Breaking Conjugation: Unusual Regioselectivity with 2-Substituted Allylic Substrates in the Tsuji-Trost Reaction

Byeong-Seon Kim,[†] Mahmud M. Hussain,[†] Per-Ola Norrby,[‡] and Patrick J. Walsh[†,*]

[†]Roy and Diana Vagelos Laboratories, Penn/Merck Laboratory for High-Throughput Experimentation, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104-6323, United States.

[‡]University of Gothenburg, Department of Chemistry and Molecular Biology, Kemigården 4, #8076, SE-412 96 Göteborg, Sweden

pwalsh@sas.upenn.edu

Table of Contents **Page**

1. General Methods. All reactions were performed under a nitrogen atmosphere with oven-dried glassware. All manipulations involving dicyclohexylborane, dimethylzinc and diethylzinc were carried out under an inert atmosphere in a Vacuum Atmospheres drybox with an attached MO-40 Dritrain or by using standard Schlenk or vacuum line techniques. Chemicals were obtained from Aldrich, Acros, or GFS Chemicals unless otherwise specified. Solvents were purchased from Fischer Scientific. Toluene was dried through an activated alumina column, and then thoroughly degassed prior to use. Tetrahydrofuran was distilled from sodium and benzophenone under N_2. B(pin)-substituted alkynes

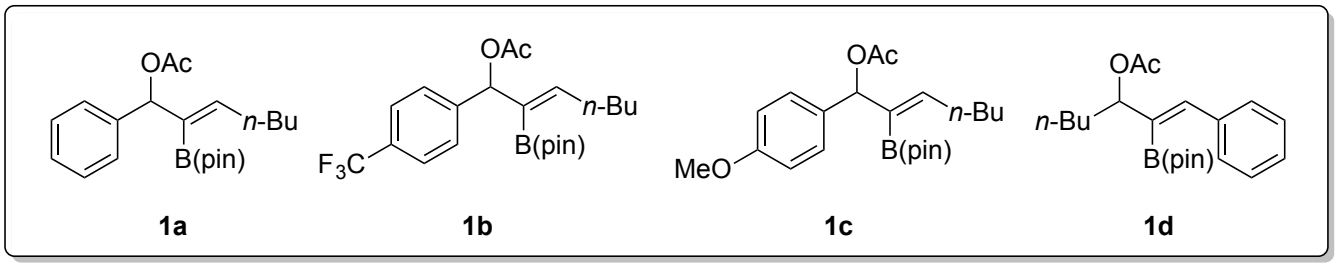
were prepared by literature methods.[1,2] Dimethylzinc and diethylzinc solutions (2.0 M in toluene) were prepared and stored in a Vacuum Atmospheres drybox. NMR spectra were obtained on Brüker 300, 360, 400 or 500 MHz Fourier transform spectrometers at the University of Pennsylvania NMR facility. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to residual solvent. $^{11}B\{^{1}H\}$ NMR spectra were referenced to $BF_3 \cdot OEt_2$. The infrared spectra were obtained using a Perkin-Elmer 1600 series spectrometer. HRMS data was obtained on a Waters LC-TOF mass spectrometer (model LCT-XE Premier) using electrospray ionization in positive or negative mode, depending on analyte. Thin-layer chromatography was performed on Whatman precoated silica gel 60 F-254 plates and visualized by ultraviolet light or by staining with ceric ammonium molybdate or phosphomolybdic acid solutions or with iodine. Silica gel (Silicaflash, P60, 40-63 μm, Silicycle) was used for air-flashed chromatography. Analysis of regioisomeric ratios was performed by analysis of ^{1}H NMR spectra of unpurified reaction products. The vinyl boronate ester is susceptible to oxidation of the B–C bond on silica under air, and hence a rapid purification is necessary to minimize oxidation to the corresponding ketone.

Caution. *Dialkylzinc reagents are pyrophoric. Care must be used when handling them.*

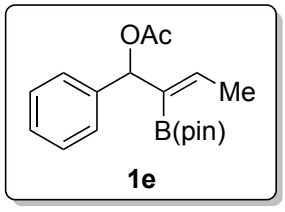
2. Preparation of 2-Substituted Allylic Substrates

General Procedure A: Synthesis of B(pin)-Substituted Allylic Acetates. To a suspension of $HBCy_2$ (770 mg, 4.32 mmol) in toluene (4.0 mL) equipped with a stir bar under N_2 was added alkyne-4,4,5,5-tetramethyl-[1,3,2]-dioxaborolane (4.32 mmol) and the reaction mixture was stirred at rt for 30 min, after which it was homogeneous. The reaction vessel was cooled to –78 °C in a dry ice bath, treated with Me_2Zn (2.16 mL, 2.0 M in toluene, 4.32 mmol), and stirred at that temperature for 30 min. The solution was then warmed to –20 °C by placing the flask in a –20 °C cold bath, and aldehyde (3.60 mmol) was added. The reaction mixture was stirred at –20 °C until TLC showed complete consumption of the aldehyde (usually 12 h). When the reaction was complete, the reaction mixture was warmed to 0 °C in

an ice bath and distilled acetic anhydride (1.1 g, 1.02 mL, 10.8 mmol) was slowly added. The reaction mixture was stirred at 0 °C until TLC showed complete consumption of the intermediate allylic alkoxide (usually 4–6 h). The reaction mixture was then diluted with EtOAc (10 mL) and quenched with saturated NH_4Cl (15 mL) at 0 °C. The organic layer was separated and the aqueous solution was extracted with EtOAc (3 x 25 mL). The combined organic solution was dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure to yield a colorless oil. The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc = 97:3) to afford the allylic acetate as a colorless oil. Importantly, the 2-B(pin) allylic acetate product is susceptible to oxidation of the B–C bond on silica under air, and hence a rapid purification is necessary to minimize oxidation to the ketone. The allylic acetate are stored under N_2 at 0 °C to preserve their purity.

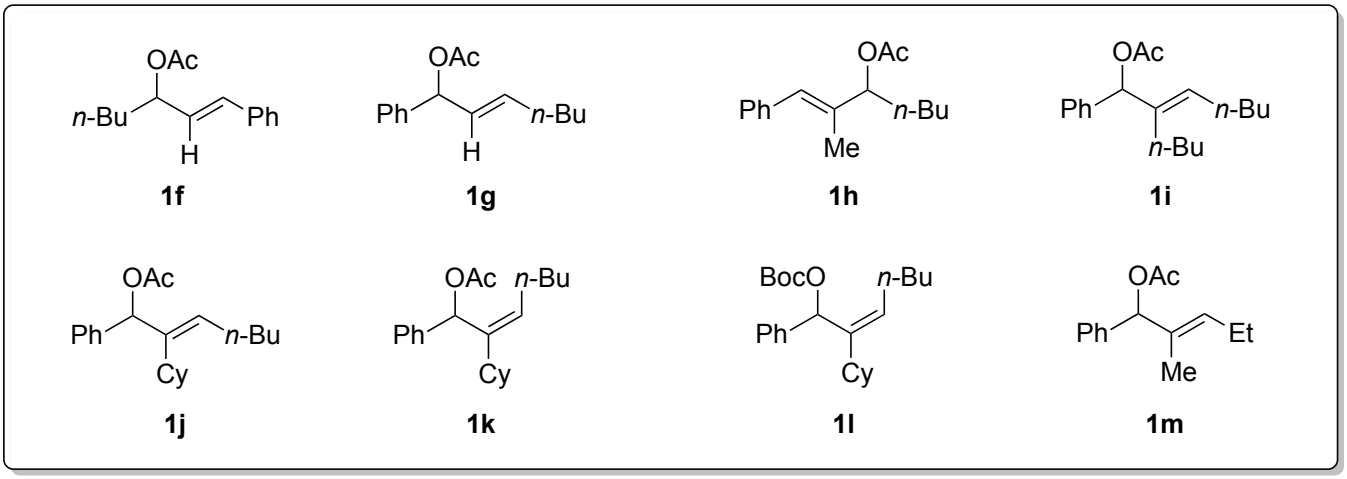


2-B(pin) substituted allylic acetates **1a–d** were prepared by General Procedure A according to our previous communication.[3]

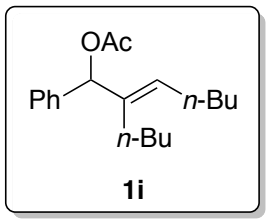


(*E*)-1-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl acetate (1e). The product was prepared by General Procedure A using 4,4,5,5-tetramethyl-2-(prop-1-yn-1-yl)-1,3,2-dioxaborolane (717 mg, 4.32 mmol), benzaldehyde (382 mg, 366 *u*L, 3.60 mmol). The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc = 97:3) to afford the allylic acetate as a colorless oil (799 mg, 70% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.22 (m, 5H), 6.42 (s, 1H), 6.21 (q, *J* = 6.9 Hz,

1H), 2.01 (s, 3H), 1.93 (d, J = 6.9 Hz, 3H), 1.19 (s, 6H), 1.16 (s, 6H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 170.1, 141.1, 140.3, 128.3, 127.9, 127.7, 83.4, 78.0, 24.9, 24.8, 21.5, 17.3 (the quaternary vinyl C bearing the boron group is not observed); ^{11}B NMR ($CDCl_3$, 128 MHz) δ 29.8; IR (neat) 2979, 2933, 1740, 1641, 1407, 1372, 1312, 1267, 1234, 1144 cm^{-1}; HRMS m/z 339.1750 $[(M+Na)^+$; calcd for $C_{18}H_{25}BO_4Na$: 339.1744].



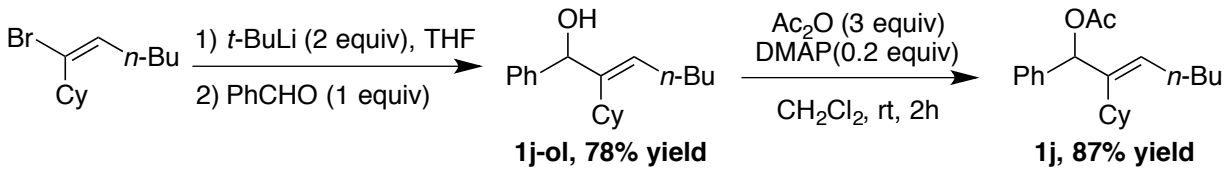
Allylic acetates **1f–h** were prepared according to our previous communication.[3]

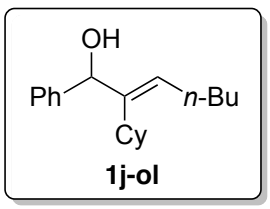


(*E*)-2-Butyl-1-phenylhept-2-en-1-yl acetate (1i). To a suspension of $HBCy_2$ (107 mg, 0.6 mmol) in toluene (1.0 mL) equipped with a stir bar under N_2 was added 5-decyne (0.11 mL, 0.6 mmol) at 0 °C in an ice bath and the reaction mixture was stirred at rt for 30 min, after which it was homogeneous. The reaction vessel was cooled to –78 °C in a dry ice bath, treated with Et_2Zn (0.45 mL, 2.0 M in toluene, 0.9 mmol), and stirred at this temperature for 30 min. The solution was then warmed to –10 °C by placing the flask in a –10 °C cold bath, and (–)-MIB (23.9 mg, 0.1 mmol) was added under positive pressure of nitrogen. The solution was stirred for 5 min and benzaldehyde (51 *u*L, 0.5 mmol) was added.

The reaction mixture was stirred at –10 °C for 12 h until TLC showed complete consumption of the aldehyde. The reaction mixture was then warmed to 0 °C in an ice bath and distilled acetic anhydride (142 *u*L, 1.5 mmol) was slowly added. The reaction mixture was stirred at 0 °C for 3 h until TLC showed complete consumption of the intermediate allylic alkoxide. The reaction mixture was then diluted with EtOAc (5 mL) and quenched with saturated NH_4Cl (5 mL) at 0 °C. The organic layer was separated and the aqueous solution was extracted with EtOAc (3 x 10 mL). The combined organic solution was washed with brine (10 mL), dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure to yield a colorless oil. The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc = 97:3) to afford the allylic acetate as a colorless oil (109 mg, 76% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 5H), 6.22 (s, 1H), 6.52 (t, *J* = 7.5 Hz, 1H), 2.11 (s, 3H), 2.10 – 2.02 (m, 2H), 2.01 – 1.94 (m, 1H), 1.92 – 1.81 (m, 1H), 1.44 – 1.18 (m, 8H), 0.91 (t, *J* = 7.0 Hz, 3H), 0.85 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 170.1, 139.6, 137.7, 129.2, 128.4, 127.9, 127.3, 79.1, 32.1, 31.5, 27.9, 27.6, 23.1, 22.7, 21.6, 14.2, 14.1; IR (neat) 2957, 2931, 2872, 2861, 1743, 1466, 1456, 1369, 1233 cm^{-1}; HRMS *m/z* 311.1985 [(M+Na)$^+$; calcd for $C_{19}H_{28}O_2Na$: 311.1987].

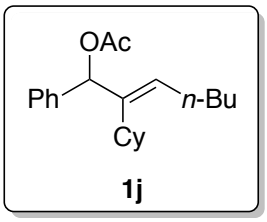
Preparation of allylic acetate 1j





(*E*)-2-Cyclohexyl-1-phenylhept-2-en-1-ol (1j-ol). To an oven-dried Schlenk flask equipped with a stir bar under N_2 was added (*E*)-(1-Bromohex-1-en-1-yl)cyclohexane[4] (245 mg, 1.0 mmol) and THF (2 mL). The reaction vessel was

cooled to –78 °C in a dry ice bath and stirred for 5 min. *t*-BuLi (1.2 mL, 2.0 mmol, 1.7 M in pentanes) was slowly added over 5 min, causing the solution to become light yellow in color. The reaction mixture was stirred at –78 °C for 20 min, and the reaction vessel was transferred to 0 °C in an ice bath. The reaction mixture was stirred at 0 °C for 10 min. The reaction vessel was again cooled to –78 °C by placing the flask in a dry ice bath. The reaction vessel was stirred at –78 °C for 5 min, before benzaldehyde (102 *u*L, 1.0 mmol) was added slowly and the reaction mixture was slowly warmed to rt over 2 h. The reaction mixture was diluted with EtOAc (5 mL) and quenched with saturated NH_4Cl (10 mL). The organic layer was separated and the aqueous solution was extracted with EtOAc (3 x 10 mL). The combined organic layer was washed with brine (10mL), dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure to yield a colorless oil. The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc = 97:3) to afford the allylic alcohol as a colorless oil (231 mg, 78% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.21 (m, 5H), 5.48 (t, *J* = 7.5 Hz, 1H), 5.21 (s, 1H), 2.30 (tt, *J* = 12.0 Hz, 3.5 Hz, 1H), 2.13 (dt, *J* = 7.5 Hz, 6.8 Hz, 1H), 1.76 – 1.58 (m, 4H), 1.48 (dq, *J* = 12.5 Hz, 3.5 Hz, 1H), 1.40 – 1.30 (m, 8H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 146.0, 143.6, 128.3, 128.2, 127.3, 127.0, 75.9, 39.7, 32.4, 32.1 (two overlapping resonances), 27.7, 27.3, 27.2, 26.4, 22.7, 14.2; IR (neat) 3369, 2928, 2852, 1493, 1449, 1379, 1239, 1188, 1172, 1014 cm^{-1}; HRMS *m/z* 295.2028 [(M+Na)$^+$; calcd for $C_{19}H_{28}ONa$: 295.2038].

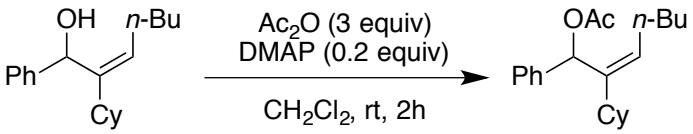


1j

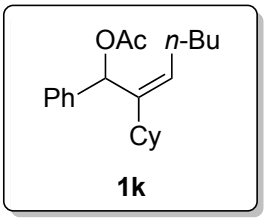
(*E*)-2-Cyclohexyl-1-phenylhept-2-en-1-yl acetate (1j). To a 20 mL glass vial equipped with a stir bar was added (*E*)-2-cyclohexyl-1-phenylhept-2-en-1-ol (136 mg, 0.5 mmol) and CH_2Cl_2 (1 mL). DMAP (12.2 mg, 0.1 mmol) was added to the solution and the reaction mixture was stirred at rt for 5 min. To the reaction mixture was added acetic anhydride (142 *u*L, 1.5 mmol) and the vial was sealed with a screw cap. The reaction mixture was stirred at rt for 2 h. The reaction mixture was diluted with CH_2Cl_2 (5 mL) and

quenched with DI water (10 mL). The organic layer was separated and the aqueous solution was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layer was dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure to yield a colorless oil. The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc = 98:2) to afford the allylic acetate as a colorless oil (130 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.21 (m, 5H), 6.29 (s, 1H), 5.41 (t, *J* = 7.0 Hz, 1H), 2.34 (tt, *J* = 12.0 Hz, 3.5 Hz, 1H), 2.13 (dt, *J* = 7.0 Hz, 7.0 Hz, 2H), 2.08 (s, 3H), 1.77 – 1.69 (m, 1H), 1.68 – 1.53 (m, 3H), 1.44 (dq, *J* = 12.5 Hz, 3.5 Hz, 1H), 1.38 – 1.04 (m, 9H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 170.1, 141.8, 140.0, 129.7, 128.3, 127.8, 127.7, 76.8, 40.0, 32.3, 32.0, 31.7, 27.6, 27.2 (two overlapping resonances), 26.3, 22.7, 21.7, 14.3; IR (neat) 2928, 2953, 1741, 1449, 1369, 1232, 1077 cm^{-1}; HRMS *m/z* 337.2140 [(M+Na)$^+$; calcd for $C_{21}H_{30}O_2Na$: 337.2144].

Preparation of allylic acetate 1k.



1k, 91% yield

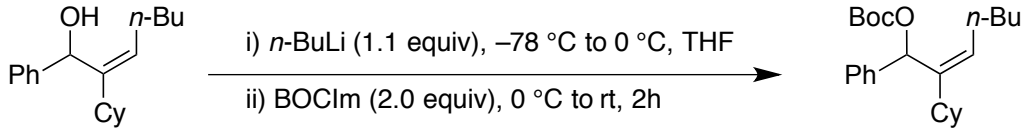


1k

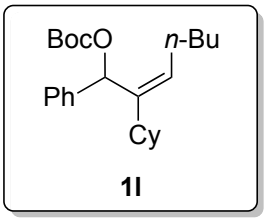
(*Z*)-2-Cyclohexyl-1-phenylhept-2-en-1-yl acetate (1k). To a 20 mL glass vial equipped with a stir bar was added (*Z*)-2-cyclohexyl-1-phenylhept-2-en-1-ol[5] (120 mg, 0.38 mmol) and CH_2Cl_2 (1 mL). DMAP (9.8 mg, 0.08 mmol) was added to the solution and the reaction mixture was stirred at rt for 5 min. To the reaction mixture was added acetic anhydride (108 *u*L, 1.14 mmol) and the vial was sealed with a screw cap. The reaction mixture was stirred at rt for 2 h. The reaction mixture was diluted with CH_2Cl_2 (5 mL) and quenched with DI water (10 mL). The organic layer was separated and the aqueous solution was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layer was dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure to yield a colorless oil. The crude product was purified by flash column

chromatography on silica gel (hexanes:EtOAc = 98:2) to afford the allylic acetate as a colorless oil (126 mg, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.22 (m, 5H), 6.77 (s, 1H), 5.47 (t, *J* = 7.5 Hz 1H), 2.33 – 2.20 (m, 2H), 2.15 (s, 3H), 1.88 (tt, *J* = 11.5 Hz, 3.0 Hz, 1H), 1.73 – 1.65 (m 2H), 1.63 – 1.55 (m, 2H), 1.42 – 1.00 (m, 10H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 170.2, 142.4, 139.7, 129.4, 128.4, 127.4, 126.2, 74.0, 40.1, 35.2, 34.5, 32.4, 28.0, 27.3, 27.2, 26.5, 22.7, 21.5, 14.3; HRMS *m/z* 255.2117 [(M–OAc)$^+$; calcd for $C_{19}H_{27}$: 255.2113].

Preparation of allylic carbonate 1l.



1l, 71% yield

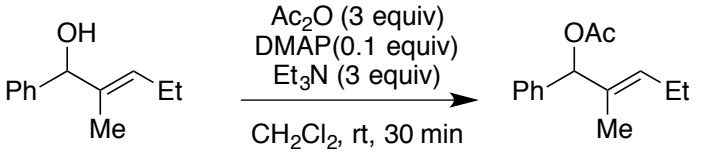


1l

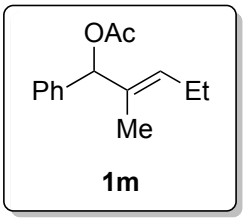
(*Z*)-*tert*-Butyl (2-cyclohexyl-1-phenylhept-2-en-1-yl) carbonate (1l). To a flame-dried round-bottomed flask equipped with a stir bar under N_2 was added (*Z*)-2-cyclohexyl-1-phenylhept-2-en-1-ol[5] (150 mg, 0.55 mmol) and THF (2 mL). The solution was cooled to –78 °C in a dry ice bath and a 2.5 M solution of *n*-BuLi in hexanes (0.24 mL, 0.61 mmol) was added dropwise. The solution was then stirred at –78 °C for 10 min and the reaction vessel was placed into a 0 °C ice bath and stirred at 0 °C for 5 min. *N*-BOC-Imidazole (185 mg, 1.1 mmol) in THF (2 mL) was added to the reaction vessel at 0 °C. The reaction mixture was allowed to warm to rt and stirred for 2 h. The reaction mixture was diluted with EtOAc (5 mL) and quenched with DI water (10 mL). The organic layer was separated and the aqueous solution was extracted with EtOAc (3 x 10 mL). The combined organic layer was washed with brine (10 mL), dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure to yield a colorless oil. The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc = 98:2) to afford the allylic carbonate as a colorless oil (205 mg, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 4H), 7.27 – 7.22 (m, 1H), 6.54 (s, 1H), 5.49 (t, *J* = 7.0 Hz, 1H), 2.35 – 2.21 (m, 2H), 1.90 (tt,

J = 11.5 Hz, 3.0 Hz, 1H), 1.75 – 1.65 (m, 2H), 1.63 – 1.53 (m, 2H), 1.49 (s, 9H), 1.43 – 1.01 (m, 10H), 0.91 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 153.3, 142.5, 139.5, 129.5, 128.3, 127.4, 126.2, 82.0, 76.7, 39.6, 35.0, 34.6, 32.4, 28.1, 27.9, 27.2 (two overlapping resonances), 26.5, 22.6, 14.3; IR (neat) 2956, 2927, 2853, 1742, 1496, 1449, 1393, 1369, 1279, 1254, 1163, 1086, cm^{-1}; HRMS *m/z* 359.2567 [$(M+Na)^+$; calcd for $C_{24}H_{36}O_3Na$: 359.2562].

Preparation of allylic acetate 1m.



