Supporting Information

Enantioselective Reductive Homocoupling of Allylic Acetates Enabled by Dual Photoredox/Palladium Catalysis: Access to C_2-Symmetrical 1,5-Dienes

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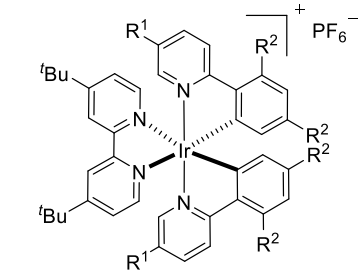
1. General information

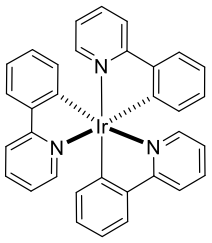
Commercial reagents were purchased from Aldrich Chemical, Alfa Aesar, TCI, Strem, Acros, Energy Chemical, J&K Chemical, Innochem and were used as received. All catalytic reactions were run in dried glassware. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light and by staining with phosphomolybdic acid or potassium permanganate, respectively. Column chromatography was performed on EMD Silica Gel 60 (300–400 Mesh) using a forced flow of 0.5–1.0 bar. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F (376 MHz) were measured on a Bruker AVANCE III–400 spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to the residual solvent peak. Coupling constants are reported as Hertz (Hz), signal shapes and splitting patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC-MS spectra were performed on Agilent 5977A Series (EI Source). High Resolution Mass spectra were performed on Agilent 1260 Series (ESI Source). High-pressure liquid chromatography (HPLC) was performed on Shimadzu SPD-20A and Agilent 1260 Series chromatographs using chiral columns as noted for each compound. Optical rotations were measured on an automatic polarimeter with $[\alpha]_D^{20}$ values reported in degrees; concentration (c) is in g/100 mL.

The allylic acetates (**1** and **3**) were prepared according to the literature procedure.[1]

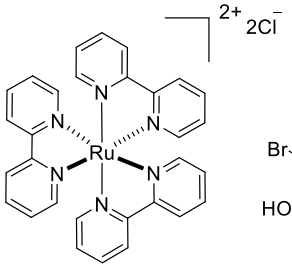
2. Numberings and structures of all compounds



R^1= R^2 = H, $Ir(ppy)_2(dtbbpy)PF_6$ (**I**)
R^1 = CF_3; R^2 = F, $Ir(dFCF_3ppy)_2(dtbbpy)PF_6$ (**V**)
R^1 = CH_3; R^2 = F, $Ir(dFMeppy)_2(dtbbpy)PF_6$ (**VI**)



fac-$Ir(ppy)_3$ (**II**)



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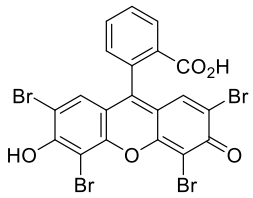

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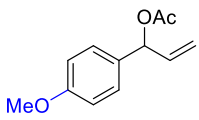

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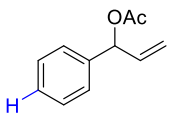

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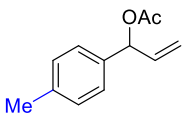

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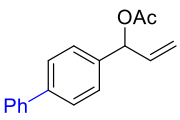

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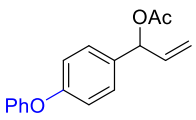

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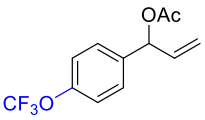

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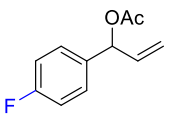

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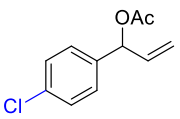

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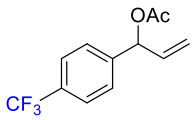

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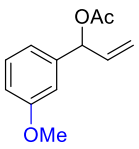

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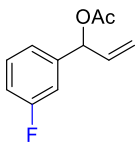

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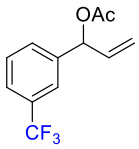

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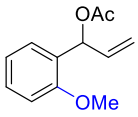

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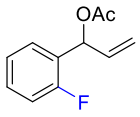

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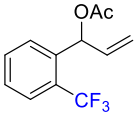

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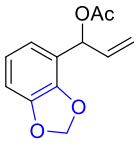

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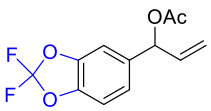

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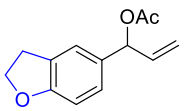

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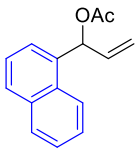

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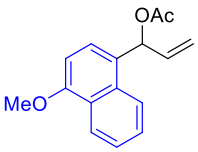

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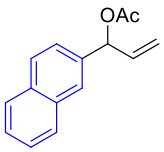

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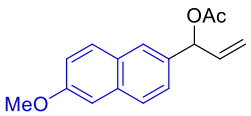

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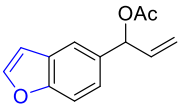

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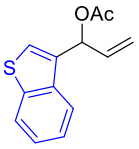

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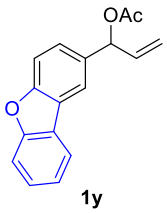

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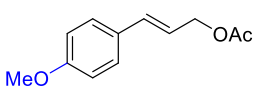

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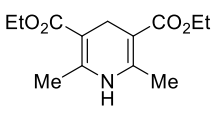

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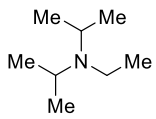

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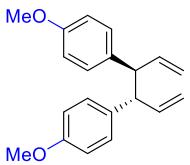

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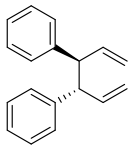

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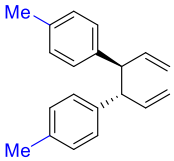

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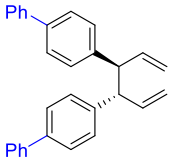

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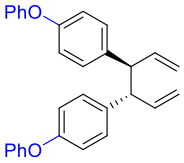

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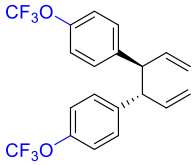

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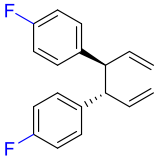

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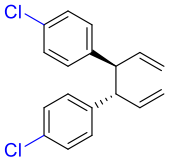

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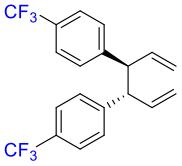

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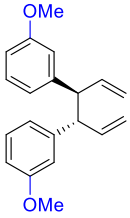

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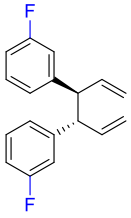

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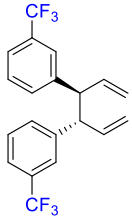

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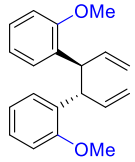

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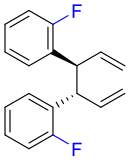

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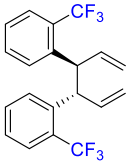

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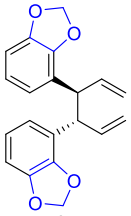

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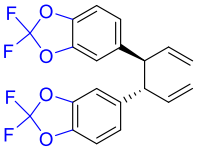

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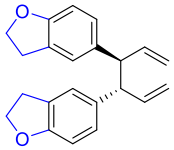

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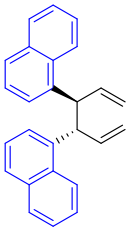

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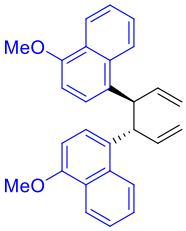

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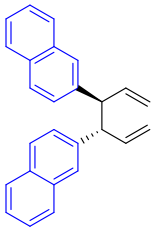

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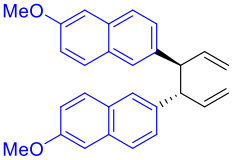

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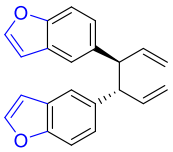

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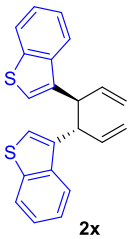

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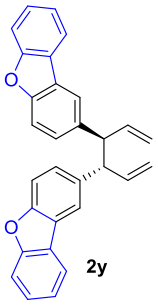

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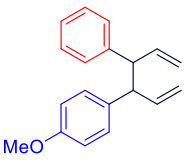

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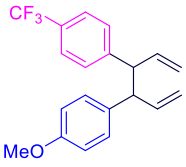

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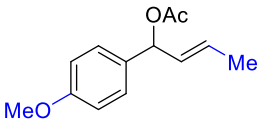

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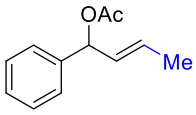

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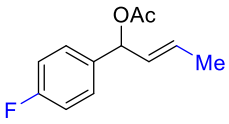

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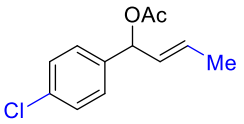

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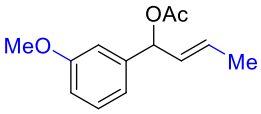

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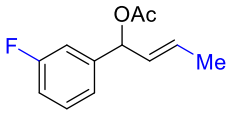

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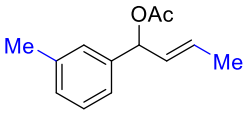

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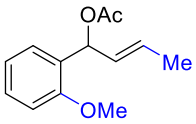

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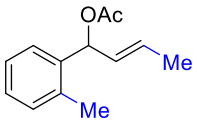

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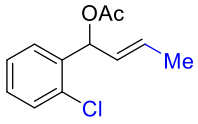

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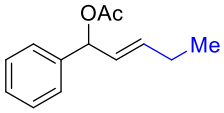

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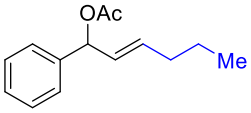

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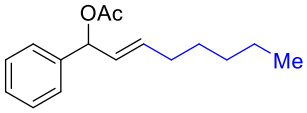

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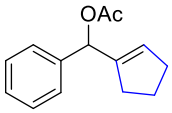

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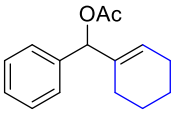

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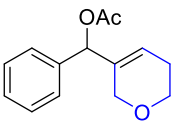

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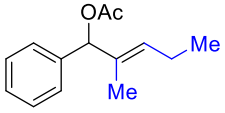

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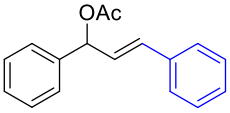

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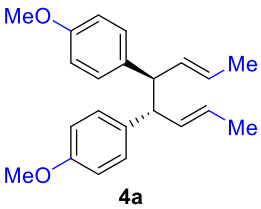

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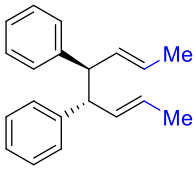

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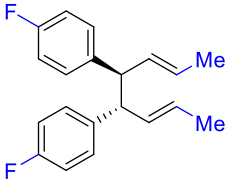

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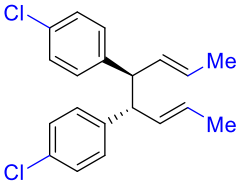

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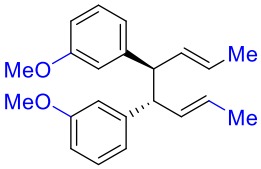

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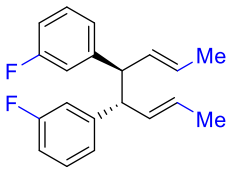

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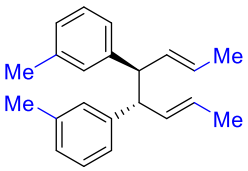

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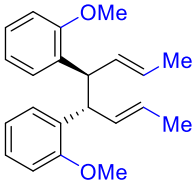

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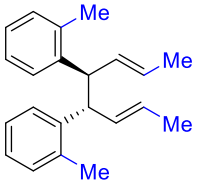

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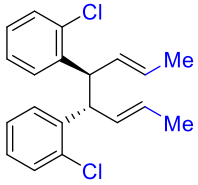

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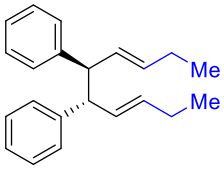

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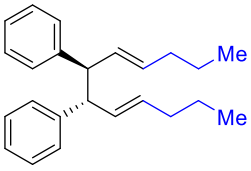

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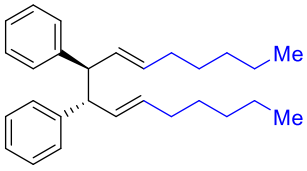

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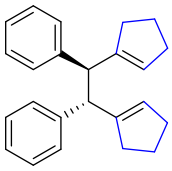

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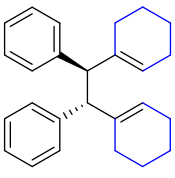

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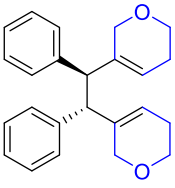

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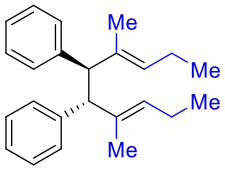

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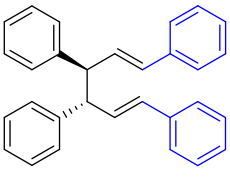

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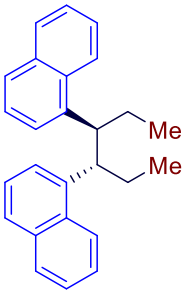

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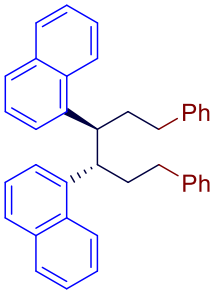

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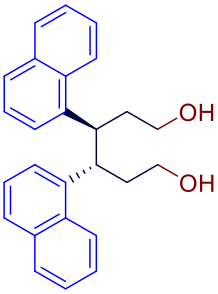

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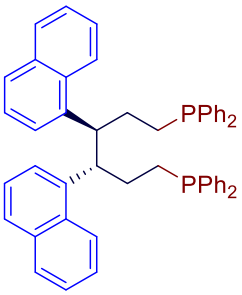

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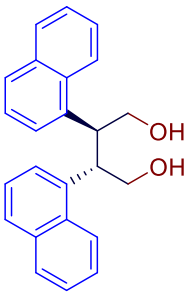

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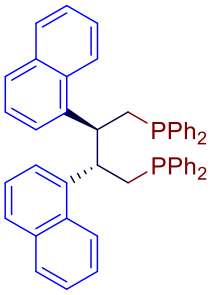

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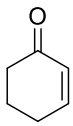

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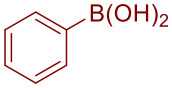

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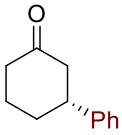

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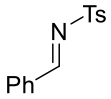

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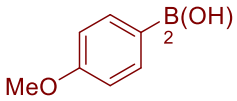

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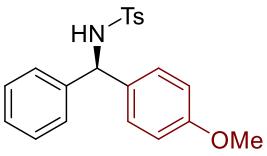

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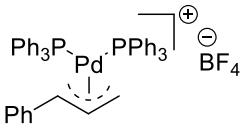

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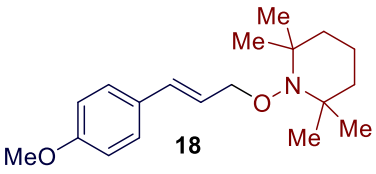

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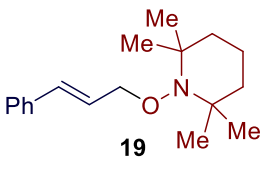

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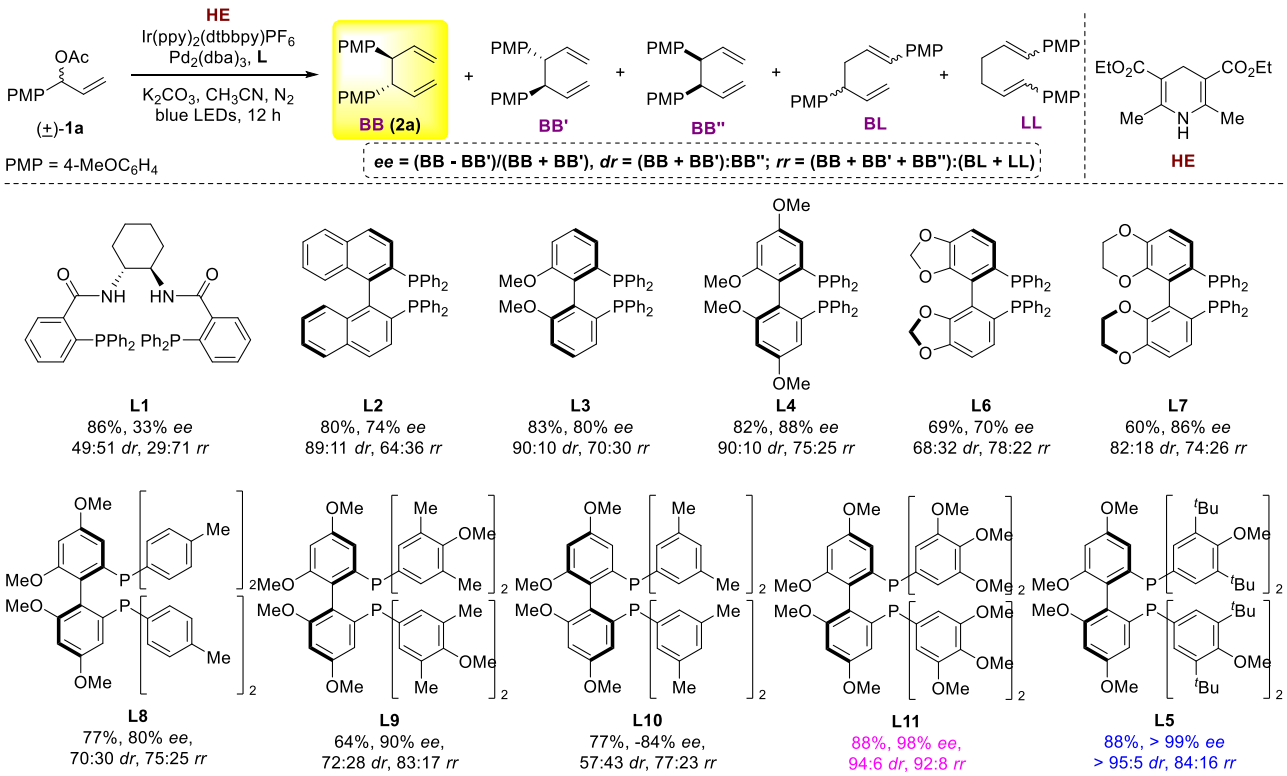
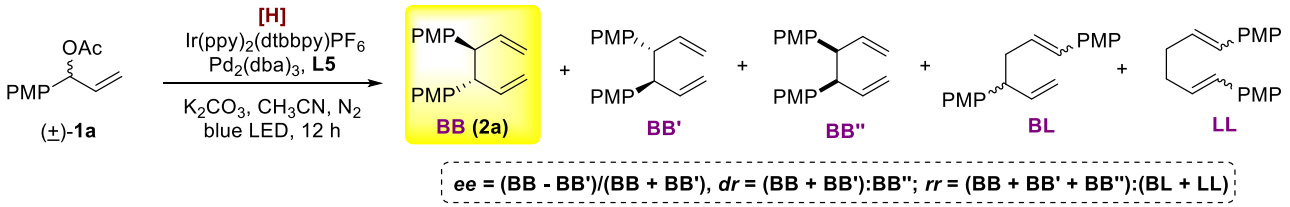
3. Optimization of the conditions for 2a

Table S1. Screening of the chiral ligands[a]



[a]Reaction conditions: **1a** (0.2 mmol), HE (0.3 mmol), K_2CO_3 (0.3 mmol), $Pd_2(dba)_3$ (1.25 mol %), ligand (3 mol %), and photocatalyst **I** (1 mol %) in CH_3CN (4.0 mL) was irradiated by 45 W blue LEDs for 12 h. The yield, diastereoselectivity (*dr*), and regioselectivity (*rr*) were determined by GC. Enantiomeric excess (*ee*) values determined by HPLC on a chiral stationary phase. PMP = *para*-methoxyphenyl.

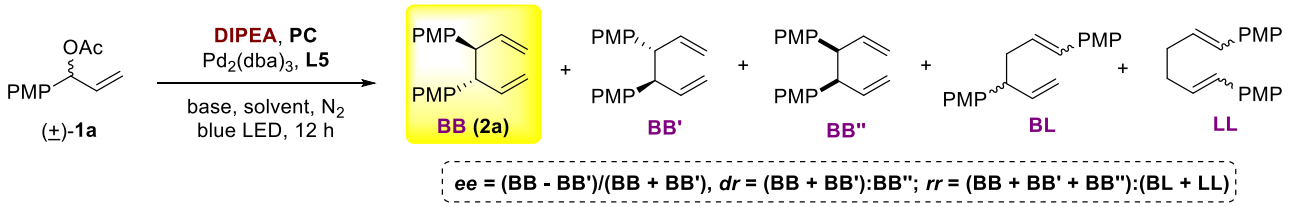
Table S2. Screening of the reductant[a]



entry	**[H]**	yield/%[b]	*ee*/%[c]	*dr*[b]	*rr*[b]
1	HE	88	> 99	> 95:5	84:16
2	DIPEA	74	> 99	> 95:5	90:10
3	Et_3N	76	> 99	> 95:5	83:17
4	$^nPr_3N$	67	> 99	> 95:5	87:13
5	$^nBu_3N$	74	> 99	> 95:5	88:12
6	NMM	57	98	85:15	38:62
7	HCO_2H	71	72	74:26	30:70
8	HCO_2NH_4	44	45	72:28	27:73

[a]Reaction conditions: **1a** (0.2 mmol), reductant (0.3 mmol), K_2CO_3 (0.3 mmol), $Pd_2(dba)_3$ (1.25 mol %), ligand **L5** (3 mol %), and photocatalyst **I** (1 mol %) in the CH_3CN (4.0 mL) was irradiated by 45 W blue LEDs for 12 h. [b]Determined by GC. [c]Enantiomeric excess (*ee*) values determined by HPLC on a chiral stationary phase. PMP = *para*-methoxyphenyl.

Table S3. Optimization of the conditions for **2a**[a]



entry	PC	solvent	base	yield/%[b]	*ee*/%[c]	*dr*[b]	*rr*[b]
1	**I**	CH_3CN	K_2CO_3	74	> 99	> 95:5	90:10
2	**II**	CH_3CN	K_2CO_3	63	> 99	88:12	41:59
3	**III**	CH_3CN	K_2CO_3	49	> 99	> 95:5	48:52
4	**IV**	CH_3CN	K_2CO_3	50	> 99	94:6	34:66
5	**V**	CH_3CN	K_2CO_3	45	> 99	94:6	64:36
6	**VI**	CH_3CN	K_2CO_3	57	> 99	95:5	70:30
7	**I**	THF	K_2CO_3	71	> 99	> 95:5	87:13
8	**I**	DMF	K_2CO_3	68	> 99	> 95:5	86:14
9	**I**	DMAC	K_2CO_3	28	ND	ND	ND
10	**I**	DMSO	K_2CO_3	68	> 99	> 95:5	69:31
11	**I**	Tol	K_2CO_3	66	> 99	> 95:5	84:16
12	**I**	DCM	K_2CO_3	14	ND	ND	ND
13	**I**	CH_3CN	$KHCO_3$	63	> 99	> 95:5	90:10
14	**I**	CH_3CN	K_3PO_4	85	> 99	> 95:5	94:6
15	**I**	CH_3CN	K_2HPO_4	50	> 99	> 95:5	93:7
16	**I**	CH_3CN	Na_2CO_3	67	> 99	> 95:5	90:10
17	**I**	CH_3CN	Cs_2CO_3	90	> 99	> 95:5	94:6
18	**I**	CH_3CN	Li_2CO_3	41	> 99	> 95:5	91:9
19	**I**	CH_3CN	-	36	> 99	> 95:5	86:14
20[d]	**I**	CH_3CN	Cs_2CO_3	96 (92)[e]	> 99	> 95:5	> 95:5

[a]Reaction conditions: **1a** (0.2 mmol), DIPEA (0.3 mmol), base (0.3 mmol), $Pd_2(dba)_3$ (1.25 mol %), ligand **L5** (3 mol %), and photocatalyst (1 mol %) in the indicated solvent (4.0 mL) was irradiated by 45 W blue LEDs for 12 h. [b]Determined by GC. [c]Enantiomeric excess (*ee*) values determined by

HPLC on a chiral stationary phase. [d]CH_3CN (2.0 mL) was used. [e]Isolated yields. PMP = *para*-methoxyphenyl.

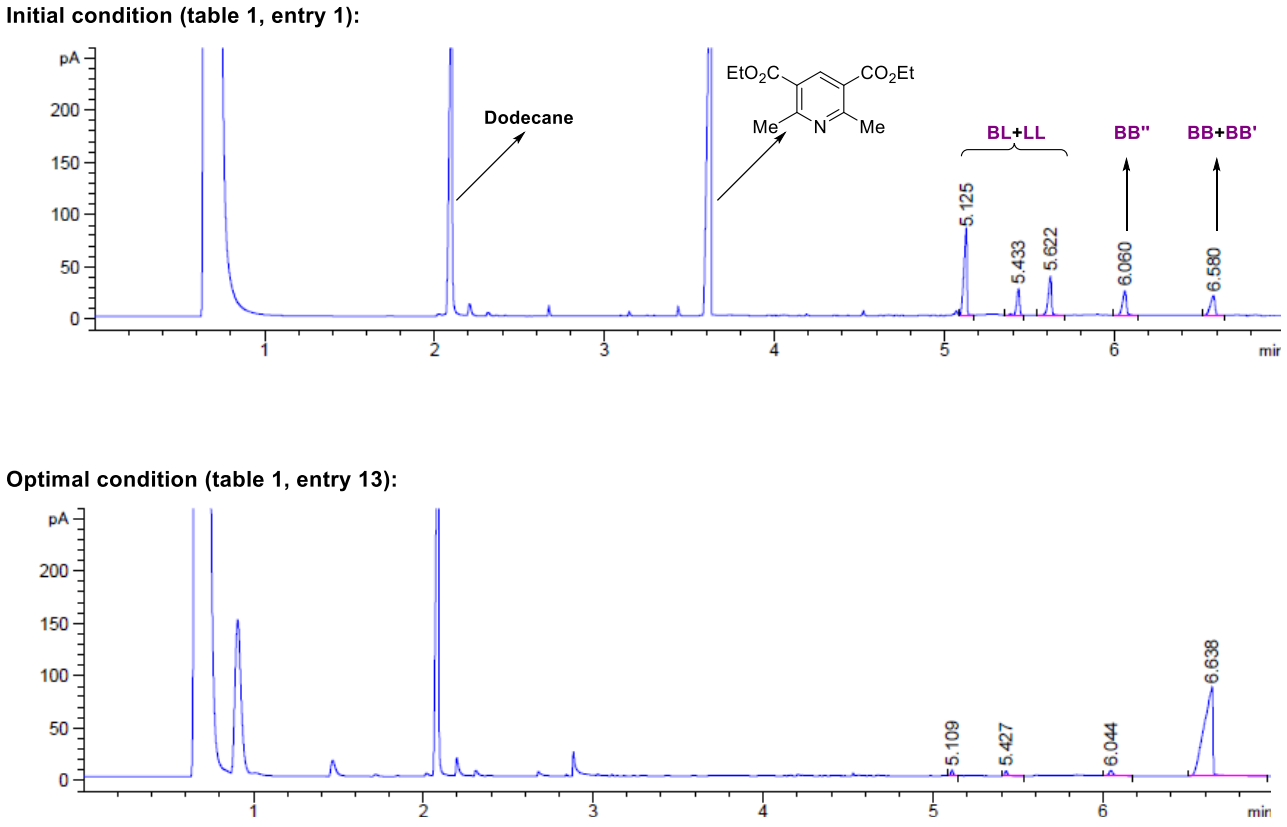
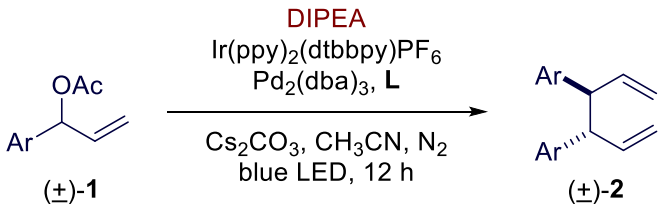


Figure S1. GC spectrum of the reaction under initial condition and optimal condition.

4. General procedure for the synthesis of products 2

4.1 Synthesis of racemic products 2

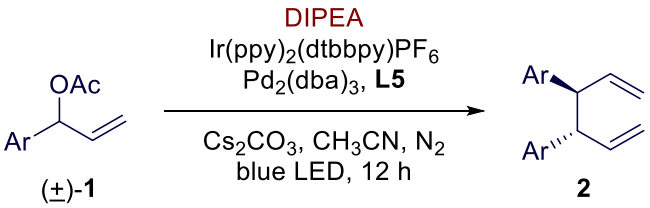


***General Procedure A*:** In a nitrogen-filled glovebox, an 8 mL screw-cap test tube, equipped with a magnetic stir bar, charged with $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol, 1.25 mol%), (±)-BINAP (3.7 mg, 0.006 mmol, 3 mol%), anhydrous CH_3CN (1.0 mL) was added and the mixture was stirred for 30 min. Then the following chemicals were added in turn: $Ir(ppy)_2(dtbbpy)PF_6$ (2.0 mg, 0.002 mmol, 1.0 mol%), Cs_2CO_3 (97.8 mg, 0.3 mmol, 1.5 equiv), allylic acetates **1** (0.2 mmol, 1.0 equiv), DIPEA (40 mg, 0.3 mmol, 1.5 equiv) and anhydrous CH_3CN (1.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously under 45W blue LED lights at room temperature for 12 h. Next, the reaction mixture was transferred to a 250 mL separatory funnel, rinsed/diluted with 100 mL ether, and washed with 100 mL deionized water (twice) and finally 100 mL brine. The organic phase was concentrated under vacuum and purified by chromatography.

General Procedure B*:** In a nitrogen-filled glovebox, an 8 mL screw-cap test tube, equipped with a magnetic stir bar, charged with $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol, 1.25 mol%), (*R*)-2,2'-Bis[bis-(4-methoxy-3,5-di-*t*-butylphenyl)phosphino]-4,4',6,6'-tetramethoxy)-1,1'-biphenyl (R*-L5**) (3.7 mg, 0.003 mmol, 1.5 mol%), (*S*)-2,2'-Bis[bis(4-methoxy-3,5-di-*t*-butylphenyl)phosphino]-4,4',6,6'-tetramethoxy)-1,1'-biphenyl (***S*-L5**) (3.7 mg, 0.003 mmol, 1.5 mol%), anhydrous CH_3CN (1.0 mL) was added and the mixture was stirred for 30 min. Then the following chemicals were added in turn: $Ir(ppy)_2(dtbbpy)PF_6$ (2.0 mg, 0.002 mmol, 2.0 mol%), Cs_2CO_3 (97.8 mg, 0.3 mmol, 1.5 equiv), allylic acetates **1** (0.2 mmol, 1.0 equiv), DIPEA (40 mg, 0.3 mmol, 1.5 equiv) and anhydrous CH_3CN (1.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously under 45W blue LED lights at room temperature for 12 h. Next, the reaction mixture was transferred to a 250 mL separatory funnel, rinsed/diluted

with 100 mL ether, and washed with 100 mL deionized water (twice) and finally 100 mL brine. The organic phase was concentrated under vacuum and purified by chromatography.

4.2 Synthesis of chiral products 2

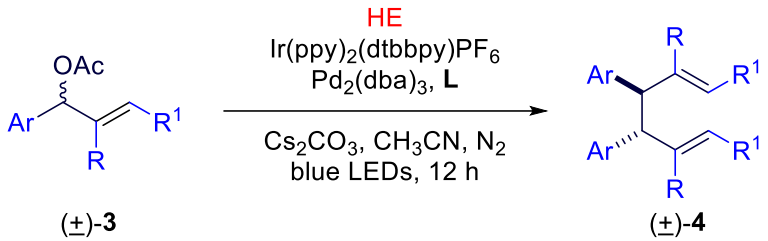


General Procedure C **(in-glovebox):** In a nitrogen-filled glovebox, an 8 mL screw-cap test tube, equipped with a magnetic stir bar, charged with $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol, 1.25 mol%), (*R*)-2,2'-Bis[bis(4-methoxy-3,5-di-*t*-butylphenyl)phosphino]-4,4',6,6'-tetramethoxy)-1,1'-biphenyl (**L5**) (7.3 mg, 0.006 mmol, 3 mol%), anhydrous CH_3CN (1.0 mL) was added and the mixture was stirred for 30 min. Then the following chemicals were added in turn: $Ir(ppy)_2(dtbbpy)PF_6$ (2.0 mg, 0.002 mmol, 1.0 mol%), Cs_2CO_3 (97.8 mg, 0.3 mmol, 1.5 equiv), allylic acetates **1** (0.2 mmol, 1.0 equiv), DIPEA (40 mg, 0.3 mmol, 1.5 equiv) and anhydrous CH_3CN (1.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously under 45W blue LED lights at room temperature for 12 h. Next, the reaction mixture was transferred to a 250 mL separatory funnel, rinsed/diluted with 100 mL ether, and washed with 100 mL deionized water (twice) and finally 100 mL brine. The organic phase was concentrated under vacuum and purified by chromatography.

General Procedure C' **(out-of-glovebox):** In air, an 8 mL screw-cap test tube, equipped with a magnetic stir bar, was charged with $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol, 1.25 mol%), (*R*)-2,2'-Bis-[bis(4-methoxy-3,5-di-*t*-butylphenyl)phosphino]-4,4',6,6'-tetramethoxy)-1,1'-biphenyl (**L5**) (7.3 mg, 0.006 mmol, 3 mol%). The tube was evacuated and backfilled with N_2 for 3 times (3 × 5 min). Degassed CH_3CN (1.0 mL) was added by syringe under N_2, and the mixture was stirred for 30 min. In air, an 8 mL screw-cap test tube, equipped with a magnetic stir bar, was charged with $Ir(ppy)_2(dtbbpy)PF_6$ (2.0 mg, 0.002 mmol, 1.0 mol%), Cs_2CO_3 (97.8 mg, 0.3 mmol, 1.5 equiv), allylic acetates **1a** (0.2 mmol, 1.0 equiv), DIPEA (40 mg, 0.3 mmol, 1.5 equiv). The tube was evacuated and backfilled with N_2 for 3 times (3 × 5 min). Degassed CH_3CN (1.0 mL) was added by

syringe under N_2. Next, the Pd/ligand slurry was transferred via a syringe to the tube in a continuous flow over 10 seconds. The reaction mixture was stirred vigorously under 45W blue LED lights at room temperature for 12 h. Next, the reaction mixture was transferred to a 250 mL separatory funnel, rinsed/diluted with 100 mL ether, and washed with 100 mL deionized water (twice) and finally 100 mL brine. The organic phase was concentrated under vacuum and purified by chromatography.

4.3 Synthesis of racemic products 4

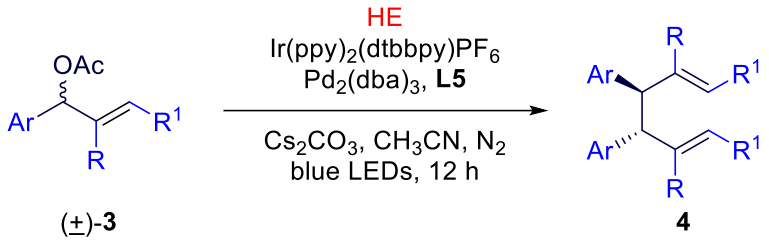


***General Procedure D*:** In a nitrogen-filled glovebox, an 8 mL screw-cap test tube, equipped with a magnetic stir bar, charged with $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol, 1.25 mol%), (±)-BINAP (3.7 mg, 0.006 mmol, 3 mol%), anhydrous CH_3CN (1.0 mL) was added and the mixture was stirred for 30 min. Then the following chemicals were added in turn: $Ir(ppy)_2(dtbbpy)PF_6$ (2.0 mg, 0.002 mmol, 1.0 mol%), Cs_2CO_3 (97.8 mg, 0.3 mmol, 1.5 equiv), allylic acetates **1** (0.2 mmol, 1.0 equiv), Hantzsch ester (HE) (76 mg, 0.3 mmol, 1.5 equiv) and anhydrous CH_3CN (1.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously under 45W blue LED lights at room temperature for 12 h. Next, the reaction mixture was transferred to a 250 mL separatory funnel, rinsed/diluted with 100 mL ether, and washed with 100 mL deionized water (twice) and finally 100 mL brine. The organic phase was concentrated under vacuum and purified by chromatography.

General Procedure E*:** In a nitrogen-filled glovebox, an 8 mL screw-cap test tube, equipped with a magnetic stir bar, charged with $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol, 1.25 mol%), (*R*)-2,2'-Bis[bis-(4-methoxy-3,5-di-*t*-butylphenyl)phosphino]-4,4',6,6'-tetramethoxy)-1,1'-biphenyl (R*-L5**) (3.7 mg, 0.003 mmol, 1.5 mol%), (*S*)-2,2'-Bis[bis(4-methoxy-3,5-di-*t*-butylphenyl)phosphino]-4,4',6,6'-tetramethoxy)-1,1'-biphenyl (***S*-L5**) (3.7 mg, 0.003 mmol, 1.5 mol%), anhydrous CH_3CN (1.0 mL) was added and the mixture was stirred for 30 min. Then the following chemicals were added in turn: $Ir(ppy)_2(dtbbpy)PF_6$ (2.0 mg, 0.002 mmol, 2.0 mol%), Cs_2CO_3 (97.8 mg, 0.3 mmol, 1.5 equiv),

allylic acetates **1** (0.2 mmol, 1.0 equiv), Hantzsch ester (HE) (40 mg, 0.3 mmol, 1.5 equiv) and anhydrous CH_3CN (1.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously under 45W blue LED lights at room temperature for 12 h. Next, the reaction mixture was transferred to a 250 mL separatory funnel, rinsed/diluted with 100 mL ether, and washed with 100 mL deionized water (twice) and finally 100 mL brine. The organic phase was concentrated under vacuum and purified by chromatography.

4.4 Synthesis of chiral products 4

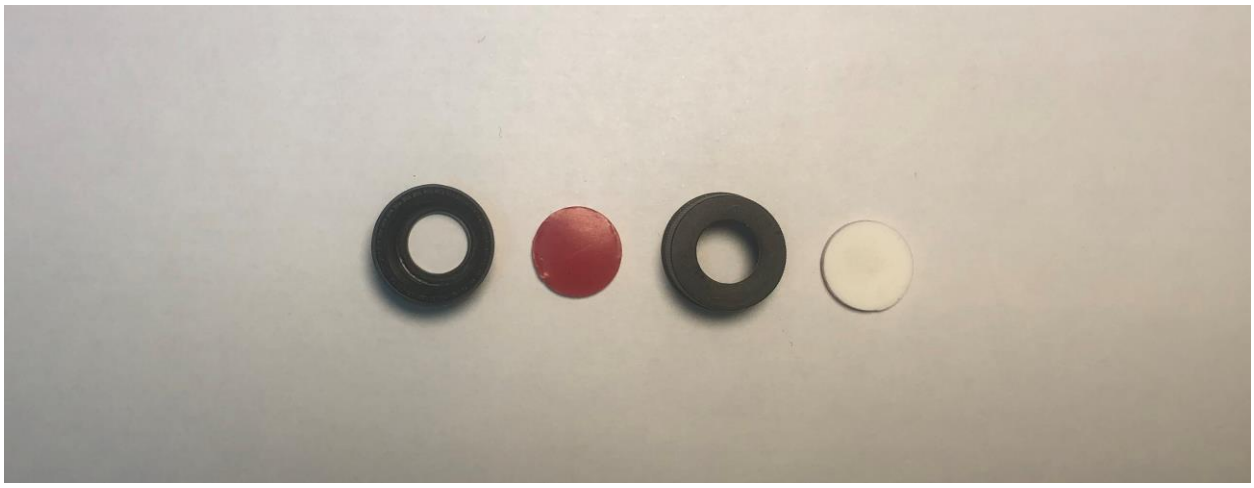


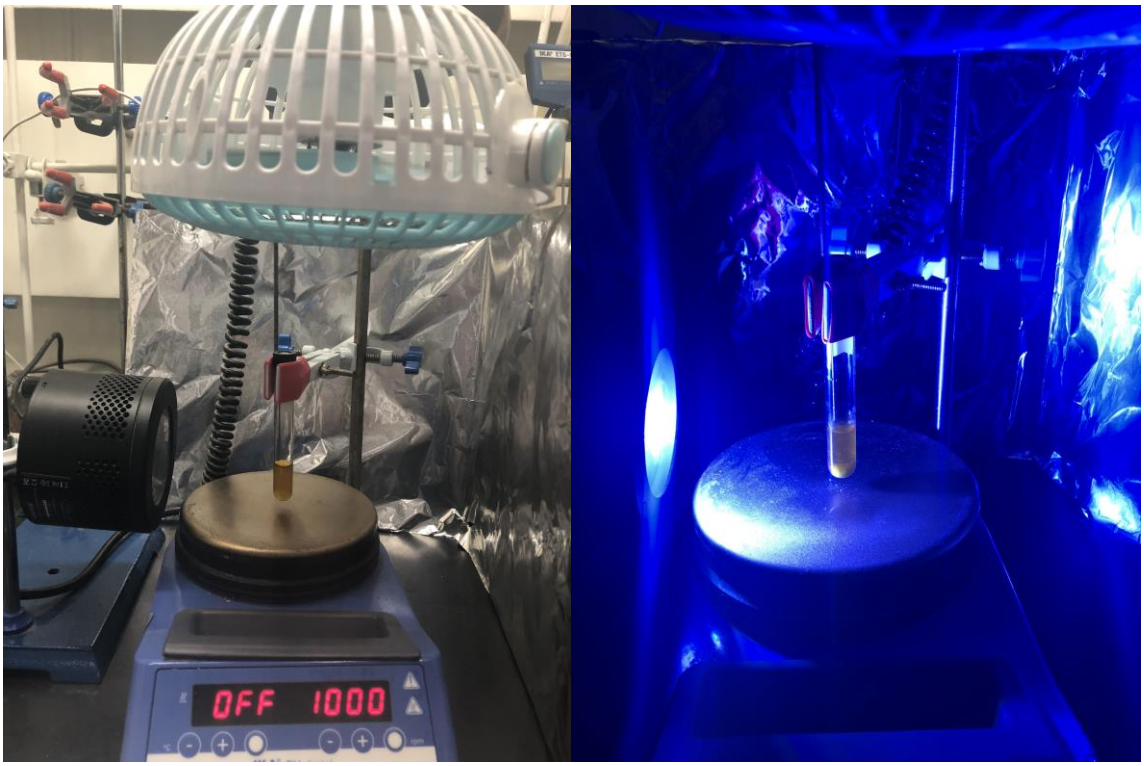
***General Procedure F*:** In a nitrogen-filled glovebox, an 8 mL screw-cap test tube, equipped with a magnetic stir bar, charged with $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol, 1.25 mol%), (*R*)-2,2'-Bis[bis(4-methoxy-3,5-di-*t*-butylphenyl)phosphino]-4,4',6,6'-tetramethoxy)-1,1'-biphenyl (**L5**) (7.3 mg, 0.006 mmol, 3 mol%), anhydrous CH_3CN (1.0 mL) was added and the mixture was stirred for 30 min. Then the following chemicals were added in turn: $Ir(ppy)_2(dtbbpy)PF_6$ (2.0 mg, 0.002 mmol, 1.0 mol%), Cs_2CO_3 (97.8 mg, 0.3 mmol, 1.5 equiv), allylic acetates **1** (0.2 mmol, 1.0 equiv), Hantzsch ester (HE) (40 mg, 0.3 mmol, 1.5 equiv) and anhydrous CH_3CN (1.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously under 45W blue LED lights at room temperature for 12 h. Next, the reaction mixture was transferred to a 250 mL separatory funnel, rinsed/diluted with 100 mL ether, and washed with 100 mL deionized water (twice) and finally 100 mL brine. The organic phase was concentrated under vacuum and purified by chromatography.

Reaction Setup

Medium-sized screw-cap test tubes (8 mL) were used for all 0.1 mmol scale reactions: Fisher13 x 100 mm tubes (Cat. No. 14-959-35C)

Cap with Septa: Thermo Scientific ASM PHN CAP w/PTFE/SIL (Cat. No. 03378316)





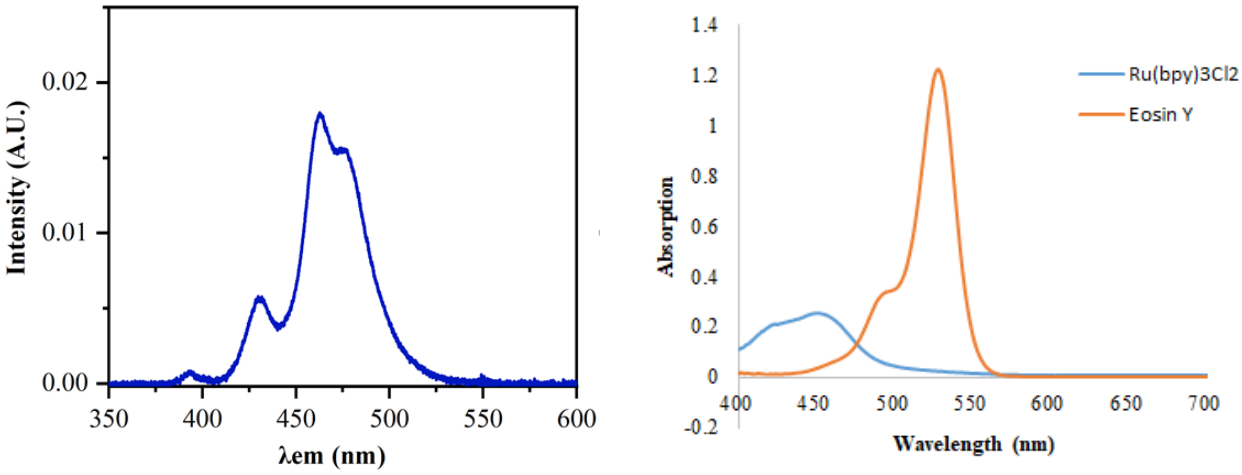
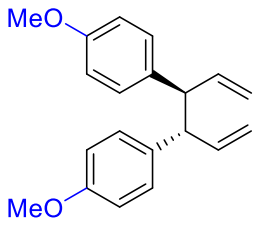


Figure S1. Spectrum of the blue LEDs source and absorption spectra of $Ru(bpy)_3Cl_2$ and Eosin Y

5. Product characterization

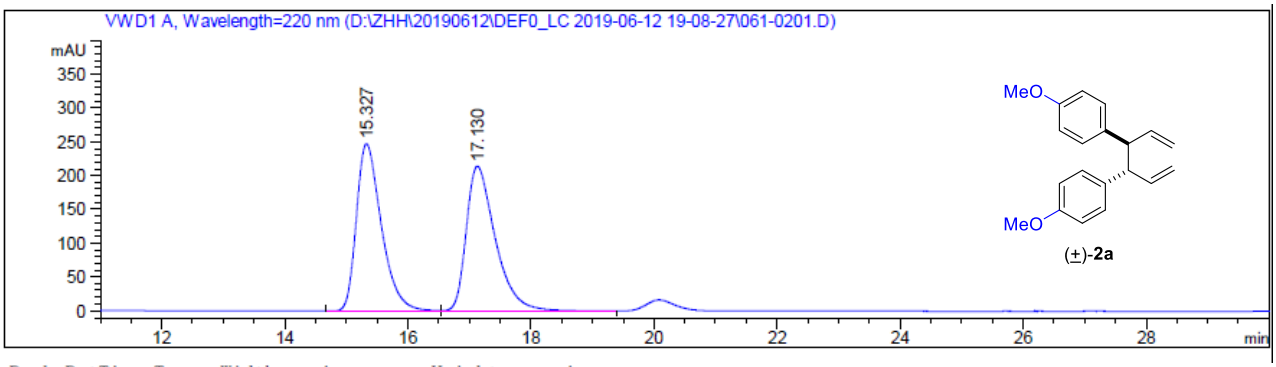


2a

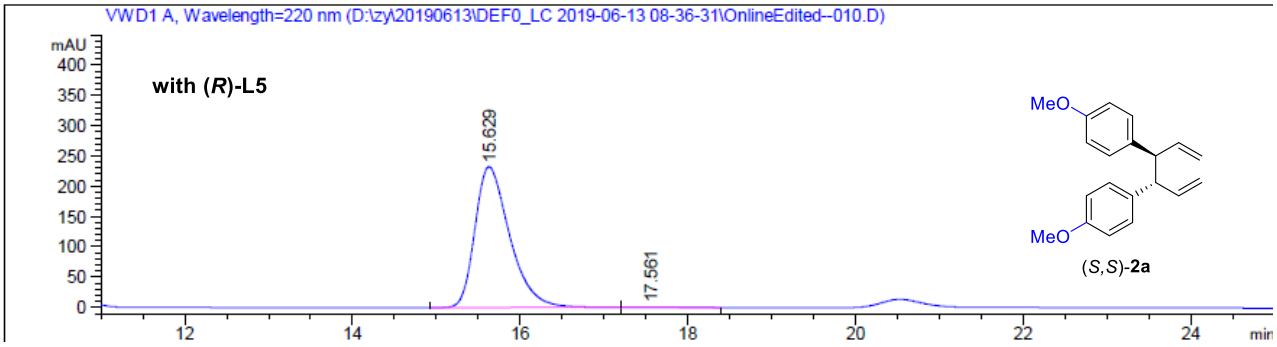
4,4'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis(methoxybenzene) (2a): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50;1; Reaction time = 12 h; yield: 92% (27.1 mg); > 95:5 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -57.5 (c 3.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.02 – 6.86 (m, 2H), 6.78 – 6.63 (m, 2H), 6.23 – 5.87 (m, 1H), 5.07 (dd, *J* = 10.2, 1.7 Hz, 1H), 5.04 – 4.96 (m, 1H), 3.55 (dd, *J* = 5.8, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 141.0, 134.8, 129.1, 115.3, 113.5, 55.1, 54.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}O_2$ 295.1693; Found 295.1683; According to ***General Procedure C'*:** **3aa** 90% GC yield, > 99% *ee*, > 95:5 *dr*, > 95:5 *rr.*

Analysis of Stereochemistry:

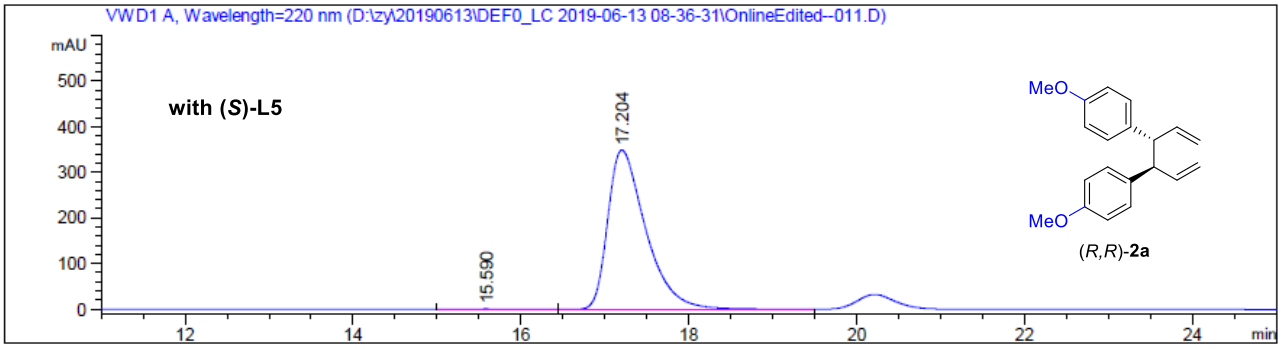
Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OJ, hexane/ethanol = 99/1, flow rate 0.8 mL/min, T = 25 °C, 220 nm): t_R = 15.63 min (major), t_R = 17.56 min (minor). (±)-**2a**: According to ***General Procedure B.***



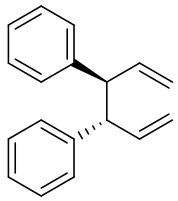
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.327	BV	0.4226	6988.11719	247.38661	49.8806
2	17.130	VB	0.4966	7021.57715	214.11304	50.1194



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.629	BB	0.4400	6689.62891	232.29607	99.8533
2	17.561	BB	0.3559	9.82925	3.31554e-1	0.1467



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.590	BB	0.4054	23.93753	8.68991e-1	0.2172
2	17.204	BV	0.4755	1.09962e4	349.10562	99.7828

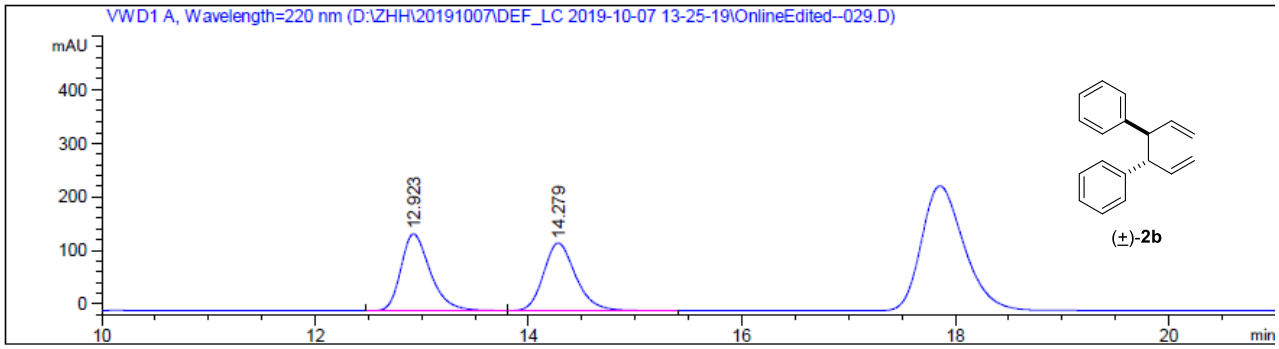


2b

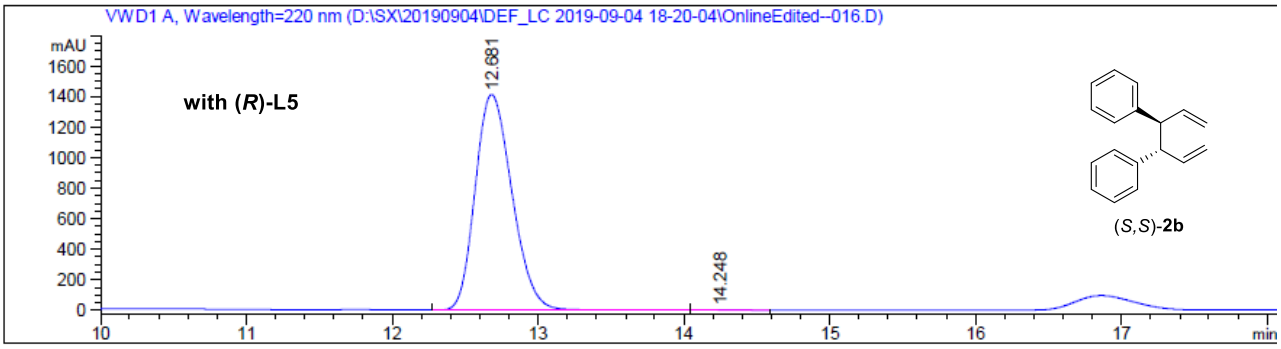
((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)dibenzene (2b)[2]: According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100;0 to 100:1; Reaction time = 12 h; yield: 84% (19.7 mg); 93:7 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -50.1 (c 0.33, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.10 (m, 4H), 7.10 – 6.98 (m, 6H), 6.19 – 6.02 (m, 2H), 5.10 (dd, *J* = 10.2, 1.7 Hz, 2H), 5.04 (dd, *J* = 17.0, 1.6 Hz, 2H), 3.67 – 3.60 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 140.6, 140.1, 128.2, 128.1, 126.0, 115.8, 55.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}$ 235.1481; Found 235.1489.

Analysis of Stereochemistry:

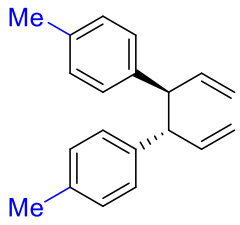
Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OJ, hexane/ethanol = 99/1, flow rate 0.5 mL/min, T = 25 °C, 220 nm): t_R = 12.68 min (major), t_R = 14.25 min (minor). (±)-**2b**: According to ***General Procedure A.***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.923	BB	0.2835	2718.28345	142.86575	50.8665
2	14.279	BB	0.3202	2625.67163	125.96497	49.1335



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.681	BV R	0.2671	2.47525e4	1411.69666	99.8869
2	14.248	BB	0.1980	28.01520	1.87873	0.1131

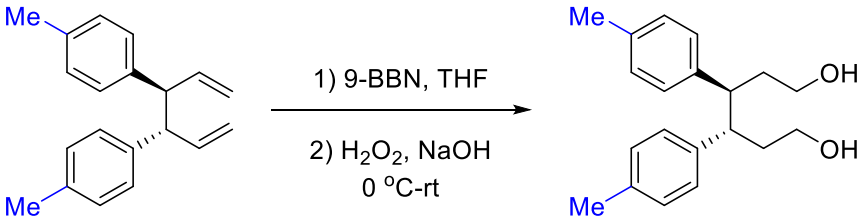


2c

4,4'-((3S,4S)-hexa-1,5-diene-3,4-diyl)bis(methylbenzene) (2c): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 94% (24.6 mg); 94:6 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -38.6 (c 1.04, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.06 – 6.88 (m, 8H), 6.06 (dddd, *J* = 16.9, 10.2, 5.9, 2.4 Hz, 2H), 5.06 (dd, *J* = 10.2, 1.7 Hz, 2H), 5.01 (dd, *J* = 17.0, 1.7 Hz, 2H), 3.61 (dd, *J* = 5.9, 2.4 Hz, 2H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 139.7, 135.4, 128.9, 128.0, 115.4, 55.2, 21.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}$ 263.1794; Found 263.1786.

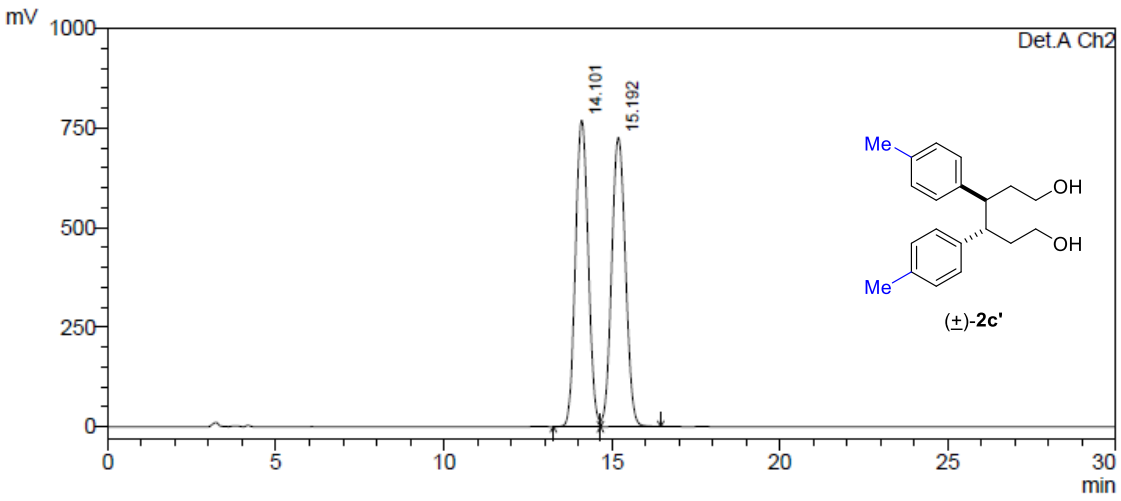
Analysis of Stereochemistry:

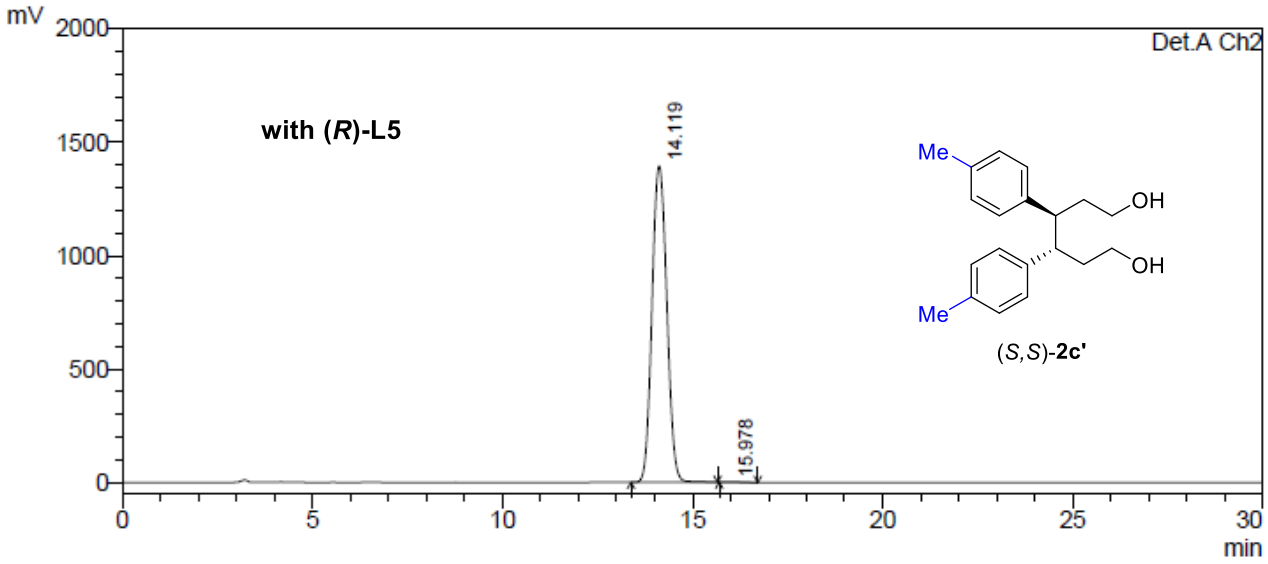
The title compound and the analogous racemic material were subjected to hydroboration and oxidation for HPLC analysis as shown below.



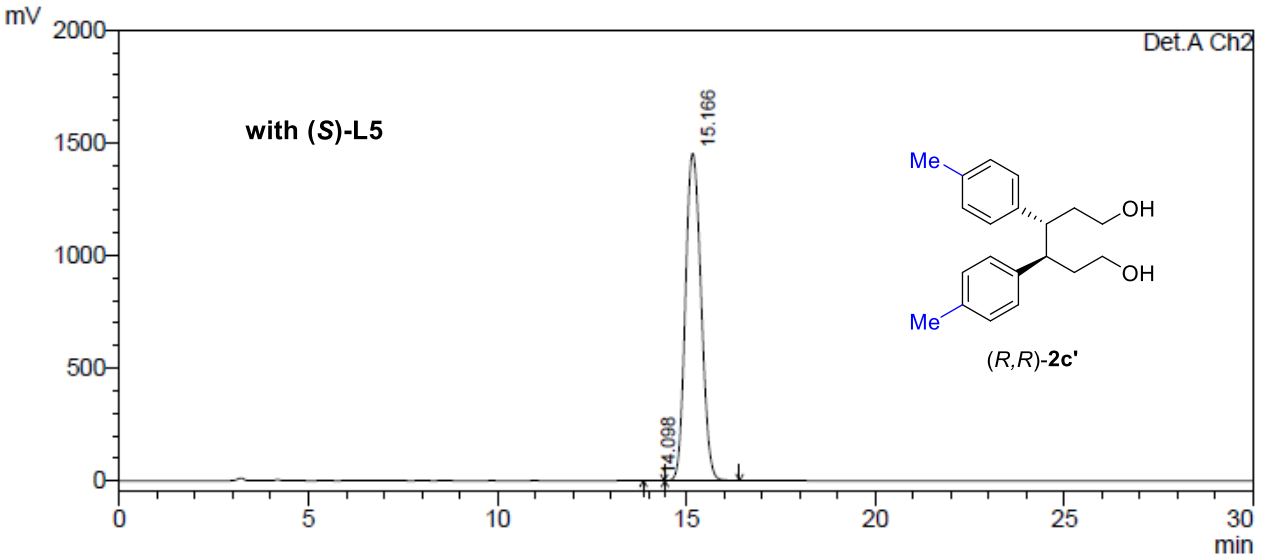
2c **2c'**

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 14.12 min (major), t_R = 15.98 min (minor).

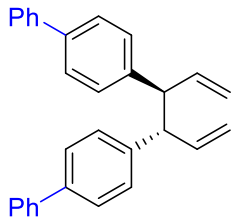




Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.117	37825337	1395638	99.934	99.924
2	15.975	25102	1062	0.066	0.076
Total		37850440	1396700	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.109	16645	940	0.040	0.065
2	15.164	41749185	1452376	99.960	99.935
Total		41765830	1453316	100.000	100.000

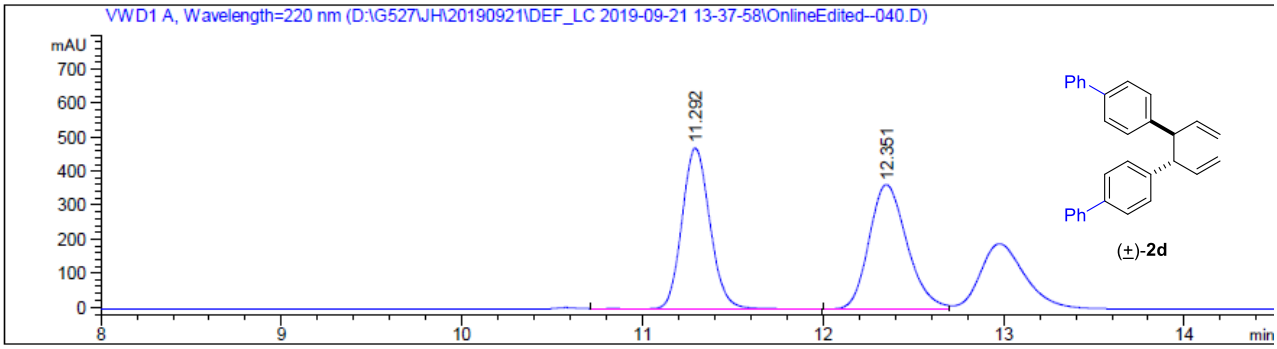


2d

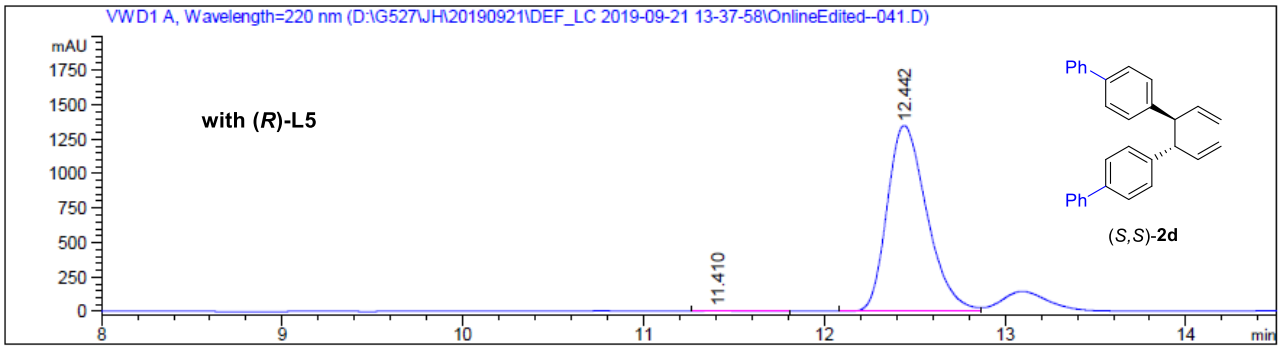
4,4''-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)di-1,1'-biphenyl (2d): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100;0 to 100:1; Reaction time = 12 h; yield: 90% (34.7 mg); 91:9 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -22.7 (c 0.79, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 4H), 7.45 – 7.35 (m, 8H), 7.33 – 7.27 (m, 2H), 7.18 – 7.12 (m, 4H), 6.22 – 6.10 (m, 2H), 5.17 – 5.06 (m, 4H), 3.73 (dd, *J* = 5.9, 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 140.8, 140.4, 138.8, 128.6, 128.6, 127.0, 126.9, 126.9, 116.0, 55.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{27}$ 387.2108; Found 387.2116.

Analysis of Stereochemistry:

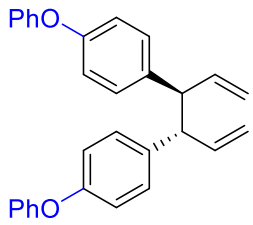
Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak AD-H, hexane/ethanol = 99/1, flow rate 0.5 mL/min, T = 25 °C, 220 nm): t_R = 12.44 min (major), t_R = 11.41 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.292	FM	0.1799	5110.66699	473.36166	49.0147
2	12.351	MF	0.2424	5316.14160	365.51367	50.9853



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.410	VB	0.1610	61.28799	5.81344	0.2957
2	12.442	MF	0.2550	2.06648e4	1350.90527	99.7043

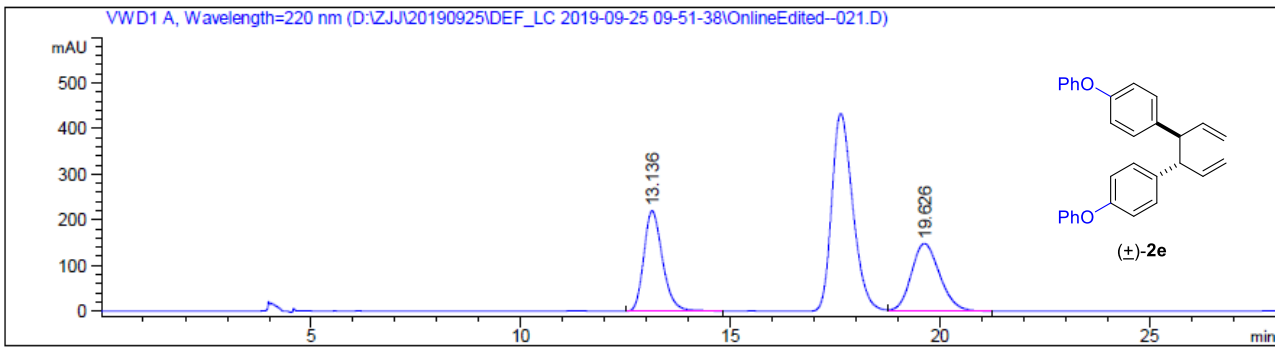


2e

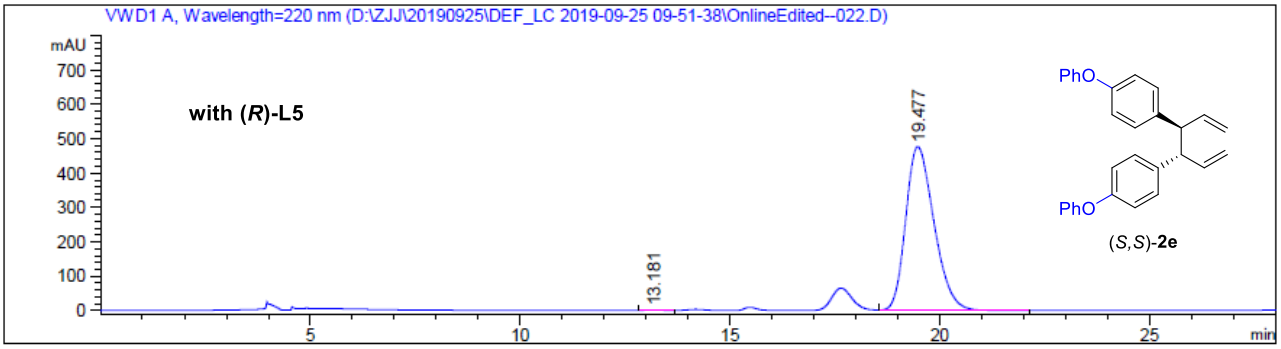
4,4'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis(phenoxybenzene) (2e): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100;1 to 50:1; Reaction time = 12 h; yield: 92% (38.5 mg); 93:7 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -24.3 (c 0.76, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 4H), 7.10 – 7.04 (m, 2H), 7.03 – 6.94 (m, 5H), 6.94 – 6.89 (m, 3H), 6.87 – 6.80 (m, 4H), 6.19 – 6.05 (m, 2H), 5.14 (dd, *J* = 10.2, 1.6 Hz, 2H), 5.11 – 5.05 (m, 2H), 3.58 (dd, *J* = 5.7, 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 155.1, 140.3, 137.7, 129.6, 129.5, 122.9, 118.9, 118.4, 116.0, 55.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{27}O_2$ requires m/z 419.2006, found m/z 419.1998.

Analysis of Stereochemistry:

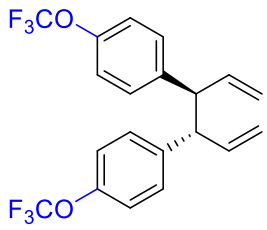
Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OJ, hexane/ethanol = 95/5, flow rate 0.5 mL/min, T = 25 °C, 220 nm): t_R = 19.48 min (major), t_R = 13.18 min (minor). (±)-**2e**: According to ***General Procedure A.***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.136	BB	0.4785	6832.14551	219.89113	49.4249
2	19.626	VB	0.7187	6991.14258	148.38348	50.5751



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.181	FM	0.5494	56.17147	1.70406	0.2498
2	19.477	VB	0.7285	2.24293e4	477.06625	99.7502

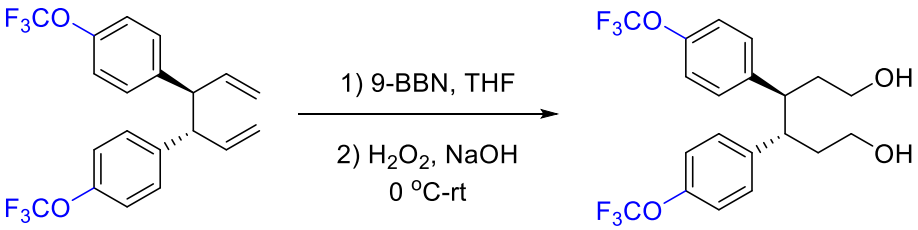


2f

4,4'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis((trifluoromethoxy)benzene) (2f): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100;0 to 100:1; Reaction time = 12 h; yield: 56% (22.5 mg); 92:8 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -11.6 (c 0.55, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.05 – 6.91 (m, 8H), 6.13 – 6.00 (m, 2H), 5.15 (dd, *J* = 10.2, 1.4 Hz, 2H), 5.08 – 5.01 (m, 2H), 3.59 (dd, *J* = 5.7, 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 140.9, 139.4, 129.3, 120.7, 120.40 (q, *J* = 256.9 Hz), 116.8, 55.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}F_6O_2$ requires m/z 403.1127, found m/z 403.1136.

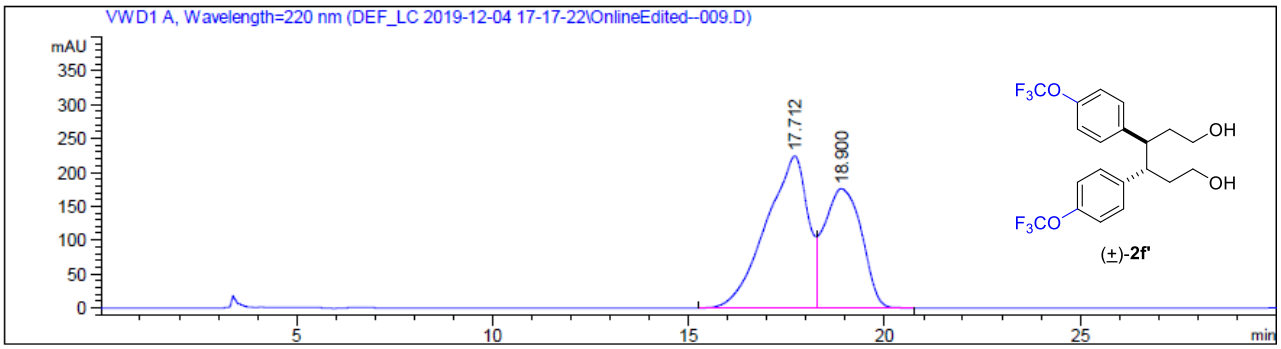
Analysis of Stereochemistry:

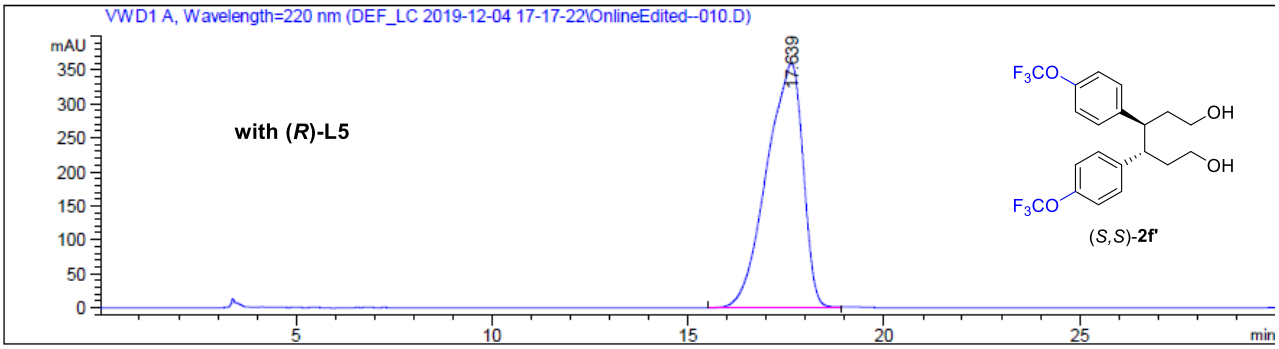
The title compound and the analogous racemic material were subjected to hydroboration and oxidation for HPLC analysis as shown below.



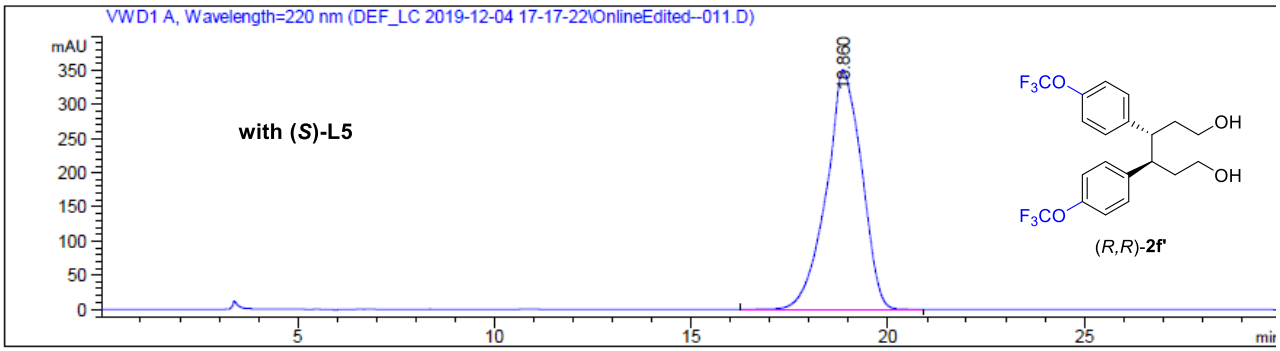
2f **2f'**

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak IC, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 17.64 min (major).

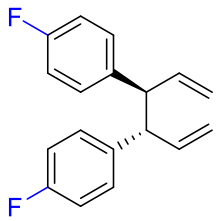




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.639	MF	1.0699	2.31129e4	360.05136	100.0000



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.860	BB	0.9620	2.19388e4	350.61435	100.0000

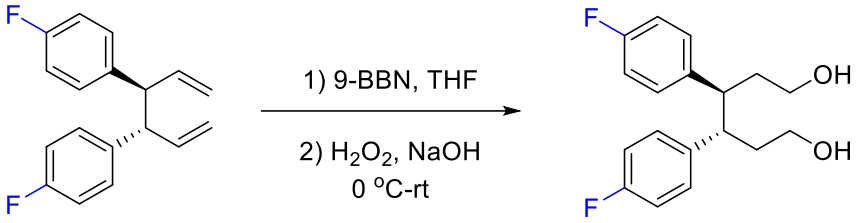


2g

4,4'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis(fluorobenzene) (2g): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100;0 to 100:1; Reaction time = 12 h; yield: 86% (23.3 mg); 90:10 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -23.8 (c 0.61, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.97 – 6.90 (m, 4H), 6.89 – 6.78 (m, 4H), 6.05 (dddd, *J* = 17.0, 10.2, 5.6, 2.4 Hz, 2H), 5.10 (dd, *J* = 10.2, 1.5 Hz, 2H), 5.01 (dd, *J* = 17.1, 1.5 Hz, 2H), 3.55 (dd, *J* = 5.7, 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, *J* = 244.2 Hz), 140.1, 138.0 (d, *J* = 3.3 Hz), 129.5 (d, *J* = 7.7 Hz), 116.2, 115.1(d, *J* = 21.3 Hz), 55.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}F_2$ requires m/z 271.1293, found m/z 271.1296.

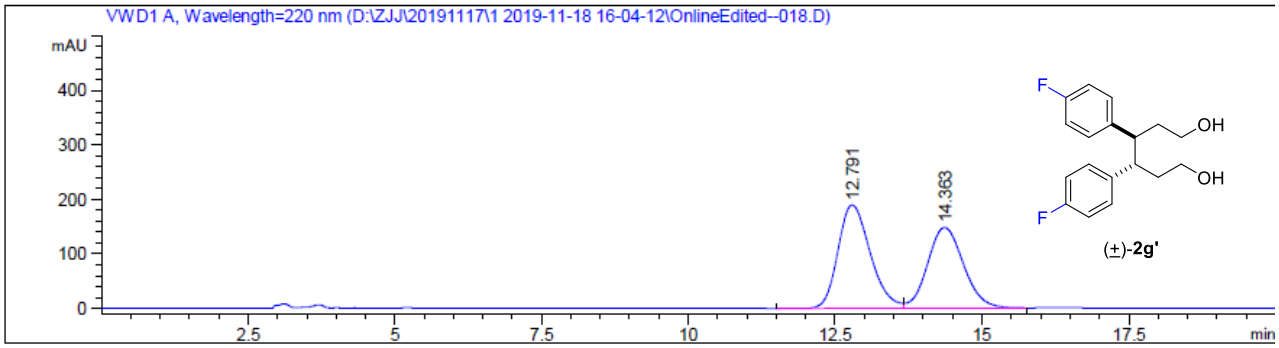
Analysis of Stereochemistry:

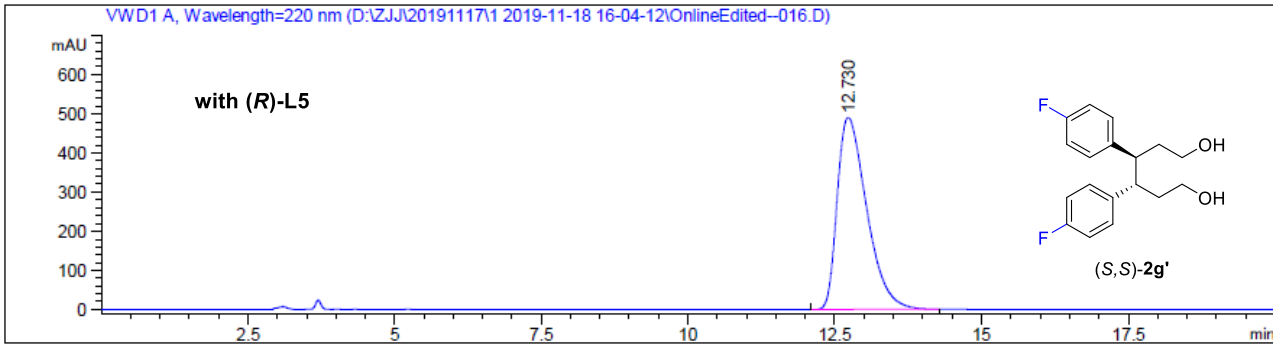
The title compound and the analogous racemic material were subjected to hydroboration and oxidation for HPLC analysis as shown below.



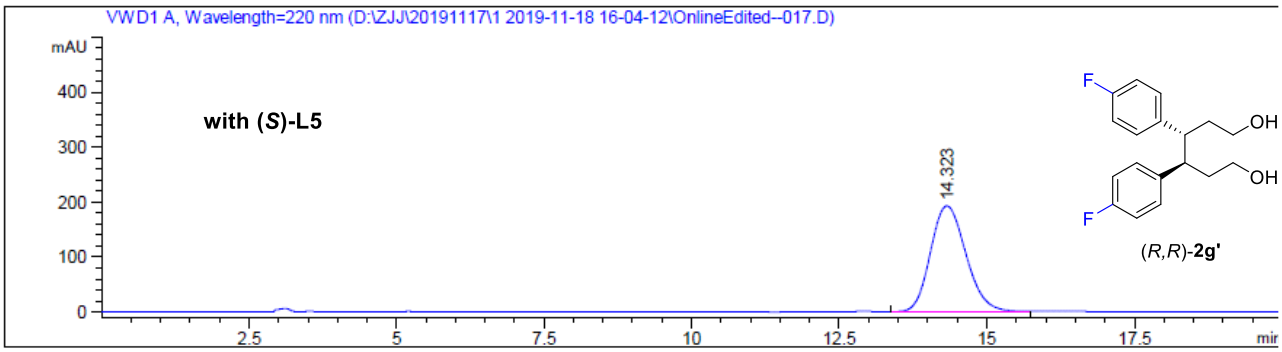
2g **2g'**

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OD, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 12.73 min (major).

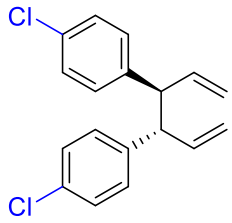




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.730	BB	0.5400	1.71054e4	490.29880	100.0000



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.323	VB	0.6473	8089.26904	192.87172	100.0000

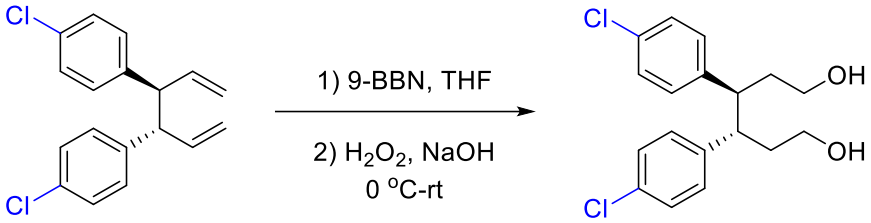


2h

4,4'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis(chlorobenzene) (2h): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100;0 to 100:1; Reaction time = 12 h; yield: 61% (18.5 mg); 92:8 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -17.4 (c 0.53, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.09 (m, 4H), 6.96 – 6.91 (m, 4H), 6.11 – 5.94 (m, 2H), 5.11 (dd, *J* = 10.2, 1.5 Hz, 2H), 5.05 – 4.99 (m, 2H), 3.58 – 3.55 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 139.7, 131.9, 129.5, 128.4, 116.5, 116.5, 55.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}Cl_2$ requires m/z 303.0703, found m/z 303.0709.

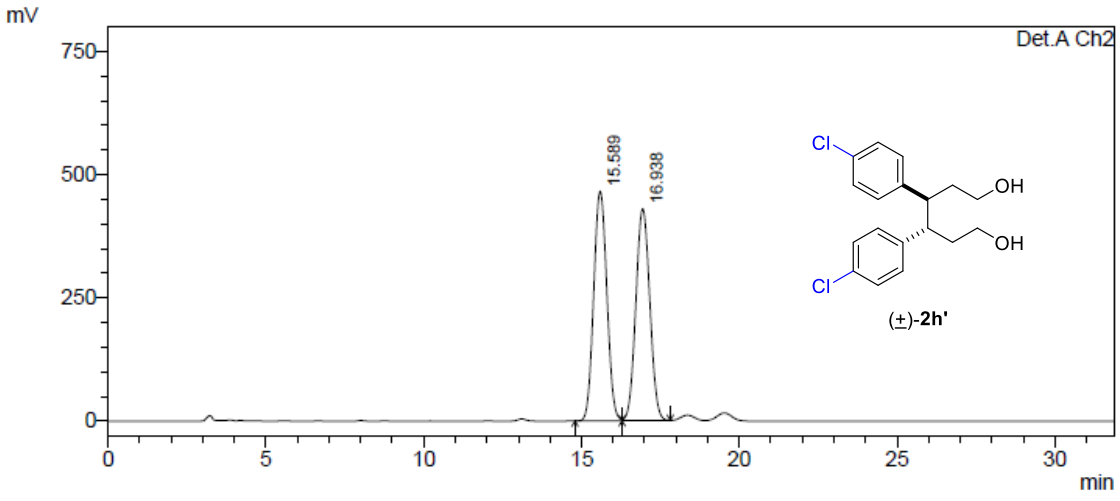
Analysis of Stereochemistry:

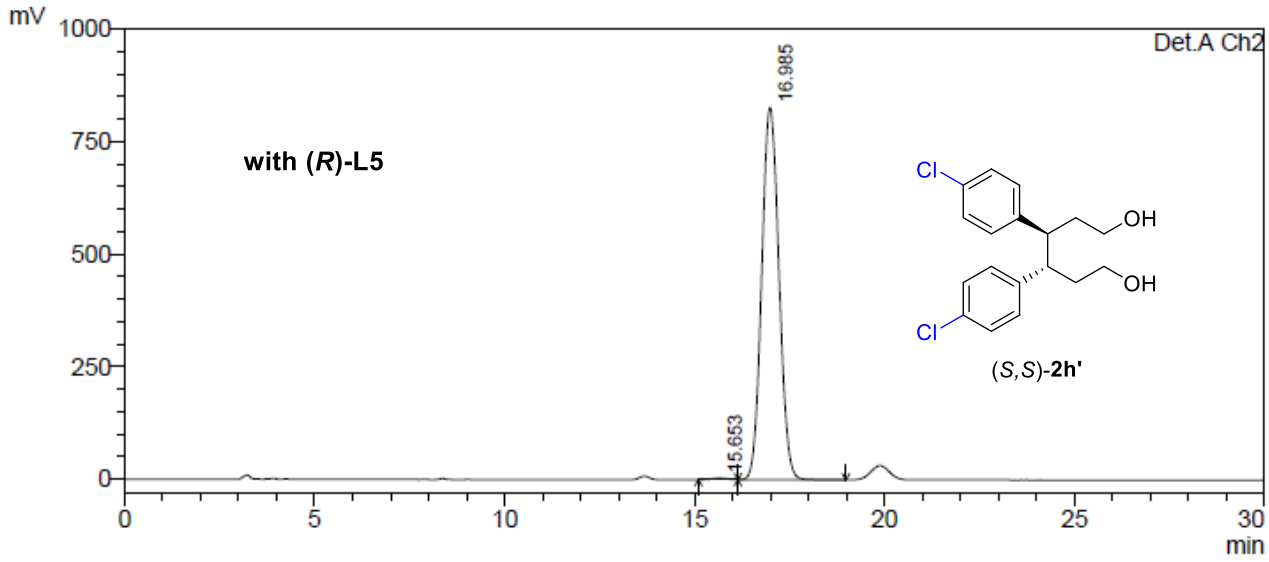
The title compound and the analogous racemic material were subjected to hydroboration and oxidation for HPLC analysis as shown below.



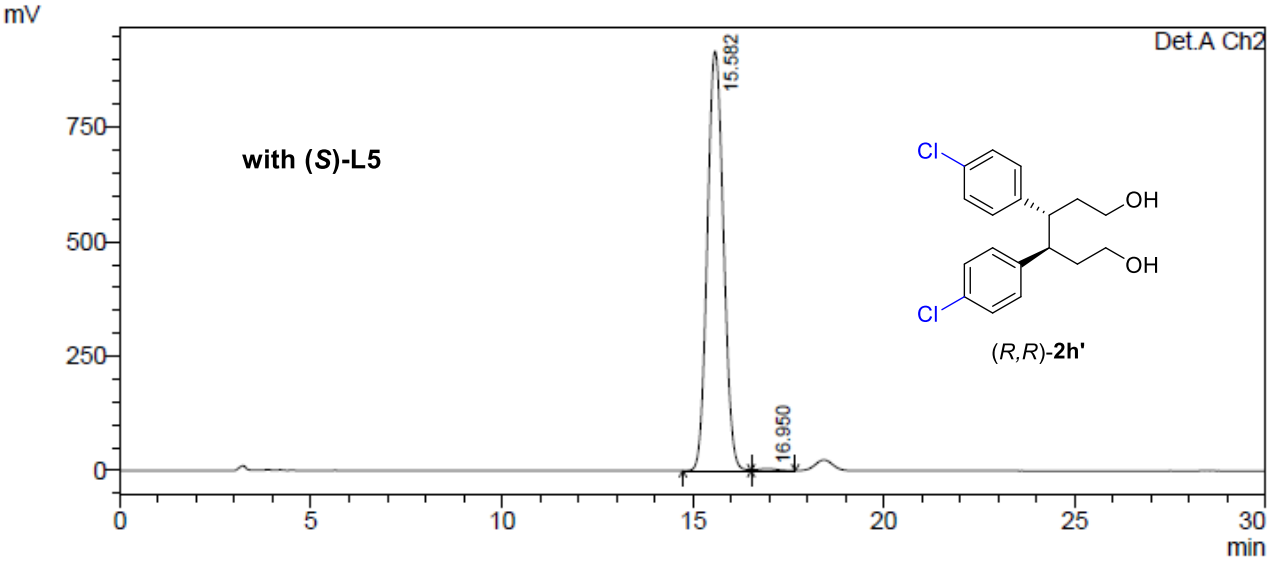
2h **2h'**

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 16.98 min (major), t_R = 15.65 min (minor).

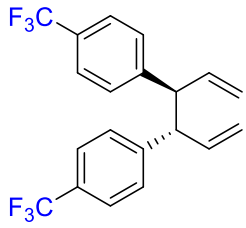




Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.649	95366	3318	0.364	0.400
2	16.983	26070991	826793	99.636	99.600
Total		26166357	830111	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.580	26978623	916538	99.480	99.537
2	16.945	140942	4267	0.520	0.463
Total		27119565	920804	100.000	100.000

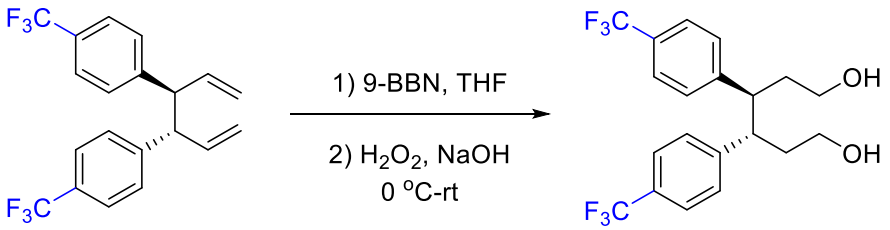


2i

4,4'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis((trifluoromethyl)benzene) (2i): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 58% (21.5 mg); 88:12 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -13.7 (c 0.45, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.38 (m, 4H), 7.21 – 7.08 (m, 4H), 6.15 – 5.96 (m, 2H), 5.16 (dd, *J* = 10.2, 1.3 Hz, 2H), 5.09 – 5.01 (m, 2H), 3.74 – 3.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 139.0, 128.4, 125.3 (q, *J* = 3.8 Hz), 117.2, 55.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5; HRMS (ESI) m/z: [M+H]+ Calcd for $C_{20}H_{17}F_6$ requires m/z 371.1230, found m/z 371.1227.

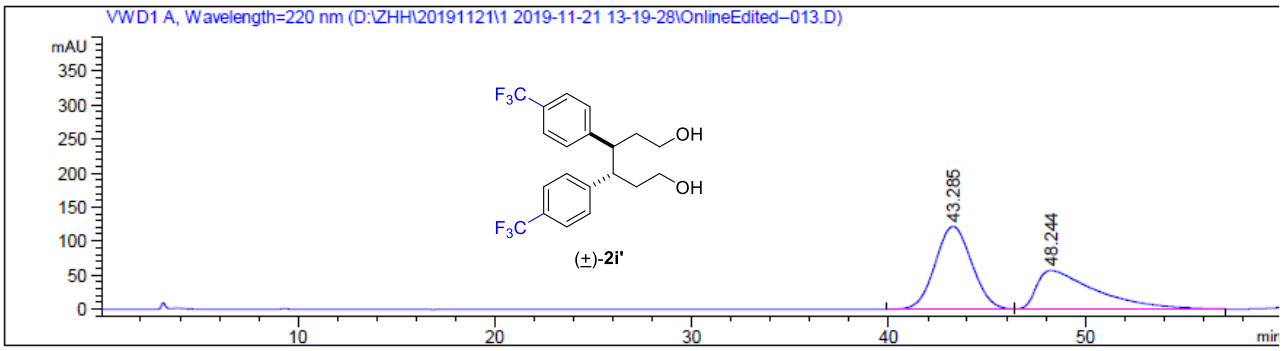
Analysis of Stereochemistry:

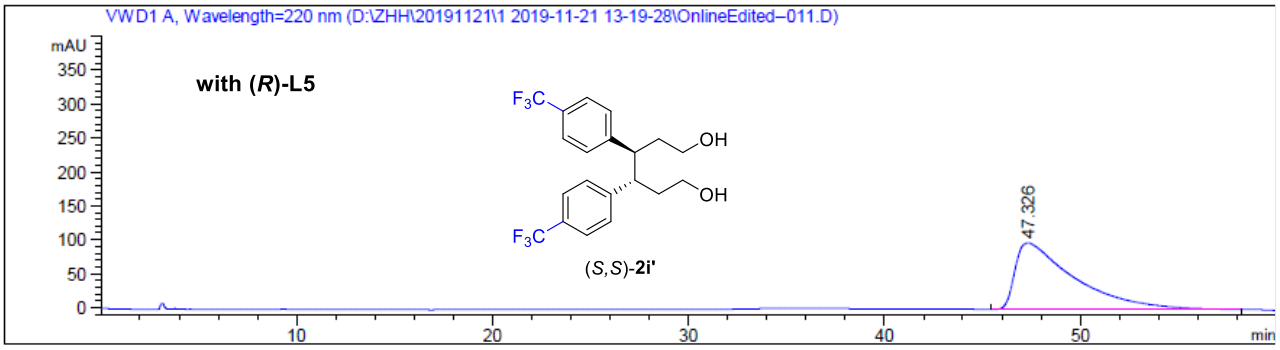
The title compound and the analogous racemic material were subjected to hydroboration and oxidation for HPLC analysis as shown below.



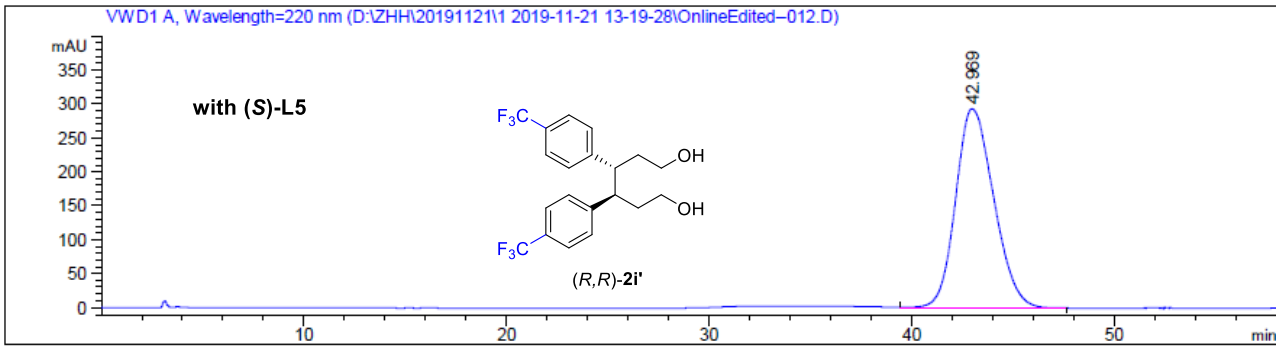
2i **2i'**

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OD, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 47.33 min (major).

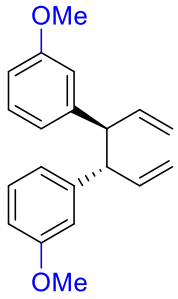




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	47.326	BB	2.7338	2.06165e4	98.18362	100.0000



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.969	VB	1.9329	3.85653e4	293.52069	100.0000

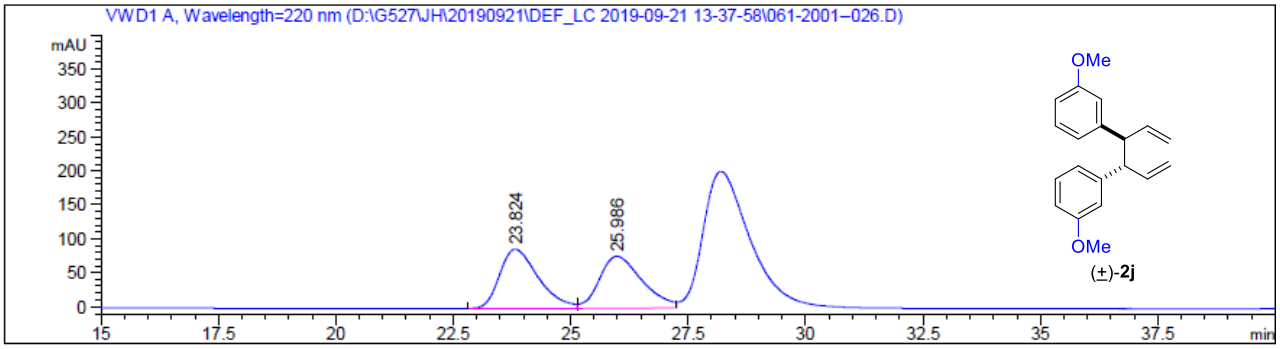


2j

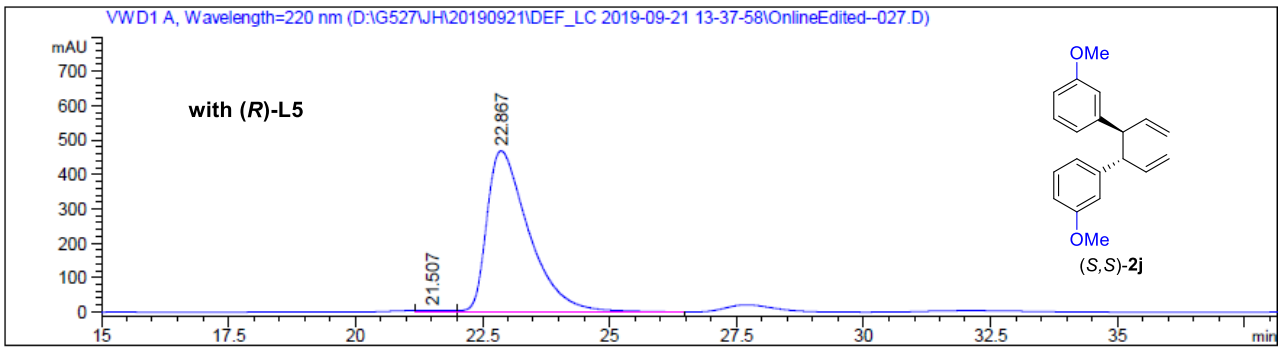
3,3'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis(methoxybenzene) (2j): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50:1; Reaction time = 12 h; yield: 90% (26.5 mg); > 95:5 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -10.0 (c 0.56, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.04 (m, 2H), 6.72 – 6.52 (m, 6H), 6.15 – 6.01 (m, 2H), 5.09 (dd, *J* = 10.2, 1.7 Hz, 2H), 5.05 (dd, *J* = 17.0, 1.6 Hz, 2H), 3.70 (s, 6H), 3.59 (dd, *J* = 5.8, 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 144.2, 140.3, 129.1, 120.6, 115.9, 114.1, 111.3, 55.7, 55.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}O_2$ requires m/z 295.1693, found m/z 295.1697.

Analysis of Stereochemistry:

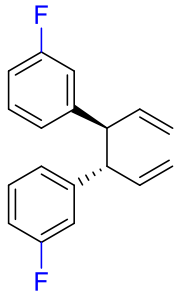
Enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak OJ, hexane/isopropanol = 99/1, flow rate 0.5 mL/min, T = 25 ^oC, 220 nm): t_R = 22.89 min (major), t_R = 21.15 min (minor). (±)-**2j**: According to ***General Procedure A.***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.824	BV	0.8279	4970.89307	87.09435	50.6502
2	25.986	VV	0.9008	4843.27881	76.37617	49.3498



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.507	FM	0.8070	274.28778	5.66490	1.0017
2	22.867	VB	0.8312	2.71067e4	469.08252	98.9983

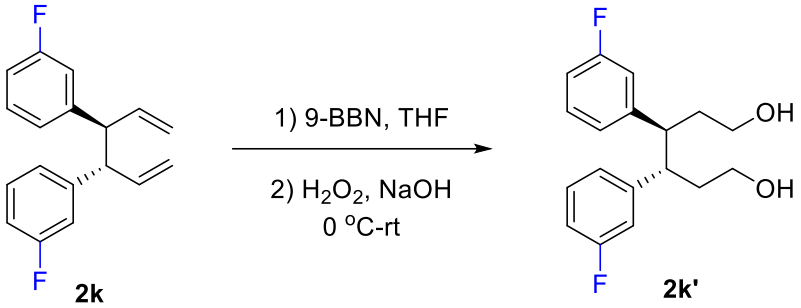


2k

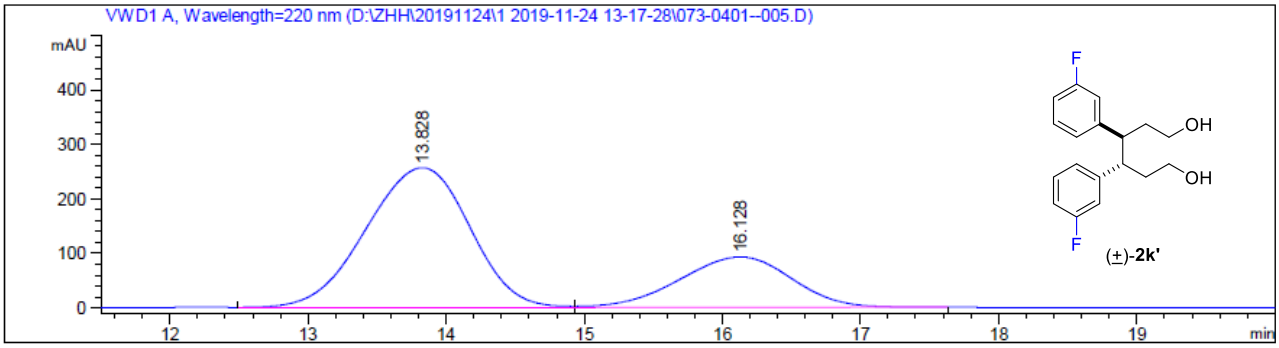
3,3'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis(fluorobenzene) (2k): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 66% (17.9 mg); 89:11 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -22.8 (c 0.54, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.06 (m, 2H), 6.86 – 6.68 (m, 6H), 6.12 – 5.95 (m, 2H), 5.13 (dd, *J* = 10.2, 1.5 Hz, 2H), 5.08 – 5.02 (m, 2H), 3.61 – 3.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, *J* = 245.3 Hz), 144.8 (d, *J* = 7.1 Hz), 139.4, 129.6 (d, *J* = 8.4 Hz), 123.8 (d, *J* = 2.7 Hz), 116.7, 114.9 (d, *J* = 21.5 Hz), 113.1 (d, *J* = 20.9 Hz), 55.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}F_2$ requires m/z 271.1294, found m/z 271.1299.

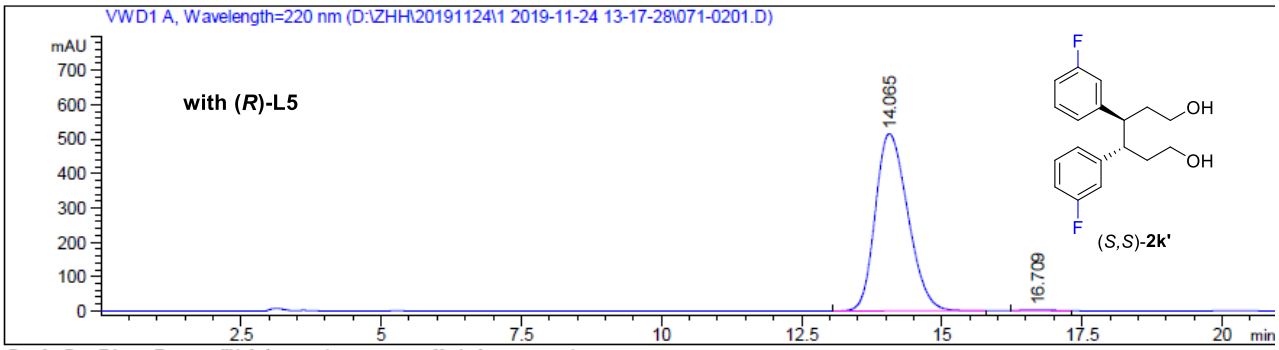
Analysis of Stereochemistry:

The title compound and the analogous racemic material were subjected to hydroboration and oxidation for HPLC analysis as shown below.

