Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Highly Efficient Asymmetric Vinylogous Mannich Reaction Induced by *O*-Pivaloylated D-Galactosylamine as the Chiral Auxiliary

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Supporting Information

Experimental Section

General Comments.

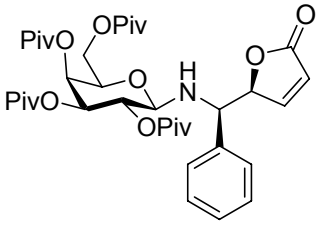
All reactions were carried out under an inert atmosphere and in heat-dried glassware. Anhydrous Et_2O were obtained by distillation from sodium. Flash column chromatography was performed on silica gel (particle size 10-40 μm, Ocean Chemical Factory of Qingdao, China). ^1H and ^{13}C NMR spectra were recorded on Brucker-400 (400 MHz for ^1H, 75 MHz for ^{13}C). Chemical shifts were reported in ppm downfield from internal $Si(CH_3)_4$. The crystal structure was determined on a Bruker SMART 1000 CCD diffractometer. Mass spectra were recorded on a LCQ advantage spectrometer with ESI resource. HR-MS were recorded on APEXII and ZAB-HS spectrometer. Melting points were determined on a T-4 melting point apparatus (uncorrected). Optical rotations were recorded on a Perkin Elemer 241 Polarimeter. HPLC analyses were recorded on a C18 column.

General procedure for the preparation of *O*-pivaloyiated *N*-Galactosylimines 3 of Aromatic Aldhydes: To a solution of 2,3,4,6-tetra-*O*-pivaloyl-β-D-galactopyranosylamine **1** (0.515 g, 1 mmol) and aldehyde **2** (1.3 mmol) in 2-propanol (2.5 ml), 2-3 drops of acetic acid were added and the mixture was stirred at room temperature for about 0.5 h. The appearance of a precipitate from the solution indicated the formation of **3**, after the precipitate was filtered off, then washed with ice cold 2-propanol and dried in vacuum, *N*-galactosylaldimines **3** was isolated as a colorless solid.

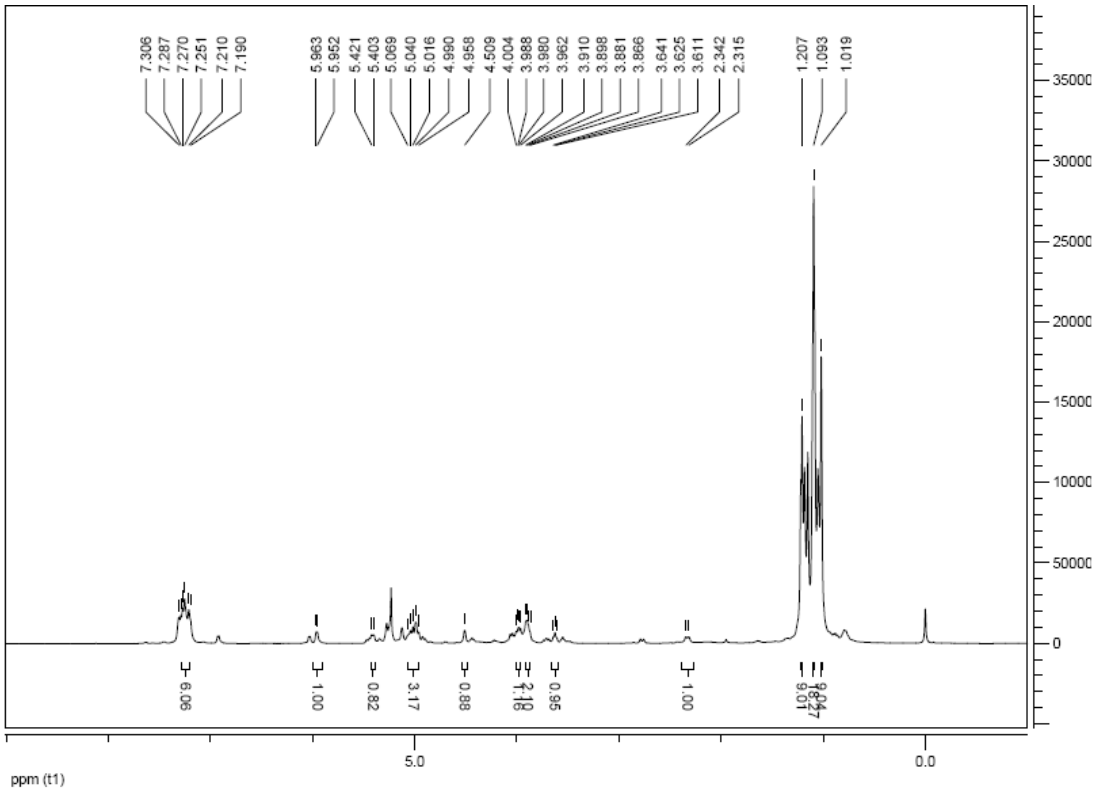
General procedure for the synthesis of *β*-*N*-glycosidic linkages γ-butenolide derivatives 5: A solution of *N*-galactosylaldimines **3** (0.3 mmol) in Et_2O (2 mL) was cooled to -78°C, and trimethylsiloxy furan (0.094 g, 0.6 mmol) and $ZnCl_2{\cdot}OEt_2$ (0.45 mL, 0.45mmol) were added. The mixture was stirred for corresponding time at -78°C. The mixture was hydrolyzed with saturated aqueous NH_4Cl (5 mL). The aqueous phase was extracted with Et_2O (3 × 10 mL), and the organic layers were dried with anhydrous $MgSO_4$, filtered, and concentrated in vacuo to yield the crude products **5**,

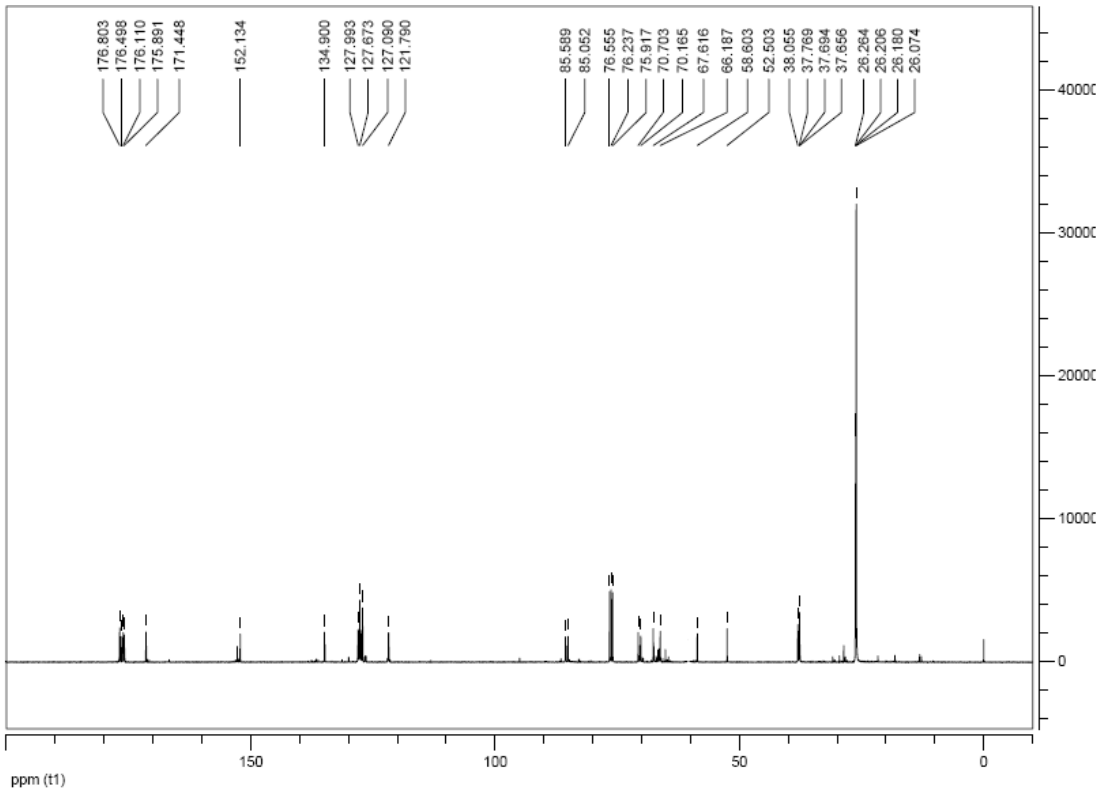
which were purified by flash column chromatography on silica gel [petroleum ether/ethyl acetate, 5:1(V/V)] to provide pure products **5**.

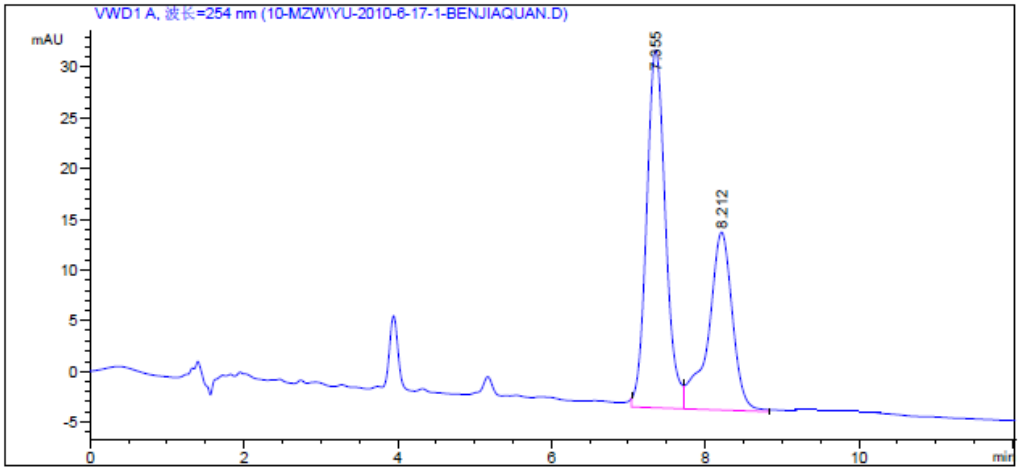
(*S*)-5-((*R*)-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-galactopyranosyl)amino(phenylmethyl)-5 *H*-furan-2-one (5a)



White solid; mp 64-68 °C; $[\alpha]_D^{25}$ = -2.6° (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.02 (s, 9H, $C(CH_3)_3$), 1.09 (s, 18H, $2C(CH_3)_3$), 1.21 (s, 9H, $C(CH_3)_3$), 2.33 (d, $^3J_{H\text{-}H}$ = 11.4 Hz, 1H, NH), 3.63 (t, $^3J_{H\text{-}H}$ = 6.0 Hz, 1H, CH), 3.88 (dd, $^3J_{H\text{-}H}$ = 11.4 Hz, $^3J_{H\text{-}H}$ = 6.0 Hz, 2H, 2CH), 4.00 (dd, $^3J_{H\text{-}H}$ = 10.2 Hz, $^3J_{H\text{-}H}$ = 7.2 Hz, 1H, CH), 4.51 (s., 1H, CH), 4.96-5.07 (m, 3H, 3CH), 5.41 (d, $^3J_{H\text{-}H}$ = 7.2 Hz, 1H, CH), 5.96 (d, $^3J_{H\text{-}H}$ = 4.4 Hz, 1H, CH), 7.19-7.31 (m, 6H, Ph, CH); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 26.07, 26.18, 26.21, 26.26, 37.66, 37.69, 37.77, 38.06, 52.50, 58.60, 66.19, 67.62, 70.17, 70.70, 85.05, 85.59, 121.79, 127.09, 127.67, 127.99, 134.90, 152.13, 171.45, 175.89, 176.11, 176.50, 176.80; ESI-MS: 710.8 ($[M+Na]^+$); HRMS calcd for $C_{37}H_{53}NO_{11}$: 710.3511 $[M+ Na]^+$. found: 710.3514.







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面积百分比报告

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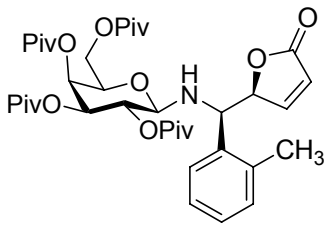
排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

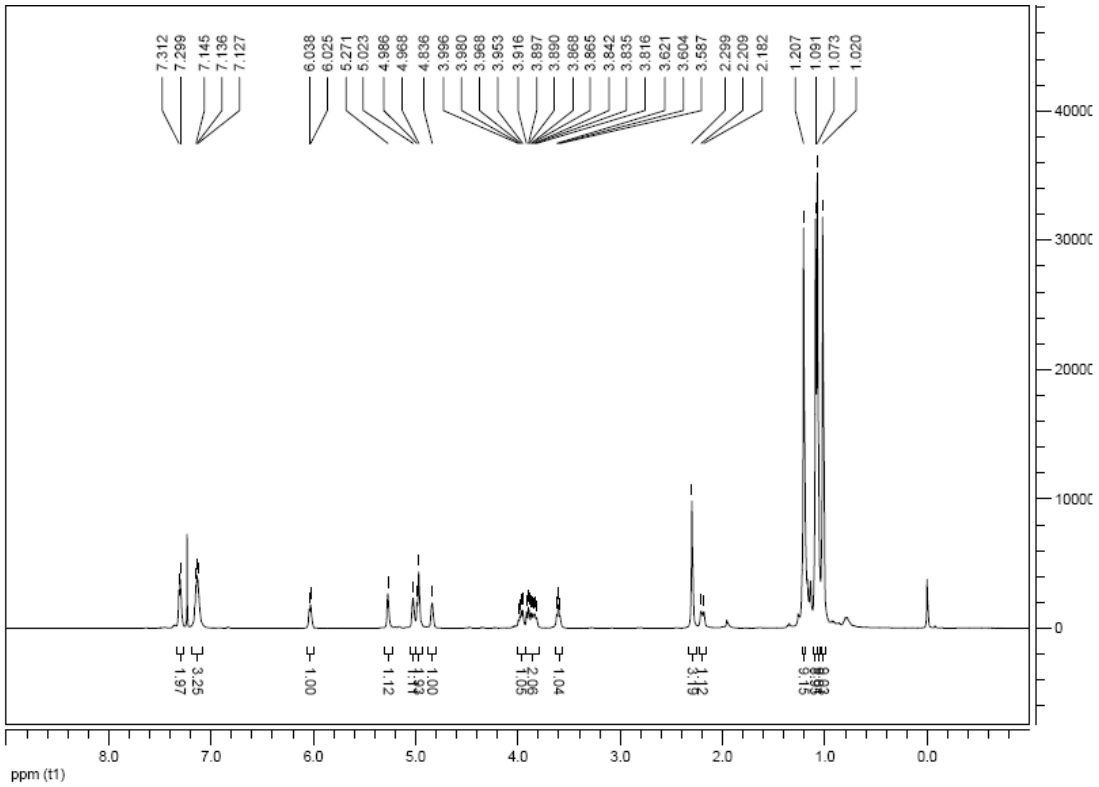
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	7.355	BV	0.2584	602.70721	35.13407	61.0409
2	8.212	VB	0.3264	384.67535	17.49660	38.9591

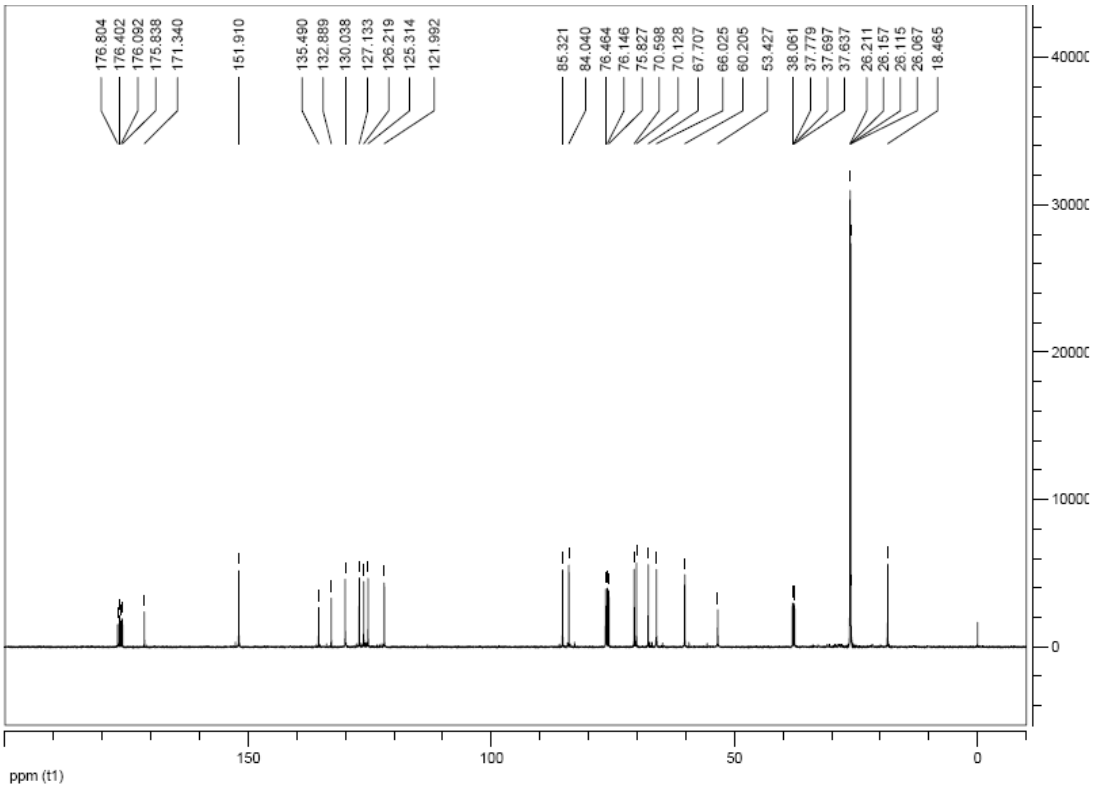
总量 : 987.38257 52.63066

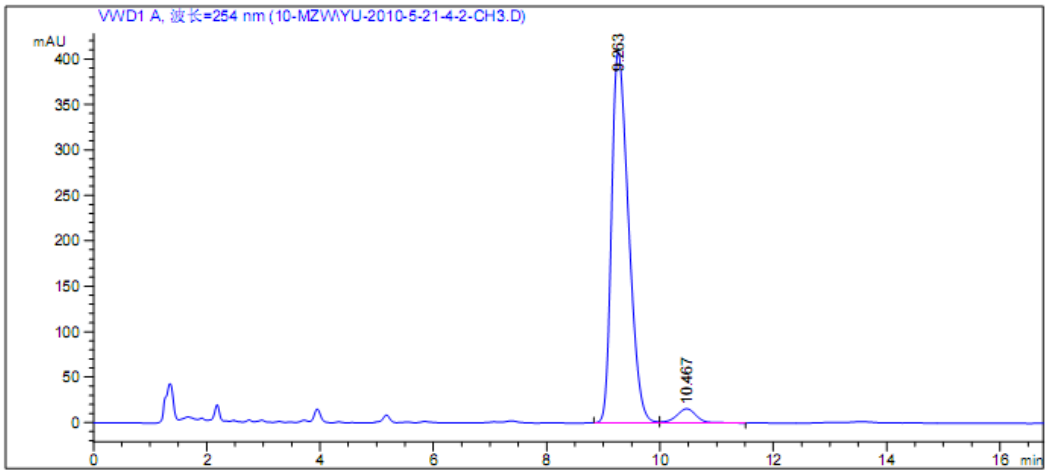
(*S*)-5-((*R*)-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-galactopyranosyl)amino(2-methylphenyl) methyl)-5*H*-furan-2-one (5b)



White solid; mp 71-72 °C; $[\alpha]_D^{25}$ = -48.4° (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.02 (s, 9H, $C(CH_3)_3$), 1.07 (s, 9H, $C(CH_3)_3$), 1.09 (s, 9H, $C(CH_3)_3$), 1.21 (s, 9H, $C(CH_3)_3$), 2.19 (d, $^3J_{H,H}$ = 10.9 Hz, 1H, NH), 2.30 (s, 3H, CH_3), 3.60 (t, $^3J_{H,H}$ = 6.6 Hz, 1H, CH), 3.82-3.92 (m, 2H, 2CH), 3.97 (dd, $^3J_{H,H}$ = 10.9 Hz, $^3J_{H,H}$ = 6.6 Hz, 1H, CH), 4.84 (s, 1H, CH), 4.97-4.99 (m, 2H, 2CH), 5.02 (s, 1H, CH), 5.27 (s, 1H, CH), 6.03 (d, $^3J_{H,H}$ = 5.2 Hz, 1H, CH), 7.13-7.15 (m, 3H, Ph), 7.30-7.31 (m, 2H, Ph, CH); ^{13}C-NMR (75MHz, $CDCl_3$): δ 18.47, 26.07, 26.12, 26.16, 26.21, 37.64, 37.70, 37.78, 38.06, 53.43, 60.21, 66.03, 67.71, 70.13, 70.60, 84.04, 85.32, 121.99, 125.31, 126.22, 127.13, 130.04, 132.89, 135.49, 151.91, 171.34, 175.84, 176.09, 176.40, 176.80; ESI-MS: 724.9 ([M+Na]$^+$); HRMS calcd for $C_{38}H_{55}NO_{11}$: 724.3667 [M+ Na]$^+$. found: 724.3674.







