Supplementary Material

Palladium-catalyzed intramolecular allylation of aldehydes through in situ generation of allylsilanes

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General

Unless otherwise noted, the reactions were carried out in flame-dried glassware under argon atmosphere. NMR spectra were recorded on Bruker AVANCE NEO 400 spectrometer. Chemical shifts (δ) are reported in ppm from the solvent resonance or tetramethylsilane (TMS) as the internal standard ($CDCl_3$: 7.26 ppm, TMS: 0.00 ppm). Peak multiplicities are designated by the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad and coupling constants (J) are provided in Hz. ^{13}C NMR spectra were recorded on Bruker AVANCE NEO 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). Some reported spectra in $CDCl_3$ include minor solvent impurities of water (^1H NMR δ 1.56 ppm) and/or silicone grease (^1H NMR δ 0.07 ppm, ^{13}C NMR δ 1.19 ppm), which do not impact product assignments.[47] Melting points were measured using open glass capillaries in a Büchi B545 apparatus. Infrared (IR) spectra were recorded on a JASCO FT/IR- 4100 spectrometer. Flash chromatography was performed with Fuji Silysia PSQ100B (100 μm) and KANTO silica gel 60N (63-210 μm). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). High-resolution mass (HRMS) spectral data were obtained on an Agilent 6546 LC/Q-TOF or a JEOL MStation JMS-700 mass spectrometer.

Materials

Dichloromethane, diethyl ether, and tetrahydrofuran (THF) were supplied from Kanto Chemical Co., Inc. as “Dehydrated solvent system”. Other solvents were purchased from commercial suppliers as dehydrated solvents and used under argon atmosphere. Triethylamine was purified by distillation from CaH_2. All commercial reagents were used as received unless otherwise noted.

Genital procedure for preparation of alkynylsilanes (GP-1)[2]

Ethynyltriphenylsilane: To a flame dried 200 mL three-necked flask equipped with a reflux condenser, dropping funnel, magnetic stir bar, and rubber septum was attached to a double manifold and cooled under vacuum. After the flask was backfilled with argon, chlorotriphenylsilane (4.43 g, 15.0 mmol), $ZnCl_2 \cdot TMEDA$ (37.88 mg, 0.15 mmol), and THF (15 mL) were added, and the flask was cooled to 0 °C. While stirring, ethynylmagnesium chloride (0.5 M in THF, 36 mL, 18.0 mmol) was added dropwise via dropping funnel over 15 min. After the addition was complete, the flask was warmed to room temperature and stirred at 70 °C for 4.5 h. The rubber septum was removed, and the reaction was quenched by saturated aqueous NH_4Cl (10 mL). The reaction was poured into a separatory funnel, and the product was extracted with Et_2O (2 × 20 mL) and washed with brine. The organic layer was dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. The residue was purified by flash chromatography on silica gel to afford ethynyltriphenylsilane as a colorless solid (3.91 g, 92%, R_f 0.60, EtOAc/hex = 1/4).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.69–7.66 (m, 6H), 7.47–7.38 (m, 9H), 2.50 (s, 1H).

The ^{1}H NMR spectrum of the title compound was identical with that reported in the literature.[3]

Ethynyltri(4-fluorophenyl)silane: Following GP-1, chlorotri(4-fluorophenyl)silane (5.0 mmol), ethynylmagnesium chloride (0.5 M in THF, 12 mL, 6.0 mmol), $ZnCl_2$·TMEDA (12.6 mg, 0.05 mmol) were used. The title compound was isolated as a yellow oil (1.1 g, 72%, R*f* 0.56, EtOAc/hex = 1/4).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.64-7.57 (tm, *J* = 6.0 Hz, 6H), 7.14-7.07 (tm, *J* = 8.4 Hz, 6H), 2.83 (s, 1H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 164.7 (d, *J* = 249.8 Hz), 137.7 (d, *J* = 7.7 Hz), 128.1 (d, *J* = 2.8 Hz), 115.7 (d, *J* = 20.0 Hz), 98.6, 84.8.

Ethynyltri(thien-2-yl)silane: Following GP-1, chlorotri(thien-2-yl)silane (5.0 mmol), ethynylmagnesium chloride (0.5 M in THF, 12 mL, 6.0 mmol), $ZnCl_2$·TMEDA (12.6 mg, 0.05 mmol) were used. The title compound was isolated as an orange oil (72%, R*f* 0.48, EtOAc/hex = 1/4).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.75 (dd, *J* = 4.8, 1.2 Hz, 3H), 7.57 (dd, *J* = 3.2, 0.8 Hz, 3H), 7.26 (dd, *J* = 4.8, 3.2 Hz, 3H), 2.86 (s, 1H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 138.5, 133.6, 131.9, 128.7, 98.1, 84.4.

Ethynyldimethyl(phenyl)silane (CAS: 17156-64-8): Following GP-1, chlorodimethyl(phenyl)silane (5.0 mmol), ethynylmagnesium chloride (0.5 M in THF, 12 mL, 6.0 mmol), $ZnCl_2$·TMEDA (12.6 mg, 0.05 mmol) were used. Purified by vacuum distillation (75 °C/6 mm Hg) to afford the title compound was isolated as a colorless oil (40%, R*f* 0.67, EtOAc/hex = 1/4).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.67–7.62 (m, 2H), 7.42–7.36 (m, 3H), 2.53 (s, 1H), 0.46 (s, 6H).

The ^{1}H NMR spectrum of the title compound was identical with that reported in the literature.[4]

Ethynylmethyl(diphenyl)silane (CAS: 17156-65-9): Following GP-1, chloromethyl(diphenyl)silane (5.0 mmol), ethynylmagnesium chloride (0.5 M in THF, 12 mL, 6.0 mmol), $ZnCl_2$·TMEDA (12.6 mg, 0.05 mmol) were used. The title compound was isolated as an orange oil (77%, R*f* 0.50, EtOAc/hex = 1/19).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ7.69-7.64 (m, 4H), 7.46-7.36 (m, 6H), 2.67 (s, 1H), 0.74 (s, 3H).

The ^{1}H NMR spectrum of the title compound was identical with that reported in the literature.[5]

Preparation of ethynyltri(4-methoxyphenyl)silane

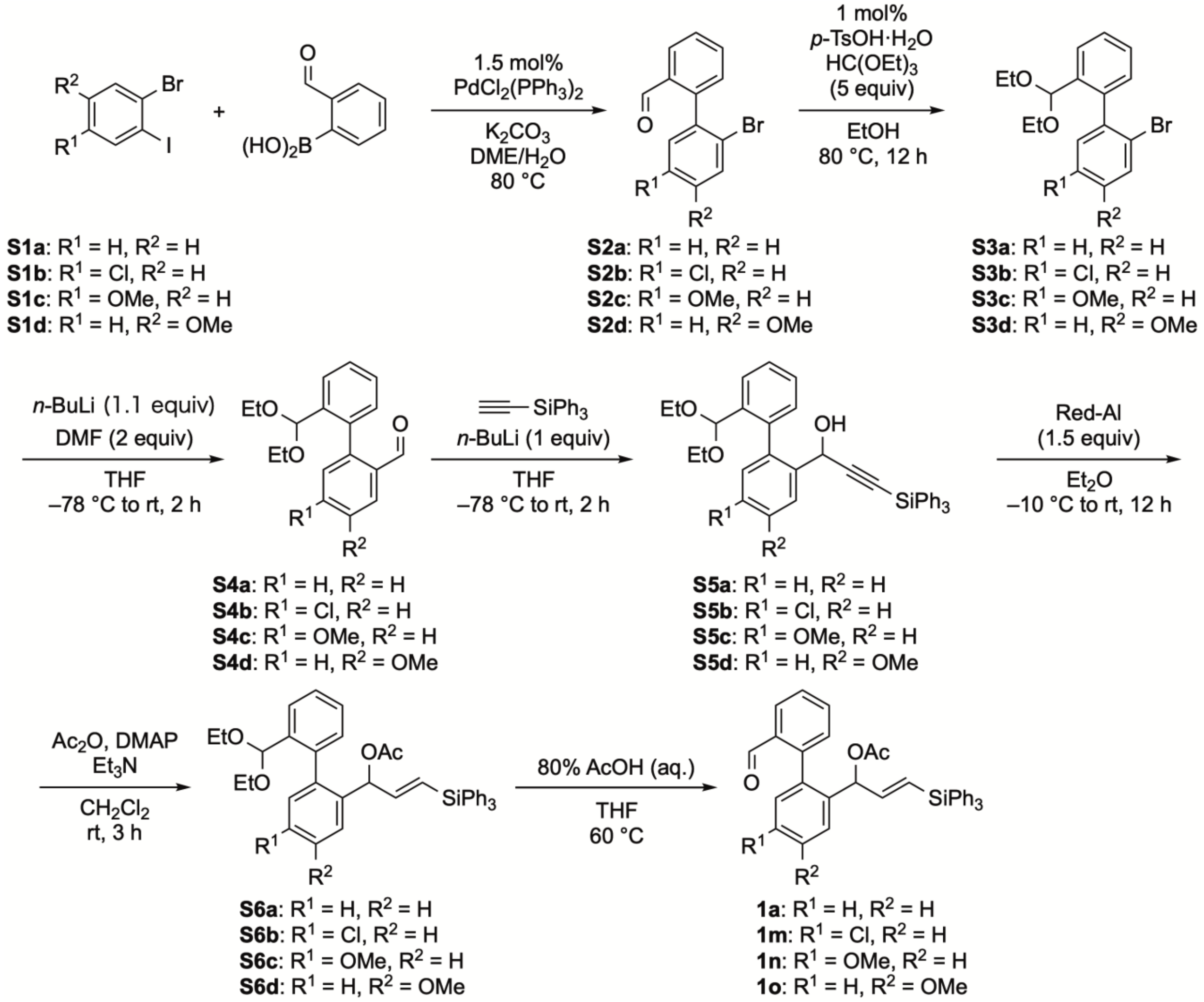
To a flame dried 50 mL three-necked flask equipped with a magnetic stir bar and a rubber septum was attached to a double manifold and cooled under vacuum. After the flask was backfilled with argon, ethynyltrimethylsilane (0.83 mL, 6 mmol) and THF (15 mL) were added, and the flask was cooled to –78 °C. While stirring, *n*-BuLi (1.6 M in hexane, 3.4 mL, 5.4 mmol) was added dropwise via a syringe. After the addition was complete, the mixture was stirred at –78 °C for 15 min. To this solution was added tris(4-methoxyphenyl)chlorosilane (5 mmol) in THF (4 mL) via cannula. After the addition was complete, the flask was warmed to room temperature and stirred for 12 h. The rubber septum was removed, and the reaction was quenched by saturated aqueous NH_4Cl (5 mL) at 0 °C. The reaction was poured into a separatory funnel, and the product was extracted with Et_2O (2 × 10 mL) and washed with brine (2 × 10 mL). The organic layer was dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. The residue was used without the necessity of purification.

To a flame dry 100 mL three-necked flask equipped with a magnetic stir bar was added 1-tris(4-methoxyphenyl)-2-trimethylsilylacethylene, K_2CO_3 (1.73 g, 12.5 mmol), THF (17.5 mL), MeOH (17.5 mL) under air. After stirring for 0.5 h at room temperature, the rubber septum was removed, and water (25 mL) was added and stirred for 10 min.

The reaction was poured into a separatory funnel, and the product was extracted with EtOAc (2 × 10 mL) and washed with brine (2 × 10 mL). The organic layer was dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. The residue was purified by flash chromatography on silica gel to afford ethynyltri(4-methoxyphenyl)silane as a pale yellow solid (mp 101.8-102.5 °C, 665.3 mg, 36% over 3 steps, R_f 0.33, EtOAc/hex = 1/4).

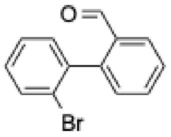
^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.56 (dt, J = 2.0, 8.0 Hz, 6H), 6.93 (dt, J = 2.4, 8.8 Hz, 6H), 3.82 (s, 9H), 2.74 (s, 1H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 161.3, 137.1, 124.4, 113.9, 97.2, 86.4, 55.1; **HRMS-EI**: $[M]^+$ calcd for $C_{23}H_{22}O_3Si^+$:374.1338, found: 374.1331.

Preparation of substrates 1a, 1m–o



General procedure for the preparation of 2'-bromo-1,1'-biphenyl-2-carbaldehyde derivatives (GP-2)

Prepared by adapting a reported procedure.[6] Water (6 mL) and degassed DME (15 mL) were poured into a round-bottomed flask, fitted with a condenser and argon flow, and bubbled through with argon. Potassium carbonate (4.14 g, 30 mmol), 1-bromo-2-iodobenzene (1.9 mL, 15.0 mmol), (2-formylphenyl)bononic acid (2.47 g, 16.5 mmol), and bis(triphenylphosphine)palladium(II) chloride (210.0 mg, 0.3 mmol) were added to the mixture, which was stirred at 80 °C for 12 h in an oil bath until substrate disappeared as judged by TLC. The mixture was filtered through a pad of Celite®. DME was evaporated, and water (40 mL) and ethyl acetate (20 mL) were added. The layers were separated, and the aqueous layer was extracted with ethyl acetate (2 × 20 mL). The combined organic layers were washed with saturated aqueous NH_4Cl (2 × 15 mL) and brine (2 × 15 mL), dried over $MgSO_4$, filtered, and evaporated, which was purified further using column chromatography on silica gel to give 2'-bromo-1,1'-(biphenyl)-2-carbaldehyde (CAS:75295-62-4) as a yellow oil (2.80 g, 72%, R_f 0.51, EtOAc/hexane = 1:4).

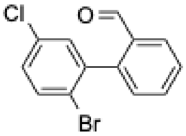


2'-Bromo-1,1'-biphenyl-2-carbaldehyde (S2a, CAS:75295-62-4)

Following GP-2, 1-bromo-2-iodobenzene (4.24 g, 15.0 mmol) was reacted with 2-bromophenylboronic acid (2.89 g, 18 mmol). The title compound was isolated as a yellow oil (2.80 g, 72%, R*f* 0.51, EtOAc/hexane = 1:4).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 8.04 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.69 (dm, *J* = 8.0 Hz, 1H), 7.65 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.55 (tm, *J* = 8.0 Hz, 1H), 7.41 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.34–7.28 (m, 3H).

The ^{1}H NMR spectrum of title compound was identical with that reported in the literature.[7]

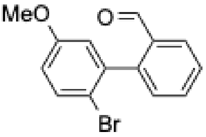


2'-Bromo-5’-chloro-(1,1'-biphenyl)-2-carbaldehyde (S2b, CAS: 2808306-67-2)

Following GP-2, 2-bromo-5-chlorobenzaldehyde (3.29 g, 15 mmol) was reacted with 2-bromophenylboronic acid (2.89 g, 18 mmol). The title compound was isolated as a brown amorphous solid (2.9 g, 66%, R*f* 0.53, EtOAc/hex = 1/4).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 9.81 (d, *J* = 0.8 Hz, 1H), 8.04 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.68 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.63-7.55 (m, 2H), 7.34 (d, *J* = 2.4 Hz, 1H), 7.31–7.27 (m, 2H).

The ^{1}H NMR spectrum of title compound was identical with that reported in the literature.[8]

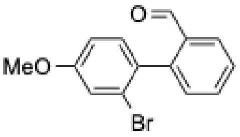


2′-Bromo-5’-methoxy-(1,1′-biphenyl]-2-carboxaldehyde (S2c, CAS: 790220-95-0)

Following GP-2, 2-bromo-5-methoxybenzaldehyde (3.44 g, 16.0 mmol) was reacted with 2-bromophenylboronic acid (3.86 g, 19.2 mmol). The title compound was isolated as a yellow oil (2.7 g, 58%, R*f* 0.52, EtOAc/hex = 3/7).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 9.81 (d, *J* = 0.8 Hz, 1H), 8.04 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.66 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.58-7.52 (m, 2H), 7.32 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.88-6.85 (m, 2H), 3.81 (s, 3H).

The ^{1}H NMR spectrum of title compound was identical with that reported in the literature.[9]



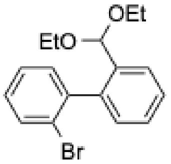
2′-Bromo-4’-methoxy-(1,1′-biphenyl]-2-carboxaldehyde (S2d, CAS: 1459238-35-7)

Following GP-2, 2-bromo-4-methoxybenzaldehyde (4.30 g, 20.0 mmol) was reacted with 2-bromophenylboronic acid (4.82 g, 24 mmol). The title compound was isolated as a yellow solid (4.3 g, 75%, R_f = 0.53, EtOAc/hex = 1/4).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 9.84 (d, *J* = 0.8 Hz, 1H), 8.05 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.67 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.55 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.35-7.32 (dm, *J* = 7.6 Hz, 1H), 7.27 (t, *J* = 8.8 Hz, 2H), 6.98 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.89 (s, 3H).

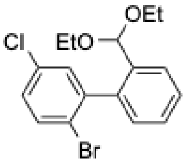
The ^{1}H NMR spectrum of title compound was identical with that reported in the literature.[10]

General procedure for the preparation of 2-bromo-2'-diethoxymethyl-1,1'-biphenyl derivatives (GP-3)



A 100 mL flask with a stir-bar was charged with 2'-bromo-(1,1'-biphenyl)-2-carbaldehyde (6.97 g, 20.8 mmol) and *p*-toluenesulfonic acid monohydrate (395.7 mg, 2.08 mmol). EtOH (40 mL) and trimethyl orthoformate (17.3 mL, 104 mmol) were added, and the solution was heated to 70 °C for 12 h. A saturated aqueous $NaHCO_3$ solution (10 mL) was then added, and most of the EtOH was evaporated. The solution was extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with brine (2 × 15 mL), dried over $MgSO_4$, and evaporated, which was purified by column chromatography on silica gel to give 2- bromo-2'-diethoxymethyl-1,1'-biphenyl (**S3a**, yellow oil, 6.1 g, 18.1 mmol, 87%, R_f 0.60, EtOAc/hex = 1/4).

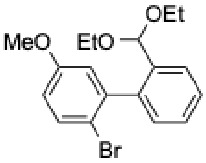
^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.68 (dt, *J* = 8.0, 1.2 Hz, 2H), 7.41 (ddq, *J* = 9.2, 7.6, 1.6 Hz, 3H), 7.30 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.26 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.12 (m, 1H), 5.10 (s, 1H), 3.51 (ddq, *J* = 9.6, 6.8, 5.2 Hz, 2H), 3.39 (dq, *J* = 9.6, 7.2 Hz, 1H), 3.21 (dq, *J* = 9.2, 7.2 Hz, 1H), 1.15 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 6.8 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 142.3, 141.5, 37.9, 133.4, 132.8, 130.8, 130.2, 129.1, 128.8, 128.0, 127.0, 124.2, 101.5, 63.6, 63.3, 15.5, 15.4; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{17}H_{20}BrO_2^+$:335.0647, found: 335.0647.



2’-Bromo-5’-chloro-2-(diethoxymethyl)-1,1'-biphenyl (S3b)

Following GP-3, 2'-bromo-5’-chloro-(1,1'-biphenyl)-2-carbaldehyde (9.9 mmol) was used. The title compound was isolated as a yellow oil (3.6 g, 97%, R_f 0.64, EtOAc/hex = 1/4).

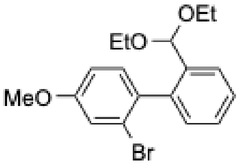
^{1}H-NMR (C_6D_6, 400 MHz) δ 7.76 (d, *J* = 8.4 Hz, 1H), 7.39 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.19 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.07 (d, *J* = 2.0 Hz, 1H), 7.00 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.88 (dt, *J* = 7.2, 1.2 Hz, 1H), 6.75-6.70 (m, 1H), 5.21 (s, 1H), 3.39 (dq, *J* = 9.2, 7.2 Hz, 2H), 3.29 (dq, *J* = 9.2, 7.2 Hz, 1H), 3.12 (dq, *J* = 9.2, 6.8 Hz, 1H), 1.06 (t, *J* = 6.8 Hz, 3H), 0.97 (t, *J* = 6.8 Hz, 3H); **^{13}C-NMR** (C_6D_6, 100 MHz) δ 141.8, 140.1, 136.1, 133.7, 132.3, 131.6, 129.7, 129.1, 128.2, 126.6, 123.2, 99.5, 62.0, 61.2, 15.0, 14.9; **HRMS (ESI-TOF)** *m/z*: [M+H]$^+$ calcd for $C_{17}H_{19}BrClO_2^+$:369.0257, found: 369.0259.



2’-Bromo-5’-methoxy-2-(diethoxymethyl)-1,1'-biphenyl (S3c)

Following GP-3, 2′-bromo-5’-methoxy-(1,1′-biphenyl]-2-carboxaldehyde (9.2 mmol) was used. The title compound was isolated as a colorless oil (2.7 g, 81%, R_f 0.58, EtOAc/hex = 3/7).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.74 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.44 (dt, *J* = 7.2, 1.2 Hz, 1H), 7.38 (dt, *J* = 7.2, 1.2 Hz, 1H), 7.15 (dd, *J* = 1.2, 7.2 Hz, 1H), 6.85-6.79 (m, 2H), 5.13 (s, 1H), 3.78 (s, 3H), 3.58 (dq, *J* = 9.2, 7.2 Hz, 1H), 3.51 (dq, *J* = 9.2, 7.2 Hz, 1H), 3.43 (dq, *J* = 9.2, 7.2 Hz, 1H), 3.27 (dq, *J* = 9.2, 7.2 Hz, 1H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 158.5, 142.0, 140.4, 137.0, 133.1, 129.7, 128.23, 128.19, 126.1, 117.0, 115.5, 113.9, 100.3, 62.7, 62.4, 55.6, 15.23, 15.20; **HRMS (ESI-TOF)** *m/z*: [M+H]$^+$ calcd for $C_{18}H_{22}BrO_3^+$:365.0752, found: 365.0752.

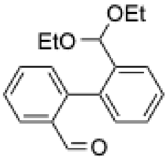


2’-Bromo-4’-methoxy-2-(diethoxymethyl)-1,1'-biphenyl (S3d)

Following GP-3, 2′-bromo-4’-methoxy-(1,1′-biphenyl]-2-carboxaldehyde (15.0 mmol) was used. The title compound was isolated as a colorless oil (4.9 g, 90%, R_f 0.55, EtOAc/hex = 3/7).

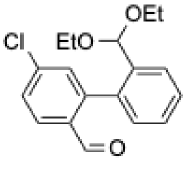
^{1}H-NMR (C_6D_6, 400 MHz) δ 8.04 (d, *J* = 7.6 Hz, 1H), 7.34-7.15 (m, 5H), 6.70 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.43 (s, 1H), 3.62-3.47 (m, 2H), 3.45 (dq, *J* = 9.6, 7.2 Hz, 1H), 3.31 (dq, *J* = 9.2, 7.2 Hz, 1H), 3.19 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H); **^{13}C-NMR** (C_6D_6, 100 MHz) δ 159.9, 140.5, 138.2, 134.0, 132.7, 130.7, 128.2, 128.0, 127.0, 124.2, 117.6, 113.5, 100.5, 62.2, 61.6, 55.0, 15.5, 15.4; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{18}H_{22}BrO_3^+$: 365.0752, found: 365.0751.

General procedure for the preparation of 2’-(diethoxymethyl)-(1,1'-biphenyl)-2-carbaldehyde derivatives (GP-4)



To a flame dried 50 mL three-necked flask equipped with a dropping funnel, magnetic stir bar, and rubber septum was attached to a double manifold and cooled under vacuum. After the flask was backfilled with argon, 2-bromo-2'-diethoxymethyl-1,1'-biphenyl (938.4 mg, 3.3 mmol) and THF (10 mL) were added, and the flask was cooled to –78 °C. While stirring, *n*-BuLi (1.6 M in hexane, 2.27 mL, 6,96 mmol) was added dropwise via dropping funnel over 0.5 h. *N*,*N*-Dimethylformamide（50.38 µL, 2.27 mmol) was added dropwise via dropping funnel over 15 minutes at –78 °C. After the addition was complete, the flask was warmed to room temperature and stirred for 1 h. The rubber septum was removed, and the reaction was quenched by saturated aqueous NH_4Cl (10 mL). The reaction was poured into a separatory funnel, and the product was extracted with Et_2O (2 × 10 mL) and washed with brine. The organic layer was dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. The residue was purified by flash chromatography on silica gel to afford the product as a yellow oil (780.0 mg, 81%, R_f 0.49, EtOAc/hex = 1/4).

