

Supplementary data

Minghua Li ^a, Nan Ji ^a, Ting Lan ^a, Wei He ^{a,*}, Rui Liu ^{b,*}

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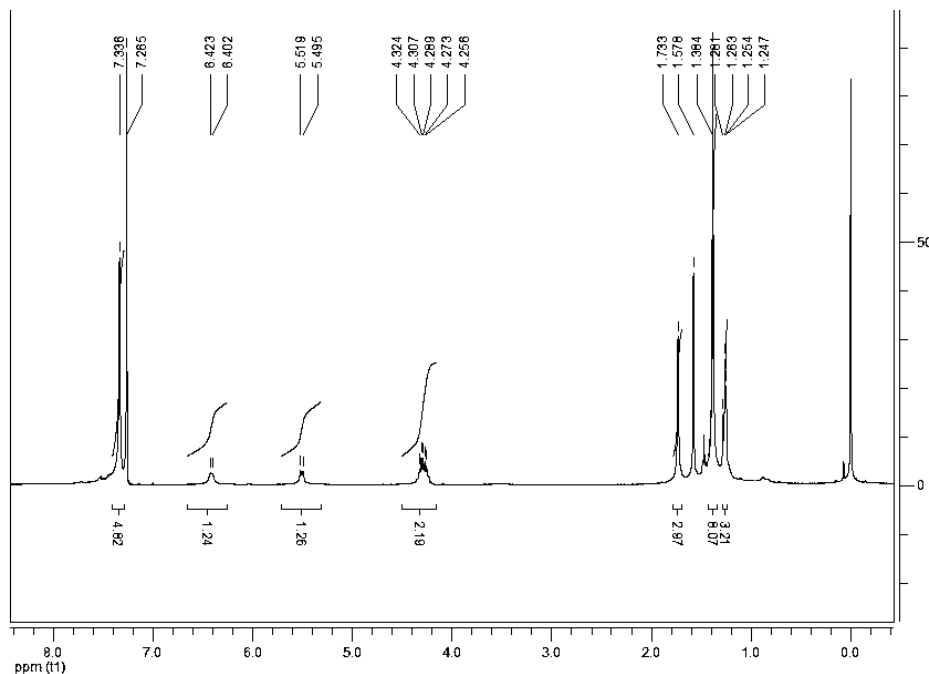
1. General

All the starting materials and reagents were purchased from commercial suppliers and used without further purification. Solvents were purified by standard procedures. CH_2Cl_2 and Toluene were freshly distilled prior to use. The reactions were monitored by thin layer chromatography (TLC) and analysis of TLCs was done either via UV light (254 nm) or iodine vapor. NMR spectra were recorded as CDCl_3 solution on 400MHz instrument. The ^1H NMR chemical shifts are reported as δ value in parts per million (ppm) relative to tetramethylsilane (TMS, $\delta = 0.00$)/ CHCl_3 ($\delta = 7.26$) as internal standard. The ^{13}C NMR chemical shifts are reported as δ values in parts per million (ppm) downfield from TMS and referenced with respect to the CDCl_3 signal (triplet, centerline $\delta = 77.0$ ppm). The yields are of materials isolated by column chromatography on gel plates, *N*-Boc benzaldimine 2a were synthesized and 2-nitropanoate commercially available. Anhydrous Potassium carbonate was dried in the oven at 110 °C. All glassware was flame-dried under a high vacuum. Low temperature baths were prepared using alcohol. All reactions were conducted in the mixed solvents in flasks fitted with a rubber septum.

2. ¹H NMR spectra of the compounds

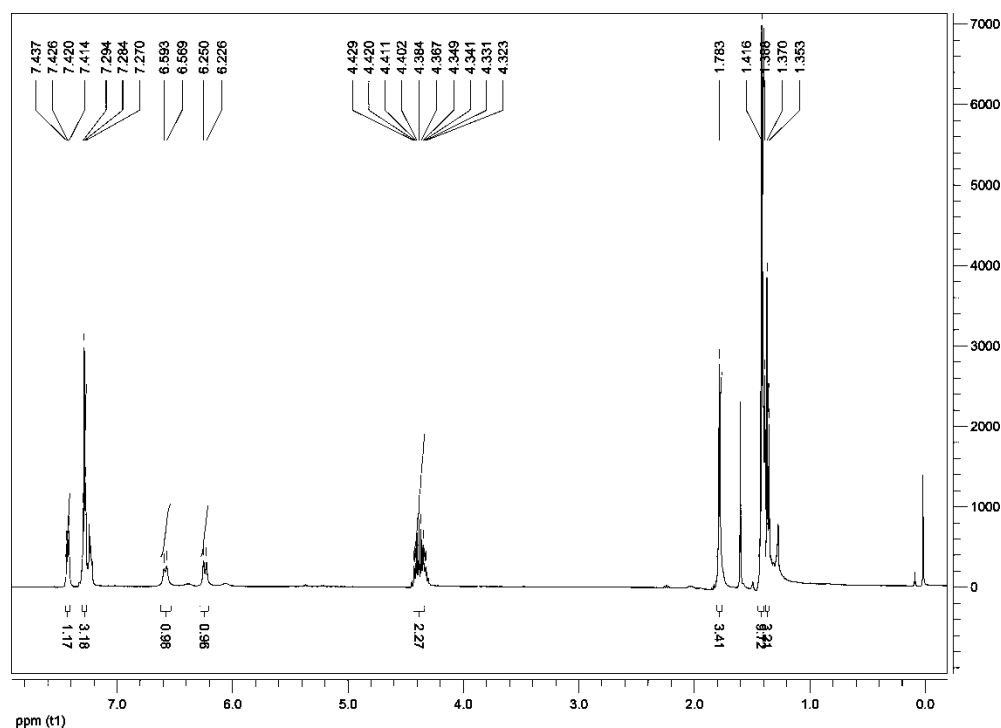
2.1 ¹H NMR of 4a

¹H NMR (400 MHz, CDCl₃): δ=7.33(s, 5H), 6.41(d, J=8.4 1H), 5.51(d, J=9.6, 1H), 4.32-4.25(m, 2H), 1.73(s, 3H), 1.38(s, 9H), 1.26-1.22(m, 3H) ppm



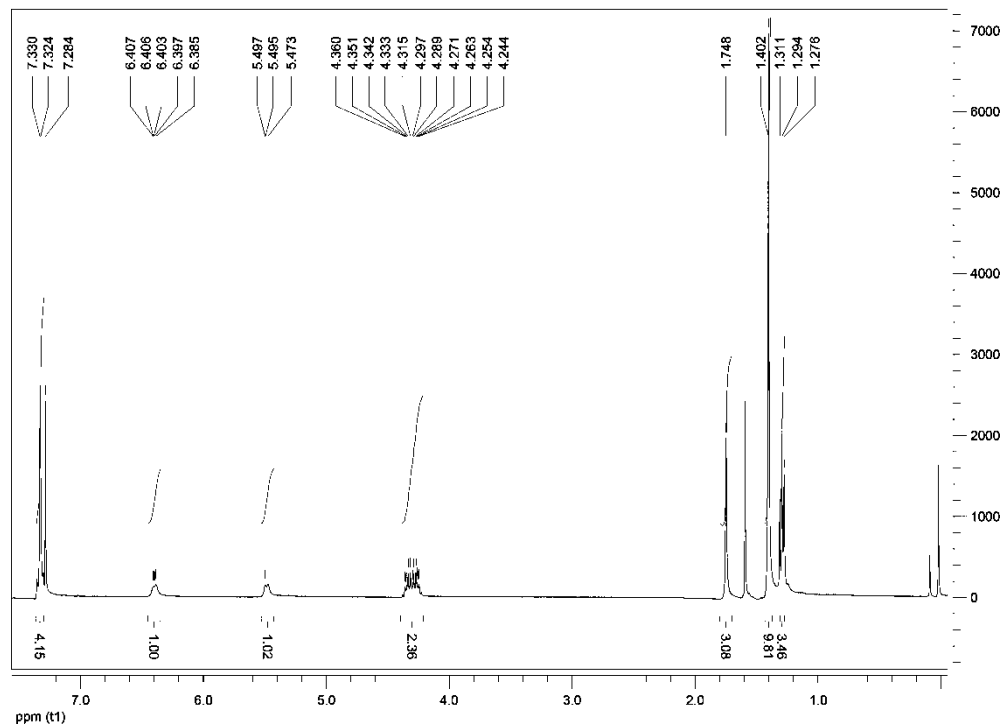
2.2 ¹H NMR of 4b

¹H NMR (400 MHz, CDCl₃): δ=7.44-7.41(m, 1H), 7.29-7.27 (m, 3H), 6.58(d, J=9.6 1H), 6.24(d, J=9.6, 1H), 4.43-4.32(m, 2H), 1.78(s, 3H), 1.42(s, 9H), 1.37(t, J=7.2, 3H) ppm



