Supplementary Information

NEW SUGAR BASED γ-AMINO SILYL ETHER ORGANOCATALYSTS FOR ASYMMETRIC MICHAEL ADDITION OF β-KETO ESTERS WITH NITROOLEFINS

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1. Experimental method

1.1 General method

Reagents and analytical grade solvents were obtained from commercial suppliers and used without further purification. All reactions were carried out under a positive atmosphere of argon, glass wares were flame-dried and cooled in desiccator. The reactions were monitored by thin layer chromatography (TLC). TLC was performed on Merck pre-coated silica gel 60 F-254 plates. Spots were visualized by exposure to UV light, by immersion into a solution of *p*-anisaldehyde followed by heating at ca. 200 °C. Column chromatography was performed on Kanto Chemical silica gel 60 N (Spherical, neutral, 40-50 μm). The melting points were determined using a micro-melting point apparatus. IR spectra were recorded on JASCO FT/IR-4100 and the major absorbance bands are all reported in wavenumbers (cm^{-1}). High-resolution mass spectra (HRMS) were measured on EI and FAB using sector instruments [Hitachi RMG-GMG and JEOL JNK-DX303]. NMR spectra were recorded on a JEOL JNM-ECA500 spectrometer, operating at 500 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR. Chemical shifts in $CDCl_3$ were reported downfield from TMS (δ = 0 ppm) for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported downfield from TMS (δ = 0 ppm) or in the scale relative to the solvent signal [$CHCl_3$ (77.0 ppm)] as an internal reference. Coupling constants (*J*) are reported as hertz (Hz). Splitting patterns are indicated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. The enantiomeric excess (*ee*) was determined by HPLC analysis. HPLC was measured at column, CHIRALPAK IC, CHIRALCEL OD-H (4.6 mm Å~ 25 cm) and 2-propanol/hexane system was employed as a mobile phase.

1.2 General procedure for the Michael addition of β-keto esters 3a-g to *trans*-β-nitroolefins 4a-f

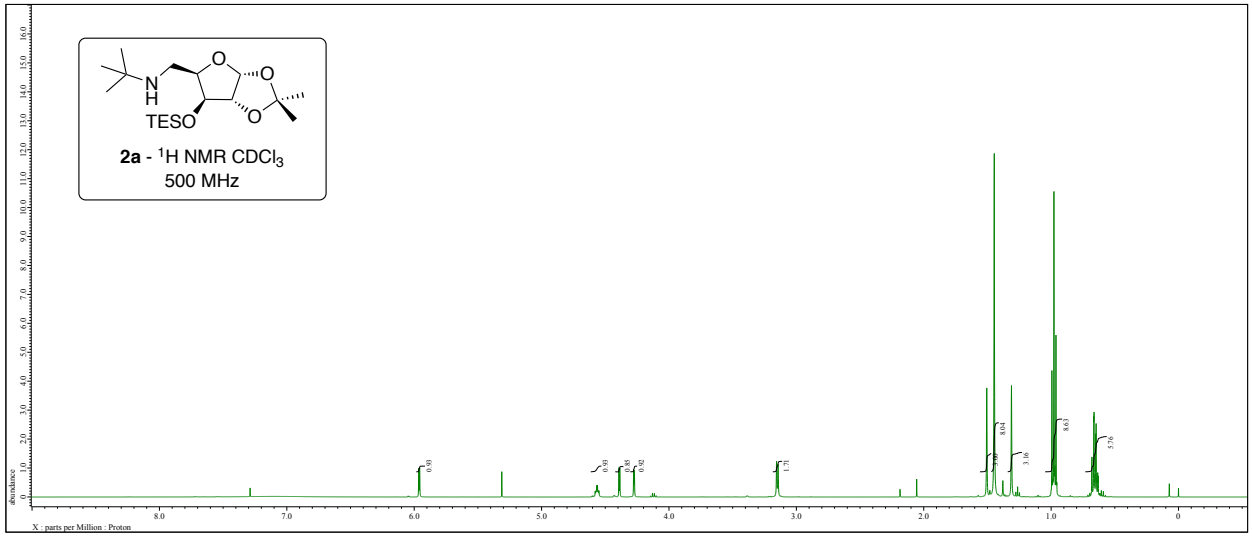
To a stirred solution of *trans*-β-nitroolefins **4a-f** (0.34 mmol) and organocatalysts **2a-k** (0.06 mmol, 20 mol%) in *i*-Pr_2O (0.5 mL) were added β-keto esters **3a-g** (0.67 mmol) at room temperature. After the reaction completion was monitored by TLC, the mixture was extracted with CH_2Cl_2 and the organic layer was dried over anhydrous Na_2SO_4, filtered and concentrated under a reduced pressure. The residue was purified by flash column chromatography on SiO_2 (*n*-hexane/EtOAc = 9:1) to afford the corresponding chiral Michael adducts **7a-j**. The ee were determined by HPLC using DAICEL CHIRALCEL OD-H or CHIRALPAK IC columns.

1.3 General procedure for the preparations of catalysts 2a-k

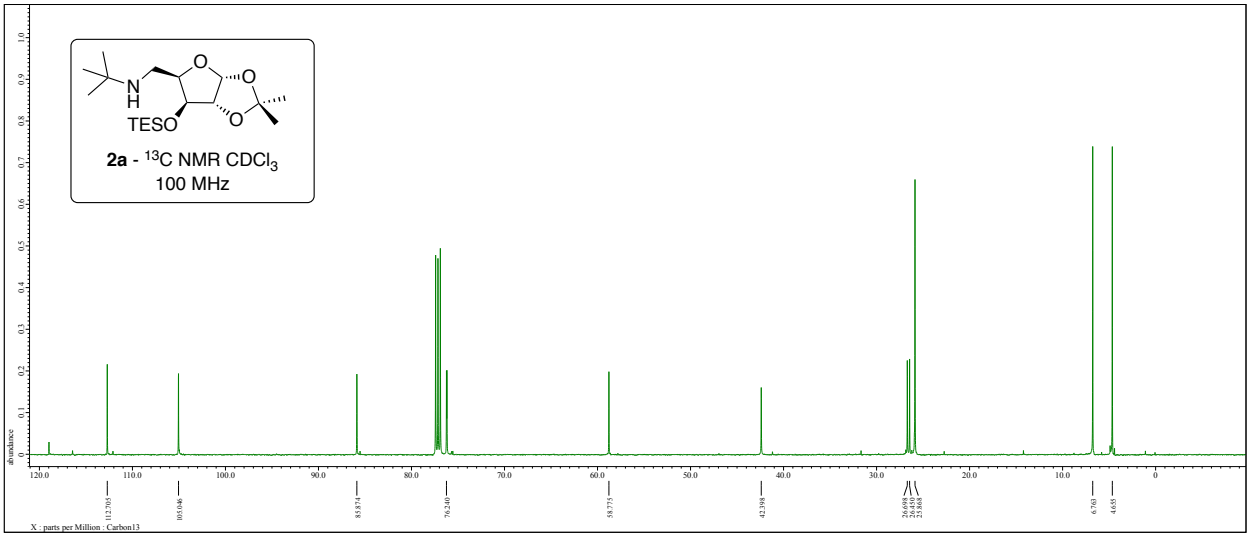
To a stirred solution of compounds **1a-k** (0.20 g, 0.82 mmol) and Et_3N (2.05 mmol) in CH_2Cl_2 (15 mL) was added corresponding silyl protecting reagents (1.2 mmol) at 0 ^{o}C for 30 mins. After that, reaction mixture was allowed to stir at room temperature for 24 h. Upon completion of reaction that was monitored by TLC, solvents were evaporated under reduced pressure and organic layer was extracted using CH_2Cl_2 as three portions (3 × 10 mL) from aqueous layer. The obtained combined organic layers were dried on Na_2SO_4, concentrated and purified by flash chromatography using on SiO_2 (CH_2Cl_2/MeOH = 9:1) afforded the compounds **2a-k**.

2. ^{1}H and ^{13}C NMR copies of compound 2a-k:

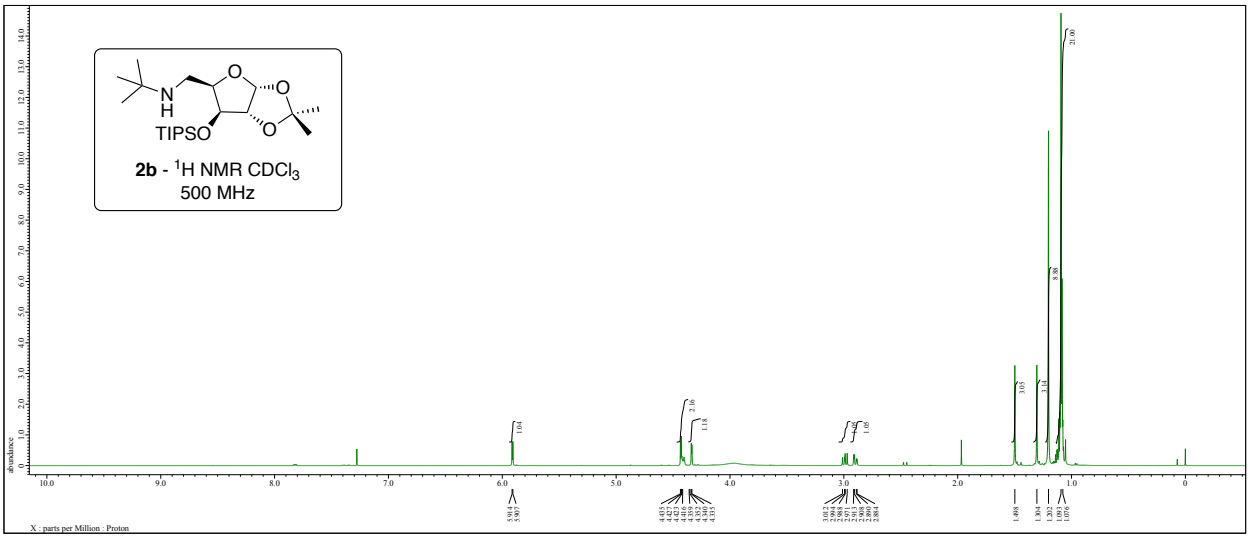
1,2-*O*-isopropylidene-3-*O*-triethylsilyl-5-*N*-(*t*-butylamine)-α-D-xylofuranose 2a:



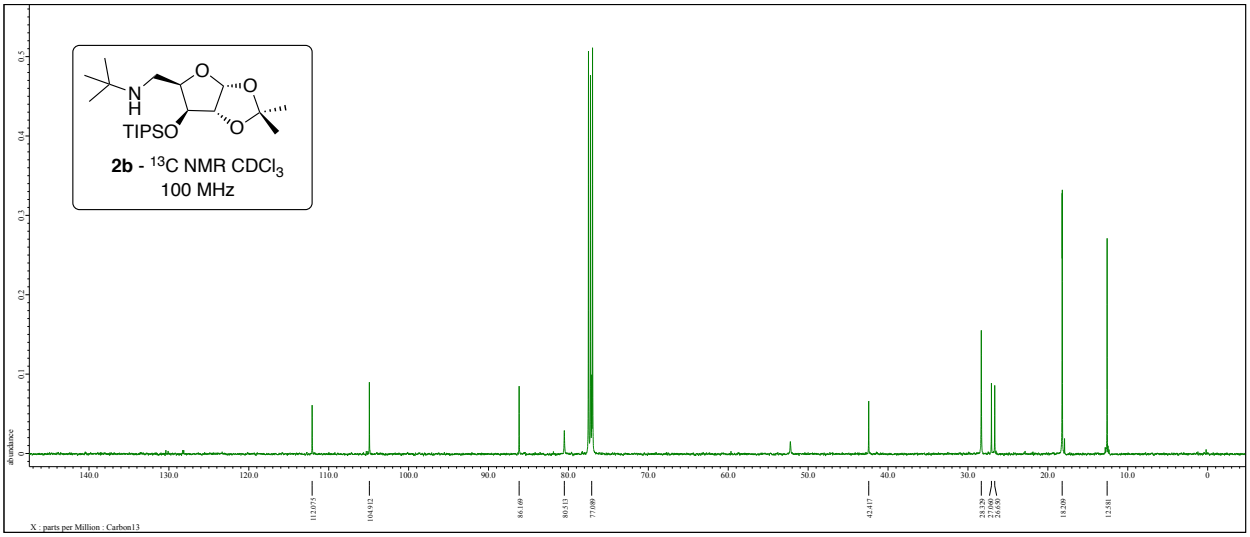
1,2-*O*-isopropylidene-3-*O*-triethylsilyl-5-*N*-(*t*-butylamine)-α-D-xylofuranose 2a:



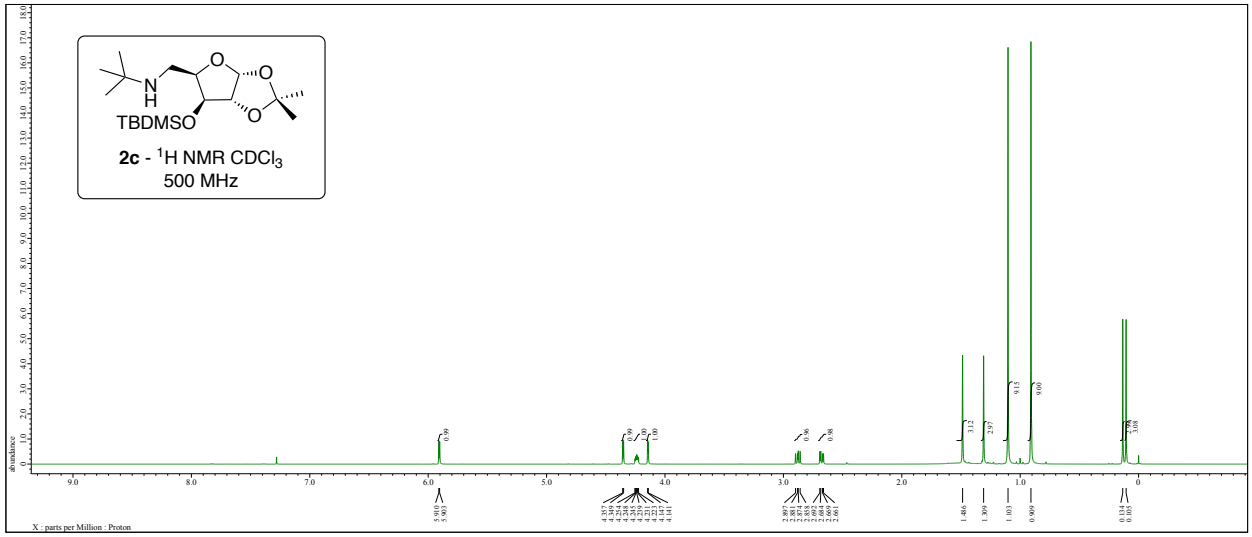
1,2-*O*-isopropylidene-3-*O*-triisopropylsilyl-5-*N*-(*t*-butylamine)-α-D-xylofuranose 2b:



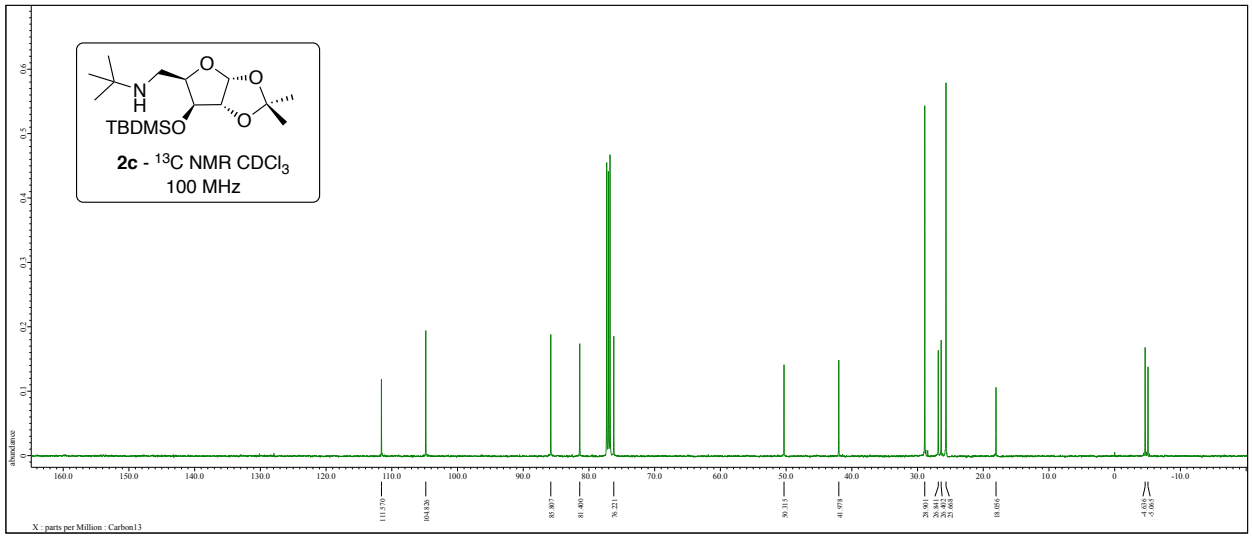
1,2-*O*-isopropylidene-3-*O*-triisopropylsilyl-5-*N*-(*t*-butylamine)-α-D-xylofuranose 2b:



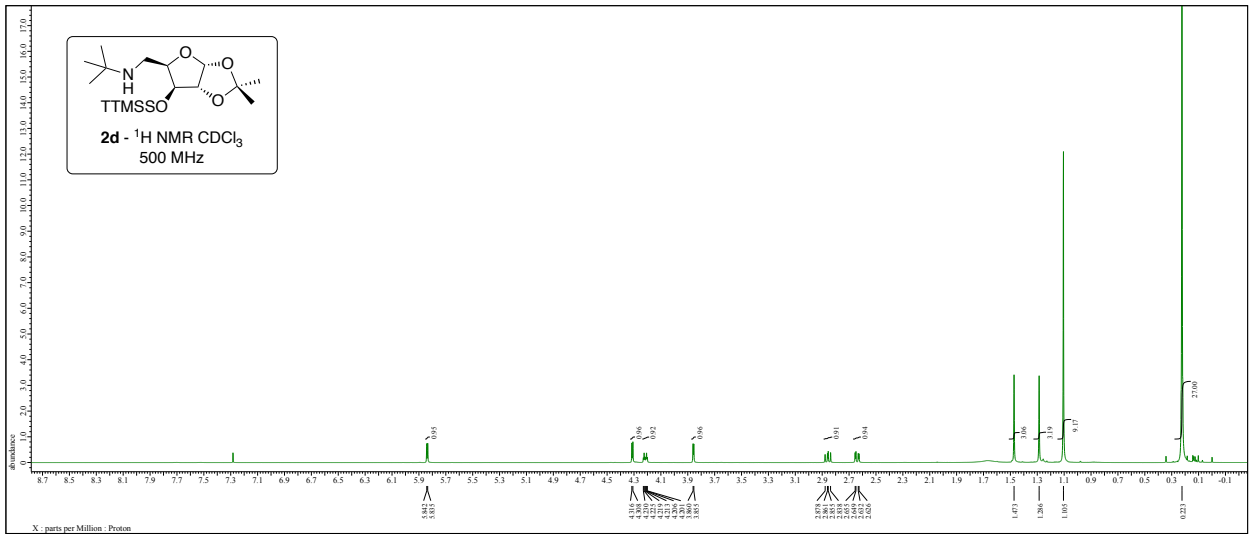
1,2-*O*-isopropylidene-3-*O*-*t*-butyldimethylsilyl-5-*N*-(*t*-butylamine)-α-D-xylofuranose 2c:



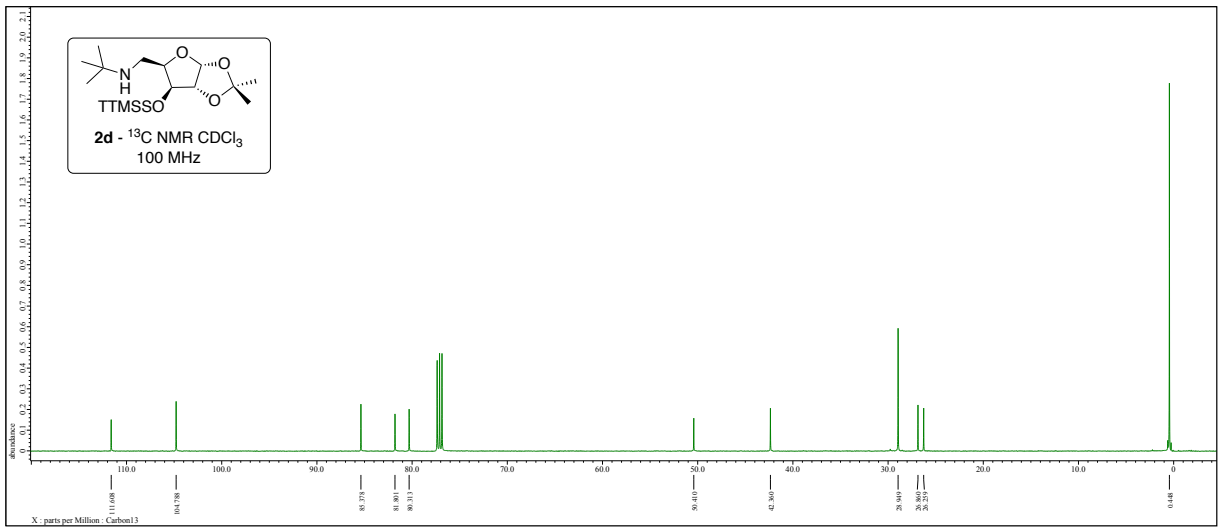
1,2-*O*-isopropylidene-3-*O*-*t*-butyldimethylsilyl-5-*N*-(*t*-butylamine)-α-D-xylofuranose 2c:



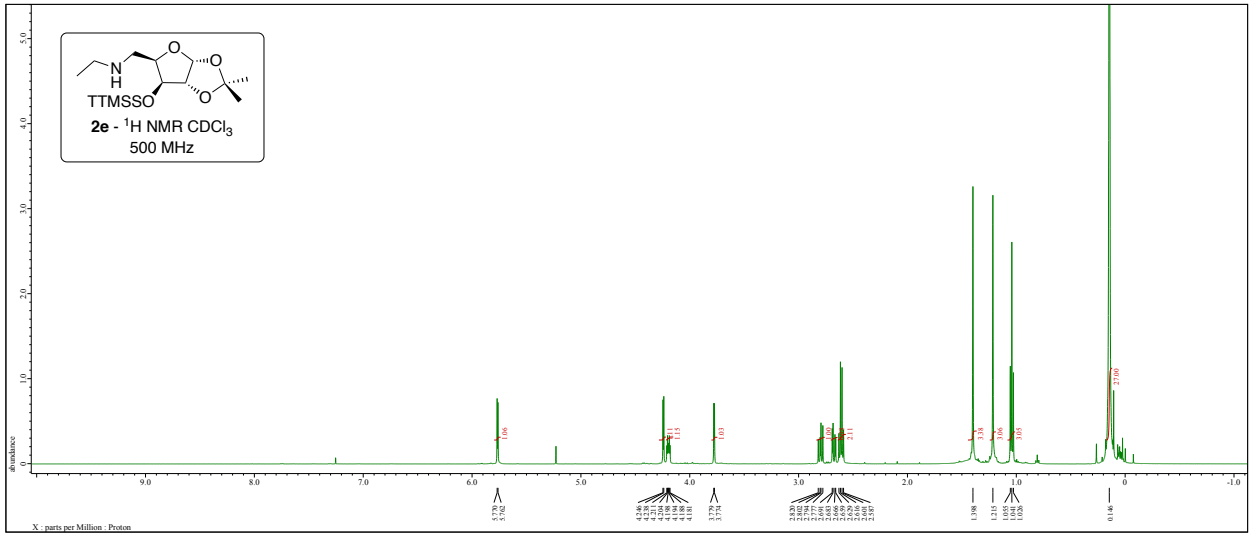
1,2-*O*-isopropylidene-3-*O*-tris(trimethylsilyl)silyl-5-*N*-(*t*-butylamine)-α-D-xylofuranose 2d:



