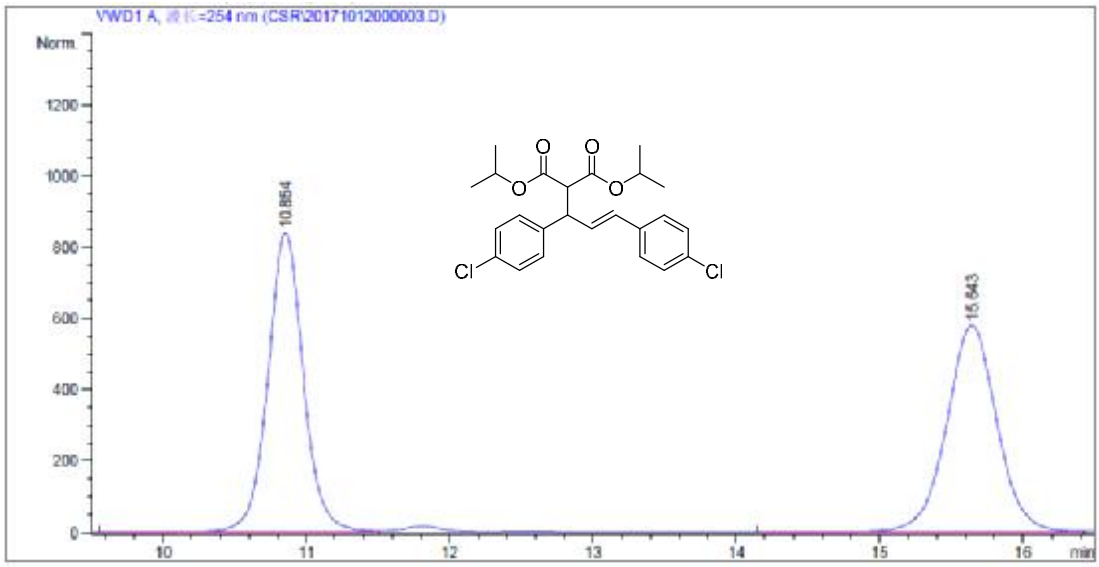


#	[min]		[min]	mAU	*s	[mAU]	%
1	14.302	VB	0.4875	8.81938e4		2817.64795	45.2876
2	20.026	VB	0.6050	1.06548e5		2740.77368	54.7124

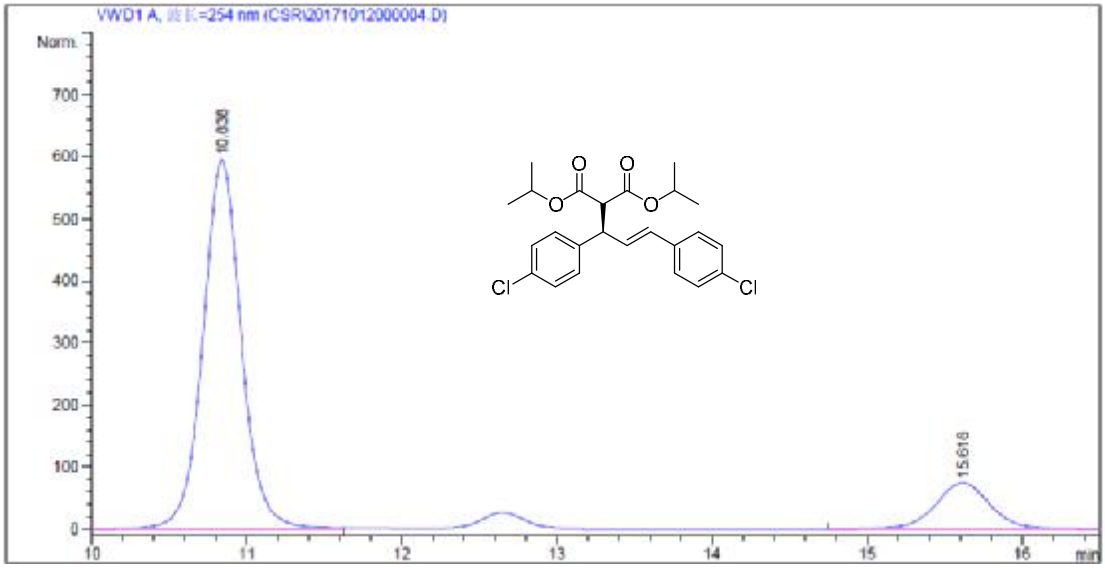


#	[min]		[min]	mAU	*s	[mAU]	%
1	14.516	VB	0.3504	7575.99219		328.78412	88.2677
2	20.245	BB	0.4861	1006.98145		31.78816	11.7323

Diisopropyl (*R*,*E*)-2-(1,3-bis(4-chlorophenyl)allyl)malonate (**4c**)

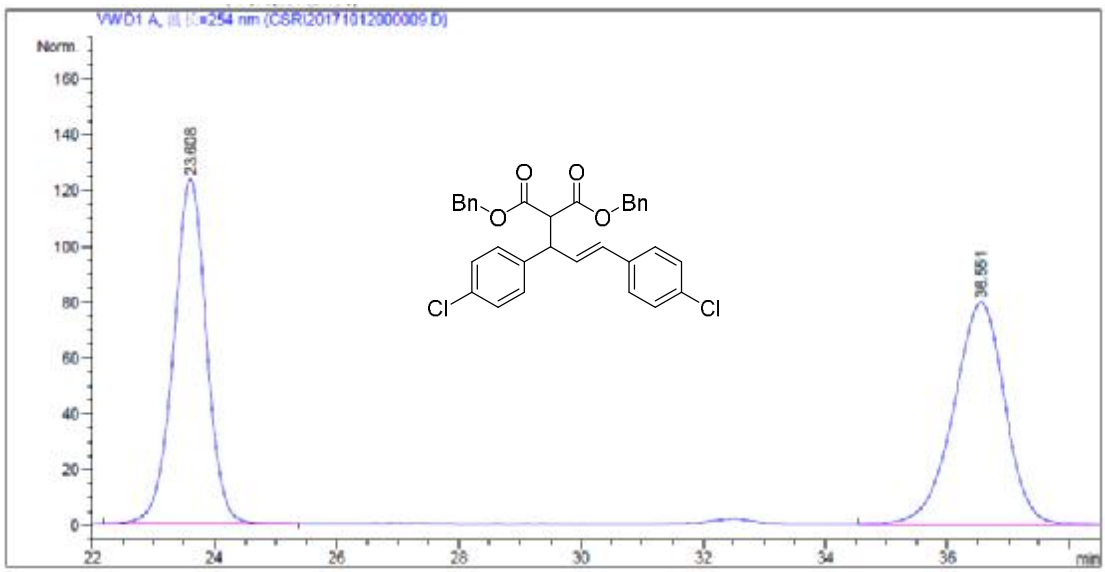


#	[min]		[min]	mAU *s	[mAU]	%
1	10.854	VV	0.2623	1.44919e4	840.38245	50.5474
2	15.643	BV	0.3757	1.41780e4	579.44623	49.4526