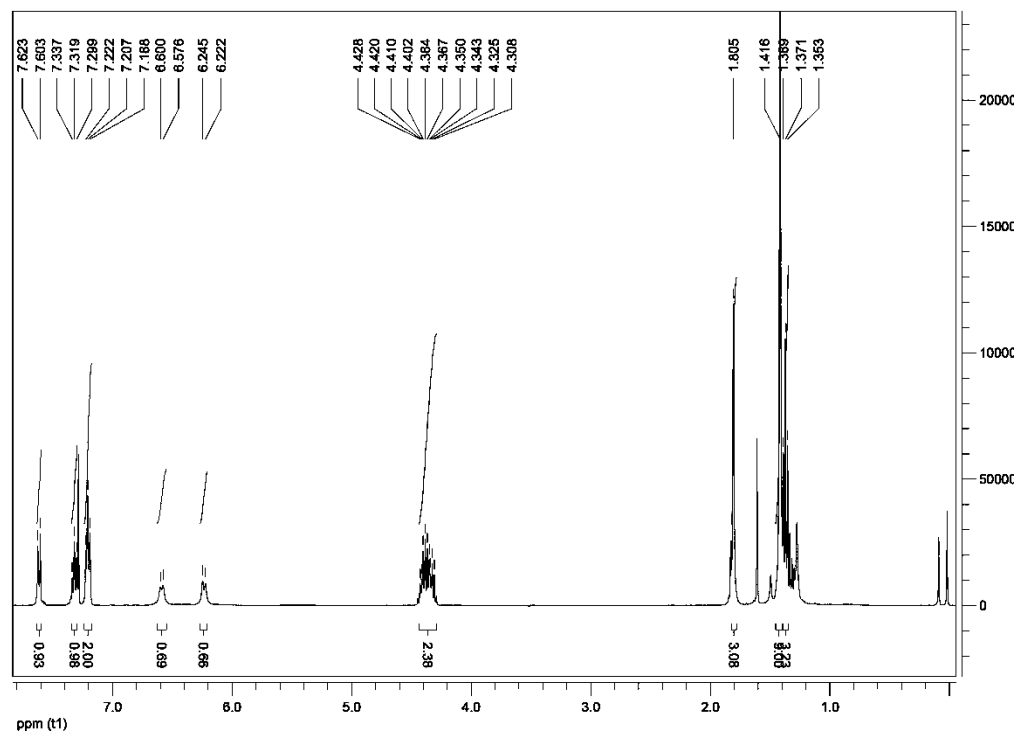
2.3 ^1H NMR of 4c

^1H NMR(400 MHz, CDCl_3): δ =7.35-7.30(m, 4H), 6.41-6.39(m, 1H), 5.49-5.47(m, 1H) 4.36-4.24(m,2H), 1.75(s,3H), 1.40(s, 9H), 1.29(t, J=7.2,3H) ppm



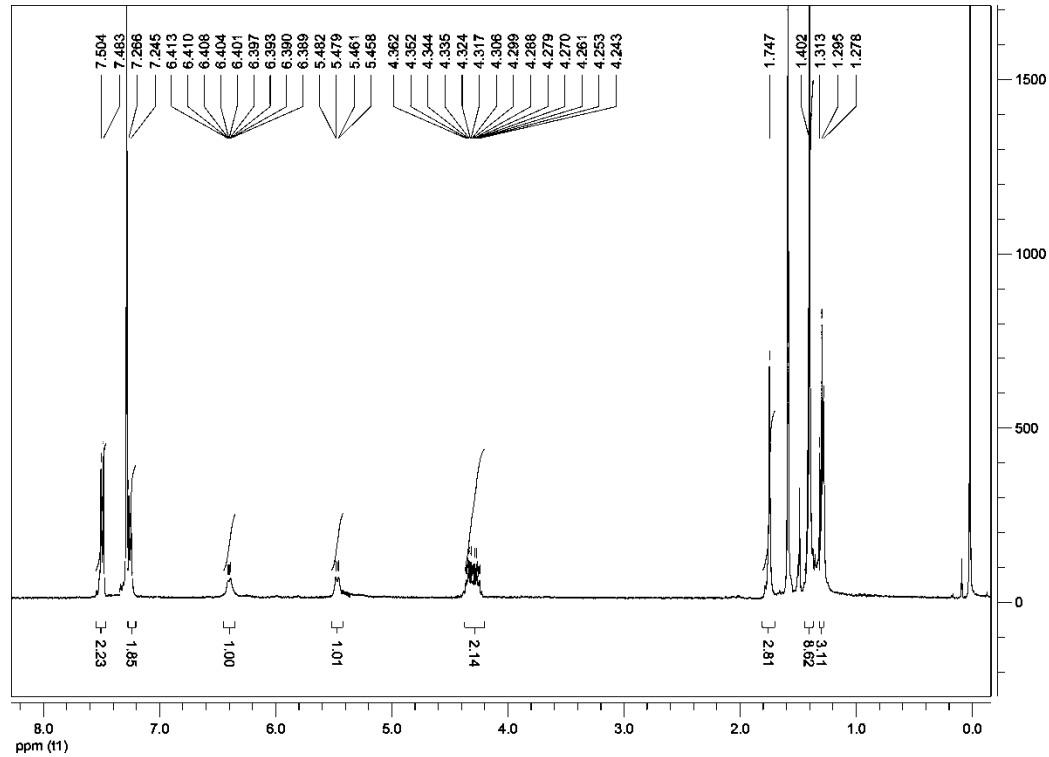
2.4 ^1H NMR of 4d

^1H NMR (400 MHz, CDCl_3): δ =7.61 (d, J=8.0, 1H), 7.31 (t, 1H), 7.2 (t, 2H), 6.58 (d, J=9.6, 1H), 6.23 (d, J=9.2, 1H), 4.43-4.31 (m, 2H), 1.80 (s, 3H), 1.42 (s, 9H), 1.37 (t, J=7.2Hz, 3H) ppm;



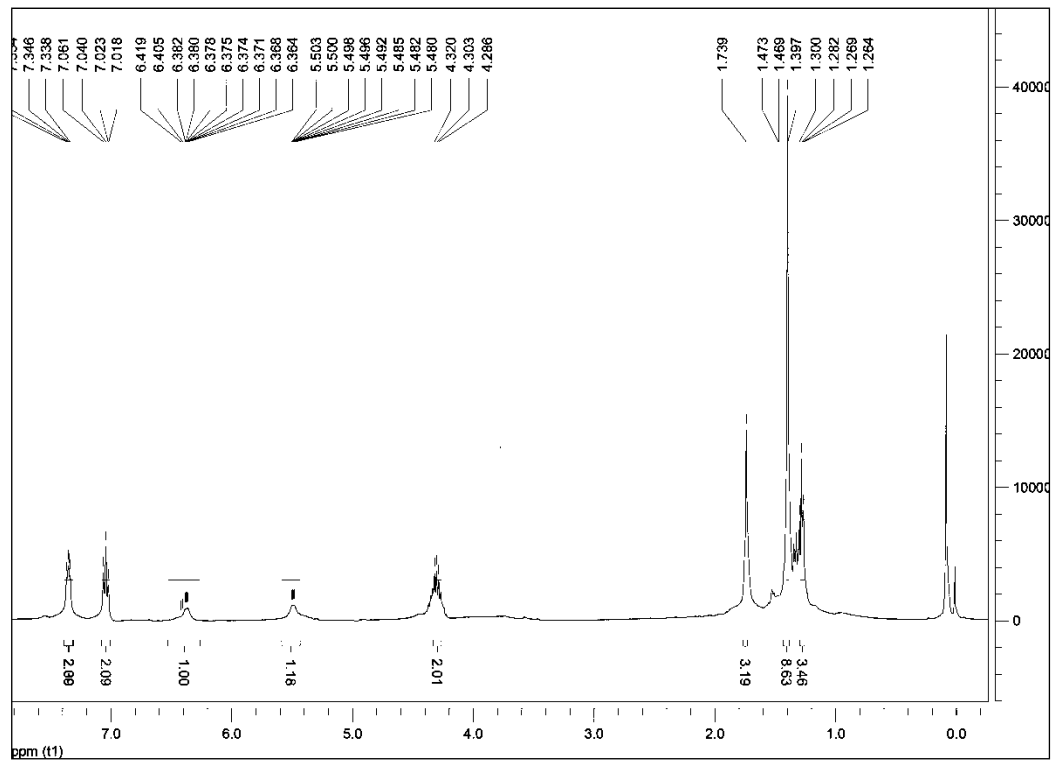
2.5 ¹H NMR of 4e

¹H NMR (400 MHz, CDCl₃): δ= 7.49 (d, J=8.4, 2H), 7.25 (d, J=8.4, 2H), 6.41-6.39 (m, 1H), 5.48-5.46 (m, 1H), 4.36-4.24 (m, 2H), 1.75 (s, 3H), 1.40 (s, 9H), 1.30 (t, J=7.2Hz, 3H) ppm;



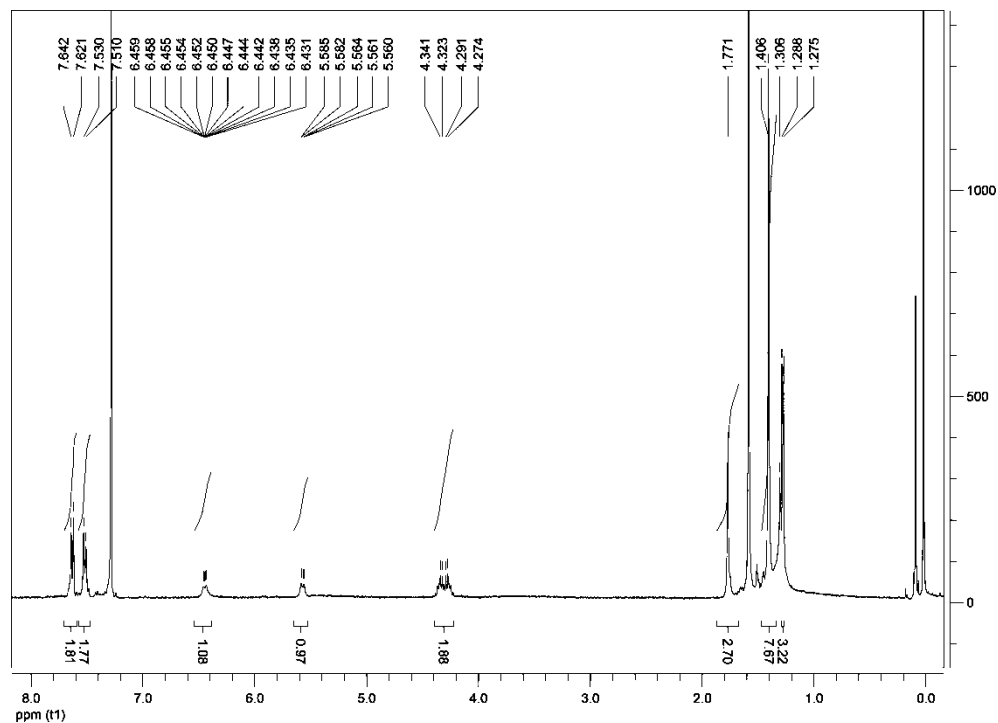
2.6 ¹H NMR of 4f

¹H NMR(400 MHz, CDCl₃): δ=7.37-7.34(m,2H), 7.06-7.02(m,2H), 6.42-6.36 (m, 1H), 5.50-5.48(m,1H), 4.32-4.29(m,2H), 1.74-1.72(m,3H), 1.40(s,9H),1.30-1.26(m, 3H) ppm;



