

Supplementary Information

Development of an α' -hydroxy enone for the aminocatalytic asymmetric formal conjugate addition of aldehydes to acrylates, vinyl ketones and acrolein

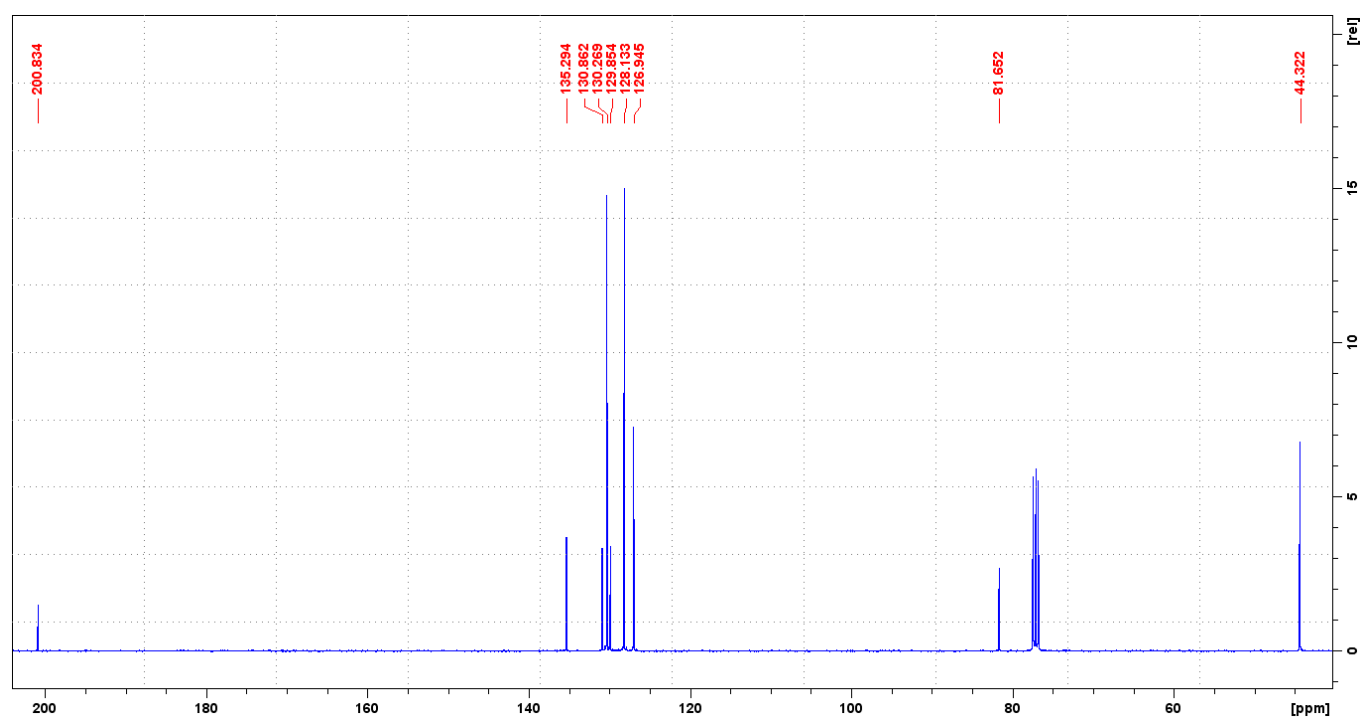
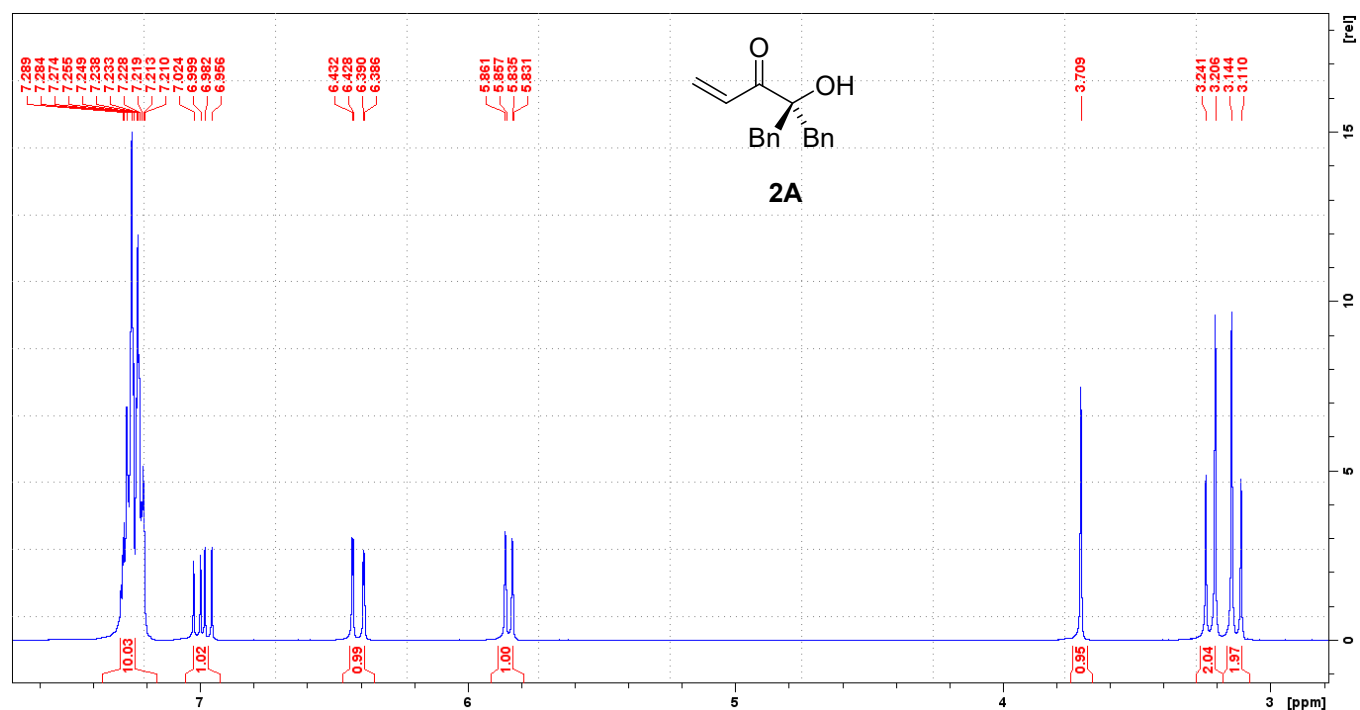
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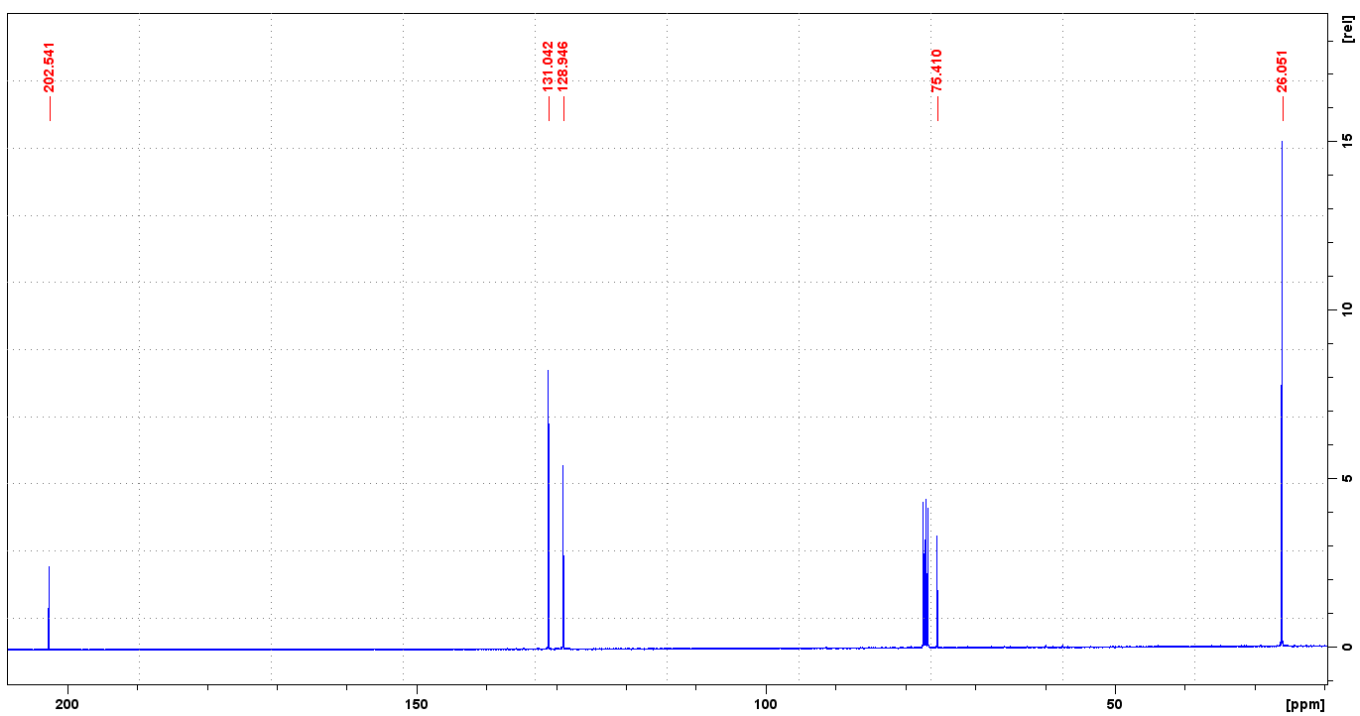
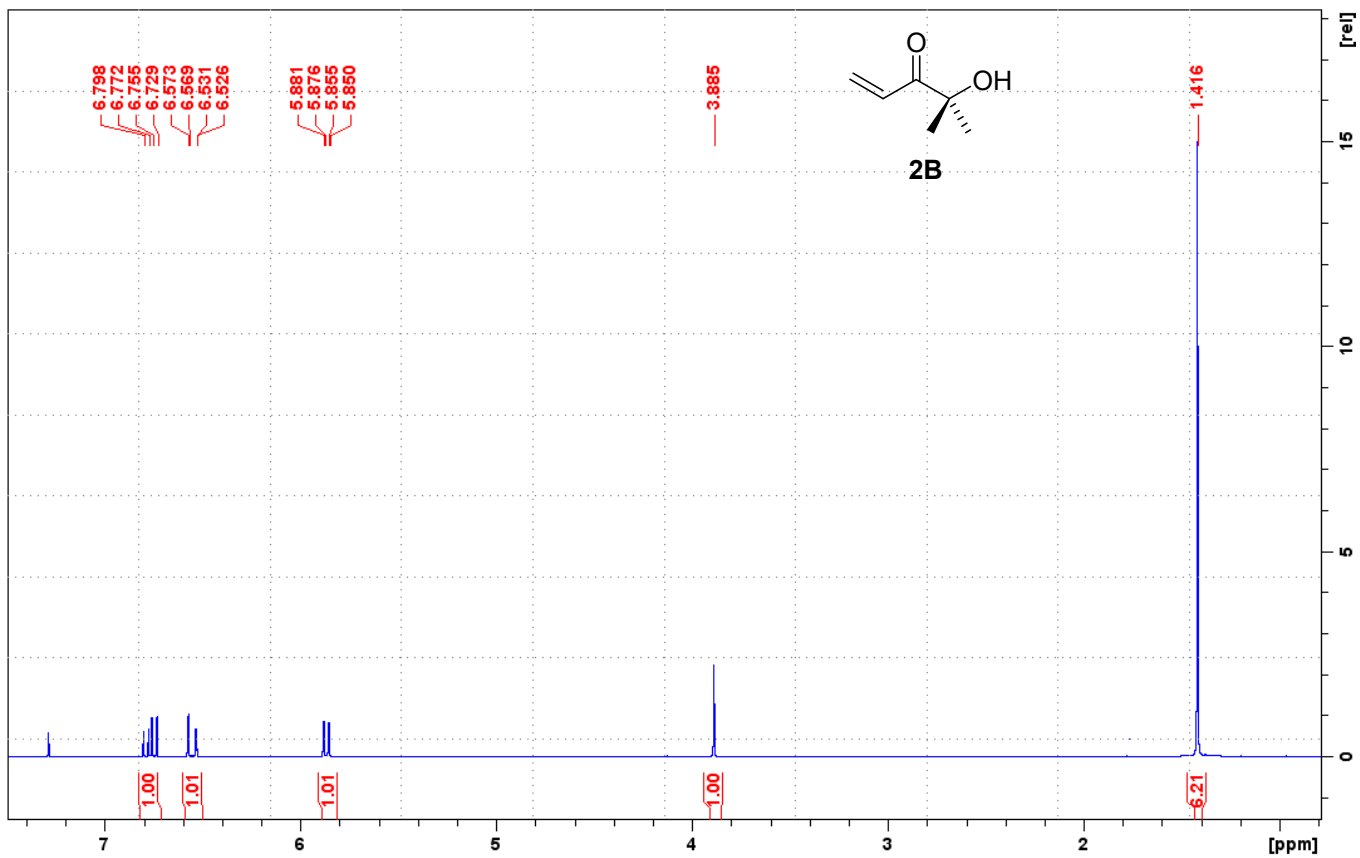
^b Departamento de Química Orgánica I. Universidad del País Vasco UPV/EHU. Manuel Lardizabal 3, 20018-San Sebastián (Spain). Fax: (+34) 943-015-270, e-mail: mikel.oiarbide@ehu.eus

¹H and ¹³C NMR spectra and HPLC analyses of products. Chromatograms correspond to both enantiomerically enriched (full-scale and inset) and racemic materials (inset)

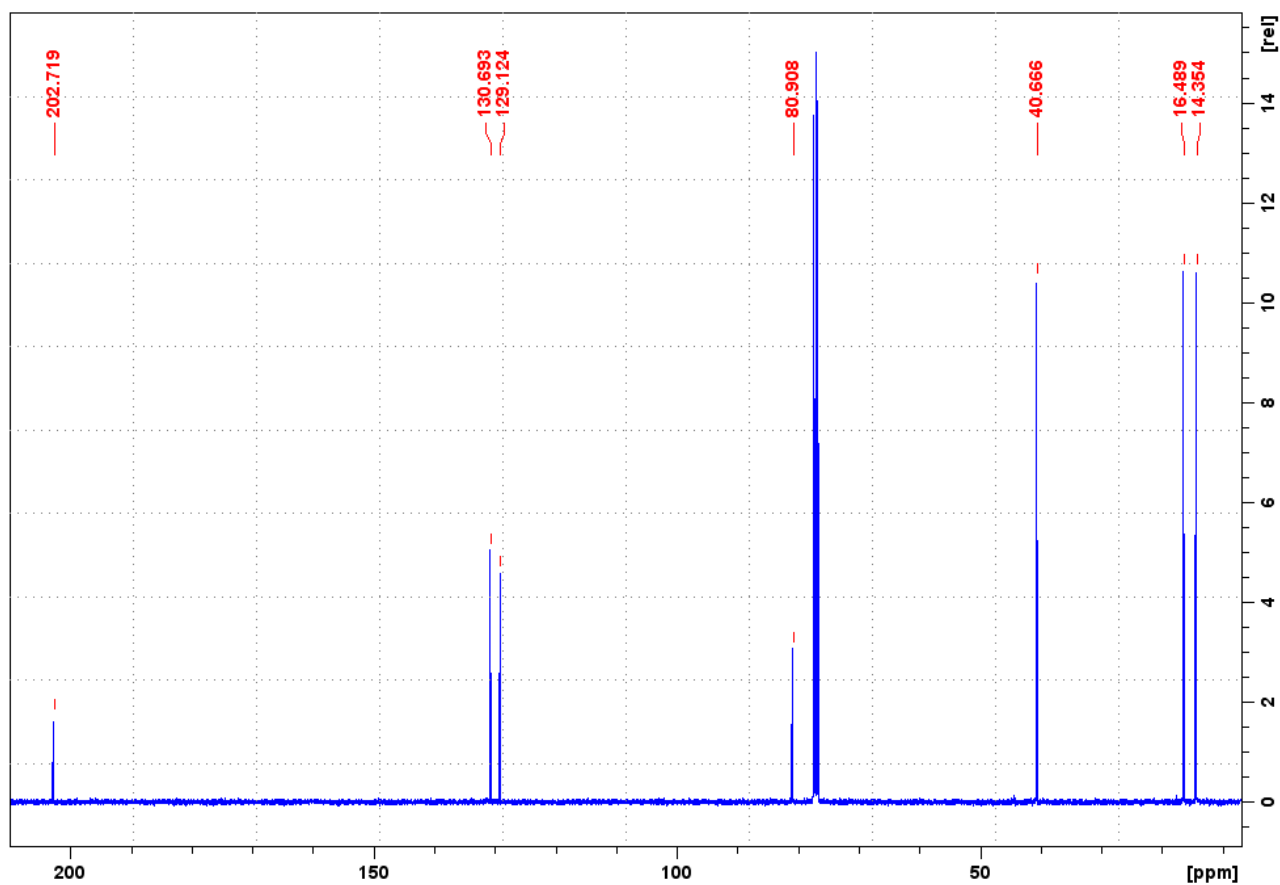
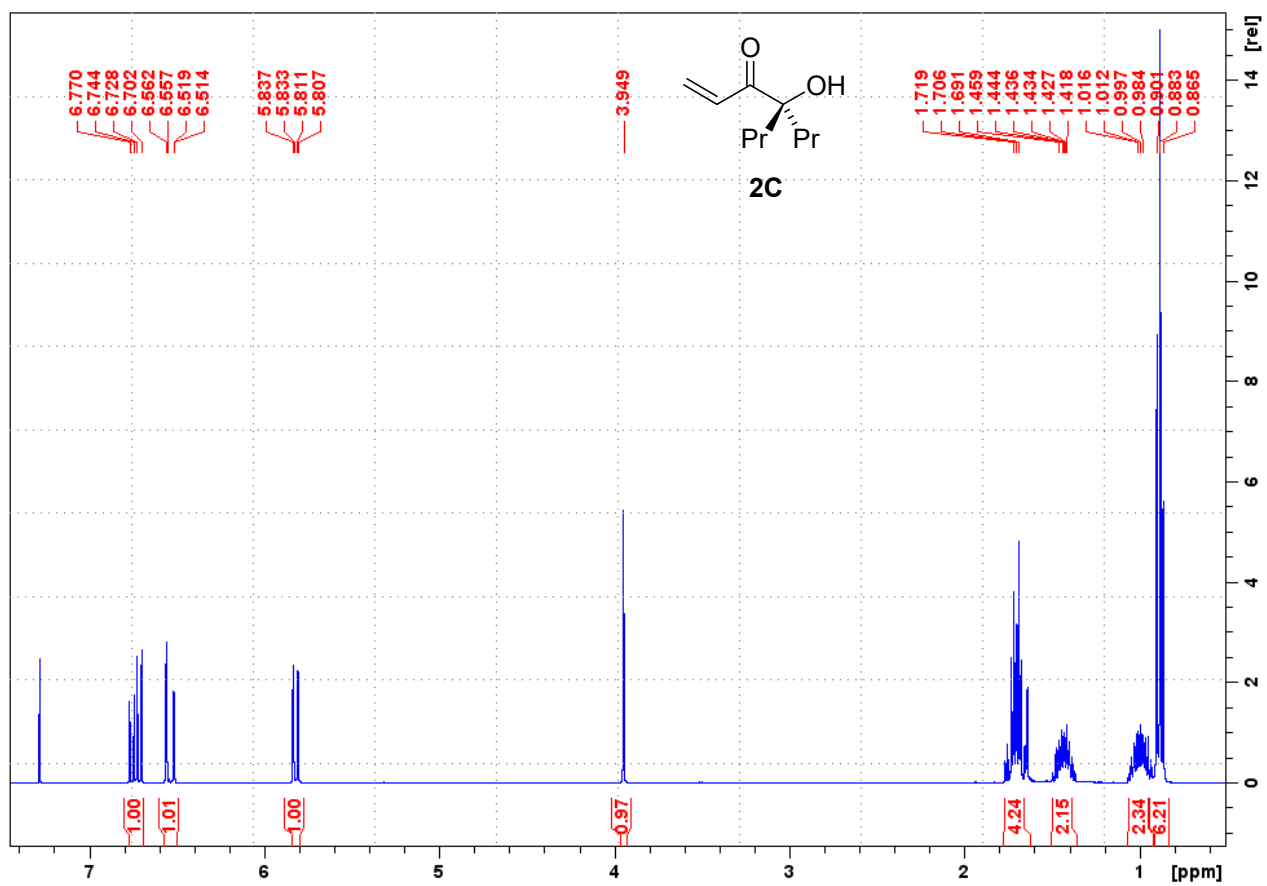
4-Benzyl-4-hydroxy-5-phenylpent-1-en-3-one (2A)



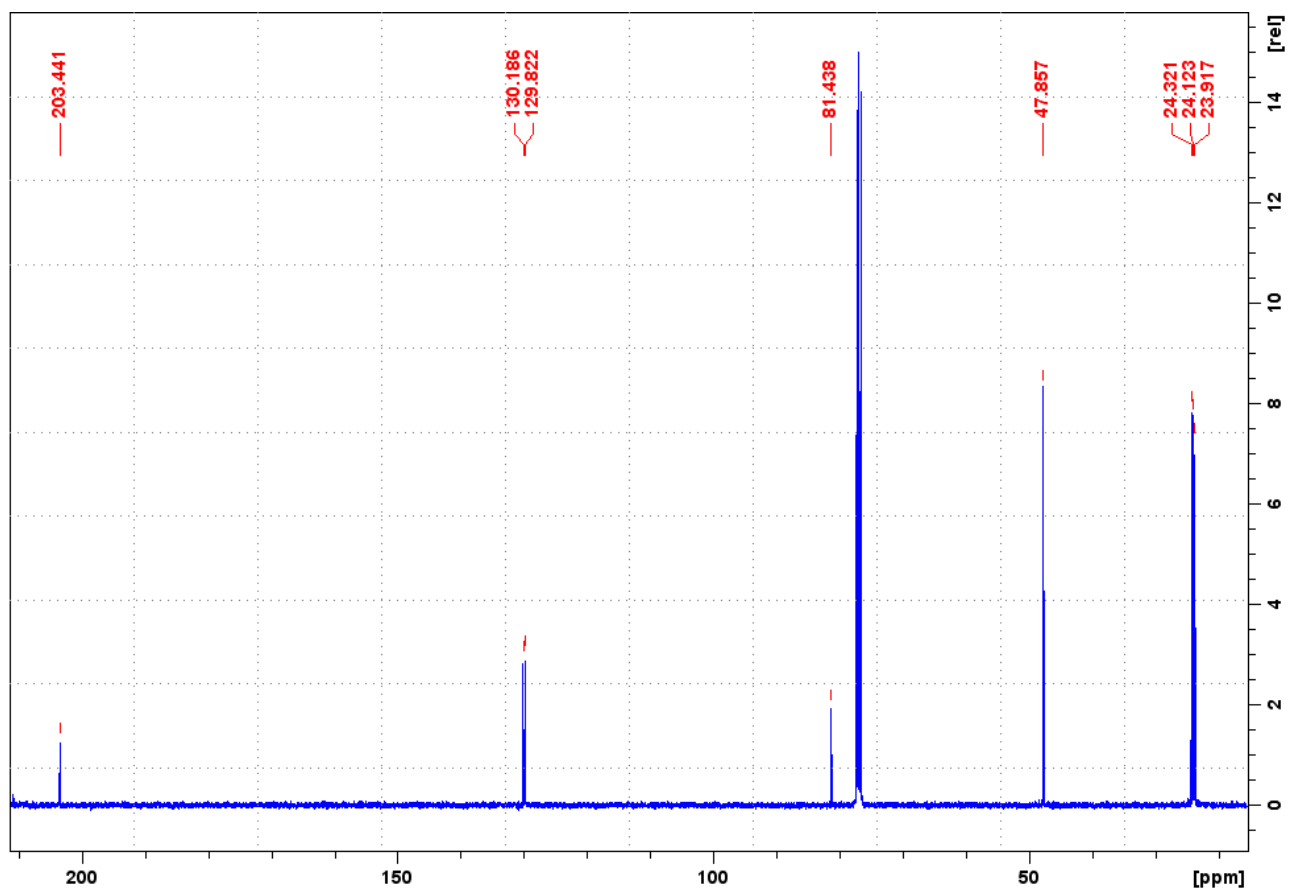
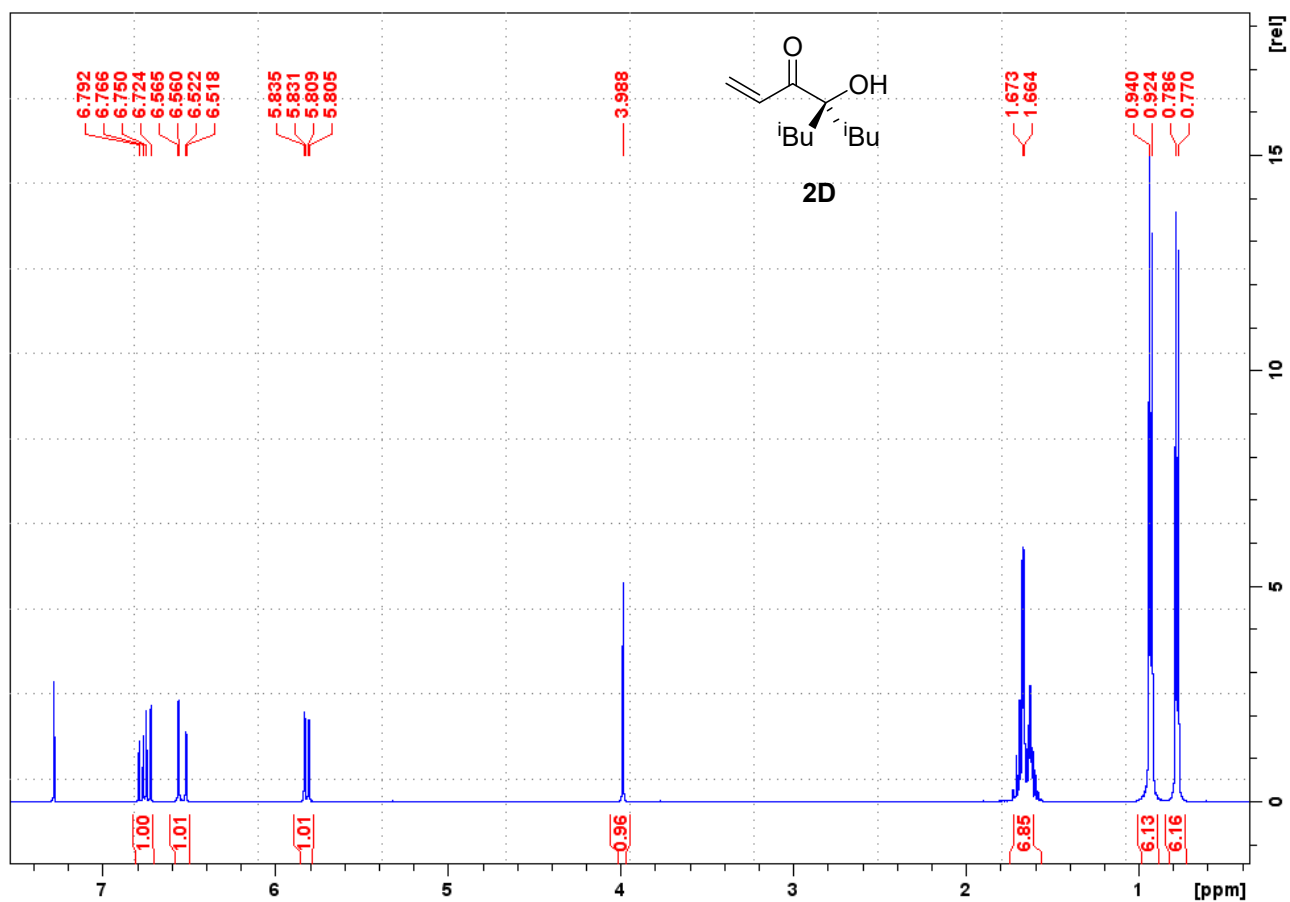
4-Hydroxy-4-methylpent-1-en-3-one (2B)



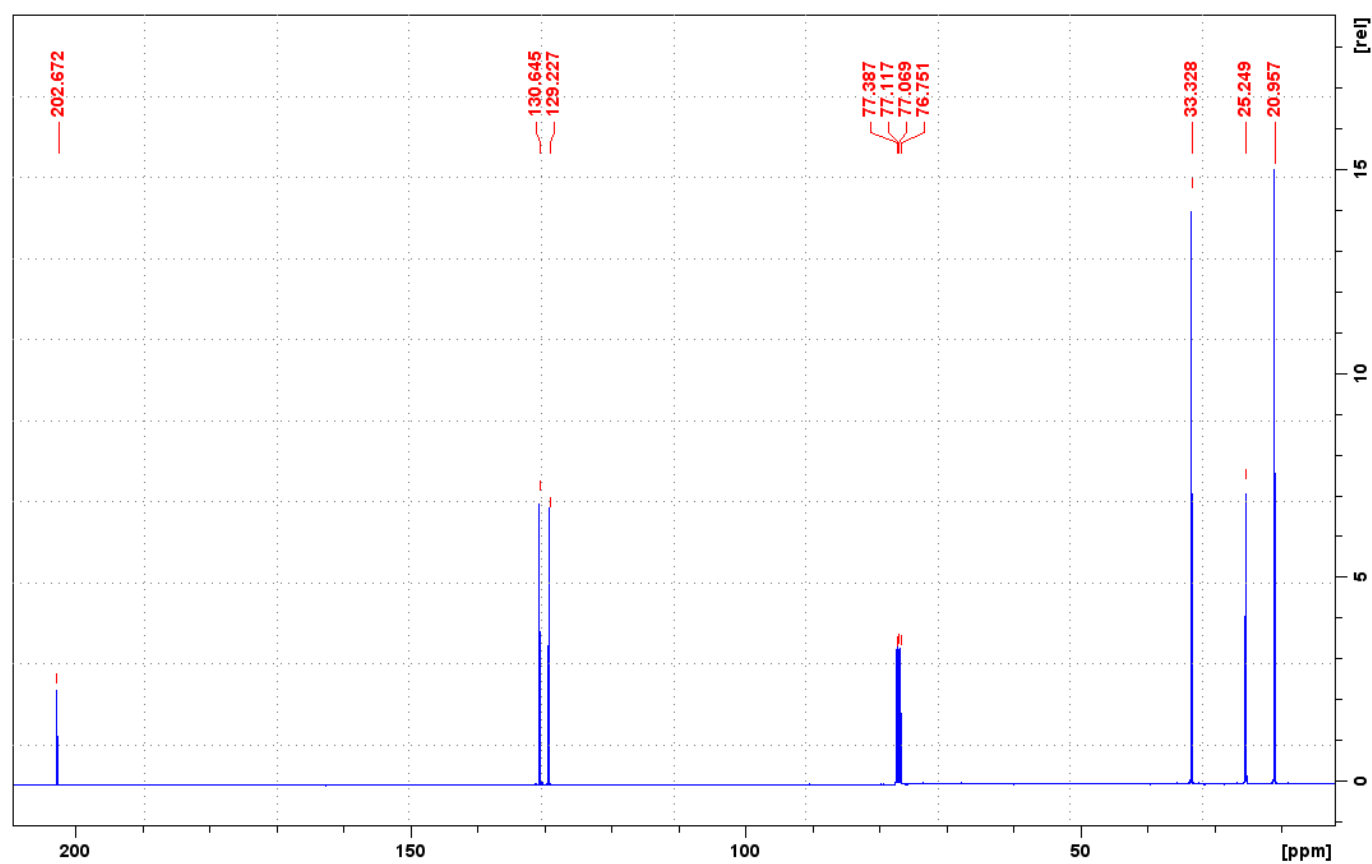
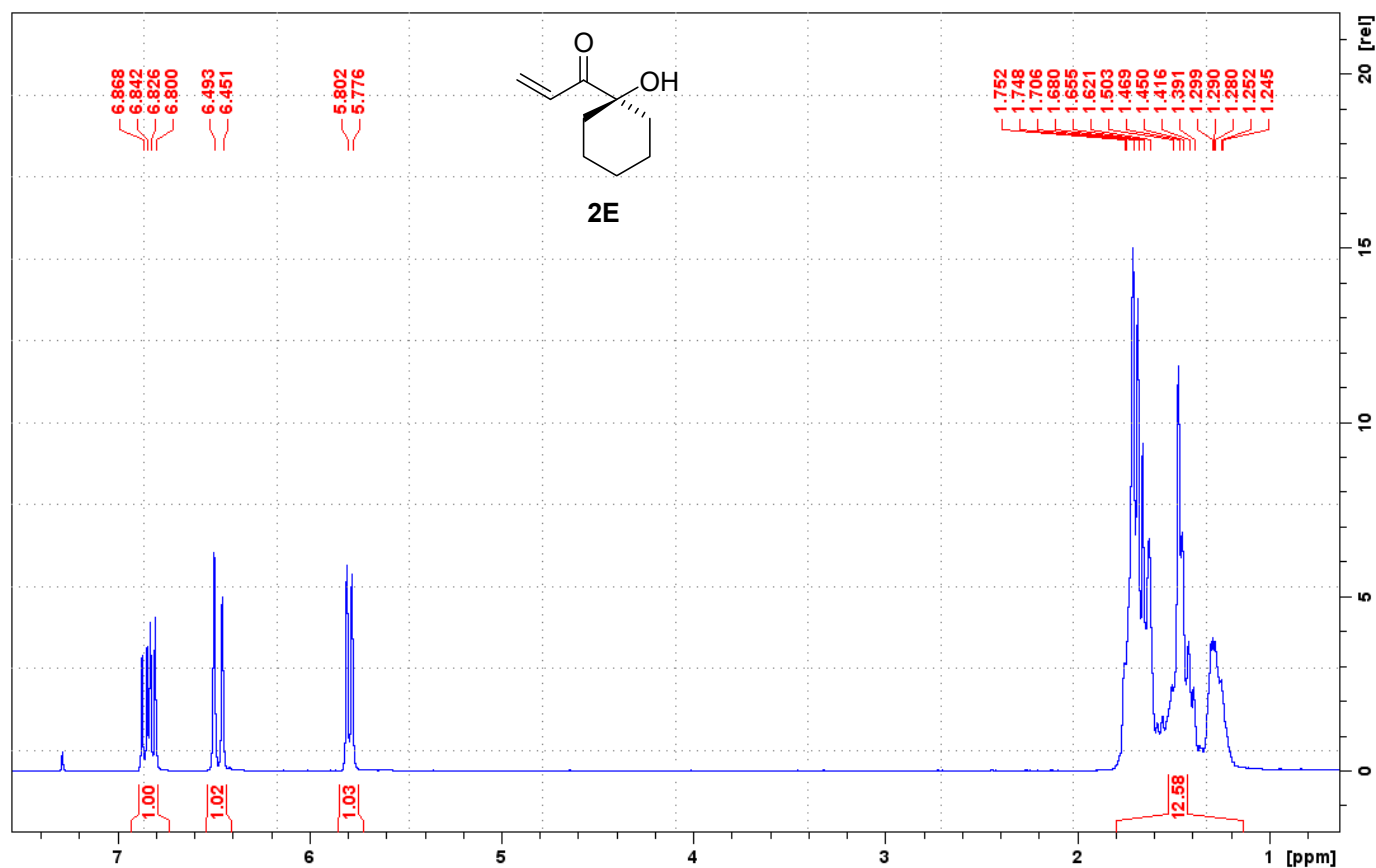
4-Hydroxy-4-propylhept-1-en-3-one (2C)



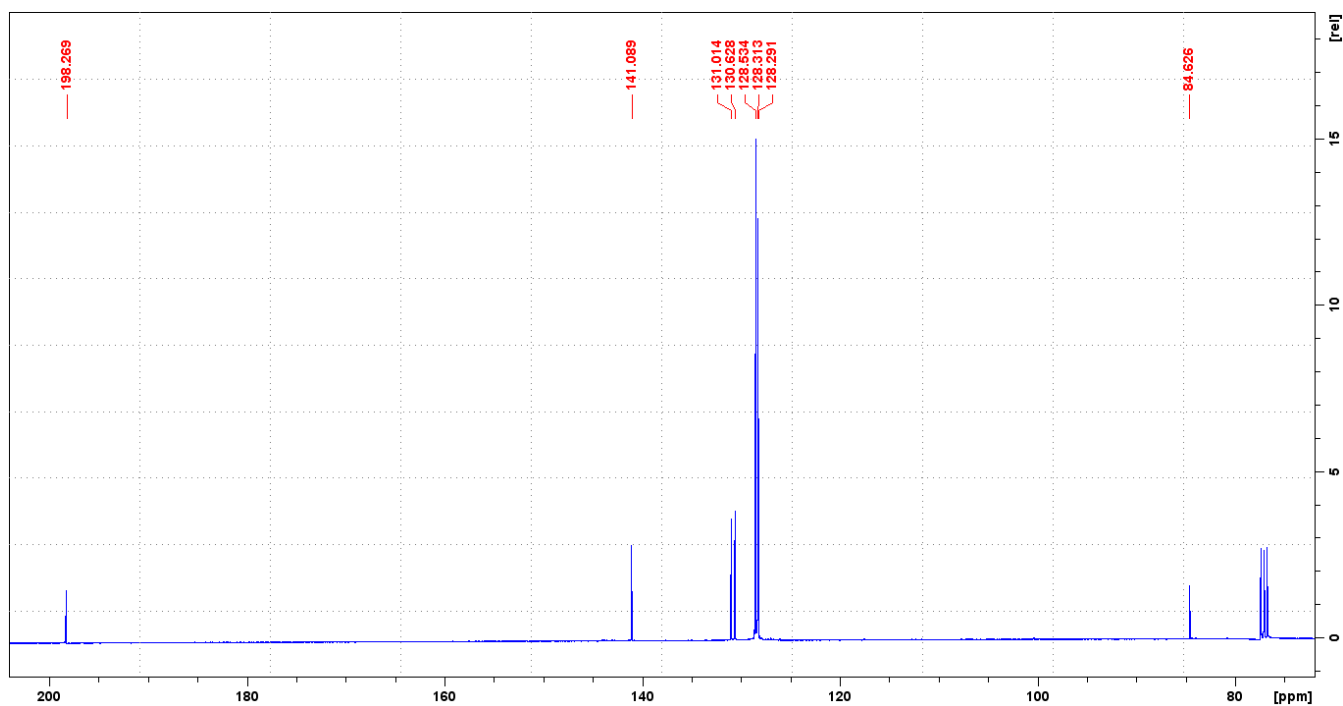
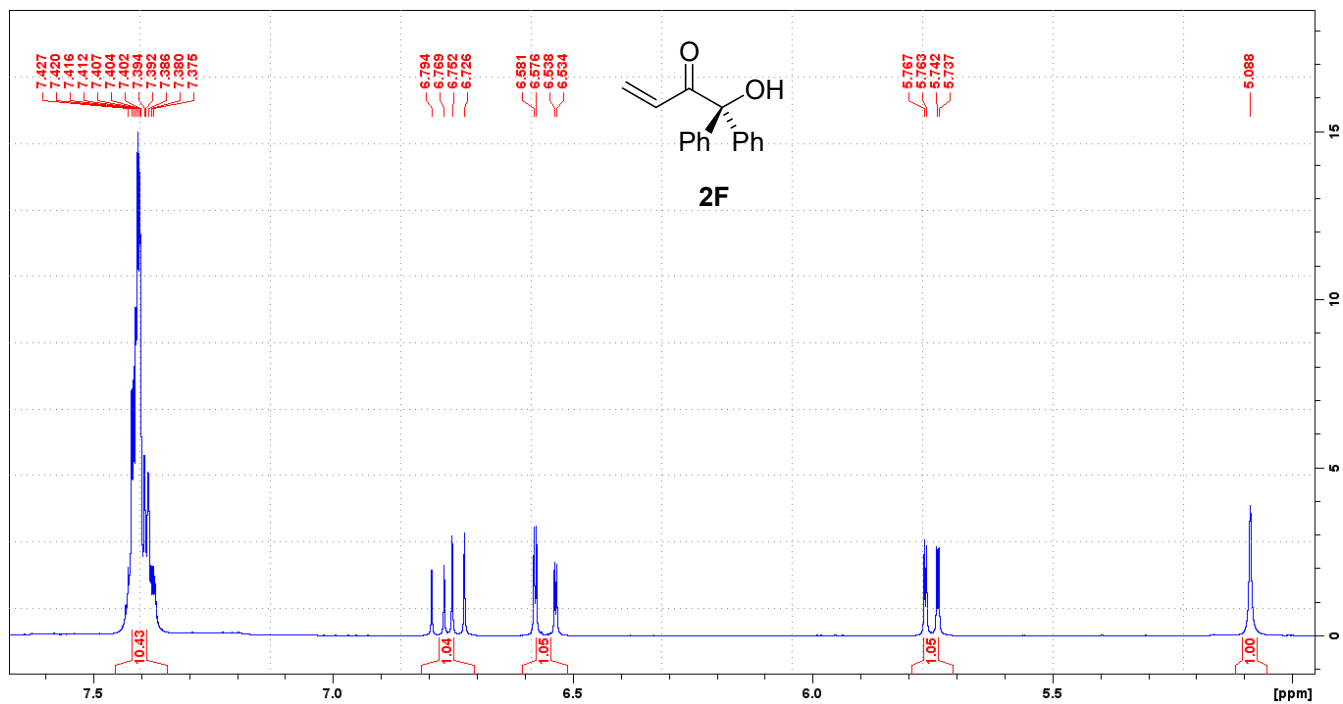
4-Hydroxy-4-isobutyl-6-methylhept-1-en-3-one (2D)



