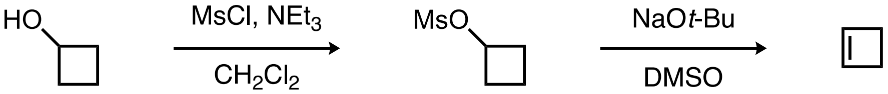
Supporting Information

A Diverted Aerobic Heck Reaction Enables Selective 1,3-Diene and 1,3,5-Triene Synthesis Through C−C Bond Scission

Neil J. McAlpine, Long Wang and Brad P. Carrow*
Department of Chemistry, Princeton University, Princeton, NJ 08544, United States
*E-mail: bcarrow@princeton.edu

General Remarks. All reagents were purchased from commercial sources and used as received unless otherwise indicated. $Pd(OAc)_2$ (Acros) was used as supplied. $Pd(OAc)_2$ was recrystallized according to the literature.[1] *p*-Benzoquinone (BQ) was sublimed under vacuum prior to use. ^1H, $^{13}C\{^1H\}$, $^{19}F\{^1H\}$ nuclear magnetic resonance spectra (NMR) were obtained on a Bruker 500 MHz or 300 MHz spectrometer and chemical shifts reported in ppm (δ) referenced against residual $CHCl_3$. Spin-spin coupling constants are described as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), broad (br) or multiplet (m), with coupling constants (J) in Hz. Flash column chromatography was performed on Teledyne IscoRediSep® prepacked silica gel columns. Preparative TLC was performed on Merck 60 F254 silica gel plates (16 cm x 16 cm x 1 mm). High resolution mass spectrometry (HR-MS) data were obtained using an Agilent 6220 High Resolution Electrospray TOFMS or an Agilent High Resolution 7200 GC TOF.



Cyclobutene. A modified literature procedure was used.[2] An oven-dried three-necked 1 L flask equipped with an overhead stirrer, thermometer and dropping funnel was cooled to -40 °C (MeCN/dry ice). CH_2Cl_2 (69 mL) was added followed by cyclobutanol (172 mmol, 13.5 mL). Methanesulfonyl chloride (1.5 equiv, 258 mmol, 20 mL) was quickly via the dropping funnel. The dropping funnel was replaced and triethylamine (1.6 equiv, 276 mmol, 38.4 mL) added dropwise (internal temperature maintained under -20 °C). The cold bath was removed and the reaction warmed at room temperature for 1 hour. The dropping funnel was replaced and the reaction cooled to 0 °C (ice/water). Cold aqueous 3 M HCl (100 mL) was added dropwise (internal temperature maintained under 4 °C) followed by cold brine (100 mL) dropwise (internal temperature maintained under 4 °C). The resulting mixture was warmed to room temperature and the organic layer separated. The aqueous phase was extracted with CH_2Cl_2 (2 x 100 mL). The combined organic phases were washed with cold brine (100 mL) then dried over anhydrous $MgSO_4$. The solvent was removed in vacuo to afford cyclobutyl methanesulfonate (25.9 g, 172 mmol, 99% yield) as yellow oil. NMR spectroscopic values are in agreement with the literature.

To an oven-dried 250 mL flask equipped with a stir bar was added DMSO (47 mL) and the flask and contents cooled to 0 °C. To the frozen DMSO is added cyclobutyl methanesulfonate (25.9 g, 172 mmol) slowly with stirring. The solution is warmed to room temperature slowly prior to addition. Note that the dissolution of cyclobutyl methanesulfonate in DMSO is strongly exothermic; the temperature must be controlled to obtain acceptable yields. Under positive pressure of nitrogen, an oven-dried 500 mL flask with stir bar is charged with sodium *tert*-butoxide (2.65 equiv, 43.9 g, 457 mmol), then equipped with a reflux condenser and dropping funnel. The reflux condenser is attached to a gas transfer manifold *via* a glass adaptor and Tygon hosing. The transfer manifold is attached to a series of two Schlenk flasks cooled to -78 °C (acetone / dry ice). The second Schlenk flask side arm is opened to atmosphere. Dry DMSO (200 mL) is added via the dropping funnel and the flask heated to 75 °C in an oil bath with vigorous stirring. The cold DMSO solution of cyclobutyl methanesulfonate above is added portion-wise via the dropping funnel and the reaction stirred for 2 hours. Sufficient positive pressure of nitrogen should be applied to push the formed product towards the traps. On completion, the transfer manifold is closed off from the reaction vessel. The first trap containing cyclobutene and trace tert-butanol is warmed to room temperature to distill the cyclobutene into the second trap. BHT (5.6 mg, 0.025 mmol) and 2-Me-THF (65 mL) were added at -78 °C. The solution was warmed to 0 °C and stored in a freezer. NMR titration indicates the final cyclobutene solution in 2-Me-THF is 1.0 M.

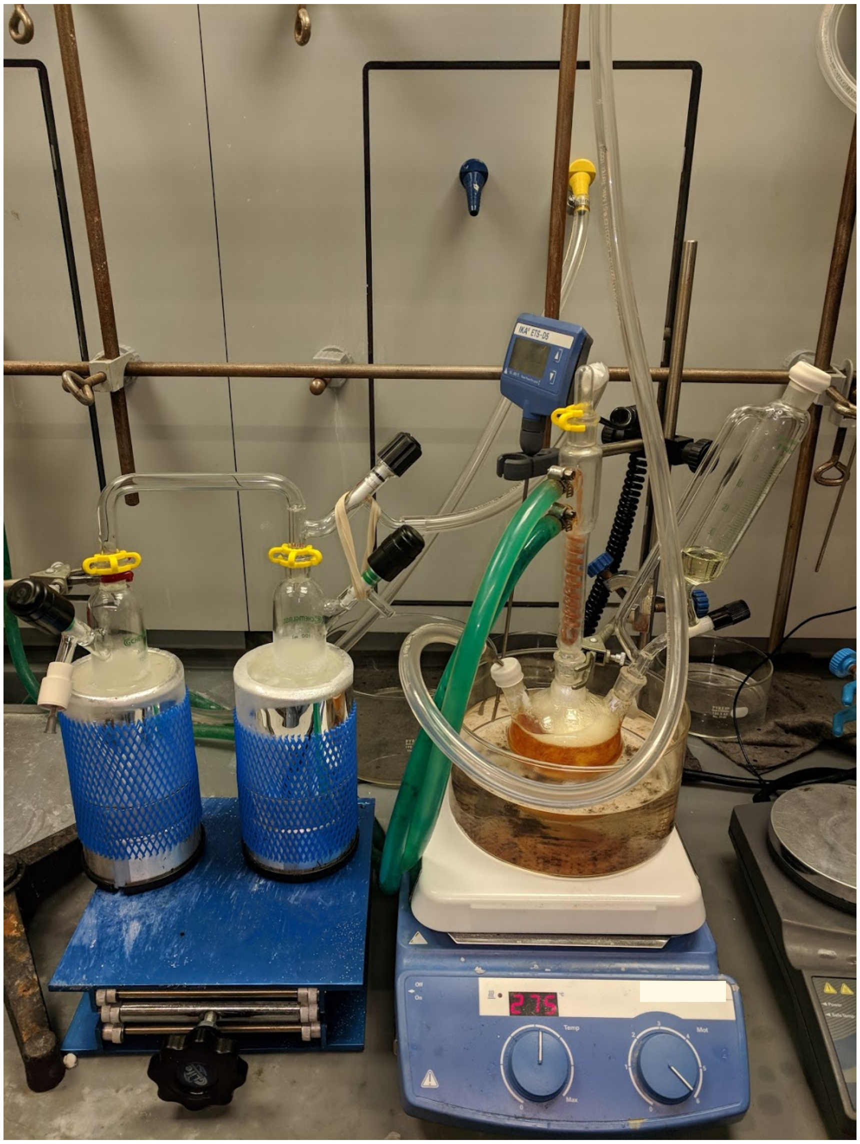


Figure S1. Experimental setup for cyclobutene preparation.

General procedure A for aerobic boron Heck reaction. A catalyst stock solution was prepared as follows: to an oven-dried 25 mL flask equipped with a stir bar was added $Pd(OAc)_2$ (84 mg, 0.38 mmol), BQ (84 mg, 0.75 mmol) and 2-Me-THF (19.5 mL). The resultant mixture was magnetically stirred under air until dissolved. To an oven-dried 10 x 75 mm culture tube equipped with a stir bar was added the appropriate boronic acid (0.25 mmol, 1 equiv) under air, which was loaded into a high-pressure vessel (HEL Group CAT-24 multi-well stainless-steel autoclave). Catalyst stock solution (0.65 mL), water (45 µL, 2.5 mmol, 10 equiv), AcOH (53 µL, 0.92 mmol, 3.7 equiv) and cyclobutene stock solution (cooled to 0 °C, 1 M, 0.65 mL) were added to the culture tube. The autoclave was sealed and pressurized with oxygen (50 psig) then heated to 45 °C with magnetic stirring in an oil bath for 72 hours. A blast shield was placed in front of the apparatus as a precaution. On completion two reactions were combined (0.50 mmol total) using diethyl ether and the solvent volume reduced *in vacuo* to *ca.* 1 mL. Product in the combined solution was then isolated by column chromatography, the eluent for which contained 100 ppm BHT inhibitor.

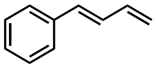
General procedure B for aerobic boron Heck reaction. Reactions were setup and conducted as described for Procedure A. If 3-arylcyclobutene side product was detected by ^{1}H NMR after 72 h in the crude reaction mixture, then a subsequent thermal treatment of the solution was applied. The autoclave was initially cooled to the room temperature after 72 h at 45 °C, then gas was vented. The autoclave is resealed under air and heated to 75 °C for 6 h to convert any 3-arylcyclobutene to the respective 1,3-diene. The work-up of the reaction is the same as described for Procedure A, except the chromatography eluent lacked any BHT inhibitor.

Yield determination by ^{1}H NMR. At the end of a reaction, $CDCl_3$ (1.5 mL) and OBn_2 (47.5 µL, 0.25 mmol, *internal standard*) were added to the culture tube and stirred for 15 min. An aliquot (ca. 0.1 mL) was filtered through silica gel into an NMR tube and diluted with $CDCl_3$ (*ca.* 0.5 mL).

Method variation for reaction using low pressure oxygen (Table 1, entry 2). A catalyst stock solution was prepared as follows: to an oven-dried 25 mL flask equipped with a stir bar was added $Pd(OAc)_2$ (10.5 mg, 0.038 mmol), BQ (10.2 mg, 0.075 mmol) and 2-Me-THF (2.4 mL). The solution was sparged with oxygen for 10 min with magnetic stirring. To an oven-dried side-arm Schlenk bomb equipped with a stir bar was added phenylboronic acid (30.5 mg, 0.25 mmol).

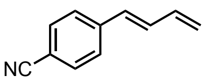
Catalyst stock solution (0.65 mL), water (45 μL, 2.5 mmol, 10 equiv), AcOH (53 μL, 0.92 mmol, 3.7 equiv) and cyclobutene stock solution (cooled to 0 °C, 1 M, 0.65 mL) were added. The vessel was sealed and pressurized with oxygen (14 psig) then heated to 45 °C with magnetic stirring in an oil bath for 72 hours.

Method variation for reaction using 10% oxygen, balance nitrogen (Table 1, entry 3). A catalyst stock solution was prepared as follows. To an oven-dried 25 mL flask equipped with a stir bar was added $Pd(OAc)_2$ (84 mg, 0.38 mmol), BQ (84 mg, 0.75 mmol) and 2-Me-THF (19.5 mL) the resultant was stirred under air until dissolved then sparged with nitrogen from a balloon for 10 min. Phenyl boronic acid (0.25 mmol, 1 equiv) was added in duplicate to an oven-dried 1 dram vial equipped with a stir bar. The vials containing the boronic acids were placed inside an oven-dried high-pressure vessel (HEL Group 50 mL stainless steel autoclave). To each vial was added catalyst stock solution (0.65 mL) followed by water (45 μL, 2.5 mmol, 10 equiv), AcOH (53 μL, 0.92 mmol, 3.7 equiv) and cyclobutene stock solution (cooled to 0 °C, 1 M, 0.65 mL). The autoclave was sealed, pressurized with 10% oxygen, balance nitrogen gas (500 psi), then heated to 45 °C in an oil bath for 72 hours behind a blast shield as a precaution. The autoclave was cooled to the room temperature and then the gases vented. The autoclave was resealed under air and heated to 75 °C for an additional 6 h. On completion, the two vials were combined using chloroform.



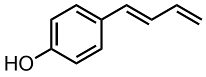
(*E*)-buta-1,3-dien-1-ylbenzene (1). According to the general procedure A using phenylboronic acid to obtain 53 mg (82%) (*E*)-buta-1,3-dien-1-ylbenzene as a colorless oil. Flash chromatography eluent: 100% pentane. Further purified by preparatory TLC (pentane) to remove trace BHT. TLC: R_f 0.55 (hexanes). NMR spectroscopic values are in agreement with the literature.[3]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.32 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.25 – 7.21 (m, 1H), 6.80 (dd, *J* = 15.7, 10.5 Hz, 1H), 6.60 – 6.46 (m, 2H), 5.34 (dd, *J* = 16.9, 1.4 Hz, 1H), 5.18 (dd, *J* = 10.0, 1.4 Hz, 1H).



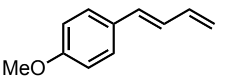
(*E*)-4-(buta-1,3-dien-1-yl)benzonitrile (2). According to the general procedure B with additional heating using (4-cyanophenyl)boronic acid to obtain 52 mg (67%) of (*E*)-4-(buta-1,3-dien-1-yl)benzonitrile as a white solid. Flash chromatography eluent: 0-40% CH_2Cl_2/pentane. TLC: R_f 0.42 (40% CH_2Cl_2/pentane). NMR spectroscopic values are in agreement with the literature.[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 2H), 7.49 – 7.45 (m, 2H), 6.92 – 6.83 (m, 1H), 6.59 – 6.46 (m, 2H), 5.44 (dd, *J* = 16.8, 1.2 Hz, 1H), 5.31 (dd, *J* = 10.0, 1.1 Hz, 1H).



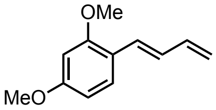
(*E*)-4-(buta-1,3-dien-1-yl)phenol (3). According to the general procedure B with additional heating using (4-hydroxyphenyl)boronic acid to obtain 44 mg (60%) of (*E*)-4-(buta-1,3-dien-1-yl)phenol as a yellow solid. Flash chromatography eluent: 20-100% CH_2Cl_2/pentane. TLC: R_f 0.38 (CH_2Cl_2). NMR spectroscopic values are in agreement with the literature.[5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 6.83 – 6.75 (m, 2H), 6.66 (dd, *J* = 15.7, 10.5 Hz, 1H), 6.54 – 6.43 (m, 2H), 5.28 (dd, *J* = 17.0, 1.7 Hz, 1H), 5.17 – 5.07 (m, 1H), 4.74 (br s, 1H).



(*E*)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene (4). According to the general procedure A using (4-methoxyphenyl)boronic acid to obtain 63 mg (79%) of (*E*)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene as a white solid. Flash chromatography eluent: 0-20% CH_2Cl_2/pentane. Further purified by preparatory TLC (20:80 CH_2Cl_2/pentane) to remove trace BHT. TLC: R_f 0.64 (20% CH_2Cl_2/pentane). NMR spectroscopic values are in agreement with the literature.[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 6.90 – 6.81 (m, 2H), 6.67 (dd, *J* = 15.5, 10.5 Hz, 1H), 6.54 – 6.44 (m, 2H), 5.31 – 5.25 (m, 1H), 5.11 (dt, *J* = 9.8, 1.4 Hz, 1H), 3.81 (s, 3H).

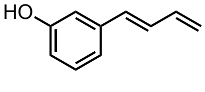


(*E*)-1-(buta-1,3-dien-1-yl)-2,4-dimethoxybenzene (5). According to the general procedure A using (2,4-dimethoxyphenyl)boronic acid to obtain 57 mg (60%) of (*E*)-1-(buta-1,3-dien-1-yl)-2,4-dimethoxybenzene as a clear oil. Flash chromatography eluent: 0-20% CH_2Cl_2/pentane. TLC: R_f 0.45 (20% CH_2Cl_2/pentane).

^{1}H NMR (500 MHz, $CDCl_3$ δ 7.39 (d, *J* = 8.5 Hz, 1H), 6.82 (d, *J* = 15.8 Hz, 1H), 6.72 (dd, *J* = 15.8, 10.2 Hz, 1H), 6.57 – 6.45 (m, 2H), 6.44 (d, *J* = 2.4 Hz, 1H), 5.25 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.08 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 160.6, 158.1, 138.3, 128.4, 127.6, 127.5, 119.3, 115.9, 105.0, 98.6, 55.6, 55.5.

HRMS (ESI$^+$) Calcd. for $C_{12}H_{14}O_2$+H, 191.1067; Found, 191.1065.



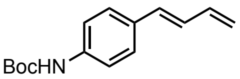
(*E*)-3-(buta-1,3-dien-1-yl)phenol (6). According to the general procedure B with additional heating using (3-hydroxyphenyl)boronic acid to obtain 69 mg (91%) of (*E*)-3-(buta-1,3-dien-1-

yl)phenol as a clear oil. Flash chromatography eluent: 50-100% CH_2Cl_2/pentane. TLC: R_f 0.46 (CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.9 Hz, 1H), 6.98 (dt, *J* = 7.6, 1.1 Hz, 1H), 6.88 (t, *J* = 2.0 Hz, 1H), 6.78 – 6.62 (m, 2H), 6.57 – 6.42 (m, 2H), 5.41 – 5.27 (m, 1H), 5.24 – 5.12 (m, 1H), 4.75 (s, 1H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 155.8, 139.0, 137.1, 132.5, 130.3, 129.9, 119.5, 118.2, 114.8, 113.0.

HRMS (ESI$^+$) Calcd. for $C_{10}H_{10}O$+H, 147.0804; Found, 147.0805.

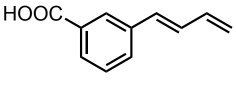


***tert*-butyl (*E*)-(4-(buta-1,3-dien-1-yl)phenyl)carbamate (7).** According to the general procedure A using (4-((*tert*-butoxycarbonyl)amino)phenyl)boronic acid to obtain 94 mg (77%) of *tert*-butyl (E)-(4-(buta-1,3-dien-1-yl)phenyl)carbamate as a cream solid. Flash chromatography eluent: 0-50% CH_2Cl_2/pentane. TLC: R_f 0.30 (50% CH_2Cl_2/pentane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 4H), 6.70 (dd, *J* = 15.5, 10.7 Hz, 1H), 6.54 – 6.44 (m, 2H), 5.30 (d, *J* = 16.6 Hz, 1H), 5.13 (d, *J* = 9.7 Hz, 1H), 1.52 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 152.7, 137.9, 137.4, 132.4, 132.2, 128.5, 127.2, 118.6, 117.1, 80.8, 28.5.

HRMS (ESI$^+$) Calcd. for $C_{15}H_{19}NO_2$+Na, 268.1308; Found, 268.1308.



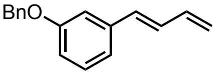
(*E*)-3-(buta-1,3-dien-1-yl)benzoic acid (8). According to the general procedure B with additional heating using 3-boronobenzoic acid to obtain 72 mg (83%) of (*E*)-3-(buta-1,3-dien-1-yl)benzoic acid as a white solid. Flash chromatography eluent: 0-20% EtOAc/CH_2Cl_2. TLC: R_f 0.35 (20% EtOAc/CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 – 8.09 (m, 1H), 7.98 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.64 (dt, *J* =

7.9, 1.4 Hz, 1H), 7.46 (dt, *J* = 26.9, 7.7 Hz, 2H), 6.88 (dd, *J* = 15.7, 10.5 Hz, 1H), 6.61 (d, *J* = 15.7 Hz, 1H), 6.53 (dt, *J* = 16.9, 10.3 Hz, 1H), 5.40 (d, *J* = 16.7 Hz, 1H), 5.24 (d, *J* = 10.0 Hz, 1H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 172.0, 137.8, 136.9, 134.0, 131.7, 131.6, 131.1, 130.4, 129.8, 129.3, 129.0, 128.6, 128.2, 118.9.

HRMS (ESI^+) Calcd. for $C_{11}H_{10}O_2$+H, 175.0754; Found, 175.0752.

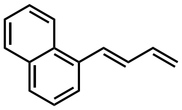


(*E*)-1-(benzyloxy)-3-(buta-1,3-dien-1-yl)benzene (9). According to the general procedure A using (3-(benzyloxy)phenyl)boronic acid to obtain 102 mg (86%) of (*E*)-1-(benzyloxy)-3-(buta-1,3-dien-1-yl)benzene as a white solid. Flash chromatography eluent: 0-20% CH_2Cl_2/pentane. TLC: R_f 0.42 (10% CH_2Cl_2/pentane).

^1H NMR (500 MHz, $CDCl_3$ δ 7.45 (d, *J* = 7.1 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.36 – 7.28 (m, 1H), 7.28 – 7.20 (m, 1H), 7.10 – 6.94 (m, 2H), 6.87 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.78 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.59 – 6.45 (m, 2H), 5.35 (d, *J* = 16.8 Hz, 1H), 5.19 (d, *J* = 10.0 Hz, 1H), 5.09 (s, 2H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 159.2, 138.7, 137.2, 137.1, 132.8, 130.1, 129.7, 128.7, 128.1, 127.7, 119.6, 118.0, 114.3, 112.8, 70.1.

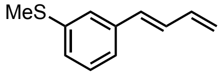
HRMS (ESI^+) Calcd. for $C_{17}H_{16}O$+H, 237.1274; Found, 236.1275.



(*E*)-1-(buta-1,3-dien-1-yl)naphthalene (10). According to the general procedure A using naphthalen-1-ylboronic acid to obtain 61 mg (68%) of (*E*)-1-(buta-1,3-dien-1-yl)naphthalene as a clear oil. The compound was protected from light during purification and drying. Flash chromatography eluent: 100% pentane. TLC: R_f 0.50 (hexanes). NMR spectroscopic values are in agreement with the literature.[7] Note that (*E*) to (*Z*) isomerization is observed during purification in the absence of BHT. The (*E*):(*Z*) ratio in the crude product mixture was initially >20:1, which later becomes 17:1 (see Figure S19). As a result, BHT (0.6 mol%) was added to the sample to inhibit (*E*) to (*Z*) isomerization.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 8.11 (m, 1H), 7.89 – 7.81 (m, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.68 (dt, *J* = 7.3, 0.9 Hz, 1H), 7.57 – 7.41 (m, 3H), 7.35 (d, *J* = 15.3 Hz, 1H), 6.86 (ddt, *J* = 15.3, 10.5, 0.8 Hz, 1H), 6.72 – 6.60 (m, 1H), 5.40 (ddt, *J* = 17.0, 1.6, 0.8 Hz, 1H), 5.24 (ddt, *J* = 10.0, 1.5, 0.8 Hz, 1H).

(1*Z*)-**10**: δ 8.02 – 7.92 (m, 1H), 6.97 (d, *J* = 11.3 Hz, 1H), 6.52 (t, *J* = 11.2 Hz, 1H), 5.17 (d, *J* = 10.1 Hz, 1H).

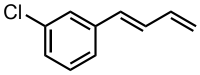


(*E*)-(3-(buta-1,3-dien-1-yl)phenyl)(methyl)sulfane (11). According to the general procedure A using (3-(methylthio)phenyl)boronic acid to obtain 79 mg (90%) of (*E*)-(3-(buta-1,3-dien-1-yl)phenyl)(methyl)sulfane as a clear oil. Flash chromatography eluent: 100% pentane. TLC: R_f 0.44 (pentane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 1.8 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.18 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.13 (dt, *J* = 7.7, 1.5 Hz, 1H), 6.82 – 6.73 (m, 1H), 6.56 – 6.42 (m, 2H), 5.35 (dd, *J* = 17.1, 1.7 Hz, 1H), 5.23 – 5.16 (m, 1H), 2.50 (s, 3H).

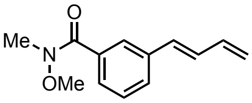
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 138.9, 137.9, 137.1, 132.4, 130.4, 129.1, 125.9, 124.7, 123.4, 118.3, 16.0.

HRMS (ESI$^+$) Calcd. for $C_{11}H_{12}S$+H, 177.0733; Found, 177.0733.



(*E*)-1-(buta-1,3-dien-1-yl)-3-chlorobenzene (12). According to the general procedure B with additional heating using (3-chlorophenyl)boronic acid to obtain 51 mg (65%) of (*E*)-1-(buta-1,3-dien-1-yl)-3-chlorobenzene as a clear oil. Flash chromatography eluent: 100% pentane. TLC: R_f 0.61 (pentane). NMR spectroscopic values are in agreement with the literature.[8]

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.57 – 7.32 (m, 2H), 7.25 – 7.18 (m, 1H), 6.85 – 6.72 (m, 1H), 6.57 – 6.41 (m, 2H), 5.37 (dd, *J* = 17.3, 1.5 Hz, 1H), 5.22 (dd, *J* = 10.0, 1.6 Hz, 1H).

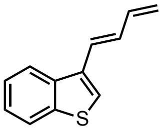


(*E*)-3-(buta-1,3-dien-1-yl)-*N*-methoxy-*N*-methylbenzamide (13). According to the general procedure B with additional heating using (3-(methoxy(methyl)carbamoyl)phenyl)boronic acid to obtain 61 mg (56%) of (*E*)-3-(buta-1,3-dien-1-yl)-*N*-methoxy-*N*-methylbenzamide as a clear oil. Flash chromatography eluent: 50-100% CH$_2$Cl$_2$/pentane. TLC: R$_f$ 0.42 (CH$_2$Cl$_2$).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.70 (t, *J* = 1.7 Hz, 1H), 7.50 (ddt, *J* = 18.5, 7.8, 1.4 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 1H), 6.82 (dd, *J* = 15.7, 10.5 Hz, 1H), 6.63 – 6.44 (m, 2H), 5.36 (dd, *J* = 17.0, 1.4 Hz, 1H), 5.24 – 5.17 (m, 1H), 3.56 (s, 3H), 3.36 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 169.9, 137.2, 137.0, 134.7, 132.1, 130.6, 128.4, 128.4, 127.3, 126.3, 118.5, 61.2, 33.9.

HRMS (ESI^{+}) Calcd. for C$_{13}$H$_{15}$NO$_2$+H, 218.1176; Found, 218.1175.

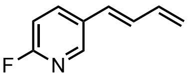


(*E*)-3-(buta-1,3-dien-1-yl)benzo[*b*]thiophene (14). According to the general procedure B with additional heating using benzo[*b*]thiophen-3-ylboronic acid to obtain 54 mg (58%) of (*E*)-3-(buta-1,3-dien-1-yl)benzo[*b*]thiophene as a clear oil. Flash chromatography eluent: 100% pentane. TLC: R$_f$ 0.50 (pentane).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.93 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.86 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.48 (s, 1H), 7.40 (dddd, *J* = 25.2, 8.2, 7.0, 1.2 Hz, 2H), 6.92 – 6.82 (m, 2H), 6.58 (dddd, *J* = 17.3, 9.9, 7.5, 2.3 Hz, 1H), 5.38 (dd, *J* = 16.8, 1.5 Hz, 1H), 5.22 (dd, *J* = 10.1, 1.5 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 140.6, 137.8, 137.4, 134.0, 131.2, 124.8, 124.7, 124.4, 123.1, 122.0, 122.0, 117.9.

HRMS (ESI$^+$) Calcd. for $C_{12}H_{10}S$+H, 187.0576; Found, 187.0578.



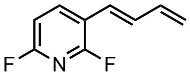
(*E*)-5-(buta-1,3-dien-1-yl)-2-fluoropyridine (15). According to the general procedure B with additional heating using (6-fluoropyridin-3-yl)boronic acid to obtain 46 mg (62%) of (*E*)-5-(buta-1,3-dien-1-yl)-2-fluoropyridine as a clear oil. Flash chromatography eluent: 0-40% CH_2Cl_2/pentane. TLC: R_f 0.34 (40% CH_2Cl_2/pentane). Due to the high volatility of this compound solvents were removed with the bath of the rotary evaporator cooled to 0 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 2.6 Hz, 1H), 7.84 (td, *J* = 8.1, 2.5 Hz, 1H), 6.90 (dd, *J* = 8.5, 3.0 Hz, 1H), 6.76 (dd, *J* = 15.7, 10.5 Hz, 1H), 6.56 – 6.42 (m, 2H), 5.39 (dd, *J* = 17.1, 1.4 Hz, 1H), 5.28 – 5.19 (m, 1H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 163.0 (d, *J* = 239.9 Hz), 146.1 (d, *J* = 14.6 Hz), 137.8 (d, *J* = 7.9 Hz), 136.6 (d, *J* = 0.8 Hz), 131.6 (d, *J* = 2.3 Hz), 131.5 (d, *J* = 4.8 Hz), 127.6, 119.3 (d, *J* = 1.1 Hz), 109.6 (d, *J* = 37.8 Hz).

$^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$) δ -69.5.

HRMS (ESI$^+$) Calcd. for C_9H_8FN+H, 150.0716; Found, 150.0712.



(*E*)-3-(buta-1,3-dien-1-yl)-2,6-difluoropyridine (16). According to the general procedure B with additional heating using (2,6-difluoropyridin-3-yl)boronic acid to obtain 48 mg (57%) of (*E*)-3-(buta-1,3-dien-1-yl)-2,6-difluoropyridine as a clear oil. Flash chromatography eluent: 0-40% CH_2Cl_2/pentane. TLC: R_f 0.55 (40% CH_2Cl_2/pentane). Due to the high volatility of this compound solvents were removed with the bath of the rotary evaporator cooled to 0 °C.

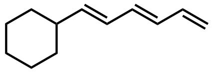
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dt, *J* = 9.4, 7.9 Hz, 1H), 6.87 – 6.72 (m, 2H), 6.63 – 6.36 (m, 2H), 5.42 (dd, *J* = 16.9, 1.2 Hz, 1H), 5.29 (d, *J* = 9.9 Hz, 1H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 161.1 (d, *J* = 14.3 Hz), 159.2 (d, *J* = 14.0 Hz), 141.3 (dd, *J* =

7.5, 4.6 Hz), 136.7, 133.5 (dd, *J* = 4.4, 2.3 Hz), 122.4, 120.1, 117.0 (d, *J* = 6.0 Hz), 106.6 (dd, *J* = 34.8, 5.6 Hz).

^{19}F{^{1}H} NMR (282 MHz, CDCl$_3$) δ -69.78 (d, *J* = 11.7 Hz), -71.16 (d, *J* = 11.9 Hz).

HRMS (ESI$^+$) Calcd. for $C_9H_7F_2N$+H, 168.0619; Found, 168.0621.

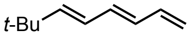


((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)cyclohexane (17). According to the general procedure A using (*E*)-(2-cyclohexylvinyl)boronic acid to obtain 58 mg (72%) of ((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)cyclohexane as a clear oil. Flash chromatography eluent: 100% pentane. Further purified by preparatory TLC (pentane) to remove trace BHT. TLC: R$_f$ 0.65 (pentane). Due to the high volatility of this compound solvents were removed with the bath of the rotary evaporator cooled to 0 °C.

^{1}H NMR (500 MHz, CDCl$_3$) δ 6.35 (dt, *J* = 16.9, 10.0 Hz, 1H), 6.24 – 6.10 (m, 2H), 6.03 (ddd, *J* = 15.3, 9.9, 1.3 Hz, 1H), 5.69 (dd, *J* = 15.3, 7.0 Hz, 1H), 5.16 (dd, *J* = 16.9, 1.7 Hz, 1H), 5.03 (dd, *J* = 10.1, 1.7 Hz, 1H), 2.01 (pd, *J* = 7.1, 6.5, 2.7 Hz, 1H), 1.82 – 1.69 (m, 4H), 1.65 (dtt, *J* = 12.3, 3.5, 1.7 Hz, 1H), 1.36 – 1.00 (m, 5H).