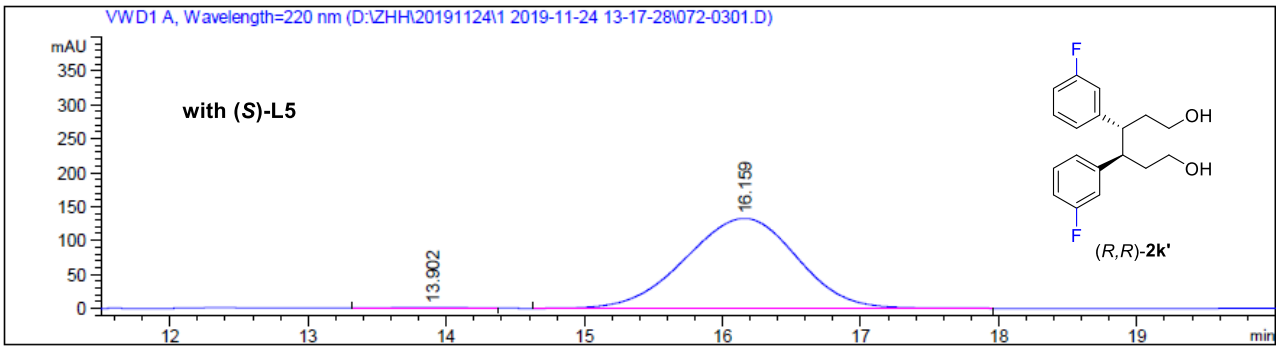


Enantiomeric excess: 99%, determined by HPLC (Daicel Chiralpak OD, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 14.06 min (major), t_R = 16.71 min (minor).

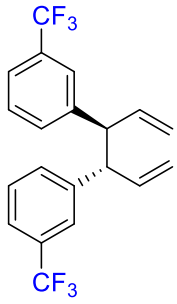




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.065	BB	0.6359	2.07868e4	515.01538	99.4873
2	16.709	FM	0.6787	107.13025	2.63059	0.5127



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.902	MF	0.7480	59.04575	1.31556	0.7836
2	16.159	VB	0.8895	7476.53369	132.66614	99.2164

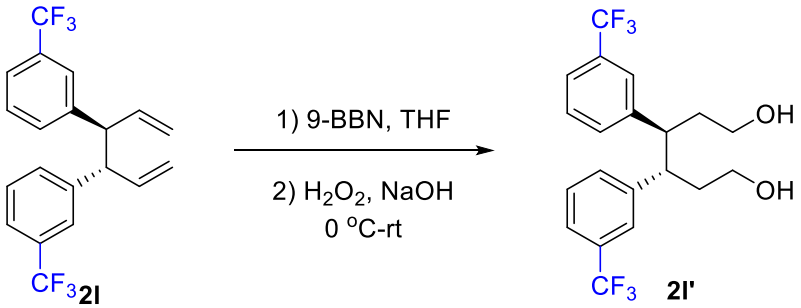


2l

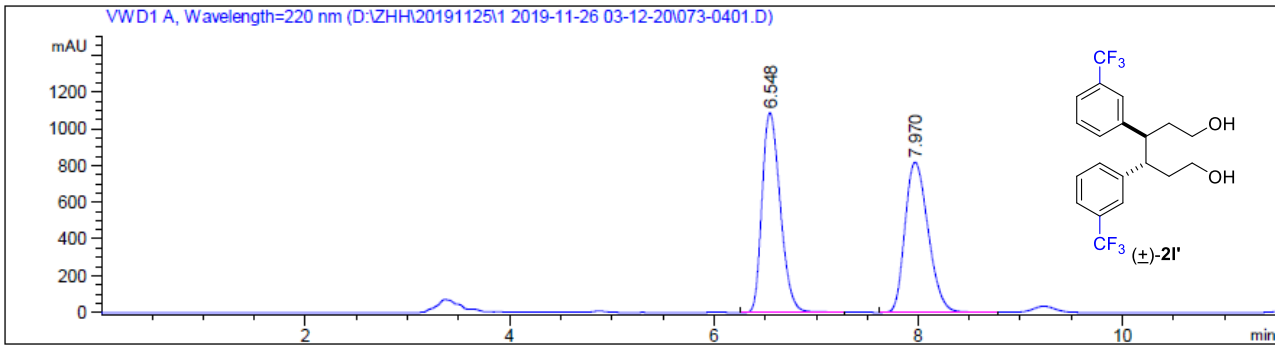
3,3'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis((trifluoromethyl)benzene) (2l): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 45% (16.7 mg); 85:15 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -12.0 (c 0.36, $CHCl_3$); ^{11}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.28 – 7.23 (m, 2H), 7.22 – 7.19 (m, 2H), 7.19 – 7.11 (m, 2H), 6.18 – 6.02 (m, 2H), 5.19 (dd, *J* = 10.1, 1.2 Hz, 2H), 5.08 (dd, *J* = 17.0, 1.2 Hz, 2H), 3.67 (dd, *J* = 5.6, 2.3 Hz, 2H); ^{113}C NMR (100 MHz, $CDCl_3$) δ 142.9, 138.8, 131.5, 128.7, 124.9 (q, *J* = 3.4 Hz), 1231 (q, *J* = 3.5 Hz), 117.3, 55.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}F_6$ requires m/z 371.1230, found m/z 371.1235.

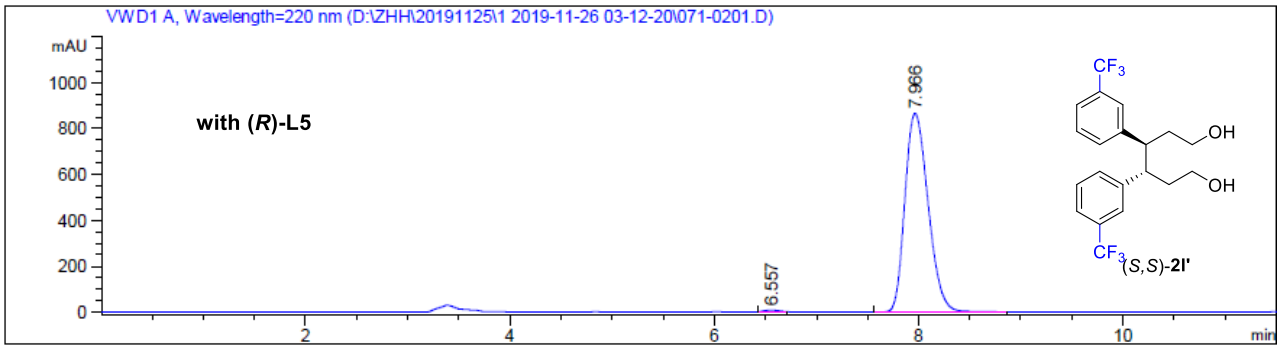
Analysis of Stereochemistry:

The title compound and the analogous racemic material were subjected to hydroboration and oxidation for HPLC analysis as shown below.

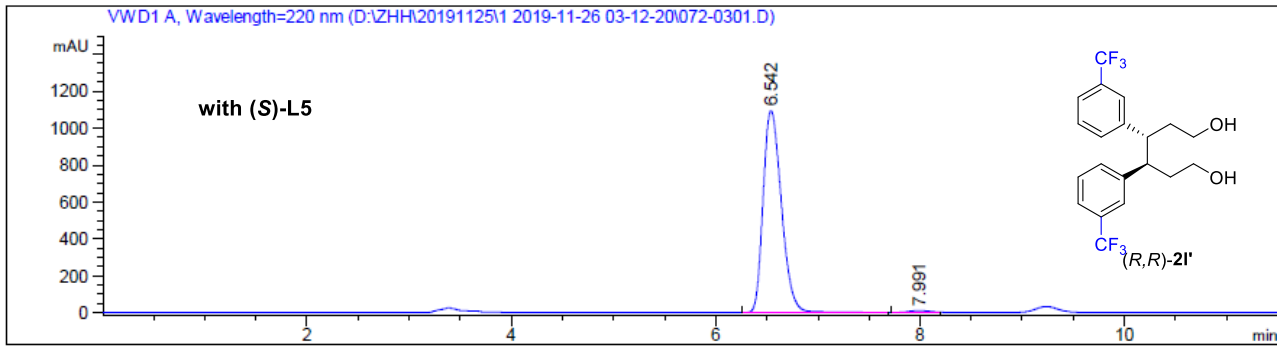


Enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak IC, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 7.97 min (major), t_R = 6.56 min (minor).

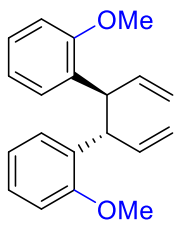




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.557	FM	0.1772	103.94921	9.77579	0.7558
2	7.966	VB	0.2481	1.36494e4	864.92529	99.2442



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.542	BB	0.1936	1.36738e4	1095.48132	98.7481
2	7.991	MF	0.2416	173.35802	11.95724	1.2519

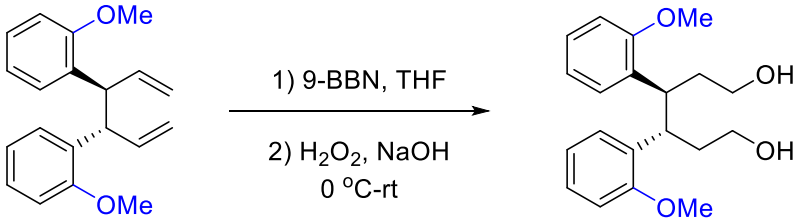


2m

2,2'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis(methoxybenzene) (2m): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50:1; Reaction time = 12 h; yield: 95% (27.9 mg); > 95:5 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -124.8 (c 1.88, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.08 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.01 – 6.95 (m, 2H), 6.75 – 6.69 (m, 2H), 6.64 (dd, *J* = 8.2, 1.1 Hz, 2H), 6.19 – 6.05 (m, 2H), 5.05 – 5.03 (m, 2H), 5.02 – 4.98 (m, 2H), 4.24 (dd, *J* = 5.4, 2.5 Hz, 2H), 3.71 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 141.0, 131.3, 128.7, 126.7, 120.1, 115.1, 110.5, 55.4, 47.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}O_2$ requires m/z 295.1693, found m/z 295.1680.

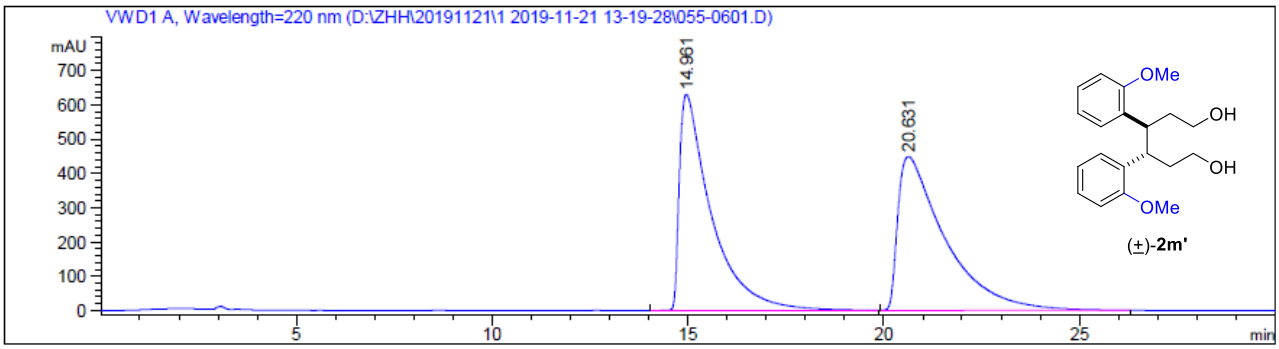
Analysis of Stereochemistry:

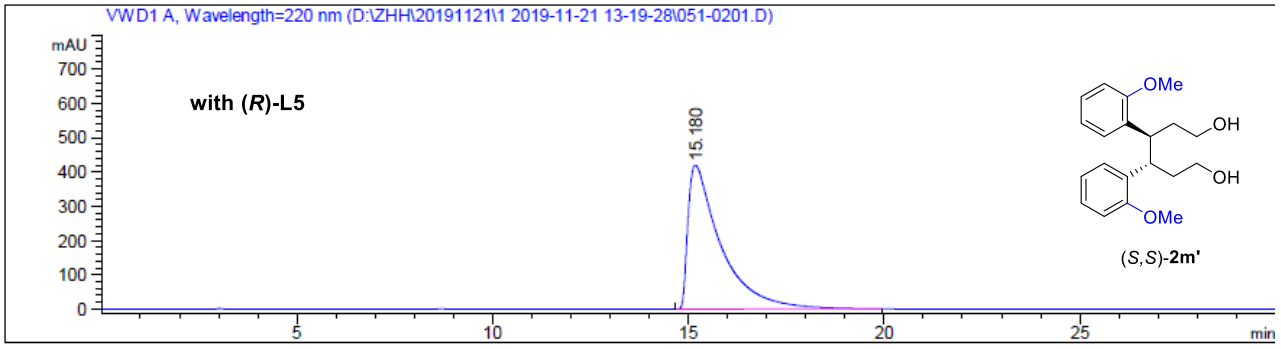
The title compound and the analogous racemic material were subjected to hydroboration and oxidation for HPLC analysis as shown below.



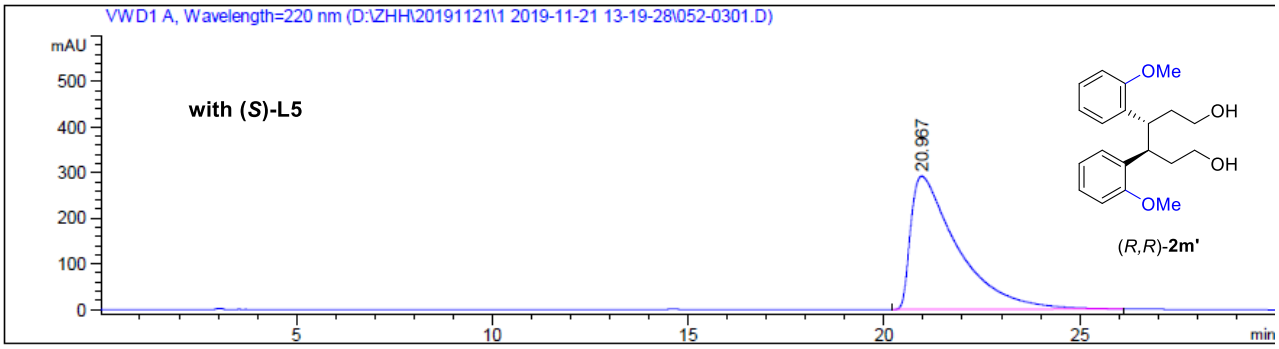
2m **2m'**

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OD, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 15.18 min (major).

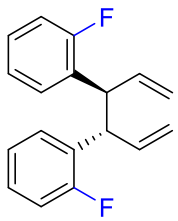




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.180	BB	0.8189	2.45954e4	420.21155	100.0000



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.967	BB	1.1607	2.43199e4	292.28589	100.0000

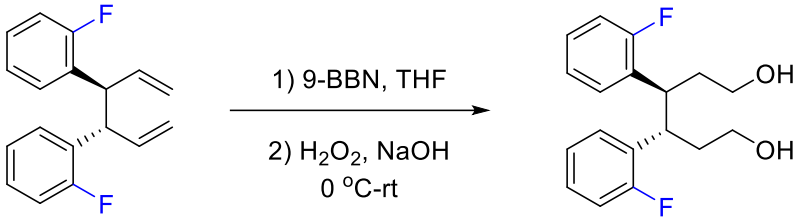


2n

2,2'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis(fluorobenzene) (2n): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 91% (24.6 mg); 94:6 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -21.0 (c 0.34, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 – 7.09 (m, 2H), 7.02 (dddd, *J* = 8.2, 7.1, 5.2, 1.8 Hz, 2H), 6.97 – 6.89 (m, 2H), 6.88 – 6.79 (m, 2H), 6.18 – 6.03 (m, 2H), 5.15 – 5.05 (m, 4H), 4.06 (dd, *J* = 5.5, 2.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4 (d, *J* = 244.8 Hz), 139.1, 129.4 (d, *J* = 5.1 Hz), 127.7 (d, *J* = 8.5 Hz), 123.8 (d, *J* = 3.2 Hz), 116.6, 115.2 (d, *J* = 23.3 Hz), 47.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}F_2$ requires m/z 271.1294, found m/z 271.1300.

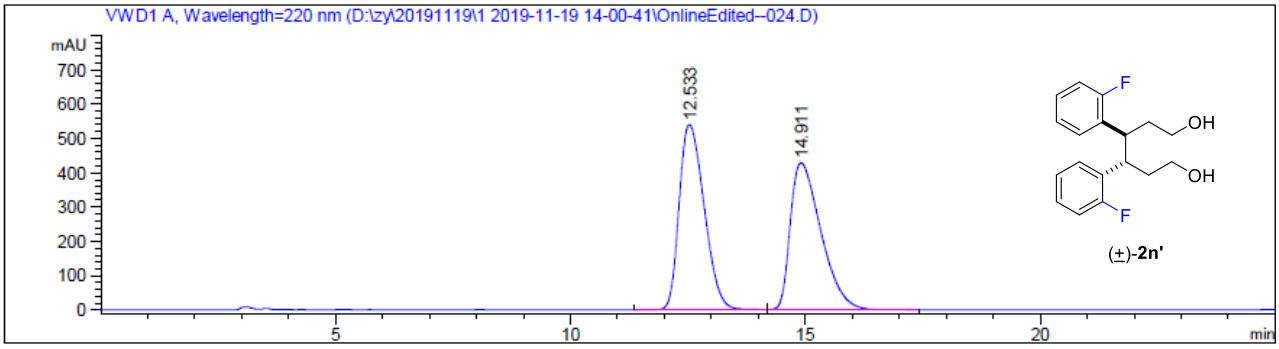
Analysis of Stereochemistry:

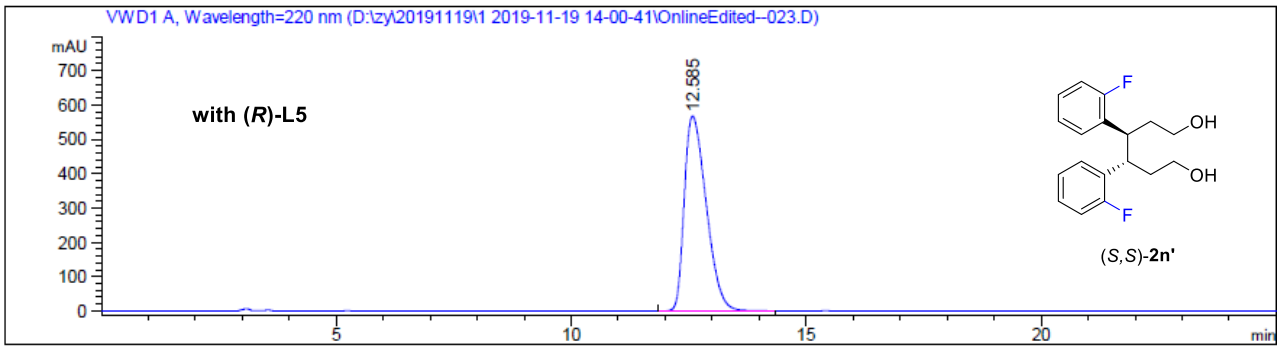
The title compound and the analogous racemic material were subjected to hydroboration and oxidation for HPLC analysis as shown below.



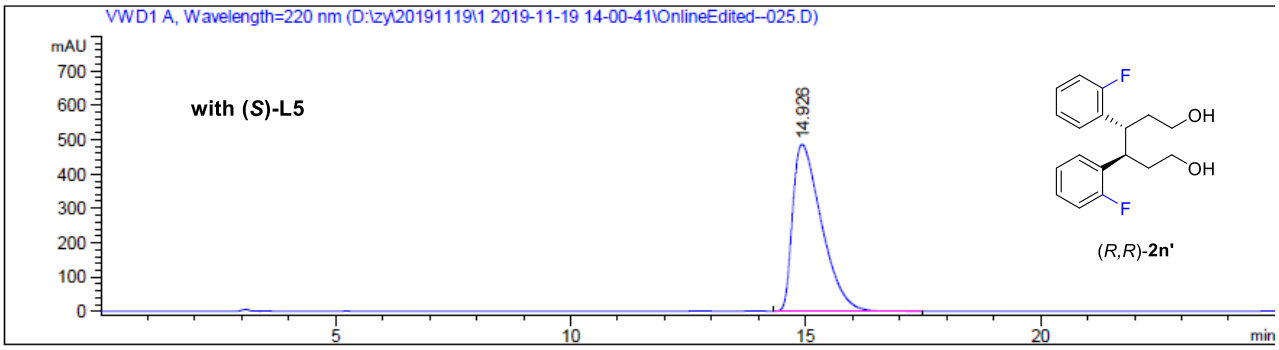
2n **2n'**

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OD, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 12.58 min (major).

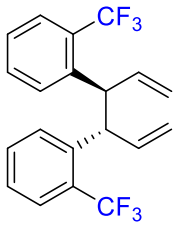




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.585	BB	0.5011	1.84465e4	567.66852	100.0000



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.926	VB	0.6432	2.08346e4	485.99048	100.0000

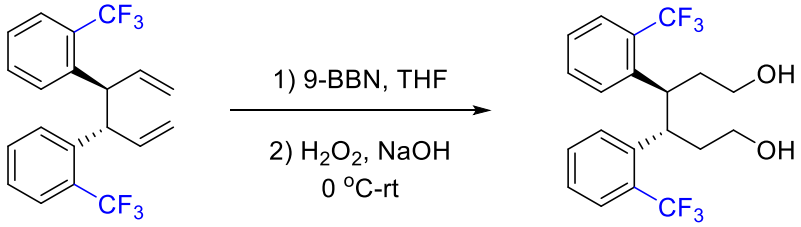


2o

2,2'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis((trifluoromethyl)benzene) (2o): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 60% (22.2 mg); > 95:5 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -53.6 (c 0.42, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.0, 1.3 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.29 (m, 2H), 7.17 – 7.07 (m, 2H), 6.11 – 5.94 (m, 2H), 5.14 (dd, *J* = 10.2, 1.2 Hz, 2H), 4.99 (d, *J* = 17.1 Hz, 2H), 4.34 – 4.23 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 140.1, 131.6, 129.5, 128.2 (q, *J* = 29.4 Hz), 126.1, 125.9 (q, *J* = 6.4 Hz), 124.5 (q, *J* = 274.4 Hz), 116.7, 49.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}F_6$ requires m/z 371.1230, found m/z 371.1238.

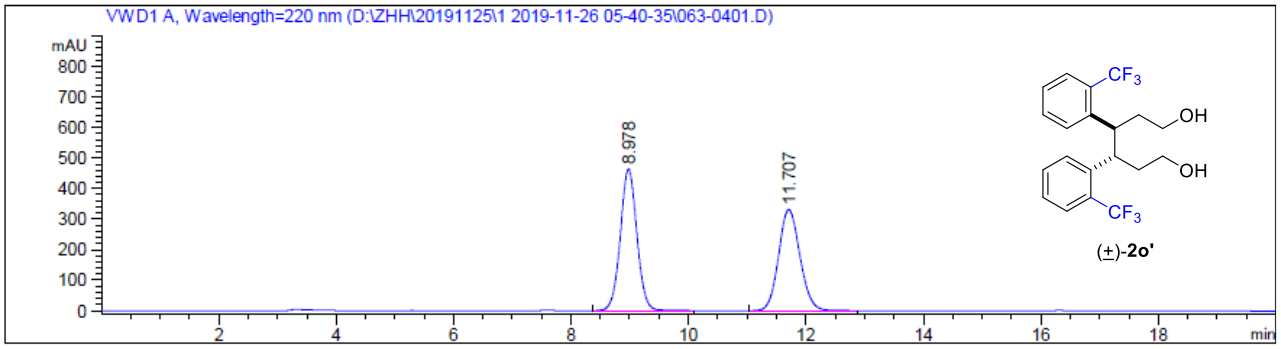
Analysis of Stereochemistry:

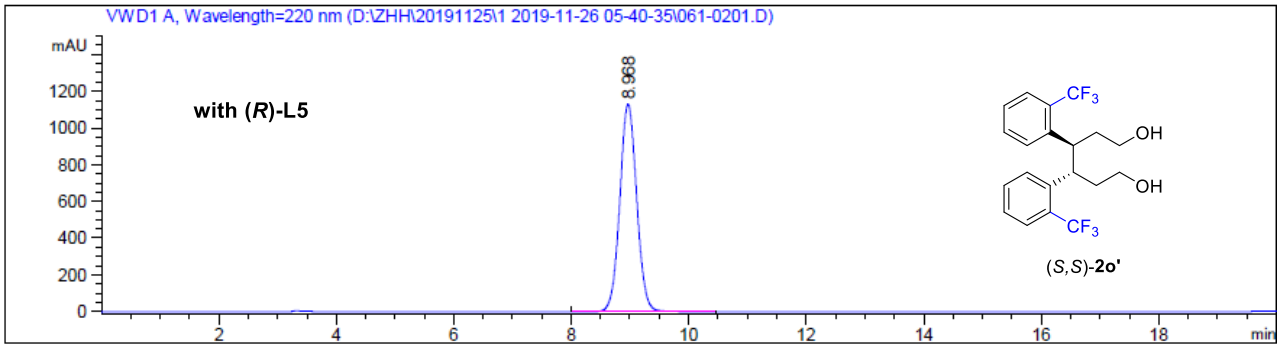
The title compound and the analogous racemic material were subjected to hydroboration and oxidation for HPLC analysis as shown below.



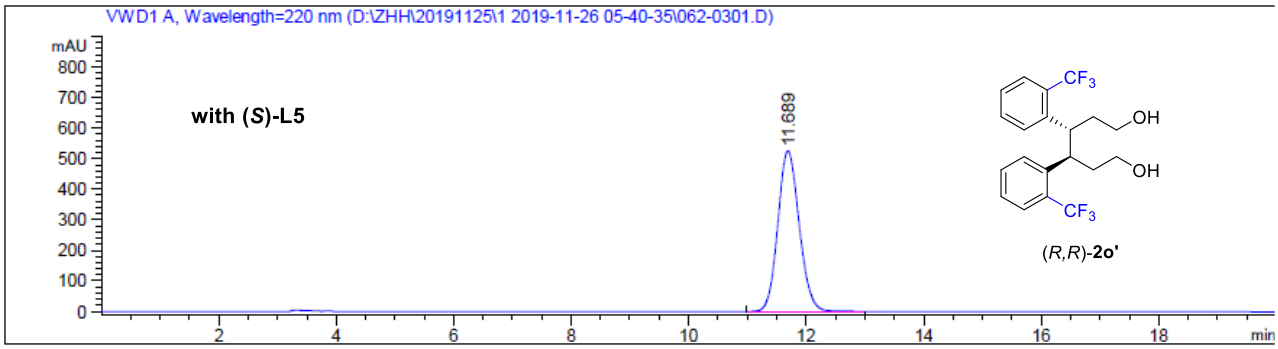
2o **2o'**

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak IC, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 8.97 min (major).

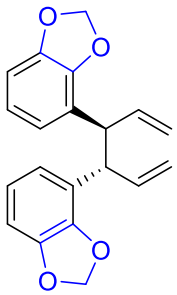




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.968	VB	0.3114	2.26843e4	1128.89404	100.0000



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.689	BB	0.3878	1.32720e4	525.31500	100.0000

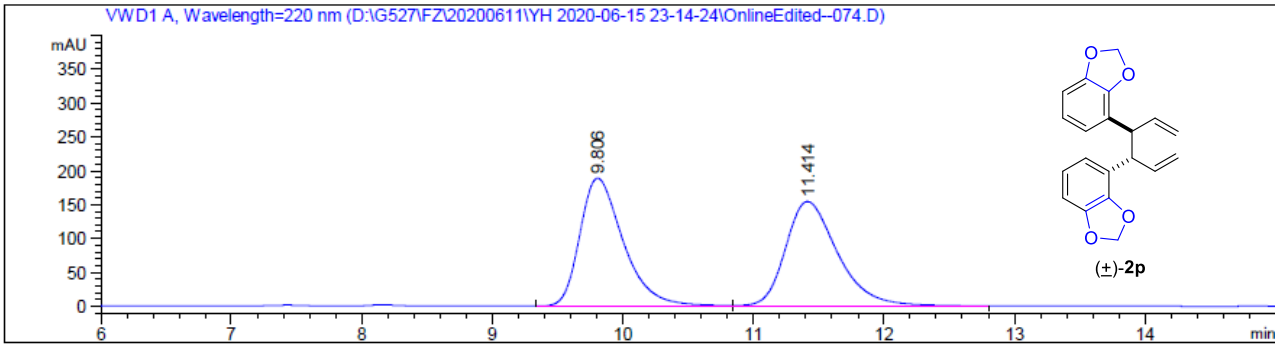


2p

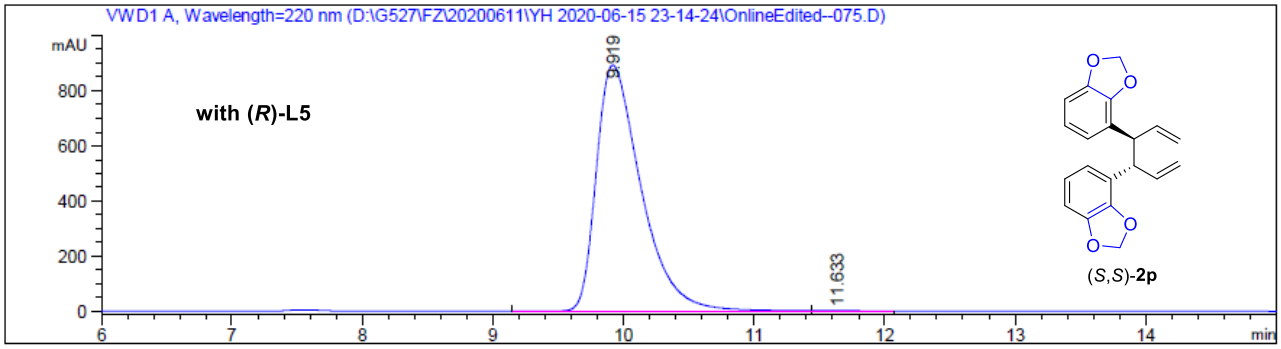
4,4'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis(benzo[*d*][1,3]dioxole) (2p): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50:1; Reaction time = 12 h; yield: 93% (30.0 mg); 93:7 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -26.8 (c 0.81, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.65 – 6.59 (m, 2H), 6.59 – 6.53 (m, 4H), 6.20 – 6.06 (m, 2H), 5.84 (d, *J* = 1.5 Hz, 2H), 5.78 (d, *J* = 1.5 Hz, 2H), 5.13 – 5.11 (m, 2H), 5.10 – 5.06 (m, 2H), 3.91 – 3.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 144.8, 138.8, 124.3, 121.6, 121.2, 116.2, 106.6, 100.3, 49.3; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}O_4$ requires m/z 323.1279, found m/z 323.1273.

Analysis of Stereochemistry:

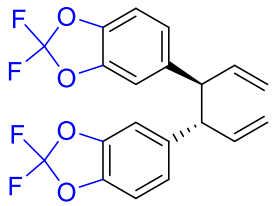
Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OJ, hexane/ethanol = 99/1, flow rate 0.8 mL/min, T = 25 ^oC, 220 nm): t_R = 9.92 min (major), t_R = 11.63 min (minor). (±)-**2p**: According to ***General Procedure B.***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.806	BV	0.3525	4378.34131	188.82907	50.5049
2	11.414	VB	0.4204	4290.80273	154.31787	49.4951



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.919	BB	0.3624	2.13743e4	892.51160	99.6928
2	11.633	BV	0.3387	65.86947	2.30960	0.3072

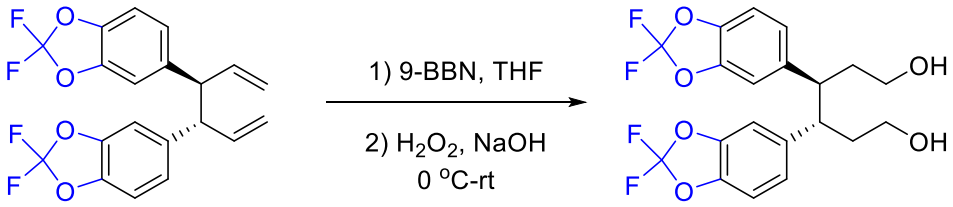


2q

5,5'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis(2,2-difluorobenzo[*d*][1,3]dioxole) (2q): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 60% (23.6 mg); 85:15 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -13.1 (c 1.21, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.86 – 6.83 (m, 2H), 6.81 – 6.77 (m, 2H), 6.74 – 6.67 (m, 2H), 6.00 (dddd, *J* = 16.9, 10.2, 5.6, 2.4 Hz, 2H), 5.14 (dd, *J* = 10.2, 1.4 Hz, 2H), 5.07 – 4.99 (m, 2H), 3.57 (dd, *J* = 5.6, 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 142.1, 139.4, 138.3, 131.6 (t, *J* = 254.8 Hz), 123.2, 116.9, 109.2, 109.0, 55.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -49.87, -49.95; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{15}F_4O_4$ requires m/z 395.0901, found m/z 395.0911.

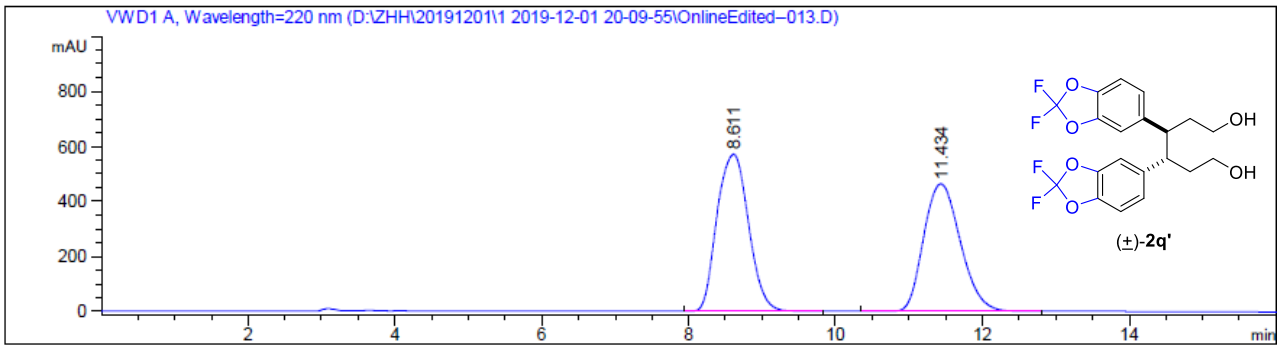
Analysis of Stereochemistry:

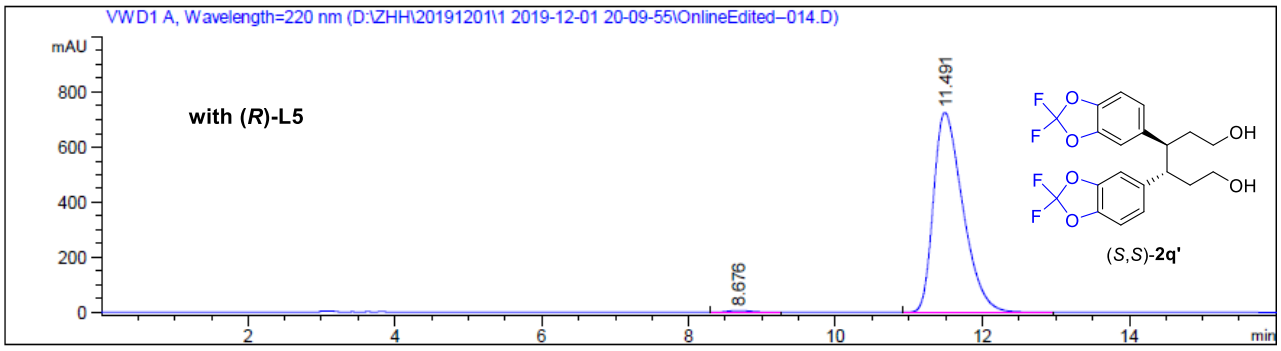
The title compound and the analogous racemic material were subjected to hydroboration and oxidation for HPLC analysis as shown below.



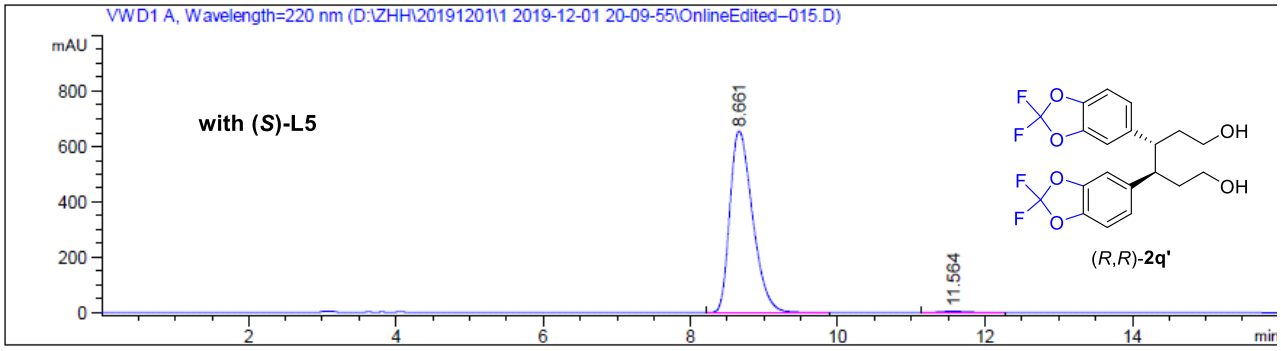
2q **2q'**

Enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 11.49 min (major), t_R = 8.68 min (minor).

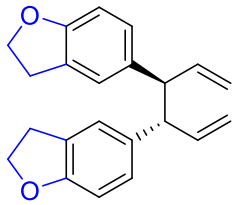




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.676	BB	0.3244	149.25414	7.12353	0.7348
2	11.491	VB	0.4224	2.01622e4	725.14301	99.2652



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.661	BB	0.3354	1.40797e4	655.94354	99.2217
2	11.564	VB	0.4069	110.43565	4.06628	0.7783

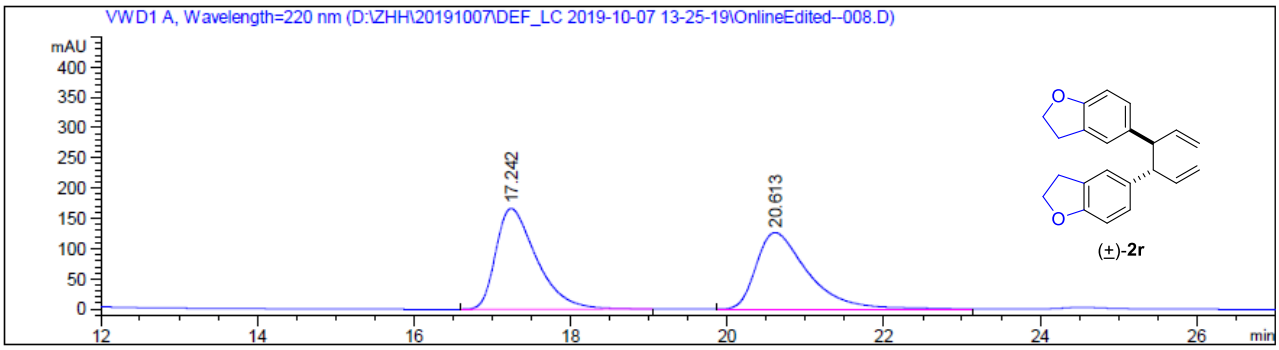


2r

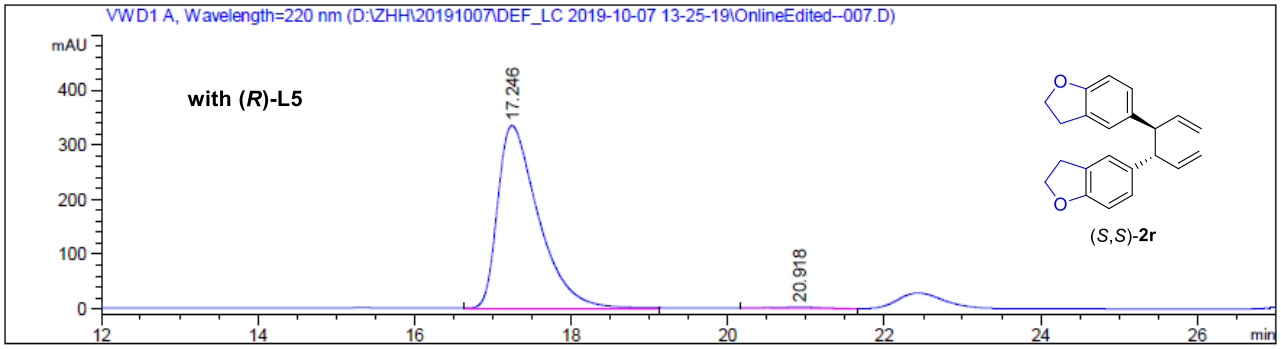
5,5'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis(2,3-dihydrobenzofuran) (2r): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50:1; Reaction time = 12 h; yield: 90% (28.6 mg); 91:9 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -25.5 (c 0.47, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.86 (d, *J* = 1.7 Hz, 2H), 6.77 (dd, *J* = 8.2, 1.9 Hz, 2H), 6.58 (d, *J* = 8.2 Hz, 2H), 6.04 (dddd, *J* = 16.9, 10.1, 5.9, 2.4 Hz, 2H), 5.05 (dd, *J* = 10.2, 1.8 Hz, 2H), 5.00 (dd, *J* = 17.0, 1.7 Hz, 2H), 4.53 – 4.44 (m, 4H), 3.52 (dd, *J* = 5.9, 2.4 Hz, 2H), 3.14 – 3.05 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 134.8, 127.7, 126.6, 124.6, 115.1, 108.7, 71.1, 55.3, 29.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{23}O_2$ requires m/z 319.1693, found m/z 319.1699.

Analysis of Stereochemistry:

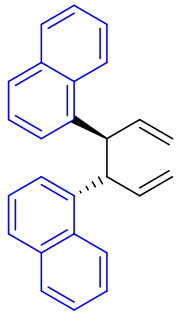
Enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak OJ, hexane/ethanol = 95/5, flow rate 0.8 mL/min, T = 25 °C, 220 nm): t_R = 17.25 min (major), t_R = 20.92 min (minor). (±)-**2r**: According to ***General Procedure B.***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.242	BB	0.5429	6019.08691	166.44412	50.9066
2	20.613	BB	0.6802	5804.70361	126.53413	49.0934



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.246	BB	0.5381	1.20319e4	334.15396	99.1146
2	20.918	BV	0.4404	107.47655	2.94750	0.8854

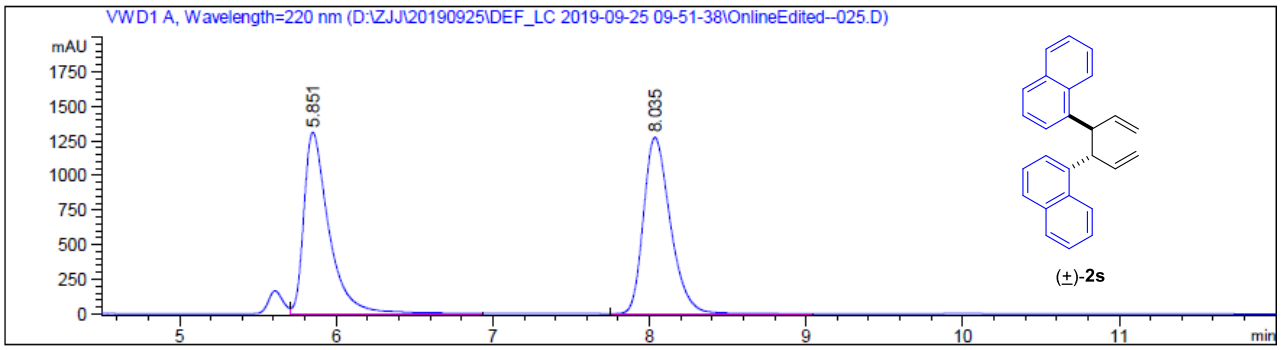


2s

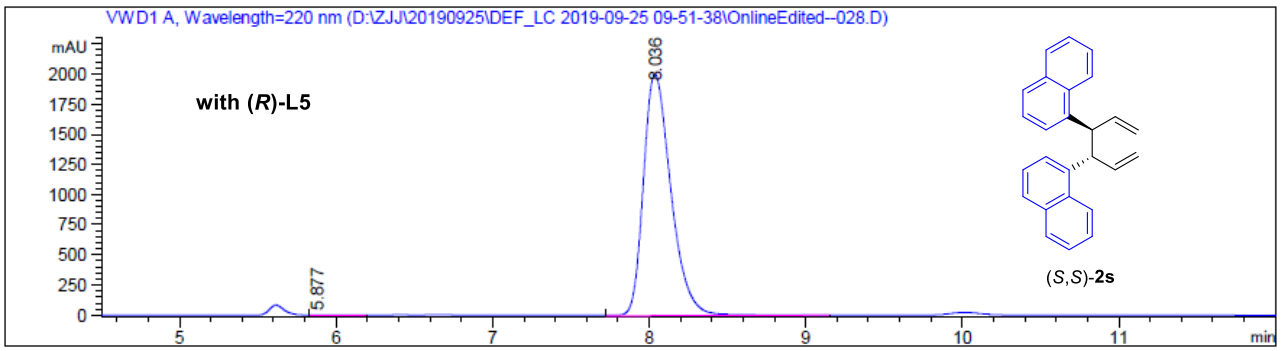
1,1'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)dinaphthalene (2s): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 94% (31.4 mg); > 95:5 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -121.2 (c 1.48, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.5 Hz, 2H), 7.77 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.53 – 7.47 (m, 2H), 7.47 – 7.41 (m, 2H), 7.36 – 7.29 (m, 2H), 7.17 (t, *J* = 7.7 Hz, 2H), 6.30 (dddd, *J* = 17.5, 10.2, 5.5, 2.3 Hz, 2H), 5.17 (dd, *J* = 10.2, 1.5 Hz, 2H), 5.07 (dd, *J* = 17.2, 1.5 Hz, 2H), 4.85 (dd, *J* = 5.4, 2.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6, 138.5, 134.0, 131.7, 129.1, 126.7, 125.9, 125.4, 125.3, 124.8, 123.3, 116.6, 48.3; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{23}$ requires m/z 335.1794, found m/z 335.1791.

Analysis of Stereochemistry:

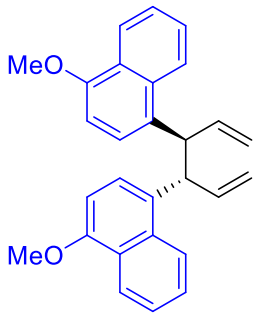
Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OD, hexane/ethanol = 95/5, flow rate 0.8 mL/min, T = 25 °C, 220 nm): t_R = 8.04 min (major), t_R = 5.88 min (minor). (±)-**2s**: According to ***General Procedure B.***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.851	VV	0.1676	1.49688e4	1317.14380	49.5153
2	8.035	VB	0.1846	1.52619e4	1275.61511	50.4847



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.877	VB	0.2466	118.79620	6.58169	0.4853
2	8.036	VB	0.1862	2.43622e4	1998.93848	99.5147

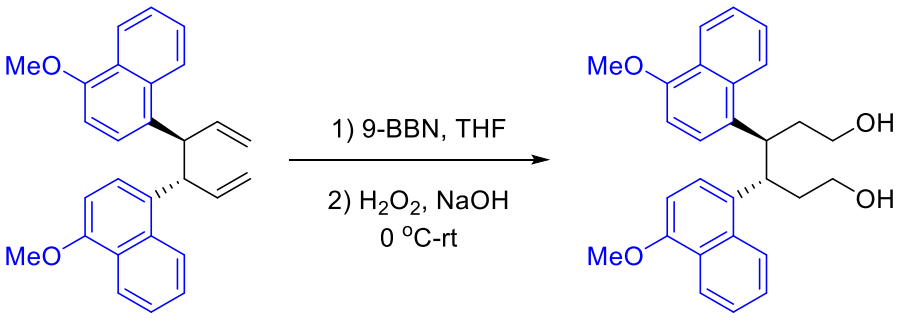


2t

4,4'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis(1-methoxynaphthalene) (2t): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50:1; Reaction time = 12 h; yield: 89% (35.1 mg); > 95:5 *dr*; > 95:5 *rr*; colorless solid, m.p. 168.4-169.7 ^{o}C; $[\alpha]_D^{20}$ = -118.5 (c 2.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (ddd, *J* = 8.3, 1.5, 0.6 Hz, 2H), 8.20 – 8.11 (m, 2H), 7.54 (ddd, *J* = 8.4, 6.7, 1.5 Hz, 2H), 7.45 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.50 (d, *J* = 8.1 Hz, 2H), 6.30 – 6.16 (m, 2H), 5.13 (dd, *J* = 10.2, 1.6 Hz, 2H), 5.08 – 4.97 (m, 2H), 4.71 (dd, *J* = 5.4, 2.2 Hz, 2H), 3.83 (s, 6H); ^{113}C NMR (101 MHz, $CDCl_3$) δ 153.7, 141.1, 132.5, 130.3, 126.3, 125.9, 124.55, 124.50, 123.0, 122.6, 115.9, 103.5, 55.2, 47.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{27}O_2$ requires m/z 395.2006, found m/z 395.2017.

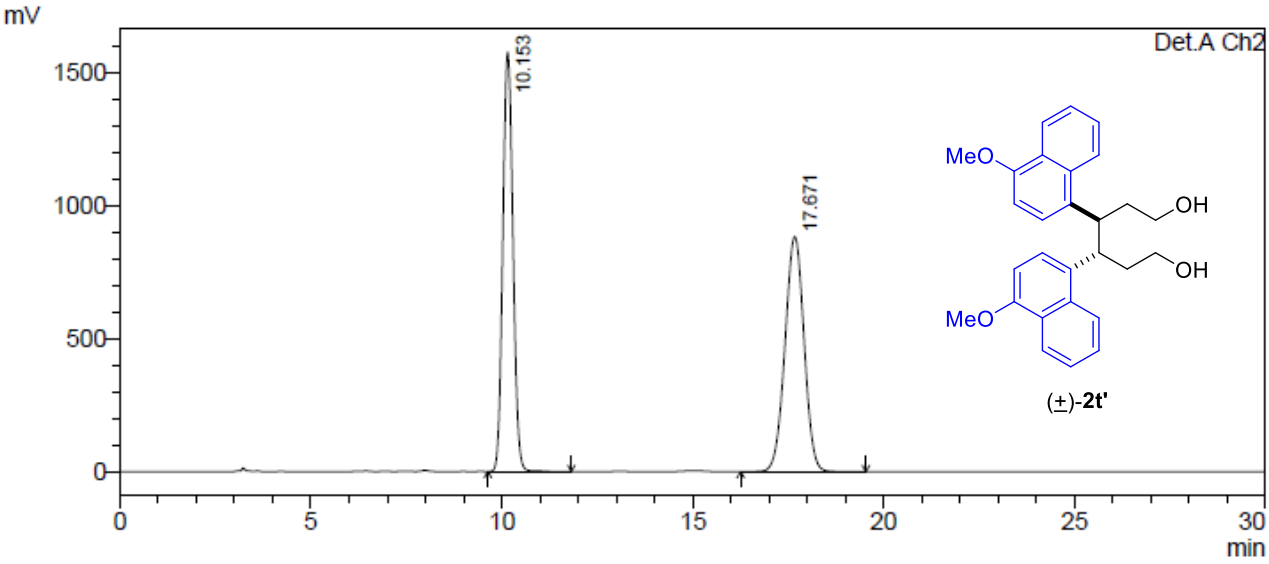
Analysis of Stereochemistry:

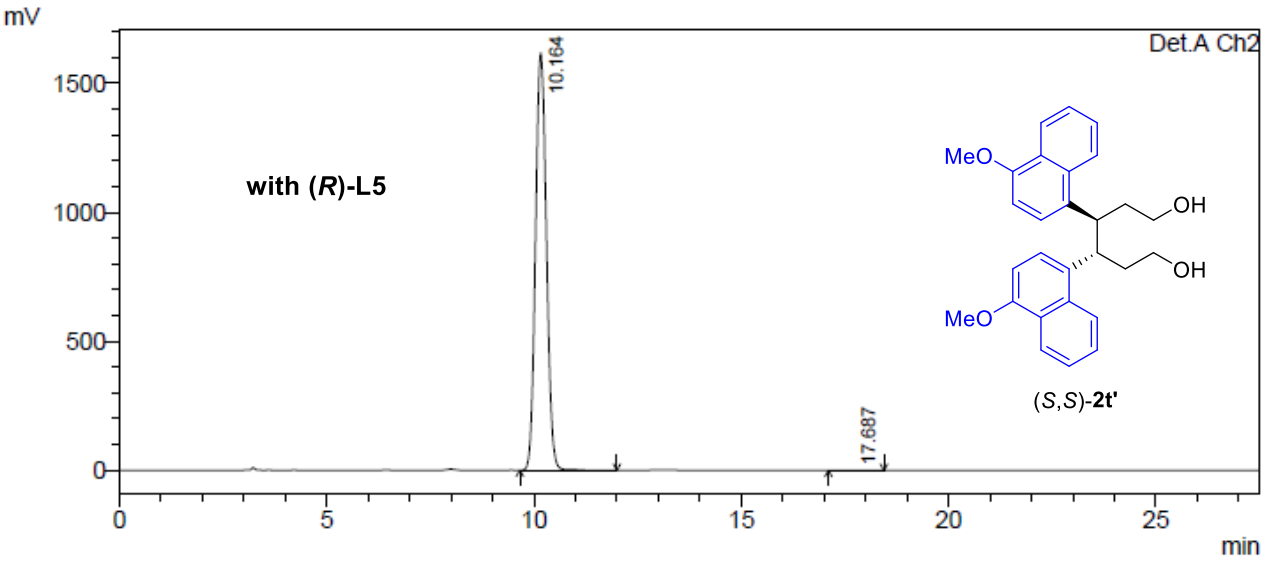
The title compound and the analogous racemic material were subjected to hydroboration and oxidation for HPLC analysis as shown below.



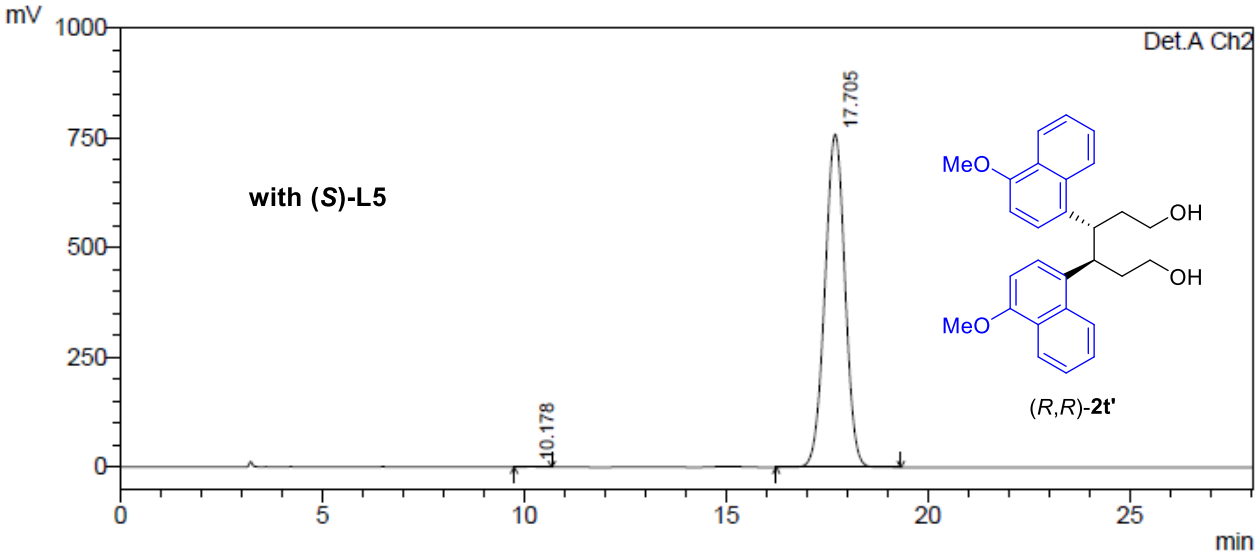
2t **2t'**

Enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, T = 25 ^{o}C, 220 nm): t_R = 10.16 min (major), t_R = 17.69 min (minor).

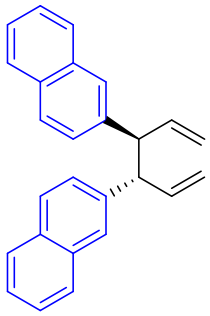




Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.163	29615131	1617407	99.910	99.951
2	17.719	26713	791	0.090	0.049
Total		29641844	1618198	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.177	27680	1514	0.105	0.199
2	17.703	26214359	758048	99.895	99.801
Total		26242038	759562	100.000	100.000

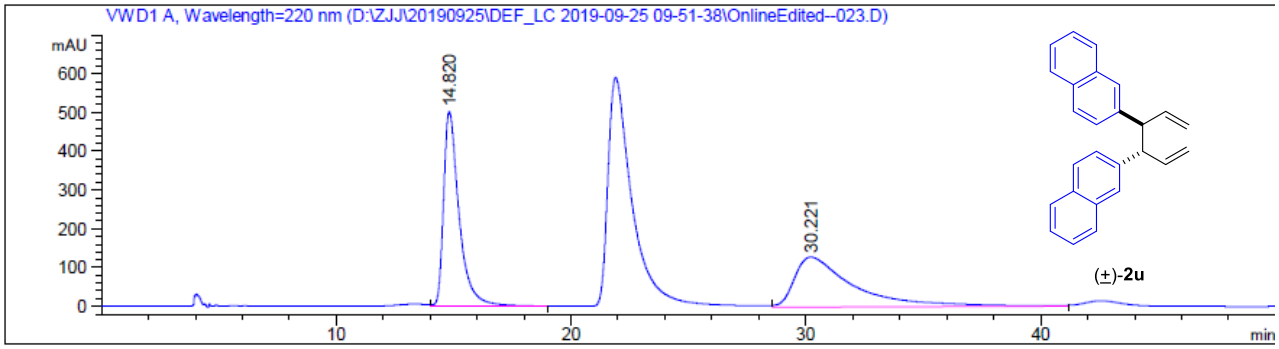


2u

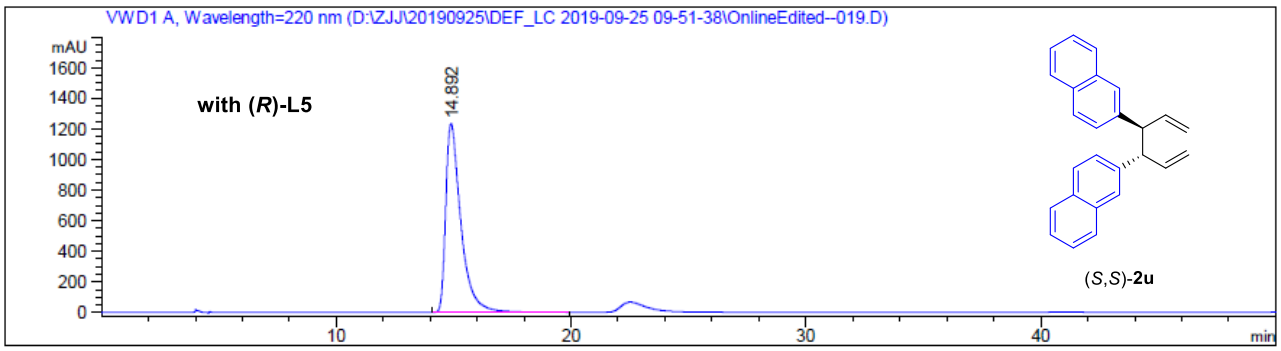
2,2'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)dinaphthalene (2u): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 60% (20.1 mg); 91:9 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -38.4 (c 0.86, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.65 (m, 4H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.54 (d, *J* = 1.7 Hz, 2H), 7.40 – 7.32 (m, 4H), 7.28 (dd, *J* = 8.5, 1.8 Hz, 2H), 6.24 (dddd, *J* = 17.0, 10.2, 5.7, 2.4 Hz, 2H), 5.16 (dd, *J* = 10.2, 1.6 Hz, 2H), 5.11 (dd, *J* = 17.0, 1.5 Hz, 2H), 3.98 (dd, *J* = 5.7, 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 140.0, 133.4, 132.1, 127.8, 127.6, 127.5, 126.9, 126.6, 125.7, 125.2, 116.1, 55.5; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{23}$ requires m/z 335.1794, found m/z 335.1787.

Analysis of Stereochemistry:

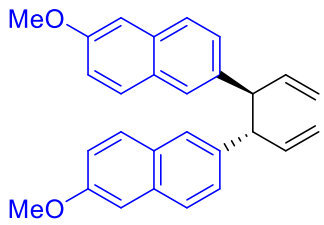
Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OJ, pentane/ethanol = 95/5, flow rate 0.8 mL/min, T = 25 °C, 220 nm): t_R = 14.89 min (major). (±)-**2u**: According to ***General Procedure A*.**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.820	VB	0.6845	2.31157e4	502.70316	50.5738
2	30.221	MM	2.9180	2.25911e4	129.03329	49.4262



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.892	BB	0.6764	5.56386e4	1233.22559	100.0000

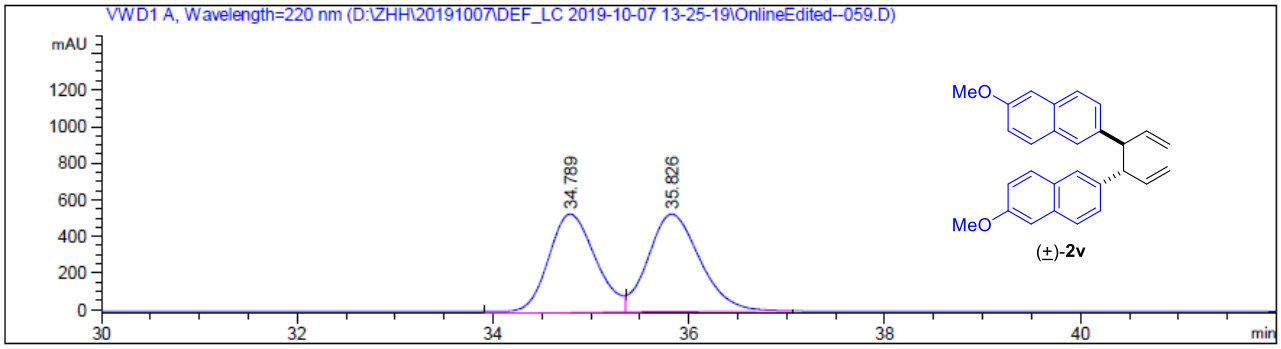


2v

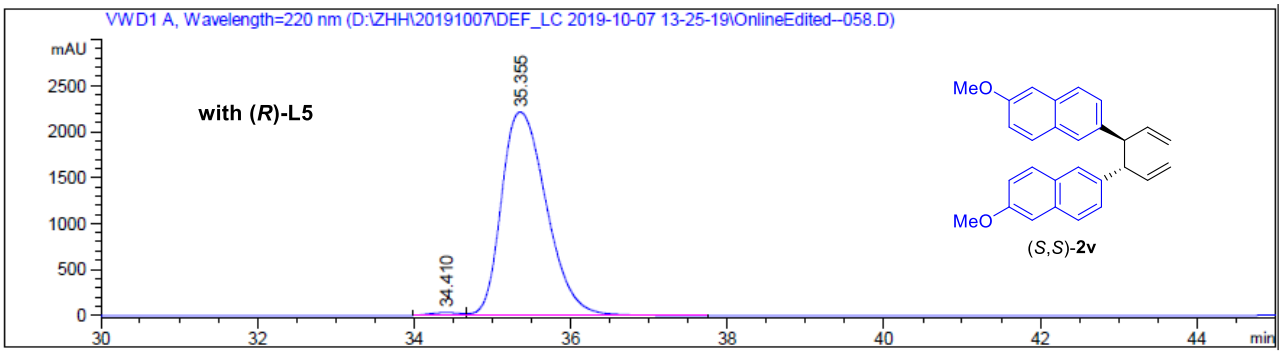
6,6'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis(2-methoxynaphthalene) (2v): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50:1; Reaction time = 12 h; yield: 94% (37.1 mg); > 95:5 *dr*; > 95:5 *rr*; olorless solid, m.p. 179.2-180.4 ^{o}C; $[\alpha]_D^{20}$ = -36.4 (c 1.76, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.49 – 7.44 (m, 2H), 7.24 (dd, *J* = 8.5, 1.7 Hz, 2H), 7.05 (dd, *J* = 8.9, 2.5 Hz, 2H), 7.00 (d, *J* = 2.5 Hz, 2H), 6.31 – 6.17 (m, 2H), 5.15 (dd, *J* = 10.3, 1.6 Hz, 2H), 5.10 (dd, *J* = 17.0, 1.5 Hz, 2H), 3.93 (dd, *J* = 5.8, 2.3 Hz, 2H), 3.85 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 140.8, 137.8, 133.1, 129.1, 128.9, 127.2, 126.7, 126.6, 118.5, 115.9, 105.5, 55.4, 55.2; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{27}O_2$ requires m/z 395.2006, found m/z 395.2019.

Analysis of Stereochemistry:

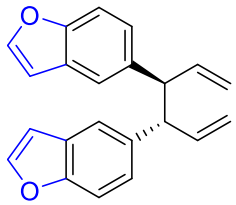
Enantiomeric excess: 98%, determined by HPLC (Daicel Chiralpak AD-H*2, hexane/ethanol = 99/1, flow rate 0.5 mL/min, T = 25 ^{o}C, 220 nm): t_R = 35.36 min (major), t_R = 34.41 min (minor). (±)-**2v**: According to ***General Procedure B.***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.789	MF	0.5612	1.81037e4	537.64087	48.0821
2	35.826	FM	0.6110	1.95480e4	533.25580	51.9179



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.410	FM	0.4634	959.42139	34.50854	1.0724
2	35.355	FM	0.6668	8.85047e4	2212.14209	98.9276

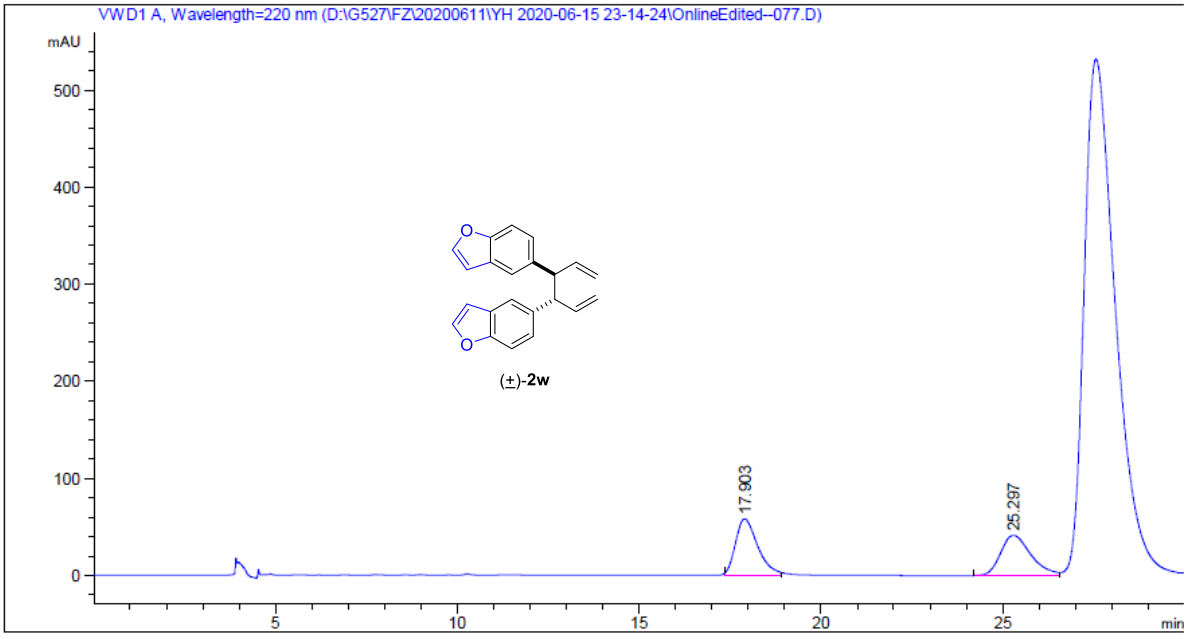


2w

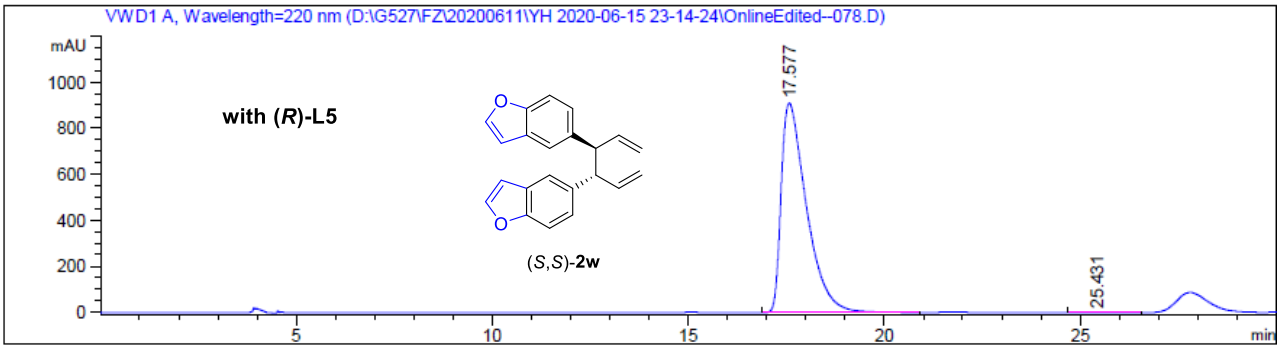
5,5'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis(benzofuran) (2w): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50:1; Reaction time = 12 h; yield: 94% (29.5 mg); 93:7 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -27.7 (c 1.11, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 2.2 Hz, 2H), 7.28 – 7.22 (m, 4H), 6.99 (dd, *J* = 8.6, 1.8 Hz, 2H), 6.60 (dd, *J* = 2.2, 0.9 Hz, 2H), 6.23 – 6.09 (m, 2H), 5.09 (dd, *J* = 10.3, 1.7 Hz, 2H), 5.07 – 5.01 (m, 2H), 3.79 (dd, *J* = 5.8, 2.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 144.9, 141.3, 137.2, 127.3, 124.6, 120.5, 115.5, 110.9, 106.5, 55.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}O_2$ requires m/z 315.1380, found m/z 315.1385.

Analysis of Stereochemistry:

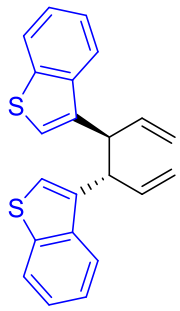
Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OJ, hexane/ethanol = 95/5, flow rate 0.8 mL/min, T = 25 °C, 220 nm): t_R = 17.58 min (major), t_R = 25.43 min (minor). (±)-**3hh**: According to ***General Procedure A.***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.903	FM	0.7095	2476.21997	58.17157	50.6813
2	25.297	BV	0.8714	2409.64429	41.62563	49.3187



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.577	BB	0.6719	4.08961e4	910.64880	99.8426
2	25.431	BV	0.6397	64.48870	1.18530	0.1574

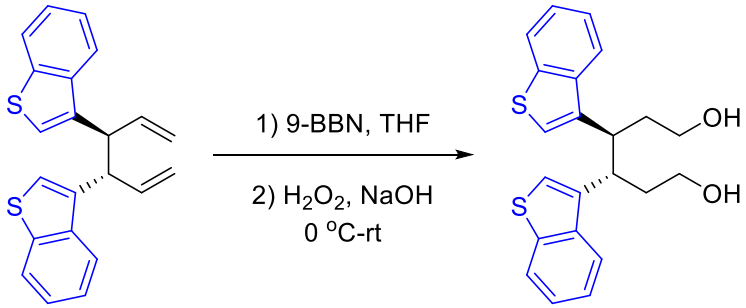


2x

3,3'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)bis(benzo[*b*]thiophene) (2x): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50:1; Reaction time = 12 h; yield: 81% (28.1 mg); 92:8 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -44.6 (c 1.34, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 4H), 7.39 – 7.31 (m, 4H), 7.11 – 7.06 (m, 2H), 6.24 – 6.09 (m, 2H), 5.19 (dd, *J* = 10.2, 1.5 Hz, 2H), 5.13 – 5.07 (m, 2H), 4.37 – 4.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3, 138.5, 138.3, 136.8, 124.2, 123.8, 122.9, 122.2, 121.8, 117.1, 47.3; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}S_2$ requires m/z 347.0923, found m/z 347.0910.

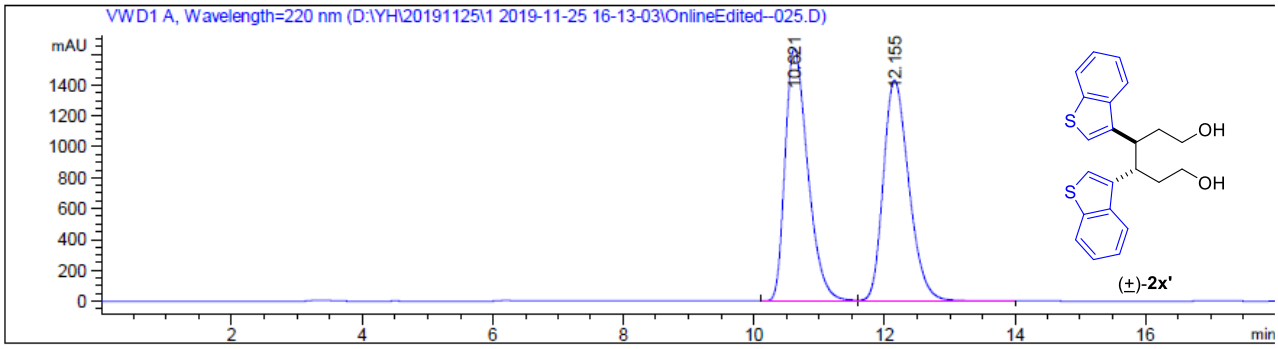
Analysis of Stereochemistry:

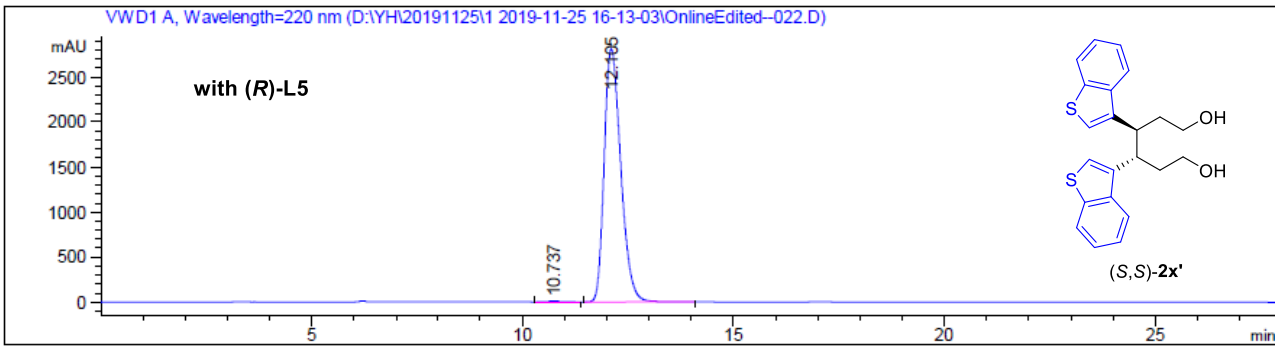
The title compound and the analogous racemic material were subjected to hydroboration and oxidation for HPLC analysis as shown below.



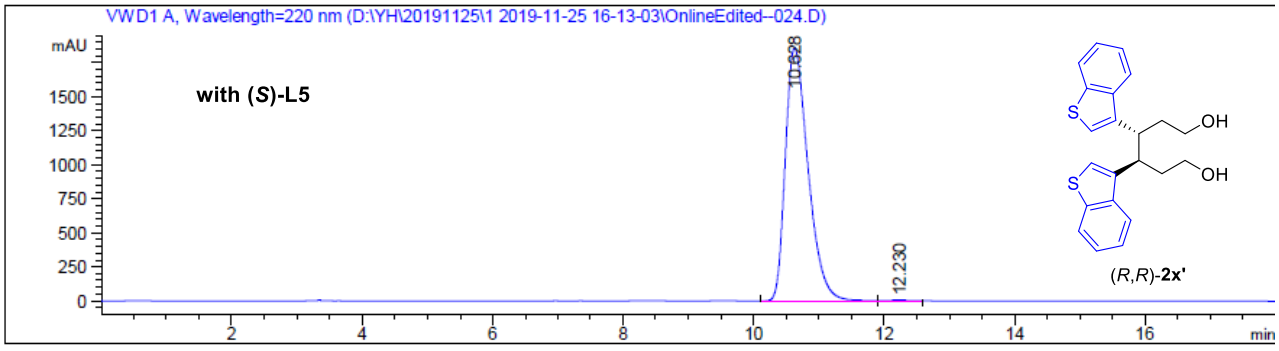
2x **2x'**

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak IC, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 12.10 min (major), t_R = 10.74 min (minor).

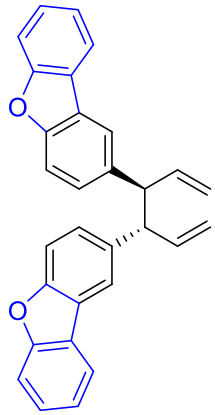




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.737	VB	0.3561	194.19537	8.23628	0.2518
2	12.105	BB	0.4273	7.69140e4	2810.59106	99.7482



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.628	BV	0.3719	4.50412e4	1857.53955	99.6972
2	12.230	MF	0.4637	136.79956	4.91662	0.3028

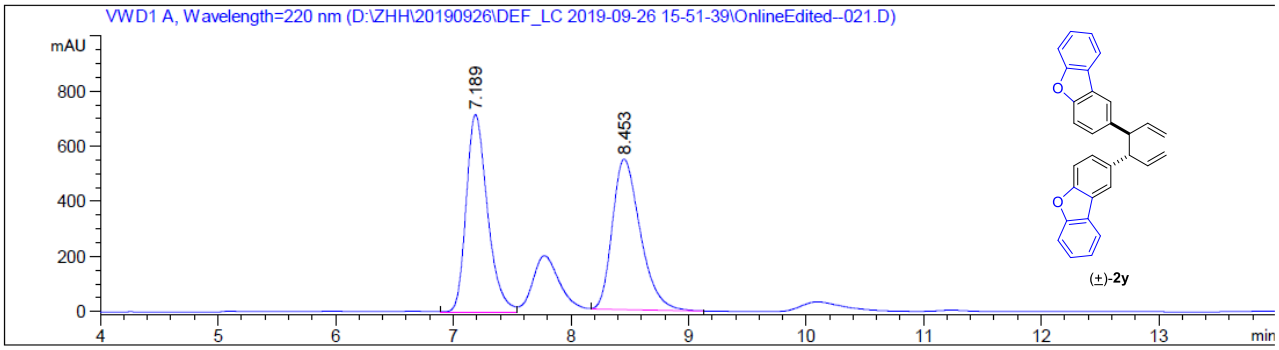


2y

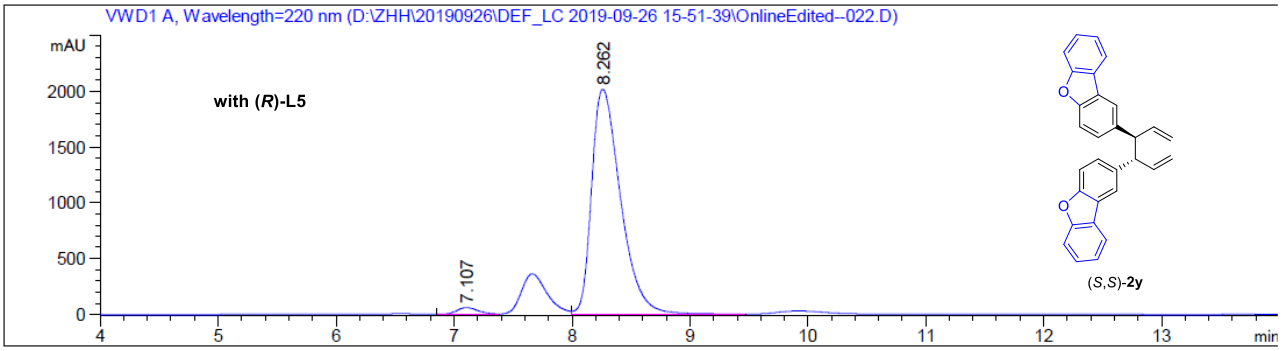
2,2'-((3*S*,4*S*)-hexa-1,5-diene-3,4-diyl)didibenzo[*b*,*d*]furan (2y): According to ***General Procedure C*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50:1; Reaction time = 12 h; yield: 91% (37.7 mg); 87:13 *dr*; > 95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -29.9 (c 1.77, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.00 – 7.93 (m, 4H), 7.53 – 7.47 (m, 2H), 7.41 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 2H), 7.36 – 7.32 (m, 4H), 7.32 – 7.27 (m, 2H), 6.36 – 6.23 (m, 2H), 5.16 – 5.07 (m, 4H), 4.09 (dd, *J* = 5.8, 2.6 Hz, 2H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 157.1, 155.4, 142.7, 138.9, 128.8, 128.0, 125.0, 124.8, 123.6, 121.5, 121.2, 115.8, 112.3, 111.8, 56.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{23}O_2$ requires m/z 415.1693, found m/z 415.1683.

Analysis of Stereochemistry:

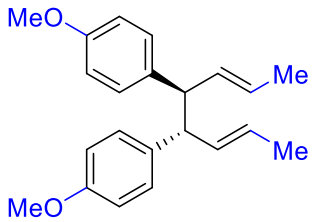
Enantiomeric excess: 96%, determined by HPLC (Daicel Chiralpak OD, hexane/isopropanol = 99/1, flow rate 1.0 mL/min, T = 25 ^{o}C, 220 nm): t_R = 8.26 min (major), t_R = 7.11 min (minor). (±)-**3hj**: According to ***General Procedure B.***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.189	VV	0.1931	9019.94531	715.60583	49.9479
2	8.453	MM	0.2761	9038.74805	545.69037	50.0521



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.107	VV	0.1976	807.74298	62.15925	2.2837
2	8.262	VV	0.2616	3.45626e4	2020.39087	97.7163

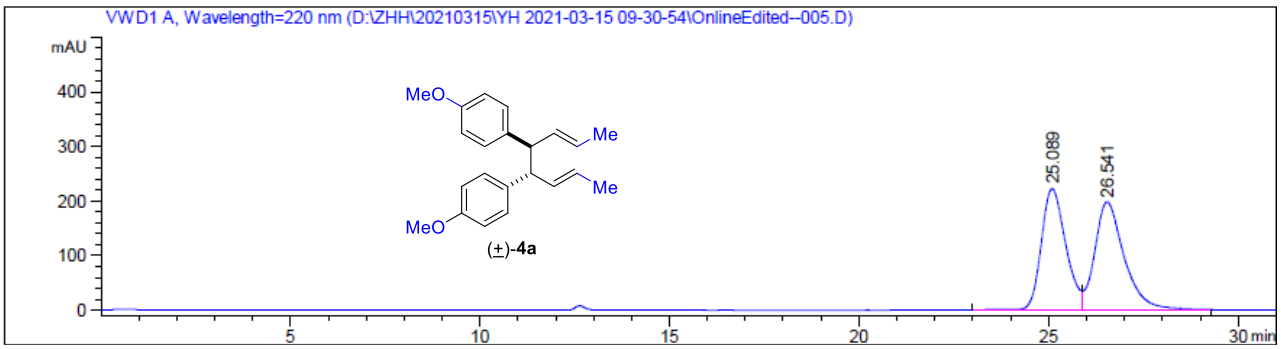


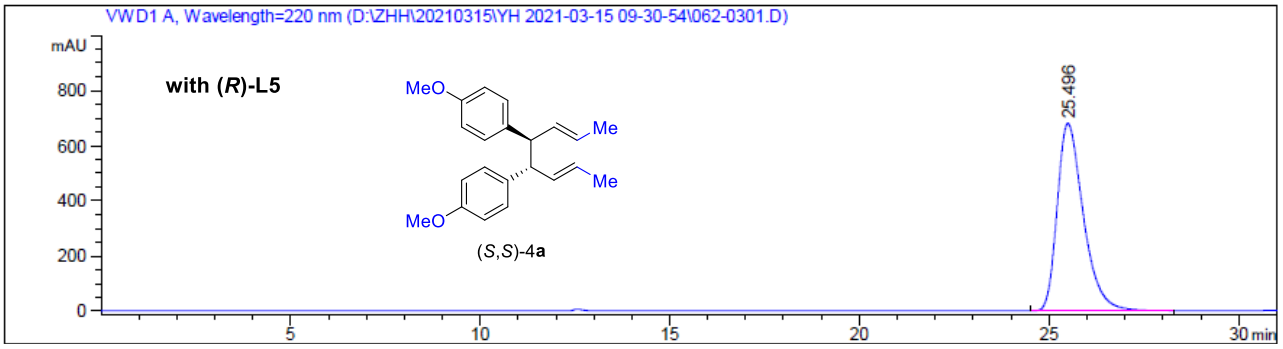
4a

4,4'-((2*E*,4*S*,5*S*,6*E*)-octa-2,6-diene-4,5-diyl)bis(methoxybenzene) (4a): According to ***General Procedure F*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50;1; Reaction time = 12 h; yield: 64% (20.6 mg); 89:11 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -36.5 (c 0.58, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.95 – 6.88 (m, 4H), 6.73 – 6.65 (m, 4H), 5.66 (ddt, *J* = 15.2, 5.9, 1.7 Hz, 2H), 5.44 – 5.29 (m, 2H), 3.72 (s, 6H), 3.44 (dd, *J* = 5.8, 2.3 Hz, 2H), 1.65 (dd, *J* = 6.4, 1.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 136.0, 133.7, 129.1, 125.8, 113.4, 55.1, 54.2, 18.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}O_2$ requires m/z 323.2006, found m/z 323.2013.

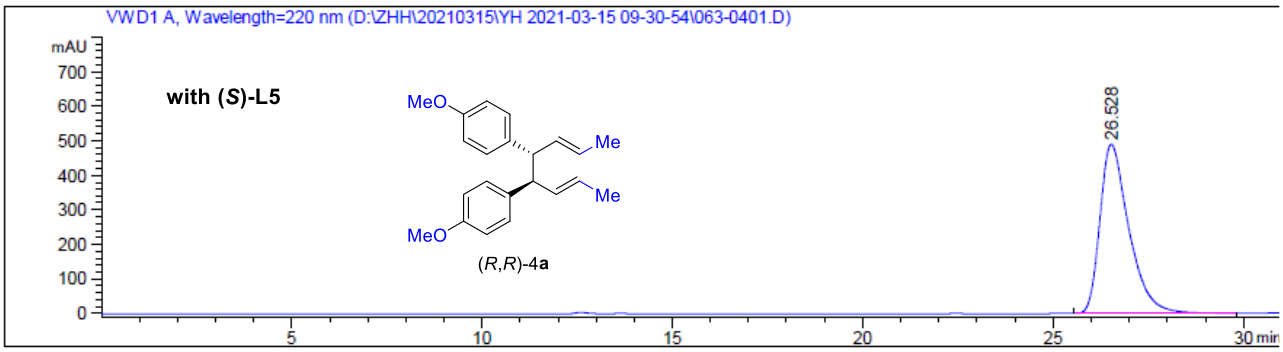
Analysis of Stereochemistry:

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OJ*2, hexane/ethanol = 99/1, flow rate 0.5 mL/min, T = 25 °C, 220 nm): t_R = 25.50 min (major. (±)-**4a**: According to ***General Procedure E.***

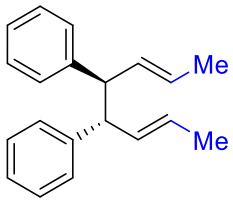




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.496	BB	0.7257	3.27339e4	681.06525	100.0000



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.528	BB	0.7927	2.60105e4	490.47394	100.0000

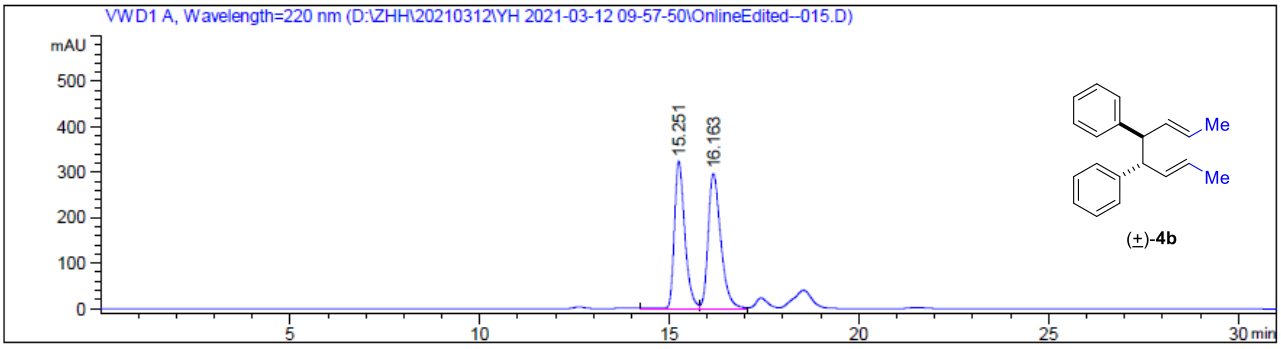


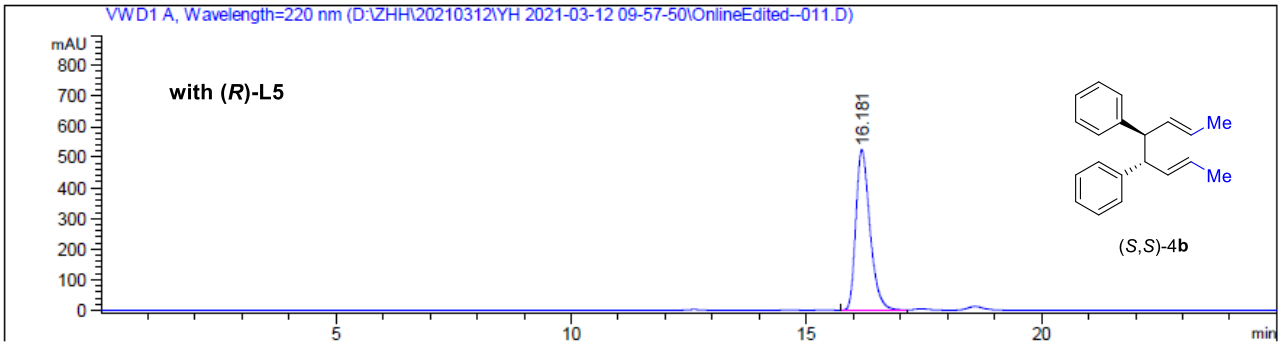
4b

((2*E*,4*S*,5*S*,6*E*)-octa-2,6-diene-4,5-diyl)dibenzene (4b): According to ***General Procedure F*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100;1; Reaction time = 12 h; yield: 87% (22.8 mg); > 95:5 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -54.3 (c 0.89, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.10 (m, 4H), 7.08 – 7.03 (m, 2H), 7.03 – 6.98 (m, 4H), 5.78 – 5.64 (m, 2H), 5.40 (dq, *J* = 15.2, 6.4 Hz, 2H), 3.53 (dd, *J* = 5.9, 2.3 Hz, 2H), 1.67 (dd, *J* = 6.4, 1.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 133.4, 128.2, 127.9, 126.3, 125.7, 55.1, 18.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}$ 263.1794; Found 263.1799.

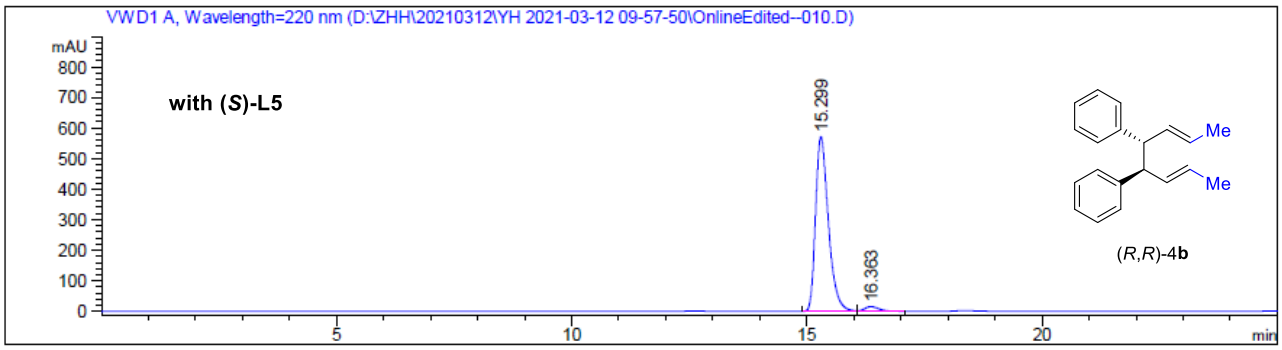
Analysis of Stereochemistry:

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OJ*2, hexane/ethanol = 99/1, flow rate 0.5 mL/min, T = 25 °C, 220 nm): t_R = 16.18 min (major. (±)-**4b**: According to ***General Procedure E.***

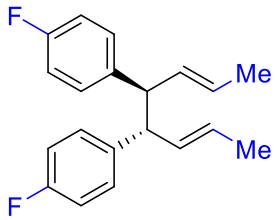




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.181	VV	0.3198	1.09737e4	525.17188	100.0000



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.299	BV	0.2879	1.08419e4	572.51379	96.9493
2	16.363	VB	0.3292	341.15826	15.41522	3.0507

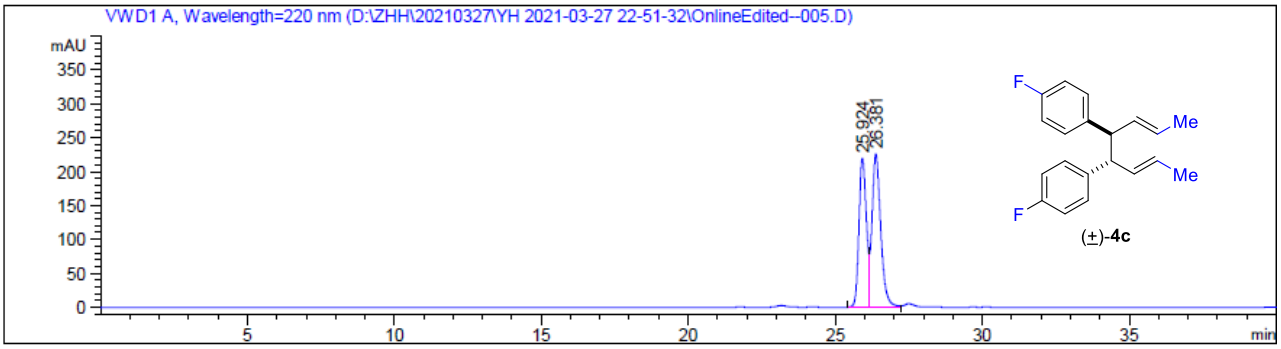


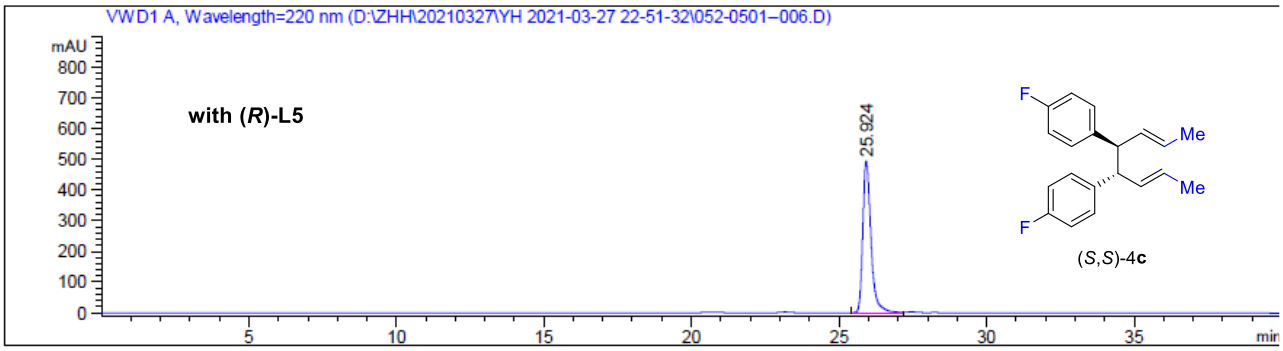
4c

4,4'-((2*E*,4*S*,5*S*,6*E*)-octa-2,6-diene-4,5-diyl)bis(fluorobenzene) (4c): According to ***General Procedure F*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100;1; Reaction time = 12 h; yield: 82% (24.4 mg); > 95:5 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -38.7 (c 0.60, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 6.95 – 6.88 (m, 4H), 6.87 – 6.79 (m, 4H), 5.73 – 5.58 (m, 2H), 5.38 (dq, *J* = 15.1, 6.4 Hz, 2H), 3.45 (dd, *J* = 5.8, 2.3 Hz, 2H), 1.67 (dd, *J* = 6.4, 1.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0 (d, *J* = 243.8 Hz), 139.2 (d, *J* = 2.6 Hz), 132.9, 129.4 (d, *J* = 7.8 Hz), 126.7, 114.8 (d, *J* = 21.0 Hz), 54.4, 18.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}F_2$ 299.1606; Found 299.1602.

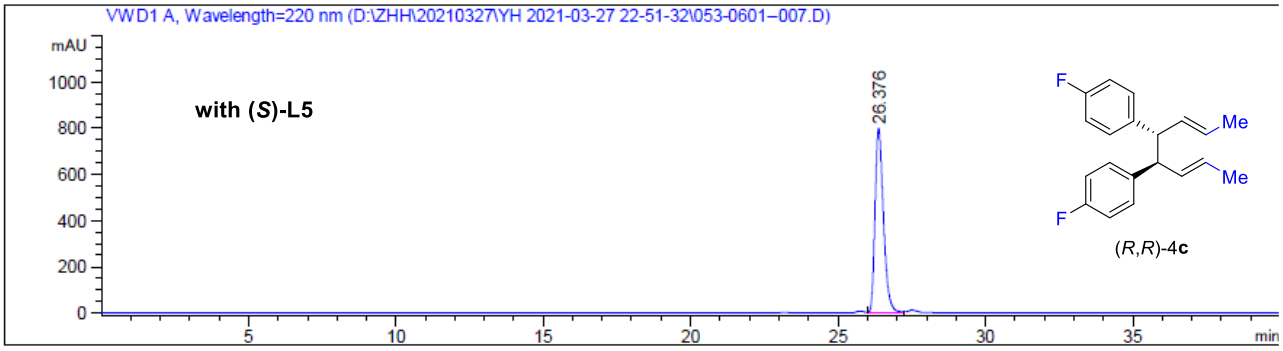
Analysis of Stereochemistry:

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OD*3, hexane/isopropanol = 99/1, flow rate 0.4 mL/min, T = 25 °C, 220 nm): t_R = 25.92 min (major). (±)-**4c**: According to ***General Procedure E.***

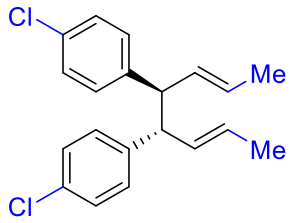




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.924	BV	0.2959	9641.22461	493.63046	100.0000



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.376	VV	0.3071	1.59615e4	798.76202	100.0000

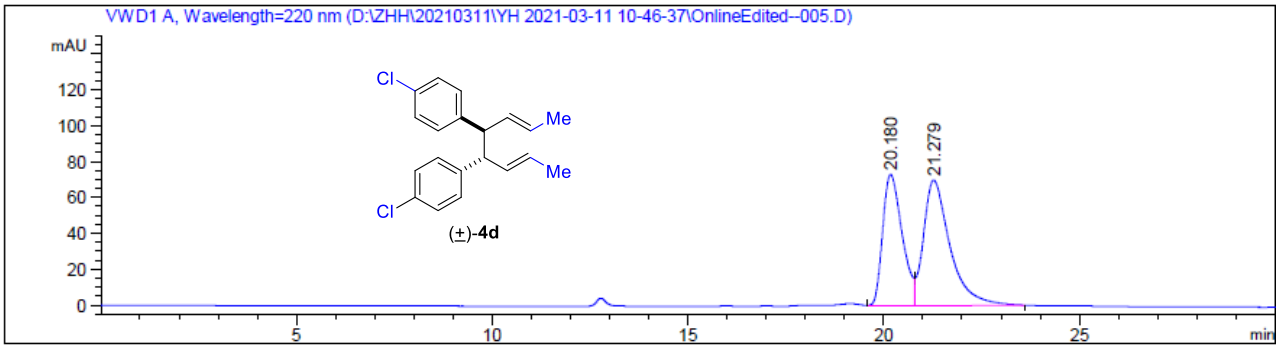


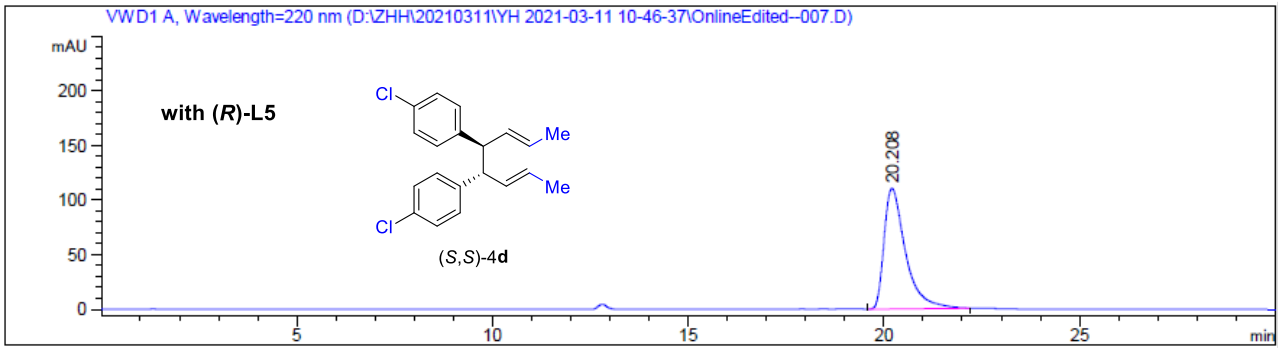
4d

4,4'-((2*E*,4*S*,5*S*,6*E*)-octa-2,6-diene-4,5-diyl)bis(chlorobenzene) (4d): According to ***General Procedure F*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100;1; Reaction time = 12 h; yield: 67% (22.1 mg); > 95:5 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -58.3 (c 0.82, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.11 (m, 2H), 7.10 – 7.03 (m, 2H), 7.01 – 6.96 (m, 2H), 6.94 – 6.89 (m, 2H), 5.75 – 5.60 (m, 2H), 5.47 – 5.31 (m, 2H), 3.54 – 3.42 (m, 2H), 1.66 (dd, *J* = 6.5, 1.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.3, 133.0, 132.9, 129.5, 128.10, 128.08, 128.06, 126.8, 126.6, 125.9, 55.0, 54.3, 18.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}Cl_2$ 331.1015; Found 331.1010.

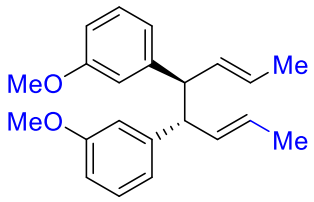
Analysis of Stereochemistry:

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak AD*2, hexane/isopropanol = 100/0, flow rate 0.5 mL/min, T = 25 °C, 220 nm): t_R = 20.2 min (major) (±)-**4d**: According to ***General Procedure E*.**





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.208	VB	0.5667	4195.69580	110.31971	100.0000

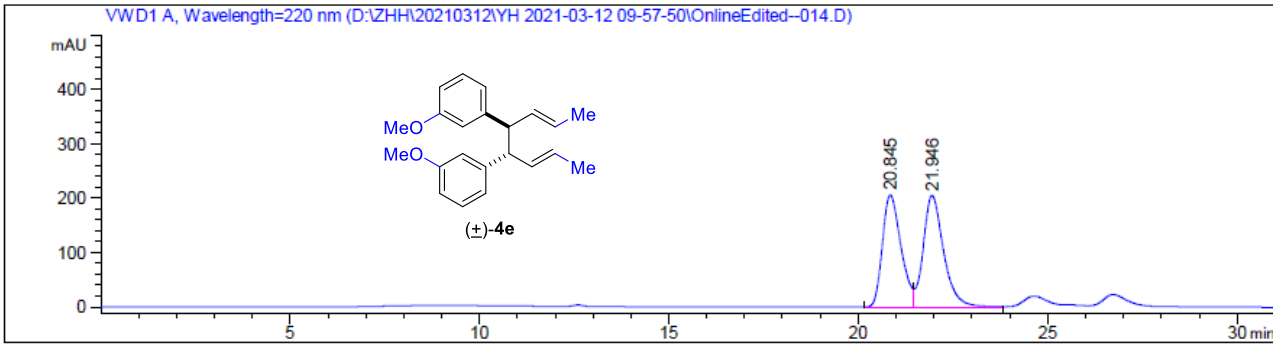


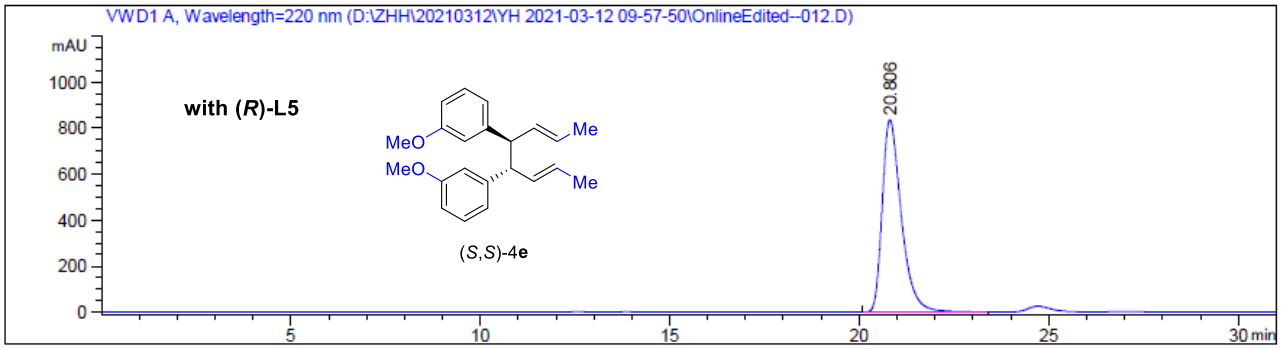
4e

3,3'-((2*E*,4*S*,5*S*,6*E*)-octa-2,6-diene-4,5-diyl)bis(methoxybenzene) (4e): According to ***General Procedure F*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50;1; Reaction time = 12 h; yield: 72% (23.2 mg); > 95:5 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -43.7 (c 0.59, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.13 – 7.02 (m, 2H), 6.68 – 6.58 (m, 4H), 6.58 – 6.54 (m, 2H), 5.76 – 5.61 (m, 2H), 5.41 (dq, *J* = 15.1, 6.4 Hz, 2H), 3.70 (s, 6H), 3.53 – 3.45 (m, 2H), 1.67 (dd, *J* = 6.4, 1.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 145.4, 133.1, 128.9, 126.4, 120.7, 114.0, 111.1, 55.1, 55.0, 18.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}O_2$ 323.2006; Found 323.2009.