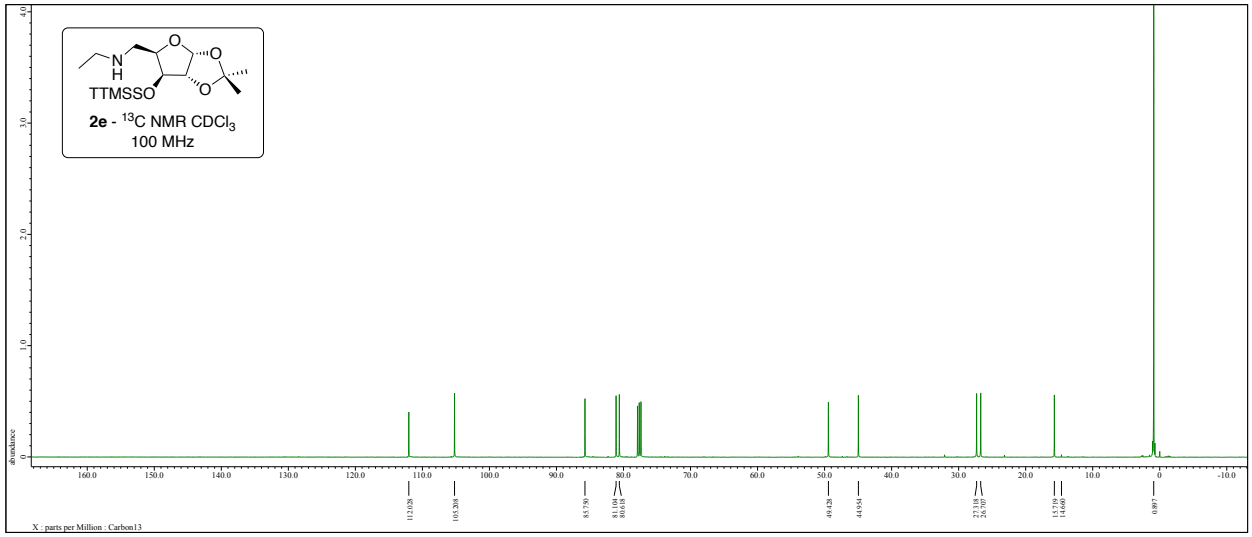
1,2-*O*-isopropylidene-3-*O*-tris(trimethylsilyl)silyl-5-*N*-(*t*-butylamine)-α-D-xylofuranose 2d:



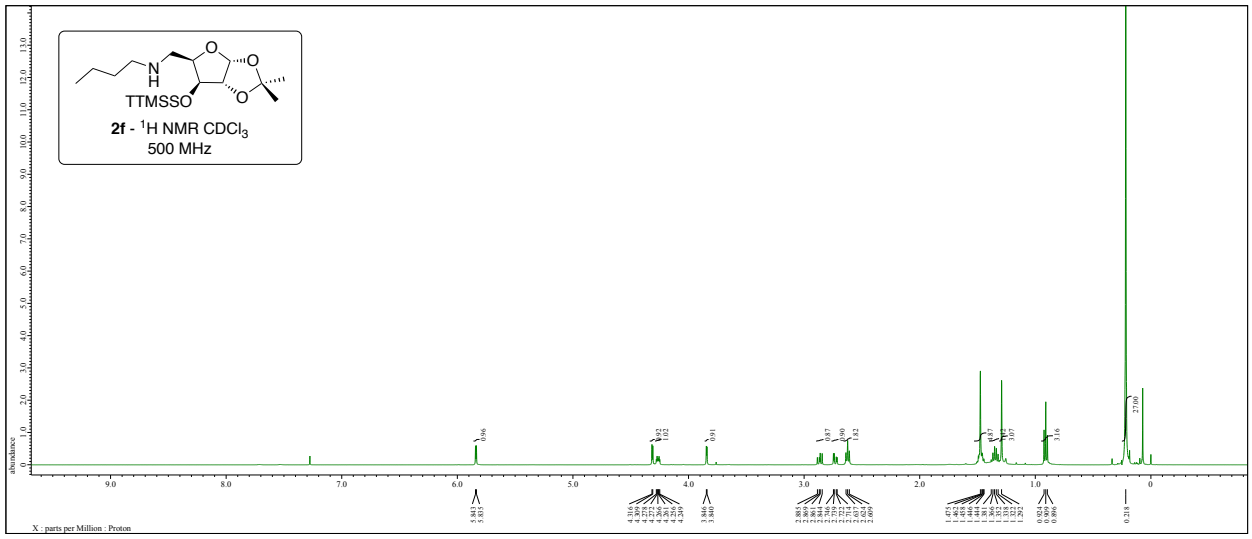
1,2-*O*-isopropylidene-3-*O*-tris(trimethylsilyl)silyl-5-*N*-(ethylamine)-α-D-xylofuranose 2e:



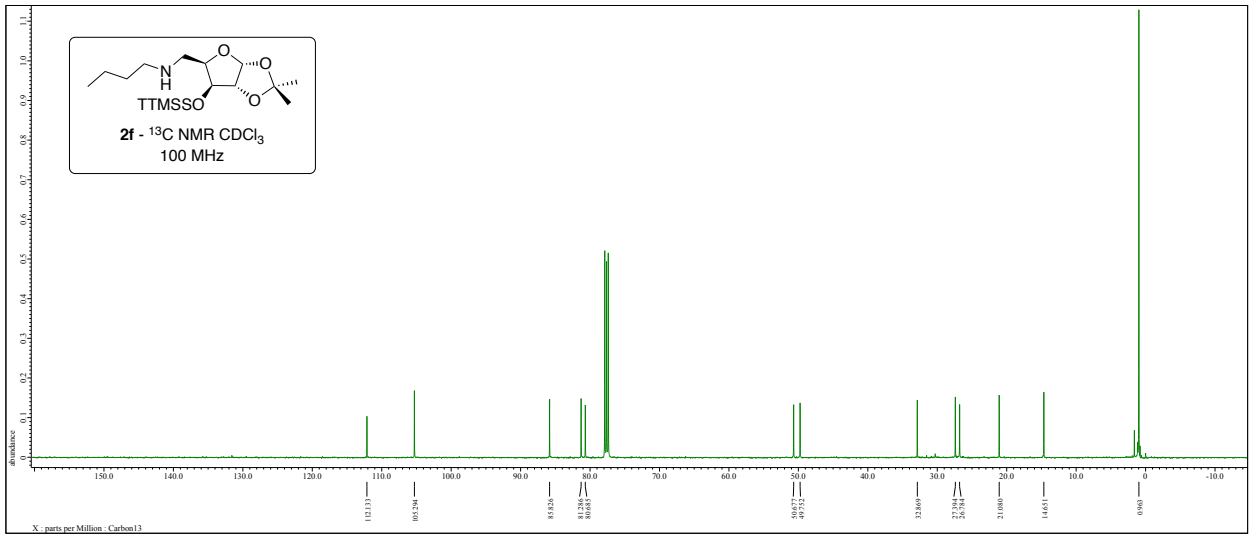
1,2-*O*-isopropylidene-3-*O*-tris(trimethylsilyl)silyl-5-*N*-(ethylamine)-α-D-xylofuranose 2e:



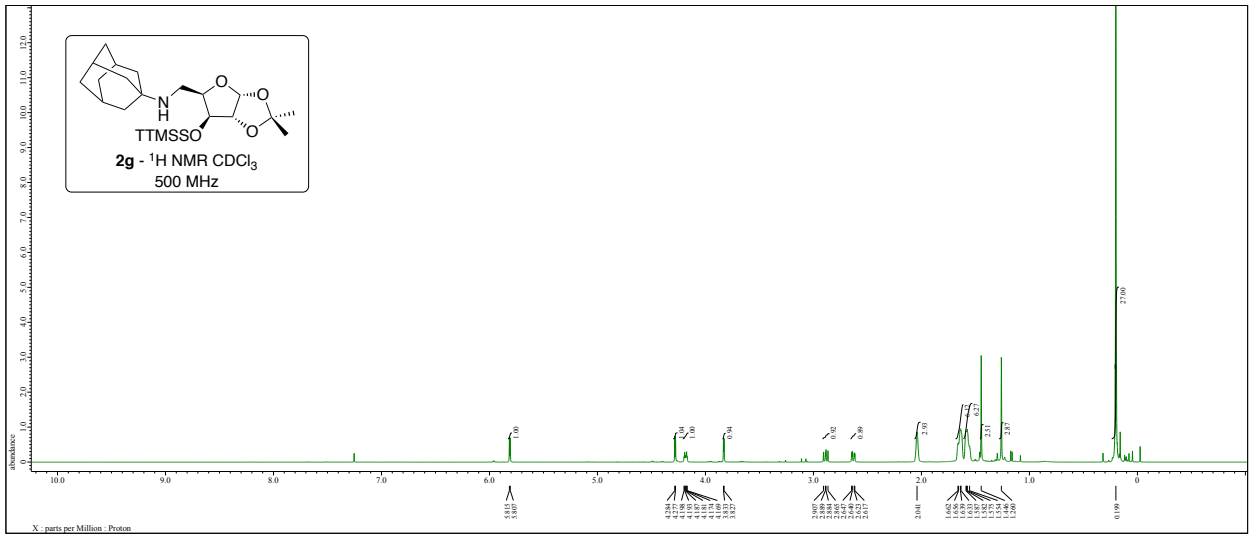
1,2-*O*-isopropylidene-3-*O*-tris(trimethylsilyl)silyl-5-*N*-(*n*-butylamine)-α-D-xylofuranose 2f:



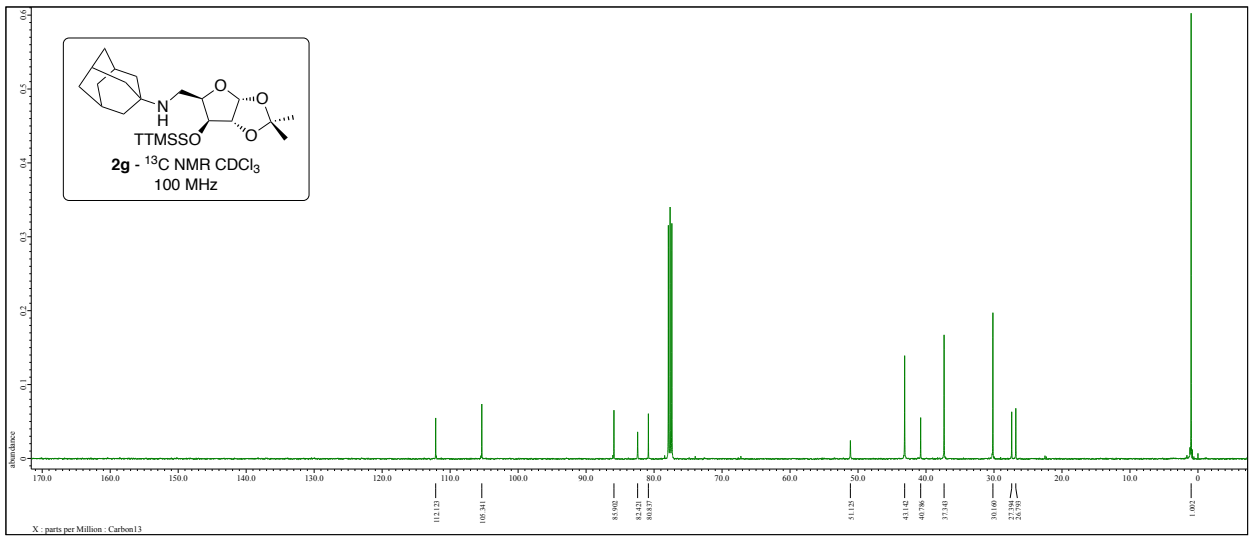
1,2-*O*-isopropylidene-3-*O*-tris(trimethylsilyl)silyl-5-*N*-(*n*-butylamine)-α-D-xylofuranose 2f:



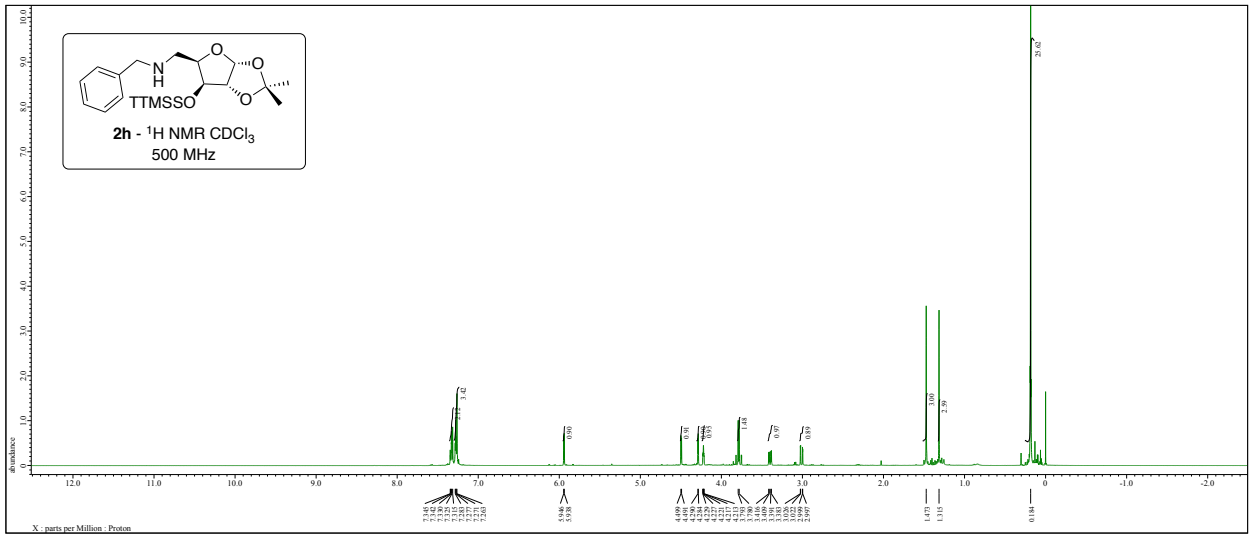
1,2-*O*-isopropylidene-3-*O*-tris(trimethylsilyl)silyl-5-*N*-(adamantyl)-α-D-xylofuranose 2g:



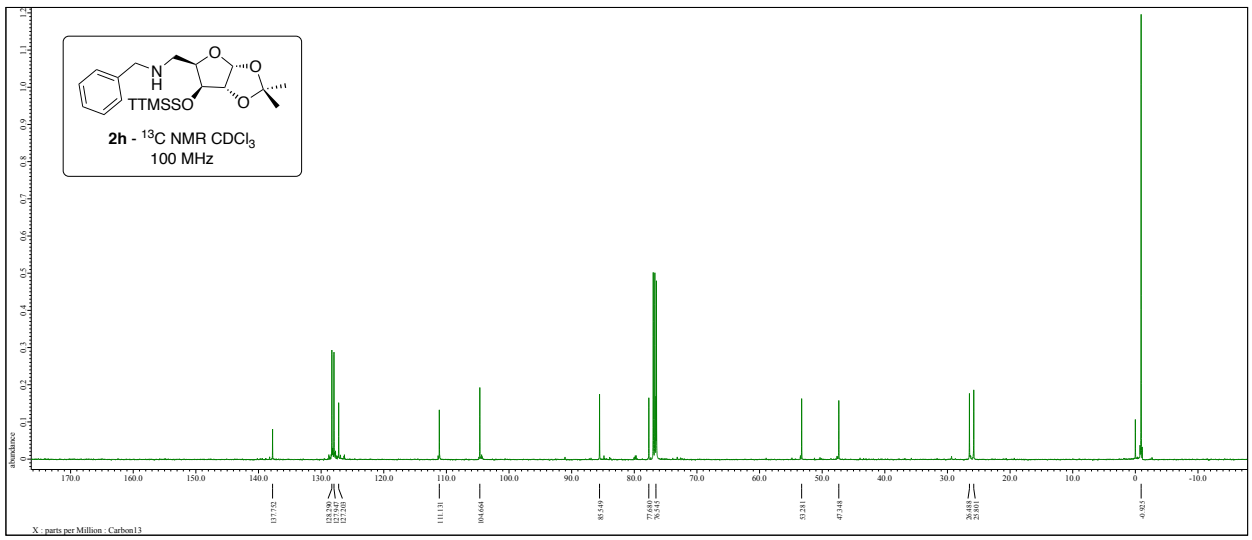
1,2-*O*-isopropylidene-3-*O*-tris(trimethylsilyl)silyl-5-*N*-(adamantyl)-α-D-xylofuranose 2g:



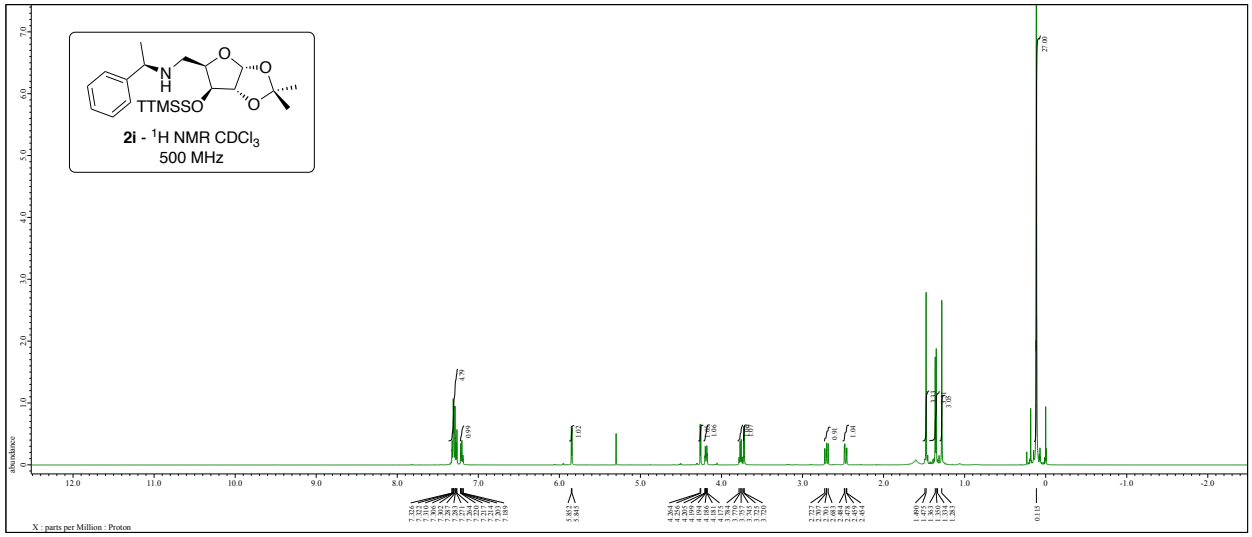
1,2-*O*-isopropylidene-3-*O*-tris(trimethylsilyl)silyl-5-*N*-(benzylamine)-α-D-xylofuranose 2h:



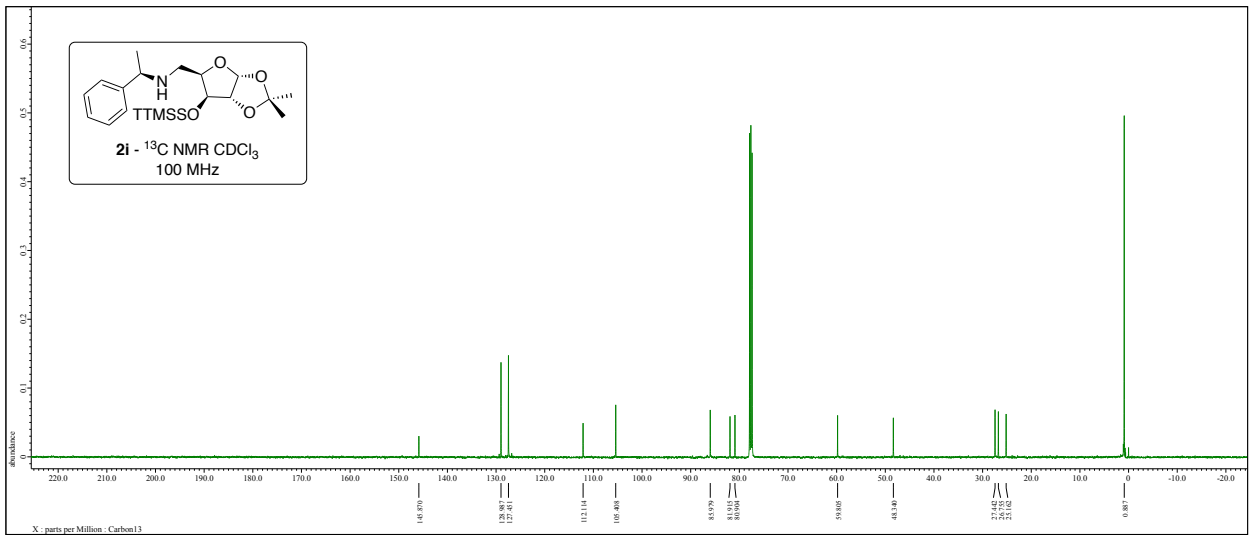
1,2-*O*-isopropylidene-3-*O*-tris(trimethylsilyl)silyl-5-*N*-(benzylamine)-α-D-xylofuranose 2h:



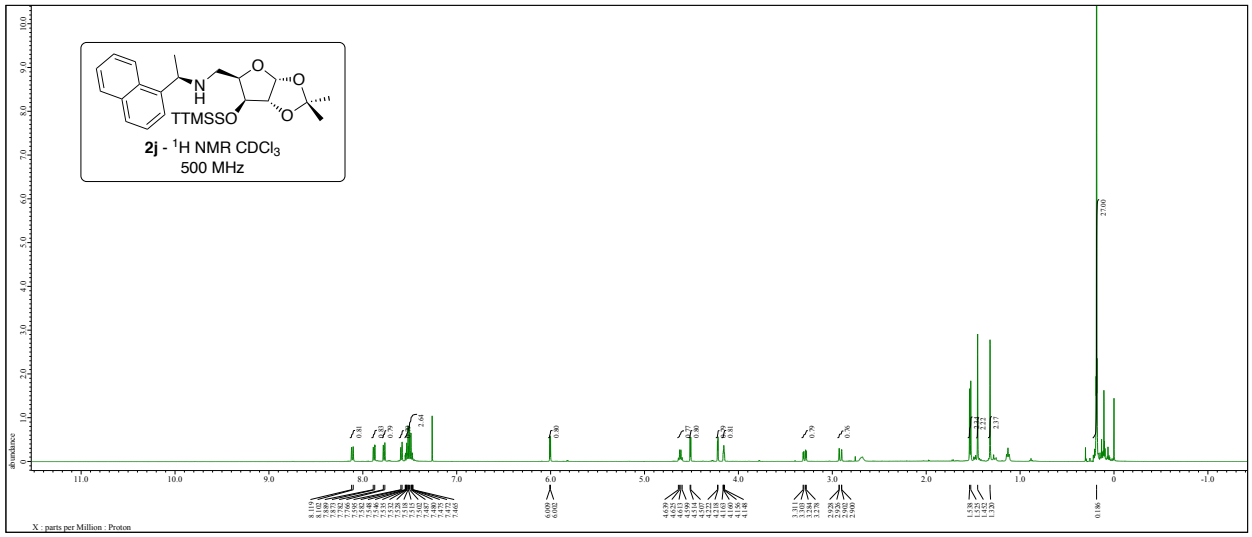
1,2-*O*-isopropylidene-3-*O*-tris(trimethylsilyl)silyl-5-*N*-(*R*-phenylethylamine)-α-D-xylofuranose 2i:



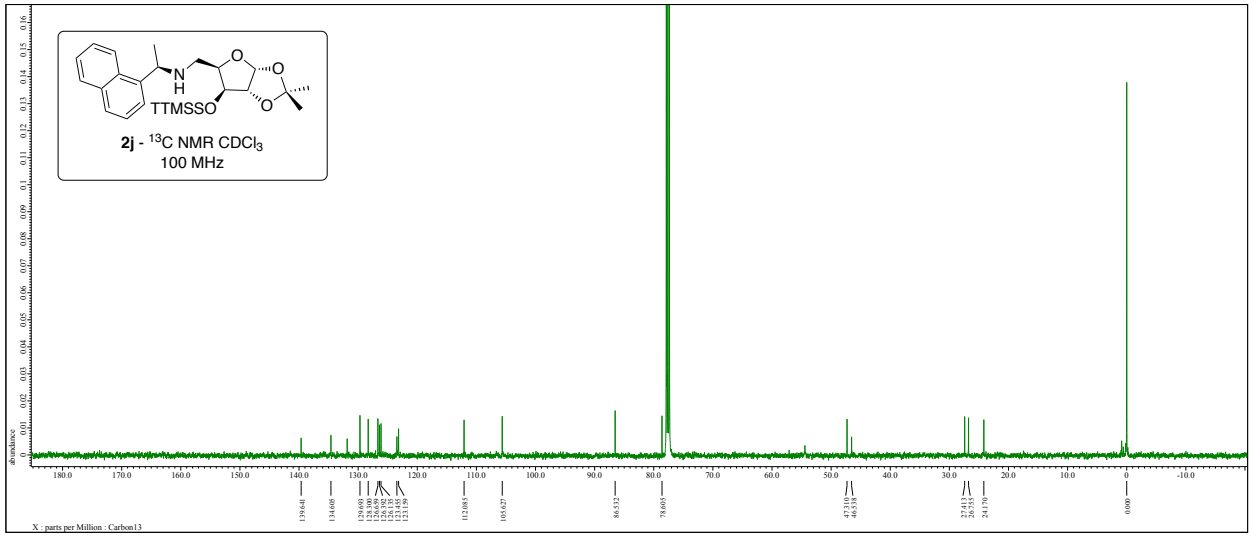
1,2-*O*-isopropylidene-3-*O*-tris(trimethylsilyl)silyl-5-*N*-(*R*-phenylethylamine)-α-D-xylofuranose 2i:



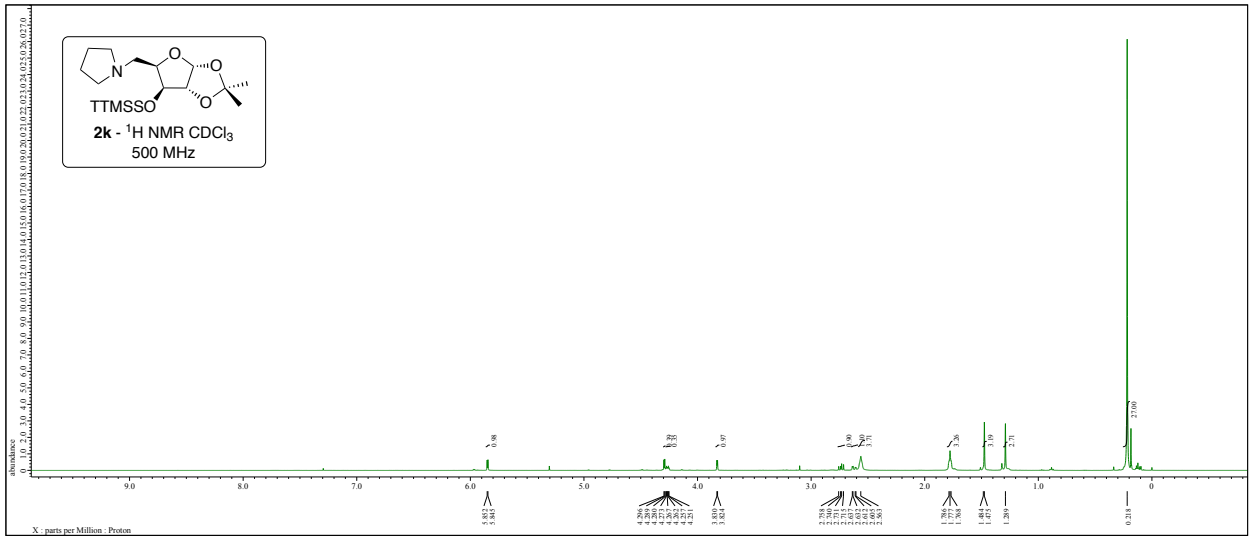
1,2-*O*-isopropylidene-3-*O*-tris(trimethylsilyl)silyl-5-*N*-(*R*-naphthylamine)-α-D-xylofuranose 2j:



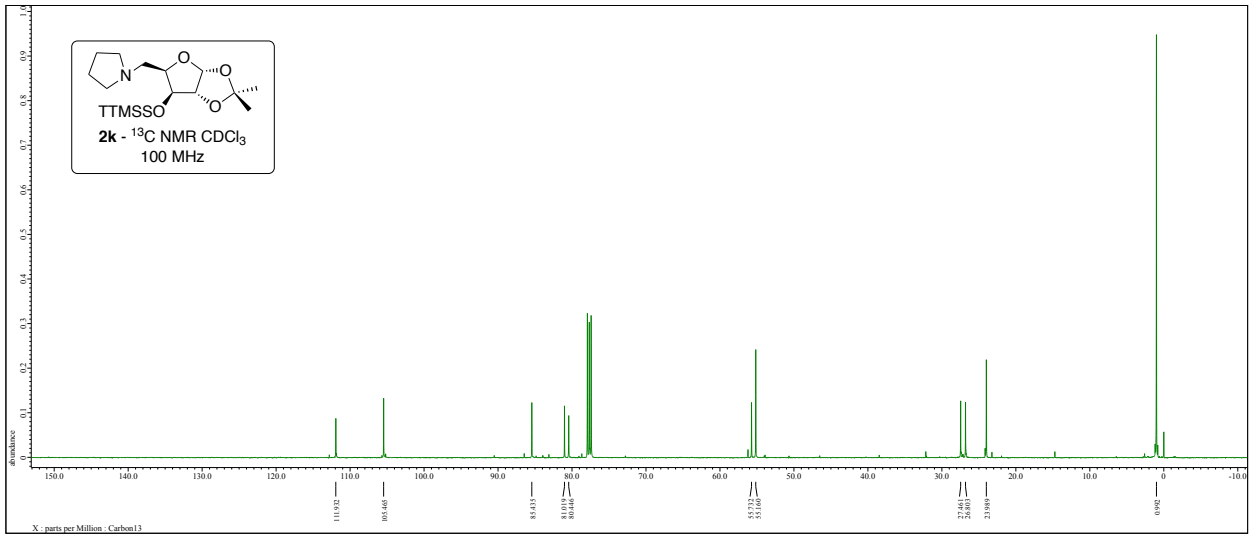
1,2-*O*-isopropylidene-3-*O*-tris(trimethylsilyl)silyl-5-*N*-(*R*-naphthylamine)-α-D-xylofuranose 2j:



1,2-*O*-isopropylidene-3-*O*-tris(trimethylsilyl)silyl-5-*N*-(pyrrolidine)-α-D-xylofuranose 2k:



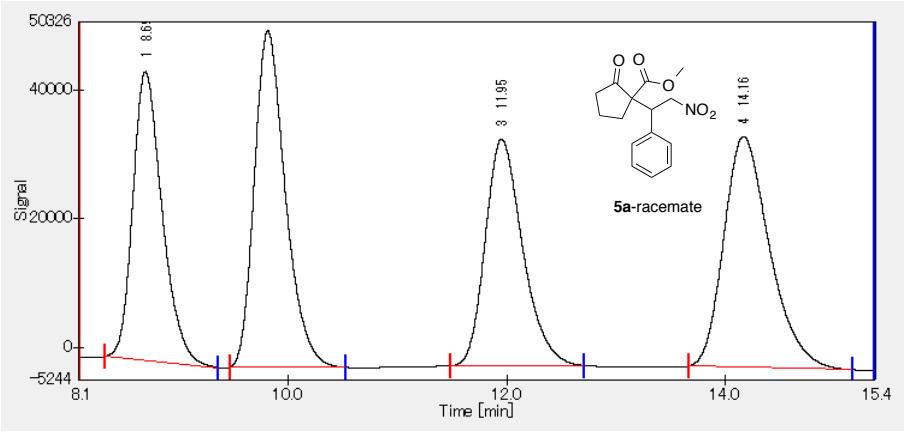
1,2-*O*-isopropylidene-3-*O*-tris(trimethylsilyl)silyl-5-*N*-(pyrrolidine)-α-D-xylofuranose 2k:



3. HPLC Chromatograph

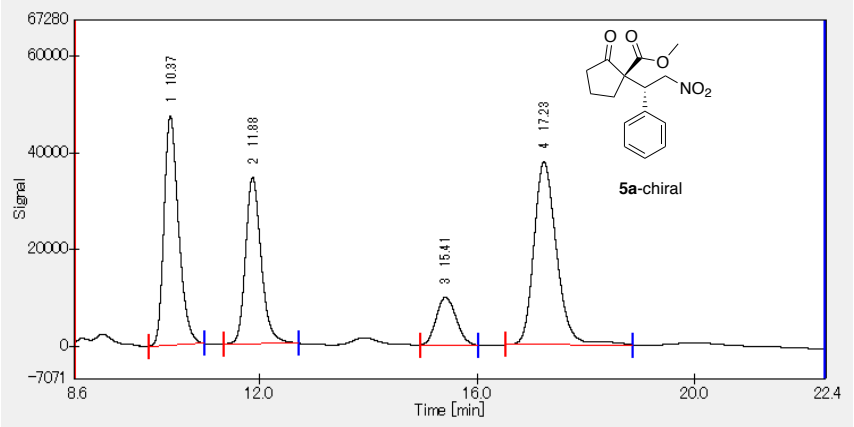
CHIRALCEL OD-H (*n*-hexane: 2-propanol = 90:10, flow rate 1.0 mL/min, λ = 213 nm)

Methyl-1-(2-nitro-1-phenylethyl)-2-oxocyclopentanecarboxylate (**5a**): Racemate



No	Rt (min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	14.4	2801974	19.3063	71187	3112.5	1.415	2.501
2	17.03	4569840	31.4874	112800	4052.6	1.416	3.626
3	21.36	2692060	18.549	53996	4204.5	1.316	3.395
4	26.31	4449372	30.6573	73608	4336.9	1.398	*****
		14513246	100	311591			