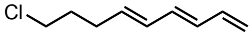
^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 142.0, 137.3, 134.1, 131.2, 127.7, 116.3, 41.0, 32.9, 26.3, 26.1.

HRMS (ESI$^+$) Calcd. for $C_{12}H_{18}$+H, 163.1481; Found, 163.1481.



(3*E*,5*E*)-7,7-dimethylocta-1,3,5-triene (18). According to the general procedure A using (*E*)-(3,3-dimethylbut-1-en-1-yl)boronic acid to obtain 43 mg (63%) of (3*E*,5*E*)-7,7-dimethylocta-1,3,5-triene as a white solid. Flash chromatography eluent: 100% pentane. TLC: R$_f$ 0.83 (pentane). Due to the high volatility of this compound solvents were removed with the bath of the rotary evaporator cooled to 0 °C. NMR spectroscopic values are in agreement with the literature.[9] BHT (0.1 mol%) was added to the sample to inhibit (*E*) to (*Z*) isomerization.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.35 (dt, *J* = 17.1, 10.0 Hz, 1H), 6.24 – 6.12 (m, 2H), 6.00 (dd, *J* = 15.3, 9.7 Hz, 1H), 5.74 (dd, *J* = 19.8, 15.4 Hz, 1H), 5.16 (dd, *J* = 16.9, 1.6 Hz, 1H), 5.05 – 5.00 (m, 1H), 1.04 (s, 12H).

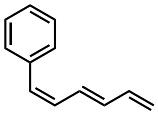


(3*E*,5*E*)-9-chloronona-1,3,5-triene (19). According to a modified general procedure B with additional heating using (*E*)-2-(5-chloropent-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane to afford 54 mg (69%) of (3*E*,5*E*)-9-chloronona-1,3,5-triene as a clear oil. Flash chromatography eluent: 100% pentane. Further purified by preparatory TLC (pentane) to remove trace BHT. TLC: R_f 0.53 (pentane). Due to the high volatility of this compound solvents were removed with the bath of the rotary evaporator cooled to 0 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.35 (dt, *J* = 16.9, 9.8 Hz, 1H), 6.23 – 6.03 (m, 3H), 5.67 (dt, *J* = 14.5, 7.2 Hz, 1H), 5.19 (dd, *J* = 16.9, 1.7 Hz, 1H), 5.07 (dd, *J* = 10.1, 1.6 Hz, 1H), 3.54 (t, *J* = 6.6 Hz, 2H), 2.27 (qd, *J* = 7.2, 1.3 Hz, 2H), 1.96 – 1.80 (m, 2H).

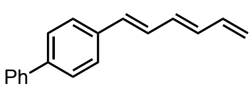
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 137.1, 133.5, 133.2, 131.9, 131.6, 117.0, 44.5, 32.1, 30.0.

HRMS (EI) Calcd. for $C_9H_{13}Cl^•$, 156.0700; Found, 156.0701.



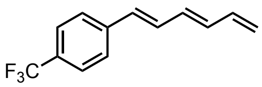
((1*Z*,3*E*)-hexa-1,3,5-trien-1-yl)benzene (20). According to a modified general procedure A using (*Z*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane to afford 44 mg (56%) of ((1*Z*,3*E*)-hexa-1,3,5-trien-1-yl)benzene as a clear oil. Flash chromatography eluent: 100% pentane. TLC: R_f 0.60 (pentane). NMR spectroscopic values are in agreement with the literature.[10]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 4H), 7.29 – 7.19 (m, 1H), 6.85 – 6.73 (m, 1H), 6.50 – 6.34 (m, 3H), 6.28 (t, *J* = 11.5 Hz, 1H), 5.30 – 5.25 (m, 1H), 5.16 – 5.11 (m, 1H).



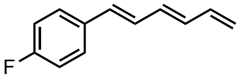
4-((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)-1,1'-biphenyl (21). According to the general procedure A using (*E*)-(2-([1,1'-biphenyl]-4-yl)vinyl)boronic acid, 52 mg (45%) of 4-((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)-1,1'-biphenyl was obtained as a clear oil. Flash chromatography eluent: 100% pentane. Further purified by preparatory TLC (pentane) to remove trace BHT. TLC: R_f 0.43 (pentane). NMR spectroscopic values are in agreement with the literature.[11]

^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 7.74 – 7.61 (m, 4H), 7.61 – 7.54 (m, 2H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.33 (m, 1H), 7.03 (dd, *J* = 15.7, 9.9 Hz, 1H), 6.70 (d, *J* = 15.6 Hz, 1H), 6.55 – 6.40 (m, 3H), 5.38 – 5.25 (m, 1H), 5.20 – 5.11 (m, 1H).



1-((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)-4-(trifluoromethyl)benzene (22). According to the general procedure A using (*E*)-(4-(trifluoromethyl)styryl)boronic acid to obtain 77 mg (69%) of 1-((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)-4-(trifluoromethyl)benzene as a clear oil. NMR spectroscopic values are in agreement with the literature.[12] Flash chromatography eluent: 100% pentane. TLC: R_f 0.57 (pentane). BHT (0.3 mol%) was added to the sample to inhibit (*E*) to (*Z*) isomerization.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.56 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 6.95 – 6.83 (m, 1H), 6.58 (d, *J* = 15.6 Hz, 1H), 6.51 – 6.34 (m, 3H), 5.38 – 5.25 (m, 1H), 5.19 (dd, *J* = 9.6, 1.5 Hz, 1H).



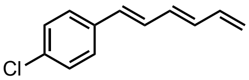
1-fluoro-4-((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)benzene (23). According to the general procedure A using (*E*)-(4-fluorostyryl)boronic acid to obtain 65 mg (75%) of 1-fluoro-4-((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)benzene as a yellow solid. Flash chromatography eluent: 100% pentane. Further purified by preparatory TLC (pentane) to remove trace BHT. TLC: R_f 0.51 (pentane). Due to the high volatility of this compound solvents were removed with the bath of the rotary evaporator cooled to 0 °C.

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.41 – 7.31 (m, 2H), 7.05 – 6.97 (m, 2H), 6.77 – 6.68 (m, 1H), 6.53 (d, *J* = 15.6 Hz, 1H), 6.48 – 6.31 (m, 3H), 5.27 (dd, *J* = 16.7, 1.5 Hz, 1H), 5.14 (dd, *J* = 9.8, 1.4 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 162.4 (d, *J* = 247.4 Hz), 137.1, 134.0 (d, *J* = 1.4 Hz), 133.6 (d, *J* = 3.4 Hz), 133.4 (d, *J* = 1.2 Hz), 131.8 (d, *J* = 1.2 Hz), 128.7 (d, *J* = 2.5 Hz), 128.0 (d, *J* = 7.9 Hz), 117.8, 115.7 (d, *J* = 21.7 Hz).

^{19}F{^{1}H} NMR (282 MHz, CDCl$_3$) δ -114.2.

HRMS (ESI$^+$) Calcd. for $C_{12}H_{11}F$+H, 175.0918; Found, 175.0916.

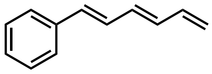


1-chloro-4-((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)benzene (24). According to the general procedure A using (*E*)-(4-chlorostyryl)boronic acid to obtain 48 mg (51%) of 1-chloro-4-((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)benzene as a yellow solid. Flash chromatography eluent: 100% pentane. Further purified by preparatory TLC (pentane) to remove trace BHT. TLC: R$_f$ 0.57 (pentane). Due to the high volatility of this compound solvents were removed with the bath of the rotary evaporator cooled to 0 °C.

^{1}H NMR (500 MHz, CDCl$_3$ δ 7.40 – 7.22 (m, 4H), 6.90 – 6.68 (m, 1H), 6.62 – 6.25 (m, 4H), 5.28 (d, *J* = 16.2 Hz, 1H), 5.15 (d, *J* = 9.2 Hz, 1H).

^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 137.0, 135.9, 134.5, 133.2, 131.6, 129.5, 128.9, 127.6, 118.1.

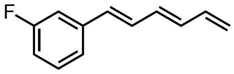
HRMS (ESI$^+$) Calcd. for $C_{12}H_{11}Cl$+H, 191.0622; Found, 191.0624.



((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)benzene (25). According to the general procedure A using (*E*)-styrylboronic acid, 46 mg (59%) of ((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)benzene was obtained as a yellow solid. Flash chromatography eluent: 100% pentane. Further purified by preparatory TLC (pentane) to remove trace BHT. TLC: R_f 0.64 (pentane). NMR spectroscopic values are in agreement with the literature.[11]

Note that (*E*) to (*Z*) isomerization is observed during purification in the absence of BHT, possibly due to a photochemical process under ambient light. The (*E*):(*Z*) ratio in the crude product mixture was >20:1, which later becomes 9:1 in the final product without added BHT.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.20 (m, 1H), 6.82 (dd, *J* = 15.6, 9.7 Hz, 1H), 6.58 (d, *J* = 15.6 Hz, 1H), 6.49 – 6.32 (m, 3H), 5.30 – 5.24 (m, 1H), 5.14 (dd, *J* = 10.1, 1.5 Hz, 1H). (*Z*)-isomer δ *inter alia* δ 6.95 (dt, *J* = 16.7, 10.7 Hz, 1H), 6.18 (t, *J* = 11.0 Hz, 1H), 6.09 (t, *J* = 11.0 Hz, 1H), 5.22 (d, *J* = 10.1 Hz, 1H).



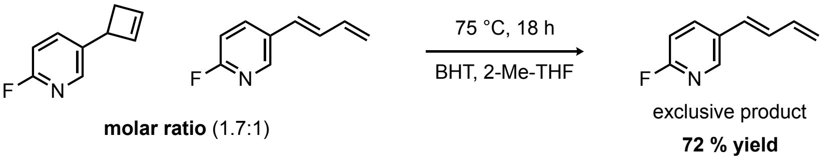
1-fluoro-3-((1E,3E)-hexa-1,3,5-trien-1-yl)benzene (26). According to the general procedure B using (E)-(3-fluorostyryl)boronic acid to afford 38 mg (44%) of 1-fluoro-3-((1E,3E)-hexa-1,3,5-trien-1-yl) as a white solid. Flash chromatography eluent: 100% pentane. TLC: R_f 0.56 (pentane). Due to the high volatility of this compound solvents were removed with the bath of the rotary evaporator cooled to 0 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.9 Hz, 1H), 7.15 (dt, *J* = 7.9, 1.3 Hz, 1H), 7.09 (dt, *J* = 10.3, 2.1 Hz, 1H), 6.91 (tdd, *J* = 8.2, 2.5, 0.9 Hz, 1H), 6.86 – 6.76 (m, 1H), 6.53 (d, *J* = 15.6 Hz, 1H), 6.48 – 6.35 (m, 3H), 5.36 – 5.21 (m, 1H), 5.19 – 5.13 (m, 1H).

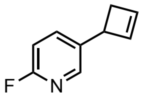
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 163.3 (d, J = 245.3 Hz), 139.8 (d, J = 7.8 Hz), 137.0, 134.9, 133.1, 131.7 (d, J = 2.9 Hz), 130.2 (d, *J* = 1.8 Hz), 130.1, 122.4 (d, J = 2.8 Hz), 118.3, 114.5 (d, J = 21.5 Hz), 112.7 (d, J = 21.8 Hz).

^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$) δ -113.6.

HRMS (ESI$^+$) Calcd. for $C_{12}H_{11}F$+H, 175.0918; Found, 175.0919.

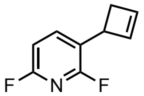


Control reaction for thermal pericyclic ring opening. According to the general procedure A with reduced reaction time (48 h), a 1.7:1 mixture of cyclobutenyl and butadienyl pyridines (+ BHT) was isolated after chromatography. 15 mg (0.1 mmol) of this mixture was dissolved in 2-Me-THF (0.52 mL, 0.2 M) and heated to 75 °C for 18 h. ^{1}H NMR analysis (OBn_2, *internal standard*) indicated complete conversion to **15** (72%). The above result was the basis for the modification of the general reaction protocol to Procedure B.



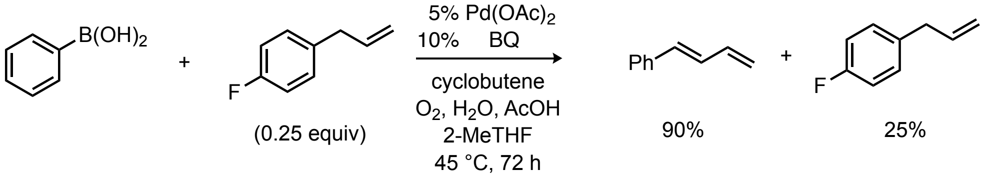
5-(cyclobut-2-en-1-yl)-2-fluoropyridine.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 2.4 Hz, 1H), 7.66 (td, *J* = 8.1, 2.6 Hz, 1H), 6.86 (dd, *J* = 8.4, 3.0 Hz, 1H), 6.29 (d, *J* = 2.7 Hz, 1H), 6.21 (d, *J* = 2.7 Hz, 1H), 4.04 (d, *J* = 4.4 Hz, 1H), 3.09 (ddd, *J* = 13.7, 4.5, 1.0 Hz, 1H), 2.36 (dt, *J* = 13.7, 1.2 Hz, 1H).

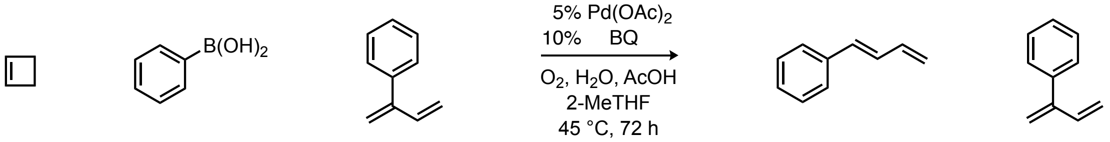


3-(cyclobut-2-en-1-yl)-2,6-difluoropyridine.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (dt, *J* = 9.5, 7.9 Hz, 1H), 6.77 (dd, *J* = 8.0, 2.8 Hz, 1H), 6.27 (dq, *J* = 2.0, 1.0 Hz, 1H), 6.22 (d, *J* = 2.8 Hz, 1H), 4.20 (d, *J* = 4.5 Hz, 1H), 3.11 (ddd, *J* = 13.7, 4.6, 1.0 Hz, 1H), 2.39 (dt, *J* = 13.6, 1.3 Hz, 1H).



Reaction to test for background alkene isomerization. A catalyst stock solution was prepared as follows: to an oven-dried 25 mL flask equipped with a stir bar was added $Pd(OAc)_2$ (10.5 mg, 0.038 mmol), BQ (10 mg, 0.075 mmol) and 2-Me-THF (2.4 mL). The solution was sparged with oxygen for 10 min with magnetic stirring. To an oven-dried side-arm Schlenk bomb equipped with a stir bar was added phenylboronic acid (31 mg, 0.25 mmol). Catalyst stock solution (0.65 mL), water (45 µL, 2.5 mmol, 10 equiv), AcOH (53 µL, 0.92 mmol, 3.7 equiv), 1-allyl-4-fluorobenzene (25 mol%, 17 µL) and cyclobutene stock solution (cooled to 0 °C, 1 M, 0.65 mL) were added. The vessel was sealed and pressurized with oxygen (50 psig) then heated to 45 °C with magnetic stirring in an oil bath for 72 hours. The reaction outcome was analyzed by ^{1}H NMR, which indicated a 90% yield of **1** and quantitative recovery of 1-allyl-4-fluoro-benzene. The absence of isomerization product (e.g., 4-fluoro-β-methylstyrene) suggests background isomerization or chain-walking by a palladium hydride species is not occurring under the catalytic conditions.



Reaction to test for degradation of the branched product isomer. A catalyst stock solution was prepared as follows: to an oven-dried 25 mL flask equipped with a stir bar was added Pd(OAc)$_2$ (10.5 mg, 0.038 mmol), BQ (10 mg, 0.075 mmol) and 2-Me-THF (2.4 mL). The solution was sparged with oxygen for 10 min with magnetic stirring. To an oven-dried side-arm Schlenk bomb equipped with a stir bar was added phenylboronic acid (31 mg, 0.25 mmol). Catalyst stock solution (0.65 mL), water (45 µL, 2.5 mmol, 10 equiv), AcOH (53 µL, 0.92 mmol, 3.7 equiv), buta-1,3-dien-2-ylbenzene (25 mol%, 9 µL) and cyclobutene stock solution (cooled to 0 °C, 1 M, 0.65 mL) were added. The vessel was sealed and pressurized with oxygen (50 psig) then heated to 45 °C with magnetic stirring in an oil bath for 72 hours. The reaction outcome was analyzed by ^{1}H NMR, which indicated a 75% yield of **1** and 16 % remaining buta-1,3-dien-2-ylbenzene. That the branched product was not fully consumed indicates that, if formed during catalysis, this minor product should be detectable by NMR.

Reaction time course analysis. Catalyst stock solution: to an oven-dried vial was added Pd(OAc)$_2$ (10.5 mg, 0.047 mmol) and BQ (10 mg, 0.094 mmol) followed by 2-Me-THF (2.4 mL). The mixture was sparged with oxygen for 10 min. To an oven-dried 25 mL flask is added phenylboronic acid (92 mg, 0.75 mmol) followed by catalyst stock solution (1.95 mL), water (135 µL, 7.5 mmol), AcOH (158 µL, 2.75 mmol), dibenzyl ether (36 µL, 0.19 mmol, *internal standard*) and cyclobutene stock solution (cooled to 0 °C, 1 M, 1.95 mL). The flask was sealed with a septum with a PTFE sleeve, then purged with oxygen from a balloon, sealed with electrical tape and heated in an oil bath to 45 °C for 72 h. Aliquots (*ca.* 50 µL) were withdrawn using a gas tight syringe backfilled with oxygen, quenched into a pad of silica, flushed with $CDCl_3$, then analyzed by ^1H NMR.

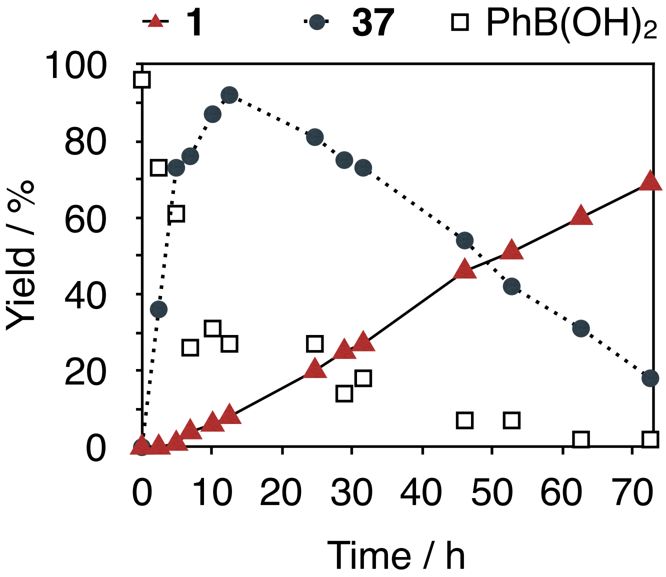
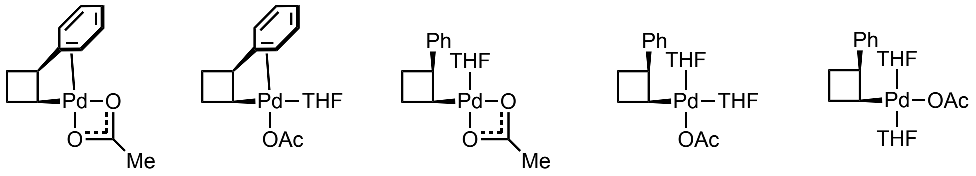


Figure S2. Kinetic profile for the reaction of phenylboronic acid and cyclobutene in 2-MeTHF under low pressure O_2 (14 psig) at 45 °C.

Computational Details for DFT Calculations. Gaussian 09 was used for all density functional theory (DFT) calculations.[13] Energy profiles were obtained using a two-step protocol: gas phase geometry optimization followed by single point solvation correction.[14] Geometry optimizations were performed with the B3LYP functional using the LANL2DZ basis set for Pd and the 6-31G(d) basis set for other atoms. Frequency calculations were performed to confirm that each optimized geometry has the appropriate number of imaginary frequency (0 for ground state and 1 for transition state). Single point calculations were performed with the M06 functional using the Stuttgart/Dresden ECP (SDD) basis set for Pd and the 6-311+G(d,p) basis set for other atoms. SMD model was employed with tetrahydrofuran as solvent, and the solvation cavity was generated using UFF radii. All thermodynamic data were calculated at the standard state (298.15 K and 1 atm).



$\Delta G_{298,\ sol}$ (kcal/mol):	0.0	5.4	7.9	9.1	15.0
	29	**S1**	**S2**	**S3**	**S4**

Figure S3. Comparison of possible alkyl-palladium species (solvent-corrected Gibbs free energies in kcal/mol).

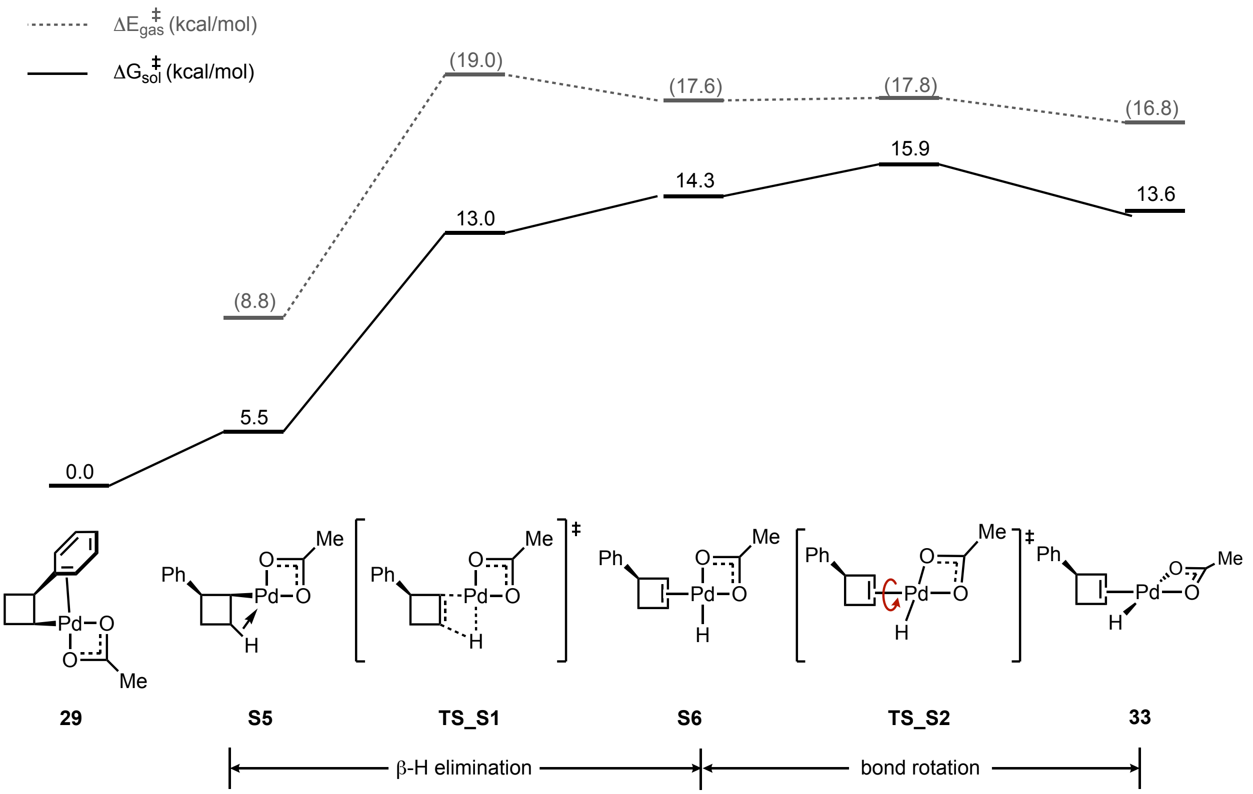


Figure S4. Reaction Energy Profile for β-Hydride Elimination (gray: gas phase electronic energies in kcal/mol, red: solvent-corrected Gibbs free energies in kcal/mol).

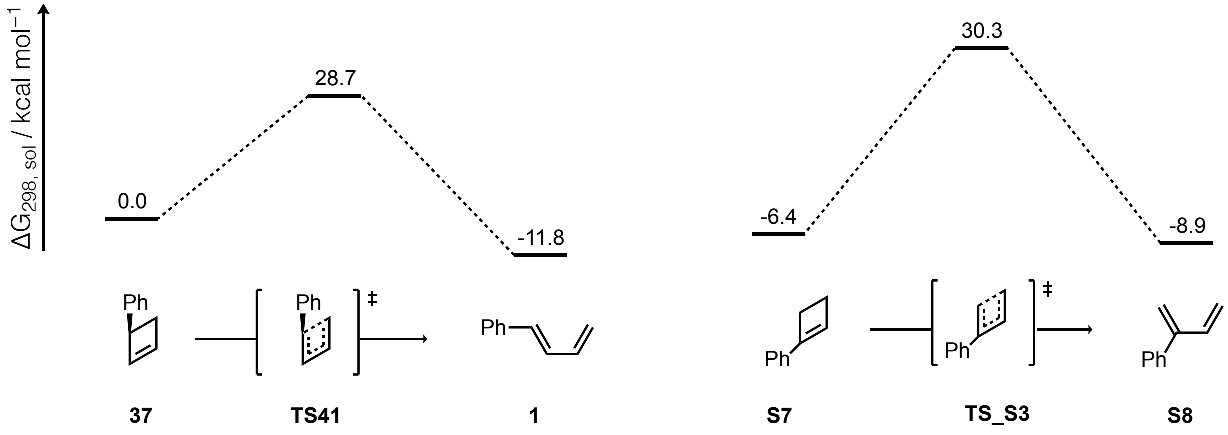


Figure S5. Reaction Energy Profile for Pericyclic Ring Opening (solvent-corrected Gibbs free energies in kcal/mol).

Energies of the Optimized Structure for 27.

B3LYP electronic energy (Hartree): -742.8678185
B3LYP zero-point energy correction (Hartree): 0.23069
B3LYP thermal correction to free energy (Hartree): 0.182403
M06 electronic energy in solution (Hartree): -743.7767768
Three lowest frequencies (cm-1): 8.909, 14.0521, 52.5324

Table S1. Cartesian Coordinates for 27.

C	-0.5127577372	2.0770321363	-0.634374431
C	0.6436982526	3.069771204	-0.527935765
C	0.3865582736	3.0642218687	1.0206548018
C	-0.7410879079	2.0721061167	0.7407119875
H	-1.1387671742	1.8000078291	-1.4769310262
H	0.4259762186	4.0320203568	-1.0059376865
H	1.626591167	2.7178363541	-0.8526589429
H	0.0249530372	4.0233656595	1.4093642508
H	1.2121715115	2.7088700968	1.6431267608
H	-1.6054722907	1.7899111058	1.3337806264
C	-1.468993944	-0.7078405381	-0.0968899175
C	-1.8642336485	-1.060738344	-1.3911021044
C	-2.2619226741	-1.0680345155	0.9973029044
C	-3.0509973784	-1.776530399	-1.5870468364
H	-1.2501270713	-0.7985004351	-2.2491486299
C	-3.4474315133	-1.7838217829	0.7938685268
H	-1.9592570125	-0.8115114865	2.0095923277
C	-3.8449034533	-2.1369124456	-0.4968652247
H	-3.3495482452	-2.0532106616	-2.5954876762
H	-4.0563542923	-2.0662191362	1.6494985977
H	-4.7661229001	-2.6921621825	-0.651953323
Pd	0.2866263727	0.186983472	0.1980100948
O	2.5103245257	0.4639769218	0.5683317501
C	2.5983284913	-0.8001629592	0.5782654857
O	1.5529886344	-1.5245571252	0.4018825513
C	3.9236756131	-1.4888120129	0.7963852909
H	4.1482499628	-2.1332037221	-0.0600924661
H	4.7204206771	-0.7542734513	0.9275122642
H	3.8618530353	-2.1325597337	1.680183449

Energies of the Optimized Structure for TS28.

B3LYP electronic energy (Hartree): -742.8433982
B3LYP zero-point energy correction (Hartree): 0.230697
B3LYP thermal correction to free energy (Hartree): 0.185986
M06 electronic energy in solution (Hartree): -743.7573221
Three lowest frequencies (cm-1): -298.3245, 35.4668, 40.4585

Table S2. Cartesian Coordinates for TS28.

C	-0.5265528086	-2.1219634506	0.3973996043
C	-0.6931615914	-2.9377670129	-0.8910888238
C	-2.1341818205	-2.3376215934	-0.9898931821
C	-1.846737535	-1.5622986568	0.3043448664
H	0.0118518568	-2.4230271032	1.2950652542
H	-0.6872174444	-4.0203581505	-0.7179400842
H	-0.0040716472	-2.7137037164	-1.7104214599
H	-2.922379714	-3.0832092106	-0.8360399802
H	-2.3784945072	-1.7567821482	-1.8808300725
H	-2.5483911467	-1.4251406208	1.1191100277
C	-1.9260942262	0.4948191535	-0.0184236226
C	-2.3394746468	1.17660395	1.138569954
C	-2.4410039498	0.8795067079	-1.2638103469
C	-3.2180810341	2.2555926898	1.0414071528
H	-1.970547401	0.8685724111	2.1138934276
C	-3.3216129817	1.9608298142	-1.3550064364
H	-2.1381041181	0.3614869197	-2.1693026096
C	-3.7126965126	2.6495558102	-0.2054493743
H	-3.5206236042	2.7852851852	1.9411477936
H	-3.6993620124	2.2639865312	-2.3281501772
H	-4.4034789999	3.4849806937	-0.2787104267
Pd	0.0526821926	-0.1808708891	-0.0222250248
O	2.1941218208	-0.3082434734	-0.1289541178
C	2.2977415658	0.9504008057	-0.3483627227
O	1.2613678509	1.6743626206	-0.418927832
C	3.6750340713	1.5531962103	-0.4983932294
H	4.1686523239	1.5750298751	0.4801325822
H	4.285867927	0.9327852261	-1.1609497971
H	3.6075347107	2.571113626	-0.8872223298

Energies of the Optimized Structure for 29.

B3LYP electronic energy (Hartree): -742.8873396
B3LYP zero-point energy correction (Hartree): 0.233106
B3LYP thermal correction to free energy (Hartree): 0.188716
M06 electronic energy in solution (Hartree): -743.8002463
Three lowest frequencies (cm-1): 40.0464, 45.9972, 50.5381

Table S3. Cartesian Coordinates for 29.

C	-1.1843390406	-1.4036902764	0.6971517779
C	-1.2636073555	-2.8391068063	0.1594018052
C	-2.8176844484	-2.7567355925	0.2242054565
C	-2.7101709332	-1.3715689489	0.9386729276
H	-0.4685688966	-1.1444248691	1.483649969
H	-0.8409620849	-3.5706212584	0.8605295247
H	-0.8172668883	-3.0193290448	-0.8235794804
H	-3.3027150909	-3.5348727563	0.8200271478
H	-3.2986755367	-2.7243853024	-0.7568661694
H	-3.0512067385	-1.3896114016	1.9827969799
C	-3.2149768034	-0.1278340907	0.2124505221
C	-2.6342579608	1.1214218291	0.5650132319
C	-4.2381302934	-0.136342558	-0.7651103065
C	-3.0708605116	2.3137550054	-0.0555308288
H	-1.9695848364	1.183811301	1.42340203
C	-4.6609688768	1.0434120178	-1.3582126741
H	-4.7053103503	-1.077046649	-1.0390336251
C	-4.0695635244	2.2730545118	-1.0141679868
H	-2.6191970753	3.2587626079	0.2315885878
H	-5.4544628161	1.0170533843	-2.1000679509
H	-4.4017272543	3.1875202601	-1.4966507196
Pd	-1.0357141663	-0.010813917	-0.7679392096
O	0.7181025763	-0.6205084785	-1.7804242942
C	0.6451980316	0.3174916683	-2.6616723401
O	-0.2994152017	1.149563056	-2.6397126099
C	1.7382747241	0.3920899682	-3.7036445908
H	2.6726631218	0.7116810487	-3.2281338485
H	1.9129793135	-0.5973124214	-4.1373104325
H	1.4701952572	1.1054244528	-4.485450863

Energies of the Optimized Structure for TS30$_{br}$.

