Supplementary Information (SI) for Chemical Communications.

Supplementary Information

Synthesis of Vinylidenecyclopropanes via Gold(I)-Catalyzed Cyclopropanation of Vinyl Arenes with *γ*-Stannylated Propargyl Esters

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General

Unless otherwise noted, the reactions were carried out in flame-dried glassware under argon atmosphere. NMR spectra were recorded on JEOL α-GX400, JNX-ECX500, and Bruker AVANCE NEO 400 spectrometer. Chemical shifts (δ) are reported in ppm from the solvent resonance or tetramethylsilane (TMS) as the internal standard ($CDCl_3$: 7.26 ppm, TMS: 0.00 ppm). Peak multiplicities are designated by the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad and coupling constants are provided in (J) Hz, and coupling constants are provided in (J) Hz. ^{13}C NMR spectra were recorded on a JEOL α-GX400 (100 MHz), JNX-ECX500 (125 MHz), and Bruker AVANCE NEO 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). Some reported spectra in $CDCl_3$ include minor solvent impurities of water (1H NMR δ 1.56 ppm) and/or silicon grease (^1H NMR δ 0.07 ppm, ^{13}C NMR δ 1.19 ppm), which do not impact product assignments.[1] Flash chromatography was performed with Fuji Silysia PSQ100B (100 μm) and KANTO silica gel 60N (63-210 μm). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). High-resolution mass (HRMS) spectral data were obtained on an Agilent 6546 LC/Q-TOF.

Materials

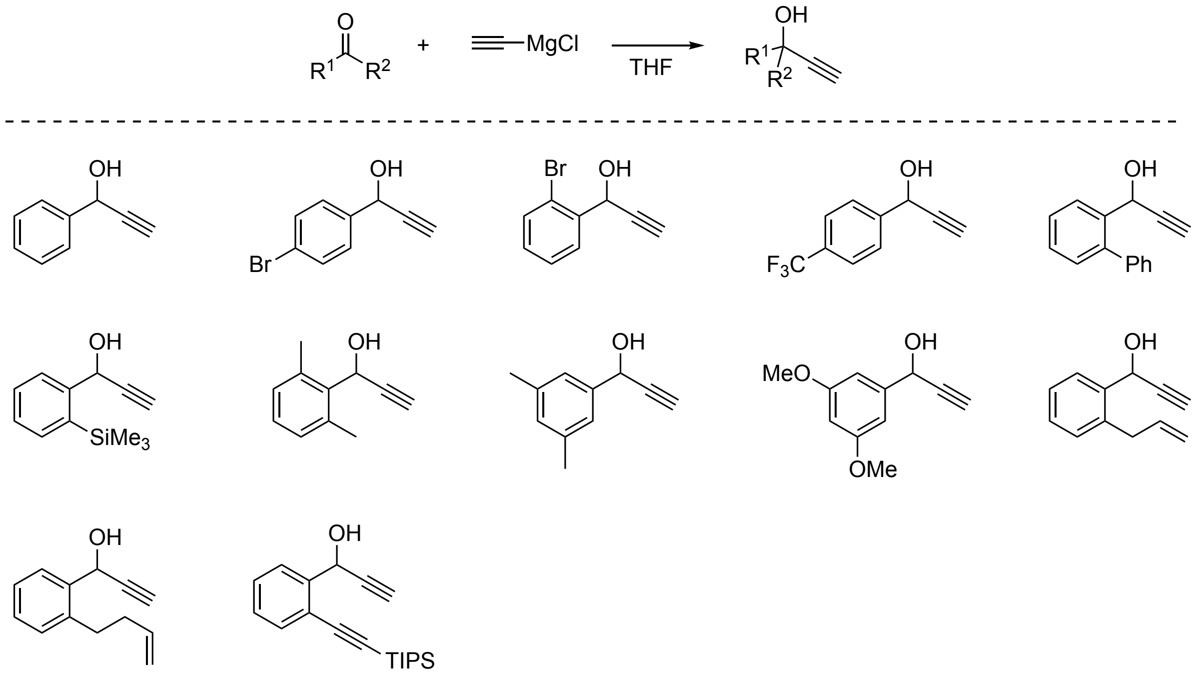
Dichloromethane, diethyl ether, and tetrahydrofuran (THF) were supplied from Kanto Chemical Co., Inc. as "Dehydrated solvent system". Other solvents were purchased from commercial suppliers as dehydrated solvents and used under argon atmosphere. Triethylamine and diisopropylamine were purified by distillation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

Tributyltin chloride (TCI), 4-chlorostyene (TCI), 4-bromostyrene (TCI), 4-methoxystyrene (TCI), 4-trifluoromethylstyrene (TCI), 2-vinylnaphtalene (TCI), α-methylstyrene (TCI), *trans*-stilbene (TCI), *cis*-stilbene (TCI), indene (TCI), dihydronaphthalene (TCI), allyltrimethylsilane (TCI), cyclohexene (TCI), 2,5-norbornadiene (TCI), 3,4-dihydro-2*H*-pyran (TCI), 2,3-benzofuran (TCI), 2-cyclopentene-1-one (TCI), triethylamine (Nakarai tesque), diisopropylamine (Nacalai tesque), 4-(dimethylamino)pyridine (TCI), acetic anhydride (TCI), pivalic anhydride (TCI), 2-methylbut-3-yn-2-ol (TCI), iodomethane (TCI), *n*-BuLi (1.6 M in hexane) (Fujifilm WAKO), ethynylmagnesium chloride (Aldrcih), trimethylsilylacetylene (TCI), chlorotrimethylsilane (TCI), chlorotriisopropylsilane (TCI), $(Ph_3P)_3AuCl$ (TCI), (IPr)AuCl (Aldrich), $AgSbF_6$ (Aldrich), $AgBF_4$ (Aldrich), $AgNTf_2$ (TCI), AuCl (Aldrich), $AuBr_3$ (Aldrich), $JohnPhosAuSbF_6{\cdot}CH_3CN$ (Aldrich), D_2O (Merck KGaA), CD_3OD (Merck KGaA), and $CDCl_3$ (ISOTEC) were purchased.

2-(Prop-2-en-1-yl)benzaldehyde,[2] 2-(but-3-en-1-yl)benzaldehyde,[3] $(4\text{-}CF_3C_6H_4)_3PAuCl$,[4] $(4\text{-}MeOC_6H_4)_3PAuCl$,[4] and 1-(3-butenyl)-2-vinylbenzene[5,6] were prepared according to literature procedure.

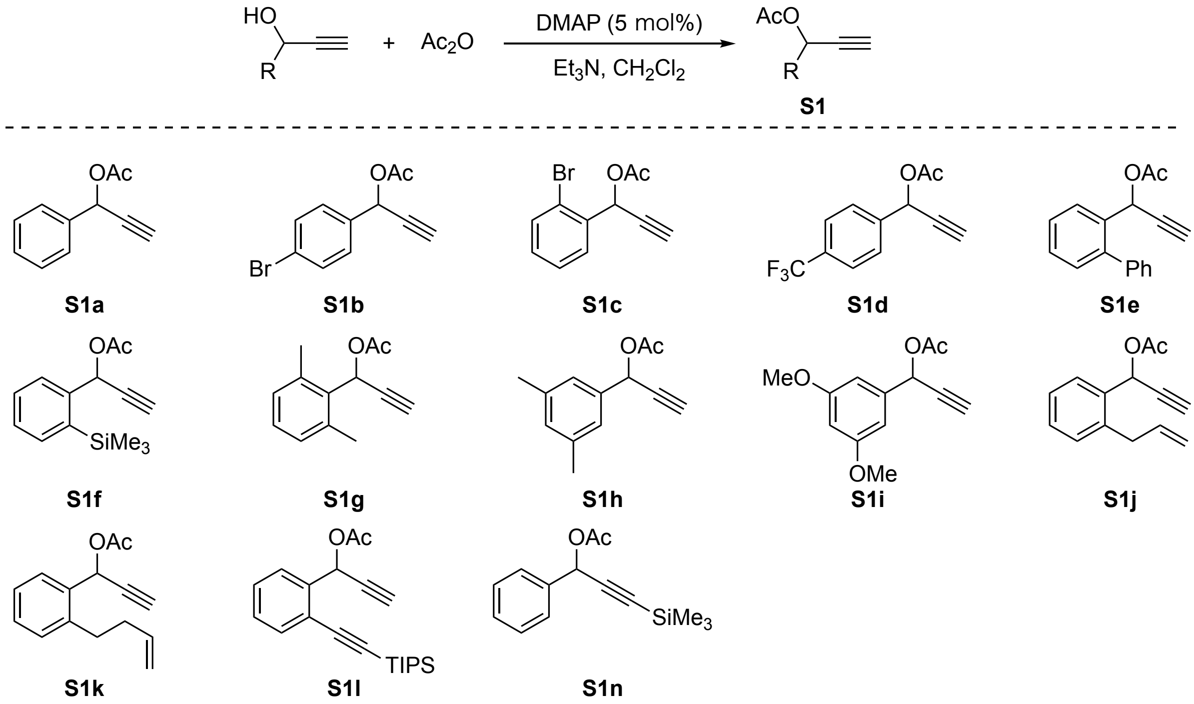
1-Phenyl-3-(trimethylsilyl)prop-2-yn-1-ol was synthesized previously.[7]

General Procedure for the Preparation of Propargyl Alcohols



(Adapted from a reported procedure)[7]: To a solution of aldehyde (1 equiv) in THF was added slowly ethynylmagnesium chloride (0.5 M in THF, 1.2 equiv) at 0 °C under argon atmosphere. The reaction mixture was allowed to warm up to room temperature, and the progress of the reaction was monitored by TLC. Upon completion, the reaction mixture was diluted with ethyl acetate, washed with water, saturated aqueous NH_4Cl, and then brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was used for the next reaction without further purification.

General Procedure for the Preparation of Propargylic Acetates



(Adapted from a reported procedure)[7]: A typical procedure for the preparation of propargyl alcohols is described for the reaction using 1-(1,1′-biphenyl)-2-ylprop-2-yn-1-ol: To a solution of crude 1-phenyl-2-propyn-1-ol (**S1**) (3.4 mmol), 4-(dimethylamino)pyridine (20.8 mg, 0.17 mmol) and triethylamine (710 μL, 5.1 mmol) in DCM (15 mL) was added acetic anhydride (388 μL, 4.1 mmol) at 0 °C under argon atmosphere. After stirring at room temperature for 2 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (2 × 20 mL). The aqueous phase was extracted with DCM (2 × 10 mL), and the combined organic extracts were washed with brine (2 × 20 mL). After the organic layer was dried over $MgSO_4$, the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (R_f = 0.50, EtOAc/hexane = 3/7) to give 1-phenyl propargyl acetate (**S1e**) as a colorless oil (0.74 g, 88% for two steps). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.85-7.81 (m, 1H), 7.48-7.35 (m, 5H), 7.35-7.27 (m, 3H), 7.32 (d, J = 2.4 Hz, 1H), 2.63 (d, J = 2.4 Hz, 1H), 2.00 (s, 3H).; **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 169.18, 141.57, 139.81, 134.31, 130.21, 129.10, 128.89, 128.36, 128.09, 127.96, 127.65, 80.94, 75.49, 63.14, 20.83.; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}O_2$: 251.1072, found: 251.1067.

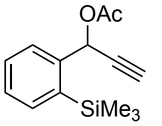
Propargyl esters: 1-phenylprop-2-yn-1-yl acetate (**S1a**), (*R*)-1-phenylprop-2-yn-1-yl acetate ((***R***)- **S1a**), 1-(4-bromophenyl)prop-2-yn-1-yl acetate (**S1b**), 1-(2-bromophenyl)prop-2-yn-1-yl acetate (**S1c**), 1-[4-(trifluoromethyl)phenyl]prop-2-yn-1-yl acetate (**S1d**), and 1-phenyl-3-(trimethylsilyl)prop-2-yn-1-yl acetate

(**S1n**), 1-phenylprop-2-yn-1-yl pivalate (**S1o**), and ethyl 1-phenylprop-2-yn-1-yl carbonate (**S1p**) were synthesized previously.[8]

1-(2,6-Dimethylphenyl)prop-2-yn-1-yl acetate (**S1g**),[9] 1-(3,5-dimethoxyphenyl)prop-2-yn-1-yl acetate (**S1i**),[10] 1-(2-allylphenyl)prop-2-yn-1-yl acetate (**S1j**),[11] and 1-(2-(but-3-enyl)phenyl)prop-2-ynyl acetate (**S1k**)[11] were synthesized according to the reported procedure.

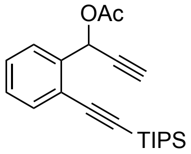
Compounds **S1f** and **S1l** are new compounds.

1-(2-trimethylsilylphenyl)prop-2-yn-1-yl acetate (S1f):



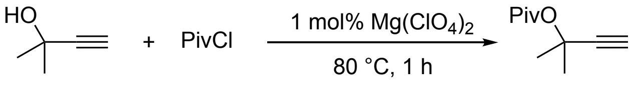
Following the general procedures, **S1f** was purified by silica gel column chromatography (16.3 mmol scale reaction, yellow oil, 3.46 g, 80% yield over two steps, R_f 0.55, EtOAc/hexane = 1/4). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.76 (dd, *J* = 0.8, 8.0 Hz, 1H), 7.53 (dd, *J* = 0.8, 7.2 Hz, 1H), 7.46 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.35 (dt, *J* = 1.2, 7.6 Hz, 1H), 6.51 (d, *J* = 2.0 Hz, 1H), 2.63 (d, *J* = 2.4 Hz, 1H), 2.12 (s, 3H), 0.38 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 169.8, 142.2, 138.5, 134.7, 129.9, 128.4, 128.2, 81.4, 75.6, 65.5, 21.2, 0.4; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{14}H_{18}O_2Si^+$: 246.1076, found: 246.1076.

1-(2-((Triisopropylsilyl)ethynyl)phenyl)prop-2-yn-1-yl acetate (S1l):



Following the general procedures, **S1l** was purified by silica gel column chromatography (7.4 mmol scale reaction, brown oil, 2.0 g, 77% yield over two steps, R_f 0.63, EtOAc/hexane = 3/7); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.72 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.52 (dd, *J* = 1.6, 7.2 Hz, 1H), 7.38 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.32 (dt, *J* = 1.6, 7.2 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 2.61 (d, *J* = 2.4 Hz, 1H), 2.10 (s, 3H), 1.19-1.11 (m, 21H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ:169.3, 138.1, 133.2, 128.9, 127.6, 122.9, 103.3, 97.3, 80.2, 75.3, 63.9, 20.1, 18.8, 11.4; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{22}H_{31}O_2Si^+$: 355.2093, found: 355.2086.

Preparation of 2-Methylbut-3-yn-2-yl Pivalate (S1m)[12]

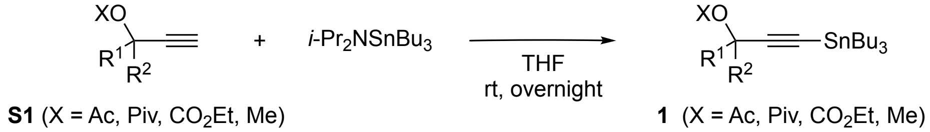


(Adapted from a reported procedure): 2-methylbut-3-yn-2-ol (4.9 mL, 50 mmol), pivalic anhydride (11.2 mL, 55 mmol, 1.1 equiv), and magnesium perchlorate (111.6 mg, 0.5 mmol, 1 mol%) were combined and the reaction mixture was stirred at 80 °C for 2 h. After cooling to room temperature, the resulting black mixture was diluted with saturated $NaHCO_3$ solution and extracted with diethyl ether. The combined organic layers were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Purification by fractionated distilling afforded 2-methylbut-3-yn-2-yl pivalate as colorless oil (3.5 g, 20.8 mmol, 42%, R_f = 0.68, EtOAc/hexane = 3/7).

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

^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.50 (s, 1H), 1.65 (s, 6H), 1.18 (s, 9H).

General Procedure for the Preparation of Stannylated Propargyl Esters (1)[8]



S1 (X = Ac, Piv, CO_2Et, Me) **1** (X = Ac, Piv, CO_2Et, Me)

(Adapted from a reported procedure)[8]: Diisopropylamine (850 µL, 6.0 mmol) was diluted with dry THF (3.3 mL) and cooled to -78 °C. *n*-BuLi (1.6 M in hexanes, 3.7 mL, 5.9 mmol) was added dropwise under an argon atmosphere. Upon completion of the addition, the mixture was warmed to room temperature and stirred for 1 hour. A solution of tributyltin chloride (1.62 mL, 6.0 mmol) in dry THF (1.5 mL) was added to the reaction mixture at room temperature, causing an immediate color change to milky white. After it was heated to 50 °C for 4 hours in an oil bath (pale yellow cloudy suspension), the supernatant was used for the next reaction without further purification.

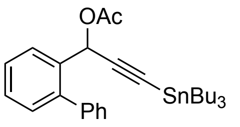
(Diisopropylamino)tributylstannane (0.55 M in THF, 1.36 mL, 0.75 mmol) was added to a flask charged with stannylated propargyl esters **1** (0.5 mmol) at room temperature under an argon atmosphere, and then it was stirred overnight at room temperature. After the reaction completed checked with TLC, the reaction mixture was quenched with water. The aqueous phase was extracted with diethyl ether (2 × 30 mL), and the combined organic extracts were washed with brine (30 mL). After the organic layer was dried over $MgSO_4$, the solvent was removed under reduced pressure. The residue was purified by neutral silica gel chromatography.

Substrates: 1-phenyl-3-(tributylstannyl)prop-2-yn-1-yl acetate (**1a**), 1-(4-bromophenyl)-3-(tributylstannyl)prop-2-yn-1-yl acetate (**1b**), 1-(2-bromophenyl)-3-(tributylstannyl)prop-2-yn-1-yl acetate (**1c**), 1-(4-trifluoromethylphenyl)-3-(tributylstannyl)prop-2-yn-1-yl acetate (**1d**), 1-(1,1′-biphenyl)-2-yl-3-(tributylstannyl)prop-2-yn-1-yl acetate (**1e**), 1-(2-trimethylsilylphenyl)-3-(tributylstannyl)prop-2-yn-1-yl acetate (**1f**), 1-(2,6-dimethylphenyl)-3-(tributylstannyl)prop-2-yn-1-yl acetate (**1g**), 1-(3,5-dimethylphenyl)-3-(tributylstannyl)prop-2-yn-1-yl acetate (**1h**), 1-(3,5-dimethoxyphenyl)-3-(tributylstannyl)prop-2-yn-1-yl acetate (**1i**), 1-(2-allylphenyl)-3-(tributylstannyl)prop-2-yn-1-yl acetate (**1j**), 1-(2-homoallylphenyl)-3-(tributylstannyl)prop-2-yn-1-yl acetate (**1k**), and 3-(tributylstannyl)-1-(2-((triisopropylsilyl)ethynyl)phenyl)prop-2-yn-1-yl acetate (**1l**), and 3-Methyl-1-(tributylstannyl)but-1-yn-3-yl pivalate (**1m**), 1-phenyl-3-(tributhylstannyl)prop-2-yn-1-yl pivalate (**1o**), ethyl (1-phenyl-3-

(tributylstannyl)prop-2-yn-1-yl) carbonate (**1p**) were known compounds and synthesized according to the general procedures.[8]

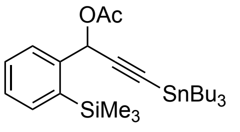
Compounds **1e**, **1f**, **1j–1l**,**1n**, and **1q** ae new compounds.

1-(1,1′-Biphenyl)-2-yl-3-(tributylstannyl)prop-2-yn-1-yl acetate (1e):



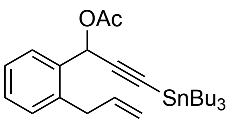
Following the general procedures, **1e** was purified by silica gel column chromatography (3.0 mmol scale reaction, yellow oil, 1.10 g, 68% yield, R_f 0.63, EtOAc/hexane = 3/7). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.87 (dd, J = 1.6, 7.6 Hz, 1H), 7.45-7.32 (m, 7H), 7.25 (dd, J = 1.6, 7.2 Hz, 1H), 6.34 (t, J = 4.0 Hz, 1H), 1.96 (s, 3H), 1.60-1.50 (m, 6H), 1.32 (sext., J = 3.2 Hz, 6H), 0.99 (t, J = 8.0 Hz, 6H), 0.88 (t, J = 7.2 Hz, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 169.10, 141.43, 140.14, 135.56, 130.00, 129.17, 128.44, 128.21, 128.19, 127.73, 127.43, 106.63, 91.70, 64.08, 28.85 ($J_{Sn\text{-}C}$ = 23.1 Hz), 26.93 ($J_{Sn\text{-}C}$ = 58.5 Hz), 20.95, 13.67, 11.15 ($J_{Sn(119)\text{-}C}$ = 379.5 Hz, $J_{Sn(117)\text{-}C}$ = 362.9 Hz); **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{29}H_{41}O_2Sn^+$: 541.2129, found: 541.2124.

1-(2-Trimethylsilylphenyl)-3-(tributylstannyl)prop-2-yn-1-yl acetate (1f):



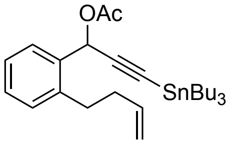
Following the general procedures, **1f** was purified by silica gel column chromatography (7.0 mmol scale reaction, yellow oil, 1.49 g, 40% yield, R_f 0.67, EtOAc/hexane = 3/7). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.30 (d, J = 7.6 Hz, 1H), 7.43 (dd, J = 1.2, 7.6 Hz, 1H), 7.30 (dt, J = 1.6, 7.6 Hz, 1H), 7.11 (dt, J = 1.2, 7.6 Hz, 1H), 7.05 (s, 1H), 1.64 (s, 3H), 1.60-1.50 (m, 6H), 1.63-1.53 (m, 6H), 1.30 (sext, J = 7.2 Hz, 6H), 1.05- 0.95 (m, 6H), 0.89 (t, J = 7.2 Hz, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 169.0, 144.5, 138.3, 134.8, 129.9, 128.6, 128.2, 108.5, 91.3, 66.6, 29.3 ($J_{Sn\text{-}C}$ = 23.3 Hz), 27.3 ($J_{Sn\text{-}C}$ = 57.9 Hz), 20.7, 13.9, 11.3 ($J_{Sn(119)\text{-}C}$ = 379 Hz, $J_{Sn(117)\text{-}C}$ = 362 Hz), 0.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{26}H_{45}O_2SiSn^+$: 537.2211, found: 537.2209.

1-(2-allylphenyl)-3-(tributylstannyl)prop-2-yn-1-yl acetate (1j):



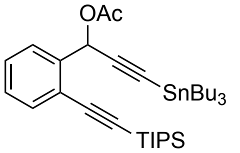
Following the general procedures, **1j** was purified by silica gel column chromatography (4.0 mmol scale reaction, yellow oil, 1.73 g, 86% yield, R_f 0.63, EtOAc/hexane = 3/7). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.70 (dd, J = 1.6, 7.6 Hz, 1H), 7.32-7.22 (m, 2H), 7.20 (dd, J = 1.6, 7.6 Hz, 1H), 6.60 (t, J = 4.0 Hz, 1H),5.97 (ddt, J = 10.0, 16.8, 6.0 Hz, 1H) 5.07 (dq, J = 10.0, 1.7 Hz, 1H), 5.01 (dq, J = 17.1, 1.7 Hz, 1H), 3.61-3.44 (m, 2H), 2.07 (s, 3H), 1.60-1.50 (m, 6H), 1.32 (sext, J = 7.2 Hz, 6H), 0.99 (t, J = 8.0 Hz, 6H), 0.88 (t, J = 7.2 Hz, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 169.6, 137.9, 136.8, 135.7, 130.1, 128.9, 128.6, 126.6, 116.1, 106.0, 91.5, 64.0, 36.7, 29.0 ($J_{Sn\text{-}C}$ = 22.9 Hz), 27.0 ($J_{Sn\text{-}C}$ = 57.4 Hz), 21.2, 13.7, 11.1 ($J_{Sn(119)\text{-}C}$ = 379.7 Hz, $J_{Sn(117)\text{-}C}$ = 362.2 Hz); **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{18}H_{41}O_2Sn^+$: 505.2129, found: 505.2136.

1-(2-(but-3-enyl)phenyl)-3-(tributylstannyl)prop-2-yn-1-yl acetate (1k):



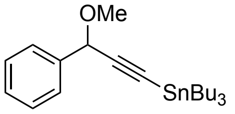
Following the general procedures, **1k** was purified by silica gel column chromatography (2.5 mmol scale reaction, yellow oil, 470.3 mg, 37% yield, R_f0.81, EtOAc/hexane = 3/7). **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.68 (dd, J = 1.2, 7.2 Hz, 1H), 7.30-7.18 (m, 3H), 6.62 (s, 1H), 5.58 (ddt, J = 10.0, 16.4, 6.4 Hz, 1H), 5.06 (dq, J = 17.2, 1.6 Hz, 1H), 4.99 (dq, J = 8.0, 1.2 Hz, 1H), 2.90 (ddd, J = 6.8, 8.8, 14.4 Hz, 1H), 2.77 (ddd, J = 6.8, 8.8, 14.4 Hz, 1H), 2.34 (dm, J = 14.4 Hz, 2H), 2.09 (s, 3H), 1.57-1.50 (m, 6H), 1.36-1.26 (m, 6H), 0.99 (t, J = 7.6 Hz, 6H), 0.88 (t, J = 7.3 Hz, 9H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 196.7, 139.9, 138.0, 135.7, 129.8, 128.8, 128.6, 126.4, 115.2, 106.4, 91.5, 64.0, 35.3, 31.9, 28.9 ($J_{Sn\text{-}C}$ = 22.9 Hz), 27.0 ($J_{Sn\text{-}C}$ = 58.2 Hz), 21.3, 13.8, 11.2 ($J_{Sn(119)\text{-}C}$ = 379.4 Hz, $J_{Sn(117)\text{-}C}$ = 363.3 Hz); **HRMS (ESI-TOF)** m/z: [M–Bu]$^+$ Calcd for C$_{23}$H$_{33}$O$_2$Sn$^+$: 461.1503, found: 461.1503.

3-(Tributylstannyl)-1-(2-((triisopropylsilyl)ethynyl)phenyl)prop-2-yn-1-yl acetate (1l):



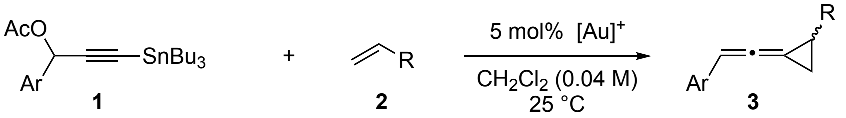
Following the general procedures, **1l** was purified by silica gel column chromatography (5.67 mmol scale reaction, pale brown oil, 731 mg, 20% yield, R_f0.75, EtOAc/hexane = 3/7). **^{1}H NMR** (C$_6$D$_6$, 400 MHz) δ 8.04 (d, J = 8.0 Hz, 1H), 7.43-7.33 (m, 2H), 7.06 (td, J = 1.2, 7.6 Hz, 1H), 6.85 (td, J = 1.2, 7.6 Hz, 1H), 1.68-1.50 (m, 9H), 1.36-1.13 (m, 27H), 0.97-0.84 (m, 15H); **^{13}C NMR** (C$_6$D$_6$, 100 MHz) δ 168.6, 140.5, 133.2, 128.9, 128.7, 123.2, 107.1, 104.5, 96.7, 91.1, 64.8, 29.3 ($J_{\text{Sn-C}}$ = 23.2 Hz), 27.3 ($J_{\text{Sn-C}}$ = 58.8 Hz), 20.6, 19.0, 13.9, 11.8 ($J_{\text{Sn(119)-C}}$ = 379.2, $J_{\text{Sn(117)-C}}$ = 362.4 Hz), 11.3; **HRMS (ESI-TOF)** m/z: [M+H]$^+$ Calcd for C$_{34}$H$_{56}$O$_2$SiSn$^+$: 645.3150, found: 645.3146.

3-Methoxy-3-phenyl-1-(tributylstannyl)prop-1-yn (1q):



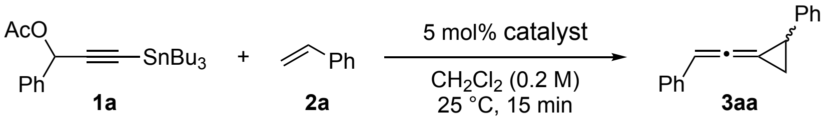
Following the general procedures, **1q** was prepared using (1-methoxyprop-2-ynyl)benzene[14,15] and purified by silica gel column chromatography (5.3 mmol scale reaction, yellow oil, 278.0 mg, 12%, $R_{f,}$ = 0.69, EtOAc/hexane = 3/7). **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.74-7.61 (m, 2H), 7.21-7.16 (m, 2H), 7.10-7.03 (m, 1H), 5.16 (s, 1H), 3.38 (s, 3H), 1.68-1.59 (m, 6H), 1.41-1.27 (sext, J = 7.4 Hz, 6H), 1.02-0.95 (m, 6H), 0.89 (t, J = 7.3 Hz, 9H); **^{13}C NMR** (CD$_3$OD, 100 MHz) δ 140.3, 129.30, 129.26, 128.7, 108.4, 92.5, 74.7, 55.8, 30.1 ($J_{Sn\text{-}C}$ = 24.5 Hz), 28.0 ($J_{Sn\text{-}C}$ = 56.1 Hz), 14.1, 12.0 ($J_{Sn(117)\text{-}C}$ = 386 Hz, $J_{Sn(119)\text{-}C}$ = 389 Hz); **HRMS (ESI-TOF)** m/z: [M–Bu]$^+$ Calcd for C$_{18}$H$_{27}$OSn: 379.1084, found: 379.1101.

General Procedure for Gold(I)-Catalyzed Cyclopropanation of Vinyl Arenes



The cationic gold catalyst was generated in a 1 dram vial with a threaded cap by addition of (Ph$_3$P)AuCl (5.0 mg, 0.01 mmol, 5 mol%), AgSbF$_6$ (3.4 mg, 0.01 mmol, 5 mol%), and dichloromethane (1 mL). After allowing the catalyst mixture to sit for 10 minutes at room temperature, the precipitate was filtered off. The resulting solution was added to the starting material **1** (0.2 mmol) and vinyl arenes **2** (2.0 mmol) in dichloromethane (4 mL), and stirred at 25 °C. The reaction mixture (0.04 M) was monitored by TLC until all starting material was consumed. Upon completion, the reaction mixture was concentrated and loaded directly onto a silica gel column chromatography resulted in isolation of analytically pure product **3**.

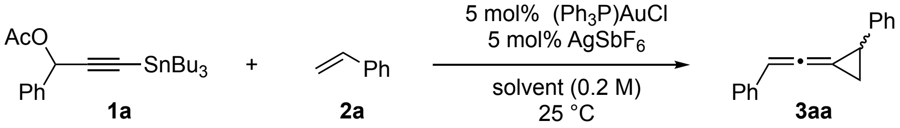
Table S1. Optimization of the Reaction.[a]



entry	catalyst	time	**3aa** (%)[b]	d.r.
1	(Ph$_3$P)AuCl/AgSbF$_6$	15 min	57	2:1
2[c]	(Ph$_3$P)AuCl/AgSbF$_6$	15 min	27	2:1
3	JohnPhosAuSbF$_6$·MeCN	7 h	57	1.3:1
4	(4-CF$_3$C$_6$H$_4$)$_3$PAuCl/AgSbF$_6$	15 min	50	1.8:1
5	(4-MeOC$_6$H$_4$)$_3$PAuCl/AgSbF$_6$	15 min	47	1.8:1
6	(*t*-Bu$_3$P)AuCl/AgSbF$_6$	1 h	48	2:1
7	(IPr)AuCl/AgSbF$_6$	24 h	14	1.2:1
8	(Ph$_3$P)AuCl/AgNTf$_2$	12 h	47	1.7:1
9	(Ph$_3$P)AuCl/AgBF$_4$	3 h	20	2:1
10	(Ph$_3$P)AuCl/NaBAr$^F_4$	48 h	26	1.5:1
11	AuCl	48 h	51	1:1
12	AuBr$_3$	28 h	31	1:1
13	(Ph$_3$P)AuCl/AgSbF$_6$	12	39	1.2:1
14[d]	(Ph$_3$P)AuCl/AgSbF$_6$	15 min	68	2:1
15	AgSbF$_6$	24 h	0	

[a]Reactions were carried out using **1a** (0.2 mmol), **2a** (2 mmol), Au (5 mol%), Ag (5 mol%), solvent (1 mL) at 25 °C. [b]Isolated yield. [c]**2a** (1 mmol) was used [d]0.04 M concentration. JohnPhos = (2-biphenylyl)di-*tert*-butylphosphine. IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

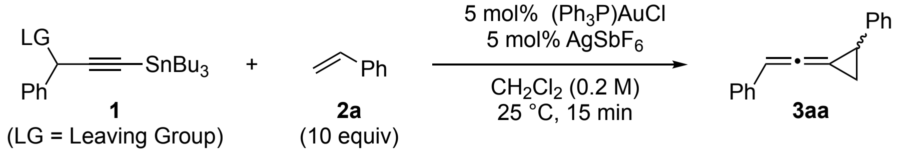
Table S2. Effects of Solvent.[a]



entry	solvent	**3aa** (%)	d.r.
1	CH_2Cl_2	57	2:1
2[b]	CH_2Cl_2	39	1.9:1
3	$ClCH_2CH_2Cl$	20	1.6:1
4	THF	0	
5	$MeNO_2$	22	–
6	EtOH	0	

[a]Reactions were carried out using **1a** (0.2 mmol), **2a** (2 mmol), $(Ph_3P)AuCl$ (5 mol%), $AgSbF_6$ (5 mol%), CH_2Cl_2 (1 mL) at 25 °C. [b]H_20 (0.2 mmol, 1 equiv) was added.

Table S3. Effects of the Leaving Group.[a]

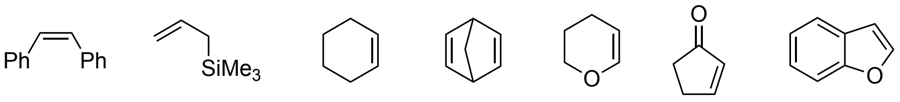


entry	**1**: LG	temp(°C)/time	**3aab** (%)	d.r.
1	**1a**: OAc	25/15 min	68	2:1
2	**1o**: OPiv	25/24 h	7	1.3:1
3	**1o**: OPiv	50/30 h	45	1:1
4	**1p**: OCO_2Et	25/15 min	10	2:1
5	**1q**: OMe	25/18 h	0	

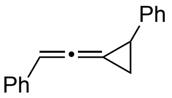
[a]Reactions were carried out using **1a** (0.2 mmol), **2a** (2 mmol), $(Ph_3P)AuCl$ (5 mol%), $AgSbF_6$ (5 mol%), CH_2Cl_2 (1 mL) at 25 °C.

When the substrate having an aryl group at the propargylic position of **1** was employed for the alkene cyclopropanation, the use of an acetoxy leaving group afforded a cyclopropanation product. On the other hand, when an alkyl substituent instead of an aryl substituent was used, a pivaloyloxy group was preferred as a leaving group. For example, although the gold(I)-catalyzed reaction of **1m** and **2c** afforded **3mc** in 20% yield, trace amount of **3mc** was observed when the substrate having an acetoxy group instead of a pivaloyloxy group of **1m** was used.

Unsuccessful Alkenes:



[2-(Phenylethenylidene)cyclopropyl]benzene (3aa)



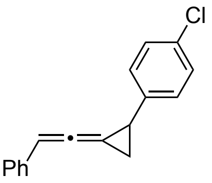
Following the general procedures, **3aa** was purified by silica gel column chromatography (0.2 mmol scale reaction, colorless oil, 30.1 mg, 69% yield, R_f 0.56, EtOAc/hexane = 1/9).

Major isomer: ^{1}**H NMR** (CDCl$_3$, 400 MHz) δ 7.24-7.09 (m, 10H), 6.31-6.27 (m, 1H), 3.11 (ddd, J = 3.2, 5.6, 8.4 Hz, 1H), 2.20 (ddd, J = 4.0, 7.6, 8.4 Hz, 1H), 1.76 (ddd, J = 4.0, 6.0, 7.6 Hz, 1H); ^{13}**C NMR** (CDCl$_3$, 100 MHz) δ 190.1, 140.4, 135.7, 128.7, 128.6, 126.79, 126.76 (two peaks), 126.6, 97.6, 85.8, 25.9, 18.6.

Minor isomer: ^{1}**H NMR** (CDCl$_3$, 400 MHz) δ 7.24-7.09 (m, 10H), 6.31-6.27 (m, 1H), 3.04 (ddd, J = 3.2, 5.6, 8.4 Hz, 1H), 2.14 (ddd, J = 4.0, 7.6, 8.4 Hz,1H), 1.83 (ddd, J = 4.0, 6.0, 7.6 Hz, 1H); ^{13}**C NMR** (CDCl$_3$, 100 MHz) δ 190.2, 140.6, 135.8, 128.7, 128.6, 126.9, 126.79, 126.76, 126.6, 97.9, 85.8, 26.3, 18.6.

HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for C$_{17}$H$_{15}$$^+$: 219.1174, found: 219.1170.

1-Chloro-4-[2-(phenylethenylidene)cyclopropyl]benzene (3ab)



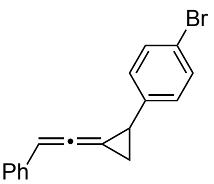
Following the general procedures, **3ab** was purified by silica gel column chromatography (0.2 mmol scale reaction, orange oil, 26.2 mg, 52% yield, R_f 0.5, EtOAc/hexane = 1/9).

Major isomer: ^{1}**H NMR** (CDCl$_3$, 400 MHz) δ 7.24-7.08 (m, 9H), 6.32 (q, J = 3.6 Hz, 1H), 3.08 (ddd, J = 3.2, 5.6, 8.8 Hz, 1H), 2.23 (ddd, J = 4.0, 7.2, 8.4 Hz, 1H), 1.73 (ddd, J = 4.0, 5.6, 7.6 Hz, 1H); ^{13}**C NMR** (CDCl$_3$, 100 MHz) δ 190.1, 138.9, 135.4, 132.3, 128.73, 128.71, 128.1, 126.9, 126.8, 98.2, 85.5, 25.2, 18.6.

Minor isomer: ^{1}**H NMR** (CDCl$_3$, 400 MHz) δ 7.40-7.36 (m, 2H), 7.24-7.08 (m, 9H), 6.31 (q, J = 3.6 Hz, 1H), 3.01 (ddd, J = 3.2, 5.6, 8.8 Hz, 1H), 2.16 (ddd, J = 4.0, 7.2, 8.4 Hz, 1H), 1.81 (ddd, J = 4.0, 5.6, 7.6 Hz, 1H); ^{13}**C NMR** (CDCl$_3$/100 MHz) δ 190.2, 139.1, 135.5, 132.3, 128.8, 128.7, 128.3, 126.9, 126.7, 98.2, 85.7, 25.6, 18.5.

HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for C$_{17}$H$_{14}$Cl$^+$: 253.0784, found: 252.0786

1-Bromo-4-[2-(phenylethenylidene)cyclopropyl]benzene (3ac)



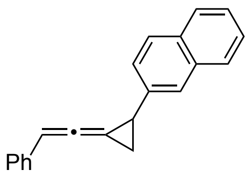
Following the general procedures, **3ac** was purified by silica gel column chromatography (0.2 mmol scale reaction, yellow oil, 23.8 mg, 40% yield, R_f 0.55, EtOAc/hexane = 1/9).

Major isomer: ^{1}**H NMR** (CDCl$_3$, 400 MHz) δ 7.40-7.36 (m, 2H), 7.26-7.20 (m, 4H), 7.13-7.02 (m, 3H), 6.34 (q, J = 3.6 Hz, 1H), 3.09 (ddd, J = 3.6, 6.0, 9.2 Hz, 1H), 2.25 (ddd, J = 4.0, 7.0, 8.8 Hz, 1H), 1.76 (ddd, J = 3.6, 6.0, 7.2 Hz, 1H); ^{13}**C NMR** (CDCl$_3$/100 MHz) δ 190.1, 139.5, 135.4, 131.4, 128.7, 128.5, 126.9, 126.8, 120.3, 98.2, 85.5, 25.3, 18.5.

Minor isomer: ^{1}**H NMR** (CDCl$_3$, 400 MHz) δ 7.40-7.36 (m, 2H), 7.26-7.20 (m, 4H), 7.13-7.02 (m, 3H), 6.34 (q, J = 3.6 Hz, 1H), 3.02 (ddd, J = 3.6, 6.0, 9.2 Hz, 1H), 2.18 (ddd, J = 4.0, 7.0, 8.8 Hz, 1H), 1.83 (ddd, J = 3.6, 6.0, 7.2 Hz, 1H); ^{13}**C NMR** (CDCl$_3$/100 MHz) δ 190.2, 139.7, 135.5, 131.7, 128.8, 128.6, 126.9, 126.7, 120.3, 98.2, 85.6, 25.6, 18.5.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}Br^+$: 297.0279, found: 297.0268.

[2-(2-Naphthylethenylidene)cyclopropyl]benzene (3af)



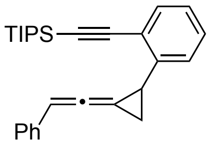
Following the general procedures, **3af** was purified by silica gel column chromatography (0.2 mmol scale reaction, yellow oil, 38.1 mg, 71% yield, R_f 0.56, EtOAc/hexane = 1/9).

Major isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.82-7.70 (m, 4H), 7.48-7.40 (m, 3H), 7.35-7.26 (m, 4H), 7.20-7.15 (m, 1H) 6.41(m, 1H), 3.36 (ddd, J = 8.8, 5.6, 3.3 Hz, 1H), 2.37 (ddd, J = 8.8, 7.2, 4.0 Hz, 1H), 1.97 (ddd, J = 7.2, 5.6, 3.8 Hz, 1H);**^{13}C NMR** ($CDCl_3$, 100 MHz) δ 190.45, 137.96, 135.77, 133.58, 132.48, 128.75, 128.34, 127.79, 127.62, 126.81 (two peaks), 126.35, 125.70, 125.63, 124.94, 97.98, 85.79, 26.14, 18.63.

Minor isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.82-7.70 (m, 4H), 7.48-7.40 (m, 3H), 7.35-7.26 (m, 4H), 7.20-7.15 (m, 1H) 6.41(m, 1H), 3.30 (ddd, J = 8.8, 5.6, 3.2 Hz, 1H) 2.31 (ddd, J = 8.8, 7.2, 4.0 Hz, 1H), 2.02 (ddd, J =7.2, 5.6, 3.8 Hz, 1H);**^{13}C NMR** ($CDCl_3$, 100 MHz) δ 190.18, 137.84, 135.65, 133.58, 132.48, 128.72, 128.32, 127.79, 127.62, 126.82 (two peaks), 126.30, 125.59, 125.34, 125.07, 97.98, 85.74, 26.52, 18.55.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}^+$: 269.1330, found: 269.1332.

1-Triisopropylsilylethynyl-2-[2-(phenylethenylidene)cyclopropyl]benzene (3ag)



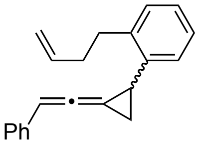
Following the general procedures, **3ag** was purified by silica gel column chromatography (0.2 mmol scale reaction, yellow oil, 44.6 mg, 56% yield, R_f 0.60, EtOAc/hexane = 1/9).

Major isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.48 (d, J = 7.6 Hz, 1H), 7.33-7.12 (m, 8H), 6.40 (m, 1H), 3.65 (ddd, J = 3.2, 5.6, 8.8 Hz, 1H), 2.33 (ddd, J = 4.0, 7.0, 8.8 Hz, 1H), 1.86 (ddd, J = 4.0, 6.0, 7.0 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 190.63, 142.33, 135.79, 132.76, 128.77, 128.66, 126.80, 126.78, 126.44, 125.63, 123.91, 105.33, 95.36, 97.86, 85.45, 25.37, 18.85, 18.50, 11.48.

Minor isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.48 (d, J = 7.6 Hz, 1H), 7.33-7.12 (m, 8H), 6.40 (m, 1H), 3.58 (ddd, J = 3.2, 5.6, 8.8 Hz, 1H), 2.27 (ddd, J = 4.0, 7.0, 8.8 Hz, 1H), 1.82 (ddd, J = 4.0, 6.0, 7.0 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 190.43, 142.18, 135.66, 132.75, 128.75, 126.87, 126.77, 126.39, 125.22, 123.88, 105.33, 97.84, 95.36, 85.34, 29.86, 24.71, 18.85, 18.50, 11.45.

HRMS (ESI-TOF) m/z: $[M-TIPS]^+$ Calcd for $C_{19}H_{13}^+$: 243.1174, found: 243.1168.

1-(But-3-en-1-yl)-2-[2-(phenylethenylidene)cyclopropyl]benzene (3ah)



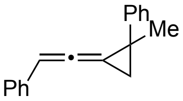
Following the general procedures, **3ah** was purified by silica gel column chromatography (0.24 mmol scale reaction, colorless oil, 37.5 mg, 57% yield, R_f 0.57, EtOAc/hexane = 1/9).

Major isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.35-7.26 (m, 4H), 7.22-7.11 (m, 5H), 6.43-6.37 (m, 1H), 5.94-5.81 (m, 1H), 5.04 (dm, J = 16.8 Hz, 1H), 4.97 (dm, J = 10.0 Hz, 1H), 3.28 (ddd, J = 3.6, 6.0, 8.8 Hz, 1H), 2.93-2.83 (m, 2H), 2.41-2.35 (m, 2H), 2.31 (ddd, J = 3.6, 6.8, 8.4 Hz, 1H), 1.80 (ddd, J = 4.0, 6.4, 6.8 Hz, 1H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 190.6, 141.3, 138.3, 137.4, 135.8, 129.1, 128.7, 127.03, 126.97, 126.7, 126.3, 115.1, 97.8, 85.0, 34.9, 32.5, 23.6, 17.7.

Minor isomer: **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.35-7.26 (m, 4H), 7.22-7.11 (m, 5H), 6.43-6.37 (m, 1H), 5.94-5.81 (m, 1H), 5.04 (dm, J = 16.8 Hz, 1H), 4.97 (dm, J = 10.0 Hz, 1H), 3.21 (ddd, J = 3.6, 6.0, 8.8 Hz, 1H), 2.93-2.83 (m, 2H), 2.41-2.35 (m, 2H), 2.24 (ddd, J = 3.6, 6.8, 8.4 Hz, 1H), 1.86 (ddd, J = 4.0, 6.4, 6.8 Hz, 1H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 190.7, 141.4, 138.3, 137.4, 135.8, 129.0, 128.7, 127.1 (2 C), 126.81, 126.75, 126.5, 115.1, 97.8, 85.2, 34.8, 32.4, 24.2, 17.7.

HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{21}H_{21}^+$: 273.1643, found: 273.1652.

[1-Methyl-2-(phenylethenylidene)cyclopropyl]benzene (3ai)



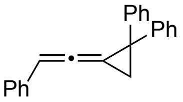
Following the general procedures, **3ai** was purified by silica gel column chromatography (0.2 mmol scale reaction, yellow oil, 7.9 mg, 17% yield, R_f 0.59, EtOAc/hexane = 1/9).

Major isomer: **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.44-7.35 (m, 2H), 7.35-7.27 (m, 4H), 7.26-7.10 (m, 4H), 6.38-6.31 (m, 1H), 2.05 (dd, J =2.0, 4.0 Hz, 1H), 1.99 (ddd, J = 4.0, 9.6 Hz, 1H), 1.68 (s, 3H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 189.3, 143.8, 136.1, 128.7 (2 peaks), 128.5, 126.9, 126.64, 126.60, 90.4, 31.2, 25.5, 25.2.

Minor isomer: **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.44-7.35 (m, 2H), 7.35-7.27 (m, 4H), 7.26-7.10 (m, 4H), 6.38-6.31 (m, 1H), 2.07 (dd, J =2.0, 4.0 Hz, 1H), 1.98 (ddd, J = 4.0, 9.6 Hz, 1H), 1.76 (s, 3H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 189.2, 144.2, 136.1, 128.7 (2 peaks), 128.5, 127.2, 126.60, 126.57, 97.5, 90.5, 31.5, 25.2, 25.0.

HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{18}H_{17}^+$: 233.1330, found: 233.1327.

[1-Phenyl-2-(phenylethenylidene)cyclopropyl]benzene (3aj)

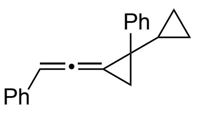


Following the general procedures, **3aj** was purified by silica gel column chromatography (0.2 mmol scale reaction, yellow oil, 37.1 mg, 63% yield, R_f 0.67, EtOAc/hexane = 1/4).

^{1}H NMR (CDCl$_3$, 400 MHz) δ: 7.33 (dm, J = 8.0 Hz, 2H), 7.28-7.08 (m, 13H), 6.38 (t, J = 4.0 Hz, 1H), 2.38 (dd, J = 11.2 Hz, 2H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ: 190.0, 143.1, 142.8, 135.7, 128.8, 128.5 (two peaks), 128.1, 127.0, 126.87, 126.86, 98.6, 89.9, 39.4, 25.5.

HRMS (ESI-TOF) m/z: [M+H]$^+$ Calcd for $C_{23}H_{19}^+$: 295.1487, found: 295.1480.

[1-Cyclopropyl-2-(2-phenylethenylidene)cyclopropyl]benzene (3ak)



Following the general procedures, **3ak** was purified by silica gel column chromatography (0.25 mmol scale reaction, yellow oil, 24.0 mg, 38% yield, R_f 0.55, EtOAc/hexane = 1/9).

