Supplementary Material

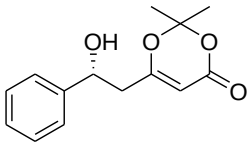
Highly enantioselective vinylogous aldol reaction of dioxinone-derived silyl diene by combined Lewis acid catalyst

Shuai Qi,[*a] Qianping Ran,[b] Chang Liu,[a] Bo Li,[a] and Xiao Zhang[a]

[a]*State Key Laboratory of High Performance Civil Engineering Materials (HPCEM), Jiangsu Sobute New Materials Co. Ltd., Nanjing 211103, Jiangsu, China*
[b]*Jiangsu Key Laboratory of Construction Materials, College of Materials Science and Engineering, Southeast University, Nanjing 211189, Jiangsu, China*
Email: gishuai@cnjsjk.cn

Table of Contents

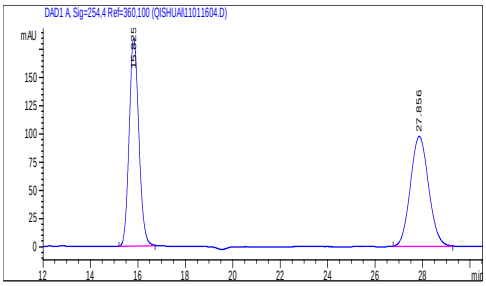
1. The analytic data for the corresponding compounds

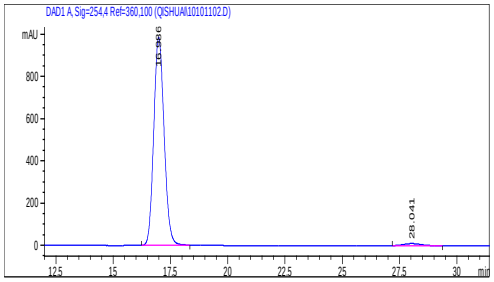


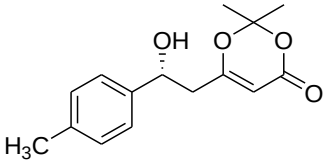
3a

(5*R*)-6-(2-hydroxy-2-phenylethyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3a)

This product was obtained as a white,crystalline solid in 91% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{19.5}$= +36.2 (*c* = 0.744, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.4-7.3 (m, 5 H), 5.29 (s, 1 H), 4.98 (m, 1 H), 2.66 (dd,*J* = 14.6, 8.2, 1 H), 2.61 (dd, *J* = 14.6, 4.8, 1 H), 2.05 (d, *J* = 3.2, 1 H), 1.65 (s, 3 H), 1.56 (s, 3 H,); Enantiomeric excess was determined to be 95% (determined by HPLC using chiralcel OD-H column, 20% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 15.8 min. (major), 27.8 min. (minor).)



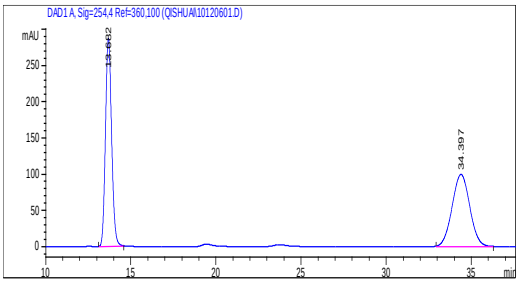


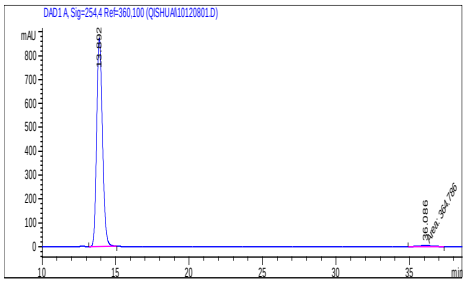


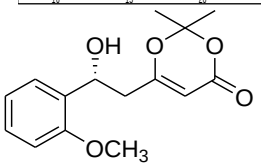
3b

(5*R*)-6-(2-hydroxy-2-(4-methylphenyl)ethyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3b)

This product was obtained as a white,crystalline solid in 92% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{19.5}$= +36.4 (*c* = 0.384, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.3-7.1 (m, 4 H), 5.29 (s, 1 H), 4.95 (m, 1 H), 2.69 (dd, *J* = 20, 8, 1 H), 2.59 (dd, *J* = 20, 4, 1 H), 2.35 (s, 3H), 2.08 (d, 1 H), 1.67 (s, 3 H), 1.61 (s, 3 H); Enantiomeric excess was determined to be 98% (determined by HPLC using chiralcel OD-H column, 20% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 13.6 min. (major), 34.4 min. (minor).)



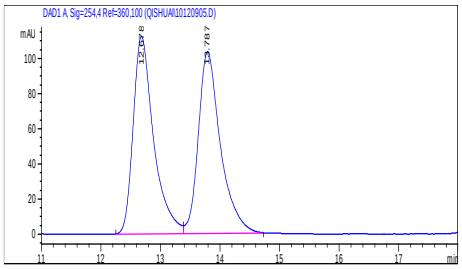


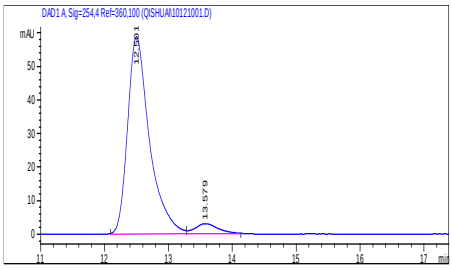


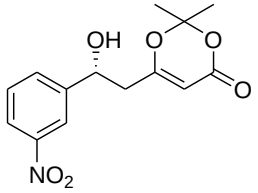
3c

(5*R*)-6-(2-hydroxy-2-(2-methoxyphenyl)ethyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3c)

This product was obtained as a white,crystalline solid in 90% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{19.5}$= +28.4 (*c* = 0.808, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.3-6.8 (m, 4 H), 5.30 (s, 1 H), 5.14 (m, 1 H), 3.88 (s, 3H), 2.75 (dd, 1 H), 2.72 (dd, 1 H), 2.72 (d, 1 H), 1.68 (s, 3 H), 1.67 (s, 3 H); Enantiomeric excess was determined to be 90% (determined by HPLC using chiralcel AD-H column, 20% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.4 mL/min, 12.7 min. (major), 13.8 min. (minor).)



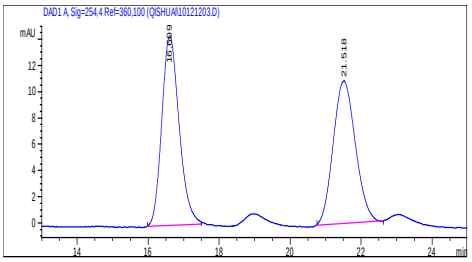


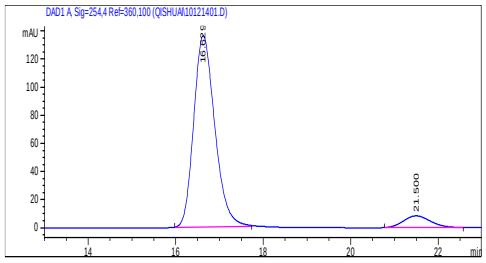


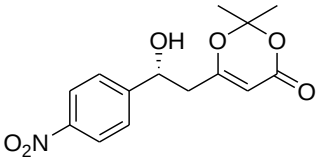
3d

(5*R*)-6-(2-hydroxy-2-(3-nitrophenyl)ethyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3d)

This product was obtained as a white,crystalline solid in 90% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{14.7}$= +32.43 (*c* = 1.033, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.3-7.5 (m, 4 H), 5.35 (s, 1 H), 5.14 (m, 1 H), 3.18 (d, 1 H), 2.66 (m, 2 H), 1.69 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8 161.3 148.4 145.2 131.8 129.7 122.9 120.7 106.9 95.6 69.9 43.3 25.3 24.7; ESI-HRMS: $(M+CH_3COO)^-$, calcd. for $C_{16}H_{18}NO_8$: 352.1032, found: 352.0851; Enantiomeric excess was determined to be 85% (determined by HPLC using chiralcel OD-H column, 20% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 16.6 min. (major), 21.5 min. (minor).)



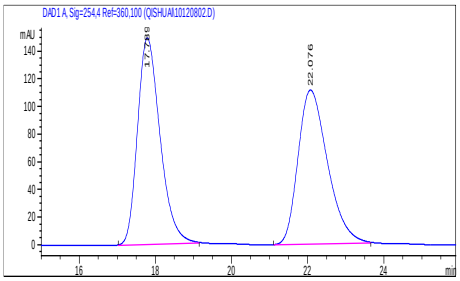


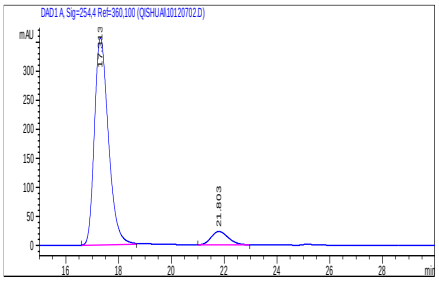


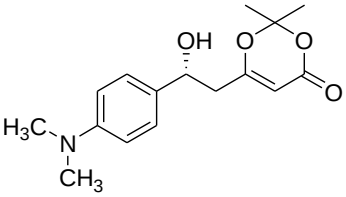
3e

(5*R*)-6-(2-hydroxy-2-(4-nitrophenyl)ethyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3e)

This product was obtained as a white,crystalline solid in 92% yield after column chromatography (acetone/petroleum ether = 1/2). $[\alpha]_D^{19.5}$= +40.1 (*c* = 0.305, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.3-7.5 (m, 4 H), 5.35 (s, 1 H), 5.14 (m, 1 H), 2.71(d, 1 H) 2.65 (m, 2 H), 1.70 (s, 3 H), 1.63 (s, 3 H); Enantiomeric excess was determined to be 85% (determined by HPLC using chiralcel OD-H column, 20% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 17.7 min. (major), 22 min. (minor).)



