

Asymmetric α -Sulfonyl- and α -Phosphoryl-oxylation of Ketones by a Chiral Hypervalent Iodine(III)

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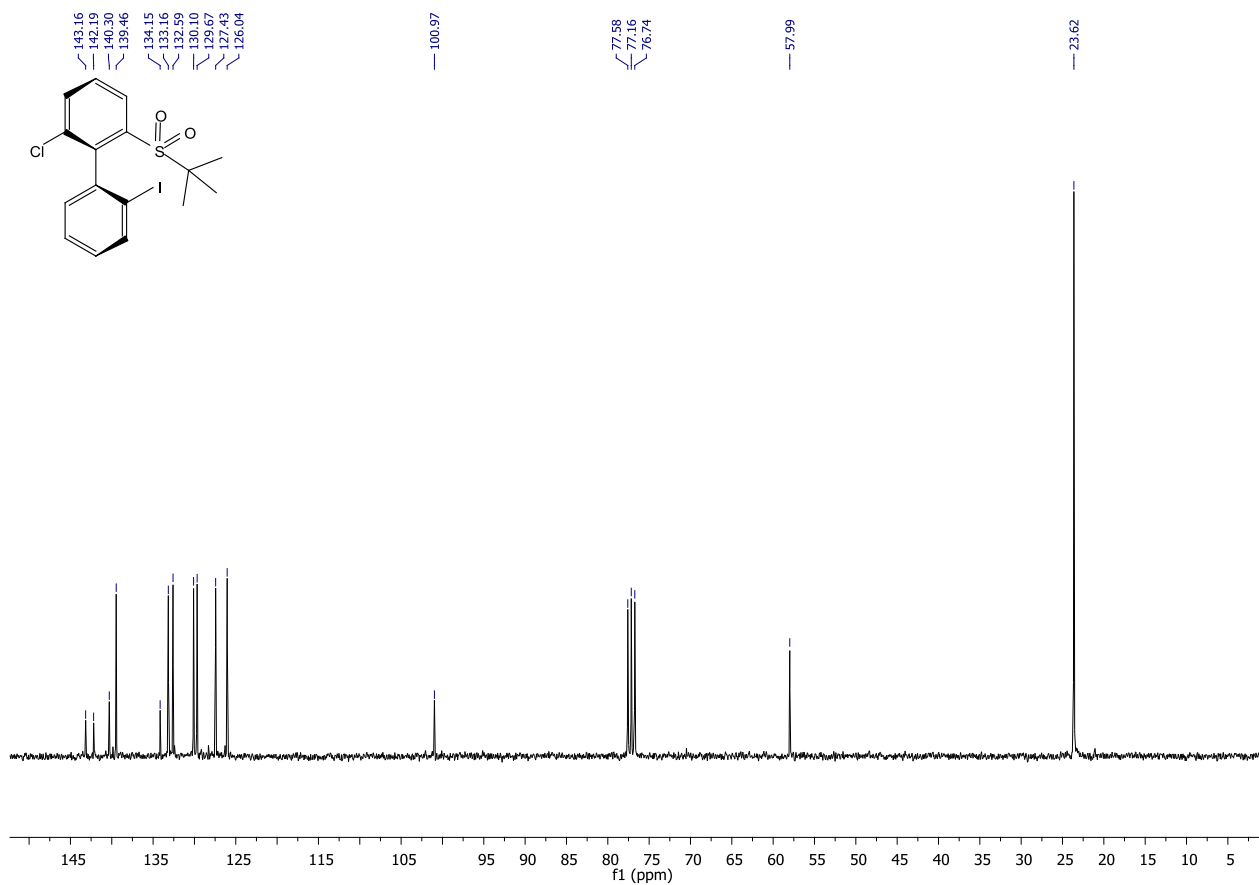
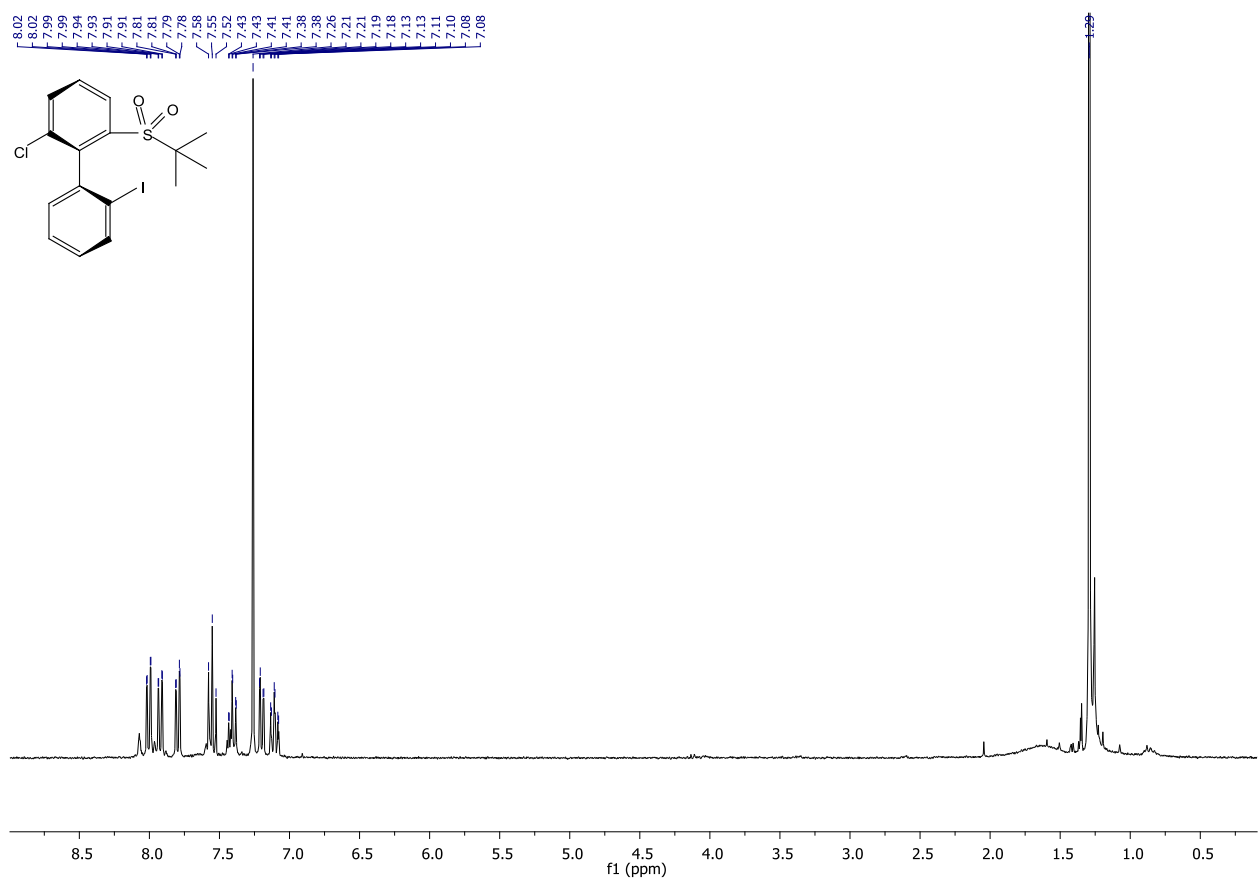
AUTHOR EMAIL ADDRESS: geraldine.masson@cnrs.fr

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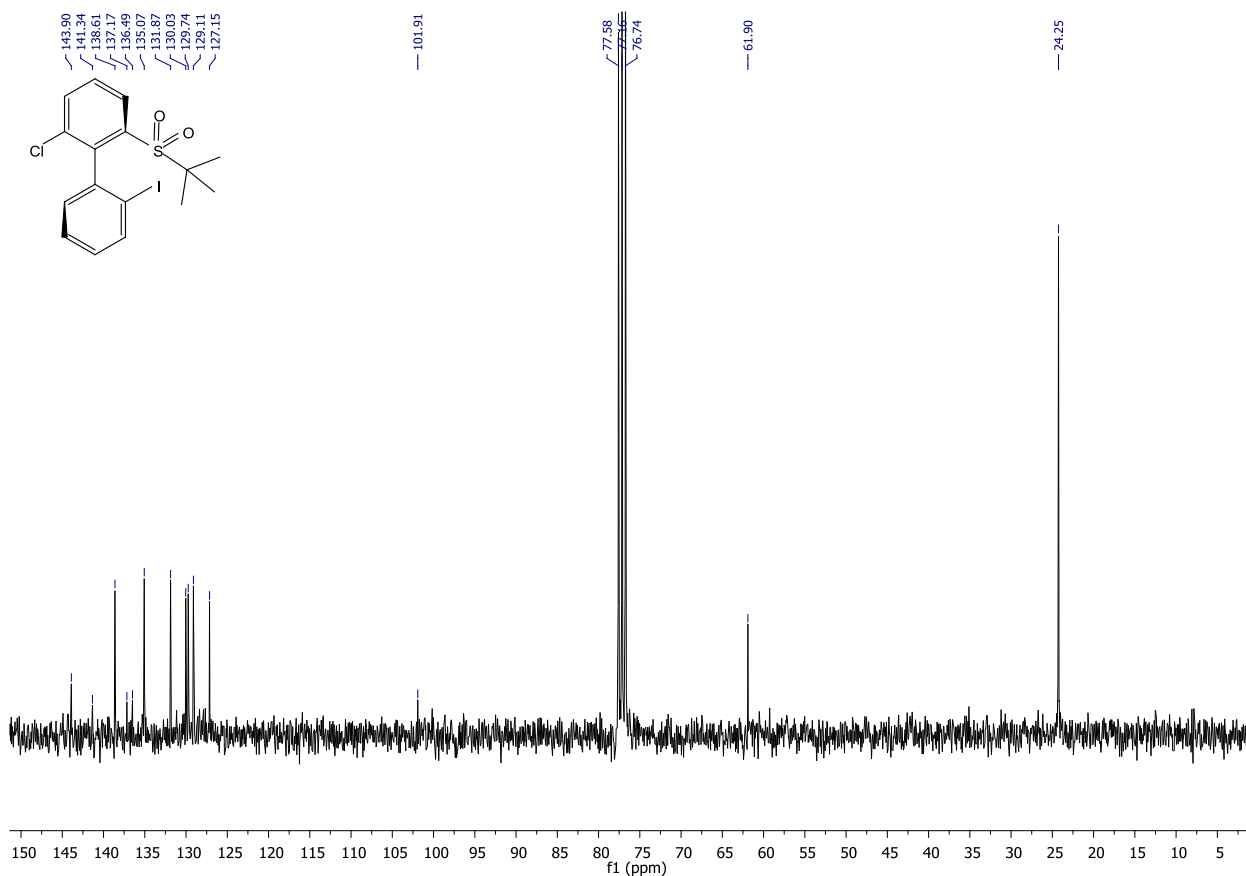
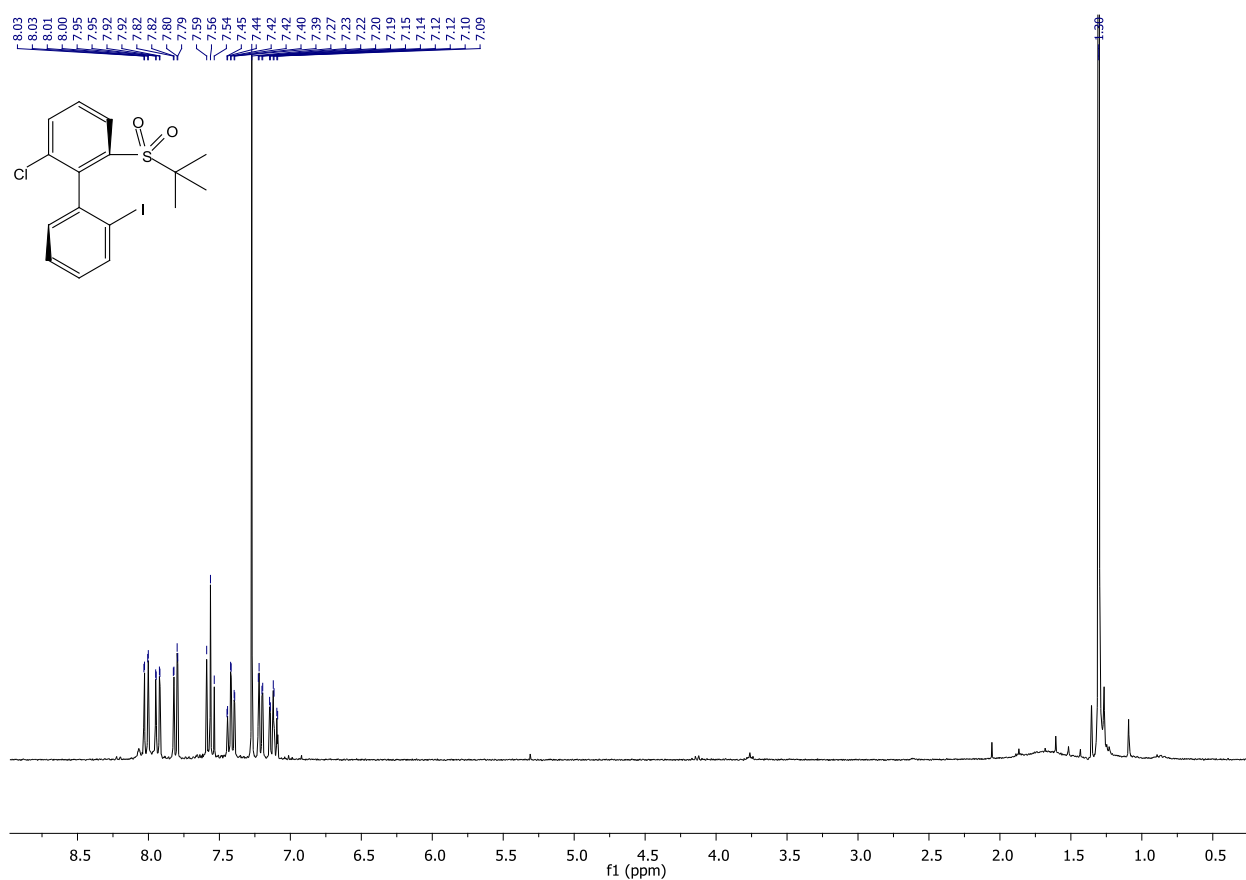
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1. ^1H and ^{13}C NMR spectra:

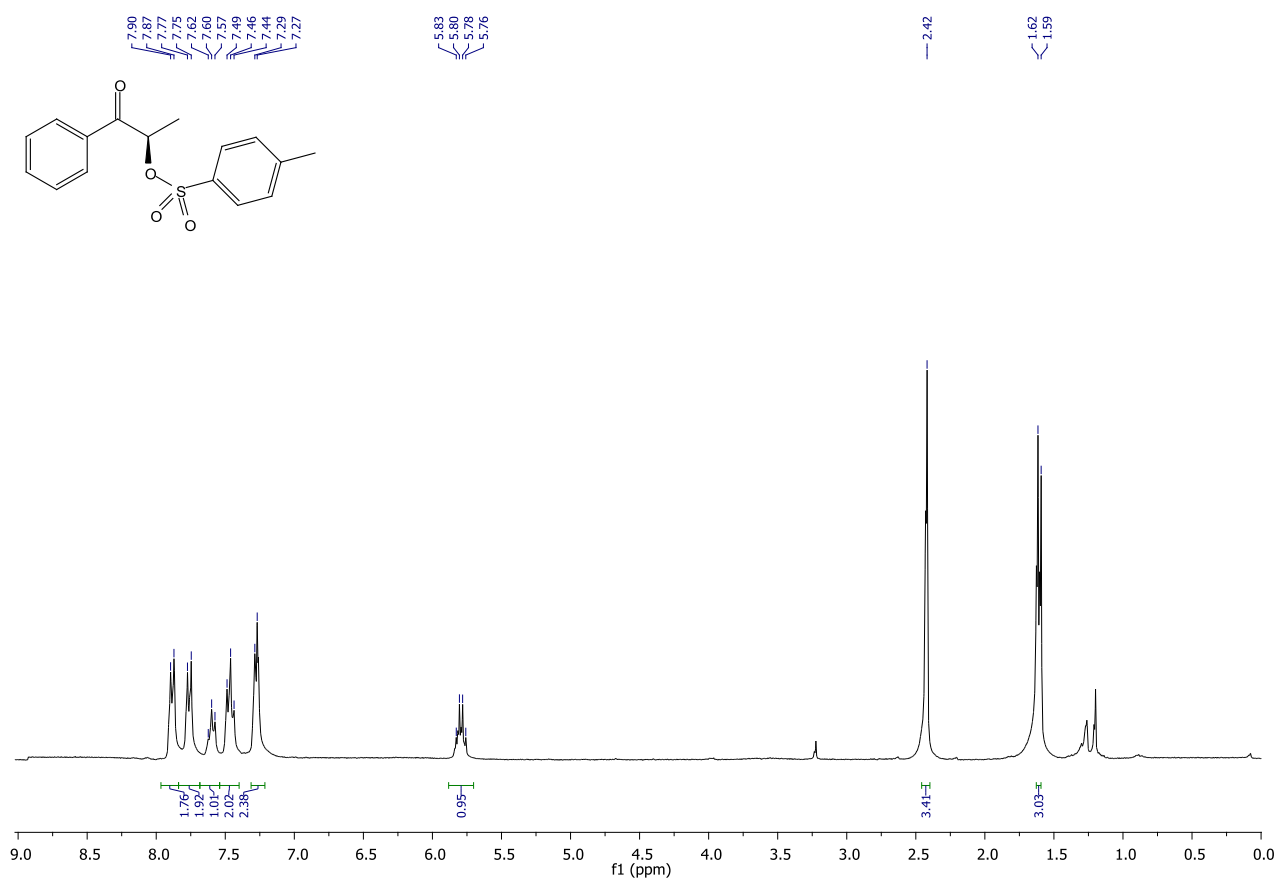
(*R*)-2-(tert-butylsulfonyl)-6-chloro-2'-iodo-1,1'-biphenyl (1m).



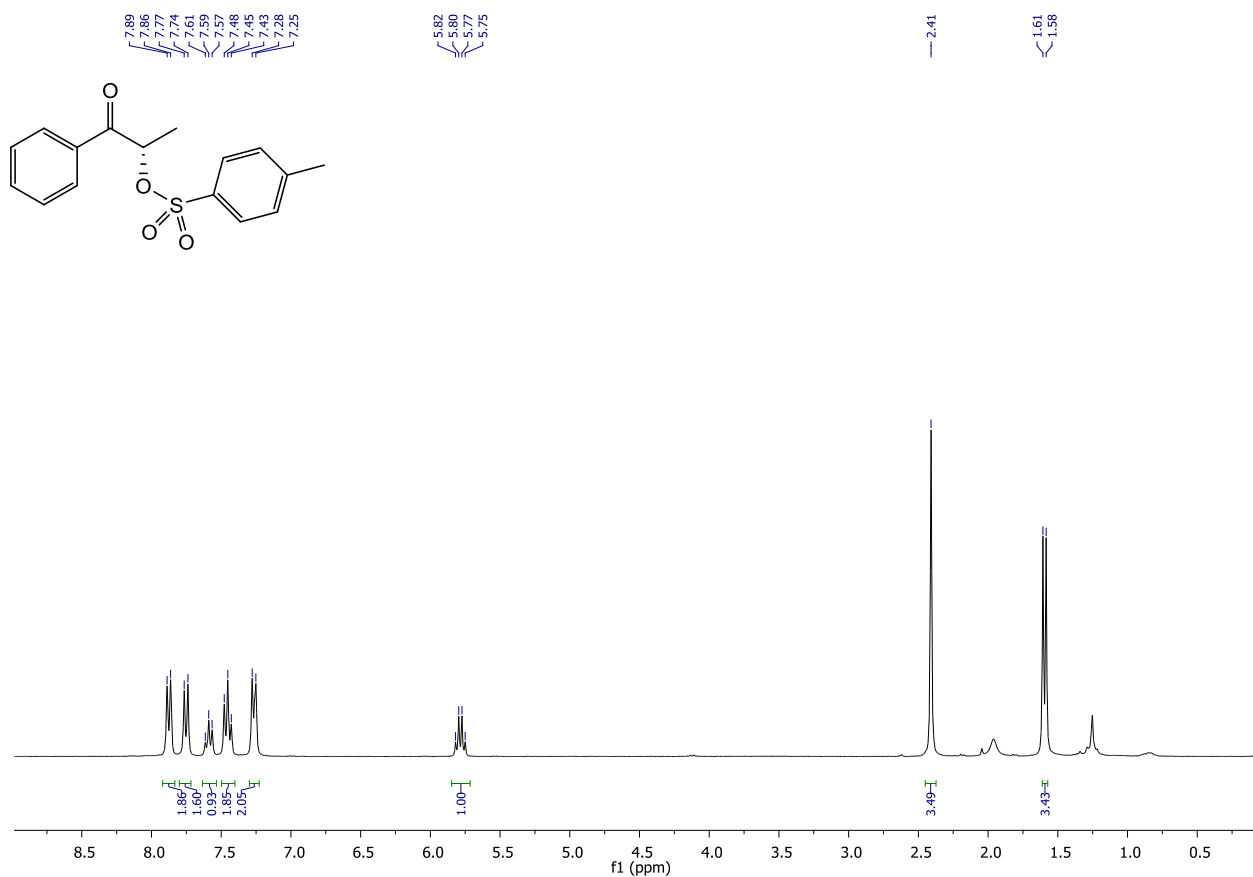
(S)-2-(tert-butylsulfonyl)-6-chloro-2'-iodo-1,1'-biphenyl (1n).



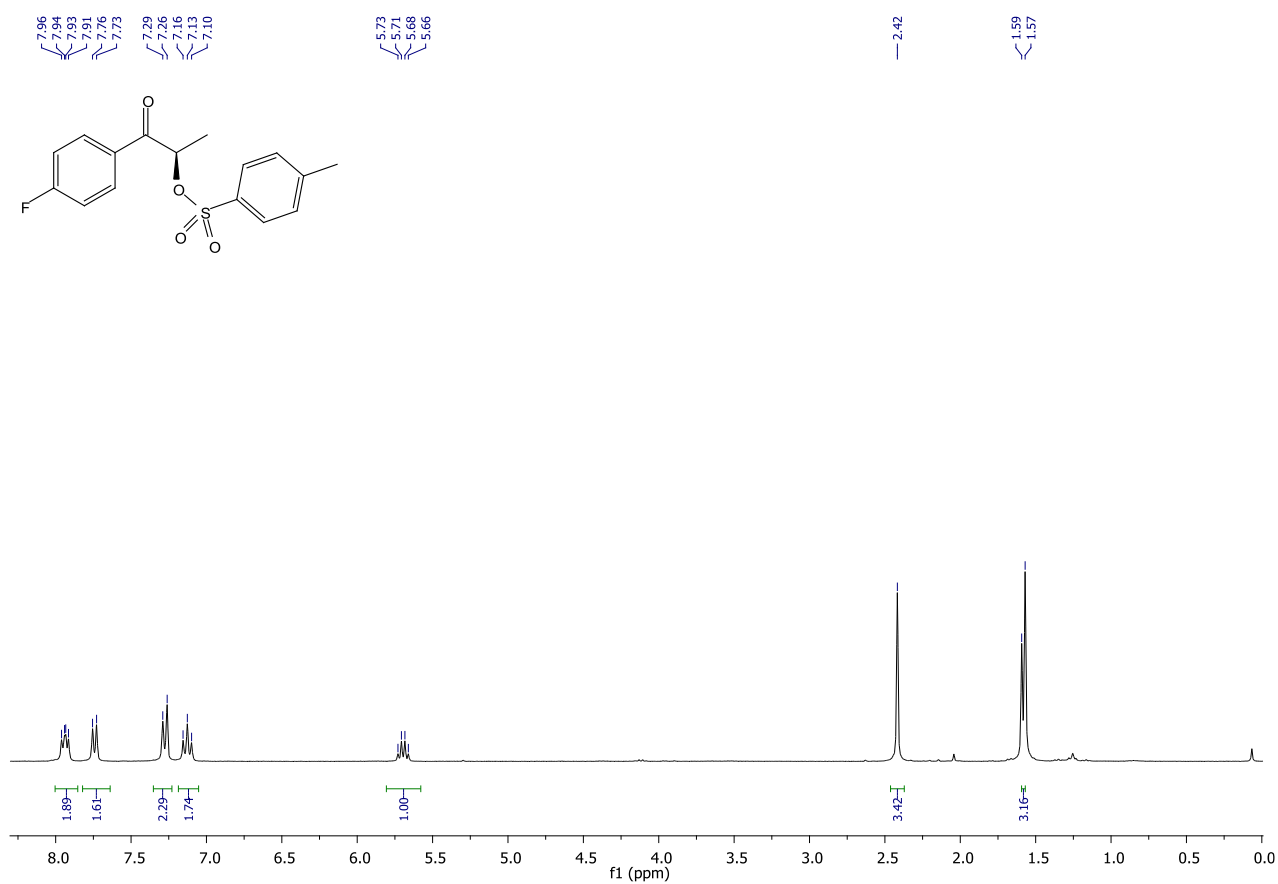
(R)-2-[(4-methylbenzenesulfonyl)oxy]-1-phenylpropan-1-one (3a).