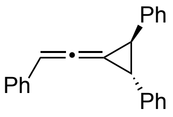
Major isomer: **^{1}H NMR** (MeOD, 400 MHz) δ 7.52-7.42 (m, 2H), 7.36-7.28 (m, 3H), 7.28-7.10 (m, 5H), 6.34 (t, J = 4.0 Hz, 1H), 2.10-1.98 (m, 1H), 2.03 (dd, J = 4.0, 7.2 Hz, 1H), 1.52 (dd, J = 5.2, 8.0

Hz, 1H), 0.64-0.37 (m, 3H), 0.33-0.22 (m, 1H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 190.0, 143.9, 136.0, 128.7, 128.4, 127.8, 126.8, 126.7, 126.6, 97.3, 86.8, 36.8, 22.8, 17.2, 4.1, 2.4.

Minor isomer: **^{1}H NMR** (MeOD, 400 MHz) δ 7.52-7.42 (m, 2H), 7.36-7.28 (m, 3H), 7.28-7.10 (m, 5H), 6.37 (t, J = 4.0 Hz, 1H), 2.10-1.98 (m, 1H), 1.95 (dd, J = 4.0, 7.2 Hz, 1H), 1.58 (dd, J = 5.2, 8.0 Hz, 1H), 0.64-0.37 (m, 3H), 0.33-0.22 (m, 1H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 189.6, 143.7, 136.0, 128.8, 128.4, 127.5, 126.74, 126.65, 126.60, 97.3, 86.6, 36.6, 22.6, 16.9, 4.5, 2.8.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}^+$: 259.1487, found: 259.1483.

***trans*-2-Phenyl-3-(2-phenylethenylidene)cyclopropyl]benzene (3al)**

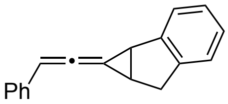


Following the general procedures, **3al** was purified by silica gel column chromatography (0.25 mmol scale reaction, yellow oil, 31.4 mg, 44% yield, R_f 0.53, EtOAc/hexane = 1/9).

^{1}H NMR (CDCl$_3$, 400 MHz) δ 7.59-7.497 (m, 1H), 7.39-7.28 (m, 11H), 7.27-7.16 (m, 3H), 6.51 (t, J = 4.0 Hz, 1H), 3.24 (dd, J = 3.6, 5.2 Hz, 1H), 3.17 (dd, J = 3.6, 5.2 Hz, 1H); **^{13}C NMR** (CDCl$_3$, 100 MHz) δ 190.86, 139.85, 139.72, 135.41, 128.81, 128.76, 128.71, 127.00, 126.96, 126.92, 126.83 (3 peaks), 98.65, 90.18, 37.06, 36.68.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}^+$: 295.1487, found: 295.1488.

(2-{1H,1aH,6H,6aH-Cyclopropa[a]inden-1-yidene}ethenyl)benzen (3am)



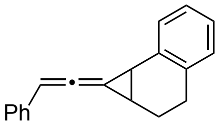
Following the general procedures, **3am** was purified by silica gel column chromatography (0.25 mmol scale reaction, yellow oil, 46.8 mg, 82% yield, R_f 0.48, EtOAc/hexane = 1/9).

Major isomer: **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.36-7.33 (m, 1H), 7.30-7.01 (m, 7H), 6.91 (m, 1H), 6.19 (t, J = 2.8 Hz, 1H), 3.58 (dm, J = 6.0 Hz, 1H), 3.41 (t, J = 6.4 Hz, 1H), 3.30 (d, J = 13.2 Hz, 1H); **^{13}C-NMR** (CDCl$_3$, 100 MHz) δ 188.1, 143.5, 142.0, 135.8, 128.7, 126.7 (two peaks), 126.4, 126.3, 125.5, 123.9, 98.0, 89.3, 36.5, 33.9, 25.7.

Minor isomer: **^{1}H NMR** (CDCl$_3$, 400 MHz) δ 7.36-7.33 (m, 1H), 7.30-7.01 (m, 7H), 6.91 (m, 1H), 6.29 (t, J = 2.8 Hz, 1H), 3.52 (dm, J = 6.0 Hz, 1H), 3.46 (t, J = 6.4 Hz, 1H), 3.26 (d, J = 13.2 Hz, 1H); **^{13}C-NMR** (CDCl$_3$, 100 MHz) δ 188.3, 144.0, 141.8, 135.8, 128.6, 126.6 (two peaks), 126.5, 126.4, 125.5, 123.8, 97.6, 90.2, 37.1, 34.3, 26.1.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{14}^+$: 231.1174, found: 231.1174.

(2-{1H,1aH,2H,3H,7bH-Cyclopropa[a] naphthalen-1-ylidene}ethenyl)benzen (3an)



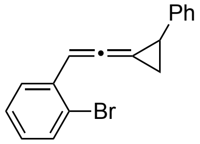
Following the general procedures, **3an** was purified by silica gel column chromatography (0.25 mmol scale reaction, light brown oil, 29.2 mg, 48% yield, R_f 0.49, EtOAc/hexane = 1/9).

Major isomer: ^{1}**H NMR** (CDCl$_3$, 400 MHz) δ 7.31-7.05 (m, 9H), 6.17 (t, *J* = 4.0 Hz, 1H), 3.23 (dd, *J* = 4.0, 8.0 Hz), 2.84-2.54 (m, 3H), 2.25 (dt, *J* = 12.0, 4.0 Hz, 1H), 1.66 (m, 1H); ^{13}**C NMR** (CDCl$_3$, 100 MHz) δ 189.90, 135.82, 135.24, 134.79, 128.66, 128.51, 128.48, 126.64, 126.51, 126.25, 125.93, 97.55, 83.99, 26.93, 26.57, 23.80, 19.55.

Minor isomer: ^{1}**H NMR** (CDCl$_3$, 400 MHz) δ 7.31-7.05 (m, 9H), 6.28 (t, *J* = 4.0 Hz, 1H), 3.14 (dd, *J* = 4.0, 8.0 Hz, 1H), 2.84-2.54 (m, 3H), 2.27 (dt, *J* = 12.0, 4.0 Hz, 1H), 1.66 (m, 1H); ^{13}**C NMR** (CDCl$_3$, 100 MHz) δ 190.12, 135.92, 135.54, 134.49, 128.64, 128.57, 128.43, 126.62, 126.60, 126.28, 125.96, 97.35, 84.32, 26.70, 26.11, 24.29, 19.56.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{17}^+$: 245.1330, found: 245.1325.

1-Bromo-2-[2-(2-phenylcyclopropylidene)ethenyl]benzene (3ba)

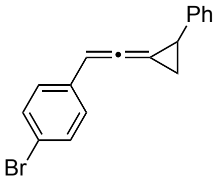


Following the general procedures, **3ba** was purified by silica gel column chromatography (0.25 mmol scale reaction, yellow oil, 31.4 mg, 43% yield, R$_f$ 0.48, EtOAc/hexane = 1/9). Major isomer: ^{1}**H NMR** (CDCl$_3$, 400 MHz) δ 7.54-7.37 (m, 2H), 7.35-7.15 (m, 6H), 7.04-6.96 (m, 1H), 6.80 (quint, *J* = 4.0 Hz, 1H), 3.21 (ddd, *J* = 4.0, 6.0, 8.8 Hz, 1H), 2.30 (ddd, *J* = 4.0, 7.2, 8.8 Hz, 1H), 1.95 (ddd, *J* = 4.0, 6.0, 7.2 Hz, 1H); ^{13}**C NMR** (CDCl$_3$, 100 MHz) δ 190.9, 140.0, 135.1, 133.1, 128.6, 128.5, 128.0, 127.4, 126.7 (two peaks), 122.2, 96.73, 85.5, 26.4, 19.0.

Minor isomer: ^{1}**H NMR** (CDCl$_3$, 400 MHz) δ 7.54-7.37 (m, 2H), 7.35-7.15 (m, 6H), 7.04-6.96 (m, 1H), 6.80 (quint, *J* = 4.0 Hz, 1H), 3.16 (ddd, *J* = 4.0, 6.0, 8.8 Hz, 1H), 2.25 (ddd, *J* = 4.0, 7.2, 8.8 Hz, 1H), 1.88 (ddd, *J* = 4.0, 6.0, 7.2 Hz, 1H); ^{13}**C NMR** (CDCl$_3$, 100 MHz) δ 191.1, 140.3, 135.2, 133.05, 128.6, 128.5, 128.0, 127.5, 126.8 (two peaks), 122.2, 96.8, 85.7, 26.7, 18.9.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}Br^+$: 297.0279, found: 297.0293.

1-Bromo-4-[2-(2-phenylcyclopropylidene)ethenyl]benzene (3ca)

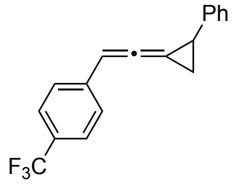


Following the general procedures, **3ca** was purified by silica gel column chromatography (0.25 mmol scale reaction, yellow oil, 40.3 mg, 55% yield, R$_f$ 0.65, EtOAc/hexane = 1/9). Major isomer: ^{1}**H NMR** (CDCl$_3$, 400 MHz) δ 7.45-7.38 (m, 2H), 7.36-7.21 (m, 5H), 7.21-7.13 (m, 2H), 6.35-6.30 (m, 1H), 3.23 (ddd, *J* = 3.6, 6.0, 8.8 Hz, 1H), 2.32 (ddd, *J* = 4.0, 7.2, 8.8 Hz, 1H), 1.89 (ddd, *J* = 4.0, 6.0, 7.2 Hz, 1H);^{13}**C NMR** (CDCl$_3$, 100 MHz) δ 190.09, 140.09, 134.78, 131.75, 128.61, 128.28, 126.84, 126.73, 120.24, 96.95, 85.96, 26.10, 18.66.

Minor isomer: ^{1}**H NMR** (CDCl$_3$, 400 MHz) δ 7.45-7.38 (m, 2H), 7.36-7.21 (m, 5H), 7.21-7.13 (m, 2H), 6.35-6.30 (m, 1H), 3.16 (ddd, *J* = 3.6, 6.0, 8.8 Hz, 1H), 2.26 (ddd, *J* = 4.0, 7.2, 8.8 Hz, 1H), 1.97 (ddd, *J* = 4.0, 6.0, 7.2 Hz, 1H);^{13}**C NMR** (CDCl$_3$, 100 MHz) δ 190.24, 140.31, 134.87, 131.79, 128.66, 128.22, 126.76, 126.71, 120.24, 96.95, 86.17, 26.46, 18.59.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}Br^+$: 297.0279, found: 297.0272.

4-(Trifluoromethyl)-4-[2-(2-phenylcyclopropylidene)ethenyl]benzene (3da)

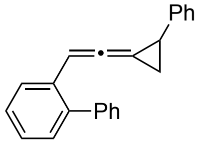


Following the general procedures, **3da** was purified by silica gel column chromatography (0.48 mmol scale reaction, yellow oil, 23.4 mg, 17% yield, R_f0.48, EtOAc/hexane = 1/9). Major isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) *δ* 7.53 (t, *J* = 8.0 Hz, 2H), 7.42-7.20 (m, 7H), 6.41-6.36 (m, 1H), 3.26 (ddd, *J* = 3.2, 6.0, 8.8 Hz, 1H), 2.35 (ddd, *J* = 4.0, 7.6, 8.8 Hz, 1H), 1.92 (ddd, *J* = 4.0, 6.0, 7.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) *δ* 190.9, 139.8, 139.6 (two peaks), 128.7, 128.3 ($J_{C\text{-}F}$ = 32 Hz), 126.7, 126.6, 125.5 ($J_{C\text{-}F}$ = 3.8 Hz), 124.4 ($J_{C\text{-}F}$ = 270 Hz), 96.9, 85.8, 26.5, 18.9

Minor isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) *δ* 7.53 (t, *J* = 8.0 Hz, 2H), 7.42-7.20 (m, 7H), 6.41-6.36 (m, 1H), 3.20 (ddd, *J* = 3.2, 6.0, 8.8 Hz, 1H), 2.28 (ddd, *J* = 4.0, 7.6, 8.8 Hz, 1H), 2.00 (ddd, *J* = 4.0, 6.0, 7.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) *δ* 191.0, 140.0, 139.7 (two peaks), 128.7, 128.3 ($J_{C\text{-}F}$ = 32 Hz), 126.74, 126.70, 125.5 ($J_{C\text{-}F}$ = 3.8 Hz), 124.4 ($J_{C\text{-}F}$ = 270 Hz), 96.9, 86.0, 26.9, 18.8.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{14}F_3^+$: 287.1048, found: 287.1045.

1-Phenyl-2-[2-(2-phenylcyclopropylidene)ethenyl]benzene (3ea)

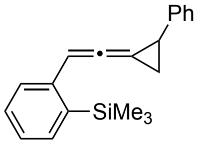


Following the general procedures, **3ea** was purified by silica gel column chromatography (0.18 mmol scale reaction, yellow oil, 11.6 mg, 22% yield, R_f0.53, EtOAc/hexane = 1/9). Major isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) *δ* 7.55 (d, *J* = 7.6 Hz, 1H),7.46-7.24 (m, 10H), 7.23-7.14 (m, 3H), 6.39-6.45 (m, 1H), 3.13 (ddd, *J* = 3.6, 5.6, 8.8 Hz, 1H), 2.23 (ddd, *J* = 4.0, 6.4, 8.4 Hz, 1H), 1.89 (ddd, *J* = 4.4, 6.0, 7.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) *δ* 190.5, 144.1, 140.5, 140.2, 133.0, 130.4, 129.9, 128.6, 128.3, 127.58, 127.56, 127.1, 126.9, 126.7, 126.6, 96.0, 85.2, 26.0, 18.81.

Minor isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) *δ* 7.55 (d, *J* = 7.6 Hz, 1H),7.46-7.24 (m, 10H), 7.23-7.14 (m, 3H), 6.39-6.45 (m, 1H), 3.09 (ddd, *J* = 3.6, 5.6, 8.8 Hz, 1H), 2.19 (ddd, *J* = 4.0, 6.4, 8.4 Hz, 1H), 1.78 (ddd, *J* = 4.4, 6.0, 7.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) *δ* 190.5, 141.1, 140.7, 140.1, 133.1, 130.4, 129.9, 128.6, 128.3, 127.6, 127.5, 127.2, 126.9, 126.6, 126.5, 96.1, 85.4, 26.3, 18.71.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{23}H_{19}^+$: 295.1487, found: 294.1480.

1-Trimethylsilyl-2-[2-(2-phenylcyclopropylidene)ethenyl]benzene (3fa)

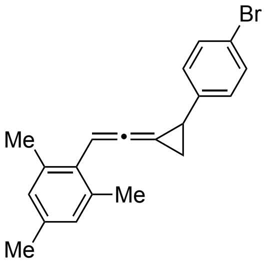


Following the general procedures, **3fa** was purified by silica gel column chromatography (0.24 mmol scale reaction, yellow oil, 22.5 mg, 33% yield, R_f0.59, EtOAc/hexane = 1/9). Major isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) *δ* 7.54-7.44 (m, 2H), 7.34-7.18 (m, 6H), 7.17-7.10 (m, 1H), 6.69-6.62 (m, 1H), 3.19 (ddd, *J* = 3.6, 6.0, 8.8 Hz, 1H), 2.27 (ddd, *J* = 4.0, 7.2, 8.8 Hz, 1H), 1.85 (ddd, *J* = 4.0, 7.2, 8.8 Hz, 1H), 0.36 (s, 9H); **^{13}C NMR** ($CDCl_3$/100 MHz) *δ* 190.3, 140.9 (two peaks), 140.4, 137.3, 134.7, 129.4, 128.6, 127.2, 126.8, 126.6, 98.3, 85.2, 25.6, 18.5, 0.32.

Minor isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) *δ* 7.55-7.44 (m, 2H), 7.34-7.18 (m, 6H), 7.17-7.10 (m, 1H), 6.69-6.62 (m, 1H), 3.13 (ddd, *J* = 3.6, 6.0, 8.8 Hz, 1H), 2.23 (ddd, *J* = 4.0, 7.2, 8.8 Hz, 1H), 1.91 (ddd, *J* = 4.0, 7.2, 8.8 Hz, 1H), 0.37 (s, 9H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ 190.3, 141.0 (two peaks), 140.6, 137.3, 134.6, 129.5, 128.6, 127.2, 126.9, 125.9, 98.4, 85.4, 26.4, 18.7, 0.32.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}Si^+$: 291.1569, found: 291.1571.

2-{2-[2-(4-Bromophenyl)cyclopropylidene]ethenyl}-1,2,3-trimethylbenzene (3gc)



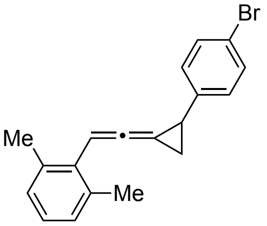
Following the general procedures, **3gc** was purified by silica gel column chromatography (0.25 mmol scale reaction, orange oil, 33.9 mg, 40% yield, R_f 0.61, EtOAc/hexane = 1/9).

Major isomer: ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ 7.35 (dm, *J* = 8.4 Hz, 2H), 7.02 (dm, *J* = 8.4 Hz, 2H), 6.82 (s, 2H), 6.50 (m, 1H), 3.00 (ddd, *J* = 4.0, 5.6, 8.8 Hz, 1H), 2.251 (s, 6H), 2.246 (s, 3H), 2.14 (m, 1H), 1.80 (ddd, *J* = 4.0, 5.6, 7.2 Hz, 1H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ 192.0, 139.9, 139.2 (2 peaks), 131.5, 129.3 (2 peaks), 128.5, 120.1, 93.7, 82.5, 25.3, 21.5, 21.1, 17.4.

Minor isomer: ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ 7.41 (dm, *J* = 8.4 Hz, 2H), 7.10 (dm, *J* = 8.4 Hz, 2H), 6.85 (s, 2H), 6.50 (m, 1H), 2.95 (ddd, *J* = 4.0, 5.6, 8.8 Hz, 1H), 2.33 (s, 6H), 2.26 (s, 3H), 2.14 (m, 1H), 1.71 (ddd, *J* = 4.0, 5.6, 7.2 Hz, 1H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ 191.6, 139.2, 136.3, 136.2, 131.6, 129.3, 129.2, 128.4, 120.2, 93.6, 82.7, 24.7, 21.4, 21.0, 18.2.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{20}Br^+$: 339.0670, found: 339.0741.

2-{2-[2-(4-Bromophenyl)cyclopropylidene]ethenyl}-1,3-dimethylbenzene (3hc)



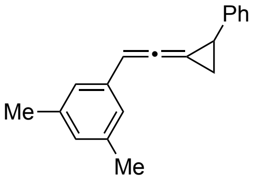
Following the general procedures, **3hc** was purified by silica gel column chromatography (0.5 mmol scale reaction, orange oil, 101.77 mg, 63% yield, R_f 0.53, EtOAc/hexane = 1/9).

Major isomer: ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ 7.36 (dm, *J* = 8.4 Hz, 2H), 7.03-6.98 (m, 5H), 6.54-6.49 (m, 1H), 3.05-3.00 (m, 1H), 2.29 (s, 6H), 2.20-2.12 (m, 1H), 1.85-1.81 (m, 1H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ 191.7, 139.1, 136.4, 132.3, 131.5, 128.5, 128.3, 126.6, 120.1, 93.67, 82.5, 25.4, 21.5, 17.4.

Minor isomer: ^{1}**H NMR** ($CDCl_3$, 400 MHz) δ 7.42 (dm, *J* = 8.4 Hz, 2H), 7.11 (dm, *J* = 8.4 Hz, 2H), 7.03-6.98 (m, 3H), 6.54-6.49 (m, 1H), 2.99-2.94 (m, 1H), 2.37 (s, 6H), 2.20-2.12 (m, 1H), 1.76-1.72 (m, 1H); ^{13}**C NMR** ($CDCl_3$, 100 MHz) δ 192.0, 139.8, 136.4, 132.3, 131.6, 128.4, 128.3, 126.7, 120.2, 93.7, 82.7, 24.8, 21.5, 18.2.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{18}Br^+$: 325.0592, found: 325.0588.

1,3-Dimethyl-5-[2-(2-phenylcyclopropylidene)ethenyl]benzene (3ia)



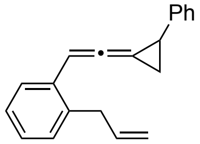
Following the general procedures, **3ia** was purified by silica gel column chromatography (0.5 mmol scale reaction, colorless oil, 40.5 mg, 33% yield, R_f 0.53, EtOAc/hexane = 1/9).

Major isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.31-7.28 (m, 2H), 7.25-7.18 (m, 3H), 6.92 (s, 2H), 6.82 (s, 1H), 6.32-6.29 (m, 1H), 3.20 (ddd, J = 3.6, 5.6, 8.8 Hz, 1H), 2.29 (ddd, J = 4.0, 7.2, 8.8 Hz, 1H), 2.29 (s, 6H), 1.83 (ddd, J = 4.0, 5.6, 7.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 190.0, 140.5, 138.2, 135.5, 128.57, 128.54, 126.8, 126.6, 124.6, 97.6, 85.4, 25.8, 21.4, 18.5.

Minor isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.31-7.28 (m, 2H), 7.25-7.18 (m, 3H), 6.91 (s, 2H), 6.81 (s, 1H), 6.32-6.29 (m, 1H), 3.12 (ddd, J = 3.6, 5.6, 8.8 Hz, 1H), 2.26 (s, 6H), 2.21 (ddd, J = 4.0, 7.2, 8.8 Hz, 1H), 1.92 (ddd, J = 4.0, 5.6, 7.2 Hz, 1H).; **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 190.3, 140.8, 138.1, 135.6, 128.62, 128.58, 126.9, 126.6, 124.7, 97.9, 85.8, 26.1, 21.4, 18.6.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}^+$: 247.1487, found: 247.1490.

1-[2-(2-Phenylcyclopropylidene)ethenyl]-2-(prop-2-en-1-yl)benzene (3ka)



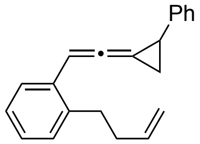
Following the general procedures, **3ka** was purified by silica gel column chromatography (0.24 mmol scale reaction, colorless oil, 27.2 mg, 44% yield, R_f 0.62, EtOAc/hexane = 1/9).

Major isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.46-7.41 (m, 1H), 7.35-7.08 (m, 8H), 6.61-6.56 (m, 1H), 6.05-5.93 (m, 1H), 5.15-5.05 (m, 2H), 3.54-3.42 (m, 2H), 3.17 (ddd, J = 3.6, 5.6, 8.4 Hz, 1H), 2.27 (ddd, J = 4.0, 7.2, 8.8 Hz, 1H), 1.86 (ddd, J = 4.0, 5.6, 7.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 190.8, 140.5, 137.0, 136.4, 133.7, 130.2, 128.6 (2 peaks), 127.7, 126.9, 126.73, 126.6, 116.0, 94.9, 84.8, 37.6, 26.0, 18.7.

Minor isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.41-7.36 (m, 4H), 7.35-7.08 (m, 8H), 6.61-6.56 (m, 1H), 6.05-5.93 (m, 1H), 5.15-5.05 (m, 2H), 3.54-3.42 (m, 2H), 3.13 (ddd, J = 3.6, 5.6, 8.4 Hz, 1H), 2.23 (ddd, J = 4.0, 7.2, 8.8 Hz, 1H), 1.92 (ddd, J = 4.0, 5.6, 7.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 190.8, 140.5, 136.9, 136.4, 133.8, 130.0, 128.6 (2 peaks), 127.7, 126.8, 126.73, 126.6, 116.1, 94.8, 85.0, 37.7, 26.4, 18.6.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}^+$: 259.1487, found: 259.1483.

1-(But-3-en-1-yl)-2-[2-(2-phenylcyclopropylidene)ethenyl]benzene (3la)



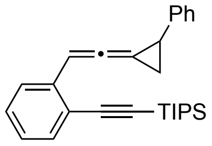
Following the general procedures, **3la** was purified by silica gel column chromatography (0.2 mmol scale reaction, colorless oil, 25.8 mg, 48% yield, R_f 0.57, EtOAc/hexane = 1/9).

Major isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.35-7.02 (m, 9H), 6.50 (q, J = 4.0 Hz, 1H), 5.80 (dt, J = 10.8, 6.4 Hz, 1H), 4.98 (dm, J = 17.2 Hz, 2H), 3.08 (ddd, J = 3.6, 5.6, 8.8 Hz, 1H), 2.72 (t, J = 7.2 Hz, 2H), 2.27 (m, 2H), 2.18 (ddd, J = 4.0, 7.2, 8.8 Hz, 1H), 1.85 (ddd, J = 3.6, 6.0, 7.6 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 190.9, 140.5, 138.7, 138.3, 133.2, 130.0, 128.6, 127.9, 126.9, 126.7, 126.5 (two peaks), 115.0, b94.9, 84.8, 35.2, 32.9, 26.0, 18.69.

Minor isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.35-7.02 (m, 9H), 6.50 (q, J = 4.0 Hz, 1H), 5.80 (dt, J = 10.8, 6.4 Hz, 1H), 4.91 (dm, J = 10.8 Hz, 2H), 3.14 (ddd, J = 3.6, 5.6, 8.8 Hz, 1H), 2.70 (t, J = 7.2 Hz, 2H), 2.27 (m, 2H), 2.24 (ddd, J = 4.0, 7.2, 8.8 Hz, 1H) 1.92 (ddd, J = 3.6, 6.0, 7.6 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 190.8, 140.6, 138.5, 138.2, 133.4, 129.8, 128.6, 127.8, 126.8, 126.6, 126.4 (2 peaks), 115.1, 94.7, 85.1, 35.2, 32.9, 26.3, 18.6.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{21}^+$: 273.1643, found: 273.1640.

1-Triisopropylsilylethynyl-2-[2-(2-phenylcyclopropylidene)ethenyl]benzene (3ma)



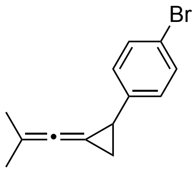
Following the general procedures, **3ma** was purified by silica gel column chromatography (0.25 mmol scale reaction, yellow oil, 63.1 mg, 64% yield, R_f 0.64, EtOAc/hexane = 1/9).

Major isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.50-7.38 (m, 2H), 7.34-7.16 (m, 6H), 7.14-7.04 (m, 1H), 7.00 (quint, J = 4.0 Hz, 1H), 3.17 (ddd, J = 4.0, 6.0, 8.8 Hz, 1H), 2.26 (ddd, J = 4.0, 7.2, 8.8 Hz, 1H), 1.96 (ddd, J = 4.0, 6.0, 7.2 Hz, 1H), 1.15 (m, 21H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 190.9, 140.5, 137.7, 133.1, 128.63, 128.56, 128.50, 126.9, 126.7, 126.3, 121.1, 105.2, 96.0, 95.6, 85.6, 26.7, 18.89, 18.88, 11.5.

Minor isomer: **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.50-7.38 (m, 2H), 7.34-7.16 (m, 6H), 7.14-7.04 (m, 1H), 7.00 (quint, J = 4.0 Hz, 1H), 3.22 (ddd, J = 4.0, 6.0, 8.8 Hz, 1H), 2.31 (ddd, J = 4.0, 7.2, 8.8 Hz, 1H), 1.87 (ddd, J = 4.0, 6.0, 7.2 Hz, 1H), 1.17-1.13 (m, 21H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 190.9, 140.2, 137.6, 133.1, 128.59, 128.56, 128.50, 126.9, 126.5, 126.4, 121.1, 105.3, 96.0, 95.8, 85.2, 26.3, 18.88, 18.80, 11.5.

HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{28}H_{35}Si^+$: 399.2508, found: 399.2500.

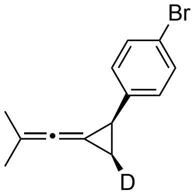
1-Bromo-4-(2-(2-methylprop-1-enylidene)cyclopropyl)benzene (3nc)



Following the general procedures, **3nc** was purified by silica gel column chromatography (0.54 mmol scale reaction, pale green oil, 37.5 mg, 28% yield, R_f 0.57, EtOAc/hexane = 1/9).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41-7.36 (m, 2H), 7.10-7.02 (m, 3H), 2.81 (dd, J = 4.8, 8.4 Hz, 1H), 2.00 (dd, J = 7.2, 8.4 Hz, 1H), 1.81 (s, 3H), 1.80 (s, 3H), 1.49 (dd, J = 4.8, 7.2 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 187.1, 140.7, 131.4, 128.1, 119.6, 100.2, 81.6, 22.9, 21.4, 21.1, 17.2; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{13}H_{14}Br^+$: 249.0279, found: 249.0266.

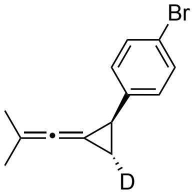
cis-1-Bromo-4-(2-deuterio-3-(2-methylprop-1-enylidene)cyclopropyl)benzene (*cis*-3mc-*d*)



Following the general procedures, **3mc** was purified by silica gel column chromatography (0.49 mmol scale reaction, pale green oil, 24.6 mg, 20% yield, R_f 0.57, EtOAc/hexane = 1/9).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.20 (dm, J = 8.4 Hz, 2H), 6.75 (dm, J = 8.4 Hz, 1H), 2.49 (d, J = 8.4 Hz, 1H), 1.79-1.64 (m, 7H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 187.3, 140.8, 131.5, 128.2, 119.7, 100.2, 81.6, 22.9, 21.5, 21.2, 17.0 (t, J = 25 Hz); **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}BrD^+$: 250.0342, found: 250.0344.

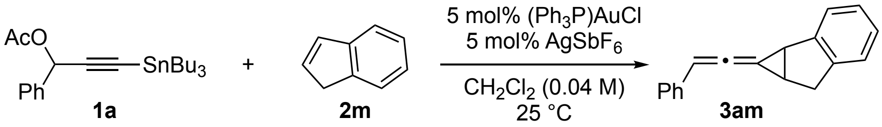
***trans*-1-Bromo-4-(2-deuterio-3-(2-methylprop-1-enylidene)cyclopropyl)benzene (*trans*-3nc-*d*)**



Following the general procedures, **3nc** was purified by silica gel column chromatography (0.49 mmol scale reaction, pale green oil, 24.5 mg, 20% yield, R_f 0.57, EtOAc/hexane = 1/9).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40-7.36 (m, 2H), 7.07-7.03 (m, 2H), 2.80 (d, J = 5.0 Hz, 1H), 1.81 (s, 3H), 1.80 (s, 3H), 1.47 (d, J = 5.0 Hz, 1H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 187.29, 140.85, 131.51, 128.28, 119.71, 100.25, 81.59, 22.91, 21.47, 21.18, 17.01 (t, J = 25.5 Hz); **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}BrD^+$: 250.0342, found: 250.0351.

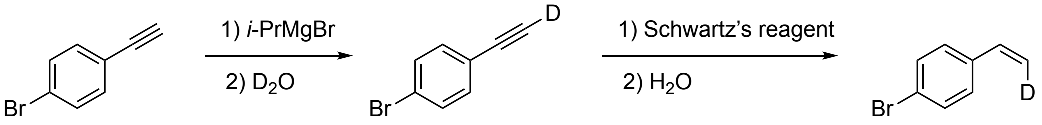
Large Scale Reaction for Gold(I)-Catalyzed Cyclopropanation of Indene



The cationic gold catalyst was generated in a 20 mL round bottom flask with a threaded cap by addition of $(Ph_3P)AuCl$ (25.0 mg, 0.01 mmol, 5 mol%), $AgSbF_6$ (17.0 mg, 0.01 mmol, 5 mol%), and dichloromethane (5 mL). After allowing the catalyst mixture to sit for 10 minutes at room temperature, the precipitate was filtered off. The resulting solution was added to the **1a** (1.0 mmol) and indene (**2m**) (20 mmol) in dichloromethane (20 mL), and stirred at 25 °C. The mixture (0.04 M) was monitored by TLC until all starting material was consumed. Upon completion, the reaction mixture was concentrated and loaded directly onto a silica gel column resulted in isolation of analytically pure product **3am** (yellow oil, 184.2 mg, 80% yield, R_f 0.48, EtOAc/hexane = 1/9).

Isotope Labeling Experiments

Synthesis of *cis*-β-Monodeuterio-4-bromostyrene



(Adapted from a reported procedure)[7]: An oven-dried schlenk flask equipped with a stir bar was charged with 4-bromophenylacetylene (3.43 g, 19 mmol, 1.0 equiv.) and anhydrous THF (30 mL). The solution was cooled to –78 ºC and isopropylmagnsium bromide prepared from isopropyl bromide and magnsium turnings (0.6 M in THF, 38 mL, 22.8 mmol, 1.2 equiv.) was added in a dropwise fashion over 10 min. The solution was stirred at -78 ºC for 1.5 h after which point D_2O (2.25 mL, 123 mmol, excess) was added. The mixture is allowed to warm to rt and stirred for 0.5 h. The reaction was quenched with 5% HCl and extracted with diethyl ether (2 × 20 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and the solvent was carefully removed with use of a rotary evaporator to give 1-bromo-4-(2-deutrioethynyl)benzene as an orange oil (3.15 g, 17.3 mmol, 91% yield, R_f 0.44, $CHCl_3$/hexane = 1/19).

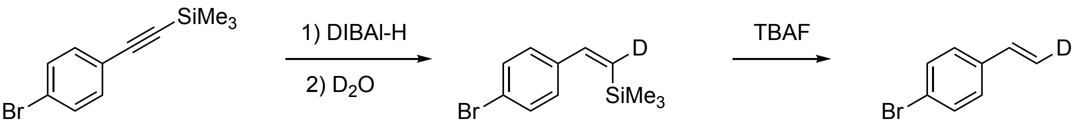
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.46 (dm, J = 8.8 Hz, 2H), 7.35 (dm, J = 8.8 Hz, 2H).

Spectroscopic data was consistent with the values reported in the literature.[16]

(Adapted from a reported procedure)[7]: A three-necked flask under Ar atmosphere was charged with Schwartz's Reagent (5.53 g, 21.5 mmol, 1.1 equiv.) in the glove box. These were then sealed and removed from the glove box, dry CH_2Cl_2 (15 mL) was added. The flask was covered with aluminum foil and the mixture was cooled to –10 °C. A solution of 1-bromo-4-(2-deutrioethynyl)benzene (1.43 g, 7.8 mmol) in dry CH_2Cl_2 (15 mL) was added dropwise over 10 min using an addition funnel. The mixture was allowed to stir at –10 °C for 15 min, then the cold bath was removed, and the stirring was continued at room temperature in the dark for 3 h. The flask was cooled to 0 °C, and the mixture was quenched with H_2O (1.0 mL, 56 mmol, 7 equiv.) and stirred vigorously at room temperature for 12 h. The mixture was diluted with CH_2Cl_2 (50 mL), followed by the addition of anhydrous $MgSO_4$, and filtration, washing with CH_2Cl_2. The filtrate was concentrated under reduced pressure until 5–10 mL of CH_2Cl_2 remained. Hexane (10 mL) was then added, and the mixture was filtered over a Celite® pad to remove the white precipitate; the filter cake was rinsed with hexane and the filtrate was again concentrated under reduced pressure. Purification by column chromatography on silica gel using hexane as eluent afforded the corresponding titled compound a colorless oil (920.6 mg, 65%). Approx. 99% D-incorporation.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 (dm, J = 8.0 Hz, 2H), 7.27 (dm, J = 12.0 Hz, 2H), 6.64 (dt, J = 8.0, 4.0 Hz, 1H), 5.72 (d, J = 16.0 Hz, 0.01H), 5.26 (d, J = 8.0 Hz, 1H); **^{13}C NMR** (CD_3OD, 100 MHz) δ 136.6, 135.8, 131.7, 127.9, 121.7, 114.5 (t, $J_{C\text{-}D}$ = 24.0 Hz); **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_8H_6DBr^+$: 183.9872, found: m/z 183.9863.

Synthesis of *trans*-β-Monodeuterio-4-bromostyrene



(Z)-(2-(4-Bromophenyl)-1-deuteriovinyl)trimethylsilane:

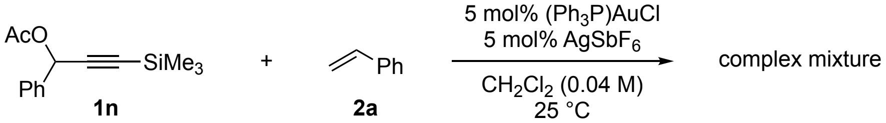
Prepared from 1-(4-bromophenyl)-2-(trimethylsilyl)acetylene according to the reported procedure.[17] To a flame-dried round bottom flask equipped with a stir bar was added dry hexane (15 mL) under Ar, after which DIBAL-H (1M in hexane, 36 mL, 36 mmol) was added. The resulting mixture was allowed to cool to 0 °C, and a solution of trimethyl(4-bromophenylethynyl)silane (3.31 g, 18 mmol) in dry THF (3 mL) was added using an addition funnel. The mixture was stirred for an additional 10 min at 0 °C and then allowed to stir for 15 h at room temperature. The solution was stirred at –0 ºC for 10 min after which point D_2O (0.75 mL, 37.5 mmol, excess) was added. The mixture was allowed to warm to rt and stirred for 0.5 h. The mixture was transferred to a separatory funnel and Rochelle's salt (40 mL) and a saturated solution of aqueous ammonium chloride (40 mL) were added. The aqueous layer was washed with Et_2O (3 × 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and the solvent was carefully removed in reduced pressure. The resulting yellow oil was purified by silica gel chromatography (100% hexane) and Kugelrohr distillation to give titled compound (2.6 g, 10.1 mmol, 56% yield).

trans-β-Monodeuterio-4-bromostyrene:

To a solution of (Z)-(2-(4-bromophenyl)-1-deuteriovinyl)trimethylsilane (2.6 g, 10.1 mmol) in THF (30 mL) was added $(n\text{-Bu})_4NF$ (1.0 M in THF, 15.2 mL, 15.2 mmol) at room temperature under Ar. The mixture was allowed to stir at 60 °C for 18 h after which it was transferred to a separatory funnel. The reaction was quenched with water (60 mL), and the layers separated. The aqueous layer was washed with Et_2O (3 × 20 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting yellow oil was purified by silica gel chromatography and Kugelrohr distillation to afford *trans*-β-Monodeuterio-4-bromostyrene as colorless liquid (962 mg, 5.2 mmol, 52% yield, 97% D, >98% *trans*).

^{1}H NMR ($CDCl_3$, 400 MHz) δ7.44 (dm, J = 8.0 HZ, 2H), 7.27 (dm, J = 8.4 Hz, 2H), 6.65 (d, J = 17.6 Hz, 2H), 5.73 (d, J = 17.6 Hz, 1H), 5.27 (dd, J = 0.6, 10.8 Hz, 0.012H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 136.6, 135.8, 131.8, 127.9, 121.7, 114.5 (t, $J_{C\text{-}D}$ = 25.0 Hz); **HRMS (ESI-TOF)** m/z: $[M+H]^+$ Calcd for $C_8H_6DBr^+$: 183.9872, found: 183.9865.

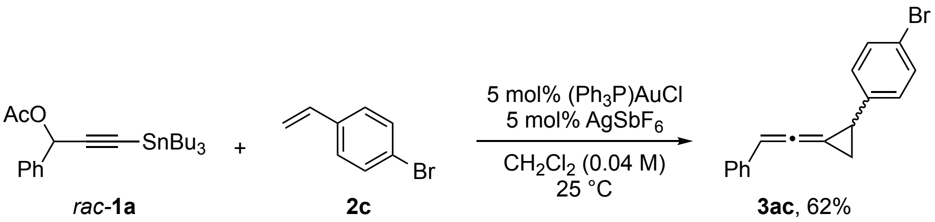
Gold(I)-Catalyzed Cyclopropanation of Styrene with Silylated Propargyl Esters (1n)



The cationic gold catalyst was generated in a 1 dram vial with a threaded cap by addition of $(Ph_3P)AuCl$ (6.2 mg, 0.0125 mmol, 5 mol%), $AgSbF_6$ (4.3 mg, 0.0125 mmol, 5 mol%), and dichloromethane (1 mL). After allowing the catalyst mixture to sit for 10 minutes at room temperature, the precipitate was filtered off. The resulting solution was added to the starting material **1n** (61.9 mg, 0.25 mmol) and styrene (**2a**) (290 µL, 2.5 mmol) in dichloromethane (5 mL), and stirred at 25 °C for 0.5 h. The mixture (0.04 M) was monitored by TLC until all starting material was consumed. Upon completion, the reaction mixture was concentrated and loaded directly onto a silica gel column resulted in complex mixture.

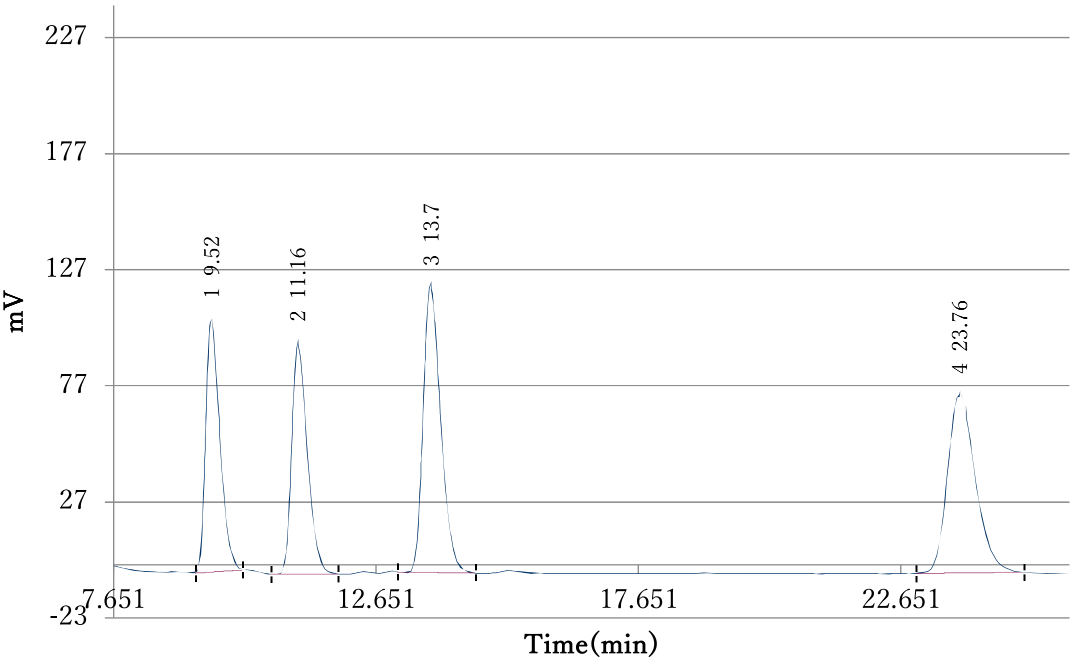
Gold(I)-Catalyzed Cyclopropanation of 2-Bromostyrene (2c) with (*R*)-1a

The cationic gold catalyst was generated in a 1 dram vial with a threaded cap by addition of $(Ph_3P)AuCl$ (5.0 mg, 0.01 mmol, 5 mol%), $AgSbF_6$ (3.4 mg, 0.01 mmol, 5 mol%), and dichloromethane (1 mL). After allowing the catalyst mixture to sit for 10 minutes at room temperature, the precipitate was filtered off. The resulting solution was added to the starting material (*R*)-**1a** (0.2 mmol) and 2-bromostyrene (**2c**) (2.0 mmol) in dichloromethane (4 mL), and stirred at 25 °C. The reaction mixture (0.04 M) was monitored by TLC until all starting material was consumed. Upon completion, the reaction mixture was concentrated and loaded directly onto a silica gel column chromatography resulted in isolation of analytically pure product **3ac** (yellow oil, 23.7 mg, 40% yield, R_f 0.55, EtOAc/hexane = 1/9).



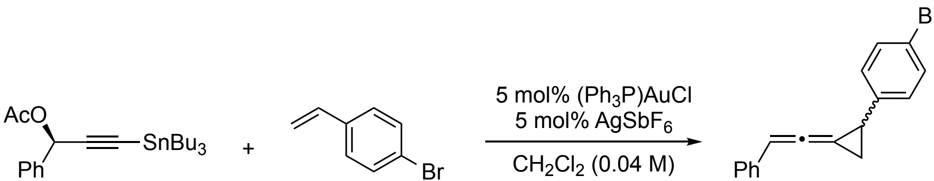
Racemic sample of **3ac**

HPLC: CHIRALPAK IJ (0.46 cm × 25 cm), MeOH= 100, flow: 1.0 mL/min, λ = 254 nm (UV)



No.	Rt	Area	Area(%)	Height
1	9.52	2040213	20.8118	109172
2	11.16	2055084	20.9635	101456
3	13.7	2861402	29.1885	125442
4	23.76	2846475	29.0363	78703
		9803174	100	414773

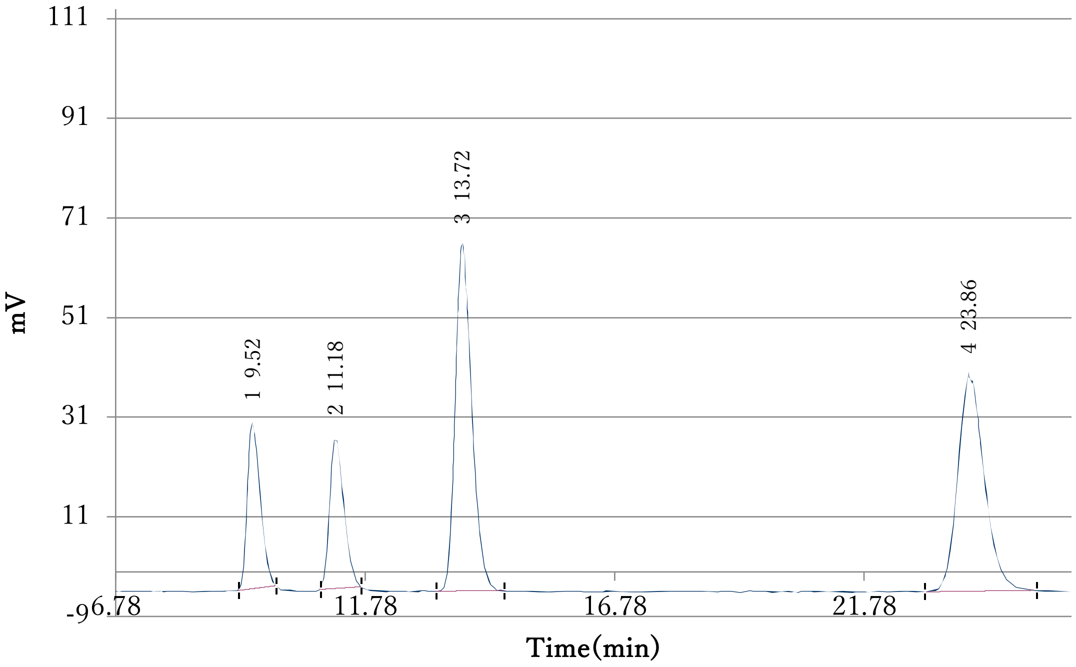
Chirality Transfer Reaction (Scheme 4c)



(*R*)-**1a**, 90% *ee* **2c** **3ac**, 45%, 2:1 *dr* 0% *ee*

HPLC data of **3ac** from a chirality transfer reaction (Scheme 4c)

HPLC: CHIRALPAK IJ (0.46 cm × 25 cm), MeOH= 100, flow: 1.0 mL/min, λ = 254 nm (UV)



No.	Rt	Area	Area(%)	Height
1	9.52	603703.4	13.6814	34161
2	11.18	603903.6	13.686	30341
3	13.72	1605776	36.3909	70411
4	23.86	1599188	36.2416	44029
		4412572	100	178942

Calculations

All structures for mechanism studies were optimized and characterized using frequency calculations at the at the ωB97XD functional with the 6-31+G(d) basis set for the organic molecules and the Def2TZVP basis set (with effective core potentials) for Au with the SCRF method based on CPCM (dichloromethane) using Gaussian 16, revision C.01.[18] It was confirmed that there is only one imaginary frequency in the vibrational spectra of all transition states. Gibbs free energies (298.15 K, 1 atm) was taken from the frequency calculation above. The natural bonding orbitals (NBO) calculations were performed at the same level of optimization using NBO 7.0 program (version 7.0.10) installed in Gaussian 16.

The generating mechanism of product **3aa** was targeted in the calculational study.

Although the reaction giving **3aa** afforded *syn*- or *anti*-isomers in a ratio of 2:1 (Table 1, entry 8), their absolute structures in both diastereomers could not be identified by instrumental analyses. Therefore, the experimental chemical shifts of both diastereomers of **3ac**, whose *dr* was 2.7:1 (scheme 2), were compared with the calculated chemical shifts. Structures of *syn*- and *anti*-**3ac** were optimized at the SMD($CHCl_3$)/B97D3/6-311+G(2d,p) level, and the chemical shifts were calculated using the GIAO method at the SMD($CHCl_3$)/mPW1PW91/6-311+G(2d,p) level. From the correlation between calculated and experimental chemical shifts (Figure S1), it was assumed that the major isomer of **3ac** was *syn*-form, and the minor isomer was *anti*-form. Therefore, we next conducted mechanistic studies on the formation of *syn*-**3aa**.