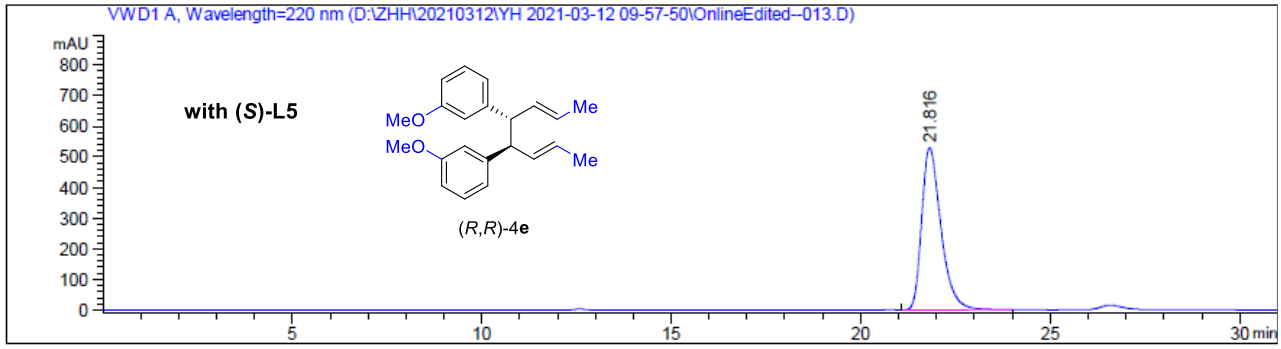
Analysis of Stereochemistry:

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OJ*2, hexane/ethanol = 99/1, flow rate 0.5 mL/min, T = 25 °C, 220 nm): t_R = 20.81 min (major. (±)-**4e**: According to ***General Procedure E.***

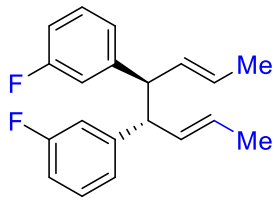




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.806	BB	0.5289	2.93099e4	836.27661	100.0000



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.816	VB	0.5394	1.87808e4	530.07782	100.0000

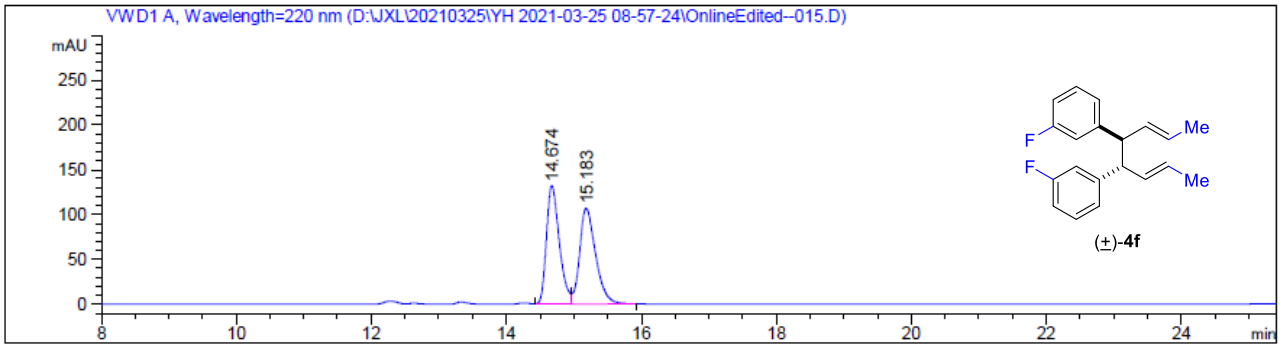


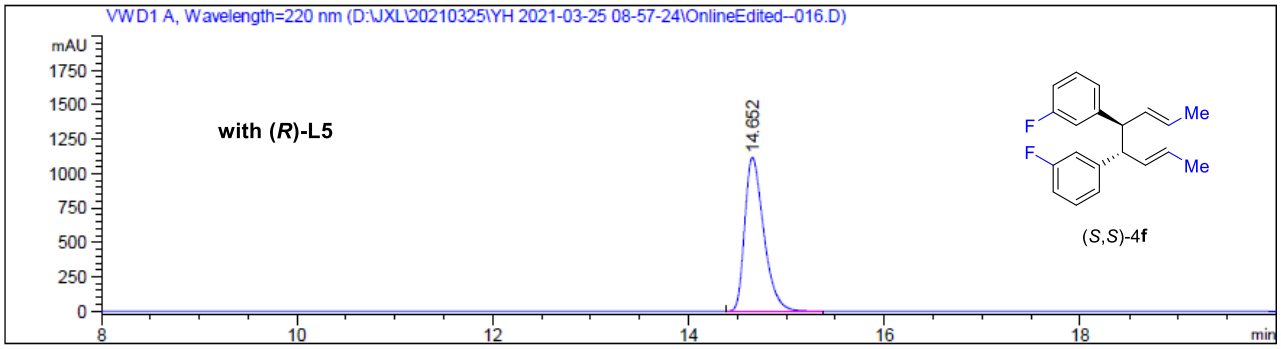
4f

3,3'-((2*E*,4*S*,5*S*,6*E*)-octa-2,6-diene-4,5-diyl)bis(fluorobenzene) (4f): According to ***General Procedure F*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100;1; Reaction time = 12 h; yield: 63% (18.8 mg); > 95:5 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -50.2 (c 0.70, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.05 (m, 2H), 6.88 – 6.69 (m, 6H), 5.71 – 5.58 (m, 2H), 5.41 (dq, *J* = 15.2, 6.4 Hz, 2H), 3.53 – 3.45 (m, 2H), 1.68 (dd, *J* = 6.4, 1.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6 (d, *J* = 245.2 Hz), 146.1 (d, *J* = 6.8 Hz), 132.3, 129.4 (d, *J* = 8.3 Hz), 127.3, 123.8 (d, *J* = 2.7 Hz), 114.8 (d, *J* = 21.2 Hz), 112.8 (d, *J* = 21.1 Hz), 54.7 (d, *J* = 1.8 Hz), 18.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}F_2$ 299.1606; Found 299.1610.

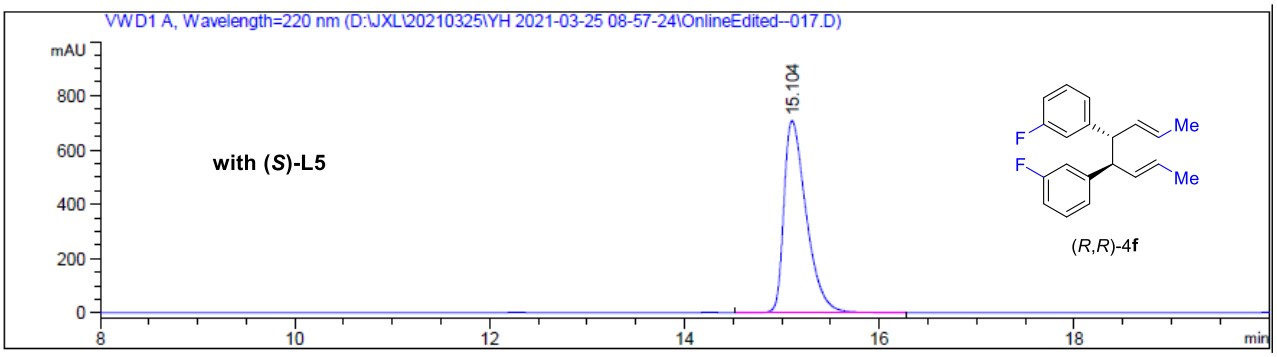
Analysis of Stereochemistry:

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OD*2, hexane/isopropanol = 99/1, flow rate 0.5 mL/min, T = 25 °C, 220 nm): t_R = 14.66 min (major). (±)-**4f**: According to ***General Procedure E.***

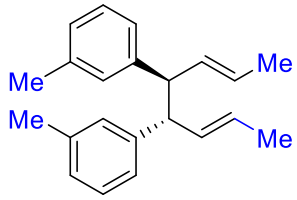




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.652	VB	0.2078	1.51062e4	1117.00781	100.0000



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.104	VB	0.2437	1.13282e4	707.81171	100.0000

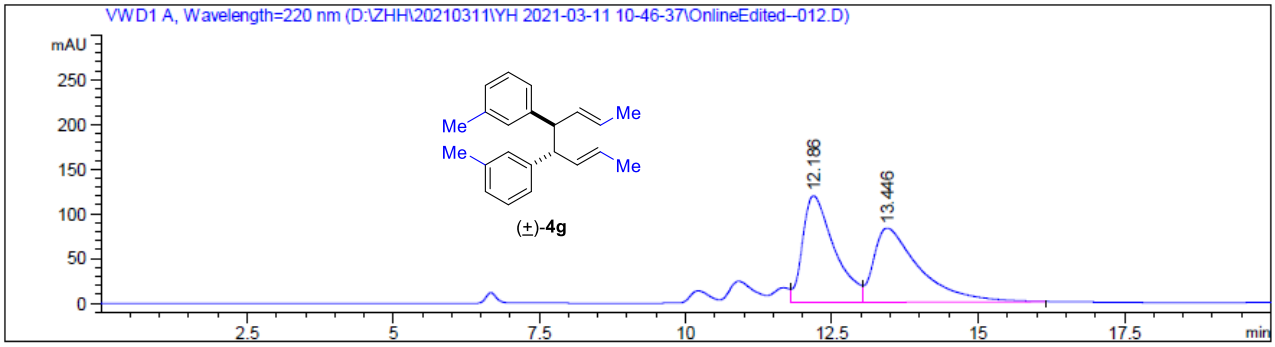


4g

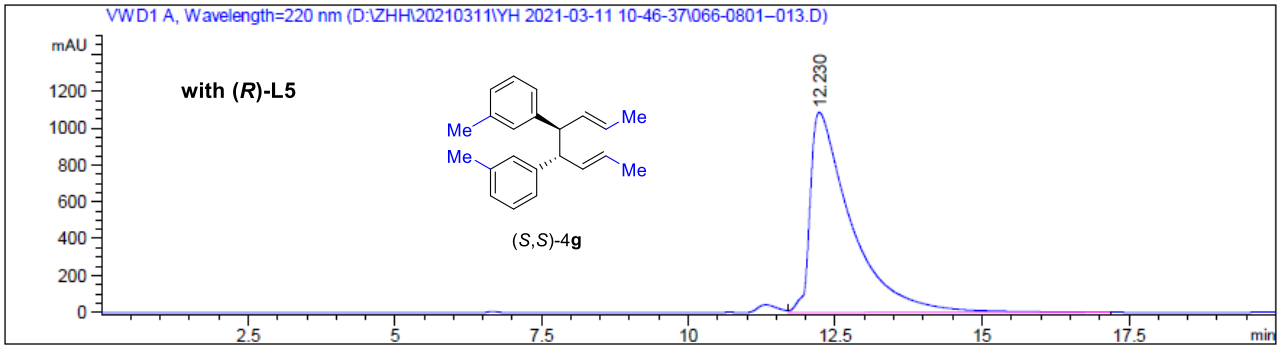
3,3'-((2*E*,4*S*,5*S*,6*E*)-octa-2,6-diene-4,5-diyl)bis(methylbenzene) (4g): According to ***General Procedure F*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100;1; Reaction time = 12 h; yield: 71% (20.6 mg); > 95:5 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -52.1 (c 0.38, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.08 – 6.99 (m, 2H), 6.91 – 6.75 (m, 6H), 5.76 – 5.61 (m, 2H), 5.38 (dq, *J* = 15.2, 6.4 Hz, 2H), 3.52 – 3.45 (m, 2H), 2.24 (s, 6H), 1.67 (dd, *J* = 6.4, 1.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 137.3, 133.4, 129.0, 127.7, 126.4, 126.1, 125.2, 54.9, 21.4, 18.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}$ 291.2107; Found 291.2103.

Analysis of Stereochemistry:

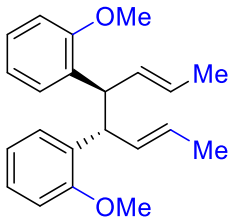
Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak IC, hexane/isopropanol = 100/0, flow rate 0.5 mL/min, T = 25 °C, 220 nm): t_R = 12.23 min (major). (±)-**4g**: According to ***General Procedure D.***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.186	VV	0.5587	4531.29932	119.40931	50.0781
2	13.446	VB	0.7720	4517.16260	82.99200	49.9219



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.230	VB	0.6854	5.28320e4	1084.36841	100.0000

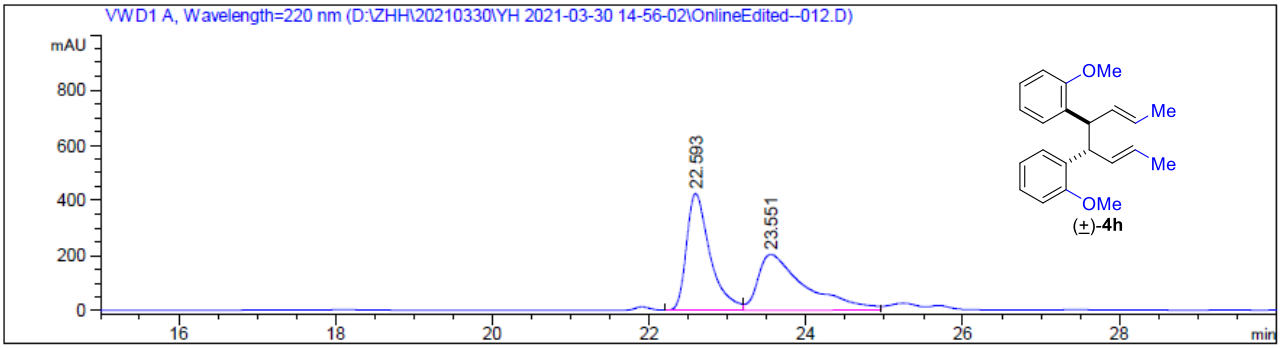


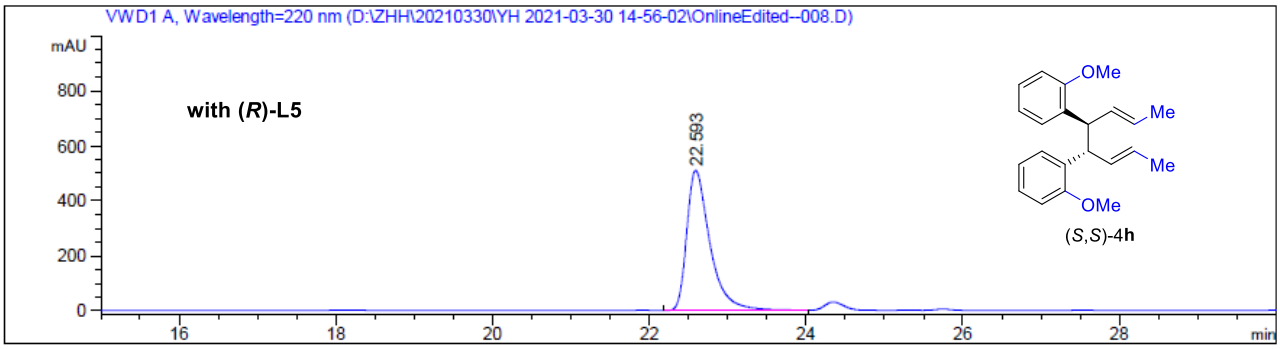
4h

2,2'-((2*E*,4*S*,5*S*,6*E*)-octa-2,6-diene-4,5-diyl)bis(methoxybenzene) (4h): According to ***General Procedure F*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50;1; Reaction time = 12 h; yield: 80% (25.8 mg); > 95:5 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -97.0 (c 0.84, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.08 (dd, *J* = 7.6, 1.7 Hz, 2H), 6.96 (ddd, *J* = 8.2, 7.4, 1.8 Hz, 2H), 6.77 – 6.68 (m, 2H), 6.63 (dd, *J* = 8.2, 1.1 Hz, 2H), 5.72 (ddq, *J* = 12.8, 5.4, 1.7 Hz, 2H), 5.39 (dq, *J* = 15.2, 6.4 Hz, 2H), 4.13 (dd, *J* = 5.4, 2.4 Hz, 2H), 3.70 (s, 6H), 1.65 (dd, *J* = 6.4, 1.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 133.8, 132.5, 128.7, 126.4, 125.6, 120.0, 110.4, 55.4, 46.1, 18.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}O_2$ 323.2006; Found 323.2001.

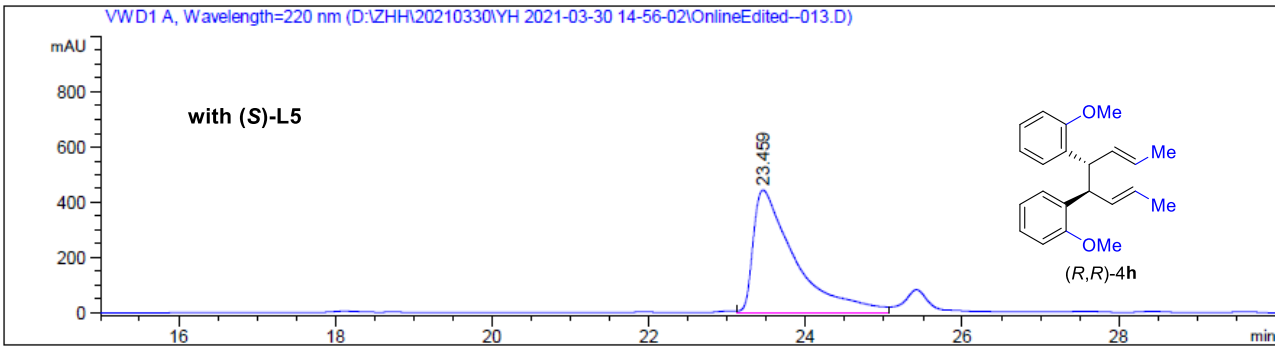
Analysis of Stereochemistry:

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OD*3, hexane/ethanol = 99/1, flow rate 0.5 mL/min, T = 25 ºC, 220 nm): t_R = 22.59 min (major). (±)-**4h**: According to ***General Procedure E.***

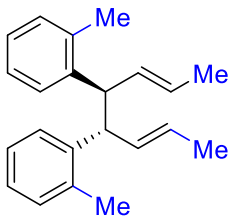




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.593	VV	0.3125	1.05981e4	509.94150	100.0000



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.459	VV	0.5119	1.64358e4	443.96310	100.0000

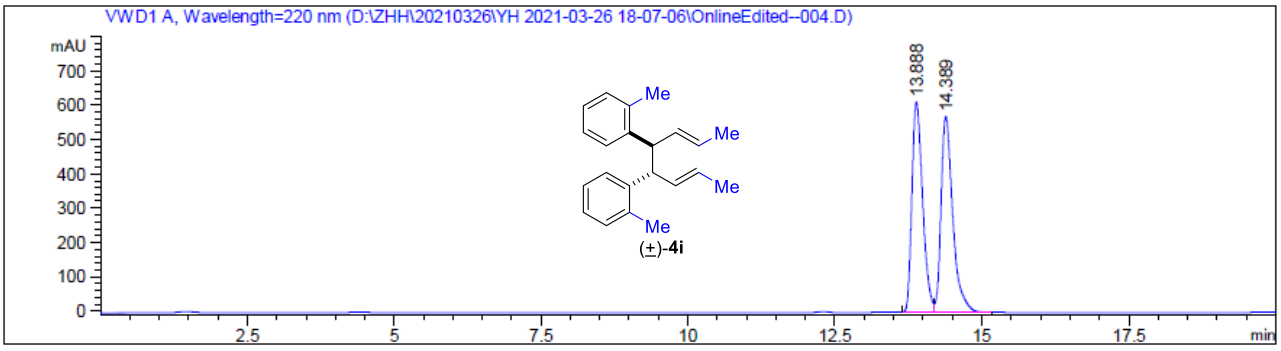


4i

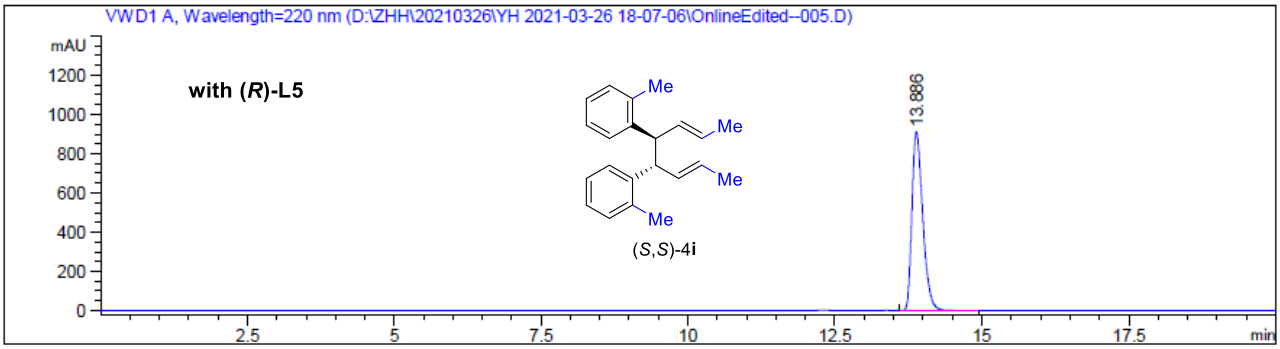
2,2'-((2*E*,4*S*,5*S*,6*E*)-octa-2,6-diene-4,5-diyl)bis(methylbenzene) (4i): According to ***General Procedure F*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100;1; Reaction time = 12 h; yield: 81% (23.5 mg); > 95:5 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -170.2 (c 0.47, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.09 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.05 – 6.98 (m, 2H), 6.98 – 6.86 (m, 4H), 5.62 (dddd, *J* = 15.1, 7.3, 3.3, 1.5 Hz, 2H), 5.35 (dq, *J* = 15.2, 6.4 Hz, 2H), 3.90 (dd, *J* = 5.4, 2.4 Hz, 2H), 2.22 (s, 6H), 1.66 (dd, *J* = 6.4, 1.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.9, 130.0, 126.8, 125.7, 125.6, 125.4, 48.6, 19.7, 18.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}$ 291.2107; Found 291.2108.

Analysis of Stereochemistry:

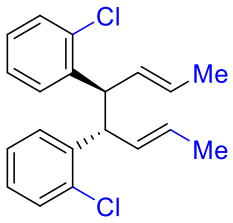
Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OD*2, hexane/isopropanol = 99/1, flow rate 0.5 mL/min, T = 25 °C, 220 nm): t_R = 13.89 min (major). (±)-**4i**: According to ***General Procedure D.***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.888	VV	0.1966	7830.94580	614.78375	49.4414
2	14.389	VB	0.2111	8007.88428	572.68475	50.5586



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.886	VB	0.1970	1.17414e4	913.15112	100.0000

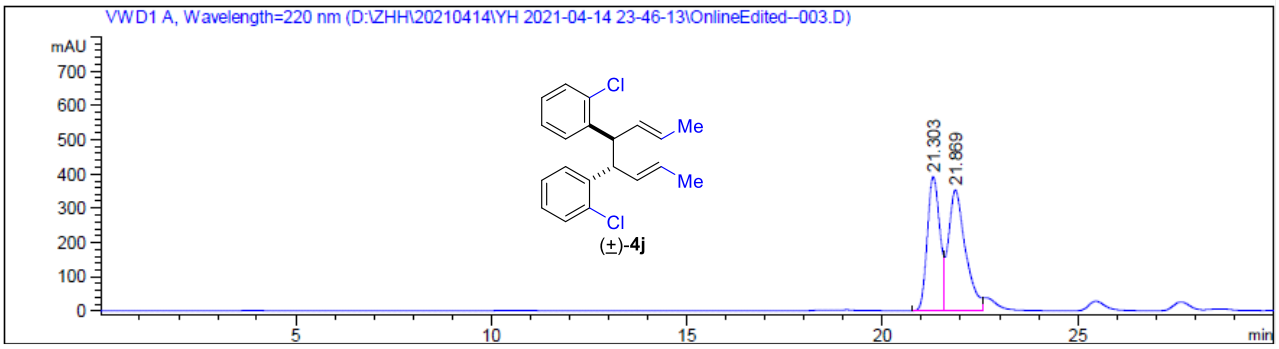


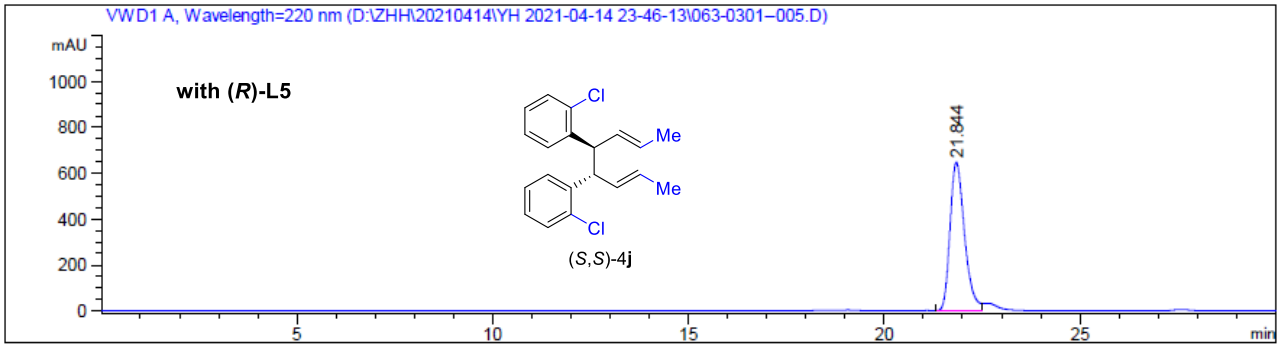
4j

2,2'-((2*E*,4*S*,5*S*,6*E*)-octa-2,6-diene-4,5-diyl)bis(chlorobenzene) (4j): According to ***General Procedure F*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50;1; Reaction time = 12 h; yield: 60% (19.9 mg); > 95:5 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -172.2 (c 0.46, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.16 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.09 – 7.02 (m, 2H), 6.97 – 6.90 (m, 2H), 5.64 – 5.52 (m, 2H), 5.46 (dq, *J* = 15.2, 6.2 Hz, 2H), 4.30 (dd, *J* = 5.0, 2.4 Hz, 2H), 1.66 (dd, *J* = 6.2, 1.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 133.6, 132.4, 129.2, 128.7, 127.1, 126.9, 126.6, 48.3, 18.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{21}Cl_2$ 331.1015; Found 331.1017.

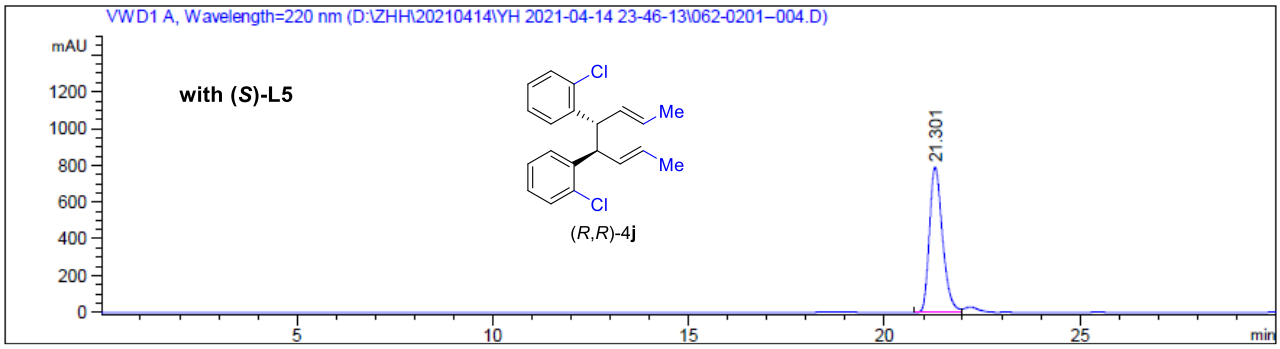
Analysis of Stereochemistry:

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OJ*3, hexane/ethanol = 99/1, flow rate 0.5 mL/min, T = 25 ºC, 220 nm): t_R = 21.84 min (major). (±)-**4j**: According to ***General Procedure E.***

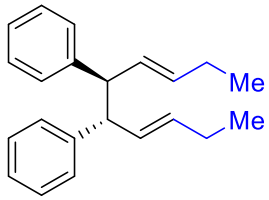




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.844	VV	0.3947	1.67211e4	648.69916	100.0000



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.301	BV	0.3586	1.84599e4	790.12030	100.0000

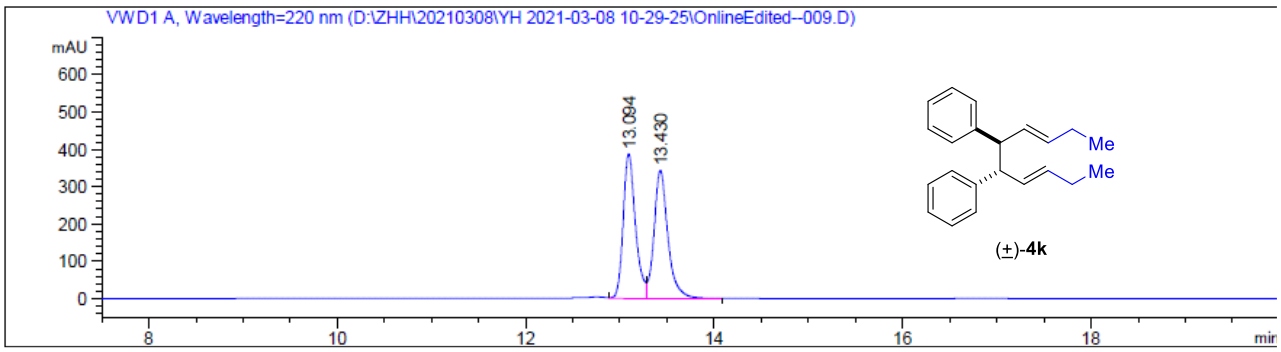


4k

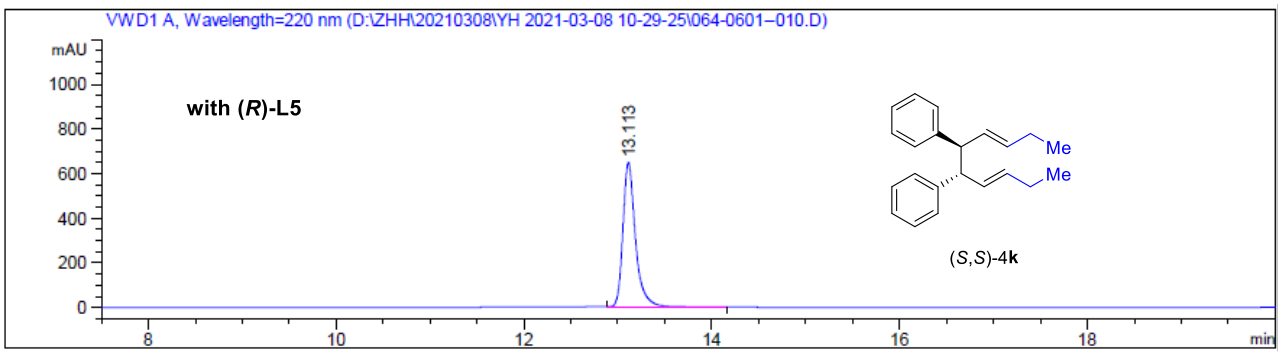
((3E,5S,6S,7E)-deca-3,7-diene-5,6-diyl)dibenzene (4k): According to ***General Procedure F*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100;1; Reaction time = 12 h; yield: 83% (24.1 mg); > 95:5 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -42.3 (c 0.53, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.09 (m, 4H), 7.09 – 6.97 (m, 6H), 5.74 – 5.60 (m, 2H), 5.44 (dt, *J* = 15.2, 6.3 Hz, 2H), 3.52 (dd, *J* = 6.0, 2.4 Hz, 2H), 2.07 – 1.96 (m, 4H), 0.97 (t, *J* = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.8, 133.4, 131.1, 128.2, 127.9, 125.7, 55.2, 25.6, 13.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}$ 291.2107; Found 291.2109.

Analysis of Stereochemistry:

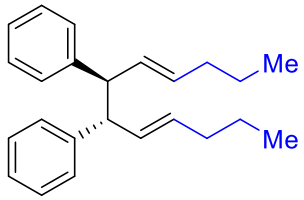
Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak IG*2, hexane/isopropanol = 99/1, flow rate 0.5 mL/min, T = 25 °C, 220 nm): t_R = 13.11 min (major). (±)-**4k**: According to ***General Procedure D.***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.094	VV	0.1365	3511.94653	388.23434	49.8276
2	13.430	VB	0.1541	3536.24634	343.56647	50.1724



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.113	VB	0.1405	6103.20313	650.49219	100.0000

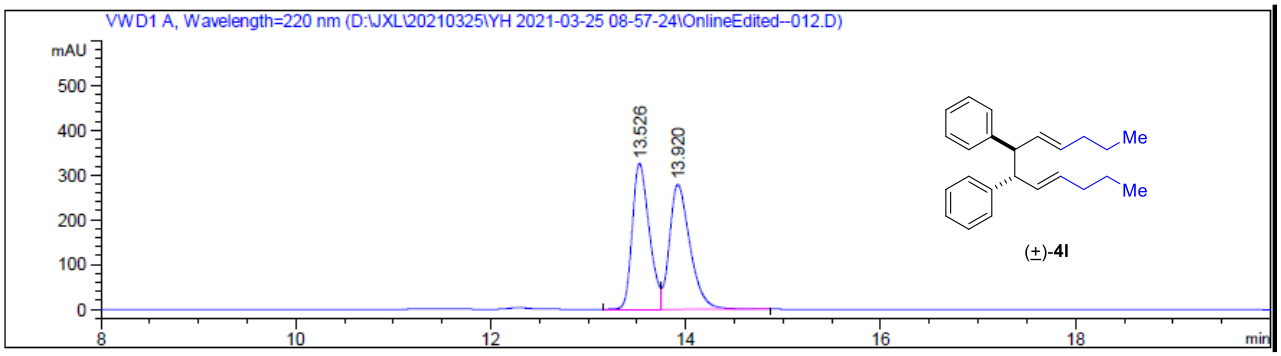


4l

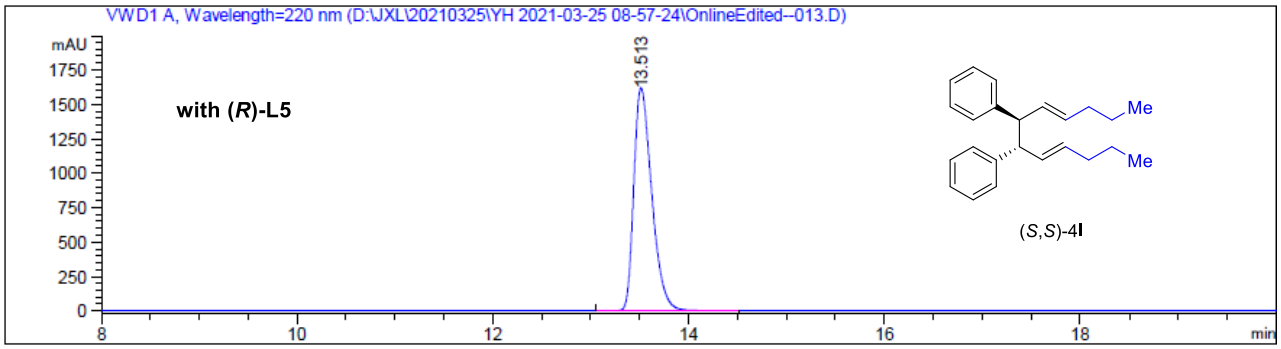
((4*E*,6*S*,7*S*,8*E*)-dodeca-4,8-diene-6,7-diyl)dibenzene (4l): According to ***General Procedure F*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50;1; Reaction time = 12 h; yield: 81% (25.8 mg); > 95:5 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -33.0 (c 0.74, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.08 (m, 4H), 7.07 – 6.95 (m, 6H), 5.76 – 5.61 (m, 2H), 5.39 (dt, *J* = 15.2, 6.8 Hz, 2H), 3.53 (dd, *J* = 6.0, 2.4 Hz, 2H), 2.04 – 1.91 (m, 4H), 1.43 – 1.30 (m, 4H), 0.87 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 132.3, 131.7, 128.2, 127.9, 125.6, 55.2, 34.7, 22.5, 13.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{31}$ 319.2420; Found 319.2424.

Analysis of Stereochemistry:

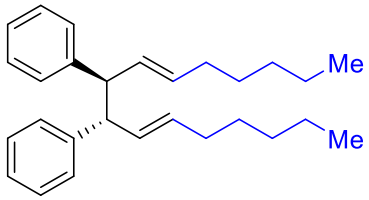
Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OD*2, hexane/isopropanol = 99/1, flow rate 0.5 mL/min, T = 25 ºC, 220 nm): t_R = 13.51 min (major). (±)-**4l**: According to ***General Procedure D.***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.526	BV	0.1857	3955.67944	325.70645	49.1852
2	13.920	VB	0.2210	4086.74316	278.87006	50.8148



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.513	VB	0.1961	2.06802e4	1617.96838	100.0000

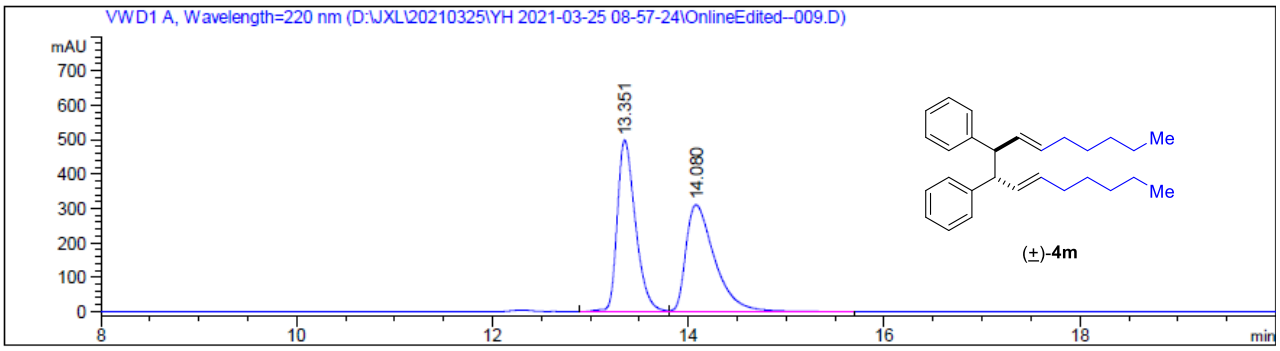


4m

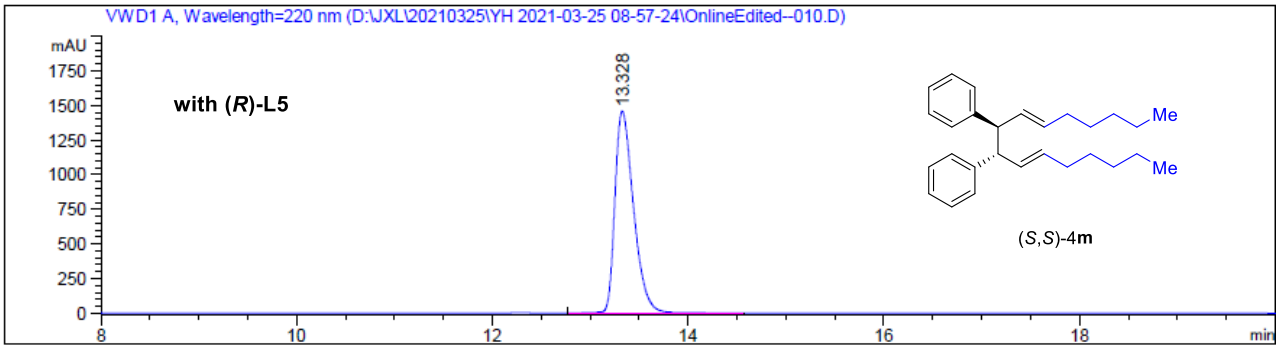
((6*E*,8*S*,9*S*,10*E*)-hexadeca-6,10-diene-8,9-diyl)dibenzene (4m): According to ***General Procedure F*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50;1; Reaction time = 12 h; yield: 85% (31.8 mg); > 95:5 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -50.9 (c 0.94, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.07 (m, 4H), 7.07 – 6.94 (m, 6H), 5.67 (ddd, *J* = 15.3, 6.1, 2.2 Hz, 2H), 5.38 (dt, *J* = 15.1, 6.7 Hz, 2H), 3.61 – 3.43 (m, 2H), 1.98 (q, *J* = 7.0 Hz, 4H), 1.38 – 1.17 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 131.99, 131.95, 128.2, 127.9, 125.6, 55.2, 32.6, 31.4, 29.1, 22.5, 14.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{39}$ 375.3046; Found 375.3048.

Analysis of Stereochemistry:

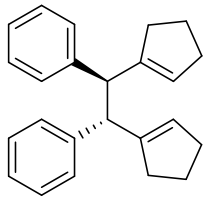
Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OD*2 hexane/isopropanol = 99/1, flow rate 0.5 mL/min, T = 25 °C, 220 nm): t_R = 13.33 min (major). (±)-**4m**: According to ***General Procedure D.***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.351	VV	0.1970	6443.70557	497.94180	50.3415
2	14.080	VB	0.3108	6356.27100	310.48056	49.6585



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.328	VB	0.2034	1.92795e4	1457.16052	100.0000

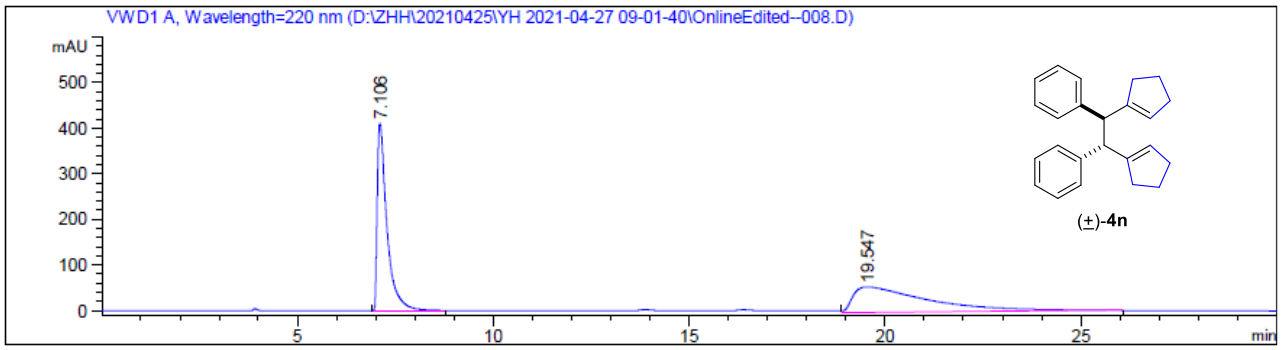


4n

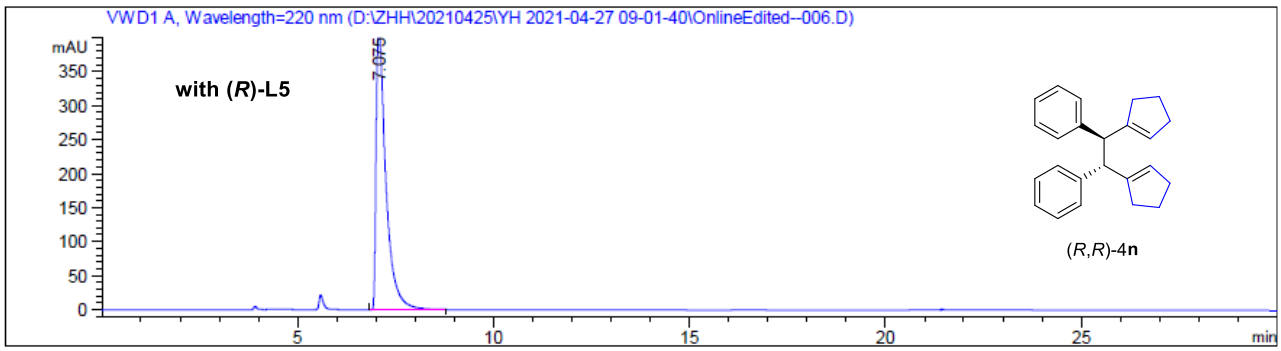
(1*R*,2*R*)-1,2-di(cyclopent-1-en-1-yl)-1,2-diphenylethane (4n): According to ***General Procedure F*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100;1; Reaction time = 12 h; yield: 78% (24.5 mg); > 95:5 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = 36.5 (c 0.49, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 – 7.01 (m, 8H), 7.01 – 6.95 (m, 2H), 5.60 (p, *J* = 2.1 Hz, 2H), 4.05 (s, 2H), 2.27 (dtt, *J* = 12.1, 7.7, 2.2 Hz, 6H), 2.20 – 2.10 (m, 2H), 1.82 – 1.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 142.3, 128.4, 127.7, 125.6, 124.7, 50.9, 32.8, 32.3, 23.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{27}$ 343.2420; Found 343.2426.

Analysis of Stereochemistry:

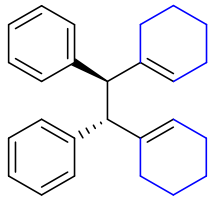
Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OD, hexane/ethanol = 99.9/0.1, flow rate 0.8 mL/min, T = 25 °C, 220 nm): t_R = 7.08 min (major). (±)-**4n**: According to ***General Procedure D.***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.106	BB	0.2516	7057.13330	410.50528	49.0447
2	19.547	MM	2.2108	7332.06641	55.27541	50.9553



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.075	BB	0.2538	7178.58643	414.92944	100.0000



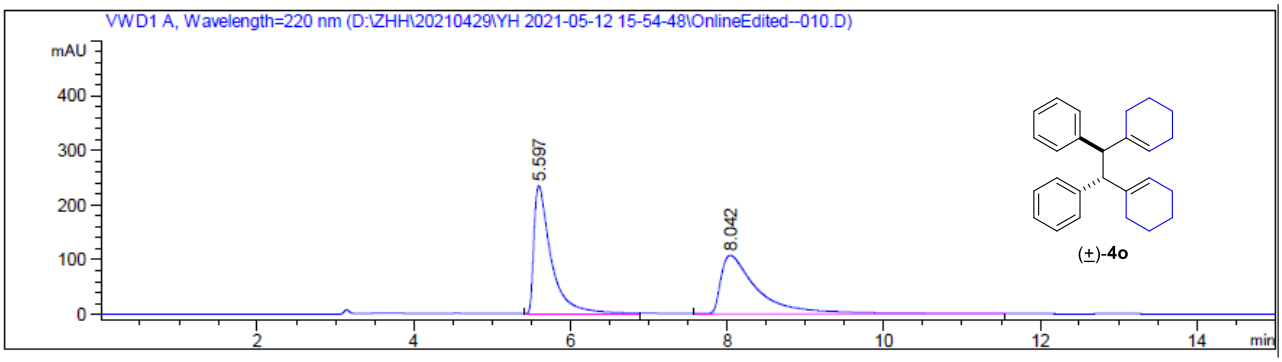
4o

(1*R*,2*R*)-1,2-di(cyclohex-1-en-1-yl)-1,2-diphenylethane (4o): According to ***General Procedure F*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100;1; Reaction time = 12 h; yield: 68% (23.2 mg); > 95:5 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -98.8 (c 0.58, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.05 (m, 8H), 7.04 – 6.94 (m, 2H), 5.74 – 5.67 (m, 2H), 3.92 (s, 2H), 2.08 – 2.00 (m, 6H), 1.73 – 1.62 (m, 2H), 1.53 – 1.43 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 139.2, 128.5, 127.7, 125.5, 122.8, 54.7, 25.6, 24.9, 23.1, 22.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{31}$ 343.2420; Found 343.2423.

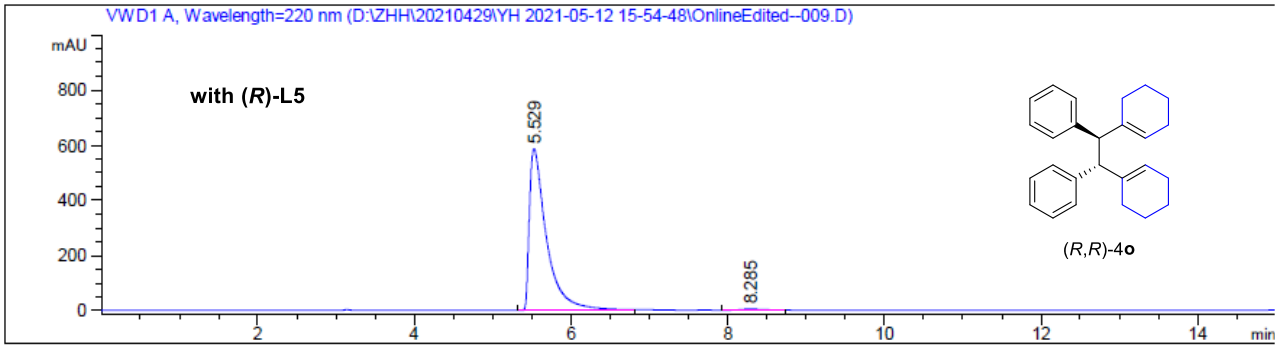
Analysis of Stereochemistry:

Enantiomeric excess: 96%, determined by HPLC (Daicel Chiralpak OD, hexane/isopropanol = 100/0, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 5.53 min (major), t_R = 8.28 min (minor).

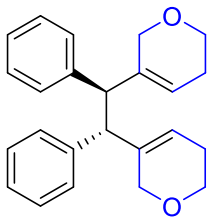
(±)-**4o**: According to ***General Procedure D.***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.597	VV	0.2291	3644.34863	234.73367	50.6715
2	8.042	VB	0.4743	3547.75513	107.14793	49.3285



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.529	BV	0.2278	9060.80176	587.82245	98.2861
2	8.285	MF	0.4617	157.99652	5.70312	1.7139

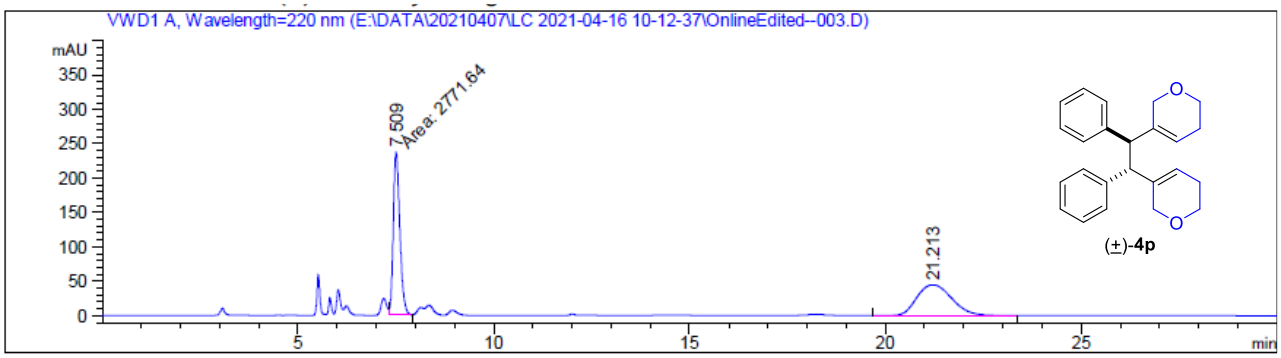


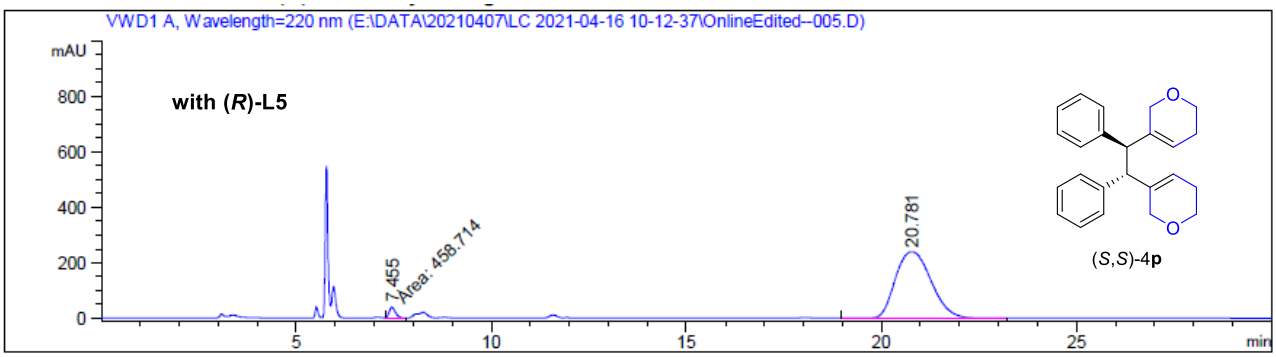
4p

(1*S*,2*S*)-1,2-bis(5,6-dihydro-2*H*-pyran-3-yl)-1,2-diphenylethane (4p): According to ***General Procedure F*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50;1; Reaction time = 12 h; yield: 66% (22.8 mg); > 95:5 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = 47.9 (c 0.61, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.10 – 7.03 (m, 4H), 7.03 – 6.99 (m, 2H), 6.99 – 6.93 (m, 4H), 5.89 (tt, *J* = 3.9, 1.8 Hz, 2H), 4.06 – 3.91 (m, 4H), 3.72 – 3.62 (m, 6H), 2.20 (ddt, *J* = 8.2, 5.4, 2.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 138.2, 128.2, 128.0, 126.1, 119.5, 66.7, 64.3, 51.8, 25.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{27}O_2$ 347.2006; Found 347.2010.

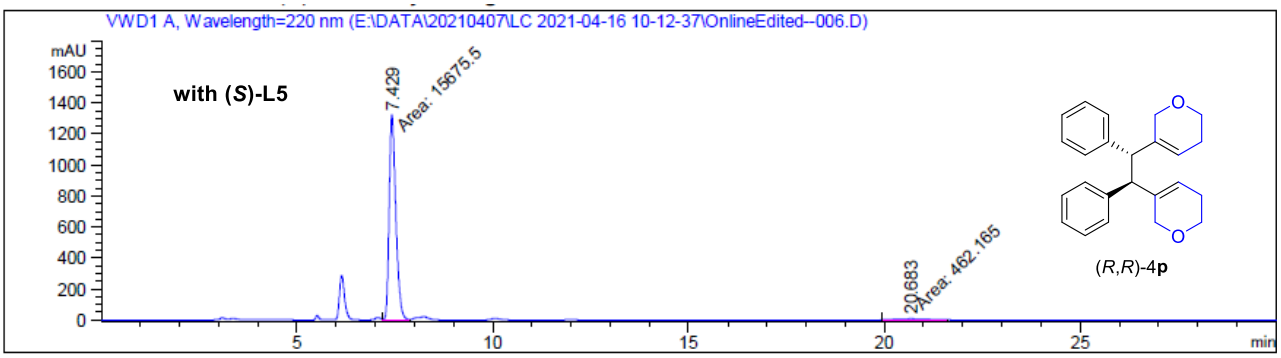
Analysis of Stereochemistry:

Enantiomeric excess: 94%, determined by HPLC (Daicel Chiralpak AD, hexane/ethanol = 95/5, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 20.78 min (major), t_R = 7.46 min (minor). (±)-**4p**: According to ***General Procedure E*.**

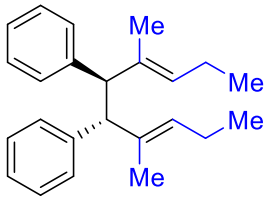




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.455	FM	0.1911	458.71402	40.01353	2.9150
2	20.781	BB	1.0216	1.52774e4	240.34894	97.0850



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.429	MF	0.1975	1.56755e4	1323.14343	97.1361
2	20.683	MF	1.0078	462.16476	7.64327	2.8639

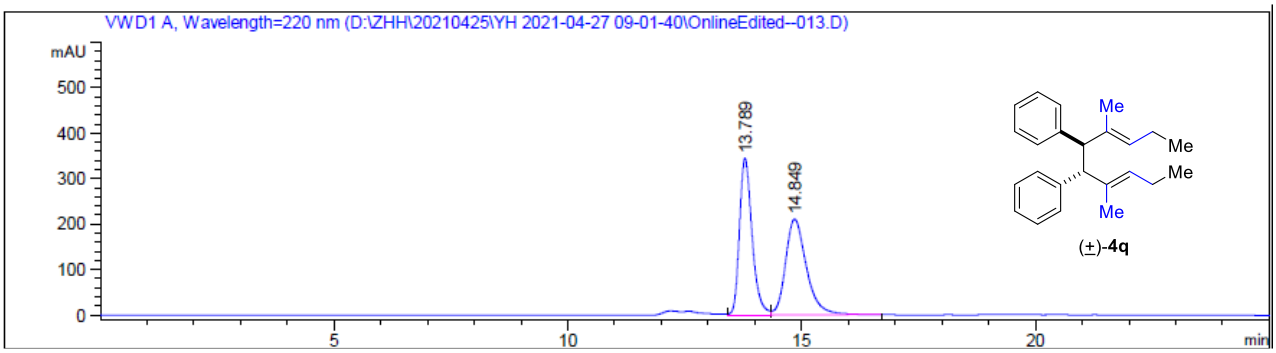


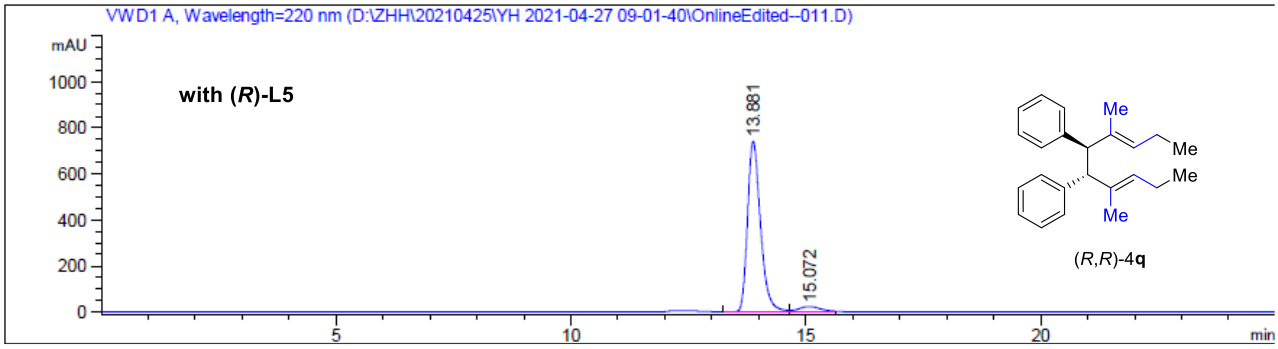
4q

((3*E*,5*R*,6*R*,7*E*)-4,7-dimethyldeca-3,7-diene-5,6-diyl)dibenzene (4q): According to ***General Procedure F*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100;1; Reaction time = 12 h; yield: 60% (19.1 mg); > 95:5 *dr*; >95:5 *rr*; a colourless sticky oil; $[\alpha]_D^{20}$ = -117.4 (c 0.54, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.06 (m, 8H), 7.06 – 6.95 (m, 2H), 5.55 – 5.43 (m, 2H), 3.98 (s, 2H), 1.98 (dq, *J* = 15.1, 7.5 Hz, 4H), 1.48 (s, 6H), 0.95 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 135.9, 128.6, 128.1, 127.7, 125.5, 55.4, 21.1, 14.2, 12.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{31}$ 319.2420; Found 319.2425.

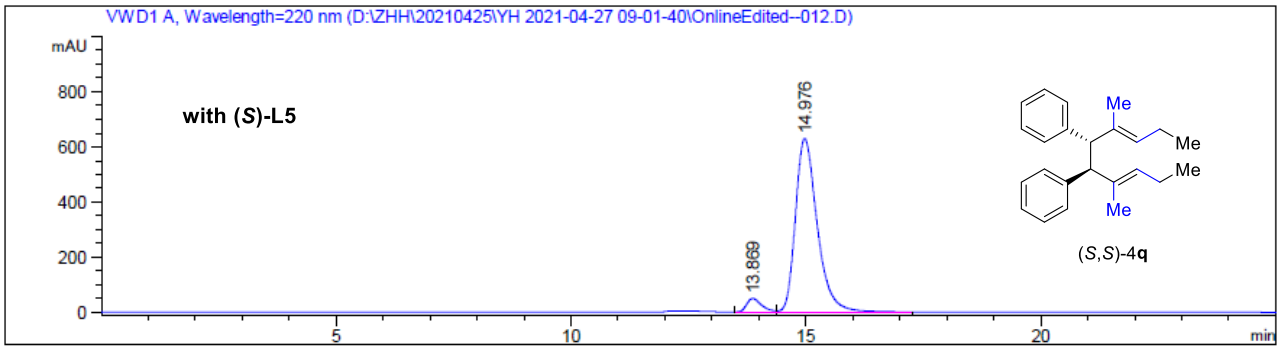
Analysis of Stereochemistry:

Enantiomeric excess: 90%, determined by HPLC (Daicel Chiralpak OJ*2, hexane/ethanol = 99/1, flow rate 0.5 mL/min, T = 25 °C, 220 nm): t_R = 13.88 min (major), t_R = 15.07 min (minor). (±)-**4q**: According to ***General Procedure E*.**

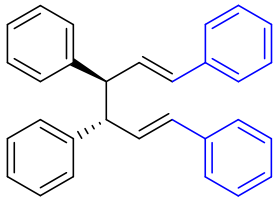




Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.881	VV	0.2959	1.43359e4	740.48389	94.4789
2	15.072	MF	0.5731	837.75256	24.36477	5.5211



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.869	BV	0.3366	1078.89075	48.86450	5.0466
2	14.976	VB	0.4920	2.02997e4	629.78424	94.9534

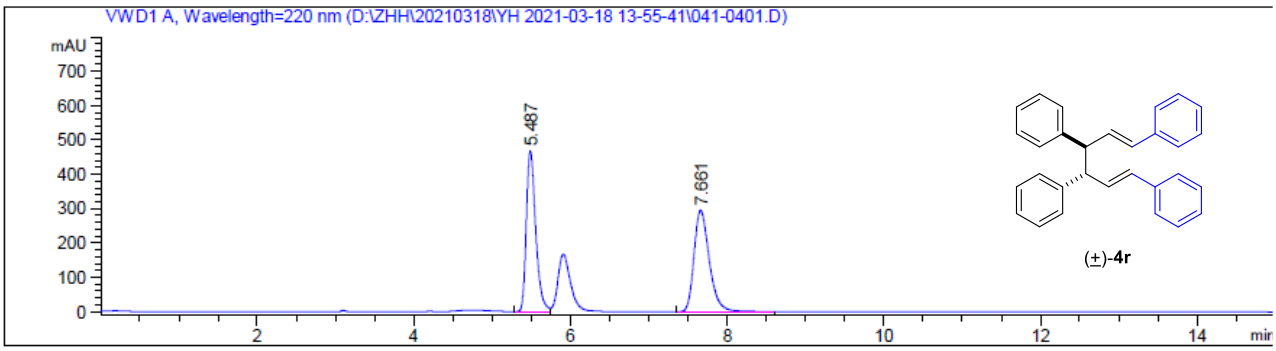


4r

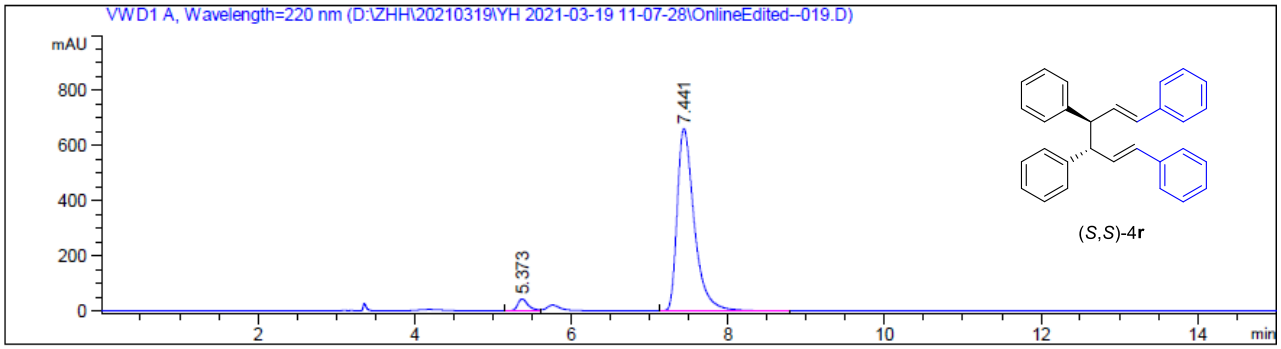
((1*E*,3*S*,4*S*,5*E*)-hexa-1,5-diene-1,3,4,6-tetrayl)tetrabenzene (4r): According to ***General Procedure F*** Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:1 to 50;1; Reaction time = 6 h; yield: 80% (30.9 mg); > 95:5 *dr*; a colourless sticky oil; $[\alpha]_D^{20}$ = 58.5 (c 0.42, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 4H), 7.29 – 7.24 (m, 5H), 7.22 – 7.16 (m, 5H), 7.15 – 7.07 (m, 6H), 6.55 (ddd, *J* = 15.7, 5.7, 2.3 Hz, 2H), 6.41 (d, *J* = 15.8 Hz, 2H), 3.90 (dd, *J* = 5.7, 2.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 137.5, 132.2, 131.4, 128.5, 128.4, 128.2, 127.2, 126.3, 126.2, 55.3; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{27}$ 387.2107; Found 387.2103.

Analysis of Stereochemistry:

Enantiomeric excess: 92%, determined by HPLC (Daicel Chiralpak IG, hexane/isopropanol = 99/1, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 7.44 min (major), t_R = 5.37 min (minor). (±)-**4r**: According to ***General Procedure D.***



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.487	VV	0.1273	3901.98682	467.93869	49.3946
2	7.661	BB	0.2080	3997.62793	295.09470	50.6054



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.373	BV	0.1420	418.11212	43.94594	3.9993
2	7.441	BB	0.2301	1.00365e4	661.06372	96.0007

6. Mechanistic Studies

6.1 Stern-Volmer fluorescence quenching experiments

A Hitachi F-7000 fluoresence spectrometer was used to record the emission intensities. All $Ir(ppy)_2(dtbbpy)PF_6$ solutions were excited at 400 nm and the emission intensity at 553 nm was observed. CH_3CN was degassed with a stream of Ar for 30 min. In a typical experiment, the emission spectrum of a 2×10^{-5} M solution of $Ir(ppy)_2(dtbbpy)PF_6$ in CH_3CN was collected. Then, appropriate amount of quencher was added to the measured solution in a quartz cuvette and the emission spectrum of the sample was collected. I_0 and I represent the intensities of the emission in the absence and presence of the quencher at 553 nm.

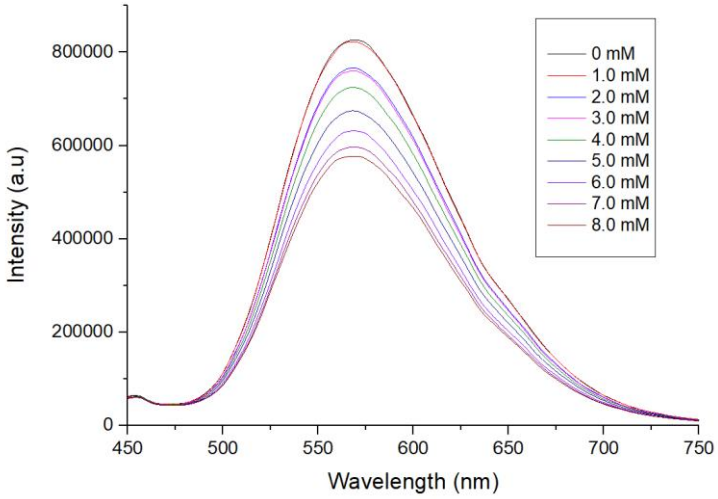


Figure S2. Emission spectra of 2×10^{-5} M Ir(ppy)2(dtbbpy)PF6 at λex = 400nm showing the quenching effect of increasing of DIPEA.

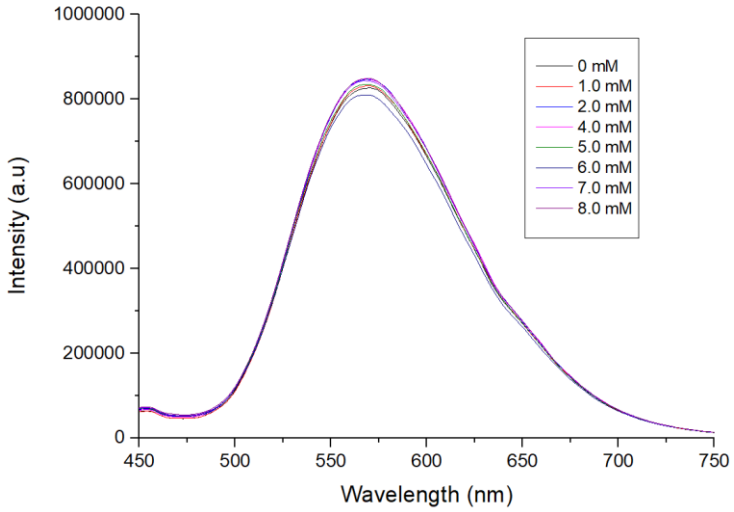


Figure S3. Emission spectra of 2×10^{-5} M Ir(ppy)2(dtbbpy)PF6 at λex = 400nm showing the quenching effect of increasing of **1a**.

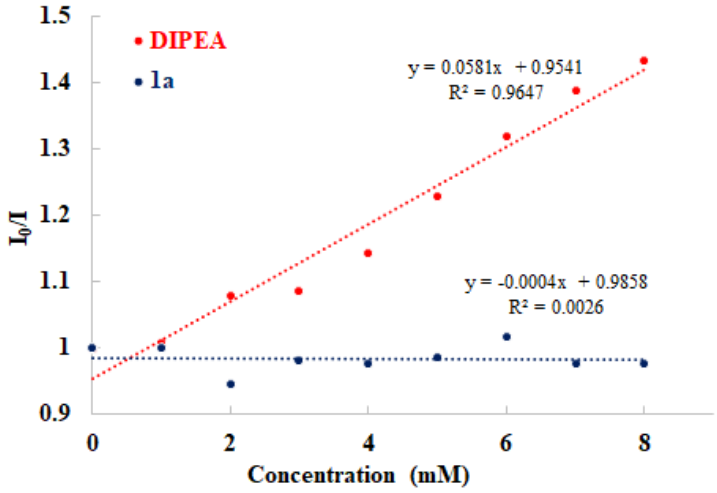
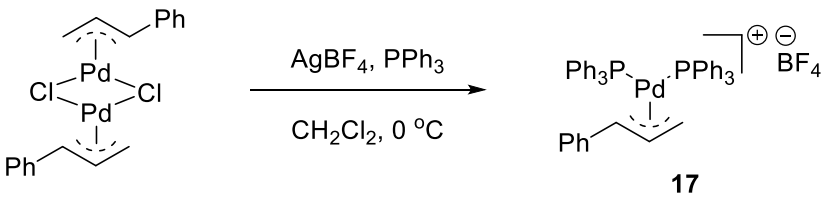


Figure S4. The Stern−Volmer plot.

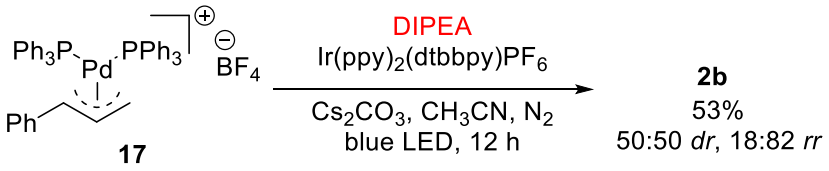
Stern–Volmer quenching experiments indicate that DIPEA quenches photoexcited catalyst **I**.

6.2 Preparation and homocoupling of π-allylpalladium complex 17



17

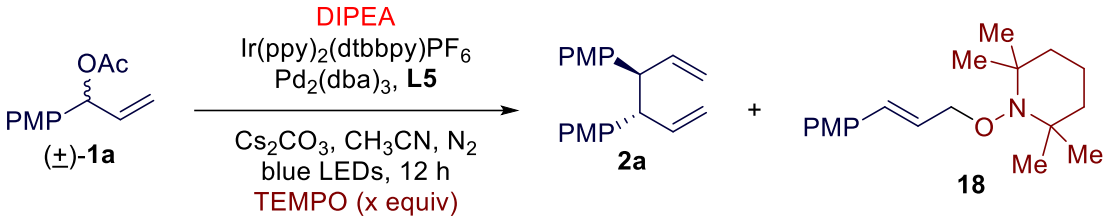
In a glove box, to a 50 mL of seal tube equipped with a stir bar was added Silver tetrafluoroborate (277 mg, 1.43 mmol). The seal tube was screw septum and brought out of the glove box. CH2Cl2 (10 mL) and [Pd(l-Phenylallyl)C1]$_2$ (300 mg, 0.57 mmol) were added to the seal tube at 0 ^{o}C. After stirring for 1 h at this temperature, a solution of PPh_3 (600 mg, 2.28 mmol) in CH_2Cl_2 (10 mL) was added at 0 ^{o}C. The paleyellow suspension was centrifugalized, and the solution was transferred to another seal tube followed by concentration under reduced pressure to give **17** (361 mg, 76%) as a pale yellow powder. This compound is known.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 6.72 (m, 35H), 6.48 – 6.28 (m, 1H), 5.49 – 5.38 (m, 1H), 3.79 (t, *J* = 11.3 Hz, 1H), 3.68 (t, *J* = 6.8 Hz, 1H).



In a nitrogen-filled glovebox, an 8 mL screw-cap test tube, equipped with a magnetic stir bar, charged with Ir(ppy)$_2$(dtbbpy)PF_6 (1.0 mg, 0.001 mmol, 1.0 mol%), Cs_2CO_3 (48.9 mg, 0.15 mmol, 1.5 equiv), π-allylpalladium complex **17** (83.5 mg, 0.1 mmol, 1.0 equiv), DIPEA (20 mg, 0.15 mmol, 1.5 equiv) and anhydrous CH_3CN (1.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously under 45W blue LED lights at room temperature for 12 h. Next, the reaction mixture was transferred to a 250 mL separatory funnel, rinsed/diluted with 100 mL ether, and washed with 100 mL deionized water (twice) and finally 100 mL brine. The organic phase was concentrated under vacuum and purified by chromatography. Flash column chromatography eluent, petroleum ether/ethyl acetate = 100;0 to 100:1; yield: 53% (6.2 mg); 50:50 *dr*; 18:82 *rr*.

This result demonstrates that π-allylpalladium complex might be the key intermediate of this reaction.

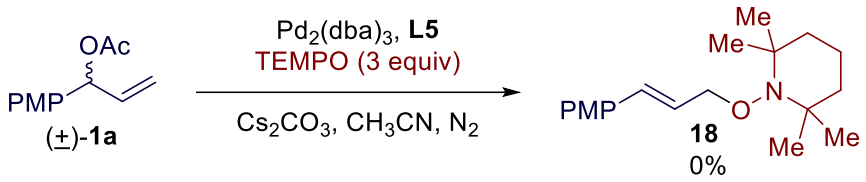
6.3 Radical trap experiments



	2a	18
TEMPO (0 equiv):	92%, >99% *ee*, >95:5 *dr*, > 95:5 *rr*	0%
TEMPO (1 equiv):	62%, >99% *ee*, 89:11 *dr*, > 95:5 *rr*	13%
TEMPO (2 equiv):	12%, >99% *ee*, 89:11 *dr*, > 95:5 *rr*	52%
TEMPO (3 equiv):	0%	64%

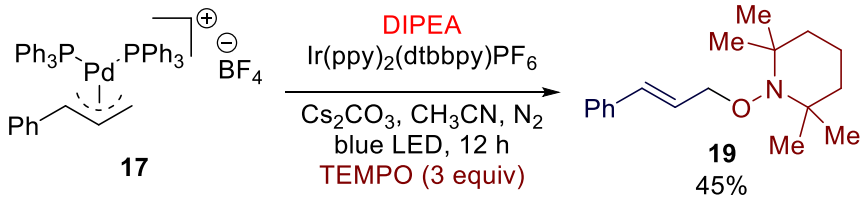
In a nitrogen-filled glovebox, an 8 mL screw-cap test tube, equipped with a magnetic stir bar, charged with $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol, 1.25 mol%), (*R*)-2,2'-Bis[bis(4-methoxy-3,5-di-*t*-butylphenyl)phosphino]-4,4',6,6'-tetramethoxy)-1,1'-biphenyl (**L5**) (7.3 mg, 0.006 mmol, 3 mol%), anhydrous CH_3CN (1.0 mL) was added and the mixture was stirred for 30 min. Then the following chemicals were added in turn: $Ir(ppy)_2(dtbbpy)PF_6$ (2.0 mg, 0.002 mmol, 1.0 mol%), Cs_2CO_3 (97.8 mg, 0.3 mmol, 1.5 equiv), allylic acetates **1a** (41.2 mg, 0.2 mmol, 1.0 equiv), DIPEA (40 mg, 0.3 mmol, 1.5 equiv), 2,2,6,6-tetramethylpiperidine-*N*-oxyl radical (TEMPO, x equiv, x = 1, 2, 3) and anhydrous CH_3CN (1.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously under 45W blue LED lights at room temperature for 12 h. Next, the reaction mixture was transferred to a 250 mL separatory funnel, rinsed/diluted with 100 mL ether, and washed with 100 mL deionized water (twice) and finally 100 mL brine. The organic phase was concentrated under vacuum and purified by chromatography.

when the radical trapping reagent TEMPO was added to the model reaction of **1a**, the reaction efficiency decreased dramatically, and the allyl-TEMPO adduct **18** was isolated. This compound is known.[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 6.91 – 6.82 (m, 2H), 6.55 (dt, *J* = 16.0, 1.5 Hz, 1H), 6.17 (dt, *J* = 15.9, 6.1 Hz, 1H), 4.43 (dd, *J* = 6.1, 1.5 Hz, 2H), 3.81 (s, 3H), 1.63 – 1.31 (m, 6H), 1.22 (s, 6H), 1.14 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 131.2, 129.9, 127.6, 123.3, 113.9, 78.3, 59.8, 55.3, 39.7, 33.1, 20.3, 17.2.



In a nitrogen-filled glovebox, an 8 mL screw-cap test tube, equipped with a magnetic stir bar, charged with $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol, 1.25 mol%), (*R*)-2,2'-Bis[bis(4-methoxy-3,5-di-*t*-butylphenyl)phosphino]-4,4',6,6'-tetramethoxy)-1,1'-biphenyl (**L5**) (7.3 mg, 0.006 mmol, 3 mol%), anhydrous CH_3CN (1.0 mL) was added and the mixture was stirred for 30 min. Then the following chemicals were added in turn: Cs_2CO_3 (97.8 mg, 0.3 mmol, 1.5 equiv), allylic acetates **1a** (41.2 mg, 0.2 mmol, 1.0 equiv), 2,2,6,6-tetramethylpiperidine-*N*-oxyl radical (TEMPO, 93.6 mg, 0.6 mmol, 3 equiv) and anhydrous CH_3CN (1.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously at room temperature for 12 h.

The allyl-TEMPO adduct **18** could not be detected in the absence of reductive photocatalysis conditions, which revealed that the radical trapping product was not formed through the directly nucleophilic addition of TEMPO to the formed π-allylpalladium complex.



In a nitrogen-filled glovebox, an 8 mL screw-cap test tube, equipped with a magnetic stir bar, charged with $Ir(ppy)_2(dtbbpy)PF_6$ (1.0 mg, 0.001 mmol, 1.0 mol%), Cs_2CO_3 (49.8 mg, 1.5 mmol, 1.5 equiv), π-allylpalladium complex **17** (83.5 mg, 0.1 mmol, 1.0 equiv), DIPEA (20 mg, 1.5 mmol, 1.5 equiv), 2,2,6,6-tetramethylpiperidine-*N*-oxyl radical (TEMPO, 46.8 mg, 0.3 mmol, 3 equiv) and anhydrous CH_3CN (1.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously under 45W blue LED lights at room temperature for 12 h. Next, the reaction mixture was transferred to a 250 mL separatory funnel, rinsed/diluted with 100 mL ether, and washed with 100 mL deionized water (twice) and finally 100

mL brine. The organic phase was concentrated under vacuum and purified by chromatography.

In the presence of TEMPO, allyl radical trapping **19** was also observed in the reaction of π-allylpalladium complex **17.** This compound is known.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.1 Hz, 2H), 7.37 – 7.29 (m, 2H), 7.26 – 7.18 (m, 1H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.31 (dt, *J* = 16.0, 5.9 Hz, 1H), 4.47 (dd, *J* = 6.0, 1.6 Hz, 2H), 1.71 – 1.55 (m, 1H), 1.50 (d, *J* = 4.3 Hz, 4H), 1.41 – 1.31 (m, 1H), 1.23 (s, 6H), 1.16 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 131.4, 128.5, 127.5, 126.5, 125.6, 78.1, 59.8, 39.7, 33.1, 20.3, 17.2.

These results suggest that allylic radical might be generated from π-allylpalladium complex in the assistance of light and photocatalyst.

6.4 Cyclic Voltammetry experiments

Cyclic Voltammetry were collected using CHI660E from Shanghai Chenhua Instruments Limited (SCHI). A solution of the sample in MeCN (0.001 M) was tested with 0.1 M Bu_4NPF_6 as the supporting electrolyte, using a glassy carbon as the working electrode, a Pt as the counter electrode, and a saturated calomel electrode reference electrode. Scan rate = 0.1 V/s.

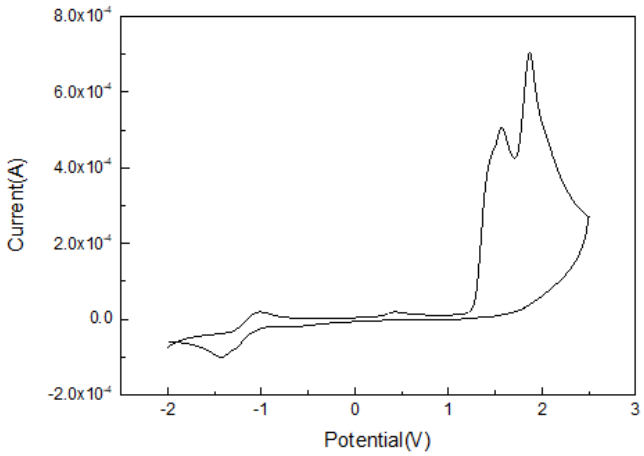


Figure S5. Cyclic Voltammogram of **1b**, $E_{1/2}$ = − 1.43 V *vs* SCE.

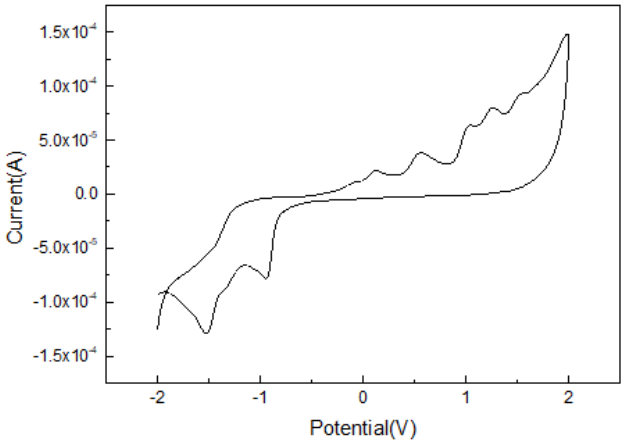


Figure S6. Cyclic Voltammogram of **17**, $E_{1/2}$ = − 0.95 V *vs* SCE.

The redox potentials indicate that the allyl radical is more likely generated from π-allylpalladium complex **17**, which is more easily reduced than allylic acetate **1b** by Ir(II) complex ($E_{1/2}$ (Ir^{III}/Ir^{II}) = − 1.51 V *vs* SCE) to give the allylic radical.

6.5 Proposed mechanism

Based on the abovementioned results and previous published work on photoredox/Pd cocatalysis, plausible mechanisms are depicted in Figure S6 and Figure S7.

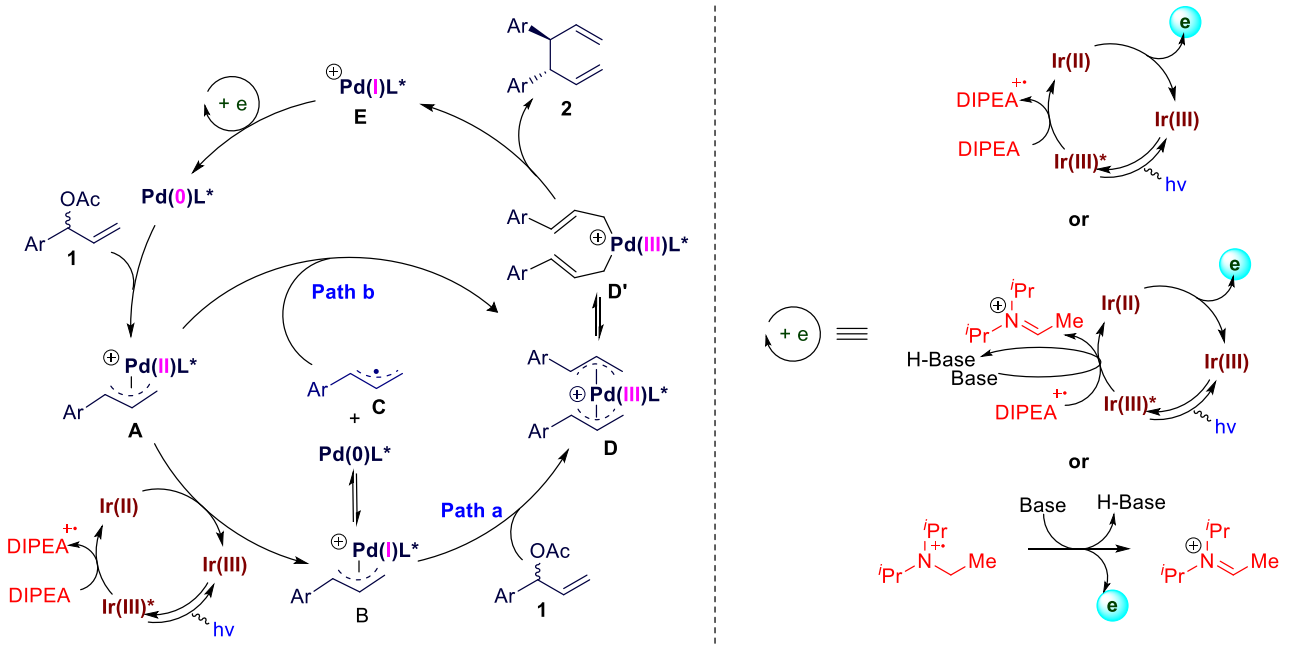


Figure S7. Pd(0/II/III/I) mechanism.

DIPEA ($E_{1/2}$ = + 0.68 V *vs* SCE) quenches visible-light excited Ir(III)* ($E_{1/2}$ (Ir^{III}*/Ir^{II}) = + 0.66 V

vs SCE) to generate low-valent Ir(II) complex and the radical cation $DIPEA^{+\bullet}$. Meanwhile, Pd(0) oxidatively adds to the allylic acetate **1** to give a π-allyl-Pd(II) complex **A**. The single-electron reduction of **A** by Ir(II) complex can generate a π-allyl-Pd(I) complex **B**, which can equilibrate with an allylic radical species **C** and a Pd(0) species. The second oxidative addition of another allylic acetate **1** to **B** would give the bis(π-allyl)-Pd(III) complex **D** equilibrated with bis(η^1-allyl)-Pd(III) complex **D'** (Path a). Alternatively, allylic radical species **C** is trapped by π-allyl-Pd(II) complex **A** to generate **D**/**D'**(Path b). Reductive elimination from **D**/**D'** yields the homocoupling product **2** and a Pd(I) species **E.** Finally single-electron reduction of **E** more likely by Ir(II) complex would regenerate Pd(0).

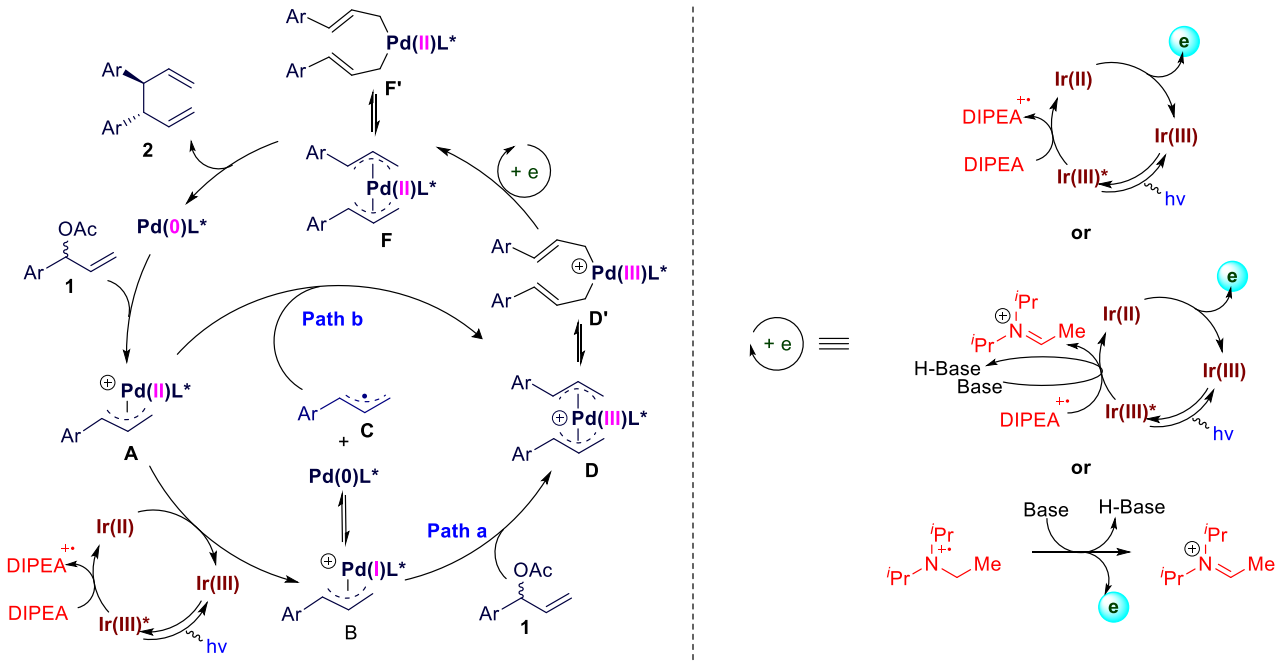


Figure S8. Pd(0/II/III/II) mechanism.

The Pd(III) intermediate **D**/**D'** could also be reduced to a bis(allyl)-Pd(II) species **F**/**F'**, and then undergo a reductive elimination to deliver the final product **2**.

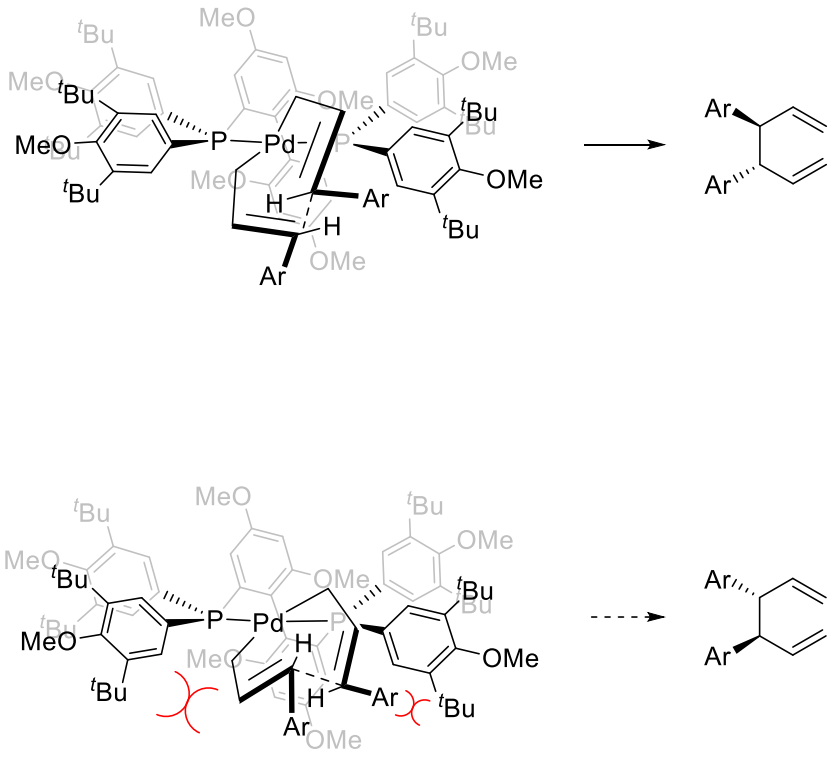
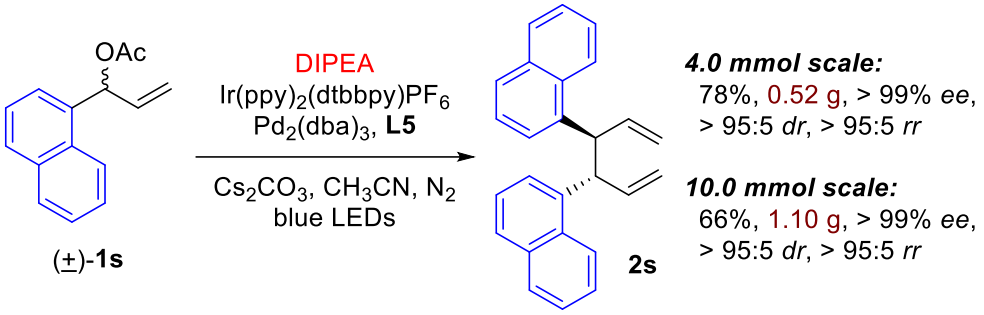
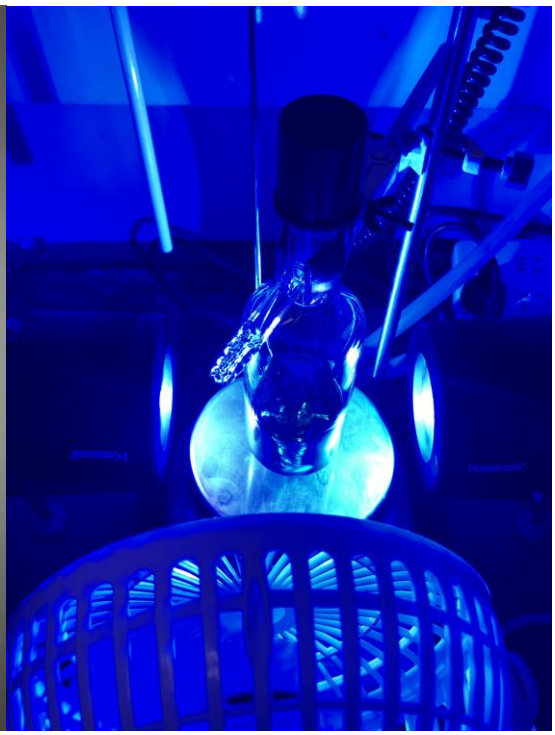


Figure S9. Proposed asymmetric induction model.

7. Gram-scale preparation of 2s

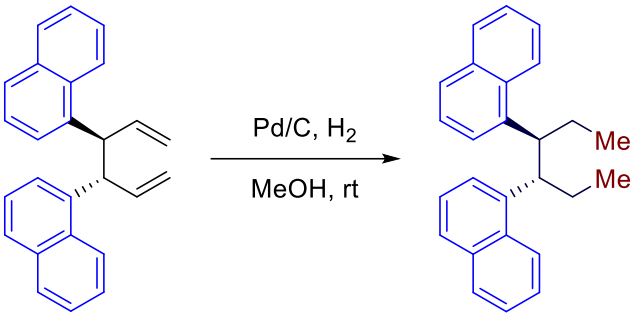


In a nitrogen-filled glovebox, a 500 mL round bottom flask, equipped with a magnetic stir bar, charged with $Pd_2(dba)_3$ (1.25 mol%, 4 mmol scale: 46 mg, 0.05 mmol; 10 mmol scale: 115 mg, 0.125 mmol), (*R*)-2,2'-Bis[bis(4-methoxy-3,5-di-t-butylphenyl)phosphine]-4,4',6,6'-tetramethoxy)-1,1'-biphenyl (**L5**) (3 mol%, 4 mmol scale:146 mg, 0.12 mmol; 10 mmol scale: 365 mg, 0.3 mmol), anhydrous CH_3CN (4 mmol scale: 20.0 mL; 10 mmol scale: 50.0 mL) was added and the mixture was stirred for 30 min. Then the following chemicals were added in turn: $Ir(ppy)_2(dtbbpy)PF_6$ (1.0 mol%, 4 mmol scale: 40 mg, 0.04 mmol; 10 mmol scale:100 mg, 0.1 mmol), Cs_2CO_3 (1.5 equiv, 4 mmol scale: 1.956 g, 6 mmol; 10 mmol scale: 4.89 g, 15 mmol), allylic acetates **1s** (1.0 equiv, 4 mmol scale: 0.904 g, 4.0 mmol; 10 mmol scale: 2.26 g, 10.0 mmol), DIPEA (1.5 equiv, 4 mmol scale: 0.8 g, 6 mmol; 10 mmol scale: 2.0 g, 15 mmol) and anhydrous CH_3CN (4 mmol scale: 20.0 mL; 10 mmol scale: 50.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously under 45 W blue LED lights at room temperature for 12 h. Next, the reaction mixture was transferred to a 500 mL separatory funnel, rinsed/diluted with 200 mL ether, and washed with 200 mL deionized water (twice) and finally 100 mL brine. The organic phase was concentrated under vacuum and purified by chromatography to **2s** (4 mmol scale: 0.52 g, 78%; 10 mmol scale: 1.10 g, 66%).

8. Derivatization of 2s

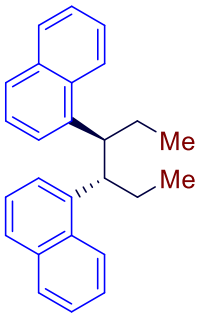
Hydrogenation of 2s



2s
> 99% *ee*

5
98%, > 99% *ee*

In an oven and vacuum-dried 10 mL two-necked round-bottom flask, a solution of **2s** (0.2 mmol, 1.0 equiv) in EtOH (2 mL), 10% Pd/C (0.01 mmol, 5 mol%) was added. The resulting mixture was degassed and stirred under H_2 balloon pressure for 12 h at room temperature. The reaction mixture was filtered and washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure and the residue was purified by chromatography on silica gel to afford compound **5**.

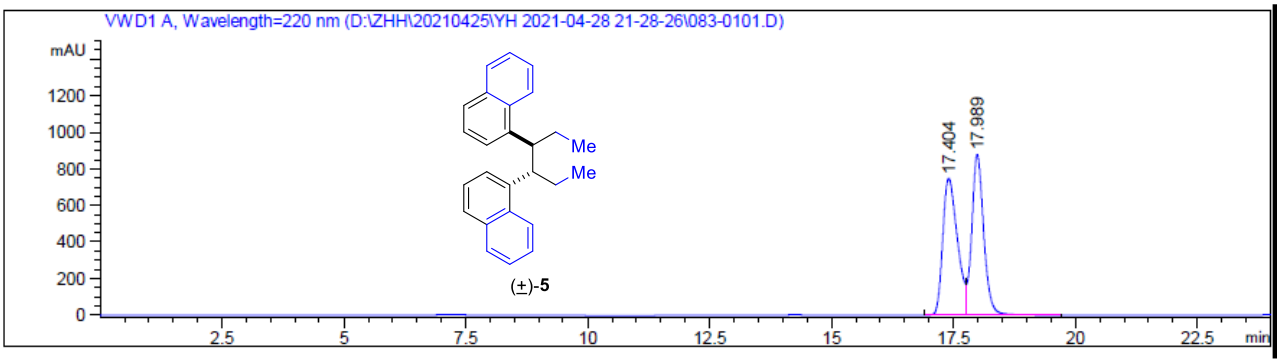


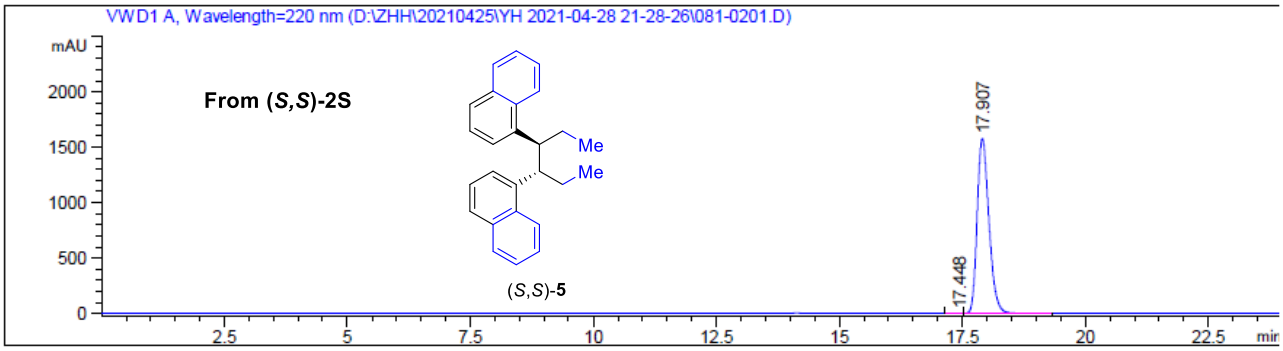
5

1,1'-((3*S*,4*S*)-hexane-3,4-diyl)dinaphthalene (5): Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100;1; yield: 98% (66.2 mg); a colourless sticky oil; $[\alpha]_D^{20}$ = -171.5 (c 1.15, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.58 – 7.45 (m, 4H), 7.45 – 7.38 (m, 2H), 7.34 – 7.15 (m, 4H), 4.20 – 3.80 (m, 2H), 2.27 – 2.11 (m, 2H), 2.03 – 1.90 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2, 133.7, 132.8, 128.8, 126.0, 125.3, 125.0, 124.9, 123.6, 44.3, 25.9, 11.7; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{27}$ 339.2107; Found 339.2110.

Analysis of Stereochemistry:

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OD, hexane/isopropanol = 99/1, flow rate 0.5 mL/min, T = 25 ºC, 220 nm): t_R = 17.91 min (major), t_R = 17.45 min (minor).





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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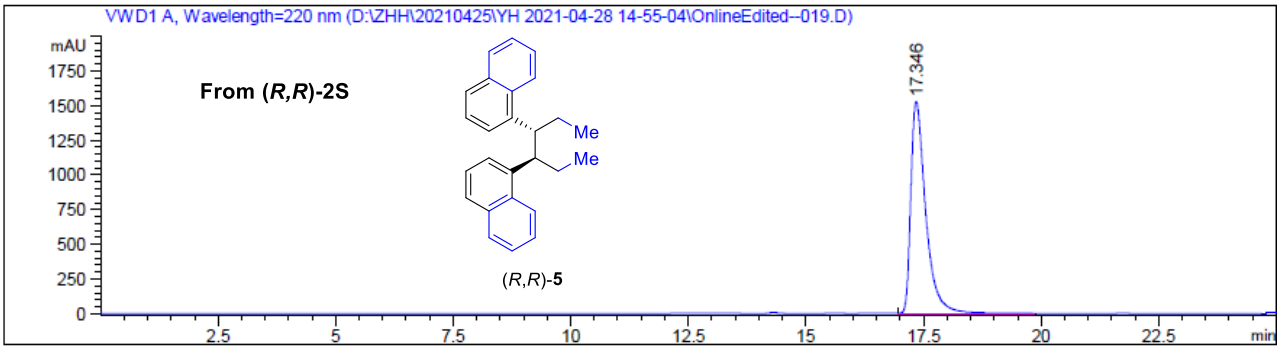
2	17.907	VB	0.2576	2.63083e4	1577.32166	99.8519



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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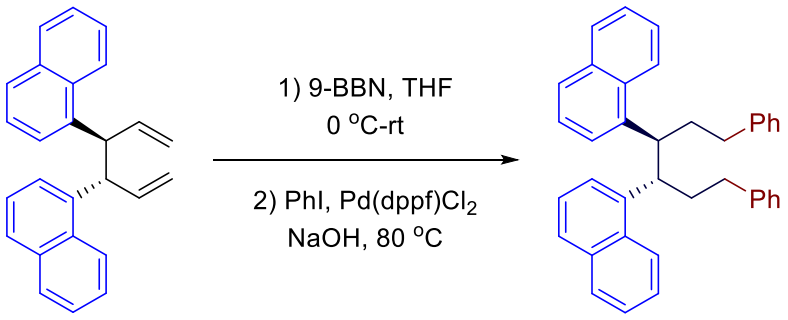
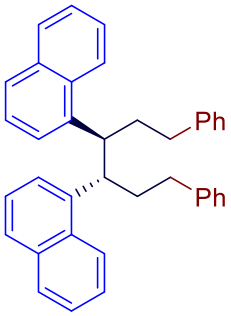
Hydroboration/Suzuki cross-coupling of 2s



2s
> 99% *ee*

6
76%, > 99% *ee*

To the dry 25 mL flask with a magnetic stirring bar was added 2s (0.2 mmol, 1.0 equiv.) and dry THF (2.0 mL) and then added the solution of 9-BBN (1.0 mL, 0.5 M, 0.5 mmol, 2.5 equiv) at 0 °C under N_2 atmosphere. After 12 h at rt, Pd(dppf)Cl_2 (10 mol%), iodobenzene (4.0 equiv) and aqueous NaOH (3.0 mL, 3 M) were added successively to the above mixture at rt and then reacted 16 h under reflux. The reaction mixture was diluted with hexane (10.0 mL), and the residual borane was oxidized by addition of H_2O_2 (30%, 2.0 mL) at rt. The mixture was extracted with CH_2Cl_2 (3 × 5.0 mL). The residue was purified by chromatography on silica gel to afford compound **6**.



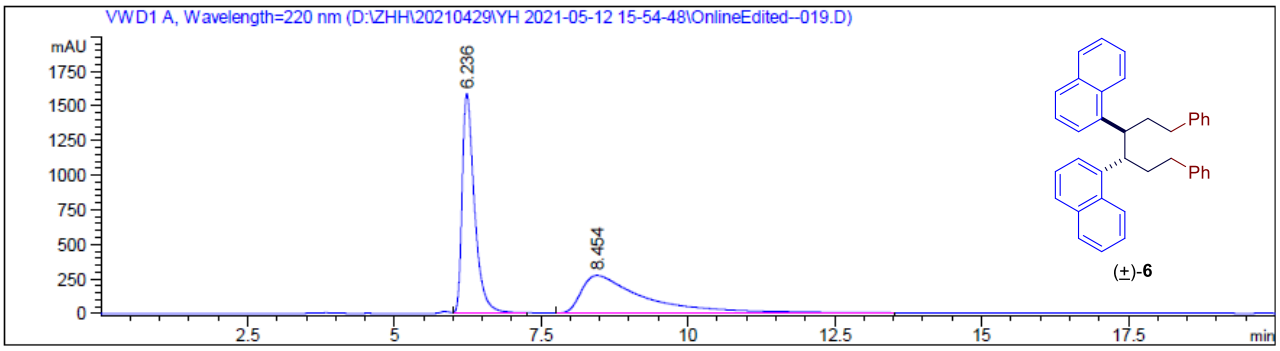
6

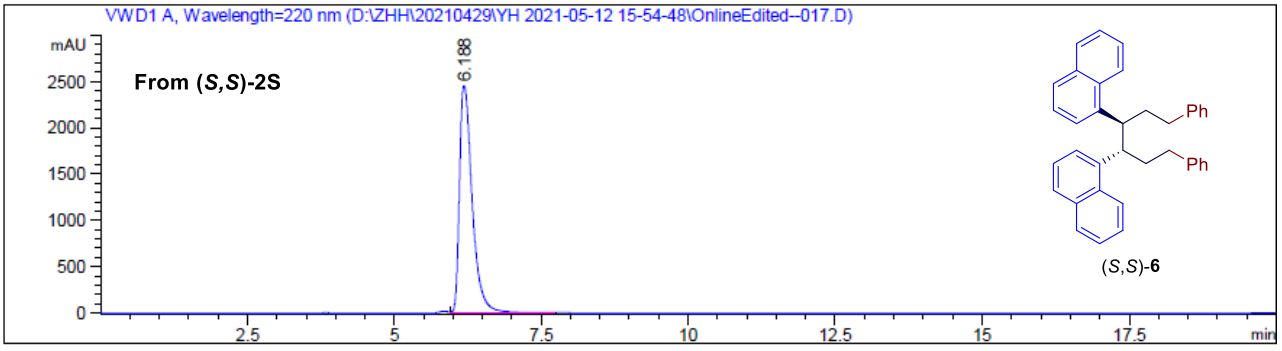
1,1'-((3*S*,4*S*)-1,6-diphenylhexane-3,4-diyl)dinaphthalene (6): Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100;1; yield: 76% (74.5 mg); a colourless sticky oil; $[\alpha]_D^{20}$ = -118.9 (c 1.37, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.01 (m, 2H), 7.85 – 7.72 (m, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.53 – 7.37 (m, 6H), 7.31 (d, *J* = 7.2 Hz, 2H), 7.25 – 7.20 (m, 4H), 7.19 – 7.14 (m, 2H), 7.05 – 6.94 (m, 4H), 4.30 – 3.88 (m, 2H), 2.62 – 2.46 (m, 2H), 2.45 – 2.25 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 139.8, 133.8, 132.7, 128.8, 128.4, 128.3, 126.5, 125.7, 125.3, 125.1, 125.0, 123.7, 43.7, 35.1, 33.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{38}H_{35}$ 491.2733;

Found 491.2738.

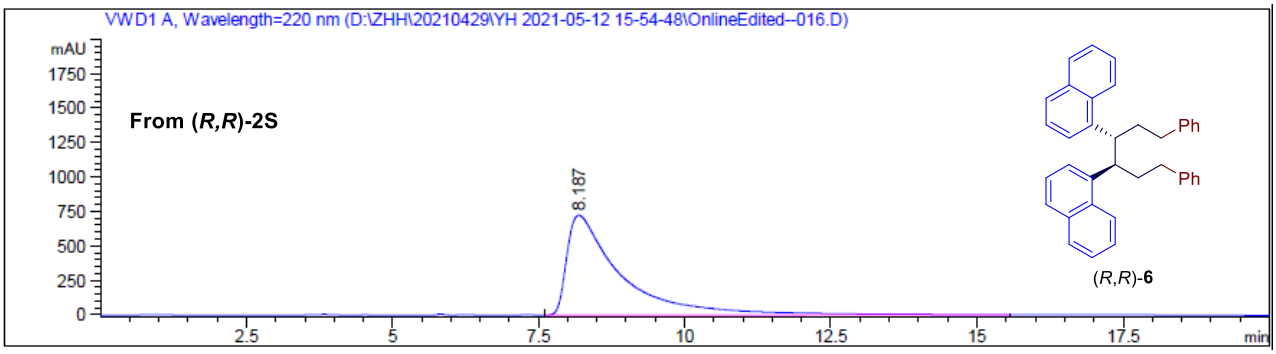
Analysis of Stereochemistry:

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak OD, hexane/isopropanol = 99/1, flow rate 0.8 mL/min, T = 25 ºC, 220 nm): t_R = 6.19 min (major).



