

Supporting Information

Electrochemical Dimerization of Phenylpropenoids and the Surprising Antioxidant Activity of the Resultant Quinone Methide Dimers

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General Procedures:

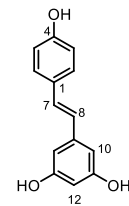
Unless specifically noted otherwise, all glassware was flame-dried under vacuum (~0.5 Torr) and cooled under inert atmosphere (N₂ or Ar) prior to use. Each reaction container was charged with a Teflon/PTFE-coated magnetic stir bar and sealed with a rubber septum to maintain a positive pressure of inert atmosphere (N₂ or Ar). Reagents sensitive to the atmosphere were transferred via syringe or cannula as necessary. Reaction conversion was evaluated using analytical thin-layer chromatography (TLC) using Merck silica gel 60 F254 TLC plates. TLC plates were visualized under a dual short wave/long wave UV lamp and/or stained using solutions of *p*-anisaldehyde or potassium permanganate or ceric ammonium molybdate. Stained plates were developed over a heat gun as needed. Reactions were purified via flash column chromatography either with RediSep®_{RF} Gold silica columns using a Teledyne Isco CombiFlash R_F automated purification system or manually using 230–400 mesh silica gel. Either sodium sulfate or magnesium sulfate were utilized to exclude water from worked up reactions, and the solvent was removed on Büchi rotary evaporators and/or a Welch vacuum pump. All electrochemical experiments were acquired using either a CH1620E electrochemical analyzer (from CH Instruments) or a uSTAT4000 4-Channel Potentiostat/Galvanostat (from Metrohm USA). Cyclic voltammetry measurements were performed in five-neck cells (3 mL) using a three-electrode set-up in which the working electrode was glassy carbon (3 mm diameter), the counter/auxiliary electrode was a platinum wire, and the reference electrode was Ag/AgCl (3 M KCl, from CH Instruments). Bulk electrolysis experiments were performed on discovery scale in open 10-mL vials and in a beaker of the appropriate size (15 – 40 mL) for the subsequent scale-up experiments. These reactions used RVC panels (reticulated vitreous carbon, 100 ppi, 0.25 inch thickness, 3% relative density, from McMaster Carr) as the working or counter/auxiliary electrodes and a Ag/AgCl (3 M KCl) reference electrode.

Reaction Materials:

Commercially available reagents were used without further purification unless specified. Organic solvents (acetonitrile, dichloromethane, diethyl ether, dimethylformamide, dimethyl sulfoxide, methanol, tetrahydrofuran, and toluene) and amine bases (triethylamine, pyridine, N,N-diisopropylethylamine, and diisopropylamine) were purified prior to use with a Phoenix Solvent Drying System from JC-Meyer Solvent Systems and PureSolv Micro amine drying columns from Innovative Technology, respectively, and kept under a pressure of argon. Solutions of organolithium reagents and Grignard reagents were purchased from Acros Organics and titrated prior to use.

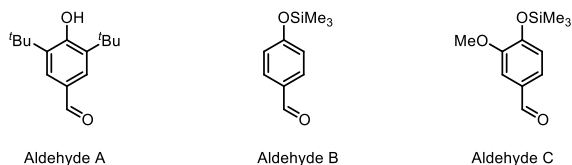
Product Analysis:

Product names were obtained using ChemDraw Professional 16.0 from Perkin Elmer. For racemic compounds, the name corresponds to the depicted structure. Nuclear magnetic resonance (NMR) spectra were obtained using an internal deuterium lock on Varian Inova 500 or Varian VNMR 500 and 700 spectrometers. For ¹H spectra, chemical shifts were referenced to the center line of the residual solvent signal (CDCl₃: δ 7.26; acetone-*d*₆: δ 2.05) and are reported in parts per million (ppm). Signal multiplicity is reported as follows: (br = broad, s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, m = multiplet), and the associated coupling constants are given in Hertz. For ¹³C spectra, experiments were completely heterodecoupled (broadband) and chemical shifts are reported as ppm using the center line of the solvent signal as reference (CDCl₃: δ 77.16; acetone-*d*₆: δ 29.92). The following resveratrol numbering scheme was used for the assignment of ¹H and ¹³C NMR signals. High-resolution mass spectra (HRMS) were acquired using a Micromass AutoSpec Ultima Magnetic Sector mass spectrometer using electrospray ionization (ESI), positive ion mode. We thank James Windak and Paul Lennon at the University of Michigan, Department of Chemistry Instrumentation Facility for conducting the HRMS experiments. Infrared spectra were acquired using a Perkin-Elmer Spectrum BX FT-IR spectrophotometer using an ATR mount with a ZnSe crystal.



General Stilbene preparation:

Unless otherwise specified, stilbene substrates were prepared from the benzyl alcohol or benzyl bromide via a Wittig olefination with one of the following aldehydes:



3,5-di-*tert*-butyl-4-hydroxybenzaldehyde (aldehyde A), commercially available;

4-((trimethylsilyl)oxy)benzaldehyde (aldehyde B), from silyl protection of 4-hydroxybenzaldehyde;

3-methoxy-4-((trimethylsilyl)oxy)benzaldehyde (aldehyde C), from silyl protection of vanillin.

Starting from the benzyl alcohol:

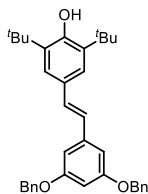
A solution of triphenylphosphine (0.97 g, 3.71 mmol) in dry THF (2.5 mL) was sparged with N₂ (18G needle, 5 min) and was added dropwise to a solution of (benzyl) alcohol (2.97 mmol) and carbon tetrabromide (1.31 3.71 mmol) in dry THF (4.5 mL) that had been previously sparged (18G needle, 5 min.) in a 50 mL flame-dried round bottom flask and chilled to 0 °C. The mixture was stirred at room temperature for 16 h followed by dropwise addition of methanol (1 mL). The mixture was diluted with EtOAc (100 mL) and added to a separatory funnel and the organic phase was washed with a 1:1:1 mixture of 10% bicarbonate solution, saturated Na₂S₂O₃, and DI water solution (100mL). The organic phase was washed with brine and dried over Na₂SO₄. The organic phase was then concentrated under reduced pressure and purified by silica gel (pre-neutralized) column chromatography and eluted with 10:1 (hexane/ ethyl acetate) to afford the brominated product.

Starting from the benzyl bromide:

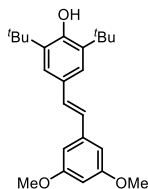
The benzyl bromide was added to a flame-dried round bottom flask charged with a stir bar and fitted with a reflux condenser and dissolved in toluene (0.15 – 0.20 M). To the stirring solution was added triphenylphosphine (1.5 equiv.), and the reaction was heated to 100 °C for 12 hours. After cooling the reaction mixture to room temperature, the white phosphonium salt was collected via vacuum filtration, and any excess triphenylphosphine was rinsed away with hexanes. The phosphonium salt was dried under vacuum for >24 hours prior to use in the Wittig olefination to ensure full removal of residual solvent and water.

The phosphonium salt was added to a flame-dried, 3-neck, round bottom flask charged with stir bar and fitted with a reflux condenser. The salt was suspended in solvent (toluene or THF, 0.1 M), and to the stirring mixture was added *n*BuLi (1.6 or 2.5 M, 1.00 equiv.). After 30 minutes, the reaction mixture had become a brilliant red, clear solution, at which point the aldehyde was added under a stream of nitrogen, and the reaction was heated at reflux for 12 hours. After cooling the reaction mixture to room temperature, the reaction was quenched with saturated aqueous ammonium chloride, diluted with ethyl acetate, and added to a separatory funnel containing additional aqueous ammonium chloride. The layers were separated, and the aqueous layer was extracted with additional ethyl acetate. The combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. The crude stilbene products were purified via flash column chromatography (see characterization data for specific chromatography conditions).

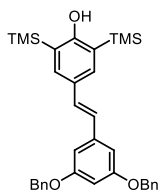
The following substrates were acquired from previous investigations reported by our group.^{1,2}



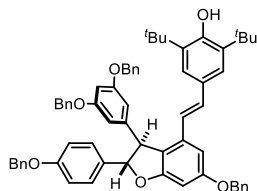
(S0) (*E*)-4-(3,5-bis(benzyloxy)styryl)-2,6-di-*tert*-butylphenol



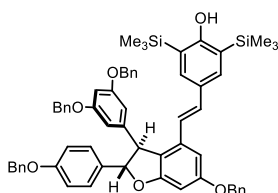
(S1) (*E*)-2,6-di-*tert*-butyl-4-(3,5-dimethoxystyryl)phenol



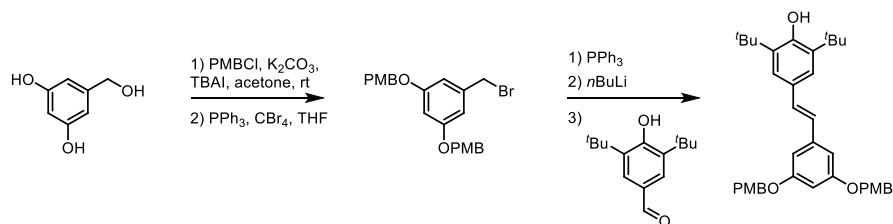
(S2) (*E*)-2,6-di-*tert*-butyl-4-(3,5-dimethoxystyryl)phenol



(21) 4-((*E*)-2-((2*S*,3*S*)-6-(benzyloxy)-2-(4-(benzyloxy)phenyl)-3-(3,5-bis(benzyloxy)phenyl)-2,3-dihydrobenzofuran-4-yl)vinyl)-2,6-di-*tert*-butylphenol



(22) 4-((*E*)-2-((2*S*,3*S*)-6-(benzyloxy)-2-(4-(benzyloxy)phenyl)-3-(3,5-bis(benzyloxy)phenyl)-2,3-dihydrobenzofuran-4-yl)vinyl)-2,6-bis(trimethylsilyl)phenol



(S3) (*E*)-4-(3,5-bis((4-methoxybenzyl)oxy)styryl)-2,6-di-*tert*-butylphenol

Commercially available 3,5-dihydroxybenzyl alcohol (2.0 g, 14.3 mmol) was added to flask charged with potassium carbonate (2.25 equiv., 4.44 g) and tetrabutylammonium iodide (0.2 equiv., 1.05 g), and the solids were dissolved/suspended in acetone (42 mL). To the stirring reaction mixture was added 4-methoxybenzyl chloride (2.20 equiv., 4.26 mL), and the reaction was allowed to stir at room temperature for 16 hours. Upon completion, the reaction was diluted with ethyl acetate and poured into a separatory funnel containing deionized water. The layers were separated, and the aqueous layer was extracted with additional portions of ethyl acetate. The combined organic layer was washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure to afford the crude product, which was carried forward without further purification. The PMB-protected material (2.18g, 5.72 mmol) was subjected to the general procedure using toluene as the solvent for the olefination with aldehyde A. The product was purified by column chromatography (4% to 28% ethyl acetate in hexanes) to afford (*E*)-4-(3,5-bis((4-methoxybenzyl)oxy)styryl)-2,6-di-*tert*-butylphenol (2.06g, 62% yield).

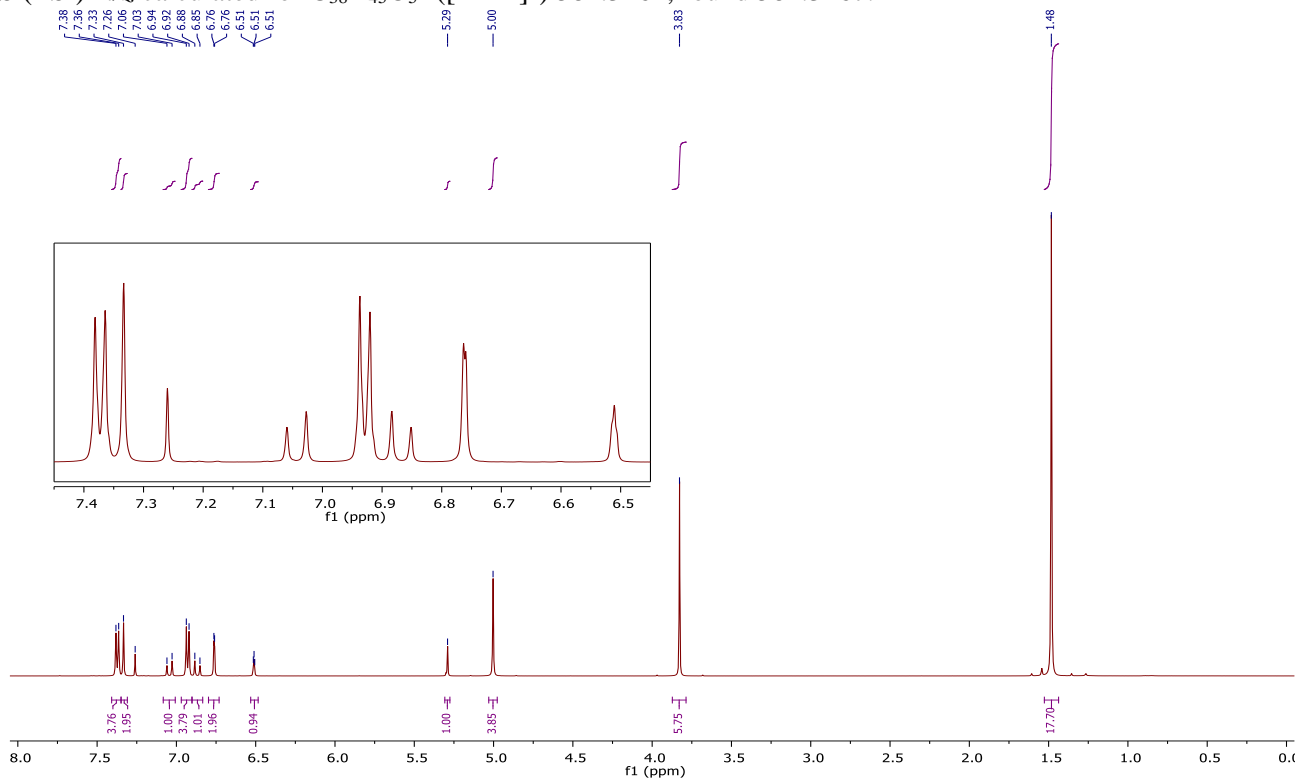
$R_f = 0.22$ (ethyl acetate/hexanes 1:9; UV)

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.37 (d, $J = 8.6$ Hz, 4H), 7.33 (s, 2H), 7.04 (d, $J = 16.1$ Hz, 1H), 6.93 (d, $J = 8.6$ Hz, 4H), 6.87 (d, $J = 16.1$ Hz, 1H), 6.76 (d, $J = 2.2$ Hz, 2H), 6.51 (t, $J = 2.2$ Hz, 1H), 5.29 (s, 1H), 5.00 (s, 4H), 3.83 (s, 6H), 1.48 (s, 18H).

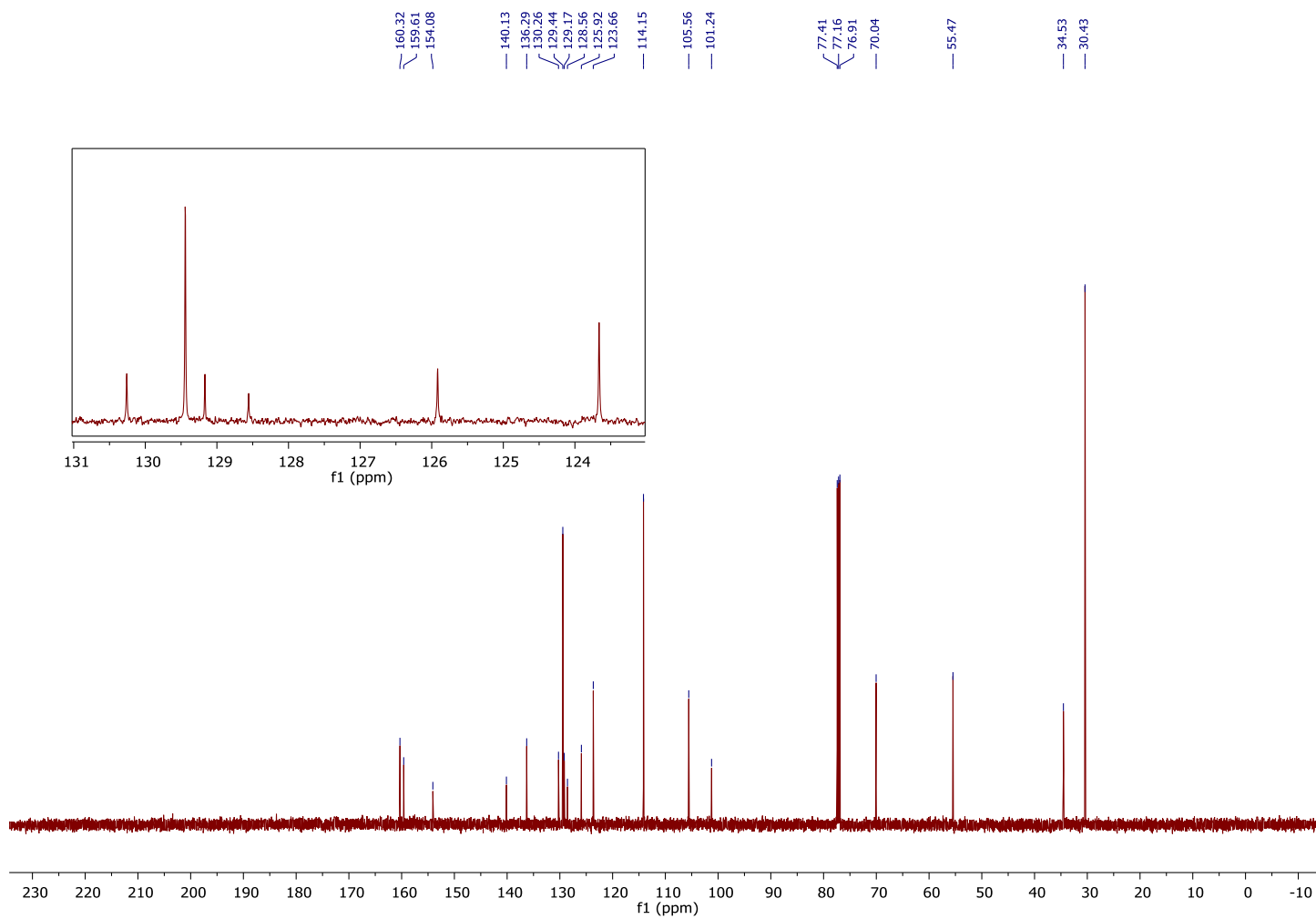
$^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 160.32, 159.61, 154.08, 140.13, 136.29, 130.26, 129.44, 129.17, 128.56, 125.92, 123.66, 114.15, 105.56, 101.24, 70.04, 55.47, 34.53, 30.43.

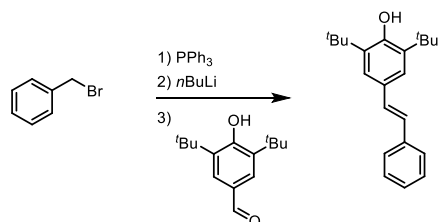
IR (Neat): 3606, 2965, 1577, 1515, 1439, 1245, 1147, 1046, 1026, 967, 858 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{C}_{38}\text{H}_{45}\text{O}_5^+$ ($[\text{M}+\text{H}]^+$) 581.3262, found 581.3267.



^{13}C NMR, 126 MHz, Chloroform-*d*, Stilbene S3





(S4) (*E*)-2,6-di-*tert*-butyl-4-styrylphenol

Commercially available benzyl bromide ((bromomethyl)benzene, 1.1 g, 6.4 mmol) was subjected to the general procedure using toluene as the solvent for the olefination with aldehyde A. The product was purified by column chromatography (2% to 12% ethyl acetate in hexanes) to afford (*E*)-2,6-di-*tert*-butyl-4-styrylphenol (1.64 g, 83% yield). The acquired ^1H and ^{13}C NMR spectra were consistent with those reported in the literature.

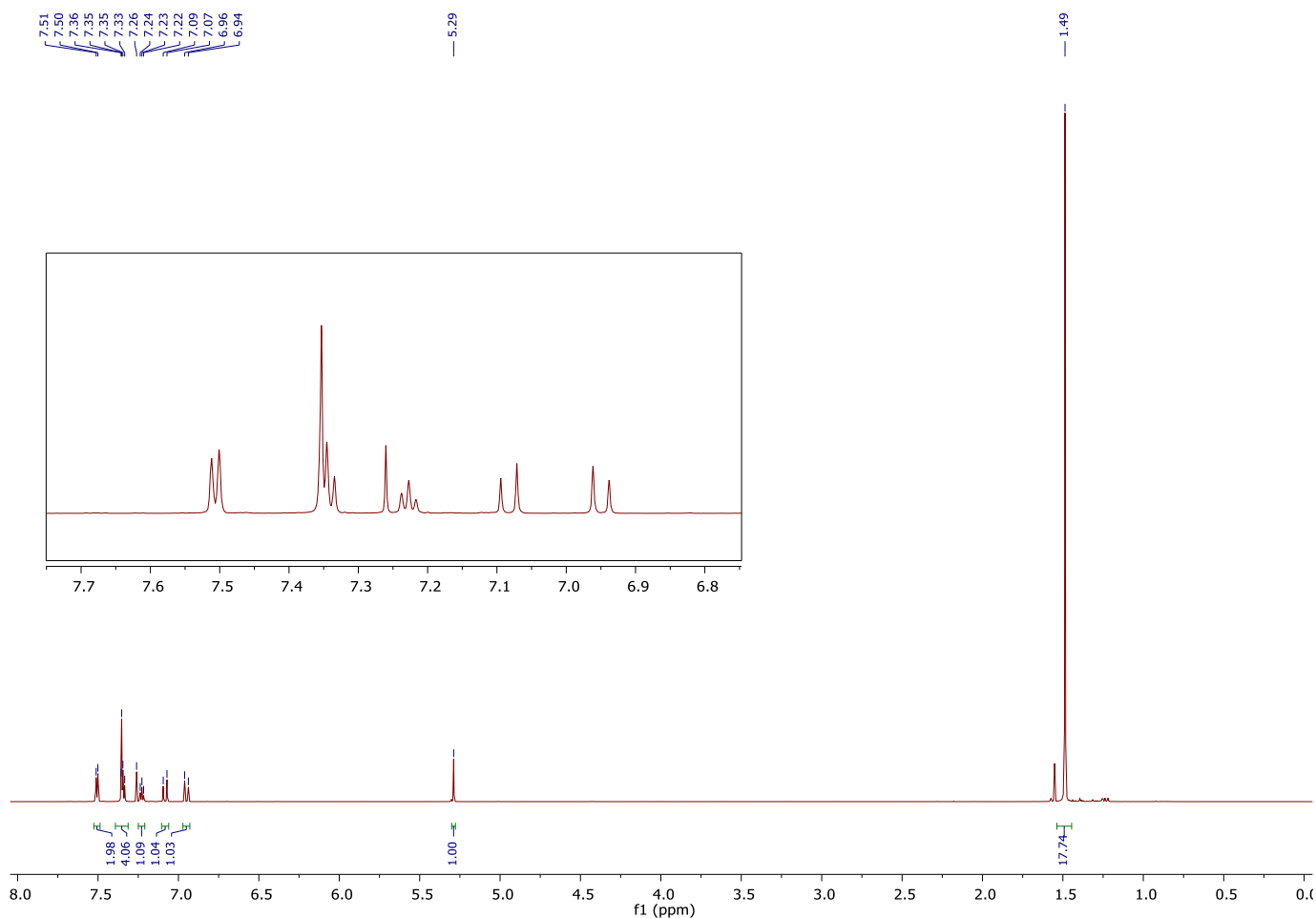
$R_f = 0.31$ (ethyl acetate/hexanes 1:9; UV)

^1H NMR (500 MHz, Chloroform-*d*) δ 7.50 (d, $J = 7.6$ Hz, 2H), 7.35 (s, 2H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.23 (t, $J = 7.3$ Hz, 1H), 7.08 (d, $J = 16.3$ Hz, 1H), 6.95 (d, $J = 16.2$ Hz, 1H), 5.28 (s, 1H), 1.49 (s, 18H).

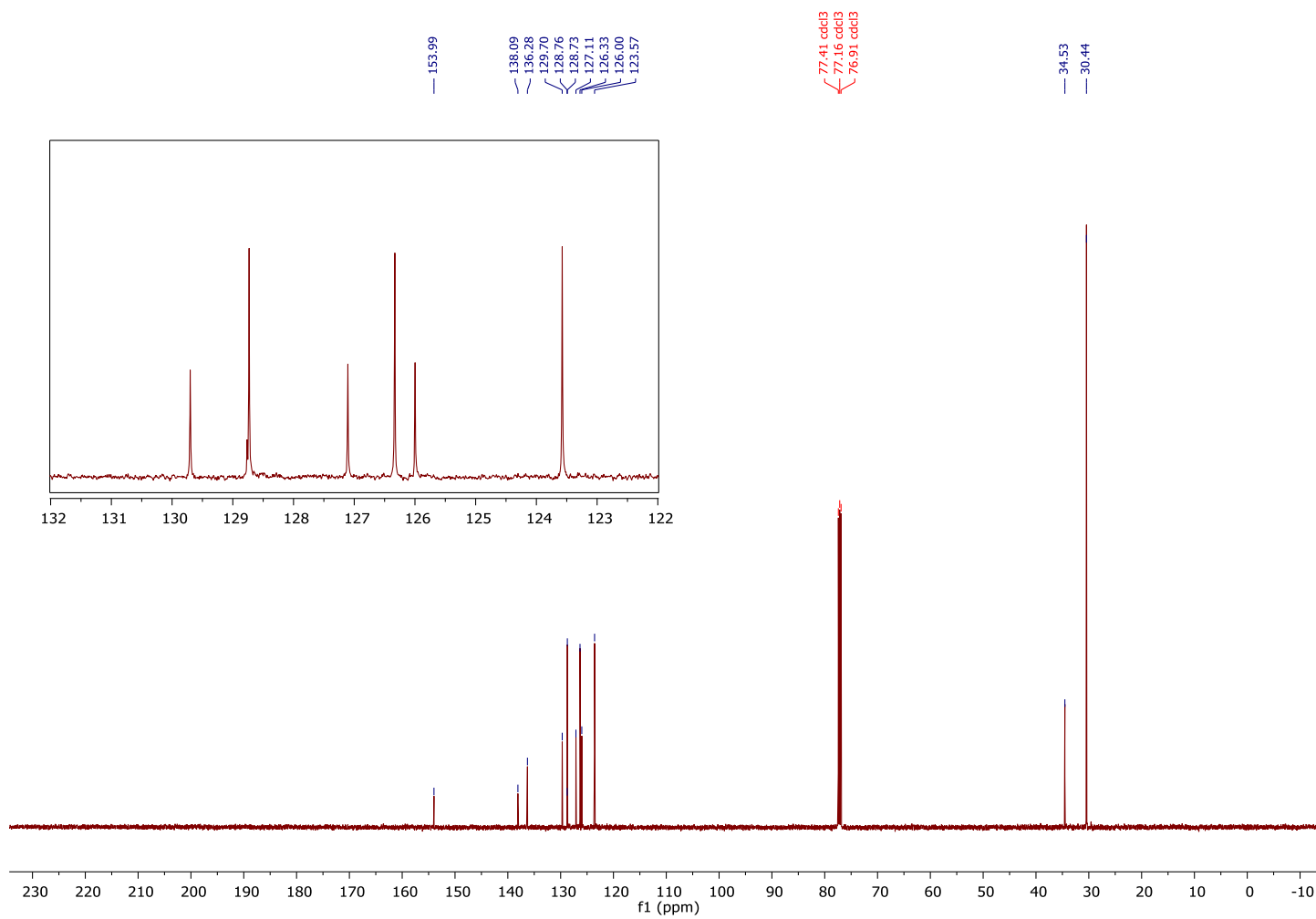
^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.99, 138.09, 136.28, 129.70, 128.73, 127.11, 126.33, 126.00, 123.57, 34.53, 30.44.

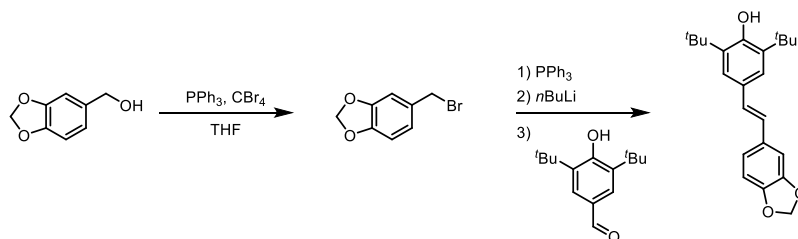
IR (Neat): 3616, 2953, 1470, 1235, 1137, 1118, 957 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{29}\text{O}^+$ ($[\text{M}+\text{H}]^+$) 309.2213, found 309.2206.



^{13}C NMR, 126 MHz, Chloroform-*d*, Stilbene S4





(S5) (*E*)-4-(2-(benzo[*d*][1,3]dioxol-5-yl)vinyl)-2,6-di-*tert*-butylphenol

Commercially available benzyl alcohol (benzo[*d*][1,3]dioxol-5-yl)methanol, 1.00g, 6.6 mmol) was subjected to the general procedure using toluene as the solvent for the olefination with aldehyde A. The product was purified by column chromatography (2% to 12% ethyl acetate in hexanes) to afford (*E*)-4-(2-(benzo[*d*][1,3]dioxol-5-yl)vinyl)-2,6-di-*tert*-butylphenol (1.72 g, 74% yield).

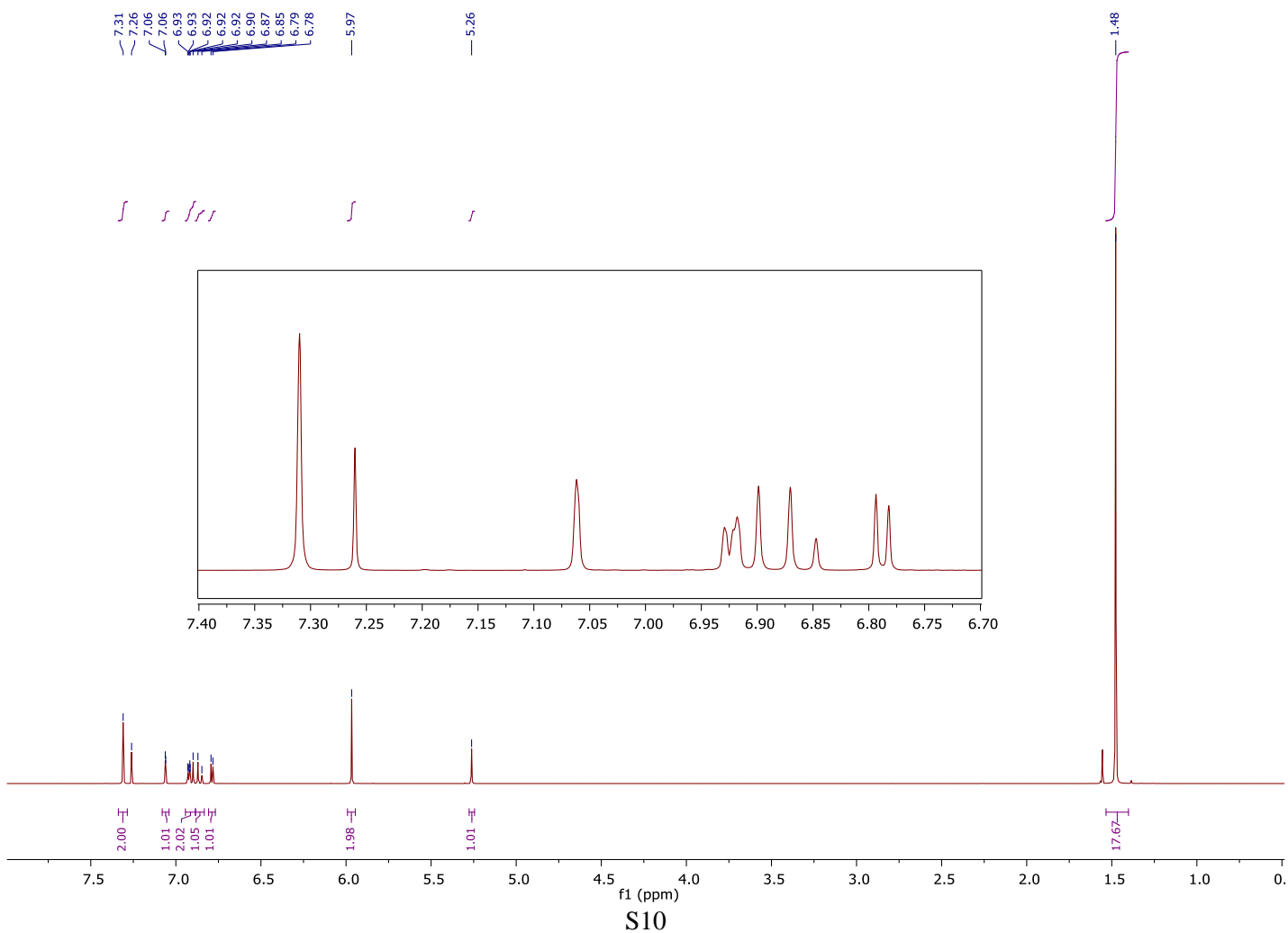
$R_f = 0.26$ (ethyl acetate/hexanes 1:9; UV)

$^1\text{H NMR}$ (700 MHz, Chloroform-*d*) δ 7.31 (s, 2H), 7.06 (s, 1H), 6.92 (d, $J = 8.0$ Hz, 1H), 6.91 (d, $J = 16.2$ Hz, 1H), 6.86 (d, $J = 16.2$ Hz, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 5.97 (s, 2H), 5.26 (s, 1H), 1.48 (s, 18H).

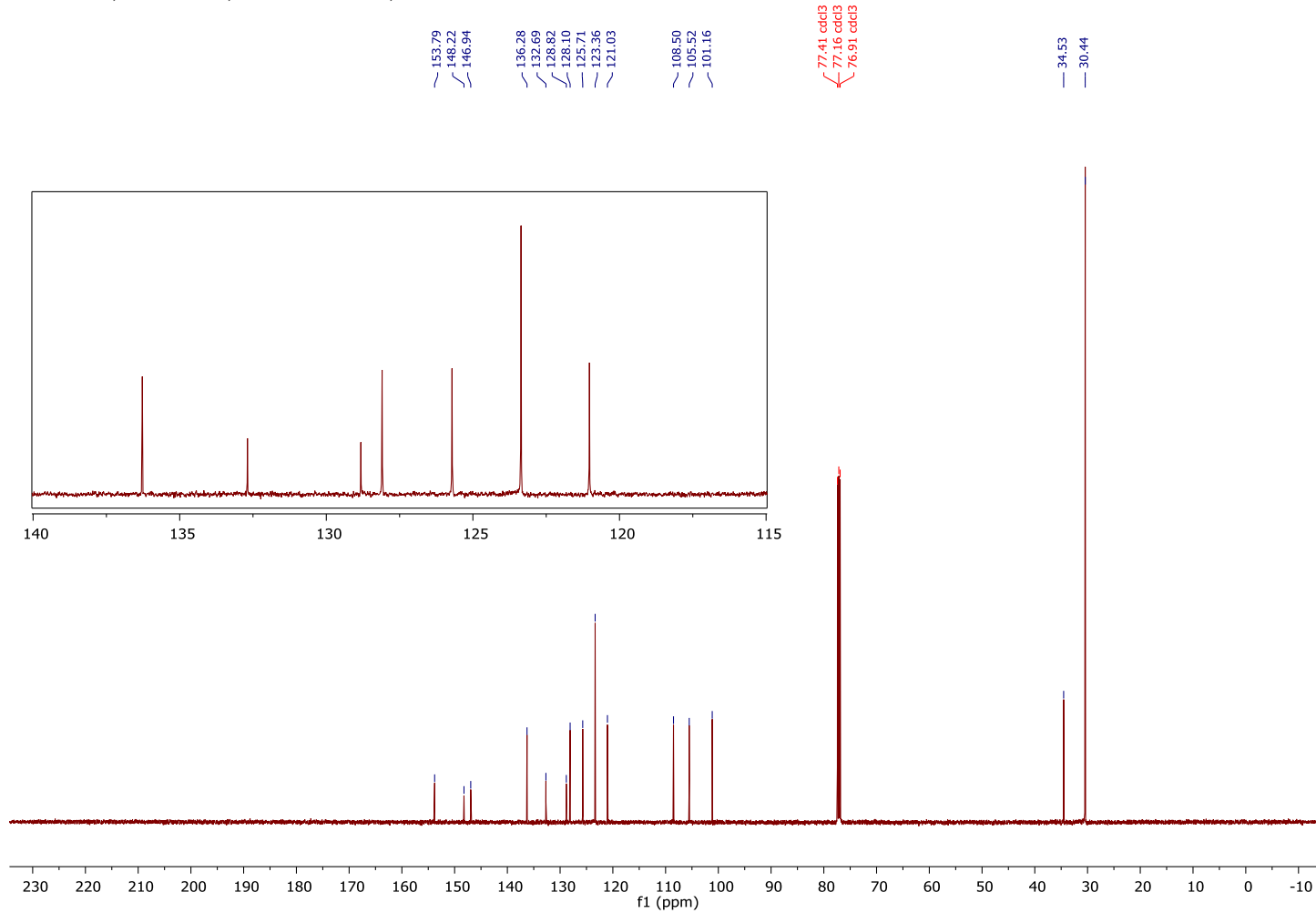
$^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 153.79, 148.22, 146.94, 136.28, 132.69, 128.82, 128.10, 125.71, 123.36, 121.03, 108.50, 105.52, 101.16, 34.53, 30.44.

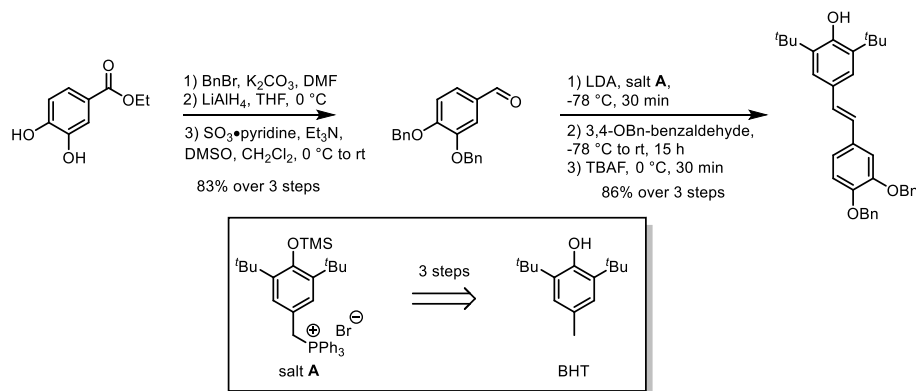
IR (Neat): 3625, 2955, 1486, 1435, 1249, 1135, 1036, 950 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{C}_{23}\text{H}_{29}\text{O}_3^+$ ($[\text{M}+\text{H}]^+$) 353.2111, found 353.2107.



^{13}C NMR, 126 MHz, Chloroform-*d*, Stilbene S5





(S6) (*E*)-4-(3,4-bis(benzyloxy)styryl)-2,6-di-*tert*-butylphenol

Freshly distilled diisopropylamine (1.04 mmol, 146 μ L) was added to a flame-dried heart-shaped flask, dissolved in freshly distilled THF (2 mL), and cooled to -78 °C. To the stirring solution was added *n*BuLi (1.00 mmol, 400 μ L, 2.5 M), and the solution was allowed to stir at the same temperature for 30 min. Meanwhile, in a 3-neck round bottom flask, the phosphonium salt **A** (1.00 mmol, 634 mg, available in 3 steps²) was suspended in freshly distilled THF (10 mL) and cooled to -78 °C. The freshly prepared LDA solution was added to the phosphonium salt suspension via cannula, and the ylid was allowed to form at the same temperature for 30 min, turning the solution deep red. To a flame-dried heart-shaped flask was added 3,4-benzyloxybenzaldehyde (0.80 mmol, 255 mg, available in 3 steps via alkylation, reduction, and oxidation), and the solid was dissolved in THF (5 mL). The aldehyde solution was added to the ylid via cannula, and the reaction was allowed to warm to room temperature overnight (~15 hours). The reaction was subsequently cooled to 0 °C, and a solution of TBAF (1.00 mmol, 1.00 mL, 1.0 M) was added. The desilylation was allowed to occur for 30 min, at which point the reaction was quenched via the addition of saturated ammonium chloride, diluted with EtOAc, and added to a separatory funnel containing deionized water. The layers were separated, and the aqueous layer was extracted with additional portions of EtOAc. The combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (10% to 60% CH₂Cl₂ in Hexanes) to afford the stilbene product (360 mg, 86% yield).

R_f = 0.30 (CH₂Cl₂/hexanes 1:1; UV)

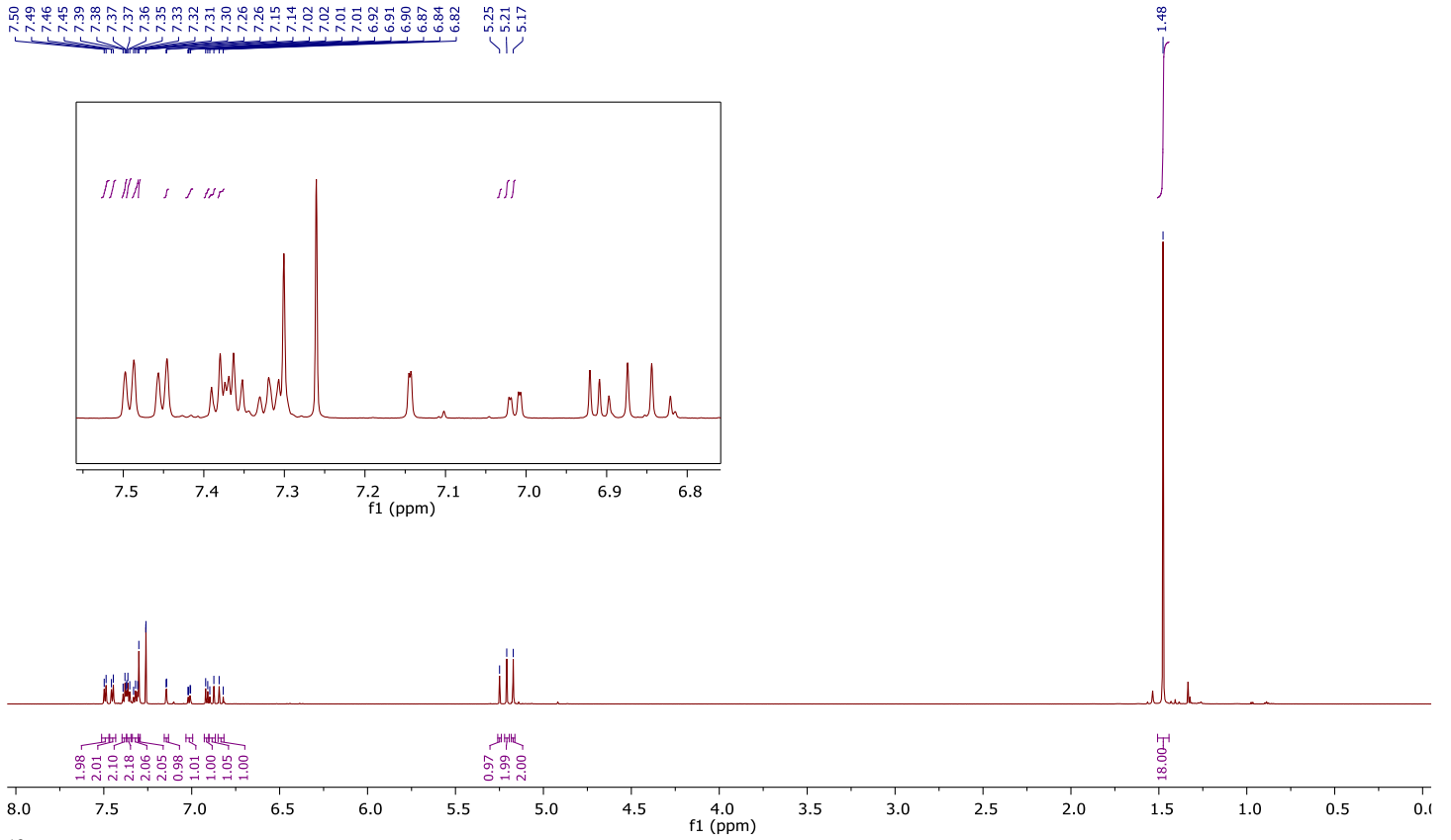
¹H NMR (700 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 7.5 Hz, 2H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.40 – 7.37 (m, 2H), 7.37 – 7.35 (m, 2H), 7.34 – 7.30 (m, 2H), 7.30 (s, 2H), 7.14 (d, *J* = 2.0 Hz, 1H), 7.01 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.89 (d, *J* = 16.2 Hz, 1H), 6.83 (d, *J* = 16.2 Hz, 1H), 5.25 (s, 1H), 5.21 (s, 2H), 5.17 (s, 2H), 1.48 (s, 18H).

¹³C NMR (176 MHz, Chloroform-*d*) δ 153.77, 149.34, 148.56, 137.52, 137.49, 136.26, 132.10, 128.90, 128.63, 128.61, 128.28, 127.95, 127.91, 127.58, 127.45, 125.64, 123.36, 120.14, 115.39, 112.86, 71.62, 71.55, 34.53, 30.45.

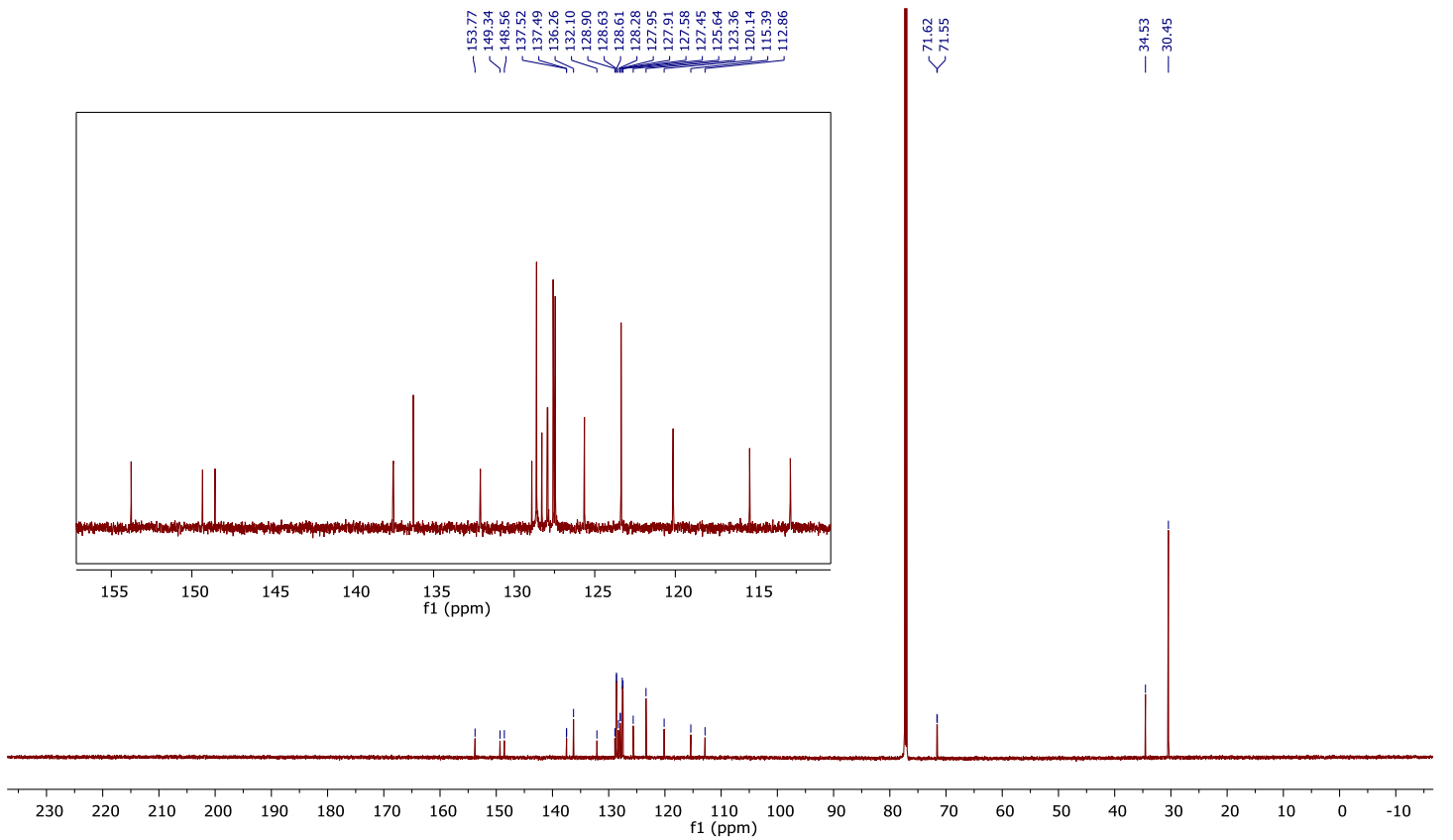
IR (Neat): 3617, 2951, 1680, 1595, 1504, 1255, 1133, 1016, 729, 695 cm⁻¹;

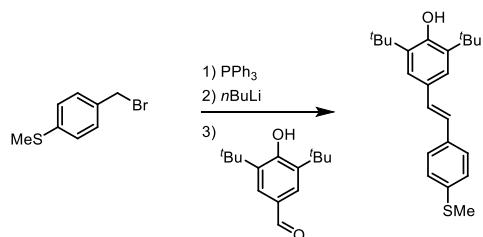
HRMS (ESI) *m/z* calculated for NaC₃₆H₄₀O₃⁺ ([M+Na]⁺) 543.2870, found 543.2873.

¹H NMR, 700 MHz, Chloroform-*d*, Stilbene S6



¹³C NMR, 176 MHz, Chloroform-*d*, Stilbene S6





(S7) (*E*)-2,6-di-*tert*-butyl-4-(4-(methylthio)styryl)phenol

Commercially available benzyl bromide ((4-(bromomethyl)phenyl)(methyl)sulfane, 1.0 g, 4.6 mmol) was subjected to the general procedure using toluene as the solvent for the olefination with aldehyde A. The product was purified by column chromatography (2% to 12% ethyl acetate in hexanes) to afford (*E*)-2,6-di-*tert*-butyl-4-(4-(methylthio)styryl)phenol (1.35 g, 82% yield).

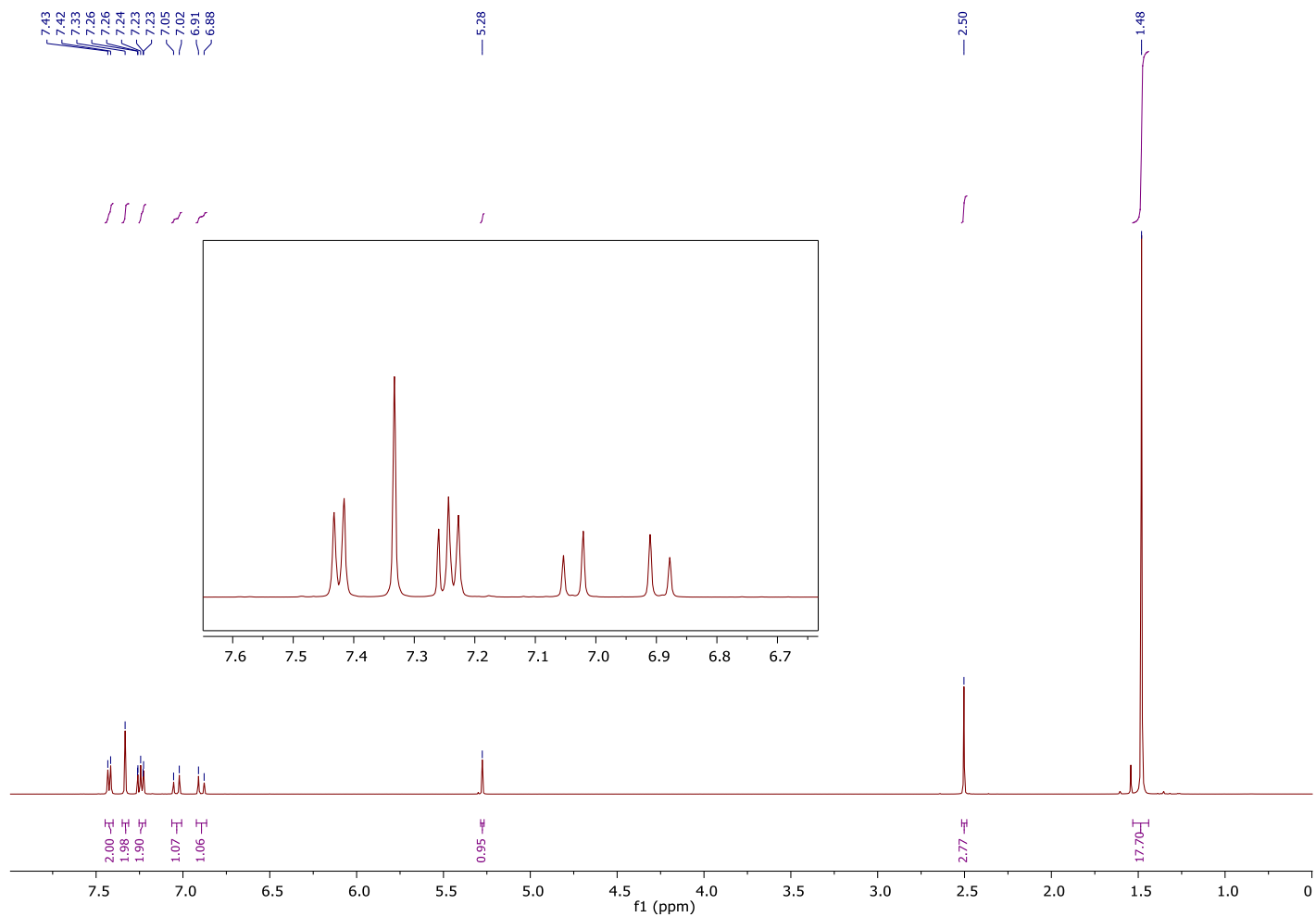
$R_f = 0.34$ (ethyl acetate/hexanes 1:9; UV)

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.42 (d, $J = 8.1$ Hz, 2H), 7.33 (s, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 7.04 (d, $J = 16.2$ Hz, 1H), 6.89 (d, $J = 16.2$ Hz, 1H), 5.28 (s, 1H), 2.50 (s, 3H), 1.48 (s, 18H).

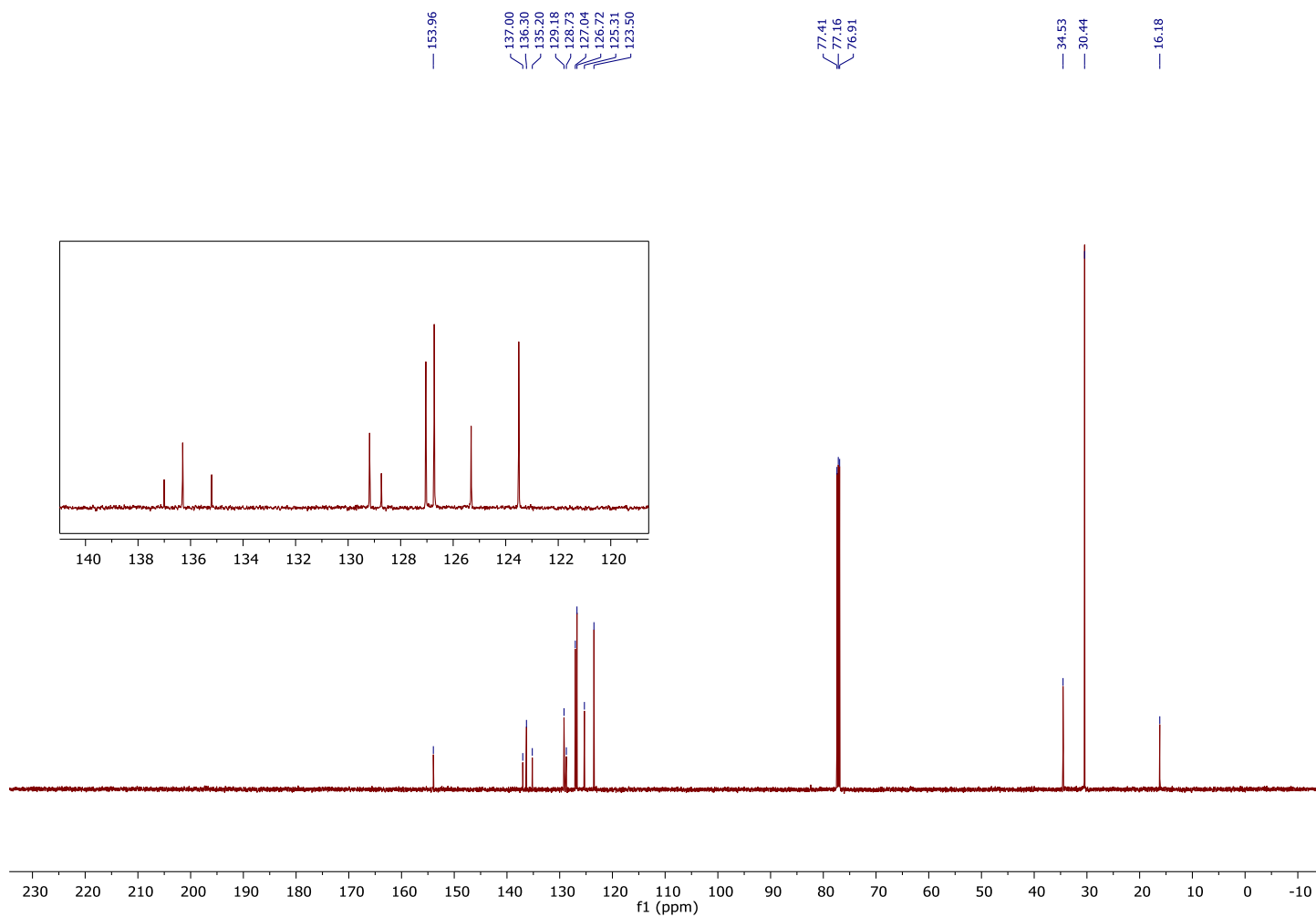
$^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 153.96, 137.00, 136.30, 135.20, 129.18, 128.73, 127.04, 126.72, 125.31, 123.50, 34.53, 30.44, 16.18.

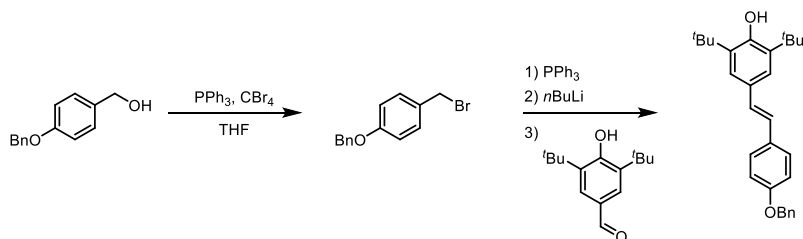
IR (Neat): 3616, 2955, 1435, 1249, 1184, 962, 800 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{C}_{23}\text{H}_{31}\text{OS}^+$ ($[\text{M}+\text{H}]^+$) 355.2090, found 355.2087.



^{13}C NMR, 126 MHz, Chloroform-*d*, Stilbene **S7**





(S8) (*E*)-4-(4-(benzyloxy)styryl)-2,6-di-*tert*-butylphenol

Commercially available benzyl alcohol ((4-(benzyloxy)phenyl)methanol, 1.00g, 4.7 mmol) was subjected to the general procedure using toluene as the solvent for the olefination with aldehyde A. The product was purified by column chromatography (2% to 12% ethyl acetate in hexanes) to afford (*E*)-4-(4-(benzyloxy)styryl)-2,6-di-*tert*-butylphenol (1.52g, 78% yield).

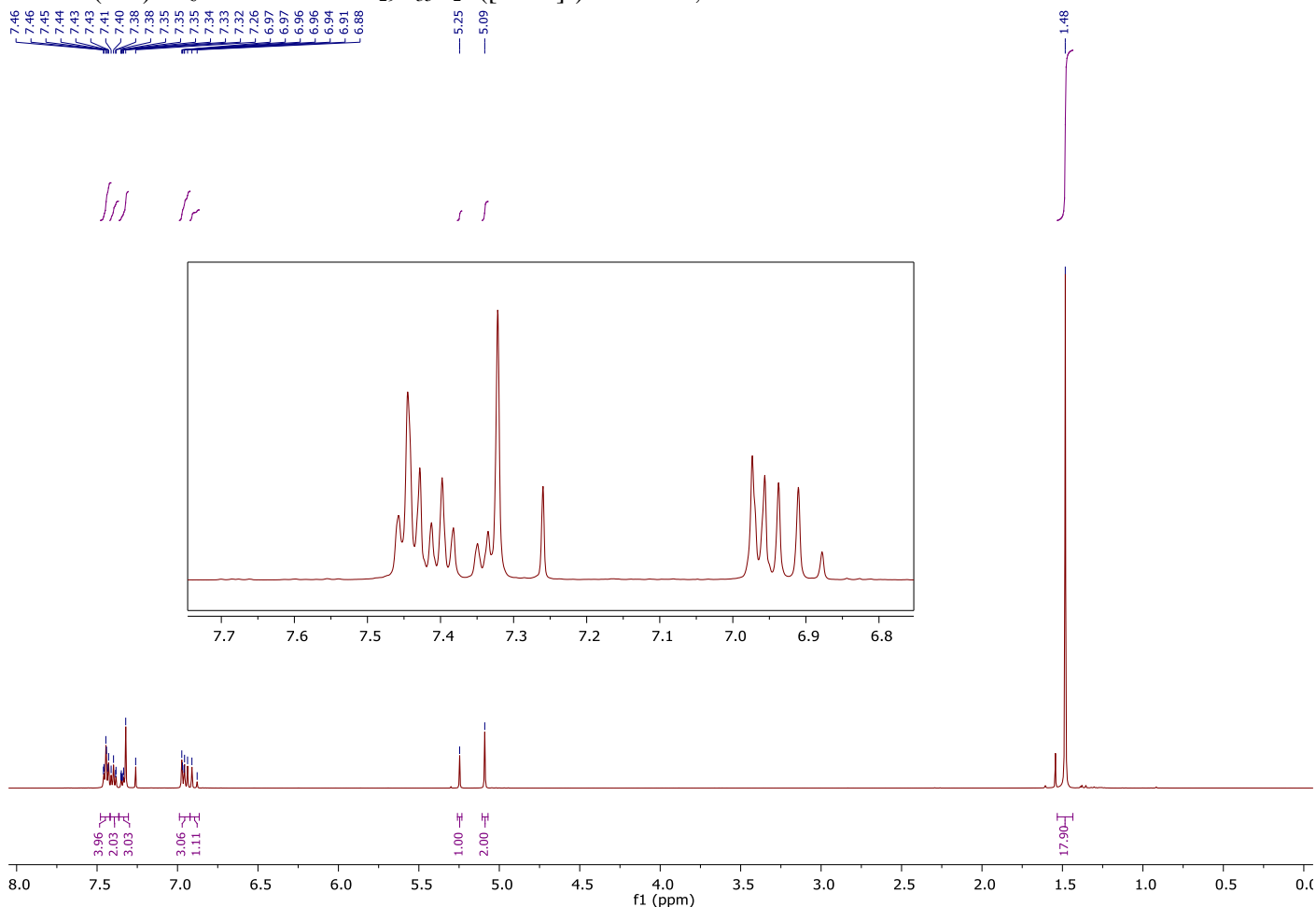
$R_f = 0.28$ (ethyl acetate/hexanes 1:9; UV)

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.44 (d, $J = 7.1$ Hz, 2H), 7.44 (d, $J = 8.6$ Hz, 2H), 7.40 (t, $J = 7.6$ Hz, 2H), 7.33 (t, $J = 7.3$ Hz, 1H), 7.32 (s, 2H), 6.96 (d, $J = 8.6$ Hz, 2H), 6.95 (d, $J = 16.2$ Hz, 1H), 6.89 (d, $J = 16.3$ Hz, 1H), 5.25 (s, 1H), 5.09 (s, 2H), 1.48 (s, 18H).