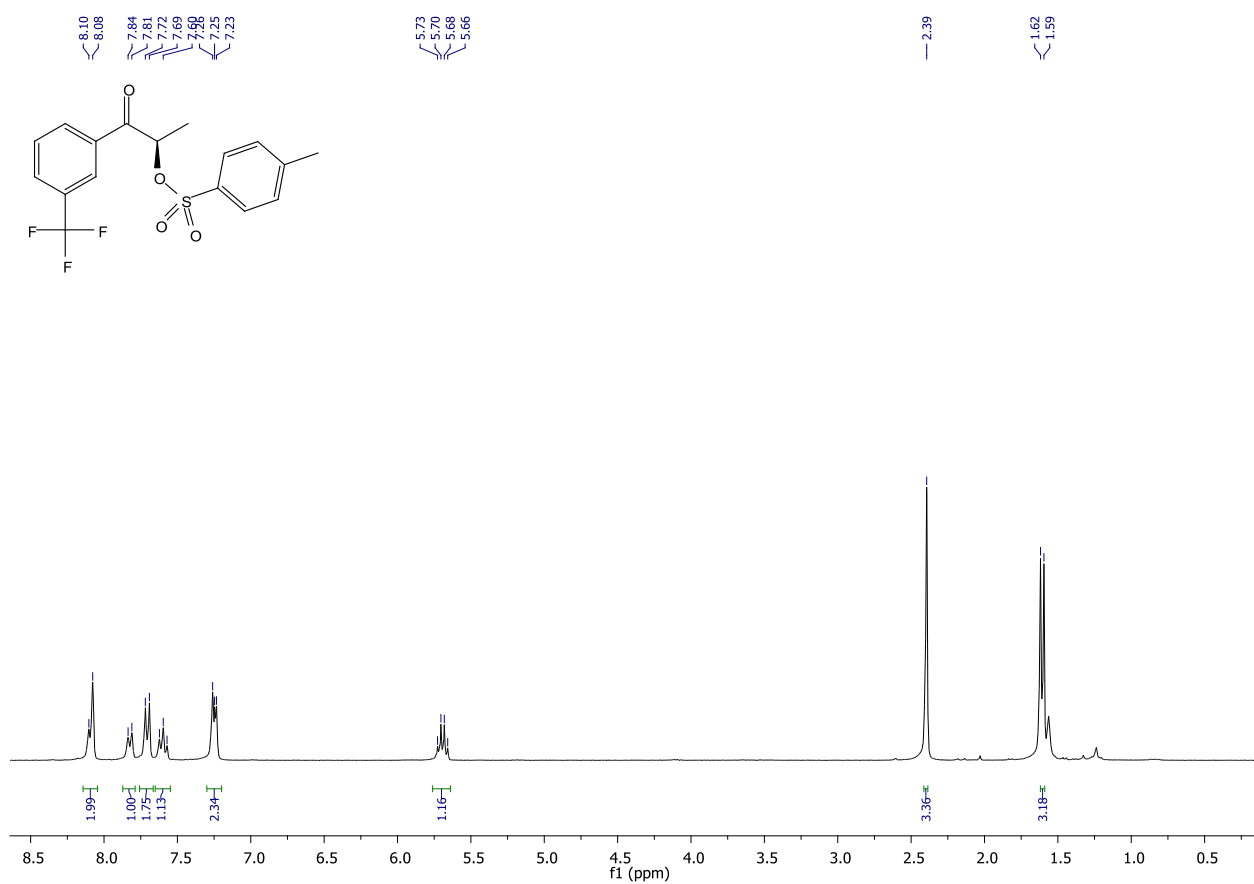
(S)-2-[(4-methylbenzenesulfonyl)oxy]-1-phenylpropan-1-one (3b).



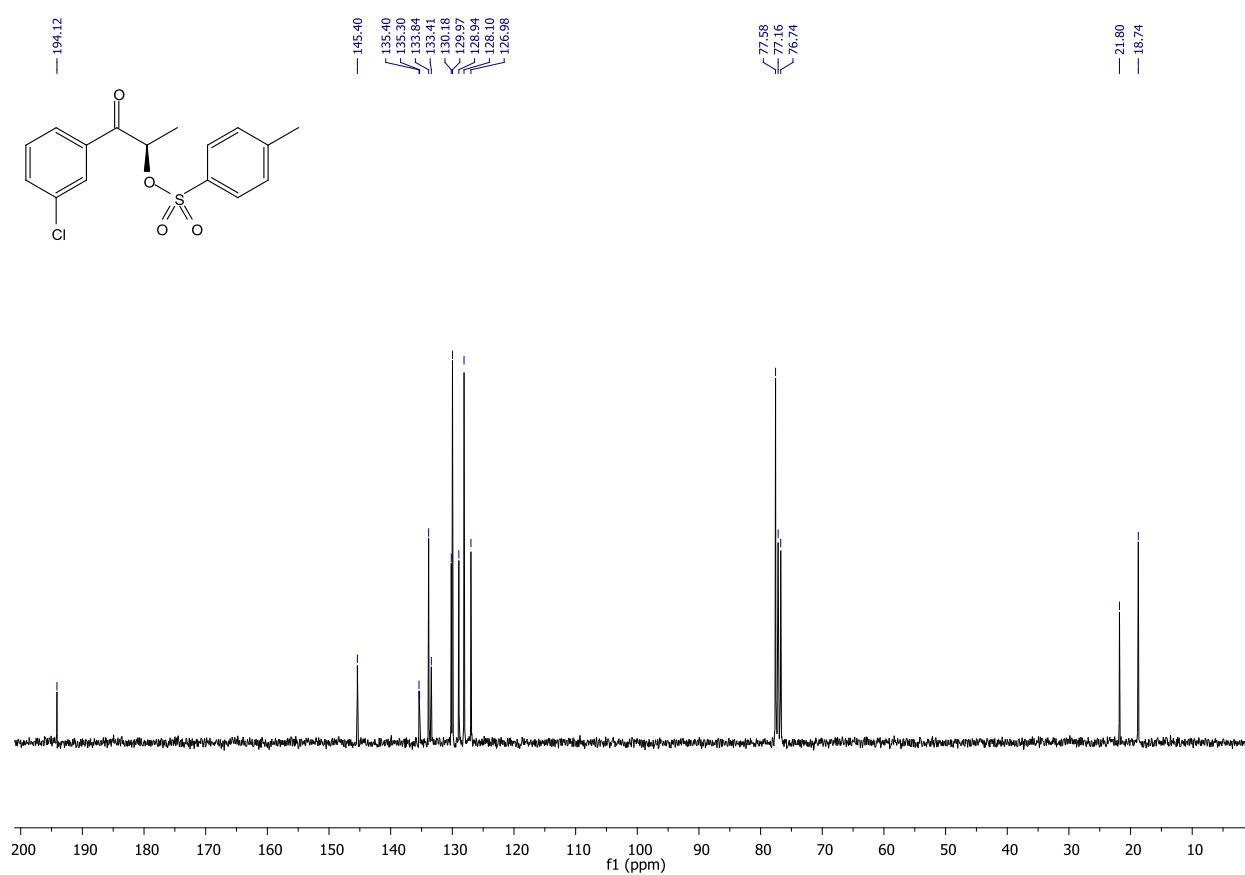
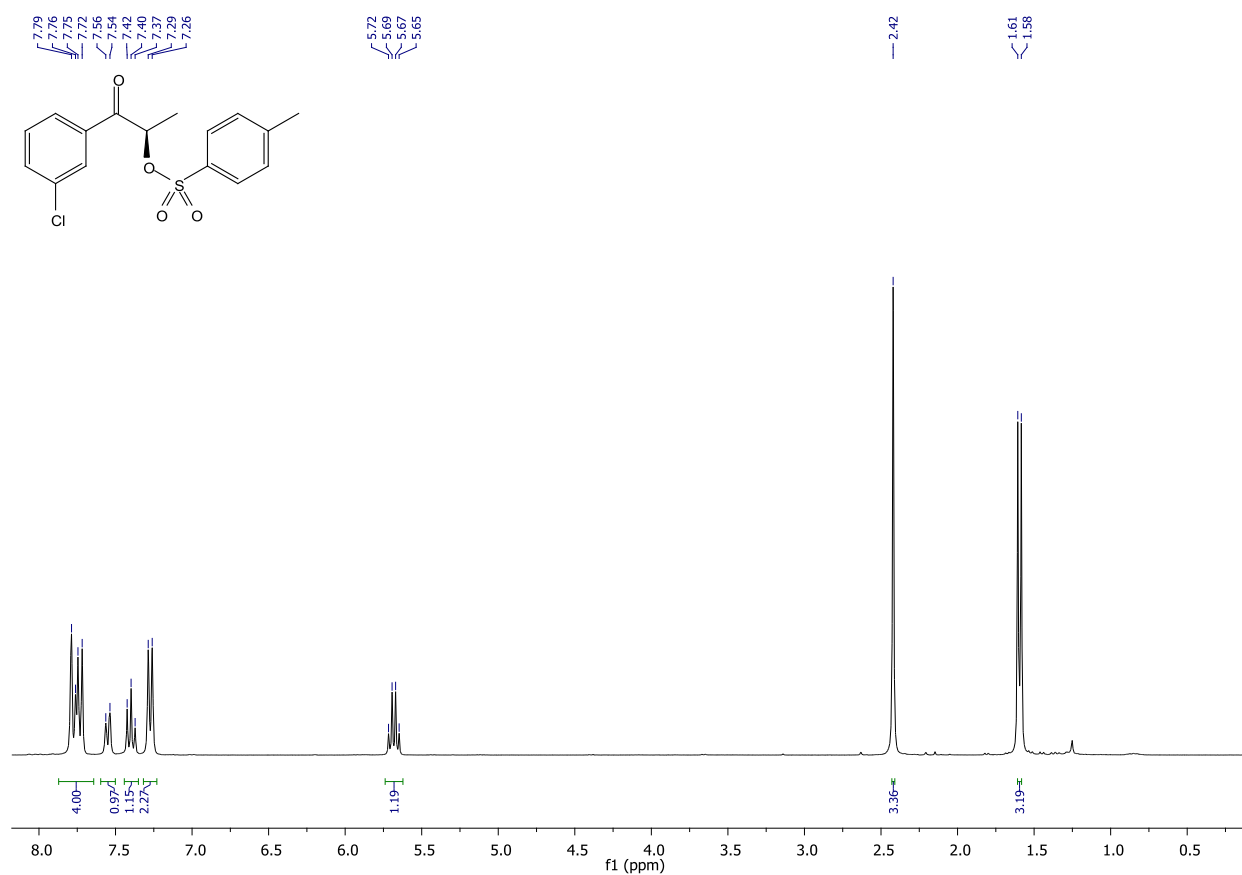
(R)-1-(4-Fluorophenyl)-1-oxopropan-2-yl 4-methylbenzenesulfonate (3c).



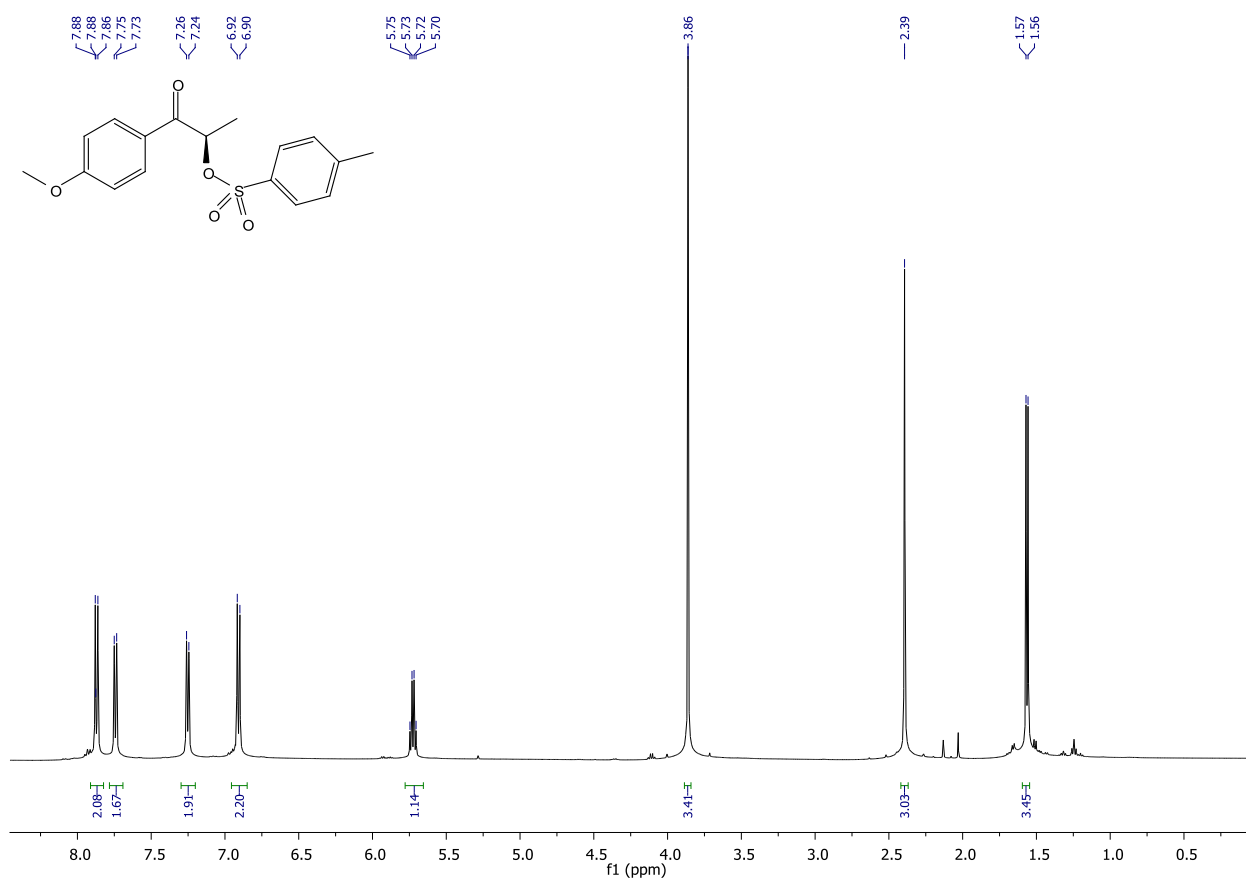
(R)-1-(3-(Trifluoromethyl)phenyl)-1-oxopropan-2-yl 4-methylbenzenesulfonate (3d).



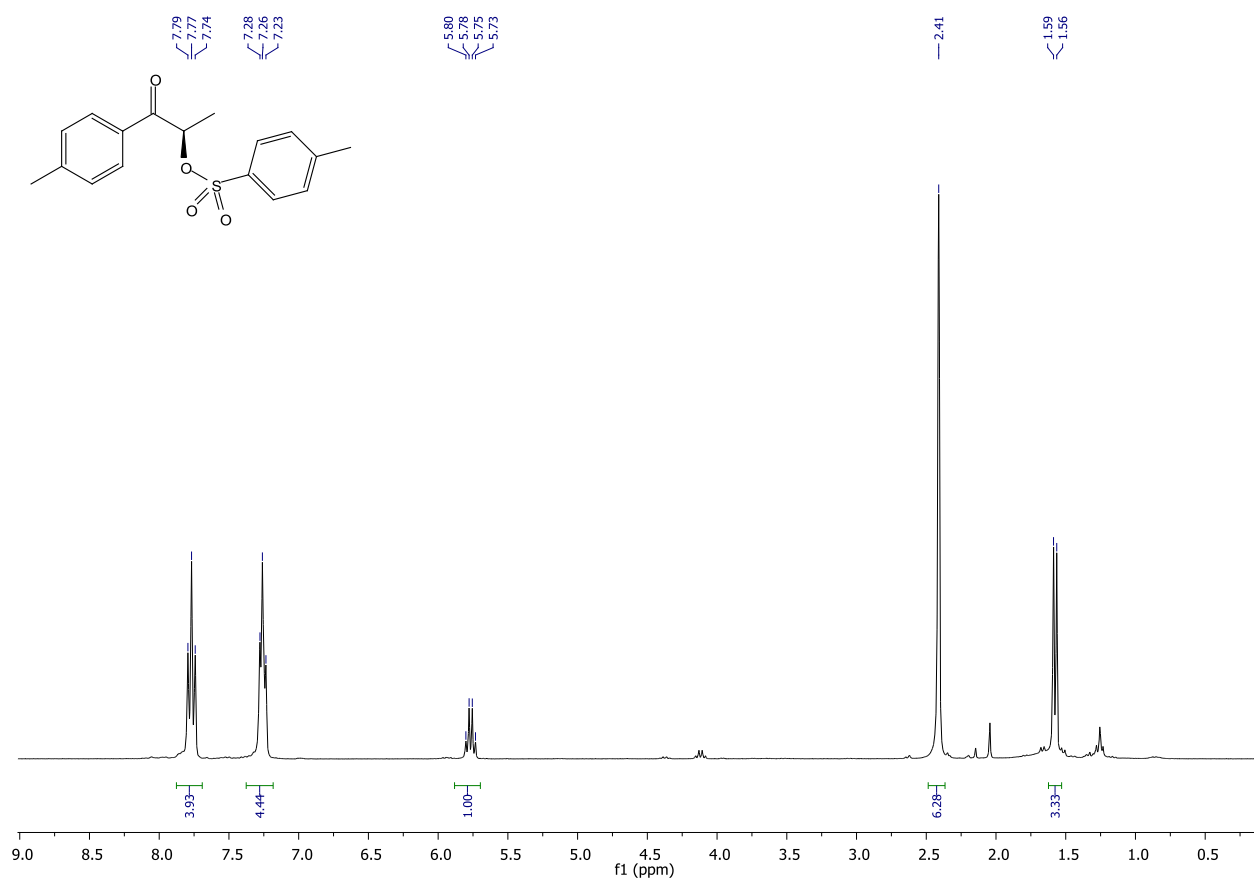
(R)-1-(3-chlorophenyl)-1-oxopropan-2-yl 4-methylbenzenesulfonate (3e).



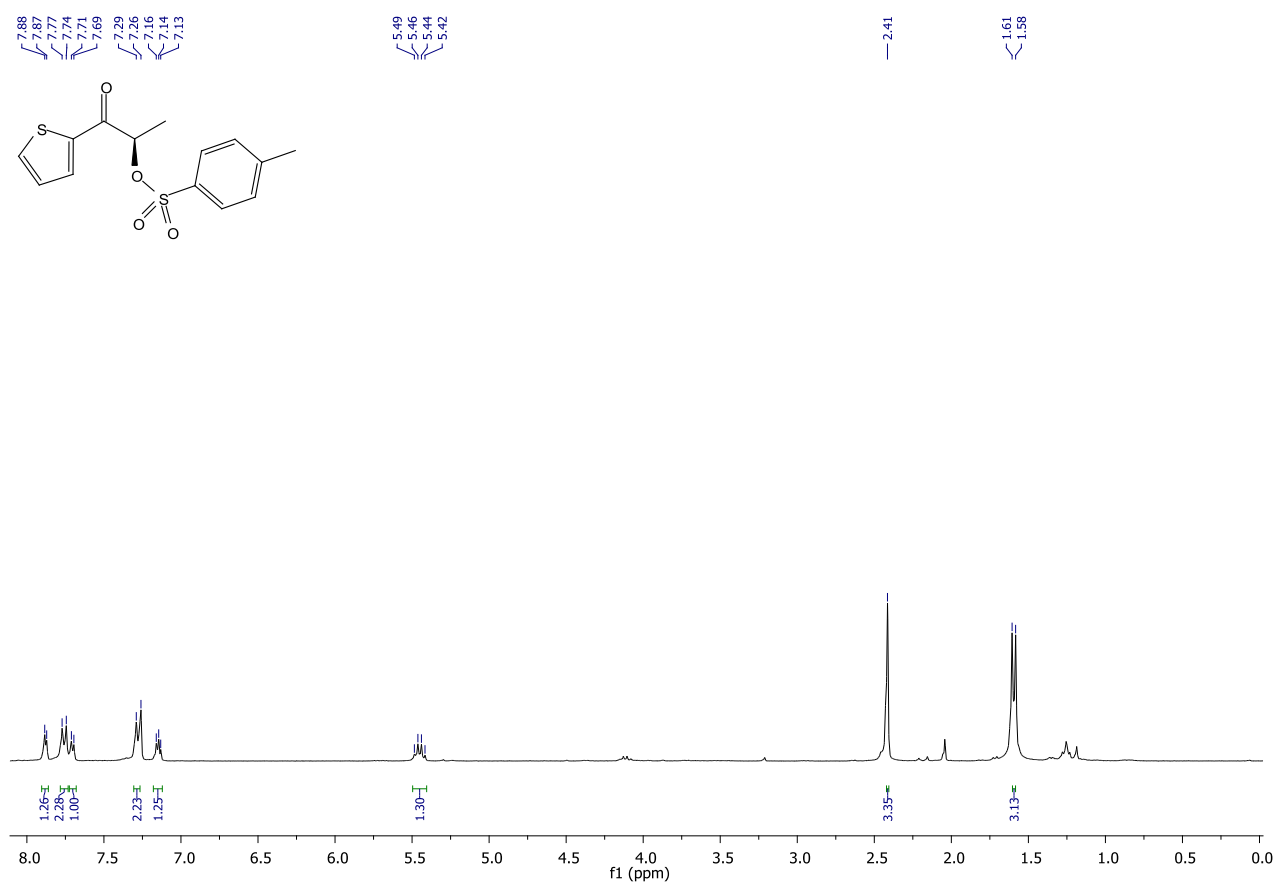
(R)-1-(4-methoxyphenyl)-1-oxopropan-2-yl 4-methylbenzenesulfonate (3f).



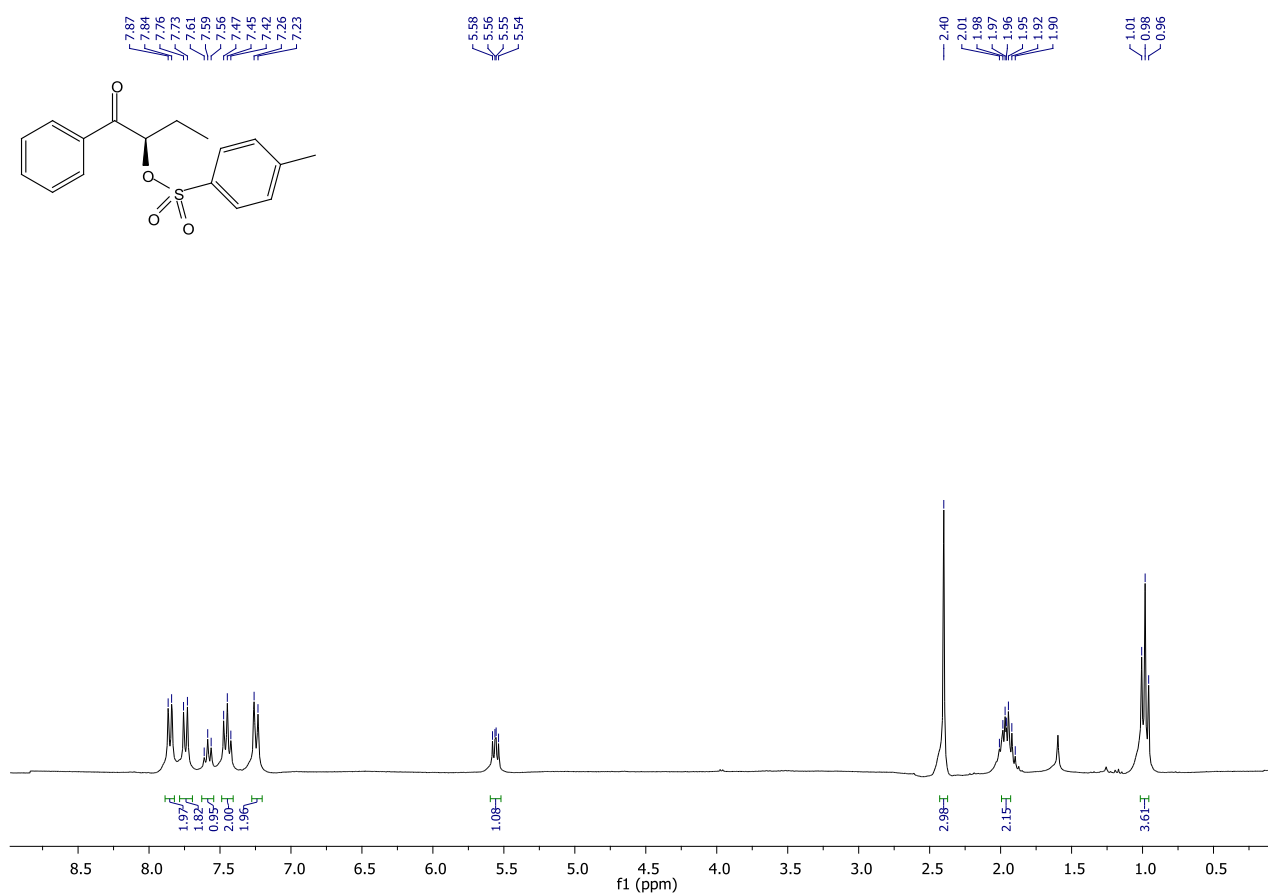
(R)-1-(4-methylphenyl)-1-oxopropan-2-yl 4-methylbenzenesulfonate (3g).