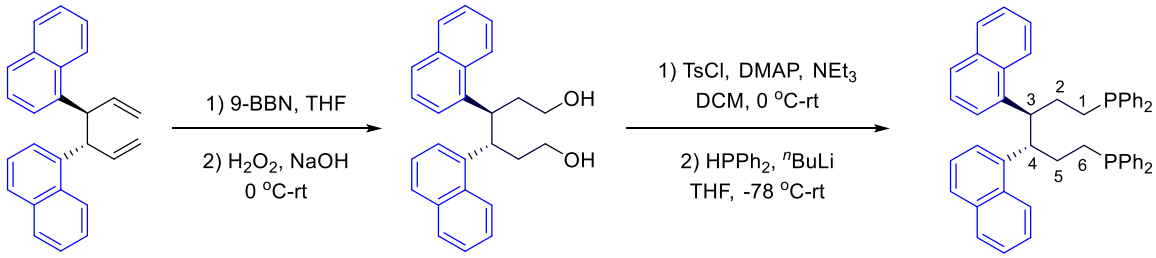


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.188	VV	0.2306	3.71713e4	2455.74634	100.0000



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.187	VB	0.8896	4.70190e4	725.06781	100.0000

Synthesis of chiral 1,6-diphosphine ligands 8

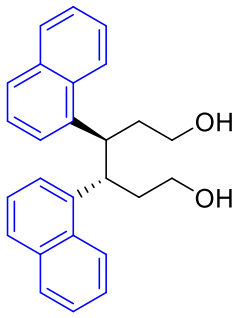


2s
> 99% *ee*

7, 88%
> 99% *ee*

8, 57%
> 99% *ee*

***Hydroboration and oxidation*:** To a suspension of **2s** (1.0 mmol, > 99% *ee*) in dry THF (10 mL) 9-BBN in THF (0.5 M, 5 mmol, 5 equiv) was added and the mixture was stirred at room temperature for 4 h. Thenan aqueous solution of NaOH (6.0 M, 4.0 mL) and H_2O_2 (30 % in water, 10 mL) were added at 0 ºC over and the reaction mixture was stirred for 2 h. The reaction was quenched with brine and the mixture extracted with ethyl acetate (3 x 10 mL). The organic layer was dried with anhydrous Na_2SO_4, filtered and the solvent evaporated in vacuo. The crude product was purified by flash chromatography on silica gel (acetate/dichloromethane = 2:1 to 5:1) to afford compound **7**.



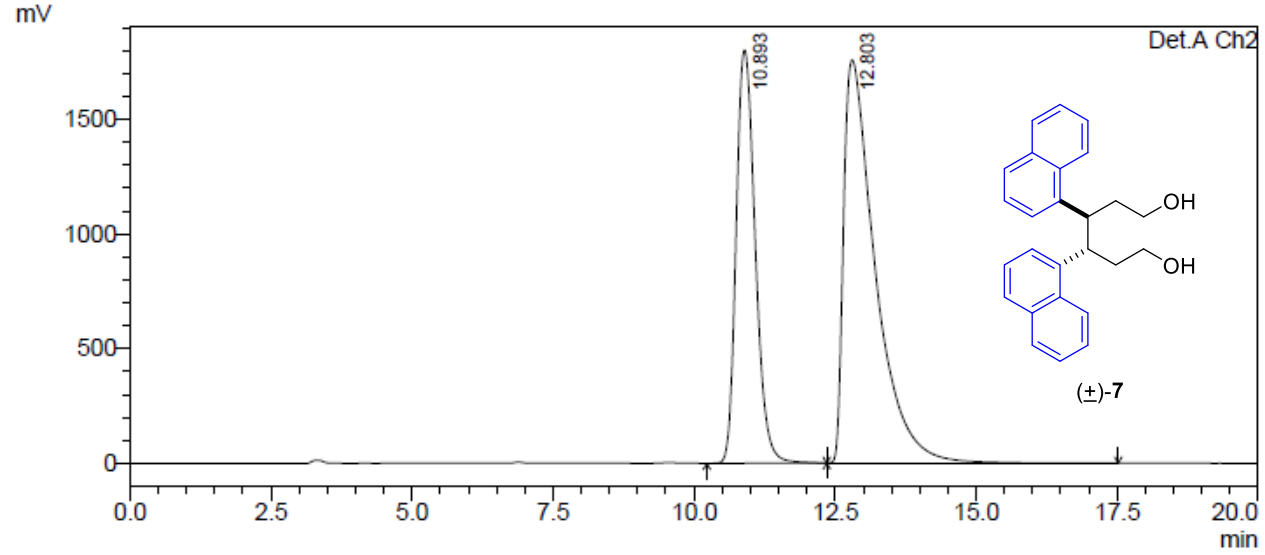
7

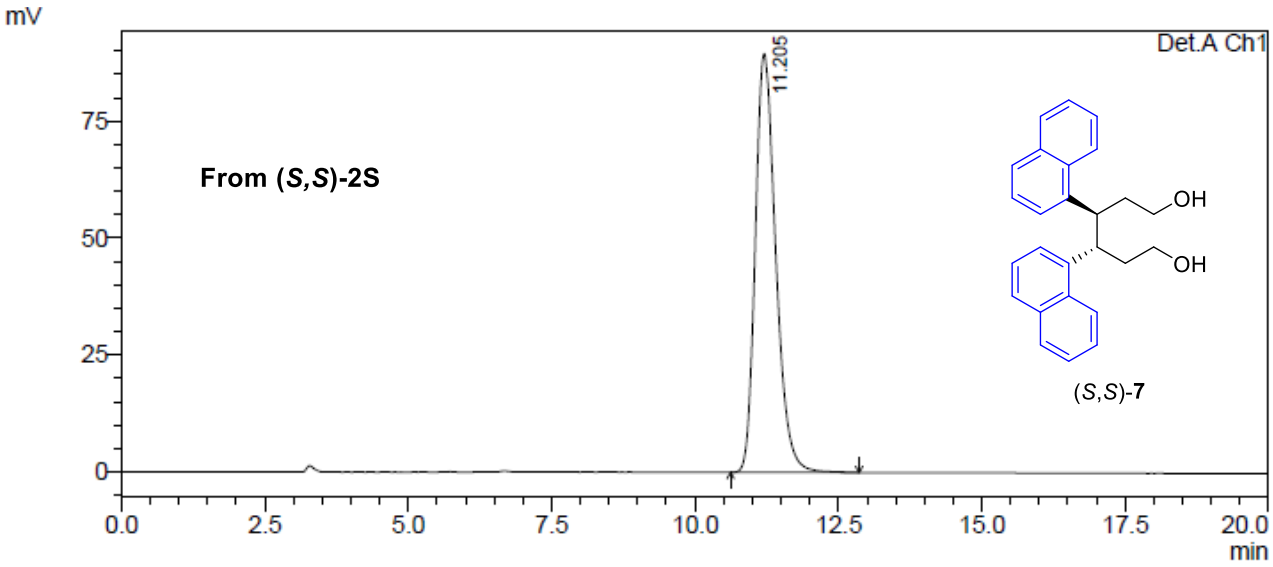
(3*S*,4*S*)-3,4-di(naphthalen-1-yl)hexane-1,6-diol (7): 88% yield (326 mg); colorless solid, m.p. 103.7-105.0 ºC; $[\alpha]_D^{20}$ = -69.7 (c 1.04, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.35 – 8.11 (m, 2H), 7.79 – 7.60 (m, 2H), 7.58 – 7.26 (m, 8H), 7.24 – 7.05 (m, 2H), 4.22 (s, 2H), 3.45 (ddd, *J* = 11.1, 7.1, 4.4 Hz, 2H), 3.32 – 3.18 (m, 2H), 2.58 – 2.39 (m, 2H), 2.24 – 2.05 (m, 2H), 1.53 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 133.7, 132.4, 128.8, 126.5, 125.6, 125.1, 125.0, 124.7, 123.3, 61.0, 40.2, 36.4; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{27}O_2$ requires m/z 371.2006, found m/z 371.1997.

Analysis of Stereochemistry:

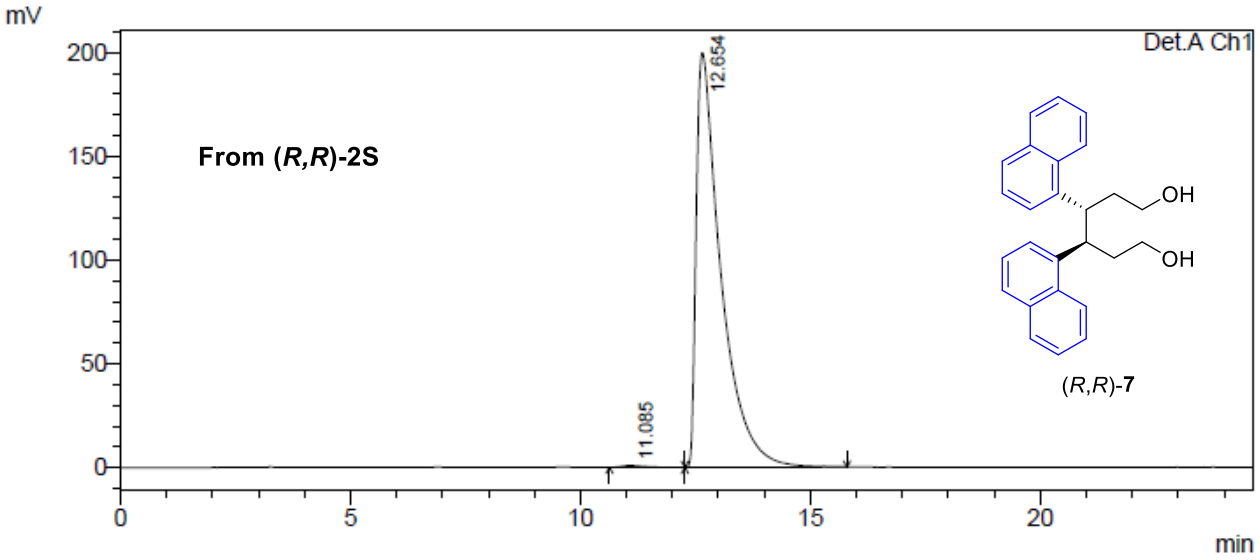
Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak IC, hexane/isopropanol =

80/20, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 11.20 min (major).



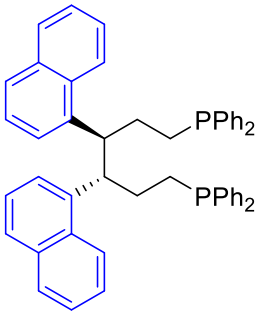


Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.205	2226289	89560	100.000	100.000
Total		2226289	89560	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.085	27823	843	0.373	0.420
2	12.654	7435514	199712	99.627	99.580
Total		7463337	200555	100.000	100.000

Tosylation and phosphorylation: Under argon atmosphere at 0 °C, **7** (1.0 mmol, > 99% ee) was dissolved in dichloromethane (10 mL), which was added DMAP (0.2 mmol) and Et_3N (2.5 mmol). Then, TsCl (2.4 mmol) was added dropwise to the reaction mixture, which was further stirred at room temperature. After the completion of the reaction indicated by TLC, the reaction mixture was diluted by dichloromethane and quenched by hydrochloric acid (1 M). The resultant mixture was extracted by dichloromethane, and the organic layer was washed successively by saturated $NaHCO_3$ aqueous solution and saturated NaCl aqueous solution. The crude was used for the next synthetic step. Diphenylphosphine (2.5 mmol) was dissolved in THF (10 mL), cooled down to -78 °C and ^{n}BuLi (2.4 M in hexane, 3.0 mmol) was carefully added. The yellow reaction mixture was allowed to come to room temperature and stirred for 2 h while a color change to orange and finally ruby red was observed. Then, crude product from previous step in THF (5 mL) was added and the mixture was stirred at room temperature over night. MeOH (1 mL) and dest. H_2O (1 mL) were added and the reaction mixture was concentrated under reduced pressure to remove THF. The residue was extracted with DCM (3 x 100 mL), the combined organic layers were washed with brine. Subsequently, the resultant organic layer was dried by anhydrous Na_2SO_4 and purified by flash column chromatography (petroleum ether/ethyl acetate = 50/1) to afford compound **8**.

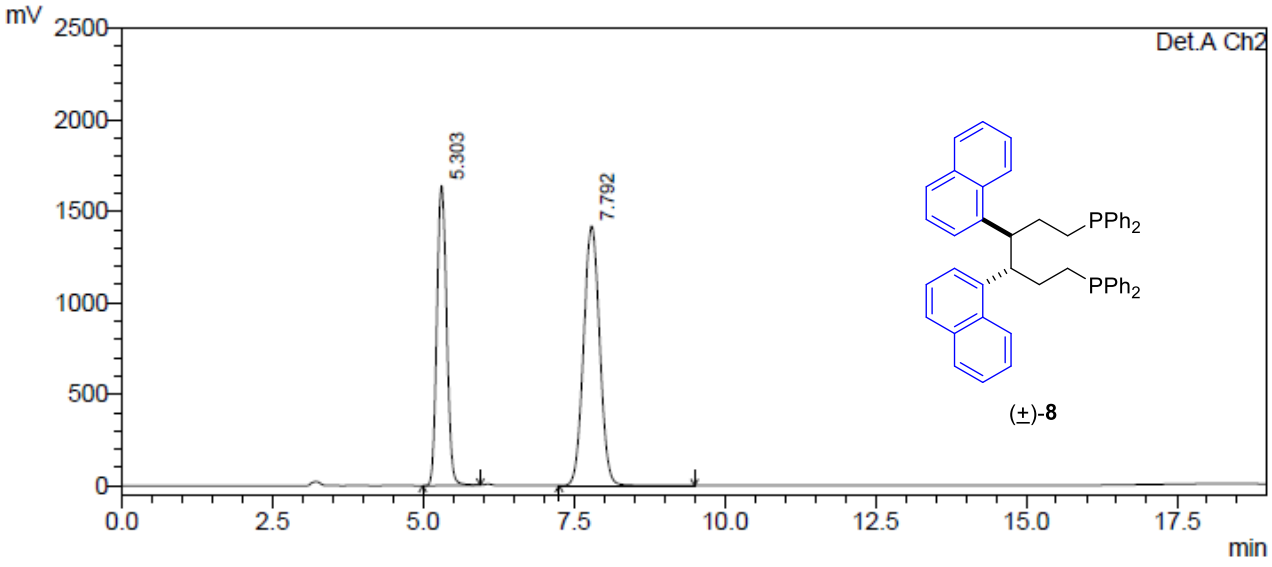


8

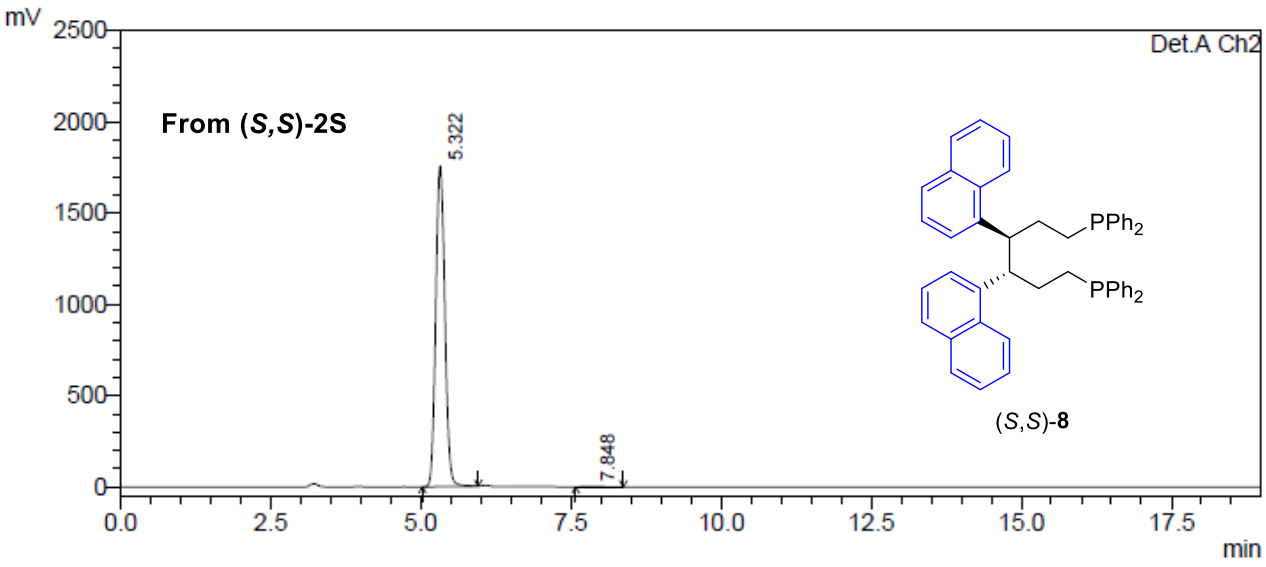
((3*S*,4*S*)-3,4-di(naphthalen-1-yl)hexane-1,6-diyl)bis(diphenylphosphane) (8): 57% yield (403 mg); white solid, m.p. 106.5-107.2 °C $[\alpha]_D^{20}$ = -84.0 (c 0.60, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-*d*) δ 8.22 – 8.03 (m, 2H), 7.80 – 7.71 (m, 2H), 7.61 – 7.53 (m, 2H), 7.48 – 7.37 (m, 4H), 7.34 – 7.26 (m, 4H), 7.25 – 7.11 (m, 16H), 7.11 – 7.04 (m, 4H), 4.16 – 3.85 (m, 2H), 2.27 – 2.08 (m, 2H), 2.06 – 1.92 (m, 2H), 1.80 – 1.74 (m, 2H), 1.68 – 1.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 138.71 (d, *J* = 12.4 Hz), 137.9 (d, *J* = 12.8 Hz), 133.9, 133.1 (d, *J* = 18.6 Hz), 132.6, 132.2 (d, *J* = 17.7 Hz), 128.9, 128.7, 128.4 (d, *J* = 6.9 Hz), 128.2 (d, *J* = 6.7 Hz), 128.17, 126.6, 125.5, 125.1 (d, *J* = 6.5 Hz), 124.6, 123.6, 44.6 (d, *J* = 9.5 Hz), 27.8 (d, *J* = 13.8 Hz), 25.4 (d, *J* = 11.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ -15.1; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{50}H_{45}P_2$ requires m/z 707.2992, found m/z 707.2993.

Analysis of Stereochemistry:

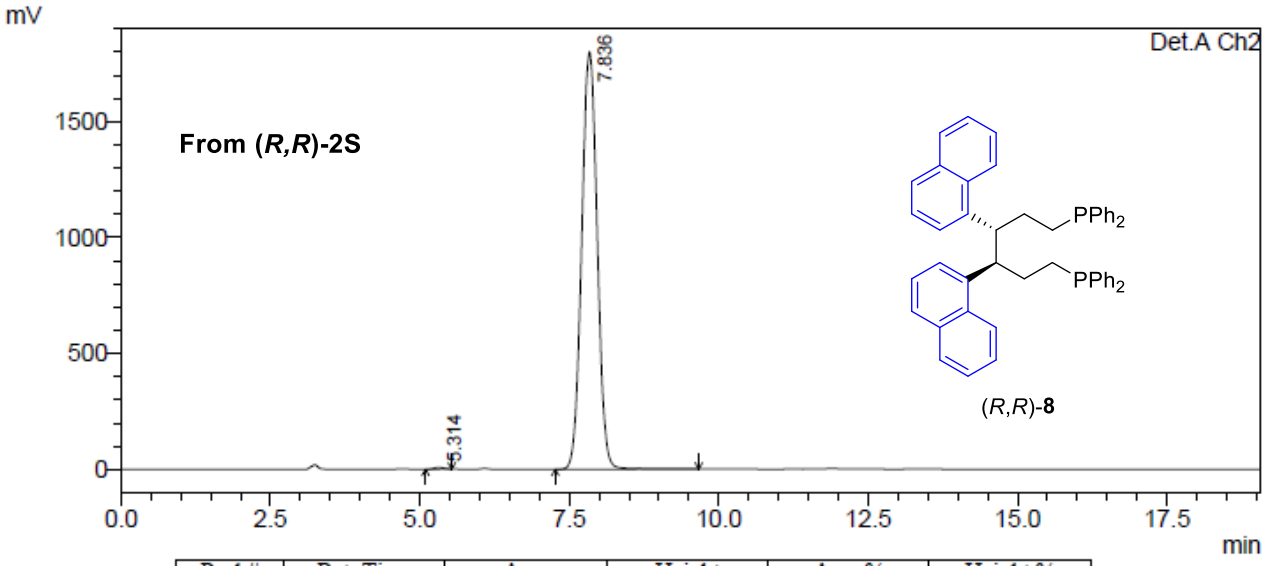
Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 5.32 min (major), t_R = 7.85 min (minor).



(±)-**8**

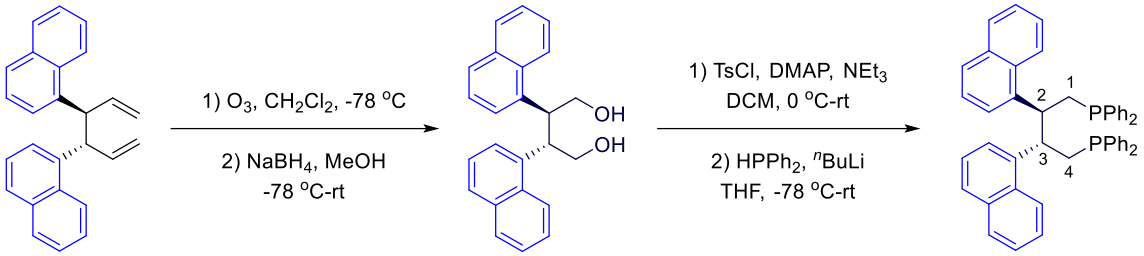


Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.320	18560061	1754706	99.899	99.944
2	7.850	18777	976	0.101	0.056
Total		18578838	1755682	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.312	79881	7000	0.244	0.387
2	7.835	32598203	1799908	99.756	99.613
Total		32678084	1806908	100.000	100.000

Synthesis of chiral 1,4-diphosphine ligands 10

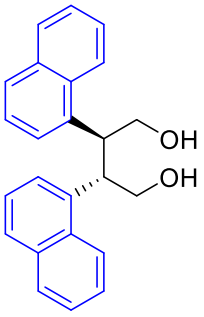


2s
> 99% *ee*

9, 54%
> 99% *ee*

10, 44%
> 99% *ee*

***Ozonolysis and reduction*:** Ozone was bubbled for 15 min through a solution of **2s** (1.0 mmol, > 99% *ee*) in a mixture of DCM (10 mL) and MeOH (10 mL) at -78°C. After stirring for 15 minutes (solution stays blue) the reaction mixture was purged with nitrogen. Sodium borohydride (5.0 mmol) was added and the mixture was warmed to room temperature and stirred for 6 h. The reaction was quenched by addition of a 1M aqueous HCl solution. The layers were separated and the aqueous layer was extracted with DCM twice. The combined organic layers were dried with sodium sulfate and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (ethyl acetate/dichloromethane = 2:1 to 5:1) to afford compound **9**.

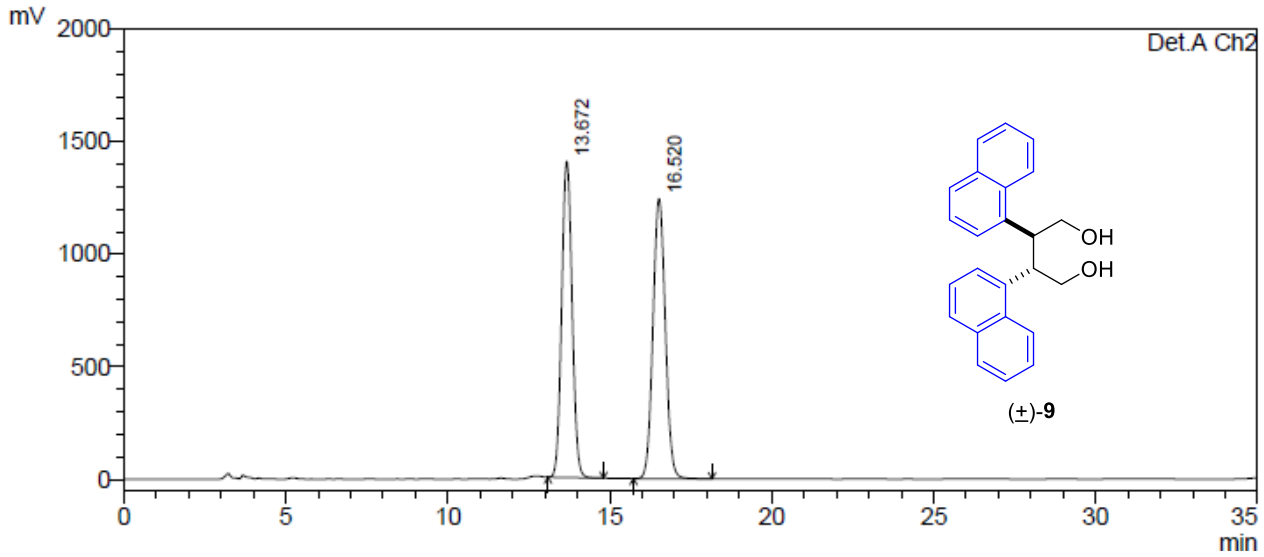


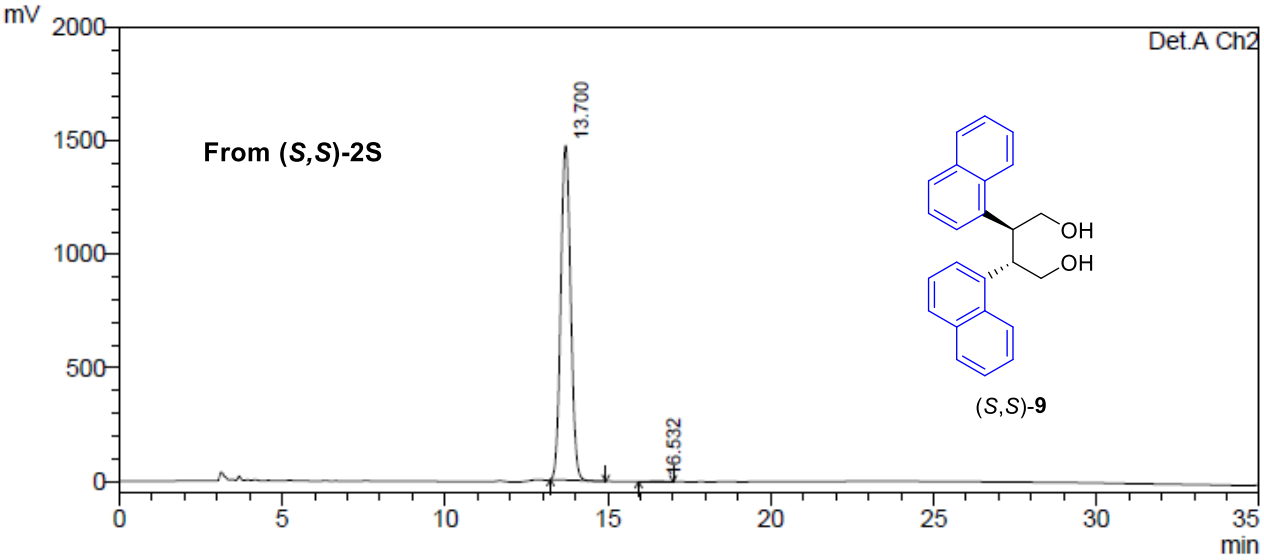
9

(2*S*,3*S*)-2,3-di(naphthalen-1-yl)butane-1,4-diol (9): 54% yield (185 mg); colorless solid, m.p. 94.6-95.7 °C; $[\alpha]_D^{20}$ = -91.0 (c 0.42, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.46 (d, *J* = 8.6 Hz, 2H), 7.75 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.59 – 7.53 (m, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.38 (m, 2H), 7.32 (dd, *J* = 7.3, 1.2 Hz, 2H), 7.14 – 6.98 (m, 2H), 4.73 – 4.62 (m, 2H), 4.62 – 4.46 (m, 2H), 4.14 – 4.01 (m, 4H); ^{13}C NMR (101 MHz, Acetone-d_6) δ 138.8, 133.9, 132.1, 128.7, 126.2, 125.7, 125.0, 124.9, 124.8, 123.3, 65.7, 44.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{23}O_2$ requires m/z 343.1693, found m/z 343.1699.

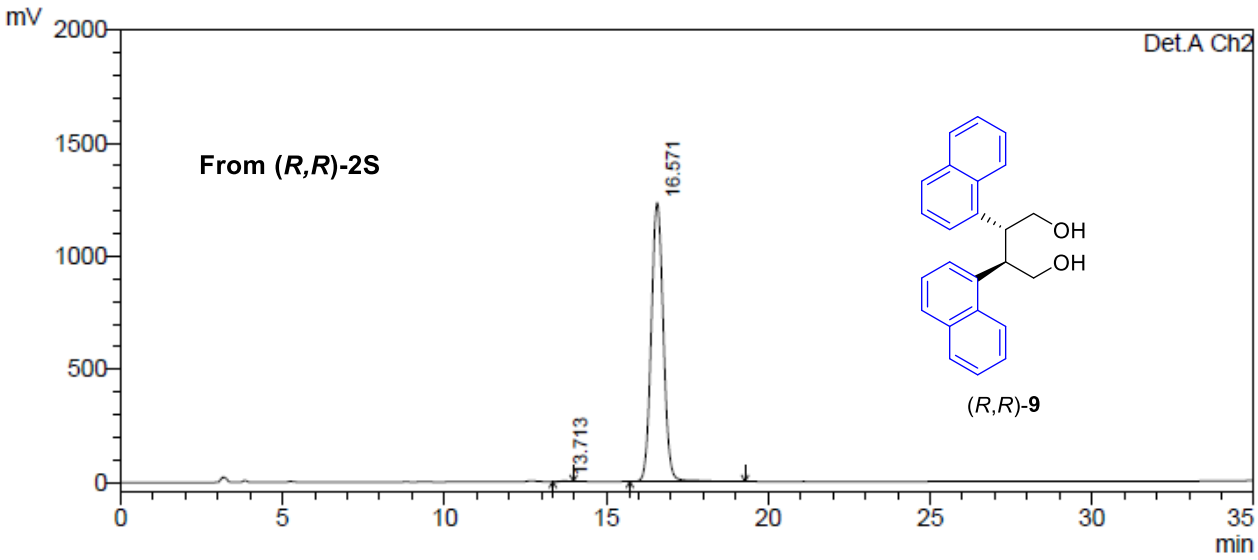
Analysis of Stereochemistry:

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak AD-H, pentane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 13.70 min (major), t_R = 16.53 min (minor).



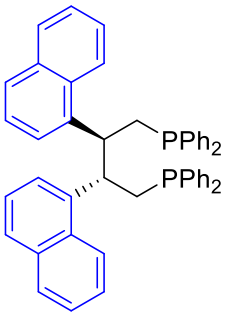


Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.699	31349353	1478420	99.794	99.834
2	16.534	64857	2464	0.206	0.166
Total		31414210	1480884	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.715	45652	2587	0.142	0.209
2	16.569	32005931	1232842	99.858	99.791
Total		32051583	1235429	100.000	100.000

Tosylation and phosphorylation: Under argon atmosphere at 0 °C, **9** (1.0 mmol, > 99% ee) was dissolved in dichloromethane (10 mL), which was added DMAP (0.2 mmol) and Et_3N (2.5 mmol). Then, TsCl (2.4 mmol) was added dropwise to the reaction mixture, which was further stirred at room temperature. After the completion of the reaction indicated by TLC, the reaction mixture was diluted by dichloromethane and quenched by hydrochloric acid (1 M). The resultant mixture was extracted by dichloromethane, and the organic layer was washed successively by saturated $NaHCO_3$ aqueous solution and saturated NaCl aqueous solution. The crude was used for the next synthetic step. Diphenylphosphine (2.5 mmol) was dissolved in THF (10 mL), cooled down to -78 °C and ^{n}BuLi (2.4 M in hexane, 3.0 mmol) was carefully added. The yellow reaction mixture was allowed to come to room temperature and stirred for 2 h while a color change to orange and finally ruby red was observed. Then, crude product from previous step in THF (5 mL) was added and the mixture was stirred at room temperature over night. MeOH (1 mL) and dest. H_2O (1 mL) were added and the reaction mixture was concentrated under reduced pressure to remove THF. The residue was extracted with DCM (3 x 100 mL), the combined organic layers were washed with brine. Subsequently, the resultant organic layer was dried by anhydrous Na_2SO_4 and purified by flash column chromatography (petroleum ether/ethyl acetate = 50/1) to afford compound **10**.

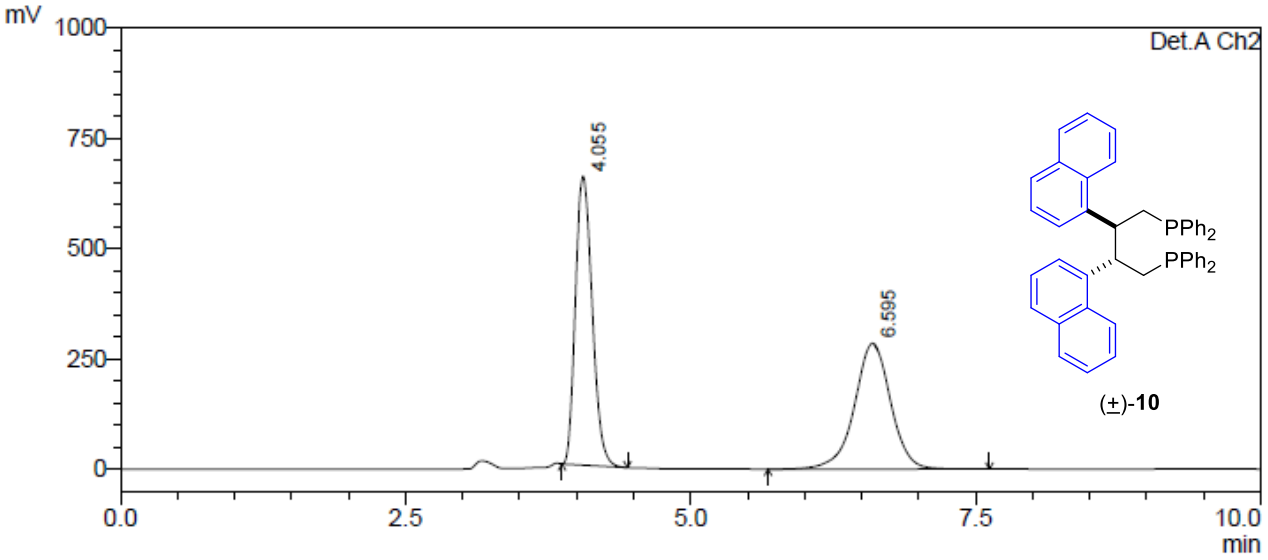


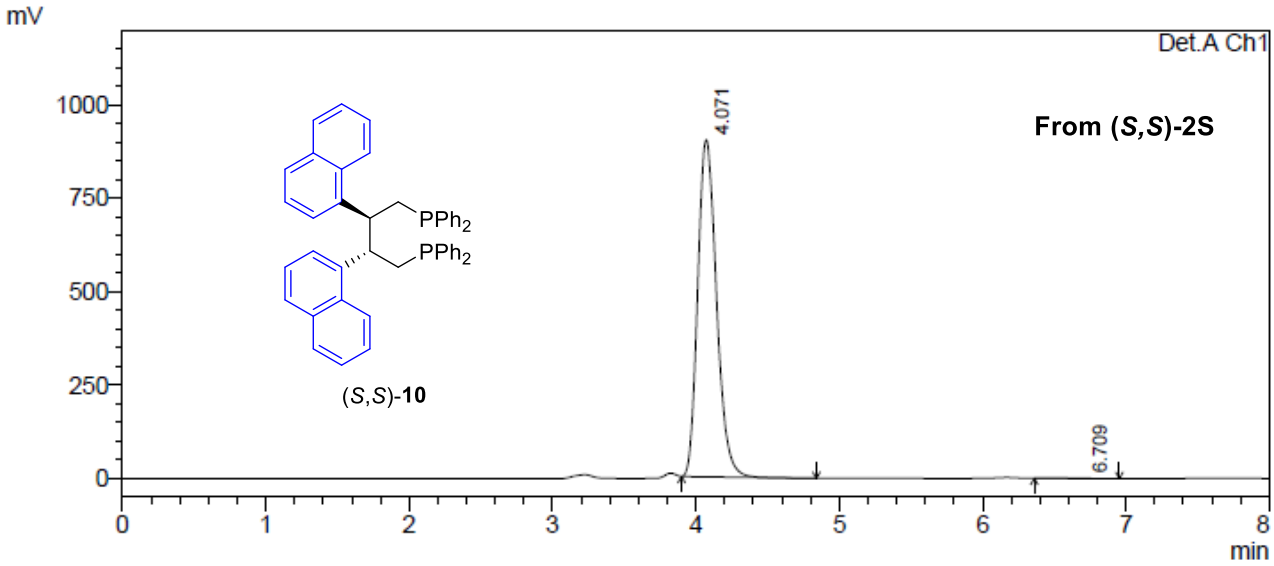
10

((2*S*,3*S*)-2,3-di(naphthalen-1-yl)butane-1,4-diyl)bis(diphenylphosphane) (10): 44% yield (299 mg); white solid, m.p. 101.1-102.4 °C $[\alpha]_D^{20}$ = -28.6 (c 1.05, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.84 (m, 2H), 7.80 – 7.72 (m, 2H), 7.66 – 7.56 (m, 2H), 7.44 – 7.31 (m, 5H), 7.25 – 7.14 (m, 16H), 7.11 – 6.98 (m, 7H), 4.32 – 4.09 (m, 2H), 2.97 – 2.74 (m, 2H), 2.67 – 2.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4 (d, *J* = 13.7 Hz), 138.5, 138.0 (d, *J* = 12.5 Hz), 133.8, 133.0 (d, *J* = 19.5 Hz), 132.5 (d, *J* = 18.6 Hz), 128.8, 128.5, 128.31, 128.25, 128.2, 127.0, 126.4, 125.4, 125.1, 124.7, 123.7, 41.28 (d, *J* = 10.8 Hz), 32.39 (d, *J* = 9.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ -19.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}NNaO_2$ requires m/z 679.2679, found m/z 679.2677.

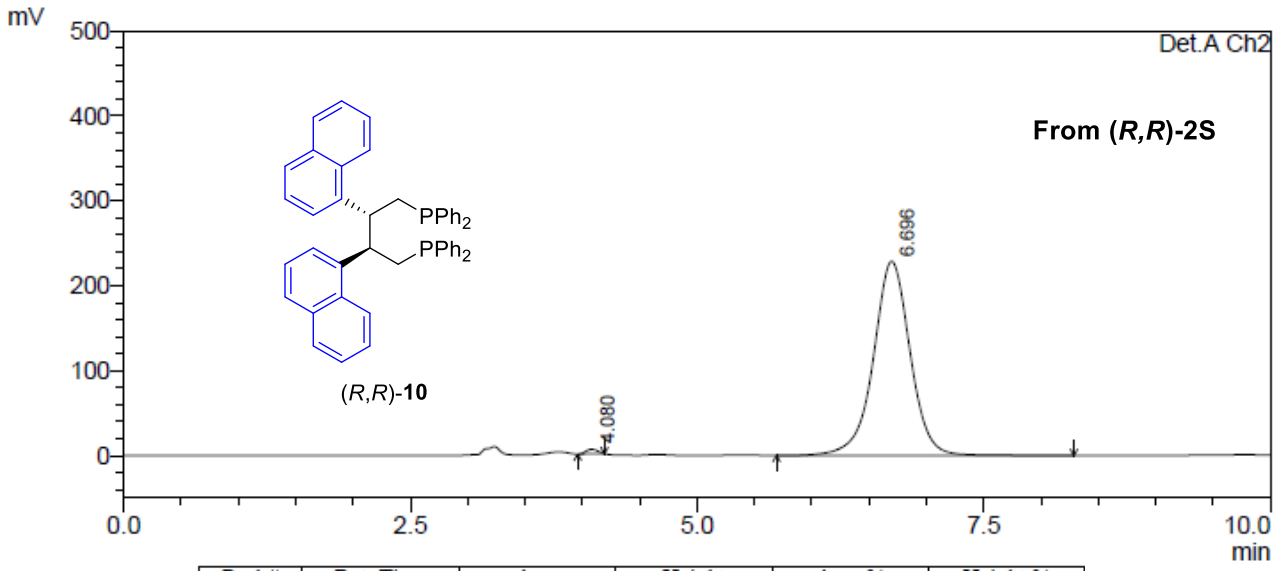
Analysis of Stereochemistry:

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak AD-H, pentane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 4.07 min (major), t_R = 6.71 min (minor).



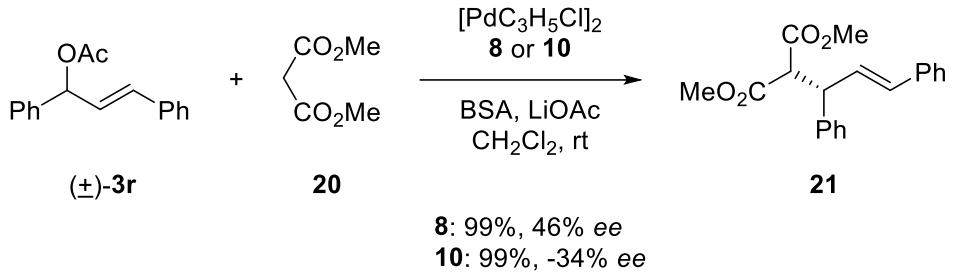


Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.071	8203959	901922	99.909	99.951
2	6.709	7491	443	0.091	0.049
Total		8211450	902365	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.078	44860	5873	0.873	2.506
2	6.694	5091775	228534	99.127	97.494
Total		5136635	234407	100.000	100.000

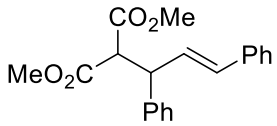
Preliminary synthetic application of 8 and 10



(±)-**3r** **20** **21**

8: 99%, 46% *ee*
10: 99%, -34% *ee*

Lithium acetate (5 mol %), *N*,*O*-bistrimethylsilyl acetamide (BSA, 0.6 mmol, 3 equiv), (*E*)-1,3-diphenylallyl acetate **3r** (0.2 mmol, 1 equiv), and dimethyl malonate **20** (0.6 mmol, 3 equiv) were added to a solution of allylpalladium dichloride dimer (5 mol %) and phosphine **8** or **10** (12 mol %) in CH_3CN (2 mL) under nitrogen. The mixture was stirred at room temperature for 6 h, poured into water, extracted into dichloromethane, dried over magnesium sulfate, and concentrated under reduced pressure to give the crude product oil. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 10/1) to give the substitution product **21**.

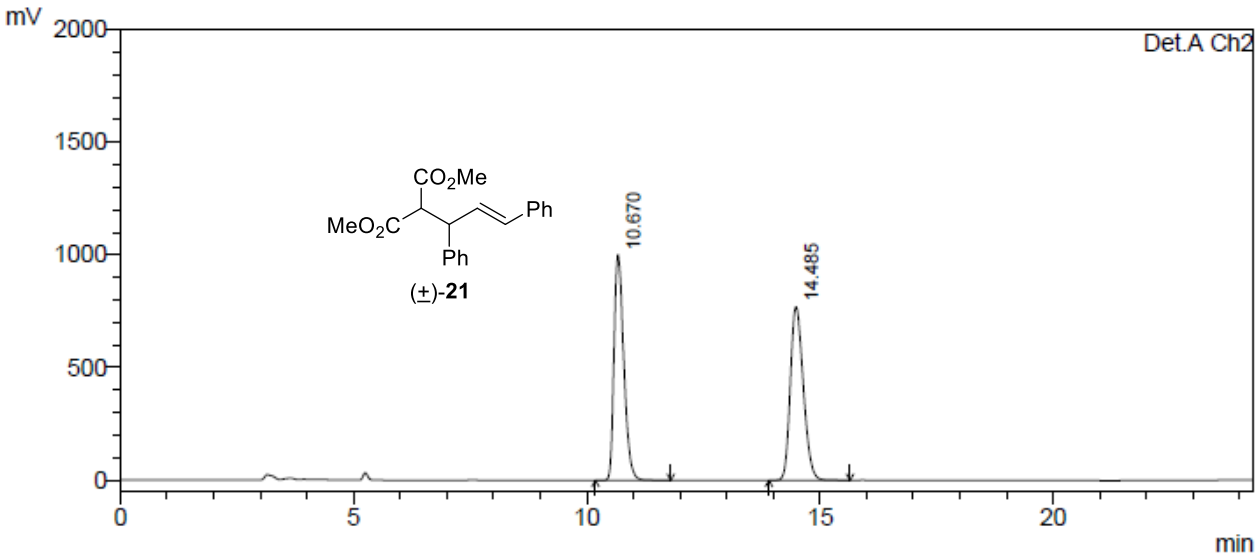


21

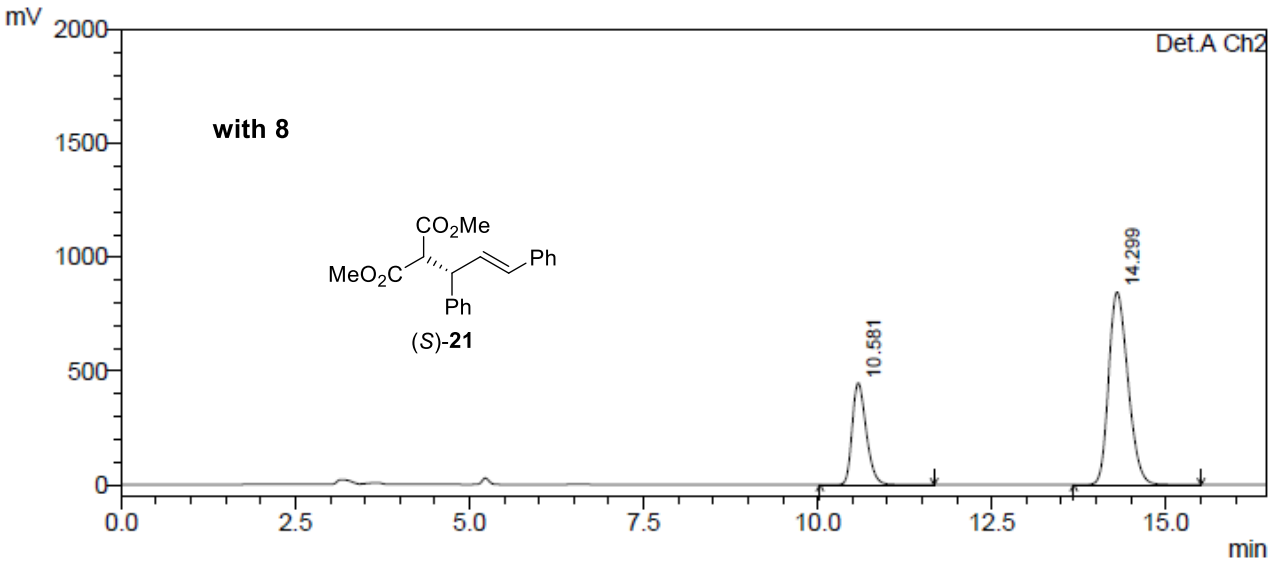
dimethyl (*E*)-2-(1,3-diphenylallyl)malonate (21): > 99% yield (64.2 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 8H), 7.26 – 7.18 (m, 2H), 6.48 (d, *J* = 15.7 Hz, 1H), 6.33 (dd, *J* = 15.7, 8.6 Hz, 1H), 4.27 (dd, *J* = 10.9, 8.6 Hz, 1H), 3.96 (d, *J* = 10.9 Hz, 1H), 3.71 (s, 3H), 3.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 167.8, 140.2, 136.8, 131.9, 129.1, 128.7, 128.5, 127.9, 127.6, 127.2, 126.4, 57.7, 52.7, 52.5, 49.2. Spectral data is in accordance with the literature.[6]

Analysis of Stereochemistry:

Enantiomeric excess: 46% (with **8**), determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 14.30 min (major), t_R = 10.58 min (minor).

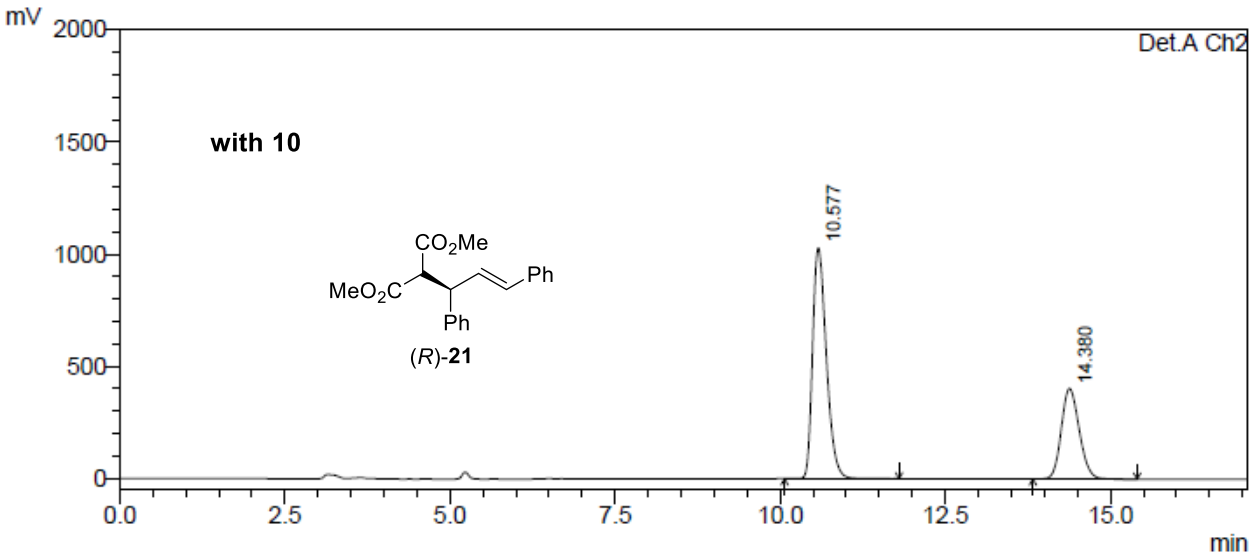


Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.668	22902418	1590369	49.683	56.686
2	14.483	23194697	1215200	50.317	43.314
Total		46097116	2805569	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.579	9536415	686912	27.281	33.892
2	14.297	25420279	1339864	72.719	66.108
Total		34956694	2026776	100.000	100.000

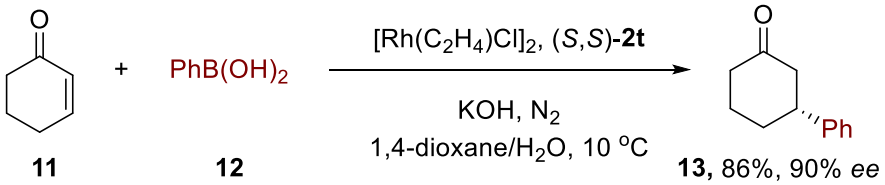
Enantiomeric excess: -34% (with **10**), determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 10.58 min (major), t_R = 14.38 min (minor).



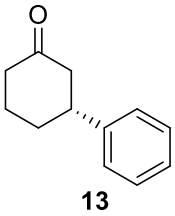
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.575	23351973	1633429	66.930	72.566
2	14.379	11538281	617512	33.070	27.434
Total		34890254	2250941	100.000	100.000

9. Applications of 2t as chiral diene ligand

Procedure for Rh(I)/2t-catalyzed asymmetric 1,4-addition of 2-cyclohexenone



To a Schlenk tube charged with phenylboronic acid **12** (73.2 mg, 0.6 mmol), $[Rh(C_2H_4)_2Cl]_2$ (3.9 mg, 0.01 mmol, 2.5 mol %), and chiral diene ligand (*S*,*S*)-**2t** (9.6 mg, 0.024 mmol, 6.0 mol %) was added degassed dioxane (0.8 mL) under Argon. The resulting mixture was heated to 50 °C and stirred for 15 min. 2-Cyclohexenone **11** (38.4 mg, 0.4 mmol) and KOH (0.03 mmol, 0.075 M in MeOH, 0.4 mL, 7.5 mol %) was added sequentially. Upon stirring at 10 °C for 12 h, the reaction mixture was concentrated, and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to give conjugated addition adduct **13**.

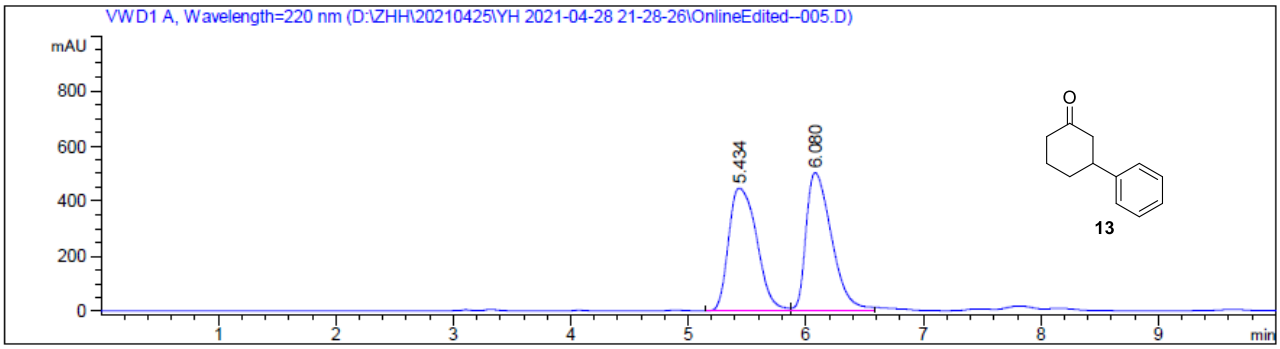


13

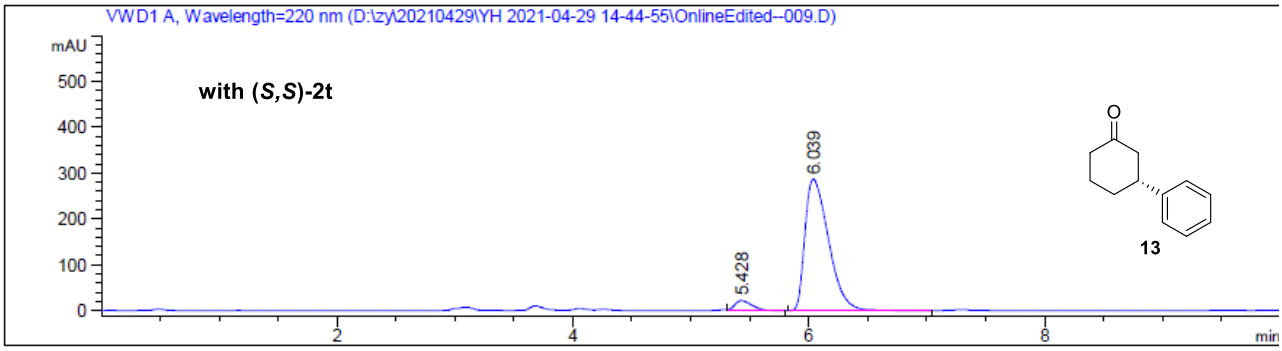
(*R*)-3-phenylcyclohexan-1-one (13): 86% yield (59.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 2H), 7.29 – 7.19 (m, 3H), 3.08 – 2.93 (m, 1H), 2.65 – 2.57 (m, 1H), 2.57 – 2.43 (m, 2H), 2.43 – 2.33 (m, 1H), 2.19 – 2.05 (m, 2H), 1.91 – 1.74 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.0, 144.3, 128.7, 126.7, 126.6, 49.0, 44.8, 41.2, 32.8, 25.6. Spectral data is in accordance with the literature.[7]

Analysis of Stereochemistry:

Enantiomeric excess: 90%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 6.04 min (major), t_R = 5.43 min (minor).

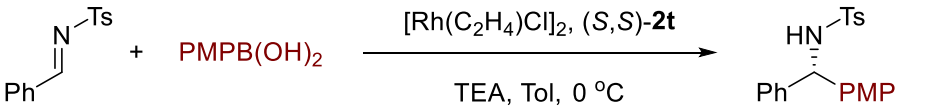


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.434	BV	0.2713	7456.26709	446.61752	49.4278
2	6.080	MF	0.2533	7628.89307	501.88501	50.5722



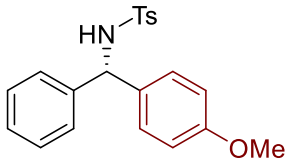
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.428	FM	0.1713	223.60545	21.75413	5.3048
2	6.039	BB	0.2215	3991.55762	286.55457	94.6952

Procedure for Rh(I)/2t-catalyzed asymmetric arylation of *N*-tosyl imines 14



14 **15** **16,** 58%, 82% *ee*

To a Schlenk tube charged with phenylboronic acid **15** (61 mg, 0.4 mmol), $[Rh(C_2H_4)_2Cl]_2$ (1.9 mg, 0.005 mmol, 2.5 mol %), and chiral diene ligand (*S*,*S*)-**2t** (4.8 mg, 0.012 mmol, 6.0 mol %) was added degassed dioxane (0.8 mL) under Argon. The resulting mixture was heated to 50 °C and stirred for 15 min. *N*-tosyl imines 14 (51.8 mg, 0.2 mmol) and TEA (40 mg, 0.4 mmol) was added sequentially. Upon stirring at 0 °C for 24 h, the reaction mixture was concentrated, and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to give conjugated addition adduct **16**.

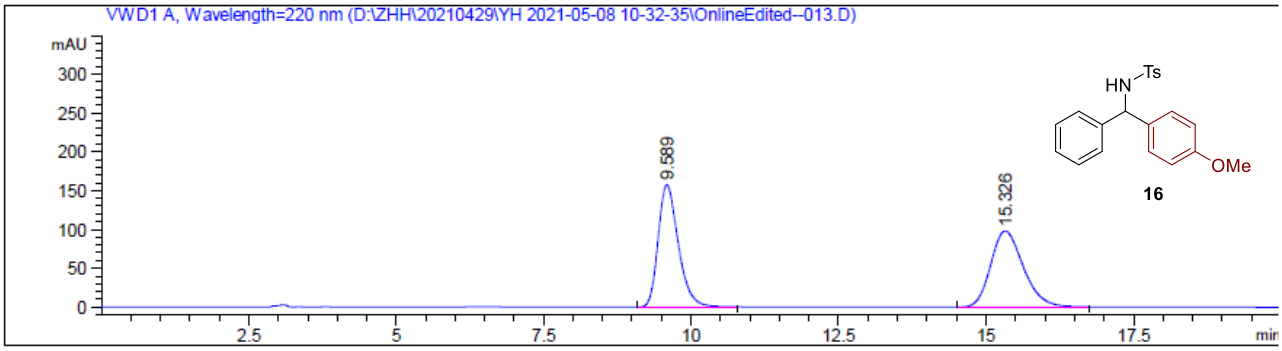


16

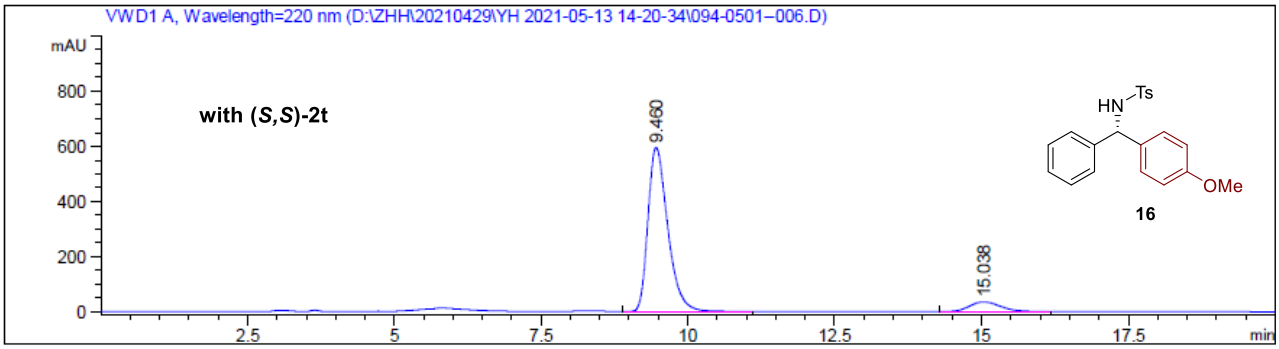
(*S*)-*N*-((4-methoxyphenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (16): 58% yield (42.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.53 (m, 2H), 7.25 – 7.17 (m, 3H), 7.15 – 7.08 (m, 4H), 7.04 – 6.96 (m, 2H), 6.77 – 6.68 (m, 2H), 5.52 (d, *J* = 7.0 Hz, 1H), 5.15 (dd, *J* = 7.1, 4.0 Hz, 1H), 3.75 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 143.1, 140.7, 137.4, 132.8, 129.3, 128.6, 128.5, 127.5, 127.3, 127.2, 113.9, 60.8, 55.3, 21.5. Spectral data is in accordance with the literature.[8]

Analysis of Stereochemistry:

Enantiomeric excess: 82%, determined by HPLC (Daicel Chiralpak OD-H, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 9.46 min (major), t_R = 15.04 min (minor).

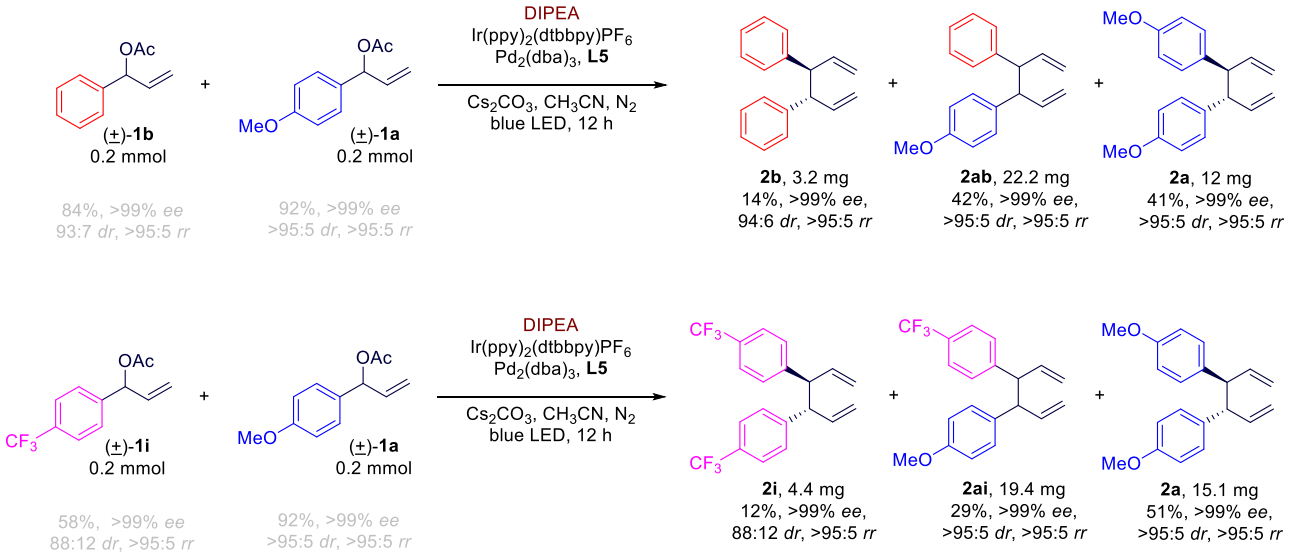


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.589	BB	0.3658	3743.20654	157.20418	49.8471
2	15.326	BB	0.5821	3766.16675	97.83757	50.1529



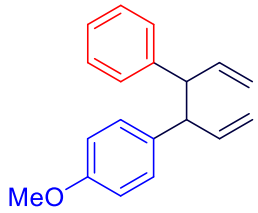
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.460	VB	0.3572	1.39974e4	595.52740	91.2946
2	15.038	BB	0.5464	1334.73096	35.76049	8.7054

10. Attempt of enantioselective reductive cross-coupling



In a nitrogen-filled glovebox, a 8 mL screw-cap test tube, equipped with a magnetic stir bar, charged with $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 2.5 mol%), (*R*)-2,2'-Bis[bis(4-methoxy-3,5-di-*t*-butylphenyl)phosphino]-4,4',6,6'-tetramethoxy)-1,1'-biphenyl (**L5**) (14.6 mg, 0.012 mmol, 6 mol%), anhydrous CH_3CN (2.0 mL) was added and the mixture was stirred for 30 min. Then the following chemicals were added in turn: $Ir(ppy)_2(dtbbpy)PF_6$ (4.0 mg, 0.004 mmol, 2.0 mol%), Cs_2CO_3 (195.6 mg, 0.6 mmol, 3.0 equiv), allylic acetates **1a** (0.2 mmol, 1.0 equiv), DIPEA (80 mg,. 0.6 mmol, 3.0 equiv), **1b** or **1i** (0.2 mmol, 1.0 equiv) and anhydrous CH_3CN (2.0 mL). The reaction tube was sealed with a Teflon screw cap, removed from the glove box. The reaction mixture was stirred vigorously under 45W blue LED lights at room temperature for 12h. Next, the reaction mixture was transferred to a 250 mL separatory funnel, rinsed/diluted with 100 mL ether, and washed with 100 mL deionized water (twice) and finally 100 mL brine. The organic phase was concentrated under vacuum and purified by chromatography.

Preliminary attempt of the enantioselective reductive cross-coupling was also made, affording the desired cross-coupling product **2ab** and **2ai** in excellent diastereo-, regio- and enantioselectivities (> 95:5 *dr*, > 95:5 *rr*, > 99 *ee*), but in poor yields (42% for **2ab**, 29% for **2ai**). Homocoupling by-products **2a**, **2b** and **2i** could also be observed. Photoredox/Pd-cocatalyzed enantioselective reductive cross-coupling is underway in our laboratory.

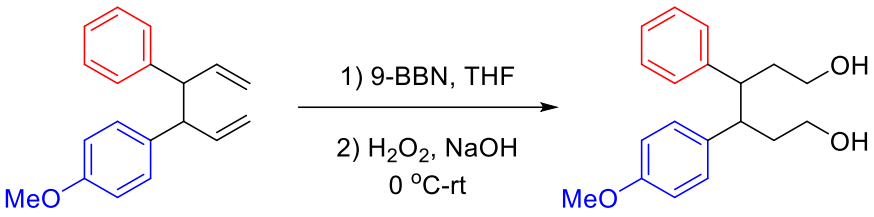


2ab

1-methoxy-4-(4-phenylhexa-1,5-dien-3-yl)benzene (2ab): Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 42% (22.2 mg); > 95:5 *dr*, > 95:5 *rr*, a colourless sticky oil; $[\alpha]_D^{20}$ = -44.3 (c 0.66, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.14 (m, 2H), 7.12 – 7.07 (m, 1H), 7.07 – 7.02 (m, 2H), 7.00 – 6.93 (m, 2H), 6.75 – 6.66 (m, 2H), 6.18 – 6.02 (m, 2H), 5.13 – 5.00 (m, 4H), 3.72 (s, 3H), 3.64 – 3.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 142.7, 140.9, 140.7, 134.7, 129.1, 128.2, 128.1, 126.0, 115.7, 115.5, 113.5, 55.9, 55.1, 54.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}O$ requires m/z 265.1588, found m/z 265.1582.

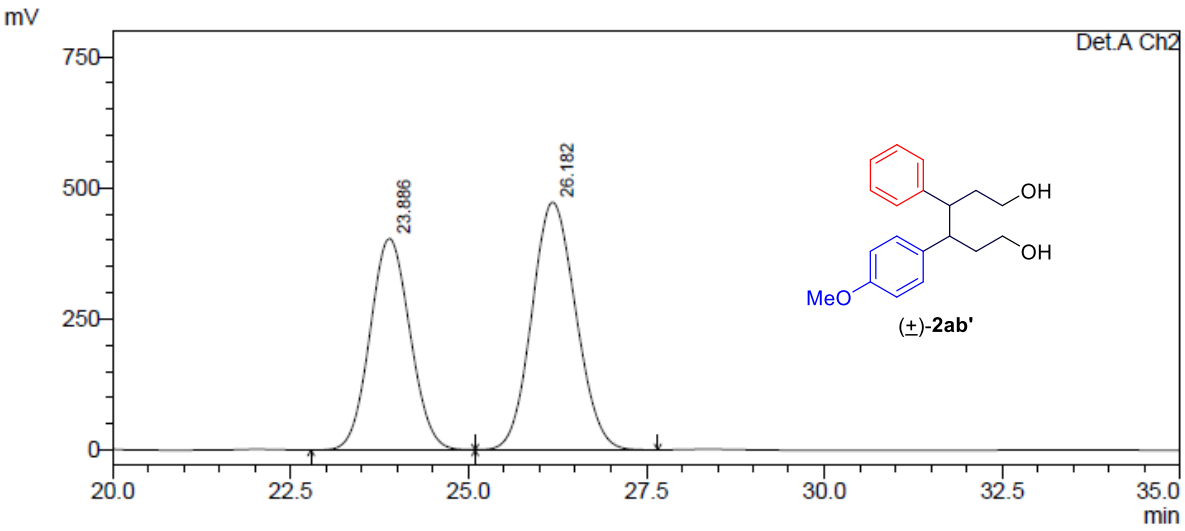
Analysis of Stereochemistry:

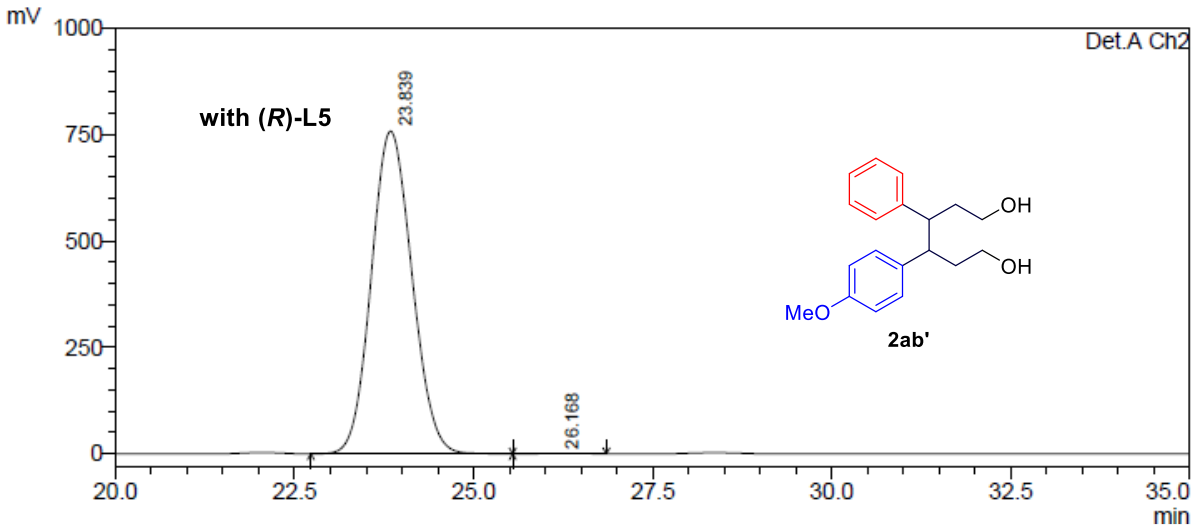
The title compound and the analogous racemic material were subjected to hydroboration and oxidation for HPLC analysis as shown below.



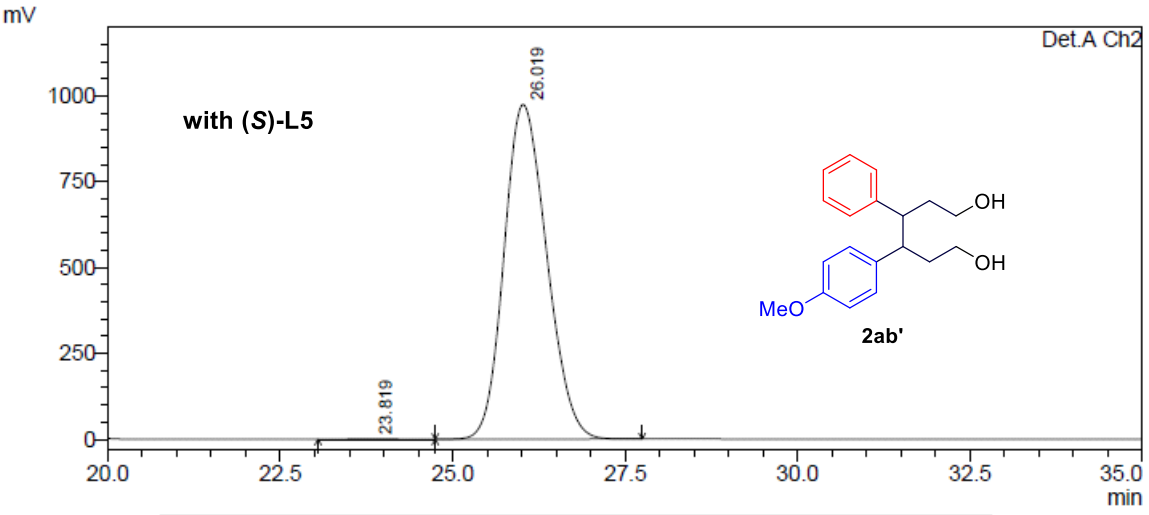
2ab **2ab'**

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 23.84 min (major), t_R = 26.17 min (minor).

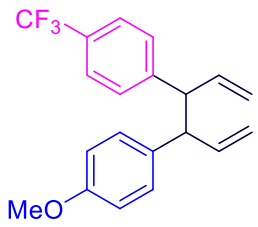




Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.837	30013907	758382	99.911	99.906
2	26.170	26628	714	0.089	0.094
Total		30040536	759096	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.848	56624	1493	0.135	0.153
2	26.017	41958659	974252	99.865	99.847
Total		42015284	975745	100.000	100.000

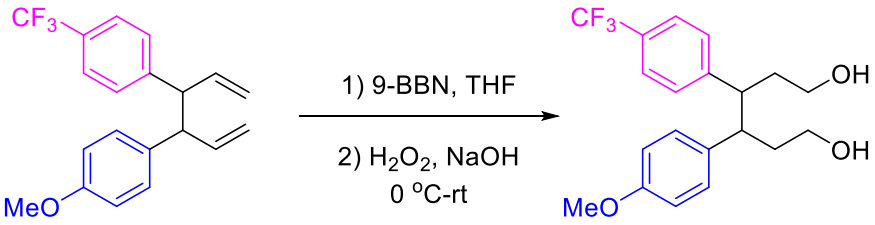


2ai

1-methoxy-4-(4-(4-(trifluoromethyl)phenyl)hexa-1,5-dien-3-yl)benzene (2ai): Flash column chromatography eluent, petroleum ether/ethyl acetate = 100:0 to 100:1; Reaction time = 12 h; yield: 29% (19.4 mg); a colourless sticky oil; $[\alpha]_D^{20}$ = -26.3 (c 0.83, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 6.98 – 6.89 (m, 2H), 6.73 – 6.68 (m, 2H), 6.07 (dddd, *J* = 16.9, 10.2, 8.2, 3.3 Hz, 2H), 5.15 – 5.08 (m, 2H), 5.06 – 4.99 (m, 2H), 3.72 (s, 3H), 3.69 – 3.64 (m, 1H), 3.62 – 3.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 146.9, 140.3, 139.8, 134.0, 129.0, 128.5, 125.05 (q, *J* = 3.7 Hz), 122.9, 116.5, 115.9, 113.7, 55.7, 55.1, 54.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.3; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}F_3O$ requires m/z 333.1462 found m/z 333.1458.

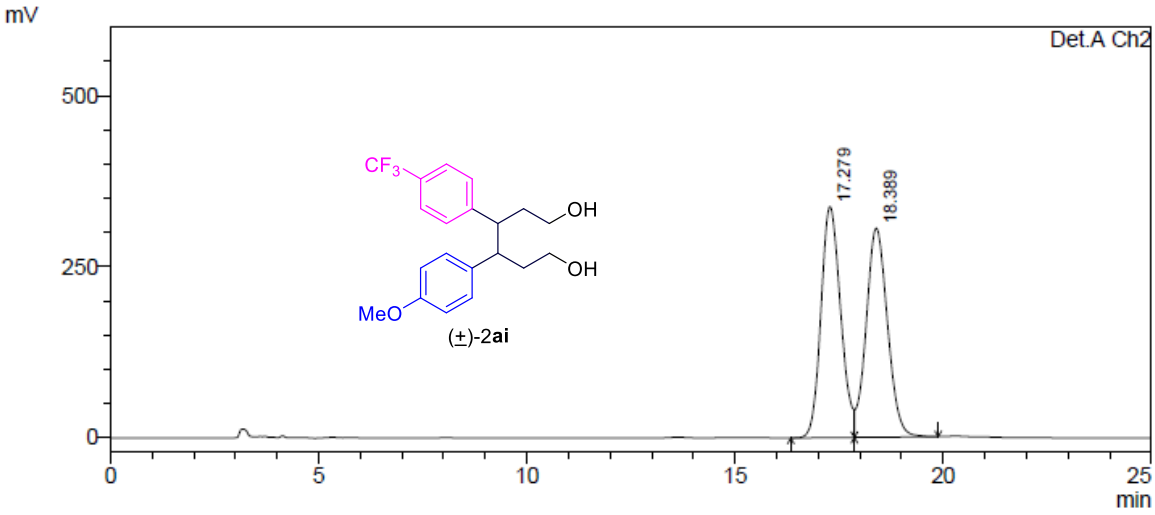
Analysis of Stereochemistry:

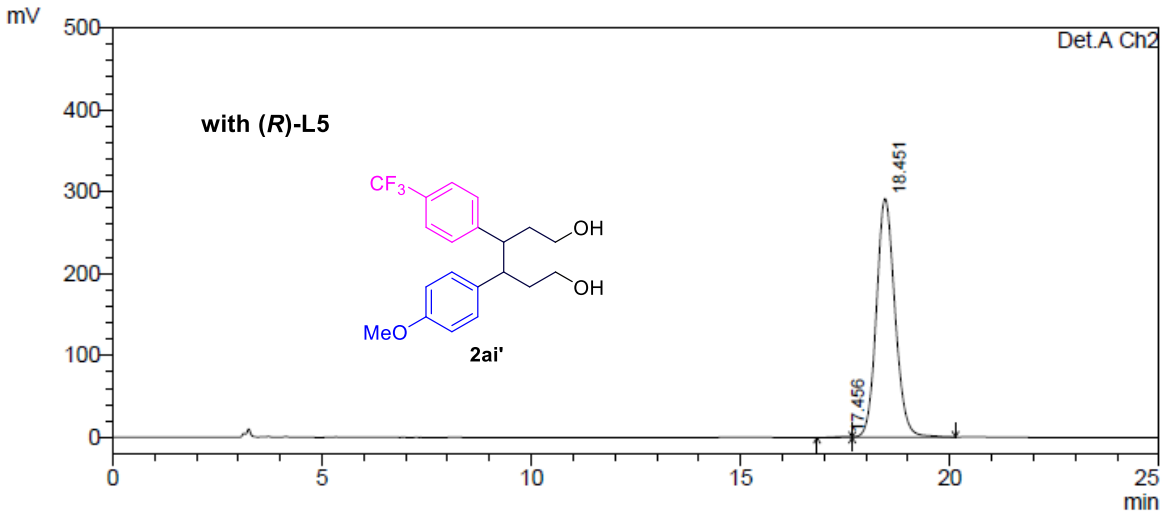
The title compound and the analogous racemic material were subjected to hydroboration and oxidation for HPLC analysis as shown below.



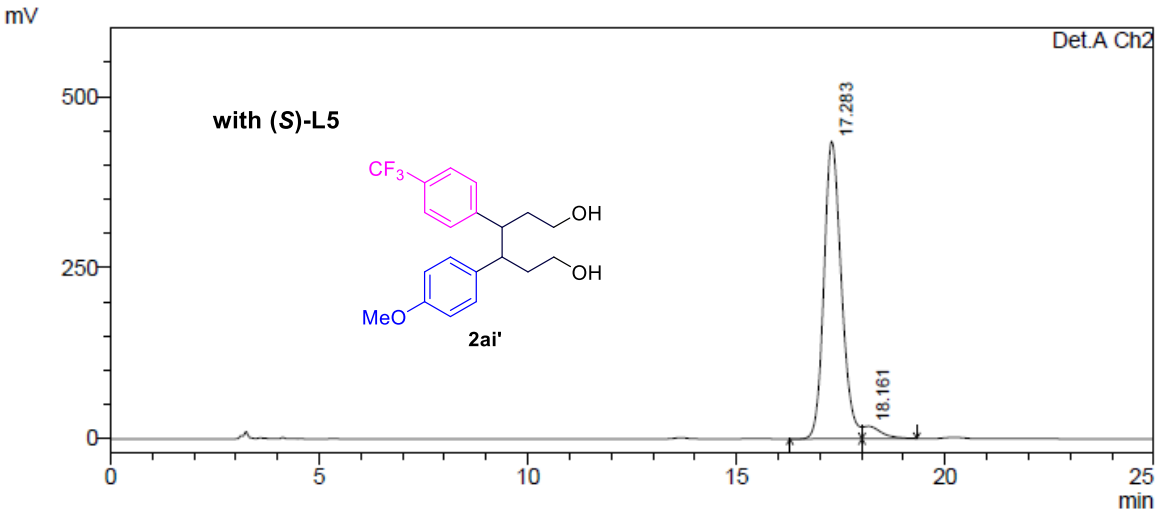
2ai **2ai'**

Enantiomeric excess: > 99%, determined by HPLC (Daicel Chiralpak IA, hexane/ethanol = 90/10, flow rate 1.0 mL/min, T = 25 °C, 220 nm): t_R = 18.45 min (major), t_R = 17.44 min (minor).



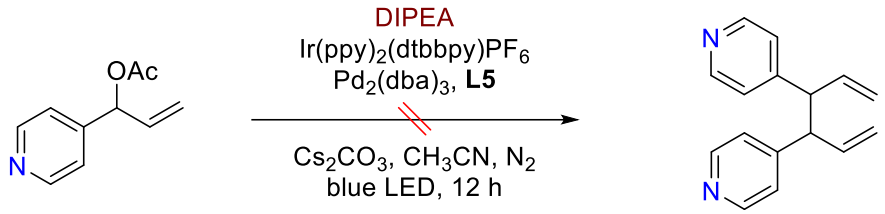


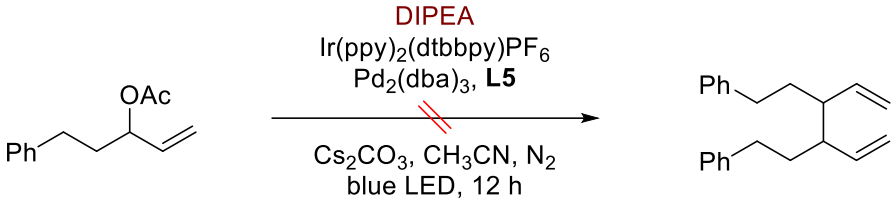
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.444	24472	967	0.271	0.330
2	18.450	9017938	291598	99.729	99.670
Total		9042410	292565	100.000	100.000

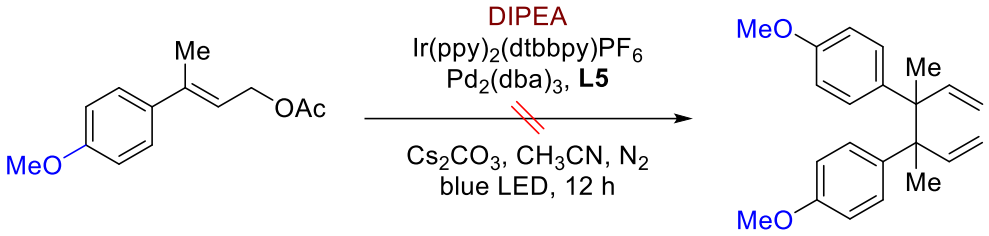


Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.282	12516663	434348	95.223	96.023
2	18.162	627910	17990	4.777	3.977
Total		13144572	452338	100.000	100.000

11. Unsuccessful substrtates







12. References

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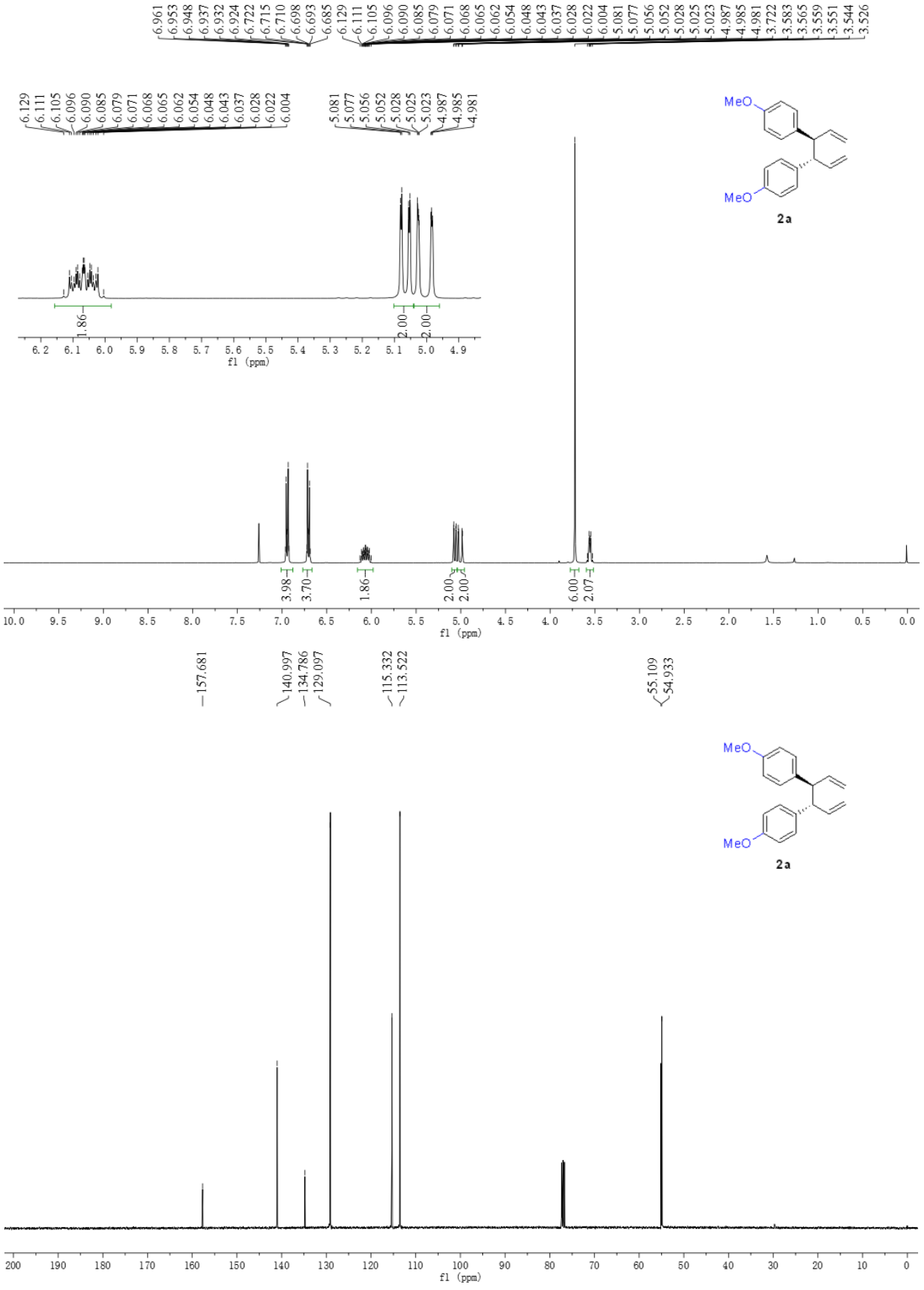
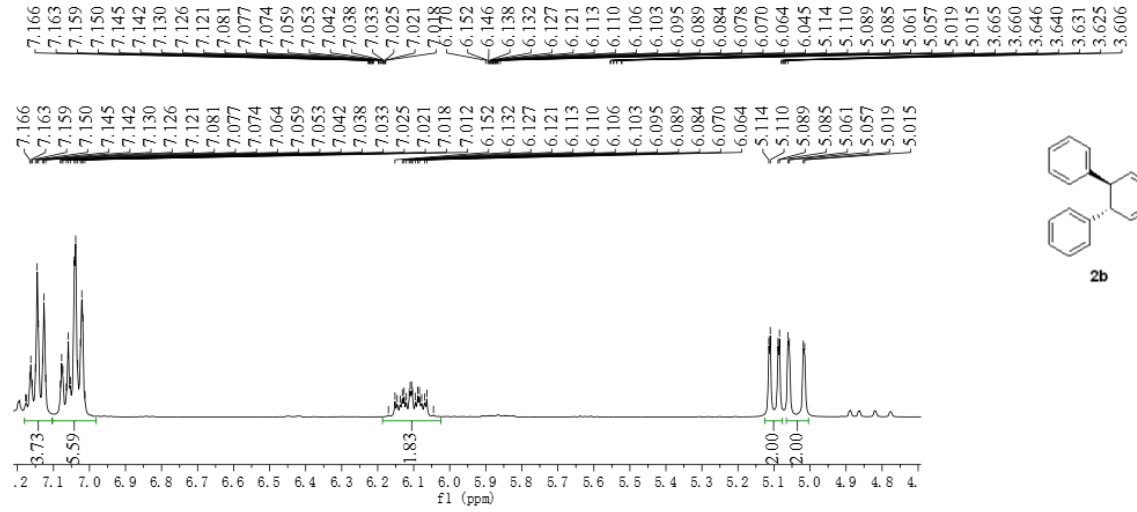
13. NMR spectra for all compounds

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7.038
7.033
7.025
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7.018
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6.146
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6.127
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6.113
6.110
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6.103
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6.070
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5.085
5.061
5.057
5.019
5.015
3.665
3.660
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3.73
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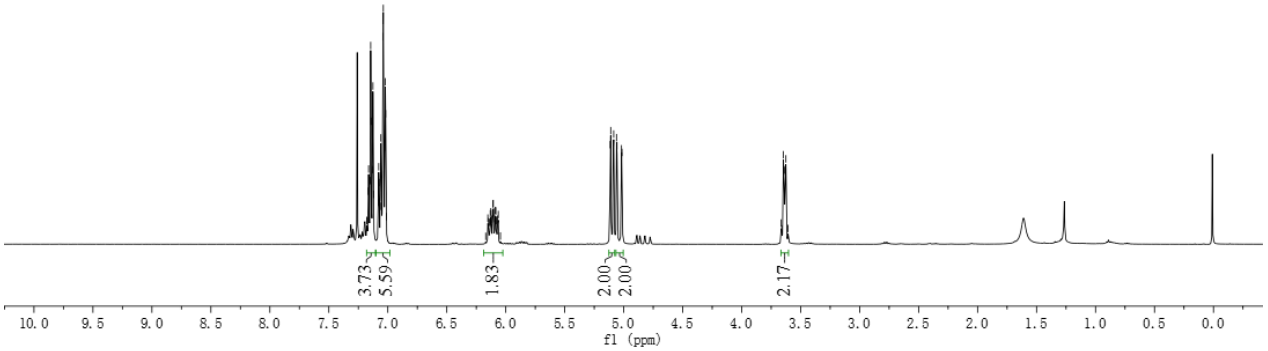
2.00
2.00
f1 (ppm)

2b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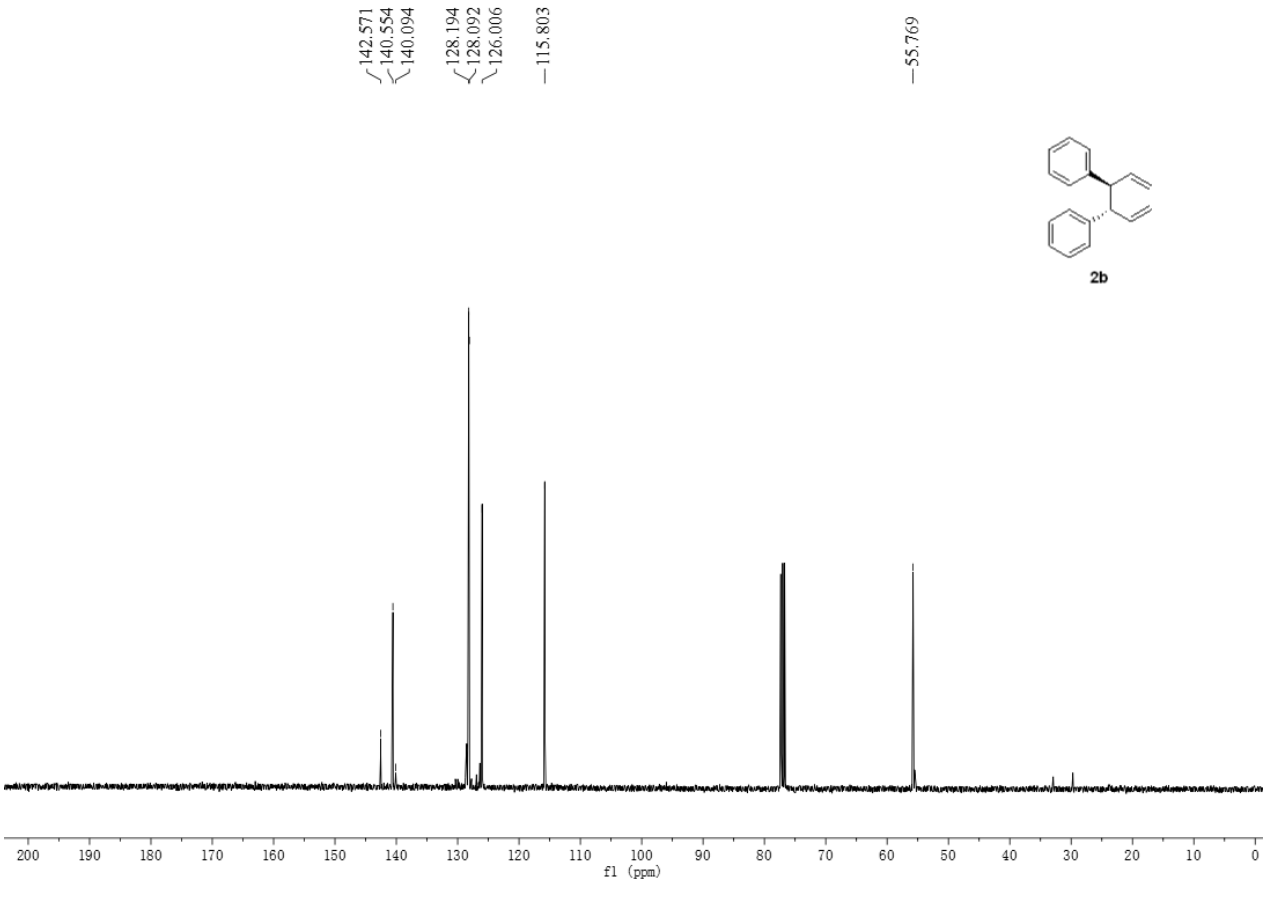
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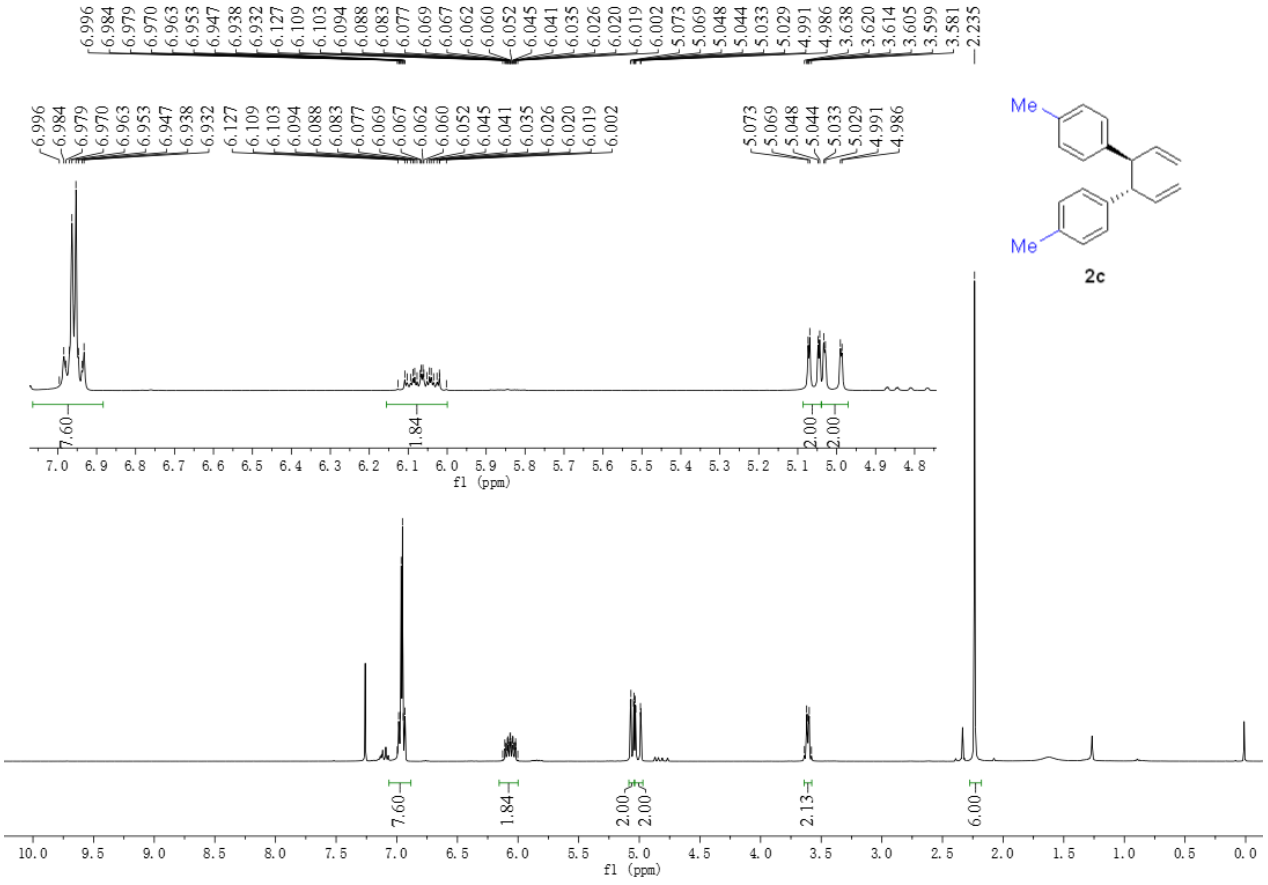
f1 (ppm)

2b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6.088
6.083
6.077
6.069
6.067
6.062
6.060
6.052
6.045
6.041
6.035
6.026
6.020
6.019
6.002
5.073
5.069
5.048
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5.033
5.029
4.991
4.986
3.638
3.620
3.614
3.605
3.599
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Me
Me
2c
7.60
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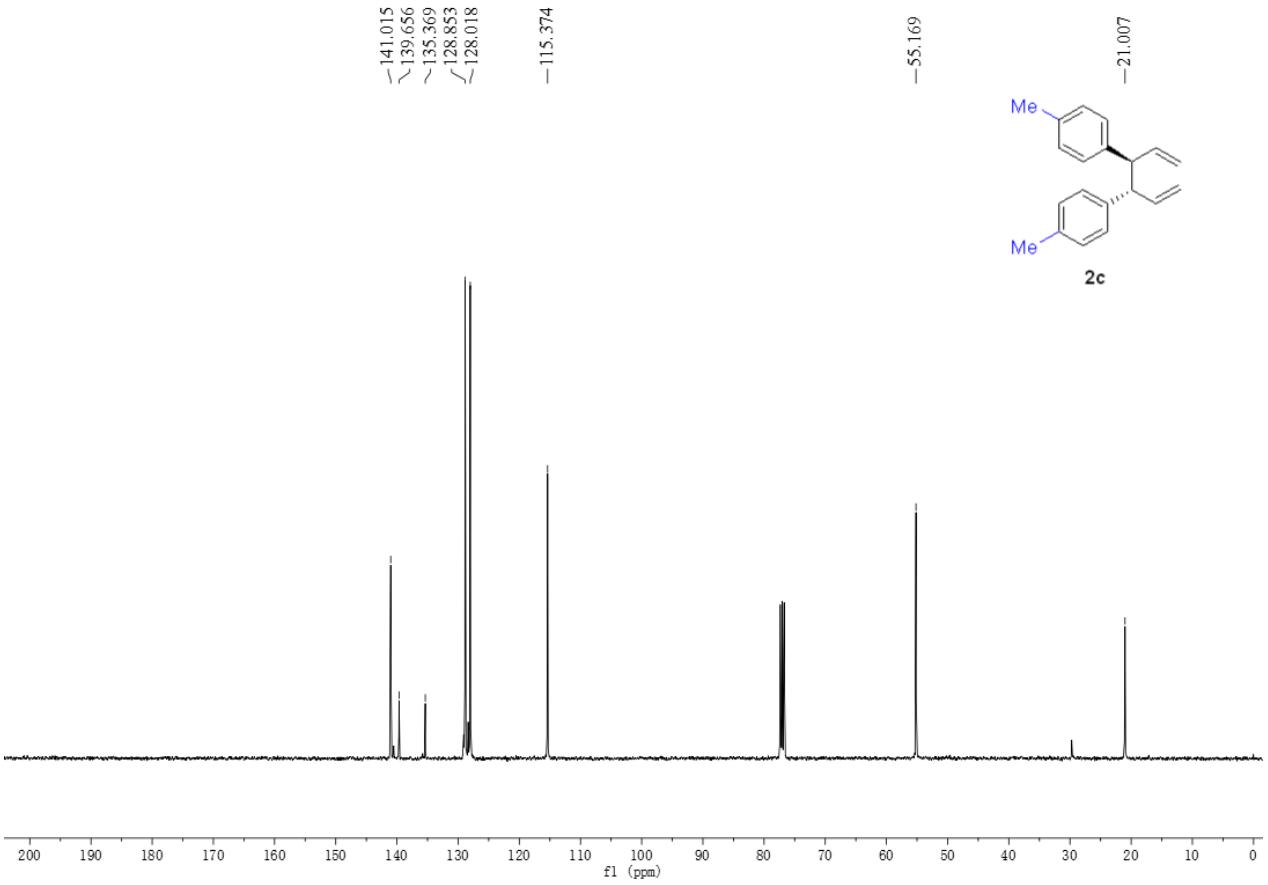
2.00
2.13
6.00
f1 (ppm)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Me
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f1 (ppm)


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7.535
7.531
7.521
7.518
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7.510
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7.410
7.406
7.388
7.384
7.372
7.368
7.314
7.311
7.308
7.298
7.293
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7.277
7.274
7.271
7.163
7.157
7.152
7.141
7.136
7.131
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6.169
6.163
6.155
6.153
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6.138
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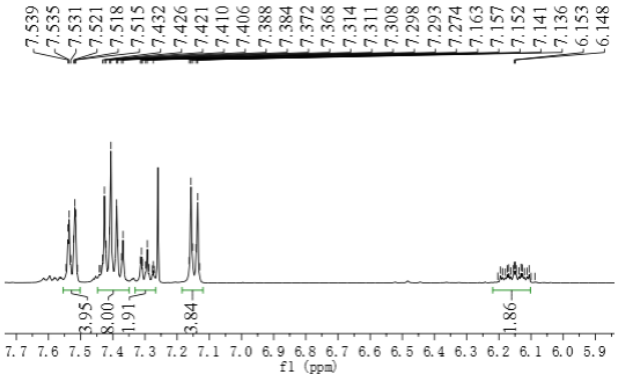
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7.368
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7.311
7.308
7.298
7.293
7.274
7.163
7.157
7.152
7.141
7.136
6.153
6.148
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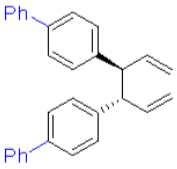
8.00
1.91
3.84
1.86
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9
f1 (ppm)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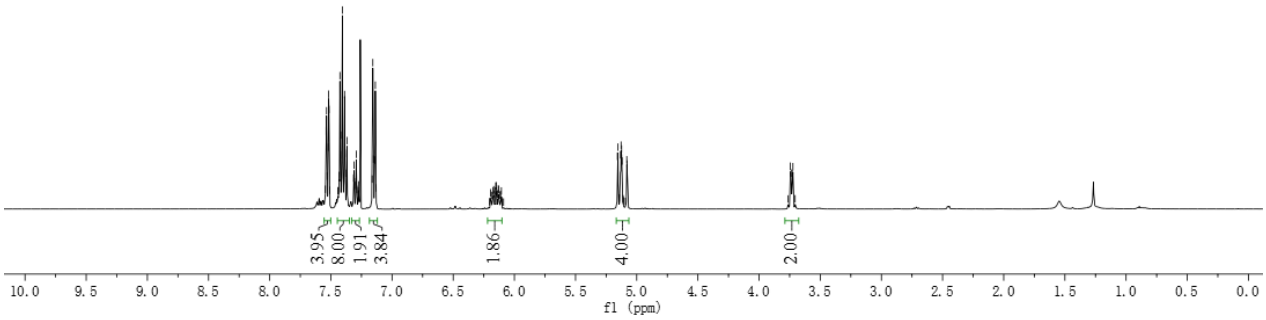
Ph

2d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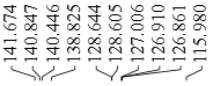
8.00
1.91
3.84
1.86
4.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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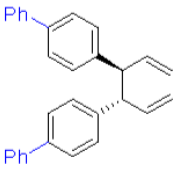
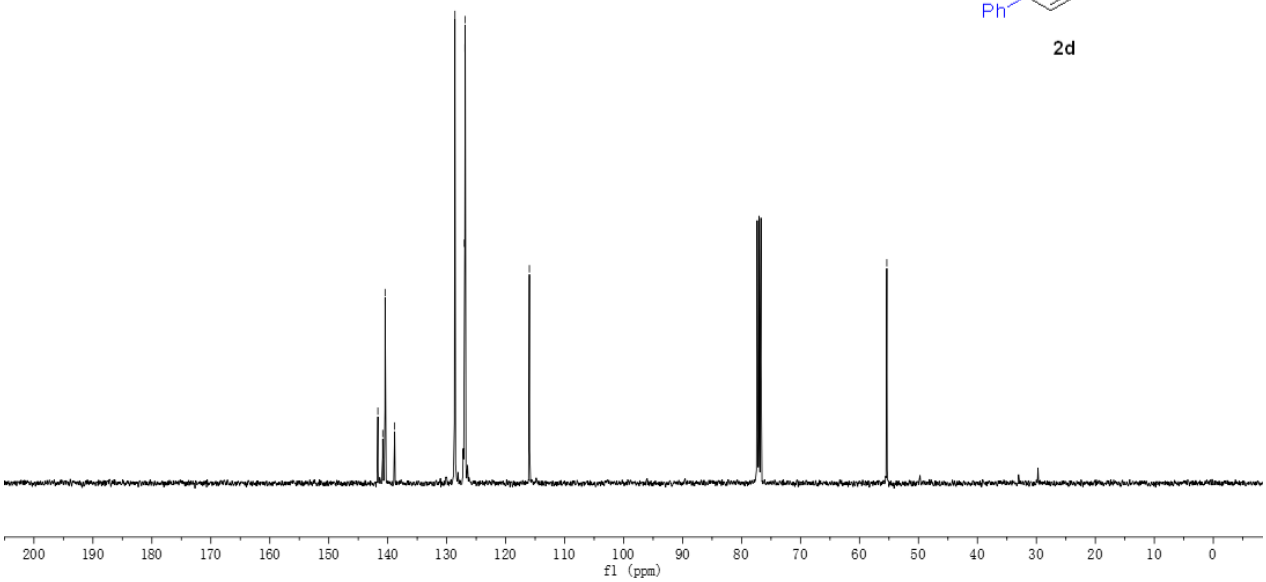
55.363