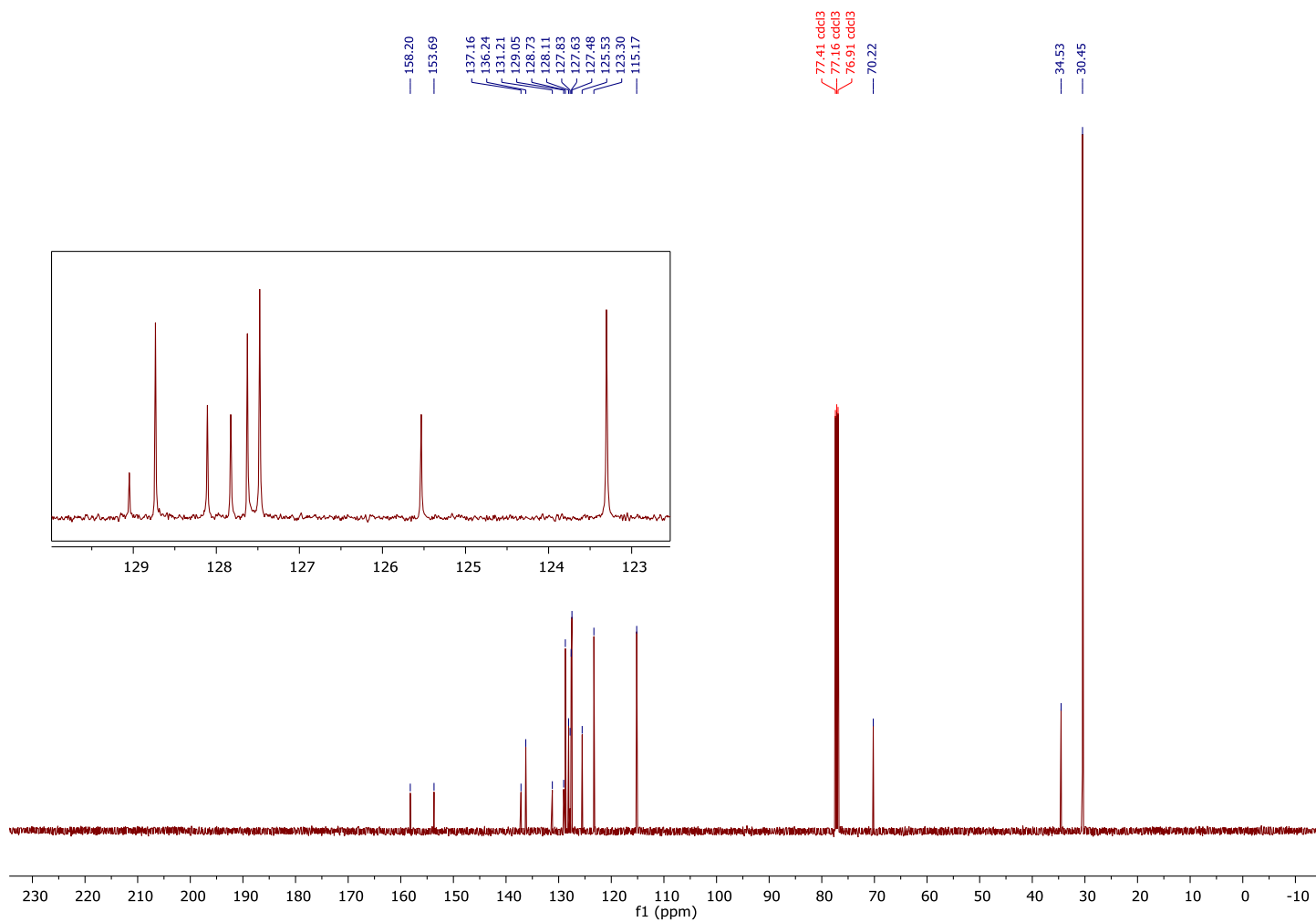
$^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 158.20, 153.69, 137.16, 136.24, 131.21, 129.05, 128.73, 128.11, 127.83, 127.63, 127.48, 125.53, 123.30, 115.17, 70.22, 34.53, 30.45.

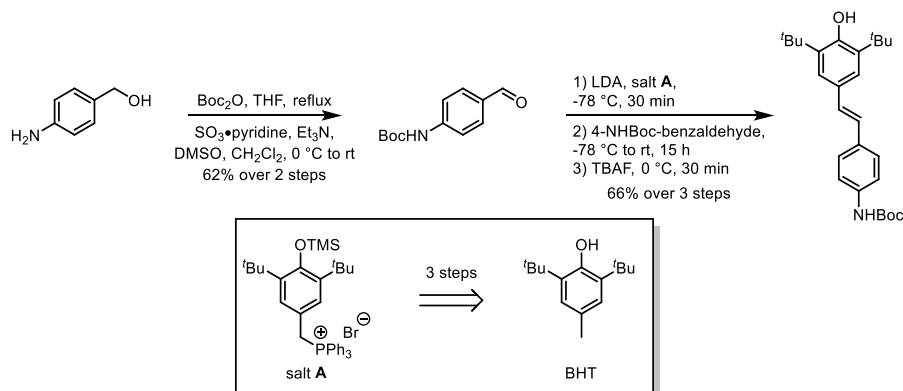
IR (Neat): 3628, 2953, 1606, 1510, 1465, 1233, 1175, 1010, 954, 745 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{C}_{29}\text{H}_{35}\text{O}_2^+$ ($[\text{M}+\text{H}]^+$) 415.2632, found 415.2632.



^{13}C NMR, 126 MHz, Chloroform-*d*, Stilbene **S8**





(S9) *tert*-butyl (*E*)-(4-(3,5-di-*tert*-butyl-4-hydroxystyryl)phenyl)carbamate

Freshly distilled diisopropylamine (3.41 mmol, 478 μ L) was added to a flame-dried heart-shaped flask, dissolved in freshly distilled THF (10 mL), and cooled to -78 °C. To the stirring solution was added *n*BuLi (3.28 mmol, 1.31 mL, 2.5 M), and the solution was allowed to stir at the same temperature for 30 min. Meanwhile, in a 3-neck round bottom flask, the phosphonium salt **A** (3.28 mmol, 2.08 g) was suspended in freshly distilled THF (25 mL) and cooled to -78 °C. The freshly prepared LDA solution was added to the phosphonium salt suspension via cannula, and the ylid was allowed to form at the same temperature for 30 min, turning the solution deep red. To a flame-dried heart-shaped flask was added 4-NHBoc-benzaldehyde (2.62 mmol, 580 mg, available in 2 steps via Boc protection and oxidation), and the solid was dissolved in THF (10 mL). The aldehyde solution was added to the ylid via cannula, and the reaction was allowed to warm to room temperature overnight (~15 hours). The reaction was subsequently cooled to 0 °C, and a solution of TBAF (3.28 mmol, 3.28 mL, 1.0 M) was added. The desilylation was allowed to occur for 30 min, at which point the reaction was quenched via the addition of saturated ammonium chloride, diluted with EtOAc, and added to a separatory funnel containing deionized water. The layers were separated, and the aqueous layer was extracted with additional portions of EtOAc. The combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (20% to 100% CH₂Cl₂ in Hexanes) to afford the stilbene product (1.00 g, 90% yield).

R_f = 0.30 (CH₂Cl₂/hexanes 3:1; UV)

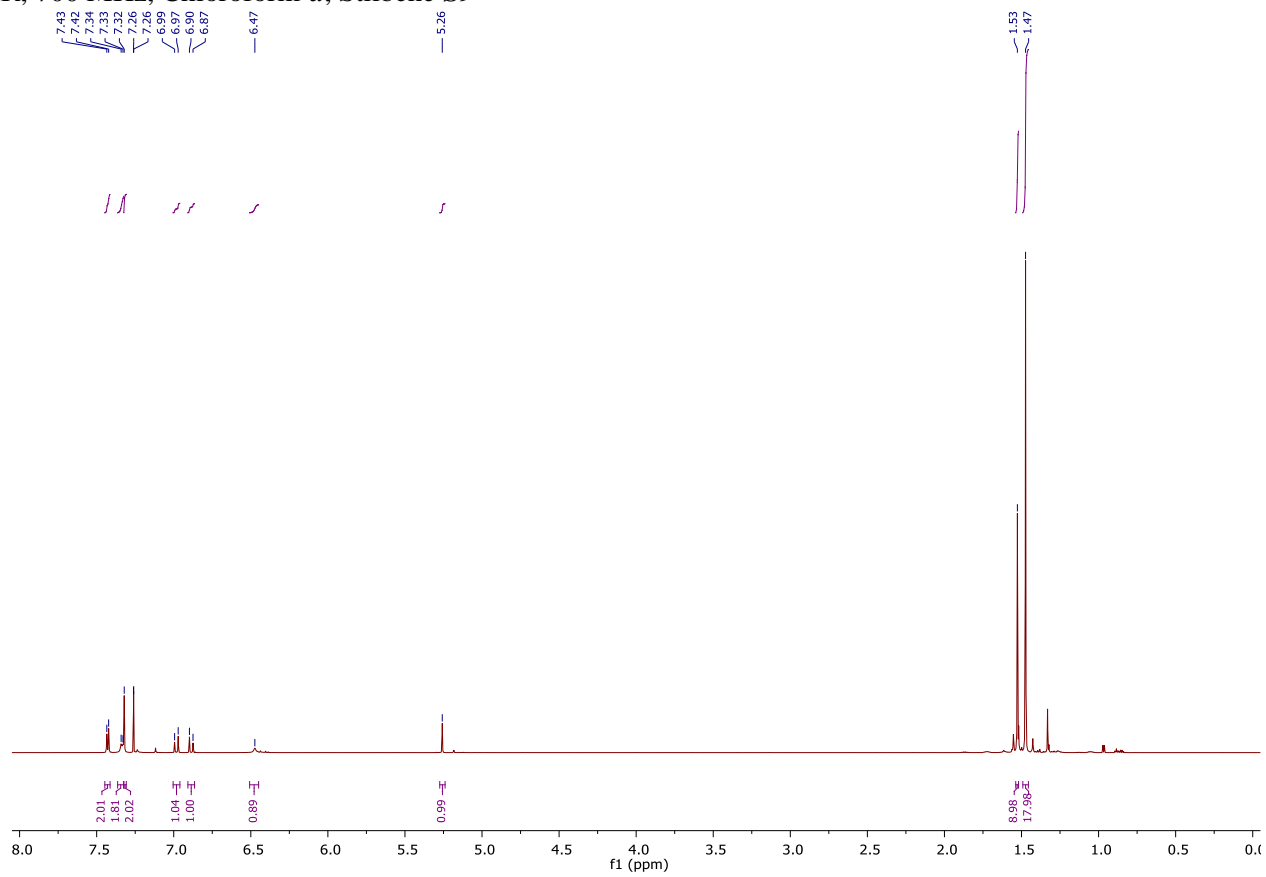
¹H NMR (700 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.32 (s, 2H), 6.98 (d, *J* = 16.2 Hz, 1H), 6.89 (d, *J* = 16.2 Hz, 1H), 6.47 (s, 1H), 5.26 (s, 1H), 1.53 (s, 9H), 1.47 (s, 18H).

¹³C NMR (176 MHz, Chloroform-*d*) δ 153.79, 152.77, 137.31, 136.22, 133.06, 128.87, 128.36, 126.93, 125.42, 123.39, 118.69, 80.71, 34.52, 30.43, 28.50.

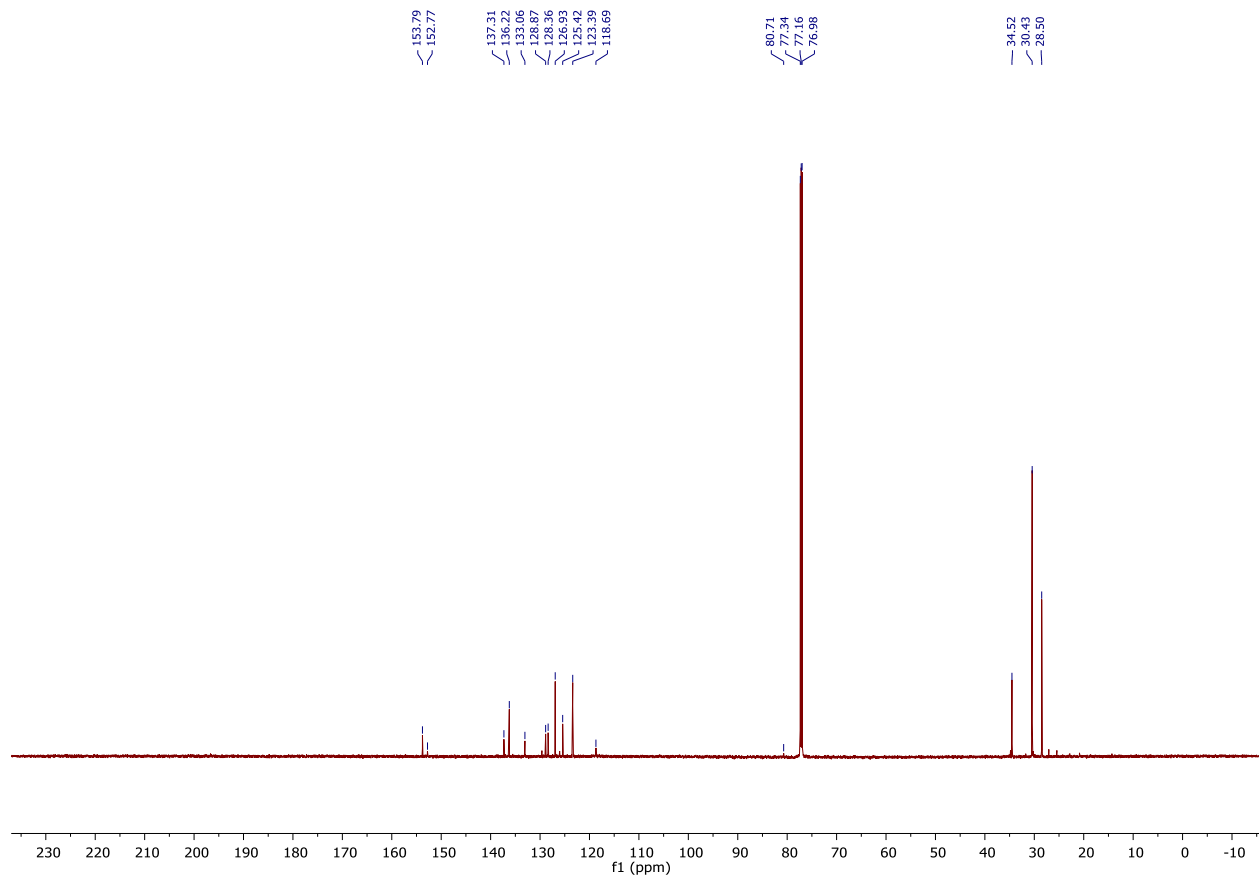
IR (Neat): 3623, 3325, 2957, 1709, 1600, 1521, 1234, 1153, 1051, 740 cm⁻¹;

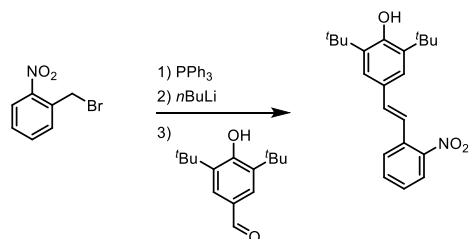
HRMS (ESI) *m/z* calculated for NaC₂₇H₃₇NO₃⁺ ([M+Na]⁺) 446.2666, found 446.2660.

¹H NMR, 700 MHz, Chloroform-*d*, Stilbene S9



¹³C NMR, 176 MHz, Chloroform-*d*, Stilbene S9





(S10) (*E*)-2,6-di-*tert*-butyl-4-(2-nitrostyryl)phenol

Commercially available benzyl bromide (1-(bromomethyl)-2-nitrobenzene, 1.0 g, 4.6 mmol) was subjected to the general procedure using toluene as the solvent for the olefination. The product was purified by column chromatography (2% to 12% ethyl acetate in hexanes) to afford (*E*)-2,6-di-*tert*-butyl-4-(2-nitrostyryl)phenol (927 mg, 57% yield).

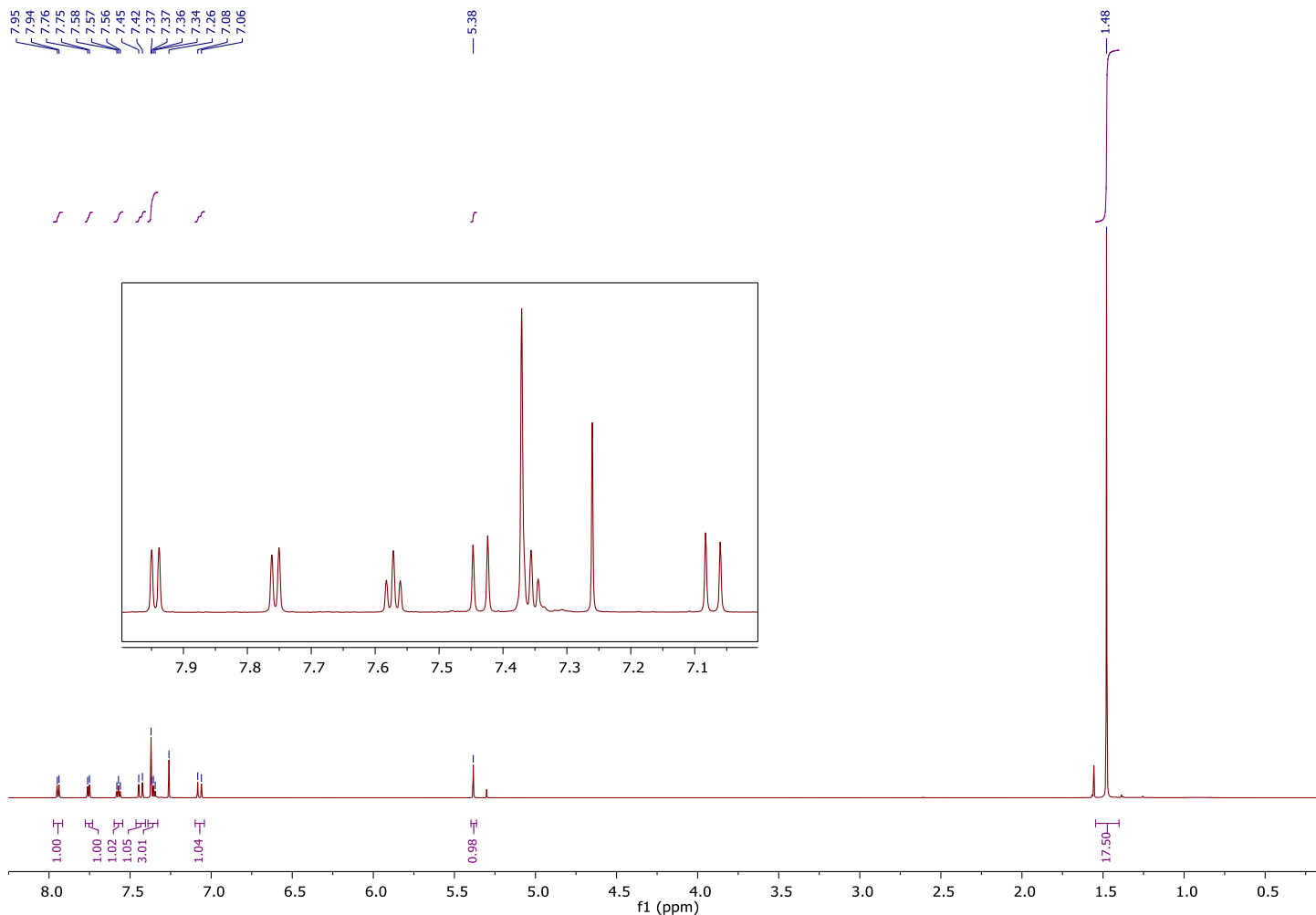
$R_f = 0.38$ (ethyl acetate/hexanes 1:9; UV)

$^1\text{H NMR}$ (700 MHz, Chloroform-*d*) δ 7.94 (d, $J = 8.1$ Hz, 1H), 7.76 (d, $J = 7.9$ Hz, 1H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.44 (d, $J = 16.0$ Hz, 1H), 7.37 (s, 3H), 7.36 (t, $J = 7.7$ Hz, 3H), 7.07 (d, $J = 16.0$ Hz, 1H), 5.38 (s, 1H), 1.48 (s, 18H).

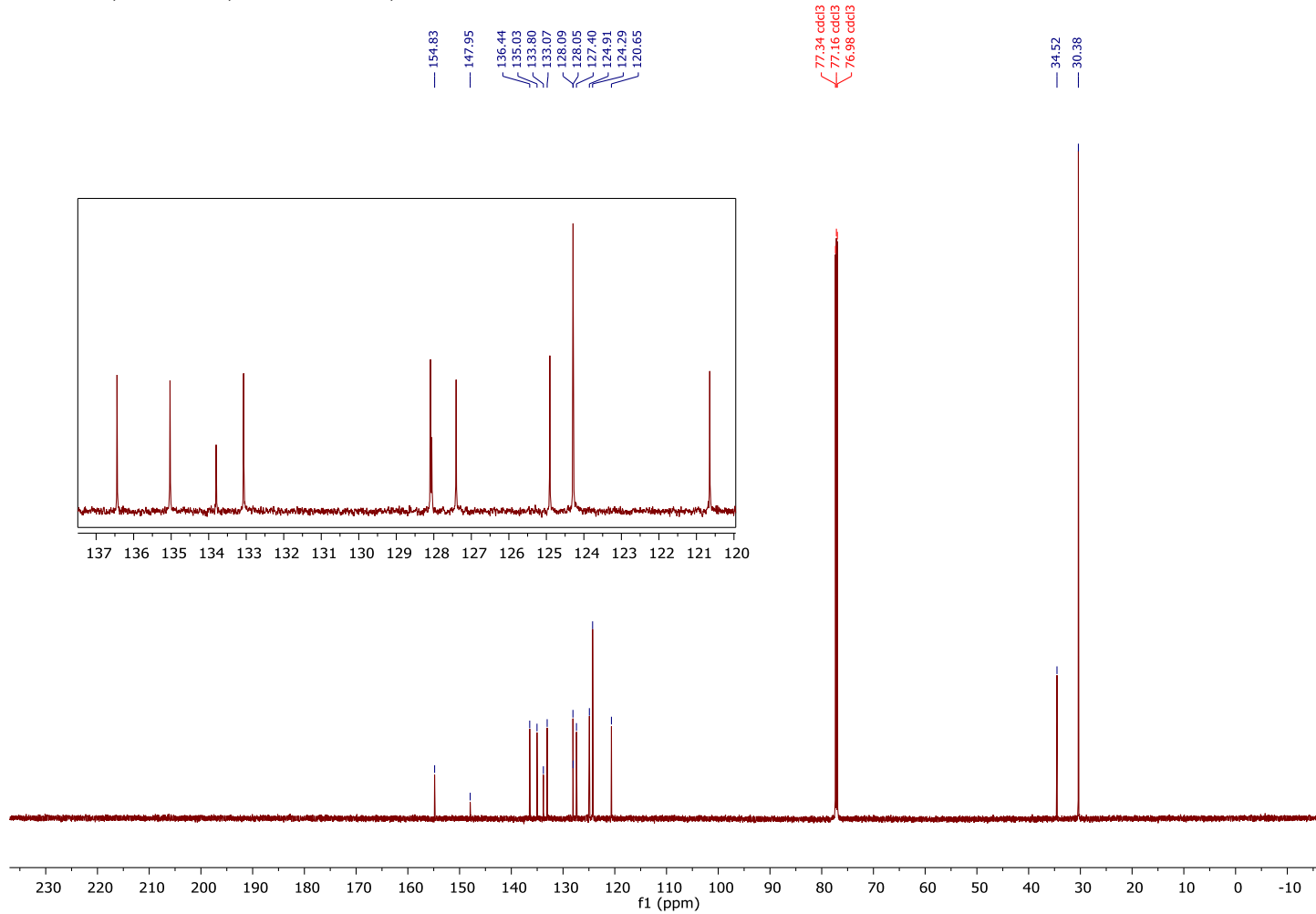
$^{13}\text{C NMR}$ (176 MHz, Chloroform-*d*) δ 154.83, 147.95, 136.44, 135.03, 133.80, 133.07, 128.09, 128.05, 127.40, 124.91, 124.29, 120.65, 34.52, 30.38.

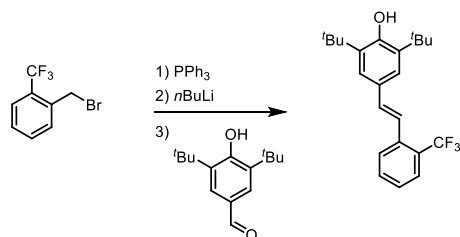
IR (Neat): 3626, 2961, 1626, 1603, 1515, 1348, 1233, 1150, 965, 742 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{28}\text{NO}_3^+$ ($[\text{M}+\text{H}]^+$) 354.2064, found 354.2064.



^{13}C NMR, 176 MHz, Chloroform-*d*, Stilbene **S10**





(S11) (*E*)-2,6-di-*tert*-butyl-4-(2-(trifluoromethyl)styryl)phenol

Commercially available benzyl bromide (1-(bromomethyl)-2-(trifluoromethyl)benzene, 0.79 g, 3.29 mmol) was subjected to the general procedure using THF as the solvent for the olefination. The product was purified by column chromatography (2% to 12% ethyl acetate in hexanes) to afford (*E*)-2,6-di-*tert*-butyl-4-(2-(trifluoromethyl)styryl)phenol (989 mg, 73% yield).

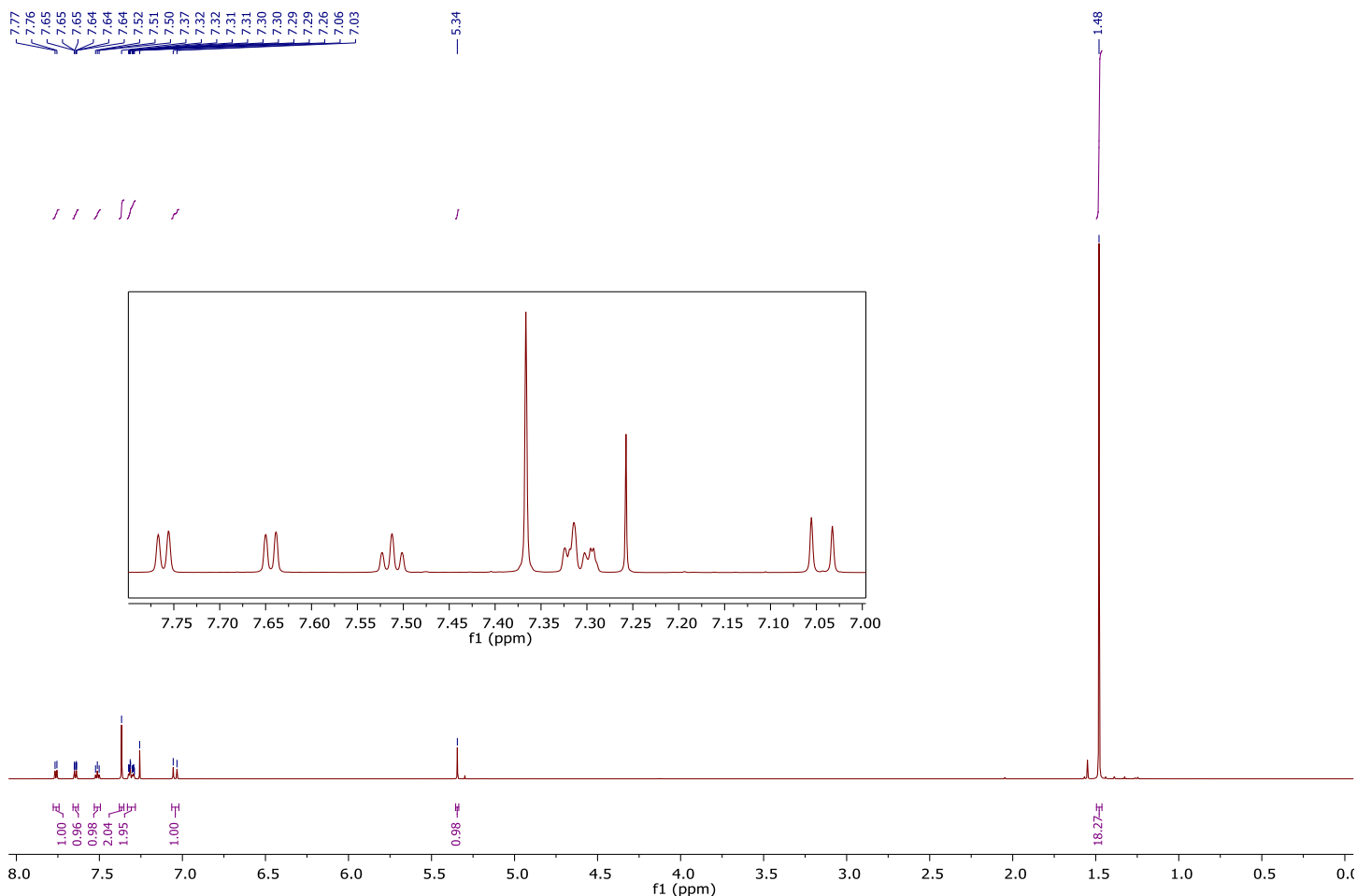
R_f = 0.40 (ethyl acetate/hexanes 1:9; UV)

¹H NMR (700 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.66 – 7.63 (m, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.37 (s, 2H), 7.33 – 7.28 (m, 2H), 7.04 (d, *J* = 16.0 Hz, 1H), 5.34 (s, 1H), 1.48 (s, 18H).

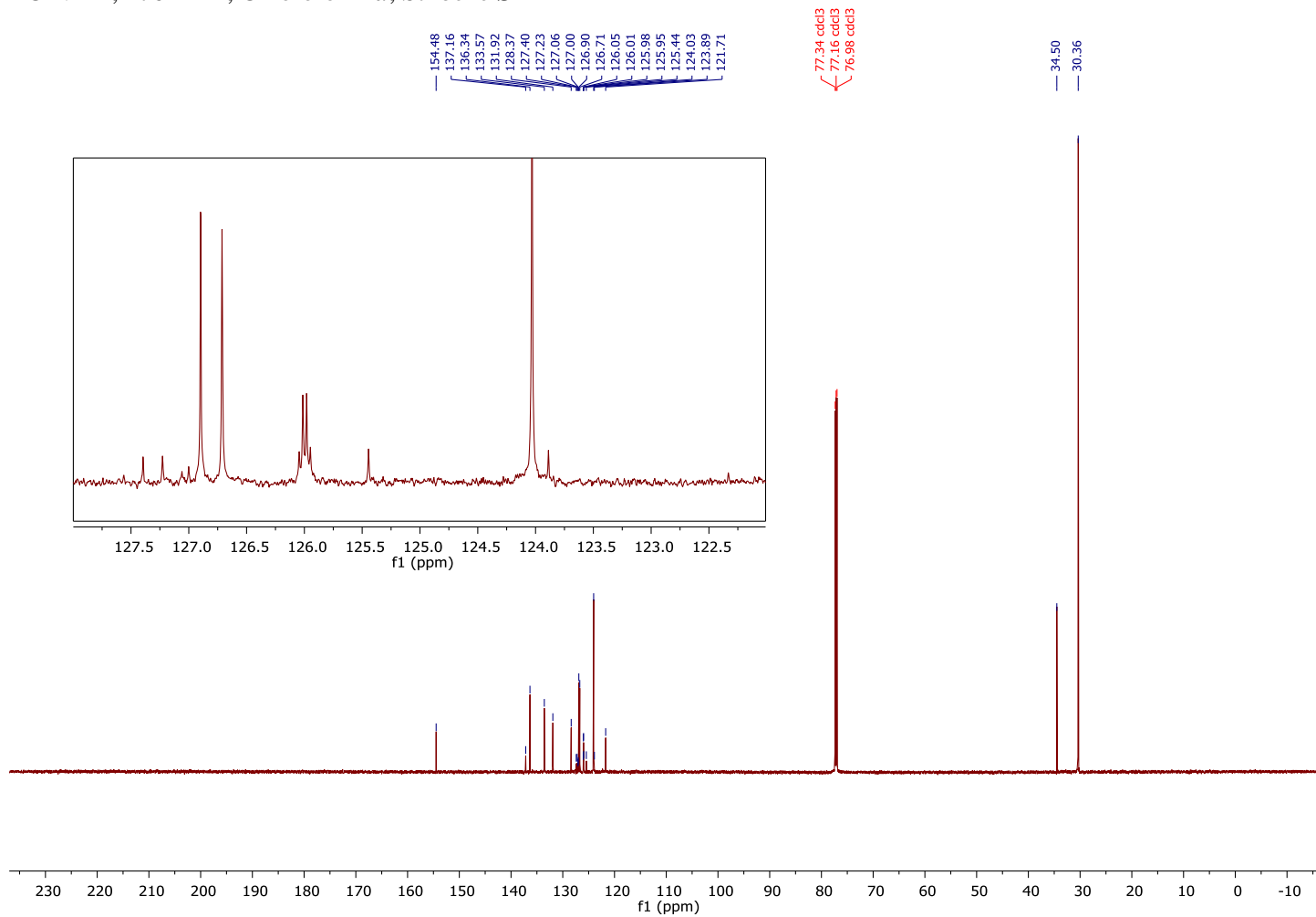
¹³C NMR (176 MHz, Chloroform-*d*) δ 154.48, 137.16, 136.34, 133.57, 131.92, 128.37, 127.32 (q, *J*_{C-F} = 29 Hz), 126.90, 126.71, 125.99 (q, *J*_{C-F} = 6.2 Hz), 124.66 (q, *J*_{C-F} = 275 Hz), 124.03, 121.71, 34.50, 30.36.

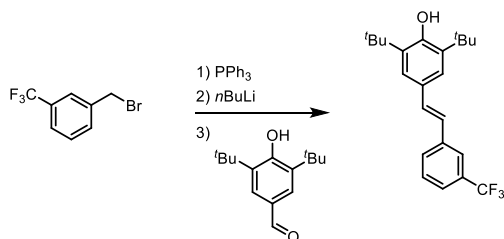
IR (Neat): 3636, 2956, 1435, 1422, 1308, 1122, 1035, 960, 753 cm⁻¹;

HRMS (ESI) *m/z* calculated for C₂₃H₂₈F₃O⁺ ([M+H]⁺) 377.2087, found 377.2084.



^{13}C NMR, 176 MHz, Chloroform-*d*, Stilbene **S11**





(S12) (E)-2,6-di-tert-butyl-4-(3-(trifluoromethyl)styryl)phenol

Commercially available benzyl bromide (1-(bromomethyl)-3-(trifluoromethyl)benzene, 0.78 g, 3.25 mmol) was subjected to the general procedure using THF as the solvent for the olefination. The product was purified by column chromatography (2% to 12% ethyl acetate in hexanes) to afford (E)-2,6-di-tert-butyl-4-(3-(trifluoromethyl)styryl)phenol (1.06 g, 87% yield).

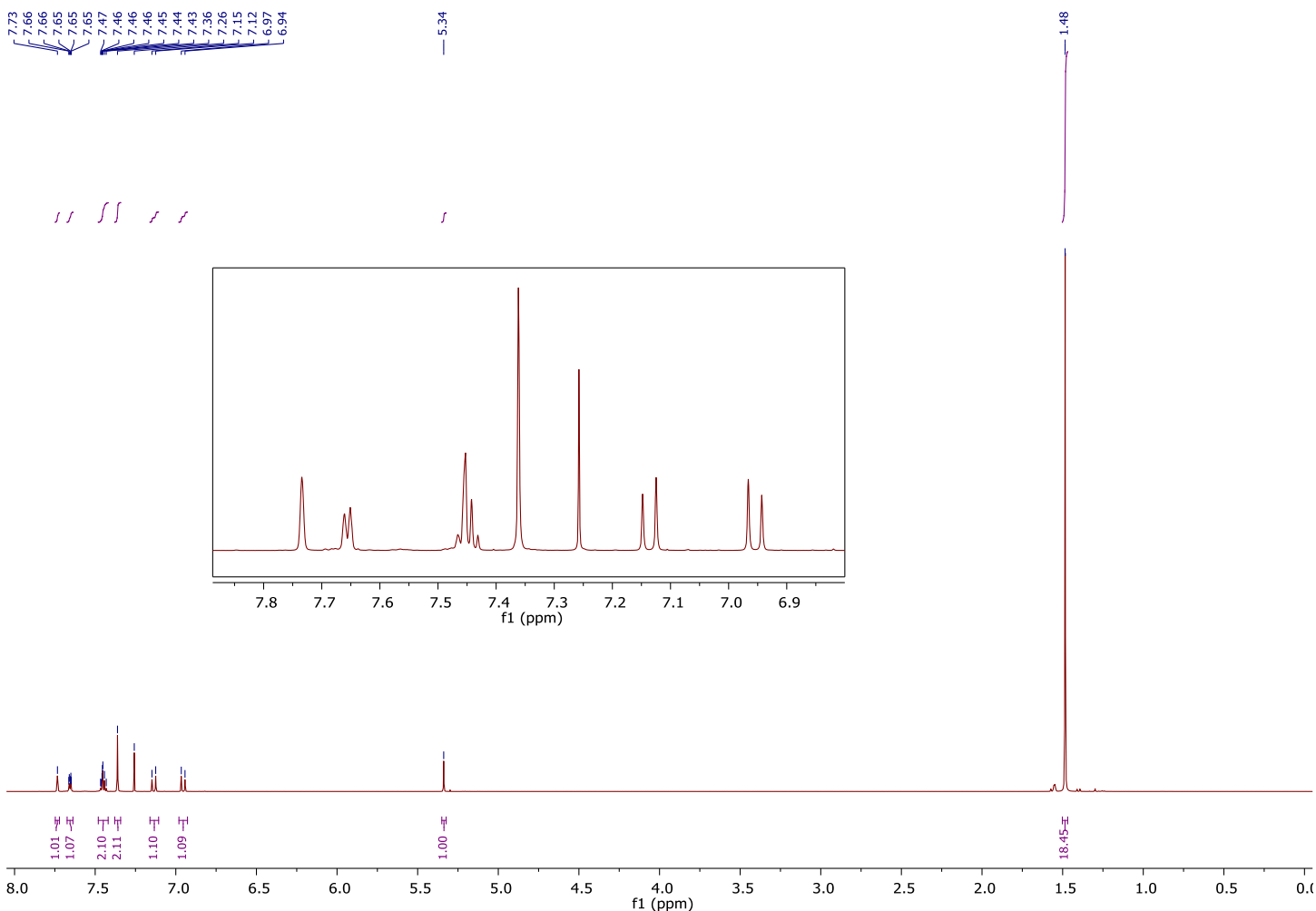
R_f = 0.40 (ethyl acetate/hexanes 1:9; UV)

¹H NMR (700 MHz, Chloroform-*d*) δ 7.73 (s, 1H), 7.66 (dd, *J* = 7.0, 1.9 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.36 (s, 2H), 7.14 (d, *J* = 16.2 Hz, 1H), 6.95 (d, *J* = 16.2 Hz, 1H), 5.34 (s, 1H), 1.48 (s, 18H).

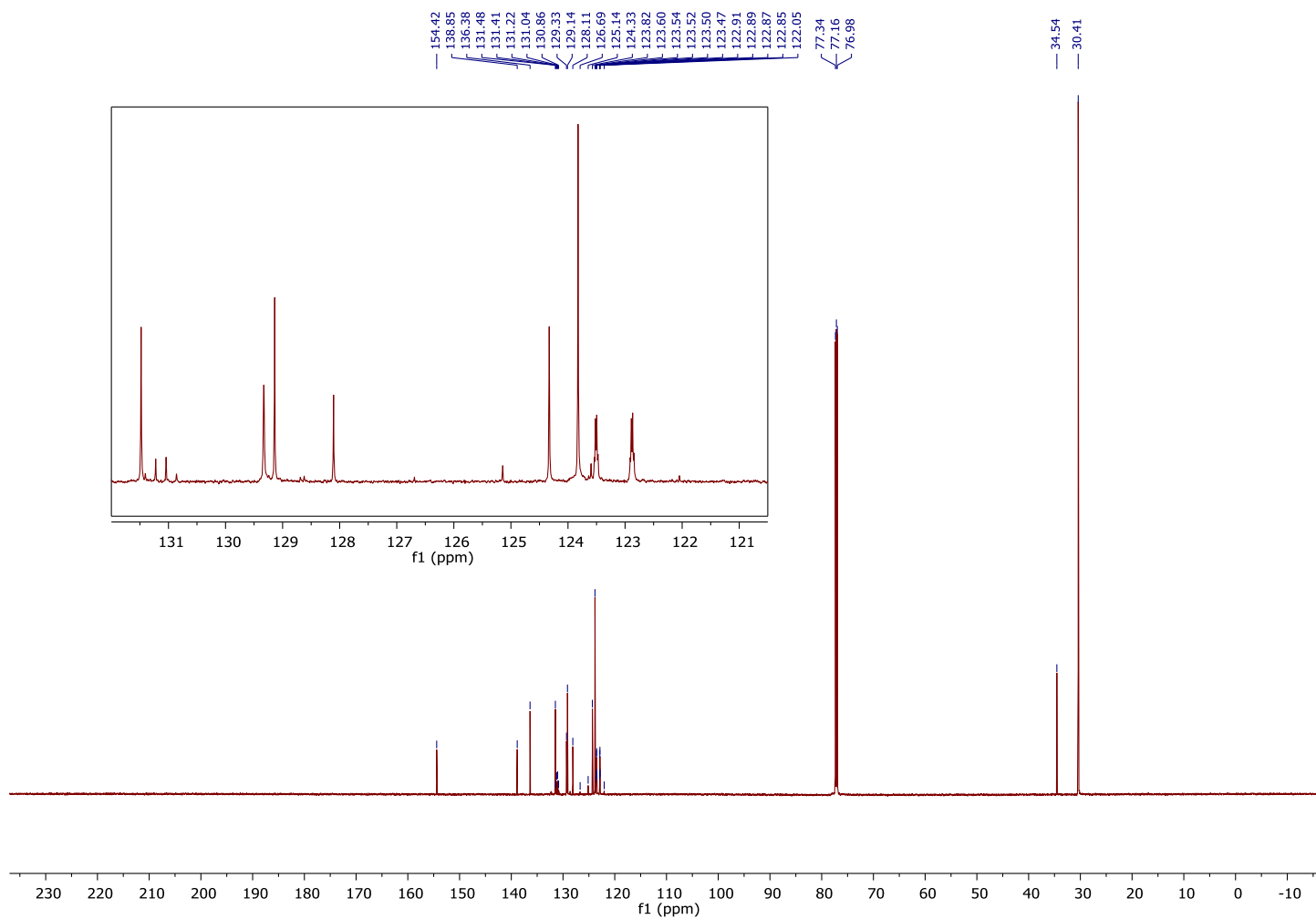
¹³C NMR (176 MHz, Chloroform-*d*) δ 154.42, 138.85, 136.38, 131.48, 131.13 (q, *J*_{C-F} = 32 Hz), 129.33, 129.14, 128.11, 124.37 (q, *J*_{C-F} = 273 Hz), 124.33, 123.82, 123.51 (q, *J*_{C-F} = 3.5 Hz), 122.88 (q, *J*_{C-F} = 3.5 Hz), 34.54, 30.41.

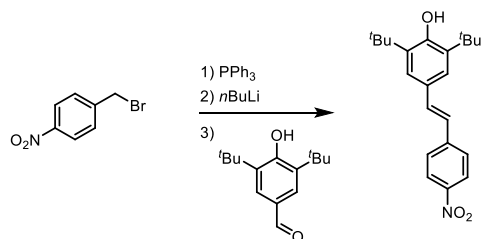
IR (Neat): 3639, 2957, 1655, 1437, 1328, 1163, 1121, 1073 cm⁻¹;

HRMS (ESI) *m/z* calculated for C₂₃H₂₈F₃O⁺ ([M+H]⁺) 377.2087, found 377.2093.



^{13}C NMR, 176 MHz, Chloroform-*d*, Stilbene **S12**





(S13) (*E*)-2,6-di-*tert*-butyl-4-(4-nitrostyryl)phenol

Commercially available benzyl bromide (1-(bromomethyl)-4-nitrobenzene, 1.0 g, 4.6 mmol) was subjected to the general procedure using toluene as the solvent for the olefination with aldehyde A. The product was purified by column chromatography (2% to 12% ethyl acetate in hexanes) to afford (*E*)-2,6-di-*tert*-butyl-4-(4-nitrostyryl)phenol (990 mg, 61% yield).

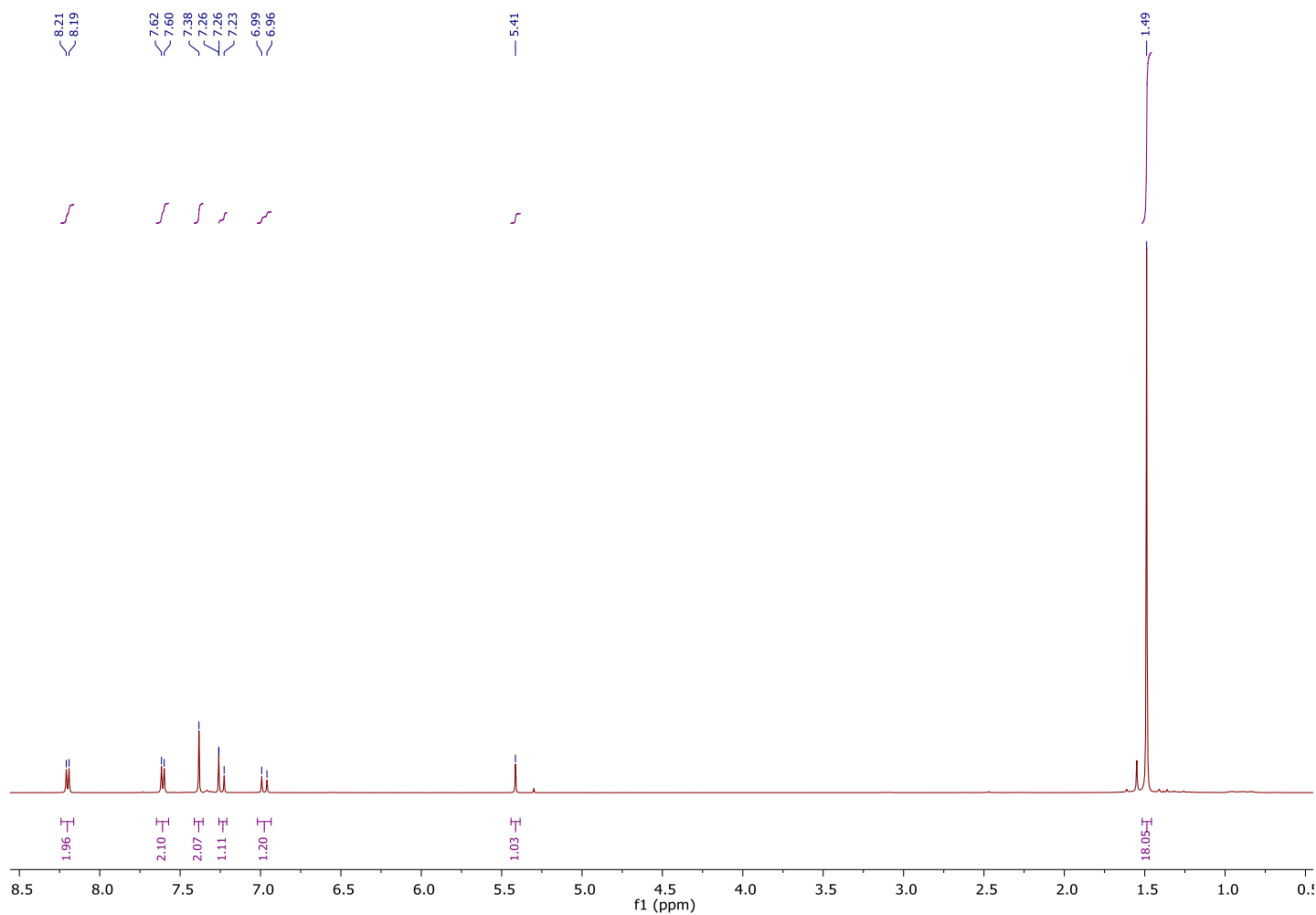
$R_f = 0.38$ (ethyl acetate/hexanes 1:9; UV)

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 8.20 (d, $J = 8.5$ Hz, 2H), 7.60 (d, $J = 8.6$ Hz, 2H), 7.38 (s, 2H), 7.24 (d, $J = 16.1$ Hz, 2H), 6.97 (d, $J = 16.2$ Hz, 1H), 5.41 (s, 1H), 1.48 (s, 18H).

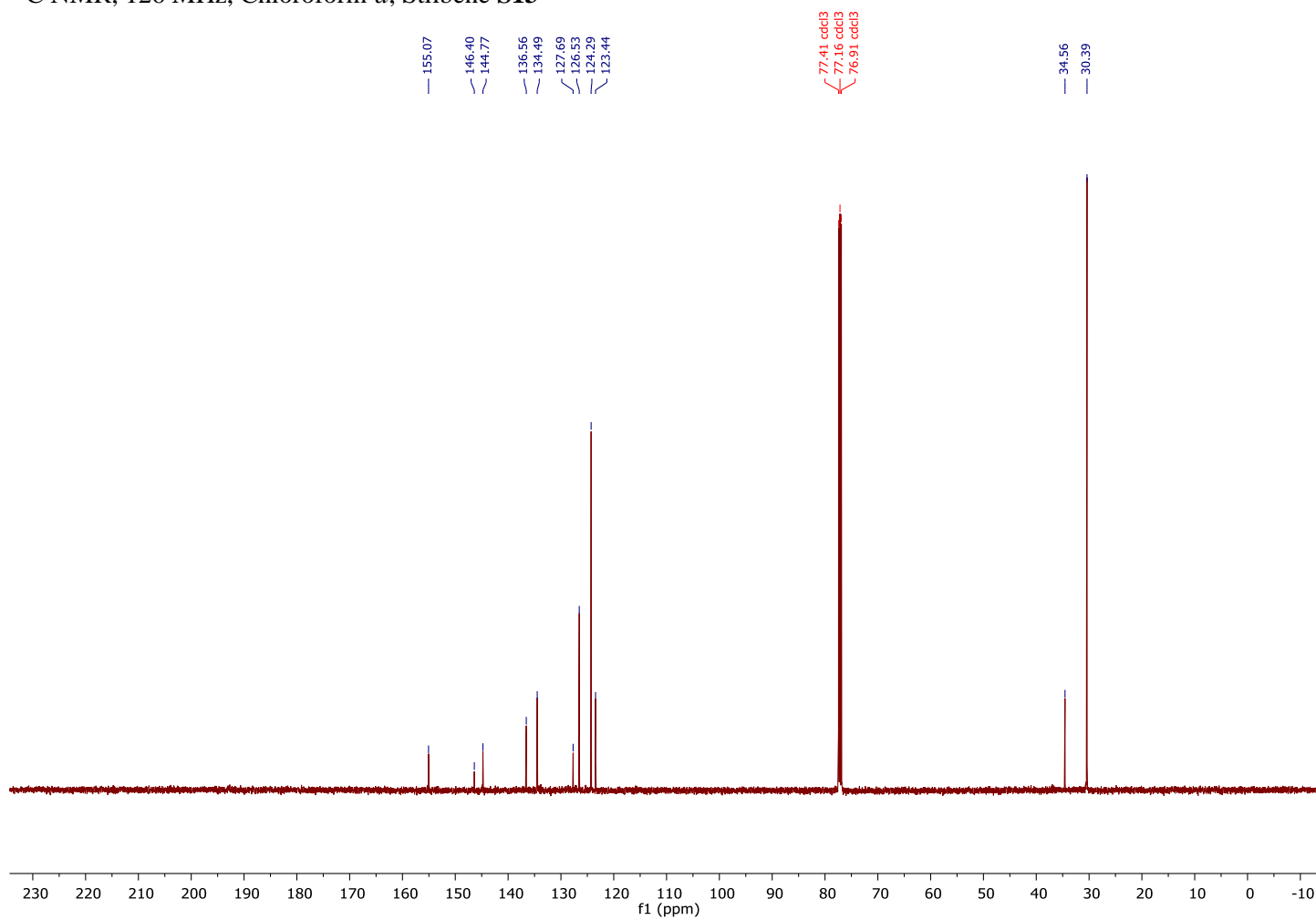
$^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 155.07, 146.40, 144.77, 136.56, 134.49, 127.69, 126.53, 124.29, 123.44, 34.56, 30.39.

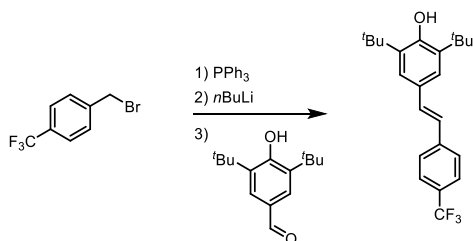
IR (Neat) 3618, 2955, 1629, 1595, 1505, 1428, 1332, 1117, 973, 861, 748 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{28}\text{NO}_3^+$ ($[\text{M}+\text{H}]^+$) 354.2064, found 354.2068.



^{13}C NMR, 126 MHz, Chloroform-*d*, Stilbene **S13**





(S14) (E)-2,6-di-tert-butyl-4-(4-(trifluoromethyl)styryl)phenol

Commercially available benzyl bromide (1-(bromomethyl)-4-(trifluoromethyl)benzene, 1.0 g, 4.18 mmol) was subjected to the general procedure using THF as the solvent for the olefination. The product was purified by column chromatography (2% to 12% ethyl acetate in hexanes) to afford (E)-2,6-di-tert-butyl-4-(4-(trifluoromethyl)styryl)phenol (1.15 g, 77% yield).

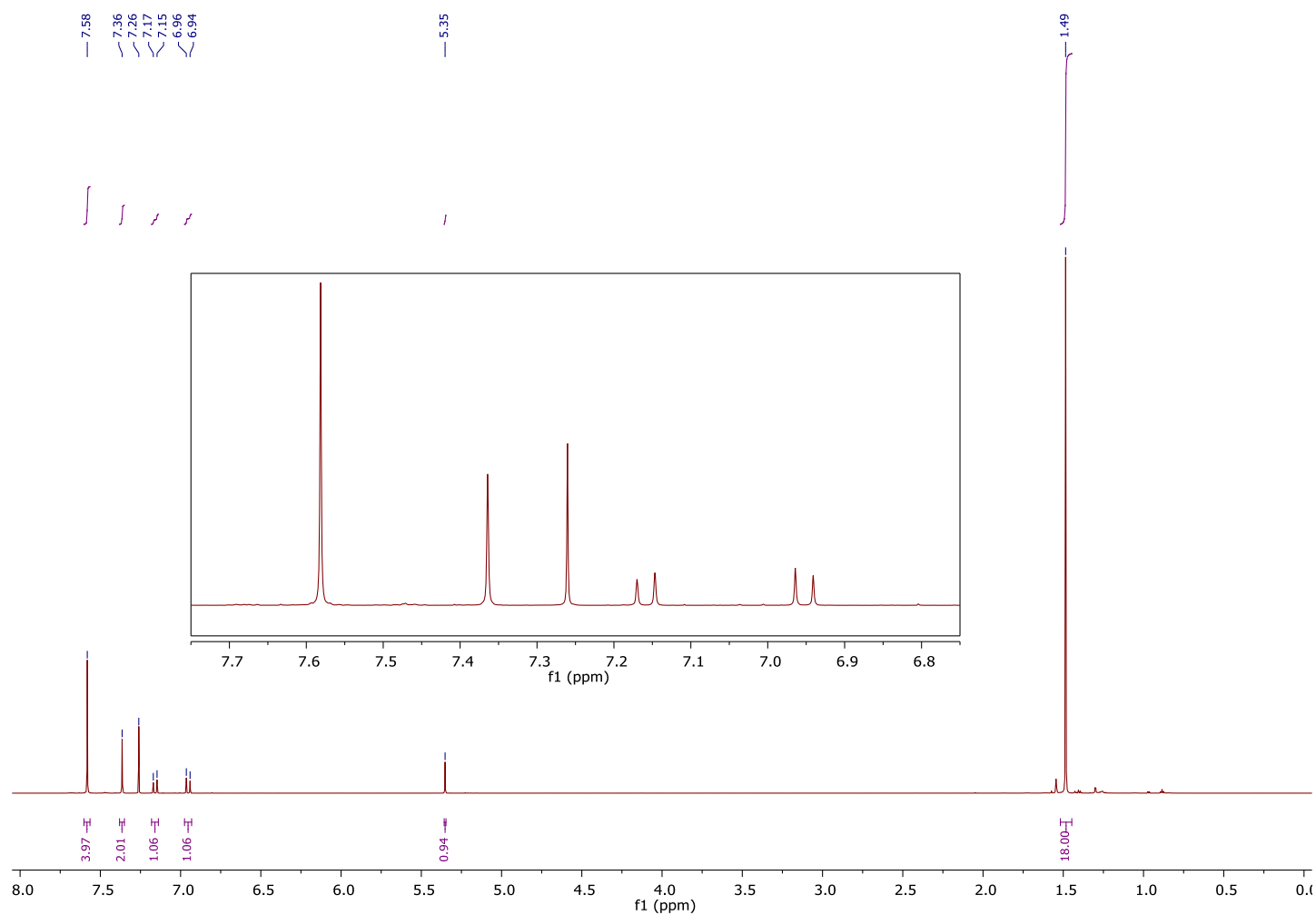
R_f = 0.40 (ethyl acetate/hexanes 1:9; UV)

¹H NMR (700 MHz, Chloroform-*d*) δ 7.58 (s, 4H), 7.36 (s, 2H), 7.16 (d, *J* = 16.3 Hz, 1H), 6.95 (d, *J* = 16.2 Hz, 1H), 5.35 (s, 1H), 1.49 (s, 18H).

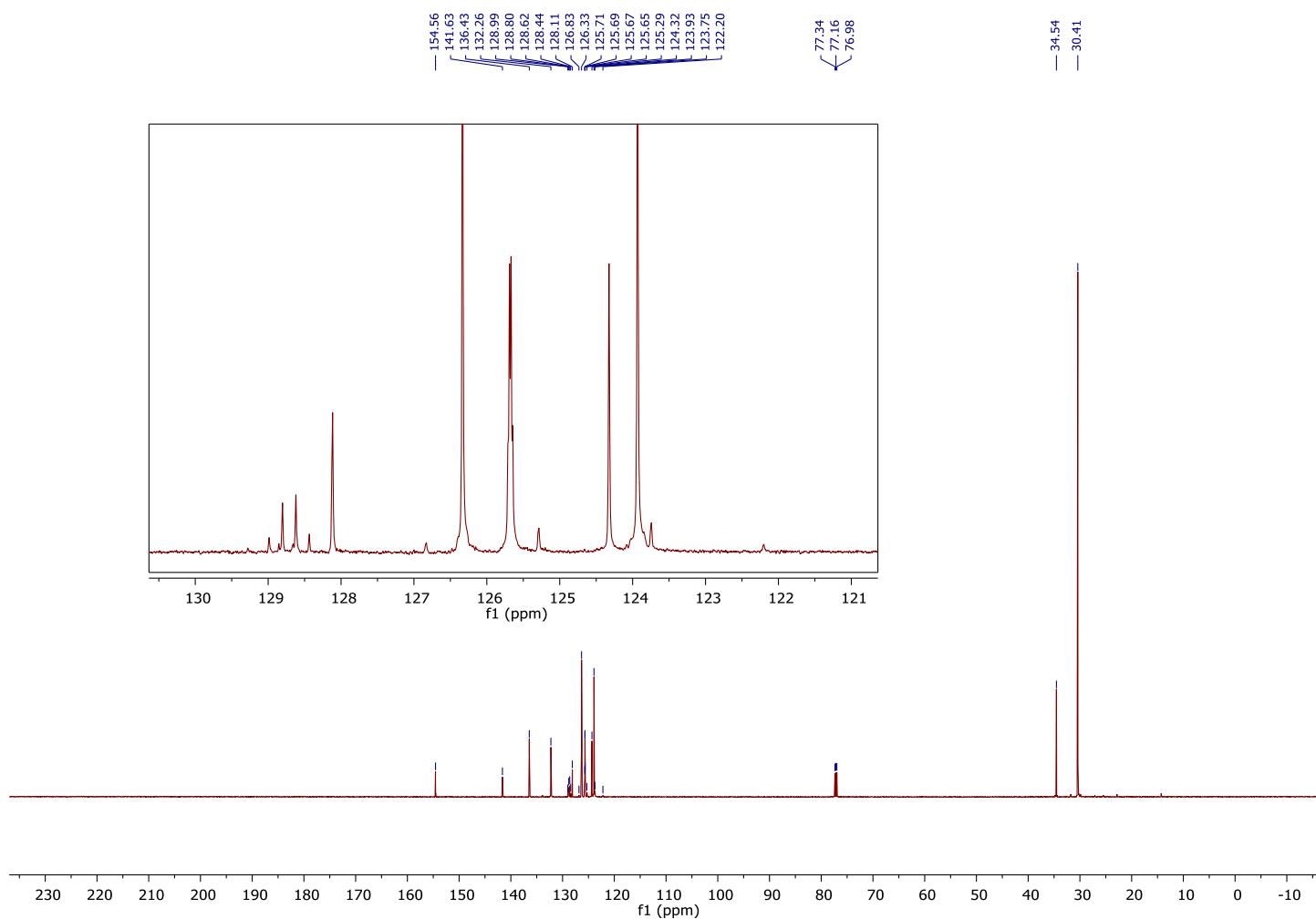
¹³C NMR (176 MHz, Chloroform-*d*) δ 154.56, 141.63, 136.43, 132.26, 128.71 (q, *J* = 32 Hz), 128.11, 126.33, 125.68 (q, *J* = 3.5 Hz), 124.52 (q, *J* = 271 Hz), 124.32, 123.93, 34.54, 30.41.

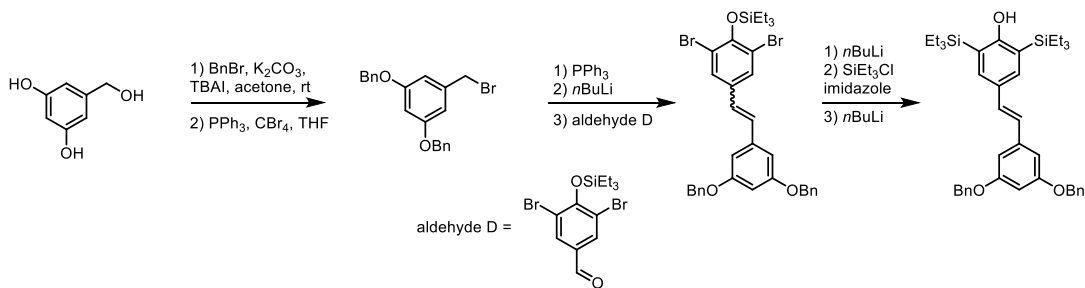
IR (Neat): 3636, 2955, 1435, 1422, 1308, 1122, 1035, 960, 753 cm⁻¹;

HRMS (ESI) *m/z* calculated for C₂₃H₂₈F₃O⁺ ([M+H]⁺) 377.2087, found 377.2084.