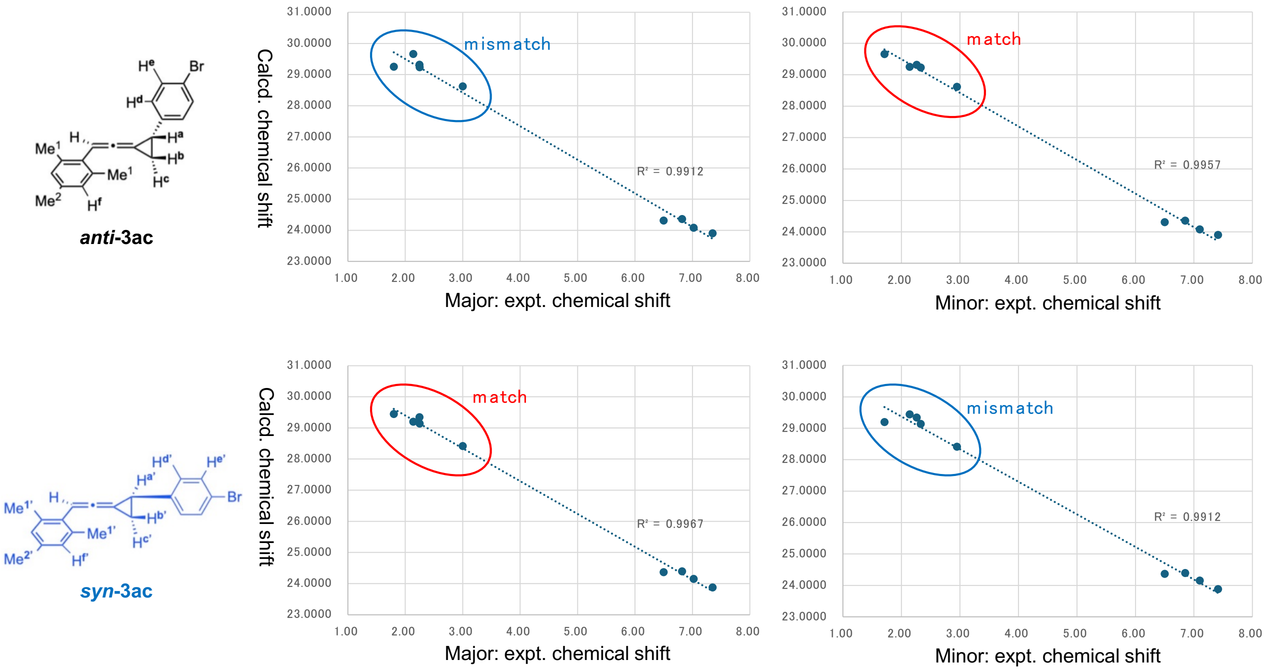
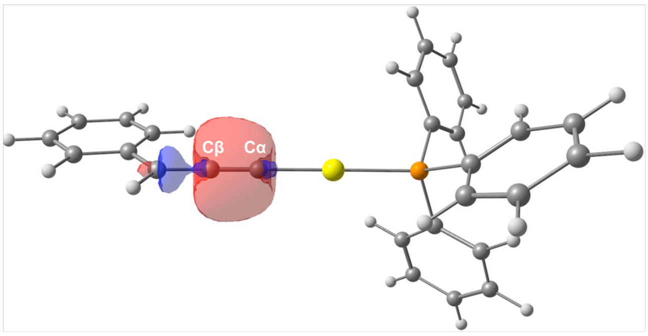


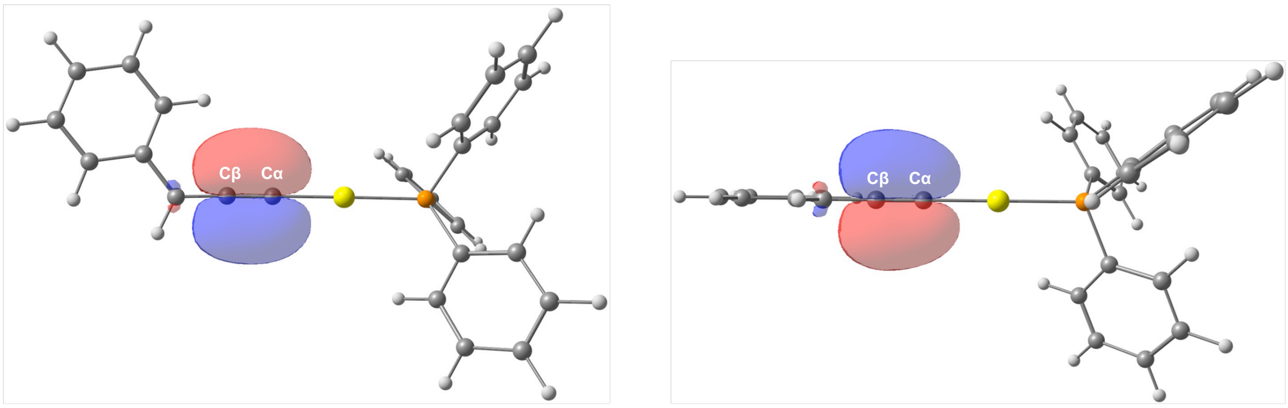
Figure S1. Correlation between calculated and experimental NMR chemical shifts of **3ac**.

Computational studies were performed at the CPCM(CH_2Cl_2)/ωB97XD/6-31+G(d) with Def2TZVP(Au) level on pathways from **C** or **D** to *syn*-**3aa** (Scheme 5).

It was evaluated whether the structure of starting complex was **C** or **D**. The NBO calculation revealed that gold(I)-coordinated allenylidene species have one C–C triple bond (Figure S2), and p orbital at the Cγ carbon in LUMO was observed (Figure S3). Thus, it was found that gold(I)-stabilized propargyl cation species **D** is generated rather than gold(I)-coordinated allenylidene species **C** in the present system.



sp hybrid bond orbital of Cα-Cβ
Cα s(51.21%) p(48.71%), Cβ s(49.29%) p(50.61%)



1st p bond orbital of Cα-Cβ
Cα s(0.01%) p(99.93%), Cβ s(0.00%) p(99.85%)

2nd p bond orbital of Cα-Cβ
Cα s(0.00%) p(100.00%), Cβ s(0.00%) p(99.84%)

Figure S2. NBO analysis of gold(I)-stabilized propargyl cation.

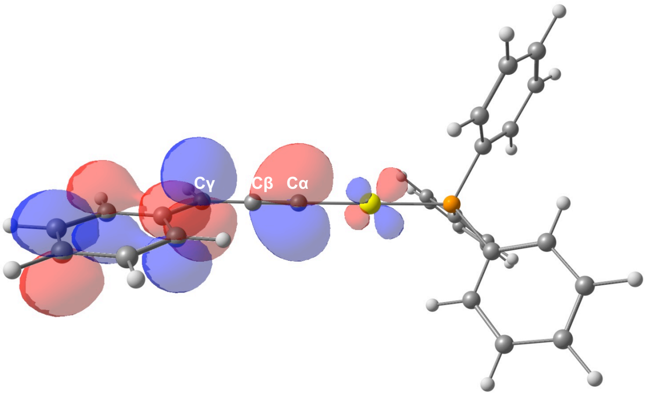


Figure S3. LUMO orbitals of gold(I)-stabilized propargyl cation.

Next, the transition state for cyclopropanation was searched.

In a first attempt, based on a previous report on the reaction of gold(I)-coordinated benzylidene species with styrene, transition states for cyclopropanation by concerted mechanisms were explored, but could not be found. Therefore, the transition state was searched using Reaction plus Pro 2 program[19] at the CPCM(CH_2Cl_2)/B97D3/SDD level. Exploration using a model complex with the phosphine ligand changed from PPh_3 to PH_3 revealed a two-step cyclopropanation mechanism (Figure S4).

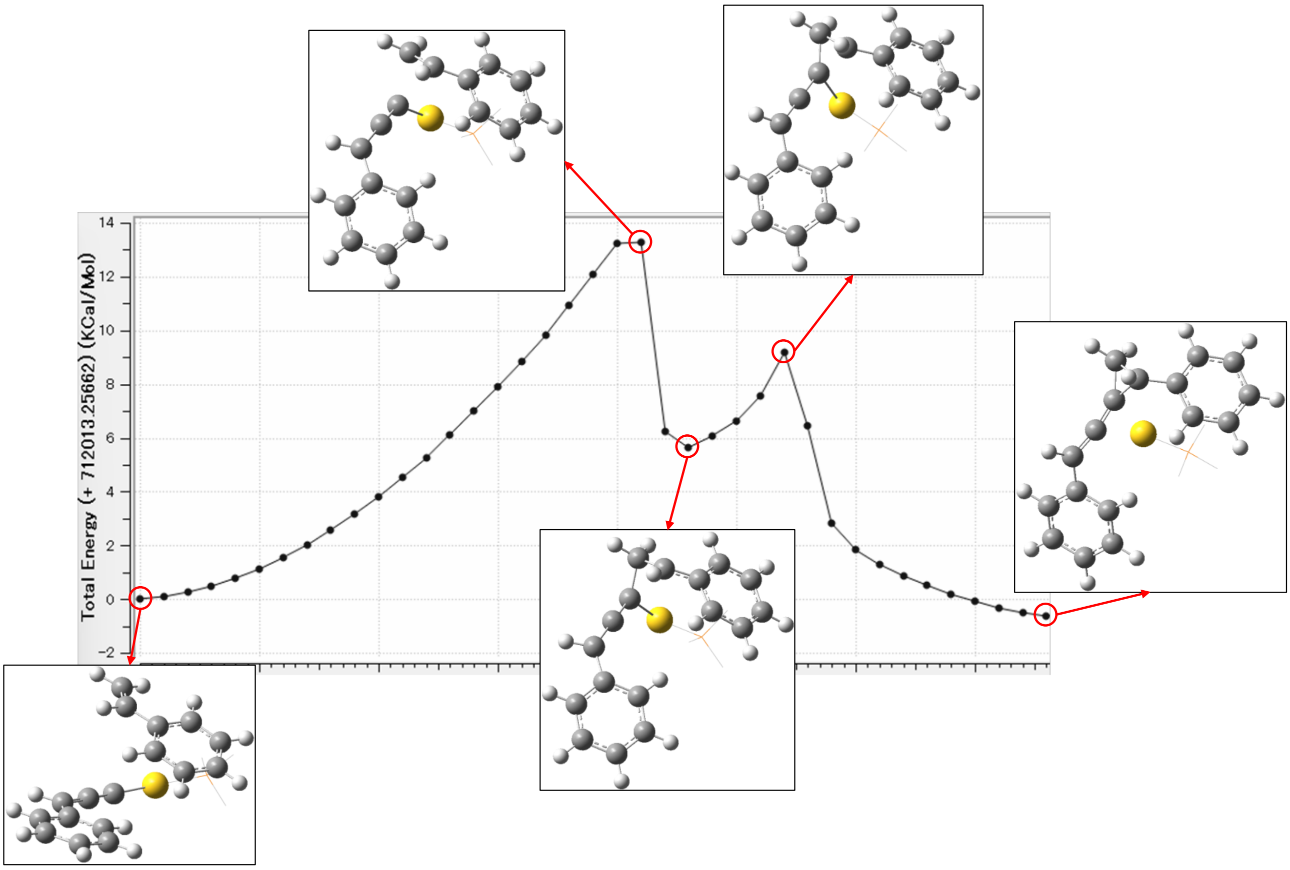


Figure S4. Transition states search of cyclopropanation.

According to the result, the transition states of cyclopropanation in real complexes having PPh_3 ligand were calculated at the CPCM(CH_2Cl_2)/ωB97XD/6-31+G(d) with Def2TZVP(Au). The mechanistic pathway from **D** to the Au-coordinated product (**3---Au**) was connected using the IRC calculations (Figure S5).

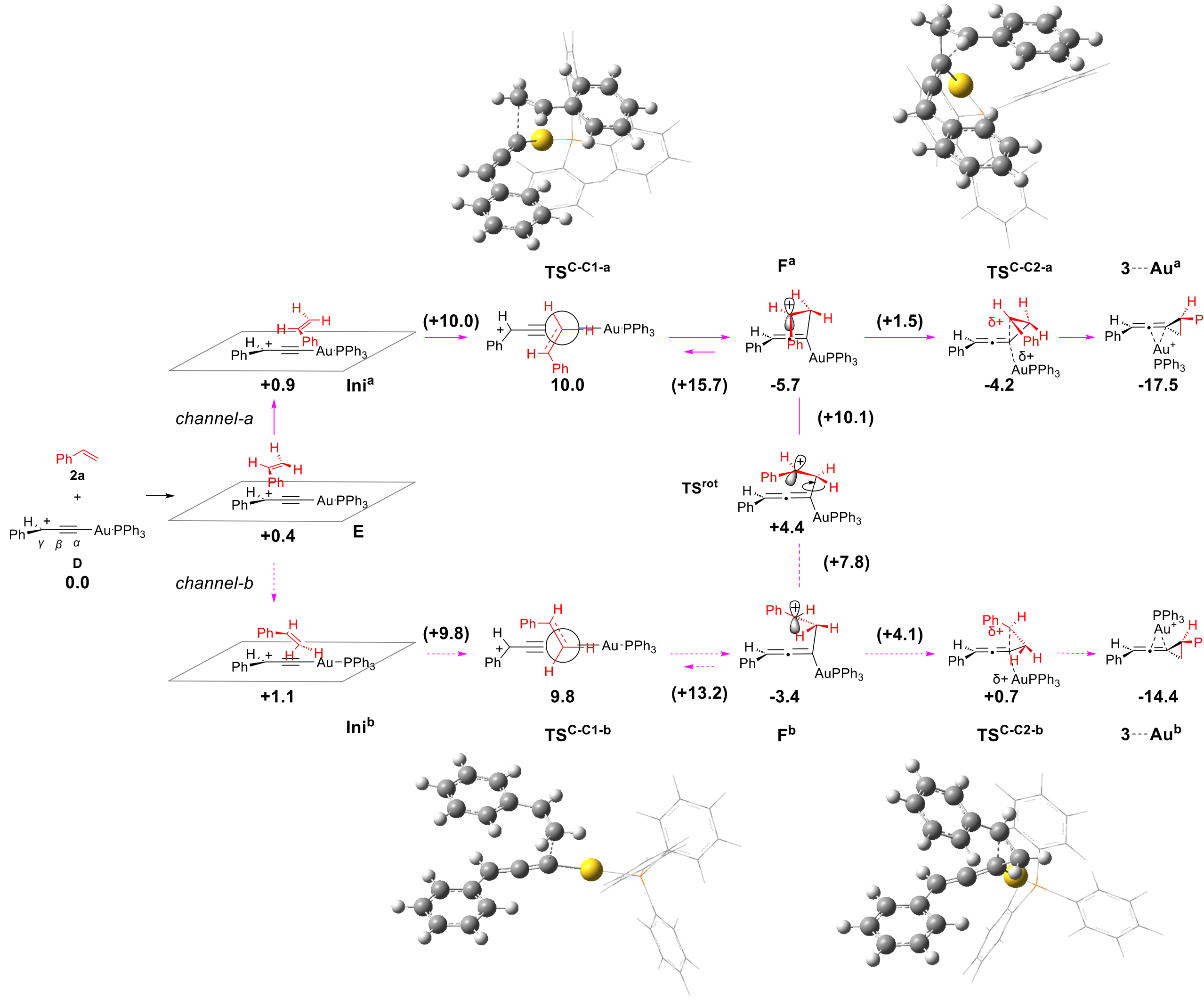


Figure S5. DFT calculations on the mechanism of gold(I)-mediated cyclopropanation of styrene (**2a**) with 1-phenyl-3-(tributylstannyl)propargyl acetates (**1a**). The geometric features of key transition structures leading to *syn*-vinylidenecyclopropane (*syn*-**3aa**) are shown.

The styrene (**2a**) attacks to Cα carbon of the gold(I)-stabilized propargyl cation species **D** to produce carbenium intermediate **F** (1st step**).** From the direction of the styrene attack, the reaction branches into two channels (channel-a and channel-b), giving **F**$^{\mathbf{a}}$ or **F**$^{\mathbf{b}}$ through transition states **TS**$^{\mathbf{C\text{-}C1\text{-}a}}$ or **TS**$^{\mathbf{C\text{-}C1\text{-}b}}$, respectively. The next carbon-carbon bond formation (2nd step) gives cyclopropane products **3---Au**$^{\mathbf{a}}$ through **TS**$^{\mathbf{C\text{-}C2\text{-}a}}$ (channel-a) or **3---Au**$^{\mathbf{b}}$ through **TS**$^{\mathbf{C\text{-}C2\text{-}b}}$ (channel-b). The activation free energies of 1st step are 10.0 kcal mol^{-1} (**2a+D→TS**$^{\mathbf{C\text{-}C1\text{-}a}}$) or 9.8 kcal mol^{-1} (**2a+D→TS**$^{\mathbf{C\text{-}C1\text{-}b}}$), and those of 2nd step are 1.5 kcal mol^{-1} (**F**$^{\mathbf{a}}$**→TS**$^{\mathbf{C\text{-}C2\text{-}a}}$) or 4.1 kcal mol^{-1} (**F**$^{\mathbf{b}}$**→TS**$^{\mathbf{C\text{-}C2\text{-}b}}$). The irreversible reactions from **F** to **Ini** do not occur due to significantly higher activation free energies (15.7 for **F**$^{\mathbf{a}}$**→TS**$^{\mathbf{C\text{-}C1\text{-}a}}$ or 13.2 kcal mol^{-1} for **F**$^{\mathbf{b}}$**→TS**$^{\mathbf{C\text{-}C1\text{-}b}}$). Although there is a possibility of equilibrium between **F**$^{\mathbf{a}}$ and **F**$^{\mathbf{b}}$ through TS$^{\text{rot}}$, higher activation free energies (10.1 or 7.8 kcal mol^{-1}) than the energies of 2nd step make this equilibrium impossible. Therefore, the reaction proceeds straightforwardly without branching along the way. From these energies relationship, the 1st step proceeds most slowly in the reaction system from **2a+D** to **3---Au**. Because the activation free energies of 1st step step in both channels are almost the same (10.0 vs. 9.8 kcal mol^{-1}), either route can proceed and give *syn*-**3aa**.

Cartesian coordinates and energies of optimized structures

All structures were optimized at the CPCM(CH_2Cl_2)/ωB97XD/6-31+G(d) with Def2TZVP(Au) level, except for *syn*- and *anti*-**3ac**, which were optimized at the SMD($CHCl_3$)/B97D3/6-311+G(2d,p) level.

Styrene (2a)

E(RwB97XD) = -309.550007941
Thermal correction to Gibbs Free Energy= 0.103040
Sum of electronic and thermal Free Energies= -309.447025

1	6	0	-0.405706	-1.280450	-0.000010
2	6	0	0.511936	-0.220663	0.000112
3	6	0	0.010334	1.090146	0.000190
4	6	0	-1.360327	1.328202	0.000062
5	6	0	-2.262300	0.262242	-0.000112
6	6	0	-1.779282	-1.044695	-0.000129
7	1	0	-0.037263	-2.303836	-0.000020
8	1	0	0.691718	1.935996	0.000383
9	1	0	-1.727446	2.350730	0.000120
10	1	0	-3.331875	0.451485	-0.000198
11	1	0	-2.470482	-1.882754	-0.000244
12	6	0	1.956178	-0.532039	0.000220
13	1	0	2.191142	-1.596371	0.000751
14	6	0	2.971834	0.337796	-0.000294
15	1	0	2.829108	1.415449	-0.000883

D

E(RwB97XD) = -1518.11994555
Thermal correction to Gibbs Free Energy= 0.335866
Sum of electronic and thermal Free Energies= -1517.784080

1	6	0	8.431250	-0.096553	-0.029954
2	6	0	7.373404	-0.987797	0.018134
3	6	0	6.041826	-0.506137	0.004212
4	6	0	5.797468	0.888200	-0.058826
5	6	0	6.860736	1.768873	-0.106386
6	6	0	8.172996	1.276425	-0.091952
7	1	0	9.453247	-0.459128	-0.019691
8	1	0	7.555260	-2.057357	0.066539
9	1	0	4.774402	1.251804	-0.069183
10	1	0	6.682992	2.837636	-0.154770
11	1	0	9.004056	1.974133	-0.129605
12	6	0	4.979794	-1.445362	0.054299
13	1	0	5.248118	-2.501543	0.101902
14	6	0	3.646714	-1.140919	0.047803
15	6	0	2.433824	-0.884504	0.040679
16	79	0	0.491038	-0.457130	0.028137
17	15	0	-1.803289	0.038682	0.012243
18	6	0	-2.190179	1.624801	-0.800313
19	6	0	-3.166155	2.490253	-0.297039
20	6	0	-1.511092	1.954545	-1.980008
21	6	0	-3.461128	3.674432	-0.971319
22	1	0	-3.697865	2.247033	0.618250
23	6	0	-1.813248	3.134581	-2.653508
24	1	0	-0.746300	1.290488	-2.375749
25	6	0	-2.788026	3.996170	-2.148646
26	1	0	-4.218265	4.344050	-0.574767
27	1	0	-1.283881	3.383822	-3.568054
28	1	0	-3.019340	4.919390	-2.671533
29	6	0	-2.511706	0.157840	1.688773
30	6	0	-3.765741	-0.377628	1.996809
31	6	0	-1.784532	0.836233	2.675325
32	6	0	-4.288382	-0.232419	3.281313
33	1	0	-4.338076	-0.908245	1.241594
34	6	0	-2.313001	0.984533	3.954318
35	1	0	-0.805880	1.251804	2.447116
36	6	0	-3.565235	0.448848	4.258629
37	1	0	-5.261796	-0.652564	3.515430
38	1	0	-1.745194	1.512558	4.714293
39	1	0	-3.974456	0.559969	5.258331
40	6	0	-2.799370	-1.216627	-0.857798
41	6	0	-3.885018	-0.862449	-1.664517
42	6	0	-2.482238	-2.568350	-0.674161
43	6	0	-4.648340	-1.853983	-2.279148
44	1	0	-4.139085	0.182395	-1.817305
45	6	0	-3.251062	-3.555311	-1.284344
46	1	0	-1.635454	-2.852862	-0.054184
47	6	0	-4.334281	-3.198505	-2.088441
48	1	0	-5.488766	-1.573093	-2.906568
49	1	0	-3.000732	-4.601472	-1.137145
50	1	0	-4.930224	-3.968709	-2.568946

E

E(RwB97XD) = -1827.68942779
Thermal correction to Gibbs Free Energy= 0.459016
Sum of electronic and thermal Free Energies= -1827.230412

1	6	0	7.755381	1.150834	0.065096
2	6	0	6.784028	0.980354	-0.906960
3	6	0	5.417299	1.100949	-0.567541
4	6	0	5.046620	1.402549	0.763768
5	6	0	6.023903	1.569982	1.727887
6	6	0	7.374087	1.442803	1.378515
7	1	0	8.805733	1.057533	-0.188824
8	1	0	7.062868	0.745034	-1.930089
9	1	0	3.994871	1.496073	1.018015
10	1	0	5.746842	1.798998	2.751350
11	1	0	8.137101	1.574564	2.139649
12	6	0	4.437777	0.879695	-1.577313
13	1	0	4.792234	0.647960	-2.581528
14	6	0	3.089112	0.939075	-1.376312
15	6	0	1.873390	0.887335	-1.139860
16	79	0	-0.042631	0.652892	-0.669885
17	15	0	-2.258459	0.242903	-0.024118
18	6	0	-3.100375	-1.022439	-1.029850
19	6	0	-4.497462	-1.110722	-1.050563
20	6	0	-2.338141	-1.941471	-1.759186
21	6	0	-5.121739	-2.114603	-1.786010
22	1	0	-5.101609	-0.398118	-0.495747
23	6	0	-2.966017	-2.946891	-2.491562
24	1	0	-1.253569	-1.872969	-1.761714
25	6	0	-4.357071	-3.034751	-2.504183
26	1	0	-6.205574	-2.177207	-1.798935
27	1	0	-2.367470	-3.656052	-3.055170
28	1	0	-4.846595	-3.816132	-3.077782
29	6	0	-3.343664	1.707449	-0.065408
30	6	0	-4.319316	1.928335	0.911748
31	6	0	-3.215109	2.603369	-1.133848
32	6	0	-5.160839	3.035488	0.817898
33	1	0	-4.425557	1.242842	1.747753
34	6	0	-4.061435	3.704859	-1.226723
35	1	0	-2.454076	2.443210	-1.893736
36	6	0	-5.034172	3.922168	-0.250202
37	1	0	-5.915274	3.202810	1.580602
38	1	0	-3.956991	4.396332	-2.057227
39	1	0	-5.690104	4.784754	-0.320279
40	6	0	-2.311158	-0.358285	1.698291
41	6	0	-2.868885	-1.590713	2.042517
42	6	0	-1.718622	0.437110	2.687863
43	6	0	-2.835752	-2.024010	3.368637
44	1	0	-3.323346	-2.221667	1.284580
45	6	0	-1.697732	0.007576	4.010231
46	1	0	-1.268313	1.391722	2.425335
47	6	0	-2.254147	-1.226901	4.351903
48	1	0	-3.265706	-2.986353	3.629242
49	1	0	-1.239314	0.630300	4.772396
50	1	0	-2.229407	-1.566757	5.382927
51	6	0	1.332086	-2.789071	-0.352820
52	6	0	0.404919	-2.693231	0.682612
53	6	0	0.755936	-2.072827	1.880197
54	6	0	2.039378	-1.546172	2.032036
55	6	0	2.967864	-1.651749	1.001178
56	6	0	2.632733	-2.283307	-0.206747
57	1	0	1.049182	-3.269496	-1.286911
58	1	0	-0.596113	-3.095774	0.552534
59	1	0	0.030404	-1.988619	2.683928
60	1	0	2.316710	-1.048010	2.956789
61	1	0	3.960962	-1.233036	1.138823
62	6	0	3.586944	-2.430087	-1.319477
63	1	0	3.145184	-2.732511	-2.268693
64	6	0	4.910998	-2.236200	-1.268588
65	1	0	5.430672	-1.959474	-0.354415
66	1	0	5.526051	-2.370980	-2.153513

Ini[a]

E(RwB97XD) = -1827.68876550
Thermal correction to Gibbs Free Energy= 0.459059
Sum of electronic and thermal Free Energies= -1827.229706

1	6	0	-7.878946	-0.960759	0.265723

2	6	0	-6.880546	-1.420899	-0.576156
3	6	0	-5.522448	-1.267452	-0.210159
4	6	0	-5.190020	-0.652144	1.021600
5	6	0	-6.194029	-0.197026	1.854619
6	6	0	-7.534438	-0.350347	1.475624
7	1	0	-8.921678	-1.072717	-0.010525
8	1	0	-7.131054	-1.895758	-1.520209
9	1	0	-4.145661	-0.543523	1.298982
10	1	0	-5.947782	0.275816	2.799352
11	1	0	-8.319121	0.009364	2.134217
12	6	0	-4.516299	-1.724394	-1.103992
13	1	0	-4.842271	-2.202665	-2.028108
14	6	0	-3.174632	-1.589226	-0.896275
15	6	0	-1.966213	-1.390268	-0.699644
16	79	0	-0.075802	-0.919177	-0.310900
17	15	0	2.129180	-0.273449	0.157896
18	6	0	2.420860	0.151849	1.905112
19	6	0	3.711677	0.132920	2.446217
20	6	0	1.341142	0.548972	2.701268
21	6	0	3.917883	0.516206	3.768928
22	1	0	4.557445	-0.180714	1.840660
23	6	0	1.552011	0.936943	4.022571
24	1	0	0.334927	0.561008	2.291418
25	6	0	2.839614	0.921237	4.556627
26	1	0	4.920876	0.497959	4.184189
27	1	0	0.709160	1.246078	4.633364
28	1	0	3.003505	1.219511	5.587869
29	6	0	3.386162	-1.522206	-0.270541
30	6	0	4.630892	-1.162089	-0.797137
31	6	0	3.101309	-2.870319	-0.021562
32	6	0	5.582260	-2.143526	-1.069480
33	1	0	4.861804	-0.119974	-0.999255
34	6	0	4.056637	-3.846915	-0.289658
35	1	0	2.133525	-3.160658	0.380360
36	6	0	5.297248	-3.484213	-0.814932
37	1	0	6.545915	-1.858178	-1.480423
38	1	0	3.829583	-4.890634	-0.095017
39	1	0	6.039649	-4.247166	-1.029350
40	6	0	2.563197	1.215622	-0.802981
41	6	0	2.936054	2.412912	-0.190306
42	6	0	2.443664	1.156293	-2.197699
43	6	0	3.177109	3.547005	-0.966459
44	1	0	3.029866	2.472776	0.889894
45	6	0	2.696349	2.285444	-2.969134
46	1	0	2.145237	0.229270	-2.682322
47	6	0	3.056528	3.485674	-2.352754
48	1	0	3.457408	4.477989	-0.483196
49	1	0	2.601172	2.232748	-4.049495
50	1	0	3.241693	4.370388	-2.954415
51	6	0	-2.992036	1.946126	-0.190447
52	6	0	-2.810933	2.231871	1.161139
53	6	0	-1.576158	2.690234	1.617239
54	6	0	-0.531441	2.869402	0.708948
55	6	0	-0.713220	2.580991	-0.639758
56	6	0	-1.944989	2.099232	-1.109068
57	1	0	-3.957577	1.586424	-0.539865
58	1	0	-3.634952	2.100323	1.857292
59	1	0	-1.428027	2.912337	2.670308
60	1	0	0.432239	3.233901	1.053575
61	1	0	0.112525	2.732429	-1.329717
62	6	0	-2.171624	1.726775	-2.519227
63	1	0	-3.216296	1.592001	-2.799359
64	6	0	-1.228733	1.511305	-3.442743
65	1	0	-0.167252	1.597695	-3.224185
66	1	0	-1.497558	1.229338	-4.456395

TS^{C-C1-a}

E(RwB97XD) = -1827.67698582

Thermal correction to Gibbs Free Energy= 0.461780

Sum of electronic and thermal Free Energies= -1827.215206

1	6	0	7.713370	1.426561	0.623542
2	6	0	6.802595	1.627097	-0.407503
3	6	0	5.493183	1.127270	-0.302449
4	6	0	5.110603	0.429640	0.858614
5	6	0	6.023151	0.232910	1.884972
6	6	0	7.325168	0.729373	1.768434
7	1	0	8.723917	1.812867	0.536415
8	1	0	7.100924	2.168989	-1.300773
9	1	0	4.095079	0.054300	0.949832
10	1	0	5.724191	-0.304731	2.779338
11	1	0	8.036563	0.573943	2.573934
12	6	0	4.569771	1.334615	-1.404386
13	1	0	4.931740	1.904768	-2.259826
14	6	0	3.315460	0.876258	-1.433863
15	6	0	2.133453	0.417476	-1.417654
16	79	0	0.214001	0.425976	-0.779072
17	15	0	-1.949308	0.473447	0.100362
18	6	0	-2.481305	2.141903	0.611066
19	6	0	-3.207232	2.357725	1.786286
20	6	0	-2.179743	3.222471	-0.227214
21	6	0	-3.629665	3.644470	2.117564
22	1	0	-3.444643	1.528085	2.446011
23	6	0	-2.608801	4.504524	0.103987
24	1	0	-1.609262	3.064591	-1.139512
25	6	0	-3.333091	4.716630	1.277817
26	1	0	-4.191270	3.806389	3.032645
27	1	0	-2.372041	5.338001	-0.550285
28	1	0	-3.662351	5.718031	1.538748
29	6	0	-2.087222	-0.562460	1.596624
30	6	0	-3.130036	-1.474026	1.777245
31	6	0	-1.108914	-0.421924	2.588603
32	6	0	-3.196458	-2.233862	2.944858
33	1	0	-3.890982	-1.599744	1.012951
34	6	0	-1.182242	-1.176471	3.754675
35	1	0	-0.284977	0.274539	2.450820
36	6	0	-2.226684	-2.084472	3.933995
37	1	0	-4.007543	-2.943505	3.077869
38	1	0	-0.419536	-1.062672	4.519021
39	1	0	-2.279712	-2.678698	4.841462
40	6	0	-3.239119	-0.120673	-1.042732
41	6	0	-4.554253	0.350316	-0.962891
42	6	0	-2.910592	-1.098599	-1.988353
43	6	0	-5.530066	-0.159295	-1.816839
44	1	0	-4.821594	1.114414	-0.238426
45	6	0	-3.889221	-1.609463	-2.837216
46	1	0	-1.889242	-1.460229	-2.066459
47	6	0	-5.199794	-1.140441	-2.751424
48	1	0	-6.548348	0.211777	-1.751446
49	1	0	-3.626010	-2.367837	-3.568294
50	1	0	-5.962175	-1.534999	-3.416503
51	6	0	2.646318	-2.092271	-1.535014
52	6	0	2.369384	-1.476773	-2.717329
53	1	0	3.172266	-1.118786	-3.351202
54	1	0	1.371547	-1.464461	-3.145304
55	6	0	1.664022	-2.684744	-0.629887
56	6	0	1.993528	-2.824437	0.726860
57	6	0	0.377694	-3.053487	-1.056780
58	6	0	1.050622	-3.285508	1.640852
59	1	0	2.988641	-2.548512	1.066814
60	6	0	-0.561175	-3.517953	-0.143702
61	1	0	0.114471	-2.985571	-2.108396
62	6	0	-0.229135	-3.626893	1.207710
63	1	0	1.310253	-3.369301	2.691754
64	1	0	-1.556030	-3.792054	-0.482638
65	1	0	-0.970533	-3.971260	1.921979
66	1	0	3.678760	-2.095044	-1.190069

F^{a}

E(RwB97XD) = -1827.70628257

Thermal correction to Gibbs Free Energy= 0.466097

Sum of electronic and thermal Free Energies= -1827.240186

1	6	0	6.048066	2.294808	0.908718
2	6	0	5.531391	2.069600	-0.365873
3	6	0	4.335412	1.360006	-0.529656
4	6	0	3.657616	0.897648	0.608009
5	6	0	4.177928	1.119133	1.878560
6	6	0	5.376801	1.817232	2.034260
7	1	0	6.977871	2.844578	1.021642
8	1	0	6.059986	2.442429	-1.239341
9	1	0	2.714410	0.367932	0.498506
10	1	0	3.643478	0.749382	2.749132
11	1	0	5.781846	1.992201	3.026496
12	6	0	3.802064	1.119342	-1.886668
13	1	0	4.195958	1.708176	-2.713600
14	6	0	2.872109	0.229841	-2.134755
15	6	0	1.866386	-0.626805	-2.244854
16	79	0	0.071868	-0.064048	-1.330855
17	15	0	-1.748268	0.431339	0.031421
18	6	0	-3.274539	-0.488318	-0.353332
19	6	0	-4.540809	0.051352	-0.106246
20	6	0	-3.163591	-1.785352	-0.868962
21	6	0	-5.683333	-0.702414	-0.369305
22	1	0	-4.641820	1.058129	0.288749
23	6	0	-4.306446	-2.538585	-1.123558
24	1	0	-2.183416	-2.208153	-1.073787
25	6	0	-5.567658	-1.996861	-0.874326
26	1	0	-6.663704	-0.276344	-0.178975
27	1	0	-4.212029	-3.544033	-1.522425
28	1	0	-6.459596	-2.581587	-1.078742
29	6	0	-2.223456	2.189041	0.097937
30	6	0	-2.629805	2.799141	1.289084
31	6	0	-2.207673	2.928233	-1.090909
32	6	0	-3.020313	4.137137	1.288012
33	1	0	-2.641239	2.236127	2.218171
34	6	0	-2.605104	4.262664	-1.089138
35	1	0	-1.882468	2.463131	-2.018445

36	6	0	-3.010491	4.868075	0.100725
37	1	0	-3.332527	4.606776	2.215893
38	1	0	-2.590788	4.830980	-2.014163
39	1	0	-3.314079	5.910736	0.102865
40	6	0	-1.318267	-0.026129	1.748175
41	6	0	-2.130348	-0.852794	2.527258
42	6	0	-0.116357	0.462319	2.277881
43	6	0	-1.745293	-1.184699	3.826411
44	1	0	-3.062012	-1.243201	2.128626
45	6	0	0.260214	0.135635	3.575944
46	1	0	0.526802	1.101401	1.676895
47	6	0	-0.553662	-0.691079	4.351877
48	1	0	-2.380149	-1.830650	4.425549
49	1	0	1.191608	0.520006	3.980591
50	1	0	-0.255317	-0.952757	5.362809
51	6	0	2.724587	-2.424925	0.938942
52	6	0	2.091084	-2.736227	2.134787
53	6	0	0.788203	-3.235054	2.120320
54	6	0	0.125991	-3.443809	0.909386
55	6	0	0.755949	-3.134842	-0.288462
56	6	0	2.058280	-2.602660	-0.285733
57	1	0	3.732580	-2.019598	0.947008
58	1	0	2.605264	-2.579468	3.077574
59	1	0	0.286029	-3.462088	3.055402
60	1	0	-0.883561	-3.842551	0.902727
61	1	0	0.236154	-3.311076	-1.224812
62	6	0	2.720818	-2.170017	-1.502829
63	1	0	3.784432	-1.961104	-1.432649
64	6	0	2.122378	-2.061916	-2.811082
65	1	0	2.809068	-2.072222	-3.653020
66	1	0	1.194881	-2.589817	-3.006044

TS$^{\text{C-C2-a}}$

E(RwB97XD) = -1827.70399082
Thermal correction to Gibbs Free Energy= 0.466175
Sum of electronic and thermal Free Energies= -1827.237816

1	6	0	5.723250	2.878241	0.847151
2	6	0	5.157922	2.627381	-0.401463
3	6	0	4.084125	1.737138	-0.526059
4	6	0	3.575893	1.116314	0.624621
5	6	0	4.144151	1.366979	1.869425
6	6	0	5.221612	2.246967	1.985316
7	1	0	6.557038	3.569228	0.930103
8	1	0	5.552472	3.122063	-1.285170
9	1	0	2.723765	0.444794	0.549038
10	1	0	3.739827	0.878743	2.751641
11	1	0	5.663090	2.443830	2.957735
12	6	0	3.494605	1.481490	-1.856817
13	1	0	3.714891	2.174390	-2.667571
14	6	0	2.708576	0.463122	-2.102658
15	6	0	1.841224	-0.537761	-2.196644
16	79	0	0.038941	-0.202923	-1.193975
17	15	0	-1.832922	0.333230	0.082647
18	6	0	-3.307491	0.793778	-0.884265
19	6	0	-4.182675	1.800321	-0.464548
20	6	0	-3.577925	0.085851	-2.061880
21	6	0	-5.320455	2.091679	-1.215326
22	1	0	-3.981431	2.360755	0.443771
23	6	0	-4.719397	0.374412	-2.804898
24	1	0	-2.896863	-0.691549	-2.400112
25	6	0	-5.590992	1.378651	-2.382360
26	1	0	-5.994533	2.876798	-0.886433
27	1	0	-4.924105	-0.179305	-3.716146
28	1	0	-6.477883	1.608226	-2.965460
29	6	0	-1.493783	1.738855	1.197277
30	6	0	-2.080110	1.826504	2.464549
31	6	0	-0.638768	2.757761	0.759054
32	6	0	-1.815655	2.924192	3.281430
33	1	0	-2.740074	1.040178	2.820146
34	6	0	-0.378990	3.854448	1.576779
35	1	0	-0.168685	2.695150	-0.219510
36	6	0	-0.966684	3.938047	2.839039
37	1	0	-2.272588	2.984934	4.264566
38	1	0	0.287938	4.638298	1.230721
39	1	0	-0.758928	4.790255	3.479257
40	6	0	-2.365778	-1.019140	1.186330
41	6	0	-3.702508	-1.410709	1.296056
42	6	0	-1.389257	-1.658425	1.960523
43	6	0	-4.059339	-2.432123	2.176658
44	1	0	-4.469022	-0.924235	0.700028
45	6	0	-1.750673	-2.669842	2.844335
46	1	0	-0.344500	-1.368264	1.873678
47	6	0	-3.086632	-3.059183	2.952717
48	1	0	-5.099411	-2.733761	2.255786
49	1	0	-0.988890	-3.159181	3.443850
50	1	0	-3.366956	-3.852709	3.639065
51	6	0	3.335924	-2.424914	0.716195
52	6	0	2.955909	-3.012112	1.916884
53	6	0	1.781434	-3.762964	1.979846
54	6	0	0.988198	-3.927573	0.842801
55	6	0	1.362532	-3.339314	-0.357884
56	6	0	2.542182	-2.578856	-0.432281
57	1	0	4.247150	-1.835099	0.664516
58	1	0	3.572784	-2.886117	2.800906
59	1	0	1.484982	-4.224794	2.917041
60	1	0	0.075003	-4.511500	0.895196
61	1	0	0.738403	-3.478902	-1.234742
62	6	0	2.979318	-1.937709	-1.663619
63	1	0	4.000661	-1.569033	-1.680190
64	6	0	2.248196	-1.868216	-2.903890
65	1	0	2.837860	-1.714813	-3.803180
66	1	0	1.397845	-2.525638	-3.048595

3---Au^{a}

E(RwB97XD) = -1827.72652700
Thermal correction to Gibbs Free Energy= 0.467599
Sum of electronic and thermal Free Energies= -1827.258928

1	6	0	5.084028	-1.236628	-0.237666
2	6	0	4.184604	-2.264810	-0.513356
3	6	0	3.031494	-2.416632	0.263787
4	6	0	2.814453	-1.550534	1.342237
5	6	0	3.713357	-0.521248	1.614117
6	6	0	4.846138	-0.357940	0.819509
7	1	0	5.968391	-1.116147	-0.856575
8	1	0	4.366241	-2.939172	-1.345955
9	1	0	1.943847	-1.698029	1.976292
10	1	0	3.528227	0.151701	2.446593
11	1	0	5.541986	0.450468	1.022694
12	6	0	2.035373	-3.469044	-0.067014
13	1	0	2.359572	-4.509769	-0.088917
14	6	0	0.771506	-3.229573	-0.351453
15	6	0	-0.515111	-3.228428	-0.685747
16	79	0	0.060265	-1.075400	-0.446511
17	15	0	-0.017306	1.239645	-0.163543
18	6	0	-1.121004	2.059945	-1.351097
19	6	0	-0.812404	3.307481	-1.900007
20	6	0	-2.330978	1.432499	-1.673041
21	6	0	-1.712855	3.923317	-2.768263
22	1	0	0.124782	3.799598	-1.655758
23	6	0	-3.230598	2.056526	-2.531519
24	1	0	-2.577921	0.461544	-1.248695
25	6	0	-2.920593	3.301240	-3.081625
26	1	0	-1.469550	4.890373	-3.197574
27	1	0	-4.169602	1.568248	-2.774270
28	1	0	-3.619905	3.784589	-3.757254
29	6	0	1.624609	2.007060	-0.308867
30	6	0	2.042976	3.015016	0.564518
31	6	0	2.479725	1.564046	-1.324985
32	6	0	3.311570	3.574601	0.419879
33	1	0	1.388598	3.362080	1.358903
34	6	0	3.740445	2.132555	-1.470858
35	1	0	2.167968	0.767576	-1.996398
36	6	0	4.158441	3.135841	-0.596484
37	1	0	3.635934	4.353692	1.103015
38	1	0	4.402360	1.780780	-2.256078
39	1	0	5.147753	3.570709	-0.703602
40	6	0	-0.654747	1.657508	1.491516
41	6	0	-1.711773	2.551962	1.669838
42	6	0	-0.080091	1.029461	2.603388
43	6	0	-2.191322	2.813957	2.953216
44	1	0	-2.171172	3.040405	0.815881
45	6	0	-0.554289	1.299893	3.882065
46	1	0	0.737690	0.326480	2.471101
47	6	0	-1.614984	2.190885	4.057693
48	1	0	-3.017509	3.505812	3.085855
49	1	0	-0.103092	0.809958	4.739451
50	1	0	-1.992181	2.395298	5.055225
51	6	0	-2.464773	-1.866555	1.510073
52	6	0	-3.225942	-0.800880	1.982736
53	6	0	-4.324260	-0.348828	1.250742
54	6	0	-4.661737	-0.974654	0.051982
55	6	0	-3.891064	-2.035075	-0.426629
56	6	0	-2.781046	-2.482308	0.292634
57	1	0	-1.601519	-2.207869	2.077172
58	1	0	-2.949629	-0.310668	2.911960
59	1	0	-4.910542	0.491022	1.612219
60	1	0	-5.517208	-0.629608	-0.521696
61	1	0	-4.149162	-2.507254	-1.370748
62	6	0	-1.898647	-3.576077	-0.241045
63	1	0	-1.984753	-4.545559	0.247455
64	6	0	-1.520646	-3.586108	-1.717849
65	1	0	-1.378847	-4.542246	-2.214153
66	1	0	-1.921240	-2.792906	-2.343178

Ini^{b}

E(RwB97XD) = -1827.68759756
Thermal correction to Gibbs Free Energy= 0.458289
Sum of electronic and thermal Free Energies= -1827.229308

1	6	0	-7.783124	1.549435	0.094968
2	6	0	-6.799556	1.053567	0.935245
3	6	0	-5.440753	1.140393	0.558930
4	6	0	-5.088316	1.734247	-0.674584
5	6	0	-6.076623	2.225829	-1.507316
6	6	0	-7.420456	2.132297	-1.122756
7	1	0	-8.828002	1.484402	0.378608
8	1	0	-7.065238	0.592046	1.881983
9	1	0	-4.042232	1.791535	-0.960437
10	1	0	-5.814203	2.680350	-2.456683
11	1	0	-8.192422	2.518236	-1.781605
12	6	0	-4.453246	0.595421	1.429080
13	1	0	-4.799681	0.132127	2.353383
14	6	0	-3.108365	0.618402	1.204961
15	6	0	-1.889450	0.590077	0.979522
16	79	0	0.050052	0.483447	0.557523
17	15	0	2.320352	0.297904	0.002264
18	6	0	2.624348	0.589508	-1.772351
19	6	0	3.711891	1.341003	-2.225014
20	6	0	1.747954	0.007727	-2.697674
21	6	0	3.921970	1.506465	-3.593913
22	1	0	4.396798	1.799469	-1.517701
23	6	0	1.965686	0.168536	-4.062463
24	1	0	0.897408	-0.576094	-2.352939
25	6	0	3.053003	0.919843	-4.511804
26	1	0	4.766980	2.093849	-3.940125
27	1	0	1.284456	-0.287427	-4.774460
28	1	0	3.219532	1.049936	-5.576977
29	6	0	3.402856	1.460332	0.894732
30	6	0	4.685471	1.091877	1.312590
31	6	0	2.943731	2.762755	1.126659
32	6	0	5.502032	2.020980	1.955167
33	1	0	5.050874	0.083423	1.141429
34	6	0	3.765125	3.689585	1.762598
35	1	0	1.944916	3.055326	0.811694
36	6	0	5.044475	3.318733	2.178210
37	1	0	6.495925	1.728730	2.280265
38	1	0	3.404056	4.698180	1.939129
39	1	0	5.682413	4.040509	2.679539
40	6	0	2.982525	-1.367463	0.337700
41	6	0	3.842362	-2.010339	-0.556942
42	6	0	2.597369	-2.015206	1.517506
43	6	0	4.306628	-3.294687	-0.276118
44	1	0	4.144100	-1.520672	-1.478137
45	6	0	3.065070	-3.295730	1.796222
46	1	0	1.920682	-1.526817	2.214594
47	6	0	3.916814	-3.938763	0.896741
48	1	0	4.969210	-3.791769	-0.978041
49	1	0	2.756822	-3.795421	2.709509
50	1	0	4.273070	-4.942221	1.109605
51	6	0	-2.896052	-2.953294	0.993699
52	6	0	-4.267884	-2.717390	0.932628
53	6	0	-4.824578	-2.118489	-0.198243
54	6	0	-3.998108	-1.742742	-1.258168
55	6	0	-2.628450	-1.974997	-1.193069
56	6	0	-2.059079	-2.605408	-0.073920
57	1	0	-2.468023	-3.422194	1.876521
58	1	0	-4.903210	-3.003709	1.766163
59	1	0	-5.893863	-1.933364	-0.248135
60	1	0	-4.421390	-1.251794	-2.130002
61	1	0	-1.990722	-1.653035	-2.011938
62	6	0	-0.616427	-2.912591	0.005325
63	1	0	-0.209054	-3.000800	1.012309
64	6	0	0.198172	-3.117299	-1.034881
65	1	0	-0.151140	-3.081251	-2.064562
66	1	0	1.250463	-3.338147	-0.880872

TS$^{C\text{-}C1\text{-}b}$

E(RwB97XD) = -1827.67417457
Thermal correction to Gibbs Free Energy= 0.458615
Sum of electronic and thermal Free Energies= -1827.215560

1	6	0	-7.214135	2.530011	0.689970
2	6	0	-6.288528	1.582520	1.113237
3	6	0	-5.006820	1.541231	0.541360
4	6	0	-4.665782	2.466704	-0.460089
5	6	0	-5.592311	3.411801	-0.878727
6	6	0	-6.867309	3.443886	-0.305891
7	1	0	-8.204187	2.556651	1.134269
8	1	0	-6.555303	0.865034	1.884649
9	1	0	-3.673393	2.439370	-0.902371
10	1	0	-5.325468	4.125763	-1.651716
11	1	0	-7.589649	4.184252	-0.636441
12	6	0	-4.076446	0.513531	0.979337
13	1	0	-4.415298	-0.161435	1.765866
14	6	0	-2.827333	0.346864	0.526398
15	6	0	-1.686415	0.087305	0.045298
16	79	0	0.331989	0.089014	0.024462
17	15	0	2.665765	0.092010	0.050697
18	6	0	3.393254	1.752885	-0.144420
19	6	0	4.530587	2.145582	0.567665
20	6	0	2.809922	2.635353	-1.062399
21	6	0	5.080126	3.410008	0.360411
22	1	0	4.990459	1.471722	1.284594
23	6	0	3.365905	3.894203	-1.271563
24	1	0	1.921097	2.341334	-1.615757
25	6	0	4.501022	4.282947	-0.558981
26	1	0	5.961540	3.710442	0.918751
27	1	0	2.909684	4.573302	-1.985340
28	1	0	4.930728	5.267478	-0.717926
29	6	0	3.371348	-0.575835	1.594189
30	6	0	4.495110	-1.407502	1.590569
31	6	0	2.782796	-0.209194	2.811081
32	6	0	5.026144	-1.866192	2.795396
33	1	0	4.959216	-1.700985	0.653474
34	6	0	3.320261	-0.663588	4.011942
35	1	0	1.904705	0.432098	2.823240
36	6	0	4.441748	-1.494070	4.004756
37	1	0	5.897472	-2.513989	2.786250
38	1	0	2.860046	-0.374794	4.951967
39	1	0	4.856917	-1.853188	4.941744
40	6	0	3.376998	-0.919085	-1.291399
41	6	0	4.496401	-0.501463	-2.017069
42	6	0	2.792454	-2.161038	-1.571234
43	6	0	5.026878	-1.321553	-3.012443
44	1	0	4.957688	0.460239	-1.812462
45	6	0	3.329171	-2.979575	-2.560567
46	1	0	1.917755	-2.491679	-1.015820
47	6	0	4.446646	-2.559362	-3.283417
48	1	0	5.894799	-0.990675	-3.574725
49	1	0	2.872011	-3.941669	-2.770898
50	1	0	4.861594	-3.195665	-4.059408
51	6	0	-4.113109	-3.361208	0.312784
52	6	0	-5.358300	-3.602577	0.874942
53	6	0	-6.453345	-2.808808	0.516343
54	6	0	-6.294450	-1.774670	-0.402488
55	6	0	-5.043222	-1.522715	-0.960058
56	6	0	-3.932766	-2.316869	-0.616192
57	1	0	-3.262952	-3.978541	0.591198
58	1	0	-5.482111	-4.408045	1.592160
59	1	0	-7.428415	-3.001483	0.953771
60	1	0	-7.141501	-1.156119	-0.682524
61	1	0	-4.942471	-0.722898	-1.686490
62	6	0	-2.606380	-2.073631	-1.144651
63	1	0	-1.844018	-2.804440	-0.880584
64	6	0	-2.212207	-0.983441	-1.867815
65	1	0	-2.913245	-0.243497	-2.239459
66	1	0	-1.218764	-0.955550	-2.300621