Ph
Ph

2d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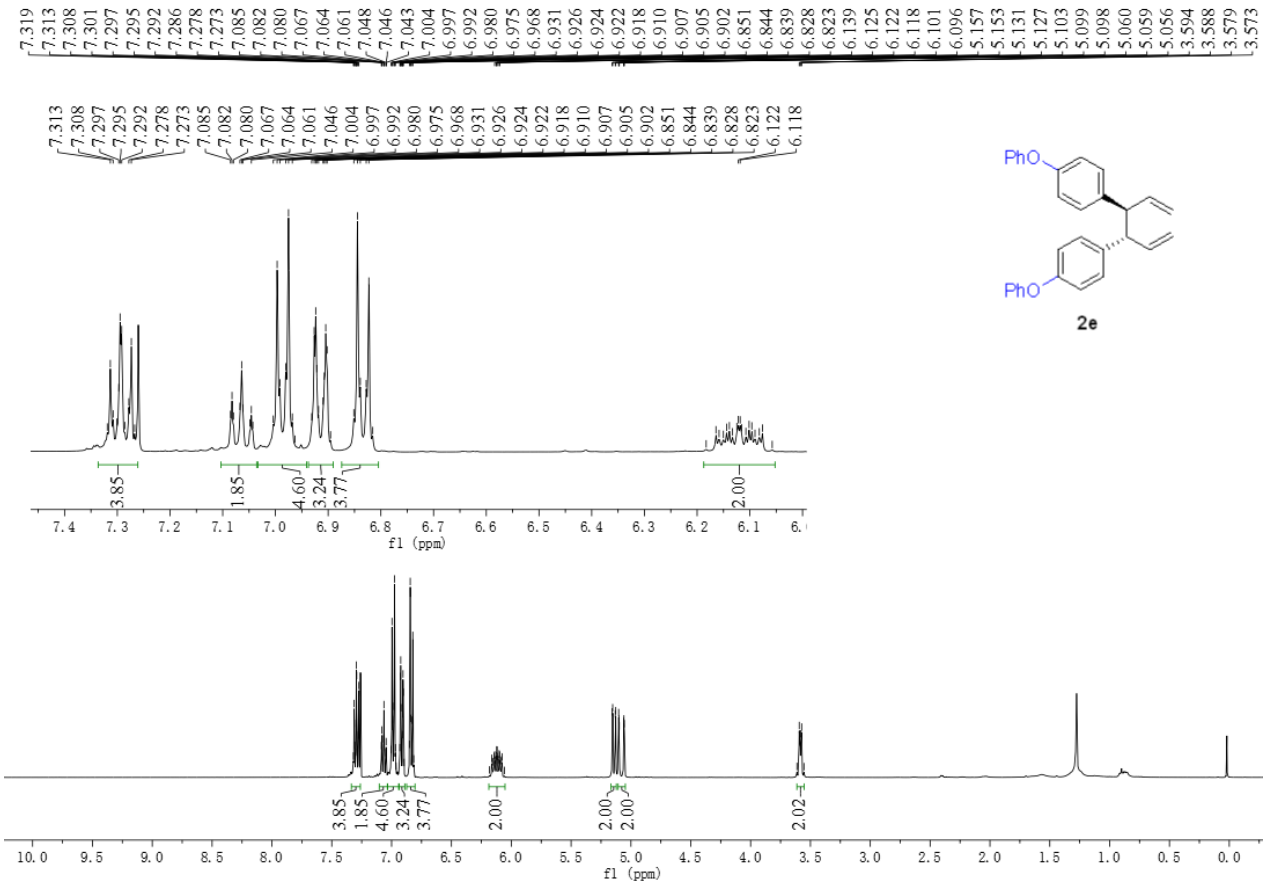
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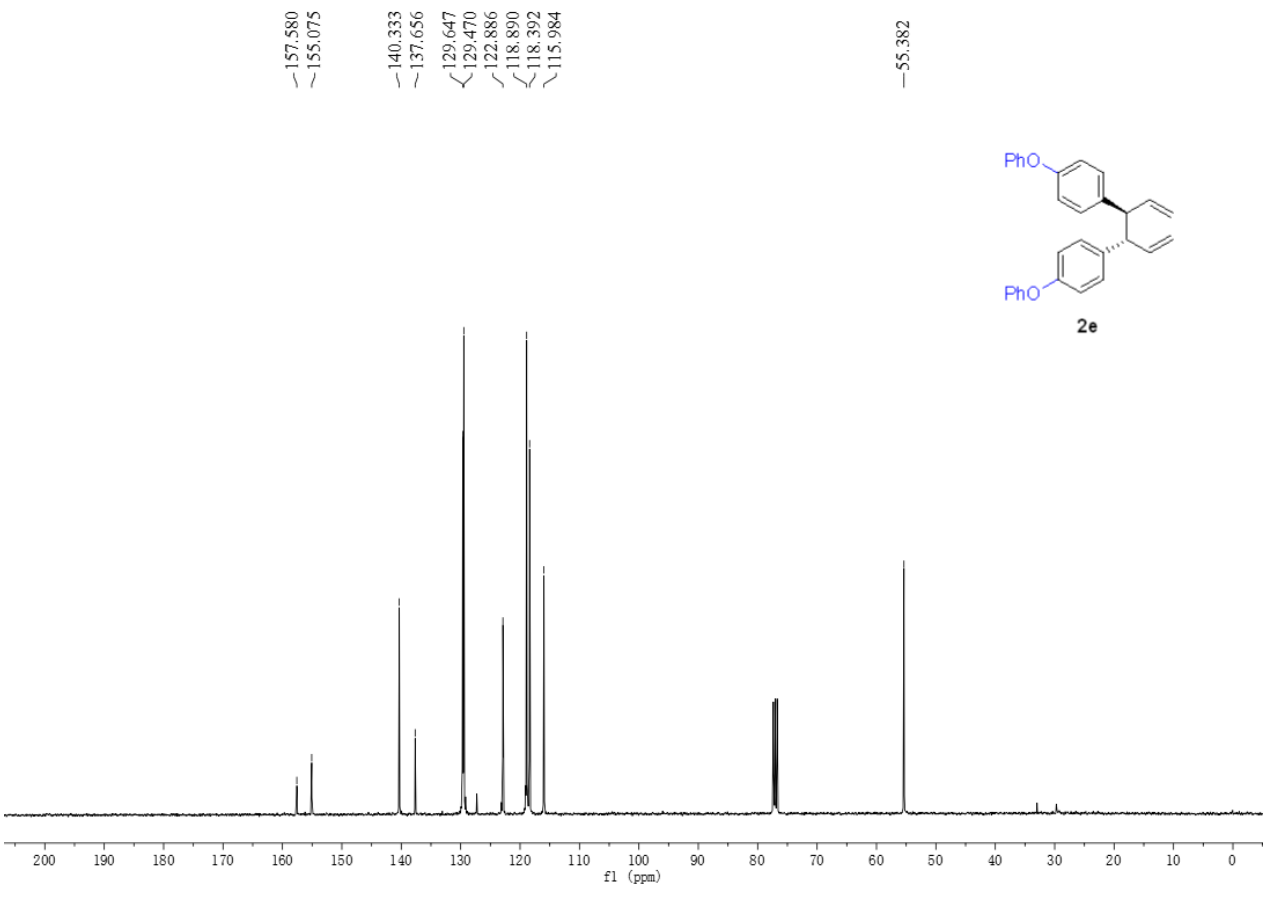
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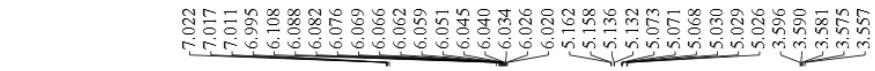
PhO
PhO
2e
f1 (ppm)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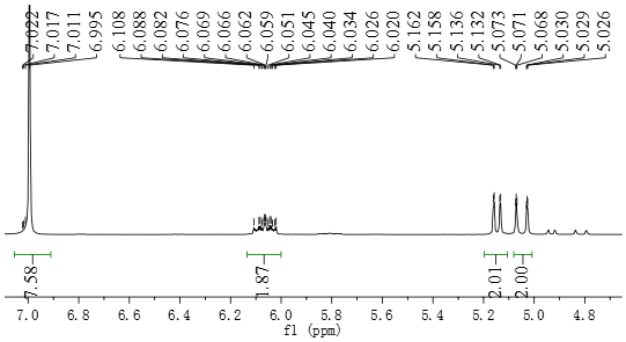
3.557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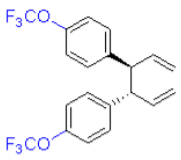
f1 (ppm)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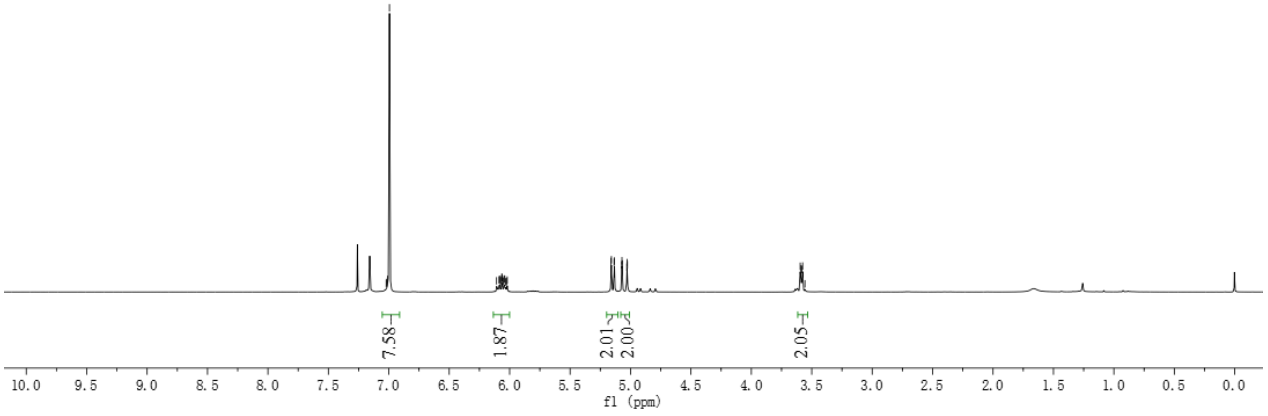
F3CO

2f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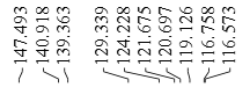
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116.573


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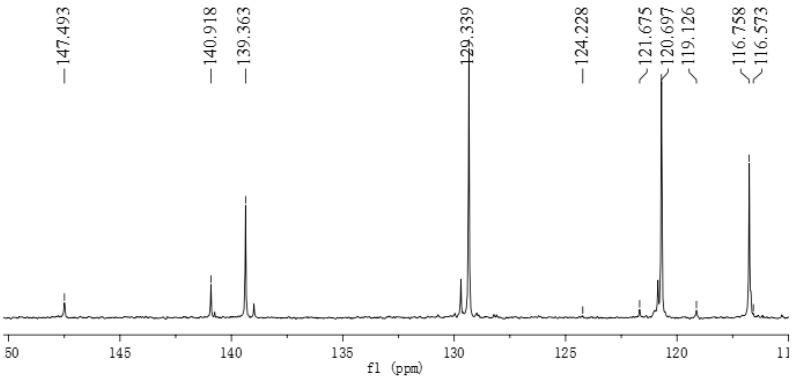
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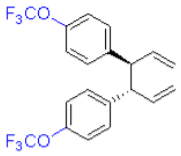
116.573
f1 (ppm)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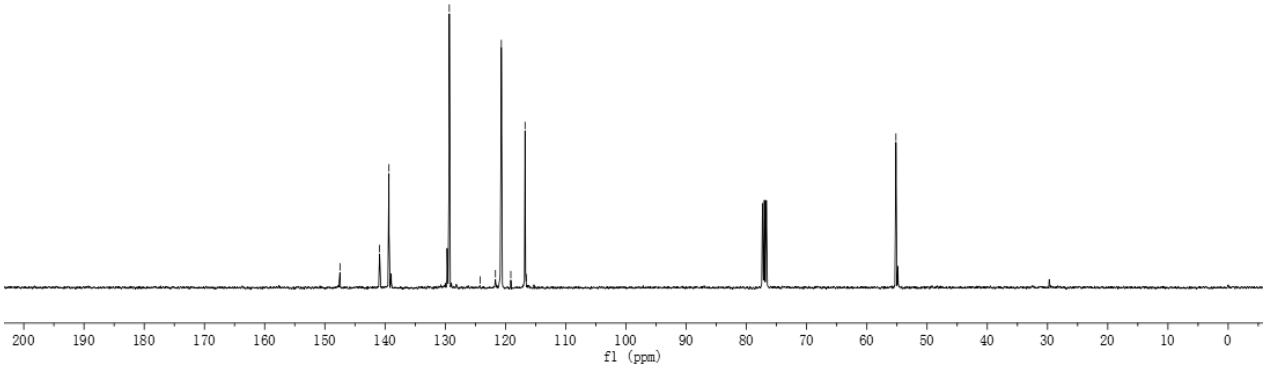
F3CO

2f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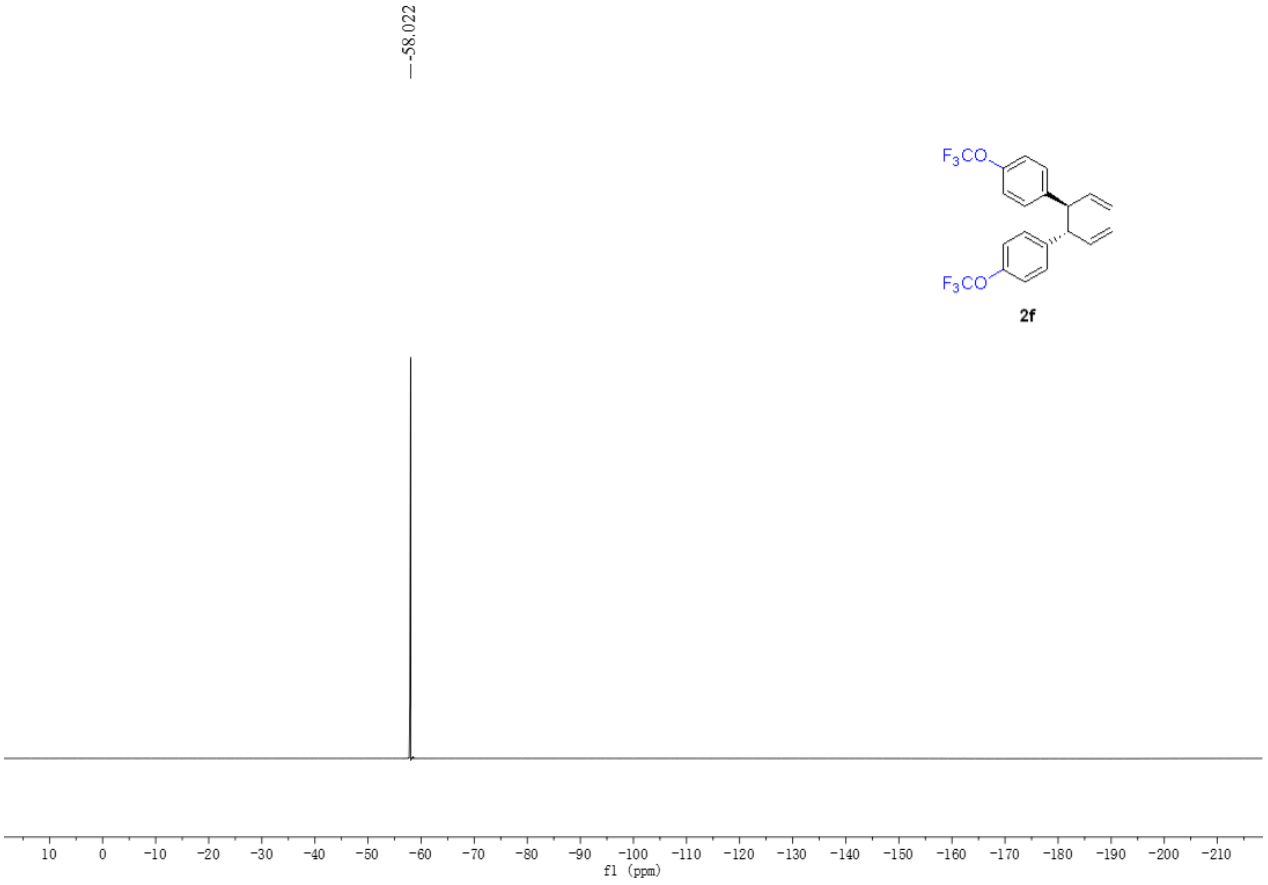
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F3CO
F3CO
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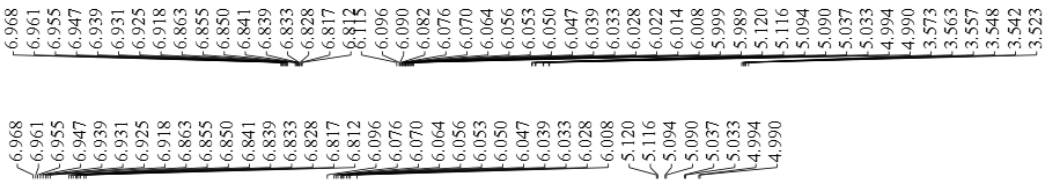
f1 (ppm)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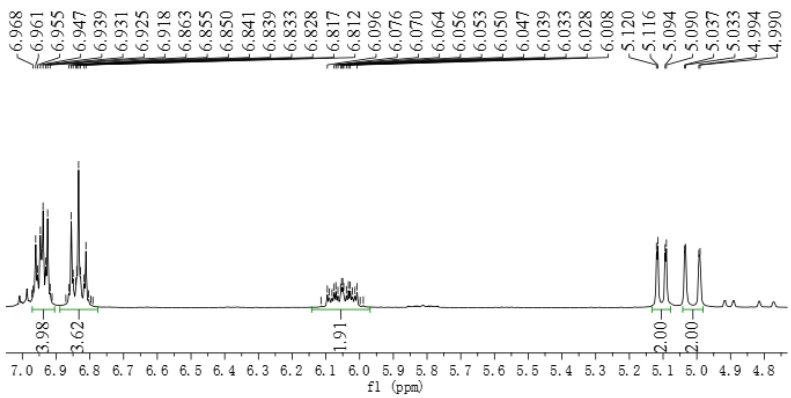
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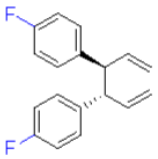

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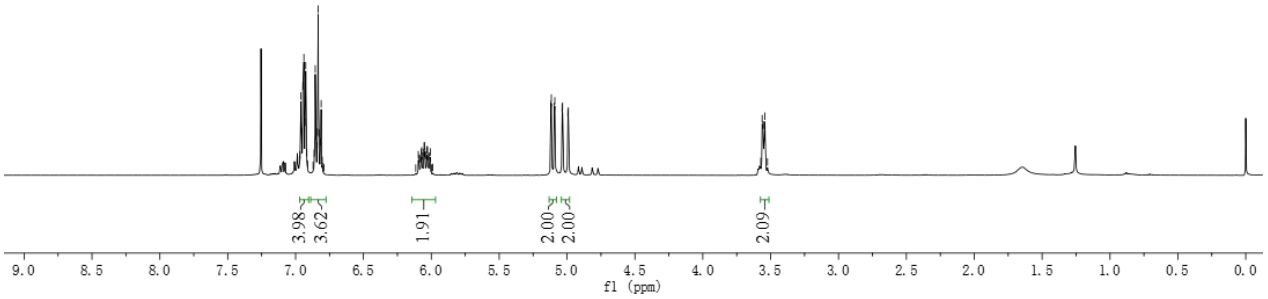
3.98
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1.91
2.00
2.00
2.09
f1 (ppm)


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129.542
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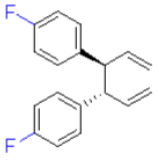
115.098
114.888
55.081



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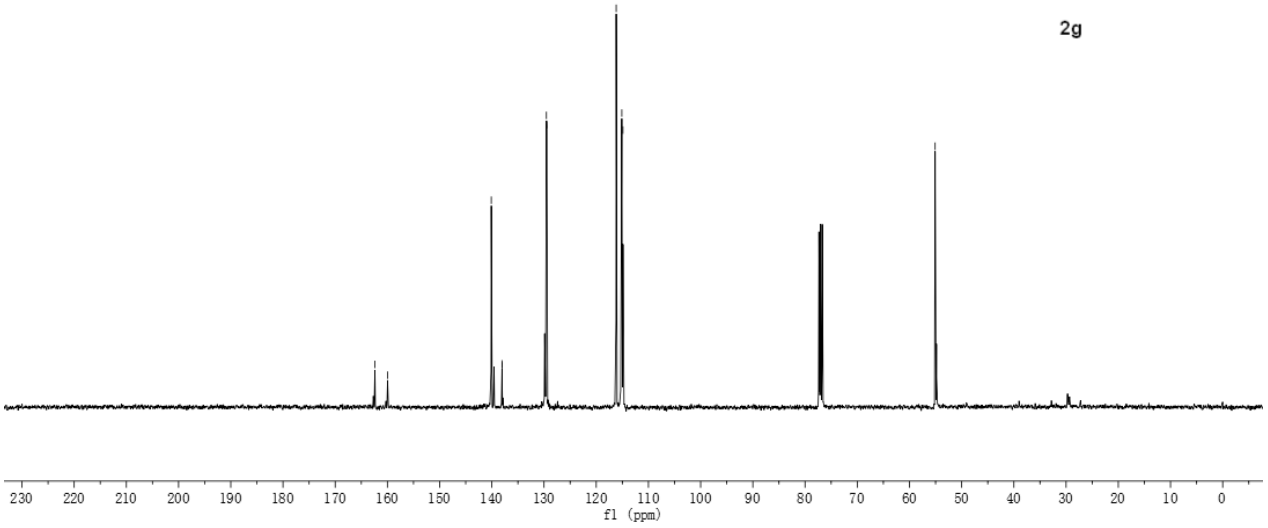
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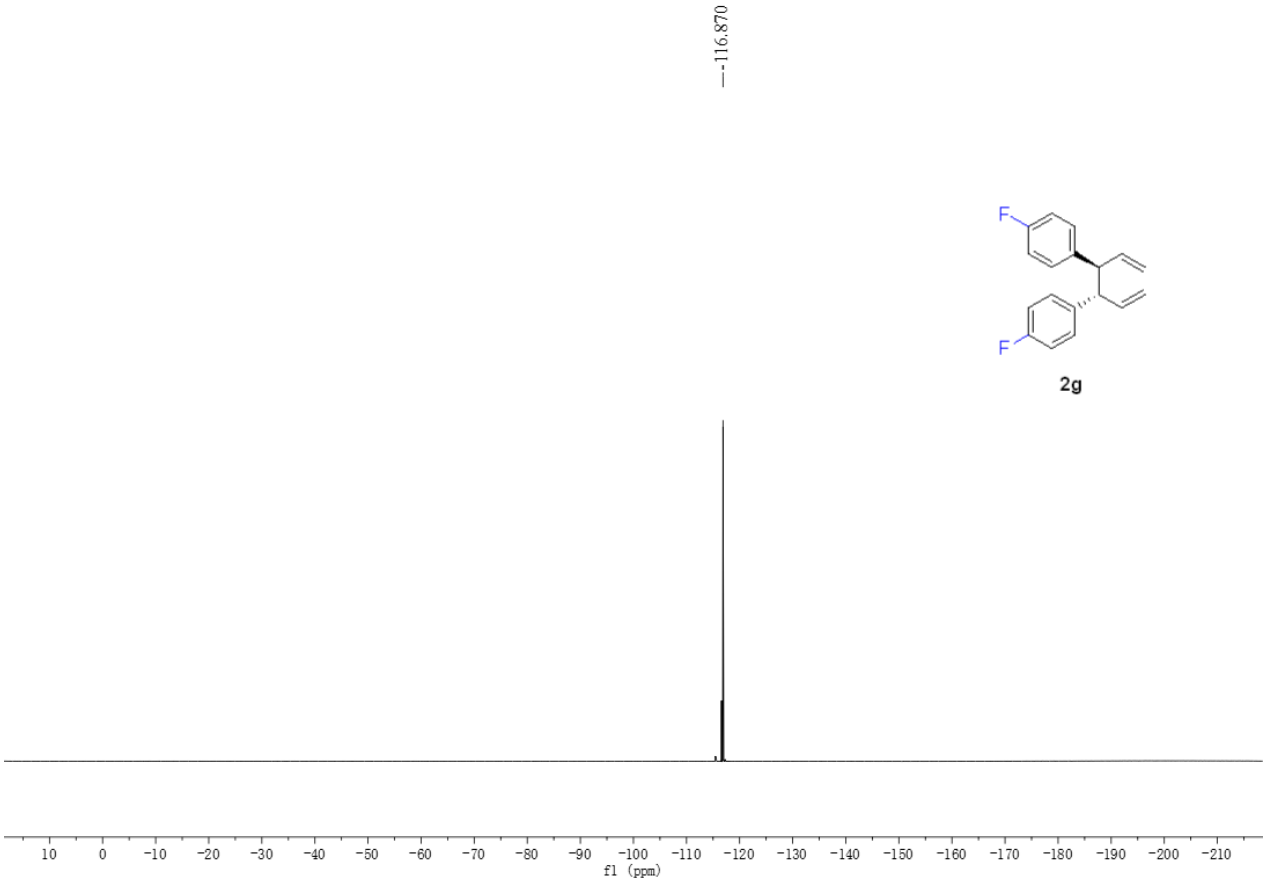
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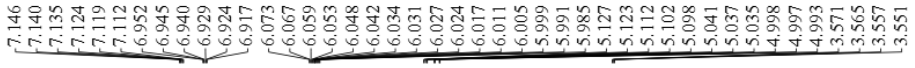
f1 (ppm)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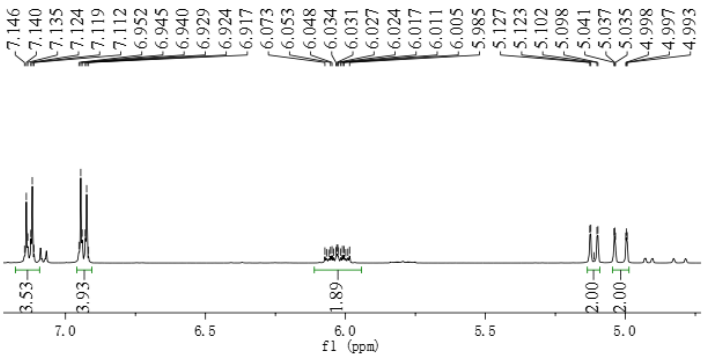
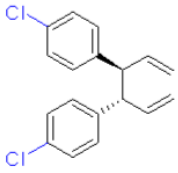
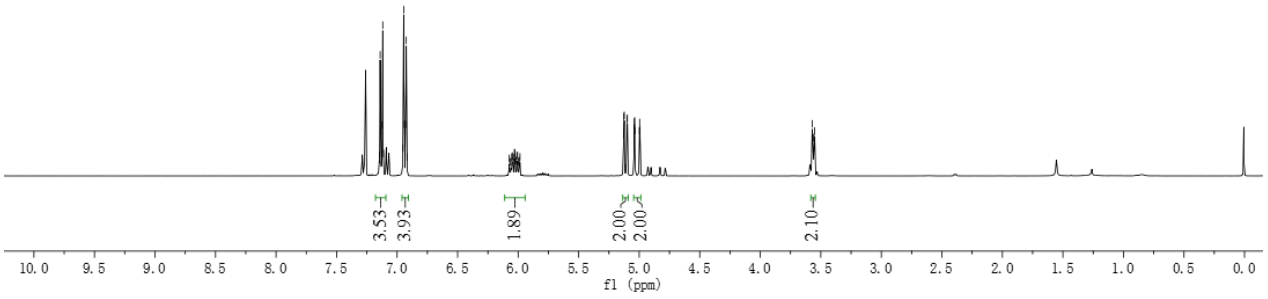
5.037
5.035
4.998
4.997
4.993
3.571
3.565
3.557
3.551

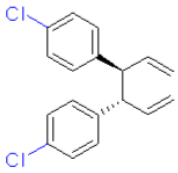

7.146
7.140
7.135
7.124
7.119
7.112
6.952
6.945
6.940
6.929
6.924
6.917
6.073
6.053
6.048
6.034
6.031
6.027
6.024
6.017
6.011
6.005
5.985
5.127
5.123
5.102
5.098
5.041
5.037
5.035
4.998
4.997
4.993
3.53
3.93
1.89
2.00
2.00
7.0
6.5
6.0
5.5
5.0
f1 (ppm)


Cl
Cl

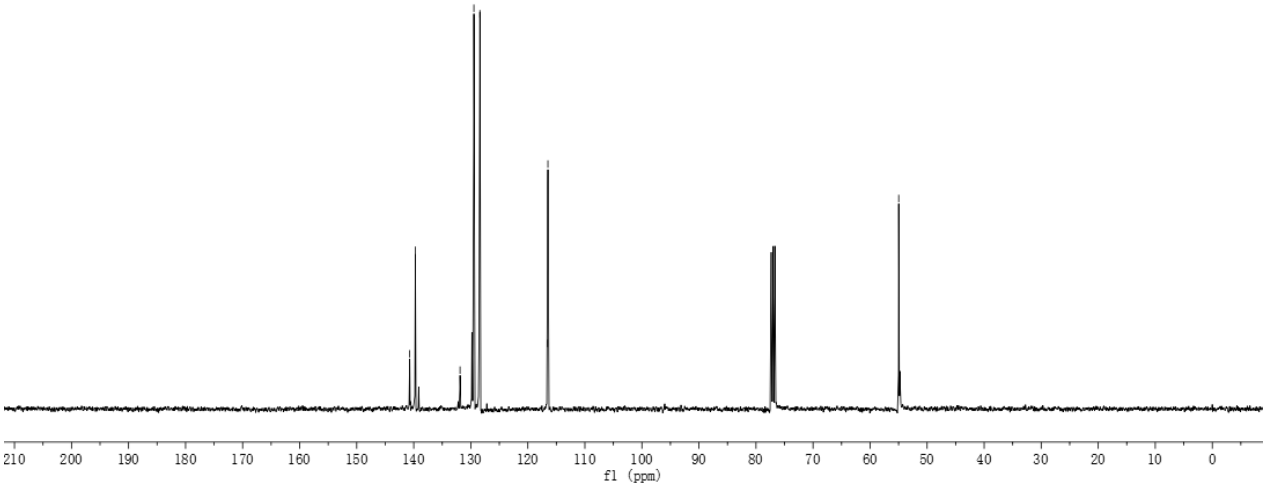
2h


3.53
3.93
1.89
2.00
2.00
2.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

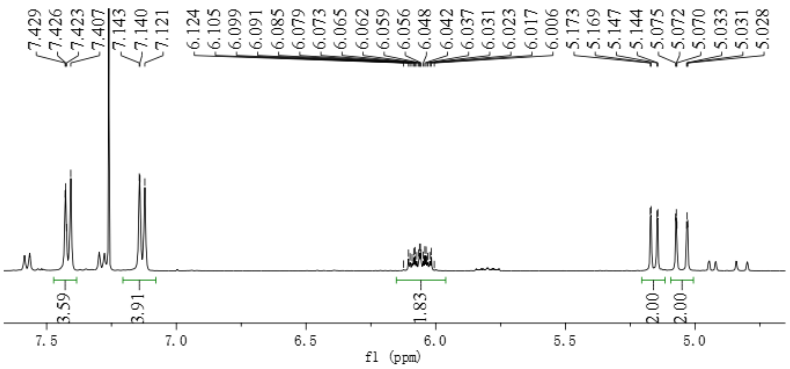

140.711
139.722
131.885
129.456
128.402
116.546
116.481
54.979

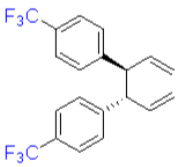

Cl
Cl

2h

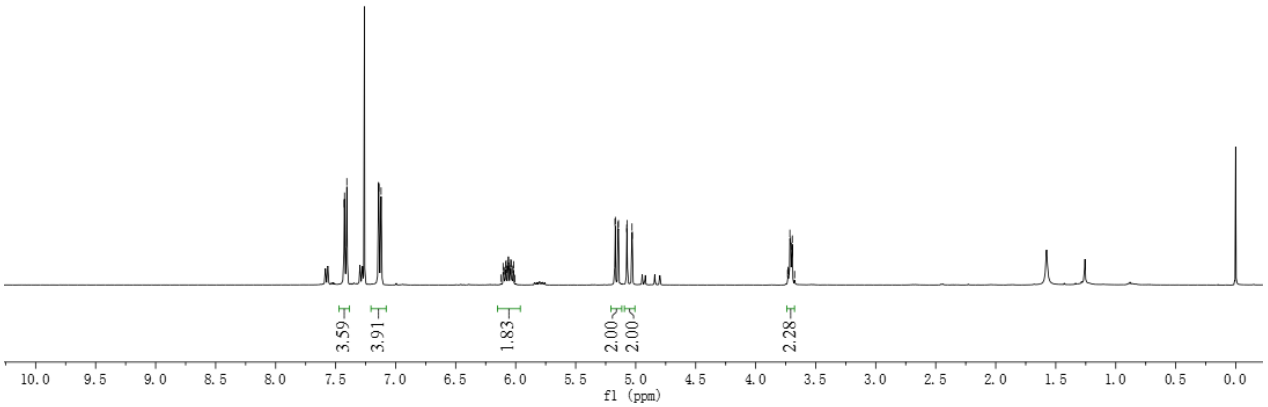

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.429
7.426
7.423
7.407
7.143
7.140
7.121
6.124
6.105
6.099
6.091
6.085
6.079
6.073
6.065
6.062
6.059
6.056
6.048
6.042
6.037
6.031
6.023
6.017
6.006
5.173
5.169
5.147
5.144
5.075
5.072
5.070
5.033
5.031
5.028
3.734
3.730
3.724
3.715
3.709
3.701
3.695
3.676

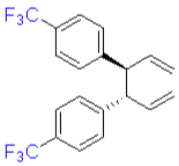

3.59
3.91
1.83
2.00
2.00
f1 (ppm)


F3C
F3C

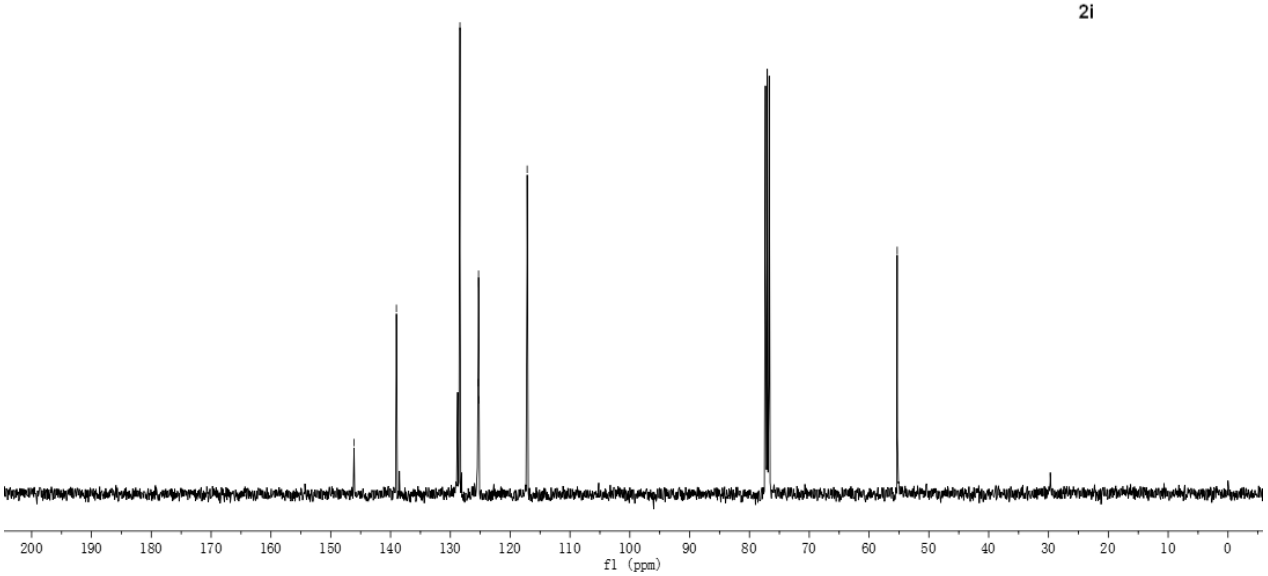
2i

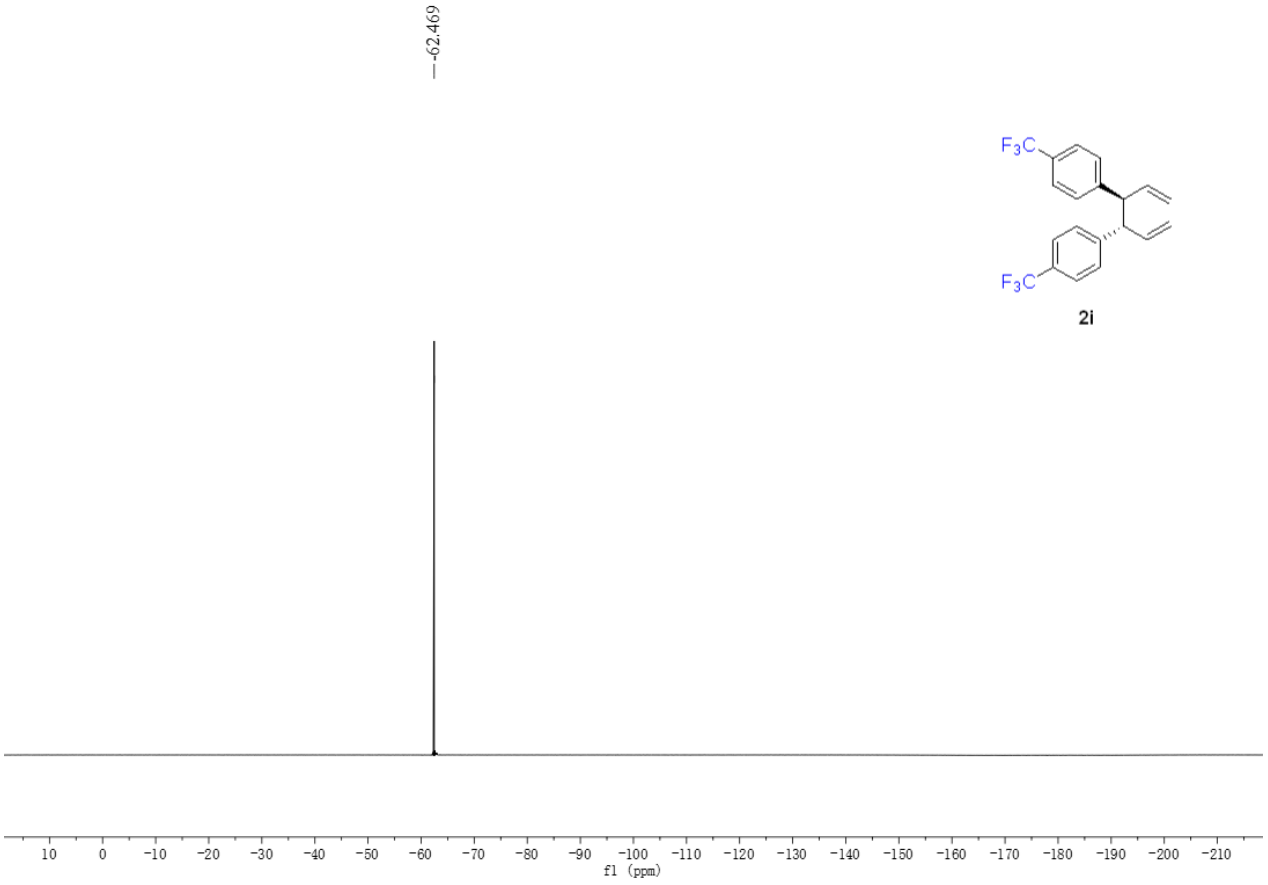

3.59
3.91
1.83
2.00
2.00
2.28
f1 (ppm)

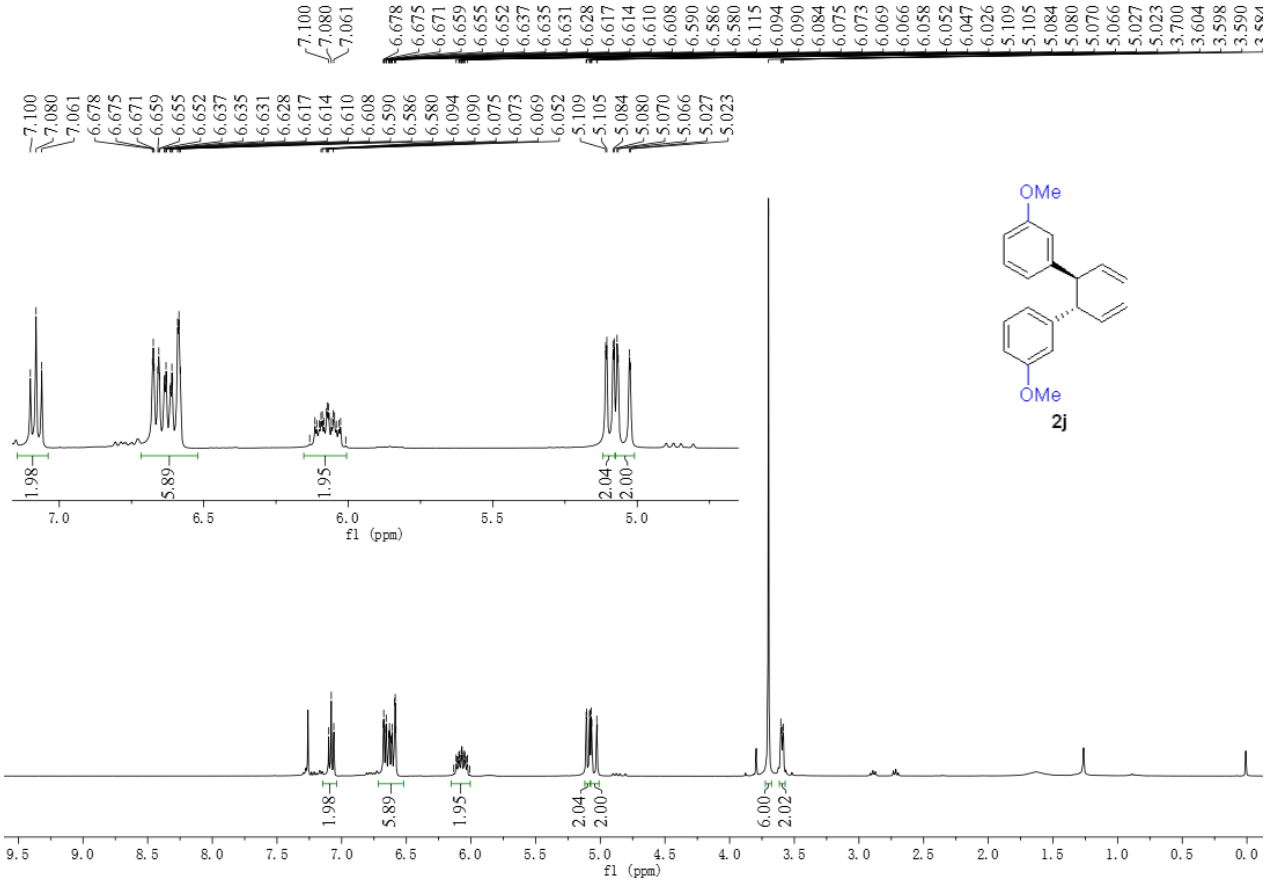

146.101
139.023
128.399
125.327
125.288
125.250
125.214
117.158
55.299

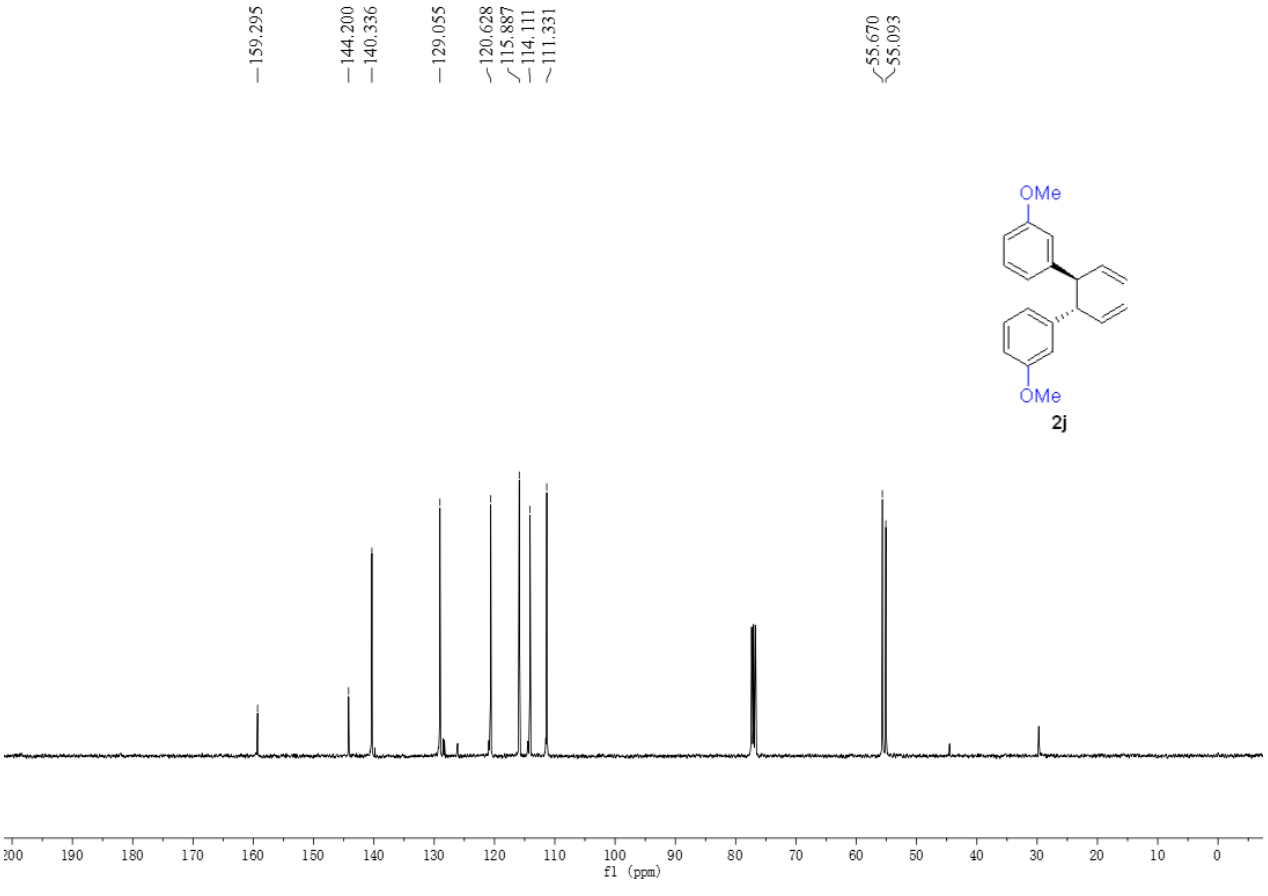

F3C
F3C

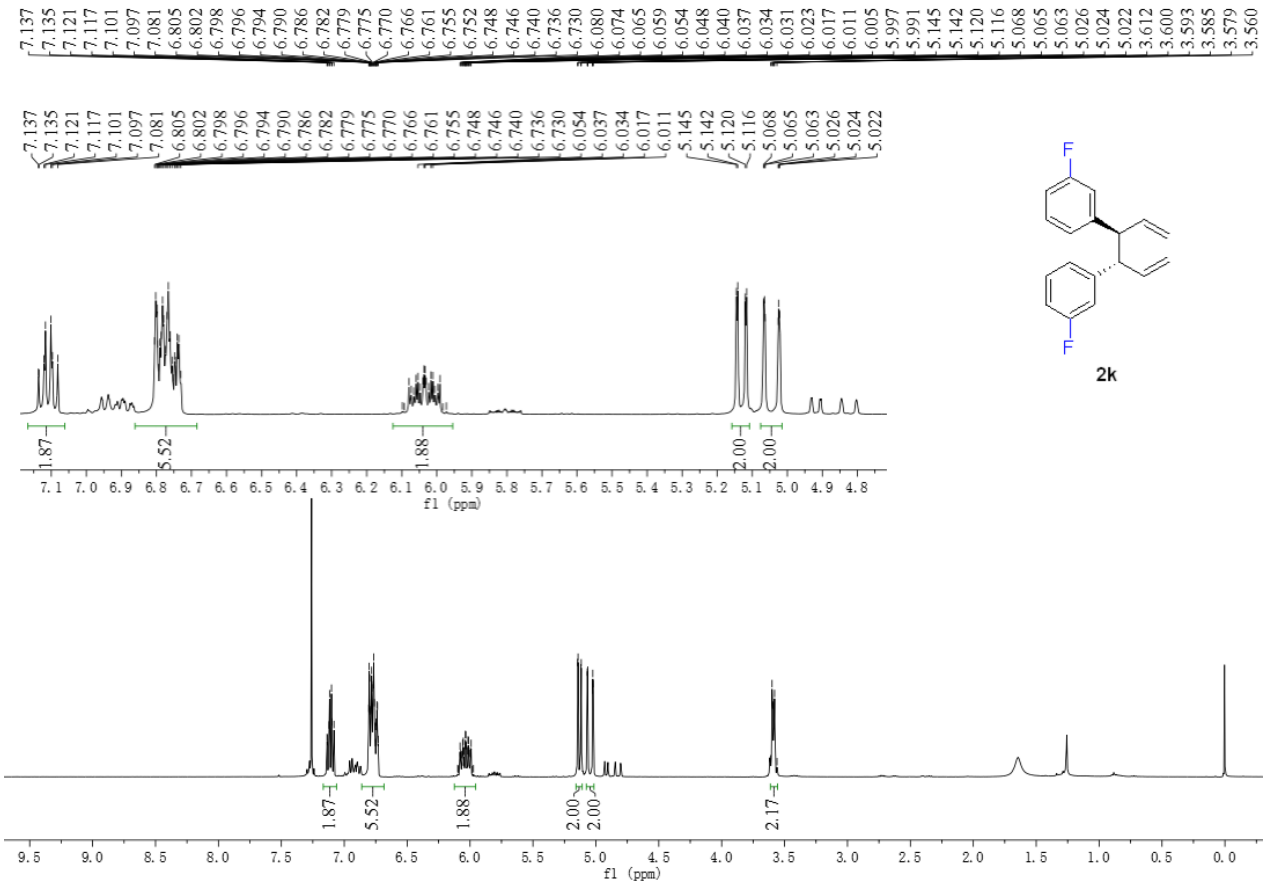
2i

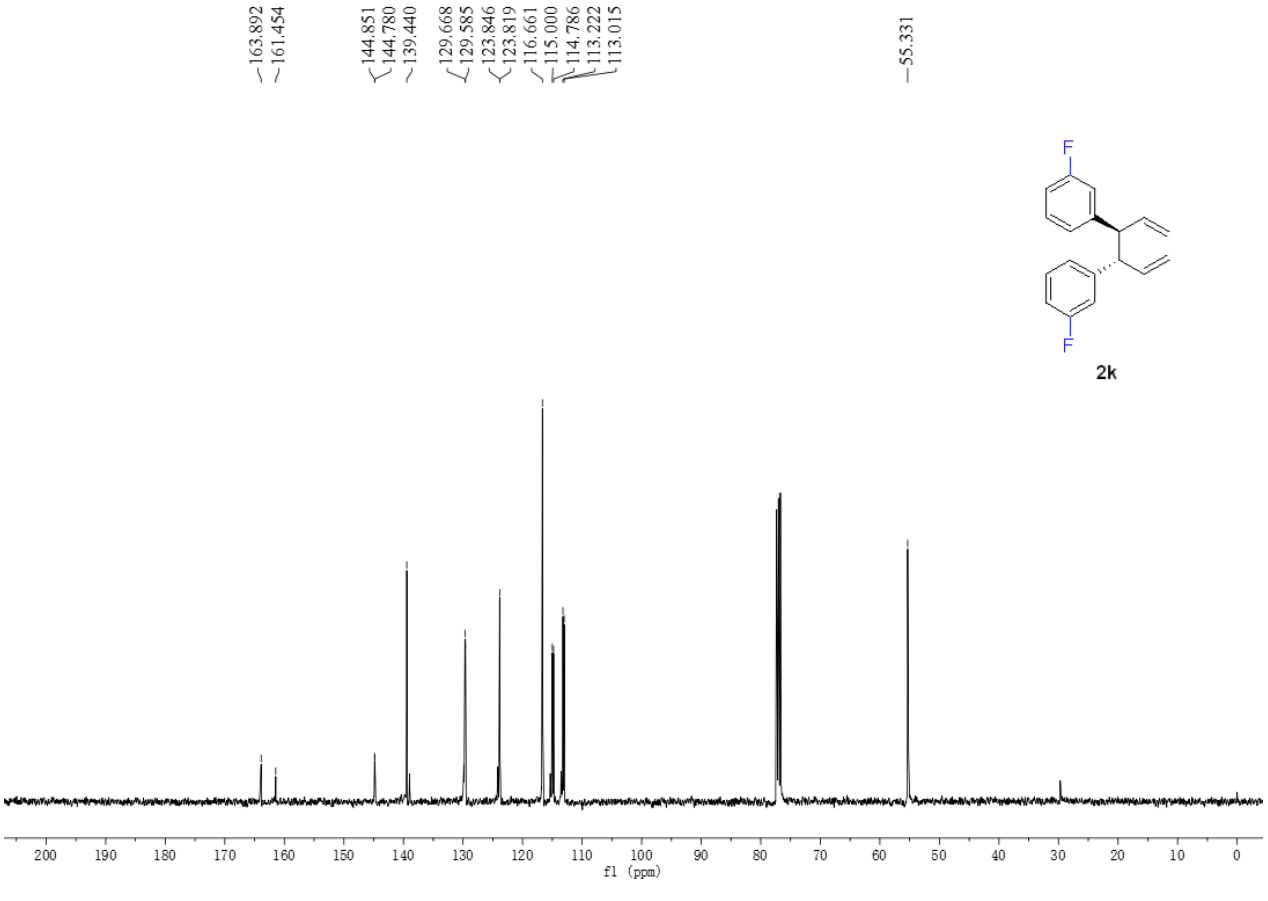

f1 (ppm)

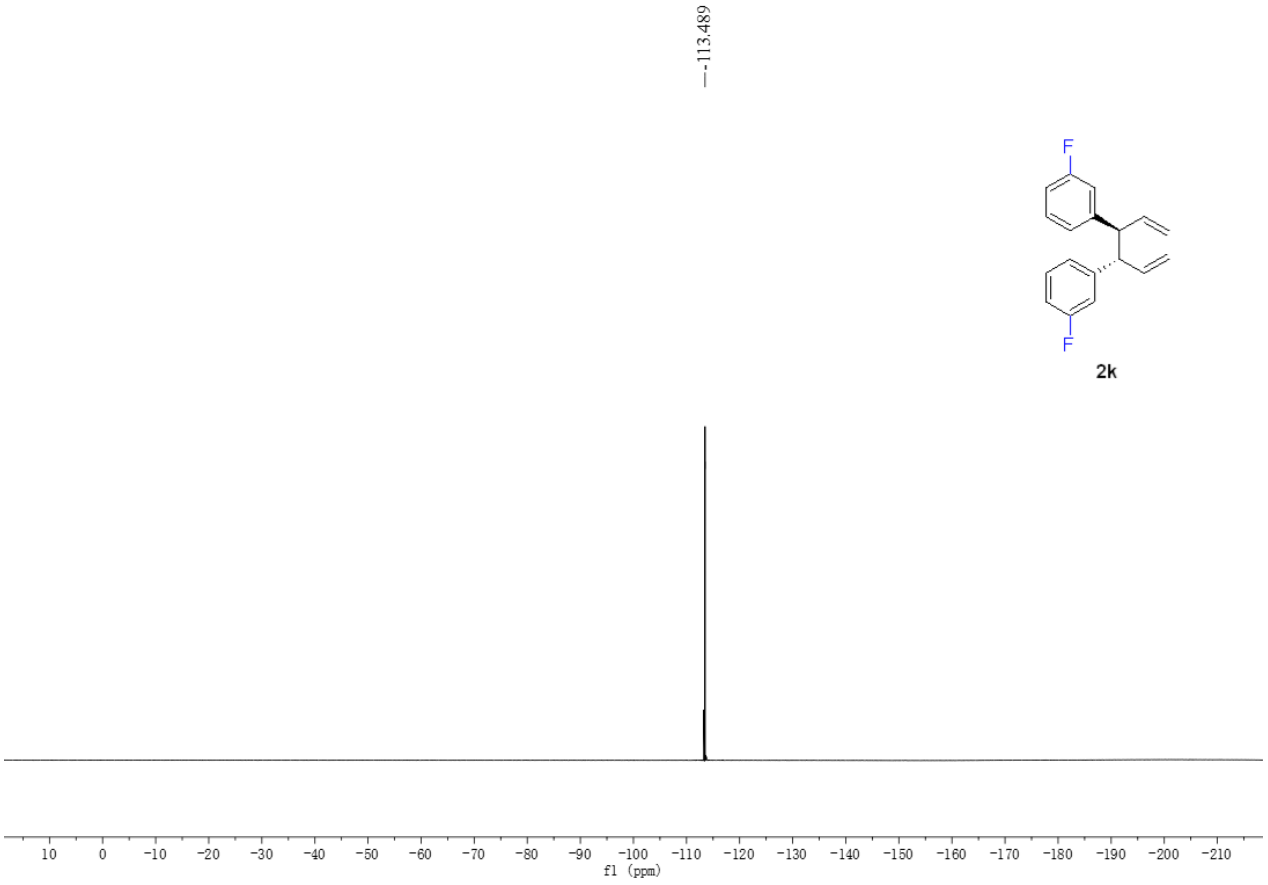

-62.469
F3C
F3C
2i
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

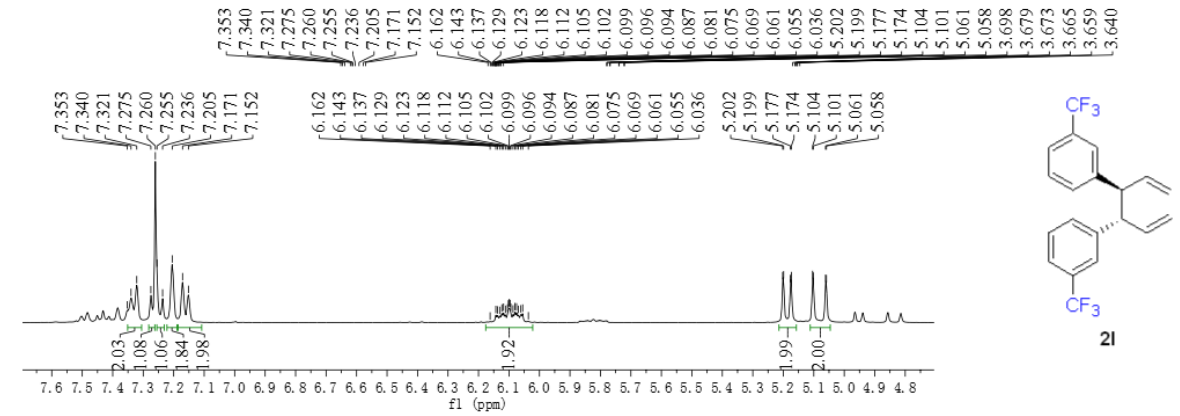

7.100
7.080
7.061
6.678
6.675
6.671
6.659
6.655
6.652
6.637
6.635
6.631
6.628
6.617
6.614
6.610
6.608
6.590
6.586
6.580
6.115
6.094
6.090
6.084
6.075
6.073
6.069
6.066
6.058
6.052
6.047
6.026
5.109
5.105
5.084
5.080
5.070
5.066
5.027
5.023
3.700
3.604
3.598
3.590
OMe
OMe
2j
1.98
5.89
1.95
2.04
2.00
6.00
2.02
f1 (ppm)


159.295
144.200
140.336
129.055
120.628
115.887
114.111
111.331
55.670
55.093
OMe
OMe
2j
f1 (ppm)


7.137
7.135
7.121
7.117
7.101
7.097
7.081
6.805
6.802
6.798
6.796
6.794
6.790
6.786
6.782
6.779
6.775
6.770
6.766
6.761
6.755
6.752
6.748
6.746
6.740
6.736
6.730
6.080
6.074
6.065
6.059
6.054
6.048
6.040
6.037
6.034
6.031
6.023
6.017
6.011
6.005
5.997
5.991
5.145
5.142
5.120
5.116
5.068
5.065
5.063
5.026
5.024
5.022
3.612
3.600
3.593
3.585
3.579
3.560
F
F
2k
1.87
5.52
1.88
2.00
2.00
2.17
f1 (ppm)

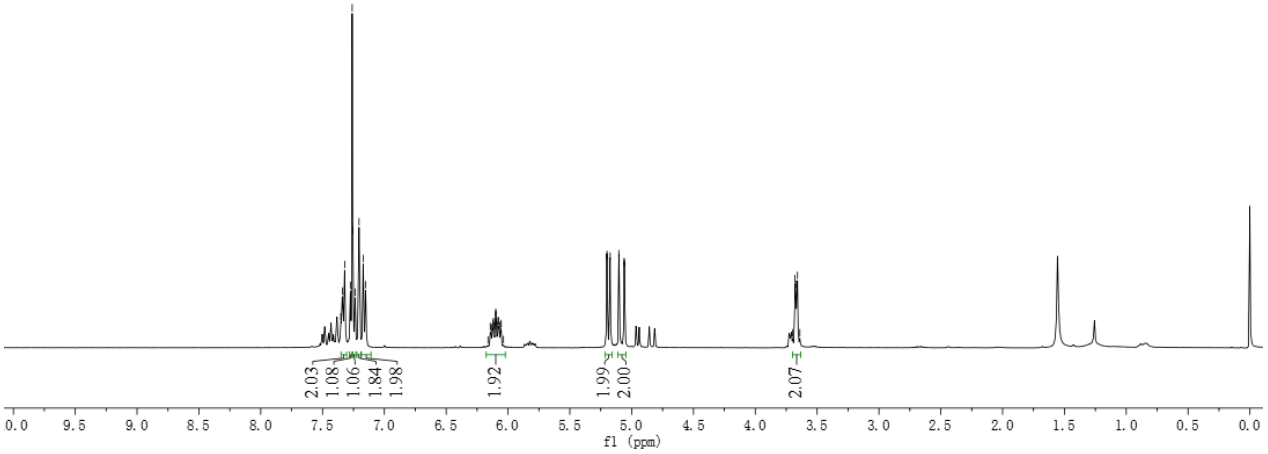

163.892
161.454
144.851
144.780
139.440
129.668
129.585
123.846
123.819
116.661
115.000
114.786
113.222
113.015
55.331
F
F
2k
f1 (ppm)

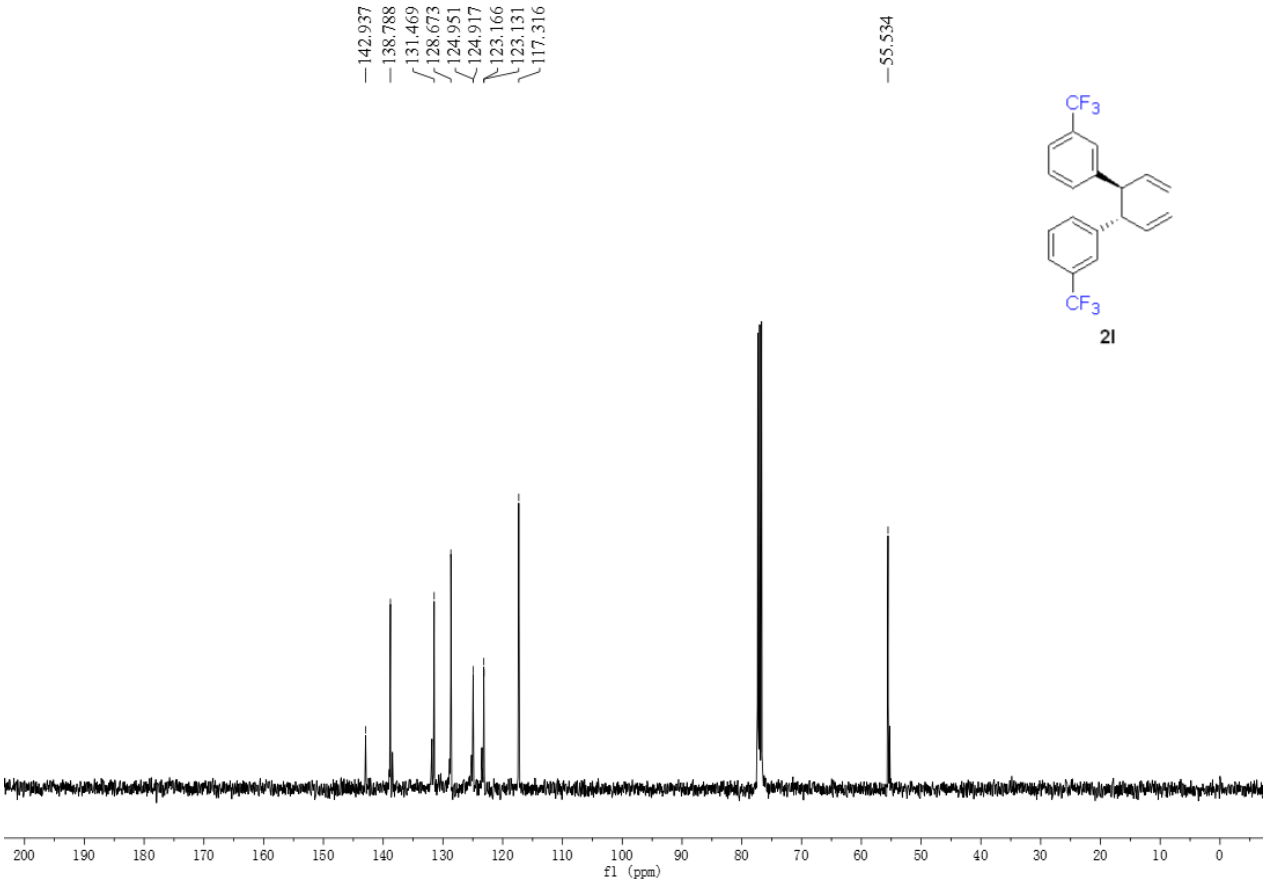

-113.489
F
F
2k
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


7.353
7.340
7.321
7.275
7.260
7.255
7.236
7.205
7.171
7.152
6.162
6.143
6.137
6.129
6.123
6.118
6.112
6.105
6.102
6.099
6.096
6.094
6.087
6.081
6.075
6.069
6.061
6.055
6.036
5.202
5.199
5.177
5.174
5.104
5.101
5.061
5.058
2.03
1.08
1.06
1.84
1.98
1.92
1.99
2.00
f1 (ppm)

CF3
CF3

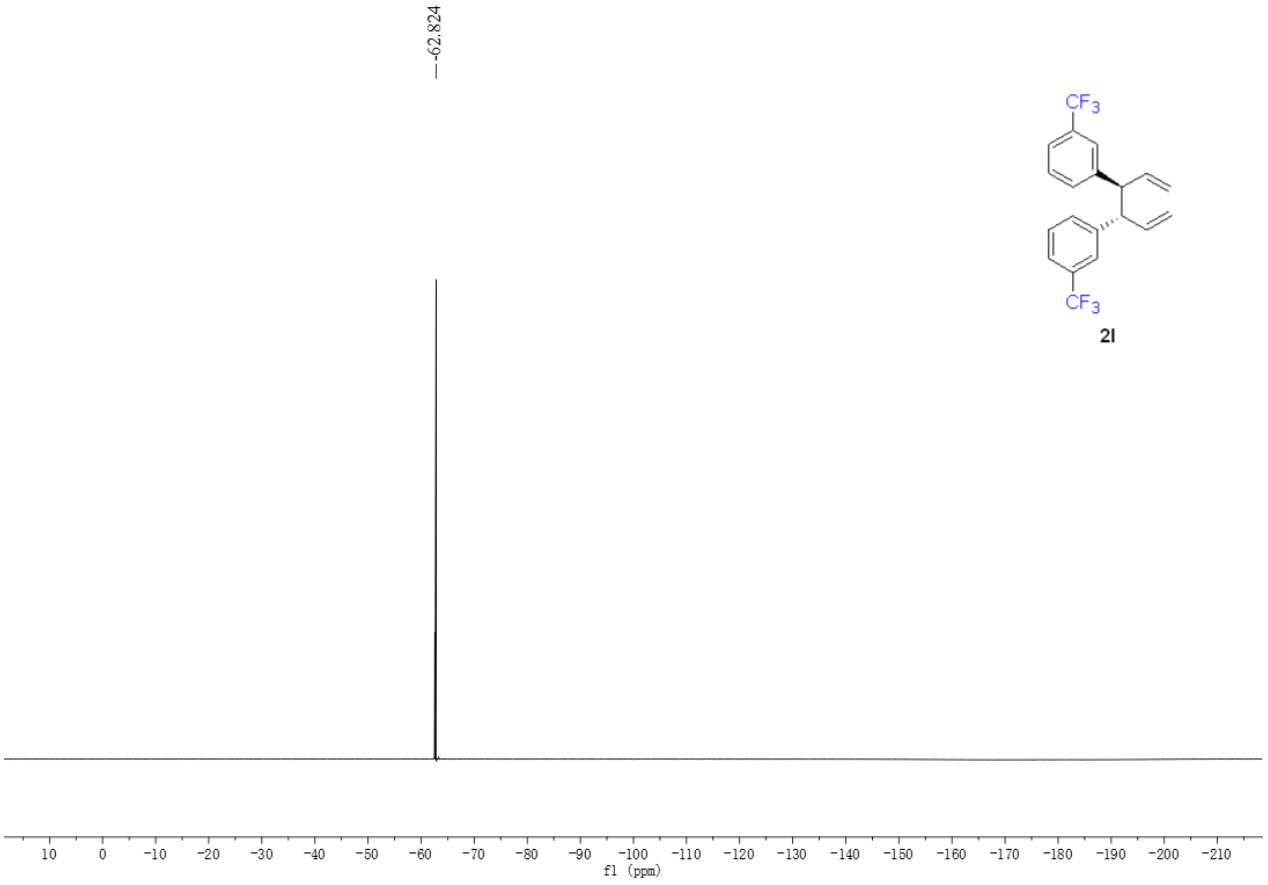
2l


2.03
1.08
1.06
1.84
1.98
1.92
1.99
2.00
2.07
f1 (ppm)

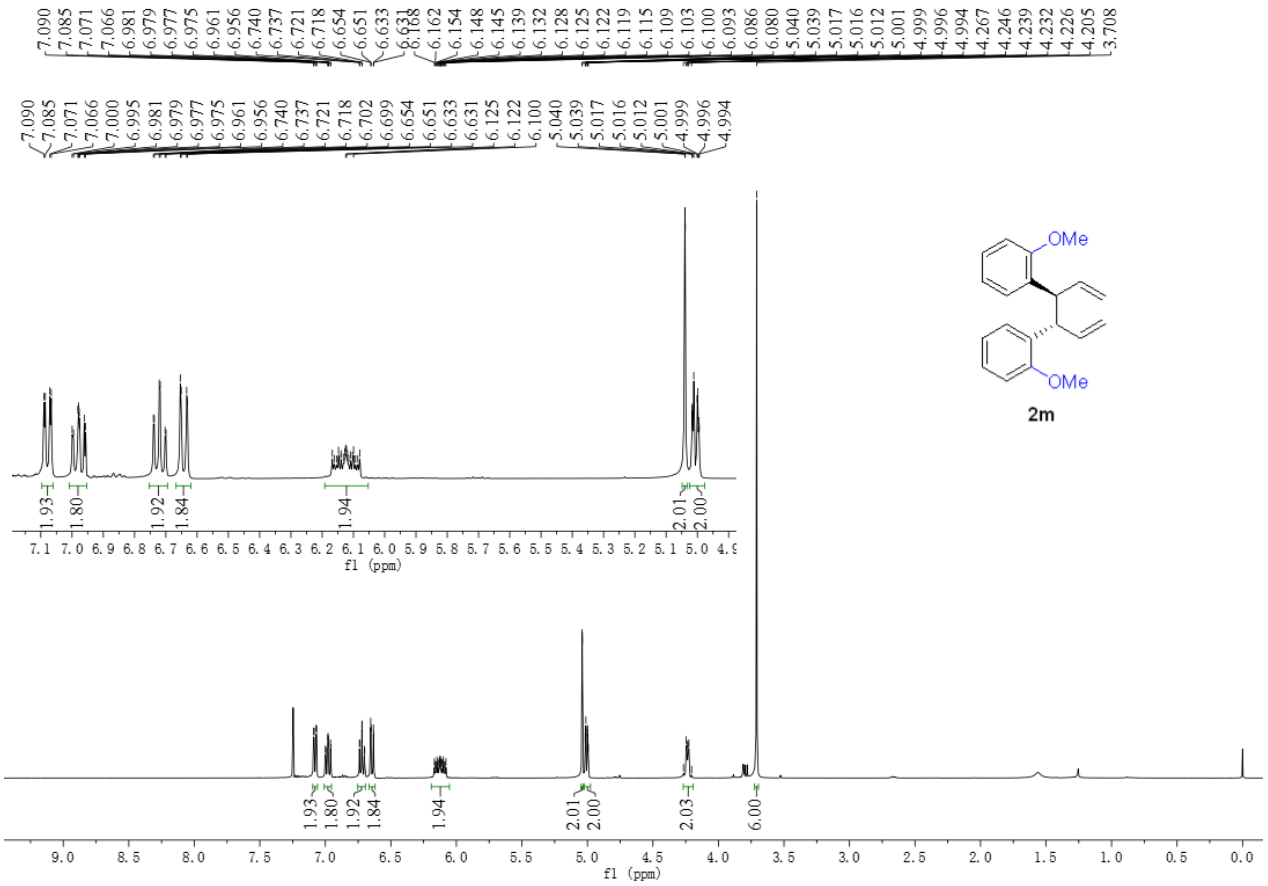

142.937
138.788
131.469
128.673
124.951
124.917
123.166
123.131
117.316
55.534
f1 (ppm)

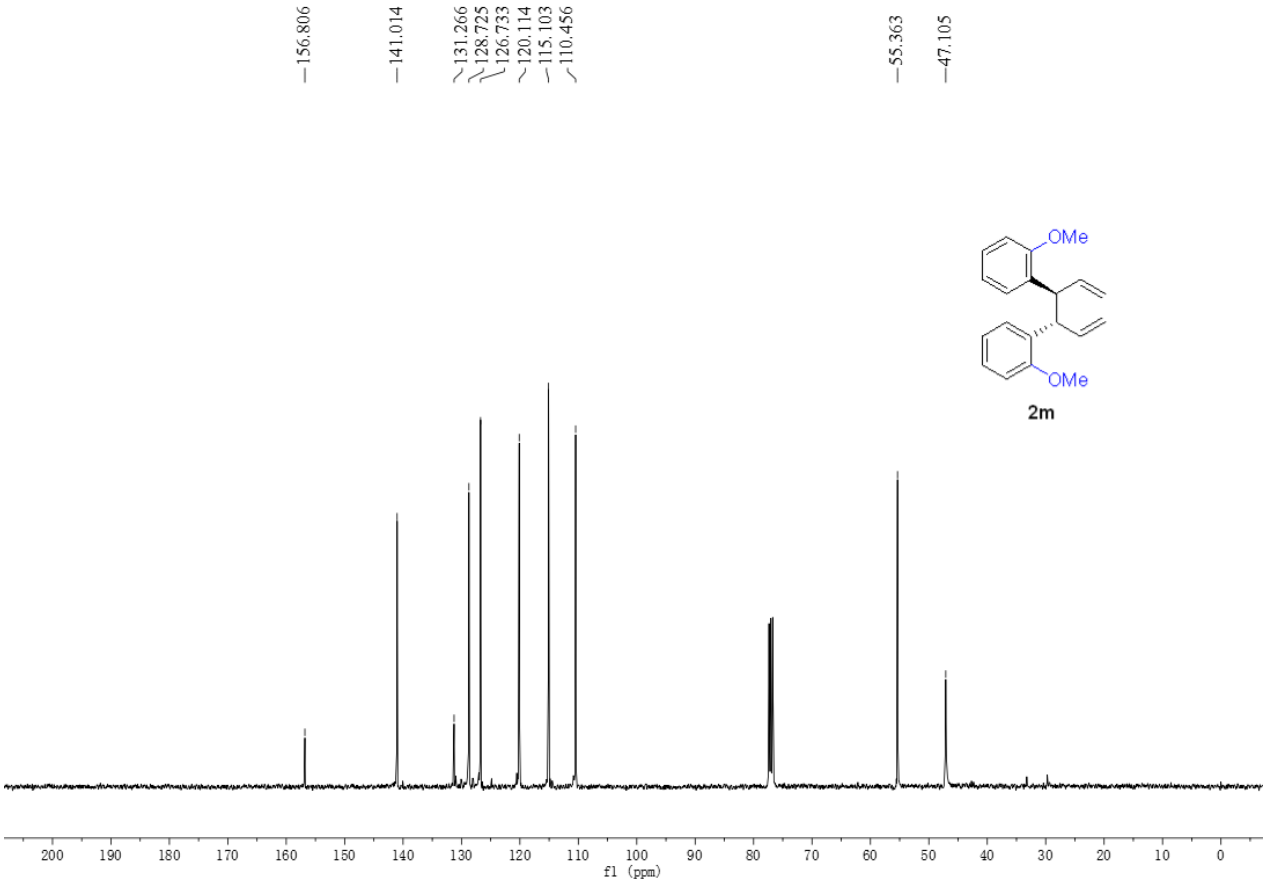
CF3
CF3

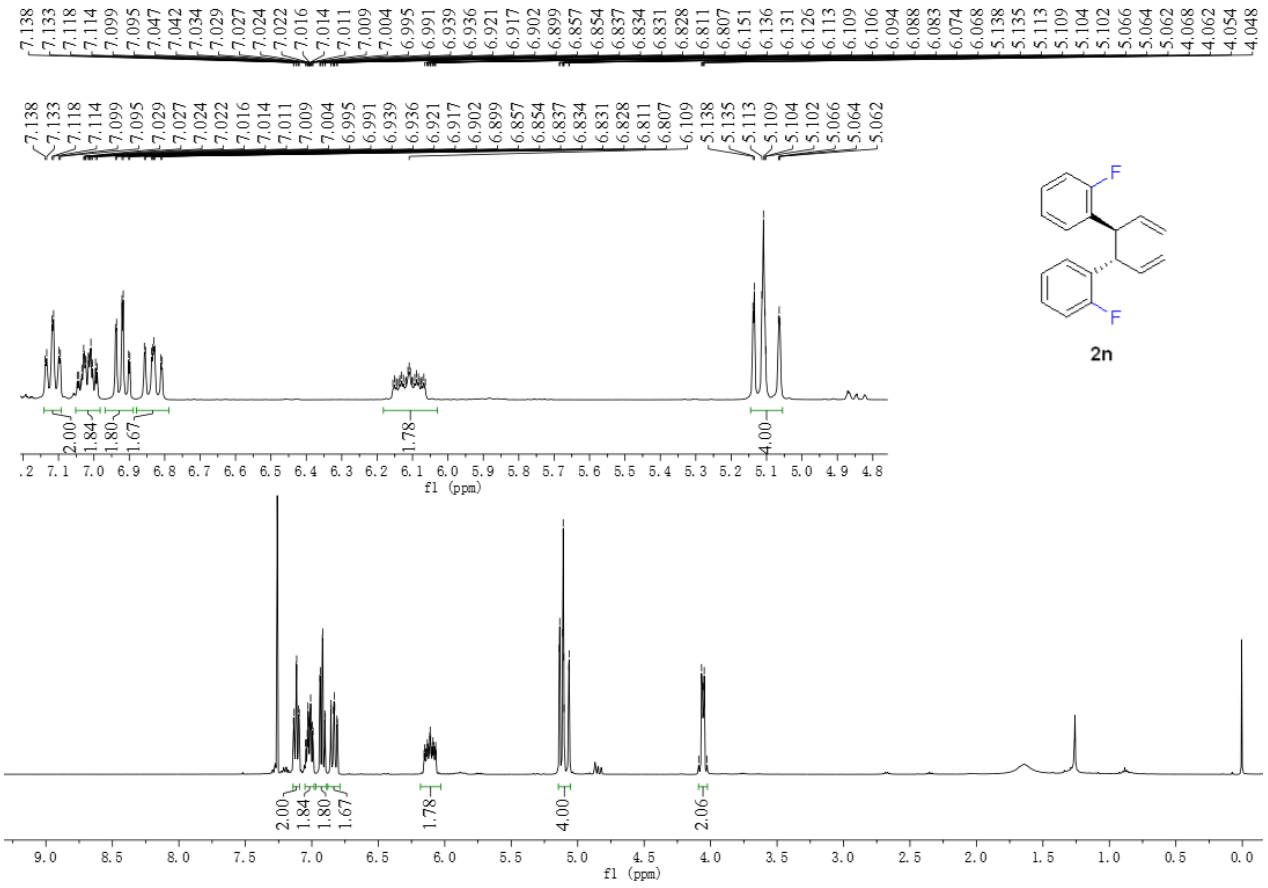
2l

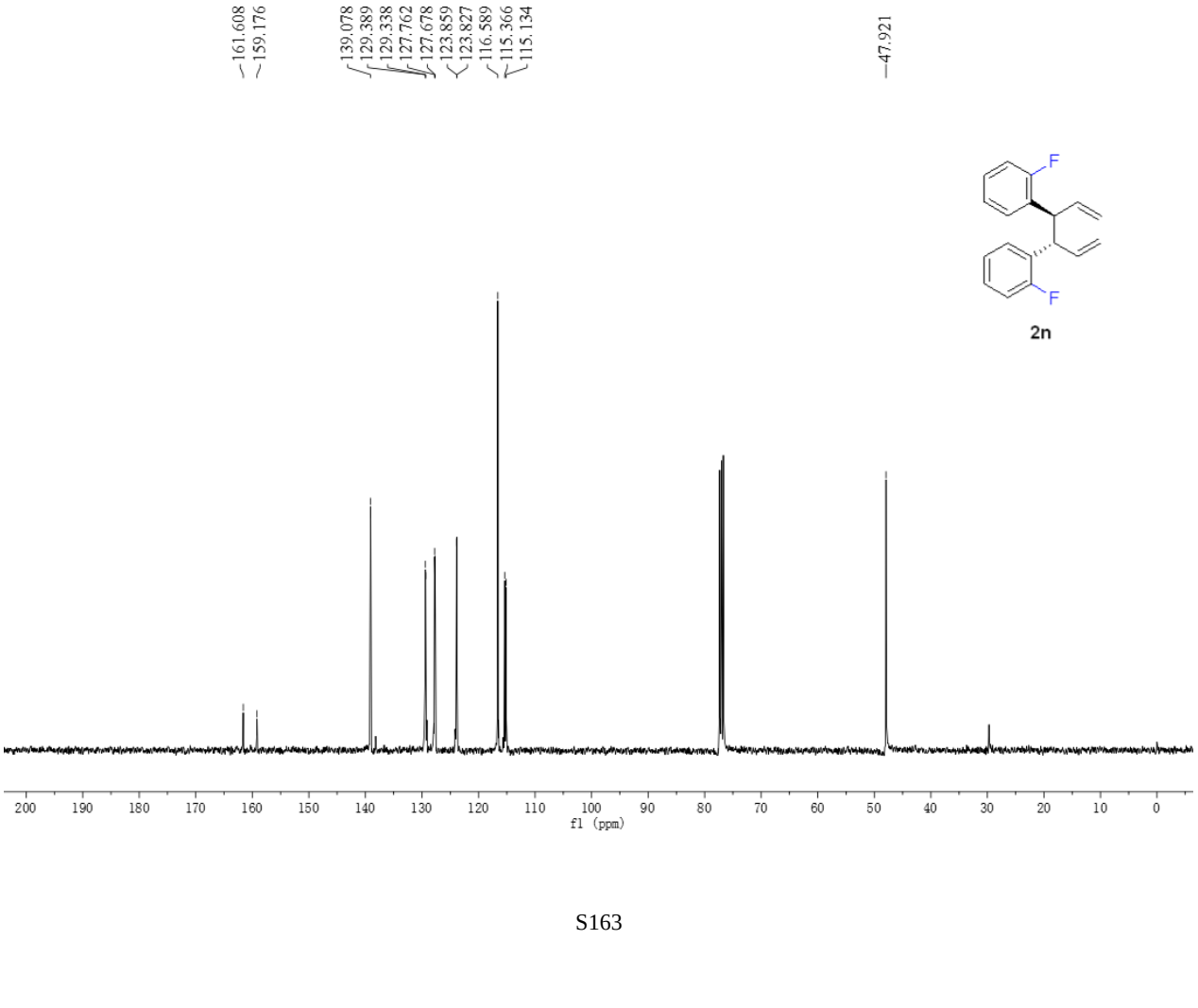

-62.824
CF3
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

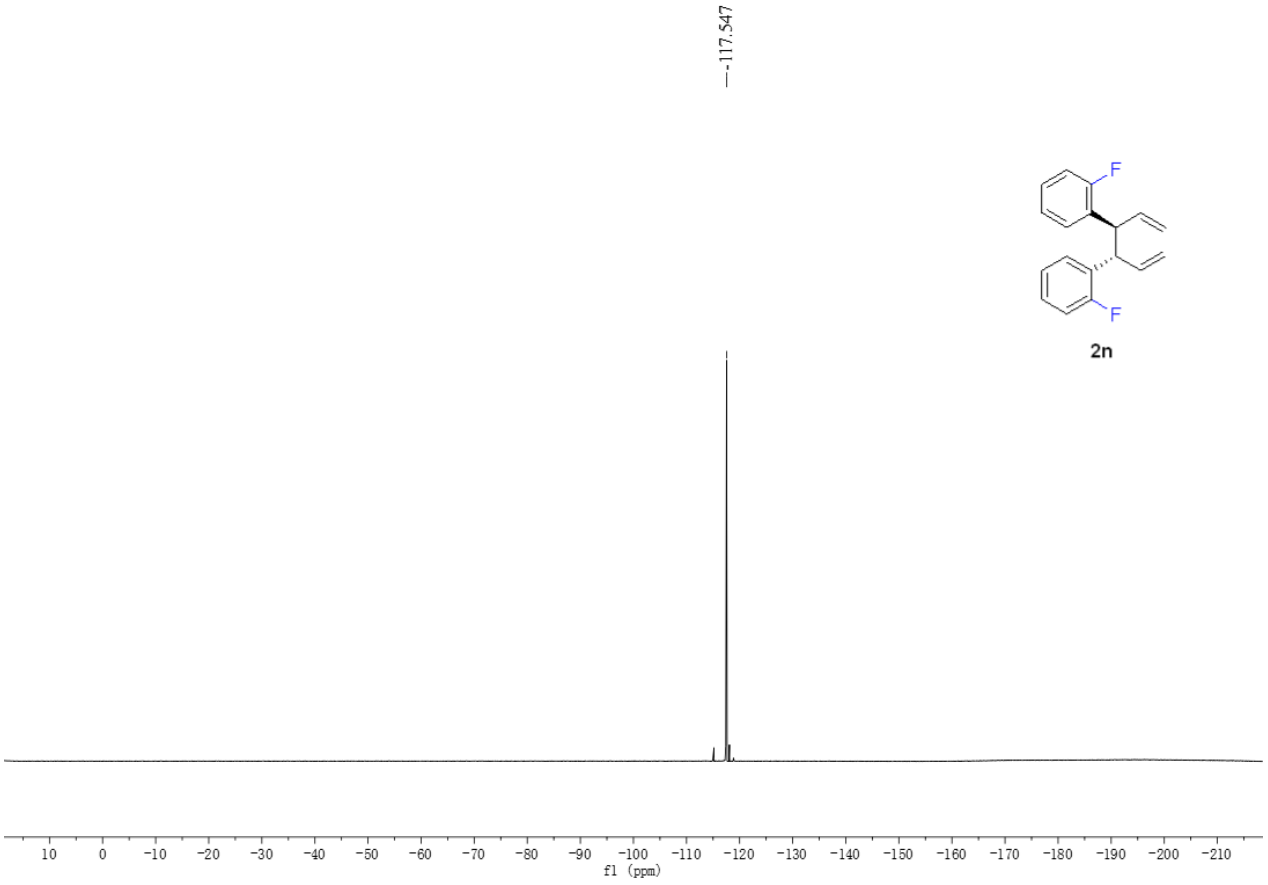
2l

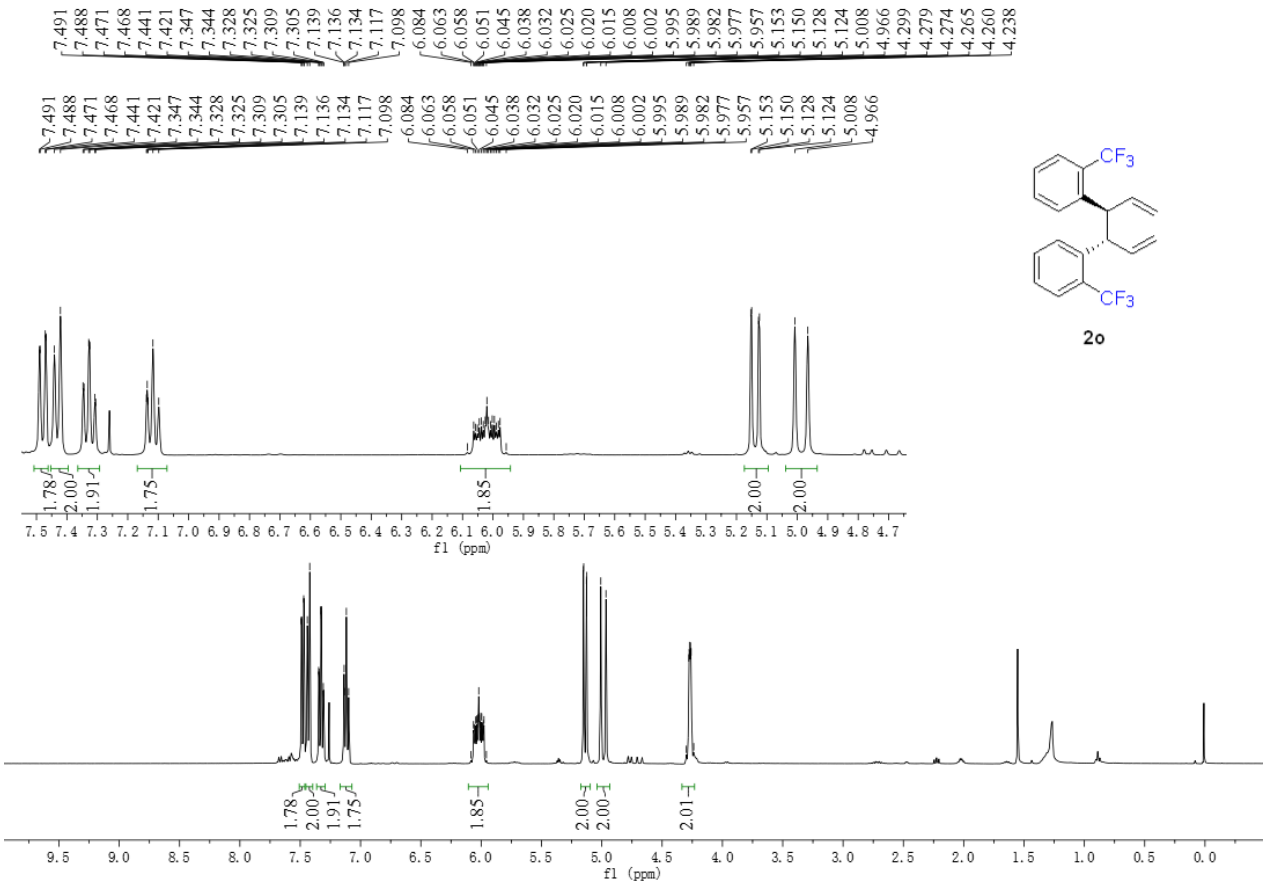

7.090
7.085
7.071
7.066
6.981
6.979
6.977
6.975
6.961
6.956
6.740
6.737
6.721
6.718
6.654
6.651
6.633
6.631
6.168
6.162
6.154
6.148
6.145
6.139
6.132
6.128
6.125
6.122
6.119
6.115
6.109
6.103
6.100
6.093
6.086
6.080
5.040
5.039
5.017
5.016
5.012
5.001
4.999
4.996
4.994
4.267
4.246
4.239
4.232
4.226
4.205
3.708
7.000
6.995
6.702
6.699
6.654
6.651
6.633
6.631
6.125
6.122
6.100
5.040
5.039
5.017
5.016
5.012
5.001
4.999
4.996
4.994
OMe
OMe
2m
1.93
1.80
1.92
1.84
1.94
2.01
2.00
2.03
6.00
f1 (ppm)

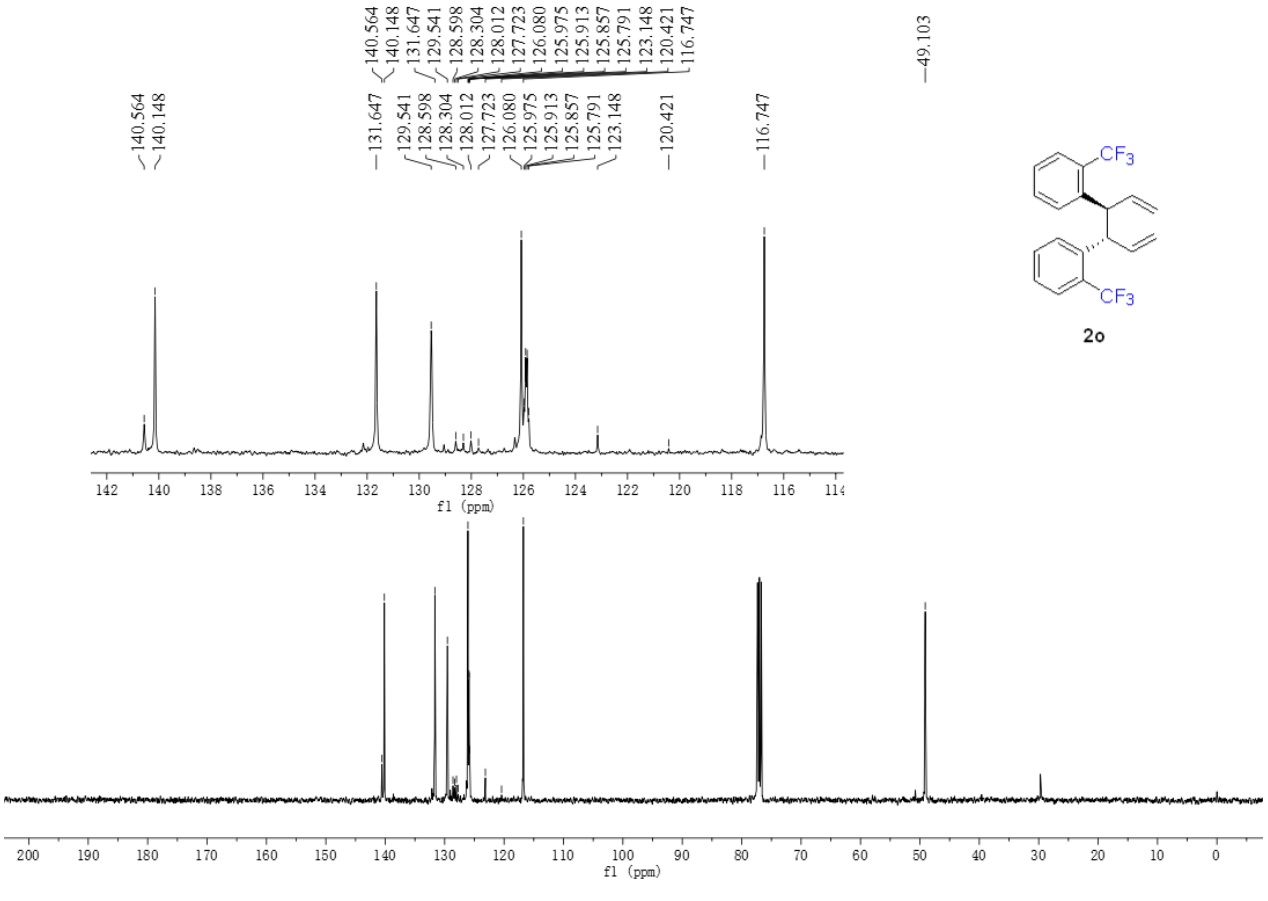

156.806
141.014
131.266
128.725
126.733
120.114
115.103
110.456
55.363
47.105
OMe
OMe
2m
f1 (ppm)

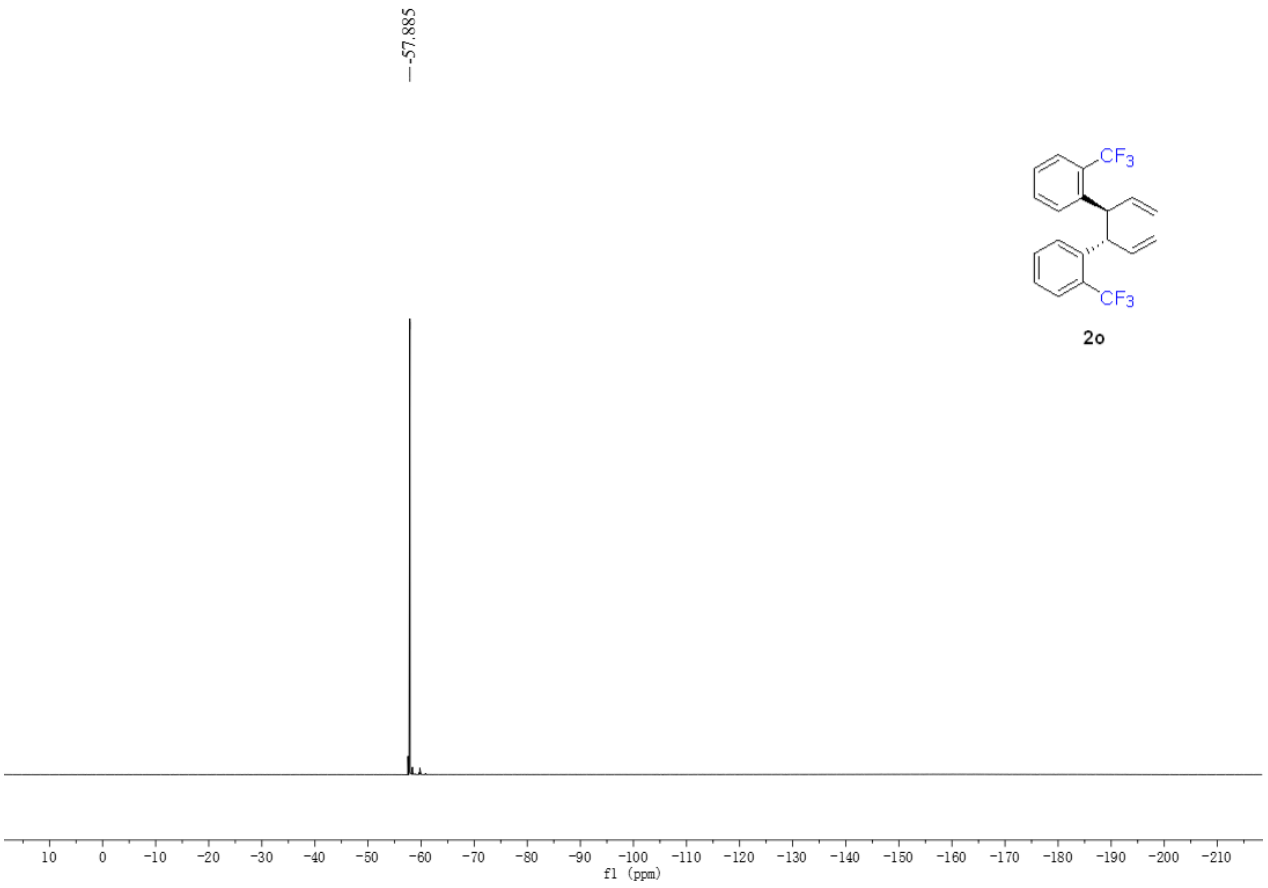

7.138
7.133
7.118
7.114
7.099
7.095
7.047
7.042
7.034
7.029
7.027
7.024
7.022
7.016
7.014
7.011
7.009
7.004
6.995
6.991
6.939
6.936
6.921
6.917
6.902
6.899
6.857
6.854
6.837
6.834
6.831
6.828
6.811
6.807
6.151
6.136
6.131
6.126
6.113
6.109
6.106
6.094
6.088
6.083
6.074
6.068
5.138
5.135
5.113
5.109
5.104
5.102
5.066
5.064
5.062
4.068
4.062
4.054
4.048
F
F
2n
2.00
1.84
1.80
1.67
1.78
4.00
2.06
f1 (ppm)

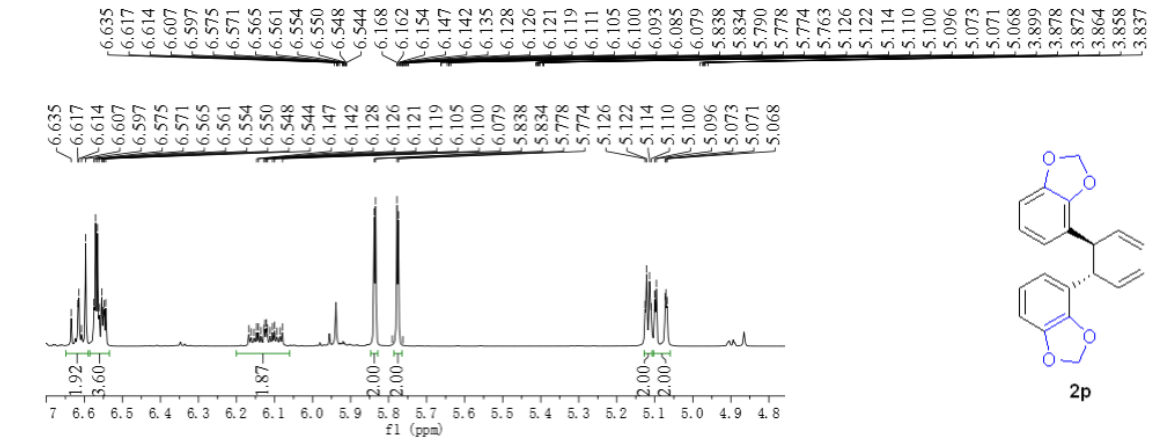

161.608
159.176
139.078
129.389
129.338
127.762
127.678
123.859
123.827
116.589
115.366
115.134
47.921
F
F
2n
f1 (ppm)


-117.547
F
F
2n
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

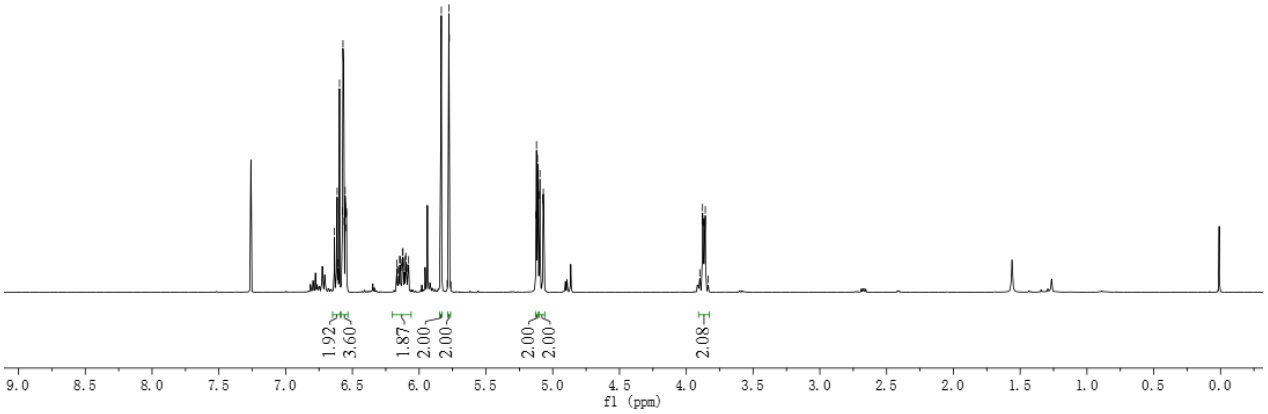

7.491
7.488
7.471
7.468
7.441
7.421
7.347
7.344
7.328
7.325
7.309
7.305
7.139
7.136
7.134
7.117
7.098
6.084
6.063
6.058
6.051
6.045
6.038
6.032
6.025
6.020
6.015
6.008
6.002
5.995
5.989
5.982
5.977
5.957
5.153
5.150
5.128
5.124
5.008
4.966
4.299
4.279
4.274
4.265
4.260
4.238
CF3
CF3
2o
1.78
2.00
1.91
1.75
1.85
2.00
2.00
f1 (ppm)
1.78
2.00
1.91
1.75
1.85
2.00
2.00
2.01
f1 (ppm)

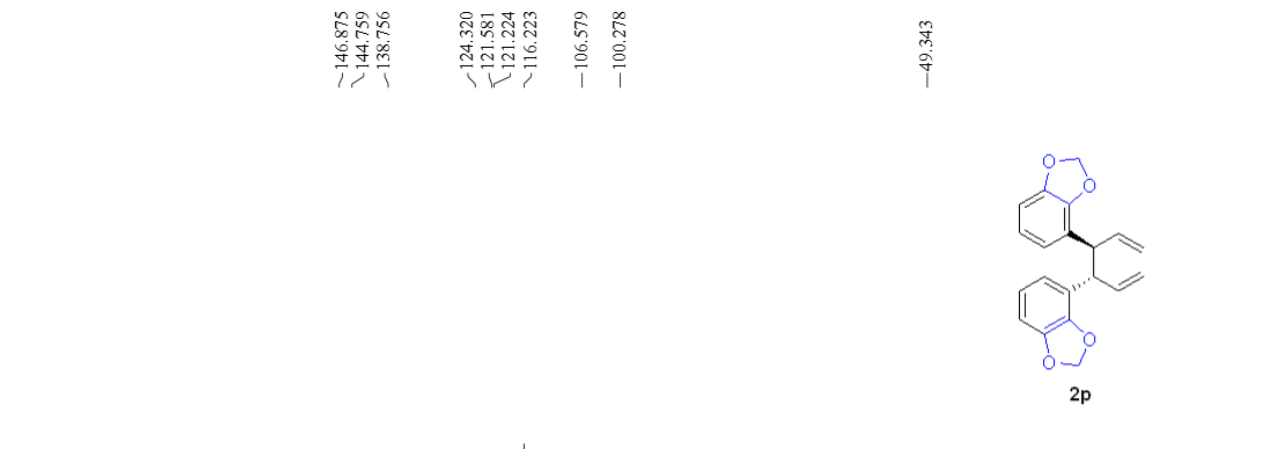

140.564
140.148
131.647
129.541
128.598
128.304
128.012
127.723
126.080
125.975
125.913
125.857
125.791
123.148
120.421
116.747
49.103
CF3
CF3
2o
f1 (ppm)
f1 (ppm)


-57.885
CF3
CF3
2o
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

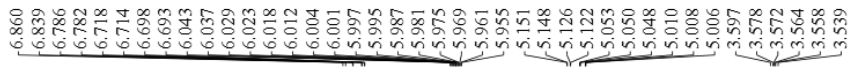

6.635
6.617
6.614
6.607
6.597
6.575
6.571
6.565
6.561
6.554
6.550
6.548
6.544
6.168
6.162
6.154
6.147
6.142
6.135
6.128
6.126
6.121
6.119
6.111
6.105
6.100
6.093
6.085
6.079
5.838
5.834
5.790
5.778
5.774
5.763
5.126
5.122
5.114
5.110
5.100
5.096
5.073
5.071
5.068
3.899
3.878
3.872
3.864
3.858
3.837
1.92
3.60
1.87
2.00
2.00
2.00
2.00
f1 (ppm)

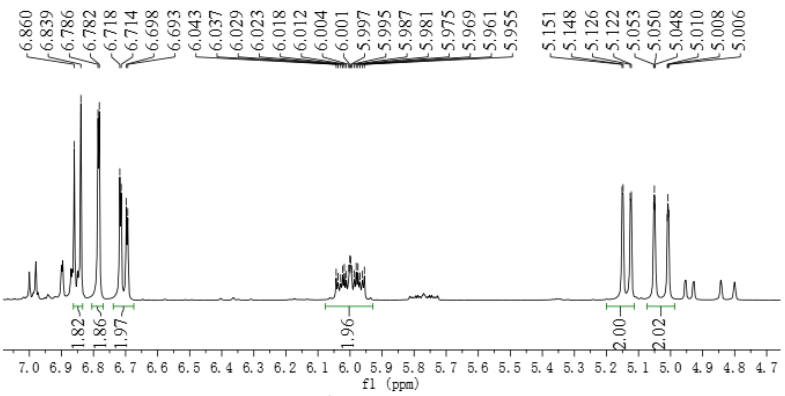
2p

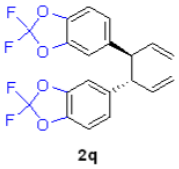

1.92
3.60
1.87
2.00
2.00
2.00
2.00
2.08
f1 (ppm)


146.875
144.759
138.756
124.320
121.581
121.224
116.223
106.579
100.278
49.343
f1 (ppm)

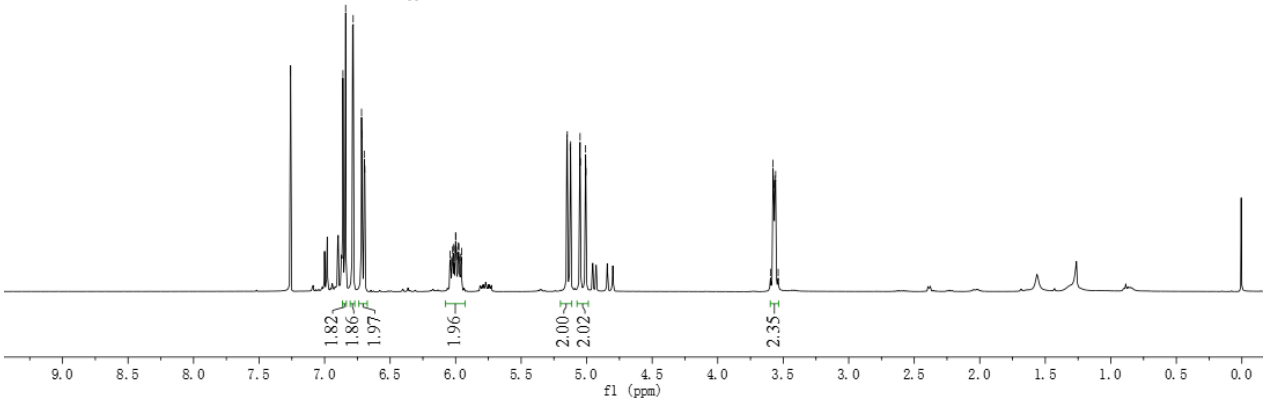
2p


6.860
6.839
6.786
6.782
6.718
6.714
6.698
6.693
6.043
6.037
6.029
6.023
6.018
6.012
6.004
6.001
5.997
5.995
5.987
5.981
5.975
5.969
5.961
5.955
5.151
5.148
5.126
5.122
5.053
5.050
5.048
5.010
5.008
5.006
3.597
3.578
3.572
3.564
3.558
3.539

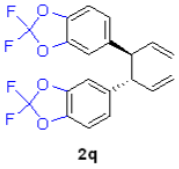

1.82
1.86
1.97
1.96
2.00
2.02
f1 (ppm)