1m, 87% yield



1m

(*E*)-2-Methyl-1-phenylpent-2-en-1-yl acetate (1m). To a 20 mL glass vial equipped with a stir bar was added (*E*)-2-methyl-1-phenylpent-2-en-1-ol[6] (550 mg, 3.12 mmol) and CH_2Cl_2 (6 mL). DMAP (38 mg, 0.31 mmol) and Et_3N (1.3 mL, 9.36 mmol) were added to the solution and the vial was sealed with a screw cap. The reaction mixture was stirred at rt for 5 min. To the reaction mixture was added acetic anhydride (0.88 mL, 9.36 mmol) and the resulting solution was stirred at rt for 30 min. The reaction mixture was then diluted with CH_2Cl_2 (5 mL) and quenched with DI water (10 mL). The organic layer was separated and the aqueous solution was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layer was dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure to yield a colorless oil. The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc = 97:3) to afford the allylic acetate as a colorless oil (126 mg, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.24 (m, 5H), 6.18 (s, 1H), 5.59 (t, *J* = 7.5 Hz, 1H), 2.13 (s, 3H), 2.06 (dq, *J* = 7.5 Hz, 7.0 Hz, 2H), 1.51 (s, 3H), 0.99 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 170.2, 139.4, 132.6, 130.7, 128.4,

127.8, 126.8, 80.2, 21.5, 21.2, 14.1, 12.6; IR (neat) 2965, 2934, 2874, 1742, 1495, 1454, 1370, 1235, 1021 cm^{-1}; HRMS *m/z* 241.1205 [$(M+Na)^+$; calcd for $C_{14}H_{18}O_2Na$: 241.1204].

3. Palladium Catalyzed Allylic Substitution of Allylic Acetates

General Procedure B[3]: Palladium Catalyzed Allylic Substitution of 2-B(pin)-Substituted Allylic Acetates with $NaCH(CO_2Me)_2$. To a Schlenk flask equipped with a stir bar was added $[Pd(allyl)Cl]_2$ (1.8 mg, 0.005 mmol, 5 mol %) and PPh_3 (5.3 mg, 0.02 mmol, 20 mol %) in 0.5 mL of dry and degassed THF at rt under N_2 and the solution stirred at rt for 30 min. To this catalyst solution was added 2-B(pin)-substituted allylic acetate (0.10 mmol) and the reaction mixture stirred for an additional 30 – 45 min. In a separate 5 mL round bottomed flask equipped with a stir bar and condenser was added sodium hydride (7.9 mg, 0.33 mmol) in 2.0 mL of dry and degassed THF under N_2, and the reaction mixture cooled to 0 °C in an ice bath. To this white suspension was added dropwise dimethyl malonate (35 μL, 39.6 mg, 0.3 mmol) at 0 °C, which was accompanied by rapid evolution of H_2. The reaction soon became clear, after which it was heated to reflux under N_2 for 15 min. The dimethyl malonate sodium solution (3 equiv) was cooled to rt, and then cannulated into the Schlenk flask containing the catalyst and 2-B(pin)-substituted allylic acetate solution at rt. The reaction mixture was warmed to 40 °C and stirred until TLC showed complete consumption of the 2-B(pin) substituted allylic acetate. The reaction mixture was then cooled to rt, diluted with EtOAc (4 mL) and quenched with saturated NH_4Cl (4 mL). The organic layer was separated and the aqueous solution was extracted with EtOAc (3 x 5 mL). The combined organic solution was dried over $MgSO_4$, filtered through celite and the solvent was removed under reduced pressure to yield a pale red oil. The crude product was dissolved in $CDCl_3$ and the ratio of regioisomers was determined by ^1H NMR spectroscopy of unpurified reaction mixtures. $CDCl_3$ was removed under reduced pressure and the crude product was purified by flash column chromatography on silica gel. The vinyl boronate ester is susceptible to oxidation of the B–C bond on silica under air, and hence a rapid purification is necessary to minimize oxidation to the corresponding ketone.

General Procedure C[3]: Palladium Catalyzed Allylic Substitution of 2-B(pin)-Substituted Allylic Acetates with BSA, $CH_2(CO_2Me)_2$ and catalytic KOAc. To a Schlenk flask equipped with a stir bar was added $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 10 mol %) and PPh_3 (5.3 mg, 0.02 mmol, 20 mol %) in 1.0 mL of dry and degassed THF at rt under N_2 and the solution stirred at rt for 30 min. To this catalyst solution was added 2-B(pin)-substituted allylic acetate (0.10 mmol) and the reaction mixture stirred for an additional 15 min, after which *N*,*O*-bis(trimethylsilyl)acetamide (BSA) (73 μL, 61.0 mg, 0.30 mmol, 3 equiv) and dimethylmalonate (34 μL, 39.6 mg, 0.3 mmol, 3 equiv) were added at rt followed by catalytic KOAc. The reaction mixture was warmed to 40 °C and stirred until TLC showed complete consumption of the 2-B(pin) substituted allylic acetate, typically 10 – 12 h. The reaction mixture was then cooled to rt, diluted with EtOAc (4 mL) and filtered through a plug of silica and the solvent was removed under reduced pressure. The crude product was dissolved in $CDCl_3$ and the ratio of regioisomers was determined by ^1H NMR spectroscopy of unpurified reaction mixtures. $CDCl_3$ was removed under reduced pressure and the crude product was purified by flash column chromatography on silica gel.

Preparation of Pd/2 equiv PPh_3 stock solution (0.143 M of Pd) in THF.

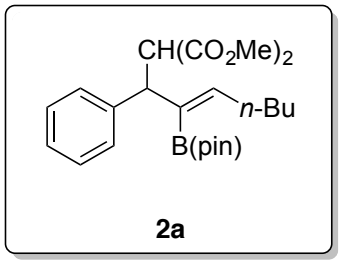
To an oven-dried microwave vial equipped with a stir bar was charged with $[Pd(allyl)Cl]_2$ (9.1 mg, 0.025 mmol) or $Pd(OAc)_2$ (11.2 mg, 0.05 mmol) and PPh_3 (26.2 mg, 0.10 mmol) and the vial was capped, and then the vial was purged with N_2. To the vial was added 3.5 mL of dry and degassed THF and the stock solution was stirred at rt for 30 min before use.

Preparation of $NaCH(CO_2Me)_2$ stock solution (0.1M) in THF.

To an oven-dried microwave vial equipped with a stir bar was charged with NaH (48 mg, 2.0 mmol) and the vial was capped, and then the vial was purged with N_2. To the vial was added dry and degassed THF (1.77 mL) at rt and the reaction mixture cooled to 0 °C in an ice bath. To this white suspension was added dropwise dimethyl malonate (229 *u*L, 264 mg, 2.0 mmol). Upon addition of the dimethyl malonate, rapid evolution of a gas, presumably H_2, was observed. Once the H_2 evolution ceased, the resulting solution was heated to reflux for 1 min. The stock solution was cooled and stirred at rt for 10 min before use.

General Procedure D: **Palladium Catalyzed Allylic Substitution of 2-B(pin)-Substituted Allylic Acetates or 2-Substituted Allylic Acetates with $NaCH(CO_2Me)_2$.** To an oven-dried microwave vial equipped with a stir bar was charged with the allylic acetate **1e** (63.2 mg, 0.20 mmol) and the vial was capped and purged with N_2. To the vial was added a stock solution of $[Pd(allyl)Cl]_2$/2 equiv PPh_3 in 0.143 M THF (1.4 mL, 10 mol% Pd and 20 mol % PPh_3) by a syringe and the reaction mixture was stirred at rt for 30 min, after which a stock solution of $NaCH(CO_2Me)_2$ in 0.1 M THF (0.6 mL, 0.6 mmol) was added by a syringe at rt. The sealed vial was warmed to 40 °C and stirred until TLC taken under positive pressure of nitrogen showed complete consumption of allylic acetate, typically 0.5 – 24 h. Note that aliquots for TLC were taken under positive pressure of nitrogen. The reaction mixture was cooled to rt, diluted with EtOAc (2 mL) and then quenched with three drops of water. The solution was filtered through a plug of $MgSO_4$ and celite. The pad was rinsed with additional ethyl acetate (5 mL) and the solvent was removed under reduced pressure to yield a pale red or yellow oil. The crude product was dissolved in $CDCl_3$ and the ratio of regioisomers and the ratio of 1,4-elimination products were determined by ^1H NMR spectroscopy of unpurified reaction mixtures. $CDCl_3$ was removed under reduced pressure and the crude product was purified by flash column chromatography on silica gel

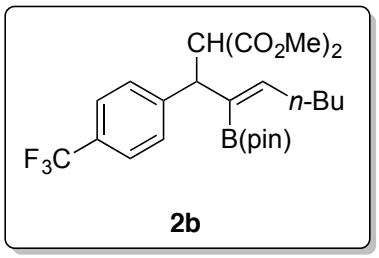
(hexanes:EtOAc = 95:5) to afford the mixture of dimethyl malonate substituted products and the mixture of 1,4-elimination products. The vinyl boronate ester is susceptible to oxidation of the B–C bond on silica under air, and hence a rapid purification is necessary to minimize oxidation to the corresponding ketone.



2a

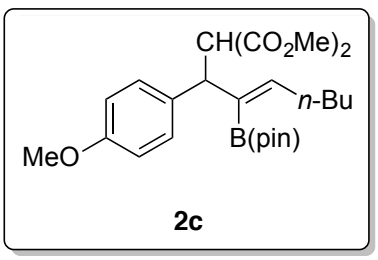
Dimethyl (*E*)-2-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-2-en-1-yl)malonate (2a). The compound was prepared by General Procedure B using **1a** and the result was reported in our previous communication (>90:10, 76% yield).[3]

The tile compound can also be prepared by General Procedure B using **1d** and the result was reported in our previous communication (>90:10, 51% yield).[3]



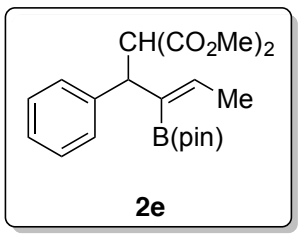
2b

Dimethyl (*E*)-2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(4-(trifluoromethyl)phenyl)hept-2-en-1-yl)malonate (2b). The compound was prepared by General Procedure C using **1b** and the result was reported in our previous communication (>95:5, 92% yield).[3]



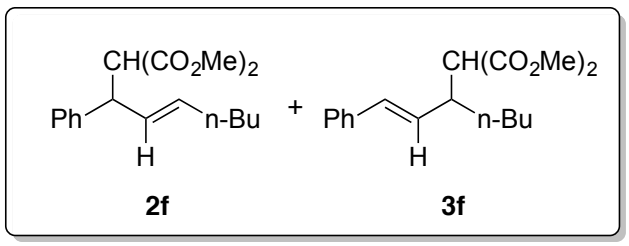
2c

Dimethyl (*E*)-2-(1-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-2-en-1-yl)malonate (2c). The compound was prepared by General Procedure C using **1c** and the result was reported in our previous communication (>95:5, 80% yield).[3]



2e

Dimethyl (*E*)-2-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)malonate (2e). The product was prepared by General Procedure D using (*E*)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl acetate **1e** (63.2 mg, 0.2 mmol), a 0.143 M $[Pd(allyl)Cl]_2/2PPh_3$ from a stock solution (1.4 mL), and 0.1 M $NaCH(CO_2Me)_2$ stock solution (0.6 mL). The reaction mixture was stirred at 40 °C for 3 h. The regioisomer **2e** (benzylic substitution product) was confirmed by ^1H NMR spectra of unpurified reaction products. The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc = 95:5) to afford dimethyl malonate substituted vinyl boronate ester as an oil (54.4 mg, 70% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.22 – 7.17 (m, 2H), 7.14 – 7.09 (m, 1H), 6.32 (q, *J* = 7.0 Hz, 1H), 4.44 (d, *J* = 12.0 Hz, 1H), 4.20 (d, *J* = 12.0 Hz, 1H), 3.69 (s, 3H), 3.48 (s, 3H), 1.88 (d, *J* = 7.0 Hz, 3H), 1.16 (s, 6H), 1.14 (s, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 169.1, 169.0, 142.4, 141.8, 128.4, 128.2, 126.5, 83.2, 55.9, 53.0, 52.4 (two overlapping resonances), 25.0, 24.9, 17.5 (the quaternary vinyl C bearing the boron group is not observed); ^{11}B NMR ($CDCl_3$, 125 MHz) δ 29.2; IR (neat) 2979, 2953, 1761, 1740, 1625, 1496, 1434, 1408, 1373, 1310, 1267, 1194, 1140, 1027 cm^{-1}; HRMS *m/z* 411.1967 [$(M+Na)^+$; calcd for $C_{21}H_{29}BO_6Na$: 411.1955].



2f **3f**

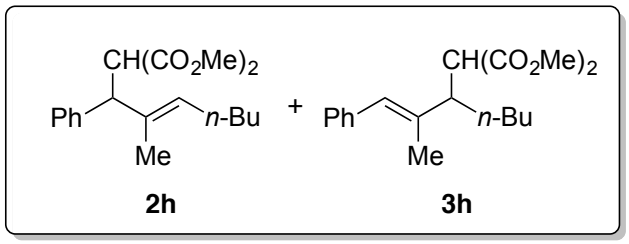
Dimethyl (*E*)-2-(1-phenylhept-2-en-1-yl)malonate (2f, minor) and Dimethyl (*E*)-2-(1-phenylhept-1-en-3-yl)malonate (3f, major). The reaction was performed following General Procedure D with **1g** (23.2 mg, 0.1 mmol) in the presence of 5 mol % of $[Pd(allyl)Cl]_2$ and 20 mol% of PPh_3 of the stock solution and 3 equiv of $NaCH(CO_2Me)_2$ from a stock solution. The reaction mixture was stirred at 40 °C for 30 min. The ratio of regioisomers was **2f**:**3f** = 13:87 determined by ^1H NMR spectra of unpurified

reaction products. The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc = 90:10) to afford the mixture of dimethyl malonate substituted products as a colorless oil (26.5 mg, 87% yield). The NMR spectral data match the previously published data.[3]

The title compound can also be made by General Procedure D with **1g** at rt for 30 min to afford the mixture of products **2f** and **3f** (16:84, 25.3 mg, 83% yield).

The title compound can also be made by General Procedure B using **1f** in the presence of 5 mol % of $Pd(OAc)_2$ and 10 mol % of PPh_3 at 40 °C for 12 h and the result was reported in our previous communication (**2f**:**3f**=10:90, 85% yield).[3]

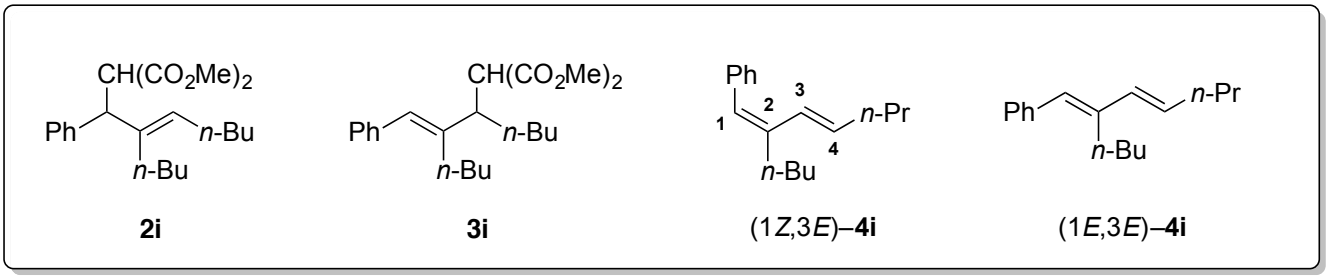
The title compound can also be made by General Procedure B using **1g** in the presence of 5 mol % of $Pd(OAc)_2$ and 10 mol % of PPh_3. (**2f**:**3f**=9:91, 95% yield). [3]



2h **3h**

Dimethyl (*E*)-2-(2-methyl-1-phenylhept-2-en-1-yl)malonate (2h, major) and dimethyl (*E*)-2-(2-methyl-1-phenylhept-1-en-3-yl)malonate (3h, minor). The reaction was performed following General Procedure D with **1h** (24.6 mg, 0.1 mmol) in the presence of 5 mol % of $[Pd(allyl)Cl]_2$ and 20 mol % of PPh_3 of the stock solution and 3 equiv of $NaCH(CO_2Me)_2$ from a stock solution. The reaction mixture was stirred at 40 °C for 3 h. The ratio of regioisomers was **2h**:**3h** = 63:37 determined by ^1H NMR spectra of unpurified reaction products. The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc = 95:5) to afford the mixture of dimethyl malonate substituted products as a colorless oil (28.0 mg, 88% yield) and characterized as the mixture of regioisomers. The reaction of **1h** provided the mixture of **2h** and **3h** (79%, 63:37) at 40 °C for 24 h, and **2h** and **3h** (65%, 64:36) at 70 °C for 24 h. **Dimethyl (*E*)-2-(2-methyl-1-phenylhept-2-en-1-yl)malonate (2h)**. ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.10 (m, 5H), 5.42 (t, *J* = 7.5 Hz, 1H), 4.09 (d,

J = 12.5 Hz, 1H), 4.03 (d, *J* = 12.5 Hz, 1H), 3.72 (s, 3H), 3.47 (s, 3H), 2.02 – 1.93 (dt, *J* = 7.5 Hz, 7.0 Hz, 2H), 1.48 (s, 3H), 1.39 – 1.15 (m, 4H) 0.89 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 168.7, 168.5, 140.1, 134.8, 128.5, 128.1, 127.1, 126.6, 55.8, 53.9, 52.7, 52.6, 32.0, 27.8, 22.5, 15.1, 14.2; **Dimethyl (*E*)-2-(2-methyl-1-phenylhept-1-en-3-yl)malonate** (**3h**). ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.22 – 7.16 (m, 3H), 6.39 (s, 1H), 3.77 (s, 3H), 3.64 (s, 3H), 3.54 (d, *J* = 11.0 Hz, 1H), 2.97 (ddd, *J* = 11.0 Hz, 8.5 Hz, 6.5 Hz, 1H), 1.77 (s, 3H), 1.52 – 1.42 (m, 2H), 1.40 – 1.15 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 169.1, 168.8, 138.0, 136.7, 129.5, 129.1, 128.3, 126.5, 56.7, 52.73, 52.61, 49.8, 30.4, 29.5, 22.7, 14.2, 13.9; **(2h+3h)** IR (neat) 2954, 2929, 2858, 1762, 1740, 1600, 1494, 1453, 1434, 1316, 1265, 1243, 1160, 1143, 1130cm^{-1}; **(2h+3h)** HRMS *m/z* 341.1730 [$(M+Na)^+$; calcd for $C_{19}H_{26}O_4Na$: 341.1729].



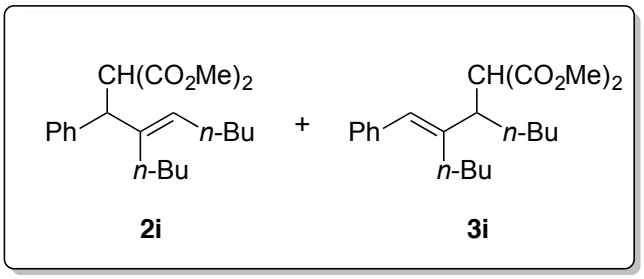
2i **3i** (1*Z*,3*E*)–**4i** (1*E*,3*E*)–**4i**

Dimethyl (*E*)-2-(2-butyl-1-phenylhept-2-en-1-yl)malonate (2i, major of 2i+3i), dimethyl (*E*)-2-(6-benzylidenedecan-5-yl)malonate (3i, minor of 2i+3i), ((1*Z*,3*E*)-2-butylhepta-1,3-dien-1-yl)benzene ((1*Z*,3*E*)-4i, minor of 4i) and ((1*E*,3*E*)-2-butylhepta-1,3-dien-1-yl)benzene ((1*E*,3*E*)-4i, major of 4i).

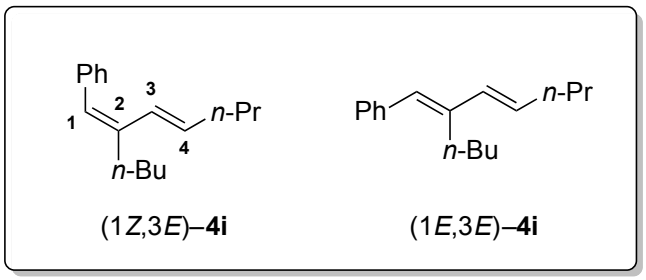
The reaction was performed following General Procedure D with **1i** (28.8 mg, 0.1 mmol) in the presence of 5 mol % of $[Pd(allyl)Cl]_2$ and 20 mol% of PPh_3 of the stock solution and 3 equiv of $NaCH(CO_2Me)_2$ stock solution. The reaction mixture was stirred at 40 °C for 8 h. The ratio of isomers was **2i:3i =** 81:19 and **(1*Z*,3*E*)-4i**:**(1*E*,3*E*)-4i** = 24:76 determined by ^1H NMR spectra of unpurified reaction products. The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc = 95:5) to

afford the mixture of dimethyl malonate substituted products as a colorless oil (27.0 mg, 75% yield) and the mixture of 1,4-elimination products as a colorless oil (4.3 mg, 15% yield).

The title compound can also be made at 70 °C for 8 h to afford the mixture of products **2i**:**3i** (81:19, 7.2 mg, 20% yield) and **(1*Z*,3*E*)-4i:(1*E*,3*E*)-4i** (27:73, 15.3 mg, 67% yield).

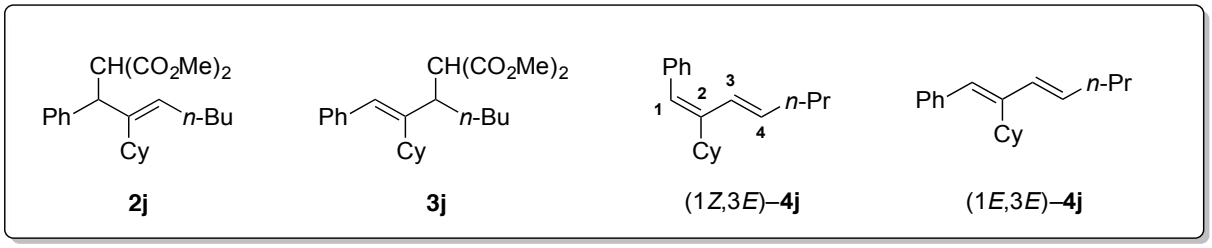


Dimethyl (*E*)-2-(2-butyl-1-phenylhept-2-en-1-yl)malonate (2i). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.15 (m, 5H), 4.04 (d, J_{AB} = 12.0 Hz, 1H), 5.36 (t, J = 7.5 Hz, 1H), 4.02 (d, J_{AB} = 12.0 Hz, 1H), 3.71 (s, 3H), 3.41 (s, 3H), 2.12 – 2.04 (m, 1H), 2.06 – 1.98 (m, 2H), 1.67 – 1.58 (m, 1H) 1.55 – 1.10 (m, 8H), 0.90 (t, J = 7.0 Hz, 3H), 0.83 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 168.7, 168.5 140.2, 139.6, 128.6, 128.4, 127.2, 125.2, 57.0, 52.6, 52.5, 51.2, 32.2, 30.7, 30.6, 27.7, 23.0, 22.5, 14.2, 14.1; **Dimethyl (*E*)-2-(6-benzylidenedecan-5-yl)malonate (3i).** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.15 (m, 5H), 6.31 (s, 1H), 3.76 (s, 3H), 3.66 (s, 3H), 3.63 (d, J = 10.5 Hz, 1H), 2.98 (ddd, J = 10.5 Hz, 9.0 Hz, 4.5 Hz, 1H), 2.24 – 2.12 (m, 2H), 1.57 – 1.10 (m, 10H), 0.94 – 0.80 (m, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 169.3, 168.9, 142.3, 138.2, 128.7, 128.3, 128.2, 126.5, 57.0, 52.7, 52.6, 49.9, 31.7, 31.0, 30.7, 29.3, 23.4, 22.9, 14.2, 14.0; **(2i+3i)** IR (neat) 2955, 2931, 2860, 1763, 1741, 1600, 1494, 1454, 1434, 1378, 1315, 1274, 1245, 1193, 1159, 1141, 1030 cm^{-1}; **(2i+3i)** HRMS *m/z* 383.2202 $[M+Na)^{+}$; calcd for $C_{22}H_{32}O_4Na$: 383.2198].