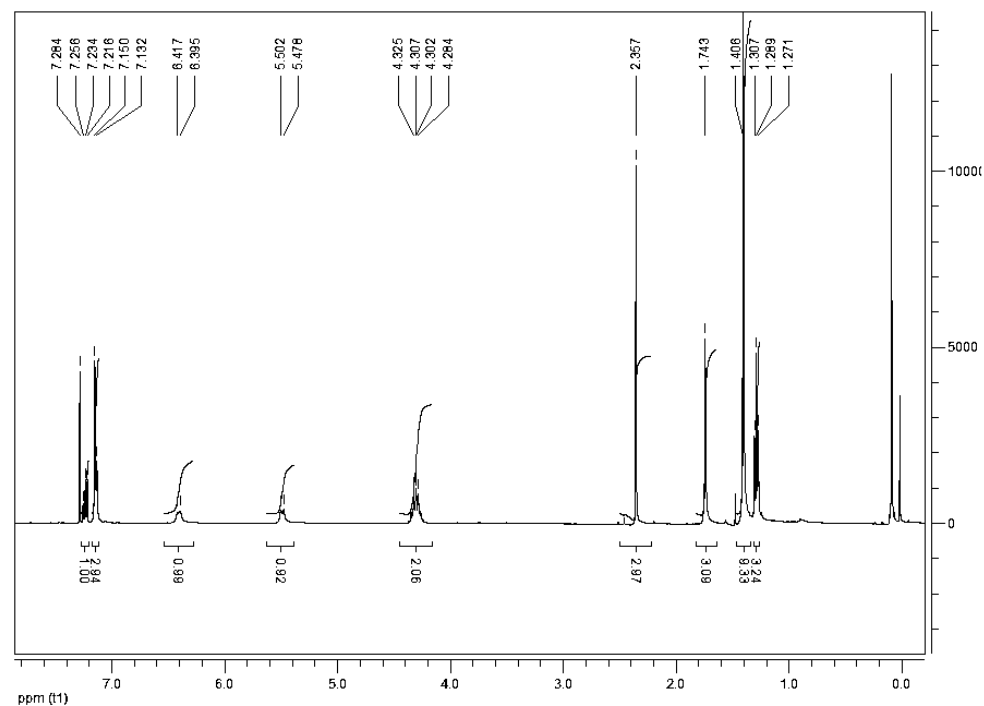
2.7 ¹H NMR of 4g

¹H NMR (400 MHz, CDCl₃): δ = 7.63 (d, J=8.4, 2H), 7.52 (d, J=8, 2H), 6.46-6.43 (m, 1H), 5.59-5.56(m, 1H), 4.34-4.27 (m, 2H), 1.77 (s, 3H), 1.41 (s, 9H), 1.29 (t, J=7.2Hz, 3H) ppm;



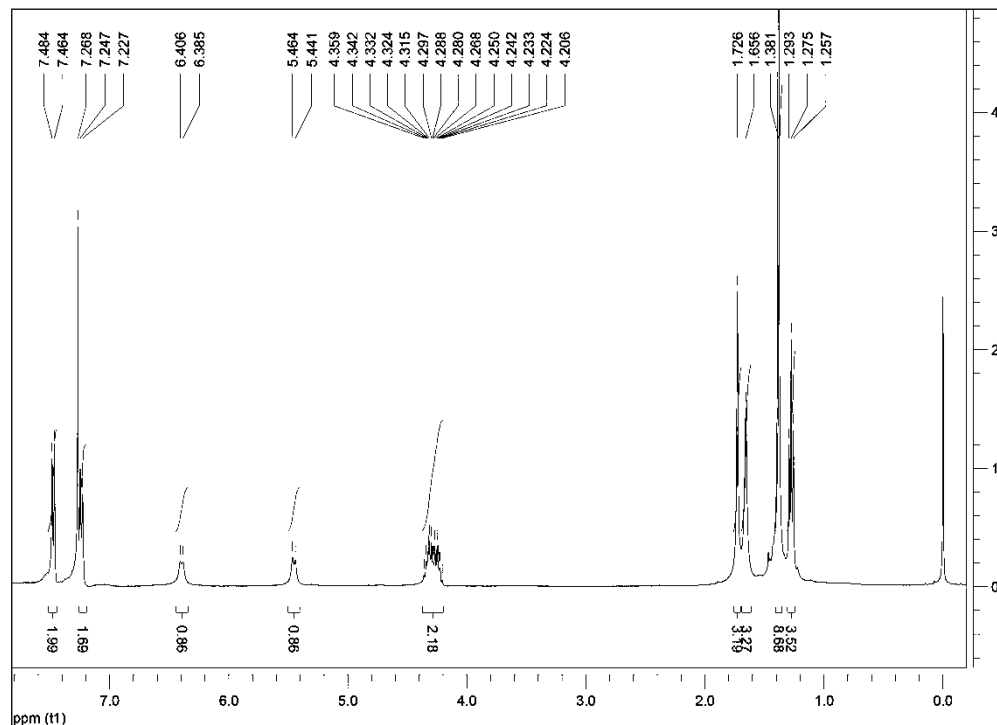
2.8 ¹H NMR of 4h

¹H NMR(400 MHz, CDCl₃): δ= 7.25-7.21(m,1H), 7.15-7.13(m,3H), 6.41(d, J=8.8, 1H), 5.49(d, J=9.6,1H), 4.33-4.28(m, 2H), 2.36(s,3H), 1.74(s,3H), 1.41(s,9H), 1.29(t, J=7.2Hz, 3H)ppm;



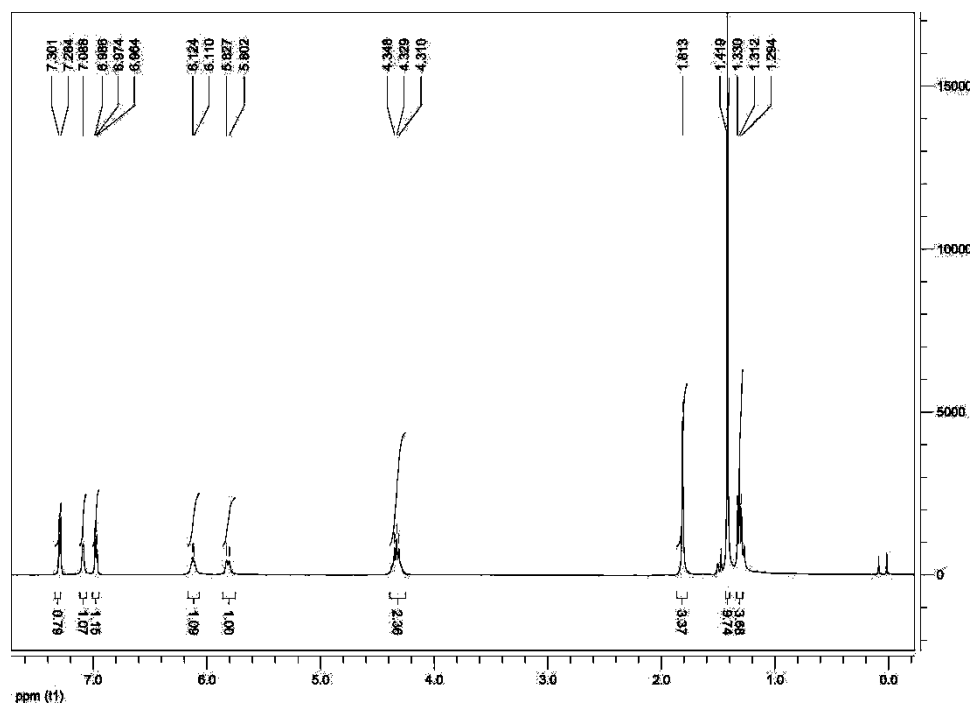
2.9 ¹H NMR of 4i

¹H NMR(400 MHz, CDCl₃): δ= 7.47(d,J=8, 2H), 7.23(d, J=8, 2H), 6.40(d, J=8.4, 1H), 5.45(d, J=9.2,1H), 4.36-4.21(m, 2H), 1.73(s,3H), 1.66(s,3H), 1.38(s,9H), 1.28(t, J=7.2Hz, 3H)ppm;