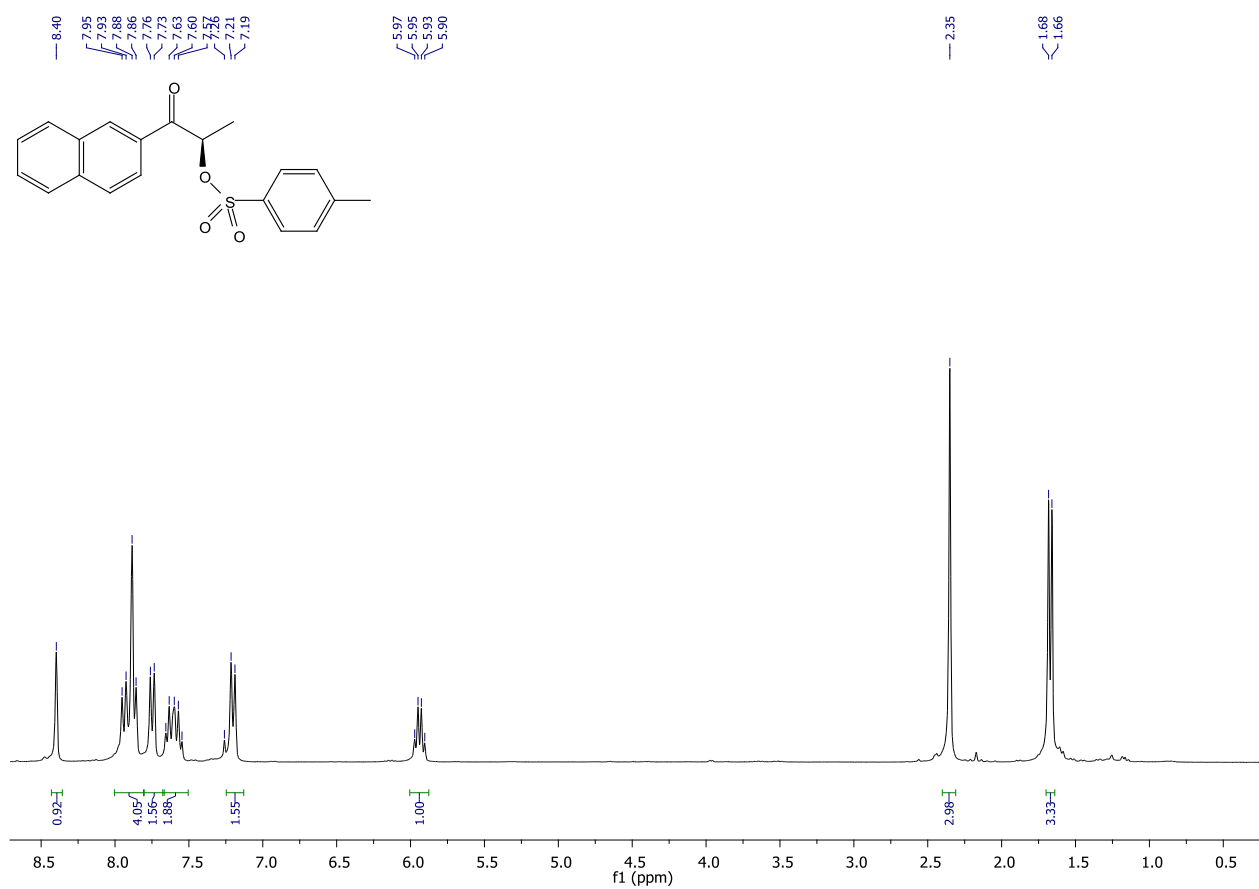
(R)-1-oxo-1-(thiophen-2-yl)propan-2-yl 4-methylbenzenesulfonate (3h).



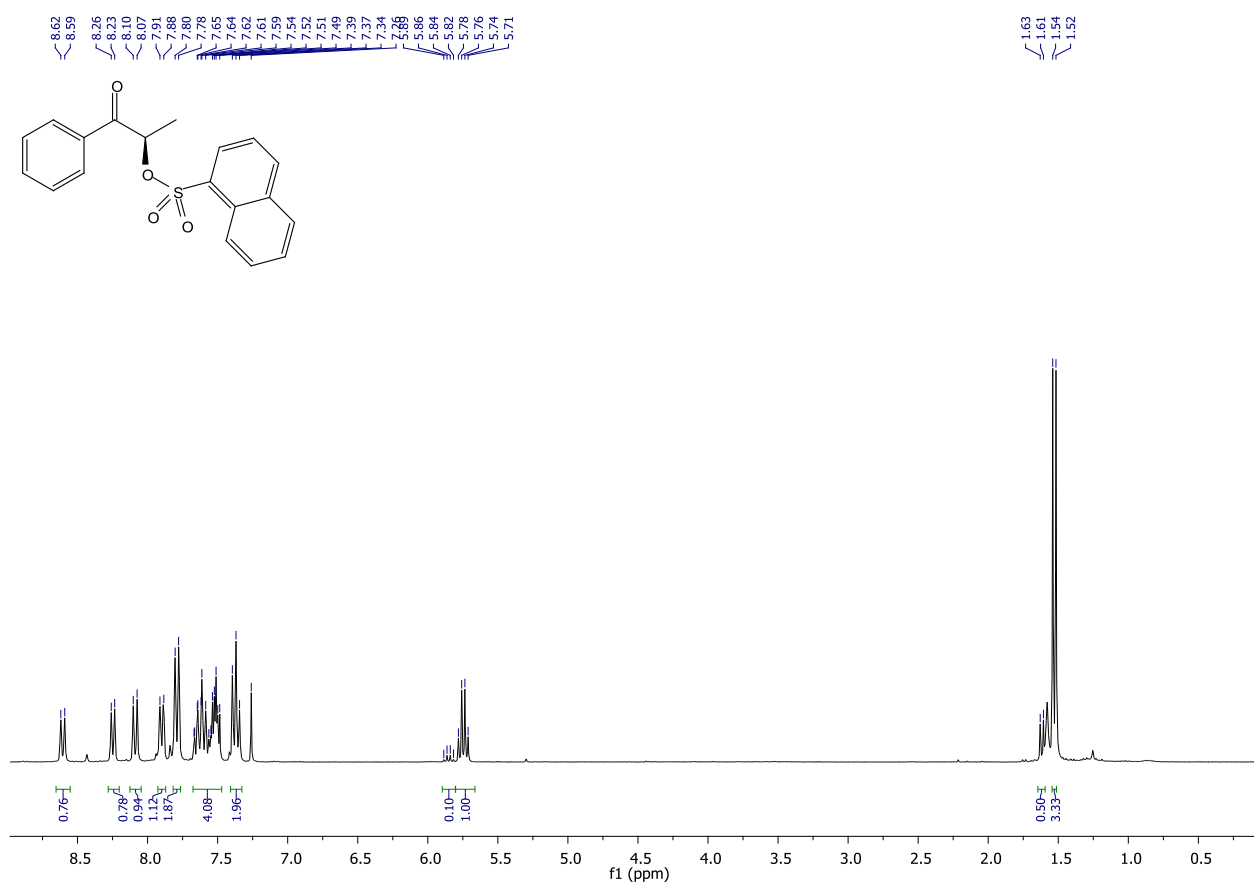
(R)-2-[(4-methylbenzenesulfonyl)oxy]-1-phenylbutan-1-one (3i).



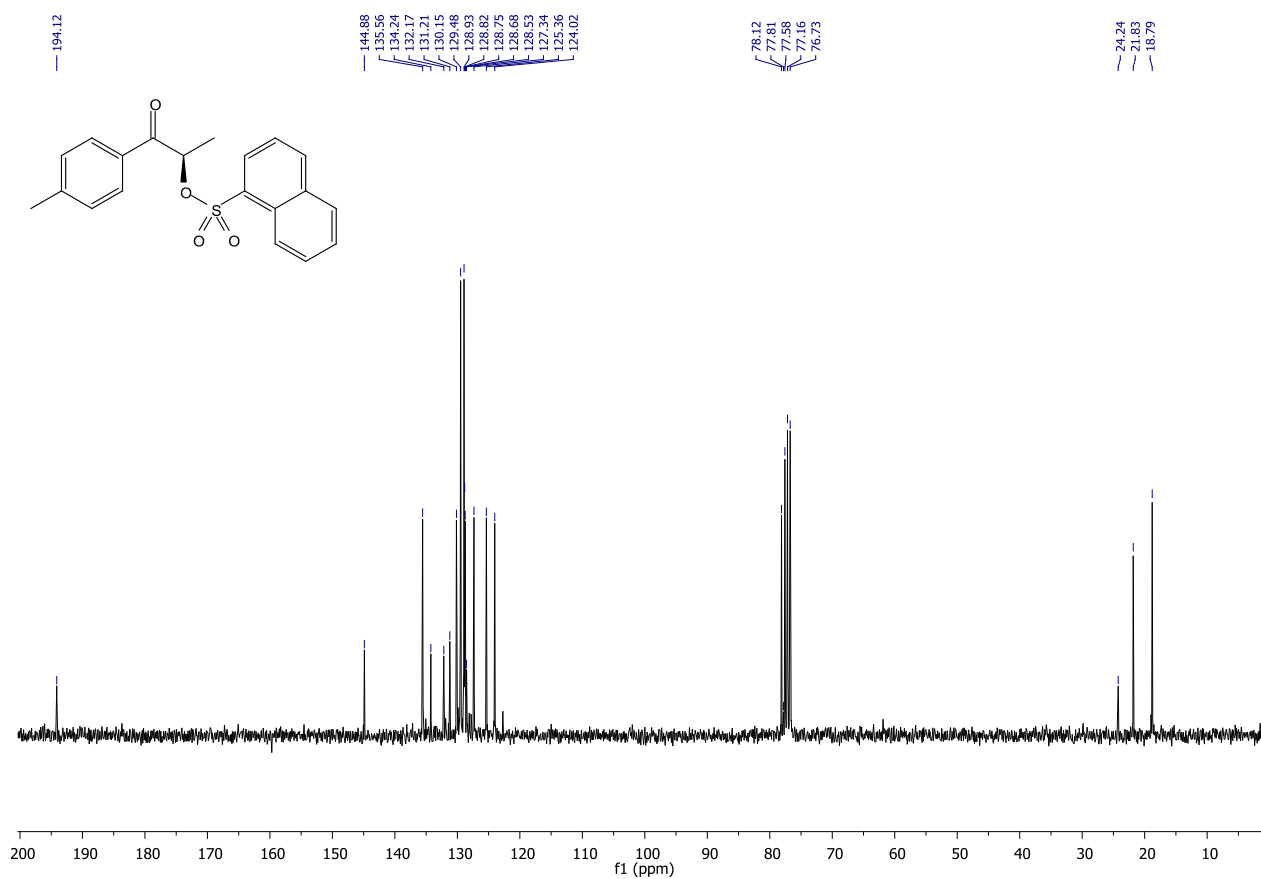
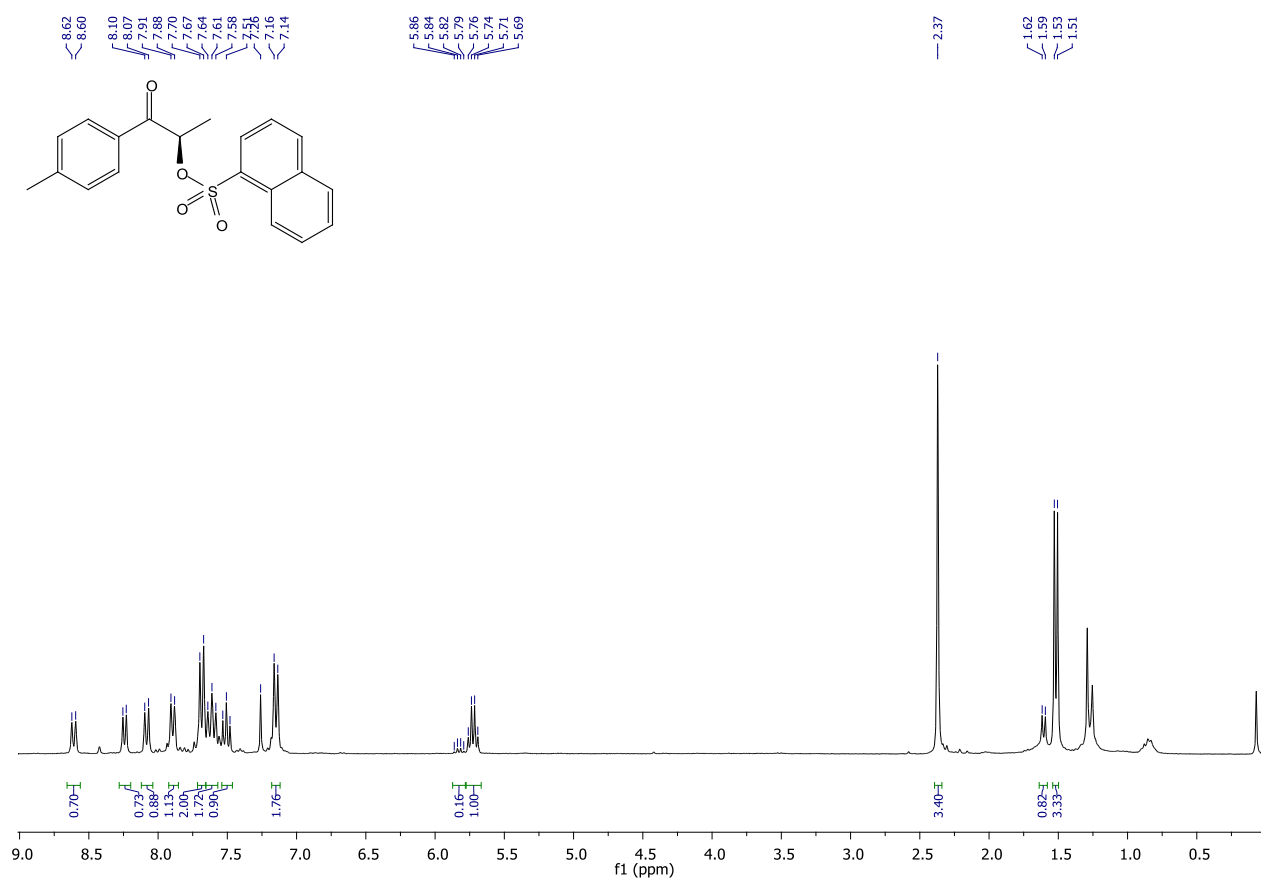
(R)-1-(naphthalen-2-yl)-1-oxopropan-2-yl-4-methylbenzenesulfonate (3j).



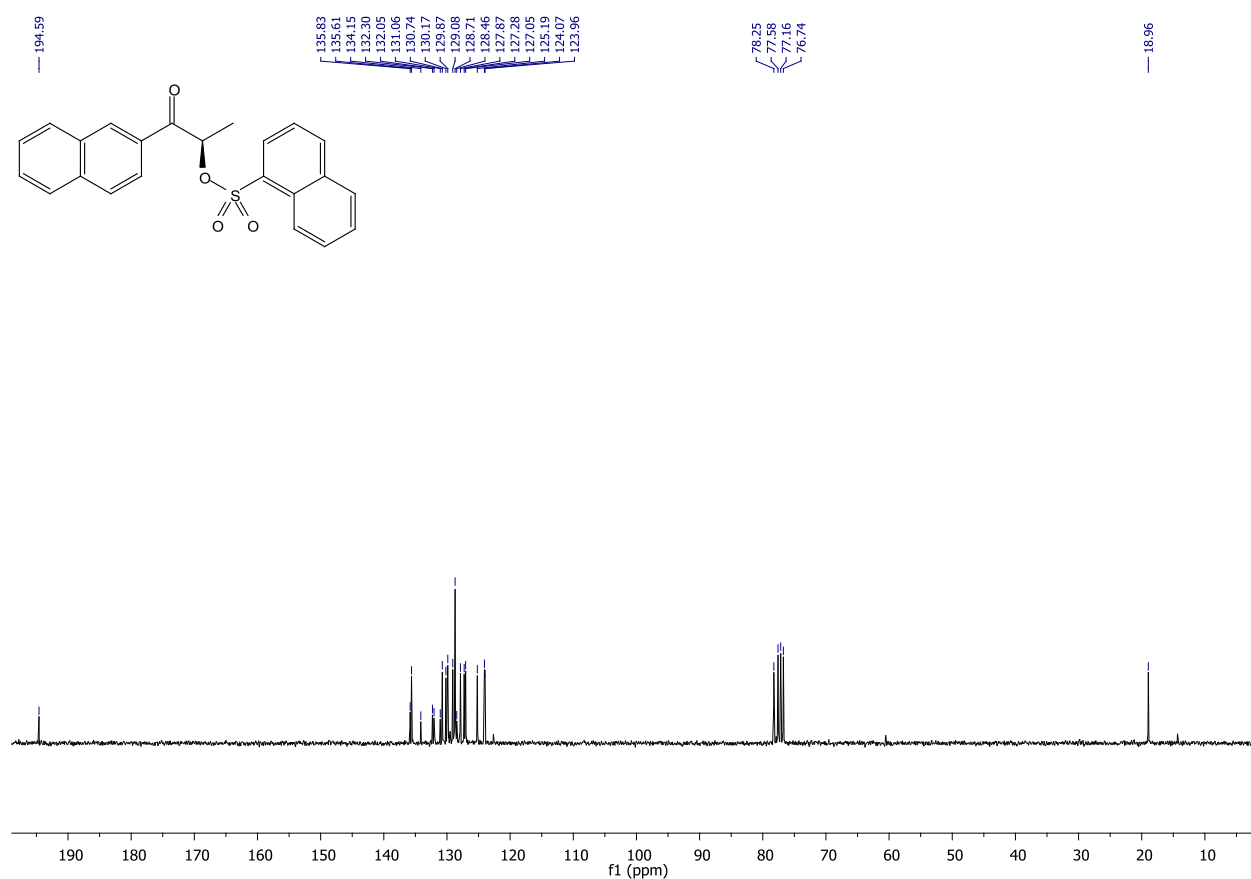
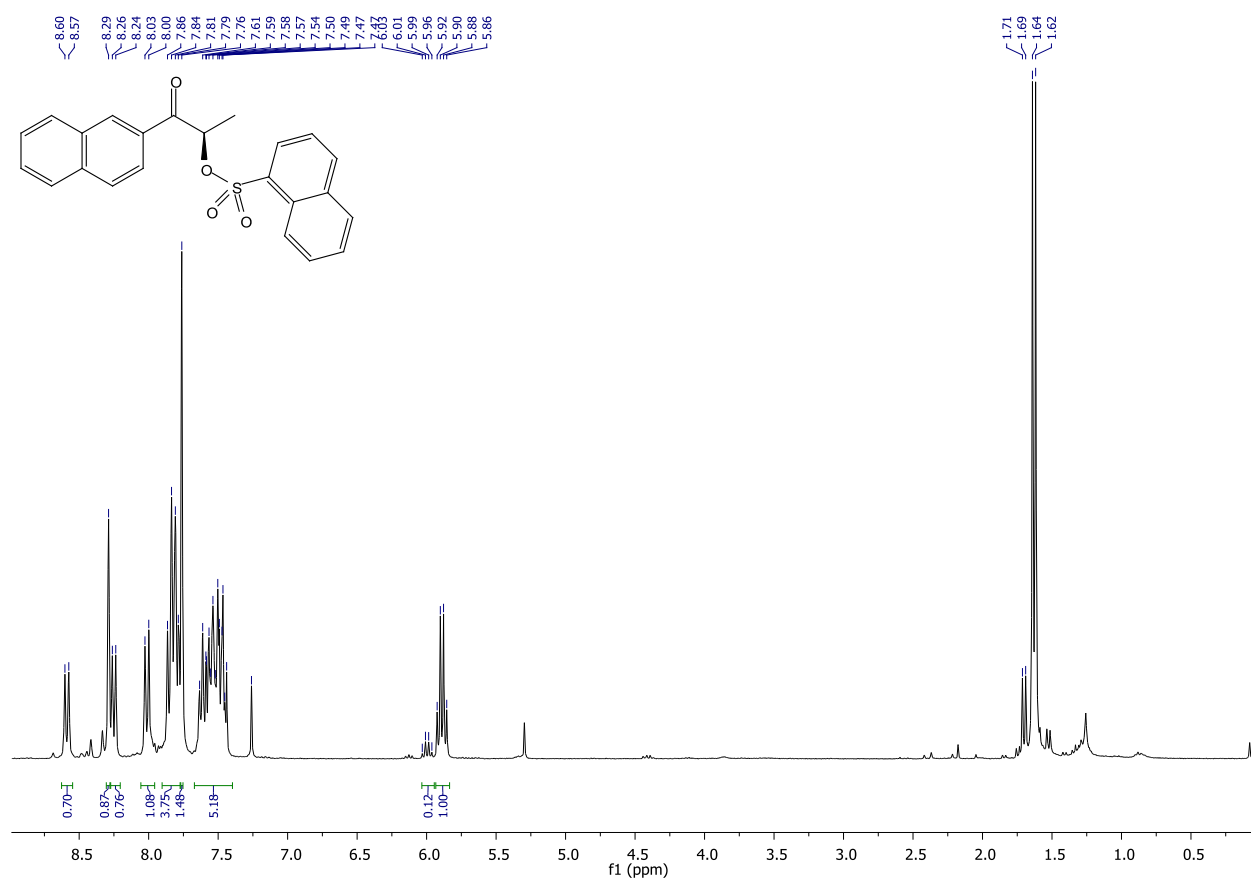
(R)- 1-oxo-1-phenylpropan-2-yl naphthalene-1-sulfonate (3k).