B3LYP electronic energy (Hartree): -742.8186545
B3LYP zero-point energy correction (Hartree): 0.23075
B3LYP thermal correction to free energy (Hartree): 0.18625
M06 electronic energy in solution (Hartree): -743.7369725
Three lowest frequencies (cm-1): -545.7951, 30.9633, 41.4262

Table S4. Cartesian Coordinates for TS30$_{br}$.

C	-0.0638347238	-1.7700849099	-1.1394699971
C	0.4460146765	-3.0031396957	-0.3940996427
C	0.1873105156	-2.2713534431	0.9620598345
C	-1.1218376357	-1.382776262	-0.2029437092
H	-0.0458272027	-1.590678879	-2.2141232188
H	-0.256852342	-3.8430713086	-0.5058082198
H	-0.4816230727	-2.7075521908	1.7010004588
H	1.0929110597	-1.9076784546	1.4671175213
H	-1.8429181838	-2.119796233	0.1518752
Pd	0.8276402174	-0.2650129315	-0.0463702088
O	2.1255311242	0.9848781097	-1.2060020442
C	2.3936299995	1.734551505	-0.1981360653
O	1.8803672198	1.4959373796	0.9312865421
C	3.3128446537	2.9159970134	-0.4040074869
H	3.6378263404	3.3183875072	0.5574566164
H	2.7788810176	3.6977726082	-0.9566829746
H	4.1778175232	2.6205639765	-1.0050702306
H	-1.6088810929	-0.4056582362	-0.2930072249
C	1.8470672964	-3.5287279623	-0.6290597478
C	2.1535266244	-4.8372499691	-0.2261506697
C	2.855448268	-2.7567323682	-1.2237283742
C	3.4343108237	-5.3608855472	-0.3992767965
H	1.3777779798	-5.4528436207	0.2253869315
C	4.1372019737	-3.2829529692	-1.4030884785
H	2.6470688024	-1.7405516588	-1.5463975667
C	4.4323424873	-4.5827751191	-0.9903187279
H	3.6504515109	-6.3770218185	-0.0798067257
H	4.9049465845	-2.6710659743	-1.8690726661
H	5.4303474447	-4.9889249877	-1.1315700485

Energies of the Optimized Structure for TS30$_{lin}$.

B3LYP electronic energy (Hartree): -742.8224011
B3LYP zero-point energy correction (Hartree): 0.230759
B3LYP thermal correction to free energy (Hartree): 0.185465
M06 electronic energy in solution (Hartree): -743.7374782
Three lowest frequencies (cm-1): -444.6343, 25.1798, 27.2711

Table S5. Cartesian Coordinates for TS30$_{lin}$.

C	-0.3960893232	-1.5410298701	1.1280534711
C	-0.1510067728	-2.9318262833	0.5408239236
C	-0.5520260183	-2.4221141575	-0.8603905091
C	-1.5852005006	-1.1984469422	0.3261528639
H	-0.2067488351	-1.2160953475	2.1525874313
H	-0.8211647377	-3.709241746	0.9357949532
H	0.879983375	-3.2908209512	0.6084295224
H	-1.3679968024	-2.8821808302	-1.4122107093
H	0.2779346239	-2.2334442336	-1.5594866074
H	-2.3479056352	-1.9770874524	0.2691521126
C	-2.2412136442	0.1360876481	0.2489886207
C	-1.7059333144	1.2925531054	0.848030959
C	-3.4886219568	0.2312288638	-0.3918786659
C	-2.4043956631	2.4974010429	0.8062955908
H	-0.7392352449	1.2515009018	1.3411308868
C	-4.1765661996	1.4418995569	-0.4505754197
H	-3.919078287	-0.6557275265	-0.8520414454
C	-3.6366824221	2.5798071247	0.1517599247
H	-1.979761548	3.3780112227	1.2802311702
H	-5.1352709358	1.494853021	-0.9592236221
H	-4.1713621308	3.5248272709	0.1117232562
Pd	0.6562108816	-0.47073856	-0.2586394819
O	2.1239874664	0.7538585146	0.6800498956
C	2.5353395517	1.2377039193	-0.4388616231
O	2.0150516653	0.8719957286	-1.5274334101
C	3.6596616347	2.2481744155	-0.4053092747
H	3.3926525873	3.0801558399	0.2544823451
H	4.5607520134	1.7812664324	0.0072452714
H	3.8671851727	2.6209362919	-1.4100224299

Energies of the Optimized Structure for 31.

B3LYP electronic energy (Hartree): -742.9123604
B3LYP zero-point energy correction (Hartree): 0.232339
B3LYP thermal correction to free energy (Hartree): 0.186334
M06 electronic energy in solution (Hartree): -743.8205069

Three lowest frequencies (cm-1): 28.1765, 42.6309, 44.796

Table S6. Cartesian Coordinates for 31.

C	-0.3883956576	-1.9128929556	0.8506278683
C	0.4969726025	-3.1259374824	0.5564573987
C	1.6035092044	-2.4773371568	-0.2757993524
C	-1.1065927668	-1.298645623	-0.1657644361
H	-0.5252610717	-1.6020811561	1.8837899646
H	-0.0538488399	-3.9150920573	0.0294150759
H	0.8765962797	-3.5506906794	1.4900208194
H	1.5969808714	-2.7262731238	-1.3400098183
H	2.610790865	-2.5300935775	0.1416142942
H	-1.1173872093	-1.7921728236	-1.1377313026
C	-2.1019569599	-0.2218796645	-0.0176912618
C	-2.1979018643	0.5808295422	1.1336127497
C	-3.0052876029	0.0050843243	-1.0702170608
C	-3.1772450784	1.5644145016	1.2302621325
H	-1.4880207689	0.4535007368	1.9451659173
C	-3.9873124262	0.989120969	-0.9721013506
H	-2.9366256414	-0.601591585	-1.9702724717
C	-4.077679935	1.770976	0.1804901166
H	-3.2324961934	2.1804383617	2.1233939598
H	-4.6778670198	1.1468928977	-1.7959041217
H	-4.8383176556	2.5428027226	0.2588624904
Pd	1.032399529	-0.5280535901	-0.1072669427
O	1.0739950524	1.784048923	0.004732263
C	2.2885416553	1.6854511958	-0.3177308225
O	2.8218570524	0.5311872825	-0.5251507067
C	3.163496737	2.9080650351	-0.4725949345
H	2.589623658	3.8159061743	-0.2775308672
H	4.0087947546	2.8465725564	0.2212258973
H	3.5764484294	2.9399962522	-1.4864544983

Energies of the Optimized Structure for 32.

B3LYP electronic energy (Hartree): -742.9039041
B3LYP zero-point energy correction (Hartree): 0.232067
B3LYP thermal correction to free energy (Hartree): 0.186341
M06 electronic energy in solution (Hartree): -743.81241
Three lowest frequencies (cm-1): 24.217, 35.7085, 38.5137

Table S7. Cartesian Coordinates for 32.

C	-0.2966299544	-1.0027039405	1.4372581869
C	0.6371048334	-1.9940797729	1.2196607207
C	-1.034051199	-0.1517536716	-0.5615532474
C	-1.594078176	-0.9175702995	0.633568861
H	-0.1230216938	-0.2418137076	2.1959937133
H	0.3933568177	-2.8715940024	0.6243575186
H	1.5402047998	-2.0553168672	1.8205119906
H	-1.2618694269	-0.5568804198	-1.5501145396
H	-1.1776523082	0.9306453981	-0.5176966429
H	-1.8615594777	-1.9359106083	0.3173903427
C	-2.7718013467	-0.3158198686	1.382535987
C	-2.9781386522	-0.6199673034	2.7356323819
C	-3.6969085912	0.5129166525	0.7355989974
C	-4.074258017	-0.1030915547	3.4270344946
H	-2.2767015904	-1.2704282039	3.254220487
C	-4.7963714471	1.0297769781	1.4238030434
H	-3.5596050127	0.7547607331	-0.3148110631
C	-4.9874849151	0.7261863286	2.772581136
H	-4.2143497149	-0.348144712	4.4766074182
H	-5.5021252035	1.6726165301	0.904328592
H	-5.8406347716	1.1316352528	3.3096229355
Pd	0.9868869961	-0.4042705611	-0.2945127218
O	3.2365240376	-0.2869460636	-0.5848539851
C	2.9937275873	0.4790407164	-1.5611015593
O	1.7795997815	0.7547951578	-1.8828664016
C	4.1099829955	1.0992977305	-2.3660866281
H	5.0752720748	0.6955539837	-2.0549421529
H	3.9487012018	0.9107348089	-3.4321832979
H	4.103898883	2.1854428763	-2.2214856272

Energies of the Optimized Structure for 33.

B3LYP electronic energy (Hartree): -742.860525
B3LYP zero-point energy correction (Hartree): 0.229457
B3LYP thermal correction to free energy (Hartree): 0.182928
M06 electronic energy in solution (Hartree): -743.7728231
Three lowest frequencies (cm-1): 20.4238, 24.4839, 35.0334

Table S8. Cartesian Coordinates for 33.

Pd	0.1752979749	-0.1917725343	0.2208227343
C	-1.8442120817	1.7928861291	1.5602236048
C	-2.4239430476	1.6403500388	0.0986182967
H	-2.0998037243	2.7462184086	2.0372721098

H	-2.06166347	0.9746365177	2.2496252213
H	-2.8508764784	2.6085293829	-0.2059208949
C	-0.9685199342	1.6010240528	-0.3753378709
C	-0.4641023454	1.7916090469	0.9110521411
H	-0.548567498	1.8059798346	-1.3573323883
H	0.4753585832	2.2076748218	1.2673222797
C	-3.4127695988	0.546472993	-0.2216746607
C	-4.5576399189	0.3936111491	0.5737360134
C	-3.2455963859	-0.2988482748	-1.3259807555
C	-5.507710151	-0.5837371344	0.2779183565
H	-4.705392885	1.0445389789	1.4329098394
C	-4.1974773502	-1.2751429382	-1.6268067818
H	-2.3609747936	-0.2009436625	-1.948990578
C	-5.3306022811	-1.4217308877	-0.8256831236
H	-6.3857103822	-0.6914943603	0.9093981441
H	-4.0479172405	-1.9251016385	-2.4847985687
H	-6.0687689073	-2.1849319492	-1.0565537627
O	1.4037317688	-1.8987440142	0.0423432045
C	2.4042475297	-1.2146352335	-0.3935524881
O	2.308717307	0.0384905592	-0.5345171389
C	3.6808795248	-1.9467264369	-0.726230858
H	4.0518875976	-2.4621787945	0.1660326924
H	3.4801835921	-2.7113455691	-1.4840780195
H	4.4362061614	-1.2489810296	-1.0924962077
H	-1.1209122353	-0.8135271859	0.7439792394

Energies of the Optimized Structure for 34.

B3LYP electronic energy (Hartree): -742.8834144
B3LYP zero-point energy correction (Hartree): 0.2339
B3LYP thermal correction to free energy (Hartree): 0.190467
M06 electronic energy in solution (Hartree): -743.7978976
Three lowest frequencies (cm-1): 40.8152, 47.5562, 57.2137

Table S9. Cartesian Coordinates for 34.

C	-0.3222247183	-1.9083898554	0.3563693111
C	0.8132639826	-2.3800189571	1.2837217324
C	1.7704604762	-1.9855543342	0.1259316576
C	0.5771092566	-2.3088712873	-0.8329726133
H	-1.3504122854	-2.2651414928	0.4570106871
H	0.7942592107	-3.4728925340	1.4003583123
H	0.9357476249	-1.9369608234	2.2761606987
H	2.7037963573	-2.5474372308	0.0028787559
H	0.5087533770	-3.3865918034	-1.0415466473
Pd	-0.3663599330	0.1244140110	0.3702814496
O	-2.4487484984	0.3265115503	0.1486638354

C	-2.4269880601	1.6166193106	0.1447206116
O	-1.3414829313	2.2426959635	0.2524633668
C	-3.7496846546	2.3365270583	0.0108047164
H	-4.3977069165	2.0765413698	0.8548698233
H	-3.5940159936	3.4167236699	-0.0145601058
H	-4.2581676660	2.0114852414	-0.9029418777
H	0.5039194969	-1.7575075899	-1.7748221661
C	2.0177336057	-0.4831545221	0.0794938577
C	2.5093657527	0.1020958209	-1.1190388066
C	1.8571504391	0.3649473612	1.2051581089
C	2.8364388492	1.4444029008	-1.1825888242
H	2.6452939533	-0.5307641150	-1.9921841718
C	2.1961954964	1.7385472046	1.1253681159
H	1.6338465535	-0.0520914321	2.1808900818
C	2.6757668980	2.2741122647	-0.0547996862
H	3.2174989997	1.8630350217	-2.1100717703
H	2.0753683626	2.3623822630	2.0058539473
H	2.9284679648	3.3284409656	-0.1157364007

Energies of the Optimized Structure for TS35.

B3LYP electronic energy (Hartree): -742.8161429
B3LYP zero-point energy correction (Hartree): 0.230657
B3LYP thermal correction to free energy (Hartree): 0.185704
M06 electronic energy in solution (Hartree): -743.73312
Three lowest frequencies (cm-1): -482.7145, 35.3742, 35.8285

Table S10. Cartesian Coordinates for TS35.

C	-0.0015988251	-1.7067914853	1.2279418953
C	0.4431106325	-3.0002174489	0.5680893339
C	0.1067008730	-2.4805110332	-0.8552062037
C	-1.0775717792	-1.3242960834	0.3075452004
H	0.0496867002	-1.4718090300	2.2916081383
H	-0.1604643703	-3.8794211289	0.8376760379
H	1.4944236597	-3.2570983455	0.7262258847
H	-0.7389587568	-2.9661658954	-1.3357688316
H	-1.8760505062	-2.0270365856	0.0713567307
Pd	1.0145888034	-0.3347564850	0.1040060575
O	2.3538366771	0.7838460712	1.3264545353
C	2.6934710394	1.5710532820	0.3666591523
O	2.2063839771	1.4304722369	-0.7862830802
C	3.6781712142	2.6774857247	0.6749054972
H	4.5314278759	2.2781476334	1.2316794166
H	4.0177636635	3.1523878703	-0.2476607258
H	3.1945366020	3.4285288363	1.3100215071
H	-1.4737068473	-0.3031617371	0.3179893616

C	1.1464197118	-2.1835722749	-1.8867654082
C	0.7236405061	-1.7716705765	-3.1668779163
C	2.5260778750	-2.3730338339	-1.6724465056
C	1.6410676490	-1.5372117288	-4.1856359041
H	-0.3384774106	-1.6270421316	-3.3516627486
C	3.4418484662	-2.1462509251	-2.6999268142
H	2.8887764982	-2.7083208963	-0.7070008811
C	3.0074964643	-1.7228929056	-3.9562878086
H	1.2904529770	-1.2130835621	-5.1616236703
H	4.5007587260	-2.3016514314	-2.5128137394
H	3.7253065839	-1.5422209203	-4.7512840811

Energies of the Optimized Structure for 36.

B3LYP electronic energy (Hartree): -742.9109921
B3LYP zero-point energy correction (Hartree): 0.23238
B3LYP thermal correction to free energy (Hartree): 0.186406
M06 electronic energy in solution (Hartree): -743.8220096
Three lowest frequencies (cm-1): 27.2384, 31.9764, 44.2222

Table S11. Cartesian Coordinates for 36.

C	-0.2355084589	-2.2852444765	0.8595190590
C	1.2583407621	-2.3715314452	0.5722514532
C	1.4502316840	-1.1757435804	-0.3653301005
C	-1.1706854265	-2.7263647152	-0.0528260989
H	-0.5627849415	-1.8812076795	1.8156463837
H	1.5062076497	-3.3149958763	0.0733945645
H	1.8567896613	-2.3115630236	1.4856943387
H	1.7410083876	-1.4598550848	-1.3796935299
H	-0.8775728282	-3.3262189619	-0.9116882449
Pd	-0.5583126399	-0.6610923788	-0.6231820720
O	-2.5032601920	0.3789894284	-1.2128037385
C	-1.7863489959	1.2713512599	-1.7505261501
O	-0.5062819761	1.1753432900	-1.7351513021
C	-2.4107032363	2.4747220877	-2.4175614082
H	-3.4998050494	2.4018491566	-2.4002092012
H	-2.0936528179	3.3858606159	-1.8985401917
H	-2.0577267989	2.5492598382	-3.4514243694
H	-2.2329030089	-2.6949016673	0.1722733120
C	2.1512077373	0.0405970350	0.1041337718
C	2.7428380016	0.9001792677	-0.8428422724
C	2.2492118697	0.3927356612	1.4646843164
C	3.4152159292	2.0530142982	-0.4474530205
H	2.6634673528	0.6554922735	-1.8985473777
C	2.9210810081	1.5473426940	1.8601090894
H	1.7919140786	-0.2362152877	2.2237257465

C	3.5096778341	2.3823506690	0.9070860485
H	3.8658814737	2.6968346889	-1.1979959824
H	2.9850166217	1.7964894926	2.9161181961
H	4.0350081488	3.2814661804	1.2172234307

Energies of the Optimized Structure for S1.

B3LYP electronic energy (Hartree): -975.3424591
B3LYP zero-point energy correction (Hartree): 0.352099
B3LYP thermal correction to free energy (Hartree): 0.296895
M06 electronic energy in solution (Hartree): -976.1600756
Three lowest frequencies (cm-1): 20.6109, 28.0234, 34.7912

Table S12. Cartesian Coordinates for S1.

C	1.426436	-1.903247	-0.697837
C	1.344946	-2.911429	0.4622
C	2.558858	-2.207376	1.136904
C	2.716416	-1.284078	-0.110545
H	1.385113	-2.25828	-1.731774
H	1.558197	-3.939544	0.142337
H	0.416424	-2.911943	1.038345
C	2.468076	0.217207	0.035775
C	2.180812	0.957634	-1.14064
C	2.569236	0.923241	1.257074
C	2.006174	2.354568	-1.084128
H	2.229922	0.46654	-2.109294
C	2.401241	2.300595	1.298322
H	2.800723	0.381292	2.168315
C	2.112861	3.021397	0.127128
H	1.799373	2.903286	-1.998646
H	2.49678	2.824943	2.245486
H	1.982717	4.099108	0.171386
Pd	0.18281	-0.326808	-0.518496
C	-2.320625	1.668248	-1.05005
C	-1.586633	1.744617	1.215934
C	-3.423795	2.306441	-0.203496
H	-2.598626	0.670535	-1.404968
H	-2.009303	2.280313	-1.90259
C	-3.114557	1.754458	1.197168
H	-1.168486	2.705387	1.542732
H	-1.175918	0.931465	1.815532
H	-3.336741	3.399752	-0.214037
H	-4.423585	2.042011	-0.561625

H	-3.537927	2.361022	2.003765
H	-3.484075	0.729506	1.302925
O	-1.179311	1.531206	-0.164531
O	-1.496436	-1.527374	-0.865852
C	-2.101518	-1.873253	0.231565
O	-1.778091	-1.522789	1.374039
C	-3.294766	-2.801059	0.002801
H	-2.941509	-3.76372	-0.384032
H	-3.833433	-2.964081	0.938609
H	-3.969757	-2.381091	-0.750264
H	3.643051	-1.46406	-0.672949
H	2.304895	-1.687786	2.064577
H	3.42464	-2.847635	1.328693

Energies of the Optimized Structure for S2.

B3LYP electronic energy (Hartree): -975.349055
B3LYP zero-point energy correction (Hartree): 0.353141
B3LYP thermal correction to free energy (Hartree): 0.29763
M06 electronic energy in solution (Hartree): -976.1568389
Three lowest frequencies (cm-1): 16.8673, 24.9486, 37.1294

Table S13. Cartesian Coordinates for S2.

C	-0.1484187398	-0.5802338085	-1.8569802874
C	-1.0294036274	-1.6769650929	-2.4914931433
C	-0.139064438	-2.7487814458	-1.8099628562
C	0.9487007892	-1.6599187456	-1.5694660147
H	0.1587861874	0.2719857263	-2.4768455883
H	-0.9424685503	-1.6829371533	-3.5866409753
H	-2.0897234151	-1.6835404769	-2.2251776898
H	0.1653557932	-3.6162346383	-2.40515516
H	-0.5879273979	-3.0993297125	-0.8772087357
H	1.6370561507	-1.6525457146	-2.4277682278
C	1.7850299142	-1.6428971356	-0.311526991
C	3.1488881422	-1.3204981337	-0.3790005528
C	1.2385692428	-1.9311386386	0.9503219336
C	3.9428994115	-1.2744396923	0.7702004461
H	3.595837069	-1.1090688424	-1.3486404868
C	2.0283841489	-1.8903642757	2.1002267959
H	0.1858631584	-2.1847819808	1.0341612327
C	3.3836155699	-1.5594075906	2.0169010358
H	4.9984924833	-1.0266316765	0.688250978
H	1.5832880325	-2.1205832396	3.0650720314
H	3.9975937885	-1.5317322846	2.9134011527
Pd	-0.9847391522	0.2835947242	-0.2344555947

C	1.3599710527	2.1274785566	0.6217013682
C	-0.1601522101	3.2301442211	-0.8060739554
C	1.7394306605	3.6243485992	0.5914477173
H	2.1878483284	1.4492933361	0.4086486496
H	0.8916907572	1.8347896257	1.5660847477
C	1.031940139	4.1707203271	-0.6677888931
H	-0.9719929676	3.4848029329	-0.1117273832
H	-0.5629258951	3.1400818485	-1.8167411468
H	1.3669876912	4.1286016319	1.4887330096
H	2.822325588	3.7708155706	0.5536315985
H	0.7306573676	5.2171669146	-0.5646260117
H	1.6785208041	4.0832395822	-1.5474295105
O	0.3943848154	1.9415652359	-0.4570220415
O	-2.4295913583	0.6270961025	1.5777184965
C	-2.8945171773	-0.4990277482	1.2663335535
O	-2.4052466623	-1.1641859026	0.273406011
C	-4.0515779279	-1.11563057	2.0195111871
H	-4.2573200466	-0.5491429455	2.9297994955
H	-4.9436586615	-1.1110925463	1.3826598895
H	-3.8296468585	-2.1588199444	2.2645669159

Energies of the Optimized Structure for S3.

B3LYP electronic energy (Hartree): -1207.8017504
B3LYP zero-point energy correction (Hartree): 0.472427
B3LYP thermal correction to free energy (Hartree): 0.407869
M06 electronic energy in solution (Hartree): -1208.525376
Three lowest frequencies (cm-1): 14.9723, 19.3081, 28.4799

Table S14. Cartesian Coordinates for S3.

C	-0.5860204848	0.1864475964	-0.0969170622
C	0.9493360626	0.0832759799	-0.2624632102
C	1.1113580322	1.4430491227	0.4656270703
C	-0.4121326623	1.6954474397	0.2741687523
H	-1.1970903498	-0.0243601295	-0.9766655302
H	1.2431272176	0.1272981652	-1.3196868672
H	1.4553136752	-0.7780711293	0.1843116766
H	1.7956944148	2.172670365	0.0192492708
H	1.3753063622	1.3082236483	1.5186095667
H	-0.5618977244	2.2783979236	-0.6493528012
C	-1.2242983015	2.3542963412	1.3662559071
C	-2.6045394117	2.1126828953	1.4727534196
C	-0.6347403836	3.2531184974	2.2659702279
C	-3.3649443029	2.7492821719	2.4550100521
H	-3.077661552	1.4132636502	0.7887822933

C	-1.3951953985	3.8892757215	3.2523303144
H	0.4295676868	3.4638777149	2.1918806658
C	-2.7642702871	3.6379129719	3.3514942645
H	-4.4318164424	2.5493023324	2.5205668256
H	-0.9163182302	4.5837764651	3.9386648715
H	-3.3584564908	4.1315700191	4.1163013516
Pd	-1.4025867238	-1.0069598422	1.3193881048
C	-0.0360417301	-0.202121374	4.0030403446
C	1.1707279527	-1.938860102	2.9368389734
C	1.2390287012	-0.4050050924	4.8125441792
H	-0.8924851071	-0.7230555233	4.4473253761
H	-0.2991532646	0.837272558	3.8015268322
C	1.6594945036	-1.8269976621	4.394582735
H	1.9759824397	-1.839921544	2.2042787299
H	0.6279651359	-2.8685882837	2.7452105176
H	1.9953794201	0.3301878553	4.5155833879
H	1.0721826304	-0.3107404411	5.8896491897
H	2.7368899542	-1.9943033914	4.4802739548
H	1.1554541567	-2.5696921562	5.02216899
C	-3.7697981128	-2.0107024466	3.2909650409
C	-2.2973343533	-3.8198087216	2.8111743998
C	-4.4633278971	-3.3149614421	3.6859178932
H	-4.2172020493	-1.5622912524	2.3979280251
H	-3.7405855493	-1.2625253599	4.0891831178
C	-3.7343169662	-4.3409526576	2.8042960332
H	-1.7199981737	-4.2147009562	3.6587134955
H	-1.7797336899	-4.0102722159	1.8705615662
H	-4.3016594188	-3.533341564	4.7487591172
H	-5.5423283872	-3.2795899213	3.5064552567
H	-3.8084380267	-5.3656978217	3.1811585364
H	-4.1175507579	-4.3157306545	1.7798127195
O	-2.4000954111	-2.3771174852	2.9801173543
O	0.2748904013	-0.8122800084	2.7248835528
O	-3.0724167703	-1.0609436258	0.1151744992
C	-3.3302296777	-2.2123289733	-0.4420570819
O	-2.7079560708	-3.2620761808	-0.2581328292
C	-4.5224535204	-2.1580157587	-1.3973444348
H	-5.3751981458	-1.6588828643	-0.9255163064
H	-4.2541504259	-1.5699660325	-2.2826618371
H	-4.803105885	-3.1662916114	-1.7090663631

Energies of the Optimized Structure for S4.

B3LYP electronic energy (Hartree): -1207.7944483
B3LYP zero-point energy correction (Hartree): 0.473057
B3LYP thermal correction to free energy (Hartree): 0.411017
M06 electronic energy in solution (Hartree): -1208.519109
Three lowest frequencies (cm-1): 19.8661, 28.7098, 37.482

Table S15. Cartesian Coordinates for S4.

C	-0.5605721627	0.5824241435	-0.1129452636
C	0.9167873785	0.194316251	-0.3799358712
C	1.3758932091	1.3859745424	0.5016500521
C	-0.0632337399	1.9670950034	0.4136625749
H	-1.2249163222	0.6189240379	-0.9845923618
H	1.1937317394	0.3175998223	-1.4357933466
H	1.2413254036	-0.804269187	-0.0665140779
H	2.1898049911	2.0097055908	0.116437186
H	1.6187174655	1.0691224009	1.5192668473
H	-0.1071846899	2.6749889416	-0.4305978372
C	-0.6867966805	2.6478002374	1.610805749
C	-2.0804238471	2.6756294293	1.7759714935
C	0.1044912785	3.3034703232	2.5641518867
C	-2.6635228498	3.3262894958	2.8646536967
H	-2.7116510297	2.1773718697	1.0446726436
C	-0.4746789474	3.9586458083	3.6544780165
H	1.1860345638	3.3012168959	2.4538715103
C	-1.8620241297	3.9692929801	3.8115850603
H	-3.7451552246	3.3291201493	2.9747811805
H	0.159847796	4.4606252746	4.3810267772
H	-2.3143610863	4.4752096489	4.6605224778
Pd	-1.5433674056	-0.6700863379	1.1583072783
C	-0.5812355482	-0.1293940837	4.029532351
C	0.8194334235	-1.6704318395	2.8506888312
C	0.483942537	-0.6255425497	4.999441192
H	-1.5385933241	-0.6403743227	4.1709551257
H	-0.7252386927	0.9514203289	4.017256608
C	0.9032086261	-1.9582698851	4.3553864717
H	1.784137238	-1.3800790713	2.4227326157
H	0.3823892725	-2.4918092595	2.2791378132
H	1.3265970194	0.0750271485	5.0347137165
H	0.0941624932	-0.7463485859	6.0147594276
H	1.9035139428	-2.2853175925	4.6546050036
H	0.1941772339	-2.7477591548	4.6264729498
O	-0.0553631048	-0.4966081704	2.7191428997
C	-4.3883618738	-1.1345081406	-0.0097707286
C	-2.6346473412	-2.1550442191	-1.2683749317

C	-4.959456032	-2.3212231684	-0.80178779
H	-4.858094588	-0.1815011787	-0.2729698153
H	-4.4184856426	-1.2869416495	1.0701112385
C	-3.9505059681	-2.5109935849	-1.9487842858
H	-2.2509672612	-2.9644483107	-0.6386639894
H	-1.8503375598	-1.8030091252	-1.9421668525
H	-4.9841829961	-3.2174732865	-0.1728543972
H	-5.9768197769	-2.1275843817	-1.1544088919
H	-3.9471904091	-3.5297890221	-2.3474447986
H	-4.1588698811	-1.8172866353	-2.7717410163
O	-2.9853206029	-1.0242484255	-0.4132798812
O	-2.6877440535	-1.9990820513	2.4893473935
C	-2.3801851242	-3.2436200494	2.3352116776
O	-1.5261416972	-3.6801773027	1.5404356068
C	-3.1670375057	-4.2132963605	3.2208424812
H	-3.0894296673	-3.9148656752	4.2721711343
H	-4.2313777996	-4.1754768946	2.9593701687
H	-2.8011571264	-5.2350367618	3.0974566698

Energies of the Optimized Structure for S5.

B3LYP electronic energy (Hartree): -742.8733079
B3LYP zero-point energy correction (Hartree): 0.231864
B3LYP thermal correction to free energy (Hartree): 0.185858
M06 electronic energy in solution (Hartree): -743.7886281
Three lowest frequencies (cm-1): 18.0478, 34.0183, 43.4603

Table S16. Cartesian Coordinates for S5.

C	-1.2732272012	-1.5515353255	1.2087229811
C	-1.0339422242	-2.72121717	0.2818429762
C	-2.4266029549	-2.4932921074	-0.3687505412
C	-2.6953135521	-1.3307301439	0.6477015008
H	-1.0914211968	-1.58994739	2.2844703136
H	-0.7700230264	-3.6976223259	0.6972683177
H	-0.1782435919	-2.5112406634	-0.4664776024
H	-3.0988770645	-3.3493326024	-0.2649848241
H	-2.3944867013	-2.1883588554	-1.4173563063
H	-3.4227912684	-1.671386962	1.4009538086
C	-3.1546530456	0.0119175481	0.1213622857
C	-2.5646110663	1.2143034633	0.5312192892
C	-4.2376830541	0.0629048389	-0.769386448
C	-3.0471261089	2.437514414	0.0573677418
H	-1.7170563414	1.20189247	1.2085270653
C	-4.7184606579	1.2831974366	-1.2432405805
H	-4.7109015015	-0.8618623539	-1.0934772237

C	-4.1231889343	2.4775519807	-0.8295035612
H	-2.5731111314	3.3599333781	0.3823705634
H	-5.5569278606	1.3015125497	-1.934827904
H	-4.4945658067	3.429913595	-1.1985147965
Pd	0.2964264236	-0.7415172458	0.2486654432
O	0.7950645516	1.1507656951	1.0334455005
C	1.8091385915	1.2807175124	0.2494969696
O	2.094392619	0.3676331946	-0.57161924
C	2.6364281617	2.5387273935	0.3560202366
H	1.988160813	3.4181074506	0.2897387761
H	3.1315673684	2.5690635842	1.3329513605
H	3.3883382219	2.5659352009	-0.4346335821

Energies of the Optimized Structure for TS_S1.

B3LYP electronic energy (Hartree): -742.8571156
B3LYP zero-point energy correction (Hartree): 0.228313
B3LYP thermal correction to free energy (Hartree): 0.183065
M06 electronic energy in solution (Hartree): -743.7739336
Three lowest frequencies (cm-1): -489.1767, 22.7608, 32.7701

Table S17. Cartesian Coordinates for TS_S1.