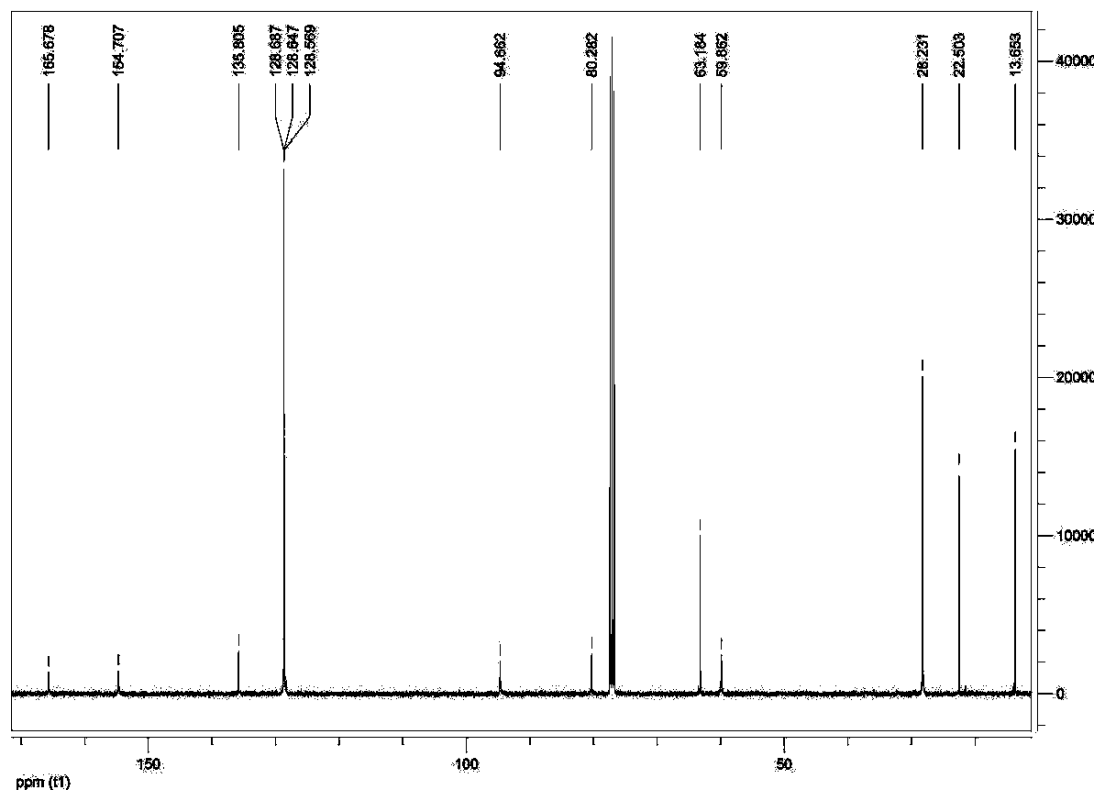
2.10 ¹H NMR of 4j

¹H NMR(400 MHz, CDCl₃): δ= 7.30(s, 1H), 7.09(s,1H), 7.0-6.97(m, 1H), 6.11(d, J=5.6, 1H), 5.81(d, J=10, 1H), 4.35-4.31(m, 2H), 1.81(s,3H), 1.42(s,9H), 1.31(t, J=7.2, 3H) ppm