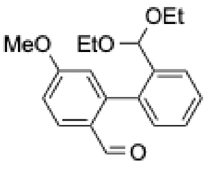
^{1}H-NMR (CD_3OD, 400 MHz) δ 9.58 (s, 1H), 7.99 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.70 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.70 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.60-7.55 (m, 1H), 7.50 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.44 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.36 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.25 (dd, *J* = 7.6, 1.2 Hz, 1H), 5.01 (s, 1H), 3.48 (dq, *J* = 9.2, 6.8 Hz, 1H), 3.43 (dq, *J* = 9.2, 6.8 Hz, 1H), 3.32 (dq, *J* = 9.2, 6.8 Hz, 1H), 3.13 (dq, *J* = 9.6, 7.2 Hz, 1H), 1.12 (t, *J* = 7.6 Hz, 3H), 0.97 (t, *J* = 7.6 Hz, 3H); **^{13}C-NMR** (CD_3OD, 100 MHz) δ 193.1, 145.4, 138.8, 138.5, 135.7, 134.6, 131.9, 131.3, 129.3, 127.7, 127.2, 101.7, 63.9, 63.2, 15.4, 15.0; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{18}H_{21}O_3^+$:285.1491, found: 285.1488.



5-Chloro-2’-(diethoxymethyl)-(1,1'-biphenyl)-2-carbaldehyde

Following GP-4, 2’-bromo-5’-chloro-2-(diethoxymethyl)-1,1'-biphenyl (9.6 mmol) was used. The title compound was isolated as a yellow oil (2.5 g, 86%, R_f 0.53, EtOAc/hex = 1/4).

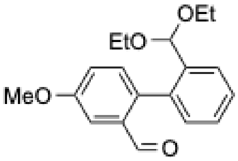
^{1}**H-NMR** (C_6D_6, 400 MHz) δ 9.61 (d, *J* = 0.8 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.76-7.72 (dm, *J* = 8.0 Hz, 1H), 7.50-7.46 (m, 2H), 7.39 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.20 (dd, *J* = 7.6, 1.2 Hz, 1H), 5.04(s, 1H), 3.54 (dq, *J* = 9.2, 7.2 Hz, 1H), 3.41 (dq, *J* = 9.2, 7.2 Hz, 1H), 3.34 (dq, *J* = 9.6, 6.8 Hz, 1H), 3.22 (dq, *J* = 9.2, 6.8 Hz, 1H), 1.16 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H); ^{13}**C-NMR** (C_6D_6, 100 MHz) δ 190.8, 145.7, 139.5, 137.5, 135.6, 132.8, 130.9, 130.3, 128.8, 128.6, 128.4, 128.3, 126.6, 100.2, 62.8, 61.9, 15.1, 14.8; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{18}H_{20}ClO_3^+$:319.1101, found: 319.1101.



5-Methoxy-2’-(diethoxymethyl)-(1,1'-biphenyl)-2-carbaldehyde

Following GP-4, 2’-bromo-5’-methoxy-2-(diethoxymethyl)-1,1'-biphenyl (9.6 mmol) was used. The title compound was isolated as a yellow solid (1.7 g, 73%, R_f 0.48, EtOAc/hex = 3/7).

^{1}**H-NMR** ($CDCl_3$, 400 MHz) δ 9.54 (d, *J* = 0.8 Hz, 1H), 8.02 (d, *J* = 8.8 Hz, 1H), 7.75 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.47 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.38 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.21 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.02 (ddd, *J* = 8.8, 2.8, 0.8 Hz, 1H), 6.81 (d, *J* = 2.8 Hz, 1H), 5.09 (s, 1H), 3.88 (s, 3H), 3.54 (dq, *J* = 9.2, 7.2 Hz, 1H), 3.42 (dq, *J* = 9.2, 6.8 Hz, 1H), 3.34 (dq, *J* = 9.2, 6.8 Hz, 1H), 3.24 (dq, *J* = 9.2, 7.2 Hz, 1H), 1.15 (t, *J* = 7.2 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H); ^{13}**C-NMR** ($CDCl_3$, 100 MHz) δ 190.8, 163.4, 146.6, 137.5, 137.0, 130.2, 129.4, 128.5, 128.24, 128.15, 126.4, 115.5, 114.4, 100.1, 62.5, 62.1, 55.8, 15.2, 14.9; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{19}H_{23}O_4^+$:315.1596, found: 315.1595.

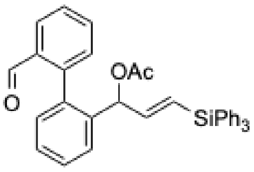


4-Methoxy-2’-(diethoxymethyl)-(1,1'-biphenyl)-2-carbaldehyde

Following GP-4, 2’-bromo-4’-methoxy-2-(diethoxymethyl)-1,1'-biphenyl (9.6 mmol) was used. The title compound was isolated as a white solid (2.7 g, 65%, R_f 0.50, EtOAc/hex = 3/7).

^{1}**H-NMR** (C_6D_6, 400 MHz) δ 9.93 (s, 1H), 7.90 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.73 (d, *J* = 2.8 Hz, 1H), 7.22 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.08 (dt, *J* = 7.6, 1.2 Hz, 1H), 7.04 (d, *J* = 8.4 Hz, 1H), 7.00 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.95 (dd, *J* = 8.4, 2.8 Hz, 1H), 5.18 (s, 1H), 3.34 (ddq, *J* = 20.0, 9.6, 7.2 Hz, 2H), 3.26 (s, 3H), 3.17 (tq, *J* = 9.2, 7.2 Hz, 2H), 1.02 (t, *J* = 7.2 Hz, 6H); ^{13}**C-NMR** (C_6D_6, 100 MHz) δ 191.0, 159.9, 138.7, 137.3, 137.1, 136.2, 132.2, 130.9, 128.2(2C), 127.1, 121.0, 109.4, 100.4, 62.4, 61.3, 55.0, 15.3, 15.0; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{19}H_{23}O_4^+$:315.1596, found: 315.1596.

General procedure for the preparation of *trans*-1-[2-(2-formylphenyl)phenyl]-3-(triphenylsilyl)prop-2-en-1-yl acetate derivatives (GP-5)



1-[2-(Dimethoxypropyl)phenyl]-3-(triphenylsilyl)prop-2-yn-1-ol

To a flame dried 50 mL three-necked flask equipped with a dropping funnel, magnetic stir bar, and rubber septum was attached to a double manifold and cooled under vacuum. After the flask was backfilled with argon, triphenylsilylacetylene[11] (3.00 g, 10.5 mmol) and THF (10 mL) were added, and the flask was cooled to –78 °C. While stirring for 0.5 h, *n*-BuLi (1.6 M in hexane, 6.02 mL, 9.64 mmol) was added dropwise via dropping funnel over 0.5 h. 2’-(Diethoxymethyl)-(1,1'-biphenyl)-2-carbaldehyde（1.83 g, 8.77 mmol) in THF (8 mL) was added via cannula at –78 °C. After the addition was complete, the flask was warmed to room temperature and stirred for 1 h. The rubber septum was removed, and the reaction was quenched by saturated aqueous NH_4Cl (5 mL). The reaction was poured into a separatory funnel, and the product was extracted with Et_2O (2 × 20 mL) and washed with brine. The organic layer was dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*, which was used without the necessity of purification (R_f = 0.42, EtOAc/hex = 3/7).

trans-1-[2-(Dimethoxypropyl)phenyl]-3-(triphenylsilyl)prop-2-en-1-ol

To a flame dried 100 mL three-necked flask equipped with a dropping funnel, magnetic stir bar, and rubber septum was attached to a double manifold and cooled under vacuum. After the flask was backfilled with argon, crude 1-[2-(dimethoxypropyl)phenyl]-3-(triphenylsilyl)-2-propyn-1-ol (8.77 mmol) and THF (23 mL) were added, and the flask was cooled to –10 °C. While stirring for 0.5 h, Red-Al（3.6 M in toluene, 3.7 mL, 13.2 mmol) was added dropwise via dropping funnel over 15 minutes. After the addition was complete, the flask was warmed to room temperature and stirred for 12 h. The rubber septum was removed, and the reaction was quenched by saturated aqueous Rochelle salt (10.0 mL) at 0 °C.

The reaction was poured into a separatory funnel, and the product was extracted with Et_2O (2 × 20 mL) and washed with brine. The organic layer was dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*, which was used without the necessity of purification (R_f 0.42, EtOAc/hex = 3/7).

trans-1-[2-(Dimethoxypropyl)phenyl]-3-(triphenylsilyl)prop-2-en-1-yl acetate

To a solution of crude *trans*-1-[2-(dimethoxypropyl)phenyl]-3-(triphenylsilyl)prop-2-en-1-ol (5.0 g, 8.77 mmol), DMAP (89.8 mg, 0.74 mmol) and Et_3N (1.33 mL, 9.55 mmol) in dichloromethane (17 mL) was added acetic acid anhydride (0.83 mL, 8.82 mmol) at 0 °C under a nitrogen atmosphere. After stirring at room temperature for 3 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (10 mL). The aqueous phase was extracted with chloroform (2 × 20 mL), and the combined organic extracts were washed with brine (2 × 20 mL). After the organic layer was dried over $MgSO_4$, the solvent was removed under reduced pressure. The residue was used without the necessity of purification (R_f 0.34, EtOAc/hexane = 1/4).

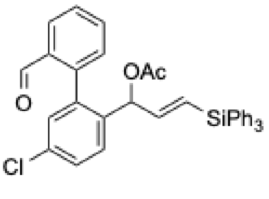
(*E*)-1-[2-(2-Formylphenyl)phenyl]-3-(triphenylsilyl)prop-2-en-1-yl acetate (1a)

To a 100 mL two-necked flask equipped with magnetic stirring bar and reflux condenser was added crude *trans*-1-[2-(dimethoxypropyl)phenyl]-3-(triphenylsilyl)prop-2-en-1-yl acetate (8.77 mmol), acetic acid (80% aq., 20 mL), and THF (8 mL). After stirring at 60 °C in an oil-bath for 3 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (5 mL).

The aqueous phase was extracted several times with EtOAc and washed with brine. The organic phases were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the product as a brown oil (2.9 g, 5.3 mmol, 61% over 4 steps, R_f = 0.49, EtOAc/hex = 3/7).

Major isomer: **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.72 (s, 1H), 8.06 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.56–7.34 (m, 20H), 7.21 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.11 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.25 (d, *J* = 18.4 Hz, 1H), 6.19 (dd, *J* = 18.4, 3.6 Hz, 1H), 5.98 (d, *J* = 3.6 Hz, 1H), 1.98 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 192.0, 169.5, 147.9, 143.6, 137.48, 137.46, 136.0, 134.1, 133.9, 133.1, 131.0, 130.6, 129.81, 128.9, 128.5, 128.03, 127.8, 127.4, 127.3, 126.3, 74.8, 20.9.

Minor isomer: **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.57 (s, 1H), 7.93 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.56–7.34 (m, 21H), 7.17 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.27 (d, *J* = 4.4 Hz, 1H), 6.10 (d, *J* = 18.0, 1H), 6.01 (dd, *J* = 18.0, 4.4 Hz, 1H), 2.06 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 191.4, 169.6, 147.5, 143.6, 137.1, 137.0, 135.9, 134.4, 133.7, 133.4, 131.3, 129.76, 128.8, 128.3, 127.99, 127.64, 127.60, 75.5, 21.2; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{36}H_{31}O_3Si^+$: 539.2042, found: 539.2035.

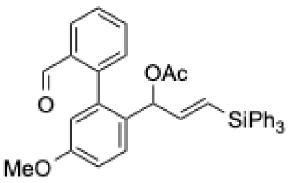


trans-1-[4-Chloro-2-(2-formylphenyl)phenyl]-3-(triphenylsilyl)prop-2-en-1-yl acetate (1m)

Following GP-5, 1-[4-chloro-2-(diethoxymethyl)phenyl]-3-(triphenylsilyl)prop-2-yn-1-ol (2.5 g, 7.9 mmol) was used. The title compound was isolated as a white amorphous solid (2.6 g, 57% over four steps, R_f 0.33, EtOAc/hex = 1/4).

Major isomer: **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.63 (d, *J* = 0.4 Hz, 1H), 7.94 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.41-7.18 (m, 18H), 7.15-7.05 (m, 2H), 6.94 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.11 (dd, *J* = 18.4, 1.2 Hz, 1H), 6.01 (dd, *J* = 18.4, 4.4 Hz, 1H), 5.78 (dd, *J* = 4.4, 0.8 Hz, 1H), 1.86 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 191.4, 169.4, 147.4, 141.9, 139.2, 136.2, 136.0, 135.1, 134.0, 133.80, 133.7, 133.3, 130.88, 130.3, 129.9, 129.1, 128.93, 128.7, 128.1, 127.8, 126.95, 74.2, 20.9.

Minor isomer: **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.50 (d, *J* = 0.4 Hz, 1H), 7.79 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.54-7.48 (m, 1H), 7.44 (dt, *J* = 7.6, 1.6 Hz, 1H), 7.41-7.18 (m, 19H), 6.05 (dd, *J* = 5.2, 0.8 Hz, 1H), 5.99 (dd, *J* = 18.4, 1.2 Hz, 1H), 5.86 (dd, *J* = 18.4, 5.2 Hz, 1H), 1.91 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 190.8, 169.5, 146.9, 141.8, 139.0, 135.9, 135.8, 134.3, 133.83, 133.62, 133.57, 130.94, 130.8, 129.8, 129.00, 128.98, 128.8, 128.3, 128.03, 127.97, 127.03, 74.9, 21.1; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{36}H_{30}ClO_3Si^+$: 573.1653, found: 573.1658.

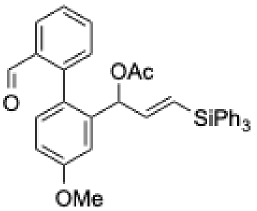


***trans*-1-[2-(2-Formylphenyl)-4-methoxyphenyl]-3-(triphenylsilyl)prop-2-en-1-yl acetate (1n)**

Following GP-5, 1-[4-methoxy-2-(diethoxymethyl)phenyl]-3-(triphenylsilyl)prop-2-yn-1-ol (1.7 g, 5.4 mmol) was used. The title compound was isolated as a white amorphous solid (1.2 g, 39% over four steps, R_f 0.42, EtOAc/hex = 3/7).

Major isomer: **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.74 (s, 1H), 7.60-7.30 (m, 19H), 7.14 (dd, *J* = 6.8, 2.0 Hz, 1H), 6.99 (dd, *J* = 8.8, 3.2 Hz, 1H), 6.74 (d, *J* = 2.8 Hz, 1H), 6.23 (d, *J* = 18.8 Hz, 1H), 6.20 (d, *J* = 3.2 Hz, 1H), 5.91 (d, *J* = 3.6 Hz, 1H), 3.81 (s, 3H), 1.96 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 192.1, 169.5, 158.89, 148.3, 139.0, 136.02, 134.2, 134.0, 133.2, 130.8, 129.81, 129.6, 129.1, 128.5, 128.1, 127.3, 125.8, 115.7, 114.7, 74.5, 55.51, 21.0; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{37}H_{33}O_4Si^+$: 569.2148, found: 569.2141.

Minor isomer: **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.62 (s, 1H), 8.05 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.95 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.60-7.30 (m, 17H), 6.98 (d, *J* = 8.8 Hz, 1H), 6.70 (d, *J* = 2.8 Hz, 1H), 6.16 (d, *J* = 4.4 Hz, 1H), 6.09 (d, *J* = 19.2 Hz, 1H), 6.01 (dd, *J* = 18.4, 4.8 Hz, 1H), 3.80 (s, 3H), 2.03 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 191.5, 169.6, 158.91, 148.0, 143.6, 138.6, 135.98, 134.4, 133.9, 133.4, 131.0, 129.77, 129.38, 129.44, 128.4, 128.0, 127.4, 116.3, 114.6, 75.2, 55.49, 21.2.



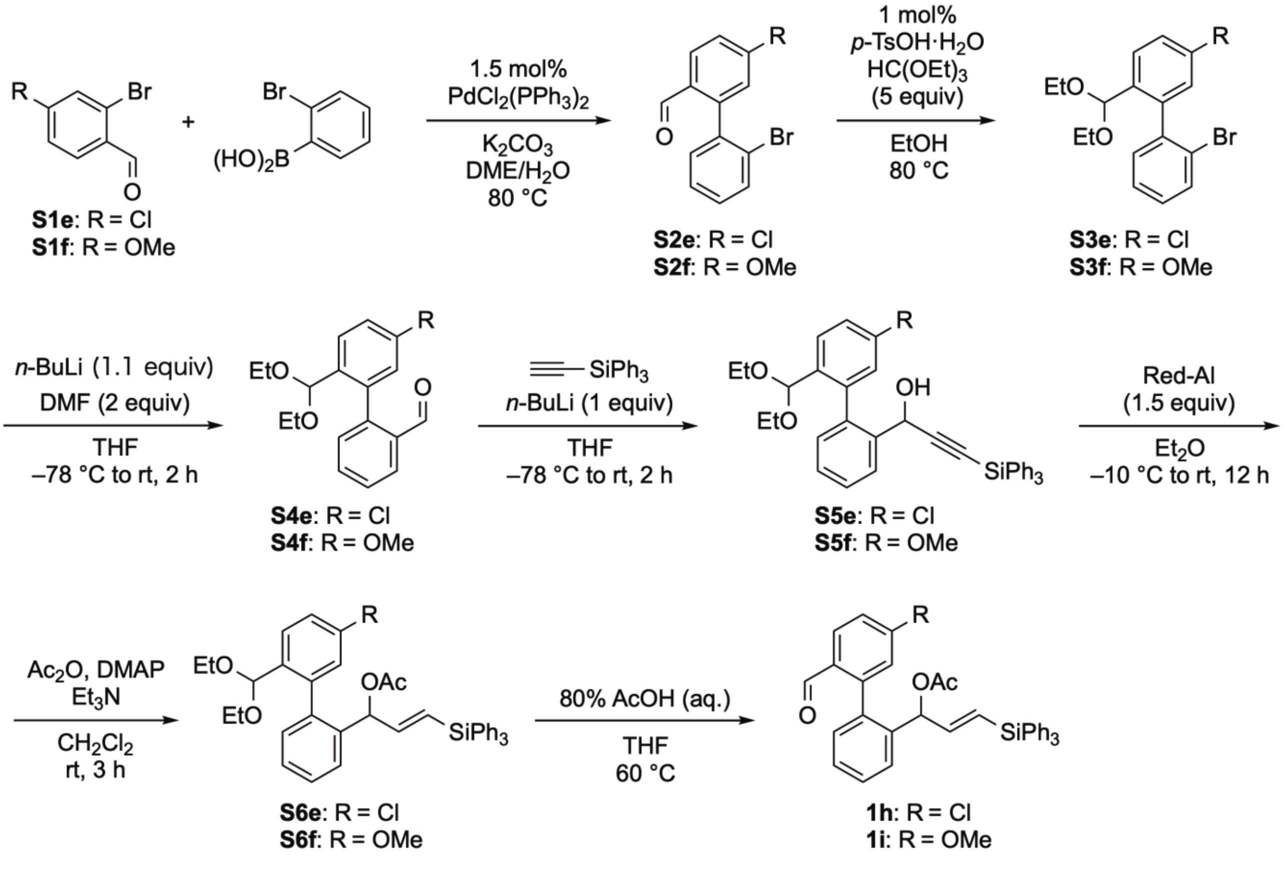
***trans*-1-[2-(2-Formylphenyl)-5-methoxyphenyl]-3-(triphenylsilyl)prop-2-en-1-yl acetate (1o)**

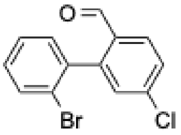
Following GP-5, 1-[5-methoxy-2-(diethoxymethyl)phenyl]-3-(triphenylsilyl)prop-2-yn-1-ol (2.7 g, 8.7 mmol) was used. The title compound was isolated as a white amorphous solid (2.4 g, 52% over four steps, R_f 0.44, EtOAc/hex = 3/7).

Major isomer: **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.73 (d, *J* = 0.4 Hz, 1H), 8.03 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.50-7.31 (m, 17H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.08 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.00 (d, *J* = 2.8 Hz, 1H), 6.91 (dd, *J* = 5.6, 2.8 Hz, 1H), 6.25 (dd, *J* = 18.4, 1.2 Hz, 1H), 6.17 (dd, *J* = 18.4, 4.0 Hz, 1H), 5.93 (dd, *J* = 4.4, 0.8 Hz, 1H), 3.837 (s, 3H), 1.98 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 192.3, 169.5, 159.91, 147.8, 143.5, 138.8, 136.0, 134.6, 133.9, 133.1, 131.6, 129.84, 129.75, 128.3, 128.1, 127.3, 126.4, 113.5, 112.6, 74.8, 55.5, 21.0; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{37}H_{33}O_4Si^+$: 569.2148, found: 569.2148.

Minor isomer: **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.58 (d, *J* = 0.4 Hz, 1H), 7.91 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.55 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.50-7.31 (m, 17H), 7.07 (d, *J* = 8.4 Hz, 1H), 7.02 (d, *J* = 2.8 Hz, 1H), 6.89 (dd, *J* = 5.6, 2.8 Hz, 1H), 6.24 (dd, *J* = 4.8, 1.2 Hz, 1H), 6.09 (dd, *J* = 18.4, 1.2 Hz, 1H), 5.98 (dd, *J* = 18.4, 4.8 Hz, 1H), 3.844 (s, 3H), 2.07 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 191.7, 169.6, 159.86, 147.3, 138.5, 135.9, 134.8, 133.8, 133.4, 132.6, 131.8, 129.79, 129.1, 128.2, 128.0, 127.7, 126.5, 113.3, 113.0, 75.4, 55.5, 21.2.

Preparation of substrates 1h and 1i



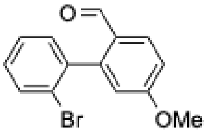


2'-Bromo-4-chloro-1,1'-biphenyl-2-carbaldehyde (S2e, CAS: 1553425-36-7)

Following GP-2, 2-bromo-4-chlorobenzaldehyde (2.19 g, 10.0 mmol) was reacted with 2-bromophenylboronic acid (2.16 g, 15 mmol). The title compound was isolated as a colorless oil (2.7 g, 92%, R*f* 0.43, EtOAc/hex = 1/4).

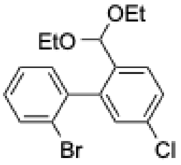
^{1}**H-NMR** ($CDCl_3$, 400 MHz) δ 9.72 (d, *J* = 0.8, 1H), 7.98 (d, *J* = 8.4, 1H), 7.73-7.67 (m, 1H), 7.52 (ddd, *J* = 8.4, 2.0, 0.8, 1H), 7.46-7.40 (m, 1H), 7.37-7.29 (m, 3H).

2'-Bromo-5-methoxy-1,1'-biphenyl-2-carbaldehyde (S2f, CAS: 1997993-98-2)



Following GP-2, 2-bromo-4-methoxybenzaldehyde (2.24 g, 10.4 mmol) was reacted with 2-bromophenylboronic acid (2.16 g, 15 mmol). The title compound was isolated as a colorless oil (1.7 g, 56%, R*f* 0.59, EtOAc/hex = 3/7).

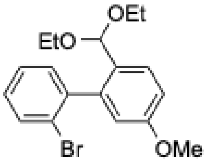
^{1}**H-NMR** ($CDCl_3$, 400 MHz) δ 9.74 (s, 1H), 7.68 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.52 (d, *J* = 2.4 Hz, 1H), 7.42-7.40 (m, 2H), 7.33-7.28 (m, 2H), 7.27-7.22 (m, 1H), 3.92 (s, 3H).



2’-Bromo-5-chloro-2-(diethoxymethyl)-1,1'-biphenyl (S3e)

Following GP-3, 2'-bromo-5’-chloro-(1,1'-biphenyl)-2-carbaldehyde (9.2 mmol) was used. The title compound was isolated as a colorless oil (3.3 g, 96%, R*f* = 0.57, EtOAc/hex = 1/4).