C	-1.2555124466	-1.5873729806	1.1043997798
C	-1.0329231312	-2.718748063	0.281053202
C	-2.3099793253	-2.4793874594	-0.5308729327
C	-2.593009427	-1.2558506989	0.4256394451
H	-0.9615431563	-1.4040987587	2.1355541829
H	-0.5644749619	-3.6683883164	0.523494557
H	0.2466433456	-2.3914230506	-0.8731847598
H	-3.0340119538	-3.2951558974	-0.428980168
H	-2.1832586996	-2.2374594603	-1.5873842104
H	-3.4037608367	-1.5371149181	1.114795277
C	-2.9100816833	0.0974121372	-0.167094272
C	-2.1317435316	1.2337579736	0.0838790999
C	-4.0477237228	0.2253954801	-0.9799745871
C	-2.4828160455	2.4682575305	-0.4715069996
H	-1.2432584555	1.1638733095	0.7030142844
C	-4.3957009624	1.4551291027	-1.5358134024
H	-4.6664410552	-0.6478717975	-1.1785480852
C	-3.611560807	2.584033065	-1.2819525671
H	-1.8649702386	3.3388430335	-0.2679882236
H	-5.2783030992	1.5333661665	-2.1654341497
H	-3.8802494116	3.5442727097	-1.7141105109
Pd	0.4533074338	-1.061080385	-0.0597437671
O	1.1783024168	0.8344439388	0.7806302908

C	2.133232178	0.813680802	-0.0622309186
O	2.2219539047	-0.1488715374	-0.894445303
C	3.1773112354	1.9020739793	-0.0589866798
H	2.7633974907	2.8248467995	0.3540138214
H	4.0188962555	1.5892035802	0.5705814198
H	3.5551813985	2.0687008362	-1.0706727799

Energies of the Optimized Structure for S6.

B3LYP electronic energy (Hartree): -742.8593561
B3LYP zero-point energy correction (Hartree): 0.229396
B3LYP thermal correction to free energy (Hartree): 0.183756
M06 electronic energy in solution (Hartree): -743.7724809
Three lowest frequencies (cm-1): 27.5768, 33.7899, 42.6502

Table S18. Cartesian Coordinates for S6.

C	-0.2239034132	-1.5858620879	1.1255167321
C	0.0269626035	-2.5599812437	0.1644166139
C	-1.3901372234	-2.4953448663	-0.4046146877
C	-1.6856791435	-1.4132760887	0.7103068622
H	0.2721406478	-1.3414444172	2.0617412823
H	0.7632149376	-3.3560768629	0.1154994399
H	0.9586994631	-1.5244059751	-1.5856702219
H	-1.9498148719	-3.4275192914	-0.2653746914
H	-1.4985433545	-2.1576926018	-1.4364700866
H	-2.3241647599	-1.8675455297	1.4832632972
C	-2.2624886557	-0.0728474233	0.320183843
C	-1.6114676761	1.1342826326	0.6047224636
C	-3.5090256187	-0.0308860573	-0.3235104817
C	-2.1935883823	2.3541721683	0.2470979418
H	-0.6450966134	1.1311623365	1.1005799746
C	-4.0880419673	1.1851522272	-0.6823244408
H	-4.0296189602	-0.96042458	-0.5457913693
C	-3.4299457072	2.3847578957	-0.3972150626
H	-1.6731463051	3.2810016644	0.4734998204
H	-5.0523564602	1.1972544302	-1.183705325
H	-3.8789956833	3.334051533	-0.6766295569
Pd	1.1776487035	-0.6775044338	-0.316483857
O	1.9434167134	0.9486260275	1.0287264348
C	2.6309878133	1.3462975987	0.0394292365
O	2.5530065813	0.7285667623	-1.0820125049
C	3.5673603876	2.5212821611	0.1628034649
H	3.2993123592	3.1303152982	1.0287513474
H	4.5914758974	2.1525407967	0.2943480896
H	3.544059018	3.1212695667	-0.7509143084

Energies of the Optimized Structure for TS_S2.

B3LYP electronic energy (Hartree): -742.8590477
B3LYP zero-point energy correction (Hartree): 0.229387
B3LYP thermal correction to free energy (Hartree): 0.185724
M06 electronic energy in solution (Hartree): -743.7719915
Three lowest frequencies (cm-1): -27.2622, 33.5978, 50.8609

Table S19. Cartesian Coordinates for TS_S2.

C	-1.2635474433	-1.4165204166	0.4788592169
C	-1.0083410145	-2.7693658993	0.2806790294
C	-1.7962349327	-2.8197121198	-1.0285104541
C	-2.0934268922	-1.2838886212	-0.796684008
H	-1.2355793844	-0.7913325272	1.3681264861
H	-0.74389409	-3.5685780883	0.9673323003
H	0.9312579792	-2.5552590238	-1.1041583805
H	-2.6943977491	-3.4442360618	-0.9572146613
H	-1.2490077578	-3.0741215205	-1.9372794192
H	-3.1521110434	-1.1620001963	-0.5214354879
C	-1.7405431709	-0.2793815734	-1.8675057834
C	-0.8901285218	0.8044918523	-1.6153211371
C	-2.30446884	-0.4089524197	-3.1455720387
C	-0.6052493295	1.7336090833	-2.6195669801
H	-0.4445193372	0.9252705639	-0.6316484496
C	-2.0193433085	0.515861976	-4.1490752327
H	-2.9717969524	-1.2424243174	-3.355743407
C	-1.166701724	1.5920629611	-3.8884837493
H	0.0596267168	2.566369588	-2.4065159745
H	-2.4623101671	0.3969978593	-5.1344693587
H	-0.9422671491	2.3128745583	-4.6700054367
Pd	0.9068052885	-1.6138294827	0.1080658552
O	1.5908291812	-0.1145916613	1.6489101665
C	2.7483877784	-0.2444544082	1.1503715552
O	2.932887881	-1.0247683587	0.1462305271
C	3.9352864936	0.4857378617	1.7267954255
H	3.6036272619	1.2759316055	2.4033311972
H	4.5601724836	-0.223060322	2.2824259381
H	4.546773078	0.9032568523	0.921678355

Energies of the Optimized Structure for (AcO)(H)Pd.

B3LYP electronic energy (Hartree): -355.7921874
B3LYP zero-point energy correction (Hartree): 0.058543
B3LYP thermal correction to free energy (Hartree): 0.026526
M06 electronic energy in solution (Hartree): -356.906447
Three lowest frequencies (cm-1): 37.7569, 123.5644, 200.9022

Table S20. Cartesian Coordinates for (AcO)(H)Pd .

Pd	-1.0375280512	0.0234618245	-0.0260691498
O	0.7194865175	-1.0146747054	0.0312837842
C	1.466340155	0.0480024915	-0.0137116951
O	0.9297204665	1.1813260797	-0.0717115801
C	2.9578159948	-0.1521100535	0.0151806854
H	3.250085218	-0.6017794102	0.9701619196
H	3.2581718108	-0.841798039	-0.7797281073
H	3.4604776165	0.8086993181	-0.1091706471
H	-1.9737647279	-1.1910015057	0.0268157903

Energies of the Optimized Structure for 37.

B3LYP electronic energy (Hartree): -387.0183993
B3LYP zero-point energy correction (Hartree): 0.168468
B3LYP thermal correction to free energy (Hartree): 0.134837
M06 electronic energy in solution (Hartree): -386.8148325
Three lowest frequencies (cm-1): 41.7072, 126.2972, 139.5369

Table S21. Cartesian Coordinates for 37.

C	0.7186167298	1.9974251877	-0.6573336678
C	1.8595785789	1.6948666031	0.4046988806
H	0.8305590312	2.945376938	-1.1992211466
H	0.5692033064	1.1909179352	-1.3840803784
H	2.5483296325	2.5440728193	0.5030219192
C	0.7274191795	1.7239219411	1.4260779585
C	-0.2269696431	2.0030263372	0.5283384621
H	0.7304892687	1.5748842996	2.5030905266
H	-1.2948570097	2.1905742459	0.6047813844
C	2.6581206906	0.4236587519	0.2308647299
C	4.0261245027	0.4776983272	-0.0674065682
C	2.0510073253	-0.8367449972	0.3417447321
C	4.7686586591	-0.6898285696	-0.2559769294
H	4.5146515408	1.4462866559	-0.1521101839
C	2.7885803866	-2.0053283627	0.1538781034

H	0.9924188846	-0.8969232381	0.582711568
C	4.1516419831	-1.9367359498	-0.1461921101
H	5.8292670436	-0.6239655743	-0.4852519627
H	2.2996427781	-2.9720391033	0.2455220278
H	4.7272371313	-2.8474002471	-0.2894803453

Energies of the Optimized Structure for 38.

B3LYP electronic energy (Hartree): -737.2808853
B3LYP zero-point energy correction (Hartree): 0.146168
B3LYP thermal correction to free energy (Hartree): 0.102697
M06 electronic energy in solution (Hartree): -738.2703813
Three lowest frequencies (cm-1): 20.7941, 38.8135, 64.1723

Table S22. Cartesian Coordinates for 38.

Pd	0.0100649789	0.3879846798	-0.4398005998
O	1.7943439151	-0.6824031674	-0.5553623673
C	2.5045238955	0.3257421103	-0.1649503159
O	1.9383494264	1.4235563616	0.1024360618
C	3.9934371376	0.1477855396	-0.0438059531
H	4.2101272956	-0.6592343875	0.6639910678
H	4.4076661734	-0.148059385	-1.0133994442
H	4.4595874524	1.0751022614	0.2936601669
H	-0.9783584282	-0.6969949399	-0.886333476
C	-2.4744824849	1.5145230149	-1.9274787201
C	-1.4890078727	1.9368240673	-0.8779043715
C	-1.6450656746	1.5339574562	0.4465393848
C	-2.8019092048	0.669026507	0.8521000904
C	-3.7305330581	0.2295507494	-0.2217070314
C	-3.5799722845	0.618235641	-1.4996469119
H	-0.8529718361	2.7756919667	-1.1517761758
H	-4.5455067765	-0.4132715576	0.0988965385
H	-4.2645834761	0.3119526547	-2.2855786098
H	-1.1376161279	2.040744856	1.2644083519
O	-2.9904249377	0.3796399352	2.0234144144
O	-2.3900851426	1.9299534165	-3.0727041997

Energies of the Optimized Structure for TS39.

B3LYP electronic energy (Hartree): -737.2598305
B3LYP zero-point energy correction (Hartree): 0.144333
B3LYP thermal correction to free energy (Hartree): 0.101369
M06 electronic energy in solution (Hartree): -738.2629126
Three lowest frequencies (cm-1): -84.2997, 32.7672, 43.7719

Table S23. Cartesian Coordinates for TS39.

Pd	0.5131235941	-0.010660605	0.3837405873
O	2.4993853996	1.1891782287	-1.2837121586
C	3.073236233	0.3078055345	-0.649531702
O	2.4722322854	-0.497170085	0.2028670777
C	4.565218662	0.0410664065	-0.7746110676
H	5.0425788131	0.0996334405	0.2088585554
H	4.7279987546	-0.9729547439	-1.154961306
H	5.0167254618	0.7674673209	-1.4519790078
H	0.3044618802	-0.5840518043	-0.9970820495
C	-2.0032977655	1.3619585004	-0.744172251
C	-1.4798373623	0.9301792075	0.5925648191
C	-1.5852336658	-0.3942893491	1.0052204099
C	-2.2247879572	-1.4235328514	0.1200175334
C	-2.6423311537	-0.9816534786	-1.236169604
C	-2.5376843942	0.2986366411	-1.6349125282
H	-1.2964544691	1.7412844082	1.2955399294
H	-3.0593949982	-1.7566599546	-1.8730121218
H	-2.8636703989	0.6304982499	-2.6165536619
H	-1.4897875707	-0.68498539	2.049613711
O	-2.4243264681	-2.560178914	0.5185814415
O	-2.0262158801	2.5402002375	-1.0615146061

Energies of the Optimized Structure for 40.

B3LYP electronic energy (Hartree): -737.3172267
B3LYP zero-point energy correction (Hartree): 0.149292
B3LYP thermal correction to free energy (Hartree): 0.102683
M06 electronic energy in solution (Hartree): -738.3188618
Three lowest frequencies (cm-1): 3.6376, 38.4204, 40.3447

Table S24. Cartesian Coordinates for 40.

Pd	-0.303992809	0.0898060186	-0.8381758527
O	-2.2249741414	-0.2274277701	1.5909023094
C	-2.979796357	-0.125423703	0.5031616566
O	-2.5075533618	0.0109705171	-0.6279542916
C	-4.453376273	-0.1948680602	0.7795407224
H	-4.6922855011	-1.1533232655	1.2521720258
H	-4.7346403713	0.5954832653	1.4829166128
H	-5.0104952729	-0.0871340333	-0.1507359743
H	-1.277766662	-0.1737659734	1.2944959248
C	2.0677439706	1.4474177197	0.2920652528

C	1.756925907	0.6587115762	-0.9319546638
C	1.6734191833	-0.7429216136	-0.8827245015
C	1.8980038261	-1.4764439731	0.3942466811
C	2.1514609977	-0.6534395314	1.6123041743
C	2.2286925843	0.6875556088	1.5654949054
H	1.9082135293	1.1873009876	-1.8708180638
H	2.2957007301	-1.2136416536	2.5327118478
H	2.438786221	1.2904153594	2.4453140421
H	1.7528315735	-1.350868328	-1.7811593535
O	1.9055620607	-2.7008128279	0.452581704
O	2.215027166	2.6640556805	0.2664008421

Energies of the Optimized Structure for TS41.

B3LYP electronic energy (Hartree): -386.9750582
B3LYP zero-point energy correction (Hartree): 0.166019
B3LYP thermal correction to free energy (Hartree): 0.13276
M06 electronic energy in solution (Hartree): -386.7670296
Three lowest frequencies (cm-1): -613.7946, 74.7245, 103.5886

Table S25. Cartesian Coordinates for TS41.

C	0.9543789511	2.5933248423	-1.0437234555
C	1.7123615822	1.4995866032	0.6444278676
H	1.2686971207	3.5227200525	-1.5298247626
H	1.1808495716	1.703782206	-1.6201416993
H	2.301070675	2.3881254973	0.8510191879
C	0.2858942785	1.6163858463	0.8340953795
C	-0.1117001596	2.5465568593	-0.0894682142
C	2.4601259831	0.2400132413	0.7055474289
C	3.8492191348	0.2374446688	0.9393667219
C	1.8140253292	-0.9978274308	0.5214992271
C	4.5626052762	-0.956223806	1.0050013339
H	4.3638733669	1.1860754102	1.0760789177
C	2.5252108229	-2.1935587861	0.5987514786
H	0.7481490973	-1.0101267209	0.3086854441
C	3.9017770862	-2.1775471346	0.8392275725
H	5.6335698732	-0.9377823329	1.1895826812
H	2.0086137659	-3.1397780179	0.4599199883
H	4.4578486068	-3.1098466984	0.8898890969
H	-0.9841051896	3.1989943983	-0.069937744
H	-0.310350503	1.0306577464	1.5321948409

Energies of the Optimized Structure for 1.

B3LYP electronic energy (Hartree): -387.0405164
B3LYP zero-point energy correction (Hartree): 0.167267
B3LYP thermal correction to free energy (Hartree): 0.132306
M06 electronic energy in solution (Hartree): -386.8310432
Three lowest frequencies (cm-1): 41.3168, 78.1658, 126.8091

Table S26. Cartesian Coordinates for 1.

C	1.1500771316	0.9636914618	-0.2101521546
C	1.6619114875	-0.2830434359	-0.135604215
H	2.7464564207	-0.390404107	-0.1484431722
C	1.9312737713	2.201245748	-0.2433083979
H	1.4348799069	3.0530170543	-0.7092191554
C	3.1631067974	2.3826709961	0.2575894146
H	3.6936469355	1.5941818488	0.7853305285
H	3.6748671848	3.3359761086	0.1647185621
H	0.0706377005	1.091037261	-0.2820514521
C	0.9198588032	-1.5456456963	-0.0720380719
C	1.6279354494	-2.7560046016	-0.1969121398
C	-0.4754868322	-1.6167305483	0.1121502117
C	0.9737995444	-3.9859465336	-0.153379595
H	2.7063954477	-2.7239034697	-0.3345535457
C	-1.1297826829	-2.8441863328	0.1537151468
H	-1.0509936494	-0.7039786931	0.2357228765
C	-0.4102068803	-4.0362142146	0.0200403011
H	1.5453741151	-4.9048205625	-0.2545844901
H	-2.2067109738	-2.8734519344	0.2981366734
H	-0.9243056671	-4.9927713488	0.0564639053

Energies of the Optimized Structure for S7.

B3LYP electronic energy (Hartree): -387.0308509
B3LYP zero-point energy correction (Hartree): 0.168569
B3LYP thermal correction to free energy (Hartree): 0.134978
M06 electronic energy in solution (Hartree): -386.82516
Three lowest frequencies (cm-1): 54.9669, 110.7433, 146.2275

Table S27. Cartesian Coordinates for S7.

C	1.1967652289	2.4359242096	-0.4309577283
C	1.186530984	0.9482911121	0.0687495132
H	2.1762524284	2.9294012081	-0.3883755958
H	0.7783792835	2.5878185201	-1.4342580422

H	2.1591073711	0.5706650814	0.407517225
C	0.2461603353	1.4354687895	1.1660977683
C	0.2623870698	2.7130750252	0.7273339714
H	0.7596192102	0.2280831527	-0.6399375399
H	-0.2162563504	3.627575729	1.0686973357
C	-0.3988180906	0.7183604505	2.26238167
C	-0.1856475282	-0.6607939661	2.4278413633
C	-1.2430207133	1.378928639	3.1754237395
C	-0.7952054421	-1.358754169	3.4705620086
H	0.4632046023	-1.1862545339	1.7319911573
C	-1.8507923008	0.6823794387	4.2153769931
H	-1.4192048661	2.4455089487	3.0626533407
C	-1.6296799977	-0.6908033182	4.3680410663
H	-0.6178386134	-2.4253472726	3.5817702722
H	-2.4995220544	1.2088796947	4.9107112142
H	-2.1051650364	-1.2332569796	5.1807654475

Energies of the Optimized Structure for TS_S3.

B3LYP electronic energy (Hartree): -386.9732458
B3LYP zero-point energy correction (Hartree): 0.165906
B3LYP thermal correction to free energy (Hartree): 0.132774
M06 electronic energy in solution (Hartree): -386.7645022
Three lowest frequencies (cm-1): -709.5187, 80.3102, 115.8617

Table S28. Cartesian Coordinates for TS_S3.

C	-3.3289059932	-0.4086317644	-0.2870080906
C	-2.0437367043	1.3083883994	-0.183659663
H	-4.3288541215	-0.6181059284	0.1080103096
H	-3.3130495007	-0.2367999541	-1.3572800775
H	-2.7324665324	1.6807169548	0.5650650214
C	-1.2188110708	0.1767340048	0.1254213263
C	-2.1449407027	-0.8292371668	0.3726560173
H	-1.7495446613	2.0566018814	-0.9283846774
H	-2.0549292251	-1.6880838198	1.0362432142
C	0.2448659936	0.1186486546	0.0666178527
C	1.0181219912	1.2917743937	0.1377910347
C	0.9137922777	-1.1132466842	-0.0634000103
C	2.4094949135	1.2369915992	0.0688695125
H	0.5184769612	2.2478996714	0.2692579792
C	2.3044670535	-1.1698895624	-0.1094181864
H	0.3287311394	-2.025073561	-0.1491432949
C	3.058557295	0.0059376401	-0.0494319751
H	2.9889659282	2.1550639739	0.1227976369
H	2.8025404528	-2.1310368861	-0.2079543726

H	4.1434945222	-0.0380485117	-0.0937904111

Energies of the Optimized Structure for S8.

B3LYP electronic energy (Hartree): -387.0359709
B3LYP zero-point energy correction (Hartree): 0.16723
B3LYP thermal correction to free energy (Hartree): 0.13324
M06 electronic energy in solution (Hartree): -386.8273535
Three lowest frequencies (cm-1): 62.6432, 105.9526, 132.4643

Table S29. Cartesian Coordinates for S8.

C	-2.6009217737	-0.1758859643	0.1918482153
C	-1.2114562129	-0.2449844031	0.2745400817
C	-0.4139025531	0.8779639612	-0.0073077314
C	-1.0581452283	2.0780490141	-0.3543077387
C	-2.4488229987	2.1484420472	-0.4368801776
C	-3.2263364333	1.0212212325	-0.1658160124
H	-3.1978220234	-1.0552797719	0.4196143842
H	-0.7352508087	-1.1707921661	0.5844572787
H	-0.4598045794	2.9563713944	-0.5806561396
H	-2.9246762579	3.0849607267	-0.7160579608
H	-4.3100484467	1.0760723575	-0.2250015776
C	1.0722575908	0.8117943798	0.056637631
C	1.7486054224	-0.3084473948	-0.2606234144
H	1.2470838161	-1.1915121459	-0.6449720402
H	2.8265825953	-0.365769408	-0.1465040848
C	1.7825472512	2.0348104239	0.4981470735
H	1.2949010708	2.6089312614	1.286424572
C	2.9407040291	2.4789655399	-0.0043258917
H	3.4377129221	1.9730967413	-0.828235074
H	3.4241052781	3.3690344342	0.3888271667

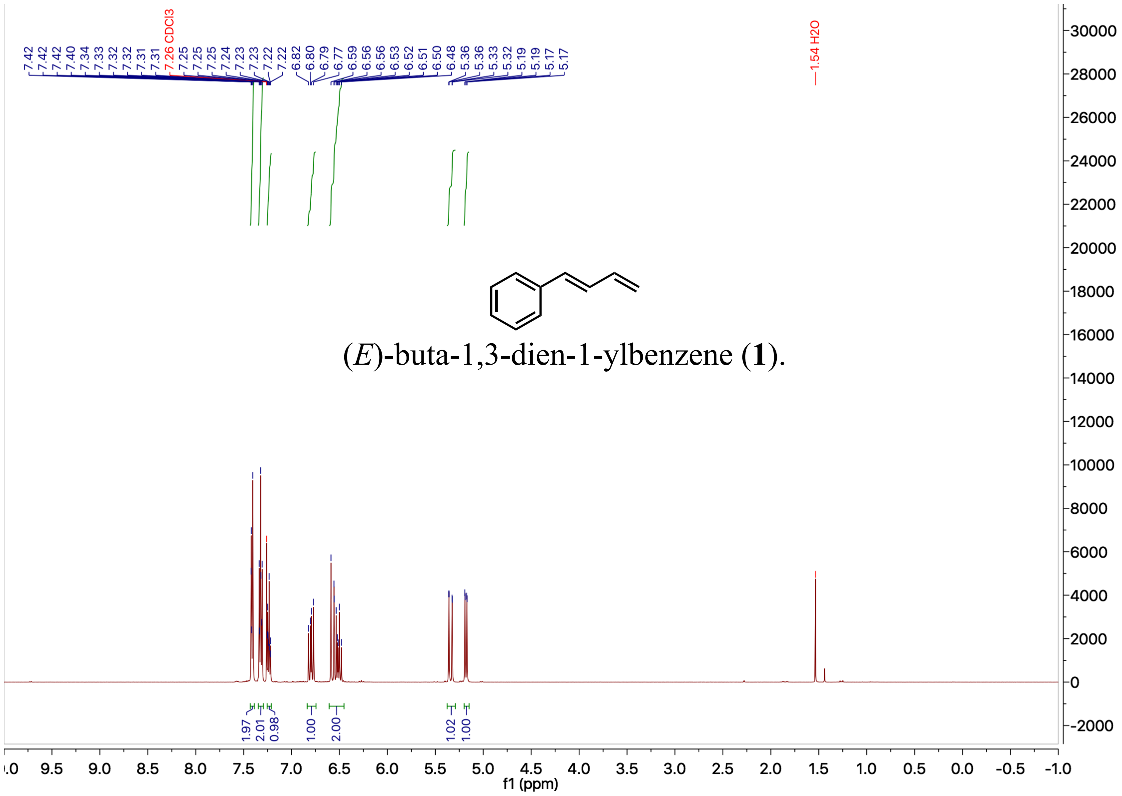


Figure S6. ^{1}H NMR (500 MHz, CDCl$_3$) of (*E*)-buta-1,3-dien-1-ylbenzene (**1**).

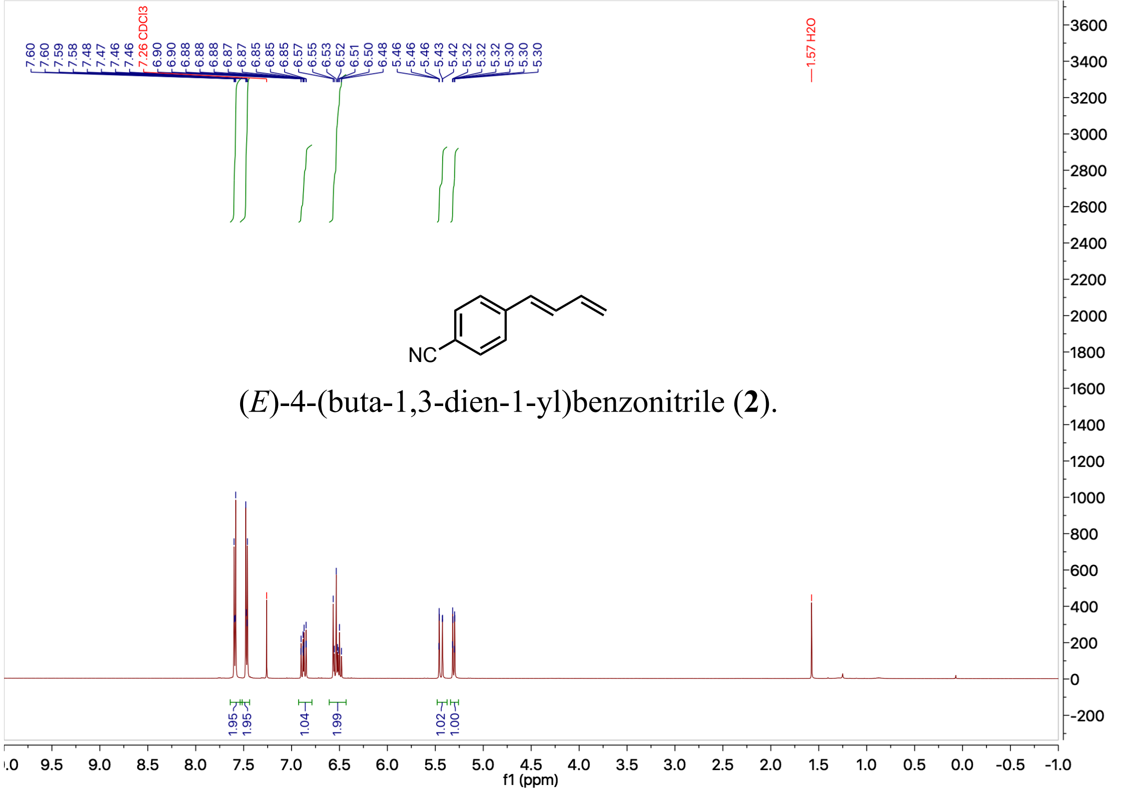


Figure S7. ^{1}H NMR (500 MHz, CDCl$_3$) of (*E*)-4-(buta-1,3-dien-1-yl)benzonitrile (**2**).

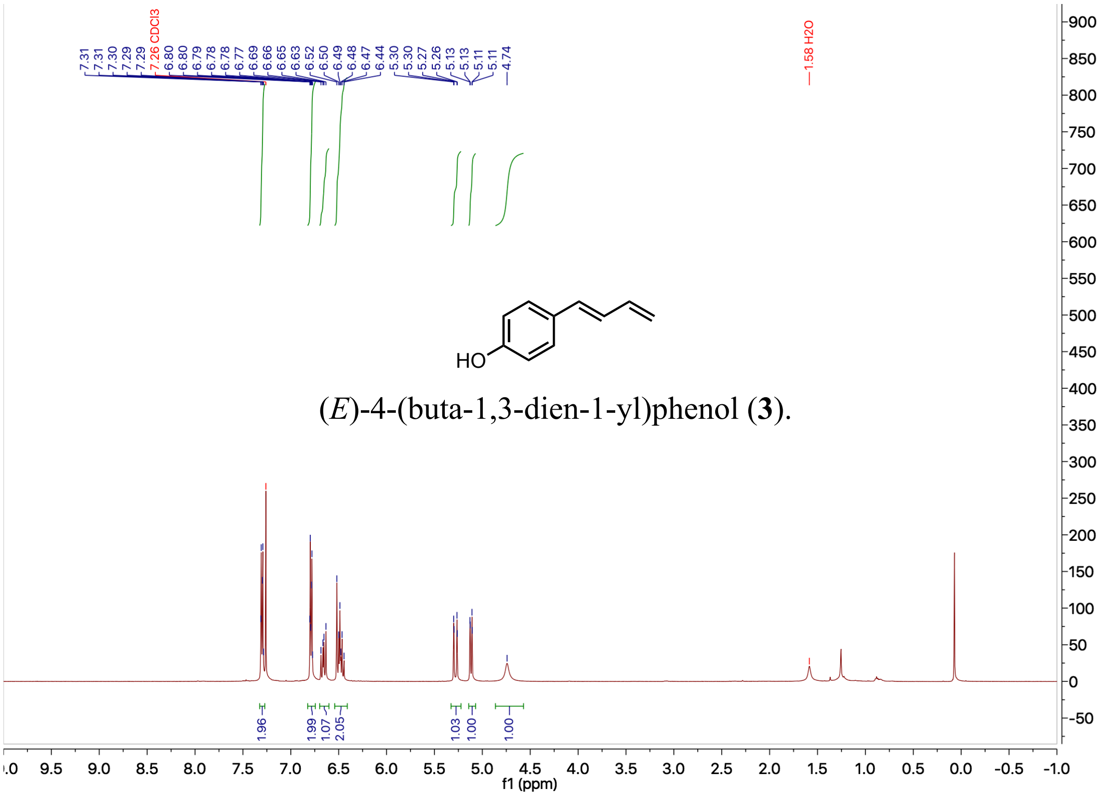


Figure S8. ^{1}H NMR (500 MHz, CDCl$_3$) of (*E*)-4-(buta-1,3-dien-1-yl)phenol (**3**).

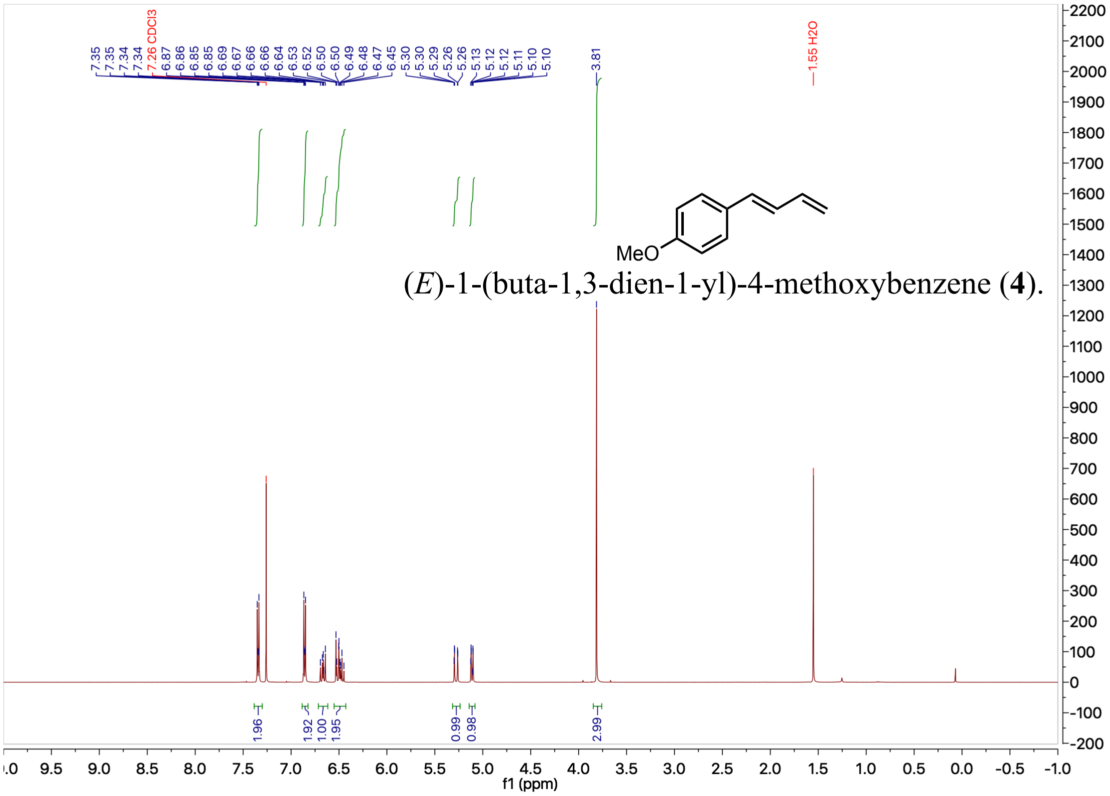


Figure S9. ^{1}H NMR (500 MHz, CDCl$_3$) of (*E*)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene (**4**).