F^{b}

E(RwB97XD) = -1827.69519944
Thermal correction to Gibbs Free Energy= 0.458628
Sum of electronic and thermal Free Energies= -1827.236572

1	6	0	-6.218984	3.393683	1.018663
2	6	0	-5.441280	2.270232	1.293973
3	6	0	-4.427028	1.875047	0.413128
4	6	0	-4.204740	2.626878	-0.750244
5	6	0	-4.981255	3.748062	-1.022153
6	6	0	-5.992270	4.135695	-0.139409
7	1	0	-7.002355	3.688303	1.710914
8	1	0	-5.622301	1.694547	2.198186
9	1	0	-3.418502	2.332631	-1.441741
10	1	0	-4.797864	4.322452	-1.925637
11	1	0	-6.597296	5.011564	-0.354280
12	6	0	-3.633496	0.672688	0.723415
13	1	0	-3.849376	0.148669	1.656534
14	6	0	-2.701657	0.156298	-0.039566
15	6	0	-1.784466	-0.419761	-0.790959
16	79	0	0.236588	-0.196961	-0.389170
17	15	0	2.508271	0.069487	0.073498
18	6	0	3.167386	1.692412	-0.438318
19	6	0	4.437606	1.828589	-1.006796
20	6	0	2.381300	2.830342	-0.217234
21	6	0	4.917150	3.092711	-1.347342
22	1	0	5.056036	0.953926	-1.186463
23	6	0	2.866361	4.091446	-0.552141
24	1	0	1.389044	2.733466	0.217240
25	6	0	4.134739	4.223398	-1.118871
26	1	0	5.903434	3.191545	-1.790636
27	1	0	2.252093	4.969386	-0.376667

28	1	0	4.510479	5.206794	−1.385469
29	6	0	3.558757	−1.165877	−0.764455
30	6	0	4.640231	−1.775967	−0.122308
31	6	0	3.279045	−1.480389	−2.100546
32	6	0	5.435723	−2.690184	−0.812355
33	1	0	4.866412	−1.543086	0.914165
34	6	0	4.079770	−2.387553	−2.788336
35	1	0	2.436011	−1.015677	−2.606621
36	6	0	5.158452	−2.994865	−2.143734
37	1	0	6.272756	−3.162445	−0.306989
38	1	0	3.858368	−2.624765	−3.824516
39	1	0	5.779414	−3.707223	−2.678781
40	6	0	2.907241	−0.078161	1.848323
41	6	0	3.852298	0.747109	2.465224
42	6	0	2.263842	−1.073051	2.595321
43	6	0	4.152394	0.575437	3.816019
44	1	0	4.355773	1.525113	1.898774
45	6	0	2.571330	−1.246381	3.941802
46	1	0	1.521300	−1.714310	2.126214
47	6	0	3.515403	−0.420809	4.553817
48	1	0	4.885225	1.221676	4.289669
49	1	0	2.069582	−2.020726	4.514140
50	1	0	3.750520	−0.552067	5.605862
51	6	0	−4.060912	−3.355338	0.669412
52	6	0	−5.300729	−3.624699	1.231020
53	6	0	−6.444019	−3.014553	0.709618
54	6	0	−6.349313	−2.138293	−0.373875
55	6	0	−5.112187	−1.868123	−0.941923
56	6	0	−3.951066	−2.478406	−0.428143
57	1	0	−3.166433	−3.821042	1.073980
58	1	0	−5.380140	−4.303913	2.073464
59	1	0	−7.414465	−3.223282	1.149707
60	1	0	−7.241540	−1.667292	−0.773261
61	1	0	−5.051733	−1.187154	−1.784075
62	6	0	−2.641195	−2.233565	−0.972075
63	1	0	−1.830015	−2.839057	−0.574554
64	6	0	−2.290635	−1.296037	−2.005105
65	1	0	−1.452264	−1.576001	−2.635734
66	1	0	−3.099419	−0.832522	−2.564577

TS$^{\text{C-C2-b}}$

E(RwB97XD) = -1827.68939471
Thermal correction to Gibbs Free Energy= 0.459384
Sum of electronic and thermal Free Energies= -1827.230010

1	6	0	6.141848	3.152153	−1.032582
2	6	0	5.086172	2.304876	−1.364616
3	6	0	4.274036	1.760779	−0.362734
4	6	0	4.529684	2.087275	0.977164
5	6	0	5.584366	2.932173	1.304368
6	6	0	6.396162	3.466542	0.301246
7	1	0	6.765648	3.565907	−1.819421
8	1	0	4.894931	2.059388	−2.405886
9	1	0	3.897648	1.685851	1.765718
10	1	0	5.771861	3.178028	2.345529
11	1	0	7.218546	4.126954	0.559484
12	6	0	3.186063	0.841733	−0.745554
13	1	0	2.938208	0.741479	−1.802686
14	6	0	2.504650	0.104434	0.091773
15	6	0	1.775327	−0.731608	0.818097
16	79	0	−0.256449	−0.321160	0.410052
17	15	0	−2.493072	0.100940	−0.063444
18	6	0	−2.748287	1.689952	−0.921184
19	6	0	−3.689436	1.827980	−1.946011
20	6	0	−2.001510	2.801227	−0.510045
21	6	0	−3.883058	3.068949	−2.551211
22	1	0	−4.272678	0.973284	−2.276193
23	6	0	−2.202643	4.039826	−1.112438
24	1	0	−1.261758	2.701543	0.280779
25	6	0	−3.142986	4.174198	−2.134710
26	1	0	−4.613638	3.169615	−3.348086
27	1	0	−1.621083	4.897528	−0.788489
28	1	0	−3.295247	5.139442	−2.608356
29	6	0	−3.240811	−1.165598	−1.141947
30	6	0	−4.536940	−1.643932	−0.928825
31	6	0	−2.496625	−1.637365	−2.230734
32	6	0	−5.083795	−2.584956	−1.800629
33	1	0	−5.123301	−1.287889	−0.086795
34	6	0	−3.048831	−2.570913	−3.102698
35	1	0	−1.485184	−1.275125	−2.399364
36	6	0	−4.343063	−3.046720	−2.887080
37	1	0	−6.090030	−2.954975	−1.628957
38	1	0	−2.467348	−2.931054	−3.945915
39	1	0	−4.771357	−3.779574	−3.564355
40	6	0	−3.546955	0.165471	1.423231
41	6	0	−4.557365	1.120722	1.567153
42	6	0	−3.350803	−0.794156	2.424561
43	6	0	−5.366943	1.112750	2.702402
44	1	0	−4.717100	1.872158	0.799475
45	6	0	−4.165946	−0.803230	3.552618
46	1	0	−2.562713	−1.536986	2.324441
47	6	0	−5.174174	0.151625	3.692960
48	1	0	−6.148336	1.858878	2.809989
49	1	0	−4.010346	−1.551047	4.324220
50	1	0	−5.805919	0.147629	4.576174
51	6	0	4.061729	−3.042828	−0.885849
52	6	0	5.319515	−3.103046	−1.478114
53	6	0	6.405460	−2.464696	−0.877337
54	6	0	6.227459	−1.774863	0.321071
55	6	0	4.971135	−1.723102	0.919423
56	6	0	3.874220	−2.356500	0.321664
57	1	0	3.214699	−3.529406	−1.363065
58	1	0	5.451468	−3.642952	−2.410928
59	1	0	7.386443	−2.506001	−1.341249
60	1	0	7.067763	−1.275538	0.794037
61	1	0	4.859782	−1.183344	1.855297
62	6	0	2.507718	−2.259875	0.865637
63	1	0	1.782816	−2.969834	0.475392
64	6	0	2.144948	−1.569412	2.082169
65	1	0	2.912884	−1.107971	2.694584
66	1	0	1.276952	−1.907585	2.634773

3---Au$^{\text{b}}$

E(RwB97XD) = -1827.71521680
Thermal correction to Gibbs Free Energy= 0.461217
Sum of electronic and thermal Free Energies= -1827.254000

1	6	0	−5.738635	−3.281455	−1.167268
2	6	0	−4.404225	−2.882489	−1.189262
3	6	0	−3.850882	−2.207902	−0.094005
4	6	0	−4.643693	−1.972771	1.035727
5	6	0	−5.977305	−2.371973	1.056287
6	6	0	−6.529940	−3.021706	−0.047718
7	1	0	−6.160823	−3.795929	−2.025471
8	1	0	−3.791111	−3.083081	−2.064053
9	1	0	−4.206230	−1.496115	1.909334
10	1	0	−6.582203	−2.183936	1.938530
11	1	0	−7.569643	−3.334942	−0.031178
12	6	0	−2.440761	−1.763671	−0.148921
13	1	0	−1.730201	−2.395877	−0.676112
14	6	0	−2.034138	−0.633823	0.399497
15	6	0	−1.930845	0.562085	0.978843
16	79	0	0.110121	−0.029947	0.350758
17	15	0	2.416321	−0.058767	−0.069882
18	6	0	2.852372	−1.187181	−1.430931
19	6	0	3.791580	−0.829363	−2.402358
20	6	0	2.253672	−2.452765	−1.471743
21	6	0	4.129769	−1.734535	−3.407475
22	1	0	4.260636	0.149902	−2.381457
23	6	0	2.599481	−3.354632	−2.473330
24	1	0	1.518939	−2.737486	−0.722226
25	6	0	3.536818	−2.995147	−3.442974
26	1	0	4.857822	−1.451731	−4.161563
27	1	0	2.133417	−4.334773	−2.500304
28	1	0	3.801634	−3.697475	−4.227634
29	6	0	3.036789	1.585810	−0.548208
30	6	0	4.242262	2.085777	−0.047597
31	6	0	2.294210	2.343195	−1.463506
32	6	0	4.701958	3.334911	−0.463260
33	1	0	4.825189	1.509105	0.664368
34	6	0	2.760883	3.585949	−1.880065
35	1	0	1.352980	1.964546	−1.855053
36	6	0	3.964832	4.083381	−1.378772
37	1	0	5.637617	3.720304	−0.069931
38	1	0	2.182567	4.167846	−2.591109
39	1	0	4.325366	5.055867	−1.700287
40	6	0	3.404685	−0.584450	1.365013
41	6	0	4.543470	−1.380898	1.209209
42	6	0	3.032417	−0.141966	2.640386
43	6	0	5.305036	−1.728921	2.323523
44	1	0	4.839544	−1.732224	0.225056
45	6	0	3.799888	−0.486996	3.749016
46	1	0	2.144774	0.472365	2.771226
47	6	0	4.935871	−1.281839	3.591113
48	1	0	6.186785	−2.349875	2.198574
49	1	0	3.507508	−0.141000	4.735640
50	1	0	5.530630	−1.555576	4.457375
51	6	0	−3.806796	3.372469	−0.659435
52	6	0	−5.026451	3.683256	−1.260053
53	6	0	−6.157420	2.916061	−0.986016
54	6	0	−6.061167	1.838251	−0.104595
55	6	0	−4.843753	1.532091	0.496563
56	6	0	−3.702707	2.294941	0.225660
57	1	0	−2.928478	3.973968	−0.880636
58	1	0	−5.090043	4.524818	−1.943778
59	1	0	−7.107073	3.154457	−1.455858
60	1	0	−6.934717	1.230898	0.114690
61	1	0	−4.790474	0.683993	1.172518

62	6	0	−2. 376449	1. 982885	0. 832525
63	1	0	−1. 588126	2. 687262	0. 576428
64	6	0	−2. 187803	1. 341692	2. 210758
65	1	0	−3. 064092	1. 053217	2. 787285
66	1	0	−1. 344702	1. 699194	2. 794204

TS^{rot}

E(RwB97XD) = -1827.68955294
Thermal correction to Gibbs Free Energy= 0.465442
Sum of electronic and thermal Free Energies= -1827.224110

1	6	0	6. 035575	2. 942859	−0. 525935
2	6	0	5. 187525	2. 265077	−1. 399767
3	6	0	4. 102323	1. 520957	−0. 914872
4	6	0	3. 878043	1. 490816	0. 469488
5	6	0	4. 724269	2. 167792	1. 341680
6	6	0	5. 810739	2. 894009	0. 850012
7	1	0	6. 874219	3. 509375	−0. 921360
8	1	0	5. 372606	2. 303283	−2. 470875
9	1	0	3. 035479	0. 925831	0. 861126
10	1	0	4. 536595	2. 127093	2. 411338
11	1	0	6. 471802	3. 420601	1. 532369
12	6	0	3. 253816	0. 767005	−1. 860315
13	1	0	3. 394959	0. 966741	−2. 921993
14	6	0	2. 402774	−0. 168194	−1. 481537
15	6	0	1. 593070	−1. 079692	−1. 010969
16	79	0	−0. 348228	−0. 565584	−0. 504855
17	15	0	−2. 512989	0. 086624	0. 079548
18	6	0	−2. 582019	1. 753125	0. 821846
19	6	0	−3. 427082	2. 052246	1. 894838
20	6	0	−1. 778495	2. 760115	0. 272001
21	6	0	−3. 469824	3. 347397	2. 409586
22	1	0	−4. 052779	1. 280073	2. 333096
23	6	0	−1. 828833	4. 053658	0. 783935
24	1	0	−1. 111036	2. 535344	−0. 556717
25	6	0	−2. 673938	4. 348117	1. 854650
26	1	0	−4. 126622	3. 572204	3. 244577
27	1	0	−1. 203508	4. 829016	0. 351764
28	1	0	−2. 708381	5. 355849	2. 257940
29	6	0	−3. 296865	−1. 017107	1. 304282
30	6	0	−4. 643804	−1. 382104	1. 221548
31	6	0	−2. 518098	−1. 480901	2. 372236
32	6	0	−5. 206094	−2. 200791	2. 200500
33	1	0	−5. 258413	−1. 032354	0. 397158
34	6	0	−3. 084531	−2. 291453	3. 351845
35	1	0	−1. 467325	−1. 208322	2. 439426
36	6	0	−4. 429633	−2. 653496	3. 265718
37	1	0	−6. 252260	−2. 482725	2. 128910
38	1	0	−2. 475116	−2. 645291	4. 177948
39	1	0	−4. 870001	−3. 291029	4. 026636
40	6	0	−3. 667366	0. 137715	−1. 333389
41	6	0	−4. 628660	1. 143680	−1. 470536
42	6	0	−3. 596672	−0. 886907	−2. 285784
43	6	0	−5. 512648	1. 121556	−2. 548687
44	1	0	−4. 692129	1. 946219	−0. 741402
45	6	0	−4. 485559	−0. 909936	−3. 356817
46	1	0	−2. 846029	−1. 668297	−2. 192187
47	6	0	−5. 443910	0. 095681	−3. 489811
48	1	0	−6. 255055	1. 907335	−2. 650939
49	1	0	−4. 425409	−1. 708141	−4. 090459
50	1	0	−6. 133092	0. 081140	−4. 328952
51	6	0	5. 790508	−1. 735855	−0. 657539
52	6	0	6. 771486	−1. 210888	0. 160985
53	6	0	6. 510267	−1. 053031	1. 525683
54	6	0	5. 275332	−1. 416418	2. 084646
55	6	0	4. 281512	−1. 919897	1. 275141
56	6	0	4. 520580	−2. 087431	−0. 119071
57	1	0	5. 967603	−1. 859255	−1. 721782
58	1	0	7. 732406	−0. 919907	−0. 248069
59	1	0	7. 280501	−0. 638566	2. 169064
60	1	0	5. 102477	−1. 283782	3. 146714
61	1	0	3. 319209	−2. 184051	1. 699336
62	6	0	3. 518126	−2. 471879	−1. 011076
63	1	0	3. 812426	−2. 587093	−2. 053680
64	6	0	2. 080701	−2. 536025	−0. 737797
65	1	0	1. 571878	−3. 221947	−1. 418757
66	1	0	1. 834167	−2. 806392	0. 289789

syn-**3ac**

E(RB97D3) = -3348.66044407
Thermal correction to Gibbs Free Energy= 0.265295
Sum of electronic and thermal Free Energies= -3348.395149

1	6	0	5. 067839	−1. 408418	−0. 150434
2	6	0	4. 584367	−0. 112846	−0. 339575
3	6	0	3. 236933	0. 193554	0. 010161
4	6	0	2. 418617	−0. 836741	0. 544239
5	6	0	2. 950797	−2. 120686	0. 710562
6	6	0	4. 269857	−2. 433199	0. 373537
7	1	0	6. 100547	−1. 626455	−0. 421731
8	1	0	2. 307752	−2. 900601	1. 117074
9	6	0	2. 762255	1. 563347	−0. 216602
10	1	0	3. 471740	2. 219425	−0. 722197
11	6	0	1. 612415	2. 148754	0. 092658
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13	6	0	−0. 841857	3. 162229	−0. 161628
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36	1	0	−1. 498321	1. 134913	1. 608493
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anti-**3ac**

E(RB97D3) = -3348.65935118
Thermal correction to Gibbs Free Energy= 0.263022
Sum of electronic and thermal Free Energies= -3348.396329

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5	6	0	−5. 520581	0. 755238	−0. 829716
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References

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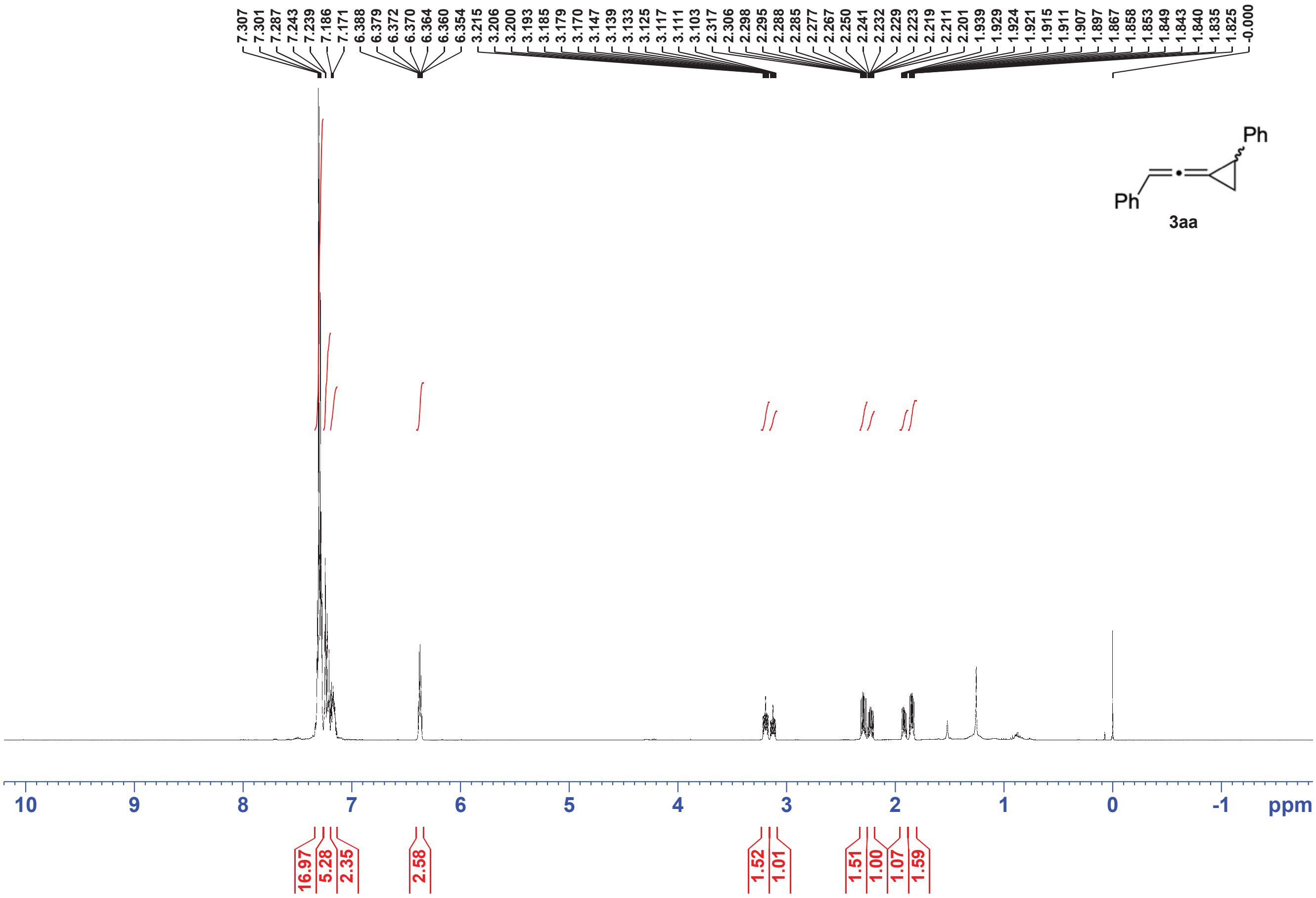
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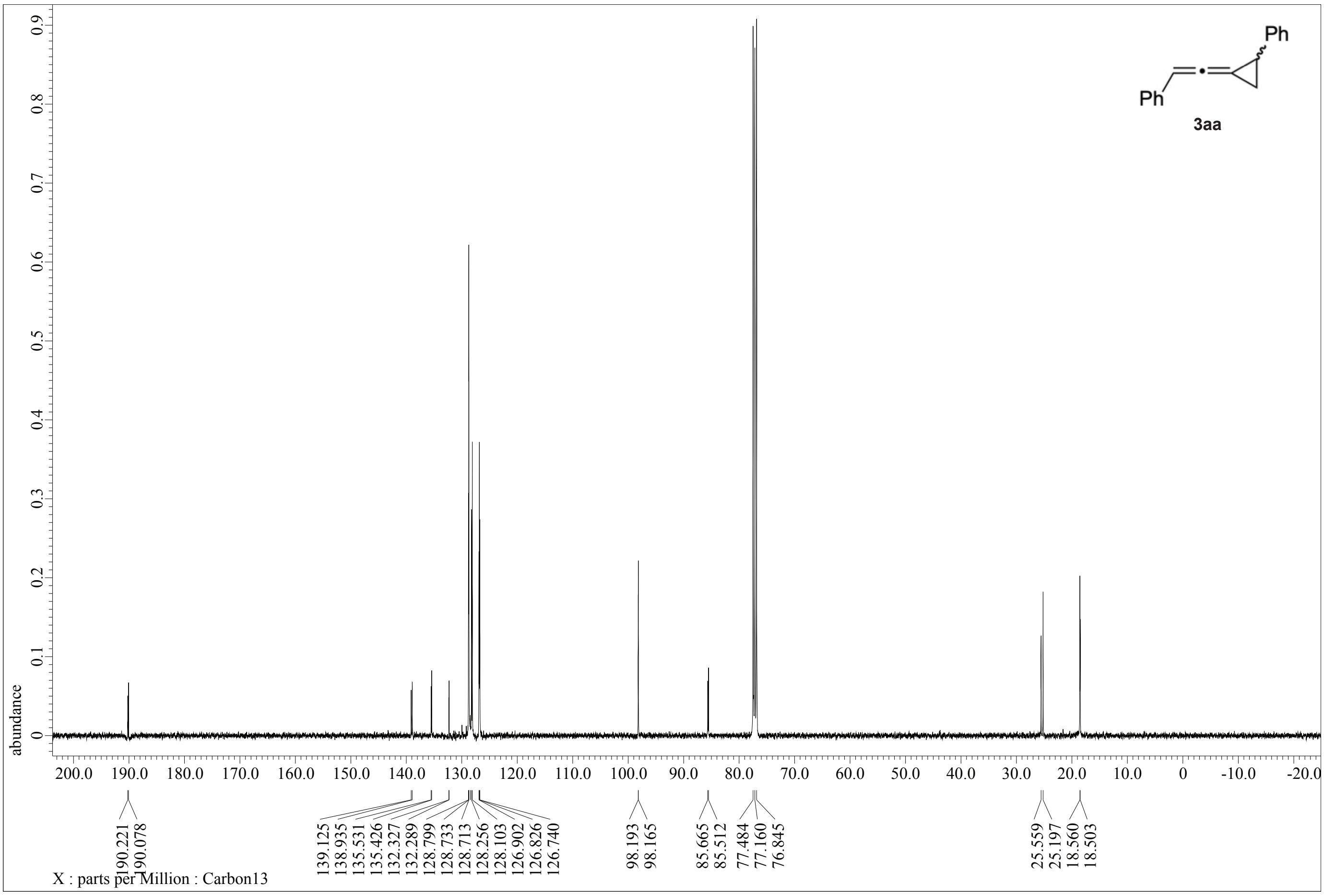
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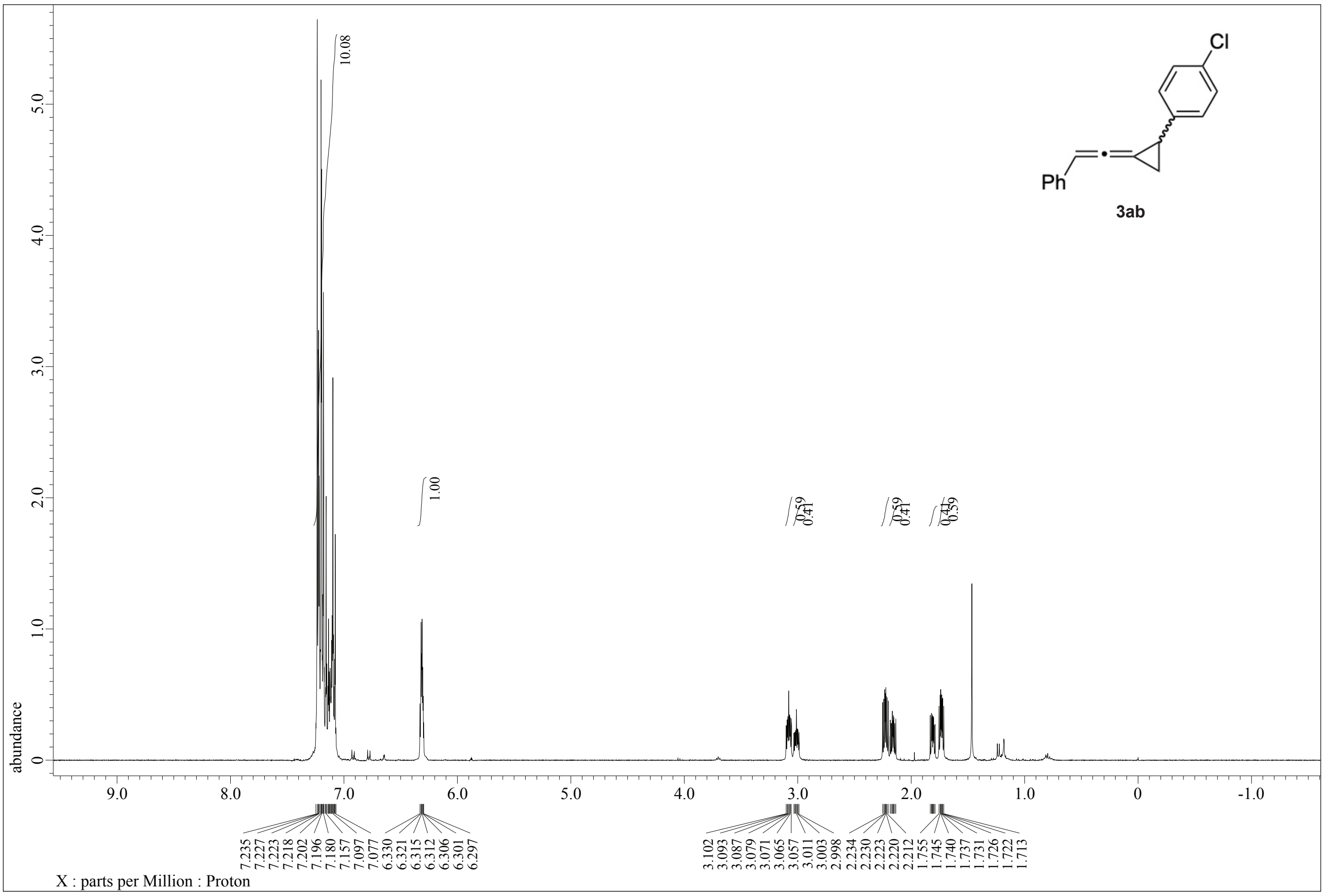
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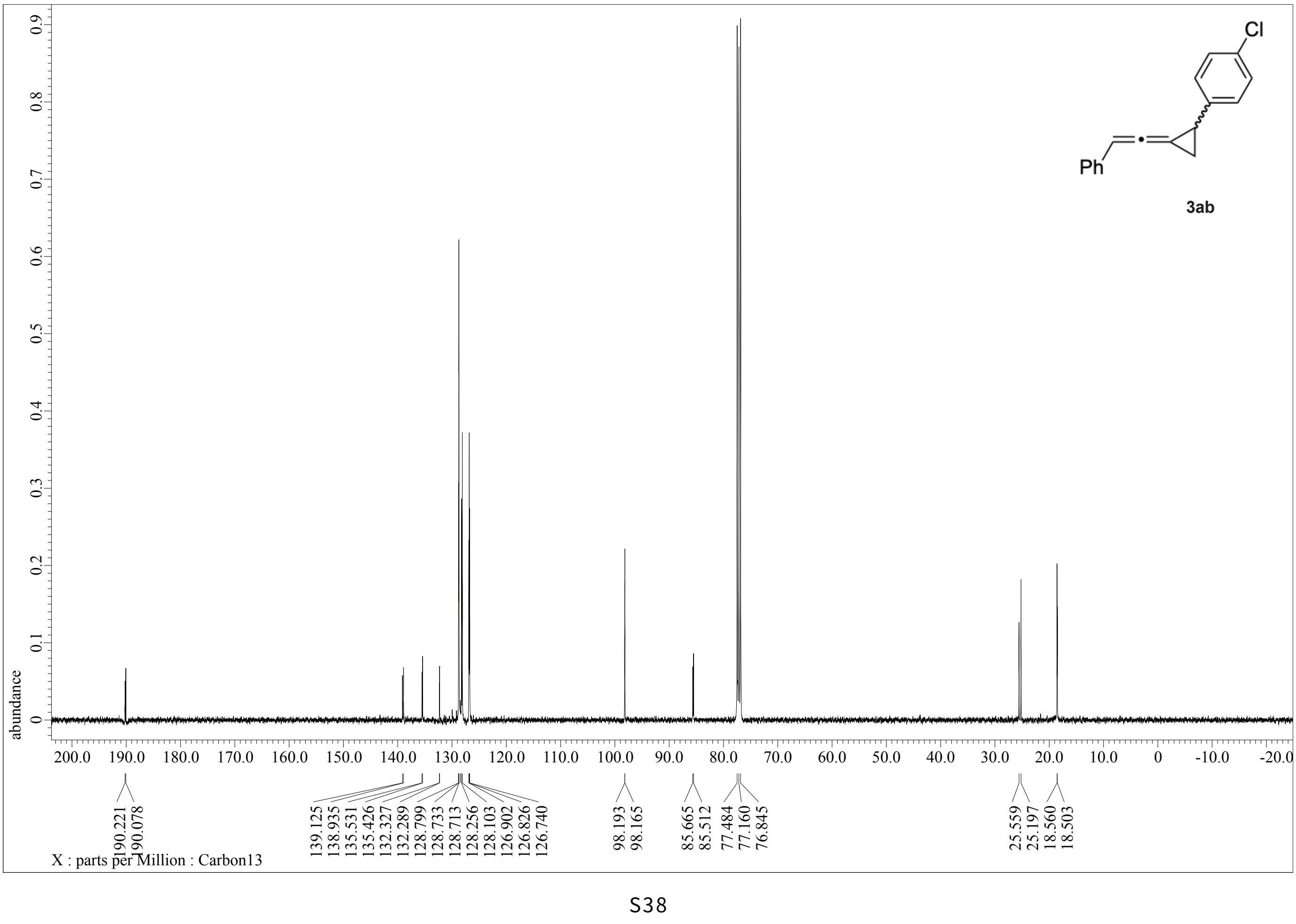
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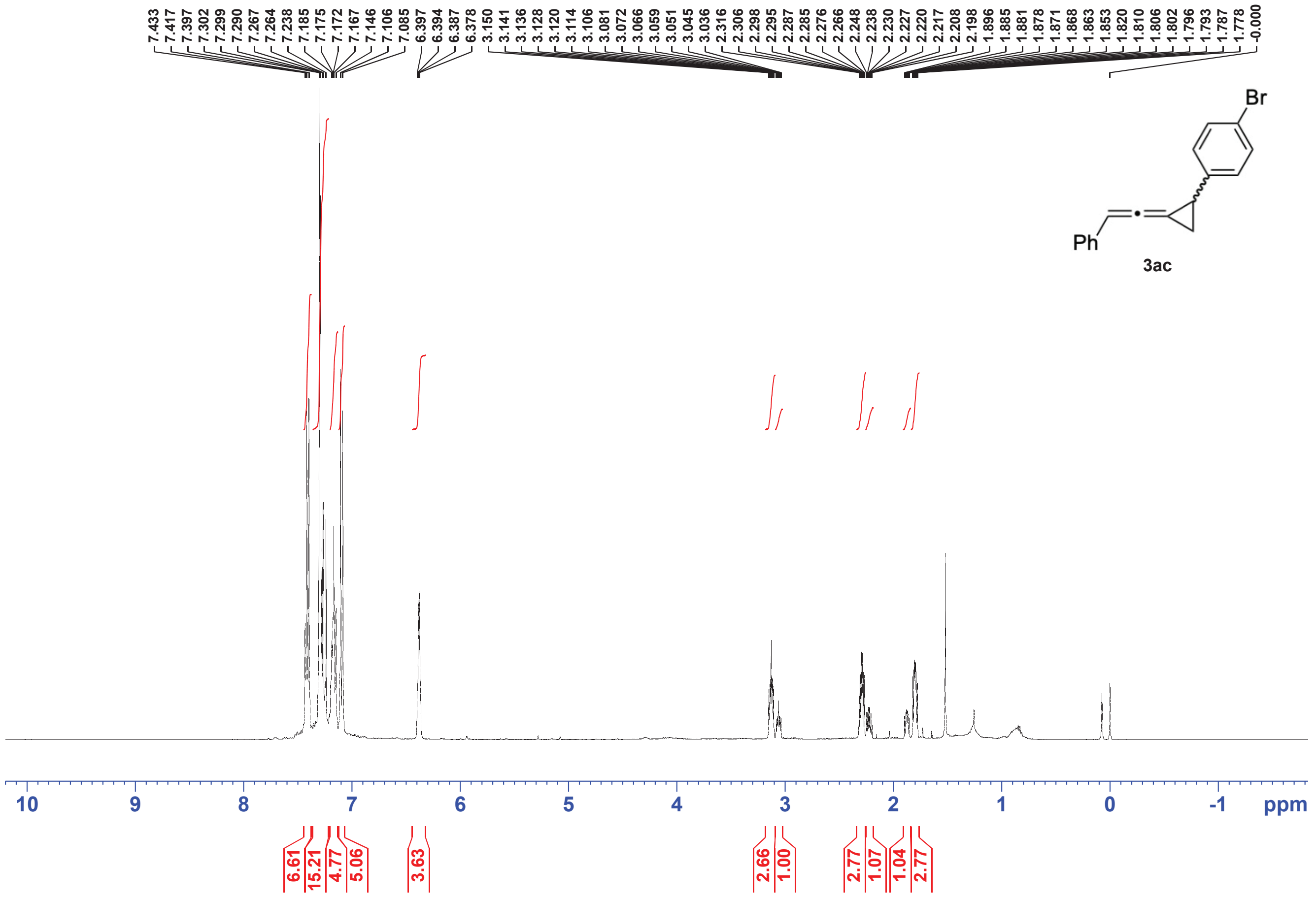
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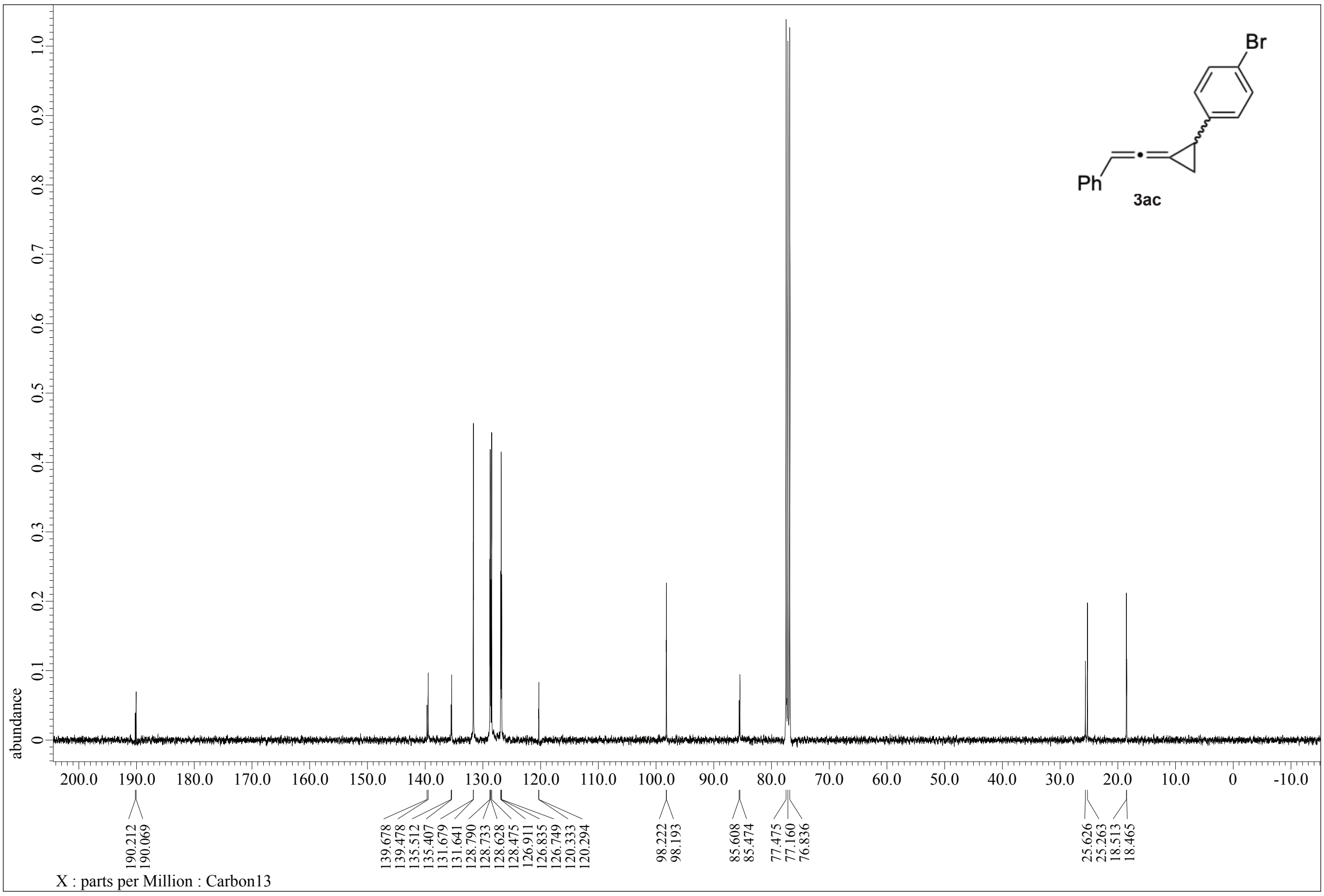
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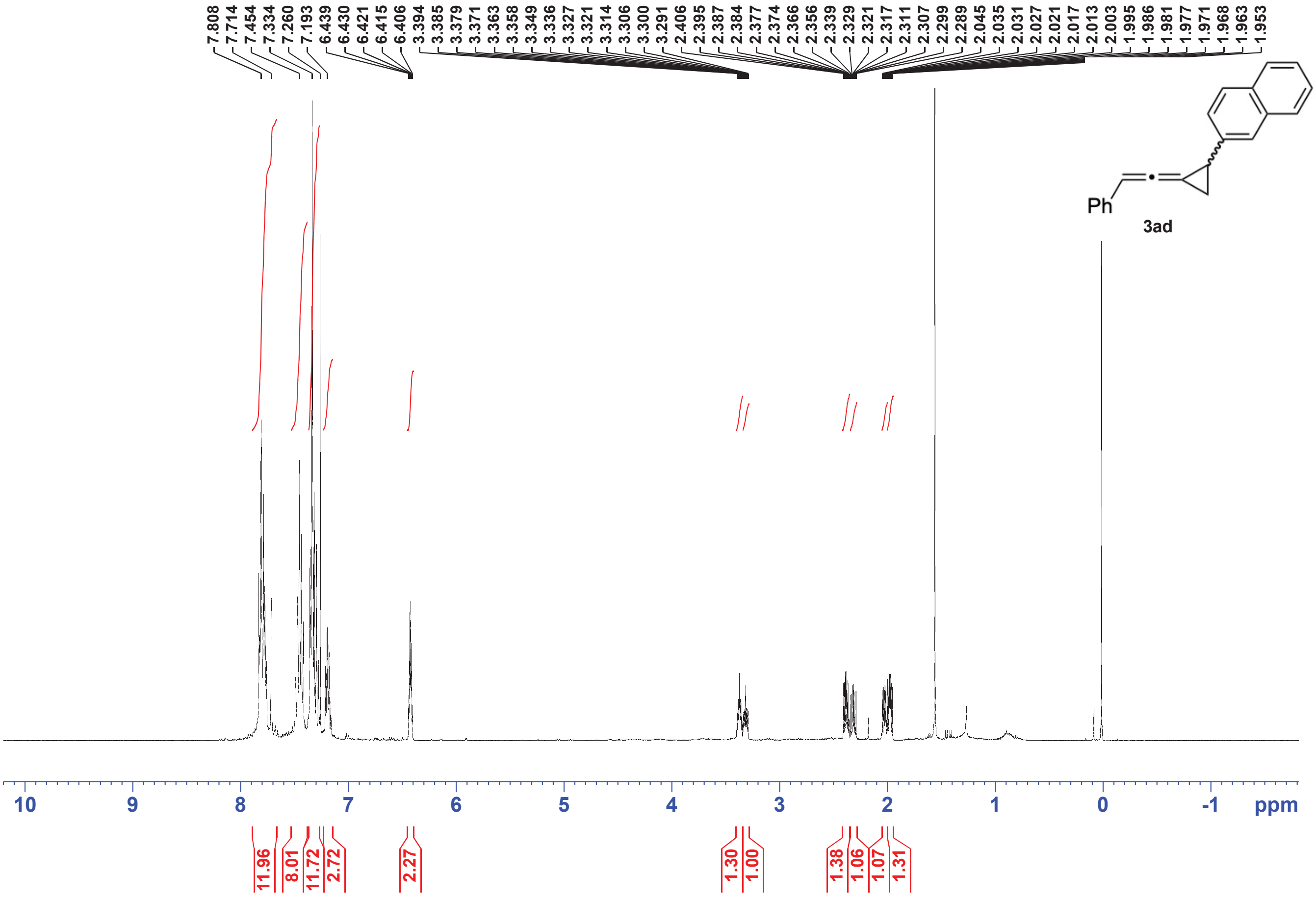
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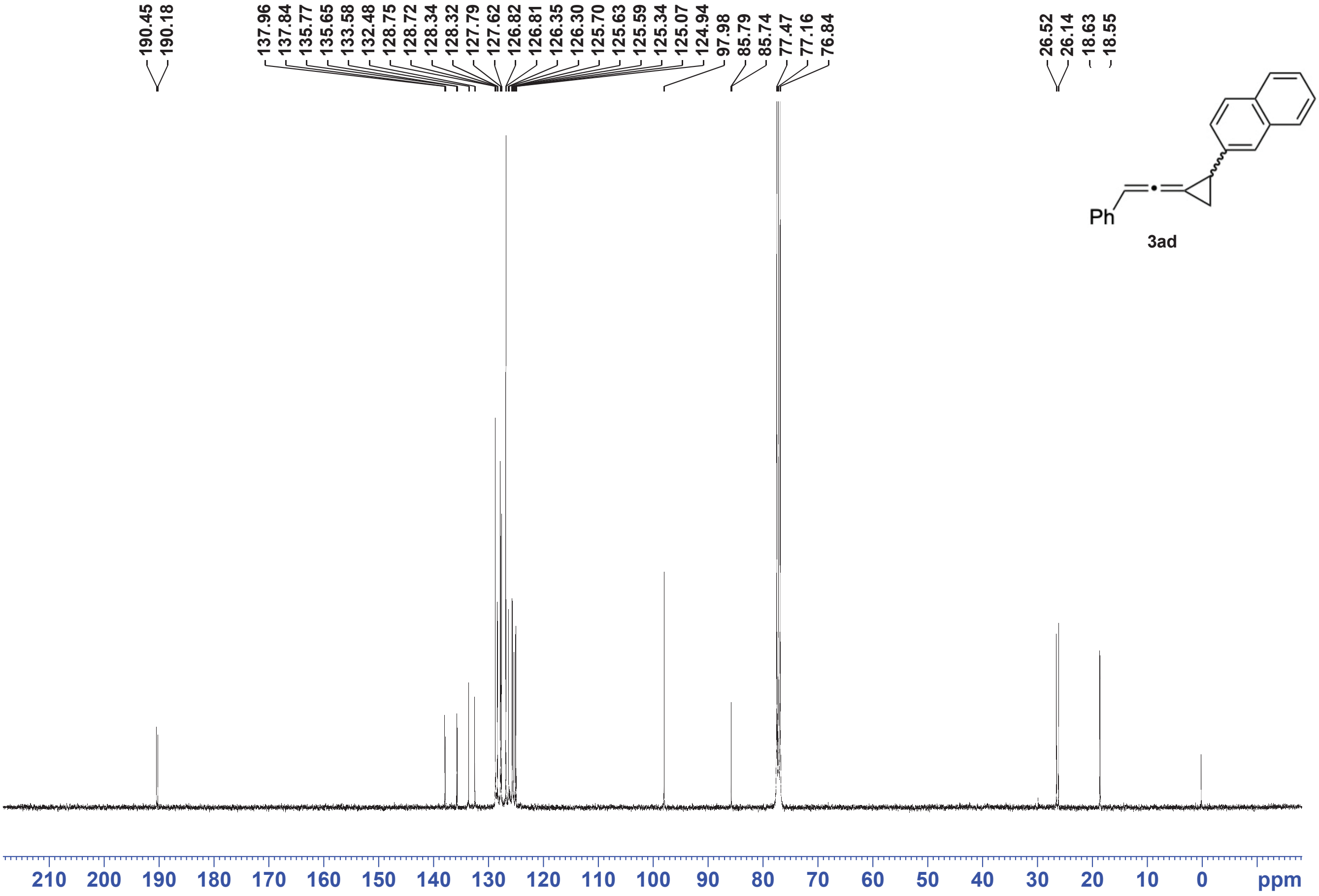
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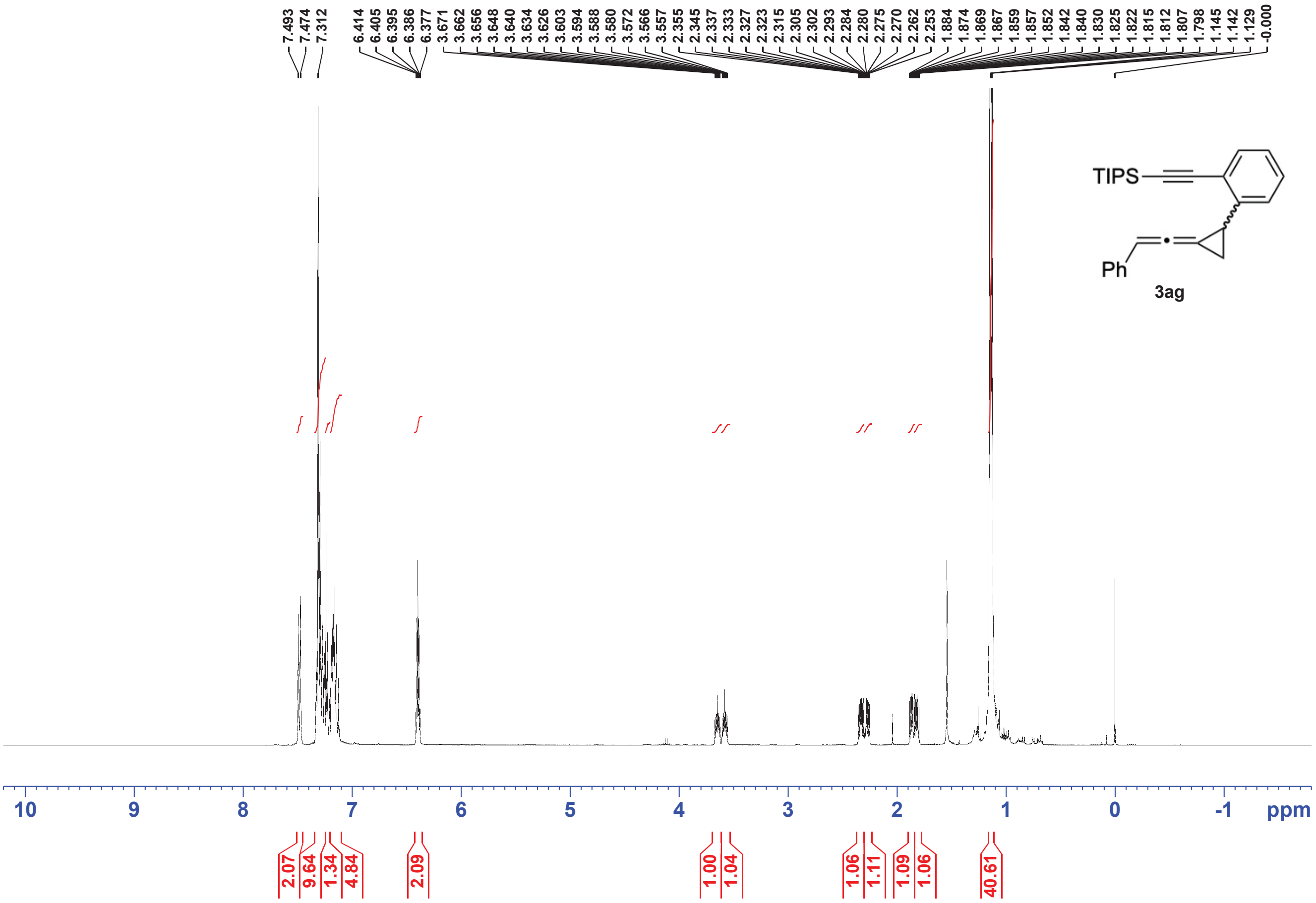
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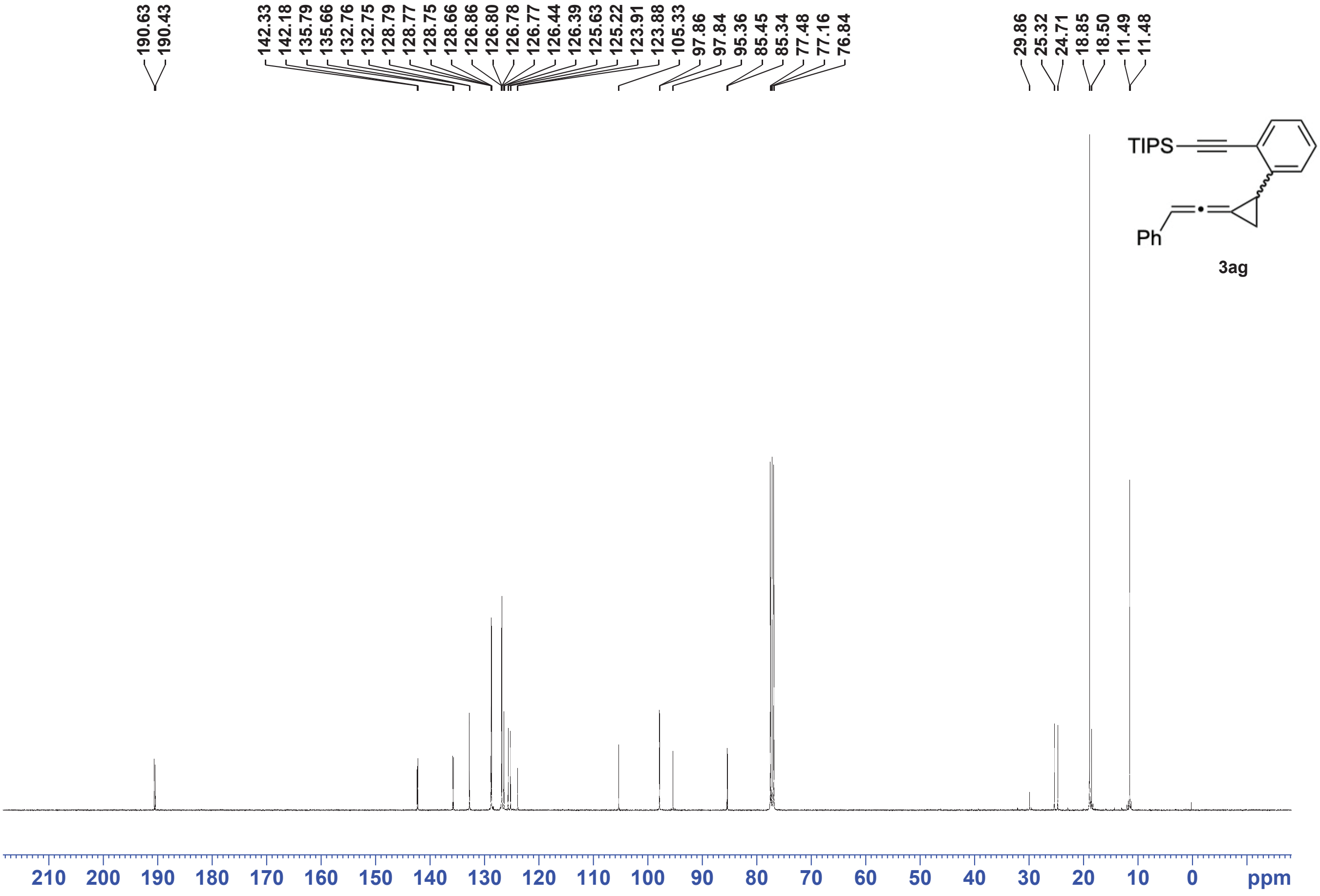
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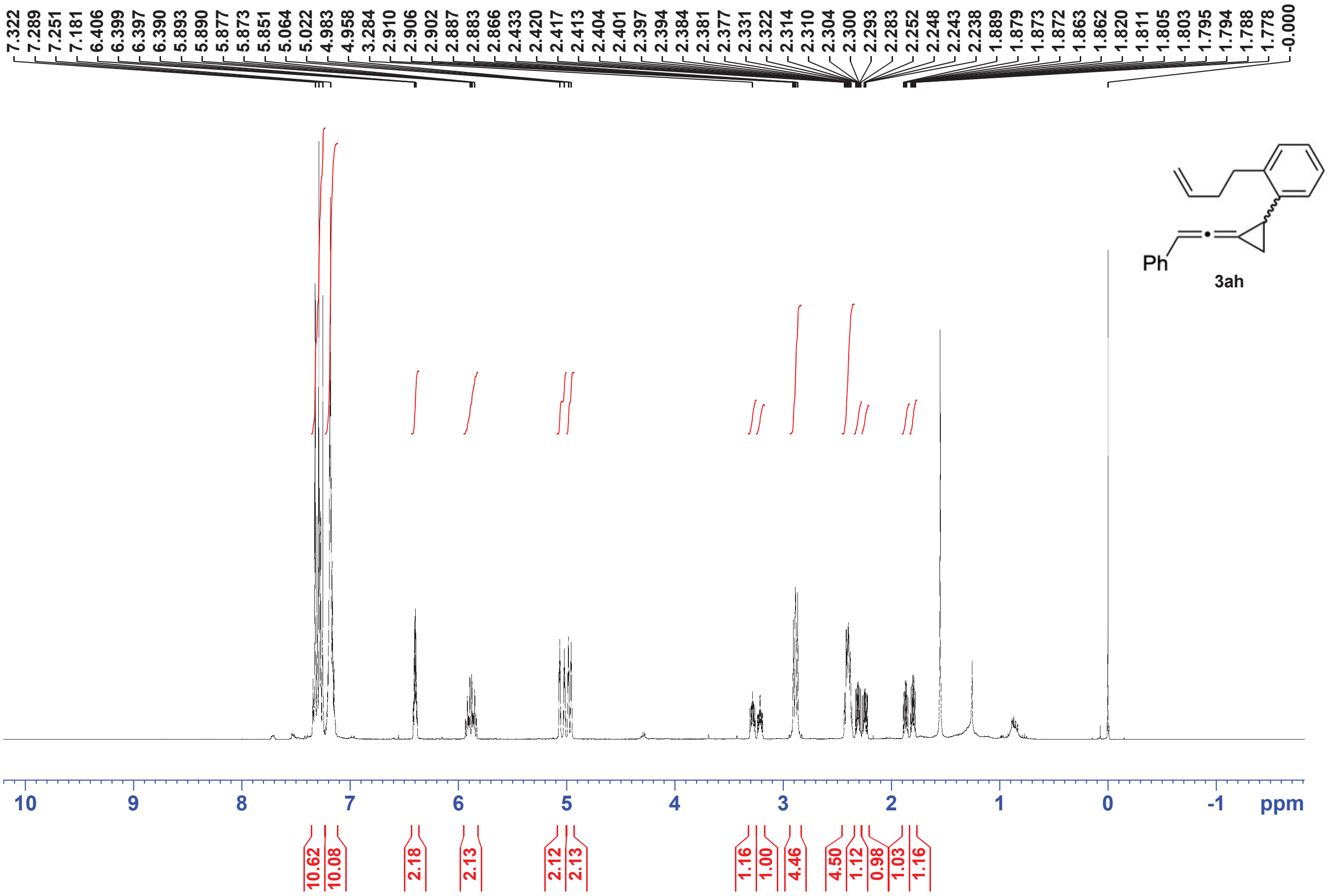
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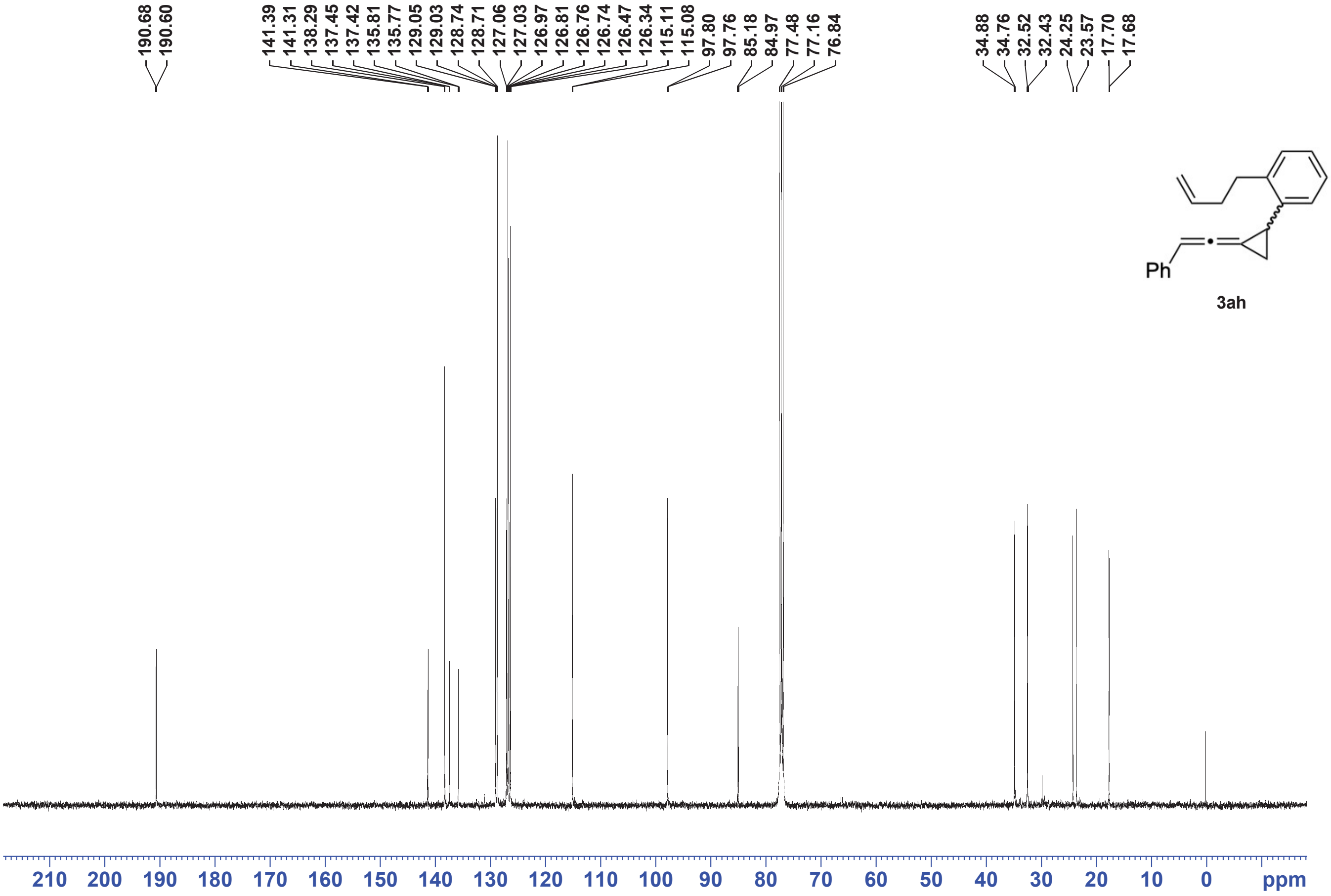
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135.77
129.05
129.03
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128.71
127.06
127.03
126.97
126.81
126.76
126.74
126.47
126.34
115.11
115.08
97.80
97.76
85.18
84.97
77.48
77.16
76.84
34.88
34.76
32.52
32.43
24.25
23.57
17.70
17.68
Ph
3ah
210
200
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180
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140
130
120
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100
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60
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20
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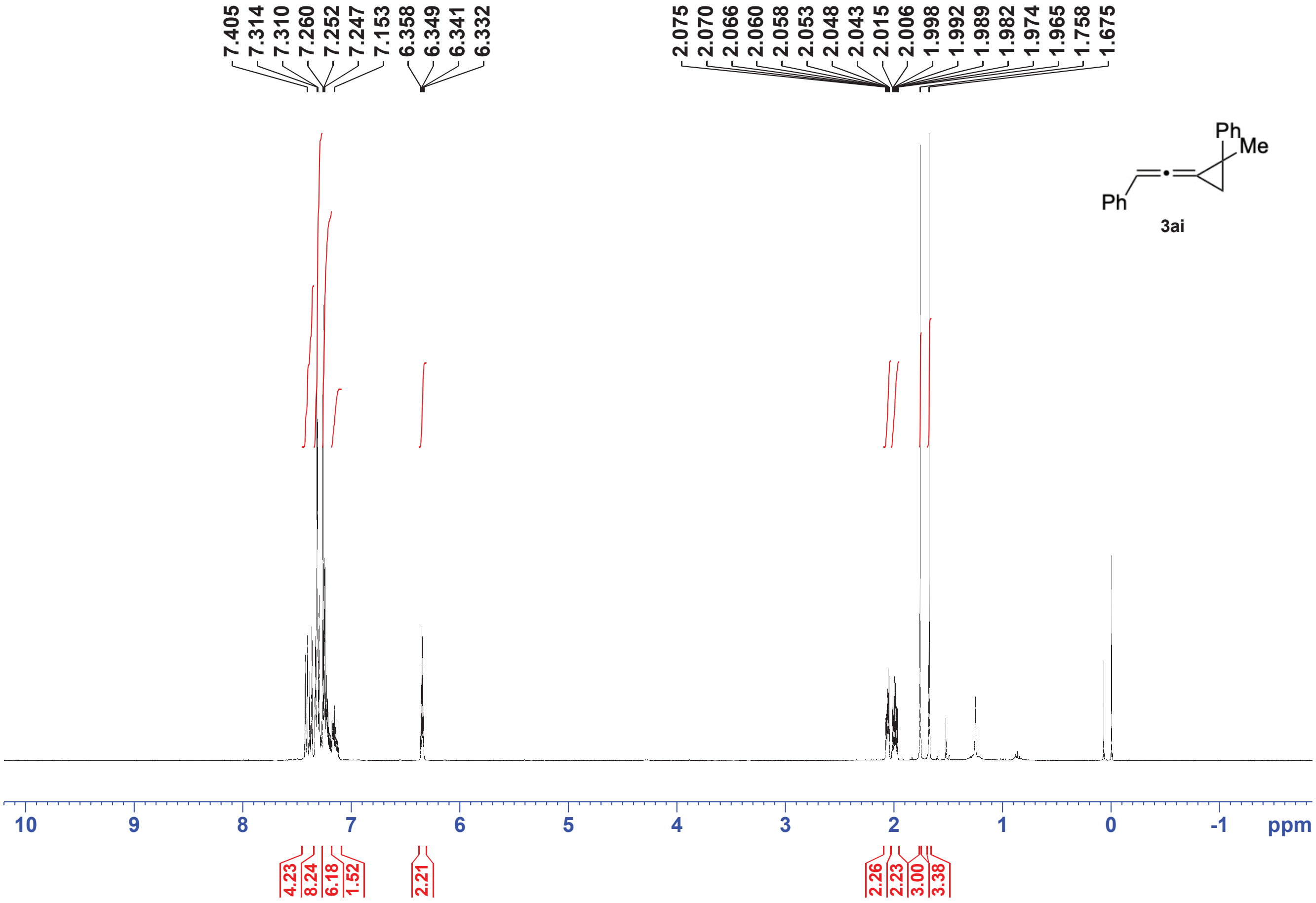
ppm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6.341
6.332
2.075
2.070
2.066
2.060
2.058
2.053
2.048
2.043
2.015
2.006
1.998
1.992
1.989
1.982
1.974
1.965
1.758
1.675
Ph
Me
Ph
3ai
10
9
8
7
6
5
4
3
2
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ppm
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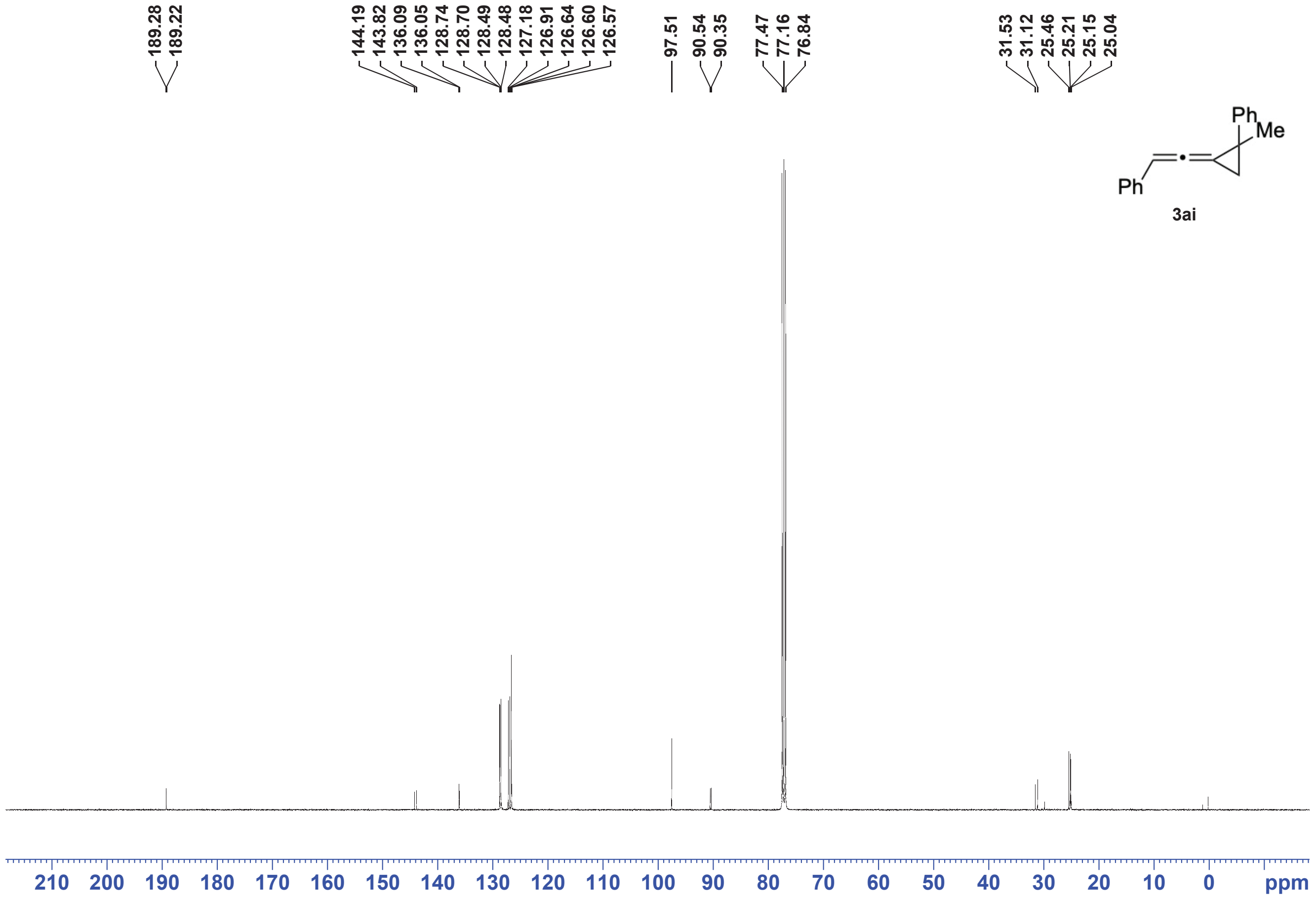
6.18
1.52
2.21
2.26
2.23
3.00
3.38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127.18
126.91
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126.60
126.57
97.51
90.54
90.35
77.47
77.16
76.84
31.53
31.12
25.46
25.21
25.15
25.04
Ph
Me
Ph
3ai
210
200
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140
130
120
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20
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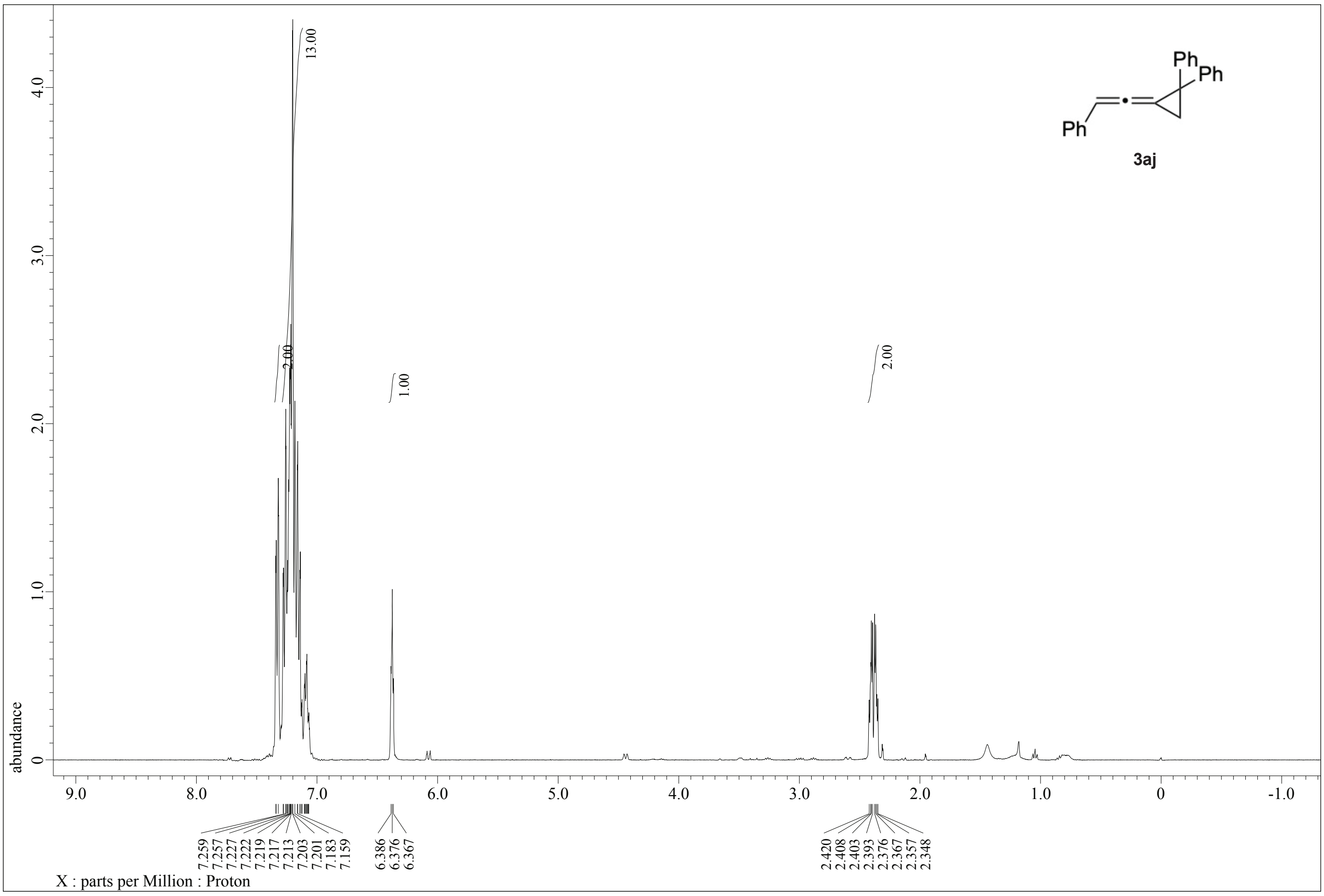
ppm