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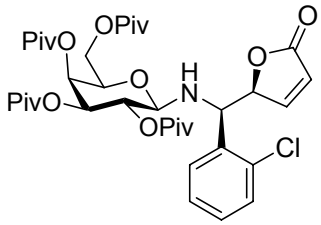
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

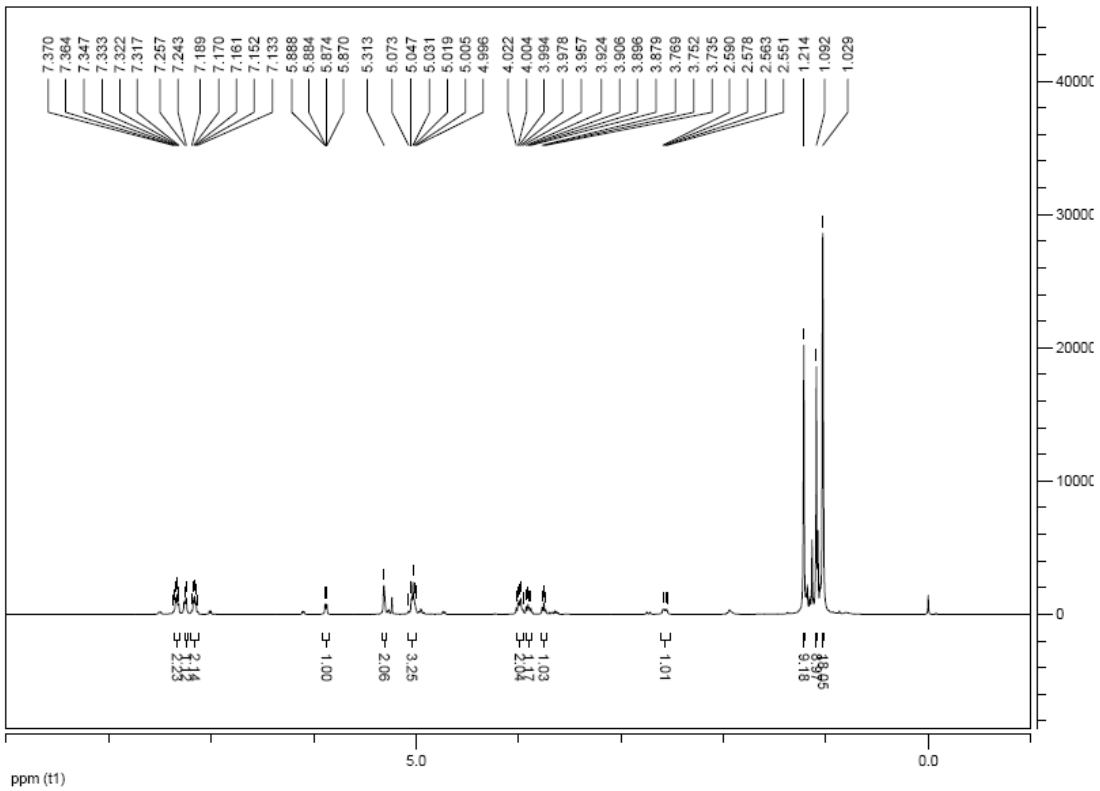
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	9.263	BV	0.3372	8519.37402	407.24039	95.4283
2	10.467	VB	0.3929	408.13660	15.88739	4.5717

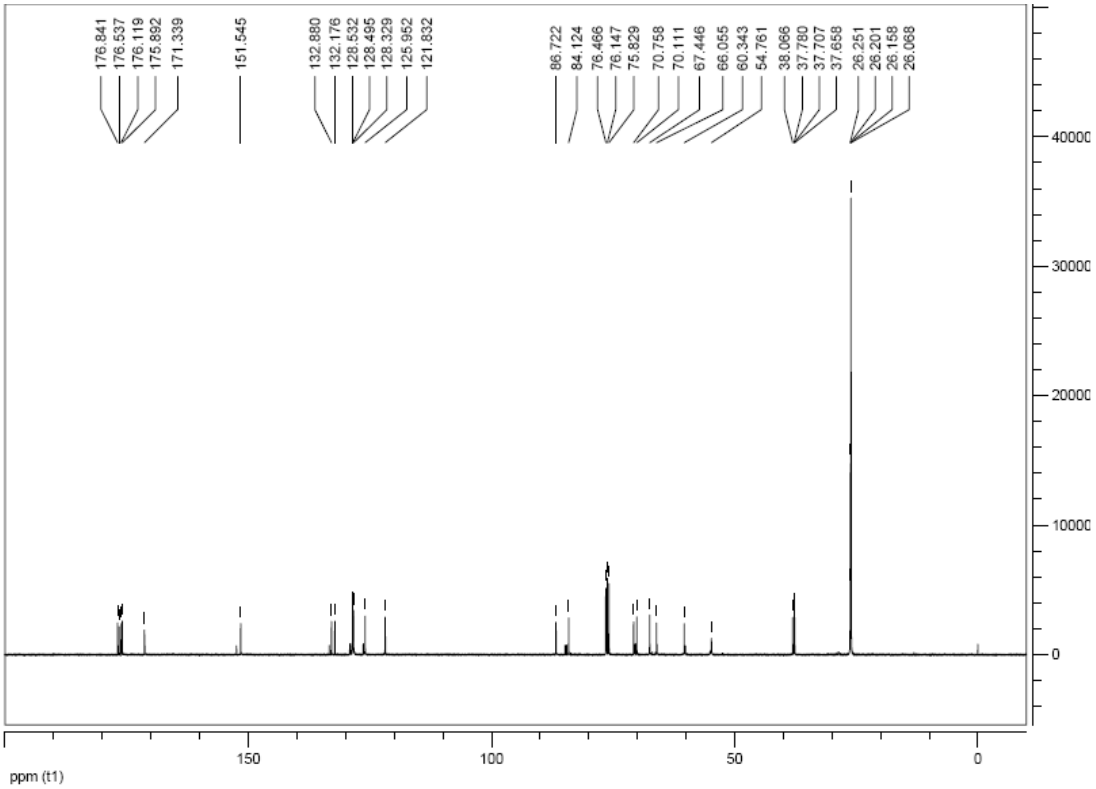
总量 : 8927.51062 423.12777

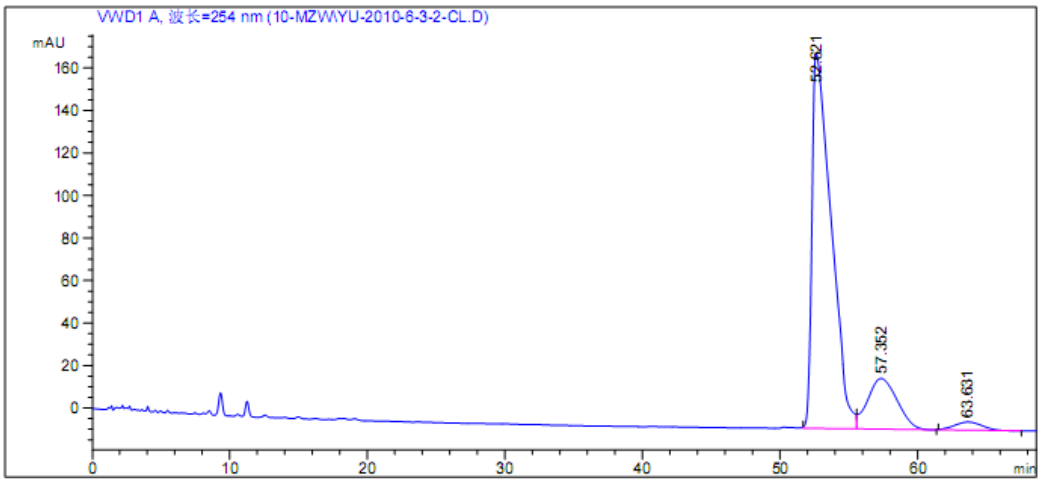
(*S*)-5-((*R*)-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-galactopyranosyl)amino(*o*-chlorophenyl) methyl)-5*H*-furan-2-one (5c)



White solid; mp 87-89 °C; $[\alpha]_D^{25} = -22.5^{\circ}$ (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 18H, 2C$(CH_3)_3$), 1.10 (s, 9H, C$(CH_3)_3$), 1.21(s, 9H, C$(CH_3)_3$), 2.57 (dd, $^3J_{H\text{-}H}$ = 11.1 Hz, $^3J_{H\text{-}H}$ = 4.8 Hz, 1H, NH), 3.75 (t, $^3J_{H\text{-}H}$ = 6.8 Hz, 1H, CH), 3.90 (dd, $^3J_{H\text{-}H}$ = 11.1 Hz, $^3J_{H\text{-}H}$ = 7.0 Hz, 1H, CH), 3.96-4.02 (m, 2H, 2CH), 5.00-5.07 (m, 3H, 3CH), 5.31 (s, 2H, 2CH), 5.88 (dd, $^3J_{H\text{-}H}$ = 5.6 Hz, $^3J_{H\text{-}H}$ = 1.4 Hz, 1H, CH), 7.13-7.19 (m, 2H, Ph), 7.25 (d, $^3J_{H\text{-}H}$ = 5.6 Hz, 1H, CH), 7.32-7.37 (m, 2H, Ph); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 26.07, 26.16, 26.20, 26.25, 37.66, 37.71, 37.78, 38.07, 54.76, 60.34, 66.06, 67.45, 70.11, 70.76, 84.12, 86.72, 121.83, 125.98, 128.33, 128.50, 128.53, 132.18, 132.88, 151.55, 171.34, 175.89, 176.12, 176.54, 176.84; ESI-MS: 744.9 ($[M+Na]^+$); HRMS calcd for $C_{37}H_{52}ClNO_{11}$: 744.3121 $(M+Na)^+$. found: 744.3126







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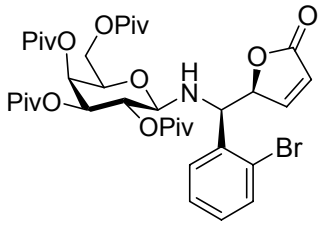
信号 1: VWD1 A, 波长=254 nm

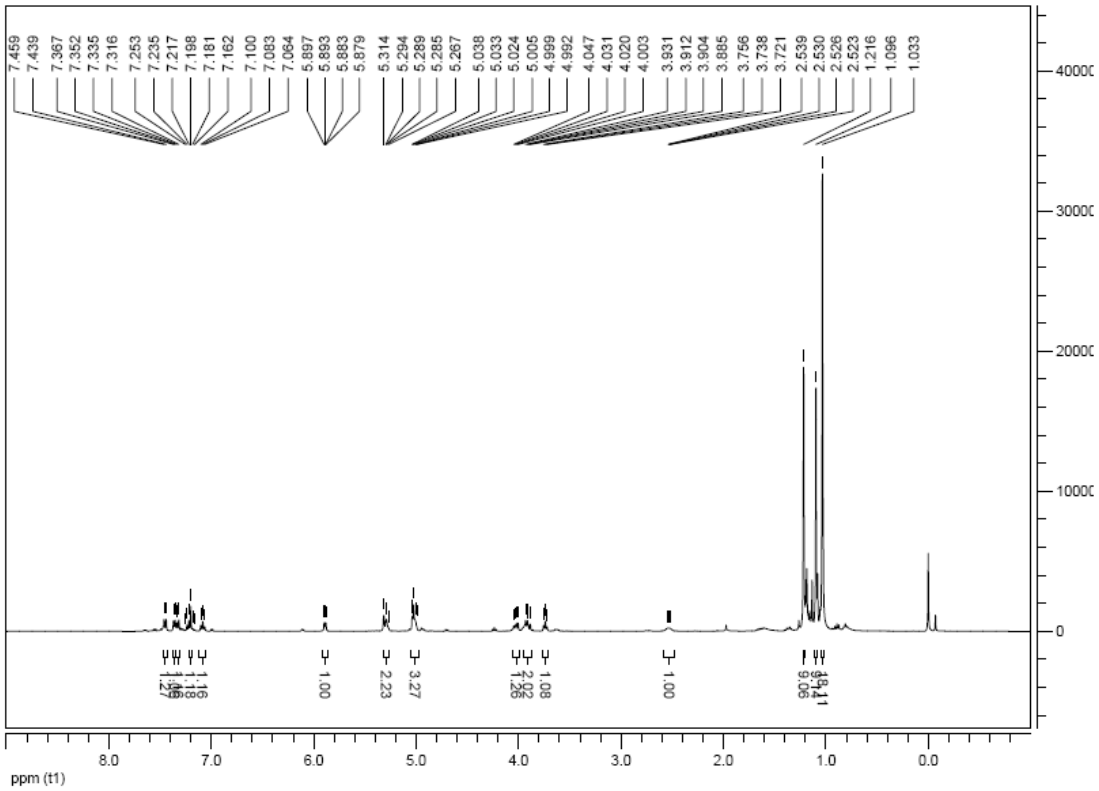
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	52.621	BV	1.3743	1.70706e4	176.29204	80.4222
2	57.352	VB	2.2742	3595.43237	23.96956	16.9386
3	63.631	BB	2.0978	560.19788	3.92100	2.6392

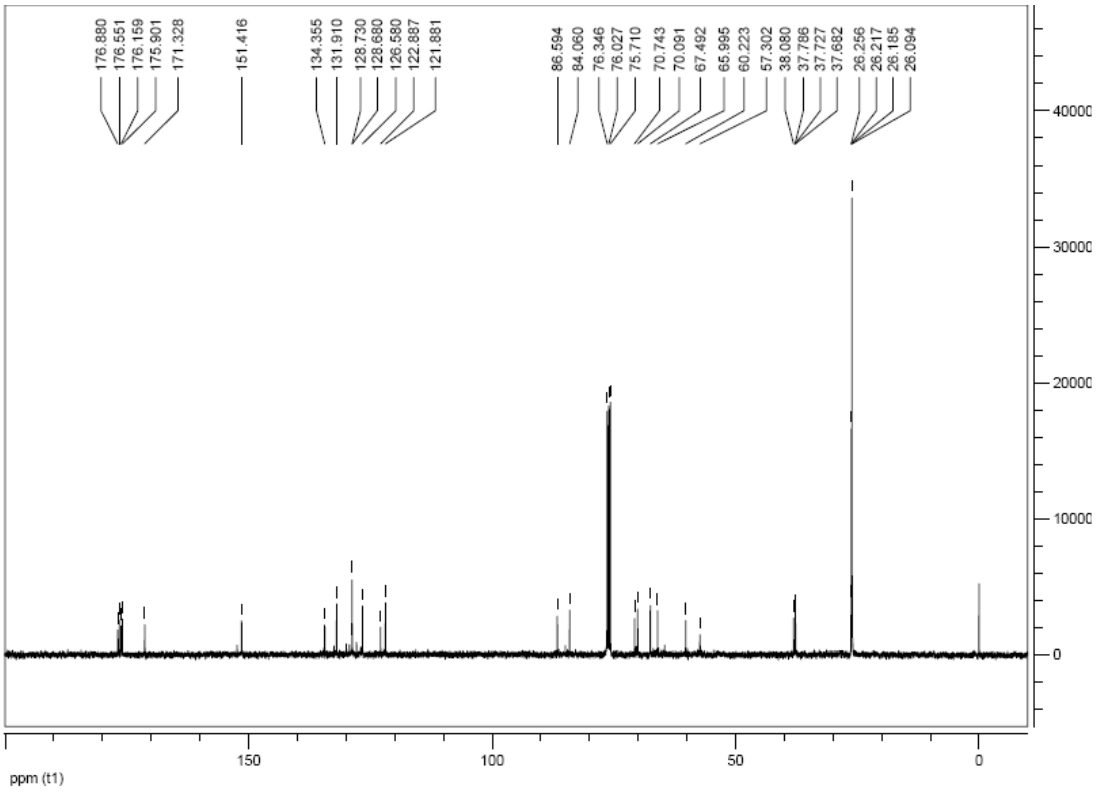
总量 : 2.12262e4 204.18260

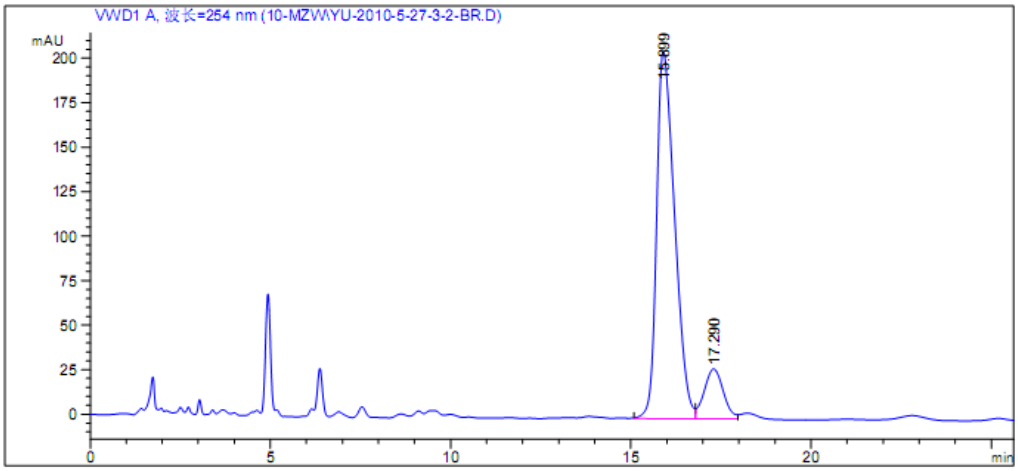
(*S*)-5-((*R*)-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-galactopyranosyl)amino(*o*-bromophenyl) methyl)-5*H*-furan-2-one (5d)



White solid; mp 64-66 °C; $[\alpha]_D^{25} = -22.6°$ (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 18H, 2C$(CH_3)_3$), 1.10 (s, 9H, C$(CH_3)_3$), 1.22 (s, 9H, C$(CH_3)_3$), 2.53 (dd, $^3J_{H-H}$ = 4.0 Hz, $^3J_{H-H}$ = 3.3Hz, 1H, NH), 3.74 (t, $^3J_{H-H}$ = 6.9 Hz, 1H, CH), 3.91 (dd, $^3J_{H-H}$ = 10.8 Hz, $^3J_{H-H}$ = 7.6 Hz, 2H, 2CH), 4.01 (dd, $^3J_{H-H}$ = 10.8 Hz, $^3J_{H-H}$ = 6.9 Hz, 1H, CH), 4.99-5.04 (m, 3H, 3CH), 5.27-5.31 (m, 2H, 2CH), 5.89 (dd, $^3J_{H-H}$ = 5.7 Hz, $^3J_{H-H}$ = 1.5 Hz, 1H, CH), 7.08 (t, $^3J_{H-H}$ = 7.7 Hz, 1H, Ph), 7.16-7.25 (m, 1H, Ph), 7.33 (d, $^3J_{H-H}$ = 7.7 Hz, 1H, Ph), 7.36 (d, $^3J_{H-H}$ = 5.7Hz, 1H, CH), 7.45 (d, $^3J_{H-H}$ = 7.7 Hz, 1H, Ph); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 26.10, 26.19, 26.22, 26.26, 37.68, 37.73, 37.79, 38.08, 57.30, 60.22, 66.00, 67.49, 70.09, 70.74, 84.06, 86.59, 121.88, 122.89, 126.58, 128.68, 128.73, 131.91, 134.36, 151.42, 171.33, 175.90, 176.16, 176.55, 176.88; ESI-MS: 788.8 ([M+Na]$^+$); HRMS calcd for $C_{37}H_{52}BrNO_{11}$: 788.2616 [M+ Na]$^+$. found: 788.2614







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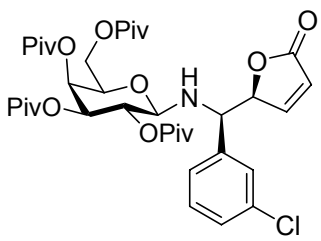
排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

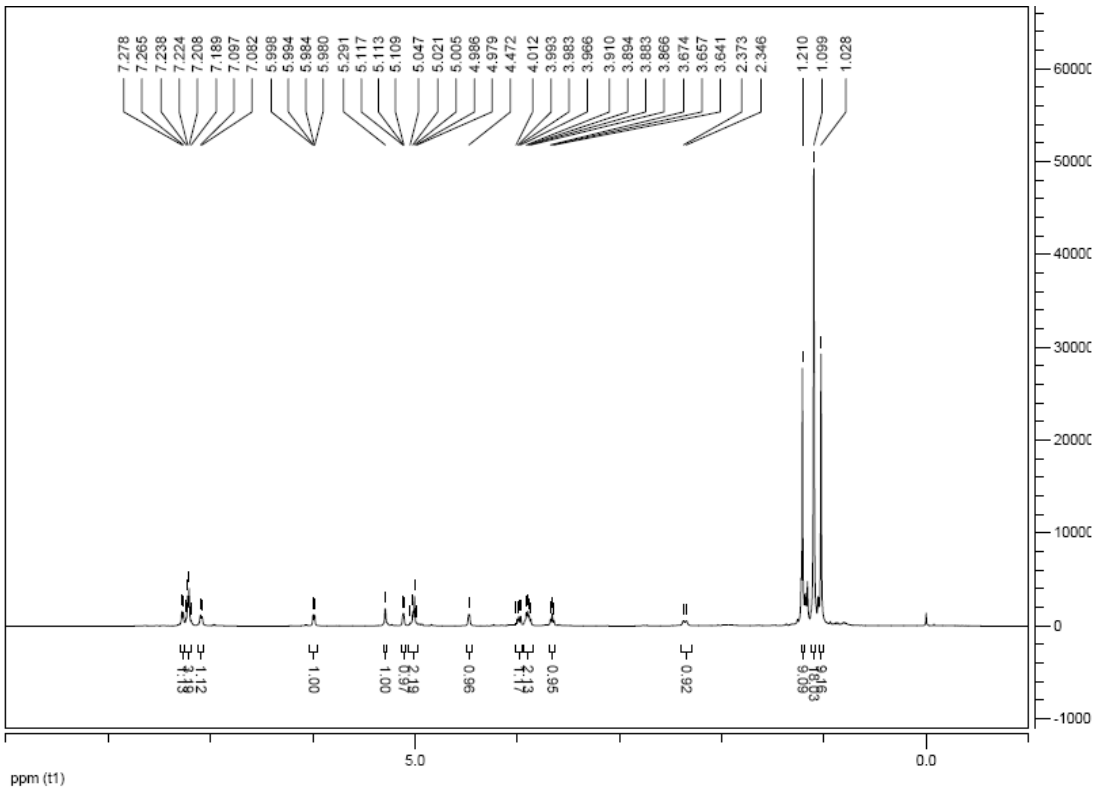
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	15.899	BV	0.5348	7186.02490	206.15181	87.2840
2	17.290	VV	0.5846	1046.89648	28.19591	12.7160