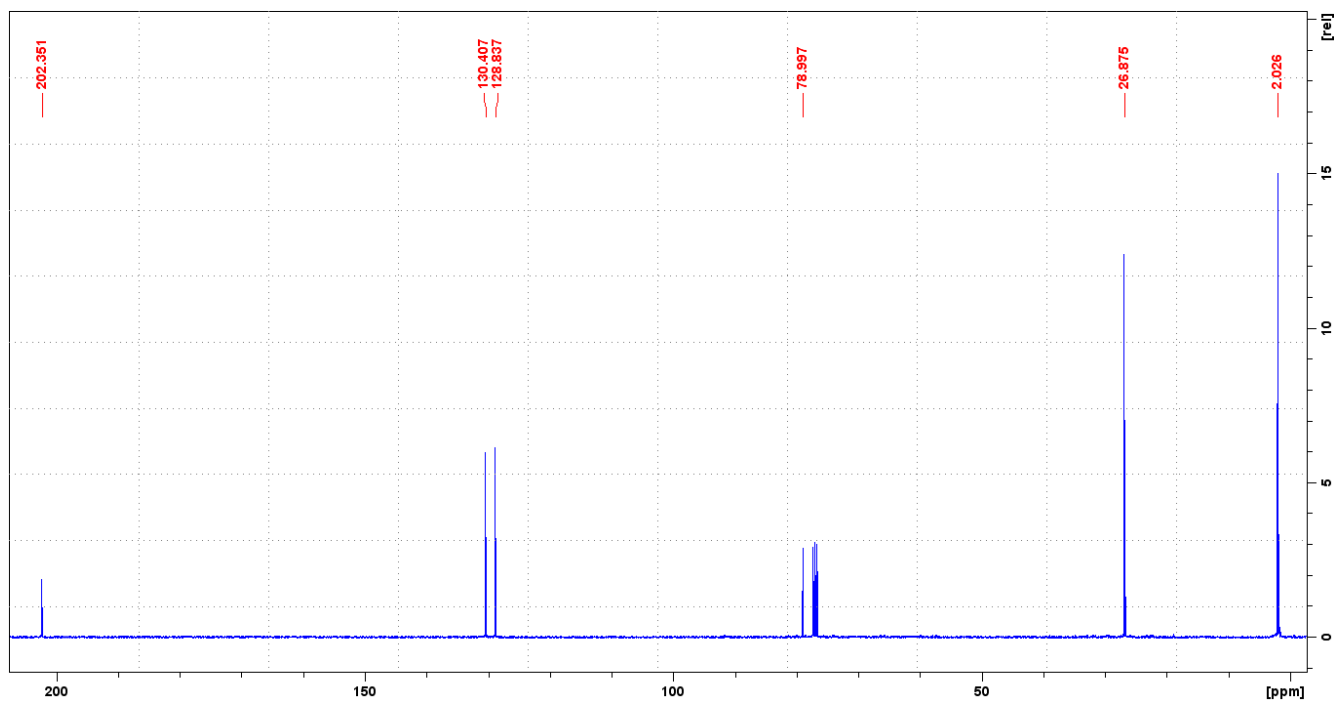
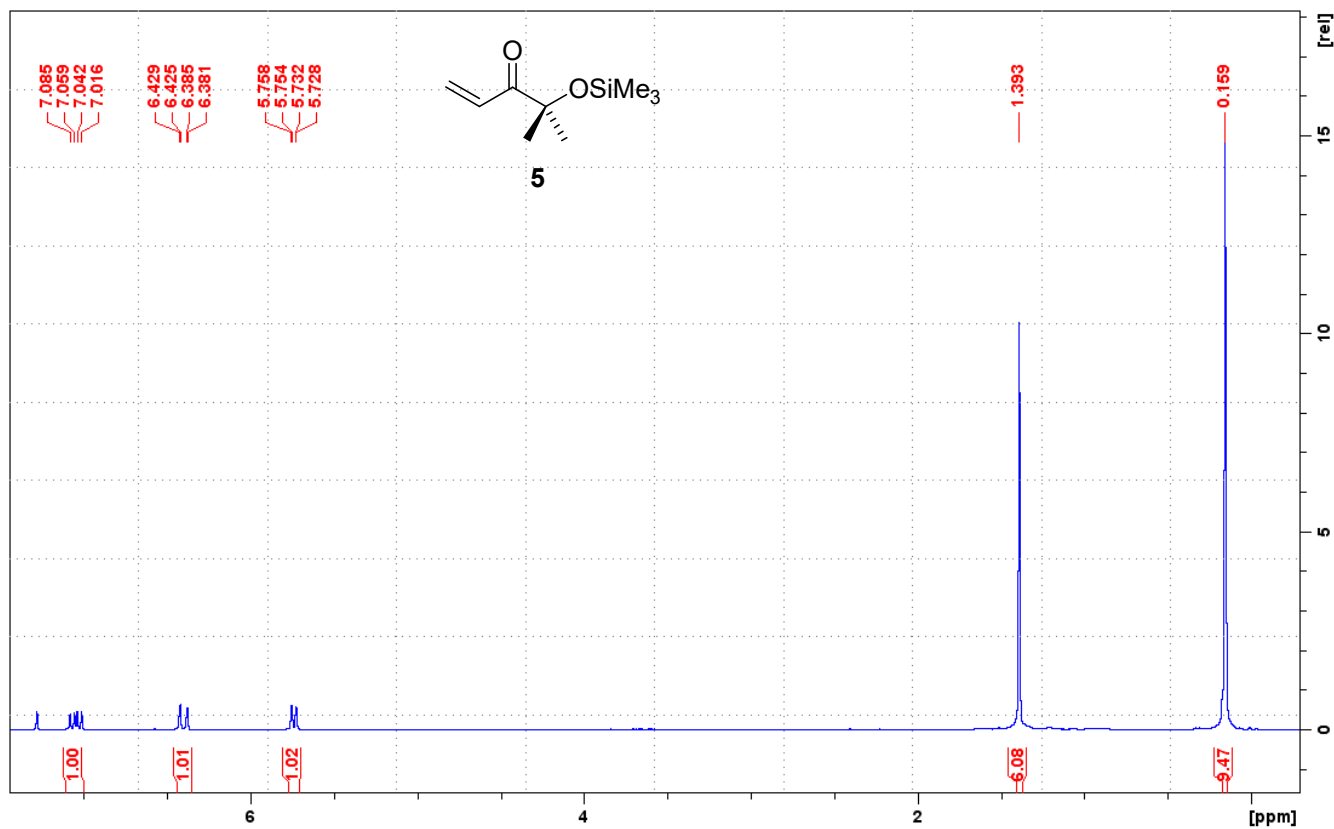
1-(1-Hydroxycyclohexyl)prop-2-en-1-one (2E)



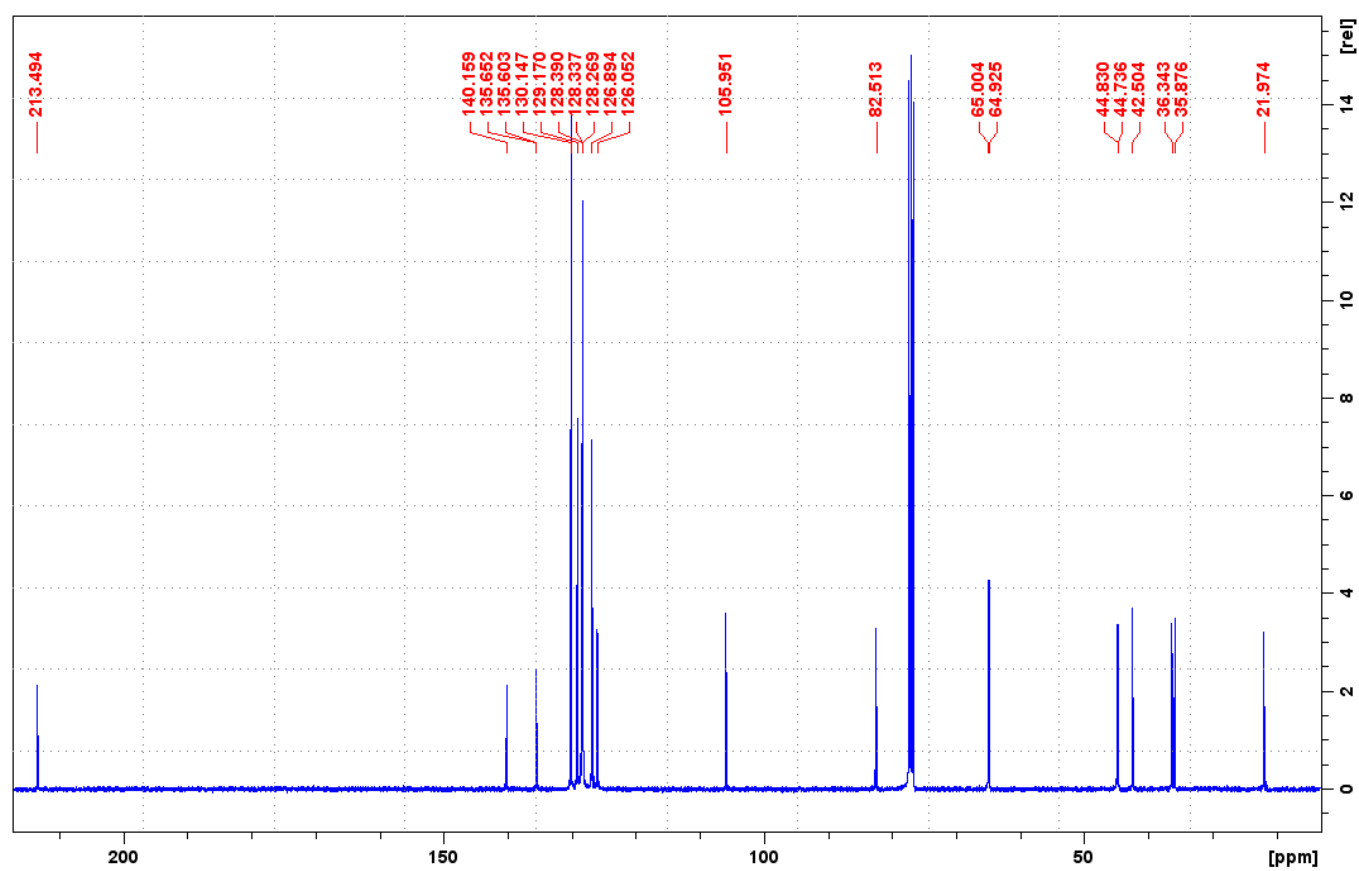
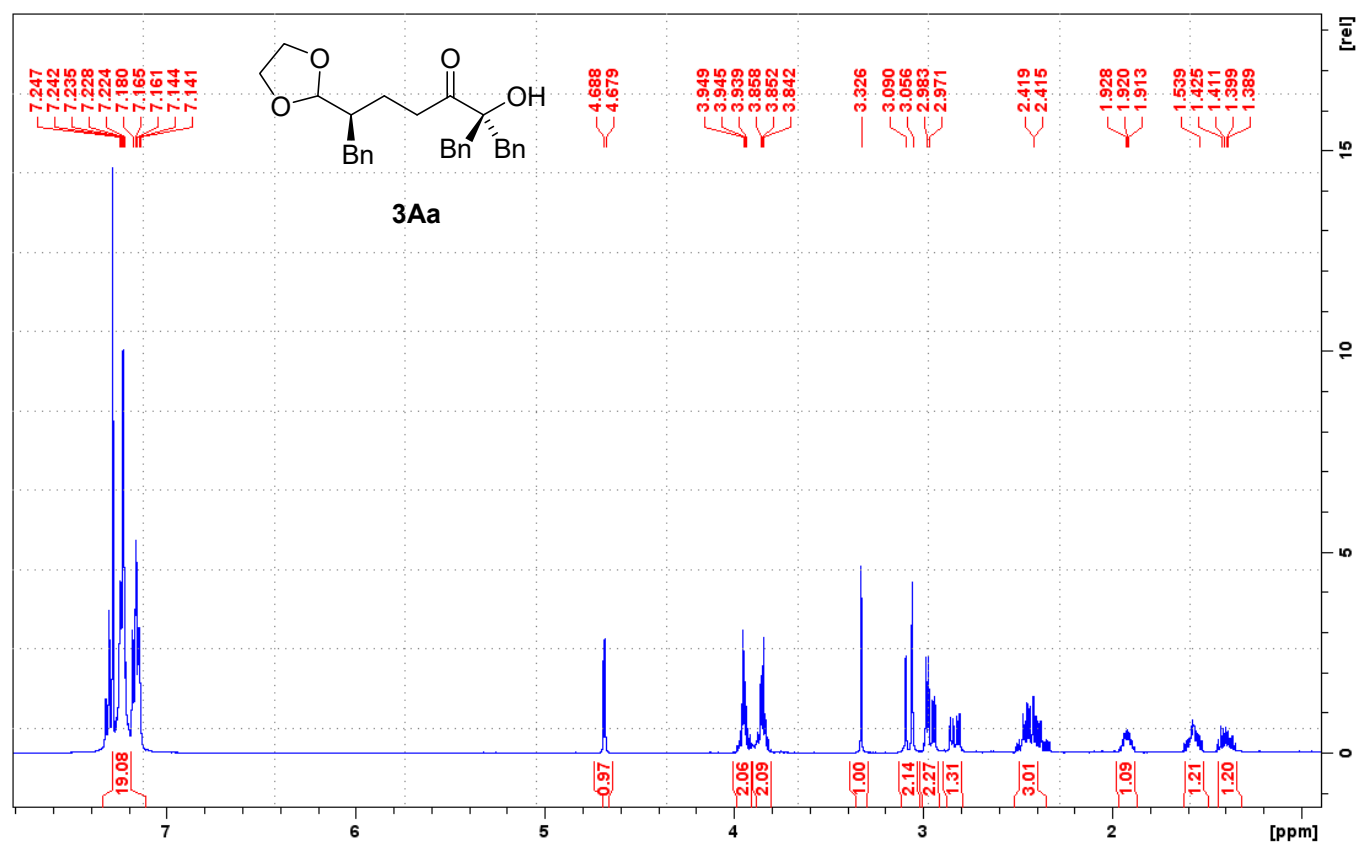
1-Hydroxy-1,1-diphenylbut-3-en-2-one (2F)

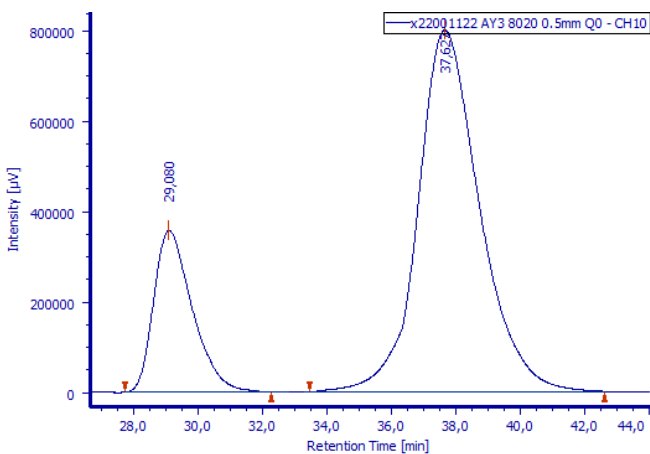
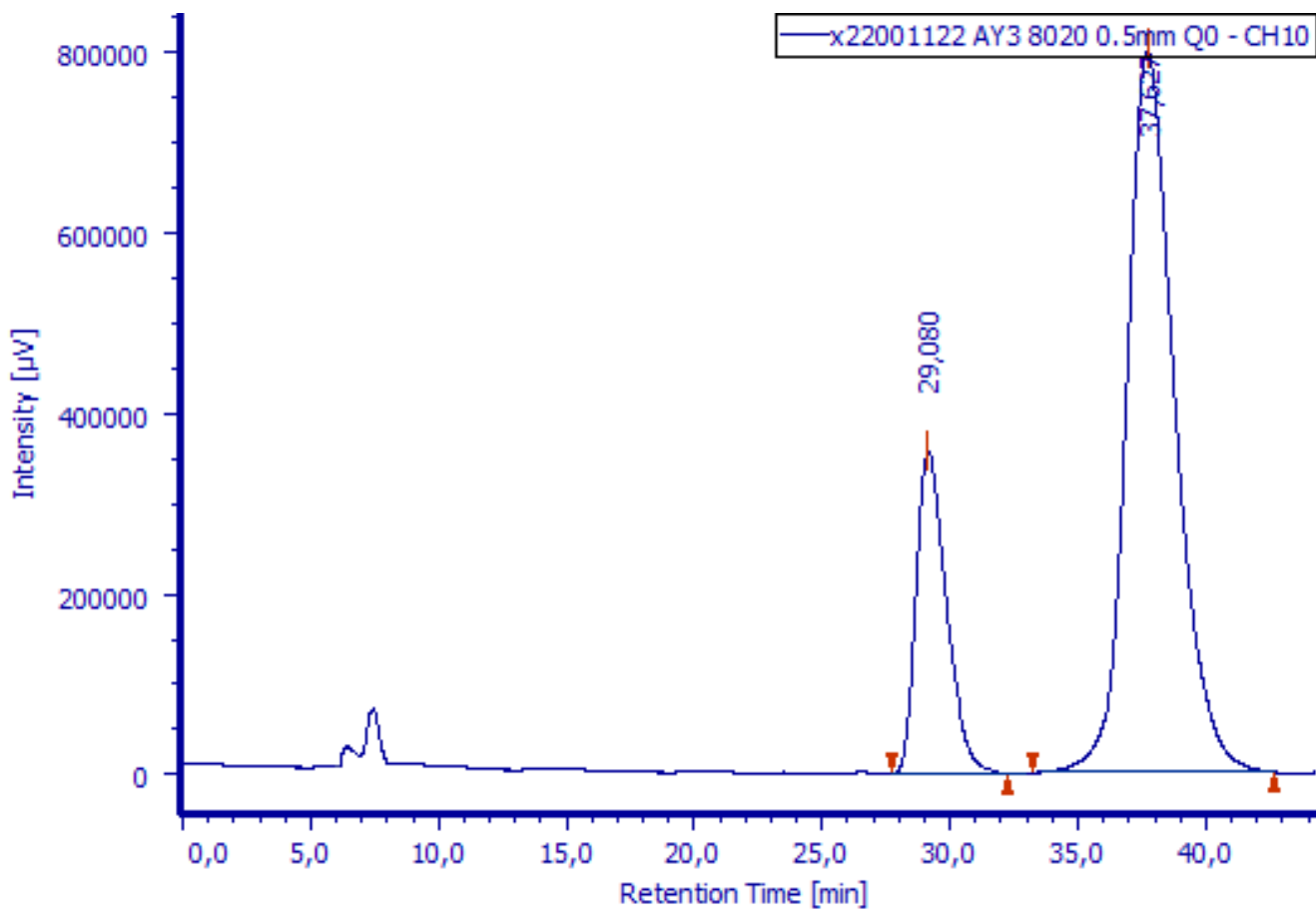


4-methyl-4-((trimethylsilyl)oxy)pent-1-en-3-one (5)

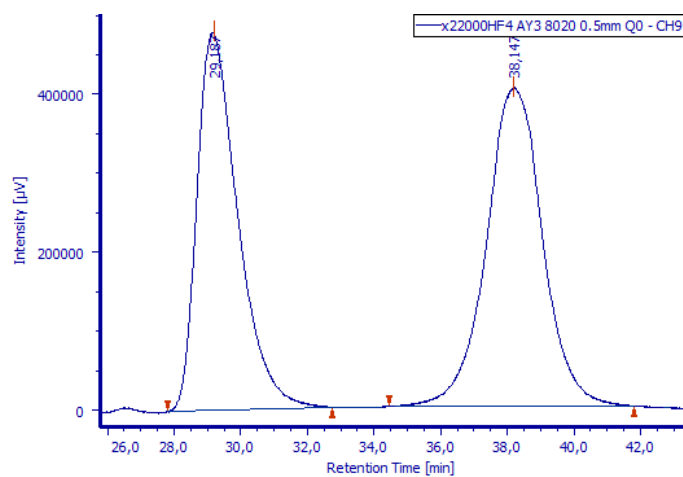


(S)-2-benzyl-6-(1,3-dioxolan-2-yl)-2-hydroxy-1,7-diphenylheptan-3-one (3Aa)



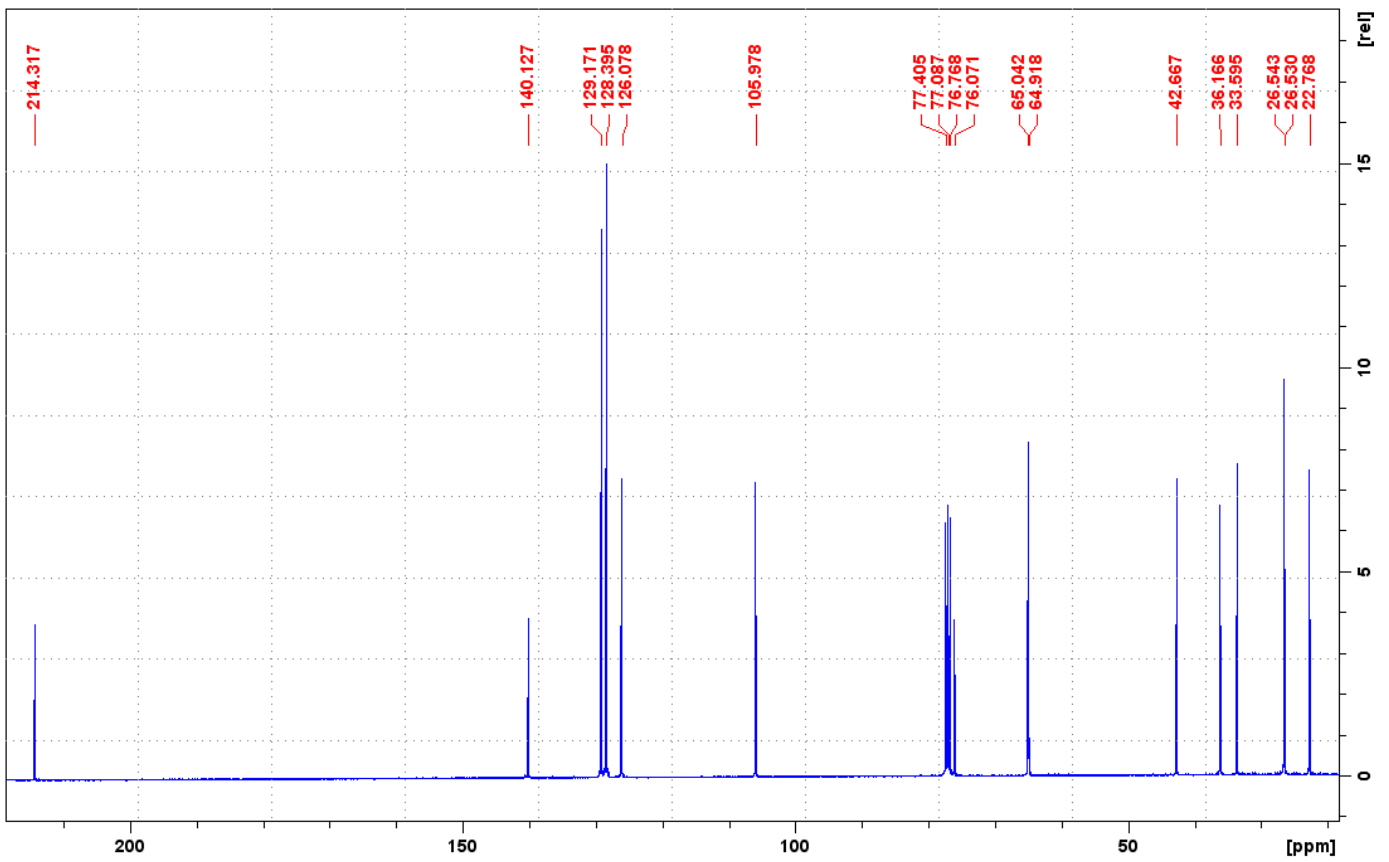
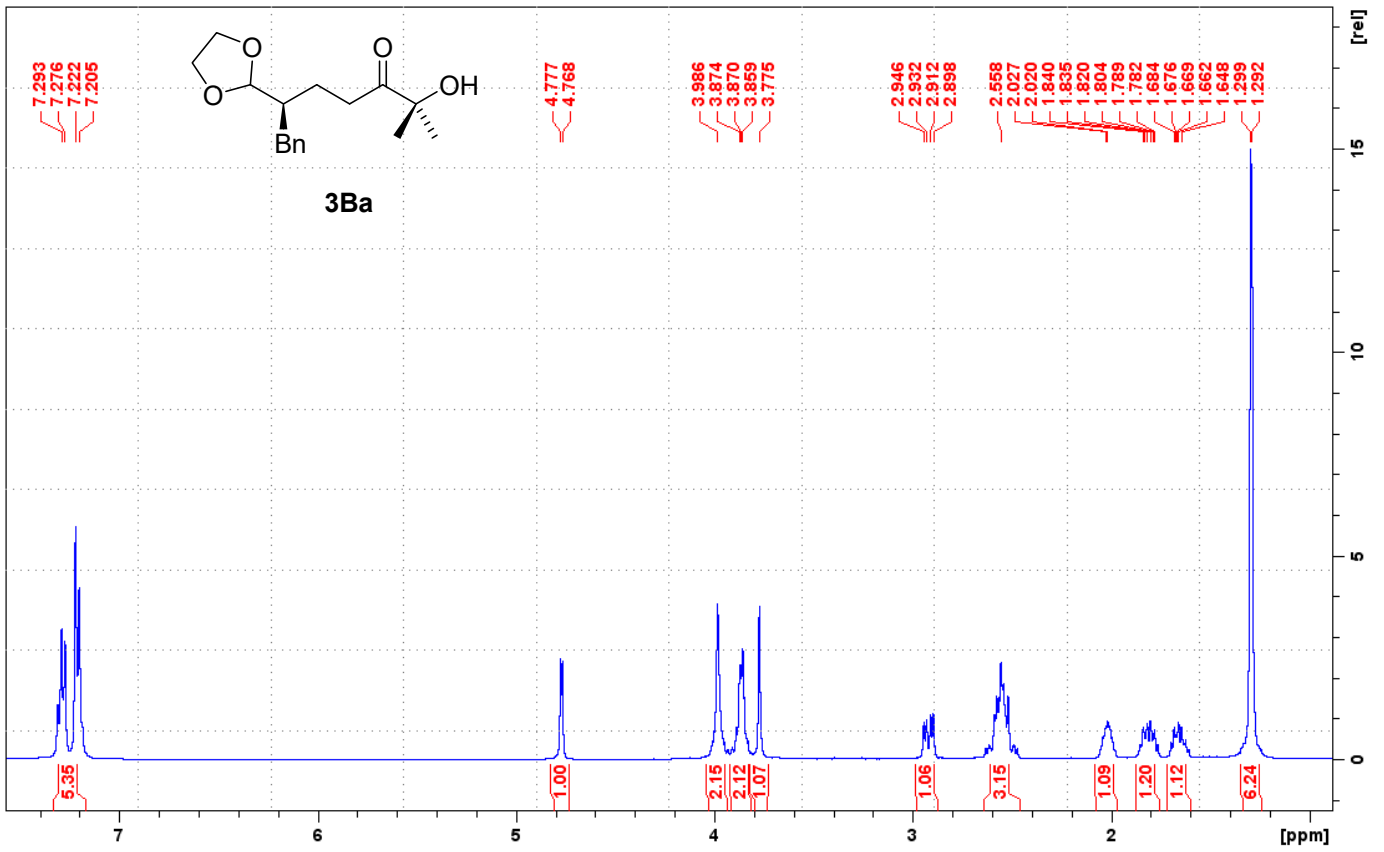


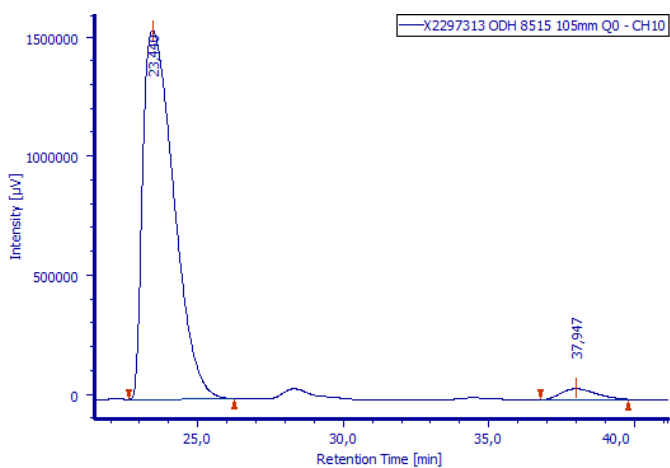
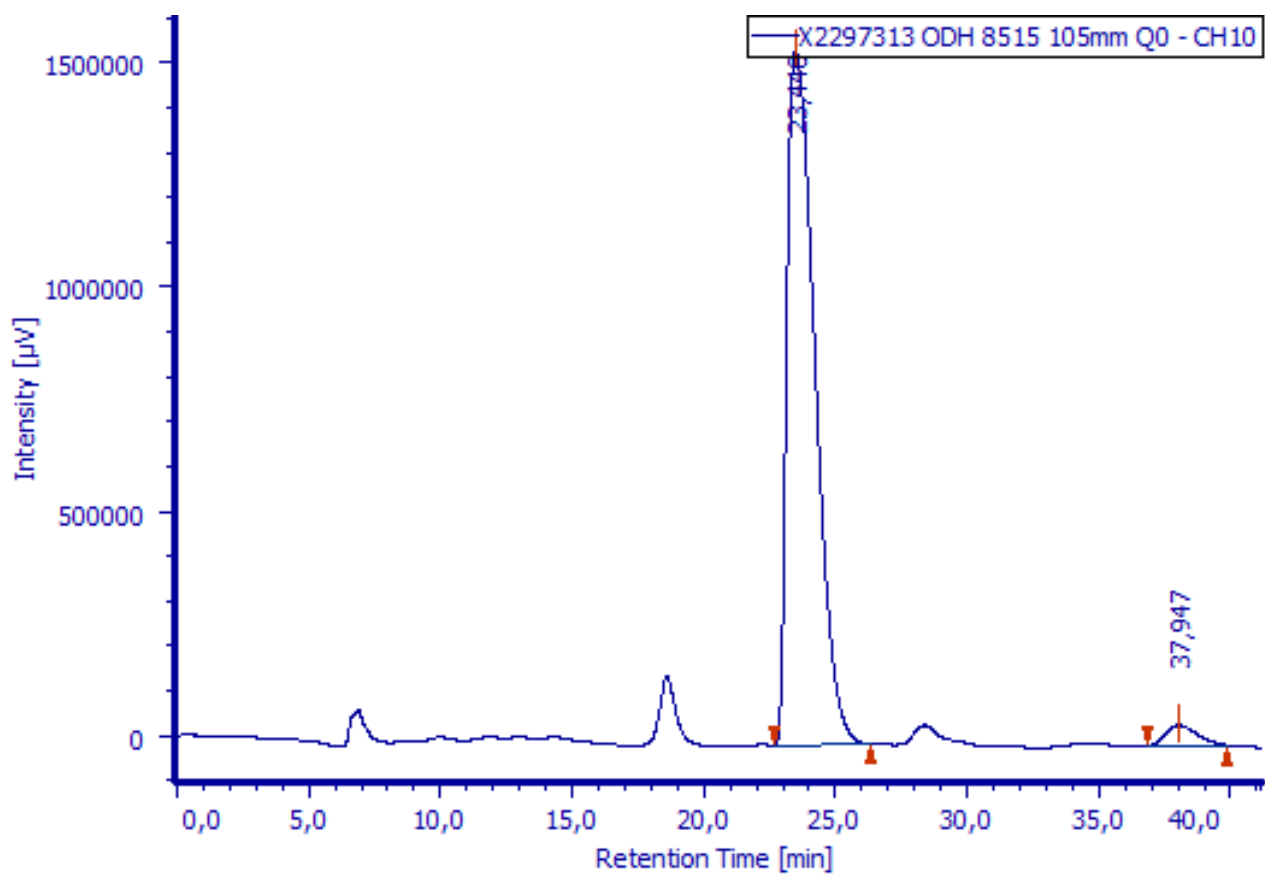
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37,627	104216673	796745	78,216	69,097



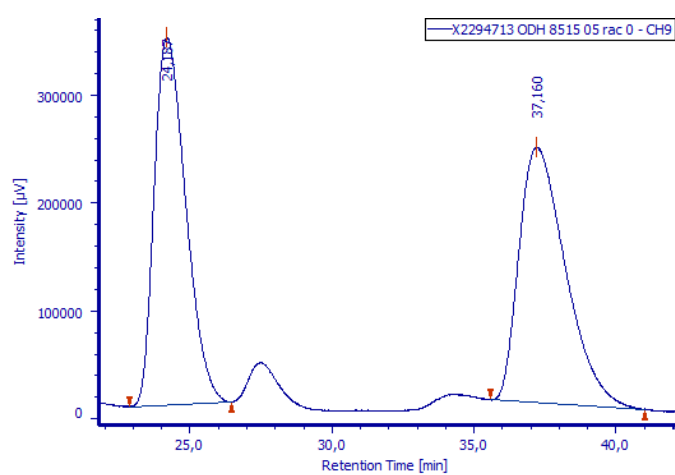
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29,187	40396853	476539	47,724	55,964
38,147	44249310	374966	52,276	44,036

(S)-6-(1,3-dioxolan-2-yl)-2-hydroxy-2-methyl-7-phenylheptan-3-one (3Ba)



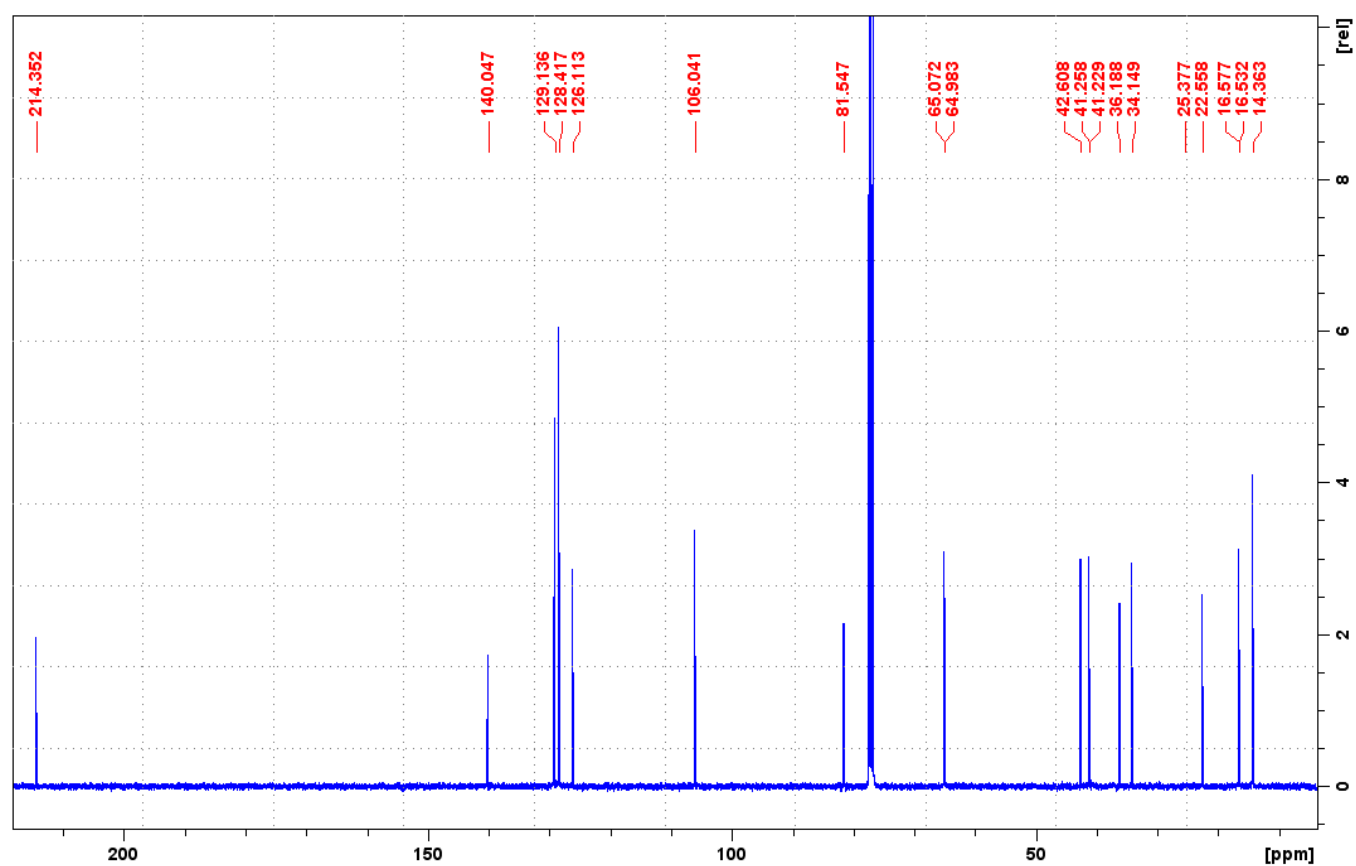
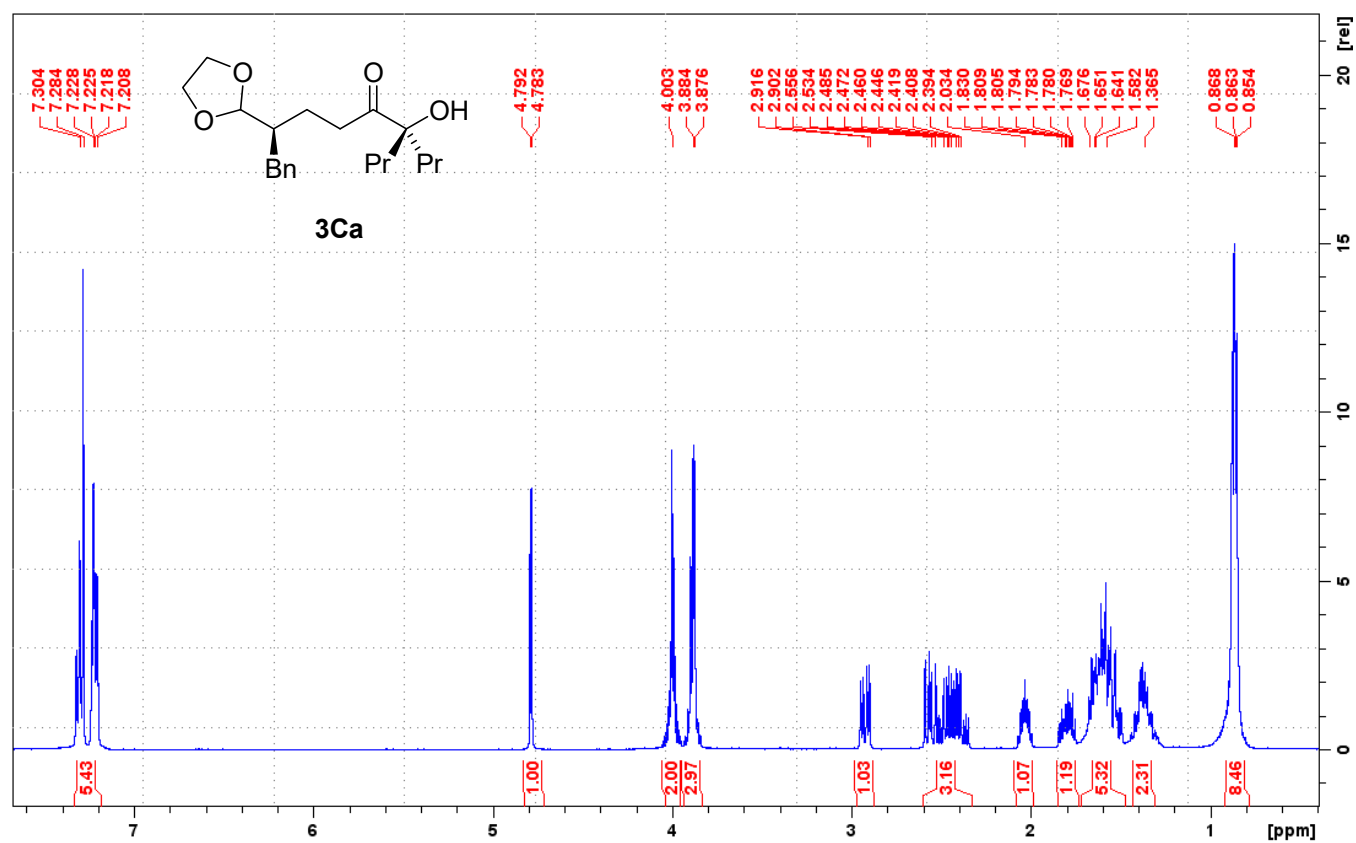