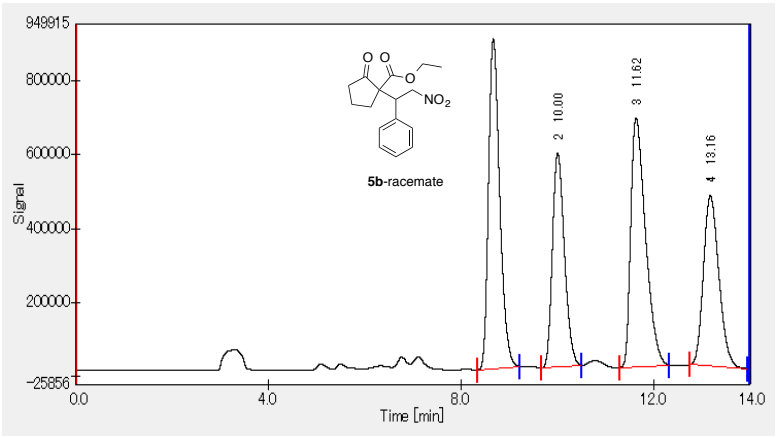
[2*R*, 3*R*]-Methyl-1-(2-nitro-1-phenylethyl)-2-oxocyclopentanecarboxylate (**5a**): Chiral



No	Rt (min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	10.37	878245.8	30.1355	47562	6746.3	1.303	2.91
2	11.88	686608.1	23.5598	34517	7957.7	1.229	5.856
3	15.41	250455	8.5939	9819	8364.6	1.156	2.524
4	17.23	1099017	37.7108	37826	8160.2	1.222	*****
		2914326	100	129724			

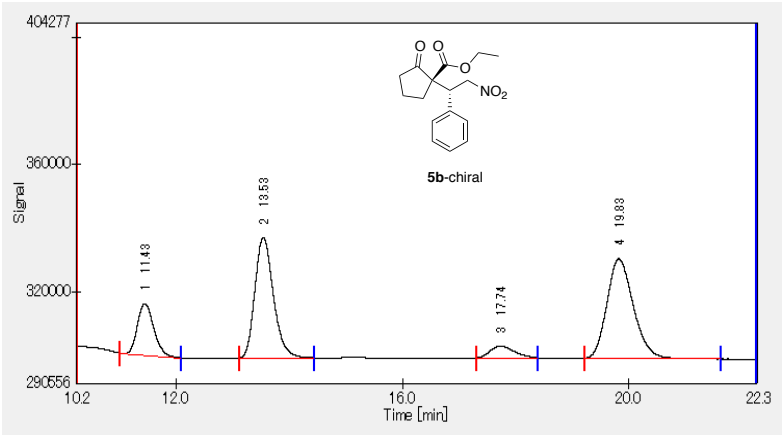
Ethyl-1-(2-nitro-1-phenylethyl)-2-oxocyclopentanecarboxylate (**5b**): Racemate

CHIRALCEL OD-H (*n*-hexane: 2-propanol = 90:10, flow rate 1.0 mL/min, λ = 213 nm)



No	Rt (min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	8.66	14346522.4	29.3218	893771	6288.6	1.336	2.96
2	10	9987199.4	20.4121	579228	7353.1	1.25	3.111
3	11.62	14331167.2	29.2904	673217	6436.9	1.605	2.608
4	13.16	10263013.4	20.9758	460642	7729.7	1.212	*****
		48927902.4	100	2606858			

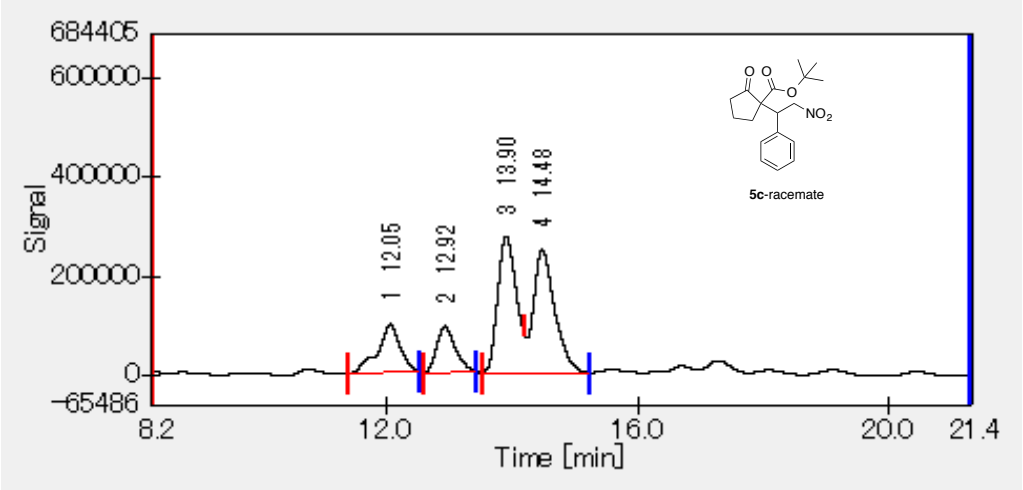
[2*R*, 3*R*]-Ethyl-1-(2-nitro-1-phenylethyl)-2-oxocyclopentanecarboxylate (**5b**): Chiral



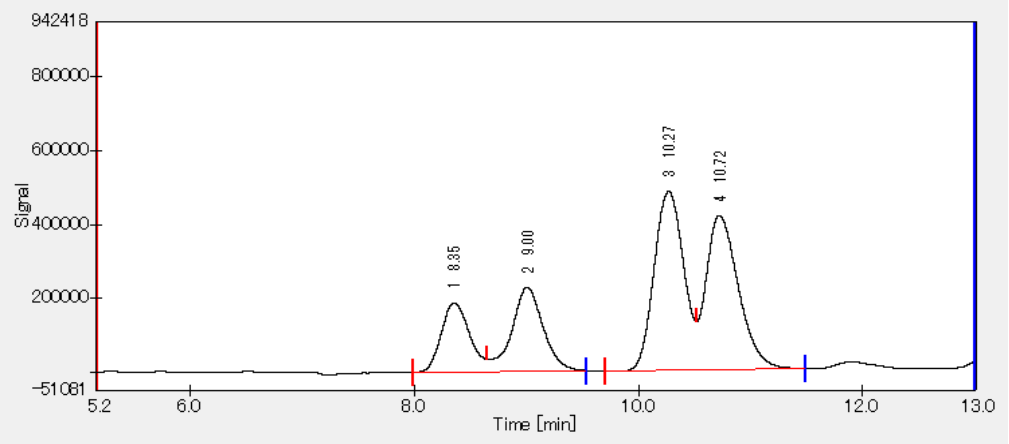
No	Rt (min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	11.43	325301.2	13.9632	16110	7162.7	1.249	3.654
2	13.53	867842.8	37.2511	38017	7845.7	1.244	5.874
3	17.74	113515.3	4.8725	3851	7484.9	1.273	2.467
4	19.83	1023050.8	43.9132	31442	8132.2	1.21	*****
		2329710.1	100	89420			

tert-butyl-1-(2-nitro-1-phenylethyl)-2-oxocyclopentanecarboxylate (**5c**): Racemate

CHIRALCEL OD-H (*n*-hexane: 2-propanol = 95:5, flow rate 1.0 mL/min, λ= 207 nm)



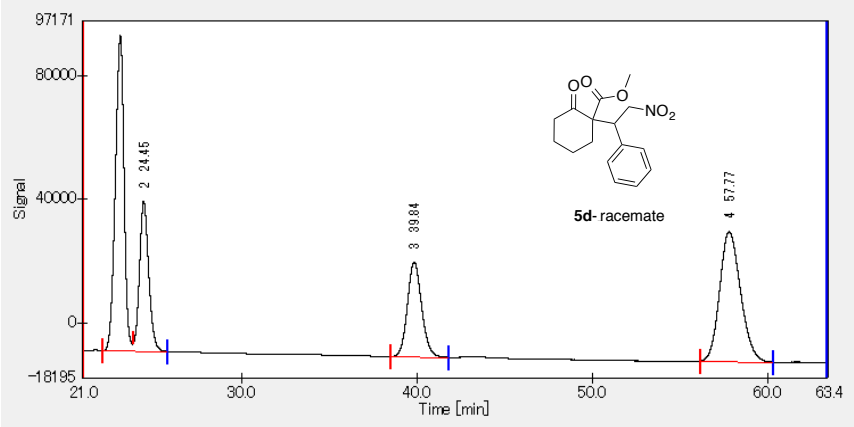
No	Rt (min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	12.05	2519992	15.6735	98236	3423.9	0.859	1.247
2	12.92	1913206	11.8995	93265	8012.9	1.327	*****
3	13.90	5700437	35.4548	275647	10214	*****	0.976
4	14.48	5944391	36.9721	247837	8240.2	*****	*****
		16078025	100	714985			



No	Rt (min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	8.35	3260561	13.1067	184964	5079.2	*****	1.32
2	9.00	4391134	17.6514	226329	4871	*****	2.515
3	10.27	8899382	35.7735	481713	6990.1	*****	0.878
4	10.72	8325955	33.4684	414774	6451	*****	*****
		24877031	100	1307780			

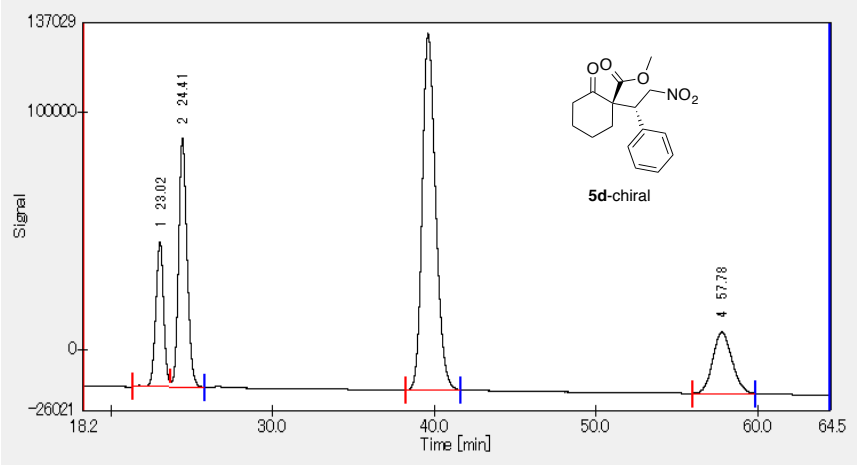
Methyl-1-(2-nitro-1-phenylethyl)-2-oxocyclohexanecarboxylate (**5d**): Racemate

CHIRALCEL OD-H (*n*-hexane: 2-propanol = 90:10, flow rate 1.0 mL/min, λ = 213 nm)



No	Rt(min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	23.12	3518457.52	33.5877	101873	10133.2	0.909	1.409
2	24.45	1767101.98	16.869	48499	10182.7	*****	12.498
3	39.84	1723653.5	16.4542	30679	11042.4	1.113	9.561
4	57.77	3466233	33.0891	41982	10697.1	1.168	*****
		10475446	100	223033			

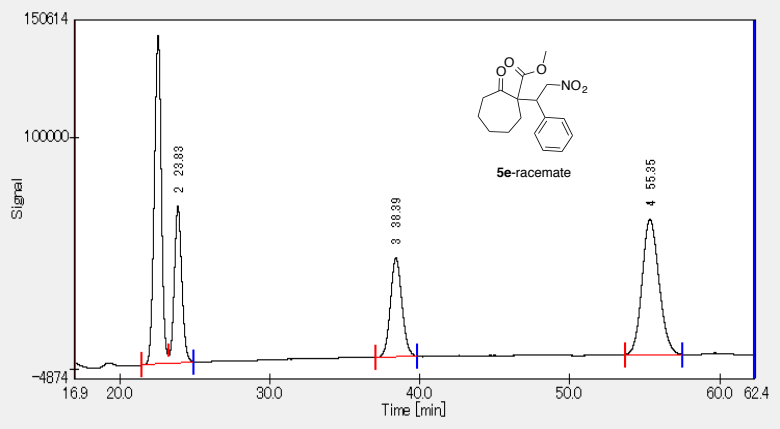
[2*R*,3*R*]-Methyl-1-(2-nitro-1-phenylethyl)-2-oxocyclohexanecarboxylate (**5d**): Chiral