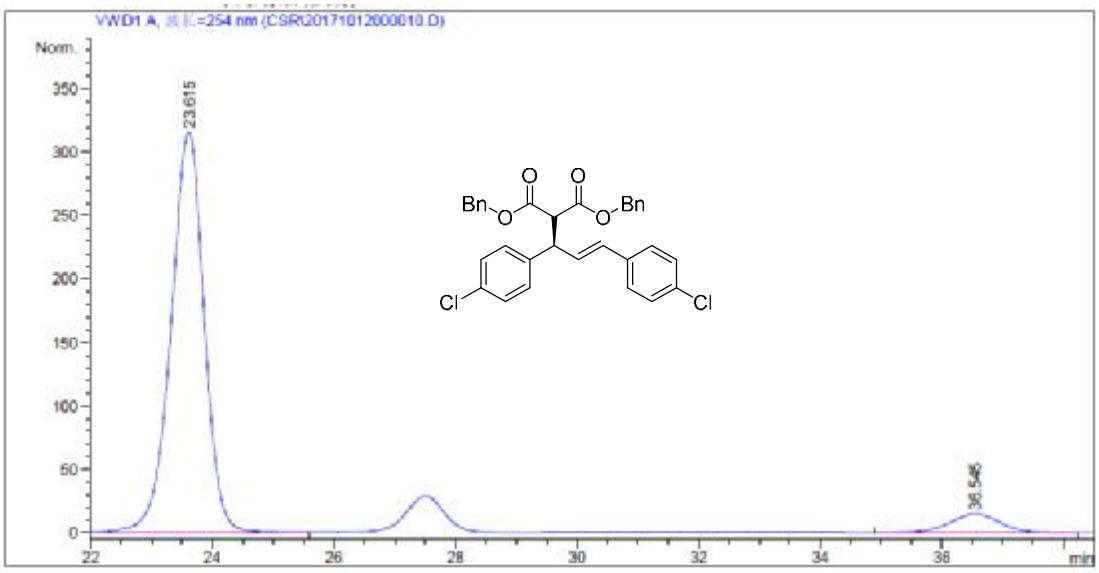


#	[min]		[min]	mAU *s	[mAU]	%
1	10.838	VV	0.2650	1.02382e4	594.29846	84.9025
2	15.616	BV	0.3729	1820.56909	74.38262	15.0975

Dibenzyl (*R*,*E*)-2-(1,3-bis(4-chlorophenyl)allyl)malonate (**4d**)

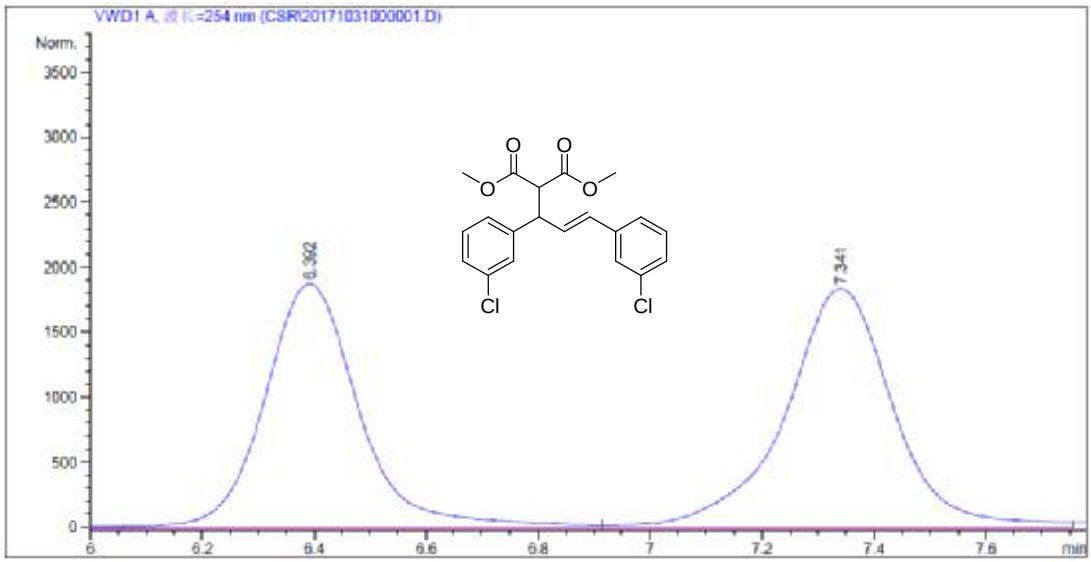


#	[min]		[min]	mAU	*s	[mAU]	%
1	23.608	VB	0.5757	4640.60107		123.37724	50.0154
2	36.551	BB	0.8958	4637.73437		79.53780	49.9846

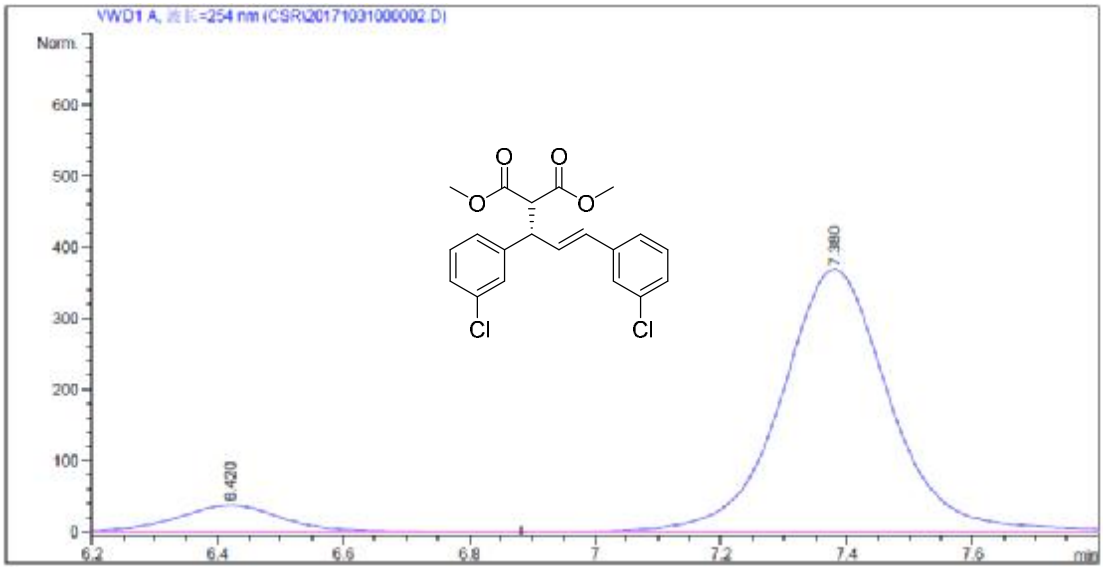


#	[min]		[min]	mAU	*s	[mAU]	%
1	23.615	VB	0.5781	1.20140e4		315.58560	93.2409
2	36.545	VB	0.9081	870.90509		14.92039	6.7591

Dimethyl (*S*,*E*)-2-(1,3-bis(3-chlorophenyl)allyl)malonate (**4e**)

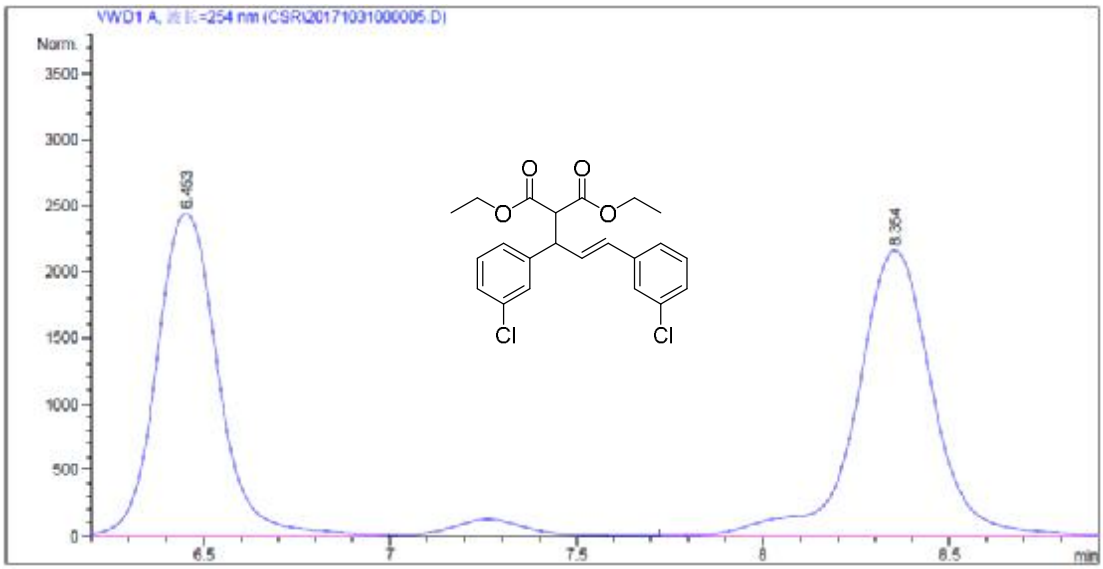


#	[min]		[min]	mAU *s	[mAU]	%
1	6.392	VV	0.1767	2.18137e4	1872.22583	47.0456
2	7.341	VV	0.1997	2.45535e4	1835.84326	52.9544