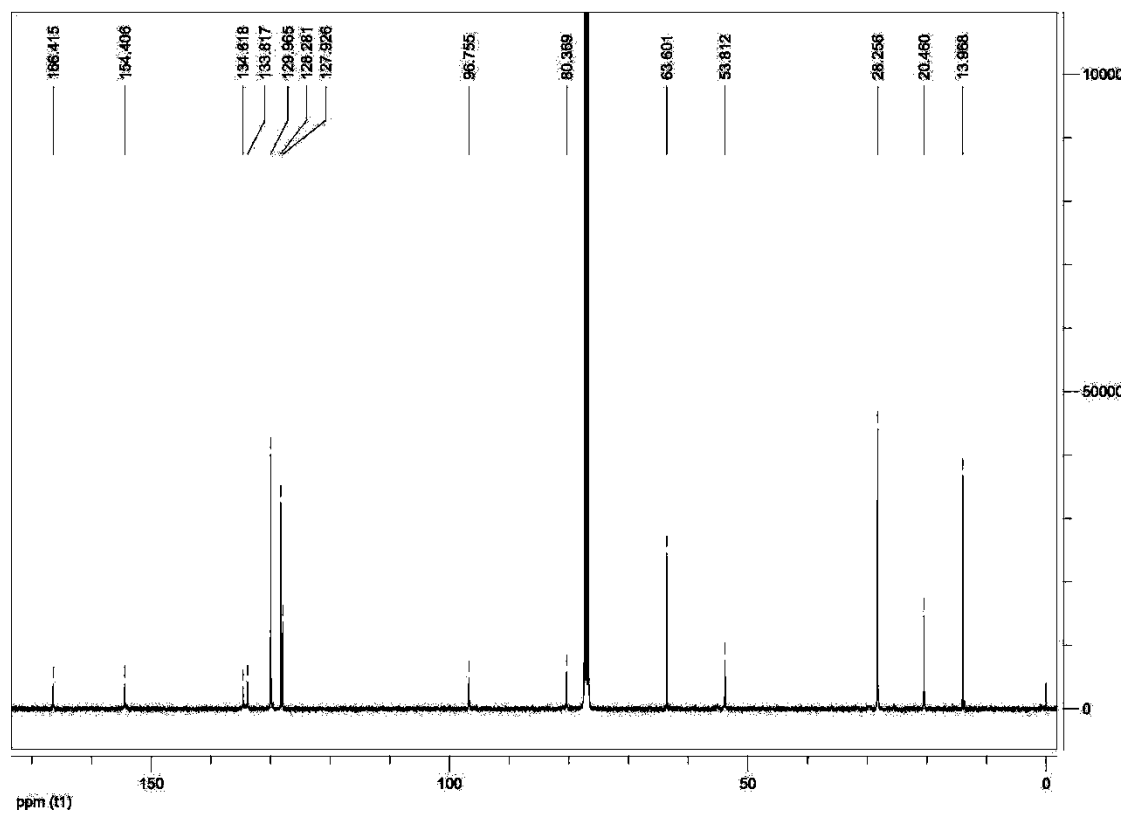


2. ^{13}C NMR spectra of the new compounds

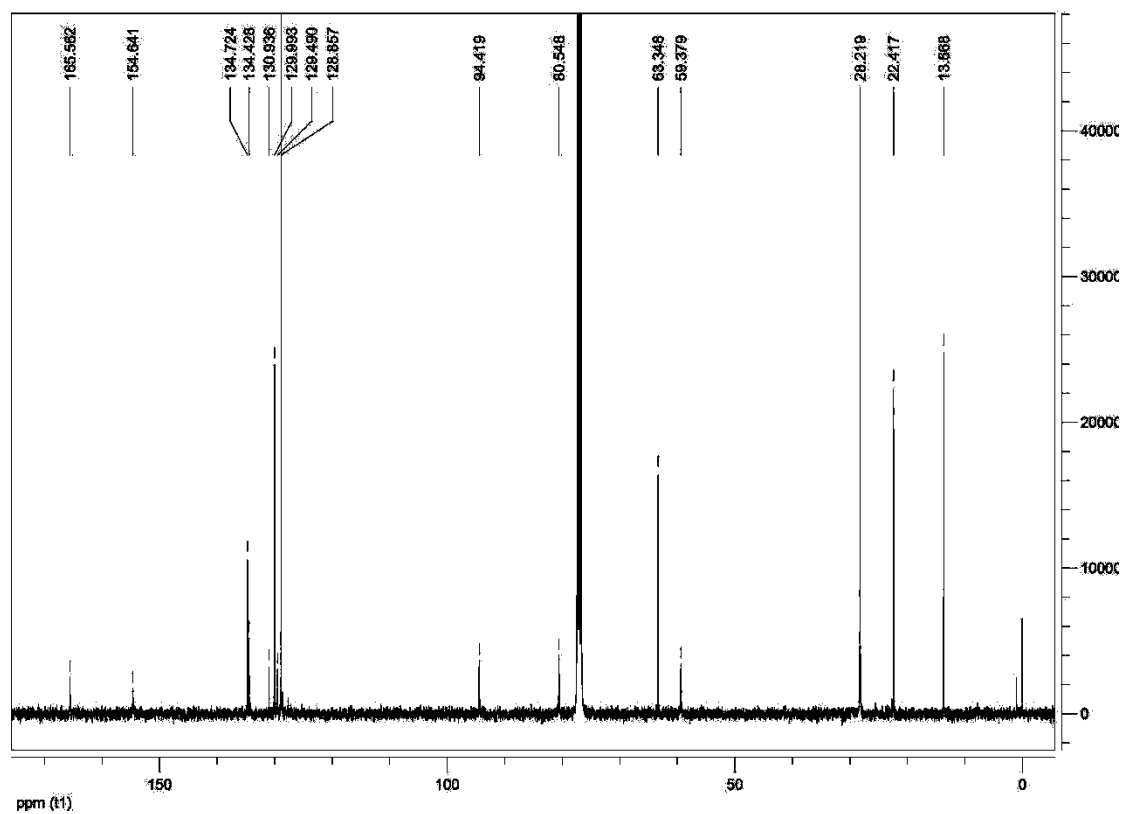
3.1 ^{13}C NMR of 4a



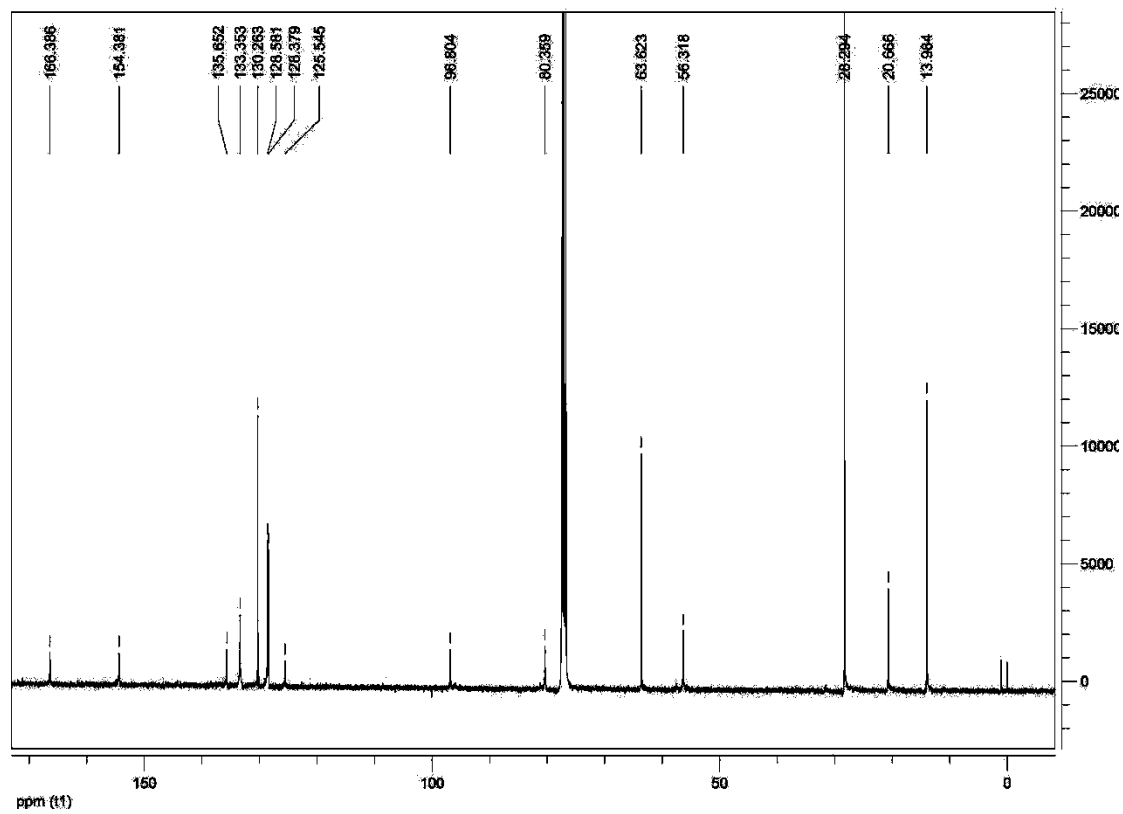
3.2 ^{13}C NMR of 4b



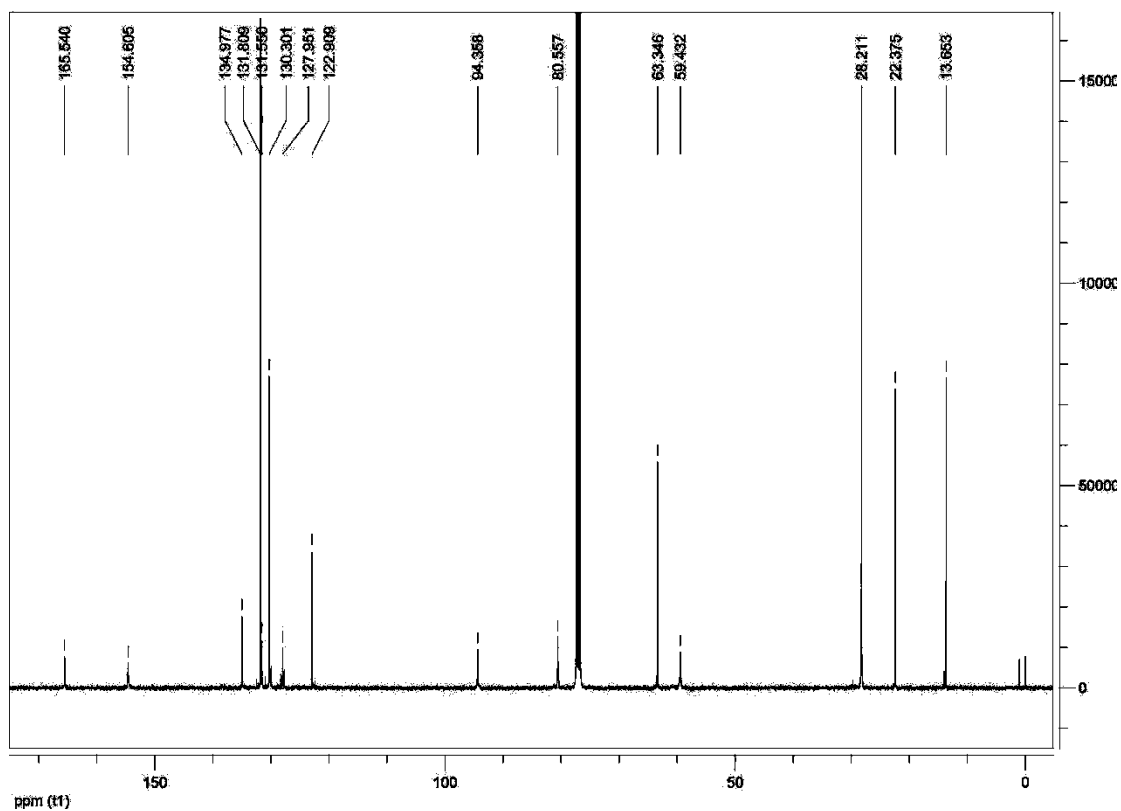
3.3 ¹³C NMR of 4c



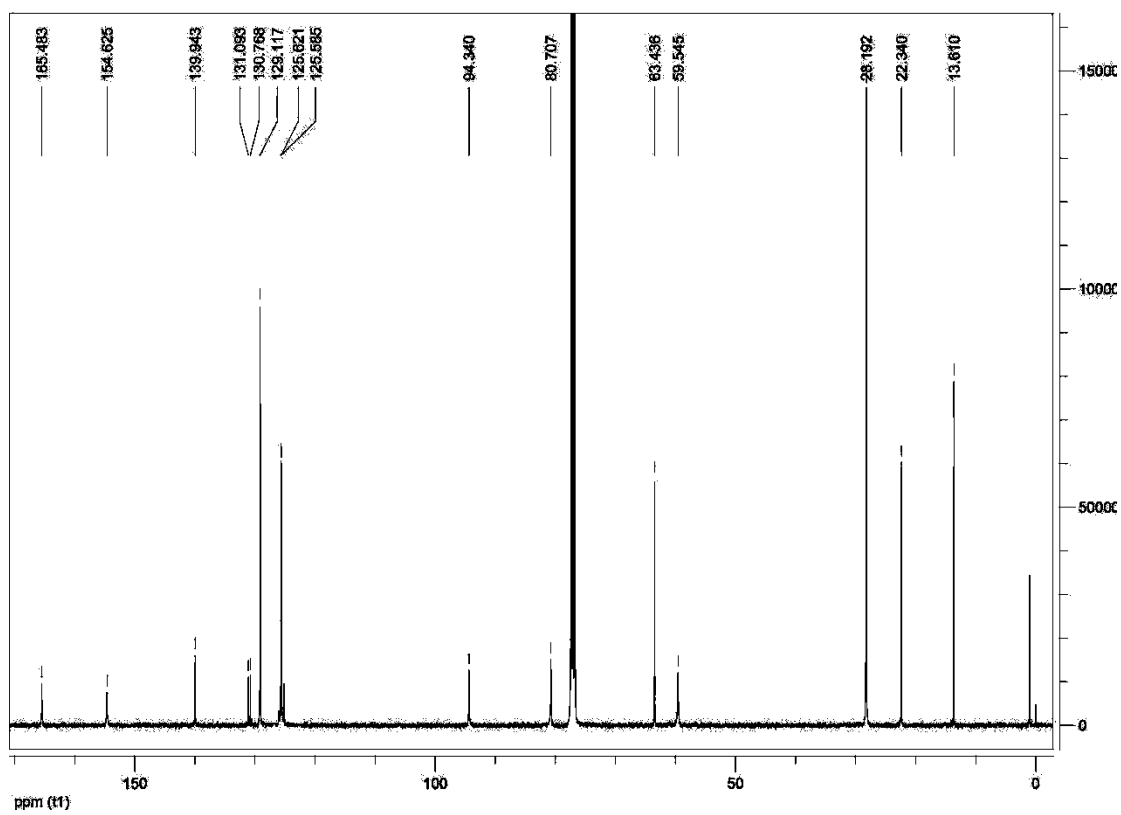
3.1 ¹³C NMR of 4d



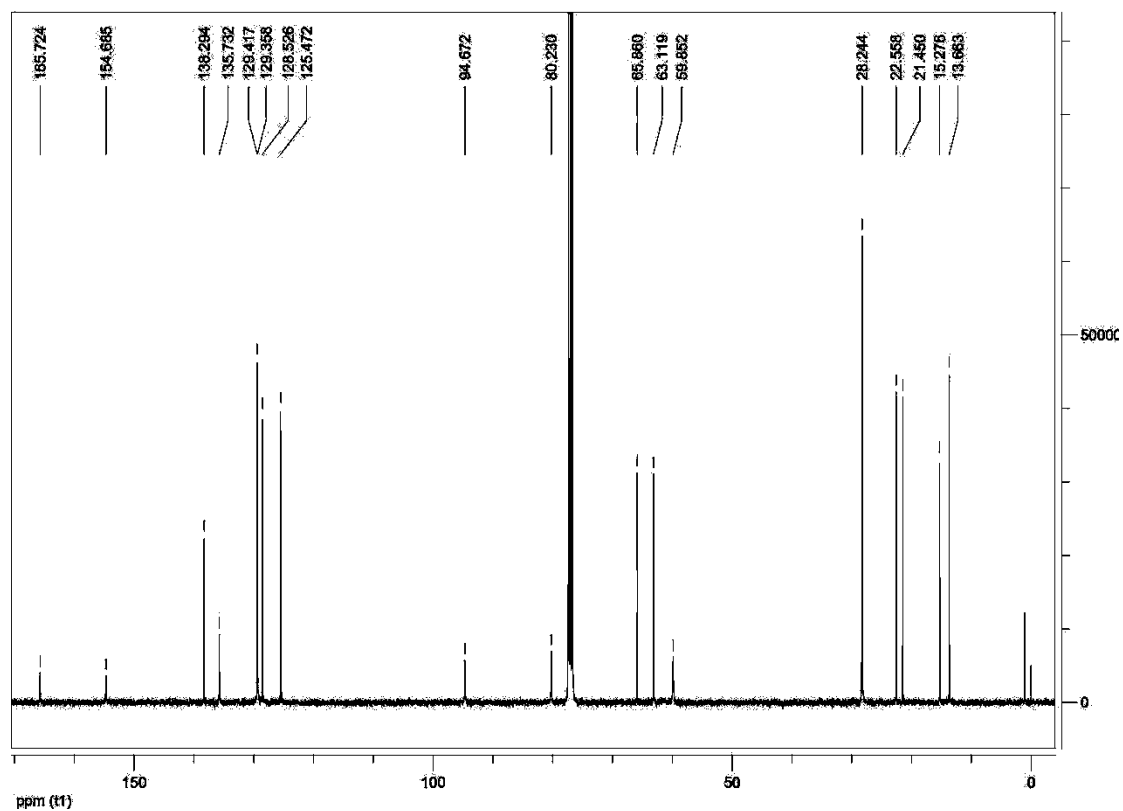
3.2 ¹³C NMR of 4e



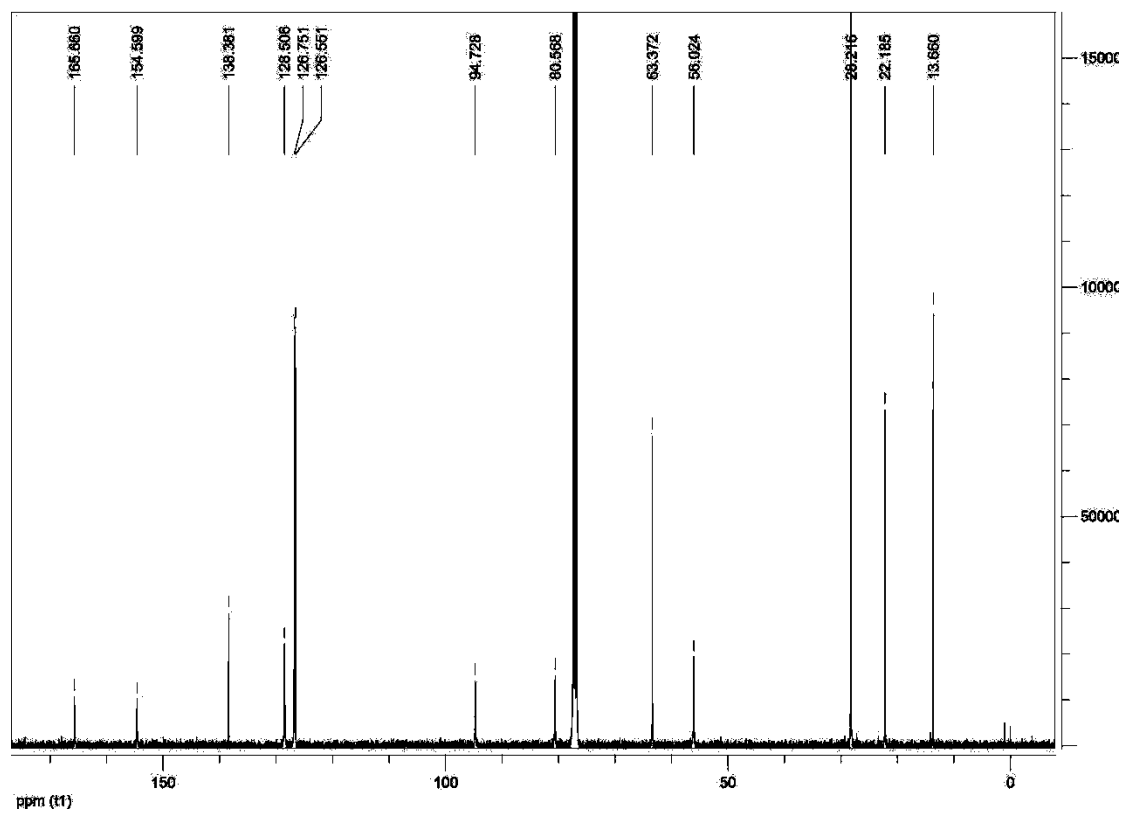
3.3 ¹³C NMR of 4g



3.4 ¹³C NMR of 4h



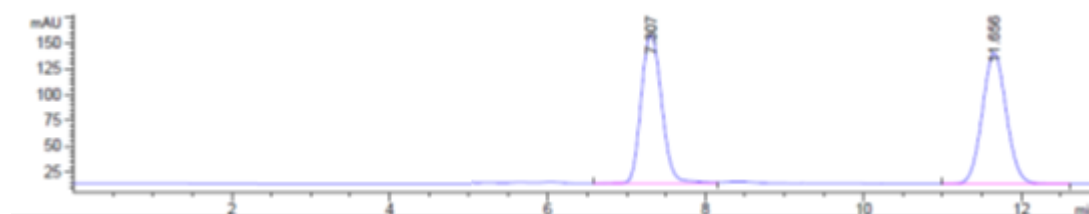
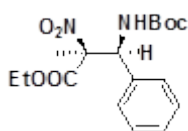
3.1 ^{13}C NMR of 4j



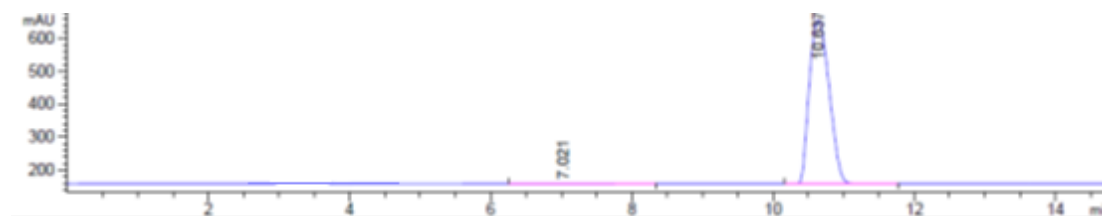
4. Chromatograms date

4.1 HPLC for 4a