^{13}C NMR, 176 MHz, Chloroform-*d*, Stilbene S14





(S15) (E)-4-(3,5-bis(benzyloxy)styryl)-2,6-bis(triethylsilyl)phenol

Commercially available 3,5-dihydroxybenzyl alcohol (2.0 g, 14.3 mmol) was added to flask charged with potassium carbonate (2.25 equiv., 4.44 g) and tetrabutylammonium iodide (0.2 equiv., 1.05 g), and the solids were dissolved/suspended in acetone (42 mL). To the stirring reaction mixture was added 4-methoxybenzyl chloride (2.20 equiv., 3.74 mL), and the reaction was allowed to stir at room temperature for 16 hours. Upon completion, the reaction was diluted with ethyl acetate and poured into a separatory funnel containing deionized water. The layers were separated, and the aqueous layer was extracted with additional portions of ethyl acetate. The combined organic layer was washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure to afford the crude product, which was carried forward without further purification. The benzyl-protected material (2.22 g, 5.79 mmol) was subjected to the general procedure using THF as the solvent for the olefination with aldehyde D, which is available from silyl protection of commercially available 3,5-dibromo-4-hydroxybenzaldehyde. The product was purified by column chromatography (2% to 12% ethyl acetate in hexanes, 2% increments, 2 column volumes each, then 2 column volumes at both 16% and 20%) to afford both olefin isomers in a ~1:1 ratio (2.26 g, 69% yield combined). The E-isomer (900 mg, 1.59 mmol) was carried forward and dissolved in THF, and the reaction mixture was cooled to -78 °C. *n*BuLi (1.0 equiv, 1.6 M in hexanes, 993 μ L) was added dropwise to the stirring solution, and the reaction was held at temperature for 15 min prior to being allowed to warm to room temperature. The retro-Brook rearrangement was quenched and worked up following the general procedure. The resulting product was silyl protected following standard conditions, then subjected to the same retro-Brook reaction to afford the product (E)-4-(3,5-bis(benzyloxy)styryl)-2,6-bis(triethylsilyl)phenol (861 mg, 85% yield).

R_f = 0.37 (ethyl acetate/hexanes 1:9; UV)

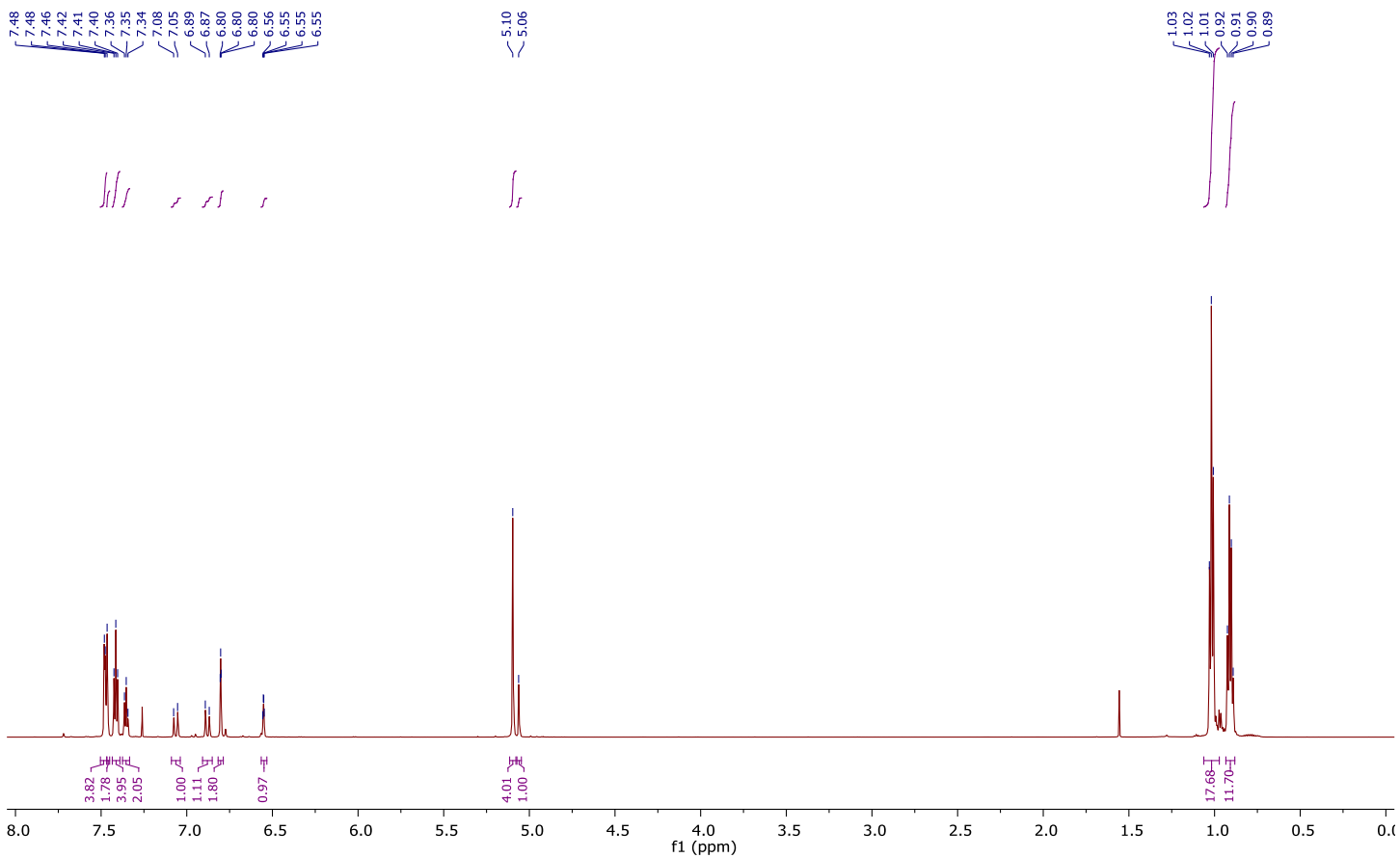
¹H NMR (700 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 3.5 Hz, 4H), 7.46 (s, 2H), 7.41 (t, *J* = 7.5 Hz, 4H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.07 (d, *J* = 16.1 Hz, 1H), 6.88 (d, *J* = 16.2 Hz, 1H), 6.80 (t, *J* = 1.8 Hz, 2H), 6.55 (q, *J* = 2.0 Hz, 1H), 5.10 (s, 4H), 5.06 (s, 1H), 1.02 (t, *J* = 8.0 Hz, 18H), 0.91 (q, *J* = 7.7 Hz, 12H).

¹³C NMR (176 MHz, Chloroform-*d*) δ 166.04, 160.27, 140.16, 137.07, 136.01, 129.77, 129.09, 128.72, 128.12, 127.72, 125.88, 121.44, 105.62, 101.18, 70.25, 7.70, 3.98.

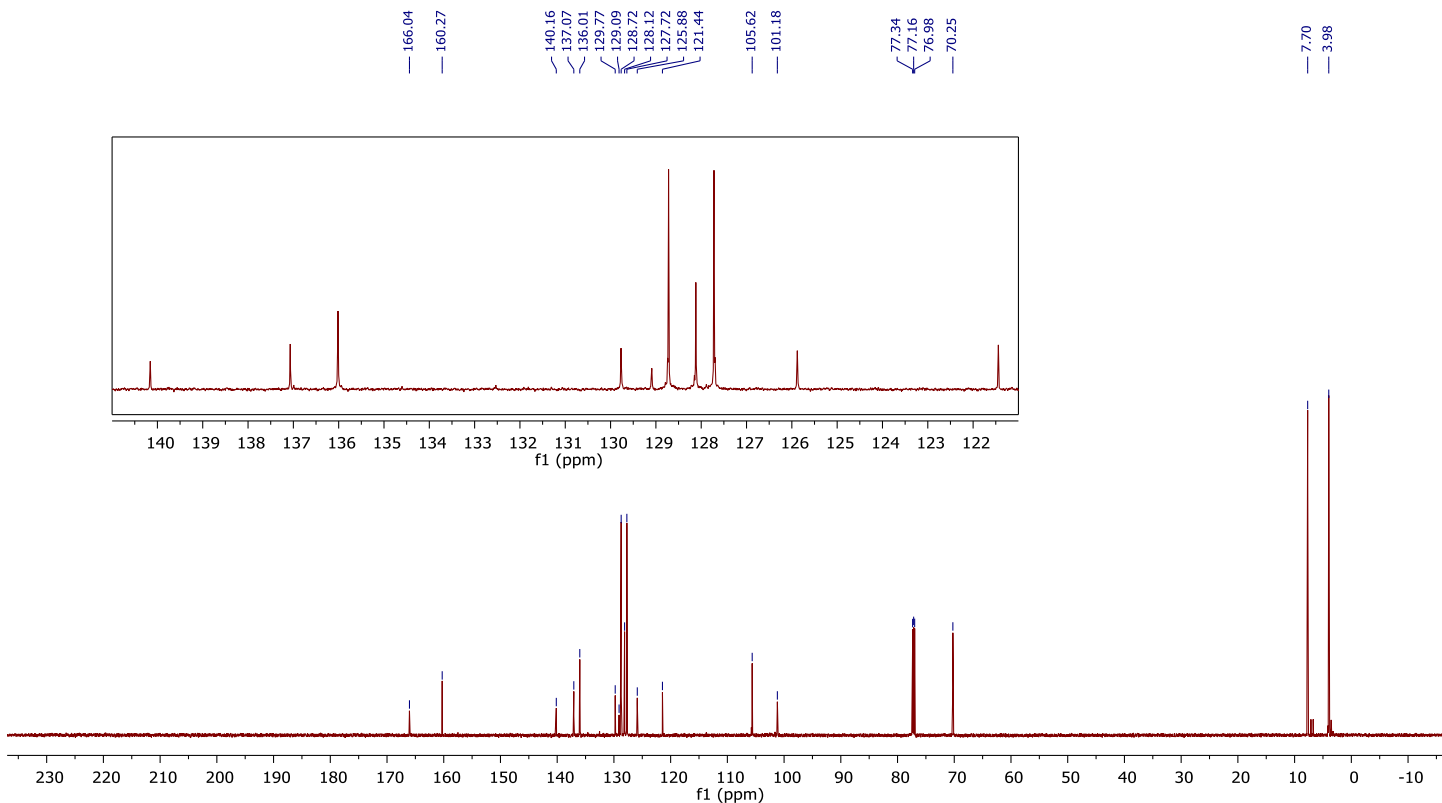
IR (Neat): 3592, 2951, 2870, 1591, 1453, 1397, 1161, 1144, 1060, 1004, 953, 723, 692 cm⁻¹;

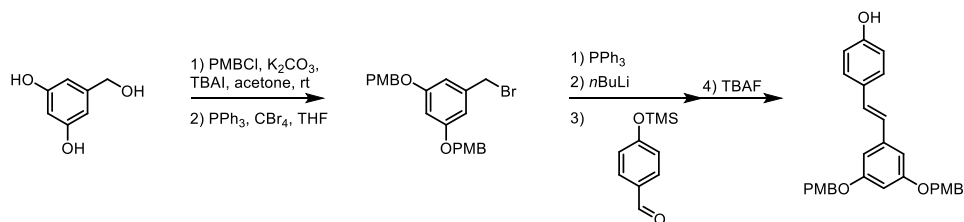
HRMS (ESI) *m/z* calculated for C₄₀H₅₃O₃Si₂⁺ ([M+H]⁺) 637.3528, found 637.3535.

¹H NMR, 700 MHz, Chloroform-*d*, Stilbene S15



¹³C NMR, 176 MHz, Chloroform-*d*, Stilbene S15





(25) (*E*)-4-(3,5-bis((4-methoxybenzyl)oxy)styryl)phenol

Commercially available 3,5-dihydroxybenzyl alcohol (2.0 g, 14.3 mmol) was added to flask charged with potassium carbonate (2.25 equiv., 4.44 g) and tetrabutylammonium iodide (0.2 equiv., 1.05 g), and the solids were dissolved/suspended in acetone (42 mL). To the stirring reaction mixture was added 4-methoxybenzyl chloride (2.20 equiv., 4.26 mL), and the reaction was allowed to stir at room temperature for 16 hours. Upon completion, the reaction was diluted with ethyl acetate and poured into a separatory funnel containing deionized water. The layers were separated, and the aqueous layer was extracted with additional portions of ethyl acetate. The combined organic layer was washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure to afford the crude product, which was carried forward without further purification. A portion of the PMB-protected benzyl alcohol (783 mg, 2.06 mmol) was subjected to the general procedure using toluene as the solvent for the olefination with aldehyde B. Upon completion of the olefination, the reaction was cooled to 0 °C, and TBAF (1.0 equiv., 1.0 M in THF, 2.06 mL) was added dropwise. The reaction was allowed to stir for 30 min, at which point it was quenched and worked up following the general procedure. The product was purified by column chromatography (8% to 40% ethyl acetate in hexanes) to afford the desired product (478 mg, 49% yield).

$R_f = 0.30$ (ethyl acetate/hexanes 3:7; UV)

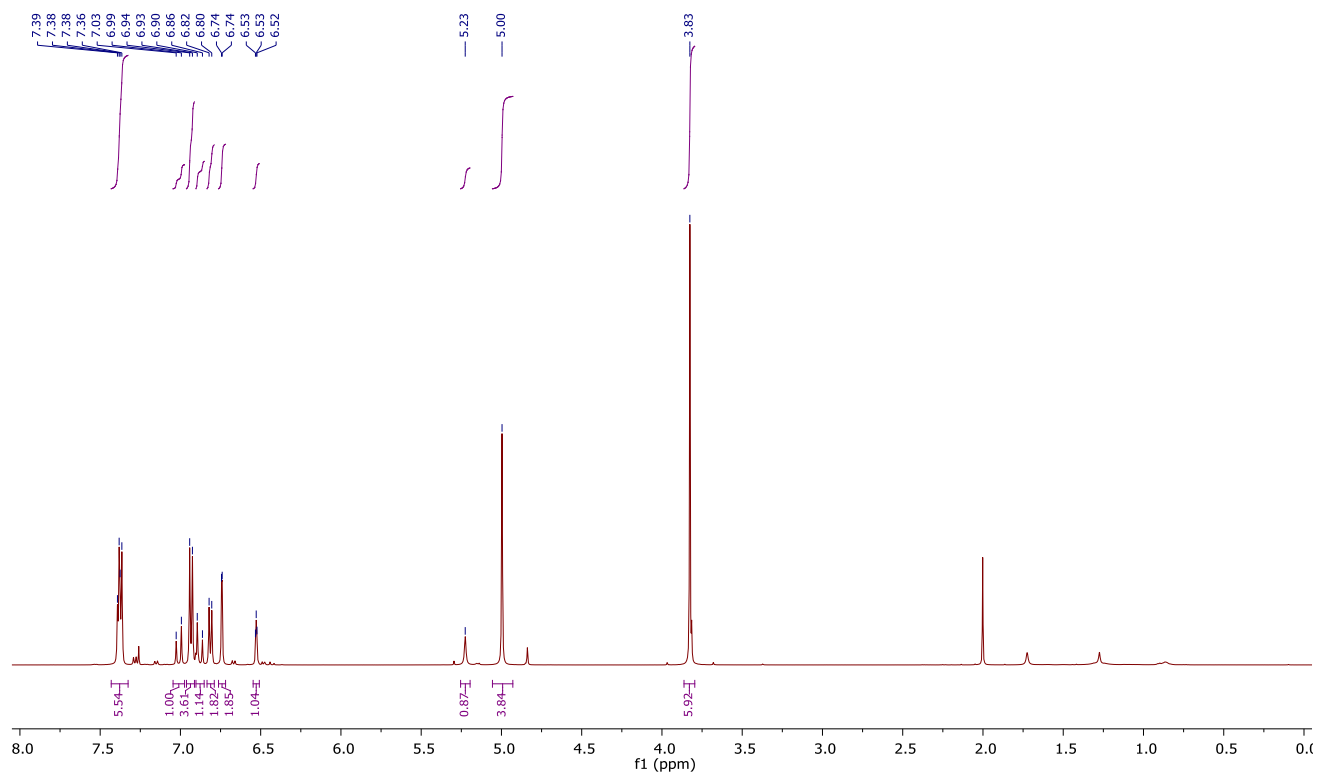
$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.38 (d, $J = 8.3$ Hz, 2H), 7.37 (d, $J = 8.5$ Hz, 4H) 7.01 (d, $J = 16.2$ Hz, 1H), 6.93 (d, $J = 8.6$ Hz, 4H), 6.88 (d, $J = 16.2$ Hz, 1H), 6.81 (d, $J = 8.3$ Hz, 2H), 6.74 (d, $J = 2.2$ Hz, 2H), 6.53 (d, $J = 2.3$ Hz, 1H), 5.23 (s, 1H), 5.00 (s, 4H), 3.83 (s, 6H).

$^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 160.14, 159.45, 155.45, 139.65, 130.02, 129.33, 128.95, 128.73, 127.99, 126.52, 115.63, 114.03, 105.57, 101.24, 69.92, 55.32.

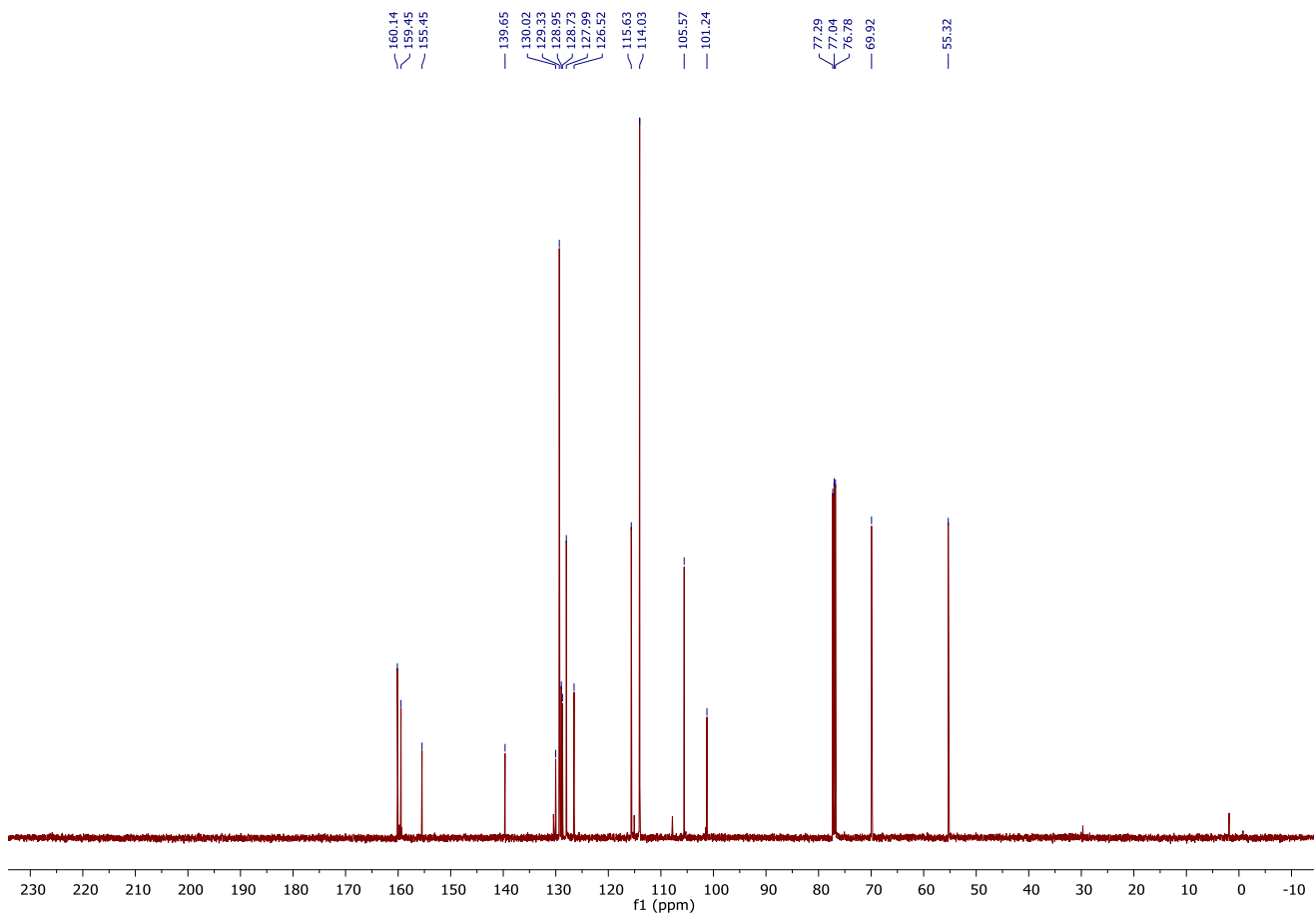
IR (Neat): 3608, 2953, 1611, 1580, 1514, 1436, 1245, 1144, 1030 cm^{-1} ;

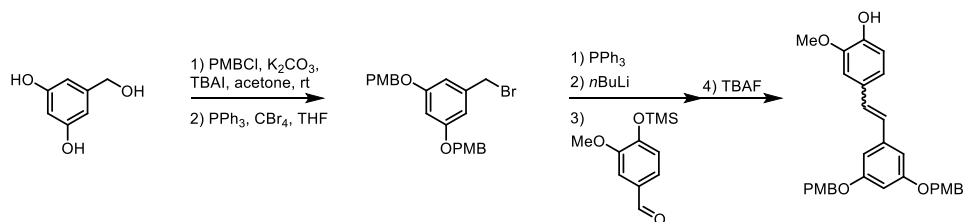
HRMS (ESI) m/z calculated for $\text{C}_{30}\text{H}_{29}\text{O}_5^+$ ($[\text{M}+\text{H}]^+$) 469.2010, found 469.2007.

¹H NMR, 500 MHz, Chloroform-*d*, Stilbene **25**



¹³C NMR, 126 MHz, Chloroform-*d*, Stilbene **25**





(26) (E)-4-(3,5-bis((4-methoxybenzyl)oxy)styryl)-2-methoxyphenol

Commercially available 3,5-dihydroxybenzyl alcohol (2.0 g, 14.3 mmol) was added to flask charged with potassium carbonate (2.25 equiv., 4.44 g) and tetrabutylammonium iodide (0.2 equiv., 1.05 g), and the solids were dissolved/suspended in acetone (42 mL). To the stirring reaction mixture was added 4-methoxybenzyl chloride (2.20 equiv., 4.26 mL), and the reaction was allowed to stir at room temperature for 16 hours. Upon completion, the reaction was diluted with ethyl acetate and poured into a separatory funnel containing deionized water. The layers were separated, and the aqueous layer was extracted with additional portions of ethyl acetate. The combined organic layer was washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure to afford the crude product, which was carried forward without further purification. A portion of the PMB-protected material (734 mg, 1.93 mmol) was subjected to the general procedure using toluene as the solvent for the olefination with aldehyde C. Upon completion of the olefination, the reaction was cooled to 0 °C, and TBAF (1.0 equiv., 1.0 M in THF, 1.93 mL) was added dropwise. The reaction was allowed to stir for 30 min, at which point it was quenched and worked up following the general procedure. The product was purified by column chromatography (8% to 40% ethyl acetate in hexanes) to afford the desired product as a ~3.6:1 E:Z mixture (762 mg, 79% yield).

R_f = 0.32 (ethyl acetate/hexanes 3:7; UV)

E-isomer:

$^1\text{H NMR}$ (700 MHz, Chloroform-*d*) δ 7.37 (d, J = 8.4 Hz, 4H), 7.03 (d, J = 1.8 Hz, 1H), 7.01 (dd, J = 8.2, 1.8 Hz, 1H), 7.00 (d, J = 15.9 Hz, 1H), 6.93 (d, J = 8.4 Hz, 4H), 6.91 (d, J = 8.1 Hz, 1H), 6.87 (d, J = 15.9 Hz, 1H), 6.52 (t, J = 2.5 Hz, 1H), 5.67 (s, 1H), 5.00 (s, 4H), 3.95 (s, 3H), 3.83 (s, 6H).

$^{13}\text{C NMR}$ (126 MHz, Acetone-*d*₆) δ 160.30, 159.58, 146.83, 145.82, 139.70, 129.90, 129.40, 129.28, 129.06, 126.55, 120.71, 114.69, 114.13, 108.42, 105.63, 101.38, 70.01, 56.03, 55.42.

Z-isomer:

$^1\text{H NMR}$ (700 MHz, Chloroform-*d*) δ 7.28 (d, J = 8.6 Hz, 4H), 6.88 (d, J = 8.6 Hz, 4H), 6.80 (dd, J = 7.6, 1.8 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 6.77 (d, J = 1.5 Hz, 1H), 6.54 (d, J = 2.2 Hz, 2H), 6.48 (d, J = 12.1 Hz, 1H), 6.46 (t, J = 2.3 Hz, 1H), 6.44 (d, J = 12.1 Hz, 1H), 5.57 (s, 1H), 4.84 (s, 4H), 3.81 (s, 6H), 3.62 (s, 3H).

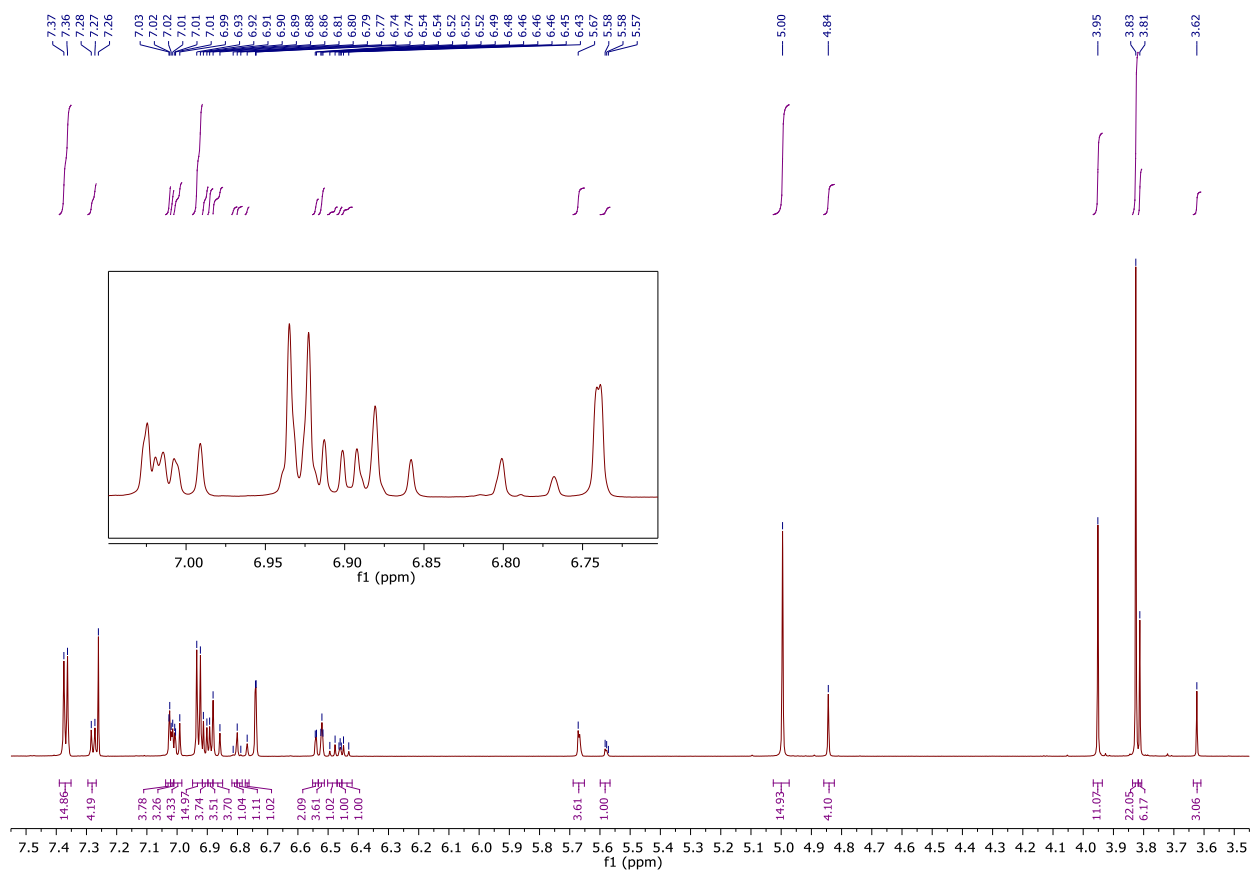
$^{13}\text{C NMR}$ (126 MHz, Acetone-*d*₆) δ 159.95, 159.51, 146.08, 145.08, 139.74, 130.53, 129.90, 128.61, 124.41, 122.87, 121.77, 114.07, 112.30, 111.42, 107.93, 101.44, 69.88, 55.75, 55.42.

Mixture of isomers:

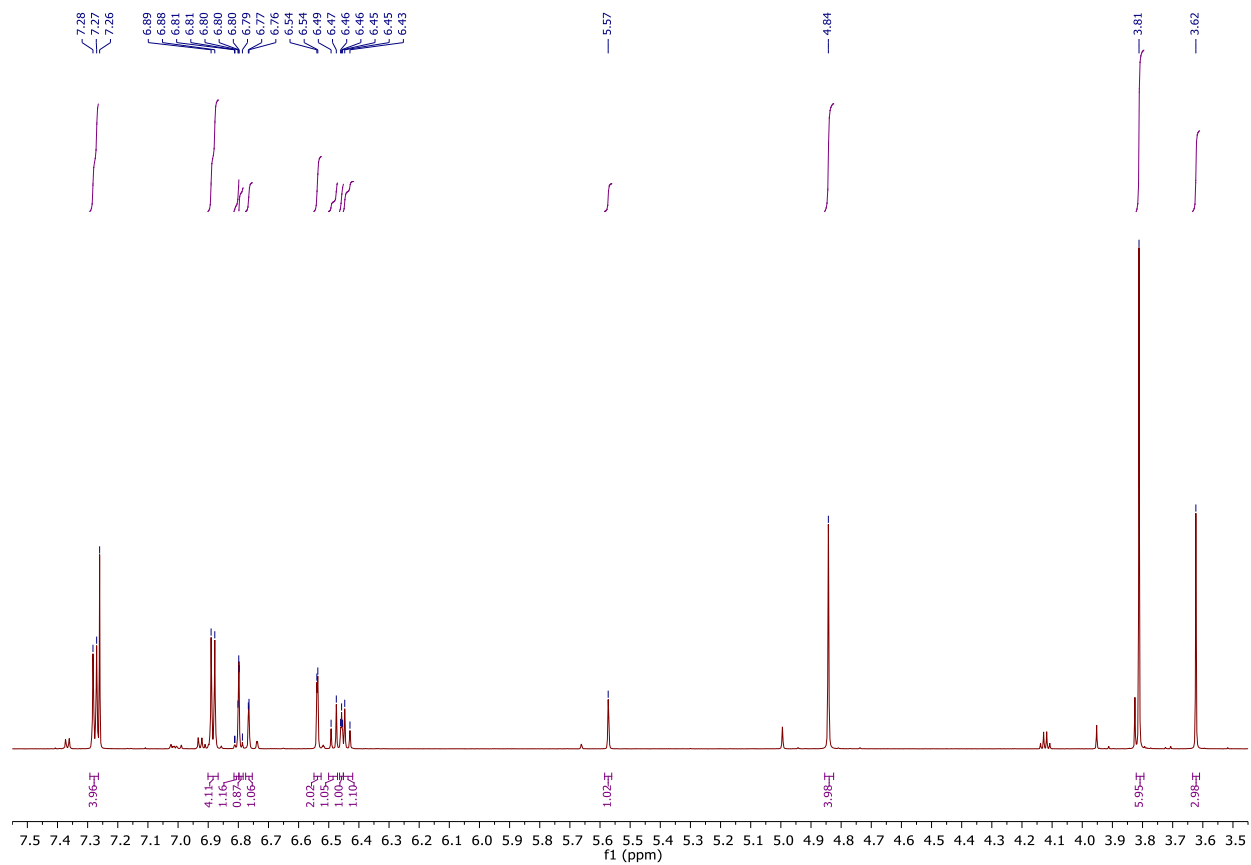
IR (Neat): 3522, 2954, 2869, 1592, 1454, 1353, 1287, 1212, 1194, 1157, 1149, 1056, 1037, 963, 828, 732, 695, 634 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{C}_{31}\text{H}_{31}\text{O}_6^+$ ($[\text{M}+\text{H}]^+$) 499.2115, found 499.2111.

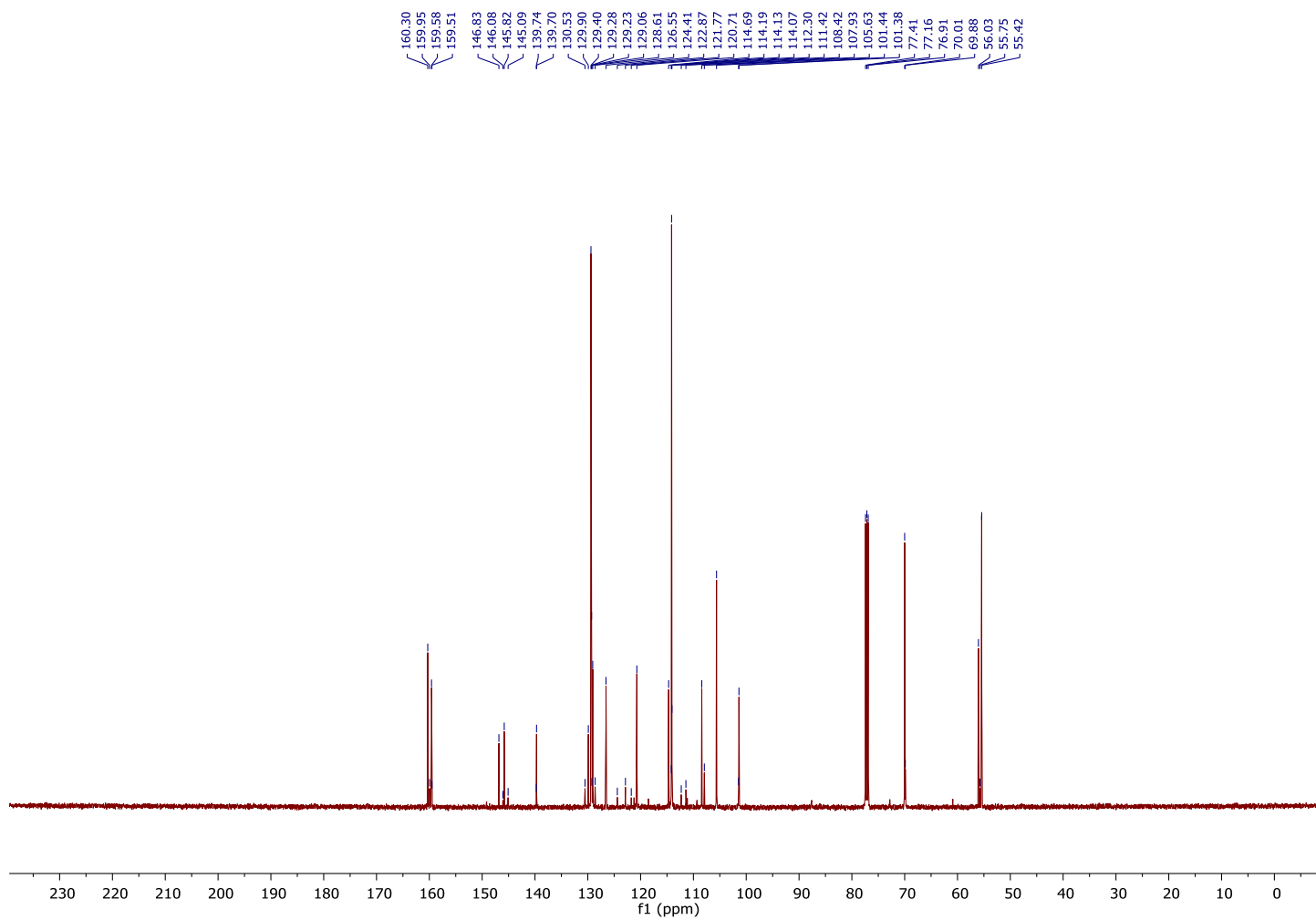
¹H NMR, 700 MHz, Chloroform-*d*, Stilbene **26** (~3.6:1 mixture of isomers)



¹H NMR, 700 MHz, Chloroform-*d*, Stilbene **26** (Z isomer)



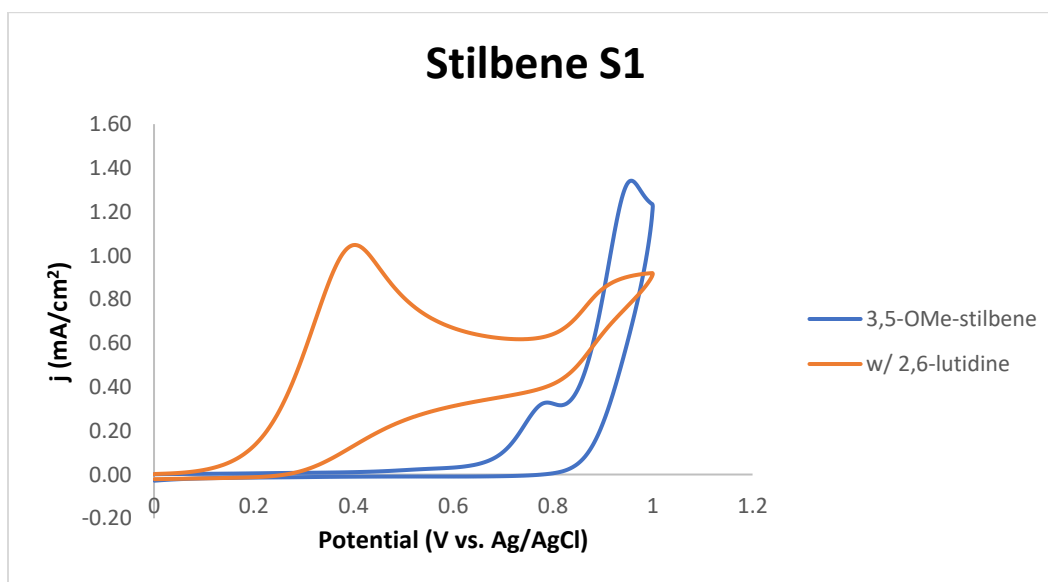
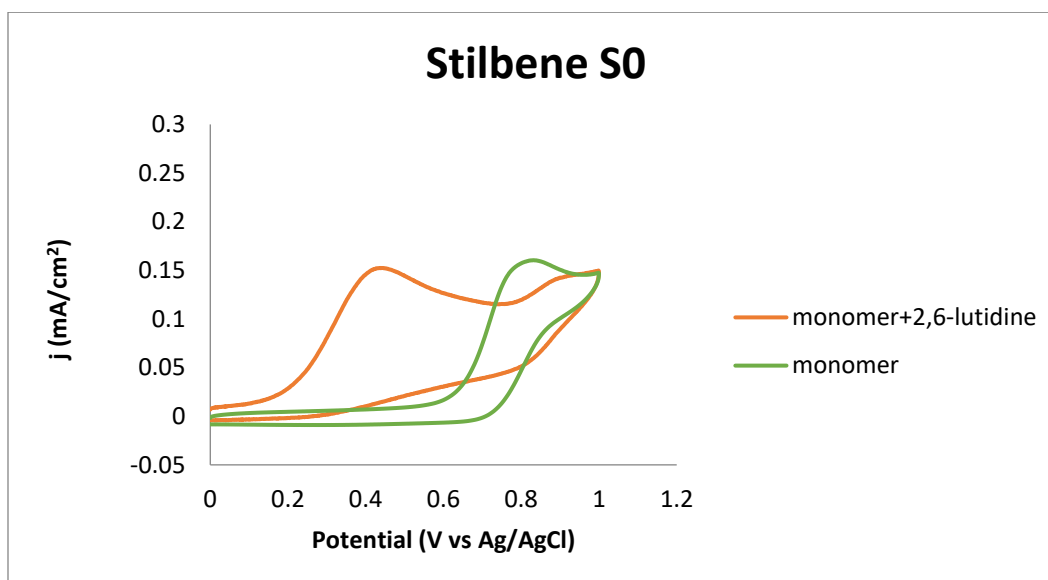
^{13}C NMR, 126 MHz, Chloroform-*d*, Stilbene **26** (~3.6:1 mixture of isomers)

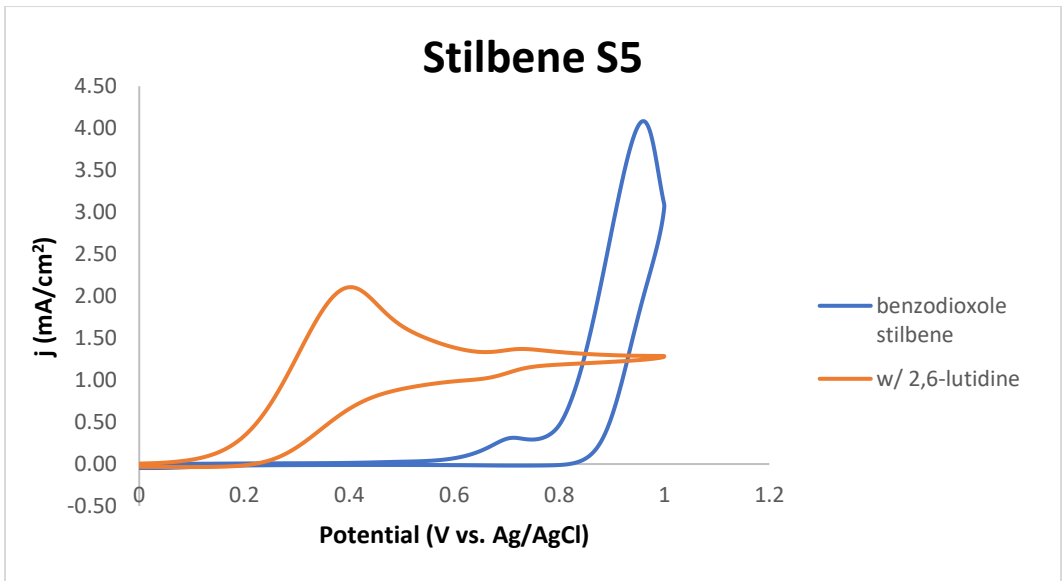
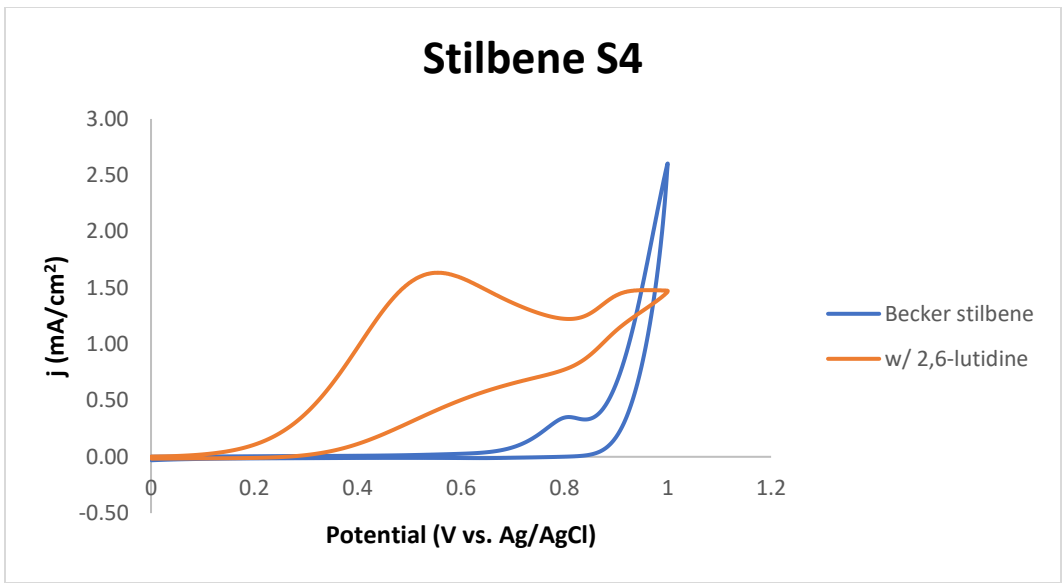
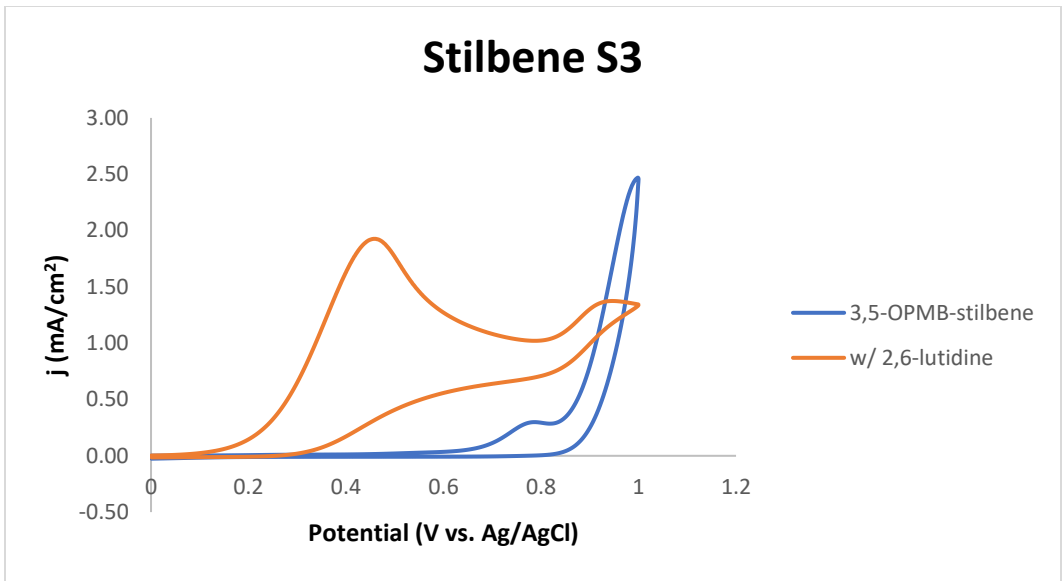


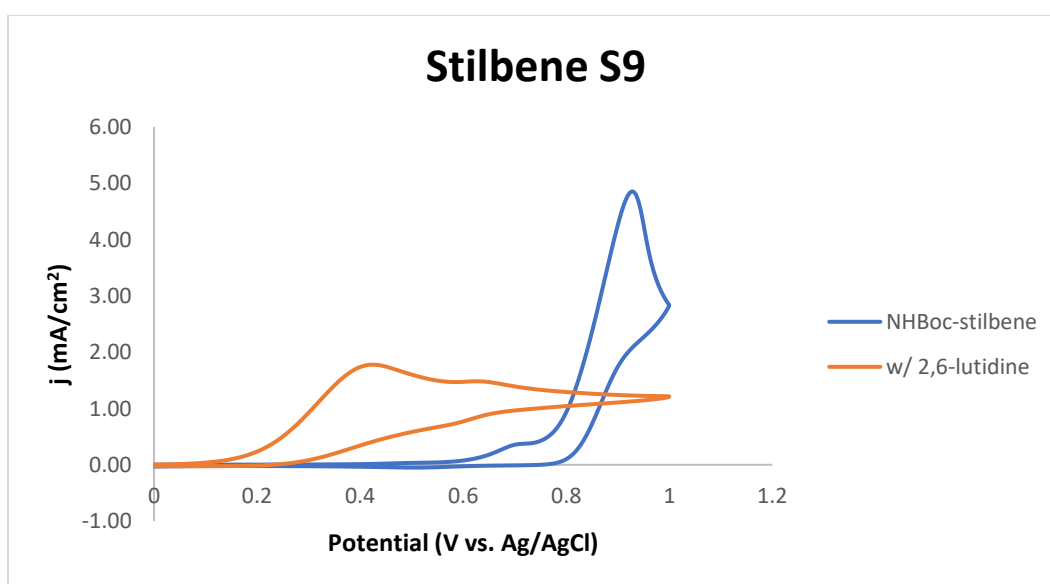
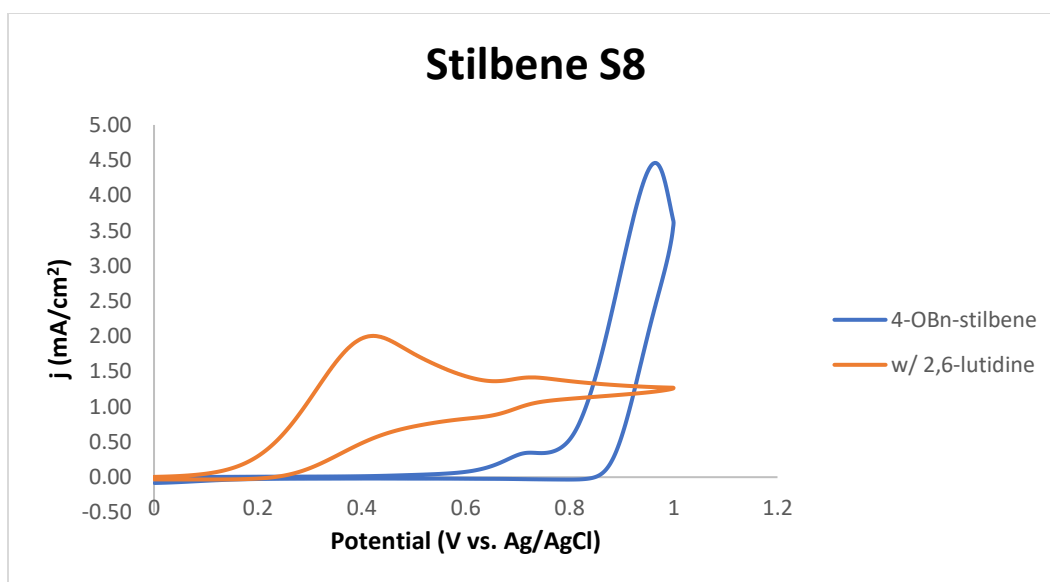
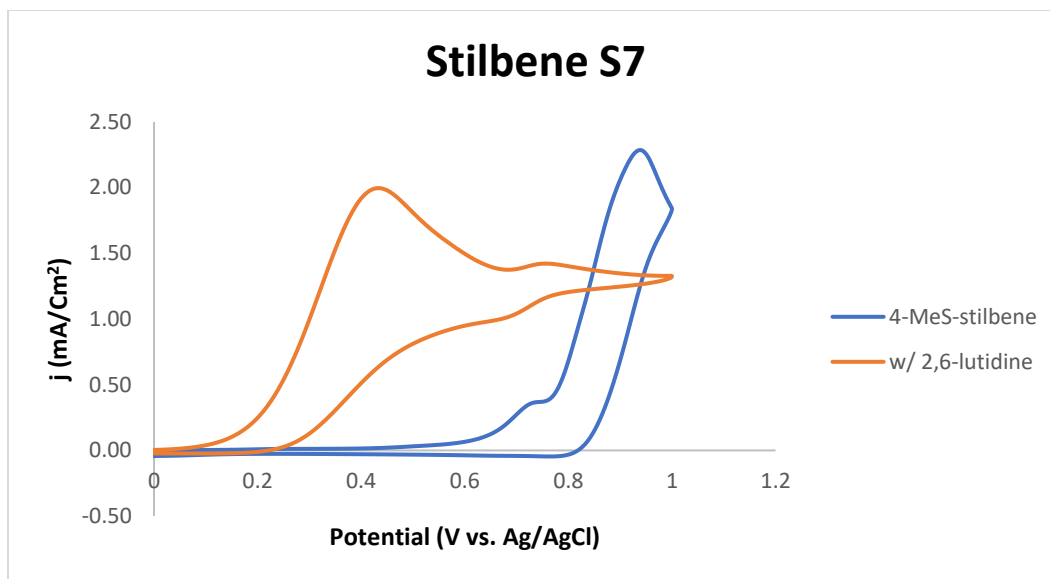
Cyclic Voltammetry Experimental Procedure:

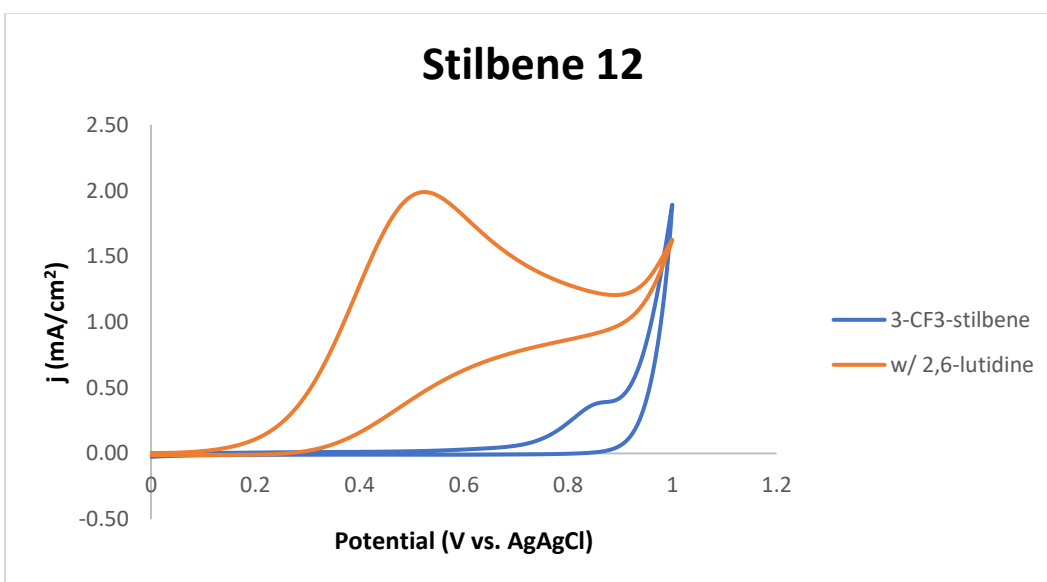
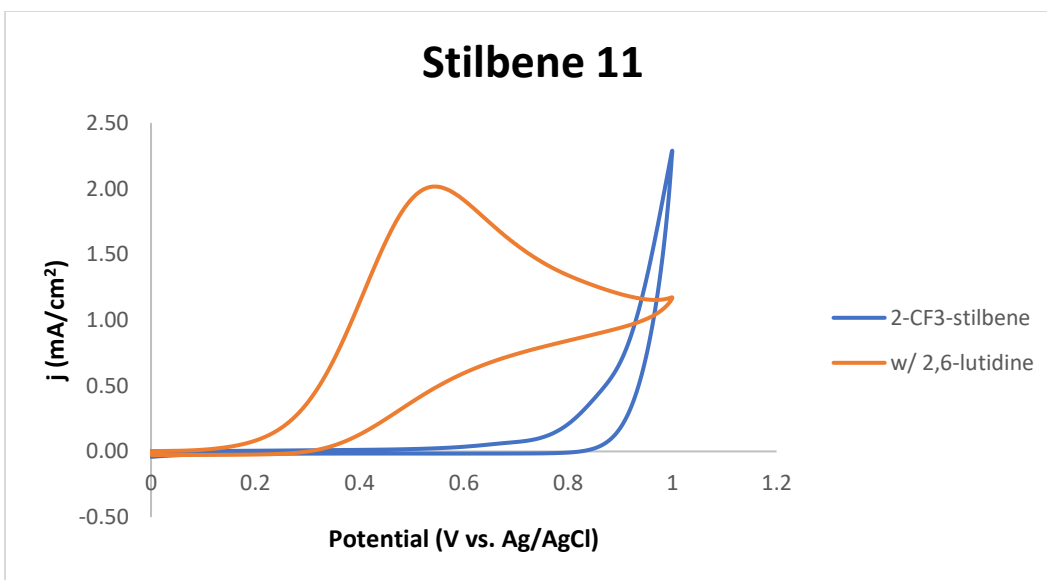
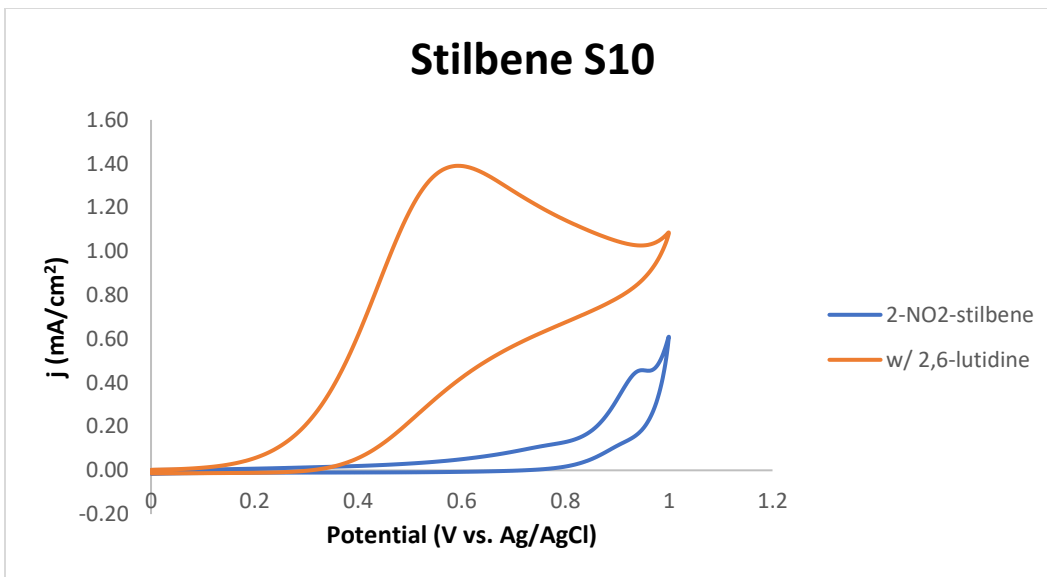
For each stilbene substrate, two cyclic voltammetry experiments were conducted. The first was to measure oxidation of the substrate (green or blue curve), while the second was to measure oxidation in the presence of 2,6-lutidine (orange curve). The stilbene substrate (0.03 mmol) and the electrolyte (Bu_4NPF_6 , 0.3 mmol, 116 mg) were dissolved in acetonitrile (3 mL). For the experiments with base, 2,6-lutidine (0.03 mmol, 3.5 μL) was added. The solution was transferred to a 5-neck electrochemical cell, which was outfitted with a working electrode (glassy carbon, 3 mm diameter, surface area = 0.0707 cm^2), reference electrode (Ag/AgCl, 3 M aq. KCl), and counter/auxiliary electrode (platinum wire). The electrochemical cell was connected to the CH1620E electrochemical analyzer, and the potential was swept from 0.0 V to +1.0 V in two sweep segments at a scan rate of 100 mV/s to afford the observed cyclic voltammograms. It can be seen in the data below that direct oxidation of the electron rich substrates occurs between +0.8 to +1.0 V, however direct oxidation of electron deficient substrates occurs beyond +1.0 V. In the presence of 2,6-lutidine, oxidation occurs below +0.6 V in all cases, suggesting that +0.6 V is a sufficient potential to attain the desired reactivity.

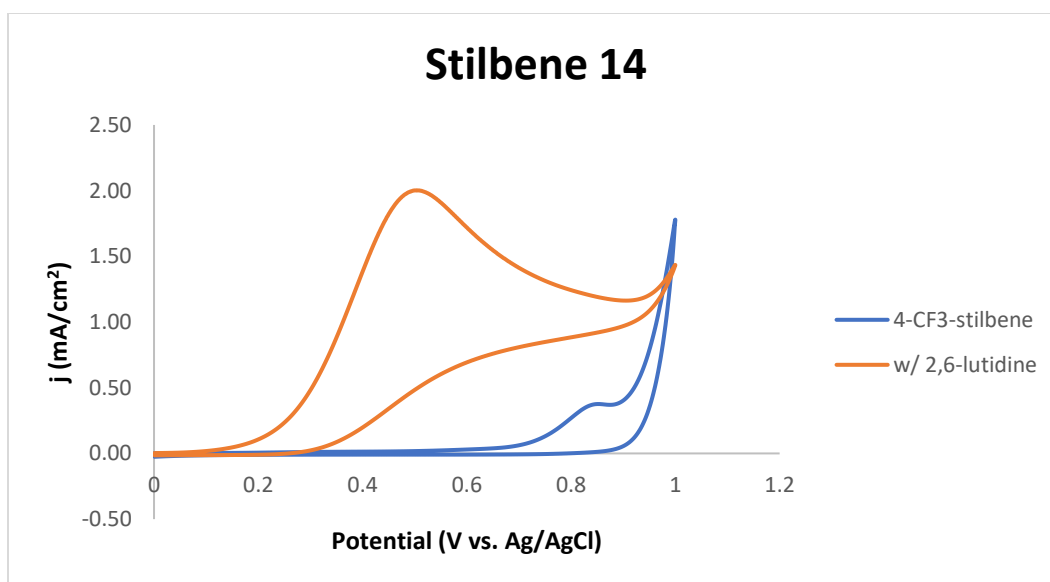
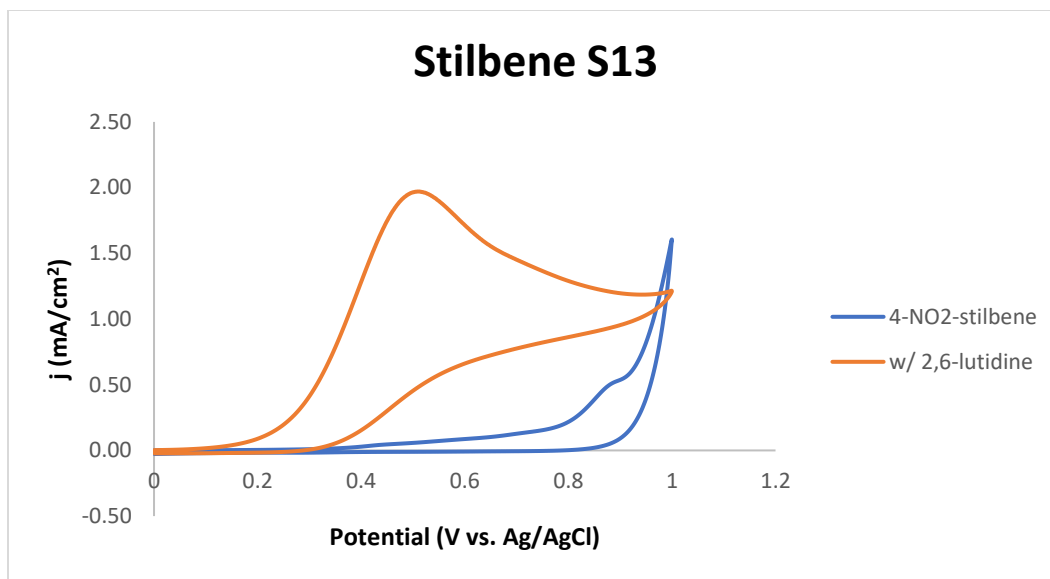
Cyclic Voltammetry Data:





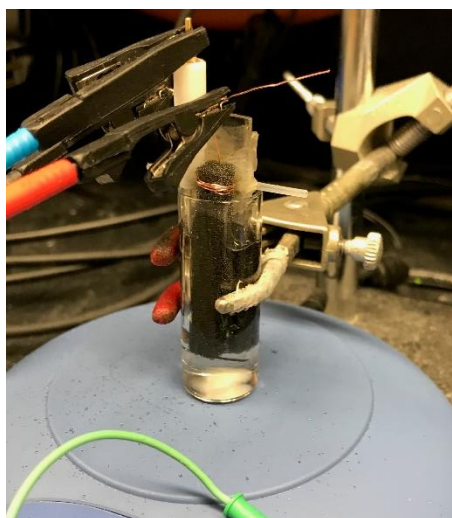






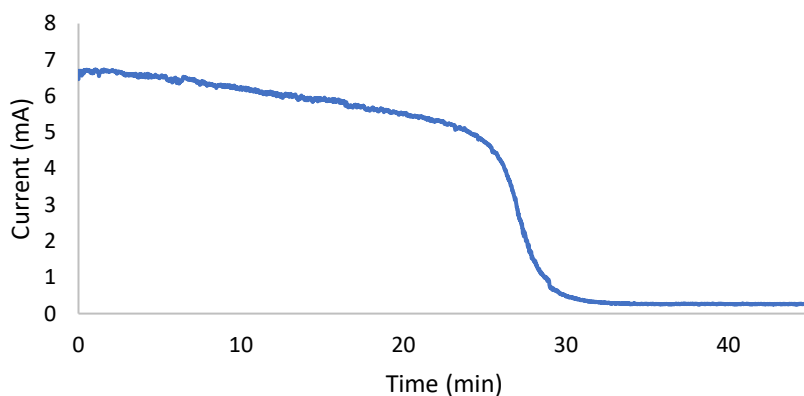
General Dimerization Procedure³:

The starting phenol (0.1 mmol) was added to a reaction vial with KPF_6 (74 mg, 0.4 mmol) and 2,6-lutidine (2.3 μL , 0.02 mmol) and dissolved in acetonitrile (8 mL). Two pieces of 0.25 x 2-inch RVC panel (0.25 inch thickness) were cut. To each, a hole was made near one end, and copper wire was placed through the hole and wrapped around the top of each electrode. One end of the wire was left free in to connect to the alligator clips. These electrodes were carefully placed into the reaction vial along with the reference electrode (Ag/AgCl in 3 M KCl) and a divider (*see image*). The alligator clips were connected such that the reference and working electrodes were adjacent to each other, while the counter electrode was opposite the divider. Care was taken to ensure the copper wire was not submerged in solvent, nor the active components of the alligator clips touching each other. The reaction was stirred at 750 rpm for 1-2 h at a constant voltage of 0.6 V. A chronoamperogram was recorded to follow the course of the reaction. Upon completion of the reaction, the electrodes were removed and rinsed into a collection flask with DCM (~40 mL). The contents of the reaction vial were also rinsed into the collection flask. The solvent was removed on the rotovap, the crude material was resuspended in DCM, and the electrolyte was filtered away with a plug of Celite. The filtrate was then concentrated to afford the product, which did not require further purification. The diastereomeric ratios were determined by integration of the aryl protons on the quinone methide. When these were overlapping with other aryl signals, the δ -protons of the quinone methide were integrated to determine dr.