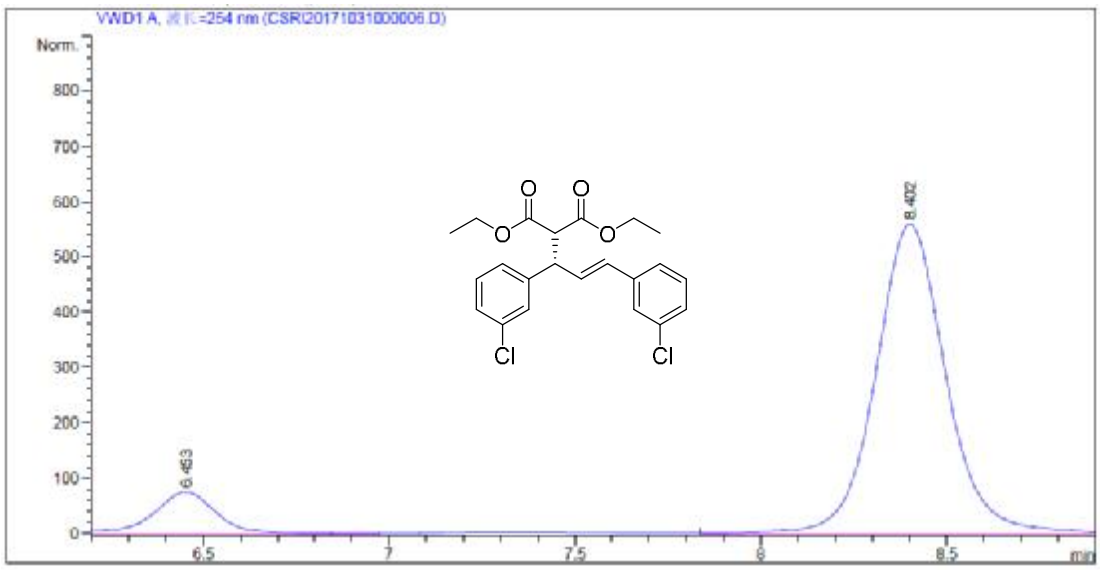


#	[min]		[min]	mAU *s	[mAU]	%
1	6.420	VV	0.1851	469.45245	37.95259	9.5350
2	7.380	VV	0.1845	4454.02148	368.88168	90.4650

Diethyl (*S*,*E*)-2-(1,3-bis(3-chlorophenyl)allyl)malonate (**4f**)

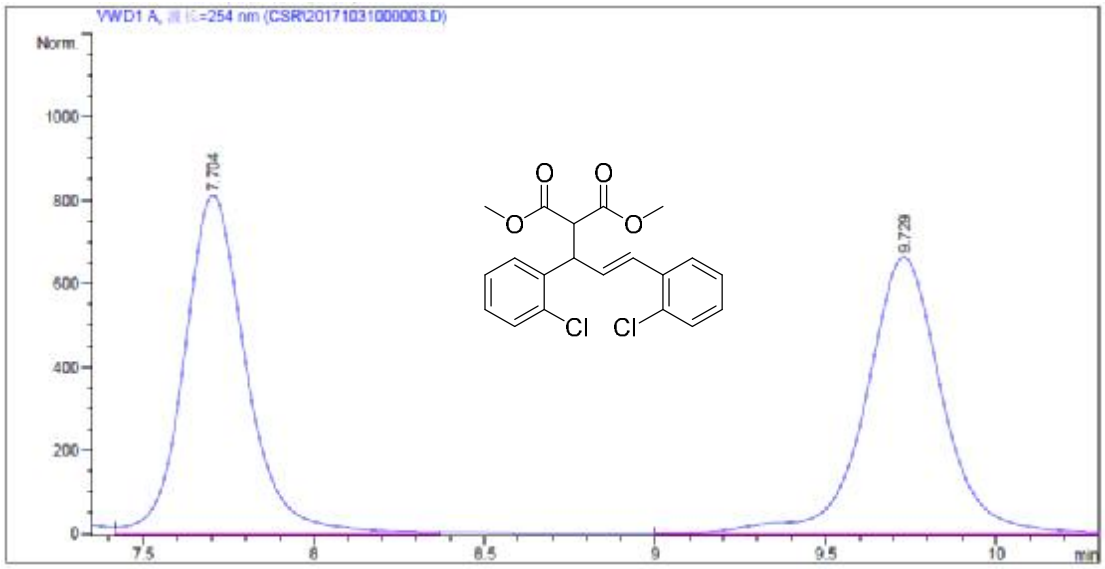


#	[min]		[min]	mAU	*s	[mAU]	%
1	6.453	VV	0.1769	2.78897e4		2442.21240	47.5465
2	8.354	VV	0.2183	3.07680e4		2163.90796	52.4535

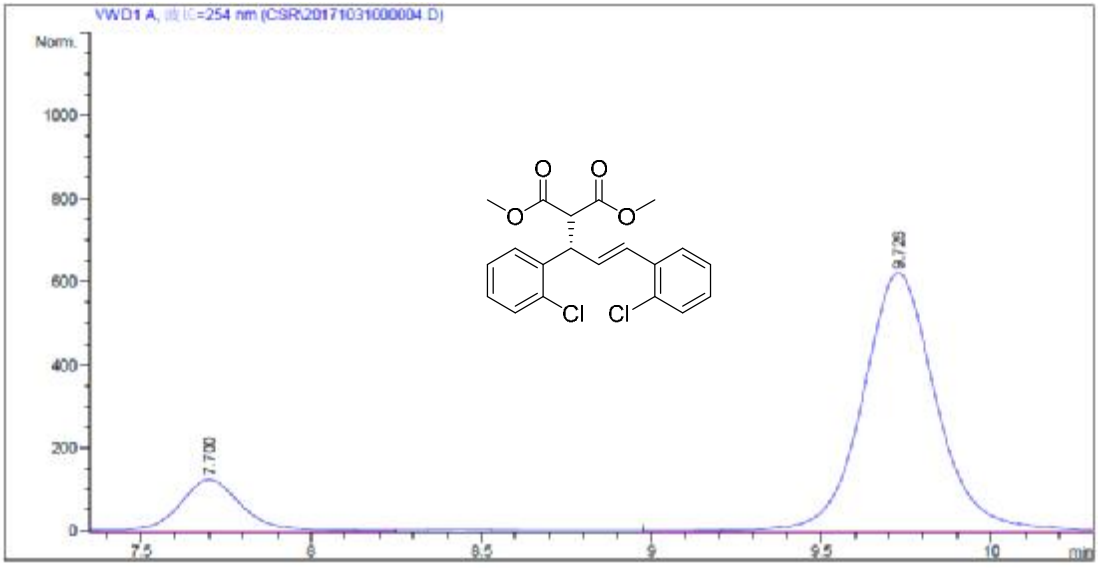


#	[min]		[min]	mAU	*s	[mAU]	%
1	6.453	VV	0.1830	921.74902		75.60696	11.0870
2	8.402	VV	0.2005	7392.03174		560.50507	88.9130