(1*Z*,3*E*)–**4i** (1*E*,3*E*)–**4i**

((1*Z*,3*E*)-2-Butylhepta-1,3-dien-1-yl)benzene ((1*Z*,3*E*)-4i). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.27 – 7.23 (m, 2H), 7.22 – 7.17 (m, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.32 (s, 1H), 5.86 (dt, *J* = 16.0 Hz, 7.0 Hz, 1H), 2.34 (t, *J* = 7.5 Hz, 2H), 2.09 (dt, *J* = 7.5 Hz, 7.0 Hz, 2H), 1.58 – 1.34 (m, 6H), 0.96 – 0.87 (m, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 139.4, 138.4, 132.4, 128.9, 128.2, 127.8, 126.9, 126.3, 35.6, 34.7, 31.5, 23.0, 22.9, 14.3, 14.0; **((1*E*,3*E*)-2-Butylhepta-1,3-dien-1-yl)benzene ((1*E*,3*E*)-4i.** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H), 7.27 – 7.23 (m, 2H), 7.22 – 7.17 (m, 1H), 6.37 (s, 1H), 6.11 (d, *J* = 15.5 Hz, 1H), 5.79 (dt, *J* = 15.5 Hz, 7.0 Hz, 1H), 2.45 –2.38 (m, 2H), 2.14 (dt, *J* = 7.5 Hz, 7.0 Hz, 2H), 1.58 – 1.34 (m, 6H), 0.94 (t, *J* = 7.5 Hz, 3H), 0.92 (t, *J* = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 141.2, 138.4, 134.4, 130.2, 129.6, 128.9, 128.4, 126.5, 35.4, 31.7, 27.6, 23.3, 23.0, 14.2, 14.0; **(1*Z*,3*E*)-4i and (1*Z*,3*E*)-4i** IR (neat) 2958, 2931, 2861, 1739, 1636, 1372, 1306, 1240, 1145 cm^{-1}; **(1*Z*,3*E*)-4i and (1*Z*,3*E*)-4i** HRMS-CI *m*/*z* 228.1884 [(M)$^{+}$; calcd for $C_{17}H_{24}$: 228.1878].



2j **3j** (1*Z*,3*E*)–**4j** (1*E*,3*E*)–**4j**

Dimethyl (*E*)-2-(2-cyclohexyl-1-phenylhept-2-en-1-yl)malonate (2j, major of 2j+3j), dimethyl (*E*)-2-(2-cyclohexyl-1-phenylhept-1-en-3-yl)malonate (3j, minor), (1*Z*,3*E*)-2-cyclohexylhepta-1,3-dien-1-yl)benzene ((1*Z*,3*E*)-4j, major of 4j) and (1*E*,3*E*)-2-cyclohexylhepta-1,3-dien-1-yl)benzene ((1*E*,3*E*)-4j, minor of 4j)

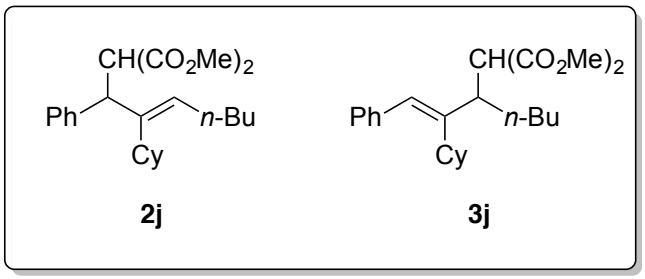
The reaction was performed following General Procedure D with **1j** (31.4 mg, 0.1 mmol) in the presence of 5 mol % of $[Pd(allyl)Cl]_2$ and 20 mol% of PPh_3 of the stock solution and 3 equiv of $NaCH(CO_2Me)_2$ stock solution. The reaction mixture was stirred at 40 °C for 24 h. The ratio of regioisomers was **2j:3j =** 84:16 and **(1*Z*,3*E*)-4j**:**(1*E*,3*E*)-4j** = 85:15 determined by ^{1}H NMR spectra of unpurified reaction products. The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc = 95:5) to afford the mixture of dimethyl malonate substituted products as a colorless oil (23.6 mg, 61% yield) and the mixture of 1,4-elimination products as a colorless oil (5.6 mg, 22% yield).

The title compound can also be made in the presence of 10 mol % of $Pd(OAc)_2$ instead of 5 mol % of $[Pd(allyl)Cl]_2$ at 40 °C for 24 h to afford the mixture of products **2j** and **3j** (86:14, 26.3 mg, 68% yield).

The title compound can also be made at 70 °C to afford the mixture of products **2j** and **3j** (5.8 mg, 15% yield) and 1,4-elimination products **((1*Z*,3*E*)-4j : (1*E*,3*E*)-4j** (86:14, 17.8 mg, 70% yield).

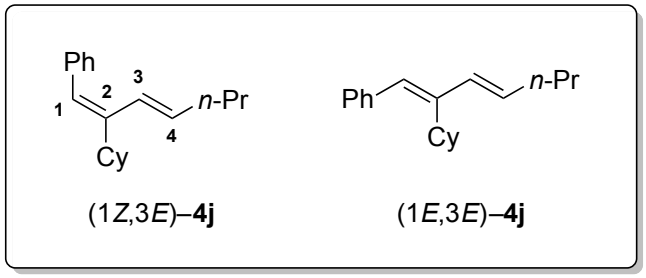
Allylic acetate **1k** (31.4 mg, 0.1 mmol) did not afford allylic substitution products in the presence of 5 mol % of $[Pd(allyl)Cl]_2$ and 20 mol% of PPh_3 of the stock solution and 3 equiv of $NaCH(CO_2Me)_2$ stock solution The reaction mixture was stirred at 40 °C for 24 h.

The title compound can also be made from **1l** instead of **1j** at 40 °C to afford the mixture of products **2j** and **3j** (83:17, 1.9 mg, 5% yield).



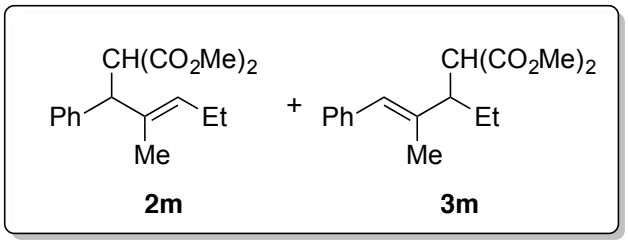
Dimethyl (*E*)-2-(2-cyclohexyl-1-phenylhept-2-en-1-yl)malonate (2j). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.06 (m 5H), 5.36 (t, *J* = 6.0 Hz, 1H), 4.18 (d, *J* = 12.5 Hz, 1H), 3.92 (d, *J* = 12.5 Hz, 1H), 3.69 (s, 3H), 3.41 (s, 3H), 2.36 (tt, *J* = 12.0 Hz, 3.5 Hz, 1H), 2.15 – 2.05 (m, 2H), 1.80 – 1.10 (m, 14H), 0.92 (t, *J* = 7.0 Hz, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 168.9, 168.4, 143.3, 141.0,

128.9, 128.3, 127.0, 125.7, 58.8, 52.6, 52.5, 48.0, 41.7, 32.5, 31.8, 31.6, 27.4, 27.2, 27.0, 26.3, 22.6, 14.3; **Dimethyl (*E*)-2-(2-cyclohexyl-1-phenylhept-1-en-3-yl)malonate (3j).** While the resonances in the ^{1}H spectrum for the major regioisomer overlap with most of those for the minor regioisomer, some of the resolved resonances for the minor regioisomer are ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.06 (m 5H), 6.28 (s, 1H), 3.10 (dt, *J* = 8.0 Hz, 4.5 Hz, 1H), 2.67 (tt, *J* = 12.0 Hz, 3.0 Hz, 1H); **2j + 3j** IR (neat) 2928, 2853, 1763, 1743, 1494, 1450, 1434, 1277, 1246, 1194, 1139, 1030 cm^{-1}; **2j + 3j** HRMS *m/z* 409.2375 [(M+Na)$^+$; calcd for $C_{24}H_{34}O_4Na$: 409.2355].



(1*Z*,3*E*)–**4j** (1*E*,3*E*)–**4j**

(1*Z*,3*E*)-2-Cyclohexylhepta-1,3-dien-1-yl)benzene ((1*Z*,3*E*)-4j): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.27 – 7.23 (m, 2H), 7.21 – 7.16 (m, 1H), 6.42 (d, *J* = 15.5 Hz, 1H), 6.30 (s, 1H), 5.72 (dt, *J* = 15.5 Hz, 7.0 Hz, 1H), 2.38 (tt, *J* = 11.5 Hz, 3.0 Hz, 1H), 2.12– 2.05 (m, 2H), 1.93 – 1.86 (m, 2H), 1.86 – 1.78 (m, 2H), 1.70 – 1.15 (m, 8H), 0.90 (t, *J* = 7.0 Hz, 3H) ; ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 144.6, 138.7, 131.1, 129.7, 128.1, 128.0, 126.2, 124.4, 41.3, 35.6, 33.6 (two overlapping resonances), 27.4 (two overlapping resonances), 26.8, 22.9, 14.0; **(1*E*,3*E*)-2-Cyclohexylhepta-1,3-dien-1-yl)benzene ((1*E*,3*E*)-4j):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.4 – 7.15 (m, 5H), 6.49 (s, 1H), 5.94 (dt, *J* = 15.5 Hz, 7.0 Hz, 1H) 2.74 (tt, *J* = 12.0 Hz, 3.5 Hz, 1H), 2.16 – 2.05 (m, 2H), 1.78 – 1.70 (m, 2H), 1.70 – 1.11 (m, 10H), 0.94 (t, *J* = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 146.2, 138.6, 131.6, 130.4, 129.1, 128.3, 126.3, 123.9, 39.4, 35.5, 33.6, 31.9, 27.4, 26.6, 26.4, 22.9, 14.0. **(1*Z*,3*E*)-4j+(1*E*,3*E*)-4j** IR (neat) 3022, 2956, 2927, 2853, 1599, 1493, 1448, 1378, 1073, 962 cm^{-1}; **(1*Z*,3*E*)-4j+(1*E*,3*E*)-4j** HRMS-CI *m/z* 254.2012 [(M)$^+$; calcd for $C_{19}H_{26}$: 254.2035].



Dimethyl (*E*)-2-(2-methyl-1-phenylpent-2-en-1-yl)malonate (2m, major) and dimethyl (*E*)-2-(2-methyl-1-phenylpent-1-en-3-yl)malonate (3m, minor): The reaction was performed following General Procedure D with **1m** (21.8 mg, 0.1 mmol) in the presence of 10 mol % of $Pd(OAc)_2$ and 20 mol% of PPh_3 of the stock solution and 3 equiv of $NaCH(CO_2Me)_2$ stock solution. The reaction mixture was stirred at 40 °C for 4 h. The ratio of regioisomers was **2m:3m =** 53:47 determined by ^1H NMR spectra of unpurified reaction products. The crude product was purified by flash column chromatography on silica gel (hexanes:EtOAc = 95:5) to afford the mixture of dimethyl malonate substituted products (**2m**+**3m**) as a colorless oil (26.1 mg, 90% yield). **Dimethyl (*E*)-2-(2-methyl-1-phenylpent-2-en-1-yl)malonate (2m).** ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.17 (m, 5H), 5.43 (t, J = 7.0 Hz, 1H), 4.11 (d, J_{AB} = 12.5 Hz, 1H), 4.00 (d, J_{AB} = 12.5 Hz, 1H), 3.71 (s, 3H), 3.47 (s, 3H), 2.00 (dt, J = 7.5 Hz, 7.0 Hz, 2H), 1.48 (s, 3H), 0.94 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 168.7, 168.5, 140.1, 134.4, 128.5, 128.2, 128.1, 127.1, 55.8, 54.0, 52.5 (two overlapping resonances), 21.4, 14.8, 14.3; **Dimethyl (*E*)-2-(2-methyl-1-phenylpent-1-en-3-yl)malonate (3m).** ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 2H), 7.23 – 7.13 (m, 3H), 6.39 (s, 1H), 3.76 (s, 3H), 3.64 (s, 3H), 3.55 (d, J = 11.0 Hz, 1H), 2.88 (ddd, J = 11.0, 11.0, 3.5 Hz, 1H), 1.77 (s, 3H), 1.60 – 1.51 (m, 1H), 1.50 – 1.39 (m, 1H), 0.88 (t, J = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 169.1, 168.7, 138.0, 136.4, 129.7, 129.1, 128.3, 126.5, 56.6, 52.74, 52.61, 51.5, 23.9, 14.0, 11.9; **2m**+**3m** IR (neat) 3027, 2958, 2934, 2874, 1760, 1739, 1600, 1494, 1453, 1435, 1319, 1261, 1241, 1193, 1161, 1144, 1031 cm^{-1}; **2m**+**3m** HRMS *m/z* 291.1595 [$(M+H)^+$; calcd for $C_{17}H_{23}O_4$: 291.1596].

The title compound can also be made in the presence of 5 mol % of $Pd(OAc)_2$ instead of 5 mol % of $[Pd(allyl)Cl]_2$ at 40 °C for 24 h to afford the mixture of products **2m** and **3m** (53:47, 13.4 mg, 56% yield).

4. Computational Studies

All structures have been optimized in solvent using Jaguar v. 7.9[7] at the B3LYP-D3/lacvp* level. B3LYP-D3 uses the hybrid B3LYP functional[8-10] augmented with dispersion corrections developed by Grimme and coworkers,[11] as implemented in Jaguar.[7] The lacvp* basis set combines 6-31G* for light elements with the Hay-Wadt ECP and basis set for Pd.[12] Continuum solvation used the PBF model[13,14] with parameters for THF.

Conformational preferences were checked for the η^3-(1-phenyl-3-ethyl-allyl)Pd(PPh_3)$_2$ moiety, with different 2-substituents (H, Me, or B(pin)). In this famework, the ethyl group has two low energy conformations (open or closed, only the former allowing nucleophilic attack at the 3-position).

The effect of the 2-BPin-substituent on nucleophilic attack was tested with the smaller η^3-(1-phenyl-3-methyl-allyl)Pd(PPh_3)$_2$ moiety, using NH_3 as a model nucleophile. The effect of continuum solvation on this transition state is significant.[†] Previous experience with very similar systems have shown that the barrier is very soft, with only a few kJ/mol variation over a range of more than 0.2 Å in the forming C–N bond. The low curvature makes transition state searches unreliable, especially with continuum solvent, but on the other hand, relaxed scans (constraining forming C–N bond, 2.0-2.5 Å in steps of 0.1 Å, full optimization of all remaining coordinates) gives reproducible structures with no hysteresis. For all calculated scans, the highest energy was found for a C–N distance of 2.2 Å; these are the structures reported herein.

Conformations:

2-unsubstituted, closed conformation

File: PhHEtAllylPd_PPh3_2_closed_thf.out
Solution phase energy: DFT(b3lyp-d3) -2626.22685903356 au

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P2	-0.7342942743	0.6718064781	-1.9161890484
P3	-0.6546857447	0.6584036515	1.8162833748
C4	-2.5326673803	3.9579073916	0.1263943049
C5	-2.9890546401	3.3026693605	1.2814574370
C6	-2.7835447266	3.4618333609	-1.1727219691
H7	-3.8245538956	2.6099767162	1.1649490915
H8	-3.6803765545	2.8550272460	-1.3244535371
C10	-3.8549397339	-0.2312724800	5.0712178708
C11	-2.5752705044	0.1671060374	5.4671300969
C12	-1.5999601285	0.4703816496	4.5136381398

C13	-1.8973337778	0.3865738531	3.1462059990
C14	-3.1927472504	0.0058456919	2.7549995052
C15	-4.1617456155	-0.3109098498	3.7090485764
H16	-4.6091341934	-0.4711490346	5.8171901045
H17	-2.3314101141	0.2457133711	6.5245420097
H18	-0.6148233423	0.7822697529	4.8457003304
H19	-3.4524801408	-0.0367464080	1.6987177729
H20	-5.1571999367	-0.6098245708	3.3873732225
C21	2.9244413109	2.9861208858	3.6371085865
C22	2.6810191050	1.6675979425	4.0352280079
C23	1.6092797819	0.9583670287	3.4932703709
C24	0.7593979156	1.5657216920	2.5516532504
C25	1.0178745150	2.8846924182	2.1537785291
C26	2.0935339433	3.5927283093	2.6926592884
H27	3.7649165437	3.5346644880	4.0570934202
H28	3.3313305716	1.1868844251	4.7629412029
H29	1.4459906440	-0.0737135956	3.7920414018
H30	0.3795126067	3.3551677112	1.4114879409
H31	2.2842357302	4.6145810407	2.3714257323
C32	1.1366368912	-3.5784626478	1.1098393306
C33	-0.1091635160	-3.4502374732	1.7268820407
C34	-0.6514959392	-2.1855770091	1.9611414609
C35	0.0479794850	-1.0301337153	1.5790745302
C36	1.3061978634	-1.1670015147	0.9698229023
C37	1.8428832813	-2.4325627564	0.7357487904
H38	1.5577218501	-4.5647577472	0.9264521892
H39	-0.6628723366	-4.3359482742	2.0309562765
H40	-1.6188199798	-2.1082318605	2.4475632060
H41	1.8755820553	-0.2886652937	0.6833705391
H42	2.8167897974	-2.5194170842	0.2600564478
C43	-2.2290231320	-3.7176452279	-2.2683348734
C44	-1.5022769103	-3.1394869351	-3.3153070125
C45	-1.0587638876	-1.8207499745	-3.2189335332
C46	-1.3235530665	-1.0625248793	-2.0621577943
C47	-2.0681751791	-1.6450083428	-1.0284456819
C48	-2.5160708885	-2.9644207852	-1.1287600978
H49	-2.5763199524	-4.7453816849	-2.3473146441
H50	-1.2870185773	-3.7138159247	-4.2138443825
H51	-0.5221309231	-1.3777267862	-4.0540879407
H52	-2.3001200097	-1.0666836293	-0.1408891727
H53	-3.0888244494	-3.4017522244	-0.3143377263
C54	3.9041112141	0.6977810022	-1.5576091495
C55	3.2735204598	-0.4055451261	-2.1411877564

C56	1.8833193039	-0.4403807649	-2.2699578151
C57	1.1031671153	0.6333780879	-1.8142700115
C58	1.7450642075	1.7440164041	-1.2401280437
C59	3.1350303353	1.7764936055	-1.1115790339
H60	4.9861159813	0.7147534770	-1.4484722434
H61	3.8645364185	-1.2498861721	-2.4896469363
H62	1.4160627440	-1.3202892099	-2.6994517278
H63	1.1560880103	2.5801803858	-0.8711235308
H64	3.6133307039	2.6382353165	-0.6521316986
C65	-1.7486111818	2.4567805333	-6.0870770701
C66	-0.4810830045	2.6653047093	-5.5383587469
C67	-0.1456597382	2.1062348100	-4.3012134308
C68	-1.0802191700	1.3315062100	-3.5998845993
C69	-2.3540317466	1.1220815303	-4.1578769841
C70	-2.6834730712	1.6791570300	-5.3934706328
H71	-2.0077558585	2.8941706308	-7.0485025863
H72	0.2537676150	3.2641728318	-6.0722343855
H73	0.8449499410	2.2781160753	-3.8894306112
H74	-3.0915034346	0.5218461187	-3.6296752217
H75	-3.6721858895	1.5077423817	-5.8138011410
C76	-2.3774007598	4.5701462304	5.3287068793
C77	-3.3947438789	3.6705434844	5.0040504448
C78	-3.5705956183	3.2624387933	3.6832966797
C79	-2.7364255095	3.7458850796	2.6583030758
C80	-1.7217622654	4.6630228042	2.9993370365
C81	-1.5437237895	5.0658212348	4.3193087453
H82	-2.2315560801	4.8838284130	6.3601109073
H83	-4.0476851810	3.2787150364	5.7799335548
H84	-4.3557852105	2.5520712865	3.4401158625
H85	-1.0616464867	5.0639038867	2.2354063162
H86	-0.7500579625	5.7675762618	4.5651456211
H87	-1.8361600622	4.7912810857	0.2260120075
C88	-2.2950982535	4.2404958939	-2.3696262864
H89	-2.2714005070	3.6001645285	-3.2510098189
H90	-1.2690225060	4.5896859552	-2.1952719439
C91	-3.2131023446	5.4476943199	-2.6464619223
H92	-3.2258956659	6.1391934112	-1.7951663488
H93	-2.8654758998	5.9971789473	-3.5289932091
H94	-4.2441671042	5.1226789234	-2.8322613929

2-unsubstituted, open conformation

File: PhHEtAllylPd_PPh3_2_thf.out

Solution phase energy: DFT(b3lyp-d3) -2626.22475144541 au

Pd1	-1.6231432005	1.9116258053	-0.0499103079
P2	-0.7448599131	0.6996557582	-1.9170706750
P3	-0.6236172236	0.6907653490	1.8017253615
C4	-2.6162174916	3.9470450996	0.1453899296
C5	-3.0553548750	3.2422941532	1.2788667159
C6	-2.8483017472	3.4697137650	-1.1626129085
H7	-3.8681904051	2.5269174433	1.1389060967
H8	-3.7186243250	2.8263931344	-1.3130444171
C10	-3.7084141726	-0.2686845325	5.1373577624
C11	-2.4359703076	0.1794380305	5.4995654266
C12	-1.4989027926	0.5151698750	4.5198726627
C13	-1.8301746683	0.4141164396	3.1619807931
C14	-3.1229646988	-0.0066221245	2.8053696018
C15	-4.0526097920	-0.3576051446	3.7853080853
H16	-4.4324293583	-0.5363010697	5.9039570069
H17	-2.1679346811	0.2696084101	6.5501998218
H18	-0.5167004909	0.8622540666	4.8239308982
H19	-3.4102851368	-0.0578967301	1.7567446950
H20	-5.0464266588	-0.6902921821	3.4927579197
C21	2.9609176745	3.0620184070	3.5575413008
C22	2.7417171416	1.7399499930	3.9576724414
C23	1.6694761802	1.0175418572	3.4340424080
C24	0.7946160444	1.6146558119	2.5090001809
C25	1.0294834275	2.9373545139	2.1082798500
C26	2.1050410011	3.6591709981	2.6290565770
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H28	3.4106716198	1.2666774543	4.6733002024
H29	1.5238400934	-0.0162439132	3.7357923623
H30	0.3715967794	3.4000188073	1.3779587780
H31	2.2768046523	4.6841394910	2.3071726225
C32	1.1687561139	-3.5603470519	1.1395616045
C33	-0.0909074929	-3.4230693575	1.7255492557
C34	-0.6311689209	-2.1547041058	1.9429122369
C35	0.0815103327	-1.0023608664	1.5732788775
C36	1.3525644099	-1.1498281980	0.9937649317
C37	1.8885083638	-2.4192226444	0.7785083864
H38	1.5896242686	-4.5494777730	0.9715449122
H39	-0.6565738968	-4.3043473762	2.0206715030
H40	-1.6079354936	-2.0723086876	2.4083055965
H41	1.9355180113	-0.2771888984	0.7195575087
H42	2.8736182876	-2.5122437567	0.3279493819
C43	-2.3408539235	-3.6515352809	-2.2206143241
C44	-1.6174256987	-3.0996403028	-3.2833256115