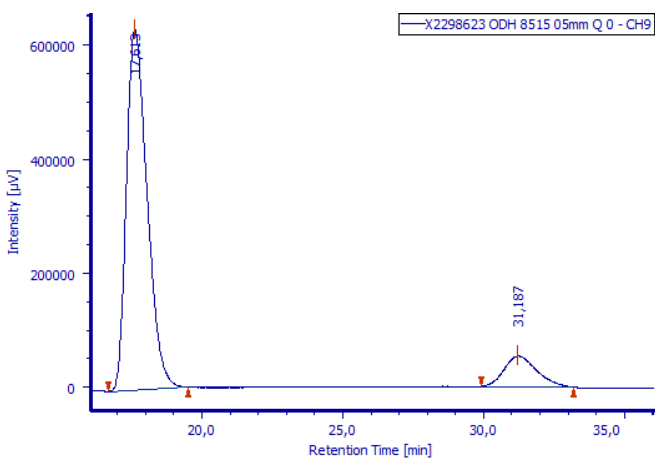
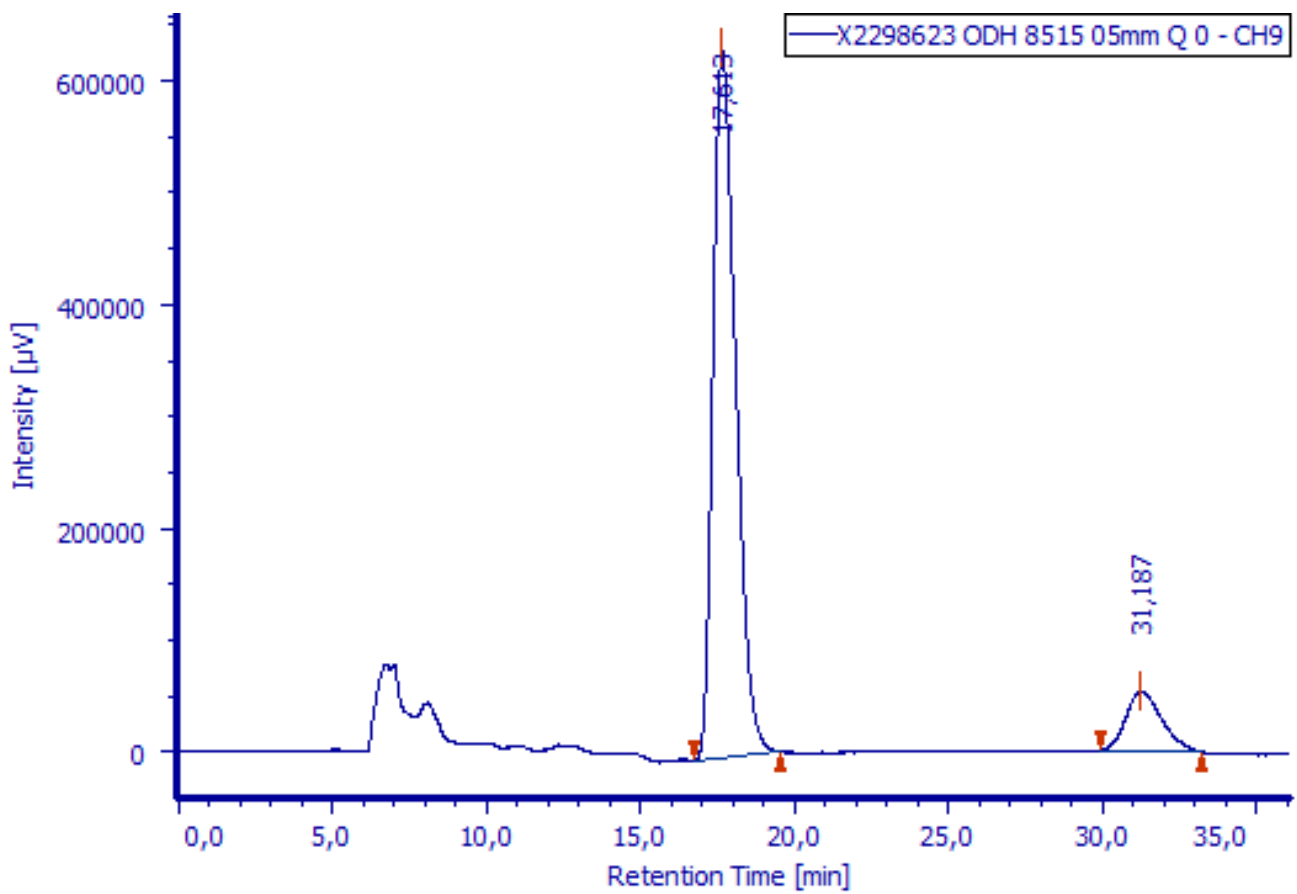
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23,440	113708897	1542742	96,725	97,104
37,947	3850552	46014	3,275	2,896



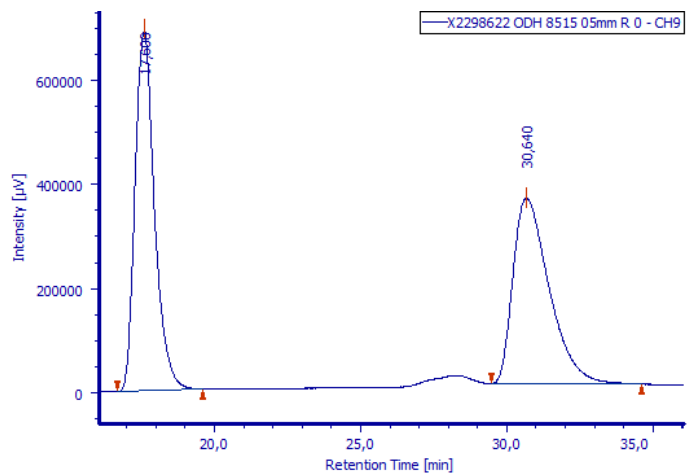
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24,187	26139182	339572	49,330	59,027
37,160	26849314	235706	50,670	40,973

(S)-2-(1,3-dioxolan-2-yl)-6-hydroxy-1-phenyl-6-propylnonan-5-one (3Ca)



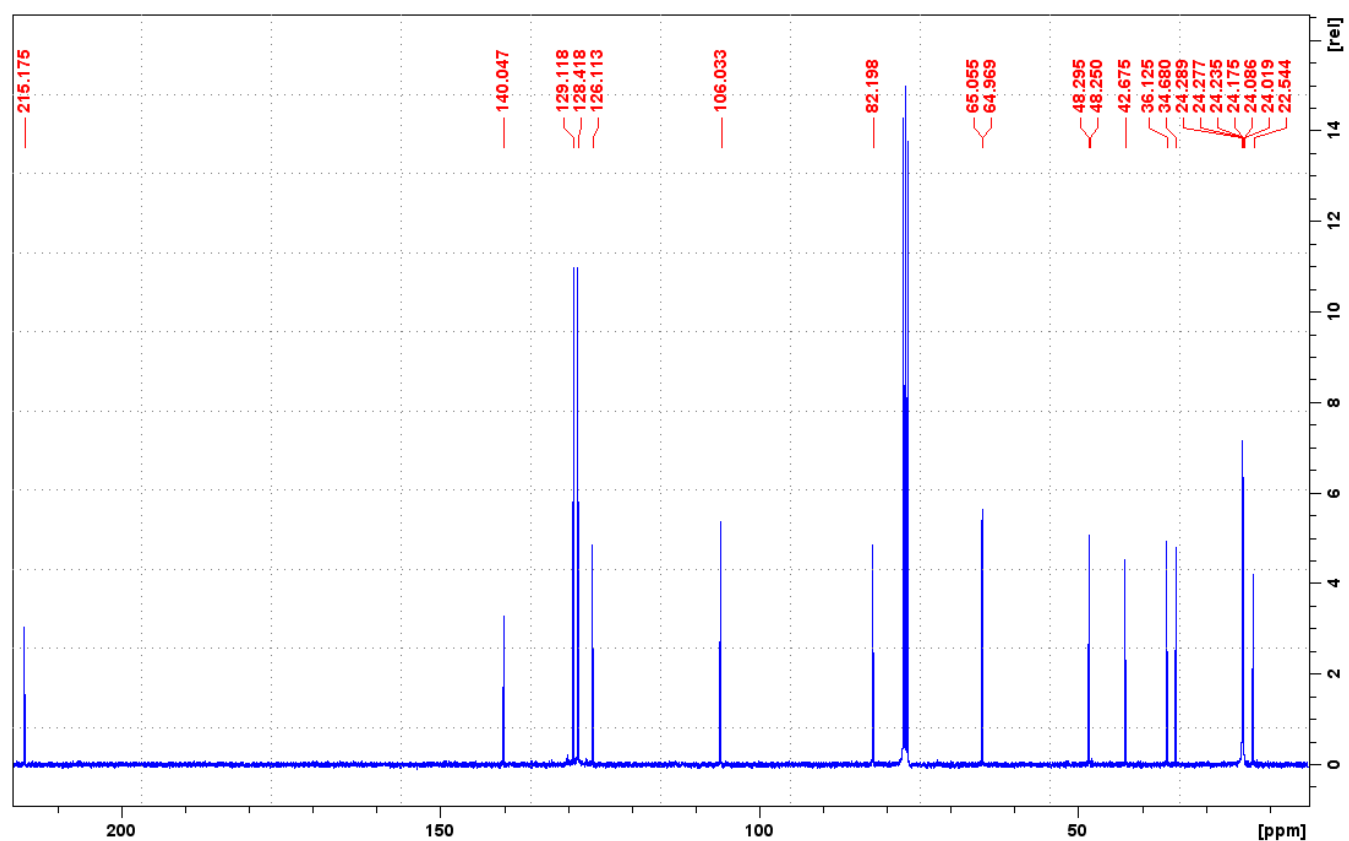
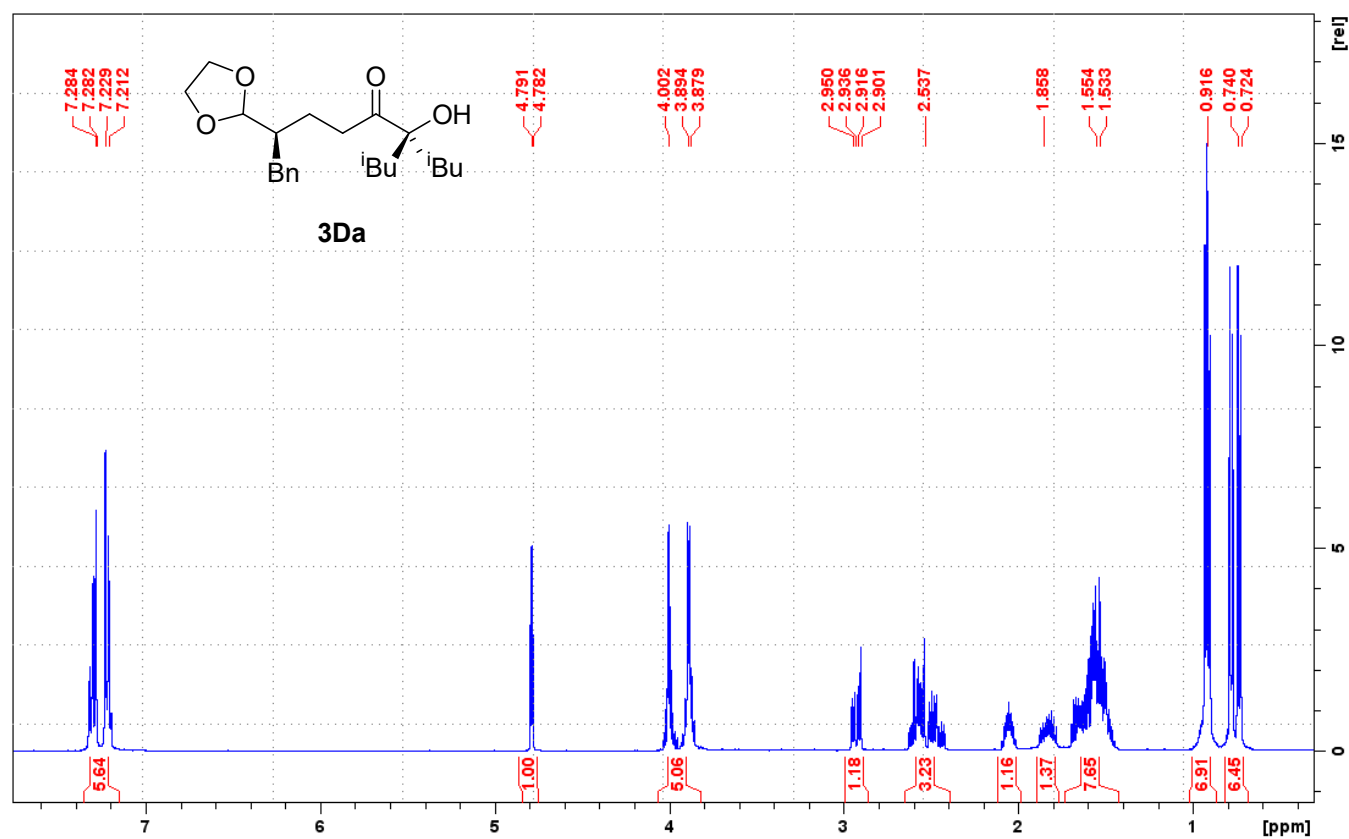


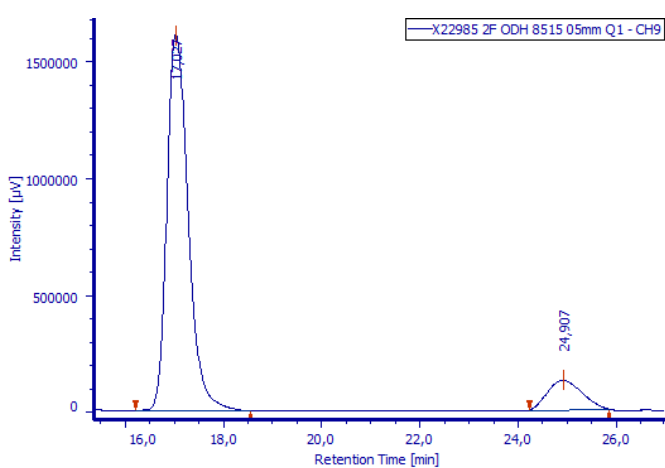
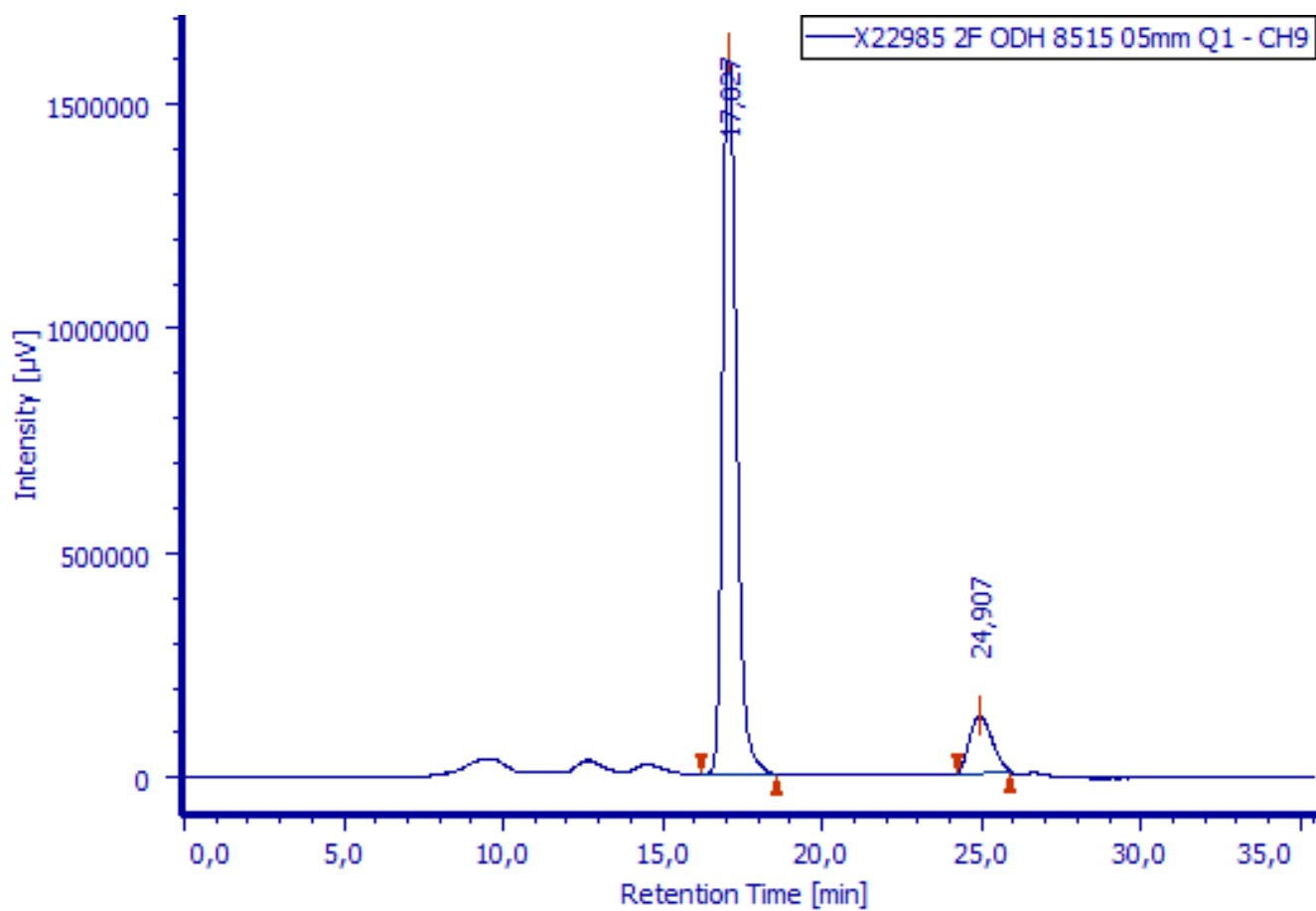
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31,187	4341126	53547	11,923	7,828



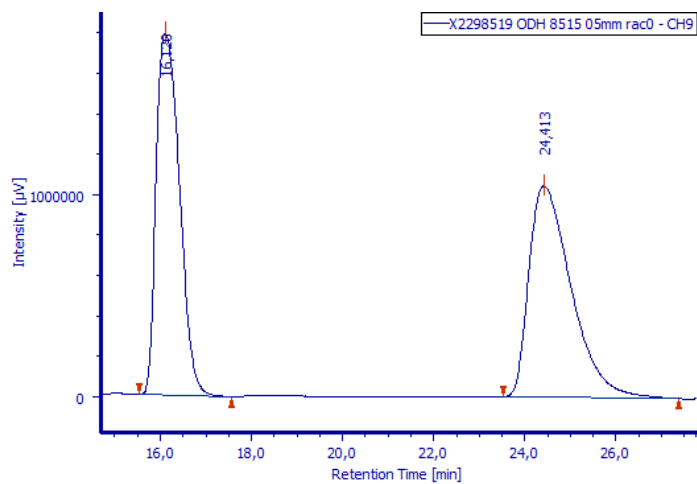
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17,600	31787540	688793	51,038	65,977
30,640	30494254	355195	48,962	34,023

(S)-2-(1,3-dioxolan-2-yl)-6-hydroxy-6-isobutyl-8 methyl-1-phenyl-5-one (3Da)



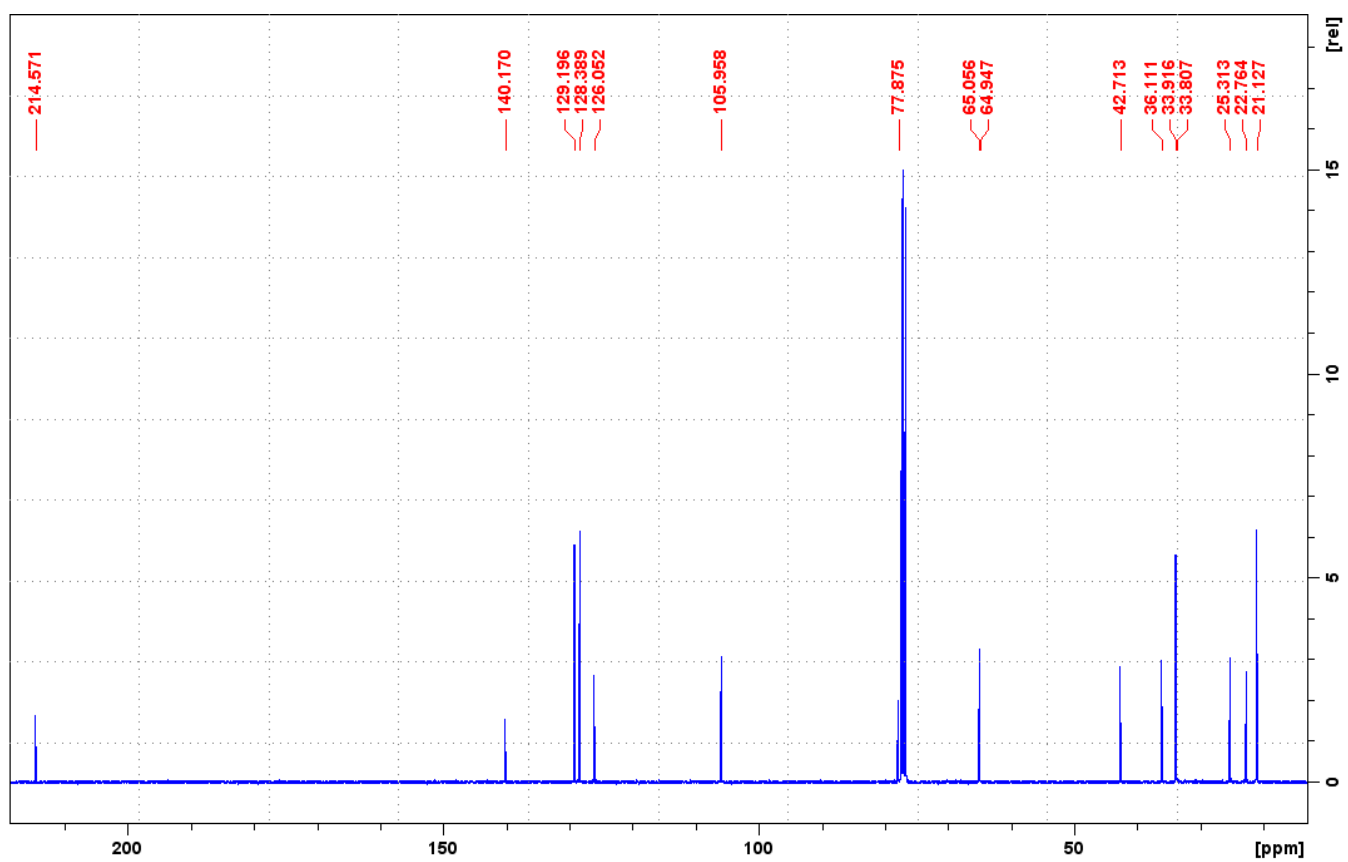
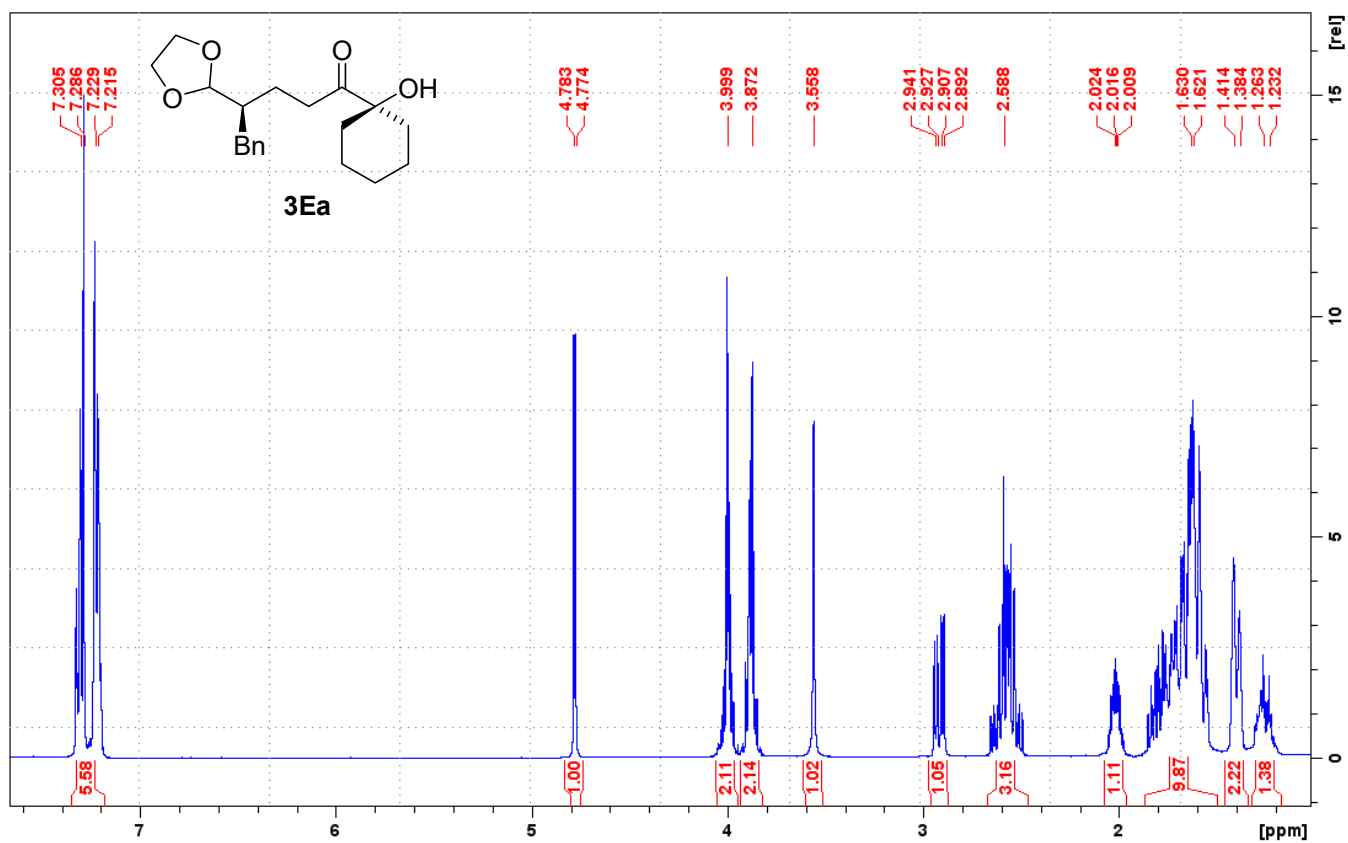


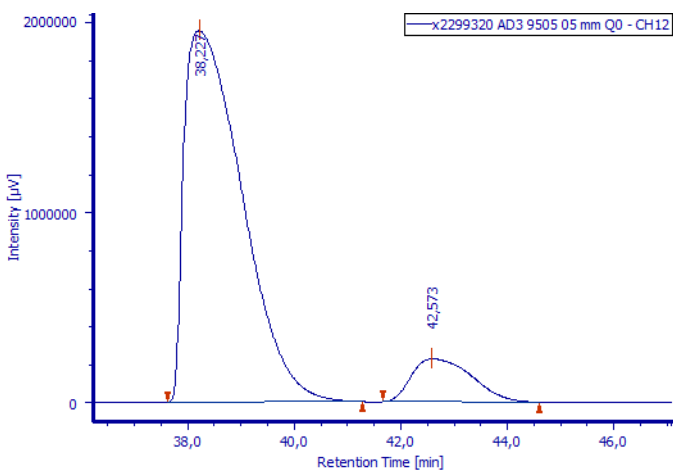
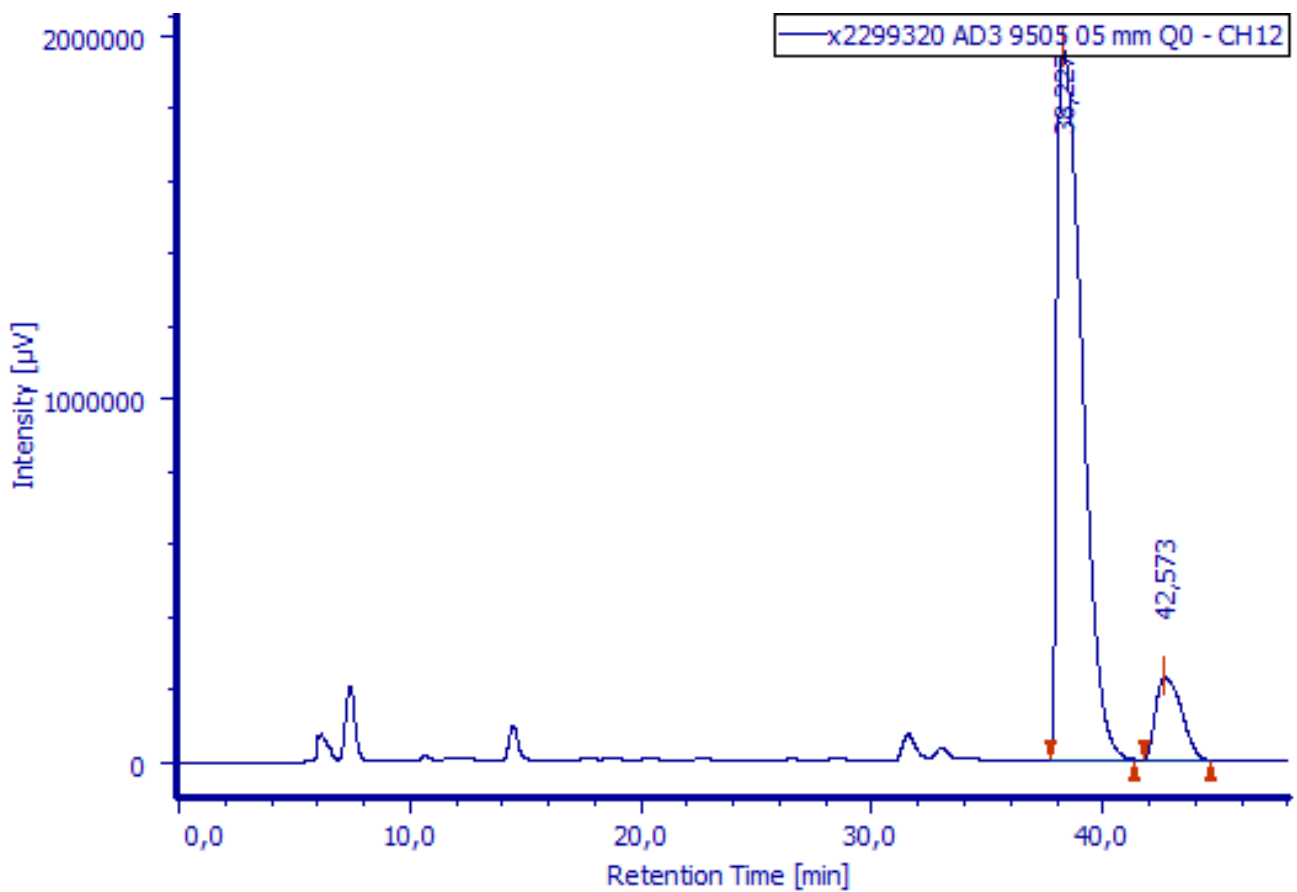
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24,907	6133093	125956	11,261	7,309



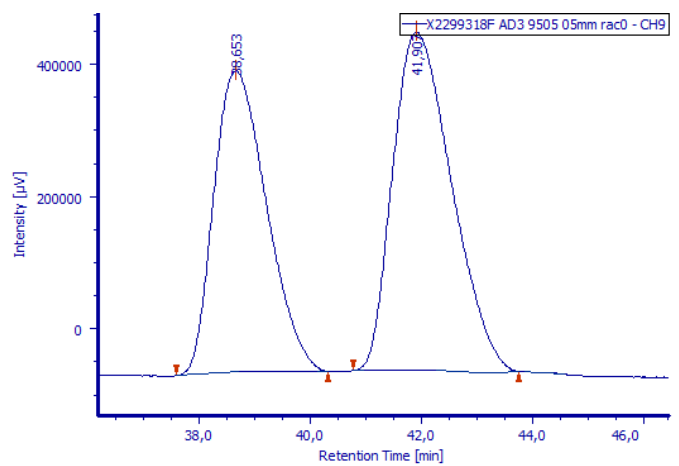
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16,120	63445701	1789035	48,613	63,191
24,413	67067284	1042117	51,387	36,809

(S)-4-(1,3-dioxolan-2-yl)-1-(1-hydroxycyclohexyl)-5-phenylpentan-1-one (3Ea)