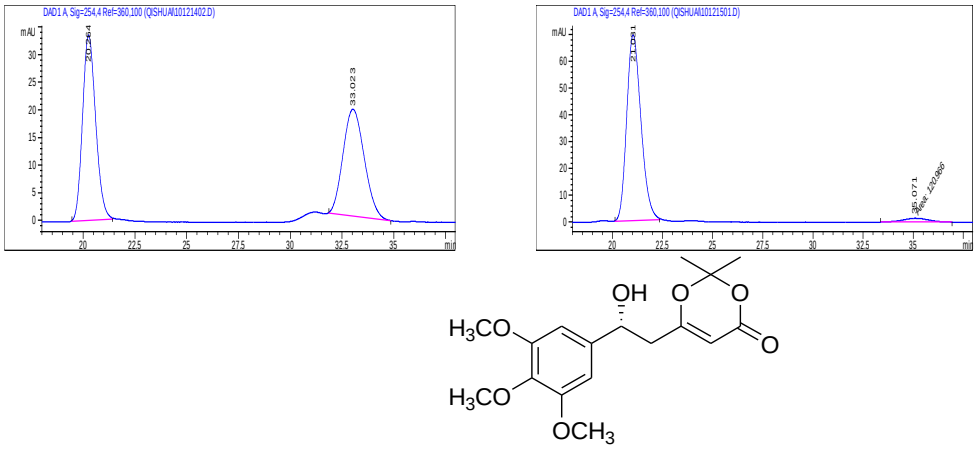




3f

(5*R*)-6-(2-hydroxy-2-(4-N,N-dimethylaminophenyl)ethyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3f)

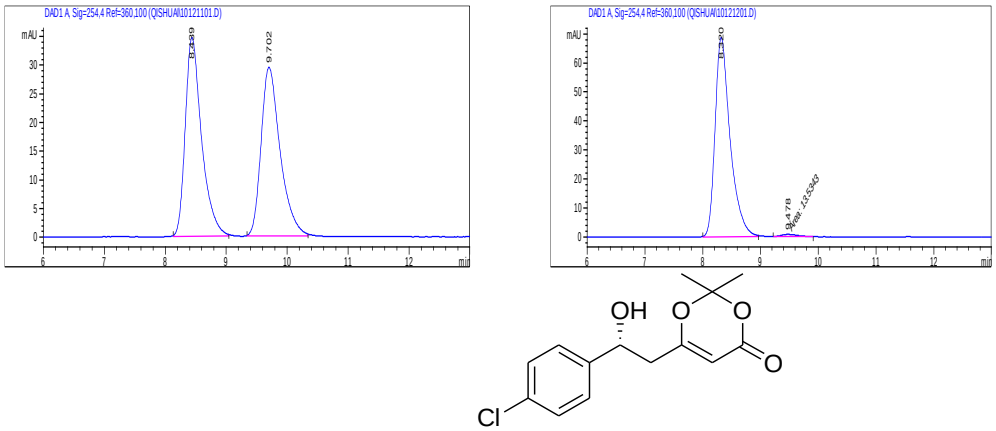
This product was obtained as a yellow,crystalline solid in 91% yield after column chromatography (acetone/petroleum ether = 1/2). $[\alpha]_D^{15.1}$= +27.7 (*c* = 0.448, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.3-6.7 (m, 4 H), 5.29 (s, 1 H), 4.9 (m, 1 H), 2.98 (s, 6 H), 2.71 (dd, *J* = 36, 8, 1 H), 2.60 (dd, *J* = 36, 4, 1 H), 2.17 (d, 1 H), 1.68 (s, 3 H), 1.65 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 168.7 161.2 150.6 130.2 126.8 112.5 106.6 95.2 71.1 42.9 40.5 25.4 24.8; ESI-HRMS: $(M+CH_3COO)^-$, calcd. for $C_{18}H_{24}NO_6$: 350.1604, found: 350.1609; Enantiomeric excess was determined to be 94% (determined by HPLC using chiralcel OD-H column, 20% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 20.2 min. (major), 33 min. (minor).)



3g

(5*R*)-6-(2-hydroxy-2-(3,4,5-trimethoxyphenyl)ethyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3g)

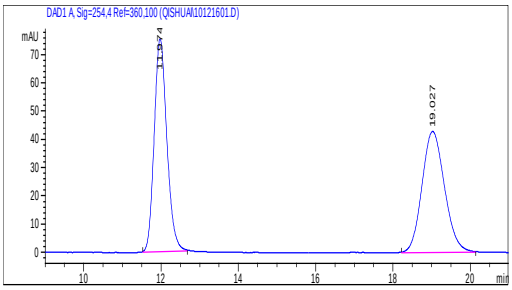
This product was obtained as a white,crystalline solid in 92% yield after column chromatography (acetone/petroleum ether = 1/2). $[\alpha]_D^{15.2}$= +27.04 (*c* = 0.548, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.59 (s, 2 H), 5.35 (s, 1 H), 4.93 (m, 1 H), 3.87 (s, 6H), 3.84 (s, 3H) 2.65 (dd, *J* = 12, 8, 1 H), 2.60 (dd, *J* = 12, 4, 1 H), 2.18 (d, 1 H), 1.71 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.4 161.1 153.4 138.7 137.6 106.7 102.5 95.4 71.3 60.9 56.2 43.4 25.5 24.6; ESI-HRMS: $(M+CH_3COO)^-$, calcd. for $C_{19}H_{25}O_9$: 397.1499, found: 397.1342; Enantiomeric excess was determined to be 97% (determined by HPLC using chiralcel AD-H column, 10% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.7 mL/min, 8.4 min. (major), 9.7 min. (minor).)

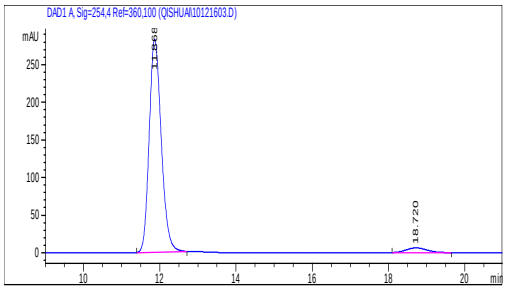


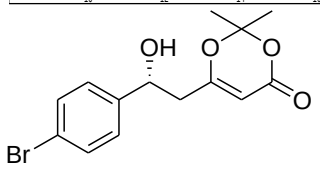
3h

(5*R*)-6-(2-hydroxy-2-(4-chlorophenyl)ethyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3h)

This product was obtained as a white,crystalline solid in 92% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{15.2}$= +36.9 (*c* = 1.079, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.3-7.2 (m, 4 H), 5.30 (s, 1 H), 4.98 (m, 1 H), 3.88 (s, 3 H), 2.65 (dd, *J* = 24, 8, 1 H), 2.58 (dd, *J* = 20, 4, 1 H), 2.39 (d, 1 H), 1.68 (s, 3 H), 1.67 (s, 3 H); Enantiomeric excess was determined to be 93% (determined by HPLC using chiralcel OD-H column, 20% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 11.9 min. (major), 19 min. (minor).)



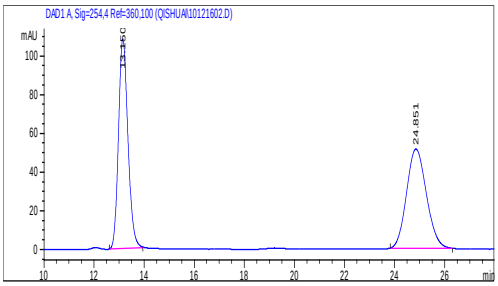


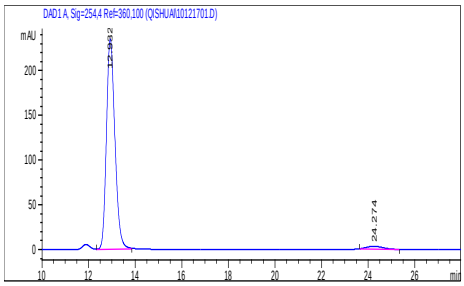


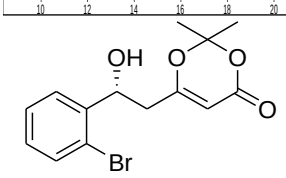
3i

(5*R*)-6-(2-hydroxy-2-(4-bromophenyl)ethyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3i)

This product was obtained as a white,crystalline solid in 90% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{15.2}$= +33.6 (*c* = 1.072, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.5-7.2 (m, 4 H), 5.30 (s, 1 H), 4.94 (m, 1 H), 3.88 (s, 3 H), 2.64 (dd, 1 H), 2.57 (dd, 1 H), 2.54 (d, 1 H), 1.67 (s, 3 H), 1.66 (s, 3 H); Enantiomeric excess was determined to be 95% (determined by HPLC using chiralcel OD-H column, 20% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 13.1 min. (major), 24.8 min. (minor).)



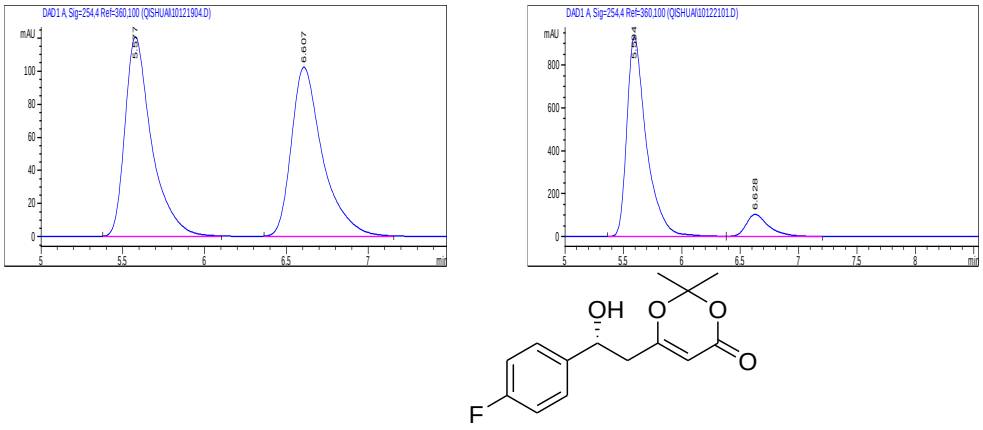




3j

(5*R*)-6-(2-hydroxy-2-(2-bromophenyl)ethyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3j)

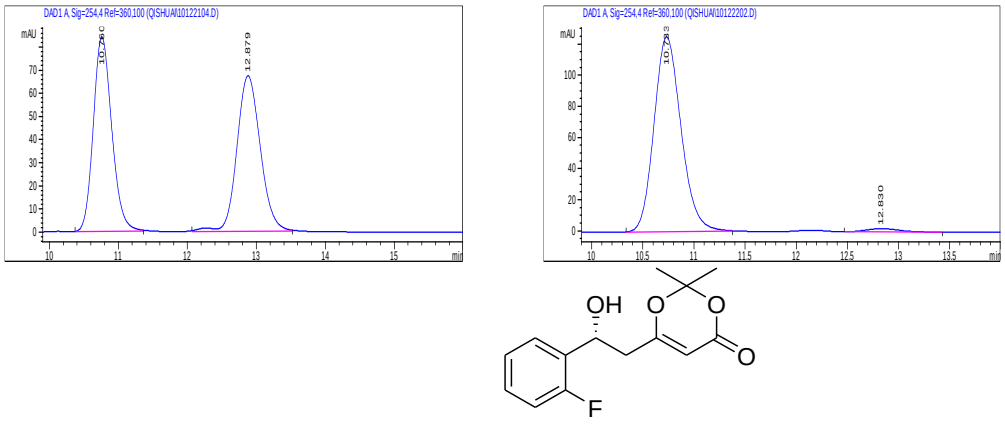
This product was obtained as a white,crystalline solid in 90% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{13.0}$= +53.9 (*c* = 1.114, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.6-7.1 (m, 4 H), 5.35 (s, 1 H), 5.32 (m, 1 H), 3.13 (s, 1 H), 2.74 (dd, *J* = 12, 4, 1 H), 2.48 (dd, *J* = 12, 4, 1 H), 1.69 (s, 3 H), 1.67 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.9 161.6 141.9 132.8 129.4 127.9 127.3 121.5 106.8 95.1 65.9 65.8 41.5 25.3 24.7 15.2; ESI-HRMS: $(M+Na)^+$, calcd. for $C_{14}H_{15}BrNaO_4$: 349.0051, found: 349.0057; Enantiomeric excess was determined to be 77% (determined by HPLC using chiralcel AD-H column, 20% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 5.6 min. (major), 6.6 min. (minor).)



