Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A chiral phosphoric acid catalyst for asymmetric construction of 1,3-dioxanes

Akira Matsumoto, Keisuke Asano,* and Seijiro Matsubara*

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyotodaigaku-Katsura, Nishikyo, Kyoto 615-8510, Japan

Contents

Instrumentation and Chemicals

^{1}H and ^{13}C Nuclear magnetic resonance spectra were taken on a Varian UNITY INOVA 500 (^{1}H, 500 MHz; ^{13}C, 125.7 MHz) spectrometer using tetramethylsilane as an internal standard for ^{1}H NMR (δ = 0 ppm) and $CDCl_3$ as an internal standard for ^{13}C NMR (δ = 77.0 ppm). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), integration. ^{19}F NMR spectra were measured on a Varian Mercury 200 (^{19}F, 188 MHz) spectrometer with hexafluorobenzene as an internal standard (δ = 0 ppm). Mass spectra were recorded on a SHIMADZU GCMS-QP2010 Plus (EI) and a Thermo Scientific Exactive (ESI, APCI) spectrometers. High performance liquid chromatography (HPLC) was performed with a SHIMADZU Prominence. Infrared (IR) spectra were determined on a SHIMADZU IR Affinity-1 spectrometer. Melting points were determined using a YANAKO MP-500D. Optical rotations were measured on a HORIBA SEPA-200. X-ray data were taken on a Rigaku XtaLAB mini diffractometer equipped with a CCD detector. TLC analyses were performed by means of Merck Kieselgel 60 F_{254} (0.25 mm) Plates. Visualization was accomplished with UV light (254 nm) and/or such as an aqueous alkaline $KMnO_4$ solution followed by heating.

Flash column chromatography was carried out using Kanto Chemical silica gel (spherical, 40–50 μm). Unless otherwise noted, commercially available reagents were used without purification.

Experimental Procedure

General procedure for asymmetric construction of 1,3-dioxane 3

To a 5-mL vial, we sequentially added δ-hydroxy-α,β-unsaturated ketones **1** (0.10 mmol), cyclohexane (2.0 mL), aldehyde **2** (0.20 mmol) and phosphoric acid catalyst **4a** (0.005 mmol). The mixture was stirred in an oil bath maintained at 35 °C for 24 h. The reaction mixture was subsequently diluted with hexane/EtOAc (v/v = 1/1), passed through a short silica gel pad to remove **4a**, and concentrated in vacuo. Purification of the reaction mixture by flash silica gel column chromatography using hexane/EtOAc (v/v = 3/1) as an eluent afforded the corresponding 1,3-dioxanes **3**.

Racemic compounds were prepared using HBF_4 or (±)-1,1'-Binaphthyl-2,2'-diyl hydrogenphosphate as a catalyst.

General procedure for the preparation of δ-hydroxy-α,β-unsaturated ketones 1

To a solution of 1,3-propanediol (2.5 g, 33 mmol) in THF (80 mL) was added *n*-BuLi (20 mL, 1.63 M in hexane, 33 mmol) dropwise at 0 °C. After the mixture was stirred for 1 h, a solution of *tert*-butyldimethylsilyl chloride (4.5 g, 30 mmol) in THF (10 mL) was added, and the reaction was allowed to warm to ambient temperature. After being stirred for additional 23 h, the reaction was quenched with H_2O (10 mL), and the mixture was subsequently extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 5/1) as an eluent gave 3-(*tert*-butyldimethylsilyloxy)-propan-1-ol as a colorless oil in 94% yield: CAS RN [73842-99-6]. ^{1}H NMR ($CDCl_3$) δ 3.84 (t, *J* = 5.0 Hz, 2H), 3.80 (t, *J* = 5.5 Hz, 2H), 1.78 (tt, *J* = 5.5, 5.0 Hz, 2H), 0.90 (s, 9H), 0.08 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 63.0, 62.5, 34.2, 25.9, 18.2, –5.5.

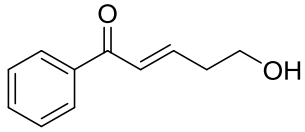
3-(*tert*-Butyldimethylsilyloxy) propan-1-ol (5.7 g, 30 mmol) was dissolved in EtOAc (100 mL, 0.30 M), and IBX (25 g, 90 mmol) was added. The resulting suspension was stirred vigorously in an oil bath maintained at 80 °C for 11 h. Subsequently, the reaction was cooled to ambient temperature and then filtered. The filter cake was washed with EtOAc, and the combined filtrates were concentrated to yield 3-(*tert*-butyldimethylsilyloxy)propanal as a colorless oil in 88 % yield, which was used for the next step without further purification: CAS RN [87184-81-4]. ^{1}H NMR ($CDCl_3$) δ 9.80 (t, *J* = 2,0 Hz, 1H), 3.99 (t, *J* = 6.0 Hz, 2H), 2.60 (dt, *J* = 6.0, 2.0 Hz, 2H), 0.88 (s, 9H), 0.06 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 202.2, 57.4, 46.5, 25.7, 18.2, –5.5.

3-(*tert*-Butyldimethylsilyloxy)propanal (0.90 g, 4.8 mmol) and a stabilized ylide (5.26 mmol) were dissolved in THF (20 mL), and the solution was refluxed in an oil bath at 100 °C for hours. After the solution was cooled to ambient temperature, solvents were removed in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 20/1) as an eluent gave the corresponding (*E*)-5-(*tert*-butyldimethylsilyloxy)pent-2-en-1-one. Subsequently, it was dissolved in CH_3CN (7.7 mL), and 46–48% aqueous HF (380 μL) was added to the solution. After being stirred for 15 min, the reaction was quenched with saturated aqueous $NaHCO_3$, and the mixture was subsequently extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 1/1) as an eluent gave the corresponding δ-hydroxy-α,β-unsaturated ketone **1**.

Ylides commercially unavailable were prepared by the literature procedure.[1]

The characterization results of **1** are as below.

(*E*)-5-Hydroxy-1-phenylpent-2-en-1-one (1a): CAS RN [946523-96-2].

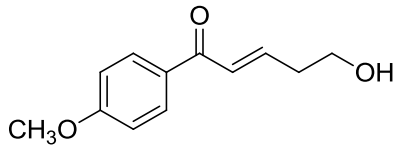


Colorless oil; 75% yield (for last 2 steps).

^{1}H NMR ($CDCl_3$) δ 7.94 (m, 2H), 7.56 (m, 1H), 7.47 (m, 2H), 7.05 (dt, *J* = 15.0, 7.0 Hz, 1H), 7.00 (dt, *J* = 15.0, 1.0 Hz, 1H), 3.85 (t, *J* = 6.0 Hz, 2H), 2.60 (m, 2H), 1.61 (br s, 1H).

^{13}C NMR ($CDCl_3$) δ 190.5, 145.5, 137.7, 132.8, 128.6, 128.0, 61.1, 36.0.

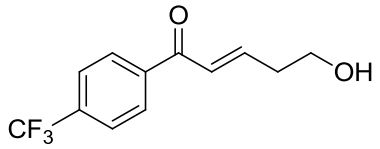
(*E*)-5-Hydroxy-1-(4-methoxyphenyl)pent-2-en-1-one (1b): CAS RN [1005326-88-4].



Colorless oil; 76% yield (for last 2 steps).

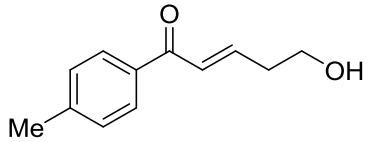
^{1}H NMR ($CDCl_3$) δ 7.96–7.94 (m, 2H), 7.05–6.98 (m, 2H), 6.95–6.92 (m, 2H), 3.87 (s, 3H), 3.83 (t, *J* = 6.5 Hz, 2H), 2.58 (m, 2H), 1.88 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 188.8, 163.4, 144.5, 130.9, 130.5, 127.7, 113.8, 61.1, 55.4, 36.0.

(*E*)-5-Hydroxy-1-(4-(trifluoromethyl)phenyl)pent-2-en-1-one (1c).



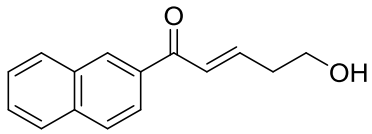
Pale yellow oil; 32% yield (for last 2 steps).
^{1}H NMR ($CDCl_3$) δ 8.02 (dd, J = 8.0, 1.0 Hz, 2H), 7.74 (dd, J = 8.0, 1.0 Hz, 2H), 7.10 (dt, J = 15.5, 7.0 Hz, 1H), 6.98 (dt, J = 15.5, 1.5 Hz, 1H), 3.87 (t, J = 6.0 Hz, 2H), 2.62 (m, 2H), 1.58 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 189.6, 147.1, 134.0 (q, J = 33.1 Hz), 128.8, 128.8, 126.1, 125.6 (q, J = 3.9 Hz), 123.6 (q, J = 272.6 Hz), 61.0, 36.0. ^{19}F NMR ($CDCl_3$) δ 98.7. TLC: R_f 0.38 (hexane/EtOAc = 1:1). IR (neat): 3381, 2937, 2888, 1672, 1624, 1616, 1411, 1326, 1229, 1169, 1128, 1068, 1016 cm^{-1}. HRMS Calcd for $C_{12}H_{10}F_3O_2$: $[M–H]^-$, 243.0638. Found: m/z 243.0640.

(*E*)-5-Hydroxy-1-(*p*-tolyl)pent-2-en-1-one (1d).



Pale yellow oil; 37% yield (for last 2 steps).
^{1}H NMR ($CDCl_3$) δ 7.85 (m, 2H), 7.27 (m, 2H), 7.02 (m, 2H), 3.84 (dt, J = 6.5, 1.0 Hz, 2H), 2.59 (ddt, J = 7.0, 1.0, 6.5 Hz, 2H), 2.42 (s, 3H), 1.68 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 190.0, 144.9, 143.7, 135.1, 129.3, 128.7, 128.0, 61.1, 36.0, 21.6. TLC: R_f 0.25 (hexane/EtOAc = 1:1). IR (neat): 3421, 2923, 2883, 1669, 1617, 1605, 1350, 1289, 1182, 1040 cm^{-1}. HRMS Calcd for $C_{12}H_{15}O_2$: $[M+H]^+$, 191.1067. Found: m/z 191.1061.

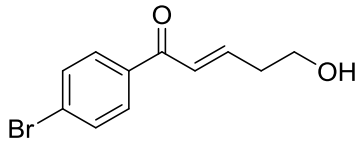
(*E*)-5-Hydroxy-1-(naphthalen-2-yl)pent-2-en-1-one (1e).



White solid; 46% yield (for last 2 steps).
^{1}H NMR ($CDCl_3$) δ 8.43 (s, 1H), 8.00 (dd, J = 8.0, 2.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.58 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 7.53 (ddd, J =8.0, 7.0, 1.0 Hz, 1H), 7.16 (d, J = 15.5 Hz, 1H), 7.11 (dt, J = 15.5, 5.5 Hz, 1H), 3.87 (t, J = 5.5 Hz, 2H), 2.63 (m 2H), 2.30 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 190.4, 145.7, 135.4, 134.9, 132.4, 130.1, 129.4, 128.4, 128.3, 127.8, 127.7, 126.7, 124.4, 61.0,

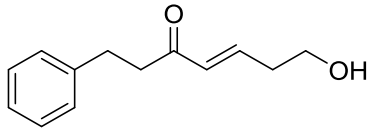
36.6. Mp. 69.7–70.5 °C. TLC: R_f 0.20 (hexane/EtOAc = 1:1). IR (KBr): 3283, 3270, 3267, 3055, 2892, 1665, 1620, 1610, 1460, 1424, 1370, 1292, 1289, 1193, 1125, 1067, 1044, 1012, 970 cm^{-1}. HRMS Calcd for $C_{15}H_{15}O_2$: $[M+H]^+$, 227.1067. Found: *m*/*z* 227.1059.

(*E*)-1-(4-Bromophenyl)-5-hydroxypent-2-en-1-one (1f).



Pale yellow oil; 23% yield (for last 2 steps).
^{1}H NMR ($CDCl_3$) δ 7.80 (m, 2H), 7.60 (m, 2H), 7.07 (dt, *J* = 15.5, 7.0 Hz, 1H), 6.95 (dt, *J* = 15.5, 1.5 Hz, 1H), 3.85 (t, *J* = 6.0 Hz, 2H), 2.60 (ddt, *J* = 7.0, 1.0, 6.0 Hz, 2H), 1.60 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 189.3, 146.2, 136.3, 131.9, 130.1, 127.9, 127.4, 61.0, 36.0. TLC: R_f 0.22 (hexane/EtOAc = 1:1). IR (neat): 3431, 3089, 3061, 2933, 2883, 1715, 1662, 1622, 1586, 1566, 1484, 1397, 1350, 1288, 1225, 1178, 1105, 1072, 1039, 1009, 976, 823, 665 cm^{-1}. HRMS Calcd for $C_{11}H_{12}BrO_2$: $[M+H]^+$, 255.0015. Found: *m*/*z* 255.0008.

(*E*)-7-Hydroxy-1-phenylhept-4-en-3-one (1g).



Pale yellow oil; 42% yield (for last 2 steps).
^{1}H NMR ($CDCl_3$) δ 7.28 (m, 2H), 7.19 (m, 3H), 6.81 (dt, *J* = 16.0, 7.0 Hz, 1H), 6.19 (dt, *J* = 16.0, 1.5 Hz, 1H), 3.77 (t, *J* = 6.0 Hz, 2H), 2.94 (m, 2H), 2.89 (m, 2H), 2.47 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 199.3, 143.4, 141.2, 132.3, 128.5, 128.4, 126.1, 61.0, 41.7, 35.6, 30.0. TLC: R_f 0.20 (hexane/EtOAc = 1:1). IR (neat): 3416, 3062, 3027, 2928, 2887, 1691, 1660, 1624, 1604, 1497, 1453, 1369, 1047, 700 cm^{-1}. HRMS Calcd for $C_{13}H_{17}O_2$: $[M+H]^+$, 205.1223. Found: *m*/*z* 205.1223.

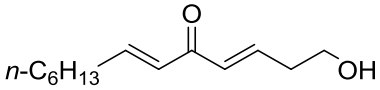
***Procedure for preparation of 1h*[2]**

To a stirred mixture of diisopropylamine (10.1 g, 100 mmol) in Et_2O (100 mL) at 0 °C was added trifluoroacetic acid dropwise (7.7 mL, 100 mmol). The reaction mixture was stirred at 0 °C for additional 5 min, and the newly formed crystals were filtered.

The filter cake was washed with Et_2O, and the combined filtrates were concentrated in vacuo to afford pure diisopropylammoium 2,2,2-trifluoroacetate as a white solid in 85 % yield. Next, to a mixture of 3-decen-2-one (3.1 g, 20 mmol) and paraformaldehyde (1.2 g, 40 mmol) in dry THF (20 mL) was added diisopropylammoium 2,2,2-trifluoroacetate (4.3 g, 20 mmol) and trifluoroacetic acid (0.31 mL, 4.0 mmol). The reaction mixture was stirred under reflux for 2 h, and then cooled down to ambient temperature, and the second addition of paraformaldehyde (1.2 g, 40 mmol) was performed. The reaction mixture was stirred under reflux for additional 6 h. The reaction mixture was cooled down to ambient temperature and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 20/1) as an eluent gave undeca-1,4-dien-3-one as a pale yellow oil in 31 % yield; CAS RN [52353-97-6] ^{1}H NMR ($CDCl_3$) δ 6.95 (dt, *J* = 15.5, 7.0 Hz, 1H), 6.61 (dd, *J* = 16.5, 10.5 Hz, 1H), 6.36 (dt, *J* = 15.5, 1.0 Hz, 1H), 6.28 (dd, *J* = 16.5, 1.0 Hz, 1H), 5.81 (dd, *J* = 10.5, 1.0 Hz, 1H), 2.25 (m, 2H), 1.48 (m, 2H), 1.35–1.25 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 190.1, 149.5, 135.1, 128.6, 128.4, 33.0, 31.8, 29.1, 28.3, 22.8, 14.3.

Hoveyda–Grubbs catalyst 2nd generation (47 mg, 0.076 mmol) was placed in a 30 mL round-bottom flask inside a glovebox. The flask was taken outside the glovebox and immediately filled with argon gas. Pure CH_2Cl_2 (5 mL), a solution of undeca-1,4-dien-3-one (1.3 g, 7.6 mmol) in CH_2Cl_2 (5 mL), and a solution of 3-buten-1-ol (0.11 g, 1.5 mmol) in CH_2Cl_2 (5 mL) were sequentially added to the flask. After the resulting mixture was stirred at ambient temperature for 10 h, the solvent was removed in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 3/1) as an eluent gave (3*E*,6*E*)-1-hydroxytrideca-3,6-dien-5-one (**1h**) in 70 % yield.

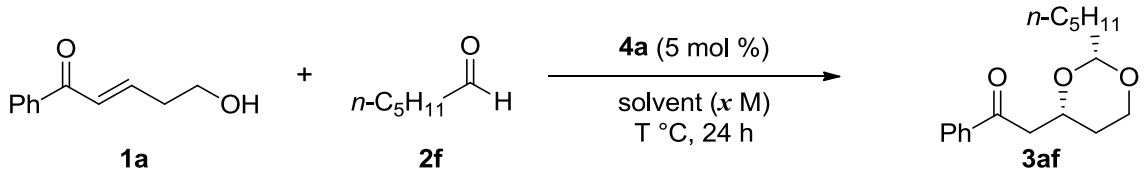
(3*E*,6*E*)-1-Hydroxytrideca-3,6-dien-5-one (**1h**)



^{1}H NMR ($CDCl_3$) δ 6.93 (dt, *J* = 15.5, 7.0 Hz, 1H), 6.89 (dt, *J* = 15.5, 7.0 Hz, 1H), 6.45 (dt, *J* = 15.5, 1.5 Hz, 1H), 6.32 (dt, *J* = 15.5, 1.5 Hz, 1H), 3.80 (dt, *J* = 5.5, 6.0 Hz, 2H), 2.51 (m 2H), 2.24 (m, 2H), 1.47 (m, 2H), 1.35–1.24 (m, 6H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 189.3, 148.7, 143.4, 130.6, 128.6, 61.1, 35.8, 32.7, 31.6, 28.9, 28.1, 22.5, 14.1. TLC: R_f 0.29 (hexane/EtOAc = 1:1). IR (neat): 3417, 2956, 2928, 2858, 1667, 1636, 1614, 1466, 1457, 1420, 1351, 1305, 1293, 1212, 1050, 980 cm^{-1}. HRMS Calcd for $C_{13}H_{23}O_2$: $[M+H]^+$, 211.1693. Found: *m*/*z* 211.1690.

All aldehydes **2** listed in this manuscript were commercially available.

Table S1. Screening of reaction conditions[a]

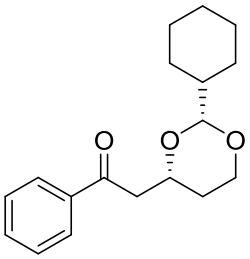


entry	solvent	T (°C)	*x* (M)	yield (%)[b,c]	ee (%)
1	benzene	25	0.5	74	86
2	toluene	25	0.5	83	87
3	hexane	25	0.5	80	83
4	*c*-hexane	25	0.5	92	85
5	EtOAc	25	0.5	29	81
6	MeCN	25	0.5	<5	58
7	CH_2Cl_2	25	0.5	76	68
8	Et_2O	25	0.5	40	82
9	CPME[d]	25	0.5	18	86
10[e]	toluene	25	0.5	40	84
11	toluene	0	0.5	22	81
12	toluene	10	0.5	62	81
13	toluene	20	0.5	80	85
14	toluene	35	0.5	81	86
15	toluene	40	0.5	87	85
16	toluene	50	0.5	76	86
17	toluene	35	0.125	63	90
18	toluene	35	0.05	38	93
19	*c*-hexane	35	0.05	75	90
20[f]	*c*-hexane	35	0.05	94	91

[a]Reactions were run using **1a** (0.1 mmol), **2f** (0.12 mmol), and **4a** (0.005 mmol) in the solvent (0.2 mL). [b]The diastereomeric ratio was ≥20:1 in all cases. [c]Isolated yields. [d]CPME = cyclopentyl methyl ether. [e]Reaction was run using 5Å molecular sieves (50 mg). [f]Reactions were run using **1a** (0.1 mmol), **2f** (0.20 mmol), and the catalyst (0.005 mmol) in *c*-hexane (2 mL).

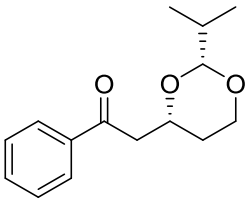
Characterization Data of Products

2-(2-Cyclohexyl-1,3-dioxan-4-yl)-1-phenylethanone (3aa).



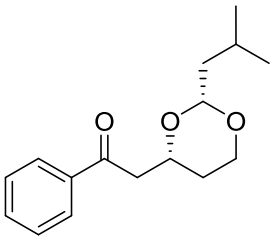
Yield: 56%, dr = >20:1, 80% *ee*, white solid. $[\alpha]_D^{23}$ +5.5 (*c* 0.40, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.97 (m, 2H), 7.57 (m, 1H), 7.46 (m, 2H), 4.28 (d, *J* = 5.5 Hz, 1H), 4.26 (m, 1H), 4.12 (ddd, *J* = 11.5, 4.5, 1.0 Hz, 1H), 3.78 (ddd, *J* = 12.0, 12.0, 3.0 Hz, 1H), 3.37 (dd, *J* = 16.0, 6.5 Hz, 1H), 2.99 (dd, *J* = 16.0, 6.5 Hz, 1H), 1.76–1.64 (m, 6H), 1.61 (m, 1H), 1.47 (m, 1H), 1.22–1.05 (m, 3H), 1.01 (dd, *J* = 12.5, 3.5 Hz, 1H), 0.96 (dd, *J* = 12.5, 3.5 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 198.0, 137.2, 133.2, 128.5, 128.3, 105.2, 73.2, 66.5, 44.9, 42.4, 31.7, 27.4, 27.3, 26.4, 25.77, 25.75. Mp. 60.5–61.4 °C. TLC: R_f 0.59 (hexane/EtOAc = 3:1). IR (KBr): 2928, 2850, 1686, 1595, 1451, 1378, 1249, 1142, 1098, 1071, 965, 754, 689 cm^{-1}. HRMS Calcd for $C_{18}H_{25}O_3$: $[M+H]^+$, 289.1798. Found: *m*/*z* 289.1791. HPLC (Daicel Chiralpak IA, hexane/*i*-PrOH = 99.0/1.0, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 7.5 min, t_{major} = 12.3 min.

2-(2-Isopropyl-1,3-dioxan-4-yl)-1-phenylethanone (3ab).



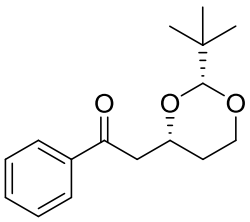
Yield: 57%, dr = >20:1, 79% *ee*, colorless oil. $[\alpha]_D^{23}$ +4.8 (*c* 0.27, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.98 (m, 2H), 7.57 (m, 1H), 7.47 (m, 2H), 4.27 (m, 1H), 4.26 (d, *J* = 5.5 Hz, 1H), 4.13 (ddd, *J* = 11.5, 4.5, 1.0 Hz, 1H), 3.79 (ddd, *J* = 11.5, 11.5, 3.0 Hz, 1H), 3.39 (dd, *J* = 16.0, 6.5 Hz, 1H), 2.98 (dd, *J* = 16.0, 6.0 Hz, 1H), 1.73(m, 2H), 1.63 (m, 1H), 0.88 (d, *J* = 6.5 Hz, 3H), 0.85 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 198.1, 137.2, 133.2, 128.5, 128.3, 73.3, 66.4, 44.8, 32.8, 31.6, 17.1, 17.0. TLC: R_f 0.48 (hexane/EtOAc = 3:1). IR (neat): 2963, 2926, 2874, 2854, 1684, 1598, 1474, 1450, 1366, 1289, 1246, 1213, 1182, 1137, 1119, 1039, 986, 963, 753, 691 cm^{-1}. HRMS Calcd for $C_{15}H_{21}O_3$: $[M+H]^+$, 249.1485. Found: *m*/*z* 249.1476. HPLC (Daicel Chiralpak IA, hexane/*i*-PrOH = 99.0/1.0, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 7.5 min, t_{major} = 10.5 min.

2-(2-Isobutyl-1,3-dioxan-4-yl)-1-phenylethanone (3ac).



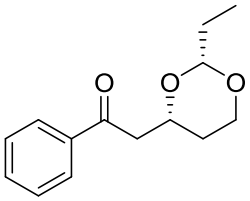
Yield: 64%, dr = >20:1, 71% *ee*, colorless oil. $[\alpha]_D^{23}$ +9.1 (*c* 0.33, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.96 (m, 2H), 7.57 (m, 1H), 7.52 (m, 2H), 4.61 (t, *J* = 5.5 Hz, 1H), 4.31 (m, 1H), 4.12 (ddd, *J* = 11.5, 4.5, 1.5 Hz, 1H), 3.82 (ddd, *J* = 11.5, 11.5, 3.0 Hz, 1H), 3.39 (dd, *J* = 16.5, 6.5 Hz, 1H), 3.01 (dd, *J* = 16.5, 6.5 Hz, 1H), 1.78–1.69 (m, 2H), 1.66 (m, 1H), 1.46 (m, 2H), 0.87 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ 197.8, 137.1, 133.2, 128.6, 128.2, 73.1, 66.4, 44.8, 43.8, 31.5, 23.8, 22.8, 22.7. TLC: R_f 0.59 (hexane/EtOAc = 3:1). IR (neat): 2957, 2927, 2869, 2857, 1685, 1449, 1369, 1126, 979, 690 cm^{-1}. HRMS Calcd for $C_{16}H_{23}O_3$: $[M+H]^+$, 263.1642. Found: *m*/*z* 263.1632. HPLC (Daicel Chiralpak IA, hexane/*i*-PrOH = 99.0/1.0, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 10.5 min, t_{major} = 16.7 min.

2-(2-*tert*-Butyl-1,3-dioxan-4-yl)-1-phenylethanone (3ad).



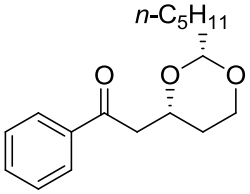
Yield: 33%, dr = >20:1, 11% *ee*, pale yellow oil. $[\alpha]_D^{23}$ –4.3 (*c* 0.40, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.99 (m, 2H), 7.57 (m, 1H), 7.47 (m, 2H), 4.23 (m, 1H), 4.12 (ddd, *J* = 11.5, 5.0, 1.5 Hz, 1H), 4.12 (s, 1H), 3.77 (dt, *J* = 11.5, 11.5, 3.0 Hz, 1H), 3.37 (dd, *J* = 16.0, 7.0 Hz, 1H), 2.93 (dd, *J* = 16.0, 6.0 Hz, 1H), 1.71 (m, 1H), 1.60 (m, 1H), 0.82 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 198.6, 137.4, 133.1, 128.5, 128.4, 107.5, 73.6, 66.5, 44.9, 34.8, 31.6, 24.6. TLC: R_f 0.30 (hexane/EtOAc = 3:1). IR (neat): 2958, 2927, 2869, 2856, 1685, 1449, 1364, 1213, 1134, 1121, 1106, 1044, 982, 690 cm^{-1}. HRMS Calcd for $C_{16}H_{23}O_3$: $[M+H]^+$, 263.1642. Found: *m*/*z* 263.1642. HPLC (Daicel Chiralpak IA, hexane/*i*-PrOH = 99.0/1.0, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 11.2 min, t_{major} = 13.7 min.

2-(2-Ethyl-1,3-dioxan-4-yl)-1-phenylethanone (3ae).



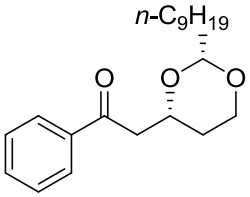
Yield: 60%, dr = >20:1, 78% *ee*, colorless oil. $[\alpha]_D^{23}$ +8.8 (*c* 0.24, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.97 (m, 2H), 7.57 (m, 1H), 7.47 (m, 2H), 4.52 (t, *J* = 5.5 Hz, 1H), 4.31 (m, 1H), 4.12 (ddd, *J* = 11.5, 5.0, 1.5 Hz, 1H), 3.82 (ddd, *J* = 11.5, 11.5, 2.5 Hz, 1H), 3.39 (dd, *J* = 16.5, 6.0 Hz, 1H), 3.01 (dd, *J* = 16.5, 6.5 Hz, 1H), 1.74 (m, 1H), 1.67 (m, 1H), 1.61 (dq, *J* = 5.5, 7.5 Hz, 2H), 0.87 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 197.8, 137.1, 133.2, 128.6, 128.2, 103.2, 73.0, 66.4, 44.8, 31.5, 28.1, 8.3. TLC: R_f 0.56 (hexane/EtOAc = 3:1). IR (neat): 2969, 2933, 2855, 1685, 1375, 1369, 1136, 1099, 974, 691 cm^{-1}. HRMS Calcd for $C_{14}H_{19}O_3$: $[M+H]^+$, 235.1329. Found: *m*/*z* 235.1322. HPLC (Daicel Chiralpak IA, hexane/*i*-PrOH = 99.0/1.0, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 8.4 min, t_{major} = 13.3 min.

2-(2-Pentyl-1,3-dioxan-4-yl)-1-phenylethanone (3af).



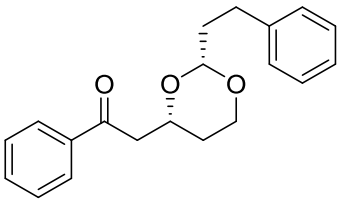
Yield: 94%, dr = >20:1, 91% *ee*, colorless oil. $[\alpha]_D^{23}$ +11.6 (*c* 0.62, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.97 (m, 2H), 7.57 (m, 1H), 7.52 (m, 2H), 4.57 (t, *J* = 5.0 Hz, 1H), 4.30 (m, 1H), 4.12 (ddd, *J* = 11.5, 4.5, 1.0 Hz, 1H), 3.81 (ddd, *J* = 11.5, 11.5, 2.5 Hz, 1H), 3.39 (dd, *J* = 16.5, 6.0 Hz, 1H), 3.01 (dd, *J* = 16.5, 6.5 Hz, 1H), 1.74 (m, 1H), 1.66 (m, 1H), 1.57 (m, 2H), 1.36–1.20 (m, 6H), 0.85 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 197.8, 137.0, 133.2, 128.6, 128.2, 102.3, 73.0, 66.4, 44.8, 35.0, 31.6, 31.5, 23.7, 22.5, 14.0. TLC: R_f 0.47 (hexane/EtOAc = 3:1). IR (neat): 2955, 2928, 2859, 1685, 1212, 1137, 1121, 1029, 990, 690, 668 cm^{-1}. HRMS Calcd for $C_{17}H_{25}O_3$: $[M+H]^+$, 277.1798. Found: *m*/*z* 277.1789. HPLC (Daicel Chiralpak IC, hexane/*i*-PrOH = 99.0/1.0, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{major} = 10.1 min, t_{minor} = 14.8 min.

2-(2-Nonyl-1,3-dioxan-4-yl)-1-phenylethanone (3ag).



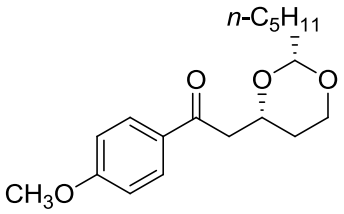
Yield: 72%, dr = >20:1, 82% *ee*, colorless oil. $[\alpha]_D^{23}$ +6.5 (*c* 0.23, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.97 (m, 2H), 7.57 (m, 1H), 7.46 (m, 2H), 4.57 (t, *J* = 5.5 Hz, 1H), 4.30 (m, 1H), 4.11 (ddd, *J* = 12.0, 5.0, 1.0 Hz, 1H), 3.81 (ddd, *J* = 12.0, 12.0, 3.0 Hz, 1H), 3.39 (dd, *J* = 11.5, 6.0 Hz, 1H), 3.00 (dd, *J* = 11.5, 6.5 Hz, 1H), 1.74 (m, 1H), 1.65 (m, 1H), 1.57 (m, 2H), 1.28 (m, 14H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 197.8, 137.1, 133.2, 128.6, 128.2, 102.3, 73.1, 66.4, 44.8, 35.1, 31.9, 31.5, 29.49, 29.48, 29.4, 29.3, 24.0, 22.3, 14.1. TLC: R_f 0.50 (hexane/EtOAc = 3:1). IR (neat): 2954, 2925, 2855, 2368, 2321, 1688, 1653, 1124, 668 cm^{-1}. HRMS Calcd for $C_{21}H_{33}O_3$: $[M+H]^+$, 333.2424. Found: *m*/*z* 333.2410. HPLC (Daicel Chiralpak IC, hexane/*i*-PrOH = 99.0/1.0, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{major} = 8.5 min, t_{minor} = 12.3 min.

2-(2-Phenethyl-1,3-dioxan-4-yl)-1-phenylethanone (3ah).



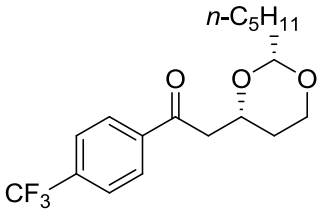
Yield: 76%, dr = >20:1, 85% *ee*, colorless oil. $[\alpha]_D^{23}$ +21.0 (*c* 0.68, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.01 (m, 2H), 7.59 (m, 1H), 7.49 (m, 2H), 7.27 (m, 2H), 7.18 (m, 3H), 4.58 (t, *J* = 5.5 Hz, 1H), 4.32 (m, 1H), 4.15 (ddd, *J* = 11.5, 5.0, 1.5 Hz, 1H), 3.81 (ddd, *J* = 11.5, 11.5, 3.0 Hz, 1H), 3.43 (dd, *J* = 16.5, 6.5 Hz, 1H), 3.02 (dd, *J* = 16.5, 6.0 Hz, 1H), 2.67 (t, *J* = 8.0 Hz, 2H), 1.91 (m, 2H), 1.79 (m, 1H), 1.67 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 197.8, 141.6, 137.2, 133.2, 128.6, 128.4, 128.3, 128.2, 125.7, 101.2, 73.2, 66.4, 44.8, 36.4, 31.5, 30.1. TLC: R_f 0.38 (hexane/EtOAc = 3:1). IR (neat): 3026, 2959, 2927, 2856, 2356, 1685, 1597, 1449, 1375, 1369, 1213, 1180, 1138, 1099, 1035, 751, 700, 691 cm^{-1}. HRMS Calcd for $C_{20}H_{23}O_3$: $[M+H]^+$, 311.1642. Found: *m*/*z* 311.1632. HPLC (Daicel Chiralpak IC, hexane/*i*-PrOH = 99.0/1.0, flow rate = 1.5 mL/min, λ = 254 nm, 40 °C): t_{major} = 16.0 min, t_{minor} = 21.2 min.