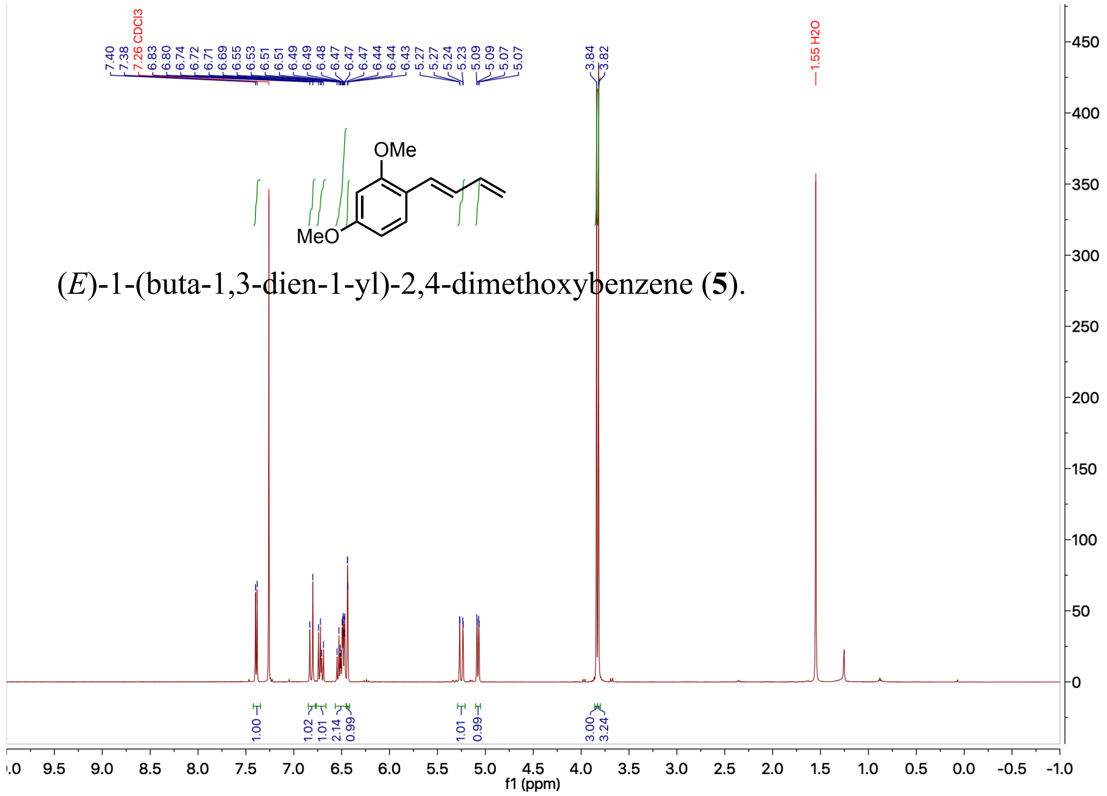


Figure S10. ^{1}H NMR (500 MHz, CDCl$_3$) of (*E*)-1-(buta-1,3-dien-1-yl)-2,4-dimethoxybenzene (**5**).

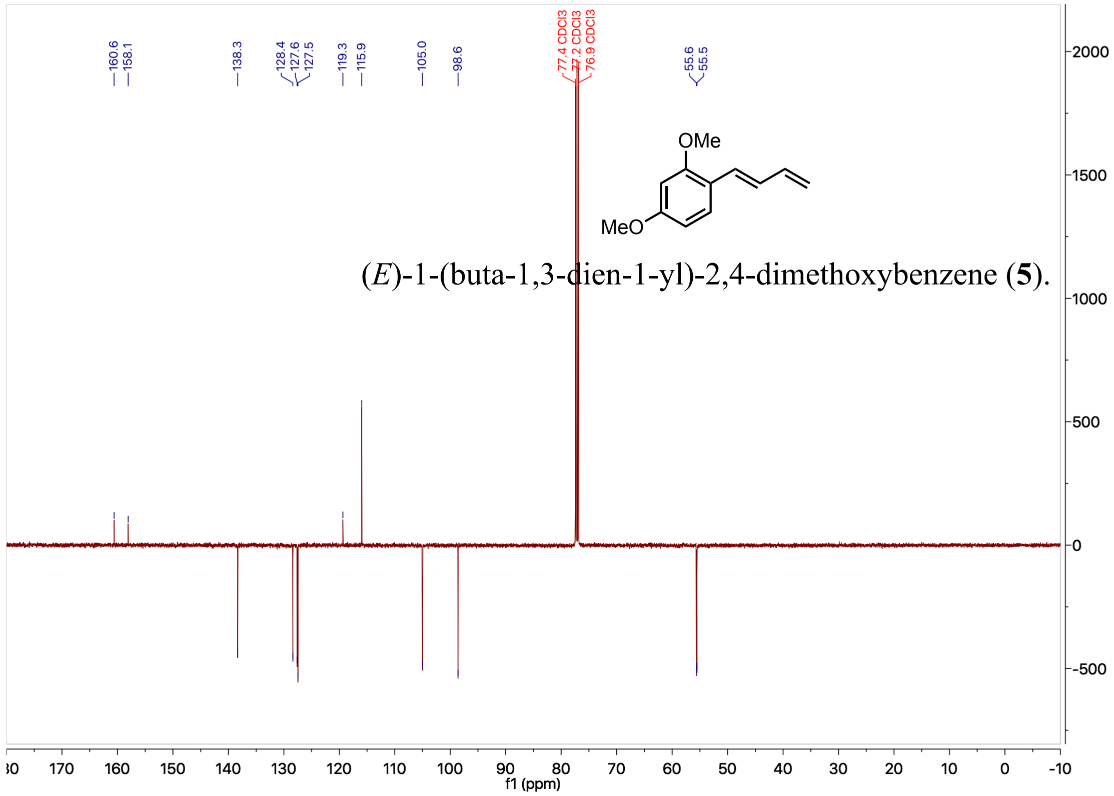


Figure S11. ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) of (*E*)-1-(buta-1,3-dien-1-yl)-2,4-dimethoxybenzene (**5**).

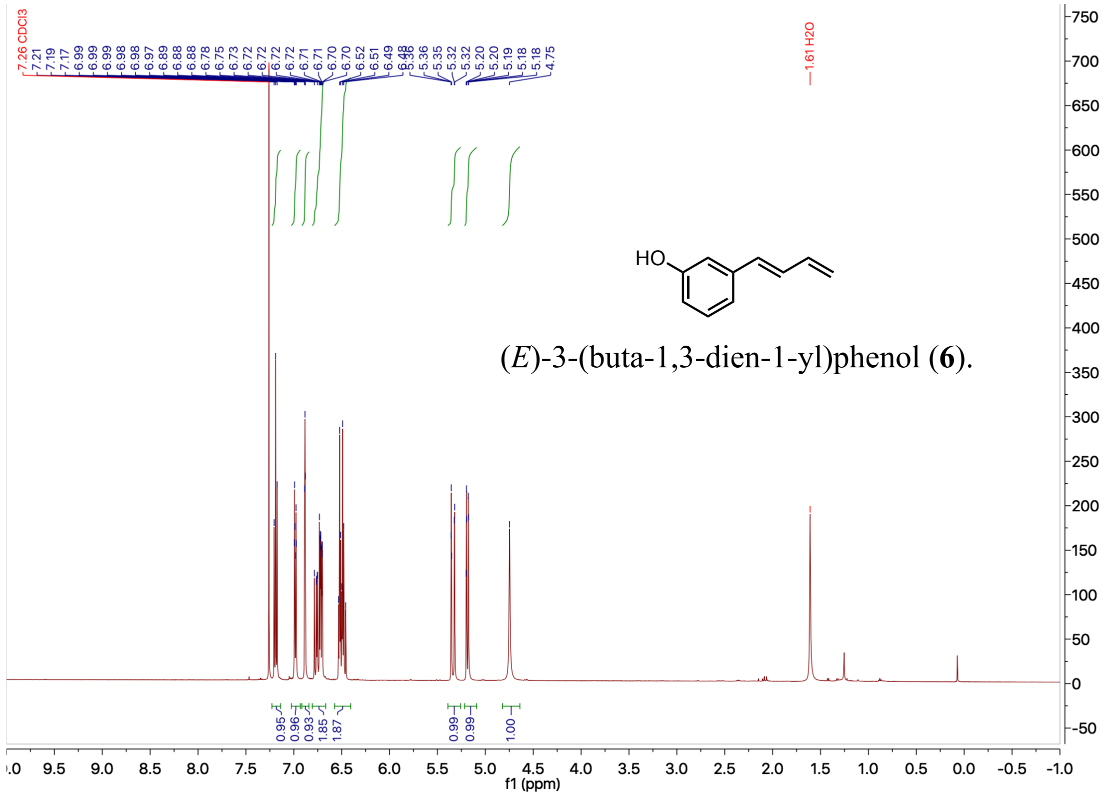


Figure S12. ^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-3-(buta-1,3-dien-1-yl)phenol (**6**).

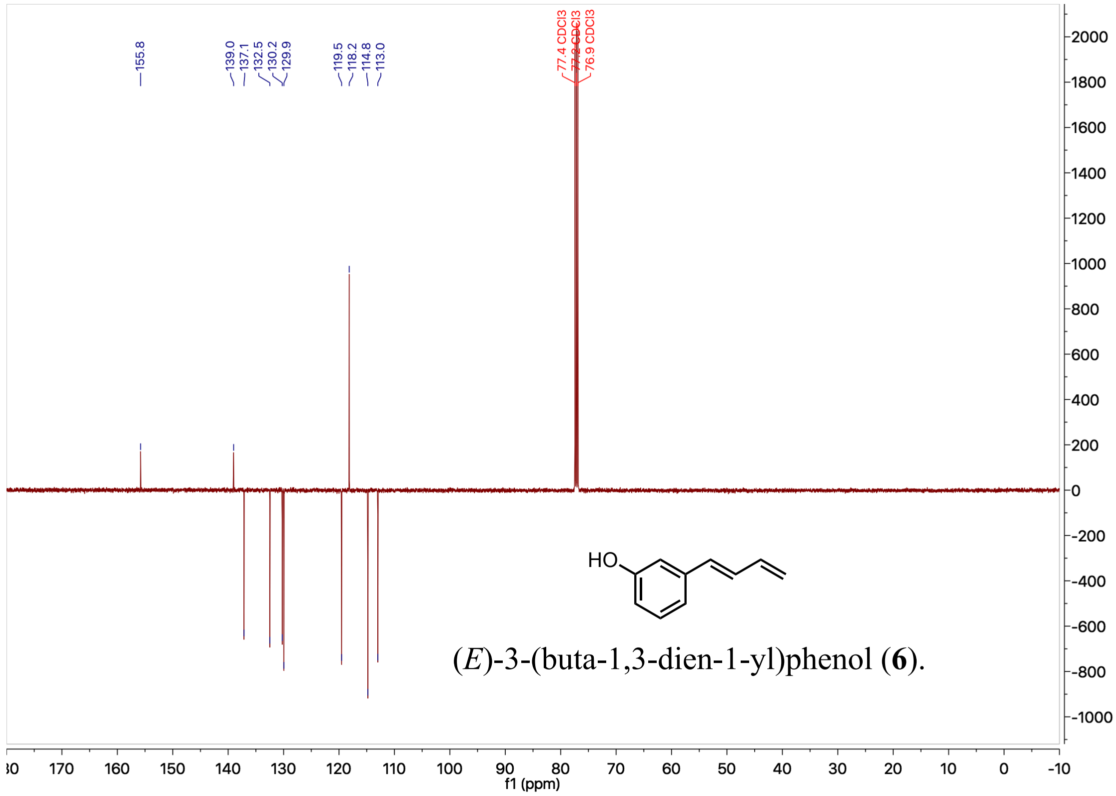


Figure S13. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of (*E*)-3-(buta-1,3-dien-1-yl)phenol (**6**).

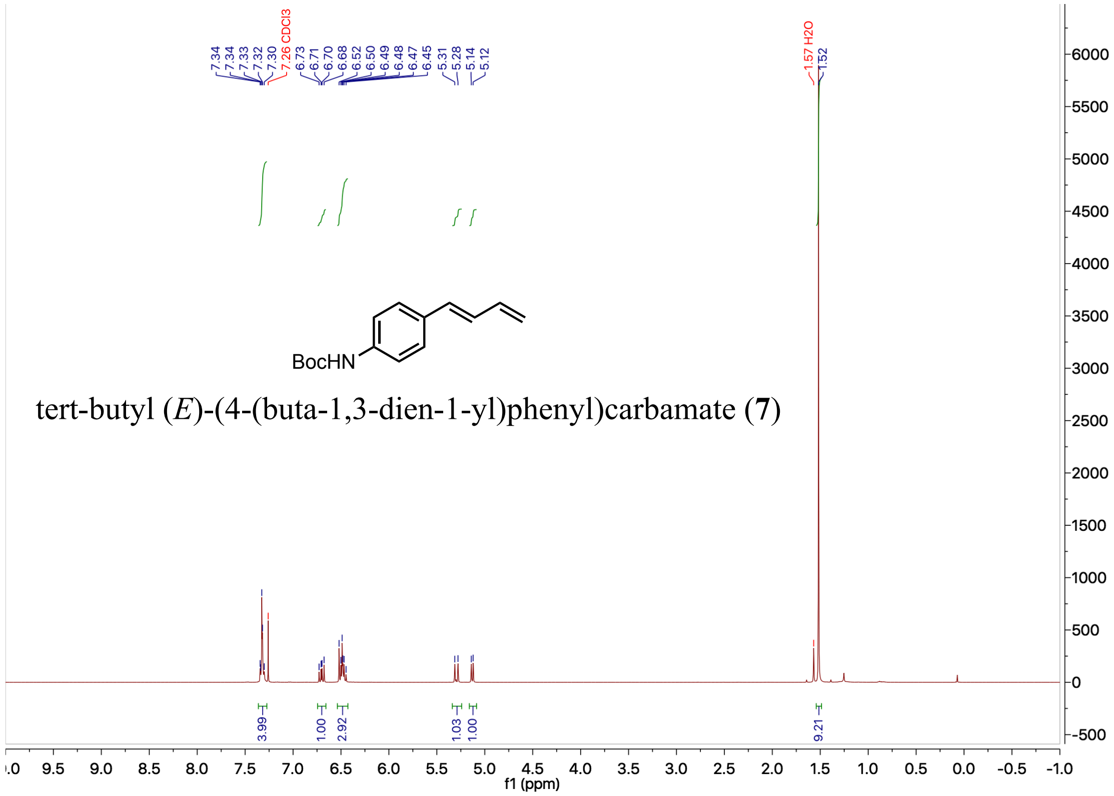


Figure S14. ^{1}H NMR (500 MHz, CDCl$_3$) of tert-butyl (*E*)-(4-(buta-1,3-dien-1-yl)phenyl)carbamate (**7**).

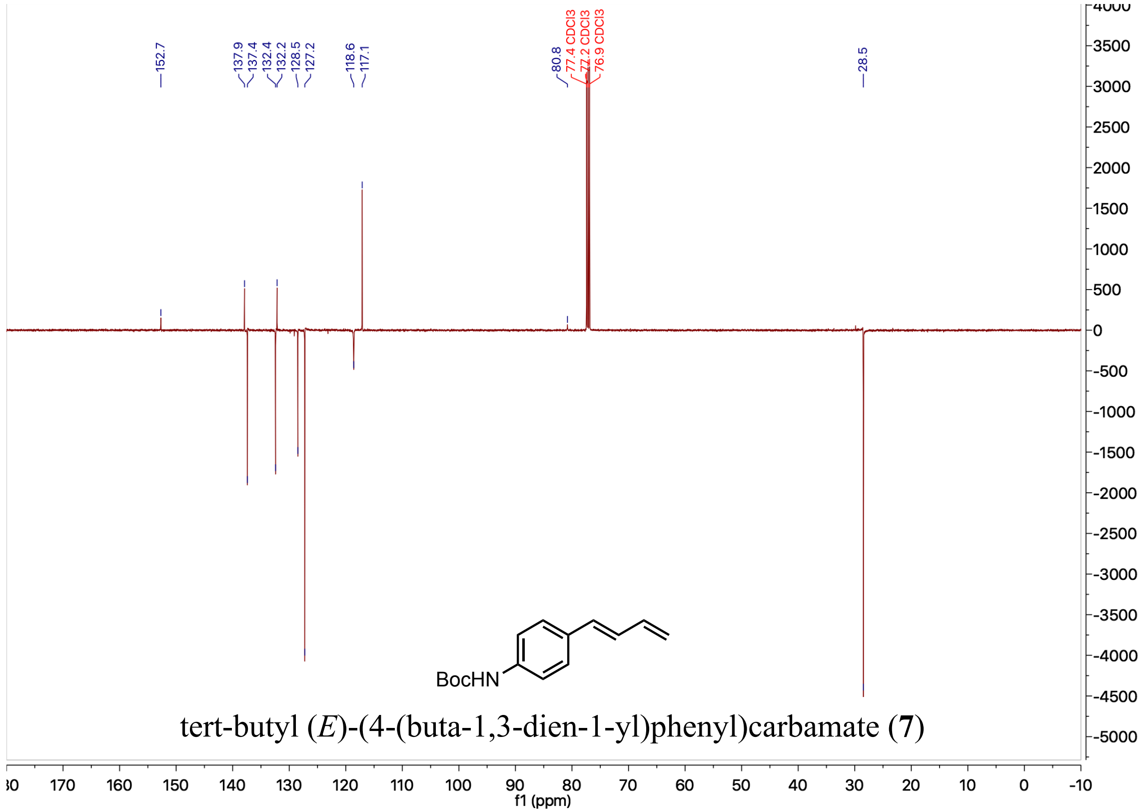


Figure S15. ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) of tert-butyl (*E*)-(4-(buta-1,3-dien-1-yl)phenyl)carbamate (**7**).

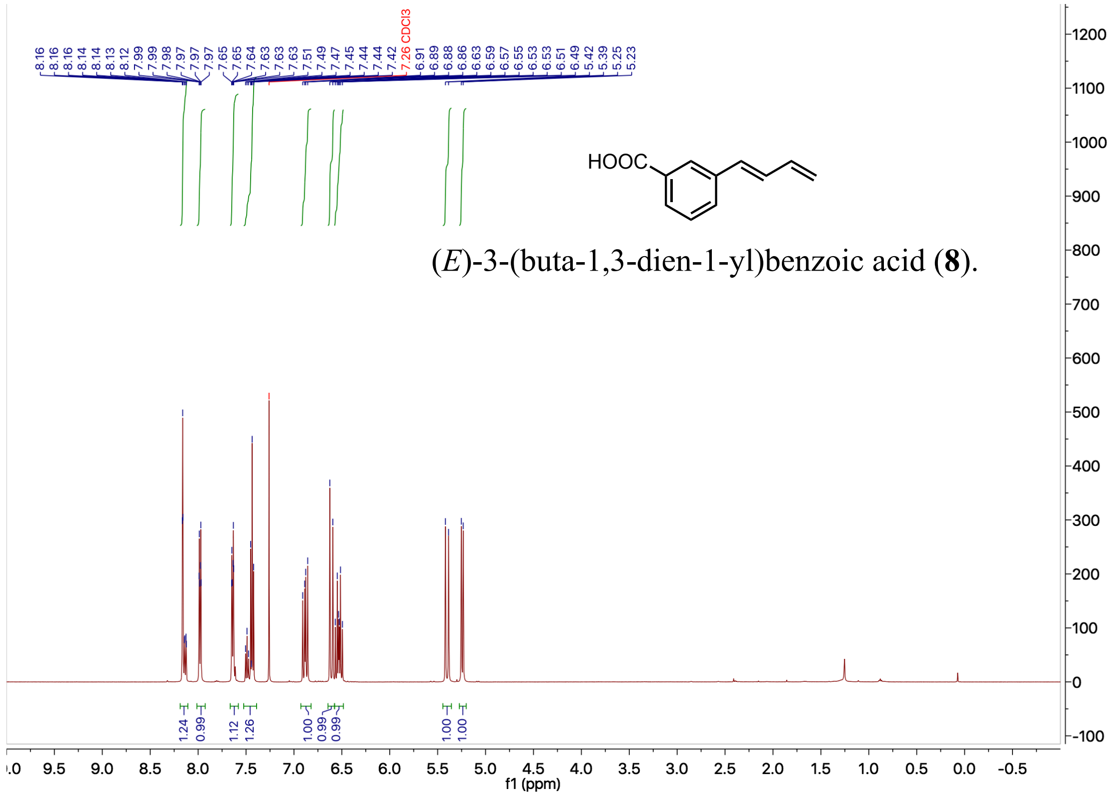


Figure S16. ^{1}H NMR (500 MHz, CDCl$_3$) of (*E*)-3-(buta-1,3-dien-1-yl)benzoic acid (**8**).

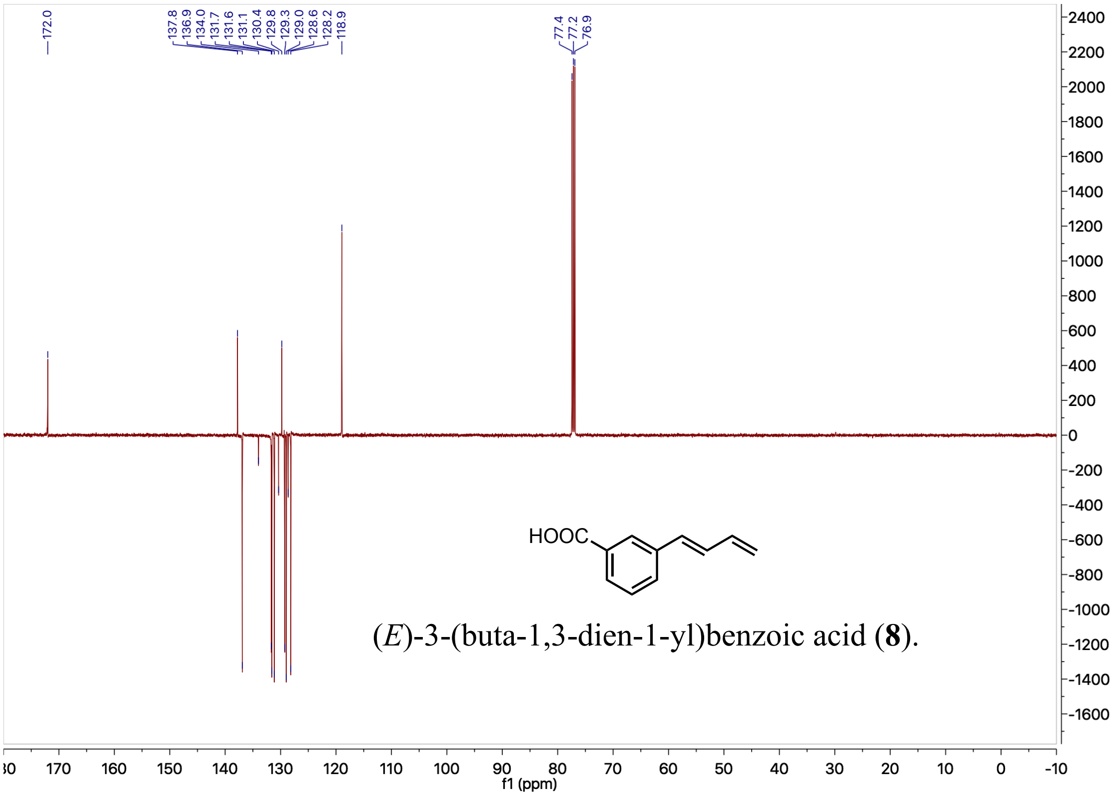


Figure S17. ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) of (*E*)-3-(buta-1,3-dien-1-yl)benzoic acid (**8**).

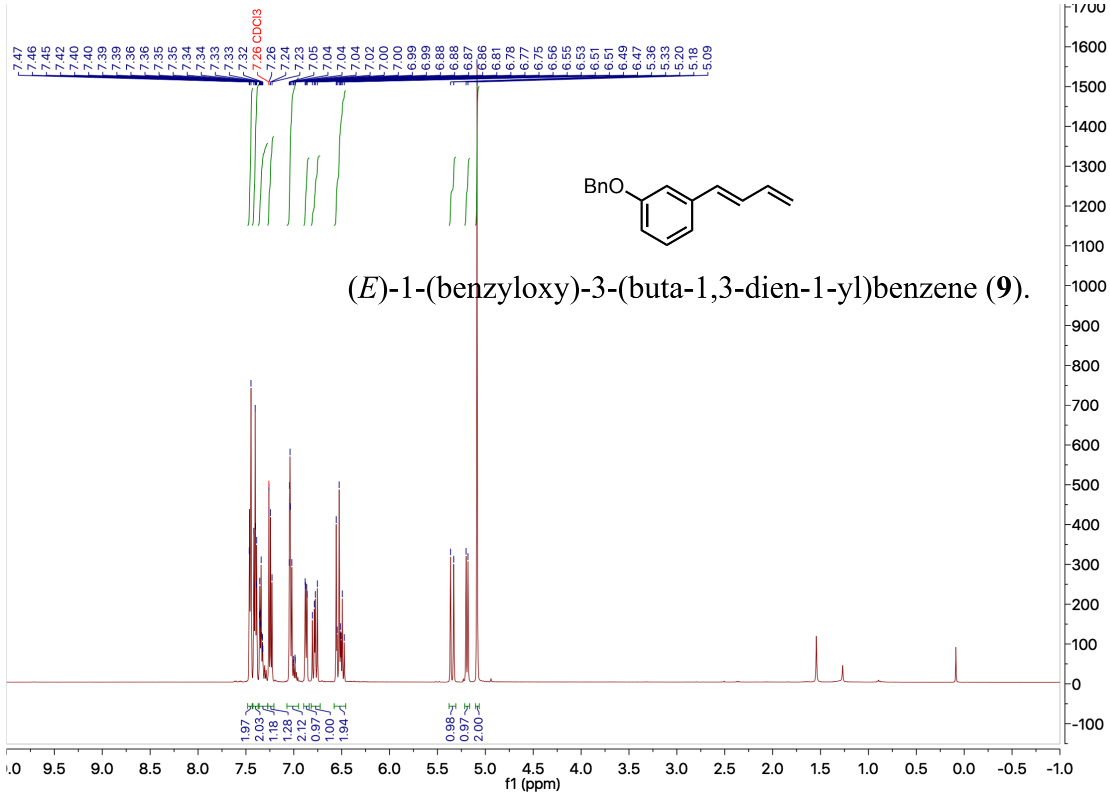


Figure S18. ^{1}H NMR (500 MHz, CDCl$_3$) of (*E*)-1-(benzyloxy)-3-(buta-1,3-dien-1-yl)benzene (**9**).

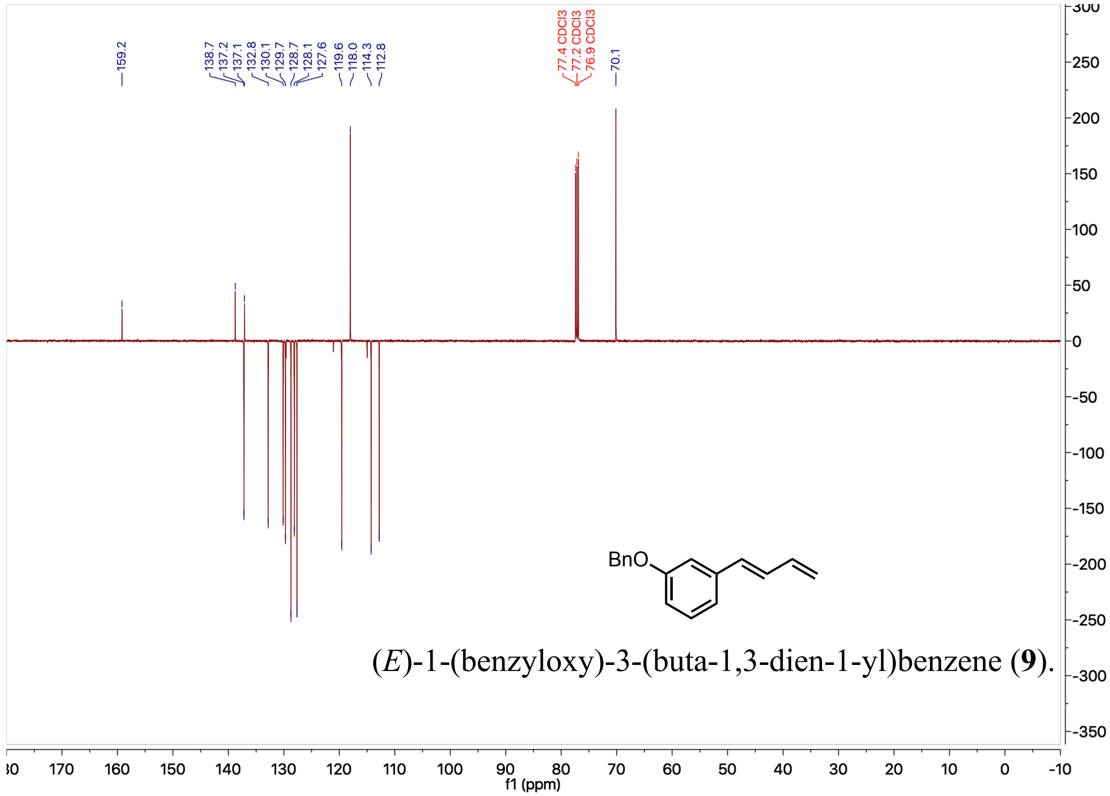


Figure S19. ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) of (*E*)-1-(benzyloxy)-3-(buta-1,3-dien-1-yl)benzene (**9**).