Ph
Ph
Ph
3aj
13.00
2.00
1.00
2.00
abundance
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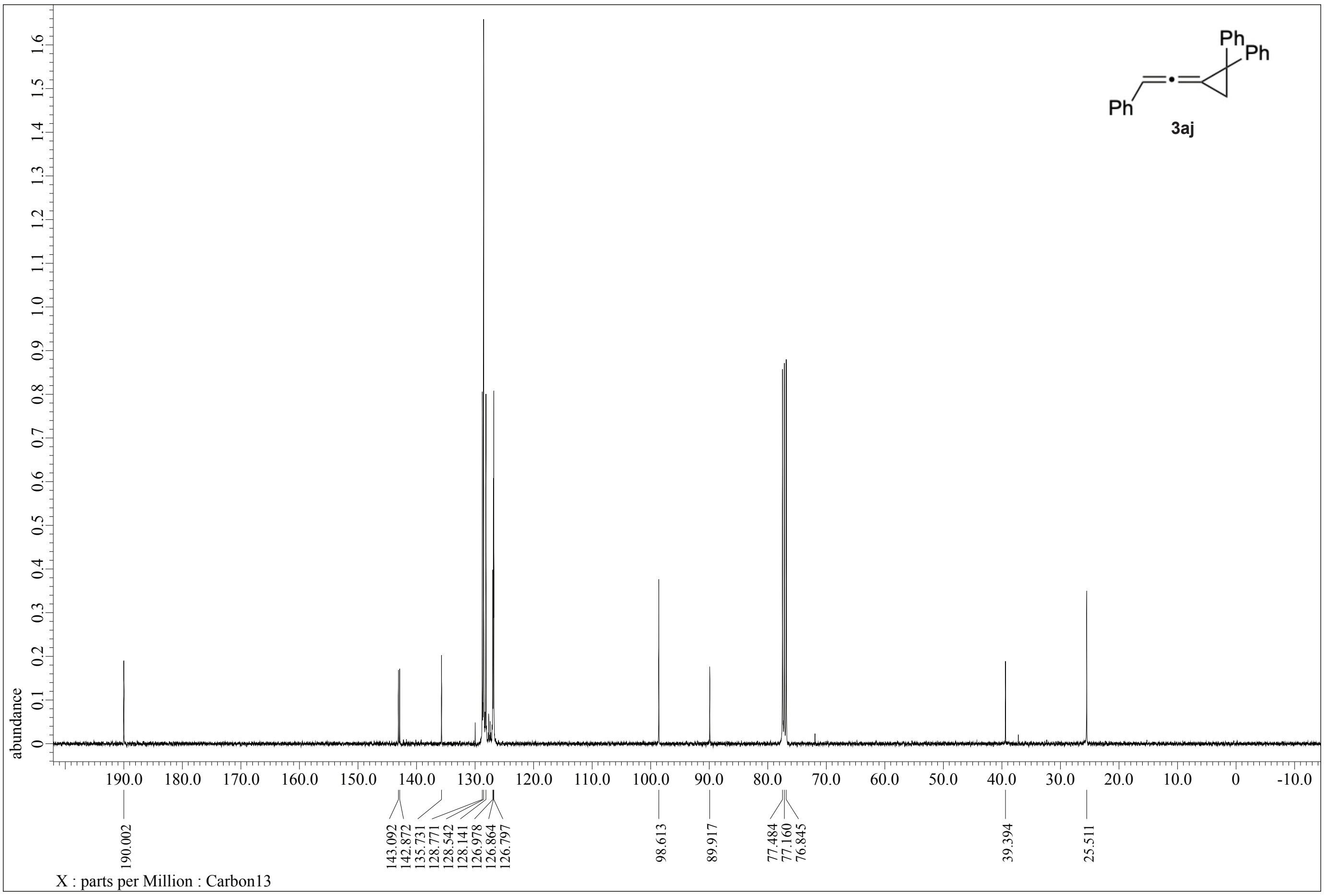
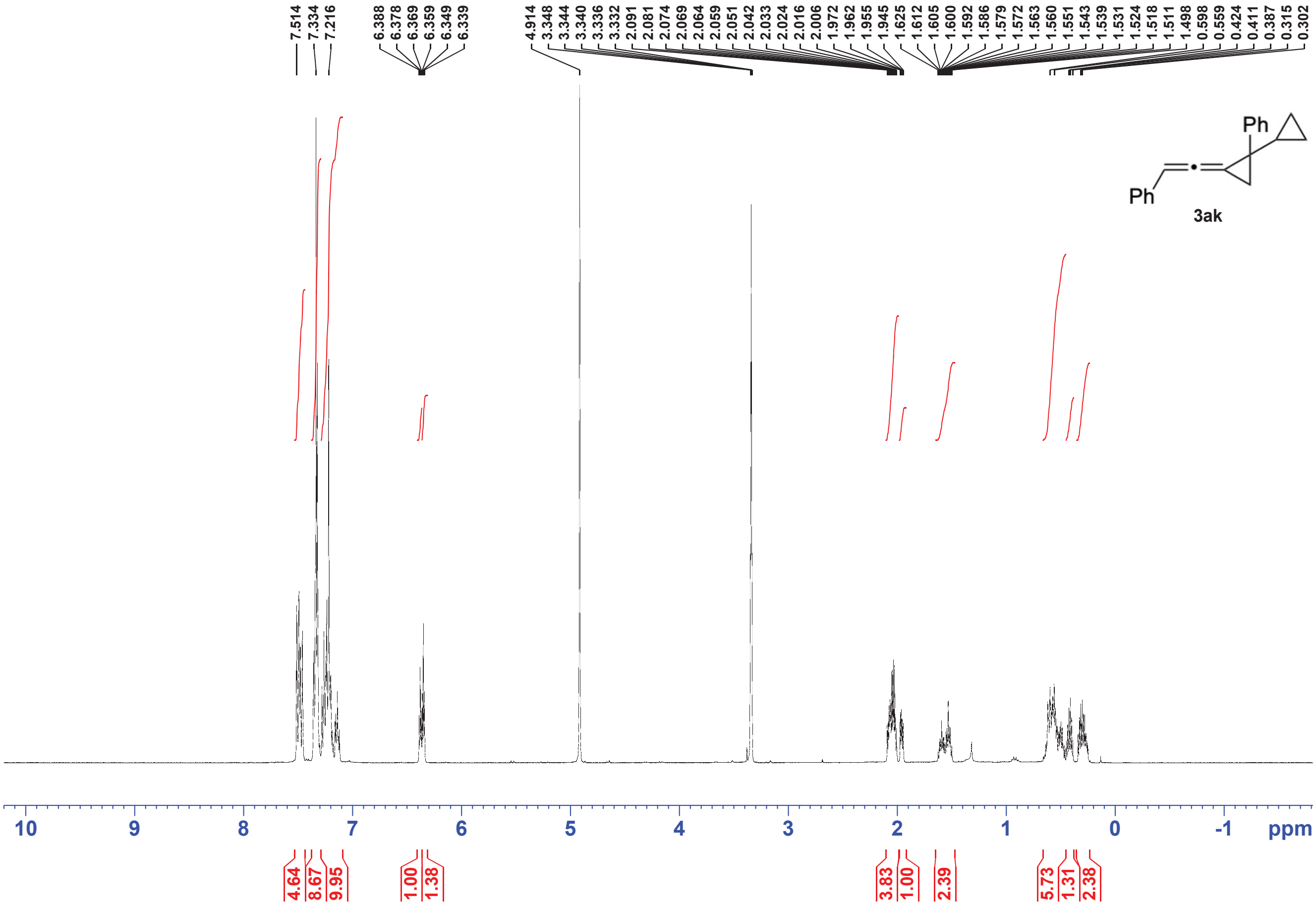
1.0
2.0
3.0
4.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.259
7.257
7.227
7.222
7.219
7.217
7.213
7.203
7.201
7.183
7.159
6.386
6.376
6.367
2.420
2.408
2.403
2.393
2.376
2.367
2.357
2.348
X : parts per Million : Proton


Ph
Ph
Ph
3aj
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
190.002
143.092
142.872
135.731
128.771
128.542
128.141
126.978
126.864
126.797
98.613
89.917
77.484
77.160
76.845
39.394
25.511
X : parts per Million : Carbon13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7.334
7.216
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6.369
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6.349
6.339
4.914
3.348
3.344
3.340
3.336
3.332
2.091
2.081
2.074
2.069
2.064
2.059
2.051
2.042
2.033
2.024
2.016
2.006
1.972
1.962
1.955
1.945
1.625
1.612
1.605
1.600
1.592
1.586
1.579
1.572
1.563
1.560
1.551
1.543
1.539
1.531
1.524
1.518
1.511
1.498
0.598
0.559
0.424
0.411
0.387
0.315
0.302
Ph
Ph
3ak
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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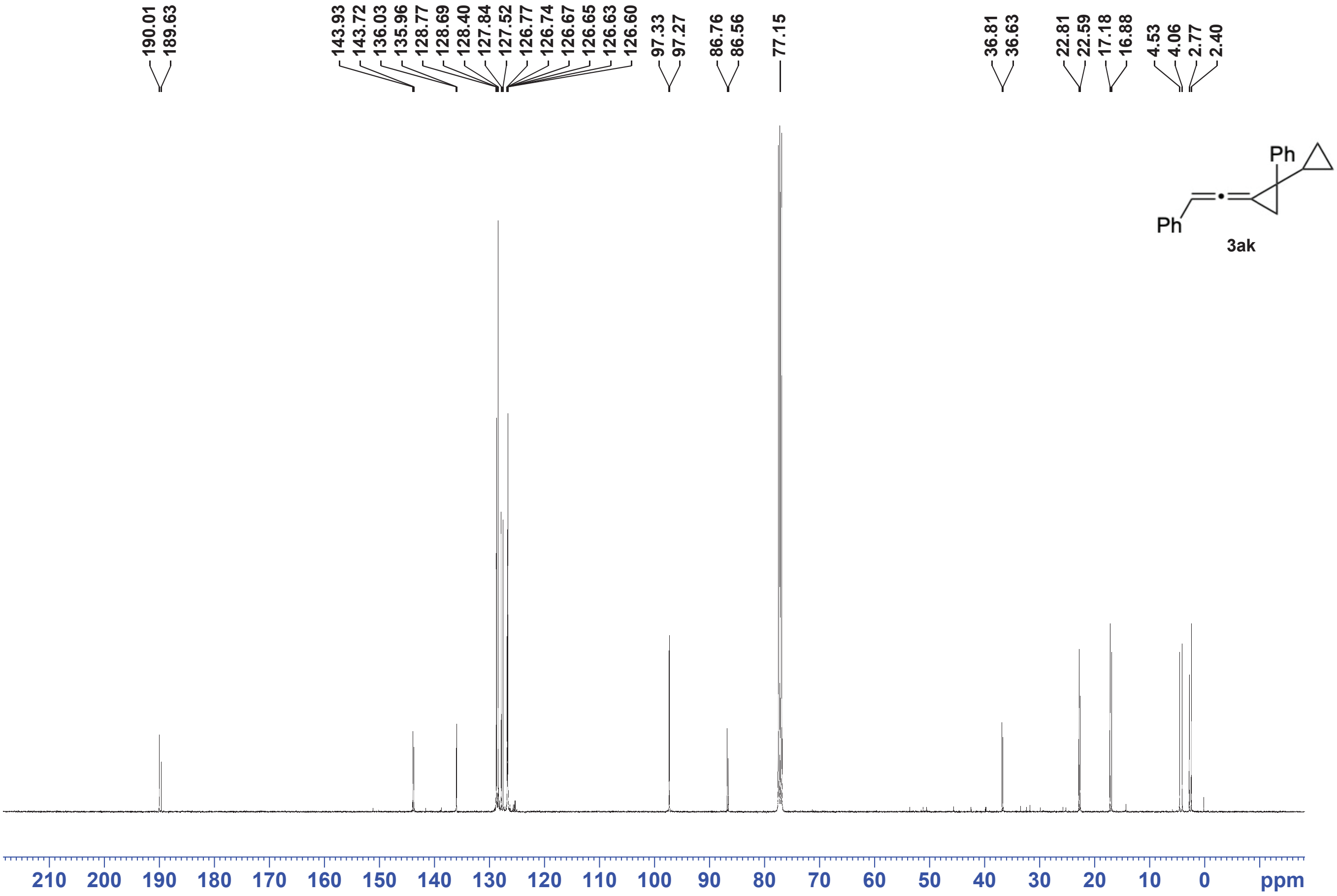
8.67
9.95
1.00
1.38
3.83
1.00
2.39
5.73
1.31
2.38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189.63
143.93
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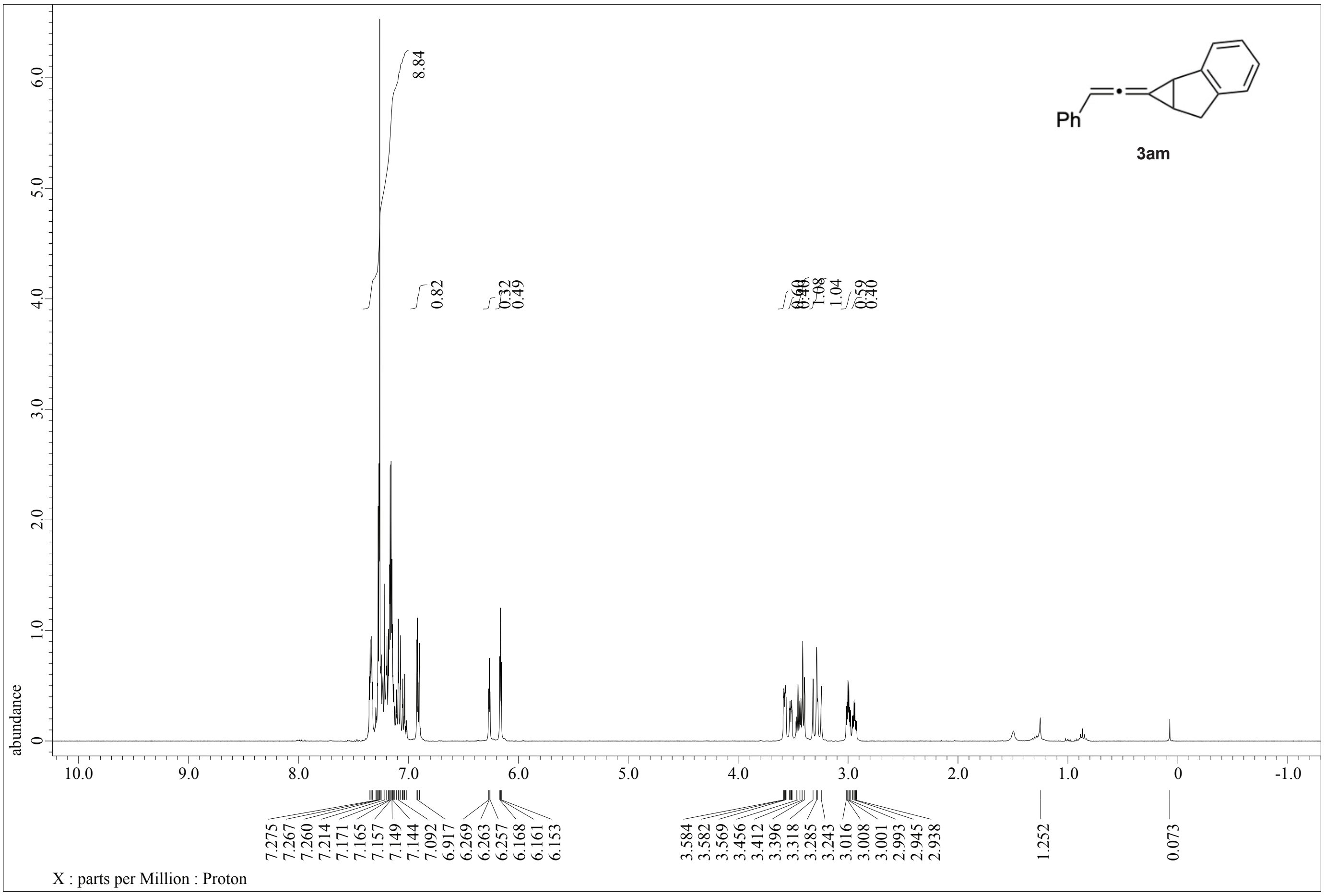
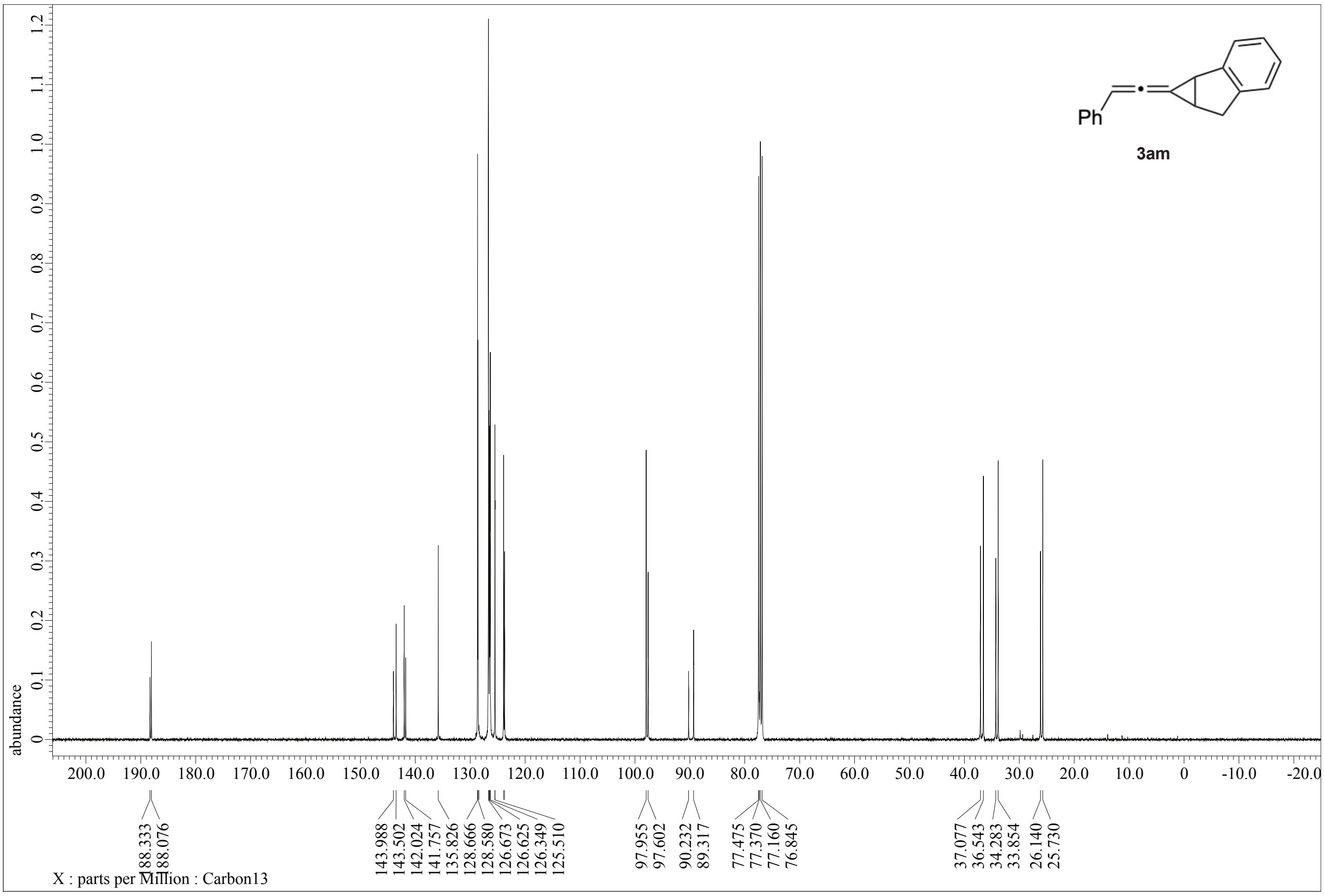
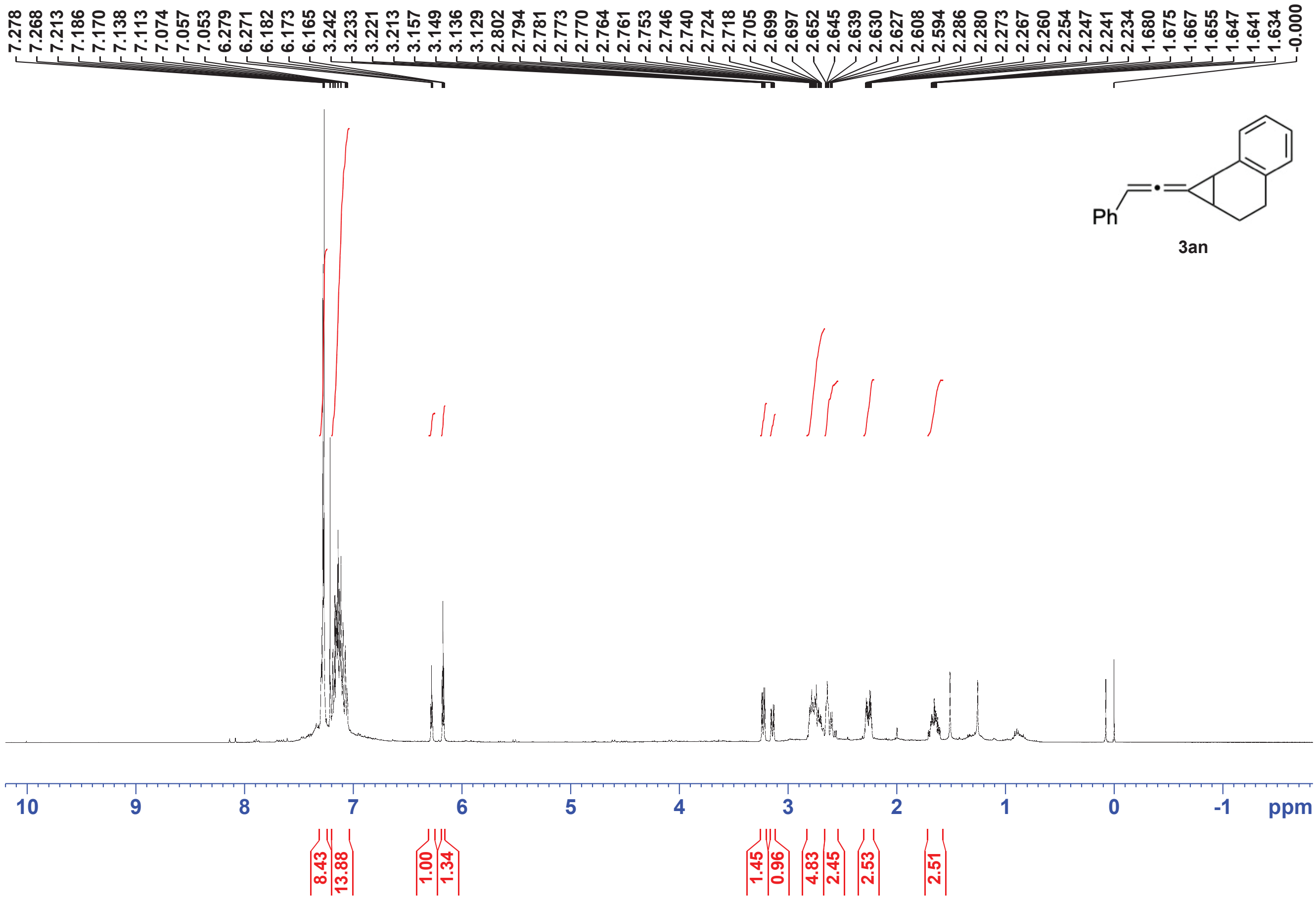
135.96
128.77
128.69
128.40
127.84
127.52
126.77
126.74
126.67
126.65
126.63
126.60
97.33
97.27
86.76
86.56
77.15
36.81
36.63
22.81
22.59
17.18
16.88
4.53
4.06
2.77
2.40
Ph
Ph
3ak
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



abundance
0
1.0
2.0
3.0
4.0
5.0
6.0
8.84
0.82
0.32
0.49
0.60
0.40
1.08
1.04
0.59
0.40
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
7.275
7.267
7.260
7.214
7.171
7.165
7.157
7.149
7.144
7.092
6.917
6.269
6.263
6.257
6.168
6.161
6.153
3.584
3.582
3.569
3.456
3.412
3.396
3.318
3.285
3.243
3.016
3.008
3.001
2.993
2.945
2.938
1.252
0.073
X : parts per Million : Proton
Ph
3am



abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
188.333
188.076
143.988
143.502
142.024
141.757
135.826
128.666
128.580
126.673
126.625
126.349
125.510
97.955
97.602
90.232
89.317
77.475
77.370
77.160
76.845
37.077
36.543
34.283
33.854
26.140
25.730
X : parts per Million : Carbon13
Ph
3am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7.170
7.138
7.113
7.074
7.057
7.053
6.279
6.271
6.182
6.173
6.165
3.242
3.233
3.221
3.213
3.157
3.149
3.136
3.129
2.802
2.794
2.781
2.773
2.770
2.764
2.761
2.753
2.746
2.740
2.724
2.718
2.705
2.699
2.697
2.652
2.645
2.639
2.630
2.627
2.608
2.594
2.286
2.280
2.273
2.267
2.260
2.254
2.247
2.241
2.234
1.680
1.675
1.667
1.655
1.647
1.641
1.634
-0.000
Ph
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
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1.00
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1.45
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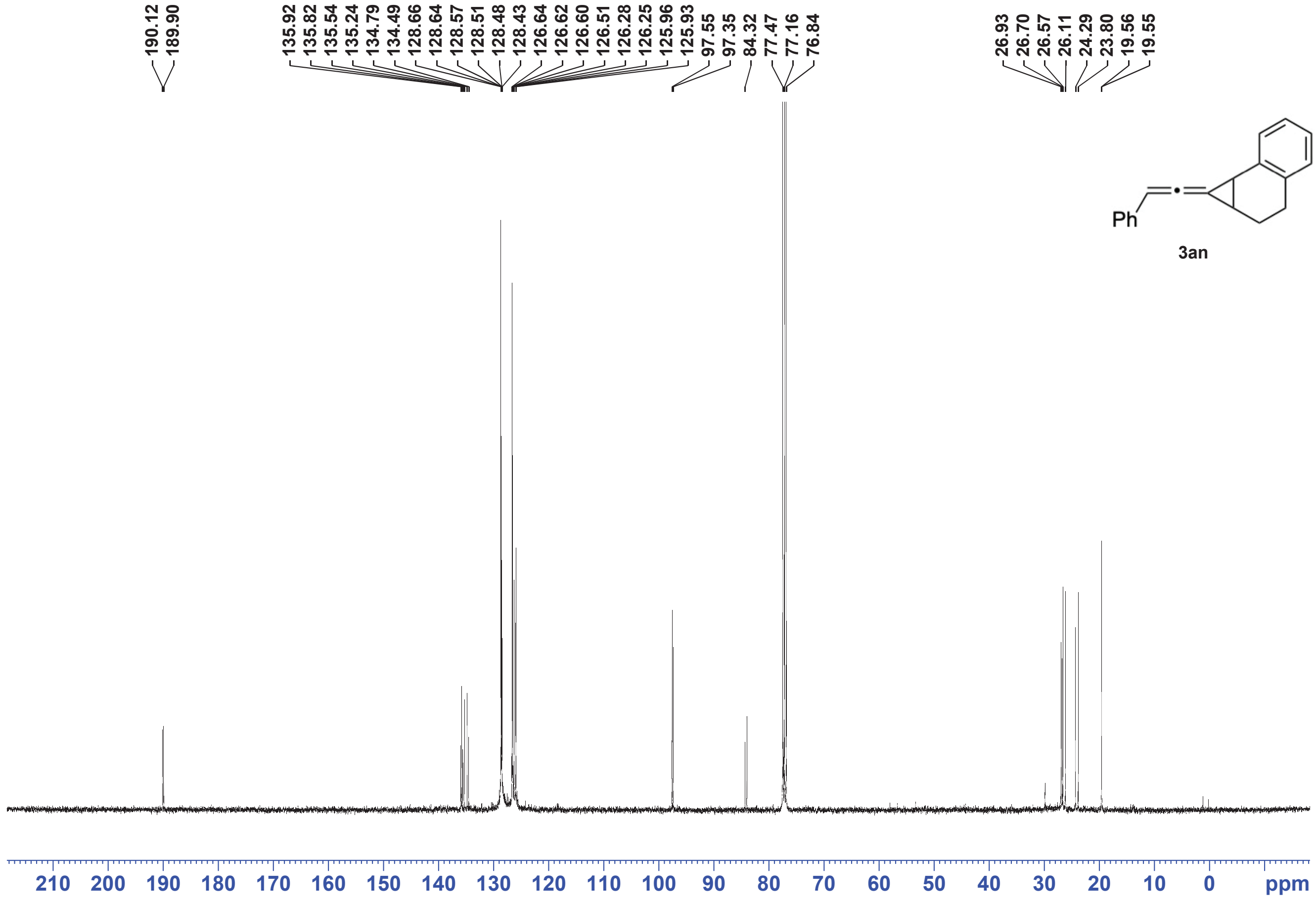
4.83
2.45
2.53
2.51