1-(4-Methoxyphenyl)-2-(2-pentyl-1,3-dioxan-4-yl)ethanone (3bf).



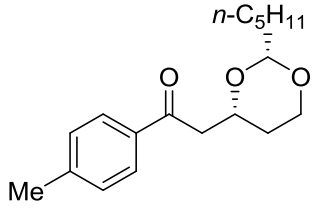
Yield: 70%, dr = >20:1, 93% *ee*, colorless oil. $[\alpha]_D^{23}$ +23.0 (*c* 2.18, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.95 (m, 2H), 6.93 (m, 2H), 4.56 (t, *J* = 5.5 Hz, 1H), 4.28 (m, 1H), 4.11 (ddd, *J* = 11.5, 5.0, 1.5 Hz, 1H), 3.87 (s, 3H), 3.81 (ddd, *J* = 11.5, 11.5, 3.5 Hz, 1H), 3.34 (dd, *J* = 16.5, 6.5 Hz, 1H), 2.96 (dd, *J* = 16.5, 6.5 Hz, 1H), 1.72 (m, 1H), 1.65 (m, 1H), 1.56 (m, 2H), 1.35–1.21 (m, 6H), 0.85 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 196.3, 163.6, 130.5, 130.2, 113.7, 102.3, 73.2, 66.4, 55.5, 44.5, 35.0, 31.62, 31.56, 23.7, 22.5, 14.0. TLC: R_f 0.29 (hexane/EtOAc = 3:1). IR (neat): 2955, 2929, 2859, 2364, 2346, 1675, 1601, 1507, 1261, 1172, 1136, 1121, 1032, 989 cm^{-1}. HRMS Calcd for $C_{18}H_{27}O_4$: $[M+H]^+$, 307.1904. Found: *m*/*z* 307.1892. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 99.0/1.0, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 13.7 min, t_{major} = 15.0 min.

2-(2-Pentyl-1,3-dioxan-4-yl)-1-(4-(trifluoromethyl)phenyl)ethanone (3cf).



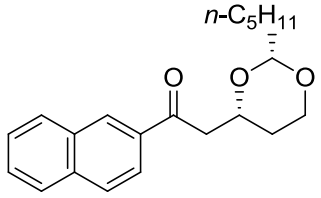
Yield: 65%, dr = >20:1, 89% *ee*, colorless oil. $[\alpha]_D^{23}$ +5.4 (*c* 0.13, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.07 (m, 2H), 7.74 (m, 2H), 4.55 (t, *J* = 5.5 Hz, 1H), 4.29 (m, 1H), 4.13 (ddd, *J* = 12.0, 5.5, 1.5 Hz, 1H), 3.81 (ddd, *J* = 12.0, 12.0, 2.5 Hz, 1H), 3.41 (dd, *J* = 16.5, 7.0 Hz, 1H), 2.99 (dd, *J* = 16.5, 6.0 Hz, 1H), 1.76 (m, 1H), 1.65 (m, 1H), 1.55 (m, 2H), 1.33–1.19 (m, 6H), 0.84 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 197.1, 139.7, 134.4 (q, *J* = 32.7 Hz), 128.6, 125.6 (q, *J* = 3.9 Hz), 123.5 (q, *J* = 272.8 Hz), 102.3, 73.0, 66.3, 45.0, 34.9, 31.6, 31.4, 23.6, 22.5, 14.0. ^{19}F NMR (C_6F_6) δ 98.6. TLC: R_f 0.29 (hexane/EtOAc = 3:1). IR (neat): 2956, 1684, 1411, 1325, 1215, 1167, 1150, 1108, 1068, 974, 855, 821 cm^{-1}. HRMS Calcd for $C_{18}H_{23}F_3O_3Na$: $[M+Na]^+$, 367.1492. Found: *m*/*z* 367.1477. HPLC (Daicel Chiralpak IC, hexane/*i*-PrOH = 99.0/1.0, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{major} = 5.8 min, t_{minor} = 8.2 min.

2-(2-Pentyl-1,3-dioxan-4-yl)-1-(*p*-tolyl)ethanone (3df).



Yield: 75%, dr = >20:1, 90% *ee*, pale yellow oil. $[\alpha]_D^{23}$ +12.9 (*c* 0.62, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.88 (m, 2H), 7.28 (m, 2H), 4.58 (t, *J* = 5.5 Hz, 1H), 4.31 (m, 1H), 4.13 (ddd, *J* = 11.5, 5.0, 1.5 Hz, 1H), 3.82 (ddd, *J* = 11.5, 11.5, 3.0 Hz, 1H), 3.37 (dd, *J* = 11.5, 6.0 Hz, 1H), 3.00 (dd, *J* = 11.5, 6.5 Hz, 1H), 2.43 (s, 3H), 1.74 (m, 1H), 1.66 (m, 1H), 1.58 (m, 2H), 1.38–1.21 (m, 6H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 197.2, 143.8, 134.3, 129.0, 128.1, 102.0, 72.9, 66.2, 44.4, 34.8, 31.4, 31.3, 23.4, 22.3, 21.4, 13.7. TLC: R_f 0.42 (hexane/EtOAc = 3:1). IR (neat): 2955, 2927, 2859, 2360, 2340, 1689, 1608, 1375, 1364, 1207, 1181, 1136, 1121, 1031, 995, 665 cm^{-1}. HRMS Calcd for $C_{18}H_{27}O_3$: $[M+H]^+$, 291.1955. Found: *m*/*z* 291.1944. HPLC (Daicel Chiralpak IC, hexane/*i*-PrOH = 99.0/1.0, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{major} = 13.1 min, t_{minor} = 20.0 min.

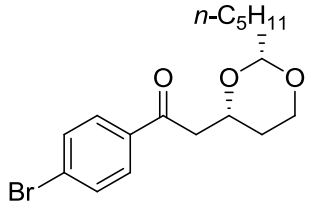
1-(Naphthalen-2-yl)-2-((2*R*,4*R*)-2-pentyl-1,3-dioxan-4-yl)ethanone (3ef).



Yield: 99%, dr = >20:1, 90% *ee*, white solid. $[\alpha]_D^{23}$ +34.5 (*c* 0.80, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.50 (s, 1H), 8.03 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.58 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 7.56 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 4.59 (t, *J* = 5.5 Hz, 1H), 4.36 (m, 1H), 4.14 (ddd, *J* = 11.5, 5.0, 1.5 Hz, 1H), 3.83 (ddd, *J* = 11.5, 11.5, 3.0 Hz, 1H), 3.54 (dd, *J* = 16.5, 6.5 Hz, 1H), 3.13 (dd, *J* = 16.5, 6.5 Hz, 1H), 1.79 (m, 1H), 1.70 (m, 1H), 1.58 (m, 2H), 1.37–1.18 (m, 6H), 0.83 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 197.8, 135.6, 134.4, 132.4, 130.2, 129.6, 128.5, 128.4, 127.7, 126.8, 123.7, 102.3, 73.2, 66.4, 44.9, 35.0, 31.6, 31.5, 23.7, 22.5, 14.0. Mp. 58.5–59.2 °C. TLC: R_f 0.43 (hexane/EtOAc = 3:1). IR (neat): 2955, 2950, 2929, 2851, 1676, 1379, 1140, 1126, 1032, 864, 836, 757 cm^{-1}. HRMS Calcd for $C_{21}H_{27}O_3$: $[M+H]^+$, 327.1955. Found: *m*/*z* 327.1940. HPLC (Daicel Chiralpak IC, hexane/*i*-PrOH = 98.0/2.0, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{major} = 11.2 min,

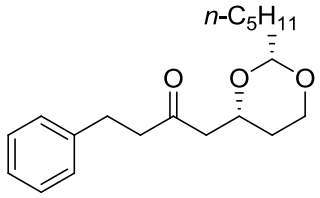
t_{minor} = 15.7 min.

1-(4-Bromophenyl)-2-(2-pentyl-1,3-dioxan-4-yl)ethanone (3ff).



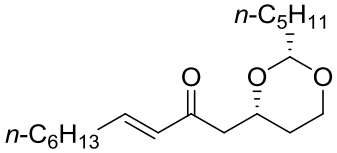
Yield: 74%, dr = >20:1, 90% *ee*, colorless oil. $[\alpha]_D^{23}$ +15.1 (*c* 0.72, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.83 (m, 2H), 7.61 (m, 2H), 4.55 (t, *J* = 5.5 Hz, 1H), 4.27 (m, 1H), 4.12 (ddd, *J* = 11.5, 5.0, 1.5 Hz, 1H), 3.80 (ddd, *J* = 11.5, 11.5, 2.5 Hz, 1H), 3.35 (dd, *J* = 16.5, 6.5 Hz, 1H), 2.94 (dd, *J* = 16.5, 6.0 Hz, 1H), 1.74 (m, 1H), 1.64 (m, 1H), 1.55 (m, 2H), 1.35–1.19 (m, 6H), 0.85 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 196.9, 135.8, 131.9, 129.8, 128.5, 102.3, 73.0, 66.4, 44.7, 35.0, 31.6, 31.4, 23.6, 22.5, 14.0. TLC: R_f 0.43 (hexane/EtOAc = 3:1). IR (neat): 2956, 2927, 2859, 2368, 2331, 1689, 1586, 1136, 1122, 1072, 668 cm^{-1}. HRMS Calcd for $C_{17}H_{24}BrO_3$: $[M+H]^+$, 355.0903. Found: *m*/*z* 355.0888. HPLC (Daicel Chiralpak IB, hexane/*i*-PrOH = 99.0/1.0, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{minor} = 7.9 min, t_{major} = 10.0 min.

1-(2-Pentyl-1,3-dioxan-4-yl)-4-phenylbutan-2-one (3gf).



Yield: 53%, dr = >20:1, 63% *ee*, colorless oil. $[\alpha]_D^{23}$ –3.99 (*c* 0.43, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.28 (m, 2H), 7.21–7.16 (m, 3H), 4.50 (t, *J* = 5.5 Hz, 1H), 4.09 (m, 1H), 4.07 (ddd, *J* = 11.5, 5.0, 1.5 Hz, 1H), 3.74 (ddd, *J* = 11.5, 11.5, 1.5 Hz, 1H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.87–2.72 (m, 3H), 2.44 (dd, *J* = 16.0 Hz, 1H), 1.63 (m, 1H), 1.56 (m, 2H), 1.37–1.22 (m, 6H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 207.9, 140.9, 128.5, 128.3, 126.1, 102.2, 72.8, 66.3, 48.9, 45.5, 34.9, 31.6, 31.2, 29.4, 23.7, 22.5, 14.0. TLC: R_f 0.43 (hexane/EtOAc = 3:1). IR (neat): 2956, 2927, 2859, 2368, 2331, 1689, 1586, 1136, 1122, 1072, 668 cm^{-1}. HRMS Calcd for $C_{19}H_{28}O_3Na$: $[M+Na]^+$, 327.1931. Found: *m*/*z* 327.1924. HPLC (Daicel Chiralpak IF, hexane/*i*-PrOH = 95.0/5.0, flow rate = 0.5 mL/min, λ = 254 nm, 40 °C): t_{minor} = 10.3 min, t_{major} = 15.0 min.

(*E*)-1-(2-Pentyl-1,3-dioxan-4-yl)dec-3-en-2-one (3hf)

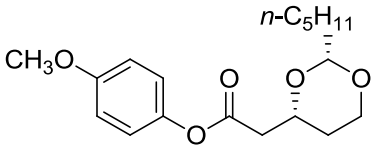


Yield: 70%, dr = >20:1, 78% *ee*, colorless oil. $[\alpha]_D^{23}$ +10.0 (*c* 0.56, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 6.85 (dt, *J* = 16.0, 7.0 Hz, 1H), 6.10 (dt, *J* = 16.0, 1.0 Hz, 1H), 4.52 (t, *J* = 5.0 Hz, 1H), 4.27 (m, 1H), 4.08 (dd, *J* = 12.0 Hz, 4.0 Hz, 1H), 3.76 (ddd, *J* = 12.0, 12.0, 3.0 Hz, 1H), 2.93 (dd, *J* = 16.0, 6.5 Hz, 1H), 2.59 (dd, *J* = 16.0 Hz, 6.5 Hz, 1H), 2.21 (m, 2H), 1.65 (m, 1H), 1.58–1.54 (m, 3H), 1.45 (m, 2H), 1.37–1.21 (m, 12H), 0.89–0.85 (m, 6H). ^{13}C NMR ($CDCl_3$) δ 198.1, 148.7, 130.9, 102.2, 73.0, 66.4, 45.9, 35.0, 32.5, 31.64, 31.56, 31.4, 28.8, 28.0, 23.7, 22.5, 14.1, 14.0. TLC: R_f 0.28 (hexane/EtOAc = 10:1). IR (neat): 2956, 2858, 1693, 1669, 1628, 1624, 1466, 1459, 1378, 1367, 1137, 1124, 1030, 994, 976 cm^{-1}. HRMS Calcd for $C_{19}H_{35}O_3$: $[M+H]^+$, 311.2581. Found: *m*/*z* 311.2573. HPLC (Daicel Chiralpak IC, hexane/*i*-PrOH = 99.0/1.0, flow rate = 1.0 mL/min, λ = 254 nm, 40 °C): t_{major} = 11.2 min, t_{minor} = 17.3 min.

Procedure for Baeyer–Villiger oxidation of 3bf [3]

The mixture of **3bf** (0.021 g, 0.070 mmol), *m*-CPBA (0.60 g, 0.35 mmol), and trifluoroacetic acid (0.003 mL, 0.04 mmol) in CH_2Cl_2 (0.6 mL) was stirred at ambient temperature for 8 h. The reaction was quenched with saturated aqueous $Na_2S_2O_3$ and saturated aqueous $NaHCO_3$, and subsequently extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 10/1) as an eluent gave 4-methoxyphenyl 2-(2-pentyl-1,3-dioxan-4-yl)acetate (**5**).

4-Methoxyphenyl 2-(2-pentyl-1,3-dioxan-4-yl)acetate (5).



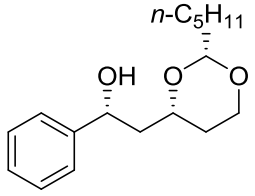
Yield: 70%, 92% *ee*, colorless oil. $[\alpha]_D^{23}$ –10.9 (*c* 0.43, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.00–6.98 (m, 2H), 6.89–6.87 (m, 2H), 4.58 (t, *J* = 5.5 Hz, 1H), 4.20 (m, 1H), 4.14 (ddd, *J* = 11.5, 5.0, 1.5 Hz, 1H), 3.80 (s, 3H), 3.80 (m, 1H), 2.83 (dd, *J* = 15.5, 8.0 Hz, 1H), 2.68 (dd, *J* = 15.5, 6.0 Hz, 1H), 1.79 (m, 1H), 1.64–1.58 (m, 3H), 1.39 (m, 2H),

1.34–1.24 (m, 4H), 0.88 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 169.8, 157.2, 144.0, 122.3, 114.4, 102.3, 73.0, 66.3, 55.6, 41.1, 35.0, 31.6, 31.0, 23.7, 22.6, 14.0. TLC: R_f 0.34 (hexane/EtOAc = 10:1). IR (neat): 2955, 2929, 2860, 2364, 2331, 1751, 1506, 1465, 1378, 1249, 1196, 1165, 1135, 1102, 1033 cm^{-1}. HRMS Calcd for $C_{18}H_{26}O_5Na$: $[M+Na]^+$, 345.1672. Found: m/z 345.1666. HPLC (Daicel Chiralpak IC, hexane/i-PrOH = 99.5/0.5, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{major} = 22.9 min, t_{minor} = 27.2 min.

Procedure for diastereoselective reduction of 3af

To a 30-mL round-bottom flask, we sequentially added 2-(2-pentyl-1,3-dioxan-4-yl)-1-phenylethanone (**3af**, 0.076 g, 0.27 mmol), Et_2O (27.4 mL), and $EuCl_3$ (0.21 g, 0.82 mmol). After the mixture was stirred under argon atmosphere at –78 °C for 0.5 h, $LiBH_4$ (0.012 g, 0.55 mmol) was added. The resulting mixture was additionally stirred at –78 °C for 2 h. The reaction was quenched with 3M aqueous NaOH, and the mixture was extracted with EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 5/1) as an eluent gave 2-(2-pentyl-1,3-dioxan-4-yl)-1-phenylethanol (**6**).

2-(2-Pentyl-1,3-dioxan-4-yl)-1-phenylethanol (6).

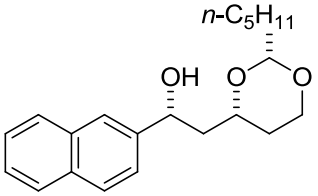


Yield: 92%, dr = 12:1, colorless oil. $[\alpha]_D^{23}$ +13.4 (c 0.90, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.37–7.32 (m, 4H), 7.27 (m, 1H), 4.97 (dd, J = 9.5, 3.5 Hz, 1H), 4.58 (t, J = 5.0 Hz, 1H), 4.01 (ddd, J = 12.0, 5.0, 1.0 Hz, 1H), 3.92 (m, 1H), 3.76 (ddd, J = 12.0, 12.0, 2.5 Hz, 1H), 2.04 (m, 1H), 1.81–1.72 (m, 2H), 1.66–1.62 (m, 2H), 1.44–1.38 (m, 3H), 1.35–1.27 (m, 4H), 0.90 (t, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 144.4, 128.6, 127.7, 126.0, 102.3, 74.1, 66.7, 45.4, 35.2, 31.9, 31.7, 24.0, 22.8, 14.3. TLC: R_f 0.37 (hexane/EtOAc = 3:1). IR (neat): 3462, 2953, 2925, 2858, 1465, 1378, 1364, 1139, 1087, 1028, 760, 700, 665 cm^{-1}. HRMS Calcd for $C_{17}H_{27}O_3$: $[M+H]^+$, 279.1955. Found: m/z 279.1945.

Procedure for diastereoselective reduction of 3ef

To a 20-mL round-bottom flask, we sequentially added 1-(naphthalen-2-yl)-2-((2*R**,4*R**)-2-pentyl-1,3-dioxan-4-yl)ethanone (**3ef**, 0.033 g, 0.10 mmol), Et_2O (1.8 mL), and $EuCl_3$ (0.078 mg, 0.30 mmol). After the mixture was stirred under argon atmosphere at –78 °C for 0.5 h, a solution of $LiBH_4$ in Et_2O (0.2 mmol, 1.0 M, 0.2 mL) was added. The resulting mixture was additionally stirred at –78 °C for 1 h. The reaction was quenched with 1 M aqueous NaOH, and the mixture was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 5/1) as an eluent gave (*R**)-1-(naphthalen-2-yl)-2-((2*R**,4*R**)-2-pentyl-1,3-dioxan-4-yl)ethanol (dihydro-**3ef**).

(*R)-1-(Naphthalen-2-yl)-2-((2*R**,4*R**)-2-pentyl-1,3-dioxan-4-yl)ethanol (dihydro-3ef)**.



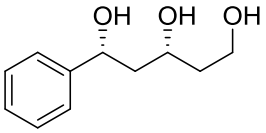
Yield: 99%, dr = 11:1, white solid. ^{1}H NMR ($CDCl_3$) δ 7.85–7.82 (m, 4H), 7.50–7.44 (m, 3H), 5.15 (dd, *J* = 9.0, 3.5 Hz, 1H), 4.60 (t, *J* = 5.5 Hz, 1H), 4.10 (ddd, *J* = 11.5, 5.0, 1.0 Hz, 1H), 3.96 (m, 1H), 3.75 (ddd, *J* = 11.5, 11.5, 3.0 Hz, 1H), 3.68 (br s, 1H), 2.11 (m, 1H), 1.88 (m, 1H), 1.78 (m, 1H), 1.69–1.64(m, 2H), 1.47–1.41 (m, 3H), 1.38–1.30 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 141.5, 133.3, 132.9, 128.1, 128.0, 127.6, 126.0, 125.7, 124.4, 124.0, 102.1, 74.0, 66.5, 45.1, 35.0, 31.7, 31.5, 23.8, 22.5, 14.0. Mp. 78.0–78.8 °C. TLC: R_f 0.33 (hexane/EtOAc = 3:1). IR (KBr): 3482, 2955, 2937, 2931, 2910, 2871, 2851, 1424, 1365, 1165, 1139, 1086, 975.1, 862.2, 822.7, 758.1 cm^{-1}. HRMS Calcd for $C_{21}H_{28}O_3Na$: $[M+Na]^+$, 351.1931. Found: *m*/*z* 351.1918.

Procedure for deacetalizaton of 6

The mixture of **6** (diastereomer mixture, dr = 12:1, 0.059 g, 0.20 mmol) and *p*-TsOH·H_2O (0.040 g, 0.21 mmol) in CH_3OH (1.6 mL) and H_2O (0.5 mL) was stirred at 100 °C for 1 h. The reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with EtOAc. The organic layers were dried over Na_2SO_4 and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc

(v/v = 1/3) as an eluent gave 1-phenylpentane-1,3,5-triol (**7**).

1-Penylpentane-1,3,5-triol (7).



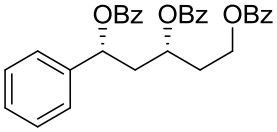
Yield: 64% (isolated yield of the major diastereomer), colorless oil. $[\alpha]_D^{23}$ +31.5 (*c* 0.72, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 7.38–7.34 (m, 4H), 7.29 (m, 1H), 5.00 (dd, *J* = 10.5, 2.5 Hz, 1H), 4.26 (m, 1H), 3.87 (m, 2H), 3.17 (br s, 3H), 1.97 (dt, *J* = 14.5, 10.5 Hz, 1H), 1.79–1.69 (m, 3H). ^{13}C NMR ($CDCl_3$) δ 144.2, 128.6, 127.7, 125.6, 75.5, 73.0, 61.6, 45.4, 38.5. TLC: R_f 0.10 (hexane/EtOAc = 1:3). IR (neat): 3322, 3088, 3064, 3031, 2944, 2920, 1455, 1428, 1329, 1101, 1059, 1029, 1003, 759, 701, 673 cm^{-1}. HRMS Calcd for $C_{11}H_{17}O_3$: $[M+H]^+$, 197.1172. Found: *m*/*z* 197.1172.

The enantiomeric excess of **7** was determined by HPLC analysis after benzoylation.

Procedure for benzoylation of 7

To a solution of **7** (0.013 g, 0.068 mmol) in CH_2Cl_2 (0.3 mL) were added benzoyl chloride (0.024 mL, 0.20 mmol) and pyridine (0.027 mL, 0.33 mmol) at ambient temperature, and the mixture was stirred overnight. The resulting mixture was diluted with H_2O and subsequently extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification by flash silica gel column chromatography using hexane/EtOAc (v/v = 10/1) as an eluent gave 1-phenylpentane-1,3,5-triyl tribenzoate.

1-Phenylpentane-1,3,5-triyl tribenzoate.



Yield: 36%, 91% *ee*, colorless oil. $[\alpha]_D^{23}$ +1.21 (*c* 0.41, CH_2Cl_2). ^{1}H NMR ($CDCl_3$) δ 8.05–8.03 (m, 2H), 7.98–7.96 (m, 2H), 7.91–7.89 (m, 2H), 7.55–7.48 (m, 3H), 7.41–7.36 (m, 6H), 7.34–7.29 (m, 4H), 7.24 (m, 2H), 6.18 (t, *J* = 7.0 Hz, 1H), 5.40 (m 1H), 4.47 (m, 1H), 4.38 (m, 1H), 2.72 (m, 1H), 2.36–2.21 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 166.4, 165.8, 165.6, 139.7, 133.03, 133.02, 132.9, 129.94, 129.87, 129.64, 129.61, 129.5, 128.7, 128.33, 128.30, 128.2, 126.4, 73.7, 69.2, 61.1, 40.8, 33.1. TLC: R_f 0.39 (hexane/EtOAc = 3:1).

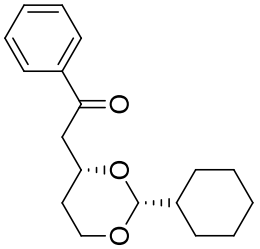
IR (neat): 3090, 3064, 3034, 2964, 2926, 2854, 1706, 1602, 1585, 1492, 1452, 1315, 1265, 1177, 1110, 1098, 1070, 1026, 1002, 974, 805, 760, 707, 687 cm^{-1}. HRMS Calcd for $C_{32}H_{28}O_6Na$: $[M+Na]^+$, 531.1778. Found: *m*/*z* 531.1774. HPLC (Daicel Chiralpak IC, hexane/*i*-PrOH = 80.0/20.0, flow rate = 2.0 mL/min, λ = 254 nm, 40 °C): t_{major} = 5.9 min, t_{minor} = 7.3 min.

References

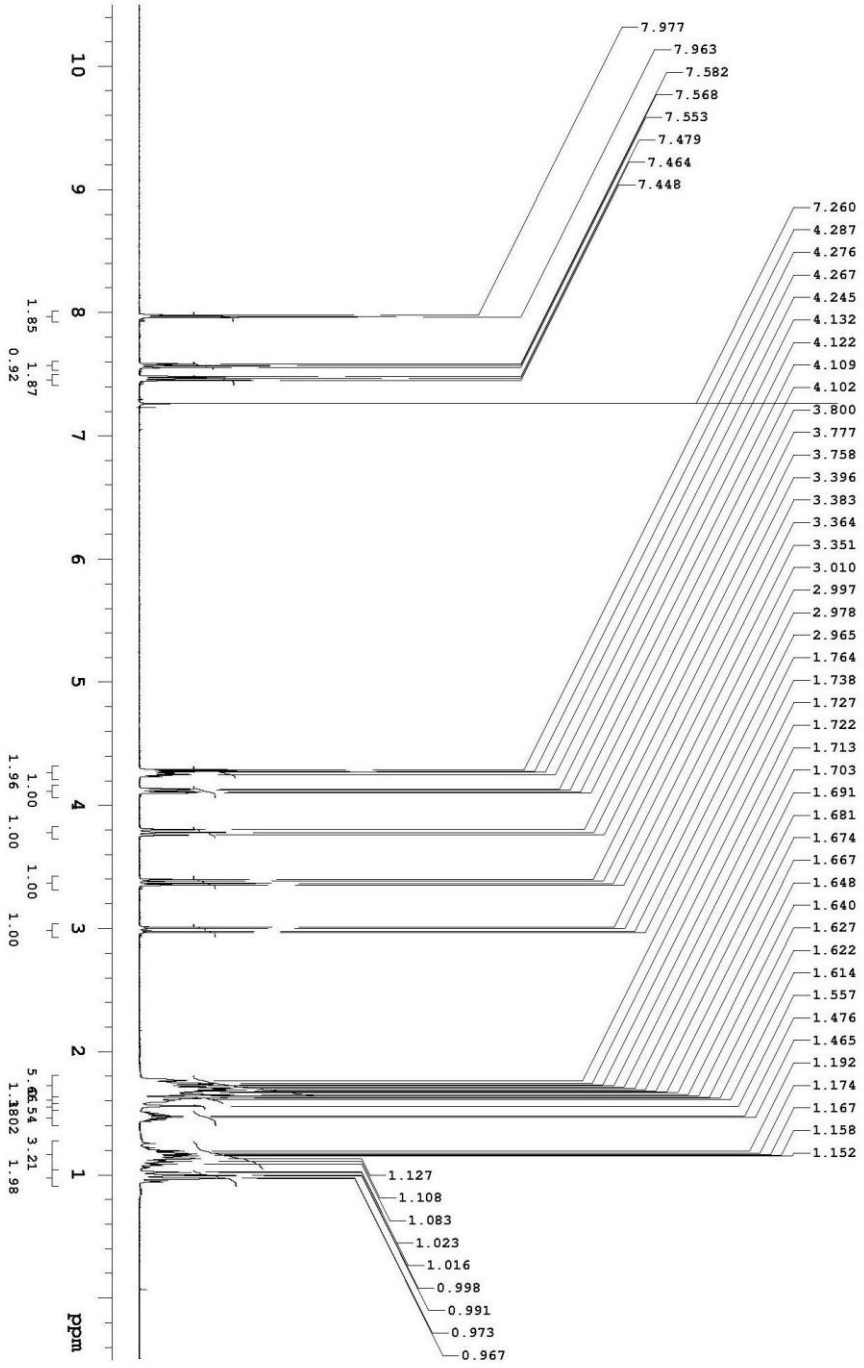
1. Oswald, C. L.; Peterson, J. A.; Lam, H. W. *Org. Lett.* **2009**, *11*, 4504.
2. Alejandro Bugarin; Kyle D. Jones; Brian T. Connell. *Chem. Commun*. **2010**, *46*, 1715.
3. Sedelmeier, J.; Hammerer, T.; Bolm, C. *Org. Lett.* **2008**, *10*, 917.

NMR Spectra (^{1}H, ^{13}C) of Products

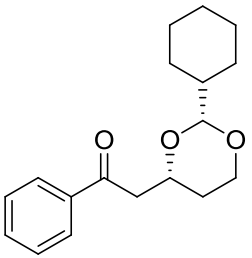
2-(2-Cyclohexyl-1,3-dioxan-4-yl)-1-phenylethanone (3aa)



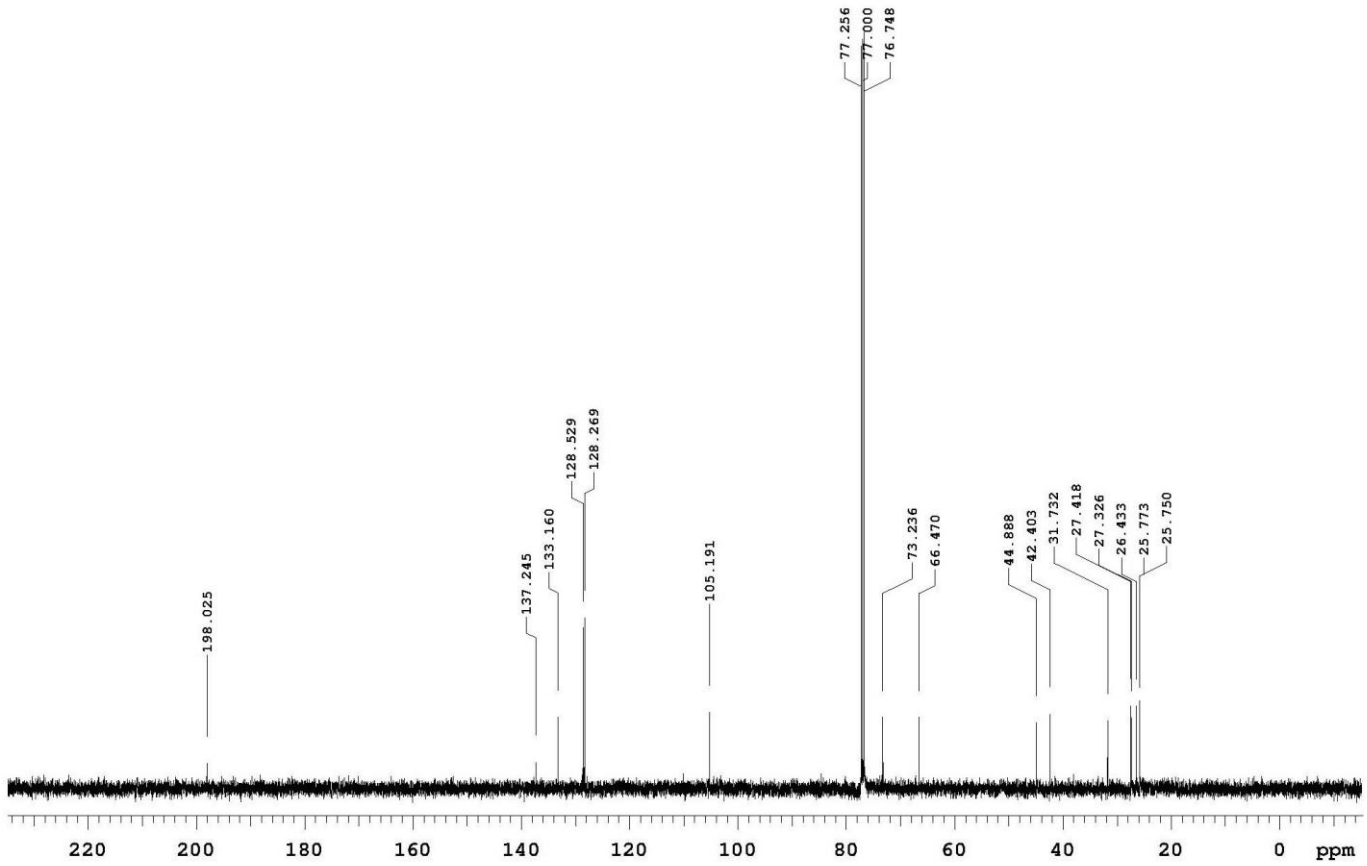
^{1}H NMR



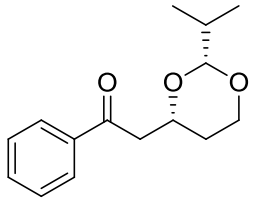
2-(2-Cyclohexyl-1,3-dioxan-4-yl)-1-phenylethanone (3aa)