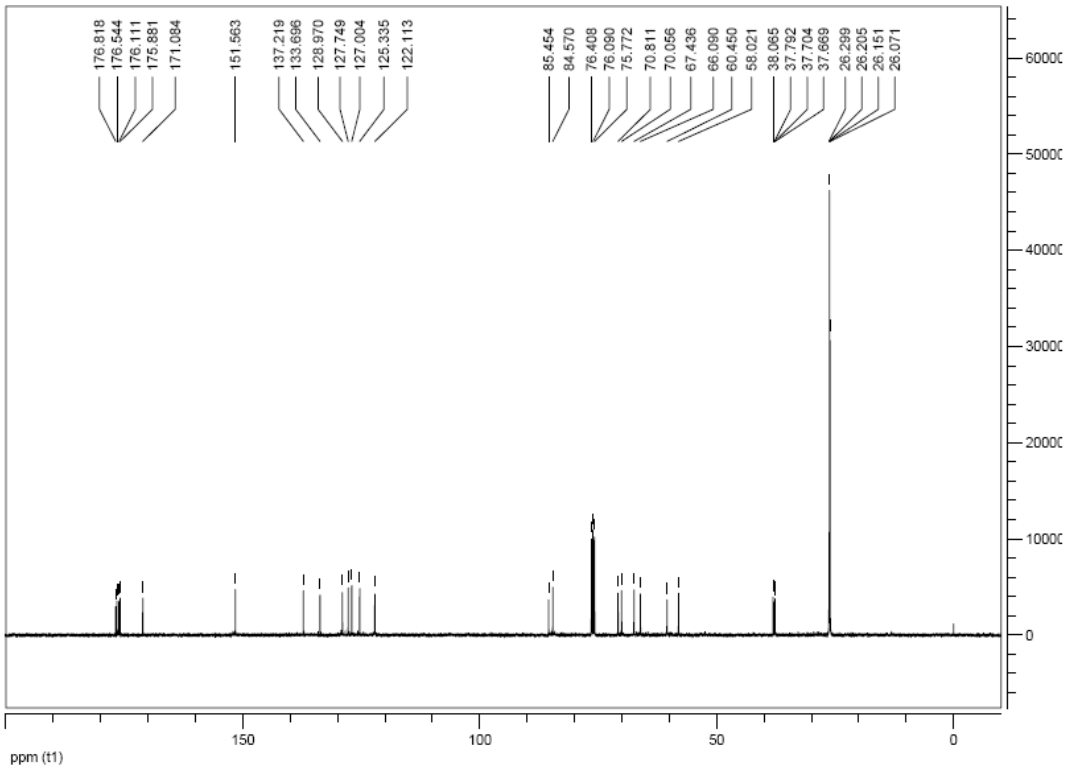
总量 : 8232.92139 234.34772

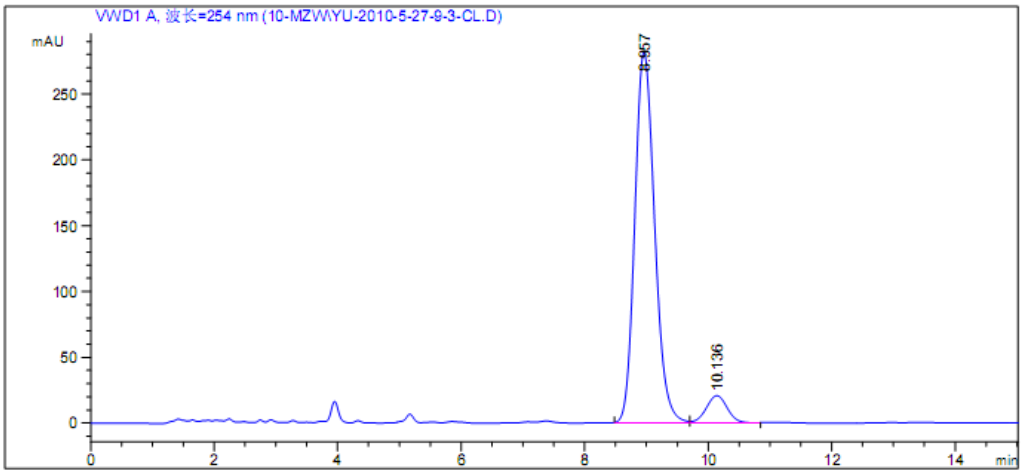
(*S*)-5-((*R*)-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-galactopyranosyl)amino(*m*-chlorophenyl) methyl)-5*H*-furan-2-one (5e)



White solid; mp 83-85 °C; $[\alpha]_D^{25} = -37.5°$ (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 1H, $C(CH_3)_3$), 1.10 (s, 18H, $2C(CH_3)_3$), 1.21 (s, 1H, $C(CH_3)_3$), 2.36 (d, $^3J_{H-H}$ = 10.7 Hz, 1H, NH), 3.66 (t, $^3J_{H-H}$ = 7.0 Hz, 1H, CH), 3.89 (dd, $^3J_{H-H}$ = 10.7 Hz, $^3J_{H-H}$ = 6.7 Hz, 2H, 2CH), 3.99 (dd, $^3J_{H-H}$ = 11.3 Hz, $^3J_{H-H}$ = 7.0 Hz, 1H, CH), 4.47 (s, 1H, CH), 4.98-5.05 (m, 2H, 2CH), 5.11 (t, $^3J_{H-H}$ = 1.7 Hz, 1H, CH), 5.29 (s, 1H, CH), 5.99 (dd, $^3J_{H-H}$ = 5.6 Hz, $^3J_{H-H}$ = 1.7 Hz, 1H, CH), 7.09 (d, $^3J_{H-H}$ = 5.9 Hz, 1H, Ph), 7.19-7.24 (m, 3H, Ph), 7.27 (d, $^3J_{H-H}$ = 5.6 Hz, 1H, CH); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 26.07, 26.15, 26.21, 26.30, 37.67, 37.70, 37.79, 38.07, 58.02, 60.45, 66.09, 67.44, 70.06, 70.81, 84.57, 85.45, 122.11, 125.34, 127.00, 127.75, 128.97, 133.70, 137.22, 151.56, 171.08, 175.88, 176.11, 176.54, 176.82; ESI-MS: 722.9 ($[M+H]^+$); HRMS calcd for $C_{37}H_{52}ClNO_{11}$: 744.3121 $[M+ Na]^+$. found: 744.3125.







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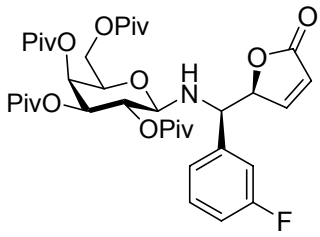
信号 1: VWD1 A, 波长=254 nm

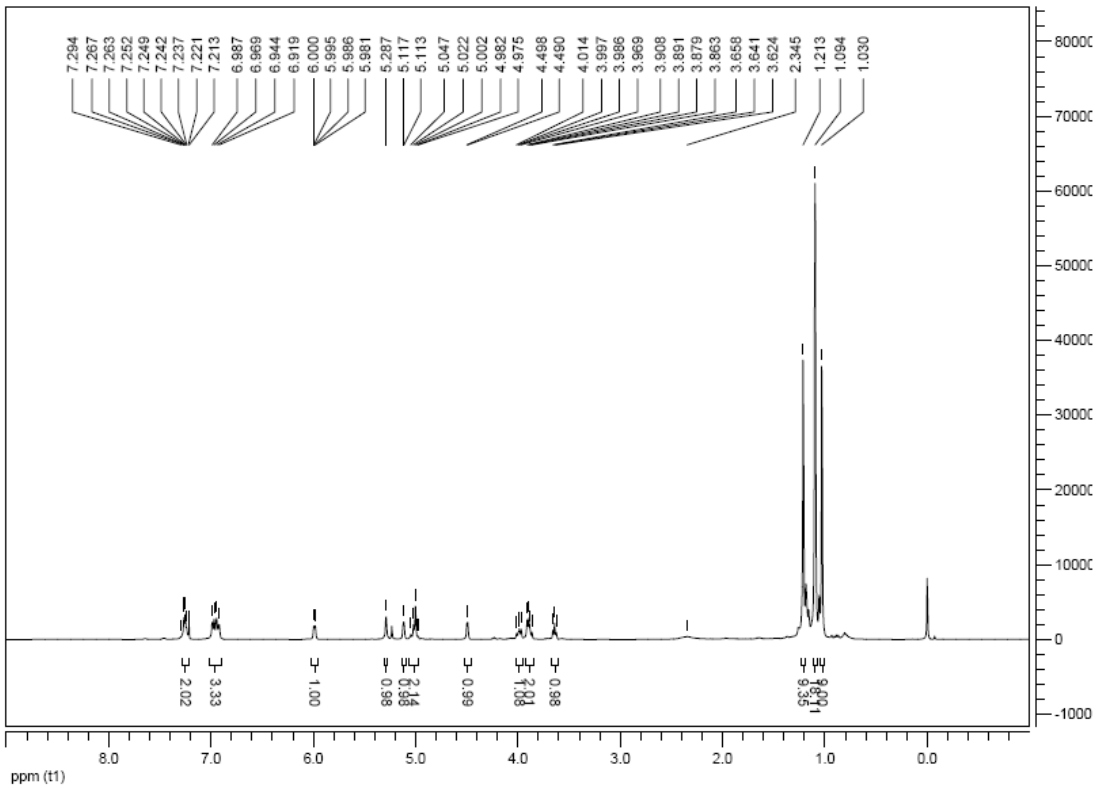
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	8.957	BV	0.3543	6294.43896	281.23871	92.6386
2	10.136	VB	0.3737	500.17831	20.80249	7.3614

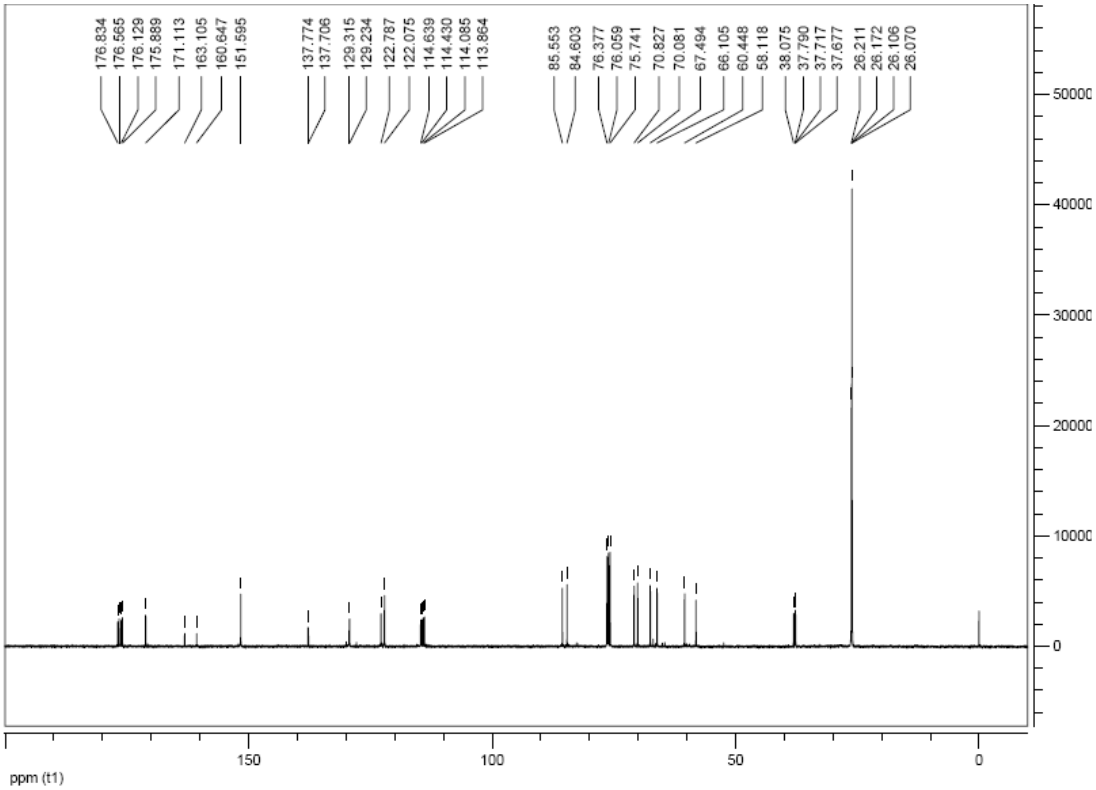
总量 : 6794.61728 302.04120

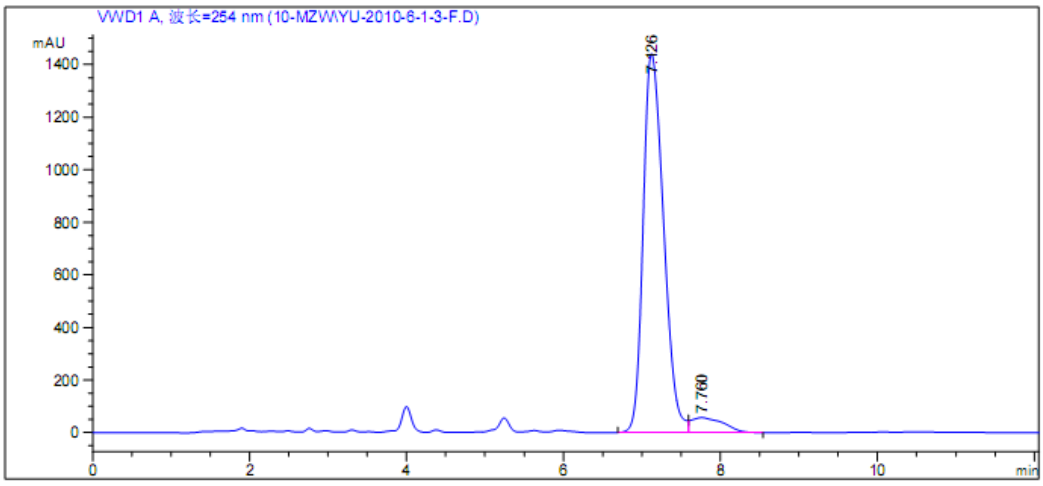
(*S*)-5-((*R*)-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-galactopyranosyl)amino(*m*-fluorophenyl) methyl)-5*H*-furan-2-one (5f)



White solid; mp 79-81 °C; $[\alpha]_D^{25}$ = -31.5° (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 9H, $C(CH_3)_3$), 1.09 (s, 18H, $2C(CH_3)_3$), 1.21 (s, 9H, $C(CH_3)_3$), 2.35 (s, 1H, NH), 3.64 (t, $^3J_{H\text{-}H}$ = 6.7 Hz, 1H, CH), 3.89 (dd, $^3J_{H\text{-}H}$ = 11.4 Hz, $^3J_{H\text{-}H}$ = 6.6 Hz, 2H, 2CH), 3.99 (dd, $^3J_{H\text{-}H}$ = 11.4 Hz, $^3J_{H\text{-}H}$ = 6.7 Hz, 1H, CH), 4.49 (d, $^3J_{H\text{-}H}$ = 3.2 Hz, 1H, CH), 4.98-5.05 (m, 2H, 2CH), 5.12 (d, $^3J_{H\text{-}H}$ = 2.1 Hz, 1H, CH), 5.29 (s, 1H, CH), 5.99 (dd, $^3J_{H\text{-}H}$ = 5.7 Hz, $^3J_{H\text{-}H}$ = 2.1 Hz, 1H, CH), 6.92-6.99 (m, 3H, Ph), 7.21-7.29 (m, 2H, Ph, CH); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 26.07, 26.11, 26.17, 26.21, 37.68, 37.72, 37.79, 38.08, 58.12, 60.45, 66.11, 67.49, 70.08, 70.83, 84.60, 85.55, 113.86, 114.09, 114.43, 114.64, 122.08, 122.79, 129.23, 129.32, 137.71, 137.77, 151.60, 160.65, 163.11, 171.11, 175.89, 176.13, 176.57, 176.83; ESI-MS: 728.9 ($[M+Na]^+$) ; HRMS calcd for $C_{37}H_{52}FNO_{11}$: 728.3417 $[M+Na]^+$. found: 728.3418.







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面积百分比报告

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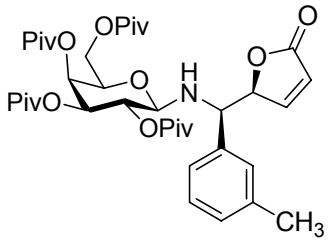
排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

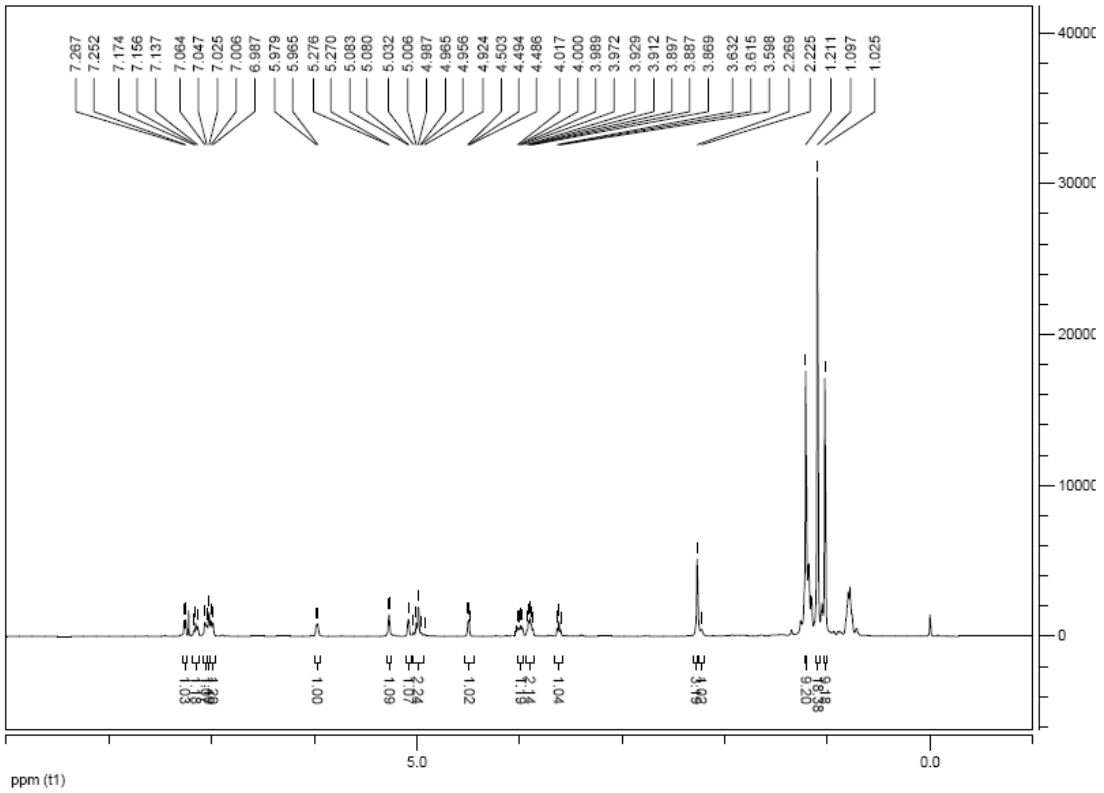
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	7.126	BV	0.2821	2.61365e4	1436.80737	94.0079
2	7.760	VV	0.3822	1665.95618	57.90705	5.9921

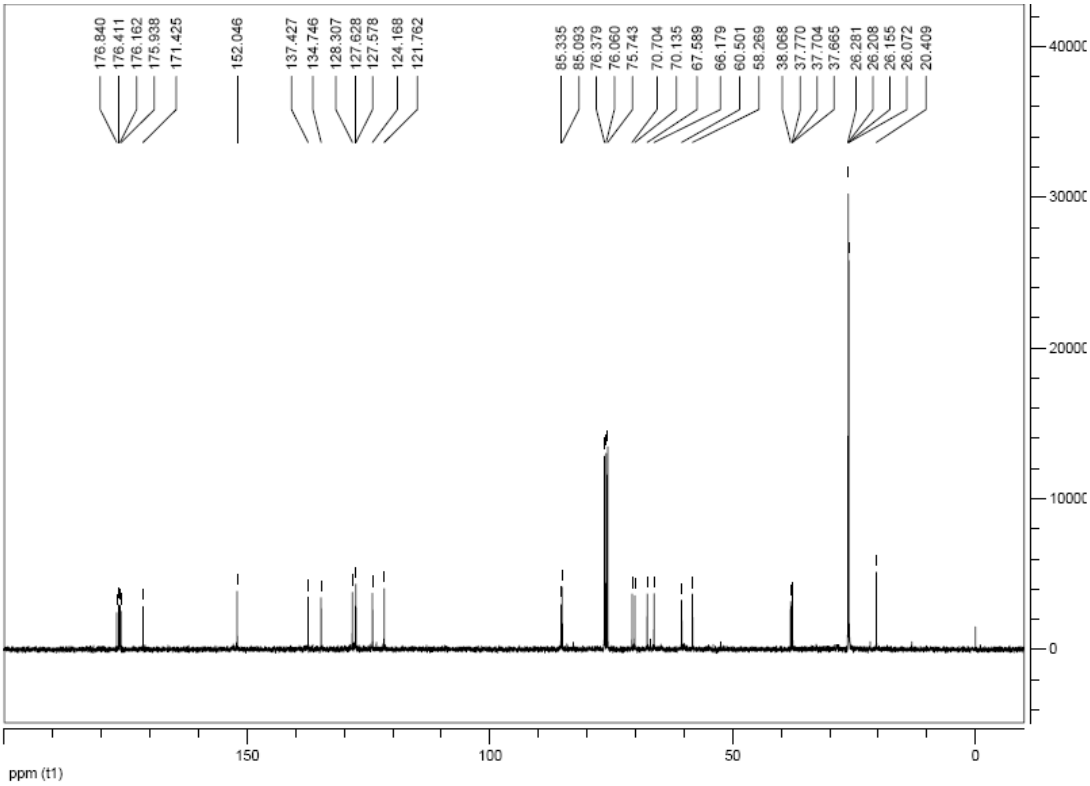
总量 : 2.78025e4 1494.71443

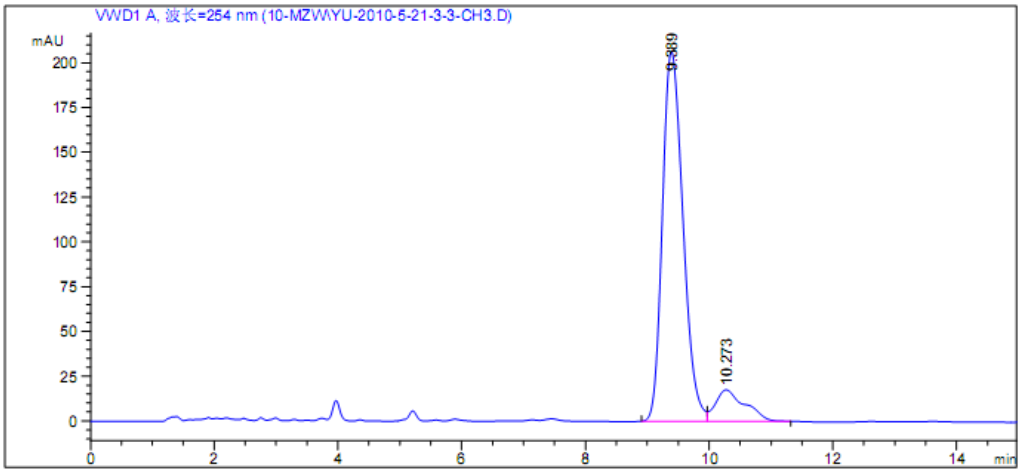
(*S*)-5-((*R*)-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-galactopyranosyl)amino(*m*-methylphenyl) methyl)-5*H*-furan-2-one (5g)