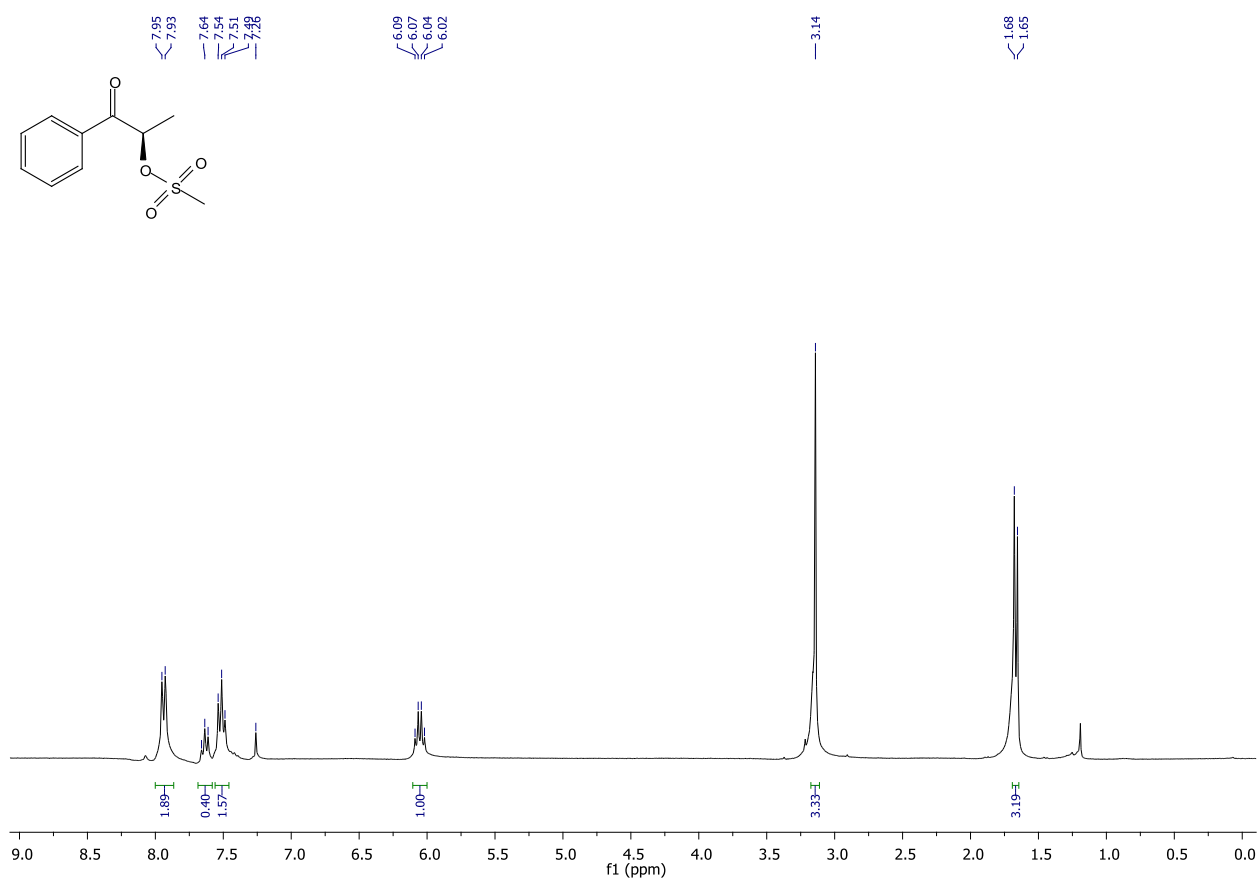
(R)- 1-oxo-1-(*p*-tolyl)propan-2-yl naphthalene-1-sulfonate (3l).



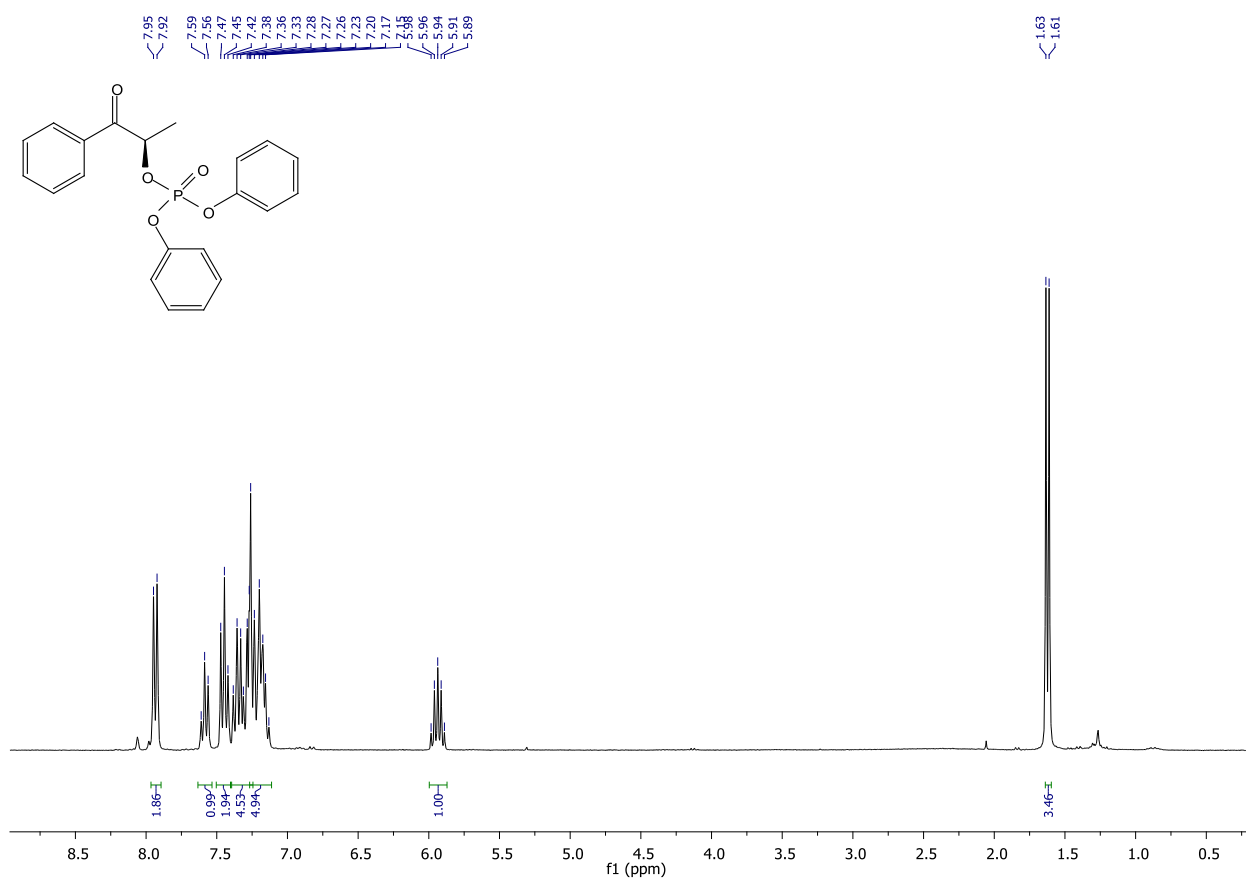
(R)- 1-(naphthalen-2-yl)-1-oxopropan-2-yl naphthalene-1-sulfonate (3m).



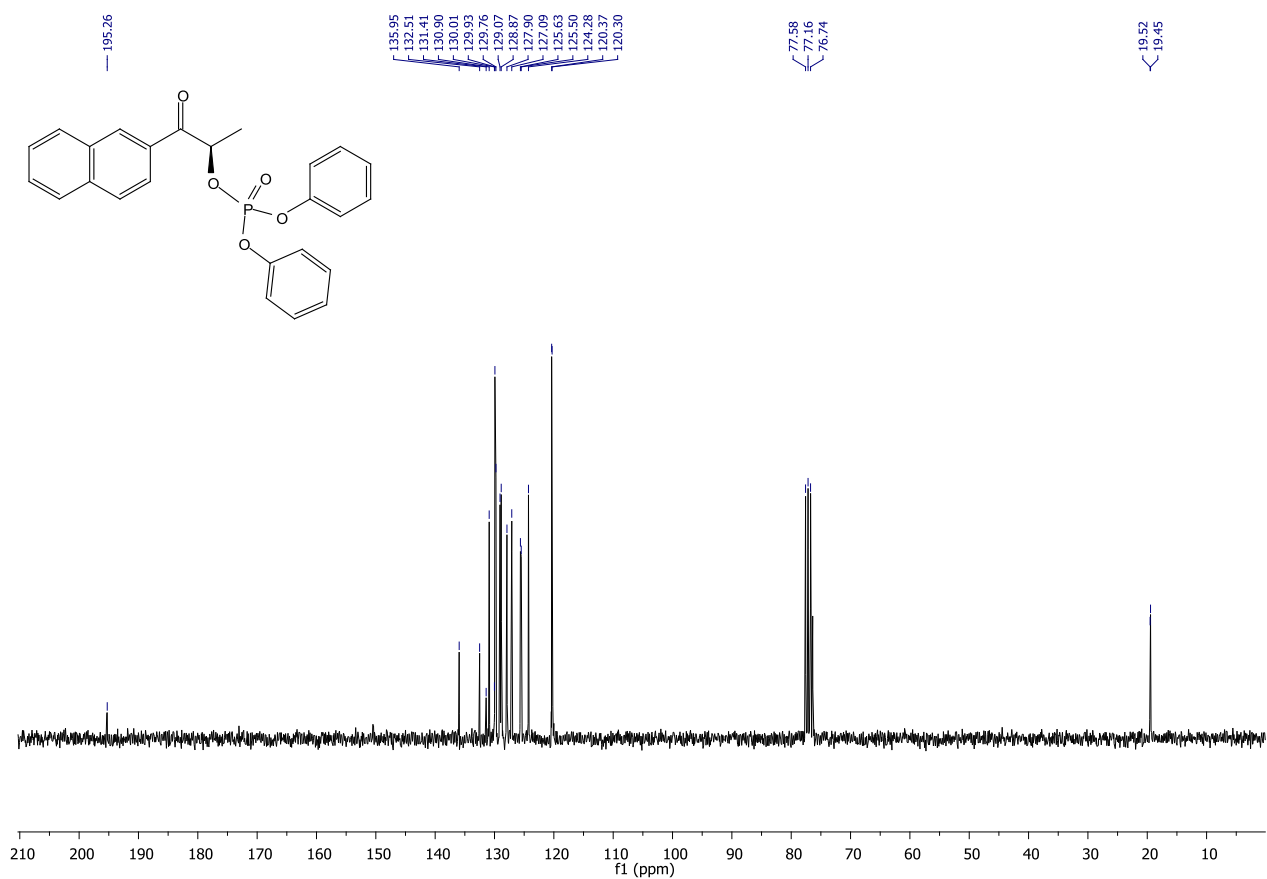
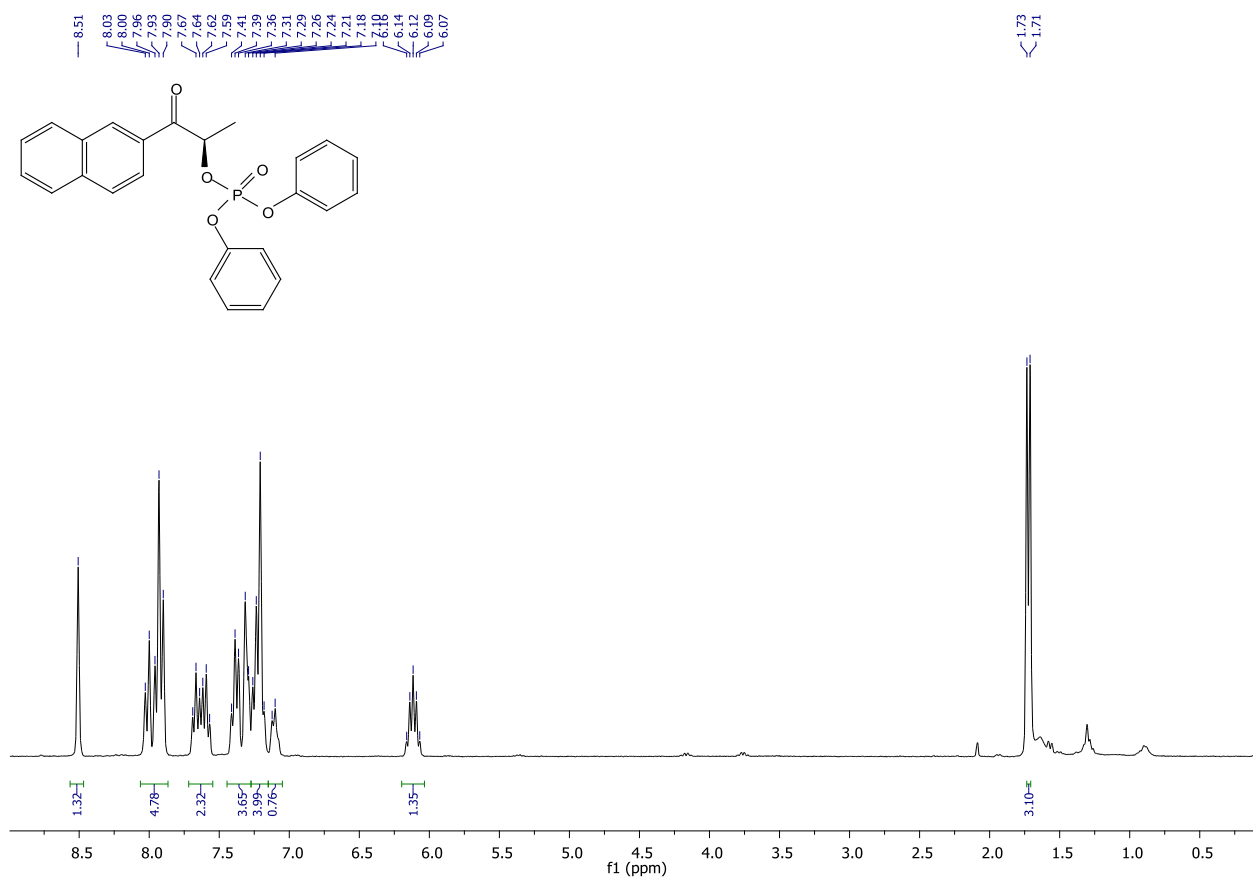
(R)-1-oxo-1-phenylpropan-2-yl methanesulfonate (3n).



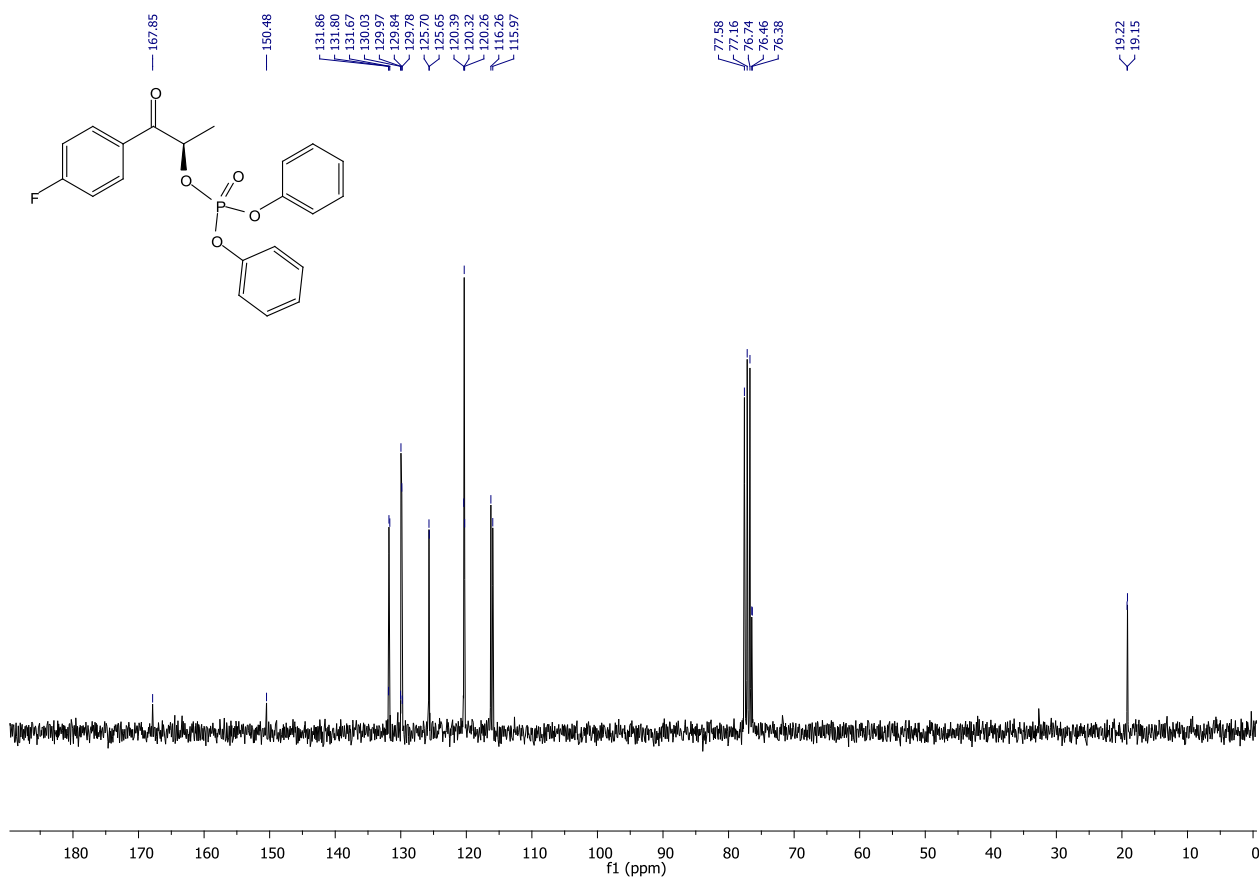
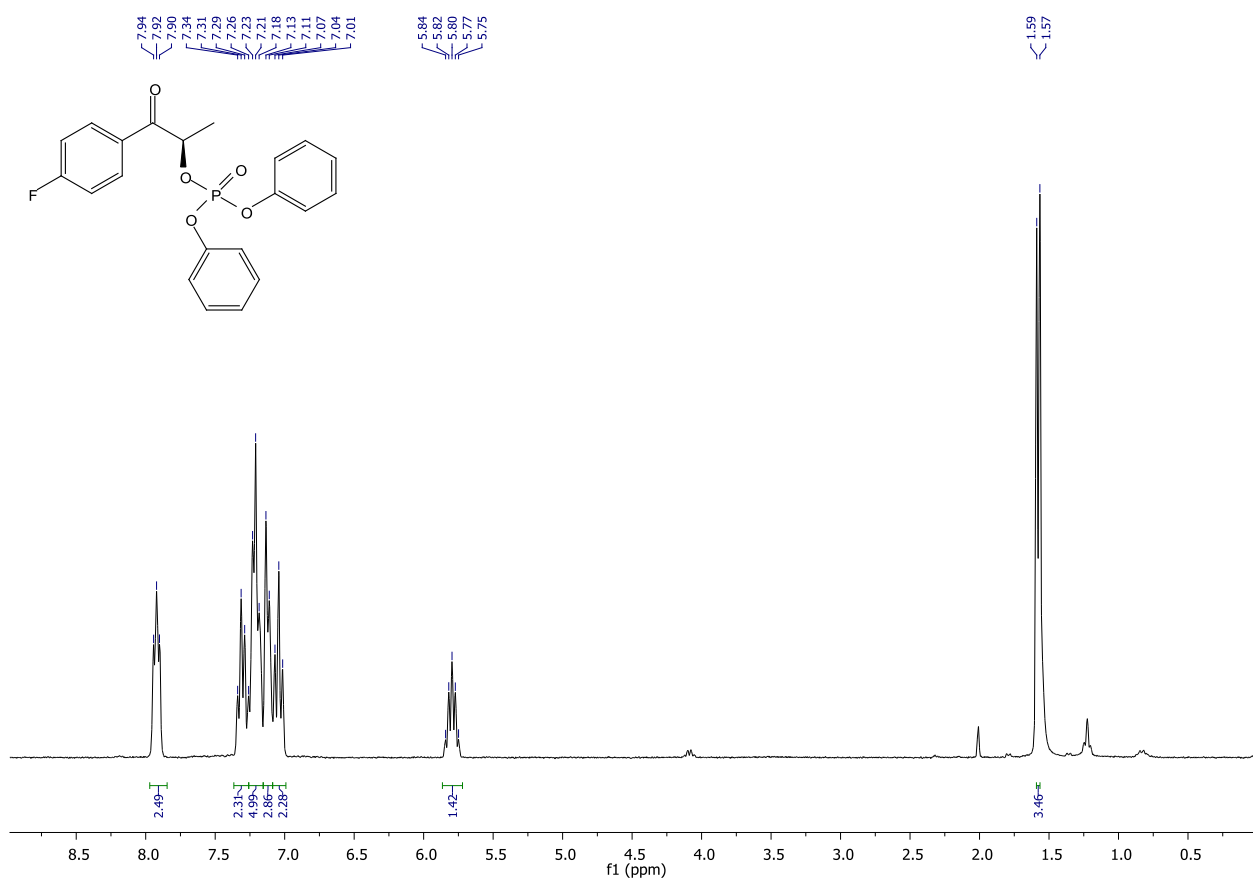
(R)-2-[(diphenoxyphosphoryl)oxy]-1-phenylpropan-1-one (3o).



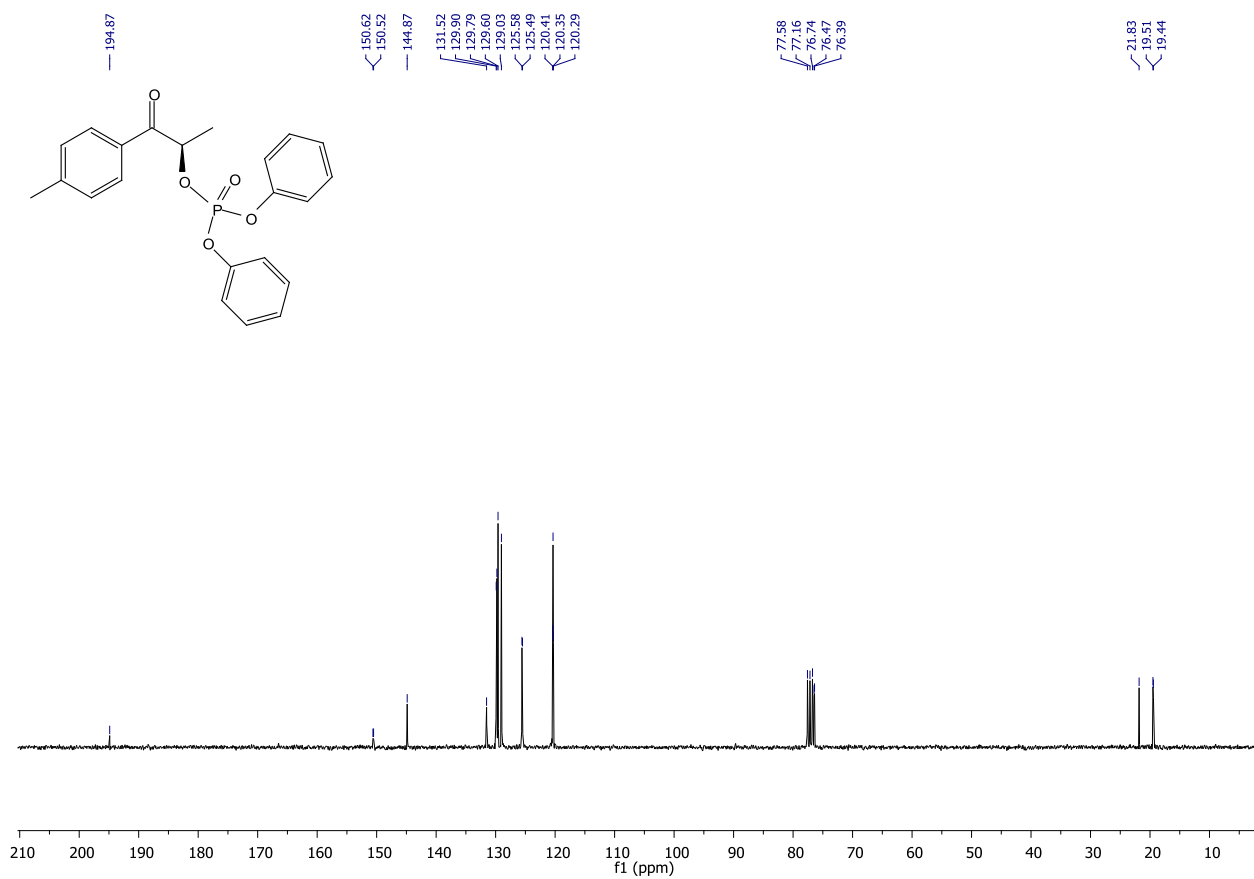
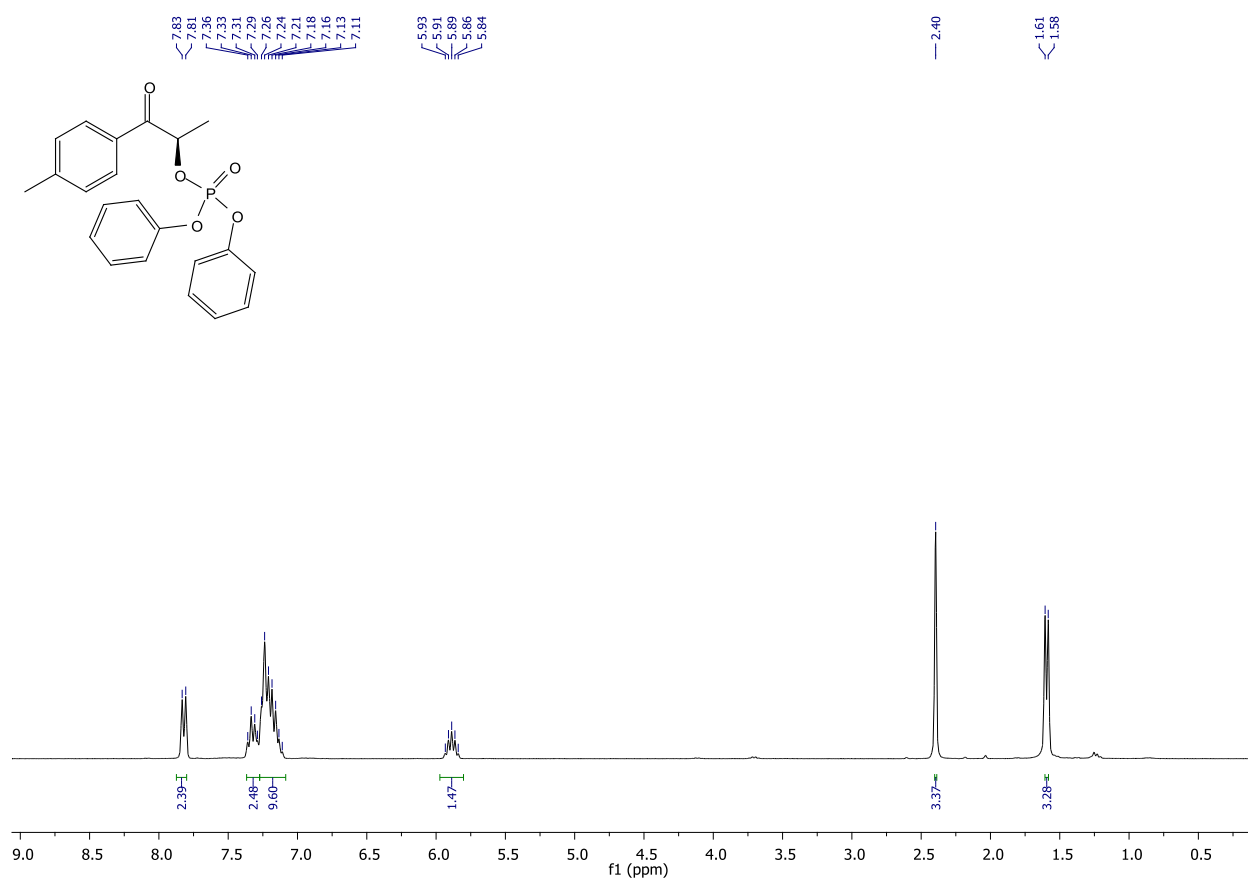
(R)-1-(naphthalen-2-yl)-1-oxopropan-2-yl diphenyl phosphate (3p).



