Supporting Information

Mastering the Potential of Well-defined ML^1L^2 Species in Asymmetric Catalysis through Ligand Immobilization ($ML^{het}L^{hom}$). Use in Highly Enantioselective Pd-catalyzed Spiroannulation

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SI.1. General considerations

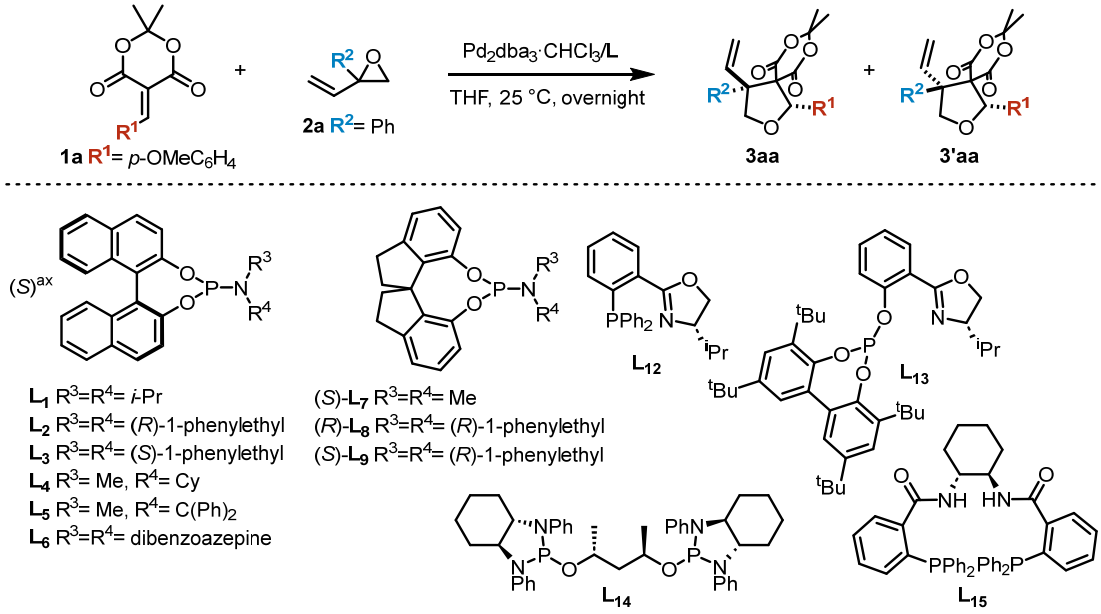
All reactions were carried out using standard Schlenk techniques under an atmosphere of argon. Solvents were purified and dried by standard procedures. $Pd_2(dba)_3 \cdot CHCl_3$ was recrystallized in chloroform twice prior to use.[1] Phosphoramidites $\mathbf{L_4}$[2] and $\mathbf{L_5}$[3]; alkylidene Meldrum's acid derivatives **1a**,[4] **1b**,[5] **1c**,[6] **1d**–**e**,[5] **1f**,[7] **1g**–**h**,[8] **1i**,[9] **1j**,[5] and **1k**[10]; and vinyl epoxides **2a**,[11] **2b**,[12] **2c**–**e**,[11] **2g**–**h**,[12] were prepared as previously reported in the literature. ^1H and $^{13}C\{1H\}$, were recorded using a 400 MHz spectrometer. Chemical shifts are relative to that of NMR solvent for ^1H and $^{13}C\{^1H\}$ and of H_3PO_4 as internal standard for $^{31}P\{^1H\}$. ^1H and ^{13}C assignments were made based on ^1H-^1H gCOSY and ^1H-^{13}C gHSQC.

SI.2. Typical batch procedure for the asymmetric cycloaddition of 5-alkyledene Meldrum's acid derivatives with vinyl epoxides

A flame dried Schlenk was charged with $Pd_2(dba)_3 \cdot CHCl_3$ (6.5 mg, 0.006 mmol), $\mathbf{L_5}$ (12.8 mg, 0.025 mmol), 5-alkylidene Meldrum's acid derivative (0.25 mmol) and vinyl epoxide (0.5 mmol). The reaction tube was sealed with rubber-septum, then purged with vacuum-argon cycles five times. Then, anhydrous THF (1 mL) was added sequentially via syringe. The resulting mixture was stirred at room temperature overnight. After that, the solvent was evaporated in vacuo. The enantiomeric excess was determined by chiral HPLC, conversions were determined by ^1H NMR and isolated yields were determined after column chromatography.

SI-3. Ligand screening and optimization of the reaction conditions

Table S1. Pd-catalyzed [3+2] cycloaddition of **1a** and **2a**.



Entry	Ligand	%Conv[b]	%Yield[c]	**3aa**:**3'aa**[b]	%ee[d]
1	(*S*)-**L1**	100	98	8:1	93 (*S*,*R*)
2	(*S*)-**L2**	<5	-	-	-
3	(*S*)-**L3**	27	19	1:1	22 (*S*,*R*)
4	(*S*)-**L4**	100	97	7:1	91 (*S*,*R*)
5	(*S*)-**L5**	100	>99	3:1	>99 (*S*,*R*)
6	(*S*)-**L6**	100	>99	3:1	90 (*S*,*R*)
7	(*S*)-**L7**	100	>99	6:1	33 (*S*,*R*)
8	(*R*)-**L8**	100	99	4:1	30 (*S*,*R*)
9	(*S*)-**L9**	50	49	2:1	63 (*S*,*R*)
10	**L12**	<5	-	-	-
11	**L13**	<5	-	-	-
12	**L14**	90	85	3:1	21 (*S*,*R*)
13	**L15**	34	30	2:1	34 (*S*,*R*)

[a] Reaction conditions: $Pd_2(dba)_3 \cdot CHCl_3$ (2.5 mol%), ligand (10 mol%), **1a** (0.1 mmol), **2a** (0.2 mmol), THF (1.0 mL), 25 ºC, overnight. [b] Measured by ^{1}H-NMR. [c] Isolated yields as a mixture of diastereomers. [d] Referred to the major diastereomer and determined by HPLC using a chiral stationary phase.

SI-4. Relative stereochemistry elucidation of 3aa and 3'aa

The relative stereochemistry of the two diastereomeric products arising from the [3+2] cycloaddition was established by 1D-NOE (Nuclear Overhauser Effect) experiments. Thus, for the major diastereomer **3aa**, there is a NOE interaction between the methine proton in the vinyl moiety and the methine proton at the 2-position of the tetrahydrofuran scaffold, which indicates that both protons belong to groups with a *cis* arrangement in the cycloadduct (Figure S1a). For isomer **3'aa**, however, the only NOE interaction observed for the methine proton in the vinyl moiety is the one with the methyl protons of the *p*-methoxy group in the aryl group, which indicates that the vinyl and the aryl substituents are in a *cis* arrangement in this diastereomer (Figure S1b).

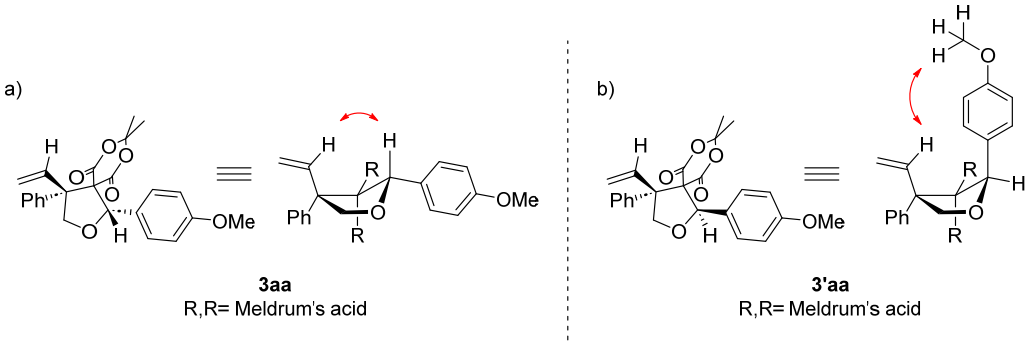


Figure S1. Representative NOE interactions involving the methine proton at the vinyl group in: a) major product **3aa**; and b) minor product **3'aa**. The tetrahydrofuran scaffold has been represented in a twisted conformation.

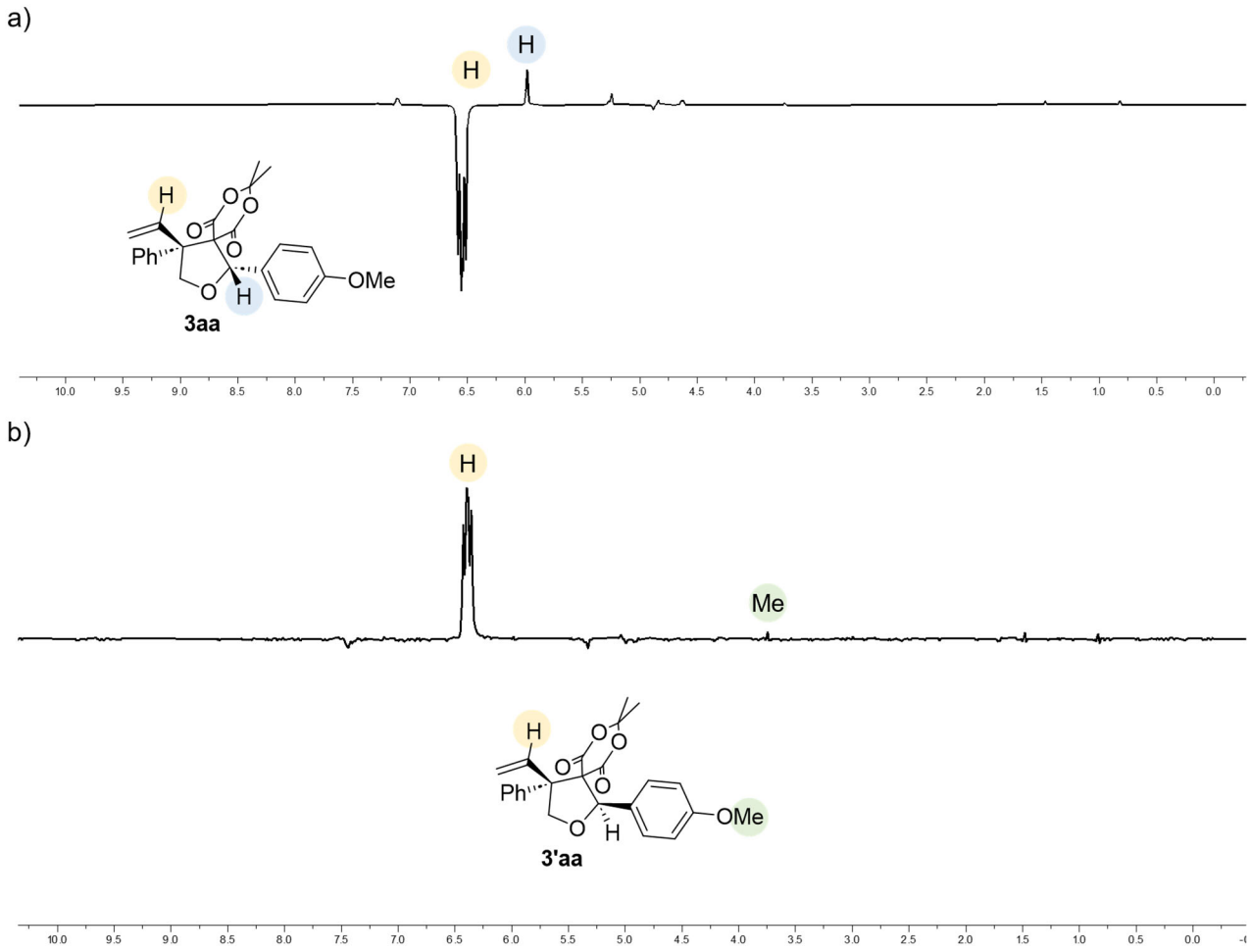


Figure S2. 1D-NOE scpectra of: a) **3aa** irradiating at 6.55 ppm (in yellow) and b) **3'aa** irradiating at 6.55 ppm (in yellow).

SI-5. Synthesis of polystyrene immobilized ligand PS-(*R*)-L_5

(*R*)-6-Bromo-2,2'-bis(ethoxymethoxy)-1,1'-binaphthalene 5. (*R*)-6-bromo-[1,1'-binaphthalene]-2,2'-diol (6.0g, 16 mmol) was dissolved in dry THF (50 mL) at 0 ºC. NaH (1.5 g, 60% in mineral oil, 38 mmol) was added portionwise and the mixture was stirred during 30 minutes at this temperature. Then chloromethyl ethyl ether (3.8 mL, 41 mmol) was added dropwise and the reaction was stirred at room temperature for 3 h. Then 30 mL of water were added to quench the reaction. The aqueous phase was extracted twice with diethyl ether and purified by column chromatography (Hexanes/Ethyl acetate, 10:1). yellow oil (5.5 g, 11 mmol, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.02 (m, 6H, CH_3), 3.38 (m, 4H, CH_2), 5.02 (m, 2H, CH_2), 5.14 (m, 2H, CH_2), 7.01 (d, 1H, CH=, $J_{H\text{-}H}$ = 9.1 Hz), 7.08 (m, 1H, CH=), 7.21-7.29 (m, 2H, CH=), 7.32-7.36 (m, 1H, CH=), 7.60 (d, 1H, CH=, $J_{H\text{-}H}$ = 9.1 Hz), 7.63 (d, 1H, CH=, $J_{H\text{-}H}$ = 9.1 Hz), 7.86 (m, 2H, CH=), 7.95 (d, 1H, CH=, $J_{H\text{-}H}$ = 9.0 Hz), 8.02 (m, 1H, CH=). 13C NMR (100.6 MHz, $CDCl_3$): δ = 15.0, 15.0, 64.1, 64.1, 93.8, 93.9, 117.3, 117.9, 118.4, 120.5, 121.5, 124.2, 125.4, 126.5, 127.6, 128.1, 128.5, 129.6, 129.7, 129.9, 129.9, 131.0, 132.7, 133.9, 152.9, 153.2.

(*R*)-(2,2'-Bis(ethoxymethoxy)-[1,1'-binaphthalen]-6-yl)methanol. (*R*)-**5** (5.5 g, 11 mmol) were dissolved in dry THF (40 mL), and cooled to -88 ºC. The reaction was maintained at this temperature for 2 hours. Then, DMF (8.8 ml, 110 mmol) was added dropwise, and the reaction was warmed to -50 ºC, and stirred for three hours. Past this time, the reaction is warmed to room temperature, quenched with water (30 mL) and extracted with ethyl acetate twice. The organic phase was dried with $MgSO_4$ and concentrated to reduced pressure. The crude aldehyde was directly dissolved in MeOH (50 mL) and cooled to 0 ºC. $NaBH_4$ (0.62 g, 17 mmol) were added, and the reaction stirred for 3 hours. 5 ml of acetone were added to quench the excess of the sodium borohydride. The solvent was evaporated, and the residue redissolved in ethyl acetate (40 mL). Water (40 mL) was added, and the aqueous phase extracted three times with ethyl acetate. The product was purified by column chromatography (Hexanes/Ethyl acetate, 10:1 → 3:1). yellow oil (2.3 g, 5.3 mmol, 48%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.01 (m, 6H, CH_3), 3.37 (m, 4H, CH_2), 4.79 (s, 2H, CH_2) 5.01 (m, 2H, CH_2), 5.12 (m, 2H, CH_2), 7.12 (m, 2H, CH=), 7.20 (m, 2H, CH=), 7.33 (m, 1H, CH=), 7.60 (d, 2H, CH=, $J_{H\text{-}H}$ = 9.1 Hz), 7.84 (s, 1H, CH=), 7.87 (d, 1H, CH=, $J_{H\text{-}H}$ = 8.1 Hz), 7.95 (m, 2H, CH=). ^{13}C NMR (100.6 MHz,

$CDCl_3$): δ = 15.0, 15.1, 64.1, 65.6, 94.0, 94.1, 117.6, 117.9, 121.2, 121.4, 122.2, 124.1, 125.6, 125.8, 126.2, 126.4, 128.0, 129.4, 129.5, 129.8, 129.9, 133.7, 134.1, 136.5, 152.9, 153.1.

PS-(*R*)-(2,2'-bis(ethoxymethoxy)-[1,1'-binaphthalen]-6-yl)methanol. (*R*)-(2,2'-bis(ethoxymethoxy)-[1,1'-binaphthalen]-6-yl)methanol (3.4 g, 7.8 mmol) was dissolved in dry THF at 0 ºC. NaH (430 mg, 60% in mineral oil, 10.8 mmol) was added portionwise and the mixture was stirred during 30 minutes at this temperature. Then Merrifield resin (10 g, f = 0.6, 6 mmol) was added and the reaction was stirred at the orbital shaker during 16 hours at room temperature. Then the mixture was filtered, and the yellowish solid was washed firstly with water, then with a 1/1 mixture water THF, two times with THF and finally, two times with acetone. The resin was dried under vacuum and characterized by NMR. All the alkyl signals could be observed in the same chemical shift as the homogeneous counterpart.

PS-(*R*)-6-(hydroxymethyl)-[1,1'-binaphthalene]-2,2'-diol (PS-(*R*)-4). The PS-(*R*)-(2,2'-bis(ethoxymethoxy)-[1,1'-binaphthalen]-6-yl)methanol (5 g, f_{max}=0.48) was suspended in dry THF (30 mL). At room temperature, 5 ml of aqueous HCl (35%) was added. The mixture was stirred 16 hours. Then the mixture was filtered and the yellowish solid was washed firstly with water two times, then with a 1/1 mixture water THF, two times with THF and finally, two times with acetone. The resin was directly used without further purification nor characterization. The resin was dried under vacuum and characterized by NMR. It could be observed that the signals corresponding to ethoxymethyl ether, have disappeared, while the CH_2 of the ether in the linker is slightly shifted.

PS-(*R*)-[1,1'-binaphthalene]-2,2'-diol-N-methyl-1,1-diphenylmethanamine-phosphoramidite (PS-(*R*)-L$_5$). The PS-(*R*)-**4** (5 g, f_{max}=0.51, 2.5 mmol) was dried azeotropically with toluene (3x10 ml). Then the resin was suspended again in 10 ml of dry toluene and freshly distilled pyridine (0.8 ml, 10 mmol) was added. Finally, PCl_3 (0.44 ml, 5 mmol), were added and the reaction was stirred 16 hours at 90 ºC at the orbital shaker. Then, the solution was cooled to room temperature, dried azeotropically with toluene (2x10 ml) to remove the PCl_3 excess and keep under vacuum for 2 hours. Pas this

time, a solution of DMAP (92 mg, 0.7 mmol) and N-methyl-1,1-diphenylmethanamine (1.5 g, 7.5 mmol) in toluene (10 ml) was added to the *in situ* generated chlorophosphite. Freshly distilled triethylamine (1.4 ml, 10 mmol) was added and the mixture was stirred 5 hours at room temperature. Then the mixture was filtered the solid was washed firstly with a 1/1 mixture water THF, two times with THF and finally, two times with dichloromethane. The resin was characterized by NMR. The functionalization (mmol of **L1**/g resin) of the resin was calculated by the elemental analysis of nitrogen using the expression: f (mmol g^{-1}) = %N × 1000 × (number of N atoms)$^{-1}$ × MW(N)$^{-1}$ × 100^{-1} = 0.41 mmol/g.

SI-6. Typical batch procedure using well-defined $PdL^{het}L^{hom}$ species for the enantioselective cycloaddition of 5-alkyledene Meldrum's acid derivatives

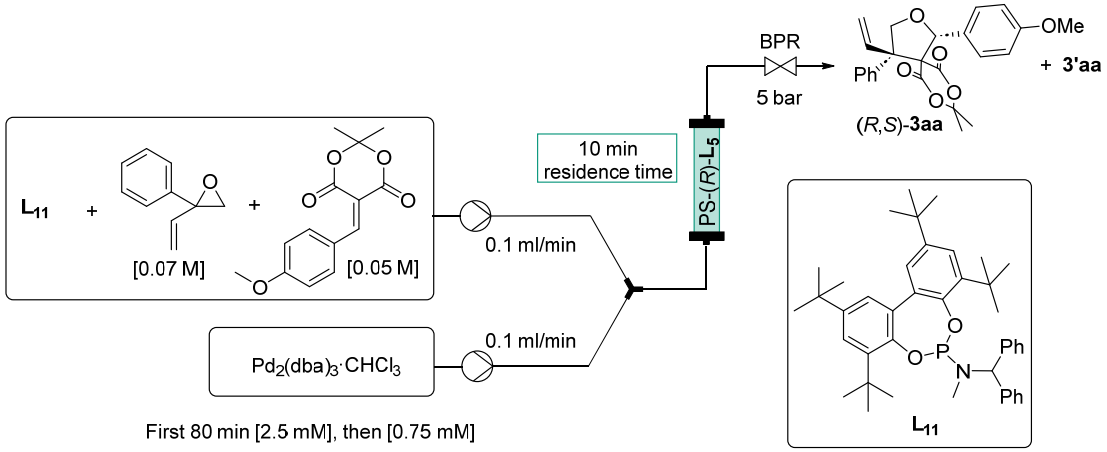
A flame dried Schlenk was charged with $Pd_2(dba)_3 \cdot CHCl_3$ (6.5 mg, 0.006 mmol), **L_5** (6.4 mg, 0.0125 mmol), PS-(*R*)-**L_5** (30.5 mg, 0.0125 mmol) 5-alkylidene Meldrum's acid derivative (0.25 mmol) and vinyl epoxide (0.5 mmol). The reaction tube was sealed with rubber-septum, then purged with vacuum-argon cycles five times. Then, anhydrous THF (1 mL) was added sequentially via syringe. The resulting mixture was stirred at room temperature overnight. After that, the solvent was evaporated in vacuo. The enantiomeric excess was determined by chiral HPLC, conversions were determined by ^{1}H NMR and isolated yields were determined after column chromatography.

SI-7. Typical flow procedure using well-defined $PdL^{het}L^{hom}$ species for the enantioselective cycloaddition of 5-alkyledene Meldrum's acid derivatives with vinyl epoxides

PS-(*R*)-**L$_5$** (0.3 g) were loaded into an Omnifit® glass column (10 mm ID). Prior to the reaction, the catalyst bed was swollen by pumping dry THF at 0.2 mL/min. The system was pressurized to 5 bars, using a back pressure regulator. Two stock solutions (A) containing **1a** (1.0 eq, 0.05 M), **2a** (1.4 eq, 0.07 M) and **L$_{11}$** (0.1 eq, 5 mM) and (B) containing the palladium precursor (0.04 eq, 2.5 mM) were prepared. Both solutions were pumped (0.1 mL/min each, 0.2 mL/min overall flow rate) by using a Syrris® Asia syringe pump and combined before the Omnifit® glass column. The different samples were collected after time periods of 10 minutes. After reaching a steady state, the palladium solution (B) was substituted by a more diluted solution (C) containing the same palladium precursor (0.015 eq, 0.75 mM), to balance the leached Pd. For all samples the yields were directly calculated by NMR samples and purified by column chromatography before checking the enantiomeric excess by chiral HPLC.

SI-8. Detailed results of the continuous flow Pd-cycloadditions using well-defined mixed Pd species containing PS-(*R*)-L_5 and L_{11}

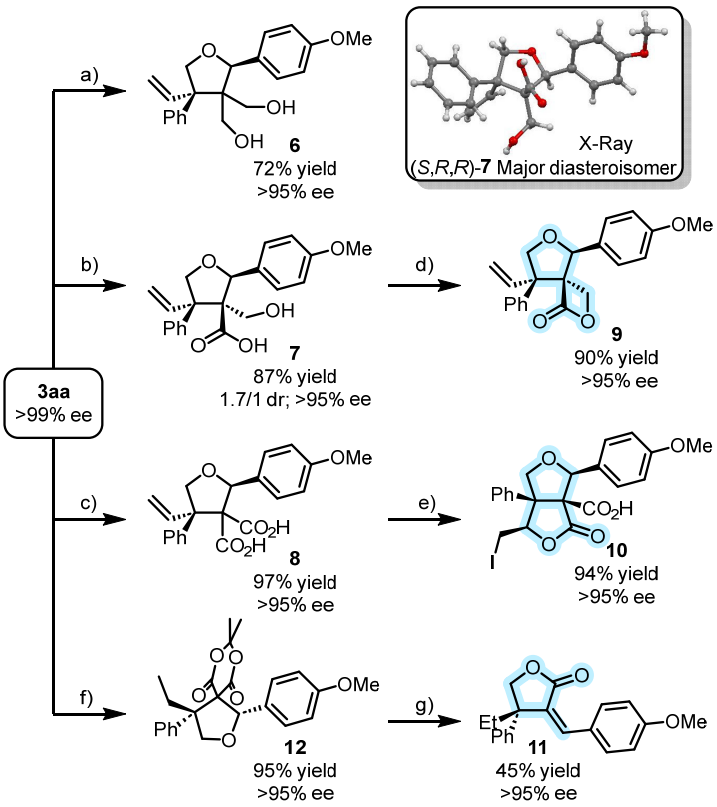
Table S2. Results of the asymmetric continuous flow Pd-cycloadditions of **1a** and **2a** well-defined mixed Pd species containing PS-(*R*)-L_5 and L_{11}.



Entry	Time (min)	Yield **3aa**+**3'aa** (%)	ee **3** (%)
1	30 - 50	72	95 (*R*,*S*)
2	50 - 70	75	95 (*R*,*S*)
3	70-90	86	95 (*R*,*S*)
4	90 - 110	92	95 (*R*,*S*)
5	110-130	79	95 (*R*,*S*)
6	130 - 160	64	95 (*R*,*S*)
From 30 min to 160 min → 66 % isolated yield, 3/1 dr, 95 % ee			

SI-9. Post-spiroannulation experiments. Preparation of rare lactone motifs

As previously stated, the Meldrum's acid-type fragment in **3** represents a very appealing platform for the preparation a wide array of synthetically relevant molecules due to its unique structure and the range of substituents that can be attached to it. To demonstrate the synthetic potential of the [3+2]-cycloaddition reaction established in this study, we first transformed selectively the Meldrum's moiety in compound **3aa** to the corresponding diol **6**, hydroxy-acid **7** and diacid derivative **8** (Scheme S1).



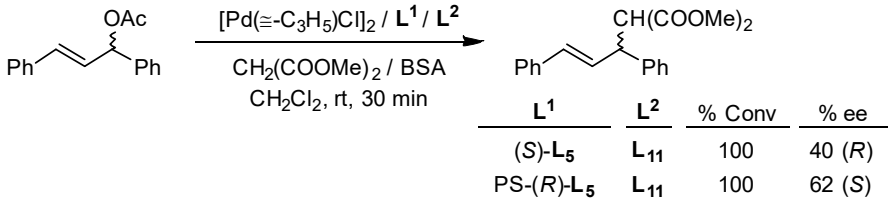
Scheme S1. Derivatization of model product (*S*,*R*)-**3aa**. Reaction conditions: a) $LiAlH_4$, THF, 70 ºC, 24 h; b) $LiAlH_4$, THF, rt, 2 h; c) NaOH (10%), $EtOH/H_2O$ (2:1), 80 ºC, 16 h; d) DEAD, PPh_3, THF, rt, 4 h; e) NIS, DMAP, CH_2Cl_2, rt, 2 h; f) $[Ir(cod)(PCy_3)(Py)]BAr_F$, H_2 (1 bar), CH_2Cl_2, rt, 2 h; g) $Sc(OTf)_3$, CH_3NO, 100 ºC, 0.5 h. X-Ray structure of enantiopure major diastereoisomer **7** is also shown.

Albeit hydroxy-acid **7** was formed in 1.7/1 diastereomeric ratio, both diastereomers could be easily separated by column chromatography. Interestingly, the ready access to diastereo- and enantiopure hydroxyacid **7** paved the way to the synthesis

of the chiral spirocyclic-β-lactone derivative **9** in a straightforward manner. Note that the spiro[3,4]octane ring system present in 9 is highly unusual in the literature.[38] In a similar way, diacid **8** was easily transformed via iodo-lactonization to enantiopure bicyclic γ-lactone **10**. Finally, **3aa** could be transformed to the corresponding α-benzylidene γ-lactone **11** by Ir-catalyzed hydrogenation of the vinyl group to yield **12** followed by Lewis-acid activation of the tetrahydrofuran ring. Note that all the lactone motifs herein developed are very rare and difficult to attain by other means and could be very useful as organic synthons as well as pharmaceuticals warheads. In particular, α-alkylidene-g-lactones like **11** depict anticancer activity, being the subject of active research.[13]

SI-10. Application of well-defined $PdL^{het}L^{hom}$ species in the enantioselective allylic alkylation

Preliminary results indicate that this approach to control ML^1L^2 speciation can also be applied to enantioselective Pd-catalyzed allylic substitution reactions. As a model reaction, we chose the reaction of *rac*-1,3-diphenyl-3-acetoxyprop-1-ene with dimethyl malonate in dichloromethane. The catalysts were generated in situ from 0.5 mol % of π-allyl-palladium chloride dimer $[PdCl(\eta^3\text{-}C_3H_5)]_2$, the corresponding ligand mixture and a catalytic amount of KOAc. The use of equimolar amounts of PS-(*R*)-**L$_5$** with achiral **L$_{11}$** provides higher enantioselectivity than that obtained under homogeneous conditions (62% vs. 40% ee; Scheme S2).



Scheme S2. Pd-catalyzed asymmetric allylic alkylation.

Typical procedure for the allylic alkylation reaction. A degassed solution of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ (1.8 mg, 0.005 mmol), **L$_{11}$** (3.5 mg, 0.0055 mmol) and either (*S*)-**L$_5$** (2.8 mg, 0.0055mmol) or PS-(*R*)-**L$_5$** (13.5 mg, 0.0055mmol) in dichloromethane (1 mL) was stirred for 30 min. Subsequently, a solution of *rac*-1,3-diphenyl-3-acetoxyprop-1-ene (252 mg, 1 mmol) in dichloromethane (3 mL), dimethyl malonate (340 µL, 3 mmol), *N*,*O*-bis(trimethylsilyl)-acetamide (740 µL, 3 mmol) and a pinch of KOAc were added. The reaction mixture was stirred at room temperature. After 30 min the reaction mixture was diluted with Et_2O (10 mL) and a saturated NH_4Cl (aq) (25 mL) was added. The mixture was extracted with Et_2O (3 x 10 mL) and the extract dried over $MgSO_4$. Solvent was removed, conversion was measured by ^{1}H-NMR and ee was determined by HPLC.

SI-11. Synthesis and characterization details of new alkylidene Meldrum's acid 1l and vinyl epoxides 2f, 2i and 2j

Preparation of 2,2-dimethyl-5-(3-(trimethylsilyl)prop-2-yn-1-ylidene)-1,3-dioxane-4,6-dione (1l)

Following the method developed by Bigi *et al*.[4] a mixture of Meldrum's acid (5.5 mmol) and 3-(trimethylsilyl)propioaldehyde (5 mmol) in water (10 mL) was stirred at 75 °C for 2 h. After cooling to room temperature, the solid product was filtered and dried under vacuum. Recrystallisation in ethanol yielded the corresponding 5-alkylidene Meldrum's acid derivative in pure form as a white solid (570 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$), δ= 0.15 (s, 9H, CH_3), 1.61 (s, 6H, CH_3), 7.35 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ= 0.0, 28.6, 101.5, 105.9, 125.1, 128.2, 137.5, 158.8, 162.1.

Procedure for the preparation of vinyl epoxides 2f and 2i

Following a reported methodology,[11] into solution of the corresponding α-bromoacetophenone (10 mmol, 1.0 equiv) in tetrahydrofuran (50 mL, 0.2 M) was added slowly vinylmagnesium bromide (15 mL, 15 mmol, 1.0 M in THF, 1.5 equiv) at 0 ºC. The reaction mixture was kept under an ice bath for 1 hour. Then, a 1M NaOH aqueous solution (20 mL) was added. The mixture was gradually warmed to room temperature and stirred for 2 hours. Subsequently, the mixture was extracted with diethyl ether. The organic layers were combined and washed with brine, then dried using Mg_2SO_4. The organic phase was filtered, and the solvent was removed under reduced pressure using rotary evaporation. The resulting crude product was purified using Kugelrohr distillation under vacuum.

2-(3-Bromophenyl)-2-vinyloxirane (2f). Colorless oil (1.8 g, 80% using 10 mmol of the corresponding α-bromoacetophenone). ^{1}H NMR (400 MHz, $CDCl_3$), δ= 2.96 (d, 1H, CH_2, $J_{H\text{-}H}$= 5.5 Hz), 3.08 (d, 1H, CH_2, $J_{H\text{-}H}$= 5.5 Hz), 5.26 (d, CH_2=, $J_{H\text{-}H}$= 17.2 Hz, 1H), 5.35 (d, 1H, CH_2=, $J_{H\text{-}H}$= 10.3 Hz), 6.01 (dd, 1H, CH=, $J_{H\text{-}H}$= 17.2, $J_{H\text{-}H}$= 10.3 Hz), 7.22-7.56 (m, 4H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ= 56.8, 59.6, 119.6, 122.4, 125.6, 129.8, 130.0, 131.0, 136.4, 140.3.

2-(2-Methoxyphenyl)-2-vinyloxirane (2i). Colorless oil (1.37 g, 77% using 10 mmol of the corresponding α-bromoacetophenone). ^{1}H NMR (400 MHz, $CDCl_3$), δ= 2.89 (d, 1H, CH_2, $J_{H\text{-}H}$= 5.5 Hz,), 2.96 (d, 1H, CH_2, $J_{H\text{-}H}$= 5.5 Hz), 3.73 (s, 3H, CH_3), 4.97 (d, 1H,

CH_2=, J_{H-H}= 17.1), 5.10 (d 1H, CH_2=, J_{H-H}= 10.6), 5.79 (dd, 1H, CH=, J_{H-H}= 17.1, J_{H-H}= 10.6 Hz), 6.78-6.86 (m, 2H, CH=), 7.25-7.28 (m, 2H, CH=) . ^{13}C NMR (100.6 MHz, $CDCl_3$), δ= 55.4, 56.0, 58.6, 110.5, 117.7, 120.5, 126.4, 128.9, 129.3, 138.1, 157.4.

Preparation of 2-((benzyloxy)methyl)-2-vinyloxirane (2j)

Following a modified procedure from the literature[14] a solution of 2-((benzyloxy)methyl)oxirane (10.0 mmol)[15] in $CHCl_3$ (100 ml) was treated with concentrated HCl (30 mL) then stirred at room temperature until no starting material was observed (TLC). The organic phase was then washed with saturated aqueous $NaHCO_3$ and water and subsequently evaporated. The resulting crude of 1-(benzyloxy)-3-chloropropan-2-ol was used in the next step without further purification.

Then, to a stirred solution of 1-(benzyloxy)-3-chloropropan-2-ol (5.3 mmol) in acetone (11.6 mL) at 5 °C, a solution of H_2CrO_3 (prepared from H_2SO_4 (0.6 mL), CrO_3 (771 mg) and water (1.4 mL)) was added dropwise over 2 h. Next, the mixture was stirred until no starting product was observed (TLC) and subsequently quenched by the dropwise addition of 2-propanol (1.6 mL). The inorganic precipitate was then filtered off and washed with acetone (2x6 mL). The solvent was evaporated and to the resulting crude product water (70 mL) was added. The mixture was extracted with $CHCl_3$ (3x6 mL) and the organic layer washed with water (3x5 mL), dried over anhydrous Mg_2SO_4 and evaporated. The resulting crude 1-(benzyloxy)-3-chloropropan-2-ol was used in the next step without further purification. Then, the corresponding vinyl epoxide was prepared by the same means as in Section 5.1.4.2. Colorless oil (480 mg, 25% over 3 steps). ^{1}H NMR (400 MHz, $CDCl_3$), δ= 2.71 (d, 1H, CH_2, J_{H-H}= 6.3 Hz,), 2.94 (d, 1H, CH_2, J_{H-H}= 6.3 Hz), 3.63 (d, 1H, CH_2, J_{H-H}= 10.9 Hz), 3.77 (d, 1H, CH_2, J_{H-H}= 10.9 Hz), 4.57 (d, 1H, CH_2, J_{H-H}= 11.9 Hz), 4.61 (dd, 1H, CH_2, J_{H-H}= 20.9 Hz, J_{H-H}= 11.9 Hz), 5.28 (d, 1H, CH_2=, J_{H-H}= 11.0 Hz), 5.46 (d, 1H, CH_2=, J_{H-H}= 17.3 Hz), 5.86 (dd, 1H, CH=, J_{H-H}= 17.3, J_{H-H}= 11.0 Hz), 7.25-7.37 (m, 5H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ= 52.9, 57.6, 71.2, 73.2, 117.5, 127.7, 127.8, 127.9, 128.4, 134.9, 137.8.

SI-12. Isolation and characterization details of tetrahydrofuran-fused spirocyclic Meldrum's acid derivatives 3

1-(4-Methoxyphenyl)-8,8-dimethyl-4-phenyl-4-vinyl-2,7,9-trioxaspiro[4.5] decane-6,10-dione (3aa). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) as a white solid (91.9 mg, 90%). Enantiomeric excess determined by HPLC using Chiralcel AD column (hexane/2-propanol=90/10, 0.5 mL/min, 220 nm). t_R 31.7 min (*S,R*); t_R 35.7 min (*R,S*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.79 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 4.58 (d, 1H, CH_2, J_{H-H}= 7.8 Hz), 4.81 (d, 1H, CH_2=, J_{H-H}= 17.0 Hz), 5.21 (1H, CH_2=, J_{H-H}= 10.9 Hz), 5.43 (d, 1H, CH_2, J_{H-H}= 7.8 Hz), 5.93 (s, 1H, CH), 6.50 (dd, J_{H-H}= 17.0, 10.9 Hz, 1H), 6.77 (d, 2H, CH=, J_{H-H}= 8.3 Hz), 7.06 (d, CH=, 2H, J_{H-H}= 6.91 Hz), 7.19-7.30 (m, 5H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 27.9, 30.1, 55.2, 64.9, 68.2, 76.4, 87.0, 105.5, 113.9, 115.4, 127.2, 127.3, 127.5, 127.8, 128.5, 129.1, 138.3, 141.0, 160.2, 162.7, 165.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{24}O_6Na$ 431.1465; Found 431.1469. Crystals suitable for X-Ray diffraction were obtained by adding isopropanol to a dichloromethane solution.

8,8-Dimethyl-4-phenyl-1-(4-(trifluoromethyl)phenyl)-4-vinyl-2,7,9-trioxaspiro-[4.5]decane-6,10-dione (3ba). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 10:1) as a white solid (110.4 mg, 99%). Enantiomeric excess determined by HPLC using Chiralcel IA column (hexane/2-propanol=95/5, 1 mL/min, 220 nm). t_R 8.4 min (*R,S*); t_R 10.2 min (*S,R*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.83 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 4.60 (d, 1H, CH_2=, J_{H-H} 8.6 Hz), 4.93 (d, 1H, CH_2=, J_{H-H}= 16.9 Hz), 5.28 (d, 1H, CH_2=, J_{H-H}= 11.1 Hz), 5.46 (d, 1H, CH_2, J_{H-H} 8.6 Hz), 6.05 (s, 1H, CH), 6.50 (dd, 1H, CH_2, J_{H-H}= 16.9, J_{H-H}= 11.1 Hz), 7.09-7.11 (m, 2H, CH=), 7.24-7.28 (m, 4H, CH=), 7.51 (s, 3H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 27.7, 30.5, 64.8, 68.3, 76.2, 86.0, 105.7, 115.8, 116.2, 125.4, 125.5, 127.4, 128.0, 128.2, 128.6, 137.3, 140.1, 140.6, 162.4, 165.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$), δ: -62.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{21}F_3O_5Na$ 469.1233; Found 469.1238.

8,8-Dimethyl-4-phenyl-1-(*p*-tolyl)-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (3ca). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 10:1) as a white solid (97.1 mg, 99%). Enantiomeric excess determined

by HPLC using Chiralcel OX-H column (hexane/2-propanol=95/5, flow 1 mL/min, 220 nm). t_R 12.4 min (*S,R*); t_R 18.2 min (*R,S*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.77 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 2.23 (s, 3H, CH_3), 4.58 (d, 1H, CH_2, J_{H-H}= 7.9 Hz), 4.82 (d, 1H, CH_2=, J_{H-H}= 16.2 Hz), 5.21 (d, CH_2=, 1H, J_{H-H}= 10.3 Hz), 5.44 (d, CH_2, 1H, J_{H-H}= 7.9 Hz), 5.95 (s, 1H, CH), 6.51 (dd, 1H, CH=, J_{H-H}= 16.2, J_{H-H}= 10.3 Hz), 7.04-7.08 (m, 4H, CH=), 7.19-7.26 (m, 5H, CH=). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$), δ: 21.2, 28.0, 30.1, 64.9, 68.2, 76.4, 87.1, 105.5, 115.4, 127.2, 127.5, 127.8, 128.5, 129.2, 132.5, 138.2, 139.0, 141.0, 162.6, 165.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{24}O_5Na$ 415.1516; Found 415.1621.

1-(4-Bromophenyl)-8,8-dimethyl-4-phenyl-4-vinyl-2,7,9-trioxaspiro[4.5] decane-6,10-dione (3da). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 10:1) as a white solid (112.0 mg, 98%). Enantiomeric excess determined by HPLC using Chiralcel AD column (hexane/2-propanol=98/2, 1 mL/min, 220 nm). t_R 22.2 min (*R,S*); t_R 28.2 min (*S,R*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.93 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 4.65 (d, 1H, CH_2, J_{H-H}= 7.9 Hz), 4.96 (d, 1H, CH_2=, J_{H-H}= 16.8 Hz), 5.32 (d, 1H, CH_2=, J_{H-H}= 10.3 Hz), 5.50 (d, 1H, CH_2, J_{H-H}= 7.9 Hz), 6.02 (s, 1H, CH), 6.56 (dd, 1H, CH=, J_{H-H}= 16.8, J_{H-H}= 10.3 Hz), 7.14 (d, 2H, CH=, J_{H-H}= 7.2 Hz), 7.29-7.35 (m, 5H, CH=), 7.45 (d, 2H, CH=, J_{H-H}= 7.2 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$), δ: 27.7, 30.5, 64.8, 68.1, 76.2, 86.2, 105.6, 115.9, 123.1, 127.2, 128.1, 128.6, 129.3, 131.6, 134.9, 137.5, 140.3, 162.5, 165.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{21}BrO_5Na$ 479.0465; Found 479.0471.

1-(3-Bromophenyl)-8,8-dimethyl-4-phenyl-4-vinyl-2,7,9-trioxaspiro[4.5] decane-6,10-dione (3ea). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 10:1) as a white solid (112.1 mg, 98%). Enantiomeric excess determined by HPLC using Chiralcel AD column (hexane/2-propanol=98/2, 1 mL/min, 220 nm). t_R 15.3 min (*R,S*); t_R 25.6 min (*S,R*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.99 (s, 3H, CH_3), 1.49 (s, 3H, CH_3), 4.67 (d, 1H, CH_2, J_{H-H}= 8.1 Hz), 4.98 (d, 1H, CH_2=, J_{H-H}= 17.3 Hz), 5.35 (d, 1H, CH_2=, J_{H-H}= 11.0 Hz), 5.53 (d, 1H, CH_2, J_{H-H}= 8.1 Hz), 6.06 (s, 1H, CH), 6.58 (dd, 1H, CH=, J_{H-H}= 17.3, J_{H-H}= 11.0 Hz), 7.17-7.46 (m, 8H, CH=), 7.60 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 27.8, 30.5, 64.8, 68.2, 76.3, 86.0, 105.7, 116.0, 122.6, 126.1, 127.3, 128.1, 128.6 (2C), 130.1, 130.5, 132.2, 137.4, 138.3, 140.3, 162.4, 165.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{21}BrO_5Na$ 479.0465; Found 479.0470.

8,8-Dimethyl-1-(naphthalen-2-yl)-4-phenyl-4-vinyl-2,7,9-trioxaspiro[4.5] decane-6,10-dione (3fa). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 10:1) as a white solid (105.3 mg, 99%). Enantiomeric excess determined by HPLC using Chiralcel AD column (hexane/2-propanol=80/20, 1 mL/min, 220 nm). t_R 15.5 min (*R,S*); t_R 25.0 min (*S,R*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.72 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 4.72 (d, 1H, CH_2, J_{H-H}= 8.4 Hz), 4.97 (d, 1H, CH_2=, J_{H-H}= 16.5 Hz), 5.34 (d, 1H, CH_2=, J_{H-H}= 10.3 Hz), 5.60 (d, 1H, CH_2, J_{H-H}= 8.4 Hz), 6.26 (s, 1H, CH), 6.64 (dd, 1H, CH=, J_{H-H}= 16.5, J_{H-H}= 10.3 Hz), 7.17-7.19 (m, 2H, CH=), 7.26-7.34 (m, 3H, CH=), 7.46-7.56 (m, 3H, CH=), 7.79-7.81 (m, 3H, CH=), 7.93 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 27.8, 30.2, 64.9, 68.3, 76.4. 87.1, 87.2, 105.6, 115.7, 124.8, 126.4, 126.5, 127.0, 127.3, 127.6, 127.9, 128.2, 128.3, 128.5, 132.9, 133.2, 133.5, 137.8, 140.7, 140.8, 162.6, 165.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{24}O_5Na$ 451.1516; Found 451.1521.

1-(2-Bromophenyl)-8,8-dimethyl-4-phenyl-4-vinyl-2,7,9-trioxaspiro[4.5] decane-6,10-dione (3ga). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 10:1) as a white solid (112.0 mg, 98%). Enantiomeric excess determined by HPLC using Chiralcel OX-H column (hexane/2-propanol=98/2, 1 mL/min, 220 nm). t_R 16.1 min (*S,R*); t_R 20.2 min (*R,S*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.13 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 4.58 (d, 1H, CH_2, J_{H-H}= 8.4 Hz), 4.73 (d, 1H, CH_2=, J_{H-H}= 17.8 Hz), 5.25 (d, 1H, CH_2=, J_{H-H}= 11.4 Hz), 5.59 (d, 1H, CH_2, J_{H-H}= 8.4 Hz), 6.45 (s, 1H, CH), 6.73 (dd, 1H, CH=, J_{H-H}= 17.8, J_{H-H}= 11.4 Hz), 7.12-7.14 (m, 3H, CH=), 7.26-7.36 (m, 4H, CH=), 7.47 (d, 1H, CH=, J_{H-H}= 7.9 Hz), 7.75 (d, 1H, CH=, J_{H-H}= 7.9 Hz).^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 28.4, 29.9, 66.5, 66.9, 77.5. 85.4, 105.3, 115.3, 122.5, 127.4, 127.7, 128.5, 130.4, 132.0, 132.4, 136.1, 137.6, 141.2 (2C), 162.8, 164.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{21}BrO_5Na$ 479.0465; Found 479.0470.

8,8-Dimethyl-1-(naphthalen-1-yl)-4-phenyl-4-vinyl-2,7,9-trioxaspiro[4.5] decane-6,10-dione (3ha). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 10:1) as a white solid (104.5 mg, 98%). Enantiomeric excess determined by HPLC using Chiralcel AD column (hexane/2-propanol=95/5, 1 mL/min, 220 nm). t_R 17.8 min (*R,S*); t_R 35.7 min (*S,R*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.16 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 4.61 (d, 1H, CH_2, J_{H-H}= 7.9 Hz), 4.76 (d, 1H, CH_2=, J_{H-H}= 16.7 Hz), 5.21 (d, 1H, CH_2=, J_{H-H}= 10.4 Hz), 5.59 (d, 1H, CH_2, J_{H-H}= 7.9 Hz), 6.68 (dd, 1H, CH=, J_{H-H}= 16.7, J_{H-H}= 10.4 Hz), 6.84 (s, 1H, CH), 7.02-7.05 (m, 2H, CH=),

7.21-7.23 (m, 2H, CH=), 7.34-7.43 (m, 3H, CH=), 7.67-7.70 (m, 2H, CH=), 7.86-7.94 (m, 2H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 28.2, 29.0, 66.1, 67.6, 77.1, 82.8, 105.1, 115.1, 123.0, 125.6, 125.7, 126.9, 127.2 (2C), 127.8, 128.5, 128.9, 129.4, 130.6, 131.5, 133.3, 138.2, 141.6, 162.6, 165.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{24}O_5Na$ 451.1516; Found 451.1520.

1-(Furan-2-yl)-8,8-dimethyl-4-phenyl-4-vinyl-2,7,9-trioxaspiro[4.5]-decane-6,10-dione (3ia). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) as a white solid (81.0 mg, 88%). Enantiomeric excess determined by HPLC using Chiralcel AD column (hexane/2-propanol=95/5, 1 mL/min, 220 nm). t_R 14.3 min (*R,S*); t_R 31.6 min (*S,R*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.12 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 4.58 (d, 1H, CH_2, J_{H-H}= 9.2 Hz), 4.87 (d, 1H, CH_2=, J_{H-H}= 16.7 Hz), 5.27 (d, 1H, CH_2=, J_{H-H}= 10.3 Hz), 5.44 (d, 1H, CH_2, J_{H-H}= 9.2 Hz), 6.02 (s, 1H, CH, CH=), 6.35-6.36 (m, 1H, CH=), 6.46-6.53 (m, 2H, CH=), 7.12-7-14 (m, 2H, CH=), 7.26-7.35 (m, 5H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 27.7, 29.5, 64.9, 66.3, 76.2, 81.1, 105.5, 110.7, 111.2, 115.8, 127.2, 128.0, 128.6, 137.5, 140.3, 142.5. 149.0, 162.9, 165.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}O_6Na$ 391.1152; Found 391.1158.

8,8-Dimethyl-4-phenyl-1-(thiophen-2-yl)-4-vinyl-2,7,9-trioxaspiro[4.5] decane-6,10-dione (3ja). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) as a white solid (89.3 mg, 93%). Enantiomeric excess determined by HPLC using Chiralcel IA column (hexane/2-propanol=80/20, 1 mL/min, 220 nm). t_R 7.5 min (*R,S*); t_R 11.1 min (*S,R*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.95 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 4.63 (d, 1H, CH_2, J_{H-H}= 8.2 Hz), 4.93 (d, 1H, CH_2=, J_{H-H}= 17.3 Hz), 5.30 (d, 1H, CH_2=, J_{H-H}= 11.4 Hz), 5.48 (d, 1H, CH_2, J_{H-H}= 8.2 Hz), 6.27 (s, 1H, CH), 6.50 (dd, 1H, CH, J_{H-H}= 17.3, J_{H-H}= 11.4 Hz), 6.94-6.96 (m, 2H, CH=), 7.26-7.32 (m, 4H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 27.8, 30.2, 76.0, 83.5, 105.7, 115.7, 126.6, 127.1, 127.2, 127.3, 128.0, 128.6, 137.9, 138.0, 140.5, 163.1, 165.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}O_5SNa$ 407.0924; Found 407.0929.

1-(*tert*-Butyl)-8,8-dimethyl-4-phenyl-4-vinyl-2,7,9-trioxaspiro[4.5]decane -6,10-dione (3ka). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 10:1) as a white solid (88.7 mg, 99%). Enantiomeric excess determined by HPLC using Chiralcel AD column (98% hexane/2-propanol, flow 0.5 mL/min). t_R 16.8 min (*R,S*); t_R 23.2 min (*S,R*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.93 (s,

9H, CH_3), 1.21 (s, 3H, CH_3), 1.63 (s, 3H, CH_3), 4.33 (d, 1H, J_{H-H}= 7.4 Hz), 4.65 (s, 1H, CH), 4.93 (d, 1H, CH_2, J_{H-H}= 16.8 Hz), 5.23 (d, 1H, CH_2=, J_{H-H}= 11.4 Hz), 5.34 (d, 1H, CH_2, J_{H-H}= 7.4 Hz), 6.59 (dd, 1H, CH=, J_{H-H}= 16.8, J_{H-H}= 11.4 Hz), 7.16-7.26 (m, 5H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 27.1, 29.4, 29.5, 34.6, 62.9, 63.0, 73.2, 94.5, 105.8, 115.6, 128.0, 128.1, 128.5, 128.8, 137.4, 141.2, 143.4, 163.1, 164.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{26}O_5Na$ 381.1674; Found 381.1679.

8,8-Dimethyl-4-phenyl-1-((trimethylsilyl)ethynyl)-4-vinyl-2,7,9-trioxaspiro [4.5]decane-6,10-dione (3la). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 10:1) as a white solid (98.6 mg, 99%). Enantiomeric excess determined by HPLC using Chiralcel OX-H column (hexane/2-propanol= 90/10, 1 mL/min, 220 nm). t_R 5.2 min (*S,R*); t_R 6.5 min (*R,S*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.12 (s, 9H, CH_3), 1.62 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 4.43 (d, 1H, CH_2, J_{H-H}= 8.2 Hz), 4.81 (d, 1H, CH_2=, J_{H-H}= 17.9 Hz), 5.23 (d, 1H, CH_2=, J_{H-H}= 10.8 Hz), 5.36 (d, 1H, CH_2, J_{H-H}= 8.2 Hz), 5.58 (s, 1H, CH), 6.39 (dd, 1H, J_{H-H}= 17.9, J_{H-H}= 10.8 Hz), 7.10-7-12 (m, 2H, CH=), 7.30-7.33 (m, 3H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: -0.5, 27.3, 31.4, 64.7, 67.3, 74.8, 76.6, 95.9, 99.5, 105.4, 116.4, 127.4, 128.2, 128.5, 136.3, 139.4, 163.3, 165.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{26}O_5SiNa$ 421.1442; Found 421.1449.

1-(4-Methoxyphenyl)-8,8-dimethyl-4-(*p*-tolyl)-4-vinyl-2,7,9-trioxaspiro[4.5] decane-6,10-dione (3ab). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) as a white solid (103.5 mg, 98%). Enantiomeric excess determined by HPLC using Chiralcel AD column (hexane/2-propanol=98/2, 1 mL/min, 220 nm). t_R 36.0 min (*R,S*); t_R 46.1 min (*S,R*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.79 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 4.55 (d, 1H, CH_2, J_{H-H}= 7.7 Hz), 4.82 (d, 1H, CH_2=, J_{H-H}= 16.9 Hz), 5.19 (d, 1H, CH_2=, J_{H-H}= 10.0 Hz), 5.39 (d, 1H, CH_2, J_{H-H}= 7.7 Hz), 5.92 (s, 1H, CH), 6.48 (dd, 1H, CH=, J_{H-H}= 16.9, J_{H-H}= 10.0 Hz), 6.77 (d, 2H, CH=, J_{H-H}= 8.7 Hz), 6.94 (d, 2H, CH=, J_{H-H}= 8.3 Hz), 7.05 (d, 2H, CH=, J_{H-H}= 8.3 Hz), 7.28 (d, 2H, CH=, J_{H-H}= 8.7 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$), δ: 21.0, 27.9, 30.2, 55.2, 64.7, 68.3, 76.4, 86.9, 105.4, 113.9, 115.2, 127.0, 127.6, 129.0 (2C), 129.2 (2C), 135.2, 137.5, 141.1, 160.2, 162.8, 165.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{26}O_6Na$ 445.1622; Found 445.1625.

1-(4-Methoxyphenyl)-8,8-dimethyl-4-(4-(trifluoro-methyll)phenyl)-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (3ad). The title compound was isolated through

column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) as a white solid (117.9 mg, 99%). Enantiomeric excess determined by HPLC using Chiralcel IA column (hexane/2-propanol=98/2, 1 mL/min, 220 nm). t_R 31.5 min (*S,R*); t_R 41.1 min (*R,S*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.77 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 3.71 (s, 3H, CH_3), 4.60 (d, 1H, CH_2, J_{H-H}= 8.2 Hz), 4.74 (d, 1H, CH_2=, J_{H-H}= 17.0 Hz), 5.23 (d, 1H, CH_2=, J_{H-H}= 11.1 Hz), 5.41 (d, 1H, CH_2, J_{H-H}= 8.2 Hz), 5.93 (s, 1H), 6.48 (dd, CH=, J_{H-H}= 17.0 Hz, J_{H-H}= 11.1 Hz), 6.78 (d, 2H, CH=, J_{H-H}= 8.7 Hz), 7.19 (d, 2H, CH=, J_{H-H}= 8.7 Hz), 7.28 (d, 2H, CH=, J_{H-H}= 8.7 Hz), 7.52 (d, 2H, CH=, J_{H-H}= 7.4 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 28.1, 30.0, 55.3, 64.8, 67.9, 76.4, 87.2, 105.7, 114.0, 116.0, 125.6, 126.9, 127.6, 129.1, 140.4, 142.6, 160.4, 162.7, 165.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$), δ: -62.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{23}F_3O_6Na$ 499.1339; Found 499.1344.

8,8-Dimethyl-4-(*p*-tolyl)-1-(4-(trifluoromethyl)phenyl)-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (3bb). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 10:1) as a white solid (104.7 mg, 91%). Enantiomeric excess determined by HPLC using Chiralcel AD column (hexane/2-propanol=98/2, 1 mL/min, 220 nm). t_R 8.3 min (*S,R*); t_R 12.5 min (*R,S*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.84 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 4.58 (d, 1H, CH_2, J_{H-H}= 8.1 Hz), 4.94 (d, 1H, CH_2=, J_{H-H}= 17.9 Hz), 5.26 (d, 1H, CH_2=, J_{H-H}= 11.3 Hz), 5.43 (d, 1H, CH_2, J_{H-H}= 8.1 Hz), 6.05 (s, 1H, CH), 6.57 (dd, 1H, CH=, J_{H-H}= 17.9, J_{H-H}= 11.3 Hz), 6.97 (d, 2H, CH=, J_{H-H}= 8.3 Hz), 7.07 (d, 2H, CH=, J_{H-H}= 8.3 Hz), 7.51 (s, 4H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 21.0, 27.7, 30.6, 64.4, 68.3, 76.2, 85.9, 105.9, 115.9, 122.5, 125.4, 127.2, 128.0, 129.2, 131.0, 131.1, 134.1, 138.0, 140.2, 140.3, 162.4, 165.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$), δ: -62.8 HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{23}F_3O_5Na$ 483.1390; Found 4831394.

4-(4-Fluorophenyl)-8,8-dimethyl-1-(4-(trifluoro-methyl)phenyl)-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (3bc). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 10:1) as a white solid (102.1 mg, 88%). Enantiomeric excess determined by HPLC using Chiralcel AD column (hexane/2-propanol=98/2, 1 mL/min, 220 nm). t_R 12.6 min (*R,S*); t_R 15.1 min (*S,R*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.84 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 4.56 (d, 1H, CH_2, J_{H-H}= 8.5 Hz), 4.90 (d, 1H, CH_2=, J_{H-H}= 17.3 Hz), 5.28 (d, 1H, CH_2=, J_{H-H}= 10.6 Hz), 5.42 (d, 1H, CH_2, J_{H-H}= 8.5 Hz), 6.06 (s, 1H, CH), 6.50 (dd, CH, 1H, J_{H-H}= 17.3, J_{H-H}= 10.6

Hz), 6.95-7.19 (m, 4H, CH=), 7.49-7.54 (s, 4H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 27.7, 30.5, 64.4, 68.4, 76.4, 85.9, 105.8, 115.5, 115.7, 116.5, 125.4, 128.0, 129.2, 129.3, 131.1, 131.6, 132.9, 133.0, 139.8, 140.0, 162.4, 165.1. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$), δ: -113.1, -62.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{20}F_4O_5Na$ 487.1139; Found 487.1145.