White solid; mp 69-72 °C; $[\alpha]_D^{25}$ = -37.4° (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 9H, $C(CH_3)_3$), 1.10 (s, 18H, $2C(CH_3)_3$), 1.21 (s, 9H, $C(CH_3)_3$), 2.23 (s, br, 1H, NH), 2.27 (s, 1H, CH_3), 3.62 (t, $^3J_{H,H}$ = 6.6 Hz, 1H, CH), 3.87- 3.93 (m, 2H, 2CH), 4.00 (dd, $^3J_{H,H}$ = 11.1 Hz, $^3J_{H,H}$ = 6.6 Hz, 1H, CH), 4.49 (t, $^3J_{H,H}$ = 3.4 Hz, 1H, CH), 4.92-5.03 (m, 2H, 2CH), 5.08 (d, $^3J_{H,H}$ = 1.3 Hz, 1H, CH), 5.27 (d, $^3J_{H,H}$ = 2.3 Hz, 1H, CH), 5.97 (d, $^3J_{H,H}$ = 5.8Hz, 1H, CH), 7.00 (d, $^3J_{H,H}$ = 7.5 Hz, 1H, Ph), 7.03 (s, 1H, Ph), 7.05 (d, $^3J_{H,H}$ = 6.9 Hz, 1H, Ph), 7.16 (t, $^3J_{H,H}$ = 7.5 Hz, 1H, Ph), 7.26 (d, $^3J_{H,H}$ = 5.8 Hz, 1H, CH); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 20.41, 26.07, 26.16, 26.21, 26.28, 37.67, 37.70, 37.77, 38.07, 58.27, 60.50, 66.18, 67.59, 70.14, 70.70, 85.09, 85.34, 121.76, 124.17, 127.58, 127.63, 128.31, 134.75, 137.43, 152.05, 171.43, 175.94, 176.16, 176.41, 176.84; ESI-MS: 724.9 ($[M+Na]^+$); HRMS calcd for $C_{38}H_{55}NO_{11}$: 724.3667 $[M + Na]^+$. found: 724.3669.







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面积百分比报告

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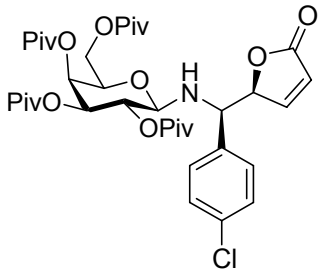
排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

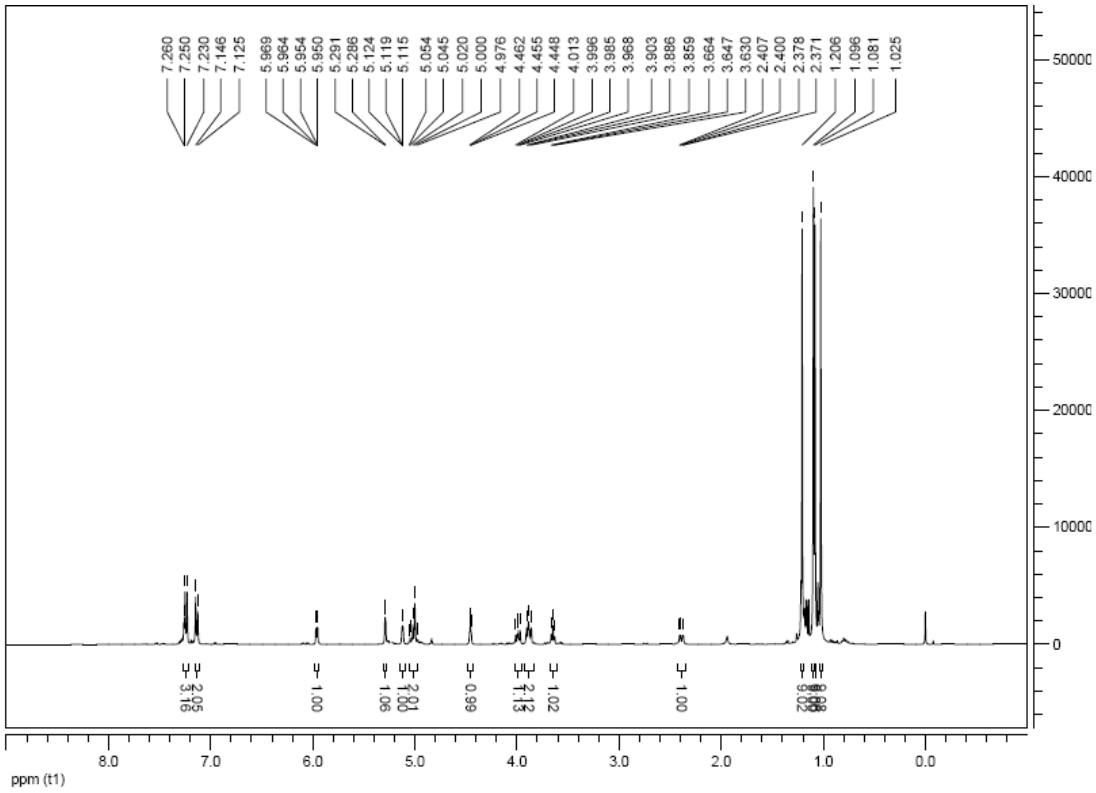
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	9.389	BV	0.3638	4786.21875	206.31972	88.8319
2	10.273	VB	0.4758	601.73389	17.80652	11.1681

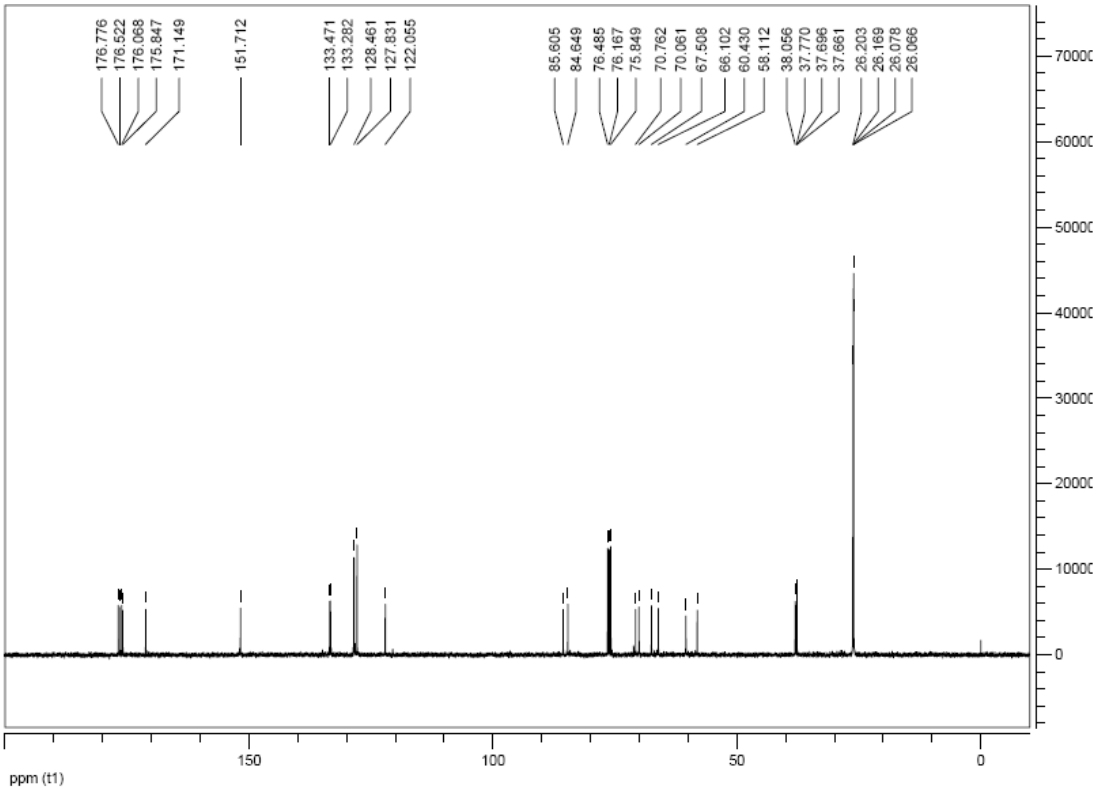
总量 : 5387.95264 224.12624

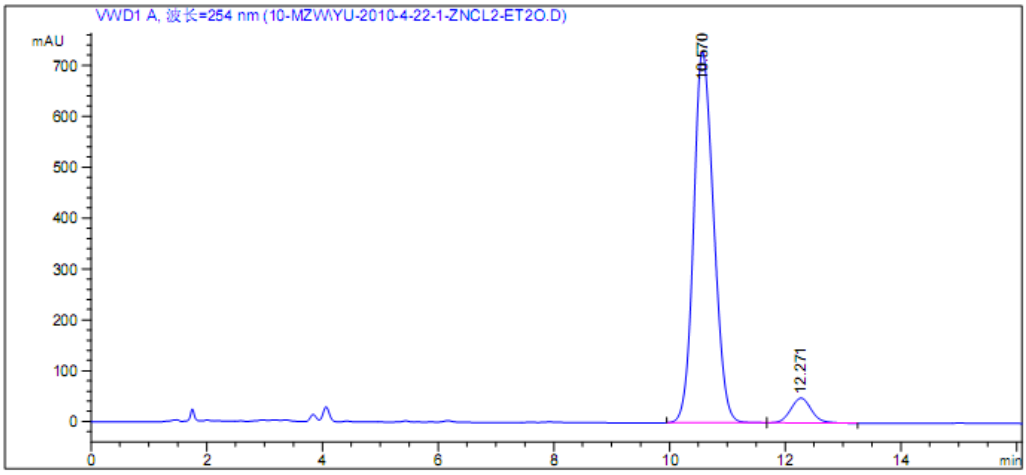
(*S*)-5-((*R*)-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-galactopyranosyl)amino(4-chlorophenyl) methyl)-5*H*-furan-2-one (5h)



White solid; mp 96-98 °C; $[\alpha]_D^{25}$ = -37.9° (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 9H, $C(CH_3)_3$), 1.08 (s, 9H, $C(CH_3)_3$), 1.10 (s, 9H, $C(CH_3)_3$), 1.21 (s, 9H, $C(CH_3)_3$), 2.39 (dd, $^3J_{H,H}$ = 11.8 Hz, $^3J_{H,H}$ = 2.9 Hz, 1H, NH), 3.65 (t, $^3J_{H,H}$ = 6.8 Hz, 1H, CH), 3.86-3.90 (m, 2H, 2CH), 4.00 (dd, $^3J_{H,H}$ = 11.8 Hz, $^3J_{H,H}$ = 6.8 Hz, 1H, CH), 4.46 (t, $^3J_{H,H}$ = 2.9 Hz, 1H, CH), 4.98-5.05 (m, 2H, 2CH), 5.12 (t, $^3J_{H,H}$ = 1.7 Hz, 1H, CH), 5.29 (d, $^3J_{H,H}$ = 1.7 Hz, 1H, CH), 5.96 (dd, $^3J_{H,H}$ = 5.7 Hz, $^3J_{H,H}$ = 1.7 Hz, 1H, CH), 7.13 (d, $^3J_{H,H}$ = 8.3 Hz, 2H, Ph), 7.23-7.26 (m, 3H, Ph, CH); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 26.07, 26.08, 26.17, 26.20, 37.66, 37.70, 37.77, 38.06, 58.11, 60.43, 66.10, 67.51, 70.06, 70.76, 84.65, 85.61, 122.06, 127.83, 128.46, 133.28, 133.47, 151.71, 171.15, 175.85, 176.07, 176.52, 176.78; ESI-MS: 744.9 ([M+Na]$^+$); HRMS calcd for $C_{37}H_{52}ClNO_{11}$: 744.3121 [M+ Na]$^+$. found: 744.3121.







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面积百分比报告

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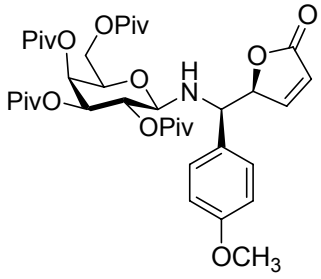
排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

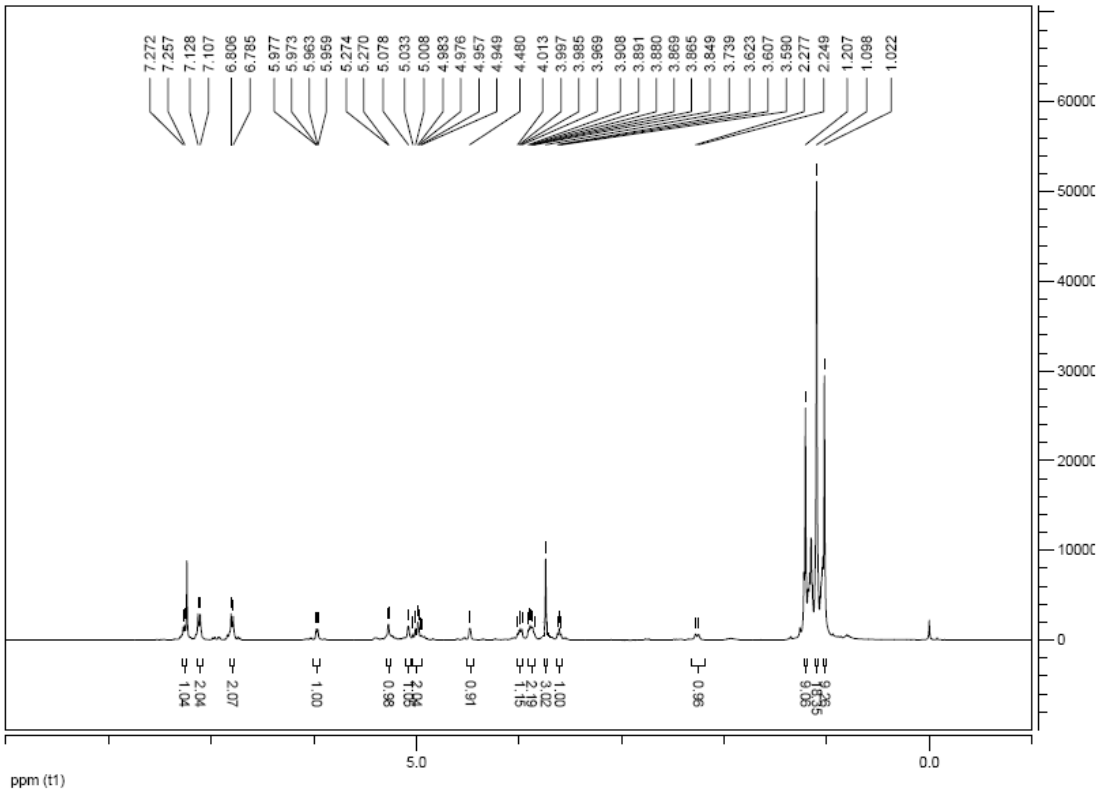
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	10.570	BV	0.3755	1.75901e4	726.84259	93.4060
2	12.271	VB	0.3879	1241.77051	49.15197	6.5940

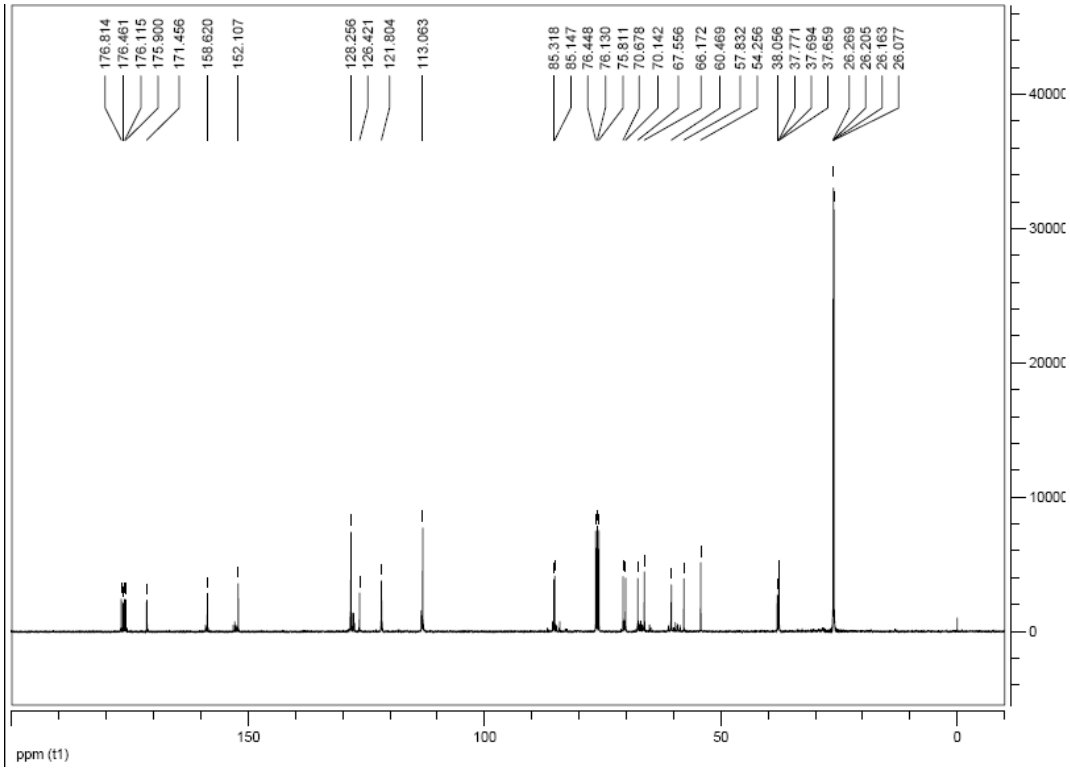
总量 : 1.88319e4 775.99456

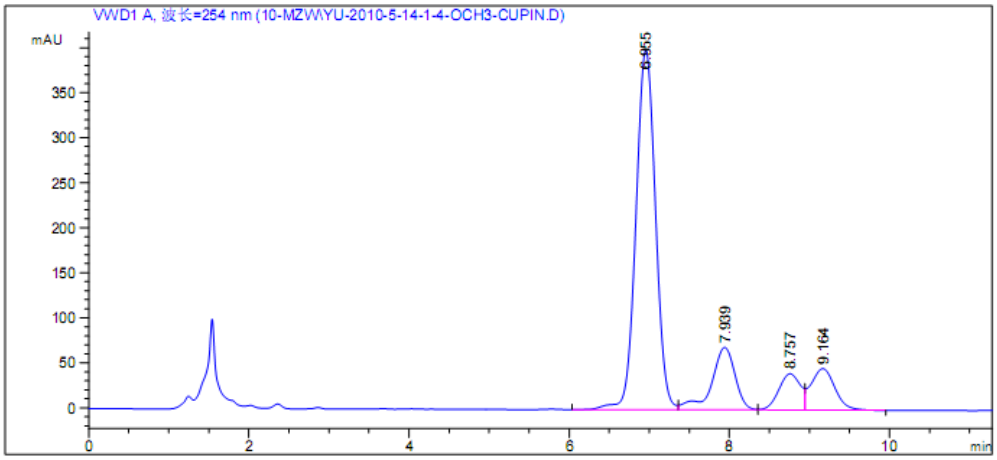
(*S*)-5-((*R*)-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-galactopyranosyl)amino(4-methoxypheny l) methyl)-5*H*-furan-2-one (5i)



White solid; mp 80-82 °C; $[\alpha]_D^{25}$ = -20.2° (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.02 (s, 9H, $C(CH_3)_3$), 1.10 (s, 18H, $2C(CH_3)_3$), 1.21 (s, 9H, $C(CH_3)_3$), 2.26 (d, $^3J_{H,H}$ = 1.4 Hz, 1H, NH), 3.61 (t, $^3J_{H,H}$ = 6.7 Hz, 1H, CH), 3.74 (s, 3H, CH_3), 3.87-3.91 (m, 2H, 2CH), 3.99 (dd, $^3J_{H,H}$ = 11.1 Hz, $^3J_{H,H}$ = 6.7 Hz, 1H, CH), 4.48 (s, 1H, CH), 4.95-5.03 (m, 2H, 2CH), 5.08 (s, 1H, CH), 5.27 (d, $^3J_{H,H}$ = 1.7 Hz, 1H, CH), 5.96 (dd, $^3J_{H,H}$ = 5.8 Hz, $^3J_{H,H}$ = 1.7 Hz, 1H, CH), 6.80 (d, $^3J_{H,H}$ = 6.4 Hz, 2H, Ph), 7.11 (d, $^3J_{H,H}$ = 6.4 Hz, 2H, Ph), 7.26 (d, $^3J_{H,H}$ = 5.8 Hz, 1H, CH); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 26.08, 26.16, 26.20, 26.27, 37.66, 37.69, 37.77, 38.06, 54.26, 57.83, 60.47, 66.17, 67.56, 70.14, 70.68, 85.15, 85.32, 113.06, 121.80, 126.42, 128.26, 152.11, 158.62, 171.46, 175.90, 176.12, 176.46, 176.81; ESI-MS: 740.9 ([M+Na]$^+$); HRMS calcd for $C_{38}H_{55}NO_{12}$: 740.3617 [M+ Na]$^+$. found: 740.3623.