Dimethyl (*S*,*E*)-2-(1,3-bis(2-chlorophenyl)allyl)malonate (**4g**)

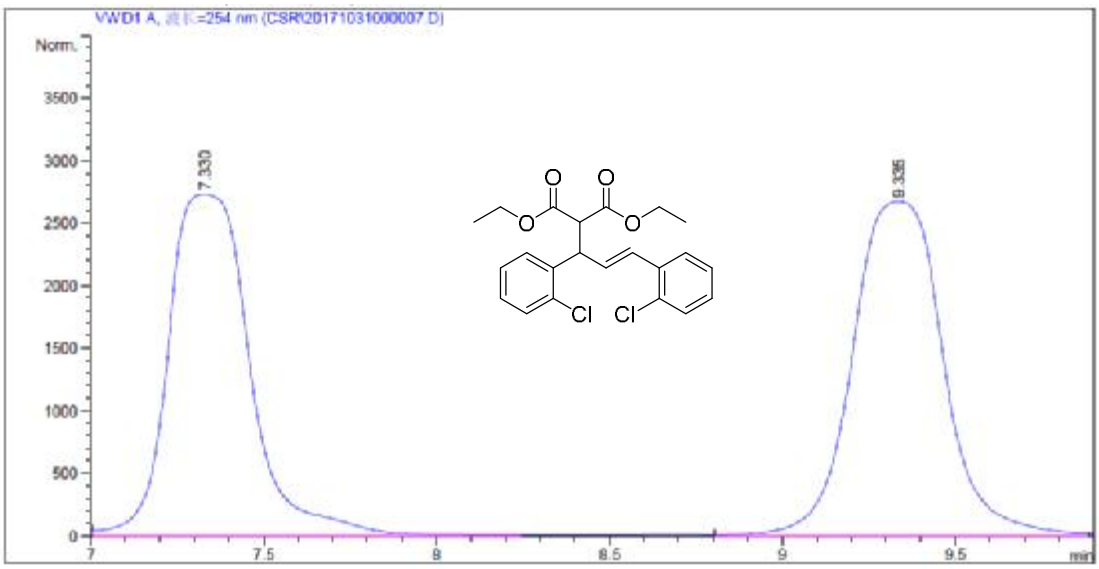


#	[min]		[min]	mAU	*s	[mAU]	%
1	7.704	VV	0.1935	1.02252e4		811.81317	49.6610
2	9.729	VV	0.2376	1.03648e4		663.48474	50.3390

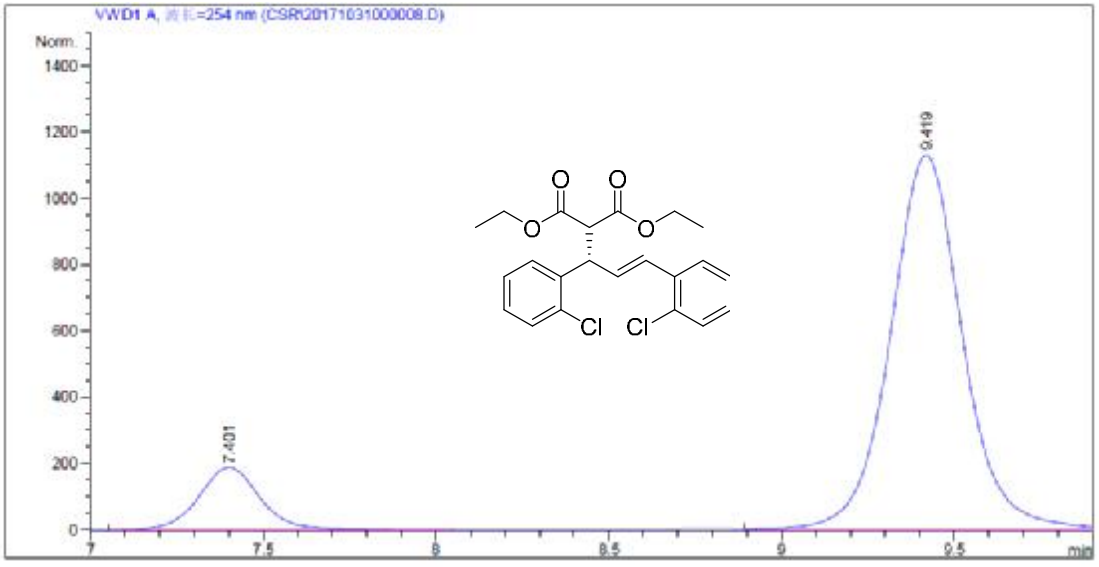


#	[min]		[min]	mAU	*s	[mAU]	%
1	7.700	VV	0.1946	1589.27808		122.82204	14.5588
2	9.726	VV	0.2280	9326.97070		619.89569	85.4412

Diethyl (*S*,*E*)-2-(1,3-bis(2-chlorophenyl)allyl)malonate (**4h**)

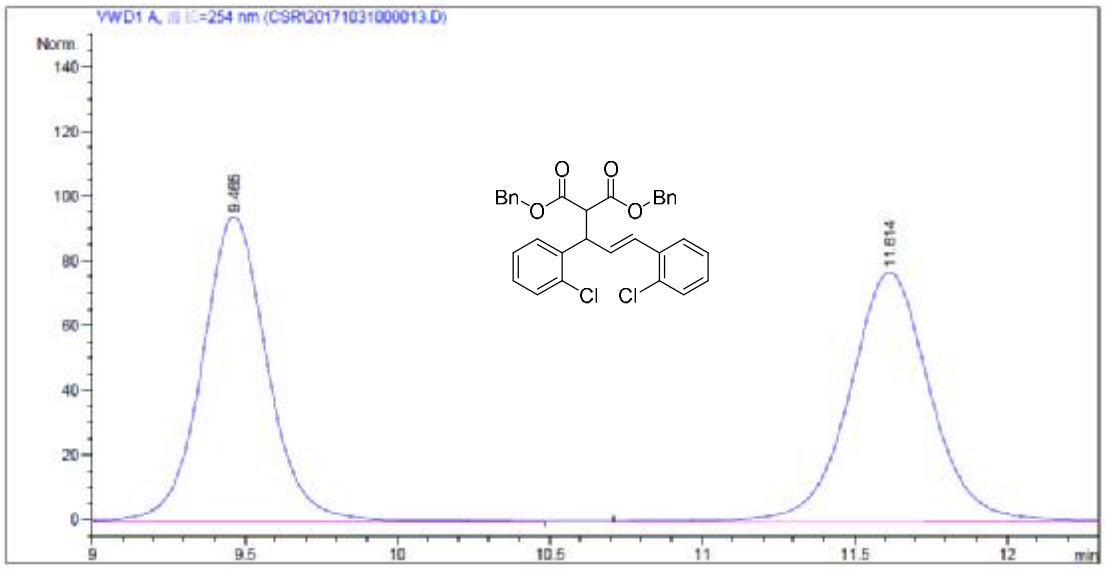


#	[min]		[min]	mAU	*s	[mAU]	%
1	7.330	VV	0.2554	4.48223e4		2733.52417	48.0120
2	9.335	VV	0.2847	4.85343e4		2672.32617	51.9880