4-(4-Bromophenyl)-8,8-dimethyl-1-(4-(trifluoro-methyl)phenyl)-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (3be). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 10:1) as a white solid (130.0 mg, 99%). Enantiomeric excess determined by HPLC using Chiralcel AD column (hexane/2-propanol=95/5, 1 mL/min). t_R 8.3 min (*R,S*); t_R 11.5 min (*S,R*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.83 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 4.56 (d, 1H, CH_2, J_{H-H}= 8.5 Hz), 4.89 (d, 1H, CH_2=, J_{H-H}= 16.9 Hz), 5.28 (d, 1H, CH_2=, J_{H-H}= 10.8 Hz), 5.40 (d, 1H, CH_2, J_{H-H}= 8.5 Hz), 6.05 (s, 1H, CH), 6.46 (dd, 1H, CH, J_{H-H}= 16.9, J_{H-H}= 10.8 Hz), 6.97 (d, 2H, CH=, J_{H-H}= 8.6 Hz,), 7.40 (d, 2H, CH=, J_{H-H}= 8.6 Hz), 7.48-7.54 (m, 4H, CH=). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$), δ: 27.8, 30.5, 64.5, 68.1, 76.3, 86.1, 105.6, 116.6, 122.43, 125.5, 128.0, 129.1, 131.2, 131.5, 131.8, 136.3, 139.6, 139.8, 139.9, 162.4, 165.0. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$), δ: -62.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{20}BrF_3O_5Na$ 547.0338; Found 547.0342.

4-(4-(Trifluoromethyl)phenyl)- 8,8-dimethyl-1-(2-bromophenyl)- 4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (3gd). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 10:1) as a white solid (120 mg, 92%). Enantiomeric excess determined by HPLC using Chiralcel AD column (hexane/2-propanol=98/2, 1 mL/min). t_R 13.1 min (*R,S*); t_R 21.8 min (*S,R*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.13 (s, 3H), 1.56 (s, 3H), 4.61 (d, 1H, J_{H-H}= 7.9 Hz), 4.68 (d, 1H, J_{H-H}= 17.1 Hz), 5.29 (d, 1H, J_{H-H}= 10.7 Hz), 5.55 (d, 1H, J_{H-H}= 7.9 Hz), 6.47 (s, 1H), 6.73 (dd, 1H, J_{H-H}= 17.1 Hz, J_{H-H}= 10.7 Hz), 7.17 (td, 1H, J_{H-H}= 7.8 Hz, J_{H-H}= 1.7 Hz), 7.27 (d, 2H, J_{H-H}= 8.3 Hz), 7.35 (m, 1H), 7.49 (dd, 1H, J_{H-H}= 8.0 Hz, J_{H-H}= 1.2 Hz), 7.60 (d, 1H, J_{H-H}= 8.3 Hz), 7.72 (dd, 1H, J_{H-H}= 8.0 Hz, J_{H-H}= 1.2 Hz).^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$), δ: 28.7, 29.8, 66.2, 66.9, 77.5. 85.6, 105.6, 116.0, 122.6, 125.5 (q, J_{C-F}= 32.0 Hz) 127.9, 127.9, 130.2 (q, J_{C-F}= 32.0 Hz), 130.6, 131.8, 132.6, 135.7, 140.6, 142.1, 162.7, 164.1. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$), δ: -62.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{20}BrF_3O_5Na$ 547.0338; Found 547.0339.

4-(3-Bromophenyl)- 8,8-dimethyl-1-(2-bromophenyl)- 4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (3gf). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 10:1) as a white solid (101 mg, 76%). Enantiomeric excess determined by HPLC using Chiralcel OX column (hexane/2-propanol=98/2, 1 mL/min). t_R 13.6 min (*R,S*); t_R 15.9 min (*S,R*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.06 (s, 3H), 1.61 (s, 3H), 4.57 (d, 1H, J_{H-H}= 7.9 Hz), 4.71 (d, 1H, J_{H-H}= 17.0 Hz), 5.28 (d, 1H, J_{H-H}= 10.6 Hz), 5.51 (d, 1H, J_{H-H}= 7.9 Hz), 6.45 (s, 1H), 6.69 (dd, 1H, J_{H-H}= 17.0 Hz, J_{H-H}= 10.6 Hz), 7.04 (m, 1H), 7.15 (m, 1H), 7.22 (t, 1H, J_{H-H}= 7.9 Hz), 7.29 (t, 1H, J_{H-H}= 1.8 Hz), 7.35 (m, 1H), 7.43 (m, 1H), 7.48 (dd, 1H, J_{H-H}= 8.0 Hz, J_{H-H}= 1.7 Hz), 7.73 (dd, 1H, J_{H-H}= 8.0 Hz, J_{H-H}= 1.7 Hz). ^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$), δ: 28.6, 30.0, 66.1, 66.8, 77.6. 85.6, 105.6, 115.7, 122.6, 122.7, 126.0, 127.8, 130.2, 130.5, 130.6, 131.2, 132.0, 132.6, 135.8, 140.2, 140.7, 162.8, 164.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{20}Br_2O_5Na$ 556.9570; Found 556.9572.

4-(3-Methoxyphenyl)-8,8-dimethyl-1-(4-(trifluoro-methyl)phenyl)-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (3bg). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 10:1) as a white solid (109.5 mg, 92%). Enantiomeric excess determined by HPLC using Chiralcel AD column (hexane/2-propanol= 95/5, 1 mL/min, 220 nm). t_R 11.1 min (*R,S*); t_R 13.8 min (*S,R*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.83 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 3.72 (s, 3H, CH_3), 4.60 (d, 1H, CH_2, J_{H-H}= 7.9 Hz), 4.97 (d, 1H, CH_2=, J_{H-H}= 16.8 Hz), 5.27 (d, 1H, CH_2=, J_{H-H}= 10.9 Hz), 5.41 (d, 1H, CH_2, J_{H-H}= 7.0 Hz), 6.03 (s, 1H, CH), 6.45 (dd, 1H, CH=, J_{H-H}= 16.8, J_{H-H}= 10.9 Hz), 6.64-7.77 (m, 3H, CH=), 7.17-7.21 (m, 1H, CH=), 7.49-7.54 (m, 4H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 27.6, 30.5, 55.2, 64.7, 68.1, 76.9, 86.1, 105.8, 112.2, 114.6, 116.1, 119.5, 125.4, 128.0, 129.7, 131.1, 131.4, 138.9, 139.9, 140.1, 159.5, 162.3, 165.1. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$), δ: -62.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{23}F_3O_6Na$ 499.1339; Found 499.1342.

1-(4-Methoxyphenyl)-8,8-dimethyl-4-(naphthalen-2-yl)-4-vinyl-2,7,9-tri oxaspiro[4.5]decane-6,10-dione (3ah). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) as a white solid (108.8 mg, 95%). Enantiomeric excess determined by HPLC using Chiralcel OJ-H column (hexane/2-propanol=95/5, 1 mL/min). t_R 29.6 min (*R,S*); t_R 37.6 min (*S,R*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.88 (s, 3H, CH_3), 1.54 (s, 3H, CH_3), 3.80 (s, 3H, CH_3), 4.77 (d, 1H, CH_2, J_{H-H}= 8.1 Hz), 4.89 (d, 1H, CH_2=, J_{H-H}= 16.7 Hz), 5.32 (d, 1H, CH_2=, J_{H-H}= 10.4

Hz), 5.67 (d, 1H, CH_2, J_{H-H}= 8.1 Hz), 6.09 (s, 1H, CH), 6.69 (dd, 1H, CH=, J_{H-H}= 16.7, J_{H-H}= 10.4 Hz), 6.87 (d, 2H, CH=, J_{H-H}= 9.1 Hz), 7.25-7.27 (m, 1H, CH=), 7.40 (d, 2H, CH=, J_{H-H}= 8.3 Hz), 7.50-7.53 (m, 2H, CH=), 7.63 (s, 1H, CH=), 7.79-7.85 (m, 3H, CH=). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$), δ: 28.0, 30.2, 55.3, 65.1, 68.2, 77.2, 87.1, 105.6, 114.0, 115.6, 125.1, 126.2, 126.5, 126.6, 127.5, 127.9, 128.3, 129.1, 132.5, 133.0, 135.6, 140.9, 160.3, 162.7, 165.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{26}O_6Na$ 481.1622; Found 481.1628.

8,8-Dimethyl-4-(naphthalen-2-yl)-1-(4-(trifluoromethyl)phenyl)-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (3bh). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 10:1) as a white solid (122.8 mg, 99%). Enantiomeric excess determined by HPLC using Chiralcel AD column (hexane/2-propanol=95/5, 1 mL, min, 220 nm). t_R 10.8 min (*R,S*); t_R 14.7 min (*S,R*). ^1H NMR (400 MHz, $CDCl_3$), δ: 0.84 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 4.70 (d, 1H, CH_2, J_{H-H}= 8.1 Hz), 4.93 (d, 1H, CH_2=, J_{H-H}= 16.8 Hz), 5.29 (d, 1H, CH_2=, J_{H-H}= 10.7 Hz), 5.61 (d, 1H, CH_2, J_{H-H}= 8.1 Hz), 6.12 (s, 1H, CH), 6.60 (dd, 1H,CH=, J_{H-H}= 16.8, J_{H-H}= 10.7 Hz), 7.19-7.22 (m, 1H, CH=), 7.43-7.45 (m, 2H, CH=), 7.53-7.56 (m, 5H, CH=), 7.71-7.76 (m, 3H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 27.7, 30.5, 65.1, 68.2, 76.6, 86.2, 105.8, 116.4, 125.1, 125.5, 126.5, 126.7, 127.6, 128.0, 128.3, 132.6, 132.9, 134.6, 140.1, 162.4, 165.7. $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$), δ: -62.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{23}F_3O_5Na$ 519.1390; Found 519.1392.

4-(2-Methoxyphenyl)- 8,8-dimethyl-1-(2-bromophenyl)- 4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (3gi). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 10:1) as a white solid (114 mg, 94%). Enantiomeric excess determined by HPLC using Chiralcel IA column (hexane/2-propanol=98/2, 1 mL/min). t_R 23.6 min (*R,S*); t_R 28.8 min (*S,R*). ^1H NMR (400 MHz, $CDCl_3$), δ: 0.92 (s, 3H), 1.56 (s, 3H), 3.72 (s, 3H), 4.66 (d, 1H, J_{H-H}= 7.8 Hz), 4.72 (d, 1H, J_{H-H}= 16.5 Hz), 5.13 (d, 1H, J_{H-H}= 10.6 Hz), 5.64 (d, 1H, J_{H-H}= 7.8 Hz), 6.40 (s, 1H), 6.77 (dd, 1H, J_{H-H}= 16.5, 10.6 Hz), 6.89 (m, 1H), 6.99 (m, 2H), 7.15 (m, 1H), 7.28 (m, 1H), 7.33 (m, 1H), 7.50 (dd, 1H, J_{H-H}= 7.8 Hz, J_{H-H}= 1.2 Hz), 7.67 (dd, 1H, J_{H-H}= 8.3 Hz, J_{H-H}= 1.2 Hz). $^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$), δ: 28.5, 29.4, 54.6, 65.5, 78.8. 86.7, 105.0, 112.2, 121.6, 123.2, 127.9, 128.6, 129.3, 130.6, 131.6, 132.7, 136.1, 140.4, 156.2, 162.7, 164.1. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{23}BrO_6Na$ 509.0570; Found 509.0574.

4-((Benzyloxy)methyl)-8,8-dimethyl-1-(4-(trifluoromethyl)phenyl)-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (3bj). The title compound was isolated through column chromatography (SiO_2, petroleum ether/ethyl acetate 4:1) as a white solid (120.1 mg, 98%). Enantiomeric excess determined by HPLC using Chiralcel IA column (hexane/2-propanol=98/2, 0.5 mL/min, 220 nm). t_R 27.9 min (*S,S*); t_R 31.7 min (*R,R*). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.21 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 3.56 (d, 1H, CH_2, J_{H-H}= 8.7 Hz), 3.82 (d, J_{H-H}= 9.7 Hz, 1H), 4.04 (m, 2H, CH_2), 4.24 (d, 1H, CH_2, J_{H-H}= 11.2 Hz), 4.33 (d, 1H, CH_2, J_{H-H}= 11.2 Hz), 5.34 (m, 2H, CH_2), 5.74 (s, 1H), 6.11 (dd, 1H, CH=, J_{H-H}= 17.5, J_{H-H}= 10.5 Hz), 7.21-7.22 (m, 5H, CH=), 7.36 (d, 1H, CH=, J_{H-H}= 7.8 Hz), 7.50 (d, 2H, CH=, J_{H-H}= 7.8 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 28.3, 29.6, 60.9, 64.9, 72.3, 73.4, 74.9, 89.5, 106.0, 117.6, 122.5, 125.1, 125.2, 126.5, 128.0, 128.3, 128.5, 130.1, 130.4, 130.7, 131.1, 136.7, 136.8, 139.9, 163.4, 166.4. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$), δ: -62.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{25}F_3O_6Na$ 513.1495; Found 513.1501.

SI-13. Synthesis and characterization details of new achiral phosphoramidite ligands L_{10} and L_{11}

Synthesis of *N*-benzhydryl-*N*-methyldibenzo[d,f][1,3,2]dioxaphosphepin-6-amine (L_{10}). *N*-methyl-1,1-diphenylmethanamine (395 mg, 2 mmol), was dried azeotropically with dry toluene (3 x 5 mL), then was solved in dry CH_2Cl_2 and cooled to 0 ºC. Then triethylamine (1.39 ml, 10 mmol) and PCl_3 (0,23 mL, 2.6 mmol) were added dropwise in this order. The mixture was stirred during 5 hours. Then, was evaporated and dried azeotropically with toluene to remove traces of PCl_3. Then it was redissolved in dry CH_2Cl_2 and cooled to 0 ºC. Freshly distilled triethylamine (1.39 mL, 10 mmol) and [1,1'-biphenyl]-2,2'-diol (0.37 g, 2 mmol) were added in this order. The mixture was stirred at room temperature overnight. The crude was directly poured into a 500 mL round bottom flask, diluted with dichloromethane, coated with SiO_2 and chromatographed (Hexanes/Ethyl acetate, 5:1). White solid (350 mg, 0.9 mmol, 43%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 149.2. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.34 (d, 3H, CH_3, J_{H-P} = 4.7 Hz), 6.07 (d, 1H, CH, J_{H-P} = 10.3 Hz), 6.85-6.98 (m, 6H, CH=), 7.04-7.14 (m, 6H, CH=), 7.18 (m, 2H, CH=), 7.26 (m, 4H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 28.7, 64.6, 65.1, 121.9, 124.3, 127.1, 127.4, 127.7, 127.9, 128.2, 129.1, 129.6, 129.7, 131.1, 131.2, 140.0, 140.1, 151.8, 151.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{22}NO_2PNa$ 434.1280; Found 434.1278.

Synthesis of *N*-benzhydryl-2,4,8,10-tetra-*tert*-butyl-*N*-methyldibenzo[d,f][1,3,2]-dioxaphosphepin-6-amine (L_{11}). *N*-methyl-1,1-diphenylmethanamine (395 mg, 2 mmol), was dried azeotropically with dry toluene (3 x 5 mL), then was solved in dry CH_2Cl_2 and cooled to 0 ºC. Then freshly distilled triethylamine (1.39 ml, 10 mmol) and PCl_3 (0,23 mL, 2.6 mmol) were added dropwise in this order. The mixture was stirred during 5 hours. Then, was evaporated and dried azeotropically with toluene to remove traces of PCl3. Then it was redissolved in dry CH_2Cl_2 and cooled to 0 ºC. Freshly distilled triethylamine (1.39 mL, 10 mmol) and 3,3',5,5'-tetra-*tert*-butyl-[1,1'-biphenyl]-2,2'-diol (0.82 g, 2 mmol) were added in this order. The mixture was stirred at room temperature overnight. The crude was directly poured into a 500 mL round bottom flask, diluted with dichloromethane, coated with SiO_2 and chromatographed with 100% hexanes. White solid (500 mg, 0.8 mmol, 40%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 146.9. 1H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 18H, CH_3), 1.49 (b, 18H, CH_3), 2.51 (b, 3H, CH_3), 6.03 (b, 1H, CH), 7.07-7.20 (m, 8H, CH=), 7.21-7.35 (b, 4H, CH=), 7.59 (m, 2H, CH=). ^{13}C NMR

(100.6 MHz, $CDCl_3$): δ = 29.6, 30.7, 30.7, 31.3, 34.3, 35.3, 65.6, 124.0, 126.3, 127.0, 129.5, 135.0, 139.9, 140.9, 146.4, 148.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{42}H_{54}NO_2PNa$ 658.3784; Found 658.3781.

SI-14. Synthesis of post-spiroannulation products

Synthesis of ((2*S*,4*R*)-2-(4-methoxyphenyl)-4-phenyl-4-vinyltetrahydrofuran-3,3-diyl)dimethanol (6). A solution of $LiAlH_4$ (70 mg, 1.8 mmol) in dry THF (10 mL) was cooled to 0 ºC. Then, a solution of **3aa** (65 mg, 0.18 mmol) in THF (4 mL) was also prepared. The **3aa** solution was added dropwise over the $LiAlH_4$ one. The reaction was refluxed for 48 h. Then the mixture was filtered through a celite plug and the crude was purified by column chromatography (CH_2Cl_2/MeOH, 95:5). Colorless oil (45 mg, 0.13 mmol, 72%). 1H NMR (400 MHz, $CDCl_3$): δ = 0.43 (m, 1H, OH), 2.60 (m, 1H, OH), 3.30 (dd, 1H, CH_2, J_{H-H} = 12.5 Hz, J_{H-H} = 4.8 Hz), 3.37 (dd, 1H, CH_2 J_{H-H} = 12.5 Hz, J_{H-H} = 8.4 Hz), 3.79 (s, 3H, CH_3), 4.01 (dd, 1H, CH_2, J_{H-H} = 11.8 Hz, J_{H-H} = 5.6 Hz), 4.18 (dd, 1H, CH_2, J_{H-H} = 11.8 Hz, J_{H-H} = 6.7 Hz), 4.33 (d, 1H, CH_2, J_{H-H} = 8.9 Hz), 4.74 (d, 1H, CH_2, J_{H-H} = 8.9 Hz), 4.98 (s, 1H, CH). 4.99 (d, 1H, CH_2=. J_{H-H} = 17.5 Hz), 5.26 (d, 1H, CH_2=, J_{H-H} = 11.0 Hz), 6.63 (dd, 1H, CH=, J_{H-H} = 11.0 Hz, J_{H-H} = 17.5 Hz), 6.88 (d, 2H, CH=, J_{H-H} = 8.7 Hz), 7.25 (m, 1H, CH=), 7.35 (m, 4H, CH=), 7.57 (m, 2H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 55.4, 55.7, 57.6, 64.7, 65.3, 75.5, 85.6, 114.2, 115.3, 126.9, 128.3, 128.4, 128.5, 130.8, 141.4, 141.5, 159.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{24}O_4Na$ 363.1567; Found 363.1563.

Synthesis of hydroxy-acids 7. A solution of $LiAlH_4$ (49.5 mg, 1.30 mmol) in dry THF (8 mL) was cooled to 0 ºC. Then, a solution of **3aa** (213 mg, 0.52 mmol) in THF (4 mL) was also prepared. The **3aa** solution was added dropwise over the $LiAlH_4$ one. The reaction was maintained at room temperature for 2 hours. Then the mixture was filtered through a celite plug and the crude was purified by gradient column chromatography. (Hexanes/AcOEt, 5:1 → 1:1 to CH_2Cl_2/EtOH 10:1). **(2*S*,3*S*,4*R*)-3-(Hydroxymethyl)-2-(4-methoxyphenyl)-4-phenyl-4-vinyltetrahydrofuran-3-carboxylic acid**. White solid (60 mg, 0.17 mmol, 32%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 3H, CH_3), 4.05 (d, 1H, CH_2, J_{H-H} = 12.4 Hz), 4.23 (d, 1H, CH_2, J_{H-H} = 12.4 Hz), 4.58 (d, 1H, CH_2, J_{H-H} = 7.9 Hz), 4.88 (d, 1H, CH_2=, J_{H-H} = 17.2 Hz), 5.03 (d, 1H, CH_2, $^3J_{H-H}$ = 7.9 Hz), 5.22 (s, 1H, CH), 5.24 (d, 1H, CH=, J_{H-H} = 10.6 Hz), 5.51 (b, 2H, OH), 6.27 (dd, 1H, CH=, J_{H-H} = 17.2 Hz, J_{H-H} = 10.6 Hz), 6.76 (d, 2H, CH=, J_{H-H} = 9.0 Hz), 7.24-7.32 (m, 7H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 55.3, 60.6, 64.5, 64.8, 78.0, 86.8, 113.3, 115.6, 126.7, 127.4, 128.5, 128.5, 130.5, 141.5, 141.9, 159.3, 175.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{22}O_5Na$ 377.1359; Found 377.1348. **(2*S*,3*R*,4*R*)-3-(Hydroxymethyl)-2-(4-methoxyphenyl)-4-phenyl-4-vinyltetrahydrofuran-3-carboxylic acid.** White solid

(102 mg, 0.29 mmol, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.41 (s, 1H, OH), 3.75 (s, 3H, CH_3), 4.03 (d, 1H, CH_2, J_{H-H} = 12.3 Hz), 4.22 (d, 1H, CH_2, J_{H-H} = 12.3 Hz), 4.57 (d, 1H, CH_2, J_{H-H} = 7.9 Hz), 4.87 (d, 1H, CH_2=, J_{H-H} = 17.2 Hz), 5.06 (d, 1H, CH_2, J_{H-H} = 7.9 Hz), 5.23 (m, 2H, CH and =CH_2), 5.65 (b, 1H, OH), 6.25 (dd, 1H, CH=, J_{H-H} = 17.2 Hz, J_{H-H} = 10.6 Hz), 6.75 (d, 2H, CH=, J_{H-H}= 8.8 Hz), 7.24-7.31 (m, 7H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 55.2, 60.5, 64.5, 64.6, 77.9, 86.9, 113.2, 115.5, 126.6, 127.4, 128.4, 128.6, 130.6, 141.5, 141.9, 159.2, 175.6.

Synthesis of (2*S*,4*R*)-2-(4-methoxyphenyl)-4-phenyl-4-vinyldihydrofuran-3,3(2H)-dicarboxylic acid (8). 3aa (80 mg, 0.20 mmol) was dissolved in 3 mL of EtOH/10% NaOH aqueous solution (2:1) and was stirred at 80 ºC during 16 h. Then, 20 mL of HCl (2M) were added and the product was extracted with dichloromethane and used without further purification. White solid. (70 mg, 0.19 mmol, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.64 (s, 3H, CH_3), 4.69 (d, 1H, CH_2, J_{H-H} = 8.0 Hz), 4.89 (d, 1H, CH_2, J_{H-H} = 8.0 Hz), 5.10 (d, 1H, CH=, J_{H-H} = 17.1 Hz), 5.26 (d, 1H, CH=, J_{H-H} = 10.7 Hz), 5.96 (s, 1H, CH), 6.18 (dd, 1H, CH=, J_{H-H} = 17.1 Hz, J_{H-H} = 10.7 Hz), 6.74 (d, 2H, CH=, J_{H-H} = 8.8 Hz), 7.28 (m, 1H, CH=), 7.37 (m, 2H, CH=), 7.42 (d, 2H, CH=, J_{H-H} = 8.0 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 42.3, 55.1, 60.9, 71.0, 84.4, 113.2, 116.6, 126.7, 127.8, 128.1, 128.5, 129.2, 140.2, 140.9, 159.3, 172.0, 172.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}O_6Na$ 391.1152; Found 391.1145.

Synthesis of (4*R*,5*S*,8*R*)-5-(4-methoxyphenyl)-8-phenyl-8-vinyl-2,6-dioxaspiro[3.4]octan-1-one (9). To a stirred solution of PPh_3 (118 mg, 0.45 mmol) in THF (5 mL) at 0 ºC, a commercial solution of diethyl azodicarboxylate (0.2 mL, 0.45 mmol) in toluene was added dropwise. Then a solution (2*S*,3*R*,4*R*)-**7** (40 mg, 0.11 mmol) in THF (1mL) was added at the same temperature and it was stirred at 0 ºC for an additional hour. Then, the mixture was stirred at room temperature for 4 hours. The volatiles were evaporated under reduced pressure and the product purified by column chromatography (Hexanes/Ethyl acetate, 4:1). Colorless oil (34 mg, 0.10 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.80 (s, 3H, CH_3), 4.27 (d, 1H, CH_2, J_{H-H} = 6.2 Hz), 4.64 (d, 1H, CH_2, J_{H-H} = 8.6 Hz), 4.70 (d, 1H, CH_2, J_{H-H} = 6.2 Hz), 4.89 (d, 1H, CH_2, J_{H-H} = 8.6 Hz), 5.16 (d, 1H, CH=, J_{H-H} = 17.3 Hz), 5.38 (d, 1H, CH=, J_{H-H} = 10.7 Hz), 6.14 (dd, 1H, CH_2, J_{H-H} = 17.3 Hz, J_{H-H} = 10.7 Hz), 6.91 (d, 2H, CH=, J_{H-H} = 8.7 Hz), 7.28 (m, 3H, CH=), 7.37 (m, 4H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 55.4, 55.6, 62.3, 74.5,

75.7, 83.8, 114.2, 117.2, 126.6, 127.9, 128.0, 128.5, 129.2, 138.5, 139.7, 160.2, 168.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}O_4Na$ 359.1254; Found 359.1260.

Synthesis of (1*R*,3a*R*,4*S*,6a*S*)-1-(iodomethyl)-4-(4-methoxyphenyl)-3-oxo-6a-phenyldihydro-1H,3H-furo[3,4-c]furan-3a(4H)-carboxylic acid (10). 8 (50 mg, 0.14 mmol) and DMAP (1.7 mg, 0.014 mmol), were dissolved in dry CH_2Cl_2 and cooled to 0 ºC. Then NIS (37 mg, 0.16 mmol) was added, and the reaction mixture was protected from light. After two hours, the reaction mixture was quenched using 1 mL of sodium thiosulfate saturated solution. 10 mL of water were added, and the aqueous phase extracted twice with dichloromethane to obtain the pure product. Yellow solid (65 mg, 0.13 mmol, 94 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.69 (dd, 1H, CH-I, $^2J_{H-H}$ = 11.0 Hz, $^3J_{H-H}$ = 6.0 Hz), 2.78 (dd, 1H, CH-I, J_{H-H} = 11.0 Hz, J_{H-H} = 7.7 Hz), 3.77 (s, 3H, CH_3), 4.90 (d, 1H, CH_2, J_{H-H} = 8.6 Hz), 5.06 (d, 1H, CH_2, J_{H-H} = 8.6 Hz), 5.23 (dd, 1H, CH, J_{H-H} = 7.7 Hz, J_{H-H} = 6.0 Hz), 5.68 (s, 1H, CH), 6.83 (d, 1H, CH=, J_{H-H} = 8.8 Hz), 6.96 (b, 2H, CH=), 7.24 (d, 2H, J_{H-H} = 9.0 Hz), 7.33 (m, 3H, CH=). ^{13}C NMR (100.6 MHz, CDCl3): δ = -1.2, 55.3, 66.5, 69.4, 76.2, 85.0, 87.2, 114.1, 126.7, 127.5, 127.6, 128.9, 129.4, 134.0, 160.2, 164.4, 174.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{19}IO_6Na$ 517.0119; Found 517.0116.

Synthesis of (1*S*,4*R*)-4-ethyl-1-(4-methoxyphenyl)-8,8-dimethyl-4-phenyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (12). 3aa (200 mg, 0.49 mmol) and [Ir(cod)(PCy3)(Py)]BAr_F (37.3 mg, 0.025 mmol), were dissolved in dry CH_2Cl_2 (20 mL). H_2 gas was bubbled for 2 minutes (discoloration of the orange solution was observed) and the hydrogen atmosphere was maintained using a rubber balloon that was purged three times. Then the reaction was stirred during three hours at room temperature. The crude was evaporated and purified by flash column chromatography (Hexanes/Ethyl acetate, 5:1). White solid (191 mg, 0.47 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.66 (t, 3H, CH_3, J_{H-H} = 7.2 Hz), 0.90 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 2.03 (m, 1H, CH), 2.39 (m, 1H, CH), 3.75 (s, 3H, CH_3), 4.45 (d, 1H, CH, J_{H-H} = 8.2 Hz), 5.30 (dd, 1H, J_{H-H} = 8.2 Hz, J_{H-H} = 2.3 Hz), 6.04 (s, 1H, CH), 6.81 (d, 2H, CH=, J_{H-H} = 8.7 Hz), 7.13 (d, 2H, CH=, J_{H-H} = 7.0 Hz), 7.24 (d, 1H, CH=, J_{H-H} = 7.0 Hz), 7.29 (m, 2H, CH=), 7.35 (d, 2H, CH=, J_{H-H} = 8.8 Hz). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 9.6, 27.6, 30.3, 30.7, 35.3, 63.6, 69.9, 73.4, 86.2, 105.4, 113.8, 127.3, 127.8, 128.3, 128.6, 129.0, 138.4, 160.0, 163.1, 166.5. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{26}O_6Na$ 433.1622; Found 433.1626.

Synthesis of (*S,Z*)-4-Ethyl-3-(4-methoxybenzylidene)-4-phenyldihydrofuran-2(3H)-one (11). $Sc(OTf)_3$ and **12** (80 mg, 0.19 mmol), were dried under vacuum during 2 hours. Then dry nitromethane (2 mL) was added, and the solution was stirred during 0.5 h at 100 ºC in a pre-heated oil bath. The solvent was evaporated under reduced pressure, and directly purified by column chromatography (Hexanes/Ethyl acetate, 5:1). Yellow oil (27 mg, 0.09 mmol, 45%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.99 (t, 3H, J_{H-H} = 7.4 Hz, CH_3), 2.10 (m, 1H, CH), 2.21 (m, 1H, CH), 3.84 (s, 3H), 4.34 (d, 1H, CH_2, J_{H-H} = 9.1 Hz), 4.54 (d, 1H, J_{H-H} = 9.1 Hz), 6.60 (s, 1H, CH=), 6.89 (d, 1H, J_{H-H} = 8.8 Hz), 7.26-7.30 (m, 1H, CH=), 7.34-7.43 (m, 4H, CH=), 7.91-7.94 (m, 2H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 8.8, 31.3, 52.8, 55.4, 113.6, 126.4, 127.0, 127.1, 128.8, 129.3, 133.3, 141.5, 143.5, 161.0, 169.7. IR (ATR) ν(cm^{-1}) = 2971, 1741 (CO), 1635, 1592, 1506, 1254, 1173, 1116, 1089, 1030, 912, 825, 787, 763, 727, 690, 643, 521. Enantiomeric excess determined by HPLC using Chiralcel OD-H column (90% hexane/2-propanol, flow 1 mL/min). t_R 11.2 min (*R*); t_R 12.4 min (*S*). HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{20}O_3Na$ 331.1305; Found 331.1313.

SI-15. Copies of NMR spectra of new alkylidene Meldrum's acid 1l and vinyl epoxides 2f, 2i and 2j

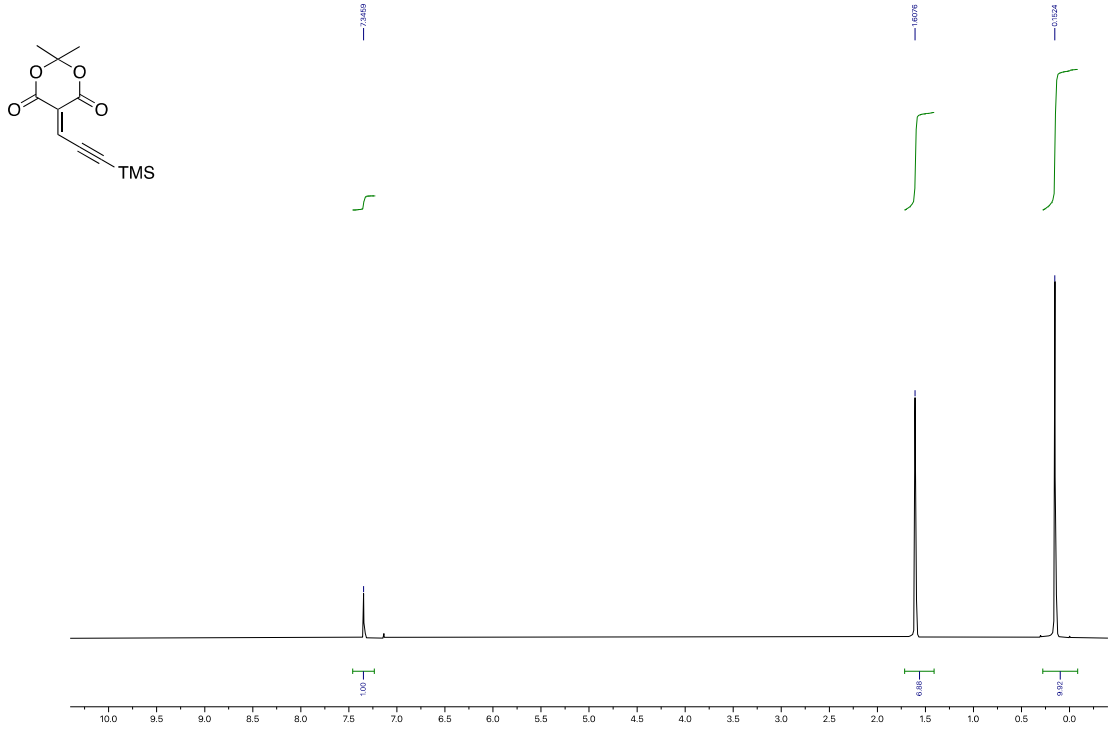


Figure S5. ^{1}H NMR (400 MHz) spectrum of 2,2-dimethyl-5-(3-(trimethylsilyl)prop-2-yn-1-ylidene)-1,3-dioxane-4,6-dione (**1l**) in $CDCl_3$.

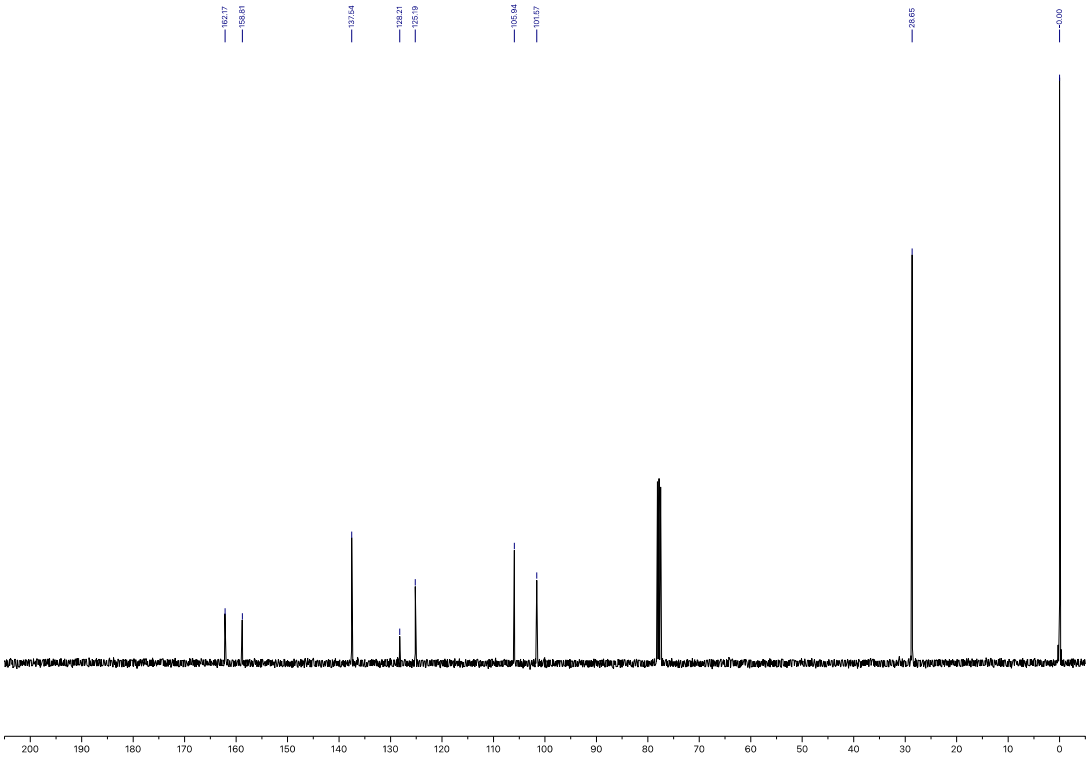


Figure S6. ^{13}C NMR (100.6 MHz) spectrum of **1l** in $CDCl_3$.

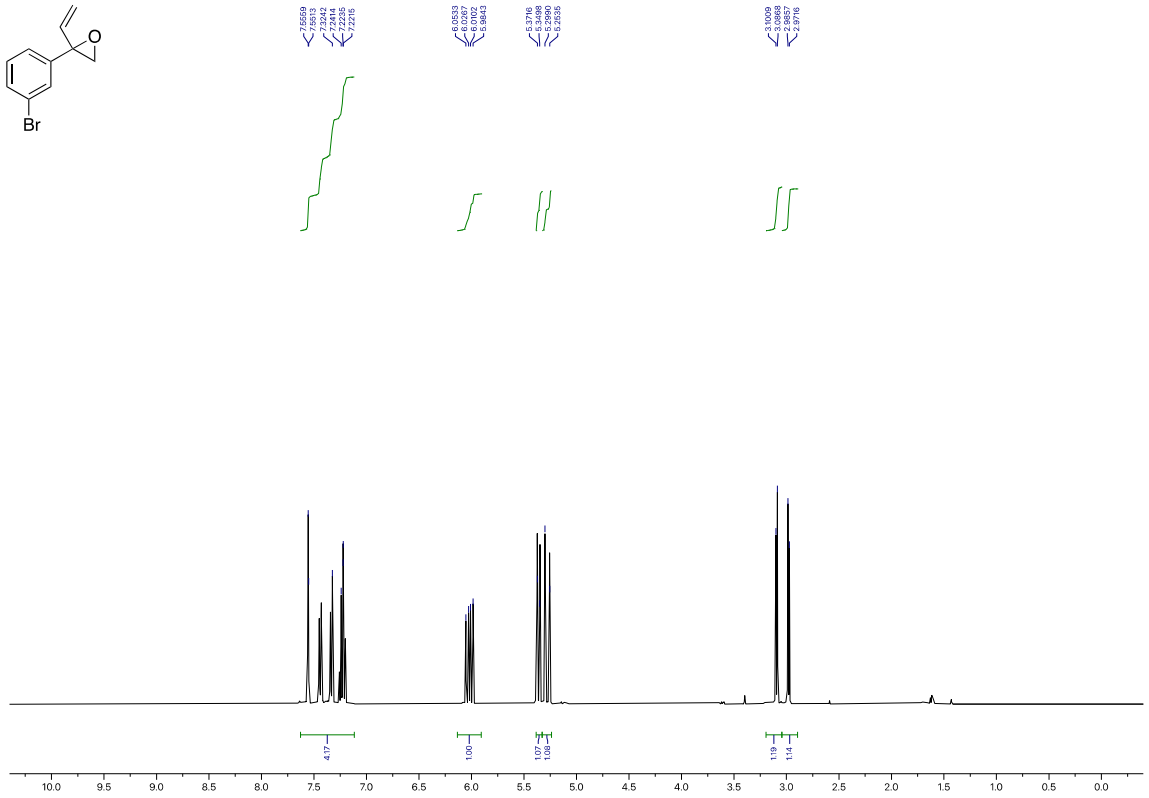


Figure S7. ^{1}H NMR (400 MHz) spectrum of 2-(3-bromophenyl)-2-vinyloxirane (**2f**) in $CDCl_3$.

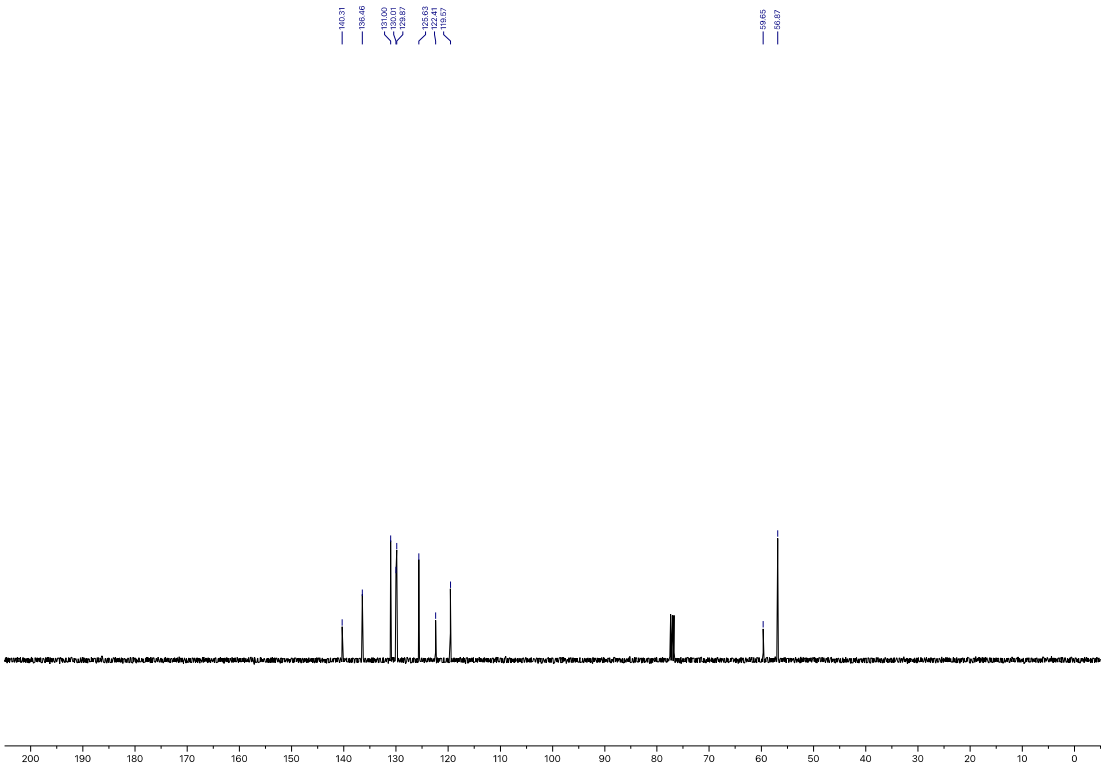


Figure S8. ^{13}C NMR (100.6 MHz) spectrum of **2f** in $CDCl_3$.

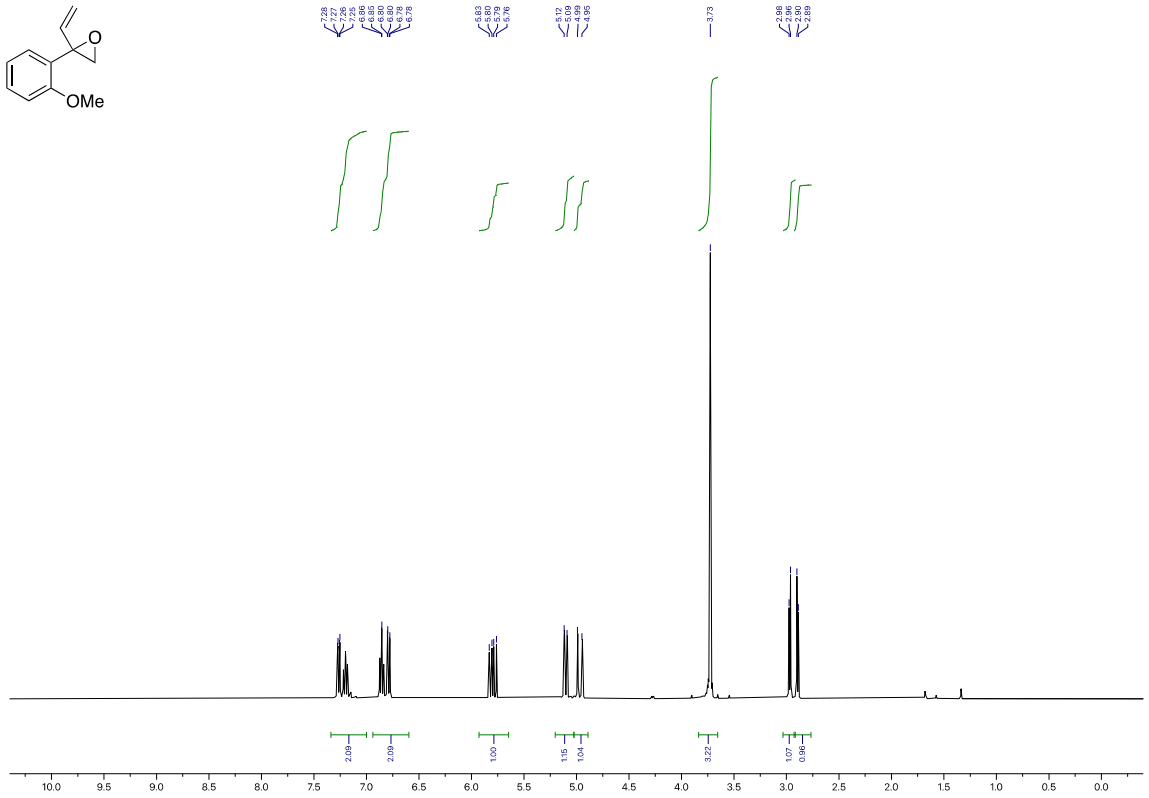


Figure S9. ^{1}H NMR (400 MHz) spectrum of 2-(2-methoxyphenyl)-2-vinyloxirane (**2i**) in $CDCl_3$.

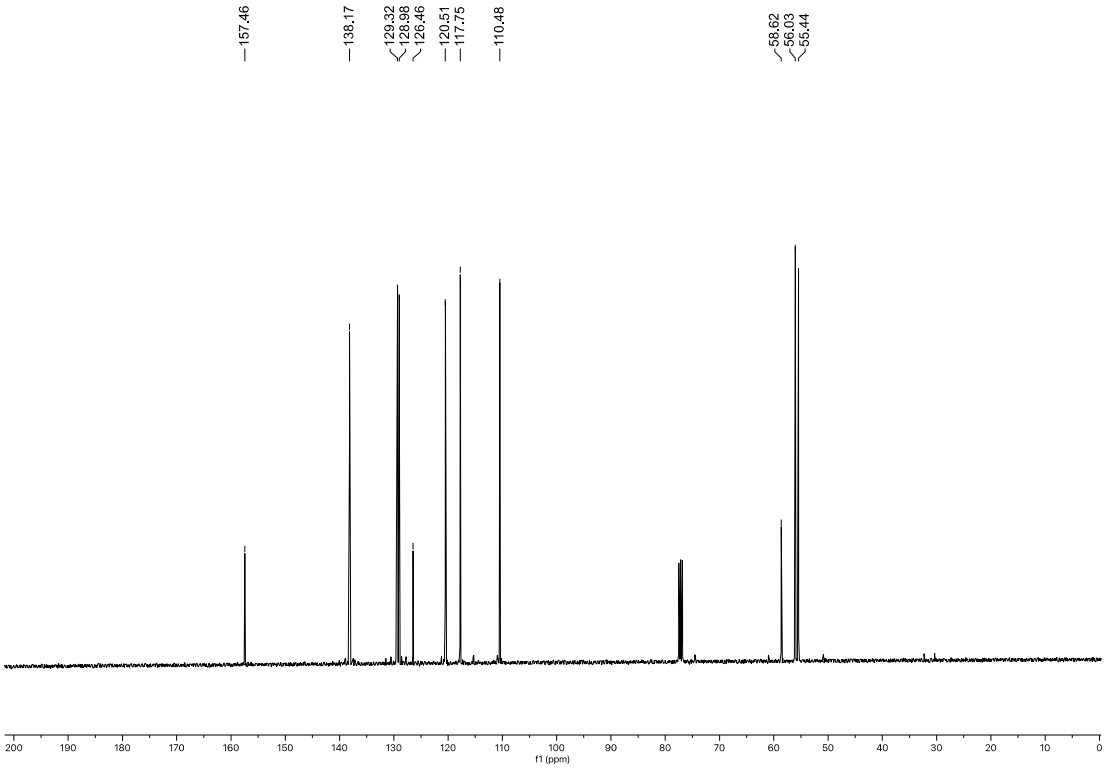


Figure S10. ^{13}C NMR (100.6 MHz) spectrum of **2i** in $CDCl_3$.

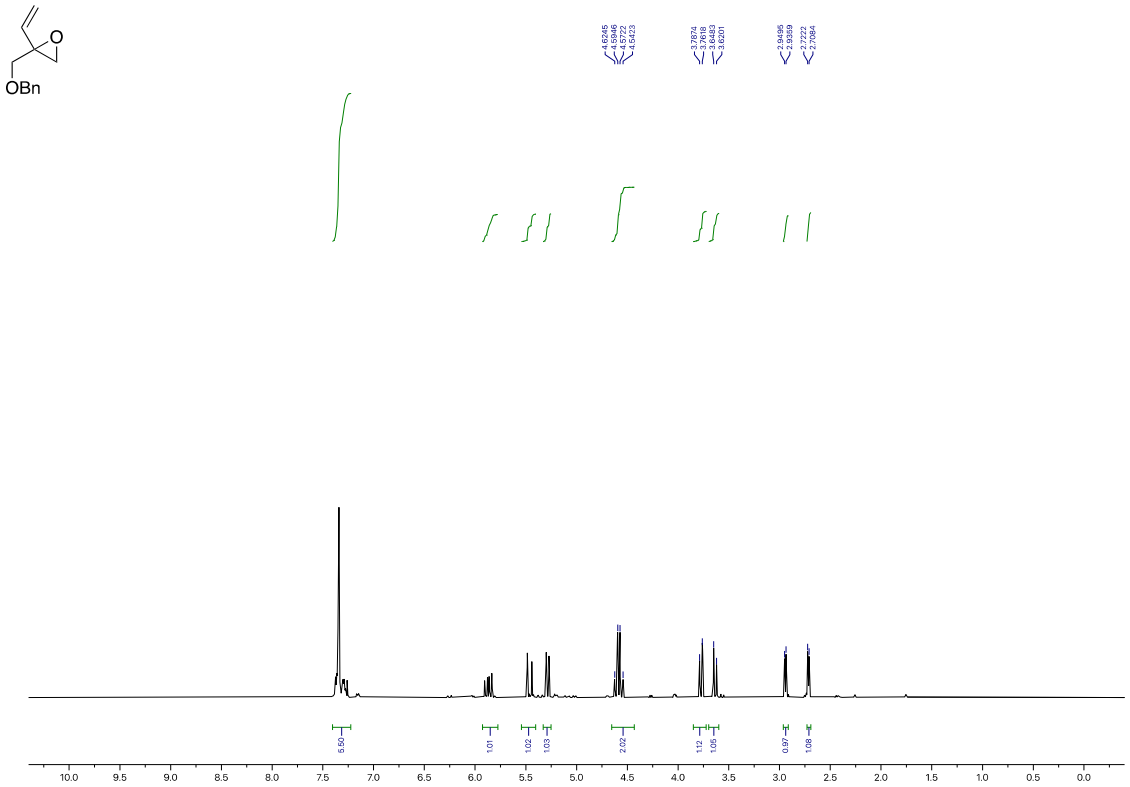


Figure S11. ^{1}H NMR (400 MHz) spectrum of intermediate 2-((benzyloxy)methyl)-2-vinyloxirane (**2j**) in $CDCl_3$.

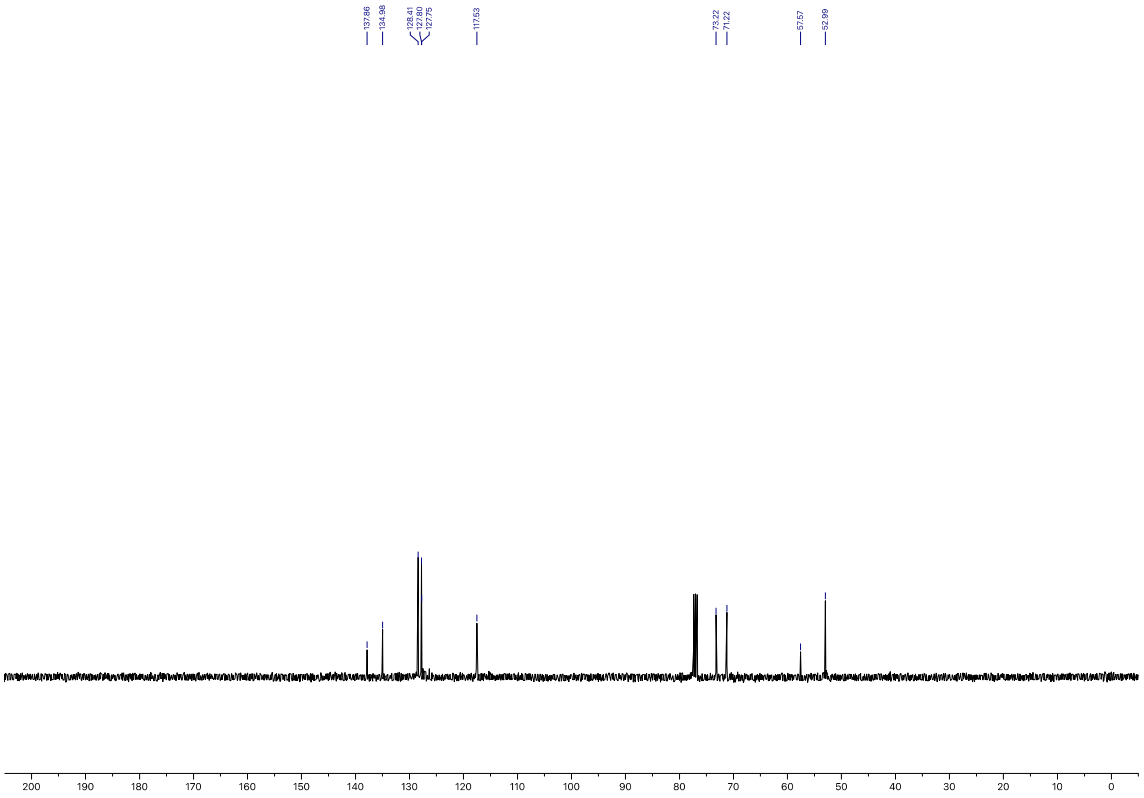


Figure S12. ^{13}C NMR (100.6 MHz) spectrum of **2j** in $CDCl_3$.

SI-16. Copies of NMR spectra and HPLC traces of [3+2]-cycloaddition products 3

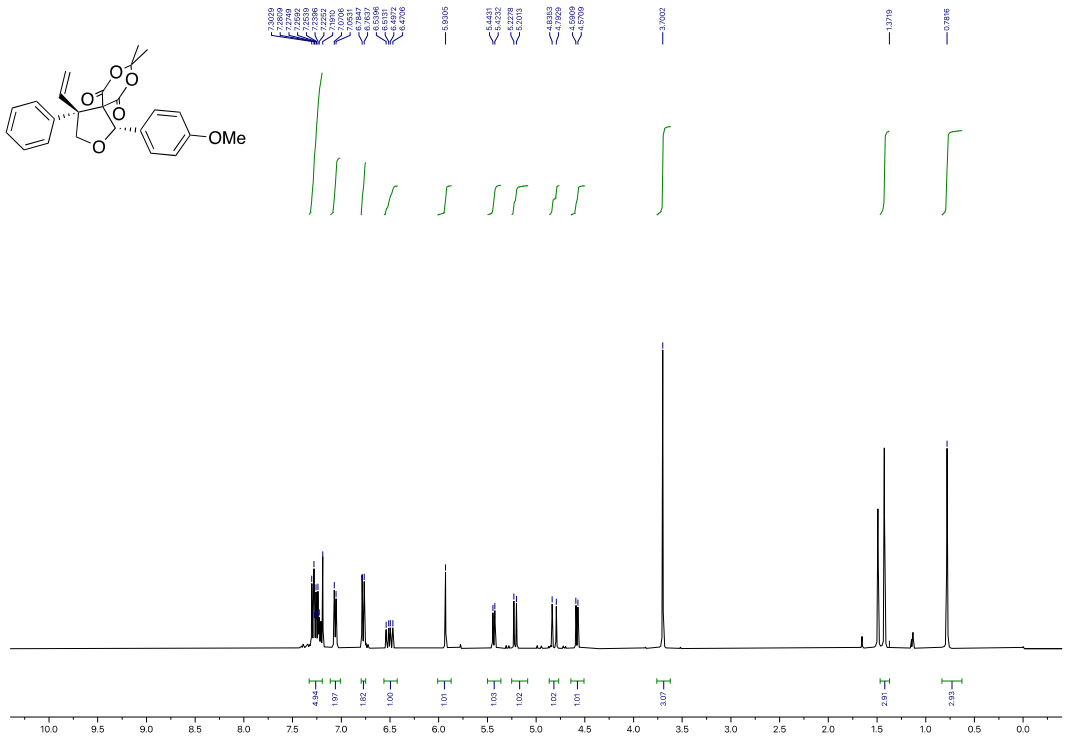


Figure S13. ^{1}H NMR (400 MHz) spectrum of 1-(4-methoxyphenyl)-8,8-dimethyl-4-phenyl-4-vinyl-2,7,9-trioxaspiro[4.5] decane-6,10-dione (**3aa**) in $CDCl_3$.