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面积百分比报告

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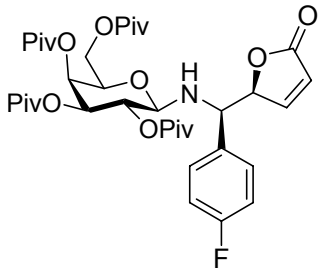
排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

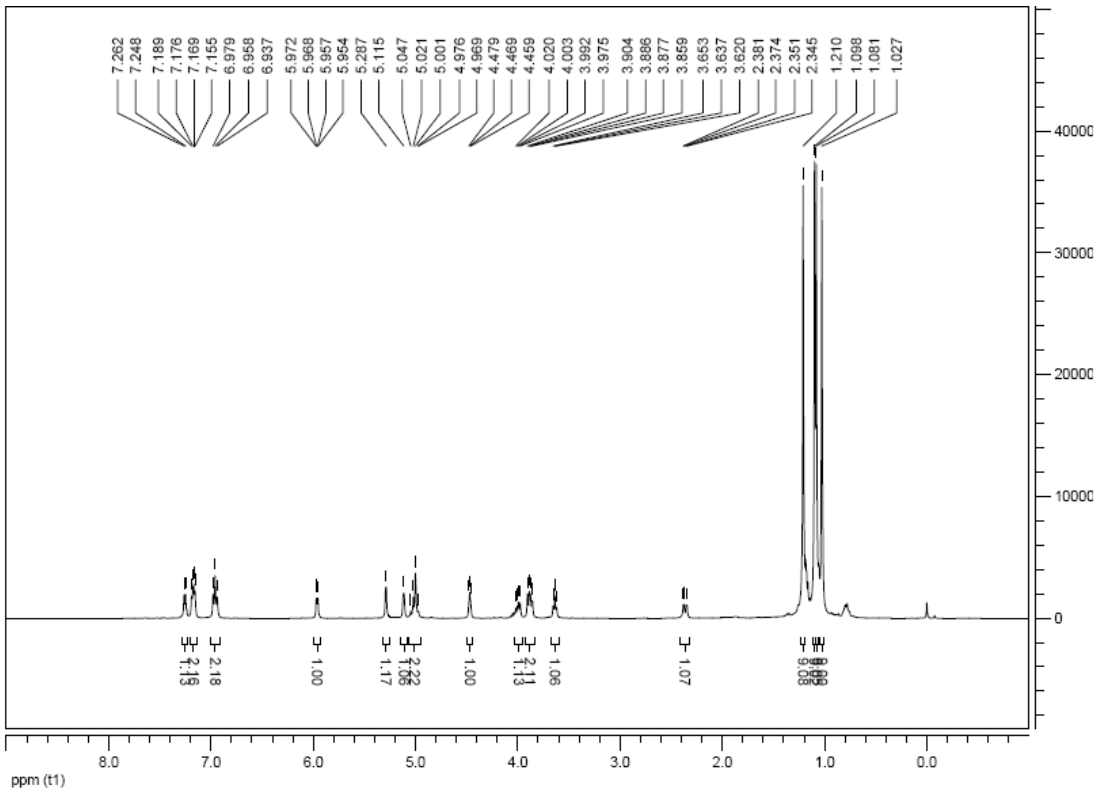
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	6.955	VV	0.2698	6802.60693	397.02127	68.2957
2	7.939	VV	0.3229	1433.58337	69.29435	14.3926
3	8.757	VV	0.2917	767.06384	40.35336	7.7010
4	9.164	VB	0.3236	957.27039	46.13245	9.6106

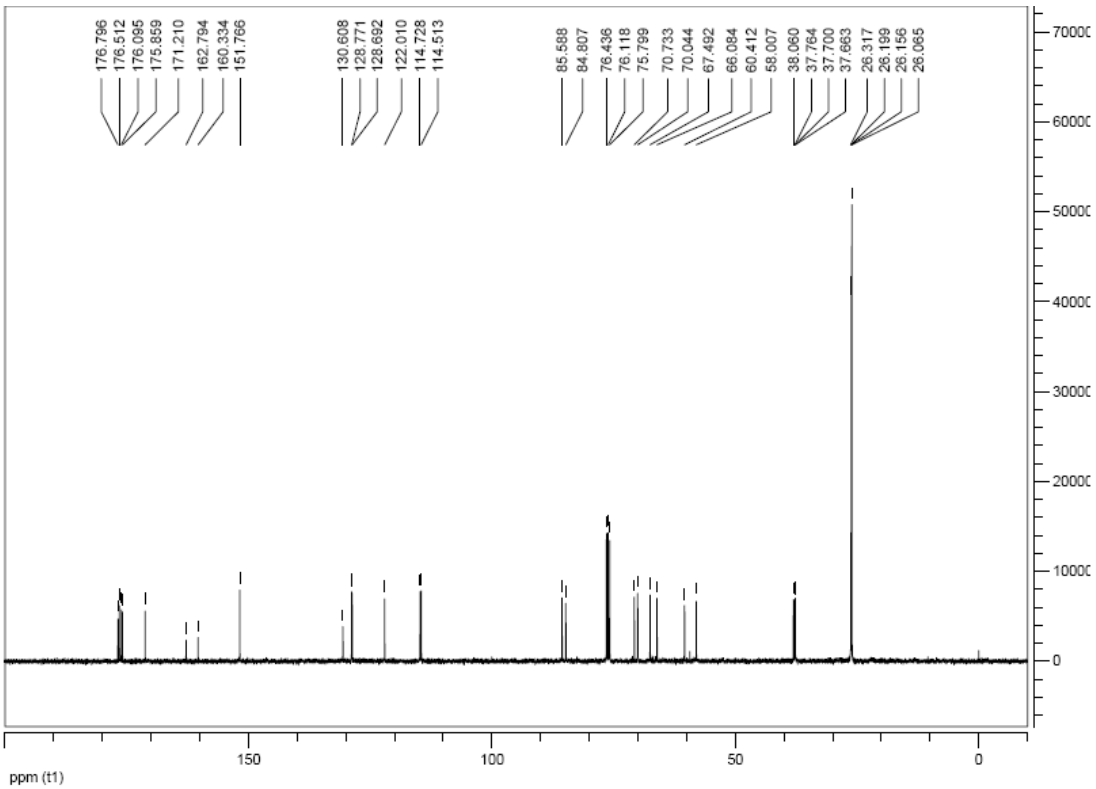
总量 : 9960.52454 552.80143

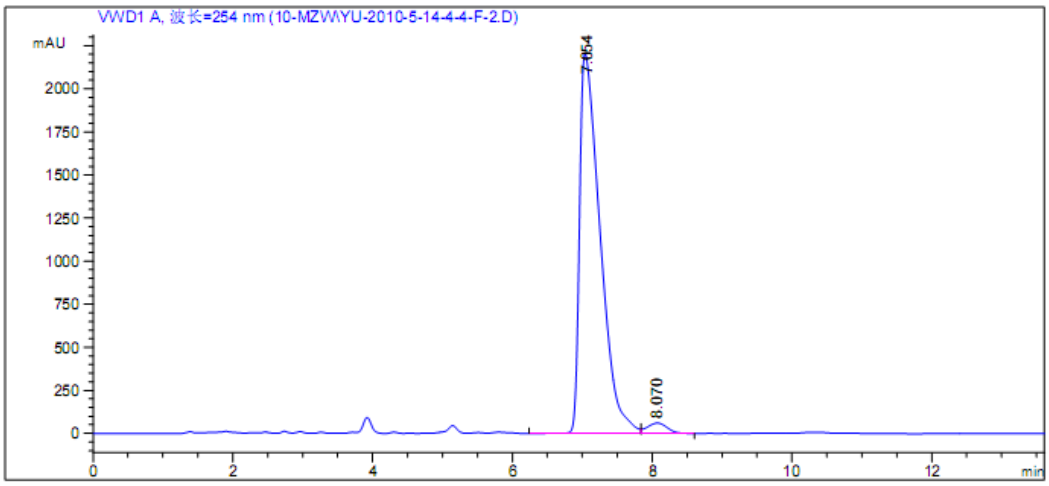
(*S*)-5-((*R*)-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-galactopyranosyl)amino(4-fluorophenyl) methyl)-5*H*-furan-2-one (5j)



White solid; mp 133-135 °C; $[\alpha]_D^{25}$ = -40.0° (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 9H, $C(CH_3)_3$), 1.08 (s, 9H, $C(CH_3)_3$), 1.10 (s, 9H, $C(CH_3)_3$), 1.21 (s, 9H, $C(CH_3)_3$), 2.36 (d, $^3J_{H,H}$ = 11.7 Hz, $^3J_{H,H}$ = 2.5 Hz, 1H, NH), 3.64 (t, $^3J_{H,H}$ = 6.6 Hz, 1H, CH), 3.88 (dd, $^3J_{H,H}$ = 11.7 Hz, $^3J_{H,H}$ = 7.2 Hz, 2H, 2CH), 4.00 (dd, $^3J_{H,H}$ = 11.1 Hz, $^3J_{H,H}$ = 6.6 Hz, 1H, CH), 4.47 (t, $^3J_{H,H}$ = 2.5 Hz, 1H, CH), 4.97-5.05 (m, 2H, 2CH), 5.12 (s, 1H, CH), 5.29 (s, 1H, CH), 5.96 (dd, $^3J_{H,H}$ = 5.8 Hz, $^3J_{H,H}$ = 1.3 Hz, 1H, CH), 6.96 (t, $^3J_{H,H}$ = 8.4 Hz, 2H, Ph), 7.16-7.19 (m, 2H, Ph), 7.26 (d, $^3J_{H,H}$ = 5.8 Hz, 1H, CH); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 26.07, 26.16, 26.20, 26.32, 37.66, 37.70, 37.76, 38.06, 58.01, 60.41, 66.08, 67.49, 70.04, 70.73, 84.81, 85.59, 114.51, 114.73, 122.01, 128.69, 128.77, 130.61, 151.77, 160.33, 162.79, 171.21, 175.86, 176.10, 176.51, 176.80. ESI-MS: 728.9 ($[M + Na]^+$); HRMS calcd for $C_{37}H_{52}FNO_{11}$: 728.3417 $[M + Na]^+$. found: 728.3411.







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面积百分比报告

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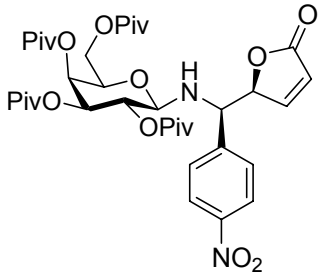
排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

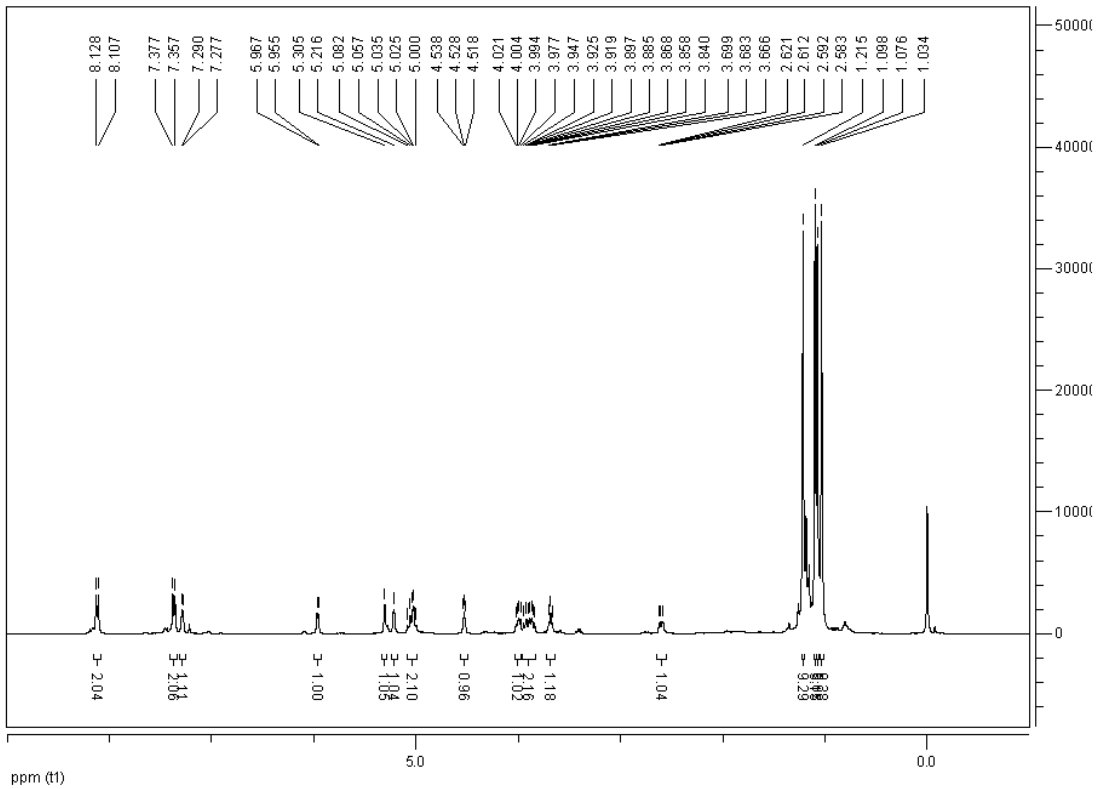
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	7.054	VV	0.3202	4.50023e4	2199.86987	97.2624
2	8.070	VV	0.3213	1266.63904	61.63151	2.7376

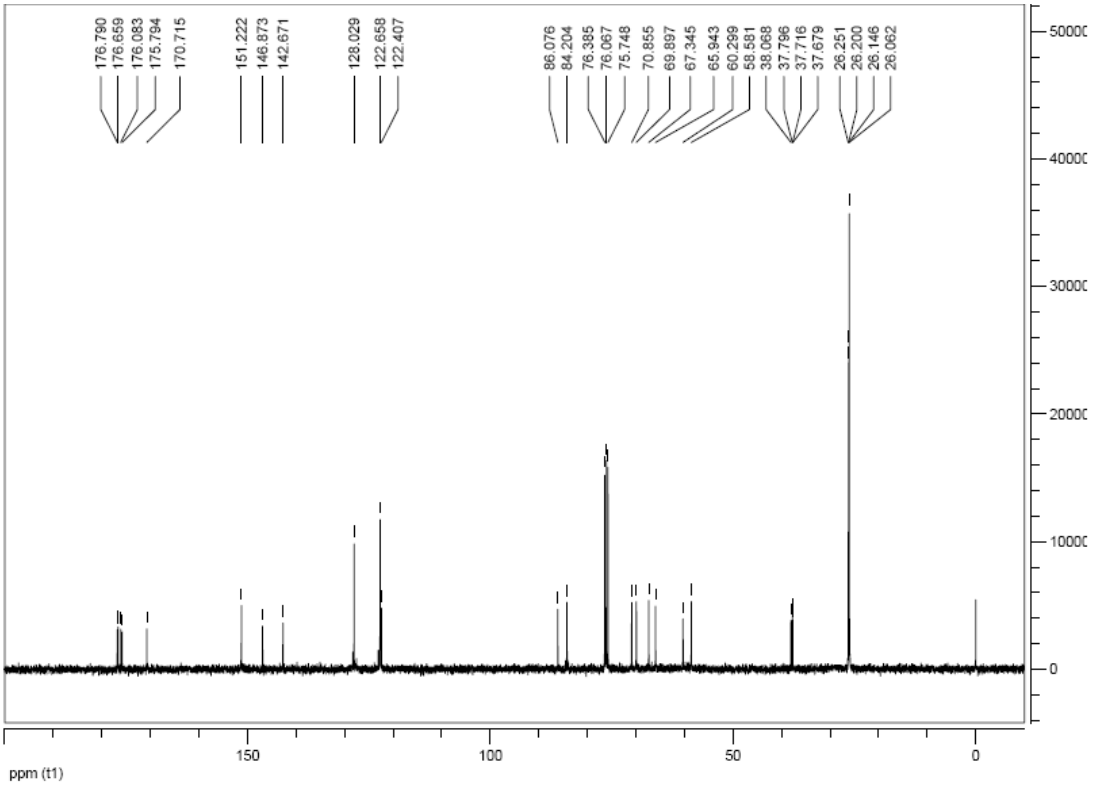
总量 : 4.62690e4 2261.50138

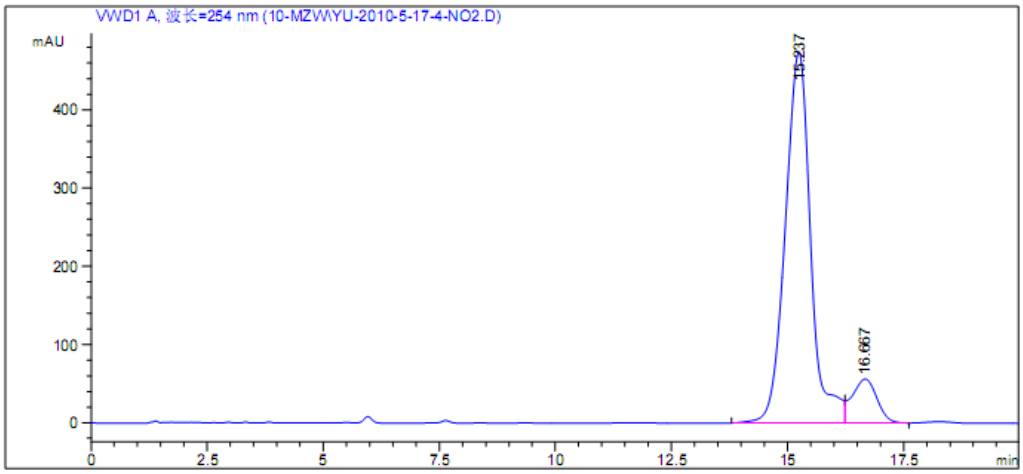
(*S*)-5-((*R*)-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-galactopyranosyl)amino(4-nitrophenyl) methyl)-5*H*-furan-2-one (5k)



White solid; mp 177-179 °C; $[\alpha]_D^{25}$ = -49.1° (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 9H, $C(CH_3)_3$), 1.08 (s, 9H, $C(CH_3)_3$), 1.10 (s, 9H, $C(CH_3)_3$), 1.22 (s, 9H, $C(CH_3)_3$), 2.61 (dd, $^3J_{H,H}$ = 11.5 Hz, $^3J_{H,H}$ = 3.7 Hz, 1H, NH), 3.68 (t, $^3J_{H,H}$ = 6.6 Hz, 1H, CH), 3.84-3.95 (m, 2H, 2CH), 4.00 (dd, $^3J_{H,H}$ = 11.5 Hz, $^3J_{H,H}$ = 6.6 Hz, 1H, CH), 4.53 (t, $^3J_{H,H}$ = 3.7 Hz, 1H, CH), 5.00-5.08 (m, 2H, 2CH), 5.31 (s, 1H, CH), 5.96 (d, $^3J_{H,H}$ = 5.4 Hz, 1H, CH), 7.28 (d, $^3J_{H,H}$ = 5.4 Hz, 1H, CH), 7.37 (d, $^3J_{H,H}$ = 8.3 Hz, 2H, Ph), 8.12 (d, $^3J_{H,H}$ = 8.3 Hz, 2H, Ph); ^{13}C-NMR (75 MHz, $CDCl_3$): δ26.06, 26.15, 26.20, 26.25, 37.68, 37.72, 37.80, 38.07, 58.58, 60.30, 65.94, 67.35, 69.90, 70.86, 84.20, 86.08, 122.41, 122.66, 128.03, 142.67, 146.87, 151.22, 170.72, 175.79, 176.08, 176.66, 176.79; ESI-MS: 755.9 ($[M + Na]^+$); HRMS calcd for $C_{37}H_{52}N_2O_{13}$: 755.3362 $[M + Na]^+$. found: 755.3358.