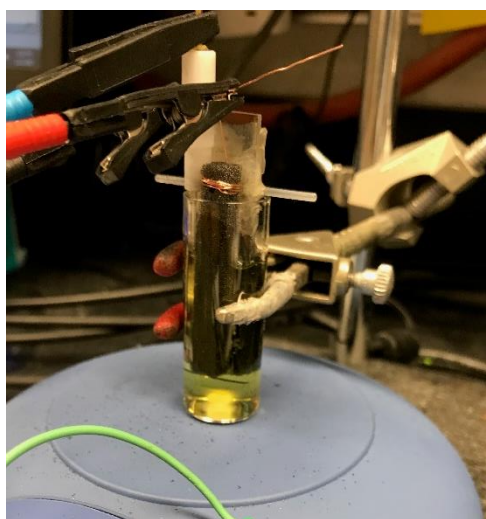


Prior to electrolysis

Monitoring Current vs. Time



Sample chronoamperogram



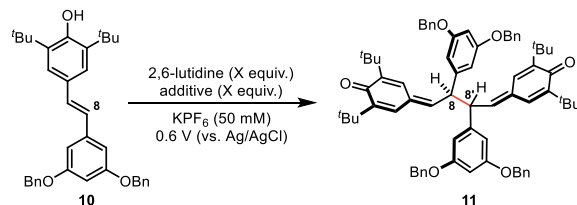
After electrolysis



Reaction components

Optimization and Scalability of Dimerization

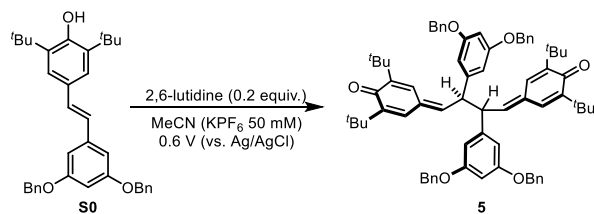
Table S1. Optimization of Electrochemical Dimerization



Entry	Scale (mmol)	Additive (equiv.)	2,6-lut. (equiv.)	Solvent (ratio)	Time (h)	Yield (%) ^a
1	0.1	Fc (0.1)	2.0	A	0.5	94
2	0.1	-	2.0	A	0.5	99
3	0.1	-	0.2	A	0.5	99
4	0.1	-	0	A	0.5	0
5	0.3	-	0.2	A	1	90
6	0.3	-	0.2	A:B (2:1)	1	95
7	0.9	-	0.2	A:B (2:1)	5	99
8	3.6	-	0.2	A:B (2:1)	12	95

^aIsolated yields. Fc = ferrocene. A = MeCN. B = CH₂Cl₂.

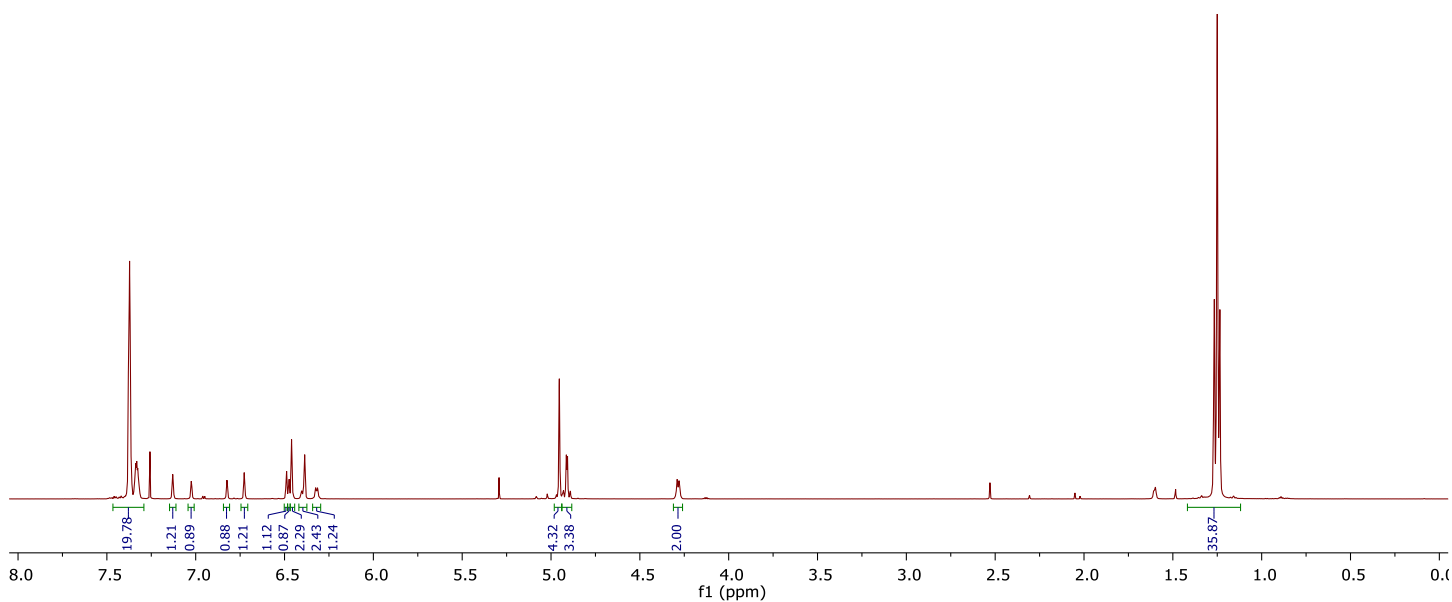
The investigation of this electrochemical dimerization strategy began with protected resveratrol analogue **10**, mimicking the key transformation in our prior syntheses of pallidol and quadrangularin A.¹ Initial attempts sought to recapitulate the ferrocenium-mediated conditions, positing that the well-known, low and reversible oxidation potential of ferrocene (E_{1/2}(Fc⁺/Fc) = 0.40 V vs SCE) would allow for the use of sub-stoichiometric equivalents of the oxidant.⁴ Gratifyingly, an excellent yield was achieved using only 10 mol% of ferrocene and 2 equivalents of 2,6-lutidine (Table S1, Entry 1). It was speculated that the oxidative dimerization of **10** could occur without the need for a metal catalyst, given the apparent selectivity window that existed between the oxidation potential of the starting material (E_{p/2} = +0.81 V vs Ag/AgCl) and the desired product **11** (E_{p/2} = +1.23 vs Ag/AgCl, see page S37 for voltammetry data). This selectivity could be further enhanced by lowering the oxidation potential through the addition of base, an effect demonstrated by Corduneanu et al. in their investigation of the effect of pH on the oxidation potential of resveratrol.⁵ Indeed, we observed a dramatic decrease in the oxidation potential of **10** upon adding 2,6-lutidine (E_{p/2} = +0.44 V (vs Ag/AgCl)), while the bis-quinone methide (BQM) product **11** was unaffected. Employing these metal-free conditions for the bulk electro-chemical processing of monomer **10** proved highly effective (Table S1, entry 2), generating the desired product in near quantitative yield after just 30 min at +0.6 V. Furthermore, it was observed that only a sub-stoichiometric amount of base was needed (Table S1, Entry 3), and the reaction did not occur at the same set potential when base was excluded (Table S1, Entry 4). Upon increasing the scale of the reaction (from 0.1 mmol to 0.3 mmol), deposition of insoluble dimeric products on the surface of the electrodes was found to inhibit the reaction (Table S1, Entry 5), an issue that was ameliorated through the addition of dichloromethane as a co-solvent. Importantly, these optimized conditions proved readily-scalable (Table S1, Entries 6-8), including operation on multi-gram scale while still maintaining high yields (≥95%). In addition to the efficiency, the operational simplicity of this method is viewed as a definitive benefit, as it is carried out on the benchtop, open to atmosphere, and only requires the addition of an electrolyte and a single, readily-available reagent. Furthermore, column chromatography is generally not required, increasing the attractiveness of this method for multi-step synthetic routes.

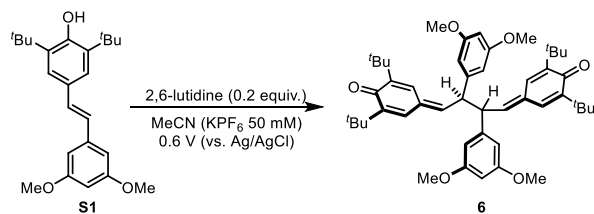


(5) 4,4'-((2R,3R)-2,3-bis(3,5-bis(benzyloxy)phenyl)butane-1,4-diylidene)bis(2,6-di-tert-butylcyclohexa-2,5-dien-1-one)

Stilbene **S0** (0.1 mmol, 52.1 mg) was subjected to the general dimerization procedure, affording bis-quinone methide **5** (51.7 mg, 99% yield, 4:3 dr). The ¹H NMR spectrum was identical to the previous report for this compound.¹

¹H NMR (CDCl₃, 500 MHz): δ 7.40 – 7.30 (m, 20H), β-H's of quinone methides: 7.12 (major diastereomer, d, *J* = 2.2 Hz, 2H), 7.02 (minor diastereomer, d, *J* = 2.0 Hz, 2H), 6.82 (minor diastereomer, d, *J* = 2.2 Hz, 2H), 6.72 (major diastereomer, d, *J* = 2.0 Hz, 2H); δ-H's of quinone methides: 6.41 – 6.37 (minor diastereomer, m, 2H), 6.33 – 6.29 (major diastereomer, m, 2H); 6.48 (major diastereomer, t, *J* = 2.1 Hz, 2H), 6.47 (minor diastereomer, t, *J* = 2.2 Hz, 2H), 6.45 (major diastereomer, d, *J* = 2.1 Hz, 4H), 6.38 (minor diastereomer, d, *J* = 2.2 Hz, 4H), 4.96 (major diastereomer, d, *J* = 11.5 Hz, 4H), 4.94 (major diastereomer, d, *J* = 11.5 Hz, 4H), 4.91 (minor diastereomer, d, *J* = 11.5 Hz, 4H), 4.89 (minor diastereomer, d, *J* = 11.5 Hz, 4H), 4.28 (m, overlap, sp³ methines of both diastereomers, 4H), 1.26 (minor diastereomer *t*Bu's, s, 18H), 1.24 (major diastereomer *t*Bu's, s, 36H), 1.23 (minor diastereomer *t*Bu's, s, 18H).

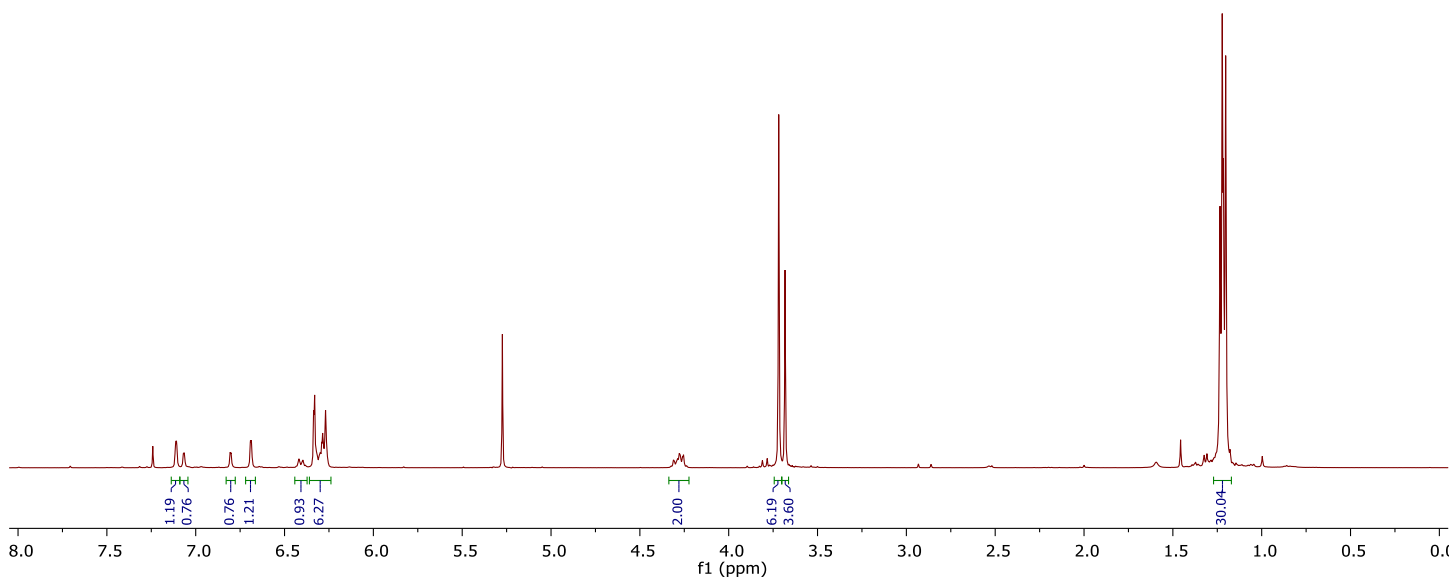


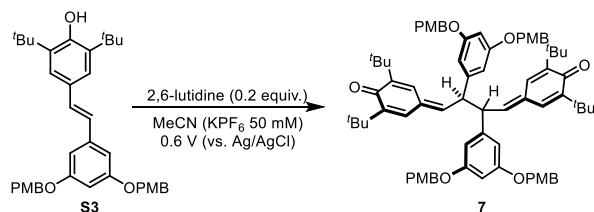


(6) 4,4'-((2*R*,3*R*)-2,3-bis(3,5-dimethoxyphenyl)butane-1,4-diyldiene)bis(2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one)

Stilbene **S1** (0.1 mmol, 36.9 mg) was subjected to the general dimerization procedure, affording bis-quinone methide **6** (36.5mg, 99% yield, 3:2 dr). The ^1H NMR spectrum was identical to the previous report for this compound.¹

^1H NMR (CDCl_3 , 700 MHz): δ β -H's of quinone methides: 7.13 (major diastereomer, d, $J = 1.9$ Hz, 2H), 7.09 (minor diastereomer, d, $J = 2.0$ Hz, 2H), 6.82 (minor diastereomer, d, $J = 2.2$ Hz, 2H), 6.71 (major diastereomer, d, $J = 2.2$ Hz, 2H); δ -H's of quinone methides: 6.43 (minor diastereomer, m, 2H), 6.33 (major diastereomer, m, 2H); 6.35 (Ar-H major diastereomer, d, $J = 2.1$ Hz, 4H), 6.31 (Ar-H major diastereomer, t, $J = 2.1$ Hz, 2H), 6.29-6.27 (Ar-H's minor diastereomer, overlap, 6H), 4.34 – 4.30 (minor diastereomer sp^3 methines, m, 2H), 4.30 – 4.26 (major diastereomer sp^3 methines, m, 2H), 3.74 (major diastereomer –OMe's, s, 12H), 3.70 (minor diastereomer –OMe's, s, 12H), 1.25 (minor diastereomer *t*Bu's, s, 18H), 1.24 (major diastereomer *t*Bu's, s, 18H), 1.23 (minor diastereomer *t*Bu's, s, 18H), 1.22 (major diastereomer *t*Bu's, s, 18H).





(7) 4,4'-((2*R*,3*R*)-2,3-bis(3,5-bis((4-methoxybenzyl)oxy)phenyl)butane-1,4-diyldiene)bis(2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one)

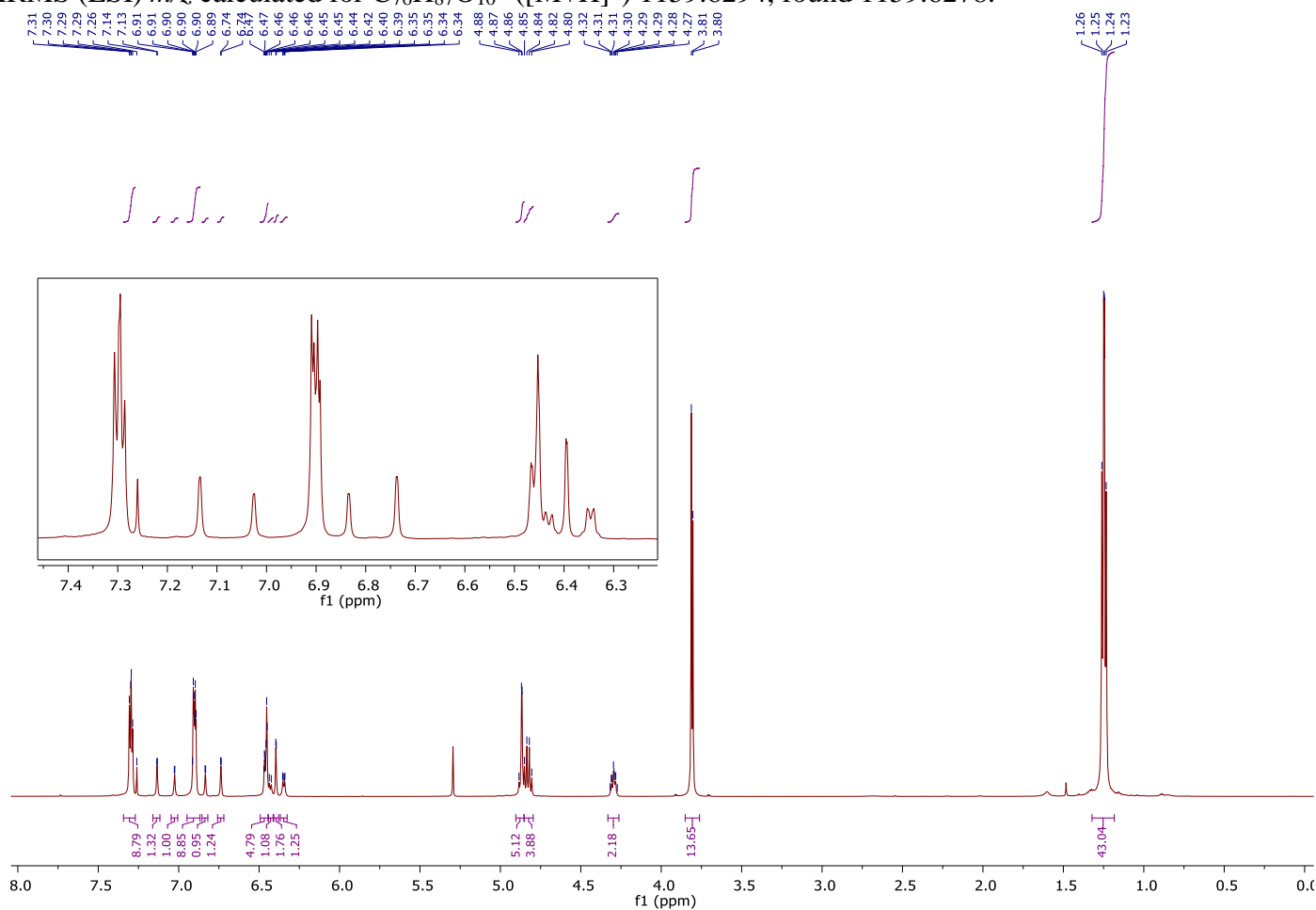
Stilbene **S3** (0.1 mmol, 58.1 mg) was subjected to the general dimerization procedure, affording bis-quinone methide **7** (57.8 mg, 99% yield, 5:4 dr).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.30 (m, 16H), 7.13 (β-H, major diastereomer, d, *J* = 2.4 Hz, 2H), 7.03 (β-H, minor diastereomer, d, *J* = 2.4 Hz, 2H), 6.90 (m, 16H), 6.83 (β-H, minor diastereomer, d, *J* = 2.4 Hz, 2H), 6.74 (β-H, major diastereomer, d, *J* = 2.4 Hz, 2H), 6.46 (m, 8H), 6.43 (δ-H, minor diastereomer, d, *J* = 8.8 Hz, 2H), 6.39 (minor diastereomer, d, *J* = 2.2 Hz, 4H), 6.35 (δ-H, major diastereomer, dd, *J* = 7.2, 2.5 Hz, 2H), 4.87 (d, *J* = 2.6 Hz, 8H), 4.83 (q, *J* = 10.6 Hz, 8H), 4.30 (m, sp³ methines of both diastereomers, 4H), 3.81 (s, 12H), 3.80 (s, 12H), ^tBu signals: 1.26 (s, 18 H), 1.25 (s, 18H), 1.24 (s, 18 H), 1.23 (s, 18 H).

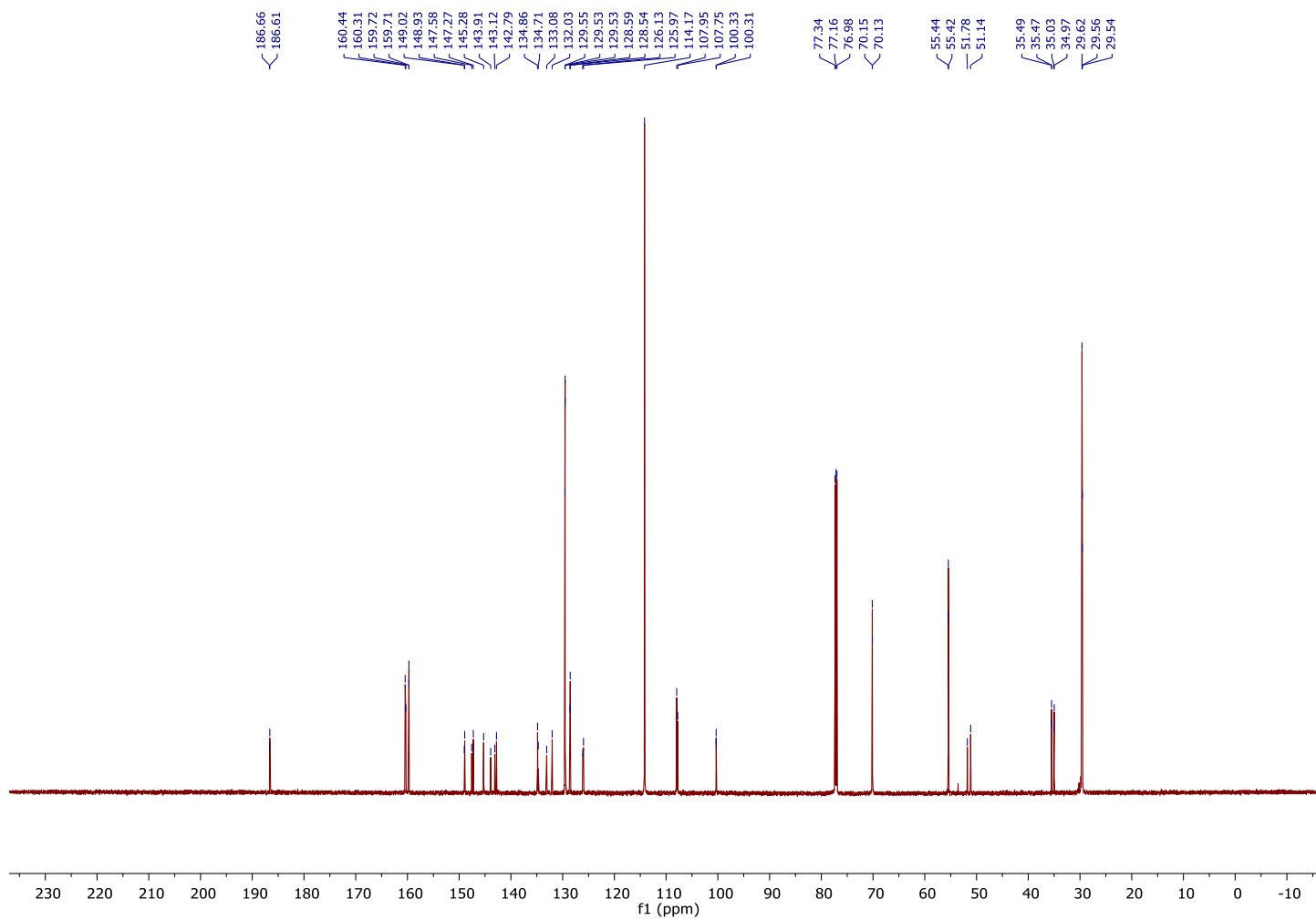
¹³C NMR (176 MHz, Chloroform-*d*) δ 186.66, 186.61, 160.44, 160.31, 159.72, 159.71, 149.02, 148.93, 147.58, 147.27, 145.28, 143.91, 143.12, 142.79, 134.86, 134.71, 133.08, 132.03, 129.55, 129.53, 128.59, 128.54, 126.13, 125.97, 114.17, 107.95, 107.75, 100.33, 100.31, 70.15, 70.13, 55.44, 55.42, 51.78, 51.14, 35.49, 35.47, 35.03, 34.97, 29.62, 29.56, 29.54.

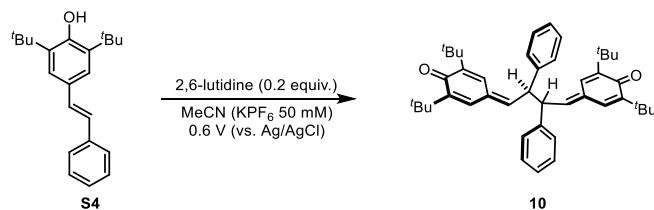
IR (Neat): 2955, 2929, 1611, 1577, 1515, 1439, 1245, 1147, 1046, 1026, 967, 858 cm⁻¹;

HRMS (ESI) *m/z* calculated for C₇₆H₈₇O₁₀⁺ ([M+H]⁺) 1159.6294, found 1159.6278.



^{13}C NMR, 176 MHz, Chloroform-*d*, Dimer 7





(10) 4,4'-((2*R*,3*R*)-2,3-diphenylbutane-1,4-diylidene)bis(2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one)

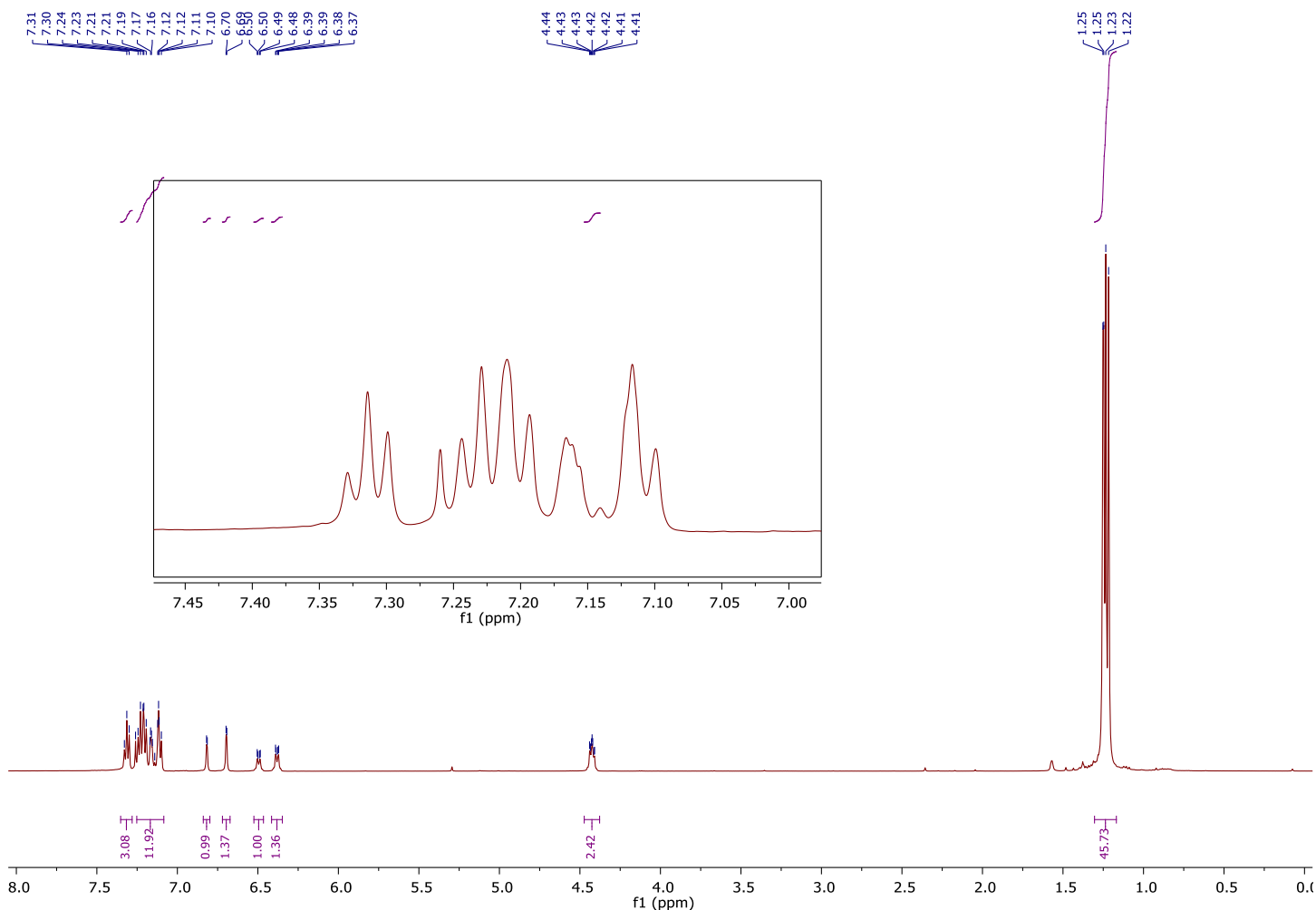
Stilbene **S4** (0.1 mmol, 33 mg) was subjected to the general dimerization procedure, affording bis-quinone methide **10** (32.6 mg, 99% yield, 4:3 dr).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.31 (t, $J = 7.5$ Hz, 4H), 7.25 – 7.08 (m, 20H), β -H's of quinone methides: 6.82 (minor diastereomer, d, $J = 2.4$ Hz, 2H), 6.70 (major diastereomer, d, $J = 2.4$ Hz, 2H), δ -H's of quinone methides: 6.52 – 6.47 (minor diastereomer, m, 2H), 6.42 – 6.35 (major diastereomers, m, 2H), 4.42 (m, sp^3 methines of both diastereomers, 4H), ^tBu signals: 1.25 (s, 18 H), 1.25 (s, 18H), 1.23 (s, 18 H), 1.22 (s, 18 H).

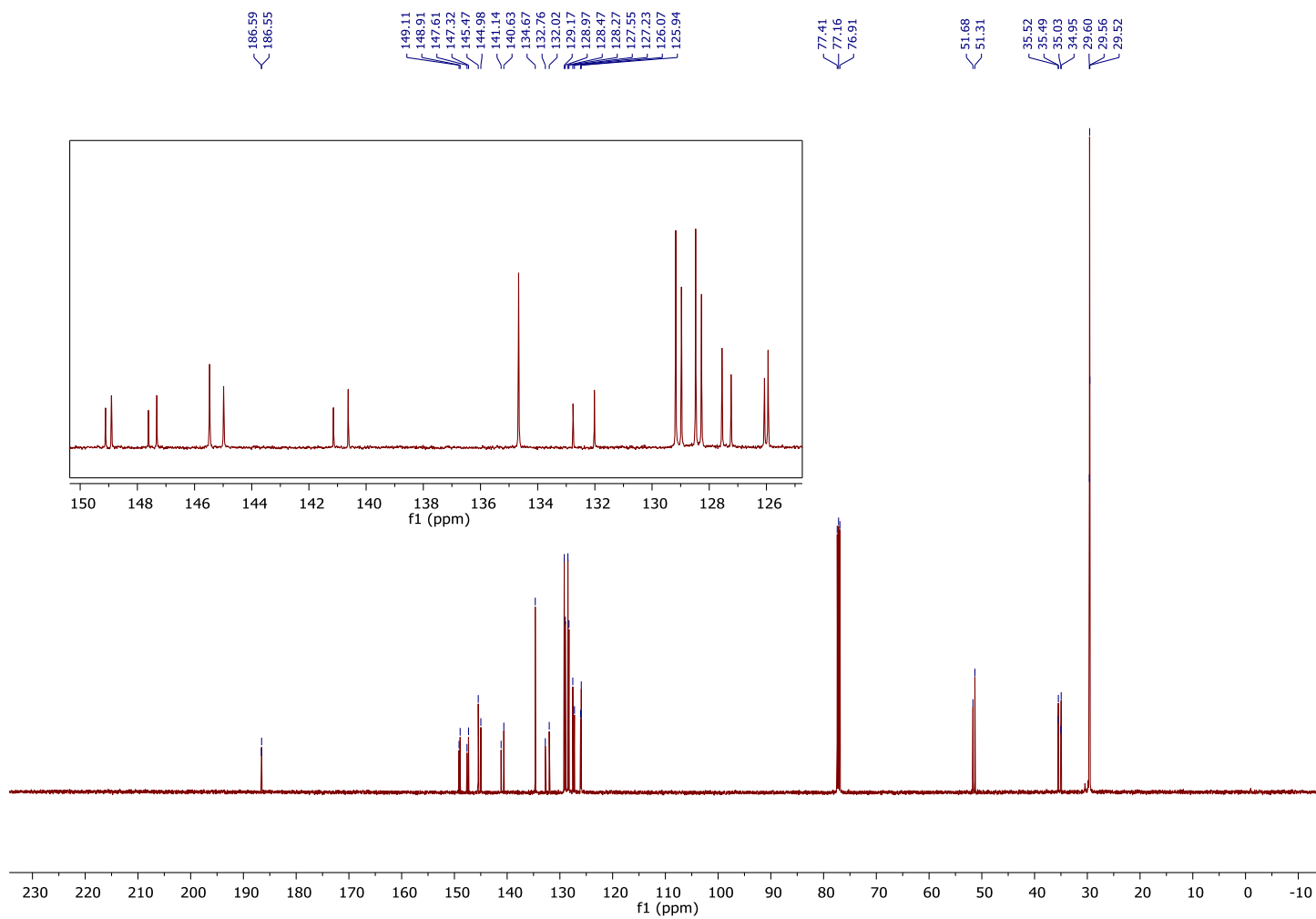
^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.59, 186.55, 149.11, 148.91, 147.61, 147.32, 145.47, 144.98, 141.14, 140.63, 134.67, 132.76, 132.02, 129.17, 128.97, 128.47, 128.27, 127.55, 127.23, 126.07, 125.94, 51.68, 51.31, 35.52, 35.49, 35.03, 34.95, 29.60, 29.56, 29.52.

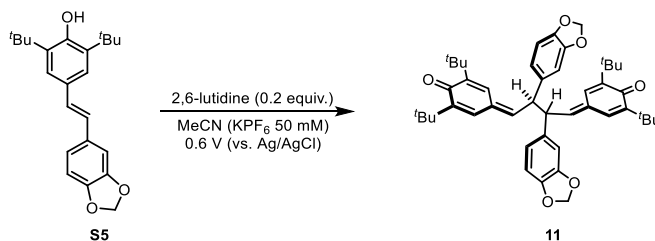
IR (Neat): 2951, 2915, 1614, 1577, 1453, 1358, 1257, 917, 883, 759, 697 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{NaC}_{44}\text{H}_{54}\text{O}_2^+$ ($[\text{M}+\text{Na}]^+$) 637.4016, found 637.4012.



^{13}C NMR, 126 MHz, Chloroform-*d*, Dimer **10**





(11) 4,4'-((2*R*,3*R*)-2,3-bis(benzo[*d*][1,3]dioxol-5-yl)butane-1,4-diyldiene)bis(2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one)

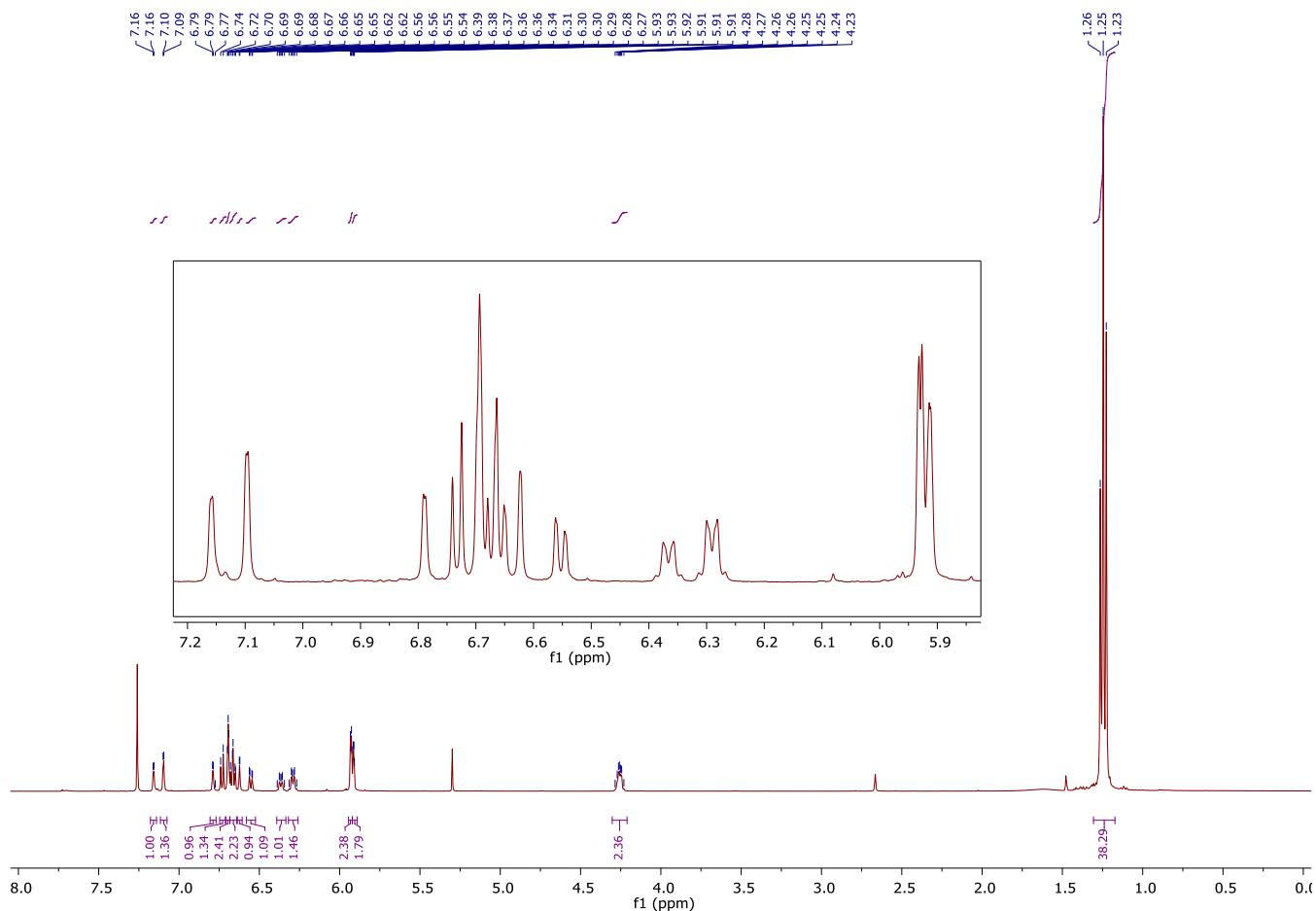
Stilbene **S5** (0.1 mmol, 35.2 mg) was subjected to the general dimerization procedure, affording bis-quinone methide **11** (34.7 mg, 99% yield, 3:2 dr).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.16 (minor diastereomer, d, $J = 2.4$ Hz, 2H), 7.10 (major diastereomer, d, $J = 2.4$ Hz, 2H), 6.79 (minor diastereomer, d, $J = 2.3$ Hz, 2H), 6.73 (minor diastereomer, d, $J = 7.9$ Hz, 2H), 6.69 (d, $J = 1.6$ Hz, 4H), 6.68 – 6.64 (m, 4H), 6.62 (d, $J = 1.7$ Hz, 2H), 6.55 (dd, $J = 8.0, 1.7$ Hz, 2H), 6.36 (δ -H, minor diastereomer, dt, $J = 8.7, 4.4$ Hz, 2H), 6.32 – 6.26 (δ -H, minor diastereomer, m, 2H), 5.93 (d, $J = 2.3$ Hz, 4H), 5.91 (d, $J = 2.1$ Hz, 4H), 4.30 – 4.21 (sp^3 methines of both diastereomers, m, 4H), ^tBu signals: 1.26 (s, 18 H), 1.25 (s, 36 H), 1.23 (s, 18 H).

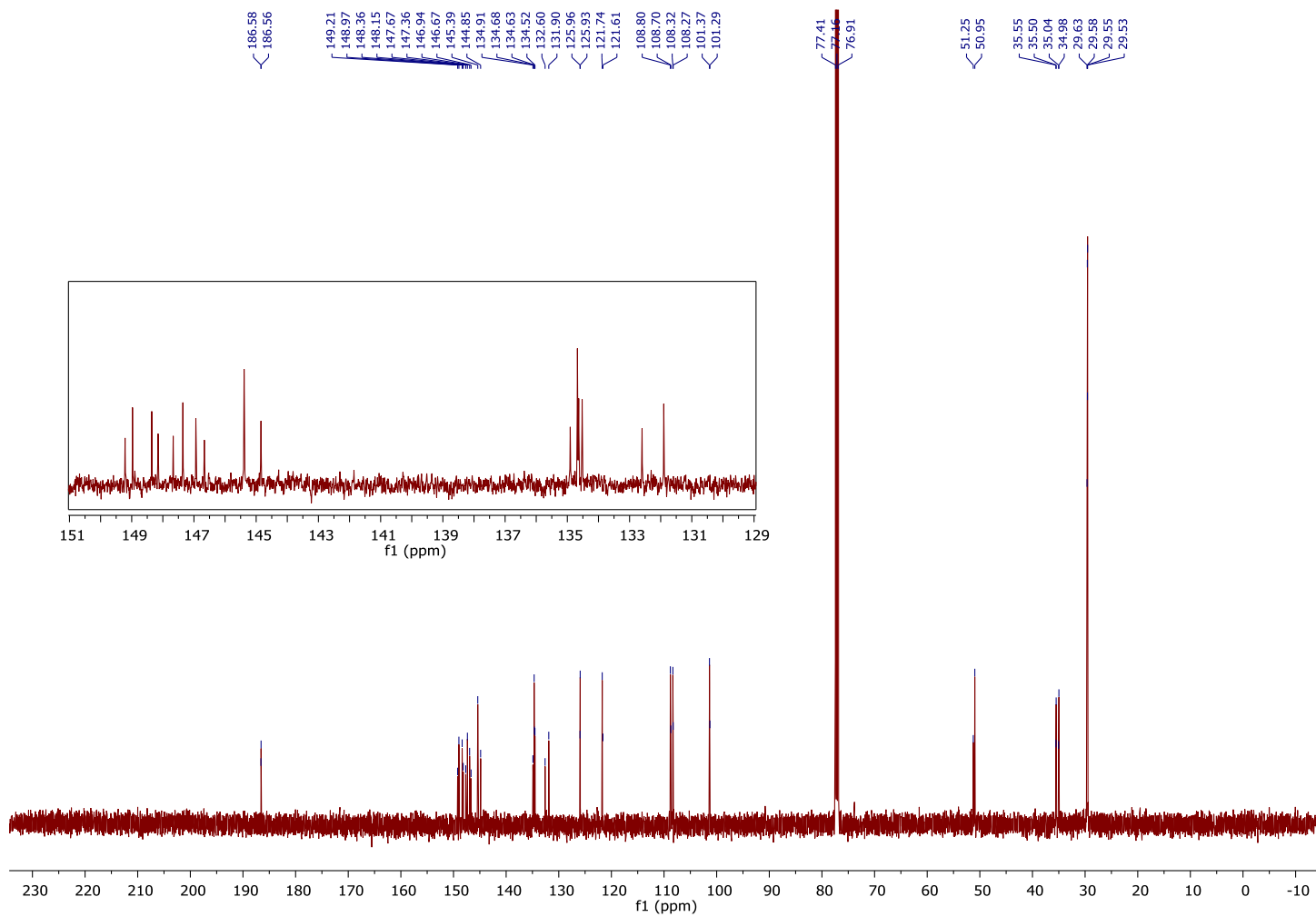
^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.58, 186.56, 149.21, 148.97, 148.36, 148.15, 147.67, 147.36, 146.94, 146.67, 145.39, 144.85, 134.91, 134.68, 134.63, 134.52, 132.60, 131.90, 125.96, 125.93, 121.74, 121.61, 108.80, 108.70, 108.32, 108.27, 101.37, 101.29, 51.25, 50.95, 35.55, 35.50, 35.04, 34.98, 29.63, 29.58, 29.55, 29.53.

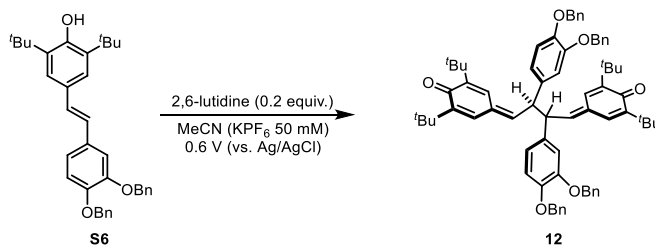
IR (Neat): 2954, 2914, 2361, 2336, 1616, 1539, 1362, 1243, 1034, 924, 808 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{NaC}_{46}\text{H}_{54}\text{O}_6^+$ ($[\text{M}+\text{Na}]^+$) 725.3813, found 725.3817.



^{13}C NMR, 126 MHz, Chloroform-*d*, Dimer **11**





(12) 4,4'-((2*R*,3*R*)-2,3-bis(3,4-bis(benzyloxy)phenyl)butane-1,4-diylidene)bis(2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one)

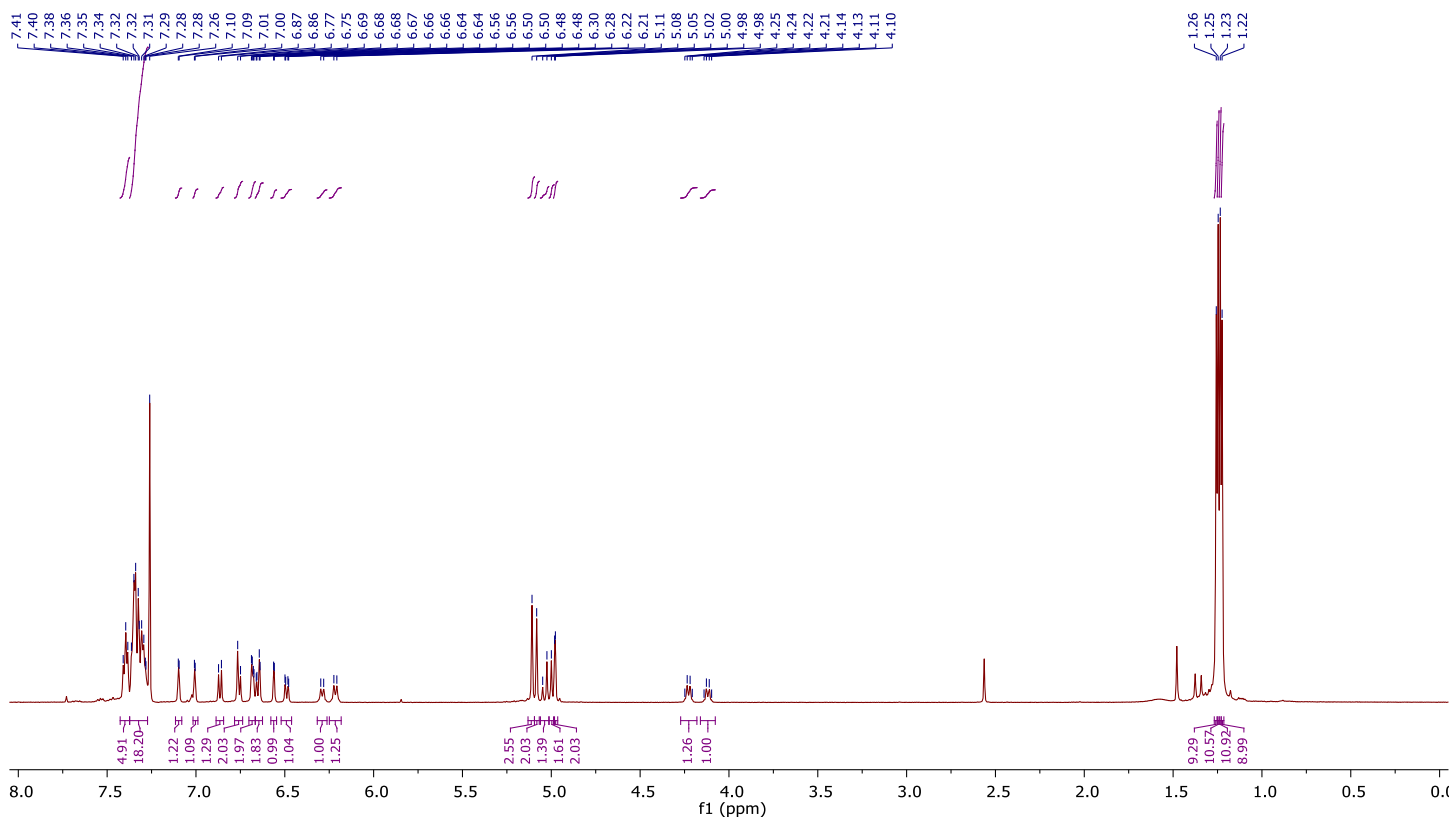
Stilbene **S6** (0.1 mmol, 52.1 mg) was subjected to the general dimerization procedure, affording bis-quinone methide **12** (48.9 mg, 94% yield, 5:4 dr).

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.40 (t, $J = 6.5$ Hz, 4H), 7.37 – 7.27 (m, 16H), 7.10 (major diastereomer, d, $J = 2.3$ Hz, 1H), 7.01 (minor diastereomer, d, $J = 2.1$ Hz, 1H), 6.86 (major diastereomer, d, $J = 8.2$ Hz, 1H), 6.77 (s, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 6.68 (m, 2H), 6.67 – 6.63 (m, 2H), 6.56 (minor diastereomer, d, $J = 2.0$ Hz, 1H), 6.49 (minor diastereomer, dd, $J = 8.3, 2.0$ Hz, 1H), 6.29 (minor diastereomer, d, $J = 8.2$ Hz, 1H), 6.22 (major diastereomer, d, $J = 8.4$ Hz, 1H), 5.11 (major diastereomer, s, 2H), 5.08 (minor diastereomer, s, 2H), 5.04 (major diastereomer, d, $J = 11.9$ Hz, 1H), 5.00 (major diastereomer, d, $J = 11.9$ Hz, 1H), 4.98 (minor diastereomer, s, 2H), 4.23 (major diastereomer, d, $J = 8.2$ Hz, 1H), 4.12 (minor diastereomer, d, $J = 8.0$ Hz, 1H), 1.26 (s, 9H), 1.25 (s, 9H), 1.23 (s, 9H), 1.22 (s, 9H).

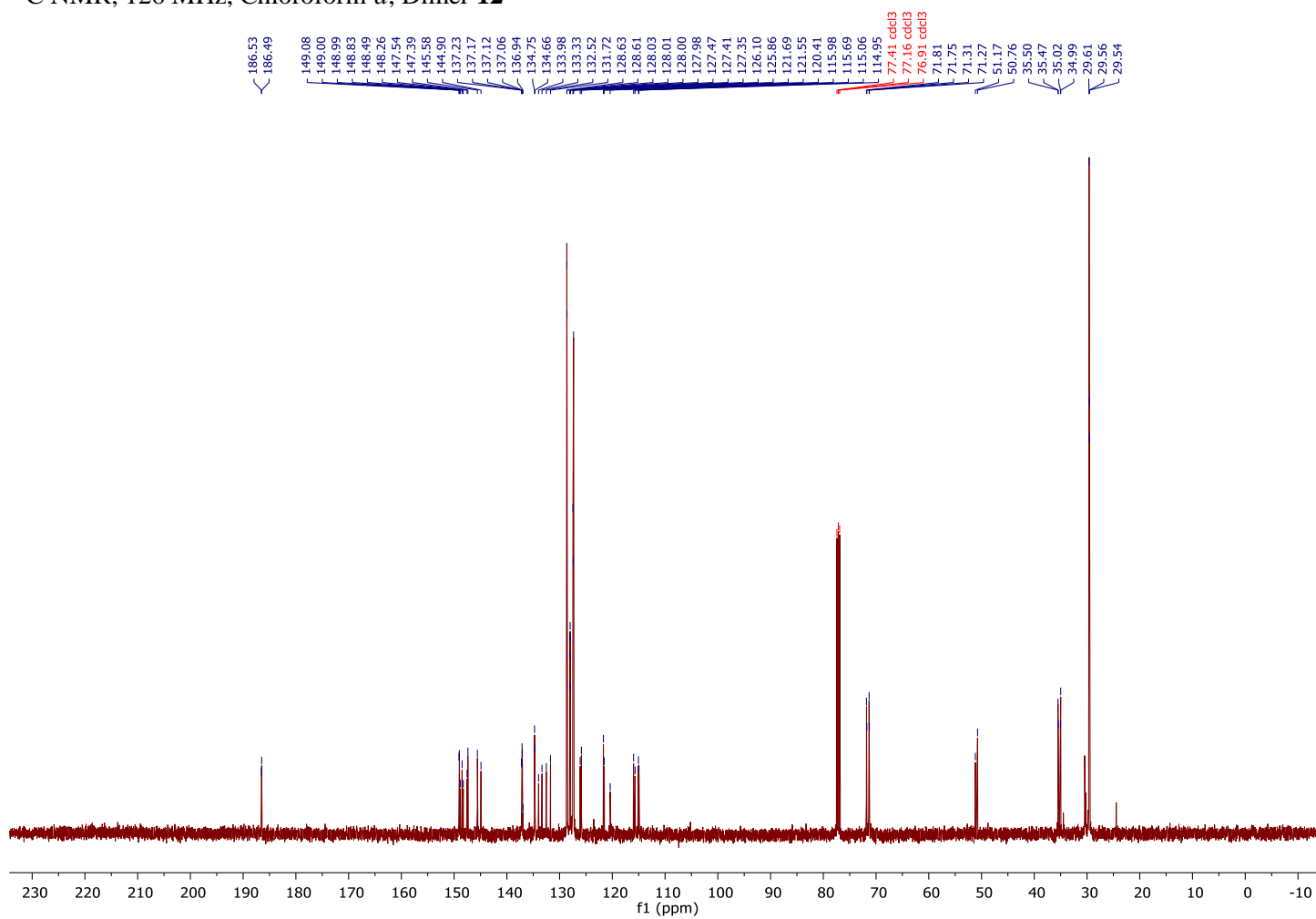
$^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 186.53, 186.49, 149.08, 149.00, 148.99, 148.83, 148.49, 148.26, 147.54, 147.39, 145.58, 144.90, 137.23, 137.17, 137.12, 137.06, 136.94, 134.75, 134.66, 133.98, 133.33, 132.52, 131.72, 128.63, 128.61, 128.03, 128.01, 128.00, 127.98, 127.47, 127.41, 127.35 (2C), 126.10, 125.86, 121.69, 121.55, 120.41, 115.98, 115.69, 115.06, 114.95, 71.81, 71.75, 71.31, 71.27, 51.17, 50.76, 35.50, 35.47, 35.02, 34.99, 29.61 (2C), 29.56, 29.54.

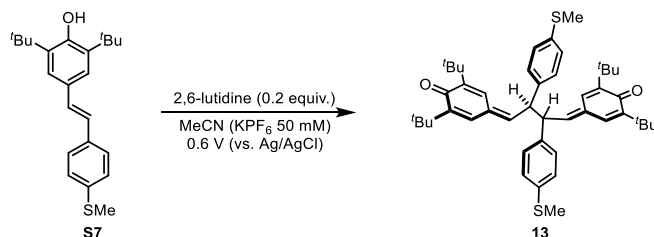
IR (Neat): 2960, 2867, 1616, 1510, 1453, 1358, 1262, 1136, 1021, 734, 697 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{NaC}_{72}\text{H}_{78}\text{O}_6^+$ ($[\text{M}+\text{Na}]^+$) 1061.5691, found 1061.5672.



¹³C NMR, 126 MHz, Chloroform-*d*, Dimer **12**





(13) 4,4'-((2*R*,3*R*)-2,3-bis(4-(methylthio)phenyl)butane-1,4-diyldiene)bis(2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one)

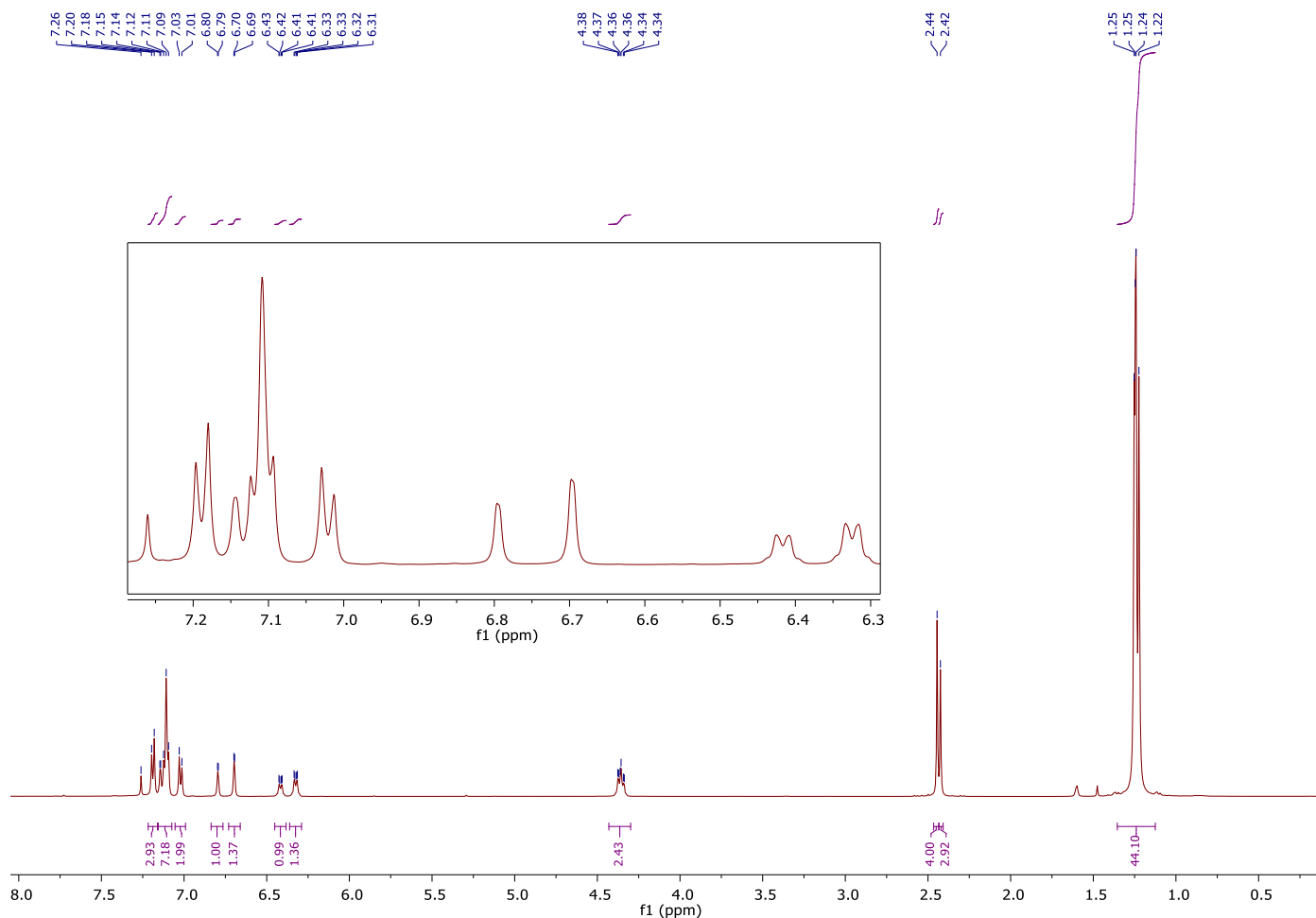
Stilbene **S7** (0.1 mmol, 35.5 mg) was subjected to the general dimerization procedure, affording bis-quinone methide **13** (32.9 mg, 93% yield, 4:3 dr).

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.19 (major diastereomer, d, $J = 8.0$ Hz, 4H), 7.12 (m, 12H), 7.02 (minor diastereomer, d, $J = 8.0$ Hz, 4H), β -H's of quinone methides: 6.80 (minor diastereomer, d, $J = 2.4$ Hz, 2H), 6.70 (major diastereomer, d, $J = 2.4$ Hz, 2H), δ -H's of quinone methides: 6.42 (minor diastereomer, dd, $J = 7.2, 2.4$ Hz, 2H), 6.36 – 6.29 (major diastereomer, m, 2H), 4.43 – 4.30 (sp^3 methines of both diastereomers, m, 4H), 2.44 (s, 3H), 2.42 (s, 3H), ^tBu signals: 1.25 (s, 18 H), 1.25 (s, 18H), 1.24 (s, 18 H), 1.22 (s, 18 H).