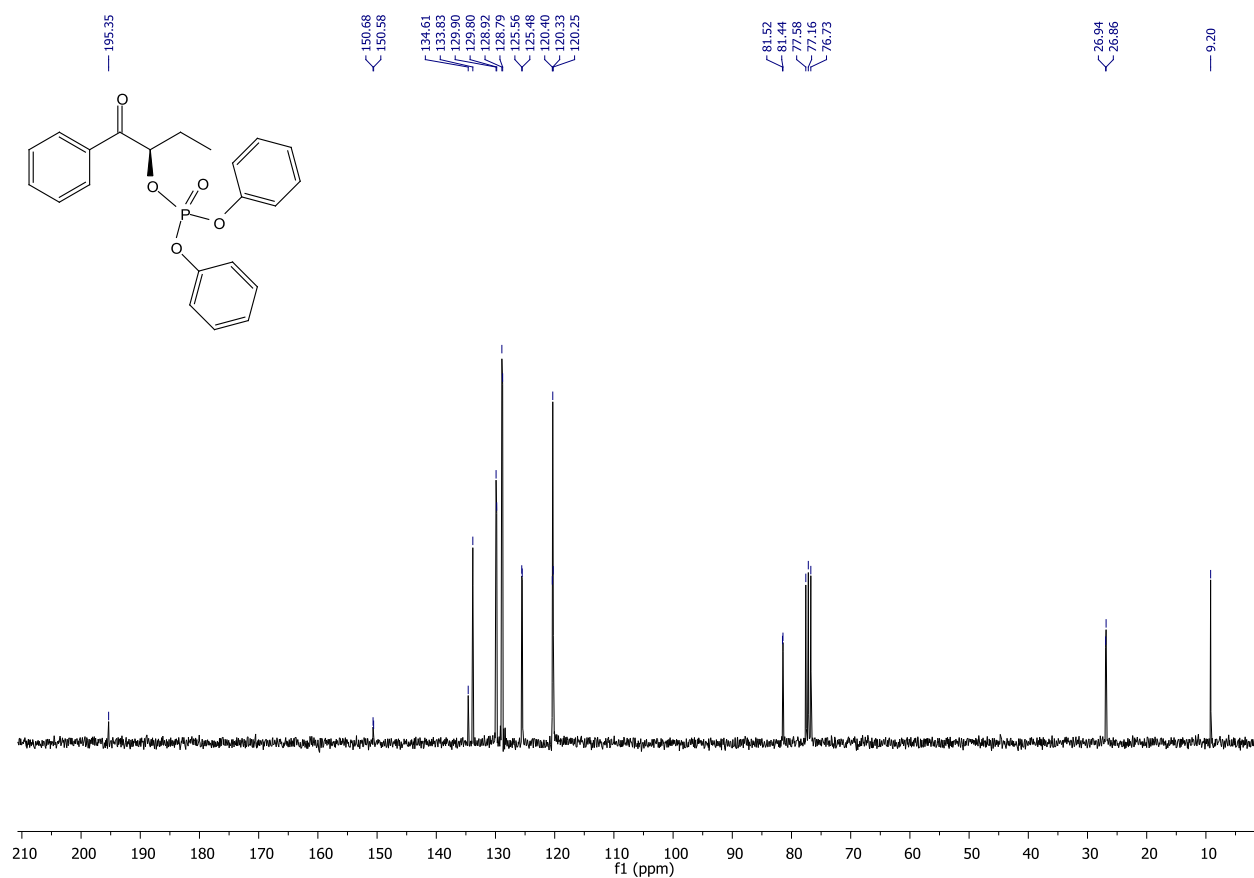
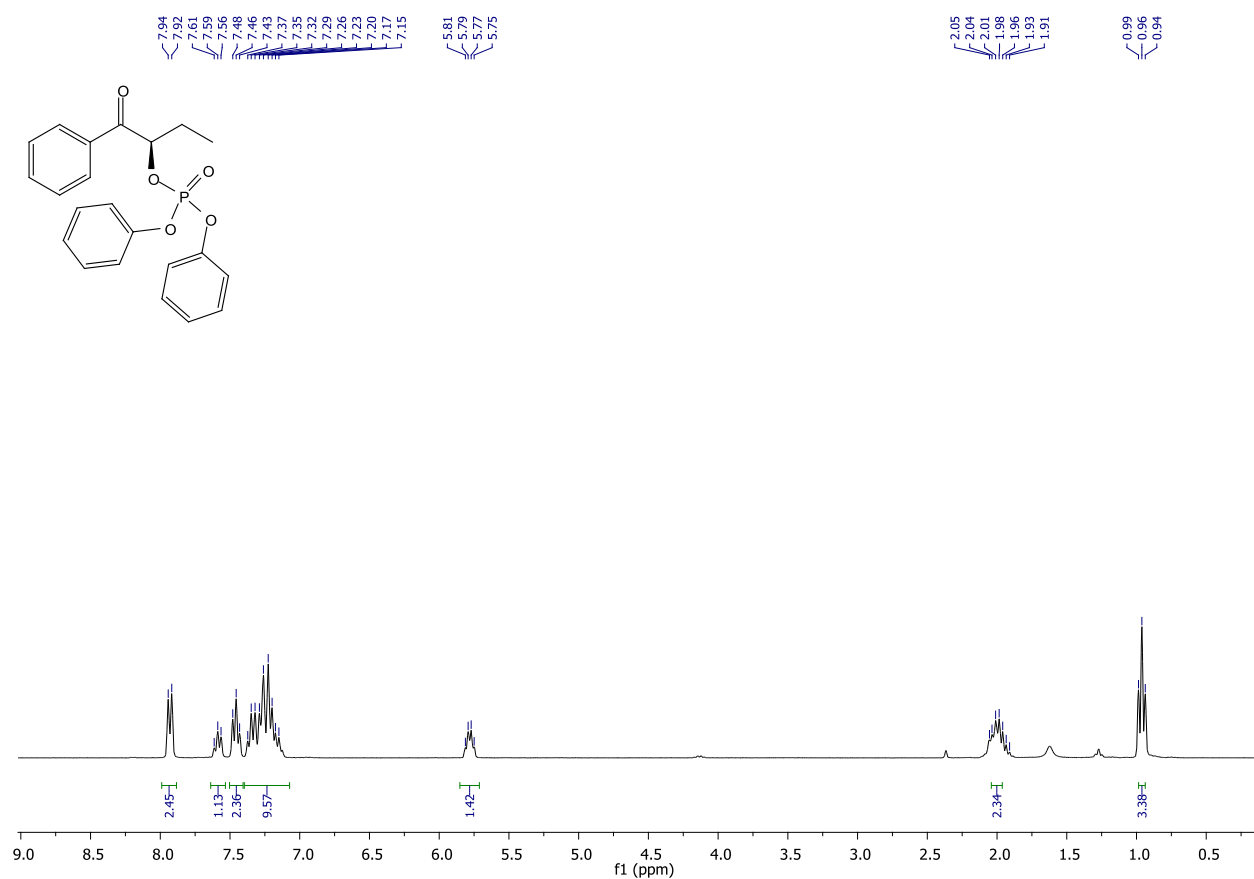
(R)-1-(4-fluorophenyl)-1-oxopropan-2-yl diphenyl phosphate (3q).



(R)-1-oxo-1-(p-tolyl)propan-2-yl diphenyl phosphate (3r).

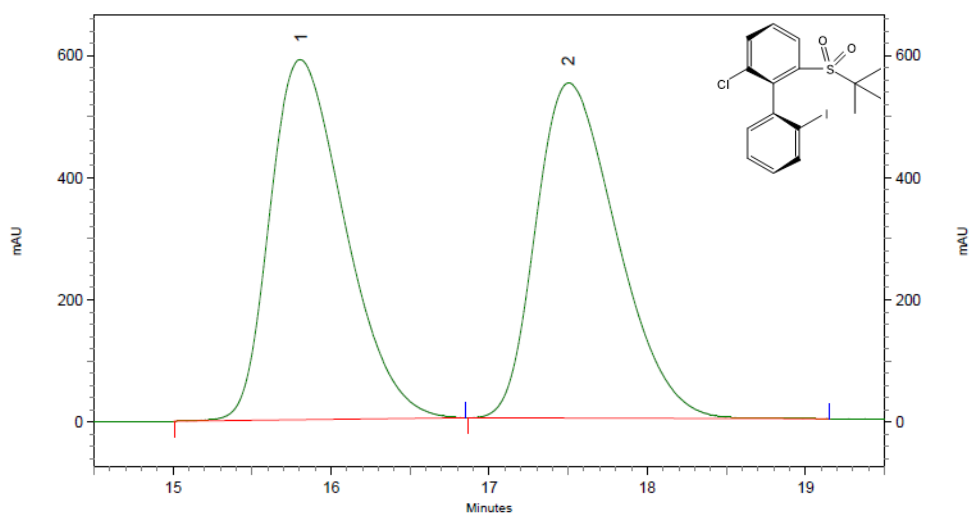


(*R*)-1-oxo-1-phenylbutan-2-yl diphenyl phosphate (3s).



2. Chiral stationary phase HPLC chromatograms:

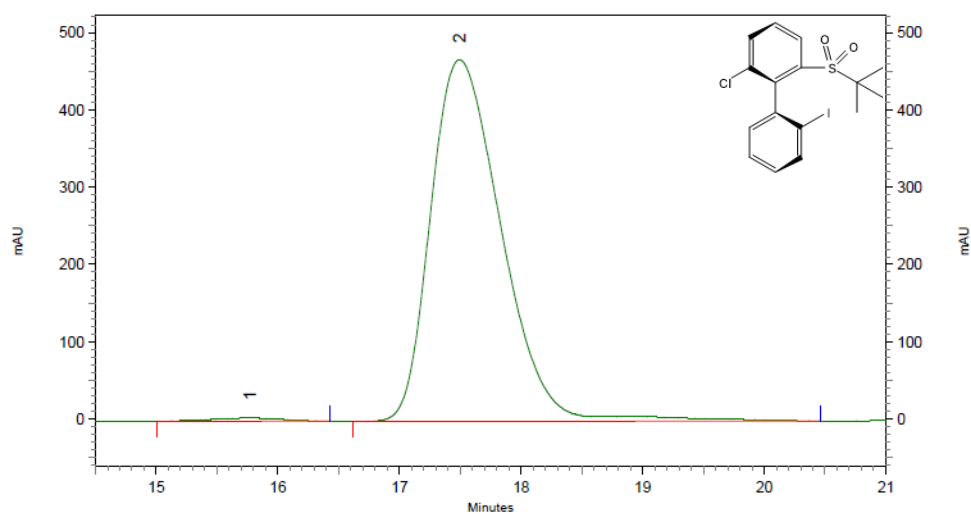
(*R*)-2-(tert-butylsulfonyl)-6-chloro-2'-iodo-1,1'-biphenyl (1m).



DAD-CH3 214 nm

Results

Pk #	Retention Time	Area	Area %
1	15,81	77888009	49,90
2	17,50	78208106	50,10

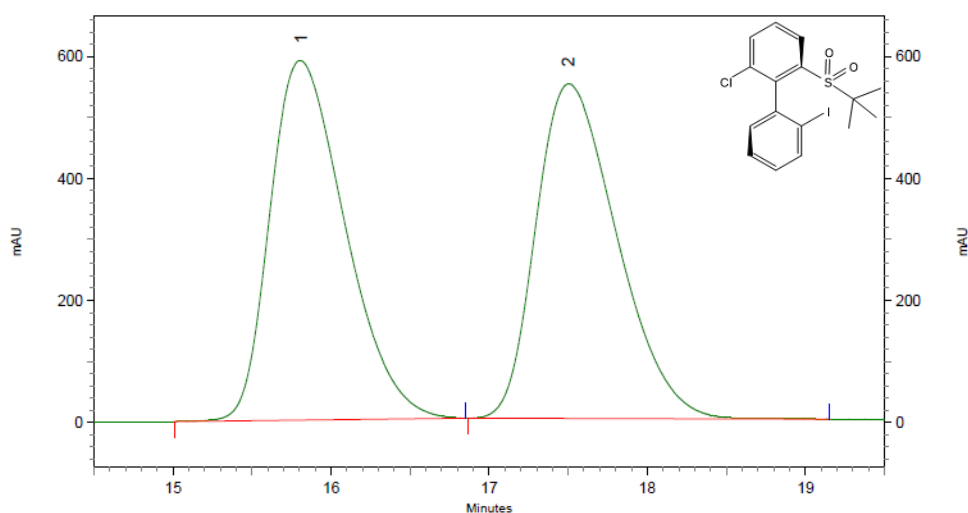


DAD-CH3 214 nm

Results

Pk #	Retention Time	Area	Area %
1	15,77	687788	0,90
2	17,49	75614733	99,10

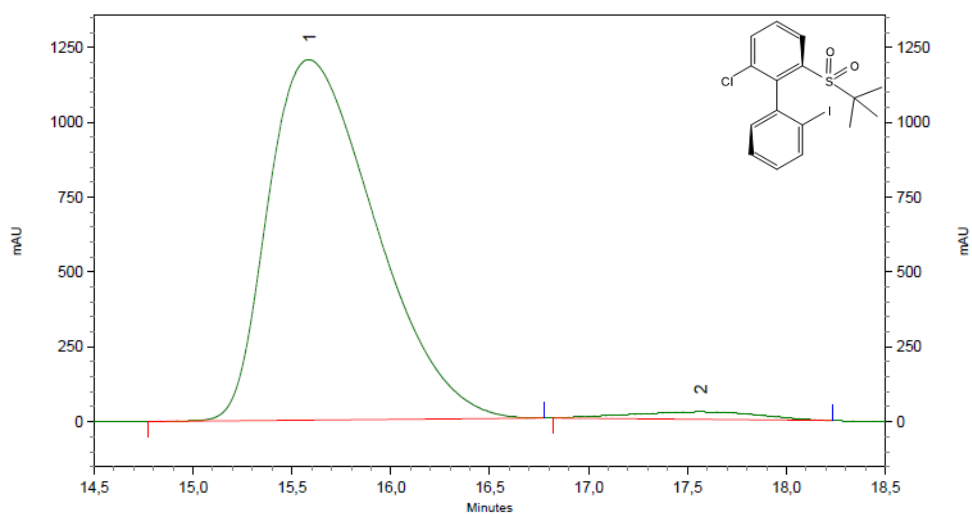
(S)-2-(tert-butylsulfonyl)-6-chloro-2'-iodo-1,1'-biphenyl (1n).



DAD-CH3 214 nm

Results

Pk #	Retention Time	Area	Area %
1	15,81	77888009	49,90
2	17,50	78208106	50,10

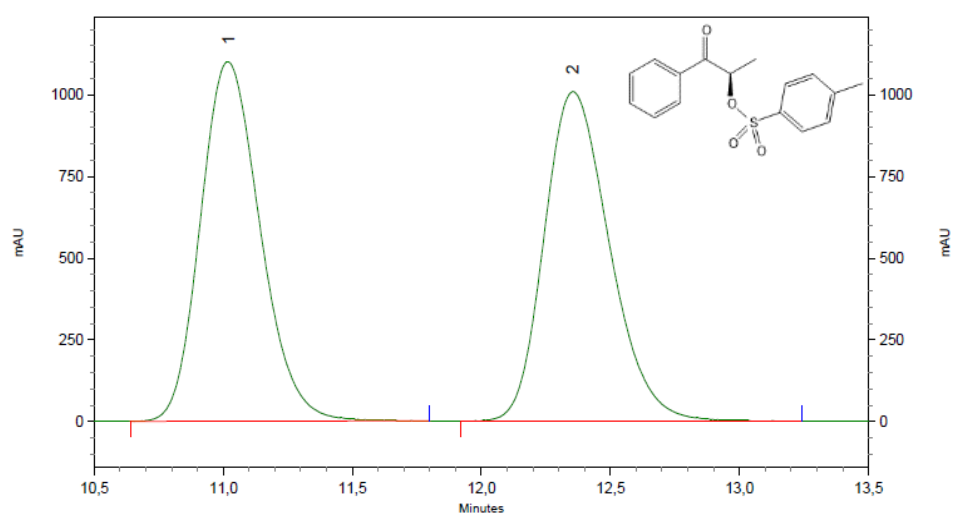


DAD-CH3 214 nm

Results

Pk #	Retention Time	Area	Area %
1	15,59	181361663	97,54
2	17,57	4575180	2,46

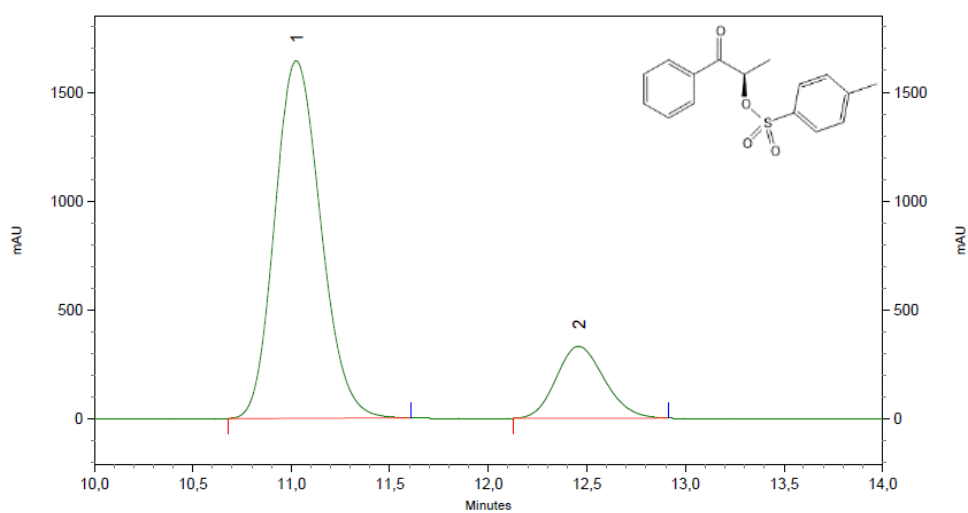
(R)-2-[(4-methylbenzenesulfonyl)oxy]-1-phenylpropan-1-one (3a).



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	11,02	70899124	50,01
2	12,35	70857771	49,99

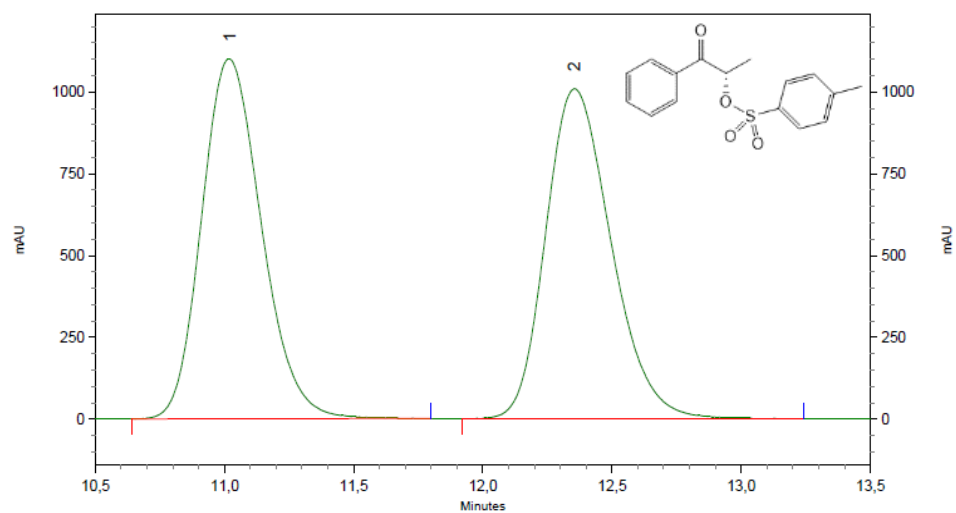


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	11,03	106677142	82,64
2	12,46	22413641	17,36

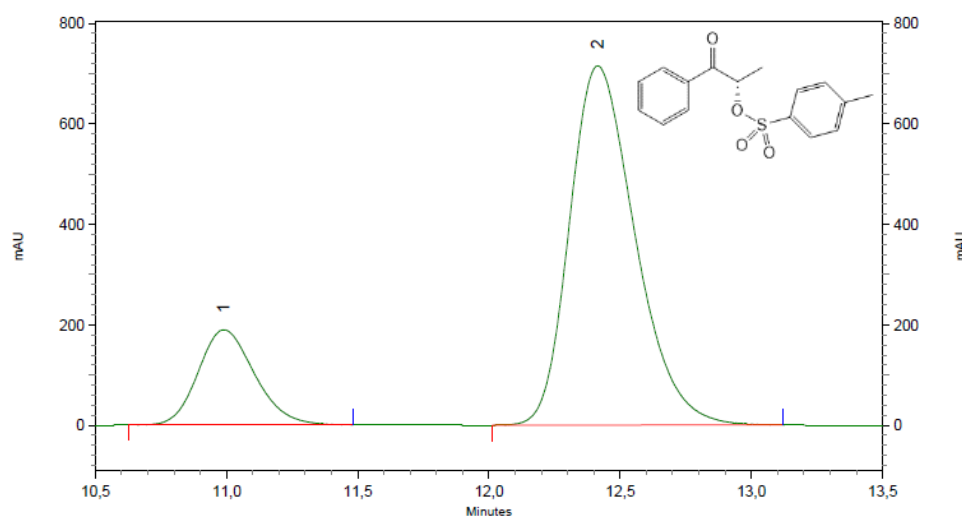
(S)-2-[(4-methylbenzenesulfonyl)oxy]-1-phenylpropan-1-one (3b).