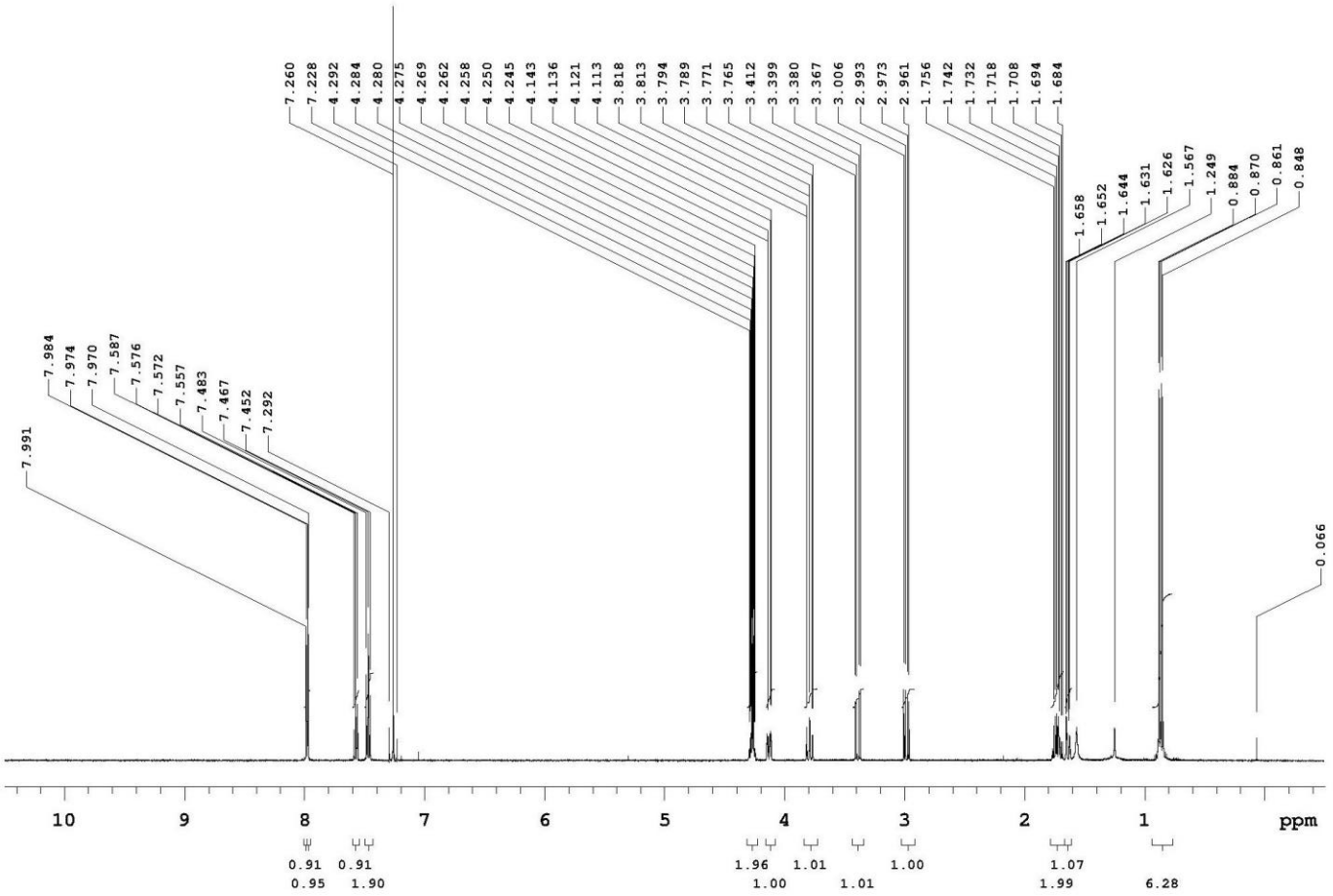
^{13}C NMR



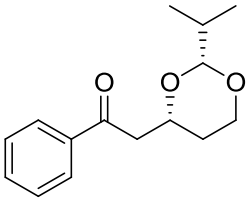
2-(2-Isopropyl-1,3-dioxan-4-yl)-1-phenylethanone (3ab)



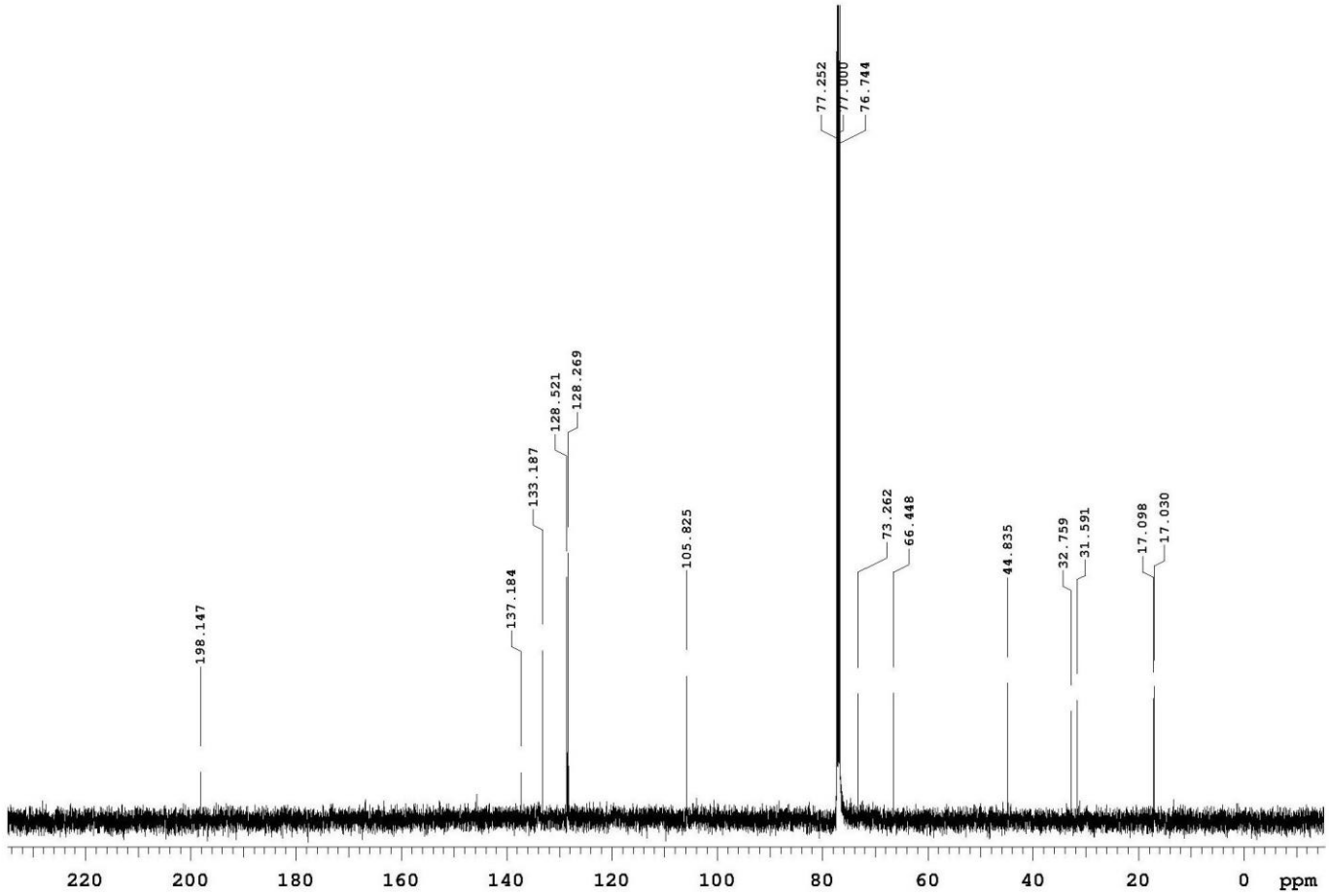
^{1}H NMR



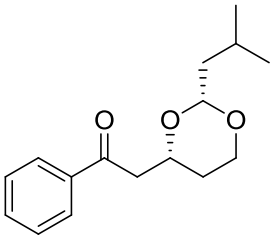
2-(2-Isopropyl-1,3-dioxan-4-yl)-1-phenylethanone (3ab)



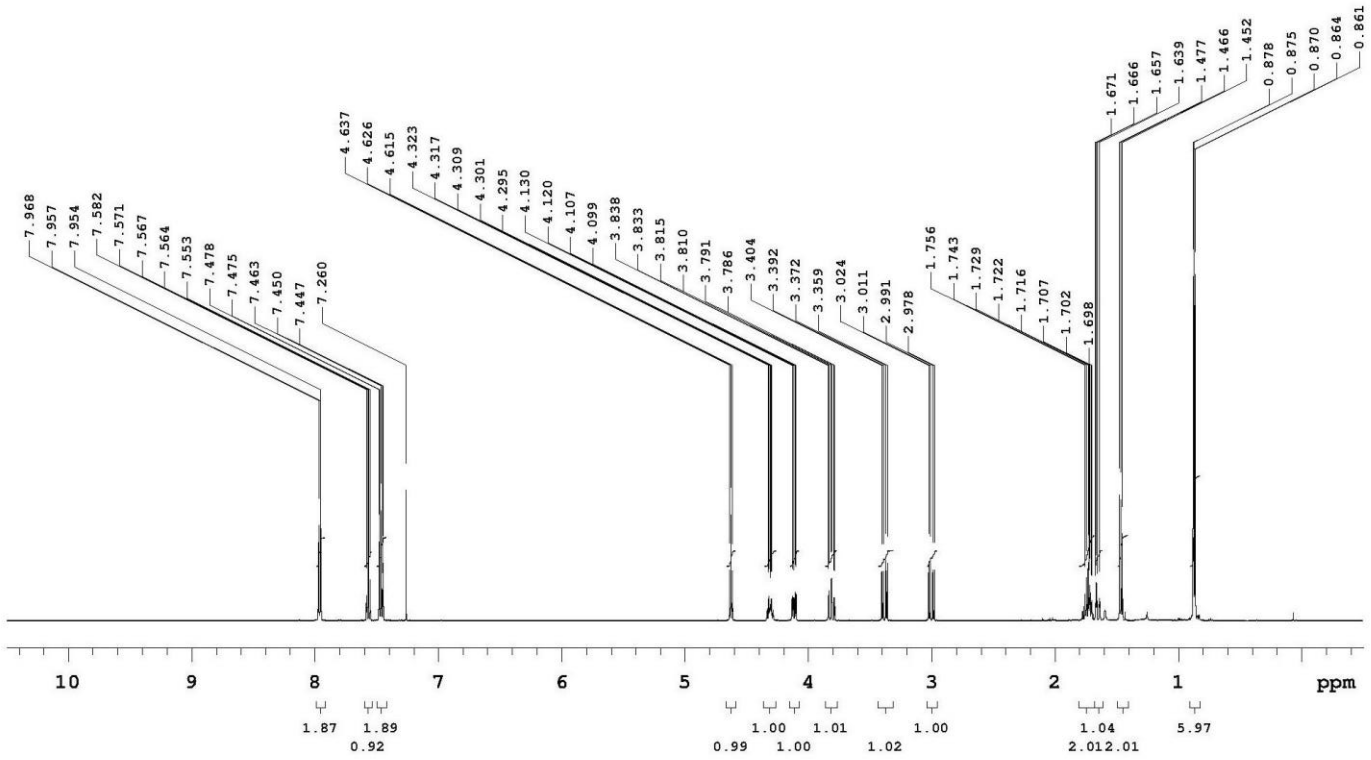
^{13}C NMR



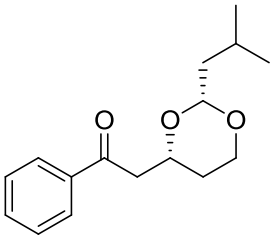
2-(2-Isobutyl-1,3-dioxan-4-yl)-1-phenylethanone (3ac)



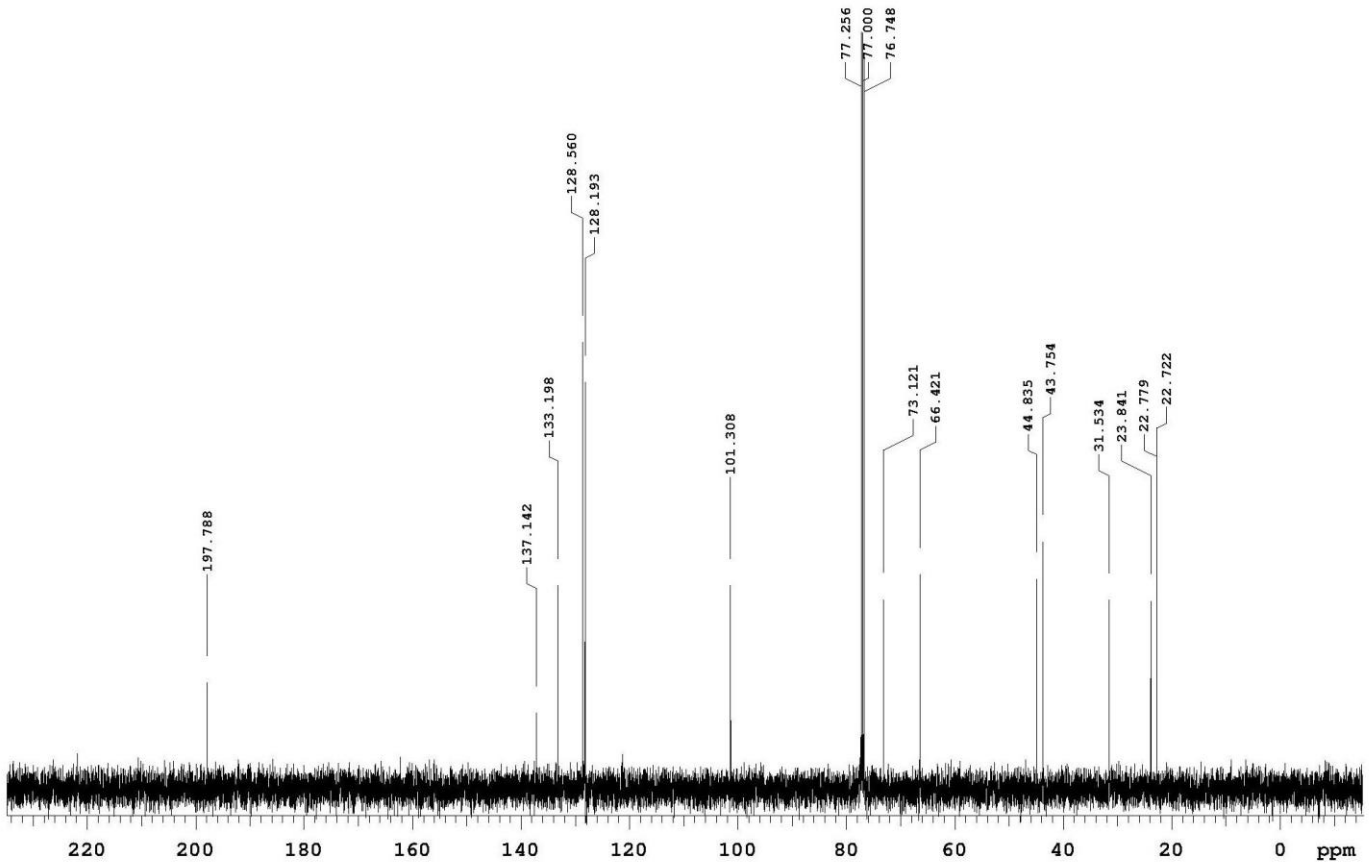
^{1}H NMR



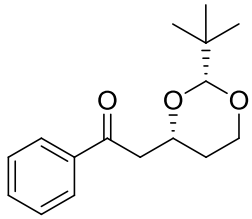
2-(2-Isobutyl-1,3-dioxan-4-yl)-1-phenylethanone (3ac)



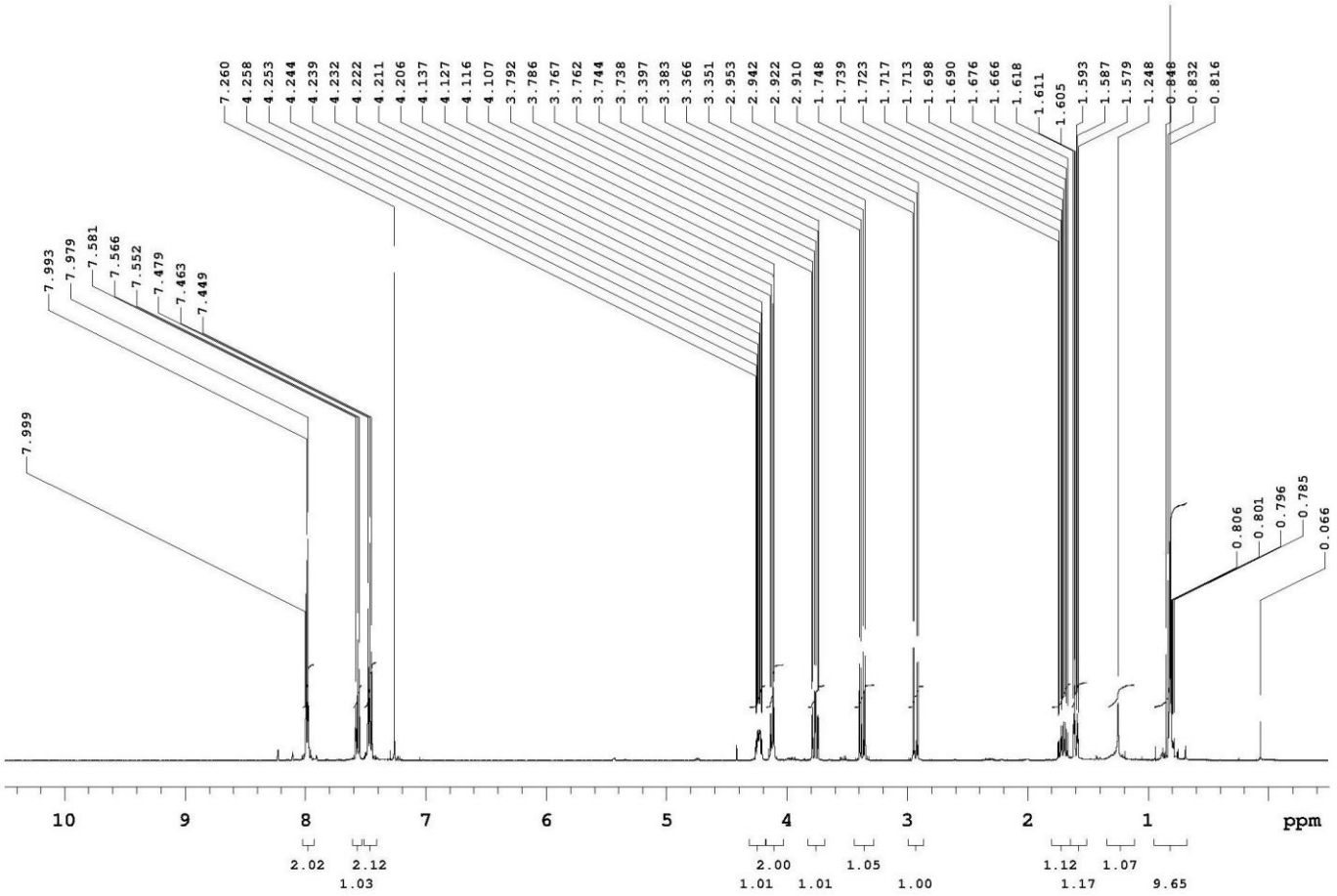
^{13}C NMR



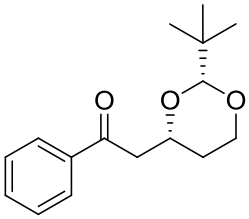
2-(2-*tert*-Butyl-1,3-dioxan-4-yl)-1-phenylethanone (3ad)



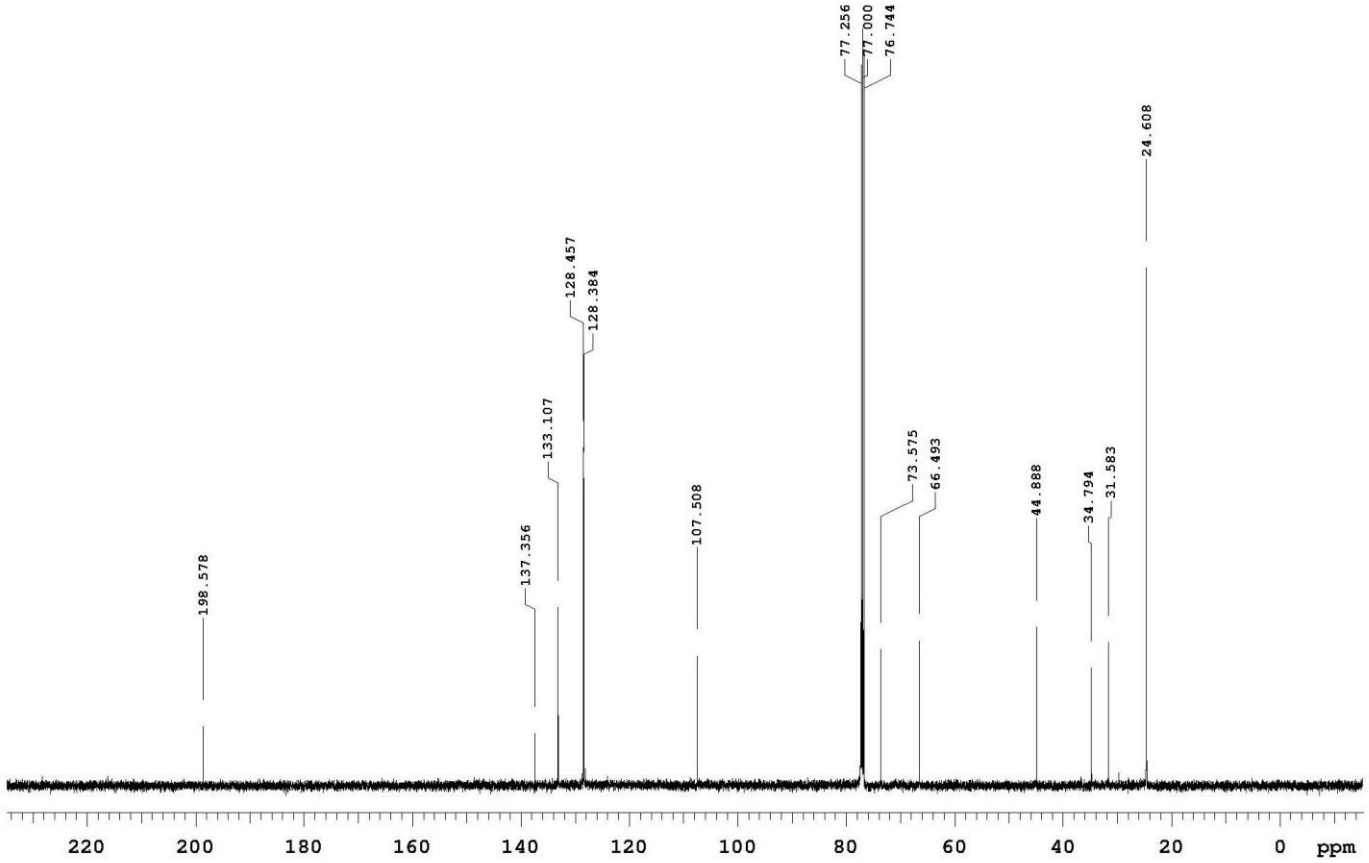
^{1}H NMR



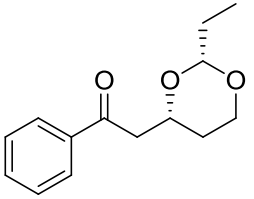
2-(2-*tert*-Butyl-1,3-dioxan-4-yl)-1-phenylethanone (3ad)



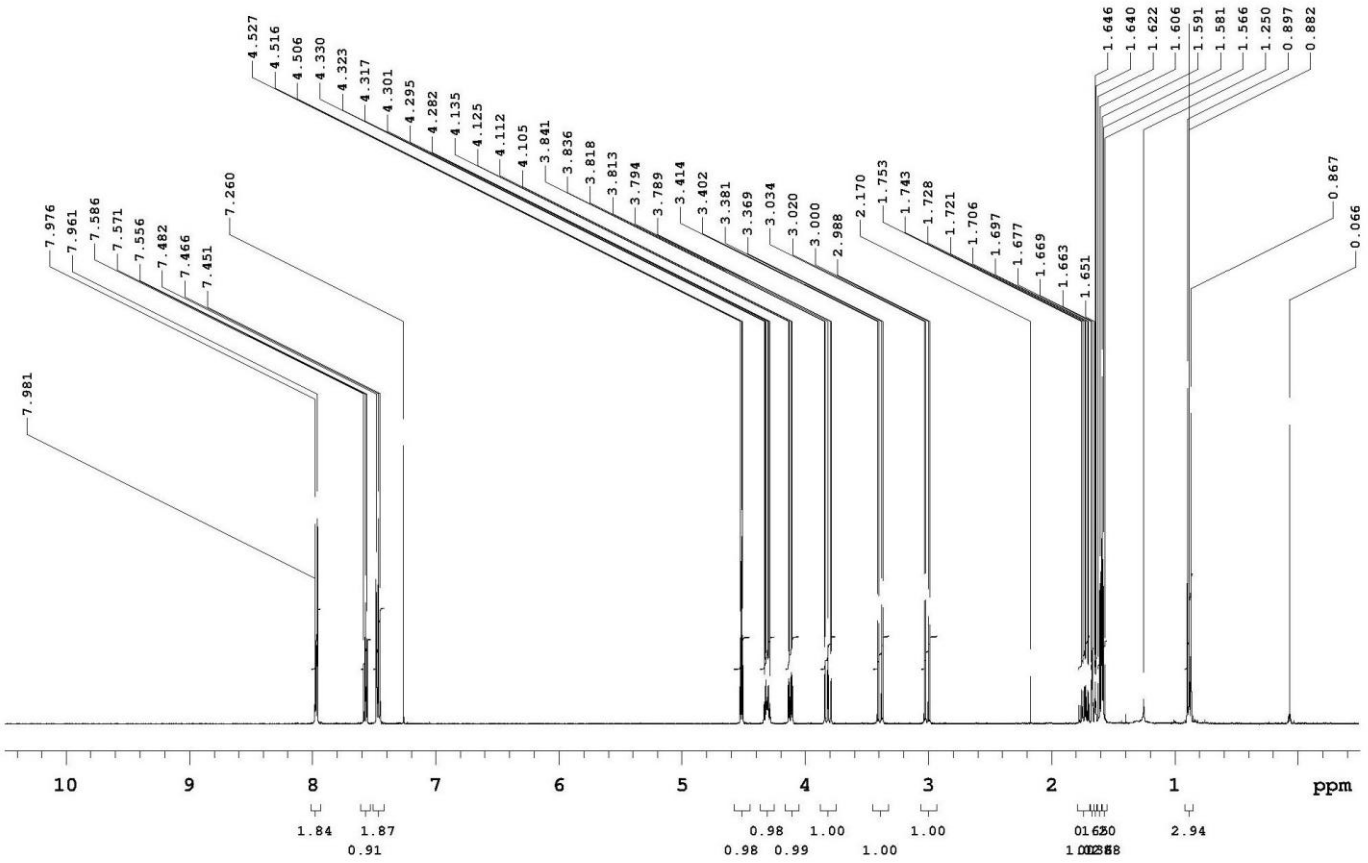
^{13}C NMR



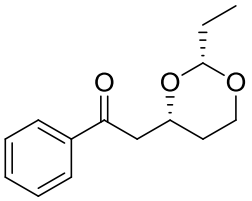
2-(2-Ethyl-1,3-dioxan-4-yl)-1-phenylethanone (3ae)



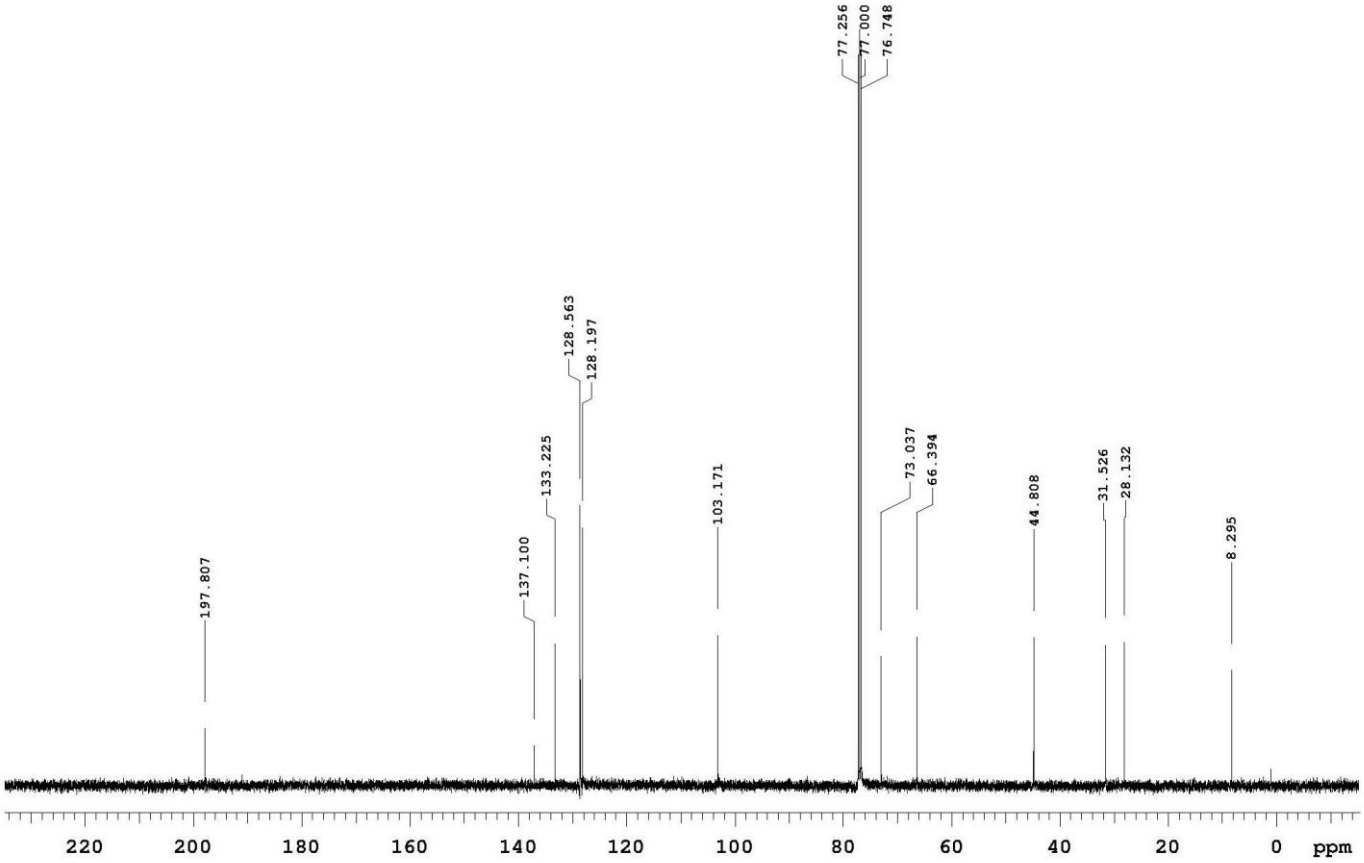
^{1}H NMR



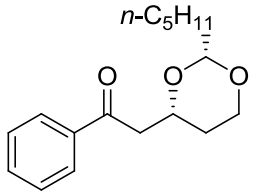
2-(2-Ethyl-1,3-dioxan-4-yl)-1-phenylethanone (3ae)



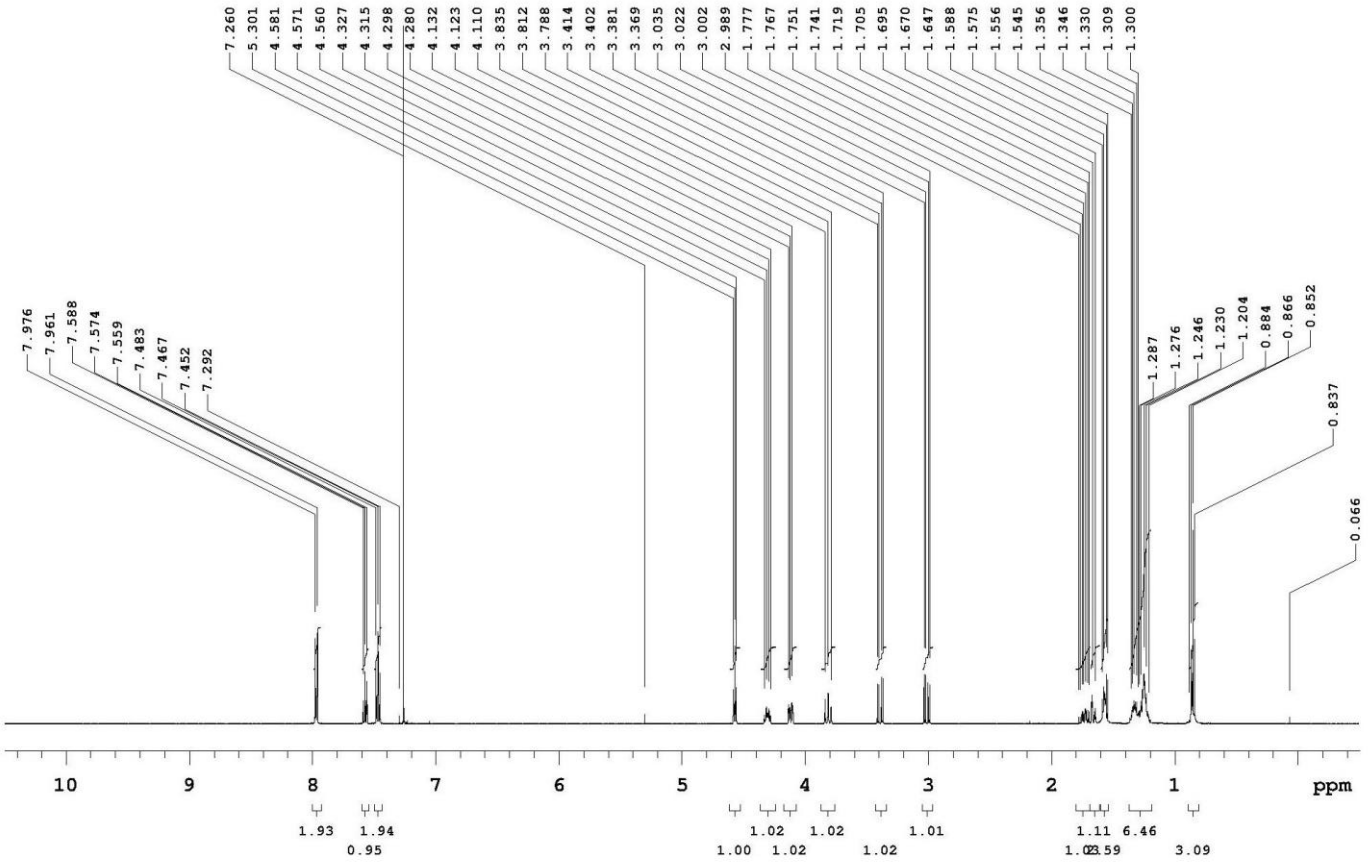
^{13}C NMR



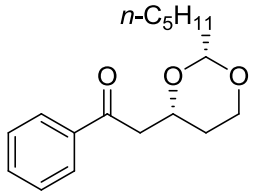
2-(2-Pentyl-1,3-dioxan-4-yl)-1-phenylethanone (3af)