HPLC analysis (Chiralpak AD-H column, n-hexane/2-propanol =90:10, flow rate = 1.0mL/min, wavelength = 220 nm), $t_{\text{major}}=10.63\text{min}$, $t_{\text{minor}}=7.02\text{min}$. $[\alpha]_D^{20} -11.8(\text{in EtOH})$



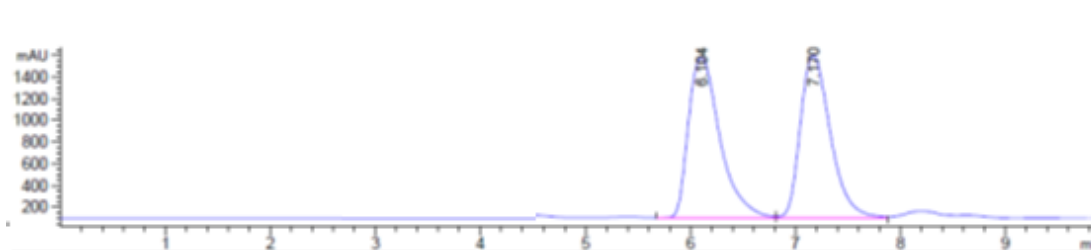
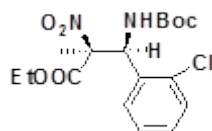
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.307	BV	0.2940	2638.50098	143.86443	49.4795
2	11.656	BB	0.3276	2694.01563	126.95264	50.5205



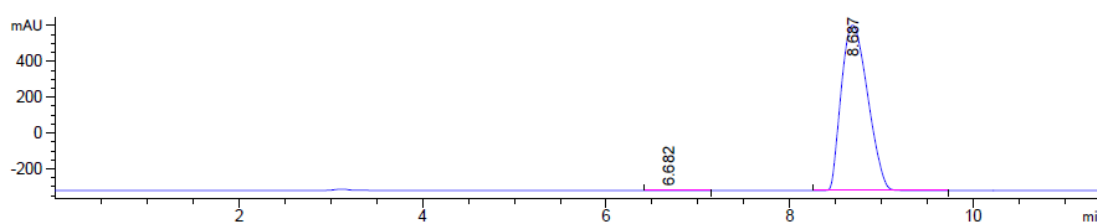
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1	7.021	VB	0.7963	53.75355	8.20549e-1	0.5516
2	10.637	VB	0.3231	9691.72852	497.82156	99.4484

4.2 HPLC for 4b

HPLC analysis (Chiralpak AD-H column, n-hexane/2-propanol =90:10, flow rate = 1.0mL/min, wavelength = 220 nm), $t_{\text{major}}=8.68\text{min}$, $t_{\text{minor}}=6.68\text{min}$. $[\alpha]_D^{20} +7.7(\text{in EtOH})$