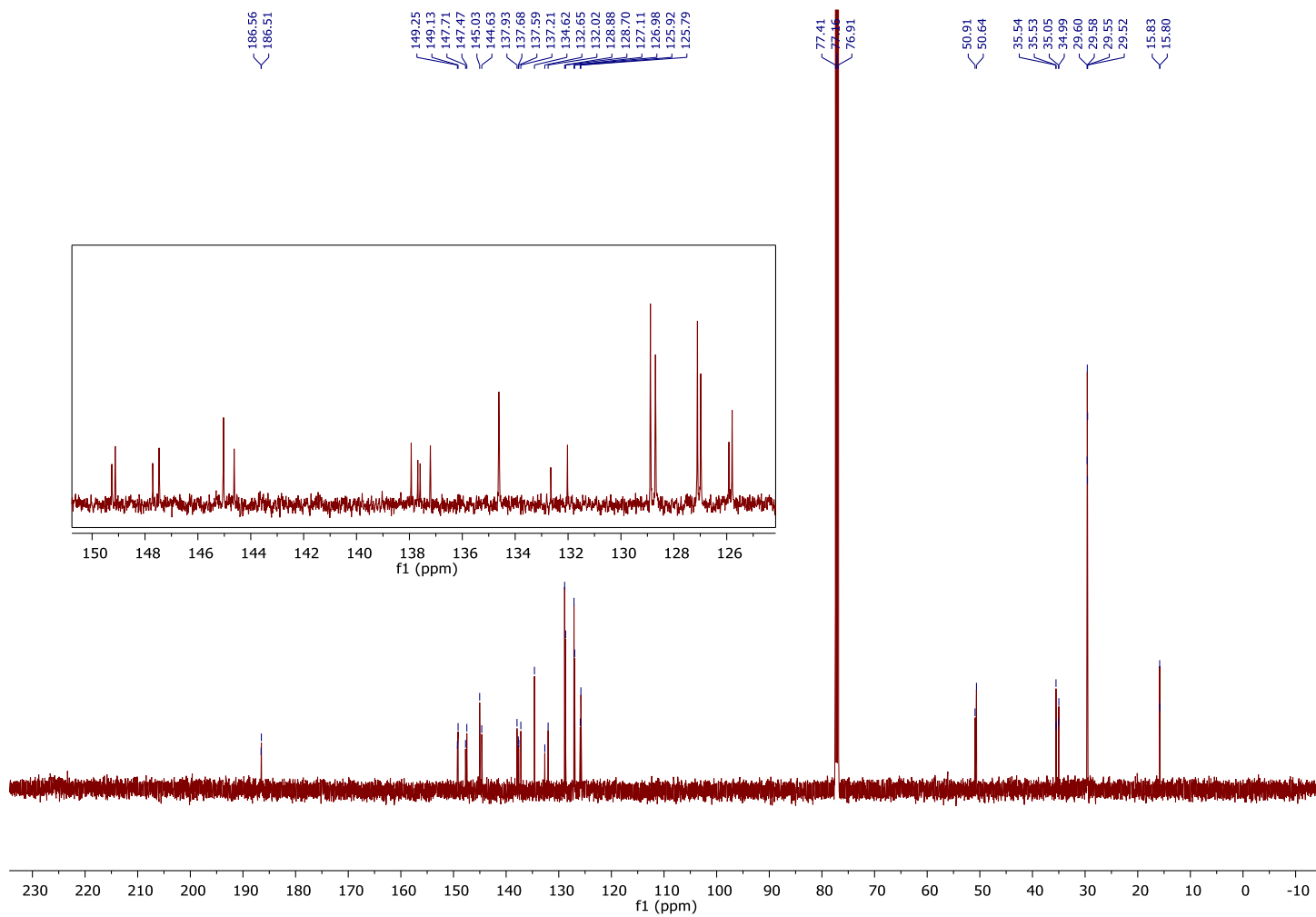
$^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 186.56, 186.51, 149.25, 149.13, 147.71, 147.47, 145.03, 144.63, 137.93, 137.68, 137.59, 137.21, 134.62, 132.65, 132.02, 128.88, 128.70, 127.11, 126.98, 125.92, 125.79, 50.91, 50.64, 35.54, 35.53, 35.05, 34.99, 29.60, 29.58, 29.55, 29.52, 15.83, 15.80.

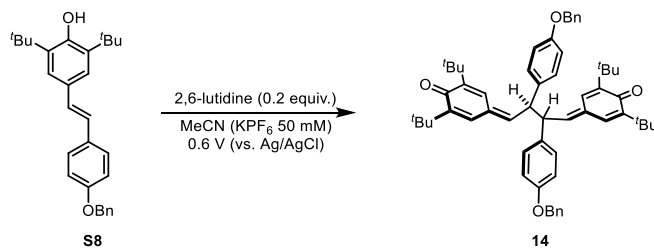
IR (Neat): 2960, 2906, 1698, 1591, 1437, 1358, 1262, 1096, 1023, 846, 815, 740 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{NaC}_{46}\text{H}_{58}\text{O}_2\text{S}_2^+$ ($[\text{M}+\text{Na}]^+$) 729.3770, found 729.3773.



^{13}C NMR, 126 MHz, Chloroform-*d*, Dimer **13**





(14) 4,4'-((2*R*,3*R*)-2,3-bis(4-(benzyloxy)phenyl)butane-1,4-diyliidene)bis(2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one)

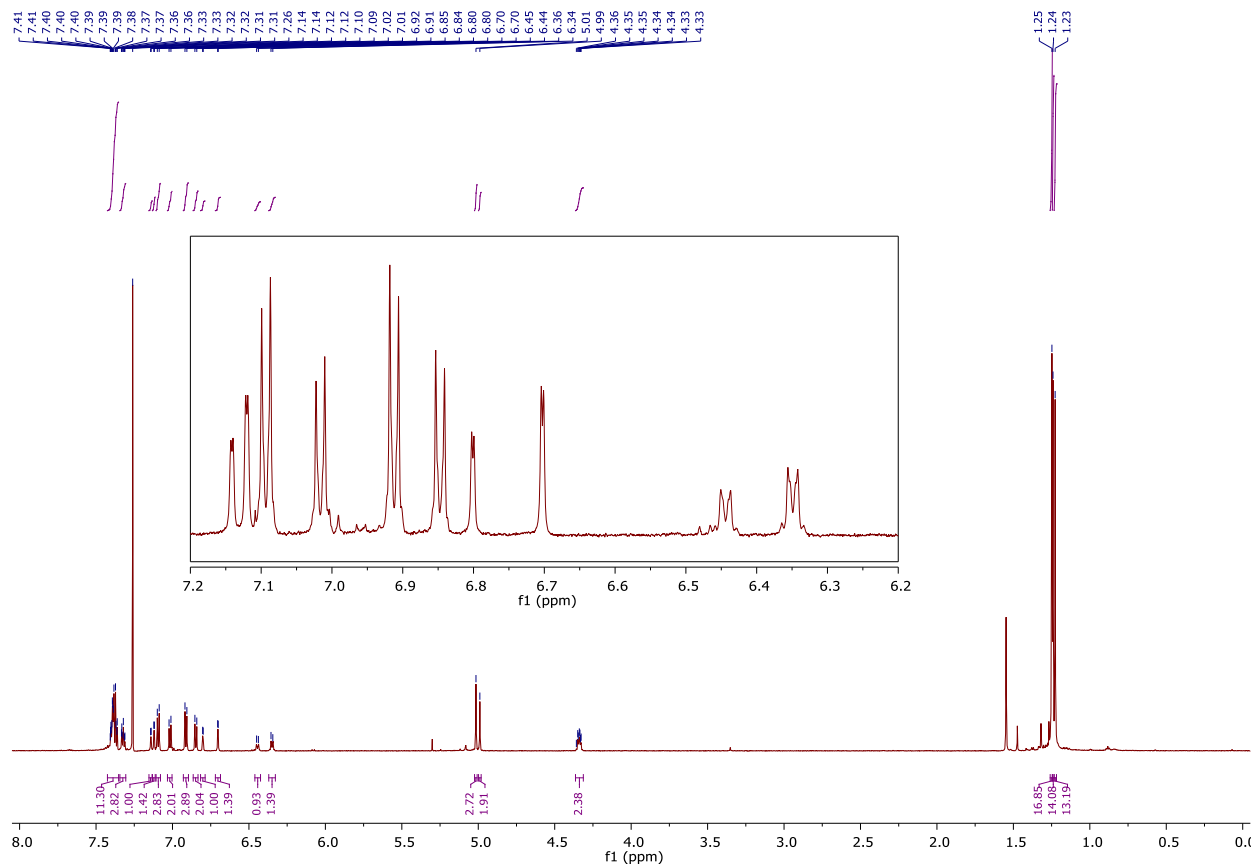
Stilbene **S8** (0.1 mmol, 41.5 mg) was subjected to the general dimerization procedure, affording bis-quinone methide **14** (39.3 mg, 95% yield, 3:2 dr).

$^1\text{H NMR}$ (700 MHz, Chloroform-*d*) δ 7.43 – 7.35 (m, 16H), 7.34 – 7.31 (m, 4H), 7.14 (β -H, minor diastereomer, d, $J = 2.4$ Hz, 2H), 7.12 (β -H, major diastereomer, d, $J = 2.4$ Hz, 2H), 7.09 (major diastereomer, d, $J = 8.7$ Hz, 4H), 7.02 (minor diastereomer, d, $J = 8.7$ Hz, 4H), 6.91 (major diastereomer, d, $J = 8.7$ Hz, 4H), 6.85 (minor diastereomer, d, $J = 8.7$ Hz, 4H), 6.80 (β -H, minor diastereomer, d, $J = 2.4$ Hz, 2H), 6.70 (β -H, major diastereomer, d, $J = 2.4$ Hz, 2H), 6.44 (δ -H, minor diastereomer, d, $J = 8.2$ Hz, 2H), 6.35 (δ -H, major diastereomer, d, $J = 8.4$ Hz, 2H), 5.01 (major diastereomer, s, 4H), 4.99 (minor diastereomer, s, 4H), 4.31 (sp^3 methines of both diastereomers, m, 4H), ^tBu signals: 1.25 (s, 36H), 1.24 (s, 18H), 1.23 (s, 18H).

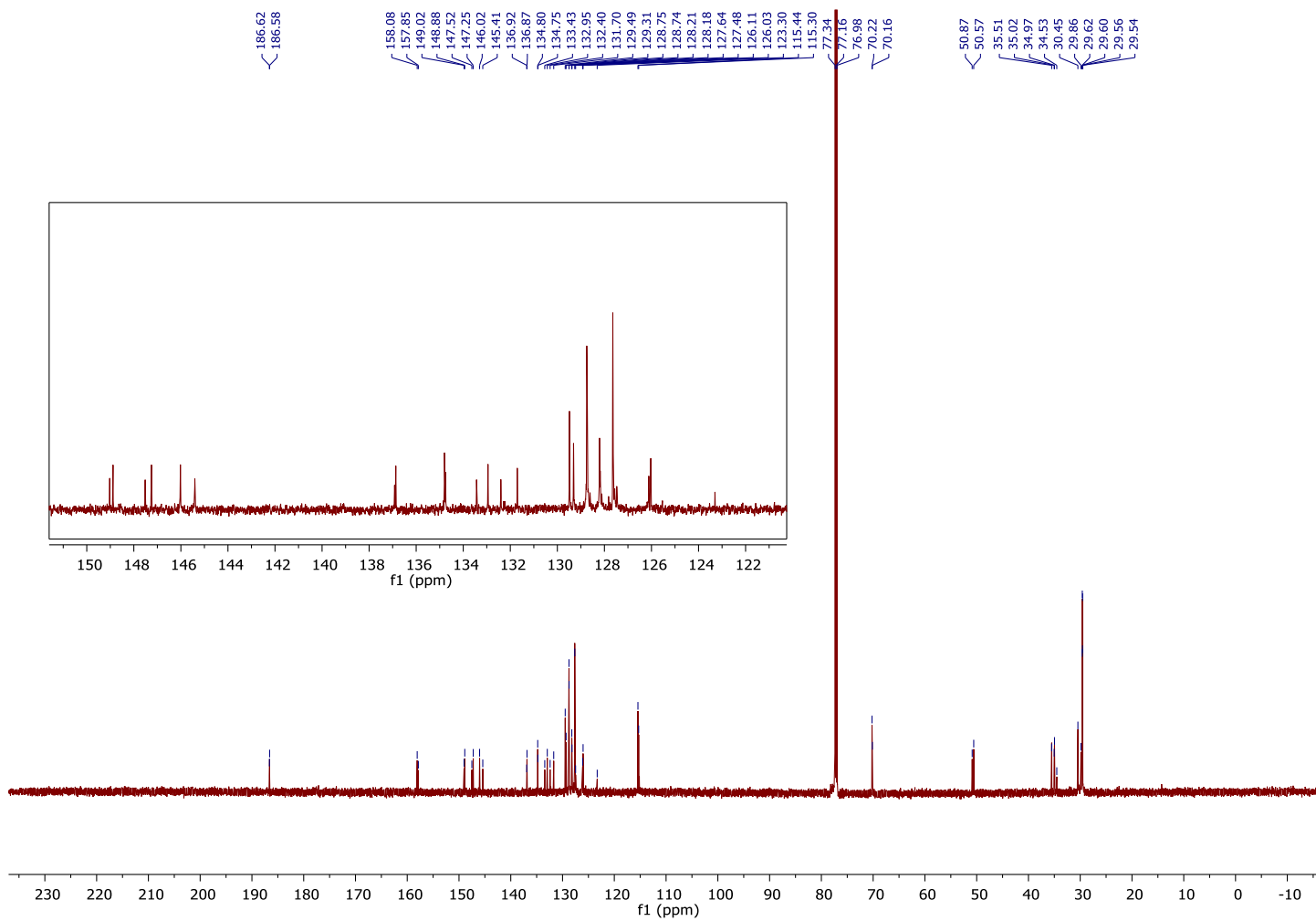
$^{13}\text{C NMR}$ (176 MHz, Chloroform-*d*) δ 186.62, 186.58, 158.08, 157.85, 149.02, 148.88, 147.52, 147.25, 146.02, 145.41, 136.92, 136.87, 134.80, 134.75, 133.43, 132.95, 132.40, 131.70, 129.49, 129.31, 128.75, 128.74, 128.21, 128.18, 127.64, 127.48, 126.11, 126.03, 123.30, 115.44, 115.30, 70.22, 70.16, 50.87, 50.57, 35.51, 35.02, 34.97, 34.53, 30.45, 29.86, 29.62, 29.60, 29.56, 29.54.

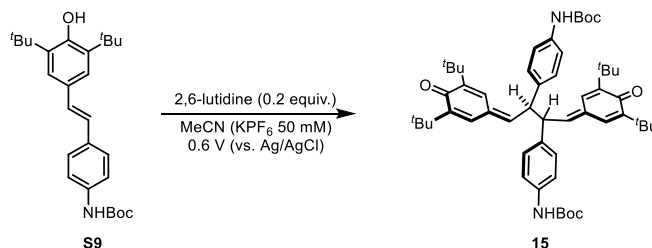
IR (Neat): 2954, 2918, 1608, 1569, 1510, 1358, 1245, 1018, 824, 740, 695 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{C}_{58}\text{H}_{67}\text{O}_4^+$ ($[\text{M}+\text{H}]^+$) 827.5034, found 827.5040.



^{13}C NMR, 176 MHz, Chloroform-*d*, Dimer **14**





(15) Di-tert-butyl (((2*R*,3*R*)-1,4-bis(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)butane-2,3-diyl)bis(4,1-phenylene))dicarbamate

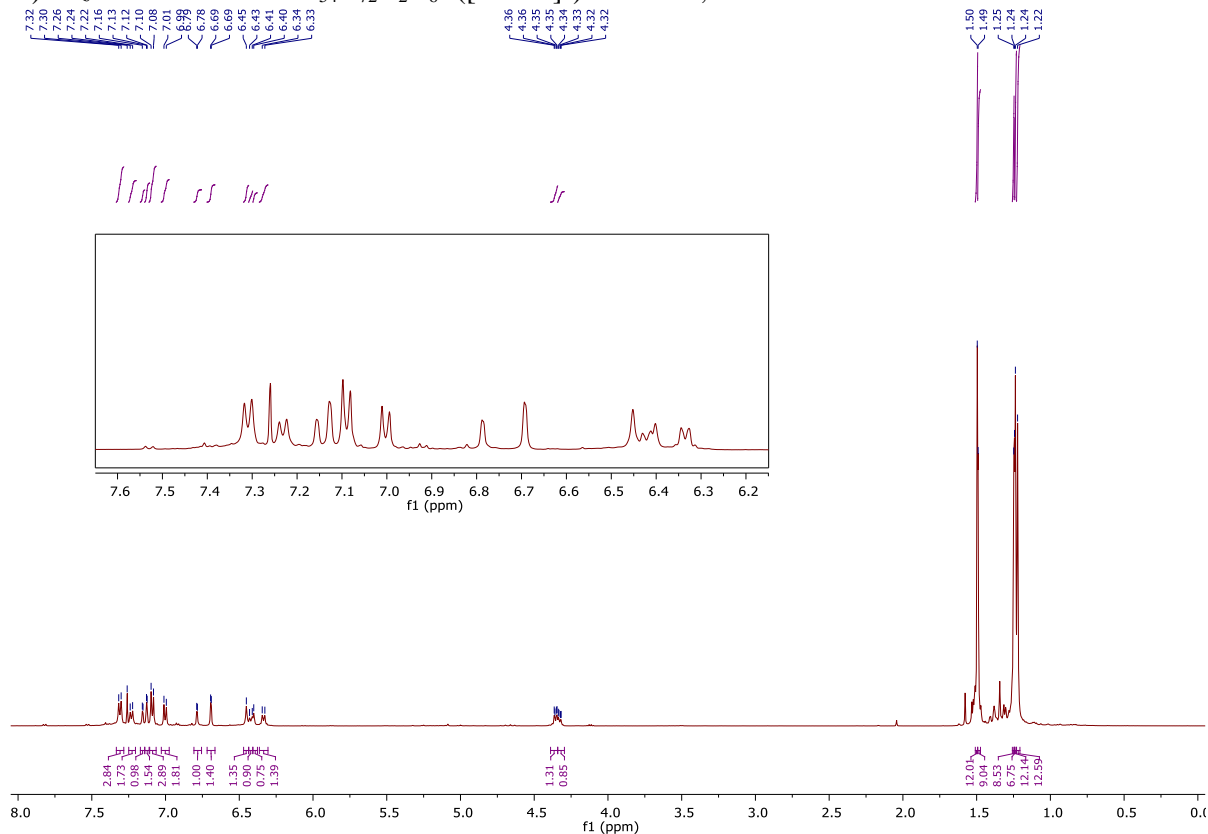
Stilbene **S9** (0.1 mmol, 42.4 mg) was subjected to the general dimerization procedure, affording bis-quinone methide **15** (40.7 mg, 95% yield, 3:2 dr).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.31 (major diastereomer, d, $J = 8.2$ Hz, 2H), 7.23 (minor diastereomer, d, $J = 8.1$ Hz, 2H), 7.16 (minor diastereomer, d, $J = 2.3$ Hz, 1H), 7.13 (major diastereomer, d, $J = 2.3$ Hz, 2H), 7.09 (major diastereomer, d, $J = 8.2$ Hz, 2H), 7.00 (minor diastereomer, d, $J = 8.1$ Hz, 2H), 6.79 (minor diastereomer, d, $J = 2.3$ Hz, 1H), 6.69 (major diastereomer, d, $J = 2.3$ Hz, 1H), 6.45 (major diastereomer, s, 1H), 6.42 (minor diastereomer, d, $J = 9.2$ Hz, 1H), 6.40 (minor diastereomer, s, 1H), 6.34 (major diastereomer, d, $J = 8.9$ Hz, 1H), 4.35 (major diastereomer, dd, $J = 7.3, 2.4$ Hz, 1H), 4.33 (minor diastereomer, dd, $J = 7.4, 2.3$ Hz, 1H), 1.50 (major diastereomer, s, 9H), 1.49 (minor diastereomer, s, 9H), 1.25 (minor diastereomer, s, 9H), 1.24 (minor diastereomer, s, 9H), 1.24 (major diastereomer, s, 9H), 1.22 (major diastereomer, s, 9H).

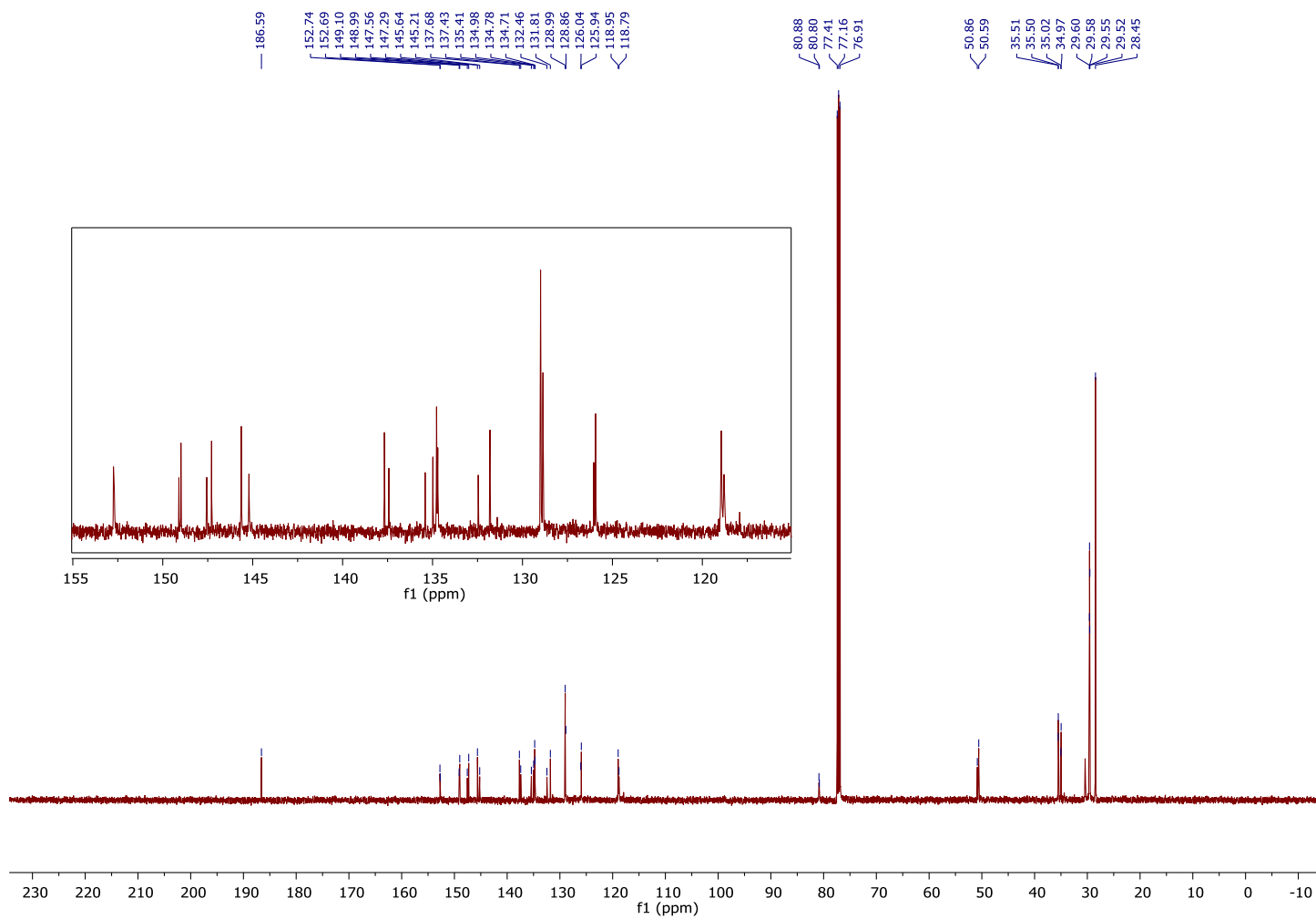
^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.60, 186.59, 152.74, 152.69, 149.10, 148.99, 147.56, 147.29, 145.64, 145.21, 137.68, 137.43, 135.41, 134.98, 134.78, 134.71, 132.46, 131.81, 128.99, 128.86, 126.04, 125.94, 118.95, 118.79, 80.88, 80.80, 50.86, 50.59, 35.51, 35.50, 35.02, 34.97, 29.60, 29.58, 29.55, 29.52, 28.45 (2C).

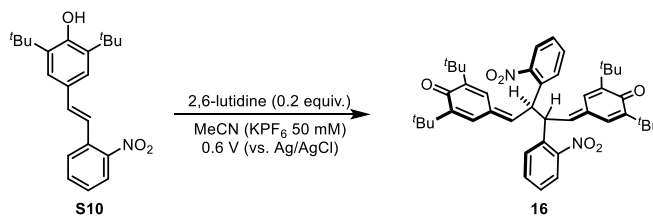
IR (Neat): 3333, 2954, 2864, 1715, 1611, 1521, 1361, 1231, 1153, 1049, 818 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{NaC}_{54}\text{H}_{72}\text{N}_2\text{O}_6^+$ ($[\text{M}+\text{Na}]^+$) 867.5283, found 867.5276.



^{13}C NMR, 176 MHz, Chloroform-*d*, Dimer **15**





(16) 4,4'-((2*R*,3*R*)-2,3-bis(2-nitrophenyl)butane-1,4-diyldiene)bis(2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one)

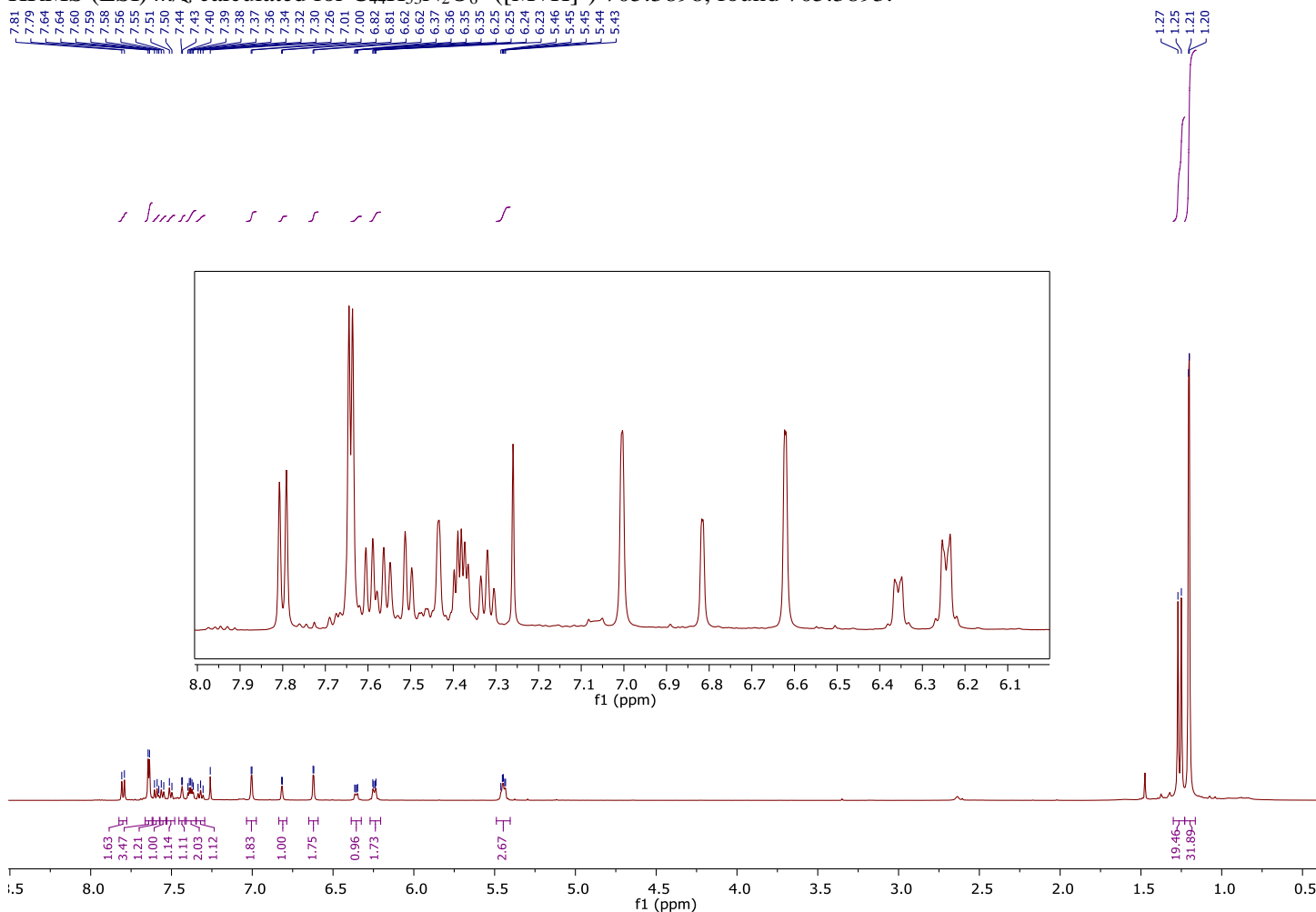
Stilbene **S10** (0.1 mmol, 35.3 mg) was subjected to the general dimerization procedure, affording bis-quinone methide **16** (32.8 mg, 93% yield, 2:1 dr).

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.80 (d, $J = 8.1$ Hz, 2H), 7.64 (d, $J = 4.3$ Hz, 4H), 7.61 – 7.57 (m, 2H), 7.56 (dd, $J = 7.5, 1.4$ Hz, 2H), 7.50 (dd, $J = 8.0, 1.4$ Hz, 2H), 7.44 (d, $J = 2.2$ Hz, 2H), 7.38 (dt, $J = 8.4, 4.3$ Hz, 2H), 7.35 – 7.30 (m, 2H), 7.00 (β -H, major diastereomer, d, $J = 2.4$ Hz, 2H), 6.82 (β -H, major diastereomer, d, $J = 2.3$ Hz, 2H), 6.62 (β -H, major diastereomer, d, $J = 2.3$ Hz, 2H), 6.36 (δ -H, minor diastereomer, dd, $J = 6.5, 2.6$ Hz, 2H), 6.25 (δ -H, major diastereomer, dd, $J = 7.1, 2.8$ Hz, 2H), 5.49 – 5.41 (m, 4H), ^tBu signals: 1.27 (s, 18 H), 1.25 (s, 18H), 1.20 (s, 18 H), 1.20 (s, 18 H).

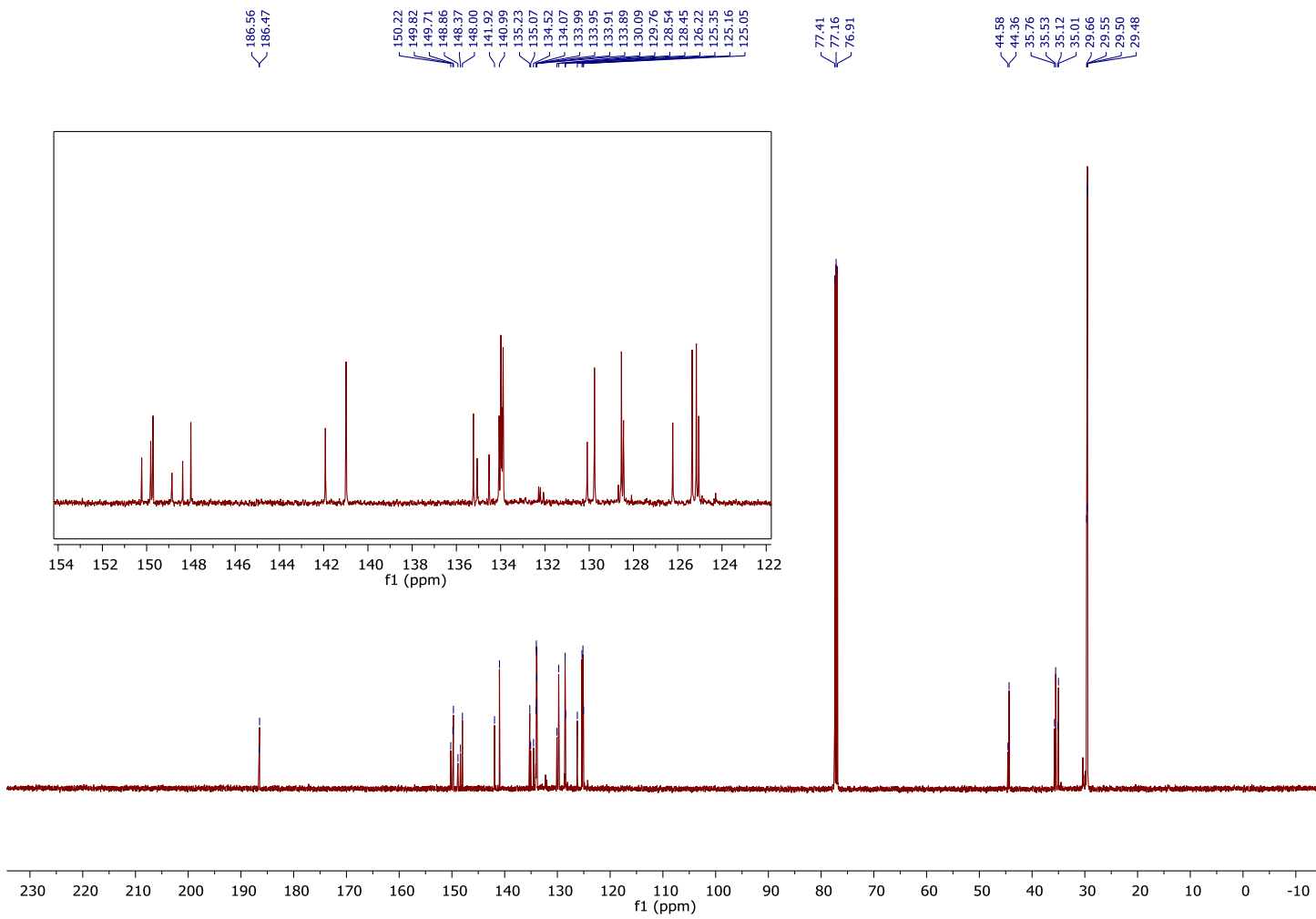
$^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 186.56, 186.47, 150.22, 149.82, 149.71, 148.86, 148.37, 148.00, 141.92, 140.99, 135.23, 135.07, 134.52, 134.07, 133.99, 133.95, 133.91, 133.89, 130.09, 129.76, 128.54, 128.45, 126.22, 125.35, 125.16, 125.05, 44.58, 44.36, 35.76, 35.53, 35.12, 35.01, 29.66, 29.55, 29.50, 29.48.

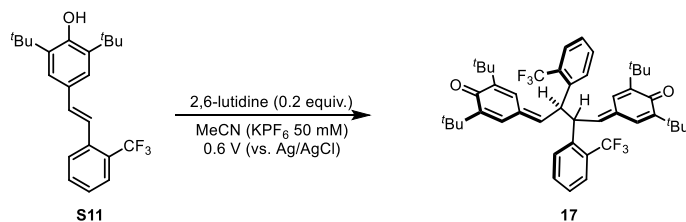
IR (Neat): 2956, 2917, 1616, 1520, 1345, 1255, 918, 886, 822, 782, 729 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{C}_{44}\text{H}_{53}\text{N}_2\text{O}_6^+$ ($[\text{M}+\text{H}]^+$) 705.3898, found 705.3893.



$^{13}\text{C NMR}$, 126 MHz, Chloroform-*d*, Dimer **16**





(17) 4,4'-((2*R*,3*R*)-2,3-bis(2-(trifluoromethyl)phenyl)butane-1,4-diyldiene)bis(2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one)

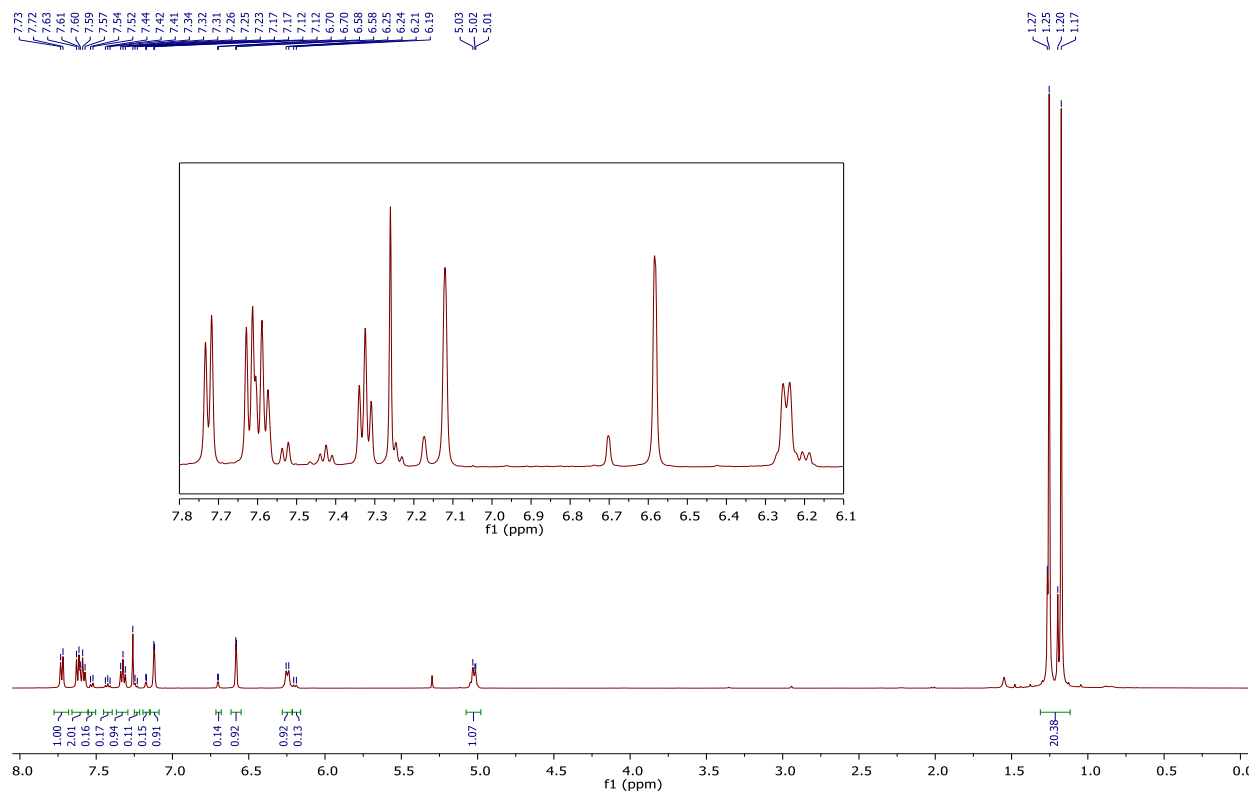
Stilbene **S11** (0.1 mmol, 37.6 mg) was subjected to the general dimerization procedure, affording bis-quinone methide **17** (36.8 mg, 98% yield, 5:1 dr).

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.73 (major diastereomer, d, $J = 7.9$ Hz, 2H), 7.62 (major diastereomer, d, $J = 8.0$ Hz, 2H), 7.59 (major diastereomer, t, $J = 7.7$ Hz, 2H), 7.53 (minor diastereomer, d, $J = 8.0$ Hz, 2H), 7.42 (minor diastereomer, t, $J = 7.7$ Hz, 2H), 7.32 (major diastereomer, t, $J = 7.7$ Hz, 2H), 7.24 (minor diastereomer, t, $J = 7.7$ Hz, 2H), β -H's of quinone methides: 7.17 (minor diastereomer, d, $J = 2.3$ Hz, 2H), 7.12 (major diastereomer, d, $J = 2.5$ Hz, 2H), 6.70 (minor diastereomer, d, $J = 2.4$ Hz, 2H), 6.58 (major diastereomer, d, $J = 2.3$ Hz, 2H), δ -H's of quinone methides: 6.25 (major diastereomer, d, $J = 8.6$ Hz, 2H), 6.20 (minor diastereomer, d, $J = 8.8$ Hz, 2H), 5.03 (sp^3 methines of both diastereomers, m, 4H), ^tBu signals: 1.27 (minor diastereomer, s, 18H), 1.25 (major diastereomer, s, 18H), 1.20 (minor diastereomer, s, 18H), 1.17 (major diastereomer, s, 18H),

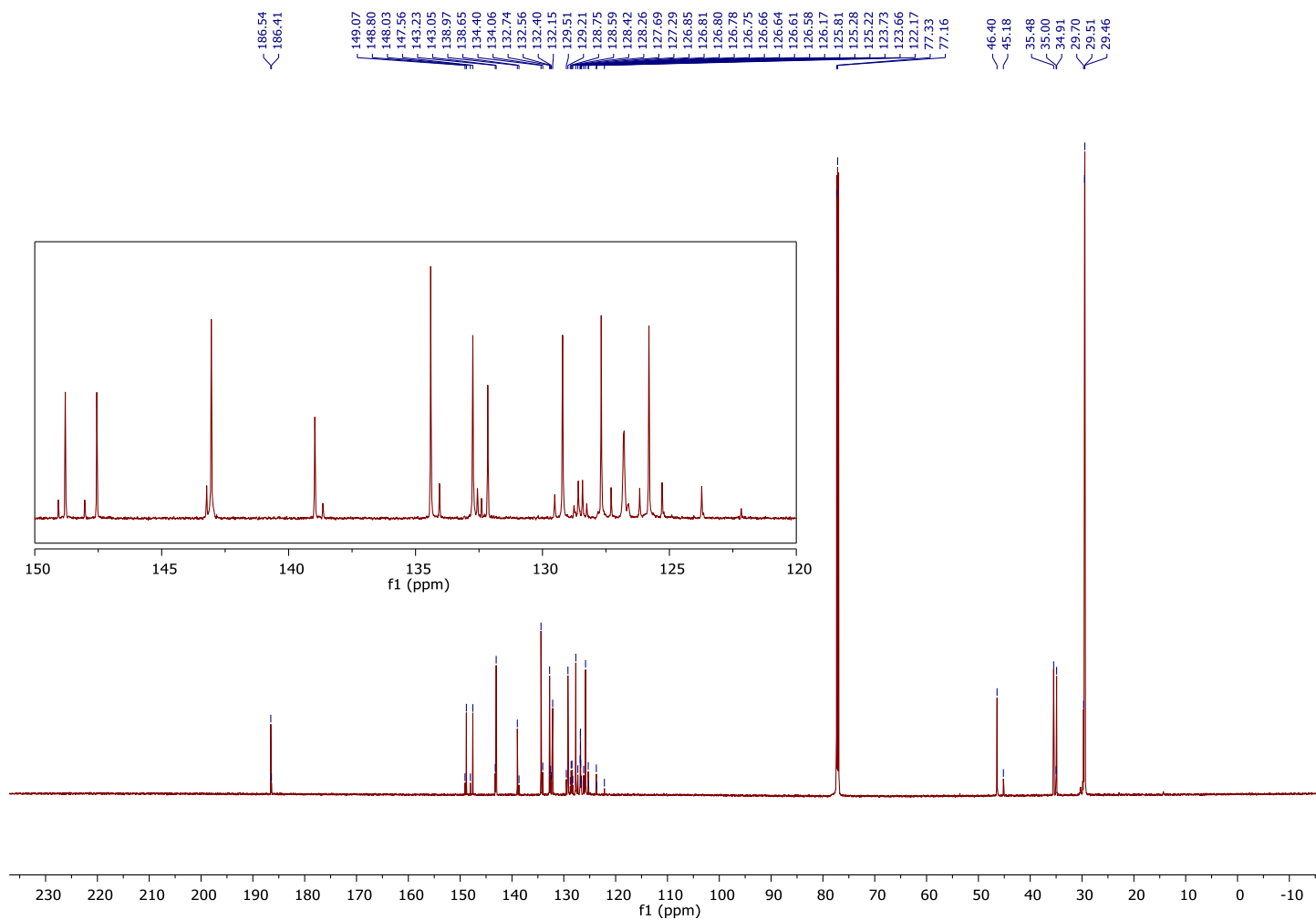
$^{13}\text{C NMR}$ (176 MHz, Chloroform-*d*) δ 186.54, 186.41, 149.07, 148.80, 148.03, 147.56, 143.23, 143.05, 138.97, 138.65, 134.40, 134.06, 132.74, 132.56, 132.40, 132.15, 129.51, 129.21, 128.50 (major diastereomer, q, $J = 28$ Hz), 128.44 (minor diastereomer, q, $J = 28$ Hz), 127.69, 127.29, 126.80 (major diastereomer, q, $J = 5.3$ Hz), 126.62 (minor diastereomer, q, $J = 5.3$ Hz), 126.17, 125.81, 124.50 (major diastereomer, q, $J = 273$ Hz), 124.43 (minor diastereomer, q, $J = 273$ Hz), 46.40, 45.18, 35.48, 35.00, 34.91, 29.70, 29.51, 29.46.

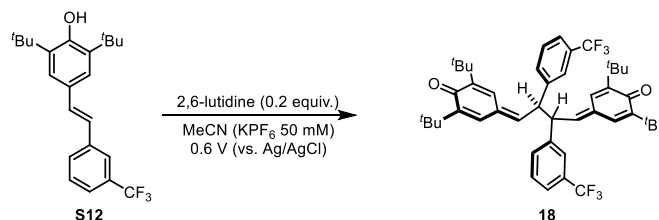
IR (Neat): 3005, 2957, 2918, 1614, 1569, 1453, 1363, 1310, 1155, 1111, 1032, 931, 765 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{NaC}_{46}\text{H}_{52}\text{F}_6\text{O}_2^+$ ($[\text{M}+\text{Na}]^+$) 773.3764, found 773.3772.



^{13}C NMR, 176 MHz, Chloroform-*d*, Dimer 17





(18) 4,4'-((2R,3R)-2,3-bis(3-(trifluoromethyl)phenyl)butane-1,4-diyldiene)bis(2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one)

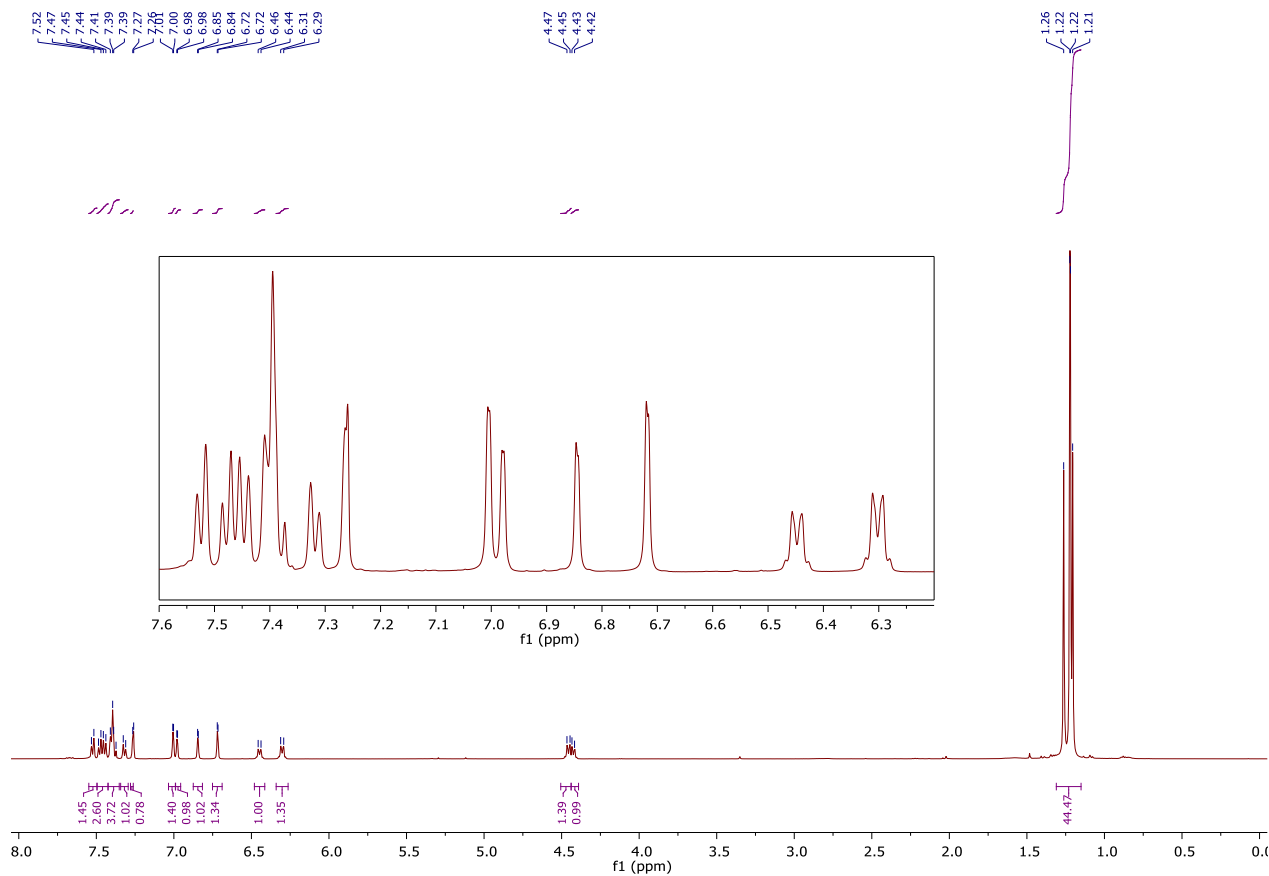
Stilbene **S12** (0.1 mmol, 37.6 mg) was subjected to the general dimerization procedure, affording bis-quinone methide **18** (36.4 mg, 97% yield, 4:3 dr).

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.52 (major diastereomer, d, $J = 7.8$ Hz, 2H), 7.46 (m, 4H), 7.43 – 7.35 (m, 6H), 7.32 (minor diastereomer, d, $J = 7.8$ Hz, 2H), 7.26 (minor diastereomer, s, 2H), β -H's of quinone methides: 7.01 (major diastereomer, d, $J = 2.4$ Hz, 2H), 6.98 (minor diastereomer, d, $J = 2.4$ Hz, 2H), 6.85 (minor diastereomer, d, $J = 2.4$ Hz, 2H), 6.72 (major diastereomer, d, $J = 2.4$ Hz, 2H), δ -H's of quinone methides: 6.45 (minor diastereomer, d, $J = 9.5$ Hz, 1H), 6.30 (major diastereomer, d, $J = 9.9$ Hz, 1H), 4.46 (sp^3 methine of major diastereomer, d, $J = 10.0$ Hz, 1H), 4.42 (sp^3 methine of minor diastereomer, d, $J = 9.6$ Hz, 1H), ^tBu signals: 1.26 (minor diastereomer, s, 18H), 1.22 (major diastereomer, s, 18H), 1.22 (major diastereomer, s, 18H), 1.21 (minor diastereomer, s, 18H),

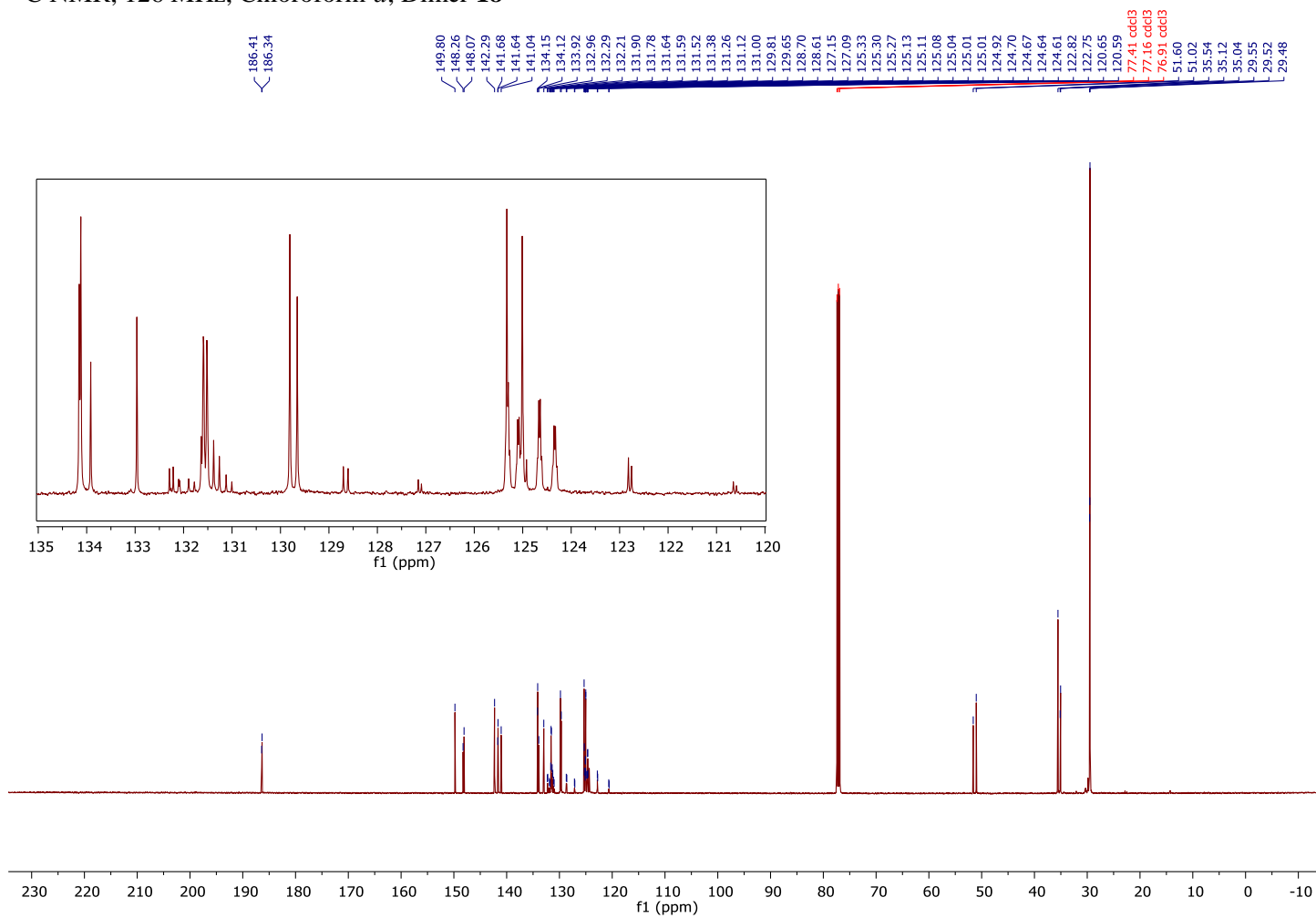
$^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 186.41, 186.34, 149.80, 148.26, 148.07, 142.29, 141.68, 141.64, 141.04, 134.15, 134.12, 133.92, 132.96, 132.29, 132.21, 131.59, 131.52, 131.51 (q, $J = 32$ Hz), 131.39 (q, $J = 32$ Hz), 129.81, 129.65, 128.70, 128.61, 125.33, 125.31 (q, $J = 3.8$ Hz), 125.09 (q, $J = 3.8$ Hz), 125.01, 124.65 (q, $J = 3.8$ Hz), 124.34 (q, $J = 3.8$ Hz), 123.90 (q, $J = 271$ Hz), 123.83 (q, $J = 271$ Hz), 51.60, 51.02, 35.54, 35.12, 35.04, 29.55, 29.52, 29.48.

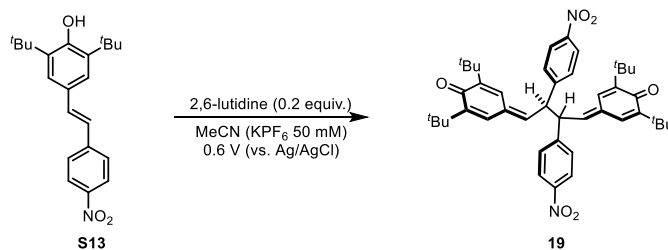
IR (Neat): 2959, 1617, 1571, 1448, 1390, 1324, 1252, 1162, 1124, 1069, 883, 813 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{NaC}_{46}\text{H}_{52}\text{F}_6\text{O}_2^+$ ($[\text{M}+\text{Na}]^+$) 773.3764, found 773.3762.



¹³C NMR, 126 MHz, Chloroform-*d*, Dimer 18





(19) 4,4'-((2*R*,3*R*)-2,3-bis(4-nitrophenyl)butane-1,4-diyldiene)bis(2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one)

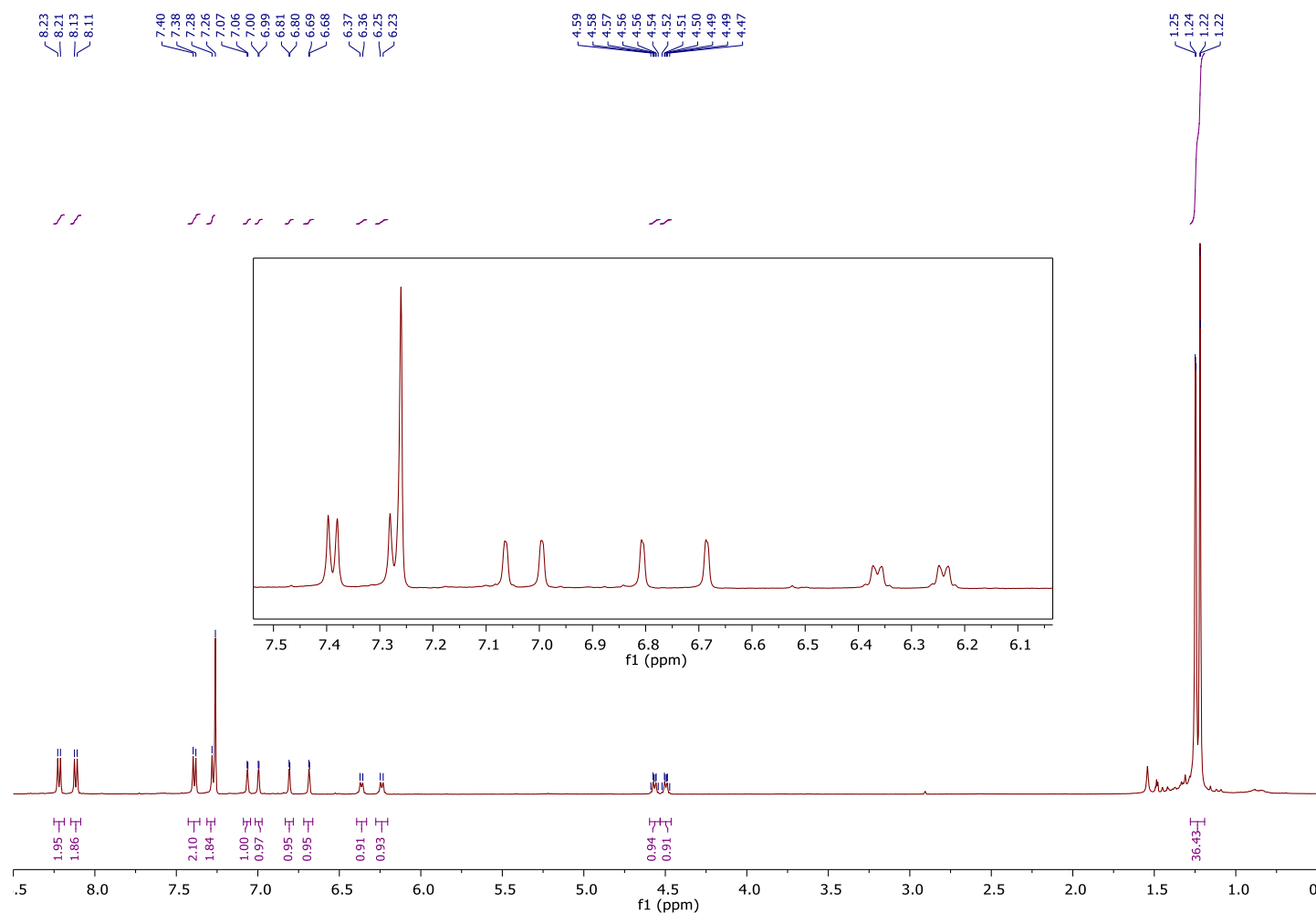
Stilbene **S13** (0.1 mmol, 35.3 mg) was subjected to the general dimerization procedure, affording bis-quinone methide **19** (32.5 mg, 92% yield, 1:1 dr).

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 8.22 (d, $J = 8.4$ Hz, 4H), 8.12 (d, $J = 8.4$ Hz, 4H), 7.39 (d, $J = 8.3$ Hz, 4H), 7.27 (d, $J = 8.4$ Hz, 4H), β -H's of quinone methides: 7.06 (d, $J = 2.4$ Hz, 2H), 7.00 (d, $J = 2.4$ Hz, 2H), 6.81 (d, $J = 2.4$ Hz, 2H), 6.68 (d, $J = 2.4$ Hz, 2H), δ -H's of quinone methides: 6.36 (d, $J = 8.5$ Hz, 2H), 6.24 (d, $J = 8.8$ Hz, 2H), sp^3 methines: 4.60 – 4.53 (m, 2H), 4.53 – 4.46 (m, 2H), 1.25 (s, 18H), 1.24 (s, 18H), 1.22 (s, 18H), 1.22 (s, 18H).

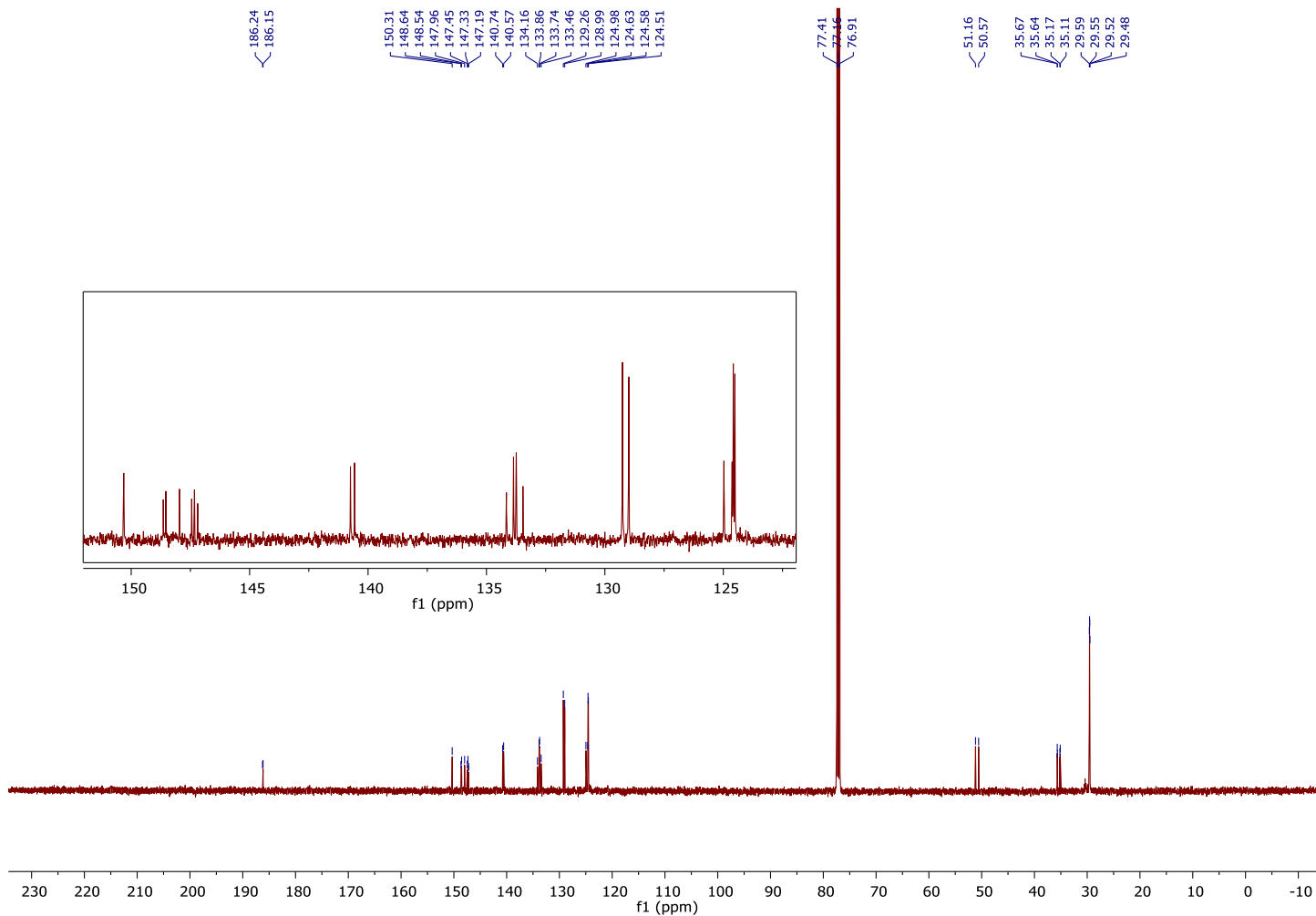
$^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 186.24, 186.15, 150.31, 148.64, 148.54, 147.96, 147.45, 147.33, 147.19, 140.74, 140.57, 134.16, 133.86, 133.74, 133.46, 129.26, 128.99, 124.98, 124.63, 124.58, 124.51, 51.16, 50.57, 35.67, 35.64, 35.17, 35.11, 29.59, 29.55, 29.52, 29.48.