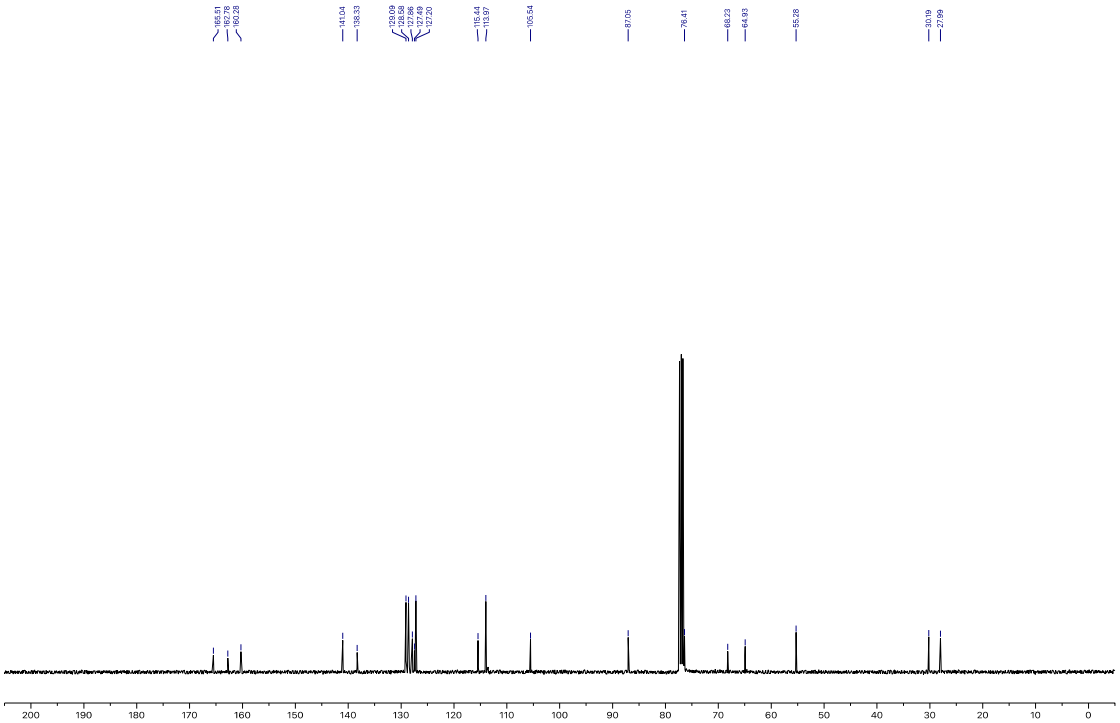
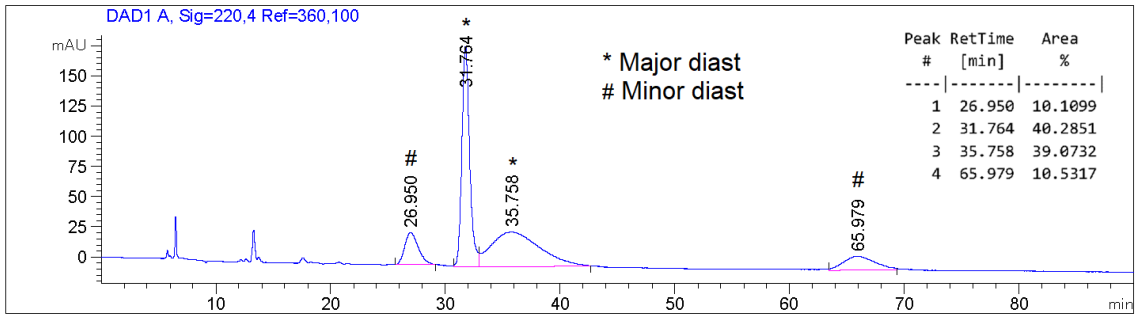
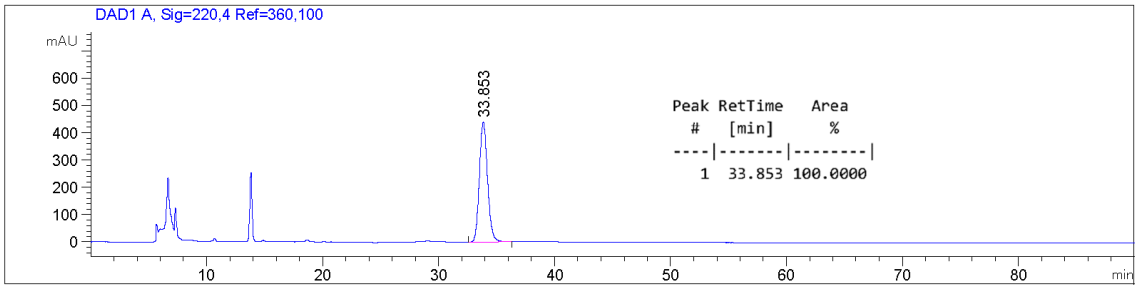


Figure S14. ^{13}C NMR (100.6 MHz) spectrum of **3aa** in $CDCl_3$.

(a)



(b)



(c)

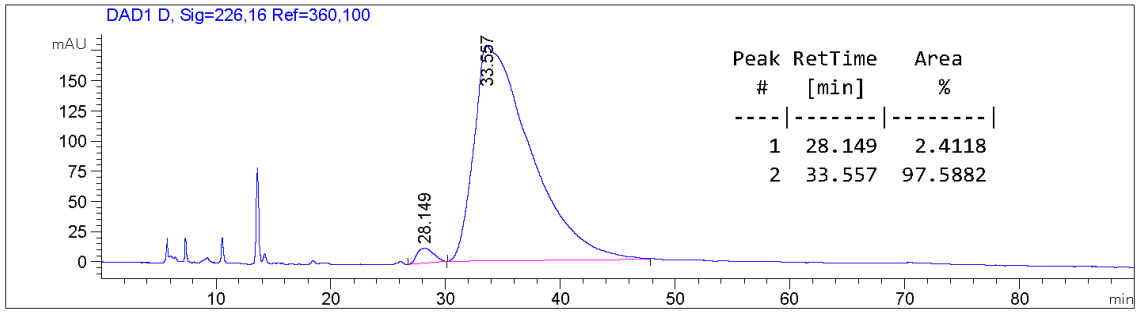


Figure S15. HPLC traces of (a) racemic, (b) enantioenriched product (*S,R*)-**3aa** (from Table 1; entry 14) and (c) enantioenriched product (*R,S*)-**3aa** (from Scheme 3).

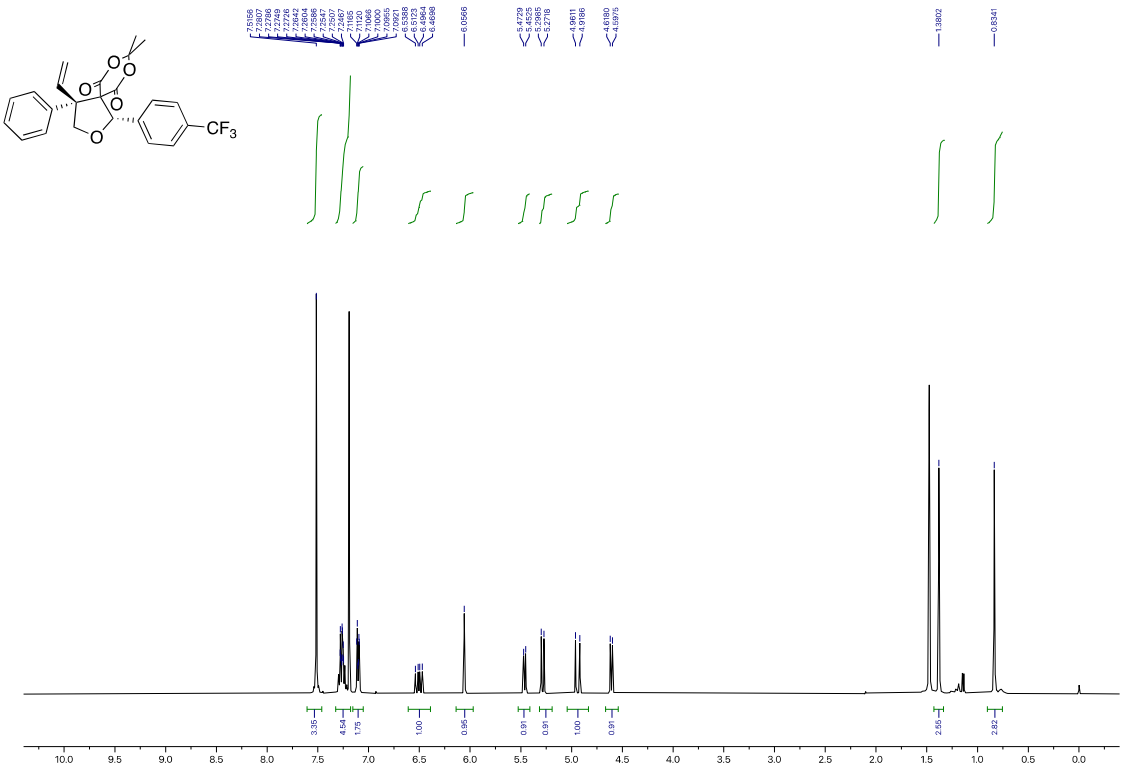


Figure S16. ^{1}H NMR (400 MHz) spectrum of 8,8-dimethyl-4-phenyl-1-(4-(trifluoromethyl)phenyl)-4-vinyl-2,7,9-trioxa spiro[4.5]decane-6,10-dione (**3ba**) in $CDCl_3$.

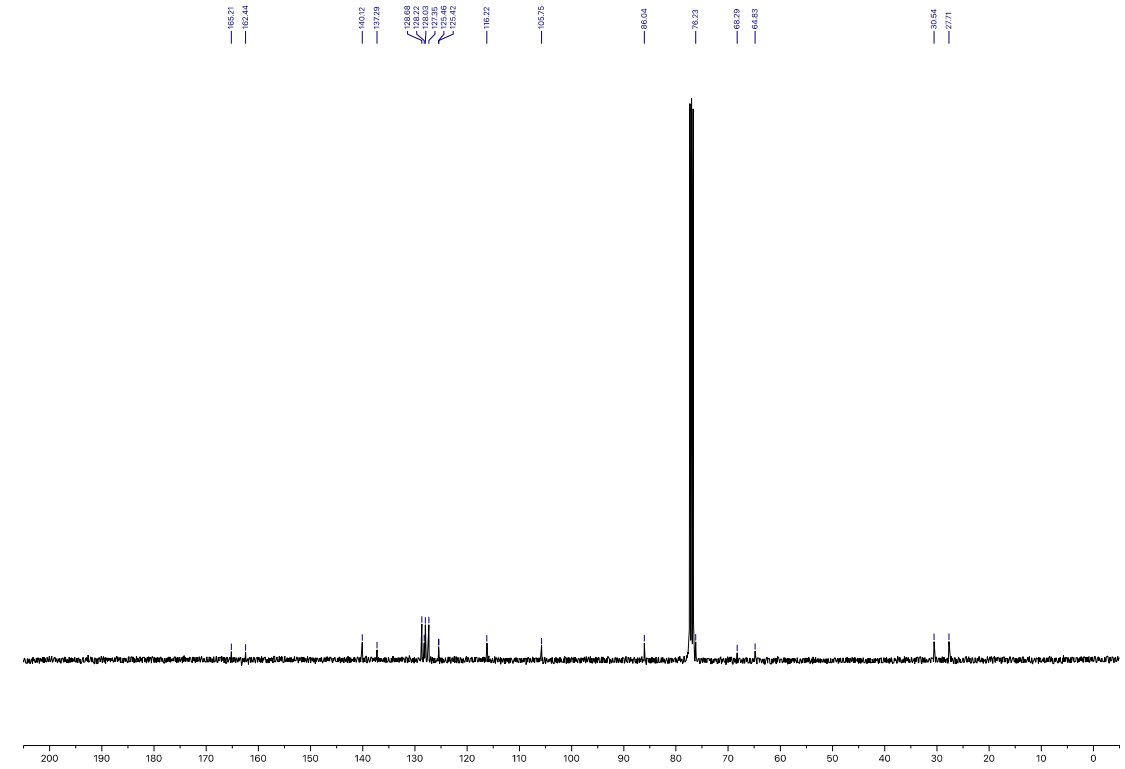


Figure S17. ^{13}C NMR (100.6 MHz) spectrum of **3ba** in $CDCl_3$.

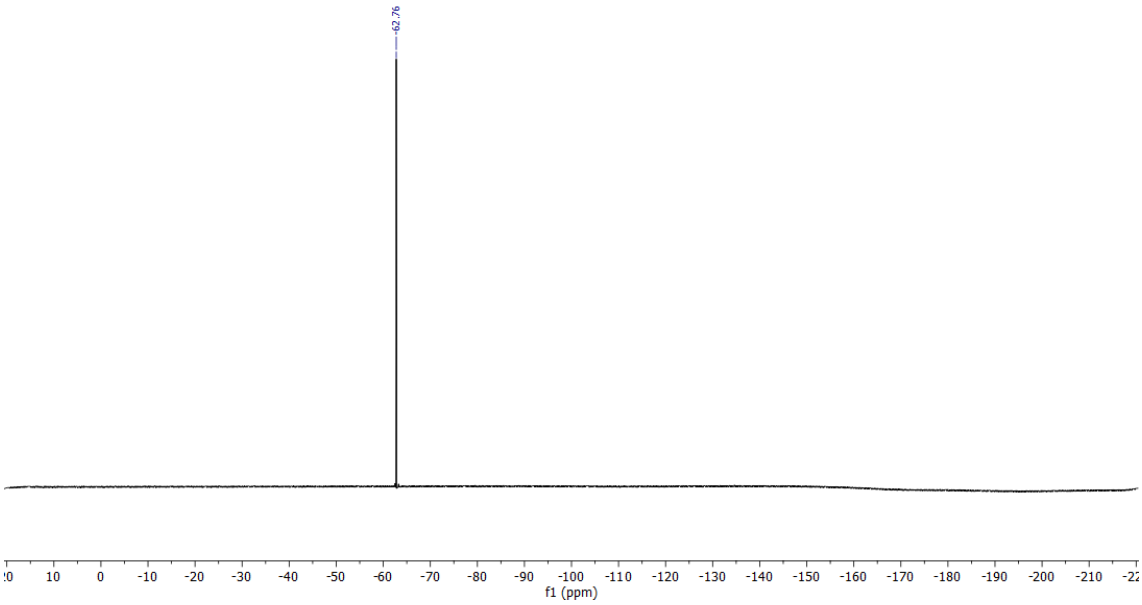
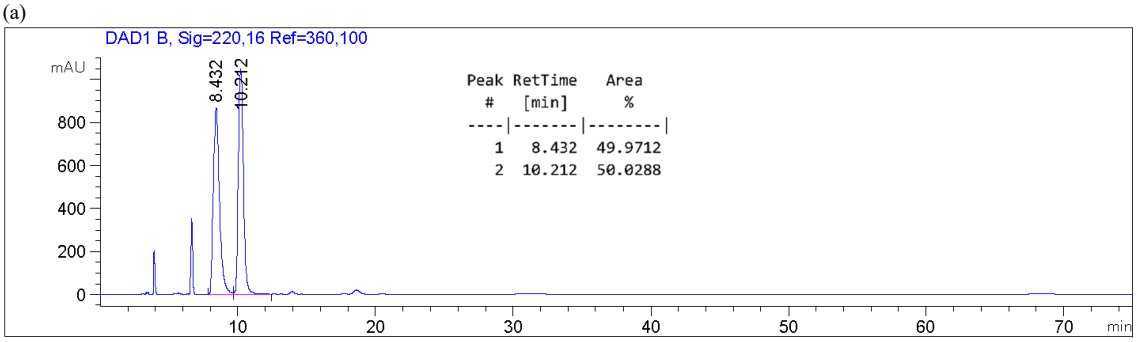
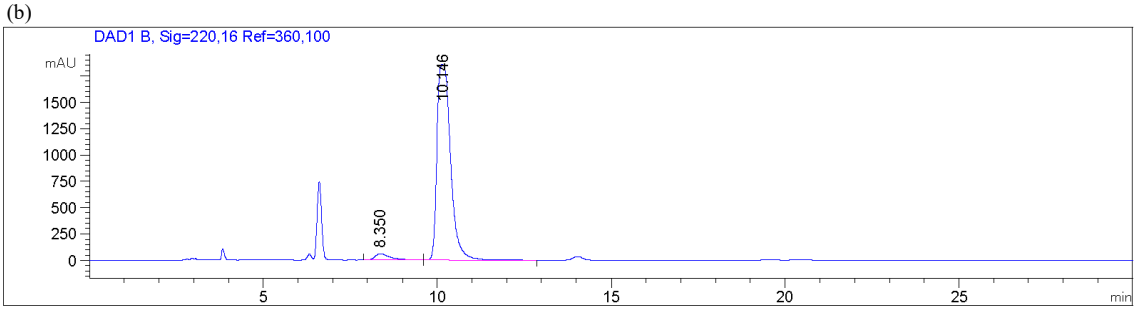


Figure S18. ^{19}F NMR (376 MHz) spectrum of **3ba** in $CDCl_3$.

(a)



(b)



(c)

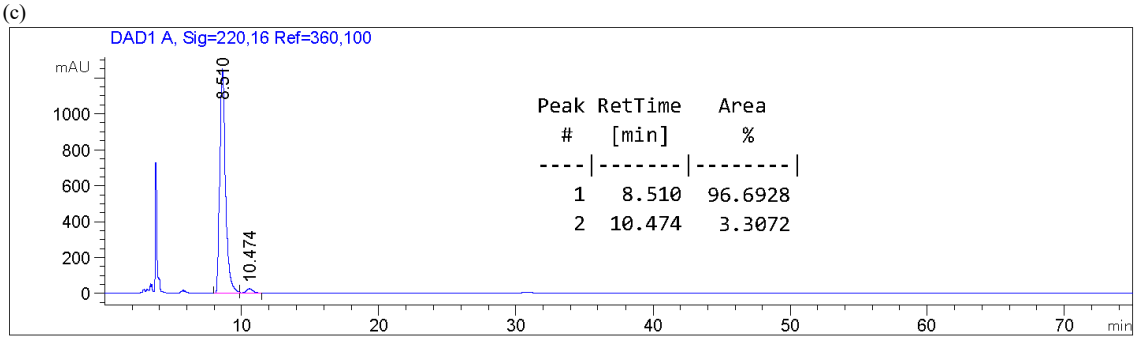


Figure S19. HPLC traces of (a) racemic, (b) enantioenriched product (*S,R*)-**3ba** (from kinetic experiments) and (c) enantioenriched product (*R,S*)-**3ba** (from Scheme 3).

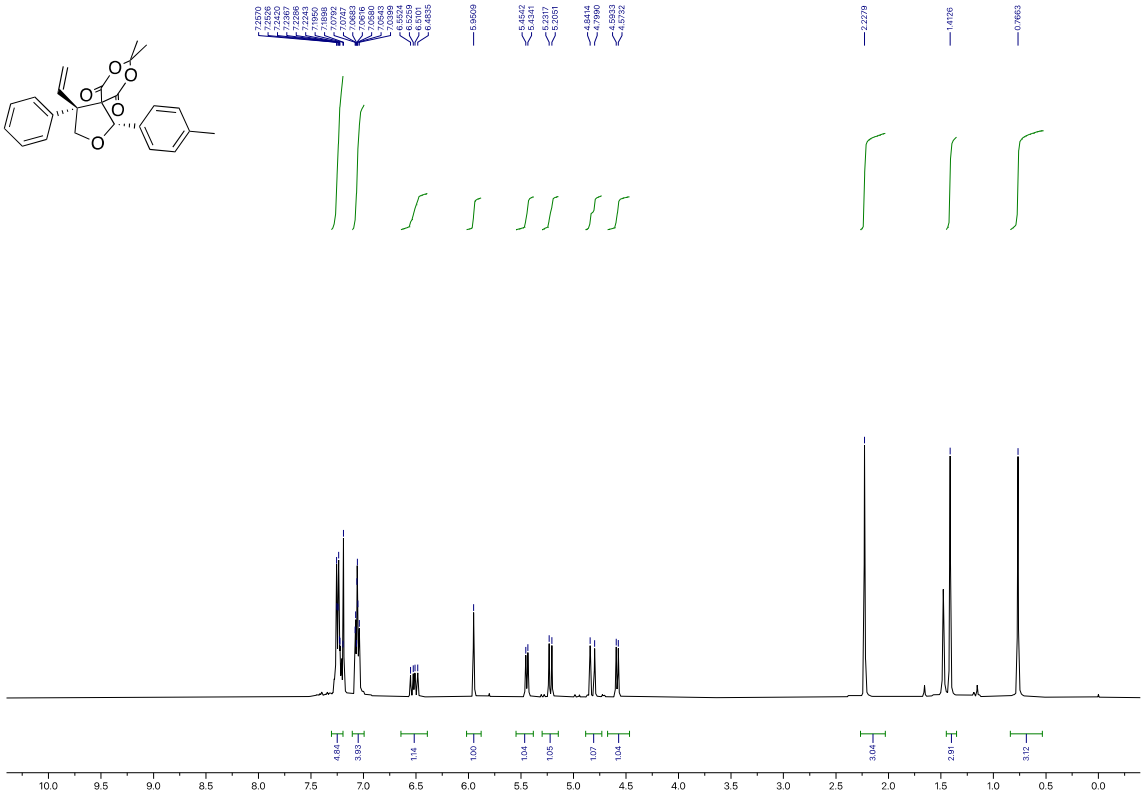


Figure S20. ^{1}H NMR (400 MHz) spectrum of 8,8-dimethyl-4-phenyl-1-(*p*-tolyl)-4-vinyl-2,7,9-trioxaspiro [4.5]decane-6,10-dione (**3ca**) in $CDCl_3$.

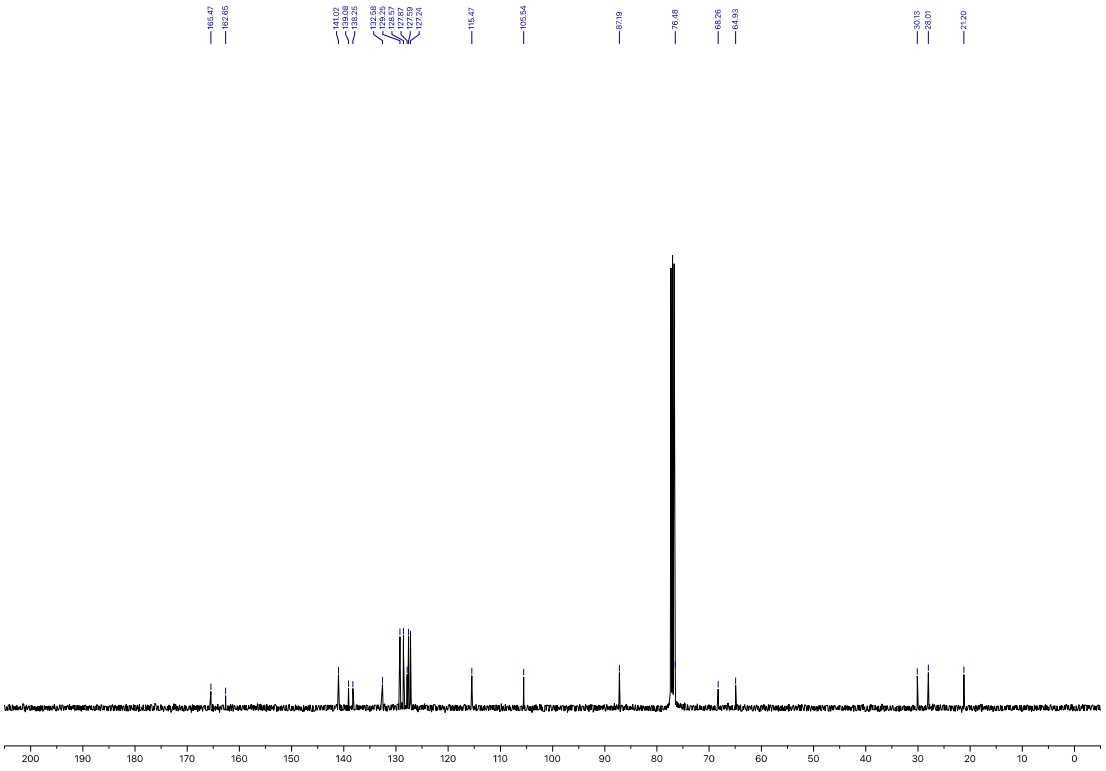
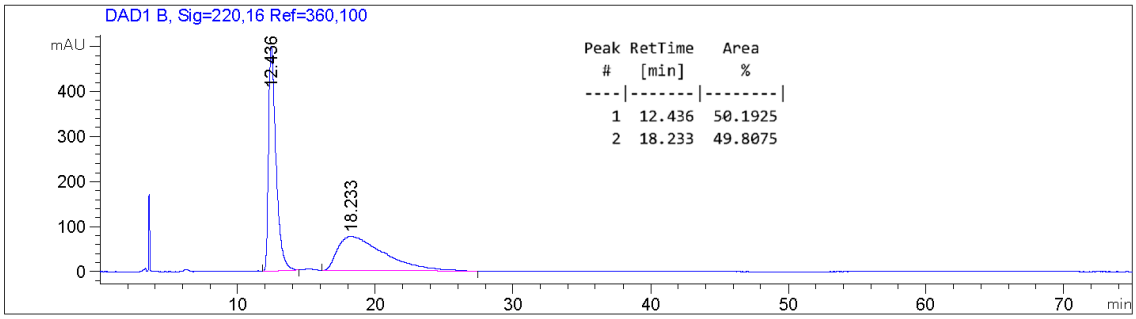


Figure S21. ^{13}C NMR (100.6 MHz) spectrum of **3ca** in $CDCl_3$.

(a)



(b)

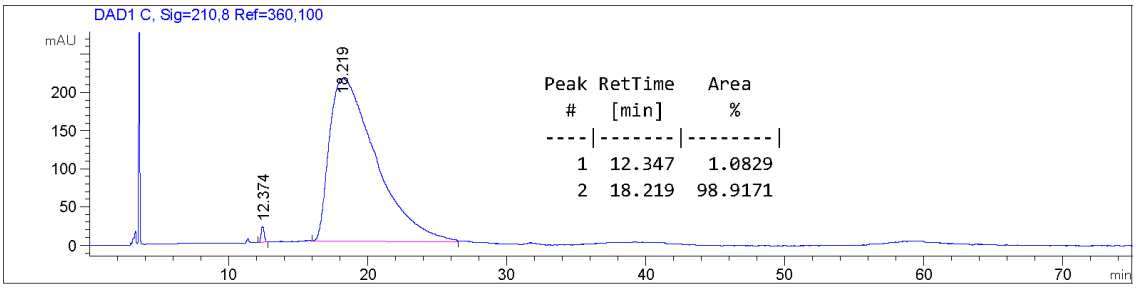


Figure S22. HPLC traces of (a) racemic and (b) enantioenriched product (*R*,*S*)-**3ca**.

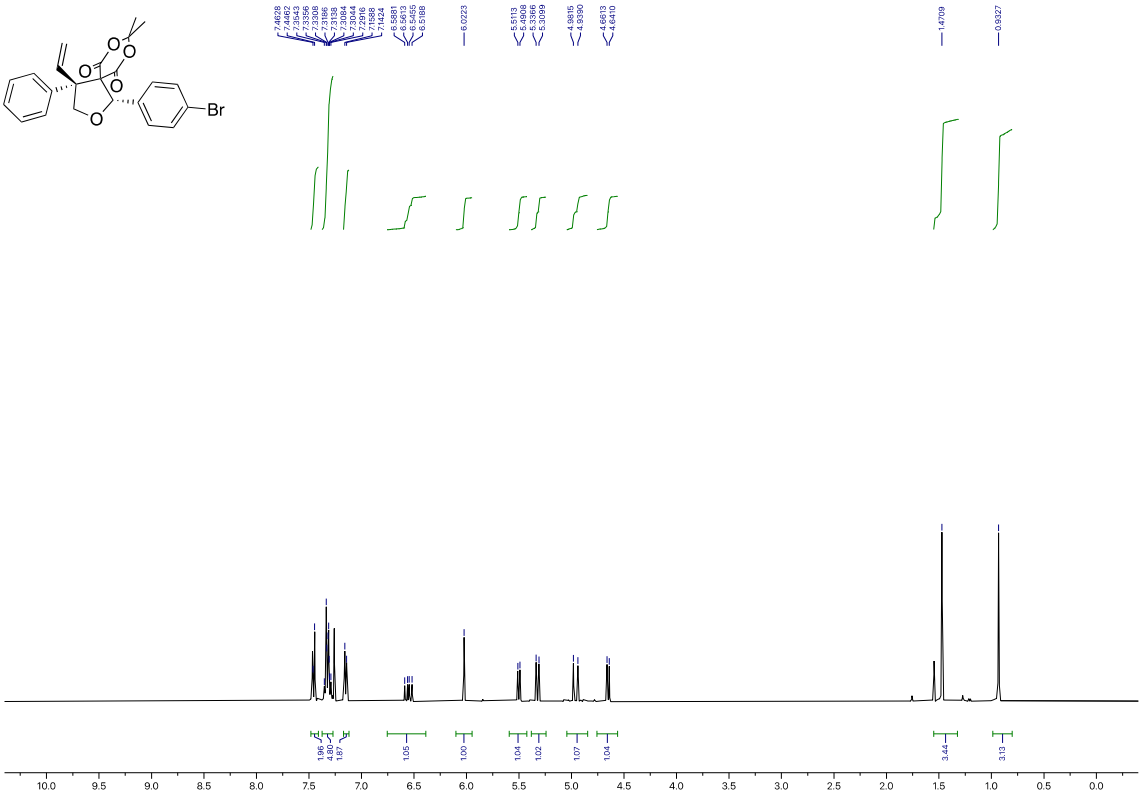


Figure S23. ^{1}H NMR (400 MHz) spectrum of 1-(4-bromophenyl)-8,8-dimethyl-4-phenyl-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3da**) in $CDCl_3$

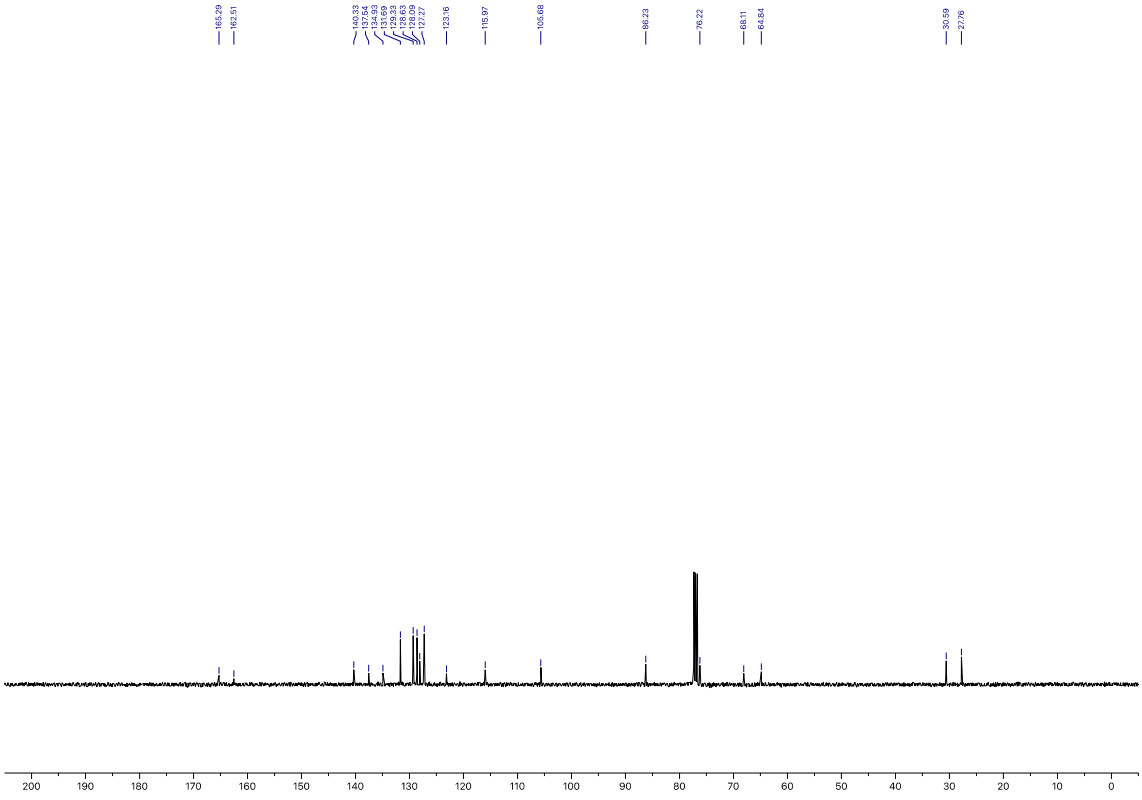
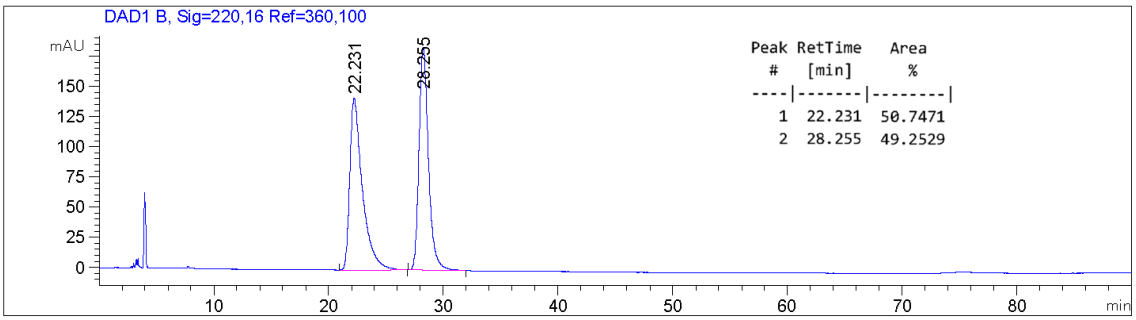


Figure S24. ^{13}C NMR (100.6 MHz) spectrum of **3da** in $CDCl_3$.

(a)



(b)

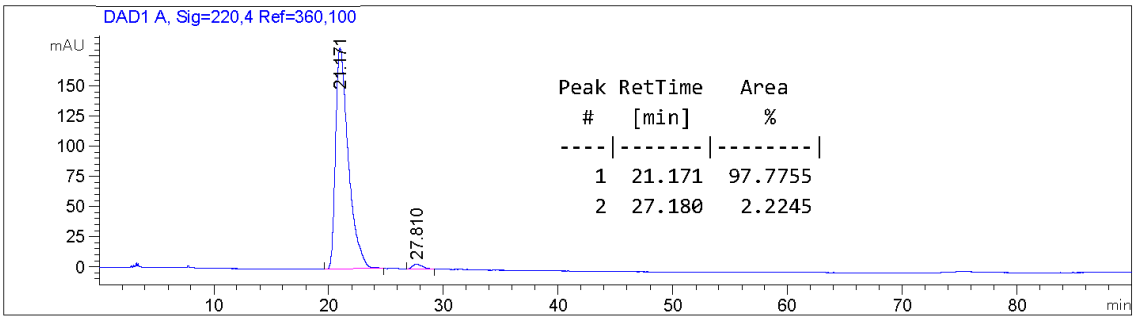


Figure S25. HPLC traces of (a) racemic and (b) enantioenriched product (*R*,*S*)-**3da**.

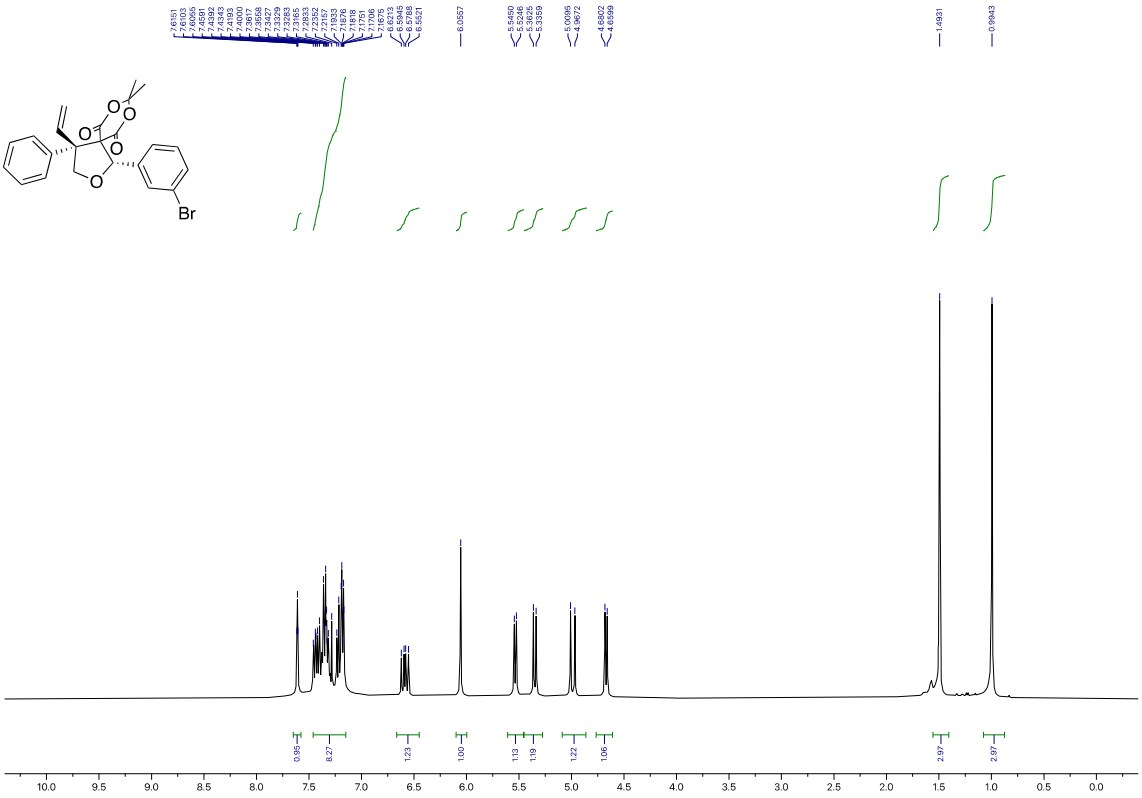


Figure S26. ^{1}H NMR (400 MHz) spectrum of 1-(3-bromophenyl)-8,8-dimethyl-4-phenyl-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3ea**) in $CDCl_3$

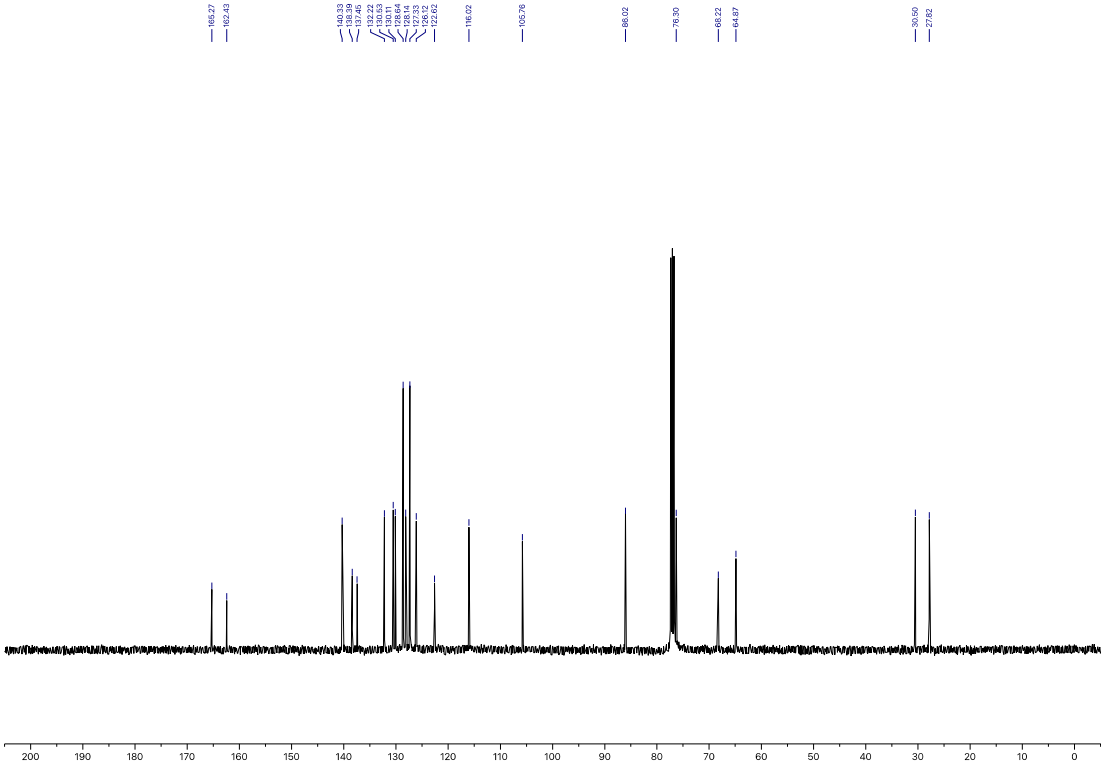
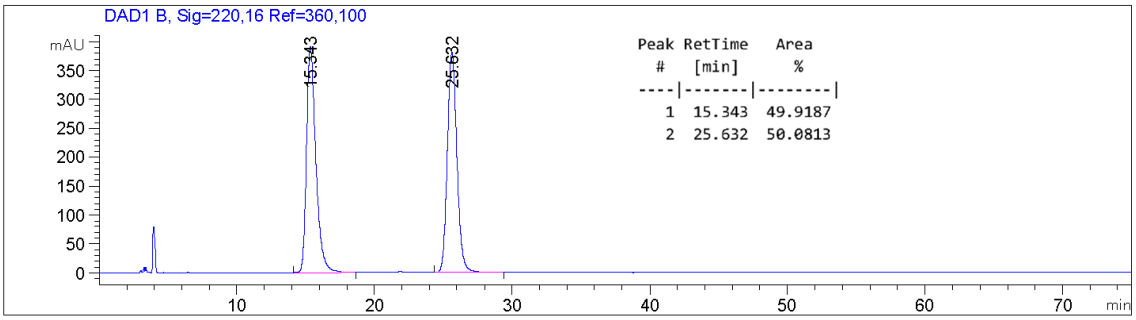


Figure S27. ^{13}C NMR (100.6 MHz) spectrum of **3ea** in $CDCl_3$.

(a)



(b)

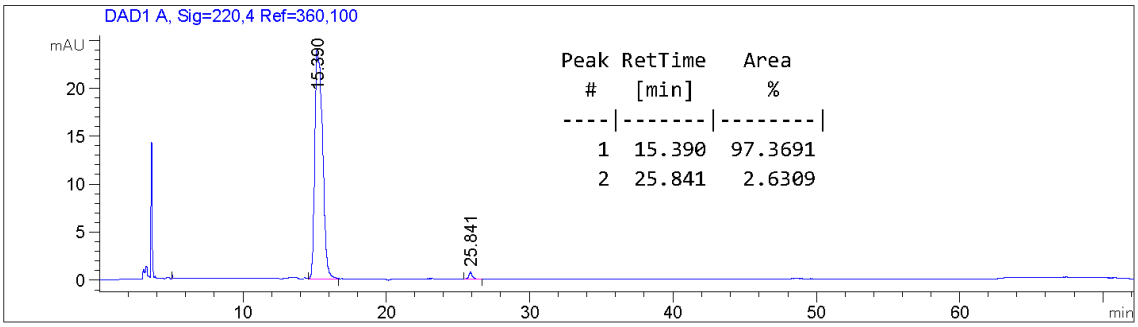


Figure S28. HPLC traces of (a) racemic and (b) enantioenriched product (*R*,*S*)-**3ea**.

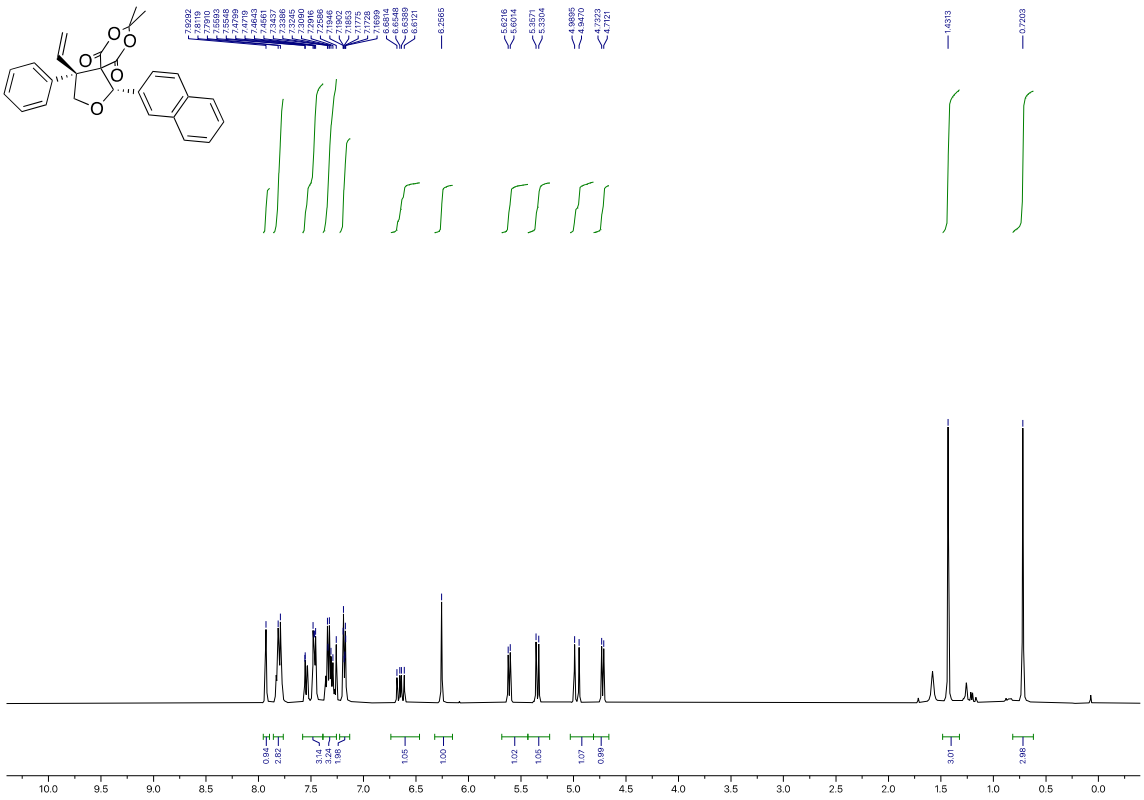


Figure S29. ^{1}H NMR (400 MHz) spectrum of 8,8-dimethyl-1-(naphthalen-2-yl)-4-phenyl-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3fa**) in $CDCl_3$

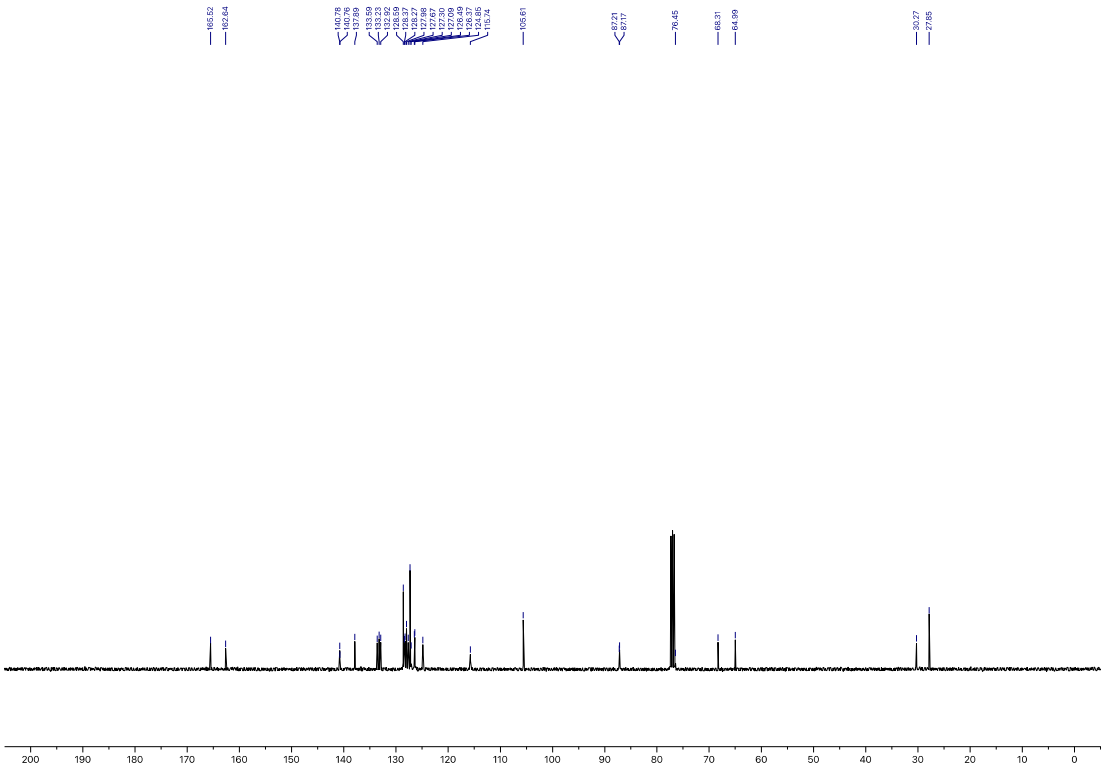
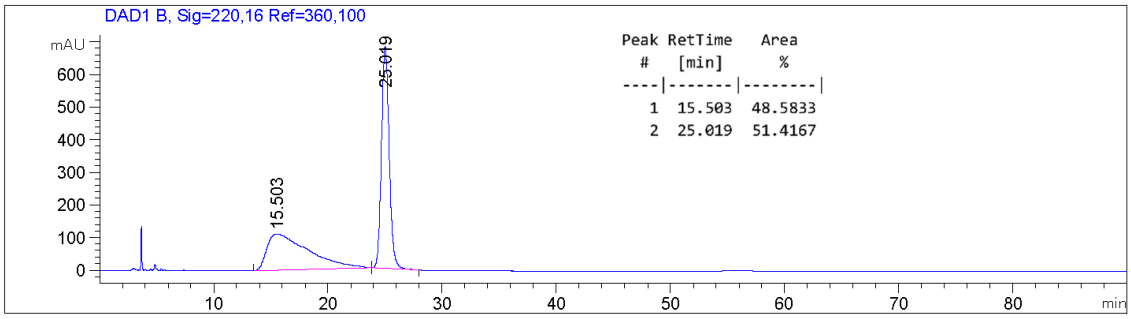


Figure S30. ^{13}C NMR (100.6 MHz) spectrum of **3fa** in $CDCl_3$.

(a)



(b)

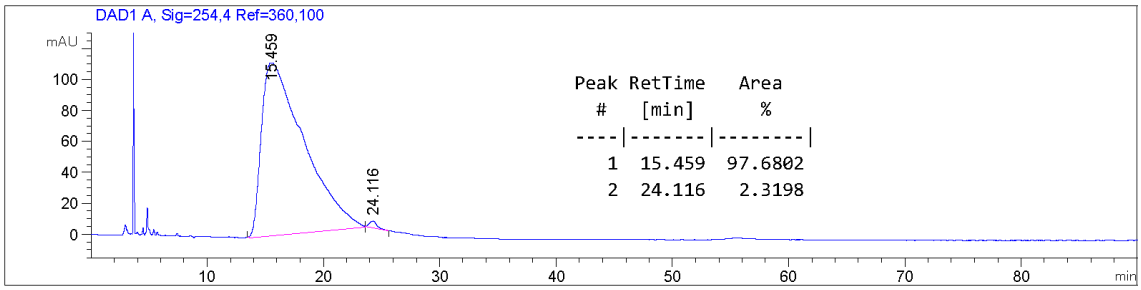


Figure S31. HPLC traces of (a) racemic and (b) enantioenriched product (*R*,*S*)-**3fa**.

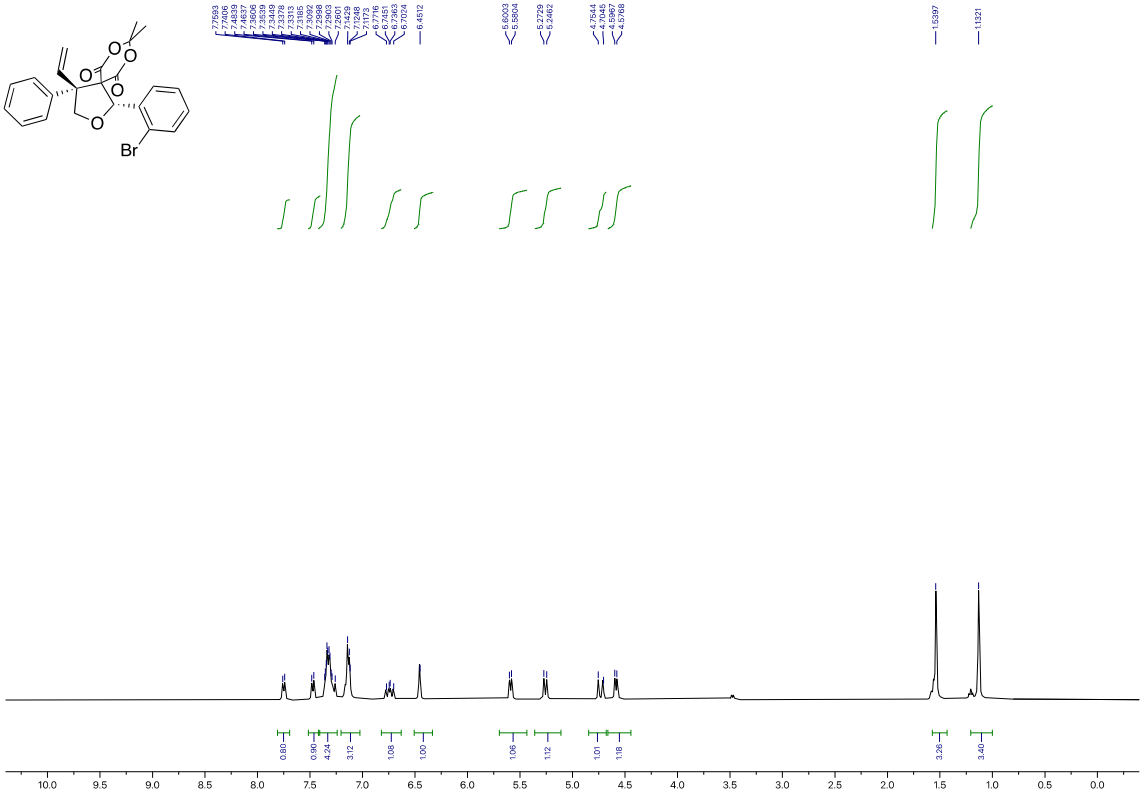


Figure S32. ^{1}H NMR (400 MHz) spectrum of 1-(2-bromophenyl)-8,8-dimethyl-4-phenyl-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3ga**) in $CDCl_3$

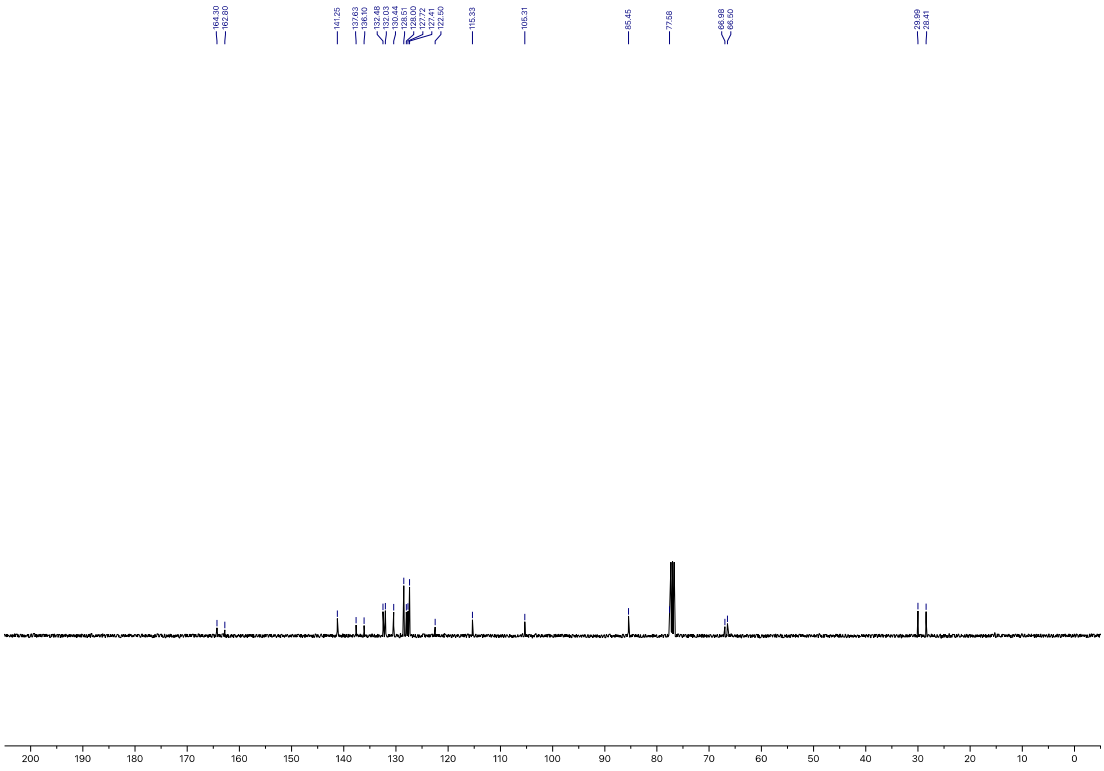
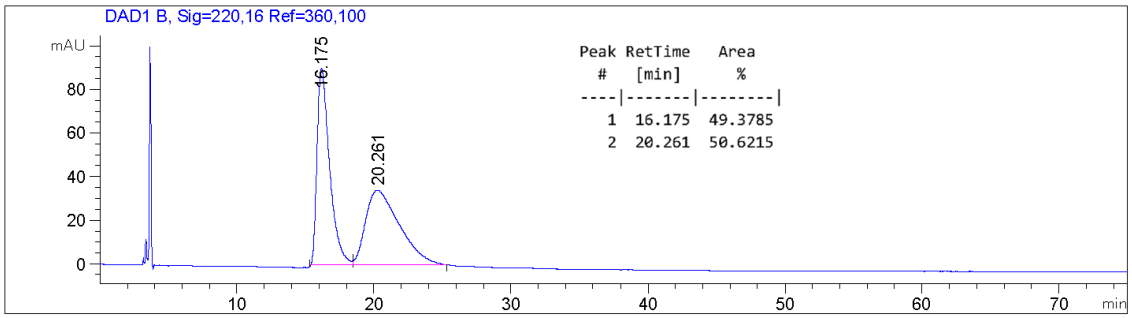


Figure S33. ^{13}C NMR (100.6 MHz) spectrum of **3ga** in $CDCl_3$

(a)



(b)

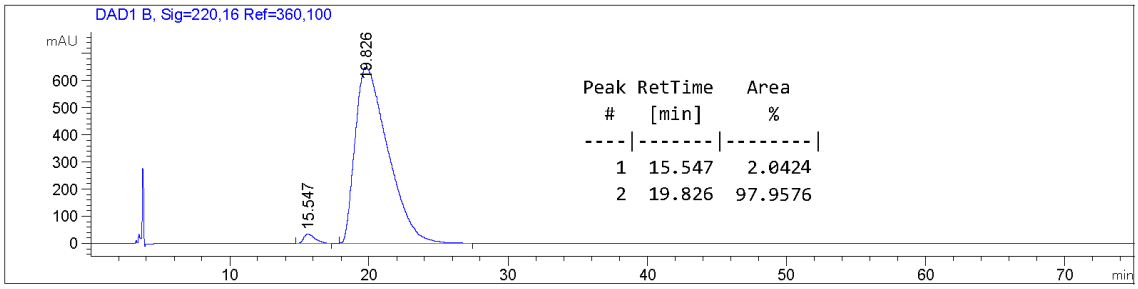


Figure 34. HPLC traces of (a) racemic and (b) enantioenriched product (*R*,*S*)-**3ga**.