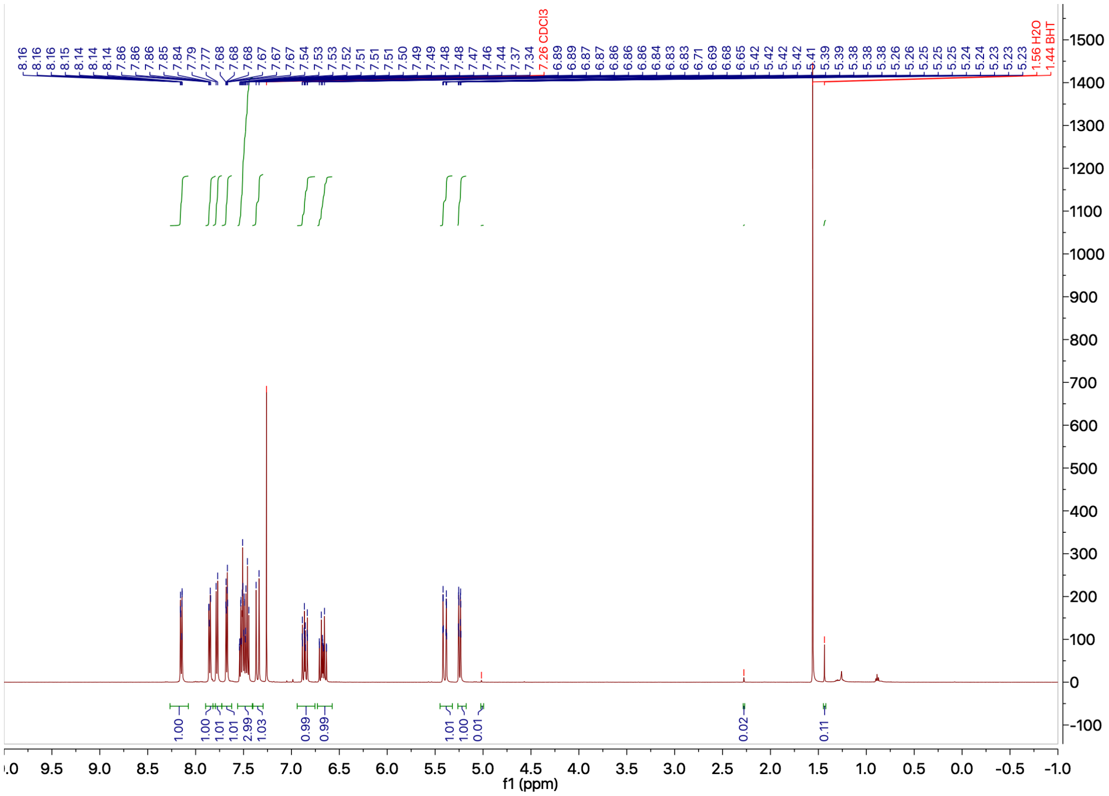
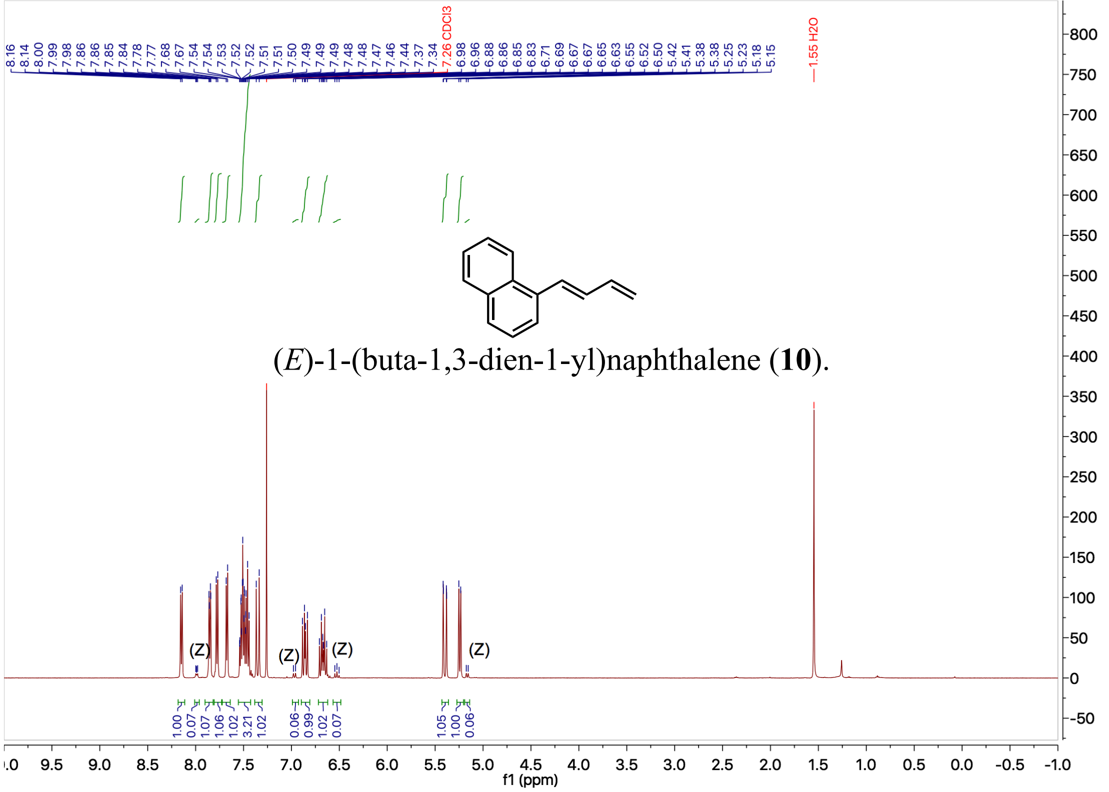


Figure S20. ^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-1-(buta-1,3-dien-1-yl)naphthalene (**10**).



(*E*)-1-(buta-1,3-dien-1-yl)naphthalene (**10**).

Figure S21. ^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-1-(buta-1,3-dien-1-yl)naphthalene (**10**) isolated in the absence of BHT inhibitor, resulting in the formation of *Z*-**10** isomer.

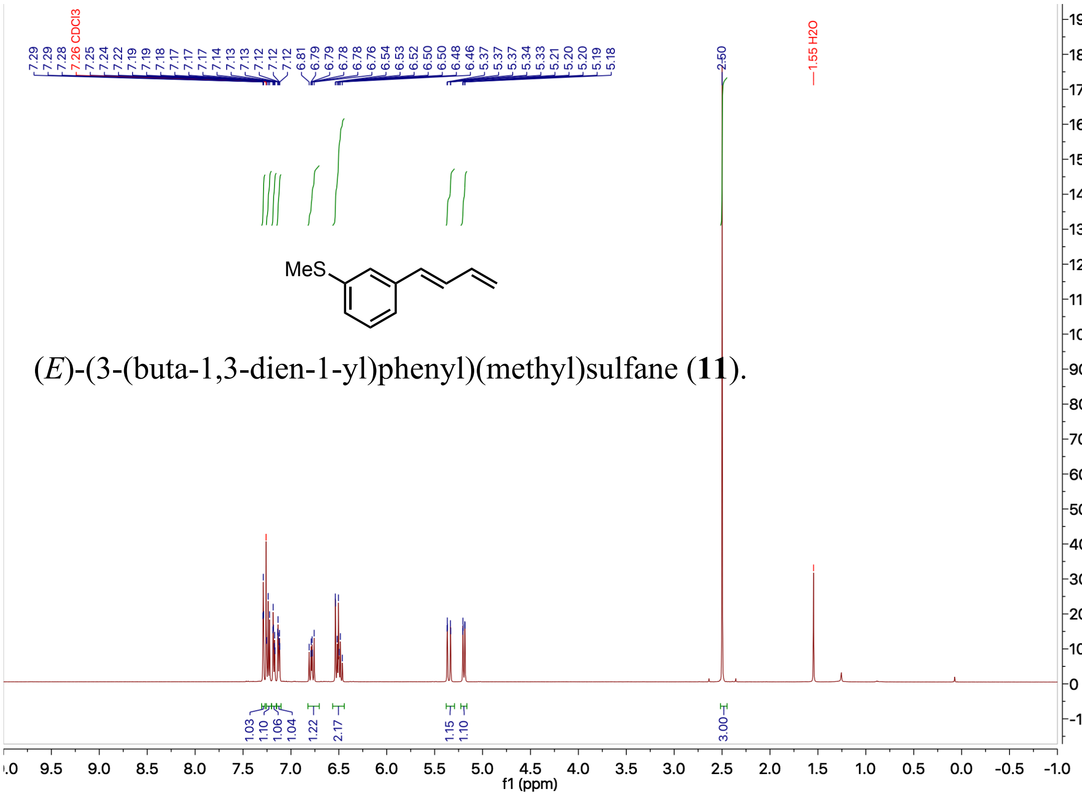


Figure S22. ^{1}H NMR (500 MHz, CDCl$_3$) of (*E*)-(3-(buta-1,3-dien-1-yl)phenyl)(methyl)sulfane (**11**).

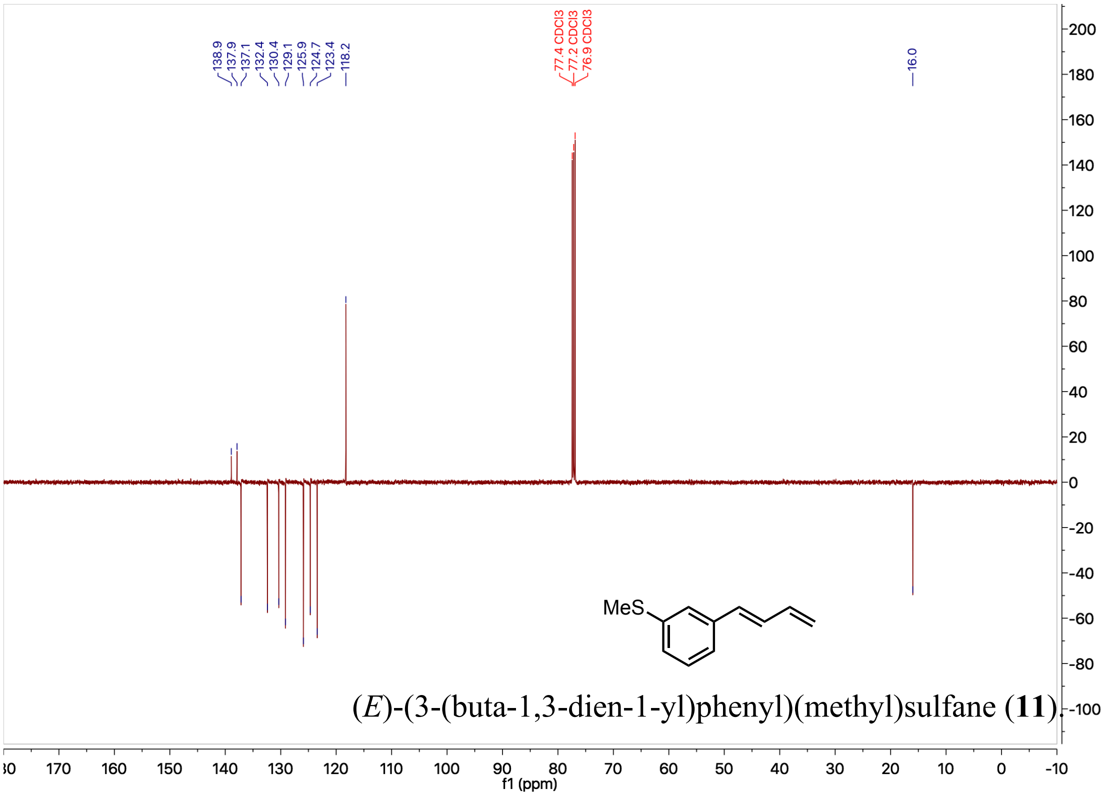


Figure S23. ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) of (*E*)-(3-(buta-1,3-dien-1-yl)phenyl)(methyl)sulfane (**11**).

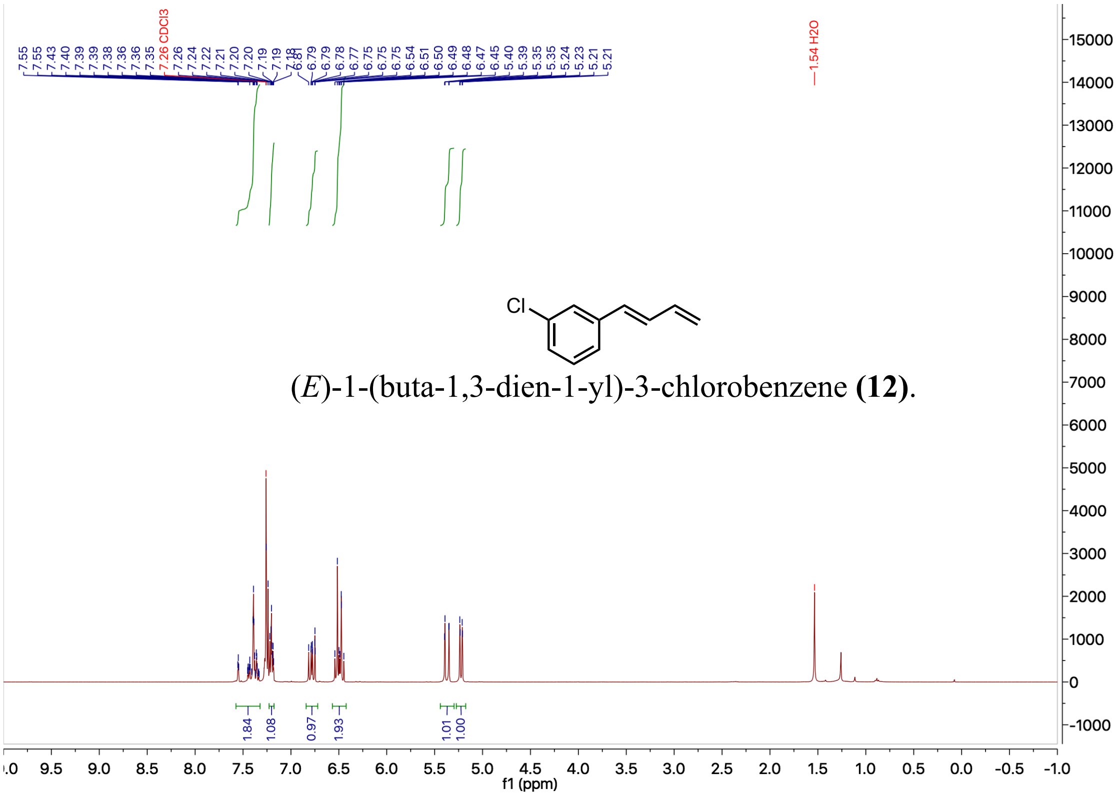


Figure S24. ^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-1-(buta-1,3-dien-1-yl)-3-chlorobenzene **(12)**.

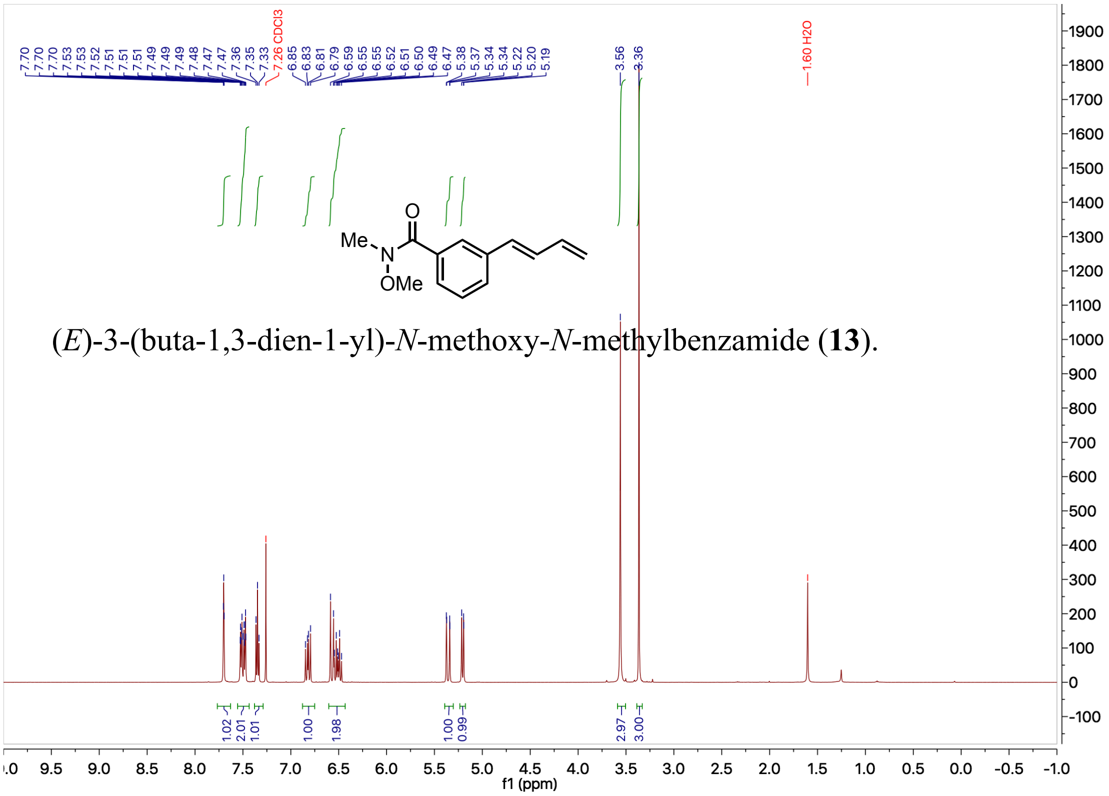


Figure S25. ^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-3-(buta-1,3-dien-1-yl)-*N*-methoxy-*N*-methylbenzamide (**13**).

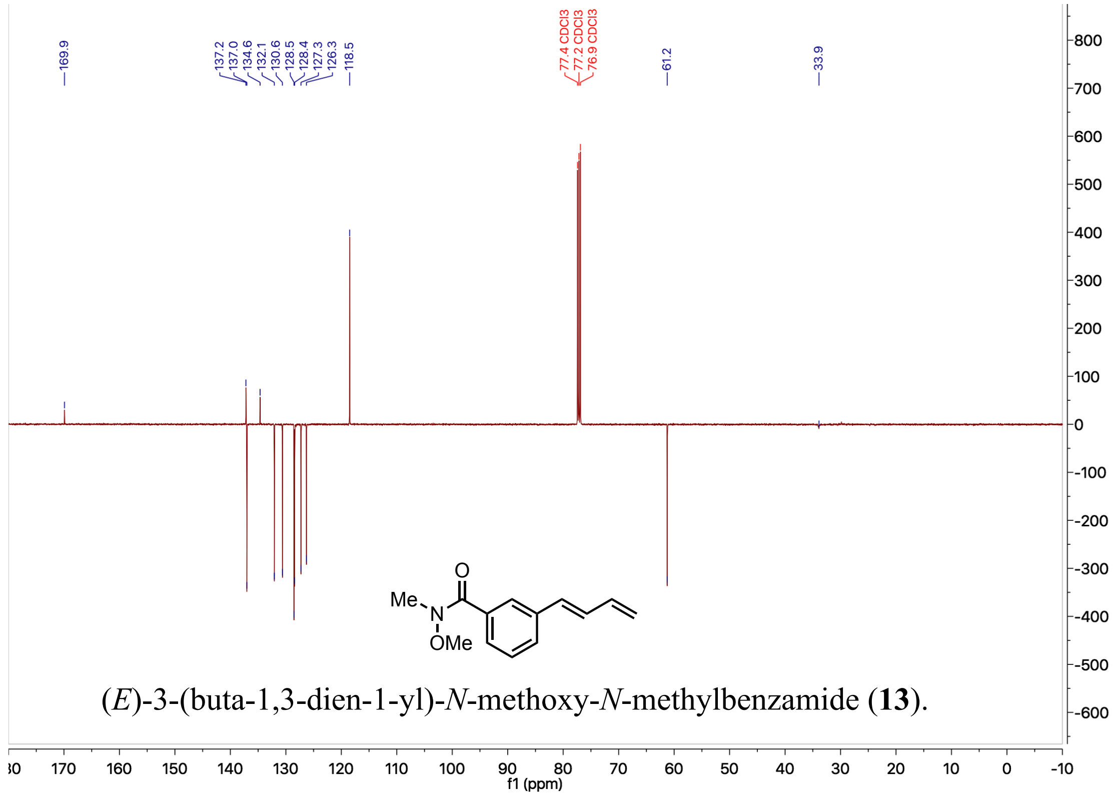


Figure S26. ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) of (*E*)-3-(buta-1,3-dien-1-yl)-*N*-methoxy-*N*-methylbenzamide (**13**).

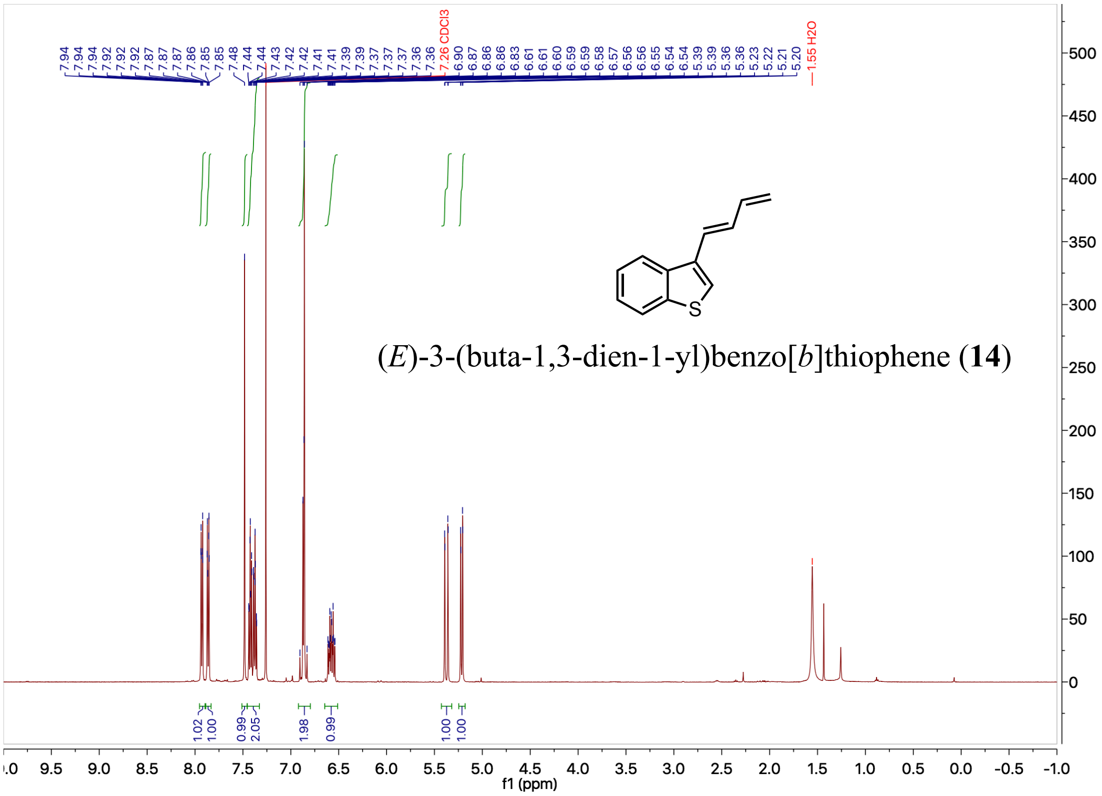


Figure S27. ^{1}H NMR (500 MHz, CDCl$_3$) of (*E*)-3-(buta-1,3-dien-1-yl)benzo[*b*]thiophene (**14**).

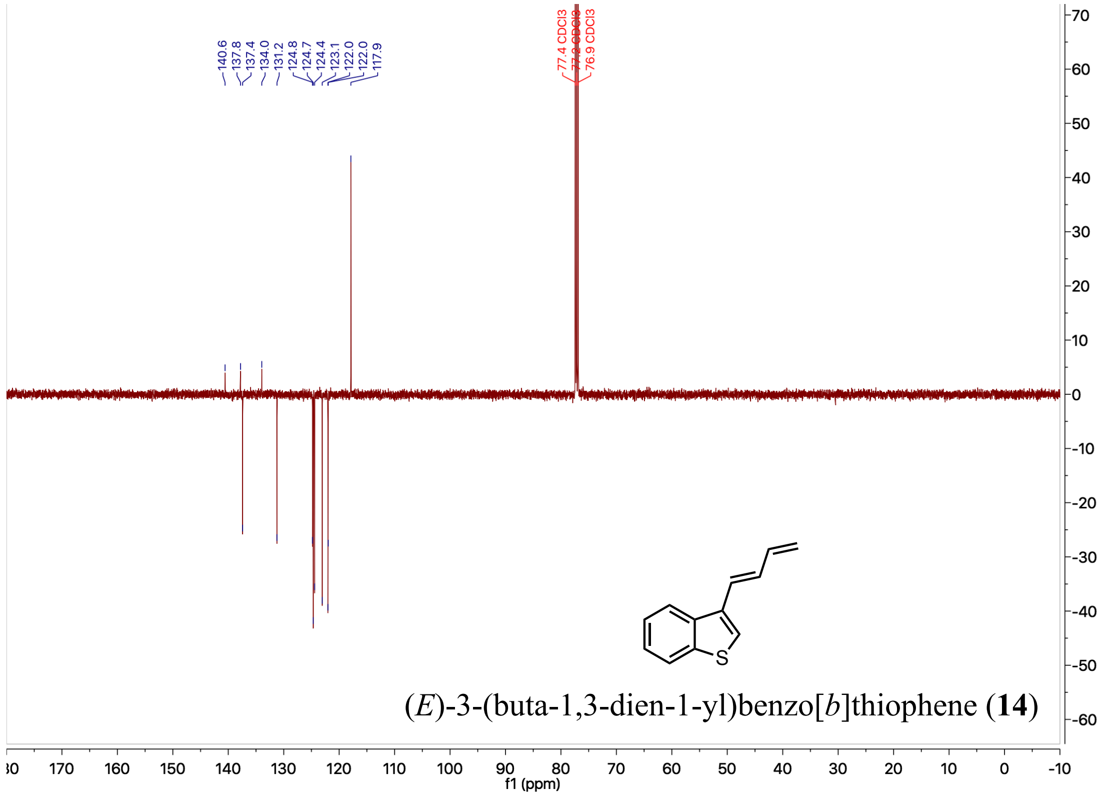


Figure S28. ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) (*E*)-3-(buta-1,3-dien-1-yl)benzo[*b*]thiophene (**14**).

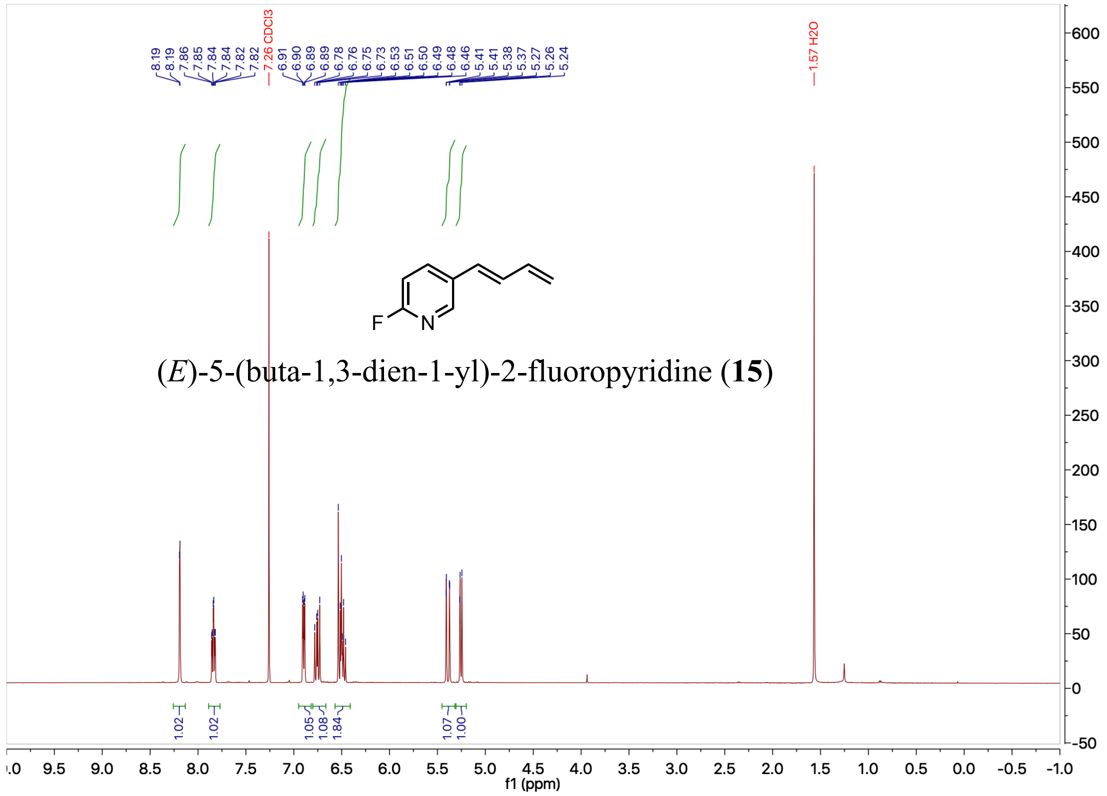


Figure S29. ^{1}H NMR (500 MHz, CDCl$_3$) of (*E*)-5-(buta-1,3-dien-1-yl)-2-fluoropyridine (**15**).

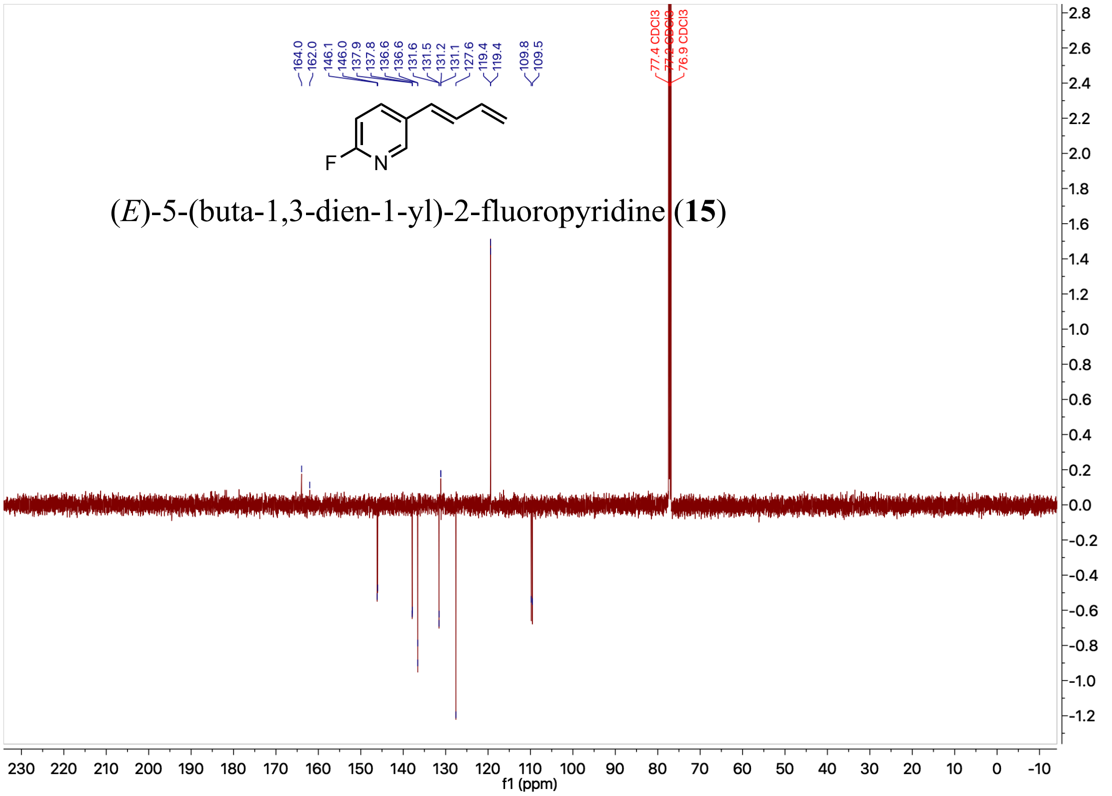


Figure S30. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of (*E*)-5-(buta-1,3-dien-1-yl)-2-fluoropyridine (**15**).