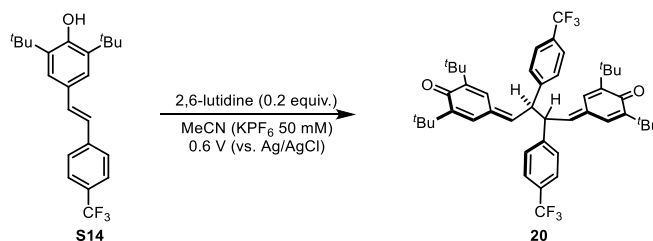
IR (Neat): 2953, 1613, 1518, 1344, 1254, 913, 857, 706 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{C}_{44}\text{H}_{52}\text{N}_2\text{O}_6^+$ ($[\text{M}+\text{Na}]^+$) 727.3718, found 727.3723.



^{13}C NMR, 126 MHz, Chloroform-*d*, Dimer **19**





(20) 4,4'-((2*R*,3*R*)-2,3-bis(4-(trifluoromethyl)phenyl)butane-1,4-diyldiene)bis(2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one)

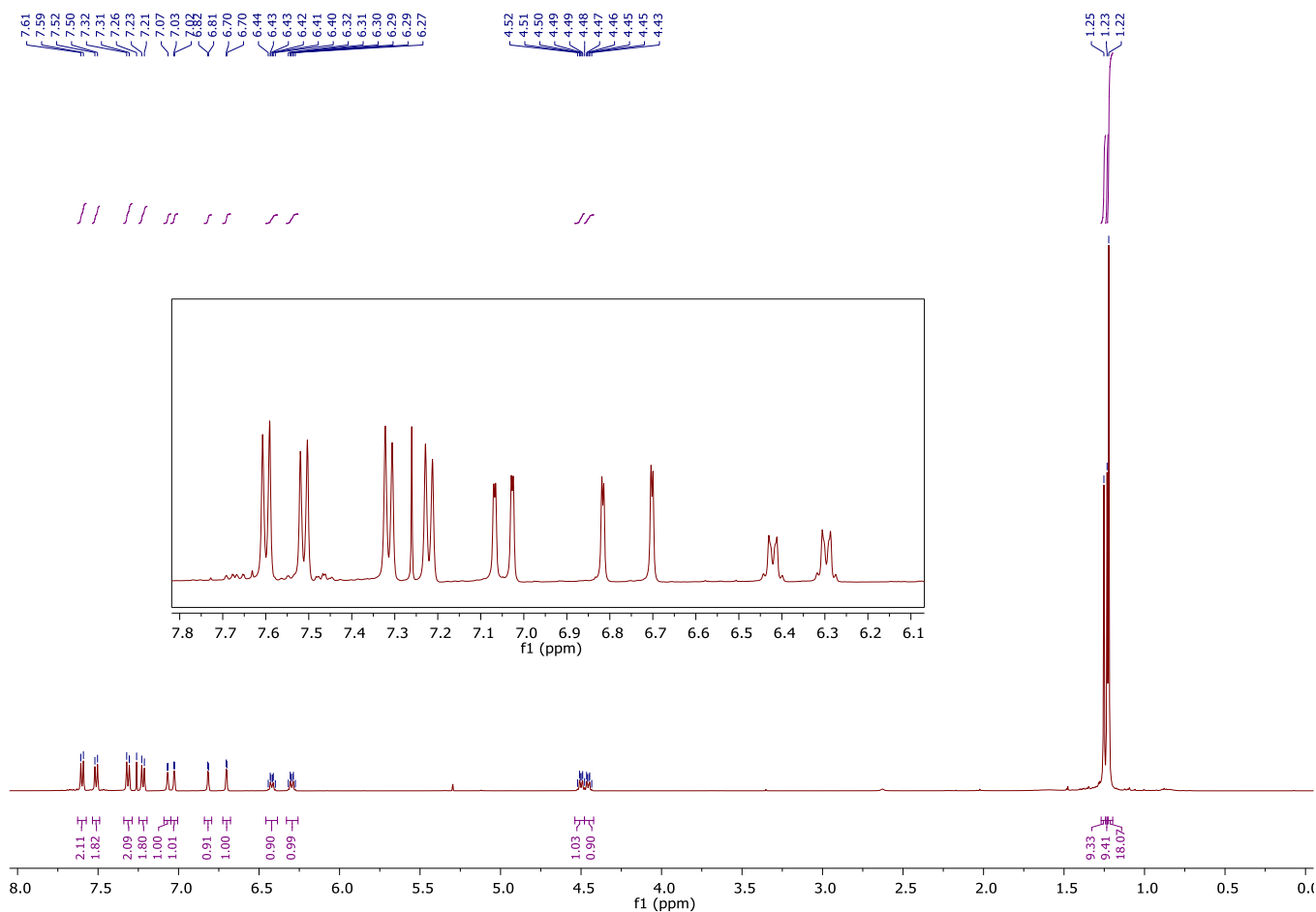
Stilbene **S14** (0.1 mmol, 37.6 mg) was subjected to the general dimerization procedure, affording bis-quinone methide **20** (33.8 mg, 90% yield, 1:1 dr).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.60 (d, $J = 8.1$ Hz, 4H), 7.51 (d, $J = 8.1$ Hz, 4H), 7.31 (d, $J = 8.0$ Hz, 4H), 7.22 (d, $J = 8.1$ Hz, 4H), 7.07 (d, $J = 2.4$ Hz, 2H), 7.03 (d, $J = 2.4$ Hz, 2H), 6.82 (d, $J = 2.4$ Hz, 2H), 6.70 (d, $J = 2.4$ Hz, 2H), 6.46 – 6.39 (m, 2H), 6.33 – 6.26 (m, 2H), 4.50 (dd, $J = 7.4, 2.4$ Hz, 2H), 4.46 (dt, $J = 8.7, 6.3$ Hz, 2H), 1.25 (s, 18H), 1.23 (s, 18H), 1.22 (s, 36H).

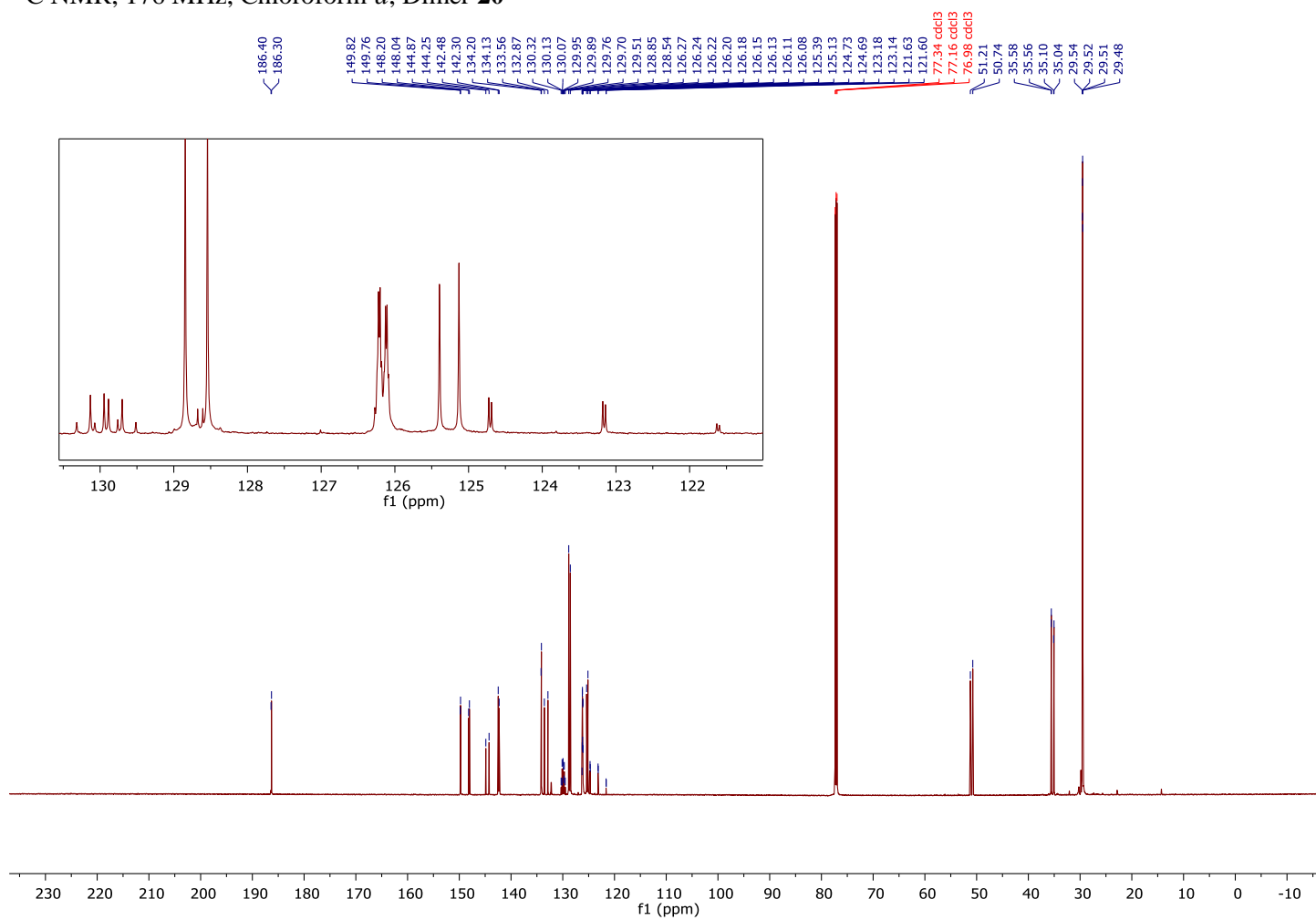
^{13}C NMR (176 MHz, Chloroform-*d*) δ 186.40, 186.30, 149.82, 149.76, 148.20, 148.04, 144.87, 144.25, 142.48, 142.30, 134.20, 134.13, 133.56, 132.87, 130.04 (q, $J = 33$ Hz), 129.80 (q, $J = 32$ Hz), 128.85, 128.54, 126.21 (q, $J = 3.5$ Hz), 126.12 (q, $J = 3.5$ Hz), 125.39, 125.13, 123.96 (q, $J = 273$ Hz), 123.92 (q, $J = 273$ Hz), 51.21, 50.74, 35.58, 35.56, 35.10, 35.04, 29.54, 29.52, 29.51, 29.48.

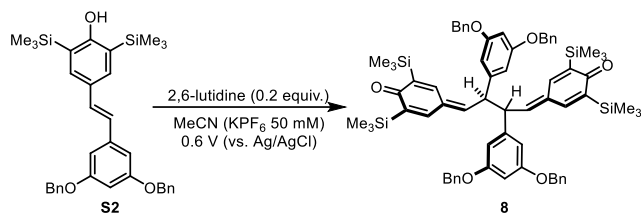
IR (Neat): 2955, 1612, 1571, 1361, 1322, 1165, 1105, 1067, 883, 834 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{NaC}_{46}\text{H}_{52}\text{F}_6\text{O}_2^+$ ($[\text{M}+\text{H}]^+$) 773.3764, found 773.3769.



^{13}C NMR, 176 MHz, Chloroform-*d*, Dimer **20**



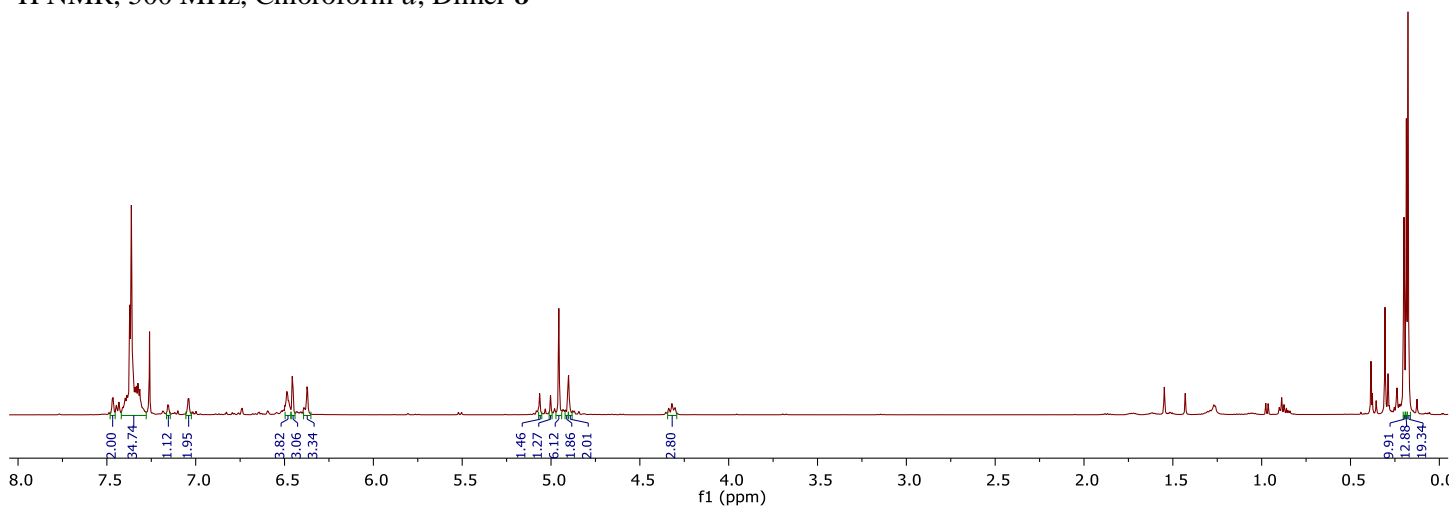


(8) 4,4'-((2*R*,3*R*)-2,3-bis(3,5-bis(benzyloxy)phenyl)butane-1,4-diylidene)bis(2,6-bis(trimethylsilyl)cyclohexa-2,5-dien-1-one)

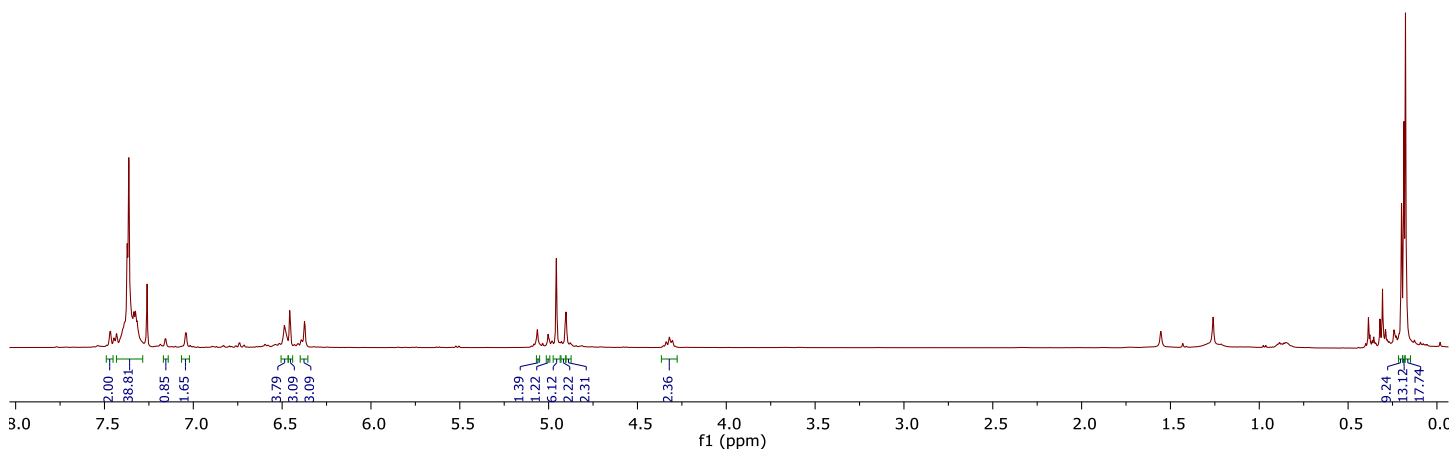
Stilbene **S2** (0.1 mmol, 55 mg) was subjected to the general dimerization procedure, and the crude reaction mixture was purified by flash column chromatography (0 to 15% EtOAc in Hexanes) to afford bis-quinone methide **8** (35.8 mg, 65% yield, 2:1 dr). The ¹H NMR spectrum was identical to the previous report for this compound.²

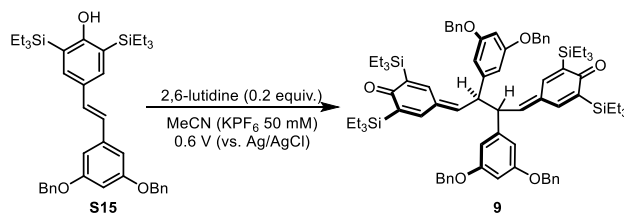
¹H NMR (500 MHz, CDCl₃, 25 °C) δ: 7.47 (d, *J* = 2.5 Hz, 2H, major), 7.45 – 7.28 (m, 32H), 7.15 (d, *J* = 2.5 Hz, 2H, minor), 7.04 (d, *J* = 2.5 Hz, 2H, major), 6.50 – 6.47 (m, overlap, 4H), 6.45 (d, *J* = 2.2 Hz, 4H, major), 6.38 (m, 4H), 6.37 (d, *J* = 2.2 Hz, 4H, minor), 5.07 (d, *J* = 9.3 Hz, 2H, minor), 4.99 (d, *J* = 9.3 Hz, 2H, minor), 4.96 (s, 8H, major/minor overlap), 4.91 (d, *J* = 11.2 Hz, 2H, major), 4.89 (d, *J* = 11.2 Hz, 2H, major), 4.36 – 4.28 (m, overlap, 4H, major/minor), 0.20 (s, 18H, minor), 0.19 (s, 18H, minor), 0.18 (s, 36H, major)

¹H NMR, 500 MHz, Chloroform-*d*, Dimer **8**



¹H NMR, 500 MHz, Chloroform-*d*, Compound **4b**²





(9) 4,4'-((2*R*,3*R*)-2,3-bis(3,5-bis(benzyloxy)phenyl)butane-1,4-diyldiene)bis(2,6-bis(triethylsilyl)cyclohexa-2,5-dien-1-one)

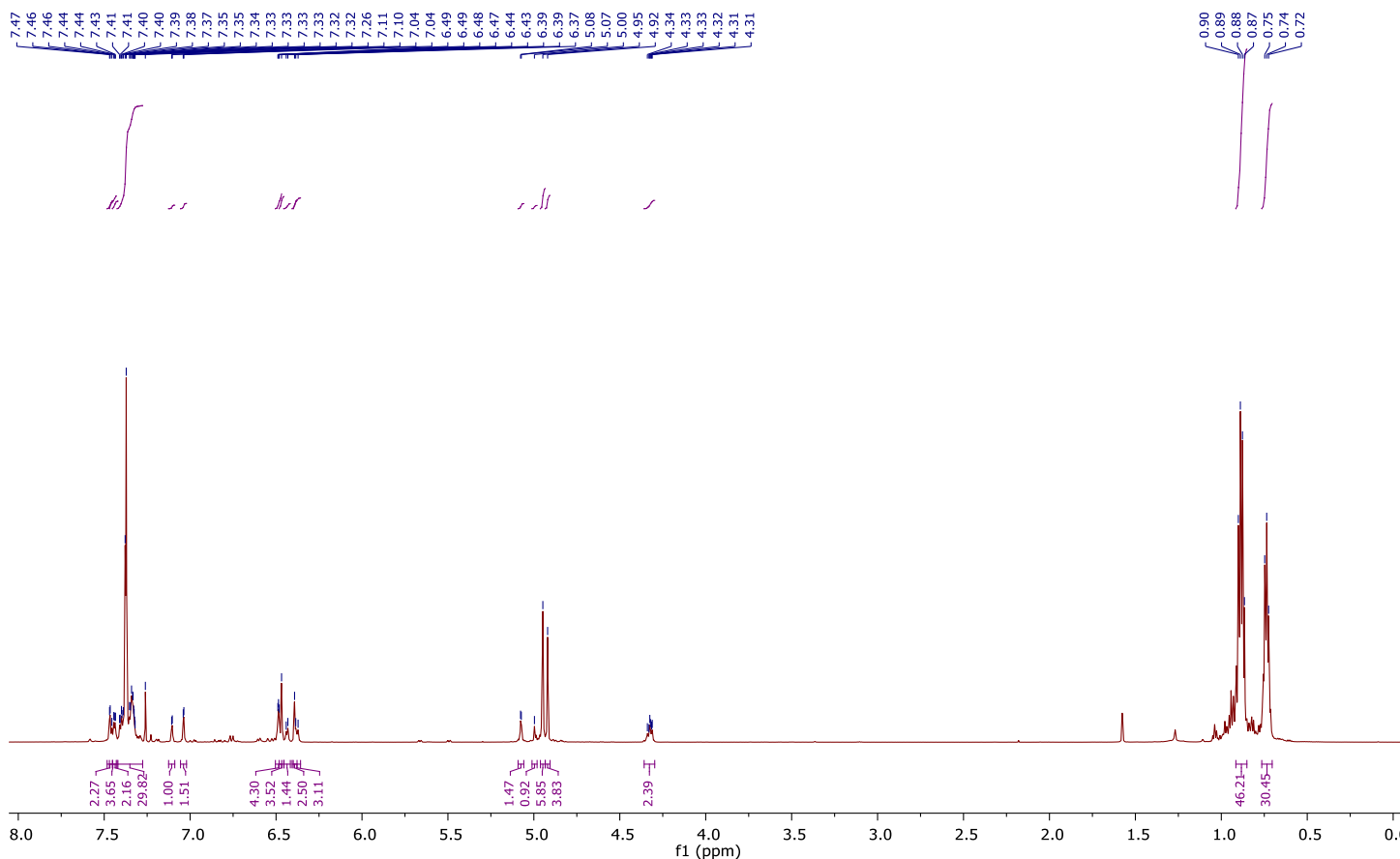
Stilbene **S15** (0.1 mmol, 63.7 mg) was subjected to the general dimerization procedure, and the crude reaction mixture was purified by flash column chromatography (0 to 15% EtOAc in Hexanes) to afford bis-quinone methide **9** (43.4 mg, 68% yield, 2:1 dr).

^1H NMR (700 MHz, Chloroform-*d*) δ 7.47 (d, $J = 2.6$ Hz, 2H), 7.45 (d, $J = 7.8$ Hz, 4H), 7.44 (d, $J = 2.6$ Hz, 2H), 7.42 – 7.28 (m, 30H), 7.11 (d, $J = 2.6$ Hz, 1H), 7.04 (d, $J = 2.6$ Hz, 2H), 6.50 – 6.47 (m, 4H), 6.47 (s, 4H), 6.44 (d, $J = 6.8$ Hz, 1H), 6.39 (s, 3H), 6.38 (d, $J = 9.6$ Hz, 3H), 5.08 (d, $J = 3.1$ Hz, 1H), 5.00 (s, 1H), 4.95 (s, 6H), 4.92 (s, 4H), 4.32 (td, $J = 8.5, 7.1, 4.5$ Hz, 2H), 0.88 (q, $J = 8.1$ Hz, 46H), 0.76 – 0.70 (m, 30H).

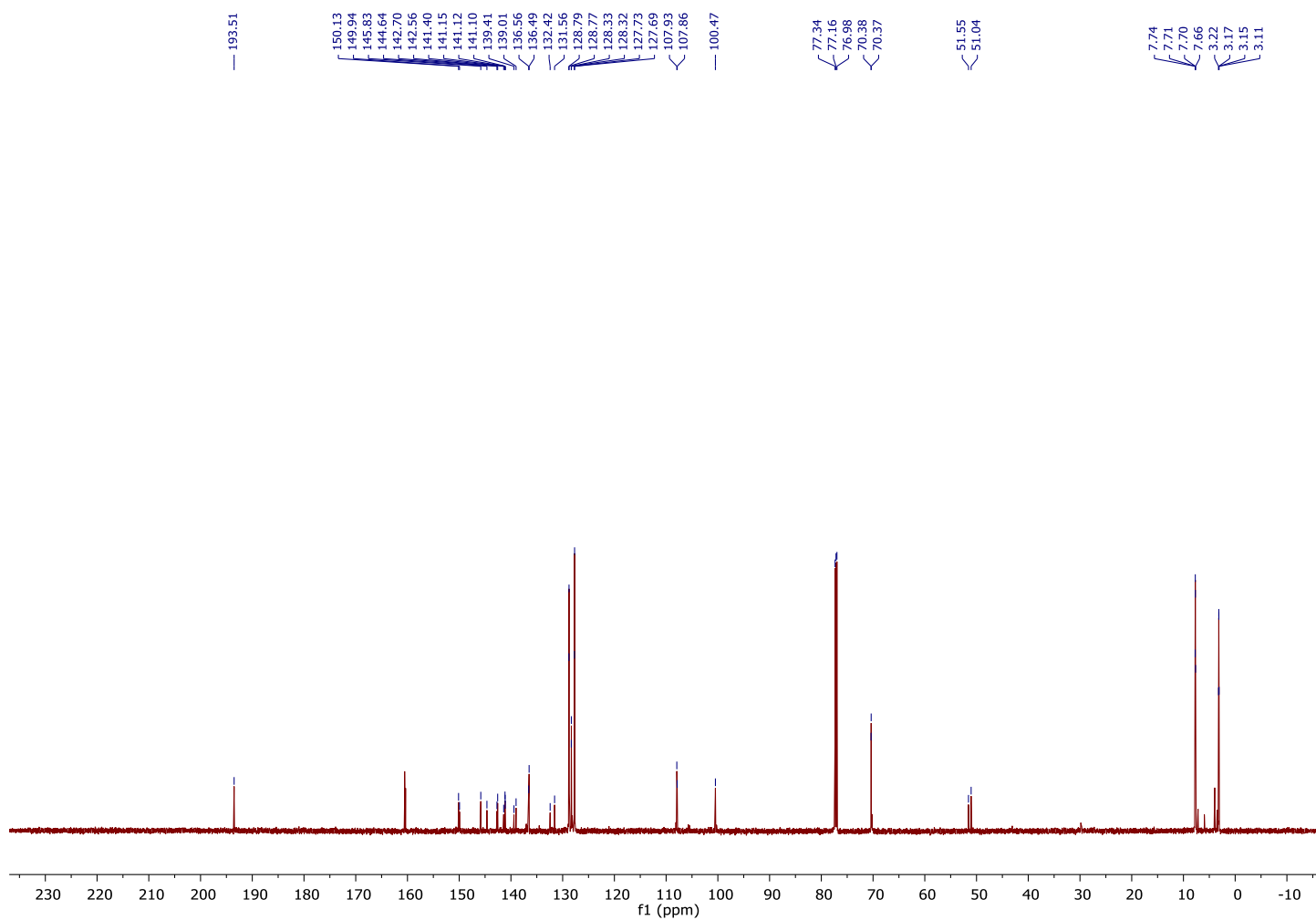
^{13}C NMR (176 MHz, Chloroform-*d*) δ 193.51, 150.13, 149.94, 145.83, 144.64, 142.70, 142.56, 141.40, 141.15, 141.12, 141.10, 139.41, 139.01, 136.56, 136.49, 132.42, 131.56, 128.79, 128.77, 128.33, 128.32, 127.73, 127.69, 107.93, 107.86, 100.47, 70.38, 70.37, 51.55, 51.04, 7.74, 7.71, 7.70, 7.66, 3.22, 3.17, 3.15, 3.11.

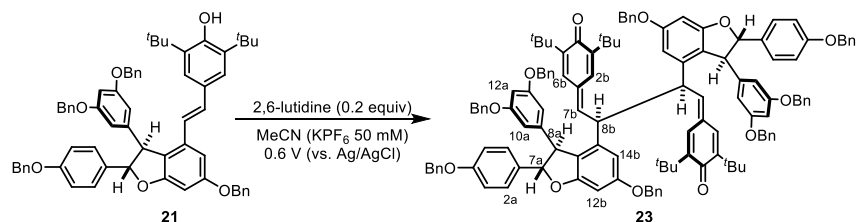
IR (Neat): 2957, 2898, 1588, 1456, 1248, 1158, 1051, 841, 734, 695, 619 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{C}_{80}\text{H}_{103}\text{O}_6\text{Si}_4^+$ ($[\text{M}+\text{H}]^+$) 1271.6826, found 1271.6816.



^{13}C NMR, 176 MHz, Chloroform-*d*, Dimer **9**



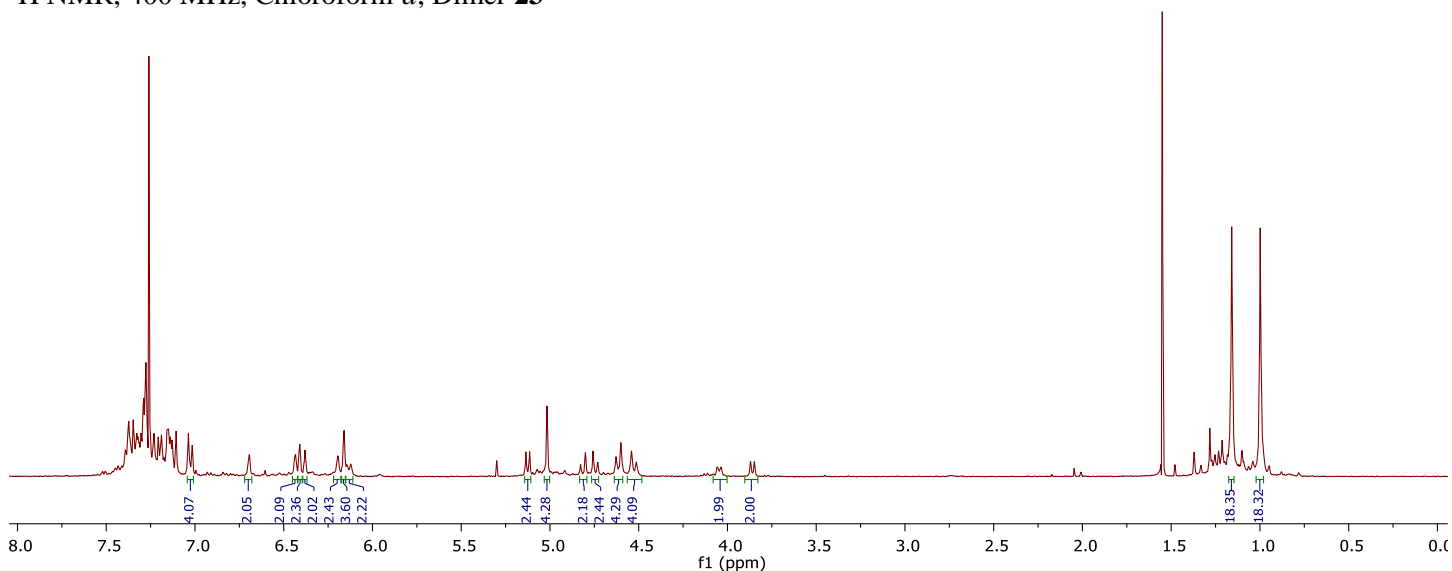


(23) 4,4'-((2*S*,3*S*)-2,3-bis((2*S*,3*S*)-6-(benzyloxy)-2-(4-(benzyloxy)phenyl)-3-(3,5-bis(benzyloxy)phenyl)-2,3-dihydrobenzofuran-4-yl)butane-1,4-diylidene)bis(2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one)

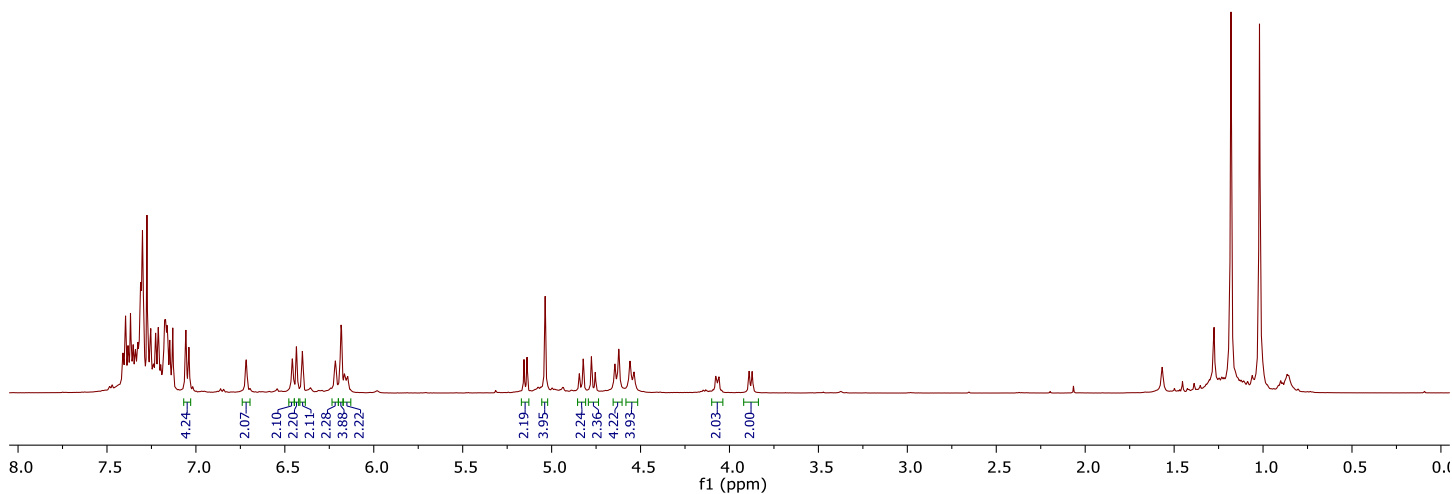
Stilbene **21** (0.05 mmol, 45 mg) was subjected to the general dimerization procedure, affording bis-quinone methide **23** (40 mg, 89% yield, >19:1 dr). The ¹H NMR spectrum was identical to the previous report for this compound.²

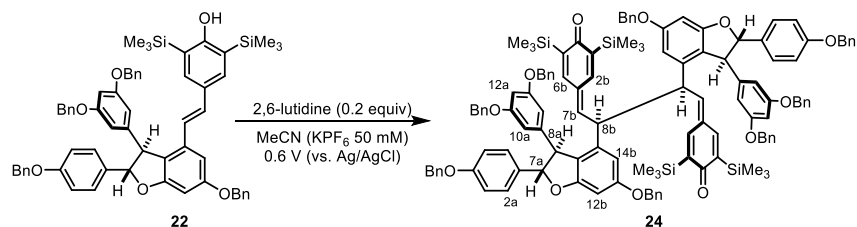
¹H NMR (700 MHz, CDCl₃, 50 °C) δ: 7.52 – 7.12 (m, 40H, –OCH₂C₆H₅), 7.10 (d, *J* = 8.5 Hz, 4H, C2a–H), 7.01 (d, *J* = 8.5 Hz, 4H, C3a–H), 6.70 (s, 2H, C14b–H), 6.42 (s, 2H, C2/6b–H), 6.39 (s, 2H, C12b–H), 6.37 (s, 2H, C12a–H), 6.23 (s, 2H, C2/6b–H), 6.16 (s, 4H, C10a–H), 6.11 (dd, br, *J* = 7.3, 9.2 Hz, 2H, C7b–H), 5.11 (d, *J* = 8.1 Hz, 2H, C7a–H), 5.04 (d, *J* = 12.5 Hz, 2H, C4a–OCH₂C₆H₅), 5.02 (d, *J* = 12.5 Hz, 2H, C4a–OCH₂C₆H₅), 4.83 (d, *J* = 10.8 Hz, 2H, C13b–OCH₂C₆H₅), 4.77 (d, *J* = 10.8 Hz, 2H, C13b–OCH₂C₆H₅), 4.62 (d, *J* = 11.1 Hz, 4H, C11a–OCH₂C₆H₅), 4.56 (d, *J* = 11.1 Hz, 4H, C11a–OCH₂C₆H₅), 4.06 (dd, br, *J* = 7.9, 9.2 Hz, 2H, C8b–H), 3.87 (d, *J* = 8.1 Hz, 2H, C8a–H), 1.17 (s, 18H, C3/5b–C(CH₃)₃), 1.00 (s, 18H, C3/5b–C(CH₃)₃).

¹H NMR, 400 MHz, Chloroform-*d*, Dimer **23**



¹H NMR, 500 MHz, Chloroform-*d*, Compound (±)-**5a**²



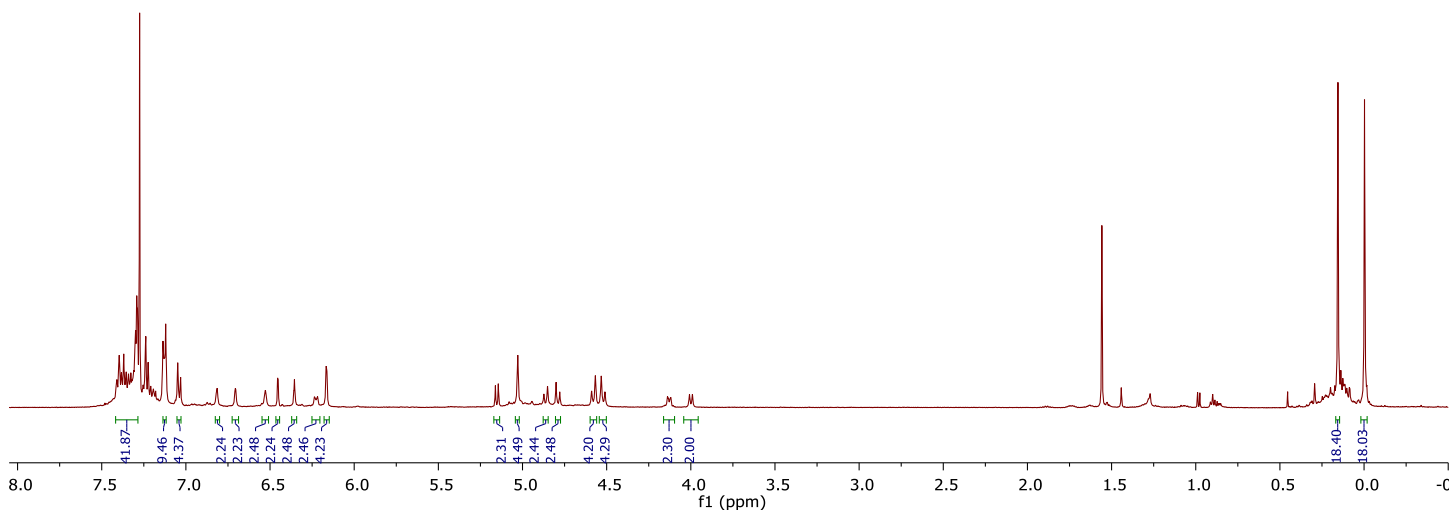


(24) 4,4'-((2*S*,3*S*)-2,3-bis((2*S*,3*S*)-6-(benzyloxy)-2-(4-(benzyloxy)phenyl)-3-(3,5-bis(benzyloxy)phenyl)-2,3-dihydrobenzofuran-4-yl)butane-1,4-diylidene)bis(2,6-bis(trimethylsilyl)cyclohexa-2,5-dien-1-one)

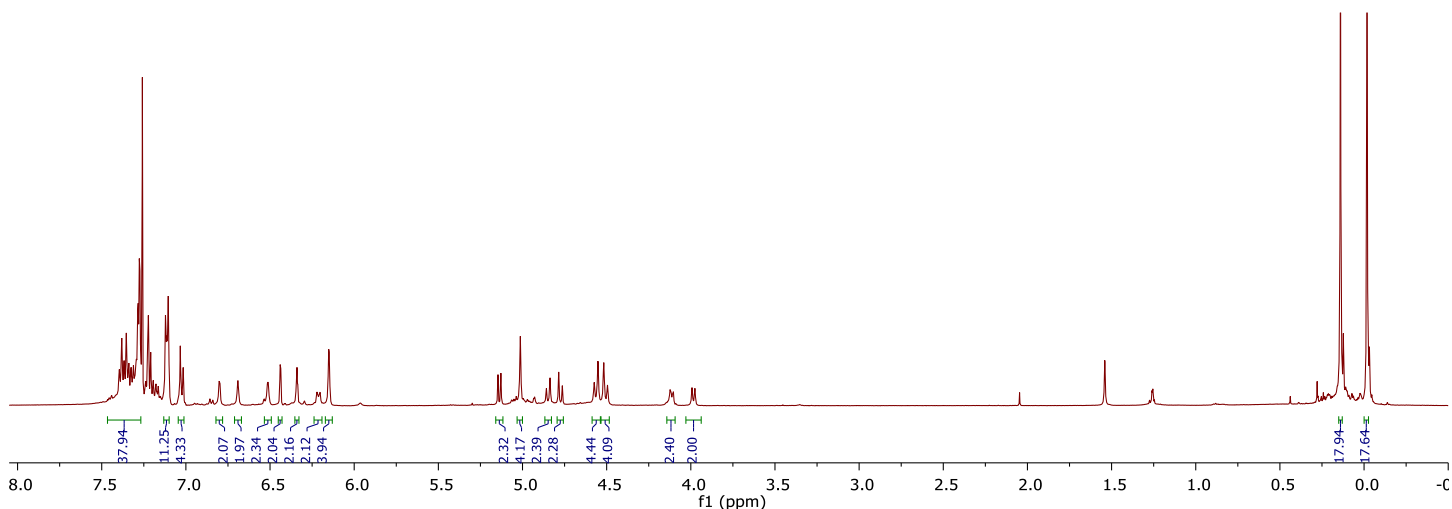
Stilbene **22** (0.039 mmol, 37 mg) was subjected to the general dimerization procedure, affording bis-quinone methide **24** (21 mg, 57% yield, >19:1). The ¹H NMR spectrum was identical to the previous report for this compound.²

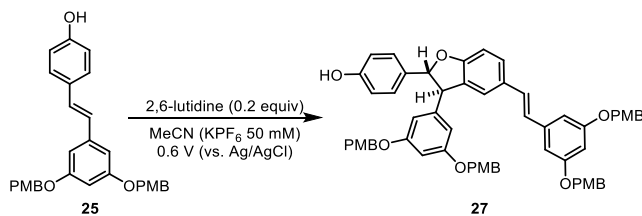
¹H NMR (500 MHz, CDCl₃, 25 °C) δ: 7.44 – 7.10 (m, 40H, –OCH₂C₆H₅), 7.11 (d, *J* = 8.6 Hz, 4H, C2a–H), 7.03 (d, *J* = 8.6 Hz, 4H, C3a–H), 6.80 (d, *J* = 2.2 Hz, 2H, C2/6b–H), 6.69 (s, br, 2H, C14b–H), 6.51 (d, br, *J* = 2.2 Hz, 2H, C2/6b–H), 6.44 (d, *J* = 2.2 Hz, 2H, C12b–H), 6.34 (t, *J* = 2.0 Hz, 2H, C12a–H), 6.21 (dd, *J* = 7.7, 9.9 Hz, 2H, C7b–H), 6.15 (d, *J* = 2.0 Hz, 4H, C10a–H), 5.14 (d, *J* = 8.6 Hz, 2H, C7a–H), 5.01 (s, 4H, C4a–OCH₂C₆H₅), 4.85 (d, *J* = 11.0 Hz, 2H, C13b–OCH₂C₆H₅), 4.77 (d, *J* = 11.0 Hz, 2H, C13b–OCH₂C₆H₅), 4.56 (d, *J* = 11.0 Hz, 4H, C11a–OCH₂C₆H₅), 4.51 (d, *J* = 11.0 Hz, 4H, C11a–OCH₂C₆H₅), 4.11 (dd, *J* = 7.7, 9.9 Hz, 2H, C8b–H), 3.99 (d, *J* = 8.6 Hz, 2H, C8a–H), 0.14 (s, 18H, C3/5b–Si(CH₃)₃), –0.02 (s, 18H, C3/5b–Si(CH₃)₃).

¹H NMR, 500 MHz, Chloroform-*d*, Dimer **24**



¹H NMR, 500 MHz, Chloroform-*d*, Compound (±)-**5b**²





(27) 4-((2*R*,3*R*)-3-(3,5-bis((4-methoxybenzyl)oxy)phenyl)-5-((*E*)-3,5-bis((4-methoxybenzyl)oxy)styryl)-2,3-dihydrobenzofuran-2-yl)phenol

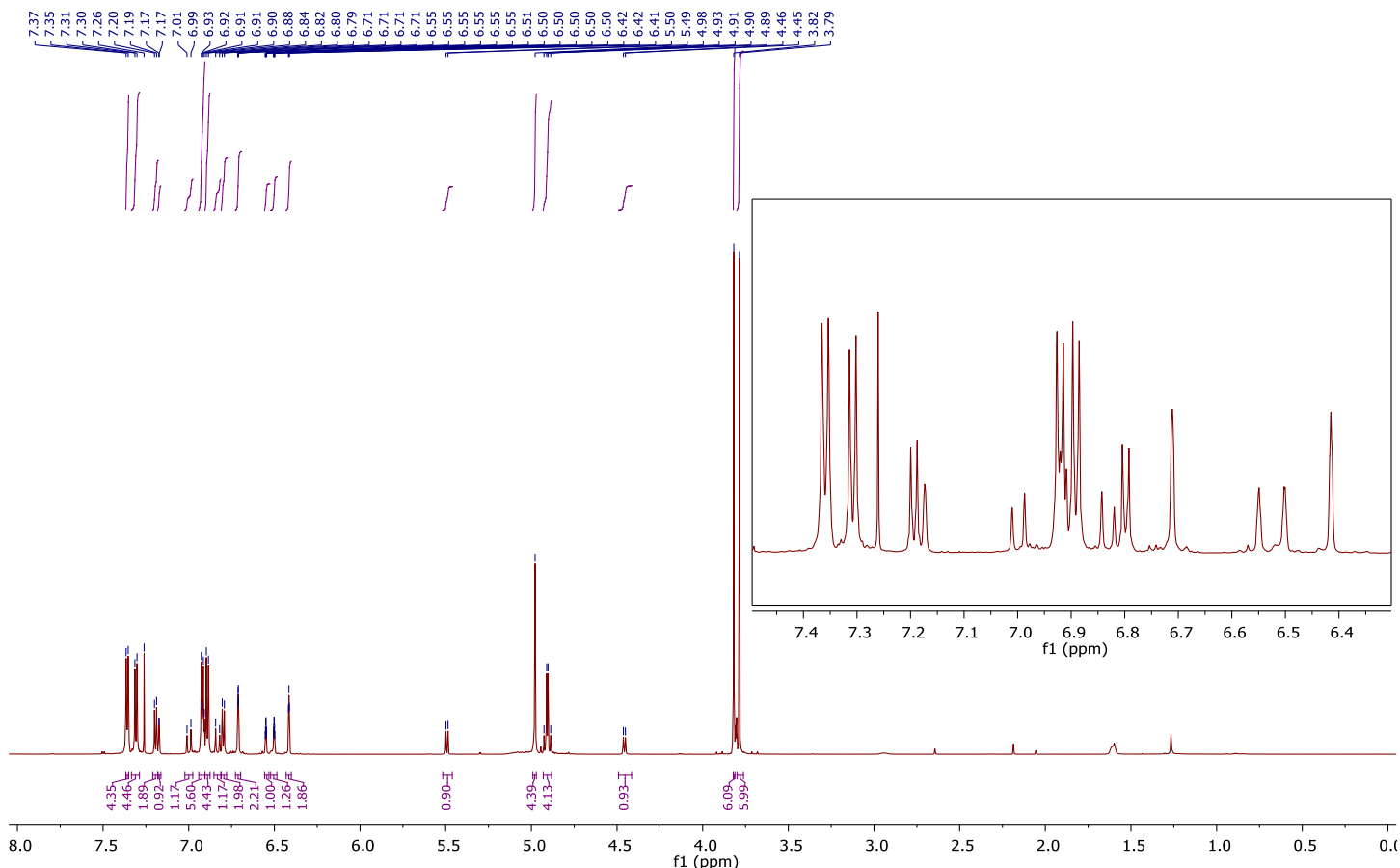
Stilbene **25** (0.1 mmol, 46.9 mg) was subjected to the general dimerization procedure. The crude product was purified via flash column chromatography (1% to 5% Acetone in CH₂Cl₂) to afford the dihydrobenzofuran **27** (27.5 mg, 59% yield, >19:1 dr).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.4 Hz, 4H), 7.31 (d, *J* = 8.6 Hz, 4H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 1.7 Hz, 1H), 7.00 (d, *J* = 16.2 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 4H), 6.91 (d, *J* = 8.5 Hz, 2H), 6.89 (d, *J* = 8.5 Hz, 4H), 6.83 (d, *J* = 16.2 Hz, 1H), 6.80 (d, *J* = 8.6 Hz, 2H), 6.71 (dd, *J* = 2.3, 1.2 Hz, 2H), 6.55 (td, *J* = 2.3, 1.0 Hz, 1H), 6.50 (td, *J* = 2.2, 1.2 Hz, 1H), 6.42 (t, *J* = 1.9 Hz, 2H), 5.49 (d, *J* = 8.2 Hz, 1H), 4.98 (s, 4H), 4.93 – 4.88 (m, 4H), 4.46 (d, *J* = 8.2 Hz, 1H), 3.82 (s, 6H), 3.79 (s, 6H).

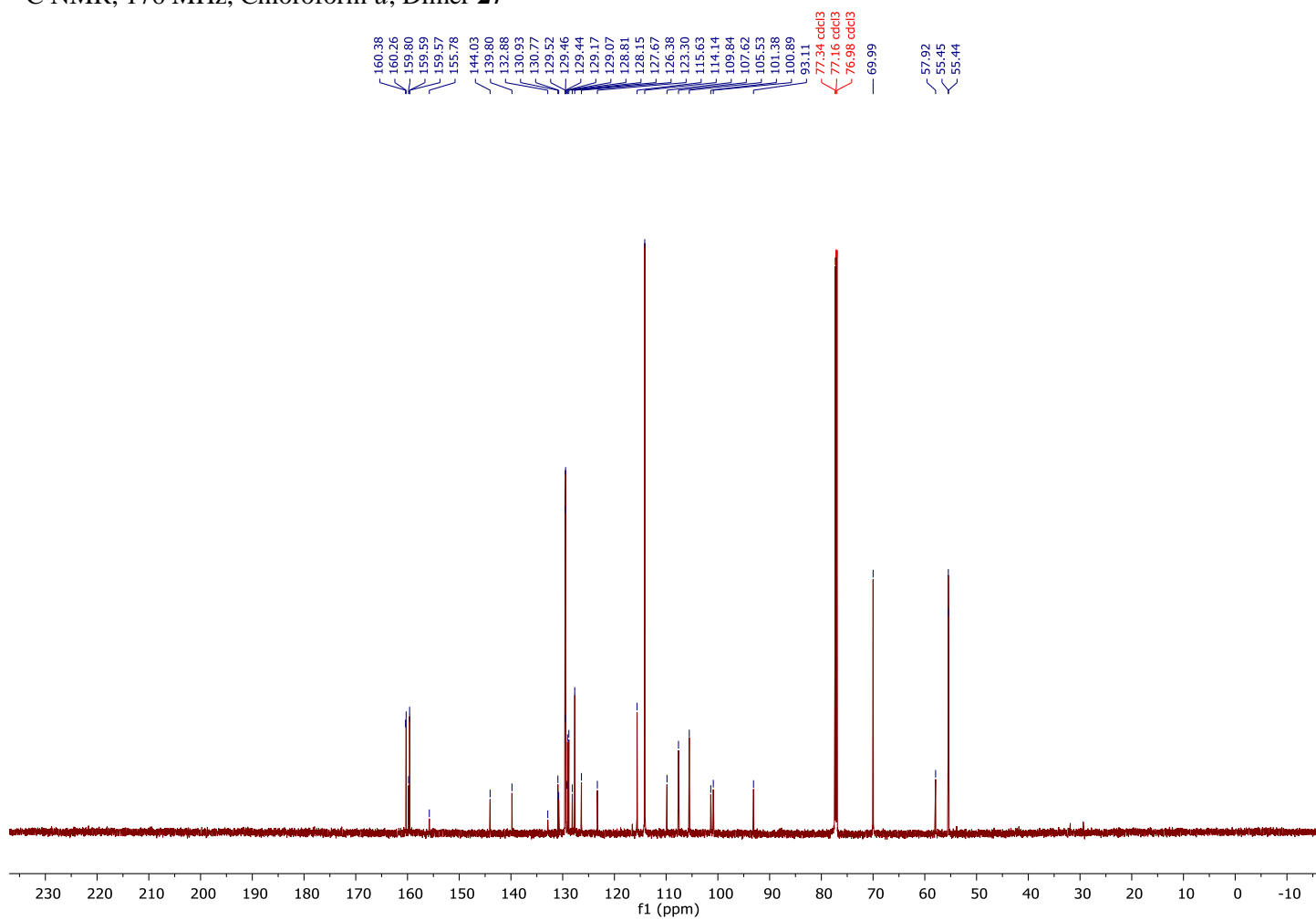
¹³C NMR (176 MHz, Chloroform-*d*) δ 160.38, 160.26, 159.80, 159.59, 159.57, 155.78, 144.03, 139.80, 132.88, 130.93, 130.77, 129.52, 129.46, 129.44, 129.17, 129.07, 128.81, 128.15, 127.67, 126.38, 123.30, 115.63, 114.14, 109.84, 107.62, 105.53, 101.38, 100.89, 93.11, 69.99, 57.92, 55.45, 55.44.

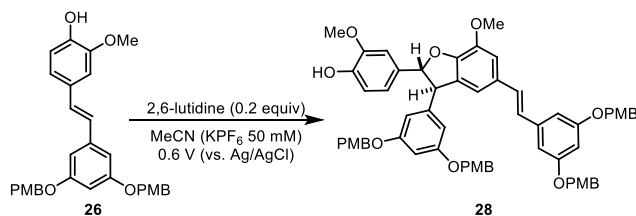
IR (Neat): 3391, 2932, 2835, 1585, 1512, 1440, 1301, 1244, 1146, 1030, 818 cm⁻¹;

HRMS (ESI) *m/z* calculated for C₆₀H₅₅O₁₀⁺ ([M+H]⁺) 935.3790, found 935.3800.



^{13}C NMR, 176 MHz, Chloroform-*d*, Dimer **27**





(28) 4-((2*R*,3*R*)-3-(3,5-bis((4-methoxybenzyl)oxy)phenyl)-5-((*E*)-3,5-bis((4-methoxybenzyl)oxy)styryl)-7-methoxy-2,3-dihydrobenzofuran-2-yl)-2-methoxyphenol

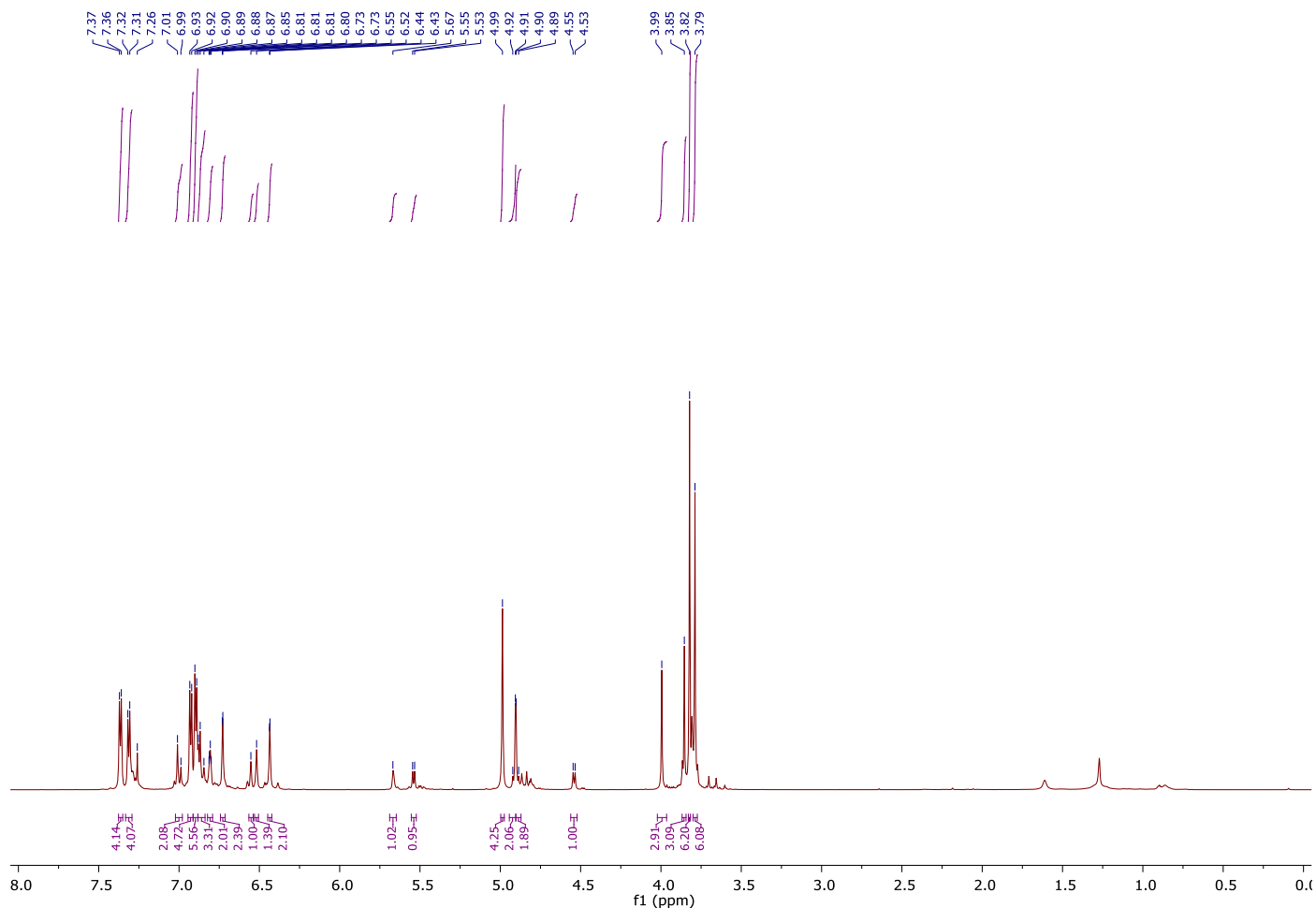
Stilbene **26** (0.1 mmol, 49.9 mg) was subjected to the general dimerization procedure. The crude product was purified via flash column chromatography (1% to 5% Acetone in CH₂Cl₂) to afford the dihydrobenzofuran **28** (28.4 mg, 57% yield, >19:1 dr).

¹H NMR (700 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 8.1 Hz, 4H), 7.31 (d, *J* = 8.3 Hz, 4H), 7.00 (d, *J* = 15.0 Hz, 2H), 6.93 (d, *J* = 8.2 Hz, 5H), 6.90 (d, *J* = 7.8 Hz, 6H), 6.88 – 6.84 (m, 3H), 6.81 (d, *J* = 4.1 Hz, 2H), 6.74 – 6.71 (m, 2H), 6.55 (s, 1H), 6.52 (s, 1H), 6.45 – 6.42 (m, 2H), 5.67 (s, 1H), 5.54 (d, *J* = 8.8 Hz, 1H), 4.99 (s, 4H), 4.91 (d, *J* = 11.2 Hz, 2H), 4.89 (d, *J* = 11.0 Hz, 2H), 4.54 (d, *J* = 8.8 Hz, 1H), 3.99 (s, 3H), 3.85 (s, 3H), 3.82 (s, 6H), 3.79 (s, 6H).

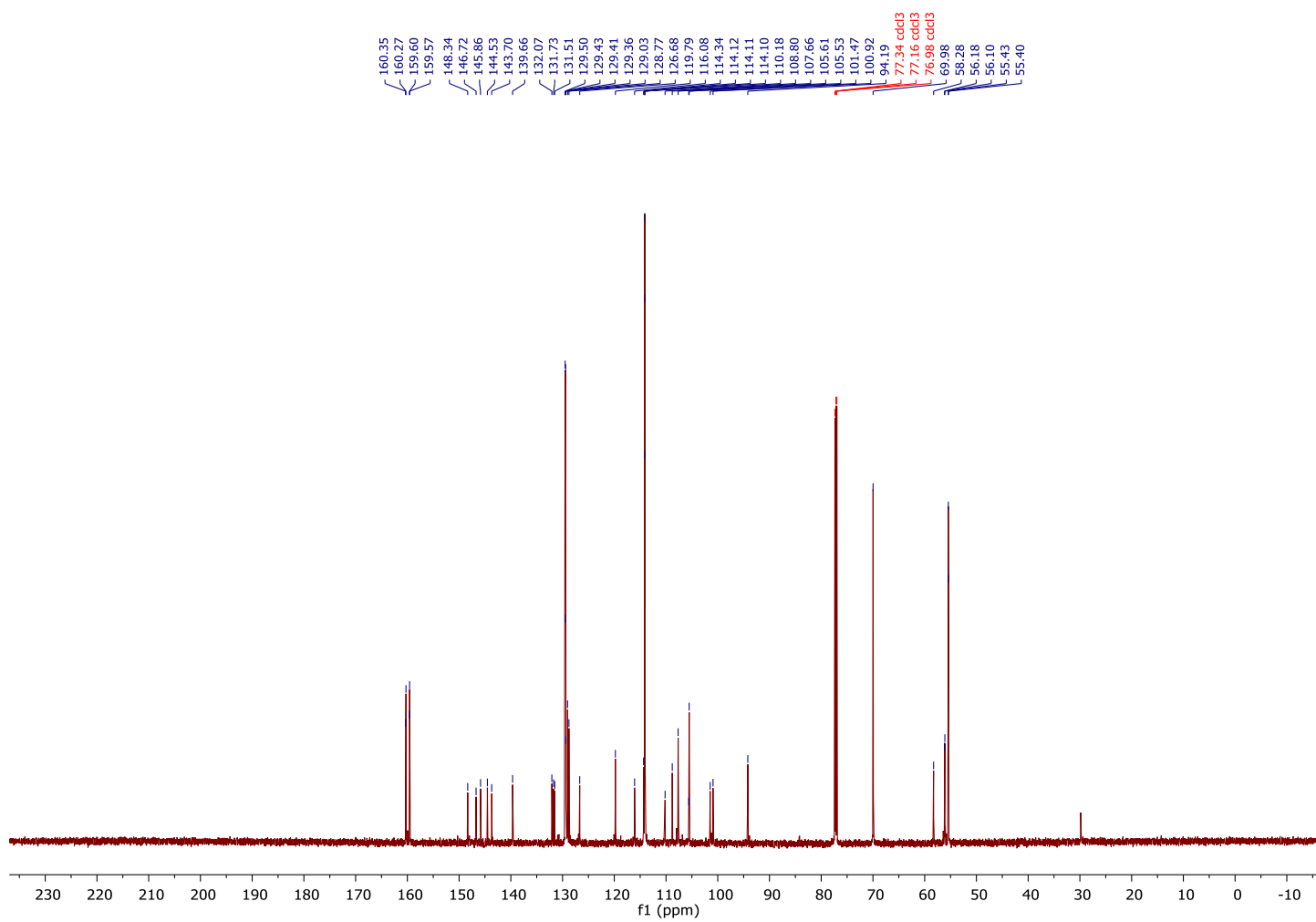
¹³C NMR (176 MHz, Chloroform-*d*) δ 160.35, 160.27, 159.60, 159.57, 148.34, 146.72, 145.86, 144.53, 143.70, 139.66, 132.07, 131.73, 131.51, 129.50, 129.43, 129.41, 129.36, 129.03, 128.77, 126.68, 119.79, 116.08, 114.34, 114.12, 114.11, 114.10, 110.18, 108.80, 107.66, 105.61, 105.53, 101.47, 100.92, 94.19, 69.98, 58.28, 56.18, 56.10, 55.43, 55.40.