3an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135.54
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134.49
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128.64
128.57
128.51
128.48
128.43
126.64
126.62
126.60
126.51
126.28
126.25
125.96
125.93
97.55
97.35
84.32
77.47
77.16
76.84
26.93
26.70
26.57
26.11
24.29
23.80
19.56
19.55
Ph
210
200
190
180
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160
150
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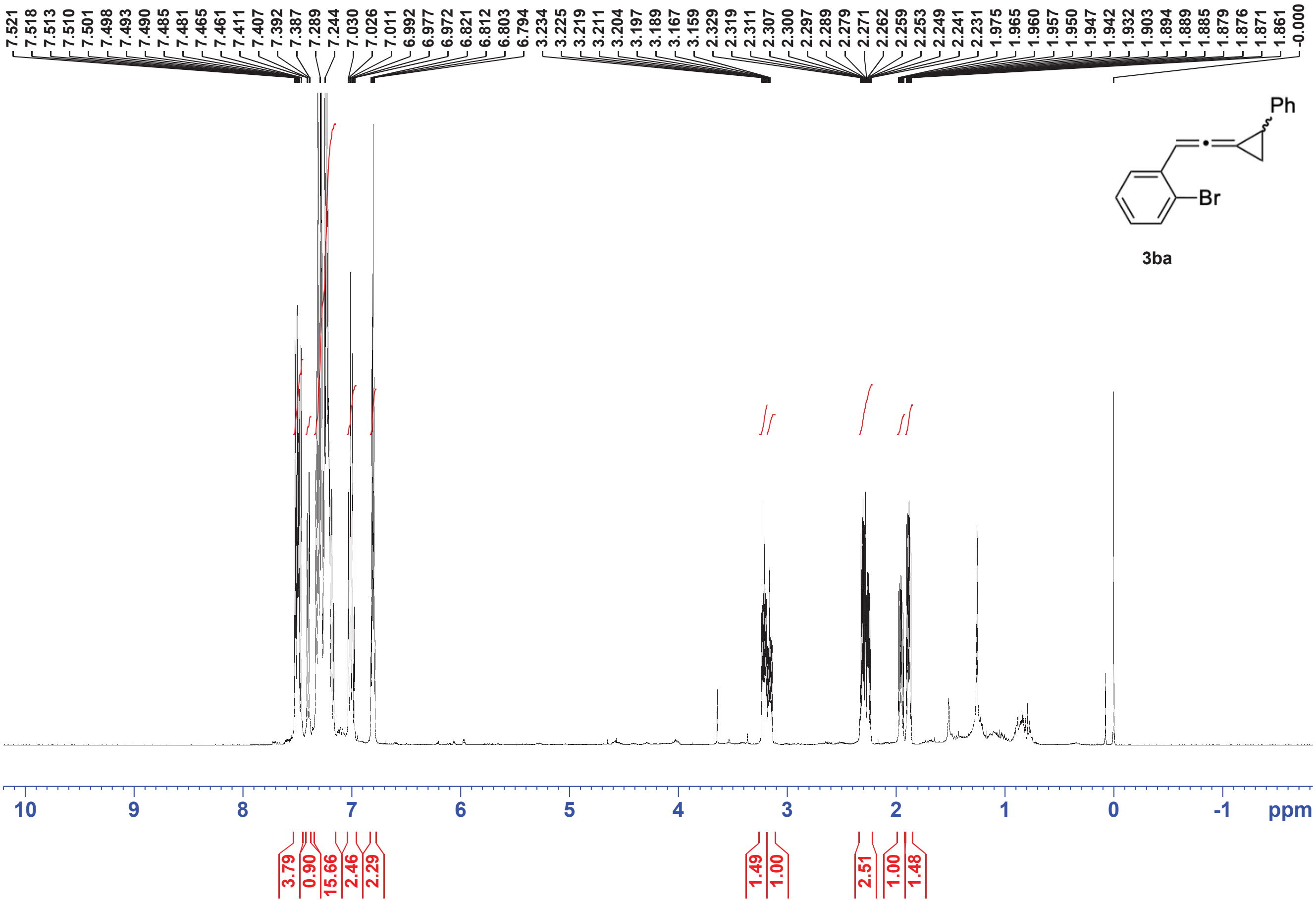
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

3an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7.510
7.501
7.498
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7.481
7.465
7.461
7.411
7.407
7.392
7.387
7.289
7.244
7.030
7.026
7.011
6.992
6.977
6.972
6.821
6.812
6.803
6.794
3.234
3.225
3.219
3.211
3.204
3.197
3.189
3.167
3.159
2.329
2.319
2.311
2.307
2.300
2.297
2.289
2.279
2.271
2.262
2.259
2.253
2.249
2.241
2.231
1.975
1.965
1.960
1.957
1.950
1.947
1.942
1.932
1.903
1.894
1.889
1.885
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1.876
1.871
1.861
-0.000
Ph
Br
3ba
10
9
8
7
6
5
4
3
2
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-1
ppm
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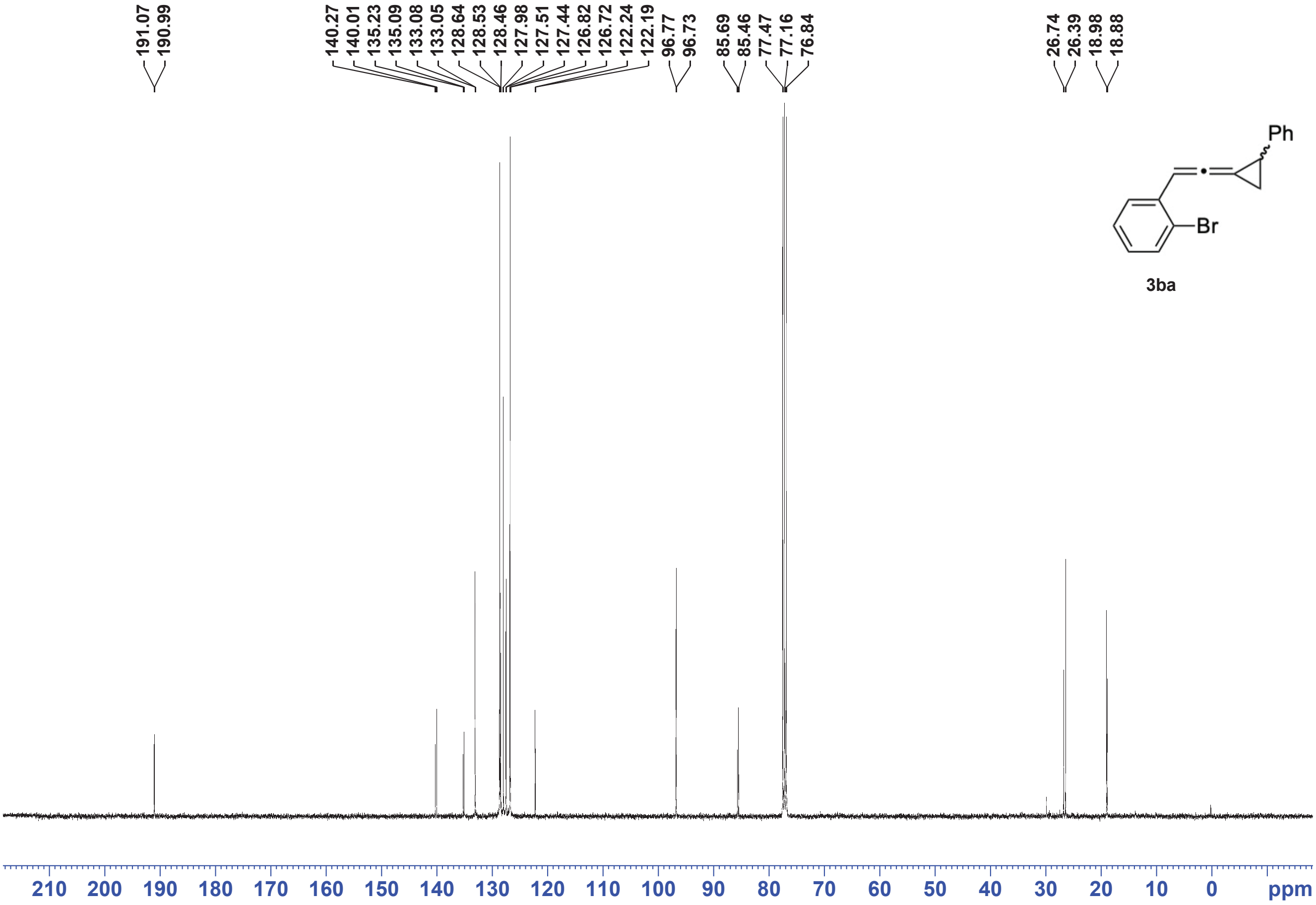
1.00
1.48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128.53
128.46
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127.51
127.44
126.82
126.72
122.24
122.19
96.77
96.73
85.69
85.46
77.47
77.16
76.84
26.74
26.39
18.98
18.88
Ph
Br
3ba
210
200
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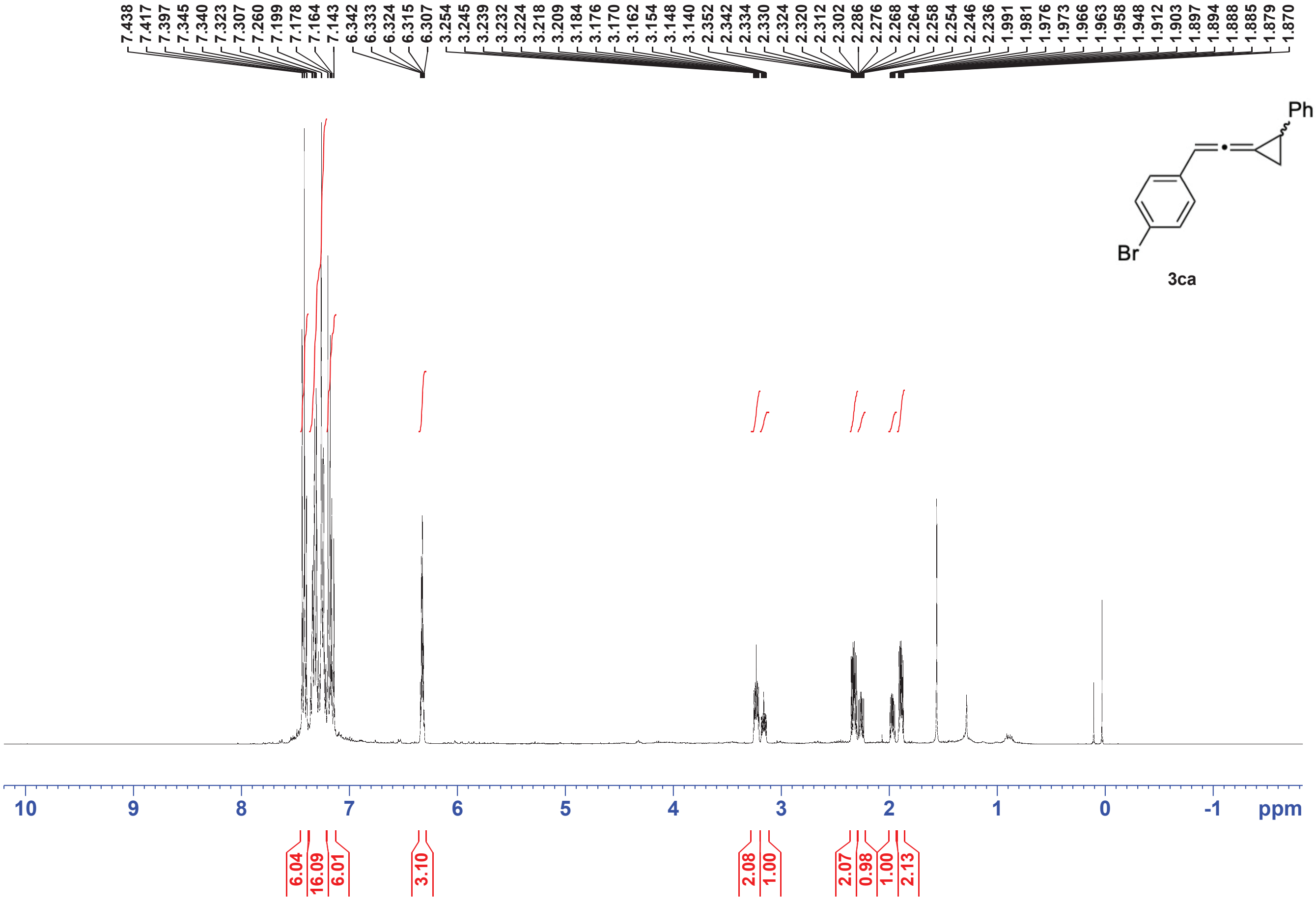
ppm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6.333
6.324
6.315
6.307
3.254
3.245
3.239
3.232
3.224
3.218
3.209
3.184
3.176
3.170
3.162
3.154
3.148
3.140
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2.342
2.334
2.330
2.324
2.320
2.312
2.302
2.286
2.276
2.268
2.264
2.258
2.254
2.246
2.236
1.991
1.981
1.976
1.973
1.966
1.963
1.958
1.948
1.912
1.903
1.897
1.894
1.888
1.885
1.879
1.870
Ph
Br
3ca
10
9
8
7
6
5
4
3
2
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-1
ppm
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3.10
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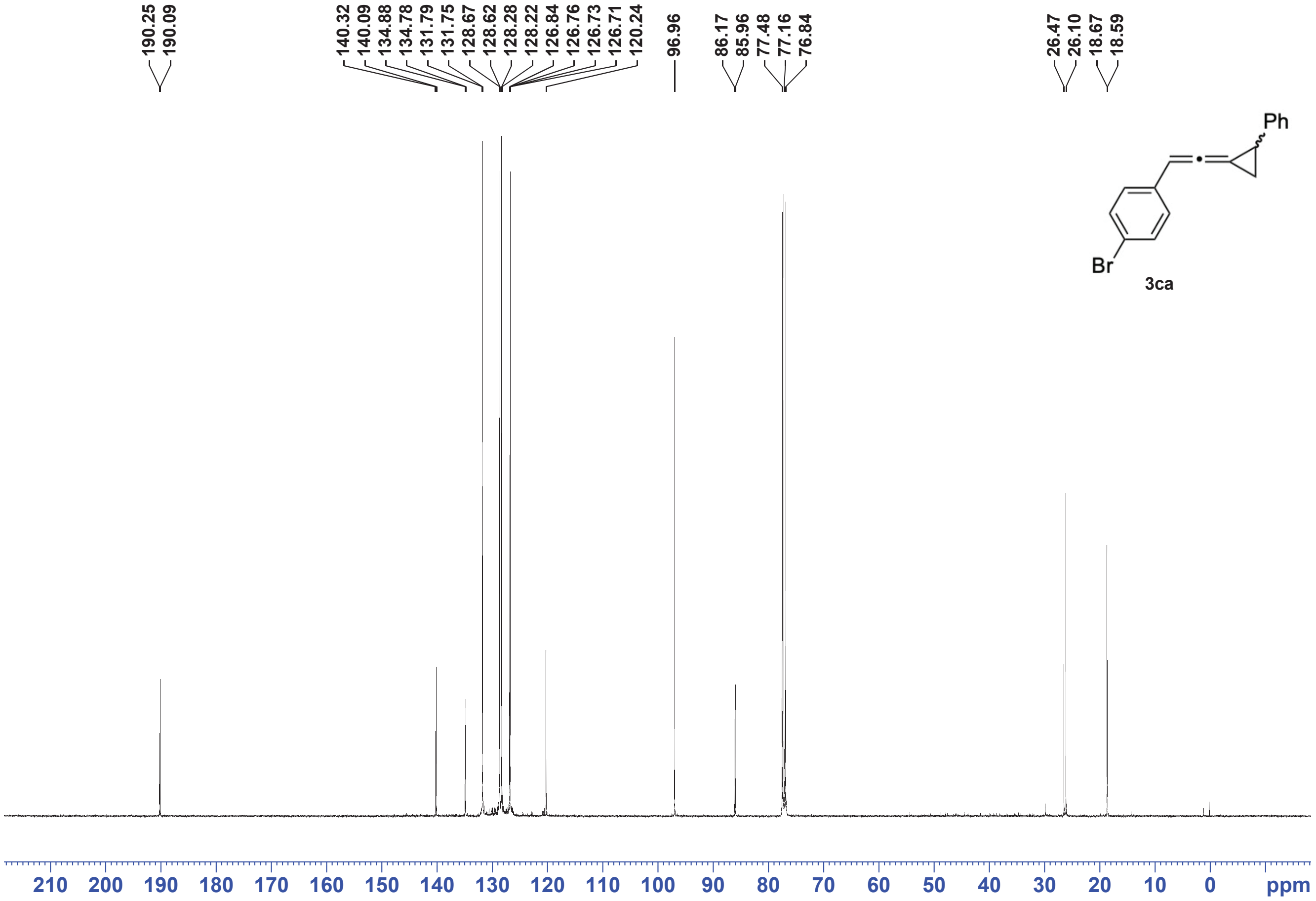
1.00
2.07
0.98
1.00
2.13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128.62
128.28
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126.84
126.76
126.73
126.71
120.24
96.96
86.17
85.96
77.48
77.16
76.84
26.47
26.10
18.67
18.59
Ph
Br
3ca
210
200
190
180
170
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140
130
120
110
100
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80
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60
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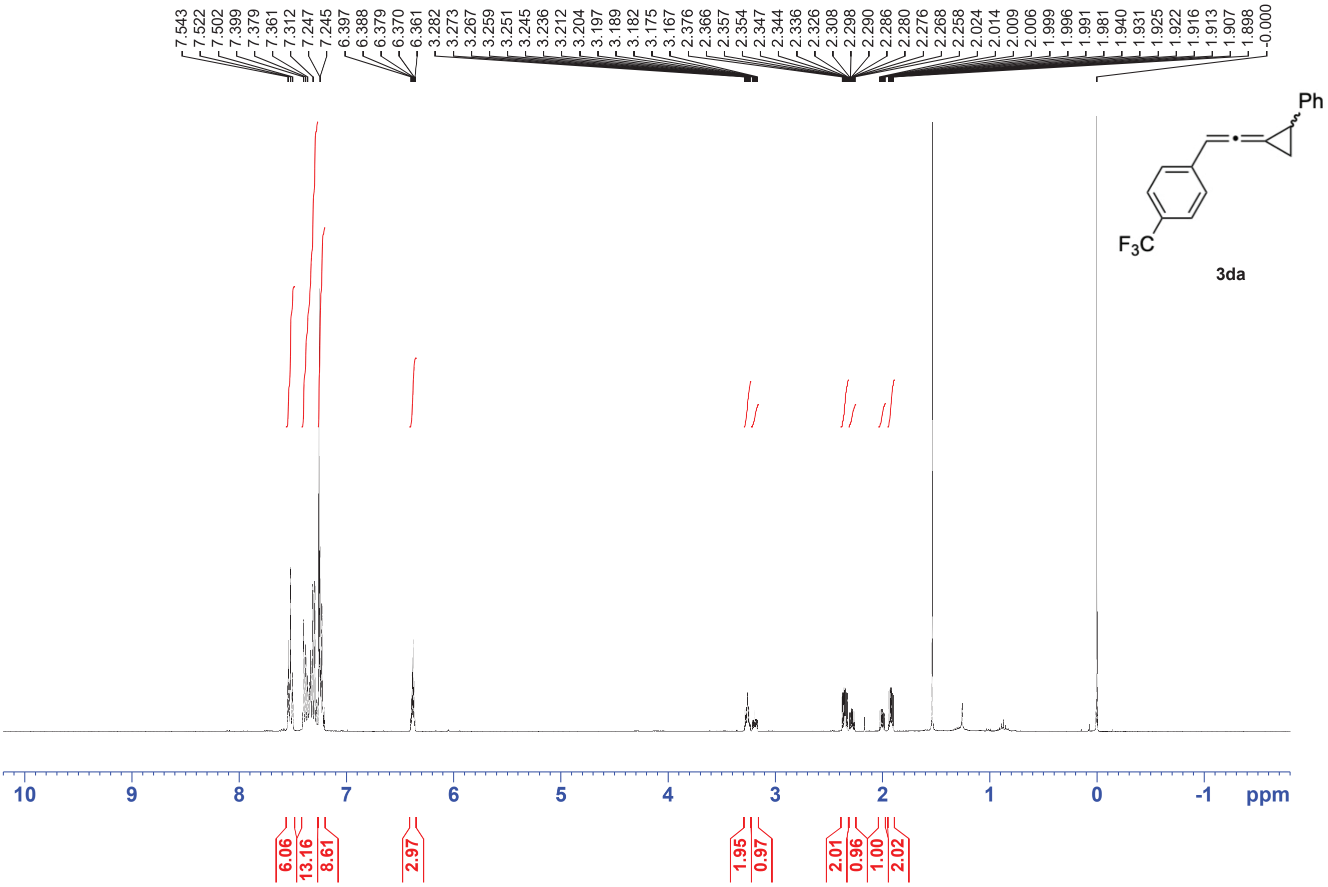
10
0
ppm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6.397
6.388
6.379
6.370
6.361
3.282
3.273
3.267
3.259
3.251
3.245
3.236
3.212
3.204
3.197
3.189
3.182
3.175
3.167
2.376
2.366
2.357
2.354
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2.336
2.326
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2.290
2.286
2.280
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2.258
2.024
2.014
2.009
2.006
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1.996
1.991
1.981
1.940
1.931
1.925
1.922
1.916
1.913
1.907
1.898
-0.000
Ph
F_3C
3da
10
9
8
7
6
5
4
3
2
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0
-1
ppm
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13.16
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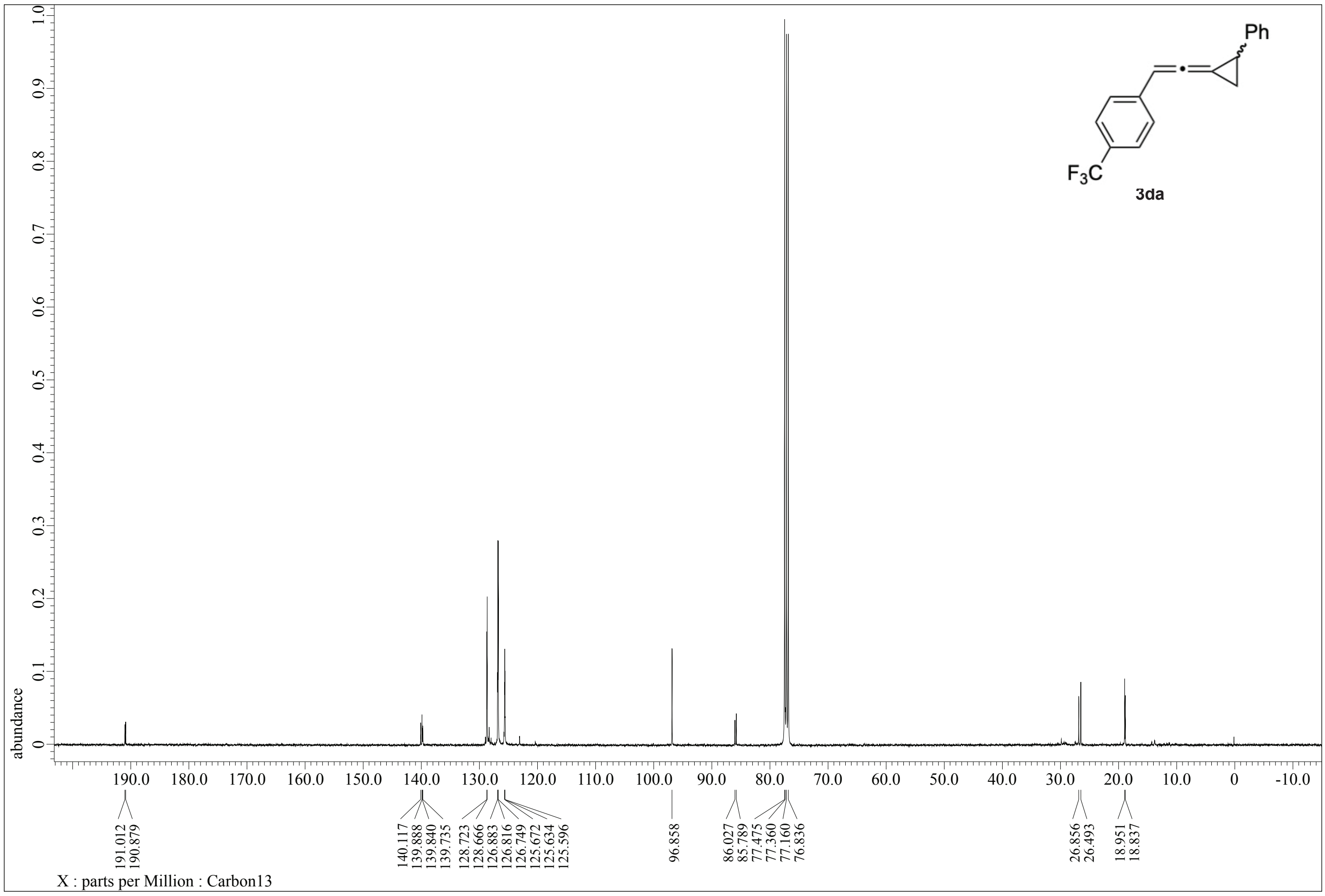
0.97
2.01
0.96
1.00
2.02


Ph
F_3C
3da
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
190.0
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170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
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60.0
50.0
40.0
30.0
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126.883
126.816
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125.596
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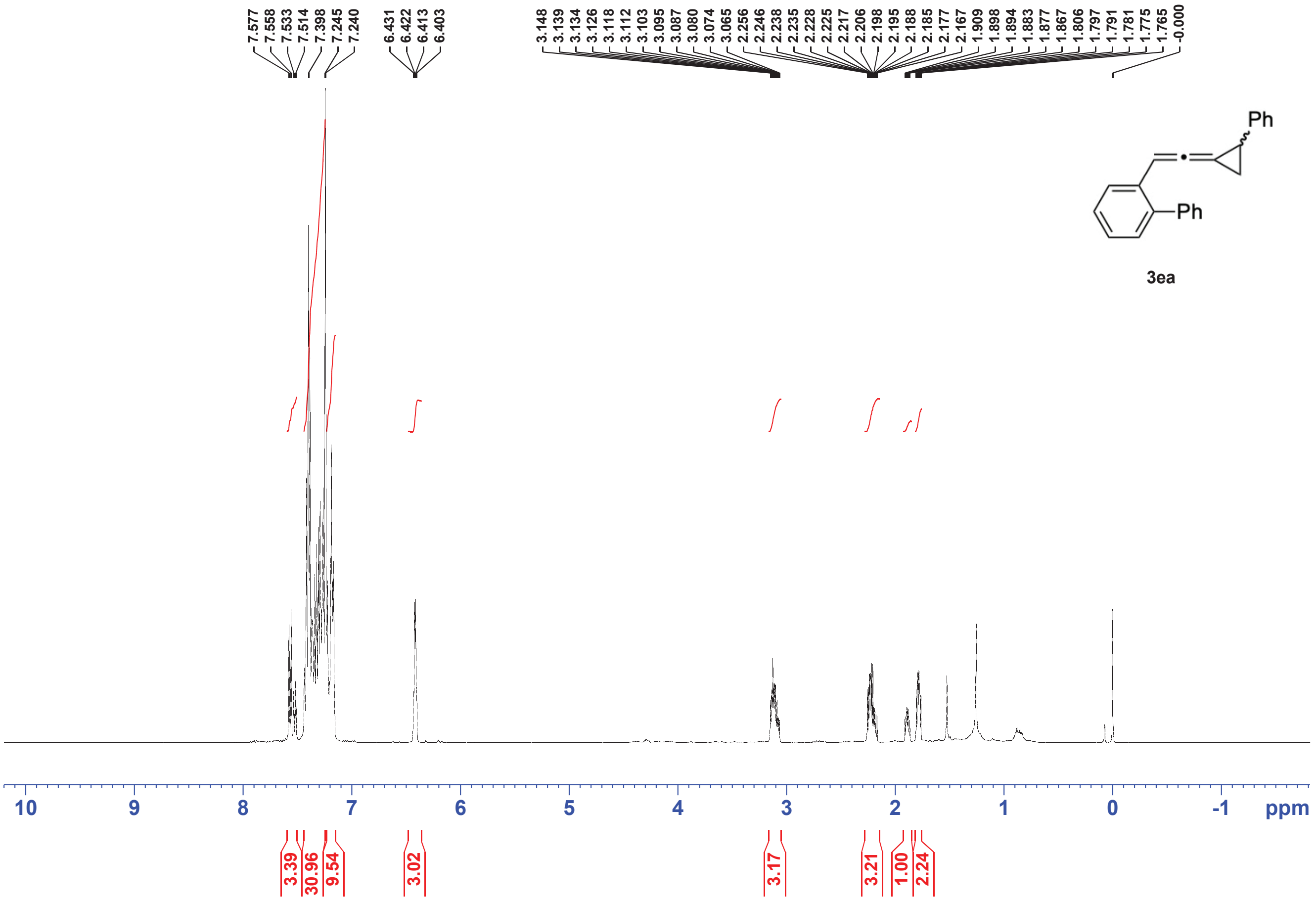
18.837
X : parts per Million : Carbon13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3.126
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3.112
3.103
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3.087
3.080
3.074
3.065
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2.246
2.238
2.235
2.228
2.225
2.217
2.206
2.198
2.195
2.188
2.185
2.177
2.167
1.909
1.898
1.894
1.883
1.877
1.867
1.806
1.797
1.791
1.781
1.775
1.765
-0.000
Ph
Ph
3ea
10
9
8
7
6
5
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-1
ppm
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3.02
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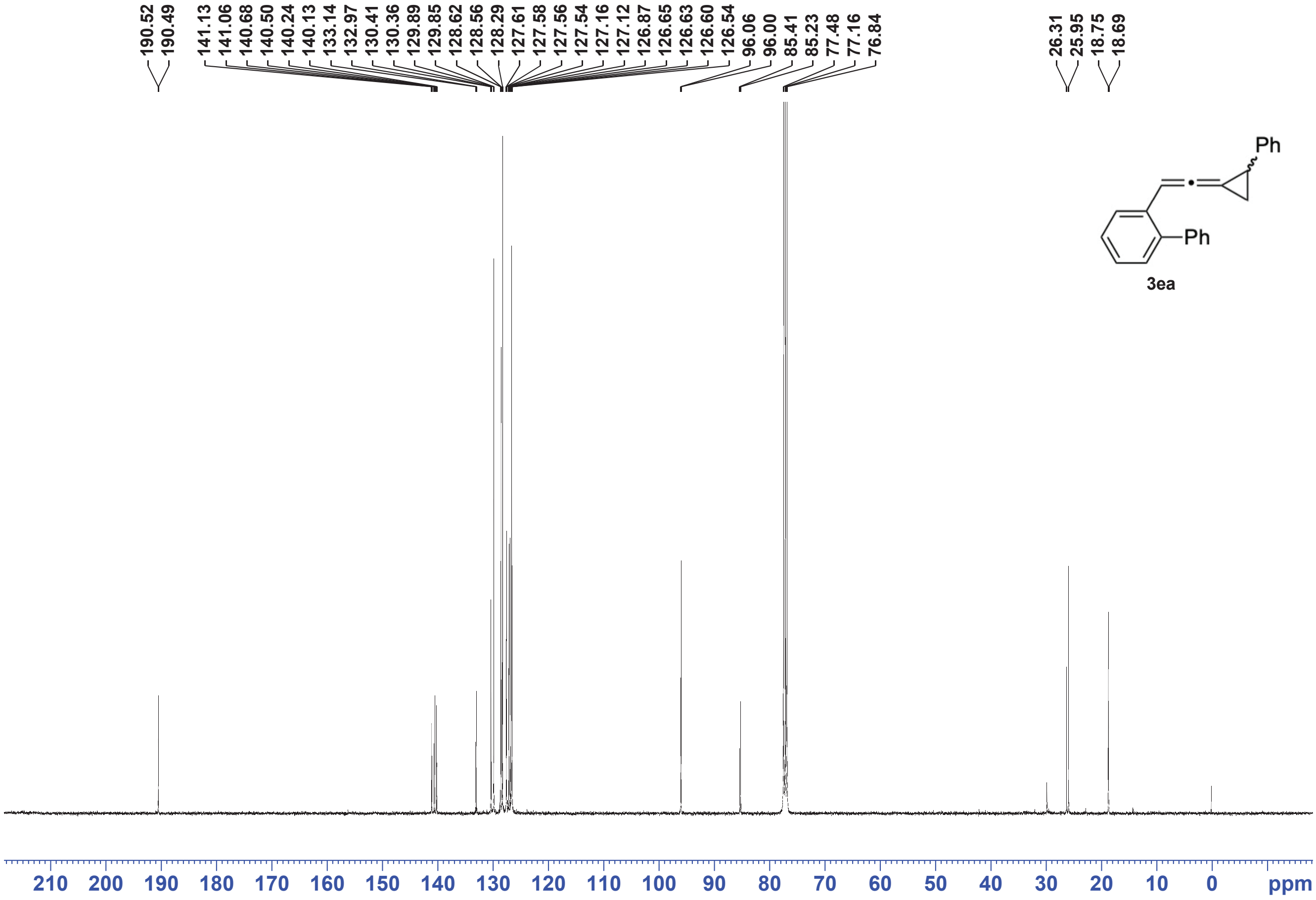
1.00
2.24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140.13
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128.56
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127.61
127.58
127.56
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127.16
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126.63
126.60
126.54
96.06
96.00
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26.31
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18.69
Ph
Ph
3ea
210
200
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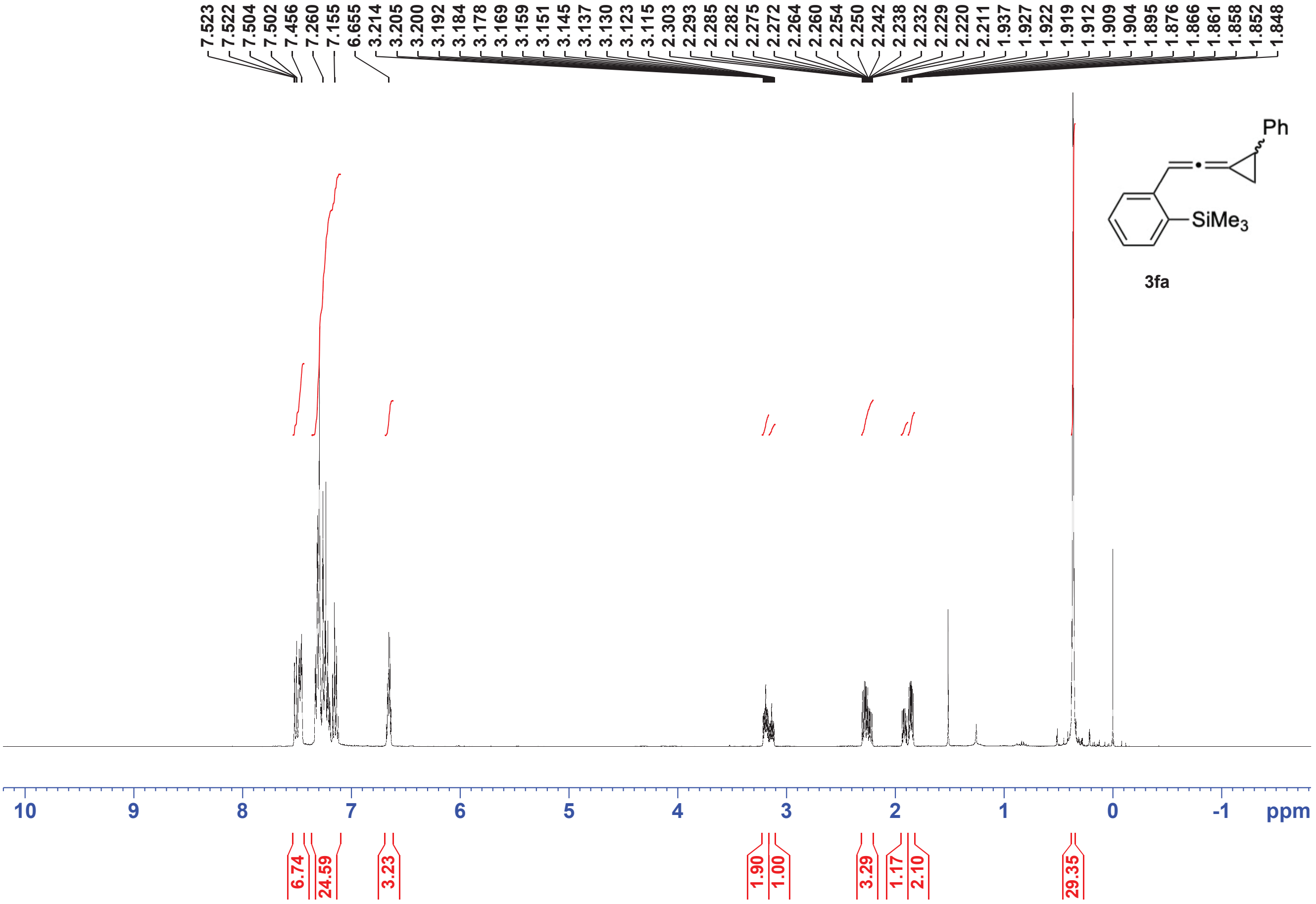
ppm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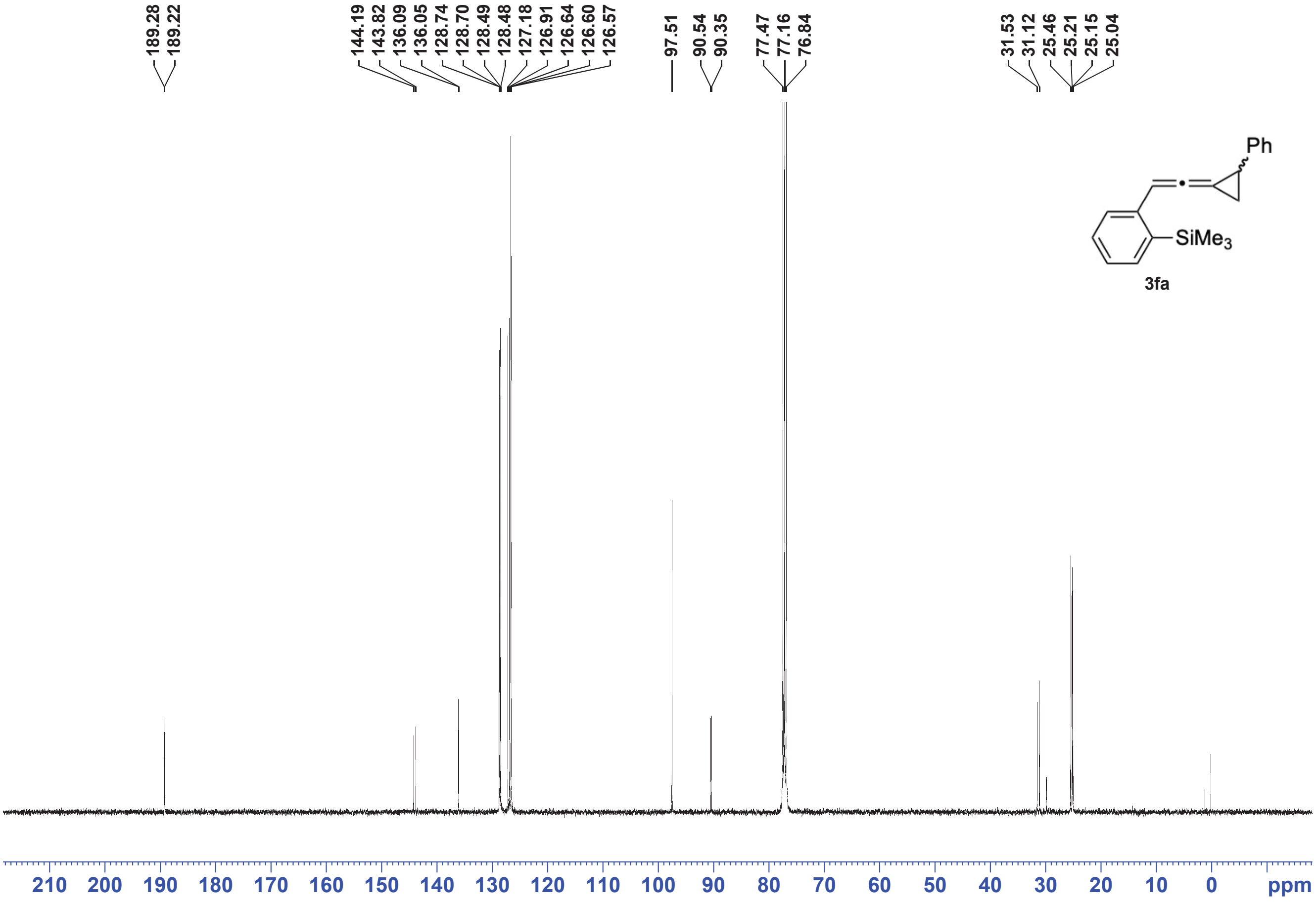
2.250
2.242
2.238
2.232
2.229
2.220
2.211
1.937
1.927
1.922
1.919
1.912
1.909
1.904
1.895
1.876
1.866
1.861
1.858
1.852
1.848
Ph
SiMe3
3fa
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
6.74
24.59
3.23
1.90
1.00
3.29
1.17
2.10
29.35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189.22
144.19
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136.09
136.05
128.74
128.70
128.49
128.48
127.18
126.91
126.64
126.60
126.57
97.51
90.54
90.35
77.47
77.16
76.84
31.53
31.12
25.46
25.21
25.15
25.04
Ph
SiMe3
3fa
210
200
190
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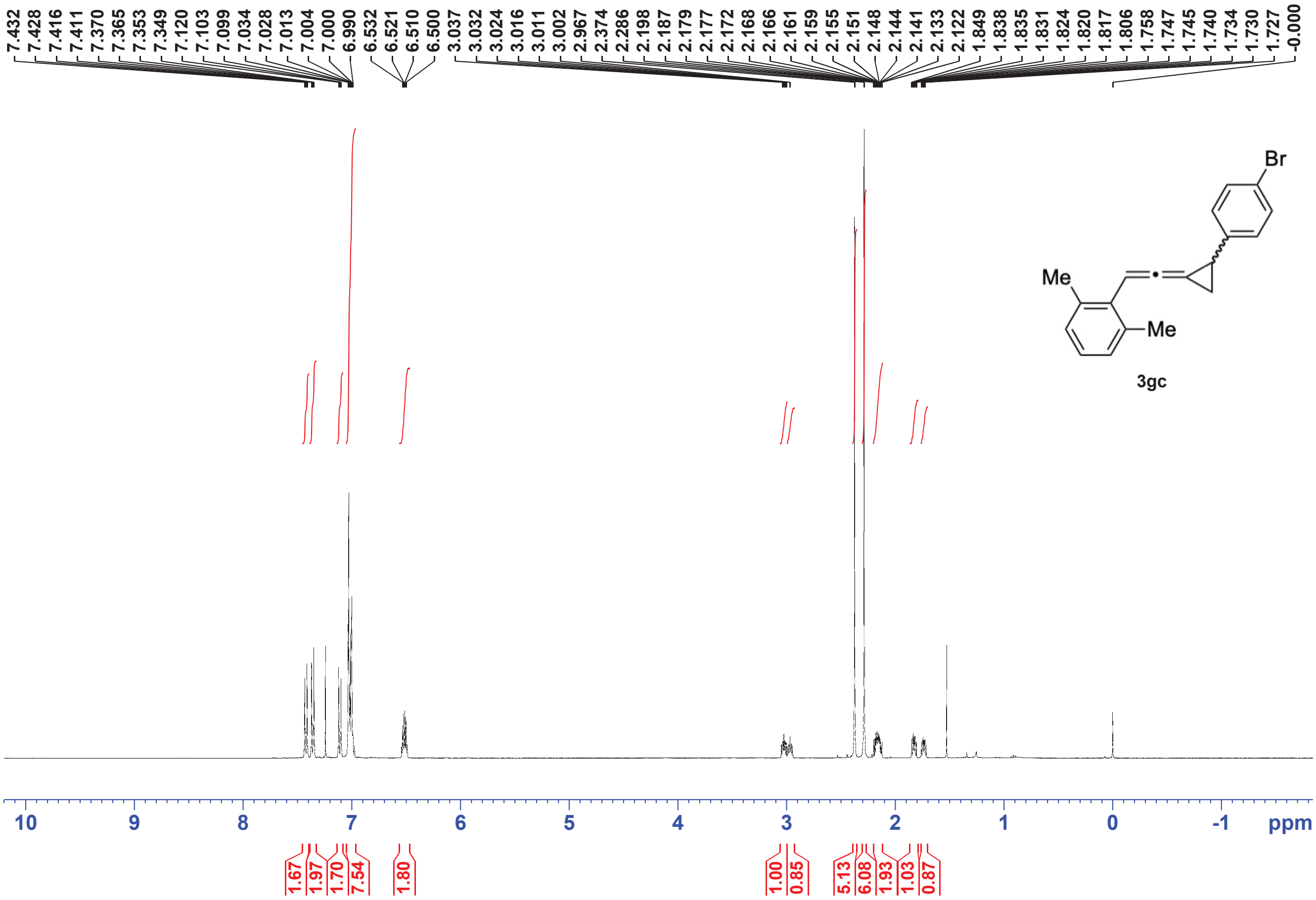
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.428
7.416
7.411
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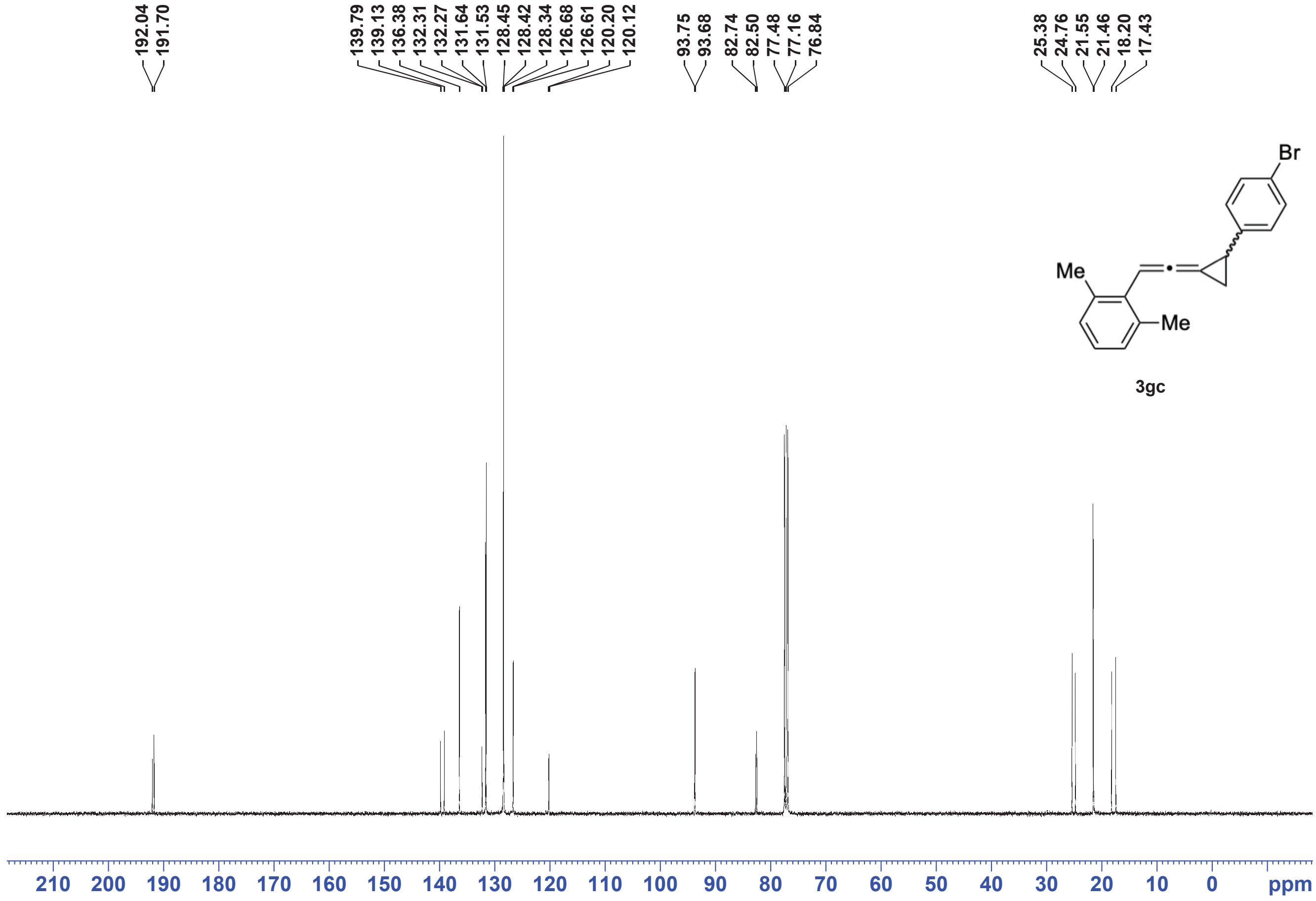
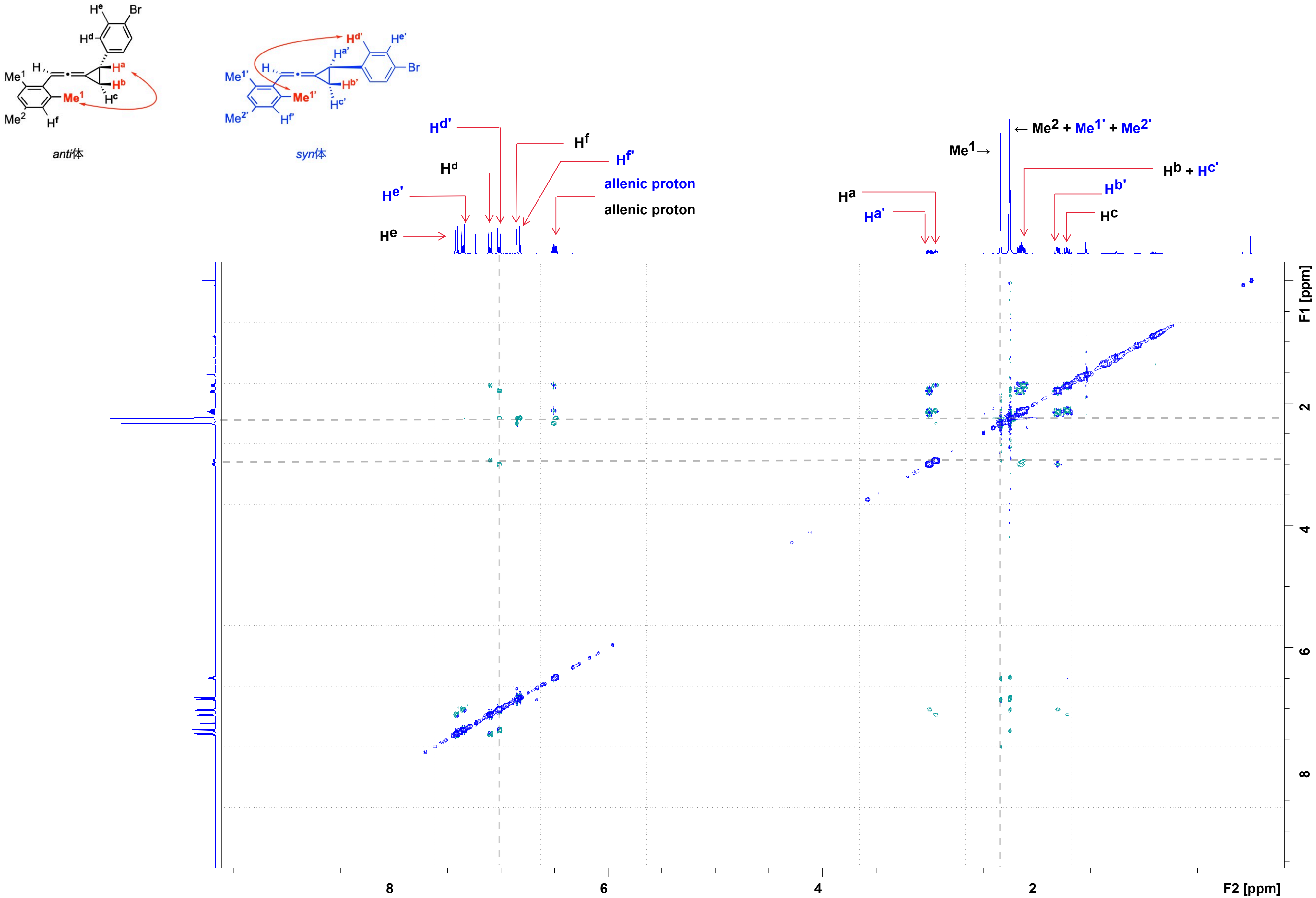
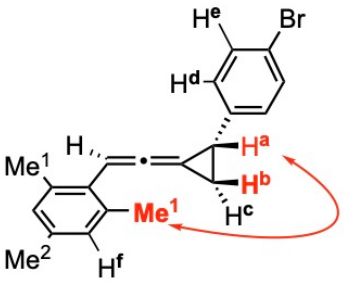
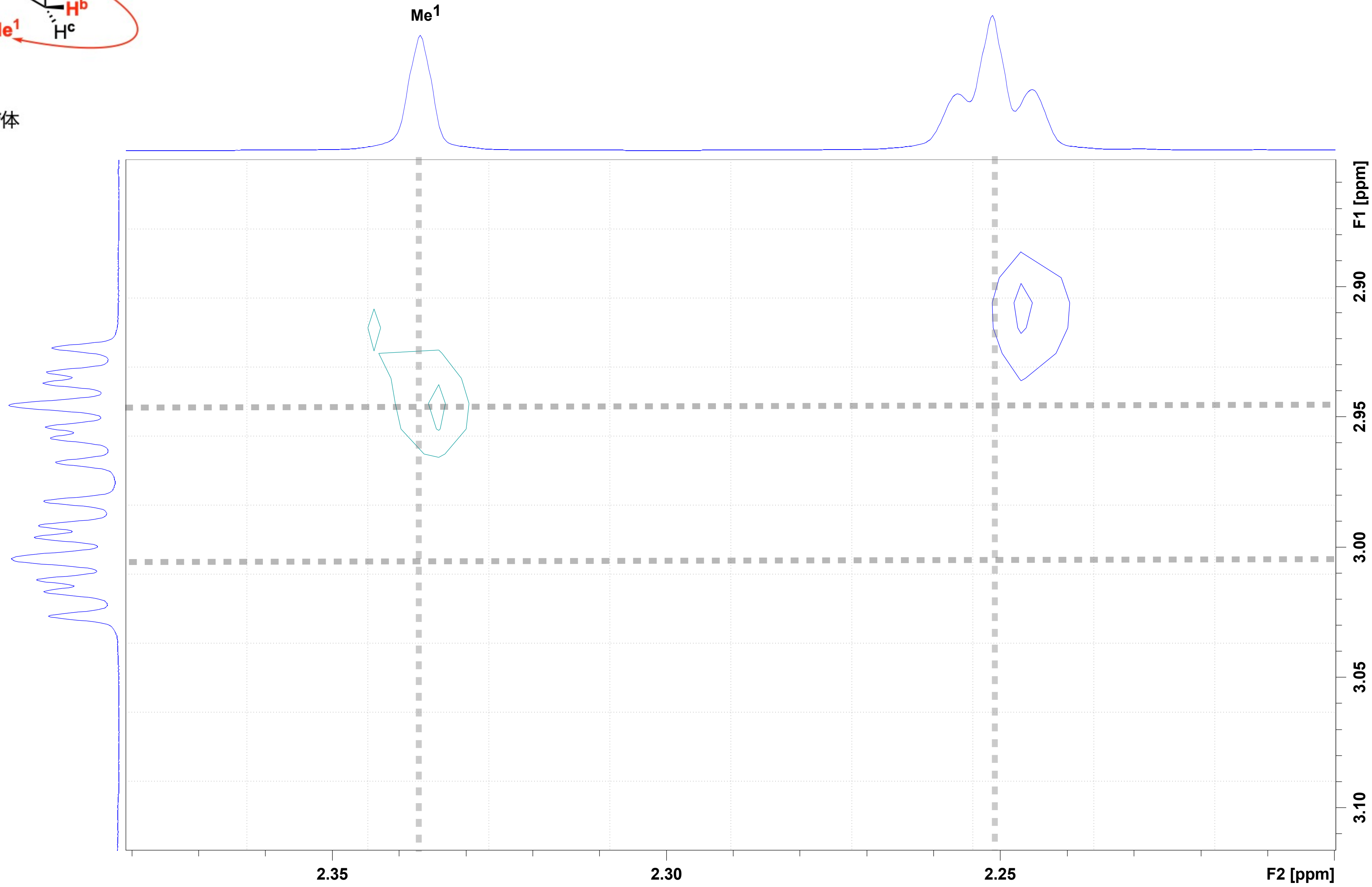
7.365
7.353
7.349
7.120
7.103
7.099
7.034
7.028
7.013
7.004
7.000
6.990
6.532
6.521
6.510
6.500
3.037
3.032
3.024
3.016
3.011
3.002
2.967
2.374
2.286
2.198
2.187
2.179
2.177
2.172
2.168
2.166
2.161
2.159
2.155
2.151
2.148
2.144
2.141
2.133
2.122
1.849
1.838
1.835
1.831
1.824
1.820
1.817
1.806
1.758
1.747
1.745
1.740
1.734
1.730
1.727
-0.000
Br
Me
Me
3gc
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.67
1.97
1.70
7.54
1.80
1.00
0.85
5.13
6.08
1.93
1.03
0.87