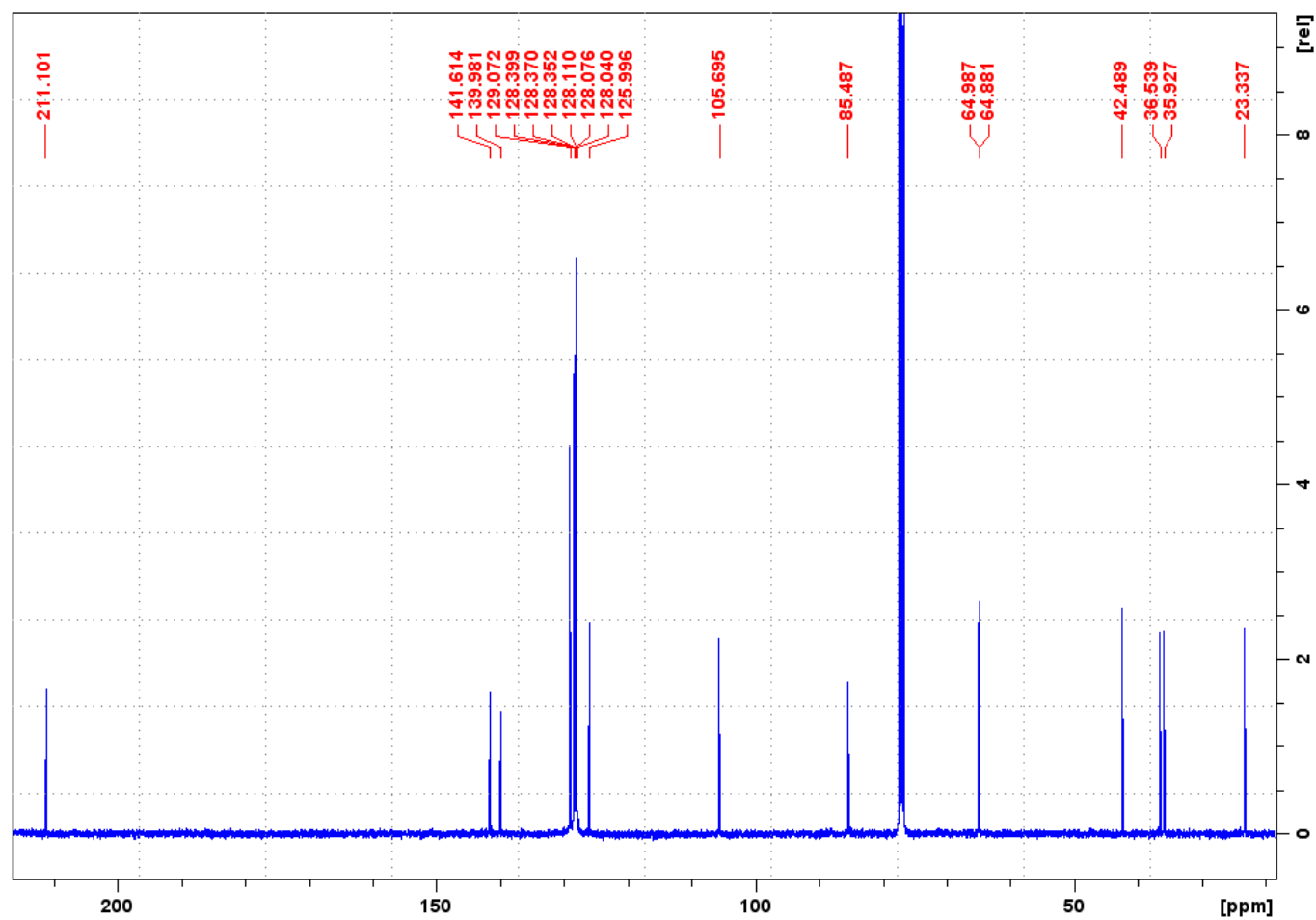
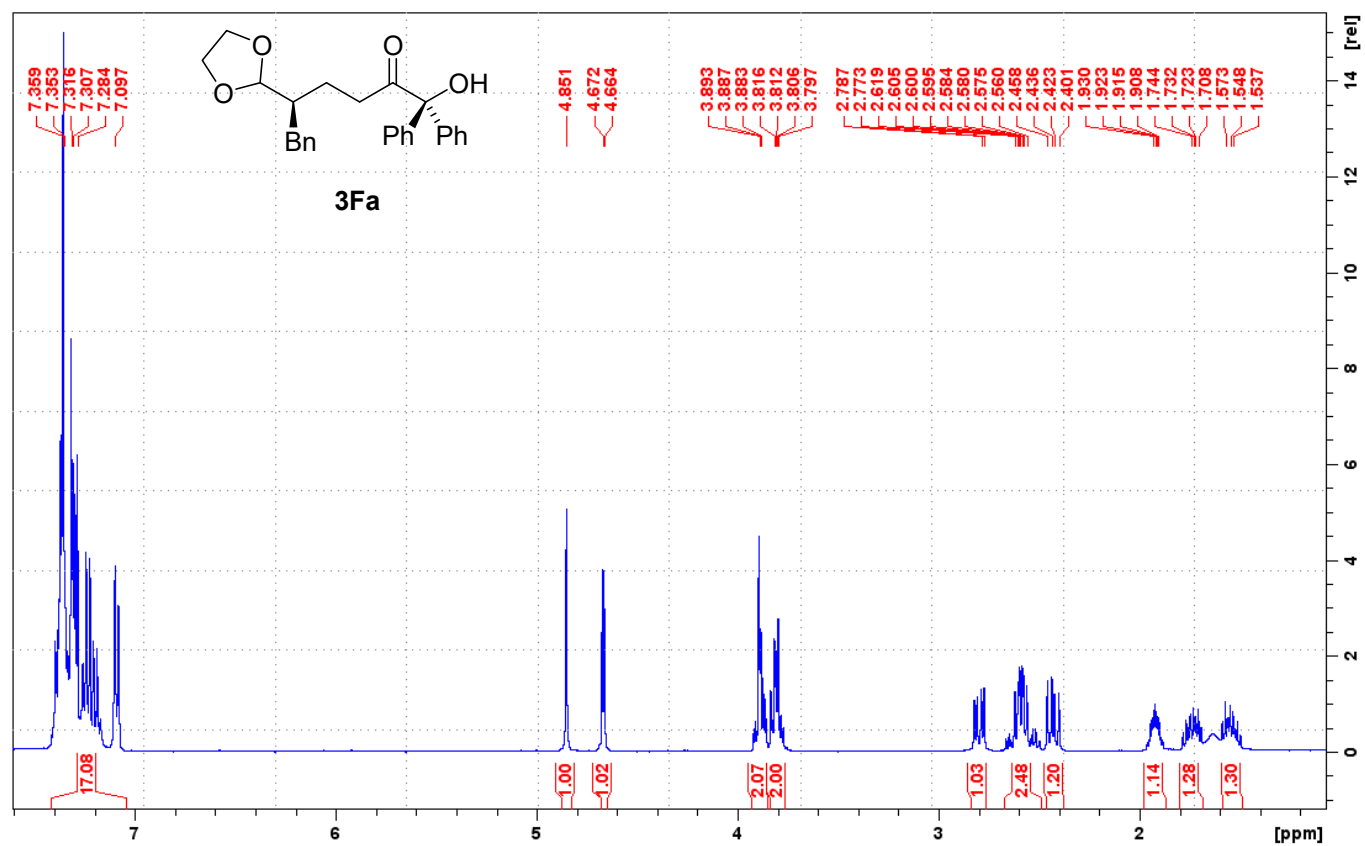


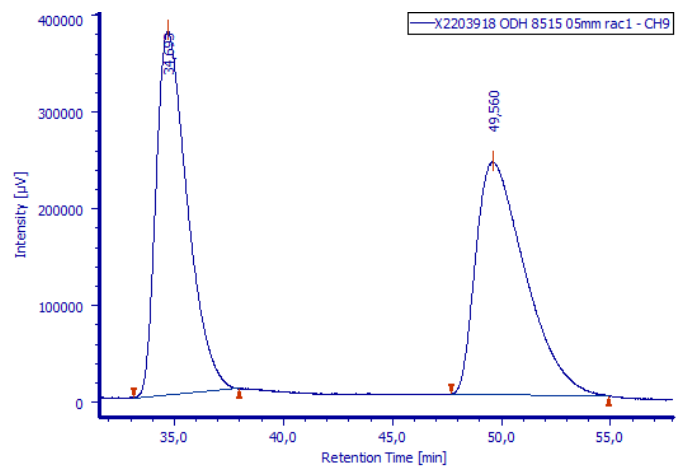
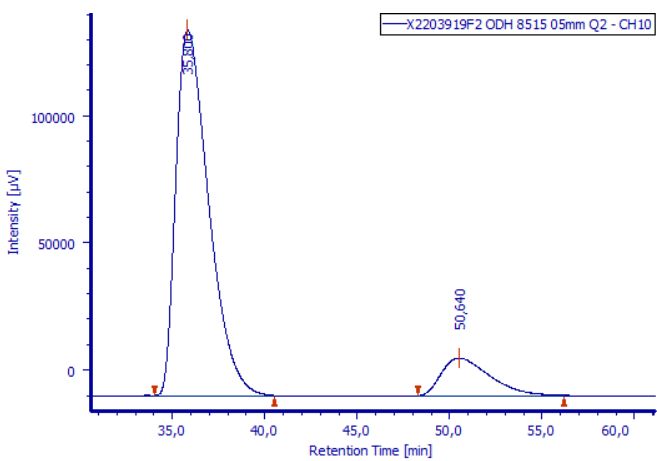
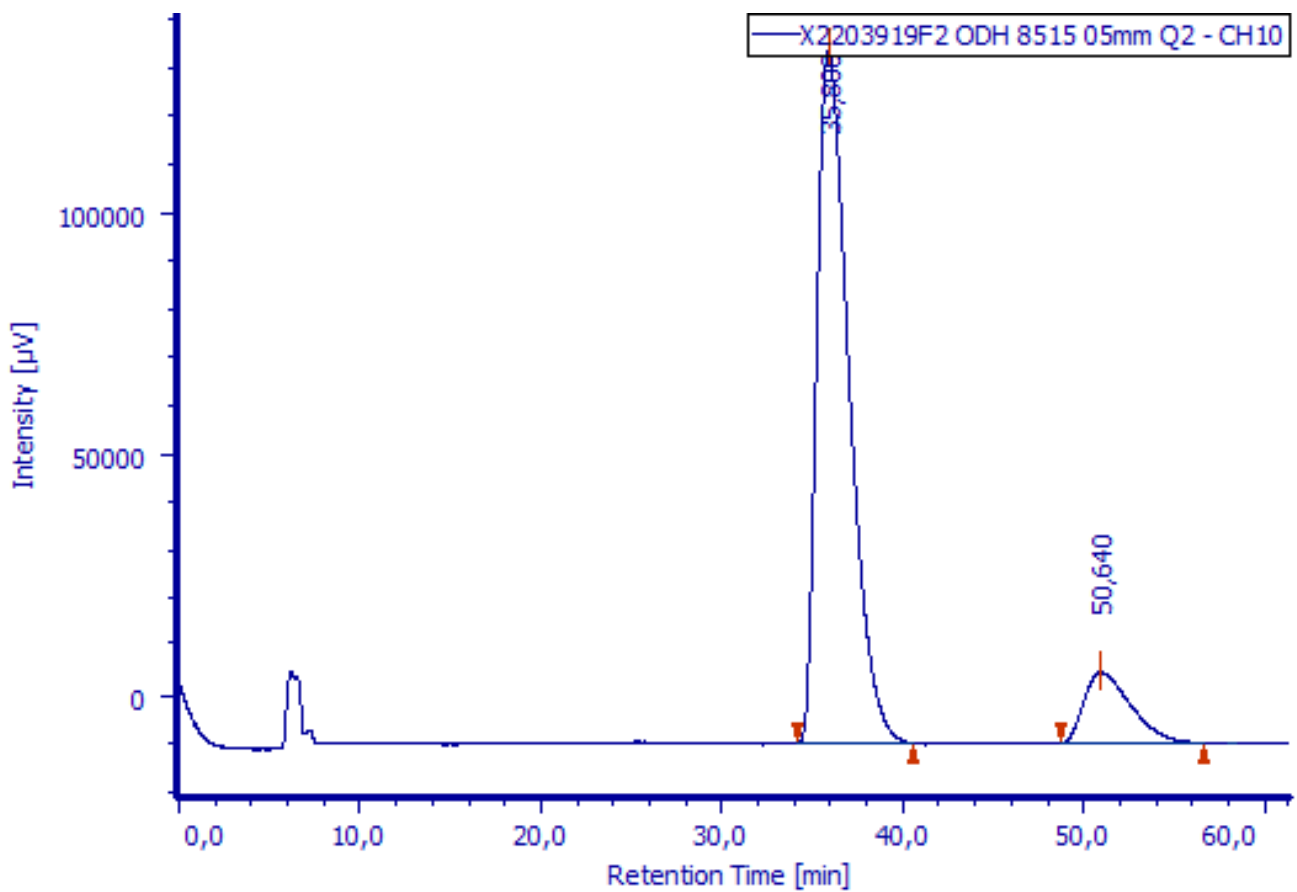
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38,227	147258823	1952495	89,295	89,637
42,573	17654548	225728	10,705	10,363



tR	Area	Height	Area%	Height%
38,653	29706631	453964	48,025	48,757
41,907	32149600	477111	51,975	51,243

(S)-5-(1,3-dioxolan-2-yl)-1-hydroxy-1,1,6-triphenylhexan-2-one (3Fa)

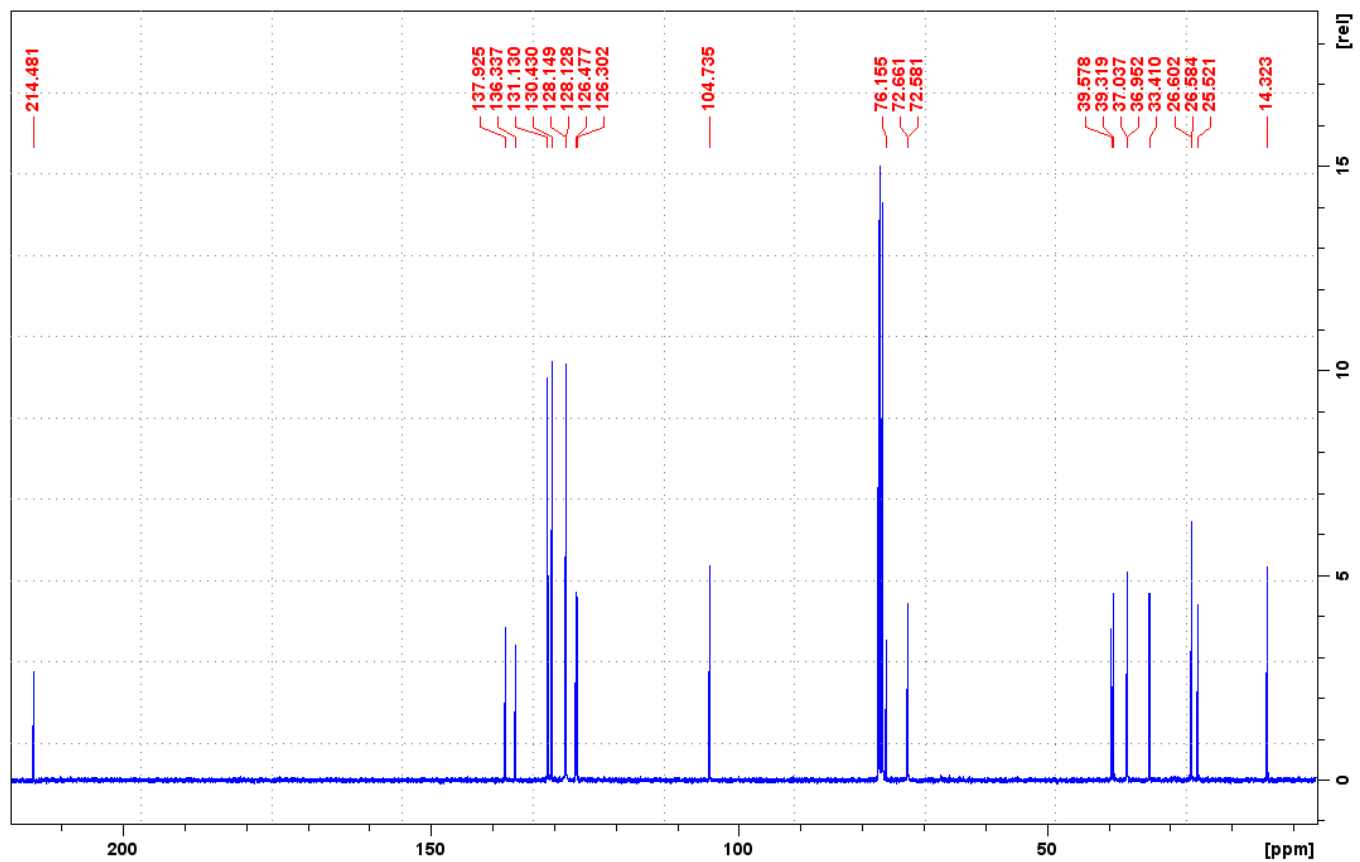
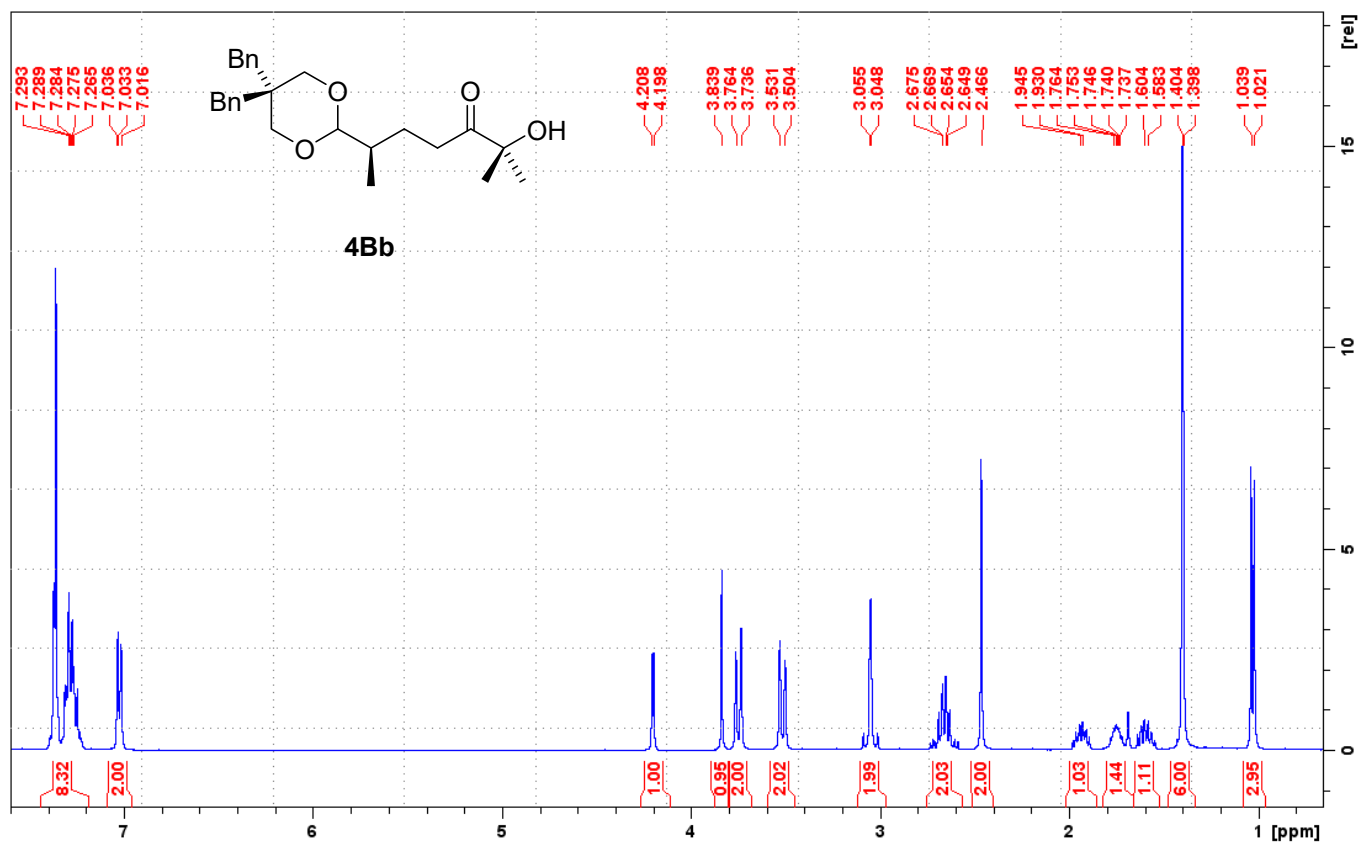


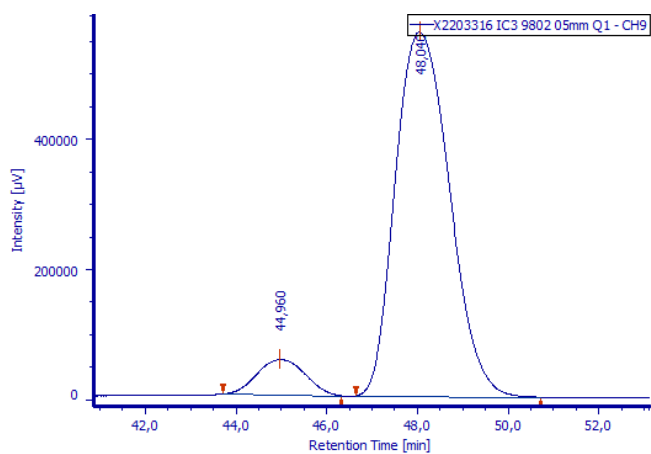
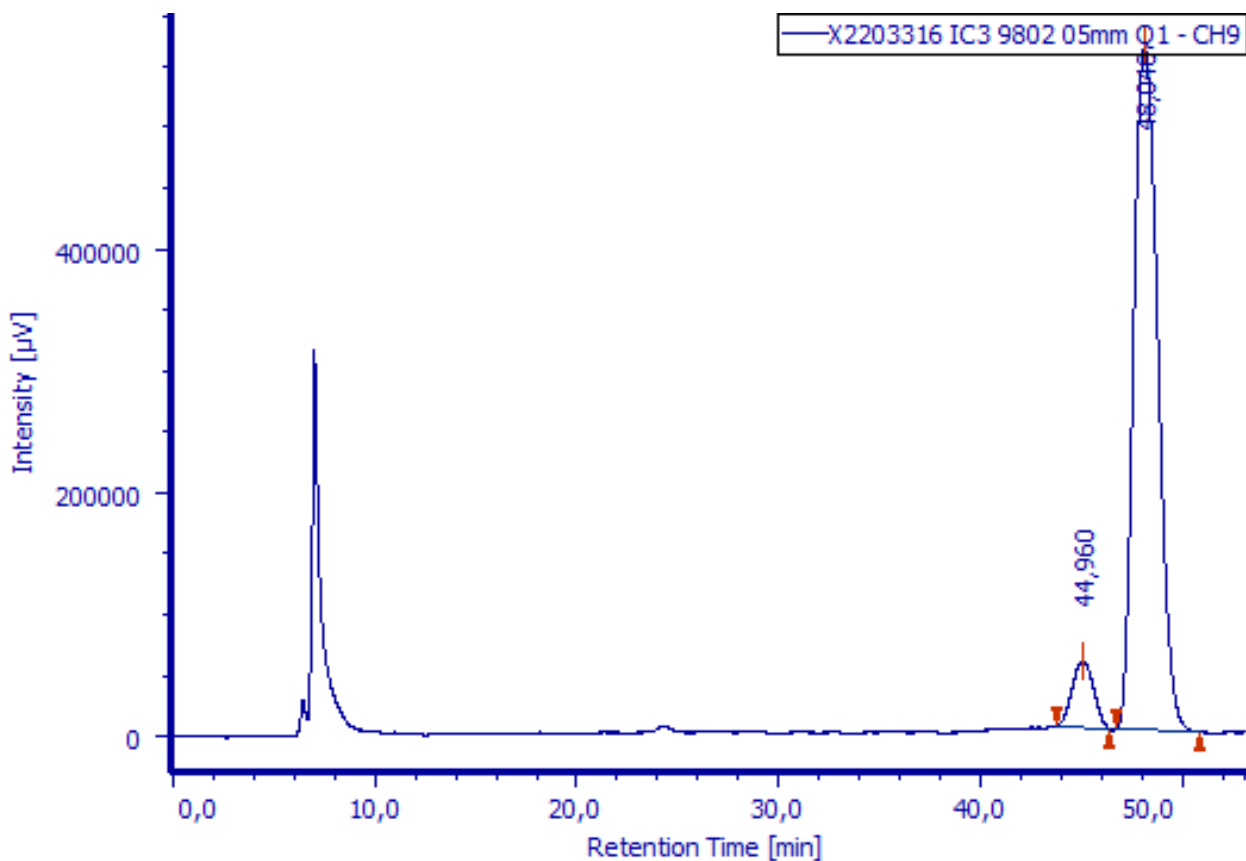


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35,800	17639513	143251	86,844	90,648
50,640	2672307	14779	13,156	9,352

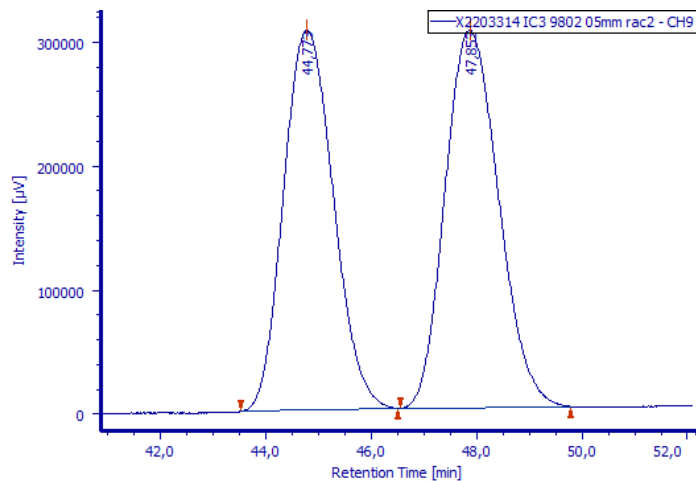
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34,693	37145392	375117	49,630	61,008
49,560	37699837	239749	50,370	38,992

(R)-6-(5,5-dibenzyl-1,3-dioxan-2-yl)-2-hydroxy-2-methylheptan-3-one (4Bb)



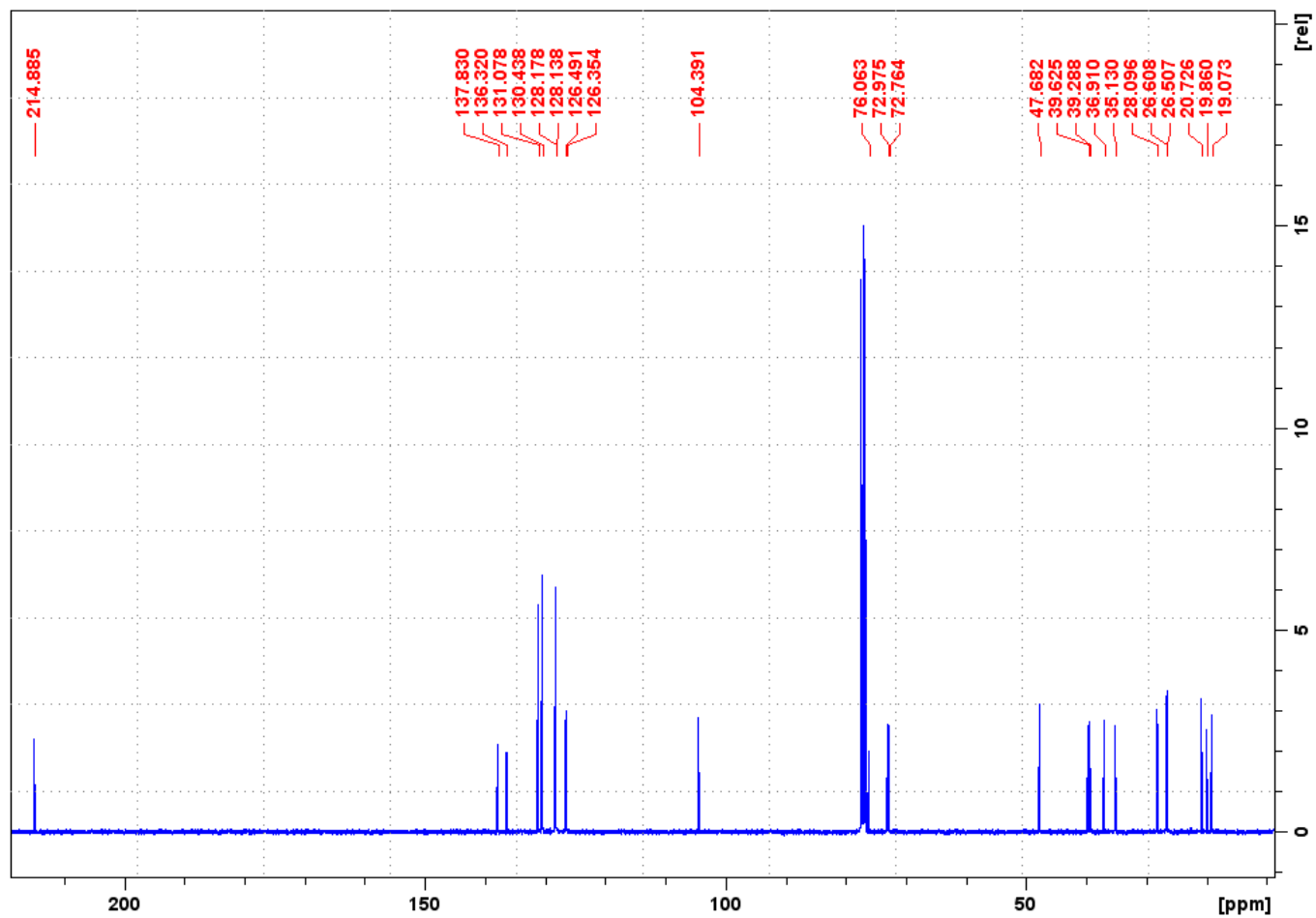
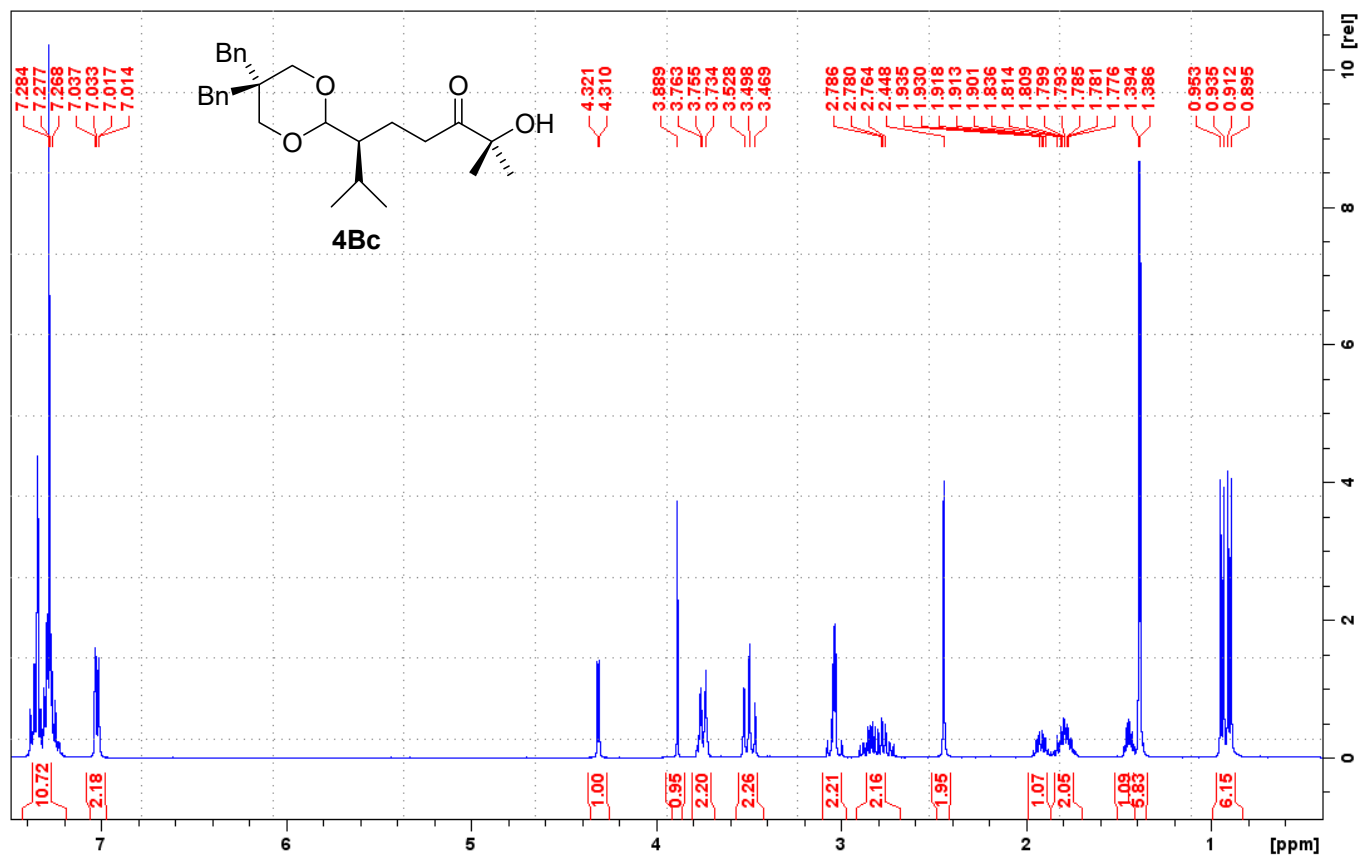


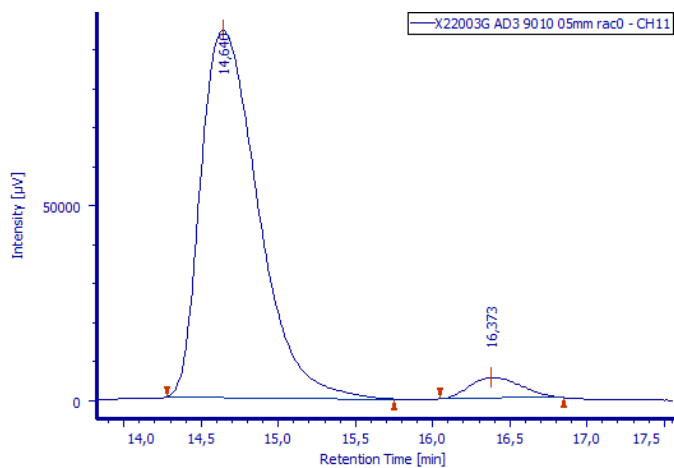
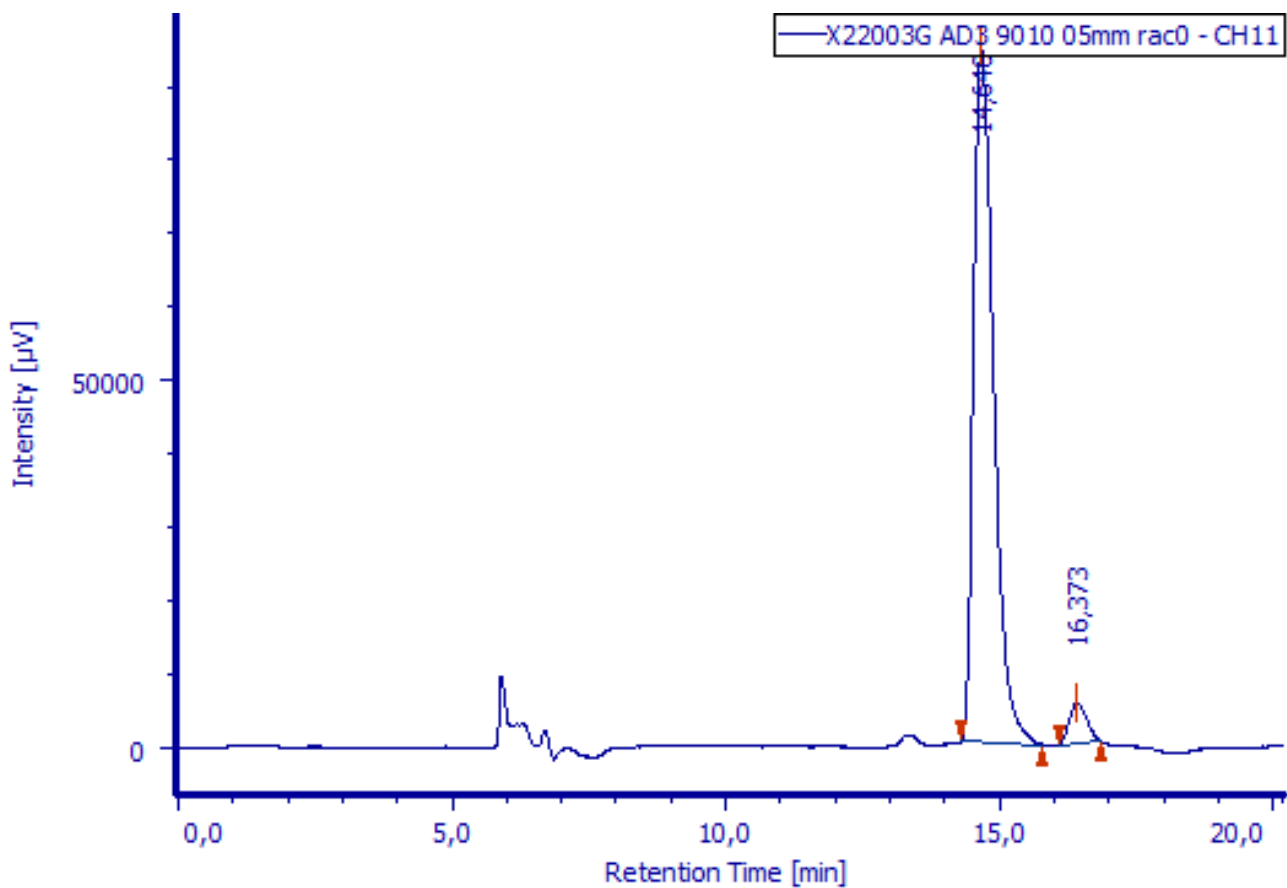
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44,960	3979798	53964	7,920	8,828
48,040	46267748	557347	92,080	91,172



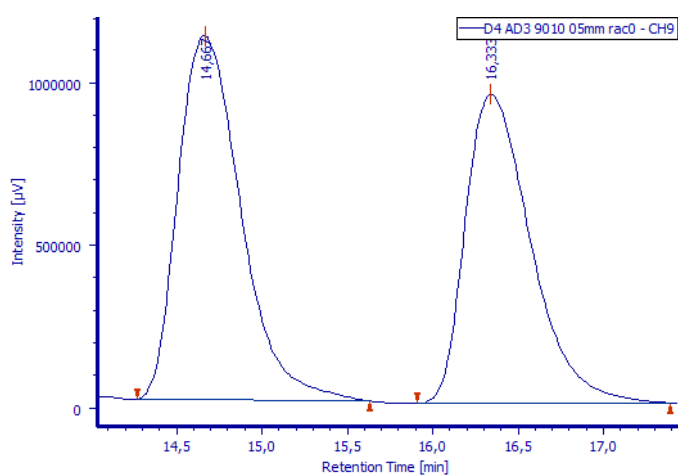
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44,773	20084225	305874	48,416	50,186
47,853	21398515	303610	51,584	49,814

(S)-6-(5,5-dibenzyl-1,3-dioxan-2-yl)-2-hydroxy-2,7-dimethyloctan-3-one (4Bc)