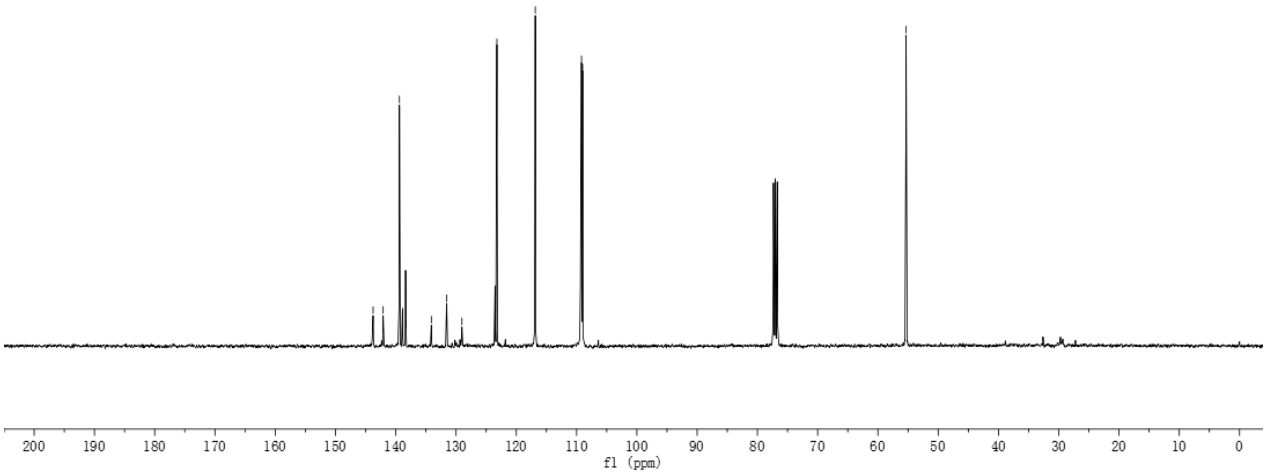
2q

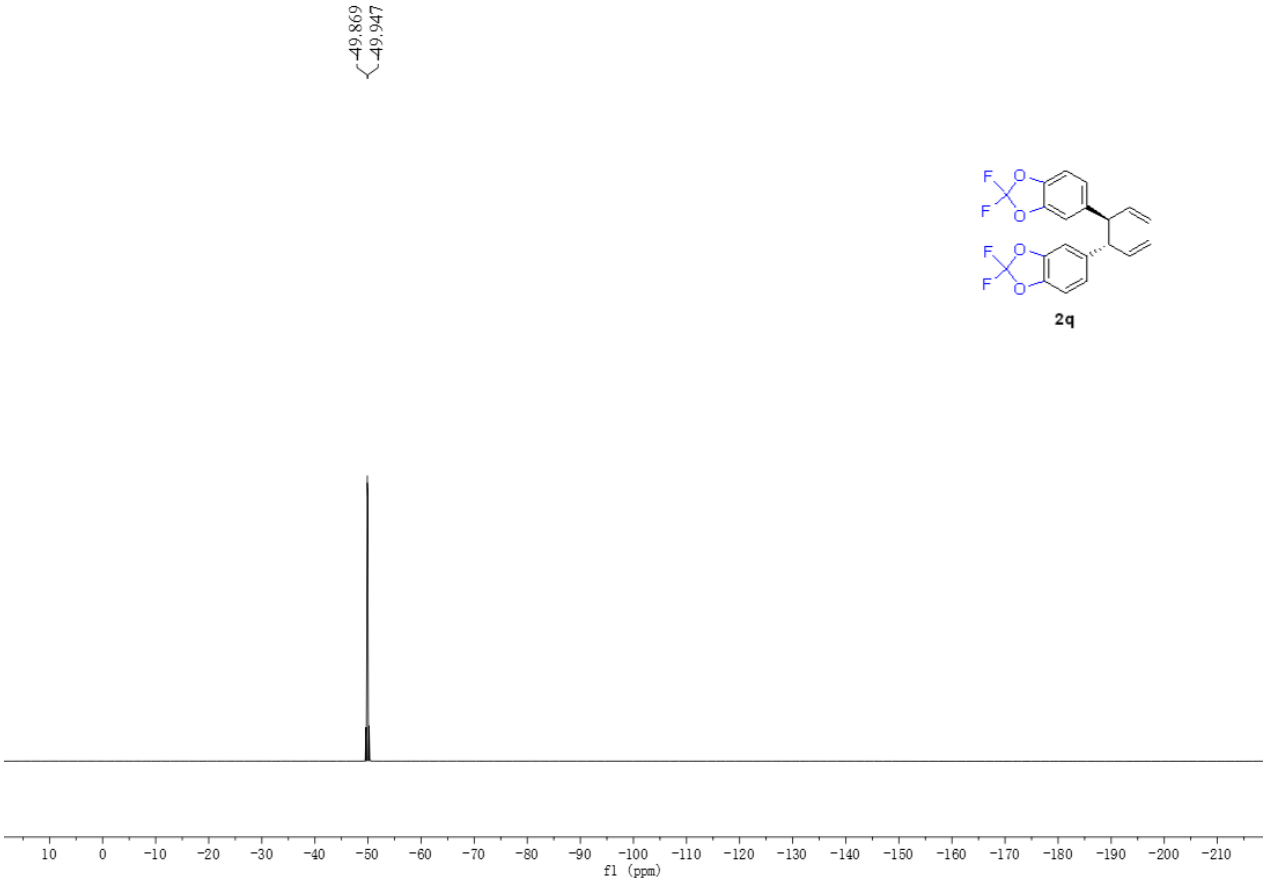

1.82
1.86
1.97
1.96
2.00
2.02
2.35
f1 (ppm)

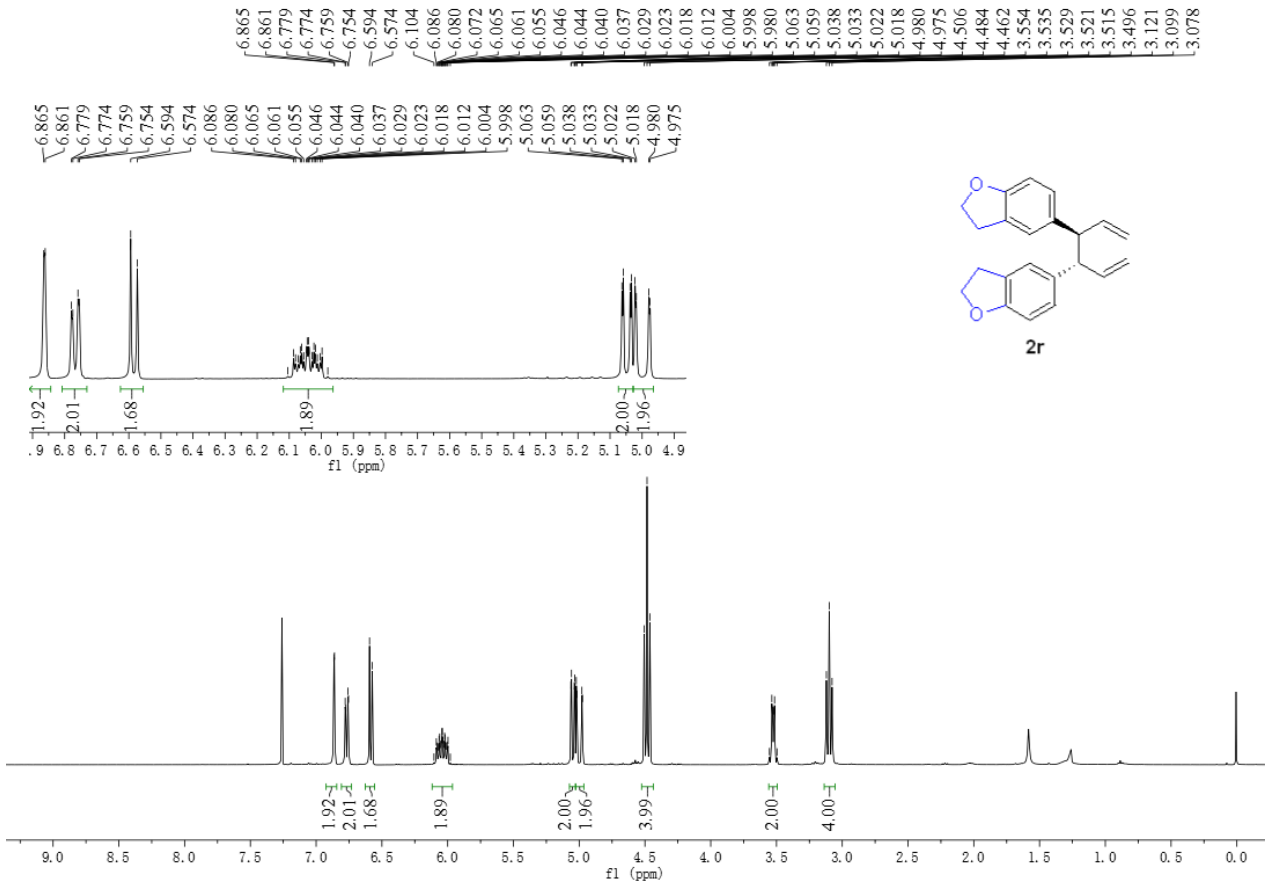

143.761
142.098
139.394
138.288
134.094
131.562
129.029
123.220
116.855
109.184
109.003
55.331



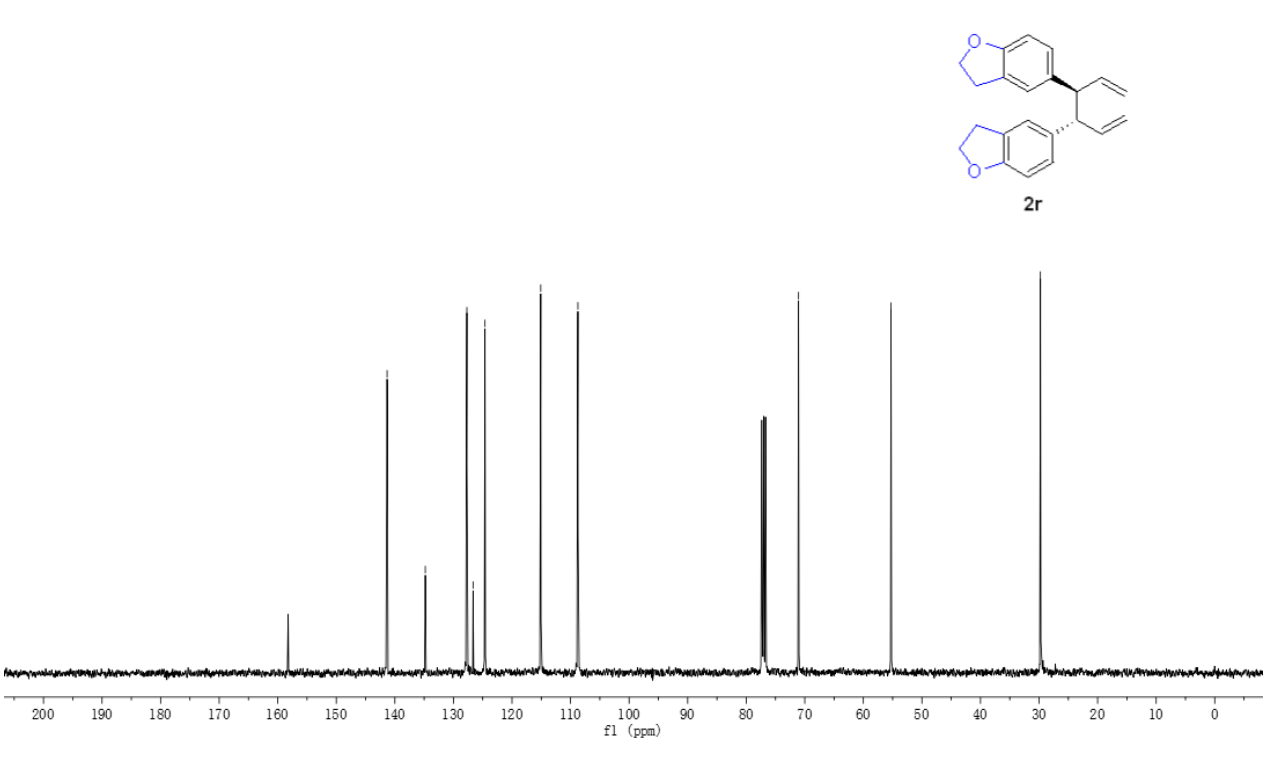
2q


f1 (ppm)

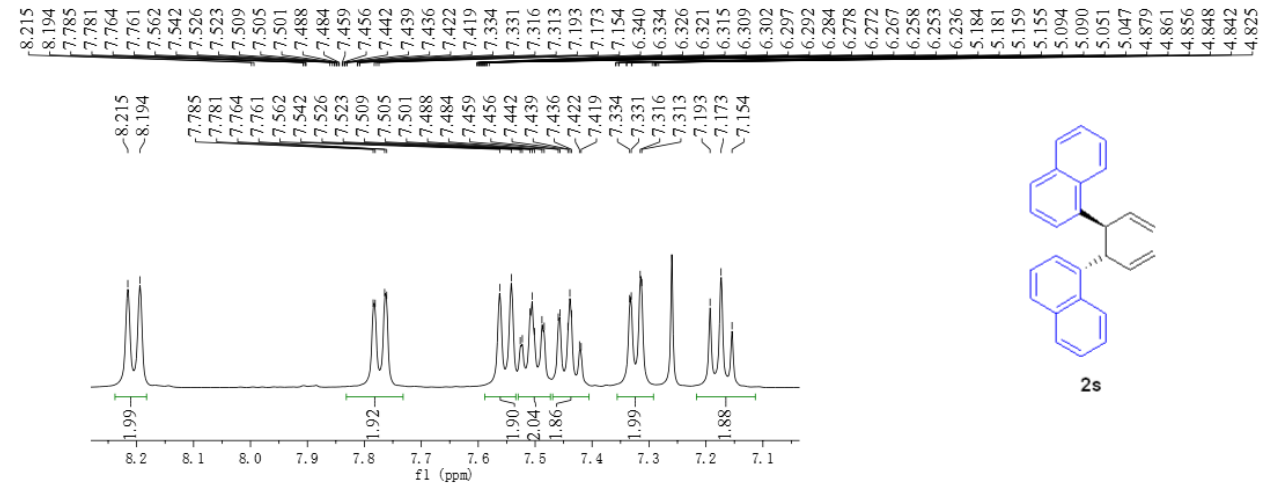

-49.869
-49.947
2q
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


6.865
6.861
6.779
6.774
6.759
6.754
6.594
6.574
6.104
6.086
6.080
6.072
6.065
6.061
6.055
6.046
6.044
6.040
6.037
6.029
6.023
6.018
6.012
6.004
5.998
5.980
5.063
5.059
5.038
5.033
5.022
5.018
4.980
4.975
4.506
4.484
4.462
3.554
3.535
3.529
3.521
3.515
3.496
3.121
3.099
3.078
1.92
2.01
1.68
1.89
2.00
1.96
3.99
4.00
f1 (ppm)

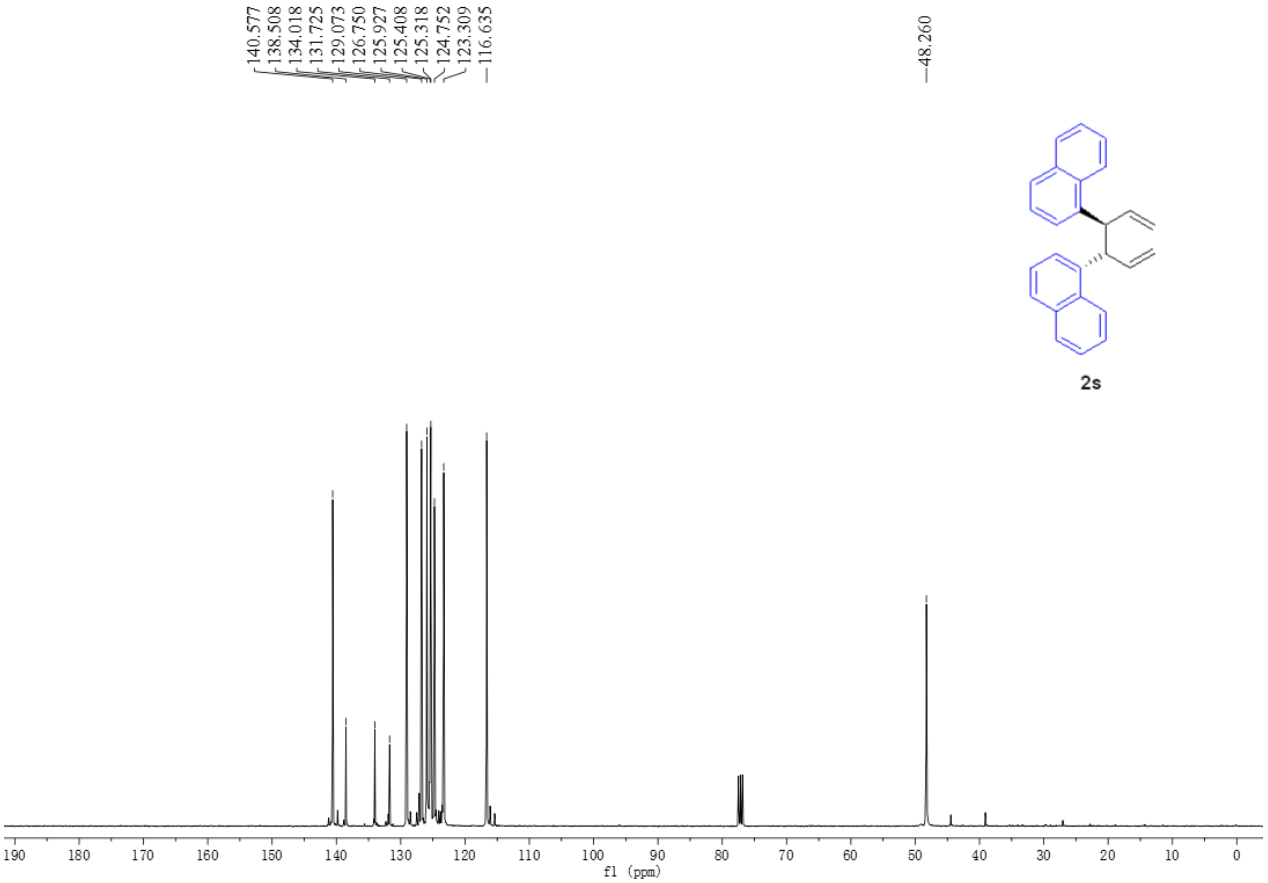
2r


141.326
134.804
127.706
126.645
124.613
115.091
108.745
71.067
55.276
29.765
f1 (ppm)

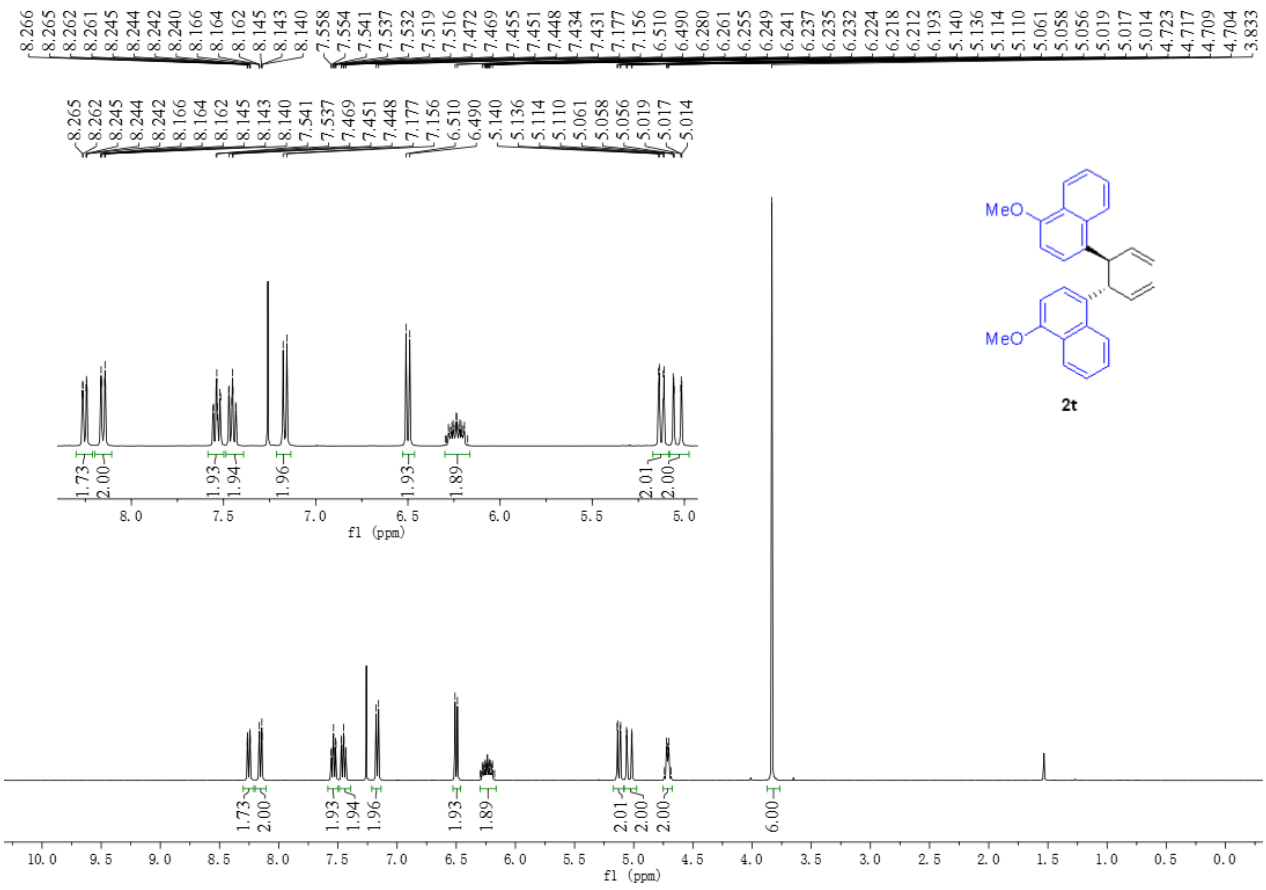
2r

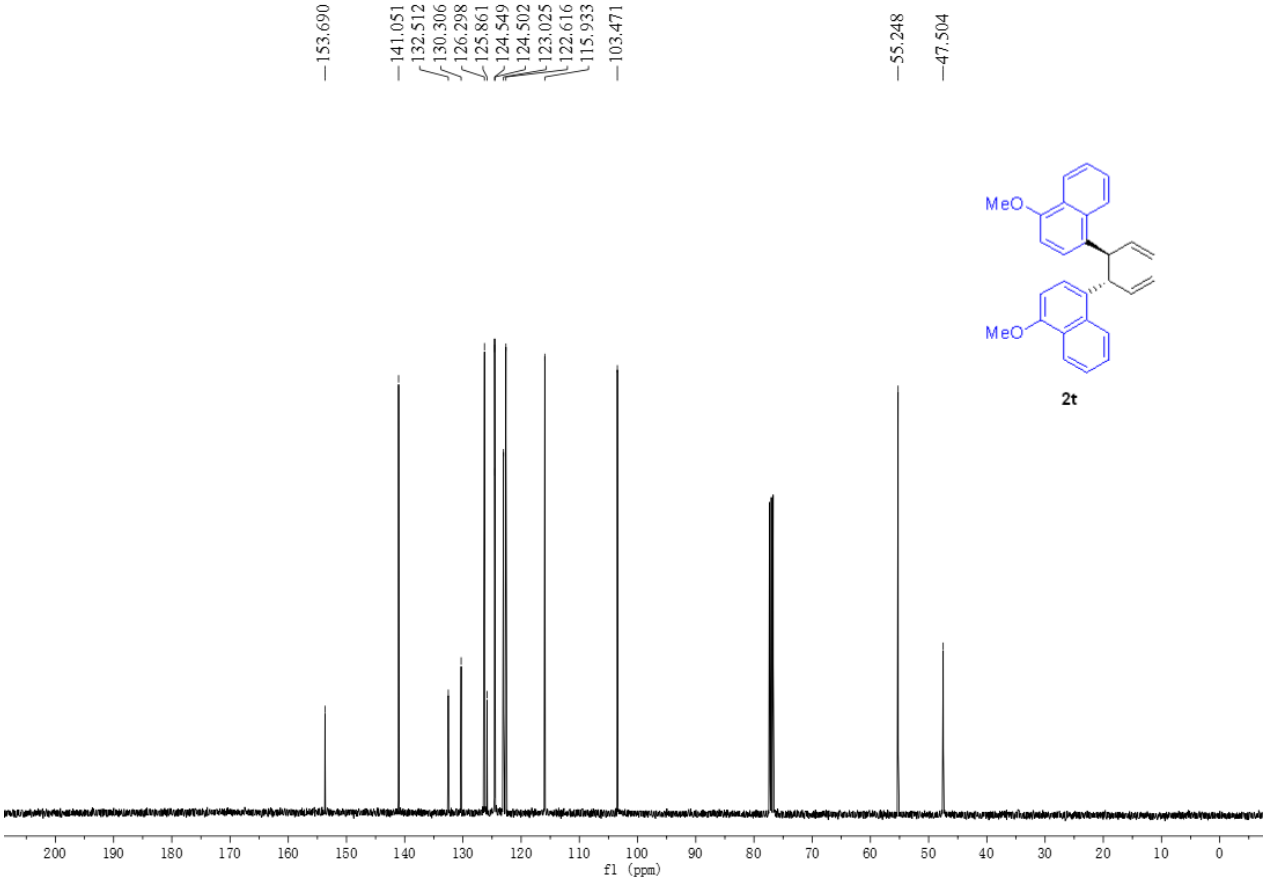

8.215
8.194
7.785
7.781
7.764
7.761
7.562
7.542
7.526
7.523
7.509
7.505
7.501
7.488
7.484
7.459
7.456
7.442
7.439
7.436
7.422
7.419
7.334
7.331
7.316
7.313
7.193
7.173
7.154
6.340
6.334
6.326
6.321
6.315
6.309
6.302
6.297
6.292
6.284
6.278
6.272
6.267
6.258
6.253
6.236
5.184
5.181
5.159
5.155
5.094
5.090
5.051
5.047
4.879
4.861
4.856
4.848
4.842
4.825
1.99
1.92
1.90
2.04
1.86
1.99
1.88
1.86
2.00
2.00
2.10
f1 (ppm)

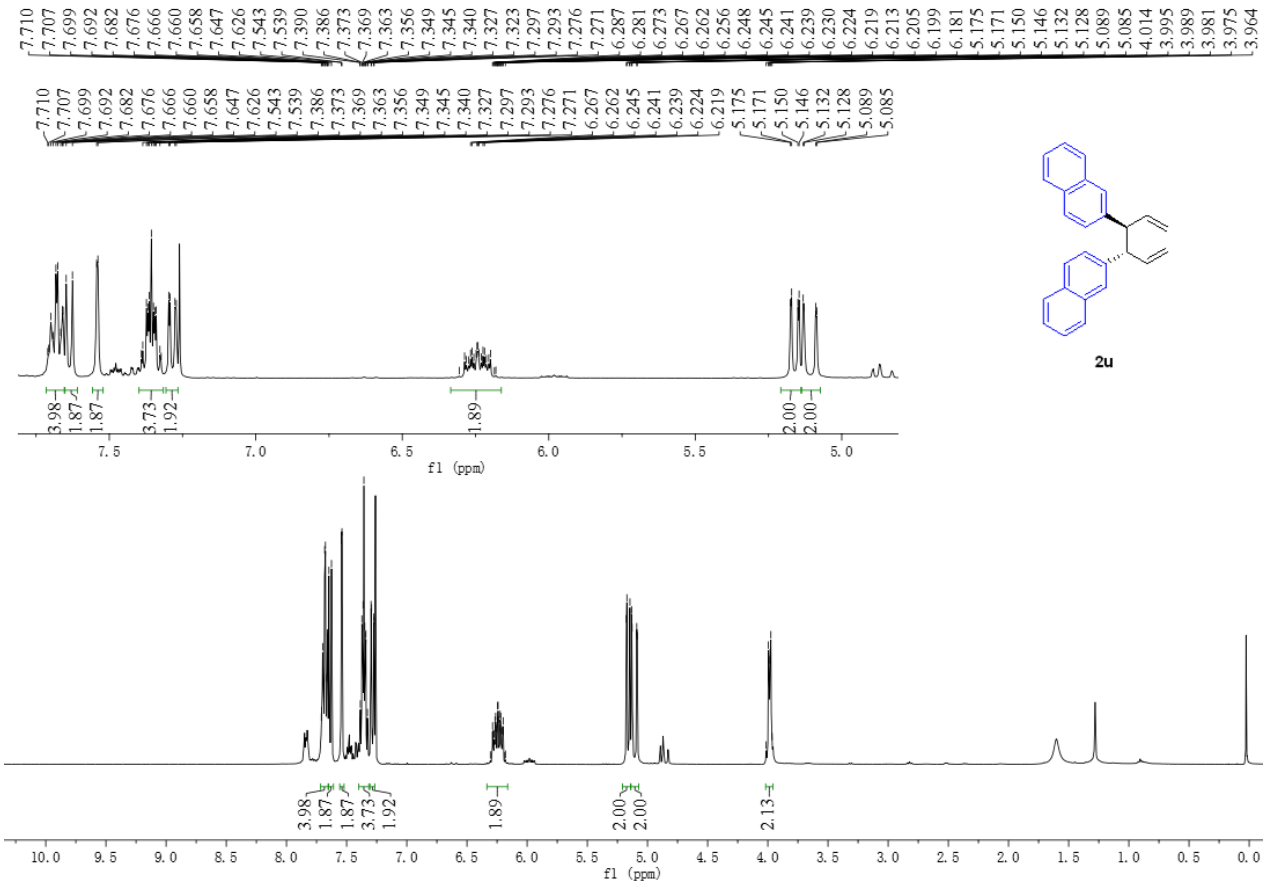
2s

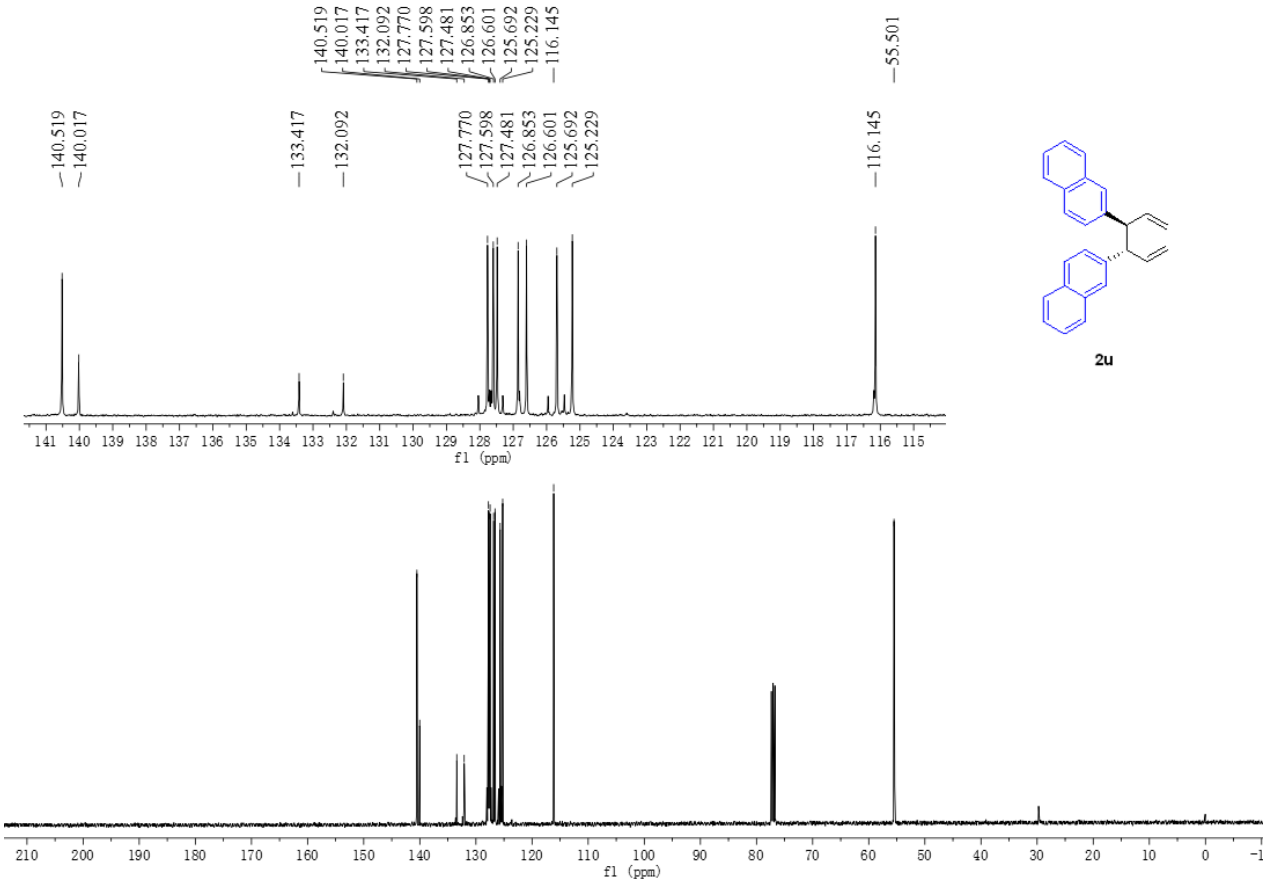

140.577
138.508
134.018
131.725
129.073
126.750
125.927
125.408
125.318
124.752
123.309
116.635
48.260
f1 (ppm)

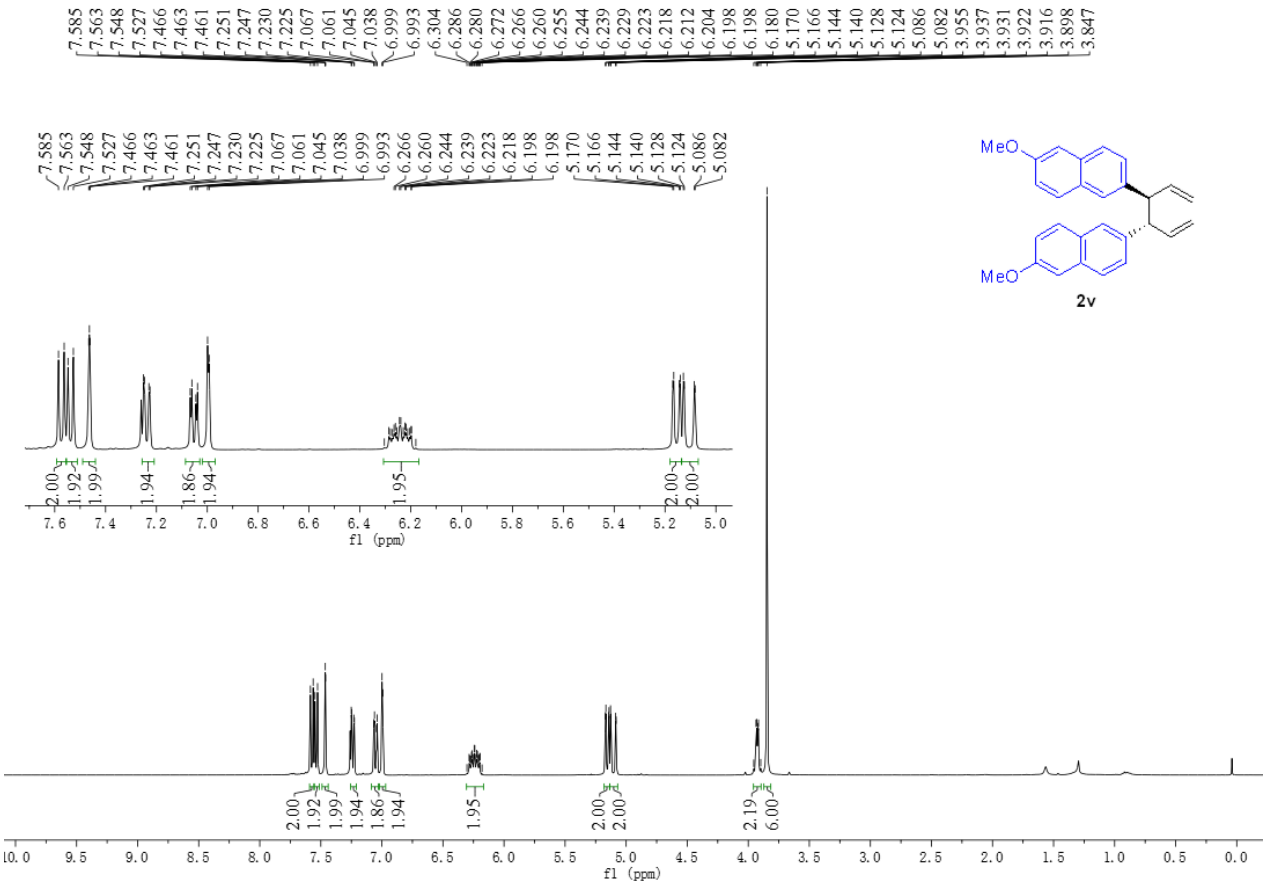
2s

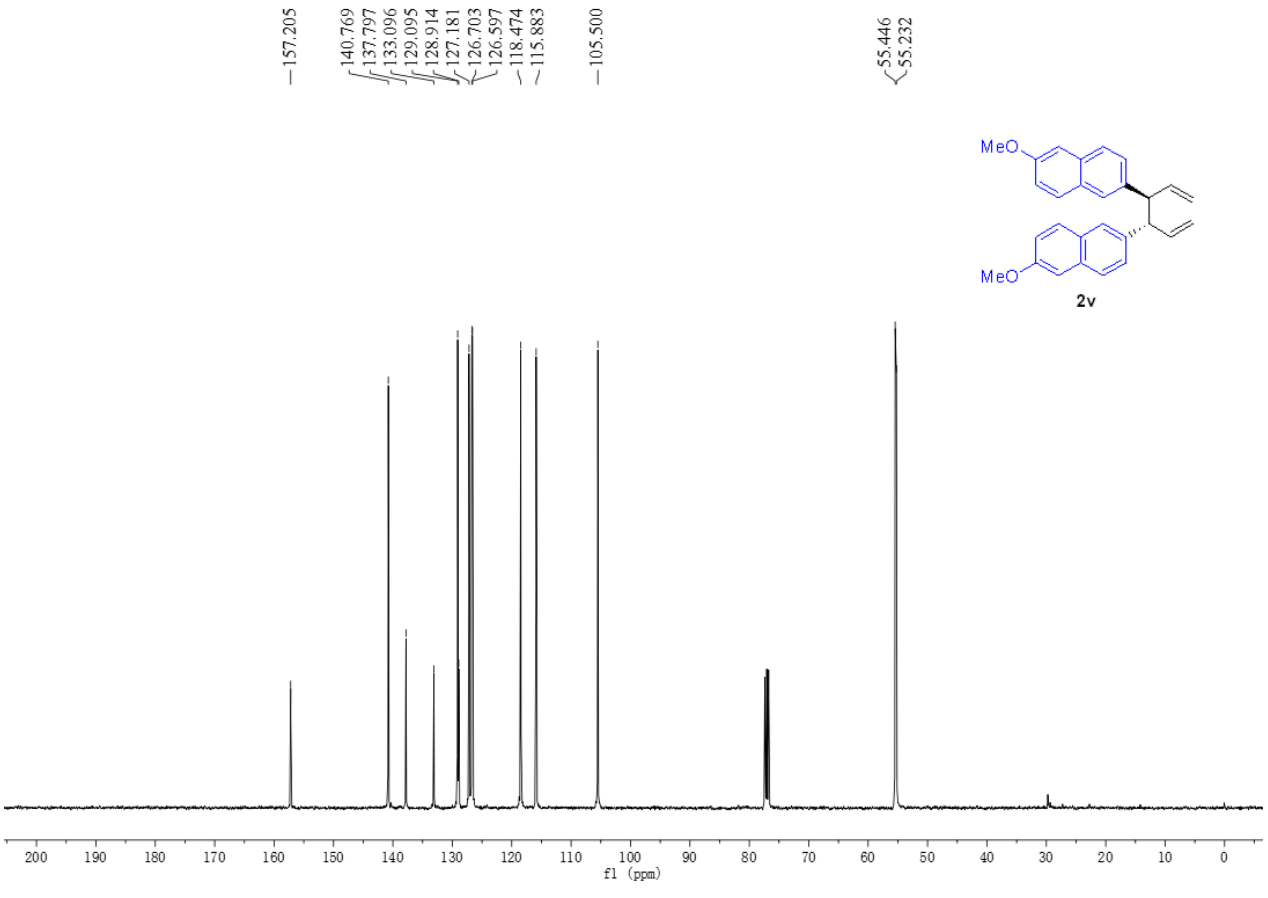

MeO
MeO
2t
f1 (ppm)

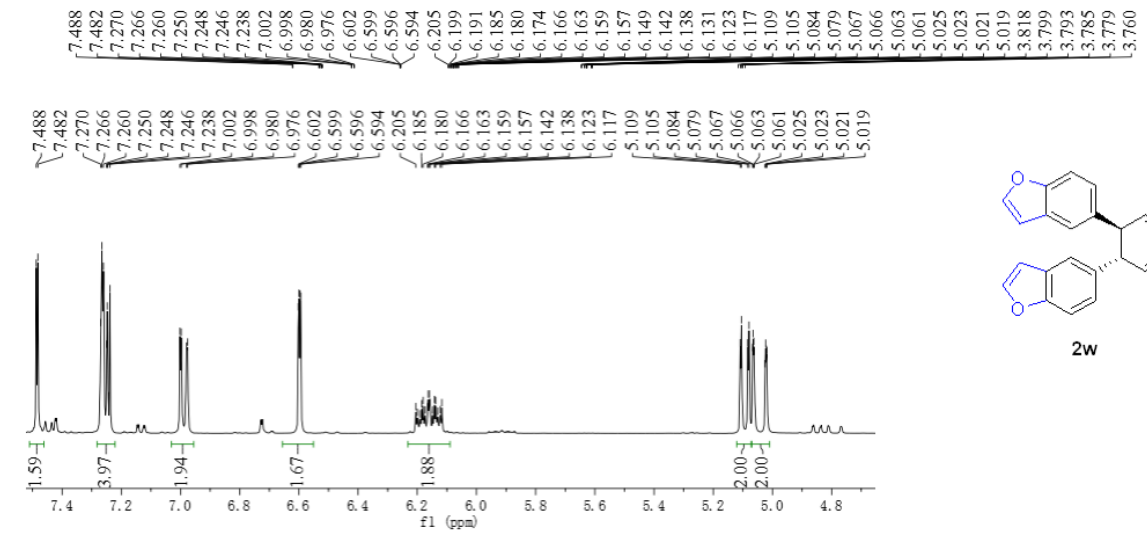

MeO
MeO
2t
f1 (ppm)


7.710 7.707 7.699 7.692 7.682 7.676 7.666 7.660 7.658 7.647 7.626 7.543 7.539 7.390 7.386 7.373 7.369 7.363 7.356 7.349 7.345 7.340 7.327 7.323 7.297 7.293 7.276 7.271 6.287 6.281 6.273 6.267 6.262 6.256 6.248 6.245 6.241 6.239 6.230 6.224 6.219 6.213 6.205 6.199 6.181 5.175 5.171 5.150 5.146 5.132 5.128 5.089 5.085 4.014 3.995 3.989 3.981 3.975 3.964
3.98 1.87 1.87 3.73 1.92 1.89 2.00 2.00
f1 (ppm)
2u
3.98 1.87 1.87 3.73 1.92 1.89 2.00 2.00 2.13
f1 (ppm)

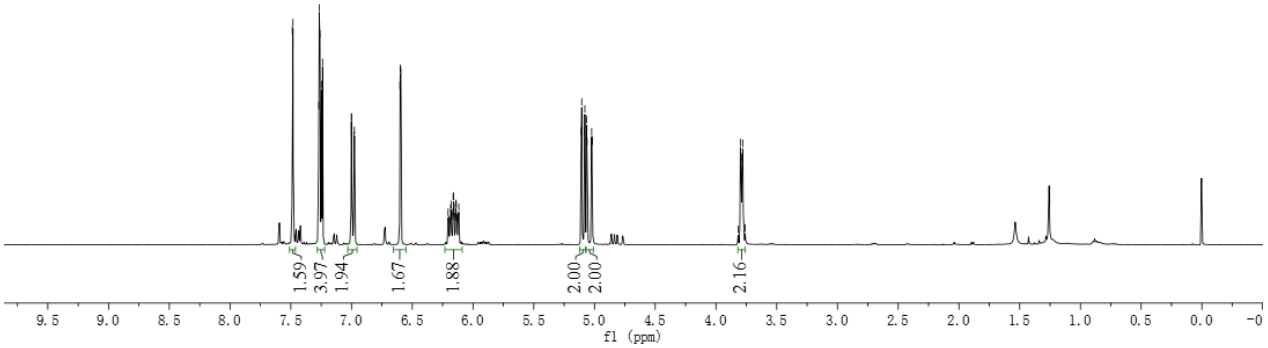

140.519 140.017 133.417 132.092 127.770 127.598 127.481 126.853 126.601 125.692 125.229 116.145 55.501
f1 (ppm)
2u
f1 (ppm)

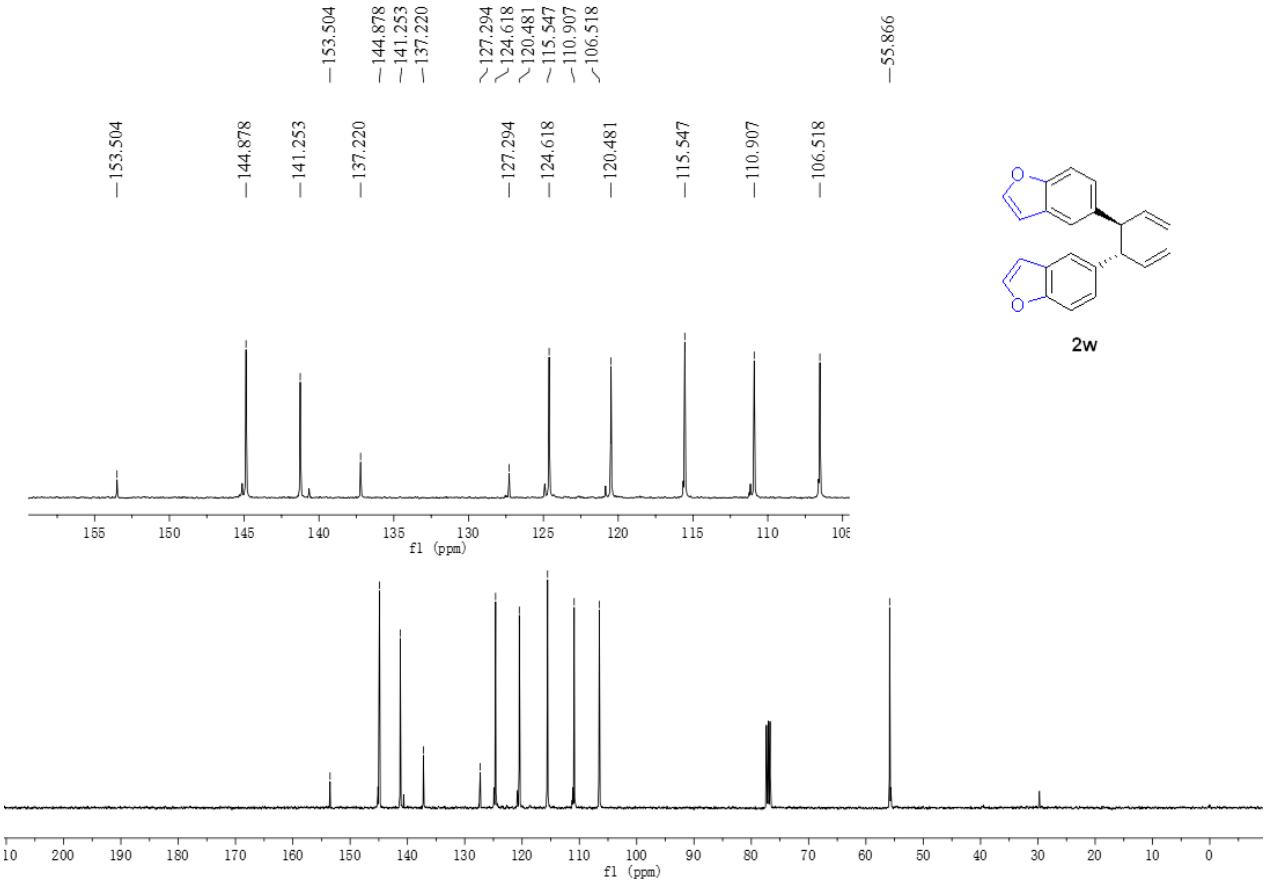

7.585
7.563
7.548
7.527
7.466
7.463
7.461
7.251
7.247
7.230
7.225
7.067
7.061
7.045
7.038
6.999
6.993
6.304
6.286
6.280
6.272
6.266
6.260
6.255
6.244
6.239
6.229
6.223
6.218
6.212
6.204
6.198
6.198
6.180
5.170
5.166
5.144
5.140
5.128
5.124
5.086
5.082
3.955
3.937
3.931
3.922
3.916
3.898
3.847
MeO
MeO
2v
2.00
1.92
1.99
1.94
1.86
1.94
1.95
2.00
2.00
2.19
6.00
f1 (ppm)


157.205
140.769
137.797
133.096
129.095
128.914
127.181
126.703
126.597
118.474
115.883
105.500
55.446
55.232
MeO
MeO
2v
f1 (ppm)

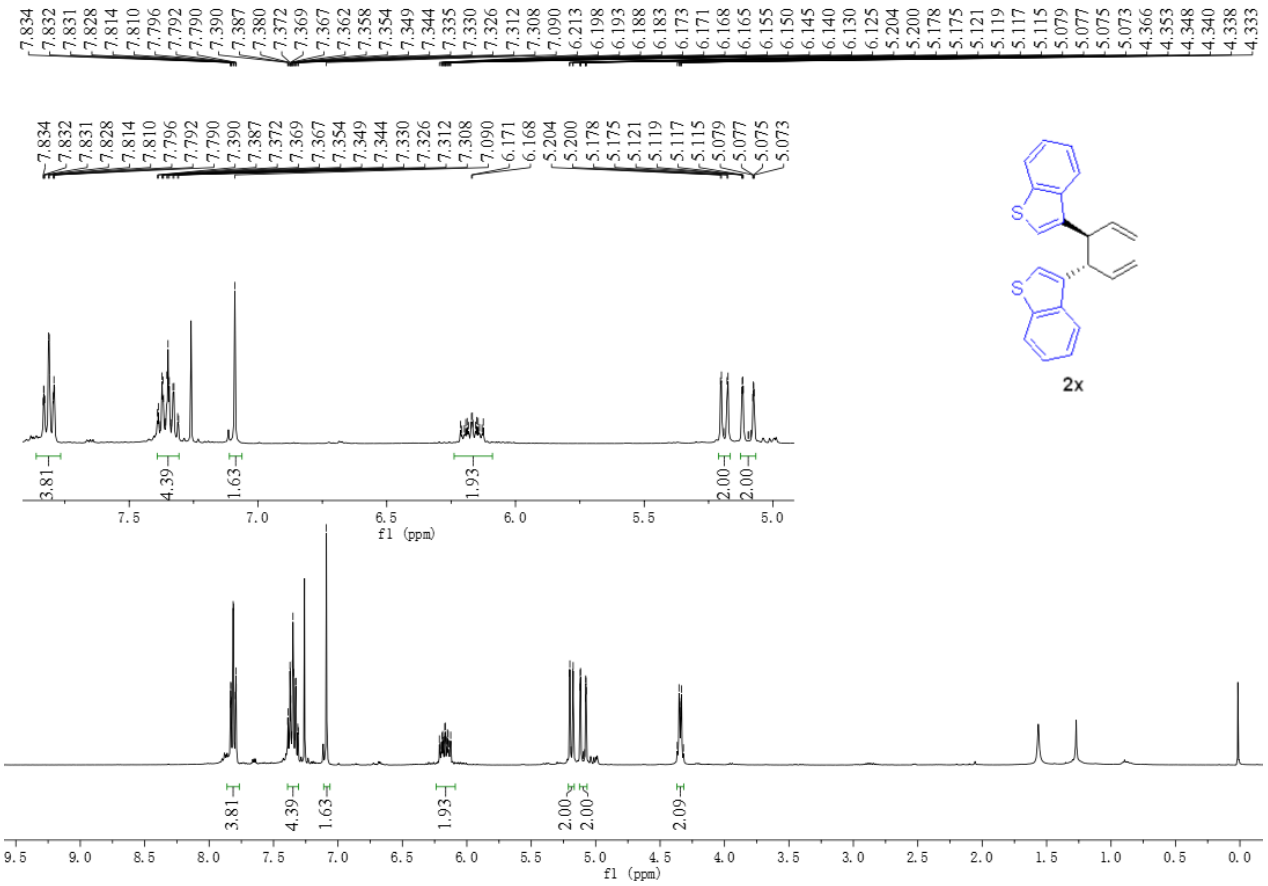

7.488
7.482
7.270
7.266
7.260
7.250
7.248
7.246
7.238
7.002
6.998
6.980
6.976
6.602
6.599
6.596
6.594
6.205
6.199
6.191
6.185
6.180
6.174
6.166
6.163
6.159
6.157
6.149
6.142
6.138
6.131
6.123
6.117
5.109
5.105
5.084
5.079
5.067
5.066
5.063
5.061
5.025
5.023
5.021
5.019
3.818
3.799
3.793
3.785
3.779
3.760
1.59
3.97
1.94
1.67
1.88
2.00
2.00
f1 (ppm)

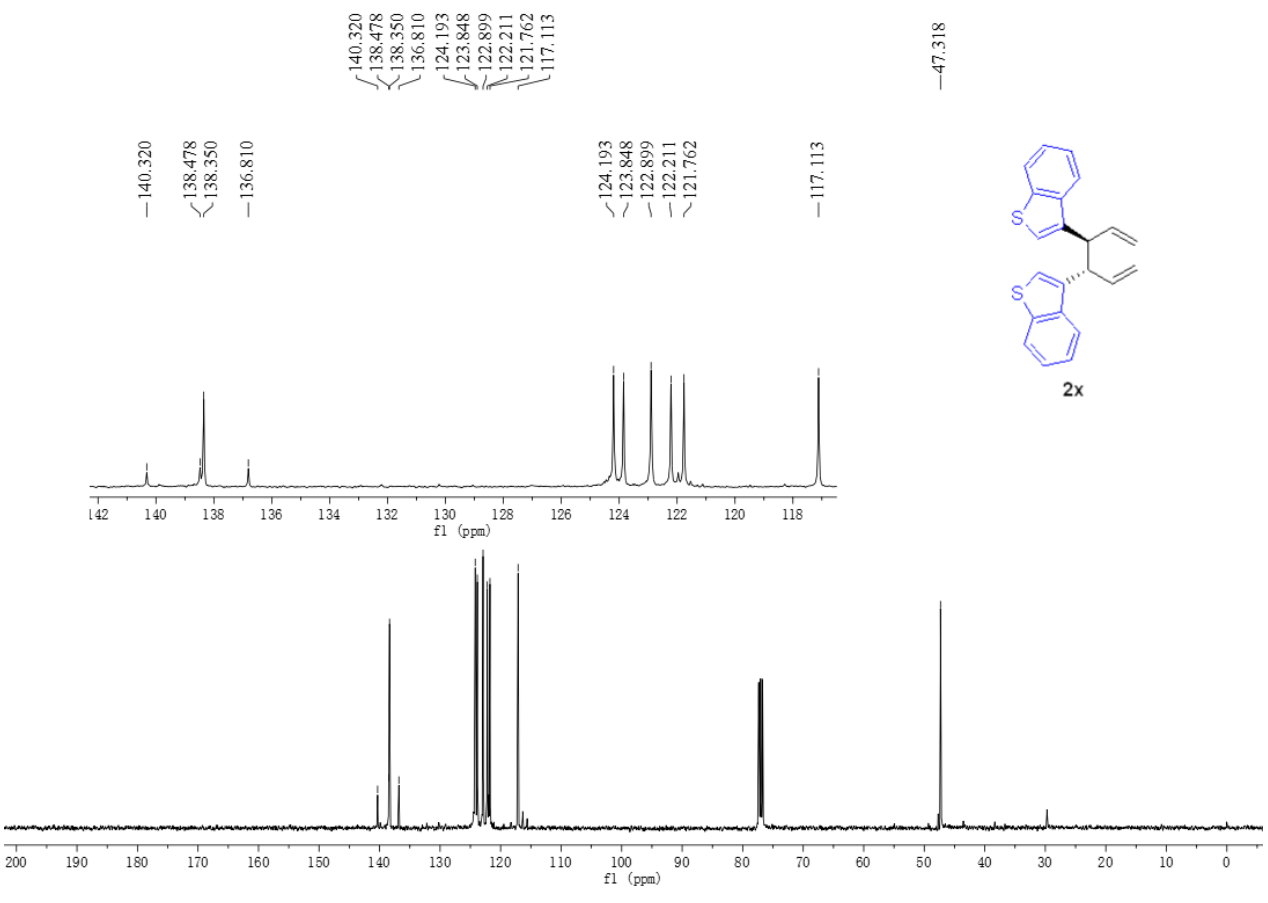
2w

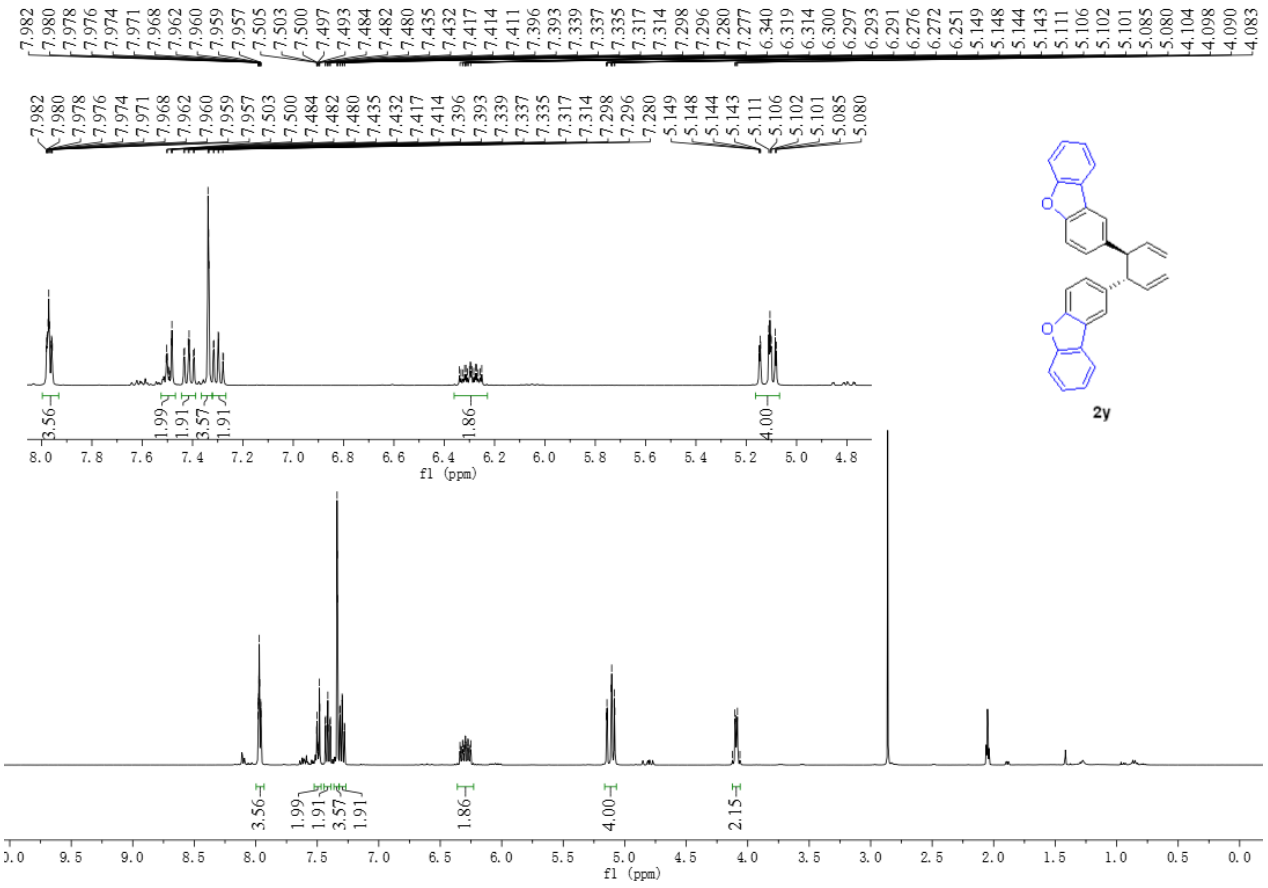

1.59
3.97
1.94
1.67
1.88
2.00
2.00
2.16
f1 (ppm)

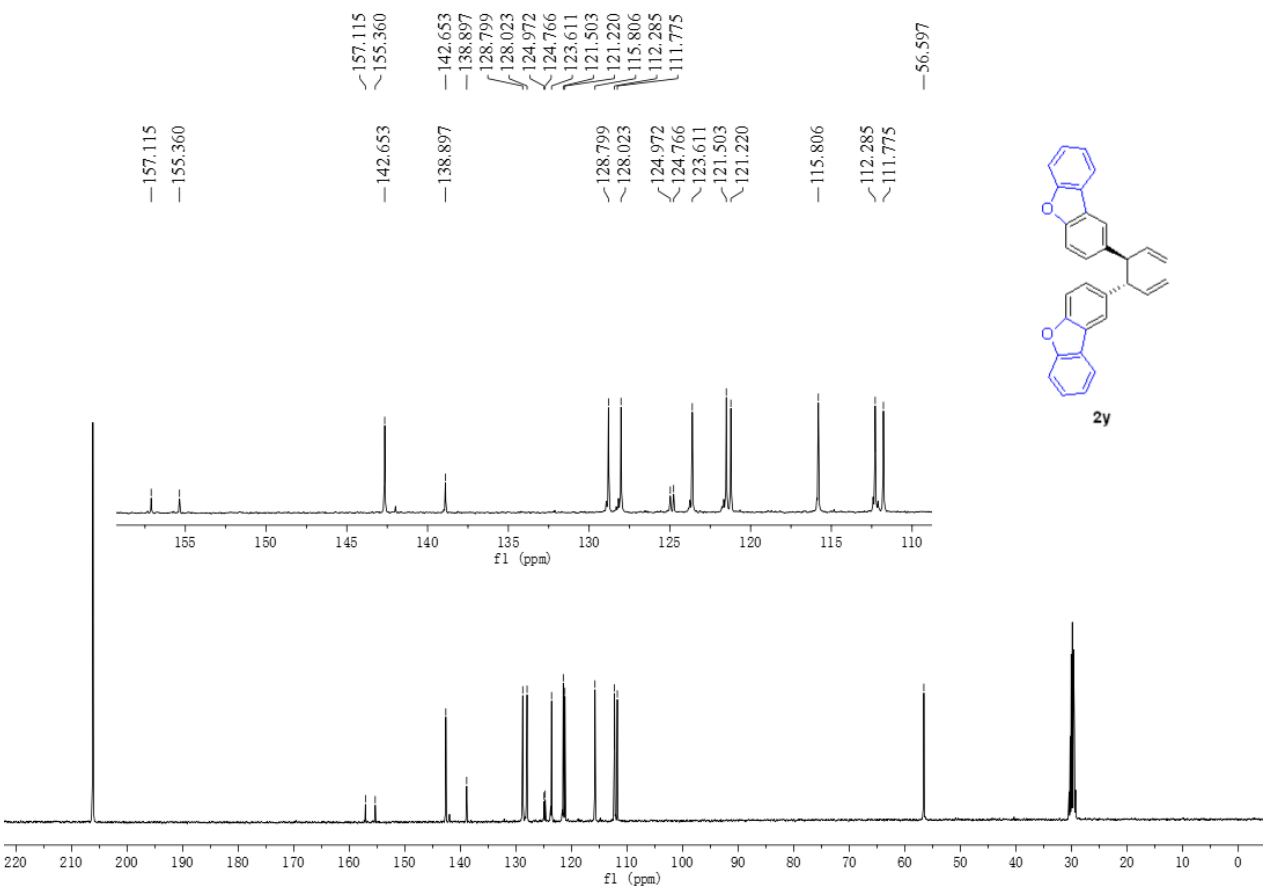

153.504
144.878
141.253
137.220
127.294
124.618
120.481
115.547
110.907
106.518
55.866
f1 (ppm)

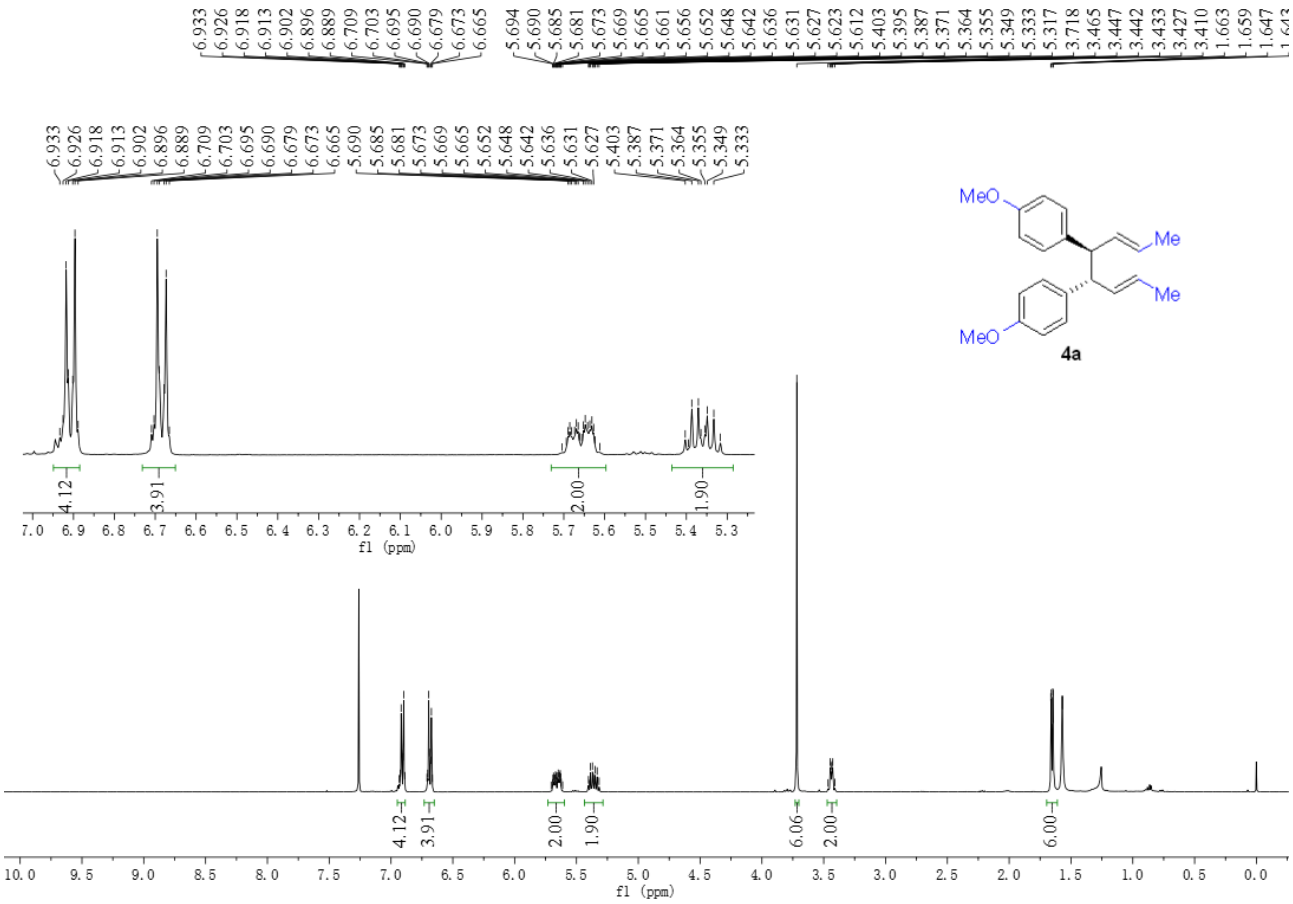
2w

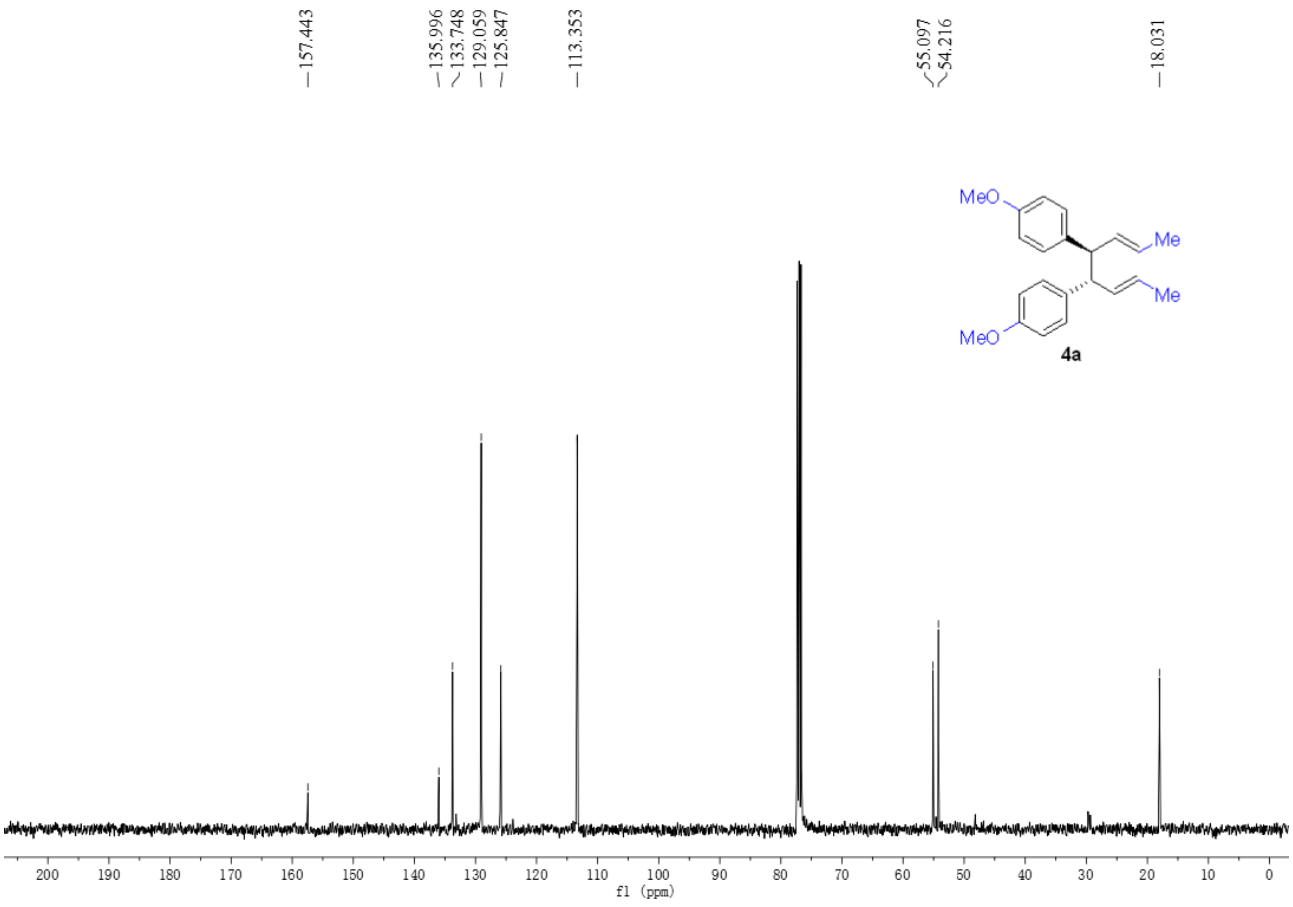

7.834 7.832 7.831 7.828 7.814 7.810 7.796 7.792 7.790 7.390 7.387 7.380 7.372 7.369 7.367 7.362 7.358 7.354 7.349 7.344 7.335 7.330 7.326 7.312 7.308 7.090 6.213 6.198 6.193 6.188 6.183 6.173 6.171 6.168 6.165 6.155 6.150 6.145 6.140 6.130 6.125 5.204 5.200 5.178 5.175 5.121 5.119 5.117 5.115 5.079 5.077 5.075 5.073 4.366 4.353 4.348 4.340 4.338 4.333
3.81 4.39 1.63 1.93 2.00 2.00 2.09
f1 (ppm)
2x

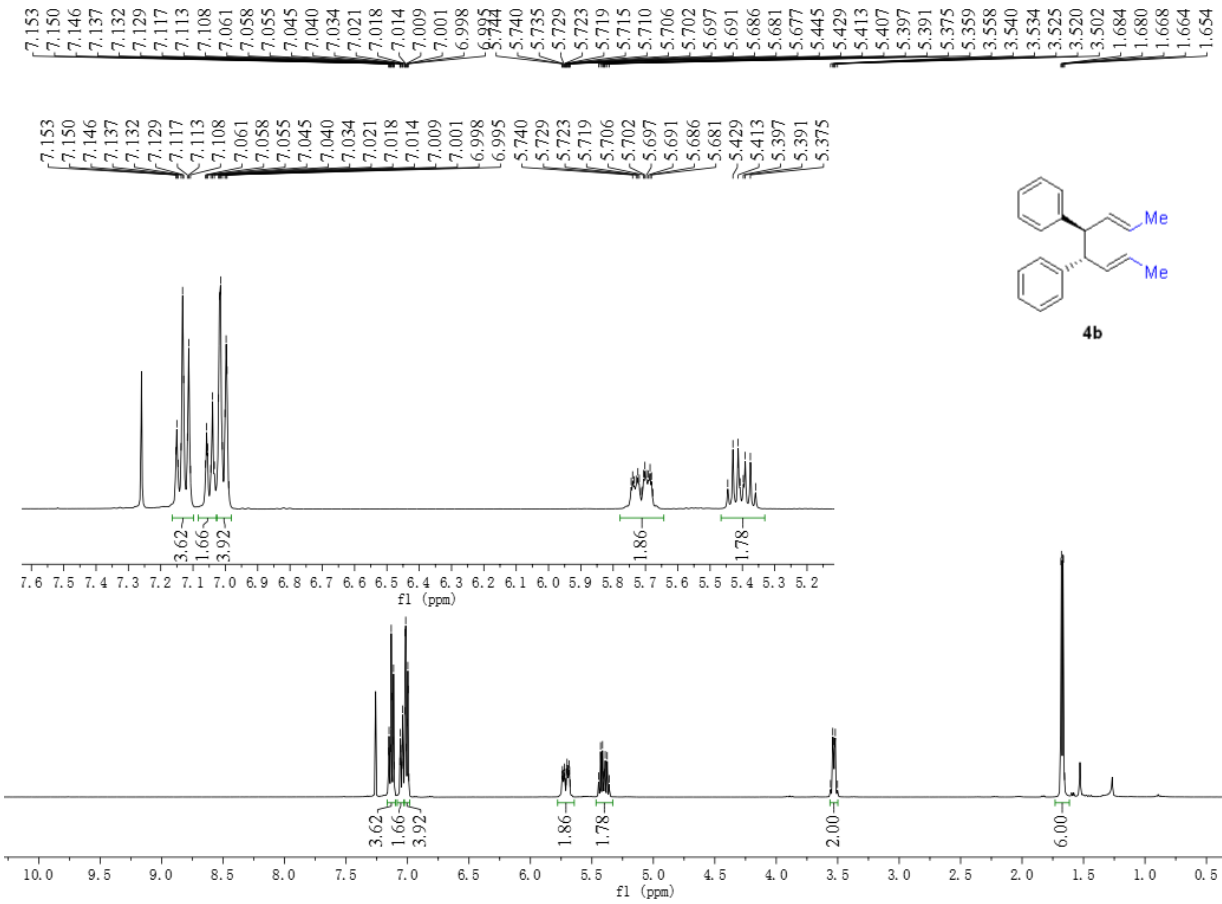

140.320 138.478 138.350 136.810 124.193 123.848 122.899 122.211 121.762 117.113 47.318
f1 (ppm)
2x

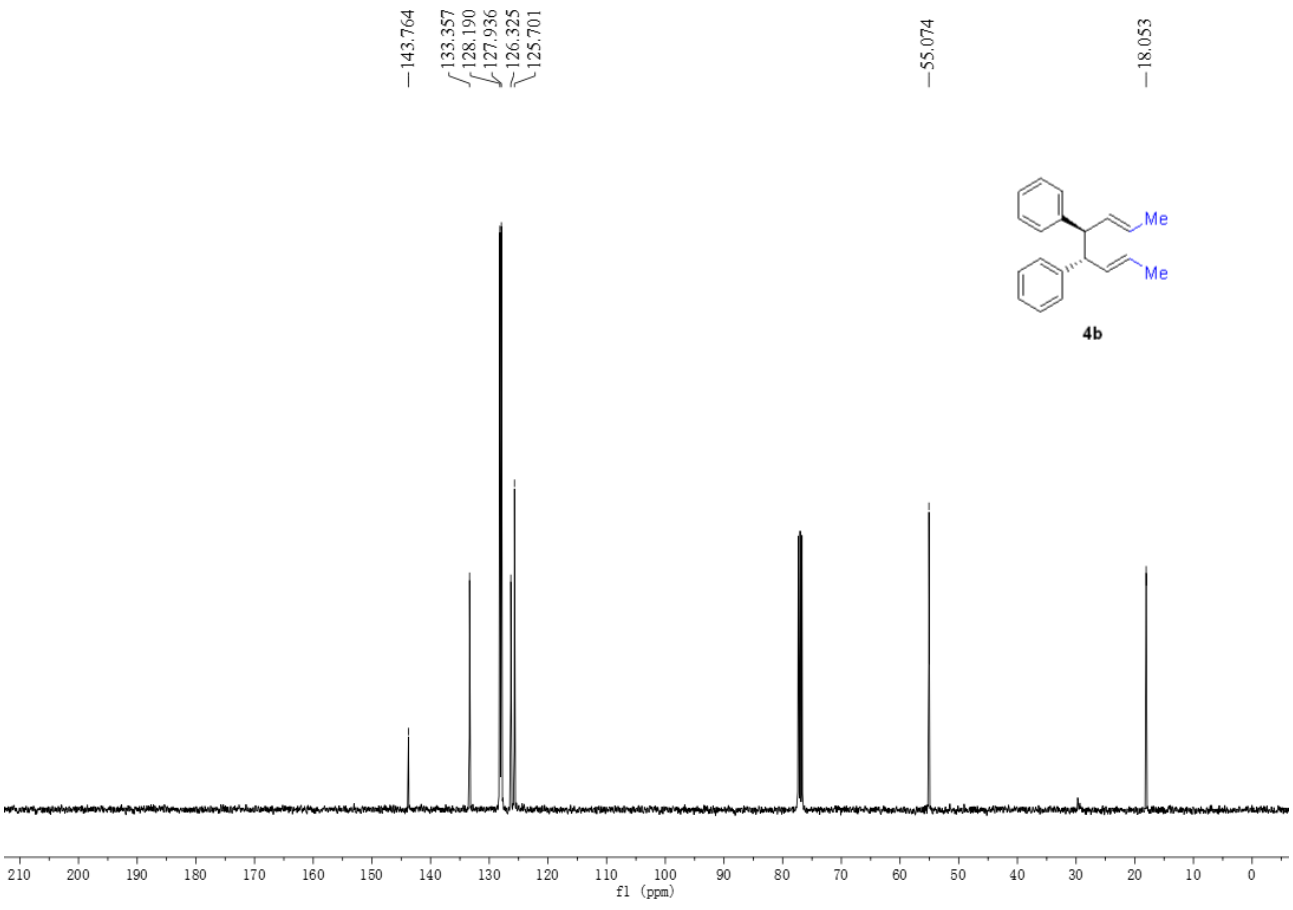

7.982 7.980 7.978 7.976 7.974 7.971 7.968 7.962 7.960 7.959 7.957 7.505 7.503 7.500 7.497 7.493 7.484 7.482 7.480 7.435 7.432 7.417 7.414 7.411 7.396 7.393 7.339 7.337 7.335 7.317 7.314 7.298 7.296 7.280 7.277 6.340 6.319 6.314 6.300 6.297 6.293 6.291 6.276 6.272 6.251 5.149 5.148 5.144 5.143 5.111 5.106 5.102 5.101 5.085 5.080 4.104 4.098 4.090 4.083
3.56 1.99 1.91 3.57 1.91 1.86 4.00 2.15
f1 (ppm)
2y

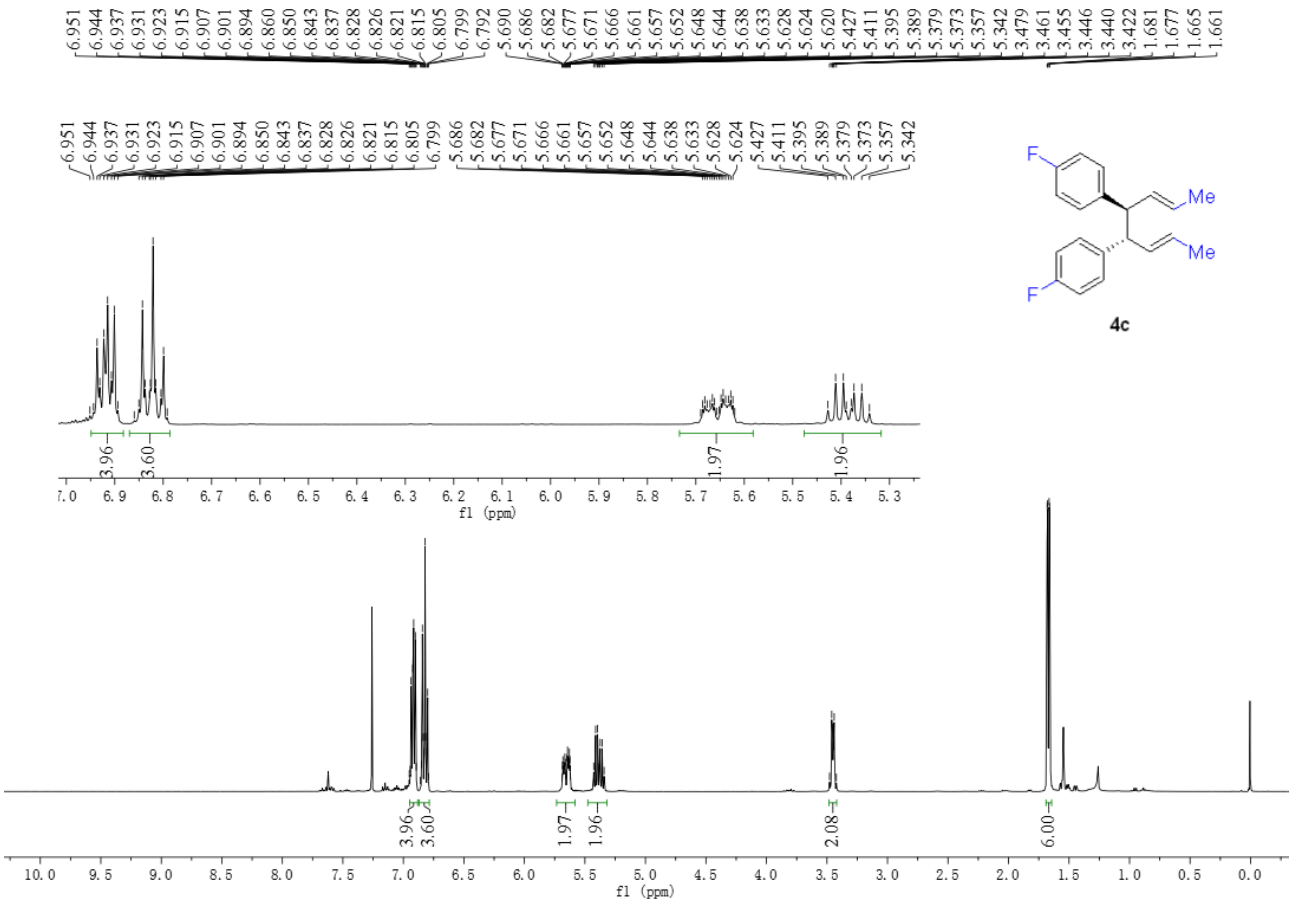

157.115 155.360 142.653 138.897 128.799 128.023 124.972 124.766 123.611 121.503 121.220 115.806 112.285 111.775 56.597
f1 (ppm)
2y

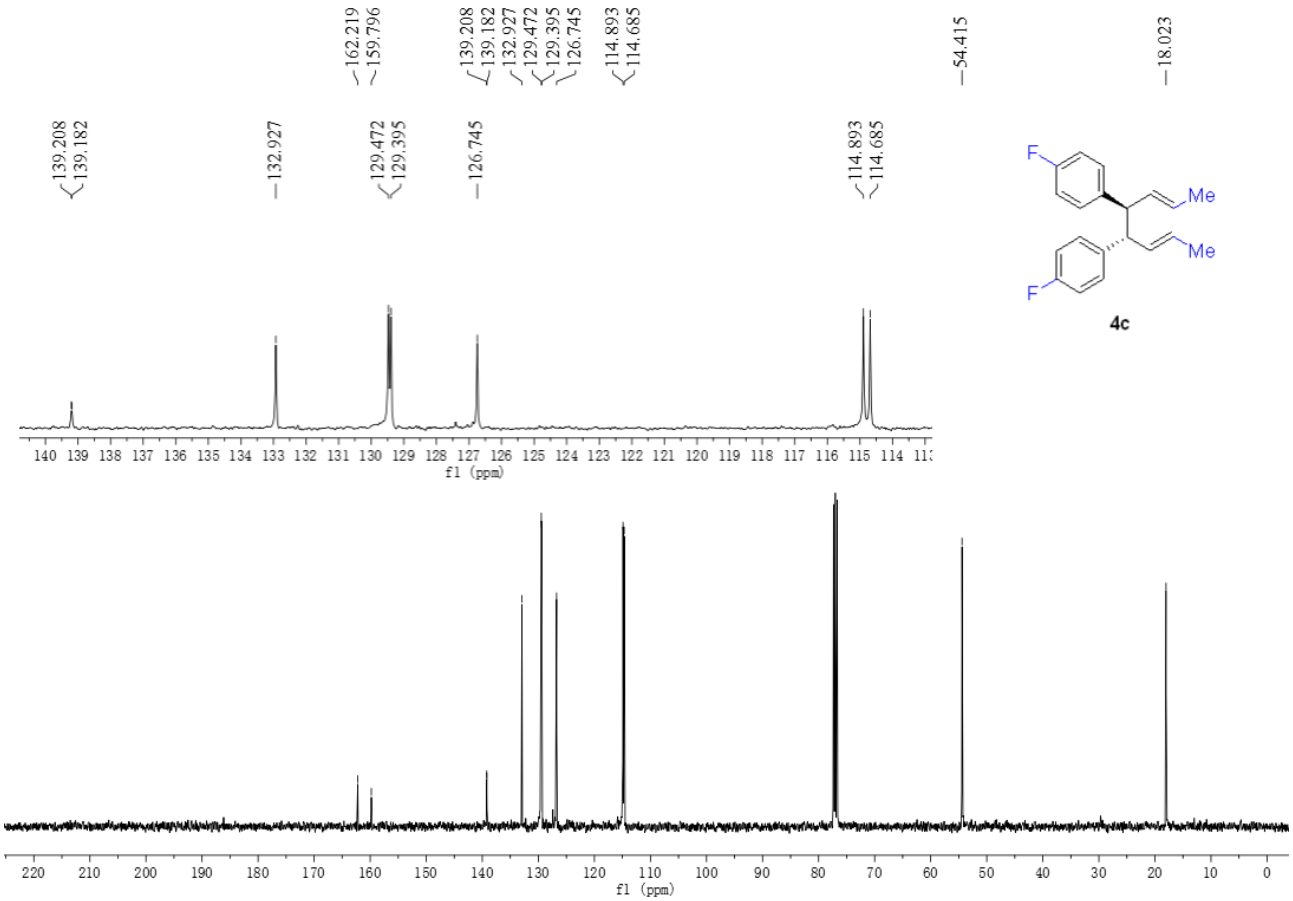

6.933
6.926
6.918
6.913
6.902
6.896
6.889
6.709
6.703
6.695
6.690
6.679
6.673
6.665
5.694
5.690
5.685
5.681
5.673
5.669
5.665
5.661
5.656
5.652
5.648
5.642
5.636
5.631
5.627
5.623
5.612
5.403
5.395
5.387
5.371
5.364
5.355
5.349
5.333
5.317
3.718
3.465
3.447
3.442
3.433
3.427
3.410
1.663
1.659
1.647
MeO
Me
Me
MeO
4a
4.12
3.91
2.00
1.90
6.06
2.00
6.00
f1 (ppm)

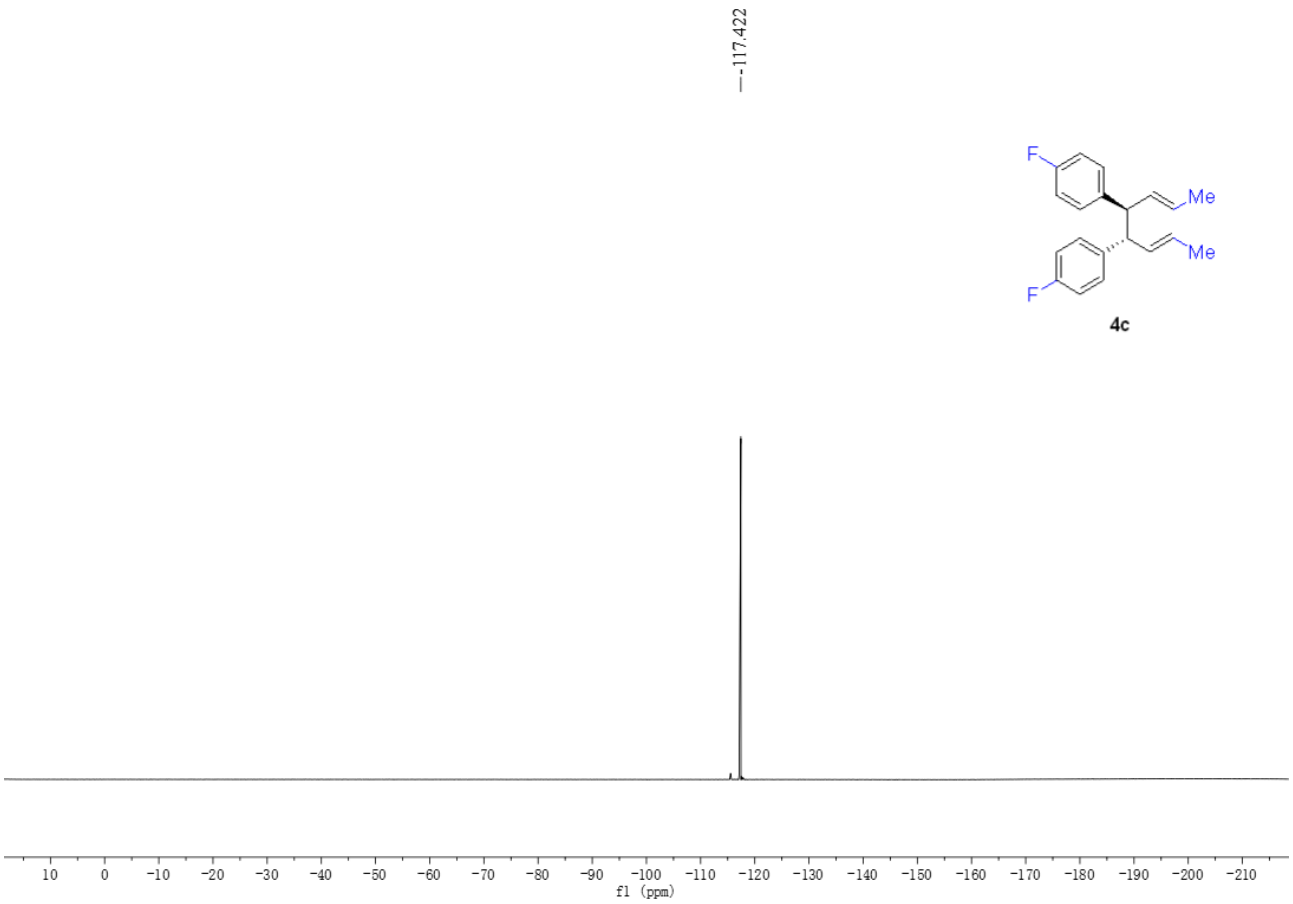

157.443
135.996
133.748
129.059
125.847
113.353
55.097
54.216
18.031
MeO
Me
Me
MeO
4a
f1 (ppm)

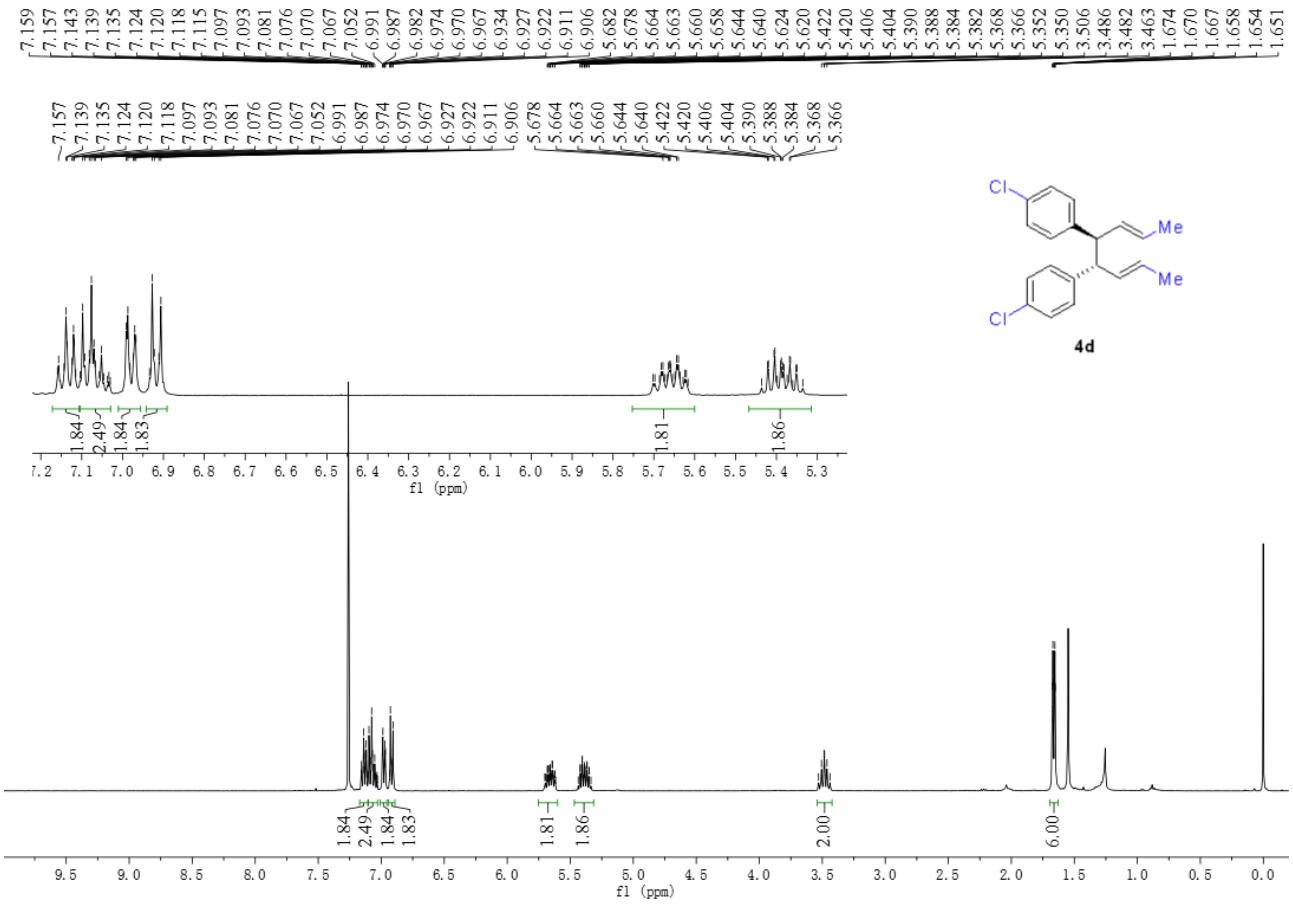

7.153
7.150
7.146
7.137
7.132
7.129
7.117
7.113
7.108
7.061
7.058
7.055
7.045
7.040
7.034
7.021
7.018
7.014
7.009
7.001
6.998
6.995
5.740
5.735
5.729
5.723
5.719
5.715
5.710
5.706
5.702
5.697
5.691
5.686
5.681
5.677
5.445
5.429
5.413
5.407
5.397
5.391
5.375
5.359
3.558
3.540
3.534
3.525
3.520
3.502
1.684
1.680
1.668
1.664
1.654
Me
Me
4b
3.62
1.66
3.92
1.86
1.78
f1 (ppm)
2.00
6.00

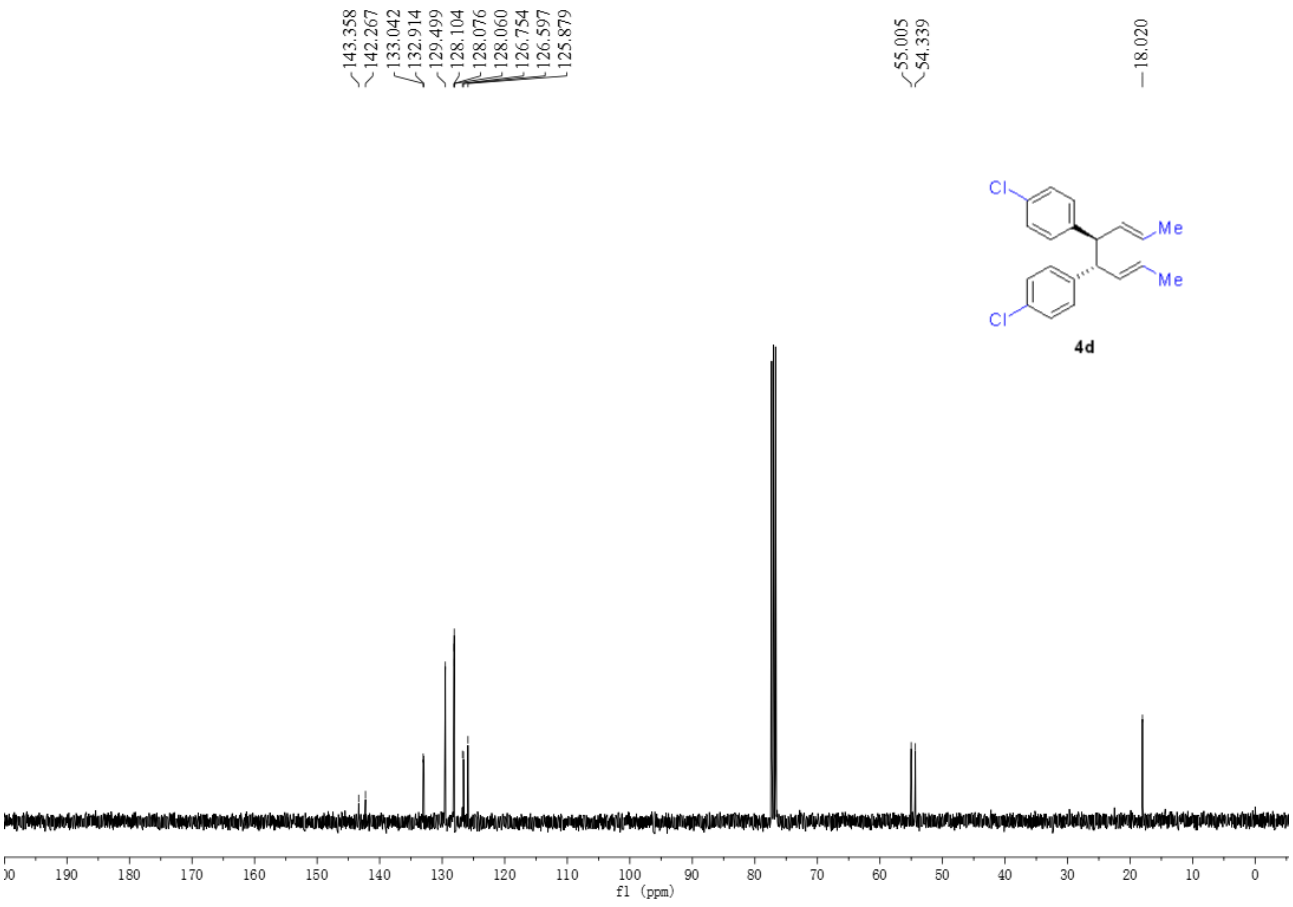

143.764
133.357
128.190
127.936
126.325
125.701
55.074
18.053
Me
Me
4b
f1 (ppm)

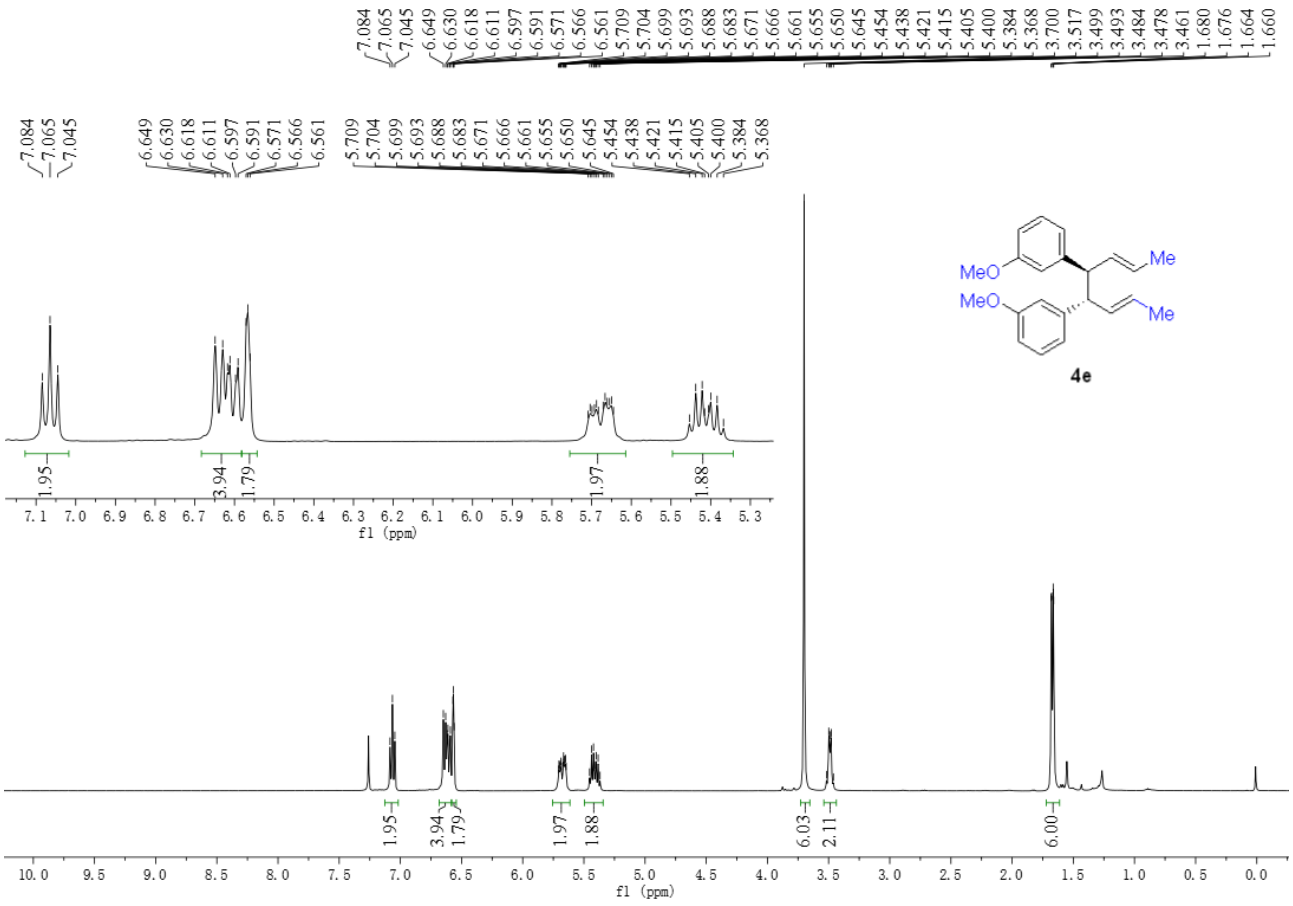

6.951 6.944 6.937 6.931 6.923 6.915 6.907 6.901 6.894 6.860 6.850 6.843 6.837 6.828 6.826 6.821 6.815 6.805 6.799 6.792
5.690 5.686 5.682 5.677 5.671 5.666 5.661 5.657 5.652 5.648 5.644 5.638 5.633 5.628 5.624 5.620 5.427 5.411 5.395 5.389 5.379 5.373 5.357 5.342
3.479 3.461 3.455 3.446 3.440 3.422 1.681 1.677 1.665 1.661
3.96 3.60 1.97 1.96
f1 (ppm)
Me
Me
F
F
4c
3.96 3.60 1.97 1.96 2.08 6.00
f1 (ppm)

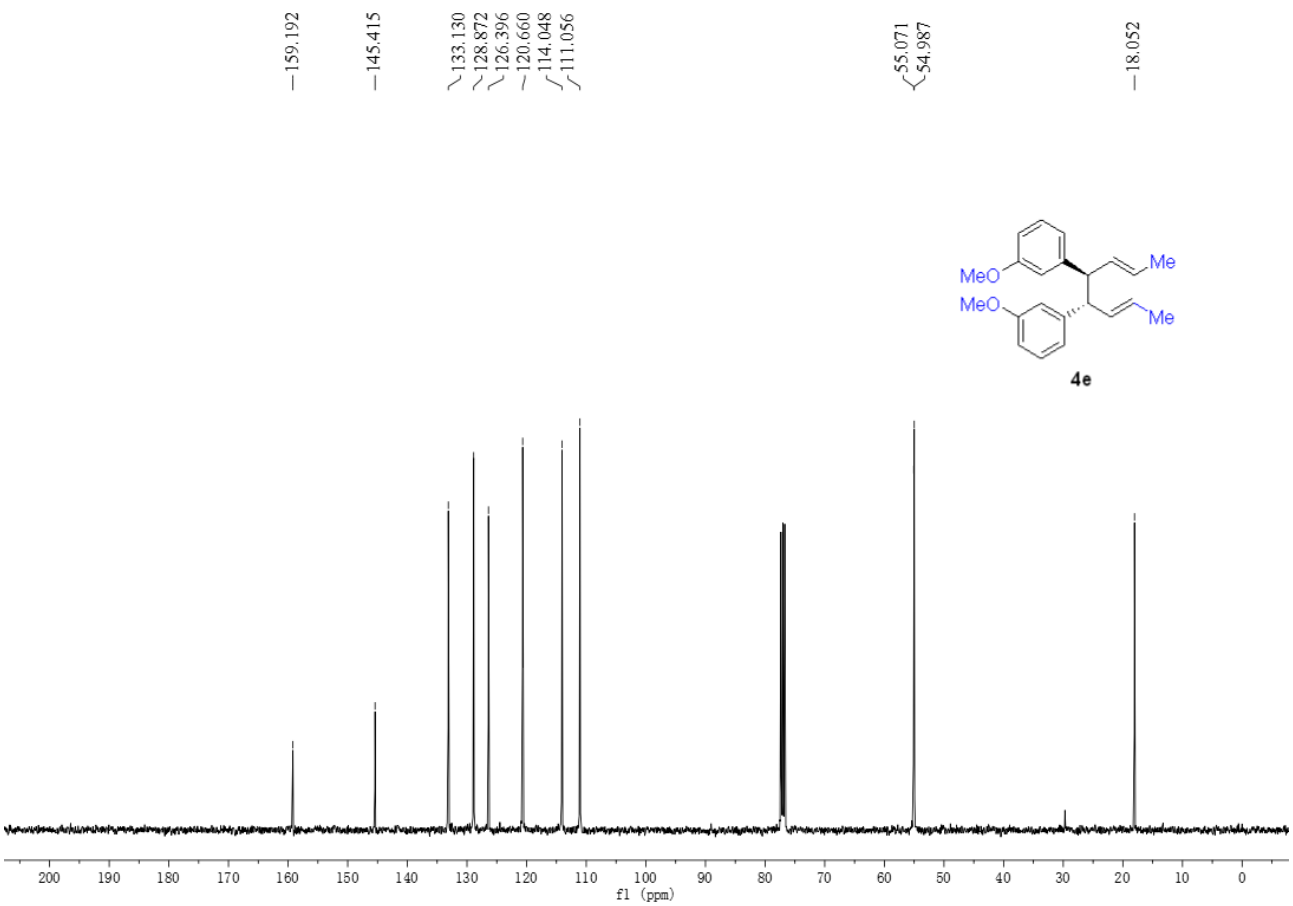

162.219 159.796
139.208 139.182 132.927 129.472 129.395 126.745 114.893 114.685
54.415
18.023
f1 (ppm)
Me
Me
F
F
4c
f1 (ppm)