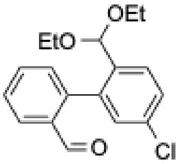
^{1}**H-NMR** (C_6D_6, 400 MHz) δ 7.76 (d, *J* = 8.4 Hz, 1H), 7.39 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.19 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.07 (d, *J* = 2.0 Hz, 1H), 7.00 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.88 (dt, *J* = 7.2, 1.2 Hz, 1H), 6.75-6.70 (m, 1H), 5.21 (s, 1H), 3.39 (dq, *J* = 9.2, 7.2 Hz, 2H), 3.29 (dq, *J* = 9.2, 7.2 Hz, 1H), 3.12 (dq, *J* = 9.2, 6.8 Hz, 1H), 1.06 (t, *J* = 6.8 Hz, 3H), 0.97 (t, *J* = 6.8 Hz, 3H); ^{13}**C-NMR** (C_6D_6, 100 MHz) δ 141.8, 140.1, 136.1, 133.7, 132.3, 131.6, 129.7, 129.1, 128.2, 126.6, 123.2, 99.5, 62.0, 61.2, 15.0, 14.9; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{17}H_{19}BrClO_2^+$: 369.0257, found: 369.0261.



2’-Bromo-5-methoxy-2-(diethoxymethyl)-1,1'-biphenyl (S3f)

Following GP-3, 2'-bromo-5-methoxy-(1,1'-biphenyl)-2-carbaldehyde (6.0 mmol) was used. The title compound was isolated as a colorless oil (2.2 g, 100%, R_f 0.58, EtOAc/hex = 1/4).

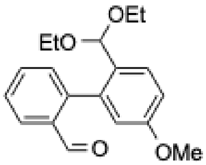
^{1}**H-NMR** (C_6D_6, 400 MHz) δ 7.66 (d, *J* = 2.8 Hz, 1H), 7.51 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.27 (dd, *J* = 7.6, 2.4 Hz, 1H), 7.05 (d, *J* =8.4 Hz, 1H), 6.97 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.83-6.76 (m, 2H), 5.32 (s, 1H), 3.53 (dq, *J* = 9.2, 6.8 Hz, 1H), 3.47 (dq, *J* = 9.6, 7.2 Hz, 1H), 3.39 (dq, *J* = 9.2, 6.8 Hz, 1H), 3.33 (s, 3H), 3.24 (dq, *J* = 9.2, 6.8 Hz, 1H), 1.10 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H); ^{13}**C-NMR** (C_6D_6, 100 MHz) δ 160.0, 141.9, 139.2, 133.1, 132.72, 132.70, 131.3, 129.0, 126.9, 124.7, 114.3, 112.0, 100.5, 62.4, 61.8, 54.9, 15.4; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{18}H_{22}BrO_3^+$: 365.0752, found: 365.0752.



5’-Chloro-2’-(diethoxymethyl)-(1,1'-biphenyl)-2-carbaldehyde (S4e)

Following GP-4 2’-bromo-5-chloro-2-(diethoxymethyl)-1,1'-biphenyl (8.0 mmol) was used. The title compound was isolated as a white solid (mp 61.1-62.4 °C, 2.5 g, 86%, R_f 0.53, EtOAc/hex = 1/4).

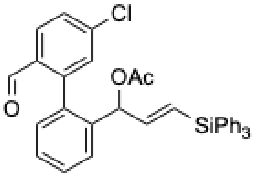
^{1}**H-NMR** (C_6D_6, 400 MHz) δ 9.76 (d, *J* = 0.4 Hz, 1H), 8.08-8.06 (m, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.20-7.10 (m, 1H), 7.08-6.99 (m, 2H), 6.92 (d, *J* = 2.4 Hz, 1H), 6.85-6.82 (m, 1H), 4.95 (s, 1H), 3.25-3.17 (m, 2H), 3.07-2.97 (m, 2H), 0.95 (dt, *J* = 14.8, 7.2 Hz, 6H); ^{13}**C-NMR** (C_6D_6, 100 MHz) δ 190.5, 142.5, 139.3, 136.9, 135.0, 134.1, 132.9, 130.6, 130.1, 128.6, 128.5, 128.4, 126.8, 99.8, 62.5, 61.4, 15.2, 14.9; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{18}H_{20}ClO_3^+$: 319.1101, found: 319.1109.



5’-Methoxy-2’-(diethoxymethyl)-(1,1'-biphenyl)-2-carbaldehyde (S4f)

Following GP-4, 2’-bromo-5-methoxy-2-(diethoxymethyl)-1,1'-biphenyl (6.0 mmol) was used. The title compound was isolated as a yellow oil (1.2 g, 61%, R_f = 0.42, EtOAc/hex = 1/4).

^{1}**H-NMR** (C_6D_6, 400 MHz) δ 10.00 (d, *J* = 0.8 Hz, 1H), 8.16 (ddd, *J* = 7.6, 1.6, 0.4 Hz, 1H), 7.53 (d, *J* = 2.8 Hz, 1H), 7.22-7.08 (m, 3H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.73 (dd, *J* = 8.4, 2.8 Hz, 1H), 5.10 (s, 1H), 3.38 (s, 3H), 3.37-3.27 (m, 2H), 3.19-3.06 (m, 2H), 0.99 (q, *J* = 6.8 Hz, 6H); ^{13}**C-NMR** (C_6D_6, 100 MHz) δ 191.4, 160.1, 144.4, 139.7, 135.6, 132.9, 131.6, 131.5, 129.5, 127.0, 114.2, 112.2, 100.5, 62.5, 61.7, 54.9, 15.3, 15.0; **HRMS (ESI-TOF)** *m/z*: [M+H]$^+$ calcd for $C_{19}H_{23}O_4^+$: 315.1596, found: 315.1595.

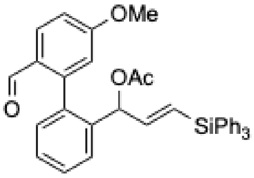


***trans*-1-[2-(5-Chloro-2-formylphenyl)phenyl]-3-(triphenylsilyl)prop-2-en-1-yl acetate (1h)**

Following GP-4, crude 1-[2-(5-chloro-2-diethoxymethylphenyl)phenyl]-3-(triphenylsilyl)prop-2-yn-1-ol (8.0 mmol) was used. The title compound was isolated as a white amorphous solid (660.0 mg, 68% over four steps, R_f 0.33, EtOAc/hex = 1/4).

Major isomer: ^{1}**H-NMR** ($CDCl_3$, 400 MHz) δ 9.62 (d, *J* = 0.8 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.54-7.33 (m, 19H), 7.21-7.13 (m, 2H), 6.29 (dd, *J* = 18.8, 0.8 Hz, 1H), 6.21 (dd, *J* = 18.8, 4.0 Hz, 1H), 5.94 (dd, *J* = 4.0, 0.8 Hz, 1H), 1.98 (s, 3H); ^{13}**C-NMR** ($CDCl_3$, 100 MHz) δ 190.8, 169.6, 147.9, 145.1, 139.4, 137.5, 136.1, 136.0, 133.8, 132.7, 130.9, 130.5, 129.86, 129.34, 128.93, 128.2, 127.89, 127.0, 74.8, 21.0.

Minor isomer: ^{1}**H-NMR** ($CDCl_3$, 400 MHz) δ 9.51 (d, *J* = 0.8 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.54-7.33 (m, 20H), 7.21-7.13 (m, 1H), 6.20 (dd, *J* = 4.8, 0.8 Hz, 1H), 6.14 (dd, *J* = 18.4, 1.2 Hz, 1H), 6.03 (dd, *J* = 18.4, 4.8 Hz, 1H), 2.08 (s, 3H); ^{13}**C-NMR** ($CDCl_3$, 100 MHz) δ 190.1, 169.6, 147.2, 145.0, 139.8, 137.1, 135.9, 135.7, 133.7, 132.8, 131.2, 131.0, 129.82, 129.29, 129.15, 128.87, 128.04, 126.7, 75.1, 21.1; **HRMS (ESI-TOF)** *m/z*: [M+H]$^+$ calcd for $C_{36}H_{30}ClO_3Si^+$: 573.1653, found: 573.1649.



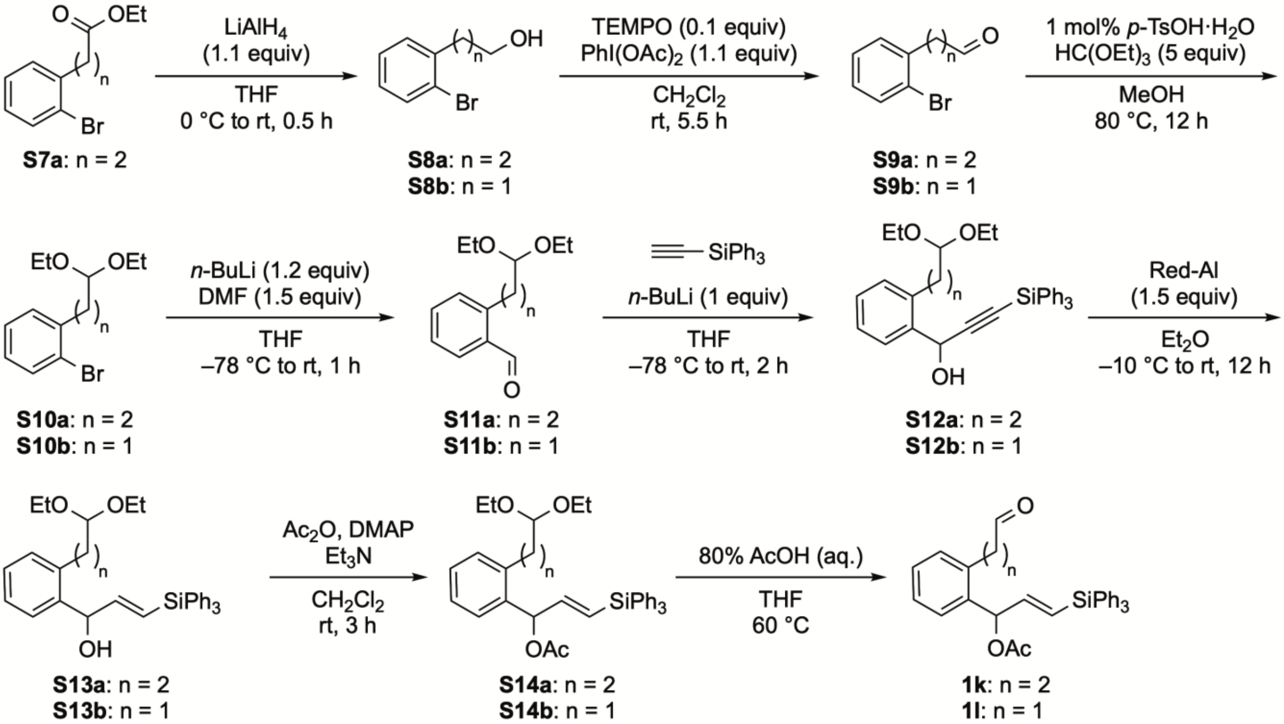
***trans*-1-[2-(2-formyl-5-metrhoxyphenyl)phenyl]-3-(triphenylsilyl)prop-2-en-1-yl acetate (1i)**

Following GP-4, crude 1-[2-(2-diethoxymethyl-5-chlorophenyl)phenyl]-3-(triphenylsilyl)prop-2-yn-1-ol (6.0 mmol) was used. The title compound was isolated as a white amorphous solid (733.7 mg 68% over four steps, R_f 0.48, EtOAc/hex = 1/4).

Major isomer: ^{1}**H-NMR** ($CDCl_3$, 400 MHz) δ 9.69 (s, 1H), 7.57 (t, *J* = 1.6 Hz, 1H), 7.55-7.32 (m, 17H), 7.19 (ddd, *J* = 17.2, 7.6, 0.8 Hz, 2H), 7.03 (d, *J* = 1.6 Hz, 2H), 6.32-6.20 (m, 2H), 6.00 (d, *J* = 3.6 Hz, 1H), 3.91 (s, 3H), 2.01 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 192.0, 169.6, 159.6, 148.1, 138.0, 137.2, 136.47, 136.0, 135.1, 133.9. 132.3, 131.1, 129.83, 128.80, 128.1, 127.8, 126.32, 120.9, 109.7, 75.0, 55.7, 21.0.

Minor isomer: **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.53 (s, 1H), 7.55-7.32 (m, 21H), 7.16 (dd, *J* = 8.4, 2.8 Hz, 1H), 6.21 (dd, *J* = 18.8, 3.6 Hz, 1H), 6.14 (dd, *J* = 18.8, 1.2 Hz, 1H), 6.04 (dd, *J* = 18.8, 4.8 Hz, 1H), 3.89 (s, 3H), 2.08 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 191.3, 169.7, 159.5, 147.7, 137.6, 136.7, 136.53, 135.9, 135.4, 133.8, 131.8, 129.78, 128.75, 128.0, 127.6, 127.3, 126.29, 121.1, 110.1, 75.5, 55.6, 21.2; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{37}H_{32}O_4Si^+$: 569.2148, found: 569.2147.

Preparation of substrates 1k and 1n



3-(2-Bromophenyl)propan-1-ol (S8a, CAS: 52221-92-8)

Under argon atmosphere, the crude ethyl 3-(2-bromophenyl)propanoate (**S7a**, 20 mmol) was dissolved in THF (20 mL) and added to a suspension of $LiAlH_4$ (868 mg, 22.9 mmol) in THF (30 mL) at 0 °C and allowed to warm to rt. After 0.5 h, the mixture was cooled to 0 °C and then quenched with saturated aqueous Rochelle salt (10 mL). The solid material was filtered. The filtrate was extracted with EtOAc (2 × 50 mL), washed with H_2O (2 × 50 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure, which was used without the necessity of purification (R_f 0.30, EtOAc/hex = 3/7).

3-(2-Bromophenyl)ethan-1-ol (S8b, CAS: 1074-16-4)

Following the procedure of **S8a**, **S8b** was synthesized and used without the necessity of purification.

3-(2-Bromophenyl)propionaldehyde (S9a, CAS: 107408-16-2)

To a 50 mL two-necked flask equipped with a magnetic stirring bar and reflux condenser was added TEMPO (238 mg, 1.52 mmol), PhI(OAc)$_2$ （7.12 g, 22.1 mmol）, and CH_2Cl_2 (15 mL) under argon atmosphere. To this mixture was added crude 3-(2-bromophenyl)propan-1-ol (**S8a**, 20 mmol as crude) in CH_2Cl_2 (8 mL) via cannula. After stirring at room temperature for 5 h, the mixture was quenched with saturated aqueous sodium thiosulfate (20 mL). The aqueous phase was extracted twice with chloroform (2 × 20 mL) and washed with brine. The organic phases were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the product as a brown oil (3.05 g, 14.3 mmol, 72% for three steps, R_f 0.51, EtOAc/hex = 3/7).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 9.84 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.33-7.18 (m. 2H), 7.14-7.05 (m, 1H), 3.08 (t, *J* = 7.6 Hz, 2H), 2.82 (t, *J* = 7.6 Hz, 2H).

The ^{1}H NMR spectrum of title compound was identical with that reported in the literature.[12]

(2-Bromophenyl)acetaldehyde (S9b, CAS: 96557-30-1)

Following the procedure of **S9a**, **S9b** was purified by silica gel column chromatography (10.0 mmol scale reaction, yellow oil, 888.3 mg, 4.5 mmol, 45%, R_f 0.40, EtOAc/hex = 1/4).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 9.76 (t, *J* = 2.0 Hz, 1H), 7.63 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.32 (dt, *J* =7.2, 1.2 Hz, 1H), 7.27-7.15 (m, 2H), 3.87 (d, *J* = 1.6 Hz, 2H).

Spectroscopic data were consistent with the values reported in the literature.[13]

1-Bromo-2-(3,3-diethoxypropyl)benzene (S10a, CAS: 595577-75-6)

To a 100 mL two-necked flask equipped with magnetic stirring bar and reflux condenser was added crude 3-(2-bromophenyl)propionaldehyde (**S9a**, 3.05 g, 14.3 mmol), trimethyl orthoformate (7.8 mL, 71.5 mmol), and *p*-TsOH·H_2O (27.22 mg, 0.14 mmol) in MeOH (30 mL) was stirred at 80 °C for 12 h. After cooling to room temperature, water was added, and the solution was neutralized with saturated aqueous Na_2CO_3. The aqueous phase was extracted several times with EtOAc and washed with brine. The organic phases were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the product as a brown oil (3.5g, 64% over 3 steps, R_f 0.64, EtOAc/hex = 3/7).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.30-7.15 (m, 2H), 7.07-7.02 (m, 1H), 4.53 (t, *J* = 6.0 Hz, 1H), 3.72-3.40 (m, 4H), 2.84-2.77 (m, 2H), 1.98-1.90 (m, 2H), 1.25-1.20 (m, 6H).

Spectroscopic data were consistent with the values reported in the literature.[14]

1-Bromo-2-(2,2-diethoxyethyl)benzene (S10b)

Following the procedure of **S10a**, **S10b** was purified by silica gel column chromatography (4.5 mmol scale reaction, yellow oil, 802.0 mg, 2.9 mmol, 65%, $R_f = 0.62$, EtOAc/hex = 1/4).

^{1}H-NMR (C_6D_6, 400 MHz) δ 7.38 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.23 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.91 (dt, *J* = 1.2, 7.6 Hz, 1H), 6.67 (dt, *J* = 1.6, 7.6 Hz, 1H), 4.78 (t, *J* = 5.2 Hz, 1H), 3.53 (dq, *J* = 9.2, 6.8 Hz, 2H), 3.27 (dq, *J* = 9.6, 6.8 Hz, 2H), 3.17 (d, *J* = 5.6 Hz, 2H), 1.04 (t, *J* = 7.2 Hz, 6H); **^{13}C-NMR** (C_6D_6, 100 MHz) δ 137.6, 132.81, 132.78, 127.3, 125.3, 102.4, 62.1, 41.4, 15.5; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{12}H_{18}BrO_2^+$: 274.1780, found: 274.1783.

2-(3,3-Diethoxypropyl)benzaldehyde (S11a)

To a flame dried 100 mL three-necked flask equipped with a dropping funnel, magnetic stir bar, and rubber septum was attached to a double manifold and cooled under vacuum.

After the flask was backfilled with argon, 3-(2-bromophenyl)propionaldehyde dimethyl acetal (**S10a**, 3.16 g, 12.2 mmol) and THF (23 mL) were added, and the flask was cooled to –78 °C. While stirring, *n*-BuLi (1.6 M in hexane, 9.83 mL, 15.7 mmol) was added dropwise via dropping funnel over 0.5 h. *N*,*N*-Dimethylformamide（1.33 mL, 17.2 mmol) was added dropwise via dropping funnel over 15 minutes at –78 °C. After the addition was complete, the flask was warmed to room temperature and stirred for 1 h. The rubber septum was removed, and the reaction was quenched by saturated aqueous NH_4Cl (20 mL). The reaction was poured into a separatory funnel, and the product was extracted with Et_2O (2 × 20 mL) and washed with brine. The organic layer was dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. The residue was purified by flash chromatography on silica gel to afford the product as a colorless oil (2.10 g, 73%, R_f 0.52, EtOAc/hex = 3/7).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ 10.3 (s, 1H), 7.82 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.50 (dt, *J* = 7.2, 1.6 Hz, 1H), 7.37 (dt, *J* = 7.2, 1.2 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 4.51 (t, *J* = 5.6 Hz, 1H), 3.66 (dq, *J* = 9.6, 7.2 Hz, 2H), 3.49 (dq, *J* = 9.2, 7.2 Hz, 2H), 3.14-3.06 (m, 2H), 1.97-1.90 (m, 2H), 1.21 (t, *J* = 7.2 Hz, 6H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 192.4, 144.7, 133.83, 133.79, 132.0, 131.1, 126.6, 102.2, 61.2 (two peaks), 35.6, 27.7, 15.4; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{14}H_{21}O_3^+$: 237.1491, found: 237.1491.

2-(3,3-Diethoxyethyl)benzaldehyde (S11b)

Following the procedure of **S11a**, 3-(2-bromophenyl)acetaldehyde diethyl acetal (581 mg, 2.9 mmol) was used. The title compound was isolated as a light yellow oil (570.9 mg, 2.6 mmol, 89%, $R_f = 0.43$, EtOAc/hex = 1/4).

^{1}H-NMR (C_6D_6/400 MHz) δ 10.16 (s, 1H), 7.66 (dm, *J* = 7.2 Hz, 1H), 7.10-7.03 (m, 2H), 6.99-6.91 (m, 1H), 4.55 (t, *J* = 5.6 Hz, 1H), 3.48 (dq, *J* = 9.2, 6.8 Hz, 2H), 3.27 (d, *J* = 5.6 Hz, 2H), 3.21 (dq, *J* = 9.2, 6.8 Hz, 2H), 1.01 (t, *J* = 7.2 Hz, 6H); **^{13}C-NMR** (C_6D_6, 100 MHz) δ 192.3, 140.3, 135.7, 133.4, 133.1, 131.6, 127.4, 104.0, 62.7, 38.1, 15.7; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{13}H_{19}O_3^+$: 223.1334, found: 223.1333.

1-[2-(Diethoxypropyl)phenyl]-3-(triphenylsilyl)-2-propyn-1-ol (S12a)

To a flame dried 50 mL three-necked flask equipped with a dropping funnel, magnetic stir bar, and rubber septum was attached to a double manifold and cooled under vacuum. After the flask was backfilled with argon, triphenylsilylacetylene[11] (3.00 g, 10.5 mmol) and THF (23 mL) were added, and the flask was cooled to – 78 °C. While stirring for 0.5 h, *n*-BuLi (1.6 M in hexane, 6.02 mL, 9.64 mmol) was added dropwise via dropping funnel over 0.5 h. 2-(3,3-Dimethoxypropyl)benzaldehyde（**S11a,** 1.83 g, 8.77 mmol) in THF (8 mL) was added via cannula at –78 °C. After the addition was complete, the flask was warmed to room temperature and stirred for 1 h. The rubber septum was removed, and the reaction was quenched by saturated aqueous NH_4Cl (5 mL). The reaction was poured into a separatory funnel, and the product was extracted with Et_2O (2 × 20 mL) and washed with brine. The organic layer was dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*, which was used without the necessity of purification (R_f 0.42, EtOAc/hex = 3/7).

1-[2-(Diethoxyethyl)phenyl]-3-(triphenylsilyl)-2-propyn-1-ol (S12b)

Following the procedure of **S12a**, **S12b** was synthesized and used without the necessity of purification.

trans-1-[2-(Diethoxypropyl)phenyl]-3-(triphenylsilyl)-2-propen-1-ol (S13a)

To a flame dried 100 mL three-necked flask equipped with a dropping funnel, magnetic stir bar, and rubber septum was attached to a double manifold and cooled under vacuum. After the flask was backfilled with argon, crude 1-[2-(dimethoxypropyl)phenyl]-3-(triphenylsilyl)-2-propyn-1-ol (**S12a**, 8.77 mmol) and THF (23 mL) were added, and the flask was cooled to –10 °C. While stirring for 0.5 h, Red-Al（3.6 M in toluene, 3.1 mL, 11.2 mmol) was added dropwise via dropping funnel over 15 minutes. After the addition was complete, the flask was warmed to room temperature and stirred for 12 h. The rubber septum was removed, and the reaction was quenched by saturated aqueous Rochelle salt (10.0 mL) at 0 °C. The reaction was poured into a separatory funnel, and the product was extracted with Et_2O (2 × 20 mL) and washed with brine. The organic layer was dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*, which was used without the necessity of purification (R_f 0.42, EtOAc/hex = 3/7).

trans-1-[2-(Diethoxyethyl)phenyl]-3-(triphenylsilyl)-2-propen-1-ol (S13b)

Following the procedure of **S13a**, **S13b** was synthesized and used without the necessity of purification.

trans-1-[2-(Diethoxypropyl)phenyl]-3-(triphenylsilyl)prop-2-en-1-yl acetate (S14a)

To a solution of crude 1-[2-(dimethoxypropyl)phenyl]-3-(triphenylsilyl)-2-propen-1-ol (**S13a**, 8.77 mmol), DMAP (89.8 mg, 0.74 mmol) and Et_3N (1.33 mL, 9.55 mmol) in dichloromethane (17 mL) was added acetic acid anhydride (0.83 mL, 8.82 mmol) at 0 °C under a nitrogen atmosphere. After stirring at room temperature for 3 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (10 mL). The aqueous phase was extracted with chloroform (2 × 20 mL), and the combined organic extracts were washed with brine (2 × 20 mL). After the organic layer was dried over $MgSO_4$, the solvent was removed under reduced pressure. The residue was used without the necessity of purification (R_f 0.34, EtOAc/hexane = 1/4).

trans-1-[2-(Diethoxyethyl)phenyl]-3-(triphenylsilyl)prop-2-en-1-yl acetate (S14b)

Following the procedure of **S14a**, **S14b** was synthesized and used without the necessity of purification.

trans-2-[1-(Acetyloxy)- 3-(triphenylsilyl)prop-2-en-1-yl]phenylpropanal (1k)

To a 100 mL two-necked flask equipped with magnetic stirring bar and reflux condenser was added crude *trans*-1-[2-(diethoxypropyl)phenyl]-3-(triphenylsilyl)prop-2-en-1-yl acetate (**S14a**, 7.35 mmol), acetic acid (80% aq., 20 mL), and THF (8 mL). After stirring at room temperature for 3 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (5 mL).