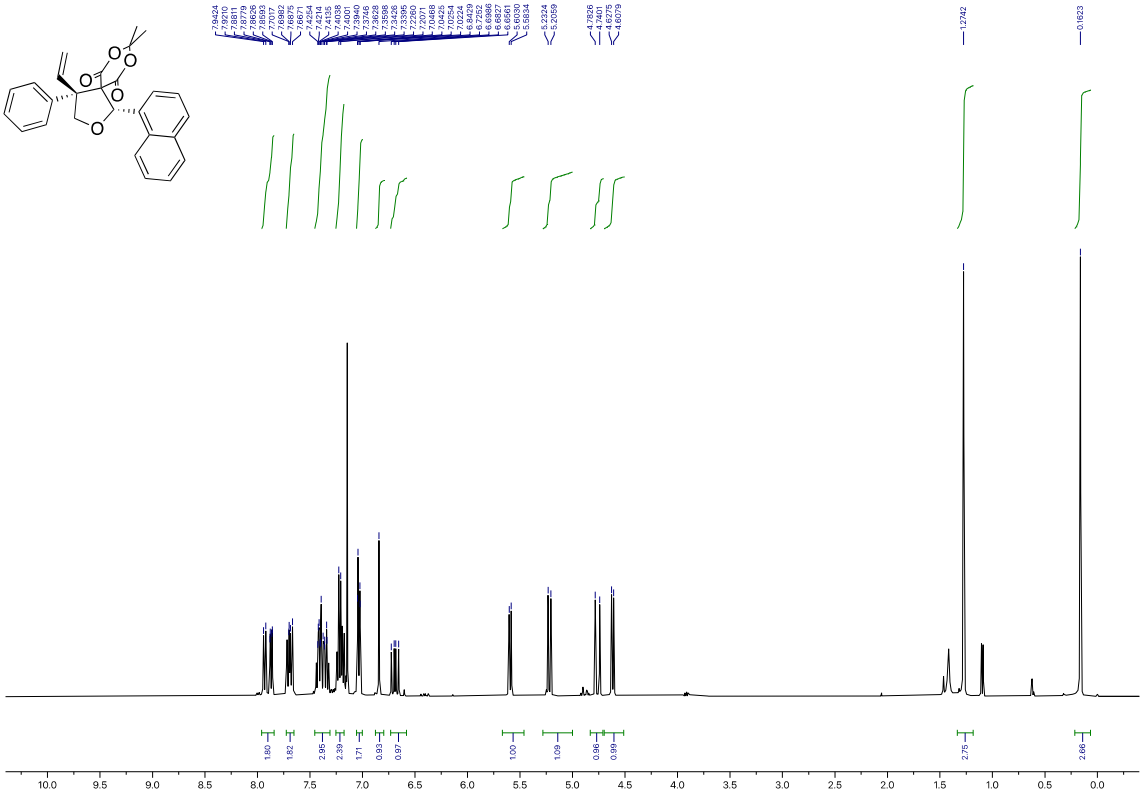


Figure S35. ^{1}H NMR (400 MHz) spectrum of 8,8-dimethyl-1-(naphthalen-1-yl)-4-phenyl-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3ha**) in $CDCl_3$.

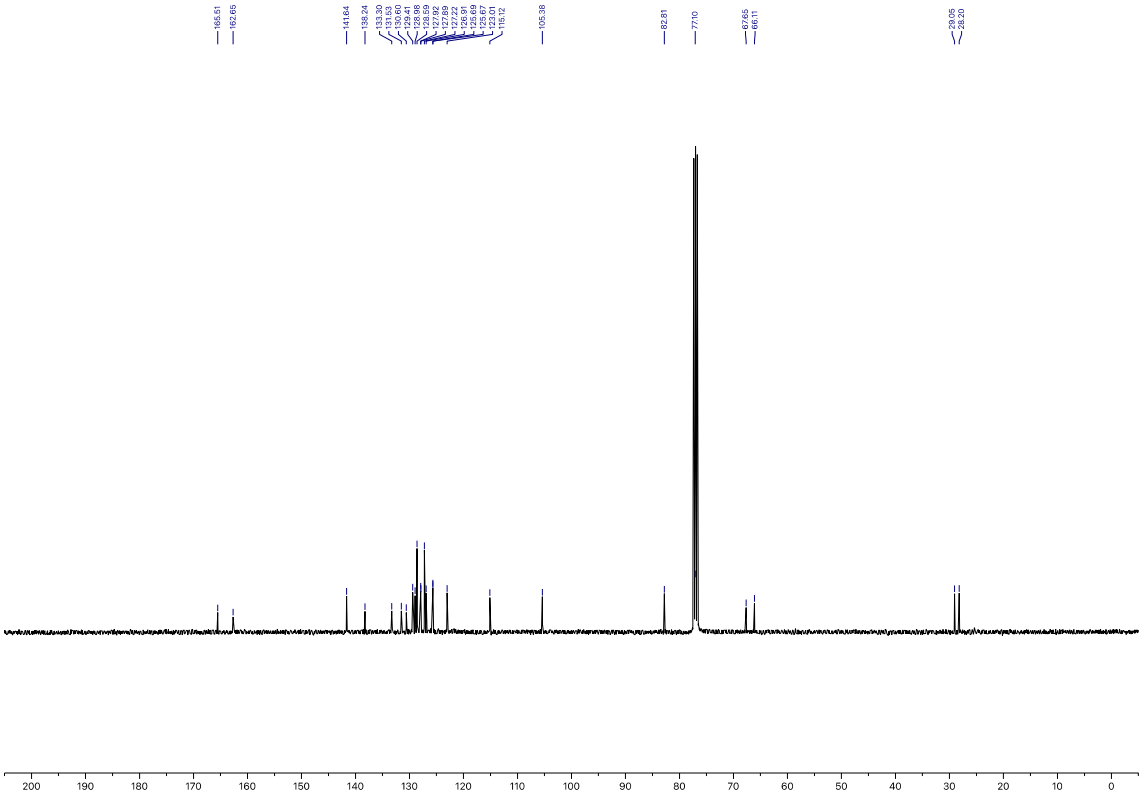
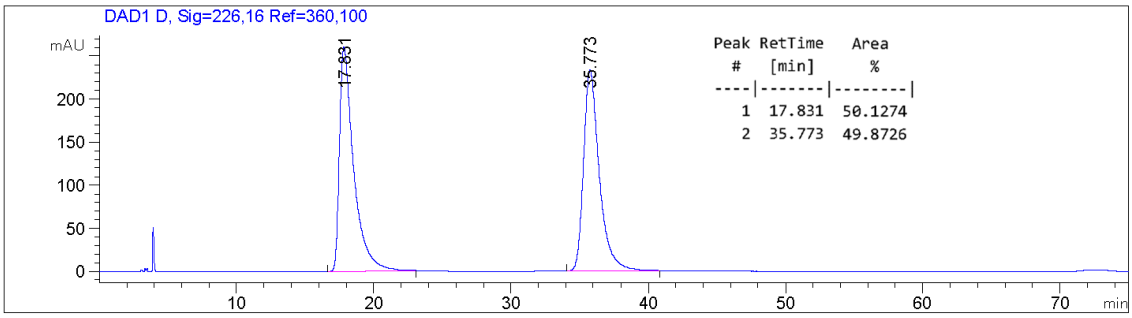


Figure S36. ^{13}C NMR (100.6 MHz) spectrum of **3ha** in $CDCl_3$.

(a)



(b)

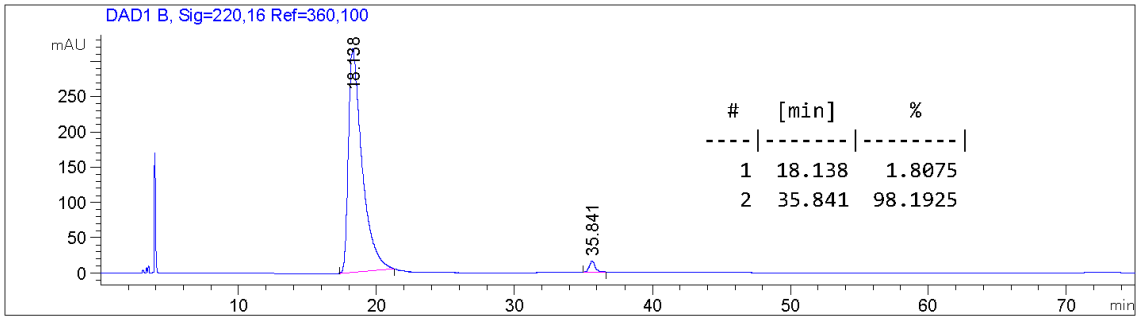


Figure S37. HPLC traces of (a) racemic and (b) enantioenriched product **3ha**.

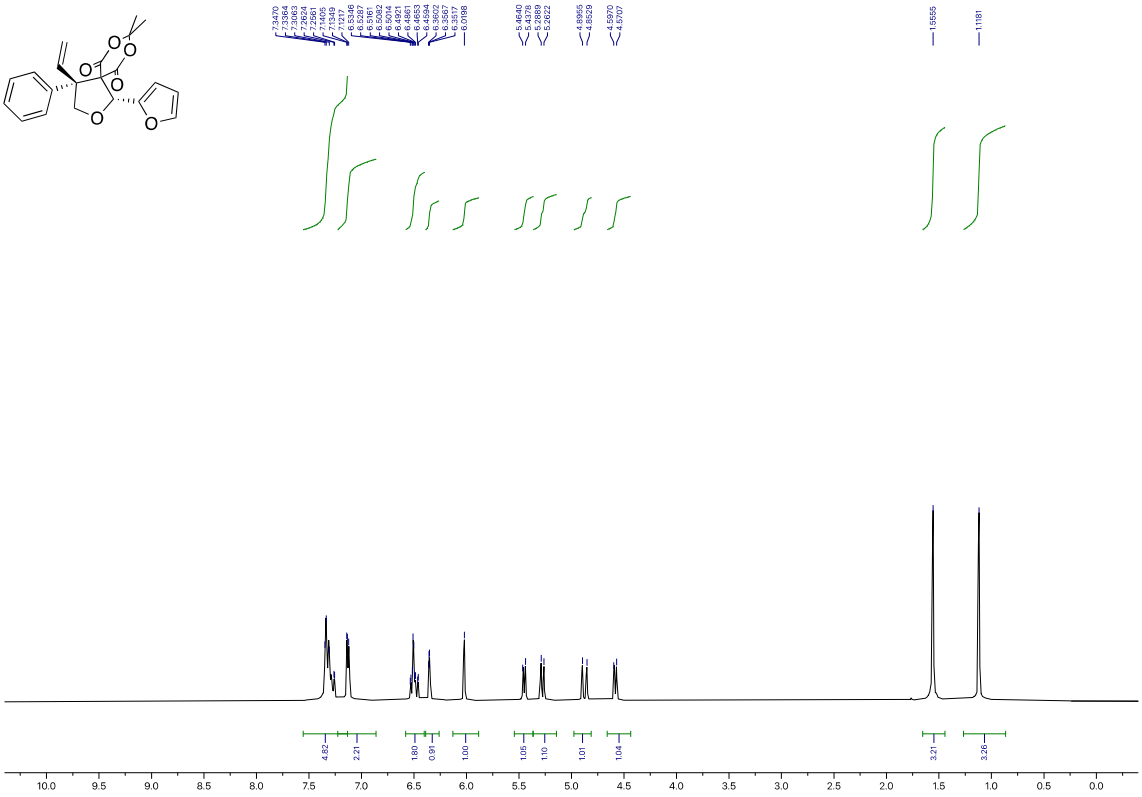


Figure S38. ^{1}H NMR (400 MHz) spectrum of 1-(furan-2-yl)-8,8-dimethyl-4-phenyl-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3ia**) in $CDCl_3$.

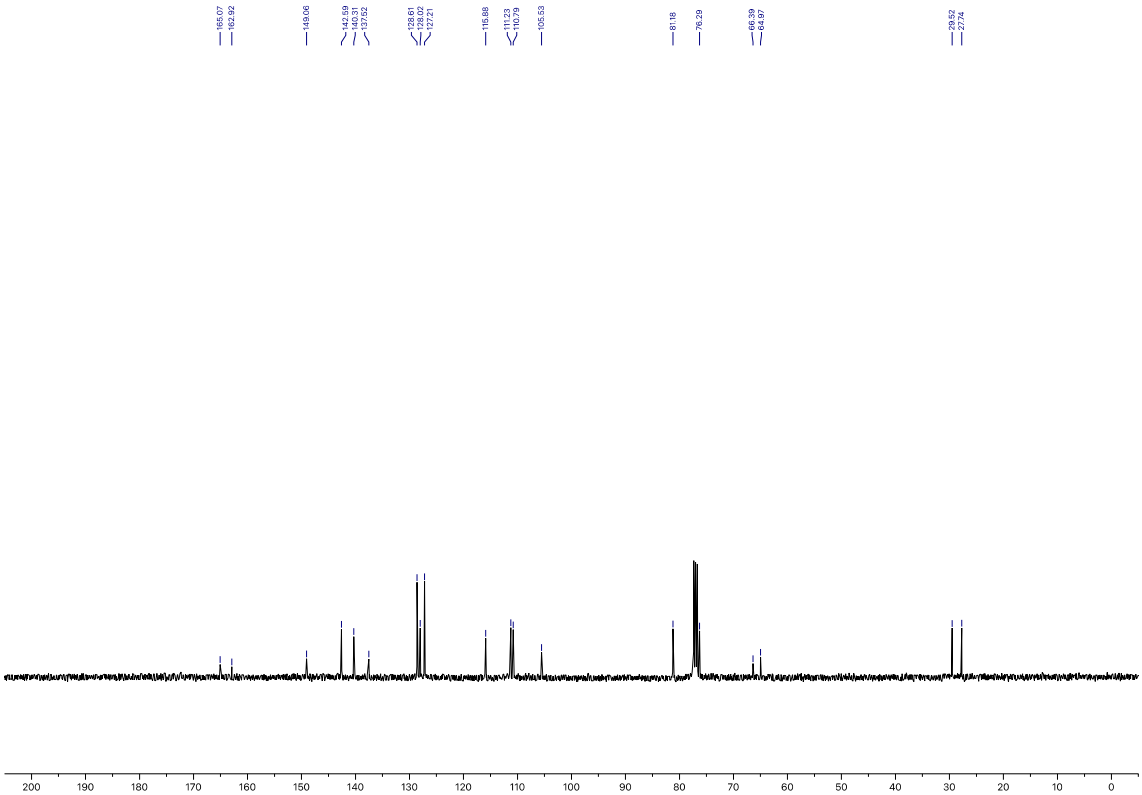
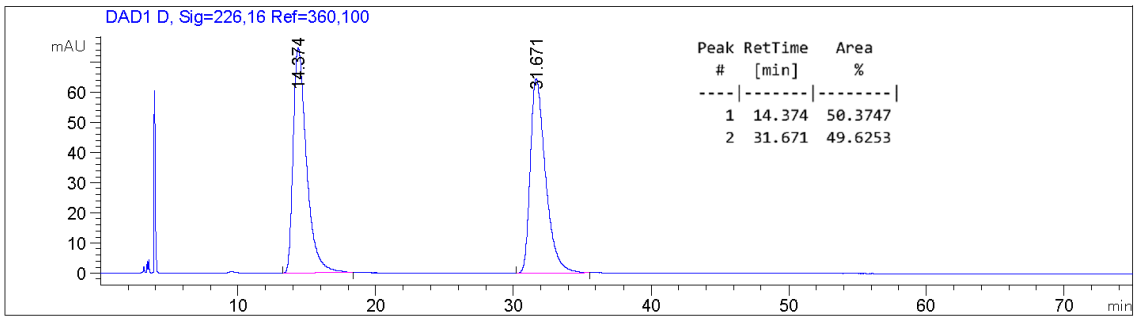


Figure S39. ^{13}C NMR (100.6 MHz) spectrum of **3ia** in $CDCl_3$.

(a)



(b)

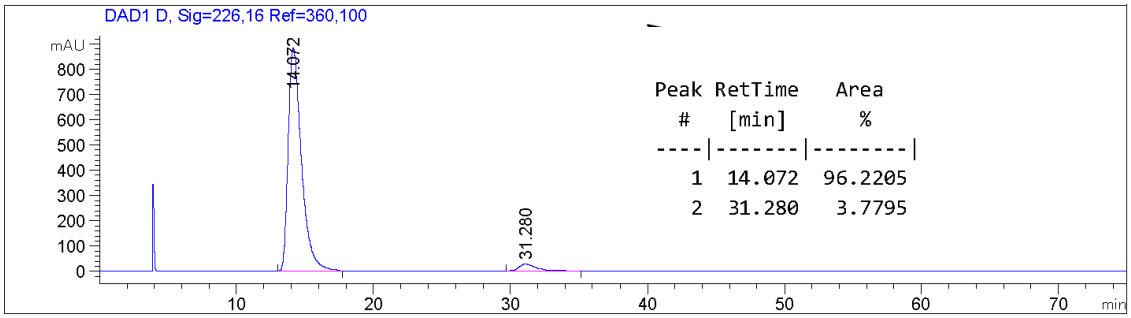


Figure S40. HPLC traces of (a) racemic and (b) enantioenriched product (*R*,*S*)-**3ia**.

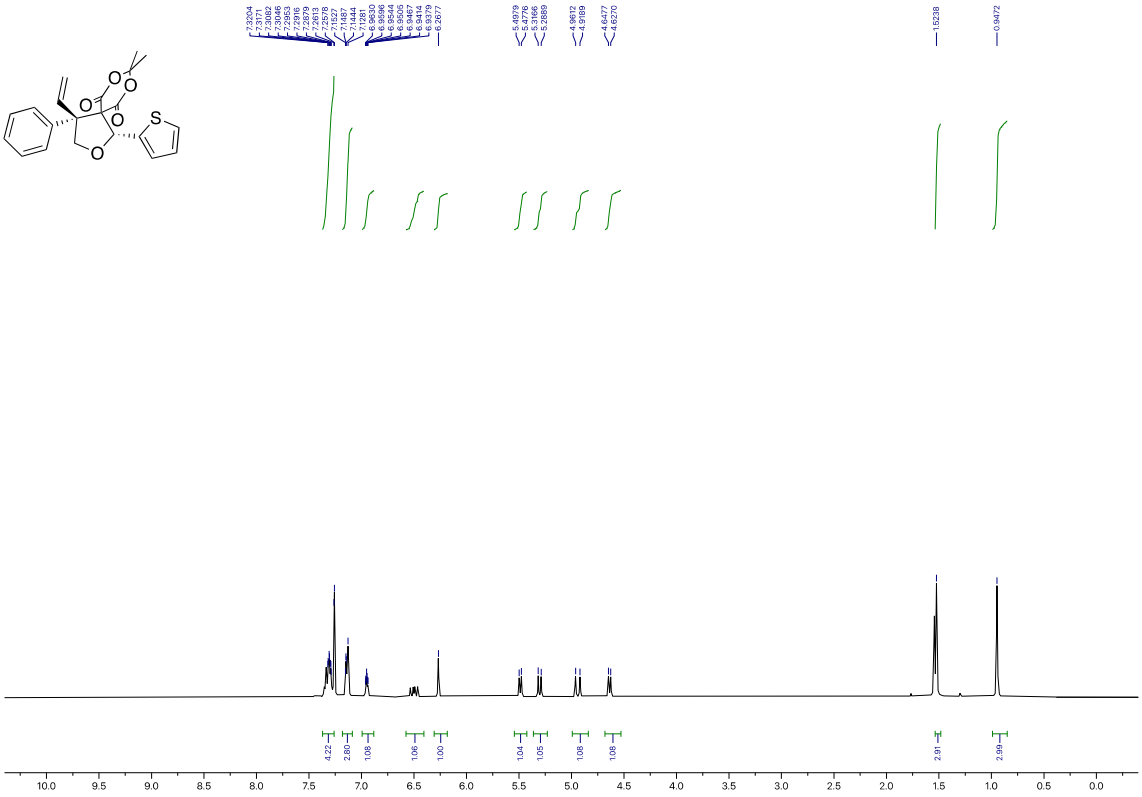


Figure S41. ^{1}H NMR (400 MHz) spectrum of 8,8-dimethyl-4-phenyl-1-(thiophen-2-yl)-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3ja**) in $CDCl_3$

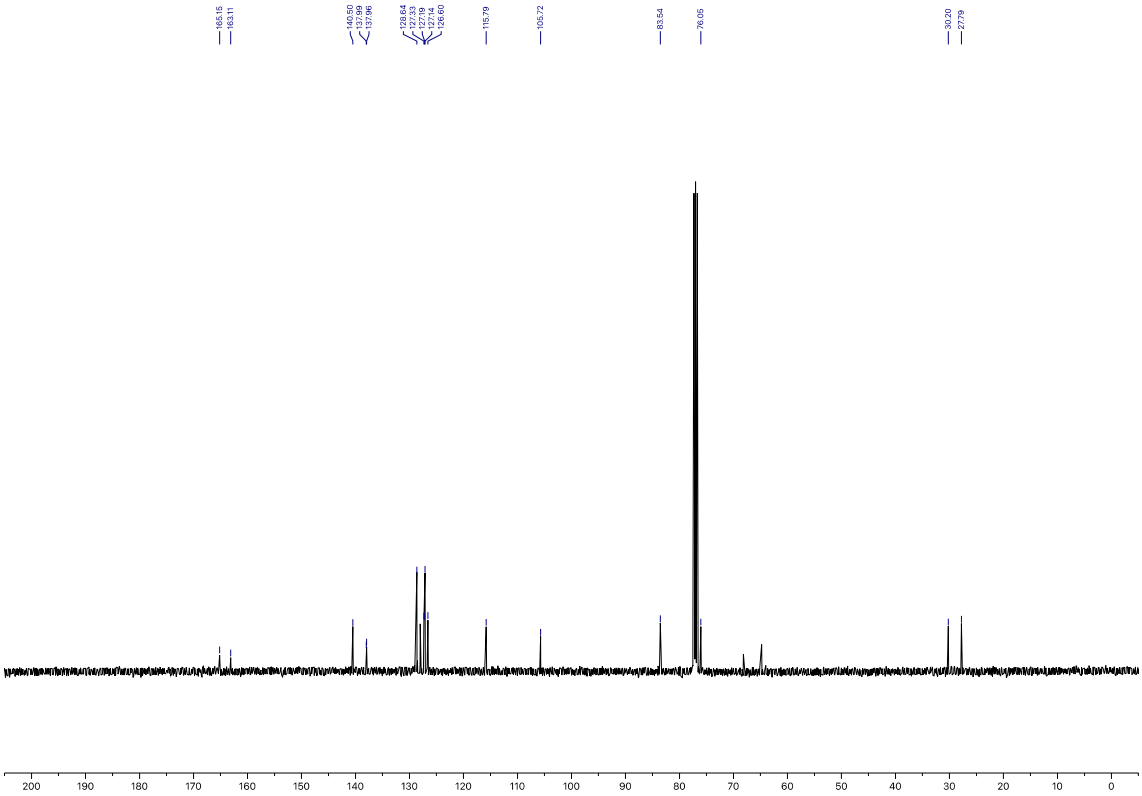
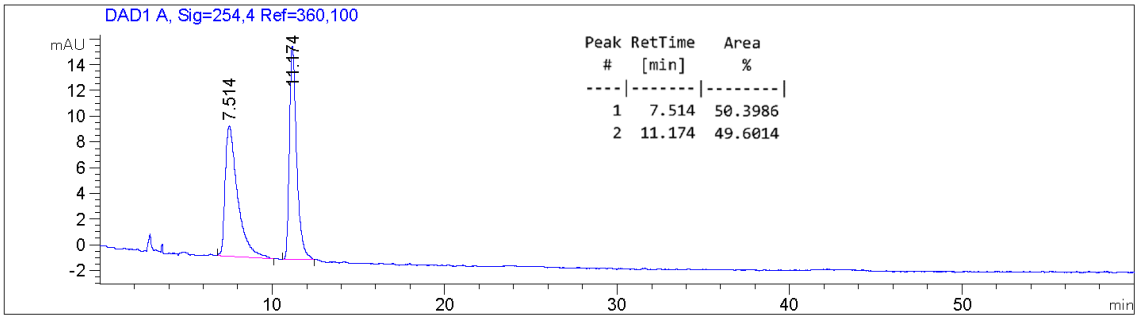


Figure S42. ^{13}C NMR (100.6 MHz) spectrum of **3ja** in $CDCl_3$.

(a)



(b)

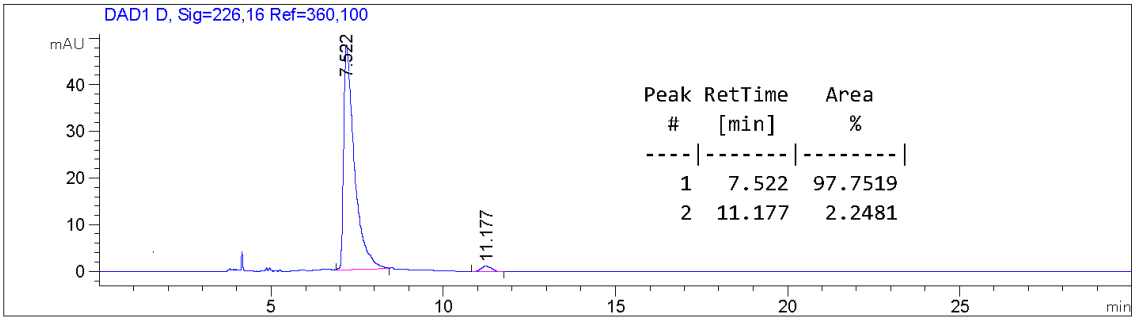


Figure S43. HPLC traces of (a) racemic and (b) enantioenriched product (*R*,*S*)-**3ja**.

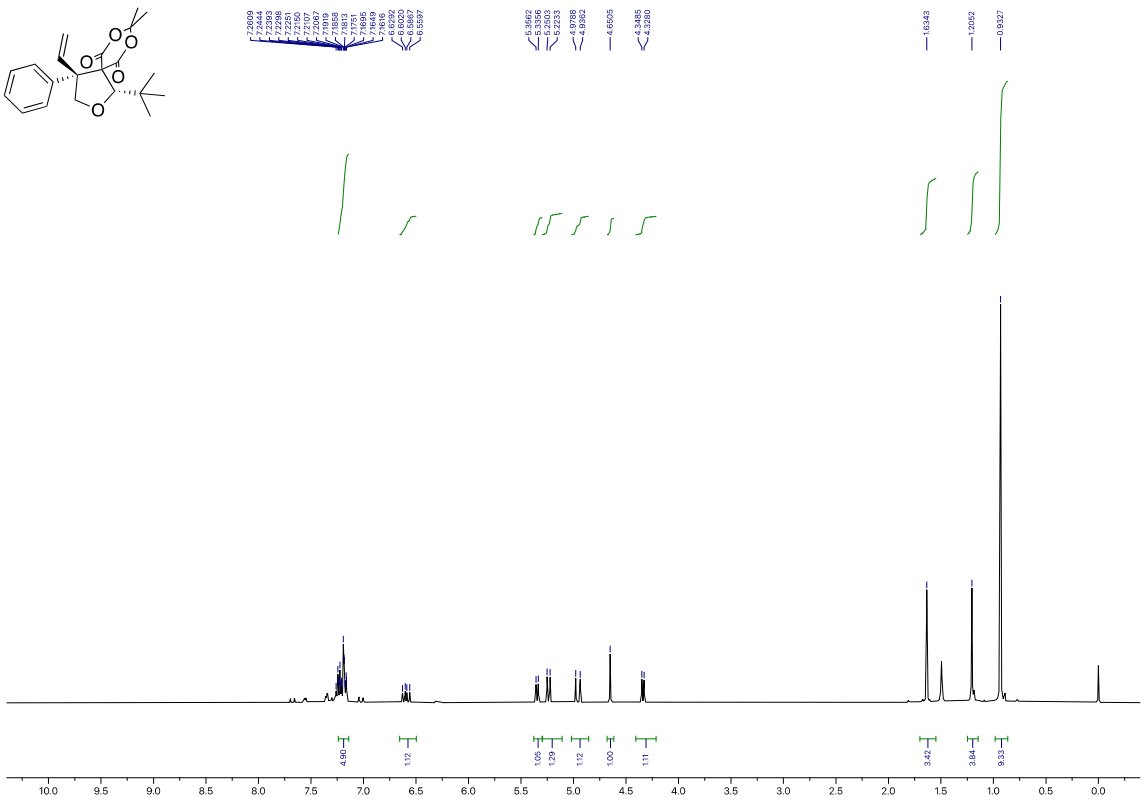


Figure S44. ^{1}H NMR (400 MHz) spectrum of 1-(*tert*-butyl)-8,8-dimethyl-4-phenyl-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3ka**) in $CDCl_3$

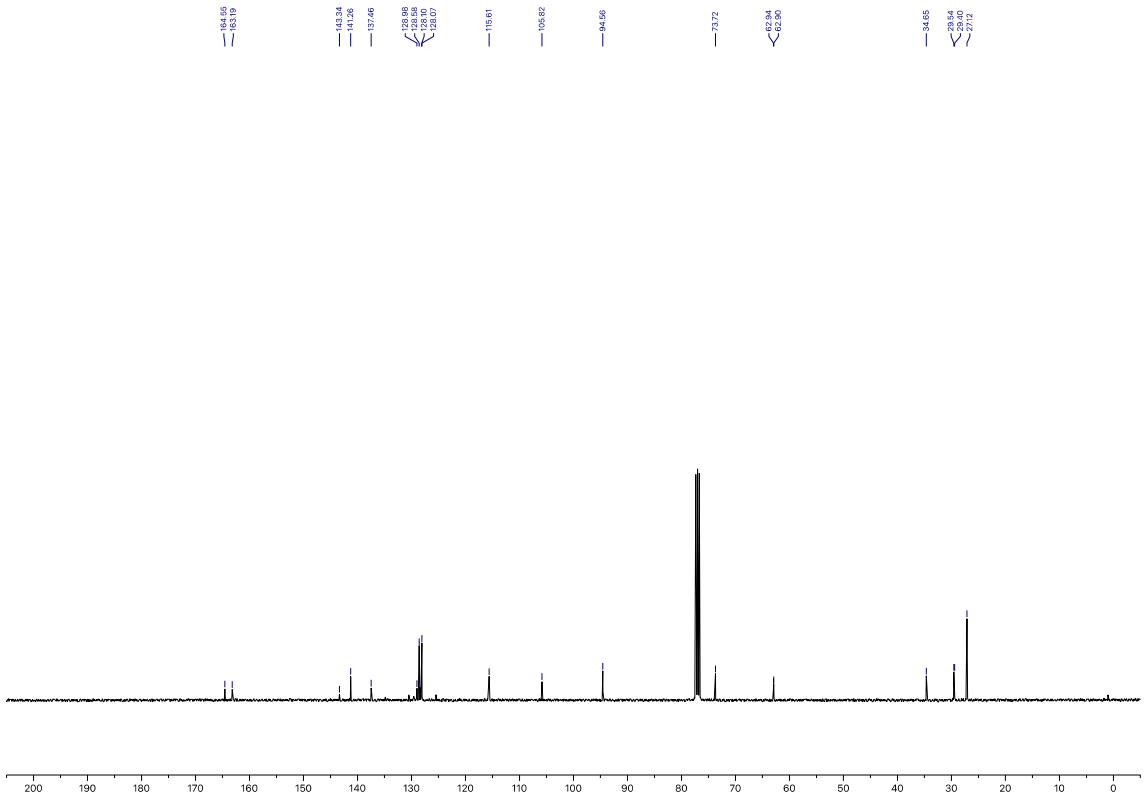
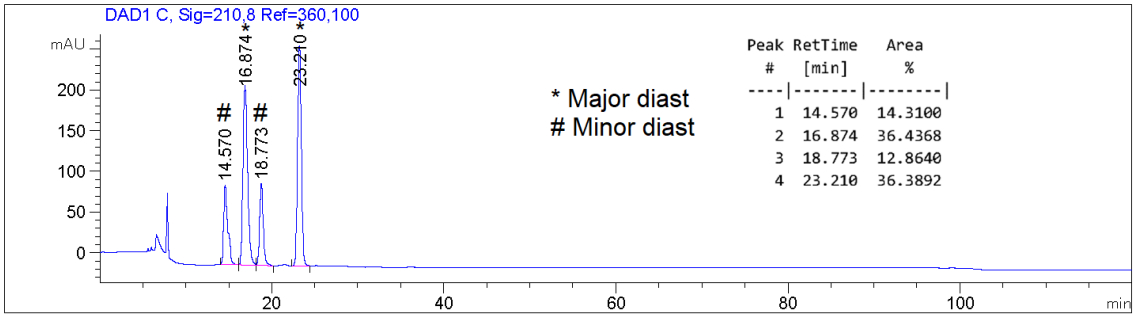


Figure S45. ^{13}C NMR (100.6 MHz) spectrum of **3ka** in $CDCl_3$.

(a)



(b)

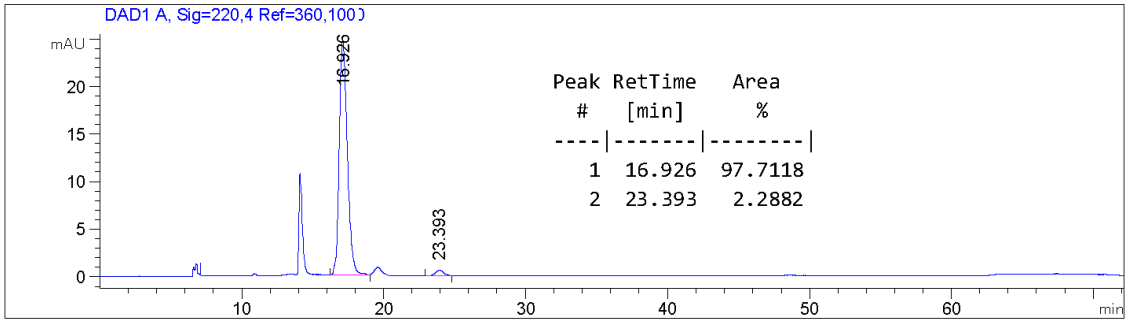


Figure S46. HPLC traces of (a) racemic and (b) enantioenriched product (*R*,*S*)-**3ka**.

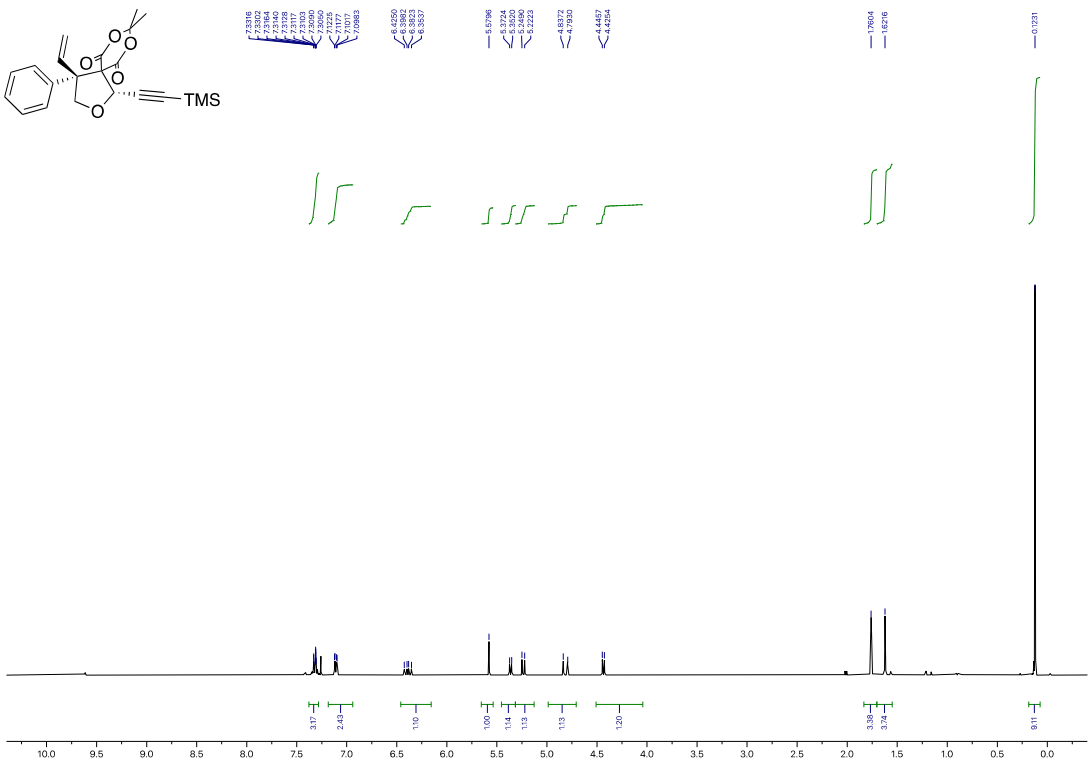


Figure S47. ^{1}H NMR (400 MHz) spectrum of 8,8-dimethyl-4-phenyl-1-((trimethylsilyl)ethynyl)-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3la**) in $CDCl_3$

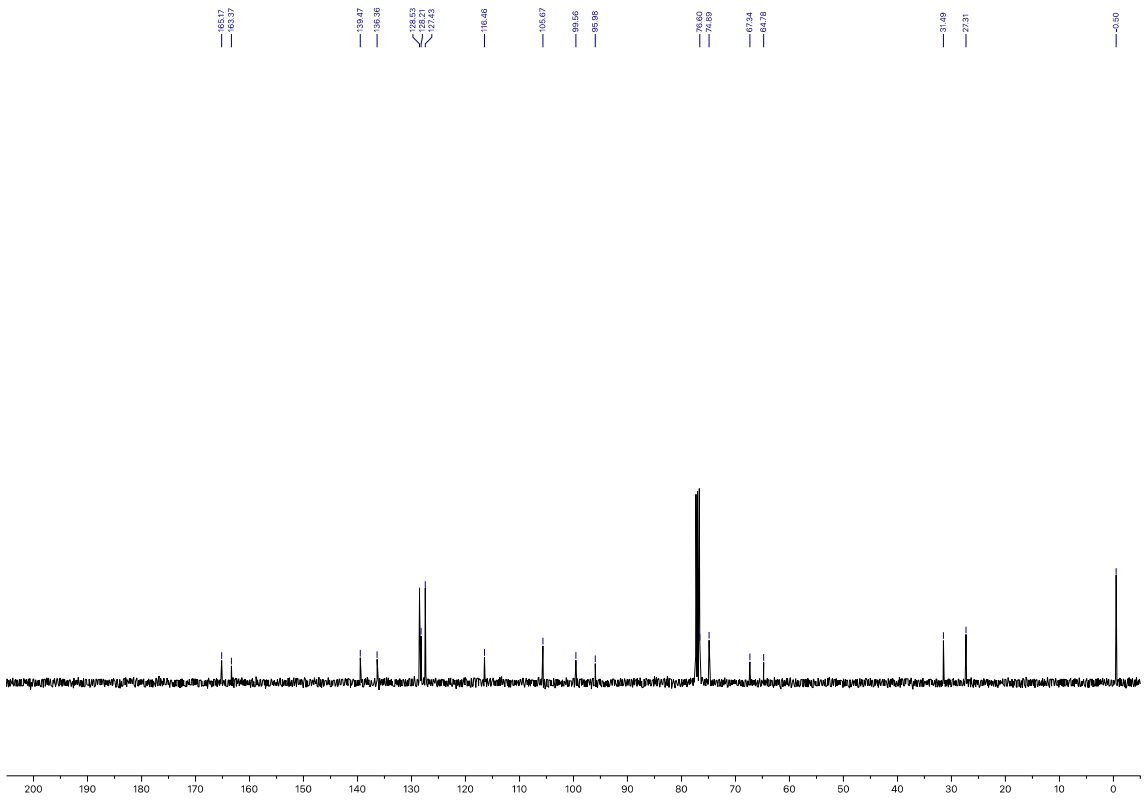
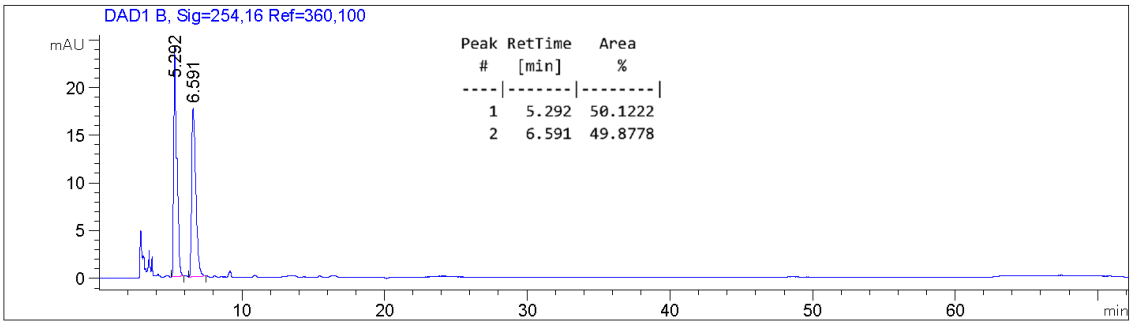


Figure S48. ^{13}C NMR (100.6 MHz) spectrum of **3la** $CDCl_3$.

(a)



(b)

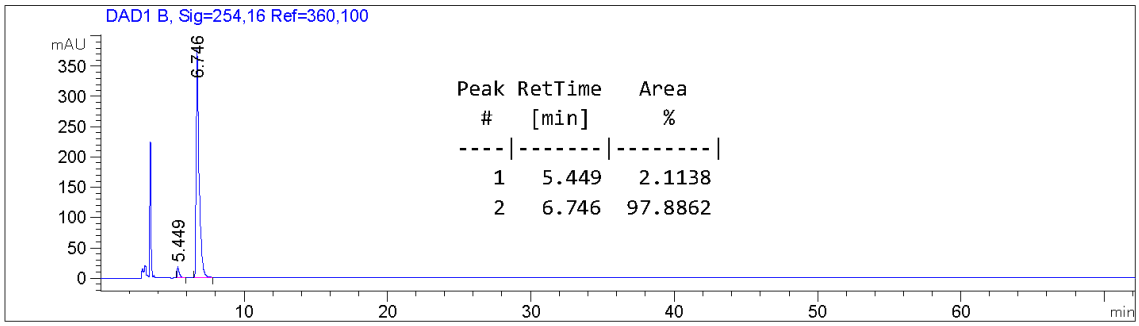


Figure S49. HPLC traces of (a) racemic and (b) enantioenriched product (*R*,*S*)-**3la**.

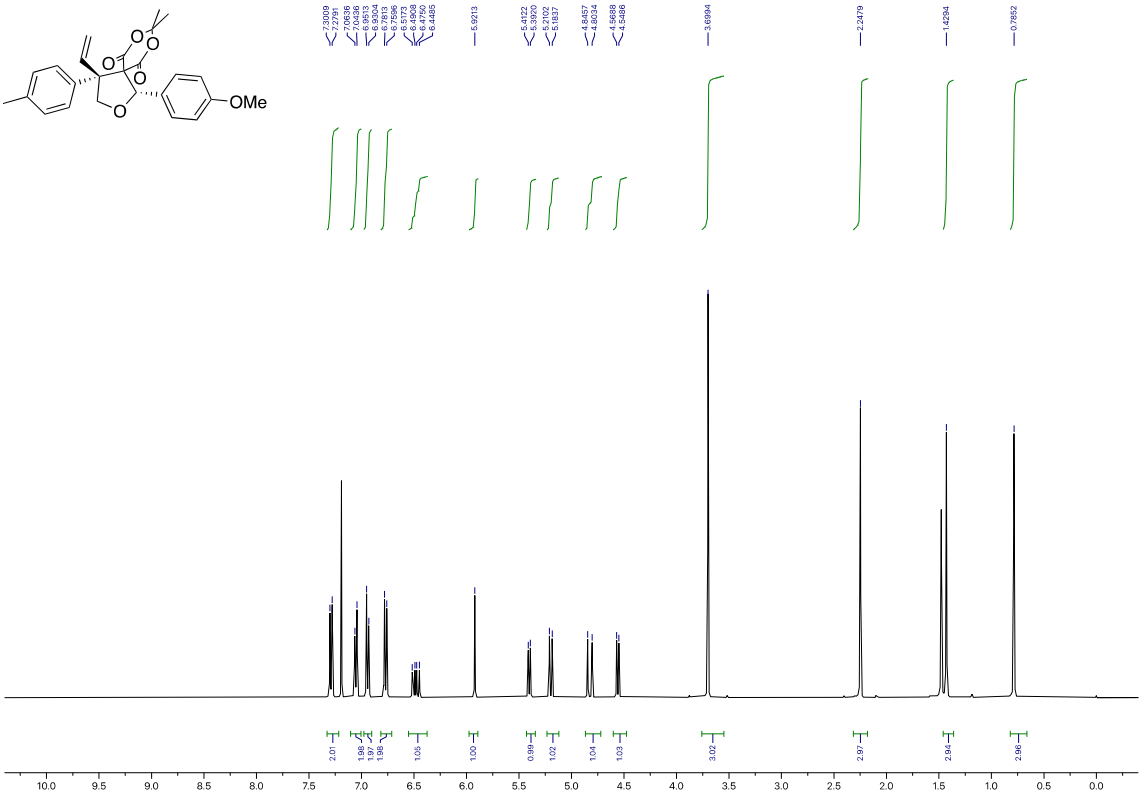


Figure S50. ^{1}H NMR (400 MHz) spectrum of 1-(4-methoxyphenyl)-8,8-dimethyl-4-(*p*-tolyl)-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3ab**) in $CDCl_3$.

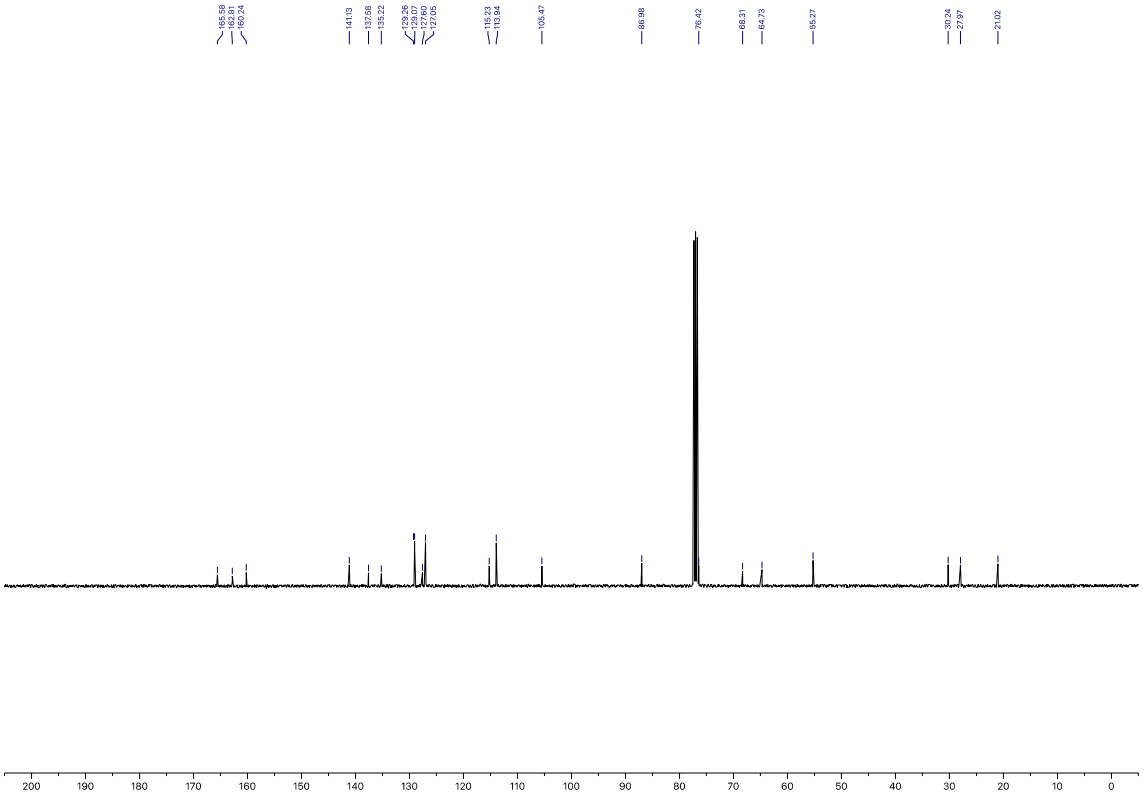
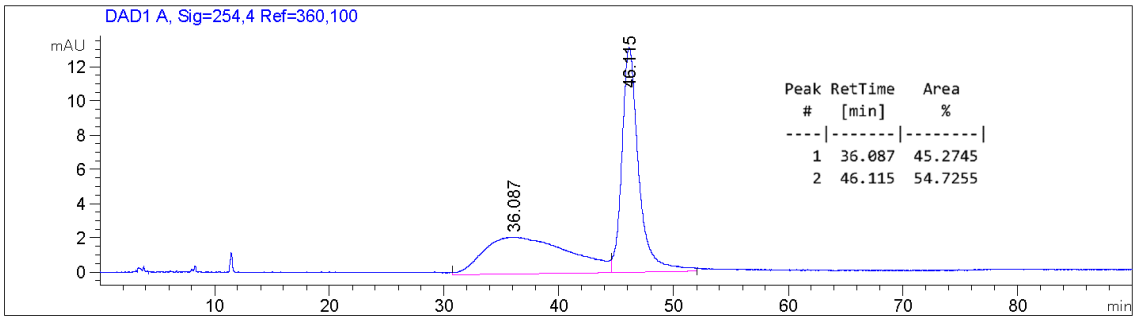


Figure S51. ^{13}C NMR (100.6 MHz) spectrum of **3ab** in $CDCl_3$.

(a)



(b)

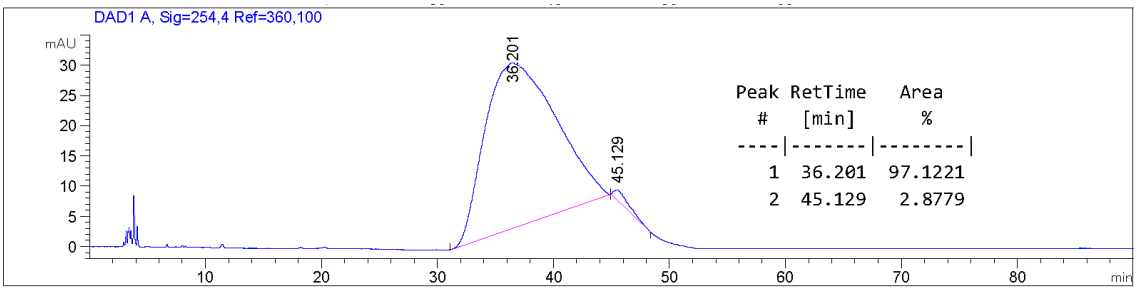


Figure S52. HPLC traces of (a) racemic and (b) enantioenriched product (*R*,*S*)-**3ab**.

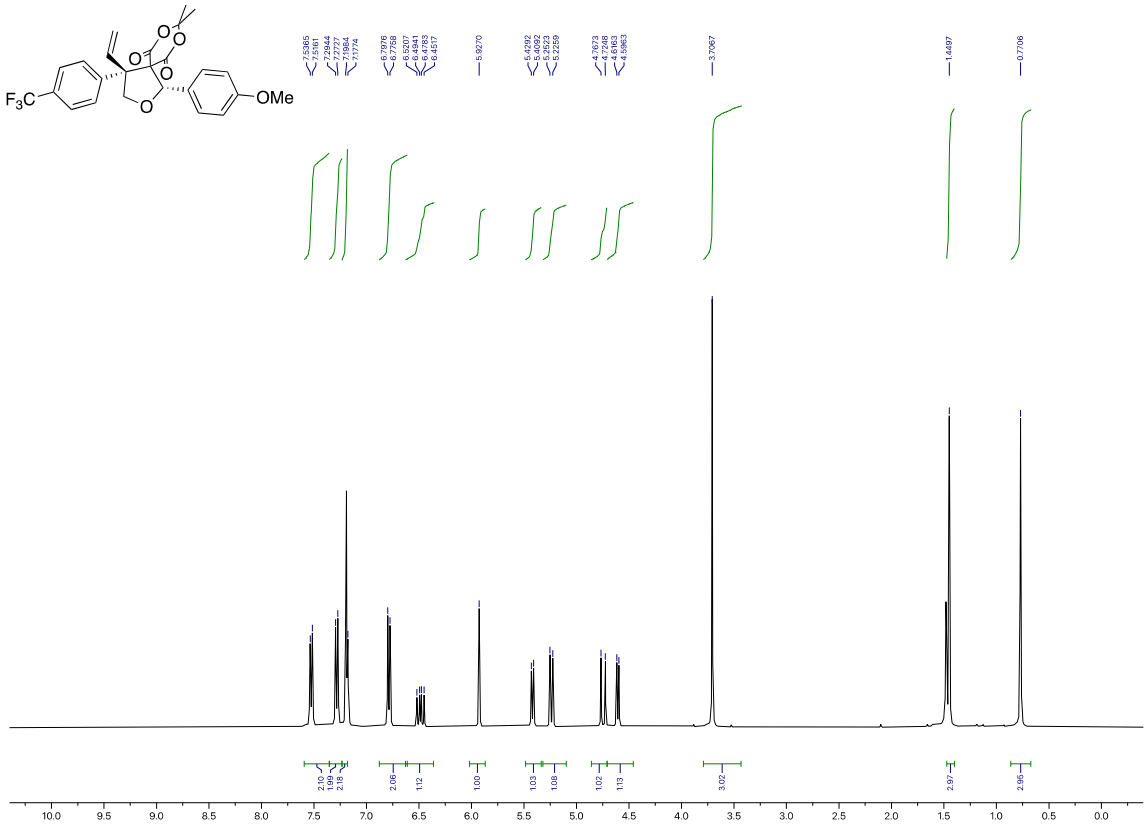


Figure S53. ^{1}H NMR (400 MHz) spectrum of 4-(4-fluorophenyl)-1-(4-methoxyphenyl)-8,8-dimethyl-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3ad**) in $CDCl_3$.

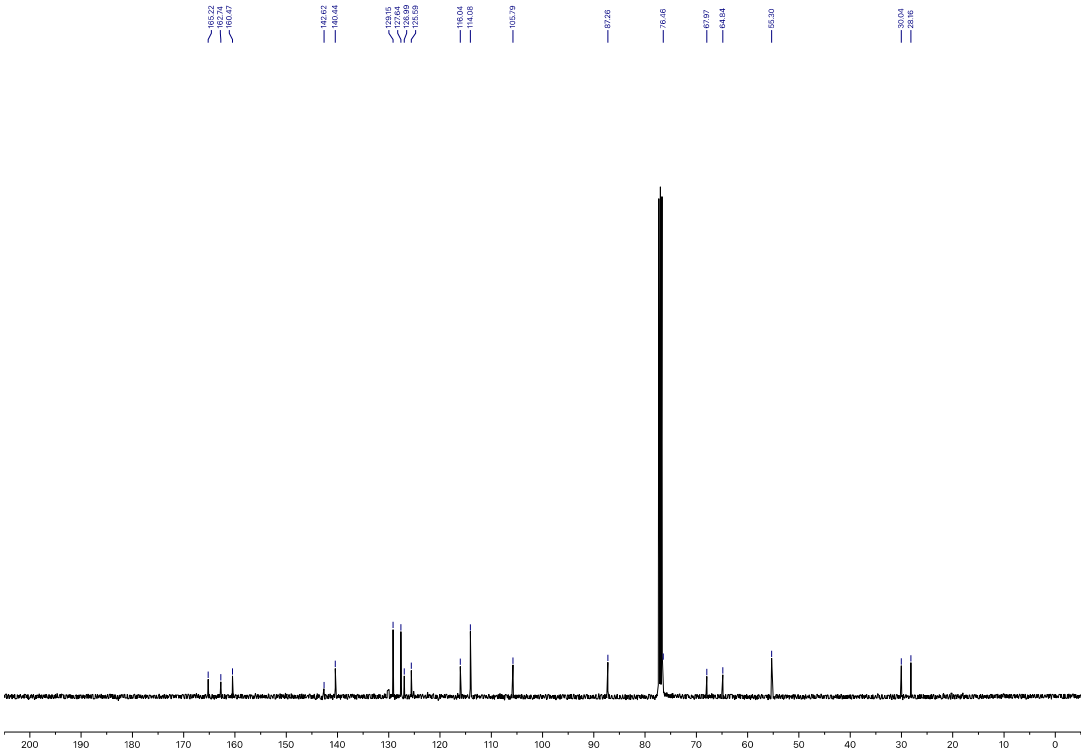


Figure S54. ^{13}C NMR (100.6 MHz) spectrum of **3ad** in $CDCl_3$.

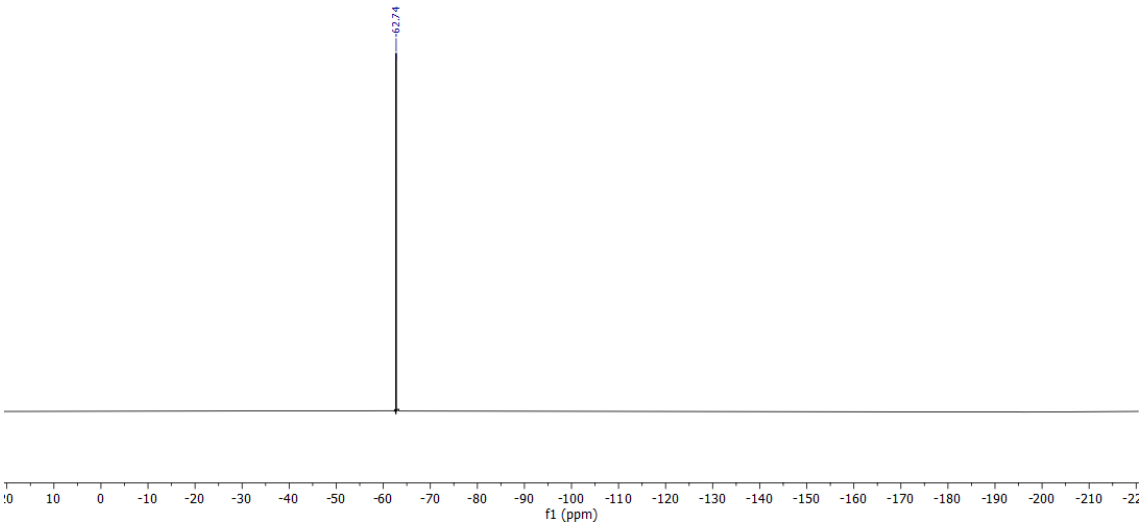
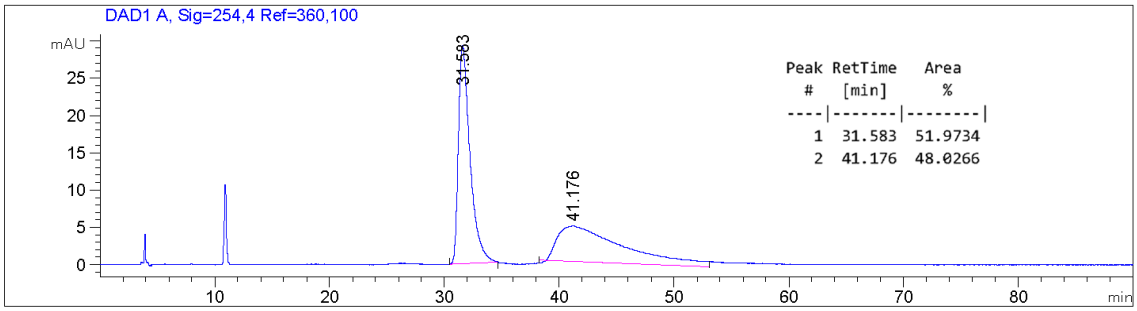


Figure S55. ^{19}F NMR (376 MHz) spectrum of **3ad** in $CDCl_3$.