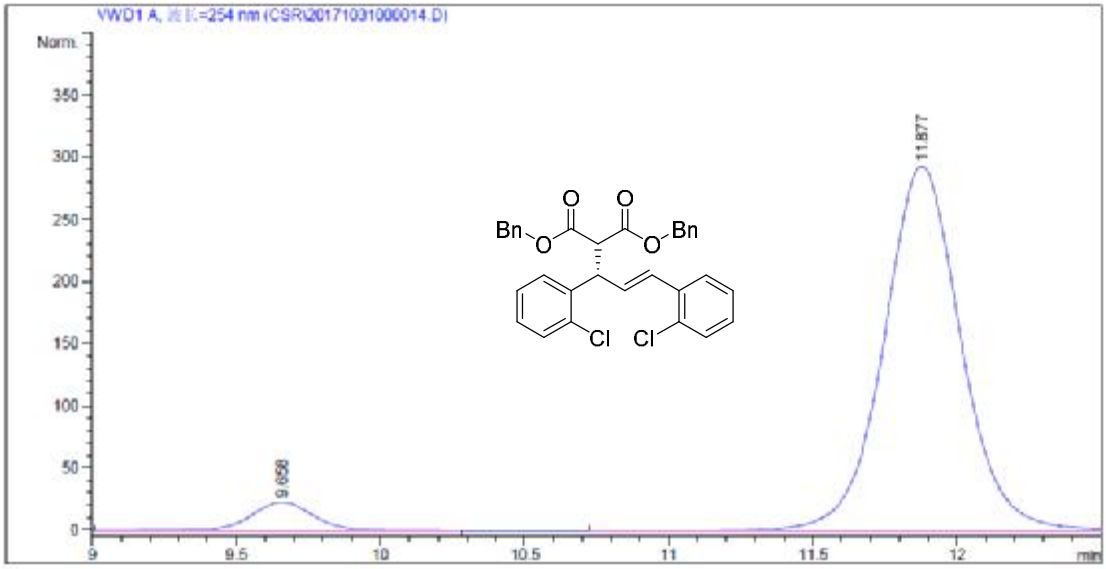


#	[min]		[min]	mAU	*s	[mAU]	%
1	7.401	VV	0.1902	2372.00610		188.82748	12.5007
2	9.419	VV	0.2209	1.66030e4		1130.41333	87.4993

Dibenzyl (*S*,*E*)-2-(1,3-bis(2-chlorophenyl)allyl)malonate (**4i**)

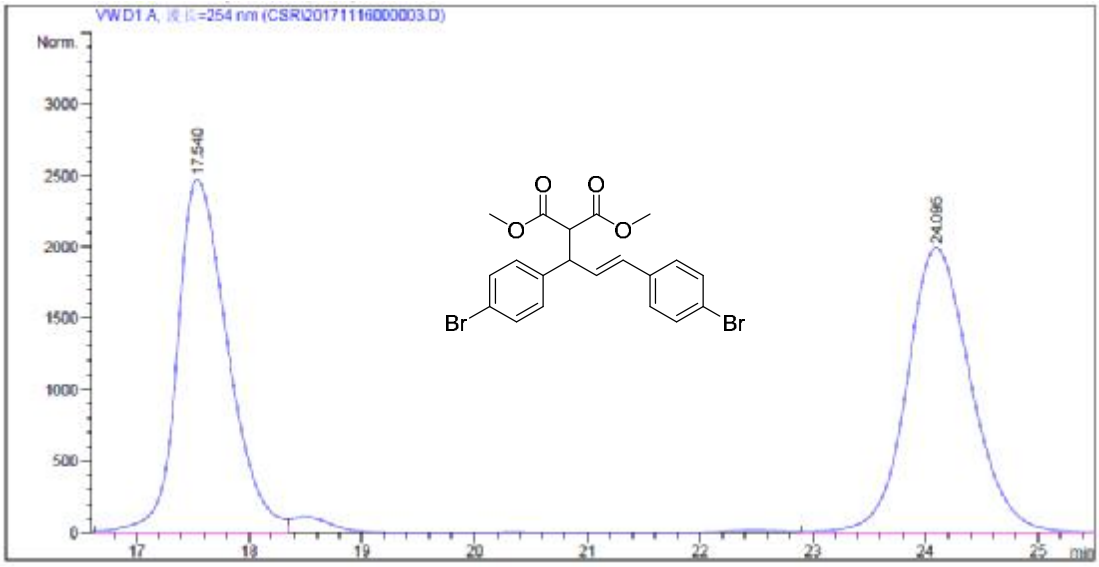


#	[min]		[min]	mAU	*s	[mAU]	%
1	9.465	VB	0.2319	1428.52979		94.39833	49.6215
2	11.614	BV	0.2862	1450.32007		77.17431	50.3785

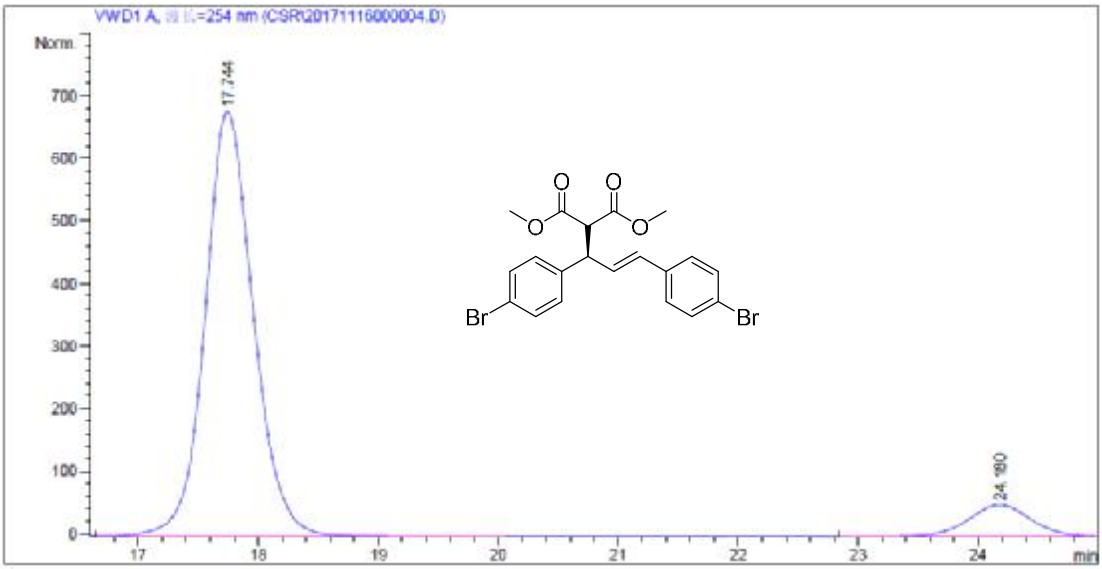


#	[min]		[min]	mAU	*s	[mAU]	%
1	9.658	VV	0.2403	367.45215		23.17325	6.2572
2	11.877	VB	0.2861	5504.99072		293.13901	93.7428

Dimethyl (*S*,*E*)-2-(1,3-bis(4-bromophenyl)allyl)malonate (**4j**)