The aqueous phase was extracted several times with EtOAc and washed with brine. The organic phases were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the product as a brown oil (2.34 g, 55% over 4 steps, R_f 0.40, EtOAc/hex = 3/7).

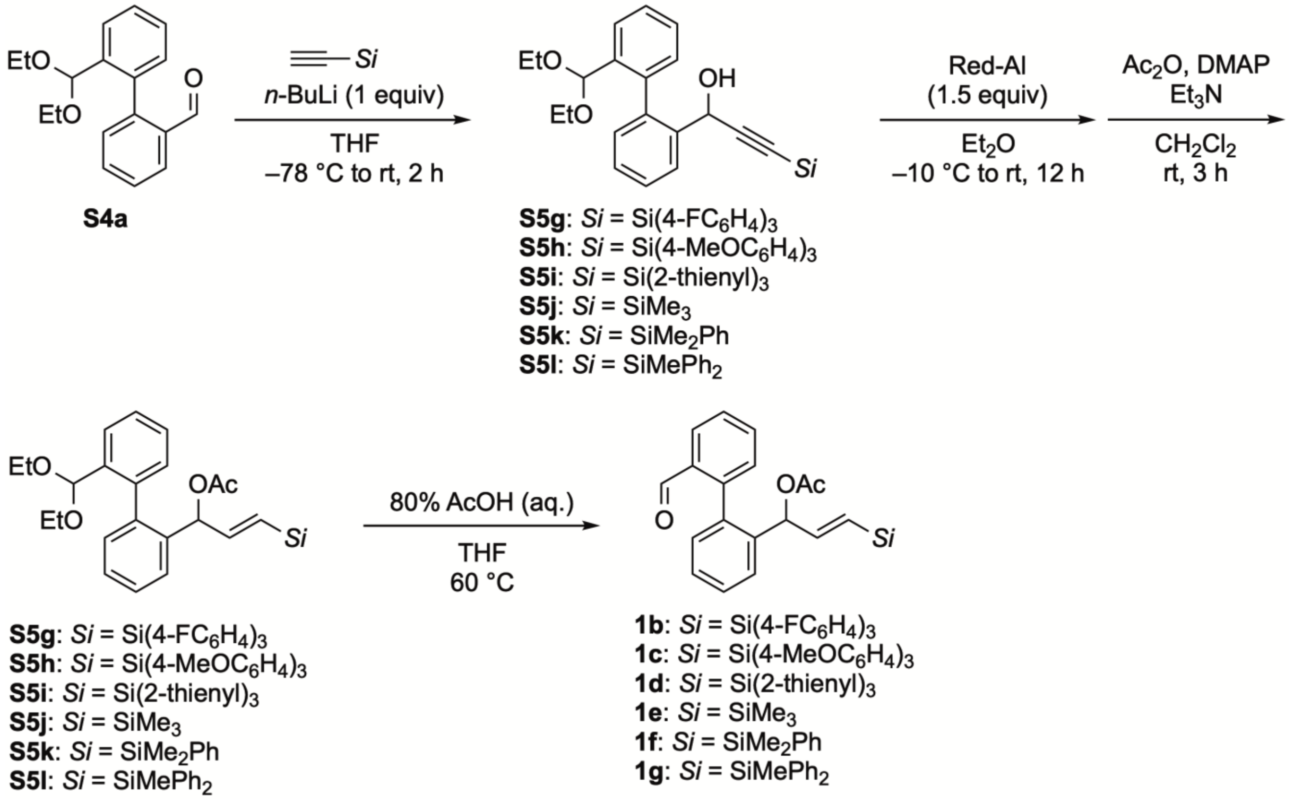
^{1}H-NMR ($CDCl_3$, 400 MHz) δ 9.73 (t, *J* = 1.2 Hz, 1H), 7.49-7.44 (m, 6H), 7.44-7.39 (m, 3H), 7.38-7.33 (m, 7H), 7.26-7.21 (m, 2H), 7.18-7.15 (m, 1H), 6.55 (dd, *J* = 4.0, 1.2 Hz, 1H), 6.35 (dd, *J* = 18.8, 1.2 Hz, 1H), 6.26 (dd, *J* = 18.8, 4.0 Hz, 1H), 3.04 (t, *J* = 7.6 Hz, 2H), 2.85-2.65 (m, 2H), 2.11 (s, 3H); **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 201.2, 170.1, 148.5, 138.6, 136.7, 136.0, 134.0, 129.9, 129.7, 128.7, 128.3, 128.1, 127.0, 126.0, 74.5, 45.1, 24.8, 21.4; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{32}H_{31}O_3Si^+$: 491.2042, found: 491.2039.

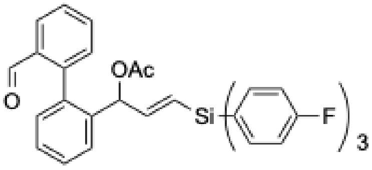
trans-2-[1-(Acetyloxy)- 3-(triphenylsilyl)prop-2-en-1-yl]phenylacetaldehyde (1l)

Following the procedure of **1k**, **S14b** was used. The title compound was isolated as a light yellow oil (729.7 mg, 59% over 4 steps, R_f = 0.34, EtOAc/hex = 1/4).

^{1}H-NMR ($CDCl_3$/400 MHz) δ 9.67 (t, *J* = 2.0 Hz, 1H), 7.94-7.44 (m, 6H), 7.44-7.29 (m, 12H), 7.21-7.15 (m, 1H), 6.43 (dd, *J* = 4.0, 1.6 Hz, 1H), 6.37 (dd, *J* = 18.4, 1.6 Hz, 1H), 6.27 (dd, *J* = 18.4, 3.6 Hz, 1H), 3.94 (dd, *J* = 17.2, 2.0 Hz, 1H), 3.75 (dd, *J* = 17.2, 2.0 Hz, 1H), 2.07 (s, 3H); **^{13}C-NMR** ($CDCl_3$/100 MHz) δ: 199.2, 169.9, 148.0, 137.6, 136.0, 133.9, 131.6, 131.1, 129.8, 129.4, 129.0, 128.1, 126.1, 77.4, 75.1, 48.0, 21.2; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{31}H_{29}O_2Si^+$: 477.1886, found: 477.1881.

Preparation of substrates 1b–g





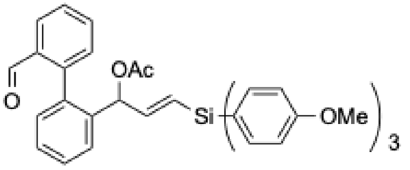
***trans*-1-Acetoxy-1-(2'-formyl-1,1'-biphenyl-2-yl)-3-tri(4-fluorophenyl)silyl-2-propene (1b)**

Following the procedure of GP-5, **1b** was purified by silica gel column chromatography (yellow amorphous solid, 45%, over 4 steps, R*f* 0.40, EtOAc/hex = 1/4).

Major isomer: **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.71 (s, 1H), 8.06 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.62–7.02 (m, 19H), 6.19 (d, *J* = 18.8 Hz, 1H), 6.12 (dd, *J* = 18.4, 4.0 Hz, 1H), 5.98 (d, *J* = 4.4 Hz, 1H), 2.07 (s, 3H).

Minor isomer: **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.56 (s, 1H), 7.93 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.62–7.02 (m, 19H), 6.22 (d, *J* = 4.4 Hz, 1H), 6.02 (d, *J* = 18.8 Hz, 1H), 5.95 (dd, *J* = 18.8, 4.4 Hz, 1H), 1.99 (s, 3H).

^{13}C-NMR ($CDCl_3$, 100 MHz) δ 191.9, 191.3, 169.6, 169.5, 165.6, 163.1, 148.6, 148.1, 143.5 (two peaks), 138.2, 138.1, 137.90, 137.86, 137.83, 137.78, 137.66, 137.57, 137.2, 137.1, 137.0, 126.9, 134.4, 134.2, 133.5, 133.1, 131.2, 131.0, 130.9, 130.7, 129.05, 129.02, 128.92, 128.89, 128.5, 128.4, 128.02, 127.96, 127.8, 127.5, 127.4, 127.3, 126.0, 125.4, 115.6, 115.5, 115.4, 115.3, 75.4, 74.7, 21.1, 20.9; **HRMS-EI**: $[M]^+$ calcd for $C_{36}H_{27}F_3O_3Si^+$: 592.1682, found: 592.1670.

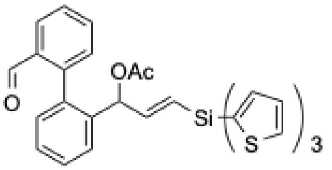


trans-1-(2'-(Dimethoxymethyl)-[1,1'-biphenyl]-2-yl)-3-(tris(4-methoxyphenyl)silyl)allyl acetate (1c)

Following the procedure of GP-5, **1c** was purified by silica gel column chromatography (yellow amorphous solid, 69% over 4 steps, R_f 0.21 and 0.27, EtOAc/hex = 3/7).

Major isomer: **^{1}H-NMR** (CDCl$_3$, 400 MHz) δ 9.71 (d, *J* = 1.2 Hz, 1H), 8.06 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.59–7.27 (m, 10H), 7.20 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.12 (dm, *J* = 7.2, Hz, 1H), 6.96–6.87 (m, 7H), 6.20 (d, *J* = 18.0 Hz, 1H), 6.13 (dd, *J* = 18.8, 4.0 Hz, 1H), 5.95 (d, *J* = 3.6 Hz, 1H), 3.824 (s, 9H), 1.97 (s, 3H).

Minor isomer: **^{1}H-NMR** (CDCl$_3$, 400 MHz) δ 9.57 (s, 1H), 7.94 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.59–7.27 (m, 11H), 7.16 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.96–6.87 (m, 7H), 6.24 (dd, *J* = 4.4, 0.8 Hz, 1H), 6.04 (dd, *J* = 18.4, 1.2 Hz, 1H), 5.95 (dd, *J* = 18.4, 4.8 Hz, 1H), 3.820 (s, 9H), 2.05 (s, 3H); **^{13}C-NMR** (CDCl$_3$, 100 MHz) δ 191.9, 191.3, 169.6, 169.4, 160.9, 160.8, 147.0, 146.6, 143.6 (two peaks), 137.5, 137.4, 137.32, 137.26, 136.8, 136.6, 134.3, 134.1, 133.4, 133.0, 131.2, 131.0 (two peaks), 130.5, 128.8, 128.4, 128.3, 127.7, 127.53, 127.48, 127.3, 127.2, 125.2, 125.1, 113.7 (two peaks), 75.4, 74.8, 55.0 (two peaks), 21.1, 20.9; **HRMS-EI**: [M]$^+$ calcd for $C_{39}H_{36}O_6Si$: 628.2281, found 628.2294.



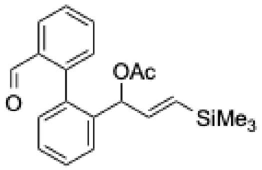
***trans* -1-Acetoxy-1-(2'-formyl-1,1'-biphenyl-2-yl)-3-tri(2-thienyl)silyl-2-propene (1d)**

Following the procedure of GP-5, **1d** was purified by silica gel column chromatography (yellow amorphous solid, 38% over 4 steps, R_f 0.44, EtOAc/hex = 3/7).

Major isomer: **^{1}H-NMR** (CDCl$_3$, 400 MHz) δ 9.71 (s, 1H), 8.06 (m, 1H), 7.73 (dd, *J* = 4.8, 0.8 Hz, 3H), 7.59–7.44 (m, 5H), 7.40–7.36 (m, 3H), 7.32 (dd, *J* = 3.2, 0.8 Hz, 1H), 7.25–7.21 (m, 3H), 7.17 (m, 1H), 6.37 (dd, *J* = 18.4, 4.4 Hz, 1H), 6.18 (dd, *J* = 18.4, 1.6 Hz, 1H), 5.97 (dd, *J* = 4.4, 1.6 Hz, 1H), 1.97 (s, 3H).

Minor isomer: **^{1}H-NMR** (CDCl$_3$, 400 MHz) δ 7.94 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.70 (dd, *J* = 4.4, 0.8 Hz, 3H), 7.59–7.44 (m, 5H), 7.40–7.36 (m, 3H), 7.32 (dd, *J* = 3.2, 0.8 Hz, 1H), 7.25–7.21 (m, 3H), 7.17 (m, 1H), 6.25 (dd, *J* = 4.4, 1.2 Hz, 1H), 6.17 (dd, *J* = 18.4, 4.8 Hz, 1H), 6.03 (dd, *J* = 18.8, 1.2 Hz, 1H), 2.06 (s, 3H).

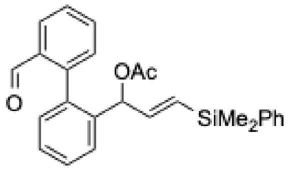
^{13}C-NMR (CDCl$_3$, 100 MHz) δ 1191.9, 191.4, 169.44, 169.35, 148.6, 148.1, 143.44, 143.42, 138.0, 137.5, 137.0, 136.7, 134.3, 134.1, 133.4, 133.2, 133.02, 132.97, 132.8, 132.6, 131.2, 131.0, 130.5, 128.9, 128.8, 128.54, 128.49, 128.4, 128.3, 127.9, 127.7, 127.6, 127.5, 127.3, 126.0, 125.5, 75.0, 74.4, 21.0, 20.8; ; **HRMS-EI**: [M]$^+$ calcd for $C_{30}H_{24}O_3S_3Si$: 556.0657, found 556.0665.



trans **-1-Acetoxy-1-(2'-formyl-1,1'-biphenyl-2-yl)-3-trimethylsilyl-2-propene (1e)**

Following the procedure of GP-5, **1e** was purified by silica gel column chromatography (yellow oil, 53% over 4 steps, R_f 0.61, EtOAc/hex = 2/3).

^{1}**H-NMR** ($CDCl_3$, 400 MHz) δ 9.71 (d, *J* = 0.8 Hz, 1H), 9.54 (d, *J* = 0.8 Hz, 1H), 8.06 (dd, *J* = 7.6, 1.2 Hz, 1H), 8.00 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.68–7.34 (m, 11H), 7.22–7.17 (m, 3H), 6.04 (dd, *J* = 6.0, 1.2 Hz, 1H), 6.02 (dd, *J* = 18.8, 6.0 Hz, 1H), 5.85 (dd, *J* = 6.0, 1.2 Hz, 1H), 5.82 (dd, *J* = 18.8, 6.0 Hz, 1H), 5.62 (dd, *J* = 18.8, 1.2 Hz, 1H), 5.34 (dd, *J* = 18.8, 1.2 Hz, 1H), 2.06 (s, 3H), 1.97 (s, 3H), 0.04 (s, 9H), -0.04 (s, 9H); ^{13}**C-NMR** ($CDCl_3$, 100 MHz) δ 192.2, 191.8, 169.8, 169.6, 144.0, 143.8, 142.2, 141.6, 137.9, 137.8, 137.4, 136.7, 134.3, 134.2, 133.9, 133.6, 133.1, 133.0, 131.1, 130.95, 130.92, 130.7, 128.9, 128.8, 128.44, 128.41, 127.7, 127.6, 127.4, 127.3, 127.2, 126.8, 76.1, 75.3, 21.3, 21.0, -1.4, -1.6; **HRMS-EI**: $[M]^+$ calcd for $C_{21}H_{24}O_3Si$: 352.1495, found 352.1488.



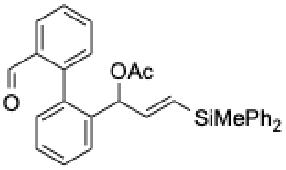
***trans*-1-Acetoxy-1-(2'-formyl-1,1'-biphenyl-2-yl)-3-tri(dimethylphenyl)silyl-2-propene (1f)**

Following the procedure of GP-5, **1f** was purified by silica gel column chromatography (yellow amorphous solid, 39% over 4 steps, R_f 0.39, EtOAc/hex = 1/4).

Major isomer: ^{1}**H-NMR** ($CDCl_3$, 400 MHz) δ 9.71 (s, 1H), 8.06 (m, 1H), 7.53–7.12 (m, 12H), 6.11 (dd, *J* = 18.4, 4.8 Hz, 1H), 5.89 (dd, *J* = 5.2, 1.2 Hz, 1H), 5.77 (dd, *J* = 18.4, 1.6 Hz, 1H), 1.97 (s, 3H), 0.32 (s, 6H).

Minor isomer: ^{1}**H-NMR** ($CDCl_3$, 400 MHz) δ 9.57 (s, 1H), 7.97 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.63 (dt, *J* = 1.6, 8.0 Hz, 1H), 7.53–7.12 (m, 11H), 6.10 (dd, *J* = 6.0, 1.2 Hz, 1H), 5.90 (dd, *J* = 18.4, 6.0 Hz, 1H), 5.53 (dd, *J* = 18.8, 1.6 Hz, 1H), 2.05 (s, 3H), 0.24 (s, 3H), 0.23 (s, 3H).

^{13}**C-NMR** ($CDCl_3$, 100 MHz) δ 192.0, 191.7, 169.6, 169.5, 144.0, 143.9, 143.7, 143.4, 138.0, 137.74, 137.68, 137.5, 137.4, 136.8, 134.4, 134.2, 133.9, 133.8, 133.5, 133.0, 131.3, 131.1, 130.9 (two peaks), 130.8, 130.6, 129.23, 129.17, 128.84, 128.82, 128.40, 128.38, 127.90, 127.86, 127.73, 127.66, 127.4, 127.34, 127.28, 127.0, 75.8, 75.1, 21.2, 21.0, -2.7, -2.80, -2.83, -2.9; **HRMS-EI**: $[M]^+$ calcd for $C_{26}H_{26}O_3Si$: 414.1651, found 414.1650.



***trans*-1-Acetoxy-1-(2'-formyl-1,1'-biphenyl-2-yl)-3-tri(methyldiphenyl)silyl-2-propene (1g)**

Major isomer: **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.71 (d, *J* = 0.4 Hz, 1H), 8.07-8.03 (dm, *J* = 7.6 Hz, 1H), 7.64-7.57 (m, 2H), 7.52-7.30 (m, 12H), 7.19 (ddd, *J* = 12.4, 7.6, 1.2 Hz, 2H), 7.13-7.10 (dm, *J* = 6.8 Hz, 1H), 6.15 (dd, *J* = 18.8, 5.2 Hz, 1H), 5.97 (dd, *J* = 18.8, 1.6 Hz, 1H), 5.93 (dd, *J* = 4.8, 1.6 Hz, 1H), 1.97 (s, 3H), 0.61 (s, 3H).

Minor isomer: **^{1}H-NMR** ($CDCl_3$, 400 MHz) δ 9.58 (d, *J* = 0.8 Hz, 1H), 7.96-7.93 (dm, *J* = 7.6 Hz, 1H), 7.64-7.57 (m, 1H), 7.52-7.30 (m, 16H), 6.17 (dd, *J* = 5.6, 1.6 Hz, 1H), 5.94 (dd, *J* = 18.8, 5.6 Hz, 1H), 5.77 (dd, *J* = 18.4, 1.2 Hz, 1H), 2.05 (s, 3H), 0.51 (s, 3H).

Mixture of major and minor isomer: **^{13}C-NMR** ($CDCl_3$, 100 MHz) δ 192.0, 191.6, 169.7, 169.5, 146.1, 145.6, 143.7, 143.6, 137.54, 137.47, 137.4, 137.3, 136.9, 135.9, 135.8, 135.70, 135.68, 134.9, 134.8, 134.6, 134.4, 134.2, 134.0, 133.5, 133.1, 131.08, 131.06, 130.98, 130.6, 129.8, 129.54, 129.49, 129.48, 128.8, 128.5, 128.43, 128.37, 127.98, 127.93, 127.80, 127.76, 127.5, 127.4, 127.33, 127.30, 75.7, 75.0 21.2, 20.9, -3.9, -4.0; **HRMS (ESI-TOF)** *m/z*: $[M+H]^+$ calcd for $C_{31}H_{29}O_3Si^+$: 477.1886, found: 477.1884.