(a)



(b)

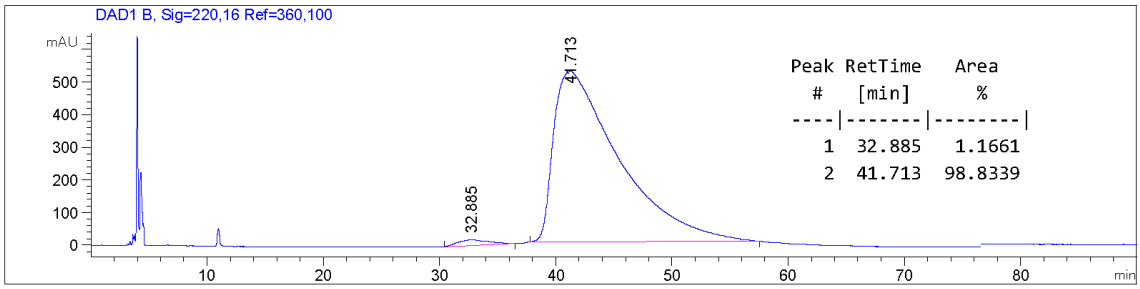


Figure S56. HPLC traces of (a) racemic and (b) enantioenriched product (*R*,*S*)-**3ad**.

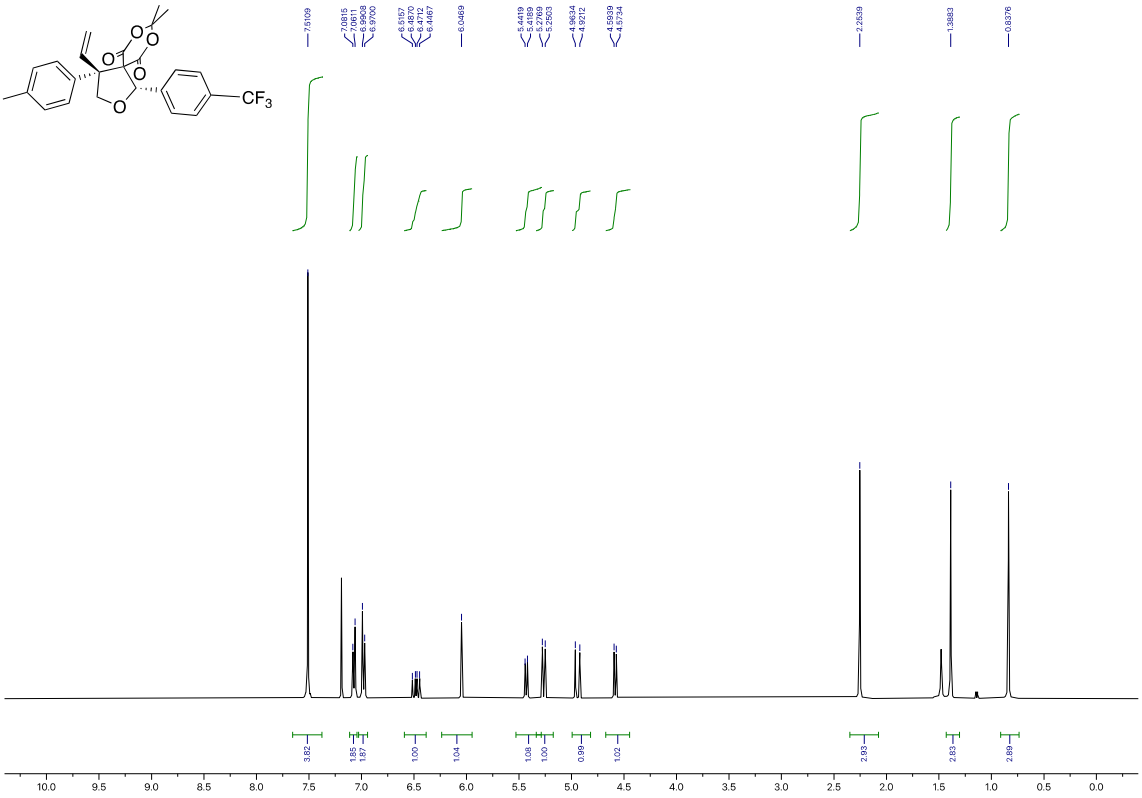


Figure S57. ^{1}H NMR (400 MHz) spectrum of 8,8-dimethyl-4-(*p*-tolyl)-1-(4-(trifluoromethyl) phenyl)-4-vinyl-2,7,9-trioxa spiro[4.5]decane-6,10-dione (**3bb**) in $CDCl_3$.

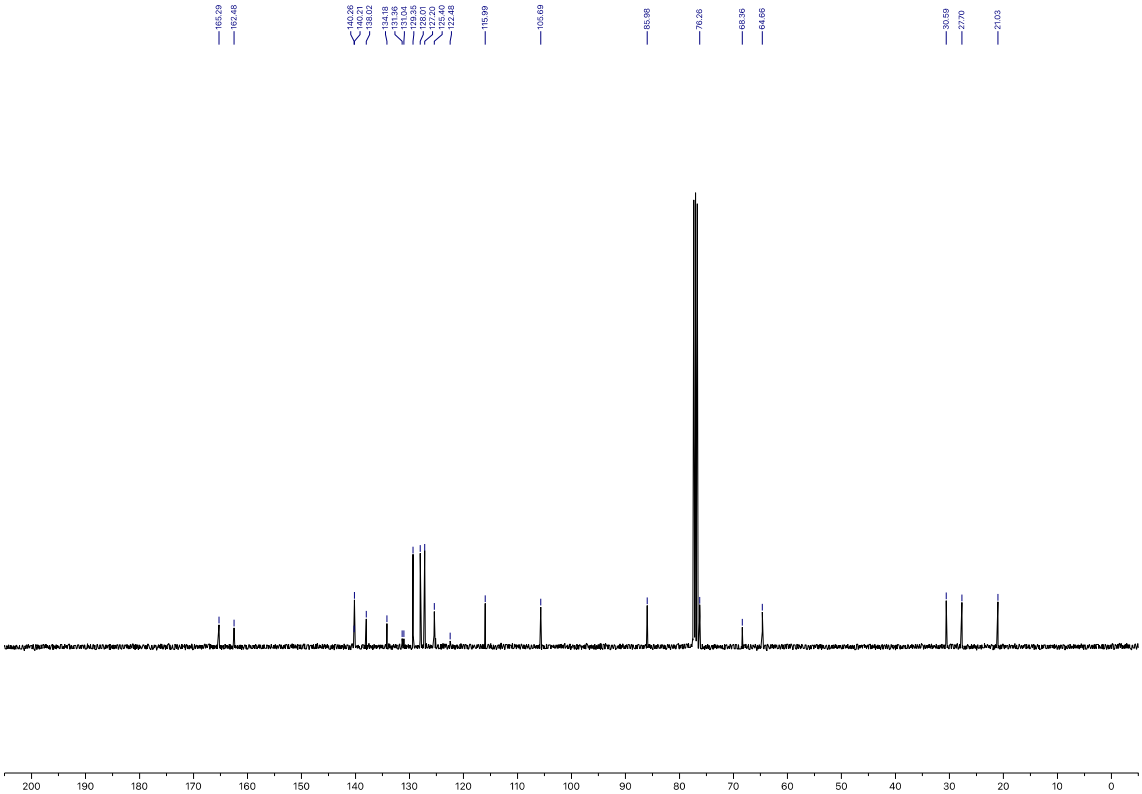


Figure S58. ^{13}C NMR (100.6 MHz) spectrum of **3bb** in $CDCl_3$.

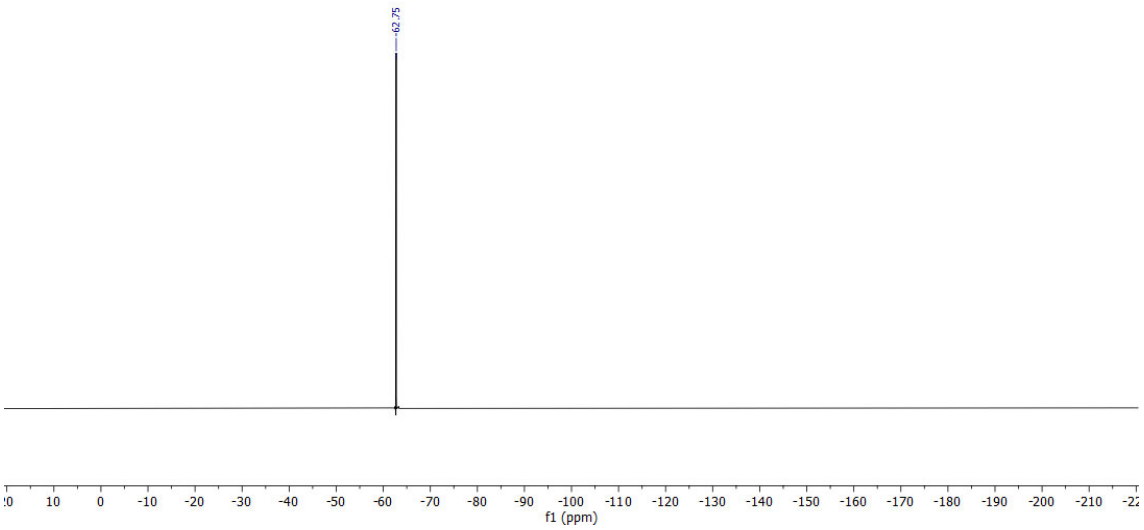
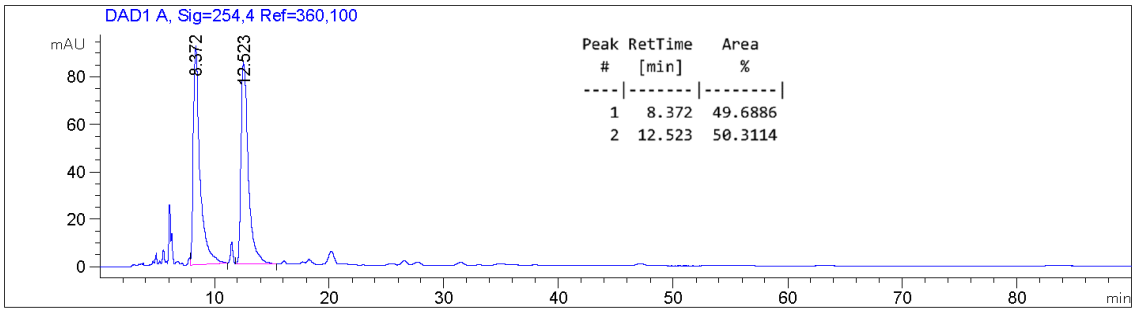


Figure S59. ^{19}F NMR (376 MHz) spectrum of **3bb** in $CDCl_3$.

(a)



(b)

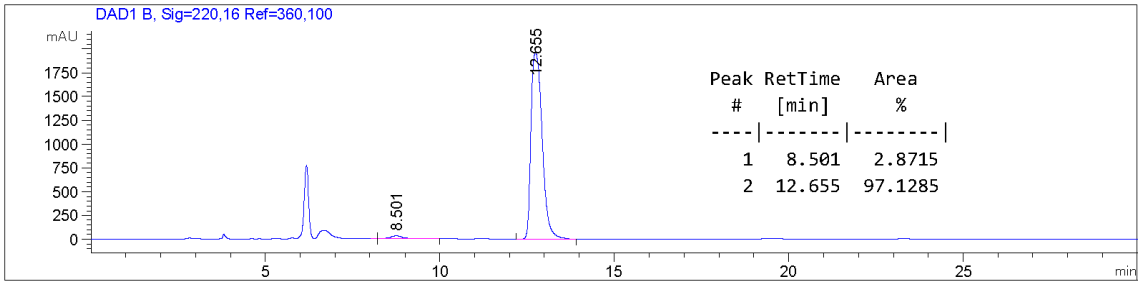


Figure S60. HPLC traces of (a) racemic and (b) enantioenriched product (*R*,*S*)-**3bb**.

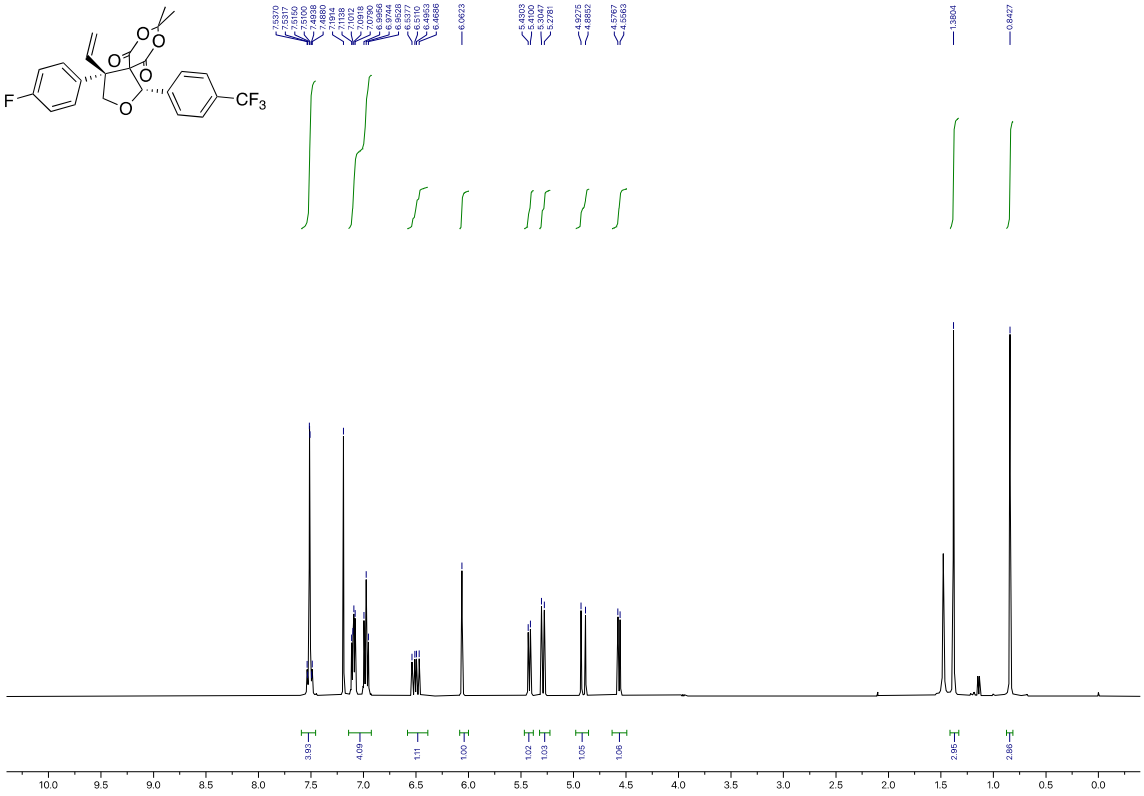


Figure S61. ^{1}H NMR (400 MHz) spectrum 4-(4-fluorophenyl)-8,8-dimethyl-1-(4-(trifluoro- methyl)phenyl)-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3bc**) in $CDCl_3$.

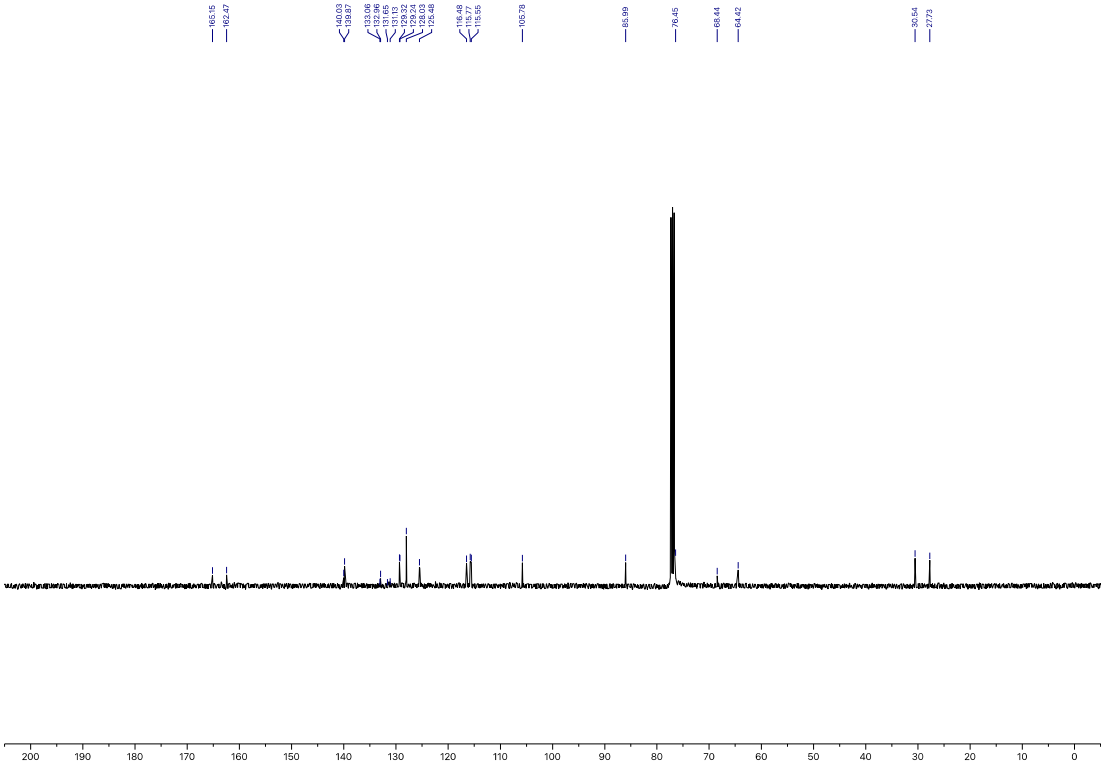


Figure S62. ^{13}C NMR (100.6 MHz) spectrum of **3bc** in $CDCl_3$.

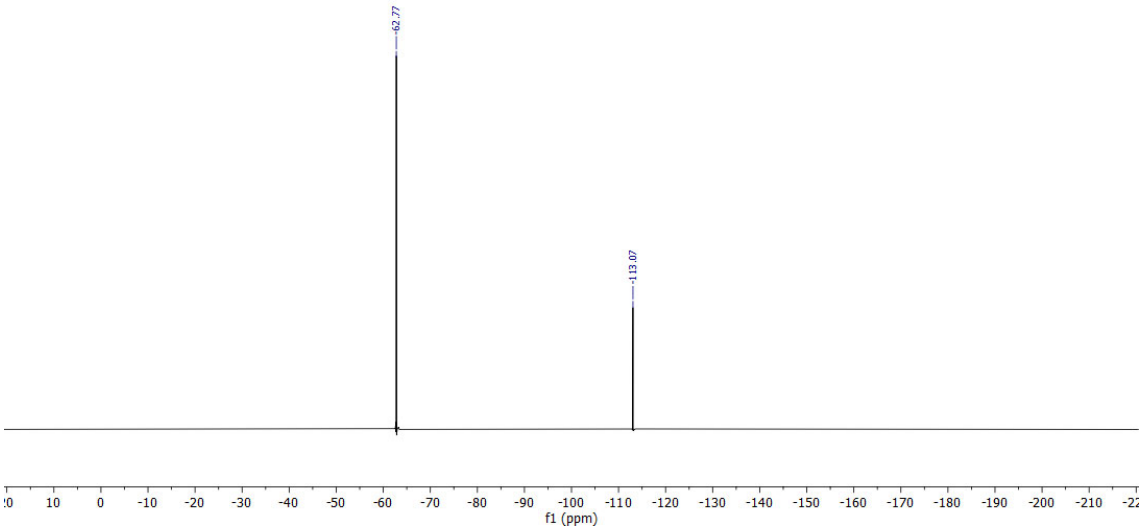
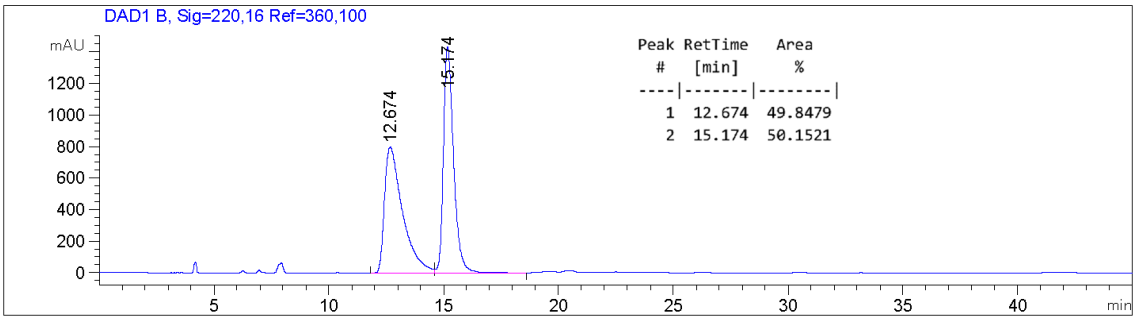


Figure S63. ^{19}F NMR (376 MHz) spectrum of **3bc** in $CDCl_3$.

(a)



(b)

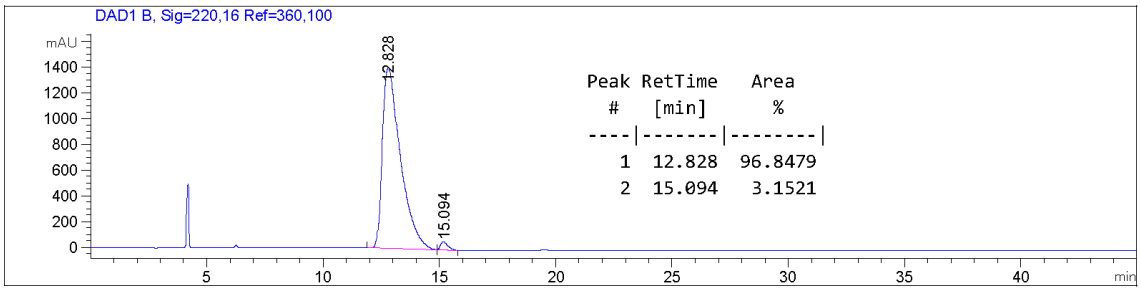


Figure S64. HPLC traces of (a) racemic and (b) enantioenriched (*R*,*S*)-**3bc**.

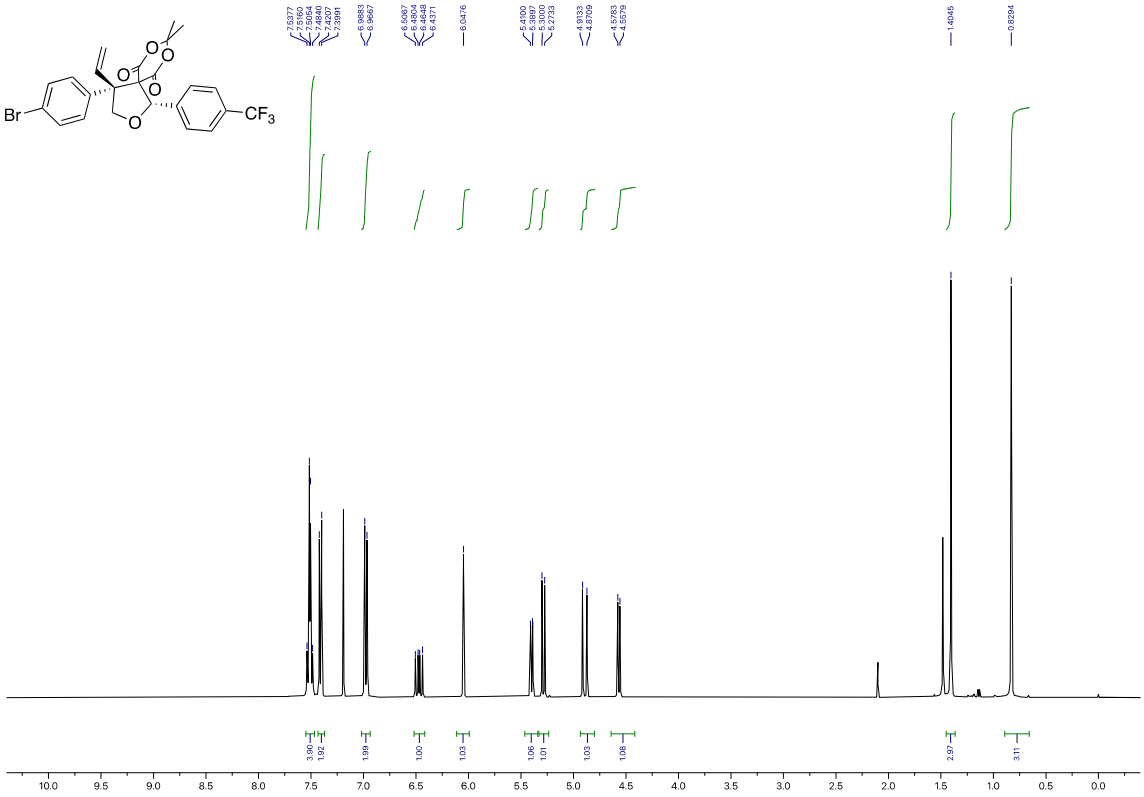


Figure S65. ^{1}H NMR (400 MHz) spectrum of 4-(4-bromophenyl)-8,8-dimethyl-1-(4-(trifluoro- methyl)phenyl)-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3be**) in $CDCl_3$.

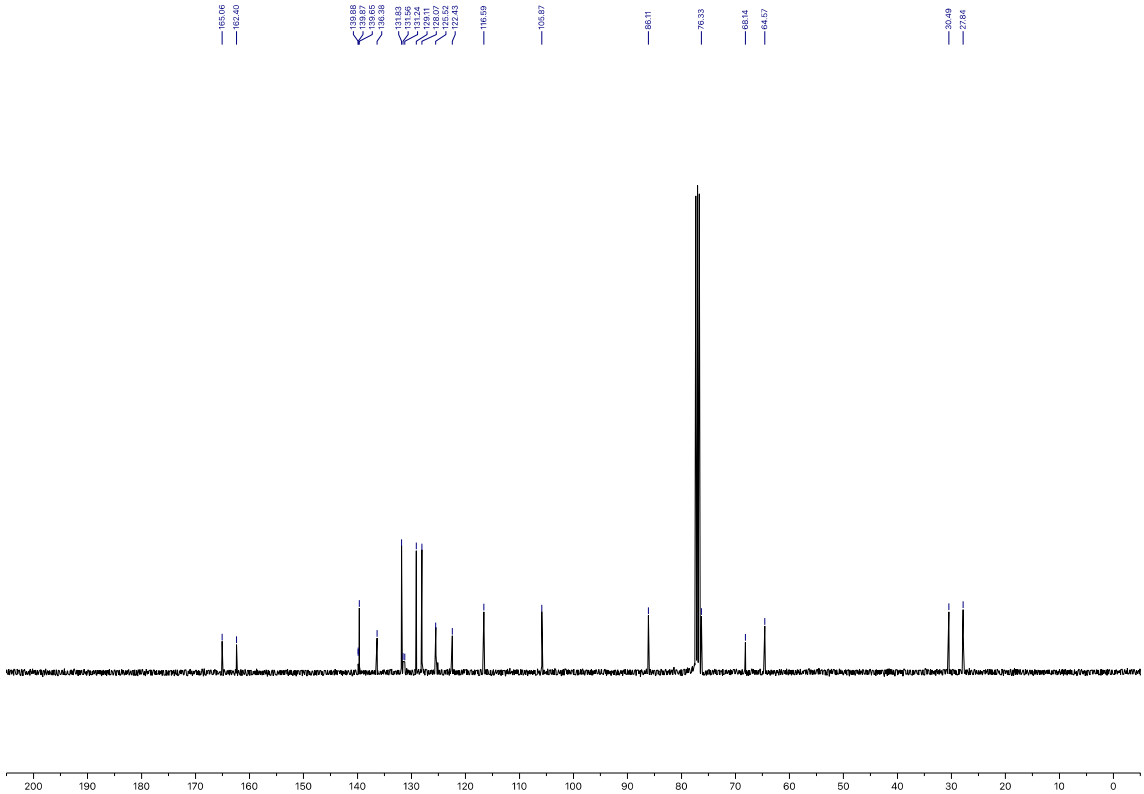


Figure S66. ^{13}C NMR (100.6 MHz) spectrum of **3be** in $CDCl_3$.

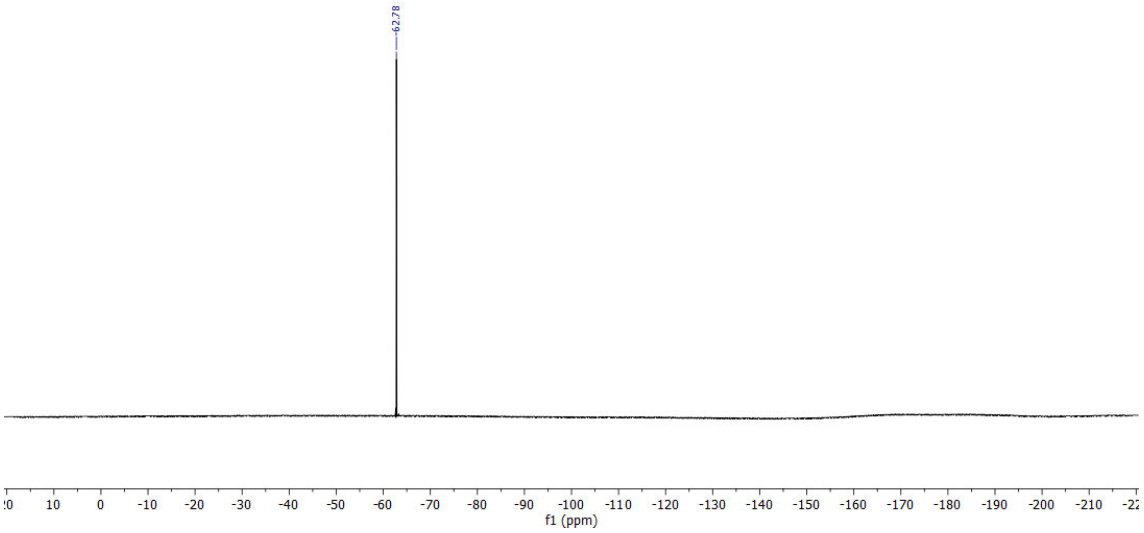
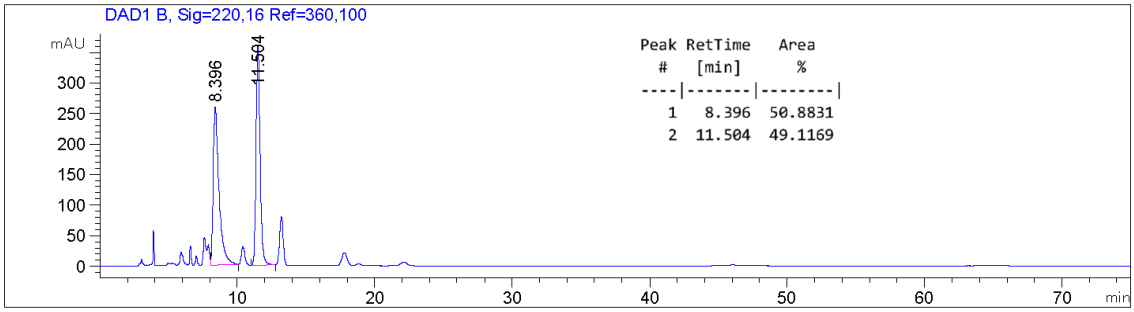


Figure S67. ^{19}F NMR (376 MHz) spectrum of **3be** in $CDCl_3$.

(a)



(b)

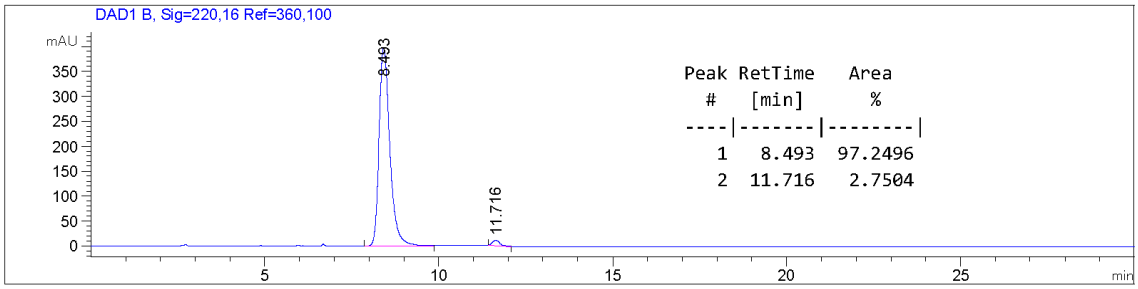


Figure S68. HPLC traces of (a) racemic and (b) enantioenriched product (*R*,*S*)-**3be**.

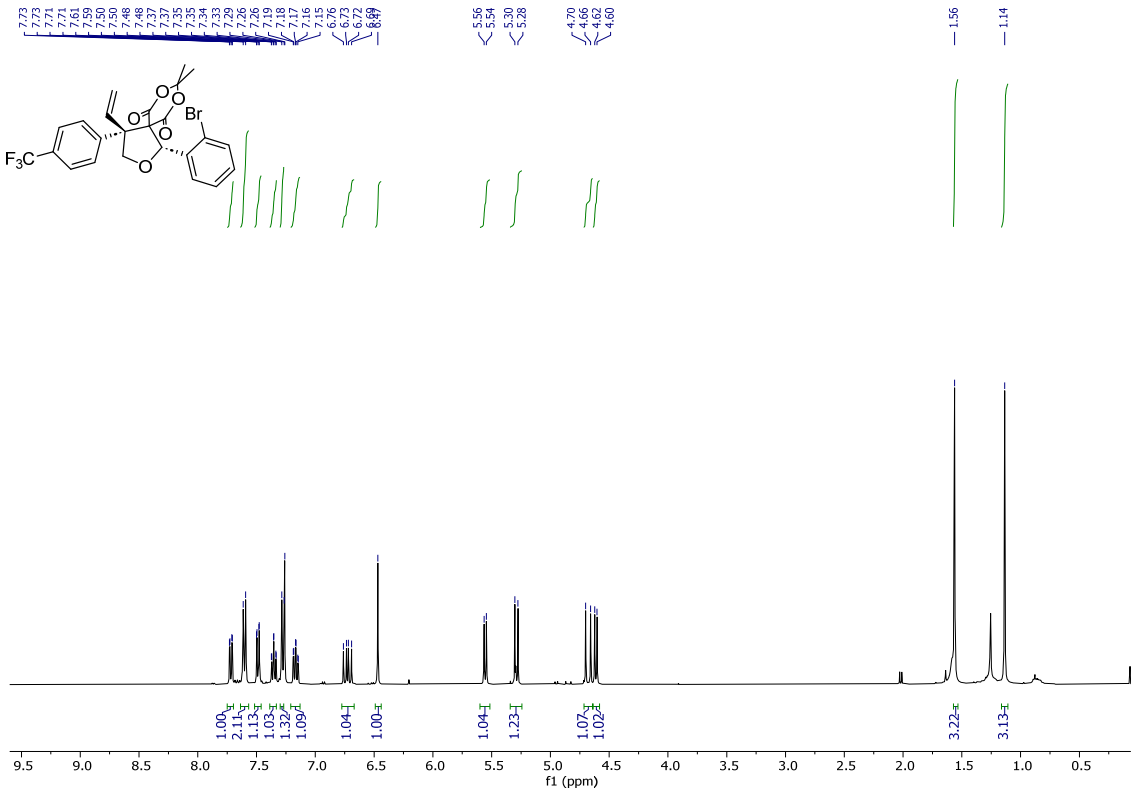


Figure S69. ^{1}H NMR (400 MHz) spectrum of 4-(4-(trifluoromethyl)phenyl)- 8,8-dimethyl-1-(2-bromophenyl)- 4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3gd**) in $CDCl_3$.

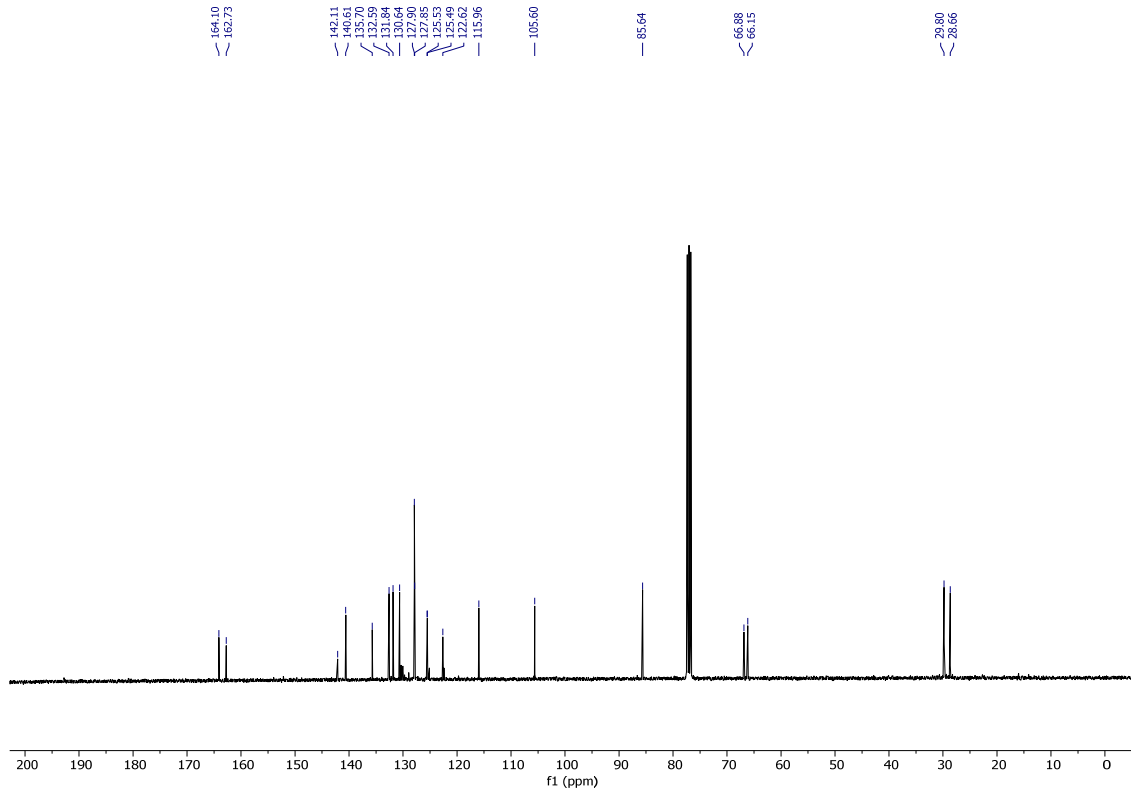


Figure S70. ^{13}C NMR (100.6 MHz) spectrum of **3gd** in $CDCl_3$.

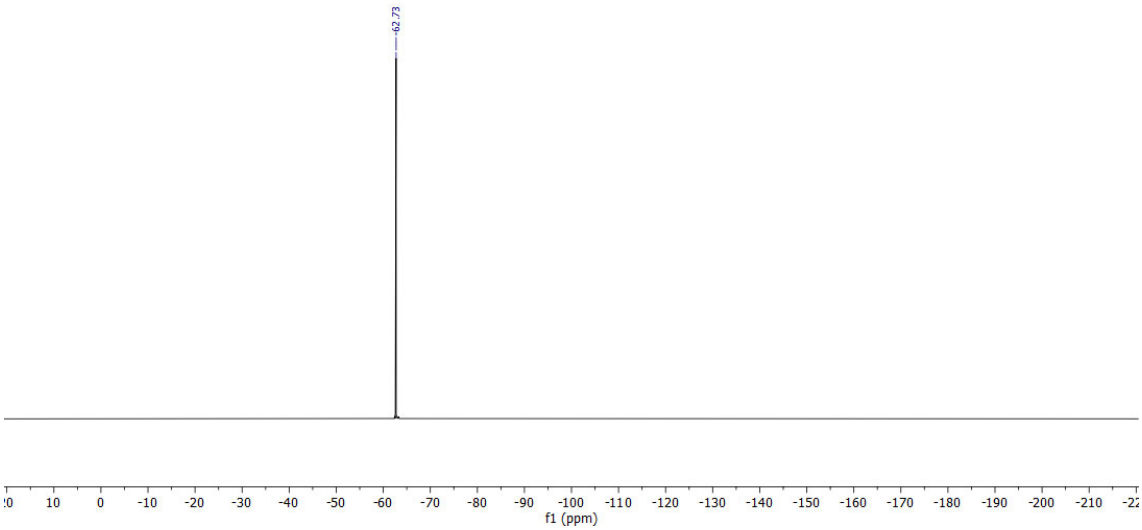
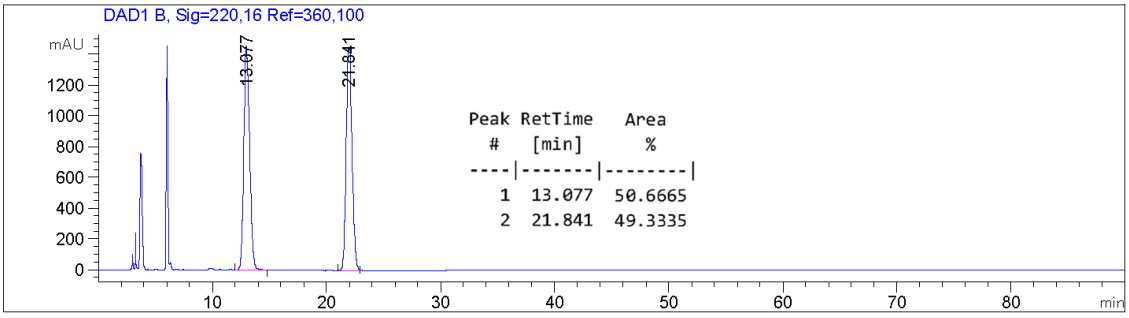


Figure S71. ^{19}F NMR (376 MHz) spectrum of **3ba** in $CDCl_3$.

(a)



(b)

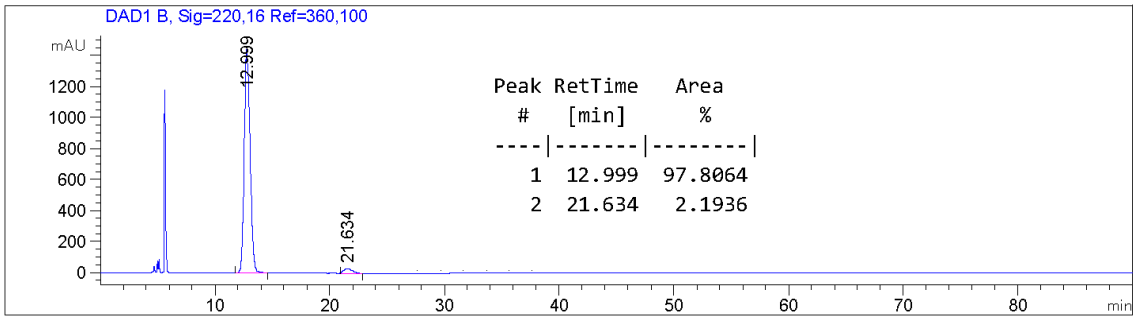


Figure S72. HPLC traces of (a) racemic and (b) enantioenriched product (*R*,*S*)-**3gd**.

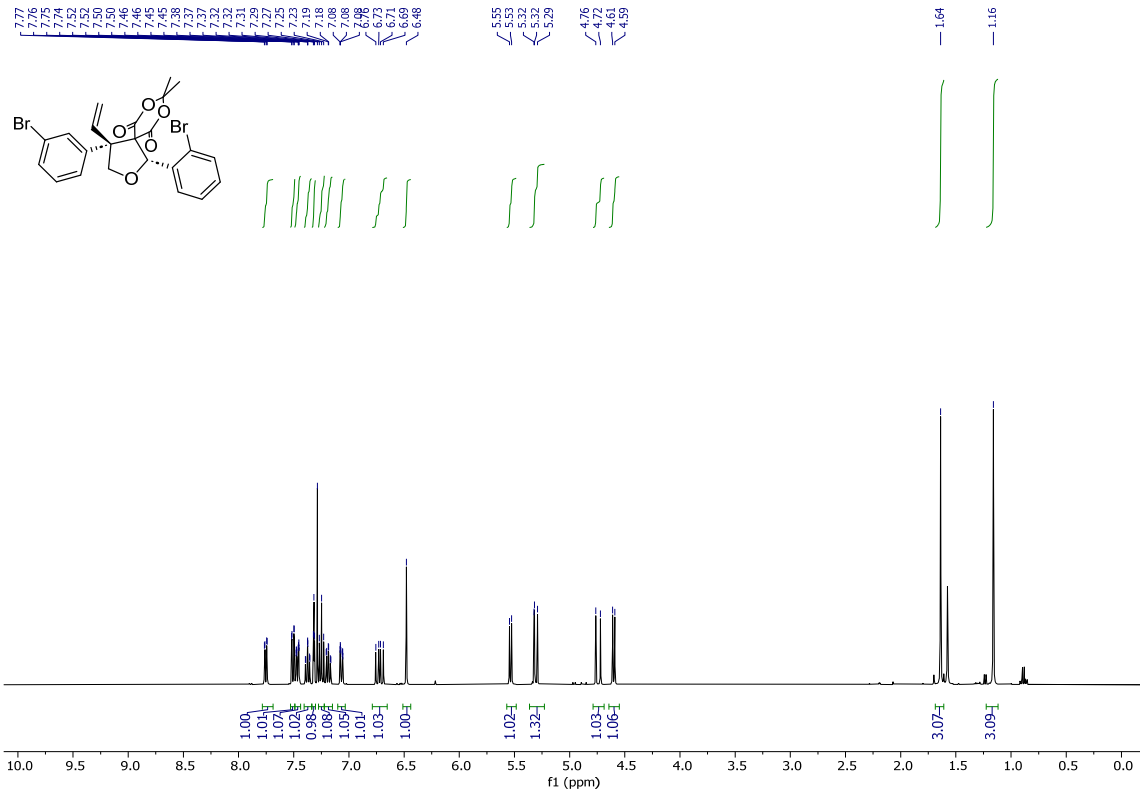


Figure S73. ^{1}H NMR (400 MHz) spectrum of 4-(3-bromophenyl)-8,8-dimethyl-1-(2-bromophenyl)- 4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3gf**) in $CDCl_3$.

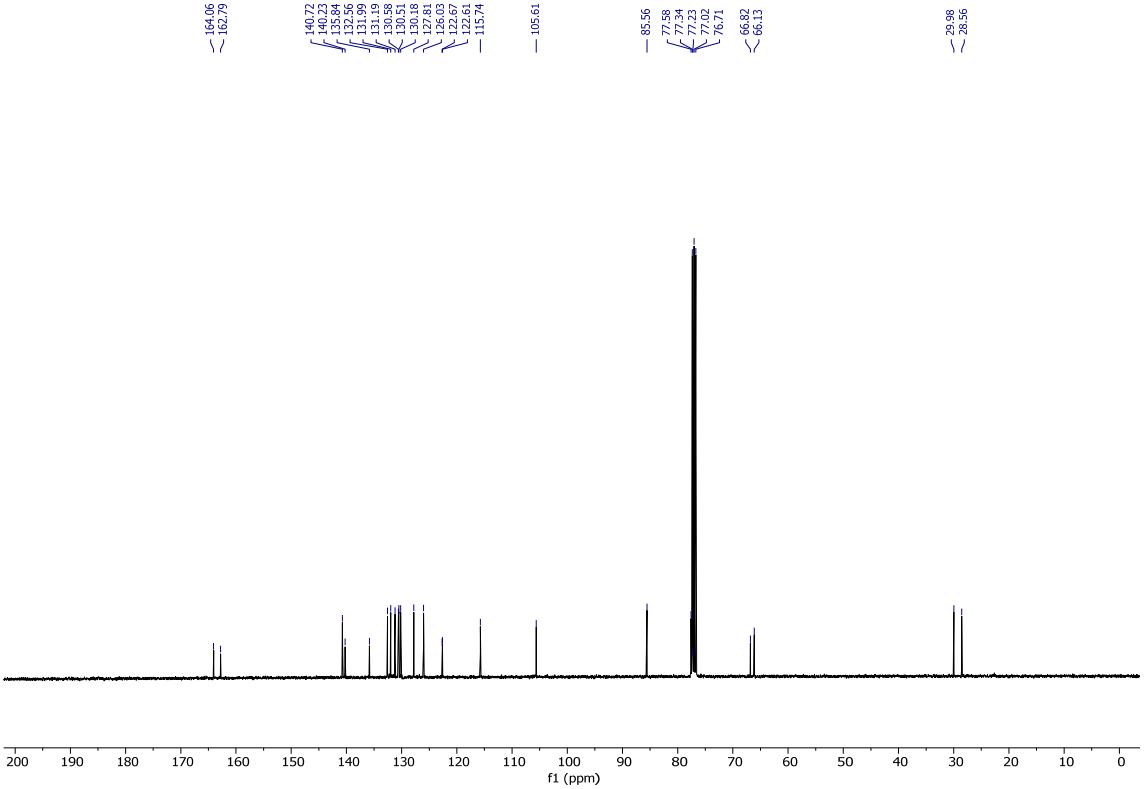
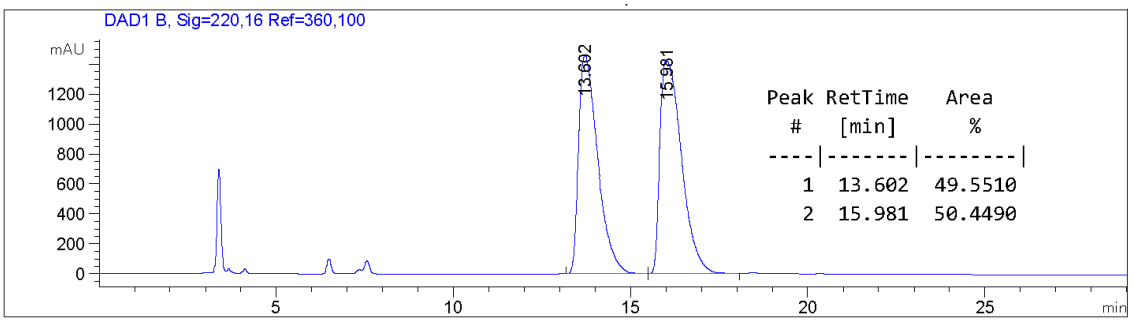


Figure S74. ^{13}C NMR (100.6 MHz) spectrum of **3gf** in $CDCl_3$.

(a)



(b)

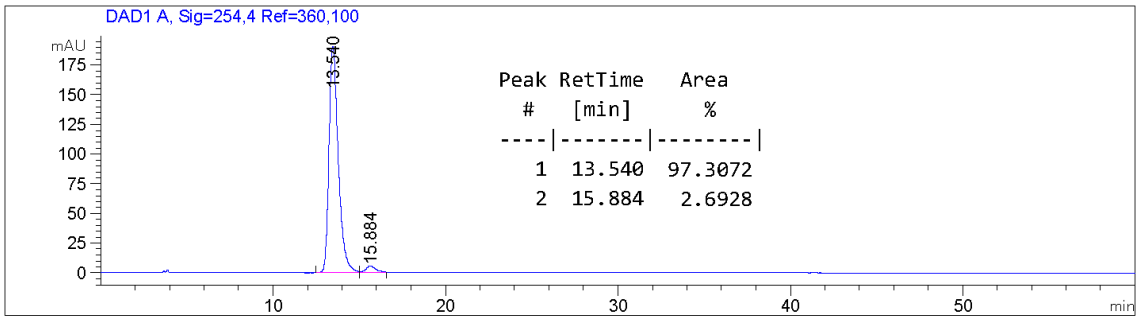


Figure S75. HPLC traces of (a) racemic and (b) enantioenriched product (*R*,*S*)-**3gf**.

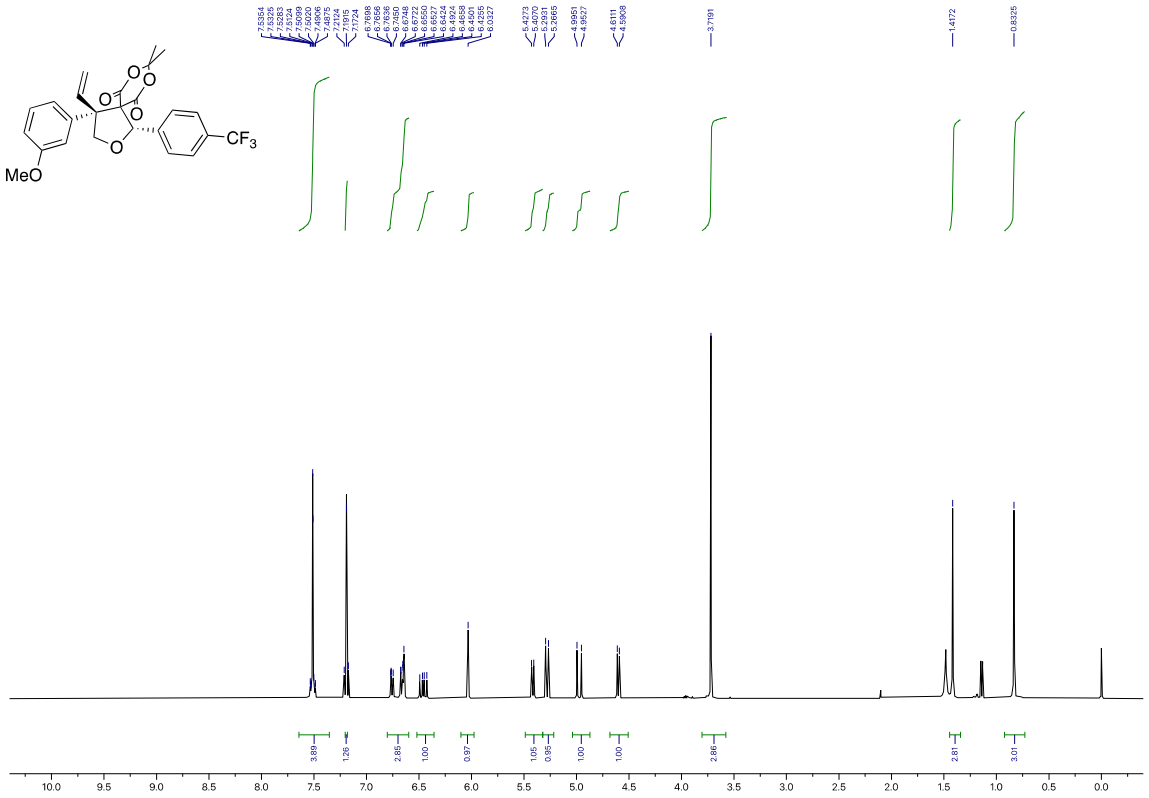


Figure S76. ^{1}H NMR (400 MHz) spectrum of 4-(3-methoxyphenyl)-8,8-dimethyl-1-(4-(trifluoro- methyl)phenyl)-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3bg**) in $CDCl_3$.

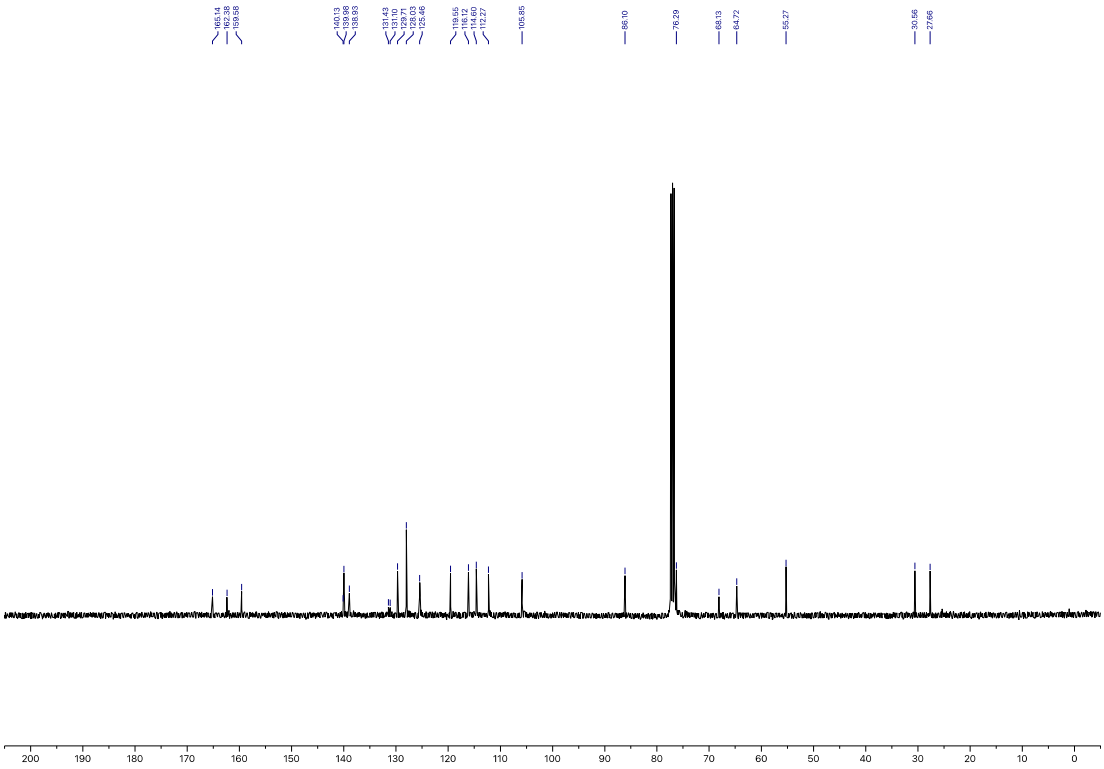


Figure S77. ^{13}C NMR (100.6 MHz) spectrum of **3bg** in $CDCl_3$.