C45	-1.1445117650	-1.7902706331	-3.2041954745
C46	-1.3779695210	-1.0182920654	-2.0502184855
C47	-2.1186128215	-1.5761020468	-1.0000891368
C48	-2.5954227006	-2.8856384642	-1.0823340477
H49	-2.7109046211	-4.6726086083	-2.2857766072
H50	-1.4272847242	-3.6870755920	-4.1790409487
H51	-0.6087481538	-1.3657581309	-4.0492123658
H52	-2.3232934416	-0.9857742011	-0.1139330104
H53	-3.1646645371	-3.3060138695	-0.2564887842
C54	3.8849806051	0.5726067562	-1.5557272398
C55	3.2197741523	-0.5033152076	-2.1510383518
C56	1.8297431071	-0.4905948802	-2.2778344002
C57	1.0872725372	0.6027084372	-1.8073380211
C58	1.7638624253	1.6826578066	-1.2172397013
C59	3.1538903021	1.6695077880	-1.0919100153
H60	4.9672813346	0.5525395402	-1.4479681608
H61	3.7833514622	-1.3622812658	-2.5092755450
H62	1.3325781393	-1.3490237131	-2.7174773192
H63	1.2011177681	2.5268535372	-0.8290160773
H64	3.6614203181	2.5070617891	-0.6195343914
C65	-1.6256807684	2.4701331284	-6.1262340270
C66	-0.3831827916	2.6924059277	-5.5275959173
C67	-0.0921317339	2.1383792208	-4.2775852018
C68	-1.0463543571	1.3569481594	-3.6106788659
C69	-2.2950474346	1.1341445878	-4.2187333108
C70	-2.5794902207	1.6842920075	-5.4690031819
H71	-1.8492174052	2.9017746621	-7.0991029938
H72	0.3676075178	3.2954468638	-6.0336867648
H73	0.8812952700	2.3175186727	-3.8299639914
H74	-3.0471873967	0.5272022404	-3.7199314816
H75	-3.5479805144	1.5000289371	-5.9290292613
C76	-2.5446627453	4.4635569169	5.3541677736
C77	-3.5698610653	3.5878705432	4.9899599838
C78	-3.7116942480	3.1933437494	3.6610360384
C79	-2.8354486826	3.6670409346	2.6676832468
C80	-1.8129436283	4.5587853097	3.0478573626
C81	-1.6683238772	4.9484234940	4.3763106452
H82	-2.4252749686	4.7659169322	6.3923612155
H83	-4.2553426422	3.2045640882	5.7416974503
H84	-4.5052460581	2.5039732482	3.3861957822
H85	-1.1177173151	4.9460794644	2.3090182216
H86	-0.8671421752	5.6299223867	4.6532533438
H87	-1.9580987420	4.8021344895	0.2839962767

C88	-2.3827265507	4.2232439964	-2.3863599654
H89	-3.1402610661	4.9941964043	-2.6028362390
H90	-2.4005529751	3.5477305104	-3.2436695344
C91	-1.0013080812	4.8767385933	-2.2763001067
H92	-0.2387103391	4.1262283503	-2.0368815736
H93	-0.7251696539	5.3428637938	-3.2278026204
H94	-0.9673812991	5.6554556195	-1.5050724305

2-Me, closed conformation

File: PhMeEtAllylPd_PPh3_2_thf.out

Solution phase energy: DFT(b3lyp-d3) -2665.53443513825 au

Pd	-1.4997062694	1.9600324884	-0.0418714055
P4	-0.6923925964	0.6638434564	-1.9000521490
P7	-0.5730207476	0.7425144099	1.8400379157
C10	-2.4016126254	4.0986385198	0.1511302348
C11	-2.9236267765	3.3072257914	1.2015145023
C12	-2.5612821322	3.5773831707	-1.1679815004
H15	-3.7346811496	2.6320292770	0.9174863725
H16	-3.4502835160	2.9688125023	-1.3562781281
C18	-3.8055103134	-0.1557954714	5.0590639717
C19	-2.5477376146	0.2921155411	5.4707822574
C20	-1.5620096462	0.6043242290	4.5308979215
C21	-1.8281652590	0.4820759690	3.1606514140
C22	-3.1065828997	0.0623987223	2.7530864868
C23	-4.0833519183	-0.2673082953	3.6935448066
H24	-4.5661280360	-0.4053698358	5.7954310045
H25	-2.3274207349	0.4007154245	6.5307000988
H26	-0.5944489292	0.9533884486	4.8764933161
H27	-3.3485624593	0.0007032601	1.6940237245
H28	-5.0638728953	-0.5983399651	3.3576503900
C28	3.0615679948	3.0936219128	3.5407886102
C29	2.7467770861	1.8315802322	4.0567611036
C30	1.6545990573	1.1198955838	3.5578625564
C31	0.8491095540	1.6694994737	2.5447454255
C32	1.1853021767	2.9269529631	2.0205457753
C33	2.2818409421	3.6368174133	2.5158353556
H34	3.9174722880	3.6431265165	3.9264165150
H35	3.3589840064	1.3939745275	4.8424750663
H36	1.4437219132	0.1264743060	3.9454591495
H37	0.5927864509	3.3453304382	1.2116555886
H38	2.5300681200	4.6097980829	2.0968914881
C38	1.2513347013	-3.4875504420	1.1704329594
C39	0.0288449848	-3.3625086429	1.8331000374

C40	-0.5206699043	-2.0999737878	2.0643734048
C41	0.1470378738	-0.9439025700	1.6316998831
C42	1.3841921606	-1.0772701878	0.9798465024
C43	1.9288063302	-2.3402449832	0.7497024879
H44	1.6764799279	-4.4721555077	0.9866166204
H45	-0.5020461186	-4.2490193134	2.1736578195
H46	-1.4712922980	-2.0248758033	2.5827672383
H47	1.9296638555	-0.1976652790	0.6532283429
H48	2.8843267609	-2.4245981804	0.2377642419
C48	-2.3790508500	-3.6690569388	-2.0600681126
C49	-1.6911979253	-3.1425831912	-3.1593799059
C50	-1.1866426080	-1.8429581508	-3.1157404070
C51	-1.3493312152	-1.0530450984	-1.9614592249
C52	-2.0548715557	-1.5833637819	-0.8741208600
C53	-2.5641161082	-2.8835624438	-0.9211652192
H54	-2.7762808594	-4.6810446091	-2.0981418817
H55	-1.5553734119	-3.7414538546	-4.0573889635
H56	-0.6817991741	-1.4385661502	-3.9893346614
H57	-2.2102545935	-0.9798812099	0.0102632437
H58	-3.1060438794	-3.2806170733	-0.0660032678
C58	3.9537411449	0.5280613701	-1.8284442193
C59	3.2492079869	-0.5737056196	-2.3216046959
C60	1.8533775398	-0.5604479220	-2.3606336653
C61	1.1427858648	0.5598103920	-1.9047481067
C62	1.8572654091	1.6671274087	-1.4195557729
C63	3.2530690949	1.6526202901	-1.3820134127
H64	5.0406175748	0.5097019112	-1.7907476647
H65	3.7865693567	-1.4528566721	-2.6707390039
H66	1.3280416251	-1.4375282625	-2.7233765494
H67	1.3201406112	2.5382465331	-1.0526318107
H68	3.7916606085	2.5143216918	-0.9951182792
C68	-1.9100574968	2.3290031867	-6.0660418950
C69	-0.5733113551	2.3959474614	-5.6664037349
C70	-0.1754384099	1.8660304004	-4.4335162127
C71	-1.1170992343	1.2633771017	-3.5874863240
C72	-2.4598888842	1.1882940442	-4.0007016484
C73	-2.8520104205	1.7159798865	-5.2304475434
H74	-2.2174714447	2.7470622289	-7.0219920286
H75	0.1670444628	2.8631009157	-6.3126273948
H76	0.8673803175	1.9311030368	-4.1361464647
H77	-3.2032114757	0.7200495371	-3.3585911042
H78	-3.8943841887	1.6529180370	-5.5355362353
C78	-2.9852359346	4.0897309581	5.4218103812

C79	-4.0832864375	3.5223977662	4.7705316490
C80	-4.0294413209	3.2669037393	3.4021922390
C81	-2.8836920373	3.5853748240	2.6479777347
C82	-1.7813468081	4.1428687387	3.3222218885
C83	-1.8326818079	4.3925545328	4.6919107870
H84	-3.0217628878	4.2808642076	6.4921962686
H85	-4.9793310400	3.2667037077	5.3314023390
H86	-4.8854547796	2.8143704846	2.9063854982
H87	-0.8634596730	4.3489925270	2.7879362409
H88	-0.9638690871	4.8143748839	5.1924727817
C88	-1.5932092279	5.3579058366	0.3911821928
H89	-1.8117250825	6.1041331077	-0.3780051278
H90	-1.8353938822	5.7938416765	1.3622169191
H91	-0.5129545392	5.1743269316	0.3628914682
C91	-2.0172382690	4.2969932254	-2.3777461959
H92	-1.8094449709	3.5765839029	-3.1676694631
H94	-1.0645477295	4.7839769105	-2.1405183363
C94	-3.0240554314	5.3303678763	-2.9195882504
H95	-3.2699617960	6.0919350977	-2.1701760173
H96	-2.6121732209	5.8377407820	-3.7994467611
H97	-3.9582339586	4.8389104193	-3.2178736445

2-Me, open conformation

File: PhMeEtAllylPd_PPh3_2_open_thf.out

Solution phase energy: DFT(b3lyp-d3) -2665.53015714998 au

Pd	-1.5035577969	1.9887941957	-0.0318753647
P4	-0.6811512516	0.7099171865	-1.8911191712
P7	-0.5610573592	0.7443763819	1.8260611991
C10	-2.4961922750	4.1044607263	0.1835700488
C11	-2.9561592062	3.2790617924	1.2381073560
C12	-2.6458757827	3.5742302274	-1.1330886952
H15	-3.7346373248	2.5601411113	0.9704393836
H16	-3.5062265215	2.9162944411	-1.2834061564
C18	-3.7253005790	-0.1632410565	5.0987467015
C19	-2.4643968820	0.2939323367	5.4873636378
C20	-1.5014193711	0.6149382769	4.5280940281
C21	-1.7966717895	0.4924784385	3.1639991865
C22	-3.0812945045	0.0696075707	2.7805248048
C23	-4.0346103989	-0.2700771604	3.7402406100
H24	-4.4684854552	-0.4208923579	5.8501334521
H25	-2.2241716427	0.4015167981	6.5430026564
H26	-0.5280622518	0.9679902452	4.8525777937
H27	-3.3442801519	0.0092770304	1.7263441358

H28	-5.0208031625	-0.6053497611	3.4262470284
C28	3.1180110372	2.9895463786	3.5558020852
C29	2.8061128632	1.7069066069	4.0180471627
C30	1.6997541453	1.0272654790	3.5079298219
C31	0.8807436824	1.6299615858	2.5368066499
C32	1.2117842354	2.9105258521	2.0705062584
C33	2.3214718052	3.5894822573	2.5775364720
H34	3.9859505560	3.5139228650	3.9499459697
H35	3.4305706115	1.2295234083	4.7701826645
H36	1.4859732350	0.0193815609	3.8538886408
H37	0.6035302626	3.3731732996	1.2970987051
H38	2.5672938645	4.5814819947	2.2046622331
C38	1.1580474663	-3.5317108290	1.1403844874
C39	-0.0692381231	-3.3770052807	1.7868841443
C40	-0.5869983817	-2.1014876102	2.0176173983
C41	0.1166664869	-0.9602567384	1.6013619343
C42	1.3590467141	-1.1244690449	0.9666237264
C43	1.8718557441	-2.4007483066	0.7363906955
H44	1.5591840874	-4.5264019029	0.9574595373
H45	-0.6286536508	-4.2501417140	2.1159257188
H46	-1.5414094371	-2.0042787854	2.5242896298
H47	1.9358714583	-0.2590508457	0.6579372918
H48	2.8327416830	-2.5077574732	0.2390834892
C48	-2.4341271462	-3.5928932242	-2.0918044226
C49	-1.6973587403	-3.0861037854	-3.1676262112
C50	-1.1705059625	-1.7967019300	-3.1109286376
C51	-1.3577934044	-0.9996101477	-1.9652359071
C52	-2.1127736890	-1.5118023387	-0.9032350328
C53	-2.6458498779	-2.8008981002	-0.9630441690
H54	-2.8492999658	-4.5973146295	-2.1406041835
H55	-1.5421794980	-3.6918140118	-4.0578976136
H56	-0.6315156807	-1.4051745000	-3.9695697686
H57	-2.2892360332	-0.9012443770	-0.0258719380
H58	-3.2267259092	-3.1833305947	-0.1269485772
C58	3.9639026670	0.5013761908	-1.7129335829
C59	3.2546365634	-0.5641023565	-2.2762354166
C60	1.8606082292	-0.5259137068	-2.3494012233
C61	1.1544001049	0.5829339988	-1.8574511245
C62	1.8749729778	1.6521216949	-1.2998999142
C63	3.2690613331	1.6133975733	-1.2285887300
H64	5.0489590261	0.4626650369	-1.6484453323
H65	3.7868961468	-1.4348772436	-2.6533389611
H66	1.3330595194	-1.3770230240	-2.7669265810

H67	1.3440426814	2.5086836119	-0.8941771329
H68	3.8094571843	2.4449686306	-0.7826090550
C68	-1.7604639114	2.1765174736	-6.1657031926
C69	-0.4364057440	2.2591243569	-5.7309242746
C70	-0.0854368587	1.8163107689	-4.4518937709
C71	-1.0621321360	1.2900583963	-3.5971232381
C72	-2.3939513884	1.2076089543	-4.0405903559
C73	-2.7398004995	1.6458383793	-5.3177942293
H74	-2.0305034428	2.5207146610	-7.1616303391
H75	0.3301072282	2.6655764604	-6.3872233490
H76	0.9495970599	1.8811162200	-4.1286056264
H77	-3.1621319324	0.7921115312	-3.3912710848
H78	-3.7729256174	1.5744389564	-5.6513602812
C78	-2.9615494744	4.1199458409	5.4468607681
C79	-4.0564597919	3.5122293270	4.8271798285
C80	-4.0228196542	3.2350324657	3.4621713889
C81	-2.9013140455	3.5723821704	2.6812524356
C82	-1.8026290258	4.1728771263	3.3232667333
C83	-1.8324287531	4.4427780183	4.6895198633
H84	-2.9825178100	4.3286593220	6.5143109305
H85	-4.9342608533	3.2430749663	5.4100597465
H86	-4.8756849065	2.7522265046	2.9901120188
H87	-0.9053920416	4.4017409744	2.7632280866
H88	-0.9669744645	4.8982957299	5.1657934685
C88	-1.8058824177	5.4285710733	0.4338268134
H89	-2.0326921013	6.1292942387	-0.3754501259
H90	-2.1538687616	5.8672275999	1.3724471232
H91	-0.7162756743	5.3366041607	0.4946309623
C91	-2.1897355668	4.2930906604	-2.3876442201
H92	-2.7796221342	5.2209852916	-2.4738357074
H94	-2.4754473924	3.6816052275	-3.2465549625
C94	-0.6956978916	4.6318956110	-2.5056096789
H95	-0.0847098211	3.7345703312	-2.3738869068
H96	-0.4832200499	5.0317874086	-3.5031807971
H97	-0.3673363206	5.3736630460	-1.7731663561

2-BPin, closed conformation

File: PhBPinEtAllylPd_PPh3_2_thf.out

Solution phase energy: DFT(b3lyp-d3) -3036.90454032419 au

Pd	-1.7943875210	1.8869742809	0.0351496713
P4	-0.8645824671	0.9198457393	-1.9509848298
P7	-0.6951036224	0.6123859179	1.7927884480
C10	-2.7768856805	3.9047624723	0.3611256824

C11	-3.1508170664	3.1560877138	1.4976339511
C12	-3.1663532668	3.3898487717	-0.9105363460
H15	-3.9921529465	2.4688442848	1.3802904277
H16	-4.0515211596	2.7460052864	-0.9369583610
C18	-3.7236051048	-0.2321109253	5.2190280514
C19	-2.4533511725	0.2484724647	5.5434355471
C20	-1.5227031492	0.5301959246	4.5398304263
C21	-1.8563649806	0.3377427828	3.1927689823
C22	-3.1461616874	-0.1221015241	2.8712266398
C23	-4.0693867471	-0.4138631914	3.8760133471
H24	-4.4435456615	-0.4515611554	6.0040607921
H25	-2.1813762455	0.4136940657	6.5837005593
H26	-0.5474073440	0.9162710978	4.8166833713
H27	-3.4330030021	-0.2521730114	1.8286797482
H28	-5.0601503536	-0.7754096771	3.6083531364
C28	3.1667921369	2.6325496625	3.3881451228
C29	2.7789507077	1.3802641549	3.8764020889
C30	1.6129412649	0.7782692727	3.4062766390
C31	0.8066236635	1.4322553860	2.4567676572
C32	1.2090082724	2.6802634653	1.9629592311
C33	2.3840611142	3.2759049023	2.4282701883
H34	4.0828905631	3.0971840982	3.7472101383
H35	3.3916721015	0.8660424409	4.6138146387
H36	1.3391824334	-0.2098736030	3.7671930711
H37	0.6187663567	3.1872388518	1.2066842318
H38	2.6923483013	4.2394443192	2.0308820437
C38	1.0095680350	-3.6034155528	0.7843822660
C39	-0.1057860741	-3.5015861914	1.6180034172
C40	-0.6300130459	-2.2488492676	1.9516810955
C41	-0.0380125559	-1.0795203515	1.4540870808
C42	1.0964833073	-1.1887783308	0.6328968926
C43	1.6122251587	-2.4391997066	0.2972069753
H44	1.4108252000	-4.5795287303	0.5217946012
H45	-0.5755771542	-4.3997289172	2.0139529304
H46	-1.4991035119	-2.1946319992	2.6000697767
H47	1.5837669425	-0.2946067758	0.2572571259
H48	2.4883321040	-2.5039787323	-0.3441944389
C48	-1.5729745904	-3.6417255591	-2.4749324765
C49	-0.8611048486	-2.9296819585	-3.4470155098
C50	-0.6439489666	-1.5603071889	-3.2963546323
C51	-1.1161930026	-0.8869783320	-2.1540775252
C52	-1.8496308759	-1.6035596878	-1.1997376139
C53	-2.0745941644	-2.9730357395	-1.3569598740

H54	-1.7432280711	-4.7092268221	-2.5956750016
H55	-0.4838838111	-3.4393310424	-4.3310970970
H56	-0.1205994460	-1.0140803348	-4.0772110015
H57	-2.2434247088	-1.0913753342	-0.3280546424
H58	-2.6380290970	-3.5149280367	-0.6014216236
C58	3.6643809263	1.9969716958	-1.9199026997
C59	3.2789151749	0.7121195767	-2.3129412308
C60	1.9287022829	0.3529448054	-2.3354949293
C61	0.9433194795	1.2768787834	-1.9543551772
C62	1.3377966939	2.5656721120	-1.5510036257
C63	2.6876593116	2.9221967599	-1.5410679200
H64	4.7167602506	2.2712827021	-1.9023315346
H65	4.0313186765	-0.0184953762	-2.6024969739
H66	1.6561695866	-0.6557141643	-2.6281353500
H67	0.5936884826	3.2918248252	-1.2310585051
H68	2.9781733072	3.9221715013	-1.2260078947
C68	-2.4907220228	2.5260416943	-6.0058104353
C69	-1.2448999692	2.9605649414	-5.5486141589
C70	-0.7201082195	2.4693790399	-4.3487601754
C71	-1.4407885331	1.5350257872	-3.5925123396
C72	-2.6914131581	1.0945121942	-4.0618169100
C73	-3.2110104316	1.5861728503	-5.2589644691
H74	-2.8978727762	2.9118254878	-6.9376314434
H75	-0.6734658597	3.6842798626	-6.1261139552
H76	0.2501240724	2.8204718018	-4.0103002767
H77	-3.2628791884	0.3645919221	-3.4925594047
H78	-4.1798018089	1.2357571052	-5.6088382794
C78	-2.3992555198	4.2096576673	5.5825971075
C79	-3.5962142752	3.5955031750	5.2065053334
C80	-3.8115821686	3.2334027223	3.8776729844
C81	-2.8413633453	3.4964200912	2.8944719767
C82	-1.6366534051	4.1043204615	3.2900533569
C83	-1.4167943948	4.4564586093	4.6186444359
H84	-2.2266030807	4.4823733324	6.6214418793
H85	-4.3607521637	3.3883308605	5.9515974878
H86	-4.7416732382	2.7459579891	3.5942278387
H87	-0.8520193699	4.2687111653	2.5622243186
H88	-0.4718117865	4.9128947307	4.9051179429
C91	-2.8935534440	4.1417401614	-2.1908381548
H92	-3.0050510953	3.4676497359	-3.0397547281
H94	-1.8571190182	4.4973084003	-2.2070396692
C94	-3.8603168698	5.3297125744	-2.3664329675
H95	-3.7461511061	6.0568442082	-1.5557699017

H96	-3.6643203133	5.8388009698	-3.3176848113
H97	-4.9027383890	4.9885482541	-2.3736500855
C96	-1.1344862671	7.3308851306	0.6857559409
C97	0.0109346650	6.4756823393	0.0103993077
C107	0.1525052363	6.7107721565	-1.4966240834
H108	0.8267893642	5.9555182014	-1.9143542322
H109	-0.8109693272	6.6273128671	-2.0087445409
H110	0.5711757796	7.7004534351	-1.7050971634
C110	1.3724845568	6.5779076510	0.6916525898
H111	2.0944357579	5.9386059145	0.1715462517
H112	1.7441661839	7.6081285437	0.6533471850
H113	1.3279598063	6.2635115752	1.7371429806
C113	-1.4802094994	8.6250870629	-0.0459042388
H114	-0.6127369934	9.2950351770	-0.0620024201
H115	-1.7974497222	8.4404606841	-1.0749868642
H116	-2.2958036152	9.1362906799	0.4763752814
C116	-0.9021063723	7.6123720730	2.1730767215
H117	-0.0670006783	8.3058882876	2.3154757692
H118	-1.8050542240	8.0646726691	2.5955821589
H119	-0.6967052404	6.6943219060	2.7300918811
B112	-1.8284729690	5.1690216620	0.4059807679
O116	-2.2953304344	6.4321726286	0.6055408624
O114	-0.4810594901	5.0999026974	0.1677487841

2-BPin, open conformation

File: PhBPinEtAllylPd_PPh3_2_open_thf.out

Solution phase energy: DFT(b3lyp-d3) -3036.89704120554 au

Pd	-1.7190739392	1.9504235434	-0.0117907903
P4	-0.9196167430	0.8347346340	-1.9933738617
P7	-0.5758416348	0.7111396983	1.7381075310
C10	-2.7327482912	3.9573634019	0.2699441333
C11	-2.9968190163	3.1963340063	1.4431479203
C12	-3.2388414382	3.3902236699	-0.9289062293
H15	-3.8305370020	2.4944848348	1.3646130430
H16	-4.0644820436	2.6817468571	-0.8105813954
C18	-3.6036651965	-0.2489918925	5.1282713525
C19	-2.3403045763	0.2359241354	5.4707896801
C20	-1.4125639924	0.5598980208	4.4776655332
C21	-1.7439893987	0.4055041076	3.1251600066
C22	-3.0286786356	-0.0561440617	2.7877658468
C23	-3.9487592001	-0.3902711792	3.7810370697
H24	-4.3207720629	-0.5037348740	5.9055193975
H25	-2.0716171123	0.3695166683	6.5165041416