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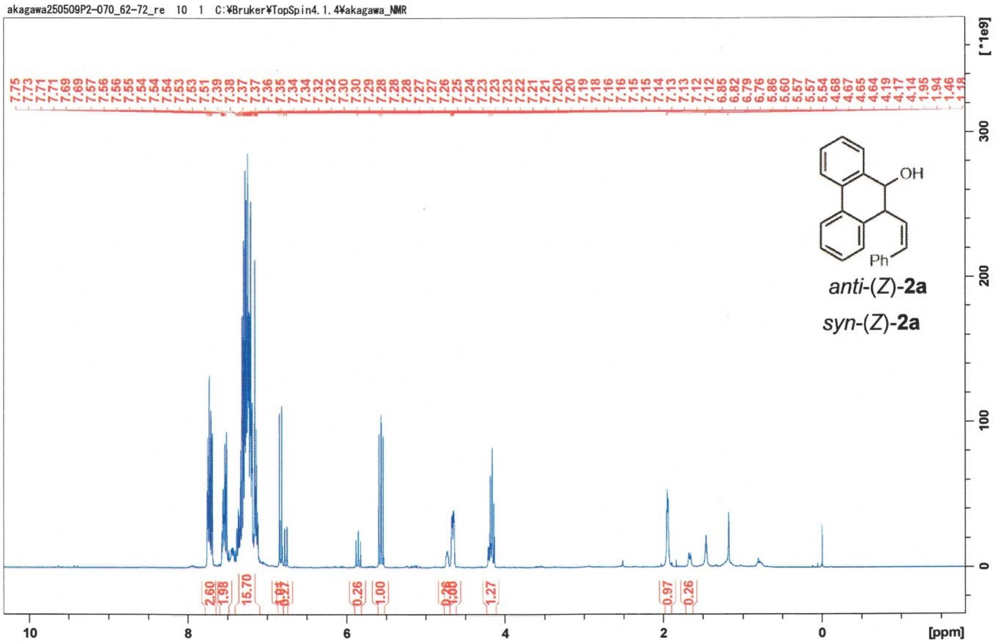
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1.27
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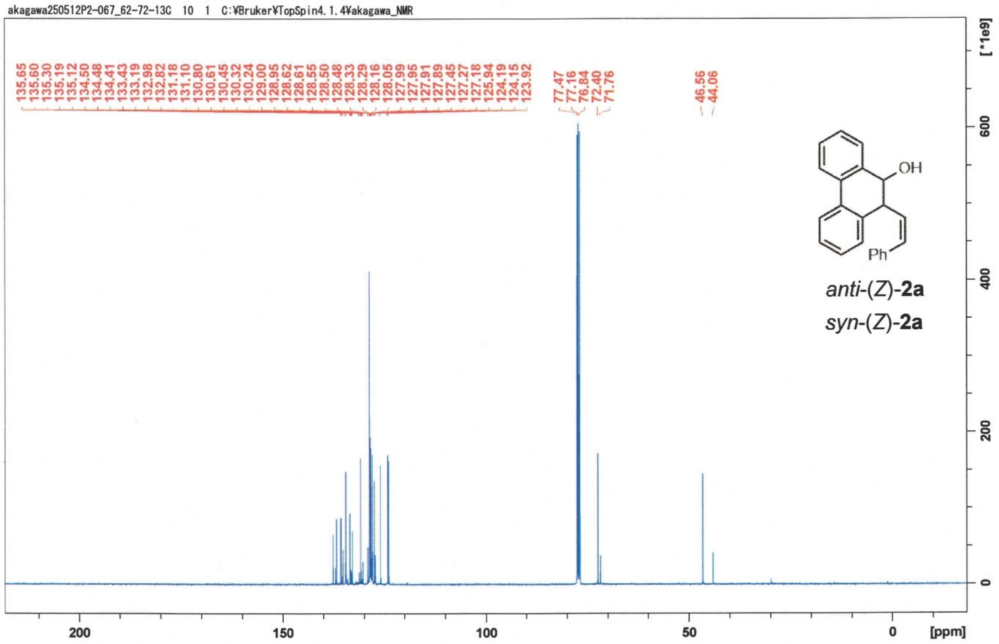
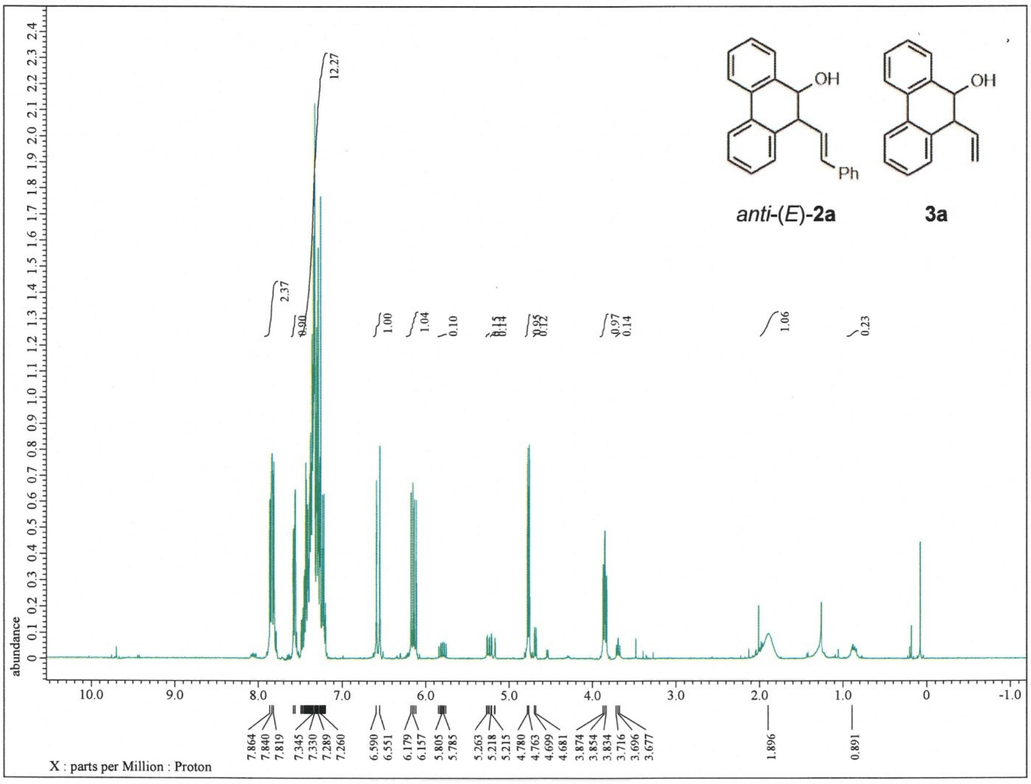
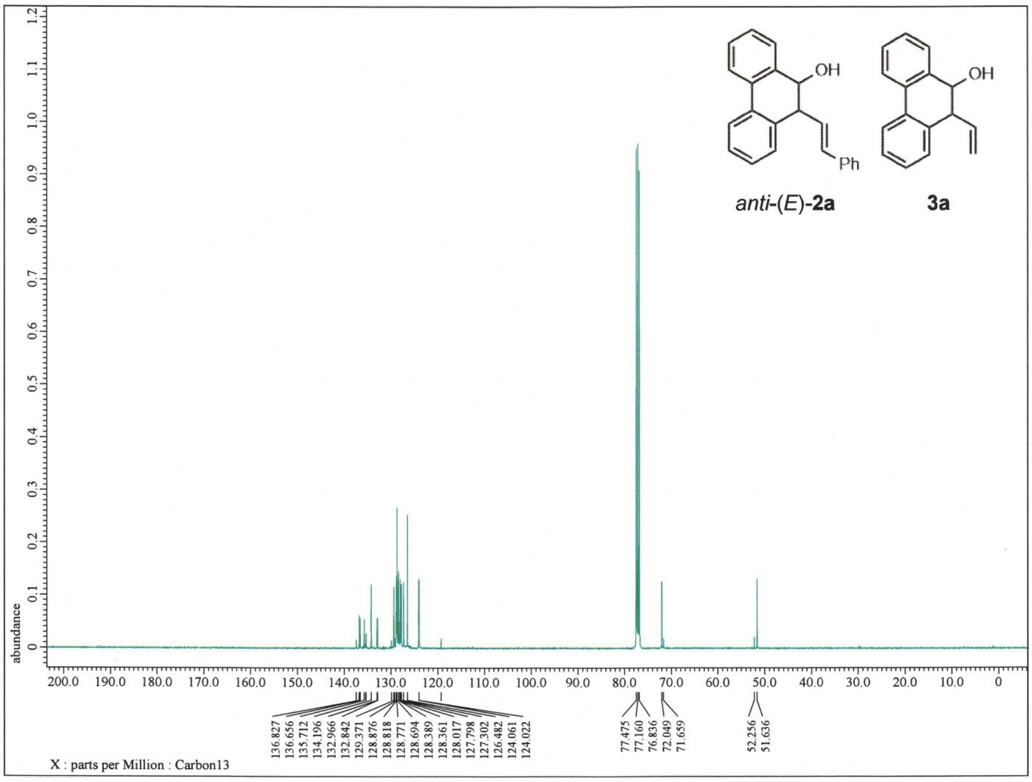
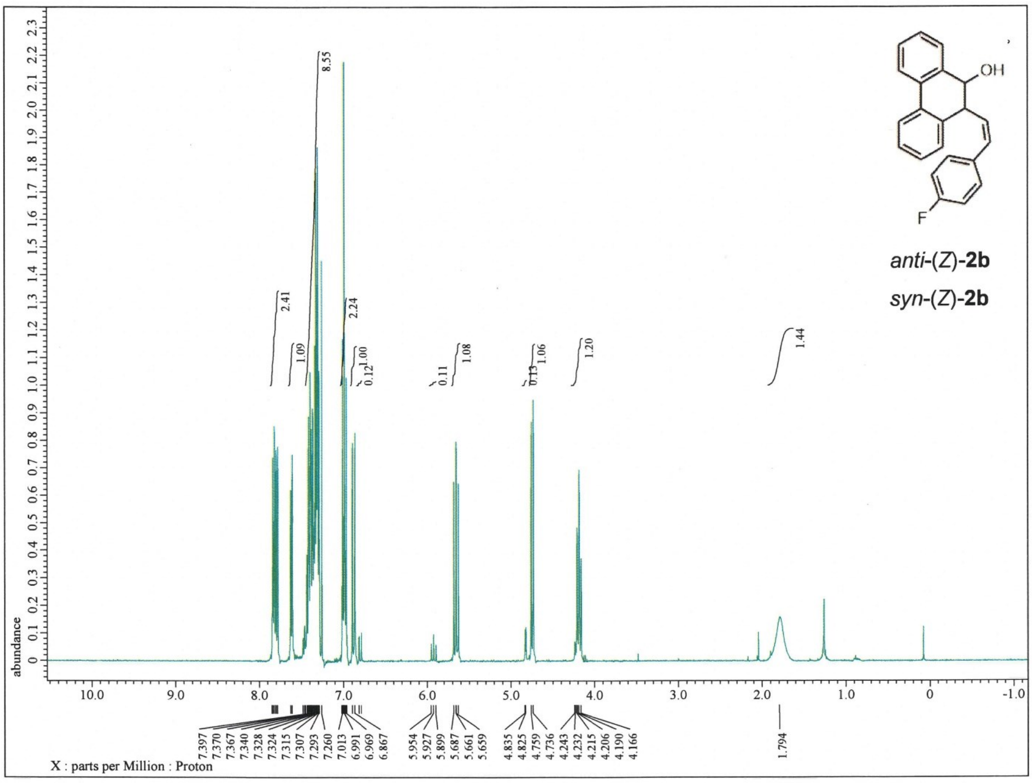
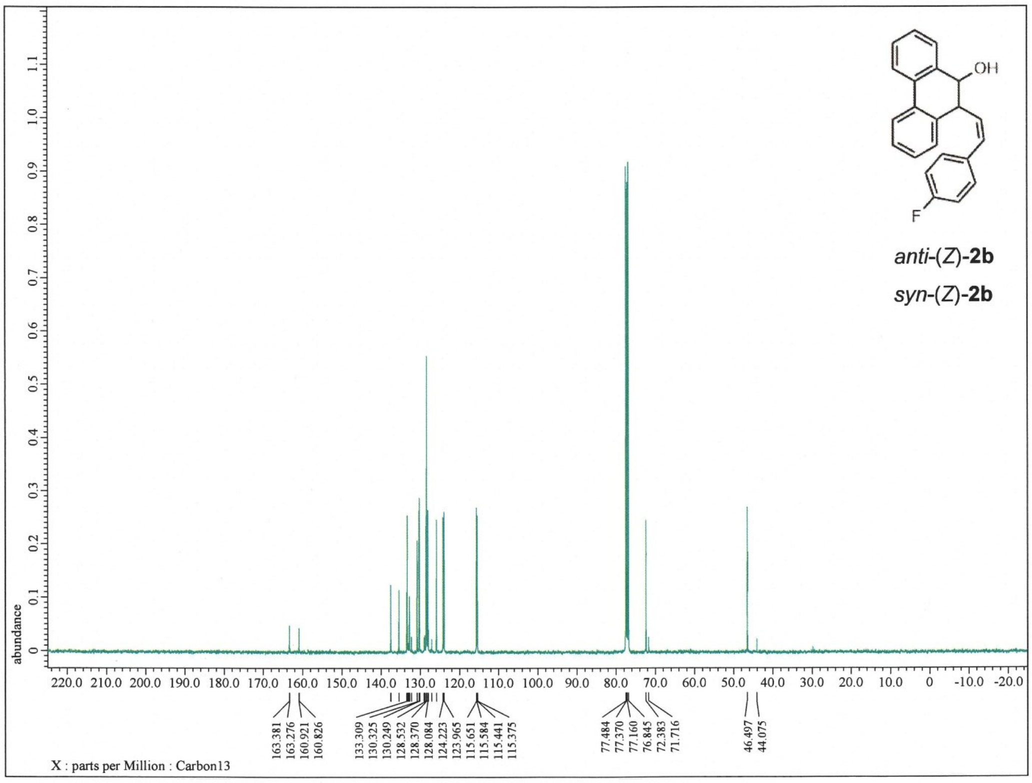
0
[ppm]

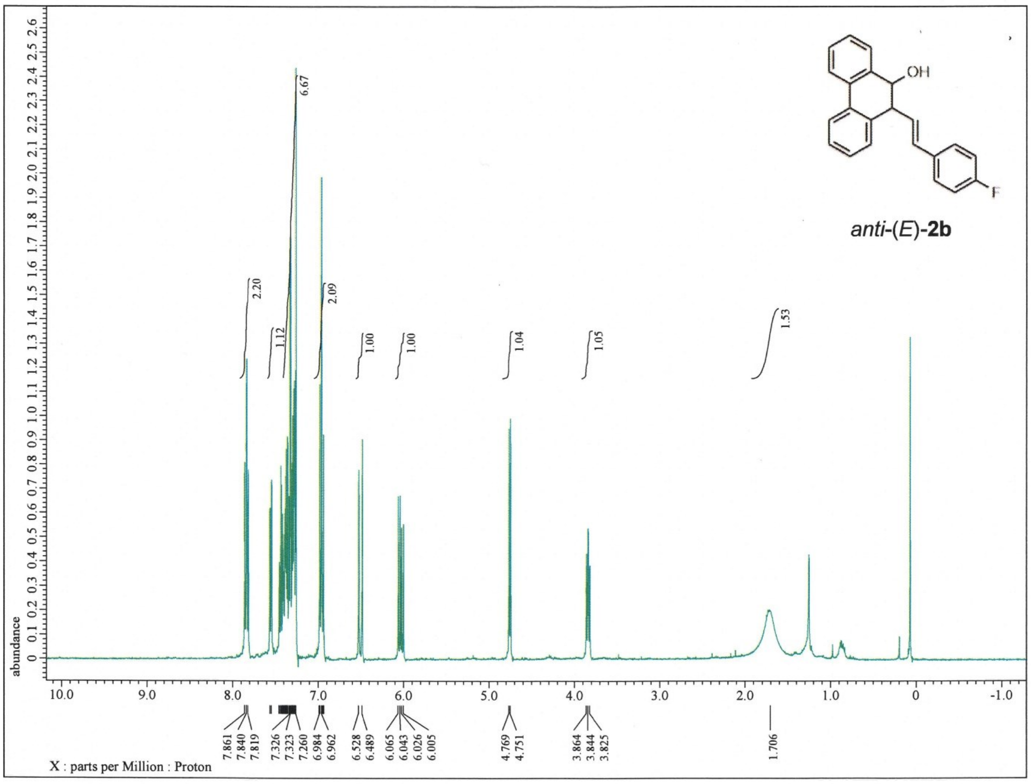

akagawa250512P2-067_62-72-13C 10 1 C:¥Bruker¥TopSpin4.1.4¥akagawa_NMR
135.65 135.60 135.30 135.19 135.12 134.50 134.48 134.41 133.43 133.19 132.98 132.82 131.18 131.10 130.80 130.61 130.45 130.32 130.24 129.00 128.95 128.62 128.61 128.55 128.50 128.48 128.33 128.29 128.16 128.05 127.99 127.95 127.91 127.89 127.45 127.27 127.18 125.94 124.19 124.15 123.92
77.47 77.16 76.84 72.40 71.76
46.56 44.06
[*1e9]
600
400
200
0
OH
Ph
anti-(*Z*)-**2a**
syn-(*Z*)-**2a**
200
150
100
50
0
[ppm]

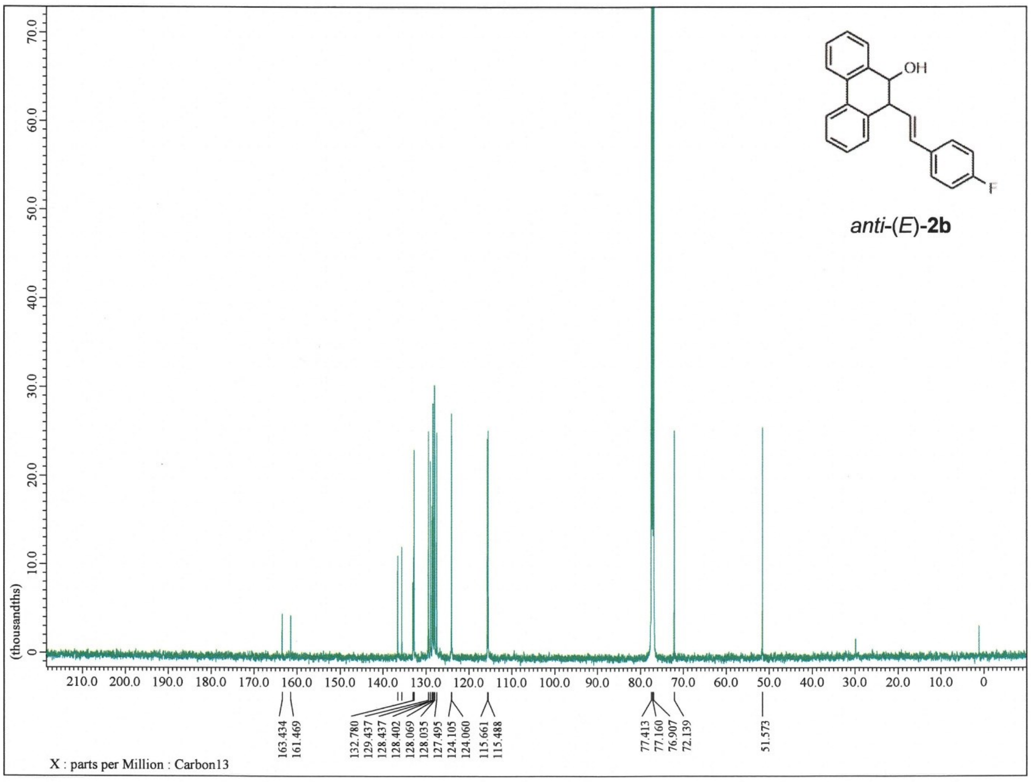

anti-(E)-2a
3a
OH
Ph
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4
2.37
0.90
12.27
1.00
1.04
0.10
0.15
0.14
0.95
0.12
0.97
0.14
1.06
0.23
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
7.864
7.840
7.819
7.345
7.330
7.289
7.260
6.590
6.551
6.179
6.157
5.805
5.785
5.263
5.218
5.215
4.780
4.763
4.699
4.681
3.874
3.854
3.834
3.716
3.696
3.677
1.896
0.891
X : parts per Million : Proton

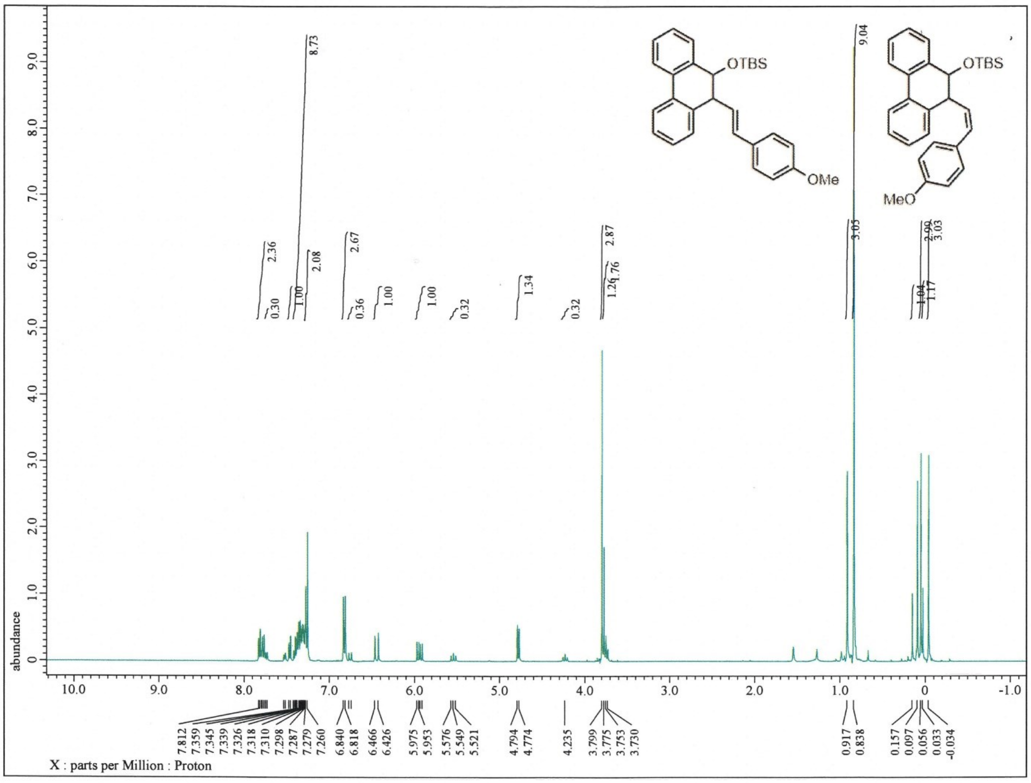

anti-(E)-2a
3a
OH
Ph
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2
200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
136.827
136.656
135.712
134.196
132.966
132.842
129.371
128.876
128.818
128.771
128.694
128.389
128.361
128.017
127.798
127.302
126.482
124.061
124.022
77.475
77.160
76.836
72.049
71.659
52.256
51.636
X : parts per Million : Carbon13

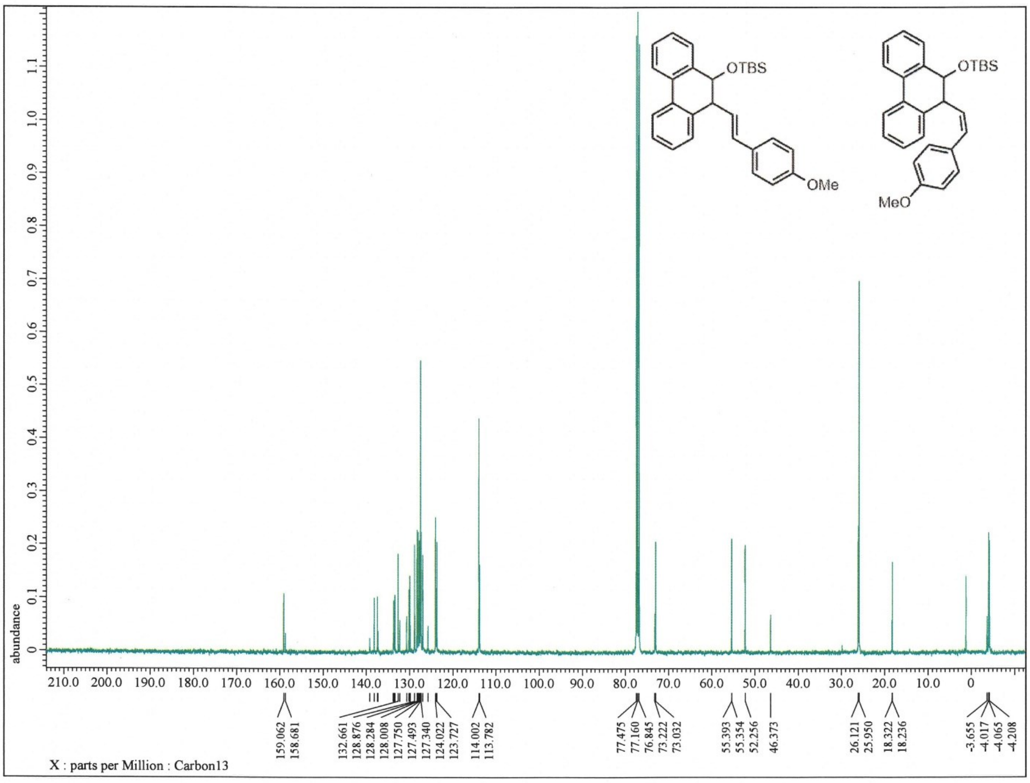

OH
F
anti-(Z)-2b
syn-(Z)-2b
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3
2.41
1.09
8.55
2.24
1.00
0.12
0.11
1.08
0.13
1.06
1.20
1.44
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
7.397 7.370 7.367 7.340 7.328 7.324 7.315 7.307 7.293 7.260 7.013 6.991 6.969 6.867
5.954 5.927 5.899 5.687 5.661 5.659
4.835 4.825 4.759 4.736 4.243 4.232 4.215 4.206 4.190 4.166
1.794
X : parts per Million : Proton