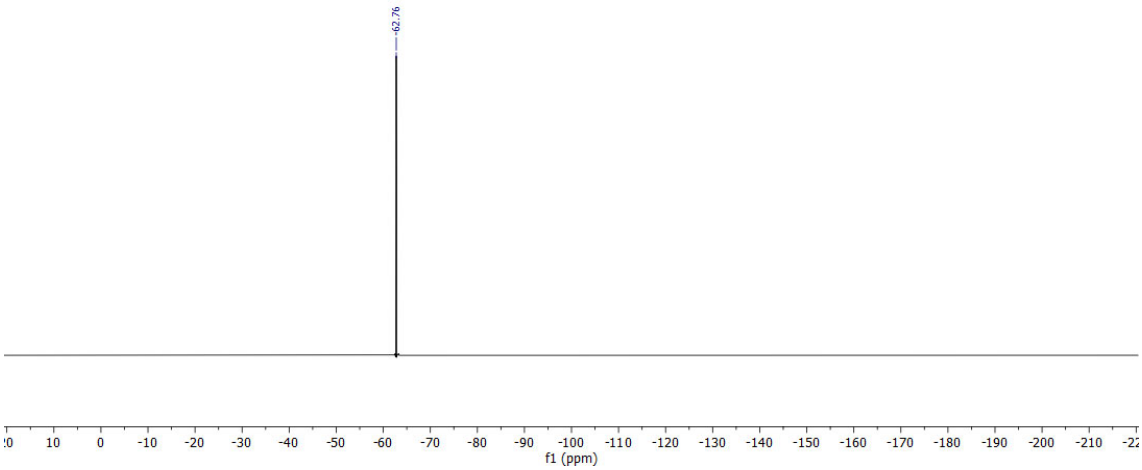
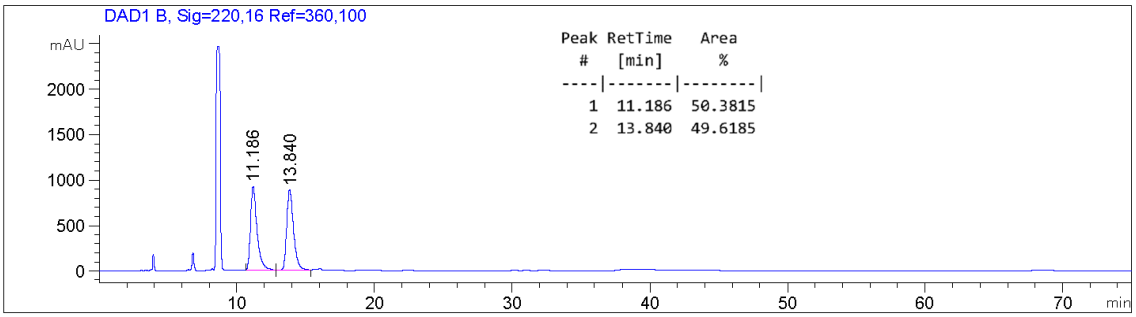


Figure S78. ^{19}F NMR (376 MHz) spectrum of **3bg** in $CDCl_3$.

(a)



(b)

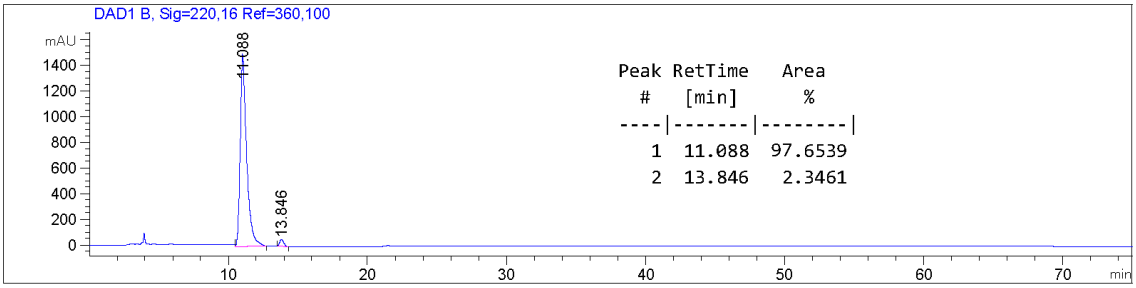


Figure S79. HPLC traces of (a) racemic and (b) enantioenriched product **3bg**.

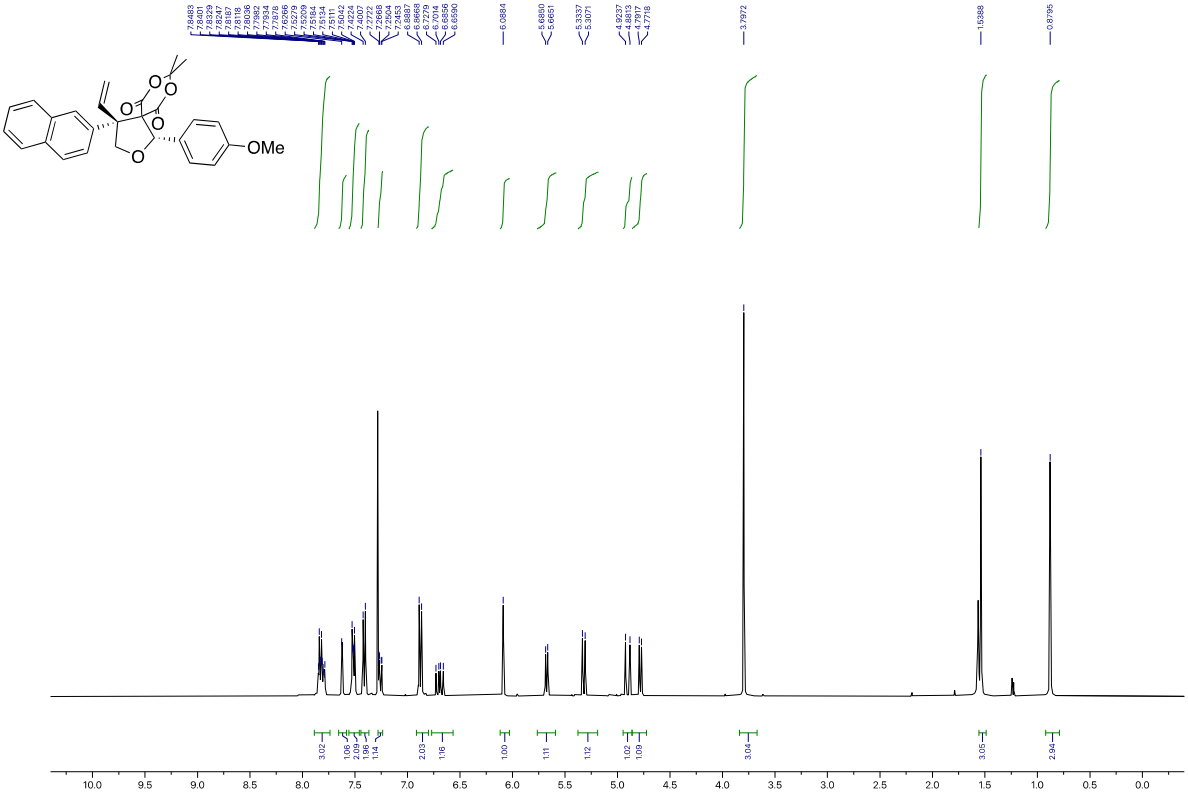


Figure S80. ^{1}H NMR (400 MHz) spectrum of 1-(4-methoxyphenyl)-8,8-dimethyl-4-(naphthalen-2-yl)-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3ah**) in $CDCl_3$.

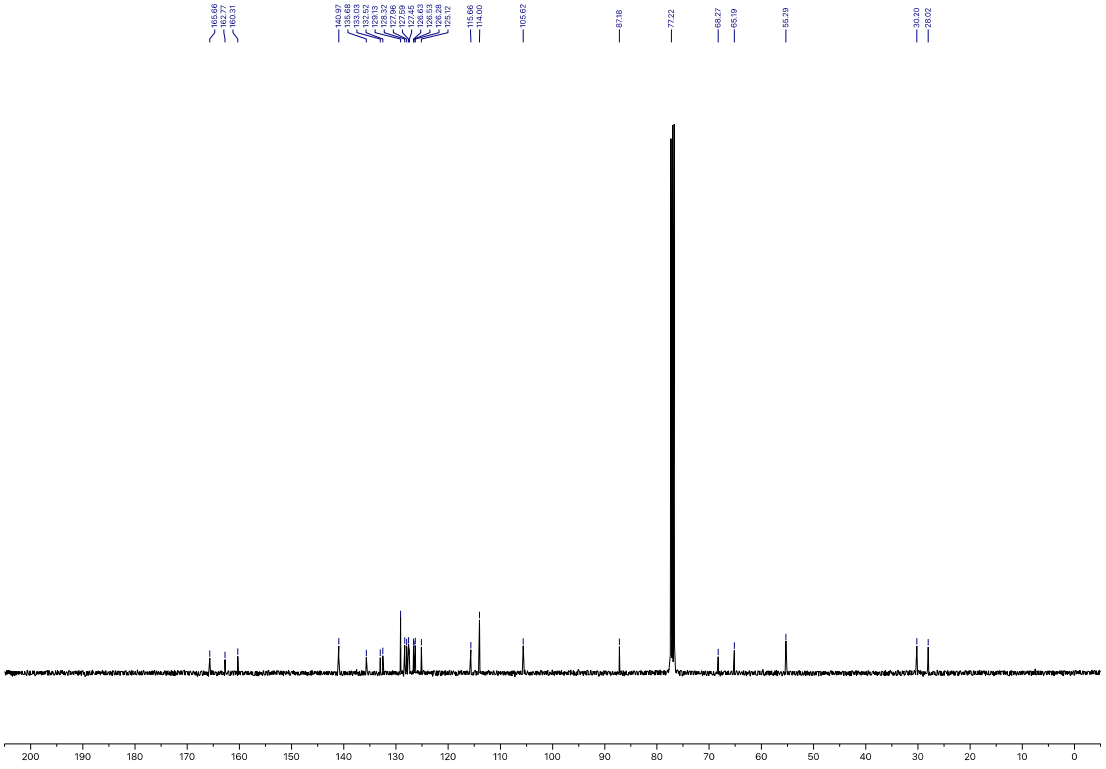
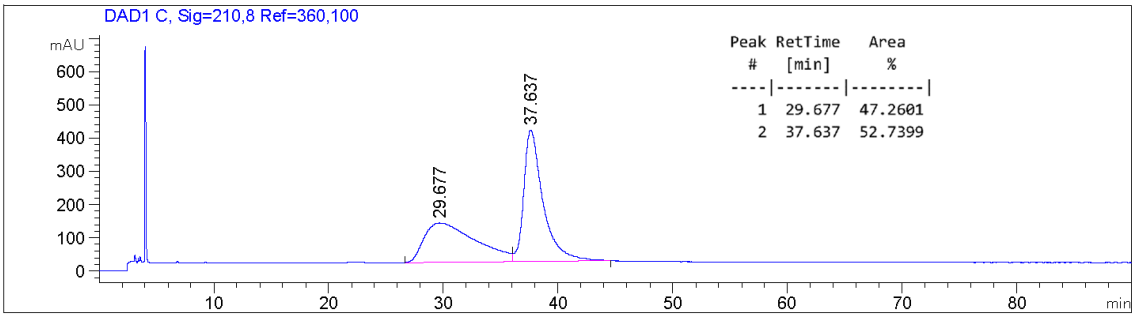


Figure S81. ^{13}C NMR (100.6 MHz) spectrum of **3ah** in $CDCl_3$.

(a)



(b)

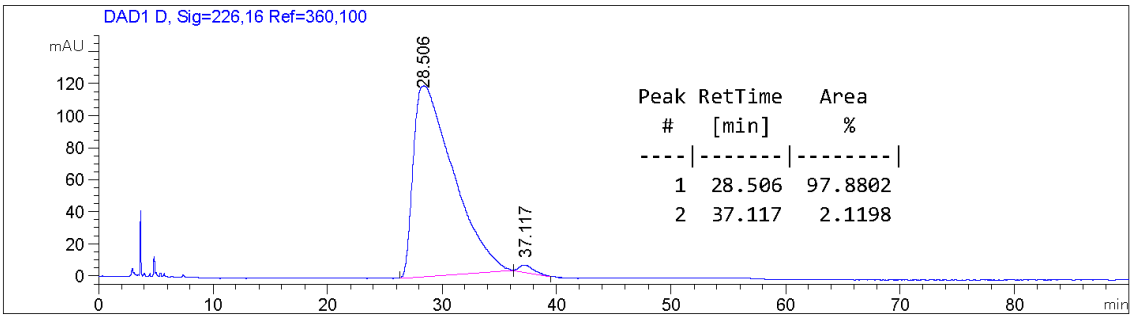


Figure S82. HPLC traces of (a) racemic and (b) enantioenriched product (*R*,*S*)-**3ah**.

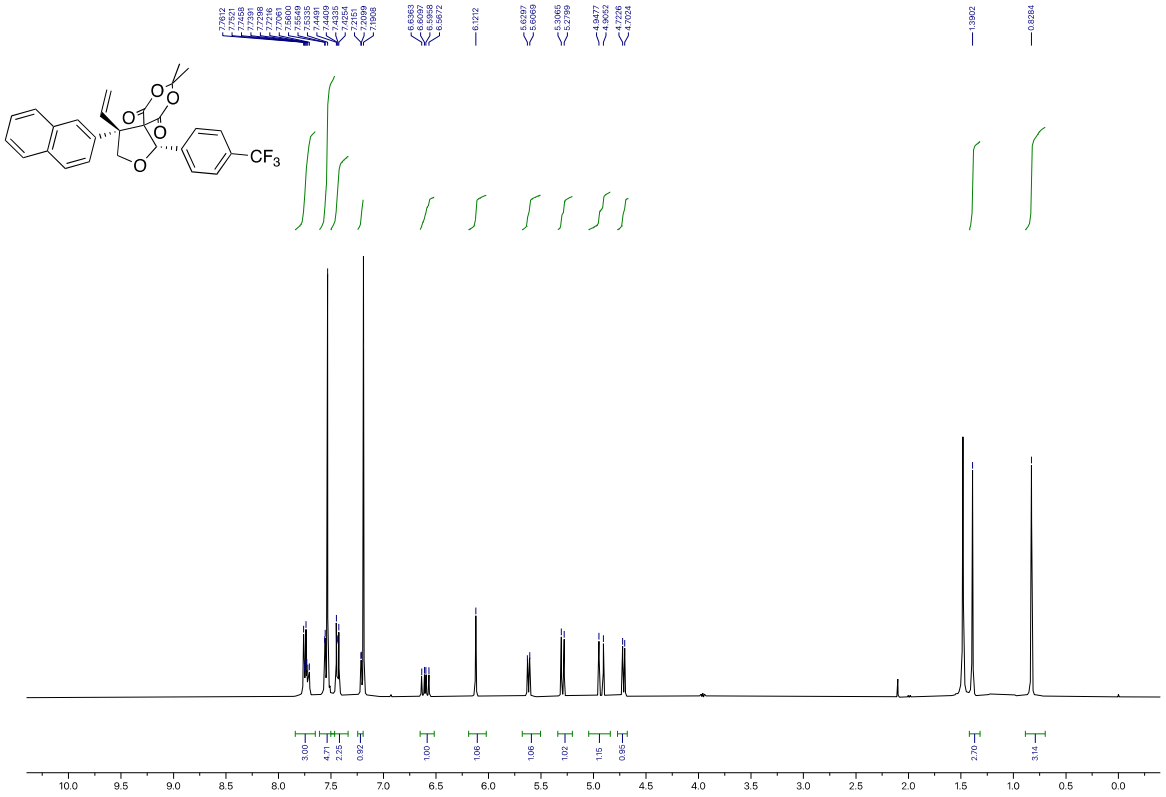


Figure S83. ^{1}H NMR (400 MHz) spectrum of 8,8-dimethyl-4-(naphthalen-2-yl)-1-(4(trifluoromethyl) phenyl)-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3bh**) in $CDCl_3$.

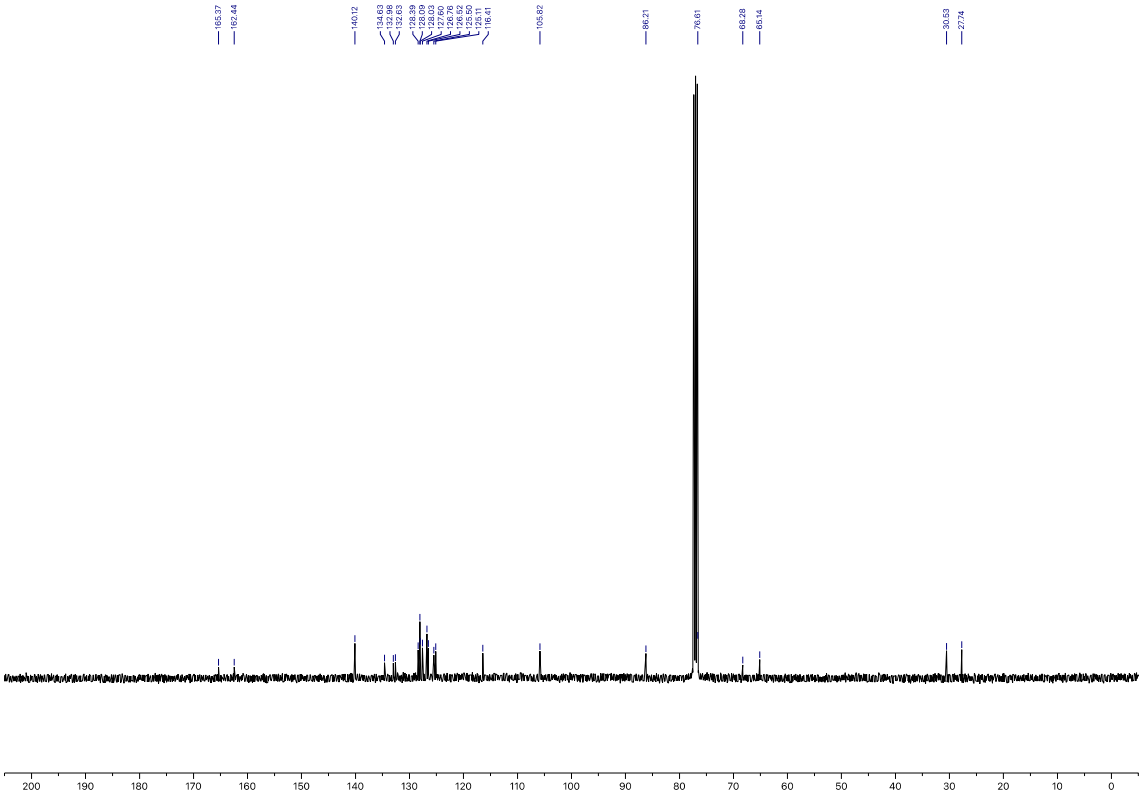


Figure S84. ^{13}C NMR (100.6 MHz) spectrum of **3bh** in $CDCl_3$.

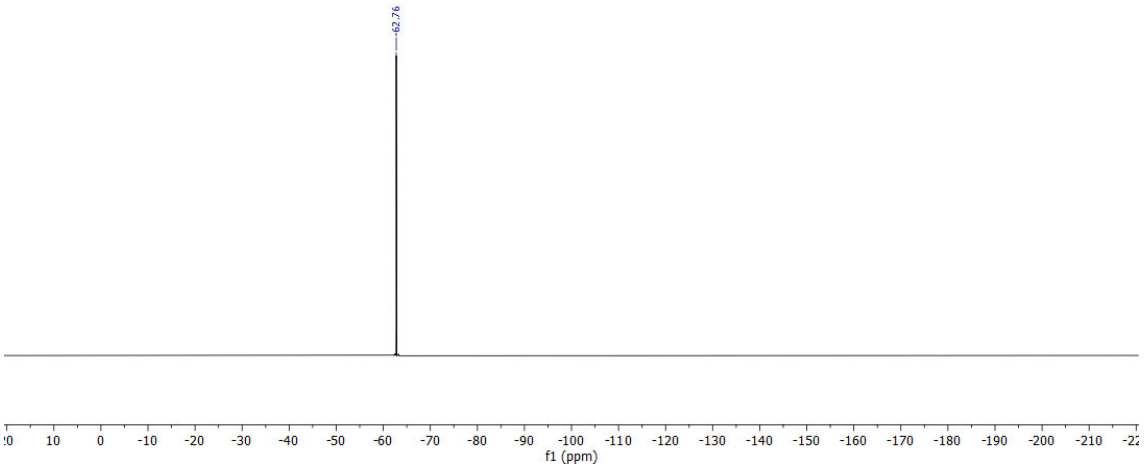
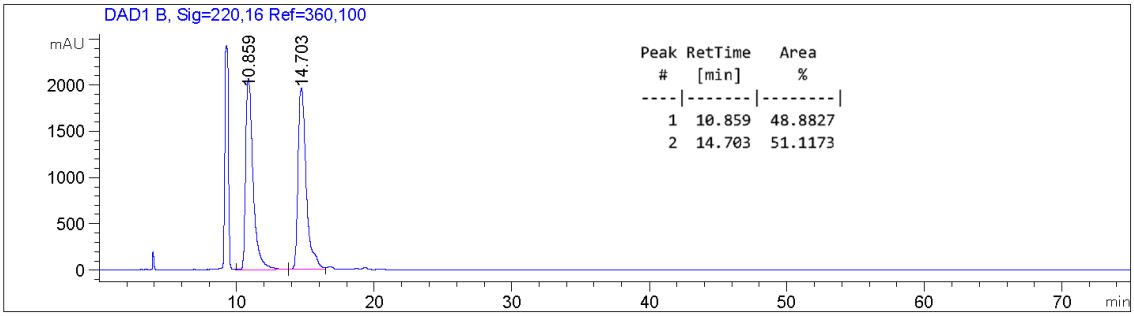


Figure S85. ^{19}F NMR (376 MHz) spectrum of **3bh** in $CDCl_3$.

(a)



(b)

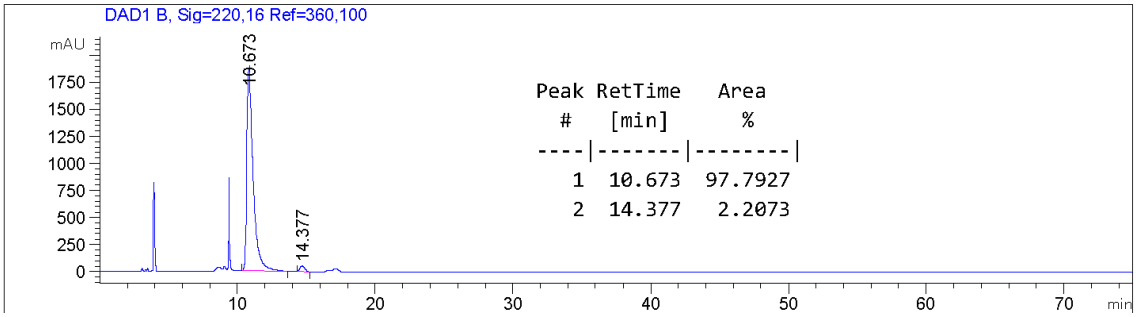


Figure S86. HPLC traces of (a) racemic and (b) enantioenriched product (*R*,*S*)-**3bh**.

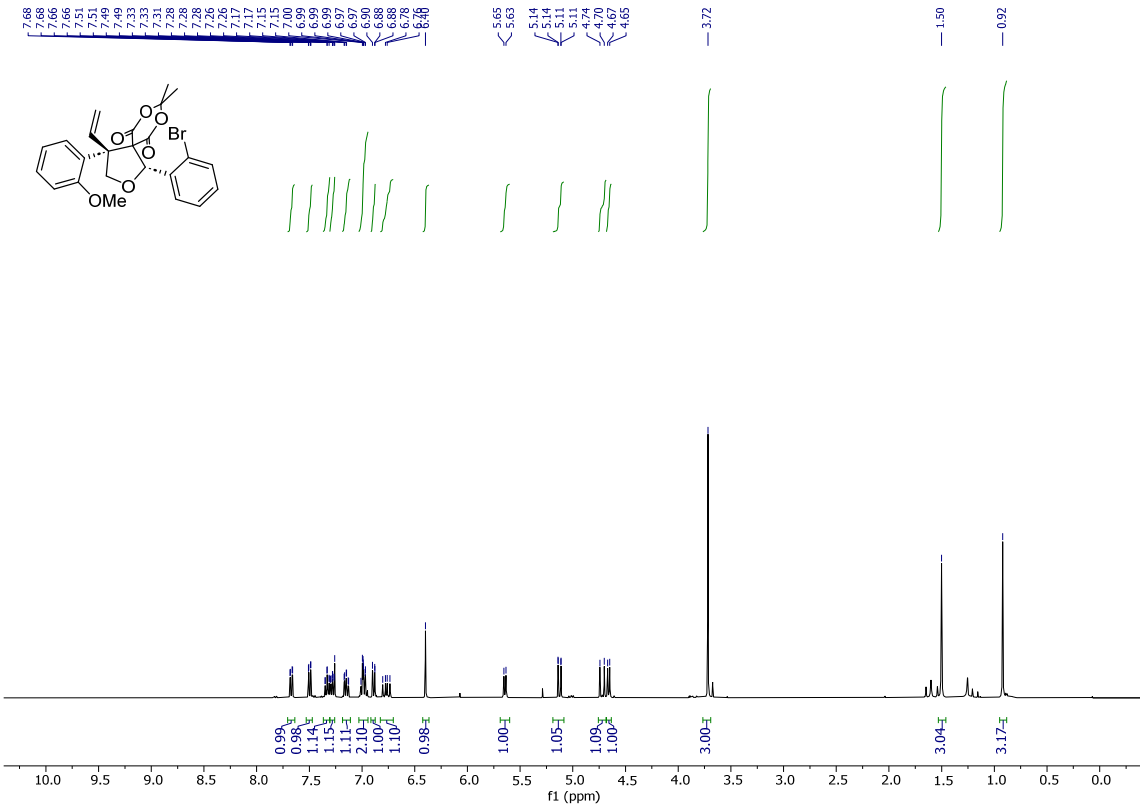


Figure S87. ^{1}H NMR (400 MHz) spectrum of 4-(2-methoxyphenyl)-8,8-dimethyl-1-(2-bromophenyl)- 4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3gi**) in $CDCl_3$.

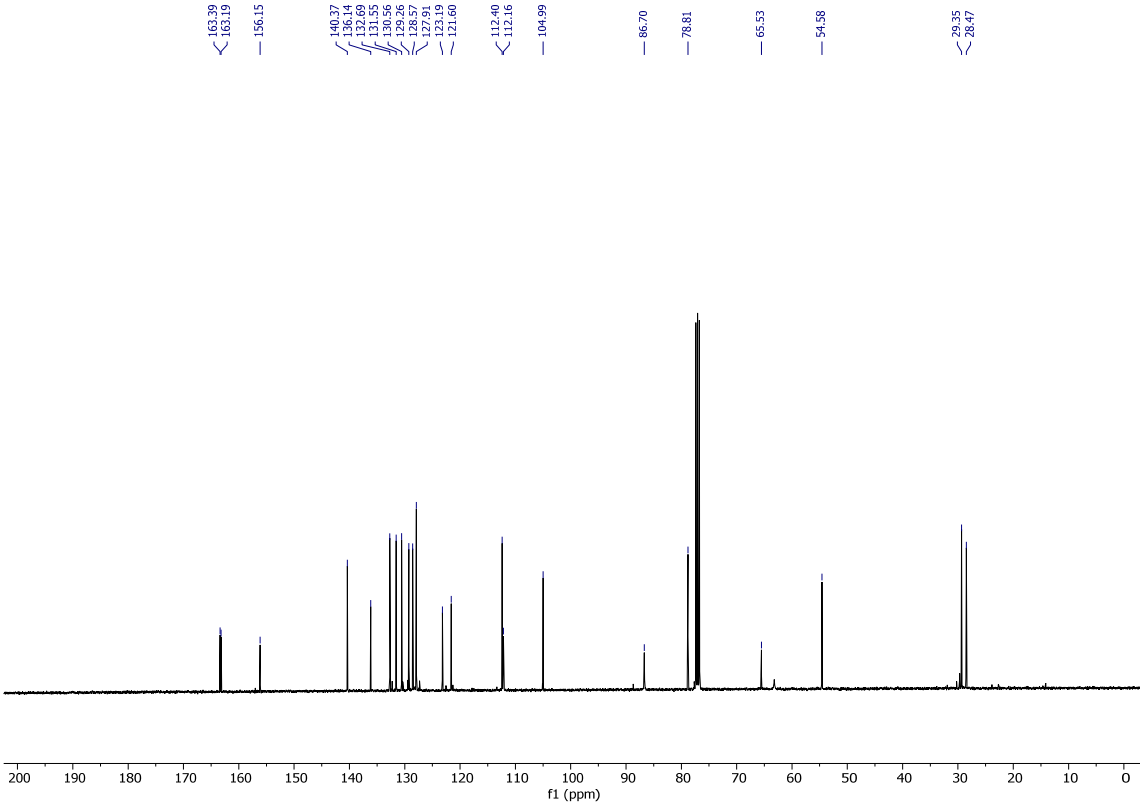
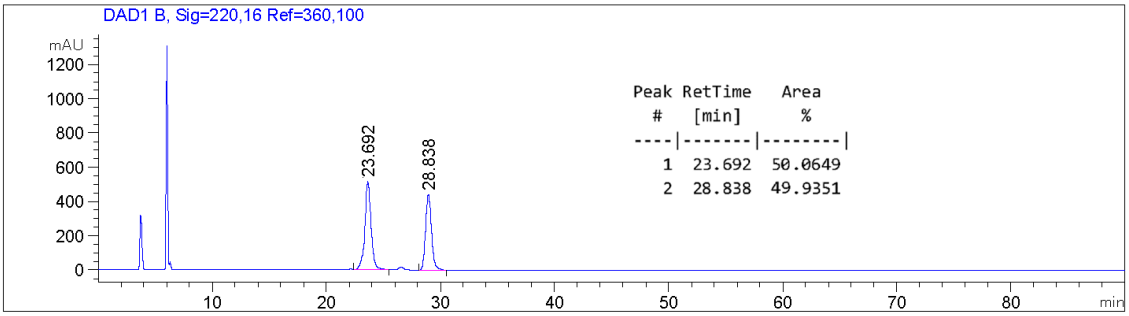


Figure S88. ^{13}C NMR (100.6 MHz) spectrum of **3gi** in $CDCl_3$.

(a)



(b)

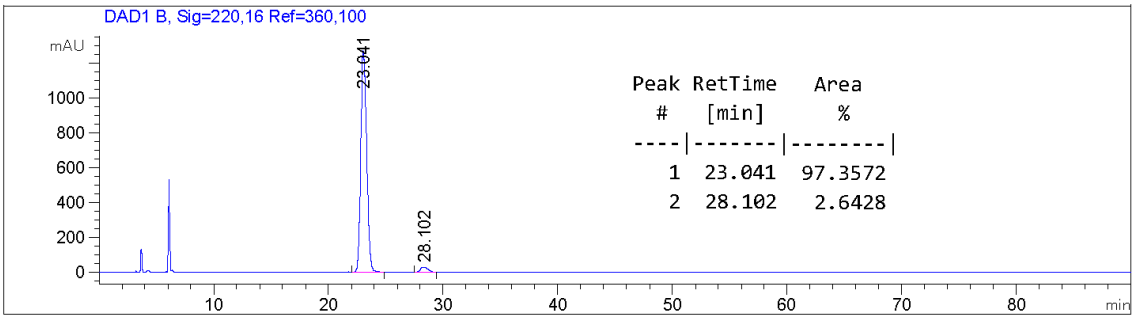


Figure S89. HPLC traces of (a) racemic and (b) enantioenriched product (*R*,*S*)-**3gi**.

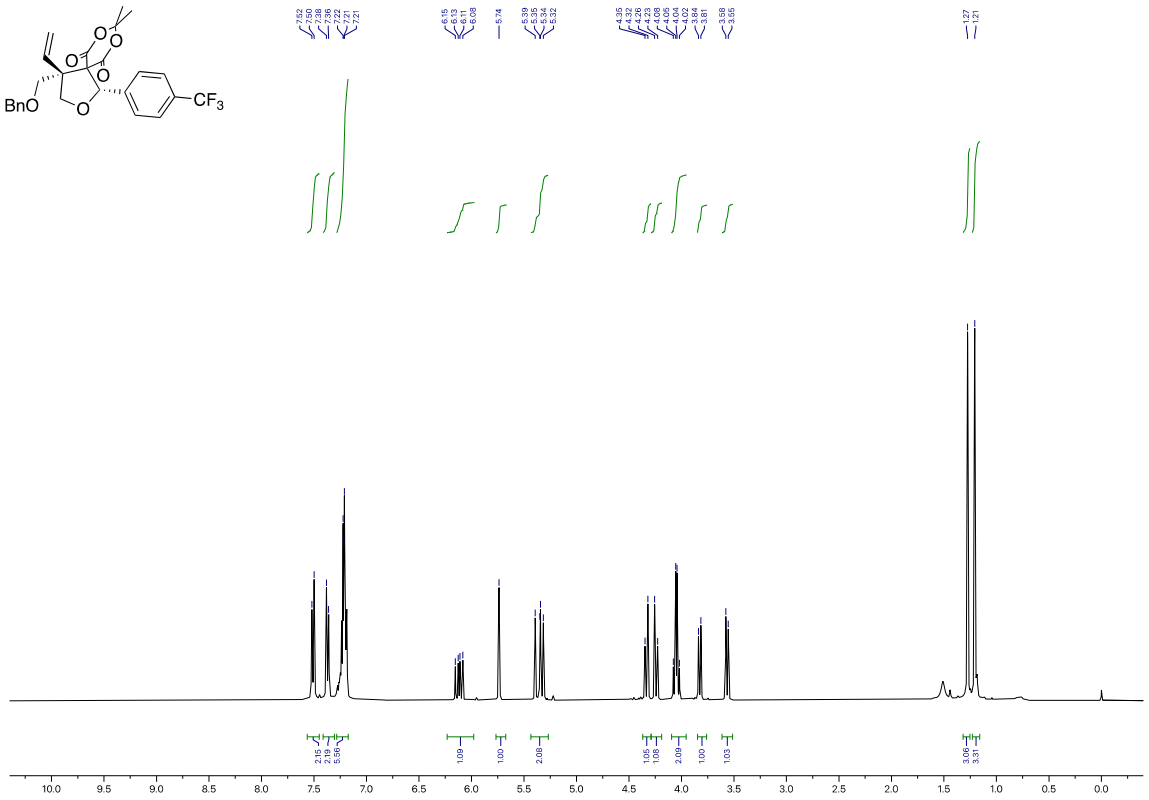


Figure S90. ^{1}H NMR (400 MHz) spectrum of 4-((benzyloxy)methyl)-8,8-dimethyl-1-(4-(trifluoromethyl) phenyl)-4-vinyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**3bj**) in $CDCl_3$

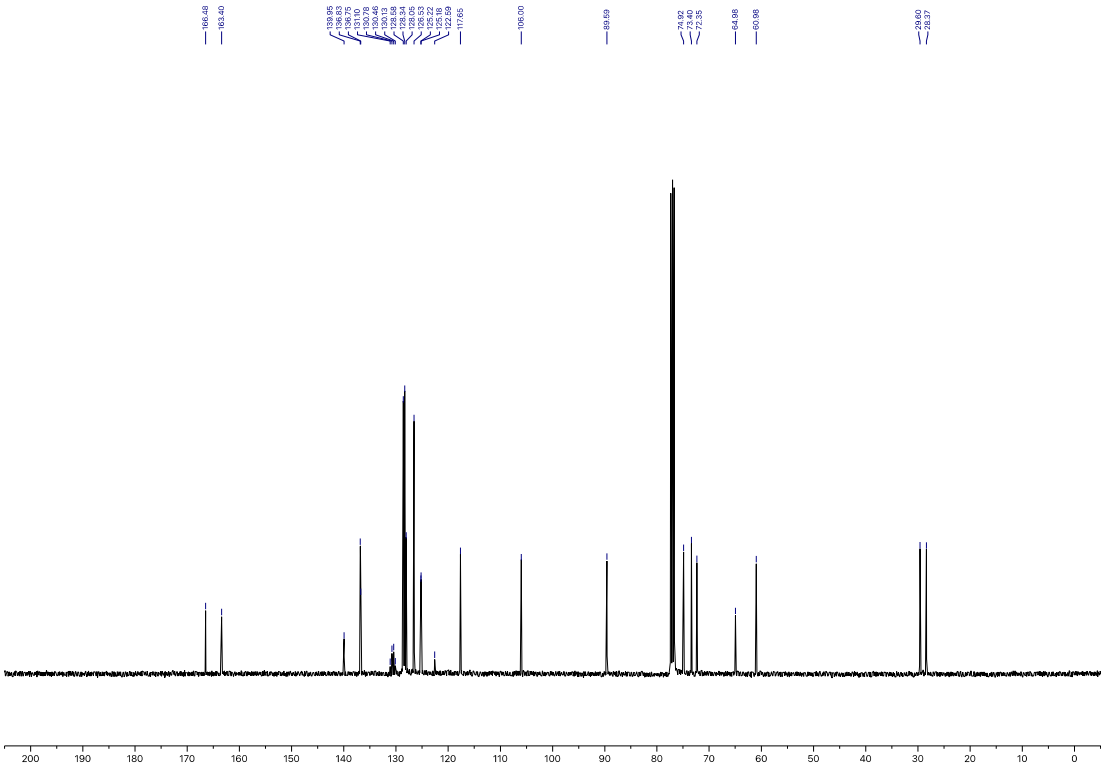


Figure S91. ^{13}C NMR (100.6 MHz) spectrum of **3bj** in $CDCl_3$.

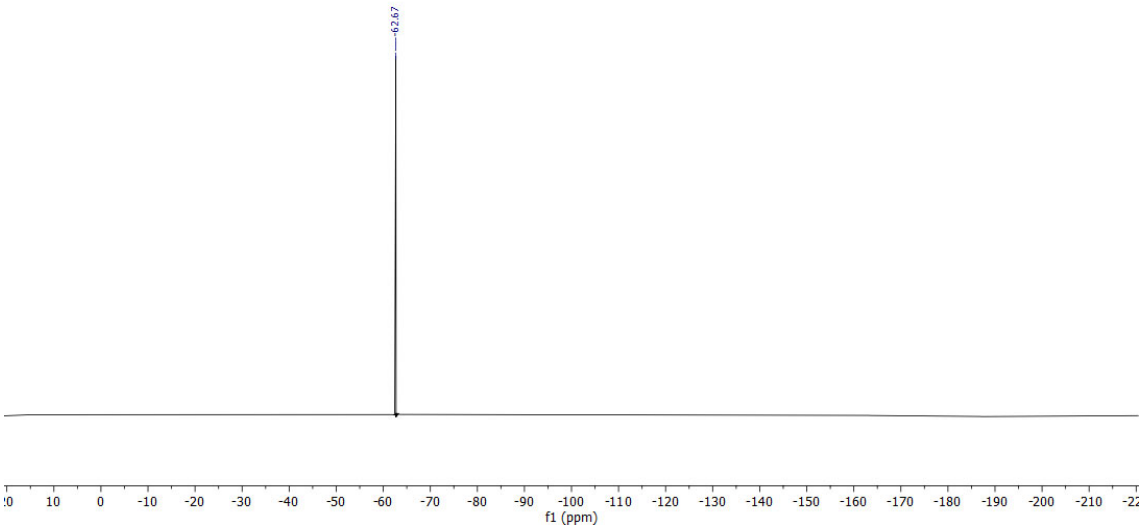
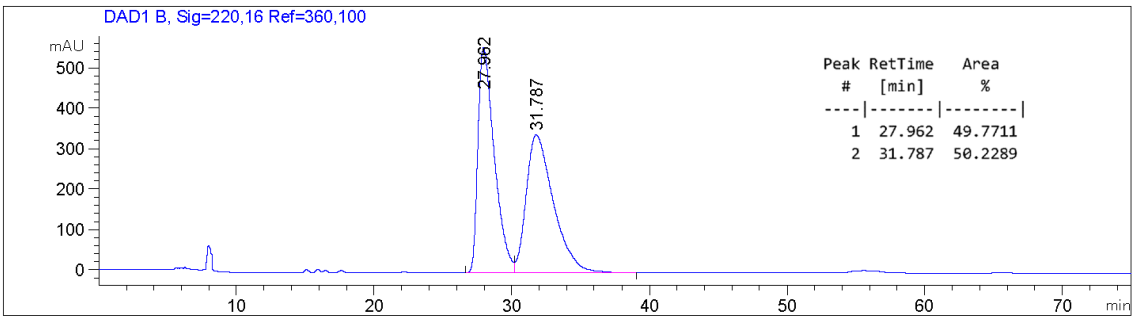


Figure S92. ^{19}F NMR (376 MHz) spectrum of **3bj** in $CDCl_3$.

(a)



(b)

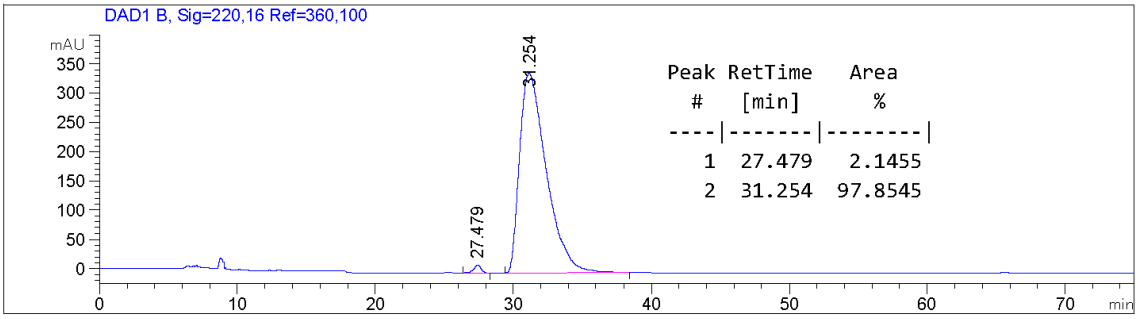


Figure S93. HPLC traces of (a) racemic and (b) enantioenriched product (*R,S*)-**3bj**.

SI-17. Copies of NMR spectra of the Pd-intermediates formed under catalytic conditions

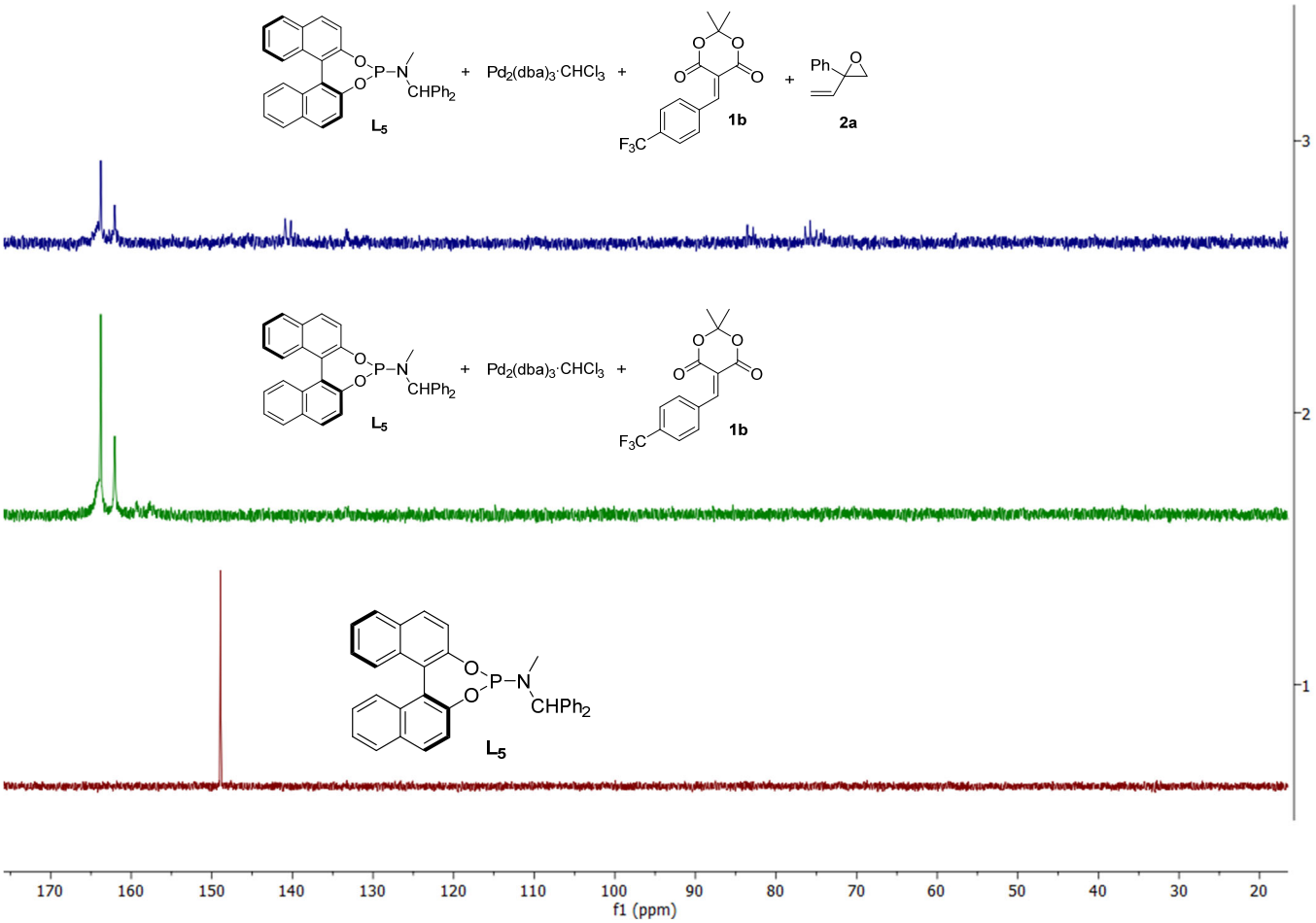


Figure S100. $^{31}P\{^{1}H\}$ NMR spectra of **L5** in red, of a mixture of $Pd_2(dba)_3{\cdot}CHCl_3$ + **L5** (2 equiv) + **1b** (10 equiv) (in green) and of a mixture of $Pd_2(dba)_3{\cdot}CHCl_3$ + **L5** (2 equiv) + **1b** (10 equiv) and **2a** (15 equiv) during the reaction (in blue).

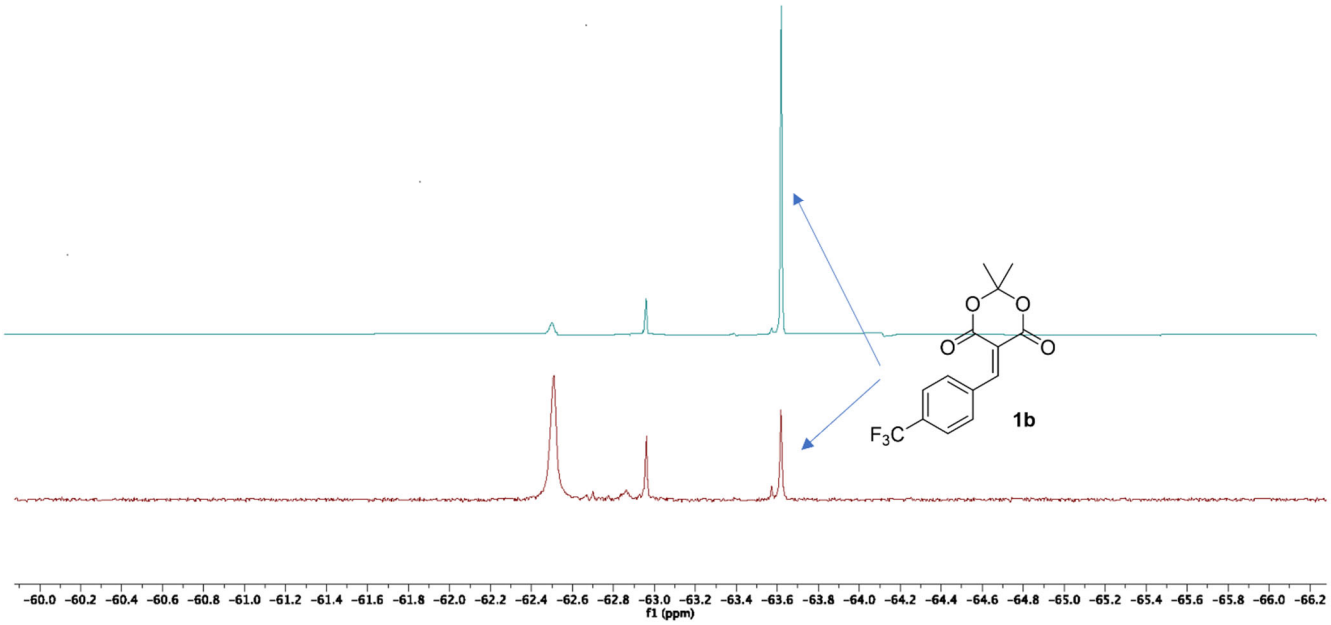


Figure S101. $^{19}F\{^{1}H\}$ NMR spectra of a mixture of $Pd_2(dba)_3 \cdot CHCl_3$ + **L5** (2 equiv) + **1b** (20 equiv) (in green) and of a mixture of $Pd_2(dba)_3 \cdot CHCl_3$ + **L5** (2 equiv) + **1b** (2 equiv) (in blue).

SI-18. Copies of NMR spectra of PS-(*R*)-L_5 and its synthetic intermediates

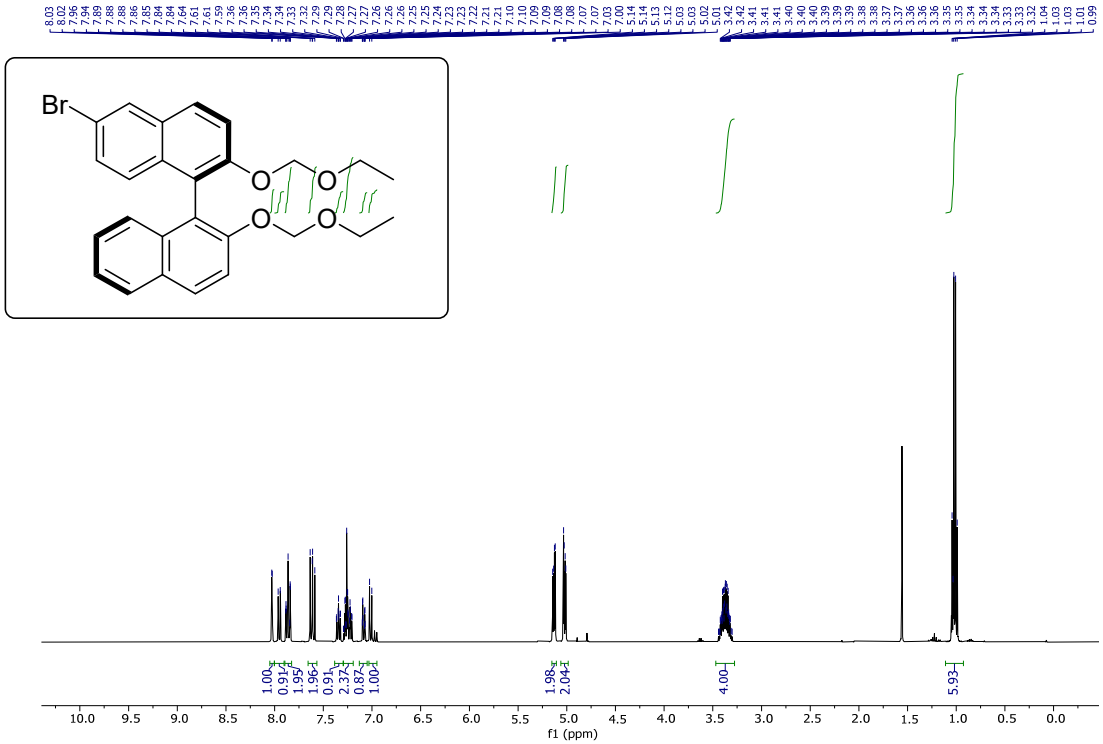


Figure S94. ^{1}H NMR spectra of (*R*)-6-bromo-2,2'-bis(ethoxymethoxy)-1,1'-binaphthalene (**5**) in $CDCl_3$.

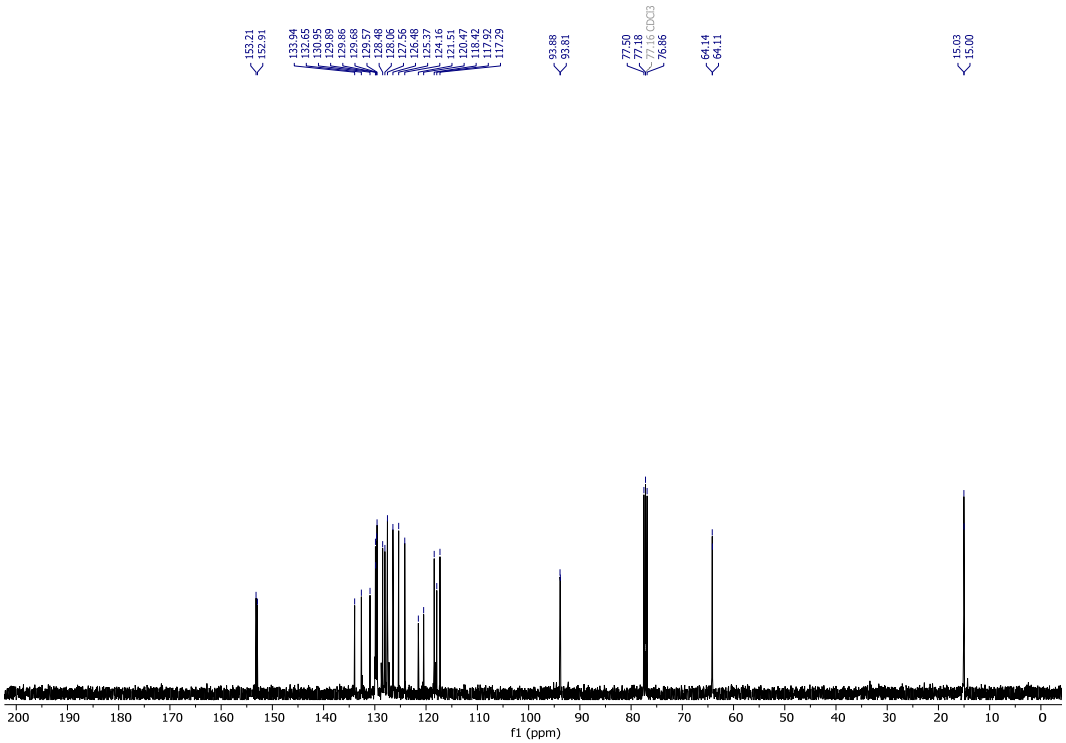


Figure S95. ^{13}C NMR spectra of (*R*)-6-bromo-2,2'-bis(ethoxymethoxy)-1,1'-binaphthalene (**5**) in $CDCl_3$.

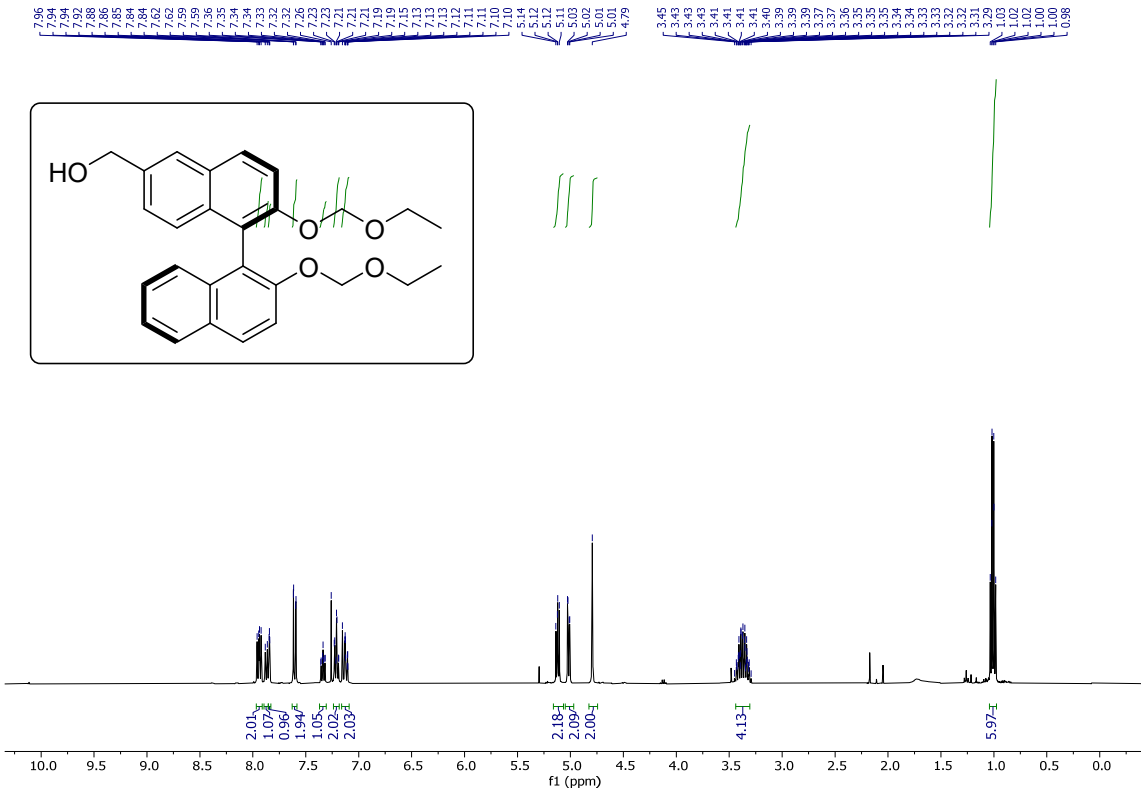


Figure S96. ^{1}H NMR spectra of (*R*)-(2,2'-bis(ethoxymethoxy)-[1,1'-binaphthalen]-6-yl)methanol in $CDCl_3$.

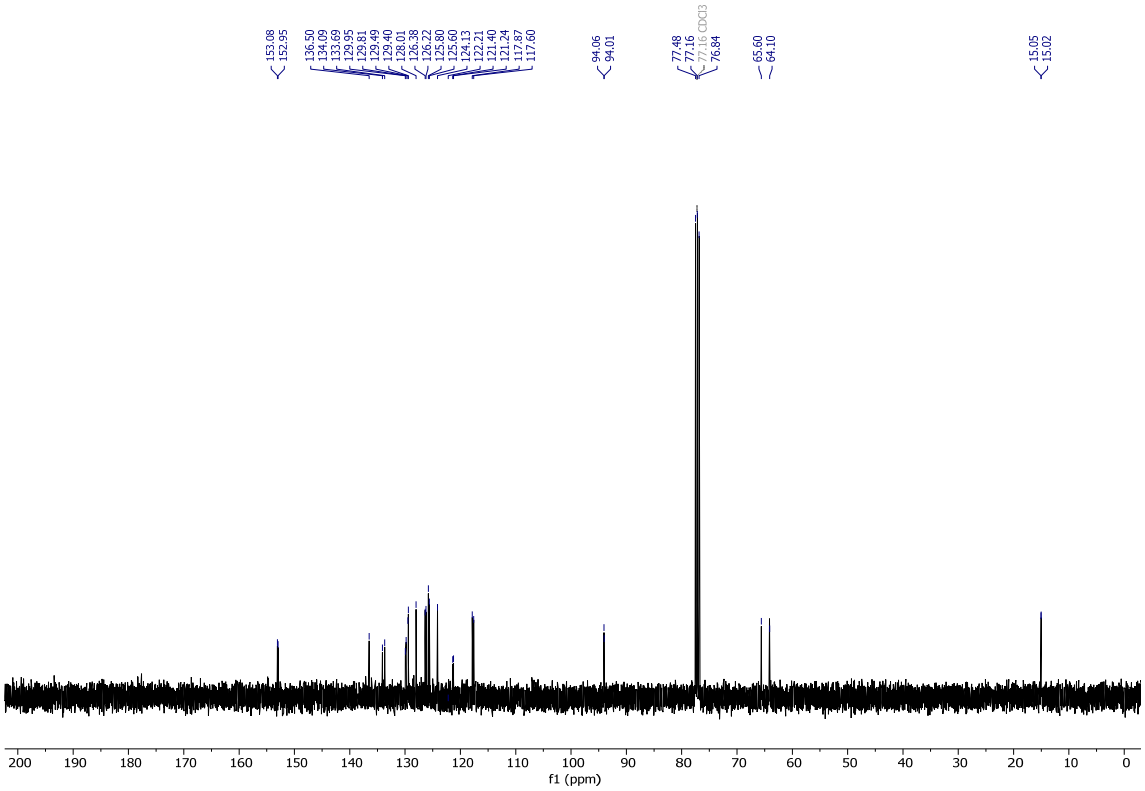


Figure S97. ^{13}C NMR spectra of (*R*)-(2,2'-bis(ethoxymethoxy)-[1,1'-binaphthalen]-6-yl)methanol in $CDCl_3$.