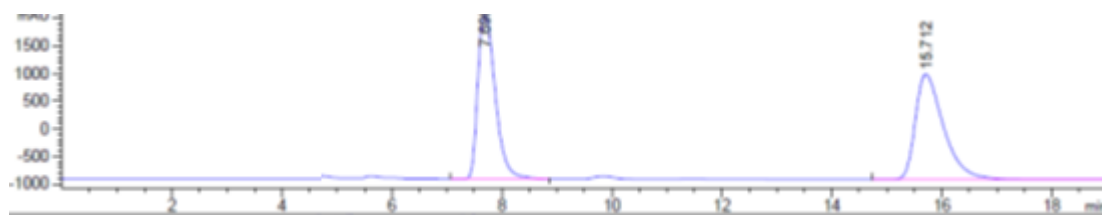
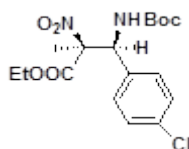
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.104	BV	0.3238	3.07966e4	1473.93555	50.8158
2	7.170	VV	0.3127	2.98077e4	1494.33838	49.1842



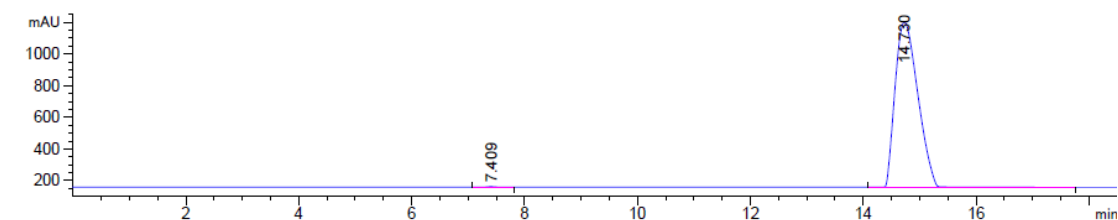
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1	6.682	VB	0.2077	8.94087	6.21838e-1	0.0485
2	8.687	BB	0.3250	1.84246e4	922.52832	99.9515

4.3 HPLC for 4c

HPLC analysis (Chiralpak AD-H column, n-hexane/2-propanol =90:10, flow rate = 1.0mL/min, wavelength = 220 nm), $t_{\text{major}}=14.73\text{min}$, $t_{\text{minor}}=7.40\text{min}$. $[\alpha]_D^{20} -22.7$ (in EtOH)



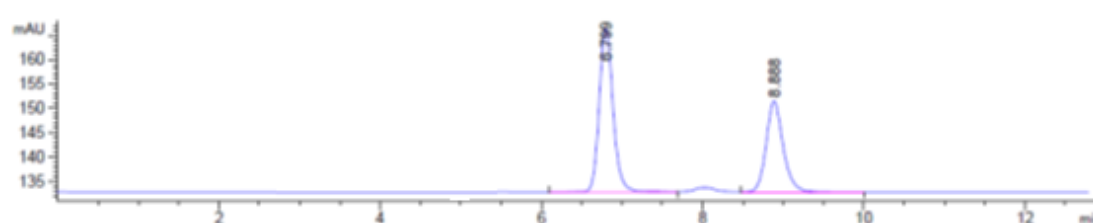
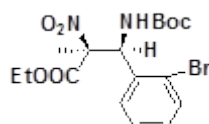
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1	7.690	BV	0.3471	6.56887e4	2957.82007	49.2209
2	15.712	BBA	0.5360	6.77682e4	1900.57263	50.7791



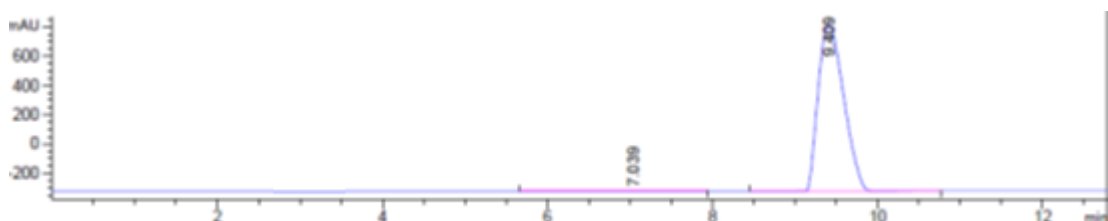
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1	7.409	BB	0.1558	39.15602	3.68980	0.1347
2	14.730	BB	0.4452	2.90382e4	1041.89771	99.8653

4.4 HPLC for 4d

HPLC analysis (Chiralpak AD-H column, n-hexane/2-propanol =90:10, flow rate = 1.0mL/min, wavelength = 220 nm), $t_{\text{major}}=9.40\text{min}$, $t_{\text{minor}}=7.03\text{min}$. $[\alpha]_D^{20}+11.3(\text{in EtOH})$



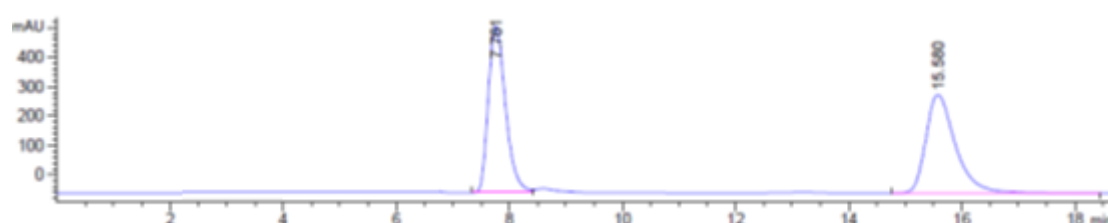
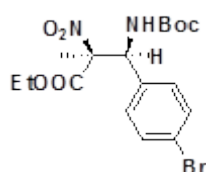
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1	6.799	BV	0.1909	408.23831	33.32938	59.5548
2	8.888	VB	0.2294	277.24557	18.65189	40.4452



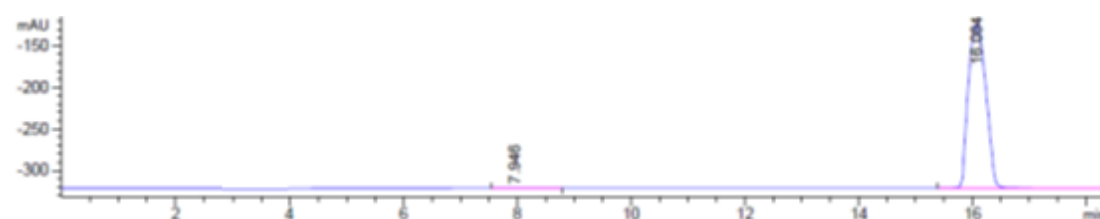
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1	7.039	VV	0.4509	37.31470	1.05944	0.1531
2	9.409	BB	0.3465	2.43387e4	1133.32007	99.8469

4.5 HPLC for 4e

HPLC analysis (Chiralpak AD-H column, n-hexane/2-propanol =90:10, flow rate = 1.0mL/min, wavelength = 220 nm), $t_{\text{major}}=16.06\text{min}$, $t_{\text{minor}}=7.94\text{min}$. $[\alpha]_D^{20} -24.5(\text{in EtOH})$



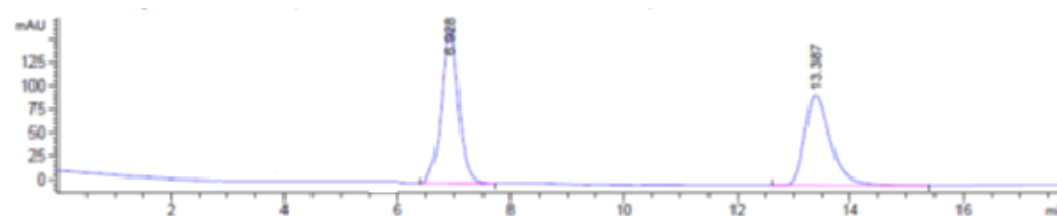
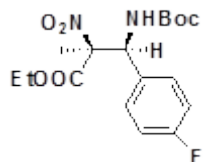
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1	7.761	BV	0.3289	1.20583e4	565.30280	49.9300
2	15.580	BBA	0.5507	1.20921e4	333.74338	50.0700



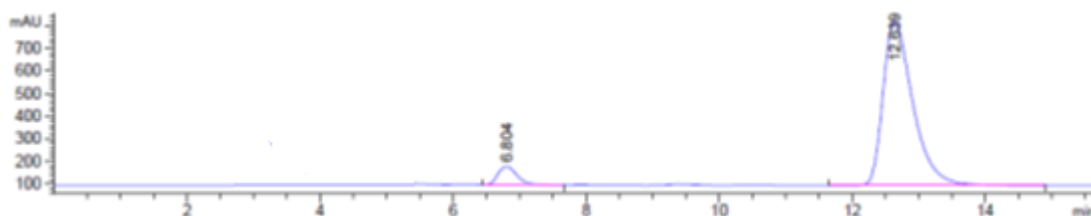
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1	7.946	VV	0.5789	23.27891	5.57742e-1	0.5464
2	16.064	BBA	0.3712	4236.89209	196.81137	99.4536

4.6 HPLC for 4f

HPLC analysis (Chiralpak AD-H column, n-hexane/2-propanol =90:10, flow rate = 1.0mL/min, wavelength = 220 nm), $t_{\text{major}}=12.63\text{min}$, $t_{\text{minor}}=6.80\text{min}$. $[\alpha]_D^{20} -7.4(\text{in EtOH})$