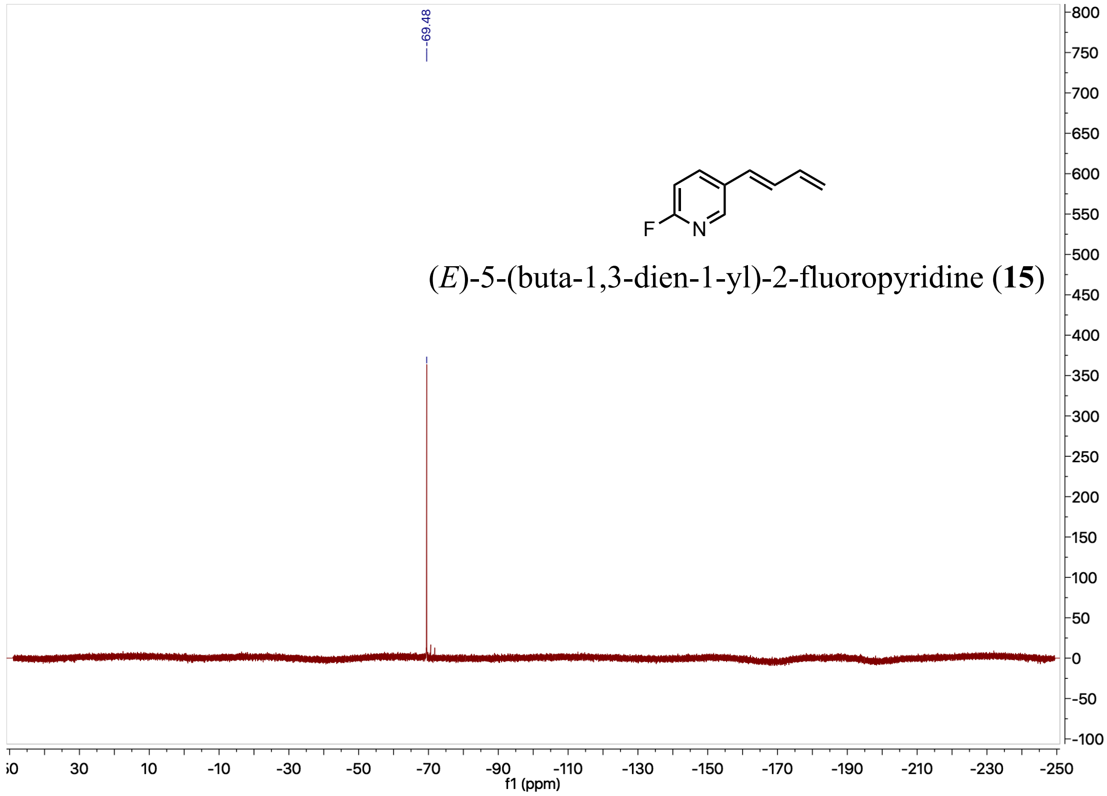


Figure S31. $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of (*E*)-5-(buta-1,3-dien-1-yl)-2-fluoropyridine (**15**).

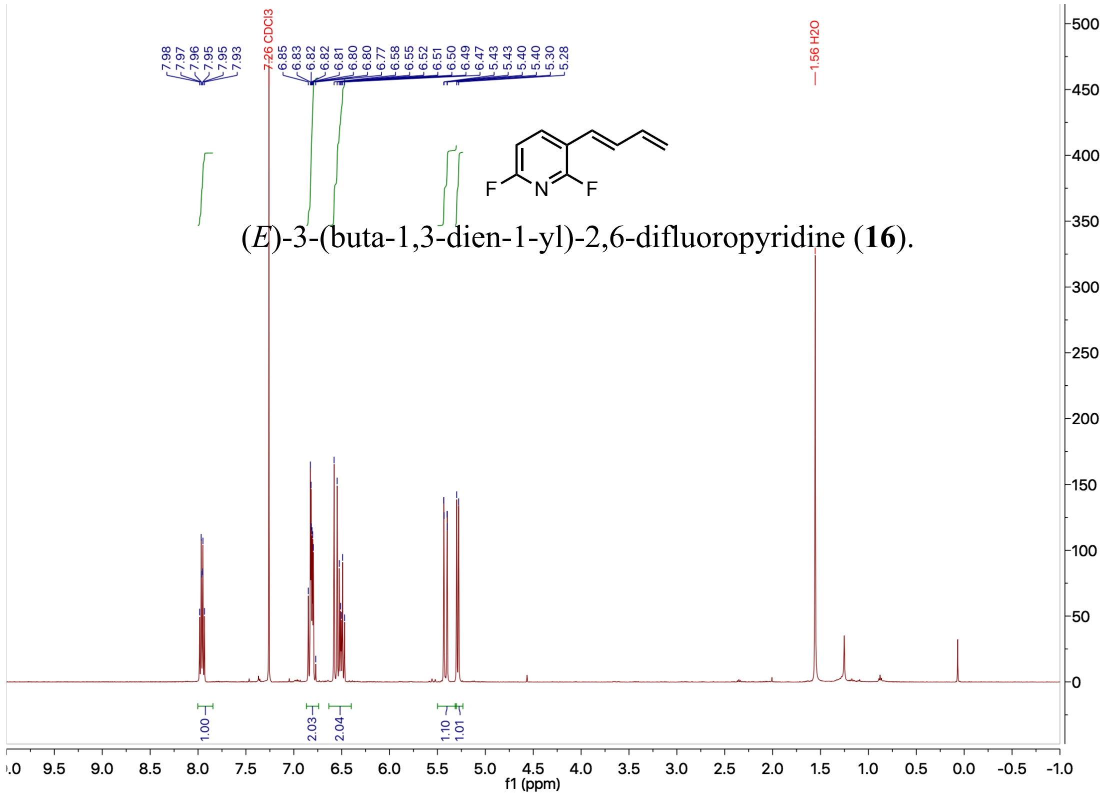


Figure S32. ^{1}H NMR (500 MHz, $CDCl_3$) of (*E*)-3-(buta-1,3-dien-1-yl)-2,6-difluoropyridine (**16**).

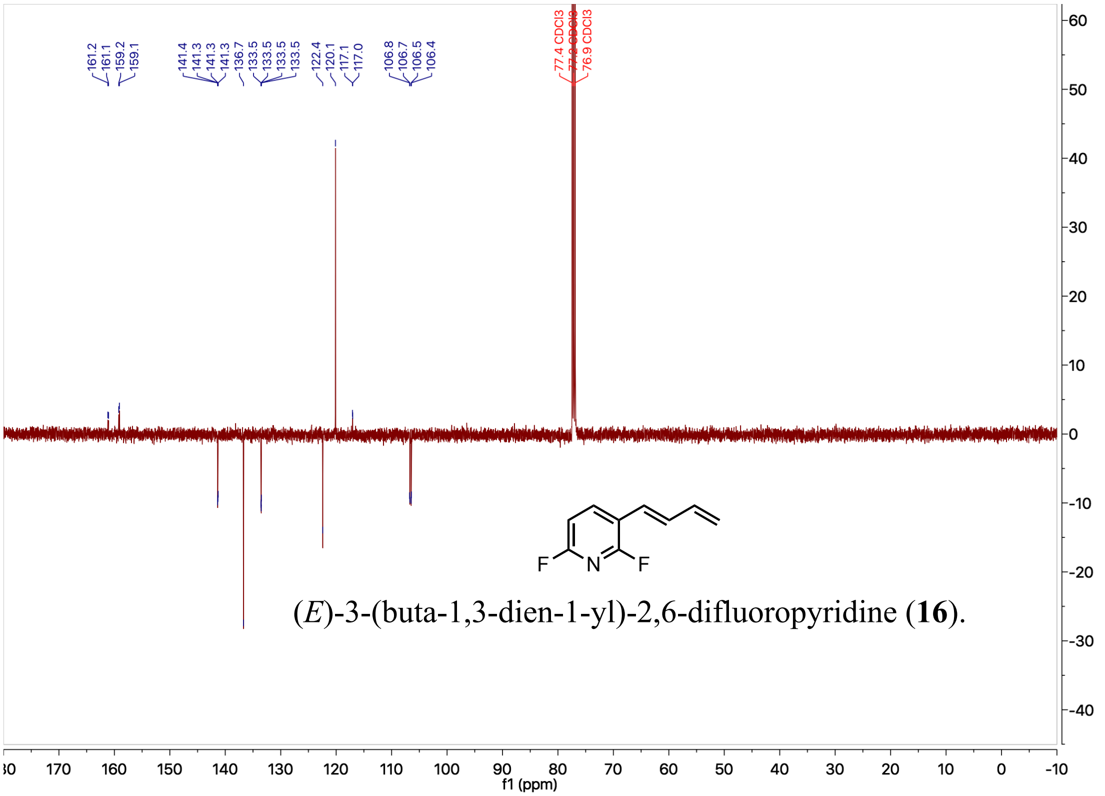


Figure S33. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of (*E*)-3-(buta-1,3-dien-1-yl)-2,6-difluoropyridine (**16**).

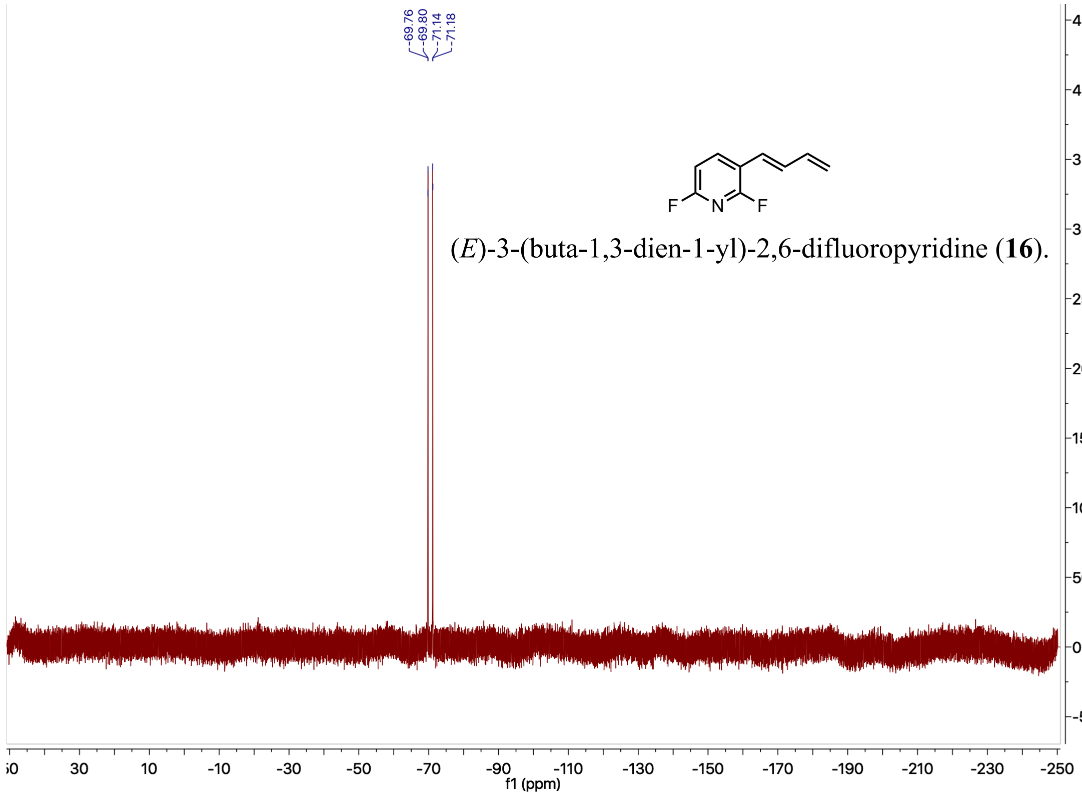


Figure S34. $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of of (*E*)-3-(buta-1,3-dien-1-yl)-2,6-difluoropyridine (**16**).

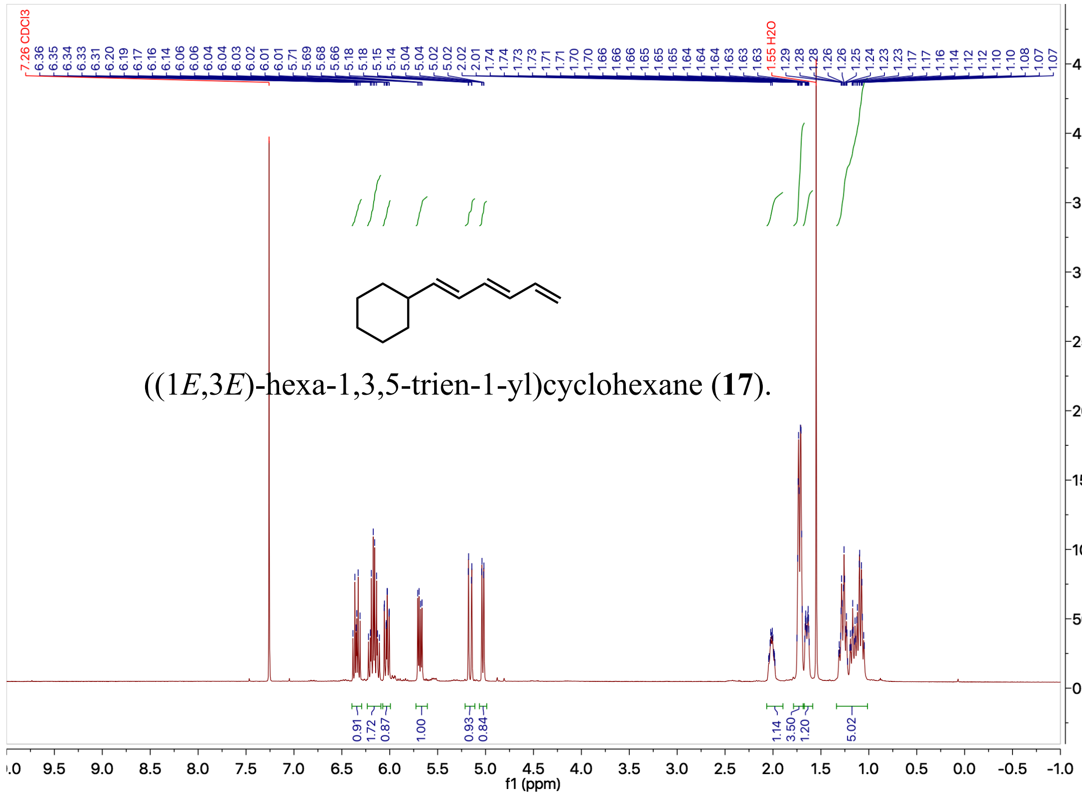


Figure S35. ^{1}H NMR (500 MHz, $CDCl_3$) of ((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)cyclohexane (**17**).

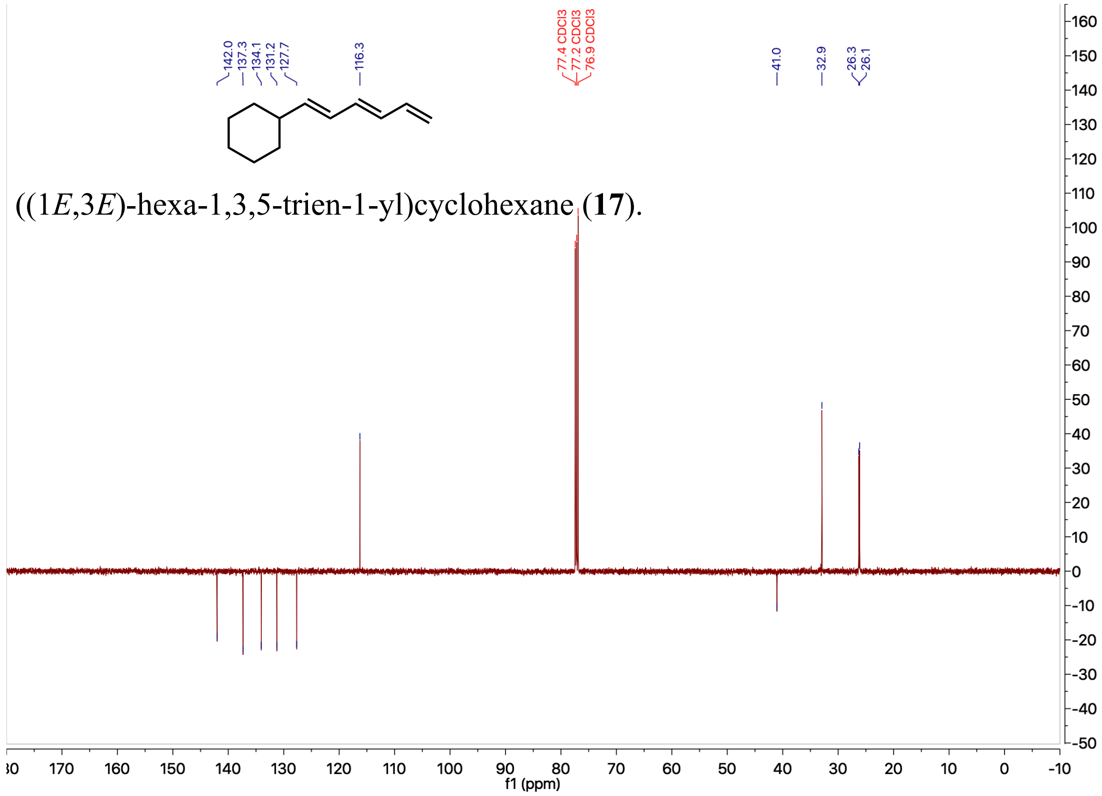


Figure S36. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of ((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)cyclohexane (**17**).

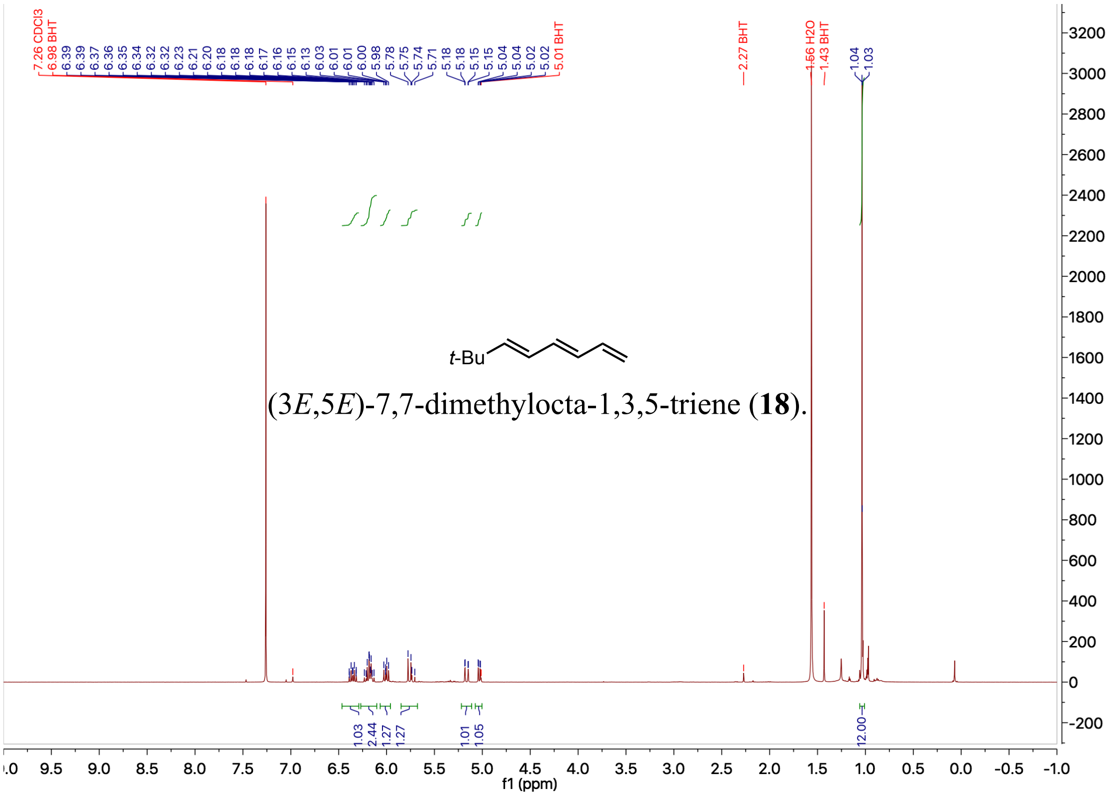
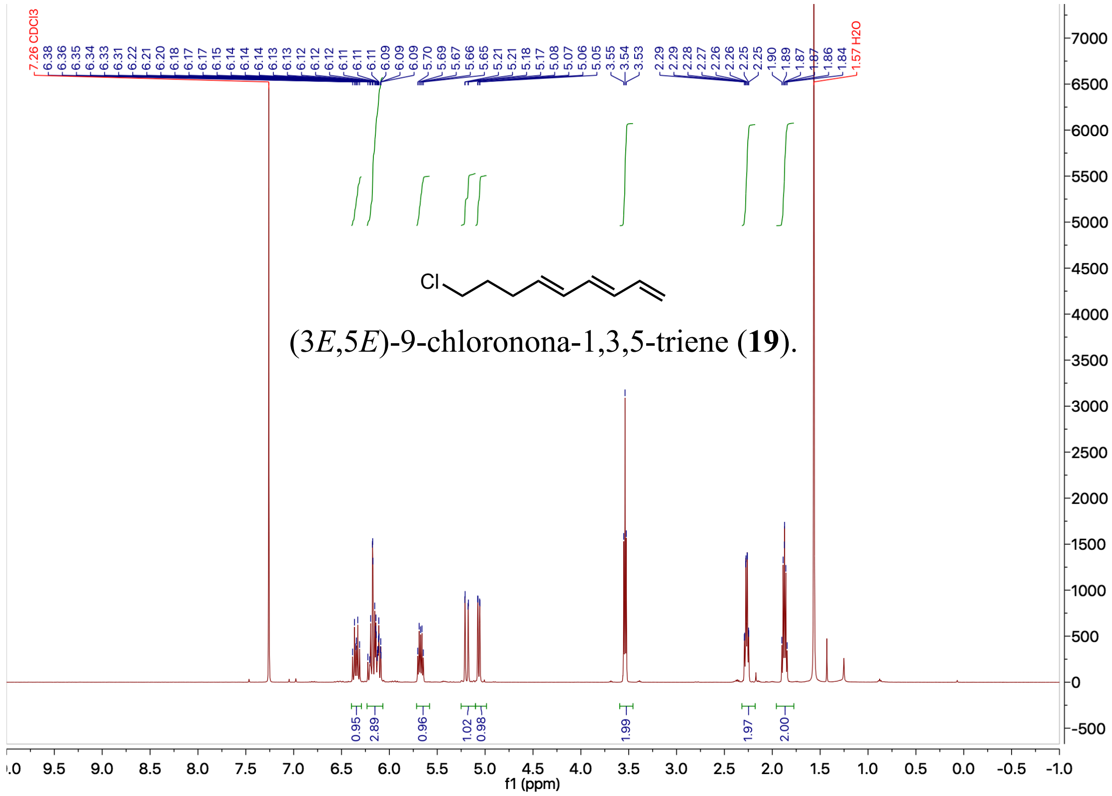
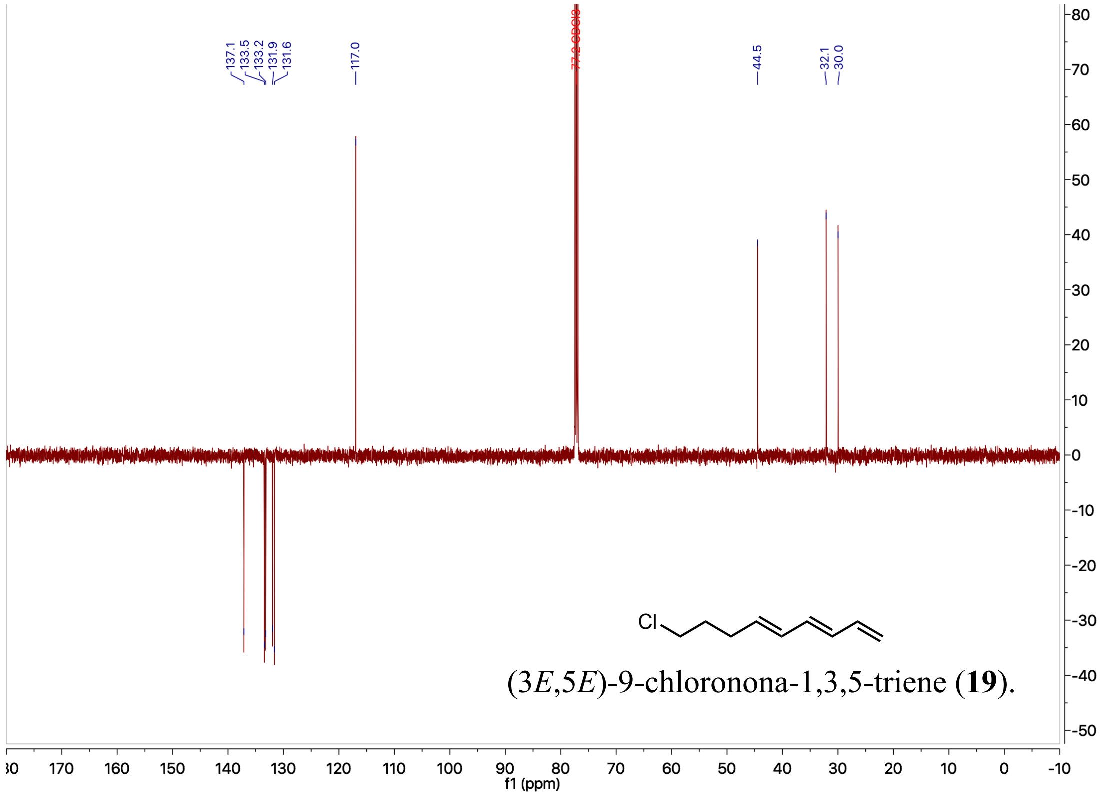


Figure S37. ^1H NMR (500 MHz, $CDCl_3$) of (3*E*,5*E*)-7,7-dimethylocta-1,3,5-triene (**18**).



(3*E*,5*E*)-9-chloronona-1,3,5-triene (**19**).

Figure S38. ^{1}H NMR (500 MHz, CDCl$_3$) of (3*E*,5*E*)-9-chloronona-1,3,5-triene (**19**).



(3*E*,5*E*)-9-chloronona-1,3,5-triene (**19**).

Figure S39. ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) of (3*E*,5*E*)-9-chloronona-1,3,5-triene (**19**).

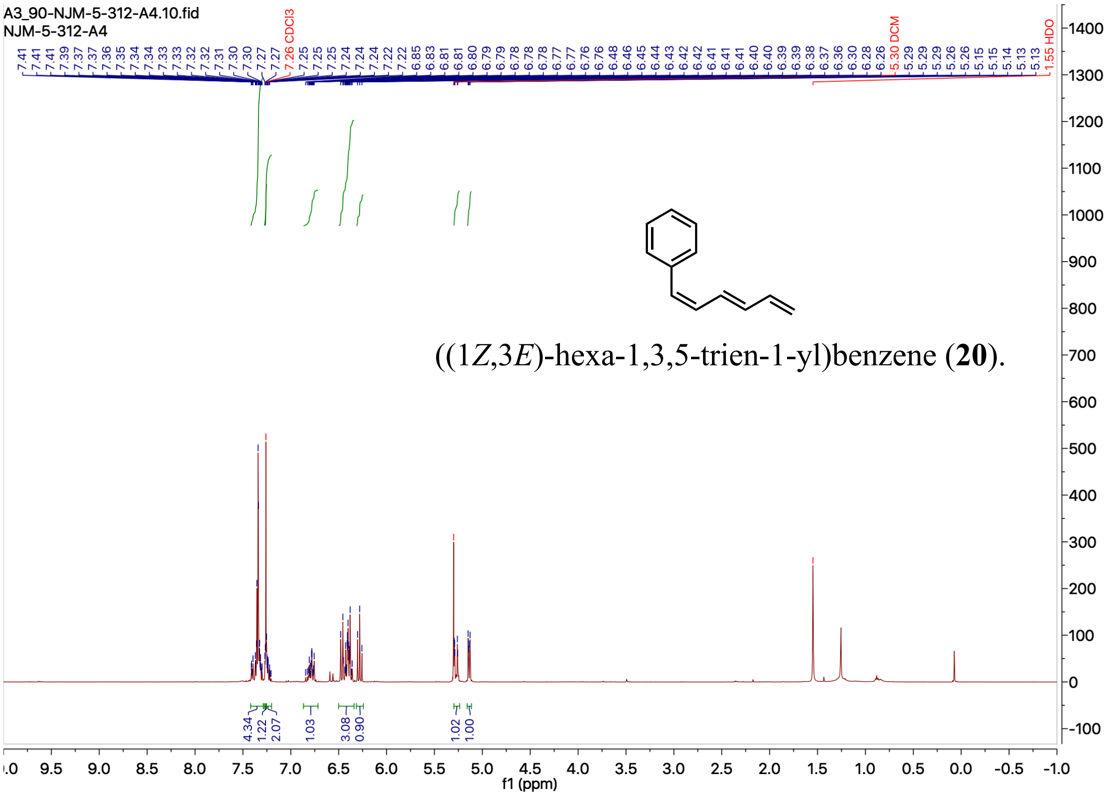


Figure S40. ^{1}H NMR (500 MHz, $CDCl_3$) of ((1*Z*,3*E*)-hexa-1,3,5-trien-1-yl)benzene (**20**).

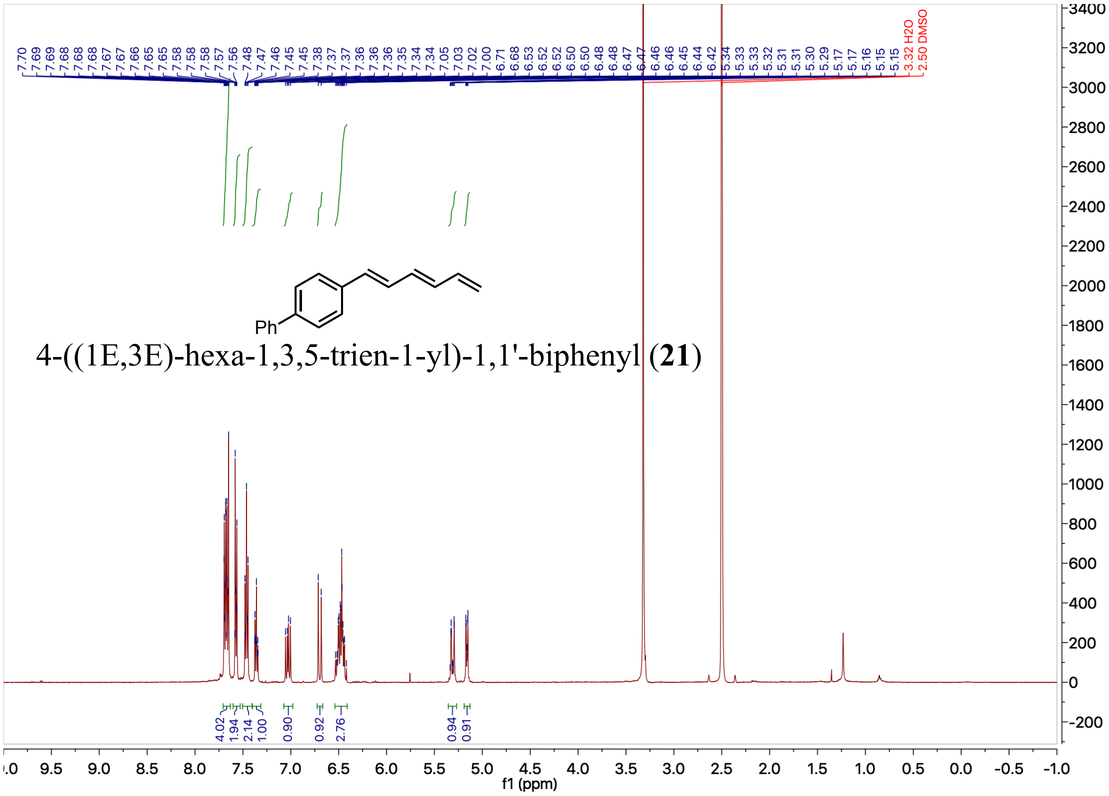


Figure S41. ^{1}H NMR (500 MHz, DMSO-d_6) of 4-((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)-1,1'-biphenyl (**21**).