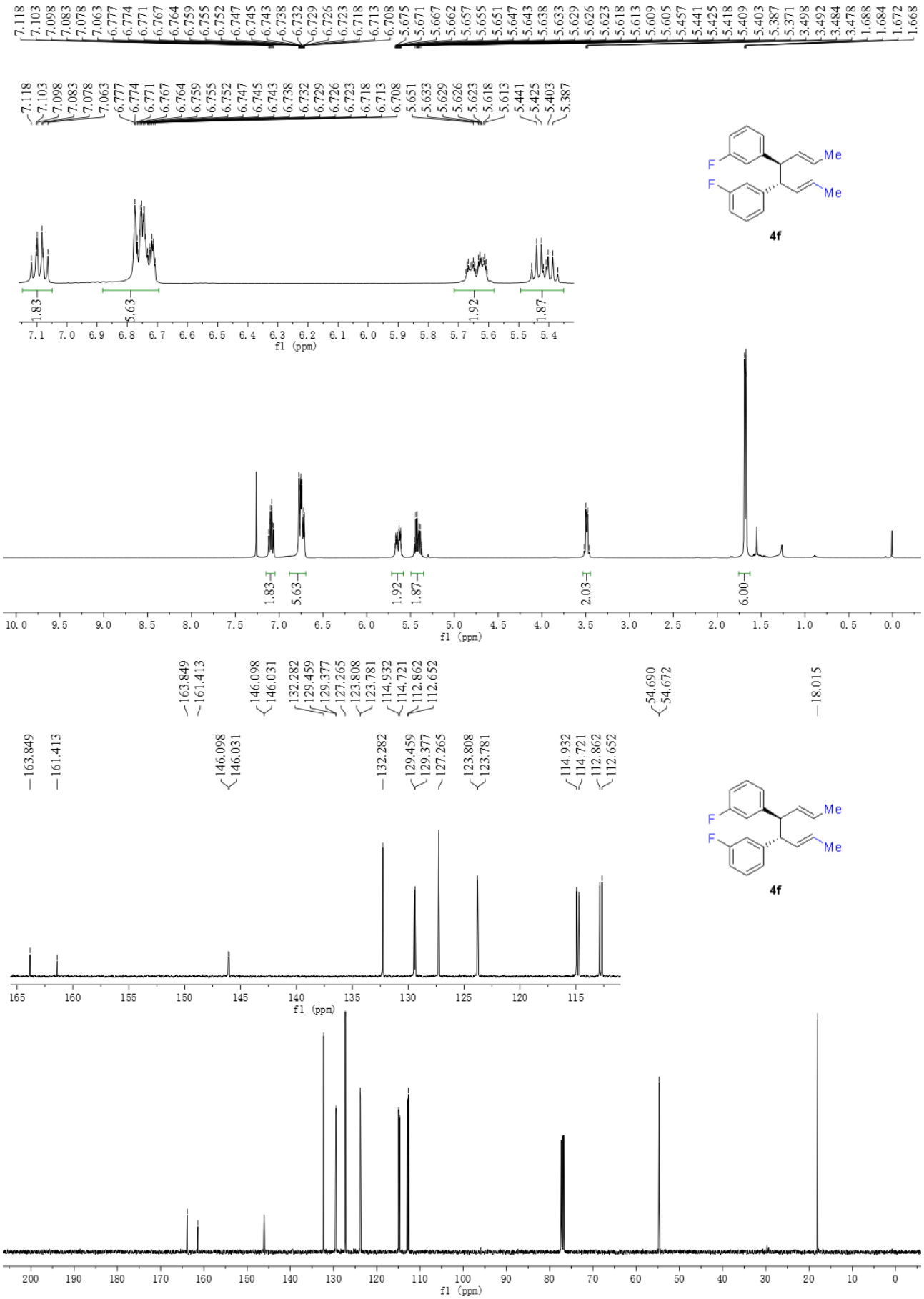

-117.422
F
Me
Me
F
4c
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

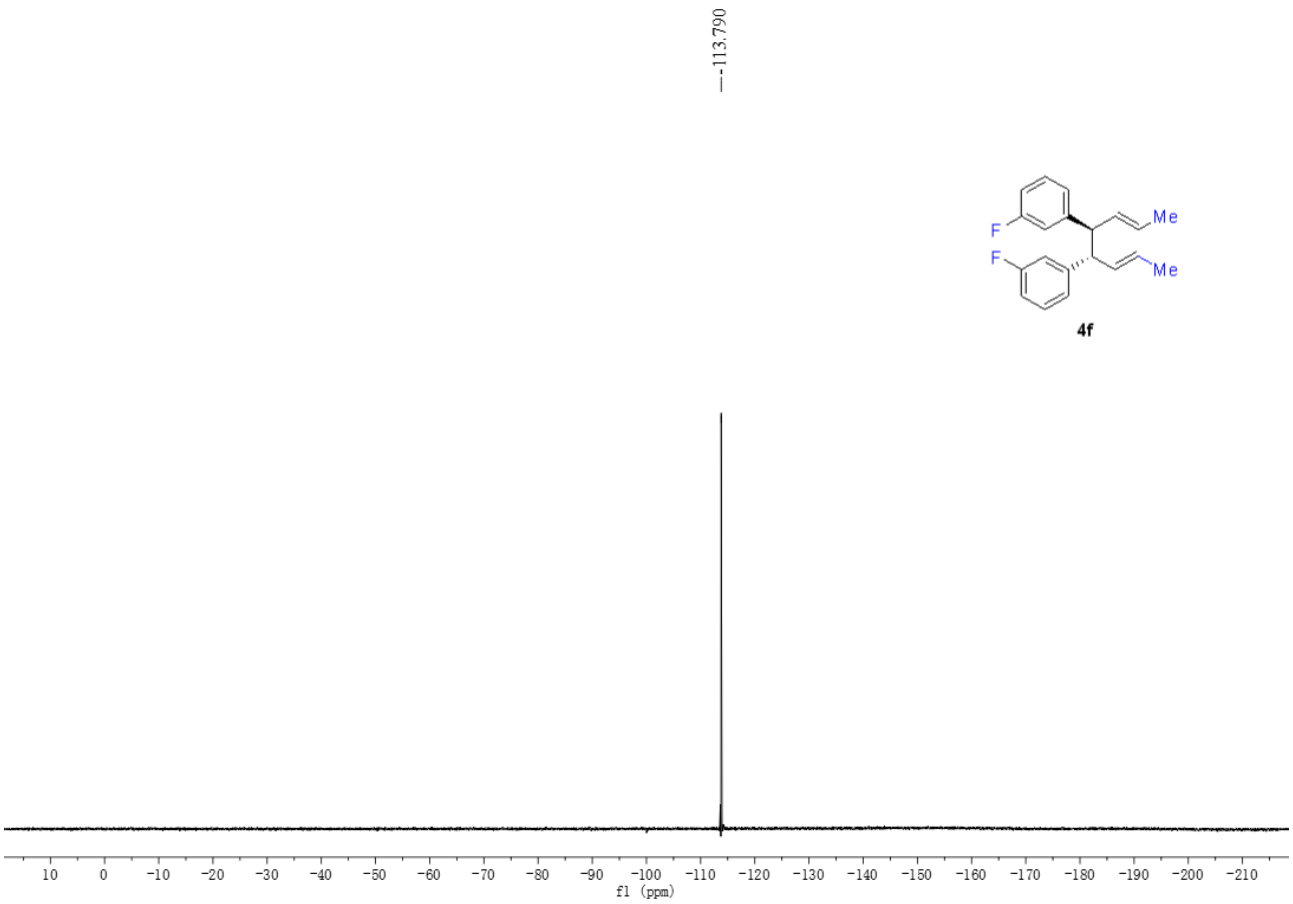

7.159 7.157 7.143 7.139 7.135 7.124 7.120 7.118 7.115 7.097 7.093 7.081 7.076 7.070 7.067 7.052 6.991 6.987 6.982 6.974 6.970 6.967 6.934 6.927 6.922 6.911 6.906 5.682 5.678 5.664 5.663 5.660 5.658 5.644 5.640 5.624 5.620 5.422 5.420 5.406 5.404 5.390 5.388 5.384 5.382 5.368 5.366 5.352 5.350 3.506 3.486 3.482 3.463 1.674 1.670 1.667 1.658 1.654 1.651
Cl
Me
Me
Cl
4d
1.84 2.49 1.84 1.83 1.81 1.86
f1 (ppm)
1.84 2.49 1.84 1.83 1.81 1.86 2.00 6.00
f1 (ppm)


143.358 142.267 133.042 132.914 129.499 128.104 128.076 128.060 126.754 126.597 125.879
55.005 54.339
18.020
Cl
Me
Me
Cl
4d
f1 (ppm)


7.084
7.065
7.045
6.649
6.630
6.618
6.611
6.597
6.591
6.571
6.566
6.561
5.709
5.704
5.699
5.693
5.688
5.683
5.671
5.666
5.661
5.655
5.650
5.645
5.454
5.438
5.421
5.415
5.405
5.400
5.384
5.368
3.700
3.517
3.499
3.493
3.484
3.478
3.461
1.680
1.676
1.664
1.660
MeO
MeO
Me
Me
4e
1.95
3.94
1.79
1.97
1.88
6.03
2.11
6.00
f1 (ppm)


159.192
145.415
133.130
128.872
126.396
120.660
114.048
111.056
55.071
54.987
18.052
MeO
MeO
Me
Me
4e
f1 (ppm)


7.118 7.103 7.098 7.083 7.078 7.063 6.777 6.774 6.771 6.767 6.764 6.759 6.755 6.752 6.747 6.745 6.743 6.738 6.732 6.729 6.726 6.723 6.718 6.713 6.708 5.675 5.671 5.667 5.662 5.657 5.655 5.651 5.647 5.643 5.638 5.633 5.629 5.626 5.623 5.618 5.613 5.609 5.605 5.457 5.441 5.425 5.418 5.409 5.403 5.387 5.371 3.498 3.492 3.484 3.478 1.688 1.684 1.672 1.668
F
F
Me
Me
4f
1.83
5.63
1.92
1.87
f1 (ppm)
2.03
6.00
163.849 161.413 146.098 146.031 132.282 129.459 129.377 127.265 123.808 123.781 114.932 114.721 112.862 112.652 54.690 54.672 18.015


-113.790
F
F
Me
Me
4f
10
0
-10
-20
-30
-40
-50
-60
-70
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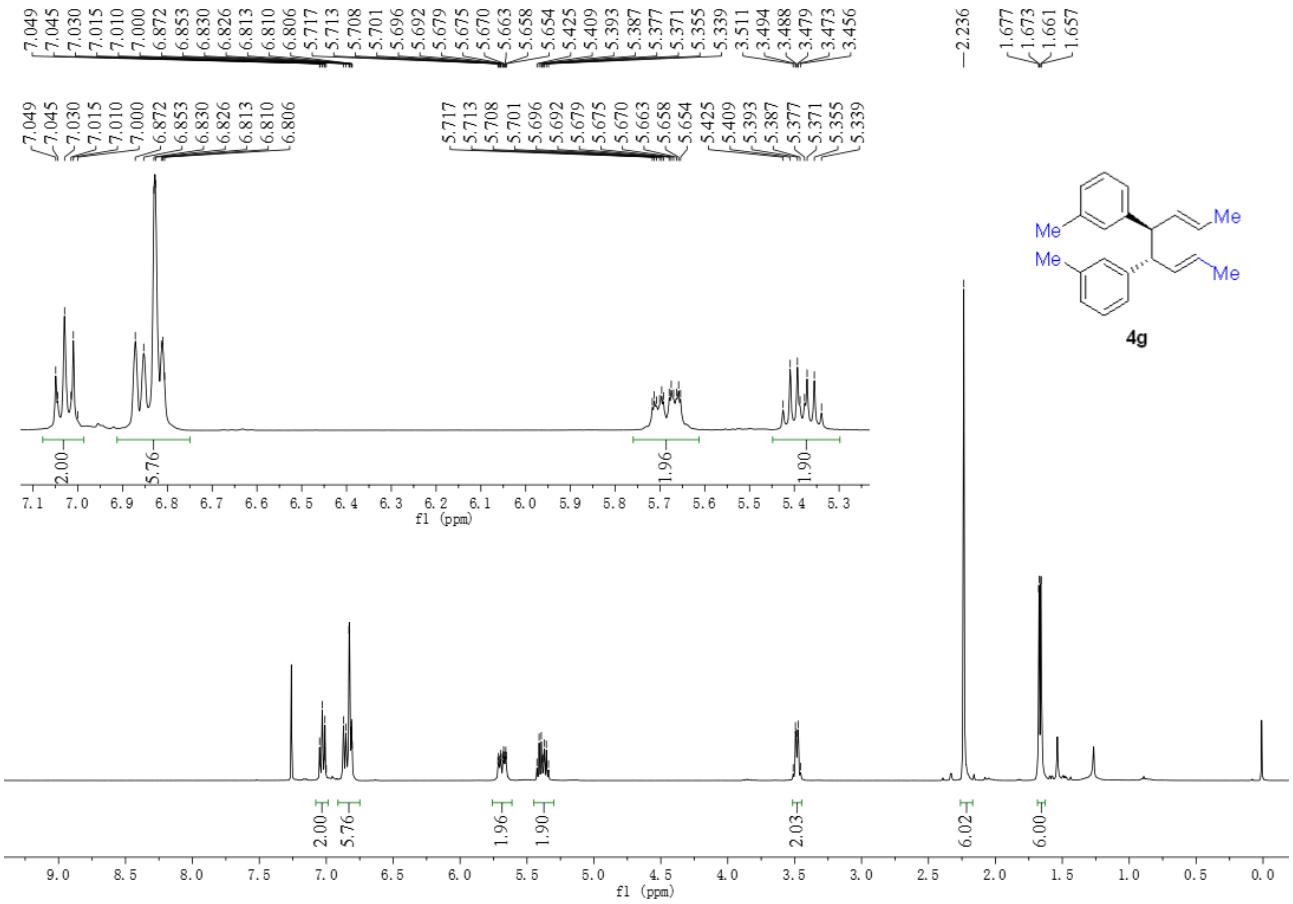
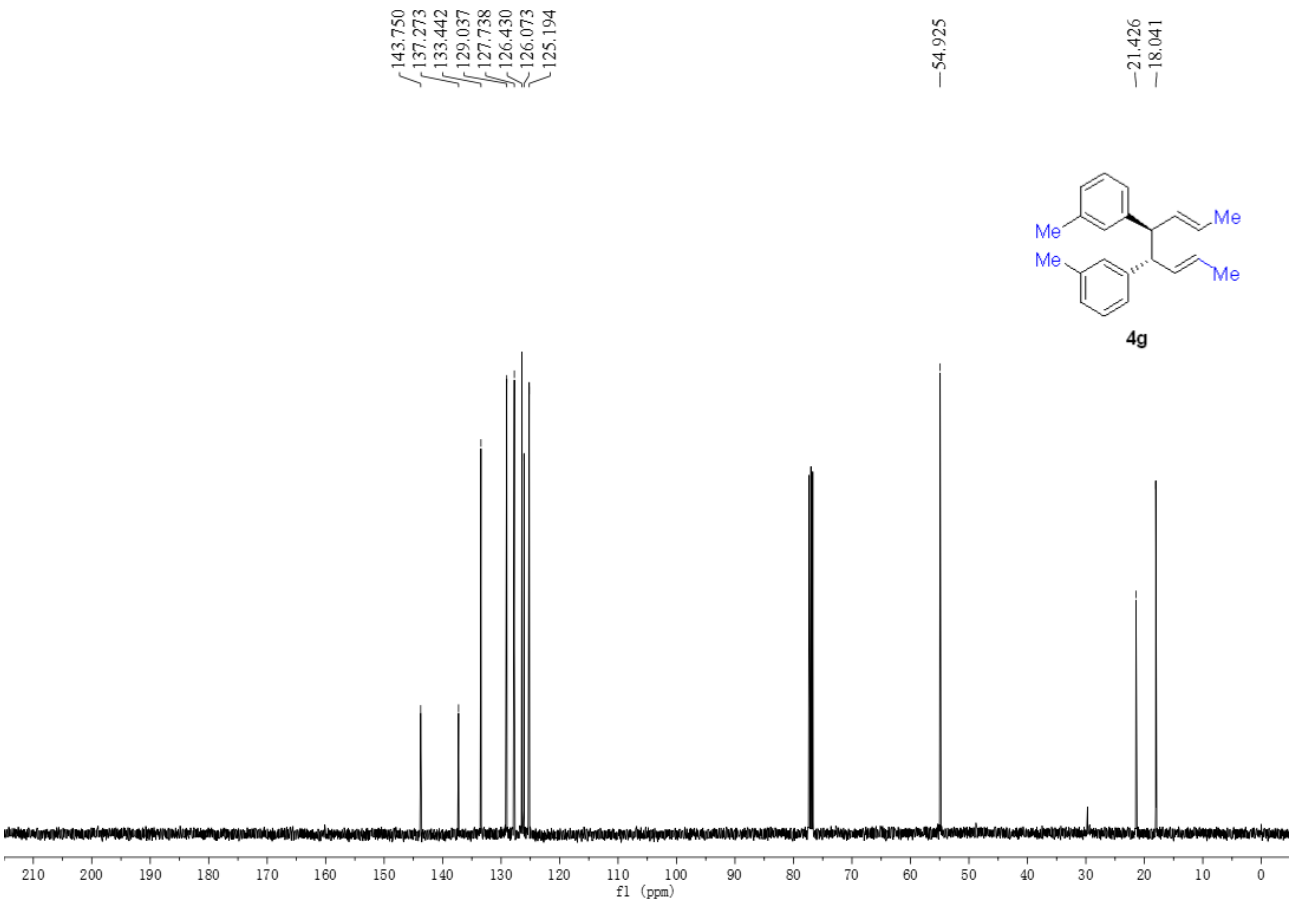
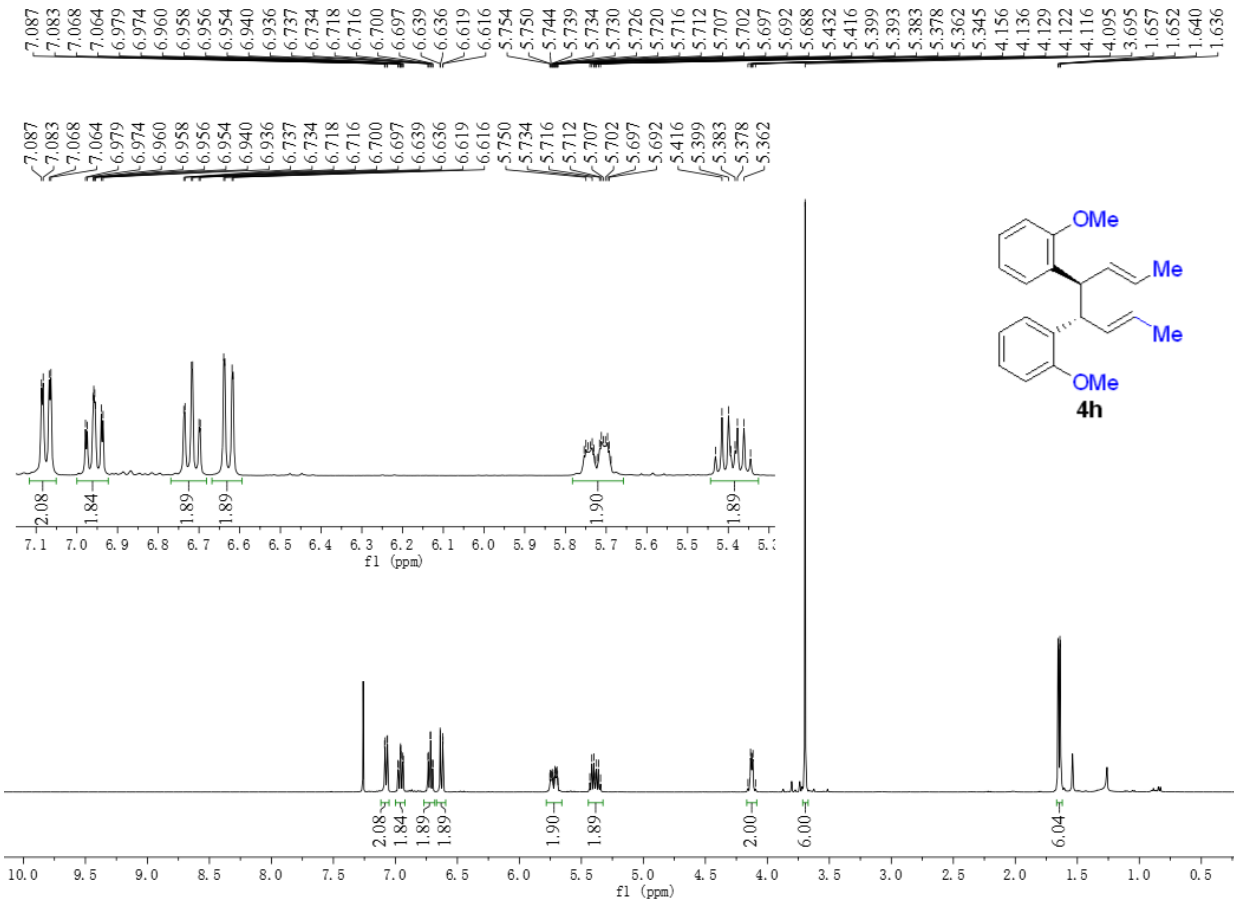
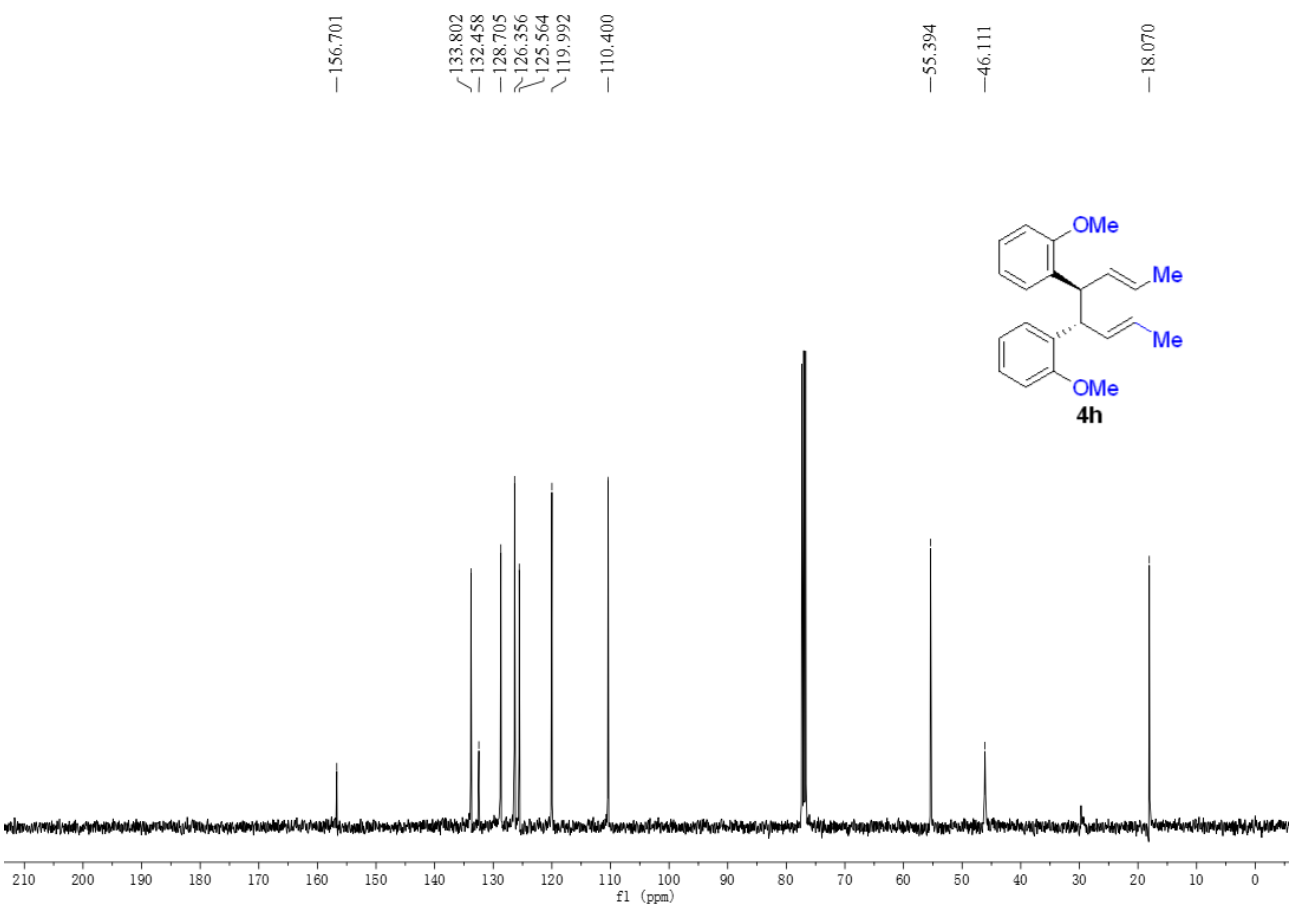
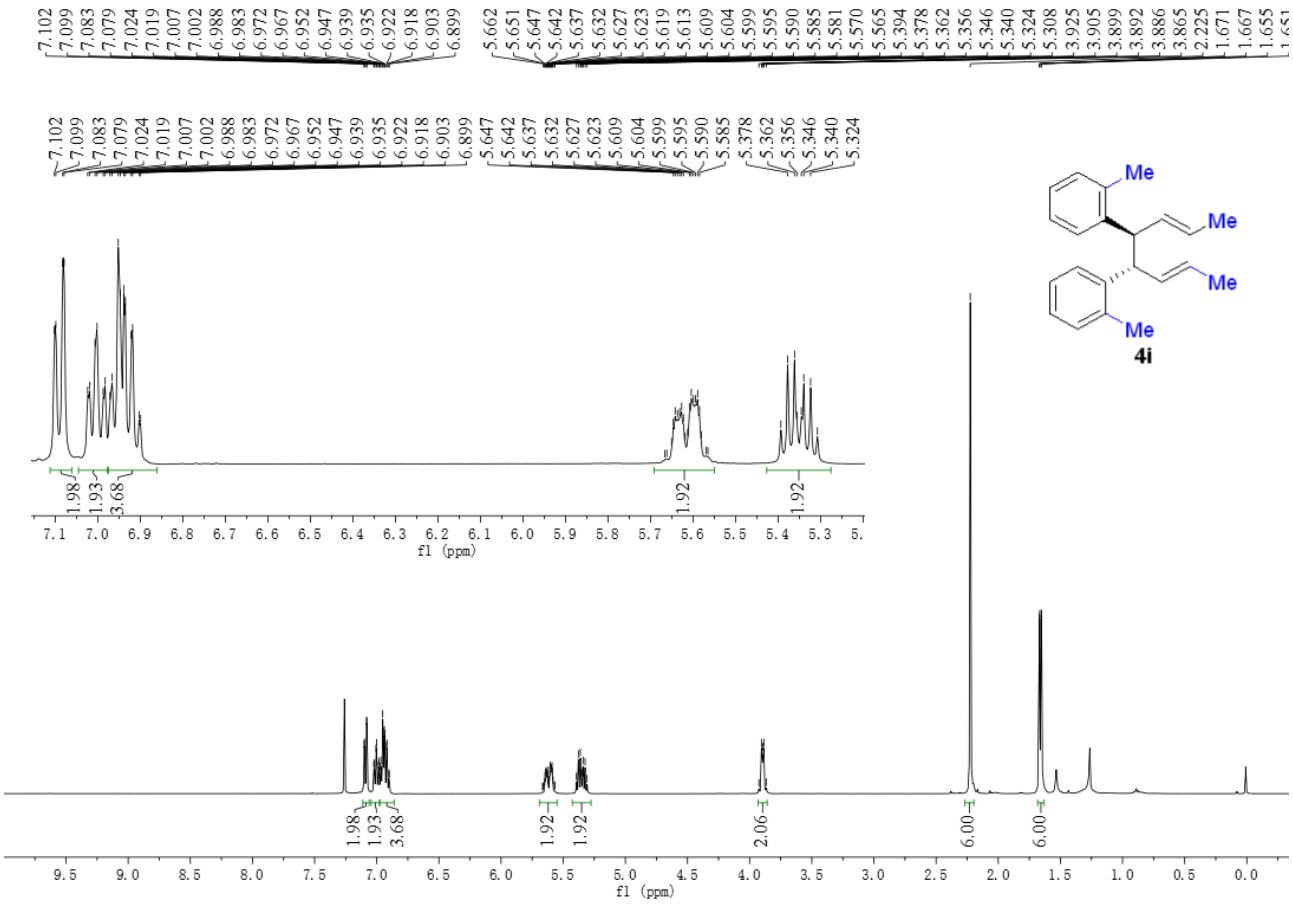
-170
-180
-190
-200
-210
f1 (ppm)

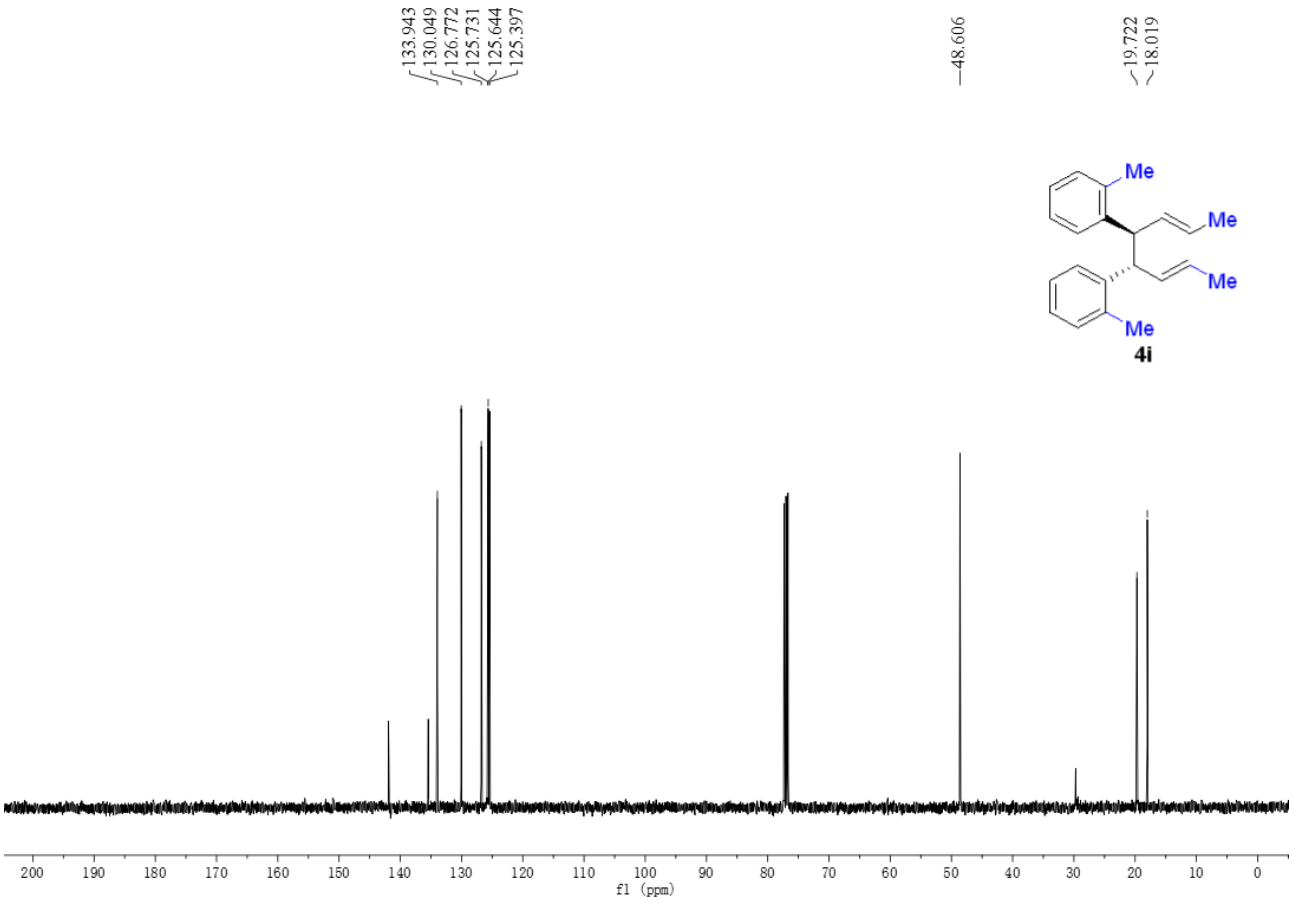

7.049
7.045
7.030
7.015
7.010
7.000
6.872
6.853
6.830
6.826
6.813
6.810
6.806
5.717
5.713
5.708
5.701
5.696
5.692
5.679
5.675
5.670
5.663
5.658
5.654
5.425
5.409
5.393
5.387
5.377
5.371
5.355
5.339
3.511
3.494
3.488
3.479
3.473
3.456
2.236
1.677
1.673
1.661
1.657
Me
Me
Me
Me
4g
2.00
5.76
1.96
1.90
2.03
6.02
6.00
f1 (ppm)

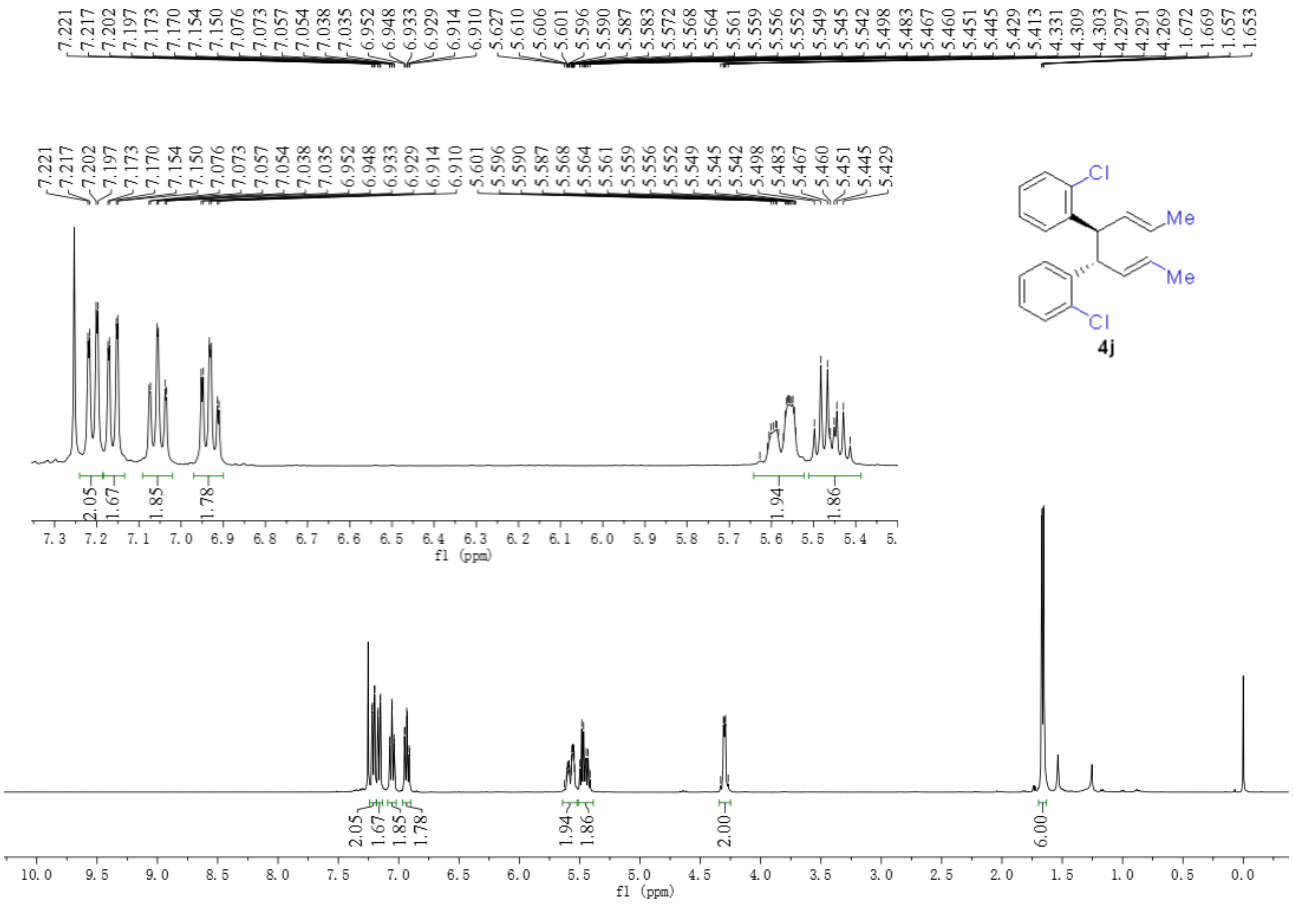

143.750
137.273
133.442
129.037
127.738
126.430
126.073
125.194
54.925
21.426
18.041
Me
Me
Me
Me
4g
f1 (ppm)

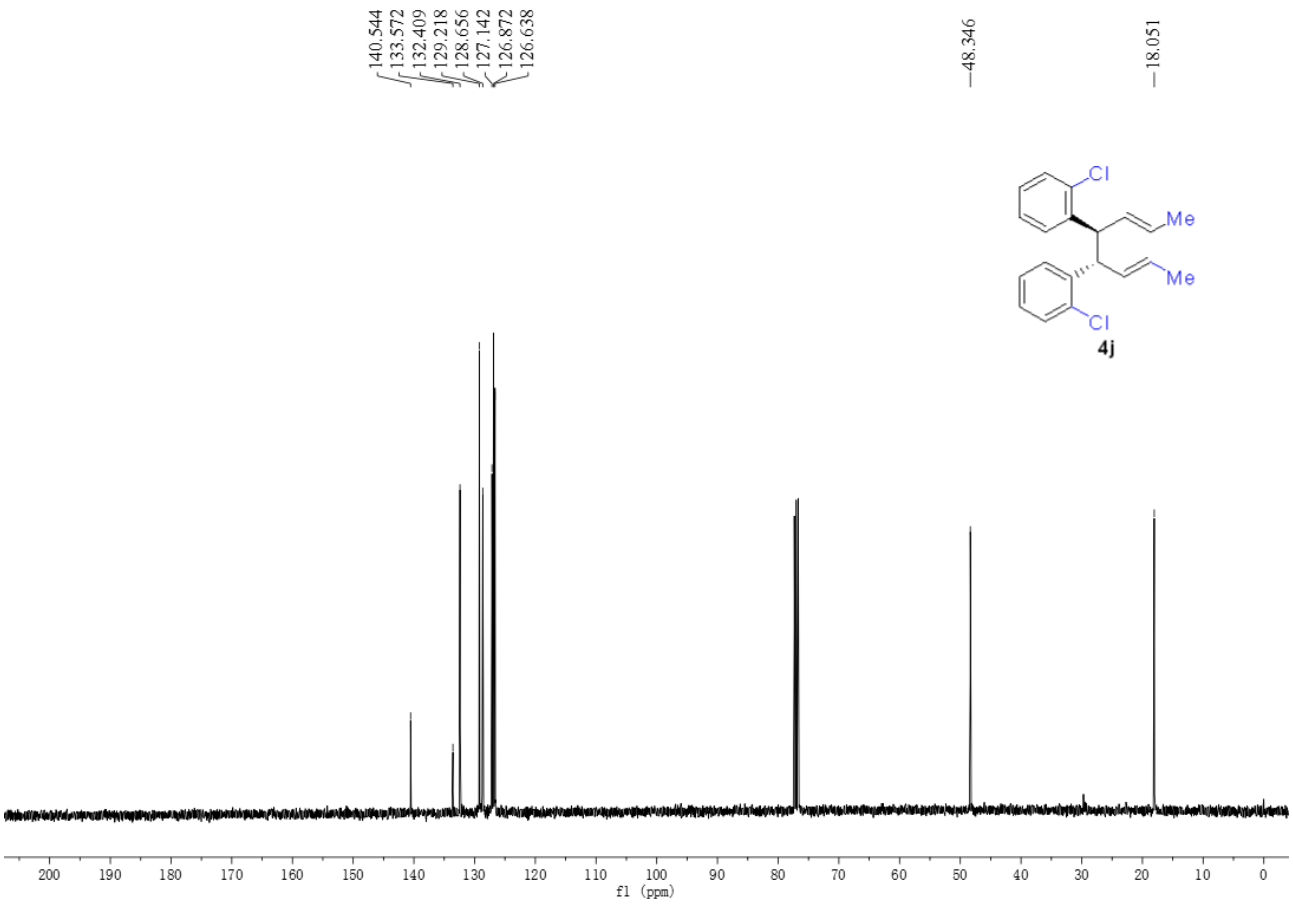

7.087
7.083
7.068
7.064
6.979
6.974
6.960
6.958
6.956
6.954
6.940
6.936
6.737
6.734
6.718
6.716
6.700
6.697
6.639
6.636
6.619
6.616
5.754
5.750
5.744
5.739
5.734
5.730
5.726
5.720
5.716
5.712
5.707
5.702
5.697
5.692
5.688
5.432
5.416
5.399
5.393
5.383
5.378
5.362
5.345
4.156
4.136
4.129
4.122
4.116
4.095
3.695
1.657
1.652
1.640
1.636
OMe
Me
Me
OMe
4h
2.08
1.84
1.89
1.89
1.90
1.89
2.00
6.00
6.04
f1 (ppm)

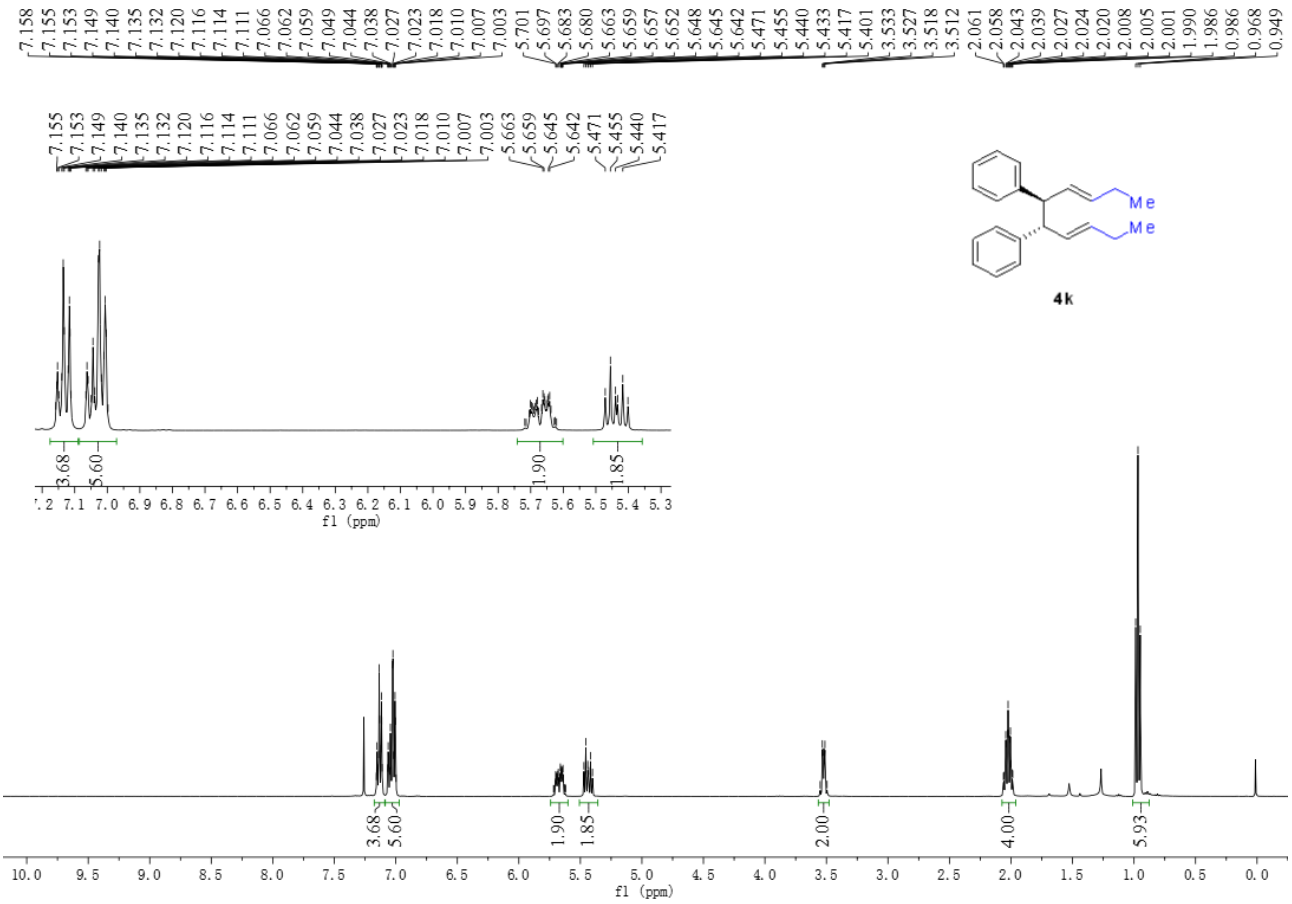

156.701
133.802
132.458
128.705
126.356
125.564
119.992
110.400
55.394
46.111
18.070
OMe
Me
Me
OMe
4h
f1 (ppm)

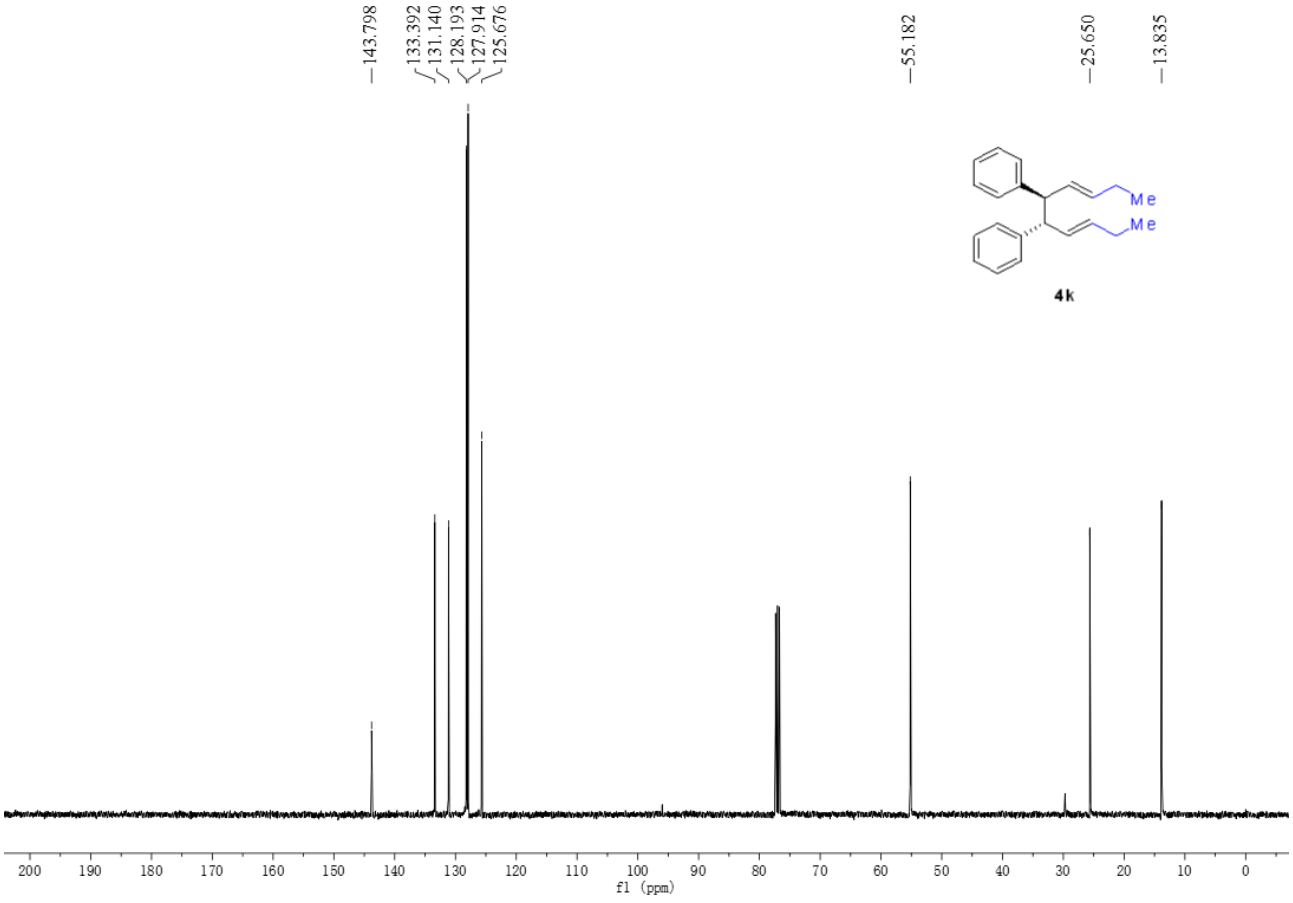

7.102
7.099
7.083
7.079
7.024
7.019
7.007
7.002
6.988
6.983
6.972
6.967
6.952
6.947
6.939
6.935
6.922
6.918
6.903
6.899
5.662
5.651
5.647
5.642
5.637
5.632
5.627
5.623
5.619
5.613
5.609
5.604
5.599
5.595
5.590
5.585
5.581
5.570
5.565
5.394
5.378
5.362
5.356
5.346
5.340
5.324
5.308
3.925
3.905
3.899
3.892
3.886
3.865
2.225
1.671
1.667
1.655
Me
Me
Me
Me
4i
1.98
1.93
3.68
1.92
1.92
2.06
6.00
6.00
f1 (ppm)

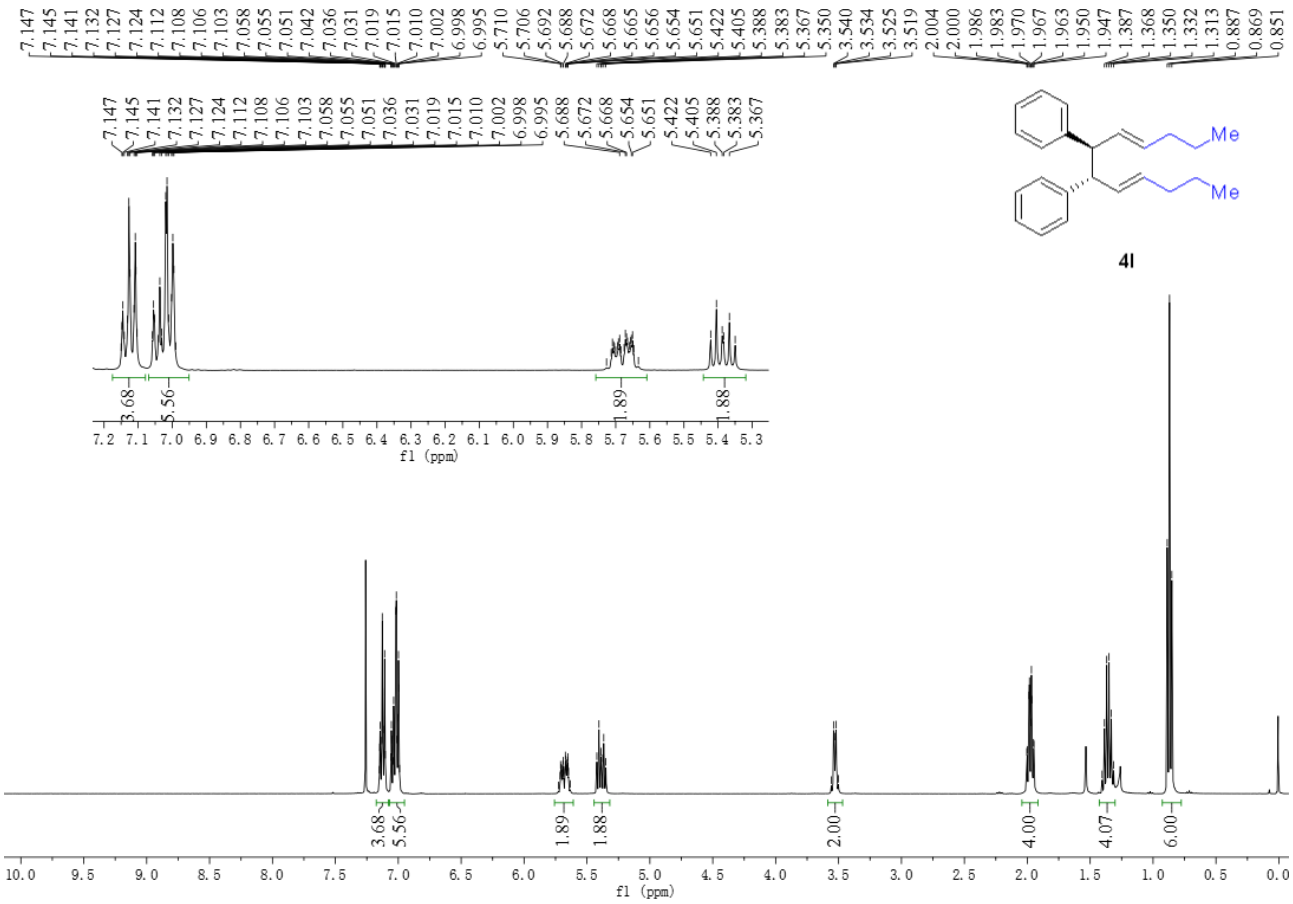

133.943
130.049
126.772
125.731
125.644
125.397
48.606
19.722
18.019
Me
Me
Me
Me
4i
f1 (ppm)

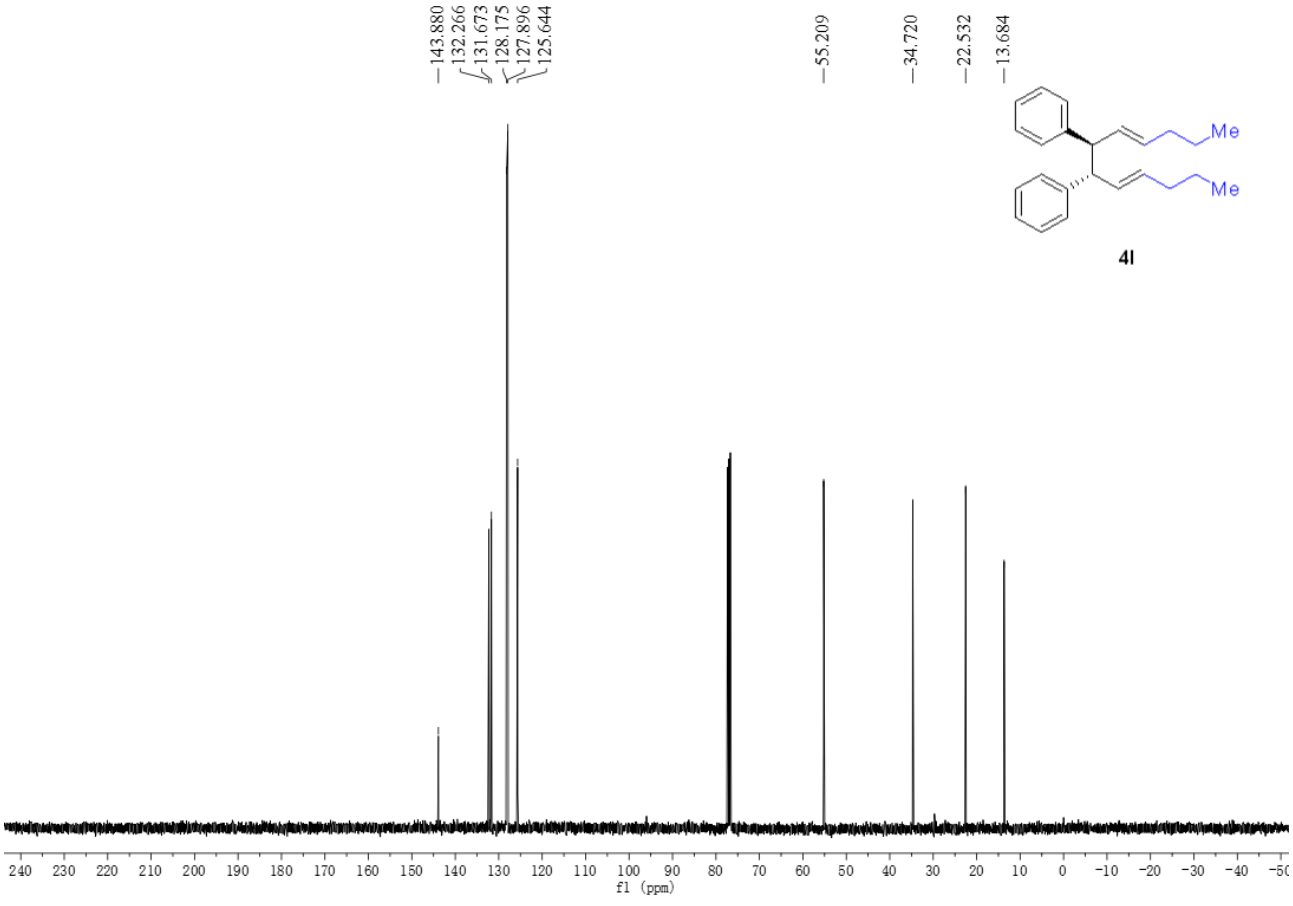

7.221
7.217
7.202
7.197
7.173
7.170
7.154
7.150
7.076
7.073
7.057
7.054
7.038
7.035
6.952
6.948
6.933
6.929
6.914
6.910
5.627
5.610
5.606
5.601
5.596
5.590
5.587
5.583
5.572
5.568
5.564
5.561
5.559
5.556
5.552
5.549
5.545
5.542
5.498
5.483
5.467
5.460
5.451
5.445
5.429
5.413
4.331
4.309
4.303
4.297
4.291
4.269
1.672
1.669
1.657
1.653
Cl
Me
Me
Cl
4j
2.05
1.67
1.85
1.78
1.94
1.86
2.00
6.00
f1 (ppm)

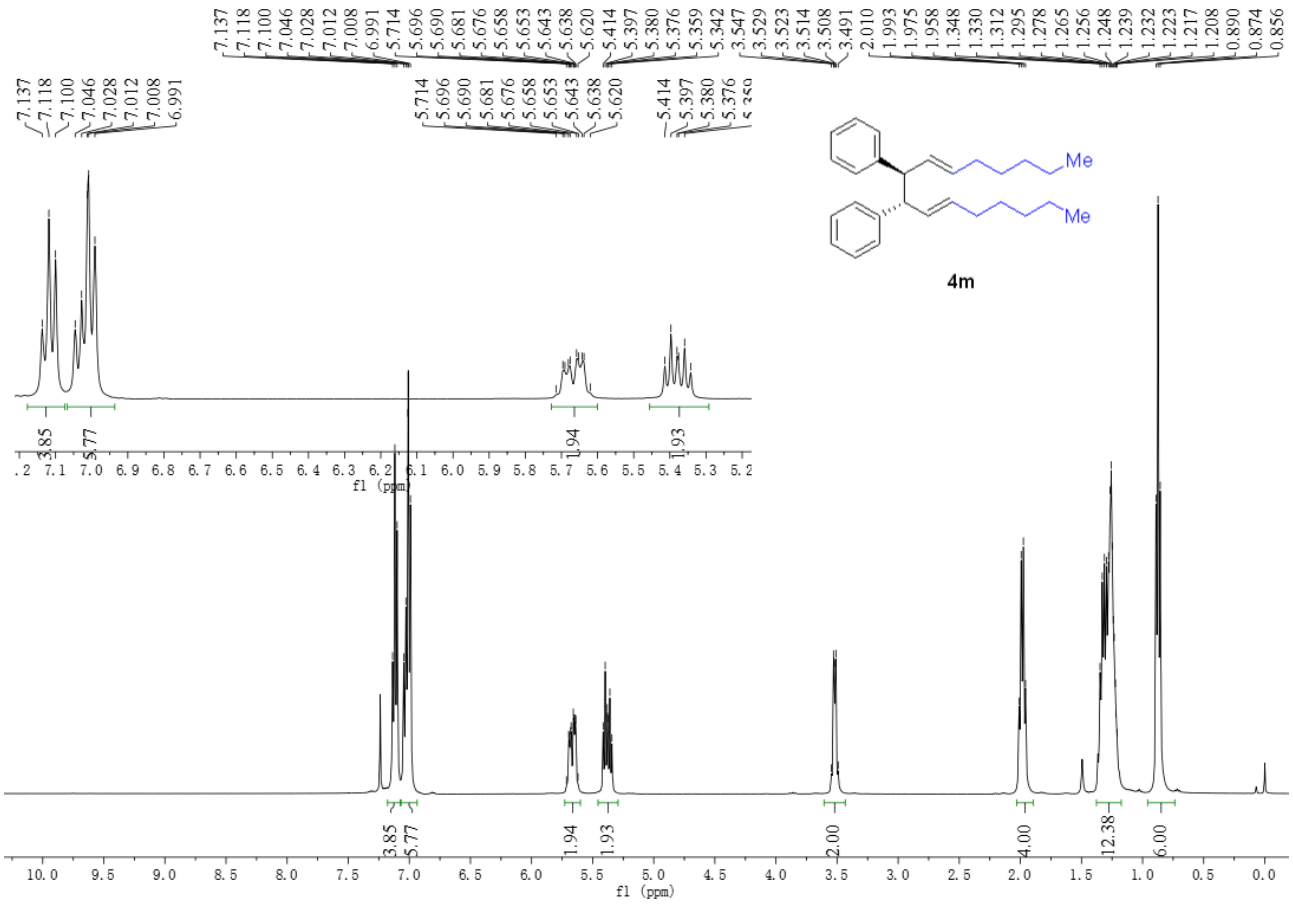

140.544
133.572
132.409
129.218
128.656
127.142
126.872
126.638
48.346
18.051
Cl
Me
Me
Cl
4j
f1 (ppm)


7.158 7.155 7.153 7.149 7.140 7.135 7.132 7.120 7.116 7.114 7.111 7.066 7.062 7.059 7.049 7.044 7.038 7.027 7.023 7.018 7.010 7.007 7.003
5.701 5.697 5.683 5.680 5.663 5.659 5.657 5.652 5.648 5.645 5.642 5.471 5.455 5.440 5.433 5.417 5.401
3.533 3.527 3.518 3.512
2.061 2.058 2.043 2.039 2.027 2.024 2.020 2.008 2.005 2.001 1.990 1.986 0.986 0.968 0.949
Me
Me
4k
3.68 5.60 1.90 1.85
f1 (ppm)
3.68 5.60 1.90 1.85 2.00 4.00 5.93
f1 (ppm)


143.798
133.392
131.140
128.193
127.914
125.676
55.182
25.650
13.835
Me
Me
4k
f1 (ppm)


7.147 7.145 7.141 7.132 7.127 7.124 7.112 7.108 7.106 7.103 7.058 7.055 7.051 7.042 7.036 7.031 7.019 7.015 7.010 7.002 6.998 6.995 5.710 5.706 5.692 5.688 5.672 5.668 5.665 5.656 5.654 5.651 5.422 5.405 5.388 5.383 5.367 5.350 3.540 3.534 3.525 3.519 2.004 2.000 1.986 1.983 1.970 1.967 1.963 1.950 1.947 1.387 1.368 1.350 1.332 1.313 0.887 0.869 0.851
Me
Me
4l
3.68 5.56 1.89 1.88
f1 (ppm)
3.68 5.56 1.89 1.88 2.00 4.00 4.07 6.00
f1 (ppm)


143.880 132.266 131.673 128.175 127.896 125.644 55.209 34.720 22.532 13.684
Me
Me
4l
f1 (ppm)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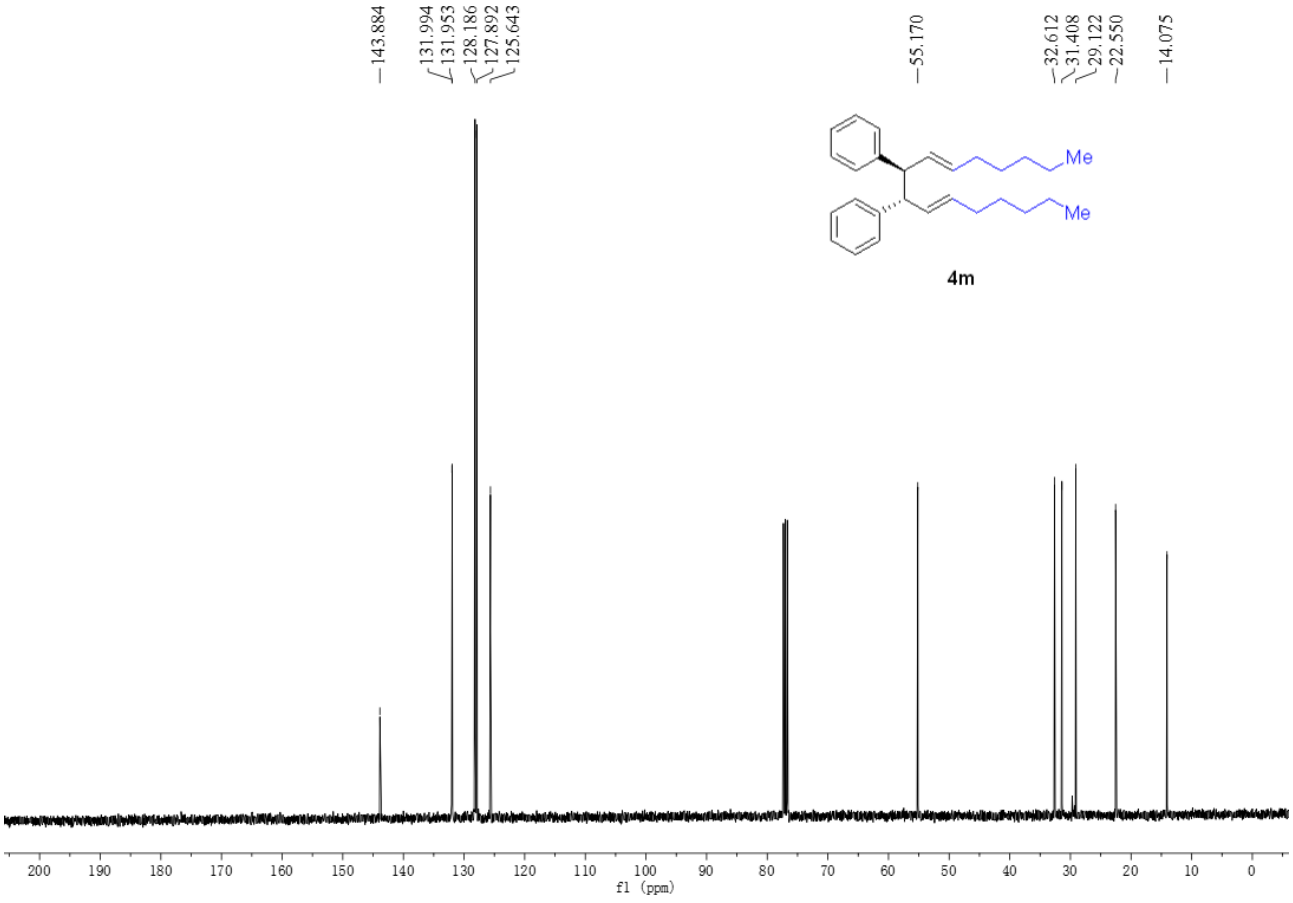
7.046
7.028
7.012
7.008
6.991
5.714
5.696
5.690
5.681
5.676
5.658
5.653
5.643
5.638
5.620
5.414
5.397
5.380
5.376
5.359
5.342
3.547
3.529
3.523
3.514
3.508
3.491
2.010
1.993
1.975
1.958
1.348
1.330
1.312
1.295
1.278
1.265
1.256
1.248
1.239
1.232
1.223
1.217
1.208
0.890
0.874
0.856
Me
Me
4m
3.85
5.77
1.94
1.93
f1 (ppm)
2.00
4.00
12.38
6.00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131.994
131.953
128.186
127.892
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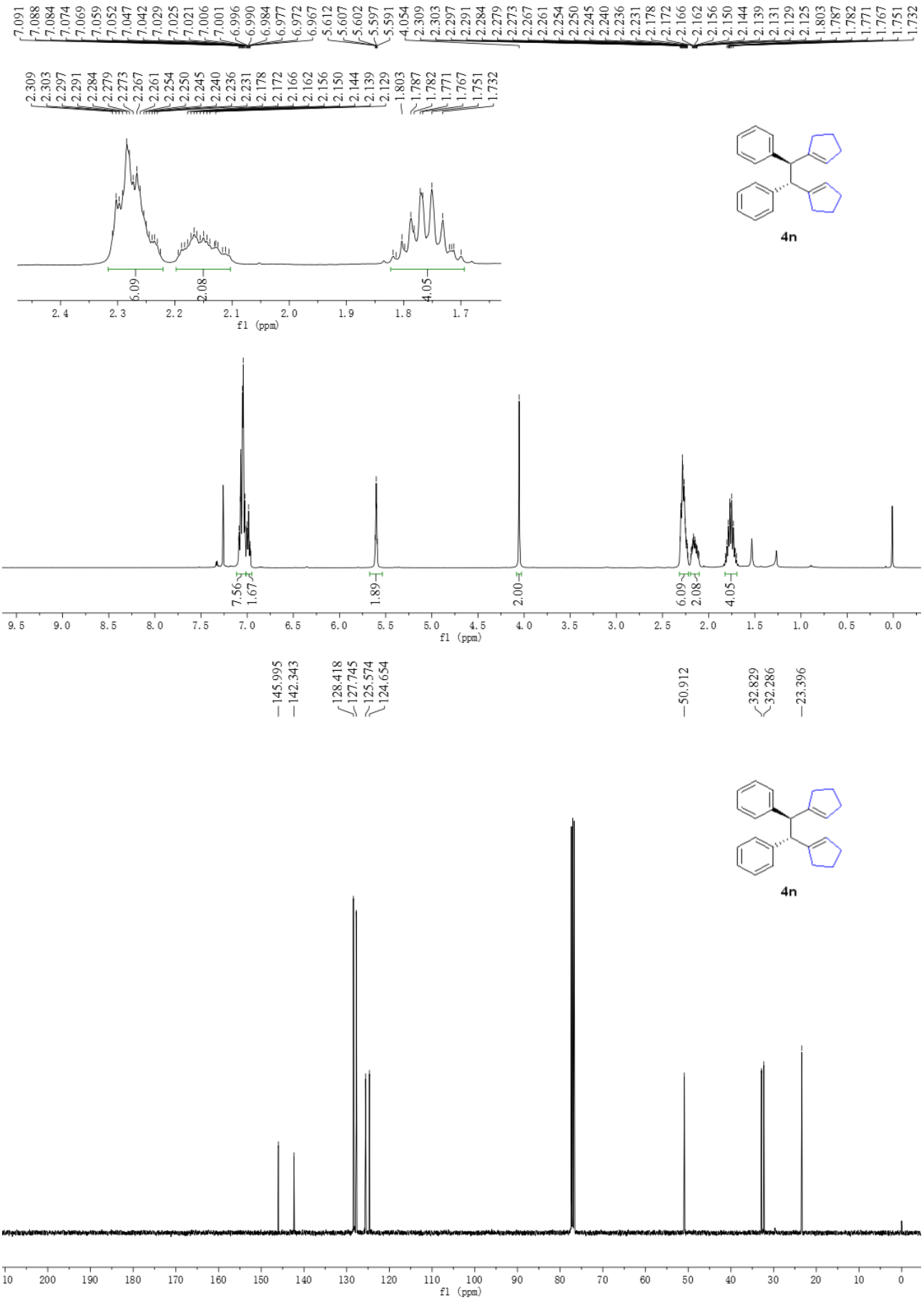
55.170
32.612
31.408
29.122
22.550
14.075
Me
Me
4m
f1 (ppm)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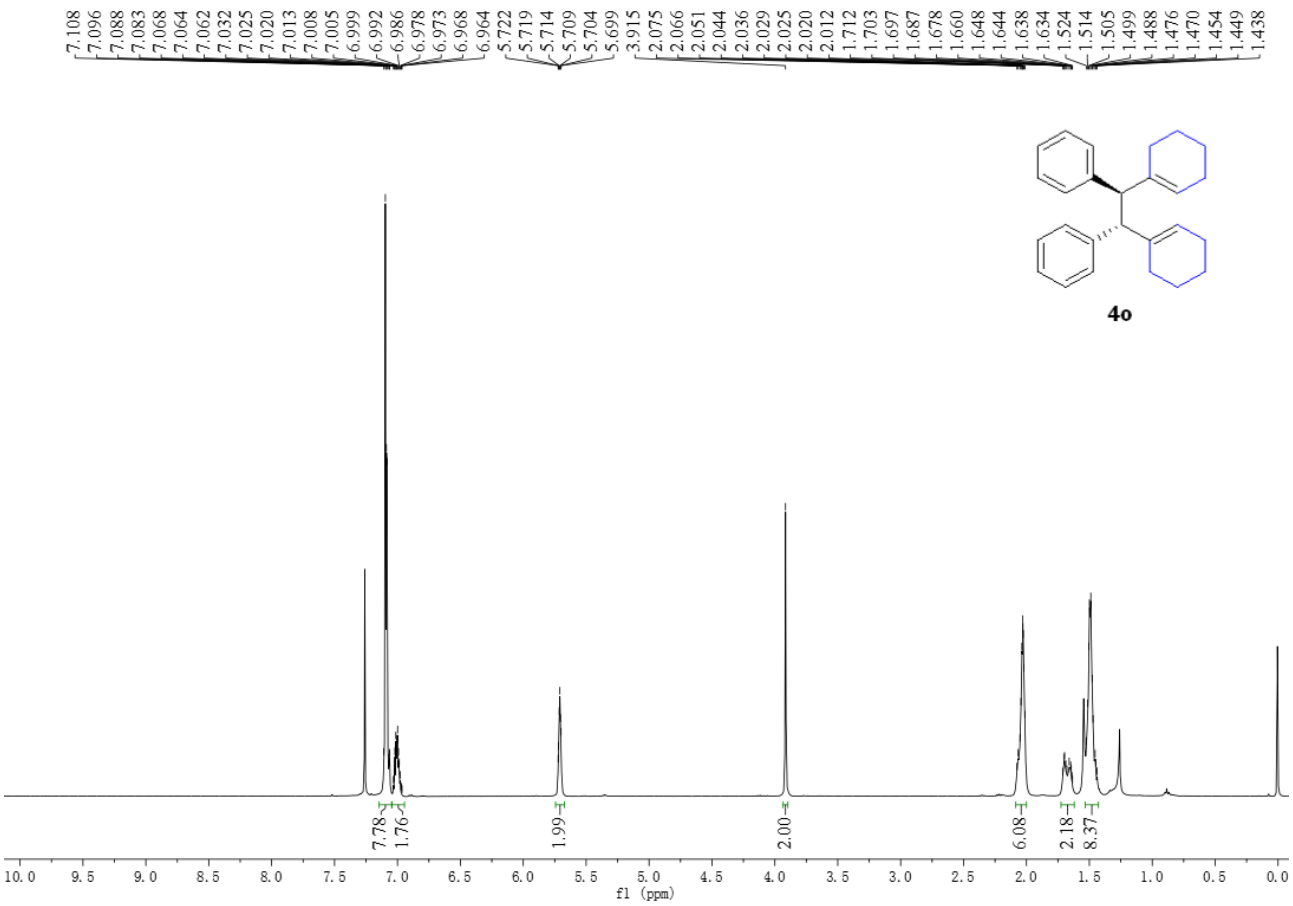
7.074
7.069
7.059
7.052
7.047
7.042
7.029
7.025
7.021
7.006
7.001
6.996
6.990
6.984
6.977
6.972
6.967
5.612
5.607
5.602
5.597
5.591
4.054
2.309
2.303
2.297
2.291
2.284
2.279
2.273
2.267
2.261
2.254
2.250
2.245
2.240
2.236
2.231
2.178
2.172
2.166
2.162
2.156
2.150
2.144
2.139
2.131
2.129
2.125
1.803
1.787
1.782
1.771
1.767
1.751
1.732
6.09
2.08
4.05
f1 (ppm)
4n
7.56
1.67
1.89
2.00
6.09
2.08
4.05
f1 (ppm)
145.995
142.343
128.418
127.745
125.574
124.654
50.912
32.829
32.286
23.396
4n
f1 (ppm)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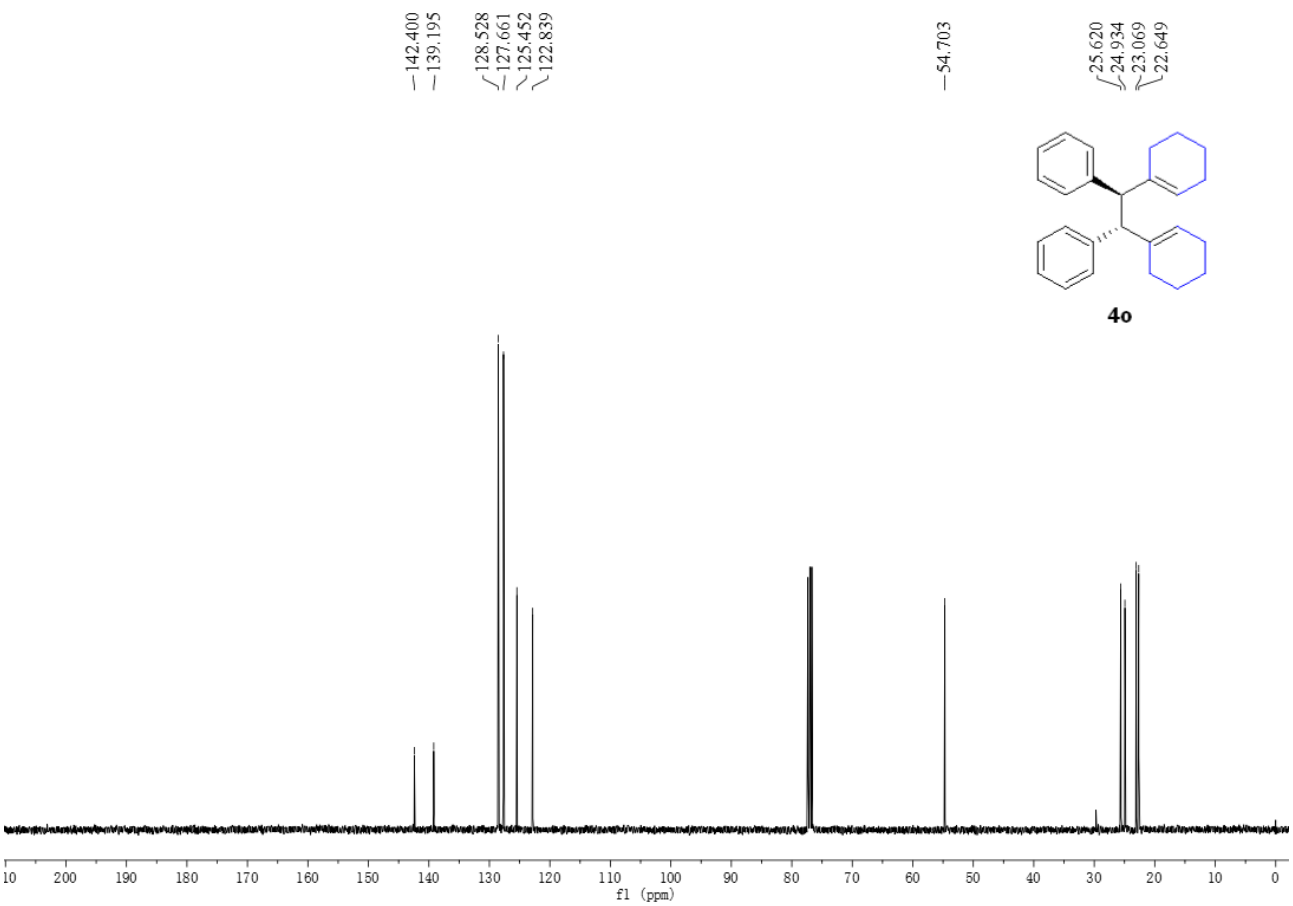
7.083
7.068
7.064
7.062
7.032
7.025
7.020
7.013
7.008
7.005
6.999
6.992
6.986
6.978
6.973
6.968
6.964
5.722
5.719
5.714
5.709
5.704
5.699
3.915
2.075
2.066
2.051
2.044
2.036
2.029
2.025
2.020
2.012
1.712
1.703
1.697
1.687
1.678
1.660
1.648
1.644
1.638
1.634
1.524
1.514
1.505
1.499
1.488
1.476
1.470
1.454
1.449
1.438
4o
7.78
1.76
1.99
2.00
6.08
2.18
8.37
f1 (ppm)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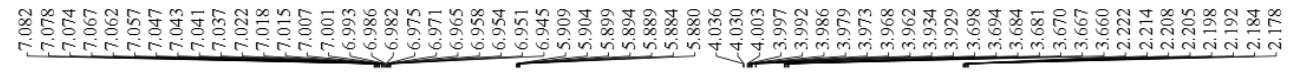
139.195
128.528
127.661
125.452
122.839
54.703
25.620
24.934
23.069
22.649
4o
f1 (ppm)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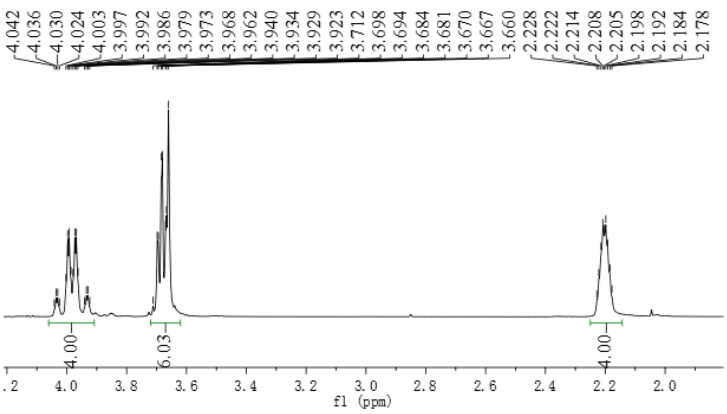
7.074
7.067
7.062
7.057
7.047
7.043
7.041
7.037
7.022
7.018
7.015
7.007
7.001
6.993
6.986
6.982
6.975
6.971
6.965
6.958
6.954
6.951
6.945
5.909
5.904
5.899
5.894
5.889
5.884
5.880
4.036
4.030
4.003
3.997
3.992
3.986
3.979
3.973
3.968
3.962
3.934
3.929
3.698
3.694
3.684
3.681
3.670
3.667
3.660
2.222
2.214
2.208
2.205
2.198
2.192
2.184
2.178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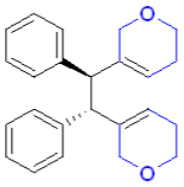
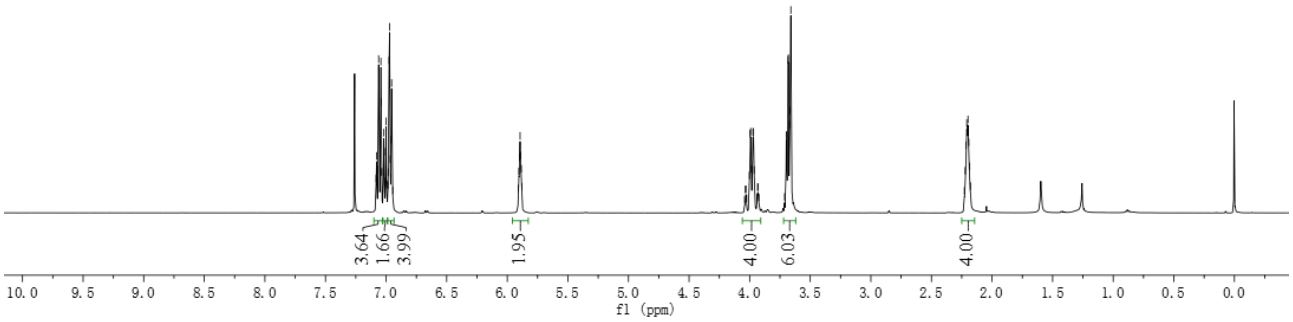
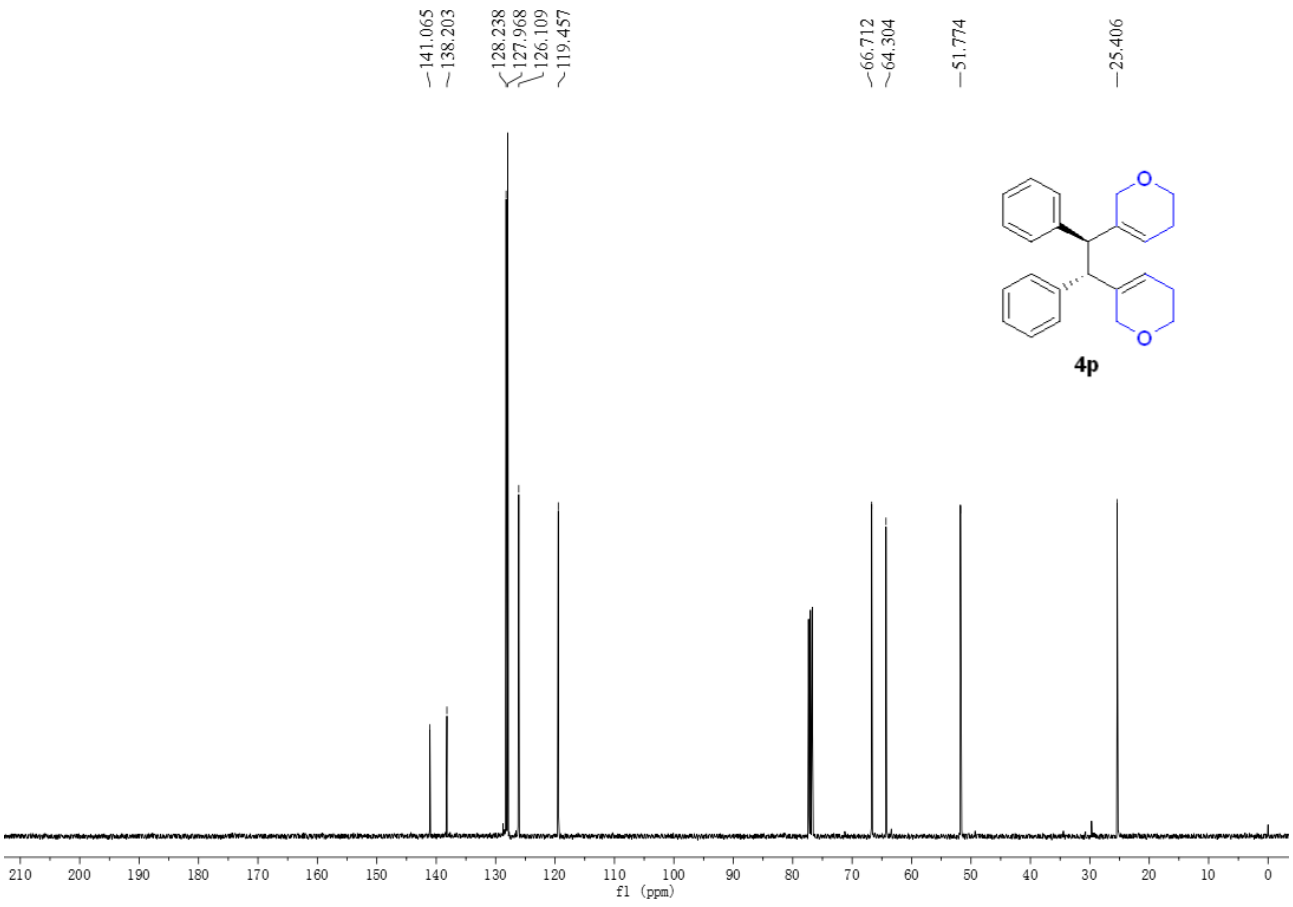
4.036
4.030
4.024
4.003
3.997
3.992
3.986
3.979
3.973
3.968
3.962
3.940
3.934
3.929
3.923
3.712
3.698
3.694
3.684
3.681
3.670
3.667
3.660
2.228
2.222
2.214
2.208
2.205
2.198
2.192
2.184
2.178
4.00
6.03
4.00
f1 (ppm)

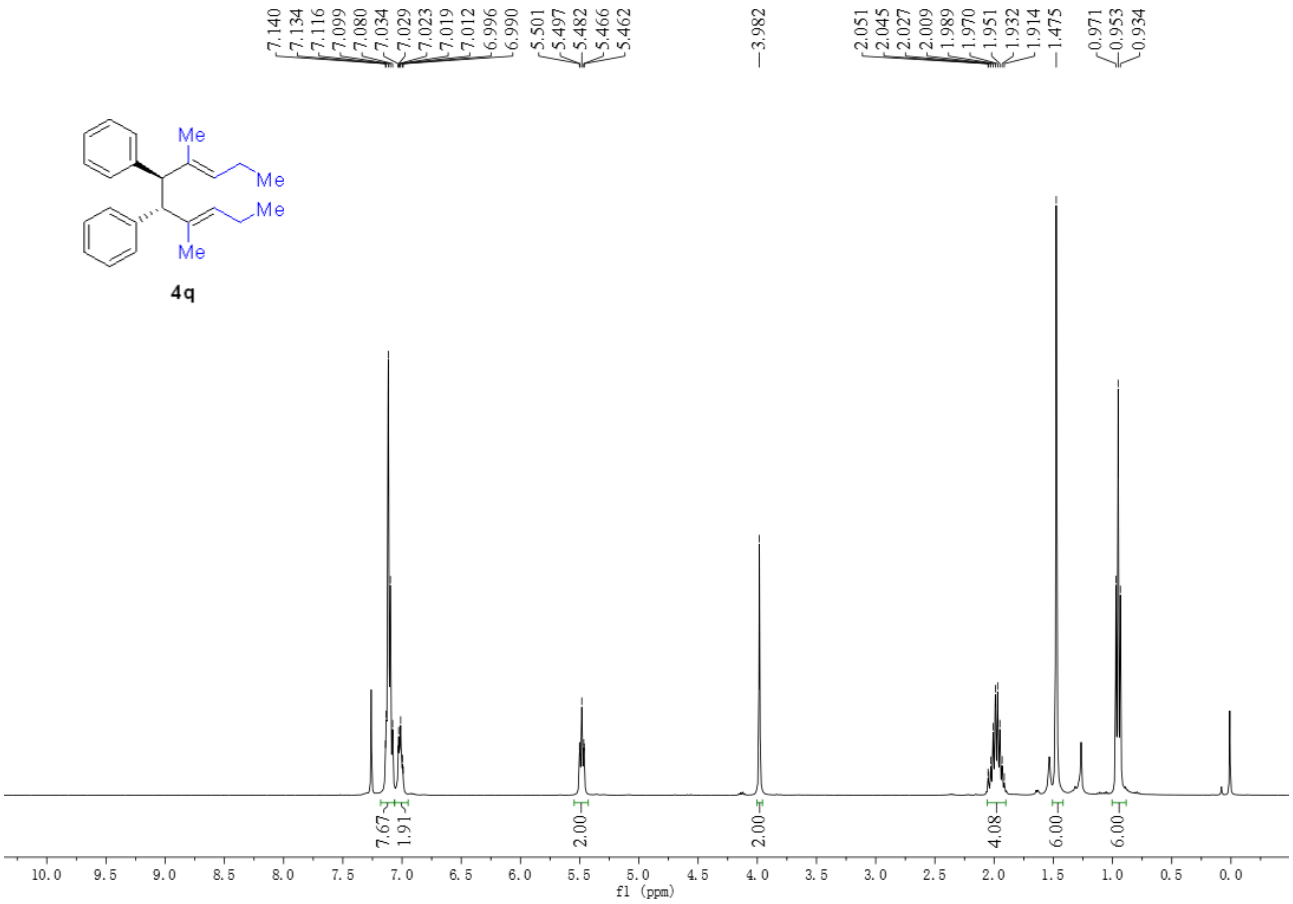


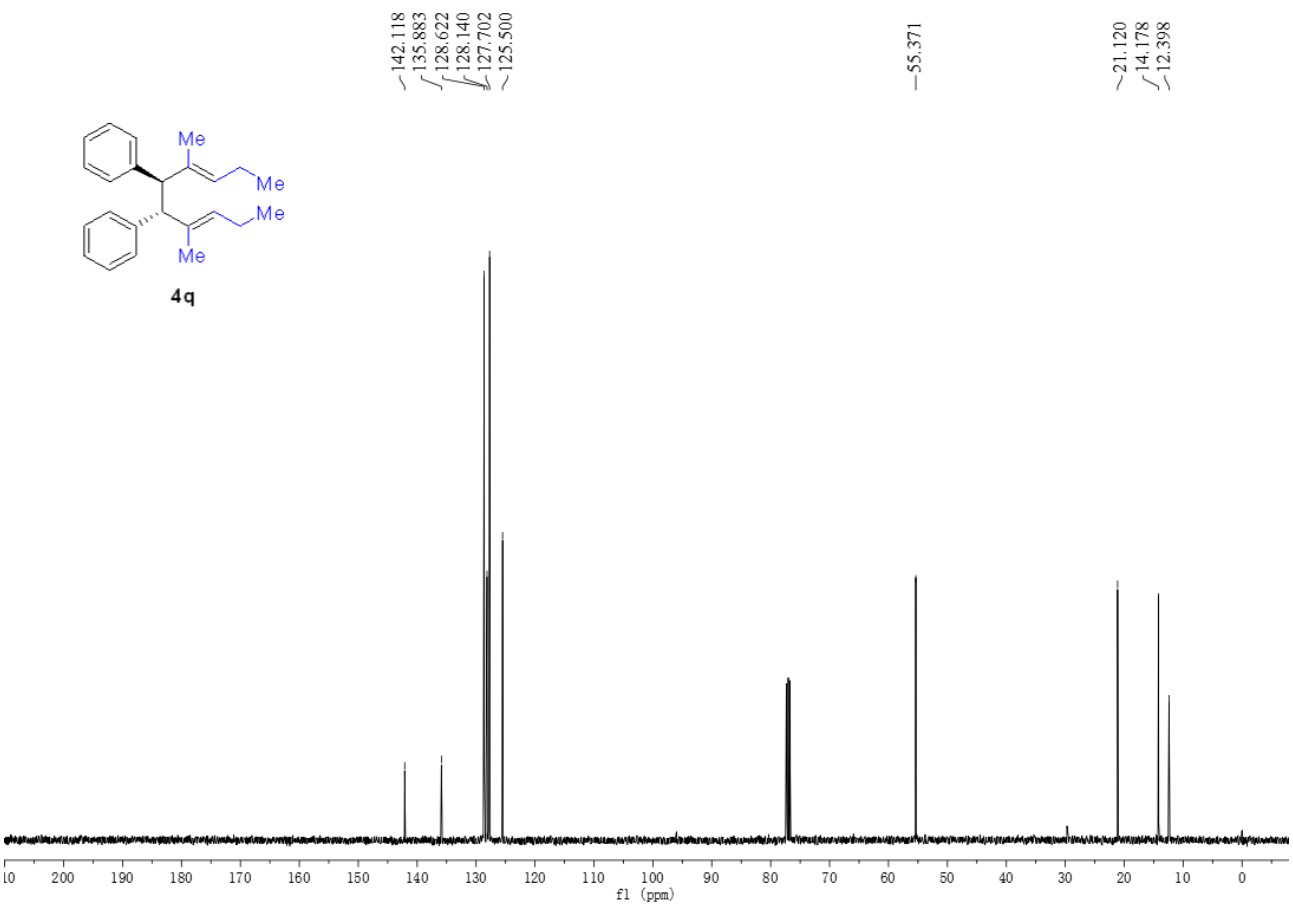
4p

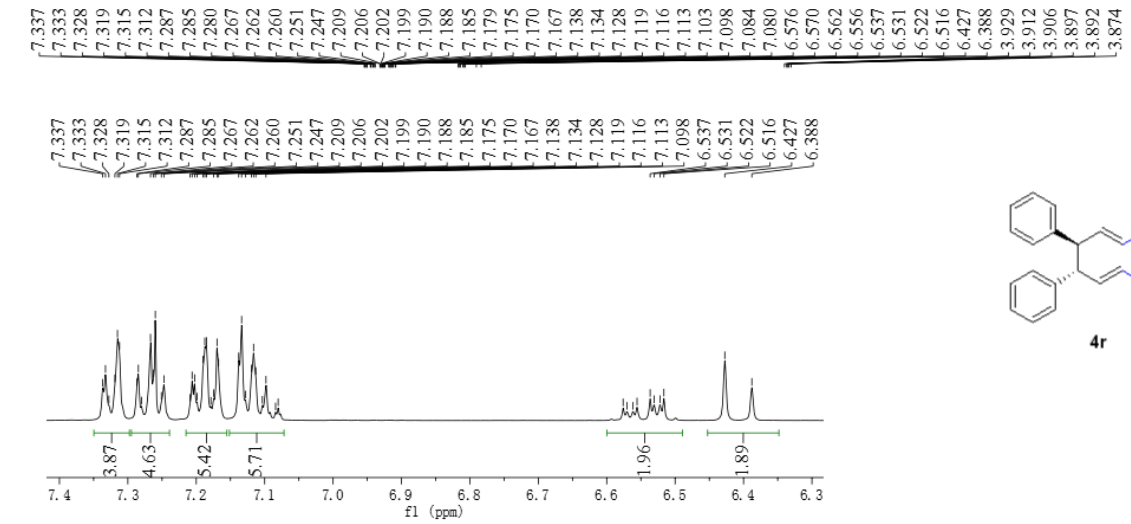

3.64
1.66
3.99
1.95
4.00
6.03
4.00
f1 (ppm)


141.065
138.203
128.238
127.968
126.109
119.457
66.712
64.304
51.774
25.406
f1 (ppm)

4p


7.140
7.134
7.116
7.099
7.080
7.034
7.029
7.023
7.019
7.012
6.996
6.990
5.501
5.497
5.482
5.466
5.462
3.982
2.051
2.045
2.027
2.009
1.989
1.970
1.951
1.932
1.914
1.475
0.971
0.953
0.934
Me
Me
Me
Me
4q
7.67
1.91
2.00
2.00
4.08
6.00
6.00
f1 (ppm)


142.118
135.883
128.622
128.140
127.702
125.500
55.371
21.120
14.178
12.398
Me
Me
Me
Me
4q
f1 (ppm)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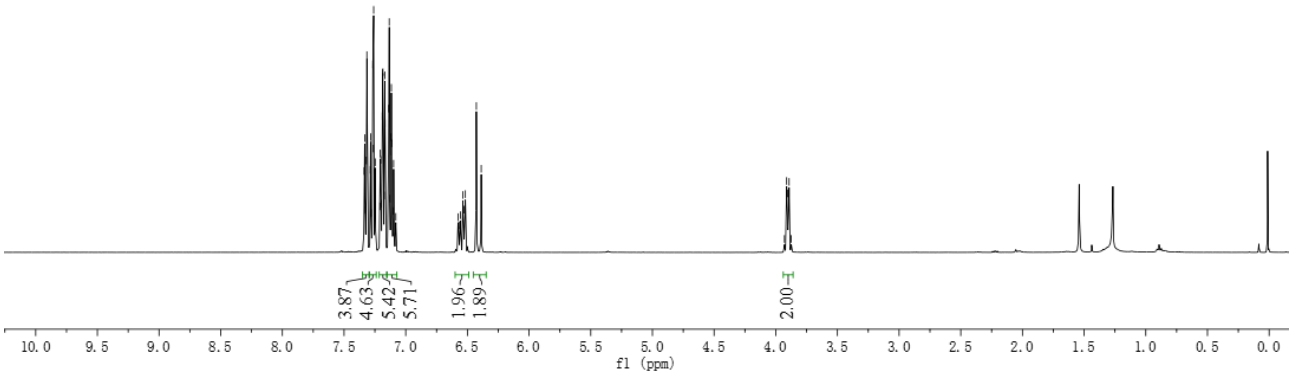
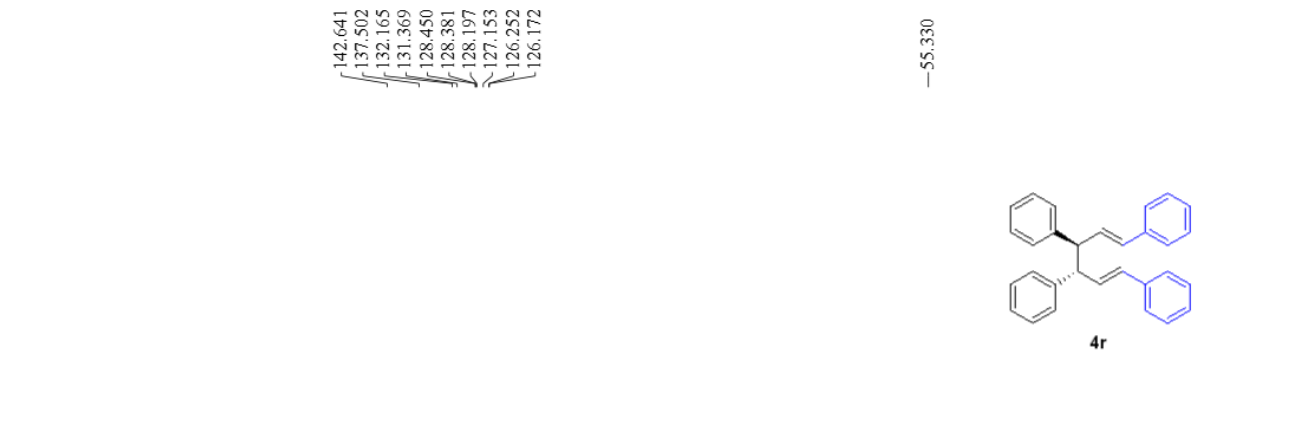
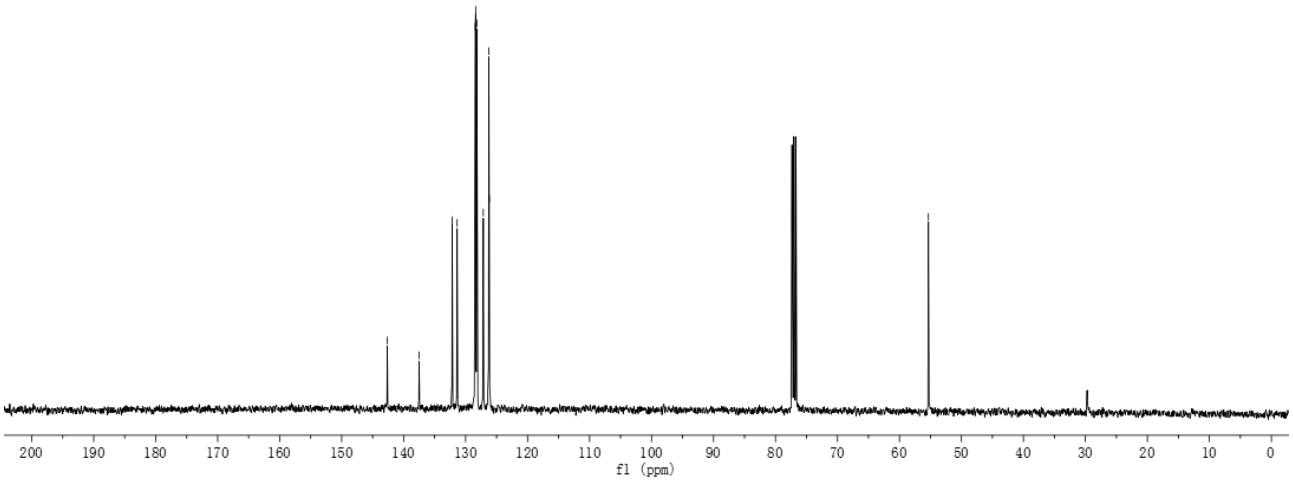
7.333
7.328
7.319
7.315
7.312
7.287
7.285
7.280
7.267
7.262
7.260
7.251
7.247
7.209
7.206
7.202
7.199
7.190
7.188
7.185
7.179
7.175
7.170
7.167
7.138
7.134
7.128
7.119
7.116
7.113
7.103
7.098
7.084
7.080
6.576
6.570
6.562
6.556
6.537
6.531
6.522
6.516
6.427
6.388
3.929
3.912
3.906
3.897
3.892
3.874
3.87
4.63
5.42
5.71
1.96
1.89
f1 (ppm)

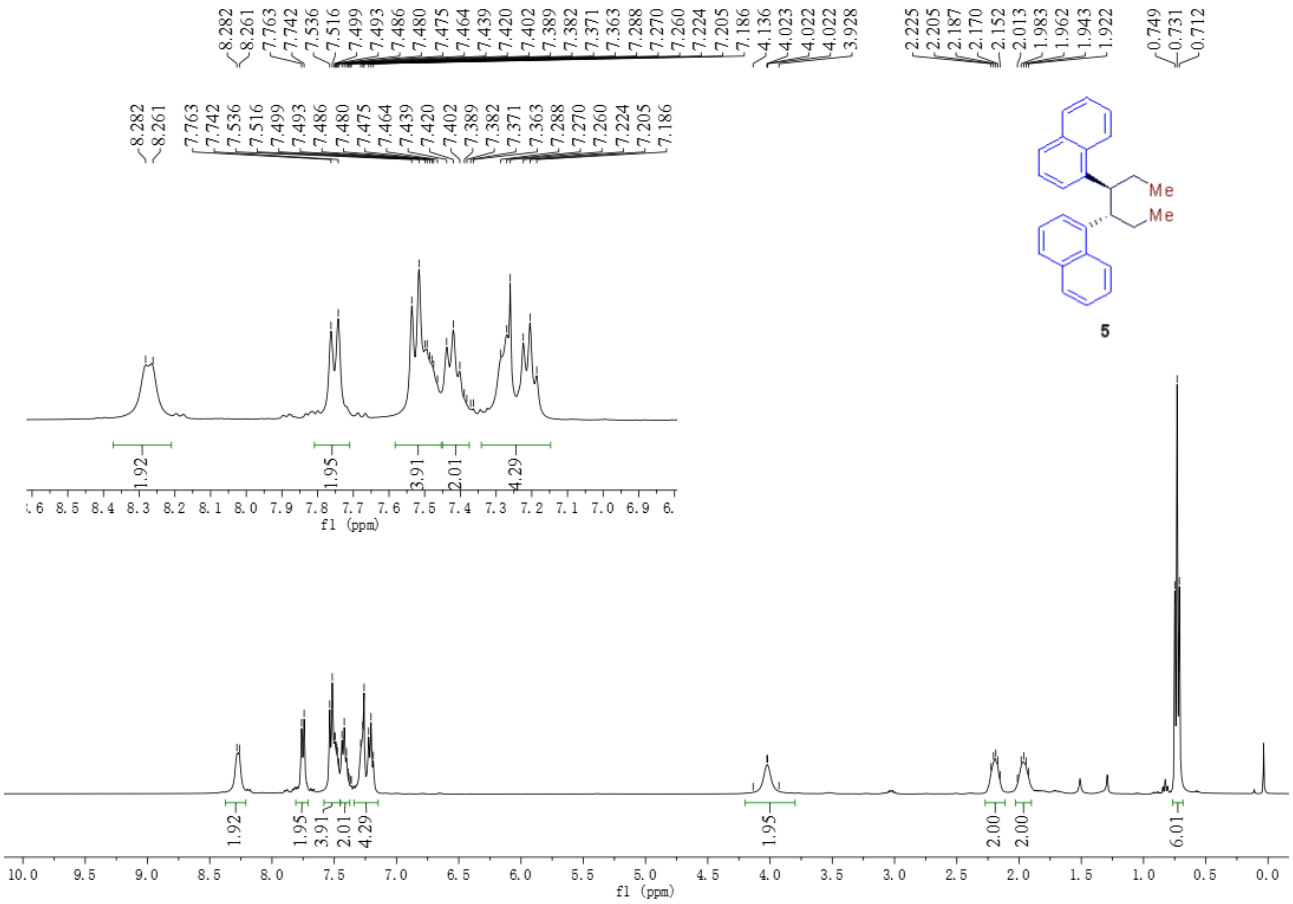

3.87
4.63
5.42
5.71
1.96
1.89
2.00
f1 (ppm)