H26	-0.4412776167	0.9467542727	4.7673313702
H27	-3.3156310482	-0.1538813608	1.7423774776
H28	-4.9355412761	-0.7537974643	3.5021658781
C28	3.2708029101	2.6643643323	3.4498855956
C29	2.8675083744	1.3997655144	3.8892965268
C30	1.7069450409	0.8227679633	3.3778743221
C31	0.9206684303	1.5129894458	2.4358794789
C32	1.3383988897	2.7739406767	1.9905482877
C33	2.5089765262	3.3437204429	2.4983977138
H34	4.1816926818	3.1118532542	3.8420390475
H35	3.4620478170	0.8567097837	4.6208758624
H36	1.4202031820	-0.1748833604	3.7005617864
H37	0.7584444053	3.3142598287	1.2494337636
H38	2.8307969044	4.3195627020	2.1456470416
C38	1.2001428968	-3.4754458993	0.7621907953
C39	0.0572799350	-3.3915795804	1.5589588253
C40	-0.4931453664	-2.1472637653	1.8751820243
C41	0.0997191213	-0.9707844281	1.3958409705
C42	1.2635048320	-1.0618940635	0.6153371173
C43	1.8044954854	-2.3049485535	0.2948158485
H44	1.6230713881	-4.4460707806	0.5124434338
H45	-0.4121721764	-4.2966788884	1.9387427939
H46	-1.3823909959	-2.1041908323	2.4957130261
H47	1.7562041680	-0.1605234384	0.2657399727
H48	2.7019344356	-2.3571452816	-0.3174094799
C48	-1.9930379109	-3.6816723590	-2.2792078604
C49	-1.3252164256	-3.0545070825	-3.3372767886
C50	-1.0042238101	-1.6996014455	-3.2609919007
C51	-1.3294311939	-0.9531728084	-2.1124078916
C52	-2.0180116307	-1.5855398189	-1.0699461520
C53	-2.3460422897	-2.9411001105	-1.1504759779
H54	-2.2444483454	-4.7381430473	-2.3419798515
H55	-1.0616531352	-3.6193888332	-4.2290218290
H56	-0.5193860322	-1.2198825011	-4.1071548147
H57	-2.3003975072	-1.0175942966	-0.1903691351
H58	-2.8739456744	-3.4161787500	-0.3271640796
C58	3.6935239767	1.4227606919	-1.9680242171
C59	3.1670297085	0.2327341741	-2.4793945562
C60	1.7864261603	0.0281241765	-2.5120423466
C61	0.9131349311	1.0134193828	-2.0272818876
C62	1.4496177193	2.2098241181	-1.5213100068
C63	2.8305883227	2.4137384017	-1.4933916602
H64	4.7705241377	1.5735466576	-1.9345717752

H65	3.8335303458	-0.5442710862	-2.8479873674
H66	1.4036336295	-0.9146012447	-2.8871631550
H67	0.7888800966	2.9821147425	-1.1333528260
H68	3.2325717623	3.3393487243	-1.0877968876
C68	-2.3504822539	2.3631058117	-6.1546755313
C69	-1.1062255807	2.7633982567	-5.6617558474
C70	-0.6527370359	2.2988979671	-4.4231668843
C71	-1.4398664822	1.4228115690	-3.6623111953
C72	-2.6911440601	1.0214676357	-4.1652165002
C73	-3.1405737265	1.4862975430	-5.4019437506
H74	-2.7011774472	2.7269886233	-7.1177786916
H75	-0.4812503763	3.4399137696	-6.2411624314
H76	0.3184639985	2.6213807094	-4.0595888827
H77	-3.3154336748	0.3364229411	-3.5956637595
H78	-4.1095884794	1.1634858976	-5.7771366563
C78	-2.2903325707	4.2029010762	5.5572591355
C79	-3.4813965755	3.5971884642	5.1493883968
C80	-3.6736723269	3.2643736560	3.8095498227
C81	-2.6890761853	3.5473198187	2.8437442039
C82	-1.4925230023	4.1502889475	3.2703678171
C83	-1.2954045628	4.4713267353	4.6122275590
H84	-2.1328681370	4.4510936003	6.6047252360
H85	-4.2569104217	3.3700754399	5.8773186980
H86	-4.5973340588	2.7783905168	3.5032687324
H87	-0.7033030081	4.3425328128	2.5576309025
H88	-0.3550768030	4.9216225666	4.9231116565
C91	-3.1982601889	4.0031660754	-2.3043417488
H92	-4.1320941035	4.5786834721	-2.4202576975
H94	-3.2714910796	3.1939002439	-3.0340088217
C94	-2.0064294162	4.8972603291	-2.6436930564
H95	-1.0590677719	4.4112381614	-2.3879233571
H96	-1.9910053800	5.1148736301	-3.7160461464
H97	-2.0621869743	5.8517774363	-2.1136984177
C96	-1.3402742503	7.4574977833	0.7429277623
C97	-0.0118771116	6.6483040702	0.4337870392
C107	0.6012931478	6.9331882119	-0.9407721484
H108	1.4069929116	6.2141654922	-1.1242251981
H109	-0.1293382030	6.8336129441	-1.7460556090
H110	1.0258058002	7.9418547779	-0.9774510499
C110	1.0664847066	6.7771644872	1.5086334478
H111	1.9523943395	6.2076208685	1.2115192099
H112	1.3654313047	7.8251263911	1.6232400368
H113	0.7280665836	6.4050069784	2.4784530972

C113	-1.5240248947	8.7218850729	-0.0926249493
H114	-0.7198094428	9.4365362296	0.1171151193
H115	-1.5267568635	8.5064756825	-1.1641310639
H116	-2.4772824695	9.1967881257	0.1630870658
C116	-1.5472342992	7.7704103232	2.2288501283
H117	-0.8137217776	8.4999820894	2.5869460794
H118	-2.5486501959	8.1916219384	2.3661557144
H119	-1.4764738849	6.8672985492	2.8418410737
B112	-1.8425786114	5.2637558603	0.3321152001
O116	-2.3987587210	6.5064096541	0.3796768268
O114	-0.4770946269	5.2542528604	0.4103702767

Transition structures, attack at either 1- or 3-position, reacting position in either *syn*- or *anti*-configuration.

Attack at 1-*syn*

File: PhBPinMeAllyl_1NH3_Pd_PPh3_2_thfd.out; structure 57

Solution phase energy: DFT(b3lyp-d3) -3054.13003134393 au

Pd1	-1.6668674134	1.9425685649	-0.0614707163
P2	-0.9427600096	0.8041123667	-2.0356044706
P3	-0.5065414577	0.8049098696	1.7747014331
C4	-2.6993822694	3.9207708302	0.4621406167
C5	-3.5340749335	3.5668421230	1.5622218898
C6	-3.0541601777	3.4031222778	-0.8395409011
H7	-4.3436894252	2.8742298583	1.3412740720
H8	-3.9976239665	2.8482297366	-0.8815222031
C9	-3.7822985533	-0.3748408895	4.8582155657
C10	-2.5692147569	0.1270173775	5.3321334472
C11	-1.5680631238	0.5200802531	4.4411546853
C12	-1.7733837965	0.4233638085	3.0594086046
C13	-3.0092345922	-0.0581673582	2.5911798977
C14	-4.0034435460	-0.4622427496	3.4812907668
H15	-4.5562654143	-0.6850753856	5.5567389943
H16	-2.3978679375	0.2165565064	6.4021545226
H17	-0.6355327880	0.9121517826	4.8323952263
H18	-3.1940950718	-0.1161947418	1.5205408914
H19	-4.9497827675	-0.8405249469	3.0997519400
C20	2.9734181823	3.1005316734	3.8470664318
C21	2.6695297527	1.7927367515	4.2393441059
C22	1.6298714063	1.0999434814	3.6183849491
C23	0.8618212095	1.7106128746	2.6107180402
C24	1.1880799836	3.0133269969	2.2049797884
C25	2.2373646807	3.7012658004	2.8229501748
H26	3.7883860570	3.6396869697	4.3248515447
H27	3.2487395859	1.3068534636	5.0219864687
H28	1.4238434937	0.0731046136	3.9103970314
H29	0.6359892491	3.4860638853	1.3965671686
H30	2.4912931440	4.7072369285	2.4982949992
C31	1.5201235818	-3.3161802761	0.9494847434
C32	0.4170882311	-3.2583483456	1.8037081659
C33	-0.1938151312	-2.0335079995	2.0899584628
C34	0.2914367363	-0.8466510459	1.5210824300
C35	1.4132876751	-0.9116534832	0.6780578903
C36	2.0194769573	-2.1344392675	0.3932219334
H37	1.9883815576	-4.2710608836	0.7213337514

H38	0.0249521200	-4.1693044133	2.2518061264
H39	-1.0526009329	-2.0127710118	2.7538716231
H40	1.8150878692	-0.0046598264	0.2380929739
H41	2.8802222218	-2.1622470423	-0.2709341221
C42	-1.7305862065	-3.7743425829	-2.3693794010
C43	-1.3083505755	-3.0574077142	-3.4945551689
C44	-1.0812558590	-1.6832465962	-3.4084989560
C45	-1.2665212915	-1.0035271943	-2.1905134109
C46	-1.7065282590	-1.7279813065	-1.0754283337
C47	-1.9311653074	-3.1041335052	-1.1611913321
H48	-1.9075007989	-4.8455471401	-2.4385412606
H49	-1.1585078856	-3.5683577173	-4.4433598343
H50	-0.7686363495	-1.1380296501	-4.2952800554
H51	-1.8667752659	-1.2178727082	-0.1333300885
H52	-2.2613958242	-3.6498272174	-0.2805952767
C53	3.6784994390	1.4055905671	-2.0966197504
C54	3.1386364916	0.2272741378	-2.6206992478
C55	1.7555832612	0.0279509180	-2.6332685400
C56	0.8918447880	1.0058936419	-2.1170405410
C57	1.4403343830	2.1943603894	-1.6018749948
C58	2.8231716310	2.3909346039	-1.5937287469
H59	4.7562048695	1.5526571987	-2.0780885969
H60	3.7959206007	-0.5451398942	-3.0152702732
H61	1.3597645915	-0.9048025285	-3.0227697913
H62	0.7882465428	2.9632224793	-1.1909300203
H63	3.2333562779	3.3100255782	-1.1813675271
C64	-2.5172430471	2.3865848765	-6.1249549072
C65	-1.2094565460	2.6789157080	-5.7335514940
C66	-0.7082385547	2.1927220844	-4.5213781529
C67	-1.5134154106	1.4091932970	-3.6841245199
C68	-2.8298187211	1.1188230286	-4.0837541854
C69	-3.3256844229	1.6001495297	-5.2952021025
H70	-2.9045095739	2.7633880254	-7.0690788481
H71	-0.5702976967	3.2833901493	-6.3739631118
H72	0.3138124254	2.4243404011	-4.2366642516
H73	-3.4704120344	0.5099524496	-3.4488383705
H74	-4.3445341742	1.3614899307	-5.5927535507
C75	-2.6803319087	3.8212568259	5.7620627445
C76	-3.9317058957	3.3932522323	5.3056702122
C77	-4.1863593969	3.3066425439	3.9395205493
C78	-3.2021089922	3.6575548635	2.9964284731
C79	-1.9456820061	4.0637646519	3.4705254267
C80	-1.6859971194	4.1480145275	4.8360658130

H81	-2.4777965022	3.8820615847	6.8288063598
H82	-4.7067599555	3.1163674183	6.0164240377
H83	-5.1606313558	2.9683065348	3.5918233271
H84	-1.1493279277	4.2763588448	2.7721332213
H85	-0.6984684646	4.4513745983	5.1751519493
C86	-2.7416666710	4.1455375367	-2.1198901853
H87	-2.9376401553	3.5205004118	-2.9916860568
H88	-1.7030014878	4.4775599828	-2.1598370554
C89	-0.8033322546	7.1541346661	1.0820171649
C90	-0.0251247549	6.5315618099	-0.1364604708
C91	-0.4646413629	7.1019017436	-1.4901774876
H92	-0.0310882167	6.4938375721	-2.2907747576
H93	-1.5538505856	7.0808999137	-1.5982632253
H94	-0.1209956345	8.1340079037	-1.6155033866
C95	1.4951227540	6.5615576552	-0.0230905253
H96	1.9386544173	6.0832756872	-0.9029021038
H97	1.8572101494	7.5950531197	0.0223265627
H98	1.8468381861	6.0320978498	0.8641309107
C99	-1.2554026239	8.5979406078	0.8893509364
H100	-0.3894691716	9.2512798118	0.7307518899
H101	-1.9304800235	8.6982271170	0.0357614463
H102	-1.7826014055	8.9425880581	1.7856439243
C103	-0.0639584933	7.0024635430	2.4161004366
H104	0.7872420920	7.6892221899	2.4721412046
H105	-0.7524509928	7.2315755498	3.2357554472
H106	0.3071424526	5.9836361454	2.5609485677
B107	-1.6921188381	5.1160162457	0.5275500826
O108	-1.9940025797	6.3011947802	1.1502597695
O109	-0.4694491178	5.1356366176	-0.1021052183
H111	-3.3842692994	5.0366748317	-2.2032248689
N112	-4.9731346838	5.2307118925	1.5368363580
H113	-4.3470172490	6.0367551903	1.5534298931
H114	-5.6123617441	5.3062882204	2.3295649747
H115	-5.5262117191	5.2719118472	0.6792585306

Attack at 1-*anti*

File: antiPhBPinMeAllyl_1NH3_Pd_PPh3_2_thfd.out; structure 56
Solution phase energy: DFT(b3lyp-d3) -3054.13528376566 au

Pd1	-1.5418942482	2.0304725205	-0.1849394863
P2	-1.0370037992	0.6434752617	-2.0518588220
P3	-0.4535476220	1.1209180942	1.7989667191
C4	-2.6918485118	4.0209444020	0.0772363581

C5	-3.7758627344	3.4805694604	0.8505464312
C6	-2.5167733917	3.6419367398	-1.2987094208
H7	-3.6106730246	3.4348210242	1.9220151628
H8	-3.3404849908	3.1338756683	-1.7891884595
C9	-3.2525363019	1.1354696956	5.5204618303
C10	-2.1878357043	2.0376352315	5.4600763372
C11	-1.3111127860	2.0291954428	4.3703984646
C12	-1.4920650852	1.1215667597	3.3165775649
C13	-2.5768815317	0.2268129478	3.3793192262
C14	-3.4419126573	0.2258246688	4.4743159635
H15	-3.9270038047	1.1377303290	6.3735117087
H16	-2.0285037348	2.7479049183	6.2689989290
H17	-0.4833348037	2.7300533596	4.3505583689
H18	-2.7425447476	-0.4826065281	2.5710515688
H19	-4.2629459351	-0.4873106378	4.5112902309
C20	3.5862834462	3.2555094567	2.6178655630
C21	3.0811645649	2.3463519829	3.5556968071
C22	1.8444322567	1.7394835021	3.3434825497
C23	1.0800975803	2.0582590543	2.2059905783
C24	1.5847760941	2.9828705879	1.2806908550
C25	2.8400527679	3.5669541234	1.4801077009
H26	4.5614767701	3.7128245246	2.7732023475
H27	3.6612938163	2.0966319578	4.4421426957
H28	1.4789268140	1.0030246621	4.0559640573
H29	1.0003711049	3.2457891374	0.4032203322
H30	3.2329811186	4.2653250976	0.7444007304
C31	1.5700852527	-3.0661952942	1.5099991054
C32	0.6746078378	-2.8338536389	2.5546489691
C33	0.0405809256	-1.5931450723	2.6820441884
C34	0.2902616925	-0.5743385891	1.7535612201
C35	1.2042564998	-0.8127286211	0.7136612044
C36	1.8387467710	-2.0460433030	0.5918636798
H37	2.0605059125	-4.0326910825	1.4142752663
H38	0.4694234585	-3.6170070218	3.2821850873
H39	-0.6381784178	-1.4306032920	3.5132193336
H40	1.4250702841	-0.0282306725	-0.0038018942
H41	2.5394151333	-2.2101445851	-0.2236798994
C42	-2.0781485389	-3.8780170354	-1.6660785264
C43	-1.7675698218	-3.3375919018	-2.9191881439
C44	-1.4782681798	-1.9781719586	-3.0458775883
C45	-1.4846188006	-1.1388570096	-1.9163782422
C46	-1.8233114002	-1.6849076580	-0.6712319834
C47	-2.1121692685	-3.0459013638	-0.5448952343

H48	-2.2975936443	-4.9391333915	-1.5683865541
H49	-1.7506637351	-3.9759000280	-3.8003296421
H50	-1.2451675591	-1.5696928350	-4.0262595330
H51	-1.8508915094	-1.0453322029	0.2031013720
H52	-2.3566886746	-3.4547138396	0.4327388086
C53	3.5273899958	0.8834311655	-2.9701459855
C54	2.8897312426	-0.3585983423	-3.0318089076
C55	1.5175166544	-0.4644667584	-2.7841353396
C56	0.7635807415	0.6757022651	-2.4621910180
C57	1.4152889481	1.9205640249	-2.3956209752
C58	2.7828992114	2.0251140258	-2.6552028887
H59	4.5956124691	0.9610287853	-3.1607813615
H60	3.4610958598	-1.2530869477	-3.2723397879
H61	1.0464253234	-1.4417698203	-2.8254004229
H62	0.8492260664	2.8111343985	-2.1325042975
H63	3.2696404242	2.9968891117	-2.6029326351
C64	-3.2718690880	1.8041907768	-5.9665028820
C65	-1.8760798832	1.7608027401	-5.9719129195
C66	-1.1747798574	1.4104831835	-4.8127065062
C67	-1.8676234486	1.1033795091	-3.6337144465
C68	-3.2728008429	1.1520650754	-3.6333913139
C69	-3.9684056575	1.4955079647	-4.7918428435
H70	-3.8146978654	2.0751206517	-6.8692552592
H71	-1.3254183116	1.9949335473	-6.8808124507
H72	-0.0890394756	1.3740016038	-4.8343795582
H73	-3.8247151766	0.9190582053	-2.7245207725
H74	-5.0558237618	1.5239790773	-4.7789203961
C75	-6.7036623874	0.6967227329	-0.5930220742
C76	-5.9847595902	0.4389434244	0.5766953048
C77	-5.0623957669	1.3732071479	1.0488010201
C78	-4.8194859502	2.5618057452	0.3422685061
C79	-5.5692159607	2.8251730563	-0.8172896695
C80	-6.5036541280	1.9000307499	-1.2789760219
H81	-7.4273158980	-0.0274170469	-0.9608243531
H82	-6.1493492115	-0.4855019101	1.1258258822
H83	-4.5077409481	1.1758356320	1.9606467858
H84	-5.4388488040	3.7656172603	-1.3448728277
H85	-7.0830214451	2.1199546850	-2.1727675898
C86	-1.6299406000	4.3979880618	-2.2611454491
H87	-1.3956142305	3.7757083975	-3.1299752911
H88	-0.7045653571	4.7383974523	-1.7943630246
C89	-1.0613480847	6.3965360764	2.5314438299
C90	-0.2946153476	6.7319888719	1.2007483397

C91	-0.8702267010	7.9438843096	0.4568711099
H92	-0.4267349988	7.9893823113	-0.5431865439
H93	-1.9571947599	7.8624371413	0.3445906067
H94	-0.6429360188	8.8786521124	0.9804422600
C95	1.2166857809	6.8692600877	1.3461435837
H96	1.6642693929	7.0738670320	0.3673692567
H97	1.4596711696	7.7043048987	2.0138863373
H98	1.6676578259	5.9597740812	1.7447035516
C99	-1.6532894235	7.6015618361	3.2558160135
H100	-0.8586477063	8.2942986509	3.5567276754
H101	-2.3655890425	8.1414934857	2.6266620645
H102	-2.1765052846	7.2697093592	4.1590852020
C103	-0.2418147000	5.5388608893	3.5009094260
H104	0.5673525580	6.1193818947	3.9568077104
H105	-0.8999613160	5.1761193838	4.2967627034
H106	0.1947780426	4.6744498047	2.9933099874
B107	-1.7739519785	5.0345819633	0.8308449407
O108	-2.1613299352	5.5627060326	2.0447175120
O109	-0.5913316132	5.5612701628	0.3735957023
H111	-2.1585402711	5.2904097580	-2.6318528054
N112	-5.0670655834	5.1998262144	1.3163268700
H113	-4.4367657109	5.8318534775	1.8092225979
H114	-5.8453761895	4.9624140824	1.9340291014
H115	-5.4456948638	5.6796206006	0.4988459586

Attack at 3-*syn*

File: PhBPinMeAllyl_3NH3_Pd_PPh3_2_thfd.out; structure 51
Solution phase energy: DFT(b3lyp-d3) -3054.13167066818 au

Pd1	-1.7823624660	1.8379318573	0.1670100233
P2	-0.7716451838	1.0126067948	-1.8999505642
P3	-0.6838017563	0.5720554550	1.8847611366
C4	-2.9996578807	3.7855027543	0.1618002749
C5	-3.1094370523	3.0455940899	1.4017018195
C6	-4.0111063591	3.5628653376	-0.8136044768
H7	-3.9765558115	2.3786873485	1.4286925355
H8	-4.6998386122	2.7397929781	-0.6315032655
C9	-3.5181045449	-0.4971005463	5.4054108992
C10	-2.2298625821	-0.0420685026	5.6912395949
C11	-1.3589460494	0.3122342160	4.6587120709
C12	-1.7734549625	0.2237024467	3.3245467913
C13	-3.0806739646	-0.2092036576	3.0462988820
C14	-3.9439078545	-0.5789120305	4.0772628867

H15	-4.1900283158	-0.7785084737	6.2128267163
H16	-1.8969605404	0.0375985788	6.7231299098
H17	-0.3624461856	0.6645870904	4.9023594912
H18	-3.4253747166	-0.2529991593	2.0153952190
H19	-4.9492605241	-0.9217620809	3.8436838693
C20	3.0837776464	2.6969048659	3.6058673982
C21	2.8686812082	1.3393953288	3.8672572981
C22	1.7451155170	0.6939897229	3.3486613409
C23	0.8166677573	1.3984081911	2.5607055259
C24	1.0478005436	2.7541584241	2.2919498886
C25	2.1709653920	3.3993563101	2.8160087857
H26	3.9609680069	3.1982343764	4.0093078563
H27	3.5779422847	0.7796611484	4.4736135228
H28	1.5959426719	-0.3635227310	3.5509116425
H29	0.3607707347	3.3037254213	1.6590621521
H30	2.3341383066	4.4527250343	2.5999576795
C31	0.9645126658	-3.6239573259	0.7057958013
C32	-0.1801591725	-3.5371411492	1.4990736443
C33	-0.6775699082	-2.2905942756	1.8869698168
C34	-0.0330576825	-1.1109073246	1.4846427146
C35	1.1260581587	-1.2091339929	0.6975160917
C36	1.6180090006	-2.4541296175	0.3100641465
H37	1.3482149585	-4.5957610599	0.4028190806
H38	-0.6901629450	-4.4419016978	1.8240601004
H39	-1.5656863268	-2.2478947161	2.5090670952
H40	1.6532688556	-0.3120399684	0.3928785988
H41	2.5147020023	-2.5073317946	-0.3027328487
C42	-1.6812391731	-3.4419850116	-2.8974464938
C43	-1.0637867442	-2.6345709993	-3.8594929472
C44	-0.7962211330	-1.2926722226	-3.5841768752
C45	-1.1372336168	-0.7364533000	-2.3370024200
C46	-1.7718047558	-1.5510239877	-1.3880816410
C47	-2.0380888891	-2.8946344839	-1.6632493357
H48	-1.8879391915	-4.4880879669	-3.1129975169
H49	-0.7922592198	-3.0490649958	-4.8281856413
H50	-0.3332511523	-0.6739392776	-4.3487378400
H51	-2.0486763349	-1.1348655644	-0.4251000720
H52	-2.5205670404	-3.5117627765	-0.9091872069
C53	3.8499566298	1.4244618798	-1.4349805358
C54	3.3373353636	0.3506373889	-2.1710072517
C55	1.9592148621	0.2094306219	-2.3525562961
C56	1.0700397789	1.1419619235	-1.7946232273
C57	1.5931669909	2.2215843697	-1.0613589352