IR (Neat): 3395, 2999, 2934, 2833, 1585, 1512, 1439, 1302, 1245, 1150, 1032, 824, 734 cm⁻¹;

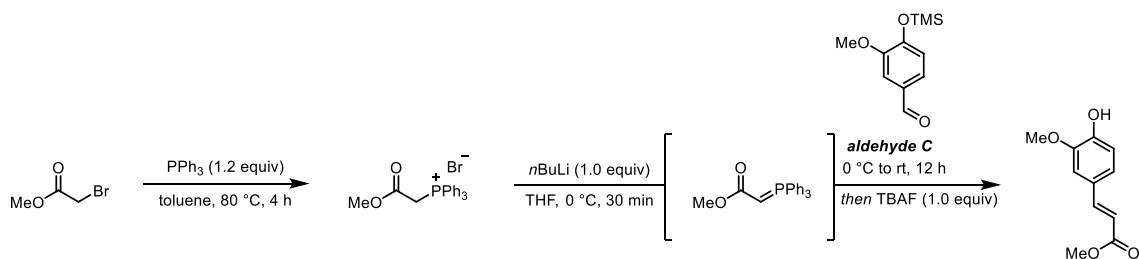
HRMS (ESI) *m/z* calculated for C₆₂H₅₉O₁₂⁺ ([M+H]⁺) 995.4001, found 995.3979.



^{13}C NMR, 176 MHz, Chloroform-*d*, Dimer **28**



Total Synthesis of (±)-hierochin D



(S16) methyl (*E*)-3-(4-hydroxy-3-methoxyphenyl)acrylate

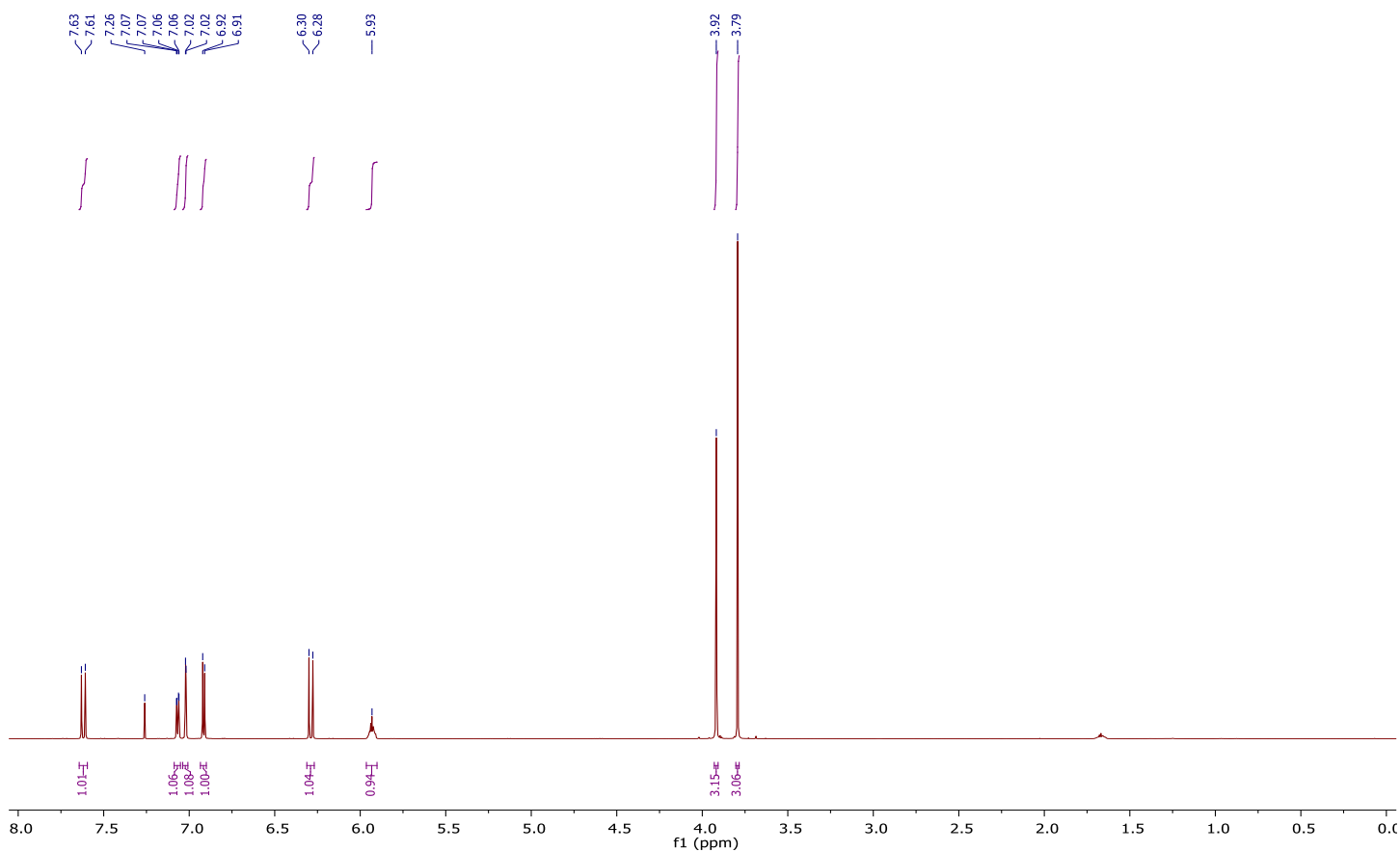
Commercially available methyl bromoacetate (1.42 mL, 15 mmol) was dissolved in toluene (60 mL) in a flame-dried round bottom flask. To the stirring solution was added triphenylphosphine (18 mmol, 4.72g), and the reaction was heated to 80 °C for 4 hours. Upon cooling the reaction mixture to room temperature, the white solid product was collected via vacuum filtration, and any excess triphenylphosphine was rinsed away with hexanes. The product was dried under vacuum for >24 hours to ensure full removal of solvent and water prior to use in the subsequent olefination.

To a flame-dried, three-neck, round bottom flask was added methyl acetophosphonium bromide (5.35 mmol, 2.22 g), which was subsequently suspended in THF (15 mL) and cooled on ice to 0 °C. To the stirring suspension was added *n*BuLi (5.35 mmol, 2.14 mL, 2.5 M in hexanes), and the reaction mixture was allowed to stir at temperature for 30 minutes to form the ylide. In a separate flame-dried, heart-shaped flask, TMS-vanillin (aldehyde C, 5.35 mmol, 1.20 g) was dissolved in THF (20 mL). The aldehyde was added to the ylide solution via cannula, and the reaction was allowed to warm to room temperature over 12 hours. The reaction was subsequently cooled on ice to 0 °C, and TBAF (5.35 mmol, 5.35 mL, 1.0 M in THF) was added. The reaction was allowed to warm to room temperature over 1 hour, at which point it was quenched by the addition of saturated ammonium chloride, diluted with EtOAc, then transferred to a separatory funnel containing additional saturated ammonium chloride. The layers were separated, and the aqueous layer was extracted with additional EtOAc. The combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. The crude product was purified via flash column chromatography (6-42% EtOAc in Hexanes, 7-step gradient, 2 column volumes per step) to afford the product **S16** as a clear, colorless, oil (857 mg, 77% yield). The ¹H and ¹³C NMR spectra of the product was consistent with the data previously reported in the literature.⁶

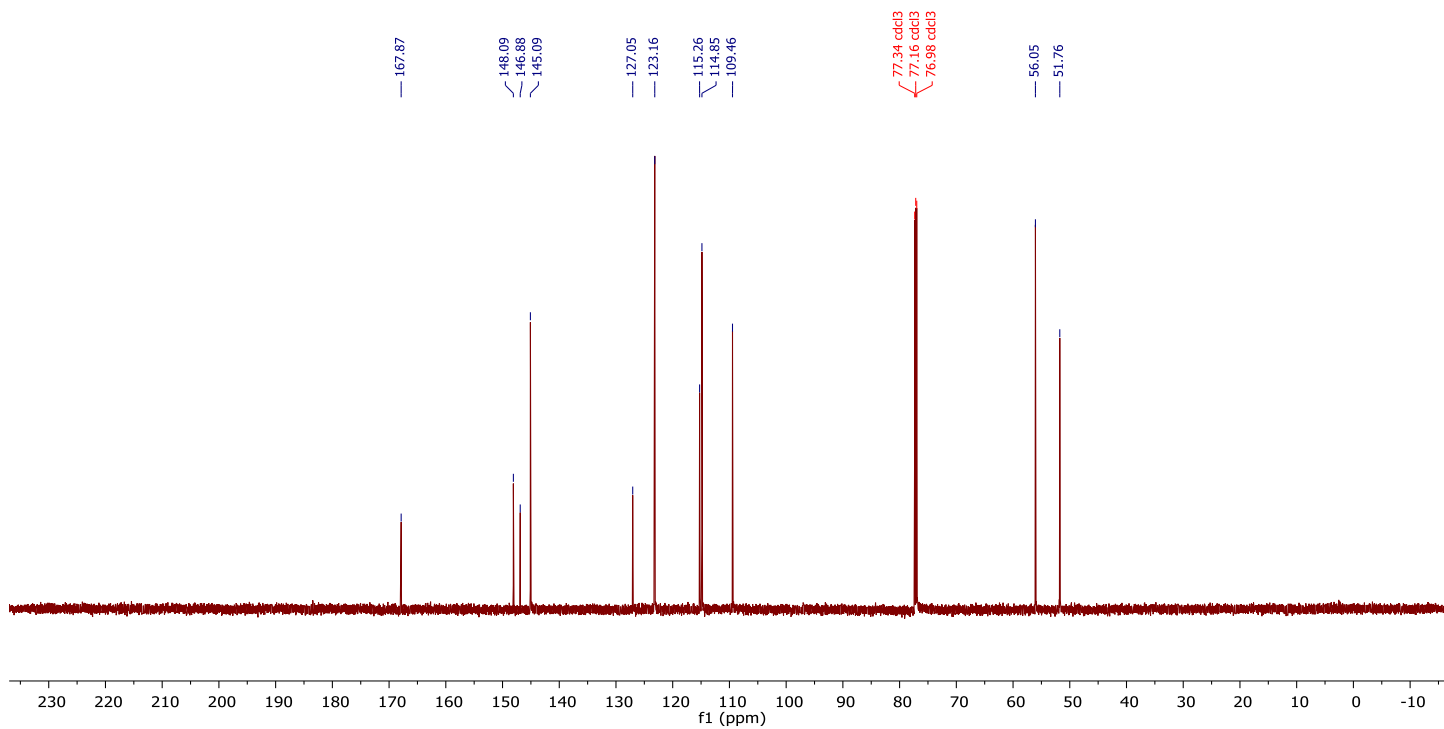
¹H NMR (700 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 15.9 Hz, 1H), 7.07 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.02 (d, *J* = 1.9 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.29 (d, *J* = 15.9 Hz, 1H), 5.93 (s, 1H), 3.92 (s, 3H), 3.79 (s, 3H).

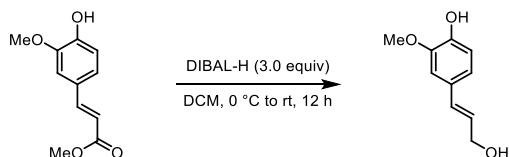
¹³C NMR (176 MHz, Chloroform-*d*) δ 167.87, 148.09, 146.88, 145.09, 127.05, 123.16, 115.26, 114.85, 109.46, 56.05, 51.76.

¹H NMR, 700 MHz, Chloroform-*d*, S16



¹³C NMR, 176 MHz, Chloroform-*d*, S16



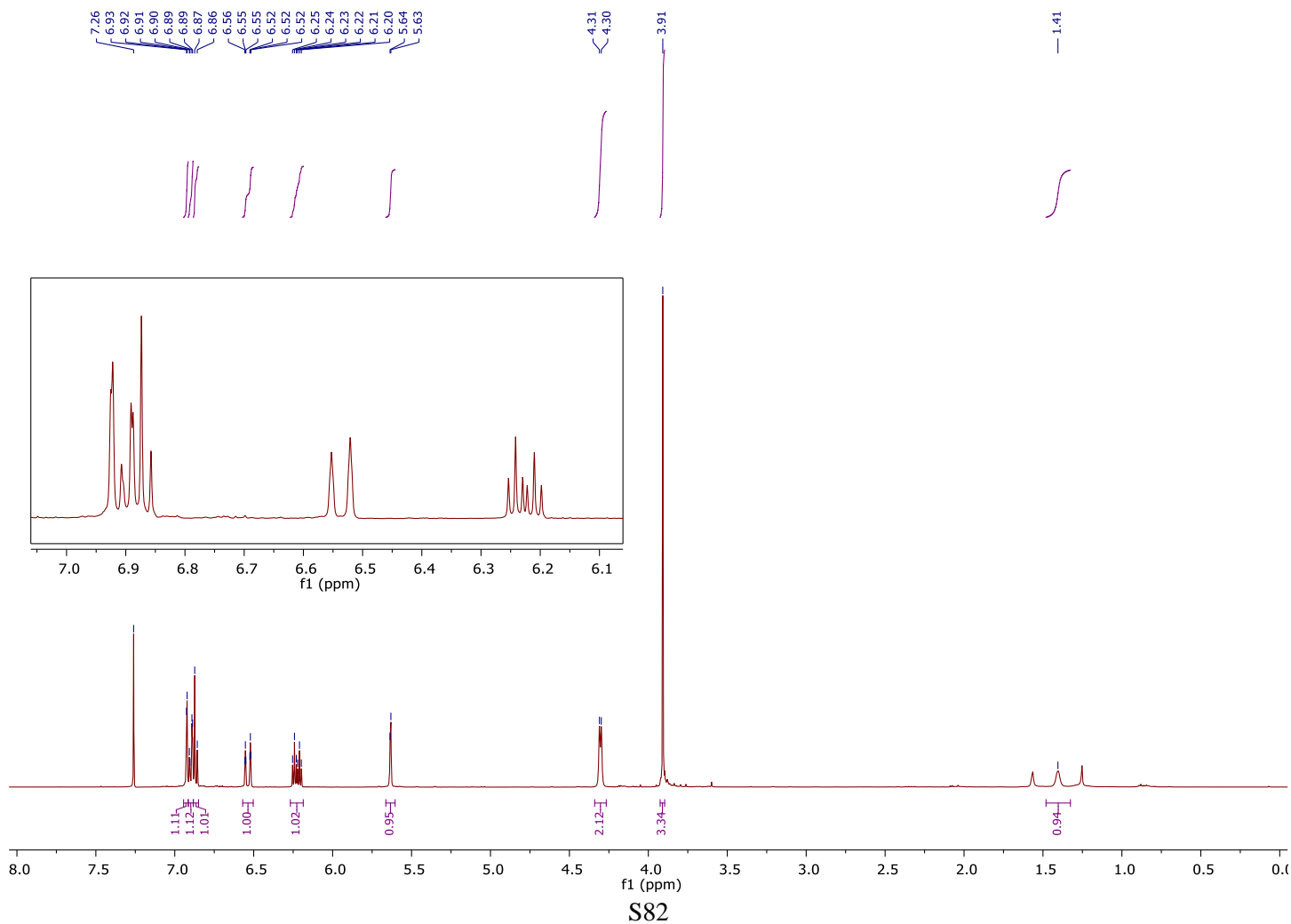


conferyl alcohol (29) ((*E*)-4-(3-hydroxyprop-1-en-1-yl)-2-methoxyphenol)

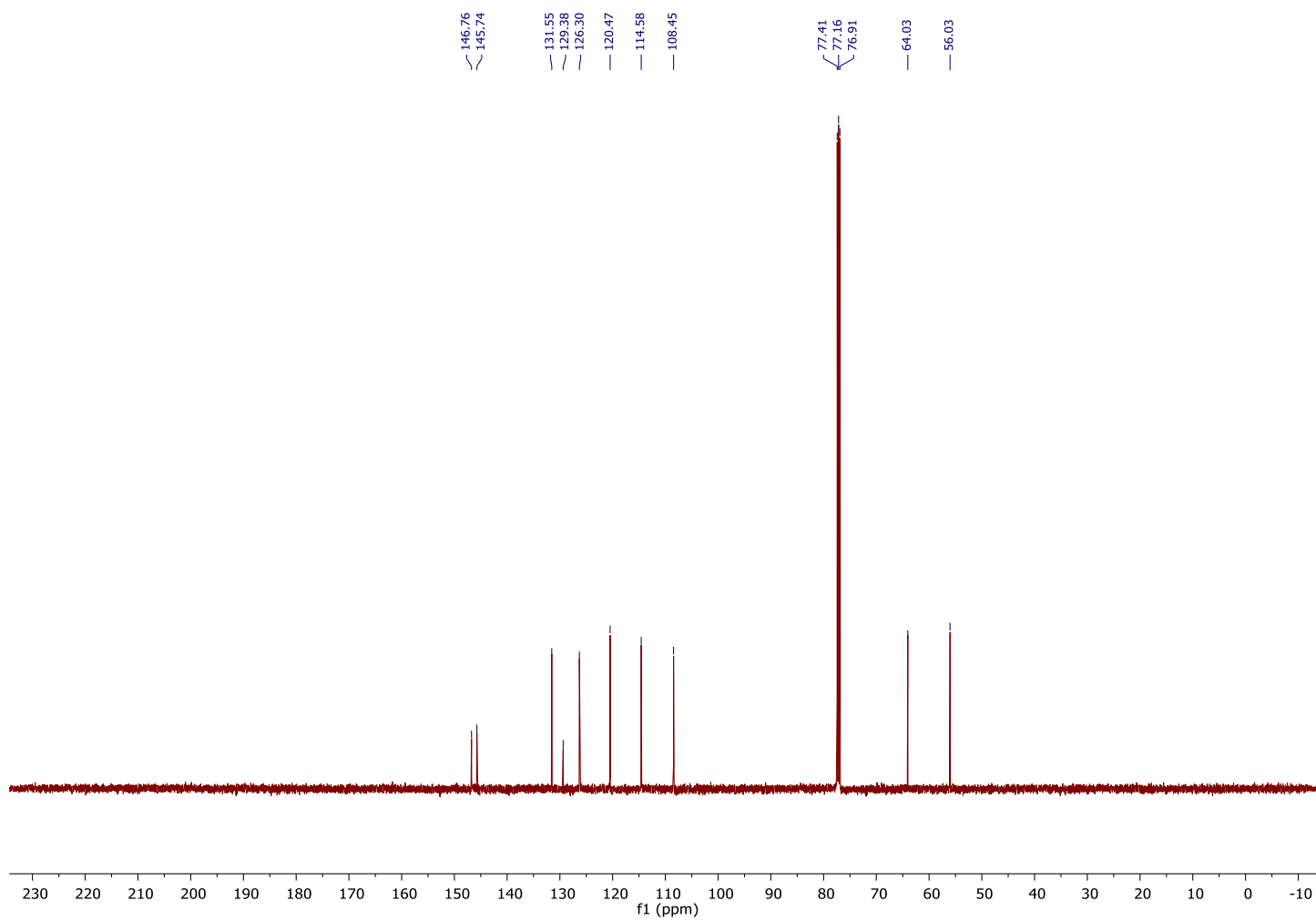
Compound **S16** (1.12 mmol, 233 mg) was dissolved in DCM under inert atmosphere, and the stirring solution was cooled to 0 °C on ice. A solution of diisobutylaluminum hydride (3.36 mmol, 3.36 mL, 1.0 M in DCM) was added dropwise to the stirring solution, causing the reaction to change from colorless to slightly yellow. The reaction mixture was held at 0 °C for 10 minutes, at which point it was allowed to warm to room temperature over 12 hours. The reaction was quenched slowly with 4mL of Rochelle's salt, turning the mixture cloudy. The mixture was let to stir at room temperature for >6 hours, at which point it was diluted with DI water and transferred to a separatory funnel. The layers were separated, and the aqueous layer was washed with multiple portions of DCM. The combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. The crude product was purified via flash column chromatography (28-98% EtOAc in Hexanes, 5 step gradient, 2 column volumes per step) to afford the product **35** as a white solid (167 mg, 83% yield). The ¹H and ¹³C NMR spectra of the product was consistent with the data previously reported in the literature.⁷

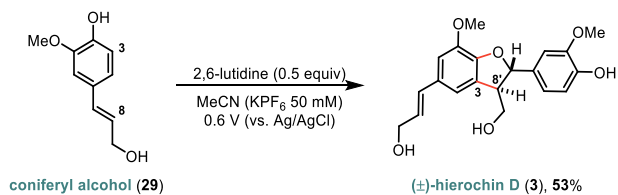
¹H NMR (500 MHz, Chloroform-*d*) δ 6.92 (d, *J* = 1.8 Hz, 1H), 6.90 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 6.54 (dt, *J* = 15.8, 1.6 Hz, 1H), 6.23 (dt, *J* = 15.8, 6.0 Hz, 1H), 5.63 (d, *J* = 2.8 Hz, 1H), 4.30 (d, *J* = 5.9 Hz, 2H), 3.91 (s, 3H), 1.41 (s, 1H).

¹³C NMR (126 MHz, Chloroform-*d*) δ 146.76, 145.74, 131.55, 129.38, 126.30, 120.47, 114.58, 108.44, 64.04, 56.03.



^{13}C NMR, 126 MHz, Chloroform-*d*, **29**



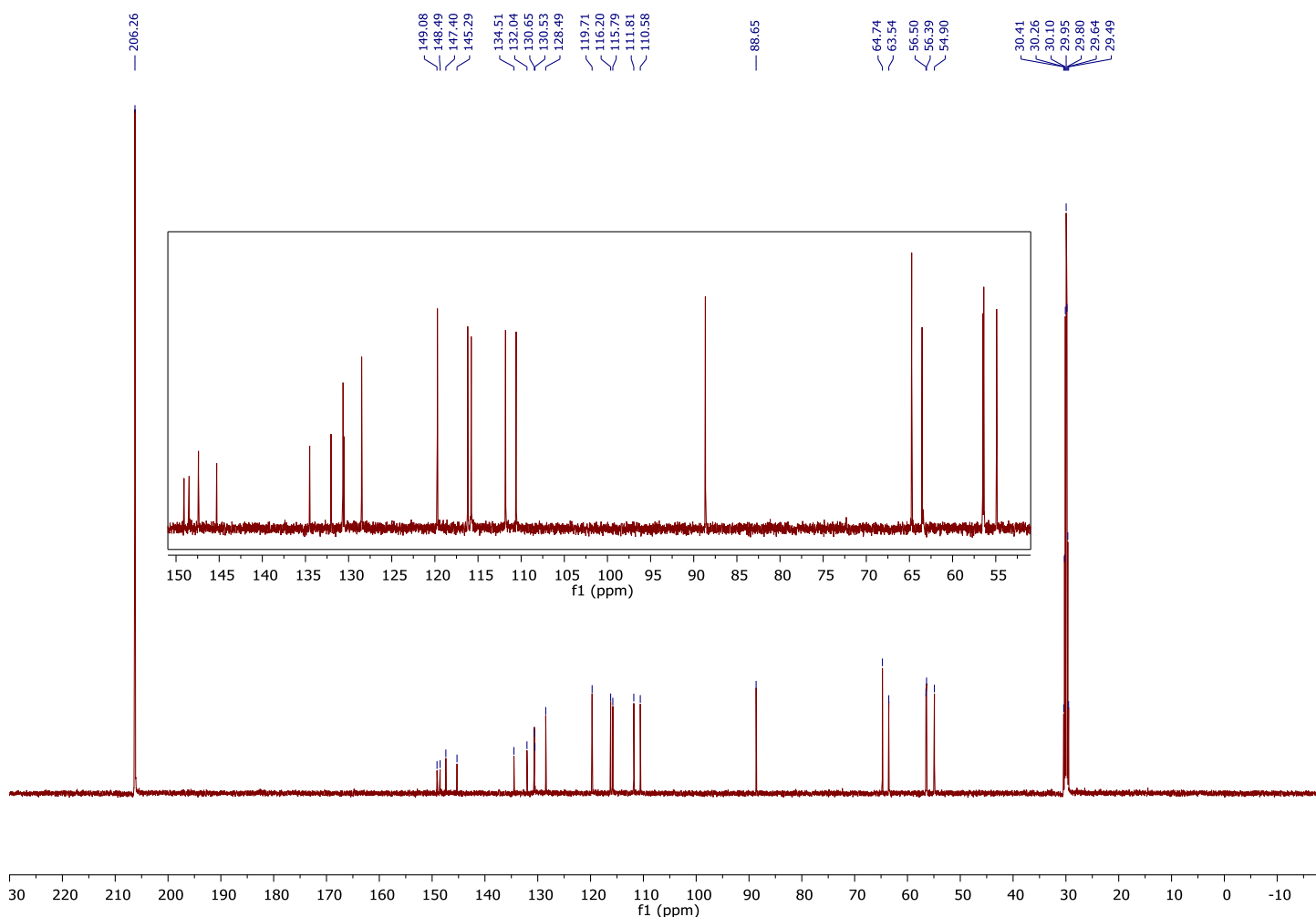


(±)-hierochin D (3) (4-((2*S*,3*R*)-3-(hydroxymethyl)-5-((*E*)-3-hydroxyprop-1-en-1-yl)-7-methoxy-2,3-dihydrobenzofuran-2-yl)-2-methoxyphenol)

Coniferyl alcohol (**29**, 0.1 mmol, 18 mg) was subjected to the general dimerization conditions (see page S42), with the only variation being the amount of 2,6-lutidine (5.8 μ L, 0.05 mmol). The crude reaction material was purified via flash column chromatography to afford (\pm)-hierochin D (**3**) as a colorless oil (9.4 mg, 53% yield). The 13 C NMR was consistent with the previous report for this compound.⁸

13 C NMR (126 MHz, Acetone- d_6) δ 148.97, 148.38, 147.29, 145.18, 134.40, 131.93, 130.54, 130.42, 128.38, 119.60, 116.09, 115.68, 111.70, 110.47, 88.54, 64.63, 63.43, 56.39, 56.28, 54.79.

13 C NMR, 126 MHz, Chloroform- d , **3**



Attempted Direct Cyclization of QMD products:

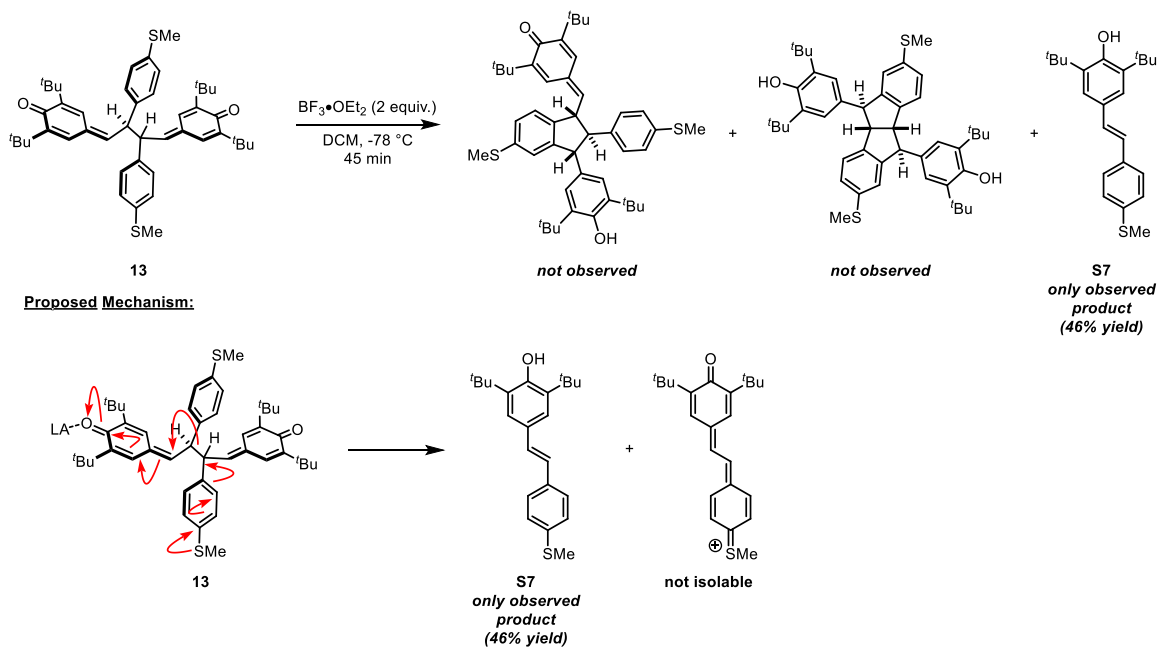
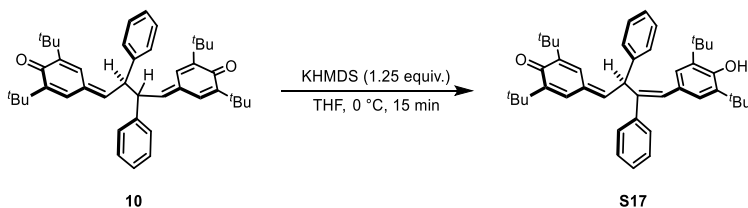


Figure S1. Attempted direct cyclization of QMDs containing electron-donating substituents at C12 results in disproportionation back to the stilbene precursor. Note that 46% yield is relative to the mass of **13**, therefore the fragmentation has a theoretical yield for **S7** of 50%.

Natural Product Analog Synthesis:

Tautomerization of BQM dimer to MQM dimer – General Procedure:

The starting BQM dimer was added to a reaction vial charged with a stir bar. The atmosphere was evacuated and replaced with nitrogen, and the starting material was dissolved in THF. The reaction solution was cooled in an ice bath to 0 °C, and potassium bis(trimethylsilyl)amide (KHMDS) was added as a solution (1.25 equiv., 0.7 M in toluene). The reaction was allowed to stir until the starting material consumed based on TLC analysis. The reaction was quenched by the addition of aqueous saturated ammonium chloride, diluted with EtOAc, and transferred to a separatory funnel containing additional aq. sat. NH₄Cl. The layers were separated, and the aqueous layer was extracted with additional portions of ethyl acetate. The combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. The crude product was further purified by flash column chromatography.



(S17) (*S,Z*)-2,6-di-*tert*-butyl-4-(4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2,3-diphenylbut-3-en-1-ylidene)cyclohexa-2,5-dien-1-one

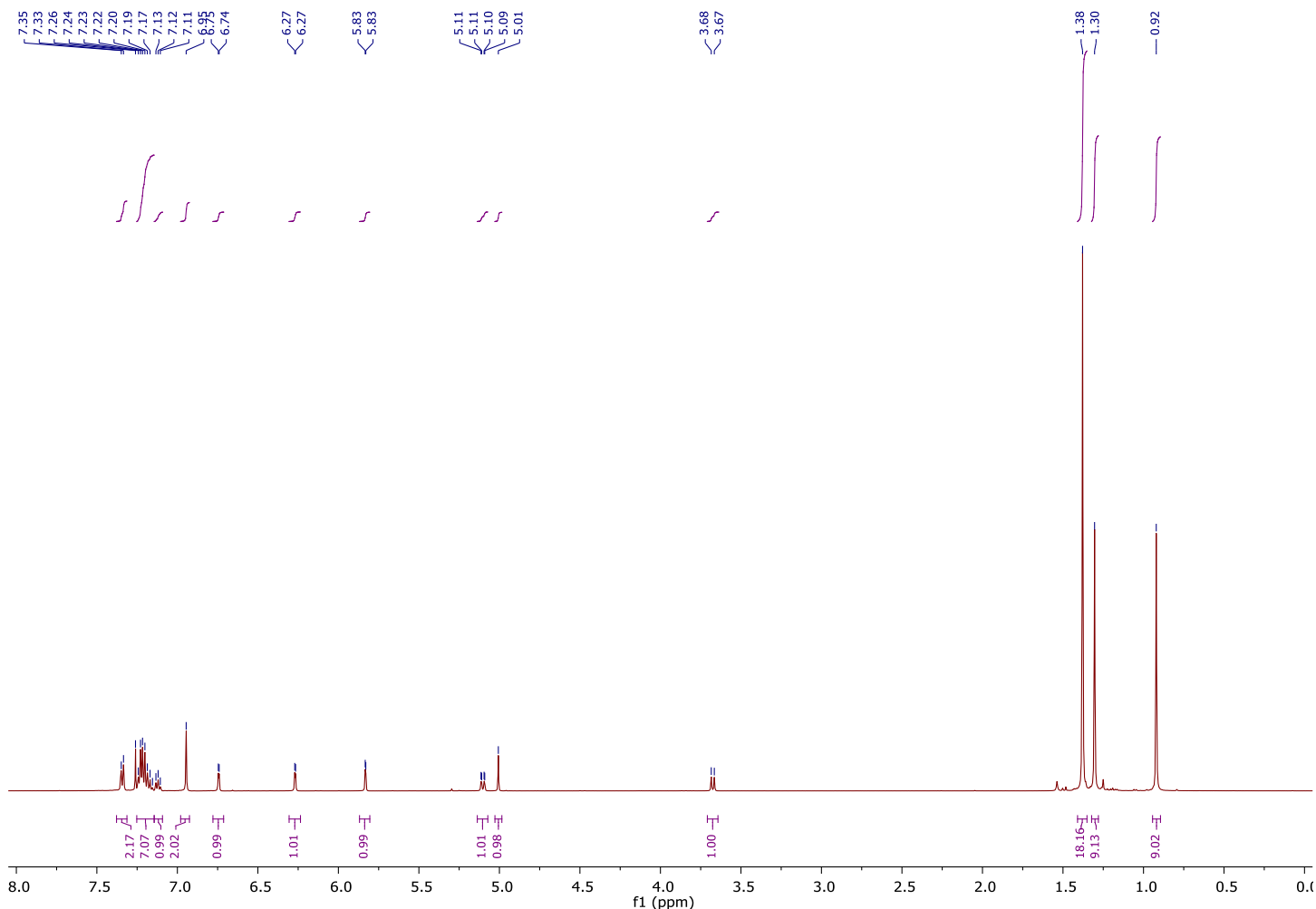
Dimer **10** (0.026 mmol, 16 mg) was subjected to the tautomerization conditions, and the crude product was purified by flash column chromatography (10–50% DCM/Hexanes) to afford MQM **S17** (10 mg, 62% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.34 (d, $J = 7.0$ Hz, 2H), 7.25 – 7.14 (m, 7H), 7.12 (t, $J = 6.8$ Hz, 1H), 6.95 (s, 2H), 6.74 (d, $J = 2.7$ Hz, 1H), 6.27 (d, $J = 2.7$ Hz, 1H), 5.83 (d, $J = 1.9$ Hz, 1H), 5.10 (dd, $J = 9.5, 2.0$ Hz, 1H), 5.01 (s, 1H), 3.67 (d, $J = 9.5$ Hz, 1H), 1.38 (s, 18H), 1.30 (s, 9H), 0.92 (s, 9H).

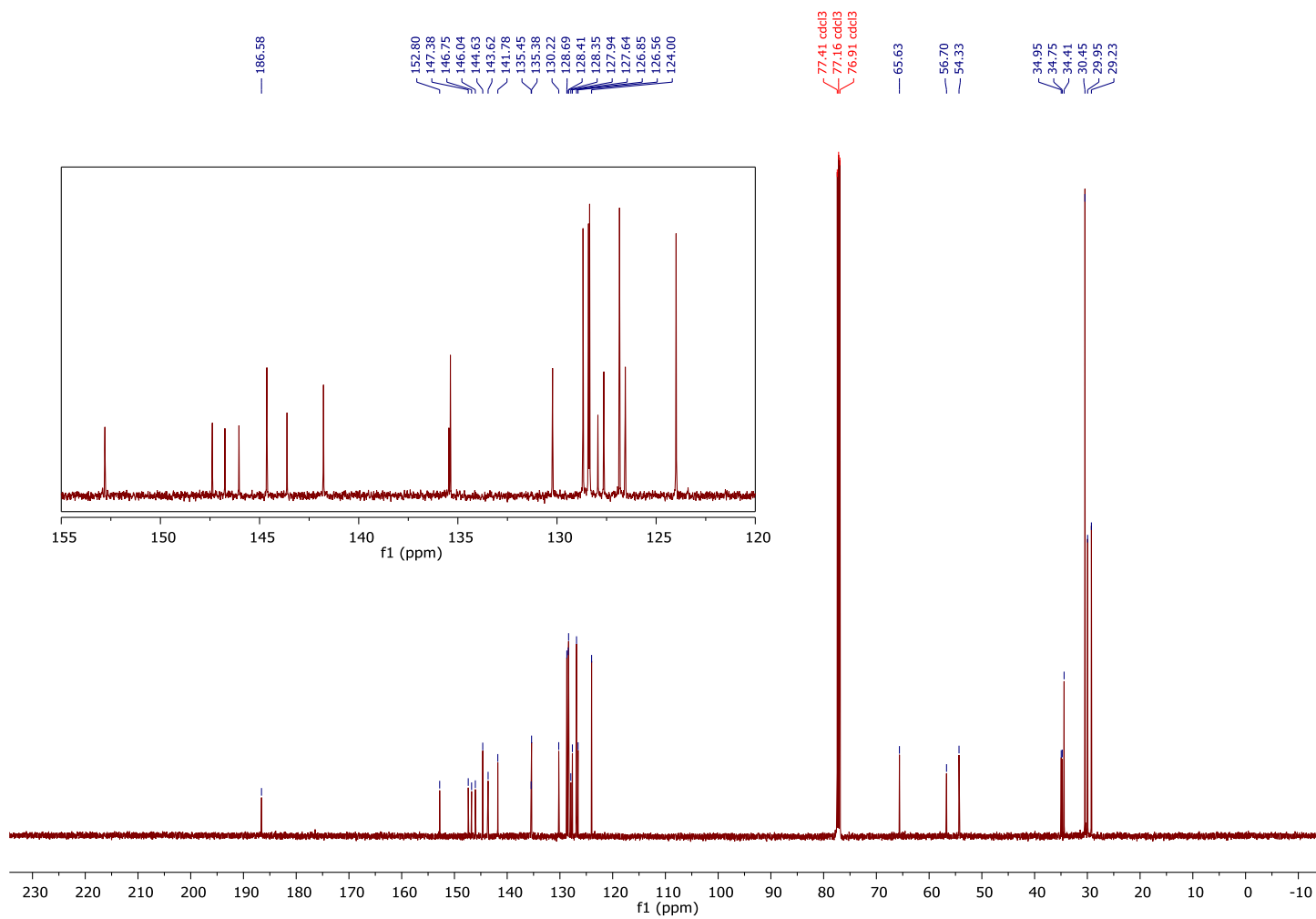
^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.41, 152.63, 147.21, 146.57, 145.86, 144.46, 143.44, 141.60, 135.28, 135.20, 130.05, 128.51, 128.24, 128.18, 127.76, 127.47, 126.68, 126.39, 123.82, 65.46, 56.53, 54.16, 34.78, 34.58, 34.23, 30.28, 29.77, 29.06.

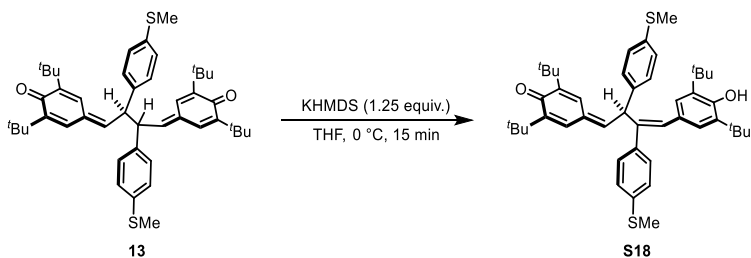
IR (Neat): 3623, 2954, 2912, 1653, 1437, 1366, 1192, 1116, 886, 734, 700 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{C}_{44}\text{H}_{55}\text{O}_2^+$ ($[\text{M}+\text{H}]^+$) 615.4197, found 615.4194.



^{13}C NMR, 126 MHz, Chloroform-*d*, Tautomer **S17**





(S18) (S,Z)-2,6-di-tert-butyl-4-(4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-bis(4-(methylthio)phenyl)but-3-en-1-ylidene)cyclohexa-2,5-dien-1-one

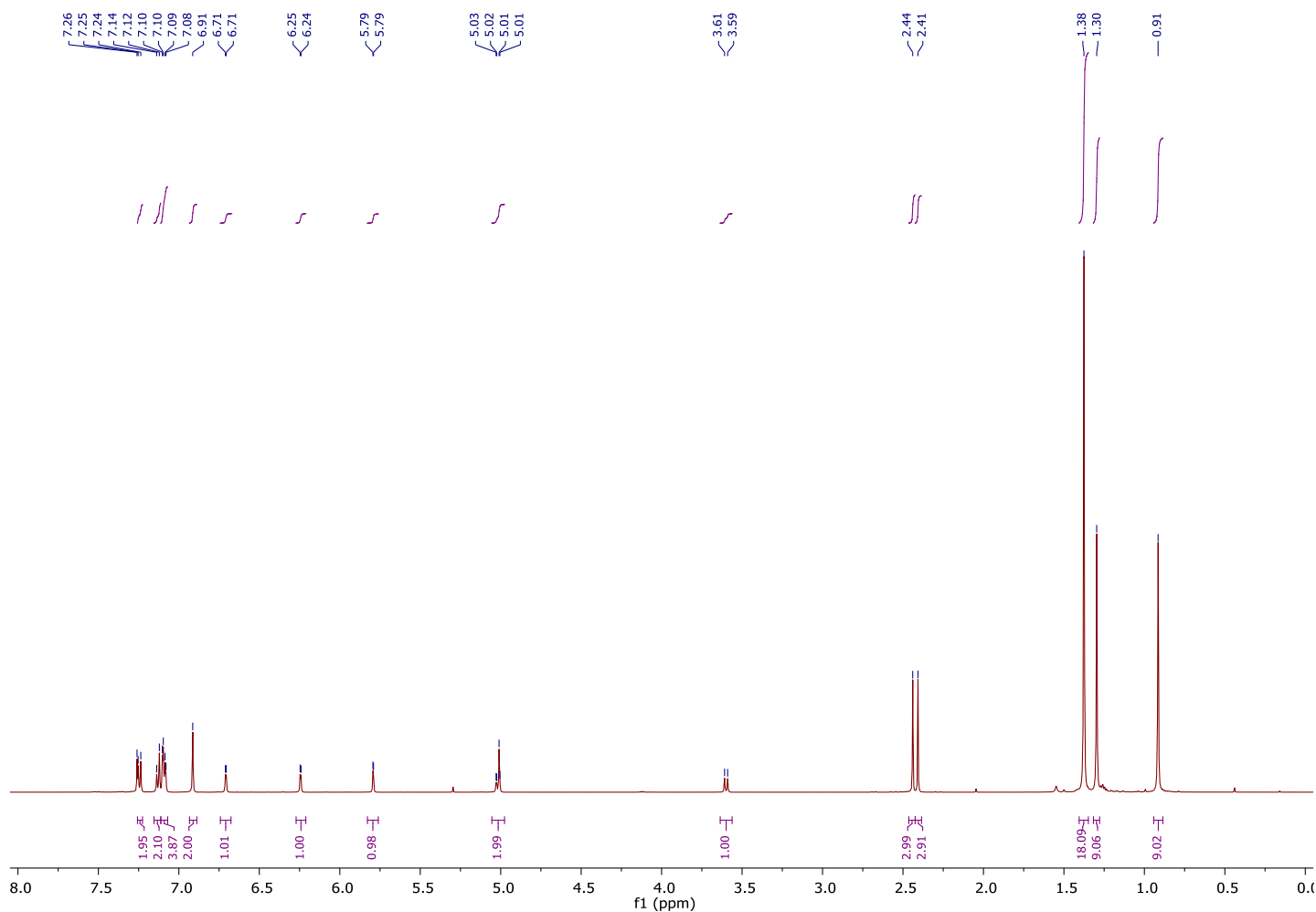
Dimer **13** (0.021 mmol, 15 mg) was subjected to the tautomerization conditions, and the crude product was purified by flash column chromatography (10-50% DCM/Hexanes) to afford MQM **S18** (14.8 mg, 99% yield).

$^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.24 (d, $J = 8.2$ Hz, 2H), 7.13 (d, $J = 8.2$ Hz, 2H), 7.10 (d, $J = 8.2$ Hz, 2H), 7.09 (d, $J = 8.2$ Hz, 2H), 6.91 (s, 2H), 6.71 (d, $J = 2.7$ Hz, 1H), 6.24 (d, $J = 2.7$ Hz, 1H), 5.79 (d, $J = 1.9$ Hz, 1H), 5.02 (dd, $J = 9.2, 2.0$ Hz, 1H), 5.01 (s, 1H), 3.60 (d, $J = 9.6$ Hz, 1H), 2.44 (s, 3H), 2.41 (s, 3H), 1.38 (s, 18H), 1.30 (s, 9H), 0.91 (s, 9H).

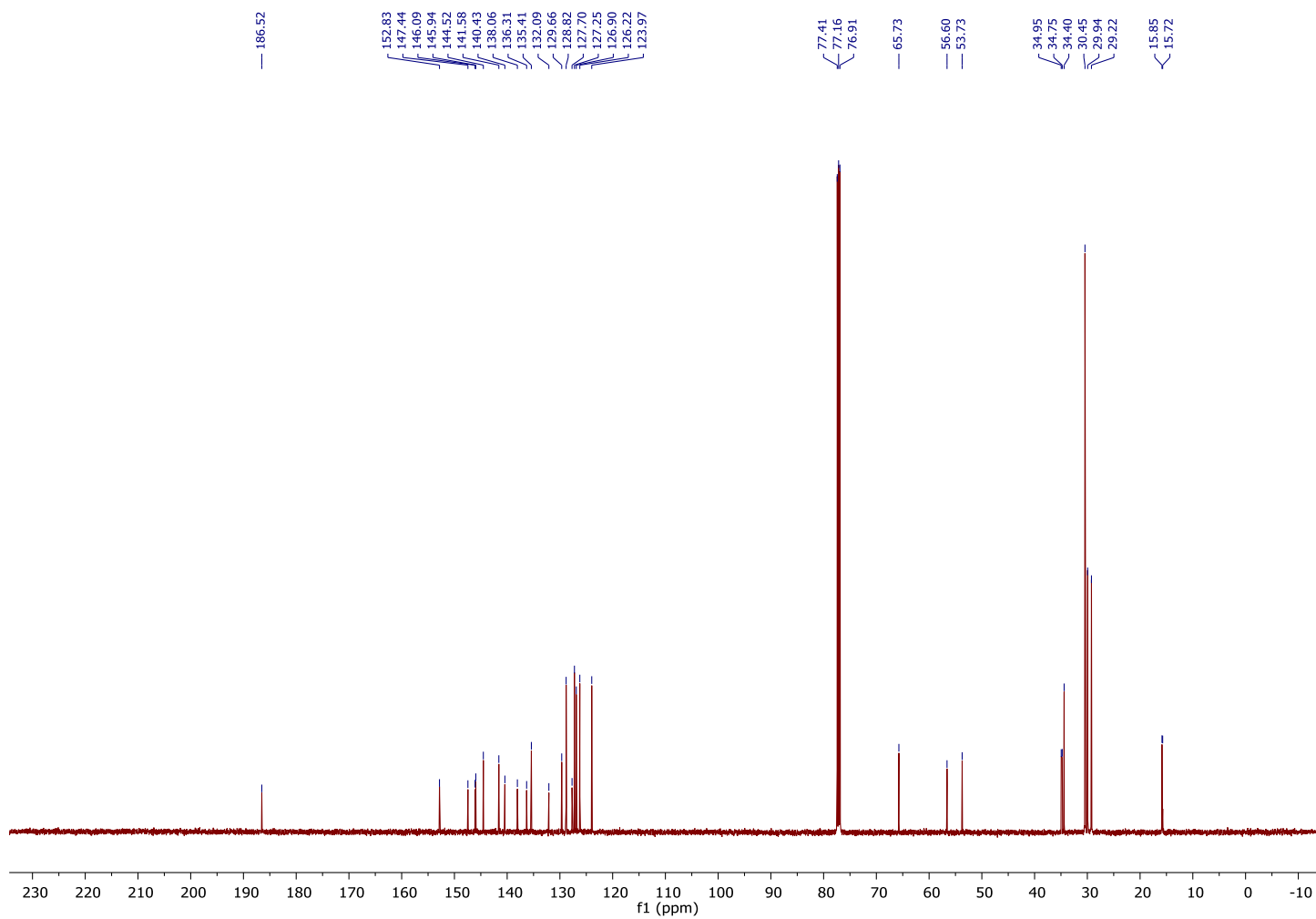
$^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 186.52, 152.83, 147.44, 146.09, 145.94, 144.52, 141.58, 140.43, 138.06, 136.31, 135.41, 132.09, 129.66, 128.82, 127.70, 127.25, 126.90, 126.22, 123.97, 65.73, 56.60, 53.73, 34.95, 34.75, 34.40, 30.45, 29.94, 29.22, 15.85, 15.72.

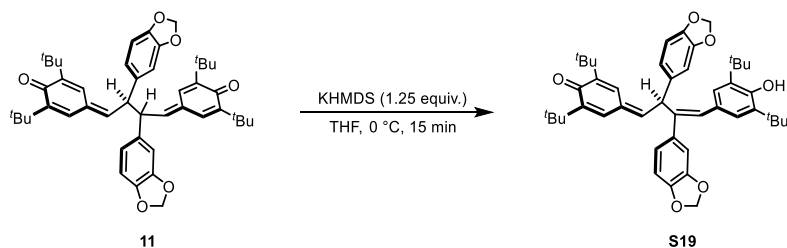
IR (Neat): 3645, 2960, 1659, 1496, 1439, 1363, 1316, 1237, 1150, 1094, 891, 814, 728 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{C}_{46}\text{H}_{59}\text{O}_2\text{S}_2^+$ ($[\text{M}+\text{H}]^+$) 707.3951, found 707.3940.



^{13}C NMR, 126 MHz, Chloroform-*d*, Tautomer **S18**





(S19) (S,Z)-4-(2,3-bis(benzo[*d*][1,3]dioxol-5-yl)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)but-3-en-1-ylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one

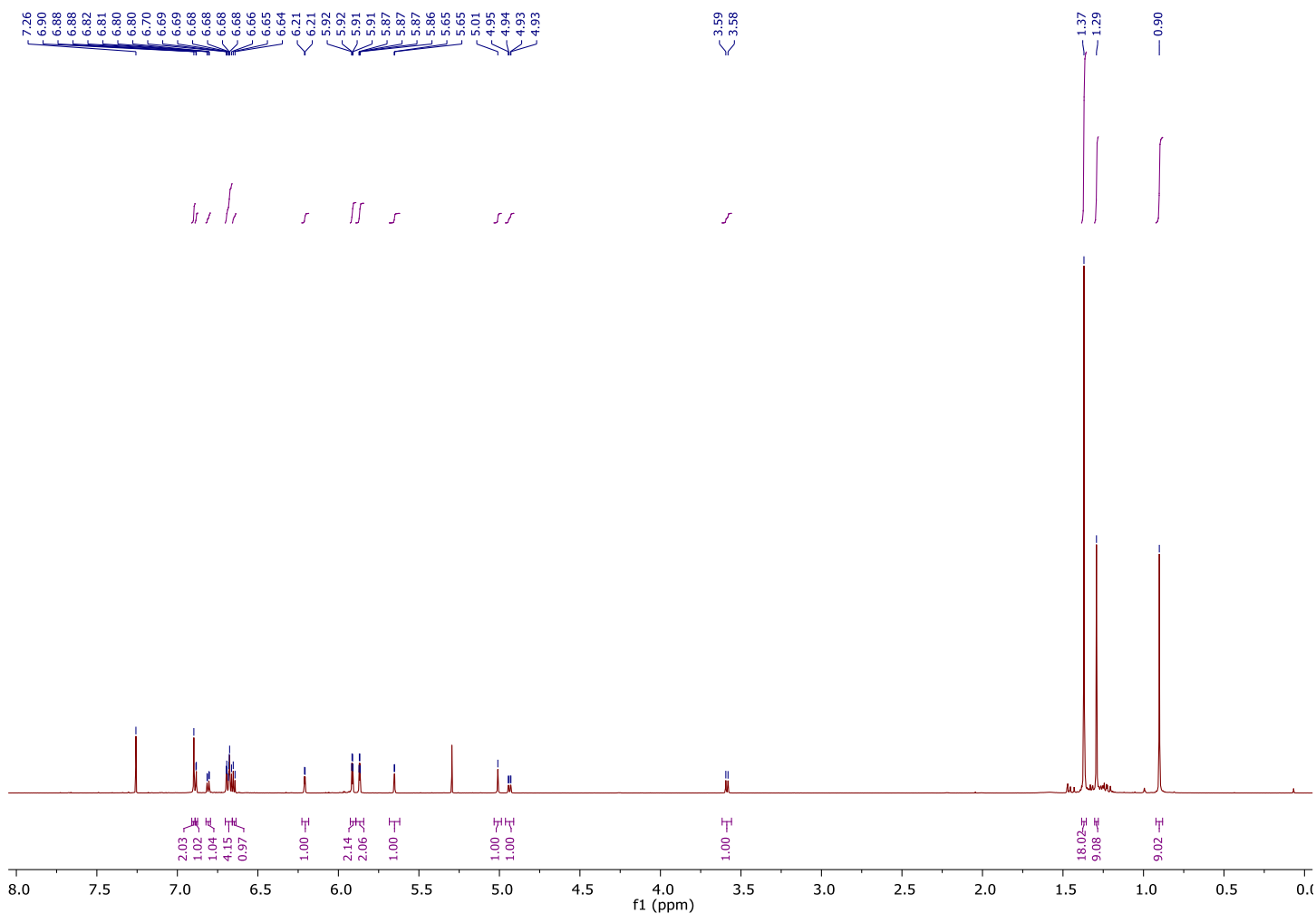
Dimer **11** (0.021 mmol, 14.7 mg) was subjected to the tautomerization conditions, and the crude product was purified by flash column chromatography (10–50% DCM/Hexanes) to afford MQM **S19** (9 mg, 61% yield).

^1H NMR (700 MHz, Chloroform-*d*) δ 6.90 (s, 2H), 6.88 (d, $J = 1.8$ Hz, 1H), 6.81 (dd, $J = 8.1, 1.8$ Hz, 1H), 6.70 – 6.66 (m, 4H), 6.65 (d, $J = 7.8$ Hz, 1H), 6.21 (d, $J = 2.7$ Hz, 1H), 5.93 – 5.89 (m, 2H), 5.89 – 5.84 (m, 2H), 5.65 (d, $J = 1.9$ Hz, 1H), 5.01 (s, 1H), 4.94 (dd, $J = 9.5, 2.0$ Hz, 1H), 3.59 (d, $J = 9.5$ Hz, 1H), 1.37 (s, 18H), 1.29 (s, 9H), 0.90 (s, 9H).

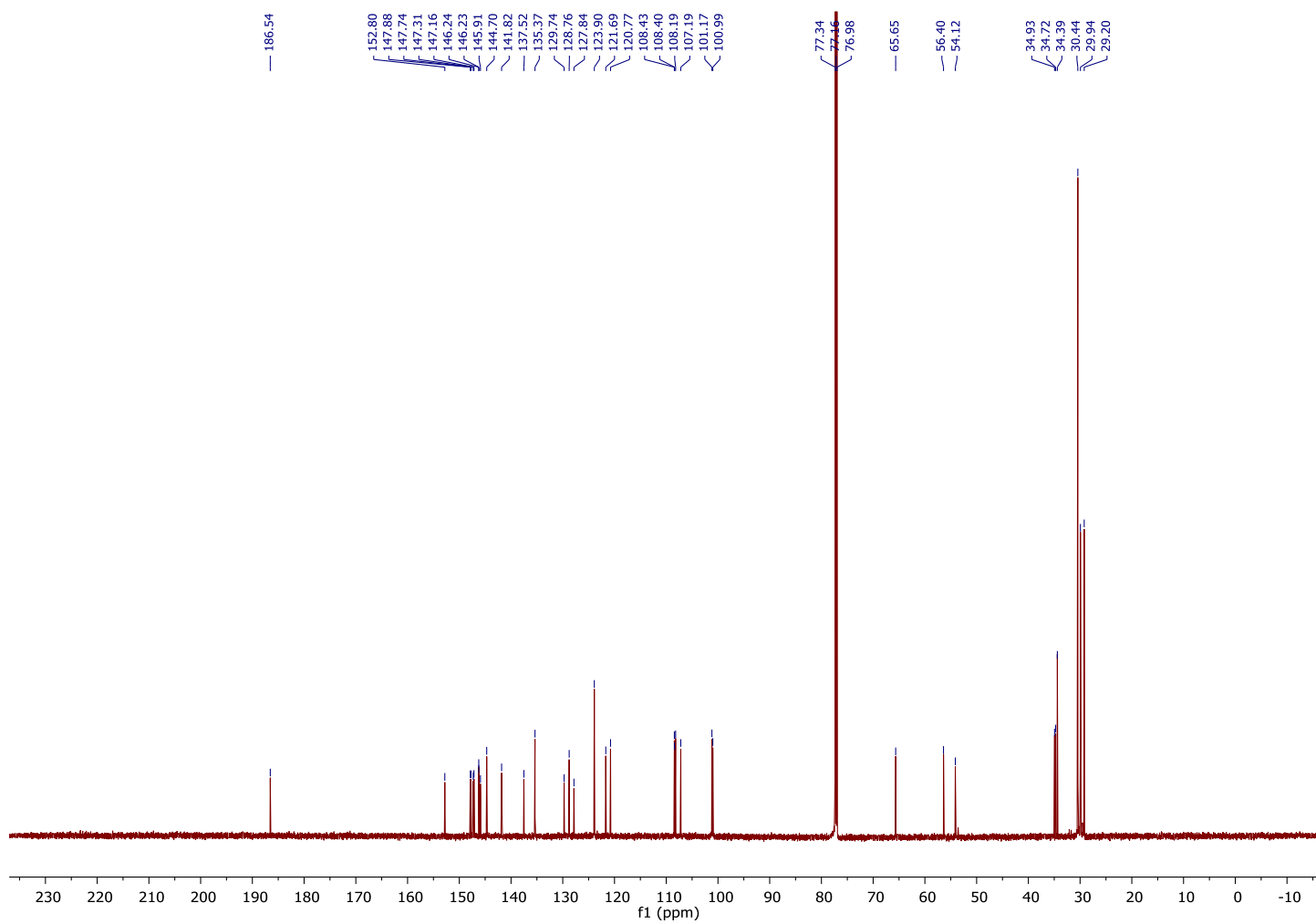
^{13}C NMR (176 MHz, Chloroform-*d*) δ 186.54, 152.80, 147.88, 147.74, 147.31, 147.16, 146.24, 146.23, 145.91, 144.70, 141.82, 137.52, 135.37, 129.74, 128.76, 127.84, 123.90, 121.69, 120.77, 108.43, 108.40, 108.19, 107.19, 101.17, 100.99, 65.65, 56.40, 54.12, 34.93, 34.72, 34.39, 30.44, 29.94, 29.20.

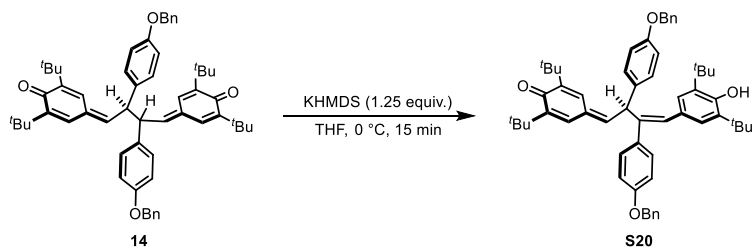
IR (Neat): 3628, 2955, 2905, 1653, 1635, 1503, 1436, 1363, 1235, 1038, 933, 809, 729 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{C}_{46}\text{H}_{55}\text{O}_6^+$ ($[\text{M}+\text{H}]^+$) 703.3993, found 703.3985.