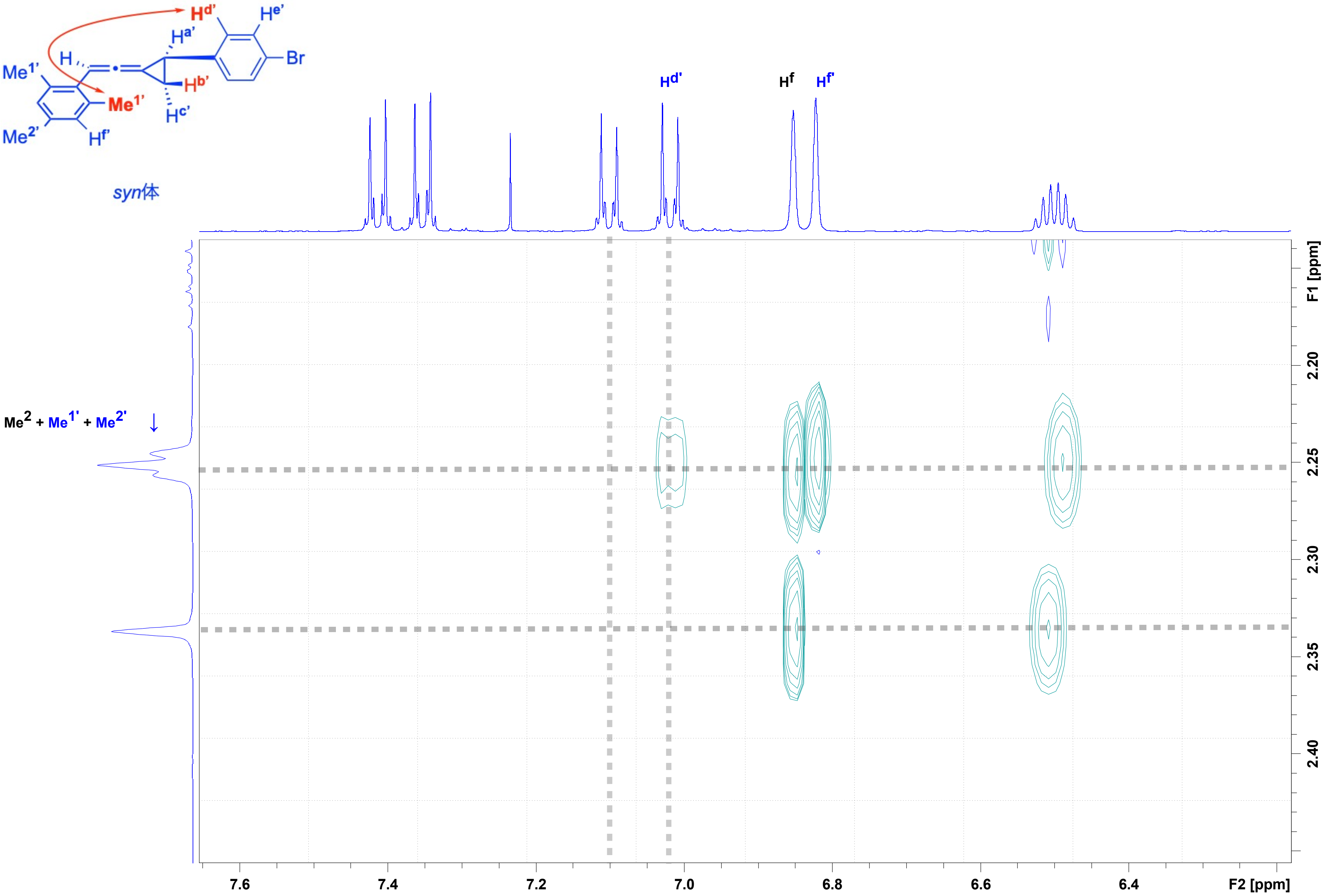

192.04
191.70
139.79
139.13
136.38
132.31
132.27
131.64
131.53
128.45
128.42
128.34
126.68
126.61
120.20
120.12
93.75
93.68
82.74
82.50
77.48
77.16
76.84
25.38
24.76
21.55
21.46
18.20
17.43
Br
Me
Me
3gc
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

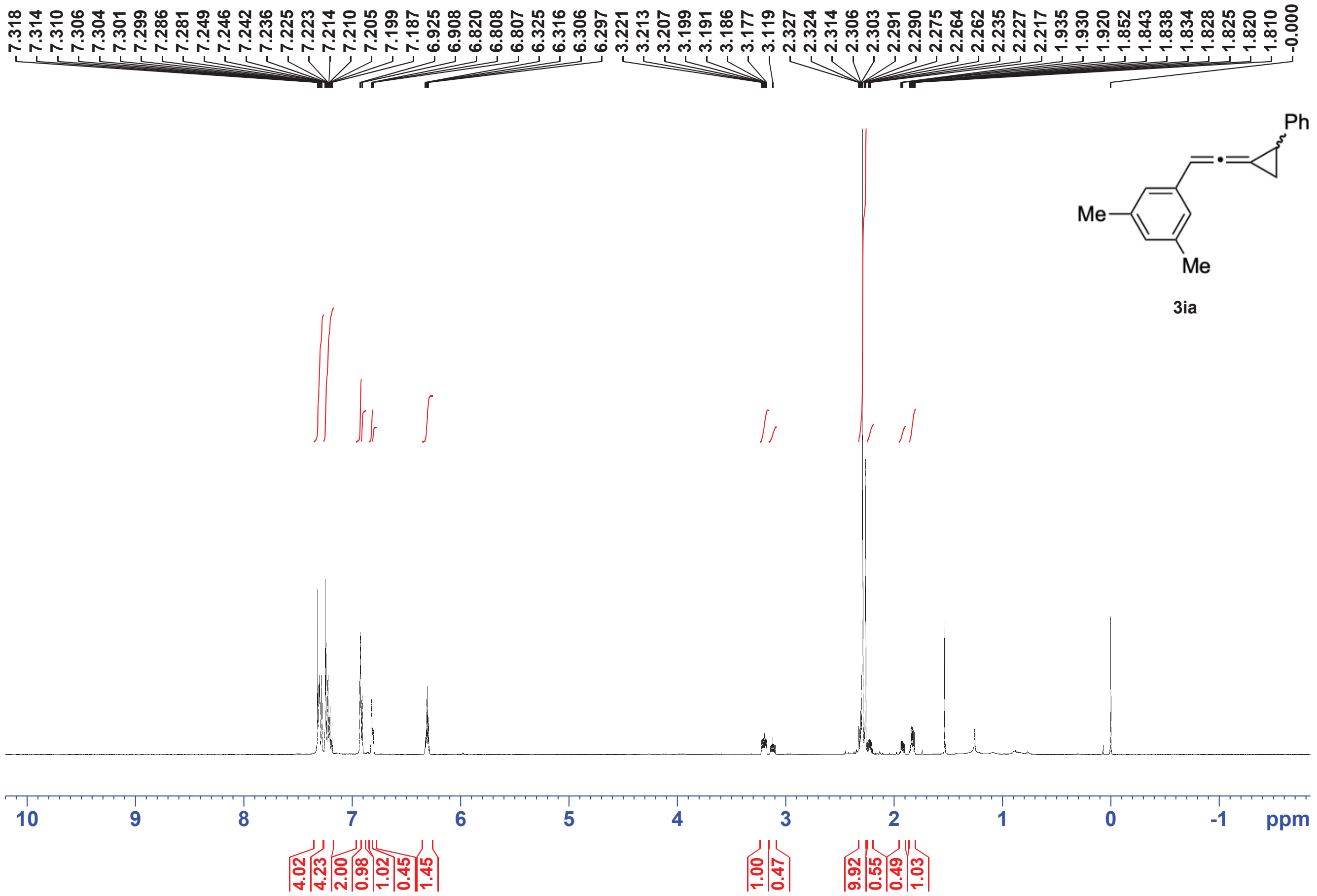

He
Br
Hd
Me1
H
Ha
Hb
Me1
Hc
Me2
Hf
anti体
Hd'
He'
Ha'
Br
Me1'
H
Hb'
Me1'
Hc'
Me2'
Hf'
syn体
Hd'
Hf
Hd
Hf'
He'
allenic proton
allenic proton
He
Me1→
← Me2 + Me1' + Me2'
Hb + Hc'
Hb'
Ha
Ha'
Hc
F1 [ppm]
2
4
6
8
F2 [ppm]


He
Br
Hd
H
Me1
Ha
Hb
Me1
Hc
Me2
Hf

*anti*体


Me1
Ha
Ha'
F1 [ppm]
2.90
2.95
3.00
3.05
3.10
2.35
2.30
2.25
F2 [ppm]


Hd'
He'
Ha'
H
Me1'
Br
Hb'
Me1'
Hc'
Me2'
Hf'
syn体
Hd'
Hf
Hf'
Me2 + Me1' + Me2'
F1 [ppm]
2.20
2.25
2.30
2.35
2.40
7.6
7.4
7.2
7.0
6.8
6.6
6.4
F2 [ppm]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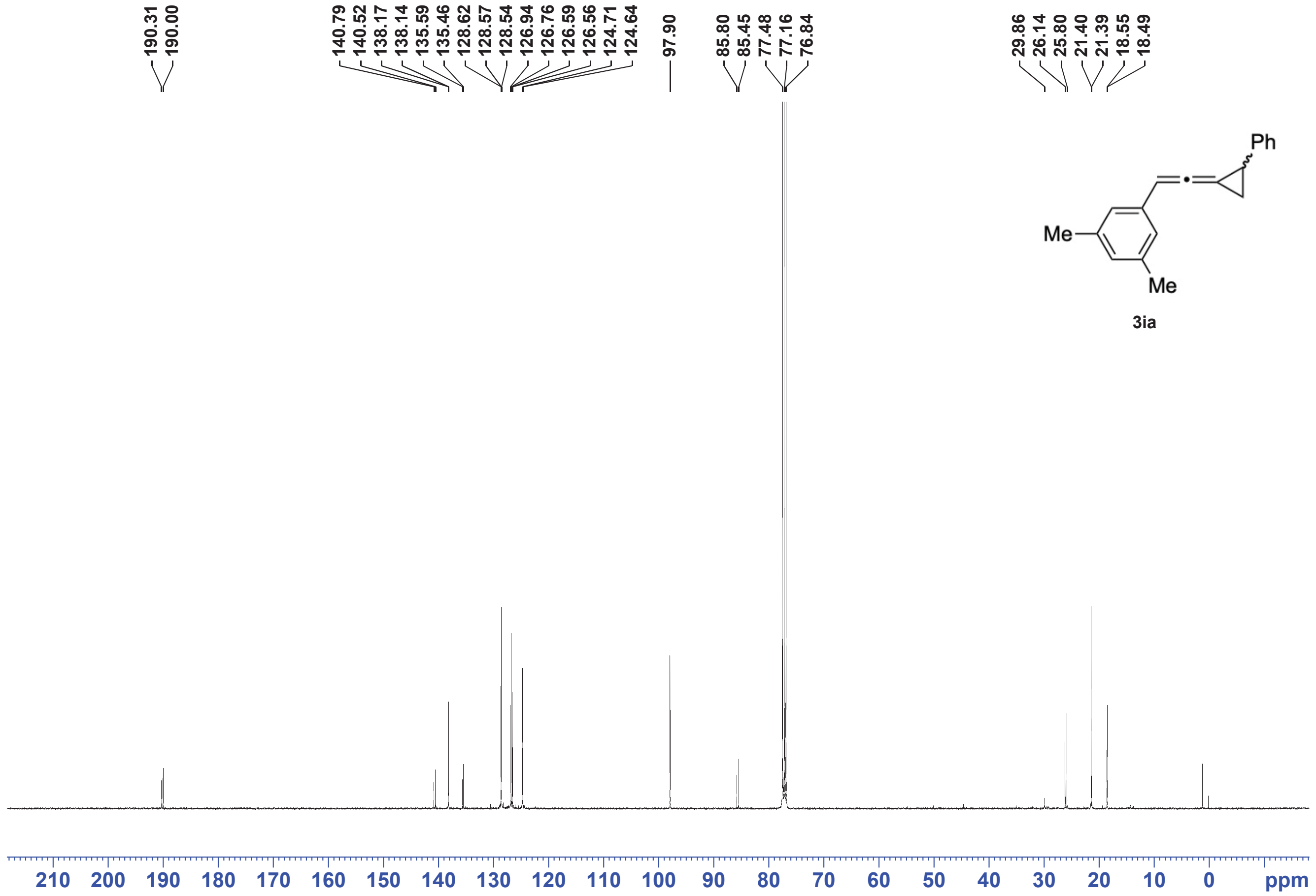
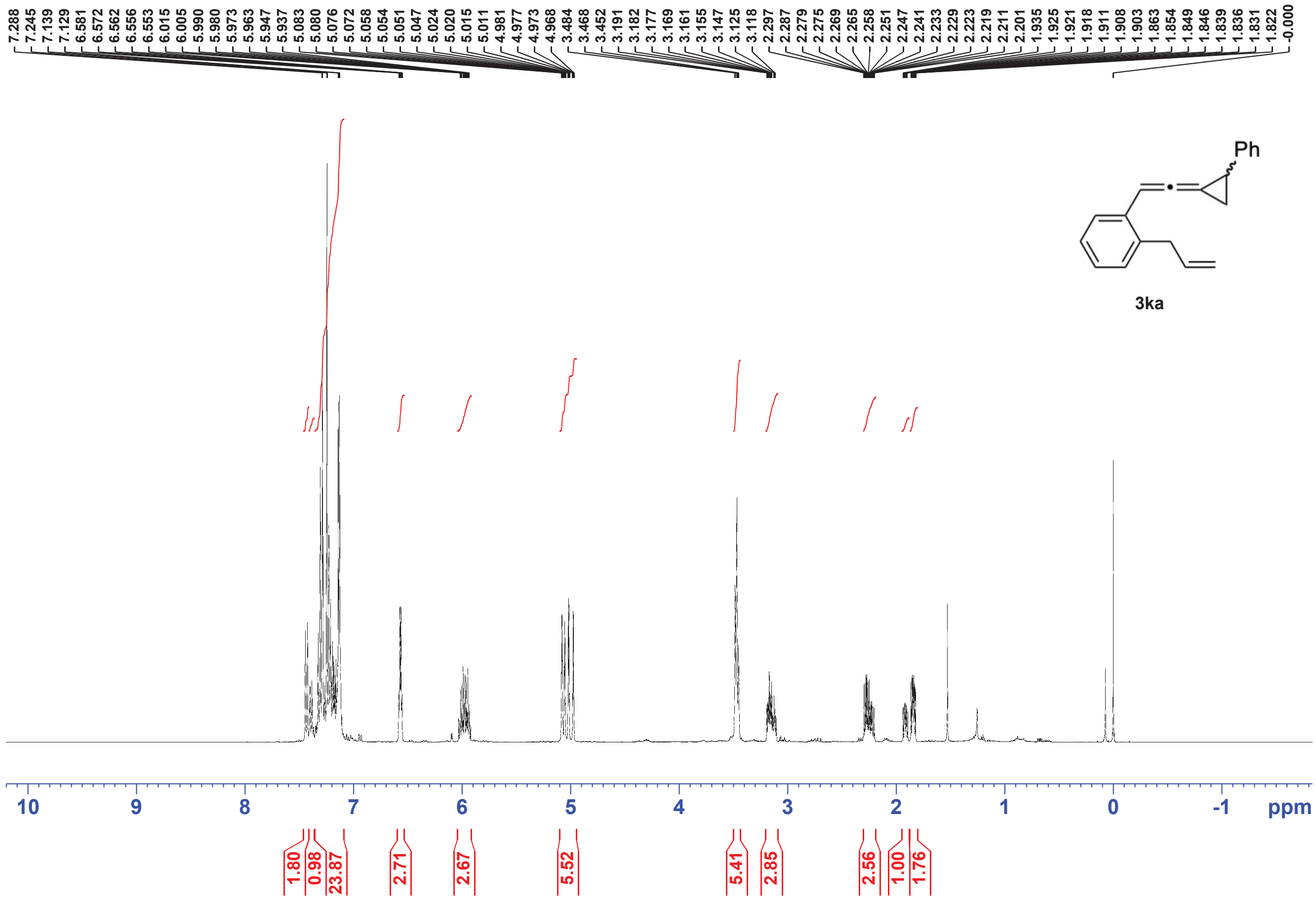
7.314
7.310
7.306
7.304
7.301
7.299
7.286
7.281
7.249
7.246
7.242
7.236
7.225
7.223
7.214
7.210
7.205
7.199
7.187
6.925
6.908
6.820
6.808
6.807
6.325
6.316
6.306
6.297
3.221
3.213
3.207
3.199
3.191
3.186
3.177
3.119
2.327
2.324
2.314
2.306
2.303
2.291
2.290
2.275
2.264
2.262
2.235
2.227
2.217
1.935
1.930
1.920
1.852
1.843
1.838
1.834
1.828
1.825
1.820
1.810
-0.000
Ph
Me
Me
3ia
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
4.02
4.23
2.00
0.98
1.02
0.45
1.45
1.00
0.47
9.92
0.55
0.49
1.03