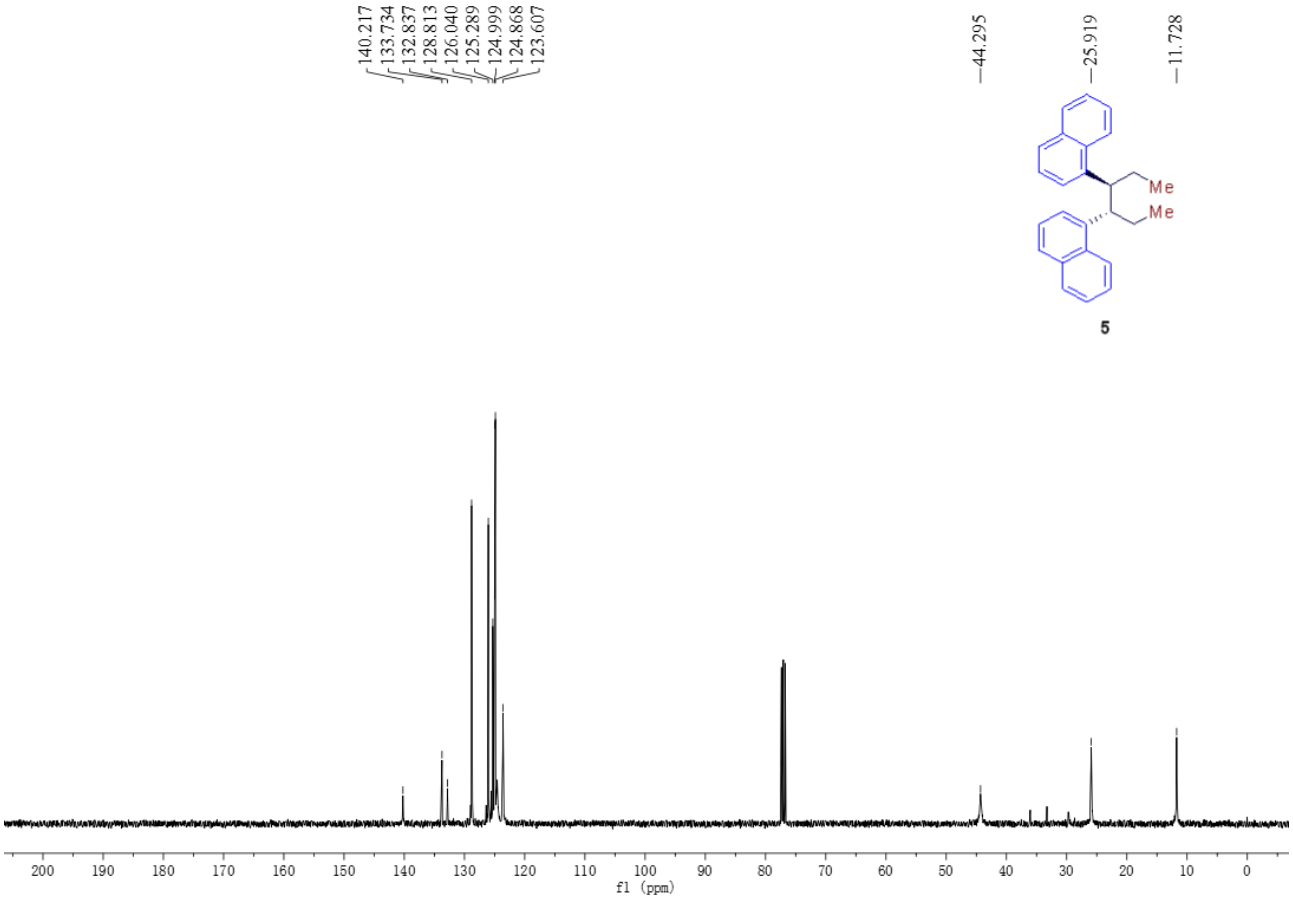
4r

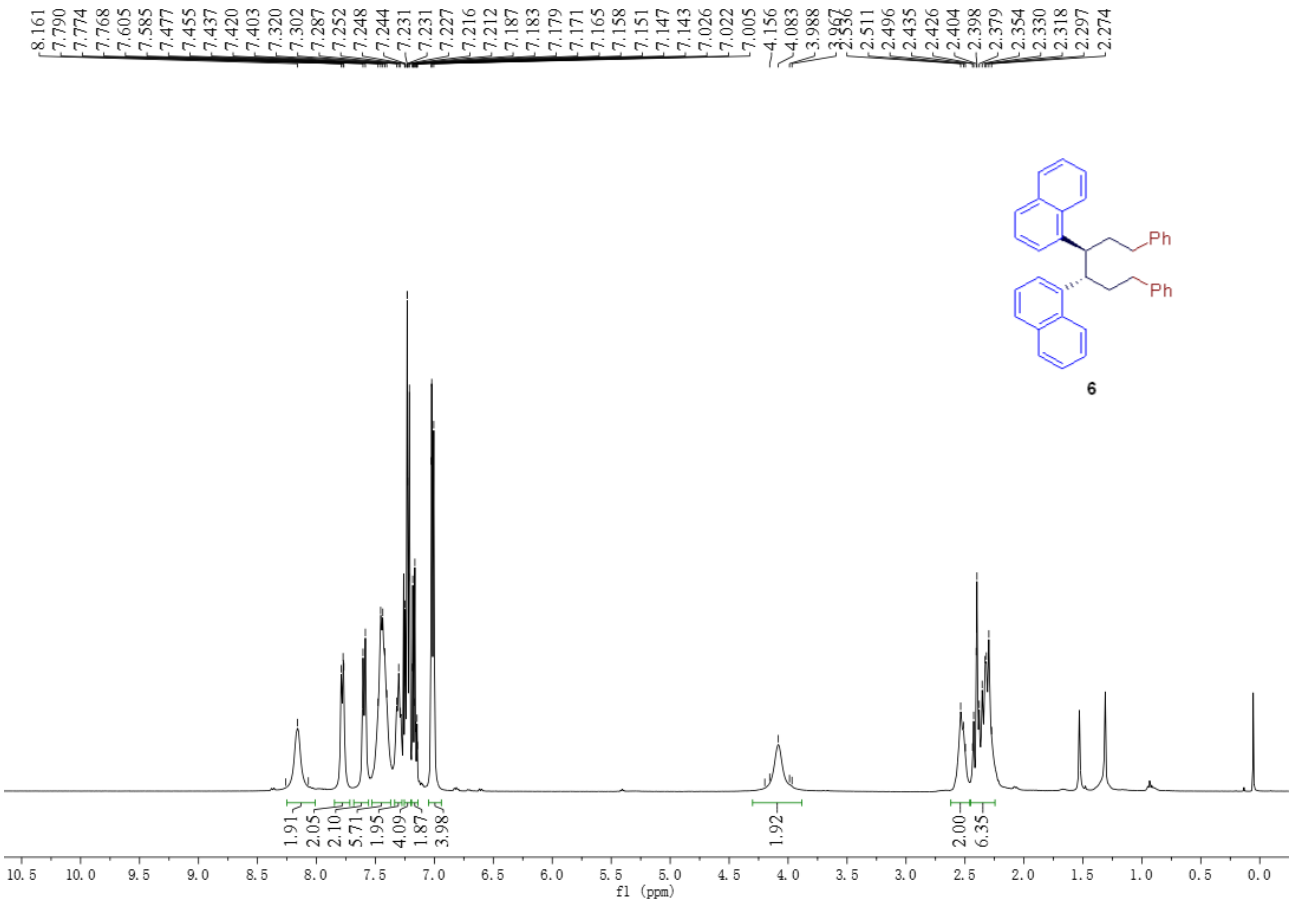

142.641
137.502
132.165
131.369
128.450
128.381
128.197
127.153
126.252
126.172
55.330
f1 (ppm)

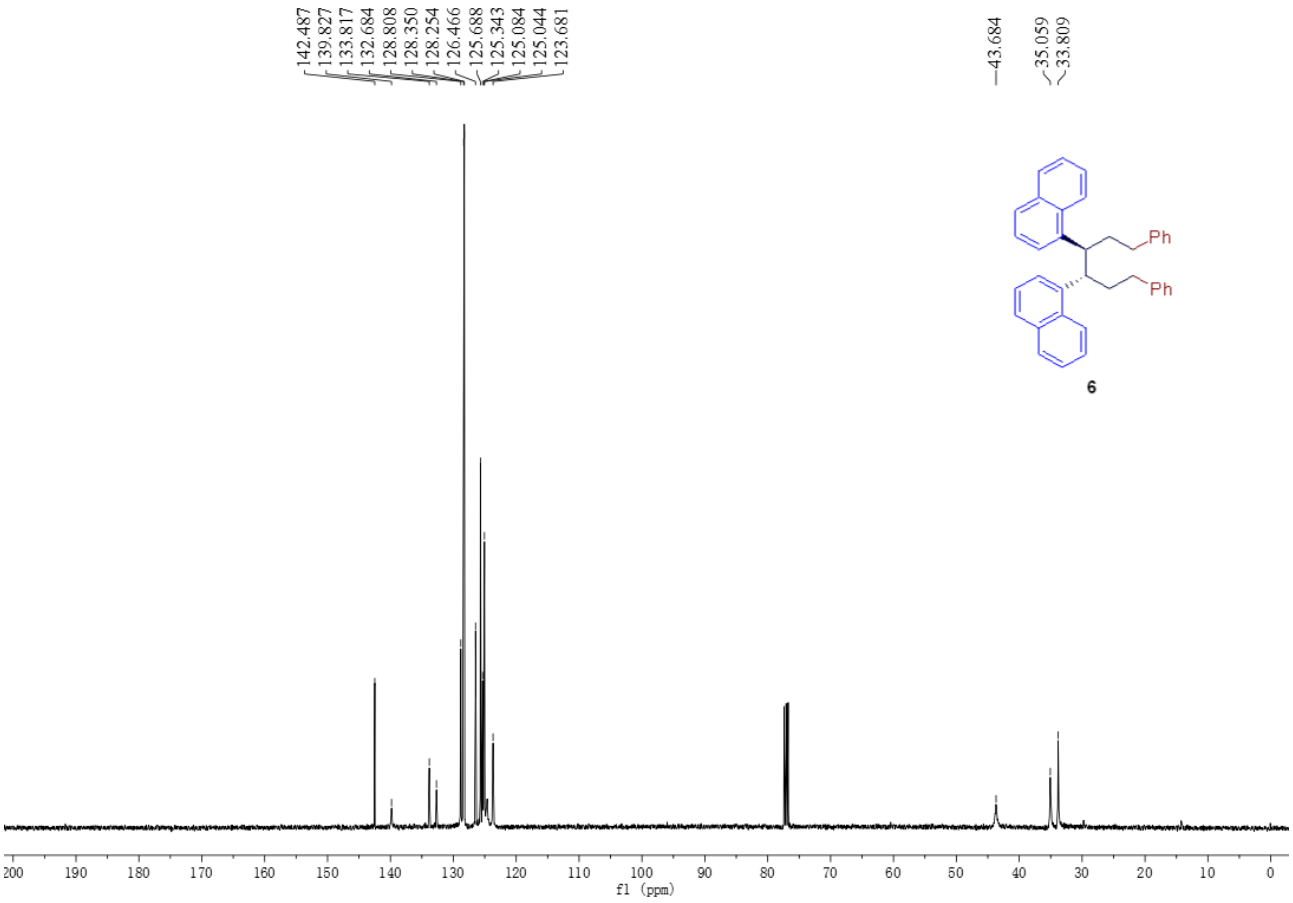
4r


f1 (ppm)


8.282
8.261
7.763
7.742
7.536
7.516
7.499
7.493
7.486
7.480
7.475
7.464
7.439
7.420
7.402
7.389
7.382
7.371
7.363
7.288
7.270
7.260
7.224
7.205
7.186
4.136
4.023
4.022
4.022
3.928
2.225
2.205
2.187
2.170
2.152
2.013
1.983
1.962
1.943
1.922
0.749
0.731
0.712
Me
Me
5
1.92
1.95
3.91
2.01
4.29
f1 (ppm)
1.92
1.95
3.91
2.01
4.29
1.95
2.00
2.00
6.01
f1 (ppm)


140.217
133.734
132.837
128.813
126.040
125.289
124.999
124.868
123.607
44.295
25.919
11.728
Me
Me
5
f1 (ppm)


8.161
7.790
7.774
7.768
7.605
7.585
7.477
7.455
7.437
7.420
7.403
7.320
7.302
7.287
7.252
7.248
7.244
7.231
7.231
7.227
7.216
7.212
7.187
7.183
7.179
7.171
7.165
7.158
7.151
7.147
7.143
7.026
7.022
7.005
4.156
4.083
3.988
3.967
3.956
2.511
2.496
2.435
2.426
2.404
2.398
2.379
2.354
2.330
2.318
2.297
2.274
Ph
Ph
6
1.91
2.05
2.10
5.71
1.95
4.09
1.87
3.98
1.92
2.00
6.35
f1 (ppm)


142.487
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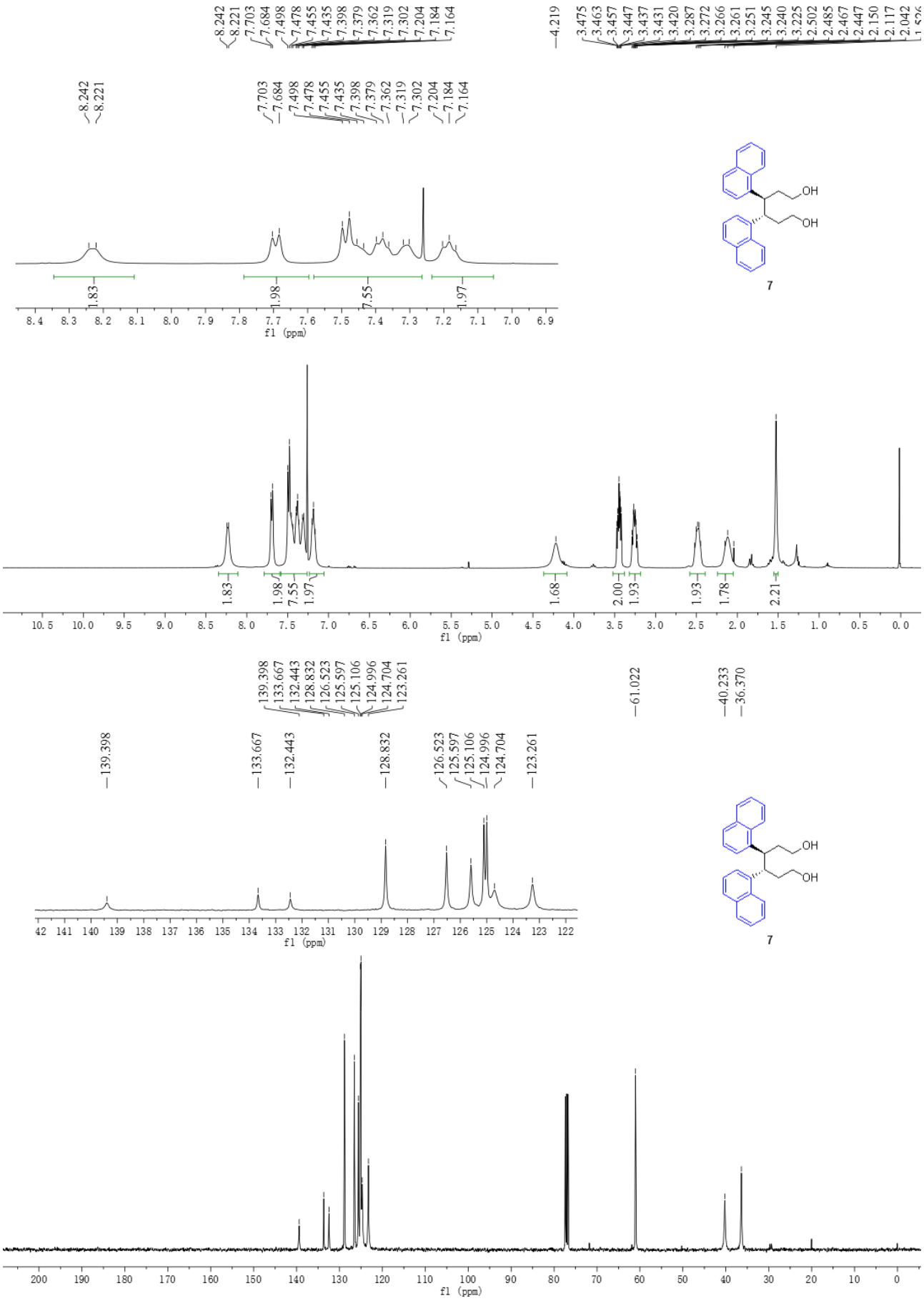
133.817
132.684
128.808
128.350
128.254
126.466
125.688
125.343
125.084
125.044
123.681
43.684
35.059
33.809
Ph
Ph
6
f1 (ppm)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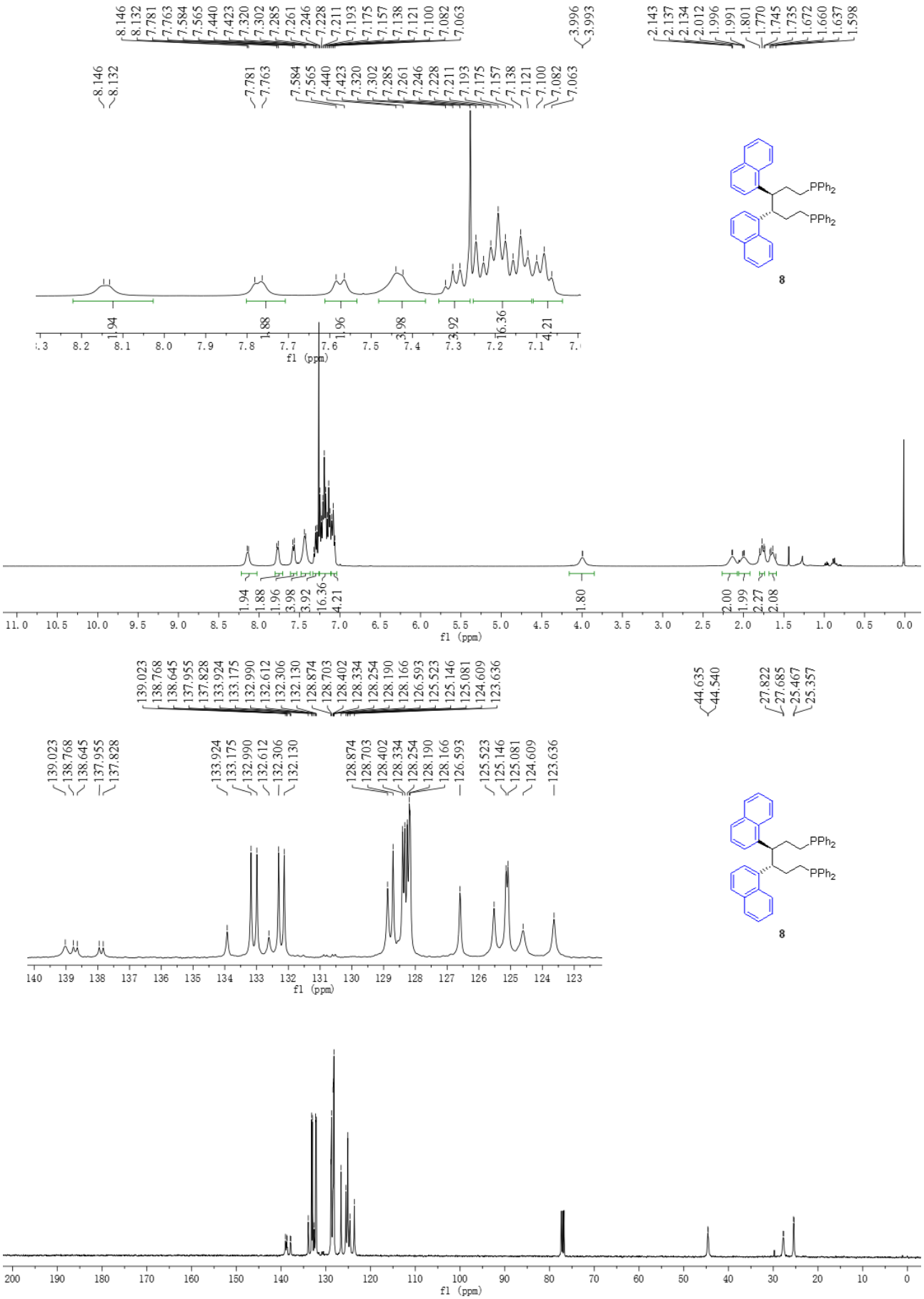
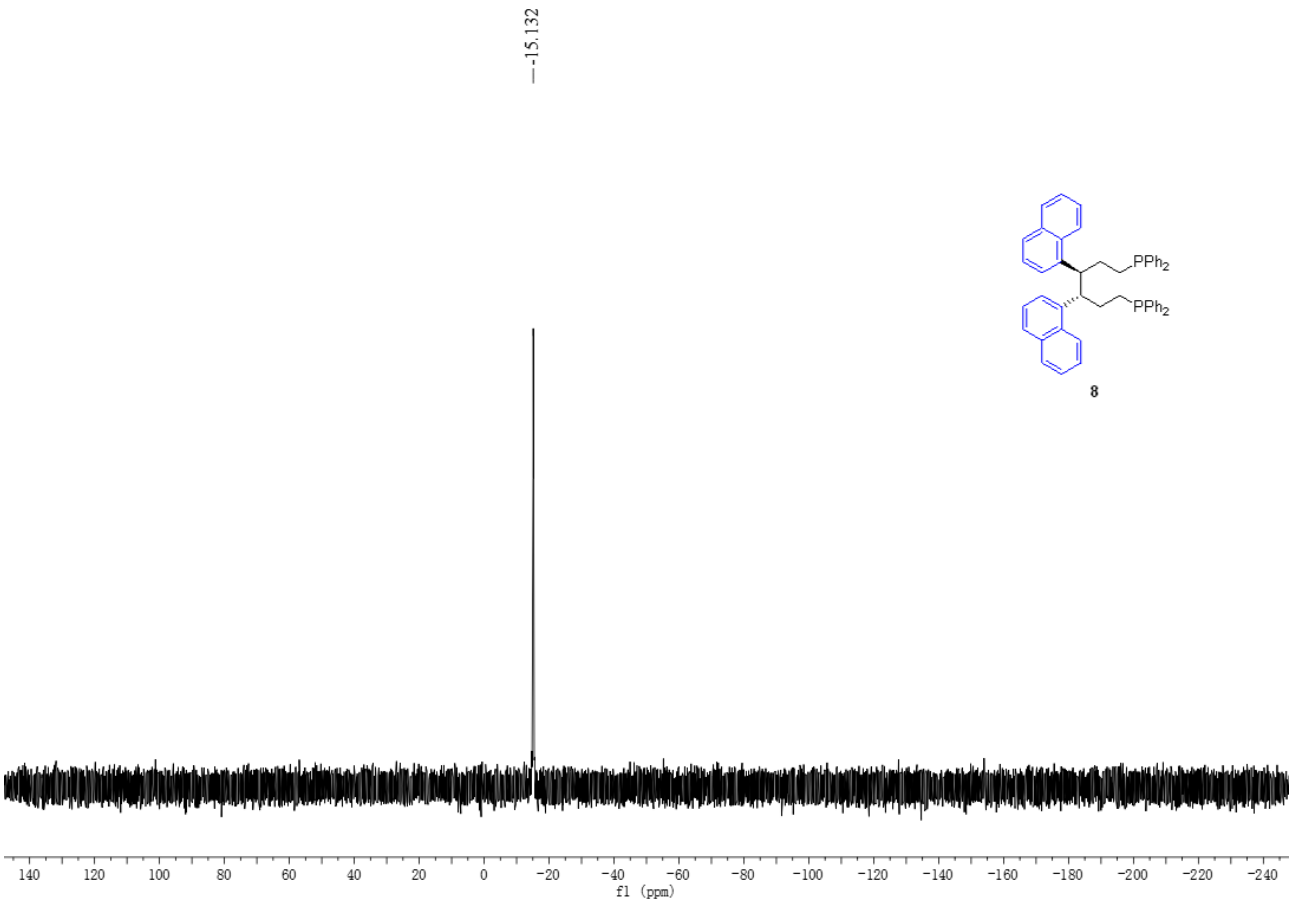
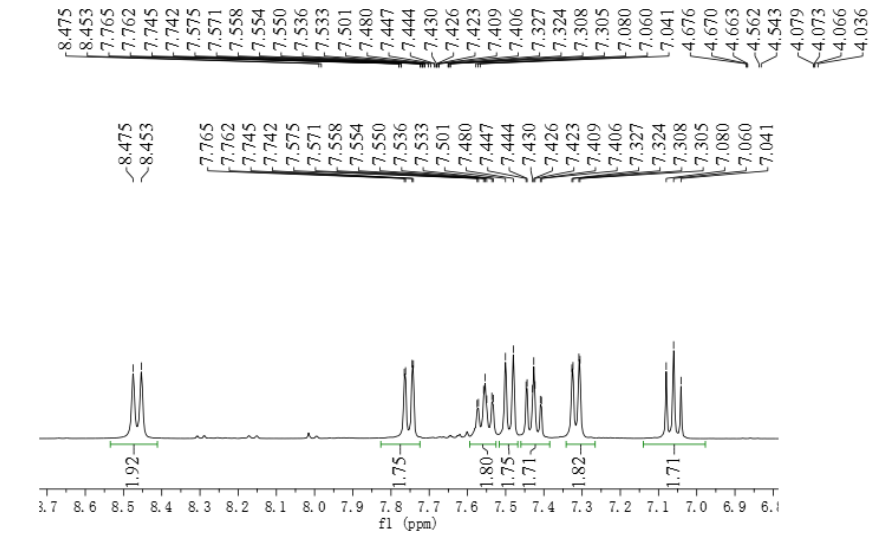
8.221
7.703
7.684
7.498
7.478
7.455
7.435
7.398
7.379
7.362
7.319
7.302
7.204
7.184
7.164
4.219
3.475
3.463
3.457
3.447
3.437
3.431
3.420
3.287
3.272
3.266
3.261
3.251
3.245
3.240
3.225
2.502
2.485
2.467
2.447
2.150
2.117
2.042
OH
OH
7
f1 (ppm)
139.398
133.667
132.443
128.832
126.523
125.597
125.106
124.996
124.704
123.261
61.022
40.233
36.370


8.146
8.132
7.781
7.763
7.584
7.565
7.440
7.423
7.320
7.302
7.285
7.261
7.246
7.228
7.211
7.193
7.175
7.157
7.138
7.121
7.100
7.082
7.063
3.996
3.993
2.143
2.137
2.134
2.012
1.996
1.991
1.801
1.770
1.745
1.735
1.672
1.660
1.637
1.598
PPh2
PPh2
8
f1 (ppm)
f1 (ppm)
139.023
138.768
138.645
137.955
137.828
133.924
133.175
132.990
132.612
132.306
132.130
128.874
128.703
128.402
128.334
128.254
128.190
128.166
126.593
125.523
125.146
125.081
124.609
123.636
44.635
44.540
27.822
27.685
25.467
25.357
PPh2
PPh2
8
f1 (ppm)
f1 (ppm)


-15.132
PPh2
PPh2
8
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)


8.475
8.453
7.765
7.762
7.745
7.742
7.575
7.571
7.558
7.554
7.550
7.536
7.533
7.501
7.480
7.447
7.444
7.430
7.426
7.423
7.409
7.406
7.327
7.324
7.308
7.305
7.080
7.060
7.041
4.676
4.670
4.663
4.562
4.543
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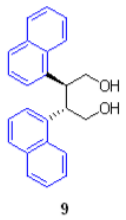
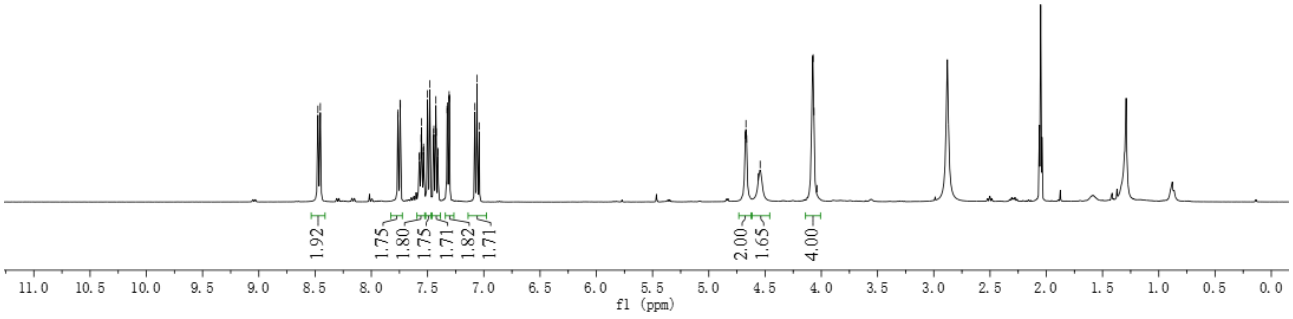
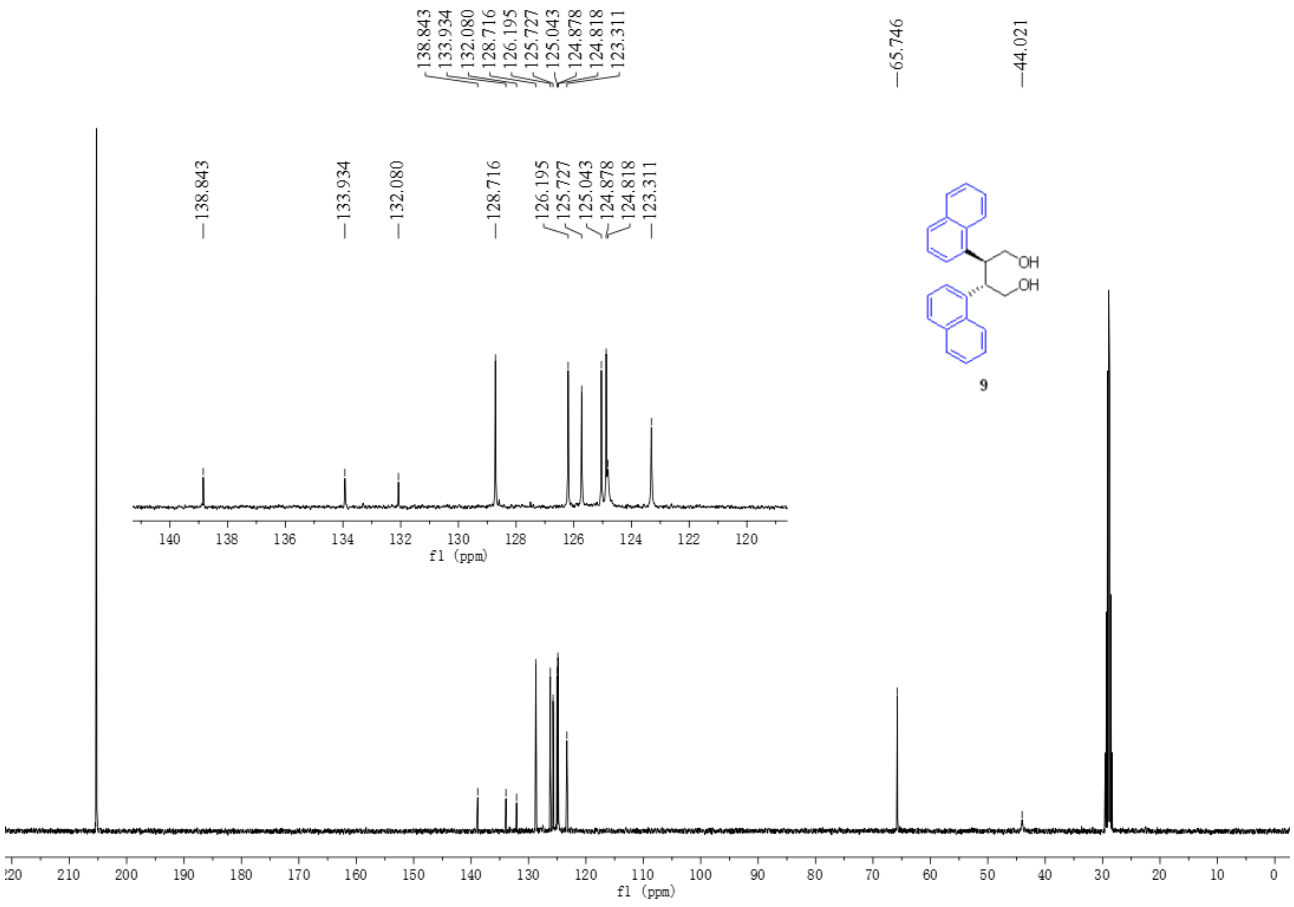
1.75
1.71
1.82
1.71
f1 (ppm)


OH
OH

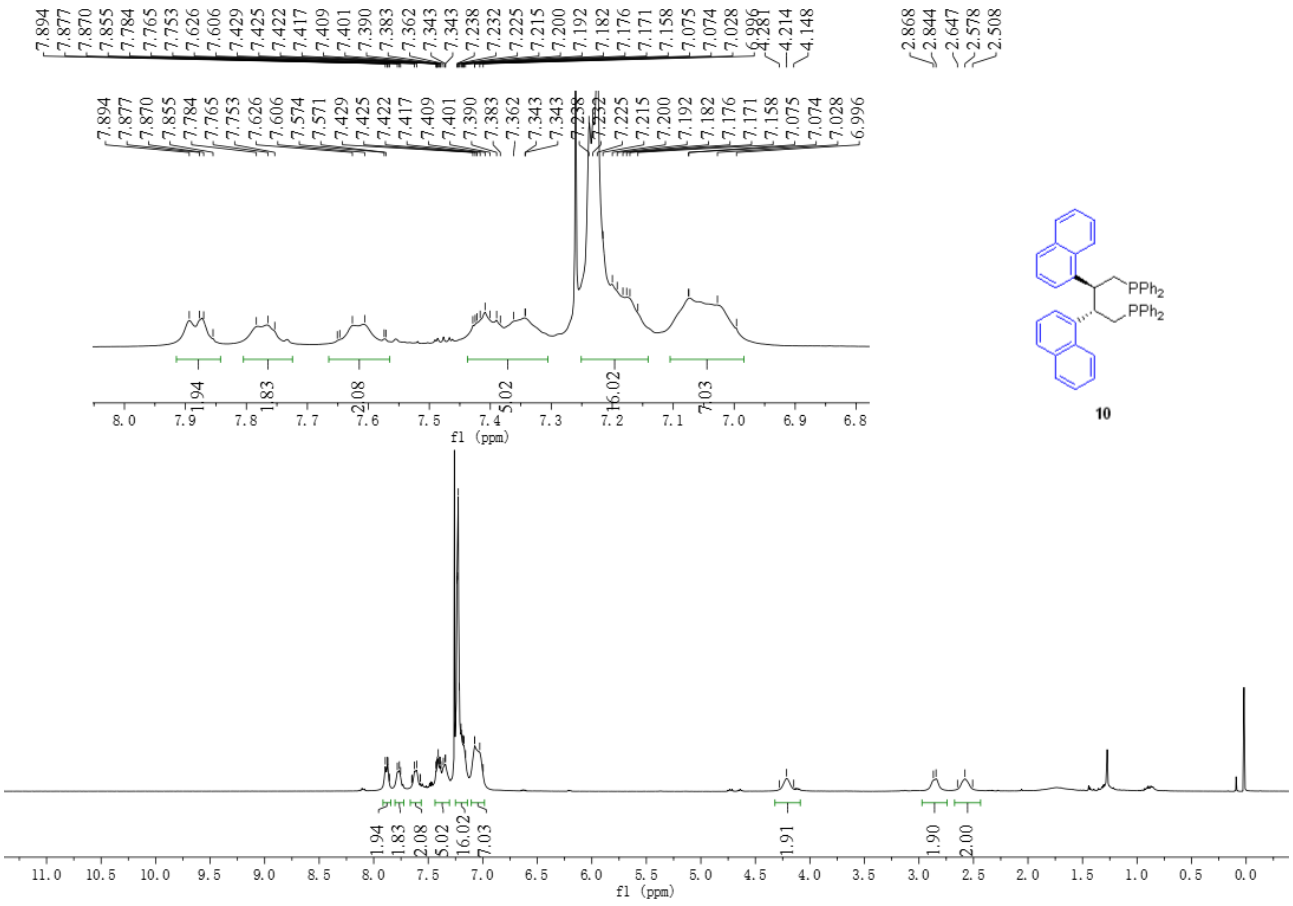
9


1.92
1.75
1.80
1.75
1.71
1.82
1.71
2.00
1.65
4.00
f1 (ppm)


138.843
133.934
132.080
128.716
126.195
125.727
125.043
124.878
124.818
123.311
65.746
44.021
f1 (ppm)

OH
OH

9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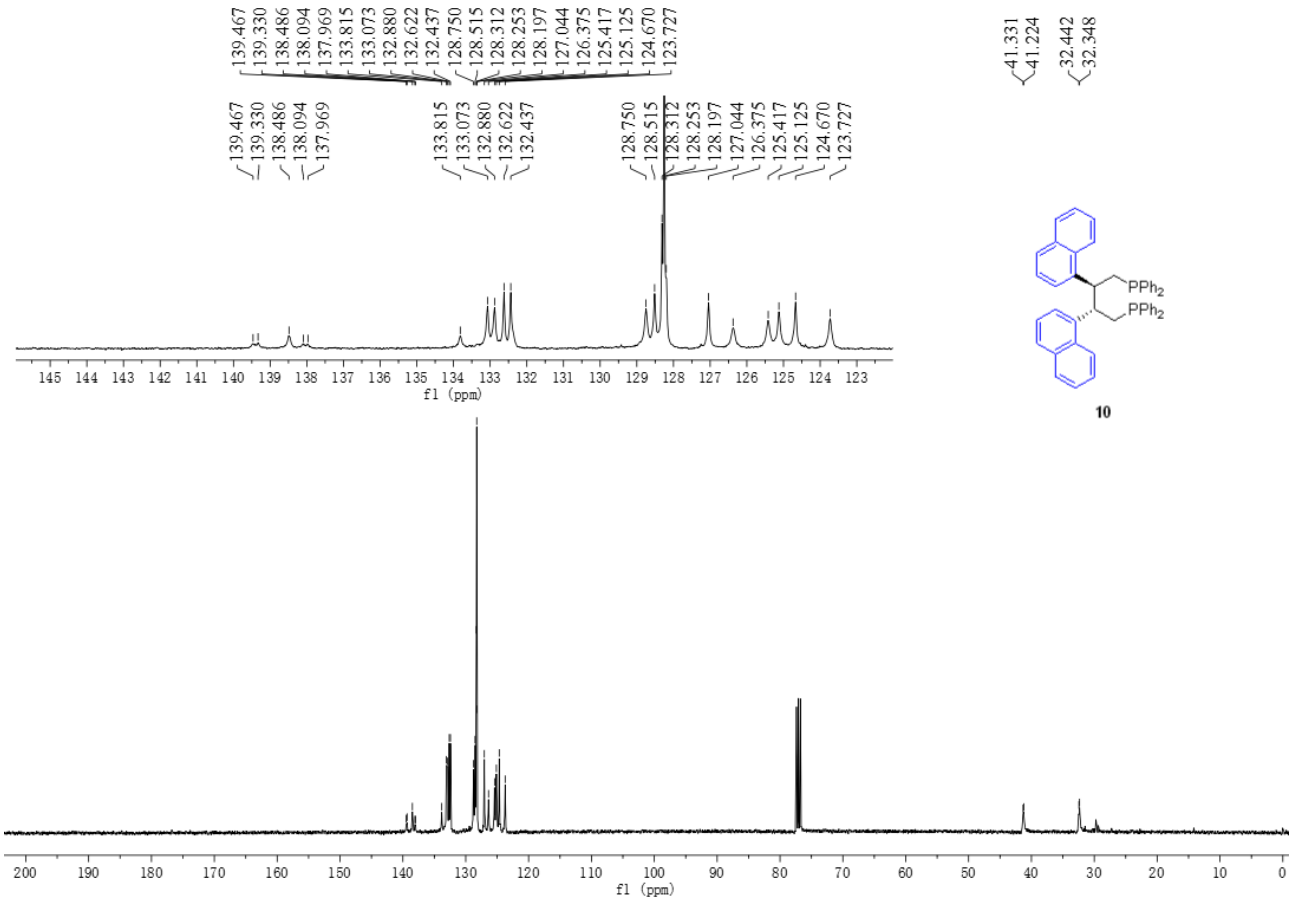
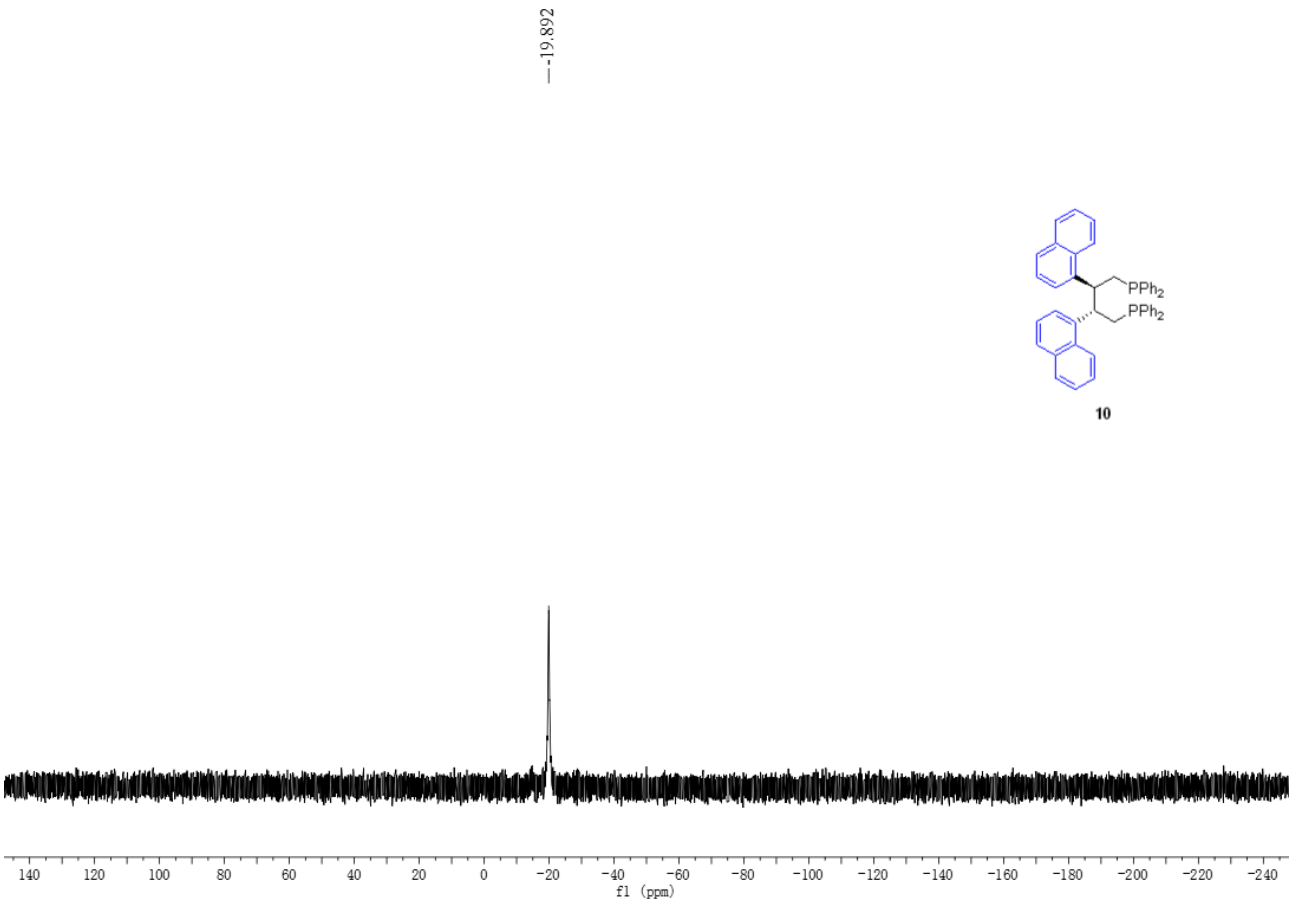
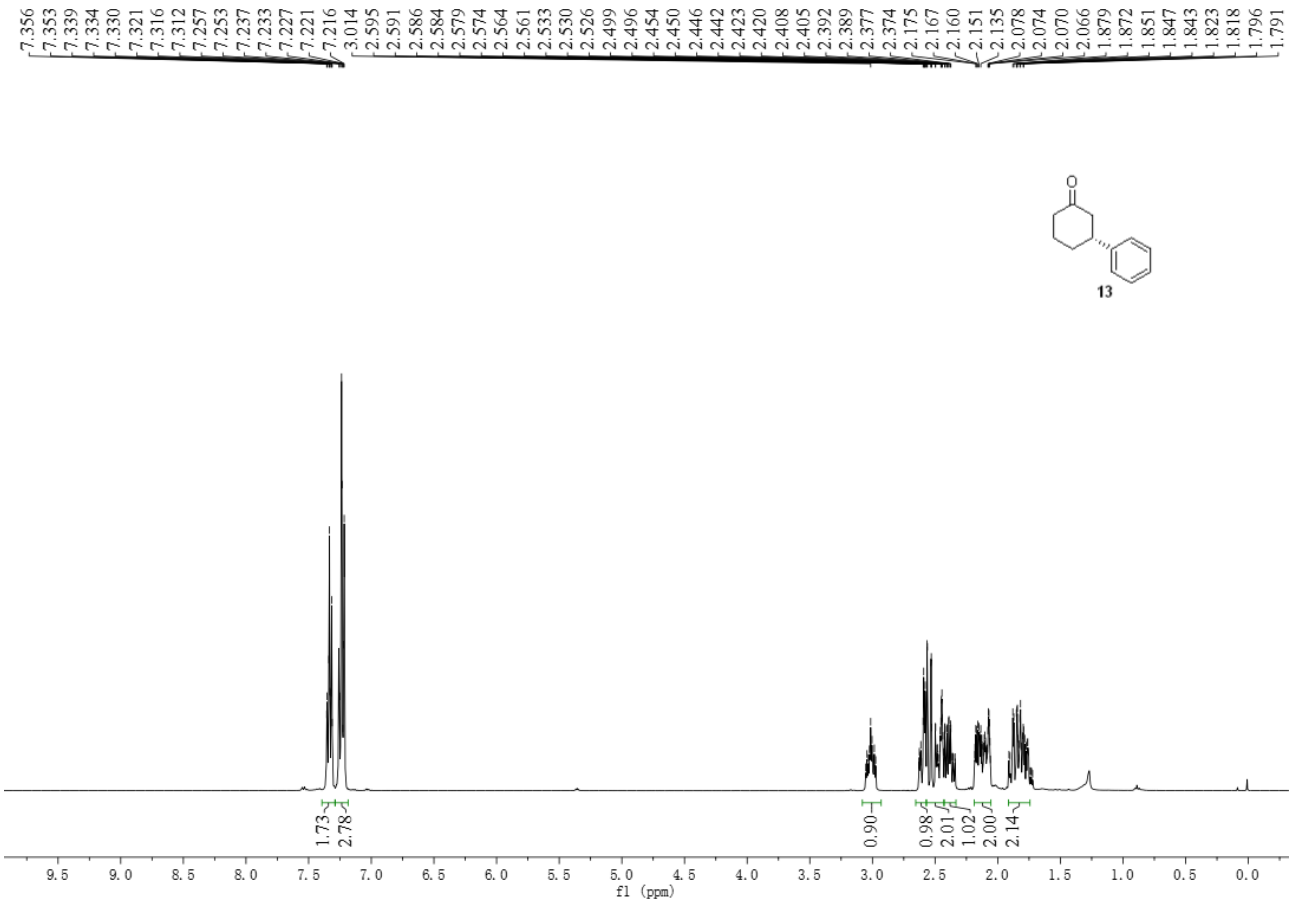
7.877
7.870
7.855
7.784
7.765
7.753
7.626
7.606
7.429
7.425
7.422
7.417
7.409
7.401
7.390
7.383
7.362
7.343
7.238
7.232
7.225
7.215
7.200
7.192
7.182
7.176
7.158
7.075
7.074
7.028
6.996
4.281
4.214
4.148
2.868
2.844
2.647
2.578
2.508
1.94
1.83
2.08
5.02
16.02
7.03
1.91
1.90
2.00
f1 (ppm)
PPh2
PPh2
10


139.467
139.330
138.486
138.094
137.969
133.815
133.073
132.880
132.622
132.437
128.750
128.515
128.312
128.253
128.197
127.044
126.375
125.417
125.125
124.670
123.727
41.331
41.224
32.442
32.348
f1 (ppm)
PPh2
PPh2
10


-19.892
PPh2
PPh2
10
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)


7.356
7.353
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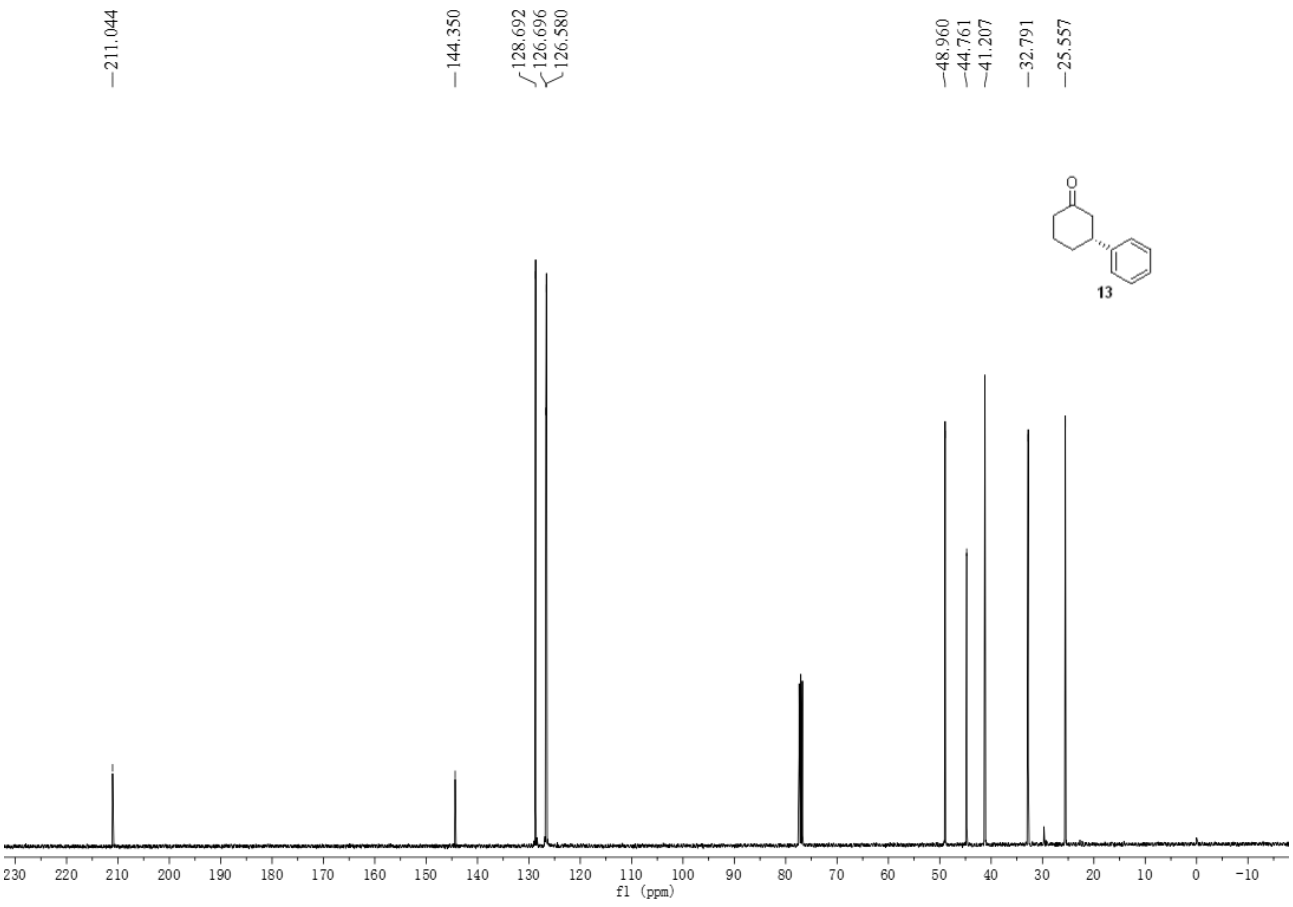
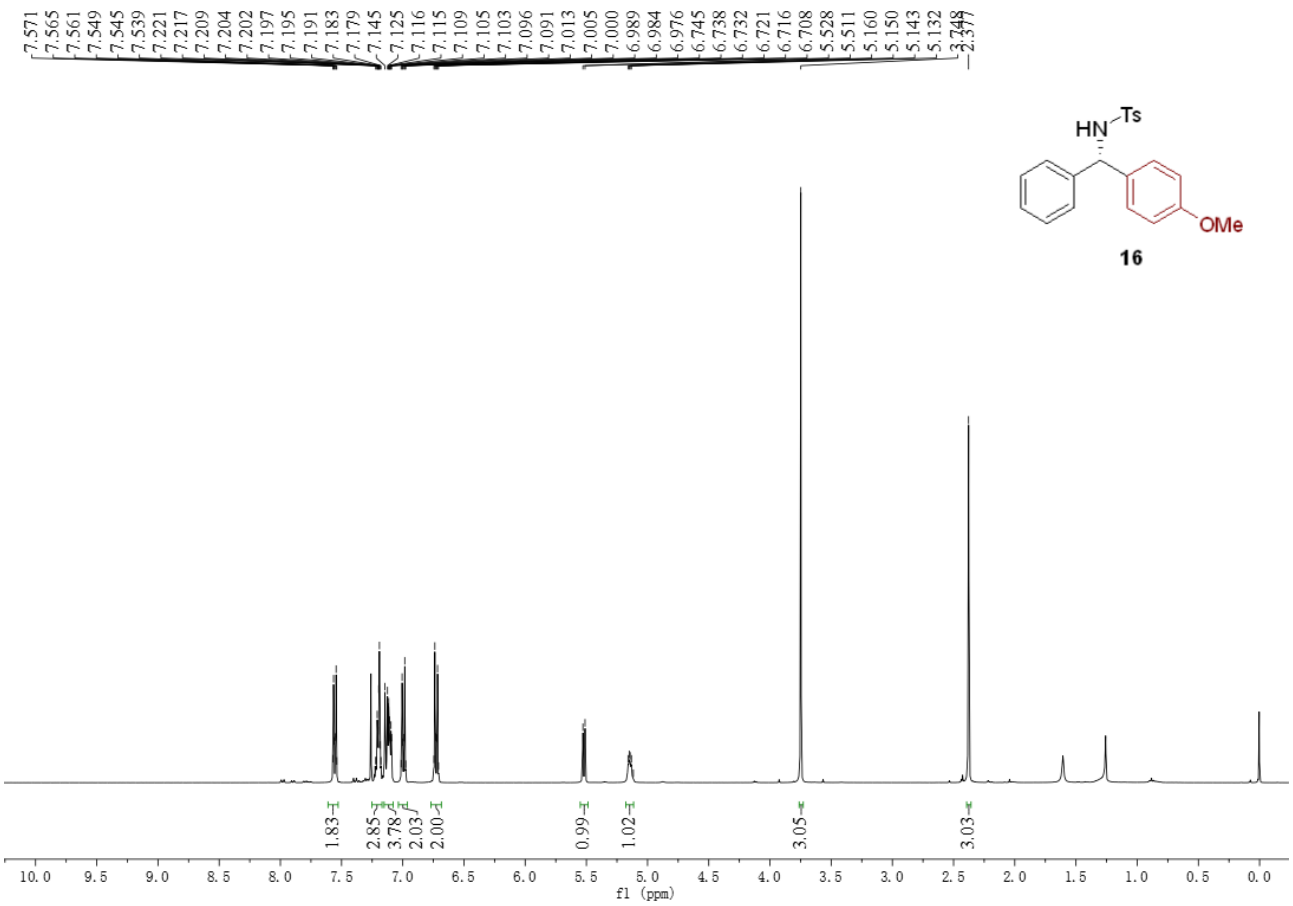
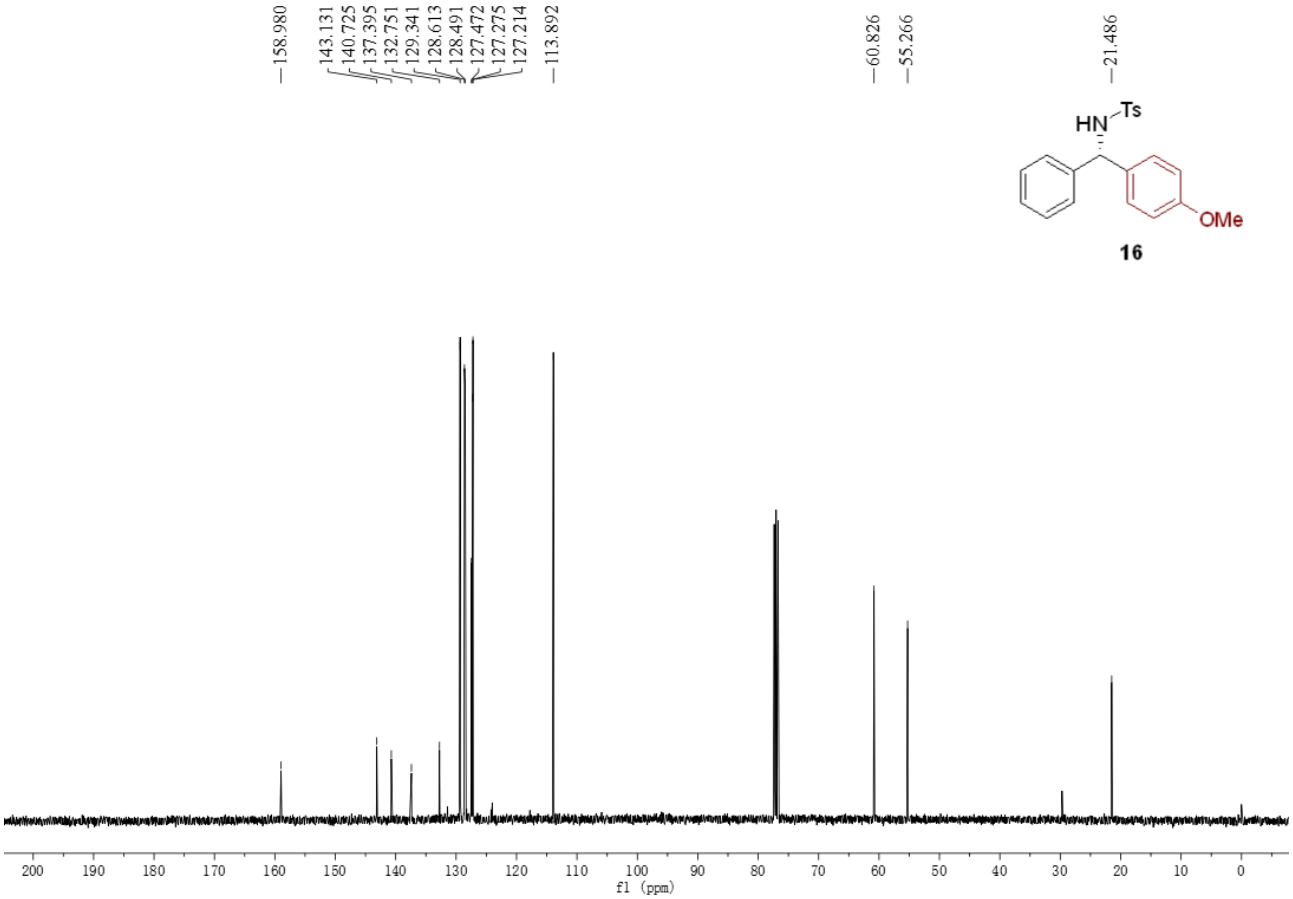
7.334
7.330
7.321
7.316
7.312
7.257
7.253
7.237
7.233
7.227
7.221
7.216
3.014
2.595
2.591
2.586
2.584
2.579
2.574
2.564
2.561
2.533
2.530
2.526
2.499
2.496
2.454
2.450
2.446
2.442
2.423
2.420
2.408
2.405
2.392
2.389
2.377
2.374
2.175
2.167
2.160
2.151
2.135
2.078
2.074
2.070
2.066
1.879
1.872
1.851
1.847
1.843
1.823
1.818
1.796
1.791
13
1.73
2.78
0.90
0.98
2.01
1.02
2.00
2.14
f1 (ppm)


211.044
144.350
128.692
126.696
126.580
48.960
44.761
41.207
32.791
25.557
13
f1 (ppm)


7.571
7.565
7.561
7.549
7.545
7.539
7.221
7.217
7.209
7.204
7.202
7.197
7.195
7.191
7.183
7.179
7.145
7.125
7.116
7.115
7.109
7.105
7.103
7.096
7.091
7.013
7.005
7.000
6.989
6.984
6.976
6.745
6.738
6.732
6.721
6.716
6.708
5.528
5.511
5.160
5.150
5.143
5.132
3.748
2.377
HN
Ts
OMe
16
1.83
2.85
3.78
2.03
2.00
0.99
1.02
3.05
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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140.725
137.395
132.751
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128.491
127.472
127.275
127.214
113.892
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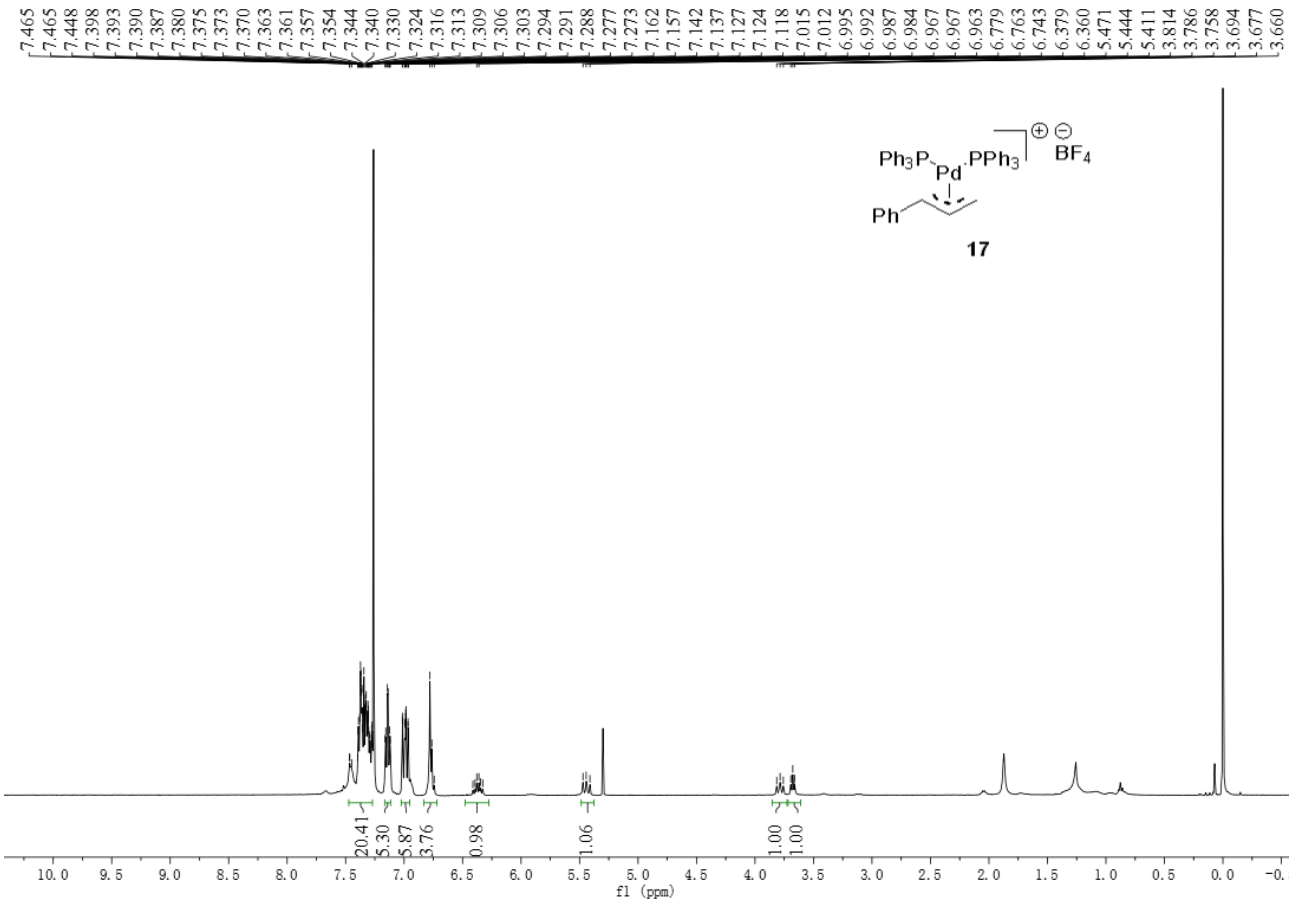
21.486
HN
Ts
OMe
16
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.361
7.357
7.354
7.344
7.340
7.330
7.324
7.316
7.313
7.309
7.306
7.303
7.294
7.291
7.288
7.277
7.273
7.162
7.157
7.142
7.137
7.127
7.124
7.118
7.015
7.012
6.995
6.992
6.987
6.984
6.967
6.967
6.963
6.779
6.763
6.743
6.379
6.360
5.471
5.444
5.411
3.814
3.786
3.758
3.694
3.677
3.660
Ph3P
Pd
PPh3
BF4
Ph
17
20.41
5.30
5.87
3.76
0.98
1.06
1.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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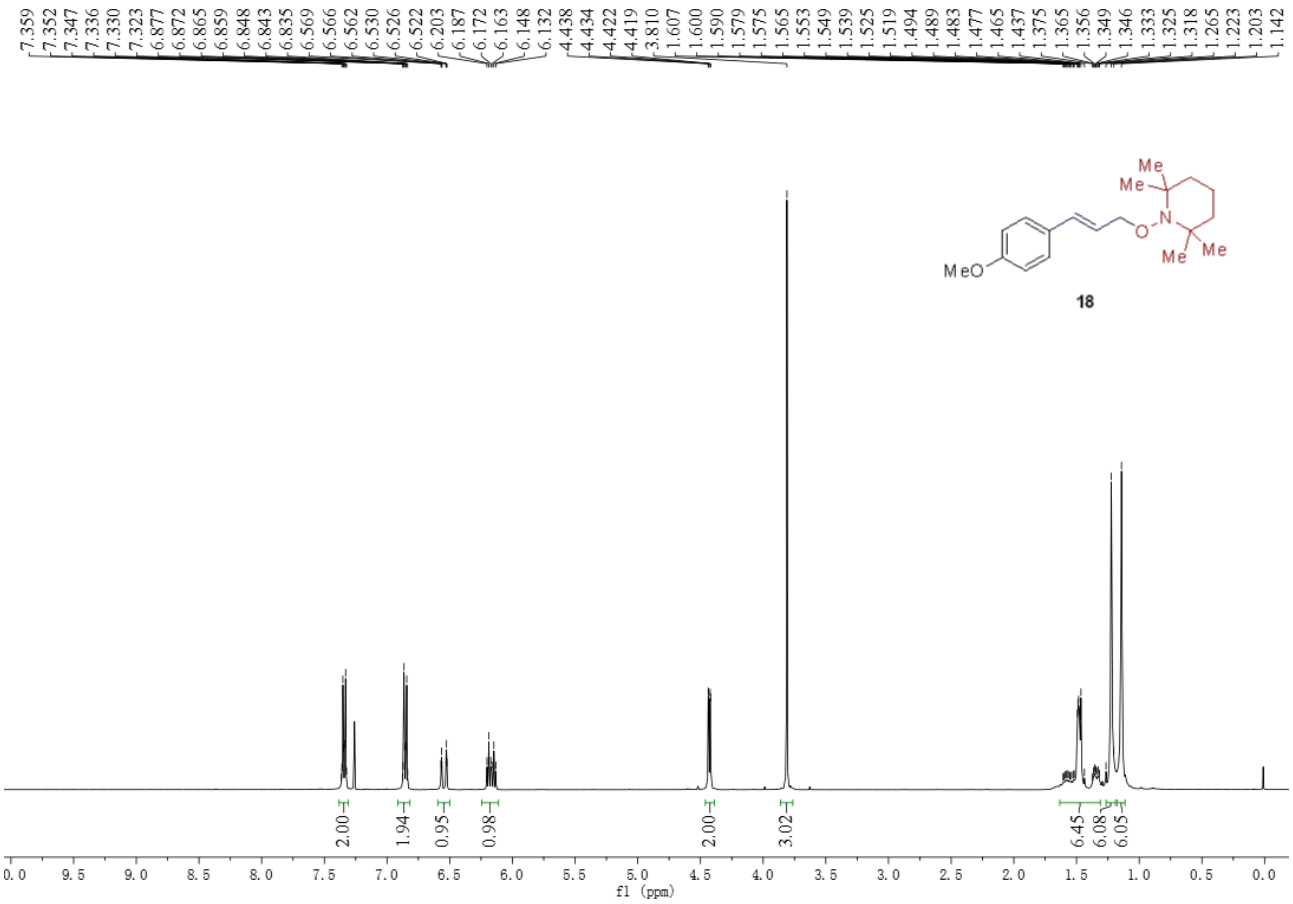
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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6.872
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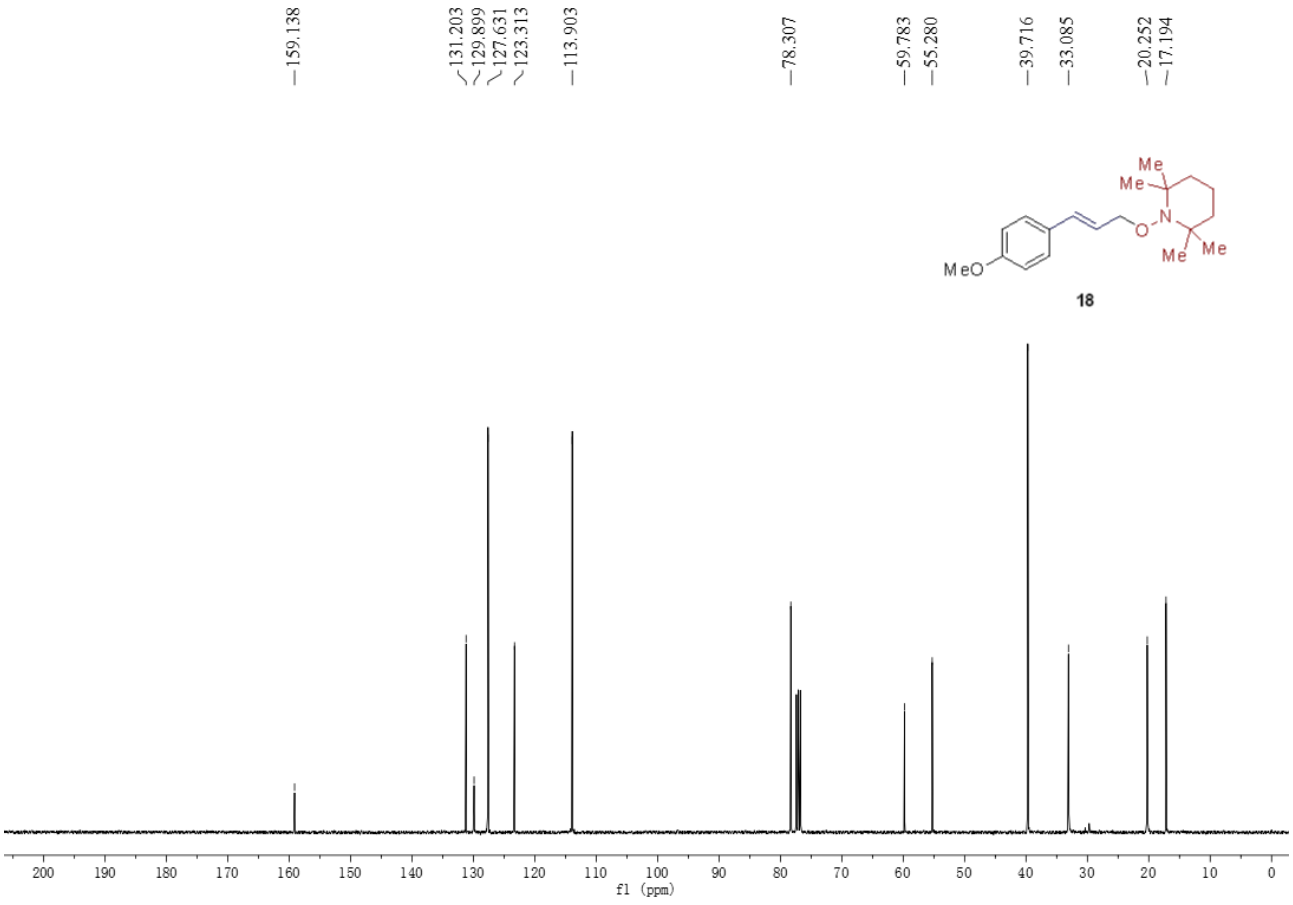
6.859
6.848
6.843
6.835
6.569
6.566
6.562
6.530
6.526
6.522
6.203
6.187
6.172
6.163
6.148
6.132
4.438
4.434
4.422
4.419
3.810
1.607
1.600
1.590
1.579
1.575
1.565
1.553
1.549
1.539
1.525
1.519
1.494
1.489
1.483
1.477
1.465
1.437
1.375
1.365
1.356
1.349
1.346
1.333
1.325
1.318
1.265
1.223
1.203
1.142
Me
Me
N
O
Me
Me
MeO
18
2.00
1.94
0.95
0.98
2.00
3.02
6.45
6.08
6.05
f1 (ppm)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131.203
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127.631
123.313
113.903
78.307
59.783
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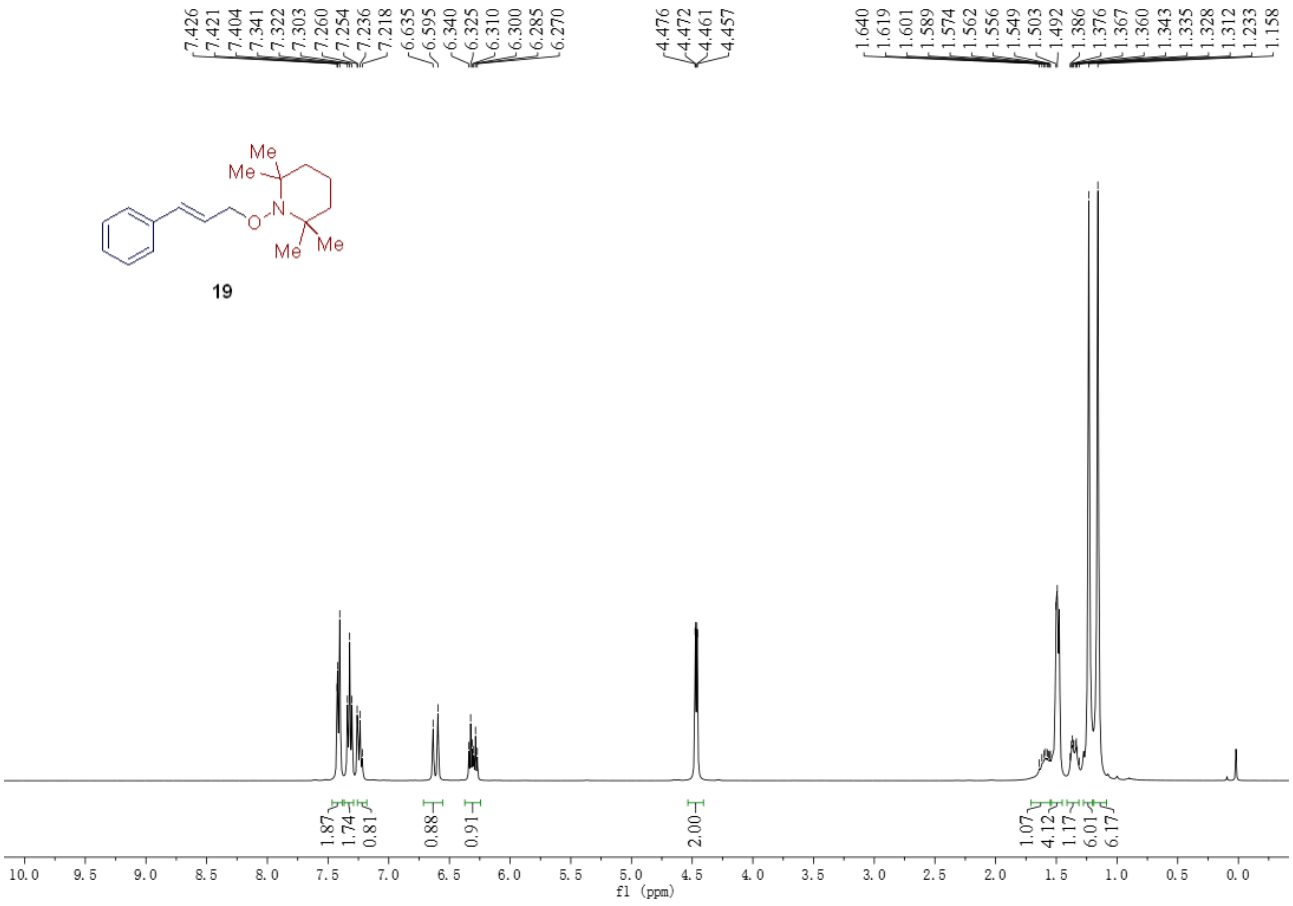
39.716
33.085
20.252
17.194
Me
Me
N
O
Me
Me
MeO
18
f1 (ppm)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6.595
6.340
6.325
6.310
6.300
6.285
6.270
4.476
4.472
4.461
4.457
1.640
1.619
1.601
1.589
1.574
1.562
1.556
1.549
1.503
1.492
1.386
1.376
1.367
1.360
1.343
1.335
1.328
1.312
1.233
1.158
Me
Me
N
O
Me
Me
19
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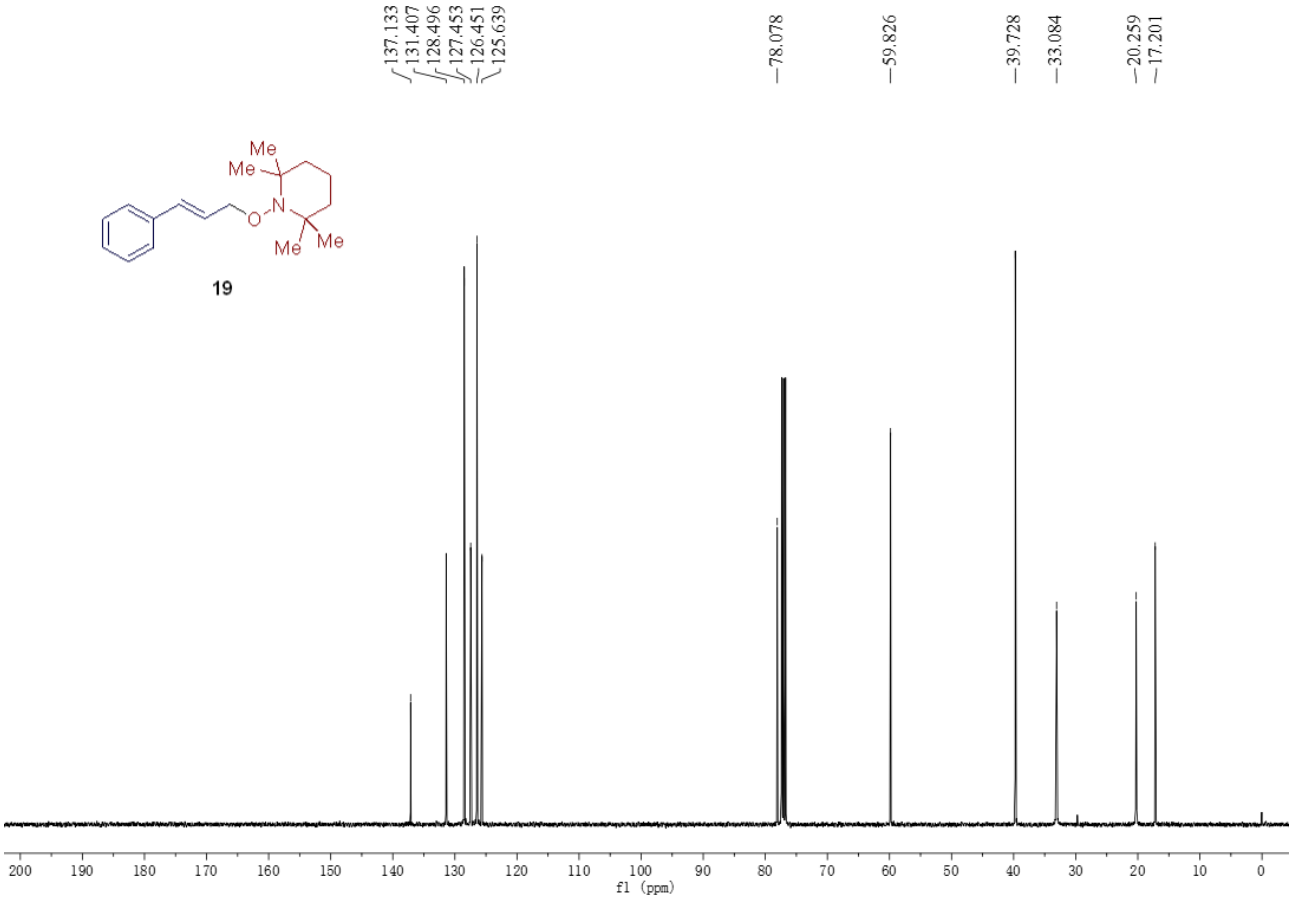
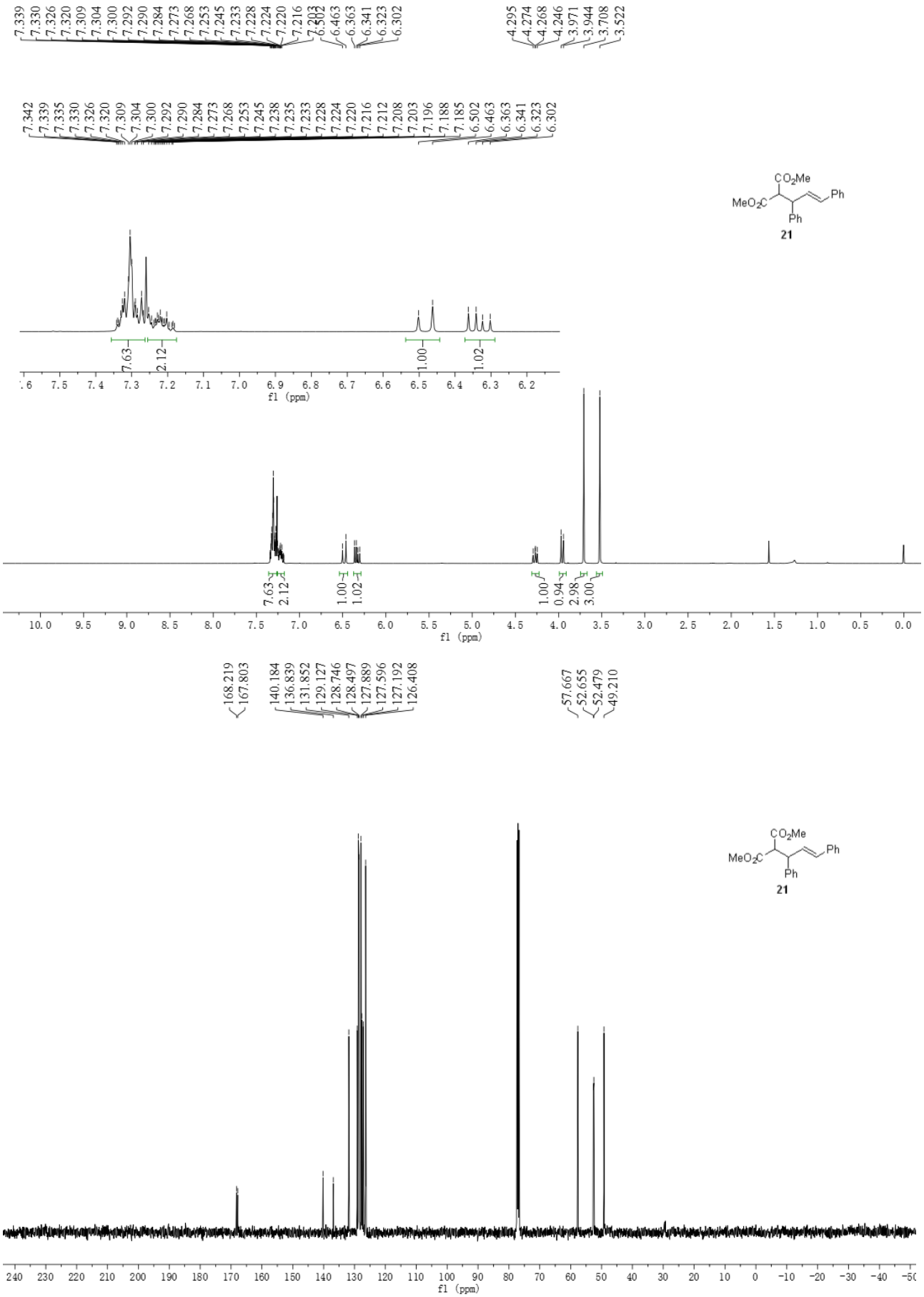
0.88
0.91
2.00
1.07
4.12
1.17
6.01
6.17
f1 (ppm)


137.133
131.407
128.496
127.453
126.451
125.639
78.078
59.826
39.728
33.084
20.259
17.201
Me
Me
N
O
Me
Me
19
f1 (ppm)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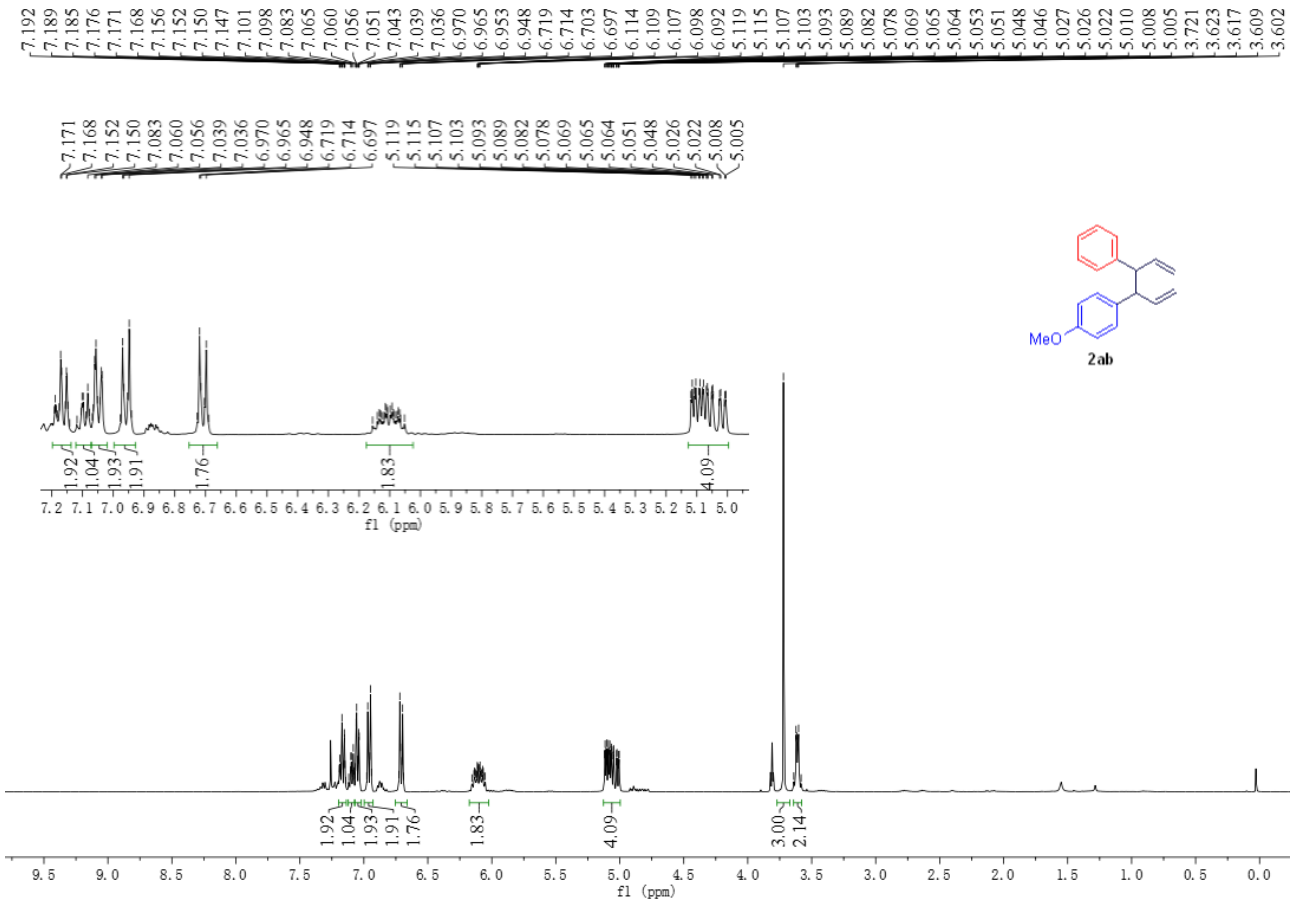
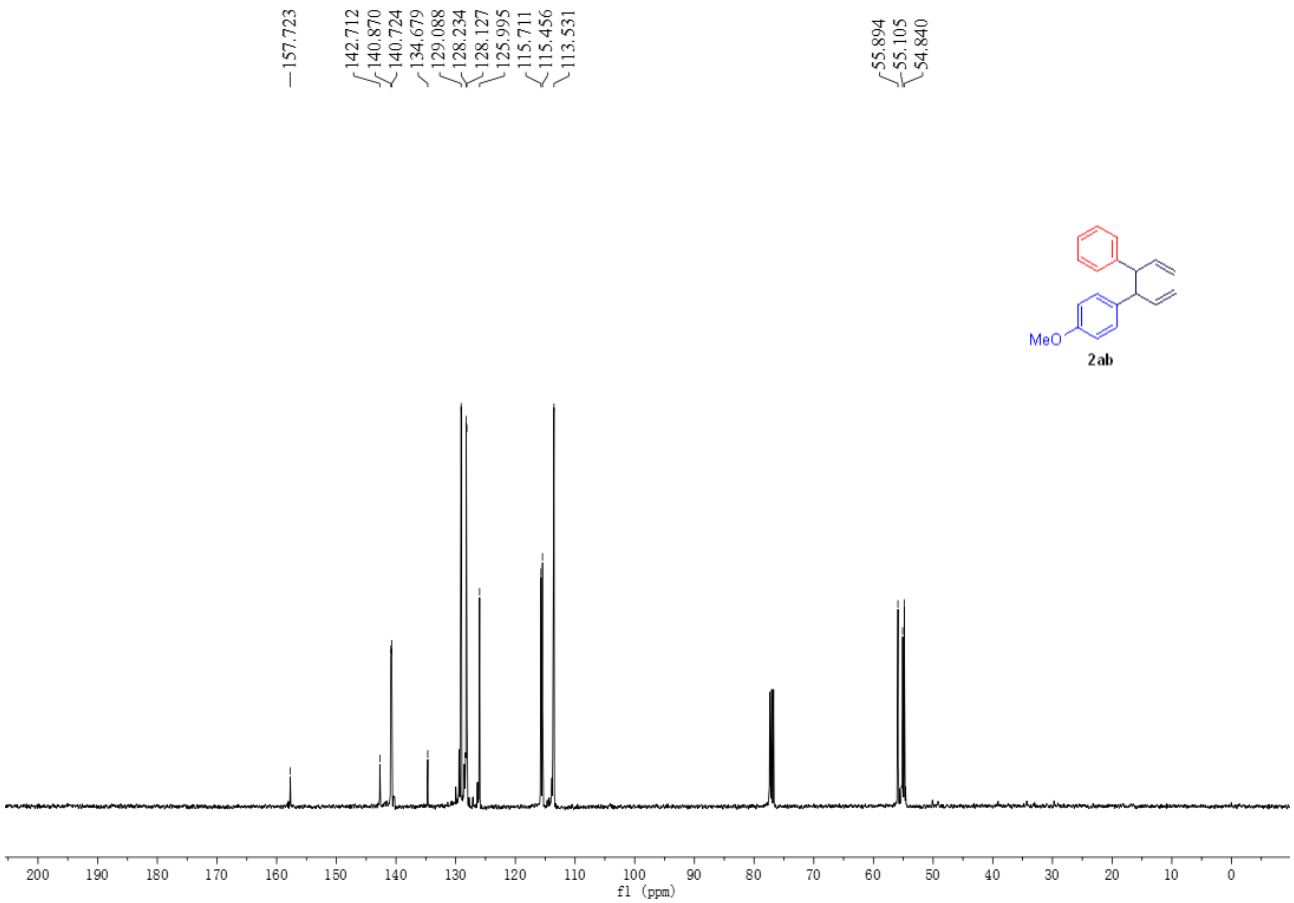
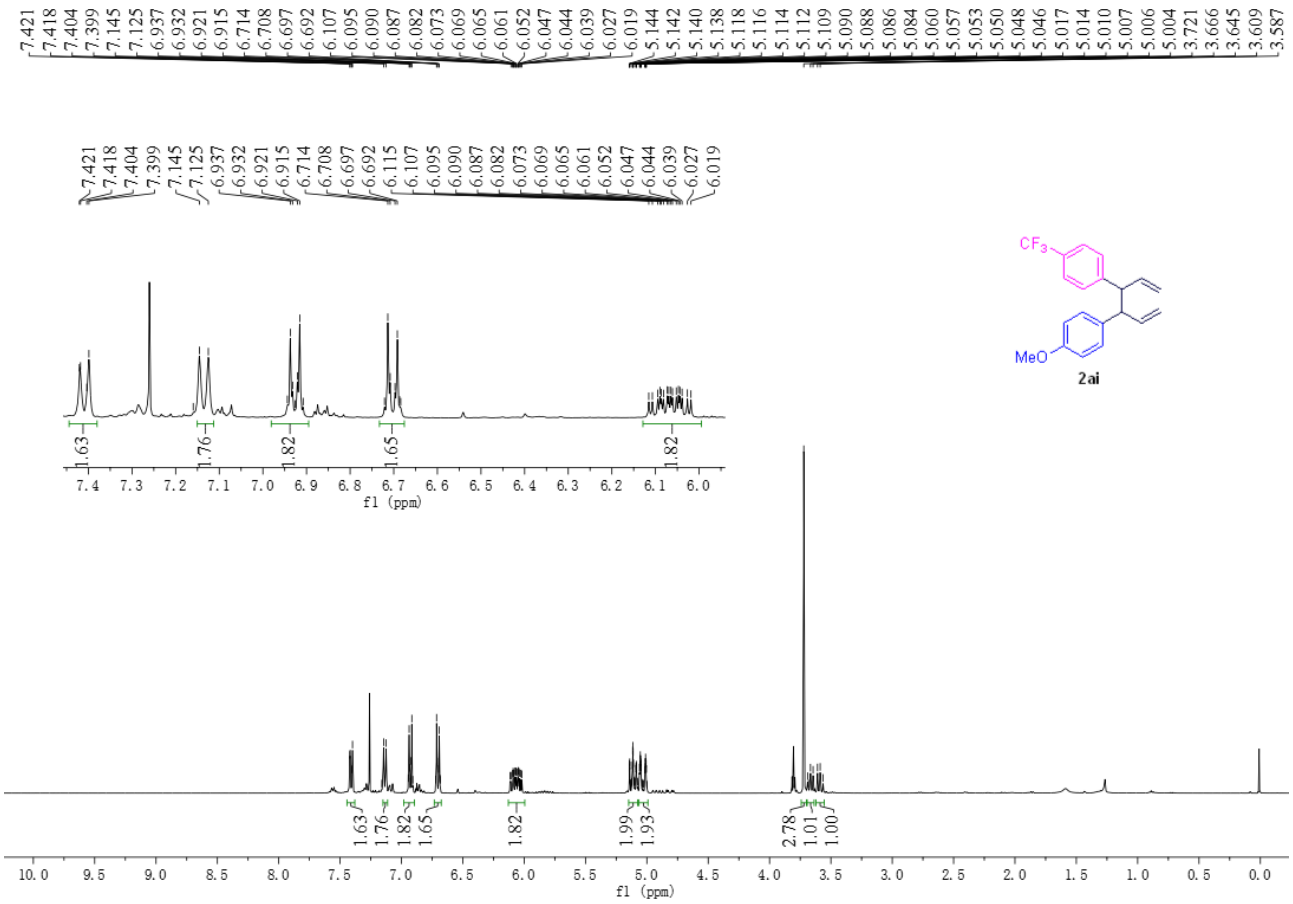
7.326
7.320
7.309
7.304
7.300
7.292
7.290
7.284
7.273
7.268
7.253
7.245
7.233
7.228
7.224
7.220
7.216
7.203
6.502
6.463
6.363
6.341
6.323
6.302
4.295
4.274
4.268
4.246
3.971
3.944
3.708
3.522
7.342
7.339
7.335
7.330
7.326
7.320
7.309
7.304
7.300
7.292
7.290
7.284
7.273
7.268
7.253
7.245
7.238
7.235
7.233
7.228
7.224
7.220
7.216
7.212
7.208
7.203
7.196
7.188
7.185
6.502
6.463
6.363
6.341
6.323
6.302
CO2Me
MeO2C
Ph
Ph
21
7.63
2.12
1.00
1.02
f1 (ppm)
7.63
2.12
1.00
1.02
1.00
0.94
2.98
3.00
f1 (ppm)
168.219
167.803
140.184
136.839
131.852
129.127
128.746
128.497
127.889
127.596
127.192
126.408
57.667
52.655
52.479
49.210
CO2Me
MeO2C
Ph
Ph
21
f1 (ppm)


MeO
2ab
f1 (ppm)


MeO
2ab
f1 (ppm)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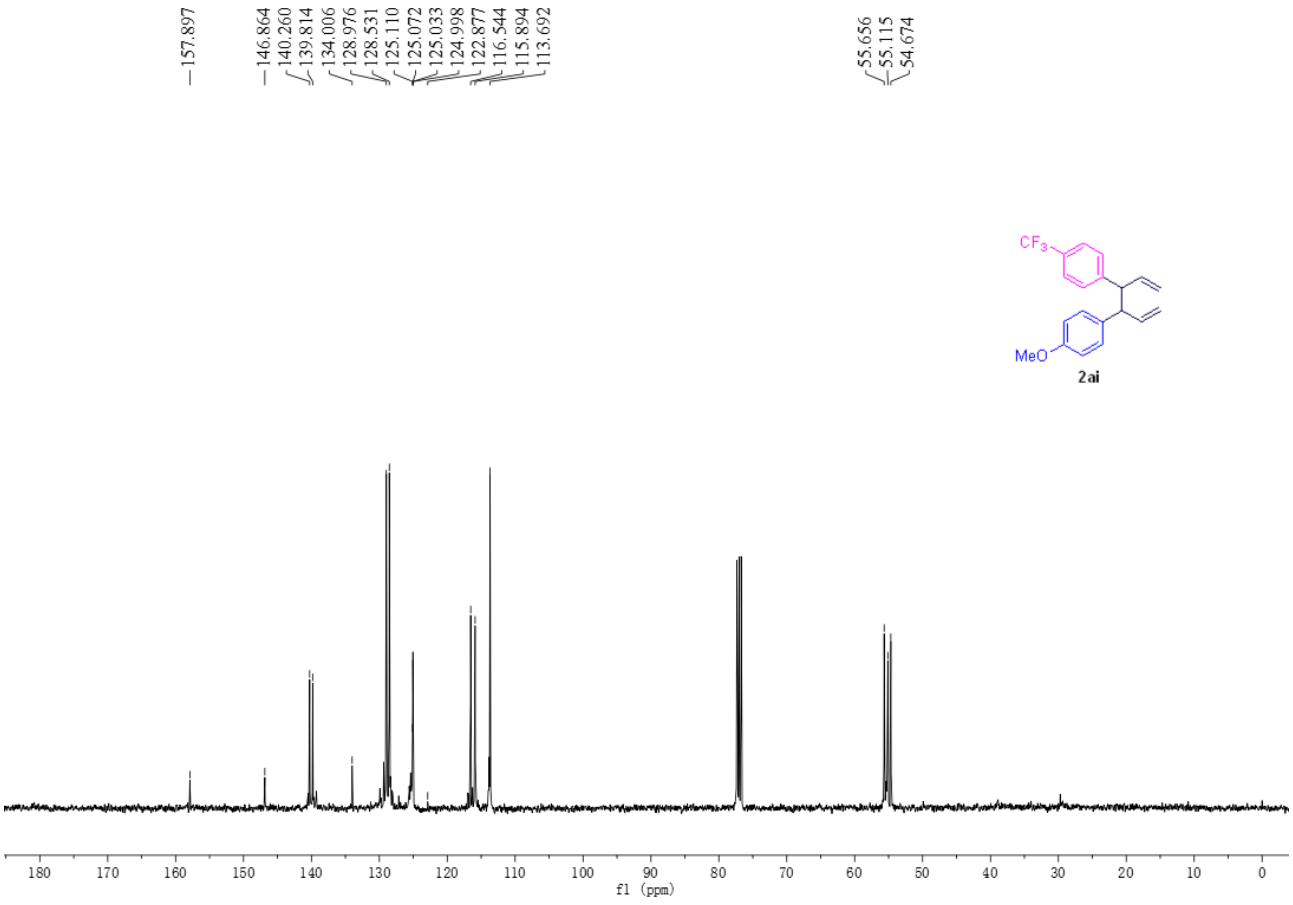
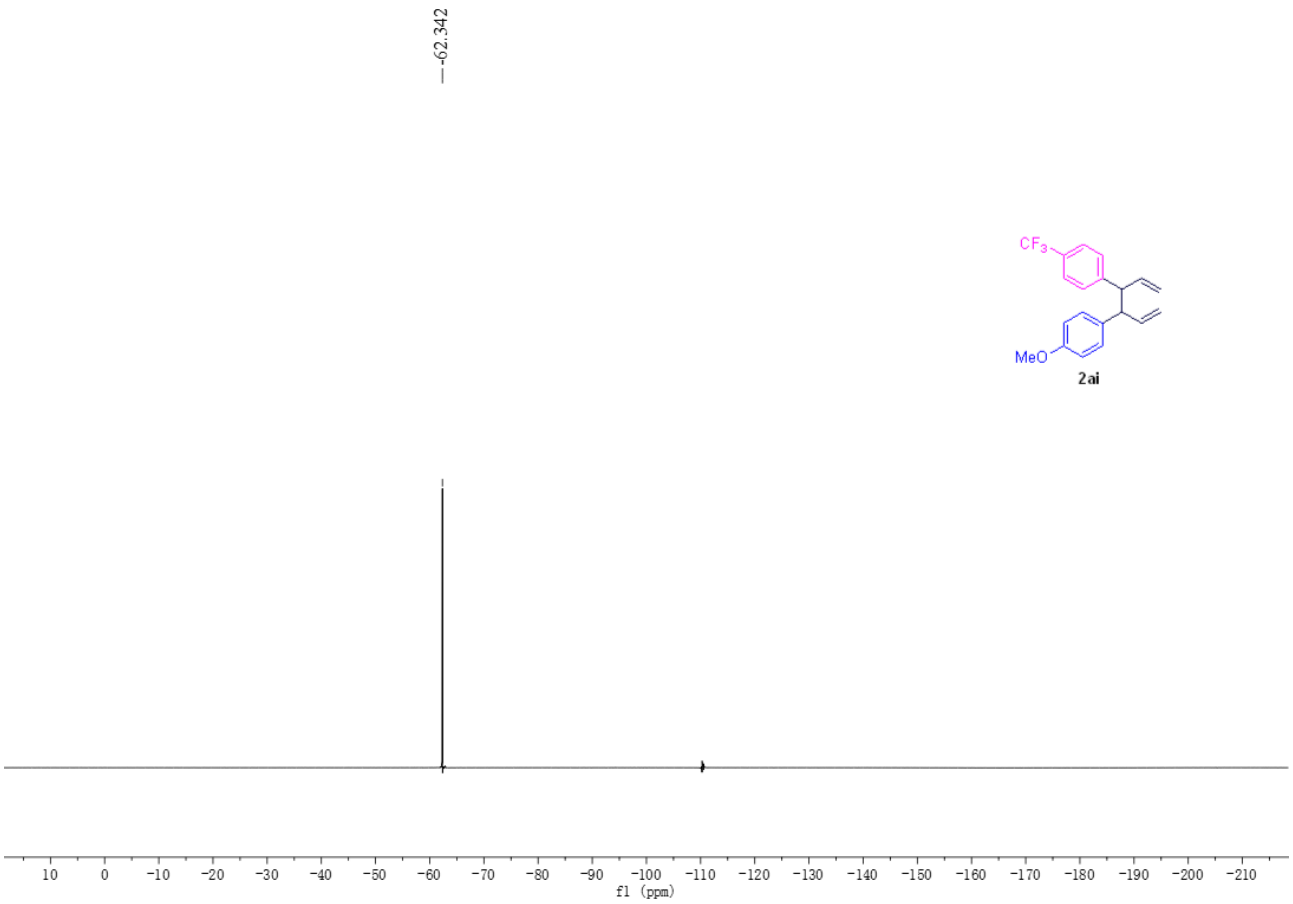
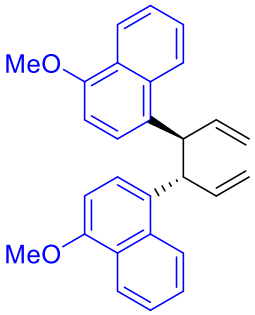
1.63 1.76 1.82 1.65 1.82
f1 (ppm)
CF3
MeO
2ai
1.63 1.76 1.82 1.65 1.82 1.99 1.93 2.78 1.01 1.00
f1 (ppm)

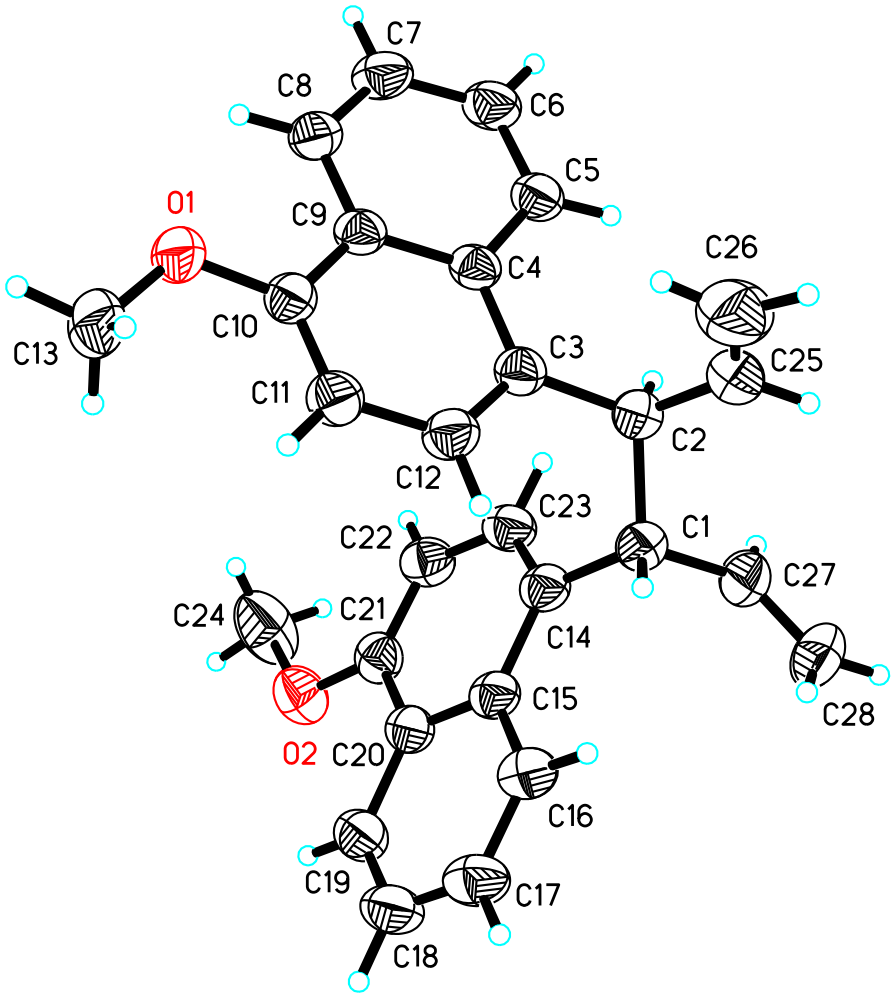

157.897
146.864 140.260 139.814 134.006 128.976 128.531 125.110 125.072 125.033 124.998 122.877 116.544 115.894 113.692
55.656 55.115 54.674
CF3
MeO
2ai
f1 (ppm)


-62.342
CF3
MeO
2ai
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

14. X-ray single crystal data for compounds 2t



2t (CCDC 2049849)



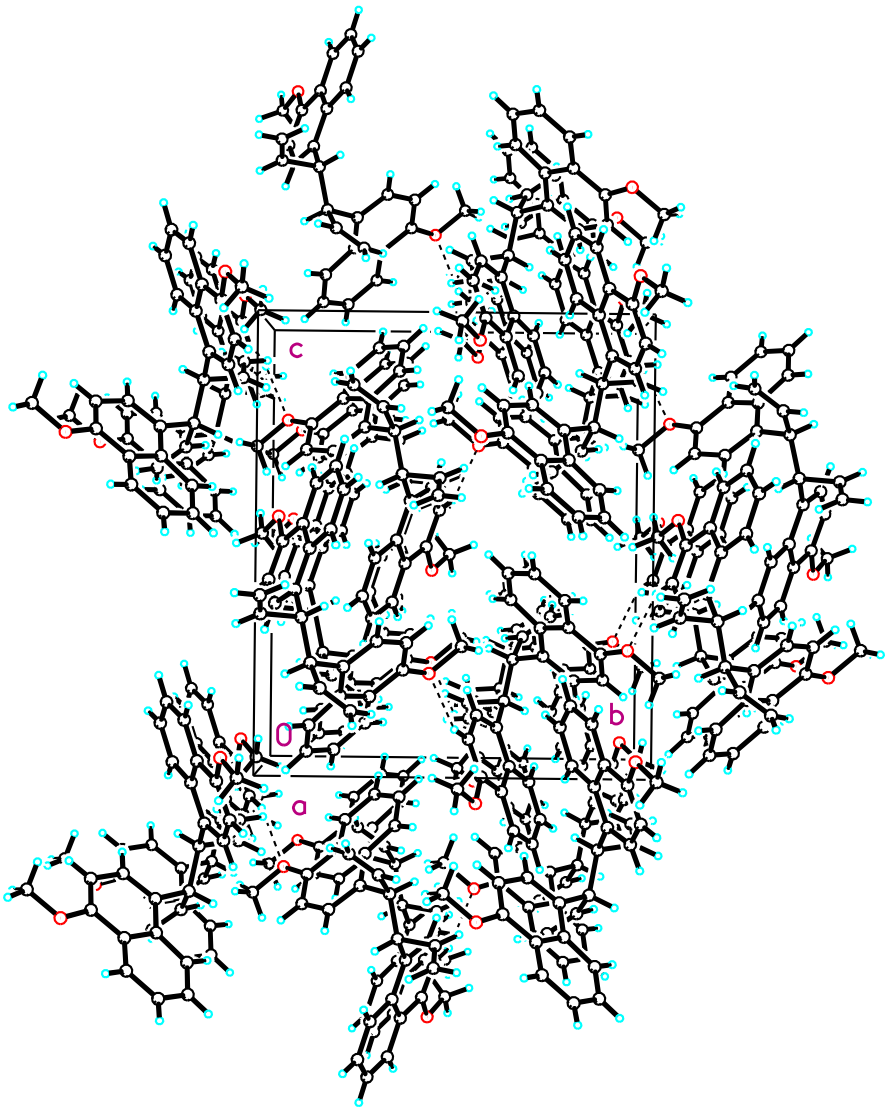

c
0
b
a

Table S4. Crystal data and structure refinement for **2t**.

Identification code	**2t**	
Empirical formula	C28 H26 O2	
Formula weight	394.49	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 10.5359(5) Å	α= 90°.
	b = 13.4642(6) Å	β= 90°.
	c = 15.7362(6) Å	γ = 90°.
Volume	2232.30(17) $Å^3$	
Z	4	
Density (calculated)	1.174 Mg/m^3	
Absorption coefficient	0.563 mm^{-1}	
F(000)	840	
Crystal size	0.200 x 0.160 x 0.140 mm^3	
Theta range for data collection	5.052 to 67.485°.	
Index ranges	-12<=h<=12, -16<=k<=16, -18<=l<=18	
Reflections collected	21085	
Independent reflections	3966 [R(int) = 0.0360]	
Completeness to theta = 67.679°	97.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.5537	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3966 / 43 / 292	
Goodness-of-fit on F^2	1.075	
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.1089	
R indices (all data)	R1 = 0.0418, wR2 = 0.1111	
Absolute structure parameter	-0.08(9)	
Extinction coefficient	0.022(4)	
Largest diff. peak and hole	0.221 and -0.144 $e.Å^{-3}$	