C58	2.9719355711	2.3631082088	-0.8855346199
H59	4.9229985026	1.5226314702	-1.2856896107
H60	4.0122015879	-0.3884047152	-2.5988244462
H61	1.5852887648	-0.6486409458	-2.9026525191
H62	0.9174820160	2.9419241678	-0.6079524248
H63	3.3563759667	3.1933518728	-0.2971396640
C64	-1.8902250116	3.4054454711	-5.7502330798
C65	-0.7914355675	3.7906248460	-4.9754934720
C66	-0.4272233071	3.0501671498	-3.8483591020
C67	-1.1600279271	1.9128134272	-3.4704184212
C68	-2.2654368720	1.5345548690	-4.2531948575
C69	-2.6216682094	2.2708473102	-5.3864782023
H70	-2.1693920868	3.9802639124	-6.6303698918
H71	-0.2067731546	4.6653381891	-5.2544466885
H72	0.4393110321	3.3555922144	-3.2702591536
H73	-2.8502437310	0.6579482676	-3.9847751559
H74	-3.4760954599	1.9556322413	-5.9821973034
C75	-2.3031342585	4.3039954145	5.4475248913
C76	-3.3393989881	3.4178760852	5.1469836330
C77	-3.5697946996	3.0305312790	3.8281529278
C78	-2.7726879925	3.5086058710	2.7691369815
C79	-1.7381918524	4.4062202276	3.0920337480
C80	-1.5059178305	4.7956611022	4.4095105379
H81	-2.1145973814	4.6040222413	6.4761816233
H82	-3.9664364938	3.0182344978	5.9408750652
H83	-4.3716582157	2.3293856482	3.6131265665
H84	-1.0904280287	4.7821835115	2.3138938613
H85	-0.6886463650	5.4799255269	4.6276979244
C86	-3.9226819571	4.0279492595	-2.2386388972
H87	-4.9070355763	4.0278448288	-2.7142149322
H88	-3.2815376884	3.3388400136	-2.7978186646
C89	-1.3073109627	7.1603262325	-0.2436471410
C90	-0.0716950483	6.1823147039	-0.3189201628
C91	0.4465130188	5.9587005406	-1.7427123399
H92	1.1882487465	5.1541441790	-1.7290300565
H93	-0.3620097419	5.6596002617	-2.4168725821
H94	0.9234557440	6.8600941861	-2.1402802225
C95	1.0840839776	6.5247680954	0.6184672317
H96	1.8779695216	5.7777768915	0.5089006565
H97	1.5052454628	7.5065396944	0.3713219257
H98	0.7705701069	6.5361829795	1.6658600998
C99	-1.3714500130	8.1991341731	-1.3588242678
H100	-0.4942868289	8.8552011379	-1.3201501590

H101	-1.4135713783	7.7305002430	-2.3449730661
H102	-2.2662341303	8.8187263655	-1.2356966290
C103	-1.4724979531	7.8351152929	1.1228704259
H104	-0.6764015952	8.5643192398	1.3051518433
H105	-2.4336417161	8.3587939367	1.1470611261
H106	-1.4685803929	7.1011161897	1.9349601958
B107	-2.0152292046	4.9901160154	-0.0425372377
O108	-2.4432211709	6.2449545917	-0.3929377525
O109	-0.6515424833	4.9095384849	0.1139401636
H111	-3.4886390659	5.0279217068	-2.3139582472
N112	-5.5667529174	5.0000022816	-0.2181204805
H113	-5.0685339671	5.8885507610	-0.1835511344
H114	-5.9082071691	4.7969158344	0.7215125852
H115	-6.3784893545	5.1109734565	-0.8275491556

Attack at 3-*anti*

File: PhBPin_antiMeAllyl_3NH3_Pd_PPh3_2_thfd.out; structure 61
Solution phase energy: DFT(b3lyp-d3) -3054.13375710818 au

Pd1	-1.7394289045	1.8631914230	0.3374056714
P2	-0.7025605205	1.2151496128	-1.7680716260
P3	-0.7070326722	0.4225440212	1.9412434520
C4	-3.0886333688	3.7146019517	0.4094761358
C5	-2.9585800071	3.0920382663	1.7088671554
C6	-4.1917159276	3.3734209709	-0.4261445211
H7	-3.7465101818	2.3801430101	1.9495873972
H8	-4.1211481146	3.7125778513	-1.4543571208
C9	-3.8183496365	-0.8326866865	5.1606474210
C10	-2.5112479801	-0.5400229755	5.5577612474
C11	-1.5550607288	-0.1591379813	4.6131854711
C12	-1.8997375788	-0.0589434252	3.2581071490
C13	-3.2178788038	-0.3486146307	2.8675260361
C14	-4.1698765719	-0.7408964726	3.8099008974
H15	-4.5605206273	-1.1273433320	5.8993705604
H16	-2.2330303591	-0.6034925072	6.6078344232
H17	-0.5481470429	0.0757337171	4.9432222328
H18	-3.5028031771	-0.2580003117	1.8208345493
H19	-5.1855783174	-0.9668648281	3.4920193239
C20	2.8515694476	2.4084468997	4.1641922866
C21	2.6908200750	1.0203487380	4.2211733460
C22	1.6329106908	0.4098173348	3.5479148529
C23	0.7219670170	1.1830503853	2.8071378584
C24	0.9003631176	2.5713916089	2.7428410735

C25	1.9546199657	3.1806580324	3.4242914292
H26	3.6762164053	2.8830353451	4.6918518310
H27	3.3899764832	0.4110503101	4.7900669886
H28	1.5230120950	-0.6704637577	3.5933112186
H29	0.2163684547	3.1792178468	2.1619533323
H30	2.0737207336	4.2604943209	3.3741400159
C31	1.0070507226	-3.6589352678	0.4709404022
C32	-0.2133676536	-3.6258211673	1.1501917999
C33	-0.7294165024	-2.4151324094	1.6198893415
C34	-0.0299092439	-1.2148531464	1.4153412906
C35	1.2033559401	-1.2592992917	0.7437590919
C36	1.7145108158	-2.4694632489	0.2749822421
H37	1.4066350109	-4.6023276129	0.1053201318
H38	-0.7678841972	-4.5461415205	1.3227539016
H39	-1.6772756287	-2.4167400971	2.1498558807
H40	1.7748400433	-0.3498902308	0.5954121688
H41	2.6702821644	-2.4788002068	-0.2440102181
C42	-1.7048043489	-3.0339076271	-3.3651593156
C43	-1.1176565403	-2.0999238856	-4.2251464747
C44	-0.8239139008	-0.8141140945	-3.7685469439
C45	-1.1088758497	-0.4501787820	-2.4407515224
C46	-1.7153631499	-1.3875671630	-1.5929395053
C47	-2.0056087255	-2.6744927658	-2.0496454207
H48	-1.9310787456	-4.0364190215	-3.7228427940
H49	-0.8896189779	-2.3722712238	-5.2538105071
H50	-0.3758602341	-0.0939588609	-4.4484539518
H51	-1.9500990993	-1.1126018132	-0.5703640465
H52	-2.4636136787	-3.3946726951	-1.3757419124
C53	3.8901723953	1.2946918095	-1.0079464208
C54	3.3643577417	0.3303224229	-1.8732345457
C55	1.9928077715	0.2933763862	-2.1416767390
C56	1.1287498612	1.2258728761	-1.5482489863
C57	1.6664783272	2.2012726062	-0.6900960847
C58	3.0359205384	2.2335737041	-0.4207499682
H59	4.9556160317	1.3106452777	-0.7885536293
H60	4.0213996680	-0.4049466606	-2.3334726878
H61	1.6001517249	-0.4815249472	-2.7932780722
H62	1.0079142035	2.9227981883	-0.2131929726
H63	3.4320392239	2.9796553211	0.2641220423
C64	-1.4457152268	3.9820324639	-5.4462142726
C65	-0.1485656699	3.5387892446	-5.1742028985
C66	0.0980524051	2.7019023738	-4.0818425405
C67	-0.9525676943	2.3004956940	-3.2438218458

C68	-2.2554687415	2.7346012014	-3.5357526360
C69	-2.5027419264	3.5676117337	-4.6279396961
H70	-1.6342966722	4.6395501254	-6.2917735526
H71	0.6790276784	3.8494709262	-5.8084303293
H72	1.1140362630	2.3767847797	-3.8769143763
H73	-3.0808116653	2.4126864705	-2.9056457987
H74	-3.5183078783	3.8964686123	-4.8397870301
C75	-1.4641486652	4.6673872789	5.4436729427
C76	-2.2532081087	3.5153409545	5.3905241816
C77	-2.7203201534	3.0380851327	4.1673831976
C78	-2.4015133580	3.6789531491	2.9522180542
C79	-1.6169656066	4.8479644076	3.0274223441
C80	-1.1585309151	5.3312583509	4.2521005608
H81	-1.0985231374	5.0446473842	6.3959419312
H82	-2.5114982789	2.9851196506	6.3043598913
H83	-3.3394128062	2.1458364040	4.1494712821
H84	-1.3272158282	5.3671322176	2.1266776239
H85	-0.5511079934	6.2342353276	4.2746952122
C86	-5.1836186502	2.2630556904	-0.1922617553
H87	-6.0395840126	2.3669592916	-0.8642110666
H88	-5.5506673239	2.2425000745	0.8379037694
C89	-1.7027877416	6.9319870941	-1.0218693834
C90	-0.3727489694	6.1168232837	-0.7886123766
C91	0.2025654383	5.5260388805	-2.0760892515
H92	0.9993840739	4.8188653317	-1.8267793926
H93	-0.5614170373	4.9836439799	-2.6361904861
H94	0.6214356444	6.3075360965	-2.7183051058
C95	0.7117558314	6.8536624076	-0.0065795950
H96	1.5794339619	6.1973090900	0.1201679837
H97	1.0379610477	7.7480043005	-0.5500110119
H98	0.3669959298	7.1561900742	0.9856908095
C99	-1.8390690097	7.5622396667	-2.4050665709
H100	-1.0321626912	8.2834551078	-2.5791343756
H101	-1.8108639632	6.8056912611	-3.1937872981
H102	-2.7941832501	8.0953656406	-2.4742402395
C103	-1.9801018956	7.9700485539	0.0727605955
H104	-1.2714665348	8.8029635965	0.0195924426
H105	-2.9922806246	8.3692116845	-0.0571271915
H106	-1.9177933103	7.5233909093	1.0716902962
B107	-2.1911745722	4.8722136881	-0.1451541963
O108	-2.7332101280	5.9003546015	-0.8800929797
O109	-0.8340240762	4.9885282618	0.0224430615
H111	-4.7061975721	1.2967755288	-0.3994512982

N112	-5.6006144253	5.0395228639	-0.1448804010
H113	-4.9969818630	5.8403915928	-0.3286008457
H114	-5.9374014054	5.0980849435	0.8170680520
H115	-6.4088679973	5.0900745697	-0.7678788126

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6. ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra

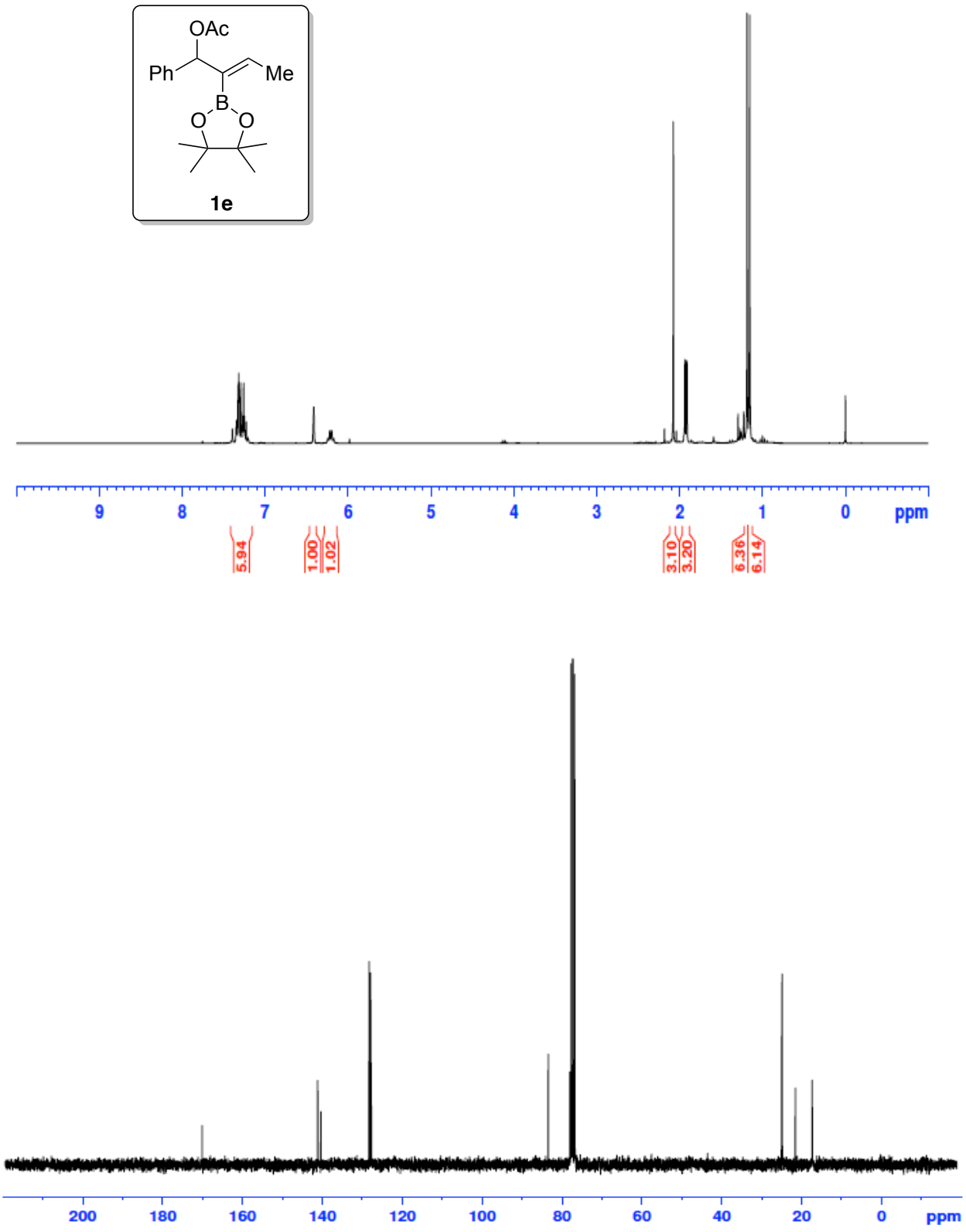

Figure A- 1. 300 MHz ^{1}H and 75 MHz $^{13}C\{^{1}H\}$ NMR of (*E*)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl acetate in $CDCl_3$.

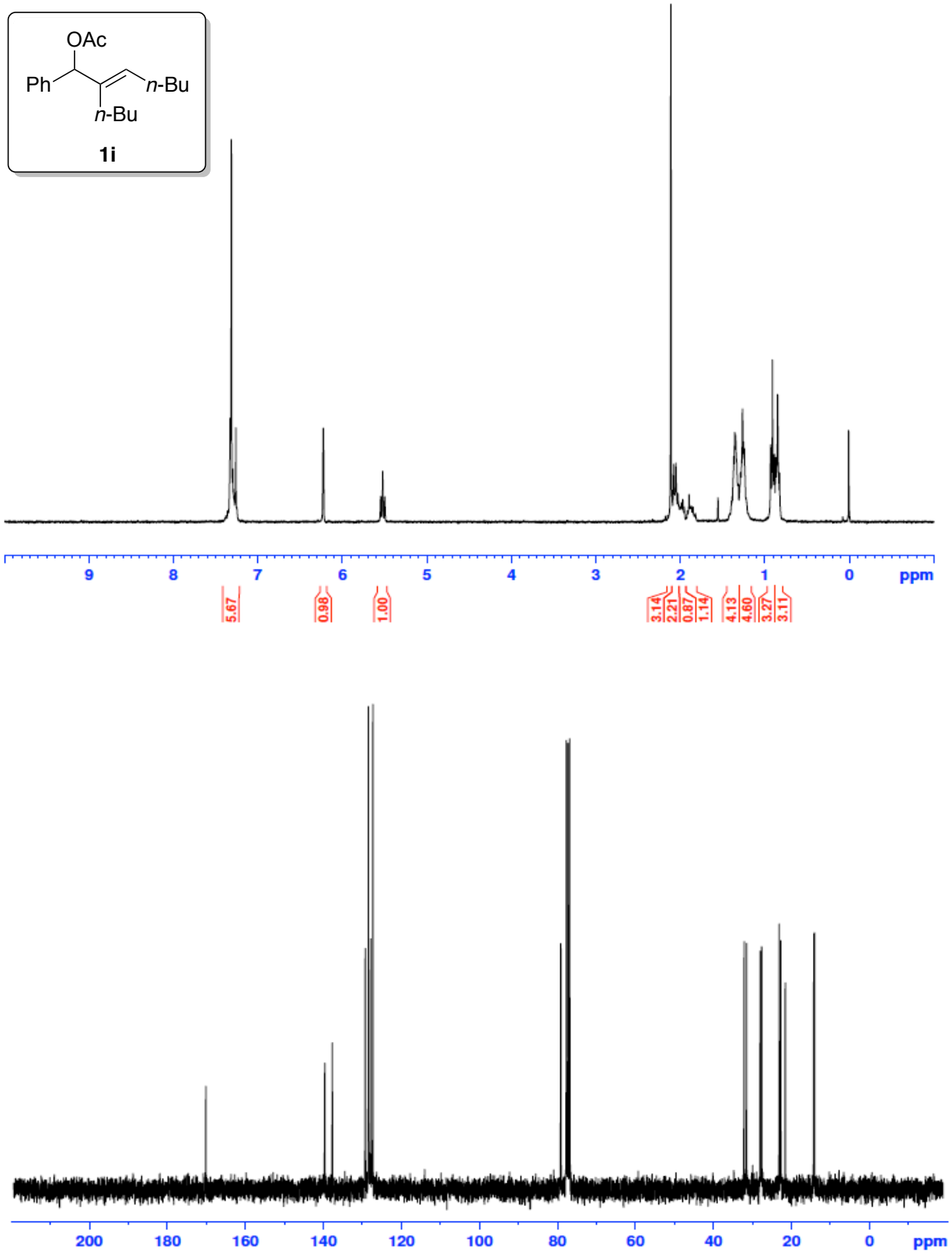

Figure A- 2. 300 MHz ^{1}H and 75 MHz $^{13}C\{^{1}H\}$ NMR of (*E*)-2-butyl-1-phenylhept-2-en-1-yl acetate in $CDCl_3$.

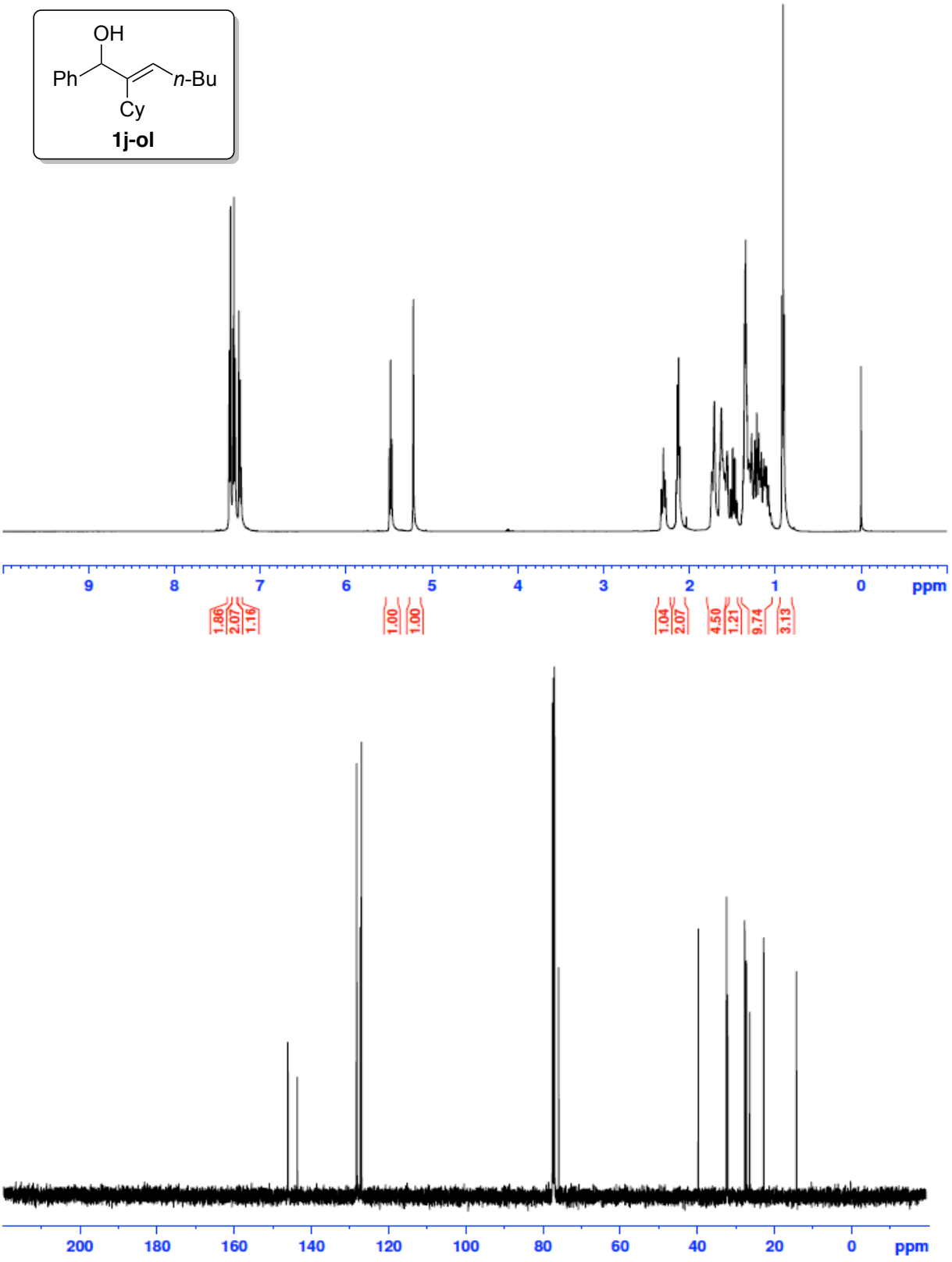

Figure A- 3. 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of (*E*)-2-cyclohexyl-1-phenylhept-2-en-1-ol in $CDCl_3$.