No	Rt(min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	23.02	2063543.853	12.435	61092	10505.9	0.98	1.487
2	24.41	3798943.247	22.8926	104523	10199.9	1.165	12.187
3	39.61	8604821.2	51.8531	149744	10404.9	1.212	9.61
4	57.78	2127305.1	12.8193	25793	10753.7	1.106	*****
		16594613.4	100	341152			

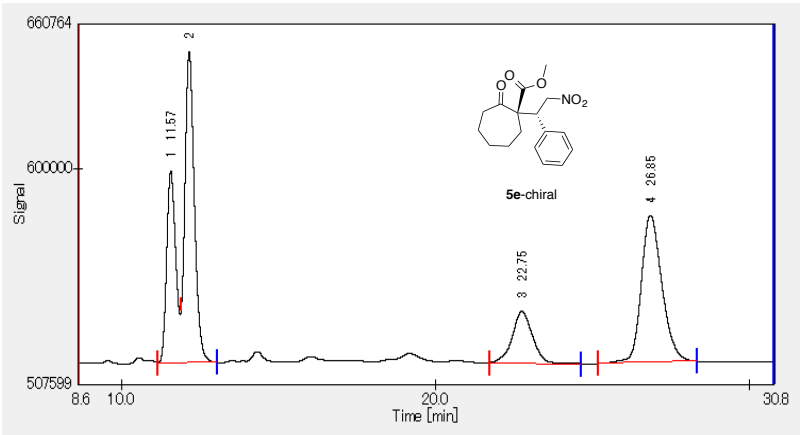
Methyl-1-(2-nitro-1-phenylethyl)-2-oxocycloheptanecarboxylate (**5e**): Racemate

CHIRALCEL OD-H (*n*-hexane: 2-propanol = 90:10, flow rate 1.0 mL/min, λ = 213 nm)



No	Rt(min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	22.52	4693140.283	33.6154	142473	10568.9	0.964	1.465
2	23.83	2354039.917	16.8612	67917	10695	1.076	12.386
3	38.39	2300703.6	16.4792	42846	11206.4	1.092	9.5
4	55.35	4613392.4	33.0442	58842	10903.1	1.13	*****
		13961276.2	100	312078			

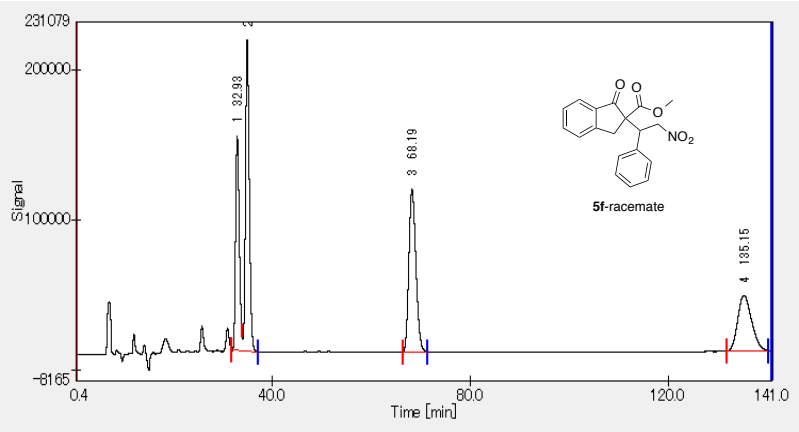
[2*R*,3*R*]-Methyl-1-(2-nitro-1-phenylethyl)-2-oxocycloheptanecarboxylate (**5e**): Chiral



No	Rt(min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	11.57	1660707.97	20.1336	81456	7280.5	*****	1.07
2	12.15	2751395.03	33.3565	132074	7698.4	*****	12.229
3	22.75	971144.8	11.7737	21908	5398.7	1.007	3.318
4	26.85	2865204.5	34.7363	62436	7610	1.234	*****
		8248452.3	100	297874			

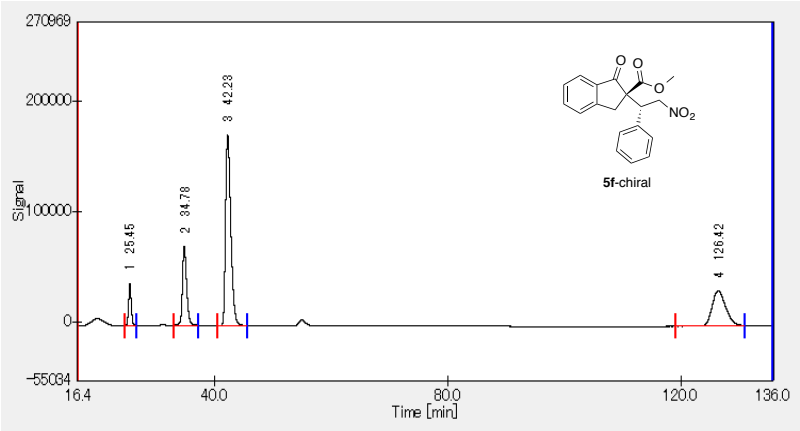
Methyl-2,3-dihydro-2-(2-nitro-1-phenylethyl)-1-oxo-1H-indene-2-carboxylate (**5f**): Racemate

CHIRALCEL OD-H (*n*-hexane: 2-propanol = 80:20, flow rate 0.5 mL/min, λ = 210 nm)



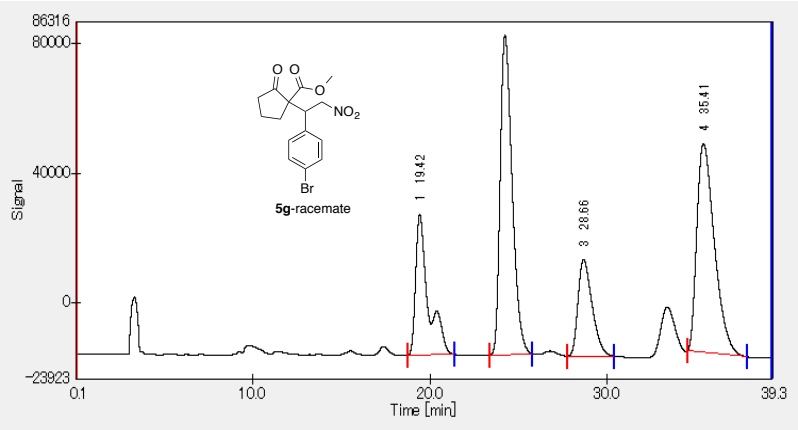
No	Rt(min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	32.93	7544157.6	20.7364	143139	8828.2	*****	1.427
2	34.93	10984763.2	30.1935	207007	9802.8	1.217	16.497
3	68.19	10667339.8	29.321	108243	10682.3	1.202	17.062
4	135.15	7184952.8	19.7491	37002	10767.8	1.223	*****
		36381213.4	100	495391			

[2*R*, 3*R*]-Methyl-2,3-dihydro-2-(2-nitro-1-phenylethyl)-1-oxo-1H-indene-2-carboxylate (**5f**): Chiral



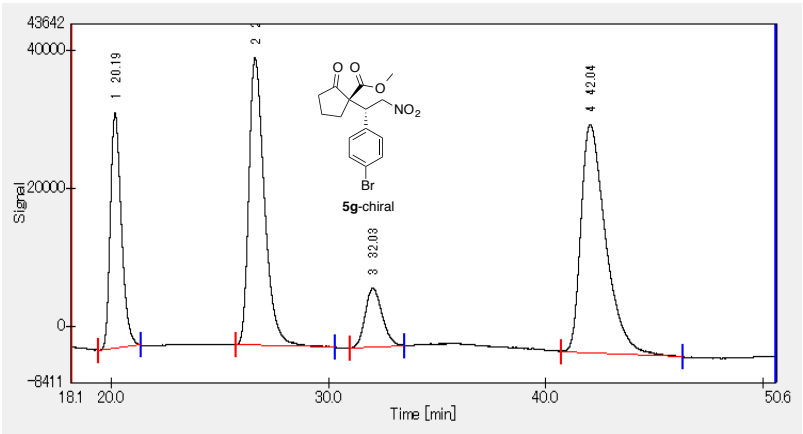
No	Rt(min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	25.45	1184217.2	5.6706	37711	14083.5	1.108	8.42
2	34.78	3671651.4	17.5817	72129	10477.2	1.298	4.905
3	42.23	10869607.8	52.0491	173042	10109.8	1.453	27.762
4	126.42	5157901	24.6986	31777	13299.5	1.233	*****
		20883377.4	100	314659			

Methyl-1-(1-(4-bromophenyl)-2-nitroethyl)-2-oxocyclopentanecarboxylate (**5g**): Racemate
CHIRALCEL OD-H (*n*-hexane: 2-propanol = 90:10, flow rate = 1.0 mL/min, λ = 213 nm)



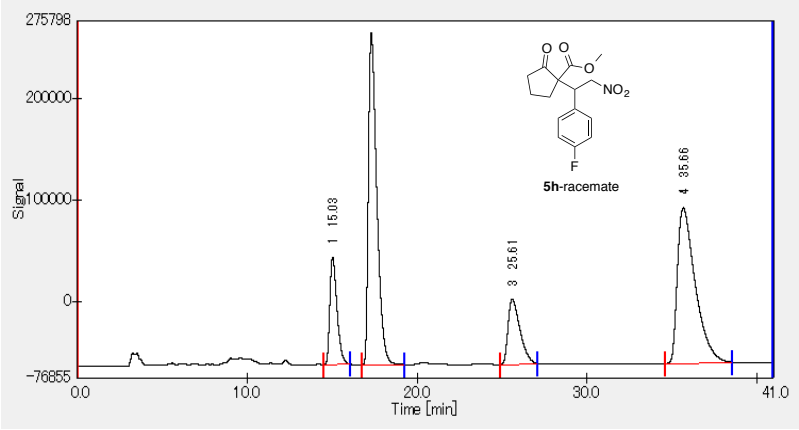
No	Rt(min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	19.42	2136021.2	16.6433	43346	2021.6	2.109	3.213
2	24.23	4607240.8	35.8983	98623	5874.5	1.416	3.198
3	28.66	1650578	12.8608	29729	5795.2	1.43	3.998
4	35.41	4440301.4	34.5976	64506	5719.1	1.565	*****
		12834141	100	236204			

[2*R*, 3*R*]-Methyl-1-(1-(4-bromophenyl)-2-nitroethyl)-2-oxocyclopentanecarboxylate (**5g**): Chiral



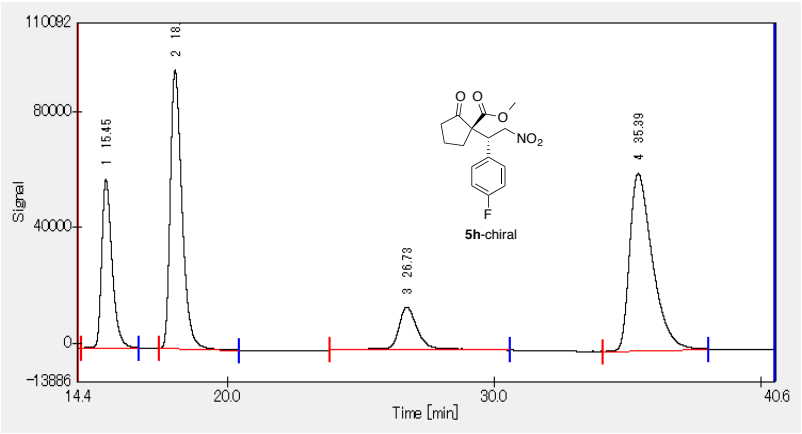
No	Rt(min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	20.19	1202653.5	18.8845	34108	7164.7	1.332	5.592
2	26.63	2089118.4	32.8041	41704	6230.7	1.447	3.867
3	32.03	459944.7	7.2222	8510	7840.6	1.194	5.563
4	42.04	2616742	41.0891	33102	6109.3	1.59	*****
		6368458.6	100	117424			