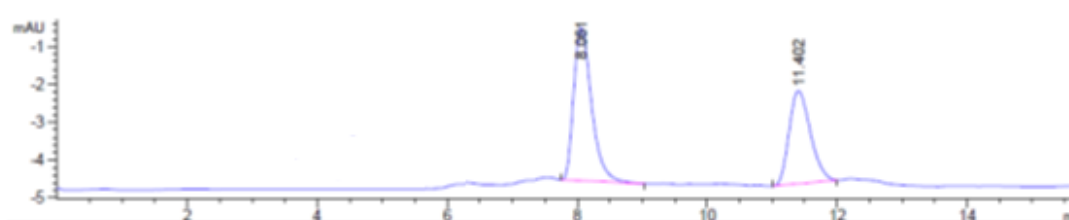
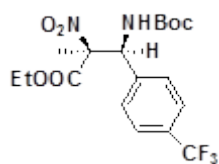
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1	6.928	BB	0.3230	3521.99585	165.00012	53.6590
2	13.387	BB	0.4825	3041.67261	95.77389	46.3410



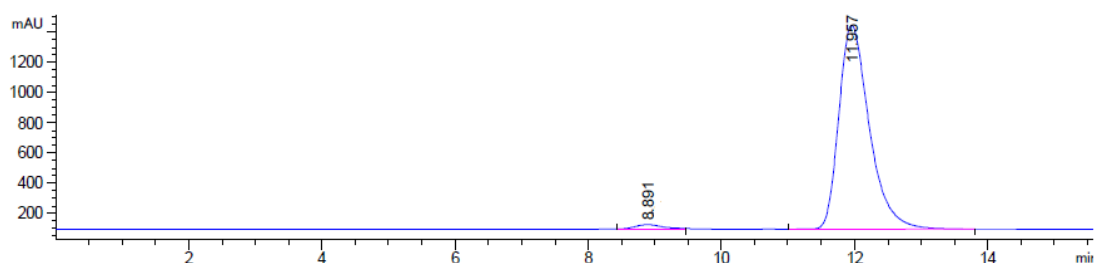
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1	6.805	BB	0.3101	165.09378	8.44515	5.5299
2	12.639	BB	0.4480	2820.37061	96.20542	94.4701

4.7 HPLC for 4g

HPLC analysis (Chiralpak AD-H column, n-hexane/2-propanol =90:10, flow rate = 1.0mL/min, wavelength = 220 nm), $t_{\text{major}}=11.95\text{min}$, $t_{\text{minor}}=8.89\text{min}$. $[\alpha]_D^{20}$ -12.3(in EtOH)



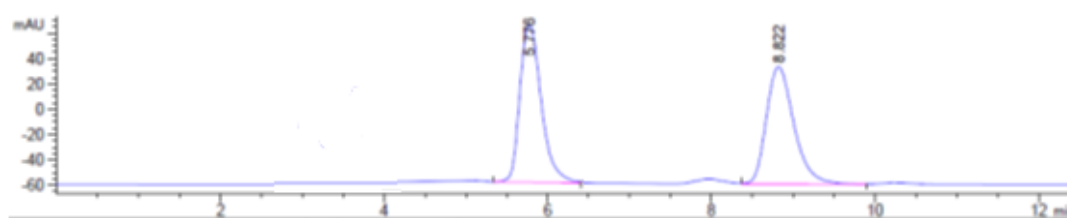
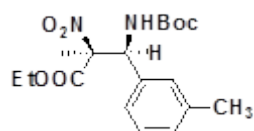
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1	8.061	BB	0.2952	77.19666	4.03475	58.0206
2	11.402	BB	0.3494	55.85385	2.45541	41.9794



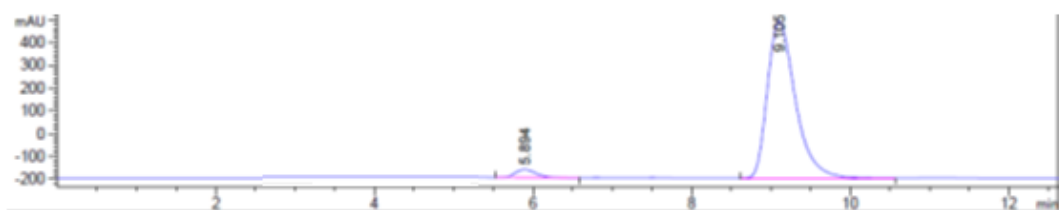
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1	8.891	MM	0.4774	838.75311	29.28064	1.9112
2	11.957	BB	0.4880	4.30479e4	1350.00024	98.0888

4.8 HPLC for 4h

HPLC analysis (Chiralpak AD-H column, n-hexane/2-propanol =90:10, flow rate = 1.0mL/min, wavelength = 220 nm), t_{major} =9.10min, t_{minor} =5.89min. $[\alpha]_D^{20}$ -9.6(in EtOH)



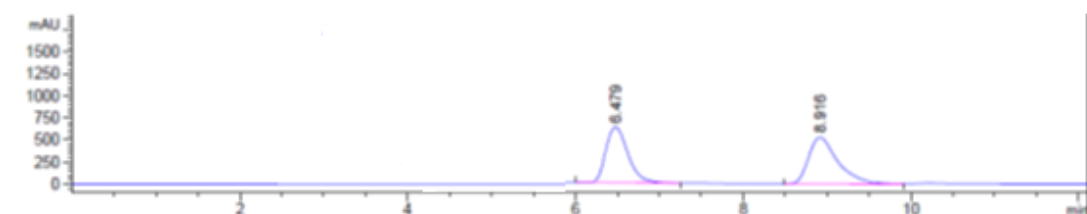
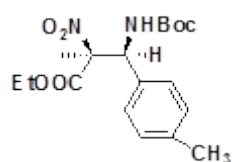
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1	5.776	BV	0.2843	2259.08081	124.15626	50.9619
2	8.822	VV	0.3623	2173.79810	92.46334	49.0381



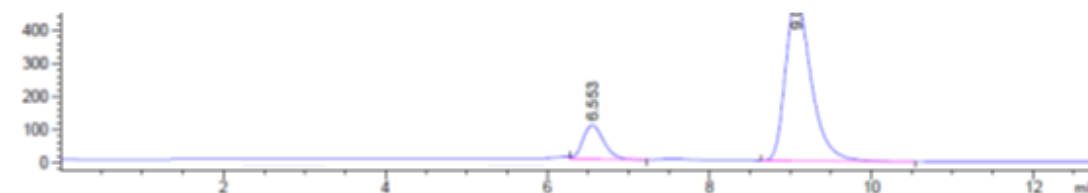
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.894	BB	0.2940	641.55316	34.65016	3.6609
2	9.105	BB	0.3790	1.68831e4	686.27600	96.3391

4.9 HPLC for 4i

HPLC analysis (Chiralpak AD-H column, n-hexane/2-propanol =90:10, flow rate = 1.0mL/min, wavelength = 220 nm), $t_{\text{major}}=9.07\text{min}$, $t_{\text{minor}}=6.55\text{min}$. $[\alpha]_D^{20} -19.0(\text{in EtOH})$



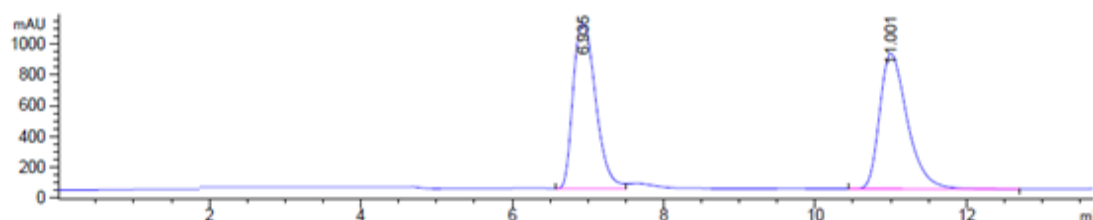
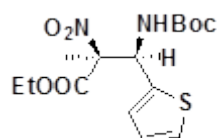
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.479	MM	0.3486	1.12620e4	538.41895	50.4396
2	8.917	MM	0.4133	1.10657e4	446.25443	49.5604



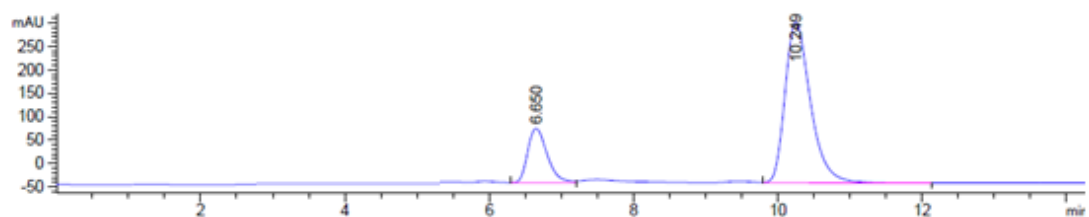
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.553	VB	0.2799	1849.34717	102.79500	14.6670
2	9.073	BB	0.3363	1.07595e4	489.78241	85.3330

4.10 HPLC for 4j

HPLC analysis (Chiralpak AD-H column, n-hexane/2-propanol =90:10, flow rate = 1.0mL/min, wavelength = 220 nm), $t_{\text{major}}=10.25$ min, $t_{\text{minor}}=6.65$ min. $[\alpha]_D^{20} -38.1$ (in EtOH)



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.935	BV	0.3302	2.22215e4	1070.45862	49.8368
2	11.001	BB	0.3908	2.23671e4	879.12732	50.1632



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.649	MM	0.3021	2241.29980	123.65408	19.7163
2	10.249	VB	0.3733	9126.44043	373.16492	80.2837