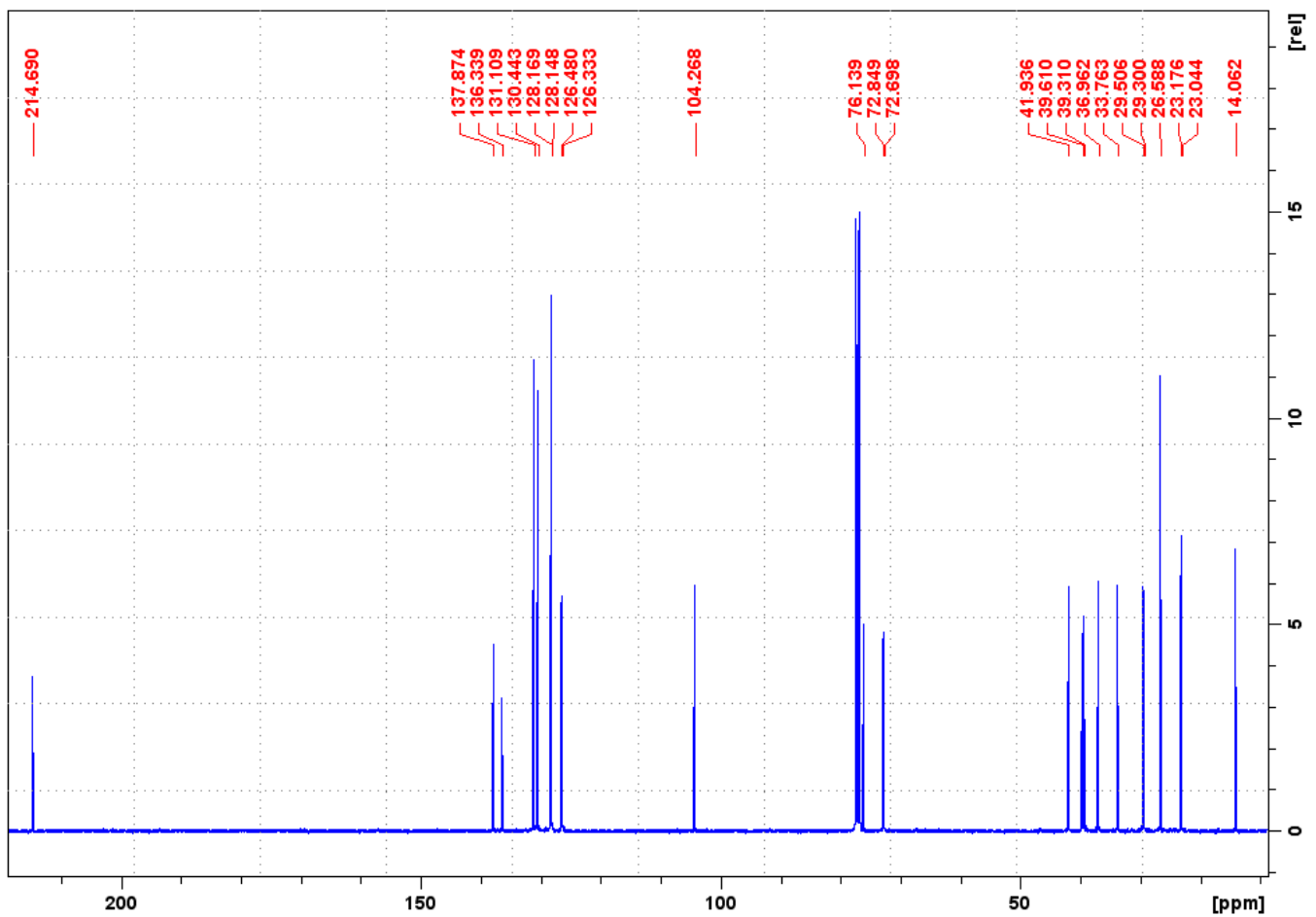
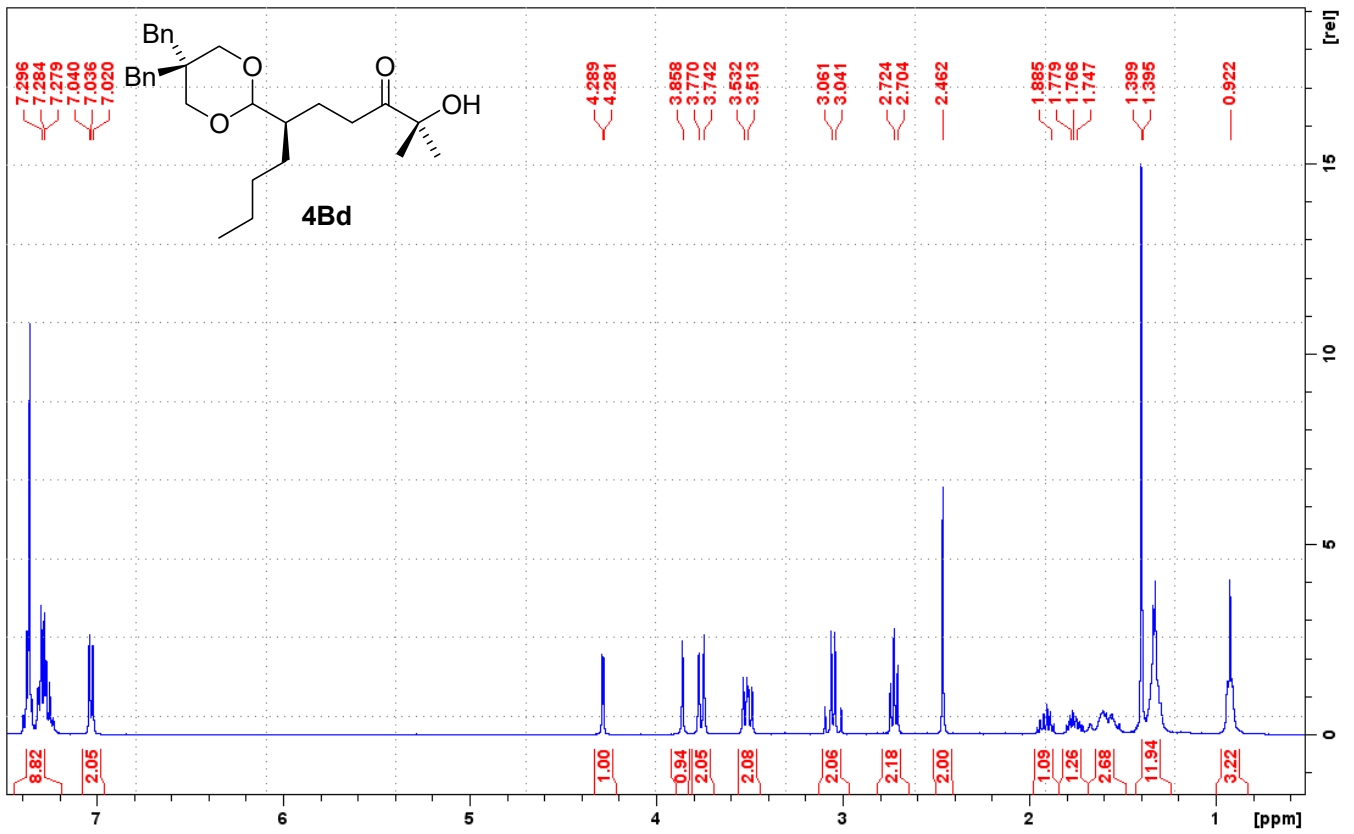


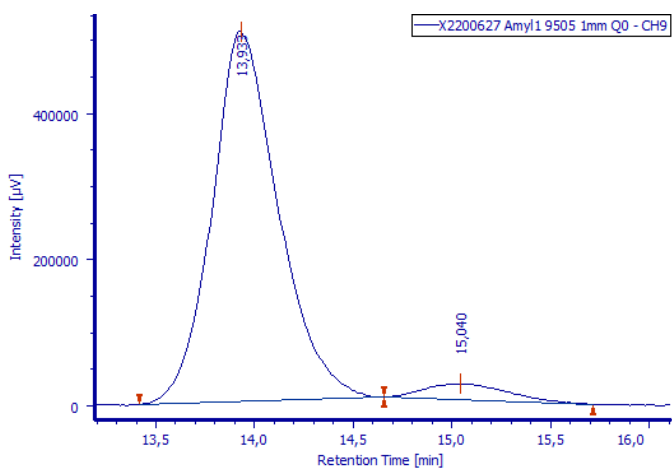
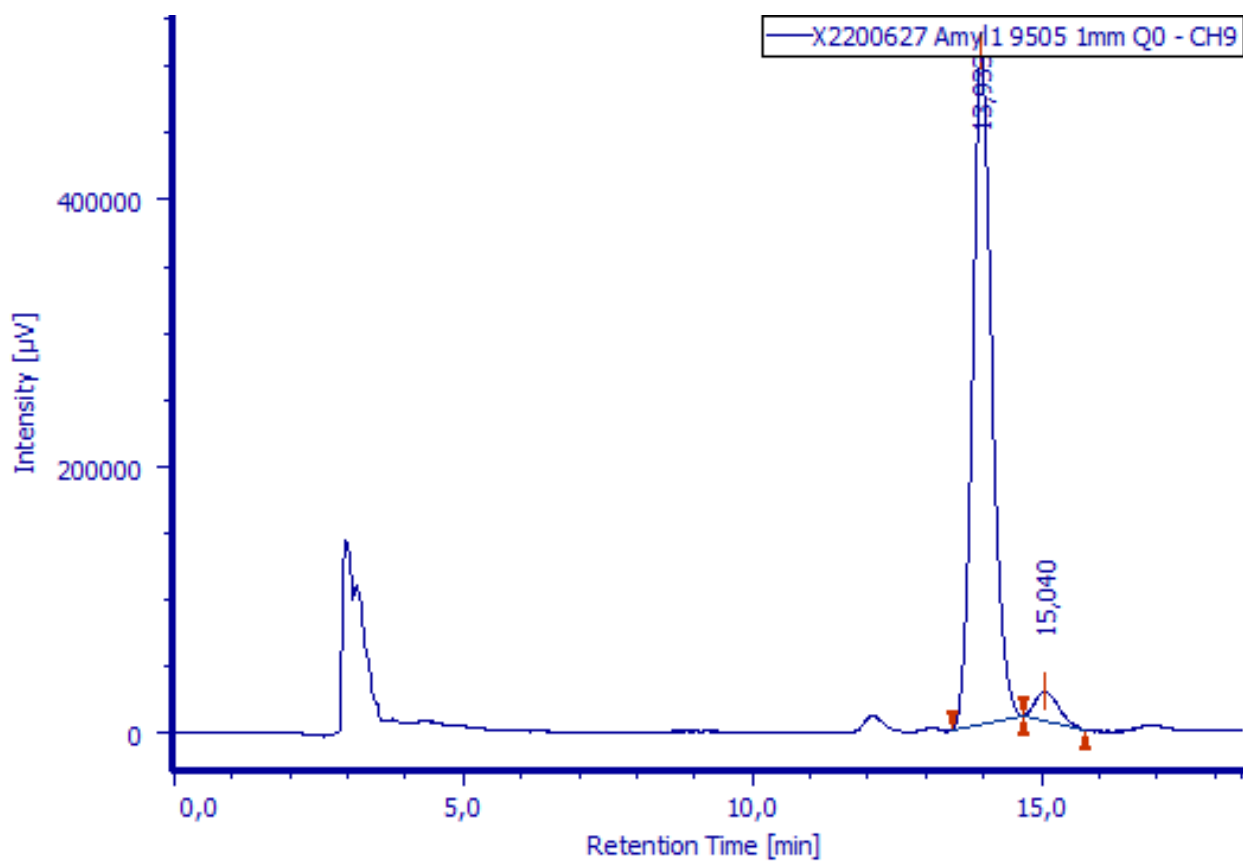
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14,640	3223443	122201	93,680	92,789
16,373	217458	9497	6,320	7,211



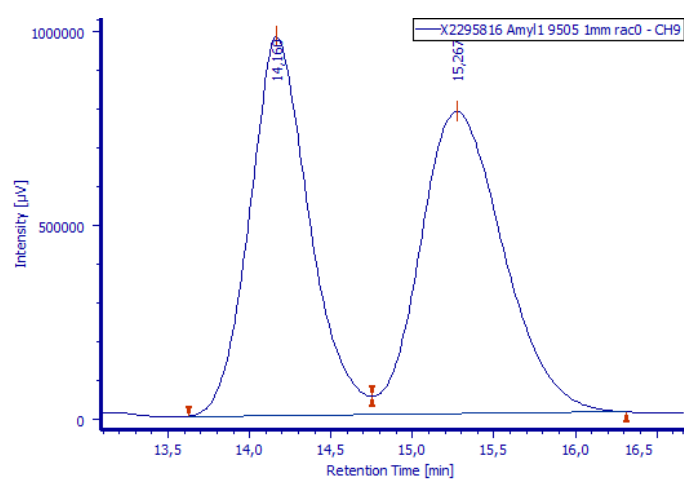
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14,667	28549665	1111975	53,128	54,003
16,333	25187891	947117	46,872	45,997

(R)-6-(5,5-dibenzyl-1,3-dioxan-2-yl)-2-hydroxy-2-methyldec-3-ona (4Bd)



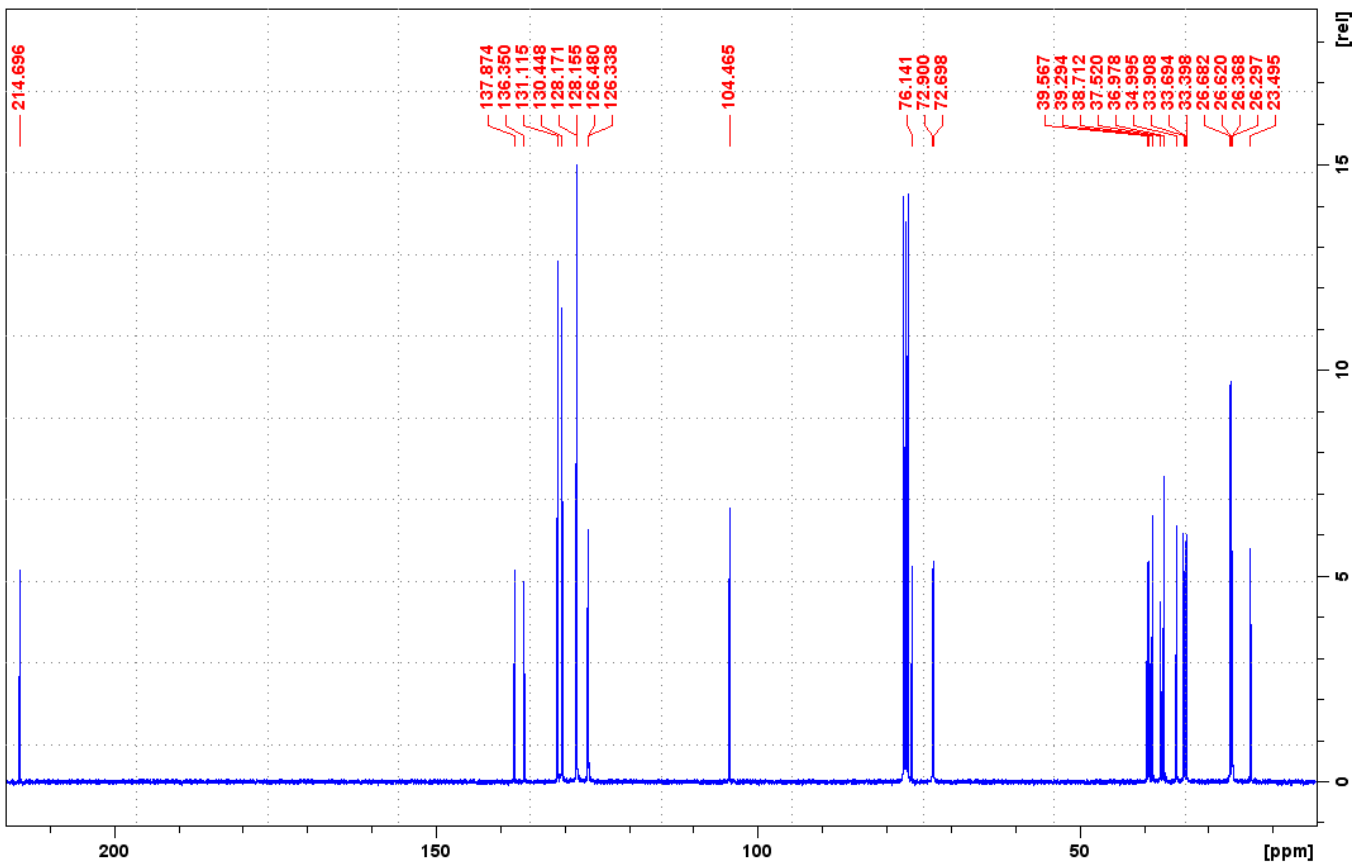
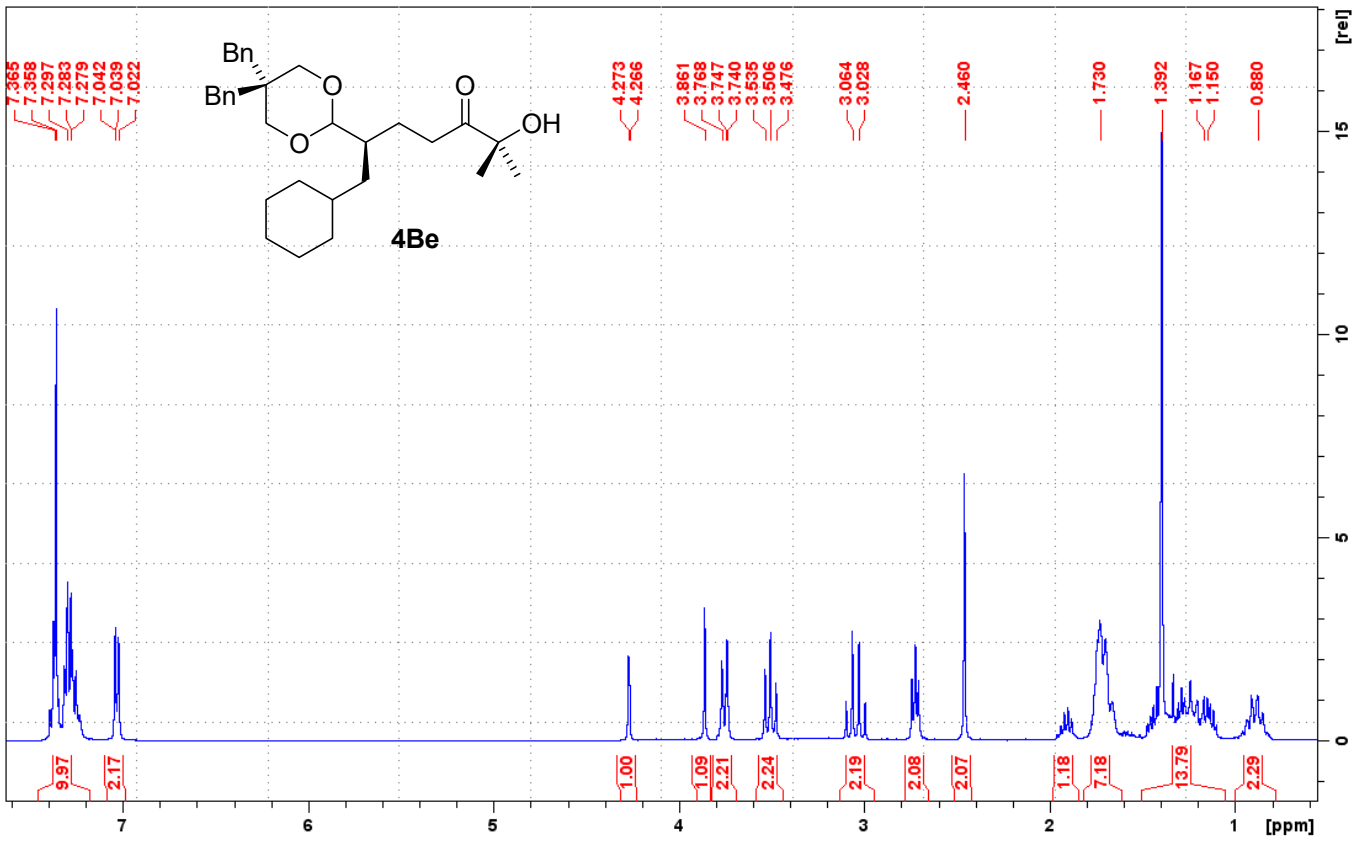


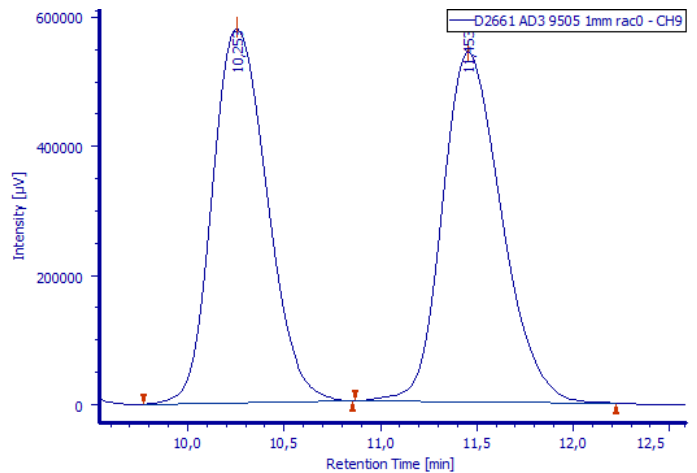
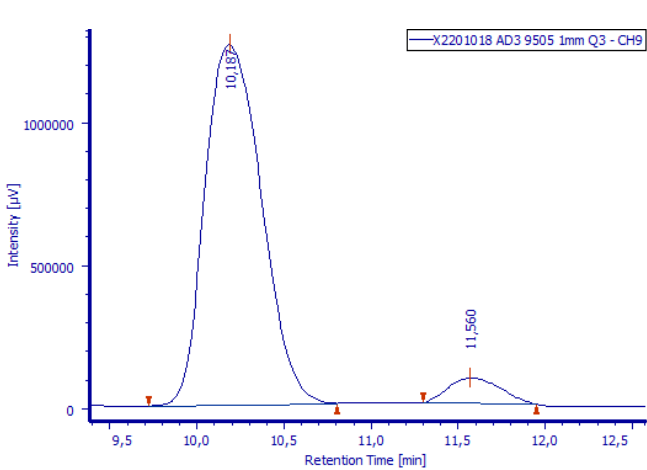
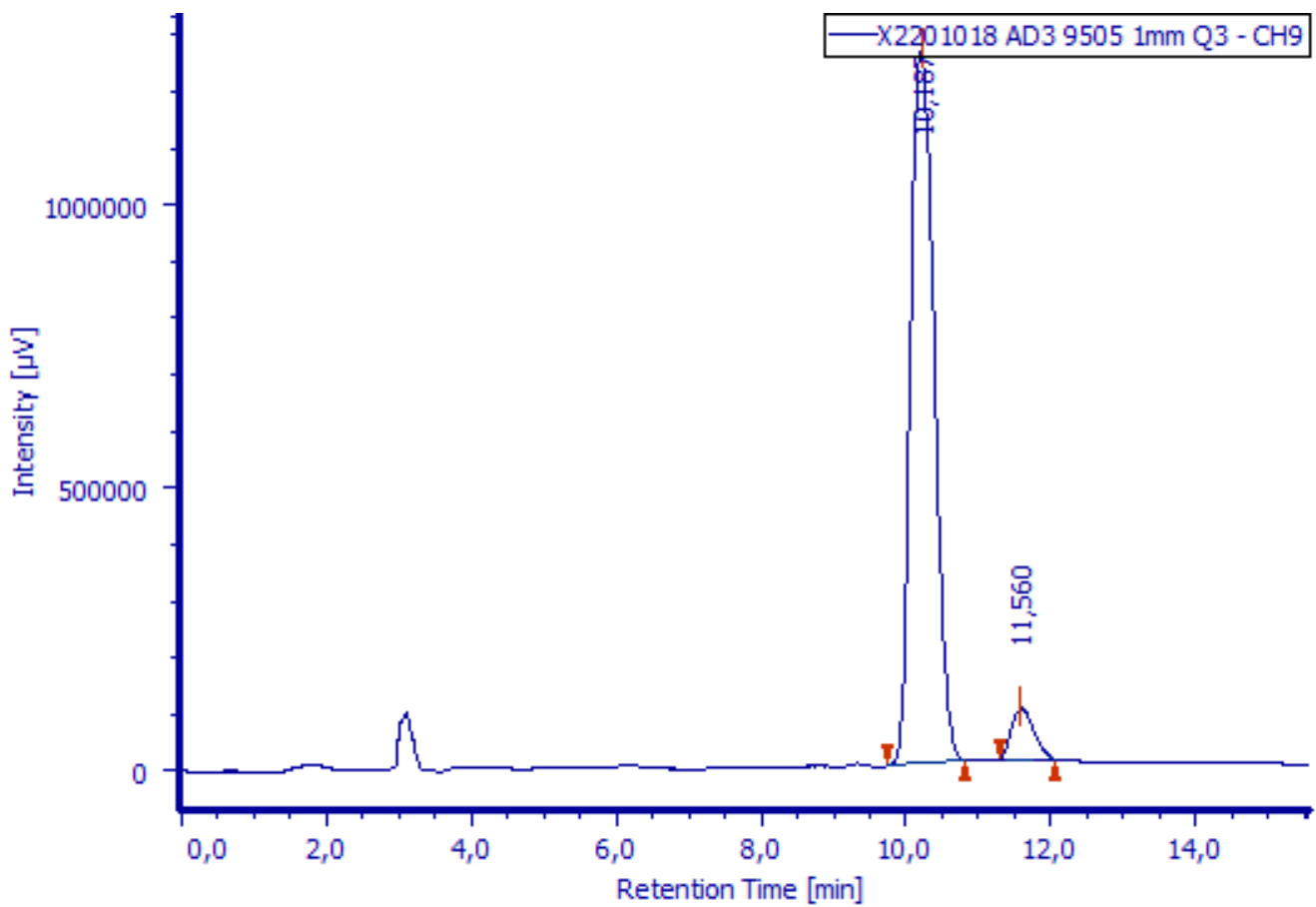
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13,933	11802611	504967	94,882	95,808
15,040	636651	22096	5,118	4,192



tR	Area	Height	Area%	Height%
14,160	24711425	974458	47,368	55,594
15,267	27457610	778362	52,632	44,406

(R)-6-(5,5-dibenzyl-1,3-dioxan-2-yl)-7-cyclohexyl-2-hydroxy-2-methylheptan-3-one (4Be)

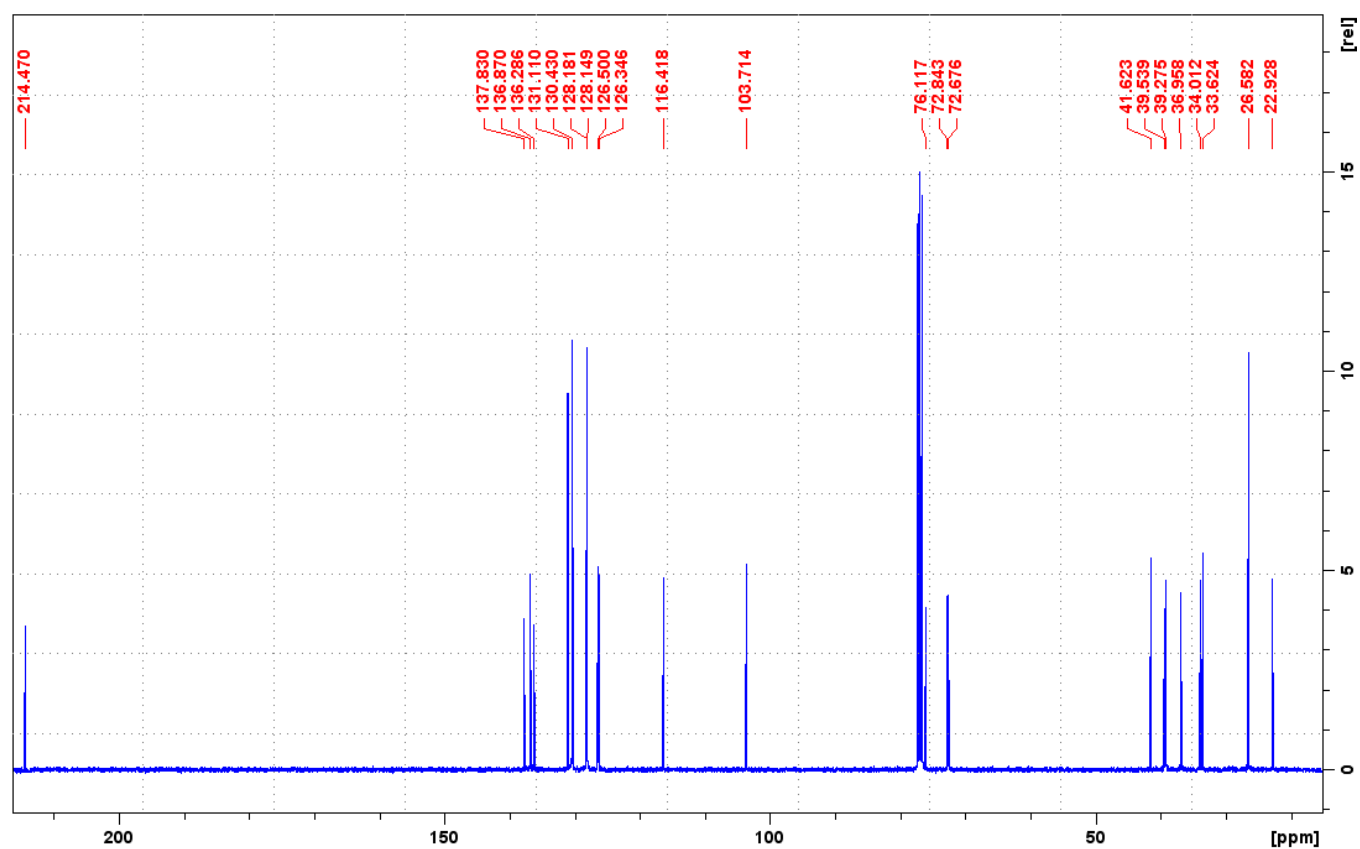
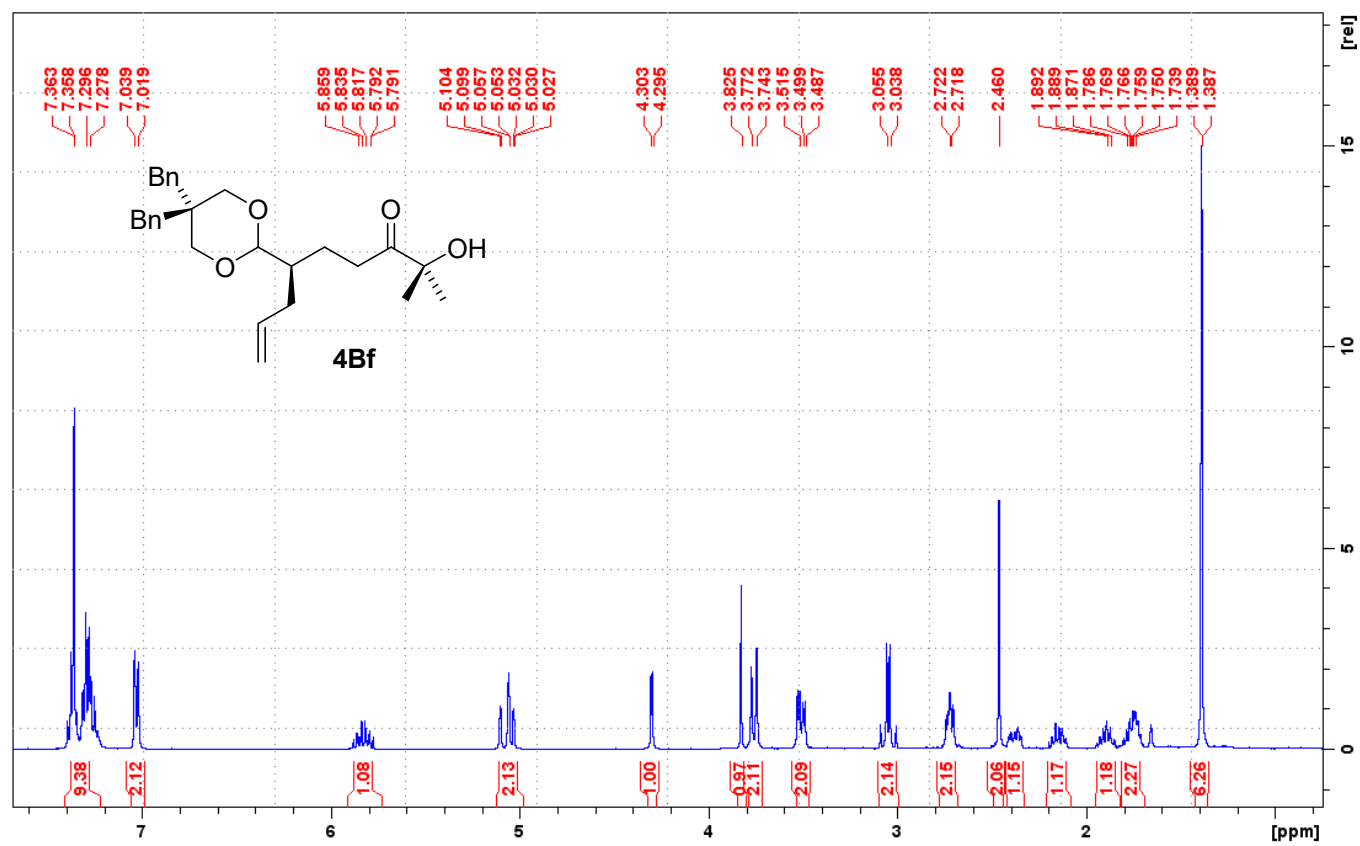


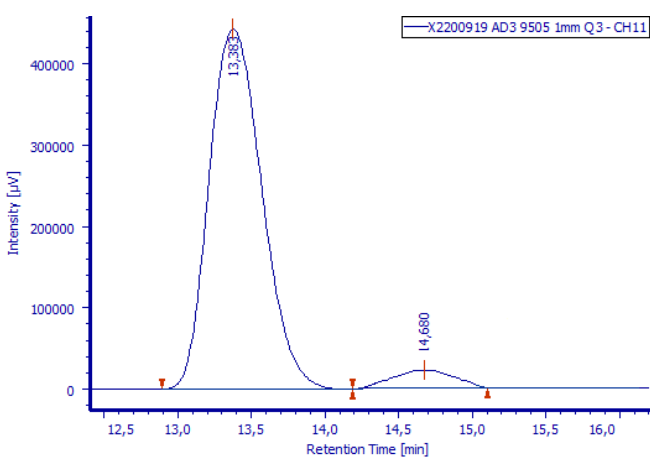
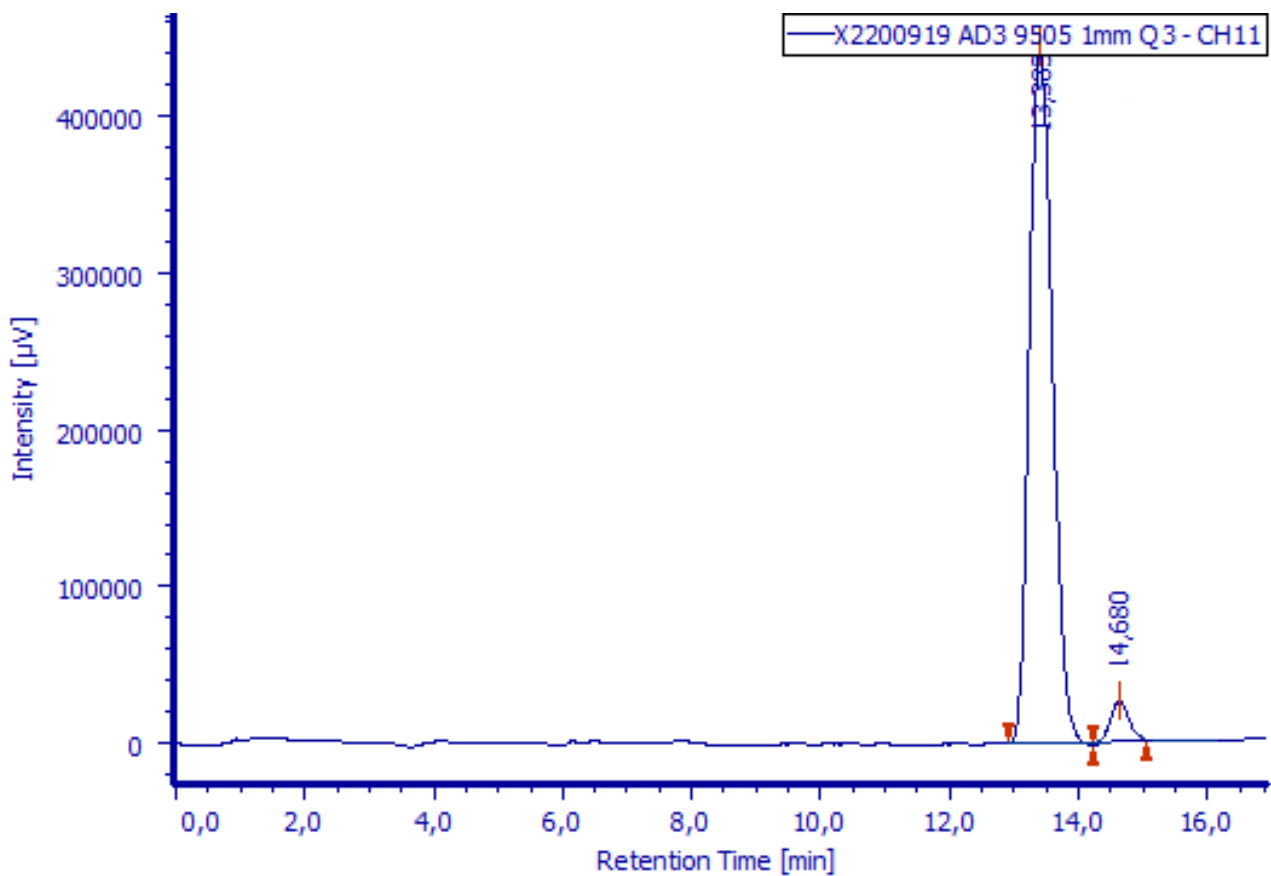


tR	Area	Height	Area%	Height%
10,187	28344277	1255796	94,788	93,913
11,560	1558464	81391	5,212	6,087

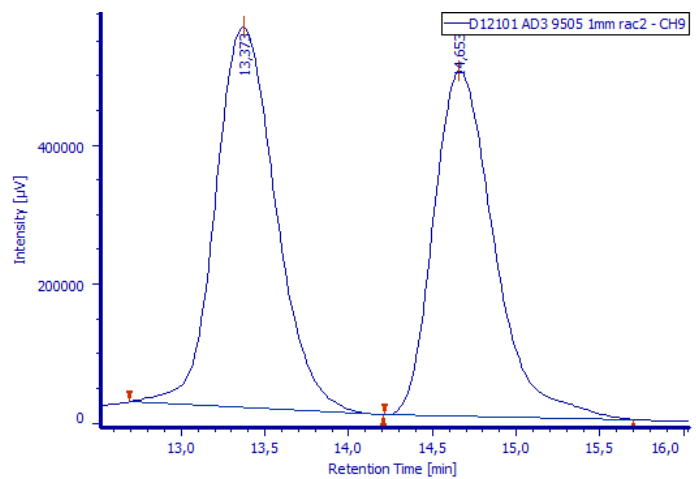
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10,253	11347853	578742	49,377	51,687
11,453	11634336	540964	50,623	48,313

(S)-6-(5,5-dibenzyl-1,3-dioxan-2-yl)-2-hydroxy-2-methylnon-8-en-3-one (4Bf)