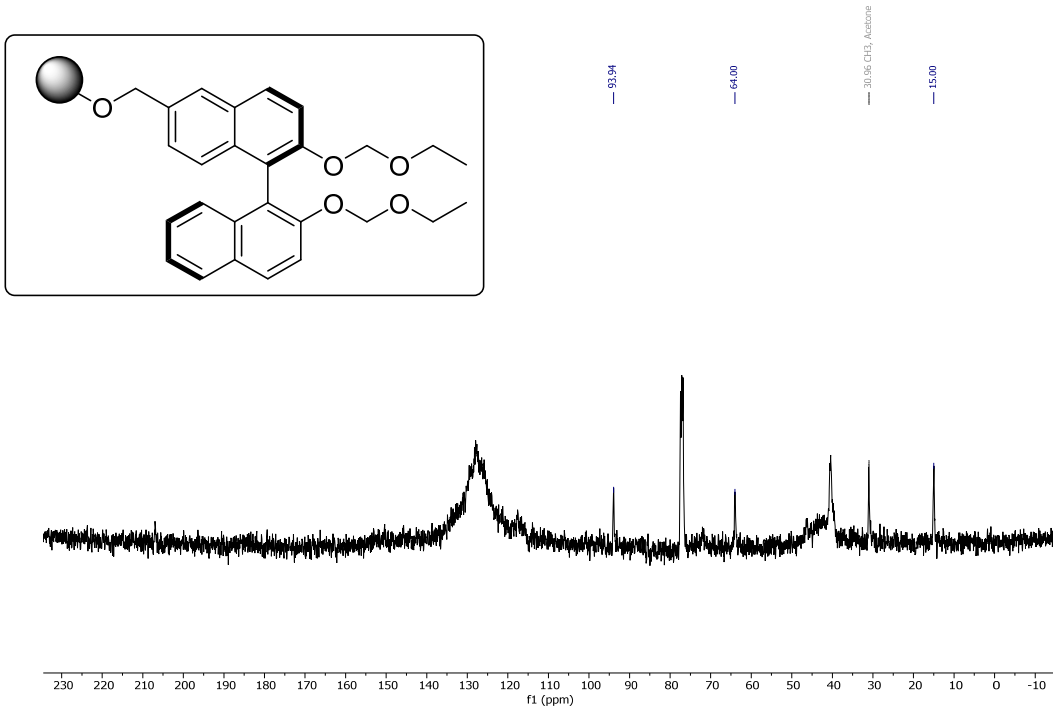


Figure S98. ^{13}C NMR spectra of PS-(*R*)-(2,2'-bis(ethoxymethoxy)-[1,1'-binaphthalen]-6-yl)methanol in $CDCl_3$.

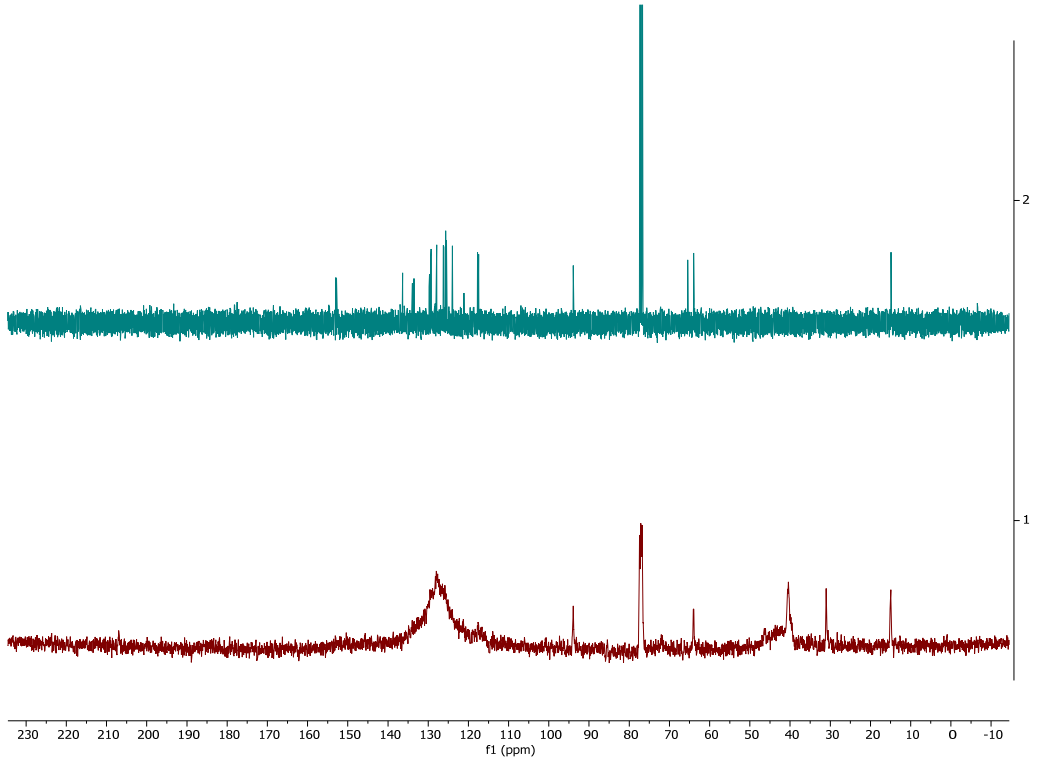


Figure S99. ^{13}C NMR spectra comparison of PS-(*R*)-(2,2'-bis(ethoxymethoxy)-[1,1'-binaphthalen]-6-yl)methanol and (*R*)-(2,2'-bis(ethoxymethoxy)-[1,1'-binaphthalen]-6-yl)methanol in $CDCl_3$.

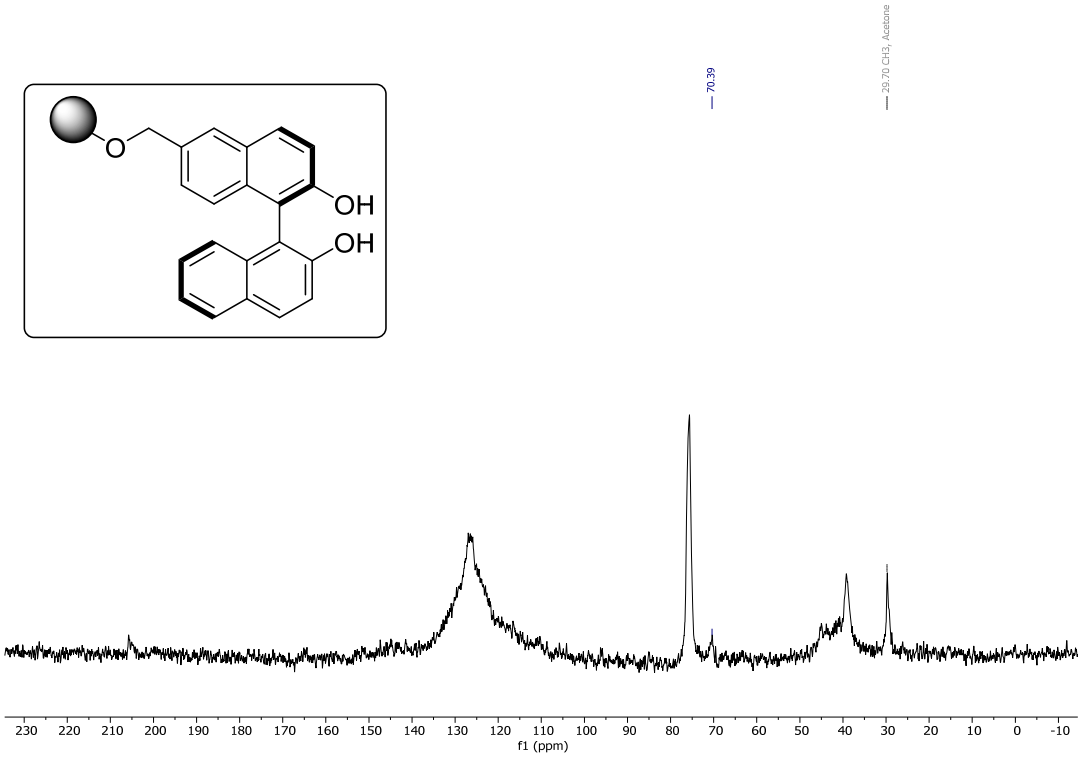


Figure S100. ^{13}C NMR spectra of PS-(*R*)-**4**.

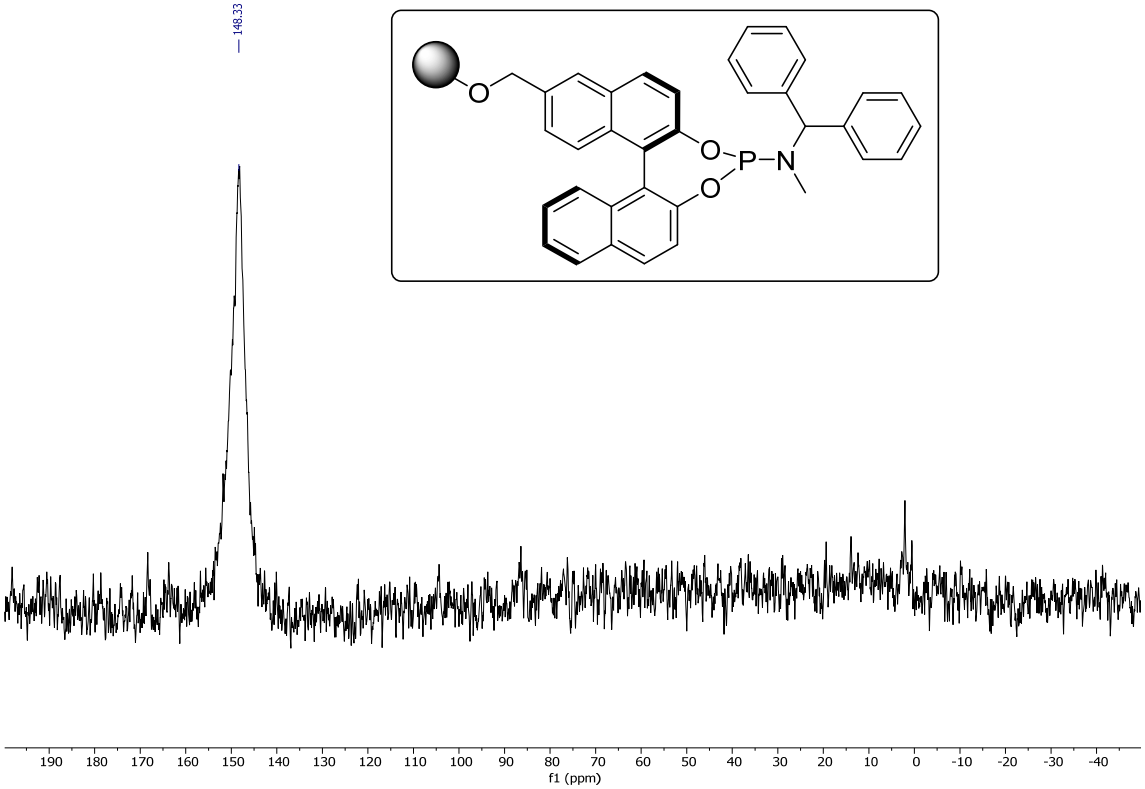


Figure S101. ^{31}P NMR spectra of PS-(*R*)-**L$_5$**.

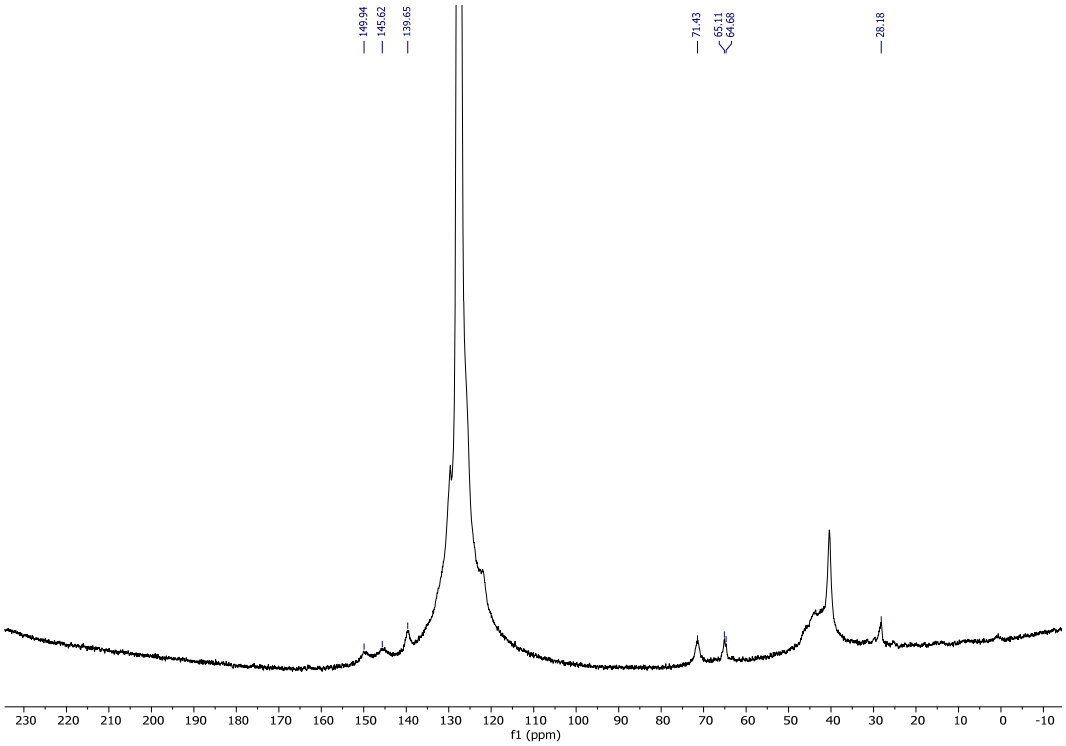


Figure S102. ^{13}C NMR spectra of PS-(*R*)-**L$_5$**

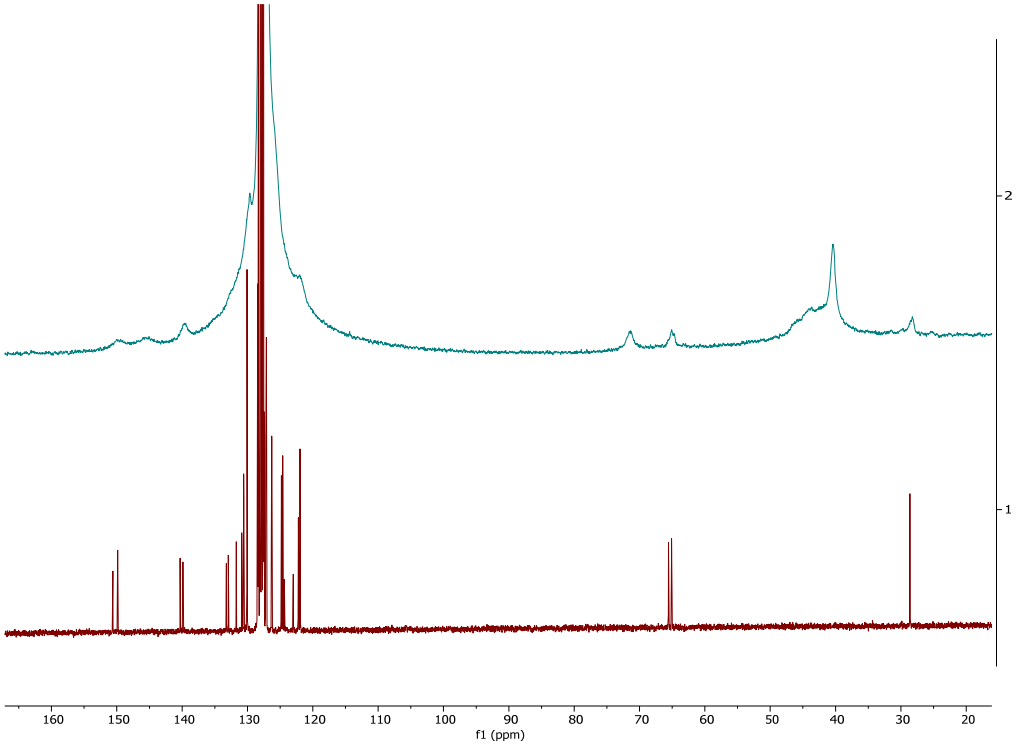


Figure S103. ^{13}C NMR spectra comparison of PS-(*R*)-**L$_5$** and (*R*)-**L$_5$** in C_6D_6.

SI-19. Copies of NMR spectra of ligands L_{10} and L_{11}

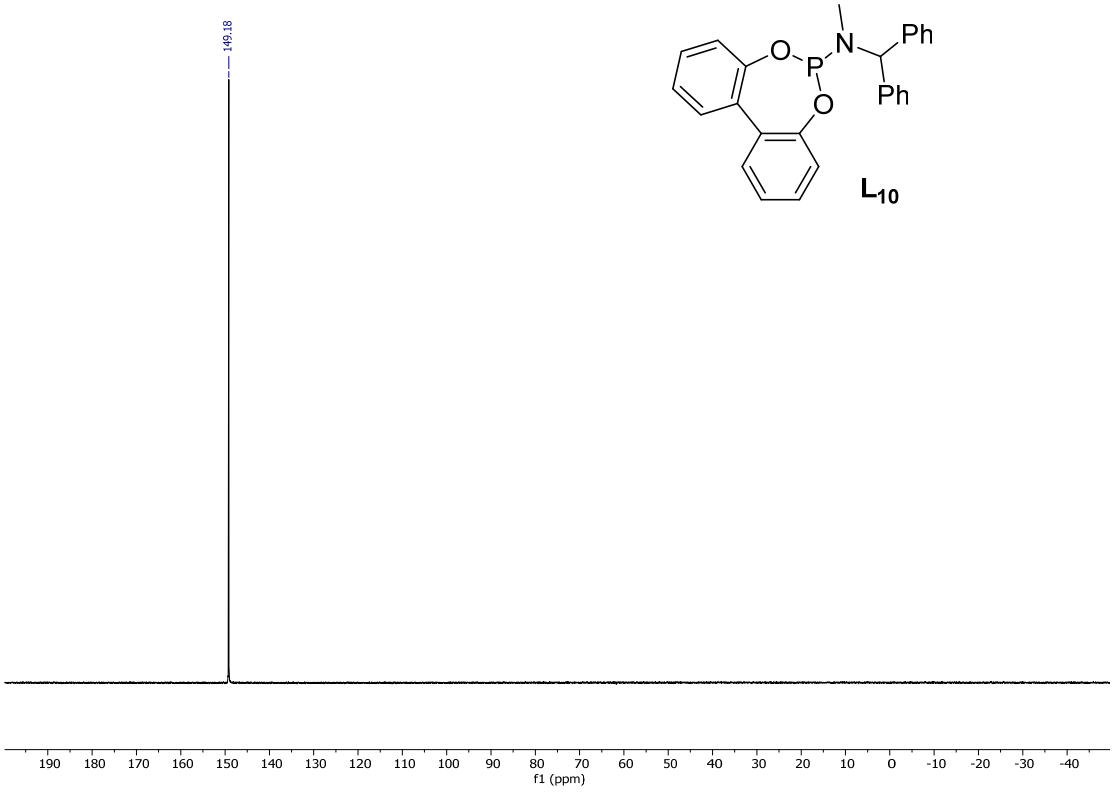


Figure S104. ^{31}P NMR of $\mathbf{L_{10}}$ in C_6D_6.

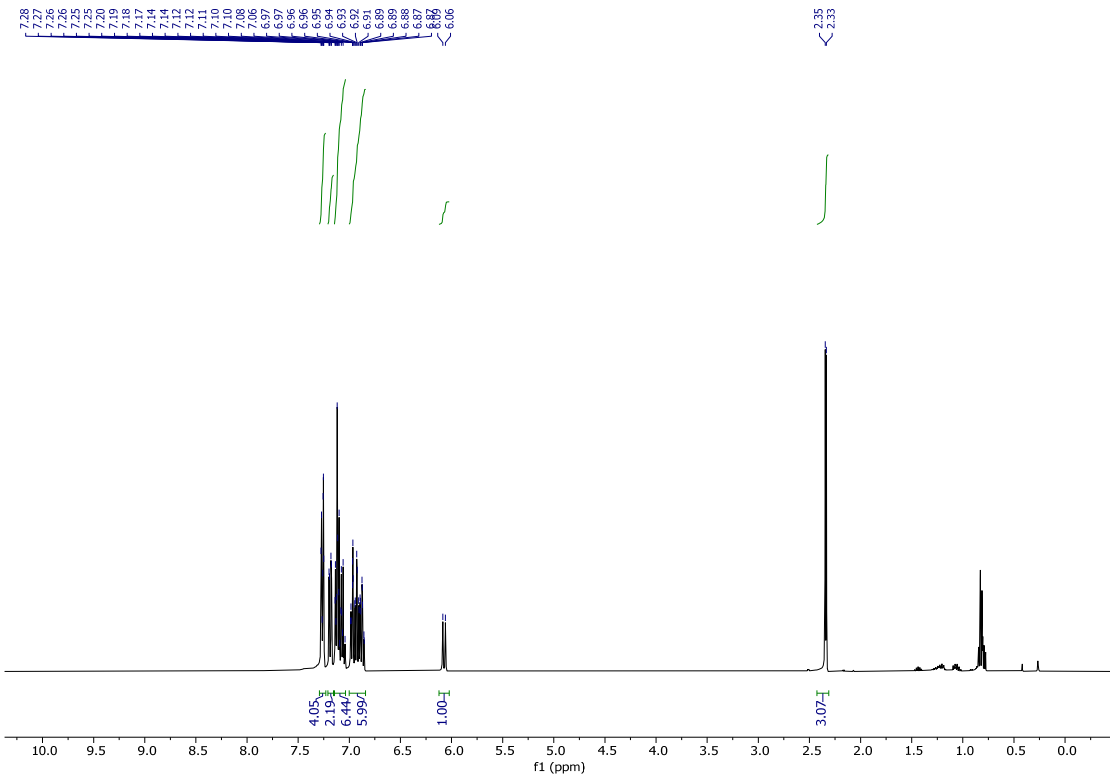


Figure S105. ^{1}H NMR of $\mathbf{L_{10}}$ in C_6D_6.

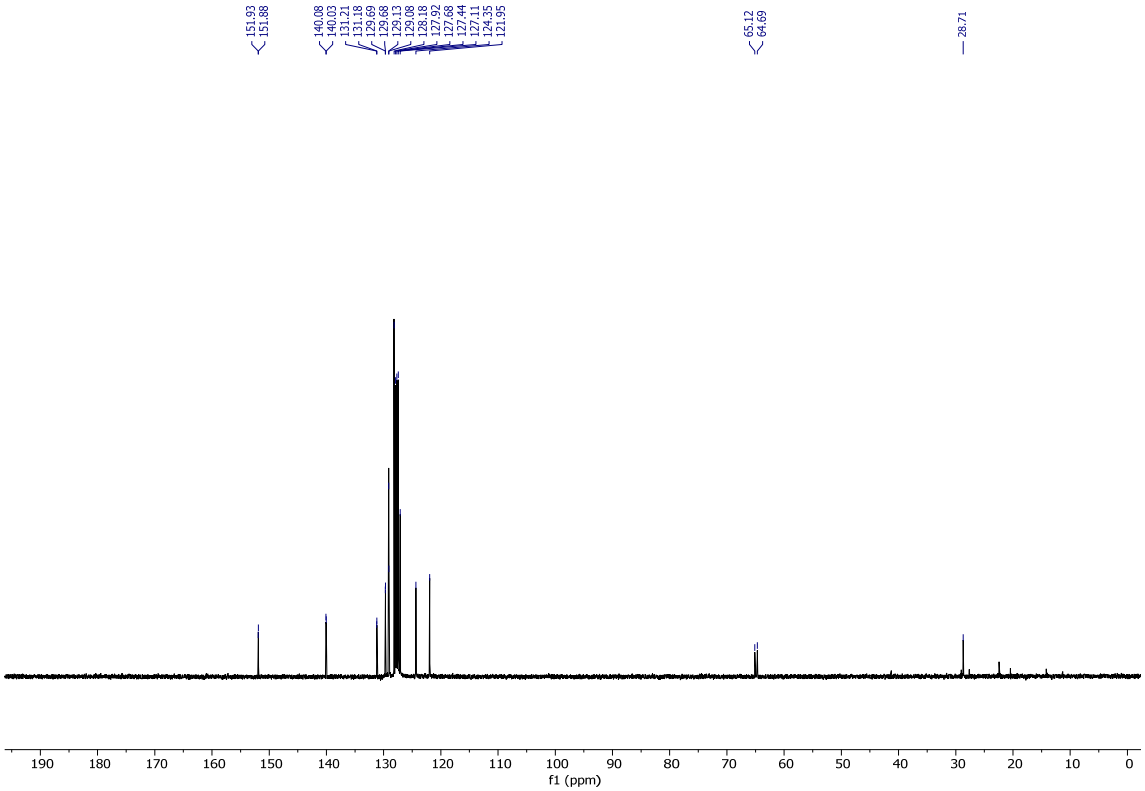


Figure S106. ^{13}C NMR of **L_{10}** in C_6D_6.

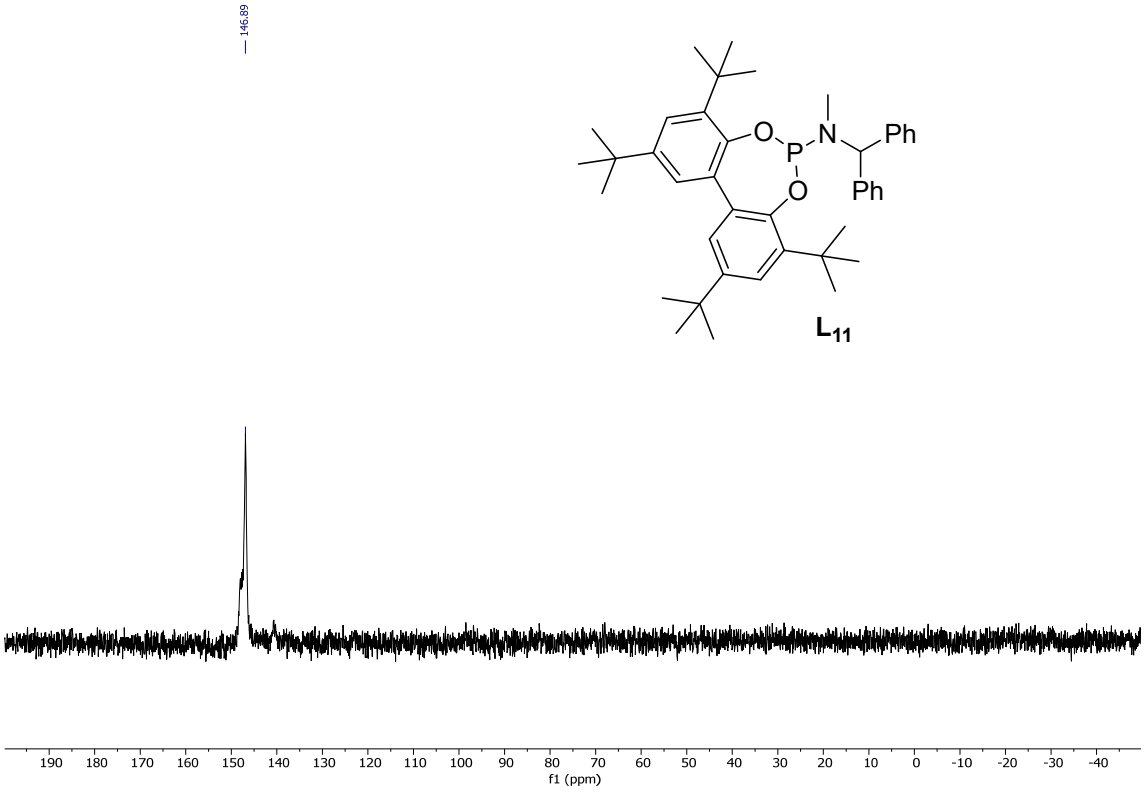


Figure S107. ^{31}P NMR of **L_{11}** in C_6D_6.

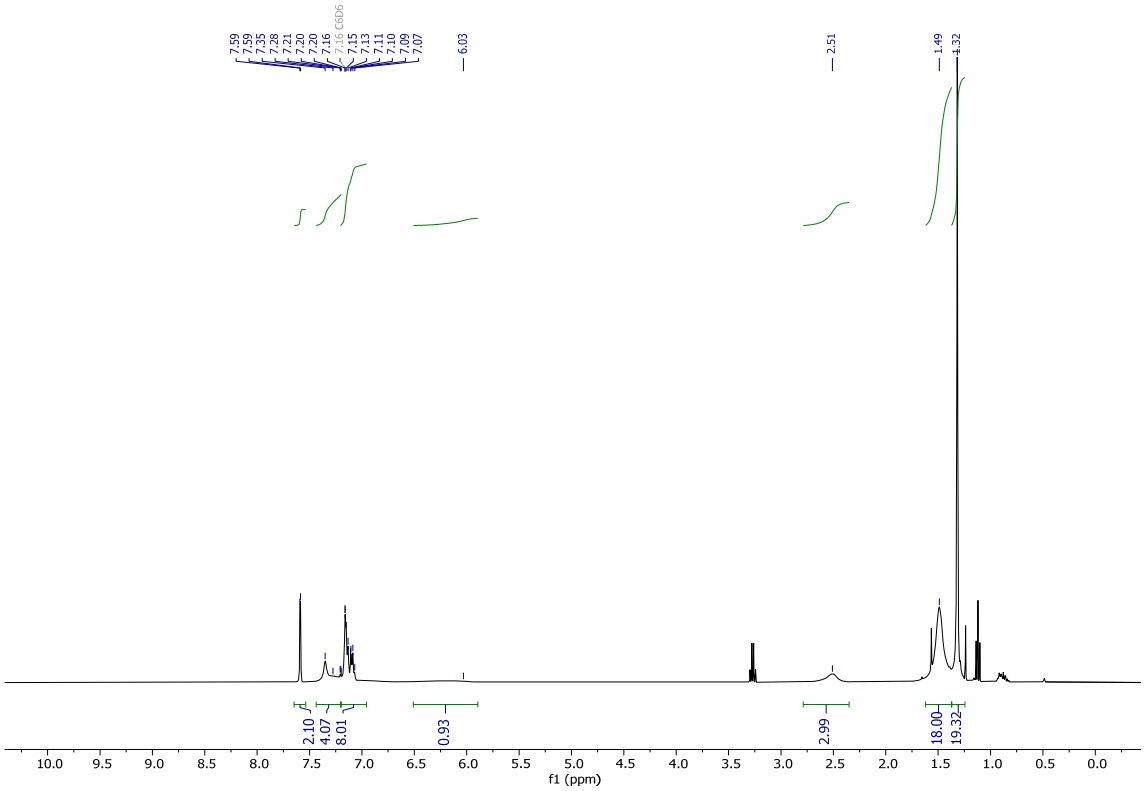


Figure S108. ^{1}H NMR **L$_{11}$** in C_6D_6.

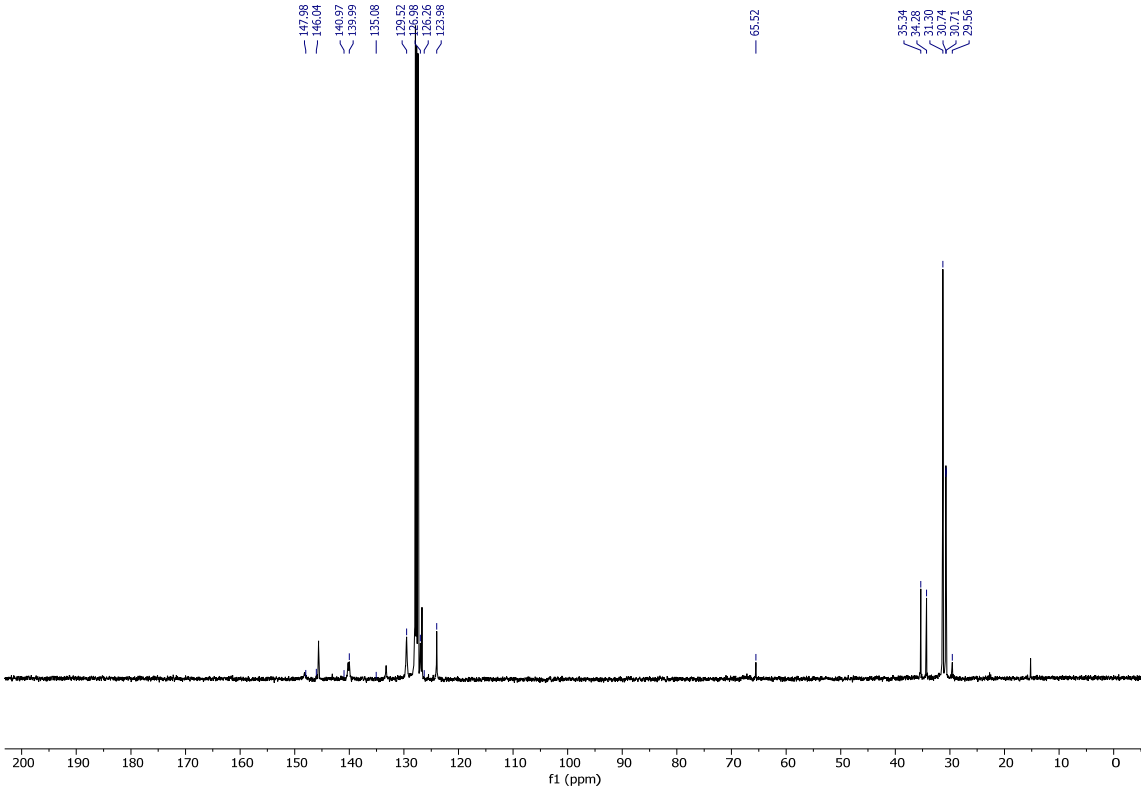


Figure S109. ^{13}C NMR **L$_{11}$** in C_6D_6.

SI-20. Sol-gel 31P{1H} NMR spectra of Pd(PS-(*R*)-L_5)L_{11} species

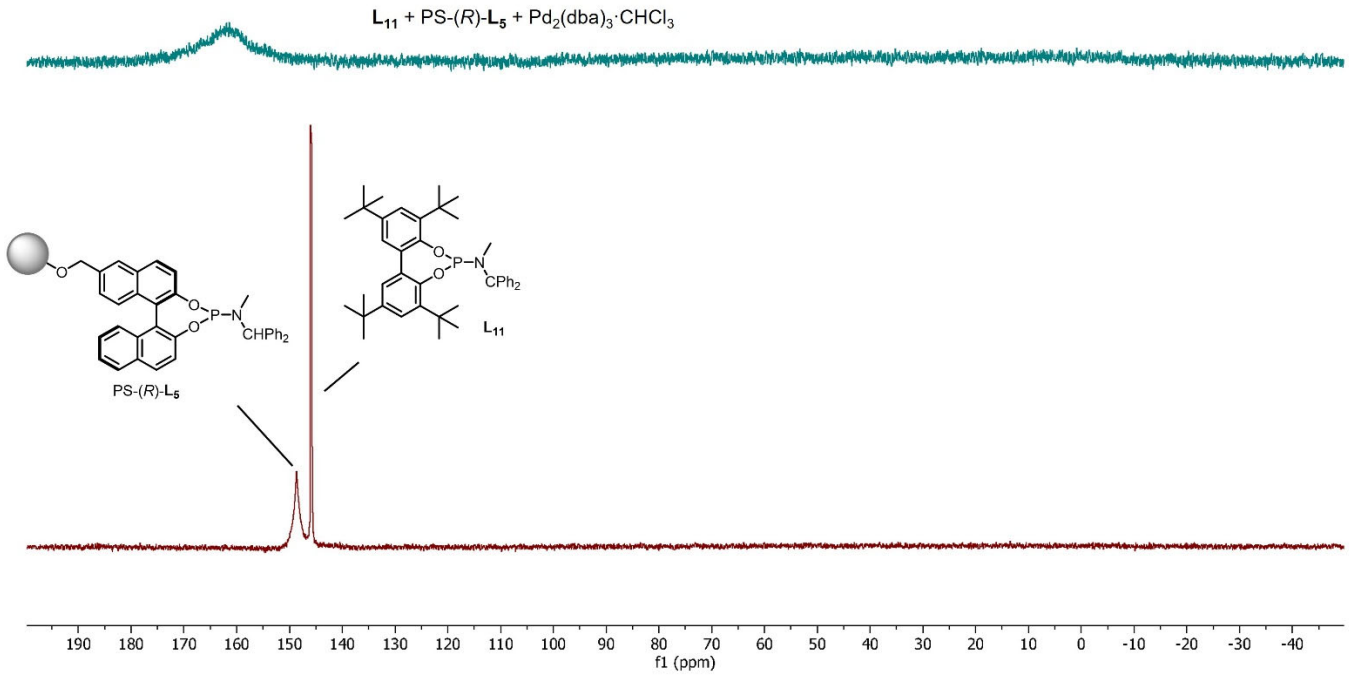


Figure S110. Sol-gel $^{31}P\{^{1}H\}$ NMR spectra of an equimolar mixture of PS-(*R*)-**L_5** and **L_{11}** in red and after addition of $Pd_2(dba)_3 \cdot CHCl_3$ in green in THF-d_8.

SI-21. Copies of NMR spectra of post-functionalized products

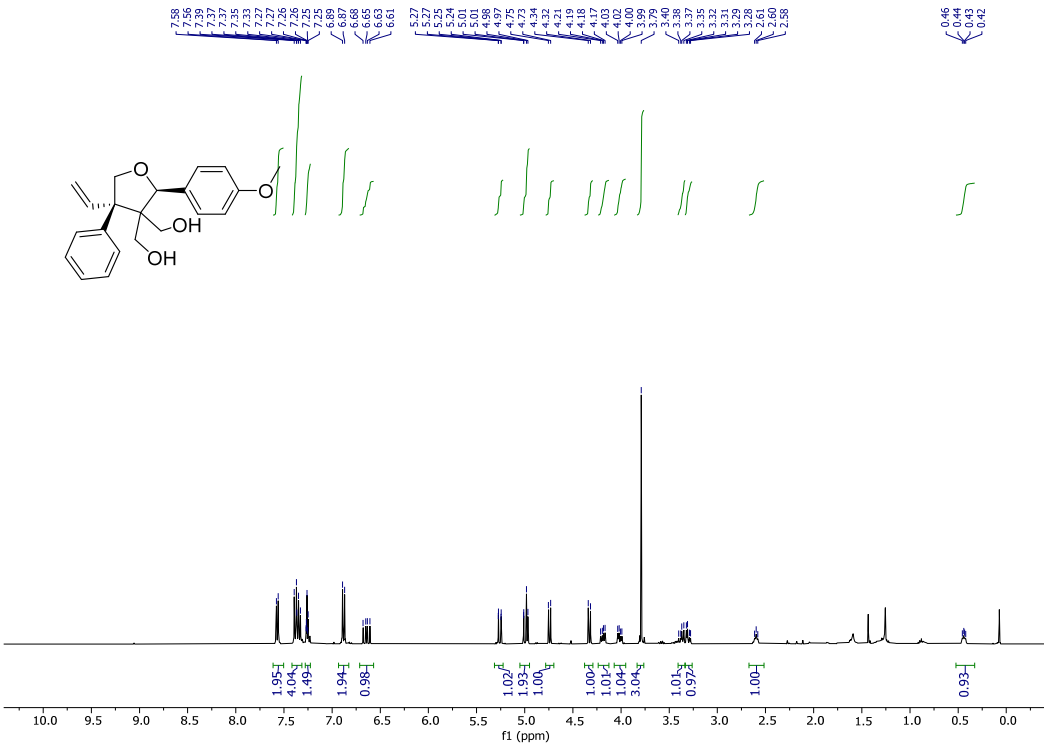


Figure S111. ^{1}H NMR of ((2*S*,4*R*)-2-(4-methoxyphenyl)-4-phenyl-4-vinyltetrahydrofuran-3,3-diyl)dimethanol (**6**) in $CDCl_3$.

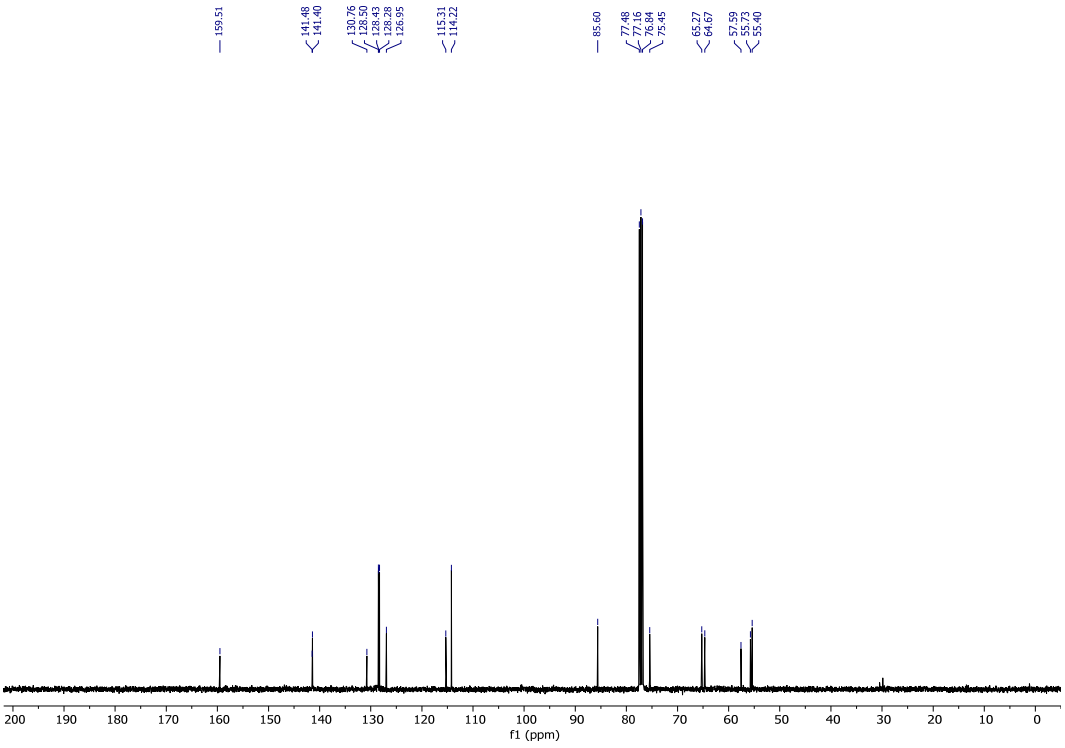


Figure S112. ^{13}C NMR of ((2*S*,4*R*)-2-(4-methoxyphenyl)-4-phenyl-4-vinyltetrahydrofuran-3,3-diyl)dimethanol (**6**) in $CDCl_3$.

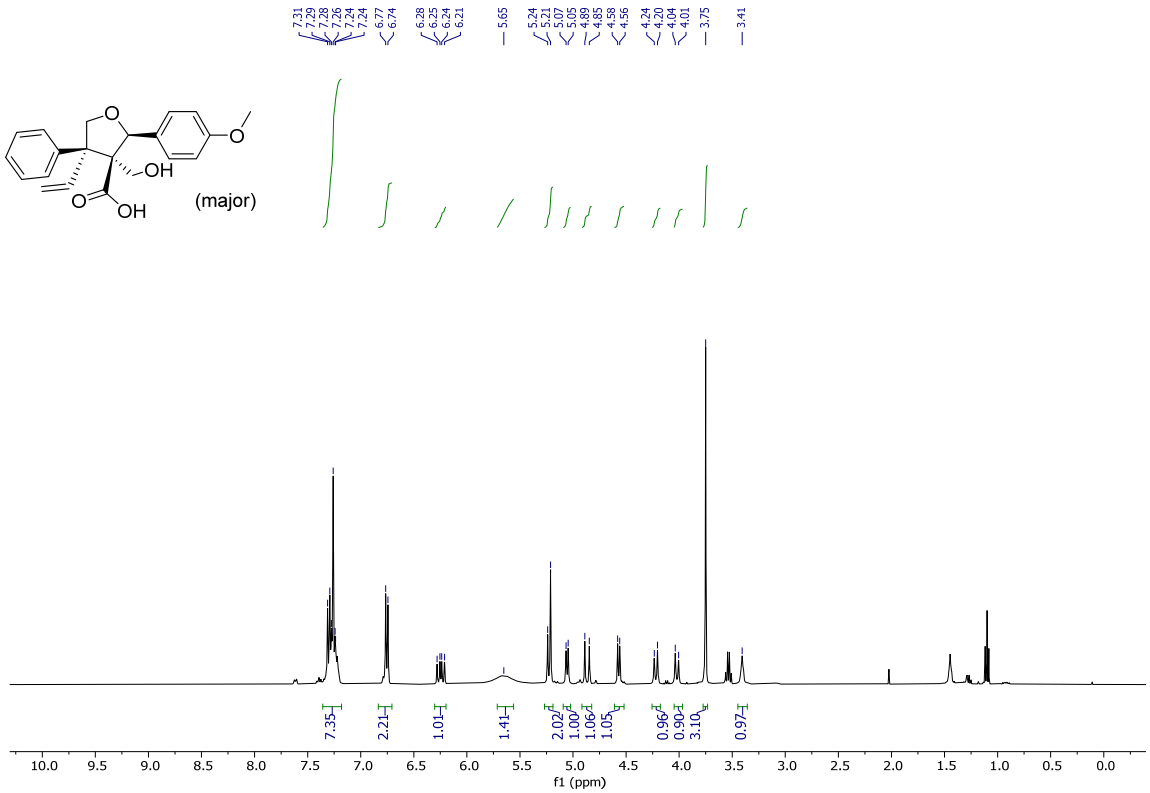


Figure S113. ^{1}H NMR of (2*S*,3*R*,4*R*)-3-(hydroxymethyl)-2-(4-methoxyphenyl)-4-phenyl-4-vinyltetrahydrofuran-3-carboxylic- acid (**7^{major}**) in $CDCl_3$.

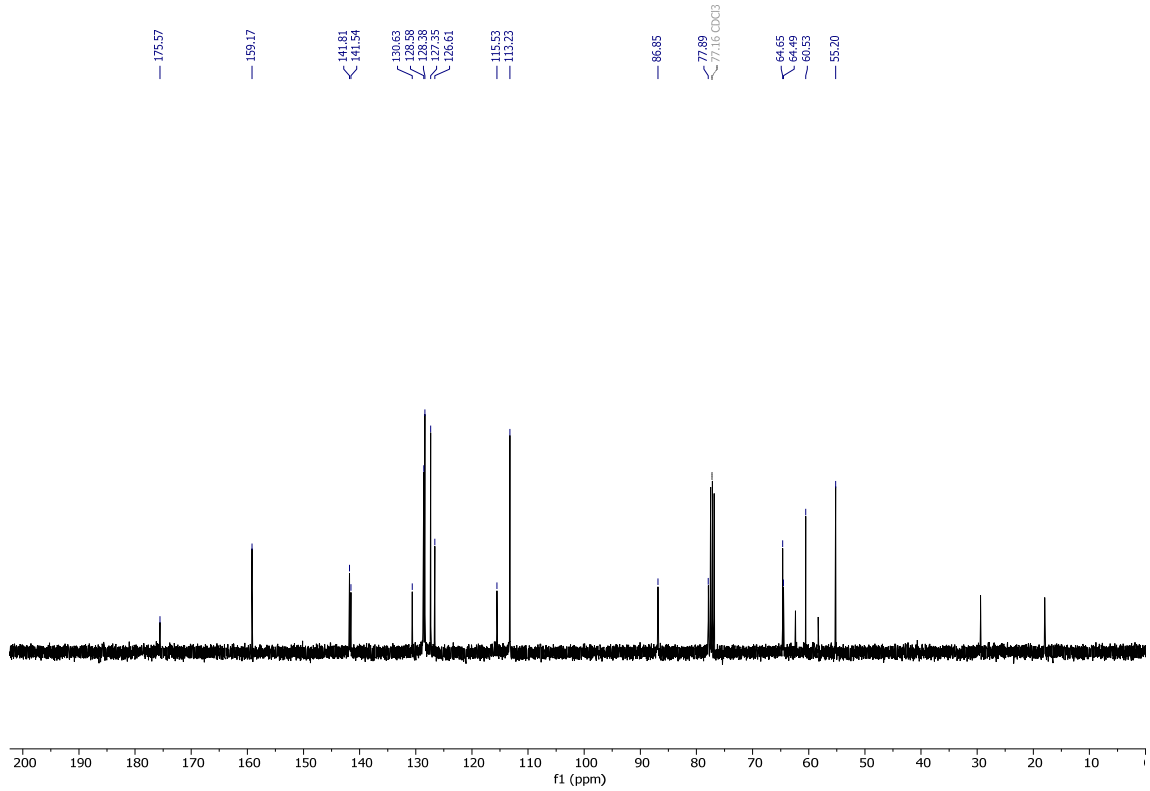


Figure S114. ^{13}C NMR of (2*S*,3*R*,4*R*)-3-(hydroxymethyl)-2-(4-methoxyphenyl)-4-phenyl-4-vinyltetrahydrofuran-3-carboxylic- acid (**7^{major}**) in $CDCl_3$.

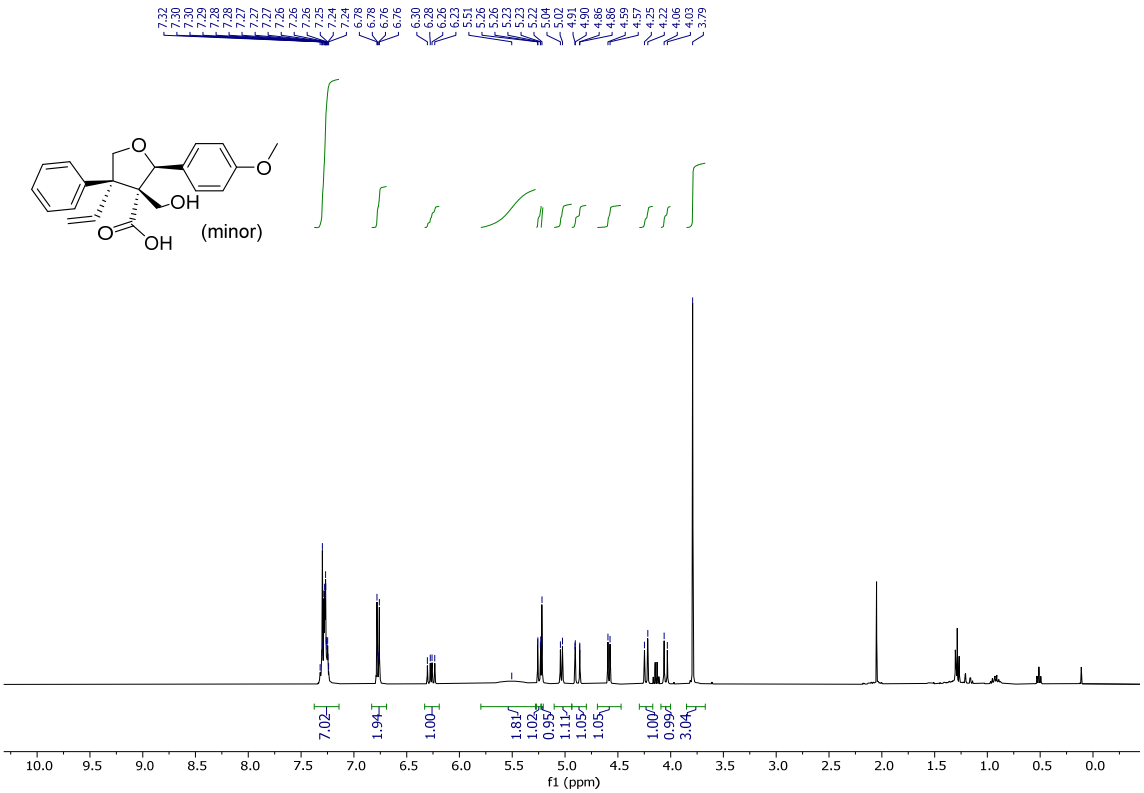


Figure S115. ^{1}H NMR of (2*S*,3*S*,4*R*)-3-(hydroxymethyl)-2-(4-methoxyphenyl)-4-phenyl-4-vinyltetrahydrofuran-3-carboxylic acid (**7**$^{\mathbf{minor}}$) in $CDCl_3$.

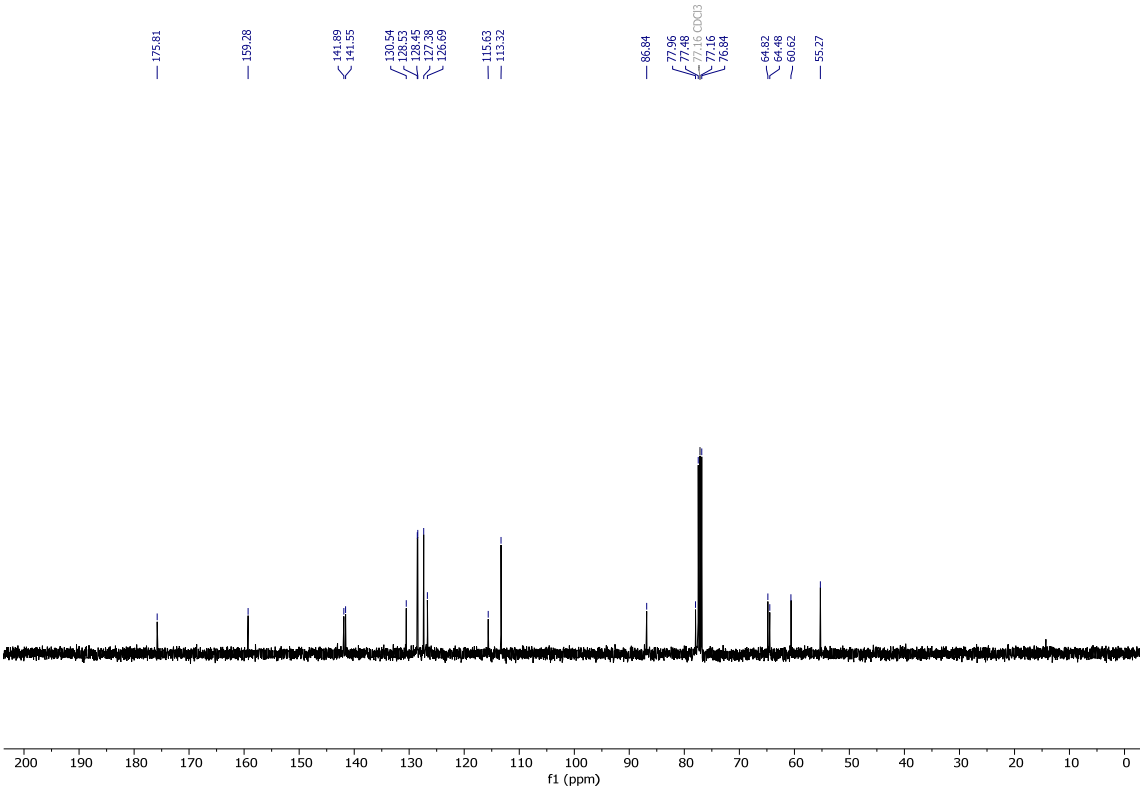


Figure S116. ^{13}C NMR of (2*S*,3*S*,4*R*)-3-(hydroxymethyl)-2-(4-methoxyphenyl)-4-phenyl-4-vinyltetrahydrofuran-3-carboxylic acid (**7**$^{\mathbf{minor}}$) in $CDCl_3$.

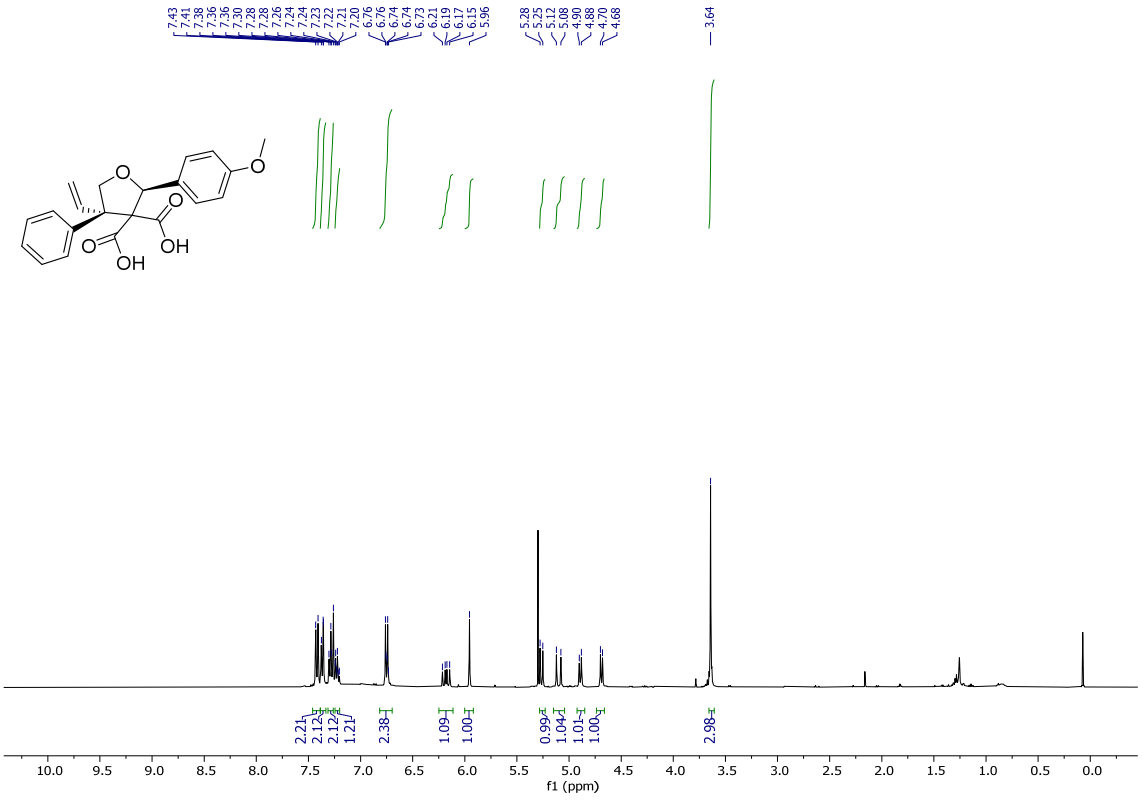


Figure S117. ^{1}H NMR of (2*S*,4*R*)-2-(4-methoxyphenyl)-4-phenyl-4-vinyldihydrofuran-3,3(2H)-dicarboxylic acid (**8**) in $CDCl_3$.