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面积百分比报告

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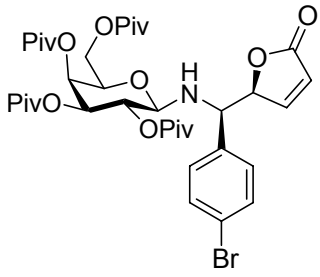
排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

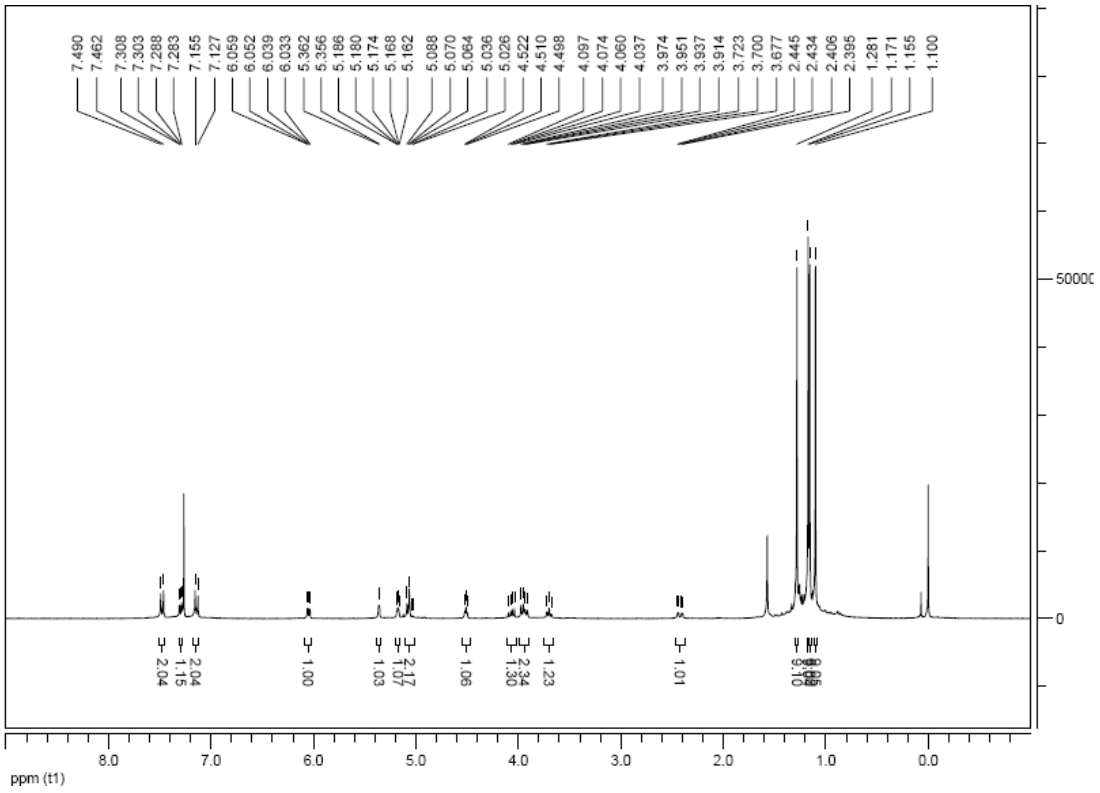
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	15.237	BV	0.5844	1.80618e4	473.91464	89.5558
2	16.667	VV	0.5746	2106.39209	56.51870	10.4442

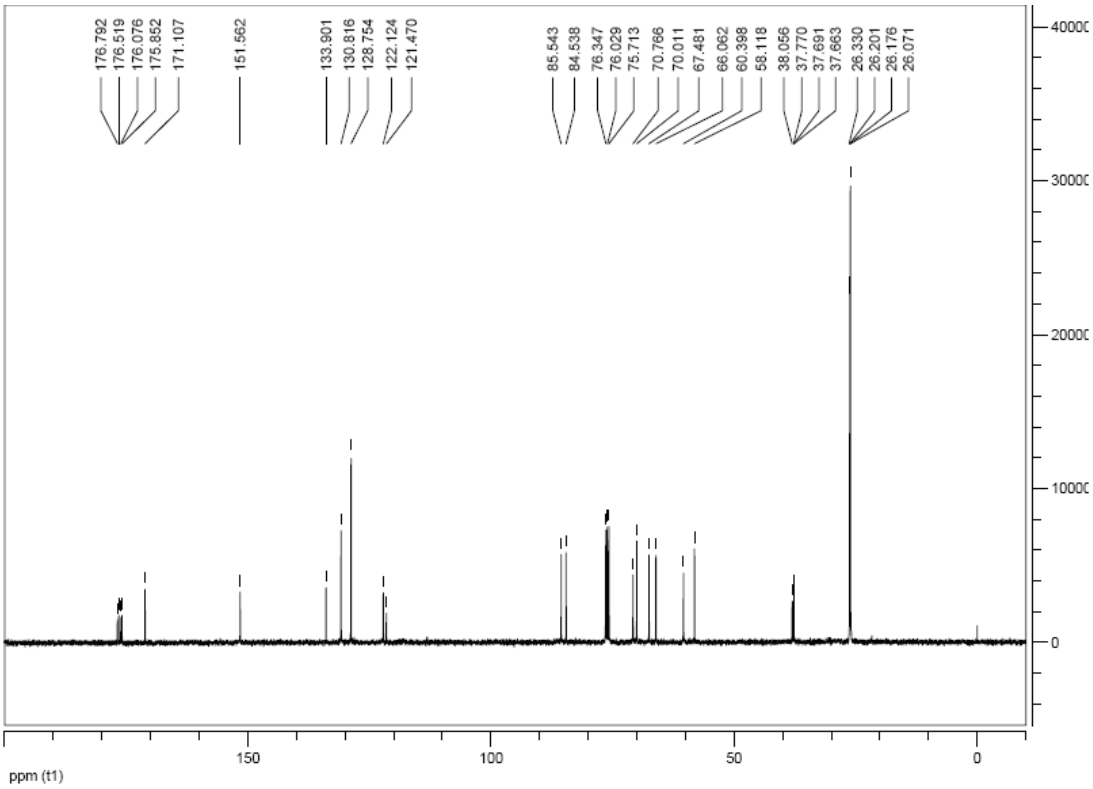
总量 : 2.01681e4 530.43334

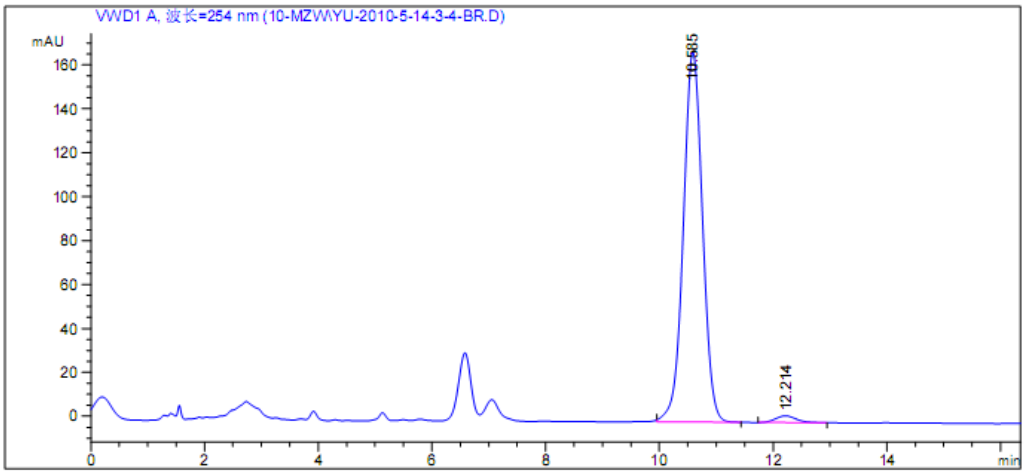
(*S*)-5-((*R*)-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-galactopyranosyl)amino(4-bromophenyl) methyl)-5*H*-furan-2-one (5l)



White solid; mp 171-173°C; $[\alpha]_D^{25}$ = -60.8° (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.10 (s, 9H, $C(CH_3)_3$), 1.16 (s, 9H, $C(CH_3)_3$), 1.17 (s, 9H, $C(CH_3)_3$), 1.28 (s, 9H, $C(CH_3)_3$), 2.42 (dd, $^3J_{H,H}$ = 12.3 Hz, $^3J_{H,H}$ = 3.5 Hz, 1H, NH), 3.70 (t, $^3J_{H,H}$ = 6.8 Hz, 1H, CH), 3.94 (dd, $^3J_{H,H}$ = 12.3 Hz, $^3J_{H,H}$ = 6.9 Hz, 2H, 2CH), 4.07 (dd, $^3J_{H,H}$ = 11.1 Hz, $^3J_{H,H}$ = 6.8 Hz, 1H, CH), 4.51 (t, $^3J_{H,H}$ = 3.5 Hz, 1H, CH), 5.03-5.09 (m, 2H, 2CH), 5.16-5.19 (m, 1H, CH), 5.36 ($^3J_{H,H}$ = 2.4 Hz, 1H, CH), 6.04 (dd, $^3J_{H,H}$ = 5.8 Hz, $^3J_{H,H}$ = 1.0 Hz, 1H, CH), 7.14 (d, $^3J_{H,H}$ = 8.4 Hz, 2H, Ph), 7.30 (dd, $^3J_{H,H}$ = 5.8 Hz, $^3J_{H,H}$ = 1.5 Hz, 1H, CH), 7.48 (d, $^3J_{H,H}$ = 8.4 Hz, 2H, Ph); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 26.07, 26.18, 26.20, 26.33, 37.66, 37.69, 37.77, 38.06, 58.12, 60.40, 66.06, 67.48, 70.01, 70.77, 84.54, 85.55, 121.47, 122.12, 128.75, 130.82, 133.90, 151.56, 171.11, 175.85, 176.08, 176.52, 176.79; ESI-MS: 788.9 ([M+Na]$^+$); HRMS calcd for $C_{37}H_{52}BrNO_{11}$: 788.2616 [M+ Na]$^+$. found: 788.2612.







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面积百分比报告

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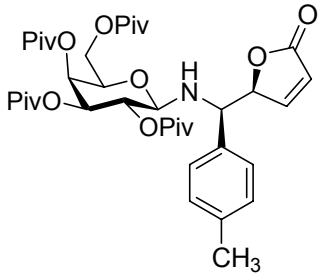
排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

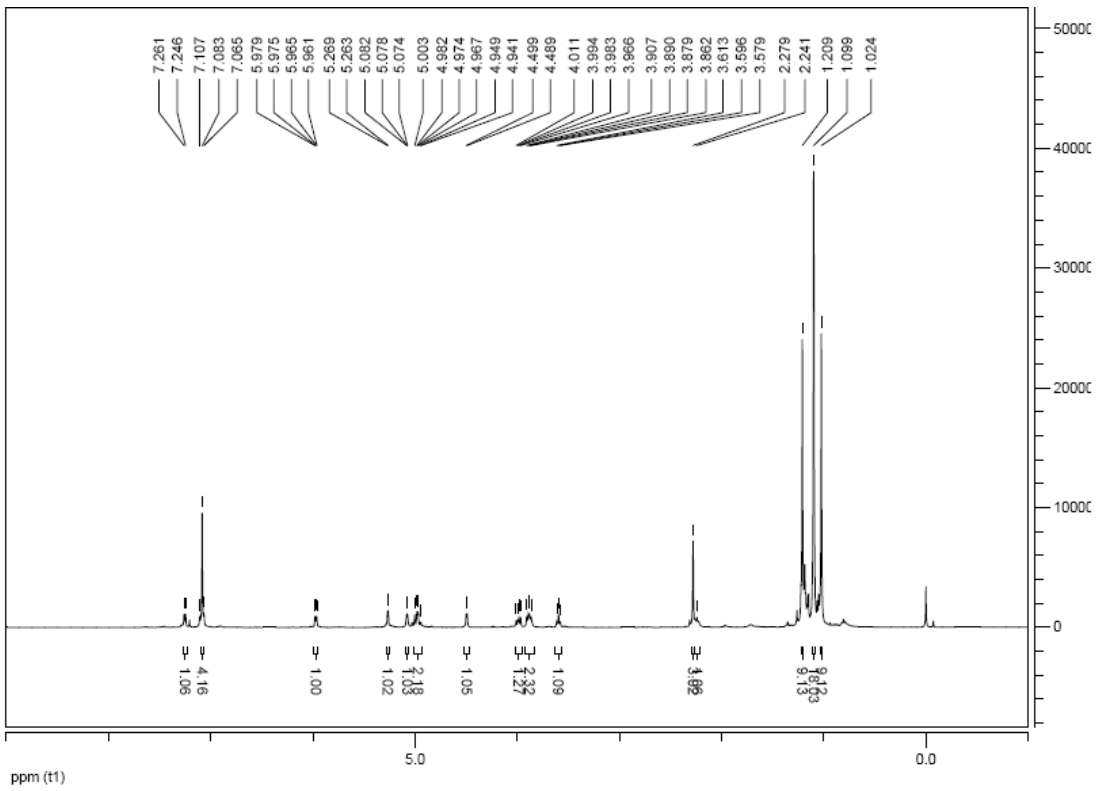
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	10.585	BB	0.3676	3953.97852	168.10014	98.0079
2	12.214	BB	0.4070	80.36739	3.10248	1.9921

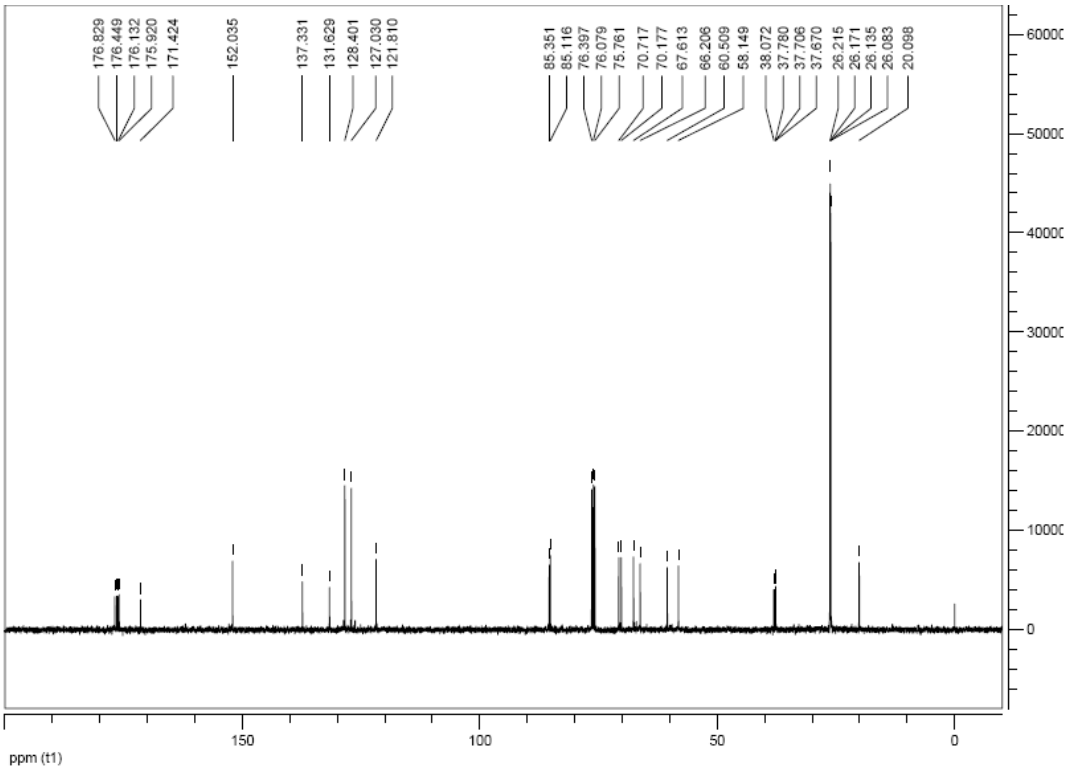
总量 : 4034.34590 171.20263

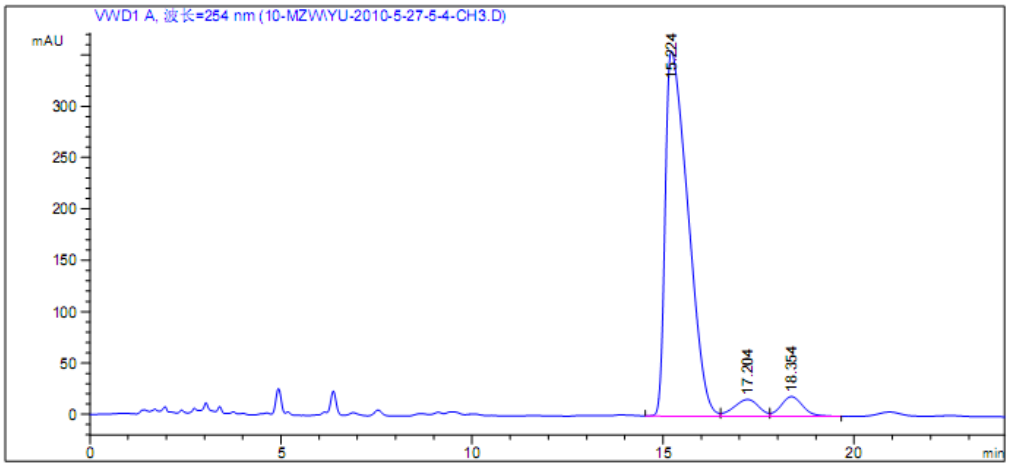
(*S*)-5-((*R*)-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-galactopyranosyl)amino(*p*-methylphenyl) methyl)-5*H*-furan-2-one (5m)



White solid; mp 75-77 °C; $[\alpha]_D^{25} = -36.6°$ (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.02 (s, 9H, $C(CH_3)_3$), 1.10 (s, 18H, $2C(CH_3)_3$), 1.21 (s, 9H, $C(CH_3)_3$), 2.24 (s, br, 1H, NH), 3.28 (s, 3H, CH_3), 3.60 (t, $^3J_{H-H}$ = 6.8 Hz, 1H, CH), 3.88 (dd, $^3J_{H-H}$ = 11.0 Hz, $^3J_{H-H}$ = 6.8Hz, 2H, 2CH), 3.99 (dd, $^3J_{H-H}$ = 11.0 Hz, $^3J_{H-H}$ = 6.8 Hz, 1H, CH), 4.49 (d, $^3J_{H-H}$ = 3.7 Hz, 1H, CH), 4.94-5.00 (m, 2H, 2CH), 5.08 (t, $^3J_{H-H}$ = 7.0 Hz, 1H, CH), 5.27 (d, $^3J_{H-H}$ = 1.7 Hz, 1H, CH), 5.97 (dd, $^3J_{H-H}$ = 5.7 Hz, $^3J_{H-H}$ = 1.7 Hz, 1H, CH), 7.07-7.11 (m, 4H, Ph), 7.25 (d, $^3J_{H-H}$ = 5.7 Hz, 1H, CH); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 20.10, 26.08, 26.14, 26.17, 26.22, 37.67, 37.71, 37.78, 38.07, 58.15, 60.51, 66.21, 67.61, 70.18, 70.72, 85.12, 85.35, 121.81, 127.03, 128.40, 131.63, 137.33, 152.04, 171.42, 175.92, 176.13, 176.45, 176.83; ESI-MS: 724.9 ($[M+Na]^+$); HRMS calcd for $C_{38}H_{55}NO_{11}$: 724.3667 $[M+ Na]^+$. found: 724.3667.







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面积百分比报告

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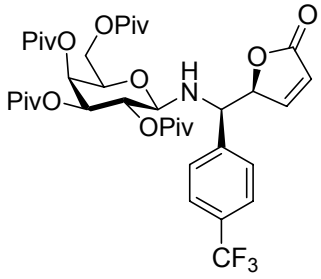
排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

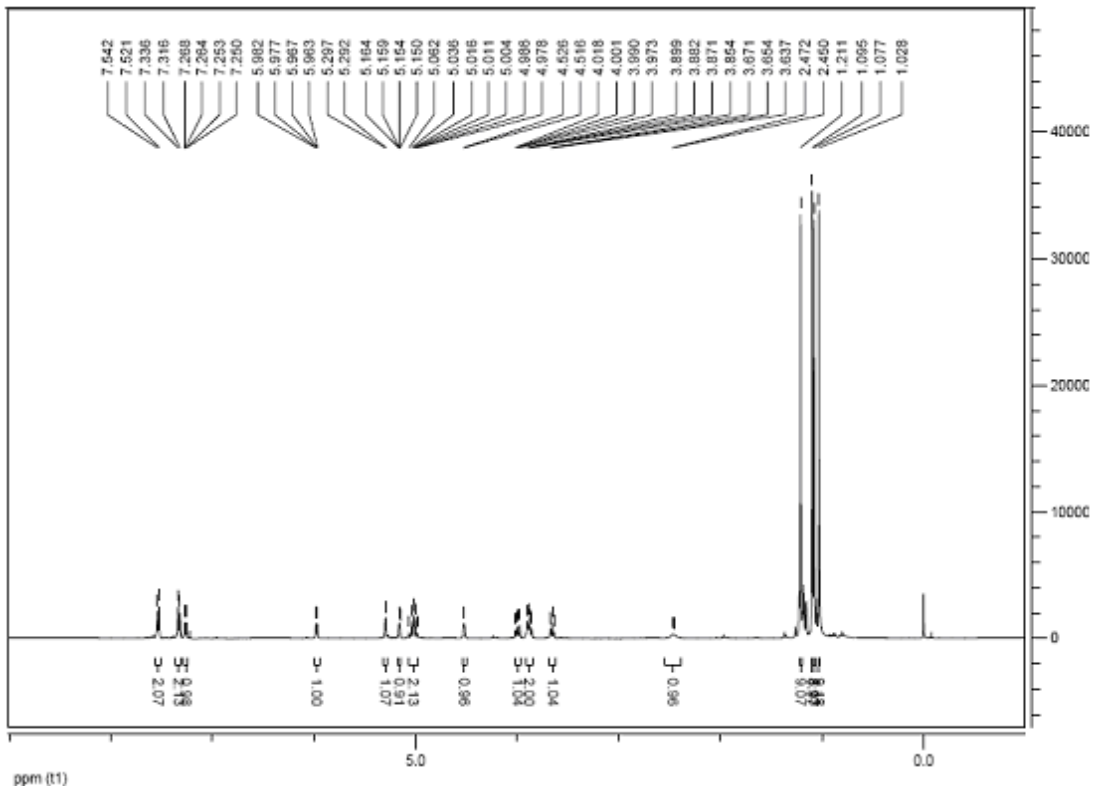
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	15.224	VV	0.6696	1.46845e4	354.52438	90.4969
2	17.204	VV	0.7162	751.06720	16.53809	4.6286
3	18.354	VB	0.6377	790.95172	19.44157	4.8744