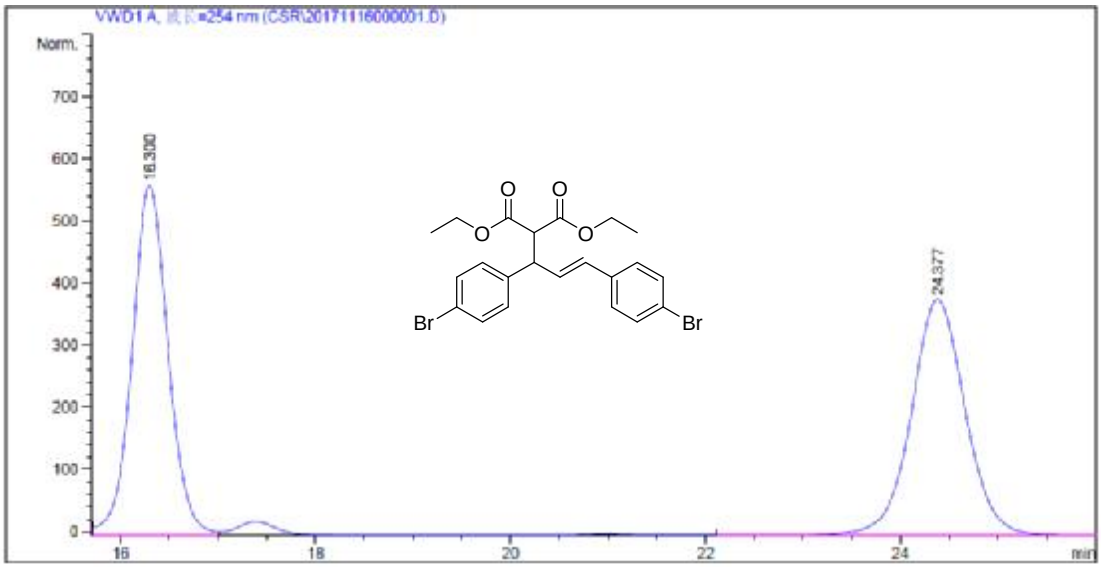


#	[min]		[min]	mAU	*s	[mAU]	%
1	17.540	VV	0.4772	7.71352e4		2474.91235	49.3187
2	24.095	VB	0.6086	7.92662e4		1997.30542	50.6813

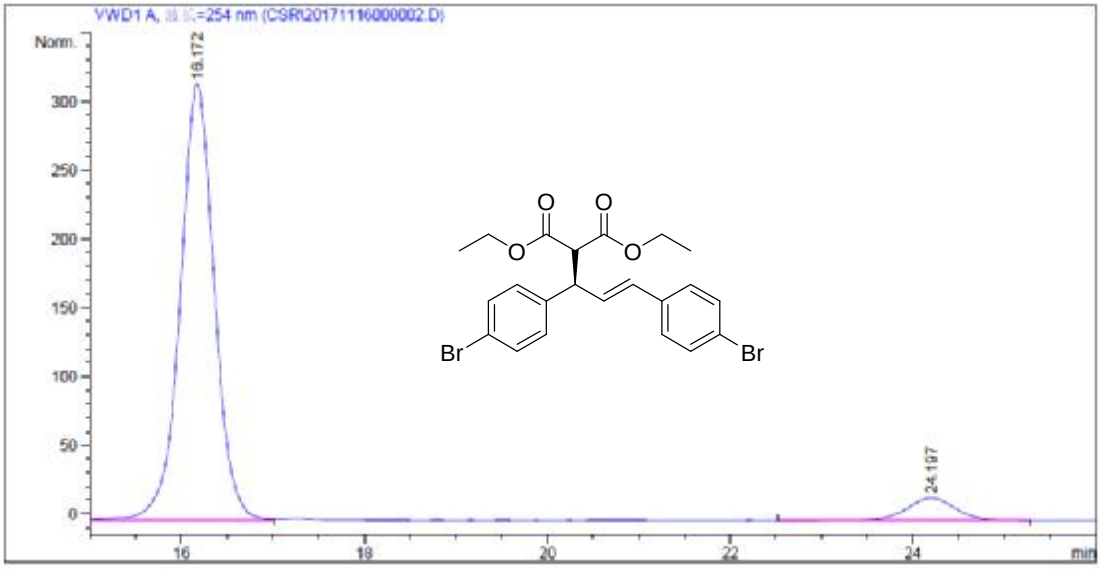


#	[min]		[min]	mAU	*s	[mAU]	%
1	17.744	VB	0.4269	1.90899e4		679.26202	91.0033
2	24.180	BB	0.5696	1887.25891		50.87957	8.9967

Diethyl (*R*,*E*)-2-(1,3-bis(4-bromophenyl)allyl)malonate (**4k**)

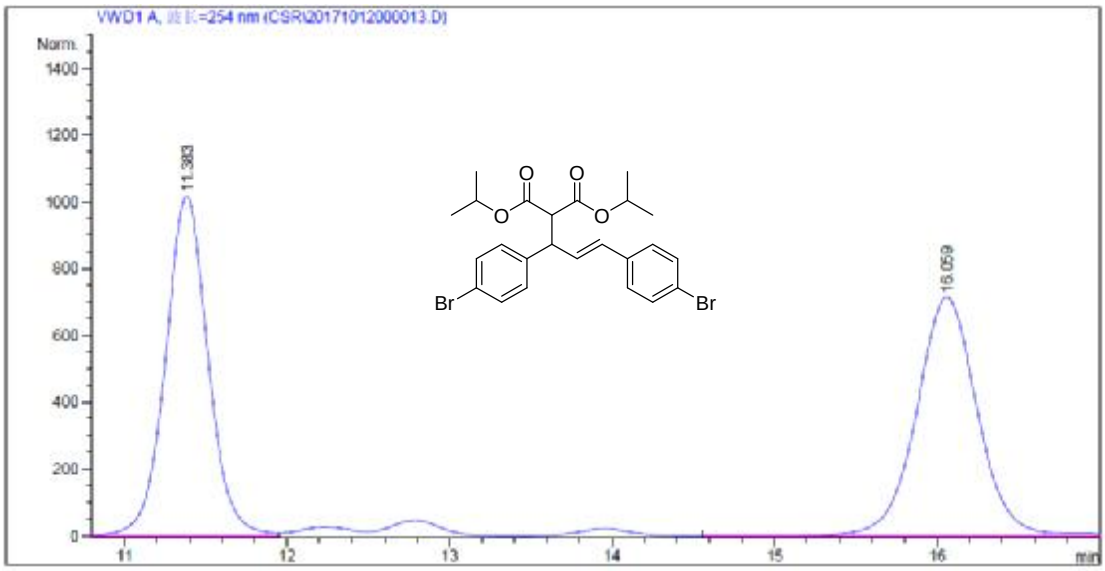


#	[min]		[min]	mAU	*s	[mAU]	%
1	16.300	VV	0.3915	1.43592e4		561.60596	49.9099
2	24.377	VB	0.5840	1.44110e4		378.48135	50.0901

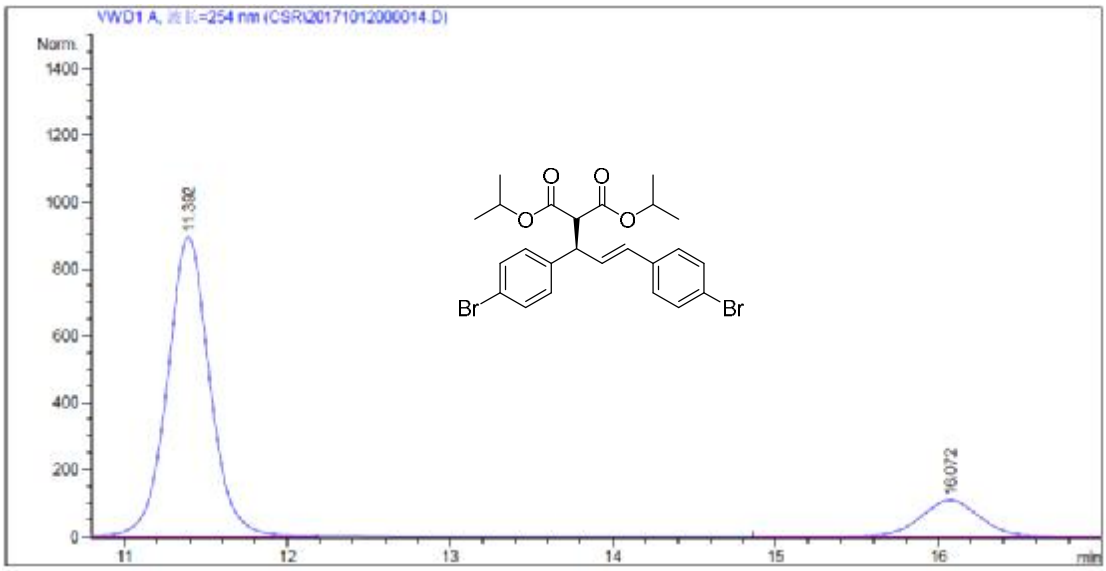


#	[min]		[min]	mAU	*s	[mAU]	%
1	16.172	VV	0.3974	8275.83789		317.42322	93.0076
2	24.197	BV	0.5719	622.18793		16.57600	6.9924