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	11,02	70899124	50,01
2	12,35	70857771	49,99

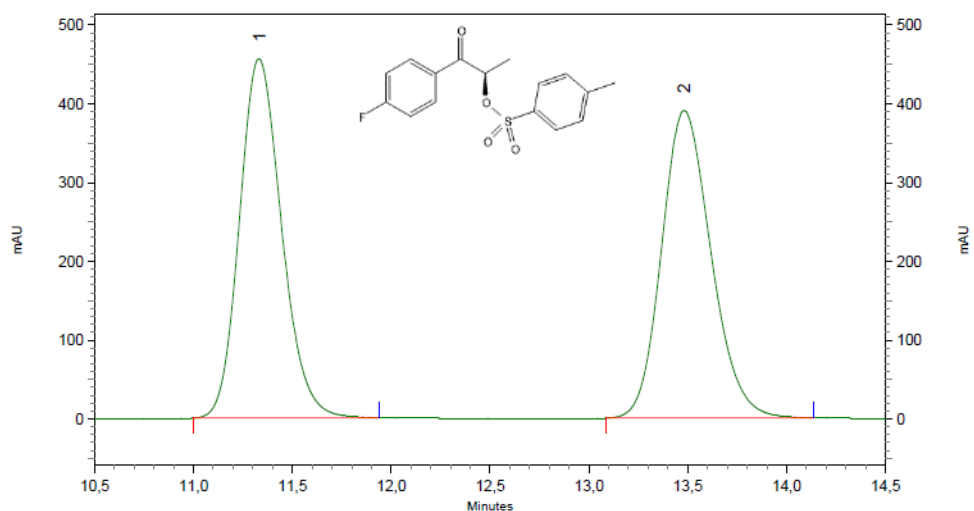


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	10,99	11350008	18,61
2	12,41	49650717	81,39

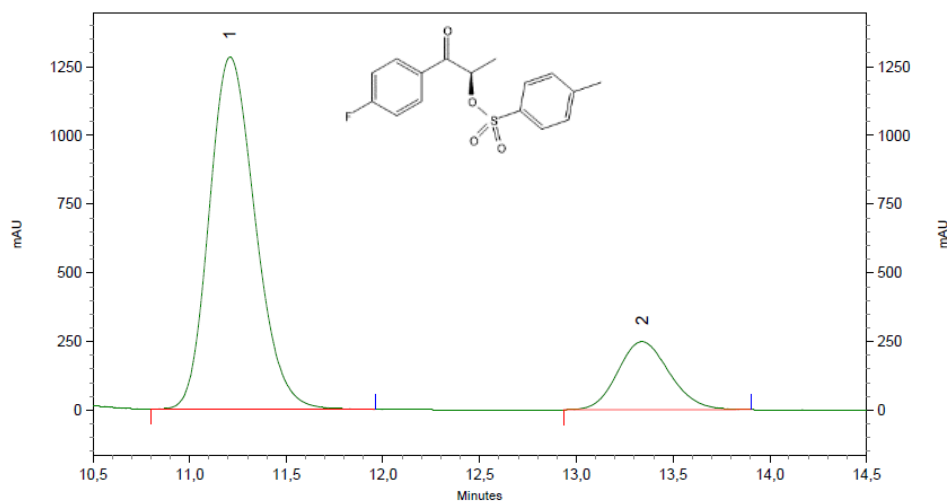
(R)-1-(4-Fluorophenyl)-1-oxopropan-2-yl 4-methylbenzenesulfonate (3c).



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	11,33	27006429	49,84
2	13,48	27185158	50,16

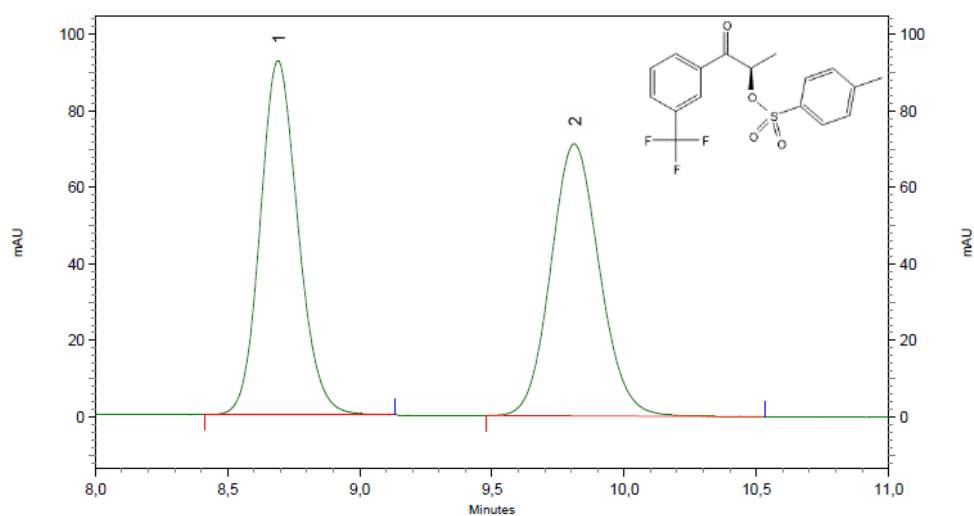


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	11,21	84614777	82,12
2	13,34	18418937	17,88

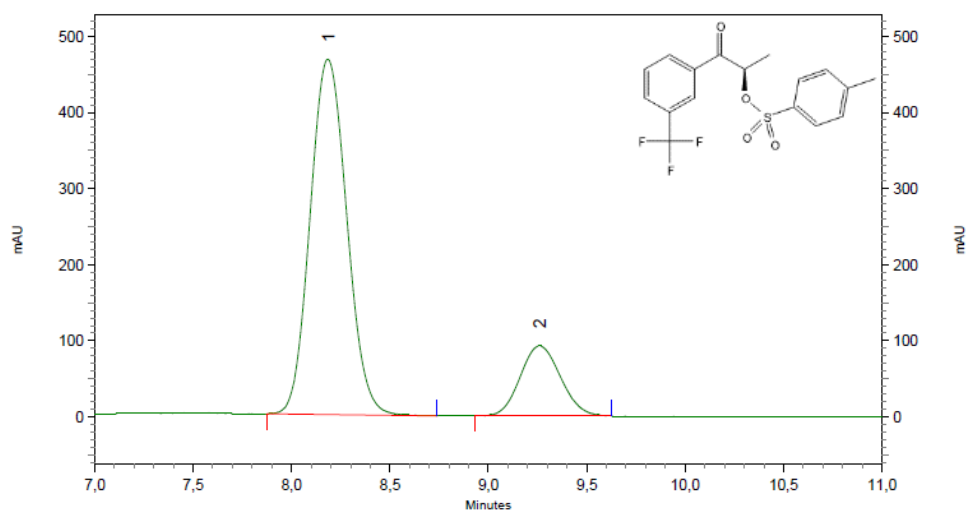
(R)-1-(3-(Trifluoromethyl)phenyl)-1-oxopropan-2-yl 4-methylbenzenesulfonate (3d).



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	8,69	3687263	50,26
2	9,81	3649306	49,74

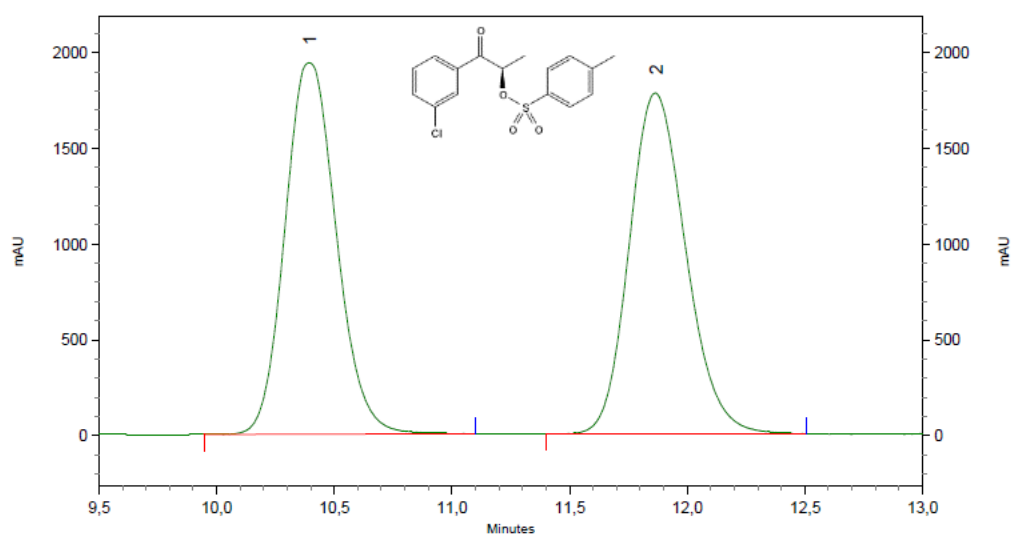


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	8,19	24109354	82,17
2	9,26	5232584	17,83

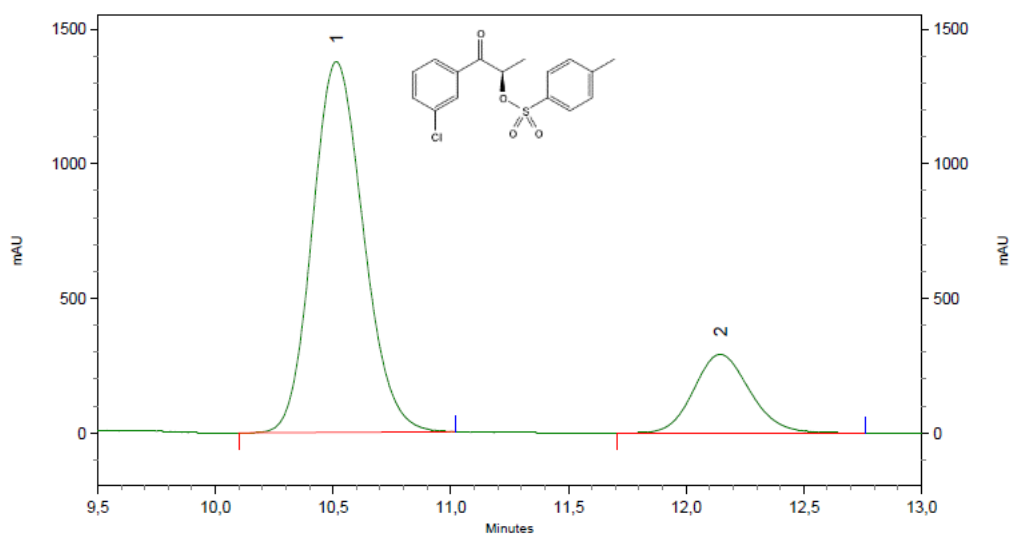
(R)-1-(3-chlorophenyl)-1-oxopropan-2-yl 4-methylbenzenesulfonate (3e).



DAD-CH2 280 nm

Results

Pk #	Retention Time	Area	Area %
1	10,39	4003529	49,91
2	11,87	4018029	50,09

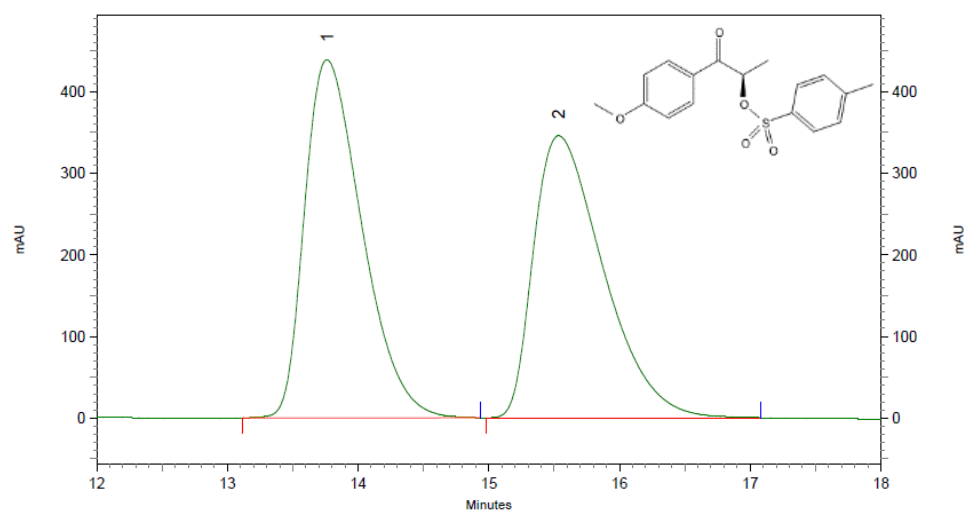


DAD-CH2 280 nm

Results

Pk #	Retention Time	Area	Area %
1	10,51	6237724	80,51
2	12,15	1509743	19,49

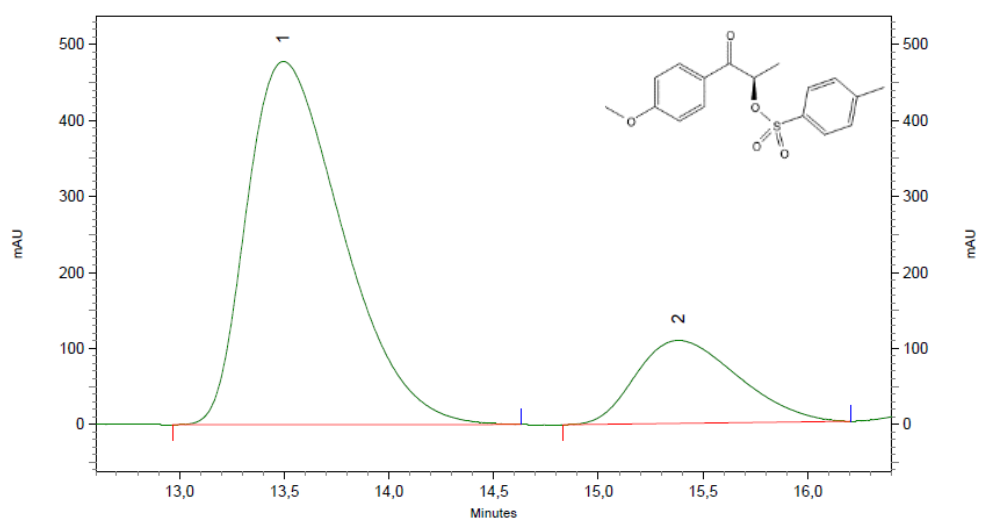
(R)-1-(4-methoxyphenyl)-1-oxopropan-2-yl 4-methylbenzenesulfonate (3f).



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	13,76	53468726	51,09
2	15,53	51194679	48,91

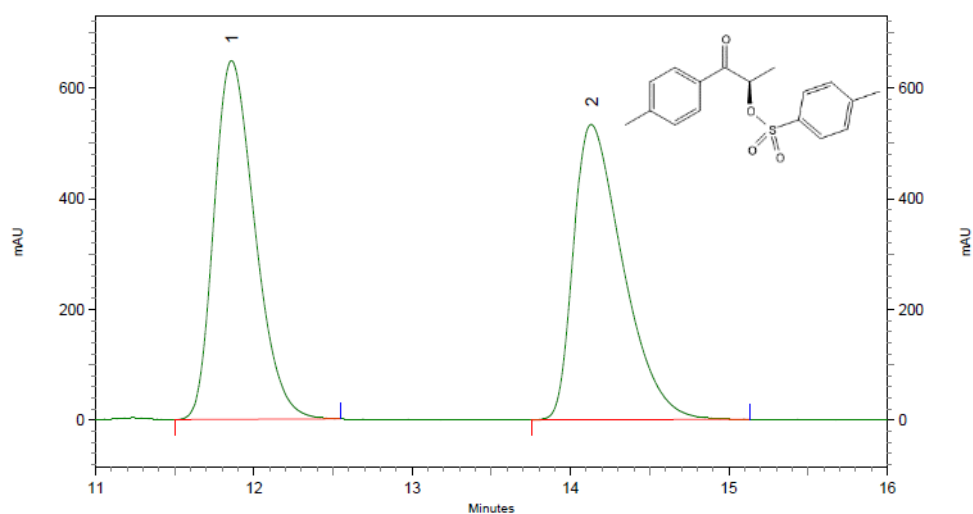


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	13,49	60704370	80,37
2	15,38	14830476	19,63

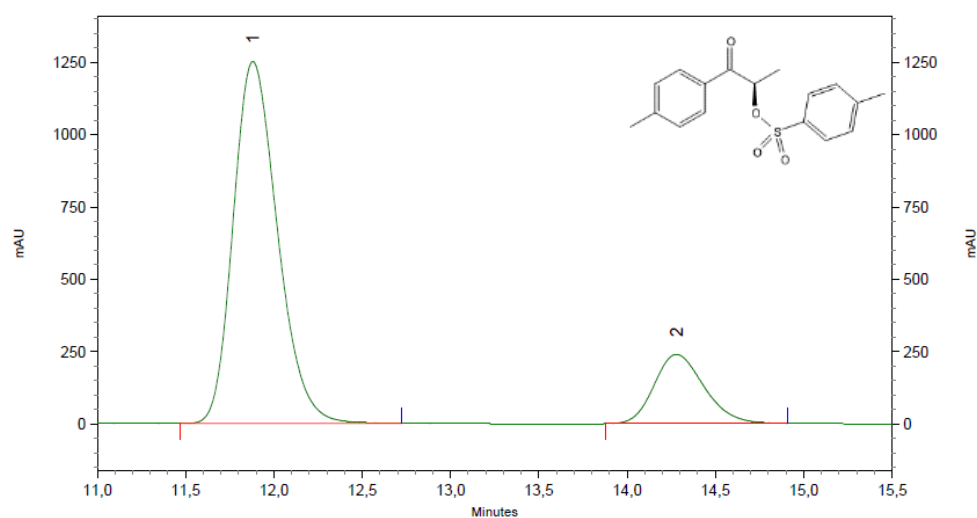
(R)-1-(4-methylphenyl)-1-oxopropan-2-yl 4-methylbenzenesulfonate (3g).



DAD-CH2 280 nm

Results

Pk #	Retention Time	Area	Area %
1	11,86	46427469	50,03
2	14,13	46366806	49,97

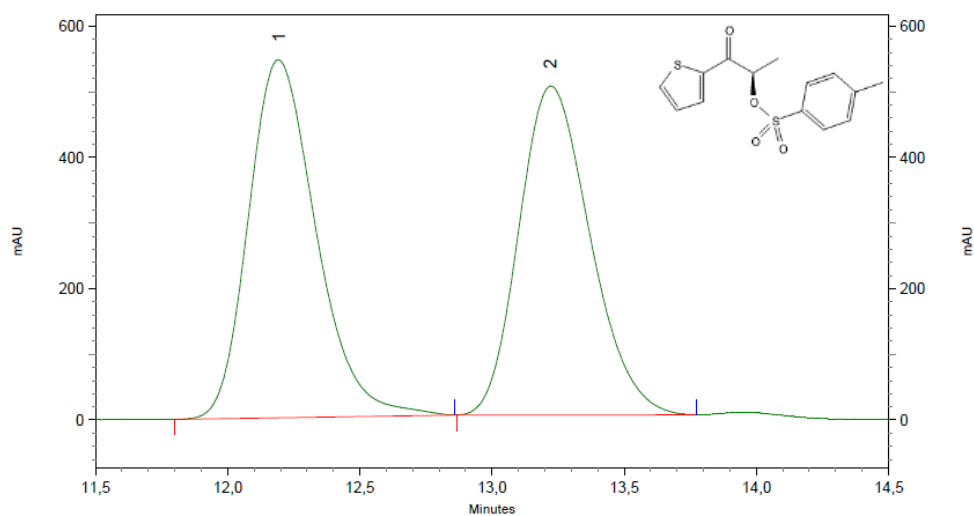


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	11,88	87204284	82,31
2	14,28	18744034	17,69

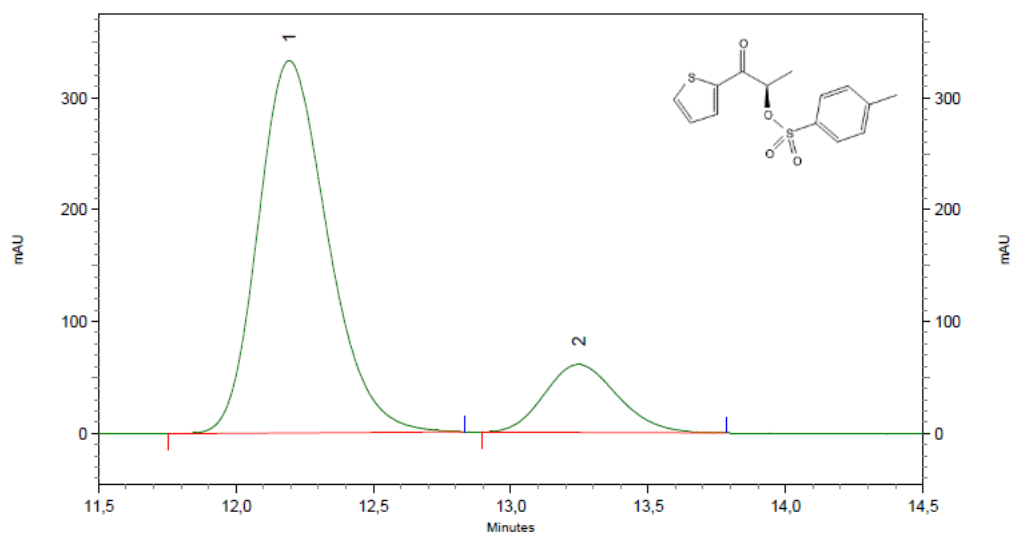
(R)-1-oxo-1-(thiophen-2-yl)propan-2-yl 4-methylbenzenesulfonate (3h).



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	12,19	38729144	50,82
2	13,22	37471833	49,18

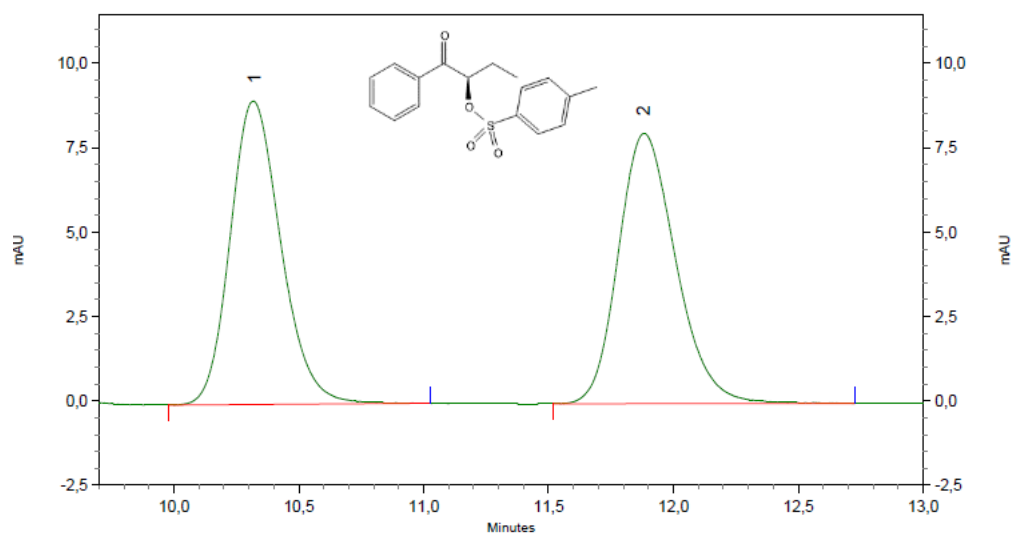


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	12,19	23423977	83,86
2	13,25	4507140	16,14

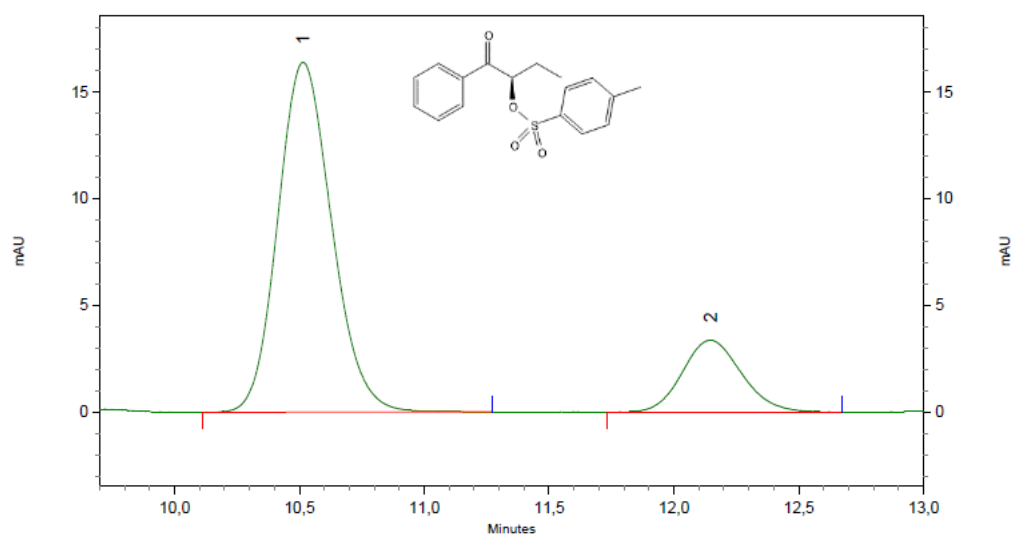
(R)-2-[(4-methylbenzenesulfonyl)oxy]-1-phenylbutan-1-one (3i).