190.31
190.00
140.79
140.52
138.17
138.14
135.59
135.46
128.62
128.57
128.54
126.94
126.76
126.59
126.56
124.71
124.64
97.90
85.80
85.45
77.48
77.16
76.84
29.86
26.14
25.80
21.40
21.39
18.55
18.49
Ph
Me
Me
3ia
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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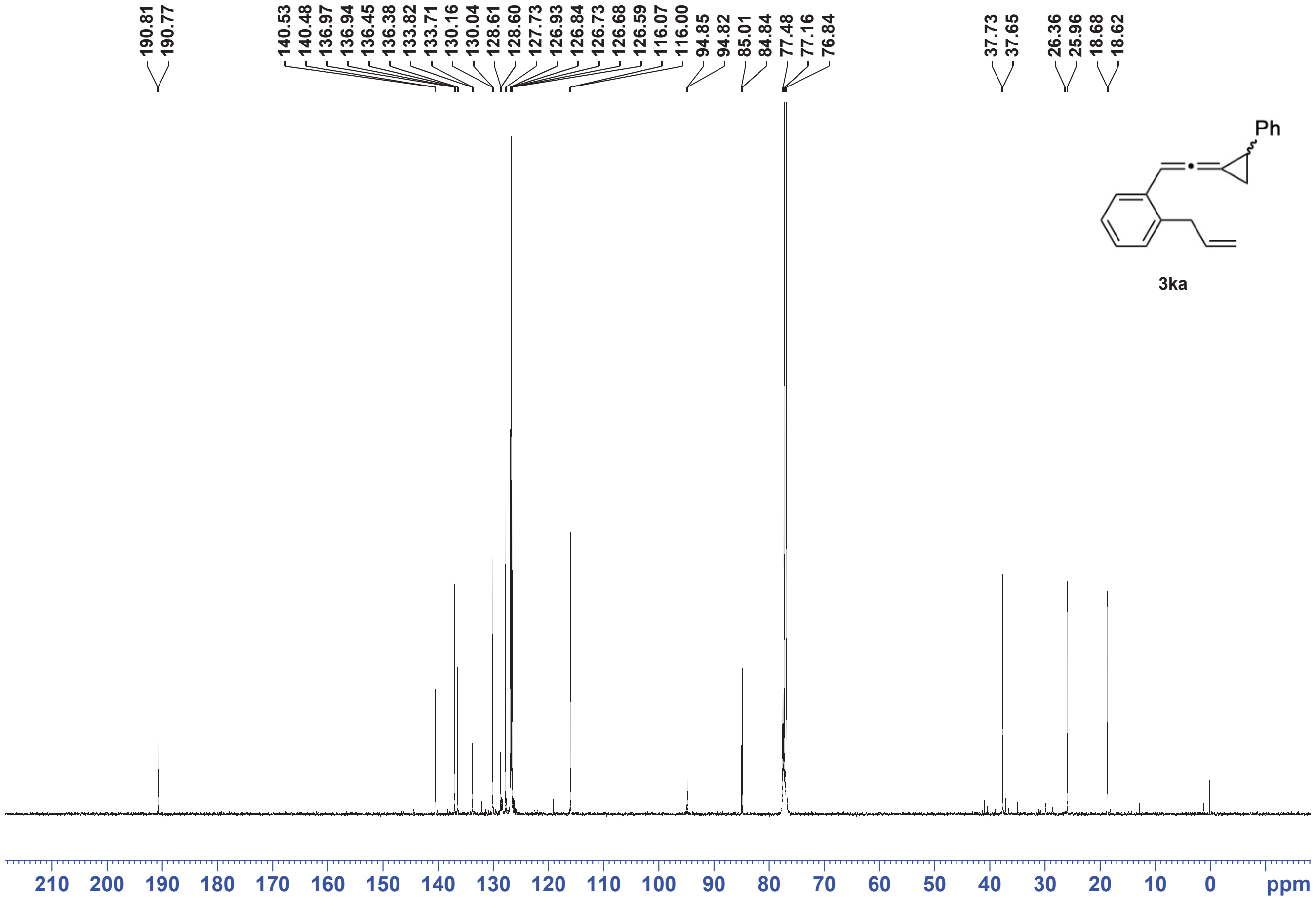
7.245
7.139
7.129
6.581
6.572
6.562
6.556
6.553
6.015
6.005
5.990
5.980
5.973
5.963
5.947
5.937
5.083
5.080
5.076
5.072
5.058
5.054
5.051
5.047
5.024
5.020
5.015
5.011
4.981
4.977
4.973
4.968
3.484
3.468
3.452
3.191
3.182
3.177
3.169
3.161
3.155
3.147
3.125
3.118
2.297
2.287
2.279
2.275
2.269
2.265
2.258
2.251
2.247
2.241
2.233
2.229
2.223
2.219
2.211
2.201
1.935
1.925
1.921
1.918
1.911
1.908
1.903
1.863
1.854
1.849
1.846
1.839
1.836
1.831
1.822
-0.000
Ph
3ka
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.80
0.98
23.87
2.71
2.67
5.52
5.41
2.85
2.56
1.00
1.76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190.77
140.53
140.48
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136.94
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136.38
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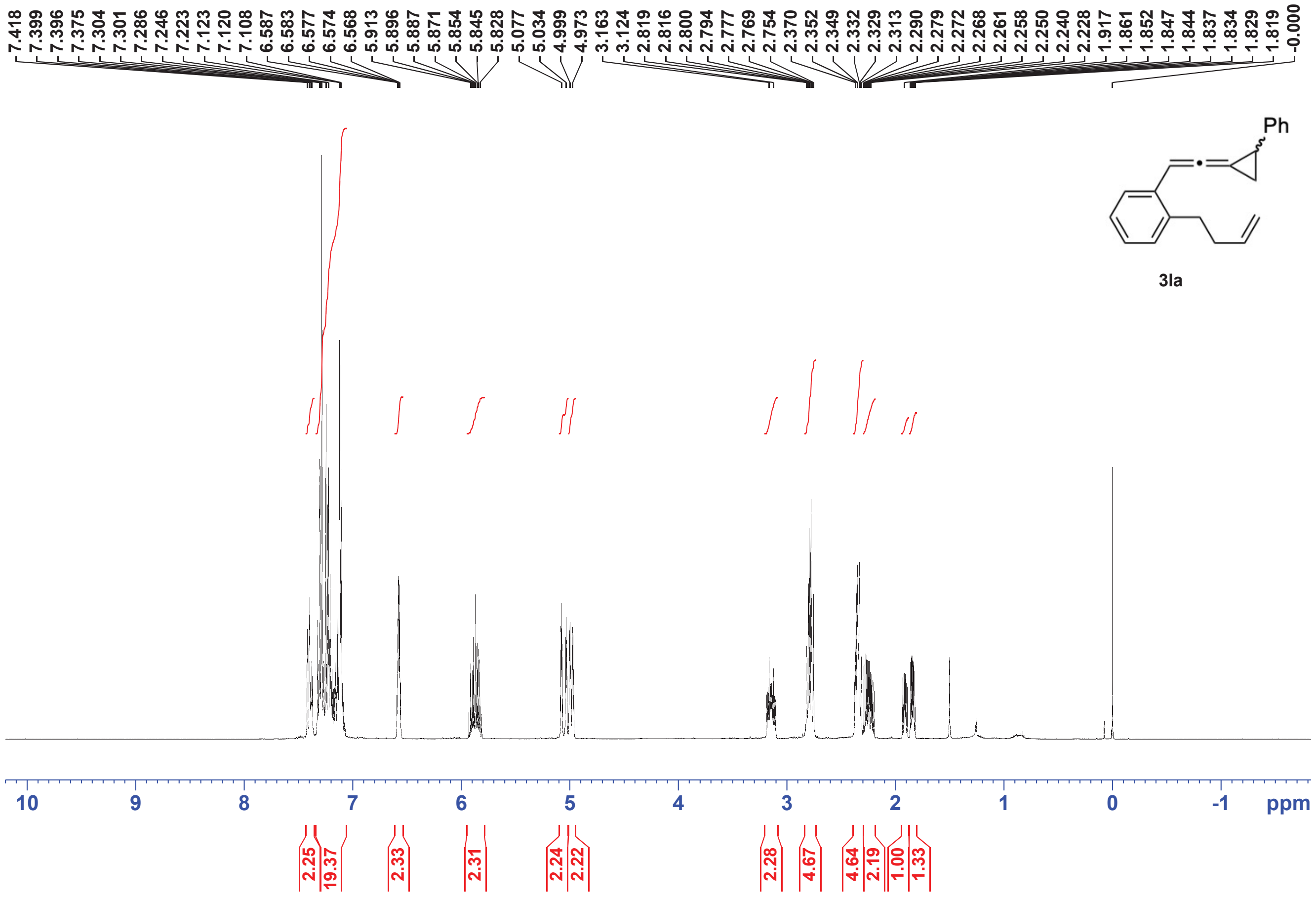
133.71
130.16
130.04
128.61
128.60
127.73
126.93
126.84
126.73
126.68
126.59
116.07
116.00
94.85
94.82
85.01
84.84
77.48
77.16
76.84
37.73
37.65
26.36
25.96
18.68
18.62
Ph
3ka
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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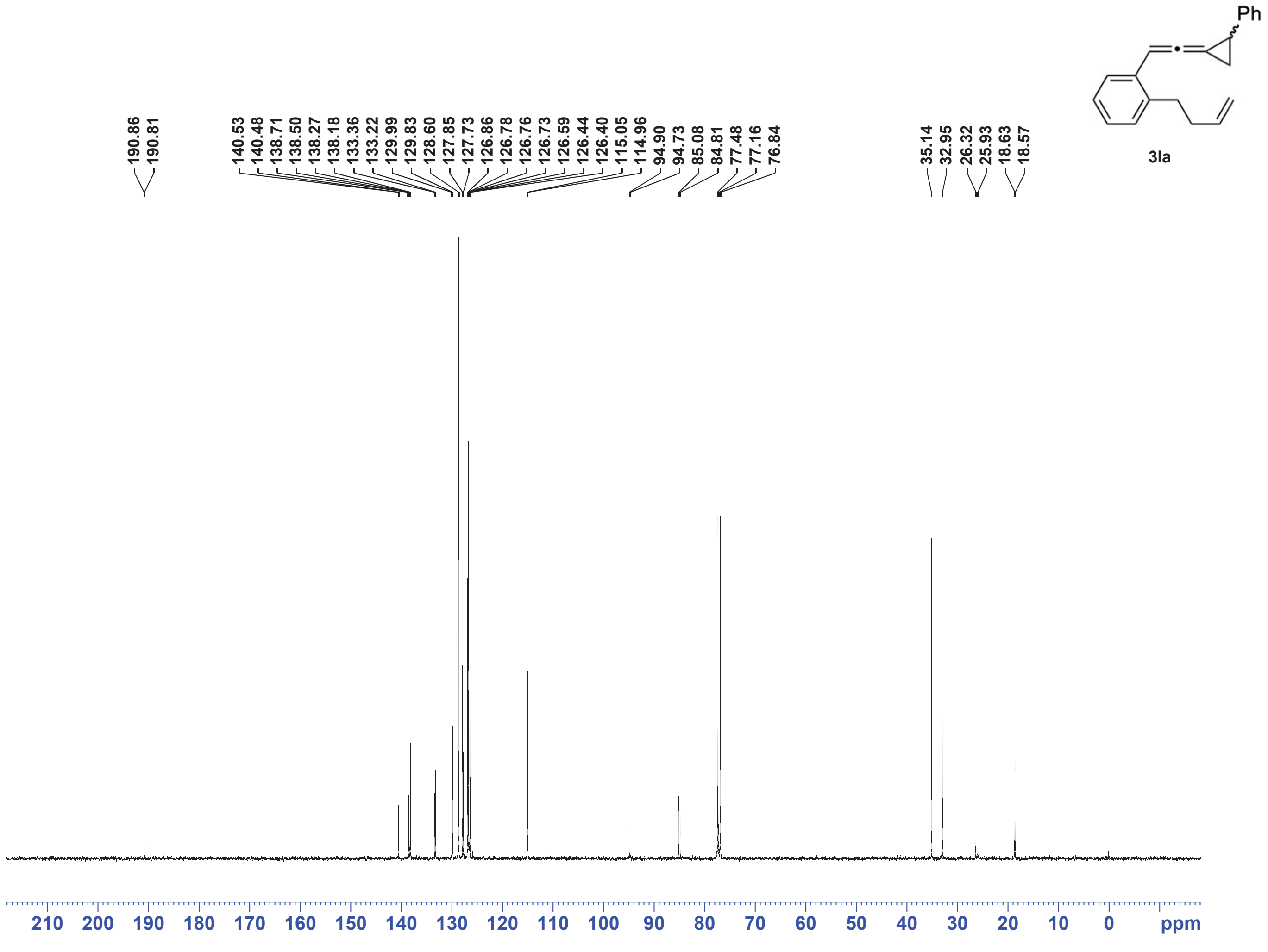
7.399
7.396
7.375
7.304
7.301
7.286
7.246
7.223
7.123
7.120
7.108
6.587
6.583
6.577
6.574
6.568
5.913
5.896
5.887
5.871
5.854
5.845
5.828
5.077
5.034
4.999
4.973
3.163
3.124
2.819
2.816
2.800
2.794
2.777
2.769
2.754
2.370
2.352
2.349
2.332
2.329
2.313
2.290
2.279
2.272
2.268
2.261
2.258
2.250
2.240
2.228
1.917
1.861
1.852
1.847
1.844
1.837
1.834
1.829
1.819
-0.000
Ph
3la
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.25
19.37
2.33
2.31
2.24
2.22
2.28
4.67
4.64
2.19
1.00
1.33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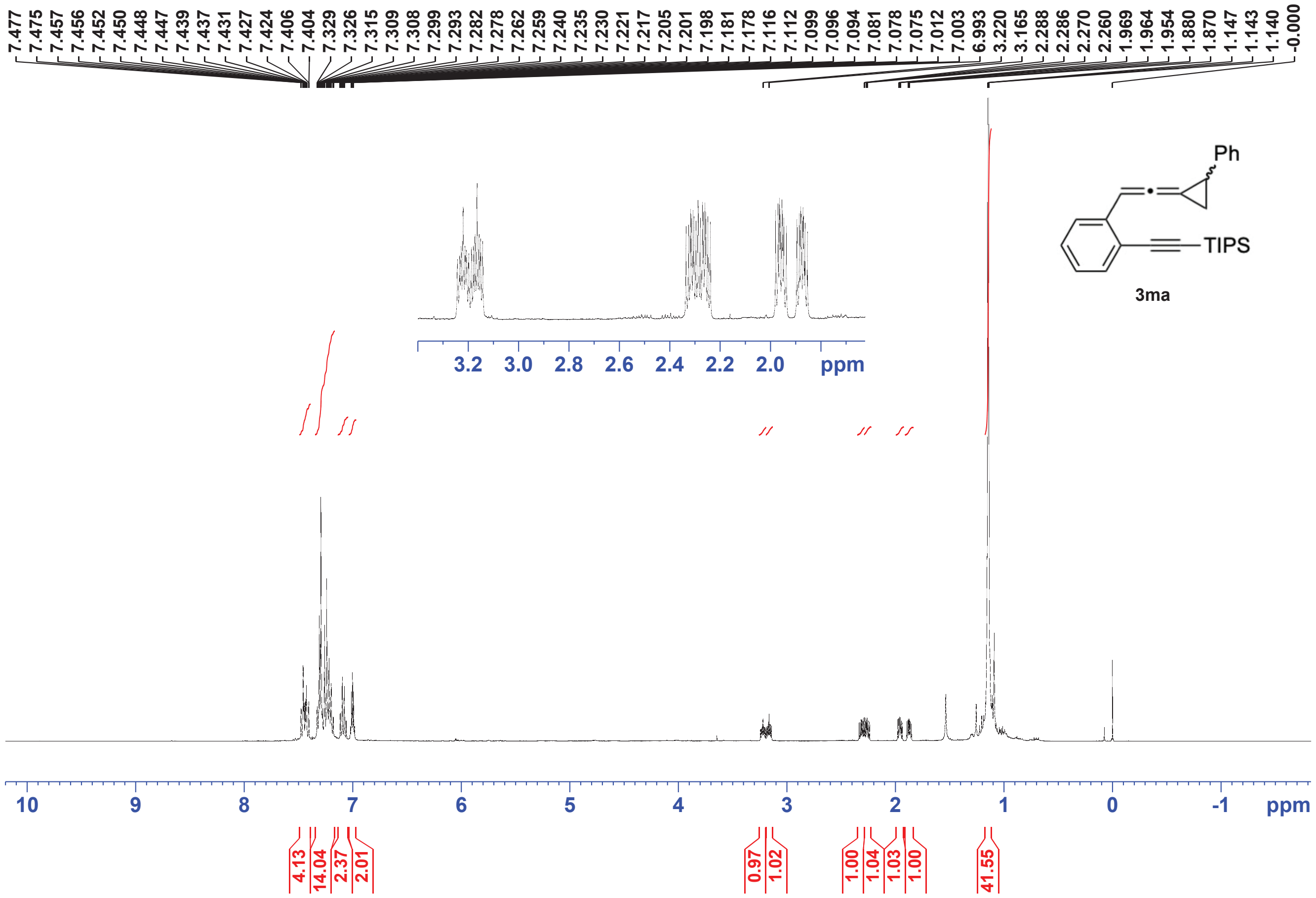
190.81
140.53
140.48
138.71
138.50
138.27
138.18
133.36
133.22
129.99
129.83
128.60
127.85
127.73
126.86
126.78
126.76
126.73
126.59
126.44
126.40
115.05
114.96
94.90
94.73
85.08
84.81
77.48
77.16
76.84
35.14
32.95
26.32
25.93
18.63
18.57
Ph
3la
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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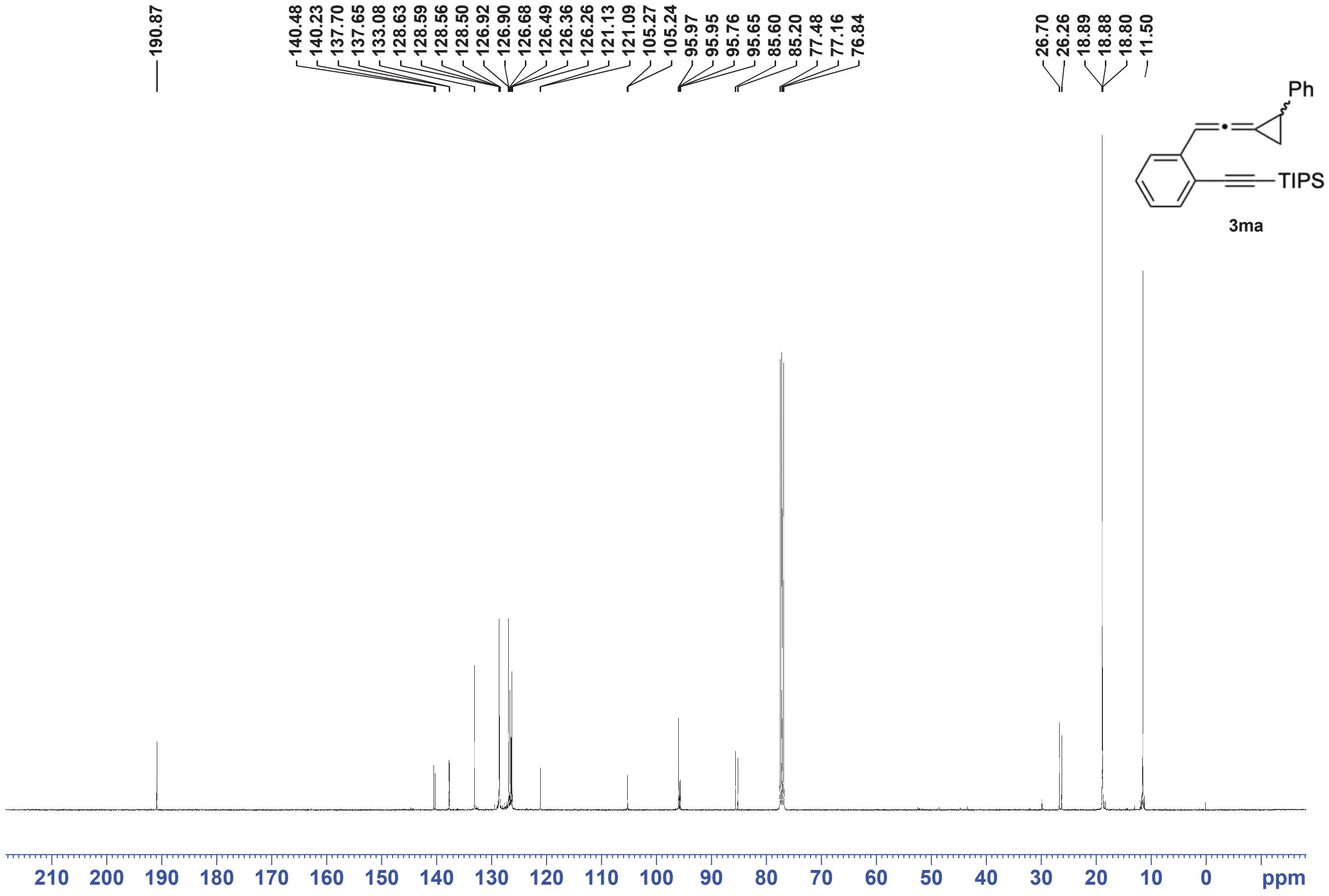
7.452
7.450
7.448
7.447
7.439
7.437
7.431
7.427
7.424
7.406
7.404
7.329
7.326
7.315
7.309
7.308
7.299
7.293
7.282
7.278
7.262
7.259
7.240
7.235
7.230
7.221
7.217
7.205
7.201
7.198
7.181
7.178
7.116
7.112
7.099
7.096
7.094
7.081
7.078
7.075
7.012
7.003
6.993
3.220
3.165
2.288
2.286
2.270
2.260
1.969
1.964
1.954
1.880
1.870
1.147
1.143
1.140
-0.000
Ph
TIPS
3ma
3.2
3.0
2.8
2.6
2.4
2.2
2.0
ppm
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
4.13
14.04
2.37
2.01
0.97
1.02
1.00
1.04
1.03
1.00
41.55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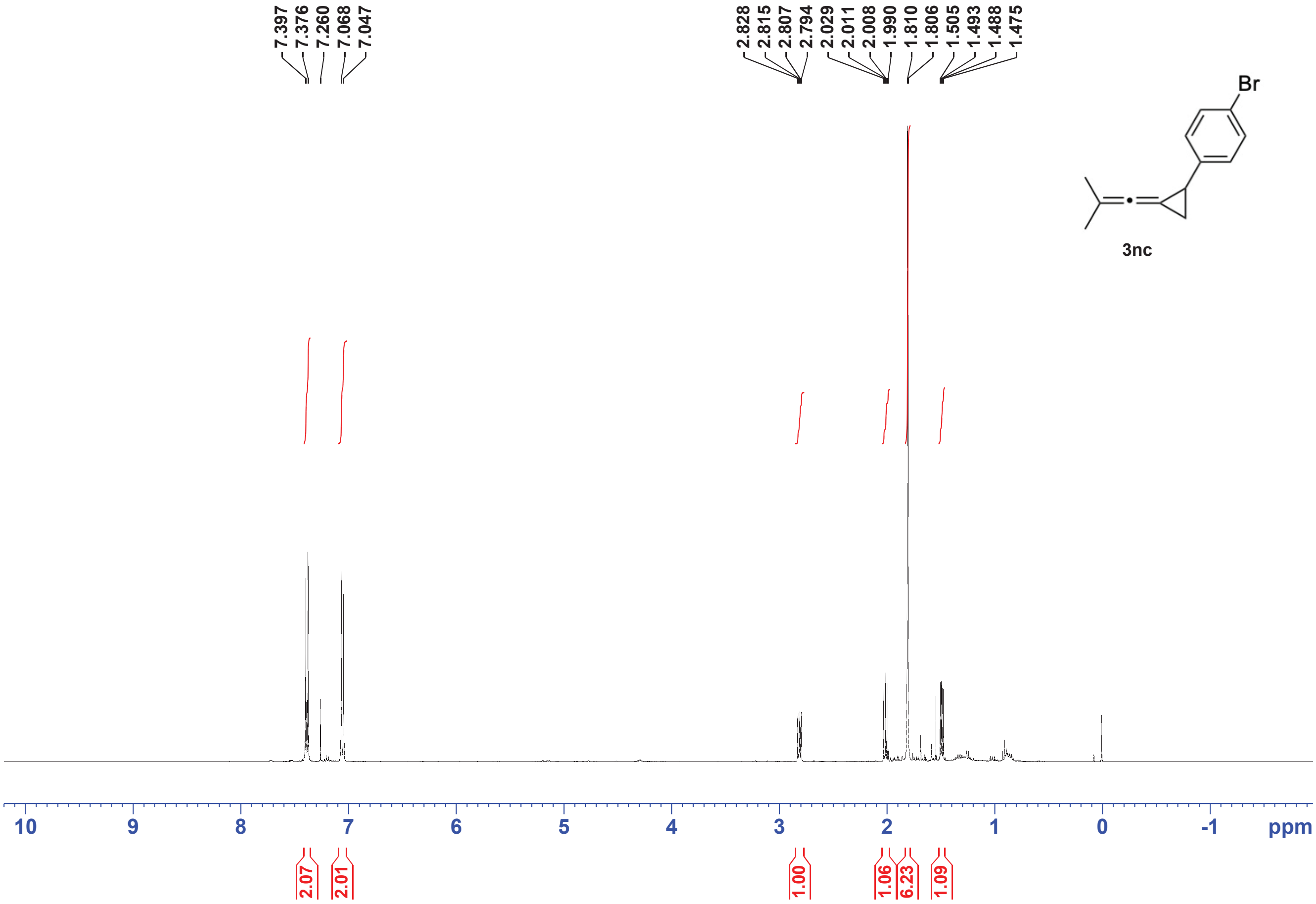
137.70
137.65
133.08
128.63
128.59
128.56
128.50
126.92
126.90
126.68
126.49
126.36
126.26
121.13
121.09
105.27
105.24
95.97
95.95
95.76
95.65
85.60
85.20
77.48
77.16
76.84
26.70
26.26
18.89
18.88
18.80
11.50
Ph
TIPS
3ma
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.260
7.068
7.047
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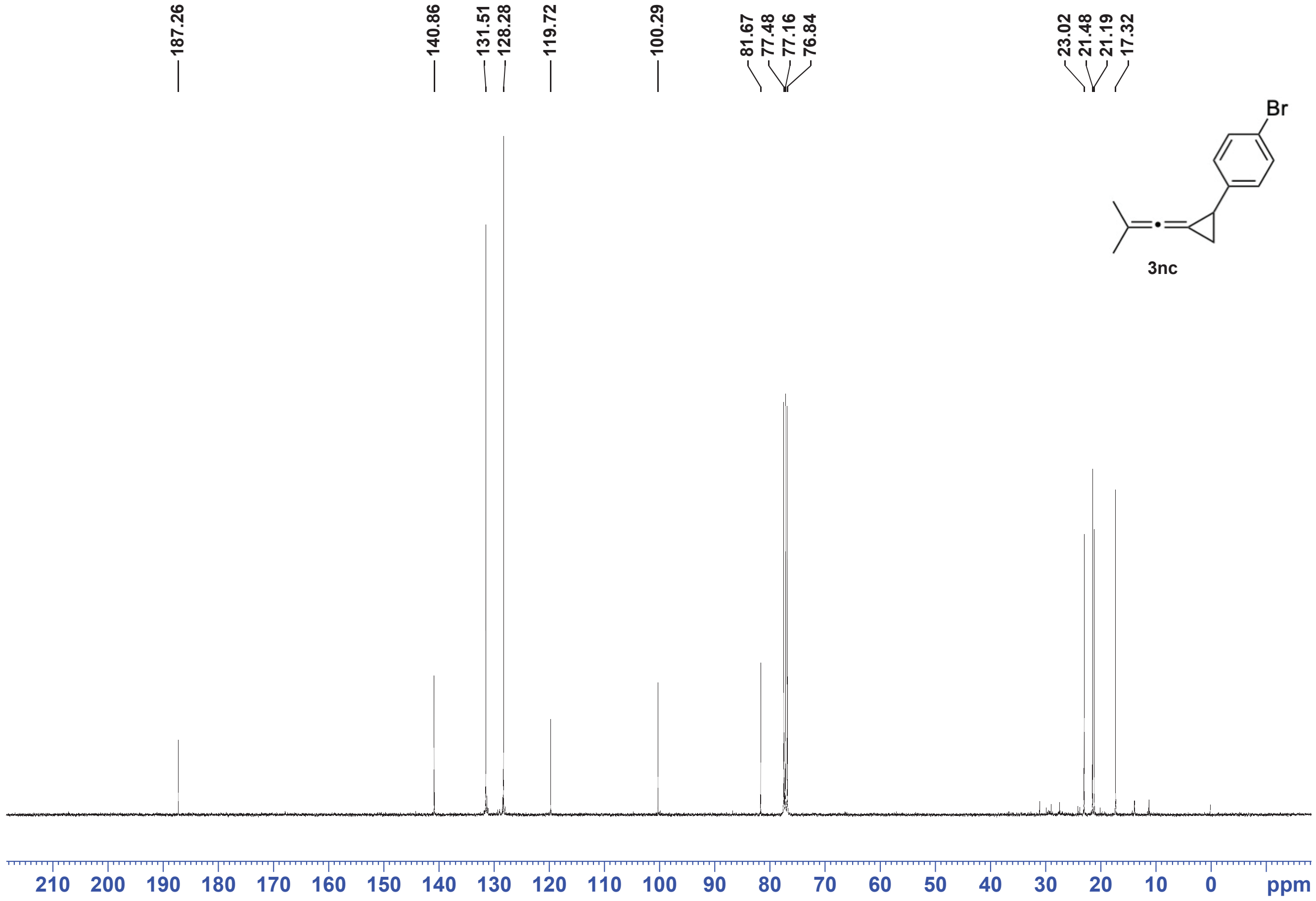
2.807
2.794
2.029
2.011
2.008
1.990
1.810
1.806
1.505
1.493
1.488
1.475
Br
3nc
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.07
2.01
1.00
1.06
6.23
1.09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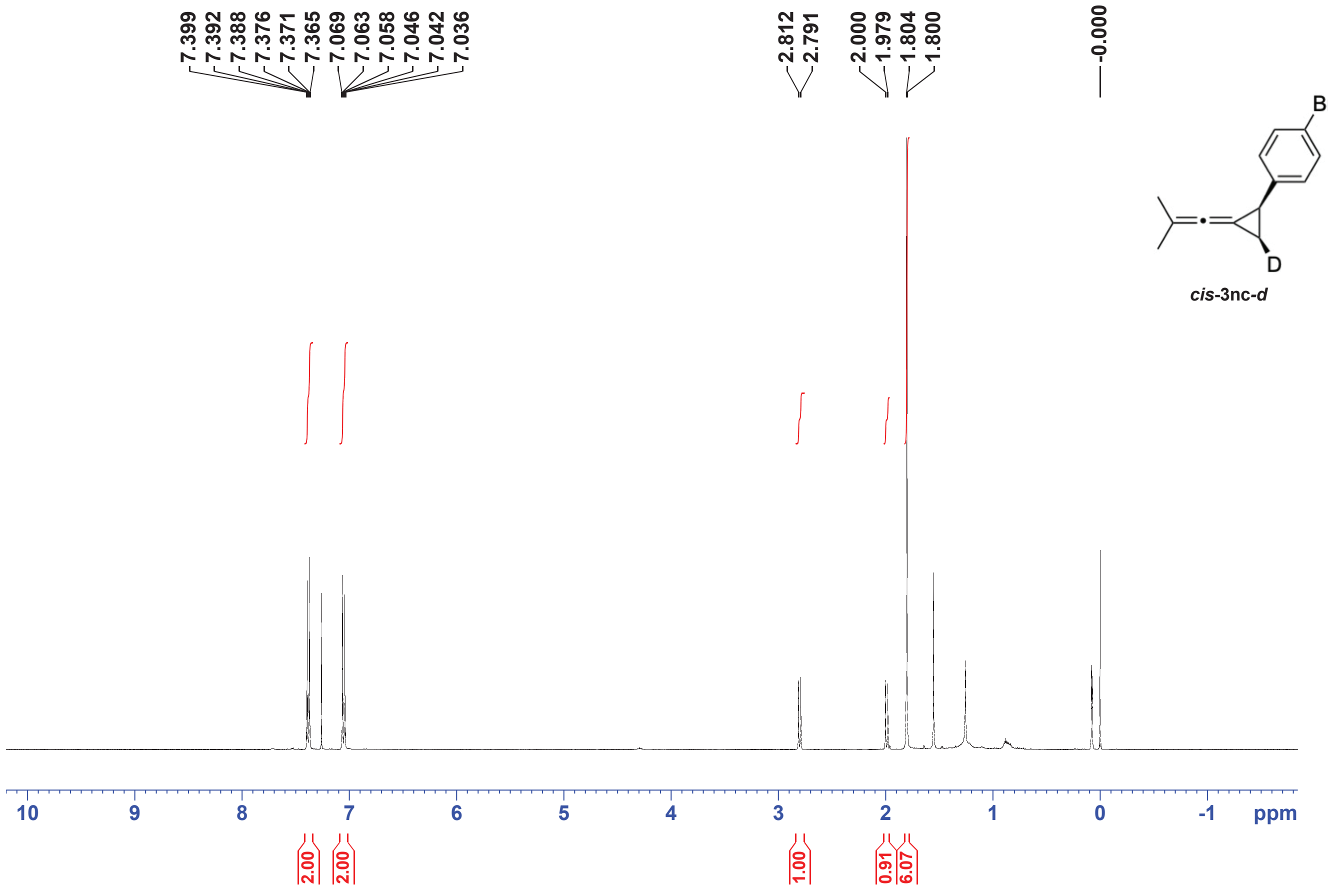
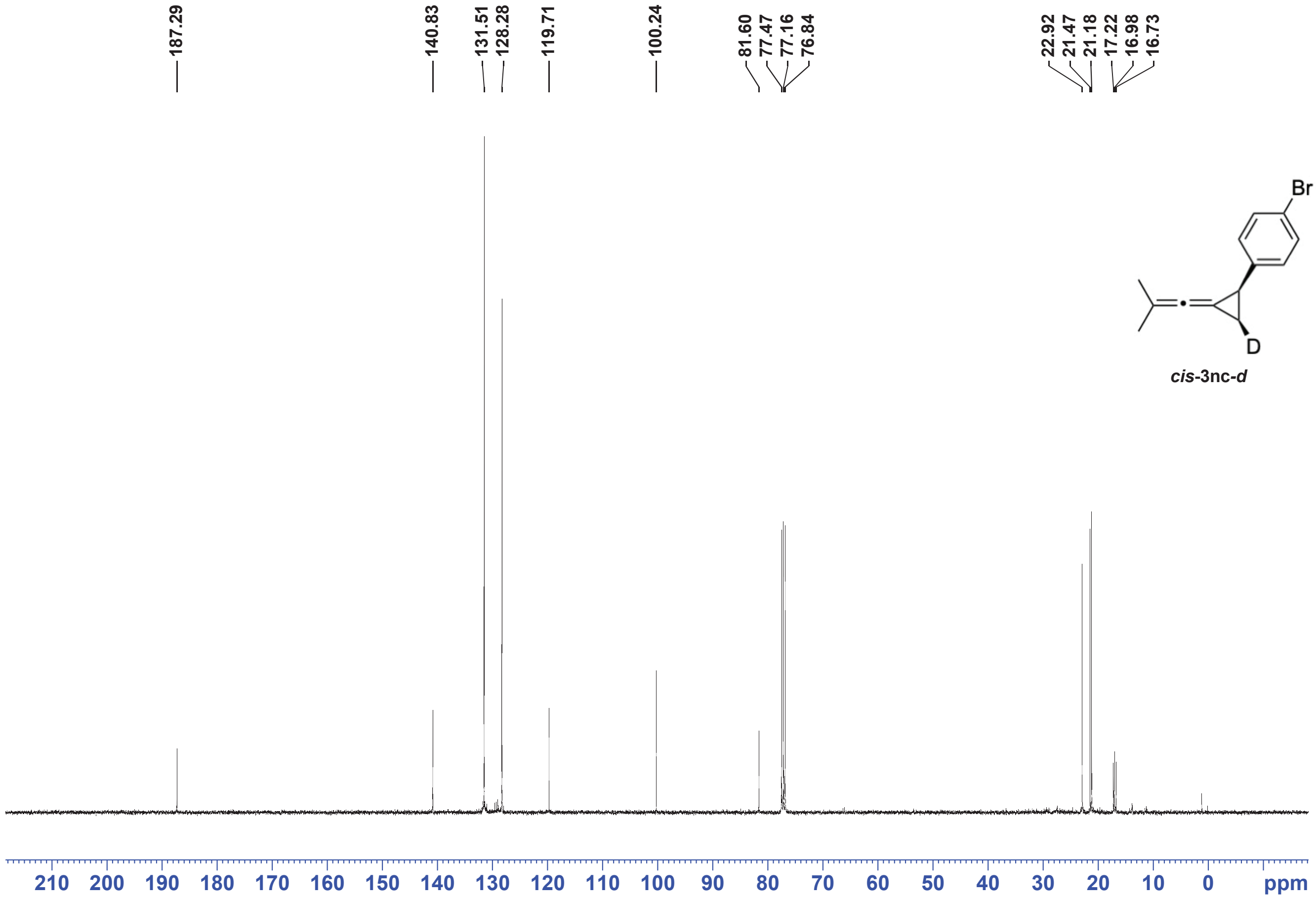
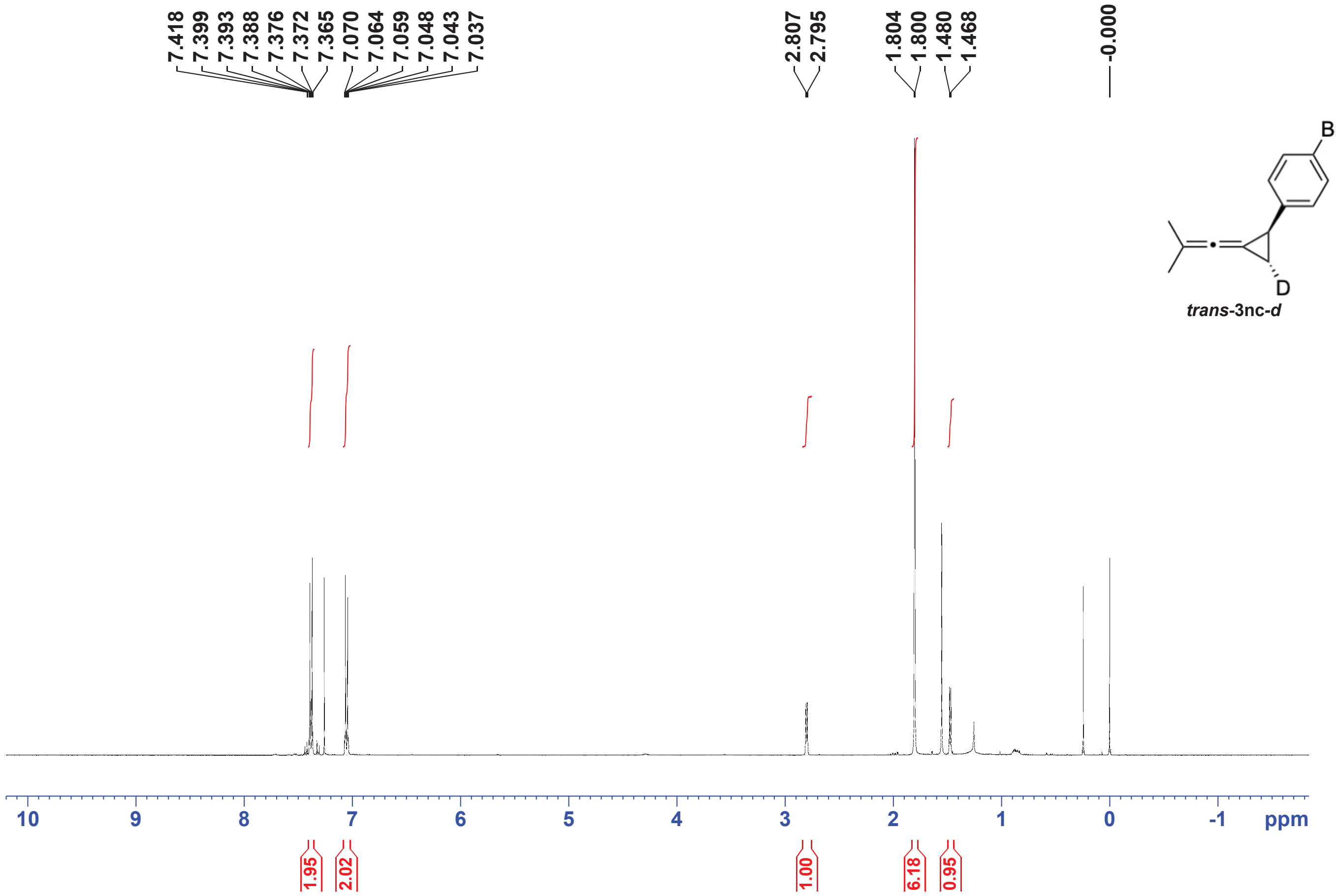
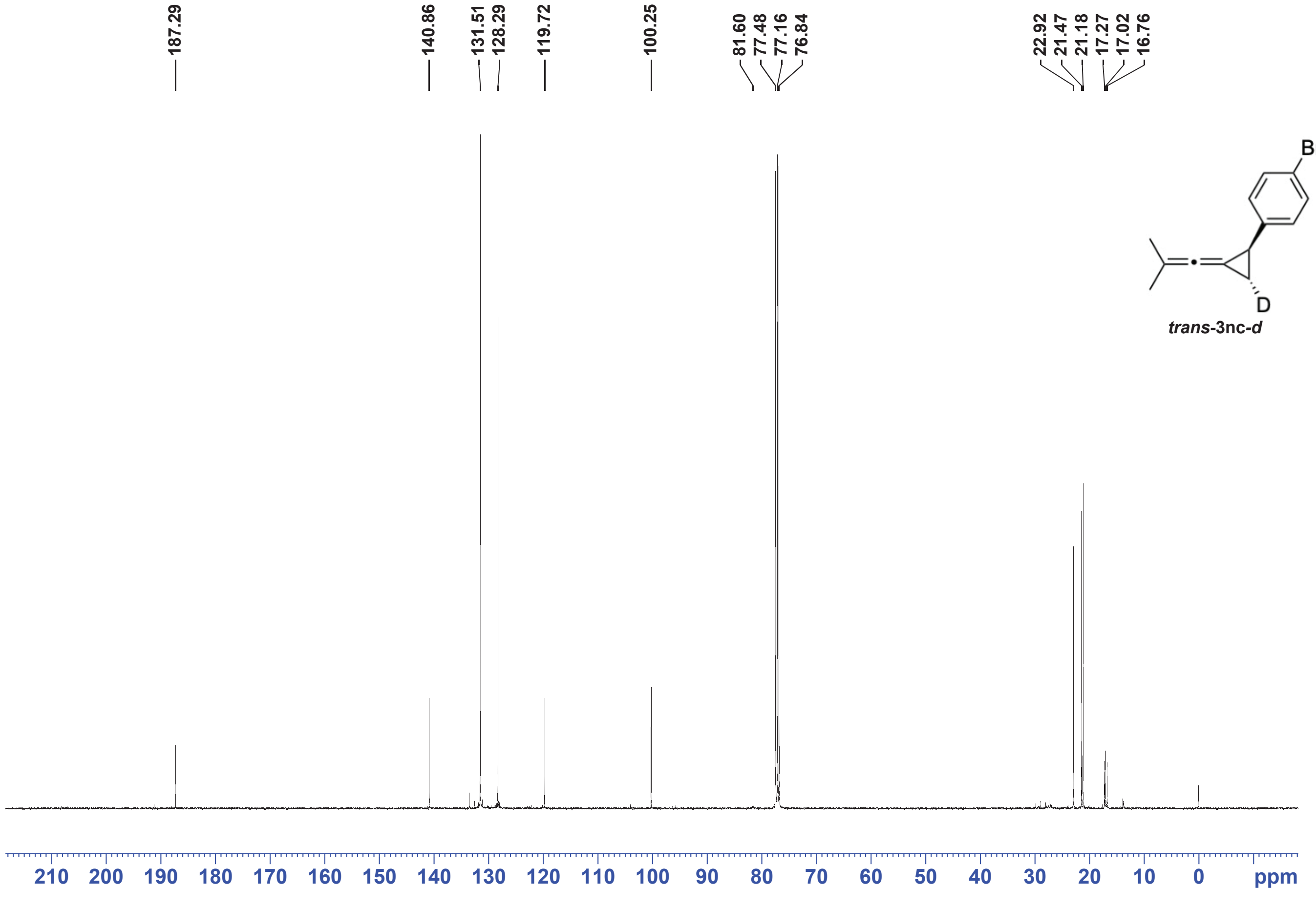
140.86
131.51
128.28
119.72
100.29
81.67
77.48
77.16
76.84
23.02
21.48
21.19
17.32
Br
3nc
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.399
7.392
7.388
7.376
7.371
7.365
7.069
7.063
7.058
7.046
7.042
7.036
2.812
2.791
2.000
1.979
1.804
1.800
-0.000
Br
D
cis-3nc-*d*
10
9
8
7
6
5
4
3
2
1
0
-1
ppm
2.00
2.00
1.00
0.91
6.07

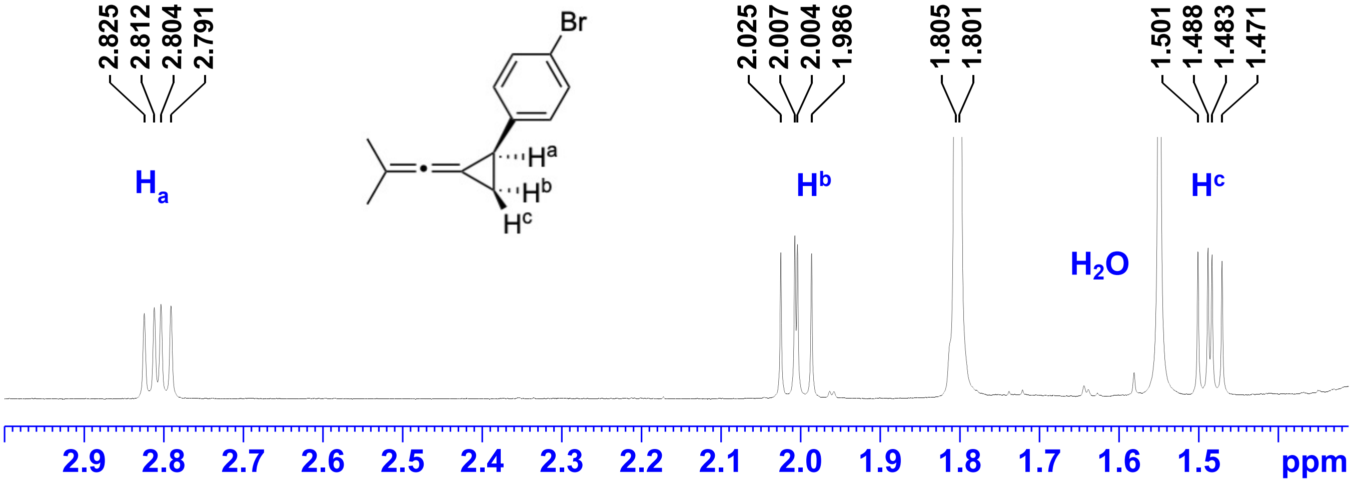

187.29
140.83
131.51
128.28
119.71
100.24
81.60
77.47
77.16
76.84
22.92
21.47
21.18
17.22
16.98
16.73
Br
D
cis-3nc-*d*
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

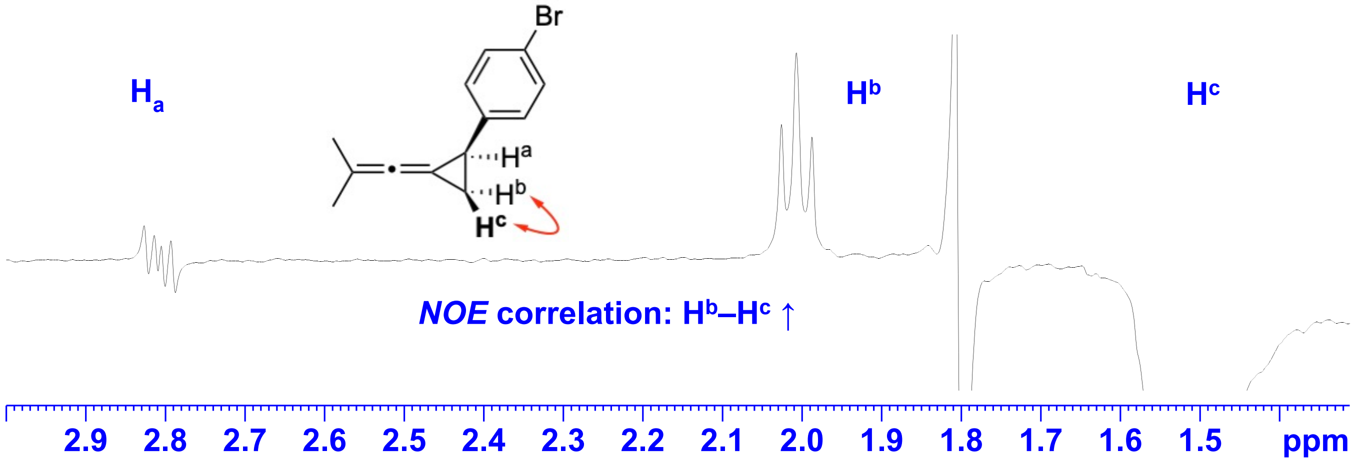


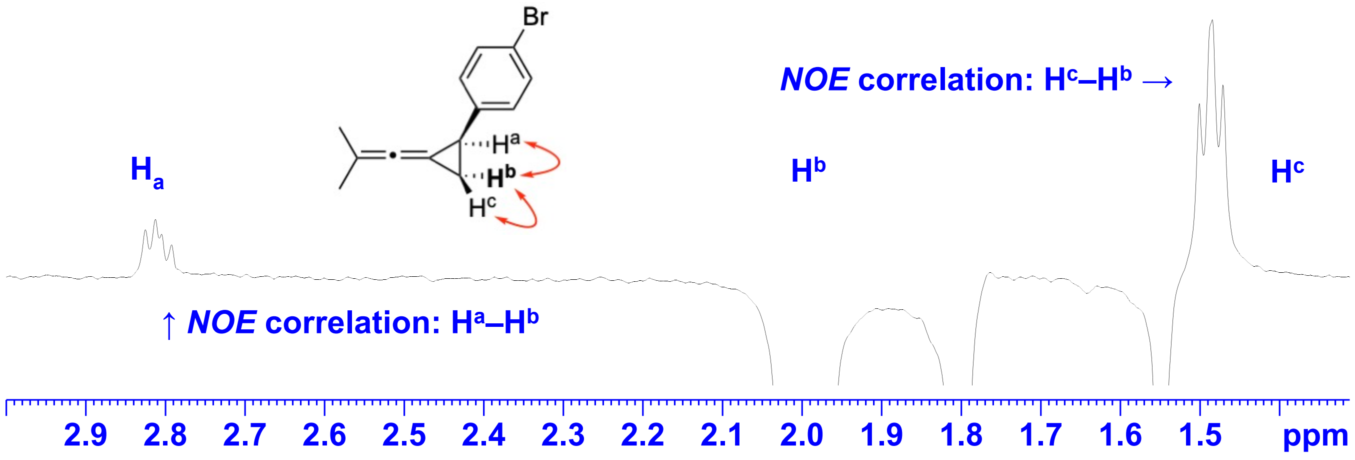
trans-3nc-*d*

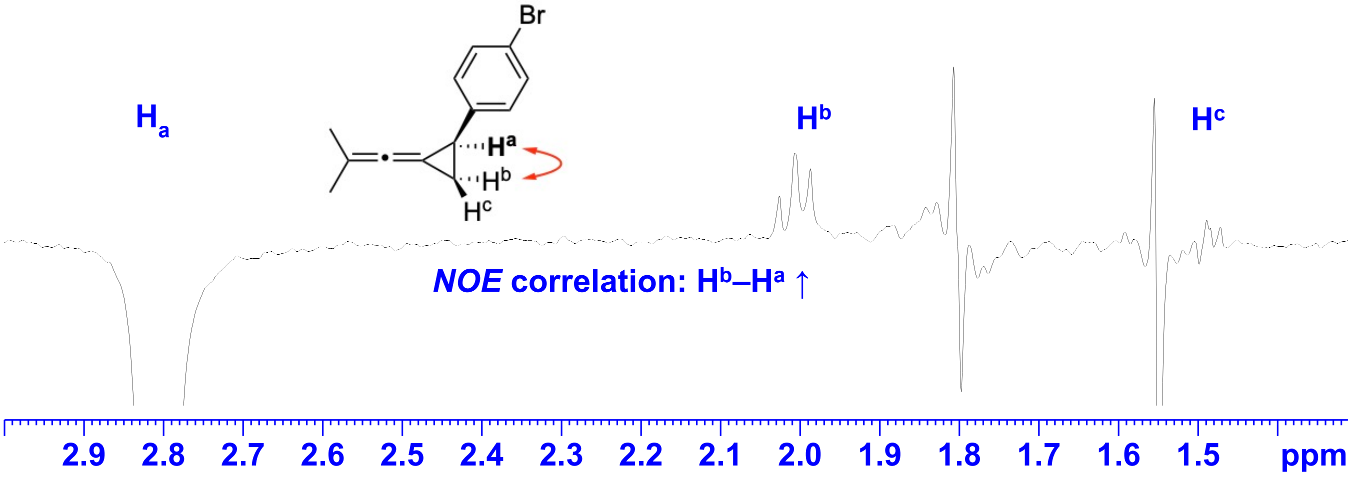


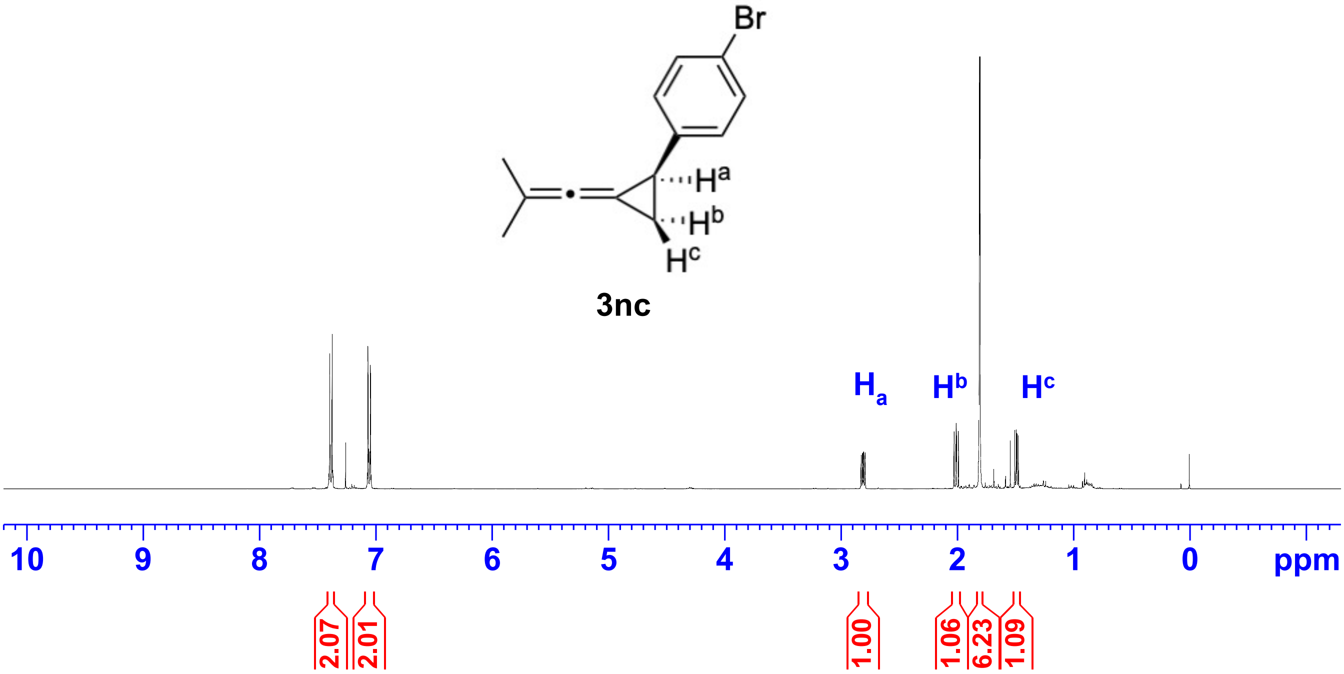
trans-3nc-*d*

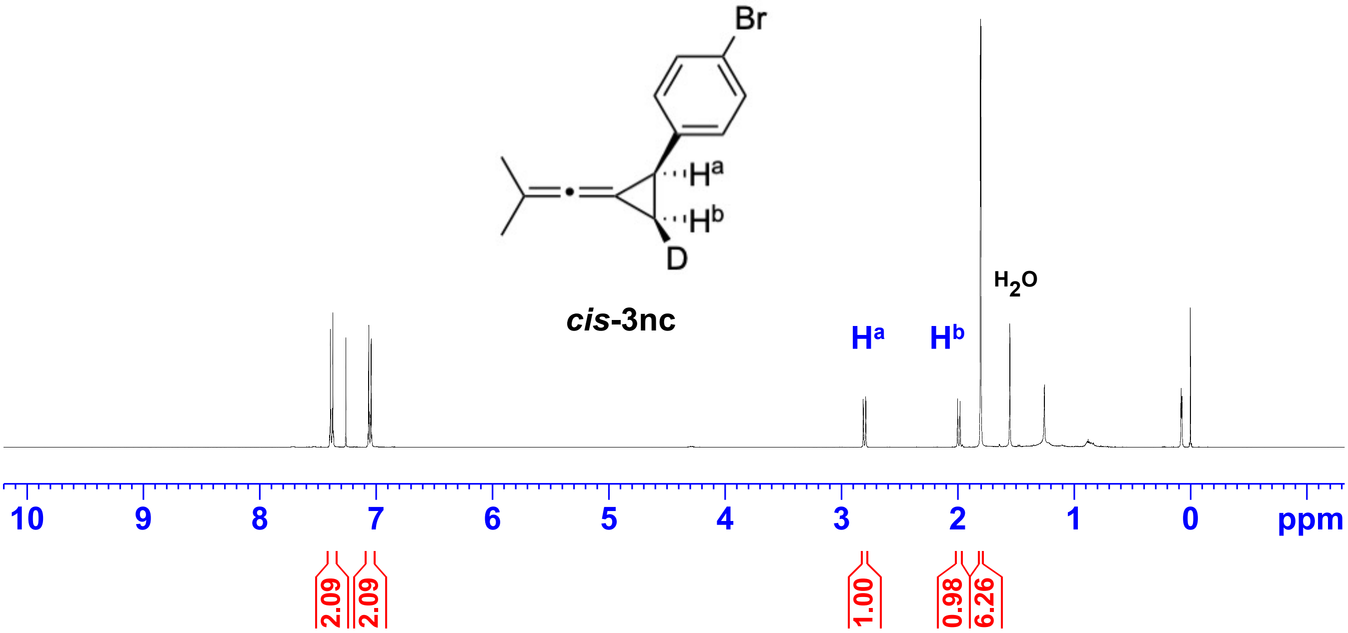

2.825
2.812
2.804
2.791
2.025
2.007
2.004
1.986
1.805
1.801
1.501
1.488
1.483
1.471
Br
Ha
Hb
Hc
H2O
2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 ppm

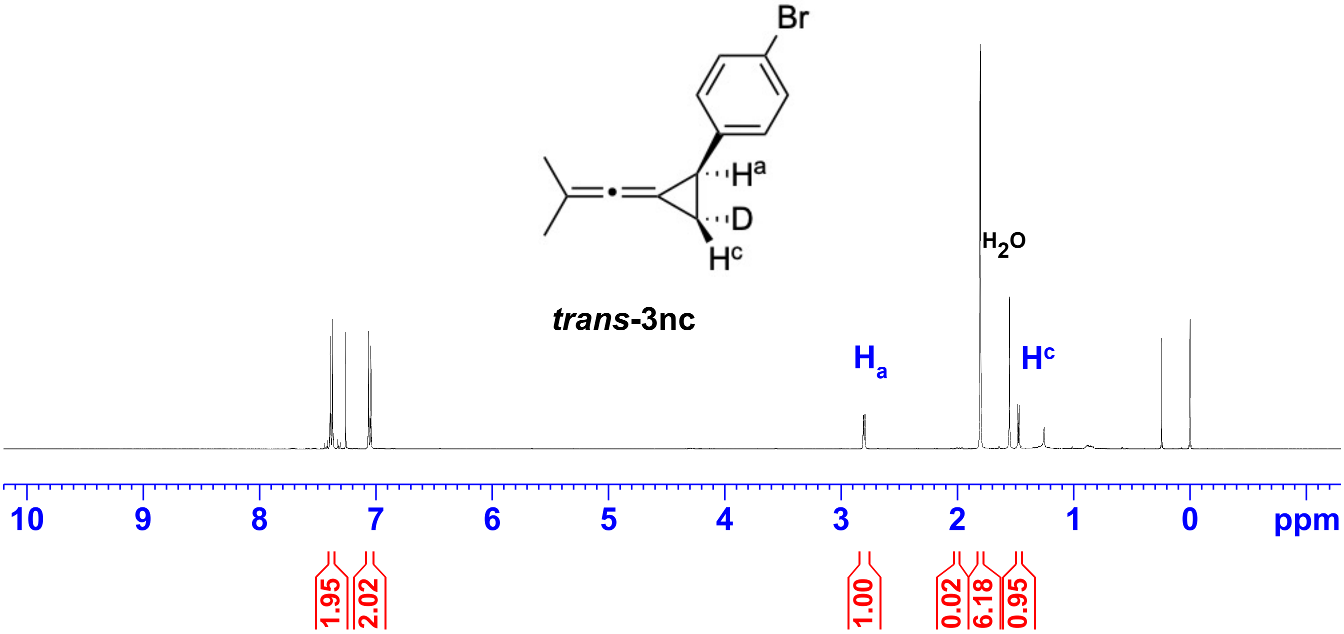

Br
Ha
Hb
Hc
NOE correlation: Hb–Hc ↑
2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 ppm

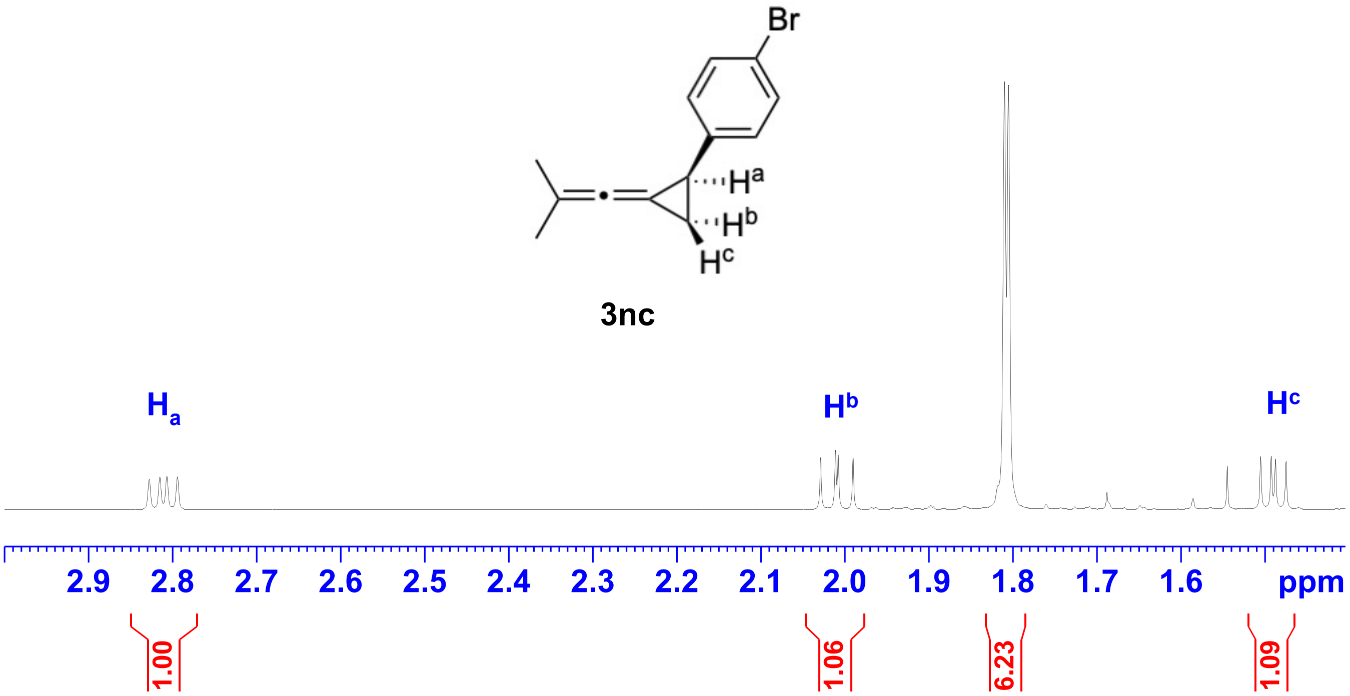

Br
Ha
Hb
Hc
NOE correlation: Hc–Hb →
↑ NOE correlation: Ha–Hb
2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 ppm

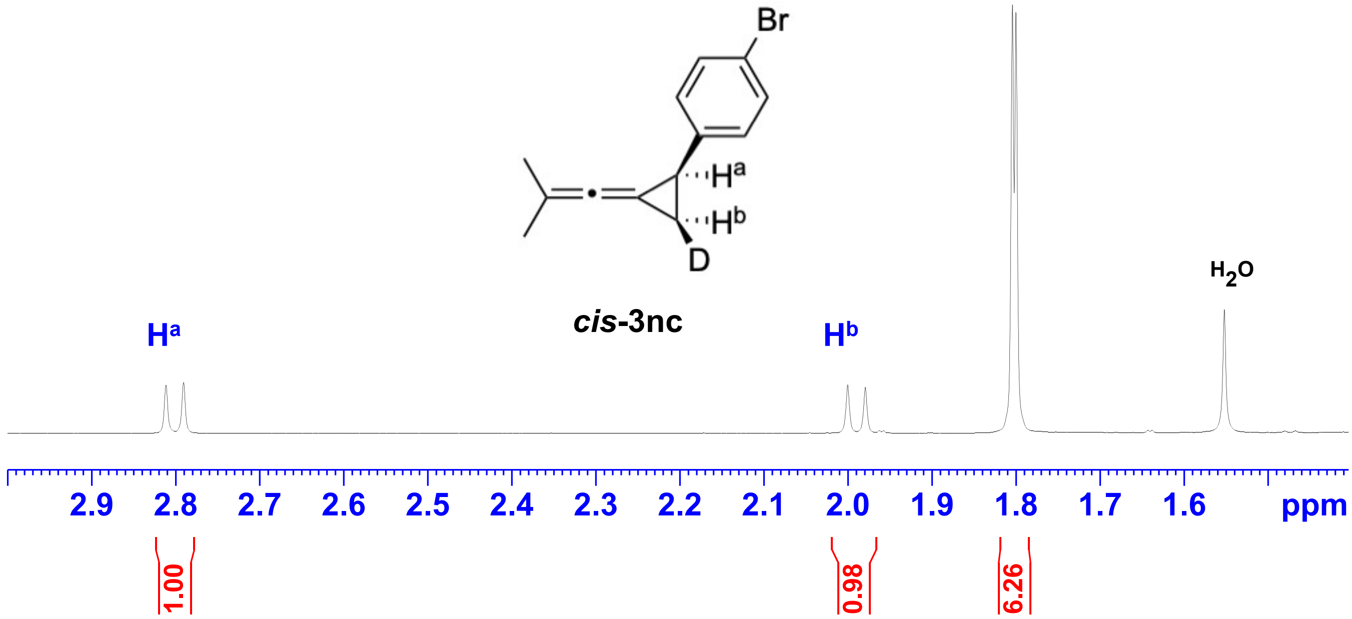

Br
Ha
Hb
Hc
NOE correlation: Hb–Ha ↑
2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 ppm

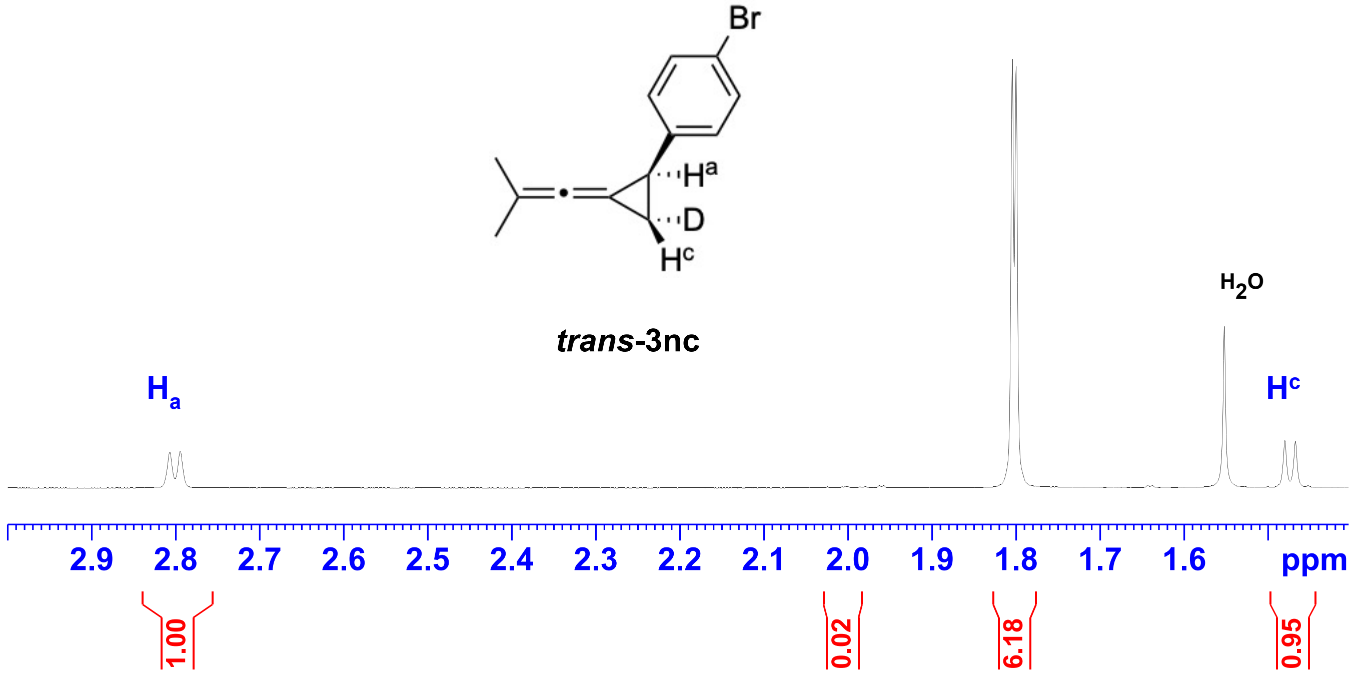

3nc


***cis*-3nc**


***trans*-3nc**


Br
Ha
Hb
Hc
3nc
Ha
Hb
Hc
2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 ppm
1.00
1.06
6.23
1.09


Br
Ha
Hb
D
cis-3nc
Ha
Hb
H2O
2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 ppm
1.00
0.98
6.26


Br
Ha
D
Hc
trans-3nc
Ha
H2O
Hc
2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8 1.7 1.6 ppm
1.00
0.02
6.18
0.95