Diisopropyl (*R*,*E*)-2-(1,3-bis(4-bromophenyl)allyl)malonate (**4l**)

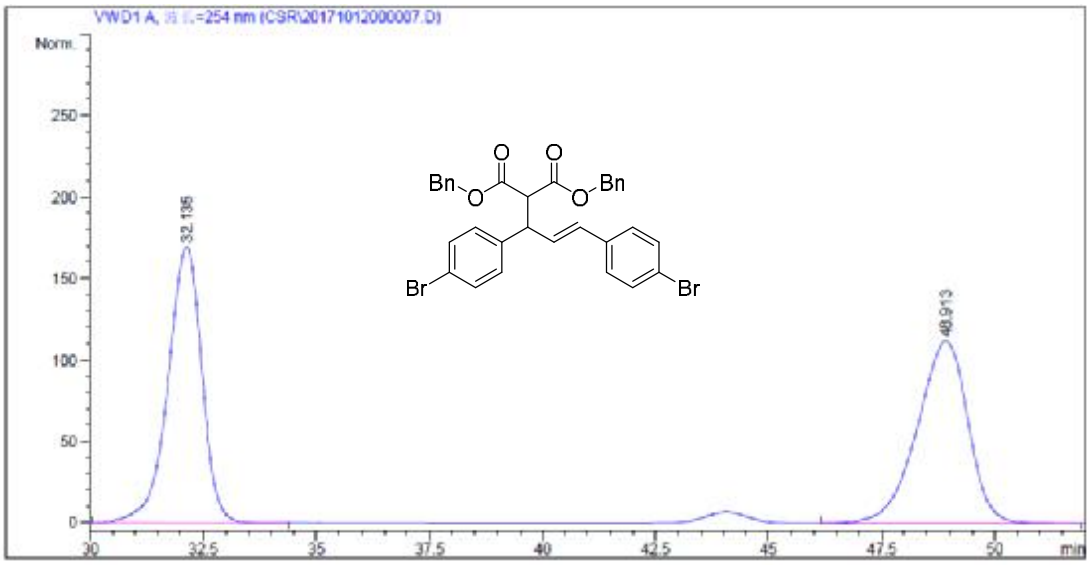


#	[min]		[min]	mAU	*s	[mAU	]	%
1	11.383	VV	0.2769	1.85537e4		1016.83105		49.8397
2	16.059	VV	0.4009	1.86730e4		714.61505		50.1603

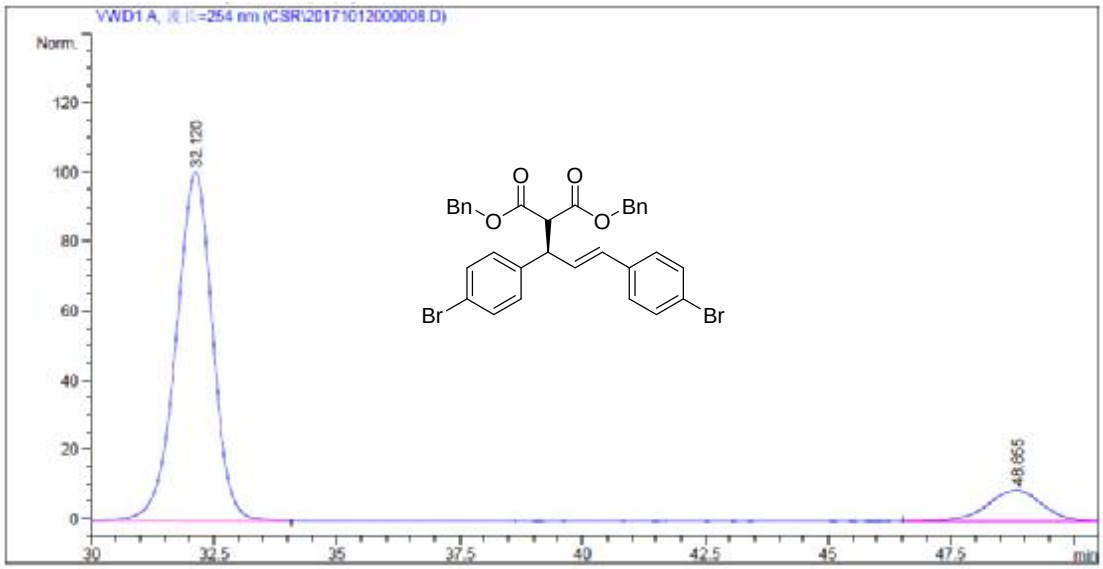


#	[min]		[min]	mAU	*s	[mAU	]	%
1	11.392	VV	0.2790	1.62385e4		893.56659		85.3863
2	16.072	VB	0.3928	2779.17529		108.22767		14.6137

Dibenzyl (*R*,*E*)-2-(1,3-bis(4-bromophenyl)allyl)malonate (**4m**)

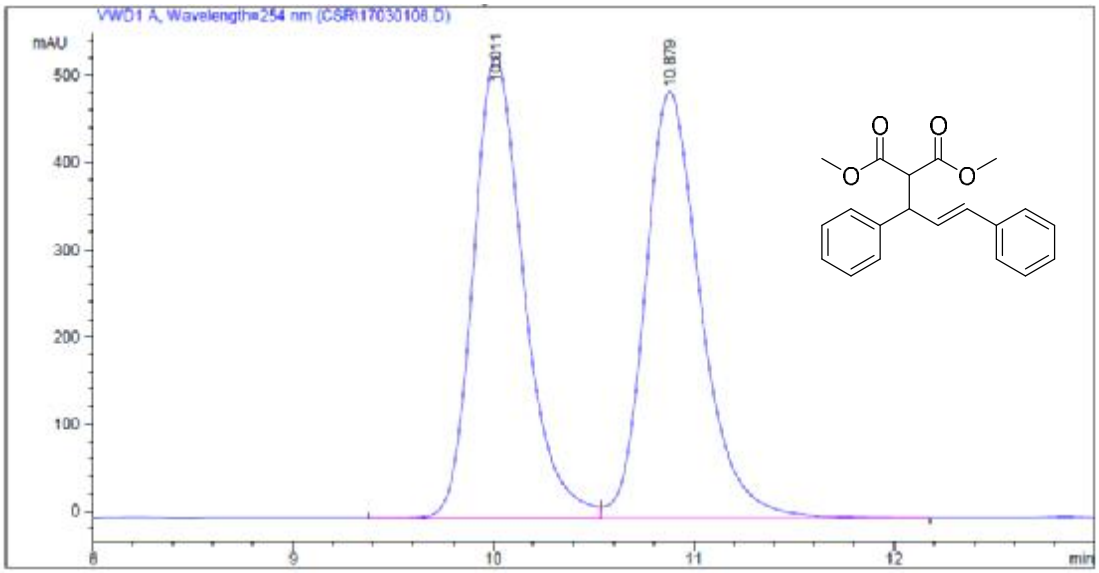


#	[min]		[min]	mAU	*s	[mAU]	%
1	32.135	VB	0.8091	8875.12207	169.43823	50.3799	
2	48.913	BB	1.1972	8741.27930	111.84412	49.6201	