DAD-CH4 300 nm

Results

Pk #	Retention Time	Area	Area %
1	10,32	508385	49,77
2	11,88	513146	50,23

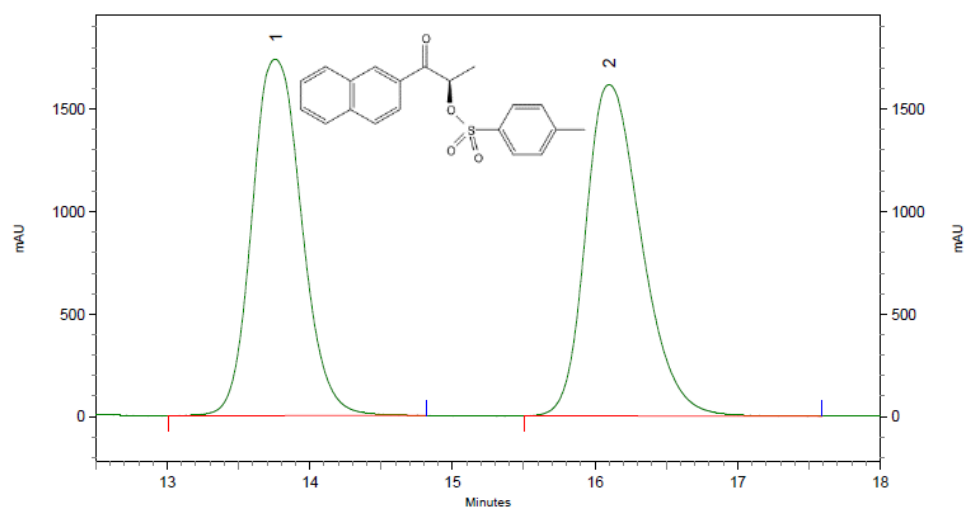


DAD-CH4 300 nm

Results

Pk #	Retention Time	Area	Area %
1	10,51	983453	81,61
2	12,15	221582	18,39

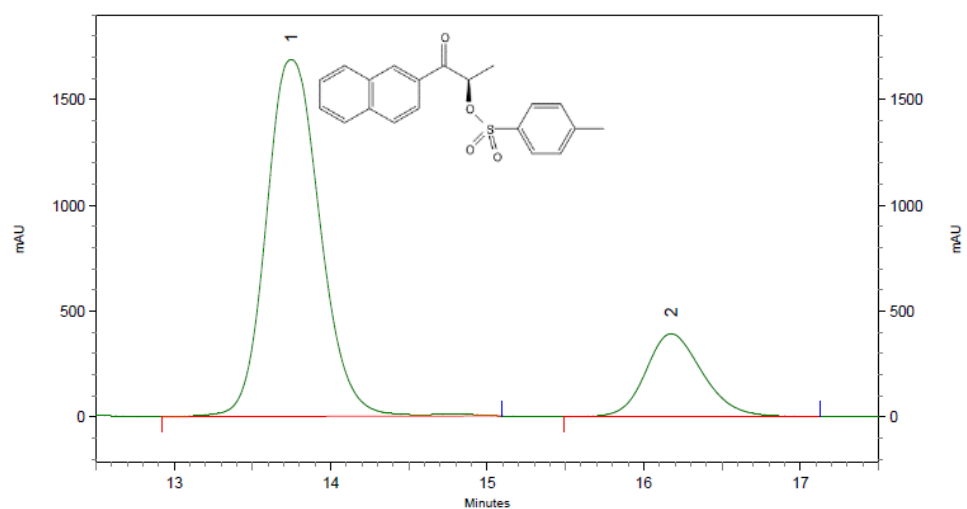
(R)-1-(naphthalen-2-yl)-1-oxopropan-2-yl-4-methylbenzenesulfonate (3j).



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	13,76	168857818	48,99
2	16,10	175845899	51,01

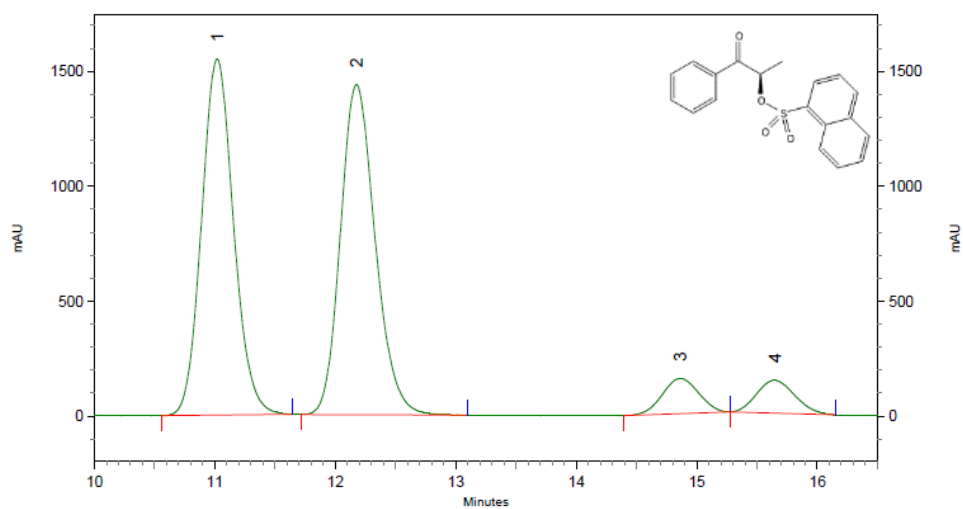


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	13,75	161841335	80,35
2	16,17	39585751	19,65

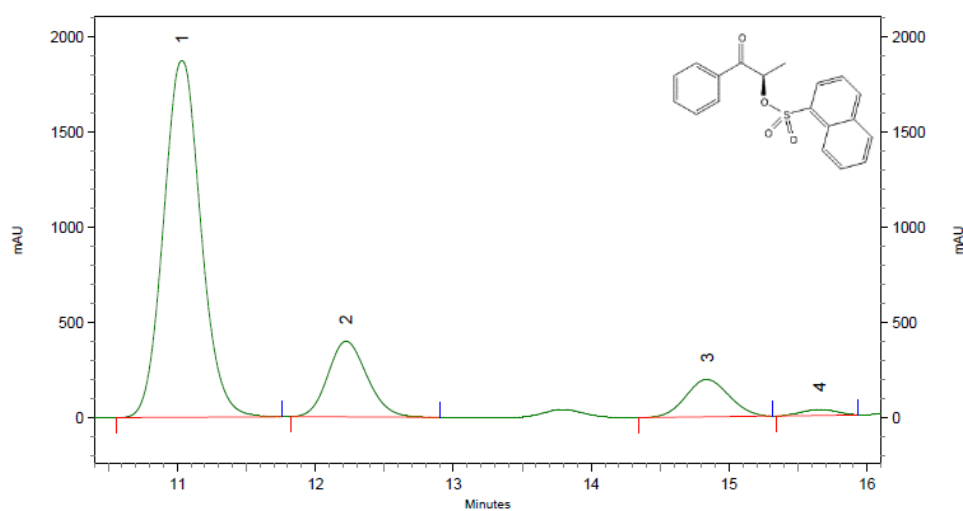
(R)- 1-oxo-1-phenylpropan-2-yl naphthalene-1-sulfonate (3k).



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	11,02	114399989	44,83
2	12,17	115310019	45,19
3	14,86	12824697	5,03
4	15,65	12631460	4,95

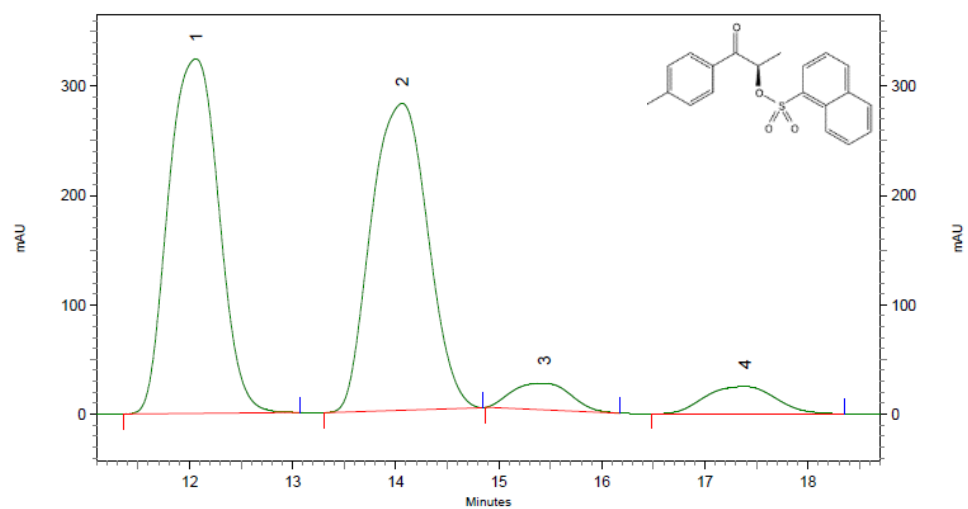


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	11,03	140753204	73,54
2	12,22	31296574	16,35
3	14,84	17120749	8,94
4	15,65	2233568	1,17

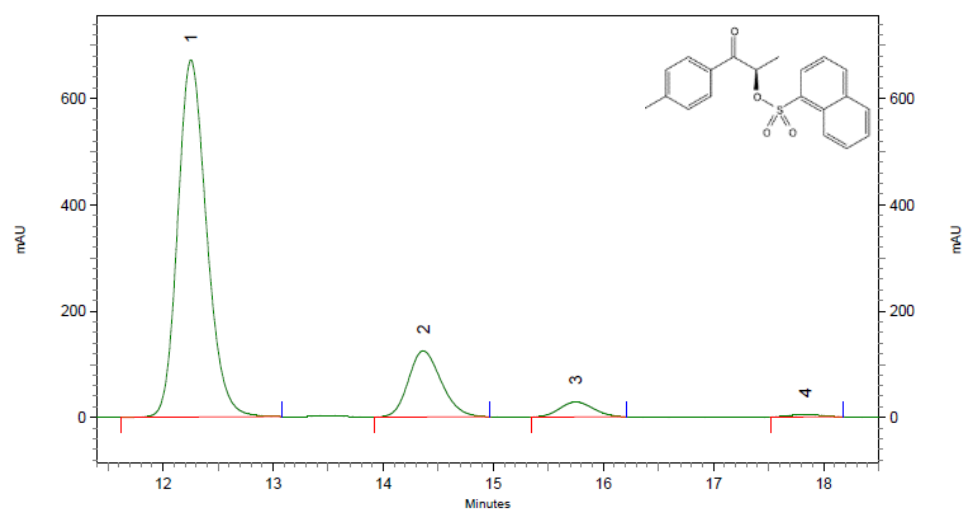
(R)- 1-oxo-1-(*p*-tolyl)propan-2-yl naphthalene-1-sulfonate (3I).



DAD-CH2 280 nm

Results

Pk #	Retention Time	Area	Area %
1	12,06	44072966	46,17
2	14,06	42931678	44,97
3	15,44	3815739	4,00
4	17,39	4639720	4,86

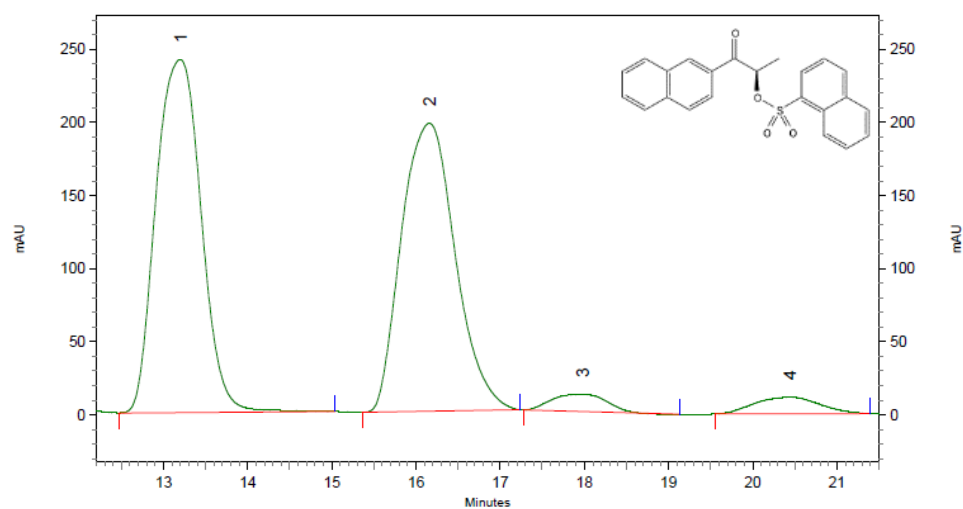


DAD-CH2 280 nm

Results

Pk #	Retention Time	Area	Area %
1	12,25	48929281	78,87
2	14,37	10285801	16,58
3	15,75	2428100	3,91
4	17,83	397392	0,64

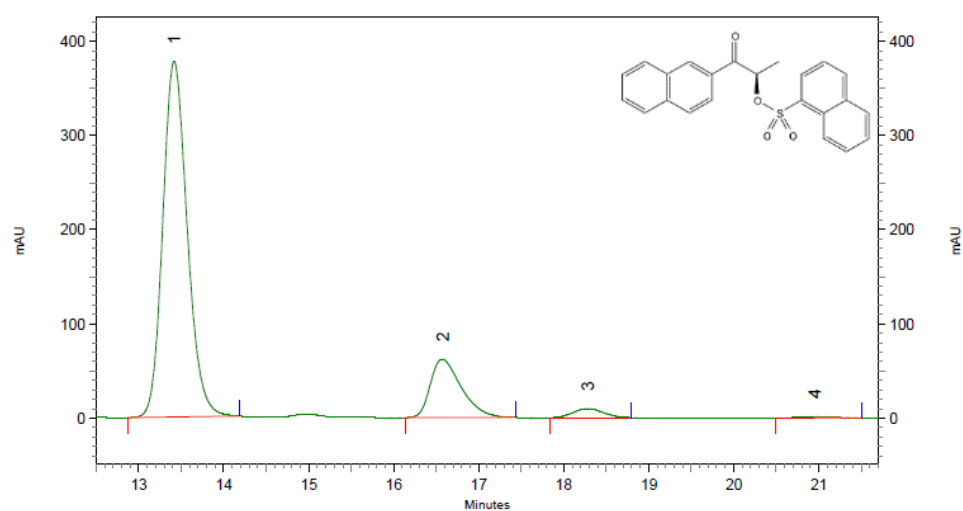
(R)- 1-(naphthalen-2-yl)-1-oxopropan-2-yl naphthalene-1-sulfonate (3m).



DAD-CH4 300 nm

Results

Pk #	Retention Time	Area	Area %
1	13,20	36050718	47,67
2	16,16	35021797	46,31
3	17,98	2103116	2,78
4	20,44	2449136	3,24

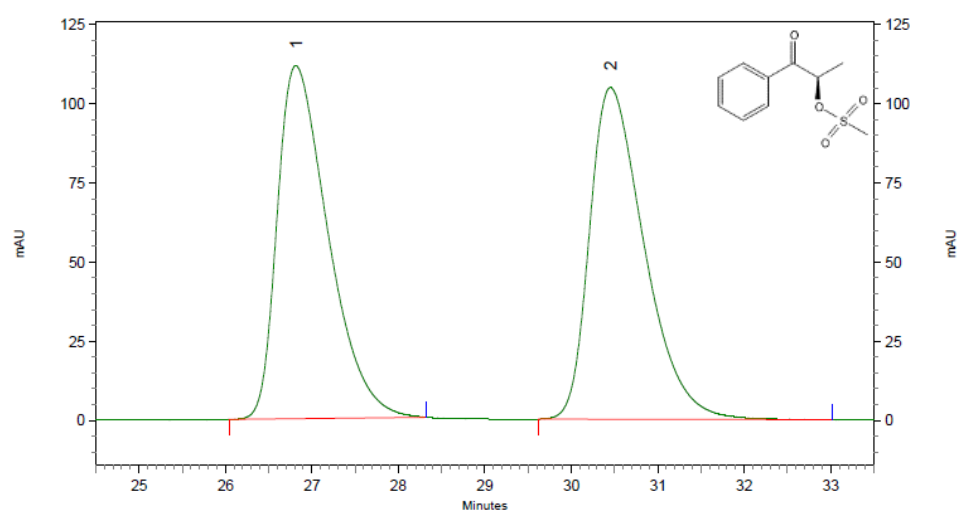


DAD-CH4 300 nm

Results

Pk #	Retention Time	Area	Area %
1	13,41	30120423	80,31
2	16,57	6261420	16,70
3	18,28	934181	2,49
4	20,95	187139	0,50

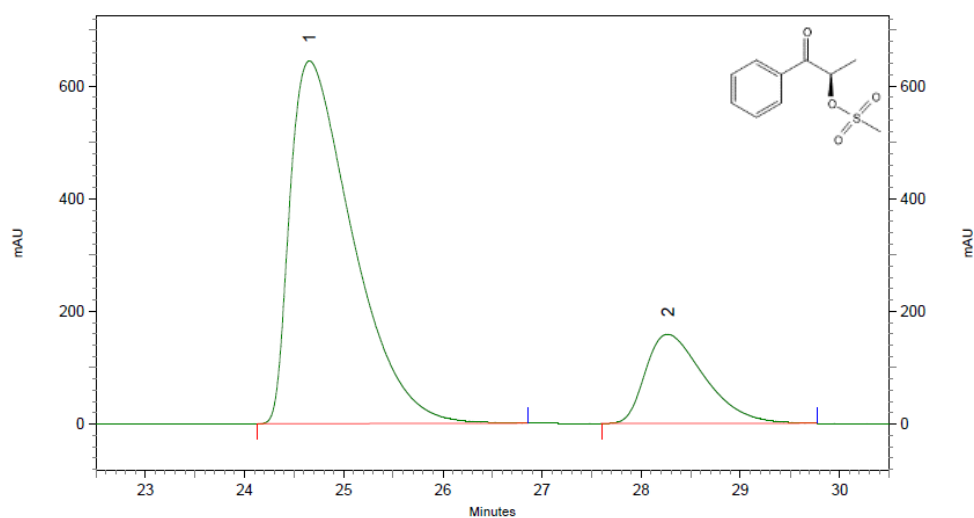
(R)-1-oxo-1-phenylpropan-2-yl methanesulfonate (3n).



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	26,81	18236556	49,67
2	30,45	18478391	50,33

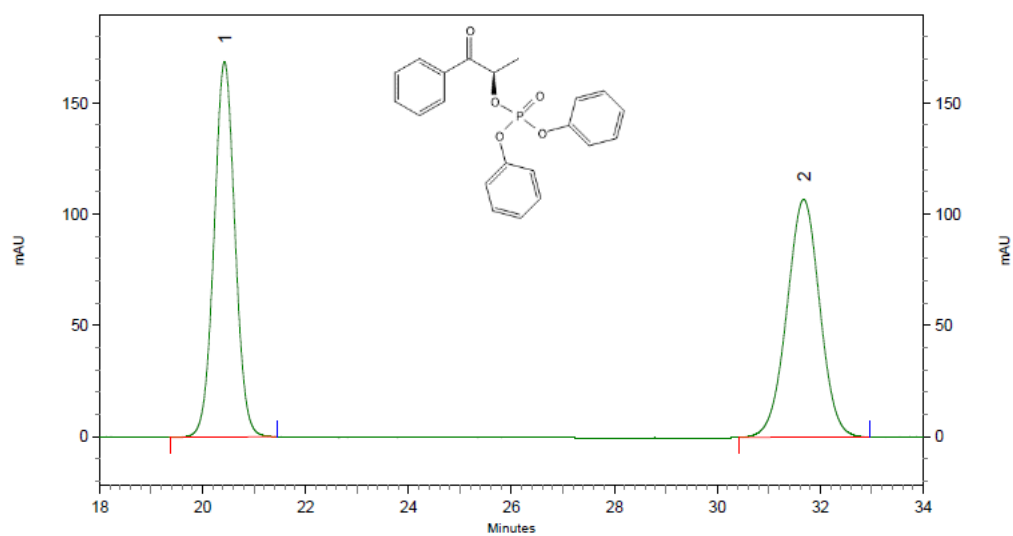


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	24,65	112820267	81,17
2	28,27	26173162	18,83

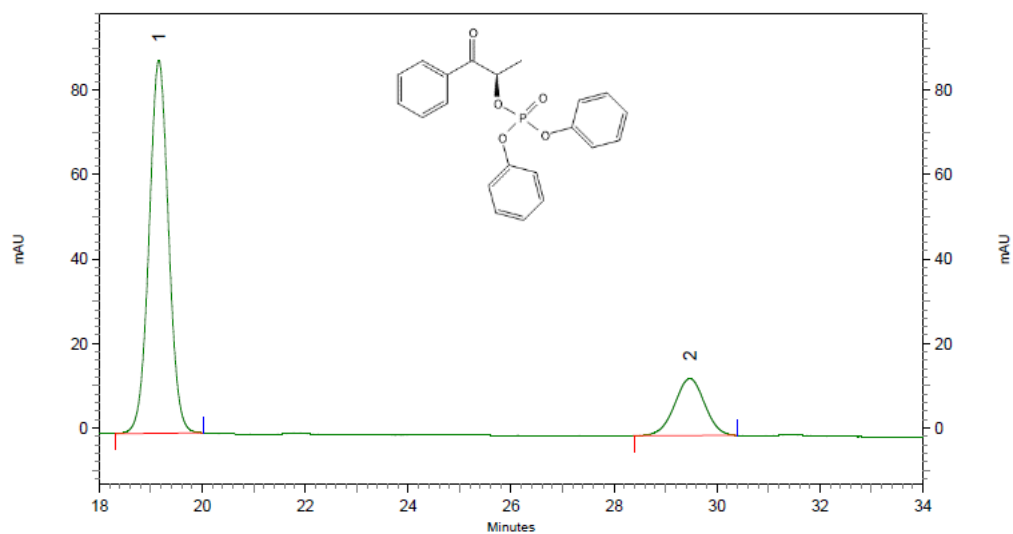
(R)-2-[(diphenoxyphosphoryl)oxy]-1-phenylpropan-1-one (3o).