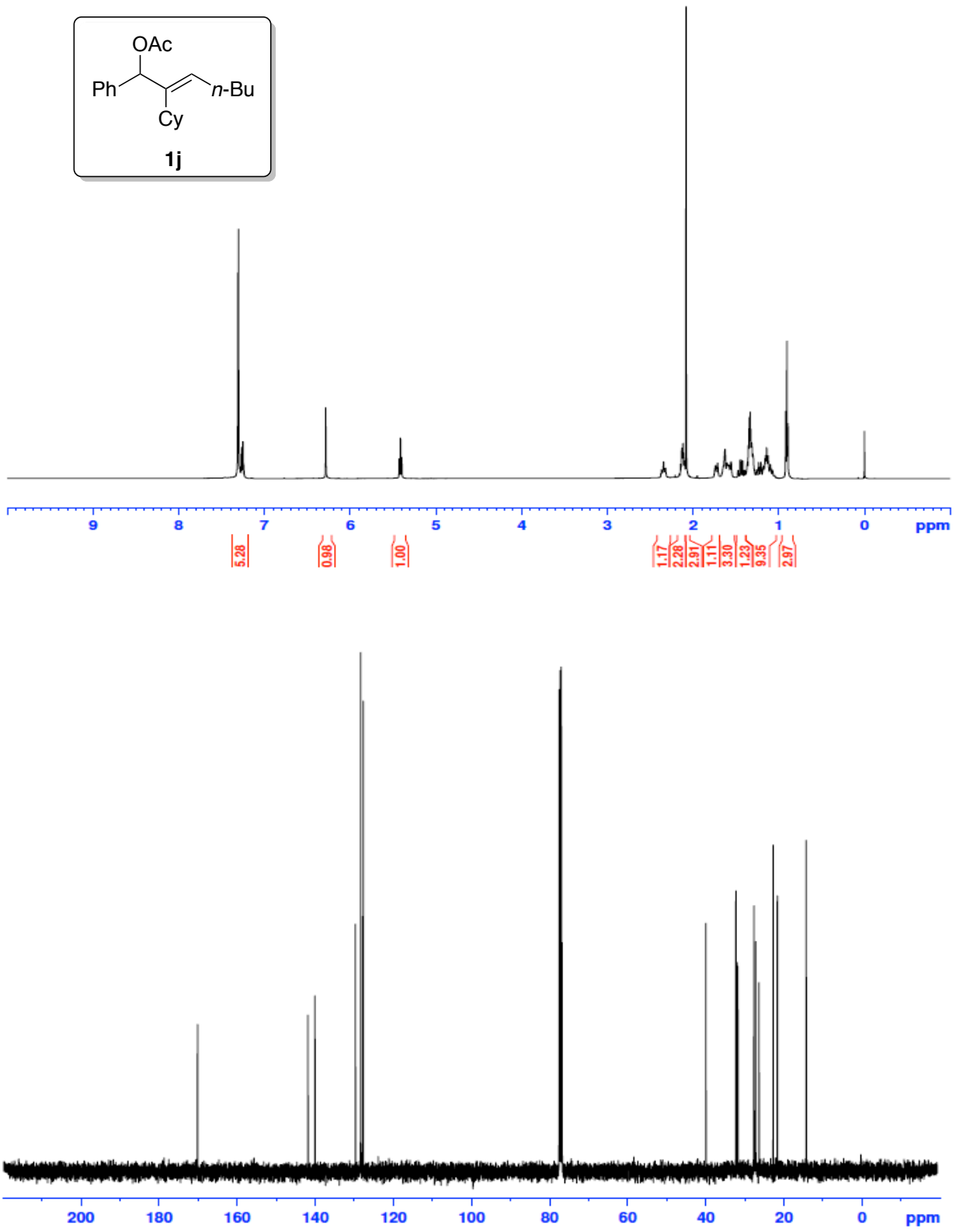

Figure A- 4. 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of (*E*)-2-cyclohexyl-1-phenylhept-2-en-1-yl acetate in $CDCl_3$.

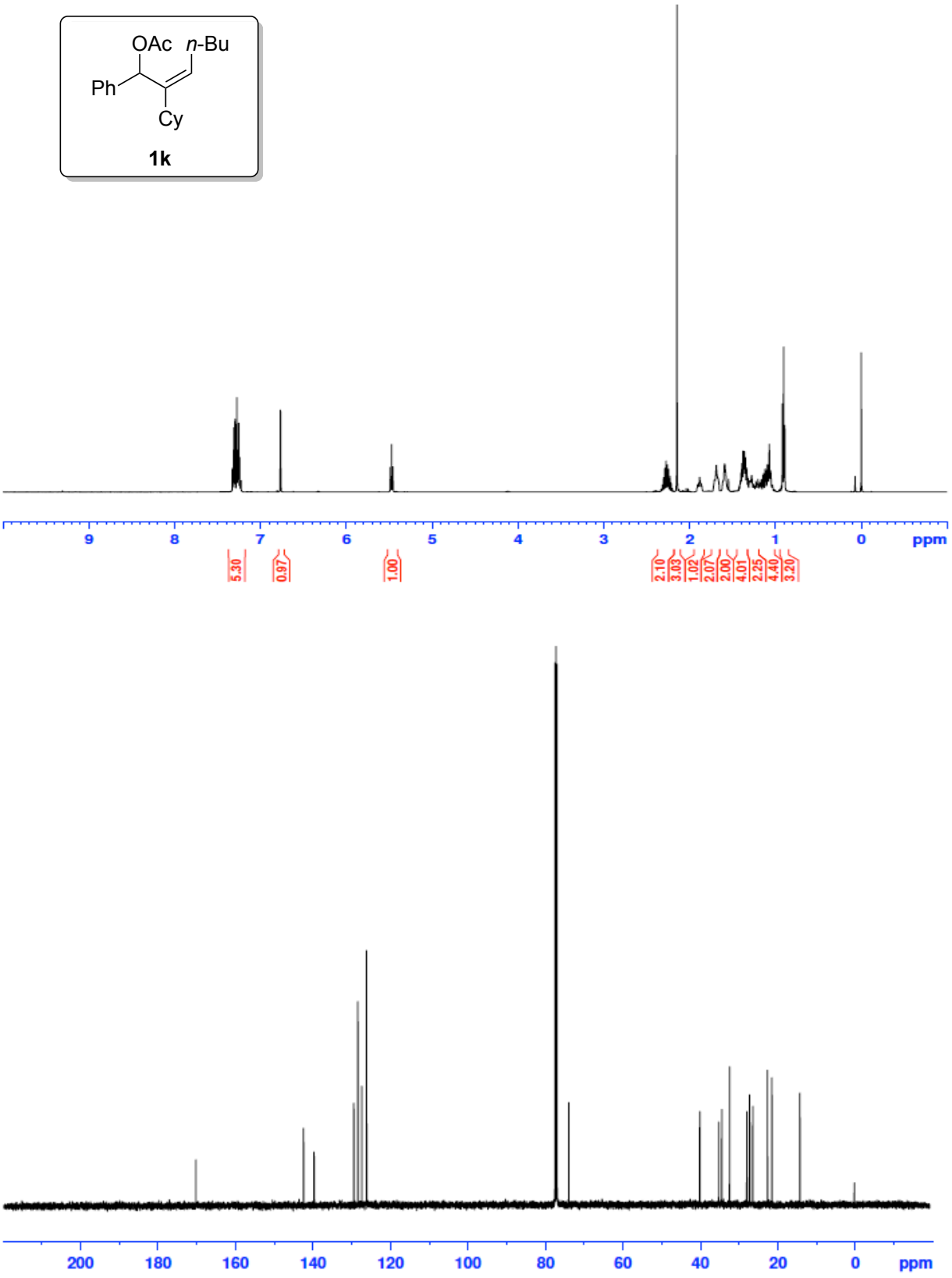

Figure A- 5. 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of (*Z*)-2-cyclohexyl-1-phenylhept-2-en-1-yl acetate in $CDCl_3$.

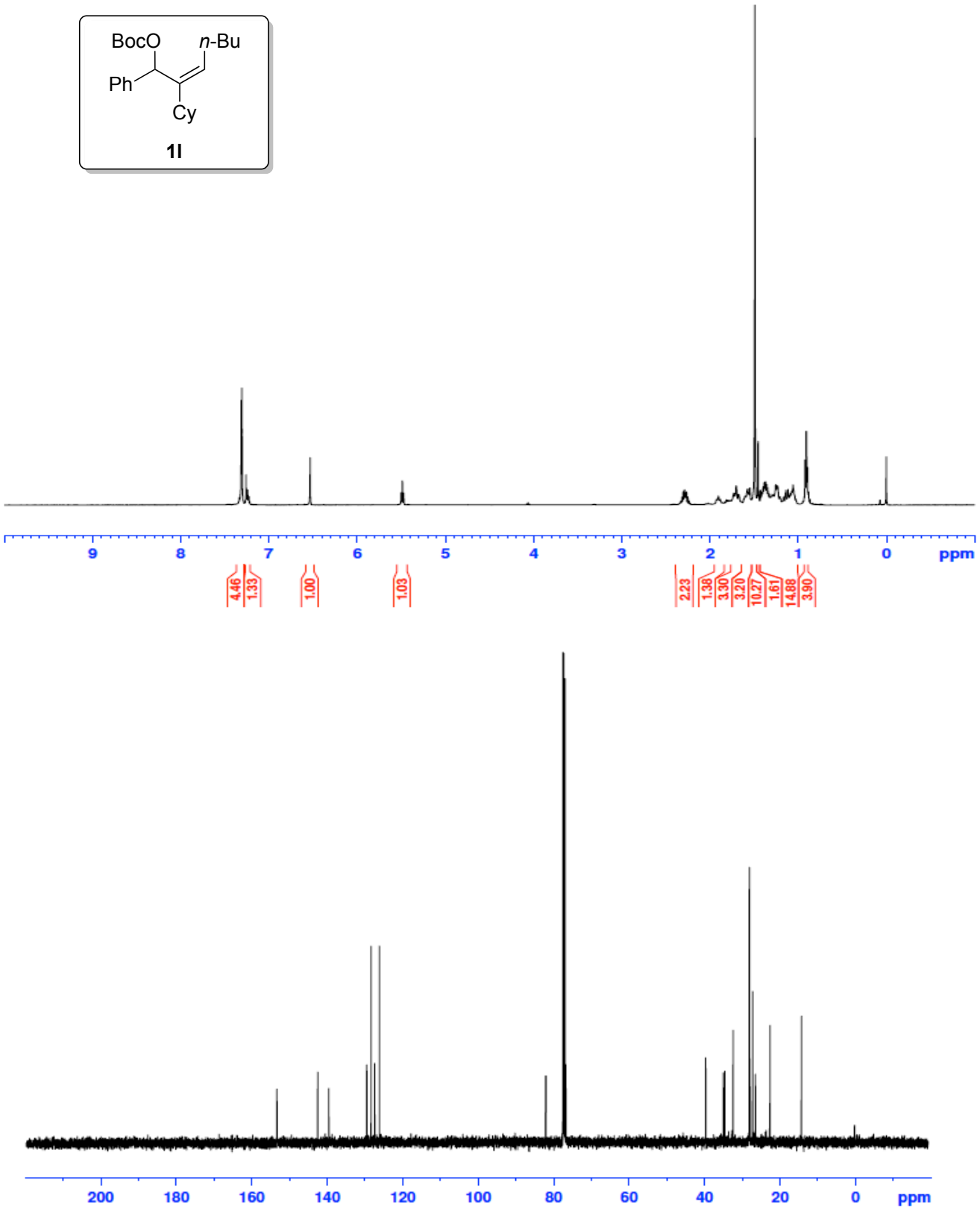

Figure A- 6. 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of (*Z*)-*tert*-butyl (2-cyclohexyl-1-phenylhept-2-en-1-yl) carbonate in $CDCl_3$.

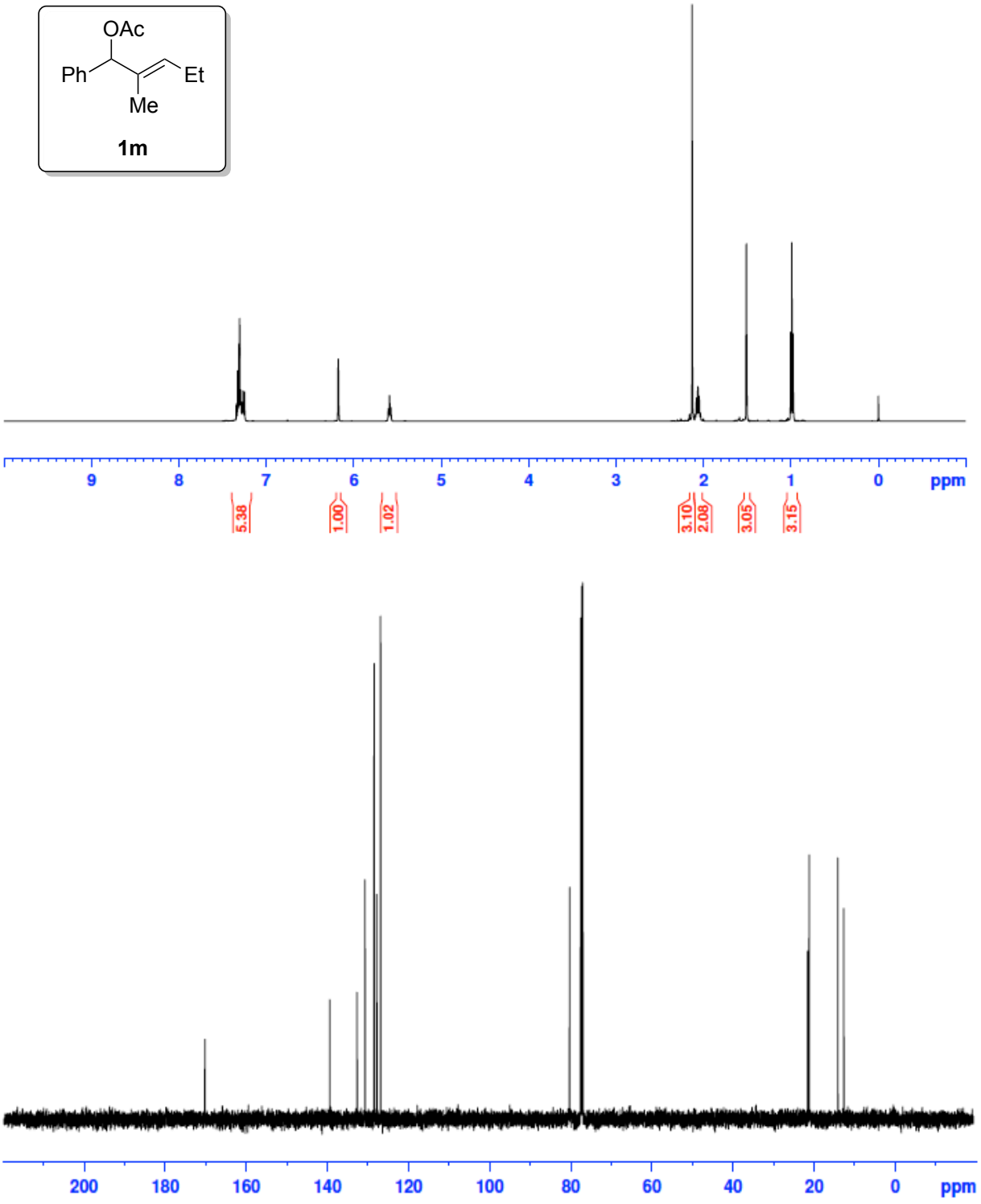

Figure A- 7. 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of (*E*)-2-methyl-1-phenylpent-2-en-1-yl acetate in $CDCl_3$.

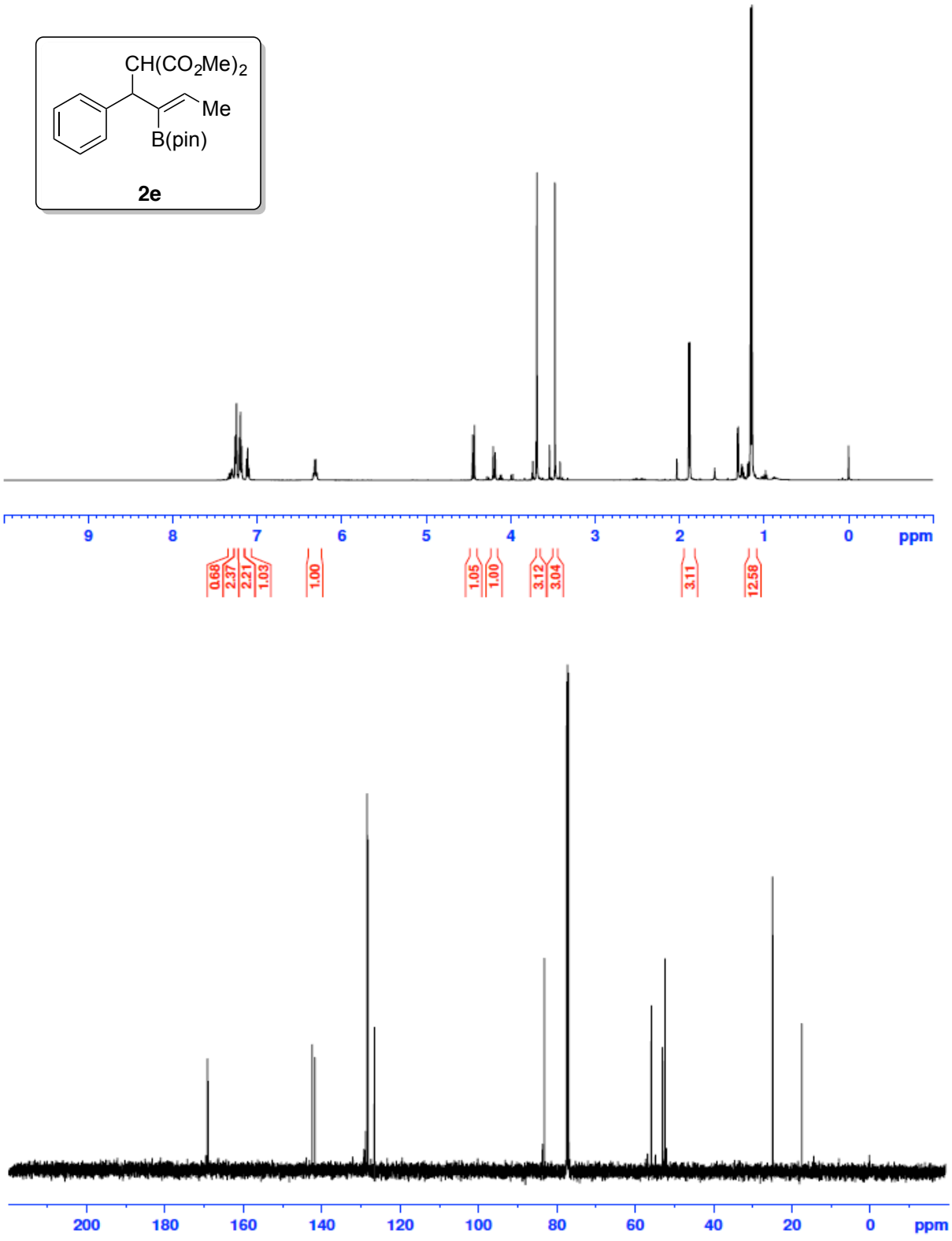

Figure A- 8. 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of dimethyl (*E*)-2-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-2-en-1-yl)malonate in $CDCl_3$. (Residual ethyl acetate solvent (~5%) peak is seen.)

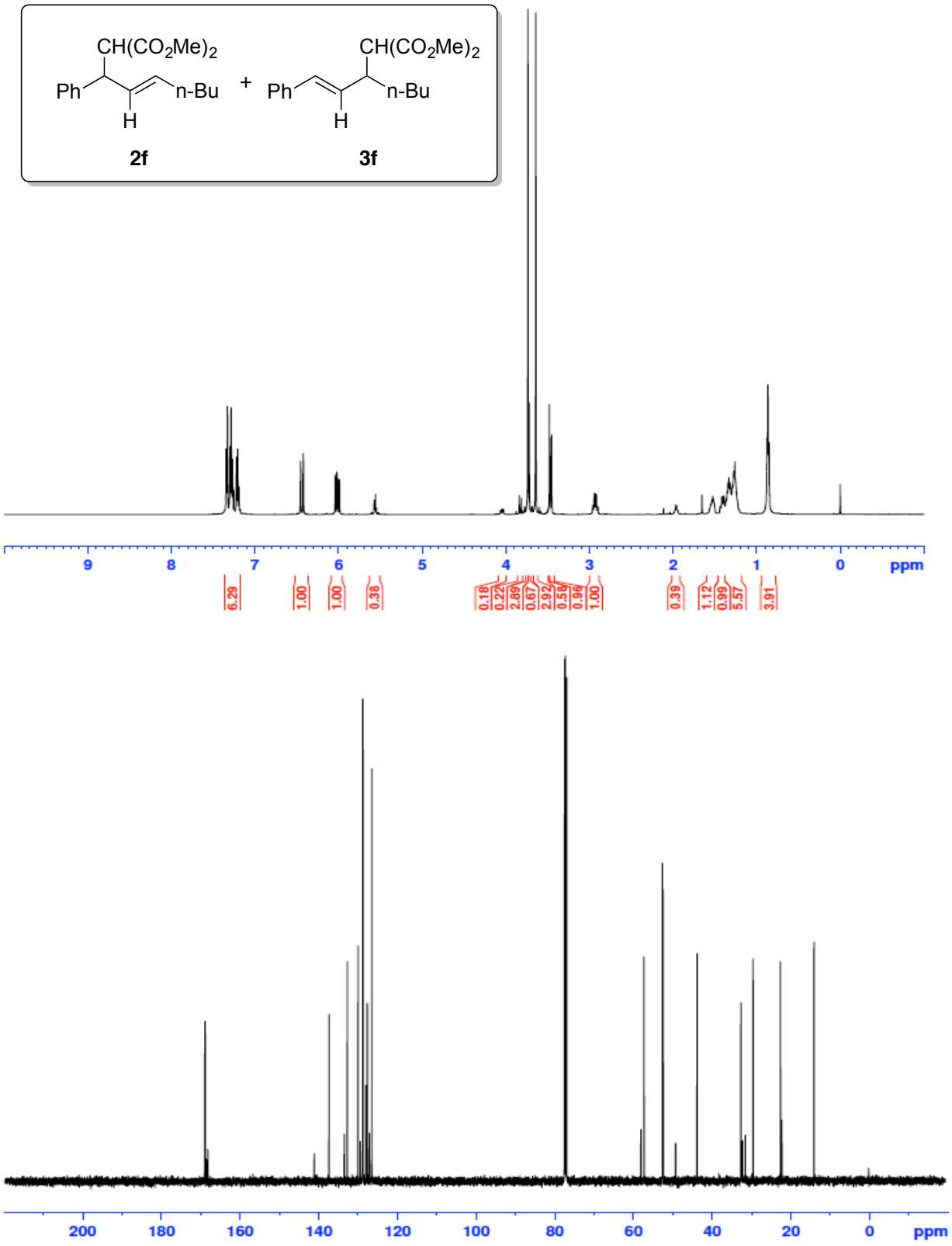

Figure A- 9. 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ of dimethyl (*E*)-2-(1-phenylhept-2-en-1-yl)malonate (minor) and dimethyl (*E*)-2-(1-phenylhept-1-en-3-yl)malonate (major) in $CDCl_3$.