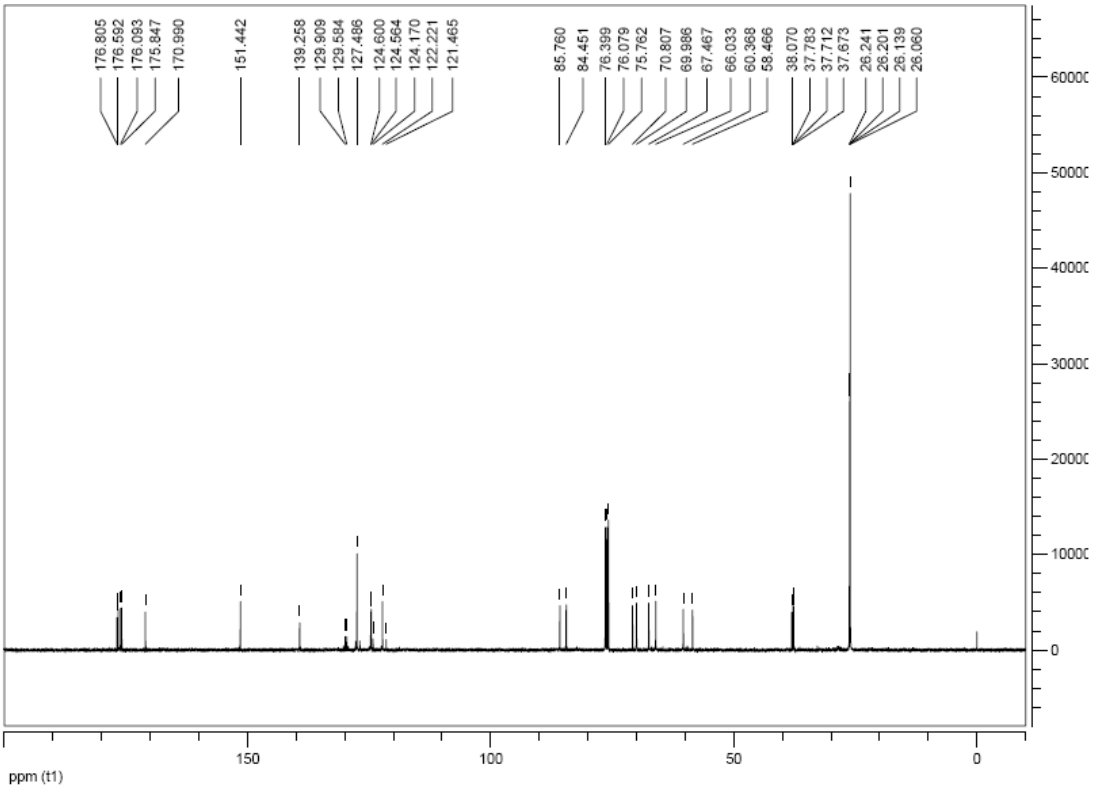
总量 : 1.62265e4 390.50405

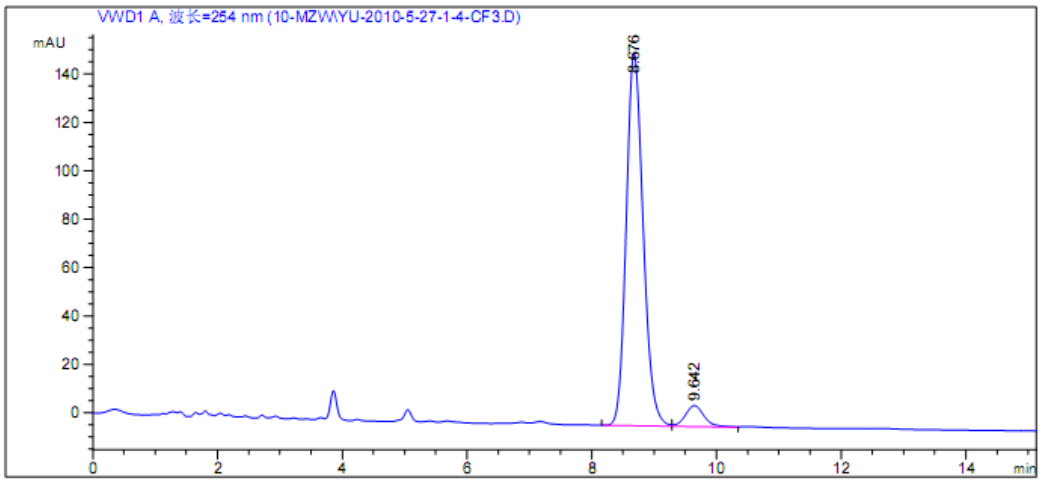
(*S*)-5-((*R*)-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-galactopyranosyl)amino(*p*-trifluoromethylphenyl) methyl)-5*H*-furan-2-one (5n)



White solid; mp 160-161°C; $[\alpha]_D^{25}$ = -41.2° (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 9H, $C(CH_3)_3$), 1.08 (s, 9H, $C(CH_3)_3$), 1.10 (s, 9H, $C(CH_3)_3$), 1.21 (s, 9H, $C(CH_3)_3$), 2.46 (d, $^3J_{H-H}$ = 8.8 Hz, 1H, NH), 3.65 (t, $^3J_{H-H}$ = 6.8 Hz, 1H, CH), 3.88 (dd, $^3J_{H-H}$ = 11.1 Hz, $^3J_{H-H}$ = 6.8 Hz, 2H, 2CH), 4.00 (dd, $^3J_{H-H}$ = 11.1 Hz, $^3J_{H-H}$ = 6.7 Hz, 1H, CH), 4.52 (d, $^3J_{H-H}$ = 3.8 Hz, 1H, CH), 4.99-5.06 (m, 2H, 2CH), 5.16 (dd, $^3J_{H-H}$ = 3.8 Hz, $^3J_{H-H}$ = 1.3 Hz, 1H, CH), 5.29 (d, $^3J_{H-H}$ = 2.0 Hz, 1H, CH), 5.97 (dd, $^3J_{H-H}$ = 5.8 Hz, $^3J_{H-H}$ = 2.0 Hz, 1H, CH), 7.26 (dd, $^3J_{H-H}$ = 5.8 Hz, $^3J_{H-H}$ = 1.3 Hz, 1H, CH), 7.33 (d, $^3J_{H-H}$ = 8.1 Hz, 2H, Ph), 7.53 (d, $^3J_{H-H}$ = 8.1Hz, 2H, Ph); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 26.06, 26.14, 26.20, 26.24, 37.67, 37.71, 37.78, 38.07, 58.47, 60.37, 66.03, 67.47, 69.99, 70.81, 84.45, 85.76, 121.47, 122.22, 124.17, 124.56, 124.60, 127.49, 129.58, 129.91, 139.26, 151.44, 170.99, 175.85, 176.09, 176.59, 176.81; ESI-MS: 778.9 ($[M+Na]^+$); HRMS calcd for $C_{38}H_{52}F_3NO_{11}$: 778.3385 $[M+ Na]^+$. found: 778.3381.







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面积百分比报告

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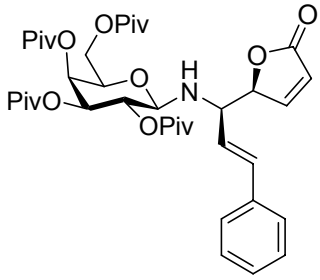
排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

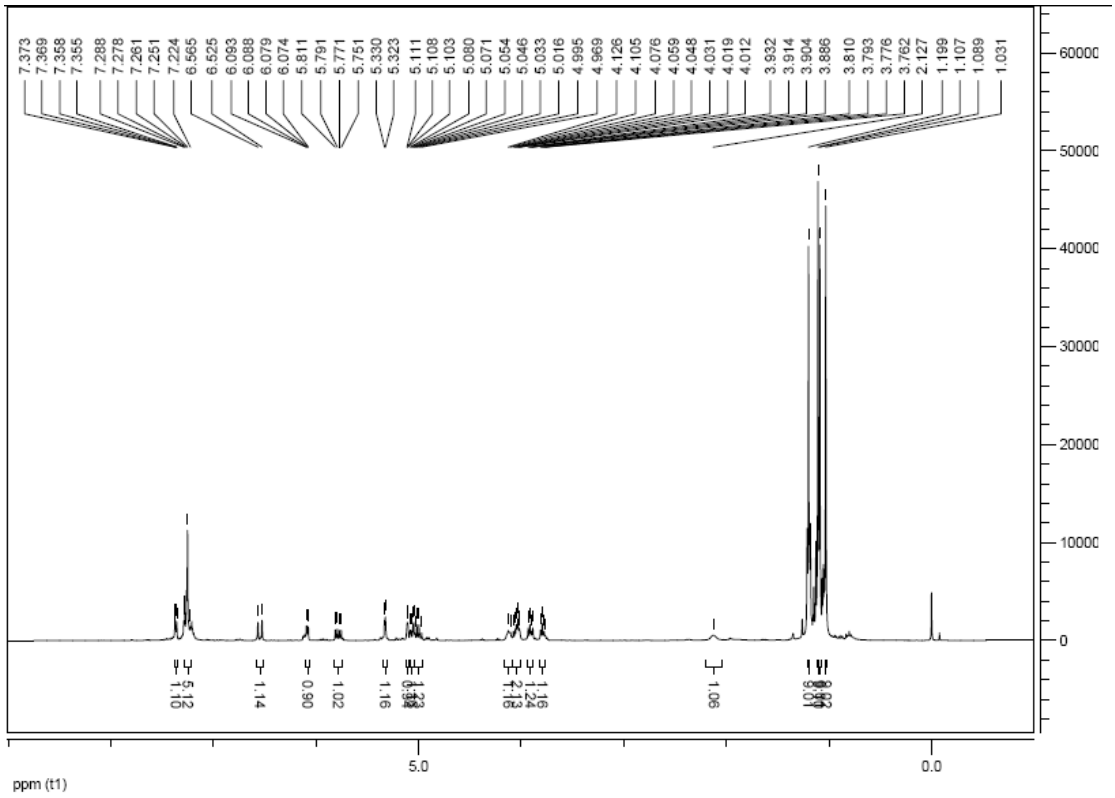
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	8.676	VV	0.3026	2902.31885	153.17349	94.0307
2	9.642	VB	0.3296	184.24573	8.66547	5.9693

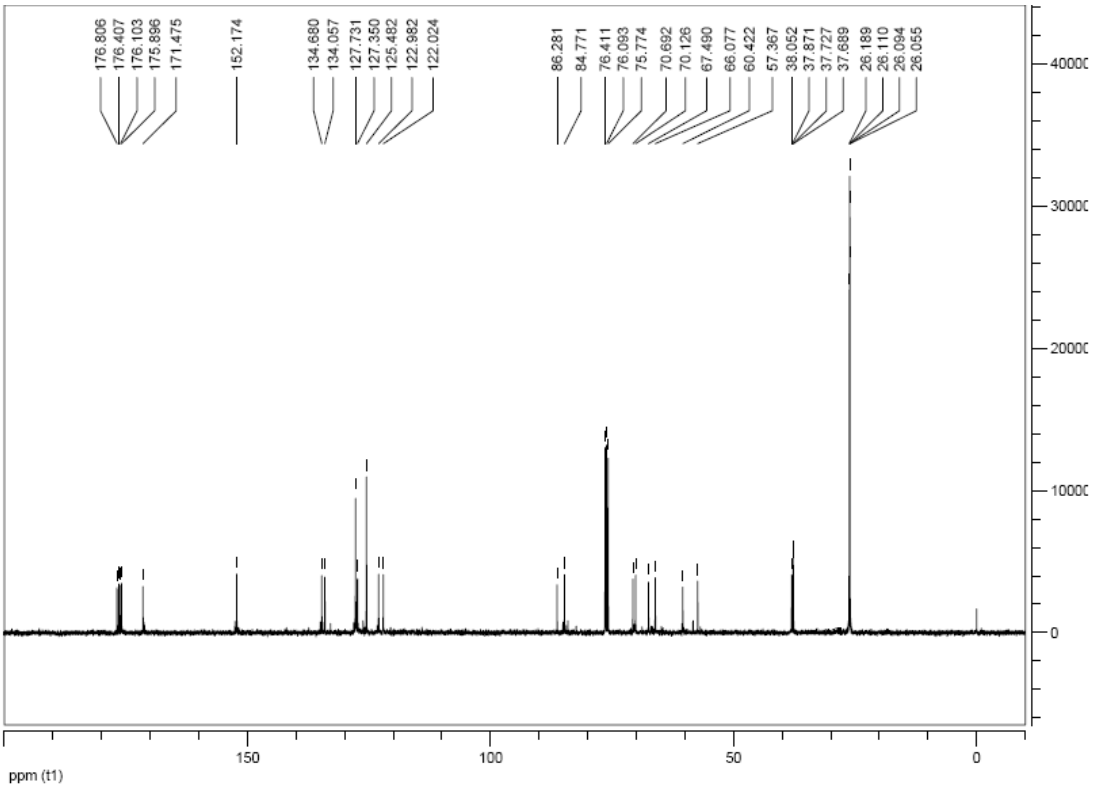
总量 : 3086.56458 161.83897

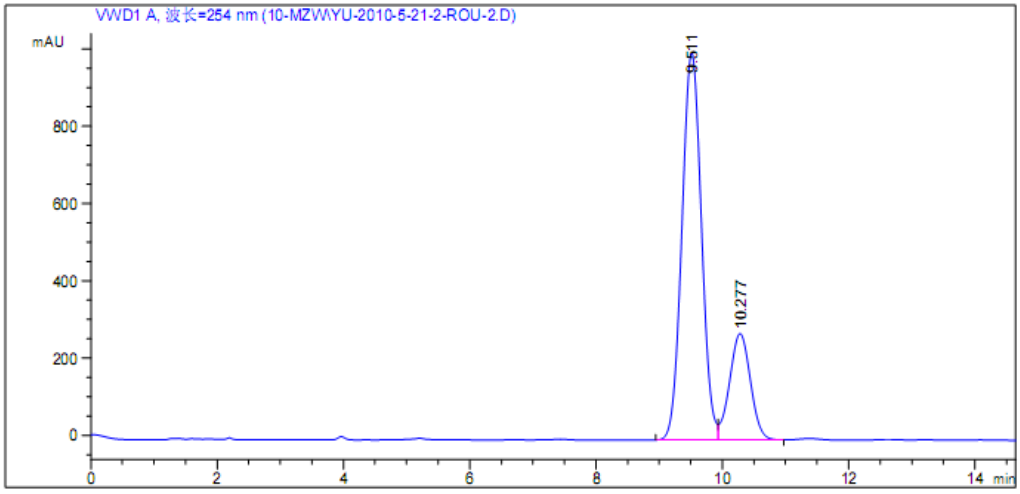
(*S*)-5-((*R*,*E*)-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-galactopyranosyl)-1-amino-3-phenylallyl)-5*H*-furan-2-one (5o)



White solid; mp 54-57 °C; $[\alpha]_D^{25}$ = -29.9° (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 9H, $C(CH_3)_3$), 1.09 (s, 9H, $C(CH_3)_3$), 1.11 (s, 9H, $C(CH_3)_3$), 1.21 (s, 9H, $C(CH_3)_3$), 2.13 (s, br, 1H, NH), 3.79 (dd, $^3J_{H-H}$ = 13.0 Hz, $^3J_{H-H}$ = 6.3 Hz, 1H, CH), 3.91 (dd, $^3J_{H-H}$ = 11.1 Hz, $^3J_{H-H}$ = 7.1 Hz, 1H, CH), 4.01-4.08 (m, 2H, 2CH), 4.12 (d, $^3J_{H-H}$ = 8.4 Hz, 1H, CH), 5.01 (q, $^3J_{H-H}$ = 8.4 Hz, 1H, CH), 5.06 (dd, $^3J_{H-H}$ =10.4 Hz, $^3J_{H-H}$= 3.3 Hz, 1H, CH), 5.11 (t, $^3J_{H-H}$ = 1.5 Hz, 1H, CH), 5.33 (d, $^3J_{H-H}$ = 3.3 Hz, 1H, CH), 5.78 (dd, $^3J_{H-H}$ = 15.9 Hz, $^3J_{H-H}$ = 8.4 Hz, 1H, CH), 6.08 (dd, $^3J_{H-H}$ = 5.8 Hz, $^3J_{H-H}$ = 1.8 Hz, 1H, CH), 6.55 (d, $^3J_{H-H}$ = 15.9 Hz, 1H, CH), 7.22-7.29 (m, 5H, Ph), 7.36 (dd, $^3J_{H-H}$ = 5.8 Hz, $^3J_{H-H}$ = 1.5 Hz, 1H, CH); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 26.06, 26.09, 26.11, 26.19, 37.69, 37.73, 37.87, 38.05, 57.37, 60.42, 66.08, 67.49, 70.13, 70.69, 84.77, 86.28, 122.02, 122.98, 125.48, 127.35, 127.73, 134.06, 134.68, 152.17, 171.48, 175.90, 176.10, 176.41, 176.81; ESI-MS: 736.9 ([M+Na]$^+$); HRMS calcd for $C_{39}H_{55}NO_{11}$: 736.3667 [M + Na]$^+$. found: 736.3659.







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面积百分比报告

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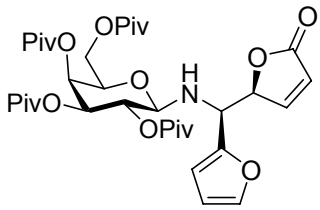
排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

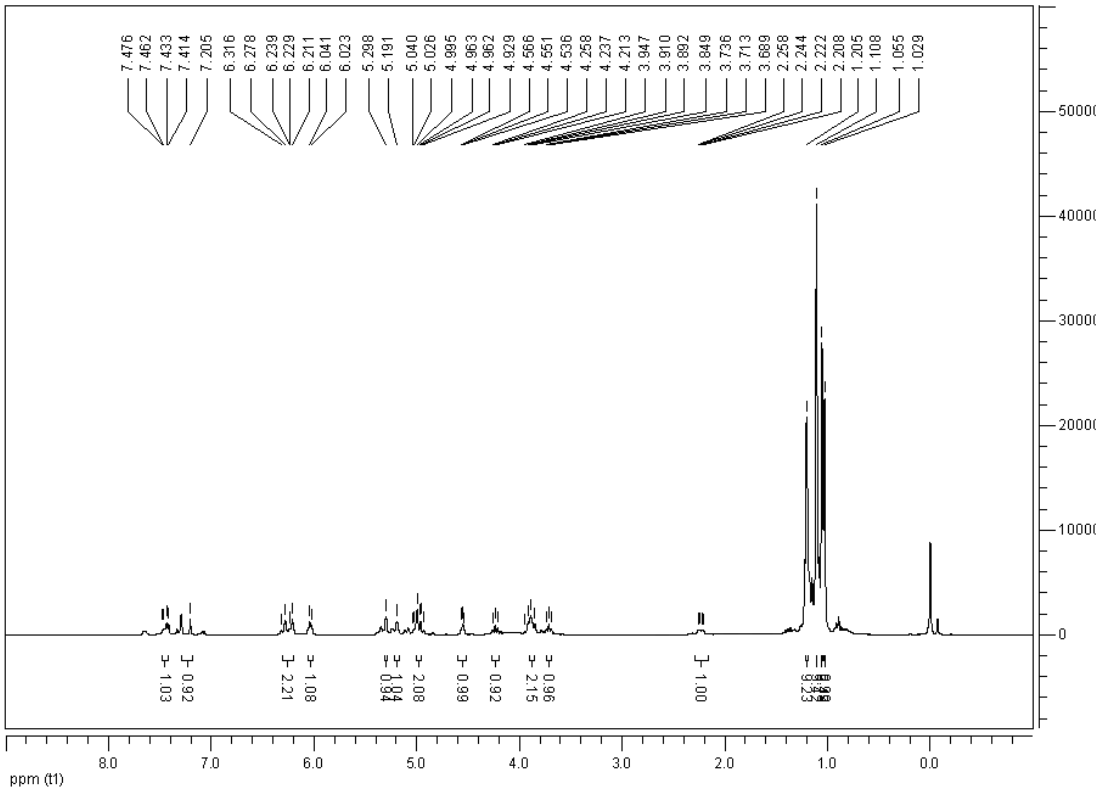
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	9.511	BV	0.3442	2.14757e4	998.08545	77.1800
2	10.277	VV	0.3626	6349.77246	274.95837	22.8200

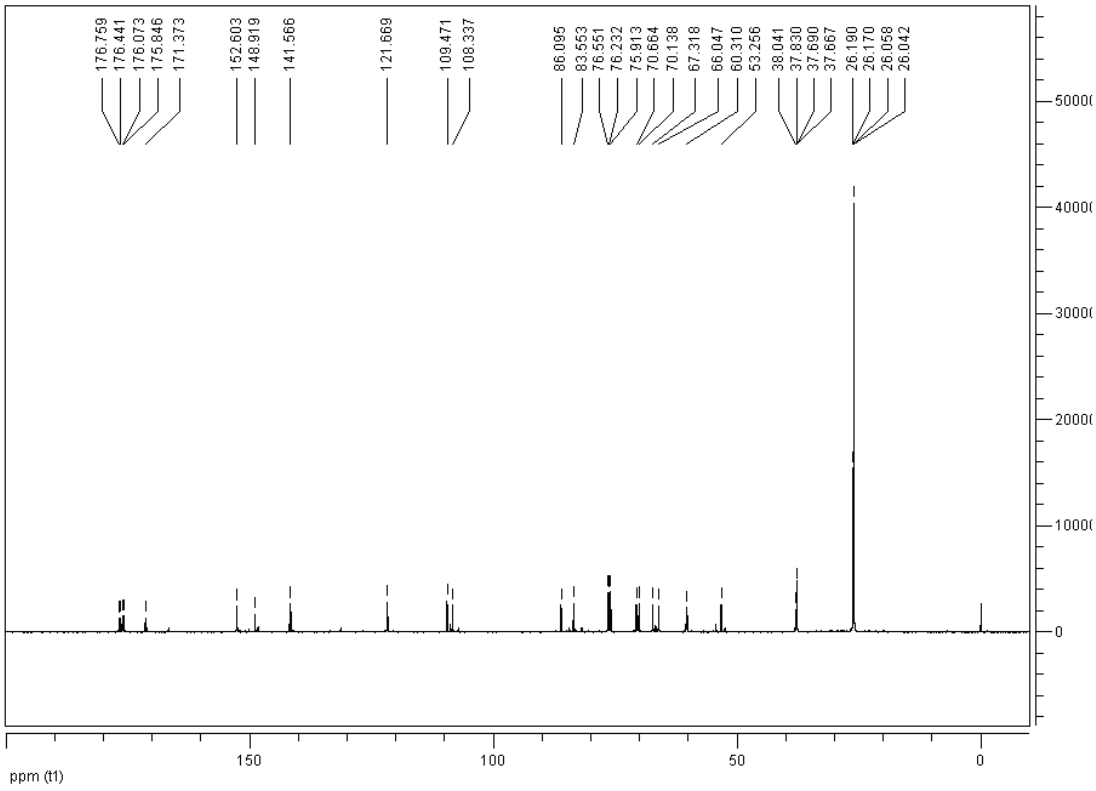
总量 : 2.78255e4 1273.04382

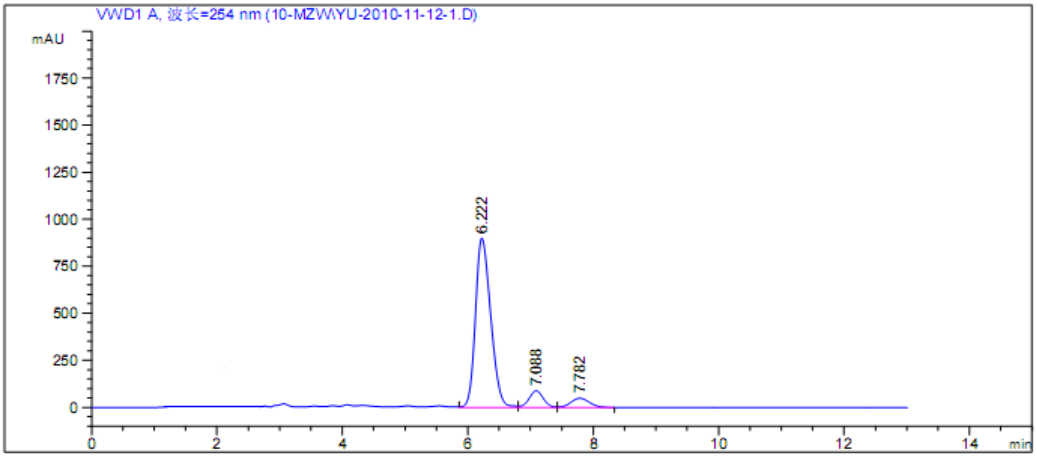
(*S*)-5-((*S*)-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-galactopyranosyl)amino(2-furyl)methyl)-5*H*-furan-2-one (5p)