3k

(5*R*)-6-(2-hydroxy-2-(4-fluorophenyl)ethyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3k)

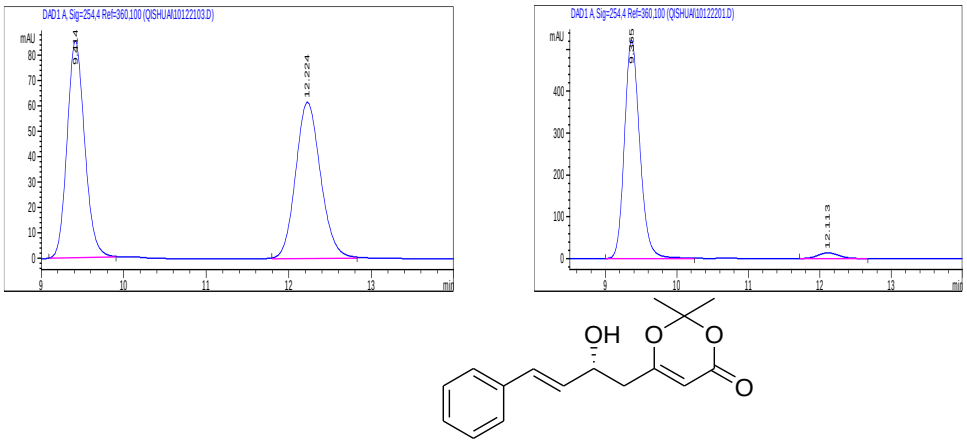
This product was obtained as a white,crystalline solid in 94% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{13.6}$= +28.5 (*c* = 0.908, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.02 (m, 4 H), 5.27 (s, 1 H), 4.95 (m, 1 H), 2.99 (s, 1 H), 2.65 (dd, 1 H), 2.55 (dd, 1 H), 1.65 (s, 3 H), 1.64 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5 163.6 161.4 161.1 138.8 138.7 127.5 127.4 115.6 115.4 106.8 95.2 70.3 43.3 25.3 24.6; ESI-HRMS: $(M+Na)^+$, calcd. for $C_{14}H_{15}BFNaO_4$: 289.0852, found: 289.0851; Enantiomeric excess was determined to be 96% (determined by HPLC using chiralcel AD-H column, 20% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 10.7 min. (major), 12.9 min. (minor).)



3l

(5*R*)-6-(2-hydroxy-2-(2-fluorophenyl)ethyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3l)

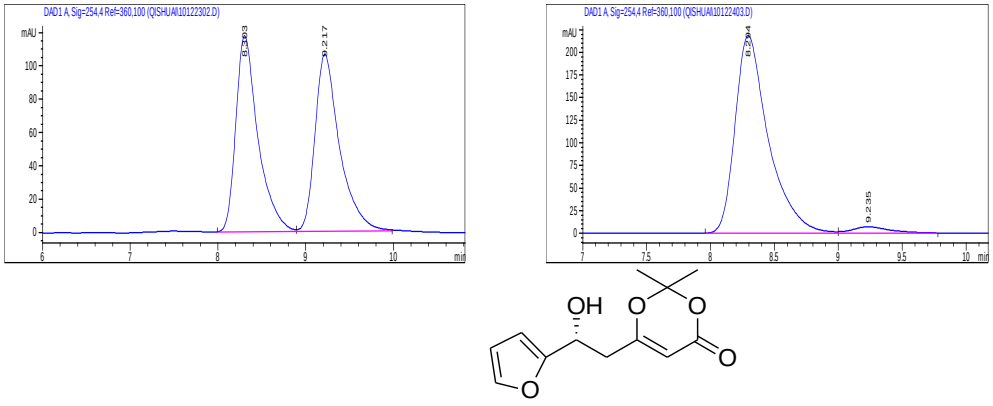
This product was obtained as a white,crystalline solid in 91% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{13.6}$= +35.2 (*c* = 0.913, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.01 (m, 4 H), 5.30 (s, 1 H), 5.26 (m, 1 H), 2.93(d, 1 H), 2.67 (m, 2 H), 1.66 (s, 3 H), 1.63 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5 161.4 160.8 158.3 129.6 129.5 127.3 127,2 124.5 115.5 115.3 106.8 95.2 65.3 41.9 25.2 24.6; ESI-HRMS: $(M+Na)^+$, calcd. for $C_{14}H_{15}BFNaO_4$: 289.0852, found: 289.0855; Enantiomeric excess was determined to be 93% (determined by HPLC using chiralcel AD-H column, 20% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 9.4 min. (major), 12.2 min. (minor).)



3m

(5*R*)-6-(2-Hydroxy-4-phenyl-3-butenyl)-2,2-dimethyl-[1,3]-dioxin-4-one(3m)

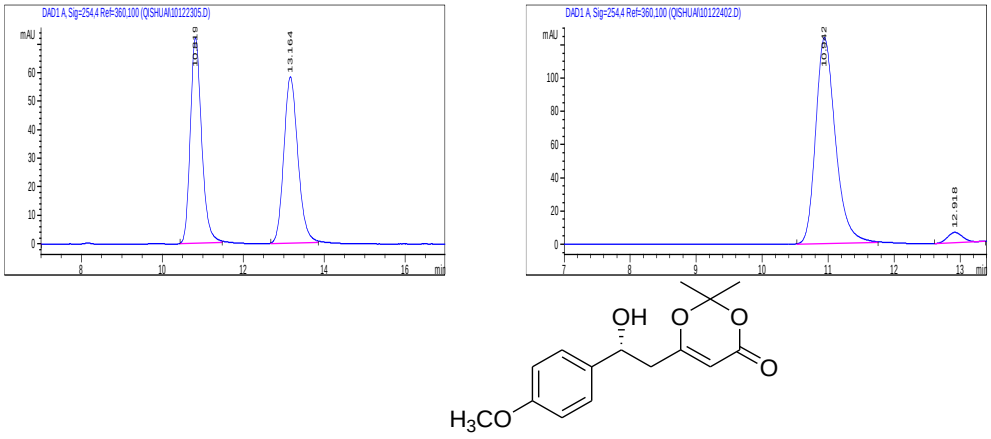
This product was obtained as a white,crystalline solid in 93% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{13.8}$= +7.4 (*c* = 1.026, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.25 (m, 5 H), 6.62 (d, 1 H), 6.21 (dd, 1 H) 5.37 (s, 1 H), 4.60 (m, 1 H), 2.56 (m, 2 H), 2.02 (s, 1 H), 1.70 (s, 3 H), 1.69 (s, 3 H); Enantiomeric excess was determined to be 93% (determined by HPLC using chiralcel AD-H column, 20% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 8.3 min. (major), 9.2 min. (minor).)



3n

(5*R*)-6-(2-hydroxy-2-furanylethyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3n)

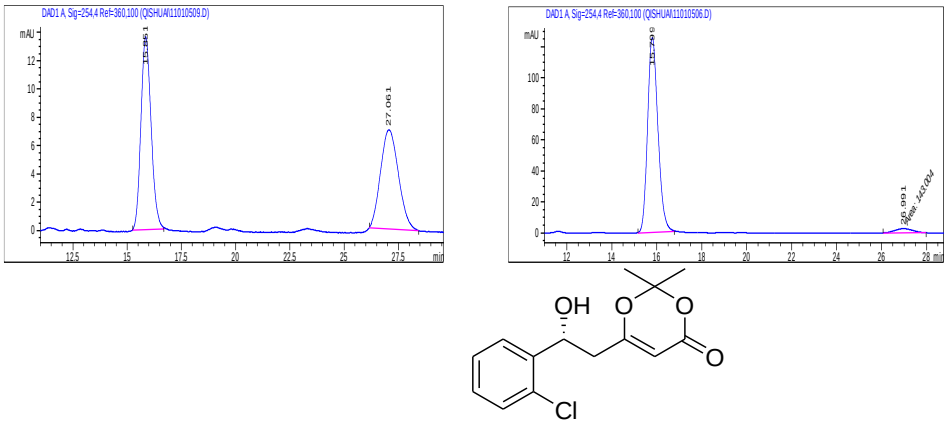
This product was obtained as a white,crystalline solid in 90% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{13.8}$= +24.5 (*c* = 0.827, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, 1 H), 6.34 (d, 1 H), 6.29 (d, 1 H) 5.32 (s, 1 H), 5.00 (m, 1 H), 2.79 (m, 2 H), 2.52 (d, 1 H), 1.68 (s, 3 H), 1.64 (s, 3 H); Enantiomeric excess was determined to be 93% (determined by HPLC using chiralcel OD-H column, 20% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 10.8 min. (major), 13.2 min. (minor).)



3o

(5*R*)-6-(2-hydroxy-2-(4-methoxyphenyl)ethyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3o)

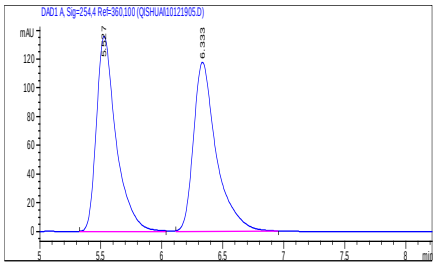
This product was obtained as a white,crystalline solid in 90% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{24.7}$= +20.5 (*c* = 0.457, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.3-6.8 (m, 4 H), 5.28 (s, 1 H), 4.93 (m, 1 H), 3.81 (s, 3 H), 2.70 (dd, *J* = 12, 4, 1 H), 2.58 (dd, *J* = 8, 4, 1 H), 2.17 (d, 1 H), 1.67 (s, 3 H), 1.65 (s, 3 H); Enantiomeric excess was determined to be 93% (determined by HPLC using chiralcel OD-H column, 20% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 15.1 min. (major), 27.1 min. (minor).)

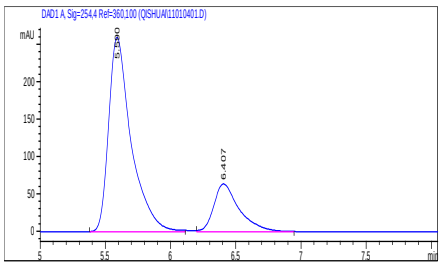


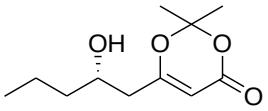
3p

(5*R*)-6-(2-hydroxy-2-(2-chlorophenyl)ethyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3p)

This product was obtained as a white,crystalline solid in 91% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{13.0}$= +53.9 (*c* = 1.114, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.6-7.2 (m, 4 H), 5.39 (m, 1 H), 5.35 (s, 1 H), 2.92 (d, 1 H), 2.73 (dd, *J* = 12, 4, 1 H), 2.52 (dd, *J* = 12, 4, 1 H), 1.69 (s, 3 H), 1.66 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7 161.5 140.3 131.5 129.5 129.1 127.4 127.0 106.8 95.2 67.8 41.4 25.3 24.7; ESI-HRMS: $(M+Na)^+$, calcd. for $C_{14}H_{15}ClNaO_4$: 305.0557, found: 305.0559; Enantiomeric excess was determined to be 56% (determined by HPLC using chiralcel AD-H column, 20% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 5.5 min. (major), 6.3 min. (minor).)



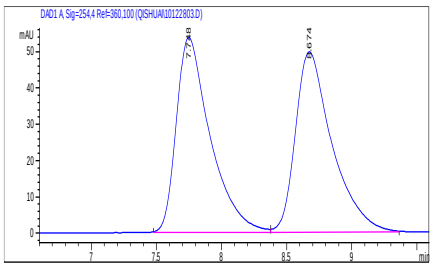


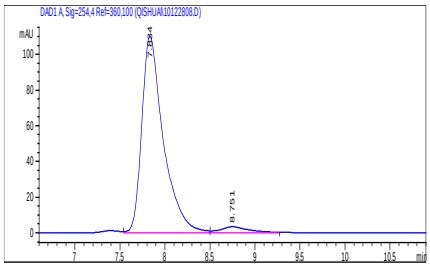


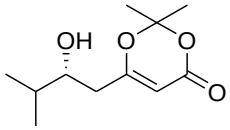
3q

(5*S*)-6-(2-hydroxypentyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3q)

This product was obtained as a colorless oil in 83% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{13.9}$= +15.1 (*c* = 0.686, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 5.32 (s, 1 H), 3.92 (m, 1 H), 2.36 (m, 2 H), 1.98 (s, 1 H), 1.70 (s, 6 H), 1.50 (m, 2 H), 1.40 (m, 2 H), 0.95 (t, 3 H); Enantiomeric excess was determined to be 93% (determined by HPLC using chiralcel AD-H column, 10% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 7.7 min. (major), 8.7 min. (minor).)