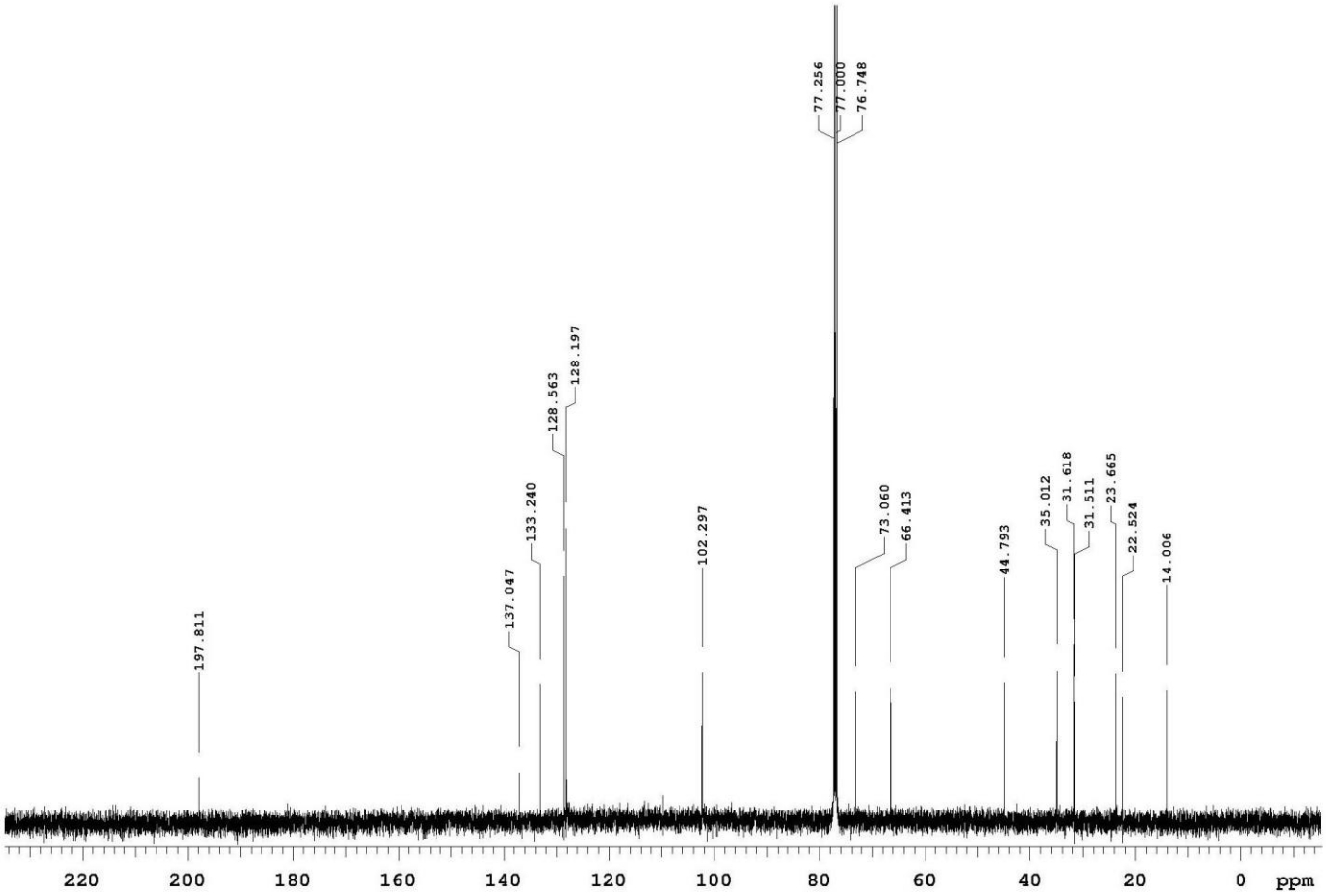
^{1}H NMR



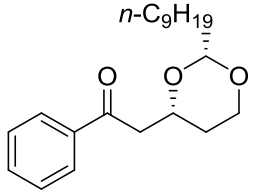
2-(Pentyl-1,3-dioxan-4-yl)-1-phenylethanone (3af)



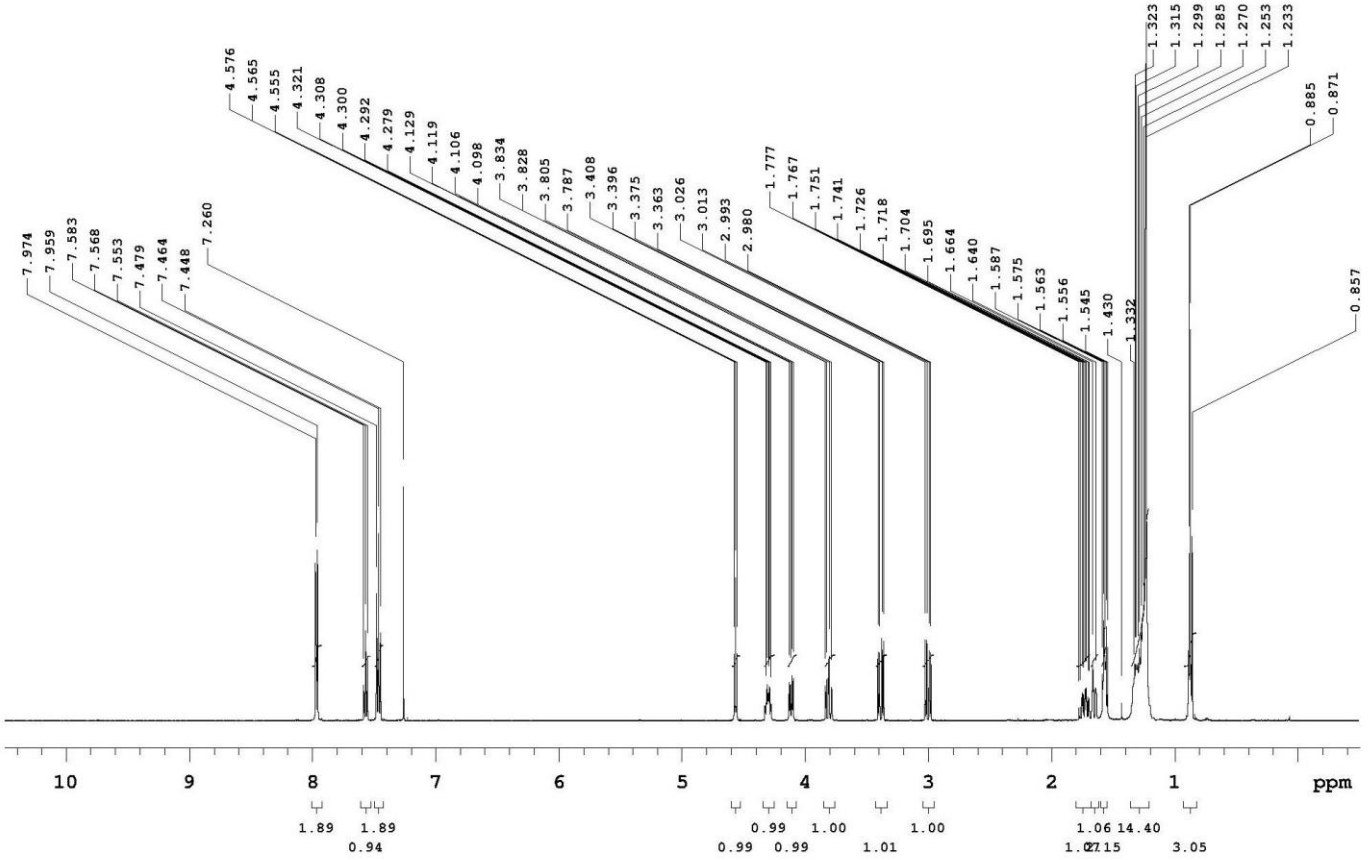
^{13}C NMR



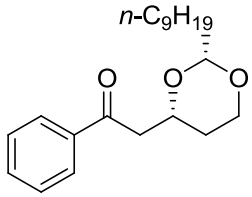
2-(2-Nonyl-1,3-dioxan-4-yl)-1-phenylethanone (3ag)



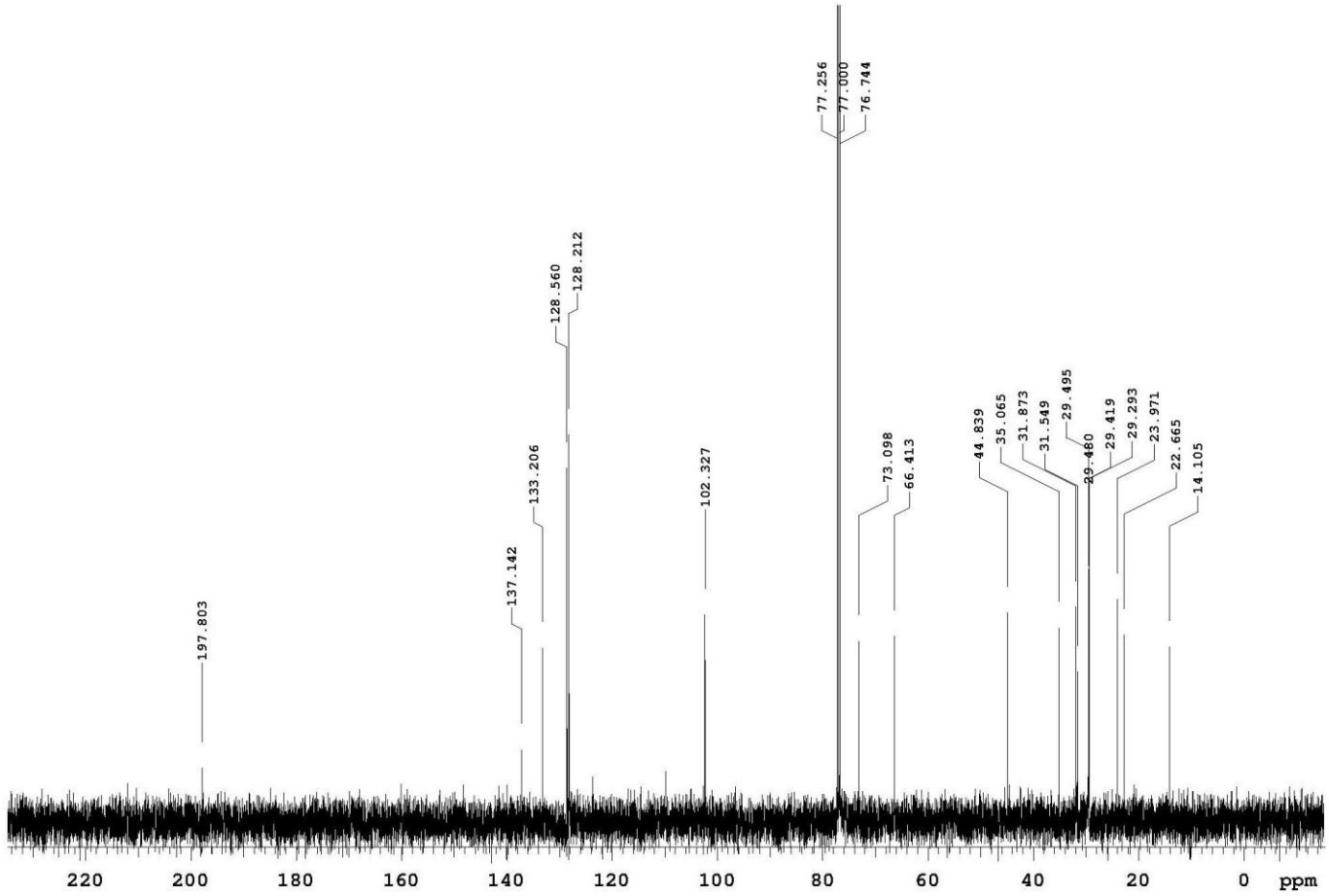
^{1}H NMR



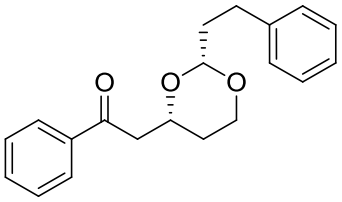
2-(2-Nonyl-1,3-dioxan-4-yl)-1-phenylethanone (3ag)



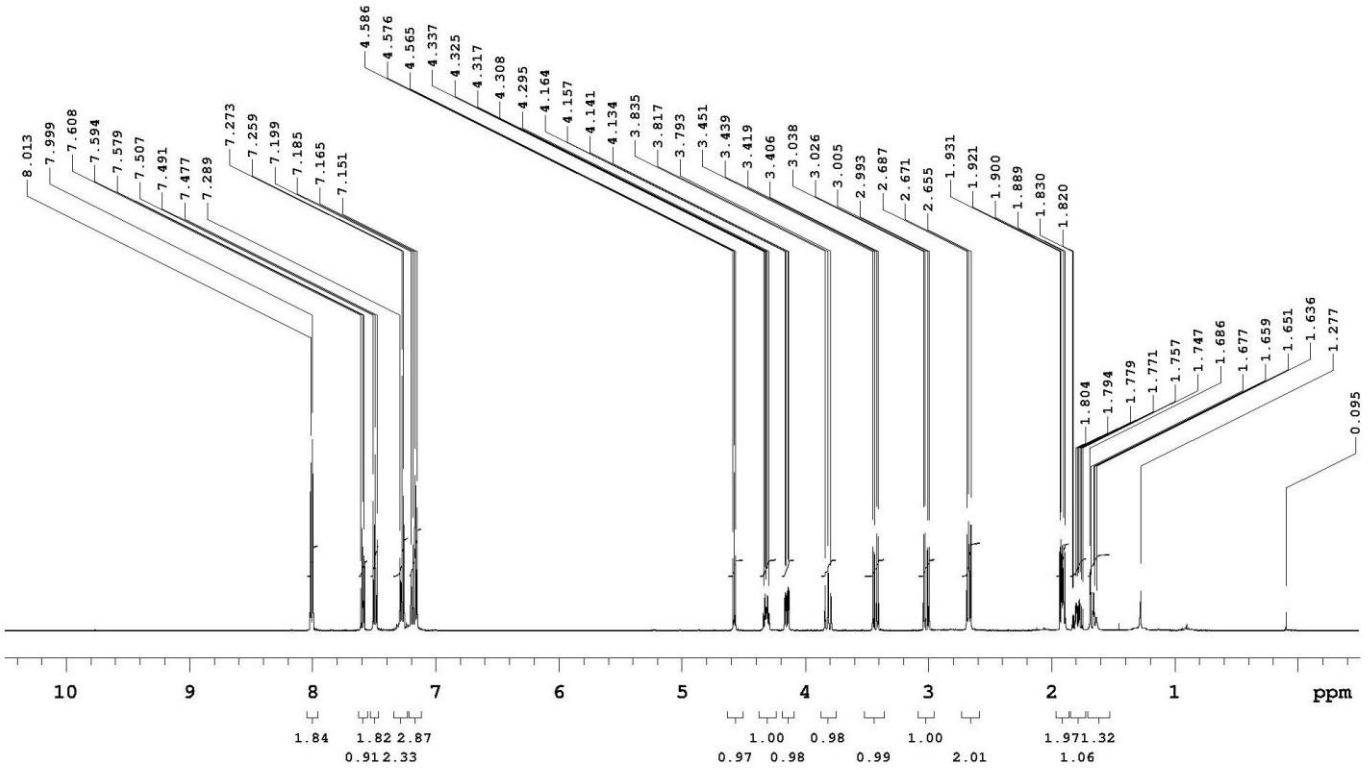
^{13}C NMR



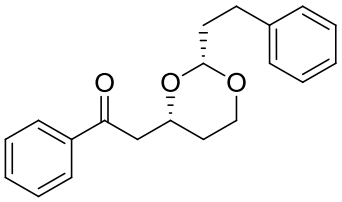
2-(2-Phenethyl-1,3-dioxan-4-yl)-1-phenylethanone (3ah)



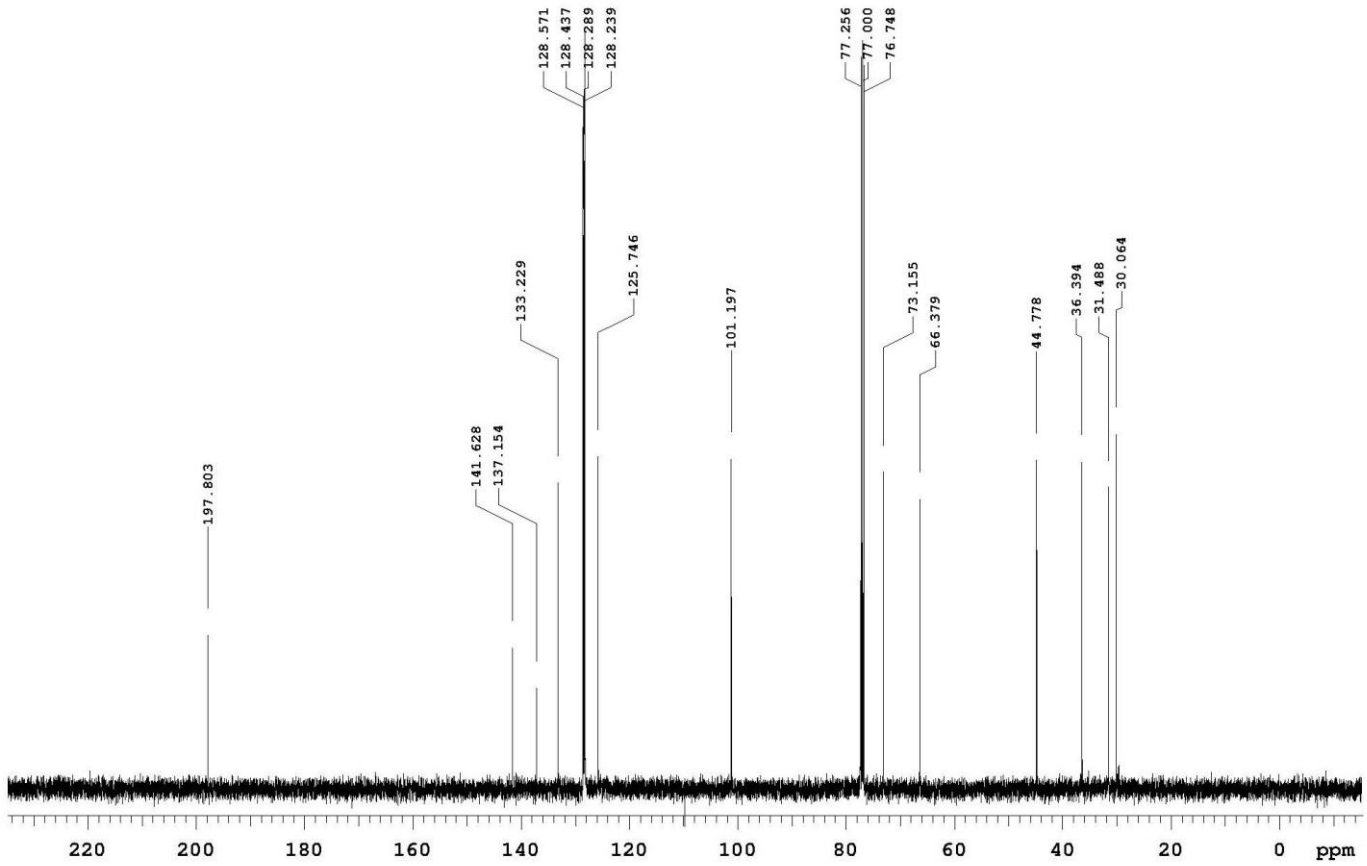
^{1}H NMR



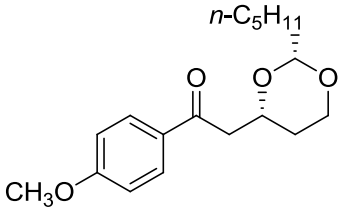
2-(2-Phenethyl-1,3-dioxan-4-yl)-1-phenylethanone (3ah)



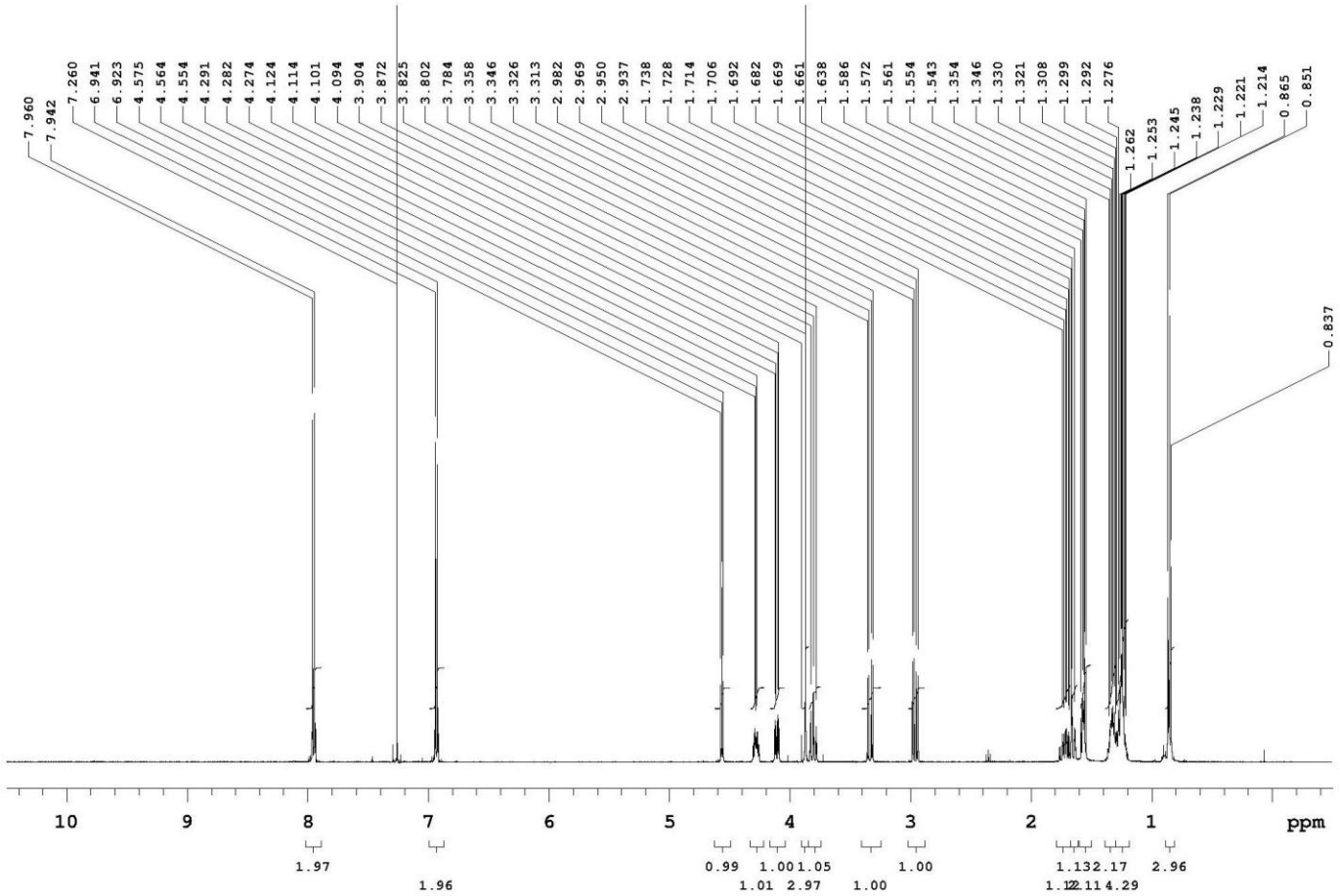
^{13}C NMR



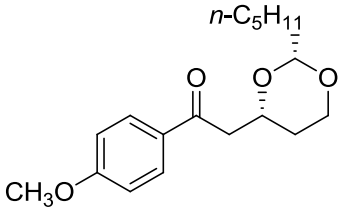
1-(4-Methoxyphenyl)-2-(2-pentyl-1,3-dioxan-4-yl)ethanone (3bf)



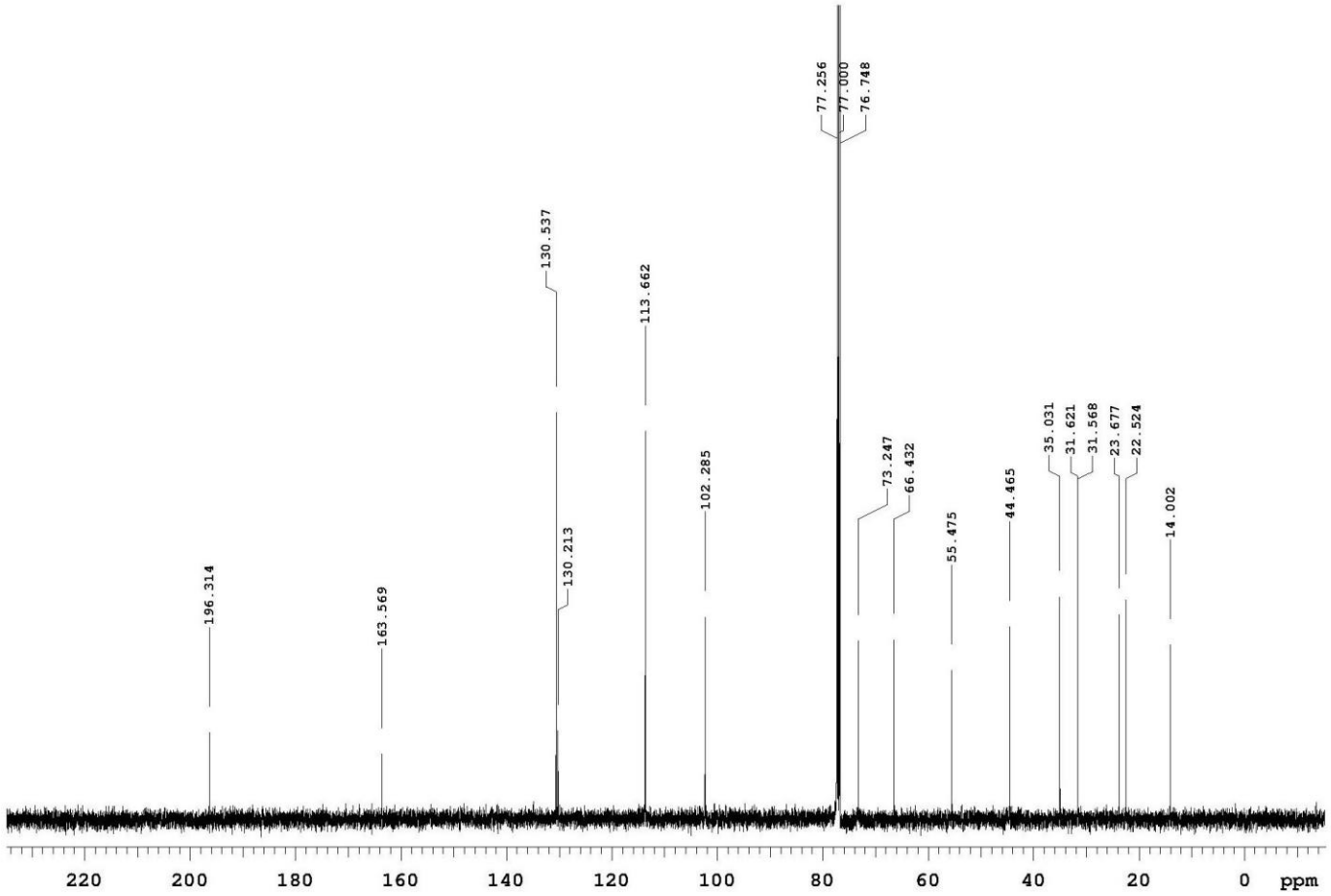
^{1}H NMR



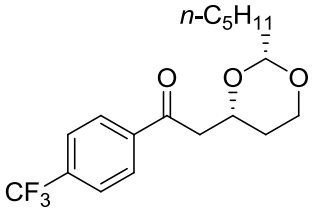
1-(4-Methoxyphenyl)-2-(2-pentyl-1,3-dioxan-4-yl)ethanone (3bf)



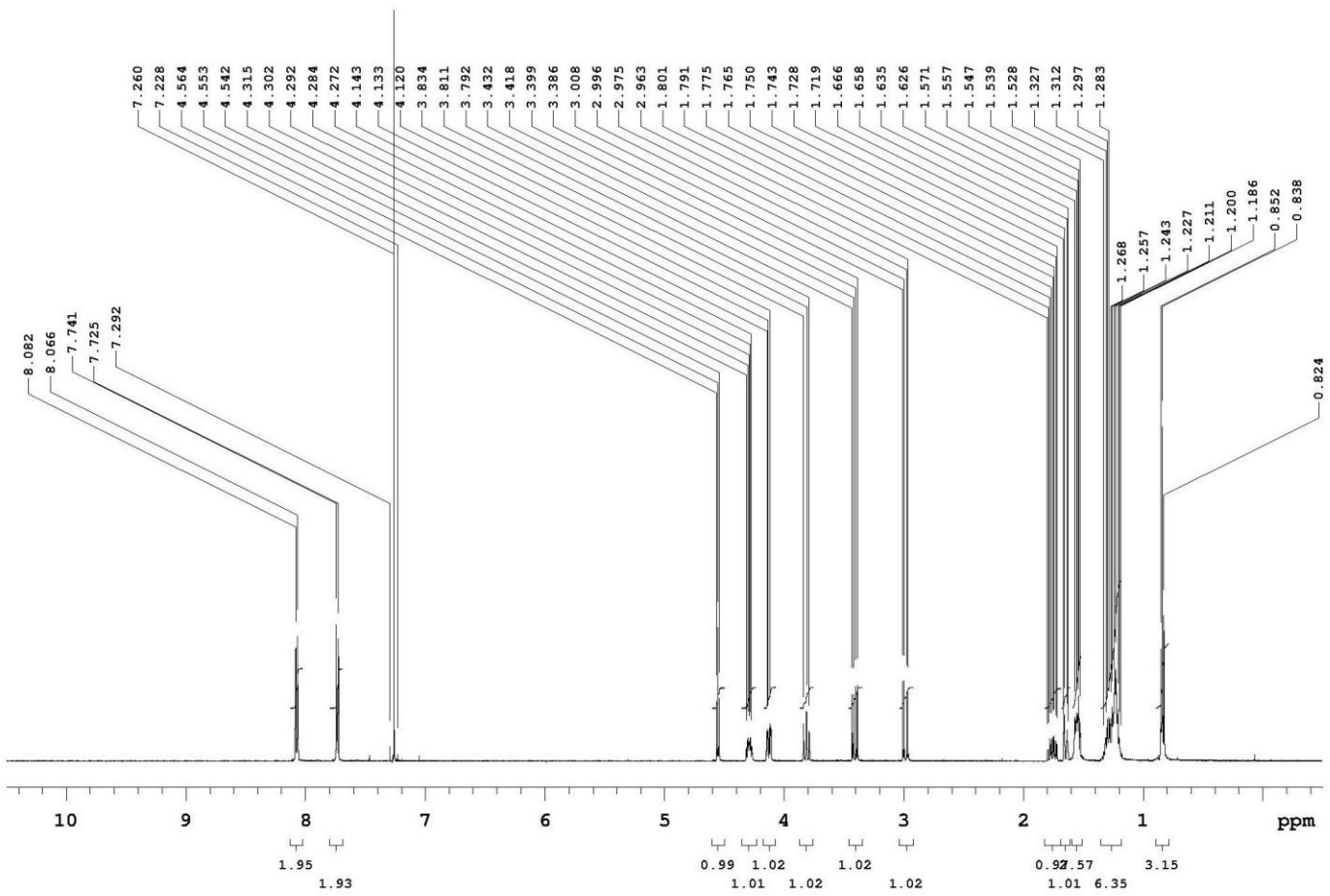
^{13}C NMR



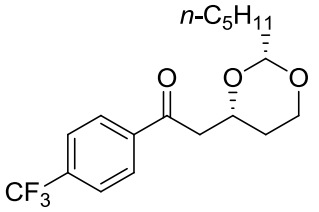
2-(2-Pentyl-1,3-dioxan-4-yl)-1-(4-(trifluoromethyl)phenyl)ethanone (3cf)



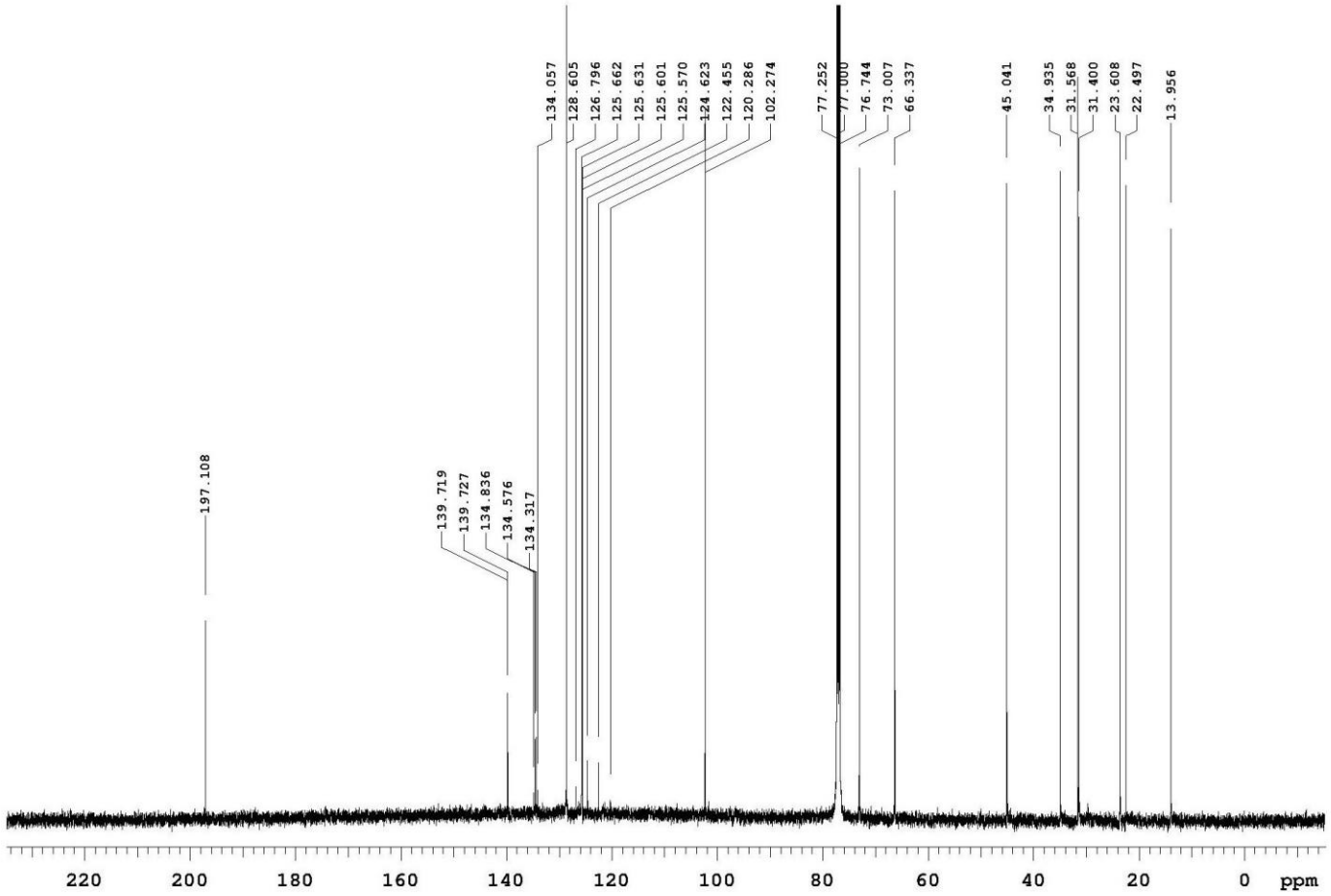
^{1}H NMR



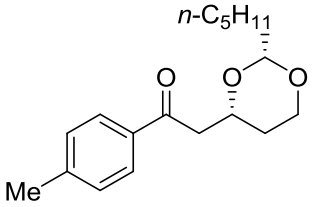
2-(2-Pentyl-1,3-dioxan-4-yl)-1-(4-(trifluoromethyl)phenyl)ethanone (3cf)