White solid; mp 39-42 °C; $[\alpha]_D^{25}$ = -11.9° (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 9H, $C(CH_3)_3$), 1.06 (s, 9H, $C(CH_3)_3$), 1.11 (s, 9H, $C(CH_3)_3$), 1.21 (s, 9H, $C(CH_3)_3$), 2.23 (dd, $^3J_{H,H}$ = 12.7 Hz, $^3J_{H,H}$ = 4.7 Hz, 1H, NH), 3.71 (t, $^3J_{H,H}$ = 7.1 Hz, 1H, CH), 3.90 (dd, $^3J_{H,H}$ = 12.7 Hz, $^3J_{H,H}$ = 11.9 Hz, 2H, 2CH), 4.24 (t, $^3J_{H,H}$ = 7.1 Hz, 1H, CH), 4.55 (t, $^3J_{H,H}$ = 4.7 Hz, 1H, CH), 4.93-5.04 (m, 2H, 2CH), 5.19 (s, 1H, CH), 5.30 (s, 1H, CH), 6.03 (d, $^3J_{H,H}$ = 5.5 Hz, 1H, CH), 6.21-6.32 (m, 2H, 2CH), 7.21 (s, 1H, CH), 7.41-7.48 (m, 1H, CH); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 26.04, 26.06, 26.17, 26.19, 37.67, 37.69, 37.83, 38.04, 53.26, 60.31, 66.05, 67.32, 70.14, 70.66, 83.55, 86.10, 108.34, 109.47, 121.67, 141.57, 148.92, 152.60, 171.37, 175.85, 176.07, 176.44, 176.76; ESI-MS: 700.33 ($[M+Na]^+$); HRMS calcd for $C_{35}H_{51}NO_{12}$: 700.3303 $[M+ Na]^+$. found: 700.3298.







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面积百分比报告

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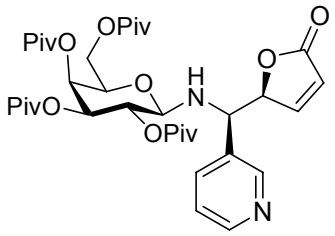
排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

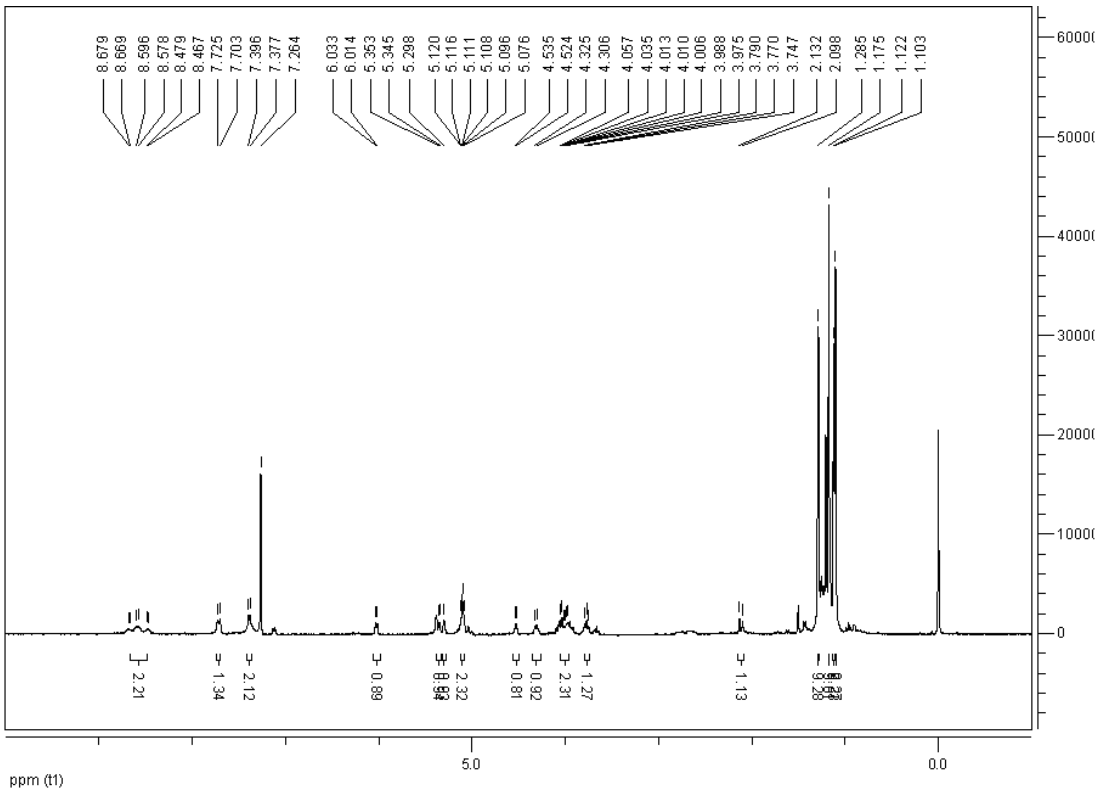
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	6.222	VV	0.2609	1.51983e4	900.68915	86.2213
2	7.088	VV	0.2461	1406.32434	88.69859	7.9782
3	7.782	VB	0.3240	1022.46014	49.19304	5.8005

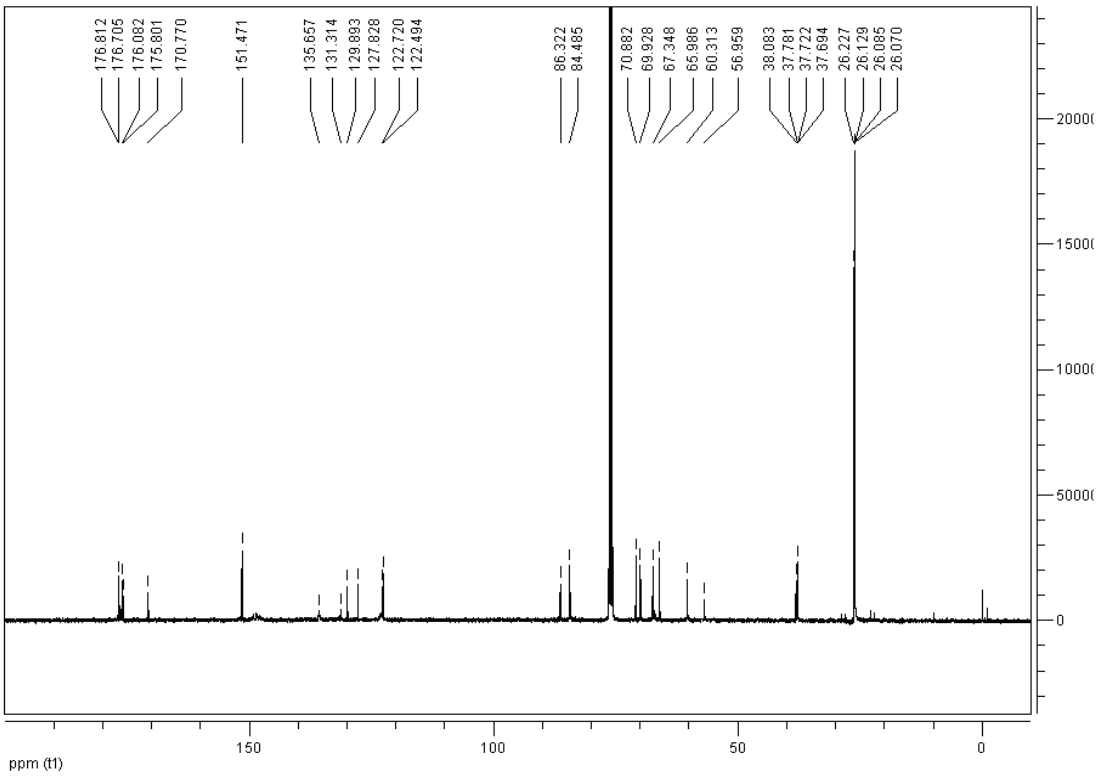
总量 : 1.76271e4 1038.58078

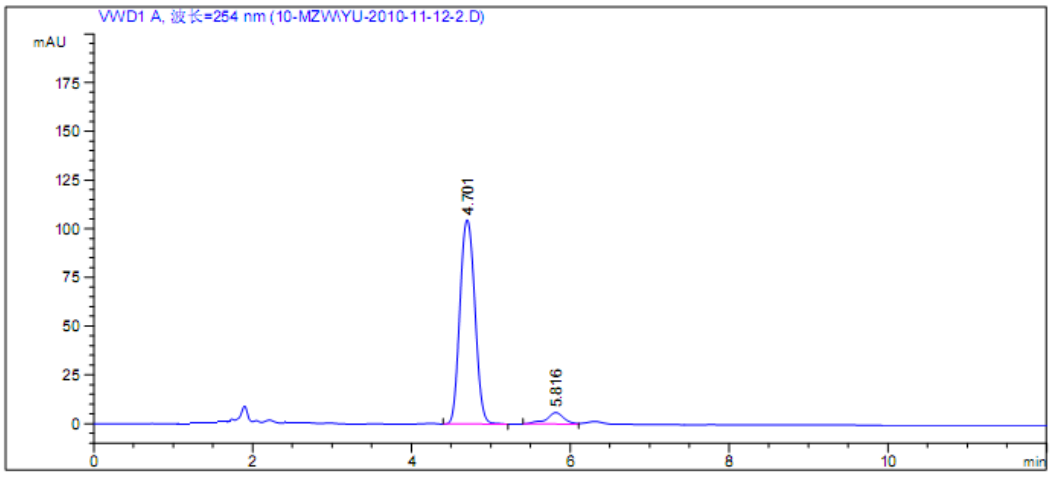
(*S*)-5-((*R*)-(2,3,4,6-tetra-*O*-pivaloyl-*β*-D-galactopyranosyl)amino(3-pyridyl)methyl)-5*H*-furan-2-one (5q)



White solid; mp 67-69 °C; $[\alpha]_D^{25}$ = -11.4° (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): 1.10 (s, 9H, $C(CH_3)_3$), 1.12 (s, 9H, $C(CH_3)_3$), 1.18 (s, 9H, $C(CH_3)_3$), 1.29 (s, 9H, $C(CH_3)_3$), 2.12 (d, $^3J_{H,H}$ = 10.1 Hz, 1H, NH), 3.77 (t, $^3J_{H,H}$ = 6.6 Hz, 1H, CH), 3.98-4.06 (m, 2H, 2CH), 4.32 (d, $^3J_{H,H}$ = 5.2 Hz, 1H, CH), 4.53 (d, $^3J_{H,H}$ = 3.0 Hz, 1H, CH), 5.08-5.12 (m, 2H, 2CH), 5.30 (s, 1H, CH), 5.35 (d, $^3J_{H,H}$ = 3.0 Hz, 1H, CH), 6.02 (d, $^3J_{H,H}$ = 5.8 Hz, 1H, CH), 7.39 (t, $^3J_{H,H}$ = 5.8 Hz, 2H, Ph, CH), 7.71 (d, $^3J_{H,H}$ = 6.5 Hz, 1H, Ph), 8.47-8.68 (m, 2H, Ph); ^{13}C-NMR (75 MHz, $CDCl_3$): *δ* 26.07, 26.09, 26.13, 26.23, 37.69, 37.72, 37.78, 38.08, 56.96, 60.31, 65.99, 67.35, 69.93, 70.88, 84.49, 86.32, 122.49, 122.72, 127.83, 129.89, 131.31, 135.66, 151.47, 170.77, 175.80, 176.08, 176.71, 176.81; ESI-MS: 689.3 ($[M+H]^+$); HRMS calcd for $C_{36}H_{52}N_2O_{11}$: 711.3460 $[M+ Na]^+$. found: 711.3463.







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面积百分比报告

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排序 : 信号
乘积因子 : 1.0000
稀释因子 : 1.0000
内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

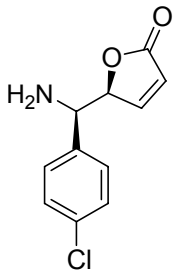
峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	4.701	VB	0.2112	1375.18201	104.87324	93.3389
2	5.816	BV	0.2347	98.13959	6.08613	6.6611

总量 : 1473.32159 110.95936

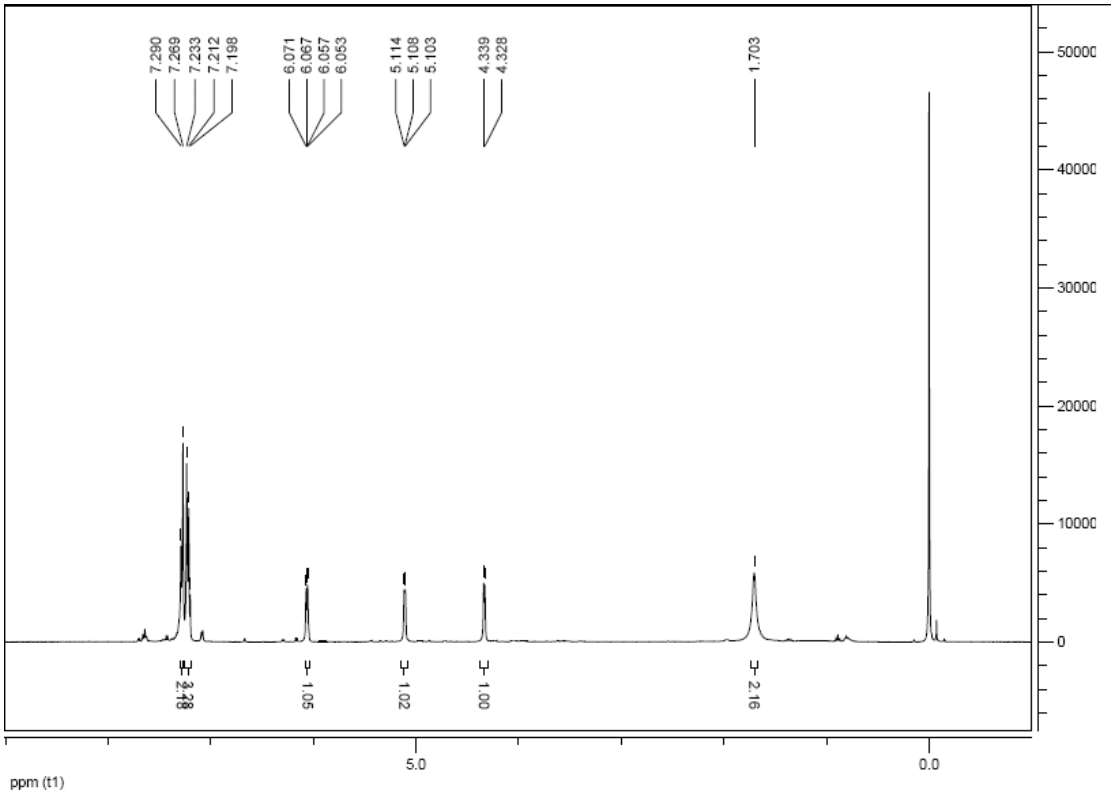
General Procedure for the synthesis of (*S*)-5-((*R*)-amino(phenyl)methyl)-5*H*-furan-2-one 8:

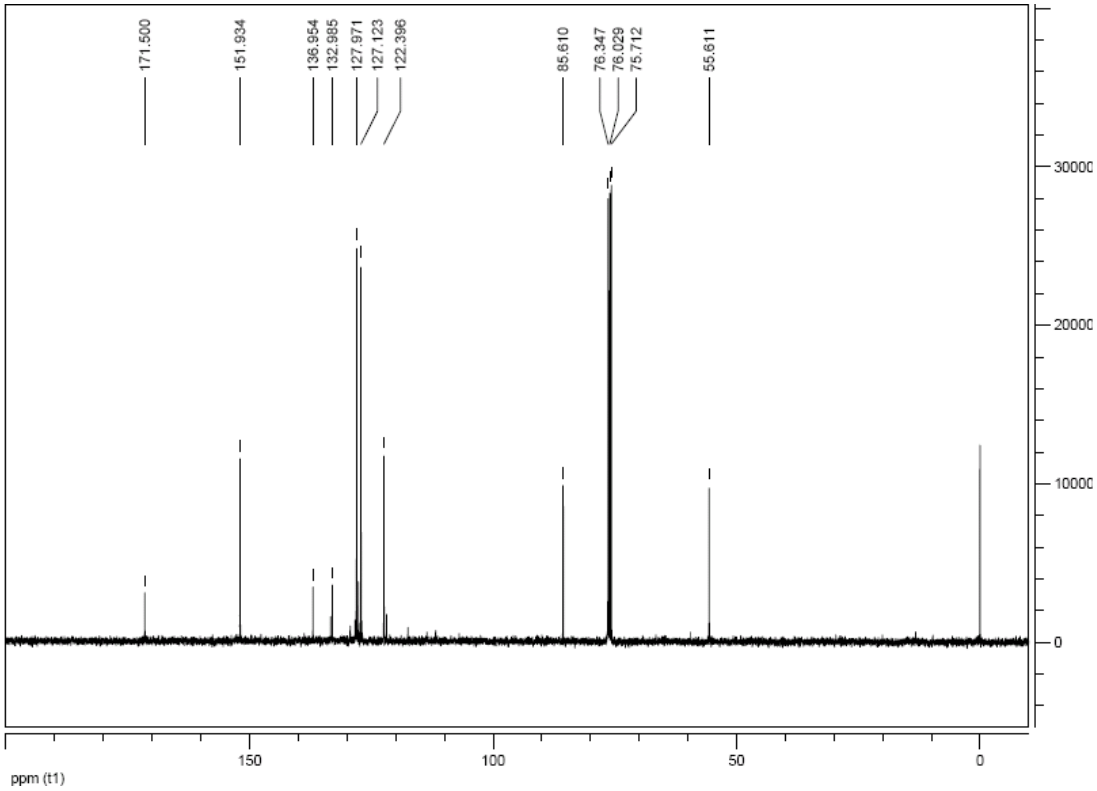
A solution of compound **5h** (0.2 mmol) in dry methanol (2 mL) was treated with freshly prepared (1M) solution of HCl/MeOH (0.5 mL). The solution was stirred for 1.5d (TLC control). Then methanol was evaporated in vacuo and the remaining residue dissolved in 0.5M HCl (5 mL) and extracted with pentane (3 × 10 mL). The aqueous solution was neutralized using saturated $NaHCO_3$ aqueous solution until that a pH value of 7 was achieved for the solution. Then, CH_2Cl_2 (5.0 mL) was added, the organic layer was separated, and the aqueous layer was washed with CH_2Cl_2 (3 × 5 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and evaporation of the solvent, and gave **8h** as yellow oil.

(S)-5-((R)-amino(4-chlorophenyl)methyl)furan-2(5H)-one (8h)



Yellow oil; $[\alpha]_D^{25}$ = -92.9° (c = 0.5, CH_2Cl_2); ^{1}H-NMR (400 MHz, $CDCl_3$): 1.70 (bs, 2H, NH_2), 4.33 (d, $^3J_{H\text{-}H}$ = 4.4 Hz, 1H, CH), 5.11 (t, $^3J_{H\text{-}H}$ = 2.4 Hz, 1H, CH), 6.06 (dd, $^3J_{H\text{-}H}$ = 5.6 Hz, $^3J_{H\text{-}H}$ = 2.4 Hz, 1H, CH), 7.20-7.23 (m, 3H, Ph, CH), 7.27-7.29 (d, $^3J_{H\text{-}H}$ = 8.36 Hz, 2H, Ph); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 55.61, 85.61, 122.40, 127.12, 127.97, 132.99, 136.95, 151.93, 171.50; ESI-MS: 206.5 (M^+-NH_3); HRMS calcd for $C_{11}H_{10}ClNO_2$: 224.0473 $[M+ H]^+$. found: 224.0476.


7.290
7.269
7.233
7.212
7.198
6.071
6.067
6.057
6.053
5.114
5.108
5.103
4.339
4.328
1.703
H= 2.18
H= 1.05
H= 1.02
H= 1.00
H= 2.16
50000
40000
30000
20000
10000
0
5.0
0.0
ppm (t1)


171.500
151.934
136.954
132.985
127.971
127.123
122.396
85.610
76.347
76.029
75.712
55.611
30000
20000
10000
0
150
100
50
0
ppm (t1)