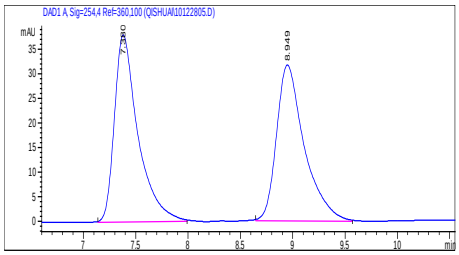


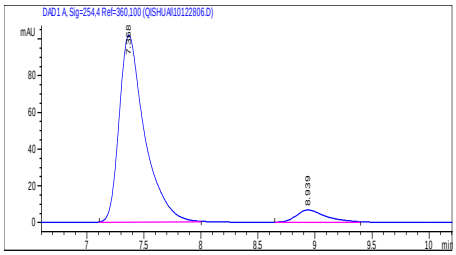


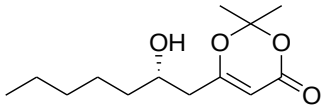
3r

(5*R*)-6-(2-hydroxy-2-methylbutyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3r)

This product was obtained as a colorless oil in 80% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{13.0}$= +53.9 (*c* = 1.114, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 5.34 (s, 1 H), 3.69 (m, 1 H), 2.35 (m, 2 H), 2.09 (s, 1 H), 1.71 (m, 1 H), 1.70 (d, 6 H), 0.96 (s, 3 H), 0.95 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 170.1 161.4 106.6 94.9 73.4 38.7 33.9 25.4 24.7 18.6 17.2; ESI-HRMS: $(M+Na)^+$, calcd. for $C_{11}H_{18}NaO_4$: 237.1103, found: 237.1107; Enantiomeric excess was determined to be 86% (determined by HPLC using chiralcel AD-H column, 20% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 7.4 min. (major), 8.9 min. (minor).)



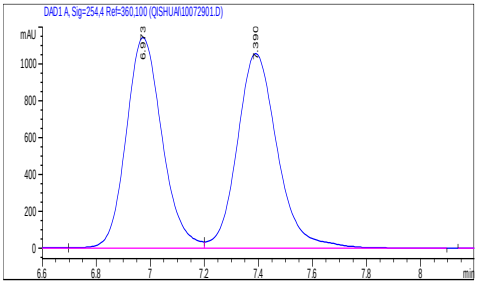


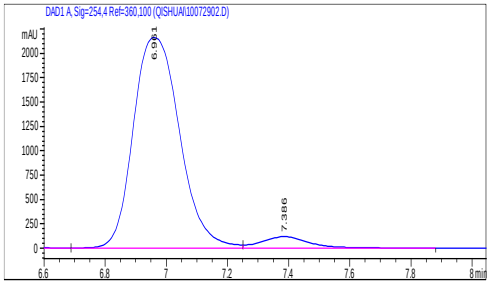


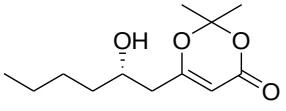
3s

(5*S*)-6-(2-hydroxyheptyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3s)

This product was obtained as a colorless oil in 87% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{23.8}$= +14.3 (*c* = 0.635, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.32 (s, 1 H), 3.91 (m, 1 H), 2.36 (m, 2 H), 1.68 (m, 5 H), 1.61 (s, 1 H), 1.50 (m, 4 H), 1.30 (m, 2 H), 0.91 (t, 3 H); Enantiomeric excess was determined to be 90% (determined by HPLC using chiralcel OD-H column, 20% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 6.9 min. (major), 7.4 min. (minor).)



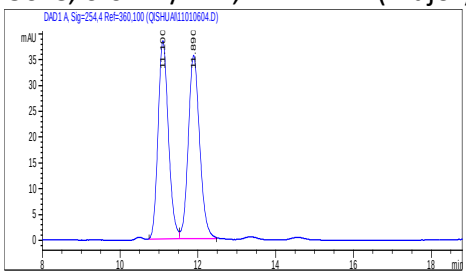


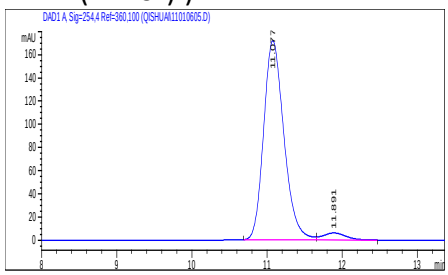


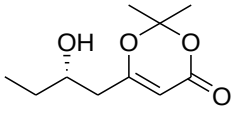
3t

(5*S*)-6-(2-hydroxyhexyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3t)

This product was obtained as a colorless oil in 84% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{23.8}$= +14.6 (*c* = 0.820, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.33 (s, 1 H), 3.90 (m, 1 H), 2.38 (m, 2 H), 2.25 (d, 1 H), 1.70 (s, 6 H), 1.50 (m, 2 H), 1.40 (m, 2 H), 1.30 (m, 2 H), 0.91 (t, 3 H); Enantiomeric excess was determined to be 92% (determined by HPLC using chiralcel OD-H column, 10% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 11.1 min. (major), 11.9 min. (minor).)



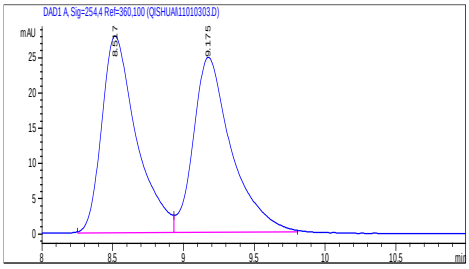


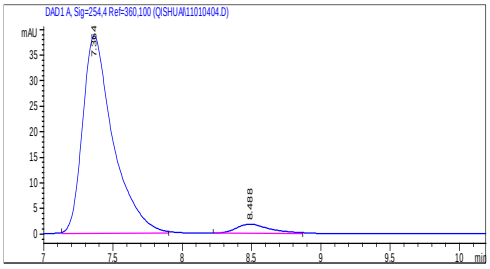


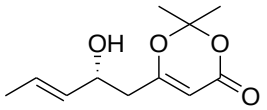
3u

(5*S*)-6-(2-hydroxybutyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3u)

This product was obtained as a colorless oil in 83% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{22.2}$= +24.4 (*c* = 0.330, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.33 (s, 1 H), 3.85 (m, 1 H), 2.37 (m, 2 H), 2.02 (d, 1 H), 1.71 (s, 6 H), 1.55 (d, 2 H), 0.99 (s, 3 H), ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.5 161.2 106.6 95.0 70.1 41.2 30.3 25.3 24.8 9.8; ESI-HRMS: $(M+Na)^+$, calcd. for $C_{10}H_{16}NaO_4$: 223.0946, found: 223.0944; Enantiomeric excess was determined to be 91% (determined by HPLC using chiralcel AD-H column, 10% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 8.5 min. (major), 9.1 min. (minor).)



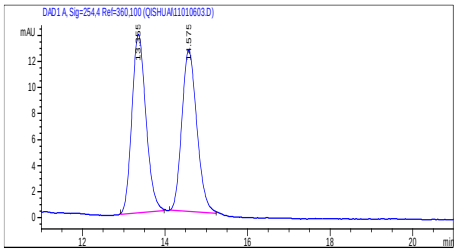


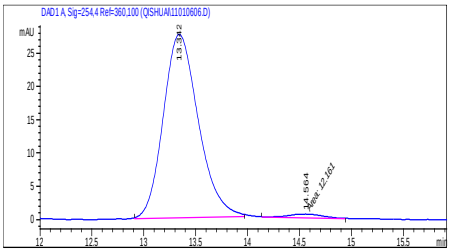


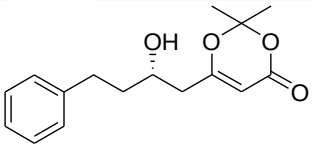
3v

(5*R*)-6-(2-hydroxy-3-butenyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3v)

This product was obtained as a colorless oil in 85% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{24.8}$= +6.5 (*c* = 0.306, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.73 (m, 1 H), 5.50 (m, 1 H), 5.32 (m, 1 H), 4.35 (m, 1 H), 2.44 (m, 2H), 1.72 (d, 1 H), 1.69 (s, 6 H); Enantiomeric excess was determined to be 97% (determined by HPLC using chiralcel OD-H column, 10% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 13.4 min. (major), 14.6 min. (minor).)



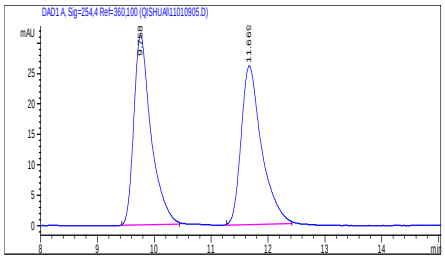


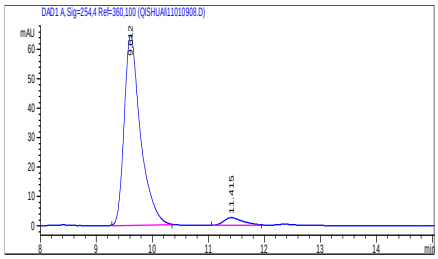


3w

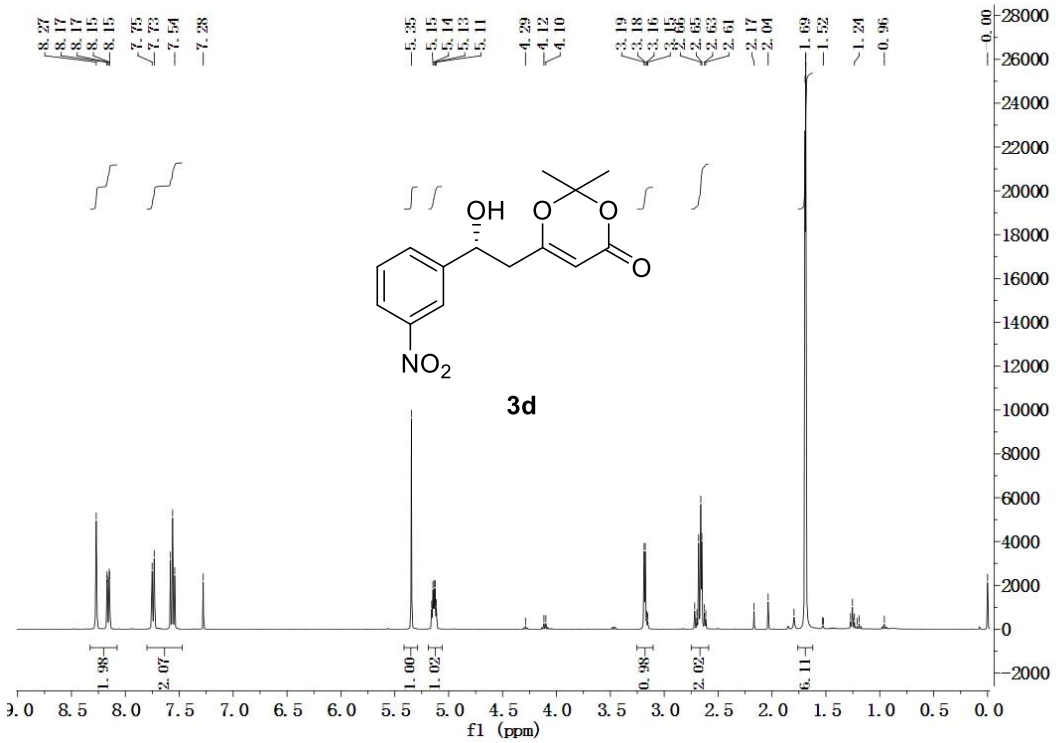
(5*S*)-6-(2-hydroxy-4-phenylbutyl)-2,2-dimethyl-4*H*-1,3-dioxin-4-one (3w)