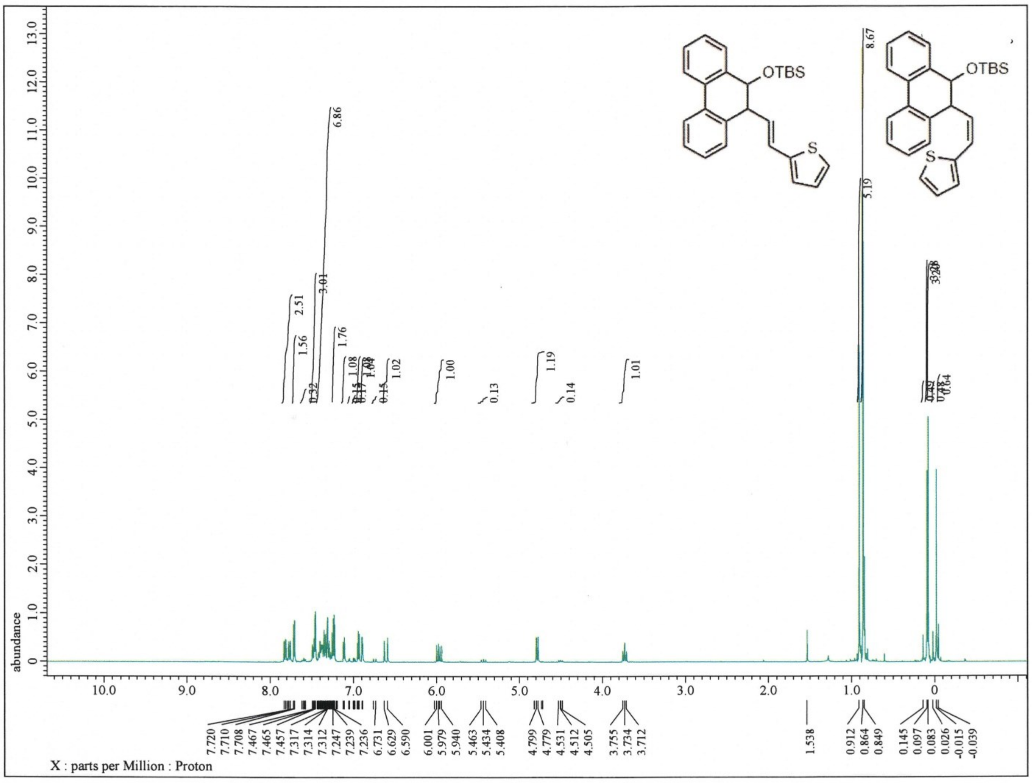

OH
F
anti-(Z)-2b
syn-(Z)-2b
abundance
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0 1.1
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
163.381 163.276 160.921 160.826
133.309 130.325 130.249 128.532 128.370 128.084 124.223 123.965 115.651 115.584 115.441 115.375
77.484 77.370 77.160 76.845 72.383 71.716
46.497 44.075
X : parts per Million : Carbon13

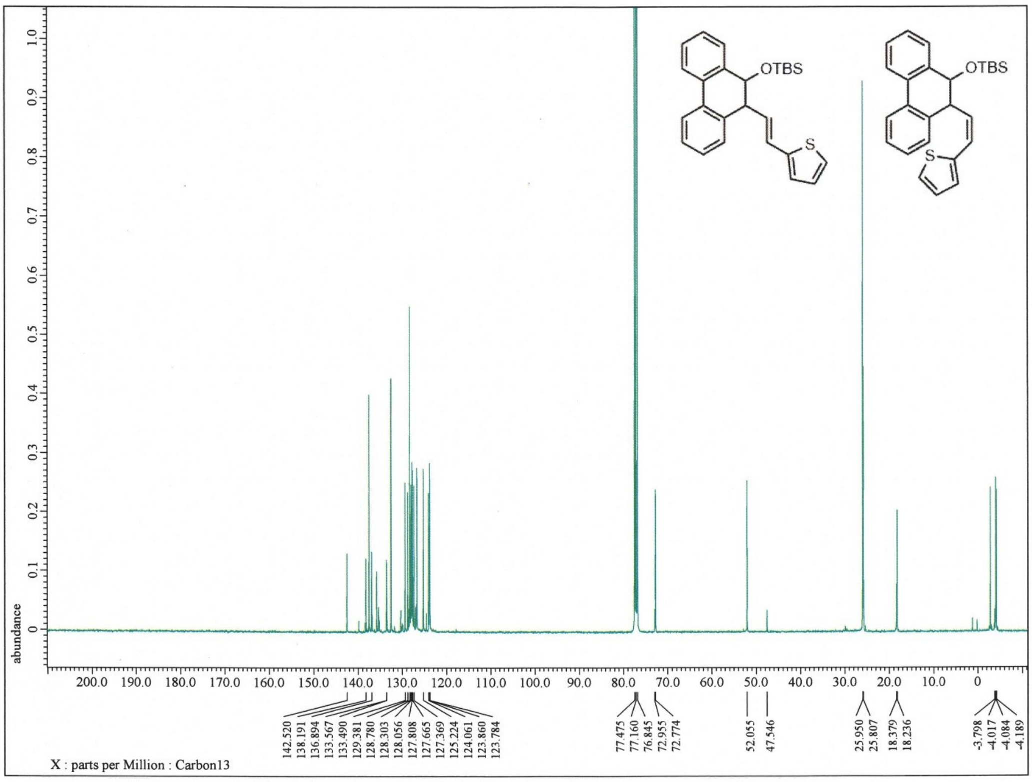

anti-(*E*)-**2b**

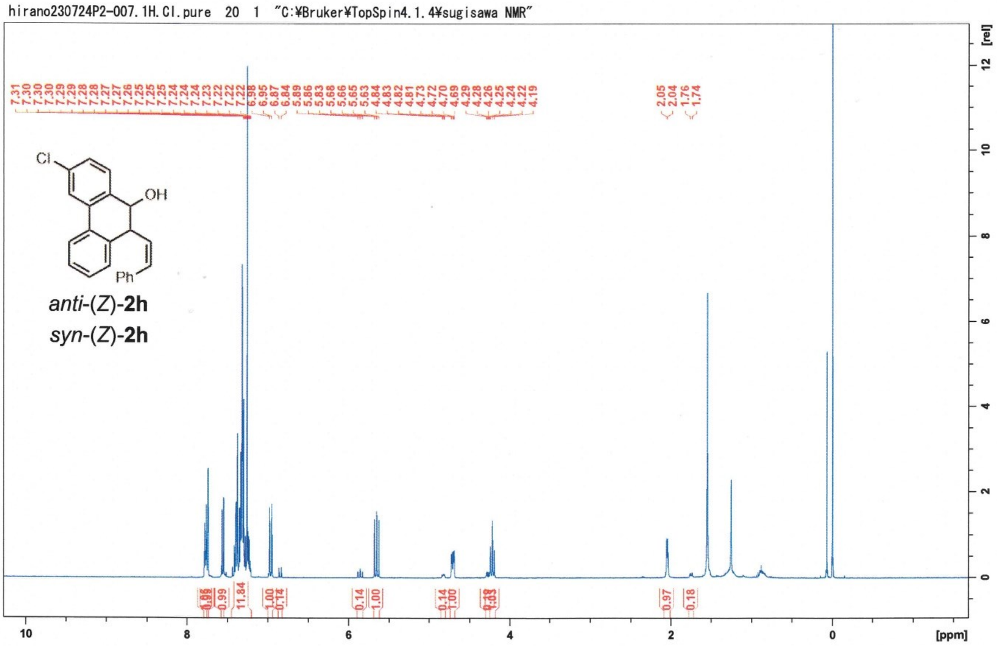

anti-(*E*)-**2b**


OTBS
OMe
OTBS
MeO
abundance
X : parts per Million : Proton
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0
0.30 2.36 1.00 2.08 8.73 0.36 2.67 1.00 1.00 0.32 1.34 0.32 1.26 1.76 2.87 3.05 9.04 1.04 1.17 2.90 3.03
7.812 7.359 7.345 7.339 7.326 7.318 7.310 7.298 7.287 7.279 7.260
6.840 6.818 6.466 6.426 5.975 5.953 5.576 5.549 5.521 4.794 4.774 4.235
3.799 3.775 3.753 3.730
0.917 0.838
0.157 0.097 0.056 0.033 -0.034

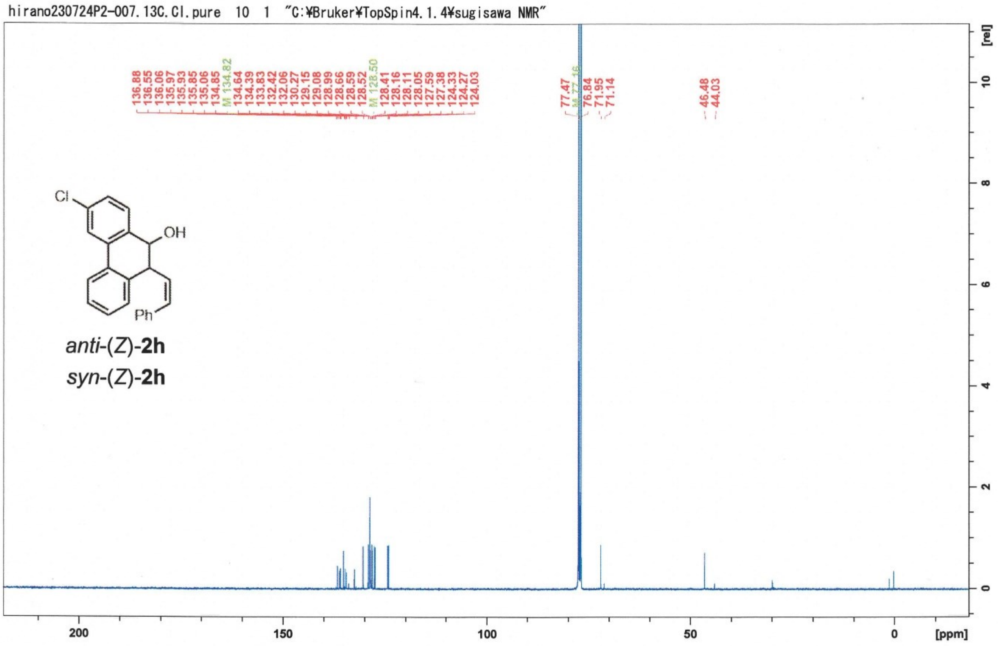

OTBS
OMe
OTBS
MeO
abundance
X : parts per Million : Carbon13
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
159.062 158.681
132.661 128.876 128.284 128.008 127.750 127.493 127.340 124.022 123.727
114.002 113.782
77.475 77.160 76.845 73.222 73.032
55.393 55.354 52.256 46.373
26.121 25.950 18.322 18.236
-3.655 -4.017 -4.065 -4.208


OTBS
S
OTBS
S
abundance
X : parts per Million : Proton
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
6.86
2.51
3.01
1.56
1.76
1.08
1.02
1.00
0.13
1.19
0.14
1.01
8.67
5.19
0.32
0.15
0.15
7.720
7.710
7.708
7.467
7.465
7.457
7.317
7.314
7.312
7.247
7.239
7.236
6.731
6.629
6.590
6.001
5.979
5.940
5.463
5.434
5.408
4.799
4.779
4.531
4.512
4.505
3.755
3.734
3.712
1.538
0.912
0.864
0.849
0.145
0.097
0.083
0.026
-0.015
-0.039

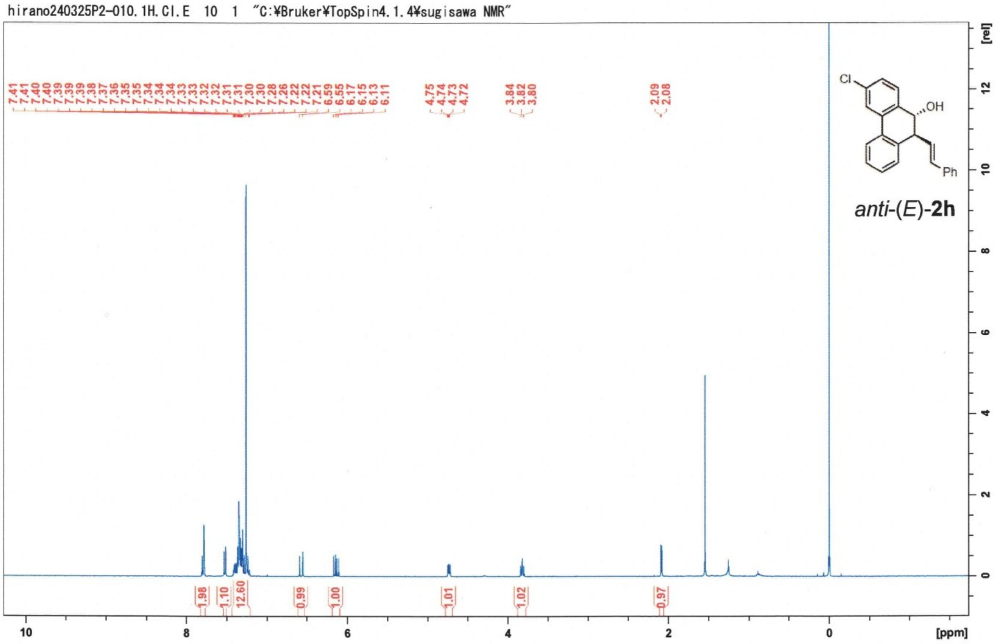

OTBS
S
OTBS
S
abundance
X : parts per Million : Carbon13
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
142.520
138.191
136.894
133.567
133.490
129.381
128.780
128.303
128.056
127.808
127.665
127.369
125.224
124.061
123.860
123.784
77.475
77.160
76.845
72.955
72.774
52.055
47.546
25.950
25.807
18.379
18.236
-3.798
-4.017
-4.084
-4.189

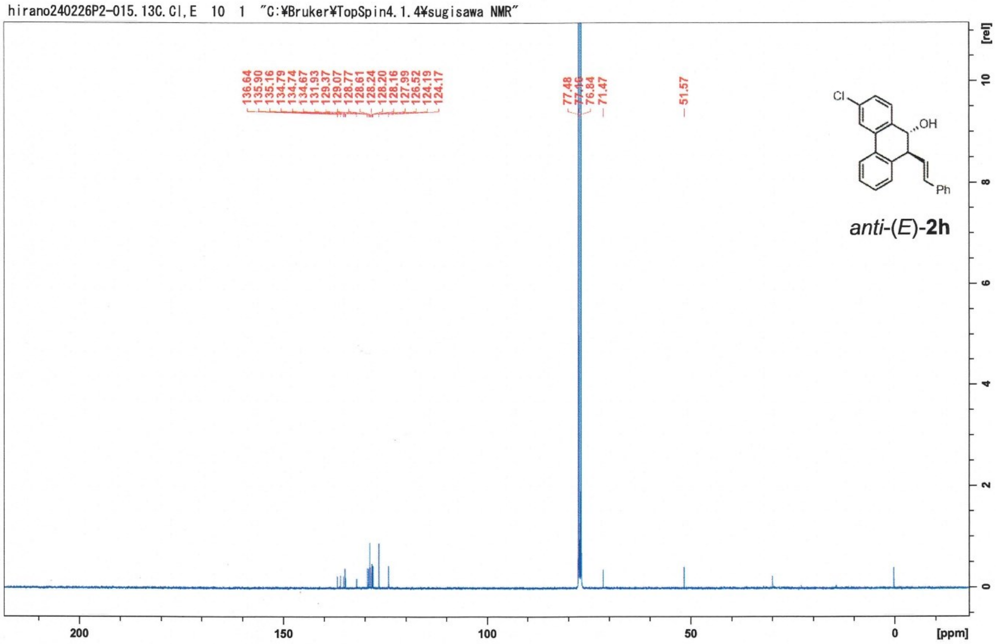


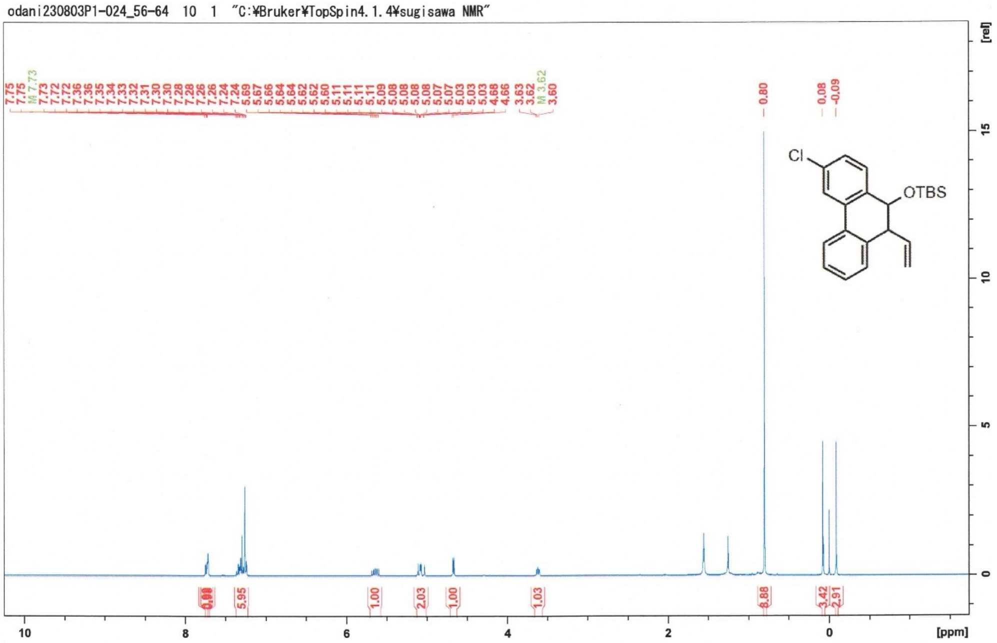
anti-(*Z*)-**2h**
syn-(*Z*)-**2h**

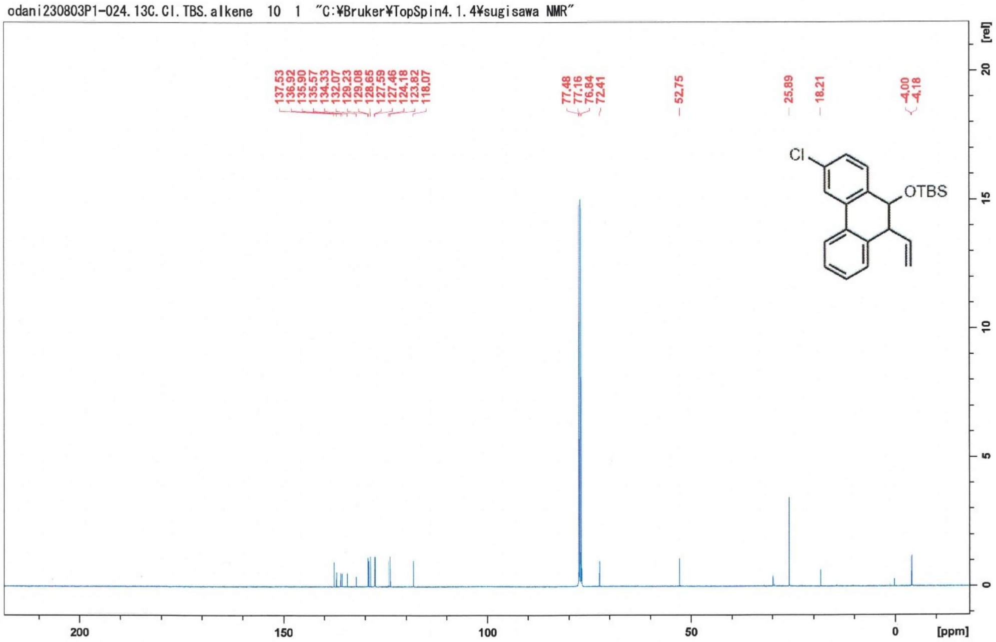


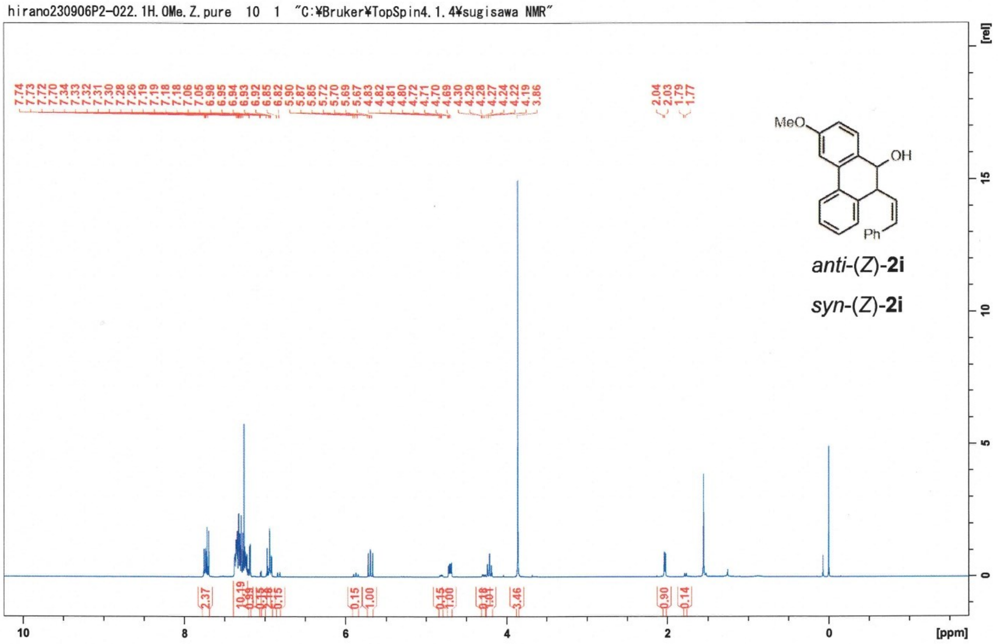
anti-(*Z*)-**2h**
syn-(*Z*)-**2h**

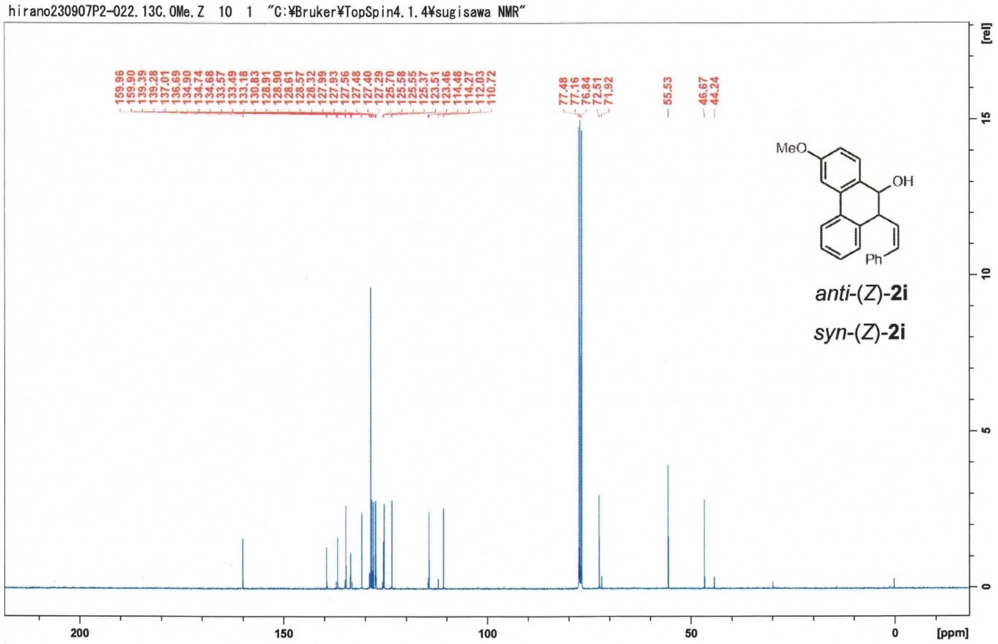

hirano240325P2-010.1H.Cl.E 10 1 "C:¥Bruker¥TopSpin4.1.4¥sugisawa NMR"
7.41 7.41 7.40 7.39 7.39 7.39 7.38 7.37 7.36 7.35 7.35 7.34 7.34 7.34 7.33 7.33 7.32 7.32 7.31 7.31 7.30 7.30 7.28 7.26 7.22 7.22 7.21 6.59 6.55 6.17 6.15 6.13 6.11
4.75 4.74 4.73 4.72
3.84 3.82 3.80
2.09 2.08
1.98
1.10
12.60
0.99
1.00
1.01
1.02
0.97
Cl
OH
Ph
anti-(E)-2h
[rel]
12
10
8
6
4
2
0
10
8
6
4
2
0
[ppm]