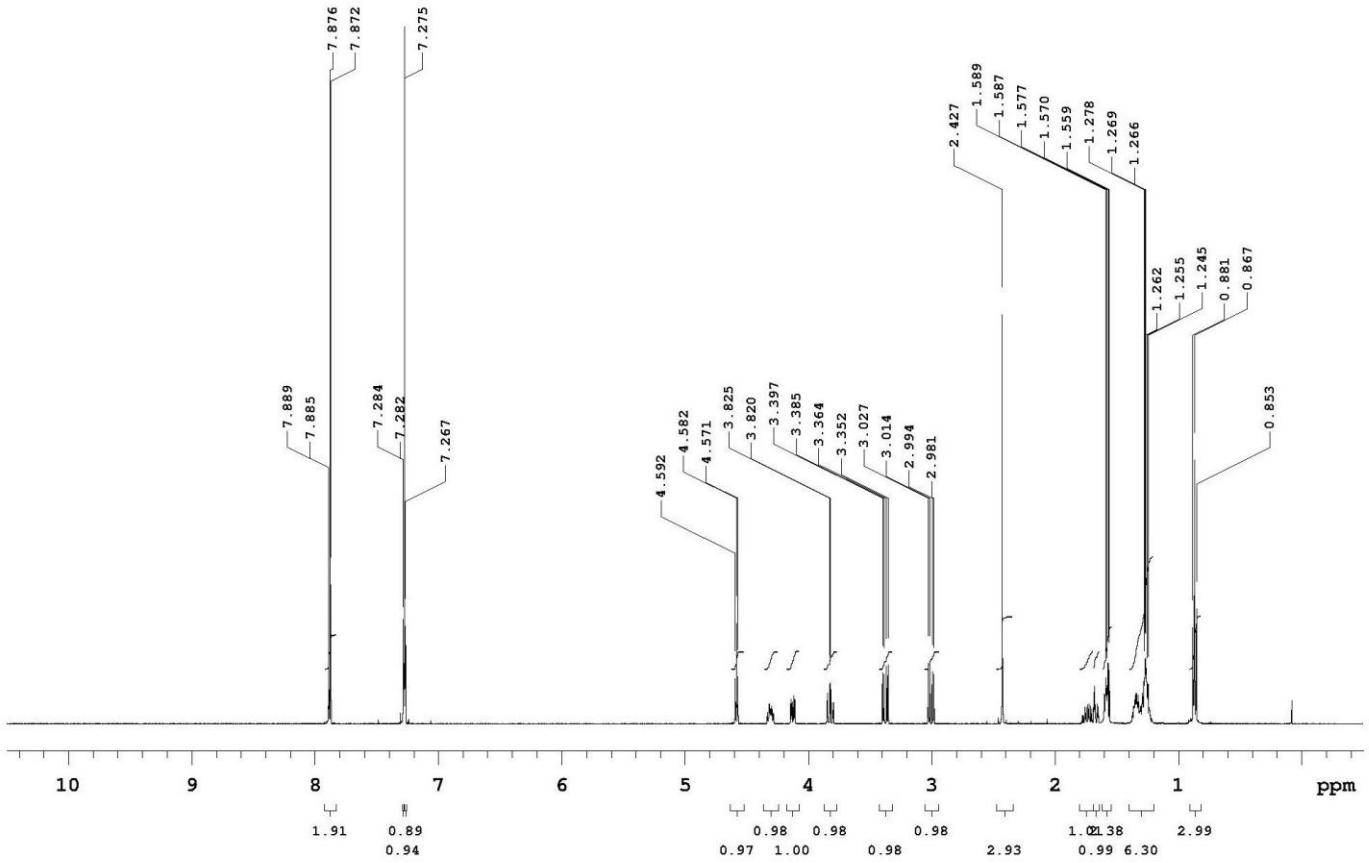
^{13}C NMR



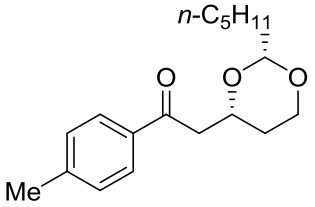
2-(2-Pentyl-1,3-dioxan-4-yl)-1-(*p*-tolyl)ethanone (3df)



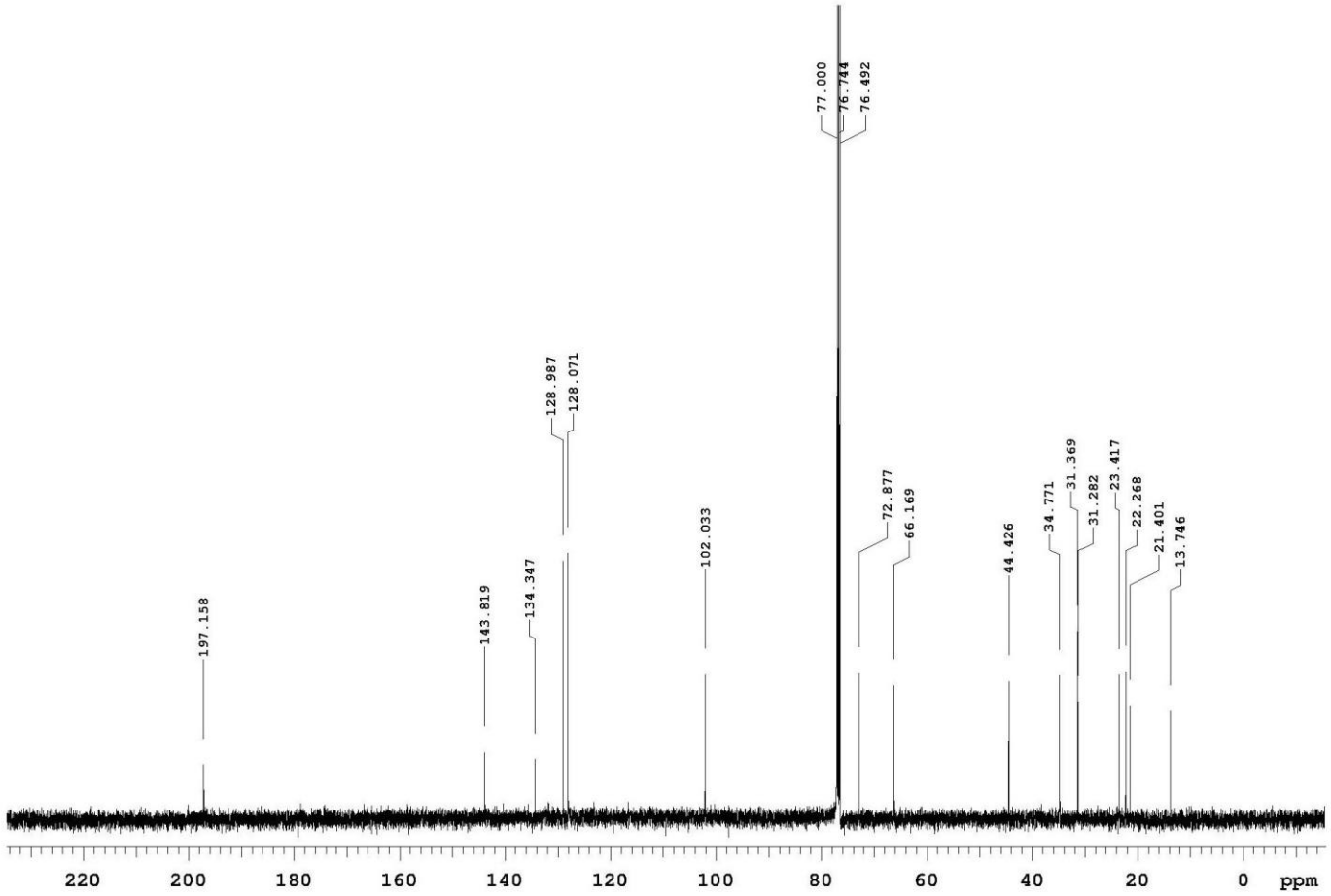
^{1}H NMR



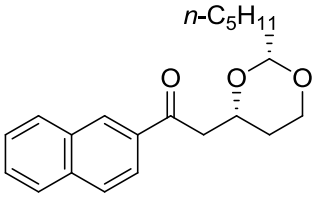
2-(2-Pentyl-1,3-dioxan-4-yl)-1-(*p*-tolyl)ethanone (3df)



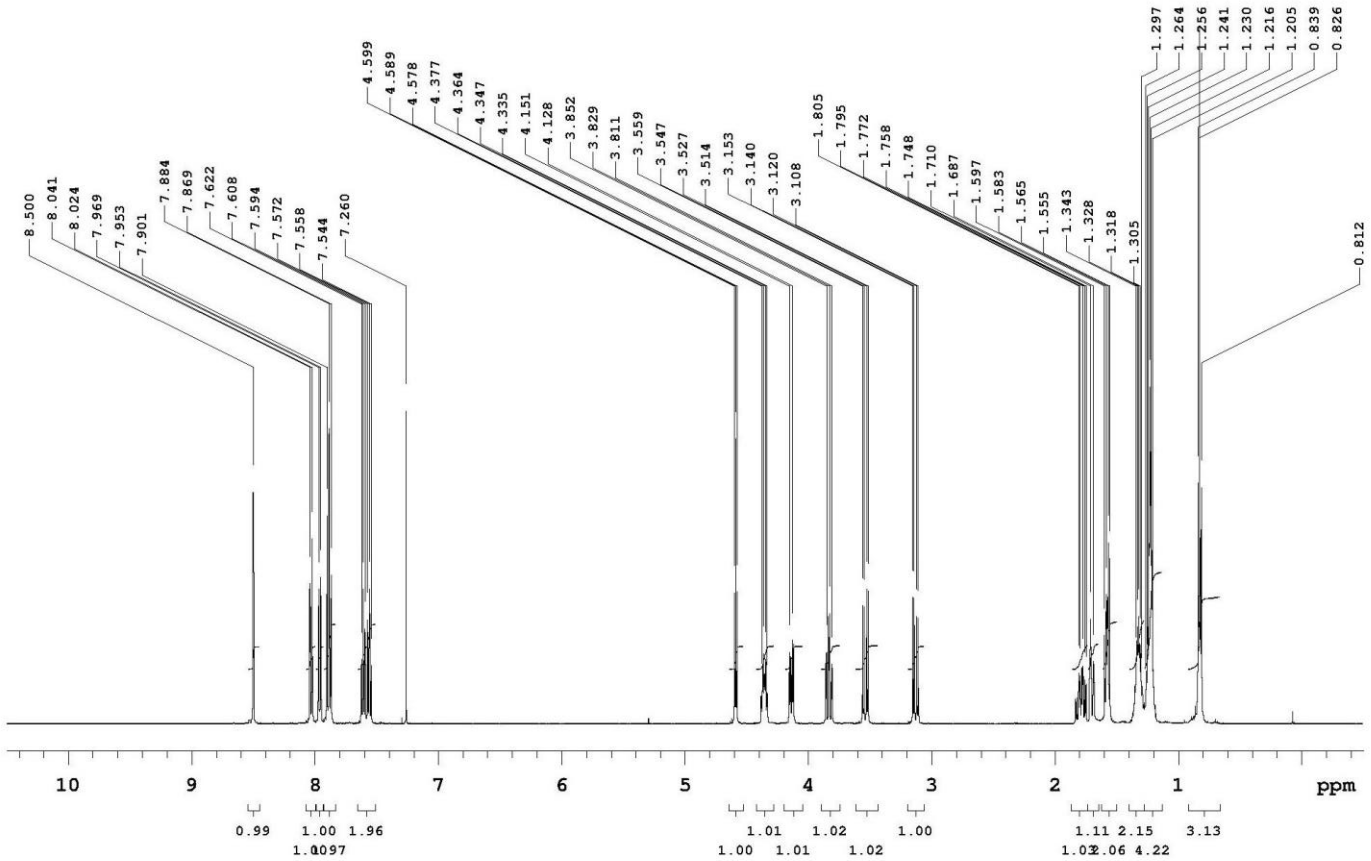
^{13}C NMR



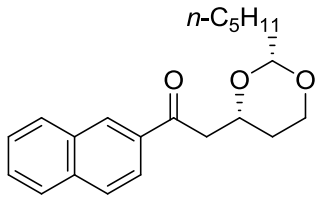
1-(Naphthalen-2-yl)-2-((2*R*,4*R*)-2-pentyl-1,3-dioxan-4-yl)ethanone (3ef)



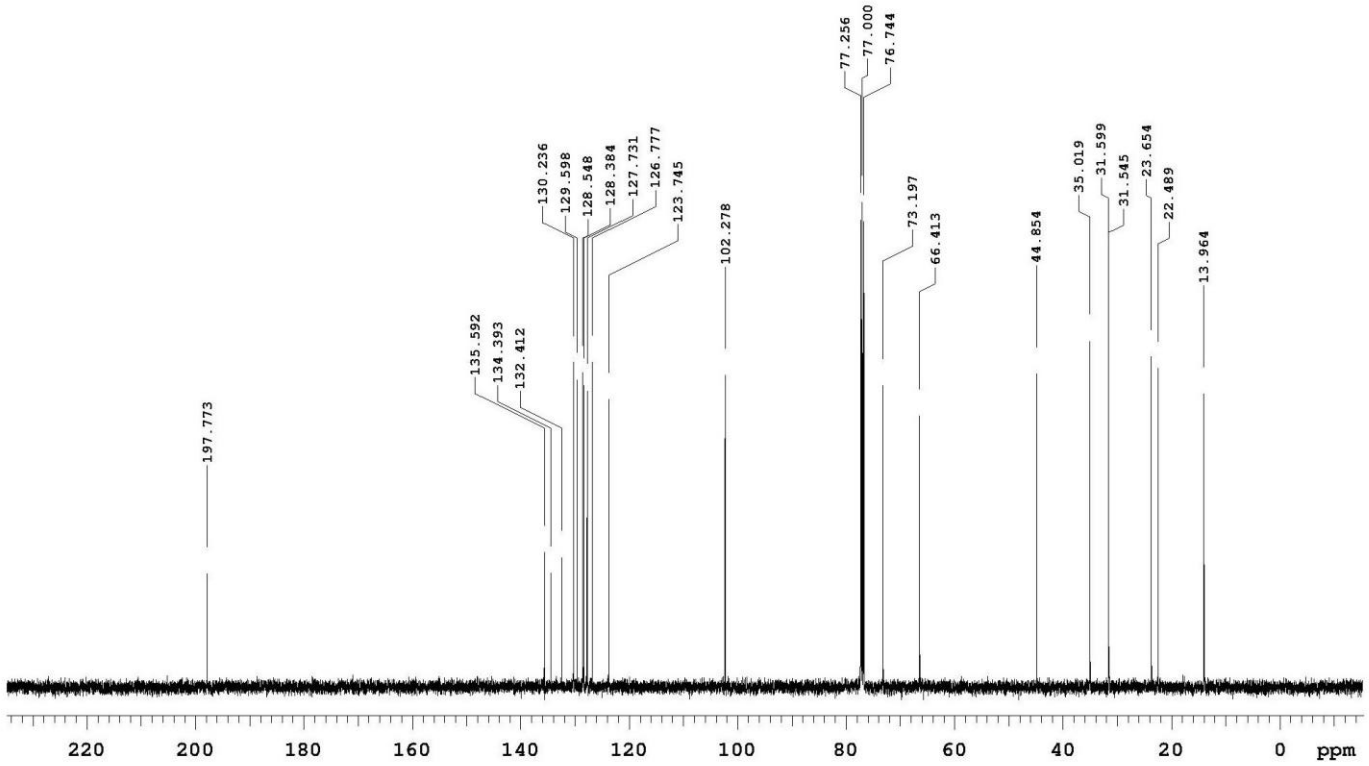
^{1}H NMR



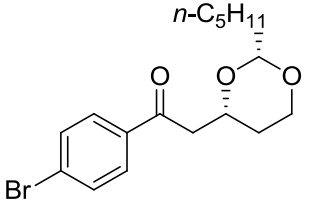
1-(Naphthalen-2-yl)-2-((2*R*,4*R*)-2-pentyl-1,3-dioxan-4-yl)ethanone (3ef)



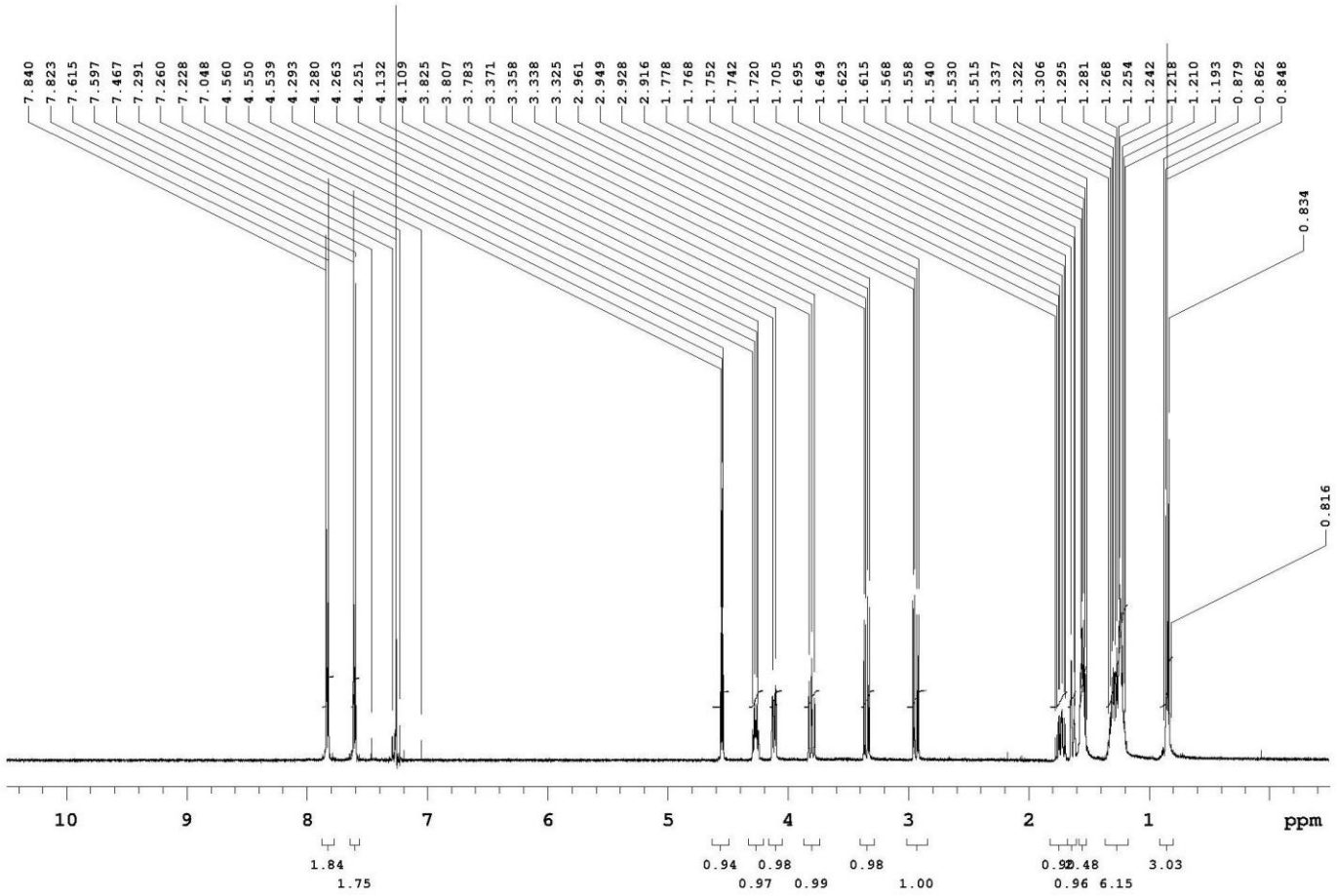
^{13}C NMR



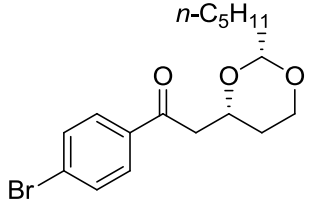
1-(4-Bromophenyl)-2-(2-pentyl-1,3-dioxan-4-yl)ethanone (3ff)



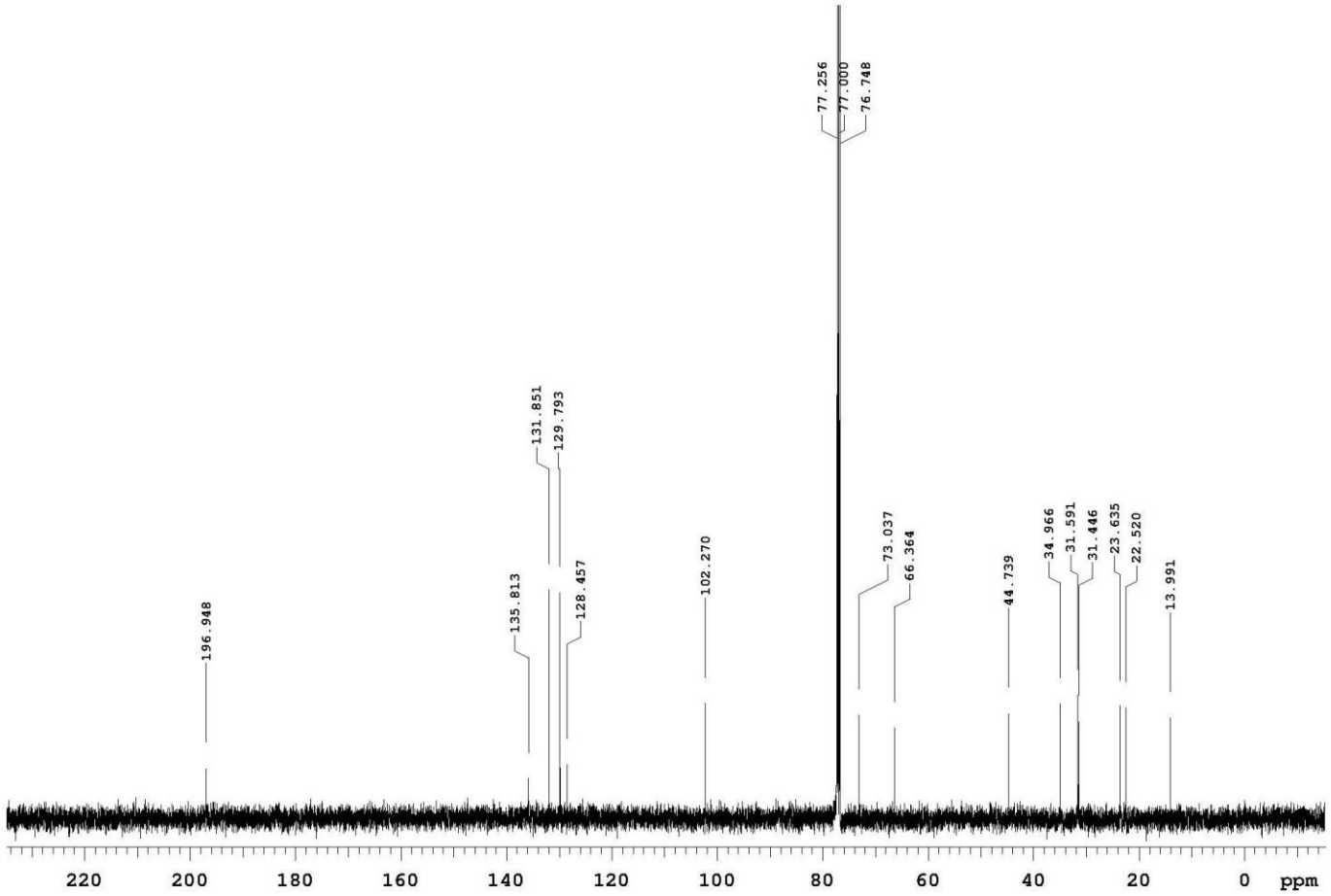
^{1}H NMR



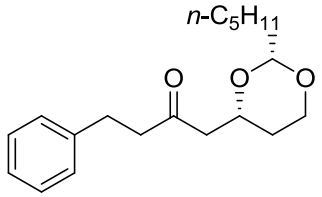
1-(4-Bromophenyl)-2-(2-pentyl-1,3-dioxan-4-yl)ethanone (3ff)



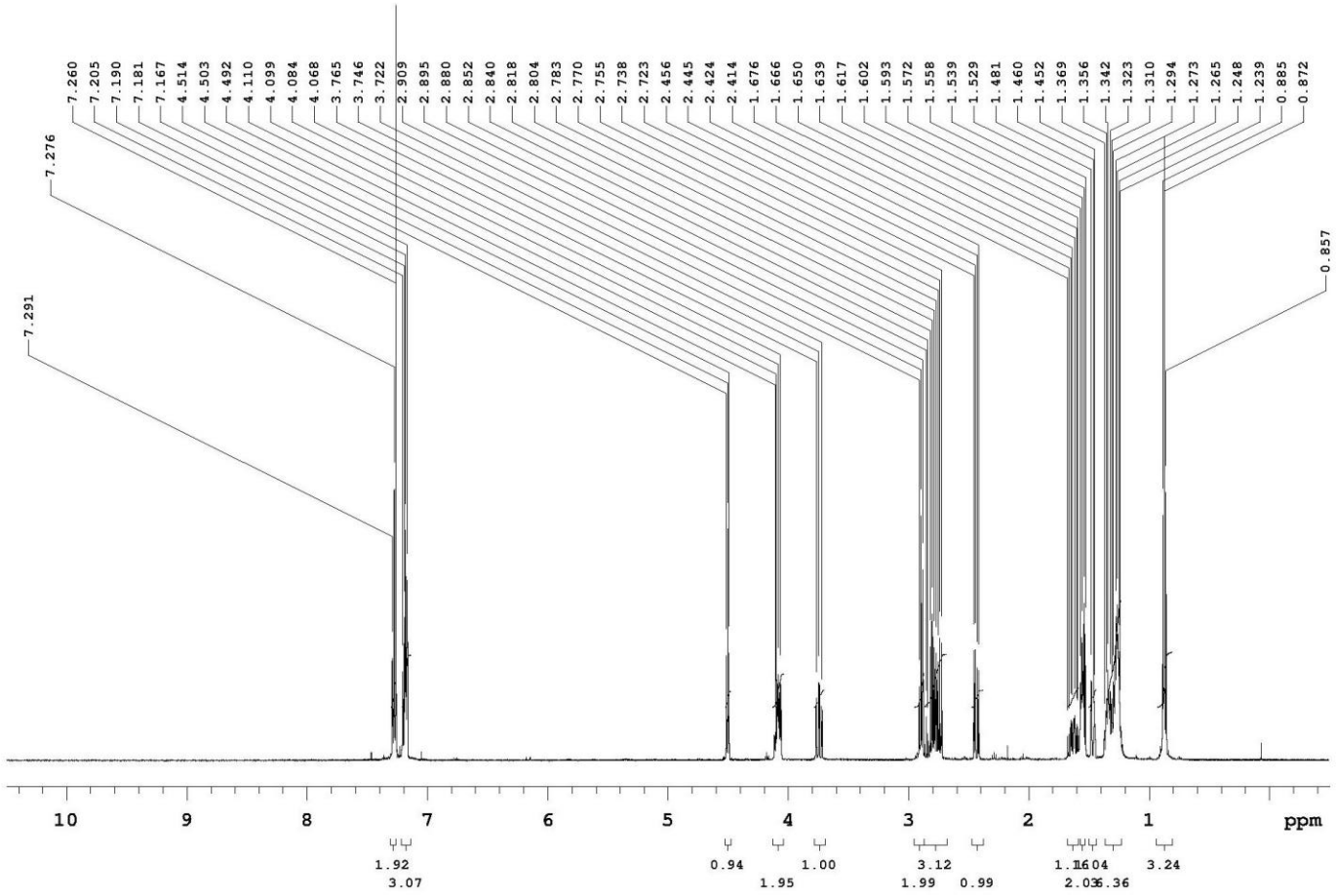
^{13}C NMR



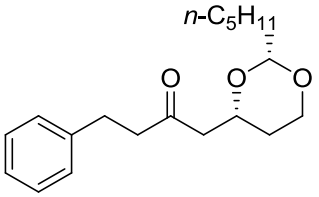
1-(2-Pentyl-1,3-dioxan-4-yl)-4-phenylbutan-2-one (3gf)



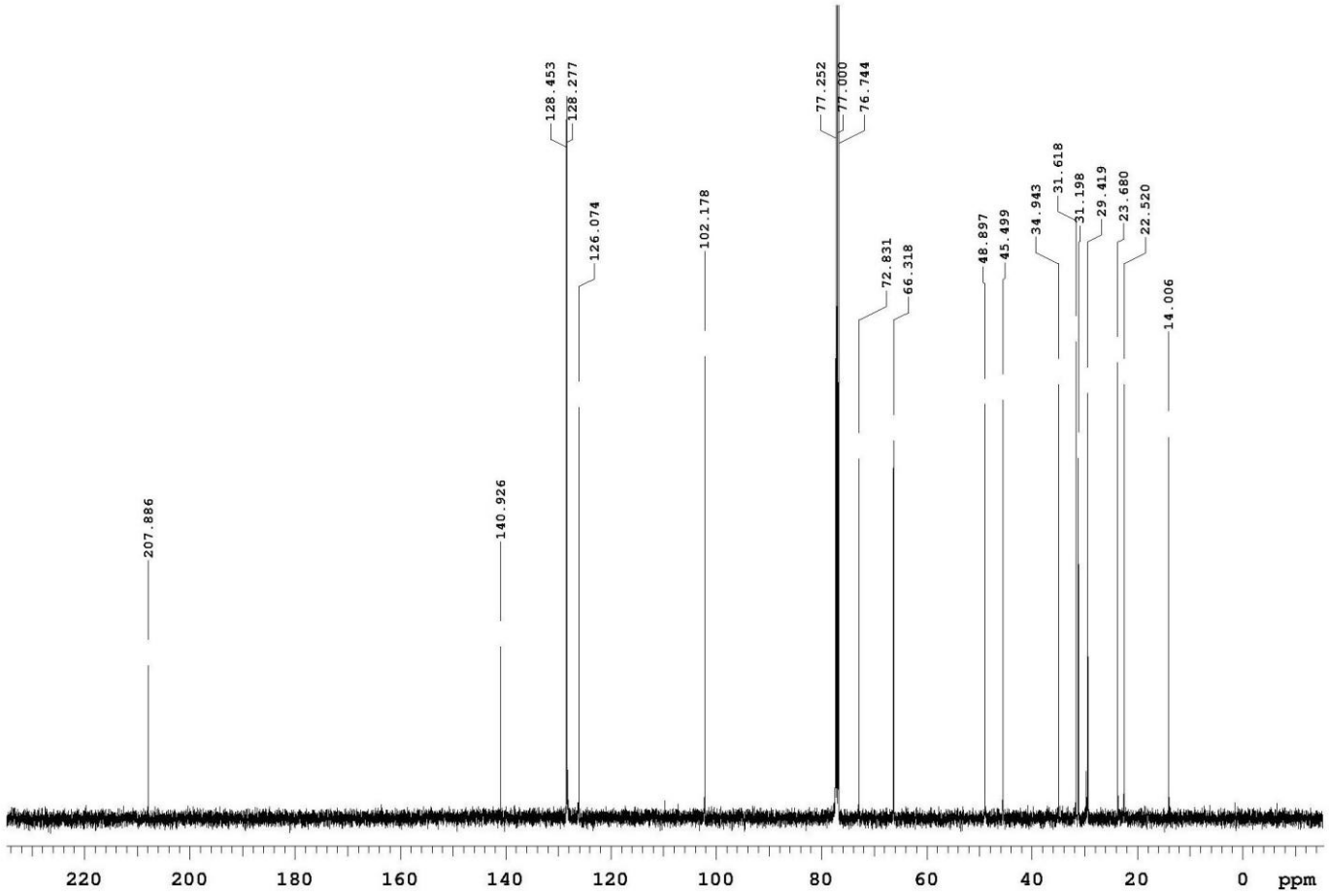
^{1}H NMR



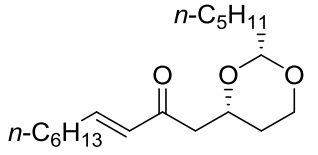
1-(2-Pentyl-1,3-dioxan-4-yl)-4-phenylbutan-2-one (3gf)



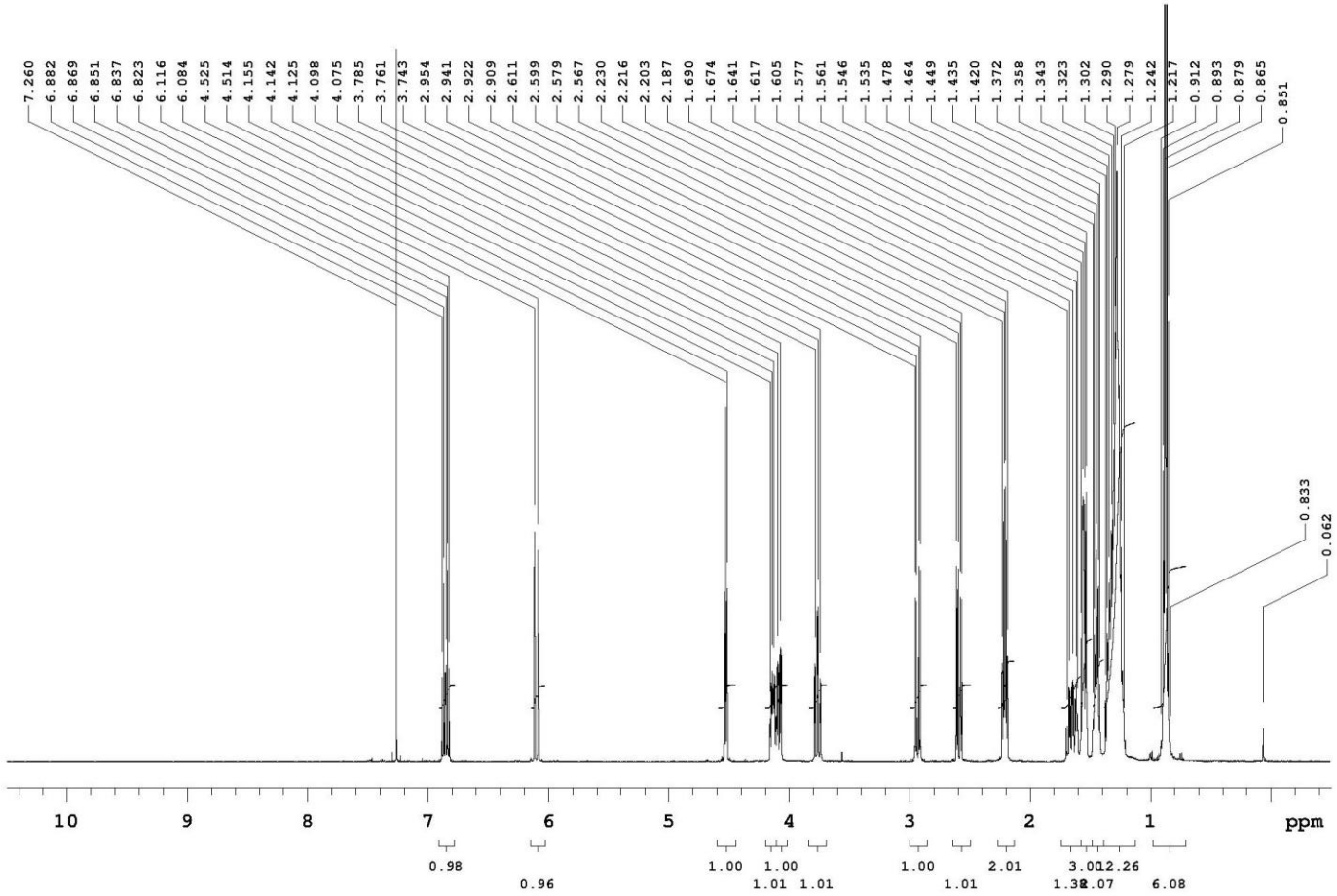
^{13}C NMR



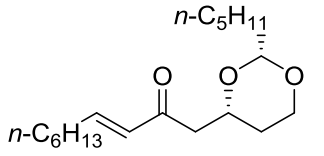
(*E*)-1-(2-pentyl-1,3-dioxan-4-yl)dec-3-en-2-one (3hf)