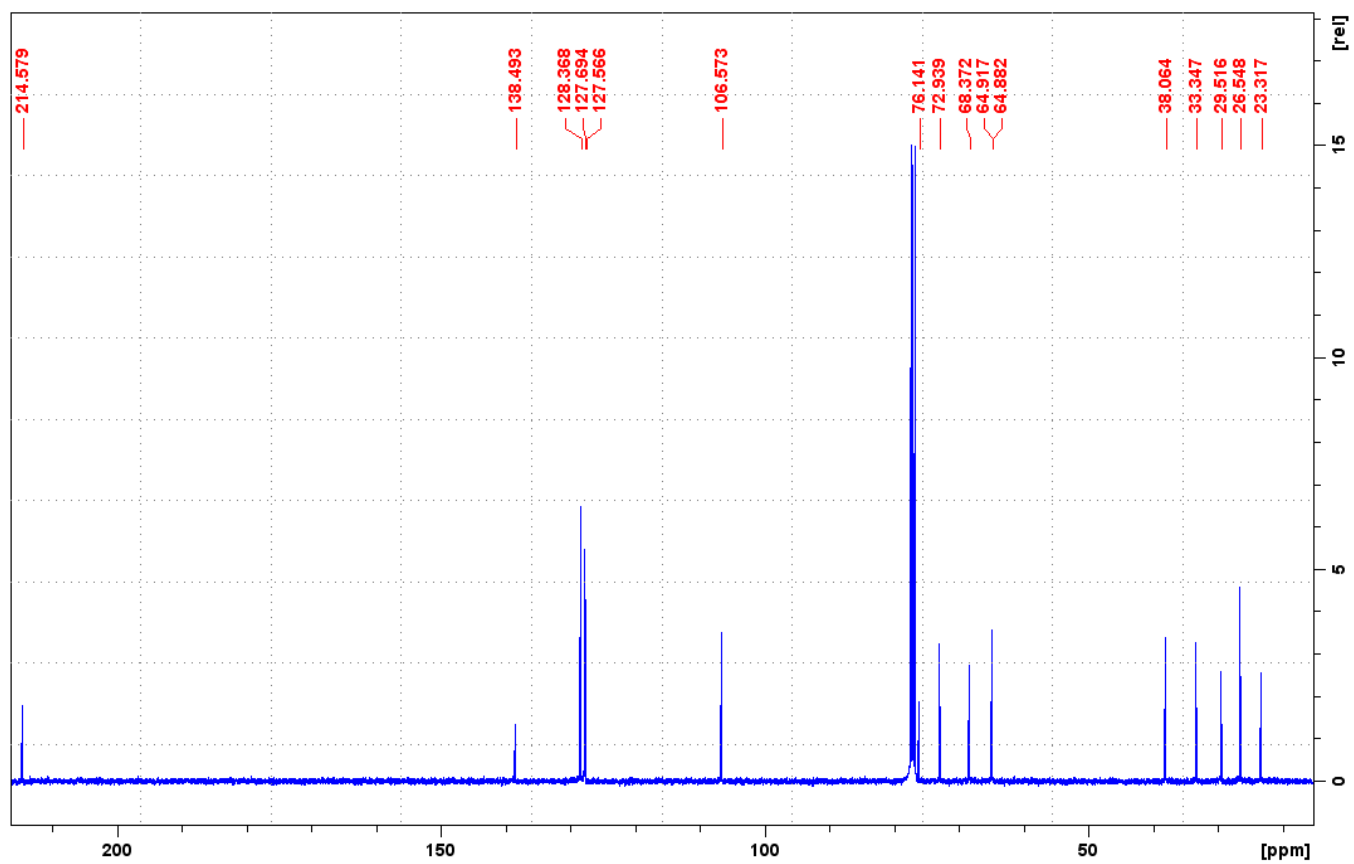
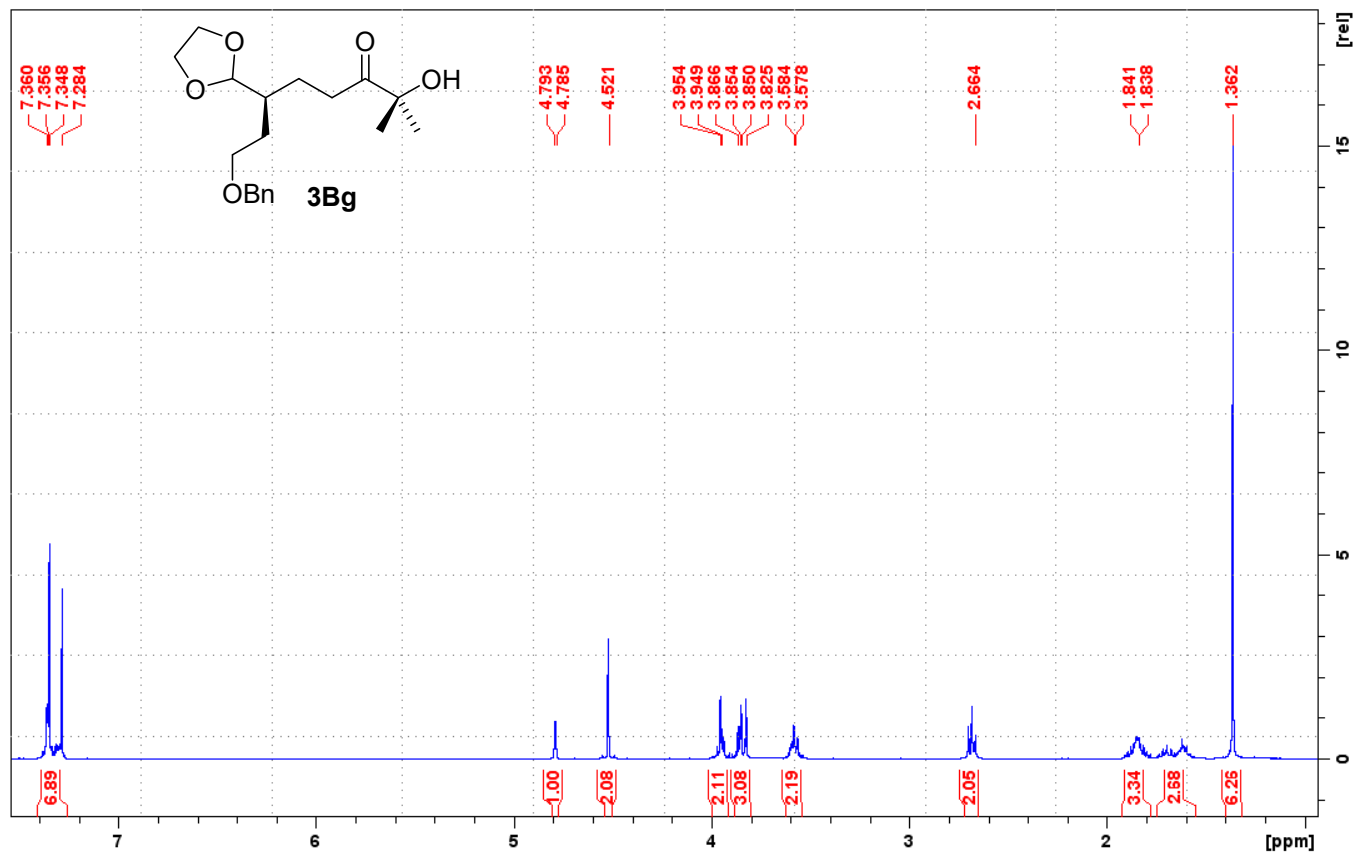


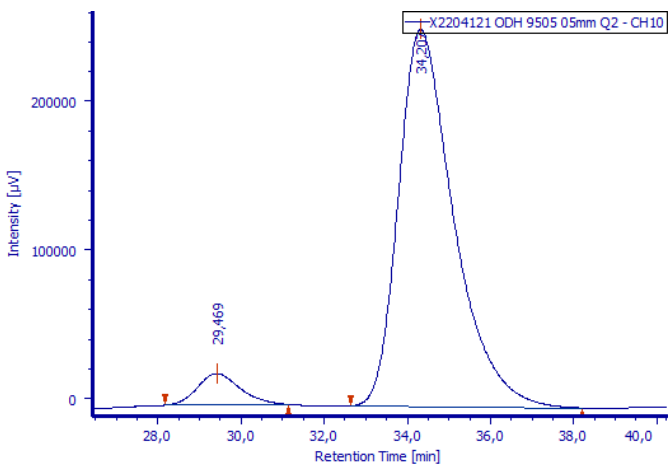
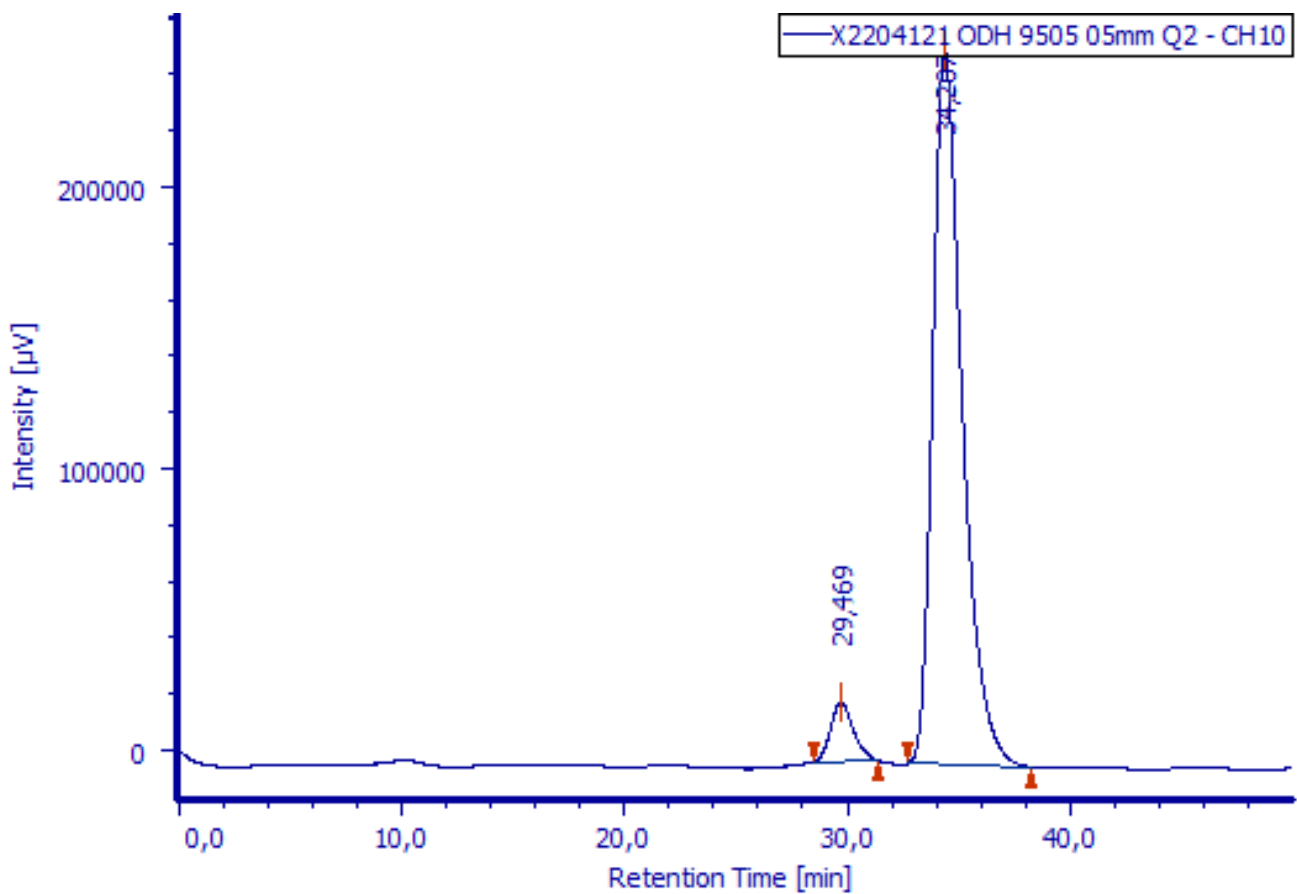
tR	Area	Height	Area%	Height%
13,383	10996210	441807	94,890	93,918
14,680	592166	28611	5,110	6,082



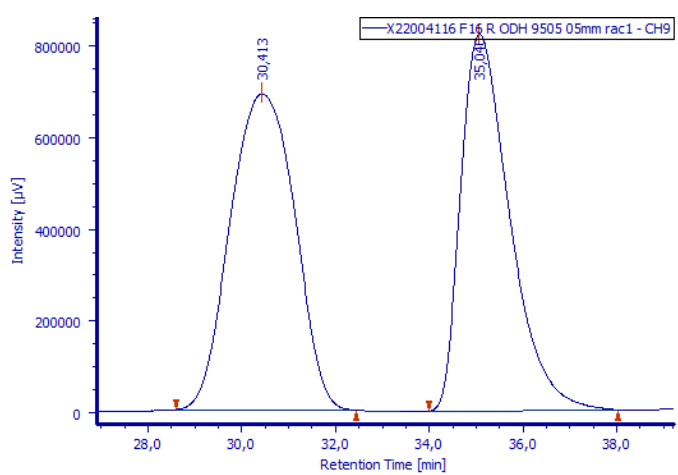
tR	Area	Height	Area%	Height%
13,373	13616065	545304	52,373	52,476
14,653	12382356	493847	47,627	47,524

(S)-8-(Benzyloxy)-6-(1,3-dioxolan-2-yl)-2-hydroxy-2-methyloctan-3-one (3Bg)



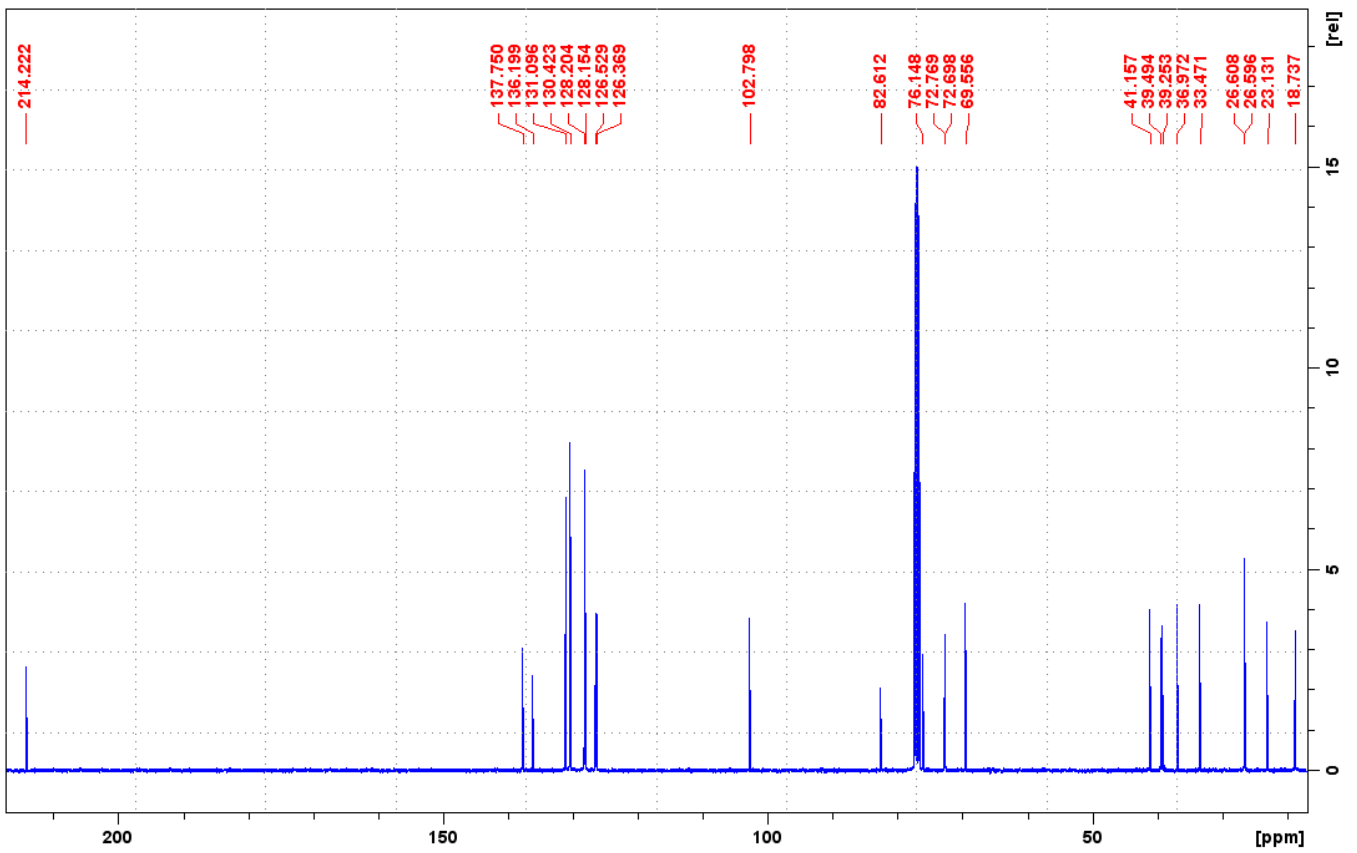
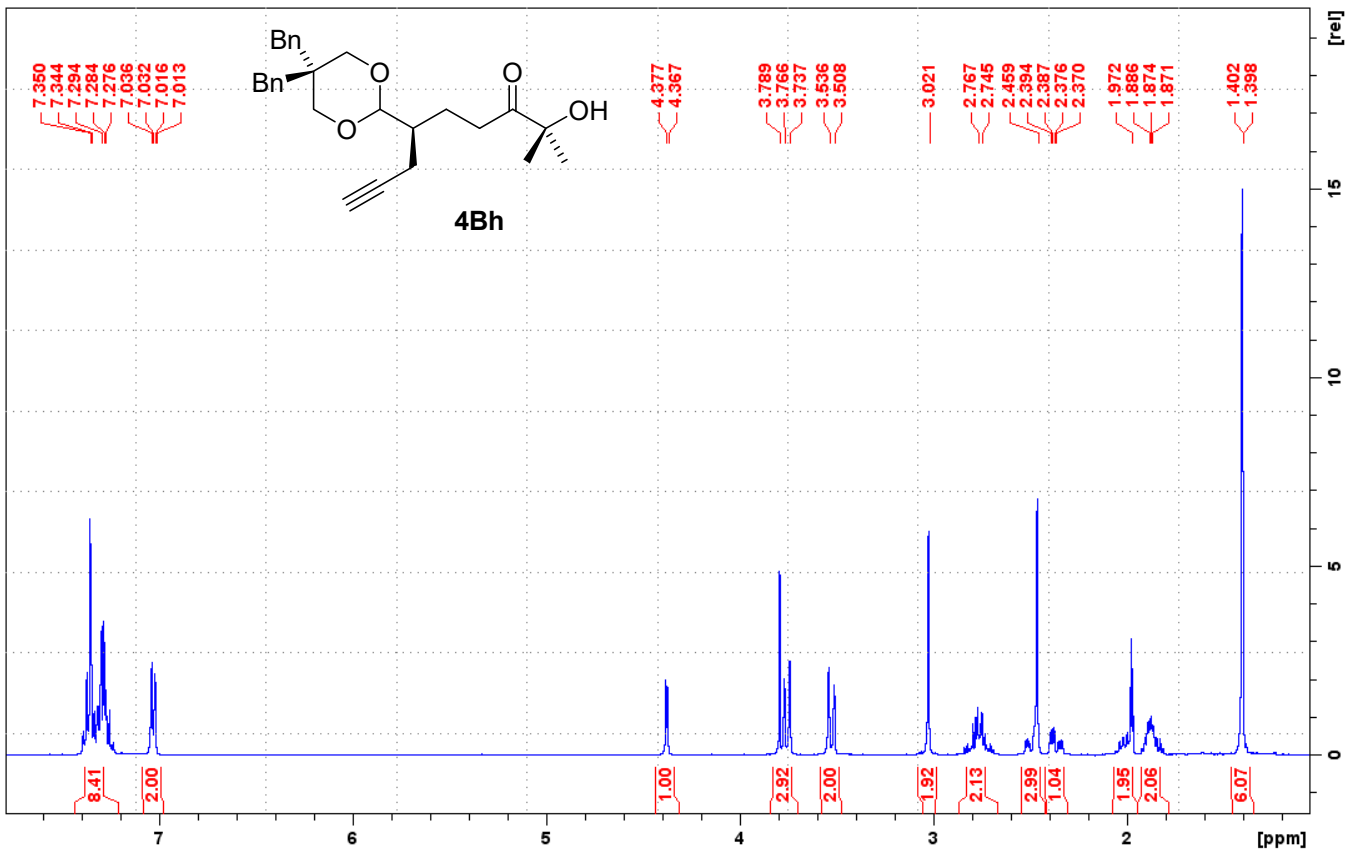


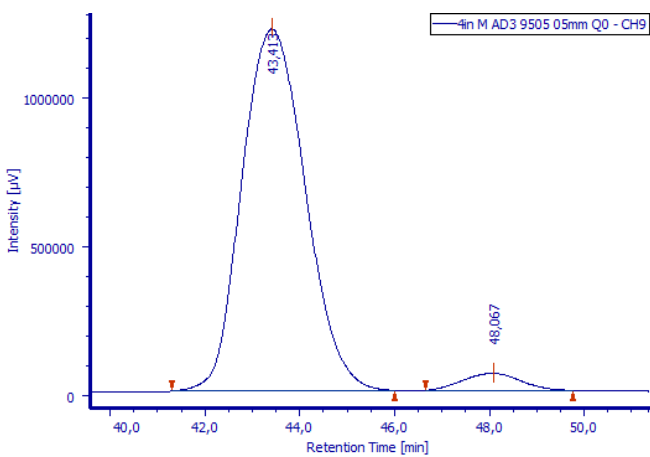
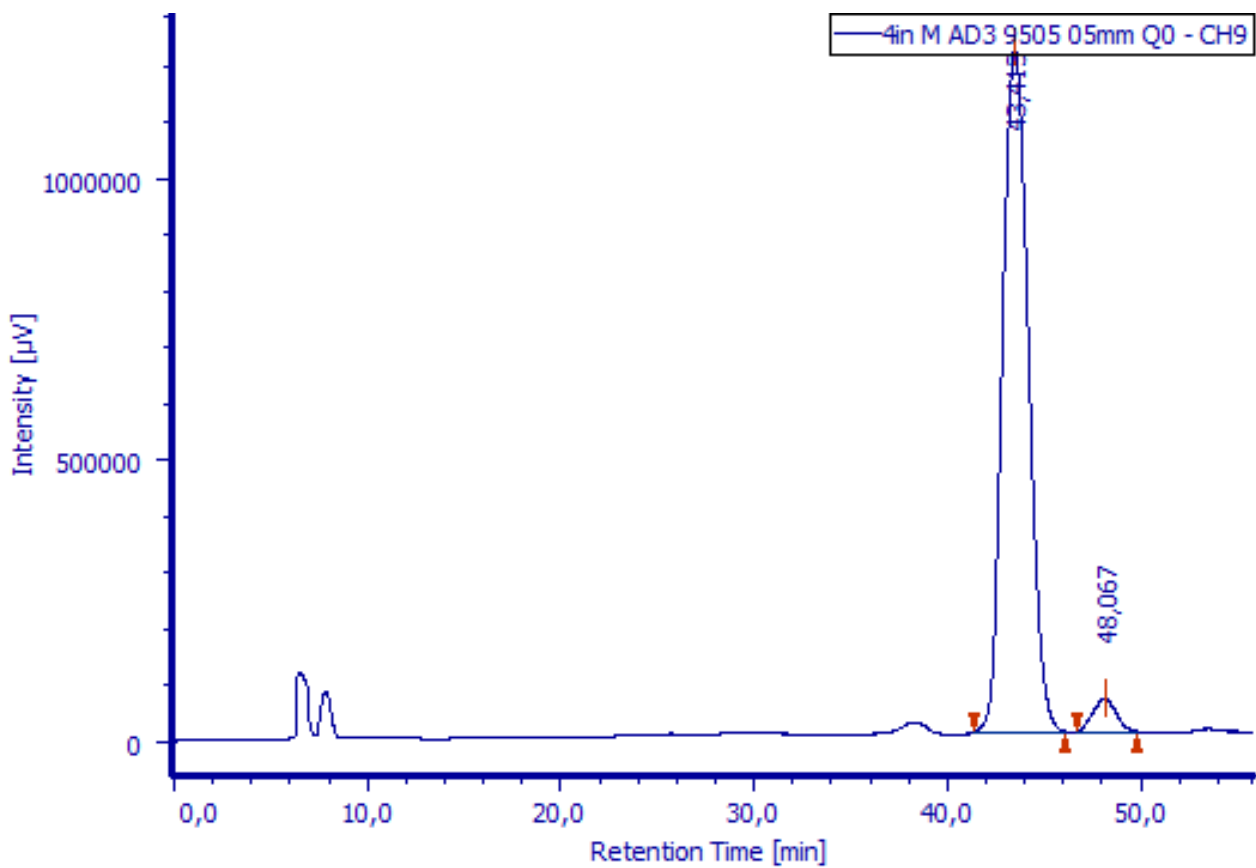
tR	Area	Height	Area%	Height%
29,469	1477623	20895	5,966	7,633
34,207	23291363	252830	94,034	92,367



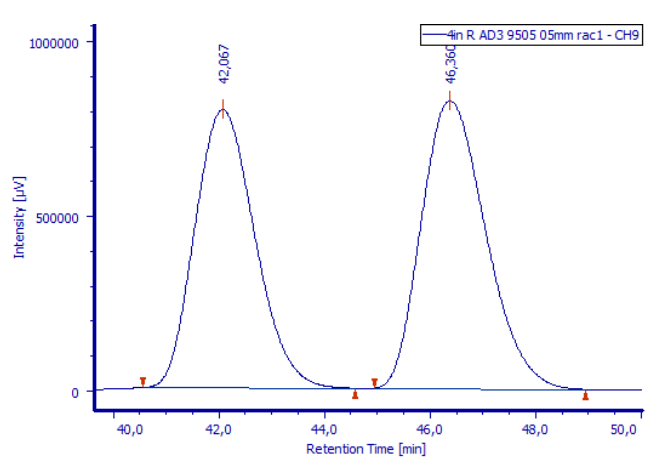
tR	Area	Height	Area%	Height%
30,413	63262657	639451	51,549	43,806
35,040	59461646	820267	48,451	56,194

(S)-6-(5,5-Dibenzyl-1,3-dioxan-2-yl)-2-hydroxy-2-methylnon-8-yn-3-one (4Bh)



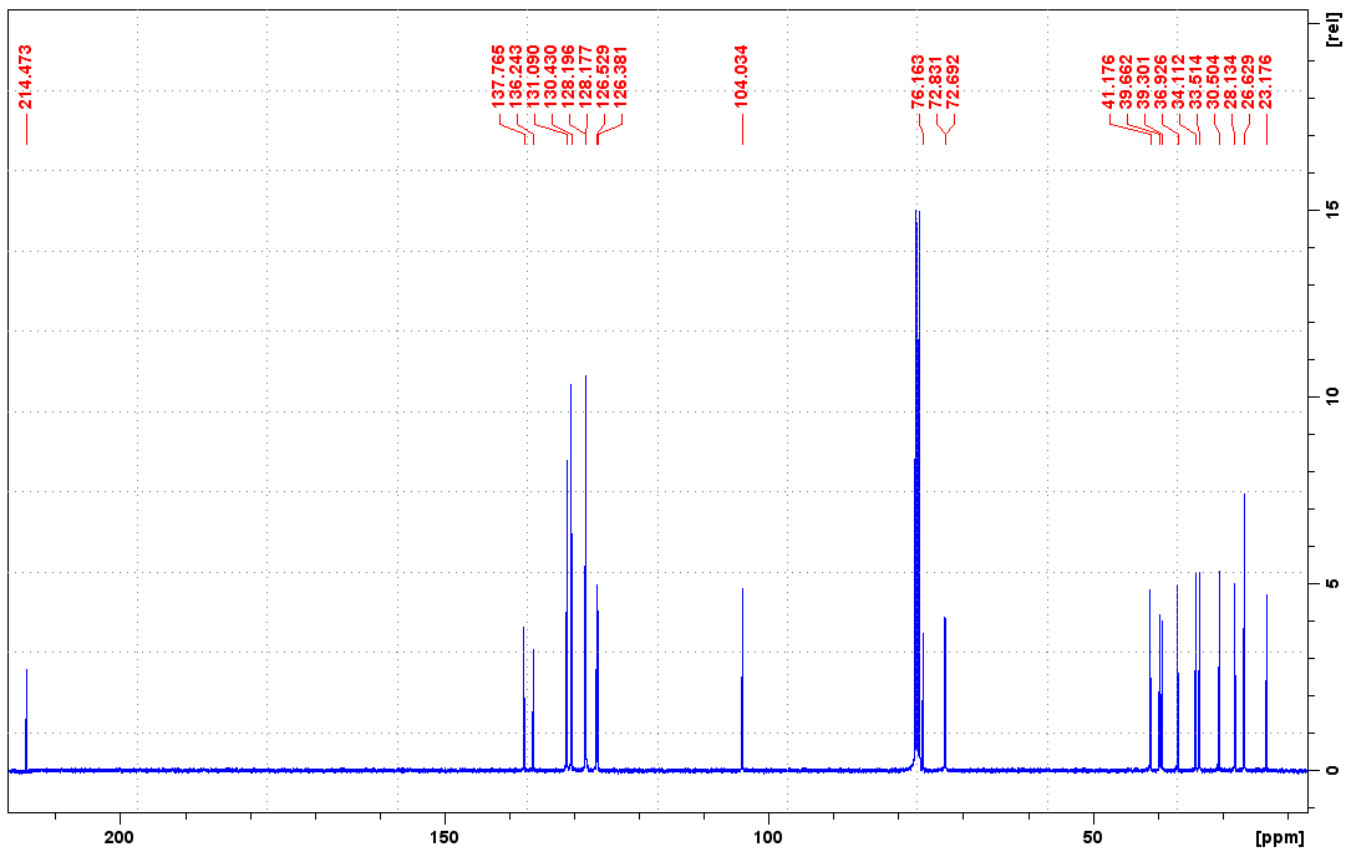
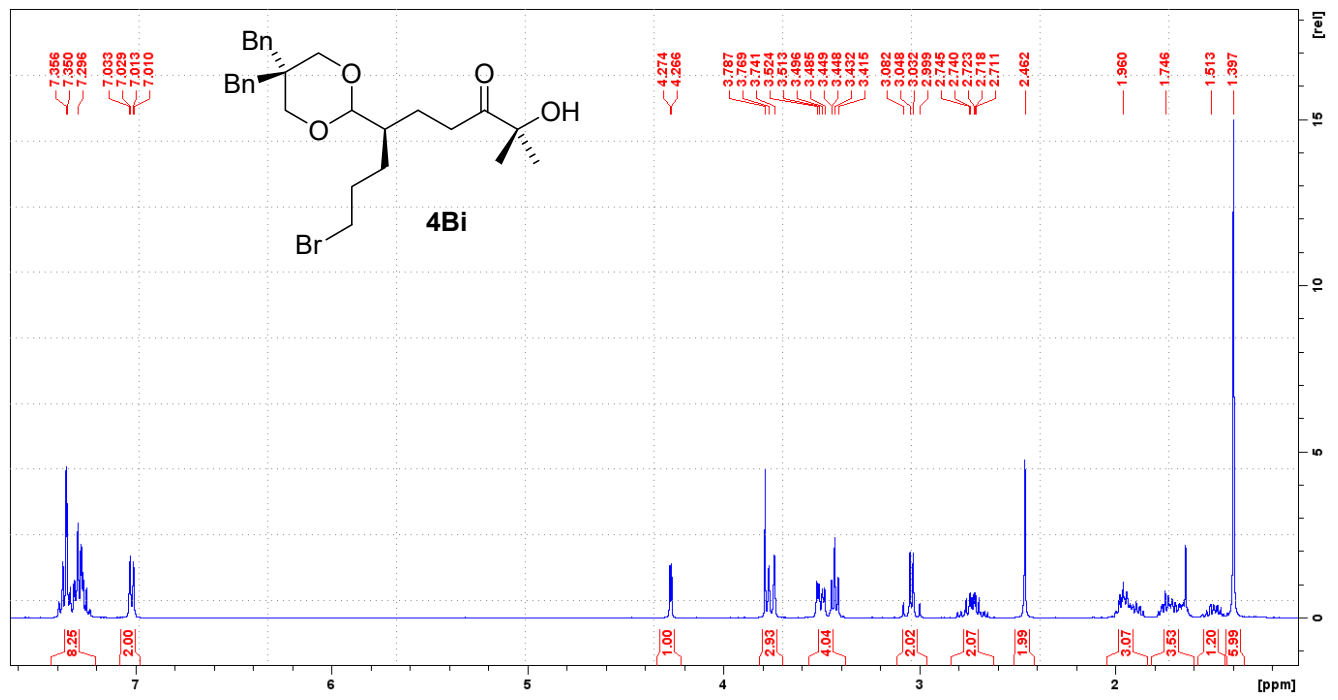


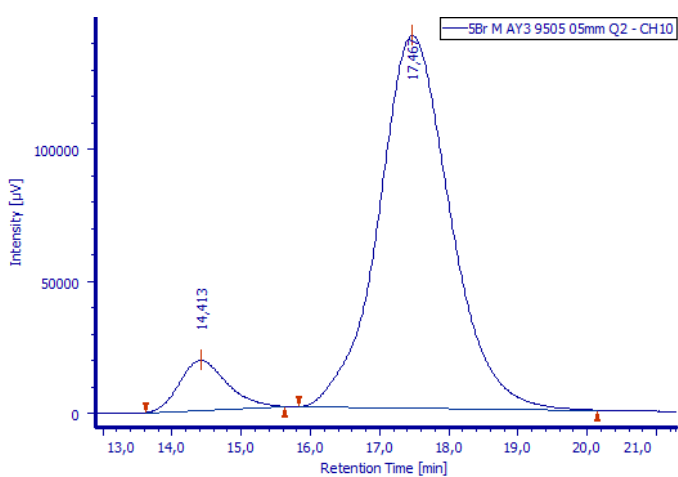
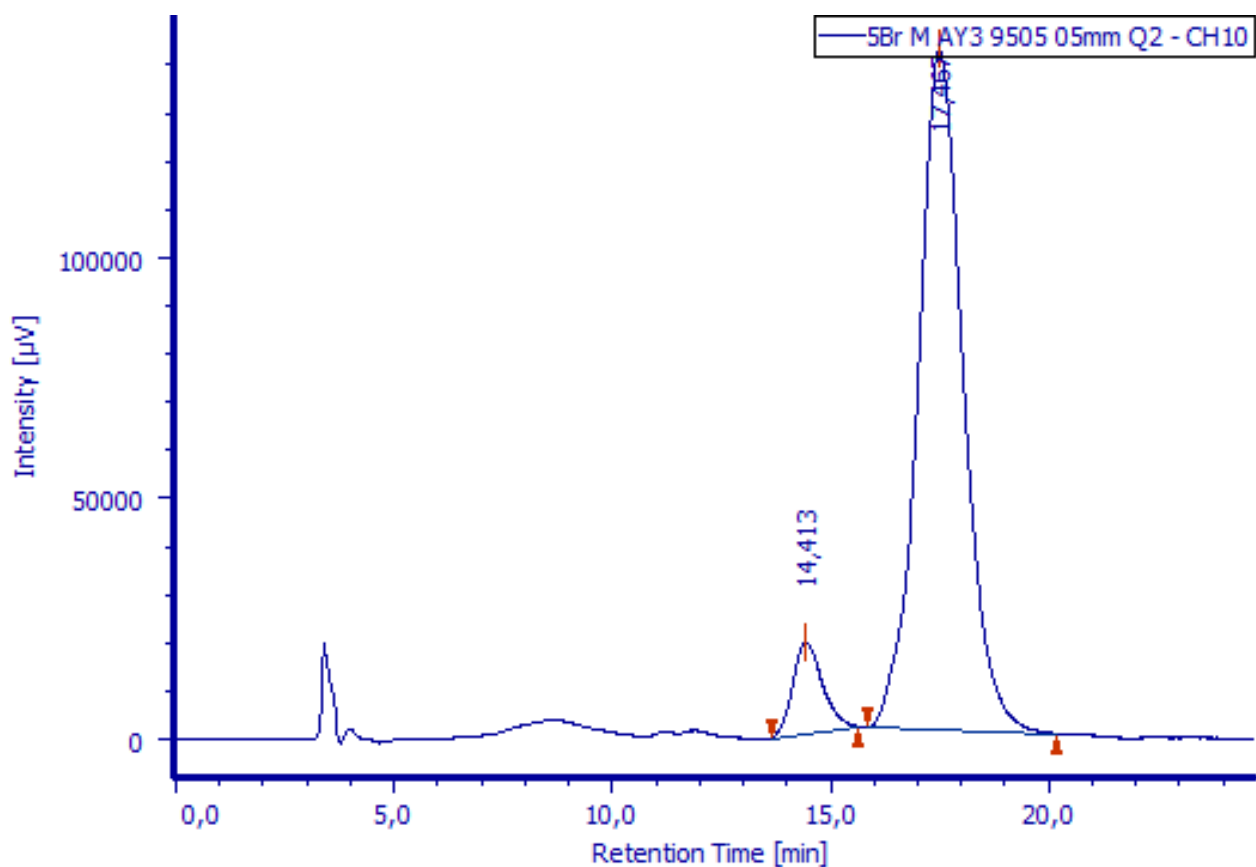
tR	Area	Height	Area%	Height%
43,413	112422587	1212551	95,878	95,490
48,067	4832941	57267	4,122	4,510



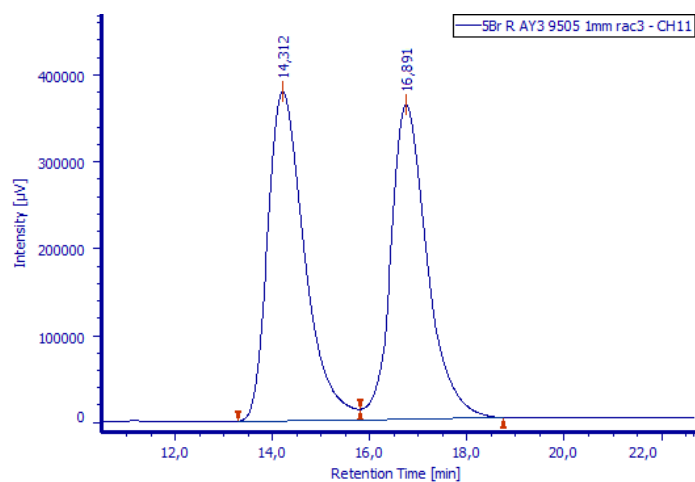
tR	Area	Height	Area%	Height%
42,067	62499942	794079	47,334	49,153
46,360	69540298	821440	52,666	50,847

(S)-6-(5,5-Dibenzyl-1,3-dioxan-2-yl)-9-bromo-2-hydroxy-2-methylnonan-3-one (4Bi)