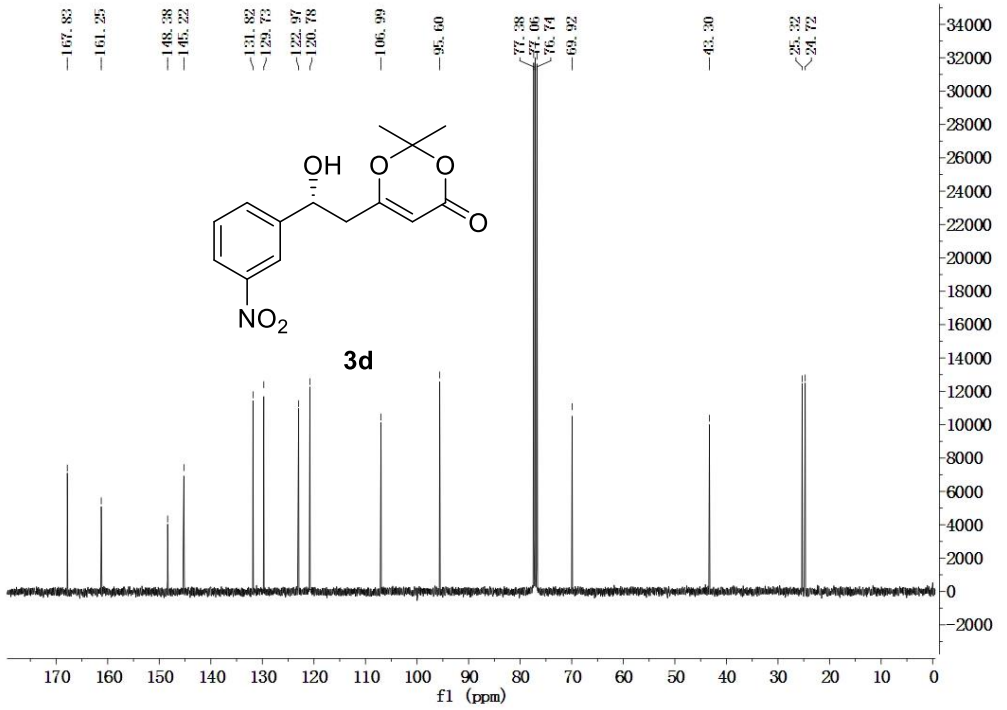
This product was obtained as a white,crystalline solid in 86% yield after column chromatography (acetone/petroleum ether = 1/3). $[\alpha]_D^{25}$= +2.7 (*c* = 0.627, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31- 7.18 (m, 5 H), 5.31 (s, 1 H), 3.92 (m, 1 H), 2.81 (m, 1 H), 2.69 (m, 1 H), 2.40 (m, 2 H), 2.37 (s, 1 H), 1.83 (q, 2 H), 1.67 (s, 3 H), 1.66 (s, 3 H); Enantiomeric excess was determined to be 91% (determined by HPLC using chiralcel AD-H column, 10% *i*PrOH/Hexanes, λ = 254 nm, 30°C, 0.6 mL/min, 9.8 min. (major), 11.6 min. (minor).)

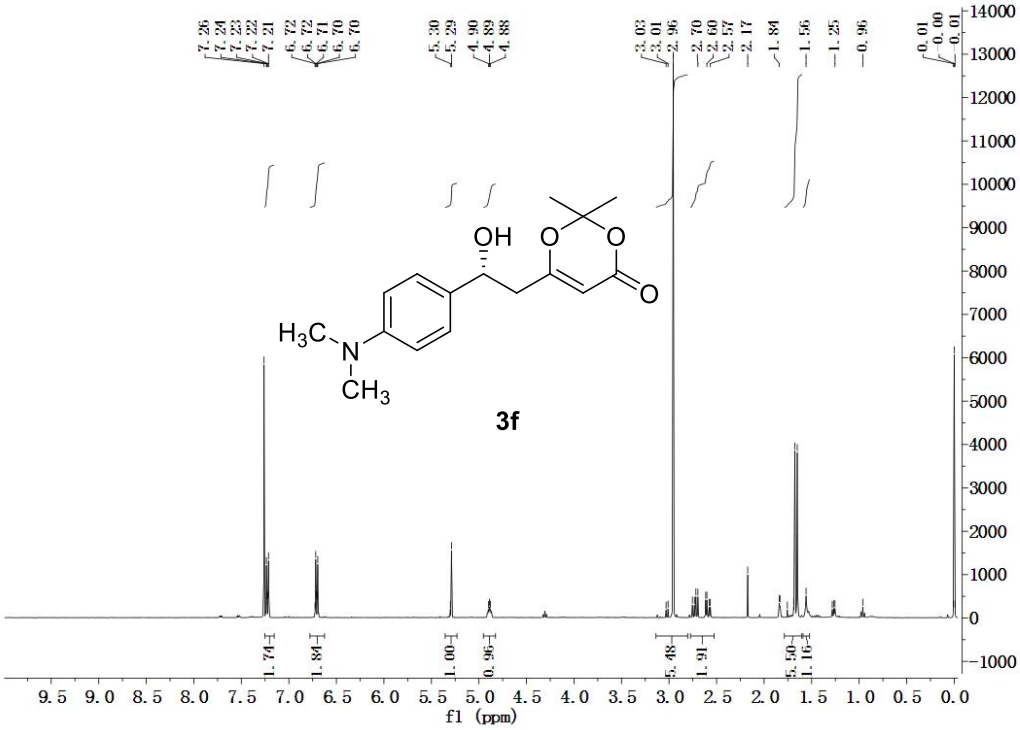


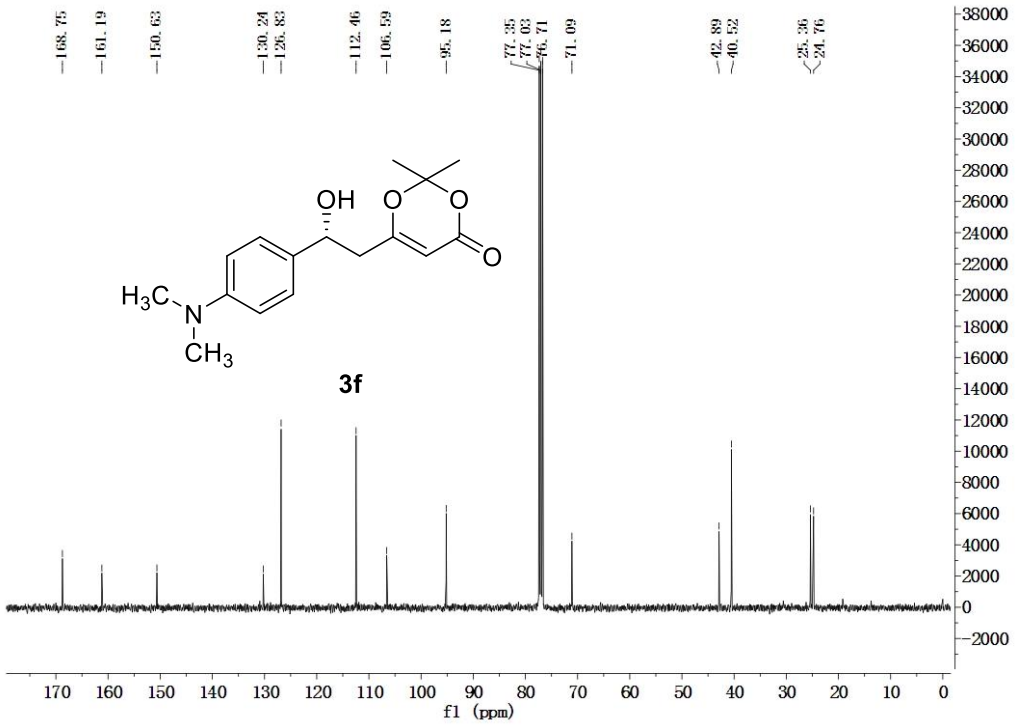


2. NMR spectra of new compounds

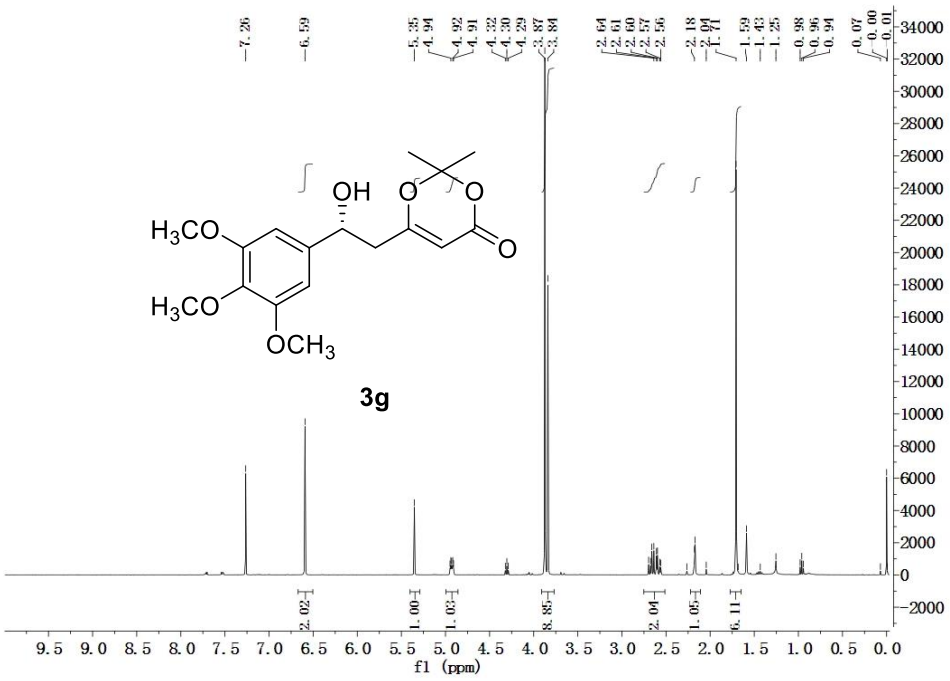



167.83
161.25
148.38
145.22
131.82
129.73
122.97
120.78
106.99
95.60
77.38
77.06
76.74
69.92
43.30
25.32
24.72
OH
O
O
O
NO2
3d
f1 (ppm)