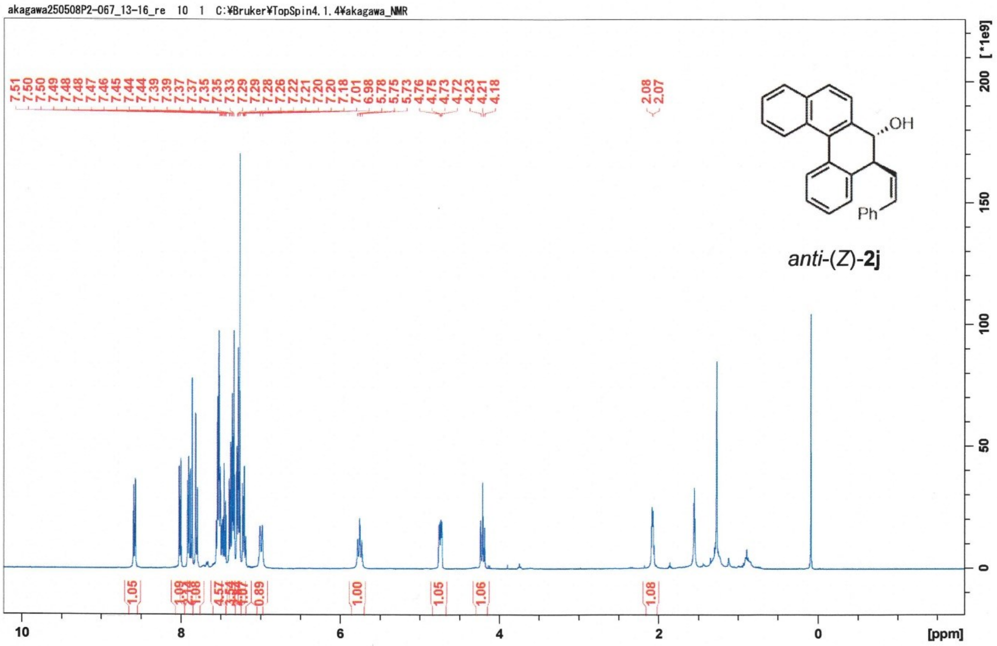

hirano240226P2-015.13C.Cl,E 10 1 "C:¥Bruker¥TopSpin4.1.4¥sugisawa NMR"
136.64 135.90 135.16 134.79 134.74 134.67 131.93 129.37 129.07 128.77 128.61 128.24 128.20 128.16 127.99 126.52 124.19 124.17
77.48 77.16 76.84 71.47
51.57
Cl
OH
Ph
anti-(E)-2h
[rel]
10
8
6
4
2
0
200
150
100
50
0
[ppm]


odani230803P1-024_56-64 10 1 "C:¥Bruker¥TopSpin4.1.4¥sugisawa NMR"
7.75
7.75
M 7.73
7.73
7.72
7.72
7.36
7.36
7.35
7.34
7.33
7.32
7.31
7.30
7.30
7.28
7.28
7.26
7.26
7.24
7.24
5.69
5.67
5.66
5.64
5.64
5.62
5.62
5.60
5.11
5.11
5.11
5.11
5.09
5.08
5.08
5.08
5.07
5.07
5.03
5.03
5.03
4.68
4.66
3.63
3.62
M 3.62
3.60
0.80
0.08
-0.09
Cl
OTBS
5.95
1.00
2.03
1.00
1.03
8.88
3.42
2.91
10
8
6
4
2
0
[ppm]
[rel]
15
10
5
0

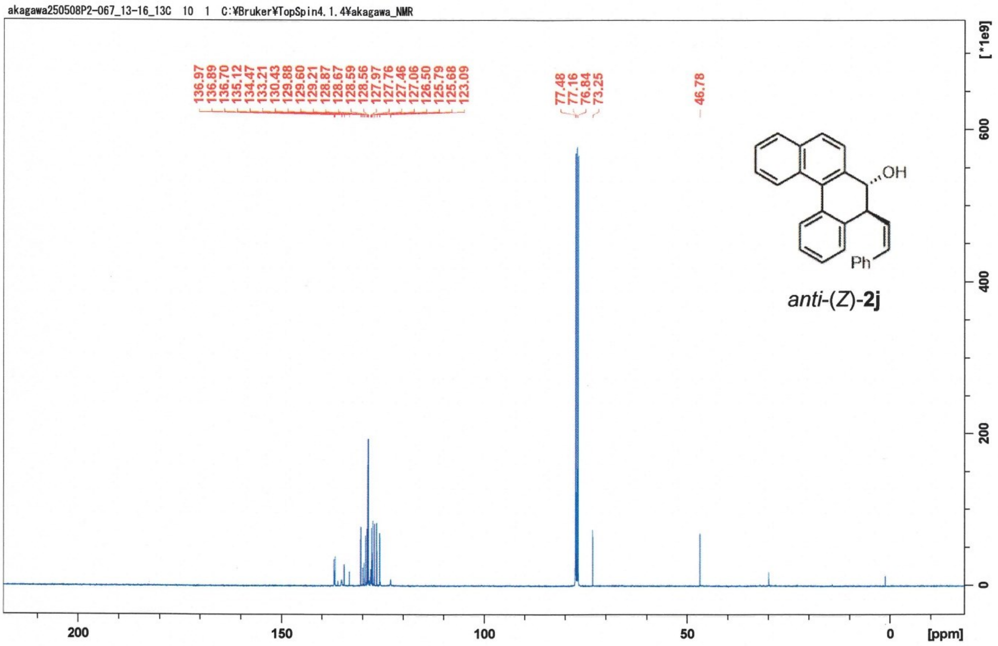

odani230803P1-024.13C.Cl.TBS.alkene 10 1 "C:¥Bruker¥TopSpin4.1.4¥sugisawa NMR"
137.53
136.92
135.90
135.57
134.33
132.07
129.23
129.08
128.65
127.59
127.46
124.18
123.82
118.07
77.48
77.16
76.84
72.41
52.75
25.89
18.21
-4.00
-4.18
Cl
OTBS
200
150
100
50
0
[ppm]
[rel]
20
15
10
5
0


hirano230906P2-022.1H.OMe.Z.pure 10 1 "C:¥Bruker¥TopSpin4.1.4¥sugisawa NMR"
MeO
OH
Ph
anti-(*Z*)-**2i**
syn-(*Z*)-**2i**
[rel]
[ppm]
10
8
6
4
2
0
5
10
15

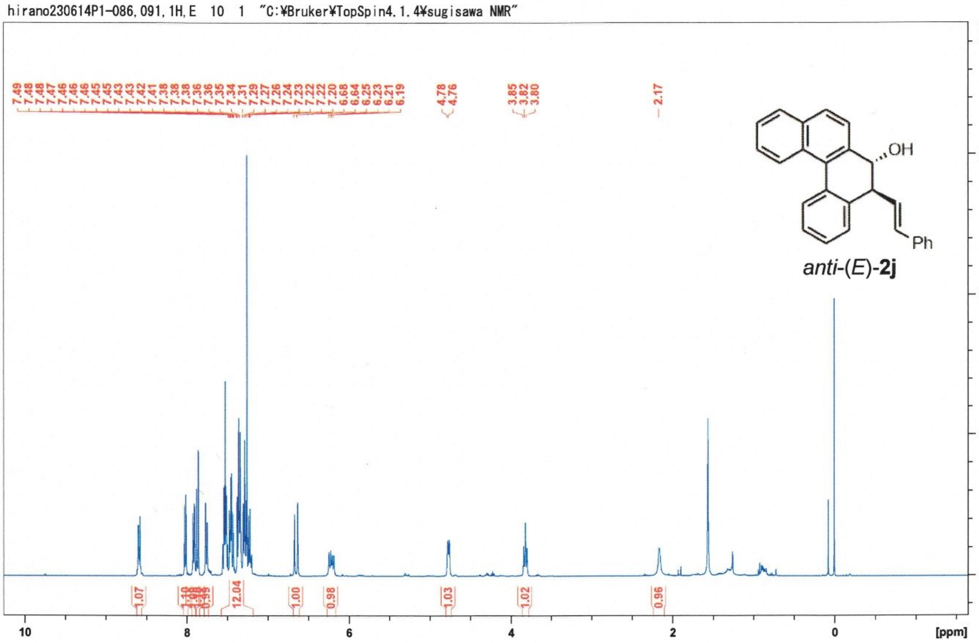

hirano230907P2-022.13C.OMe.Z 10 1 "C:¥Bruker¥TopSpin4.1.4¥sugisawa NMR"
MeO
OH
Ph
anti-(*Z*)-**2i**
syn-(*Z*)-**2i**
[rel]
[ppm]
200
150
100
50
0
5
10
15

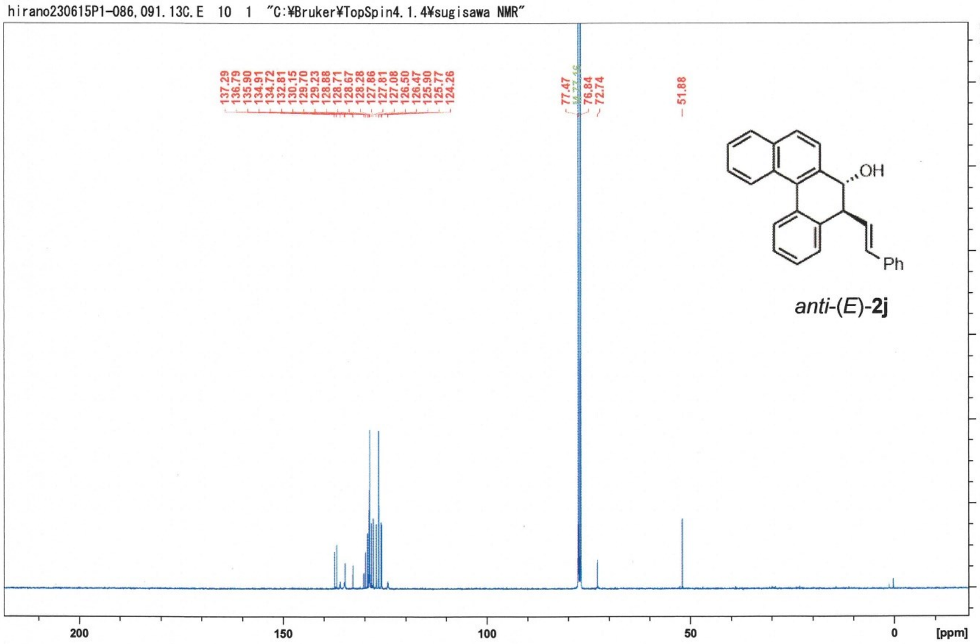


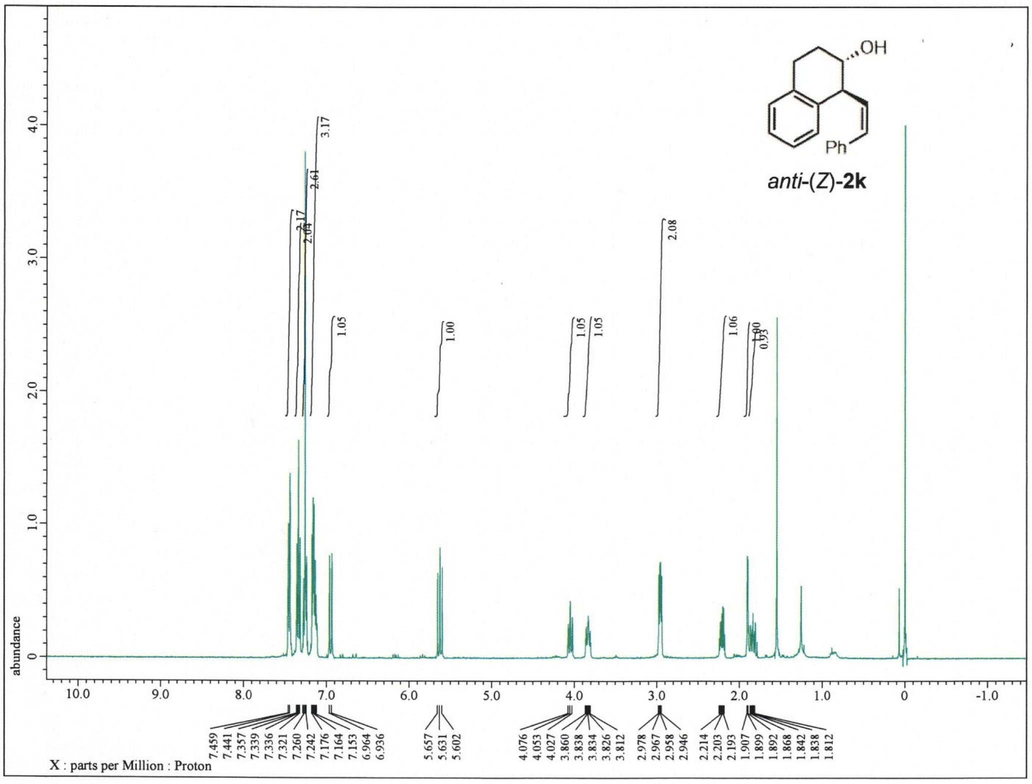
anti-(*Z*)-**2j**

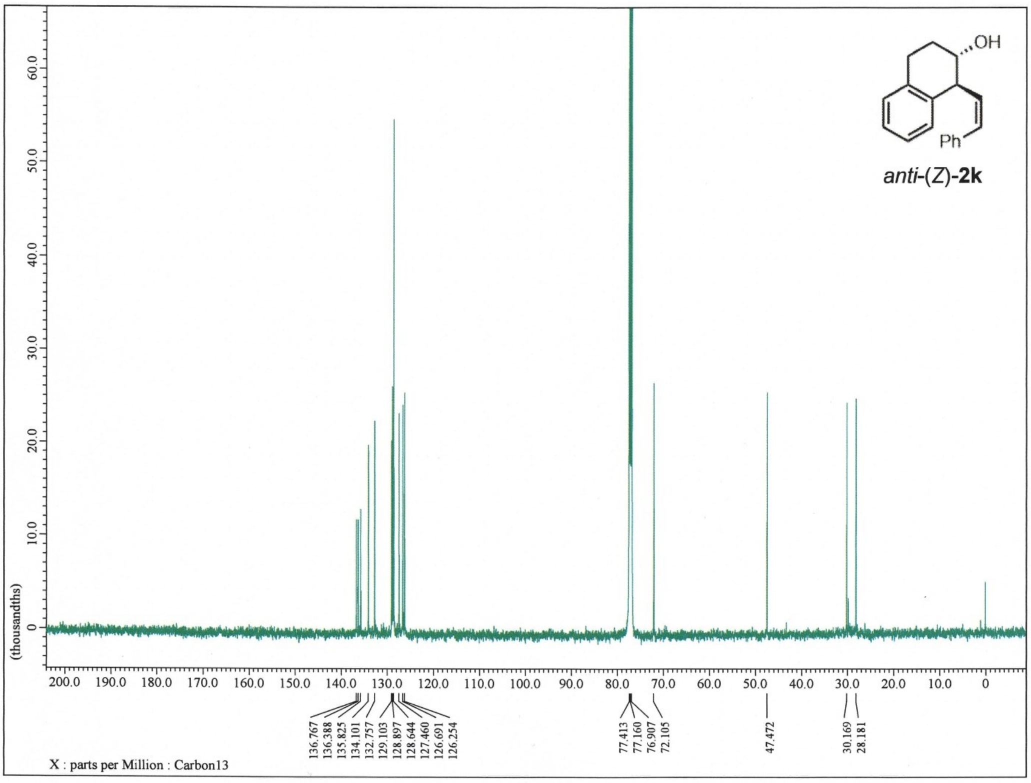


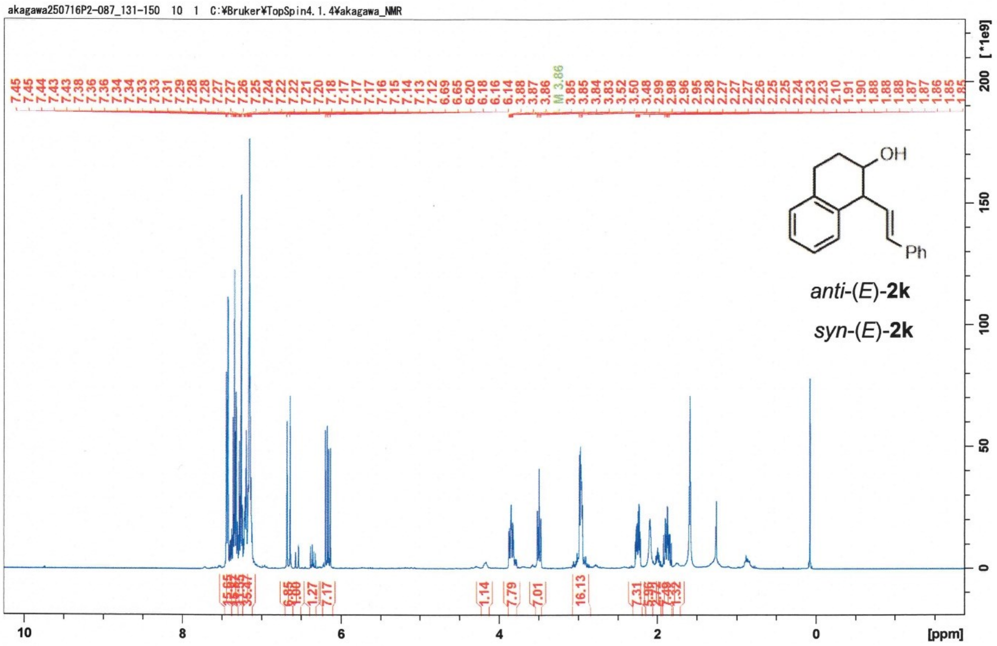
anti-(*Z*)-**2j**

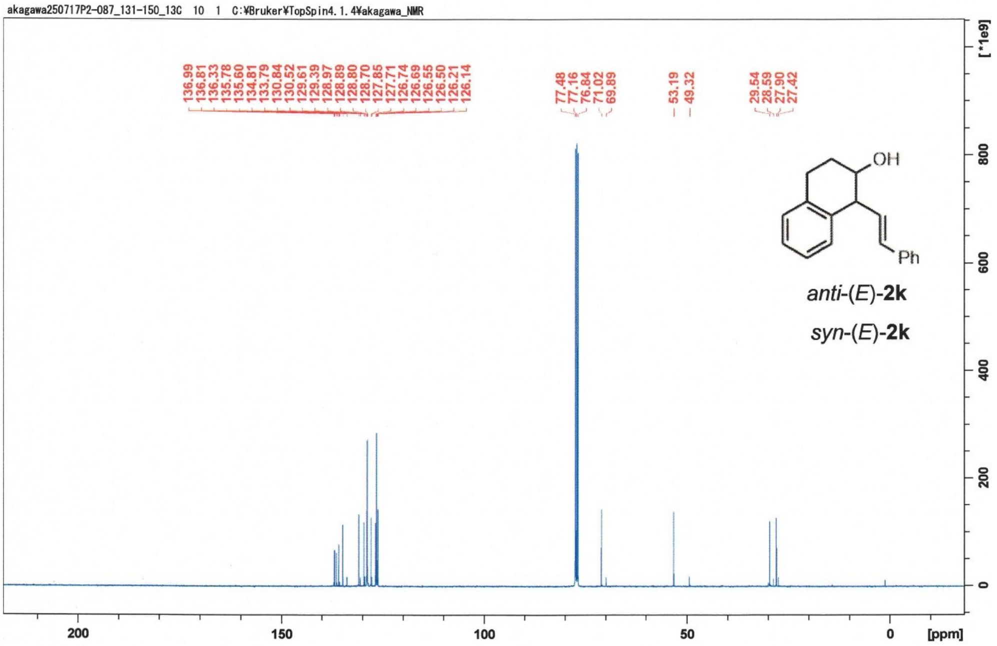

hirano230614P1-086,091,1H,E 10 1 "C:¥Bruker¥TopSpin4.1.4¥sugisawa NMR"
7.49 7.48 7.47 7.46 7.46 7.45 7.45 7.43 7.43 7.42 7.41 7.38 7.38 7.38 7.38 7.36 7.36 7.35 7.34 7.31 7.29 7.27 7.26 7.24 7.23 7.22 7.22 7.20 6.68 6.64 6.25 6.23 6.21 6.19
4.78 4.76
3.85 3.82 3.80
2.17
OH
Ph
anti-(E)-2j
1.07 12.04 1.00 0.98 1.03 1.02 0.96
[rel]
15 10 5 0
10 8 6 4 2 0 [ppm]

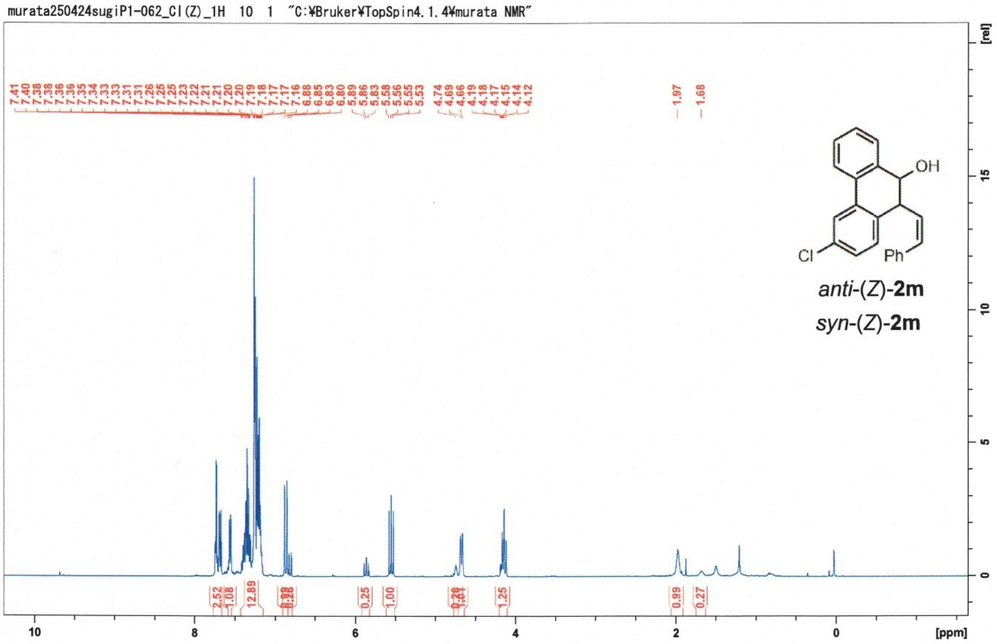

hirano230615P1-086,091,13C,E 10 1 "C:¥Bruker¥TopSpin4.1.4¥sugisawa NMR"
137.29 136.79 135.90 134.91 134.72 132.81 130.15 129.70 129.23 128.88 128.71 128.57 128.28 127.86 127.81 127.08 126.50 126.47 125.90 125.77 124.26
77.47 76.84 72.74
51.88
OH
Ph
anti-(E)-2j
[rel]
12 10 8 6 4 2 0
200 150 100 50 0 [ppm]

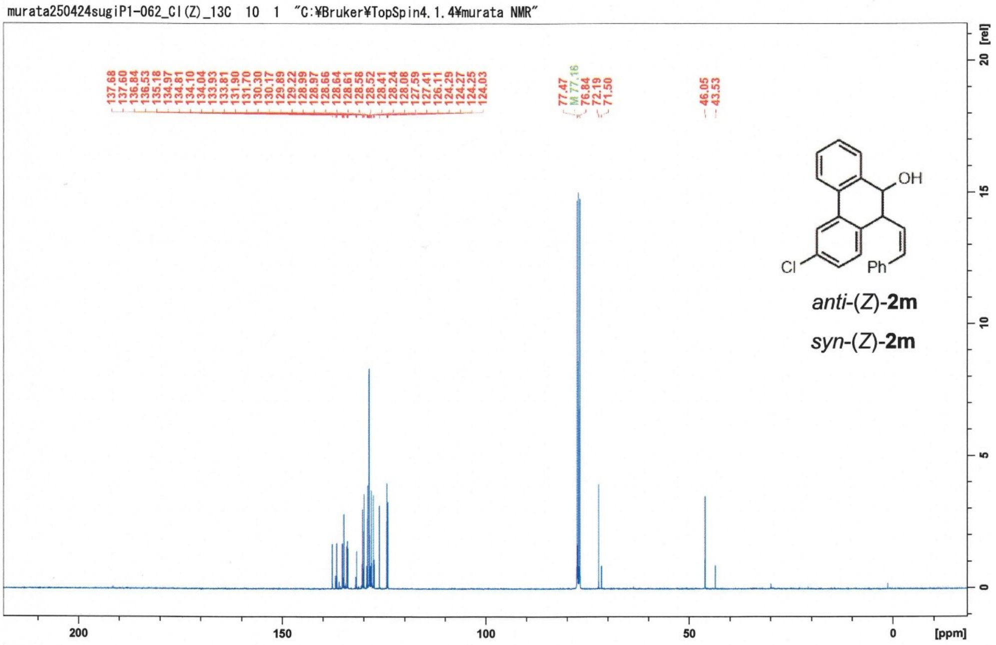

OH
Ph
anti-(Z)-2k
abundance
0
1.0
2.0
3.0
4.0
3.17
2.61
2.17
2.04
1.05
1.00
1.05
1.05
2.08
1.06
1.00
0.93
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.459
7.441
7.357
7.339
7.336
7.321
7.260
7.242
7.176
7.164
7.153
6.964
6.936
5.657
5.631
5.602
4.076
4.053
4.027
3.860
3.838
3.834
3.826
3.812
2.978
2.967
2.958
2.946
2.214
2.203
2.193
1.907
1.899
1.892
1.868
1.842
1.838
1.812
X : parts per Million : Proton