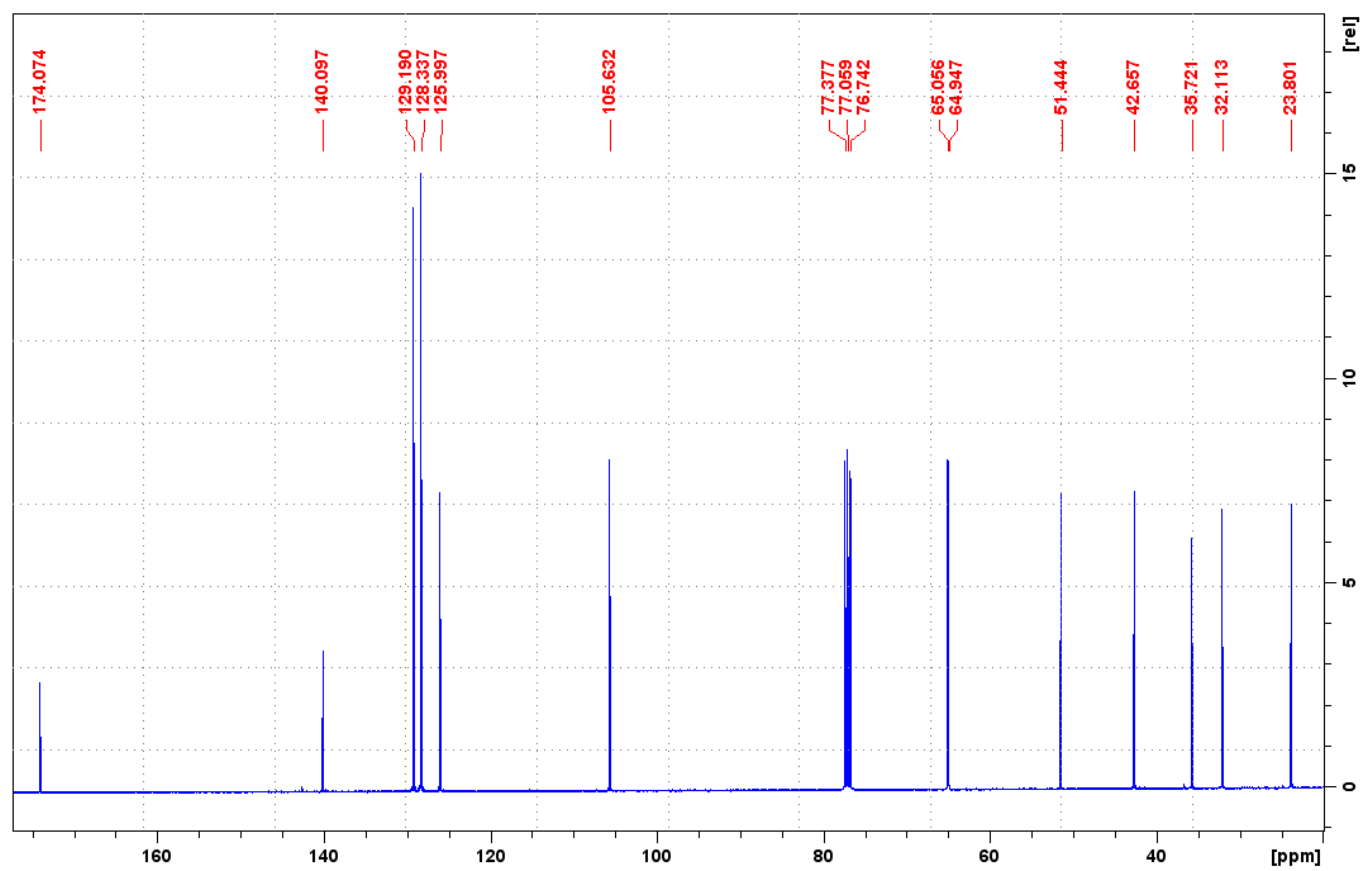
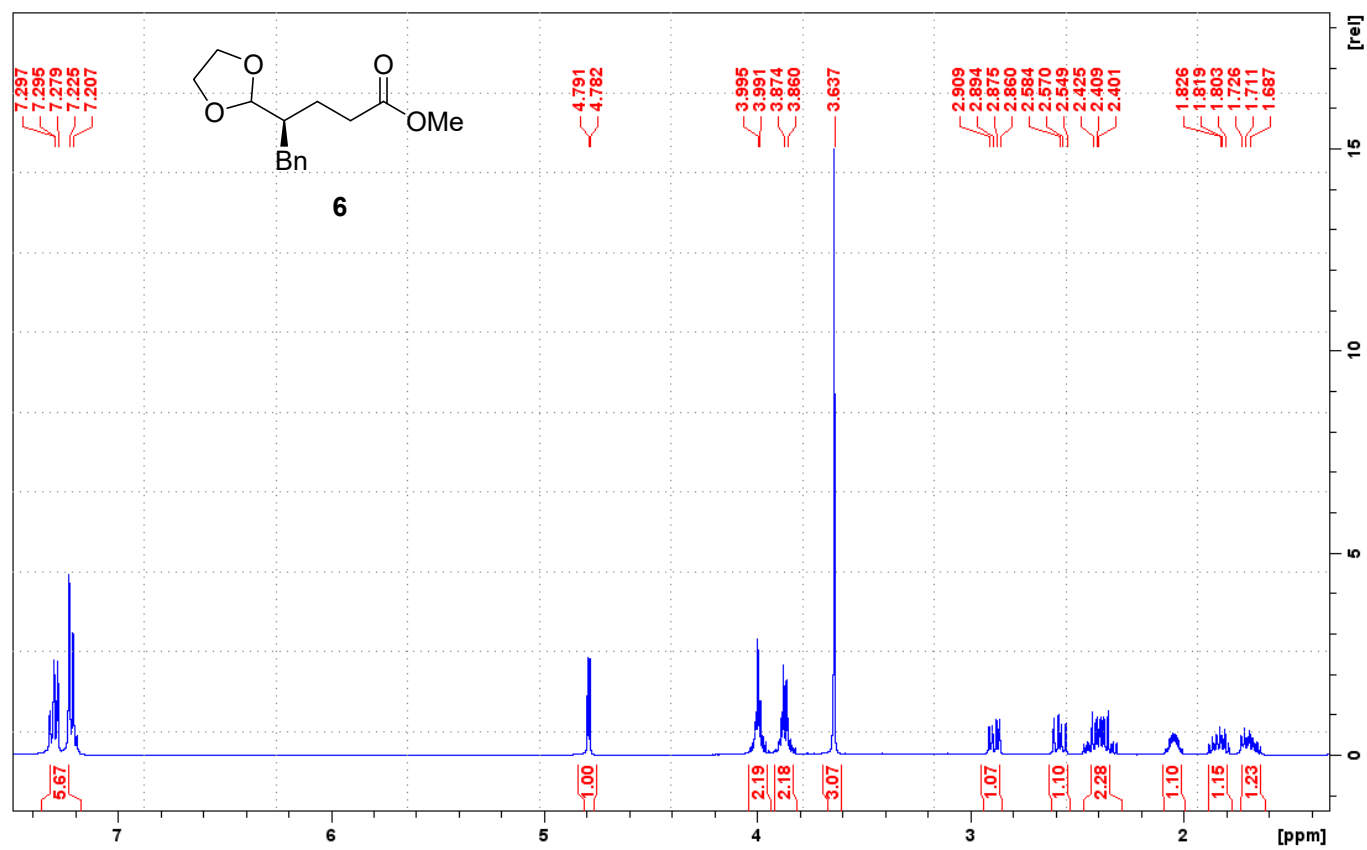


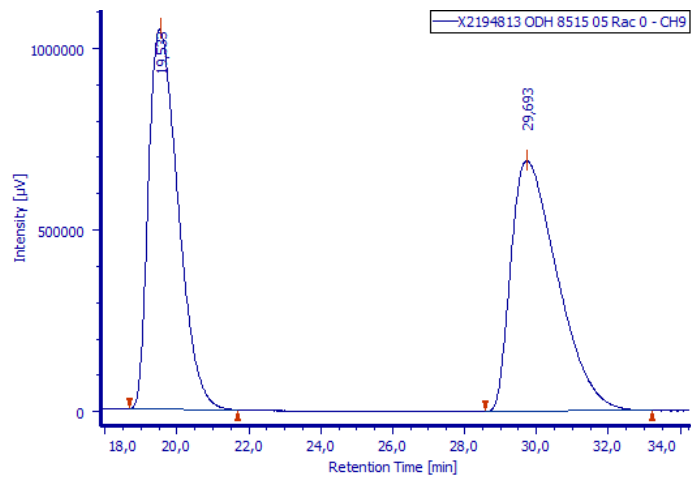
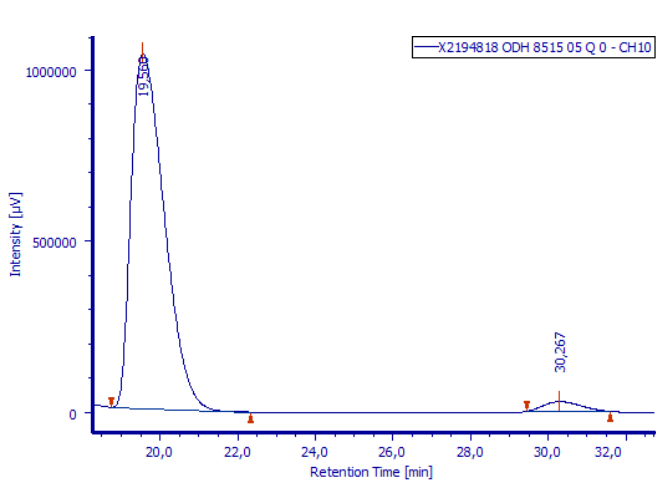
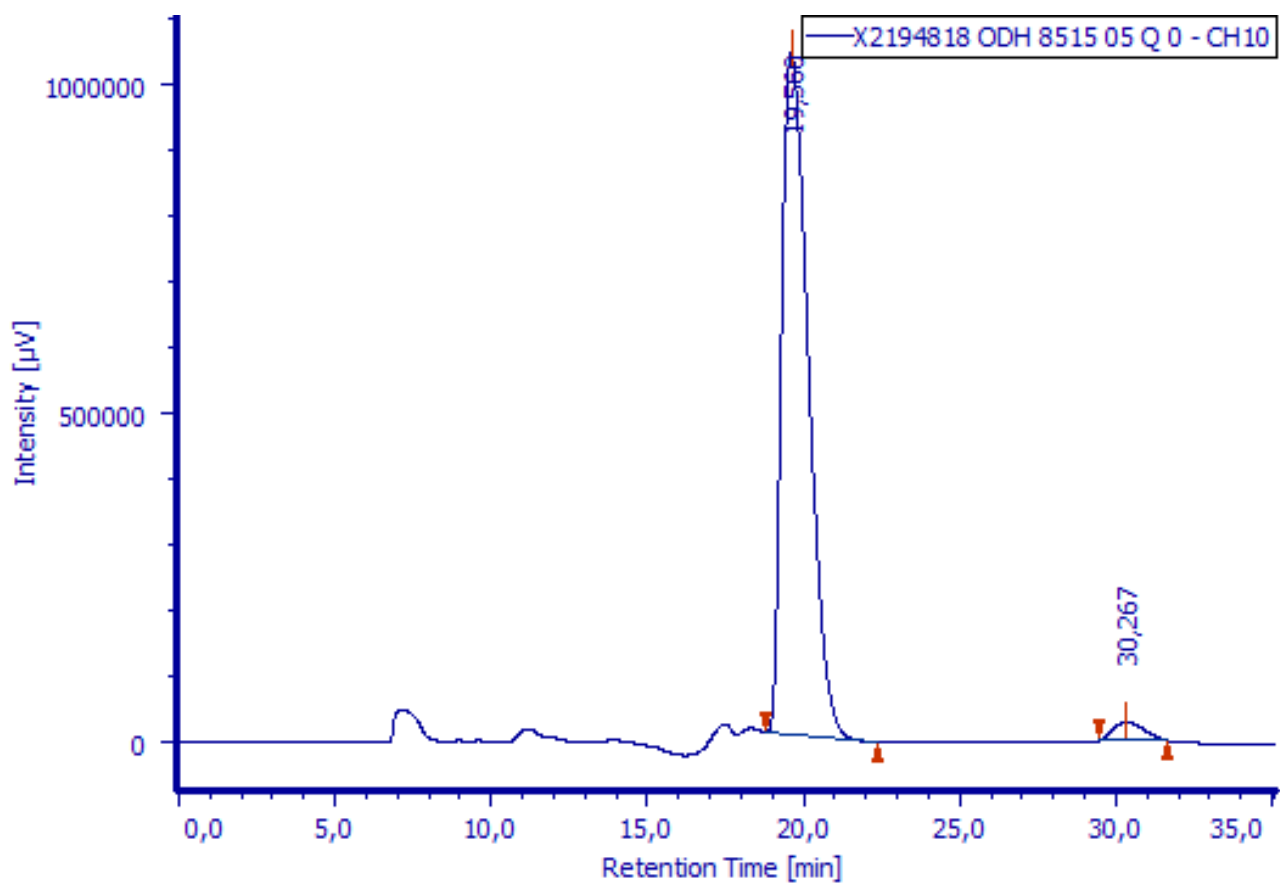
tR	Area	Height	Area%	Height%
14,413	795434	18834	7,302	11,816
17,467	10097874	140558	92,698	88,184



tR	Area	Height	Area%	Height%
14,312	20267751	387625	51,037	50,515
16,891	19443974	379725	48,963	49,485

(S)-Methyl 4-(1,3-dioxolan-2-yl)-5-phenylpentanoate (6)

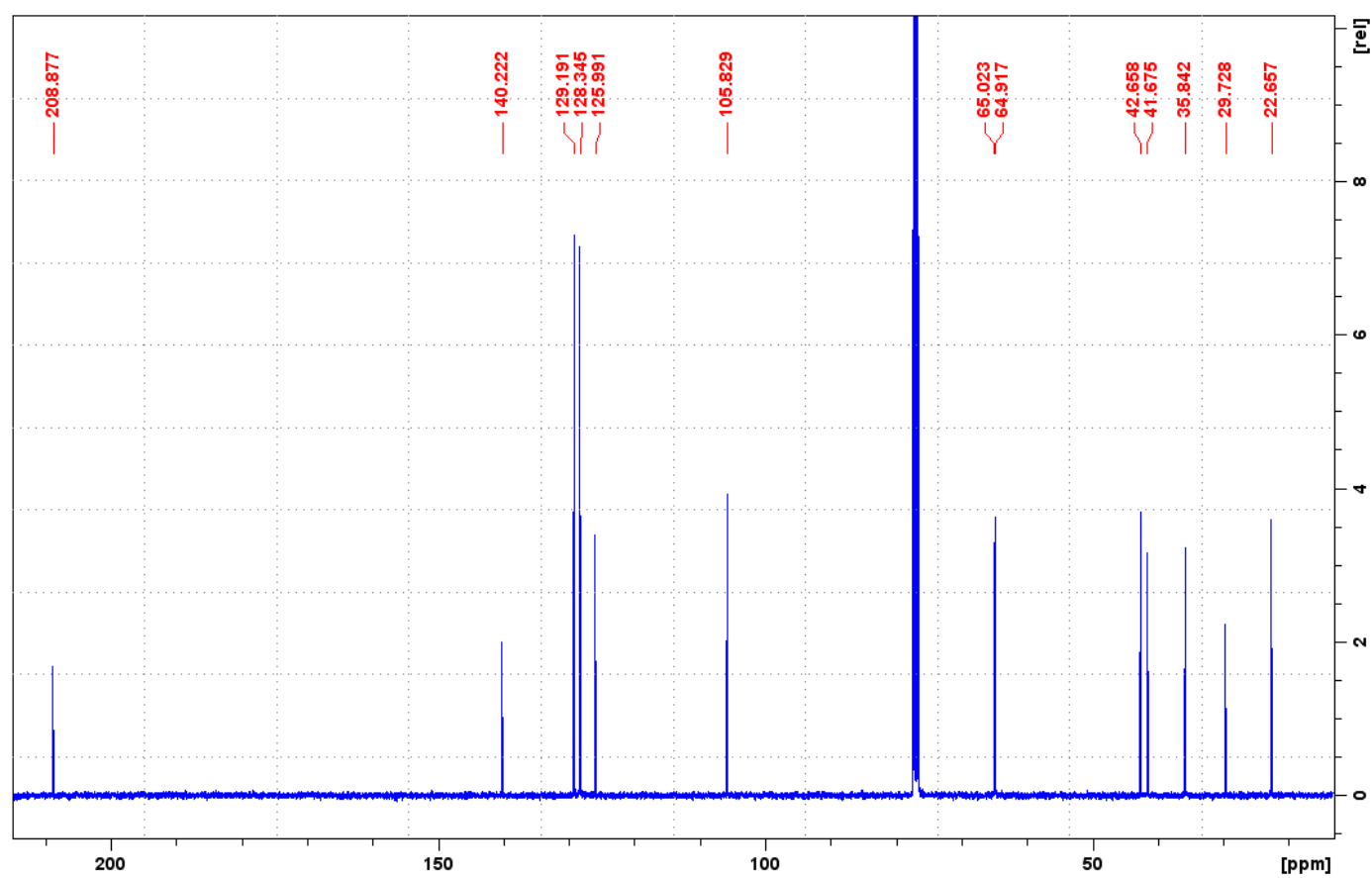
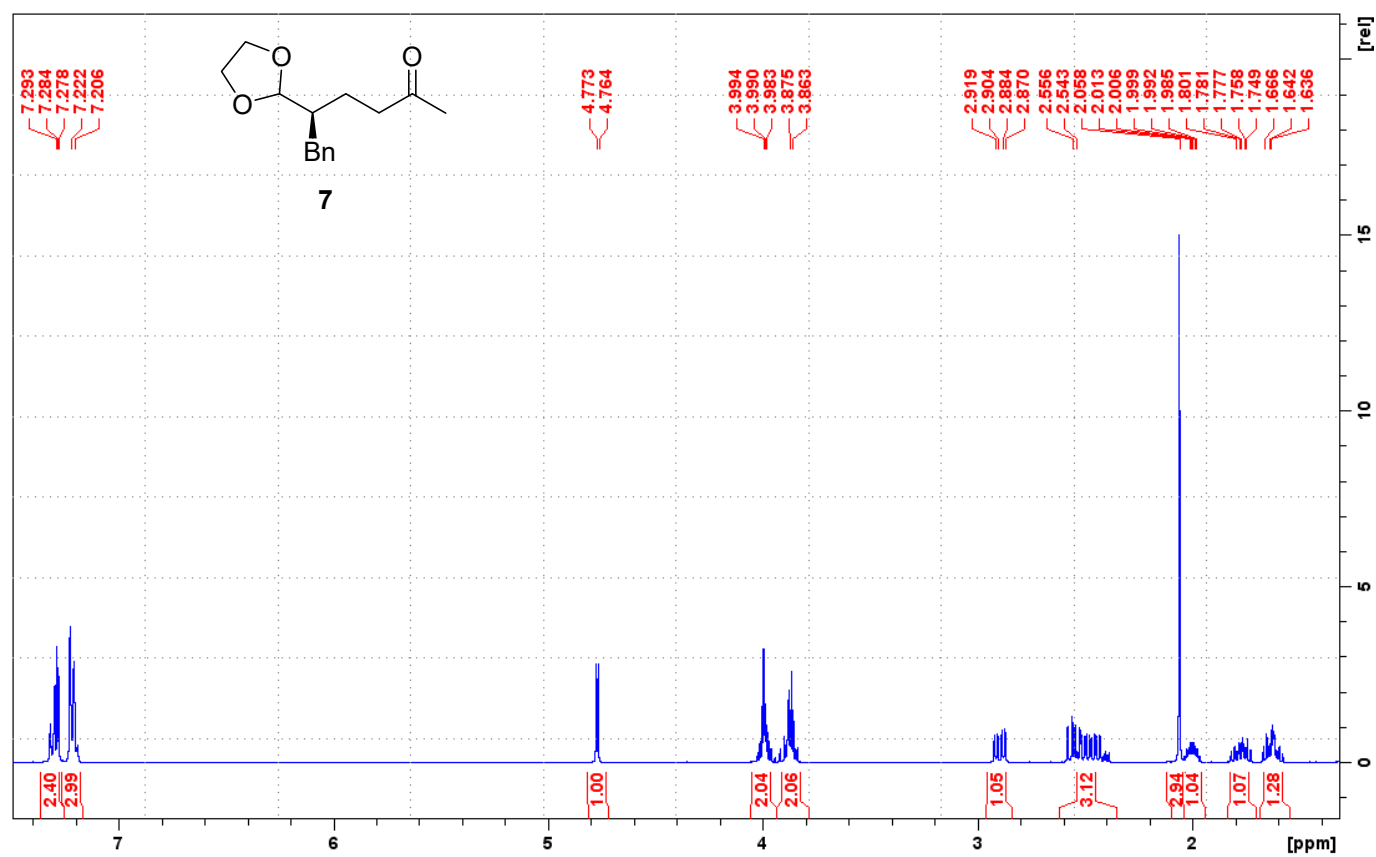


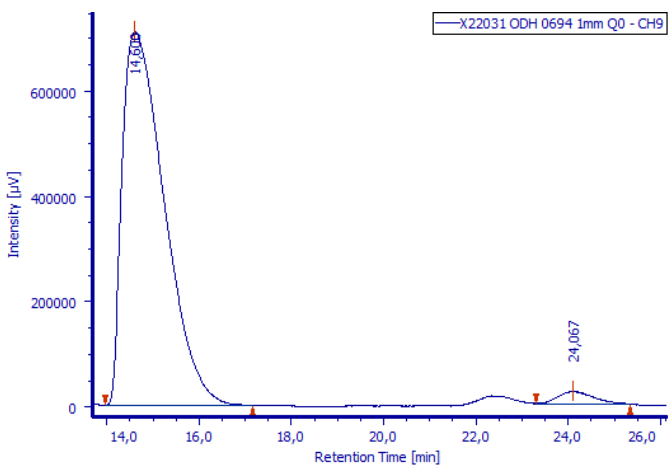
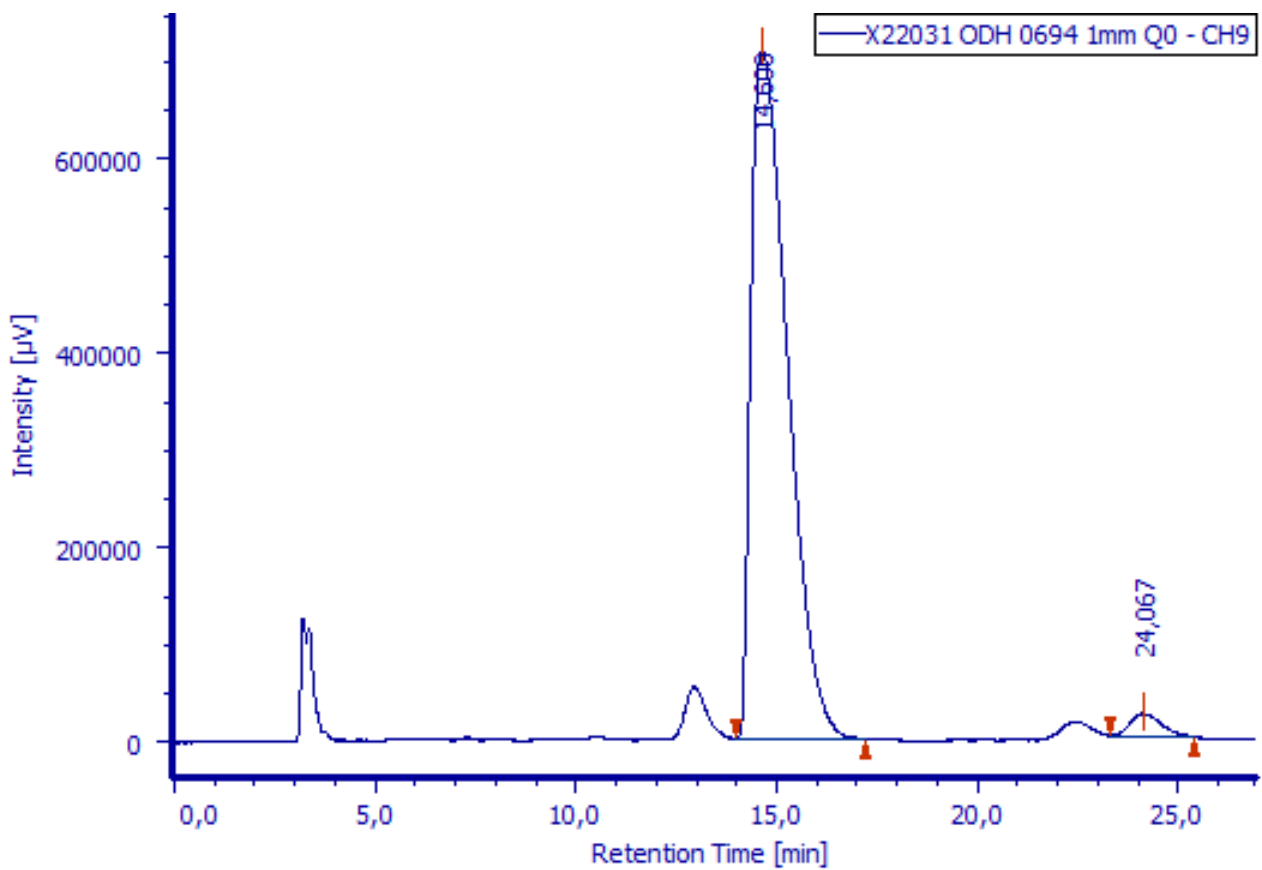


tR	Area	Height	Area%	Height%
19,560	61005327	1033986	96,982	97,329
30,267	1898717	28377	3,018	2,671

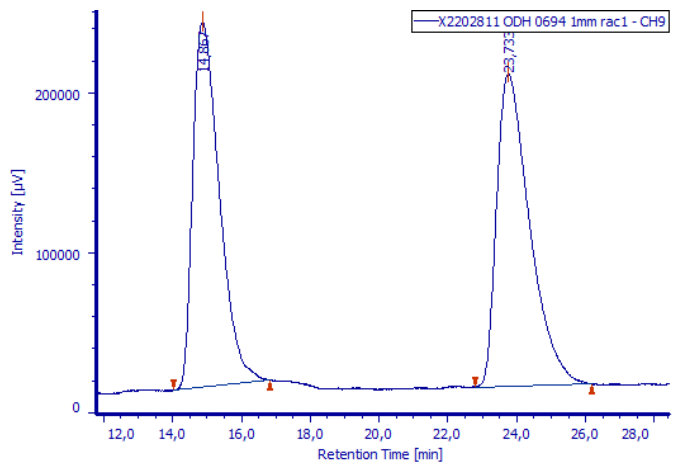
tR	Area	Height	Area%	Height%
19,533	59383223	1041670	49,037	60,207
29,693	61714823	688473	50,963	39,793

(S)-5-(1,3-dioxolan-2-yl)-6-phenylhexan-2-one (7)



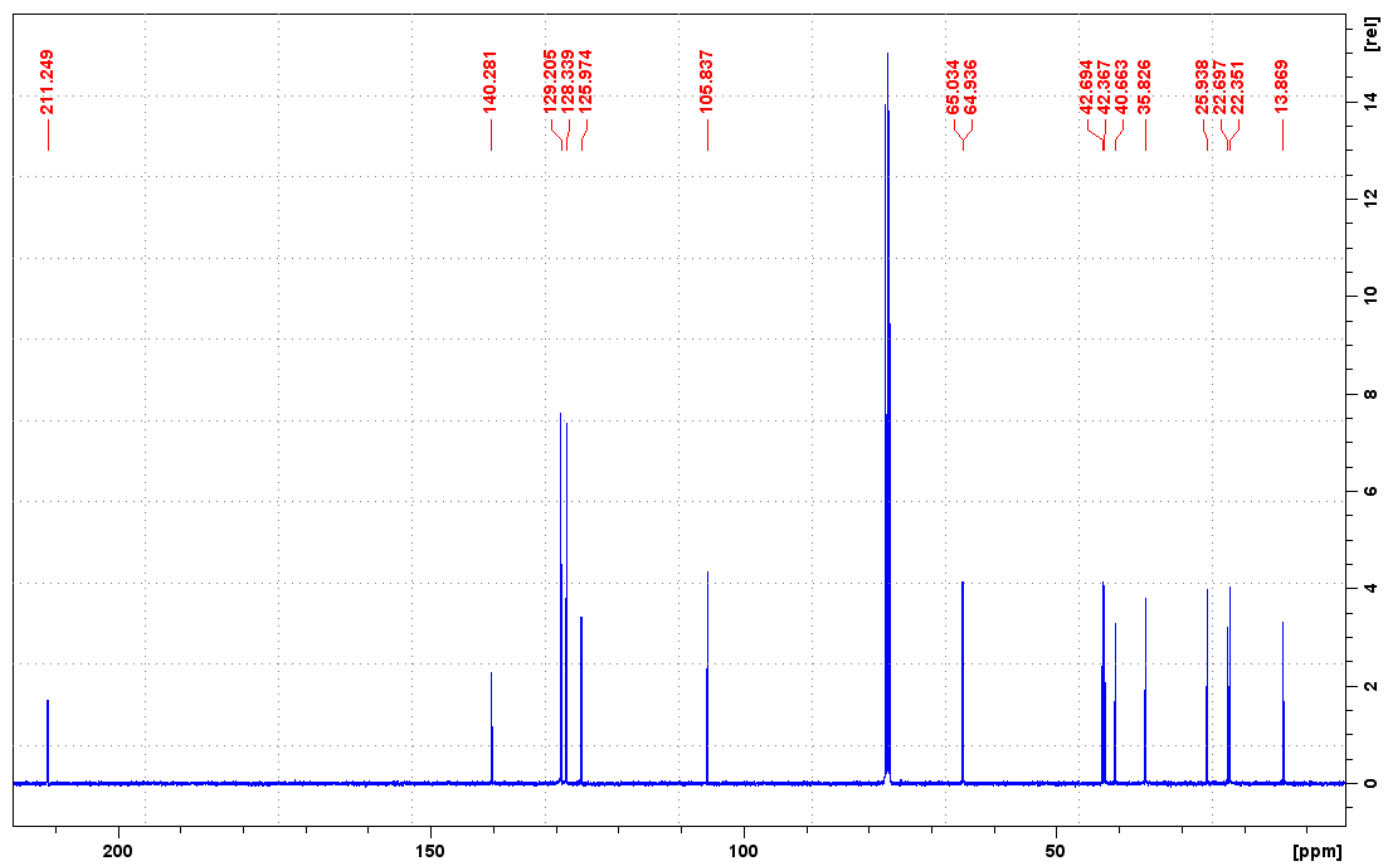
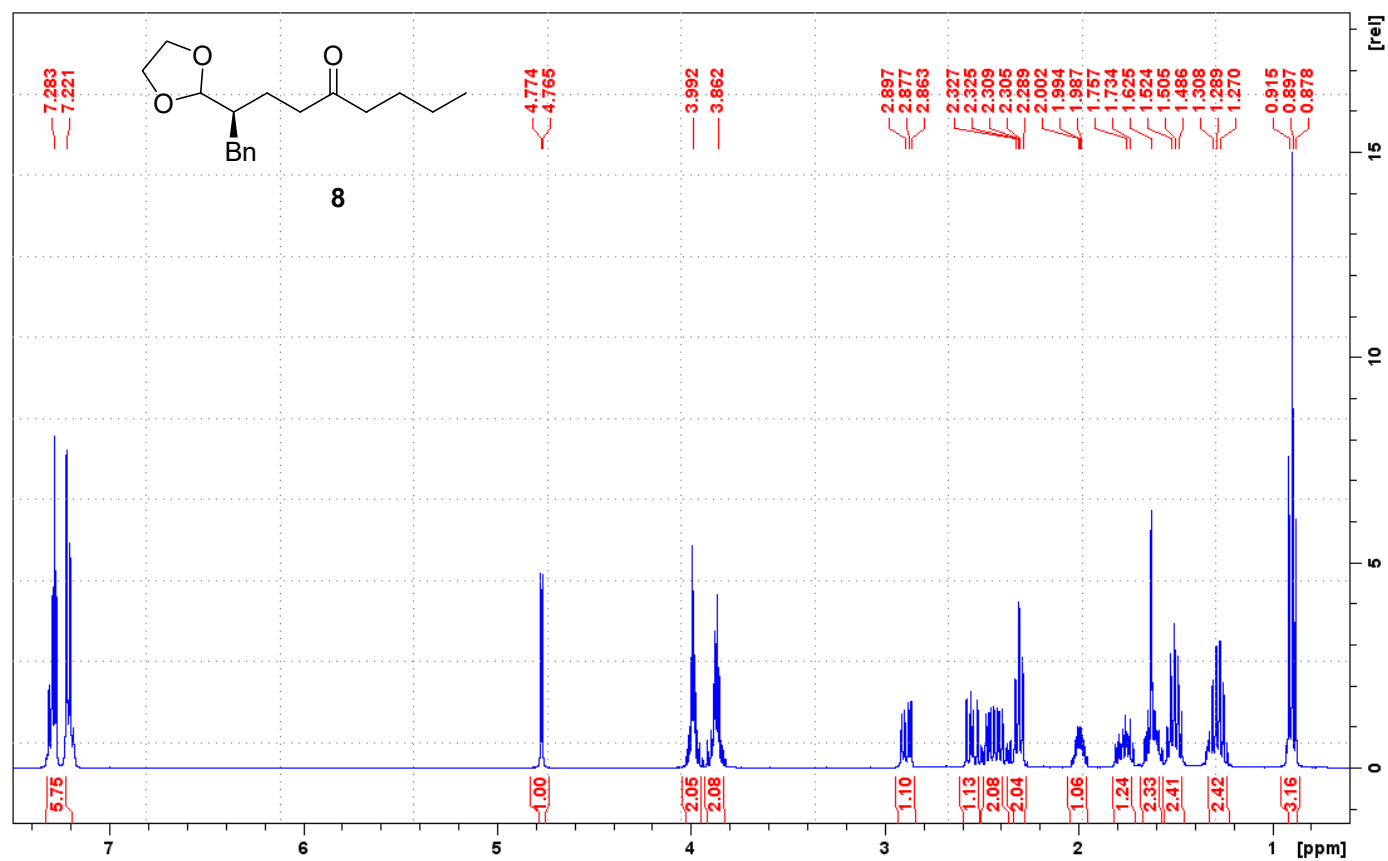


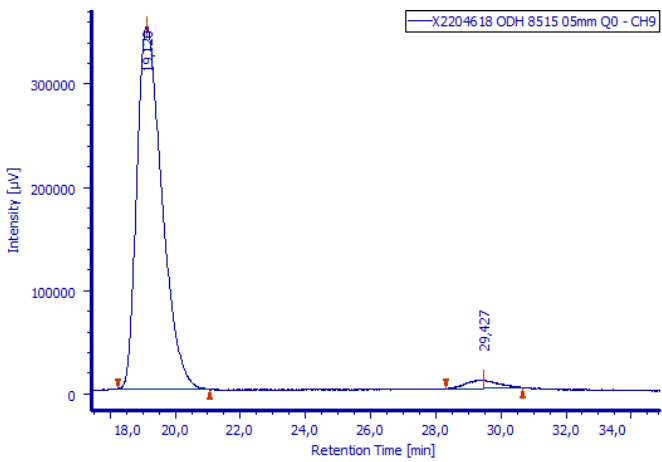
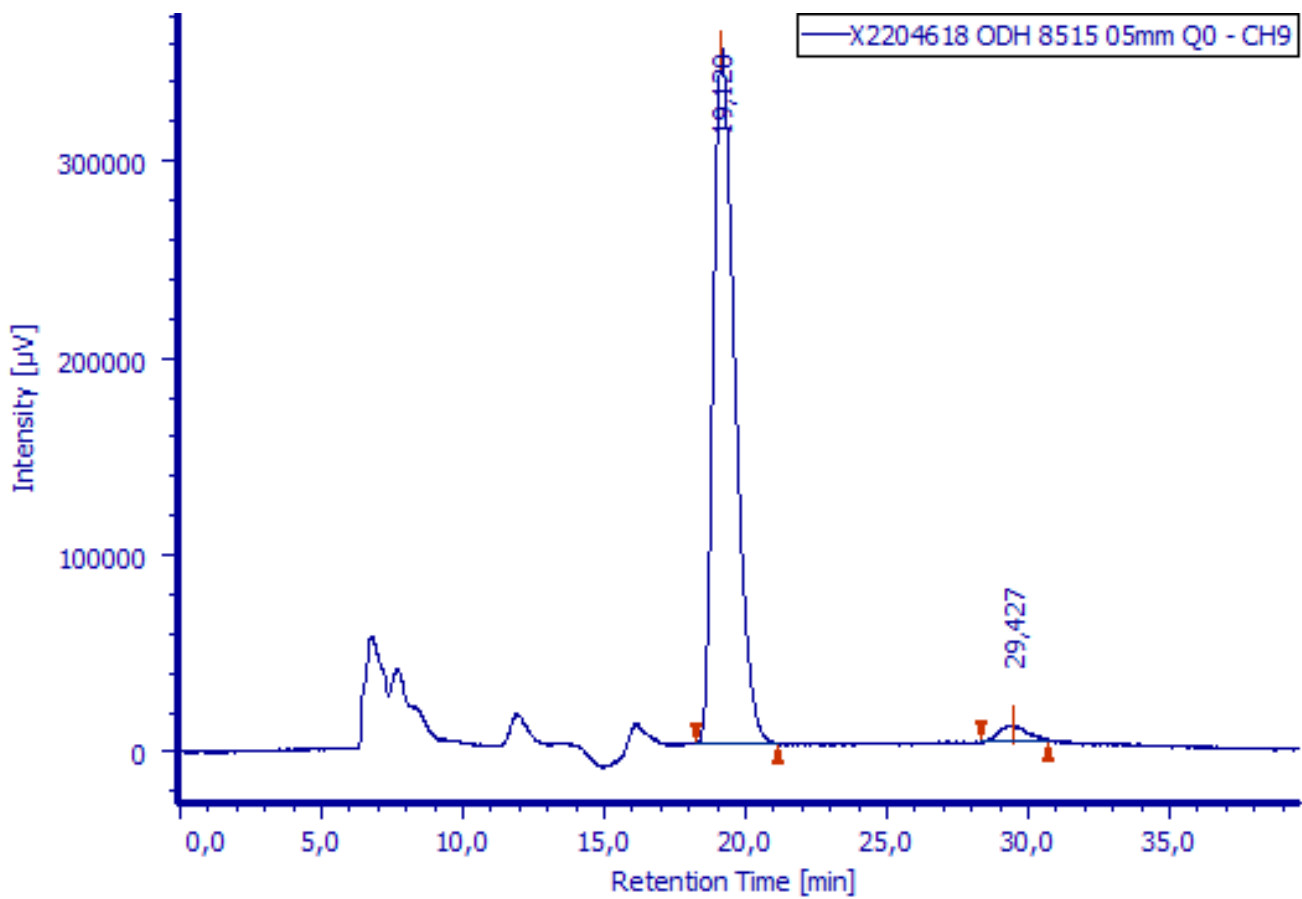
tR	Area	Height	Area%	Height%
14,600	44636853	707137	97,352	96,812
24,067	1214201	23285	2,648	3,188



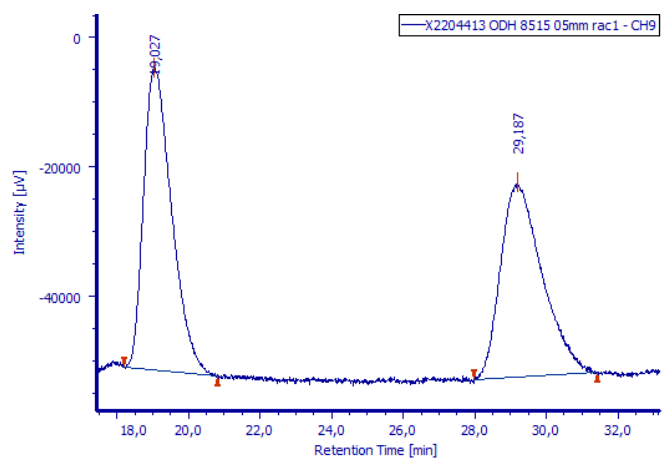
tR	Area	Height	Area%	Height%
14,867	12210511	227749	48,619	53,881
23,733	12904378	194940	51,381	46,119

(S)-2-(1,3-dioxolan-2-yl)-1-phenylnonan-5-one (8)