Methyl-1-(1-(4-fluorophenyl)-2-nitroethyl)-2-oxocyclopentanecarboxylate (**5h**): Racemate
CHIRALCEL OD-H (*n*-hexane: 2-propanol = 90: 10, flow rate = 1.0 mL/min, λ = 213 nm)



No	Rt(min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	15.03	3103407.4	10.829	106029	5684.3	1.513	2.631
2	17.31	11212232	39.124	327078	5508.4	1.755	7.303
3	25.61	3142565	10.9657	64232	5842.1	1.632	5.971
4	35.66	11200009	39.0813	153113	4951.6	1.949	*****
		28658213	100	650452			

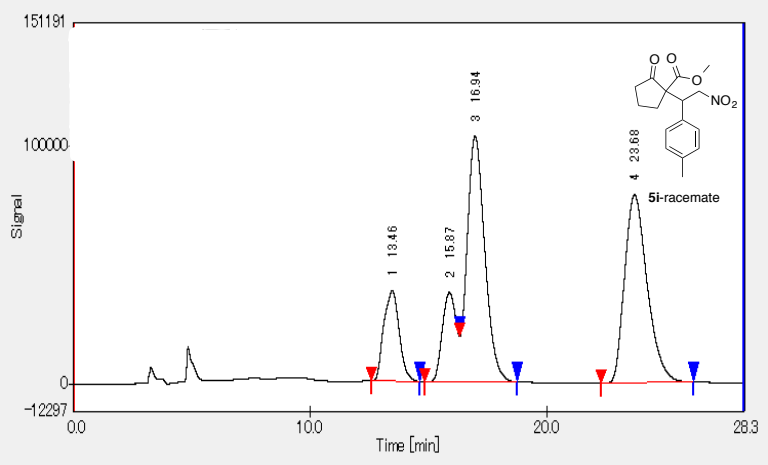
[2*R*, 3*R*]-Methyl-1-(1-(4-fluorophenyl)-2-nitroethyl)-2-oxocyclopentanecarboxylate (**5h**): Chiral



No	Rt(min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	15.45	1570163.1	17.6185	58138	7186.1	1.413	3.337
2	18.04	2947431.6	33.0726	96151	7723.3	1.419	8.303
3	26.73	767506	8.612	14860	7064.4	1.323	5.984
4	35.39	3626901.8	40.6968	61148	7605.1	1.6	*****
		8912002.5	100	230297			

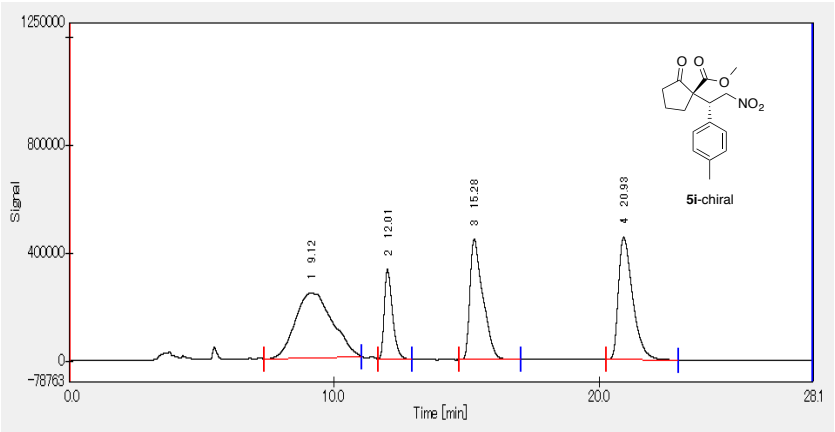
Methyl-1-(1-(4-methylphenyl)-2-nitroethyl)-2-oxocyclopentanecarboxylate (**5i**): Racemate

CHIRALCEL OD-H (*n*-hexane: 2-propanol = 90:10, flow rate = 1.0 mL/min, λ = 213 nm)



No	Rt(min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	13.46	1712345.3	12.3387	37909	2167.1	1.076	*****
2	15.87	1562807.84	11.2612	37717	3318.2	*****	0.864
3	16.94	5372488.16	38.7128	103409	2405.7	*****	4.284
4	23.68	5230171.4	37.6873	78957	2749.7	1.329	*****
		13877812.7	100	257992			

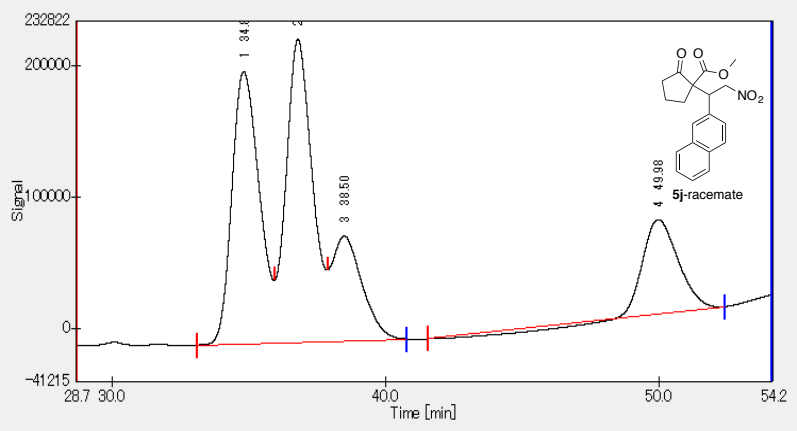
[2*R*, 3*R*]- Methyl-1-(1-(4-methylphenyl)-2-nitroethyl)-2-oxocyclopentanecarboxylate (**5i**): Chiral



No	Rt(min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	9.12	23429167	37.3033	239509	200.3	1.192	1.823
2	12.01	7139626.3	11.3675	330345	6675.4	1.507	4.254
3	15.28	15227330	24.2446	446962	4134.1	1.722	5.714
4	20.93	17011076	27.0846	453133	6677.4	1.636	*****
		62807200	100	1469949			

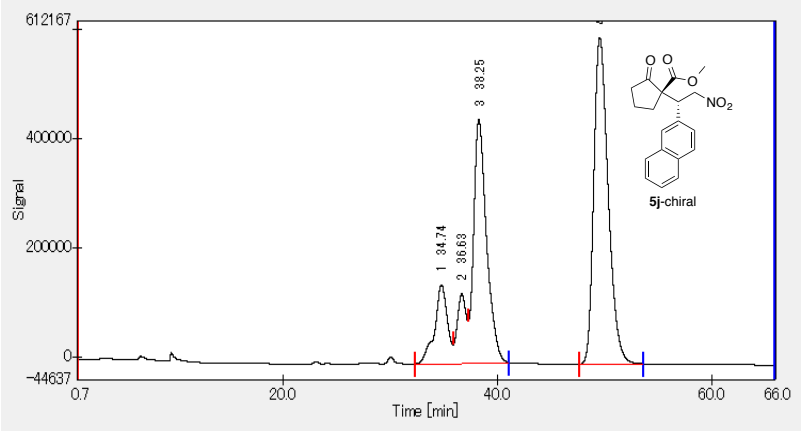
Methyl-1-(2-nitro-1-(naphthalen-2-yl)-ethyl)-2-oxocyclopentanecarboxylate (**5j**): Racemate

CHIRALCEL AS-H (*n*-hexane: 2-propanol = 90:10, flow rate 0.5 mL/min, λ = 224 nm)



No	Rt(min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	34.82	14466969.6	34.6736	206740	5601.7	*****	1.086
2	36.8	15434260.3	36.992	230057	6807	*****	0.892
3	38.5	6061327.802	14.5275	79742	5802.9	*****	5.52
4	49.98	5760714.4	13.807	71703	6546.6	1.207	*****
		41723272.1	100	588242			

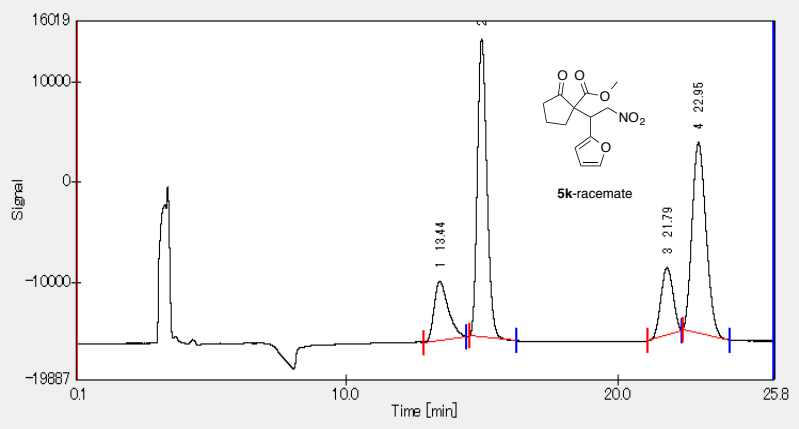
[2*R*,3*R*]-Methyl-1-(2-nitro-1-(naphthalen-2-yl)-ethyl)-2-oxocyclopentanecarboxylate (**5j**): Chiral



No	Rt(min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	34.74	12144769	10.7336	144551	3866.5	*****	0.99
2	36.63	7610389.1	6.7261	126832	8431	*****	0.847
3	38.25	37354504	33.0141	445723	4712.6	*****	4.783
4	49.54	56037305	49.5261	598026	6131.7	1.347	*****
		113146967	100	1315132			

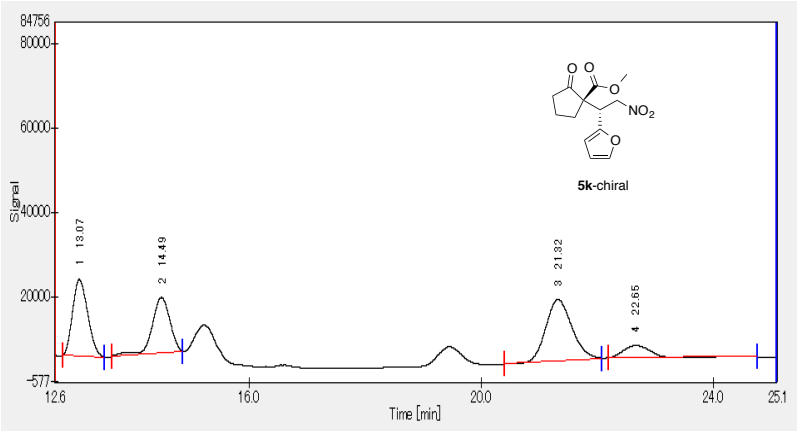
Methyl-1-((1-furan-2-yl)-2-nitroethyl)-2-oxocyclopentanecarboxylate (**5k**): Racemate

CHIRALCEL OD-H (*n*-hexane: 2-propanol = 90: 10, flow rate 1.0 mL/min, λ = 213 nm)



No	Rt(min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	13.44	213970.6	11.7589	5926	2823.3	1.497	1.857
2	14.98	722788	39.7213	29867	8488	1.207	9.332
3	21.79	207397.6	11.3977	6729	11585.2	0.991	1.31
4	22.95	675492.8	37.1221	18990	9318.9	1.195	*****
		1819649	100	61512			

[2*R*, 3*R*]-Methyl-1-((1-furan-2-yl)-2-nitroethyl)-2-oxocyclopentanecarboxylate (**5k**): Chiral



No	Rt(min)	Area	Area (%)	Height	NTP	Symmetry	Resolution
1	13.07	330075	28.7979	18168	11557.8	1.191	2.765
2	14.49	278916.8	24.3346	13110	11590.5	0.965	9.894
3	21.32	447219.9	39.0185	14444	10251.3	1.147	1.633
4	22.65	89963.7	7.849	2935	13268.5	1.127	*****
		1146175.4	100	48657			