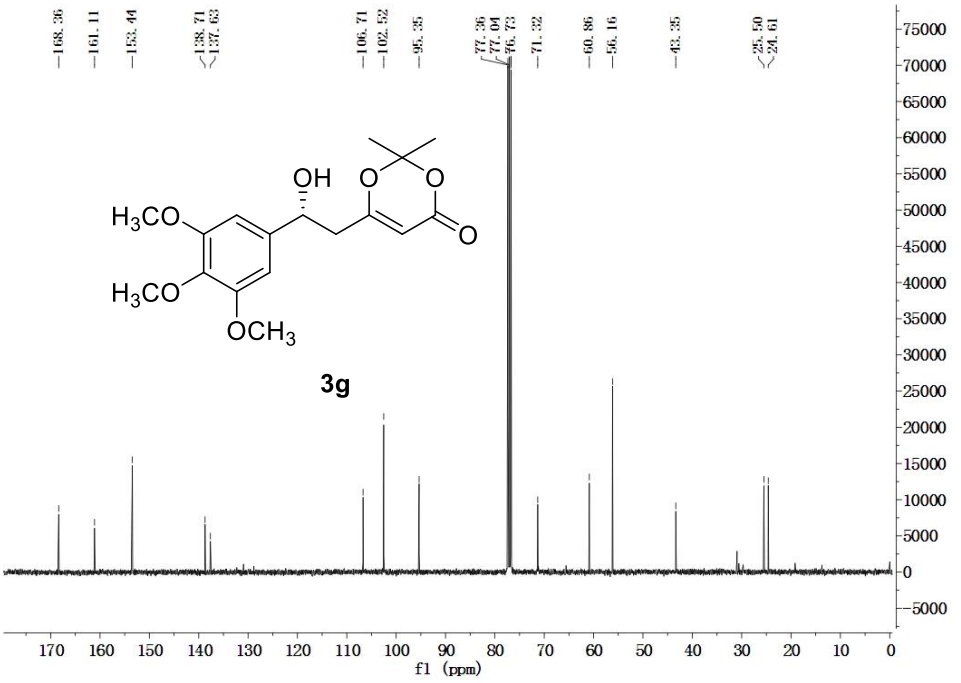

7.26
7.24
7.23
7.22
7.21
6.72
6.72
6.71
6.70
6.70
5.30
5.29
4.90
4.89
4.88
3.03
3.01
2.96
2.70
2.60
2.57
2.17
1.84
1.56
1.25
0.96
0.01
0.00
0.01
1.74
1.84
1.00
0.96
5.48
1.91
5.50
1.16
OH
O
O
O
H3C
N
CH3
3f
f1 (ppm)