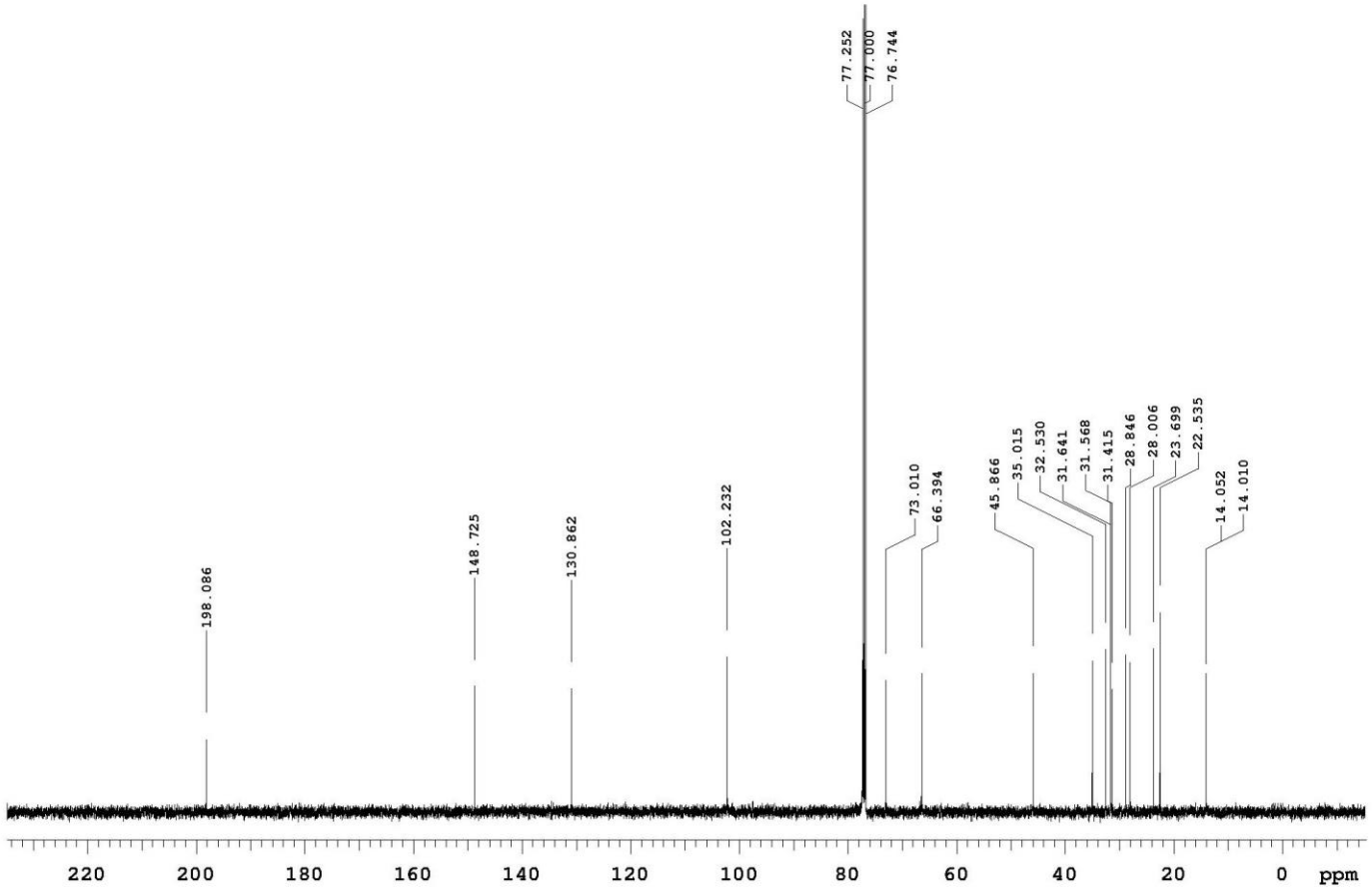
^{1}H NMR



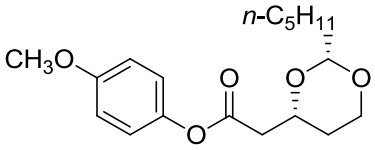
(*E*)-1-(2-pentyl-1,3-dioxan-4-yl)dec-3-en-2-one (3hf)



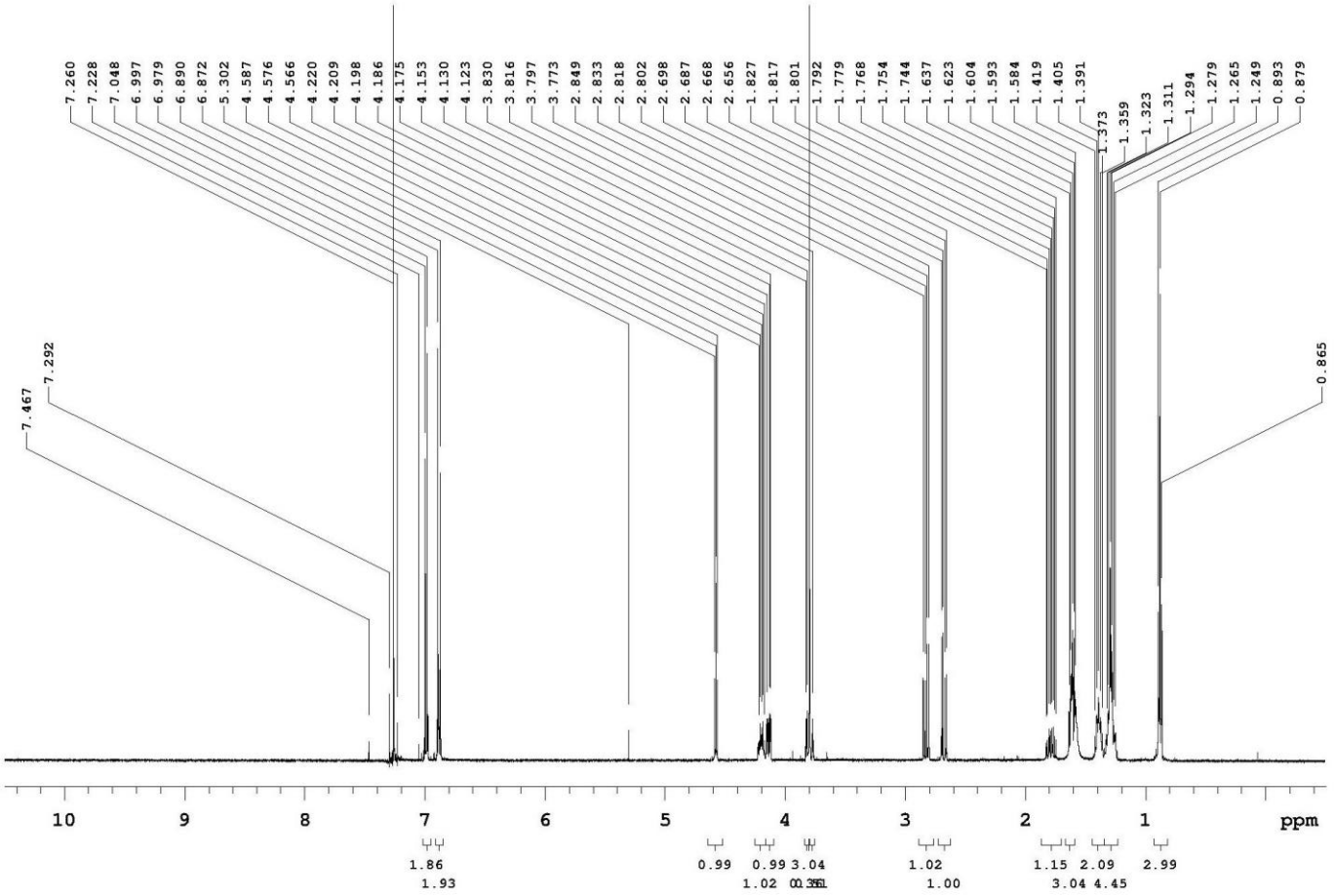
^{13}C NMR



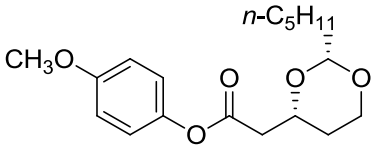
4-Methoxyphenyl 2-(2-pentyl-1,3-dioxan-4-yl)acetate (5)



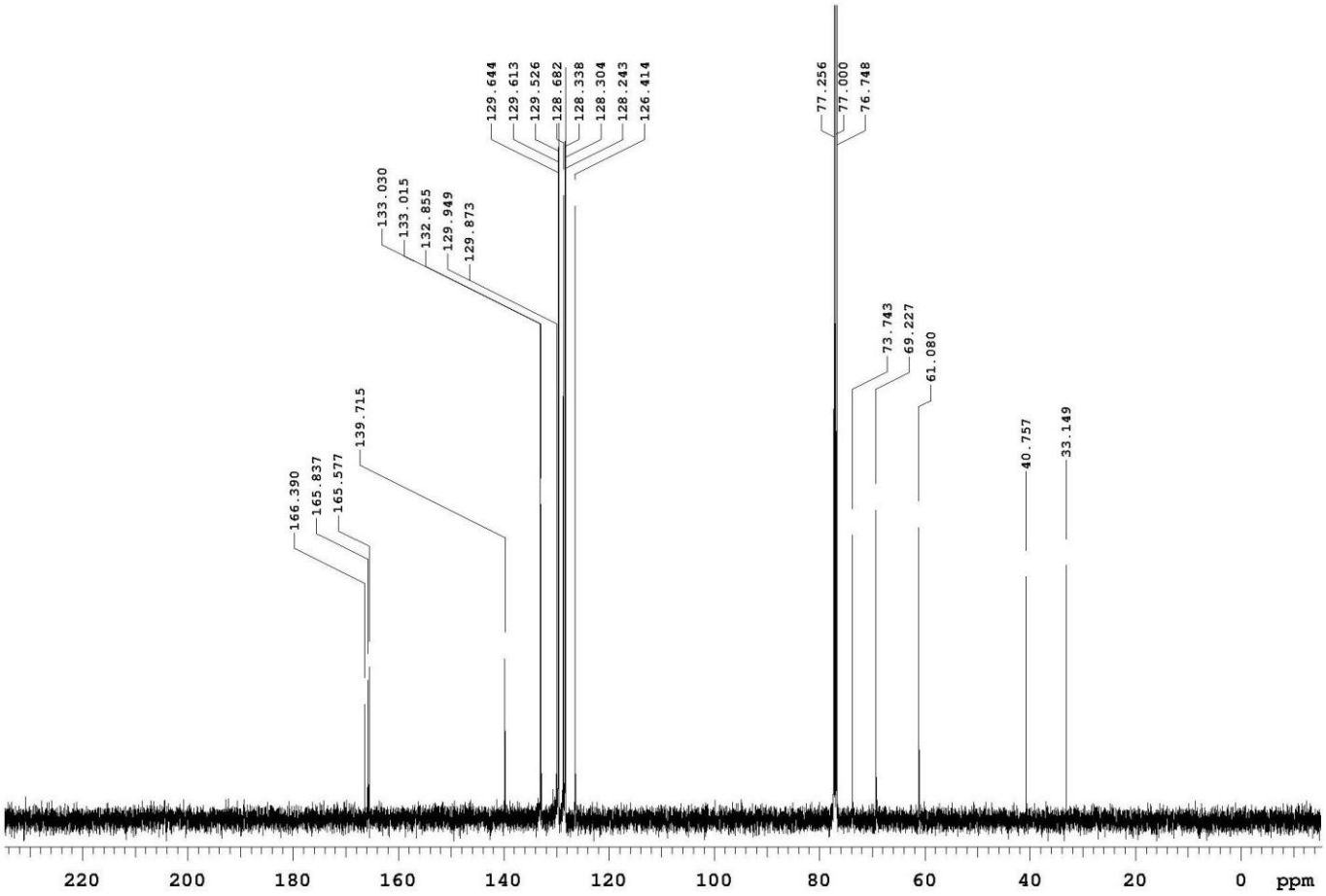
^{1}H NMR



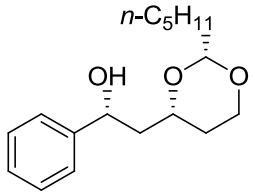
4-Methoxyphenyl 2-(2-pentyl-1,3-dioxan-4-yl)acetate (5)



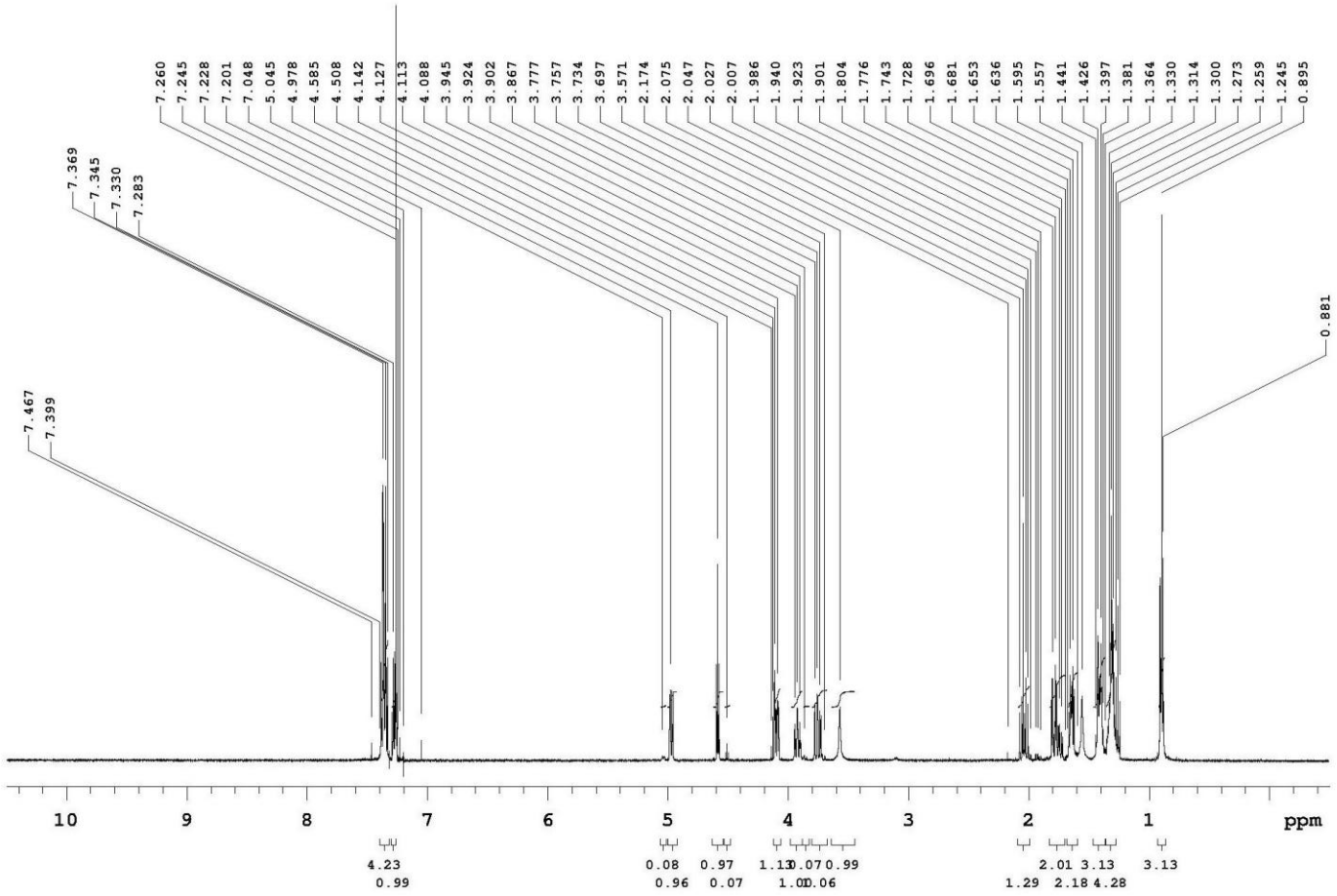
^{13}C NMR



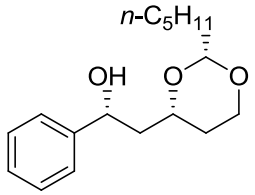
2-(2-Pentyl-1,3-dioxan-4-yl)-1-phenylethanol (6)



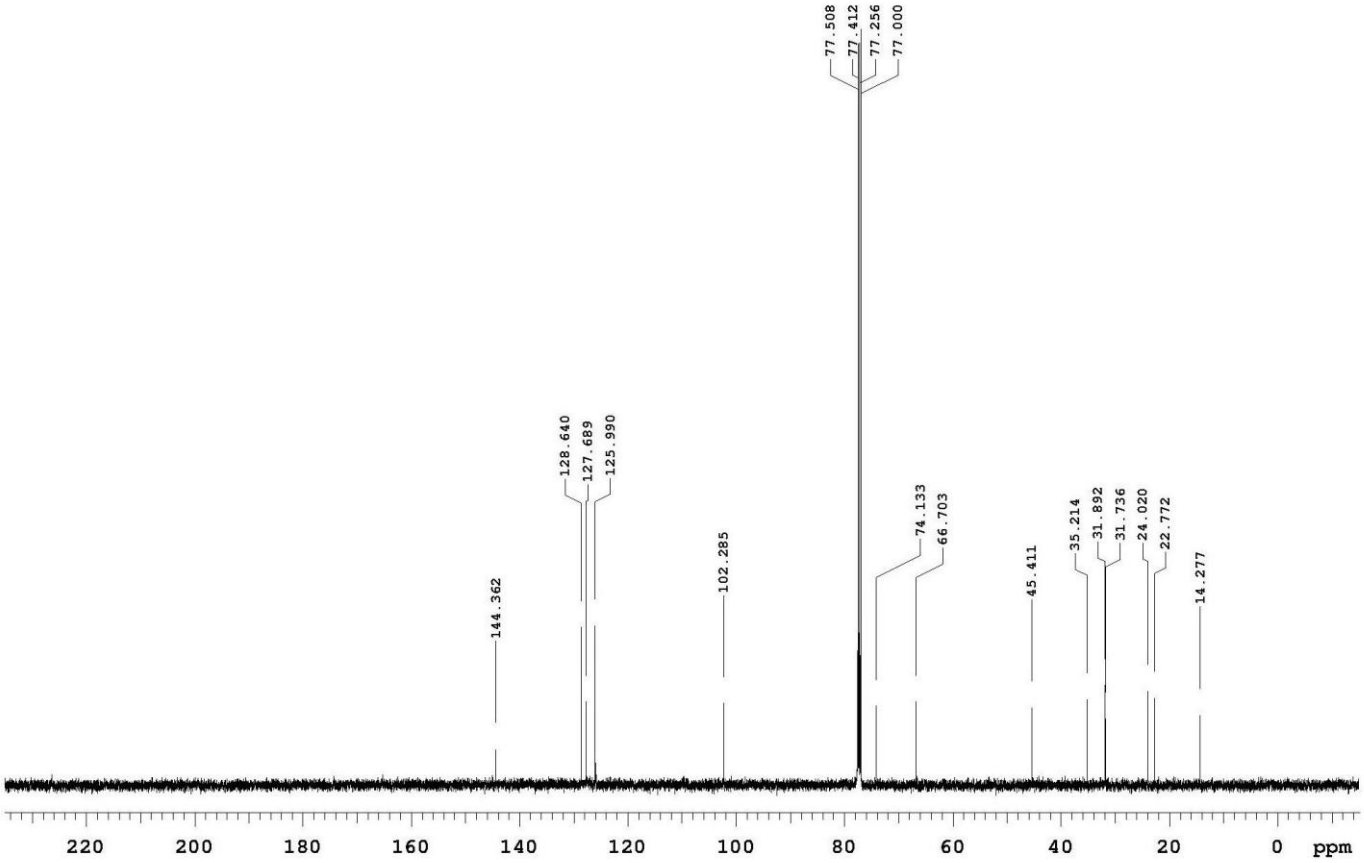
^{1}H NMR



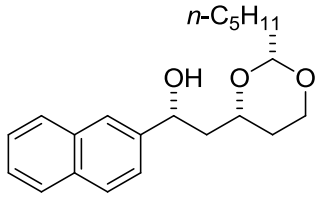
2-(2-Pentyl-1,3-dioxan-4-yl)-1-phenylethanol (6)



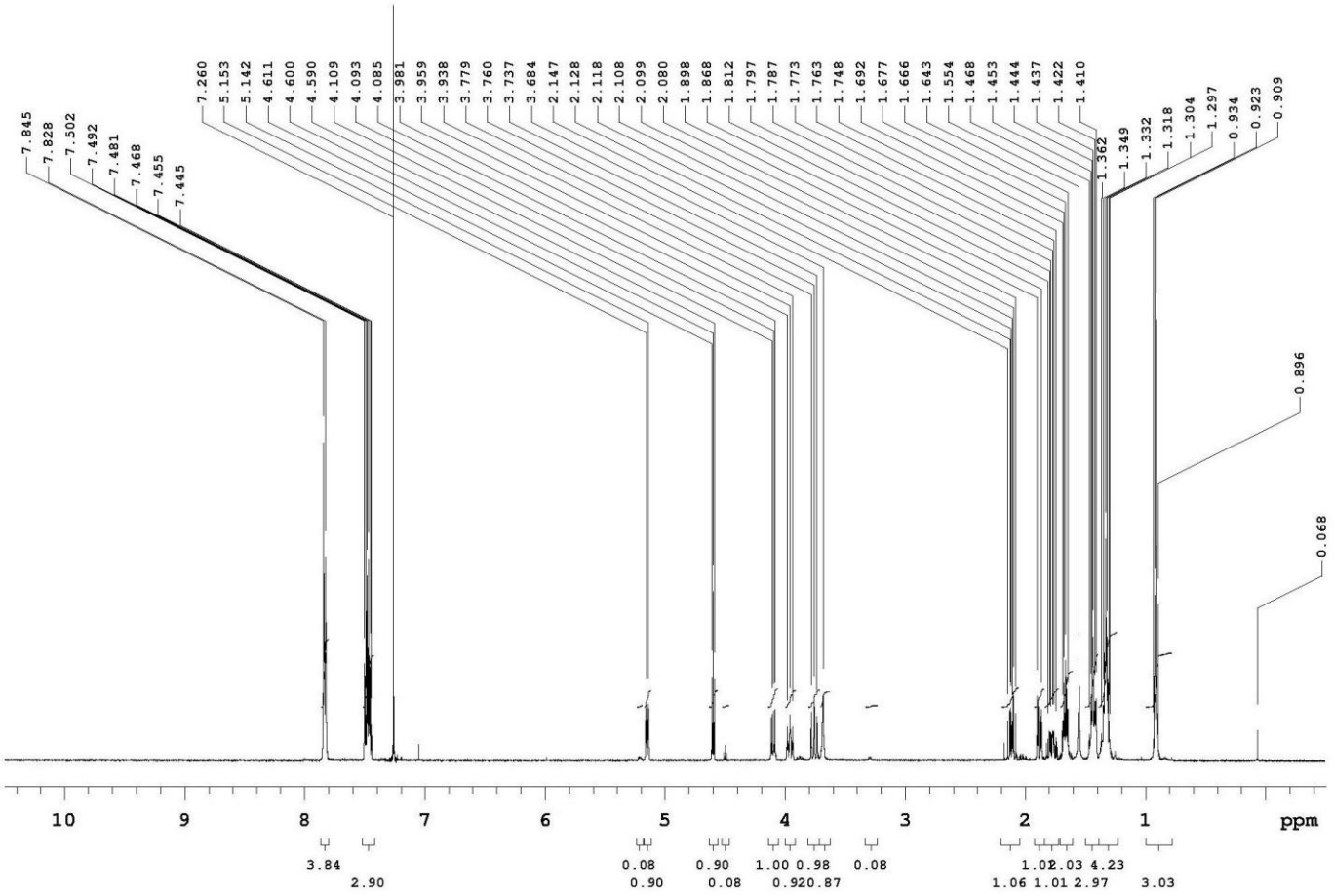
^{13}C NMR



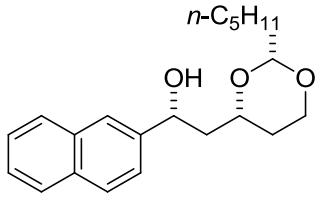
(*R)-1-(Naphthalen-2-yl)-2-((2*R**,4*R**)-2-pentyl-1,3-dioxan-4-yl)ethanol (dihydro-3ef)**



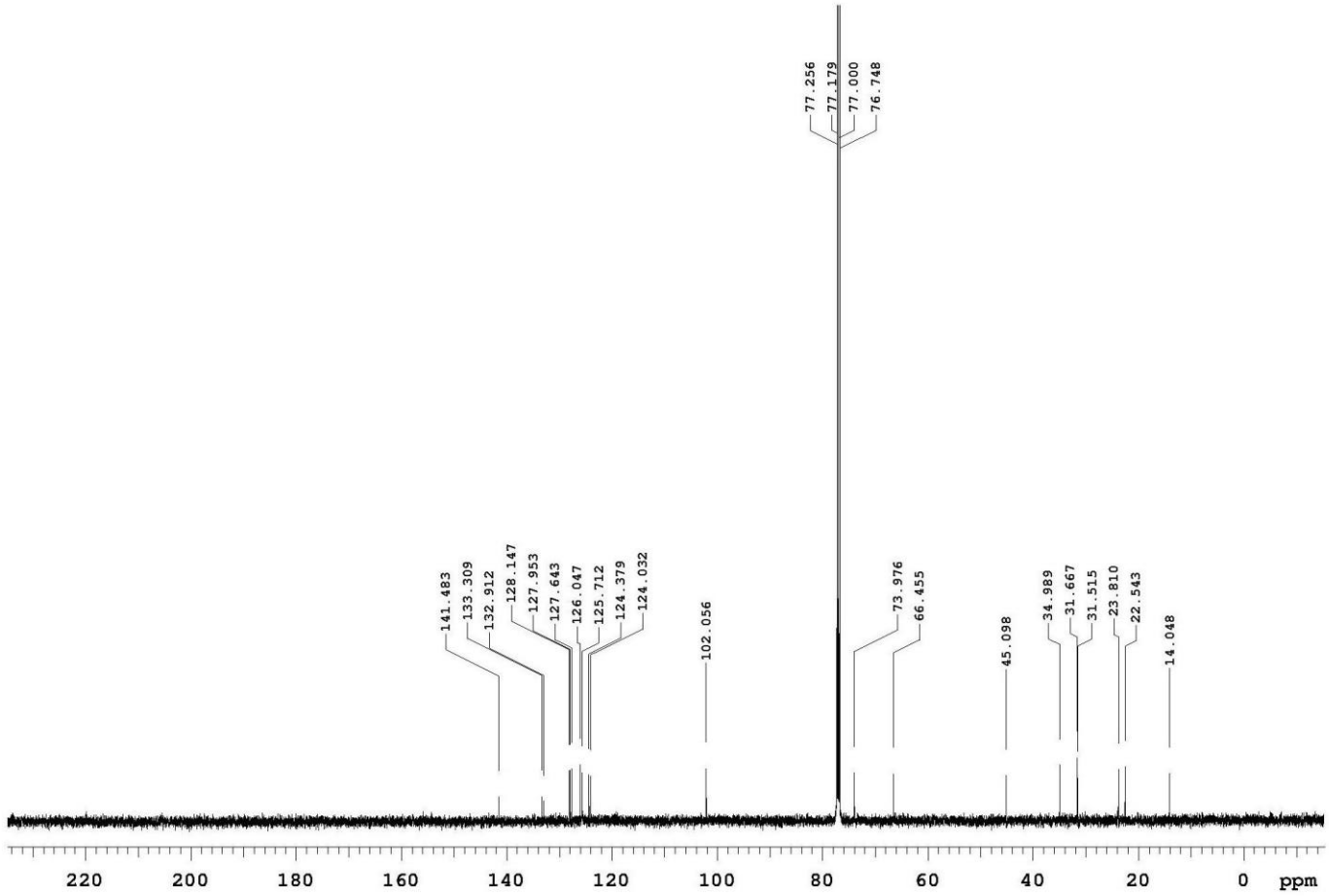
^{1}H NMR



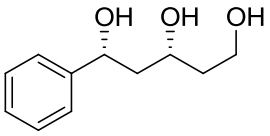
(*R)-1-(Naphthalen-2-yl)-2-((2*R**,4*R**)-2-pentyl-1,3-dioxan-4-yl)ethanol (dihydro-3ef)**



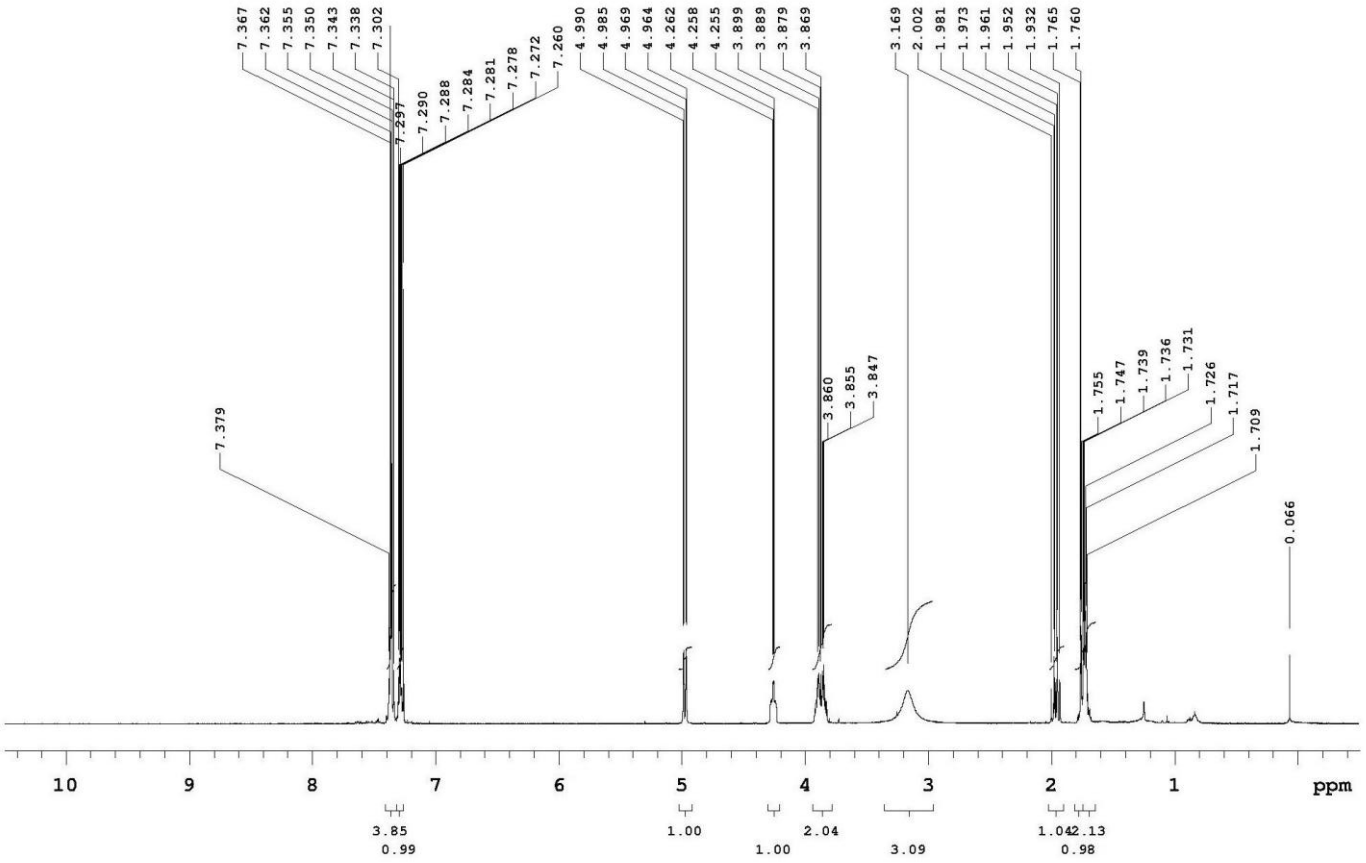
^{13}C NMR



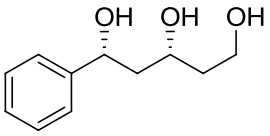
1-Phenylpentane-1,3,5-triol (7)