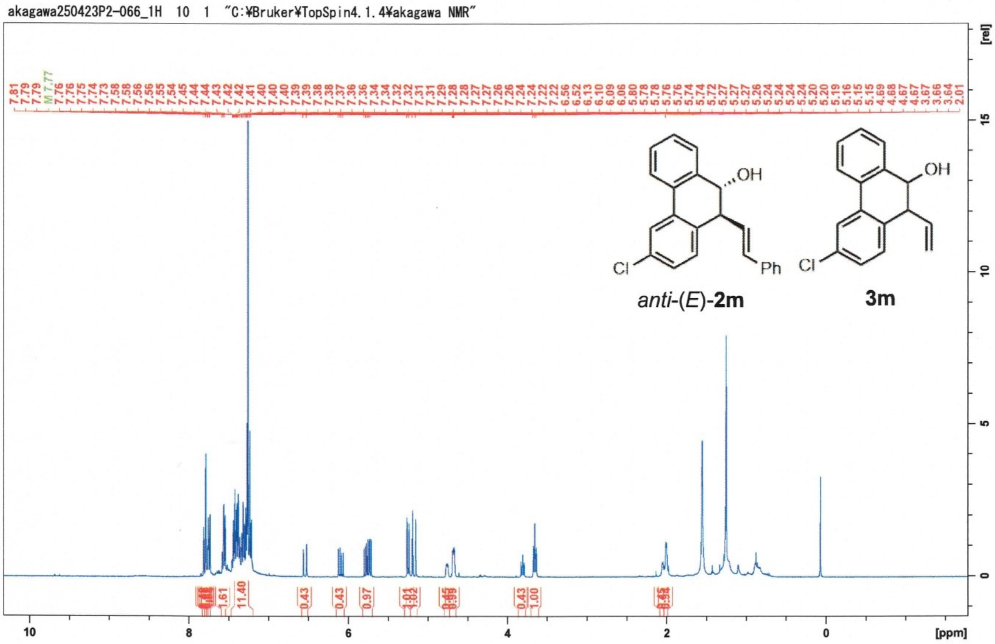

OH
Ph
anti-(Z)-2k
(thousandths)
0
10.0
20.0
30.0
40.0
50.0
60.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
136.767
136.388
135.825
134.101
132.757
129.103
128.897
128.644
127.460
126.691
126.254
77.413
77.160
76.907
72.105
47.472
30.169
28.181
X : parts per Million : Carbon13

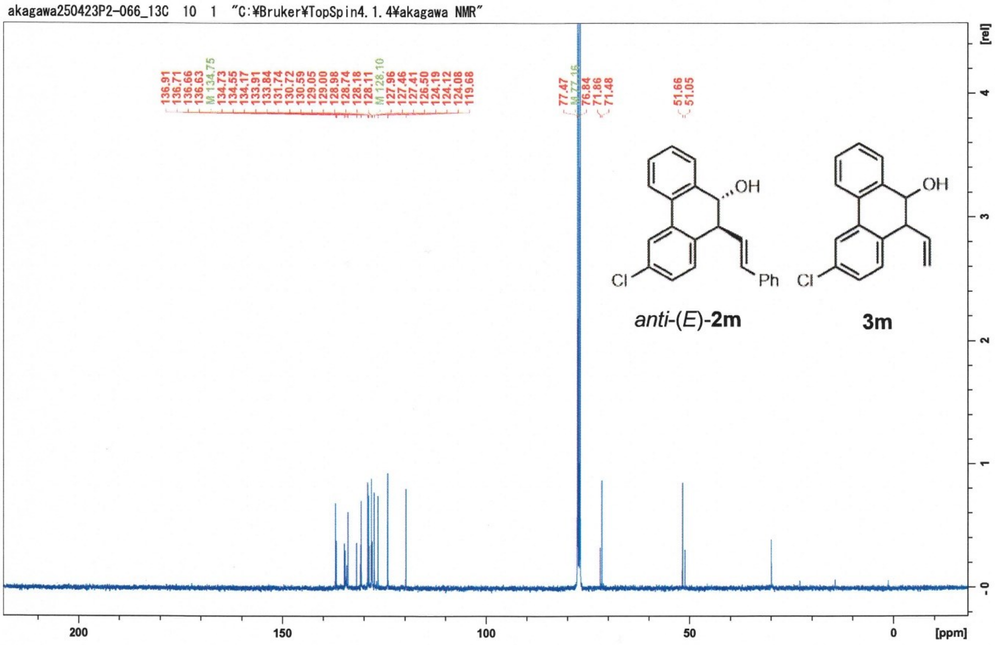

akagawa250716P2-087_131-150 10 1 C:¥Bruker¥TopSpin4.1.4¥akagawa_NMR
anti-(E)-2k
syn-(E)-2k
OH
Ph
[ppm]
[*1e9]

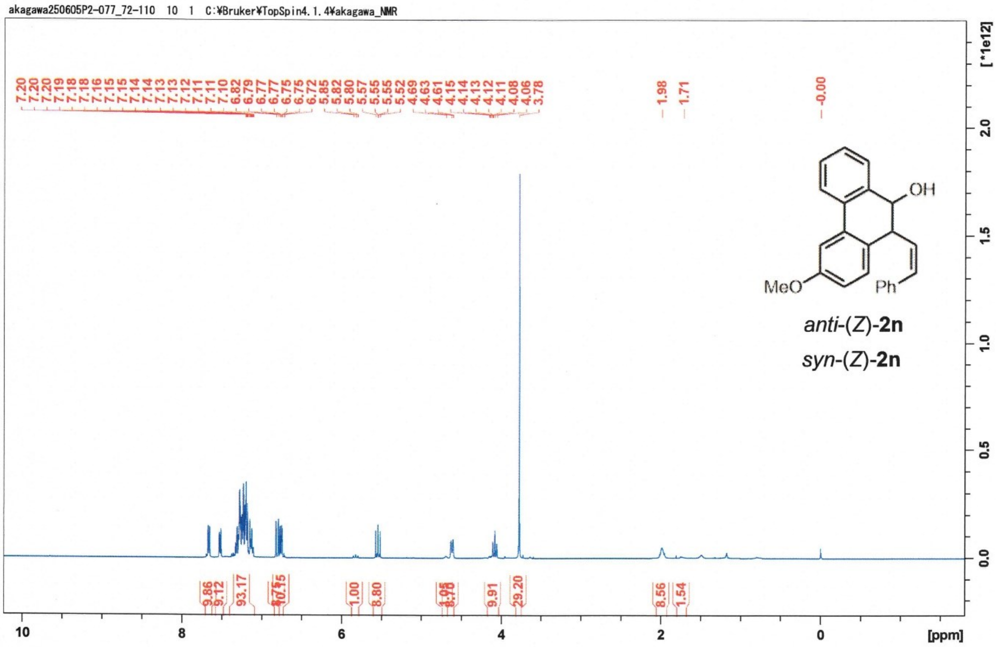

akagawa250717P2-087_131-150_13C 10 1 C:¥Bruker¥TopSpin4.1.4¥akagawa_NMR
136.99 136.81 136.33 135.78 135.60 134.81 133.79 130.84 130.52 129.61 129.39 128.97 128.89 128.80 128.70 127.85 127.71 127.74 126.69 126.55 126.50 126.21 126.14
77.48 77.16 76.84 71.02 69.89
53.19 49.32
29.54 28.59 27.90 27.42
anti-(E)-2k
syn-(E)-2k
OH
Ph
[ppm]
[*1e9]


murata250424sugiP1-062_Cl(Z)_1H 10 1 "C:¥Bruker¥TopSpin4.1.4¥murata NMR"
7.41 7.40 7.38 7.38 7.36 7.36 7.35 7.34 7.33 7.33 7.31 7.31 7.26 7.25 7.25 7.23 7.22 7.21 7.21 7.20 7.20 7.19 7.18 7.17 7.17 7.16 6.88 6.85 6.83 6.80 5.89 5.86 5.83 5.58 5.56 5.55 5.53 4.74 4.69 4.66 4.19 4.18 4.17 4.15 4.14 4.12
1.97
1.68
OH
Cl
Ph
anti-(*Z*)-**2m**
syn-(*Z*)-**2m**
2.52
1.08
12.89
0.25
1.00
1.25
0.99
0.27
10
8
6
4
2
0
[ppm]
[rel]
15
10
5
0


murata250424sugiP1-062_Cl(Z)_13C 10 1 "C:¥Bruker¥TopSpin4.1.4¥murata NMR"
137.68 137.60 136.84 136.53 135.18 134.97 134.81 134.10 134.04 133.93 133.81 131.90 131.70 130.30 130.17 129.89 129.22 128.99 128.97 128.66 128.64 128.61 128.58 128.52 128.41 128.24 128.08 127.59 127.41 126.11 124.29 124.27 124.25 124.03
77.47
M 77.16
76.84
72.19
71.50
46.05
43.53
OH
Cl
Ph
anti-(*Z*)-**2m**
syn-(*Z*)-**2m**
200
150
100
50
0
[ppm]
[rel]
20
15
10
5
0

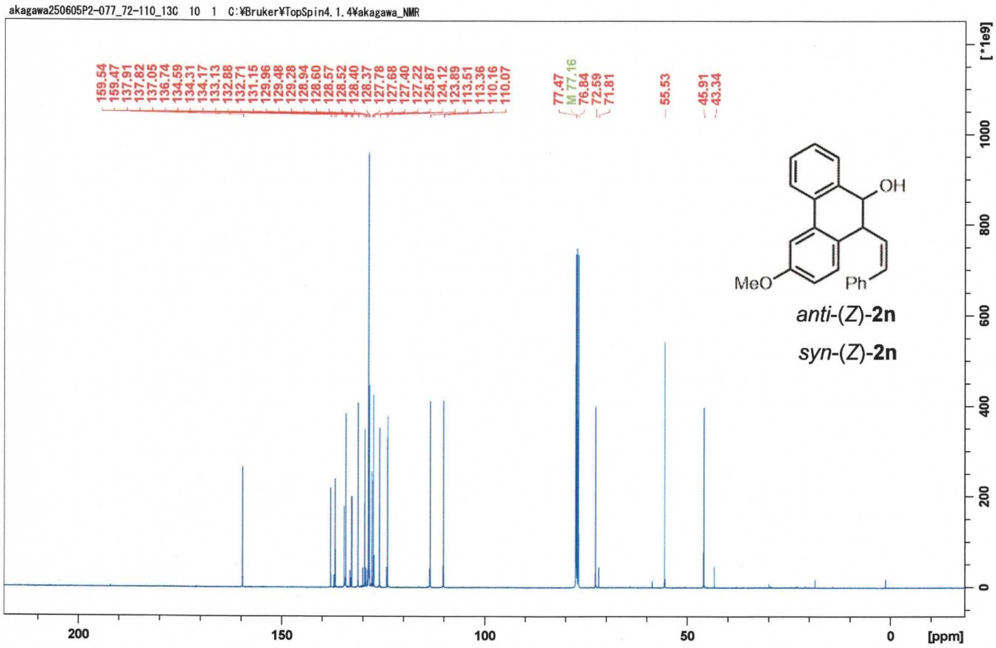

akagawa250423P2-066_1H 10 1 "C:¥Bruker¥TopSpin4.1.4¥akagawa NMR"
7.81 7.79 M 7.77 7.76 7.75 7.74 7.73 7.58 7.56 7.55 7.54 7.45 7.44 7.44 7.43 7.42 7.42 7.41 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.36 7.36 7.35 7.34 7.32 7.31 7.31 7.29 7.28 7.28 7.27 7.26 7.24 7.24 7.22 7.22 6.56 6.52 6.13 6.10 6.09 6.06 5.80 5.78 5.76 5.76 5.74 5.74 5.72 5.27 5.27 5.26 5.24 5.24 5.24 5.20 5.19 5.16 5.15 5.15 4.69 4.68 4.67 4.67 3.67 3.66 3.64 2.01
1.61
11.40
0.43
0.43
0.97
0.43
1.00
OH
Cl
Ph
anti-(*E*)-**2m**
3m
[rel]
[ppm]
10
8
6
4
2
0
15
10
5
0


akagawa250423P2-066_13C 10 1 "C:¥Bruker¥TopSpin4.1.4¥akagawa NMR"
136.91 136.71 136.66 136.63 M 134.75 134.73 134.55 134.17 133.91 133.84 131.74 130.72 130.59 129.05 129.00 128.98 128.74 128.18 128.11 M 128.10 127.96 127.46 127.41 126.50 124.19 124.12 124.08 119.68
77.47 M 77.16 76.84 71.86 71.48
51.66 51.05
OH
Cl
Ph
anti-(*E*)-**2m**
3m
[rel]
[ppm]
200
150
100
50
0
4
3
2
1
0



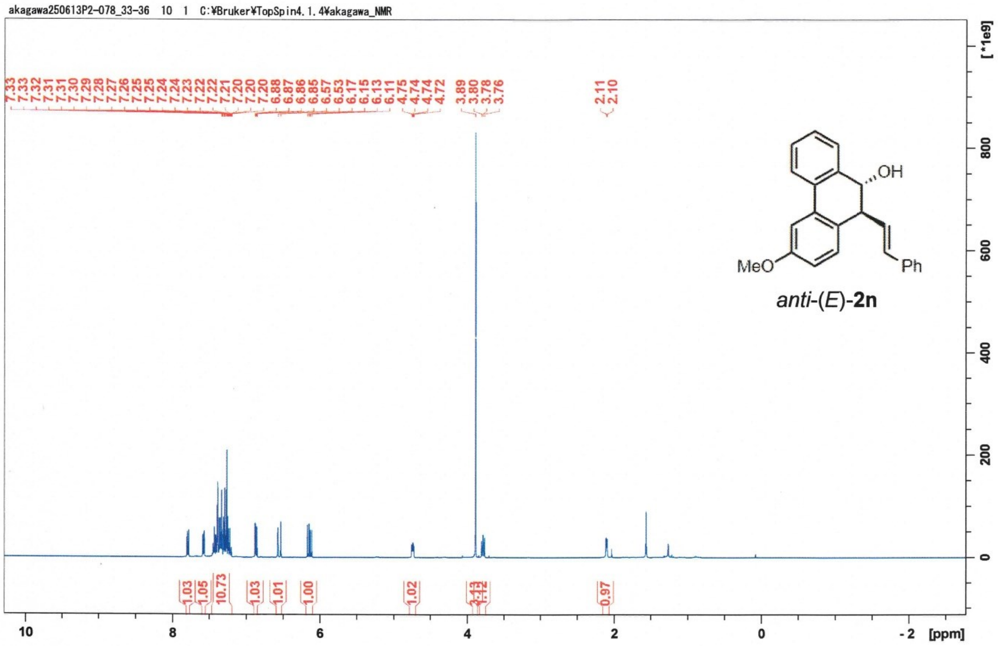
anti-(*Z*)-**2n**

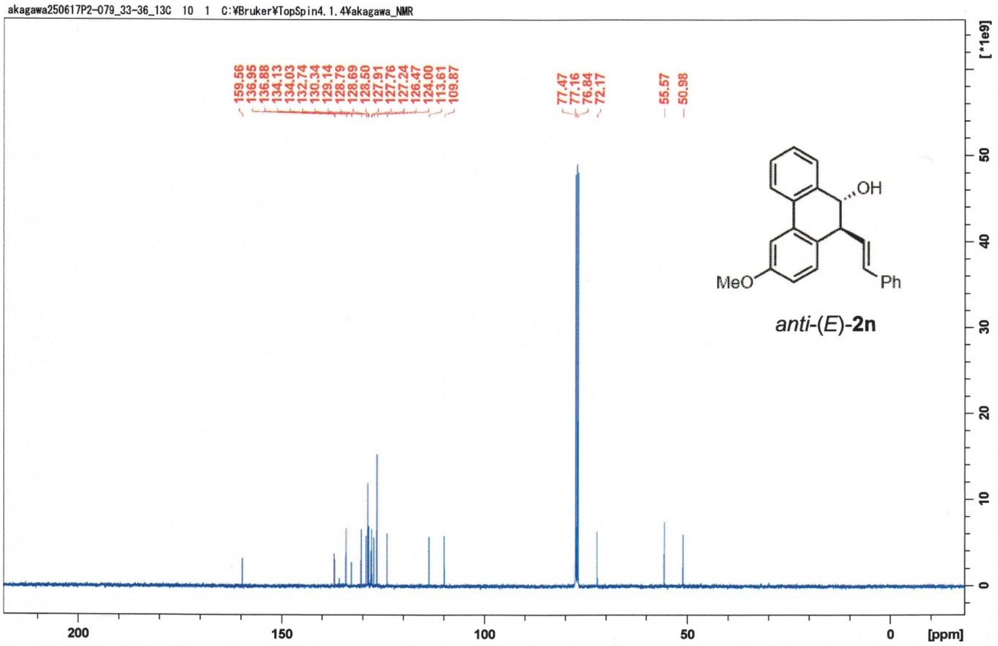
syn-(*Z*)-**2n**

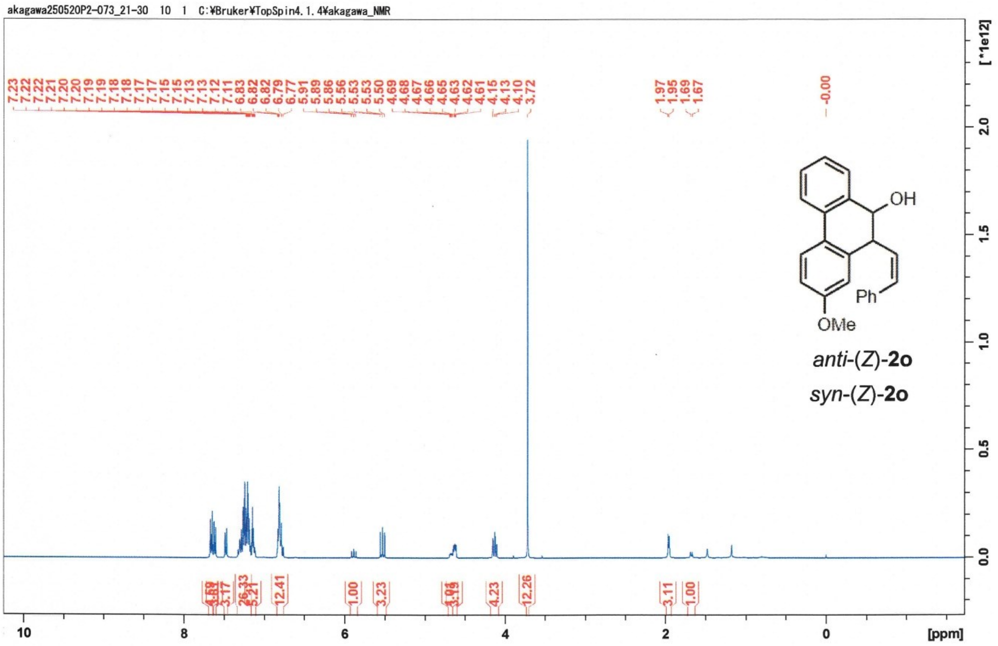


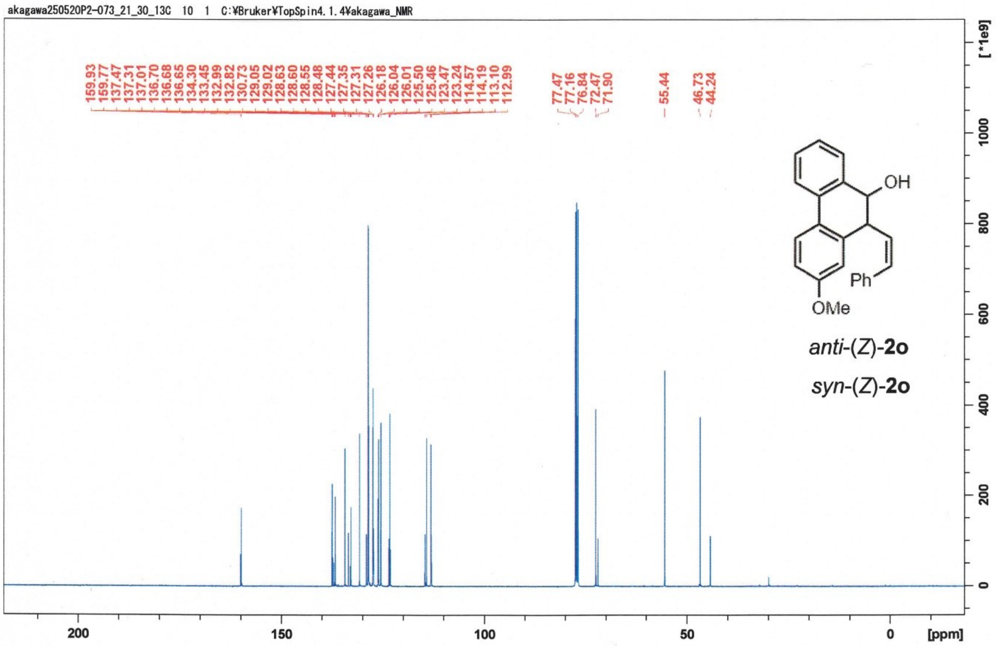
anti-(*Z*)-**2n**

syn-(*Z*)-**2n**


akagawa250613P2-078_33-36 10 1 C:¥Bruker¥TopSpin4.1.4¥akagawa_NMR
7.33
7.33
7.32
7.31
7.31
7.30
7.29
7.28
7.27
7.26
7.25
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.20
7.20
7.20
6.88
6.87
6.86
6.85
6.57
6.53
6.17
6.15
6.13
6.11
4.75
4.74
4.74
4.72
3.89
3.80
3.78
3.76
2.11
2.10
OH
MeO
Ph
anti-(E)-2n
1.03
1.05
10.73
1.03
1.01
1.00
1.02
3.13
1.12
0.97
10
8
6
4
2
0
-2
[ppm]
[*1e9]
800
600
400
200
0


akagawa250617P2-079_33-36_13C 10 1 C:¥Bruker¥TopSpin4.1.4¥akagawa_NMR
159.56
136.95
136.88
134.13
134.03
132.74
130.34
129.14
128.79
128.69
128.50
127.91
127.76
127.24
126.47
124.00
113.61
109.87
77.47
77.16
76.84
72.17
55.57
50.98
OH
MeO
Ph
anti-(E)-2n
200
150
100
50
0
[ppm]
[*1e9]
50
40
30
20
10
0


akagawa250520P2-073_21-30 10 1 C:¥Bruker¥TopSpin4.1.4¥akagawa_NMR
7.23 7.22 7.22 7.21 7.20 7.20 7.19 7.19 7.18 7.18 7.17 7.17 7.15 7.15 7.13 7.13 7.12 7.11 6.83 6.82 6.82 6.79 6.77 5.91 5.89 5.86 5.56 5.53 5.53 5.50 4.69 4.68 4.67 4.66 4.65 4.63 4.62 4.61 4.15 4.13 4.10 3.72
1.97 1.95 1.69 1.67
-0.00
[*1e12]
2.0
1.5
1.0
0.5
0.0
OH
Ph
OMe
anti-(Z)-2o
syn-(Z)-2o
3.17
26.33
5.21
12.41
1.00
3.23
4.23
12.26
3.11
1.00
10
8
6
4
2
0
[ppm]


akagawa250520P2-073_21_30_13C 10 1 C:¥Bruker¥TopSpin4.1.4¥akagawa_NMR
159.93 159.77 137.47 137.31 137.01 136.70 136.68 136.65 134.30 133.45 132.99 132.82 130.73 129.05 129.02 128.63 128.60 128.55 128.48 127.44 127.35 127.31 127.26 126.18 126.04 126.01 125.50 125.46 123.47 123.24 114.57 114.19 113.10 112.99
77.47 77.16 76.84 72.47 71.90
55.44
46.73 44.24
[*1e9]
1000
800
600
400
200
0
OH
Ph
OMe
anti-(Z)-2o
syn-(Z)-2o
200
150
100
50
0
[ppm]