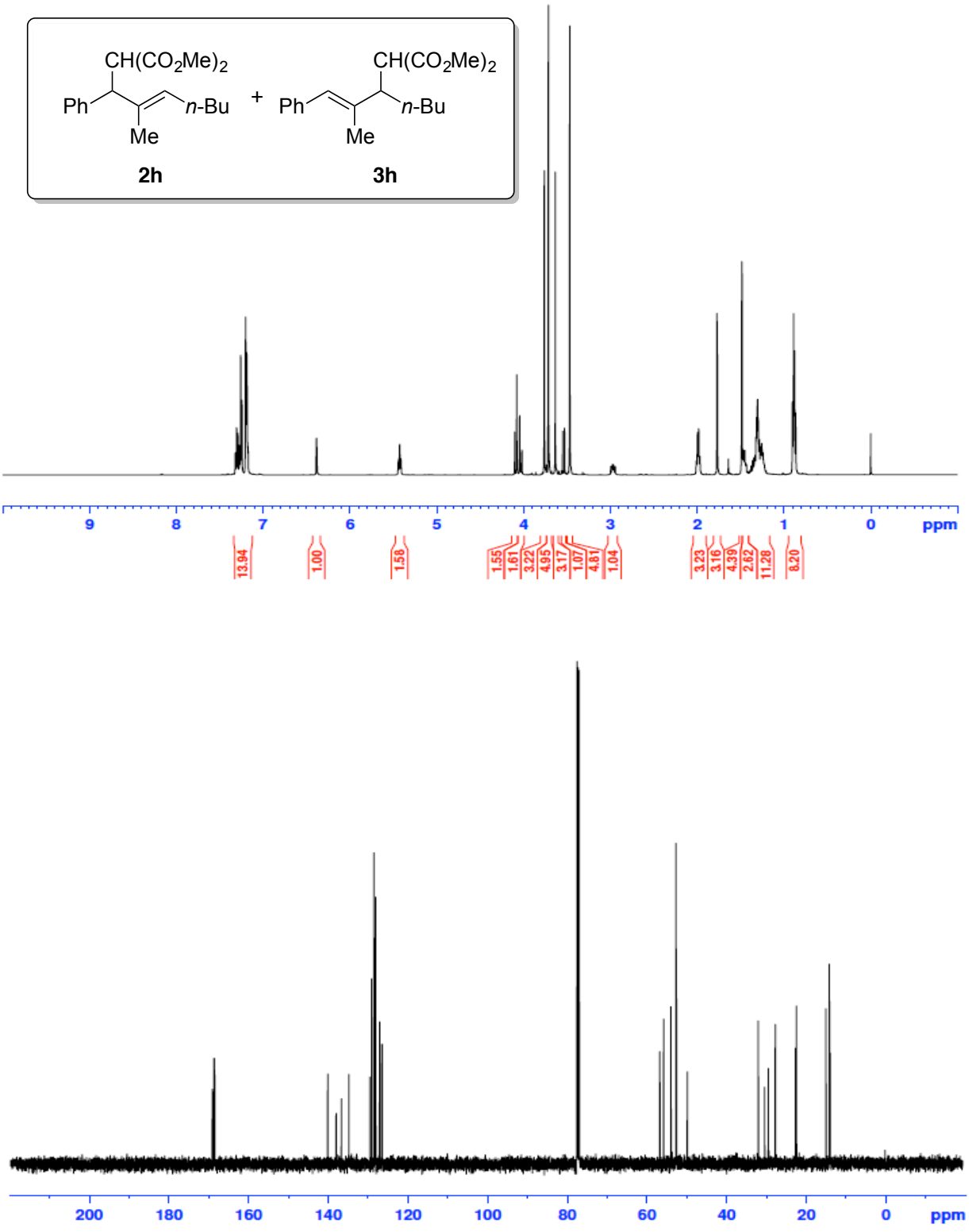

Figure A- 10. 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ of dimethyl (*E*)-2-(2-methyl-1-phenylhept-2-en-1-yl)malonate (major) and dimethyl (*E*)-2-(2-methyl-1-phenylhept-1-en-3-yl)malonate (minor) in $CDCl_3$.

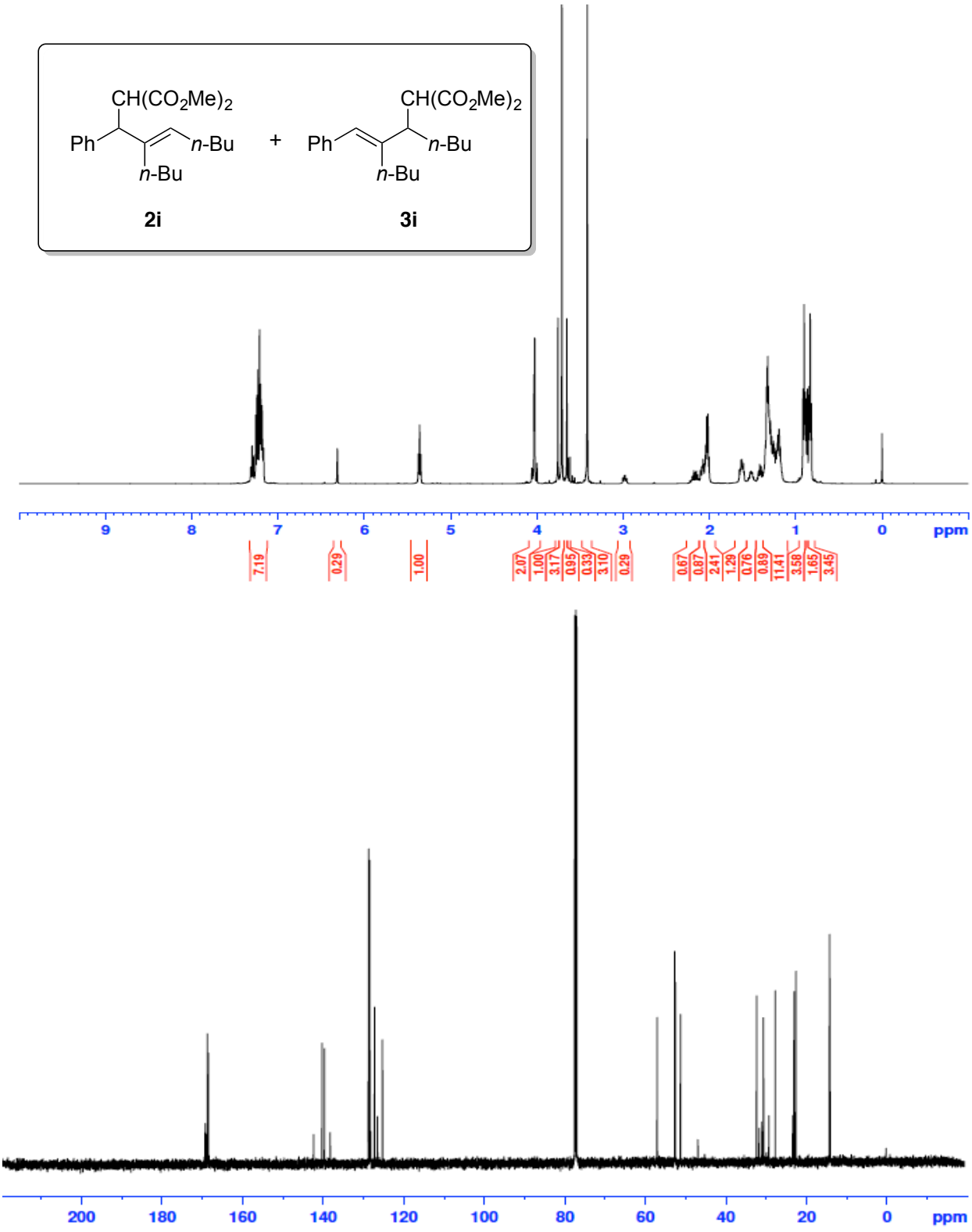

Figure A- 11. 500 MHz ^{1}H and 125 MHz ^{13}C{^{1}H} of dimethyl (*E*)-2-(2-butyl-1-phenylhept-2-en-1-yl)malonate (major) and dimethyl (*E*)-2-(6-benzylidenedecan-5-yl)malonate (minor) in $CDCl_3$.

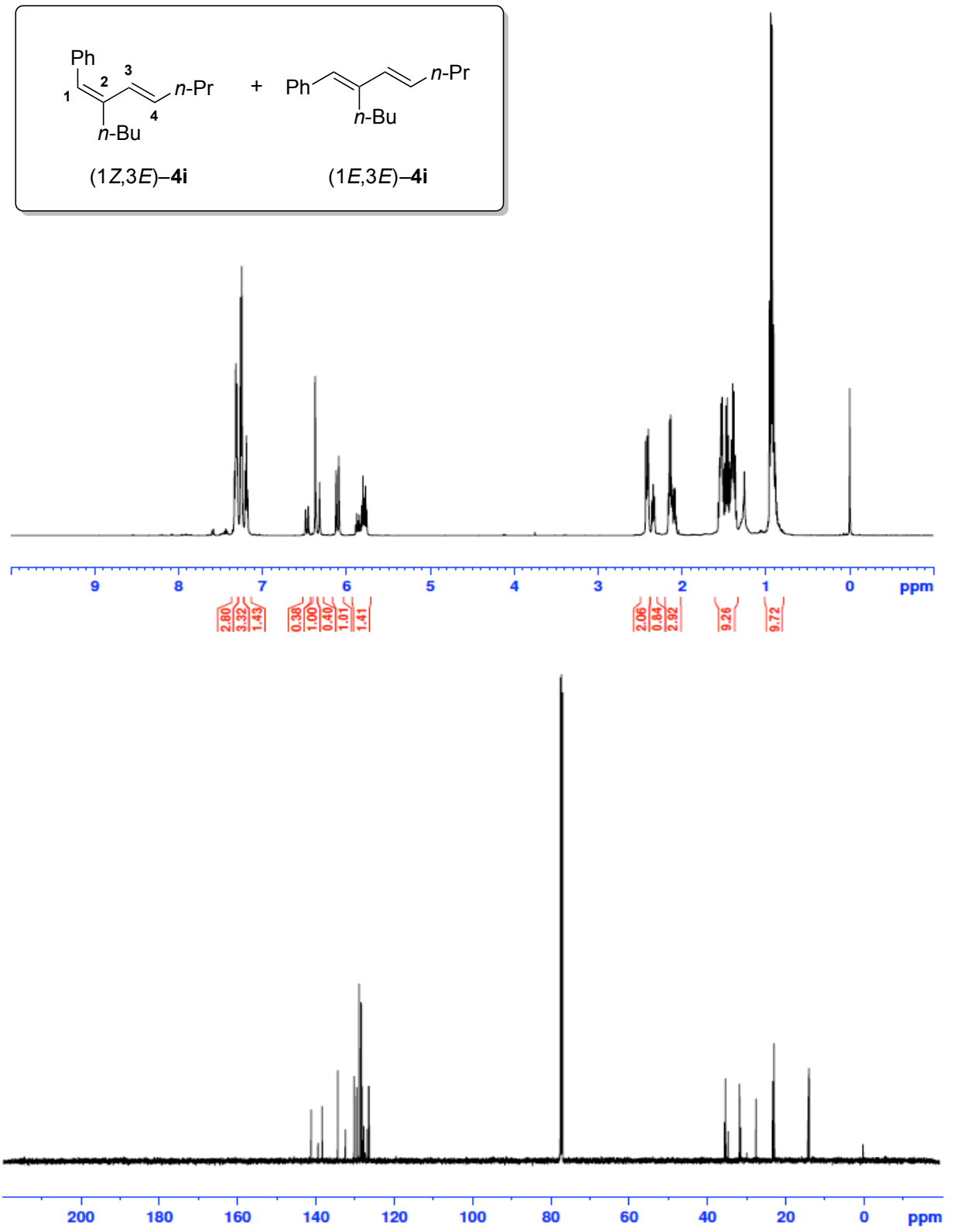

Figure A- 12. 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ of ((1*Z*,3*E*)-2-butylhepta-1,3-dien-1-yl)benzene (minor) and ((1*E*,3*E*)-2-butylhepta-1,3-dien-1-yl)benzene (major) in $CDCl_3$.

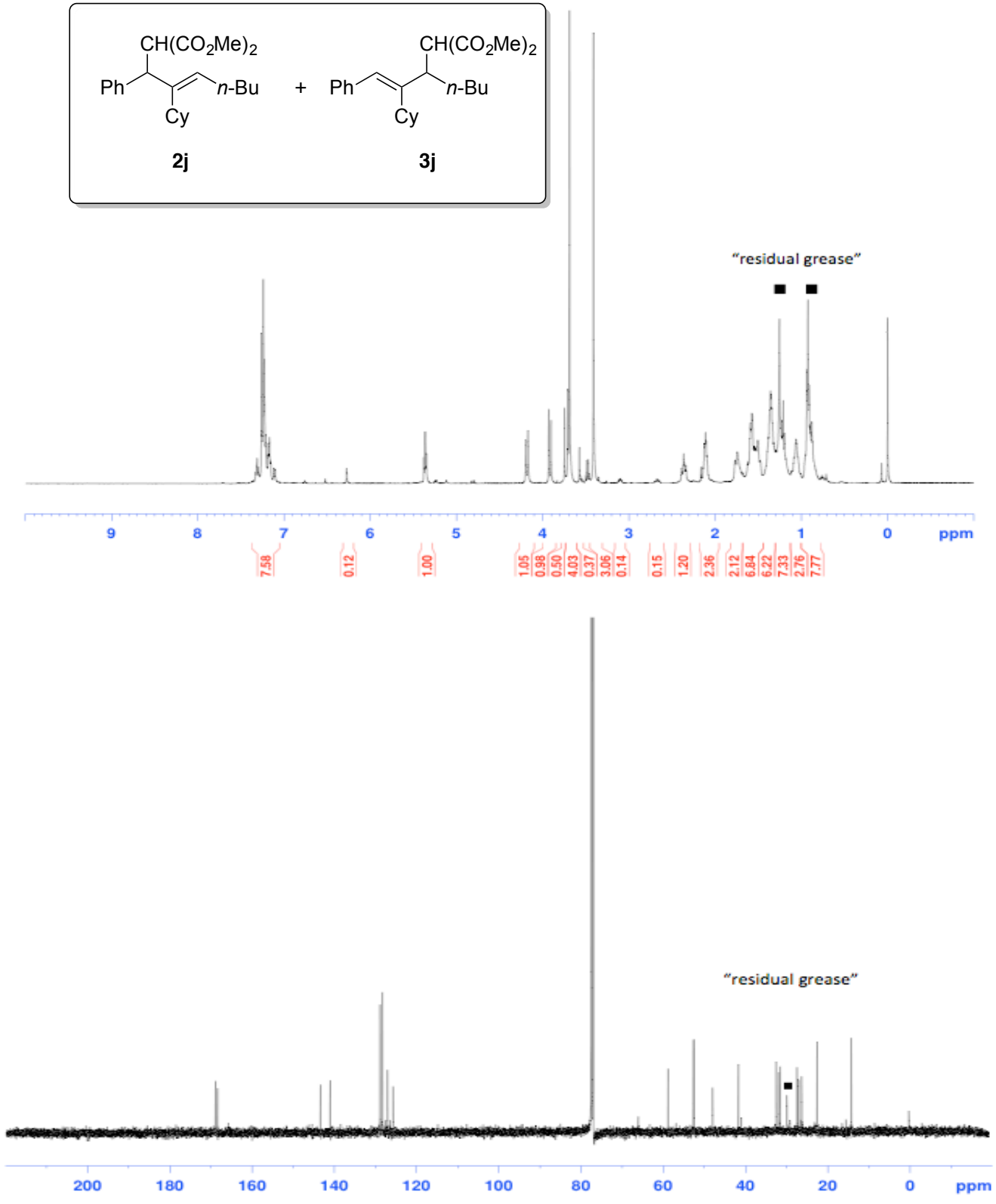

Figure A- 13. 500 MHz ^{1}H and 125 MHz ^{13}C{^{1}H} of dimethyl (*E*)-2-(2-cyclohexyl-1-phenylhept-2-en-1-yl)malonate (major) and dimethyl (*E*)-2-(2-cyclohexyl-1-phenylhept-1-en-3-yl)malonate (minor) in $CDCl_3$ (Residual "grease" peak is seen.)

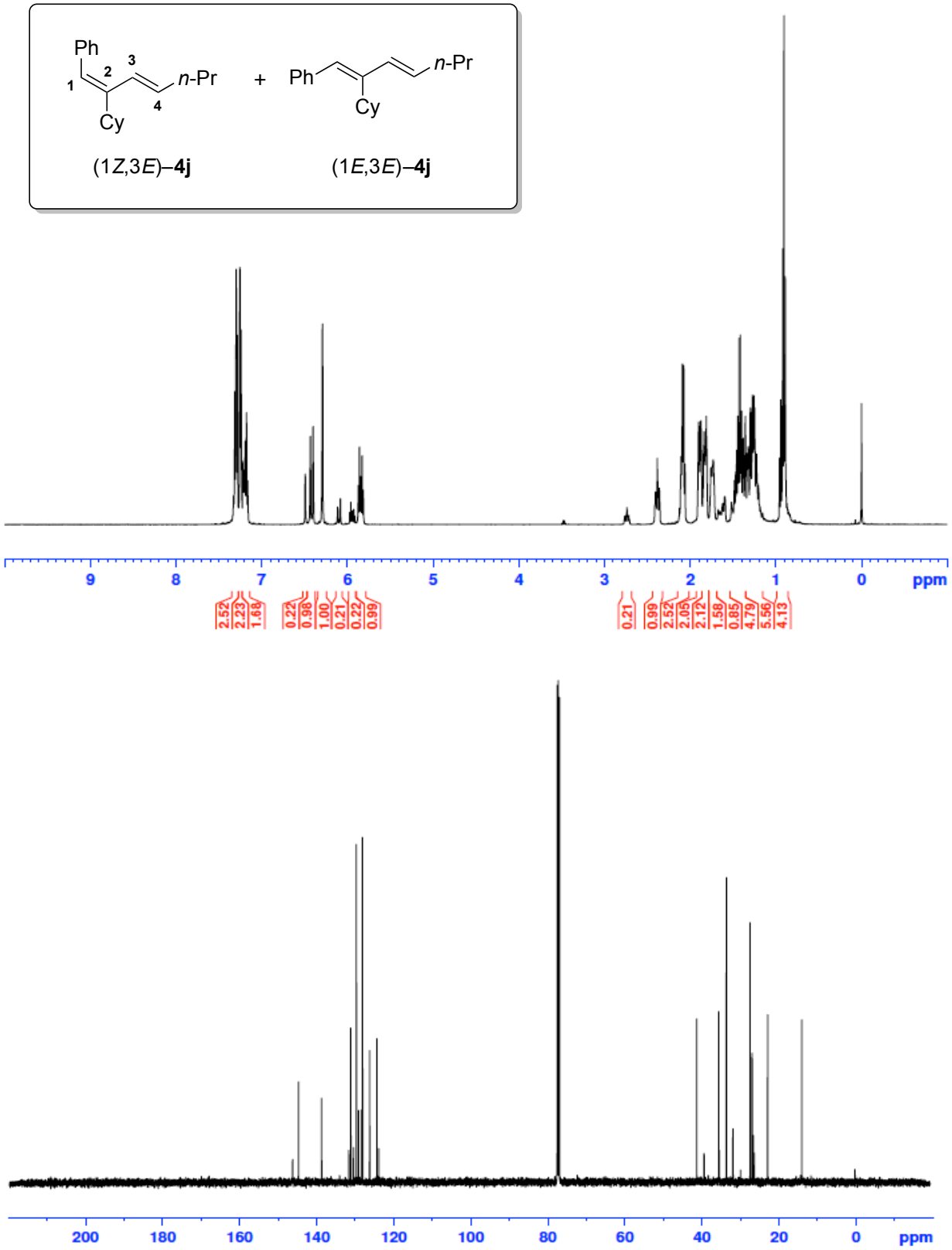

Figure A- 14. 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ of ((1*Z*,3*E*)-2-cyclohexylhepta-1,3-dien-1-yl)benzene (major) and ((1*E*,3*E*)-2-cyclohexylhepta-1,3-dien-1-yl)benzene (minor) in $CDCl_3$.

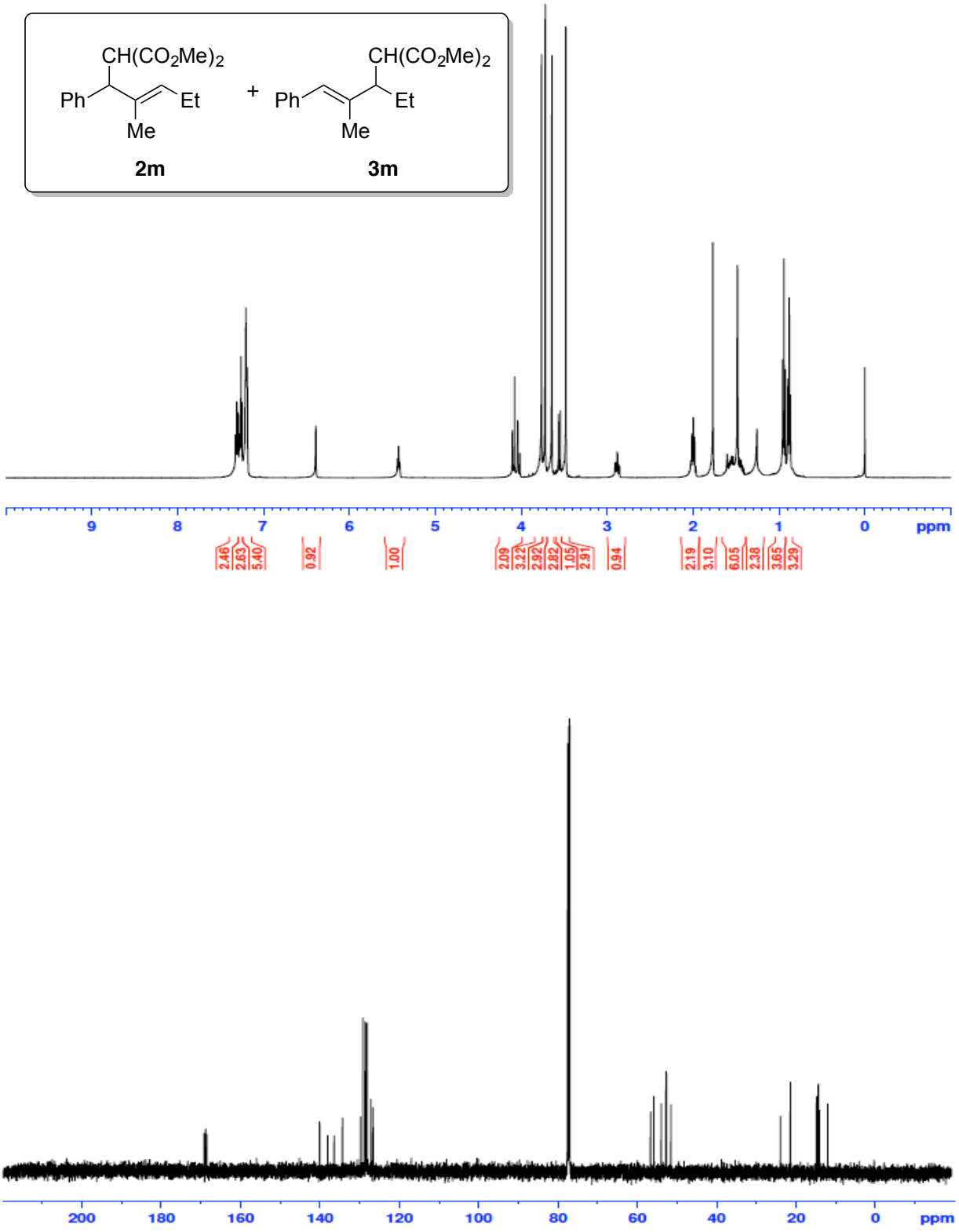

Figure A- 15. 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ dimethyl (*E*)-2-(2-methyl-1-phenylpent-2-en-1-yl)malonate (major) and dimethyl (*E*)-2-(2-methyl-1-phenylpent-1-en-3-yl)malonate (minor) in $CDCl_3$.