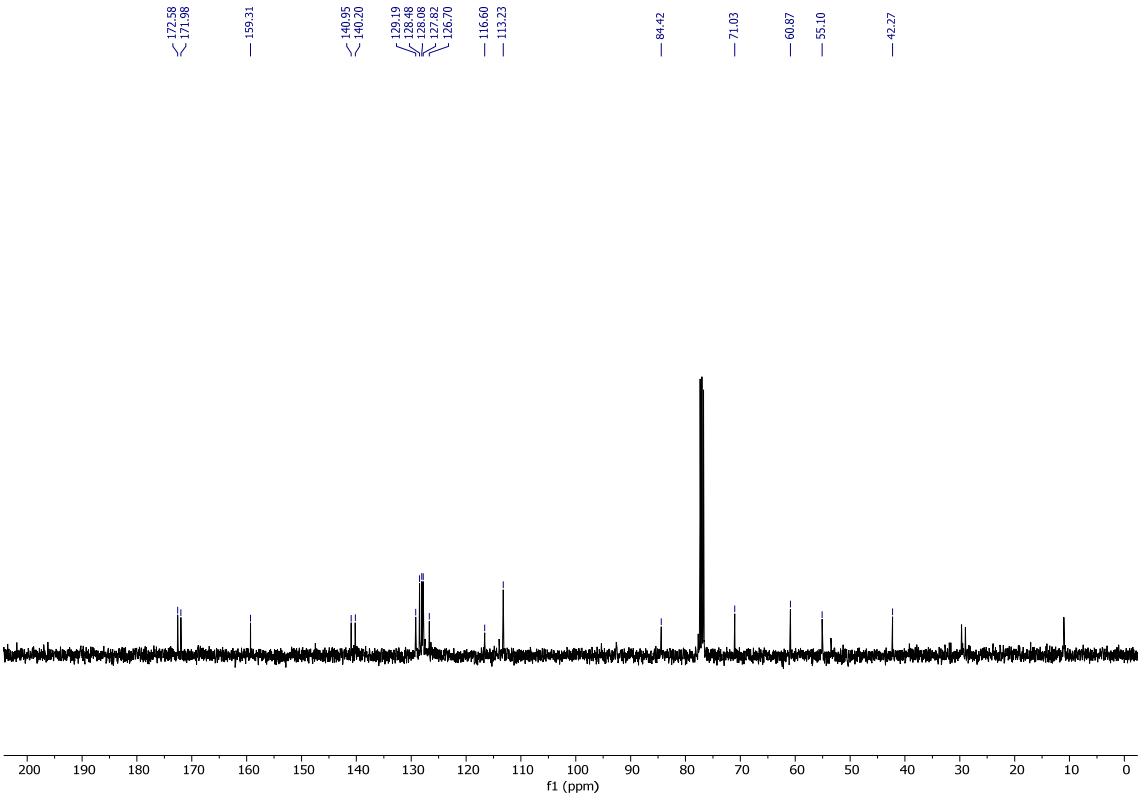


Figure S118. ^{13}C NMR of (2*S*,4*R*)-2-(4-methoxyphenyl)-4-phenyl-4-vinyldihydrofuran-3,3(2H)-dicarboxylic acid (**8**) in $CDCl_3$.

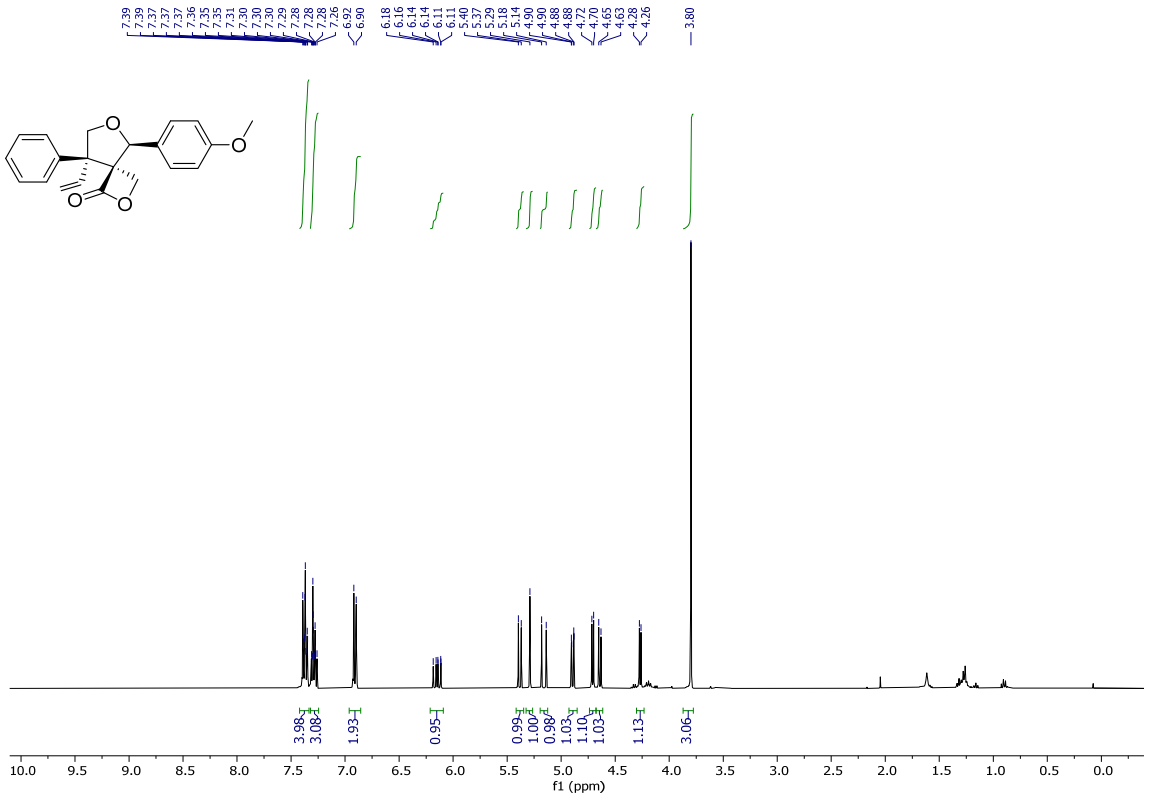


Figure S119. ^{13}C NMR of (4*R*,5*S*,8*R*)-5-(4-methoxyphenyl)-8-phenyl-8-vinyl-2,6-dioxaspiro[3.4]octan-1-one (**9**) in $CDCl_3$.

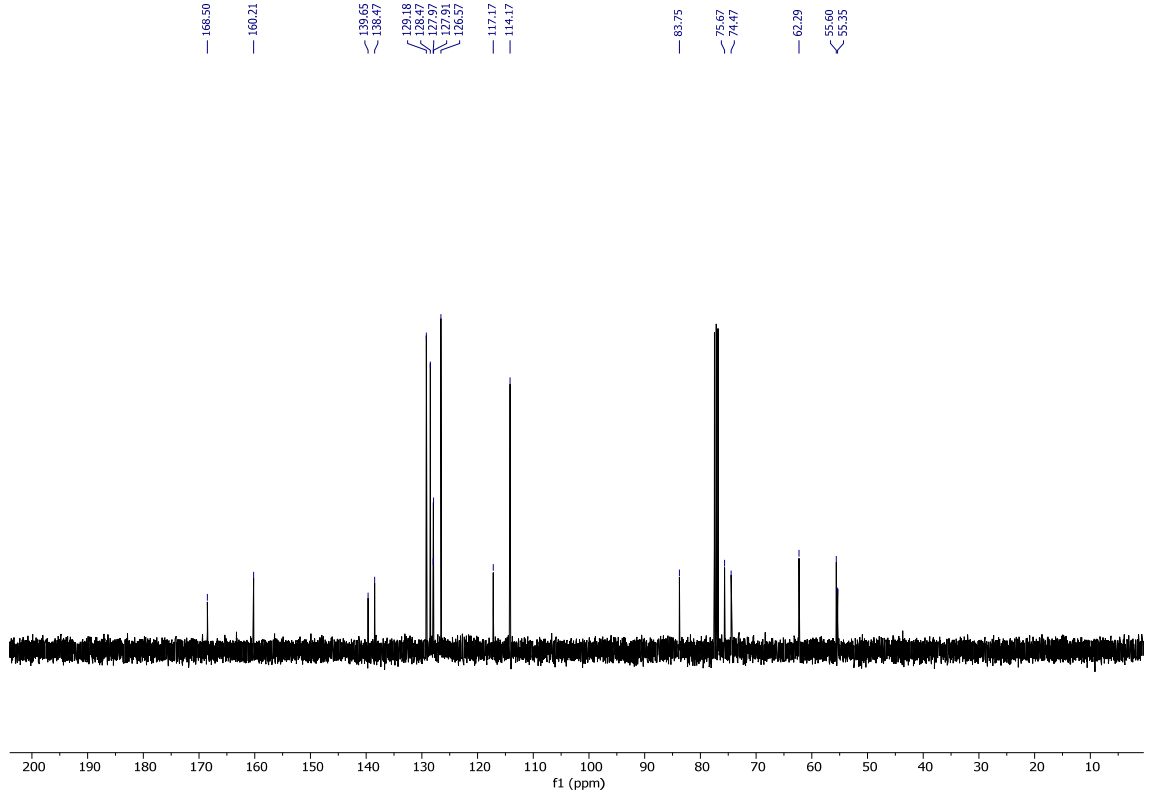


Figure S120. ^{13}C NMR of (4*R*,5*S*,8*R*)-5-(4-methoxyphenyl)-8-phenyl-8-vinyl-2,6-dioxaspiro[3.4]octan-1-one (**9**) in $CDCl_3$.

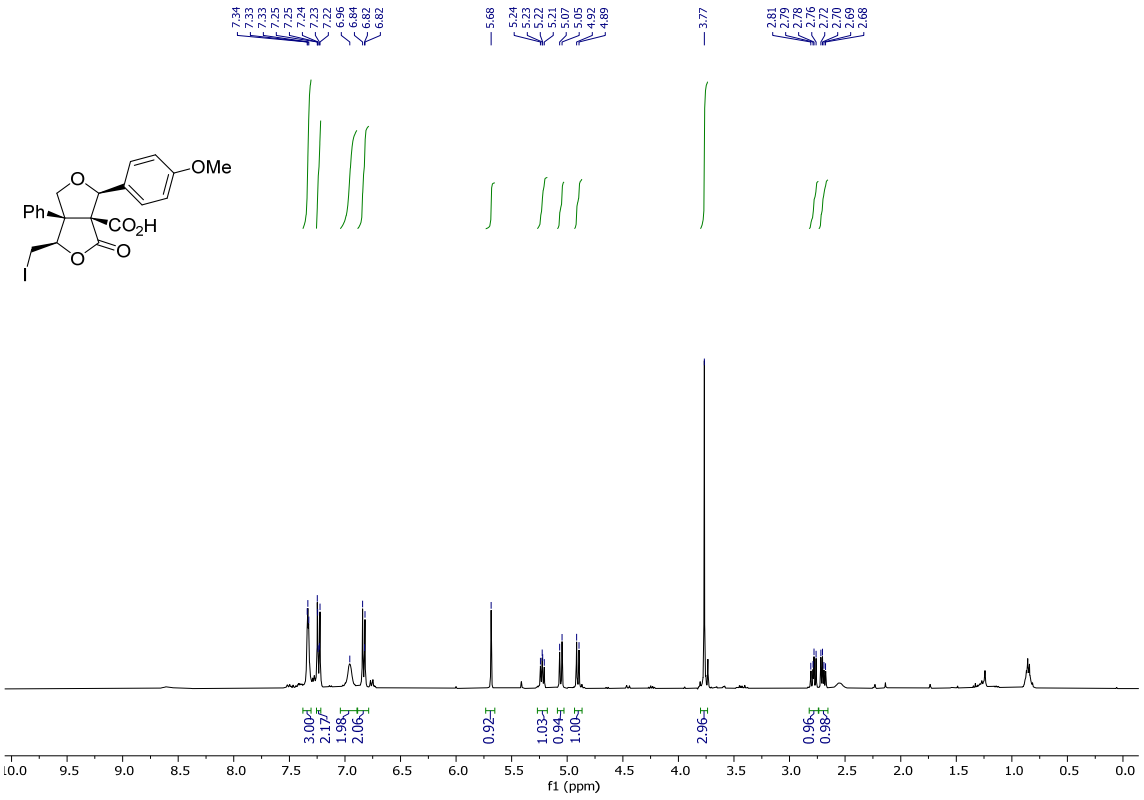


Figure S121. ^{1}H NMR of (1*R*,3*aR*,4*S*,6*aS*)-1-(iodomethyl)-4-(4-methoxyphenyl)-3-oxo-6a-phenyldihydro-1H,3H-furo[3,4-c]furan-3a(4H)-carboxylic acid (**10**) in $CDCl_3$.

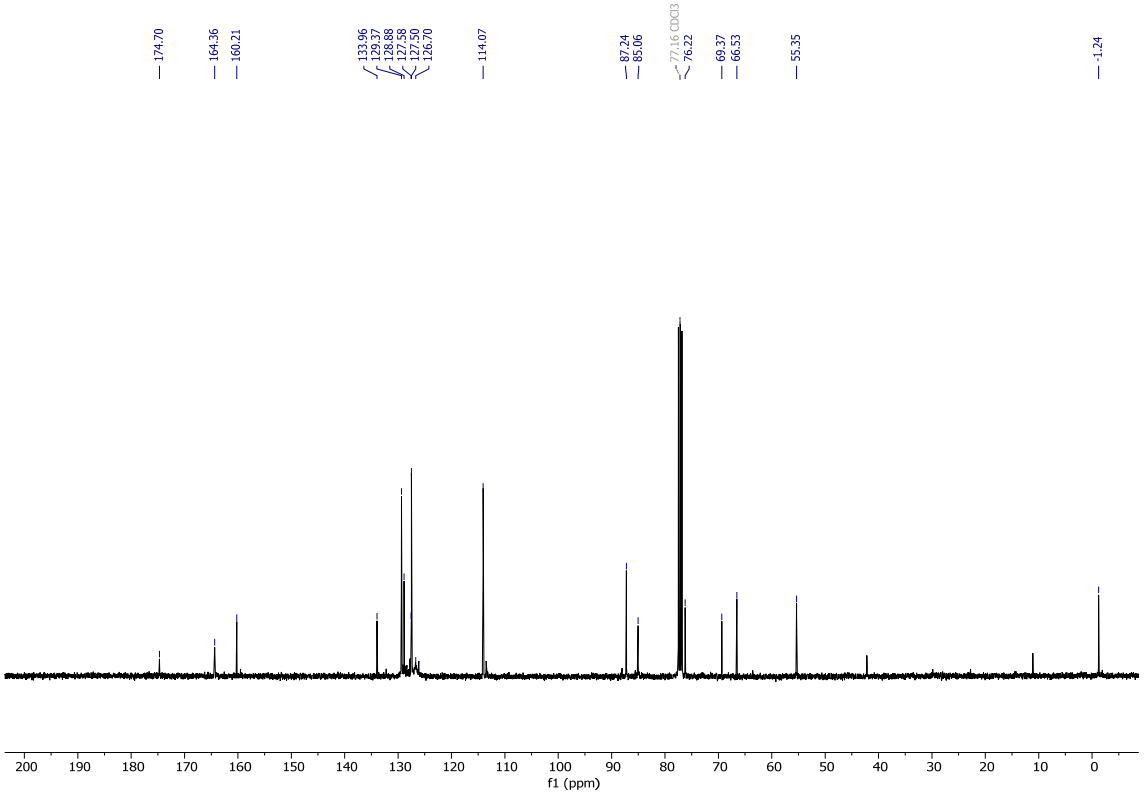


Figure S122. ^{13}C NMR of (1*R*,3*aR*,4*S*,6*aS*)-1-(iodomethyl)-4-(4-methoxyphenyl)-3-oxo-6a-phenyldihydro-1H,3H-furo[3,4-c]furan-3a(4H)-carboxylic acid (**10**) in $CDCl_3$.

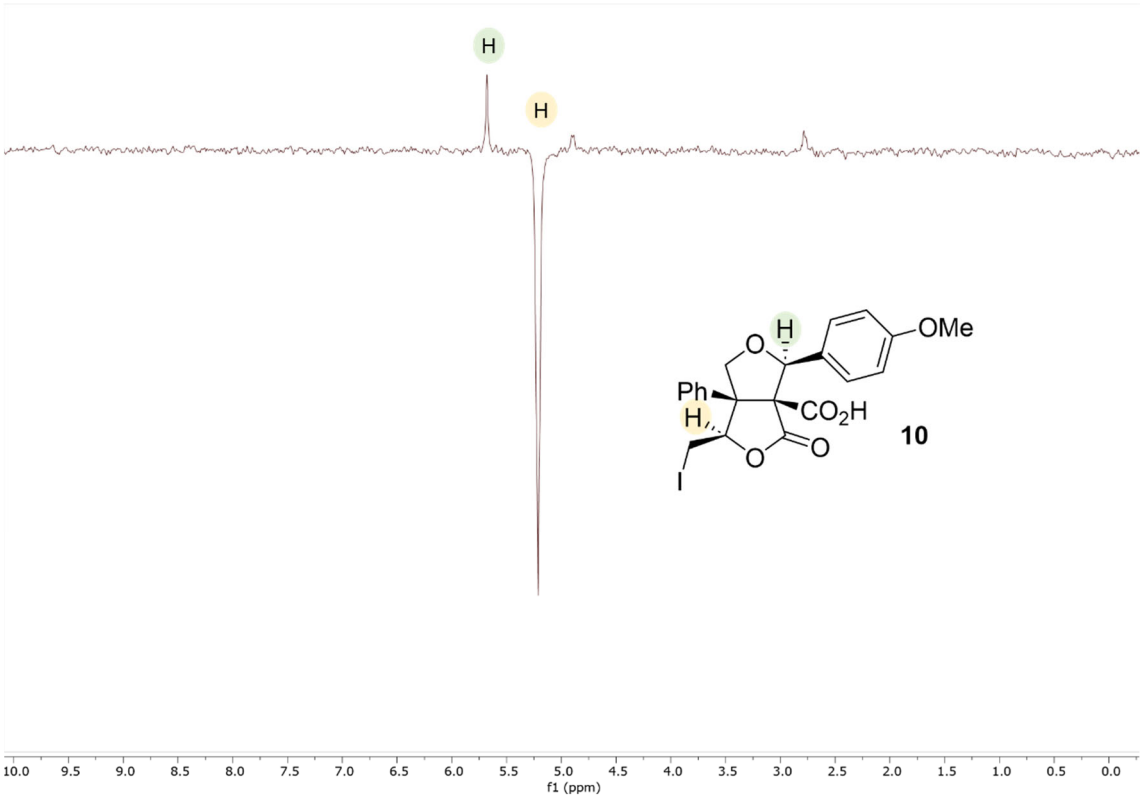


Figure S123. 1D-NOE scpectra of **10** irradiating at 5.23 ppm (in yellow).

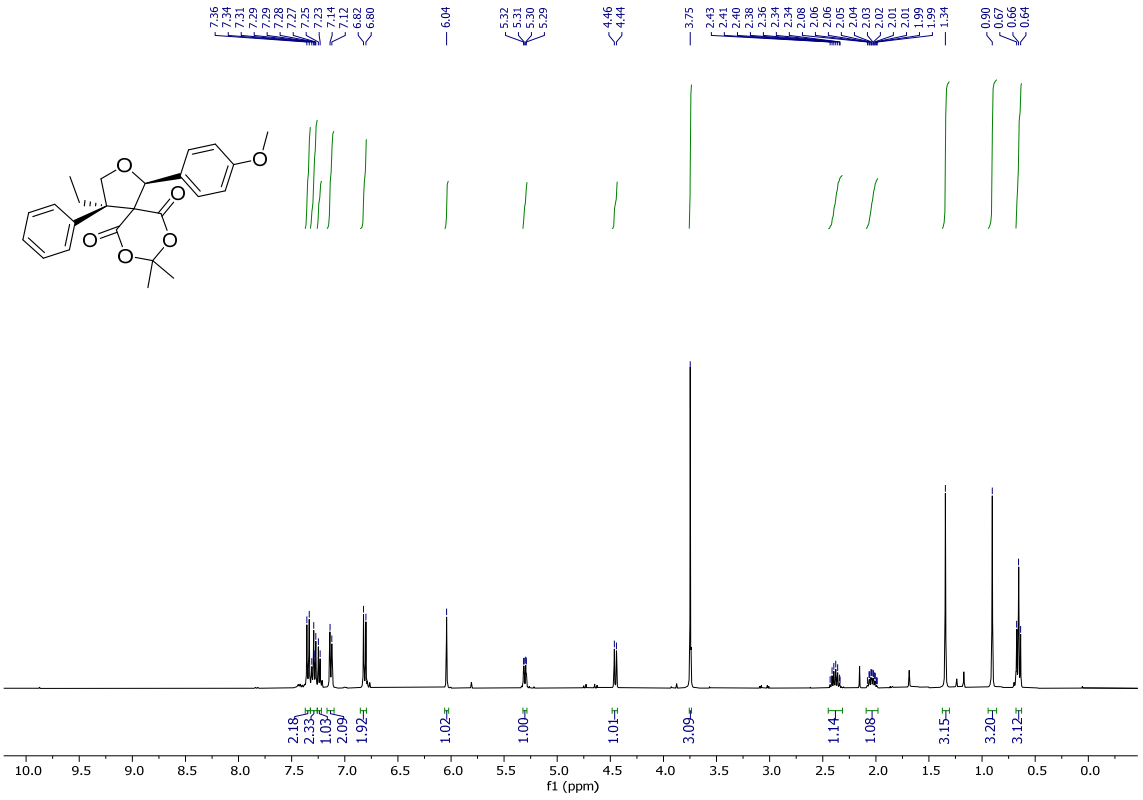


Figure S124. ^{1}H NMR of (1*S*,4*R*)-4-ethyl-1-(4-methoxyphenyl)-8,8-dimethyl-4-phenyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**12**) in $CDCl_3$.

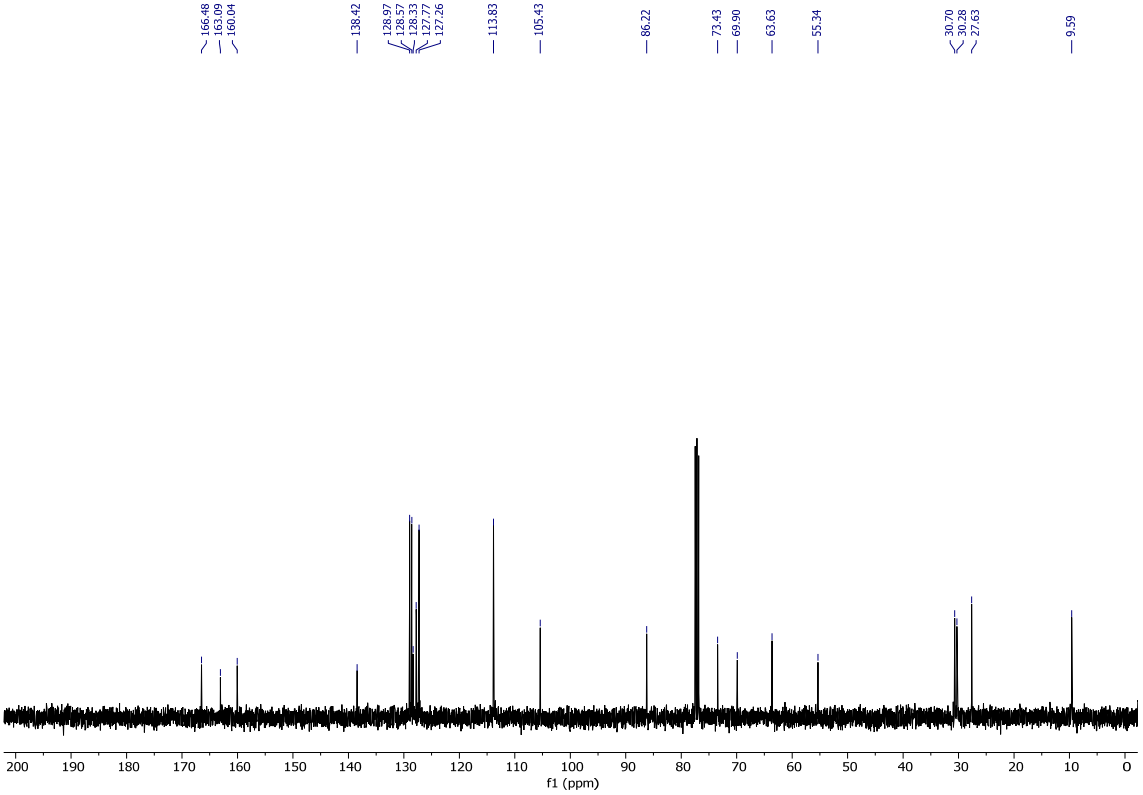


Figure S125. ^{13}C NMR of (1*S*,4*R*)-4-ethyl-1-(4-methoxyphenyl)-8,8-dimethyl-4-phenyl-2,7,9-trioxaspiro[4.5]decane-6,10-dione (**12**) in $CDCl_3$.

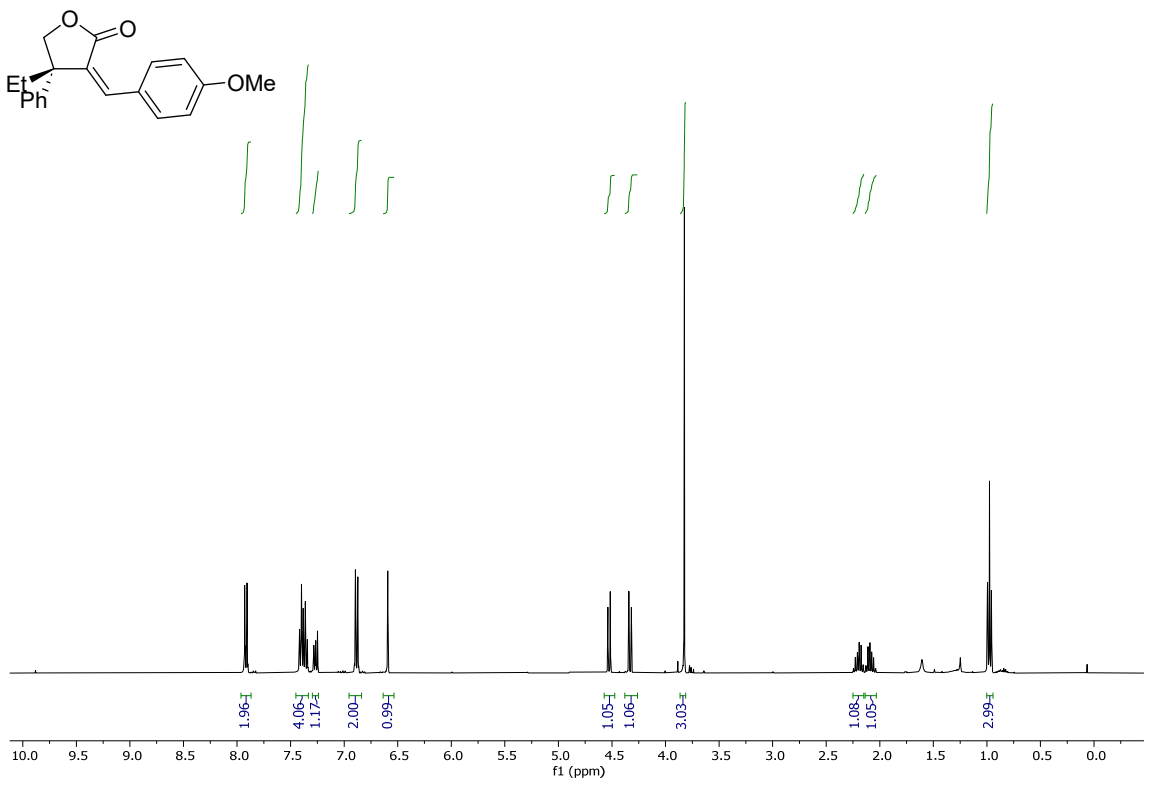


Figure S126. ^{1}H NMR of (S,Z)-4-ethyl-3-(4-methoxybenzylidene)-4-phenyldihydrofuran-2(3H)-one (**11**) in $CDCl_3$.

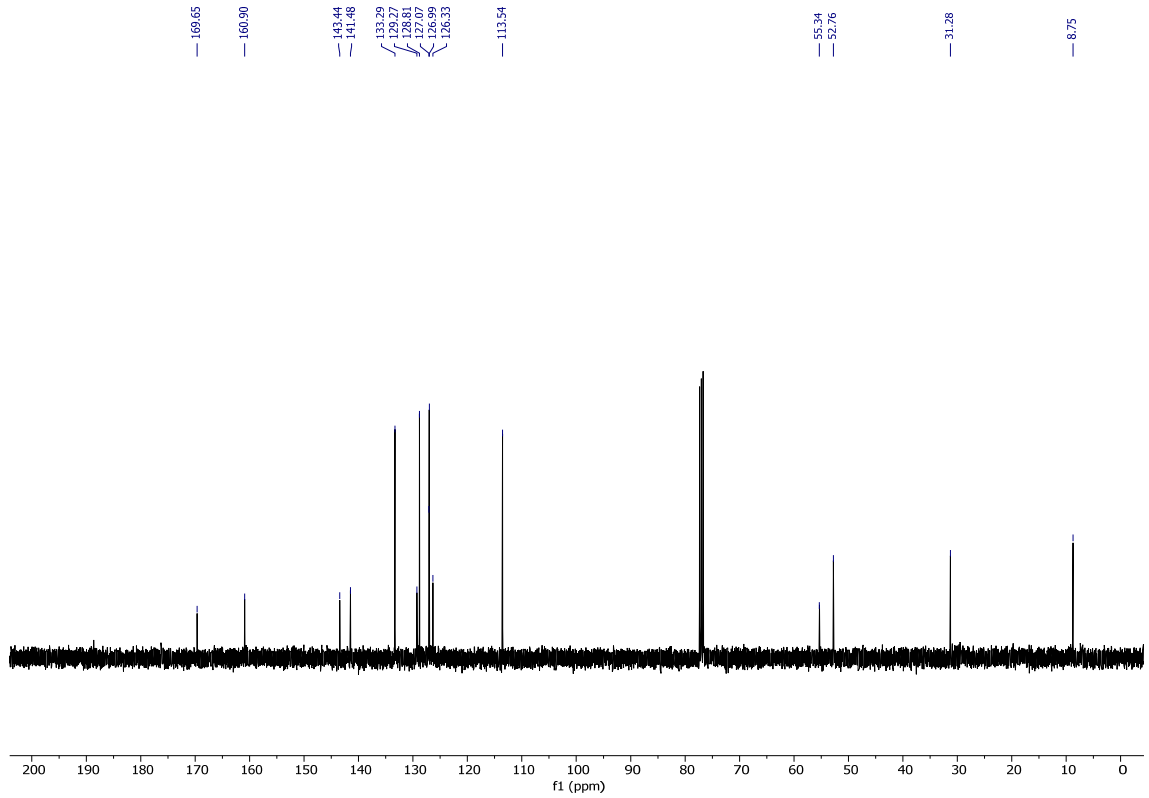


Figure S127. ^{13}C NMR of (S,Z)-4-ethyl-3-(4-methoxybenzylidene)-4-phenyldihydrofuran-2(3H)-one (**11**) in $CDCl_3$.

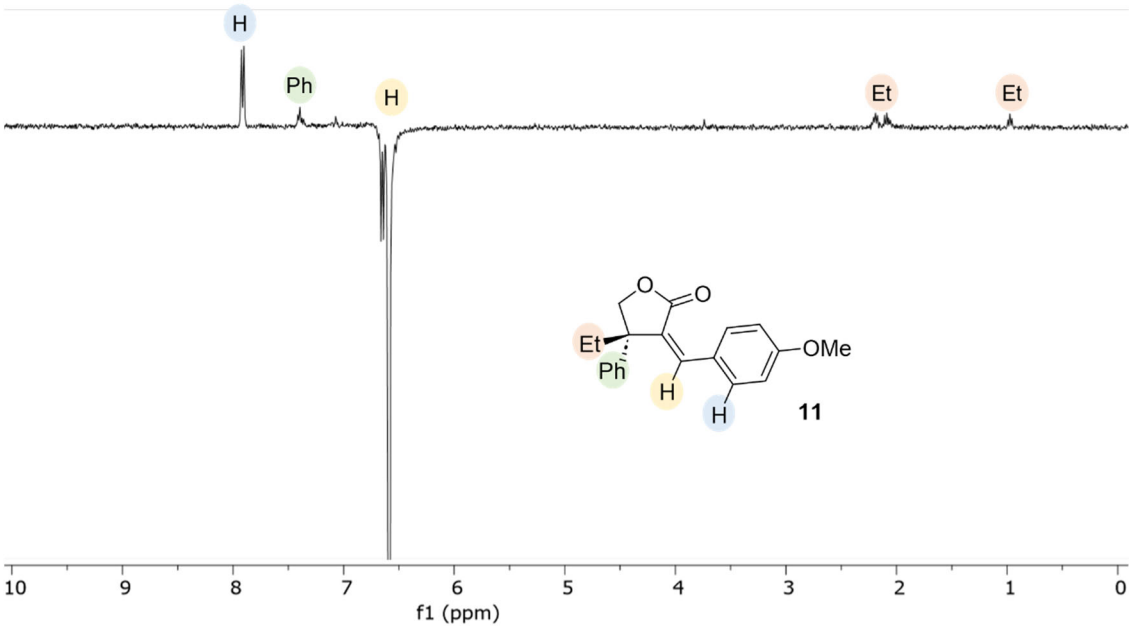


Figure S128. 1D-NOE scpectra of **11** irradiating at 6.55 ppm (in yellow).

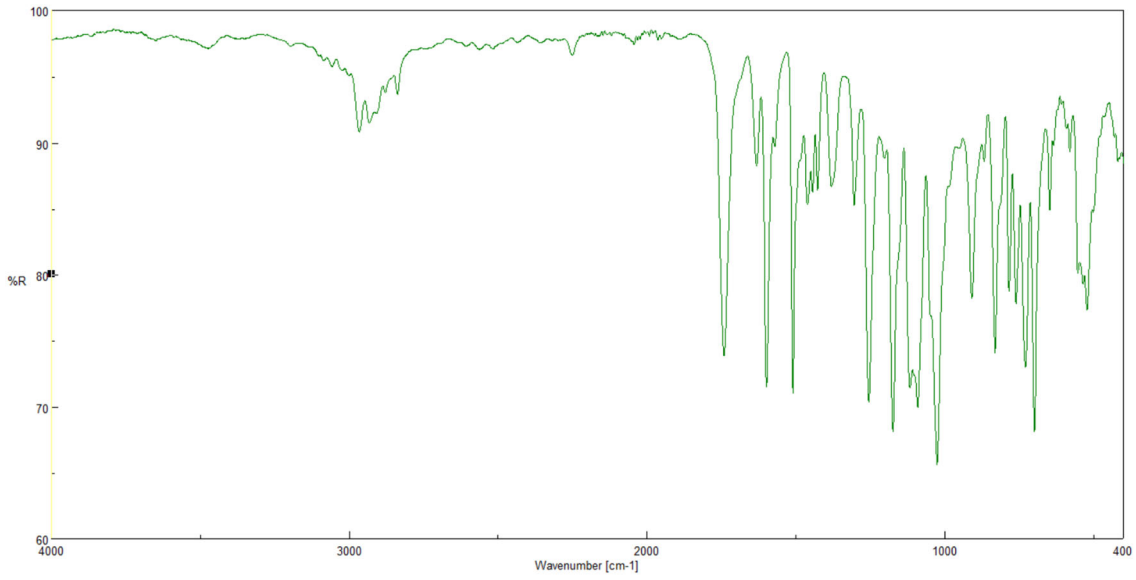
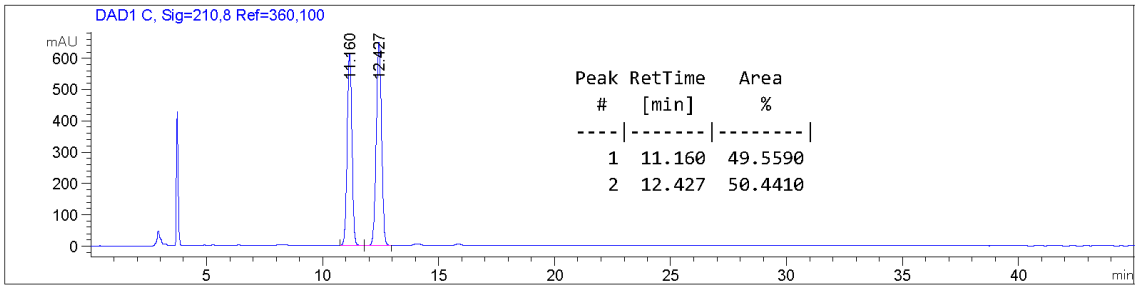


Figure S129. ATR-IR of (*S*,*Z*)-4-ethyl-3-(4-methoxybenzylidene)-4-phenyldihydrofuran-2(3H)-one (**11**).

(a)



(b)

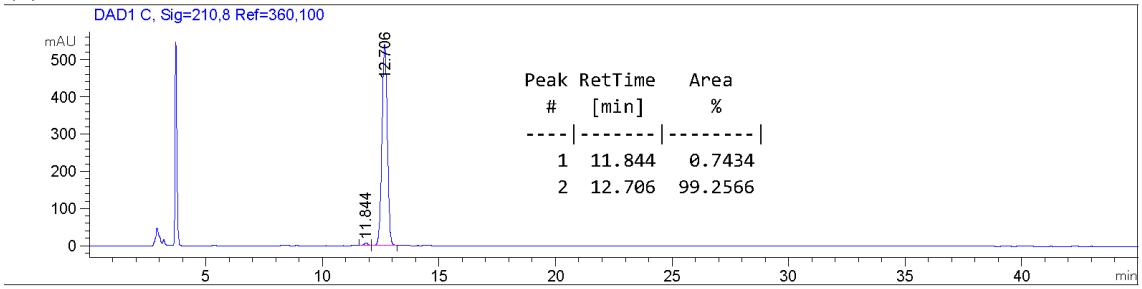
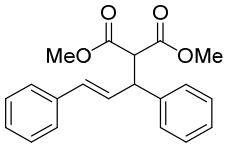


Figure S130. HPLC traces of (a) racemic and (b) enantioenriched product **11**.

SI-22. Characterization details and copies of NMR spectra and HPLC traces of allylic alkylation product



Dimethyl 2-(1,3-diphenylallyl)malonate.[16] ^{1}H NMR ($CDCl_3$), δ: 3.52 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 3.95 (d, 1H, CH, *J*=10.9 Hz), 4.26 (m, 1H, CH), 6.34 (dd, 1H, CH=, *J*=16.0 Hz, *J*= 8.4 Hz), 6.48 (d, 1H, CH=, *J*=16.0 Hz), 7.1-7.4 (m, 10H, CH=). Enantiomeric excess determined by HPLC using Chiralcel O*J*-H column (87% hexane/2-propanol, flow 0.5 mL/min). t_R 29.1 min (*R*); t_R 32.9min (*S*).

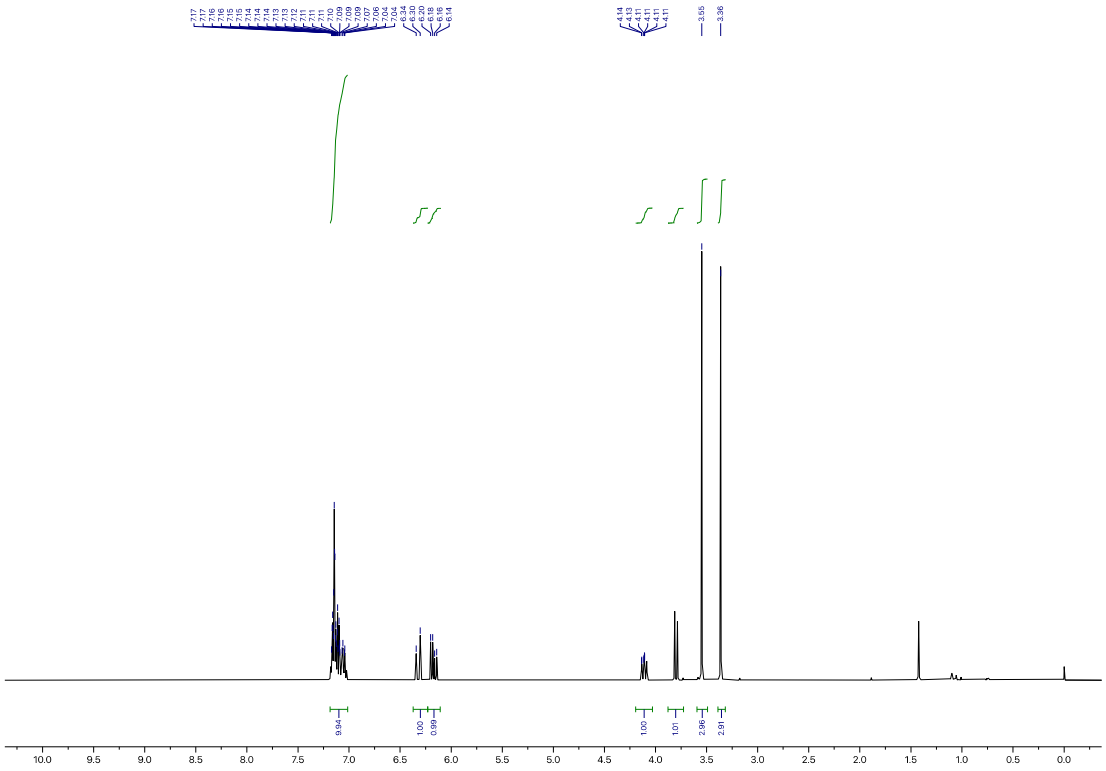
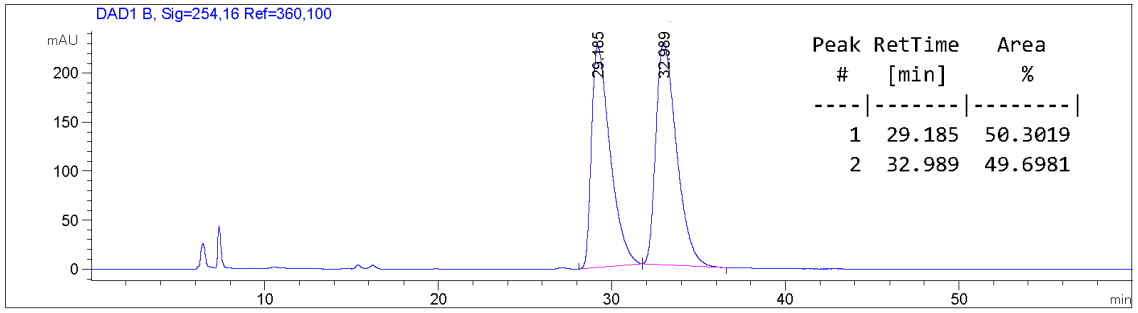
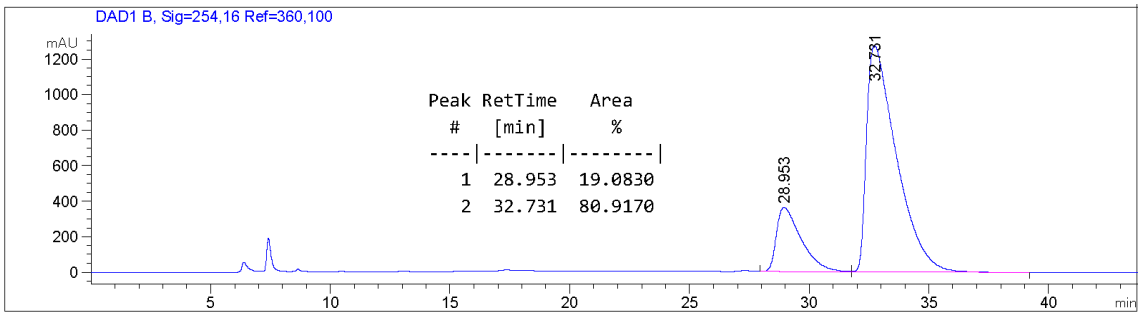


Figure S131. ^{1}H NMR of dimethyl 2-(1,3-diphenylallyl)malonate in $CDCl_3$.

a)



b)



c)

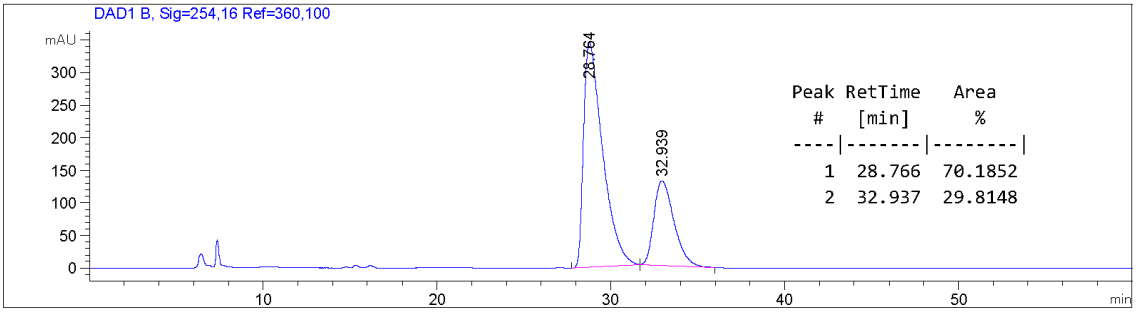


Figure S132. HPLC traces of (a) racemic, (b) enantioenriched product using Pd/PS-(*R*)-**L5**/**L11** catalytic system, and (c) enantioenriched product using (*S*)-**L5**/**L11** catalytic system.

SI-23. Kinetic data and reaction order of the catalyst

- *Epoxide kinetic order data*

[2a]= 0.2292 M

t (min)	integral IS	integral 3'ba	integral 3ba	3'ba+3ba	mmol product
-	113,4 ppm	62,5 ppm	62,6 ppm	-	-
1,500	100,000	2,350	3,530	5,880	0,002
3,000	100,000	4,590	7,120	11,710	0,004
4,500	100,000	7,010	10,130	17,140	0,006
6,000	100,000	9,420	13,860	23,280	0,008
7,500	100,000	11,570	17,060	28,630	0,010
9,000	100,000	13,390	19,750	33,140	0,012
10,500	100,000	15,820	23,230	39,050	0,014
12,000	100,000	18,480	27,270	45,750	0,016
13,500	100,000	20,380	29,970	50,350	0,018
15,000	100,000	22,480	33,180	55,660	0,020
16,500	100,000	25,640	37,150	62,790	0,022
18,000	100,000	27,810	40,830	68,640	0,024
19,500	100,000	29,190	43,580	72,770	0,026
21,000	100,000	31,320	46,900	78,220	0,028
22,500	100,000	34,840	51,280	86,120	0,031
24,000	100,000	36,480	53,950	90,430	0,032
25,500	100,000	38,030	56,740	94,770	0,034
27,000	100,000	40,170	60,730	100,900	0,036
28,500	100,000	43,710	65,000	108,710	0,039
30,000	100,000	44,560	67,410	111,970	0,040
31,500	100,000	46,080	69,810	115,890	0,041
33,000	100,000	46,780	70,290	117,070	0,042
34,500	100,000	47,170	71,070	118,240	0,042

[2a]= 0.09824 M

t (min)	integral IS	integral 3'ba	integral 3ba	3'ba+3ba	mmol product
-	113,4 ppm	62,5 ppm	62,6 ppm	-	-
1,5	100,00	1,29	1,81	3,1	0,00110112
3	100,00	2,13	3,47	5,6	0,00198912
4,5	100,00	3,36	4,83	8,19	0,00290909
6	100,00	3,99	6,33	10,32	0,00366566
7,5	100,00	4,92	7,72	12,64	0,00448973
9	100,00	5,84	9,08	14,92	0,00529958
10,5	100,00	7,23	10,65	17,88	0,00635098
12	100,00	8,01	12,21	20,22	0,00718214

[2a]= 0.045842 M

t (min)	integral IS	integral 3'ba	integral 3ba	3'ba+3ba	mmol product
-	113,4 ppm	62,5 ppm	62,6 ppm	-	-
1,5	100,00	5,8	8,04	13,84	0,00491597
3	100,00	11,16	16,43	27,59	0,00979997
4,5	100,00	16,79	24,29	41,08	0,01459162
6	100,00	21,71	32,4	54,11	0,01921987
7,5	100,00	27,78	40,9	68,68	0,02439514
9	100,00	33,22	49,04	82,26	0,02921875
10,5	100,00	39,1	56,61	95,71	0,03399619
12	100,00	44,19	65,38	109,57	0,03891926
13,5	100,00	48,14	70,74	118,88	0,04222618

- ***Meldrum's acid derivative kinetic order data***

[1b]= 0.10658 M

t (min)	integral IS	integral 3'ba	integral 3ba	3'ba+3ba	mmol product
-	113,4 ppm	62,5 ppm	62,6 ppm	-	-
1,500	100,000	2,350	3,530	5,880	0,002
3,000	100,000	4,590	7,120	11,710	0,004
4,500	100,000	7,010	10,130	17,140	0,006
6,000	100,000	9,420	13,860	23,280	0,008
7,500	100,000	11,570	17,060	28,630	0,010
9,000	100,000	13,390	19,750	33,140	0,012
10,500	100,000	15,820	23,230	39,050	0,014
12,000	100,000	18,480	27,270	45,750	0,016
13,500	100,000	20,380	29,970	50,350	0,018
15,000	100,000	22,480	33,180	55,660	0,020
16,500	100,000	25,640	37,150	62,790	0,022
18,000	100,000	27,810	40,830	68,640	0,024
19,500	100,000	29,190	43,580	72,770	0,026
21,000	100,000	31,320	46,900	78,220	0,028
22,500	100,000	34,840	51,280	86,120	0,031
24,000	100,000	36,480	53,950	90,430	0,032
25,500	100,000	38,030	56,740	94,770	0,034
27,000	100,000	40,170	60,730	100,900	0,036
28,500	100,000	43,710	65,000	108,710	0,039
30,000	100,000	44,560	67,410	111,970	0,040
31,500	100,000	46,080	69,810	115,890	0,041
33,000	100,000	46,780	70,290	117,070	0,042
34,500	100,000	47,170	71,070	118,240	0,042

[1b]= 0.2106 M

t (min)	integral IS	integral 3'ba	integral 3ba	3'ba+3ba	mmol product
-	113,4 ppm	62,5 ppm	62,6 ppm	-	-
1,500	100,000	0,470	1,080	1,550	0,001
3,000	100,000	1,510	2,680	4,190	0,001
4,500	100,000	2,580	3,730	6,310	0,002
6,000	100,000	3,610	5,050	8,660	0,003
7,500	100,000	4,220	6,310	10,530	0,004
9,000	100,000	5,280	7,660	12,940	0,005
10,500	100,000	6,070	9,140	15,210	0,005
12,000	100,000	7,210	10,000	17,210	0,006
13,500	100,000	7,880	11,740	19,620	0,007
15,000	100,000	8,410	12,690	21,100	0,007

16,500	100,000	9,630	14,270	23,900	0,008

[1b]= 0.0532 M

t (min)	integral IS	integral 3'ba	integral 3ba	3'ba+3ba	mmol product
-	113,4 ppm	62,5 ppm	62,6 ppm	-	-
1,500	100,000	2,01	3,19	5,200	0,002
3,000	100,000	4,07	6,12	10,190	0,004
4,500	100,000	6,32	9,79	16,110	0,006
6,000	100,000	8,56	13,19	21,750	0,008
7,500	100,000	11,36	17,34	28,700	0,010
9,000	100,000	13,96	21,7	35,660	0,013
10,500	100,000	17,17	26,4	43,570	0,015
12,000	100,000	20,93	32,22	53,150	0,019
13,500	100,000	28,750	42,190	70,940	0,025

- ***Catalyst kinetic order data***

[Cat]= 0.002706 M

t (min)	integral IS	integral 3'ba	integral 3ba	3'ba+3ba	mmol product
-	113,4 ppm	62,5 ppm	62,6 ppm	-	-
1,500	100,000	2,350	3,530	5,880	0,002
3,000	100,000	4,590	7,120	11,710	0,004
4,500	100,000	7,010	10,130	17,140	0,006
6,000	100,000	9,420	13,860	23,280	0,008
7,500	100,000	11,570	17,060	28,630	0,010
9,000	100,000	13,390	19,750	33,140	0,012
10,500	100,000	15,820	23,230	39,050	0,014
12,000	100,000	18,480	27,270	45,750	0,016
13,500	100,000	20,380	29,970	50,350	0,018
15,000	100,000	22,480	33,180	55,660	0,020
16,500	100,000	25,640	37,150	62,790	0,022
18,000	100,000	27,810	40,830	68,640	0,024
19,500	100,000	29,190	43,580	72,770	0,026
21,000	100,000	31,320	46,900	78,220	0,028
22,500	100,000	34,840	51,280	86,120	0,031
24,000	100,000	36,480	53,950	90,430	0,032
25,500	100,000	38,030	56,740	94,770	0,034
27,000	100,000	40,170	60,730	100,900	0,036
28,500	100,000	43,710	65,000	108,710	0,039
30,000	100,000	44,560	67,410	111,970	0,040
31,500	100,000	46,080	69,810	115,890	0,041
33,000	100,000	46,780	70,290	117,070	0,042
34,500	100,000	47,170	71,070	118,240	0,042

[Cat]= 0.0050236 M

t (min)	integral IS	integral 3'ba	integral 3ba	3'ba+3ba	mmol product
-	113,4 ppm	62,5 ppm	62,6 ppm	-	-
1,5	100,00	6,75	10,58	17,33	0,00615562
3	100,00	14,43	22,13	36,56	0,01298611
4,5	100,00	24,33	37,37	61,7	0,02191584
6	100,00	32,41	50,37	82,78	0,02940346
7,5	100,00	42,1	65,18	107,28	0,03810586
9	100,00	46,88	73,47	120,35	0,04274832

[Cat]= 0.001546 M

t (min)	integral IS	integral 3'ba	integral 3ba	3'ba+3ba	mmol product
-	113,4 ppm	62,5 ppm	62,6 ppm	-	-
1,5	100,00	0,77	1,09	1,86	0,00066067
3	100,00	1,74	2,94	4,68	0,00166234
4,5	100,00	2,8	4,34	7,14	0,00253613
6	100,00	3,54	5,43	8,97	0,00318614
7,5	100,00	4,28	6,31	10,59	0,00376157
9	100,00	4,79	7,22	12,01	0,00426595
10,5	100,00	5,33	7,91	13,24	0,00470285
12	100,00	5,89	8,83	14,72	0,00522854
13,5	100,00	6,37	9,46	15,83	0,00562282
15	100,00	6,62	9,76	16,38	0,00581818
16,5	100,00	7,2	10,44	17,64	0,00626573
18	100,00	7,45	10,88	18,33	0,00651082
19,5	100,00	7,83	11,47	19,3	0,00685536
21	100,00	8,08	11,96	20,04	0,00711821
22,5	100,00	8,54	12,22	20,76	0,00737395
24	100,00	8,71	12,56	21,27	0,0075551
25,5	100,00	9,02	13,05	22,07	0,00783926
27	100,00	9,3	13,57	22,87	0,00812342
28,5	100,00	9,54	13,87	23,41	0,00831523
30	100,00	9,74	14,24	23,98	0,0085177

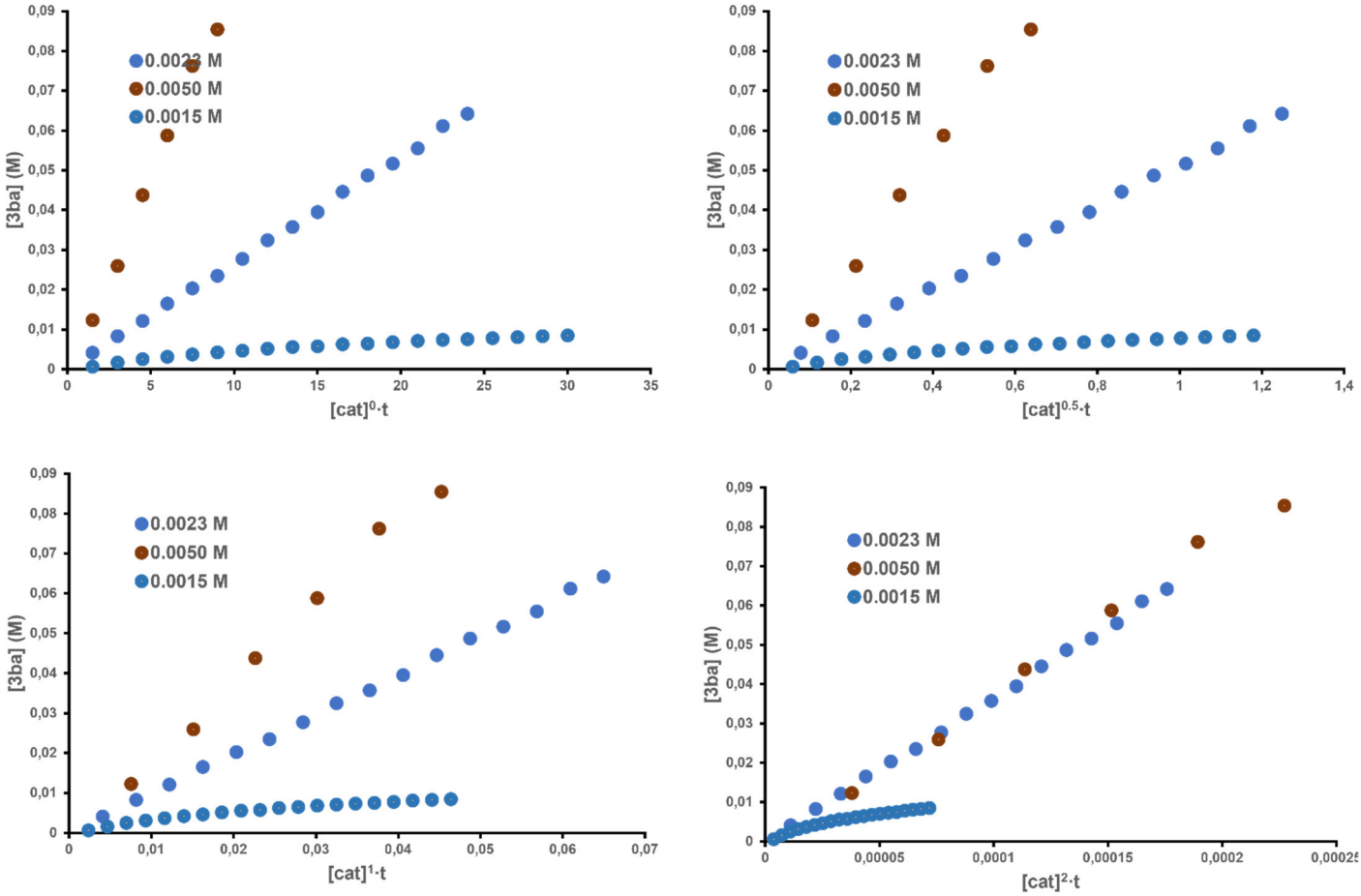


Figure S133. VTNA kinetic analysis to stablish the catalyst kinetic data.

SI-24. References

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