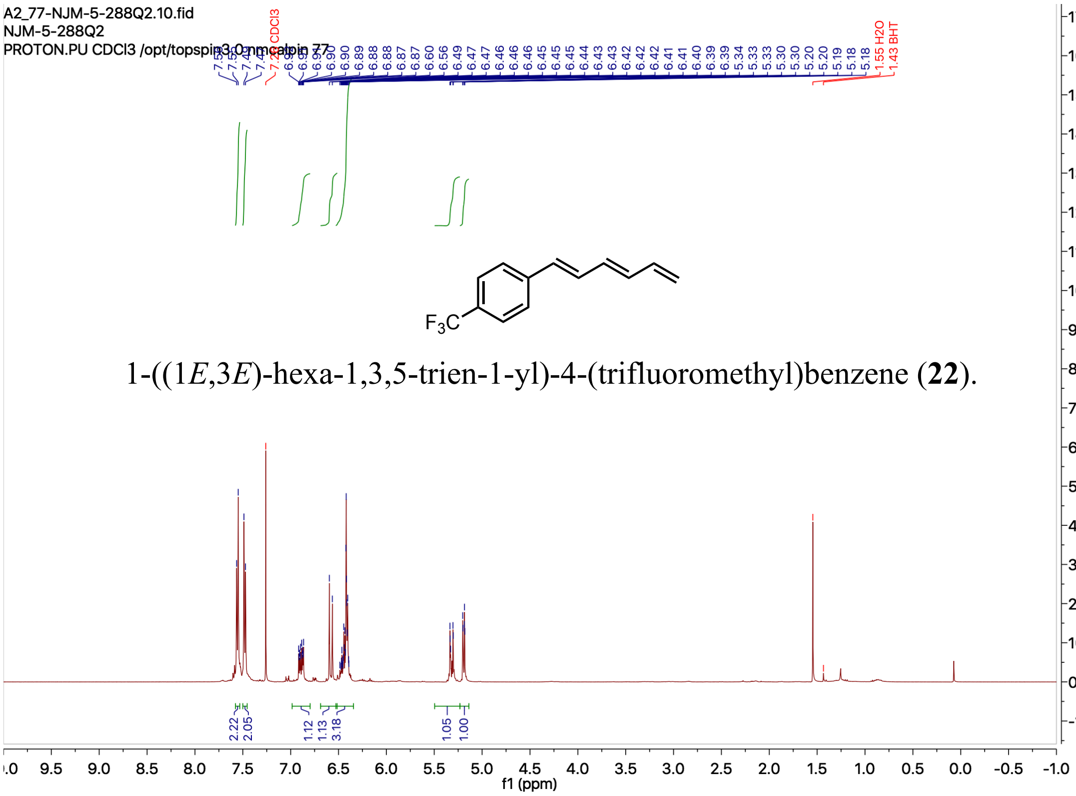


Figure S42. ^{1}H NMR (500 MHz, $CDCl_3$) of 1-((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)-4-(trifluoromethyl)benzene (**22**).

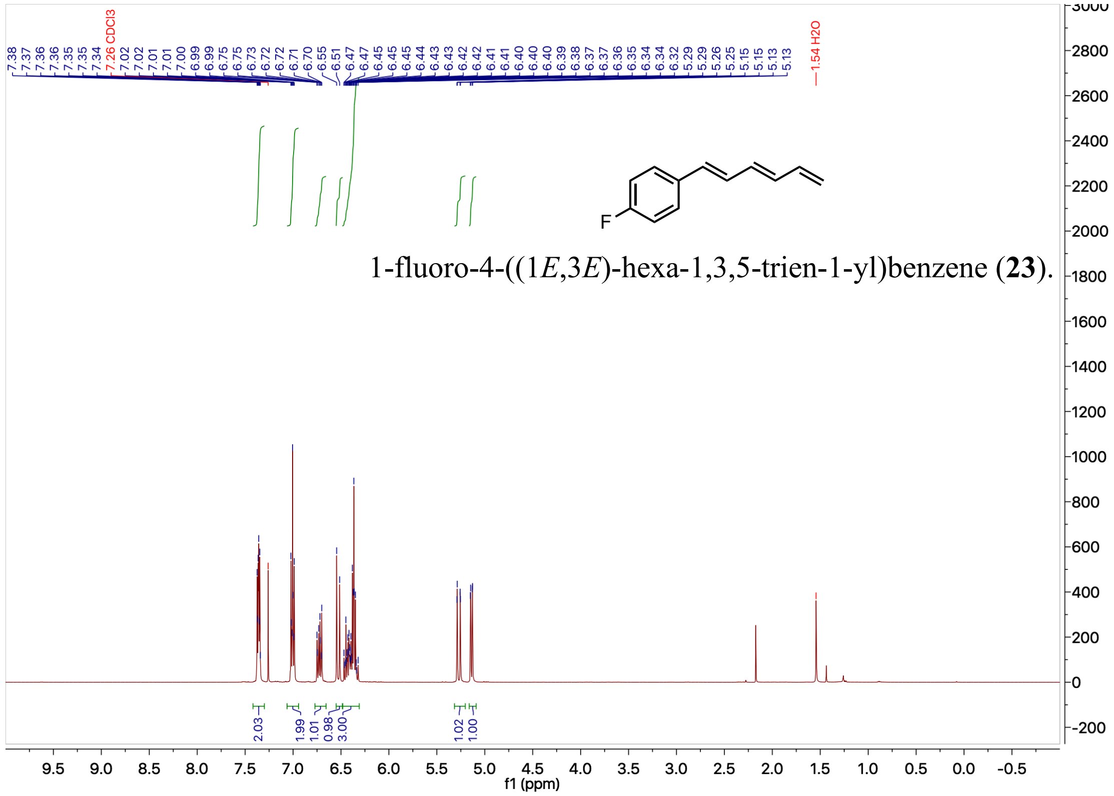


Figure S43. ^{1}H NMR (500 MHz, $CDCl_3$) of 1-fluoro-4-((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)benzene (**23**).

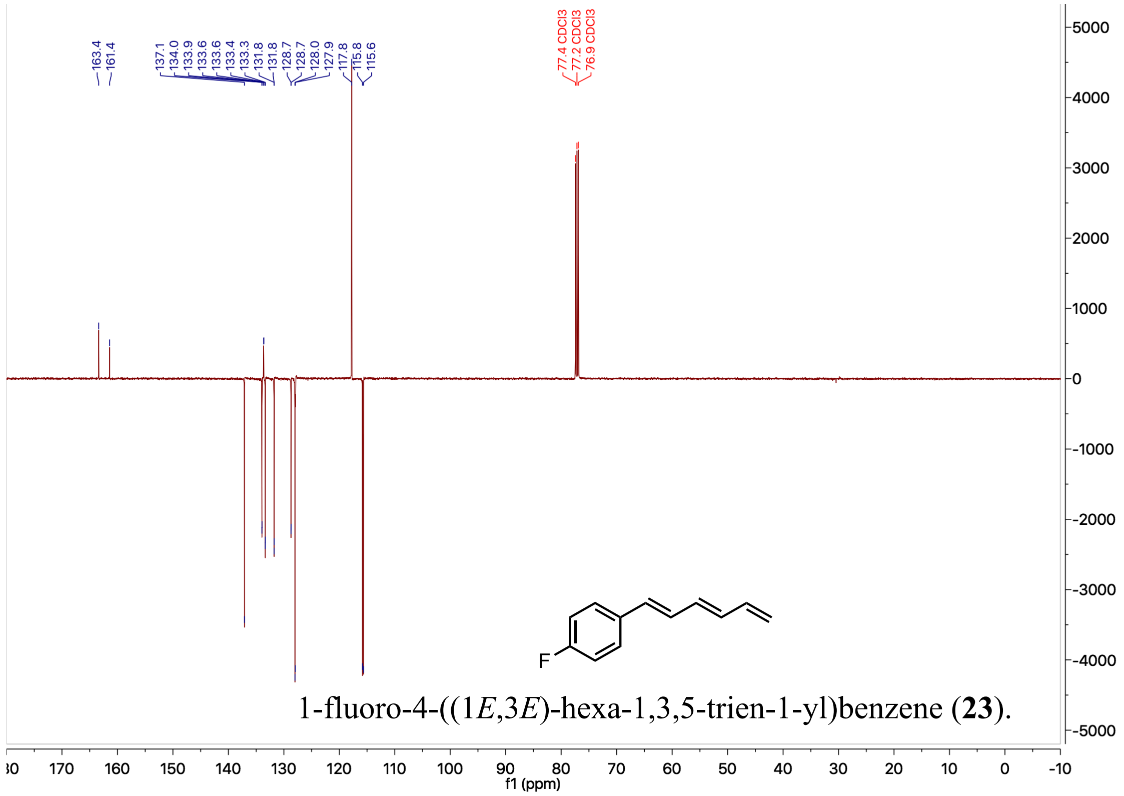


Figure S44. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) of 1-fluoro-4-((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)benzene (**23**).

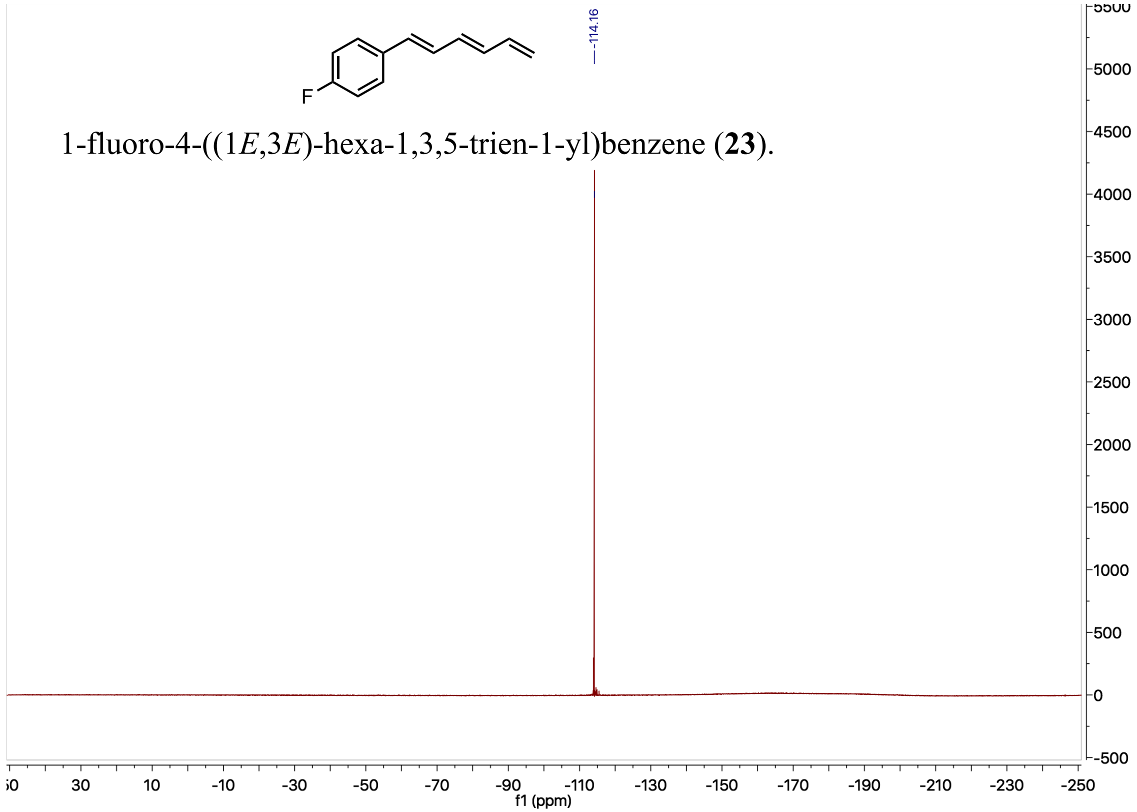


Figure S45. $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$) of 1-fluoro-4-((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)benzene (**23**).

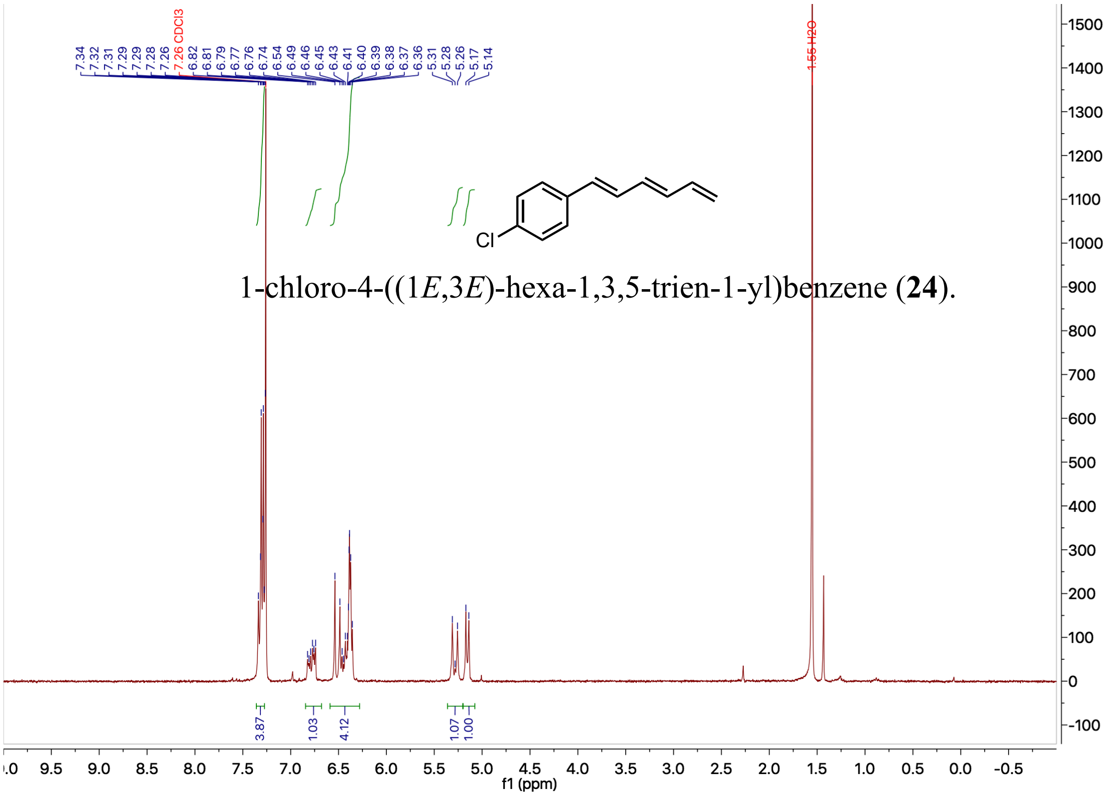


Figure S46. ^{1}H NMR (500 MHz, CDCl$_3$) of 1-chloro-4-((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)benzene (**24**).

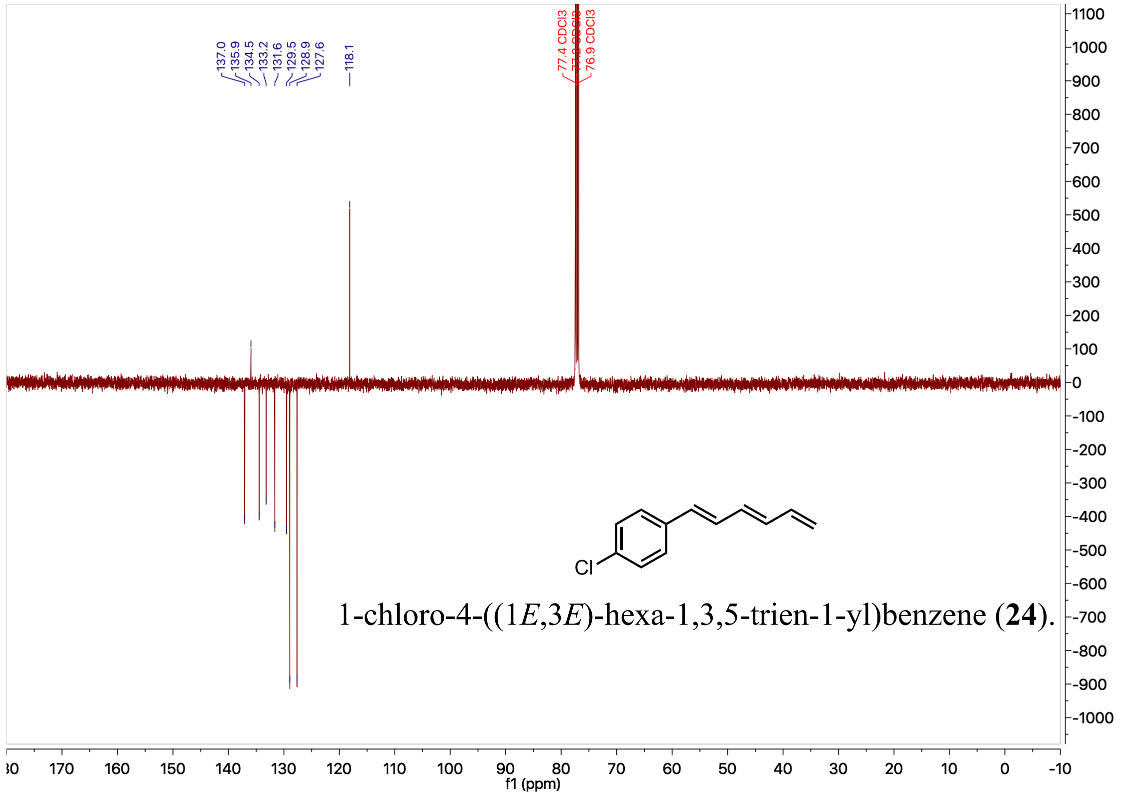


Figure S47. ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) of 1-chloro-4-((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)benzene (**24**).

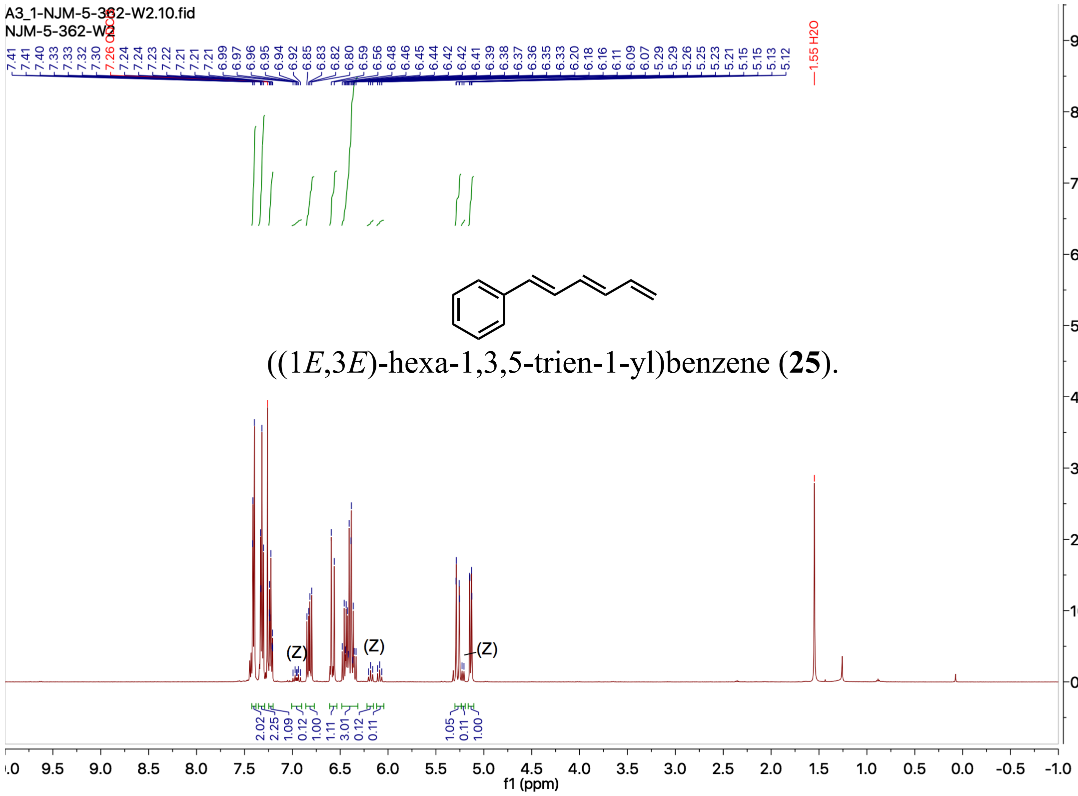


Figure S48. ^{1}H NMR (500 MHz, $CDCl_3$) of ((1*E*,3*E*)-hexa-1,3,5-trien-1-yl)benzene (**25**).

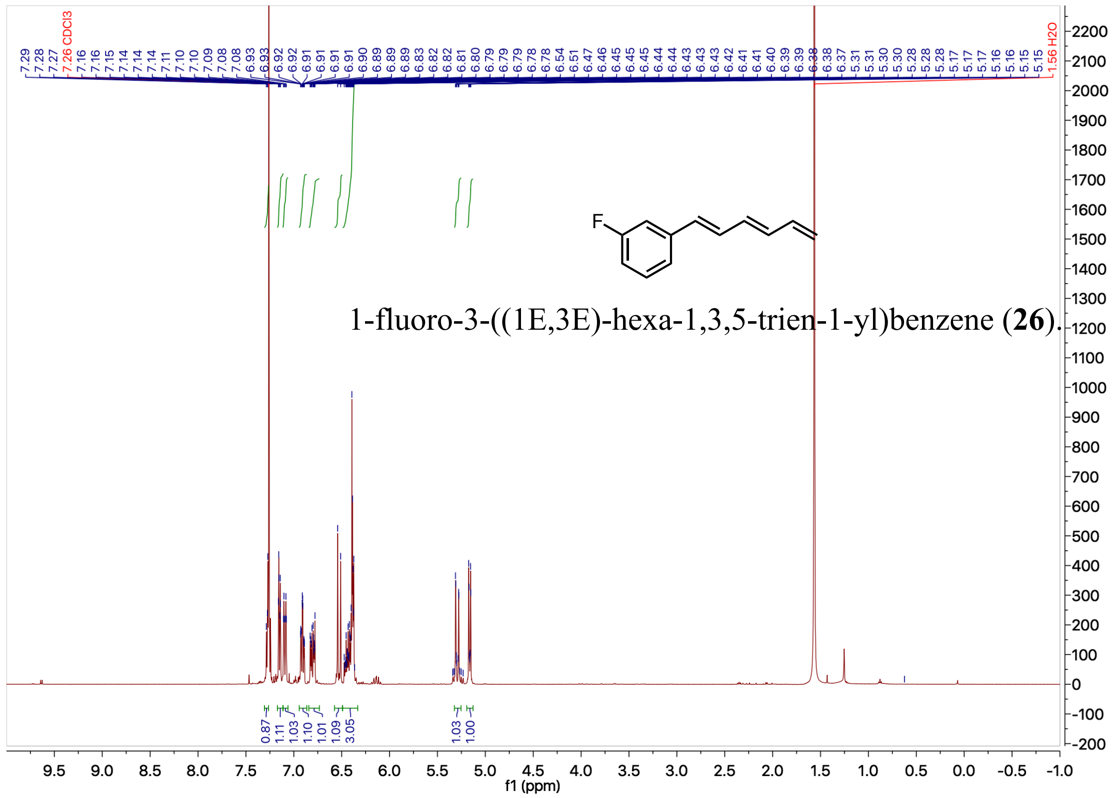


Figure S49. ^{1}H NMR (500 MHz, $CDCl_3$) of 1-fluoro-3-((1E,3E)-hexa-1,3,5-trien-1-yl)benzene (**26**).

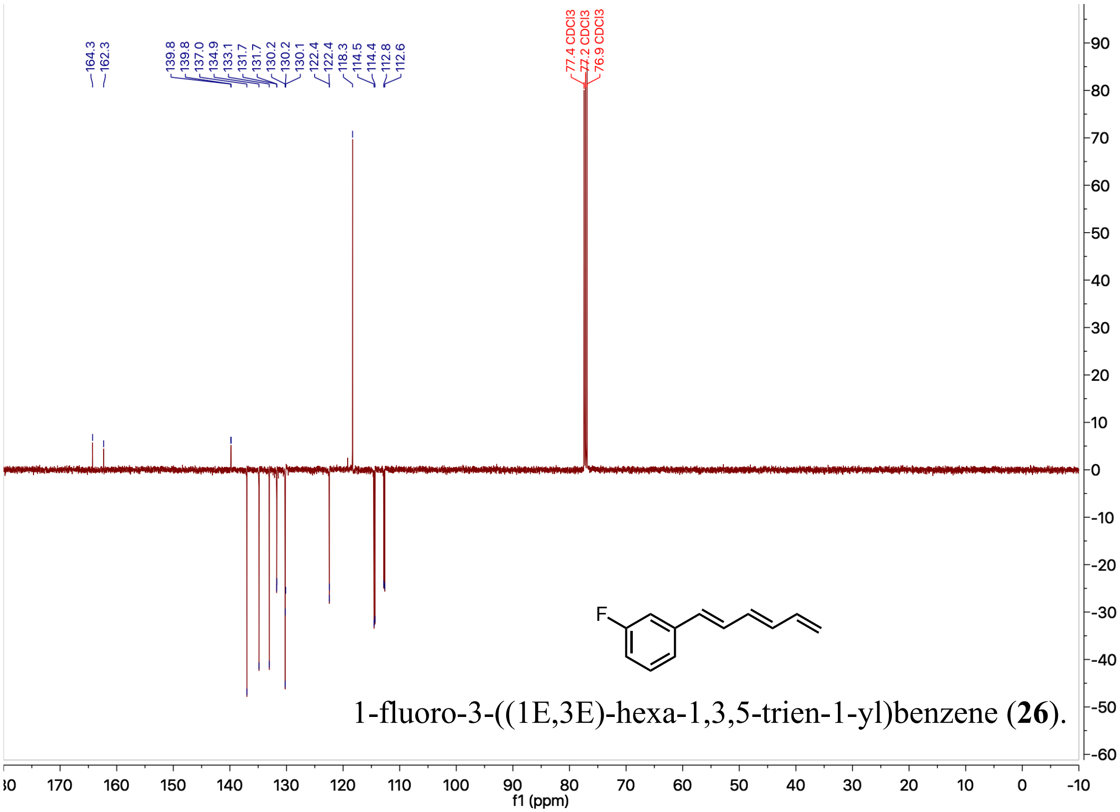


Figure S50. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of 1-fluoro-3-((1E,3E)-hexa-1,3,5-trien-1-yl)benzene (**26**).

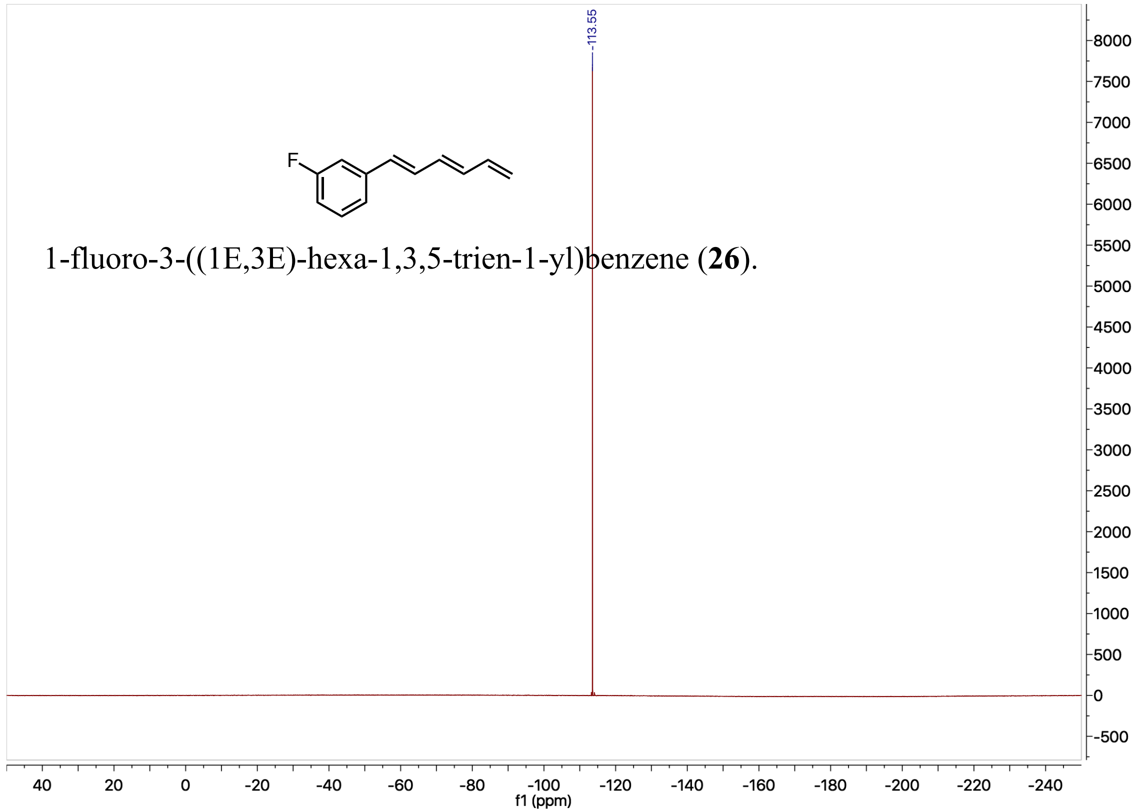


Figure S51. $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of 1-fluoro-3-((1E,3E)-hexa-1,3,5-trien-1-yl)benzene (**26**).

References

(1) Delcamp, J. H.; White, M. C.; Sequential Hydrocarbon Functionalization: Allylic C−H Oxidation/Vinylic C−H Arylation. *J. Am. Chem. Soc.* **2006**, *128*, 15076-15077.

(2) Mascitti, V.; Corey, E. J.; Enantioselective Synthesis of Pentacycloanammoxic Acid. *J. Am. Chem. Soc.* **2006**, *128*, 3118-3119.

(3) Lei, C.; Yip, Y. J.; Zhou, J. S.; Nickel-Catalyzed Direct Synthesis of Aryl Olefins from Ketones and Organoboron Reagents under Neutral Conditions. *J. Am. Chem. Soc.* **2017**, *139*, 6086-6089.

(4) Chatterjee, T.; Dey, R.; Ranu, B. C.; An easy access to styrenes: trans aryl 1,3-, 1,4- and 1,5-dienes, and 1,3,5-trienes by Hiyama cross-coupling catalyzed by palladium nanoparticles. *New J. Chem.* **2011**, *35*, 1103-1110.

(5) Kim, S.-S.; Fang, Y.; Park, H.; Synthesis and Anti-inflammatory Activity of Phenylbutenoid Dimer Analogs. *Bull. Korean Chem. Soc.* **2015**, *36*, 1676-1680.

(6) Pal, S.; Zhou, Y.-Y.; Uyeda, C.; Catalytic Reductive Vinylidene Transfer Reactions. *J. Am. Chem. Soc.* **2017**, *139*, 11686-11689.

(7) Khan, F. A.; Budanur, B. M.; Superoxide mediated isomerization of 4-aryl-but-1-ynes to 1-aryl-1,3-butadienes. *Tetrahedron* **2015**, *71*, 7600-7607.

(8) Quinn, M. P.; Yao, M.-L.; Yong, L.; Kabalka, G. W.; Boron Trihalide Mediated Haloallylation of Aryl Aldehydes and Its Application to the Preparation of (E)-1,3-Dienes. *Synthesis* **2011**, *2011*, 3815-3820.

(9) Spangler, C. W.; Jondahl, T. P.; Spangler, B.; Kinetics of thermal electrocyclic ring closure. Alkyl-1,3,5-hexatrienes. *The Journal of Organic Chemistry* **1973**, *38*, 2478-2484.

(10) Ukai, J.; Ikeda, Y.; Ikeda, N.; Yamamoto, H.; Direct, stereoselective synthesis of either E- or Z-1,3-dienes. *Tetrahedron Lett.* **1983**, *24*, 4029-4032.

(11) Wang, R.; Zhang, S.; Synthesis of conjugated dienes and polyenes via diethyl phosphite promoted carbonyl olefination. *RSC Advances* **2014**, *4*, 39497-39507.

(12) Schmidt, A.; Hilt, G.; Scope and Limitations of 1,3,5-Hexatriene Derivatives in Regioselective Cobalt-Catalyzed Reactions. *Org. Lett.* **2013**, *15*, 2708-2711.

(13) M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas,

D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople *Gaussian 03, Revision E.01*; Gaussian, Inc.: Wallingford CT, 2004.

(14) Xia, Y.; Lu, G.; Liu, P.; Dong, G.; Catalytic activation of carbon–carbon bonds in cyclopentanones. *Nature* **2016**, *539*, 546.