^{13}C NMR, 176 MHz, Chloroform-*d*, Tautomer **S19**





(S20) (S,Z)-4-(2,3-bis(4-(benzyloxy)phenyl)-4-(3,5-di-*tert*-butyl-4-hydroxyphenyl)but-3-en-1-ylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one

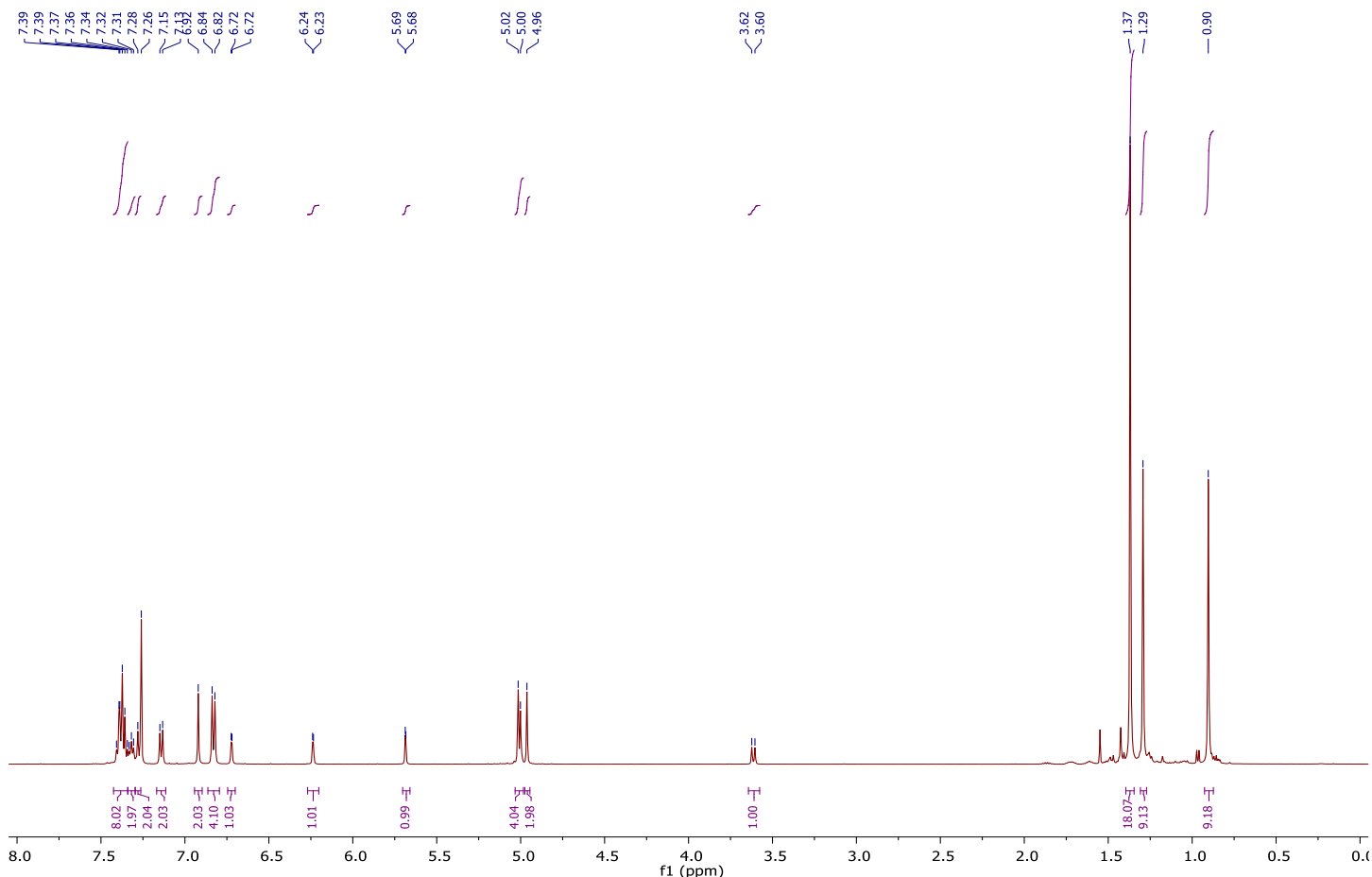
Dimer **14** (0.087 mmol, 72 mg) was subjected to the tautomerization conditions, and the crude product was purified by flash column chromatography (5–35% DCM/Hexanes) to afford MQM **S20** (50 mg, 69% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.38 (m, 8H), 7.32 (m, 2H), 7.28 (m, 2H), 7.14 (d, $J = 8.3$ Hz, 2H), 6.92 (s, 2H), 6.83 (d, $J = 8.3$ Hz, 4H), 6.72 (d, $J = 2.6$ Hz, 1H), 6.24 (d, $J = 2.6$ Hz, 1H), 5.69 (d, $J = 1.9$ Hz, 1H), 5.01 (m, 4H), 4.96 (s, 2H), 3.61 (d, $J = 9.5$ Hz, 1H), 1.37 (s, 18H), 1.29 (s, 9H), 0.90 (s, 9H).

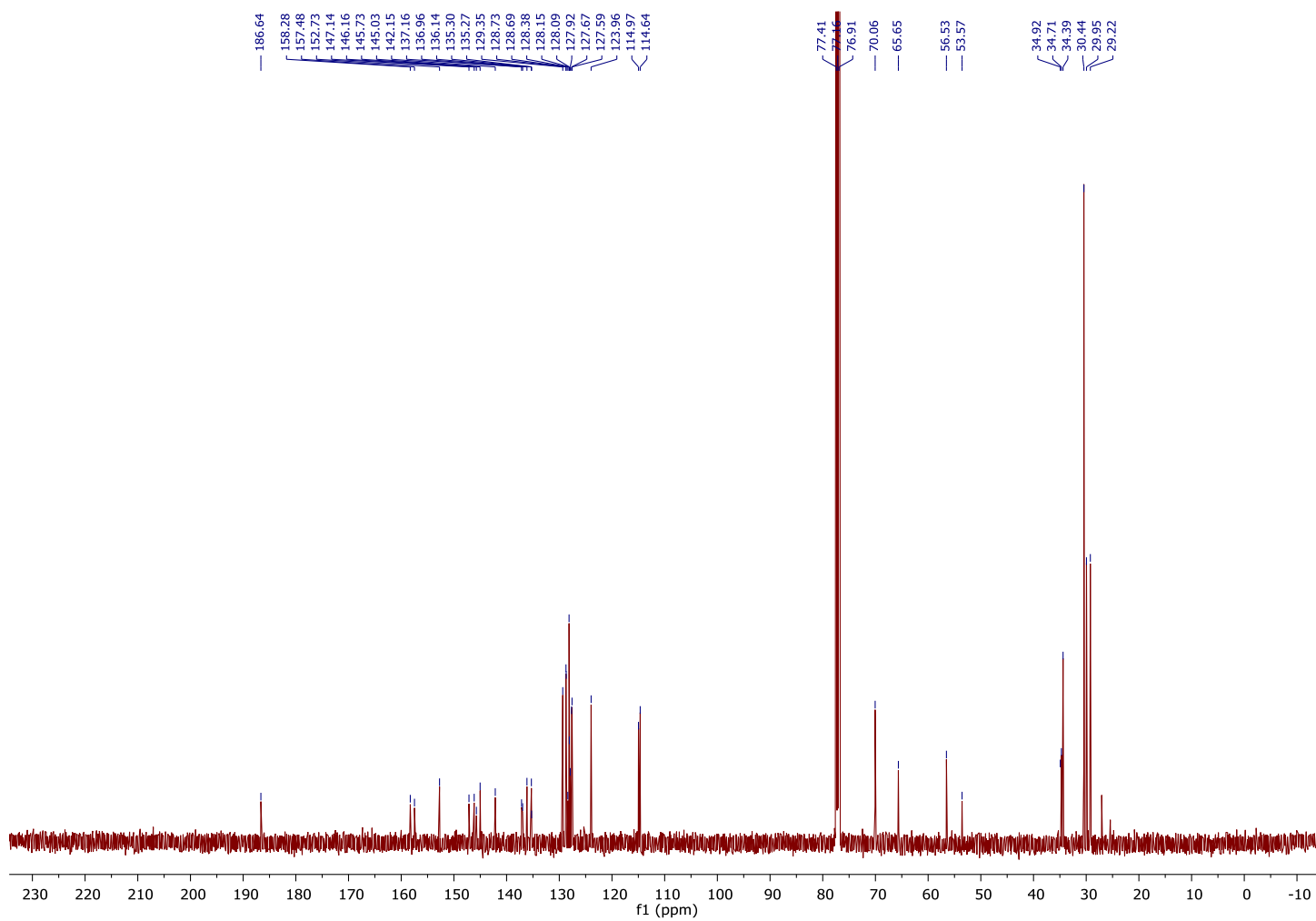
^{13}C NMR (126 MHz, Chloroform-*d*) δ 186.64, 158.28, 157.48, 152.73, 147.14, 146.16, 145.73, 145.03, 142.15, 137.16, 136.96, 136.14, 135.30, 135.27, 129.35, 128.73, 128.69, 128.38, 128.36, 128.15, 128.09, 127.92, 127.67, 127.59, 123.96, 114.97, 114.64, 70.06 (2C), 65.65, 56.53, 53.57, 34.92, 34.71, 34.39, 30.44, 29.95, 29.22.

IR (Neat): 3635, 2959, 2869, 1656, 1507, 1454, 1433, 1364, 1228, 1178, 1120, 1027, 886, 732, 695 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{C}_{58}\text{H}_{67}\text{O}_4^+$ ($[\text{M}+\text{H}]^+$) 827.5034, found 827.5010.

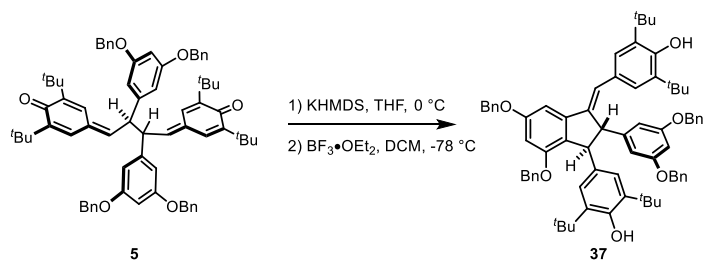


^{13}C NMR, 176 MHz, Chloroform-*d*, Tautomer **S20**



Cyclization of MQM dimer to quadrangularin A core:

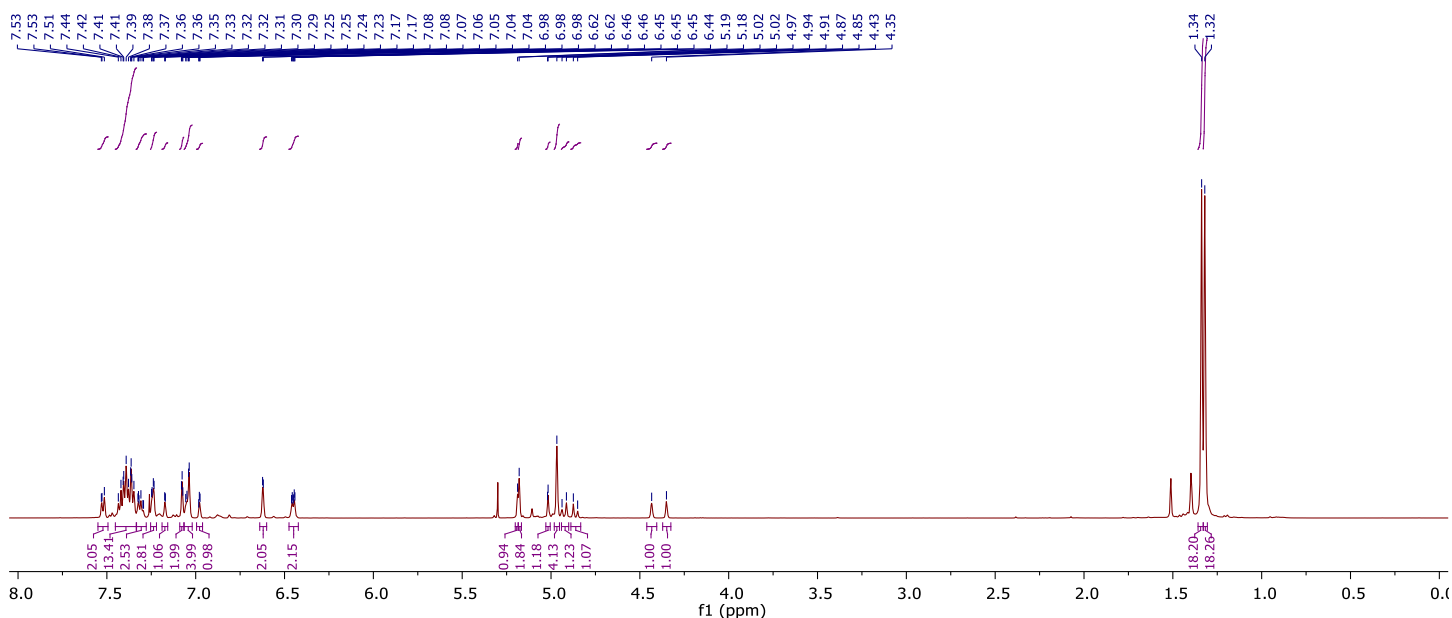
The starting material was dried down into a flame-dried round bottom flask charged with stir bar. The atmosphere was evacuated and replaced with N₂, and the starting material was dissolved in CH₂Cl₂ (0.01 M reaction concentration). The solution was cooled to the reaction temperature, and BF₃•OEt₂ (2 equiv.) was added dropwise. The reaction was allowed to stir for 3 hours, at which point it was raised from the ice bath and quenched via the addition of saturated NaHCO₃. Once the reaction had thawed, it was poured into a separatory funnel, and the layers were separated. The aqueous layer was extracted with additional portions of CH₂Cl₂, and the combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography.

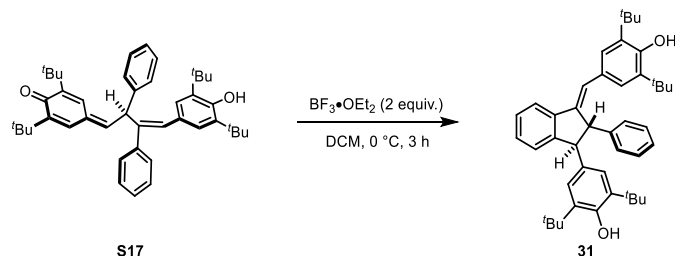


(30) 4-((1*S*,2*S*)-5,7-bis(benzyloxy)-2-(3,5-bis(benzyloxy)phenyl)-3-((*E*)-3,5-di-*tert*-butyl-4-hydroxybenzylidene)-2,3-dihydro-1*H*-inden-1-yl)-2,6-di-*tert*-butylphenol

BQM **5** (500 mg, 0.481 mmol) was subjected to the standard tautomerization conditions, and the crude product was subjected to the cyclization conditions at $-78\text{ }^{\circ}\text{C}$ with $\text{BF}_3 \bullet \text{OEt}_2$ (128 μL , 0.962 mmol, 2.0 equiv.). The product was purified by column chromatography (0% to 20% EtOAc in Hexanes) to afford compound **37** (452 mg, 90% yield). The ^1H NMR spectrum was consistent with the prior report for this compound.¹

^1H NMR (500 MHz, Chloroform-*d*) δ 7.55 – 7.49 (m, 2H), 7.45 – 7.33 (m, 13H), 7.33 – 7.28 (m, 3H), 7.24 (t, $J = 2.8$ Hz, 3H), 7.19 – 7.16 (m, 1H), 7.08 (d, $J = 1.8$ Hz, 2H), 7.05 (dd, $J = 7.2, 2.7$ Hz, 4H), 6.98 (t, $J = 1.9$ Hz, 1H), 6.62 (d, $J = 2.1$ Hz, 2H), 6.45 (dt, $J = 5.4, 2.0$ Hz, 2H), 5.19 (s, 1H), 5.18 (s, 2H), 5.02 (d, $J = 1.6$ Hz, 1H), 4.97 (s, 4H), 4.93 (d, $J = 12.4$ Hz, 1H), 4.86 (d, $J = 12.0$ Hz, 1H), 4.43 (s, 1H), 4.35 (s, 1H), 1.34 (s, 18H), 1.32 (s, 18H).





(31) 2,6-di-tert-butyl-4-((1*S*,2*S*)-3-((*E*)-3,5-di-tert-butyl-4-hydroxybenzylidene)-2-phenyl-2,3-dihydro-1*H*-inden-1-yl)phenol

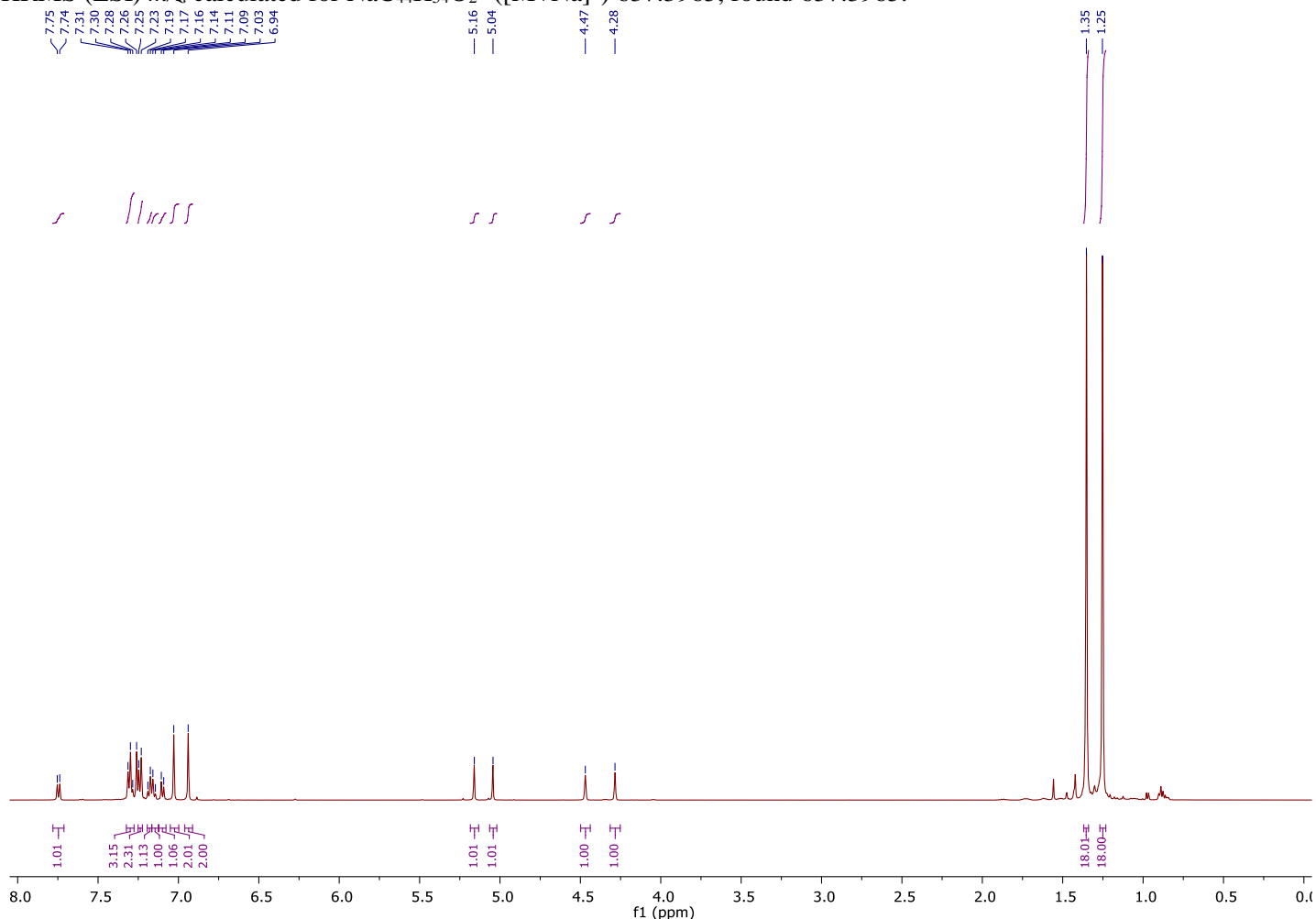
Compound **S17** (330 mg, 0.537 mmol) was subjected to the standard cyclization conditions at 0 °C with $\text{BF}_3 \cdot \text{OEt}_2$ (0.132 mL, 1.07 mmol), and the crude product was purified by column chromatography (3%, 6%, 9%, 12%, 17%, 26%, 37%, 51%, DCM/Hexanes, 2 CV per step) to afford compound **31** (154 mg, 47% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.75 (d, $J = 7.7$ Hz, 1H), 7.31 (m, 3H), 7.24 (d, $J = 7.9$ Hz, 2H), 7.18 (d, $J = 7.9$ Hz, 1H), 7.15 (d, $J = 7.9$ Hz, 1H), 7.10 (d, $J = 7.5$ Hz, 1H), 7.03 (s, 2H), 6.94 (s, 2H), 5.16 (s, 1H), 5.04 (s, 1H), 4.47 (s, 1H), 4.28 (s, 1H), 1.35 (s, 18H), 1.25 (s, 18H).

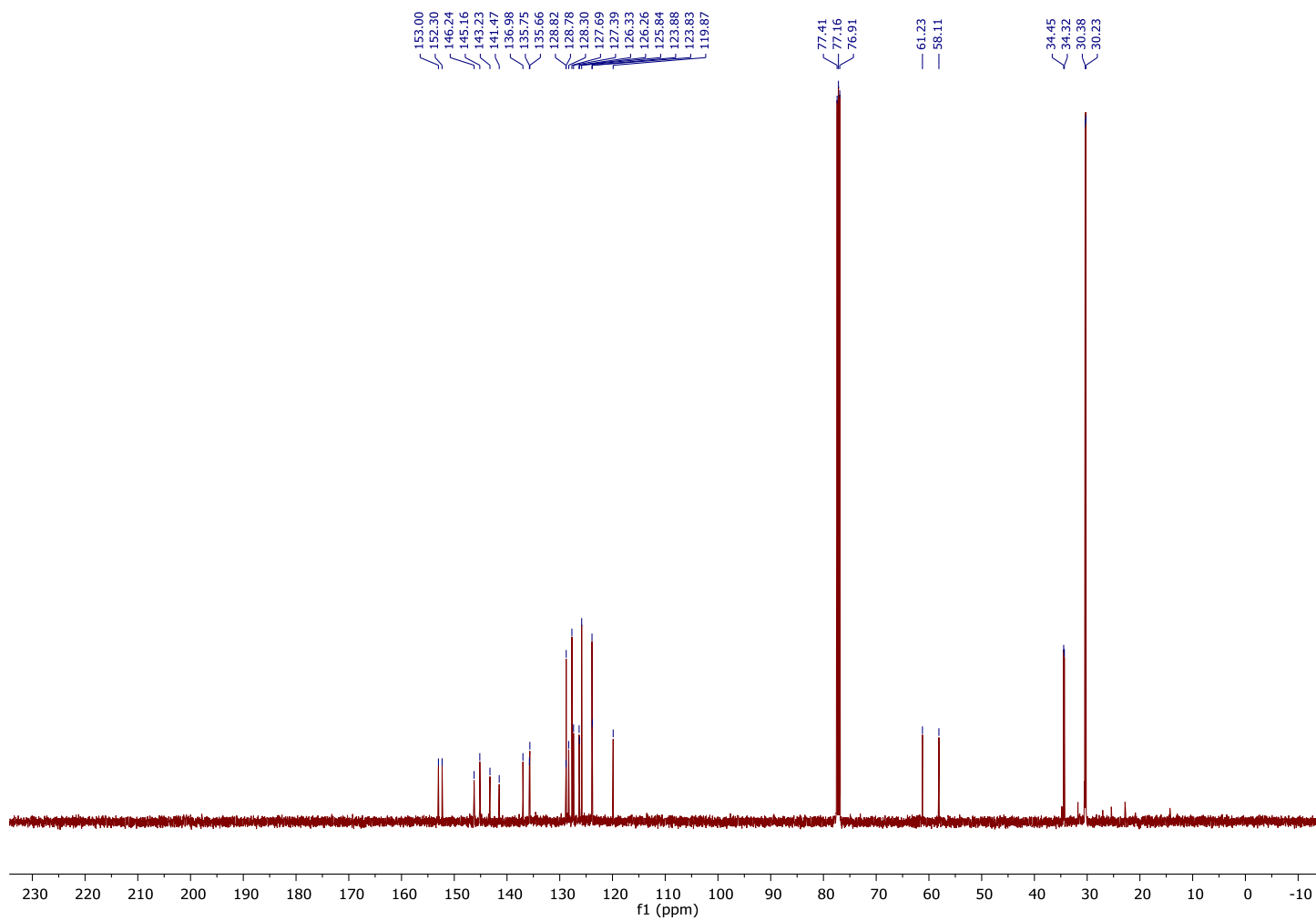
^{13}C NMR (126 MHz, Chloroform-*d*) δ 153.00, 152.30, 146.24, 145.16, 143.23, 141.47, 136.98, 135.75, 135.66, 128.82, 128.78, 128.30, 127.69, 127.39, 126.33, 126.26, 125.84, 123.88, 123.83, 119.87, 61.23, 58.11, 34.45, 34.32, 30.38, 30.23.

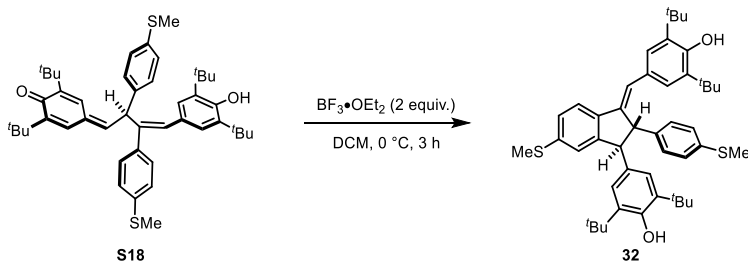
IR (Neat): 3616, 2953, 1470, 1311, 1235, 1137, 957, 767, 694 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{NaC}_{44}\text{H}_{54}\text{O}_2^+$ ($[\text{M}+\text{Na}]^+$) 637.3965, found 637.3965.



^{13}C NMR, 176 MHz, Chloroform-*d*, Analog Core **31**





(32) 2,6-di-*tert*-butyl-4-((1*S*,2*S*)-3-((*E*)-3,5-di-*tert*-butyl-4-hydroxybenzylidene)-6-(methylthio)-2-(4-(methylthio)phenyl)-2,3-dihydro-1*H*-inden-1-yl)phenol

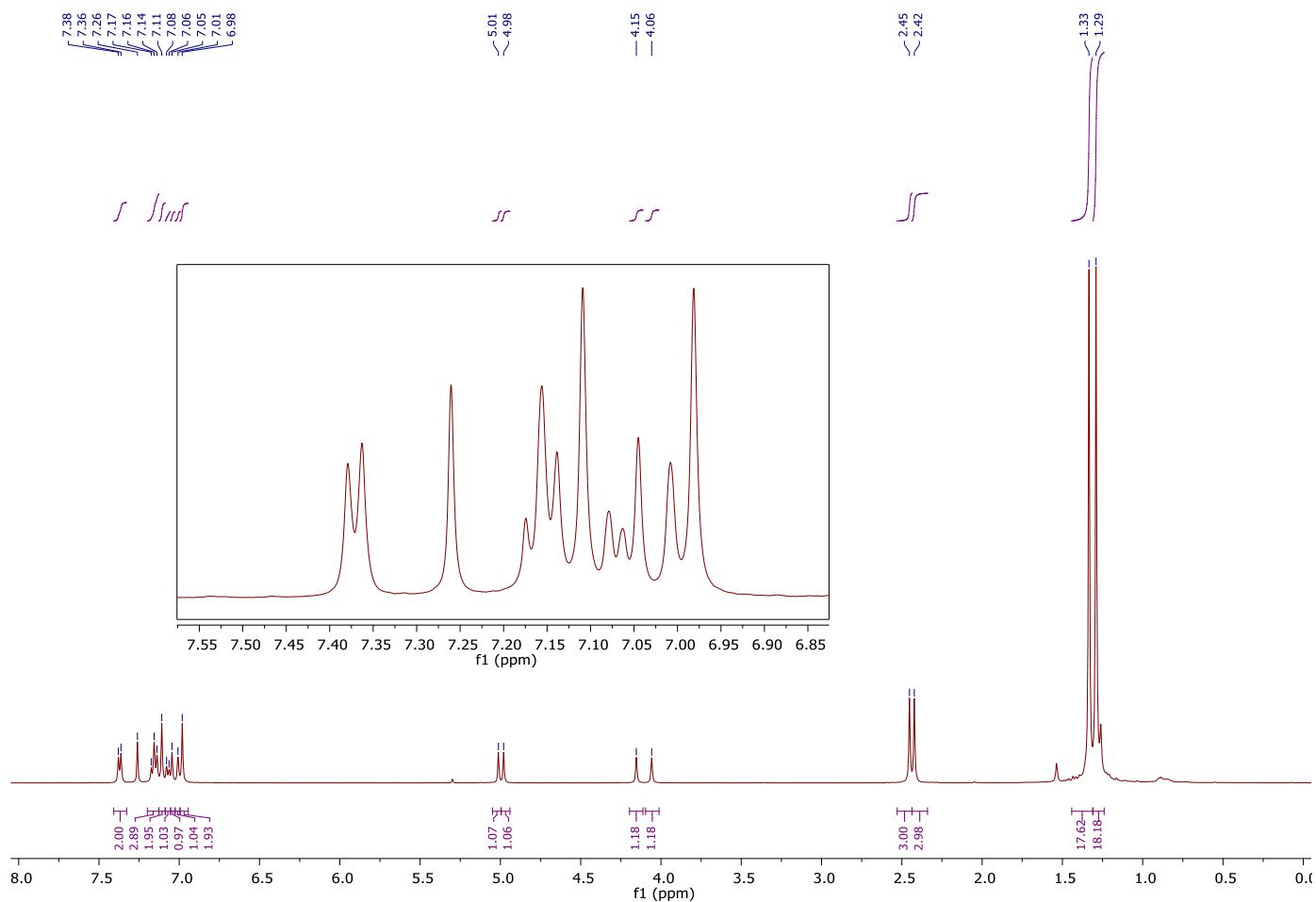
Compound **S18** (96 mg, 0.136 mmol) was subjected to the standard cyclization conditions at 0 °C with $\text{BF}_3 \cdot \text{OEt}_2$ (0.034 mL, 0.27 mmol), and the crude product was purified by column chromatography (10% to 50% DCM/Hexanes) to afford compound **32** (59 mg, 62% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.37 (d, $J = 8.1$ Hz, 2H), 7.16 (m, 3H), 7.11 (s, 2H), 7.07 (d, $J = 7.9$ Hz, 1H), 7.05 (s, 1H), 7.01 (s, 1H), 6.98 (s, 2H), 5.01 (s, 1H), 4.98 (s, 1H), 4.15 (s, 1H), 4.06 (s, 1H), 2.45 (s, 3H), 2.42 (s, 3H), 1.33 (s, 18H), 1.29 (s, 18H).

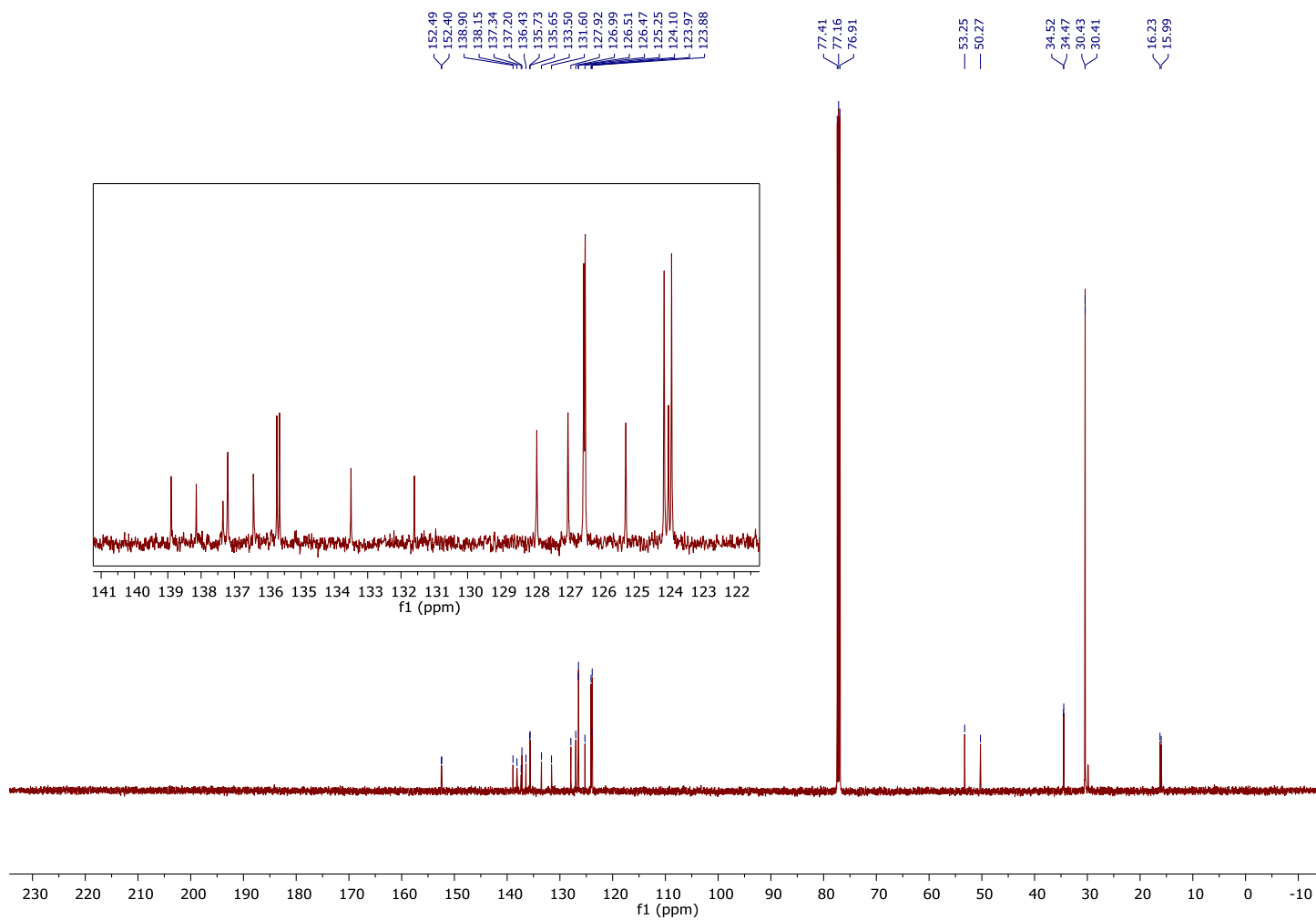
^{13}C NMR (126 MHz, Chloroform-*d*) δ 152.49, 152.40, 138.90, 138.15, 137.34, 137.20, 136.43, 135.73, 135.65, 133.50, 131.60, 127.92, 126.99, 126.51, 126.47, 125.25, 124.10, 123.97, 123.88, 53.25, 50.27, 34.52, 34.47, 30.43, 30.41, 16.23, 15.99.

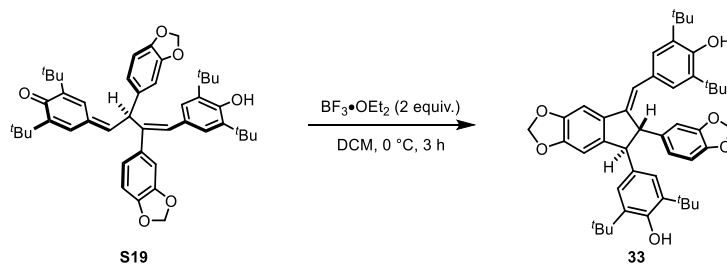
IR (Neat): 3614, 2957, 2920, 1597, 1434, 1240, 1150, 1119, 883, 821, 790, 765 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{C}_{46}\text{H}_{58}\text{O}_2\text{S}_2^+$ ($[\text{M}]^+$) 706.3873, found 706.3872.



^{13}C NMR, 126 MHz, Chloroform-*d*, Analog Core **32**





(33) 4-((1*S*,2*S*)-6-(benzyloxy)-2-(4-(benzyloxy)phenyl)-3-((*E*)-3,5-di-*tert*-butyl-4-hydroxybenzylidene)-2,3-dihydro-1*H*-inden-1-yl)-2,6-di-*tert*-butylphenol

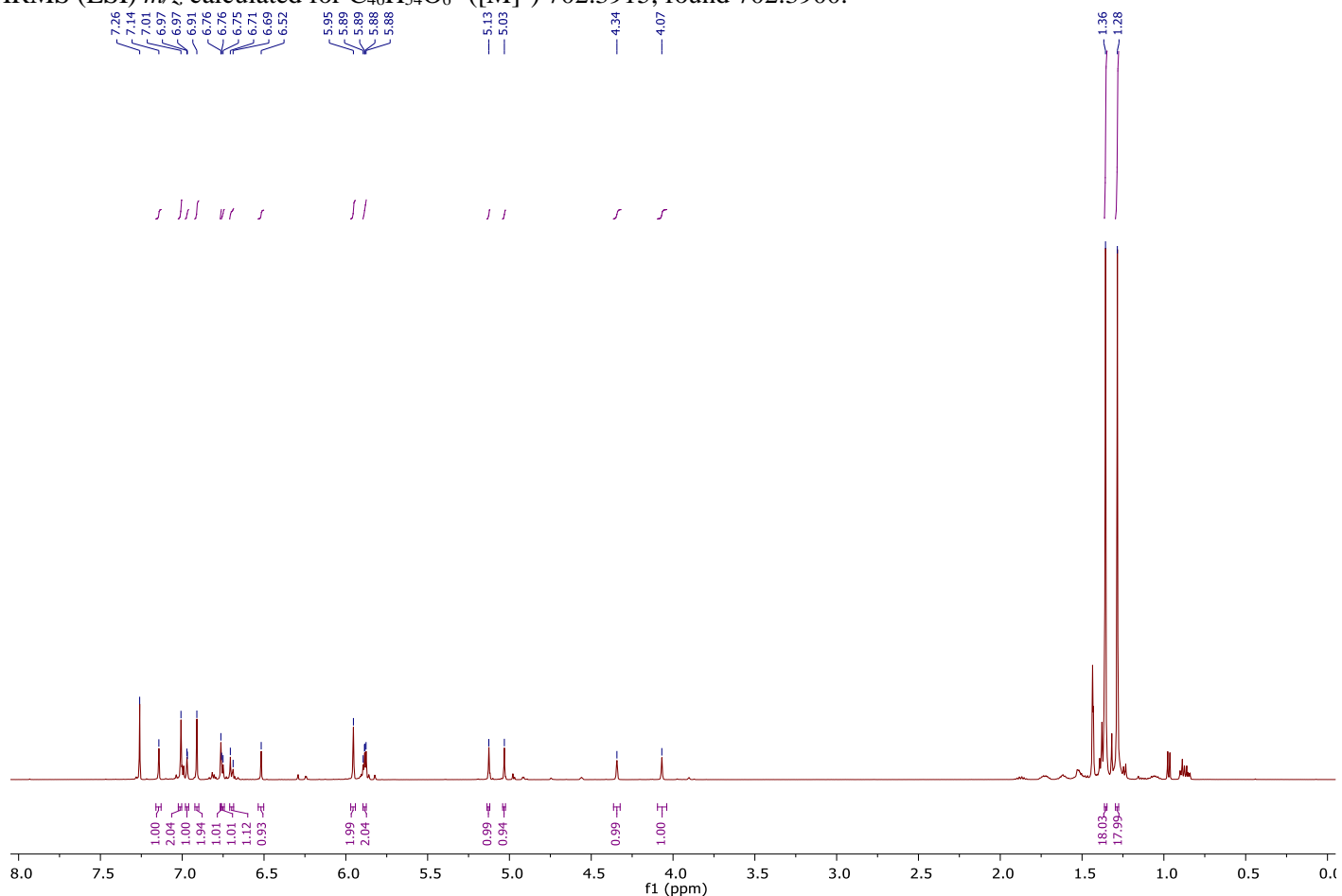
Compound **S19** (102 mg, 0.145 mmol) was subjected to the standard cyclization conditions at 0 °C with $\text{BF}_3 \cdot \text{OEt}_2$ (0.036 mL, 0.29 mmol), and the crude product was purified by column chromatography (10% to 50% DCM/Hexanes) to afford compound **33** (65 mg, 64% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.14 (s, 1H), 7.01 (s, 2H), 6.97 (d, $J = 1.4$ Hz, 1H), 6.91 (s, 2H), 6.76 (s, 1H), 6.75 (d, $J = 4.6$ Hz, 1H), 6.70 (d, $J = 8.4$ Hz, 1H), 6.52 (s, 1H), 5.95 (s, 2H), 5.88 (dd, $J = 5.2, 3.7$ Hz, 2H), 5.13 (s, 1H), 5.03 (s, 1H), 4.34 (s, 1H), 4.07 (s, 1H), 1.36 (s, 18H), 1.28 (s, 18H).

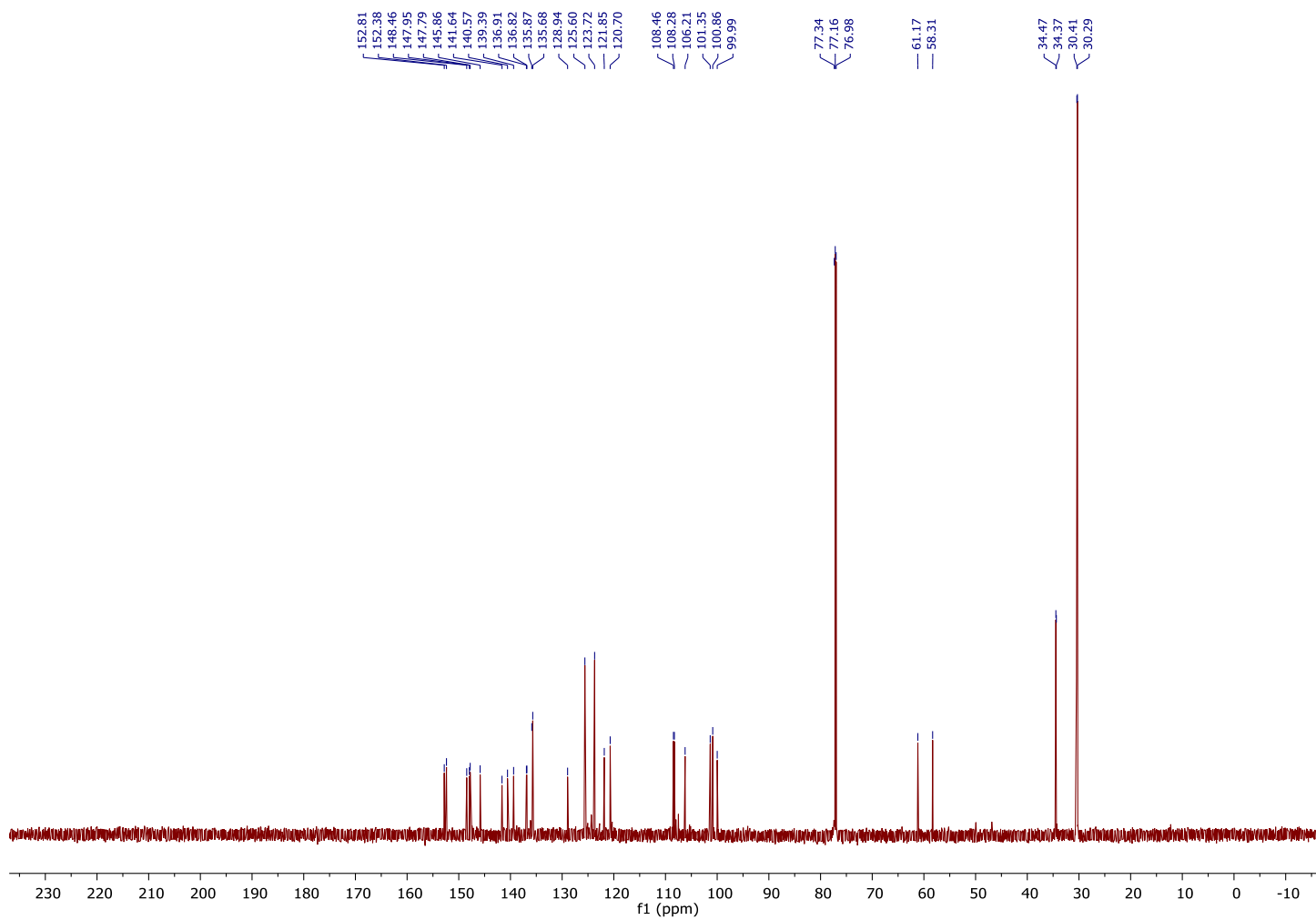
^{13}C NMR (176 MHz, Chloroform-*d*) δ 152.81, 152.38, 148.46, 147.95, 147.79, 145.86, 141.64, 140.57, 139.39, 136.91, 136.82, 135.87, 135.68, 128.94, 125.60, 123.72, 121.85, 120.70, 108.46, 108.28, 106.21, 101.35, 100.86, 99.99, 61.17, 58.31, 34.47, 34.37, 30.41, 30.29.

IR (Neat): 3634, 2957, 2912, 1476, 1431, 1231, 1150, 1035, 936, 737 cm^{-1} ;

HRMS (ESI) m/z calculated for $\text{C}_{46}\text{H}_{54}\text{O}_6^+$ ($[\text{M}]^+$) 702.3915, found 702.3900.



^{13}C NMR, 176 MHz, Chloroform-*d*, Analog Core **33**



Analysis of Radical-Trapping Antioxidant Activity:

Kinetic Data

General Procedure for Inhibited Autoxidations

The inhibited autoxidations were carried out following our reported method.⁹ All autoxidations of 1-hexadecene (2.9 M) and PBD-BODIPY (10 μ M) were initiated by AIBN (6 mM) in chlorobenzene at 37 °C. A 3.5-mL quartz cuvette was charged with PhCl (0.44 mL), 1-hexadecene (2.00 mL). The cuvette was preheated to 37 °C in a thermostatted sample holder of a UV-vis spectrophotometer and allowed to equilibrate for approximately 15 min. To the cuvette was added PBD-BODIPY (12.5 μ L of a 2.00 mM stock solution in 1,2,4-trichlorobenzene) and AIBN (50 μ L of a 300 mM stock solution in chlorobenzene). The solution was thoroughly mixed prior to monitoring the uninhibited co-autoxidation via the disappearance of the PBD-BODIPY probe at 588 nm for 10 min to ensure the reaction was proceeding at a constant rate. Finally, the antioxidant under investigation was added (5.0 μ L of a 2.5 mM solution in chlorobenzene), the solution was mixed thoroughly, and the absorbance readings were resumed. The resulting Abs vs time data were processed as previously reported.⁹ The rate of initiation ($R_i = 1.3 \times 10^{-9} \text{ M s}^{-1}$) and second order rate constant for propagation for the dye ($k_{\text{PBD-BODIPY}} = 3792 \text{ M}^{-1} \text{ s}^{-1}$) necessary to compute stoichiometric data (n) and inhibition rate constants (k_{inh}) were determined using PMC as a standard, which has an established stoichiometry of 2.^{10,11}

Table S2. Comparison of inhibition rate constants (k_{inh}) and stoichiometry (n) during inhibited co-autoxidations of 1-hexadecene (2.9 M) and PBD-BODIPY (10 μ M) initiated by AIBN (6 mM) in chlorobenzene at 37 °C.

X	<i>Quadrangularin A analogues</i>		<i>Quinone methide dimers</i>		<i>Parent phenols</i>				
	k_{inh} ($10^5 \text{ M}^{-1} \text{ s}^{-1}$)	n	k_{inh} ($10^5 \text{ M}^{-1} \text{ s}^{-1}$)	n	k_{inh} ($10^5 \text{ M}^{-1} \text{ s}^{-1}$)	n			
4-CF ₃	N/A	N/A	20	24 \pm 1	1.4 \pm 0.1	S14	1.3 \pm 0.1	2.3 \pm 0.1	
3,5-diOBn	30	1.1 \pm 0.1	3.8 \pm 0.3	5	19 \pm 5	1.7 \pm 0.1	10	1.4 \pm 0.1	2.3 \pm 0.1
H	31	1.0 \pm 0.1	4.1 \pm 0.3	10	20 \pm 1	1.4 \pm 0.1	S4	1.6 \pm 0.1	2.0 \pm 0.1
4-SMe	32	0.8 \pm 0.1	3.8 \pm 0.1	13	29 \pm 1	1.3 \pm 0.1	S7	1.7 \pm 0.1	2.2 \pm 0.1
3,4-dioxy	33	1.3 \pm 0.2	4.1 \pm 0.1	11	31 \pm 4	1.3 \pm 0.1	S5	1.9 \pm 0.3	2.1 \pm 0.1

Computational Data¹²

Table S3. Summary of enthalpies (ΔH , ΔH^\ddagger), free energies (ΔG , ΔG^\ddagger), and corresponding computed second order rate constants (k) for the addition of methyl peroxy radical to or hydrogen atom transfer (HAT) from a truncated analogue of **14** in the gas phase at 37 °C.

<i>Mechanism</i>	<i>Position</i>	ΔH , (<i>kcal mol⁻¹</i>)	ΔG , (<i>kcal mol⁻¹</i>)	ΔH^\ddagger , (<i>kcal mol⁻¹</i>)	ΔG^\ddagger , (<i>kcal mol⁻¹</i>)	k^a (<i>M⁻¹s⁻¹</i>)
HAT	C _β -H	-15.7	-15.3	7.5	19.0	6
Addition	C _α	-31.5	-19.4	-1.7	10.8	4 × 10 ⁶

^a Computed using $k = \frac{RT}{P} \cdot \frac{k_B T}{h} e^{\frac{-\Delta G^\ddagger}{RT}}$ where T = 310.15 K.

Optimized Gaussian Structures and CBS-QB3¹³ or DFT Energies (Hartree)

Methyl peroxy radical

H₃COO•

CBS-QB3 Enthalpy = -189.954731 CBS-QB3 Free Energy = -189.985243

0 2

C	1.09605900	-0.18318300	0.00000000
H	1.87467700	0.57860700	-0.00001500
H	1.14885000	-0.80070400	0.89699800
H	1.14883700	-0.80072700	-0.89698300
O	-0.15733600	0.54388600	0.00000000
O	-1.18625300	-0.27864500	0.00000000

Methyl hydroperoxide

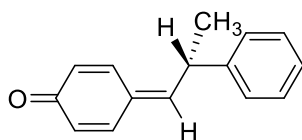
H₃COOH

CBS-QB3 Enthalpy = -190.589542 CBS-QB3 Free Energy = -190.620447

0 1

C	1.12961700	-0.22363900	0.02672600
H	1.97292100	0.47126800	0.02466400
H	1.14400500	-0.82582200	0.94203100
H	1.18954700	-0.87767200	-0.84877800
O	-0.01619300	0.60684200	-0.03138300
O	-1.16412600	-0.28550800	-0.09072600
H	-1.64161900	0.00339000	0.69859800

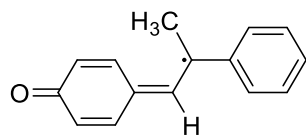
Truncated dimer



CBS-QB3 Enthalpy = -654.002976 CBS-QB3 Free Energy = -654.060994

0 1			
C	-2.28497800	0.40886900	-1.38146900
C	-3.55270400	-0.03922500	-1.32815500
C	-4.13529300	-0.56092000	-0.07890600
C	-3.23865900	-0.55847700	1.09408900
C	-1.97179800	-0.10764000	1.02679200
H	-1.87418700	0.78842400	-2.31241000
H	-4.20081500	-0.03800300	-2.19697400
H	-3.66131800	-0.94226000	2.01572400
H	-1.34982200	-0.12439600	1.91411400
C	-1.40780200	0.40947300	-0.21456200
C	-0.14133100	0.88393400	-0.33638800
H	0.15649000	1.24391200	-1.31988600
O	-5.28793700	-0.97120500	-0.01361300
C	0.93072100	0.98559600	0.71399400
C	2.15417900	0.17948500	0.27509100
C	2.43091400	-1.05007100	0.87987500
C	3.00520900	0.62664700	-0.74224100
C	3.53098300	-1.81010100	0.48913600
H	1.77888600	-1.41666800	1.66618900
C	4.10408800	-0.13185400	-1.13742500
H	2.81702700	1.57620900	-1.23132600
C	4.37188000	-1.35298100	-0.52222200
H	3.72971200	-2.75869500	0.97523300
H	4.75316900	0.23292500	-1.92573000
H	5.22845900	-1.94234200	-0.82872500
C	1.25966000	2.46665200	1.00604200
H	1.57784500	2.99577200	0.10458500
H	0.38007500	2.98079300	1.40032500
H	2.06455800	2.53733300	1.74154700
H	0.57301500	0.54030300	1.64432900

C-H HAT radical product (truncated dimer)

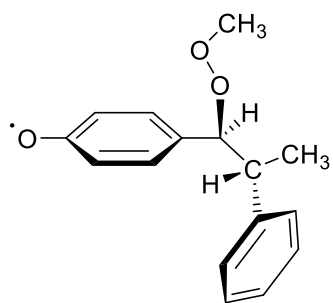


CBS-QB3 Enthalpy = -653.393246 CBS-QB3 Free Energy = -653.450284

0 2

C	1.52663700	-0.17878300	-0.06031300
C	2.26612700	1.04646900	-0.05163000
C	3.63125800	1.05609200	-0.05797800
C	4.41372500	-0.17389500	-0.07235200
C	3.64436100	-1.41088100	-0.11084300
C	2.28208000	-1.39605400	-0.11637600
H	1.74048500	1.98910300	-0.07297000
H	4.18983800	1.98508300	-0.06360700
H	4.20631700	-2.33724000	-0.13798000
H	1.73406700	-2.33262400	-0.14873300
C	0.09559100	-0.30235800	-0.05597100
H	-0.23773000	-1.30730800	-0.29735500
C	-0.90681300	0.59889900	0.18954500
C	-2.31412300	0.15072700	0.07608700
C	-3.30656300	1.03105100	-0.39201800
C	-2.71066100	-1.15268400	0.42751200
C	-4.62699500	0.61798900	-0.53178300
H	-3.03832200	2.04156900	-0.67632200
C	-4.03301100	-1.56037100	0.29989500
H	-1.98216700	-1.84097800	0.83868200
C	-4.99806500	-0.67954400	-0.18603900
H	-5.36792600	1.31206600	-0.91227100
H	-4.31363000	-2.56608300	0.59198900
H	-6.02906600	-0.99866600	-0.28584100
O	5.65560200	-0.16513300	-0.06495700
C	-0.67848700	2.04011600	0.58017800
H	0.15428900	2.12915000	1.27928800
H	-0.44885500	2.67090900	-0.28670000
H	-1.56247000	2.45544600	1.06398500

Addition radical product (truncated dimer)

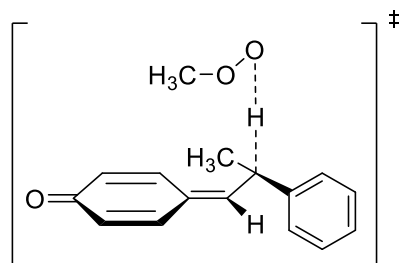


CBS-QB3 Enthalpy = -844.008115 CBS-QB3 Free Energy = -844.077218

0 2

C	1.68586100	-0.73545200	-0.94678200
C	2.03864400	-2.05690200	-1.04386900
C	1.65692100	-3.01393600	-0.01965400
C	0.89517400	-2.49267000	1.10074700
C	0.55651100	-1.16384100	1.17166500
H	1.98969400	-0.02773600	-1.70968300
H	2.61367700	-2.43783300	-1.87997300
H	0.61296200	-3.19839200	1.87314800
H	-0.01169700	-0.79243000	2.01765600
C	0.93550600	-0.26276200	0.15473600
O	1.97130500	-4.22160000	-0.09771200
O	1.58857600	2.04790200	-0.20443700
O	2.61138400	1.96629700	0.84596800
C	3.78537300	2.50236300	0.26894200
H	4.52260200	2.46789200	1.07383500
H	4.12979300	1.89716600	-0.57569200
H	3.63454500	3.53954000	-0.04808300
C	0.53023100	1.19587100	0.22243000
C	-0.67504300	1.54242800	-0.70021500
H	0.27533000	1.45818500	1.25591200
C	-1.89282900	0.70535500	-0.33377400
C	-2.36613100	-0.27753900	-1.20731200
C	-2.57489100	0.90298300	0.87332900
C	-3.48544600	-1.04383900	-0.88862100
H	-1.85000100	-0.44796500	-2.14632700
C	-3.69261200	0.13833500	1.19677100
H	-2.23685900	1.66374000	1.56895000
C	-4.15235100	-0.83895000	0.31597800
H	-3.83382500	-1.80139600	-1.58165800
H	-4.20687700	0.30800700	2.13631100
H	-5.02313000	-1.43390300	0.56681800
C	-0.98133300	3.05080000	-0.68657800
H	-1.22038800	3.40135600	0.32101200
H	-0.12719900	3.62451100	-1.04555200
H	-1.84128200	3.26025700	-1.32687200
H	-0.37898200	1.26472500	-1.71711200

C-H HAT TS (truncated dimer)



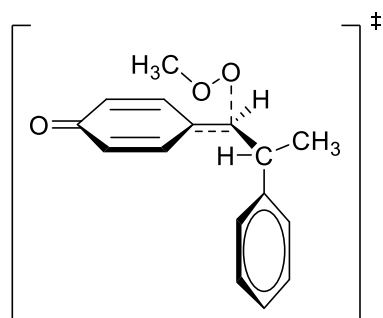
TS frequency: -1557.85 cm^{-1}

CBS-QB3 Enthalpy = -843.945793 CBS-QB3 Free Energy = -844.015840

0 2

C	2.25564500	-0.81459400	-1.31202000
C	3.59164400	-1.00867700	-1.27621500
C	4.34095000	-0.94392700	-0.01493100
C	3.53661400	-0.67398800	1.18686700
C	2.19873300	-0.47972300	1.13376700
H	1.72389600	-0.86184400	-2.25735800
H	1.65699900	-0.30200500	2.05014700
C	1.47427800	-0.52309700	-0.12151100
C	0.11527300	-0.32322000	-0.28906400
H	-0.22338500	-0.43776100	-1.31608500
O	5.55794900	-1.10835800	0.03910700
C	-0.95338200	0.11339200	0.59345900
H	-0.98829400	1.32936100	0.26126100
O	-0.99624200	2.63019100	-0.02807000
O	-0.04681900	2.76958300	-1.00881500
C	1.15191800	3.32650200	-0.45026100
H	1.58793500	2.64444600	0.28311000
H	1.82813900	3.45106200	-1.29669400
H	0.93127600	4.29146200	0.01023200
C	-0.78138600	0.19480600	2.11318300
H	-0.60022900	-0.79575900	2.54330900
H	0.03185600	0.86149900	2.40191900
H	-1.69744200	0.58282100	2.56083200
C	-2.32405400	-0.39026600	0.18827000
C	-3.44985900	0.43555600	0.30836200
C	-2.50351700	-1.70092100	-0.27188600
C	-4.71588900	-0.03568000	-0.02300300
H	-3.32776700	1.46076400	0.63874700
C	-3.77214400	-2.17439200	-0.60011000
H	-1.64639200	-2.36002900	-0.35910000
C	-4.88216500	-1.34322800	-0.47742900
H	-5.57354200	0.62163600	0.06581100
H	-3.89129700	-3.19433200	-0.94836100
H	-5.86931600	-1.70967500	-0.73514600
H	4.16560400	-1.21728600	-2.17165600
H	4.07690800	-0.64693800	2.12640000

Addition TS (truncated dimer)



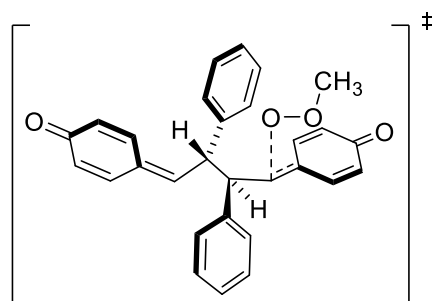
TS frequency: -343.37 cm^{-1}

CBS-QB3 Enthalpy = -843.960367 CBS-QB3 Free Energy = -844.028986

0 2

C	0.96314500	-0.76857400	-0.75517100
C	1.83634300	-1.75262400	-1.08048400
C	2.84270300	-2.24399300	-0.12820700
C	2.84016200	-1.60372700	1.19251200
C	1.96163900	-0.62042300	1.49770000
H	0.22717400	-0.43962100	-1.47830900
H	1.82743000	-2.22622800	-2.05555400
H	3.57672000	-1.95858700	1.90398000
H	1.98057100	-0.15155200	2.47654100
C	0.97599200	-0.15653500	0.55037100
O	3.63885800	-3.13567600	-0.42560300
O	1.35833300	2.52336000	0.56707000
O	1.45649800	2.81734500	-0.75543500
C	2.78161800	2.51858200	-1.22898300
H	2.79283600	2.84364900	-2.26985300
H	3.51406800	3.07645700	-0.64293800
H	2.97189500	1.44691100	-1.15775400
C	0.11111800	0.87785900	0.91263100
C	-1.10441000	1.33029600	0.13304000
H	-0.76303100	1.59726800	-0.87257200
H	0.14440000	1.17923200	1.95527200
C	-1.73255800	2.58771200	0.76472600
H	-2.57633300	2.93237100	0.16356300
H	-2.10800700	2.36997500	1.76906300
H	-0.99437700	3.38714100	0.83252300
C	-2.14961600	0.22465600	-0.01552300
C	-2.75441500	-0.00316100	-1.25515700
C	-2.56682600	-0.54188100	1.07849300
C	-3.74636600	-0.97085000	-1.40242800
H	-2.44737600	0.58550300	-2.11425100
C	-3.55574100	-1.51108400	0.93481700
H	-2.11460600	-0.38633700	2.05227600
C	-4.14944200	-1.72962700	-0.30691000
H	-4.20104800	-1.13240100	-2.37351500
H	-3.86193900	-2.09794800	1.79366400
H	-4.91795600	-2.48583000	-0.41895600

Addition TS (dimer)



TS frequency: -398.43 cm^{-1}

DFT Enthalpy = -1420.677955

DFT Free Energy = -1420.774397

0 2

C	0.60031500	2.05824600	-0.77530600
C	0.75794700	2.68832800	-2.01173100
C	1.55020200	3.82910900	-2.13686000
C	2.19360300	4.35635900	-1.02139000
C	2.03749900	3.73949600	0.21969400
C	1.24612200	2.60228100	0.34237400
H	0.25358100	2.28765000	-2.88553500
H	1.65988900	4.30507700	-3.10482300
H	2.81086000	5.24239300	-1.11549500
H	2.53569300	4.14404000	1.09344200
H	1.12928000	2.13182200	1.31290800
C	-0.26601800	0.80745700	-0.65062800
H	-0.65354100	0.58365300	-1.64854100
C	0.58847600	-0.45477700	-0.21551700
H	0.70380600	-0.41268100	0.86323600
C	-0.09534900	-1.77858300	-0.56242100
C	-0.57209500	-2.61394400	0.45107800
C	-0.23990800	-2.19606200	-1.89276900
C	-1.18412900	-3.82841500	0.14669800
H	-0.48070200	-2.29802400	1.48299800
C	-0.85186000	-3.40854500	-2.19920000
H	0.12826900	-1.57519900	-2.70275000
C	-1.32742200	-4.23009800	-1.17855700
H	-1.55098700	-4.46020200	0.94790300
H	-0.95236300	-3.71394000	-3.23473300
H	-1.80262400	-5.17505700	-1.41541800
C	1.94713100	-0.42463400	-0.86423100
H	1.95496400	-0.26059900	-1.93908900
C	3.15304500	-0.61833900	-0.27149600
C	3.33403600	-0.85067100	1.15626800
C	4.36065200	-0.59801200	-1.09043500
C	4.55484800	-1.04107200	1.69126700
H	2.45971200	-0.87193200	1.79590100
C	5.58667100	-0.78537200	-0.56832200
H	4.23704300	-0.42258000	-2.15498300
C	5.78329600	-1.02375900	0.87262700
H	4.69372400	-1.21472500	2.75235800
H	6.48169800	-0.76914800	-1.17951300
C	-2.79696000	0.78924200	-0.00077400

C	-3.20596700	-0.26628500	-0.89096000
C	-3.83191900	1.52426900	0.68723200
C	-4.51622300	-0.55791500	-1.08332400
H	-2.44820900	-0.84131600	-1.40644800
C	-5.14645400	1.24916000	0.50544900
H	-3.52542700	2.32092700	1.35695700
C	-5.58433400	0.17857900	-0.39767200
H	-4.83088200	-1.34823500	-1.75490300
H	-5.92639000	1.80772700	1.00998700
O	6.89284500	-1.19451600	1.36391300
O	-6.77616500	-0.08491000	-0.57011800
C	-1.46158100	1.14673700	0.23837500
H	-1.33283400	2.05465700	0.81129200
O	-1.02977200	0.19349100	2.02623500
O	-1.67266300	0.82133800	3.05310100
C	-2.64791700	-0.06212400	3.63054900
H	-2.15070500	-0.94196400	4.04459000
H	-3.11966800	0.51642200	4.42559700
H	-3.38238700	-0.35591500	2.87988800

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