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	20,43	1911847	50,09
2	31,68	19045637	49,91

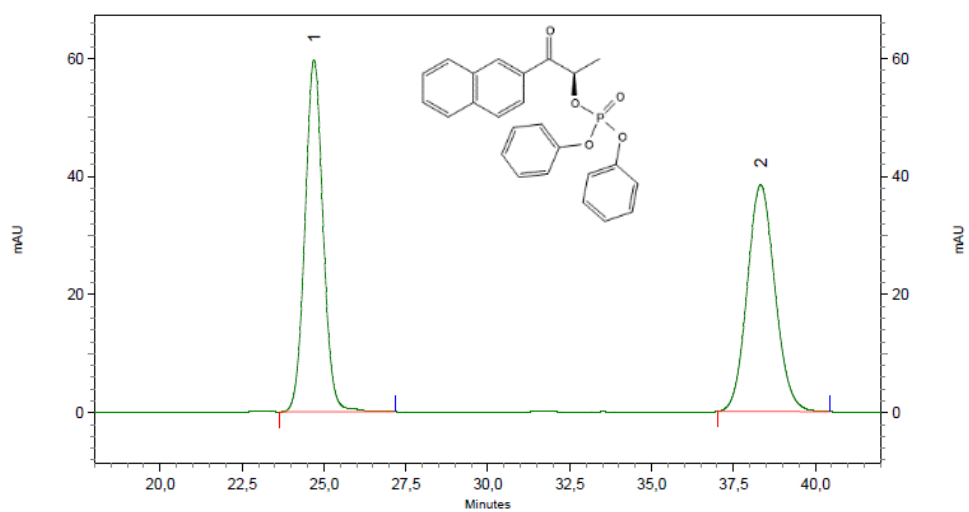


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	19,15	9299599	80,86
2	29,47	2201590	19,14

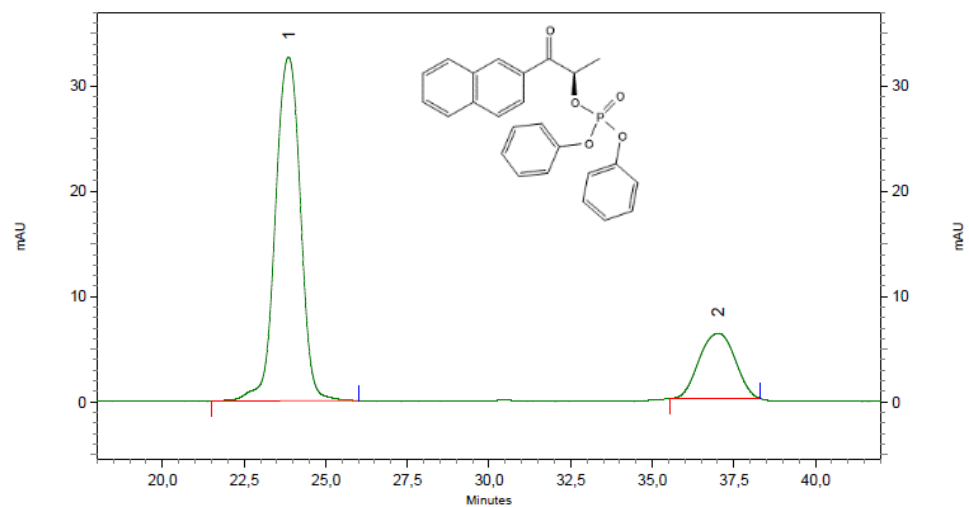
(R)-1-(naphthalen-2-yl)-1-oxopropan-2-yl diphenyl phosphate (3p).



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	24,70	72622429	49,82
2	38,33	73141262	50,18

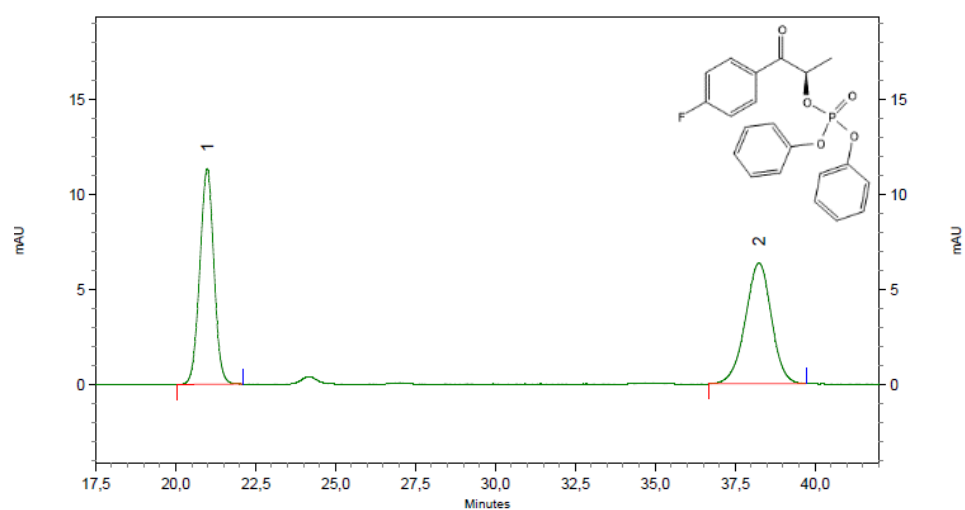


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	23,86	58640678	78,75
2	37,01	15822374	21,25

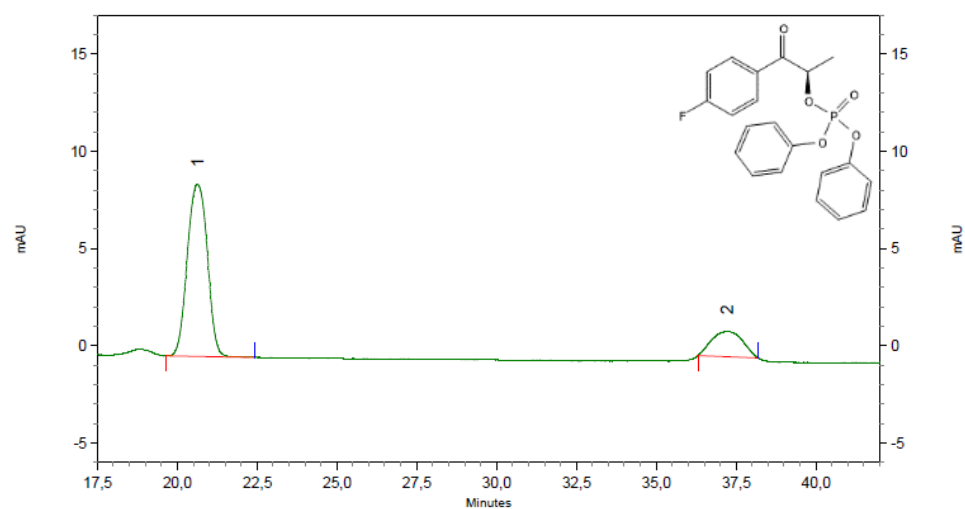
(R)-1-(4-fluorophenyl)-1-oxopropan-2-yl diphenyl phosphate (3q).



DAD-CH2 280 nm

Results

Pk #	Retention Time	Area	Area %
1	20,98	1394773	49,19
2	38,25	1440655	50,81

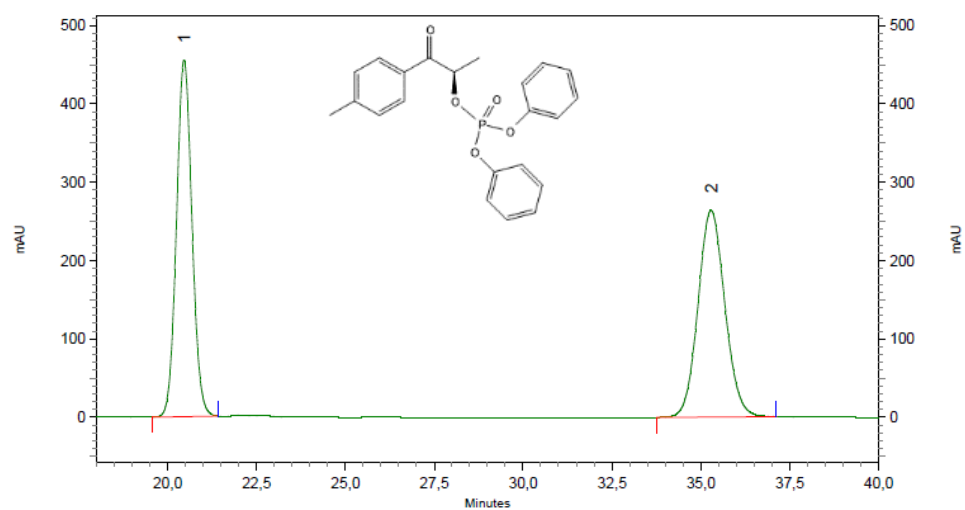


DAD-CH2 280 nm

Results

Pk #	Retention Time	Area	Area %
1	20,63	1544520	81,50
2	37,21	350641	18,50

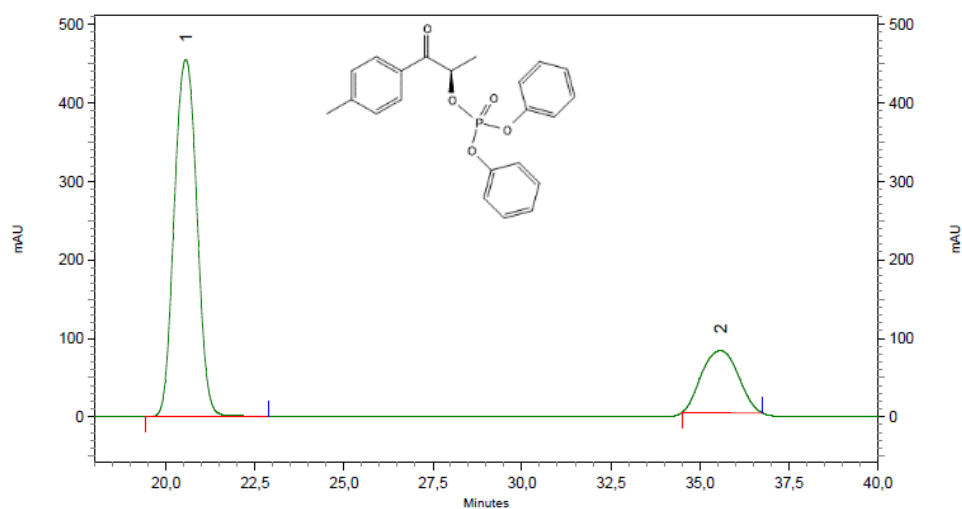
(R)-1-oxo-1-(p-tolyl)propan-2-yl diphenyl phosphate (3r).



DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	20,47	55301899	49,94
2	35,29	55444862	50,06

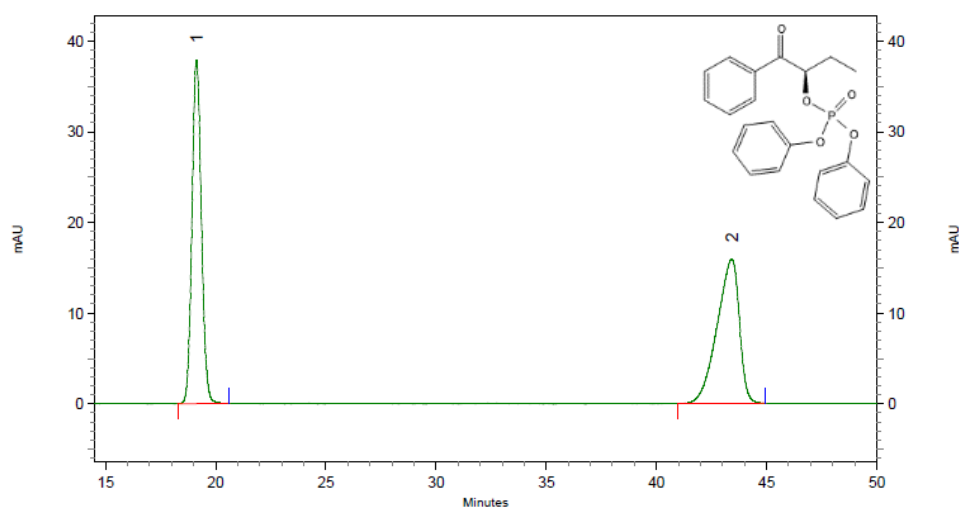


DAD-CH1 254 nm

Results

Pk #	Retention Time	Area	Area %
1	20,56	80199354	77,94
2	35,57	22702598	22,06

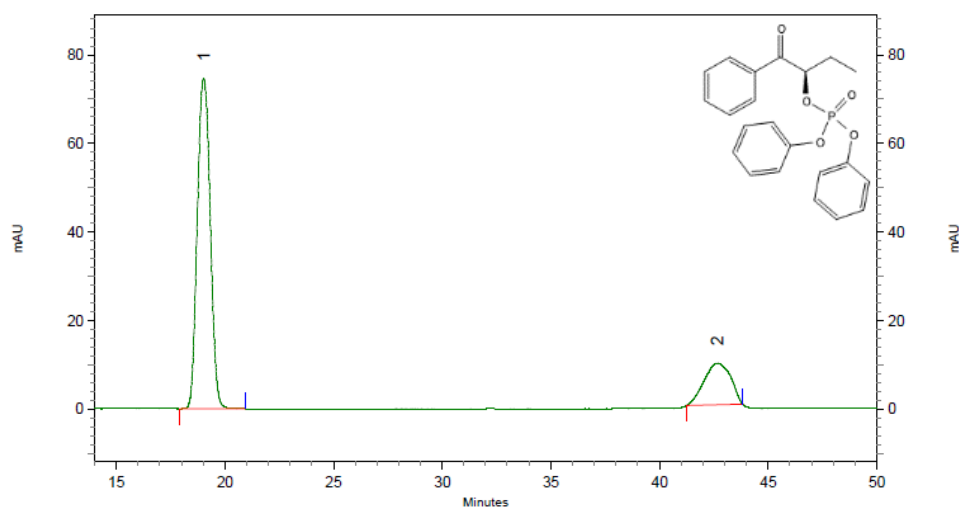
(R)-1-oxo-1-phenylbutan-2-yl diphenyl phosphate (3s).



DAD-CH2 280 nm

Results

Pk #	Retention Time	Area	Area %
1	19,13	4475726	50,05
2	43,41	4466607	49,95



DAD-CH2 280 nm

Results

Pk #	Retention Time	Area	Area %
1	19,03	12379465	79,46
2	42,65	3200272	20,54

3. X-Ray crystallographic data:

Good-quality colourless parallelepipedic crystals of **1** were obtained from a mixture of ethyl acetate and hexane by slow evaporation. The crystal chosen was attached to the tip of a 200 μ m nylon loop with paratone-N oil. X-ray diffraction measurements were carried out using a Rigaku XtaLabPro diffractometer equipped with a microfocus source (MicroMax003) delivering Mo K α radiation, λ = 0.71073 Å through Rigaku confocal Max-Flux® multilayer double bounce optic. The initial crystal orientation and unit cell were indexed using a least-squares analysis of a random set of reflections collected from three series of 0.5° w-scans, 0.6 second per frame and 10 frames per series, that were distributed in reciprocal space. For complete redundant (≥ 5) dataset collection, four w-scan frame series were collected with 0.5° wide scans, four second frames for a total of 486 frames at varying k (19, 38°) and j (-150, -180, -60°) angles. The crystal-to-detector distance was set to 4 cm. Cell refinement and data reduction were performed using CrysAlisPro¹, which corrects for Lorentz and polarization effects in particular and applies a multi-scan absorption correction (CrysAlisPro). The structure

¹ Rigaku Oxford Diffraction, CrysAlisPro Software system, version 38.41o, Rigaku Corporation, Oxford, UK. (2015).

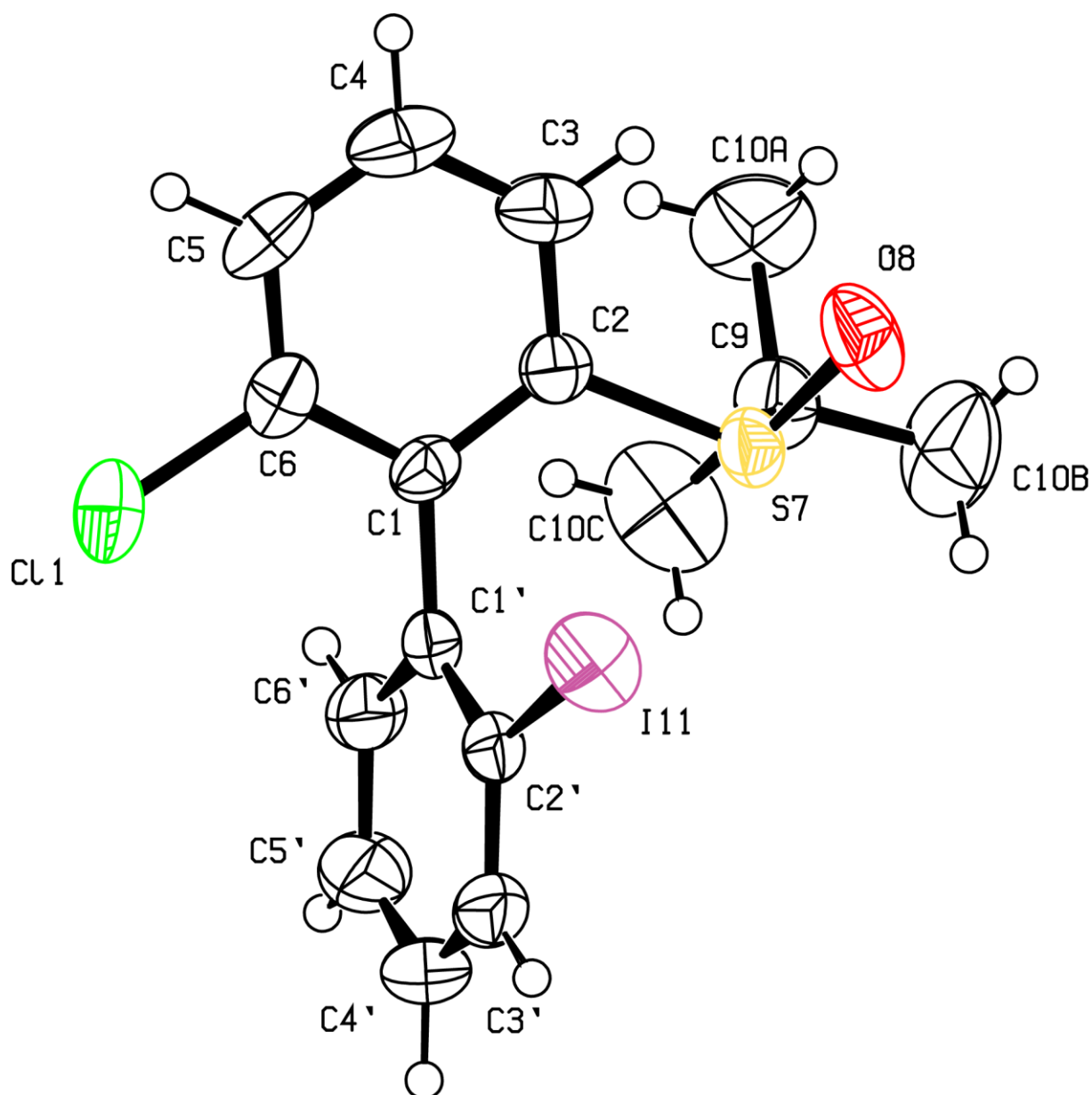


Figure was solved by intrinsic phasing methods with the ShelXT² program and refined using a full-matrix least-squares method on F^2 with the ShelXL³. All non-hydrogen atoms were refined with anisotropic displacement parameters and H atoms, although located in residual density, were included at geometrically idealized positions and treated as riding on their parent atoms. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2Ueq of the parent carbon of 1.5Ueq for methyl ones. The absolute structure of **1** was characterized as (*R*)-2-((*R*)-*tert*-butylsulfinyl)-6-chloro-2'-iodo-1,1'-

² Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Crystallogr. Sect. Found. Adv.* **2015**, *71*, 3.

³ Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3.

biphenyl with an non-ambiguous absolute structure Flack parameter,⁴ $x = -0.002(12)$ using 1192 quotients [(I+)-(I-)]/[(I+)+(I-)], from about 80% of Bijvoet pair coverage.

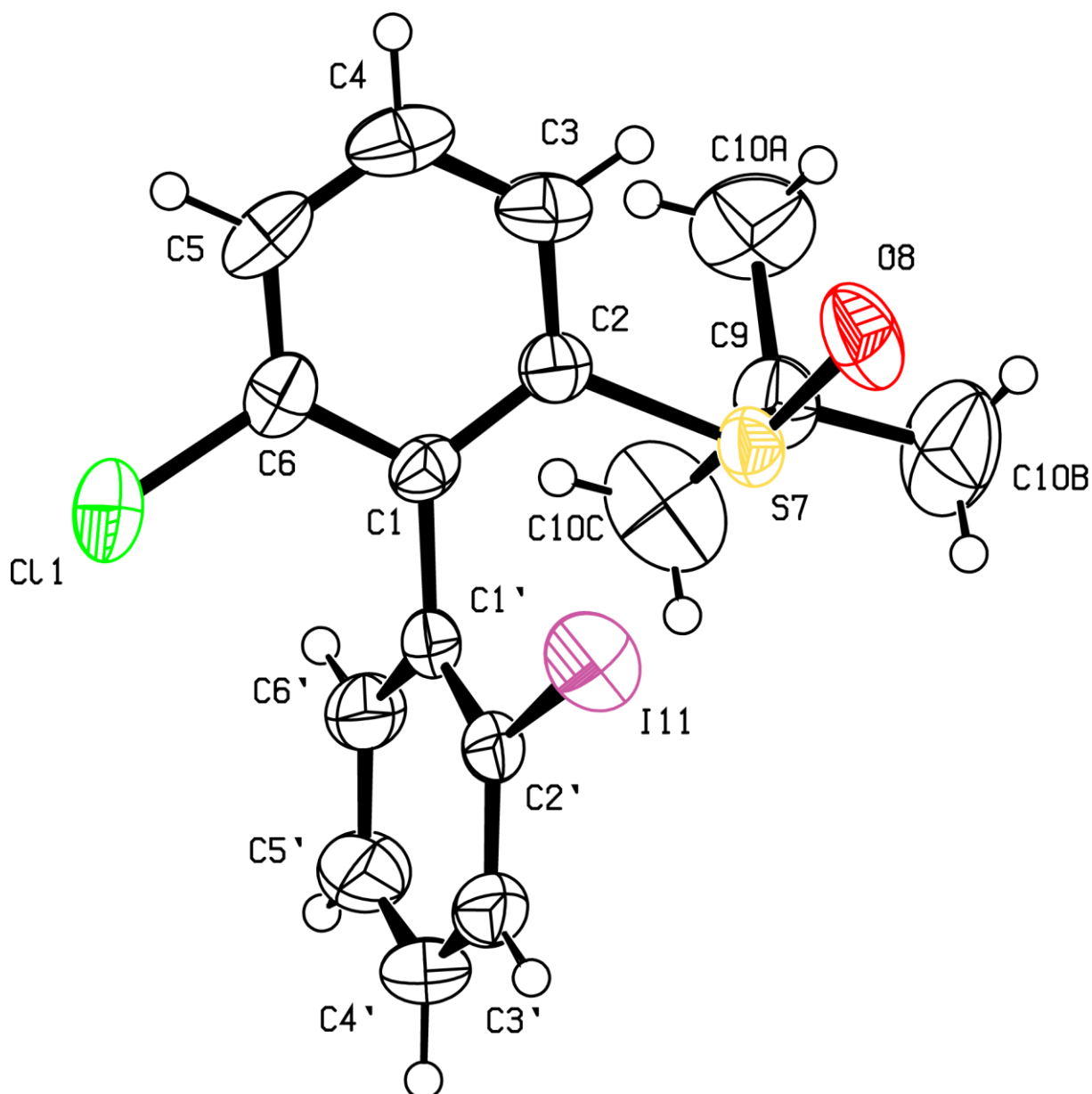


FIGURE S1: ORTEP-III⁵ PLOT OF **1**. ELLIPSOIDS ARE DRAWN AT THE 50% PROBABILITY LEVEL AND H ATOMS ARE SHOWN AS SPHERES OF ARBITRARY RADIUS.

⁴ Parsons, S., Flack, H.D. & Wagner, T. (2013) *Acta Cryst. B*69, 249-259.

⁵ Burnett, M. N. & Johnson, C. K. (1996). *ORTEP-III*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Table S1. Crystal data and structure refinement for *GL-III-85-deposit*.

Identification code		<i>GL-III-85-deposit</i>
Empirical formula		C ₁₆ H ₁₆ Cl I O S
Formula weight		418.70
Temperature	(K)	293(2)
Wavelength	(Å)	0.71073
Crystal system		Orthorhombic
Space group		P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions a	(Å)	7.6895(4)
b		12.8374(5)
c		17.1516(6)
α, β, γ	(°)	90
Volume	(Å ³)	1693.09(12)
Z		4
Density (calculated)	(Mg/m ³)	1.643
Absorption coefficient	(mm ⁻¹)	2.166
F(000)		824
Crystal size	(mm ³)	0.25 x 0.1 x 0.1
θ range for data collection	(°)	3.559 to 28.867
Index ranges		-8 ≤ h ≤ 10, -17 ≤ k ≤ 16, -22 ≤ l ≤ 19
Reflections collected		11923
Independent reflections		3756 [R(int) = 0.0274]
Completeness to θ _{full} = 25.242° (%)		99.3
Absorption correction		Semi-empirical from equivalents
Max. and min. transmission		1.00000 and 0.62326
Refinement method		Full-matrix least-squares on F ²
Data / restraints / parameters		3754 / 0 / 185
Goodness-of-fit on F ²		1.068
Final R indices [I > 2σ(I)]		R1 = 0.0265, wR2 = 0.0549
R indices (all data)		R1 = 0.0337, wR2 = 0.0571

Absolute structure parameter	-0.002(12)
Extinction coefficient	0.0026(5)
Largest diff. peak and hole (e.Å ³)	0.324 and -0.389
CCDC deposit number	1541444

CCDC 1541444 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.