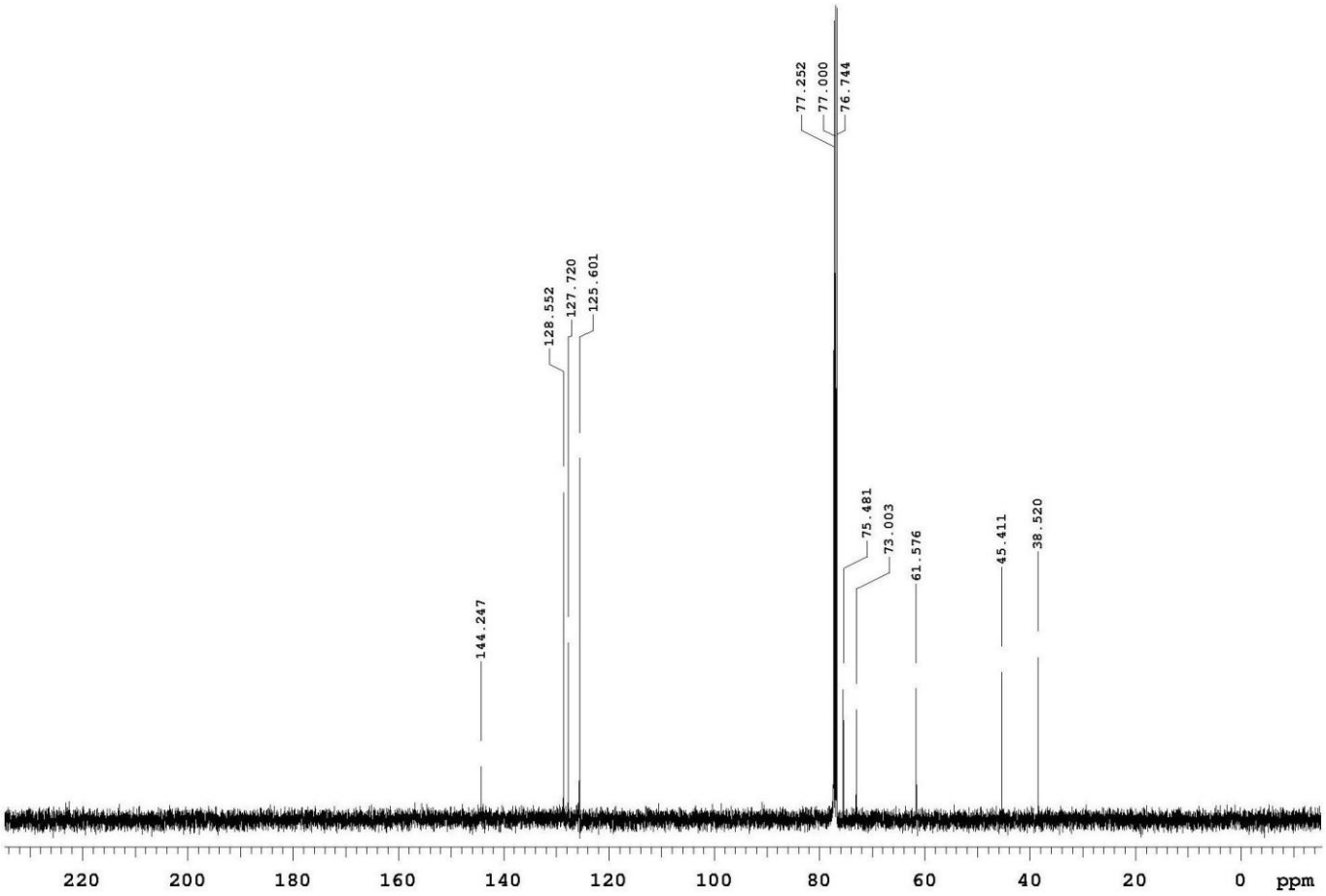
^{1}H NMR



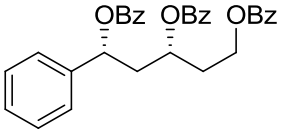
1-Phenylpentane-1,3,5-triol (7)



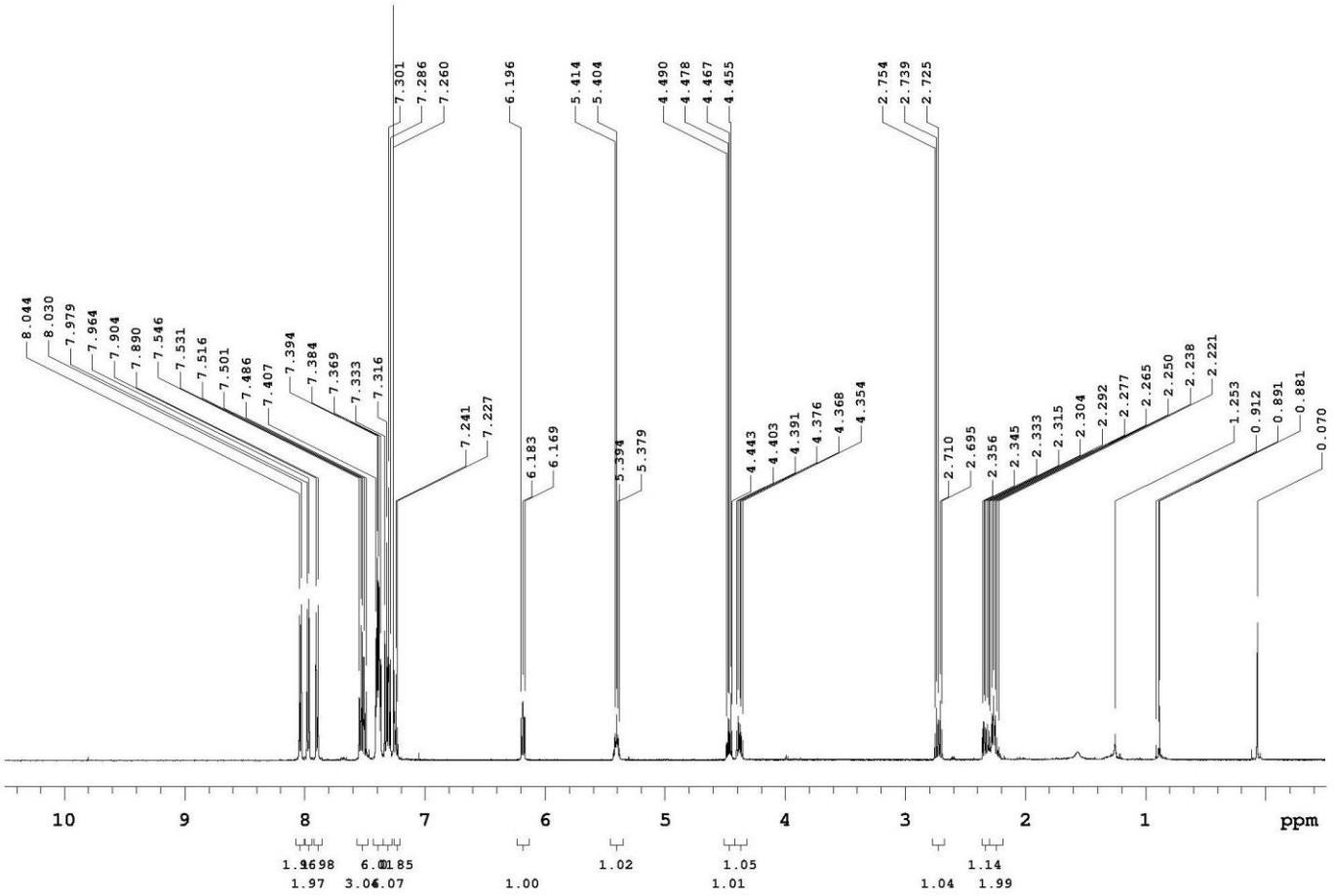
^{13}C NMR



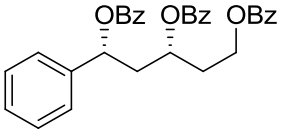
1-Phenylpentane-1,3,5-triyl tribenzoate



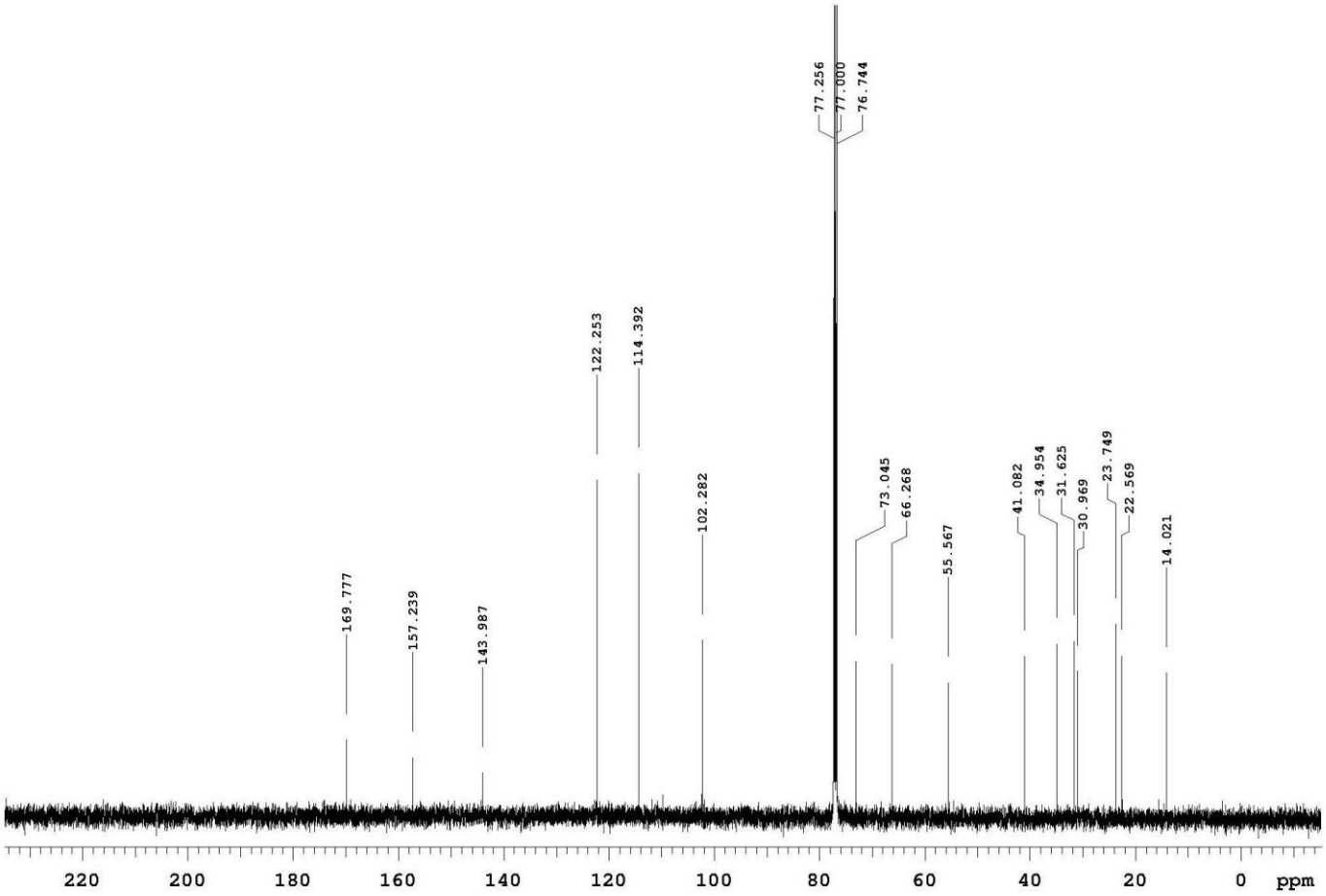
^{1}H NMR



1-Phenylpentane-1,3,5-triyl tribenzoate

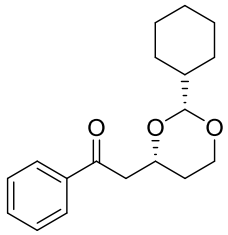


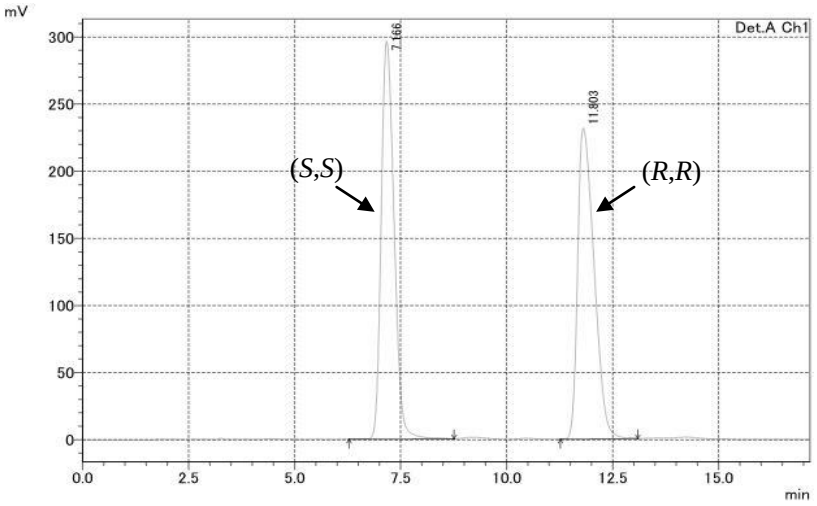
^{13}C NMR



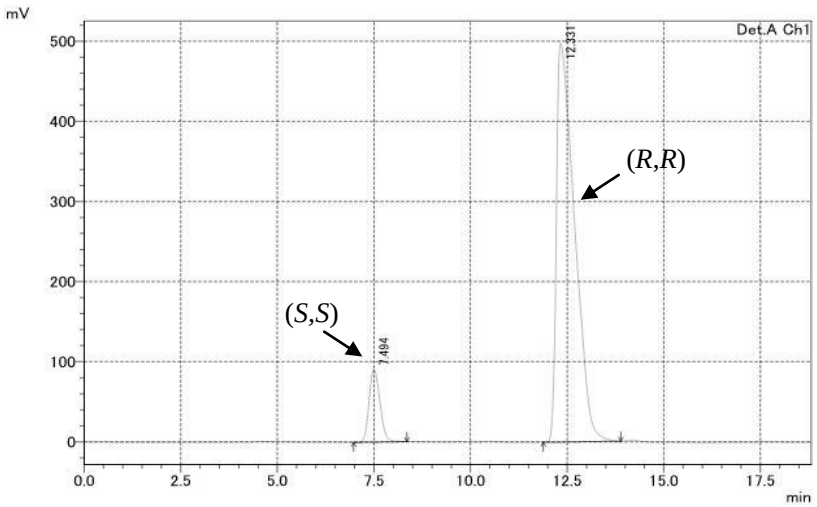
HPLC Chromatogram Plofiles

2-(2-Cyclohexyl-1,3-dioxan-4-yl)-1-phenylethanone (3aa).



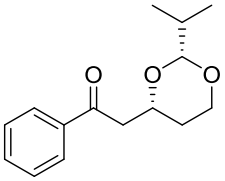


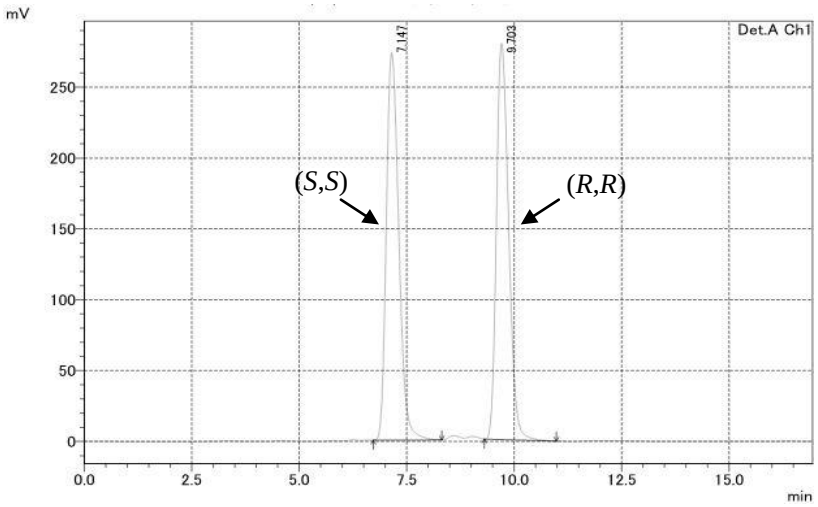
peak	retention time (min)	area %
1	7.166	50.110
2	11.803	49.890



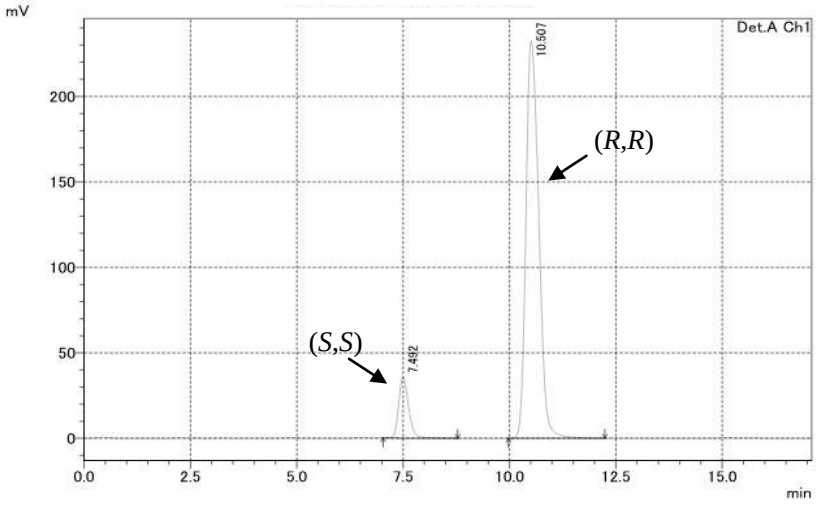
peak	retention time (min)	area %
1	7.494	9.885
2	12.331	90.115

2-(2-Isopropyl-1,3-dioxan-4-yl)-1-phenylethanone (3ab).



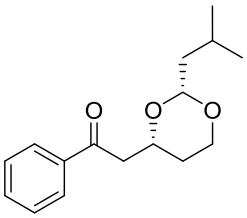


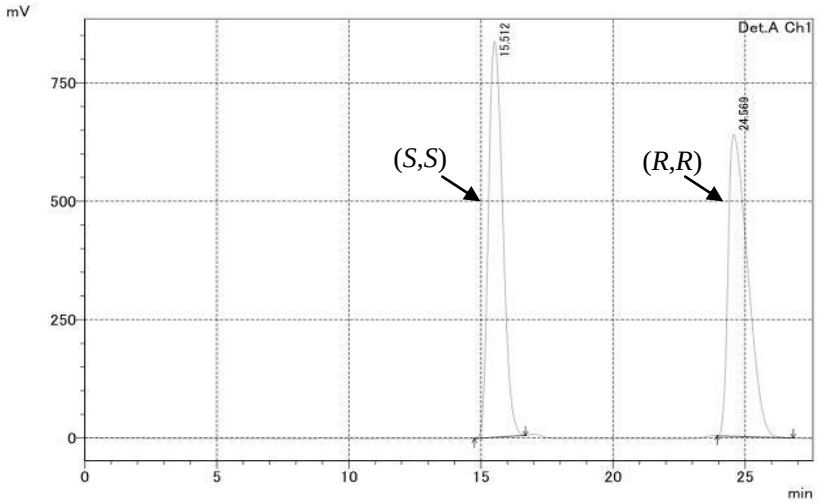
peak	retention time (min)	area %
1	7.147	50.076
2	9.703	49.924



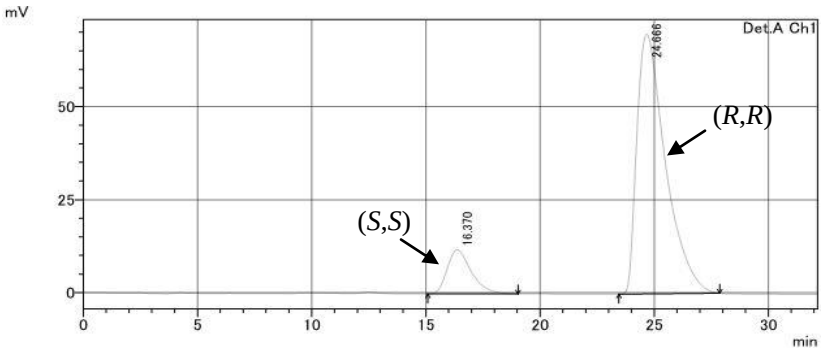
peak	retention time (min)	area %
1	7.492	10.652
2	10.507	89.348

2-(2-Isobutyl-1,3-dioxan-4-yl)-1-phenylethanone (3ac).



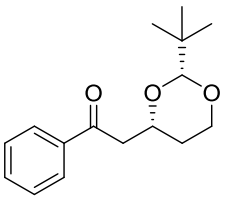


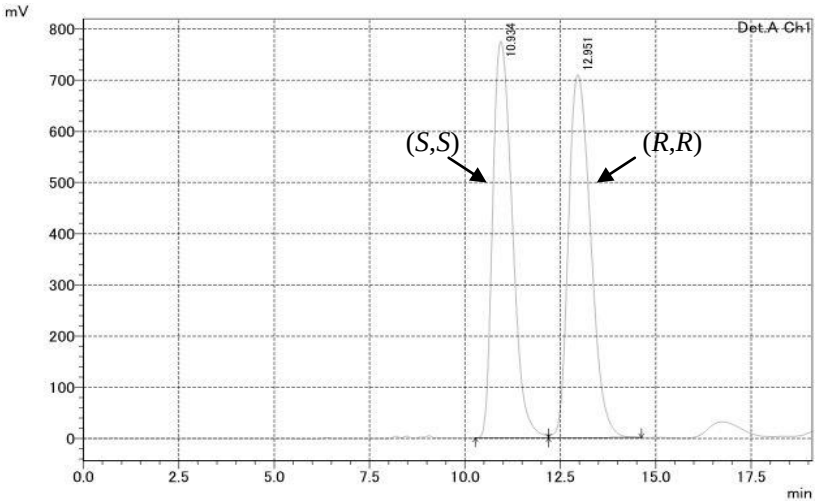
peak	retention time (min)	area %
1	15.512	49.023
2	24.569	50.977



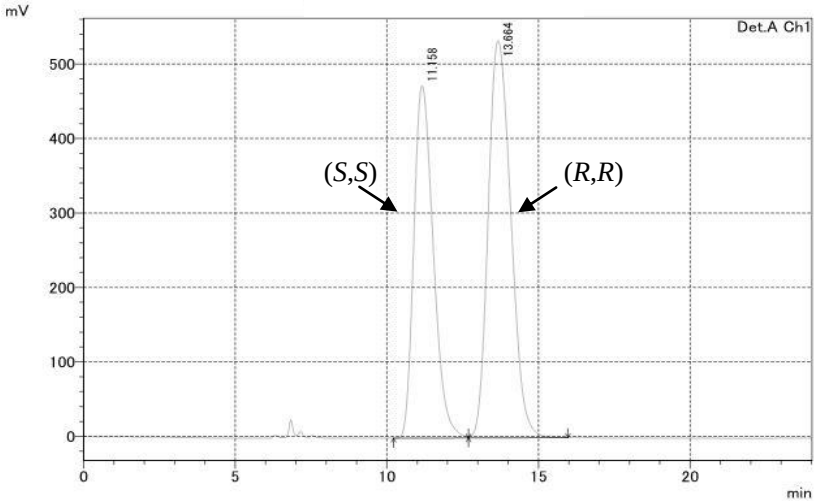
peak	retention time (min)	area %
1	10.474	13.384
2	16.657	86.616

2-(2-*tert*-Butyl-1,3-dioxan-4-yl)-1-phenylethanone (3ad).



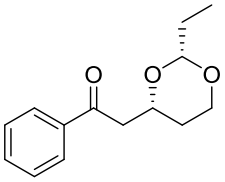


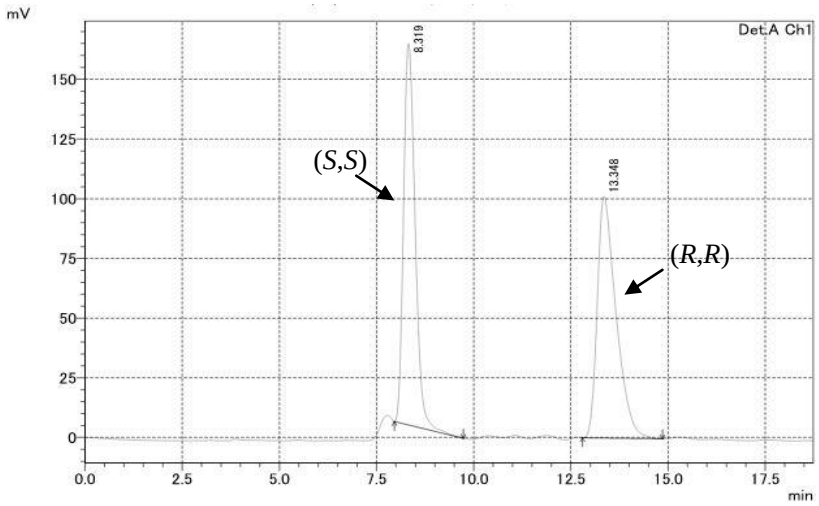
peak	retention time (min)	area %
1	10.934	48.959
2	12.951	51.041



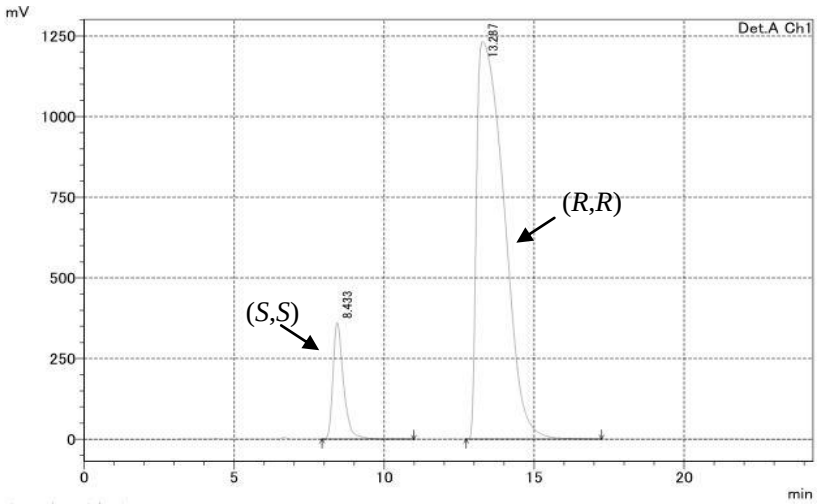
peak	retention time (min)	area %
1	11.158	43.265
2	13.664	56.735

2-(2-Ethyl-1,3-dioxan-4-yl)-1-phenylethanone (3ae).



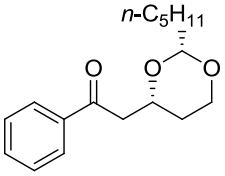


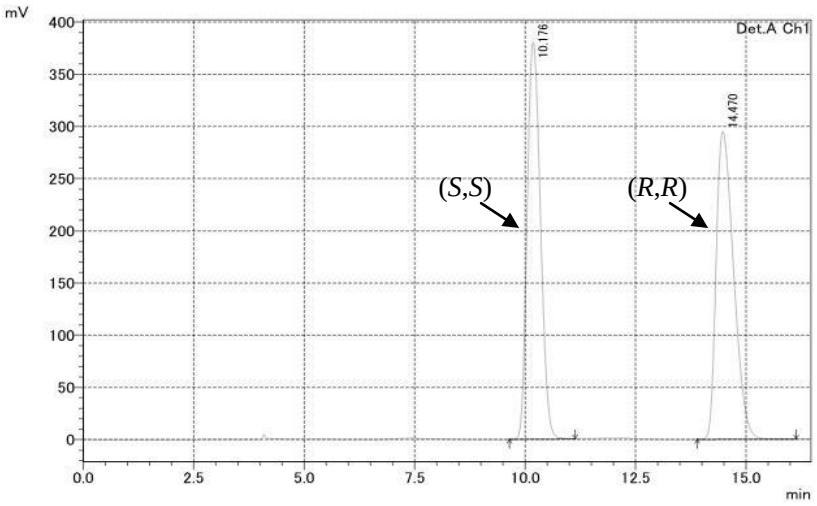
peak	retention time (min)	area %
1	8.319	49.245
2	13.348	50.755



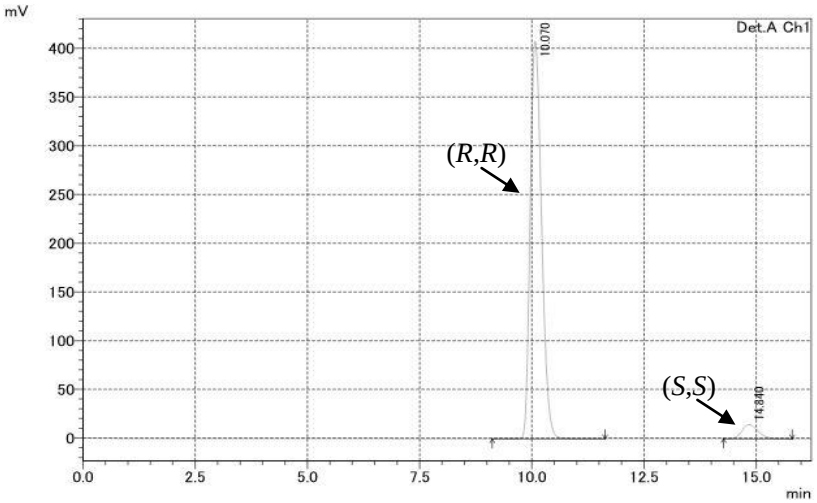
peak	retention time (min)	area %
1	8.433	10.122
2	13.287	89.878

2-(2-Pentyl-1,3-dioxan-4-yl)-1-phenylethanone (3af).



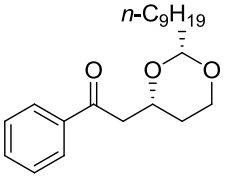


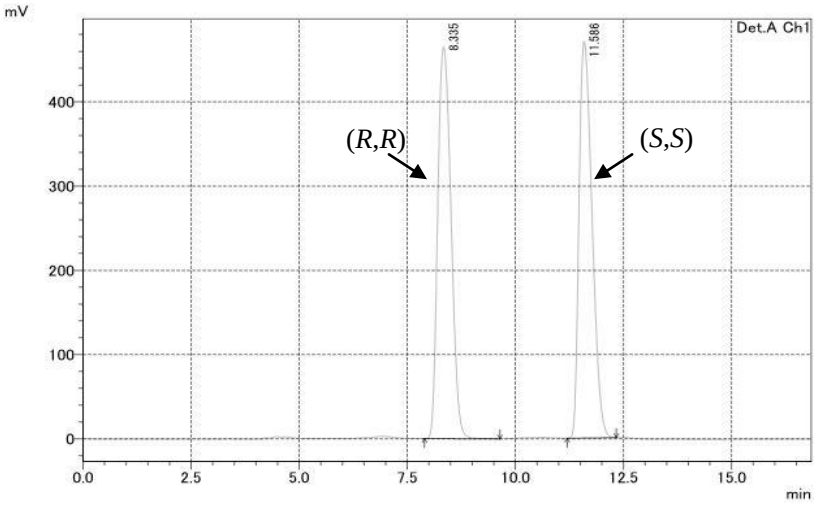
peak	retention time (min)	area %
1	10.176	49.535
2	14.470	50.465



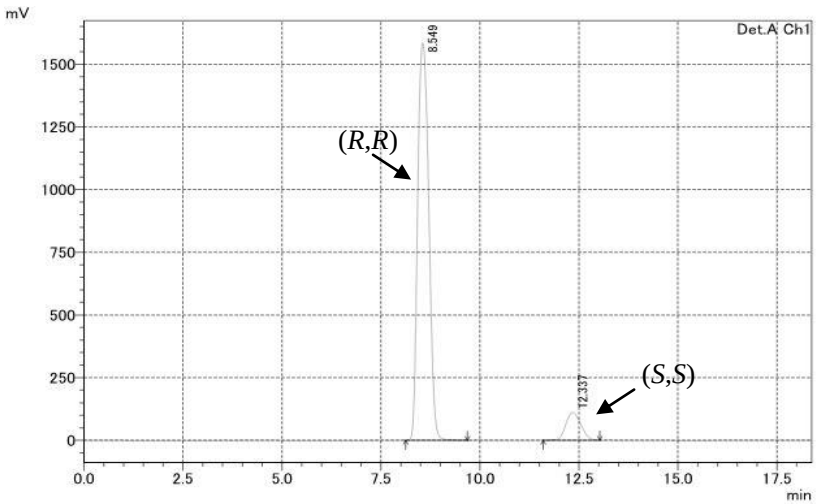
peak	retention time (min)	area %
1	10.070	95.240
2	14.840	4.760

2-(2-Nonyl-1,3-dioxan-4-yl)-1-phenylethanone (3ag).



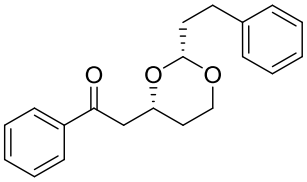


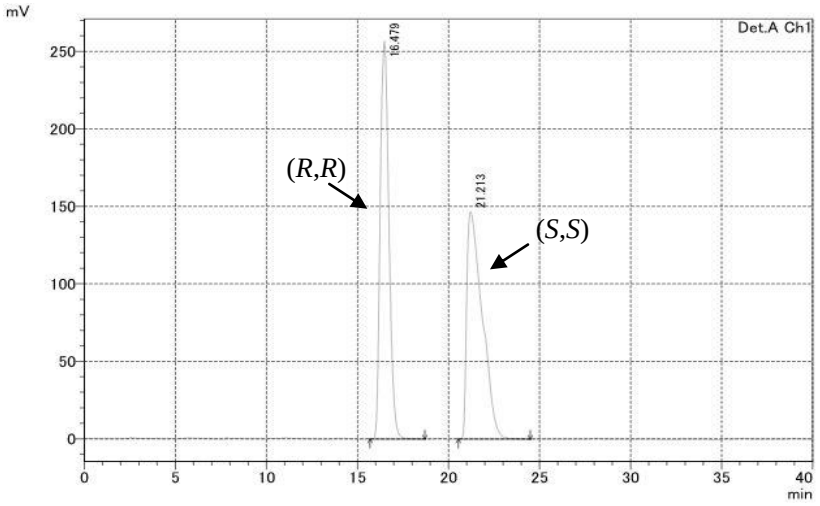
peak	retention time (min)	area %
1	8.335	50.098
2	11.586	49.902



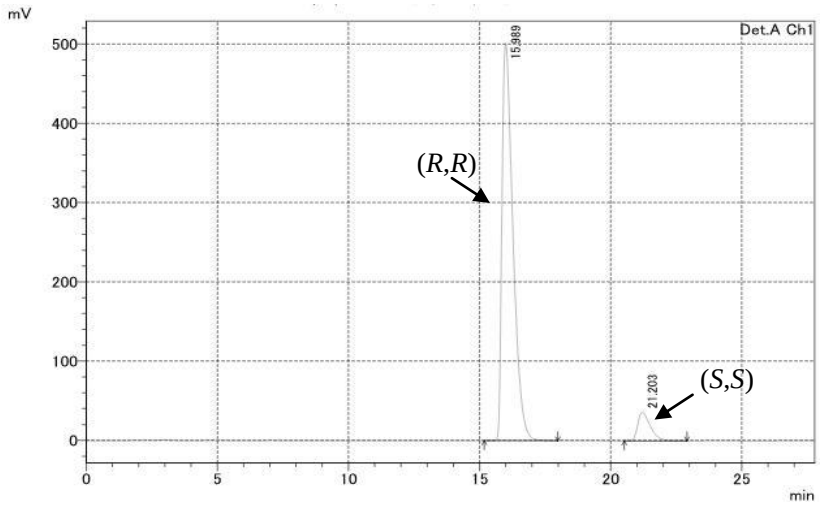
peak	retention time (min)	area %
1	8.549	91.281
2	12.337	8.719

2-(2-Phenethyl-1,3-dioxan-4-yl)-1-phenylethanone (3ah).