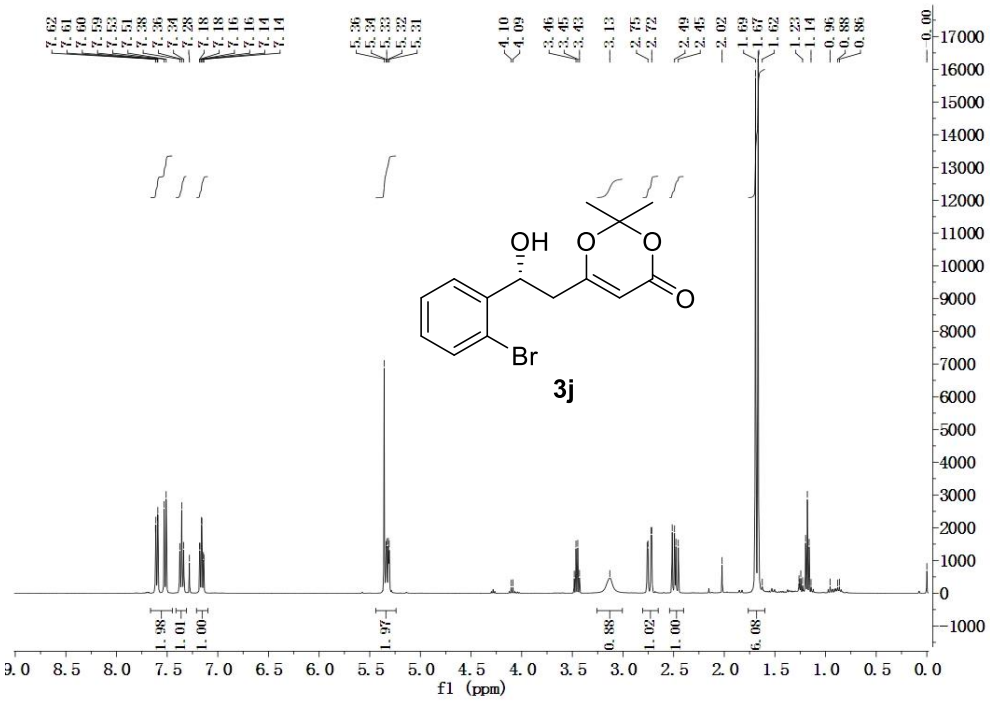


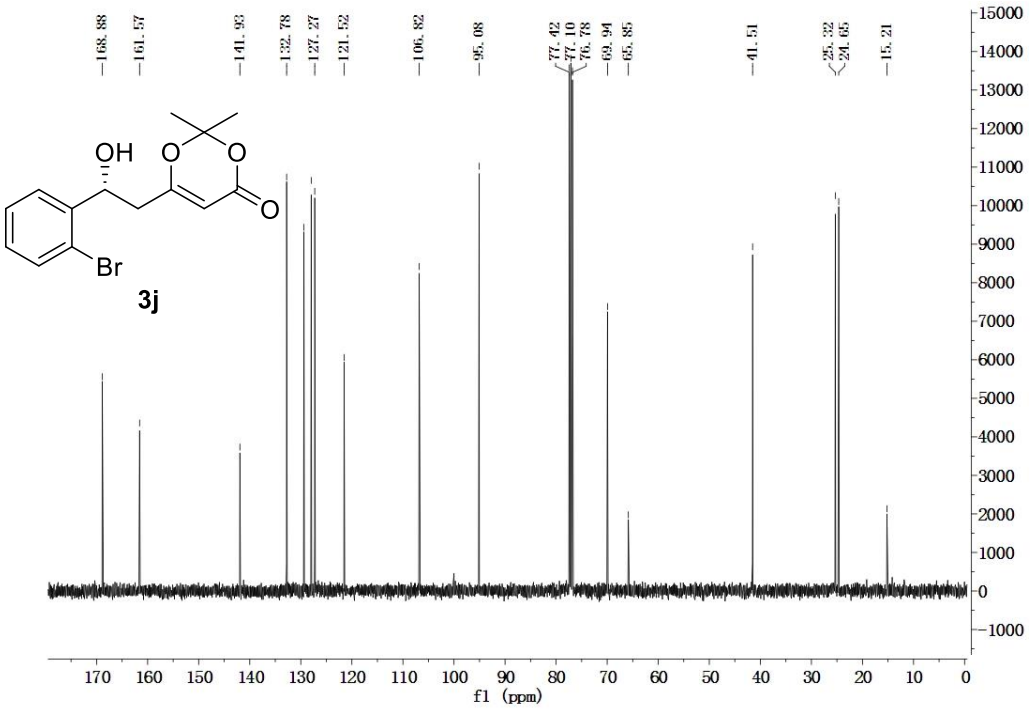
3f

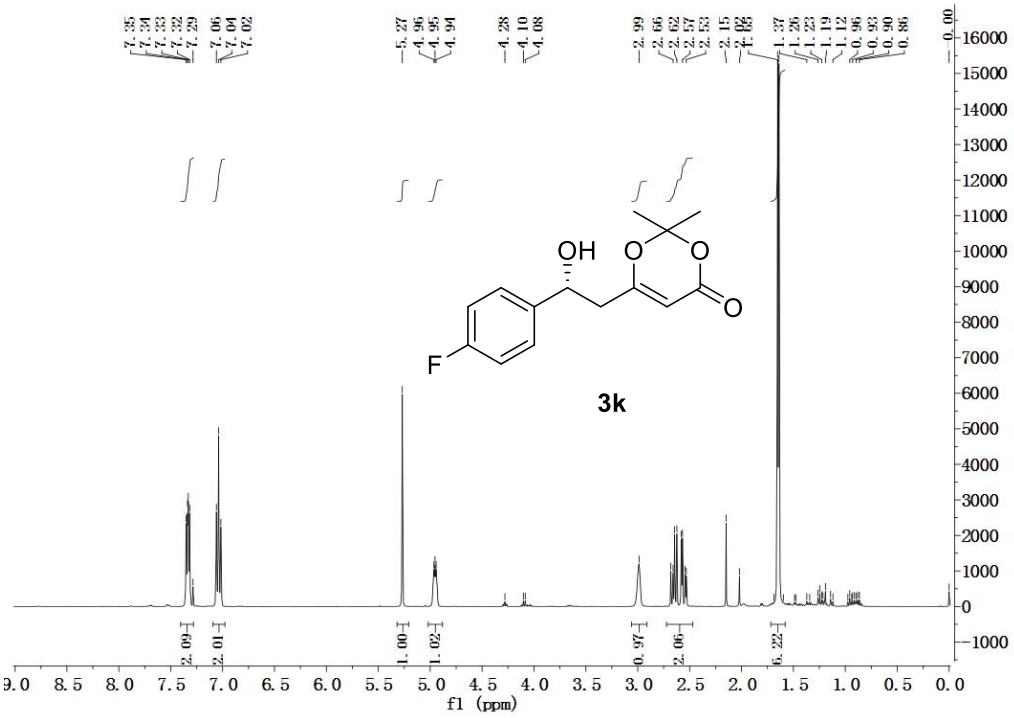


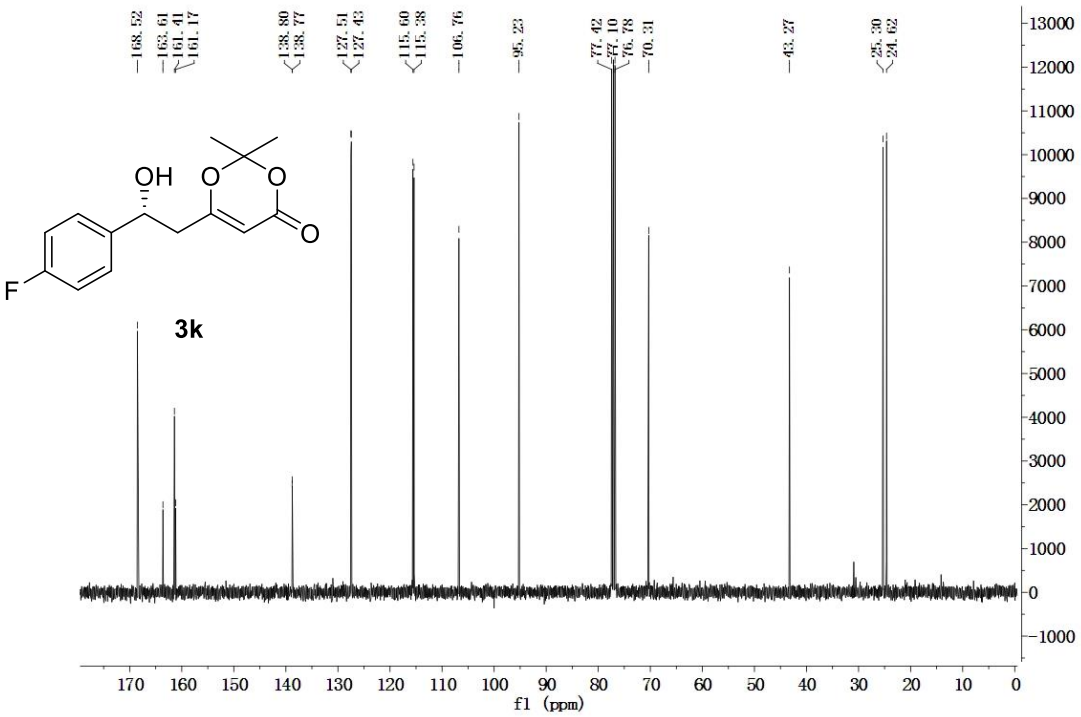
3g

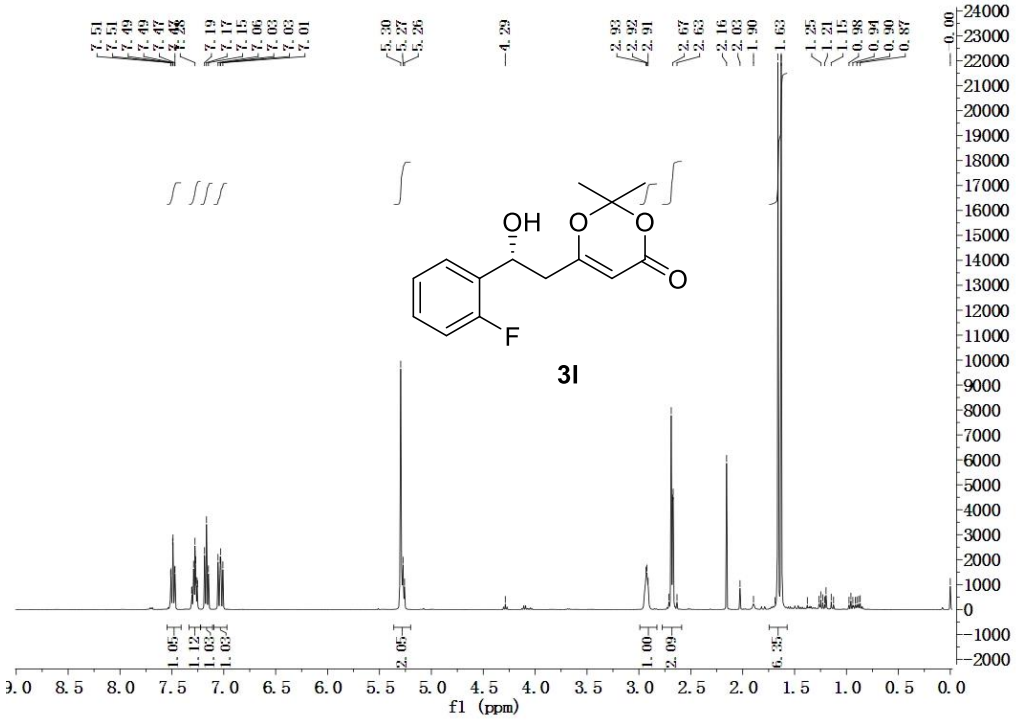


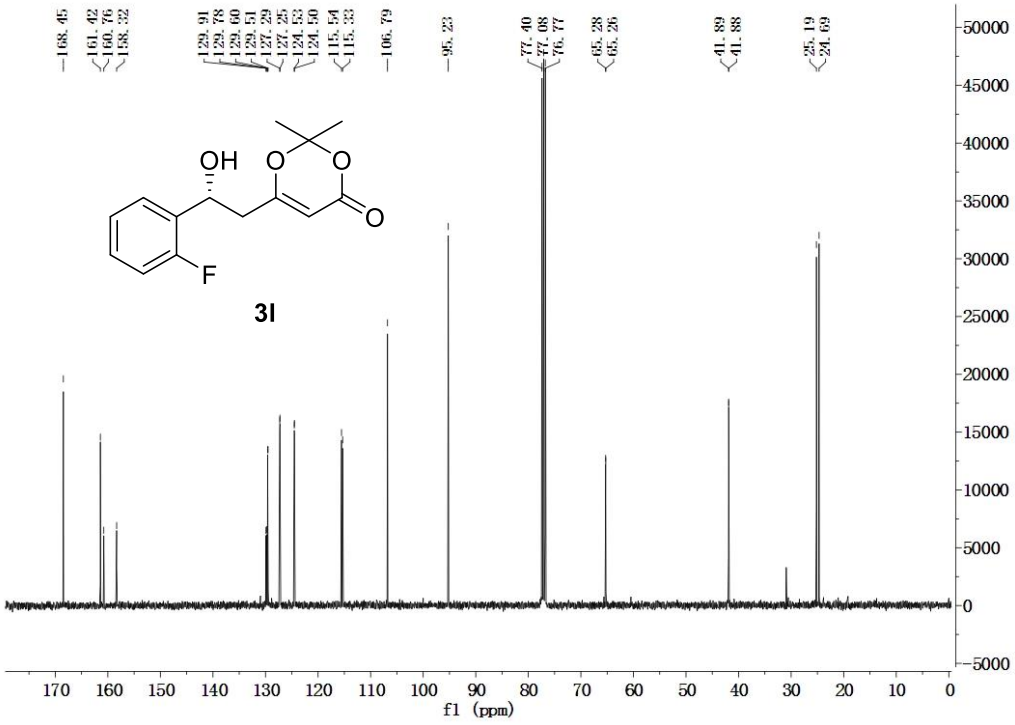


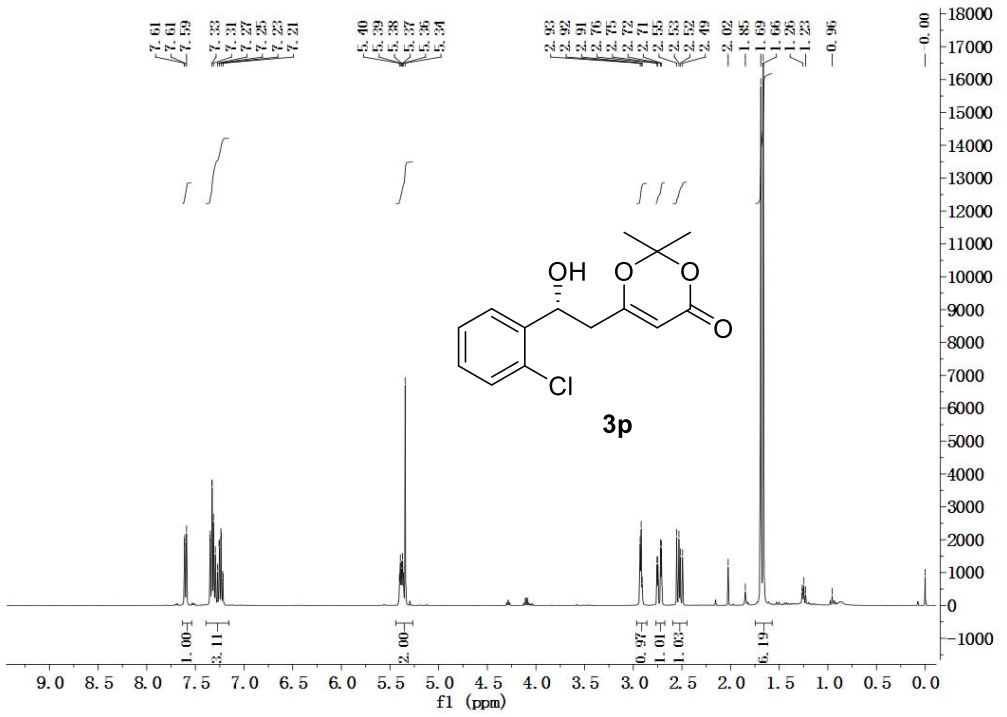

168.88
161.57
141.93
132.78
127.27
121.52
106.82
95.08
77.42
77.10
76.78
69.94
65.85
41.51
25.32
24.65
15.21
OH
O
O
O
Br
3j
f1 (ppm)

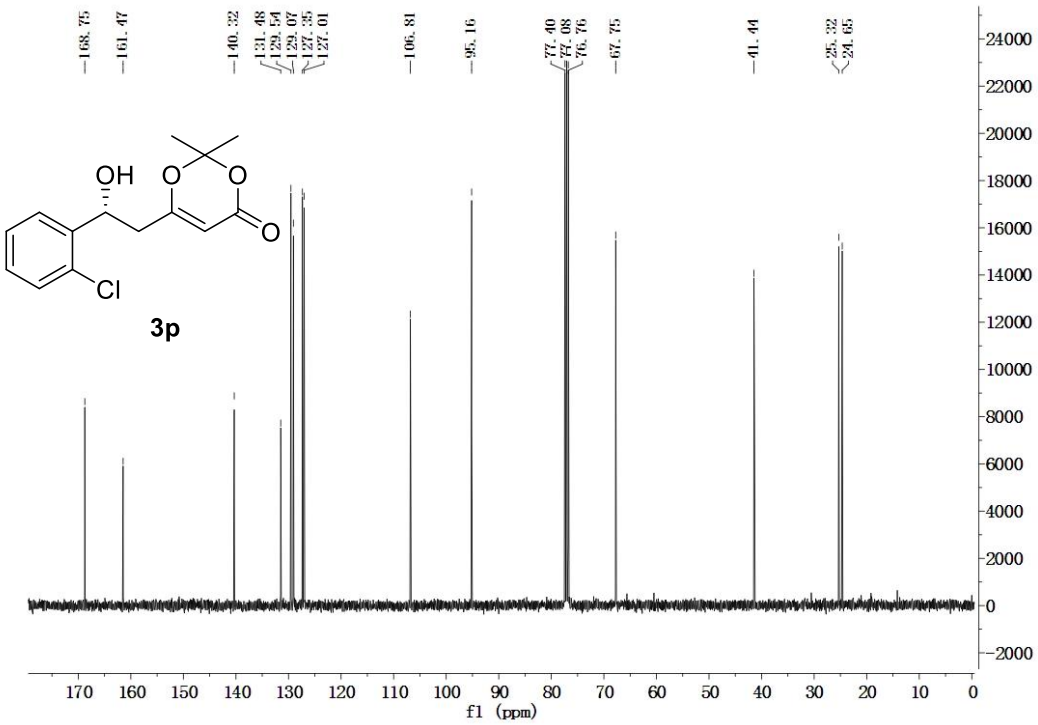

7.35
7.34
7.33
7.32
7.29
7.06
7.04
7.02
5.27
4.96
4.95
4.94
4.28
4.10
4.08
2.99
2.66
2.62
2.57
2.53
2.15
1.37
1.26
1.23
1.19
1.12
0.96
0.93
0.90
0.86
0.00
OH
O
O
O
F
3k
2.09
2.01
1.00
1.02
0.97
2.06
6.22
f1 (ppm)

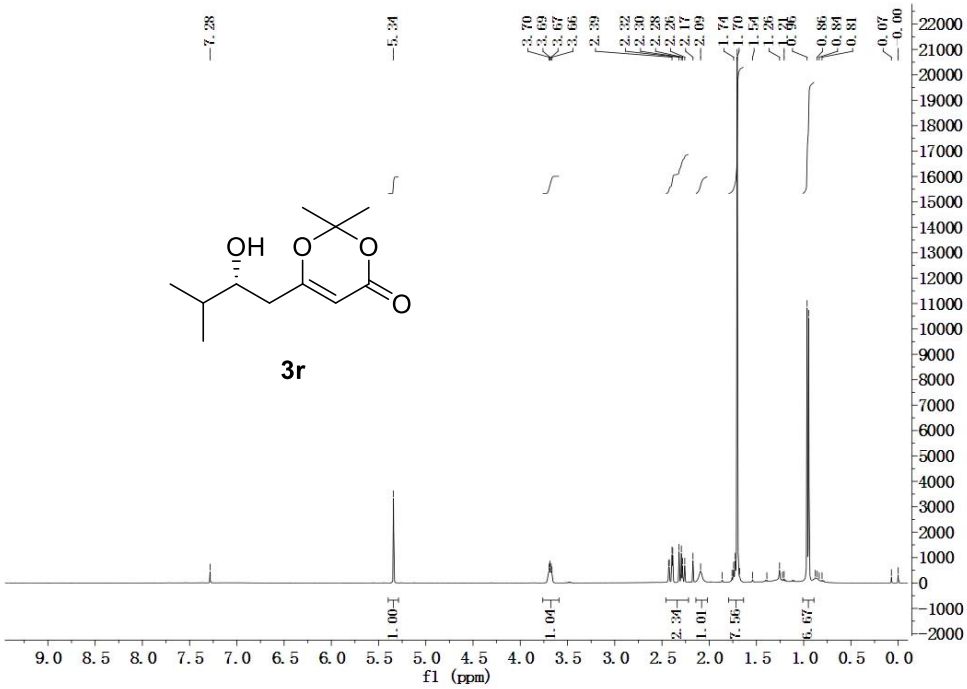

168.52
163.61
161.41
161.17
138.80
138.77
127.51
127.43
115.60
115.38
106.76
95.23
77.42
77.10
76.78
70.31
43.27
25.30
24.62
OH
O
O
O
F
3k
f1 (ppm)