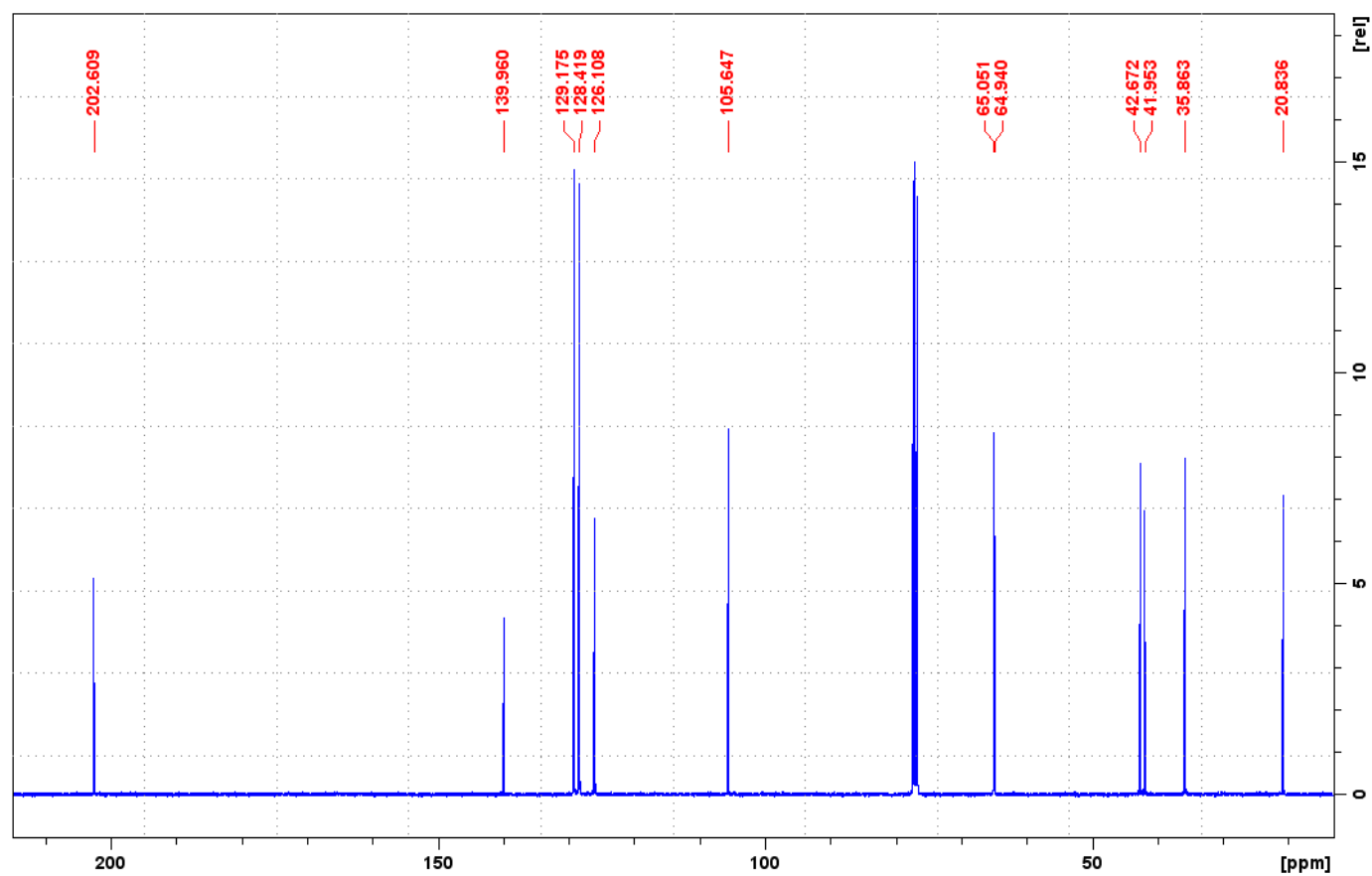
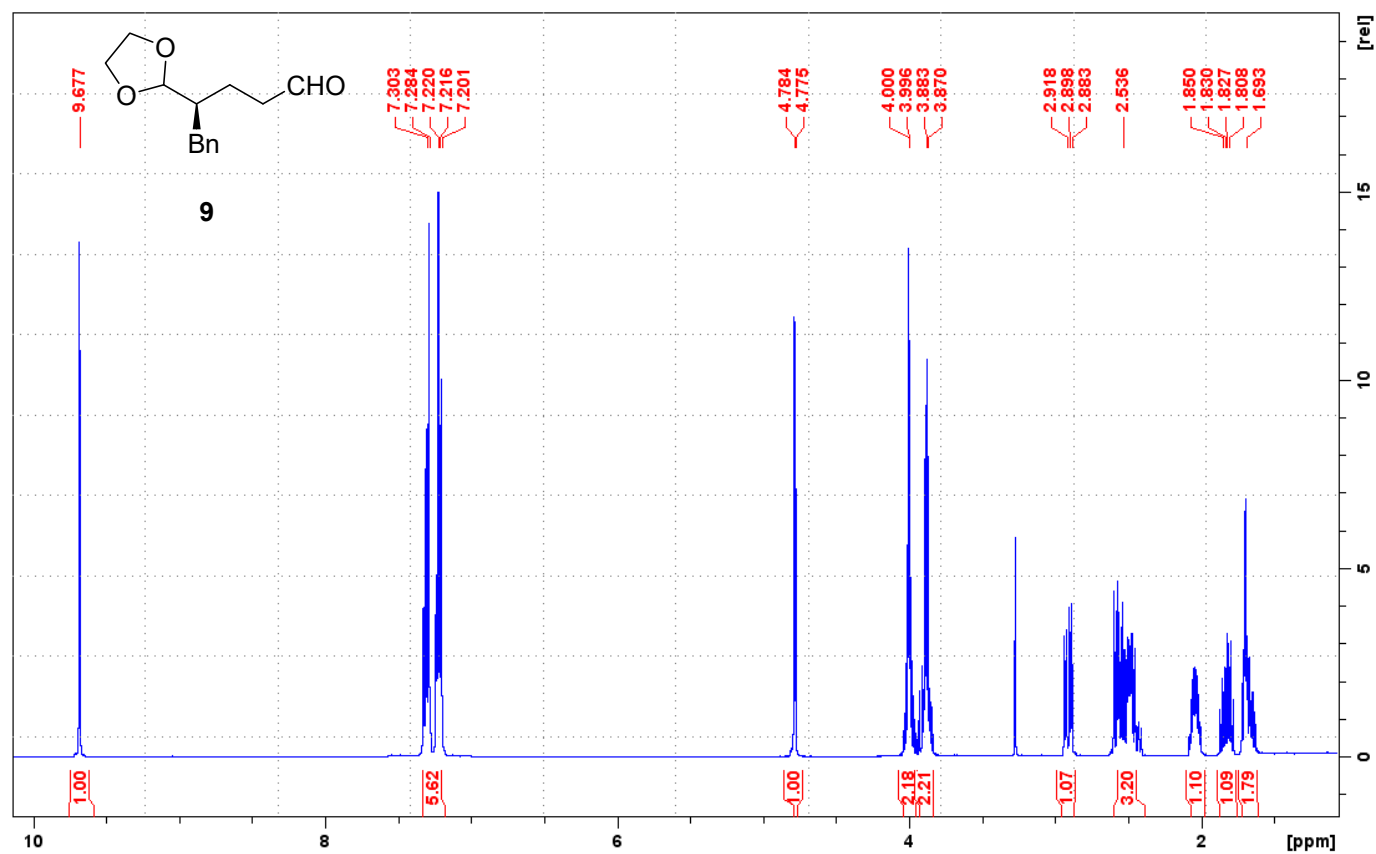


tR	Area	Height	Area%	Height%
19,120	18729645	350177	97,347	97,856
29,427	510432	7673	2,653	2,144

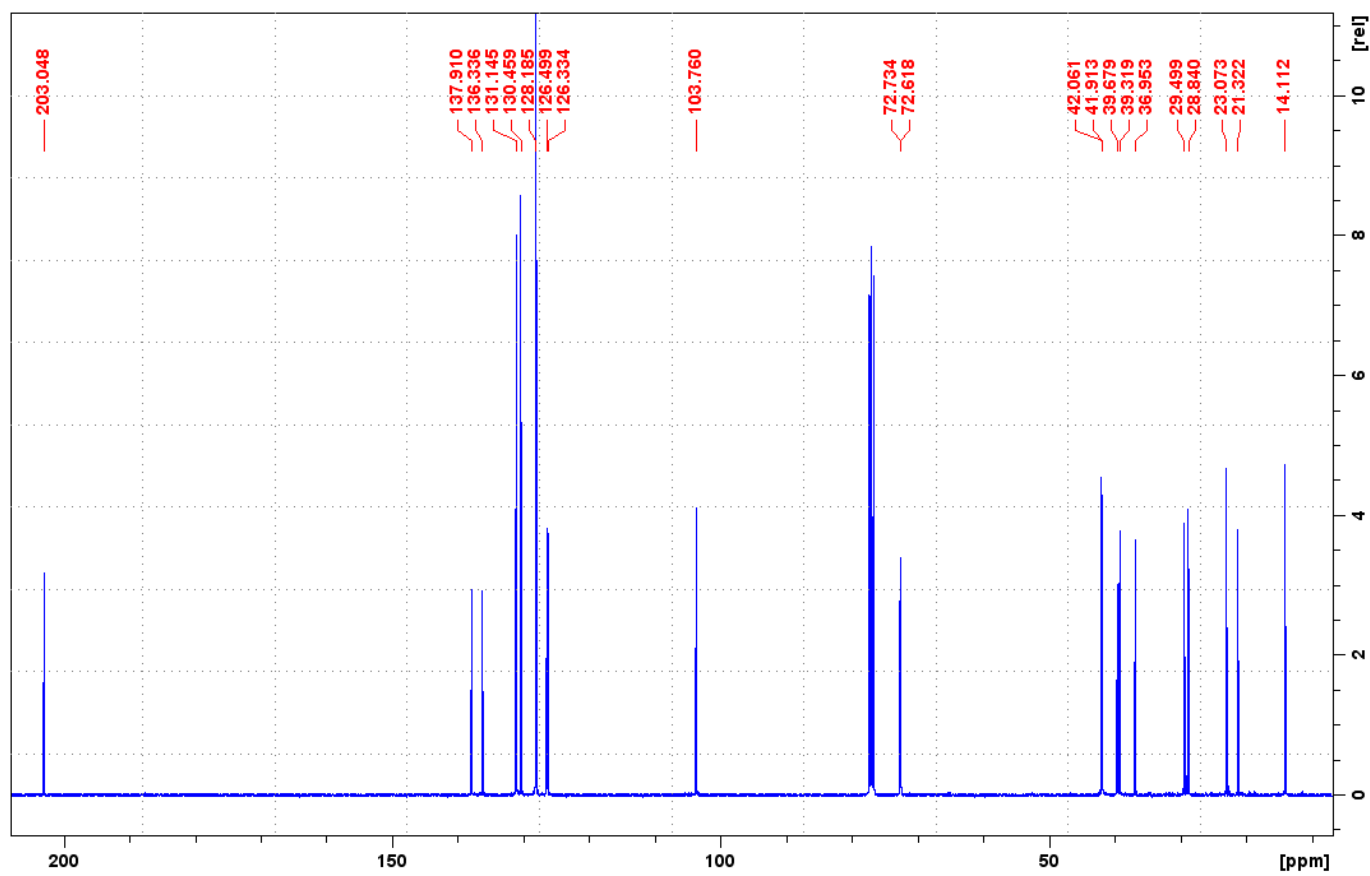
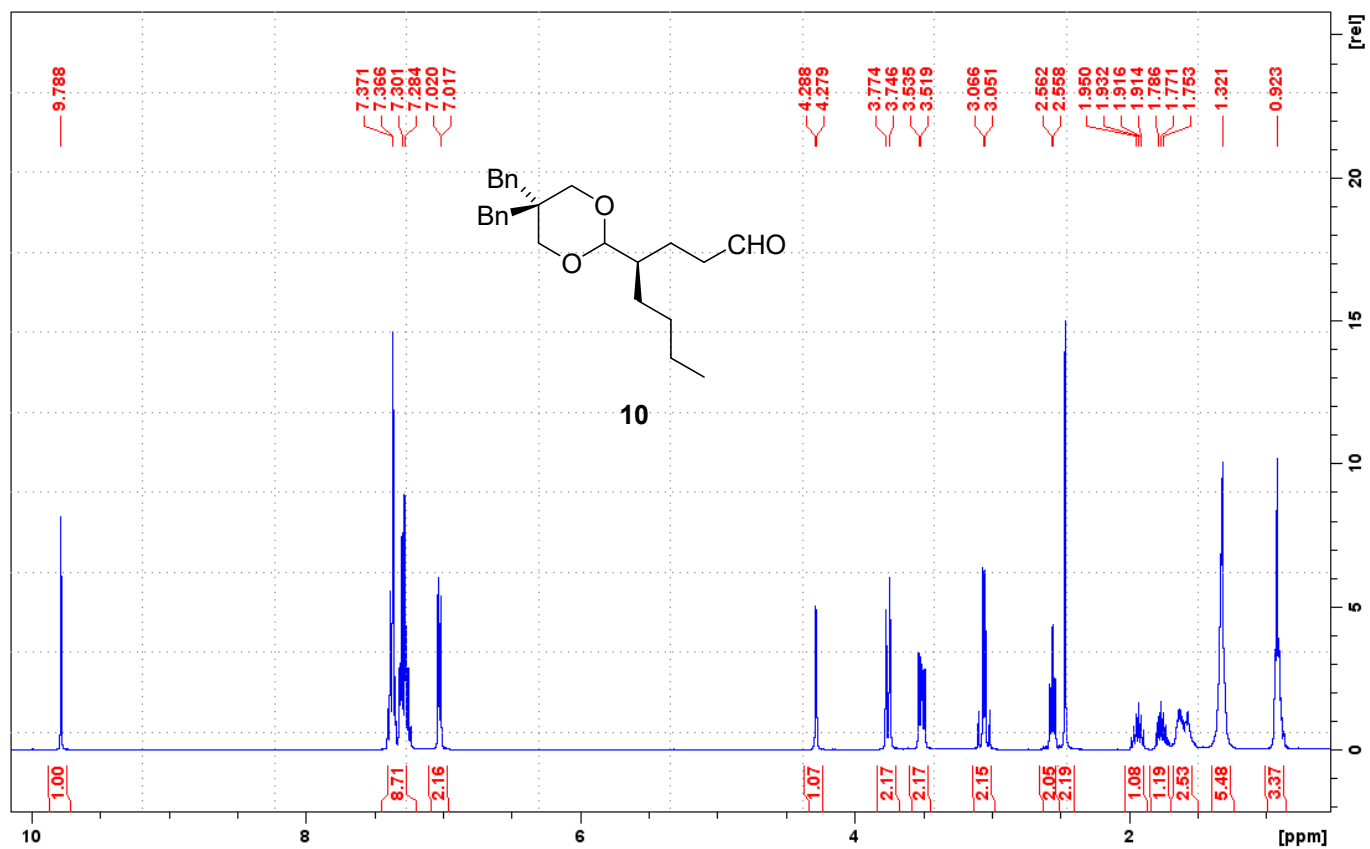


tR	Area	Height	Area%	Height%
19,027	2531938	46503	51,445	60,910
29,187	2389746	29844	48,555	39,090

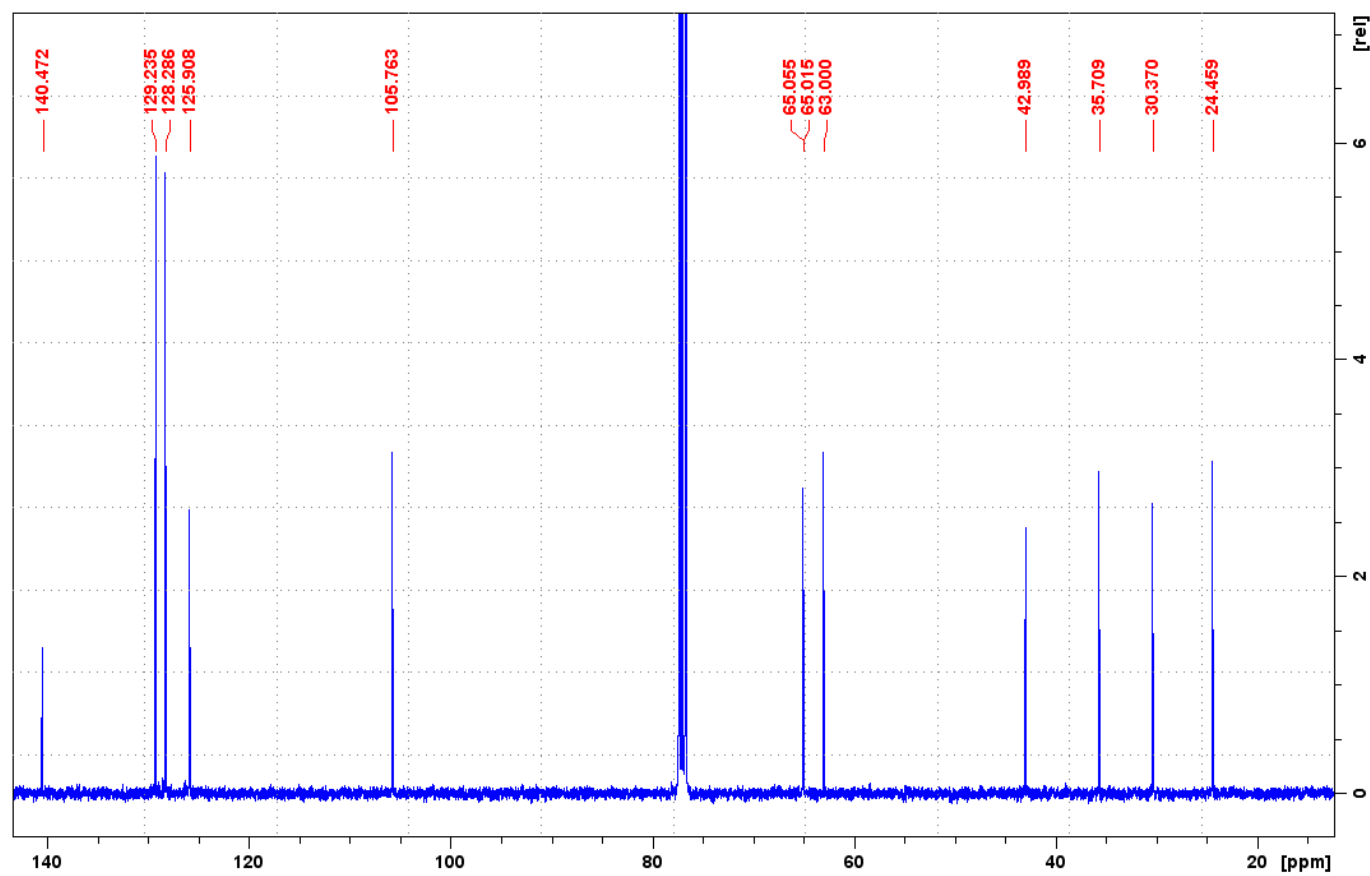
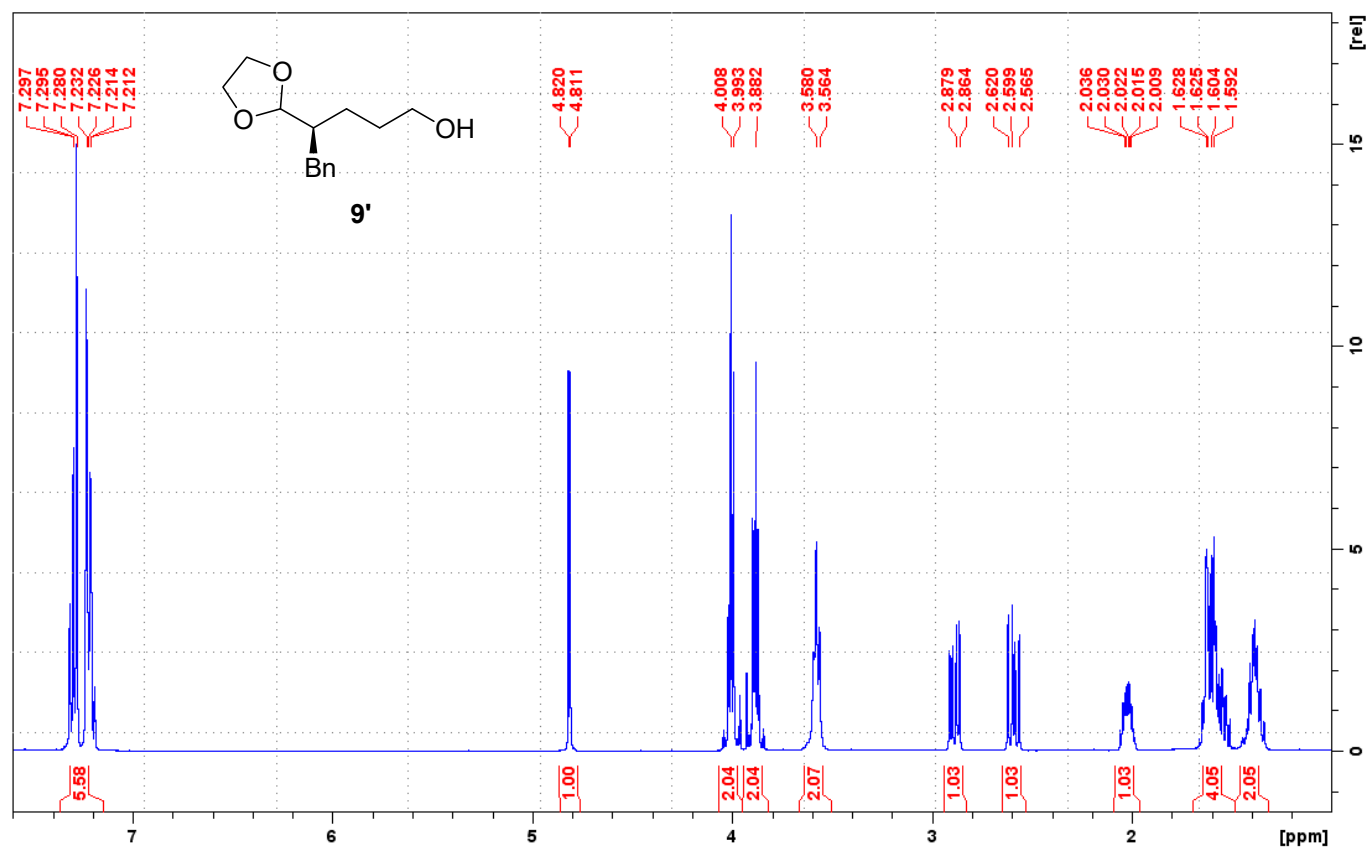
(S)-4-(1,3-dioxolan-2-yl)-5-phenylpentanal (9)

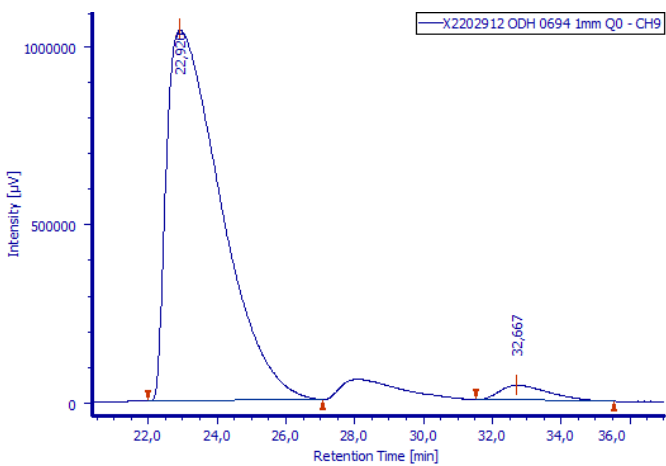
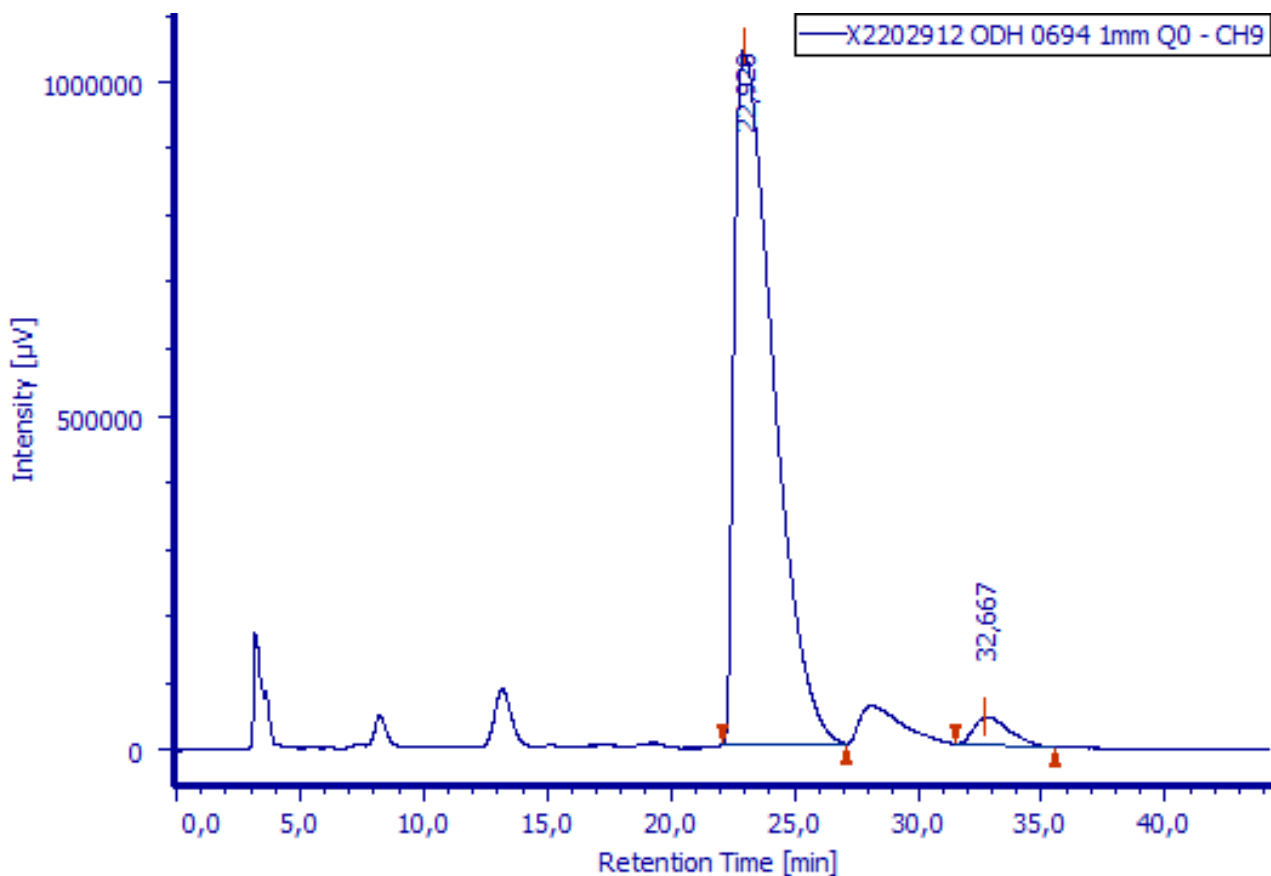


(R)-4-(5,5-dibenzyl-1,3-dioxan-2-yl)octanal (10)

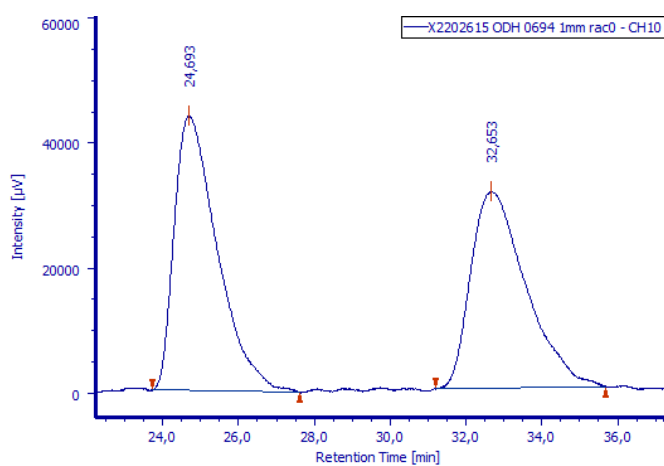


(S)-4-(1,3-dioxolan-2-yl)-5-phenylpentan-1-ol (9')



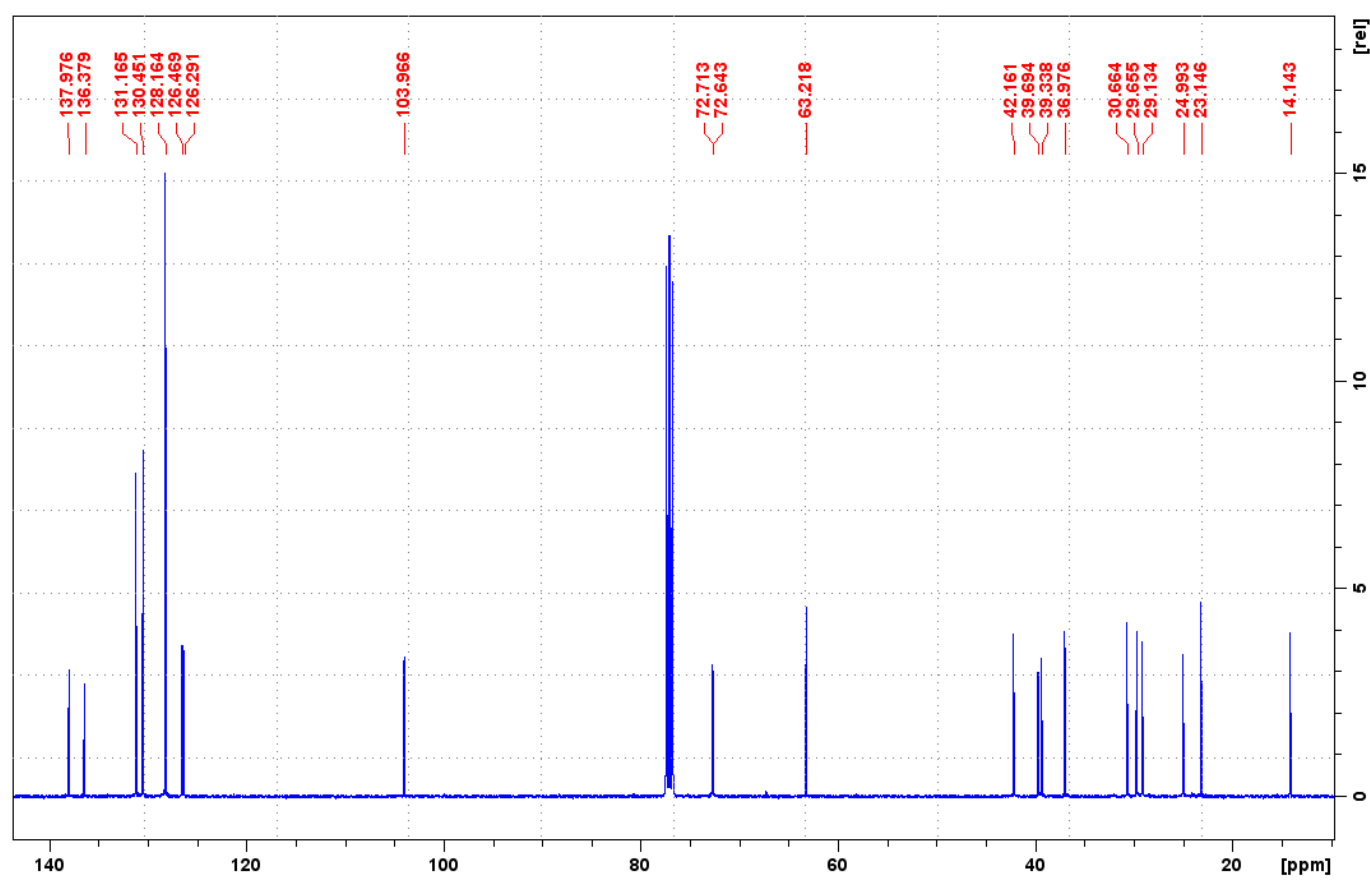
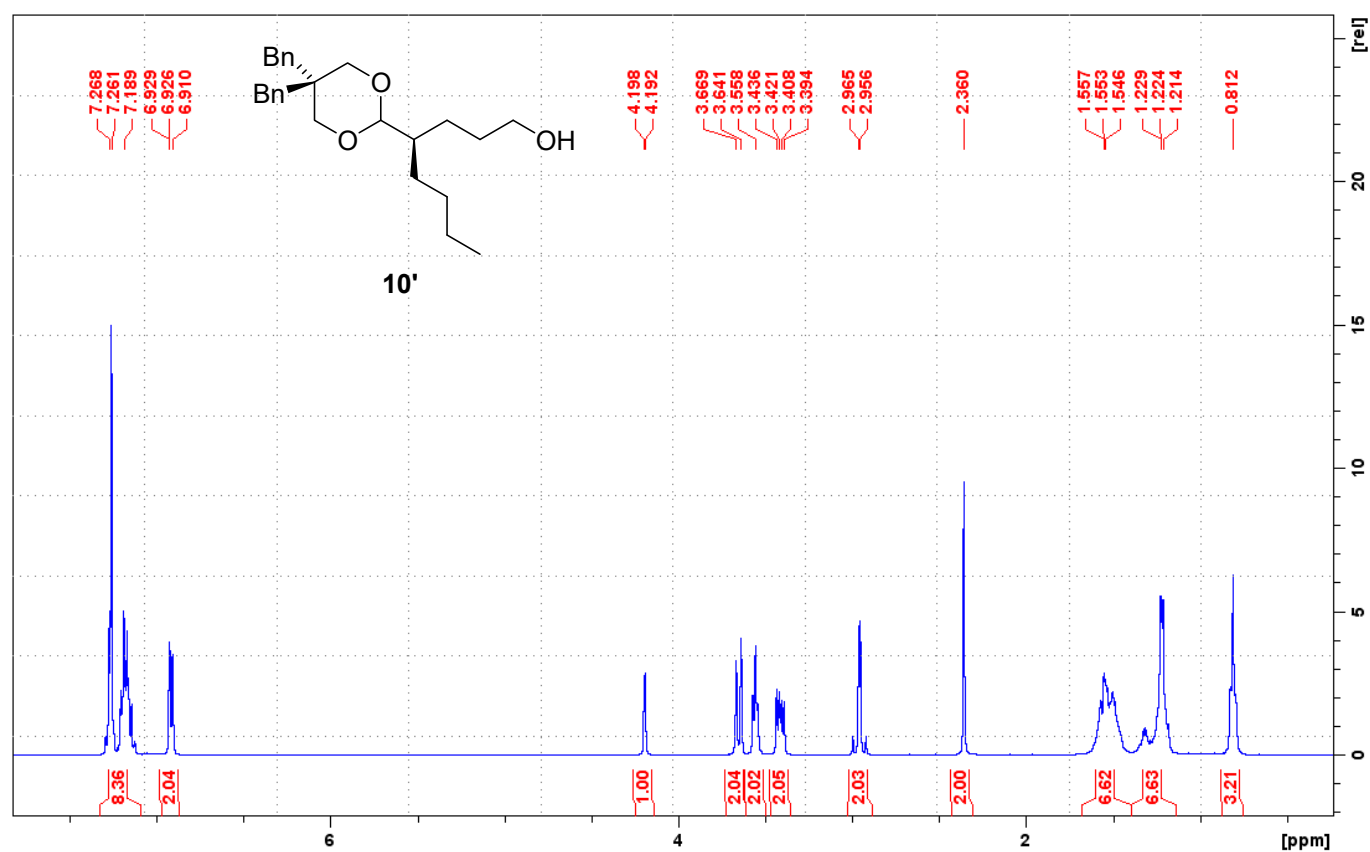


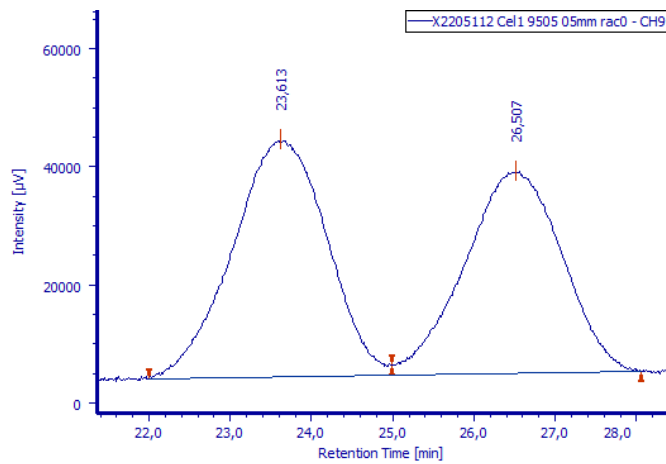
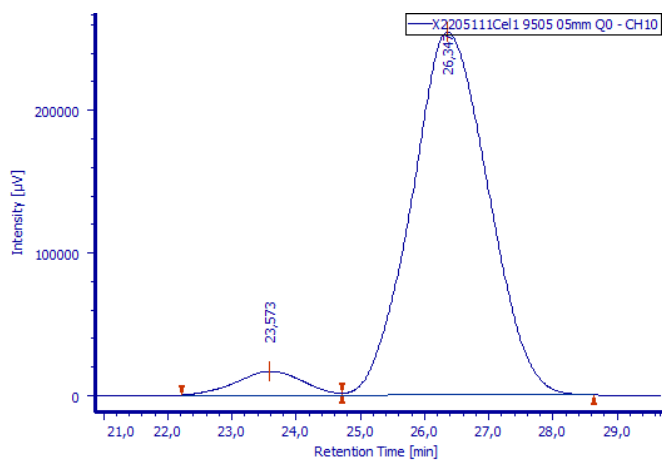
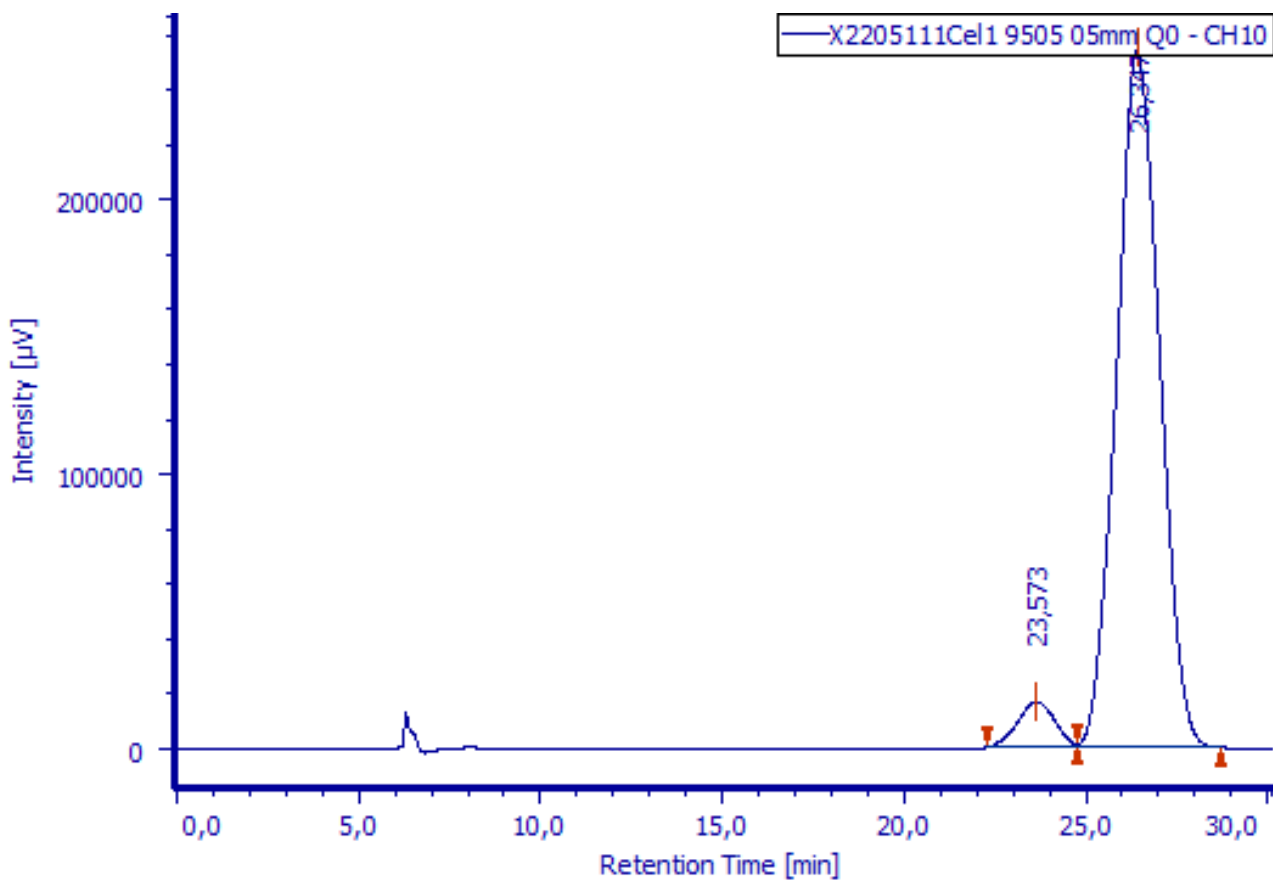
tR	Area	Height	Area%	Height%
22,920	85029089	779791	96,888	96,297
32,707	2730700	29989	3,112	3,703



tR	Area	Height	Area%	Height%
24,693	3454331	43799	52,141	58,316
32,653	3170631	31308	47,859	41,684

(R)-4-(5,5-dibenzyl-1,3-dioxan-2-yl)octan-1-ol (10')





tR	Area	Height	Area%	Height%
23,573	1188176	16593	5,368	6,140
26,347	20944924	253668	94,632	93,860

tR	Area	Height	Area%	Height%
23,613	3218006	40034	53,193	53,996
26,507	2831655	34108	46,807	46,004