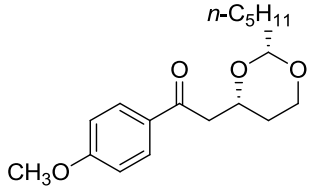


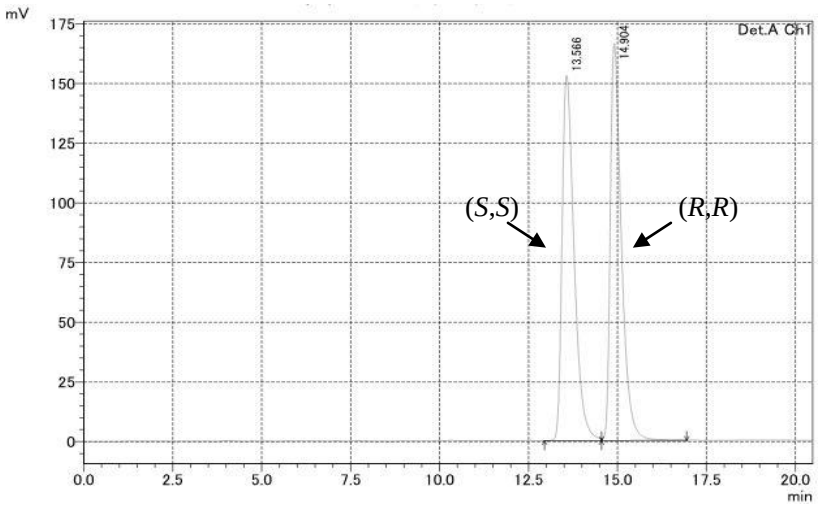
peak	retention time (min)	area %
1	16.479	49.690
2	21.213	50.310



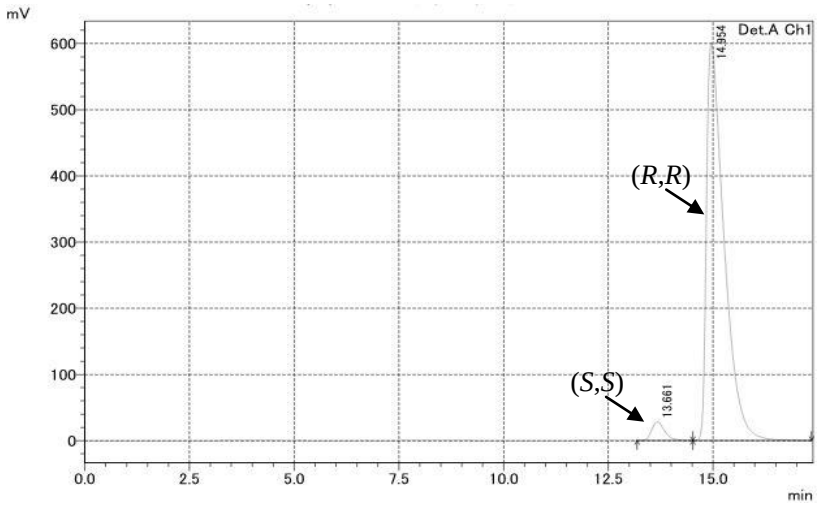
peak	retention time (min)	area %
1	15.989	92.407
2	21.203	7.593

1-(4-Methoxyphenyl)-2-(2-pentyl-1,3-dioxan-4-yl)ethanone (3bf).



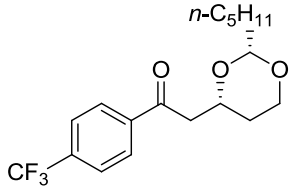


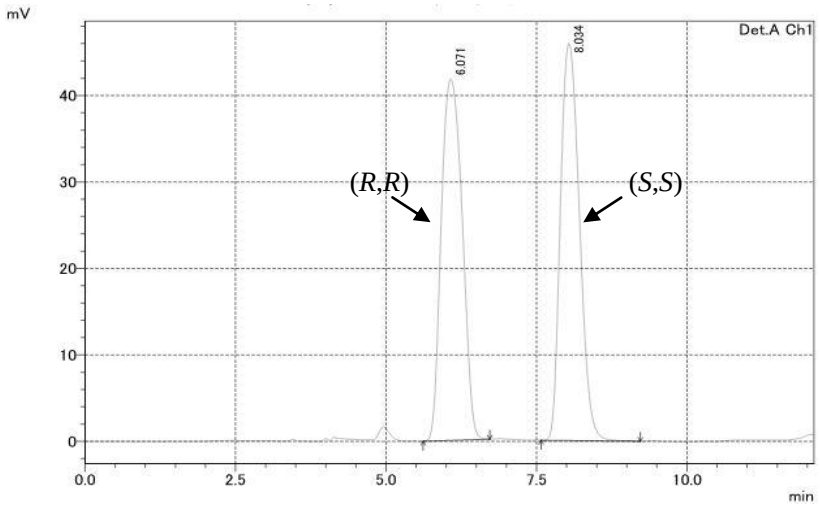
peak	retention time (min)	area %
1	13.566	50.016
2	14.904	49.984



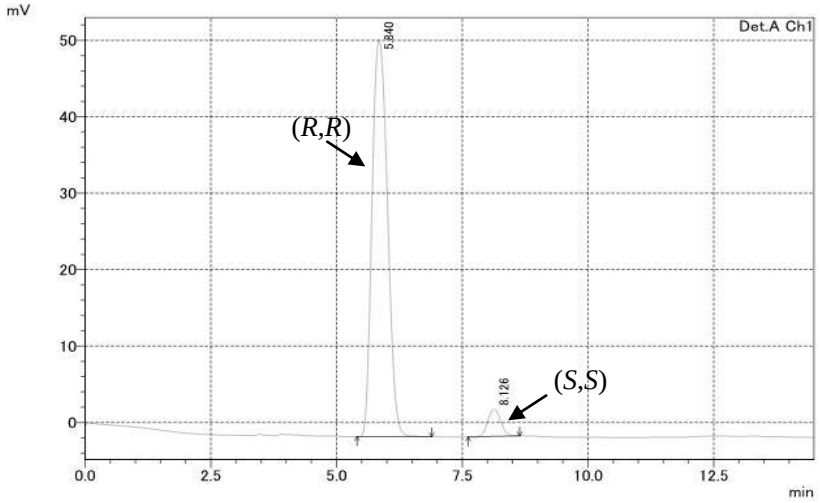
peak	retention time (min)	area %
1	13.661	3.432
2	14.954	96.568

2-(2-Pentyl-1,3-dioxan-4-yl)-1-(4-(trifluoromethyl)phenyl)ethanone (3cf).



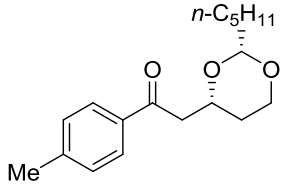


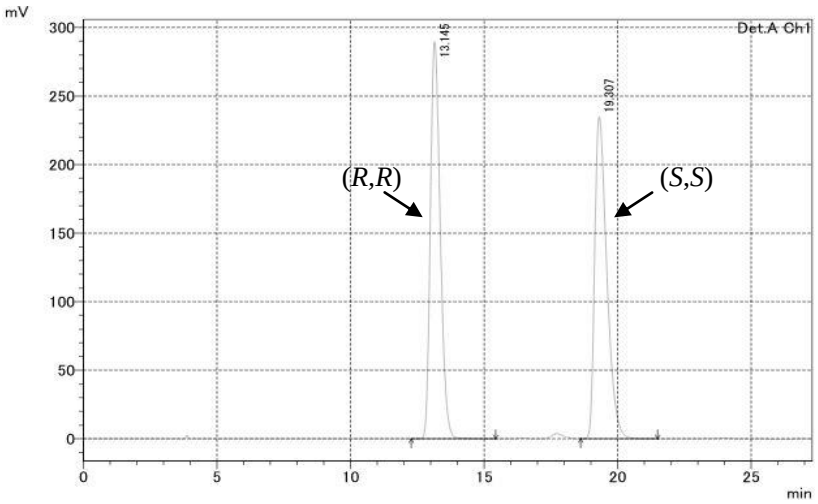
peak	retention time (min)	area %
1	6.071	50.099
2	8.034	49.901



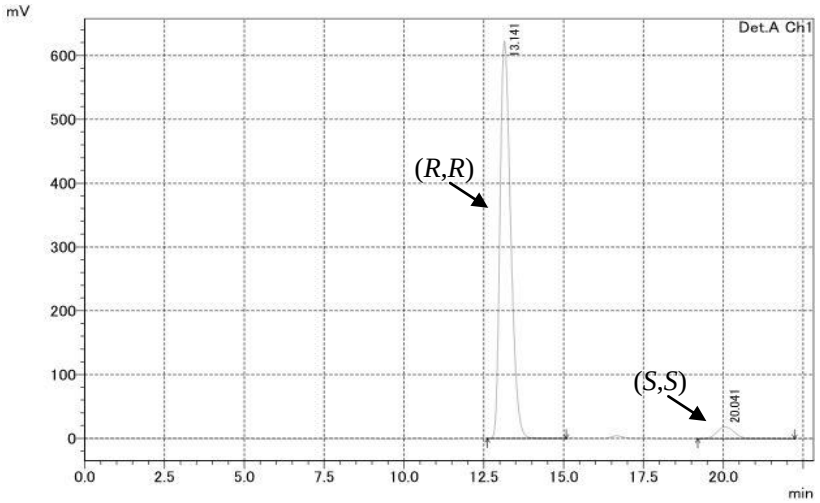
peak	retention time (min)	area %
1	5.840	94.648
2	8.126	5.352

2-(2-Pentyl-1,3-dioxan-4-yl)-1-(*p*-tolyl)ethanone (3df).



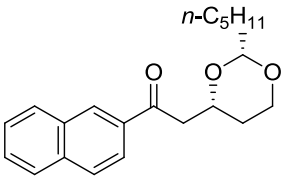


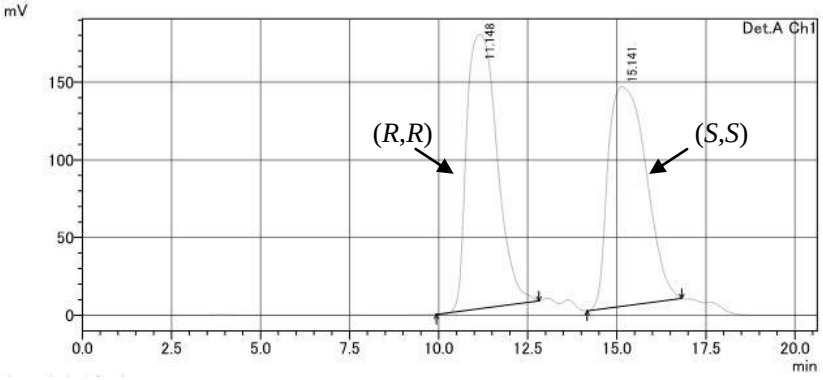
peak	retention time (min)	area %
1	13.145	50.138
2	19.307	49.862



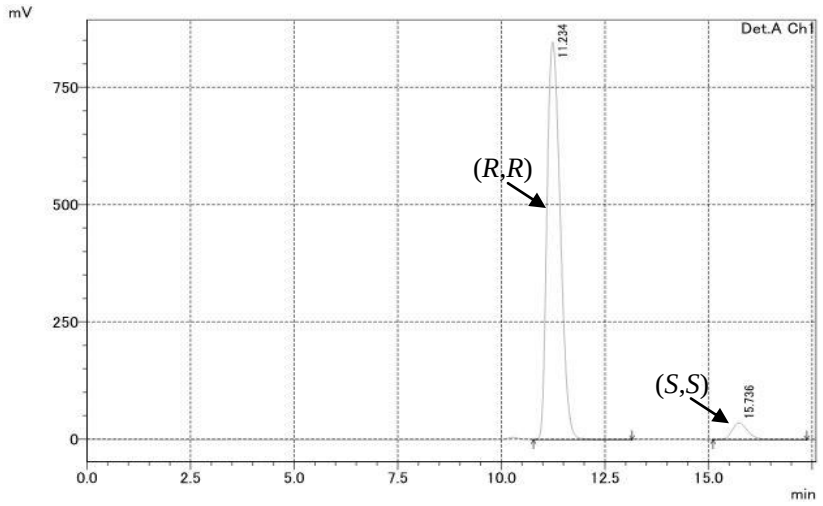
peak	retention time (min)	area %
1	13.141	95.374
2	20.041	4.626

1-(Naphthalen-2-yl)-2-((2*R*,4*R*)-2-pentyl-1,3-dioxan-4-yl)ethanone (3ef).



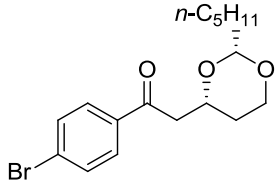


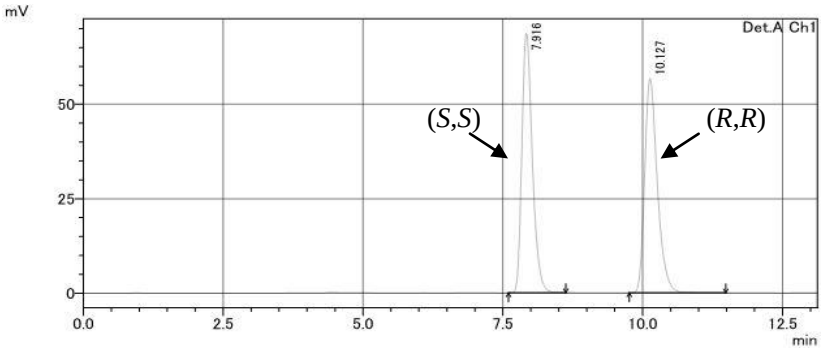
peak	retention time (min)	area %
1	11.148	50.000
2	15.141	50.000



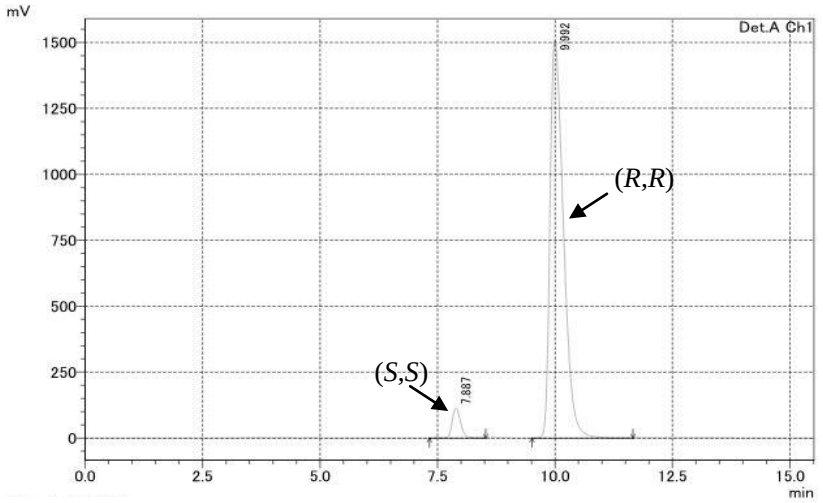
peak	retention time (min)	area %
1	11.234	95.155
2	15.736	4.845

1-(4-Bromophenyl)-2-(2-pentyl-1,3-dioxan-4-yl)ethanone (3ff).



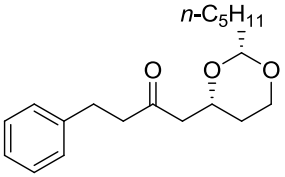


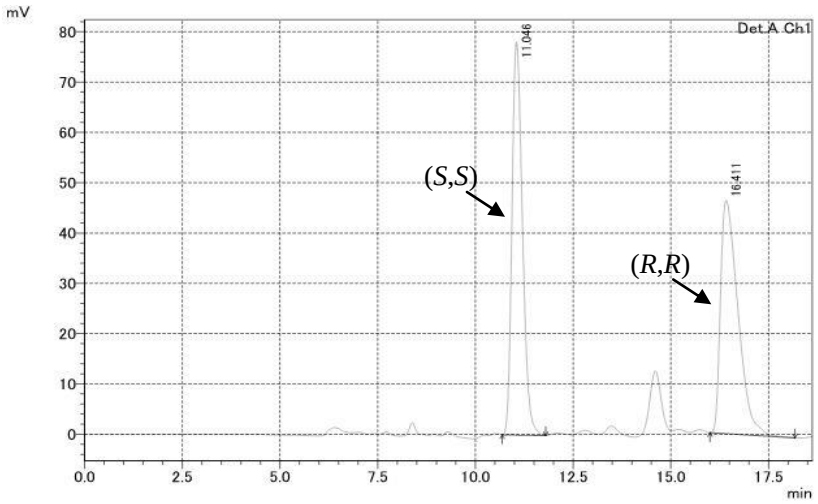
peak	retention time (min)	area %
1	7.916	49.929
2	10.127	50.071



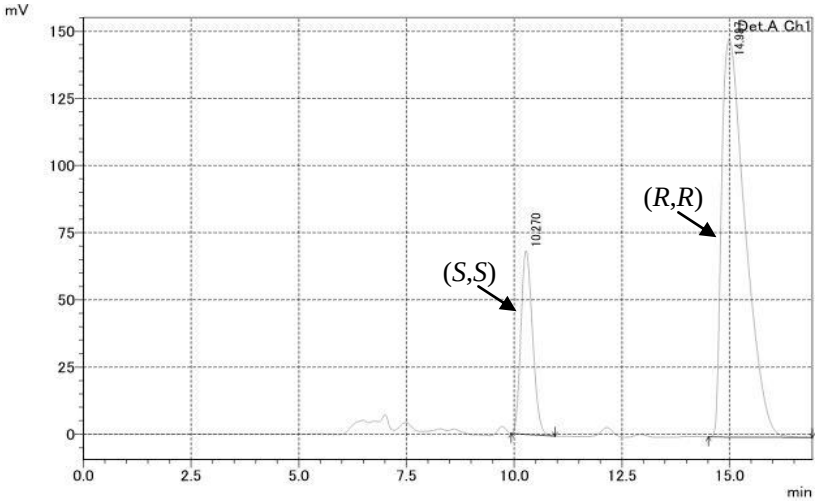
peak	retention time (min)	area %
1	7.887	4.476
2	9.992	95.524

1-(2-Pentyl-1,3-dioxan-4-yl)-4-phenylbutan-2-one (3gf).



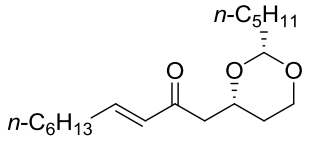


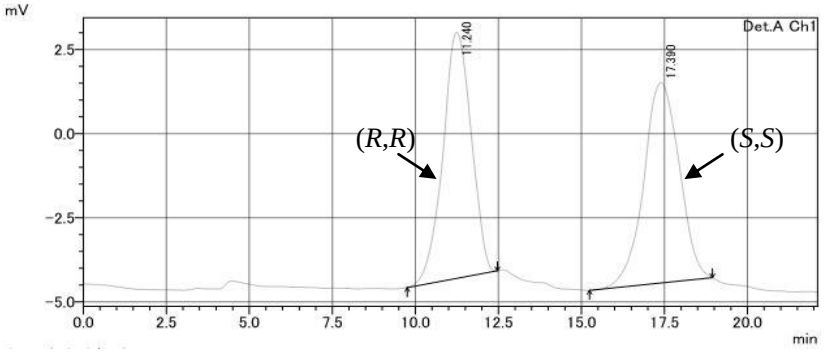
peak	retention time (min)	area %
1	11.046	50.352
2	16.411	49.648



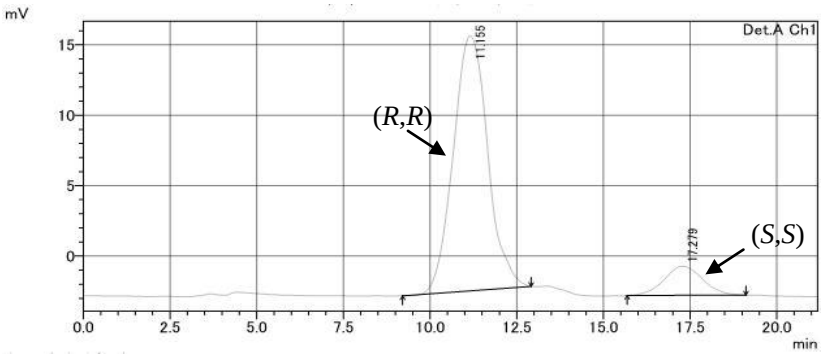
peak	retention time (min)	area %
1	10.270	18.623
2	14.987	81.377

(*E*)-1-(2-Pentyl-1,3-dioxan-4-yl)dec-3-en-2-one (3hf).



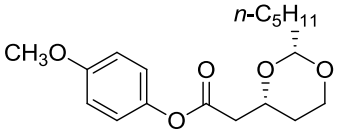


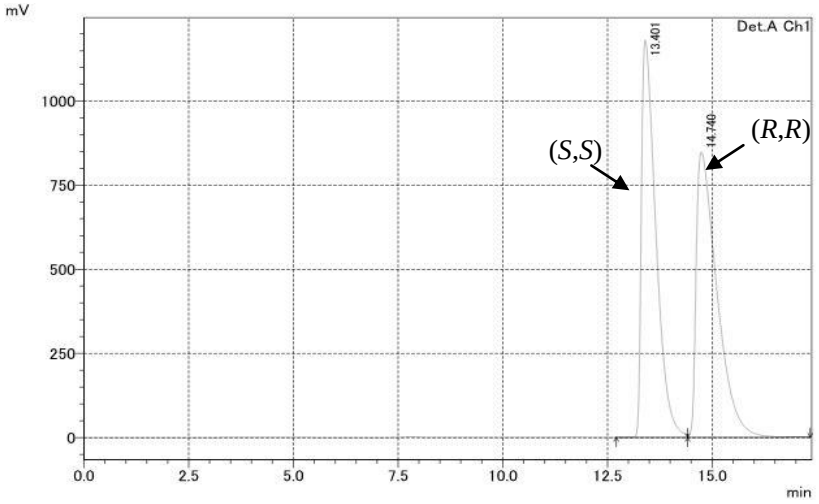
peak	retention time (min)	area %
1	11.240	49.713
2	17.390	50.287



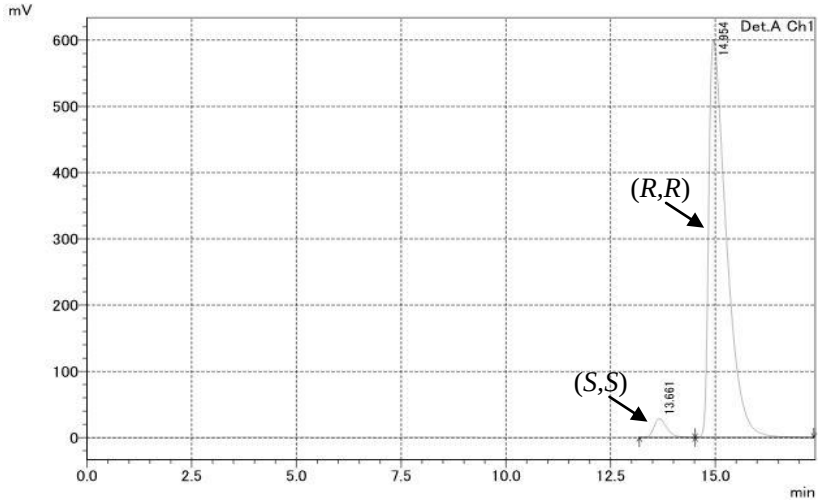
peak	retention time (min)	area %
1	11.155	88.788
2	17.279	11.212

4-Methoxyphenyl 2-(2-pentyl-1,3-dioxan-4-yl)acetate (5).



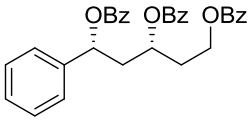


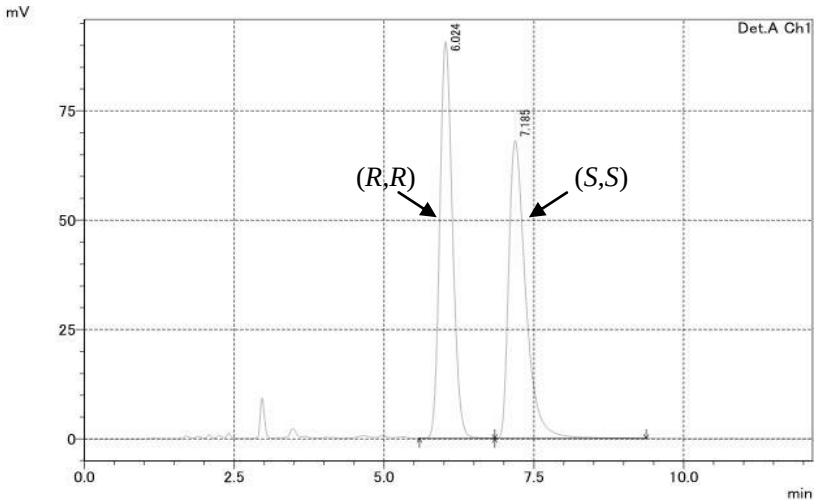
peak	retention time (min)	area %
1	13.401	49.353
2	14.740	50.647



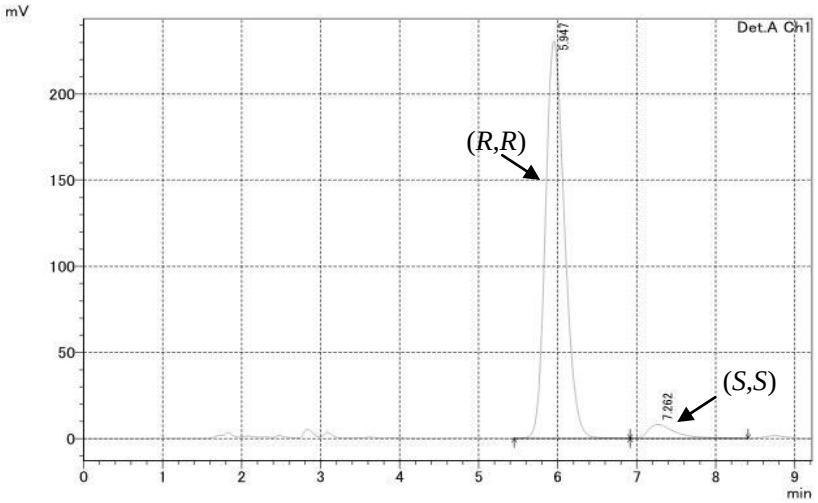
peak	retention time (min)	area %
1	13.661	3.432
2	14.954	96.568

1-Phenylpentane-1,3,5-triyl tribenzoate.



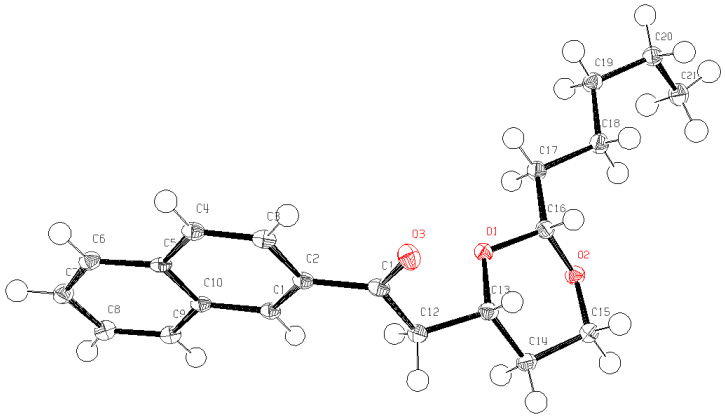


peak	retention time (min)	area %
1	6.024	50.045
2	7.185	49.955



peak	retention time (min)	area %
1	5.947	95.329
2	7.262	4.671

ORTEP Drawing of 3ef



A. Crystal Data

Empirical Formula	$C_{21}H_{26}O_3$
Formula Weight	326.43
Crystal Color, Habit	Colorless, Needle
Crystal Dimensions	0.244 × 0.070 × 0.060 mm
Crystal System	Orthorhombic
Lattice Type	Primitive
Lattice Parameters	a = 5.7682(2) Å
	b = 7.7444(3) Å
	c = 39.9505(14) Å
	V = 1784.64(11) Å^3
Space Group	$P2_12_12_1$ (#19)
Z value	4
D_{calc}	1.215 g/cm^3
F_{000}	704.00
μ(CuKα)	6.326 cm^{-1}

B. Intensity Measurements

Diffractometer	R-AXIS RAPID
Radiation	CuKα (λ = 1.54187 Å)
	Multi-layer mirror monochromated
Voltage, Current	40kV, 30mA

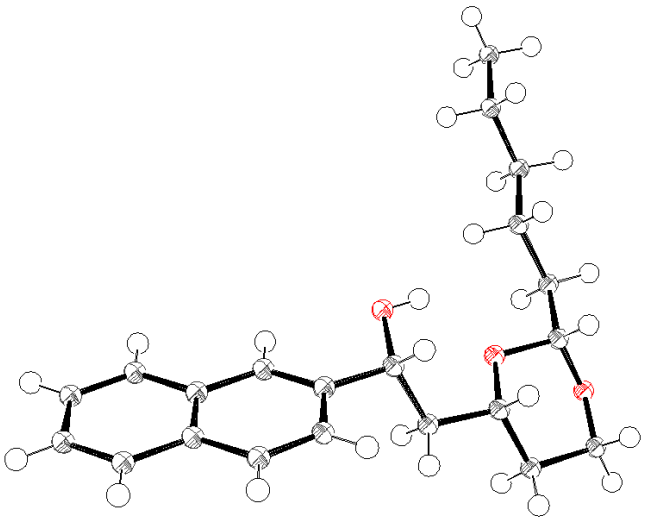
Temperature	–180.0 °C
Detector Aperture	460.0 × 256.0 mm
Data Images	180 exposures
ω Oscillation Range (χ = 54.0, φ = 0.0)	80.0–260.0°
Exposure Rate	20.0 sec./°
ω Oscillation Range (χ = 54.0, φ = 90.0)	80.0–260.0°
Exposure Rate	20.0 sec./°
ω Oscillation Range (χ = 54.0, φ = 180.0)	80.0–260.0°
Exposure Rate	20.0 sec./°
ω Oscillation Range (χ = 54.0, φ = 270.0)	80.0–260.0°
Exposure Rate	20.0 sec./°
ω Oscillation Range (χ = 0.0, φ = 0.0)	80.0–260.0°
Exposure Rate	20.0 sec./°
Detector Position	127.40 mm
Pixel Size	0.100 mm
$2\theta_{max}$	136.4°
No. of Reflections Measured	Total: 20325 Unique: 3254 (R_{int} = 0.0784) Parsons quotients (Flack x parameter): 1047
Corrections	Lorentz-polarization Absorption (trans. factors: 0.687–0.963)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELXS2013)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma\ w\ (F_0^2 - F_c^2)^2$
Least Squares Weights	$w = 1/ [\ \sigma^2(F_0^2) + (0.1161 \cdot P)^2 + 0.2777 \cdot P\ ]$ where $P = (Max(F_0^2,0) + 2F_c^2)/3$
$2\theta_{max}$ cutoff	136.4°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	3254

No. Variables	217
Reflection/Parameter Ratio	15.00
Residuals: R1 (I>2.00σ(I))	0.0683
Residuals: R (All reflections)	0.0732
Residuals: wR2 (All reflections)	0.1857
Goodness of Fit Indicator	1.110
Flack parameter (Parsons' quotients = 1047)	0.0(2)
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.33 $e^{-}/Å^{3}$
Minimum peak in Final Diff. Map	–0.36 $e^{-}/Å^{3}$

ORTEP Drawing of dihydro-3ef



A. Crystal Data

Empirical Formula	$C_{21}H_{28}O_3$
Formula Weight	328.45
Crystal Color, Habit	Colorless, Prism
Crystal Dimensions	0.410 × 0.380 × 0.200 mm
Crystal System	Monoclinic
Lattice Type	Primitive
Lattice Parameters	a = 28.83(4) Å
	b = 7.923(11) Å
	c = 7.876(11) Å
	ß = 89.14(2)°
	V = 1799(5) $Å^3$
Space Group	$P2_1/c$ (#14)
Z value	4
D_{calc}	1.213 g/cm^3
F_{000}	712.00
μ(MoKα)	0.791 cm^{-1}

B. Intensity Measurements

Diffractometer	XtaLAB mini
Radiation	MoKα (λ = 0.71075 Å) graphite monochromated
Voltage, Current	50kV, 12mA
Temperature	20.0 °C
Detector Aperture	75 mm (diameter)
Data Images	1080 exposures
ω Oscillation Range	–60.0–120.0°
Exposure Rate	96.0 sec./°
Detector Swing Angle	30.50°
ω Oscillation Range	–60.0–120.0°
Exposure Rate	96.0 sec./°
Detector Swing Angle	30.50°
ω Oscillation Range	–60.0–120.0°
Exposure Rate	96.0 sec./°
Detector Swing Angle	30.50°
Detector Position	49.00 mm
Pixel Size	0.146 mm
$2\theta_{max}$	55.6°
No. of Reflections Measured	Total: 11513 Unique: 3684 (R_{int} = 0.0874)
Corrections	Lorentz-polarization Absorption (trans. factors: 0.967–0.984)

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SHELX97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	$\Sigma\, w\, (F_0^2 - F_c^2)^2$
Least Squares Weights	$w = 1/ [\, \sigma^2(F_0^2) + (0.1000 \cdot P)^2 + 0.0000 \cdot P\,]$ where $P = (\mathrm{Max}(F_0^2,0) + 2F_c^2)/3$

$2\theta_{max}$ cutoff	55.6°
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (All reflections)	3684
No. Variables	217
Reflection/Parameter Ratio	16.98
Residuals: R1 (I>2.00σ(I))	0.1052
Residuals: R (All reflections)	0.1523
Residuals: wR2 (All reflections)	0.2984
Goodness of Fit Indicator	1.270
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.33 $e^{-}/Å^{3}$
Minimum peak in Final Diff. Map	–0.35 $e^{-}/Å^{3}$