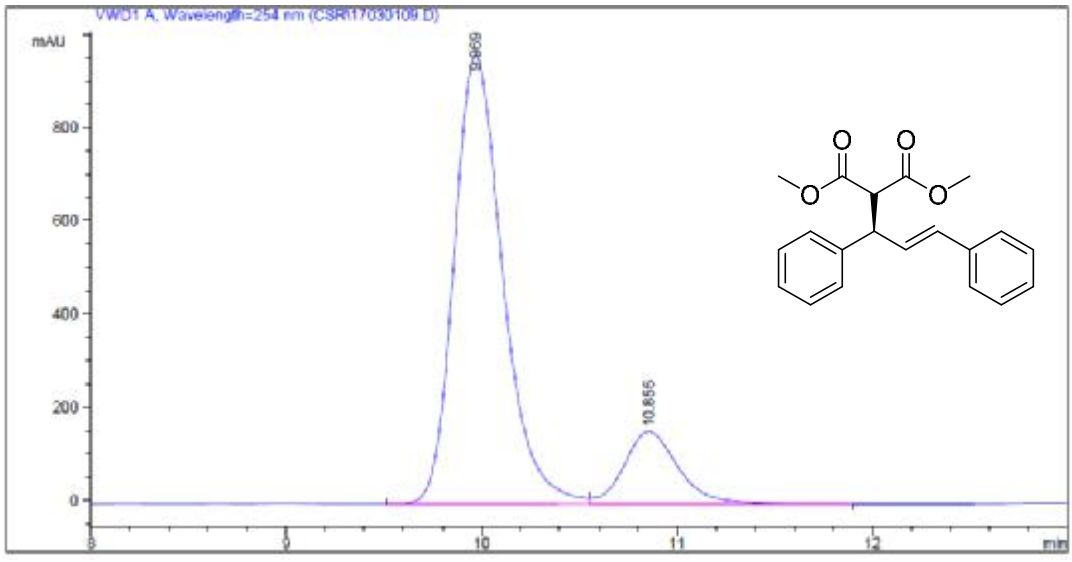


#	[min]		[min]	mAU	*s	[mAU]	%
1	32.120	VB	0.7921	5178.66602	100.71088	87.9487	
2	48.855	VB	1.1205	709.61121	9.03130	12.0513	

Dimethyl (*R*,*E*)-2-(1,3-diphenylallyl)malonate (**4n**)

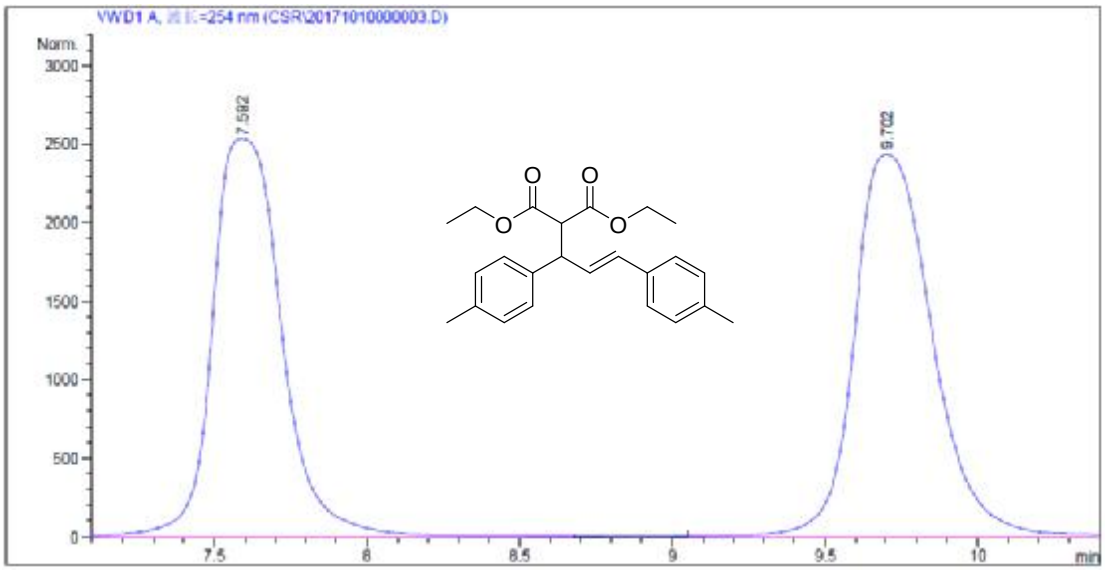


#	[min]		[min]	mAU	*s	[mAU	]	%
1	10.011	VV	0.2687	9286.42578		529.40094		49.6297
2	10.879	VB	0.2947	9425.01367		489.06870		50.3703

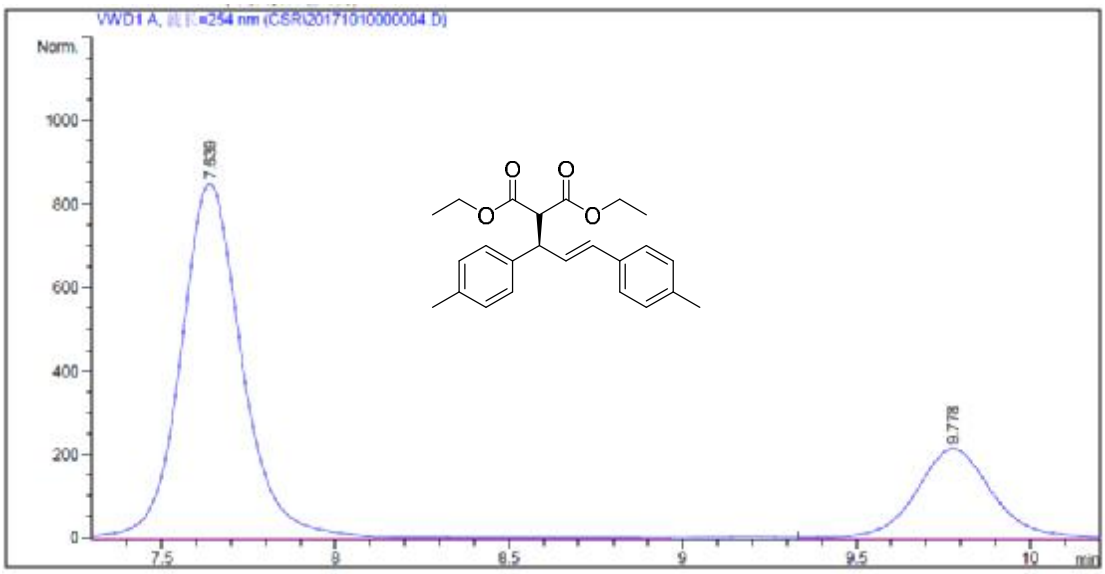


#	[min]		[min]	mAU	*s	[mAU	]	%
1	9.969	VV	0.2659	1.66708e4		963.49475		84.7215
2	10.855	VB	0.2937	3006.37622		155.70625		15.2785

Diethyl (*R*,*E*)-2-(1,3-di-p-tolylallyl)malonate (**4o**)



#	[min]		[min]	mAU	*s	[mAU	]	%
1	7.592	VV	0.2456	4.00662e4		2534.49878		47.9400
2	9.702	VV	0.2751	4.35096e4		2439.51489		52.0600



#	[min]		[min]	mAU	*s	[mAU	]	%
1	7.639	VV	0.1870	1.04217e4		848.62018		76.2079
2	9.778	VV	0.2334	3253.64673		213.12358		23.7921