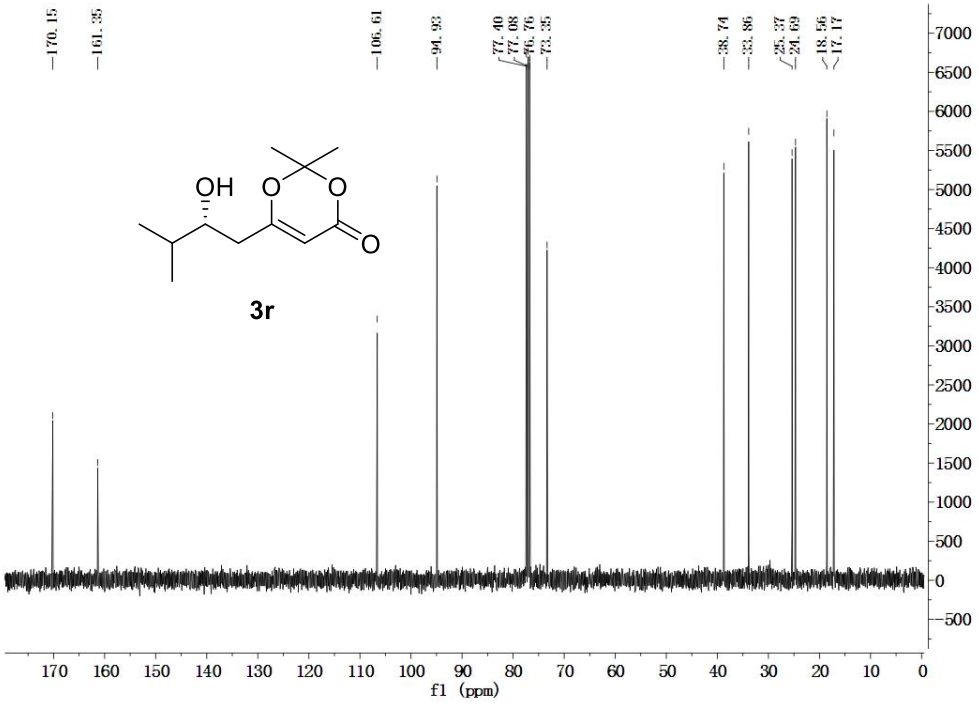

7.51
7.51
7.49
7.49
7.47
7.47
7.19
7.17
7.15
7.06
7.03
7.03
7.01
5.30
5.27
5.26
4.29
2.93
2.92
2.91
2.67
2.63
2.16
2.03
1.90
1.63
1.25
1.21
1.15
0.98
0.94
0.90
0.87
0.00
1.05
1.12
1.03
1.03
2.05
1.00
2.09
6.35
OH
O
O
O
F
3l
f1 (ppm)


168.45
161.42
160.76
158.32
129.91
129.78
129.60
129.51
127.29
127.25
124.53
124.50
115.54
115.33
106.79
95.23
77.40
77.08
76.77
65.28
65.26
41.89
41.88
25.19
24.69
OH
O
O
O
F
3l
f1 (ppm)

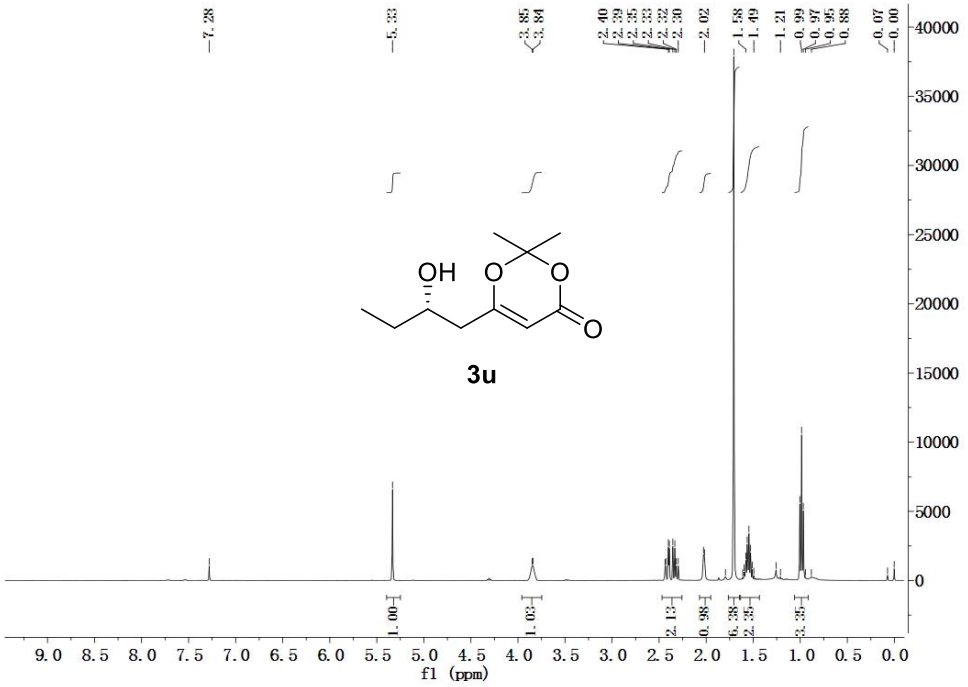

7.61
7.61
7.59
7.33
7.31
7.27
7.25
7.23
7.21
5.40
5.39
5.38
5.37
5.36
5.34
2.93
2.92
2.91
2.76
2.75
2.72
2.71
2.55
2.53
2.52
2.49
2.02
1.85
1.69
1.66
1.26
1.23
0.96
0.00
OH
O
O
O
Cl
3p
1.00
3.11
2.00
0.97
1.01
1.03
6.19
f1 (ppm)


168.75
161.47
140.32
131.48
129.54
129.07
127.35
127.01
106.81
95.16
77.40
77.08
76.76
67.75
41.44
25.32
24.65
OH
O
O
O
Cl
3p
f1 (ppm)

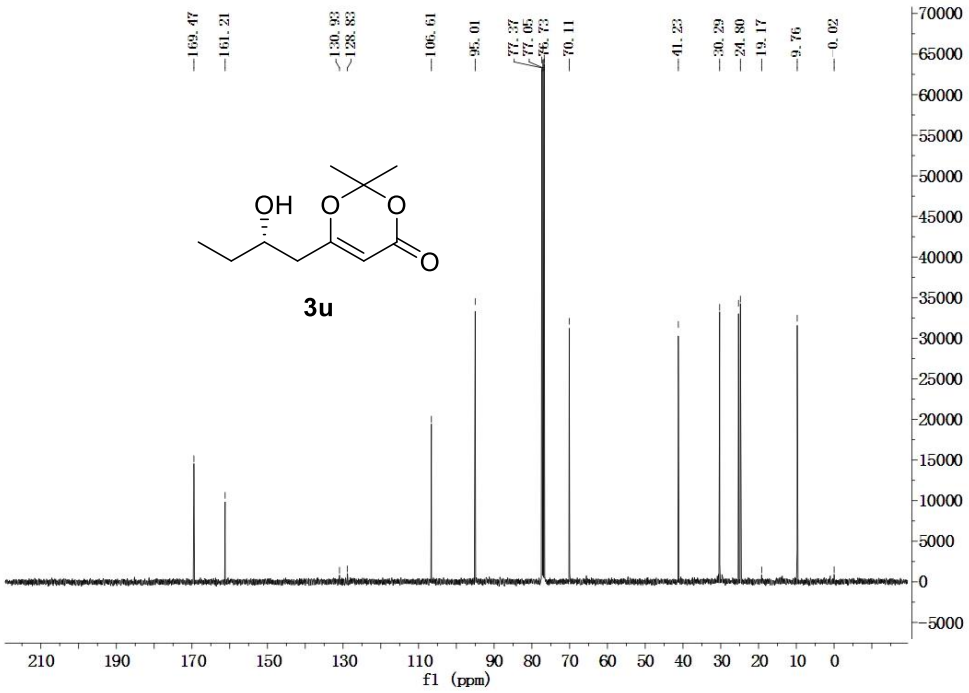

7.28
5.34
3.70
3.69
3.67
3.66
2.39
2.32
2.30
2.28
2.26
2.17
2.09
1.74
1.70
1.54
1.26
1.21
0.96
0.86
0.84
0.81
0.07
0.00
OH
O
O
O
3r
1.00
1.04
2.34
1.01
7.56
6.67
f1 (ppm)

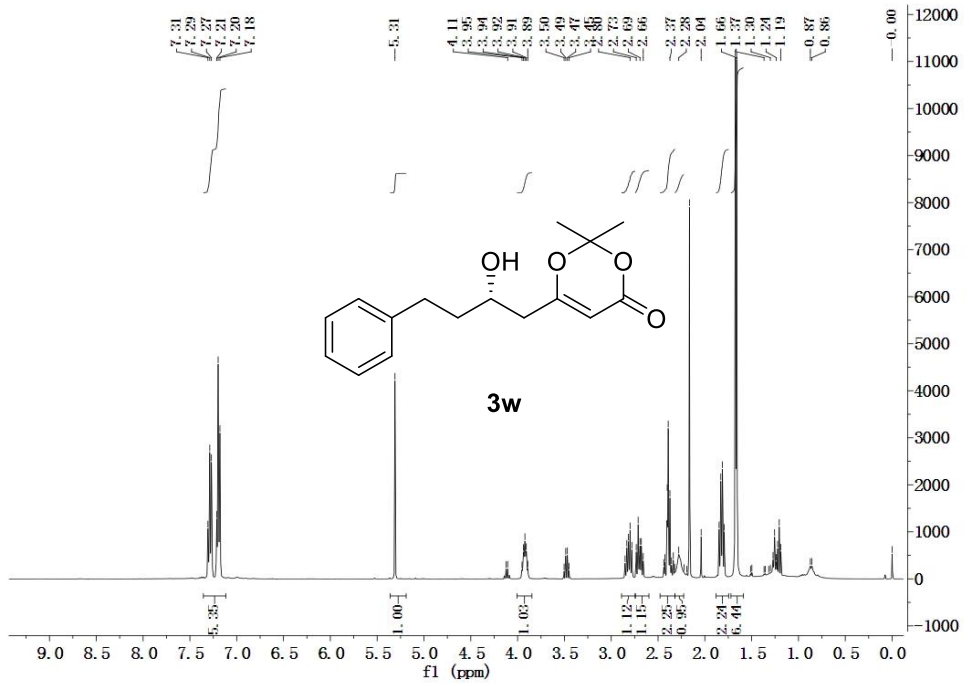


3r



3u


169.47
161.21
130.93
128.83
106.61
95.01
77.37
77.05
76.73
70.11
41.23
30.29
24.80
19.17
9.76
0.02
OH
O
O
O
3u
f1 (ppm)


7.31
7.29
7.27
7.21
7.20
7.18
5.31
4.11
3.95
3.94
3.92
3.91
3.89
3.50
3.49
3.47
2.73
2.69
2.66
2.37
2.28
2.04
1.66
1.37
1.30
1.24
1.19
0.87
0.86
0.00
OH
O
O
O
3w
5.35
1.00
1.03
1.12
1.15
2.25
0.95
2.24
6.44
f1 (ppm)