Supporting Information

Cyclopropane–Alkene Metathesis by Gold(I)-catalyzed Decarbenation of Persistent Cyclopropanes

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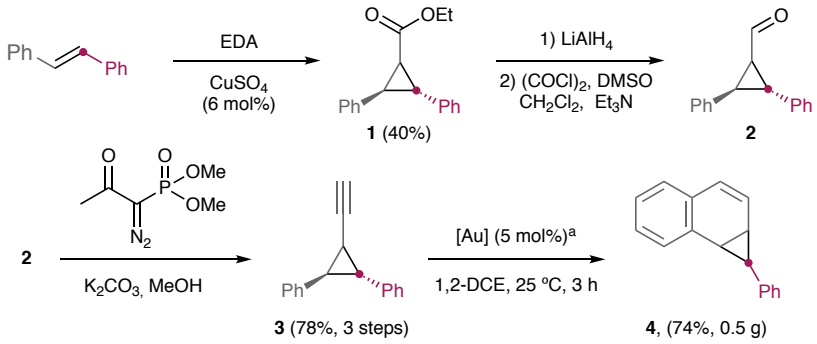
1. General Considerations

All gold-catalyzed reactions were performed using HPLC-grade solvents, without a protective inert atmosphere. Unless otherwise stated, all the other reactions reported herein were carried out under argon atmosphere in solvents dried by passing through an activated alumina column on a PureSolv^{TM} Solvent Purification System (SPS, Innovative Technologies, Inc., MA). Yields refer to chromatographically and spectroscopically pure (^{1}H NMR) homogeneous material, unless otherwise stated. Thin layer chromatography was carried out using TLC aluminum sheets coated with 0.2 mm of silica gel (Merck Gf234) using short-wave UV light as visualizing agent and phosphomolybdic acid, $KMnO_4$ or acidic vanillin followed by heat as developing agents. Chromatographic purifications were carried out using flash grade silica gel (SDS Chromatogel 60 ACC, 40-60 μm) as the stationary phase manually, or using a CombiFlash®R_f instrument with normal phase disposable columns of different sizes (Teledyne Isco). Preparative TLC was performed on 20 cm x 20 cm silica gel plates (2.0 mm thick, catalogue number 02015, Analtech or 1.0 mm thick, catalogue number P02013 Analtech). NMR spectra were recorded at 23 ºC on a Bruker Avance 400 Ultrashield or Bruker Avance 500 Ultrashield apparatus. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane, using the residual undeuterated solvent ($CHCl_3$ at 7.26 ppm ^{1}H NMR, 77.2 ppm ^{13}C NMR) or tetramethylsilane as reference. Coupling constants are reported in hertz (*Hz*). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, m = multiplet, br = broad. Mass spectra were recorded on a Waters LCT Premier Spectrometer (ESI and APCI) or on a Autoflex Bruker Daltonics (MALDI and LDI), or a GC instrument (Agilent Network GC System) coupled with a MS (Agilent Technologies, inert XL MSD). Melting points were determined using a MP70 Melting Point System (Mettler Toledo). Microwave reactions were carried out in a Biotage Initiator 2.5 MW reactor. Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification.

Handling of Gold(I) Catalysts

Gold complexes were synthesized according to our previously reported procedures,[1] or purchased from Sigma Aldrich, such as (acetonitrile)[(2-biphenyl)di-*tert*-butyl-phosphine]gold(I) hexafluoroantimonate. The bottles were not stored under inert atmosphere.

2. Preparation of Phenyl Cyclopropyl Dihydronaphthalene (4)



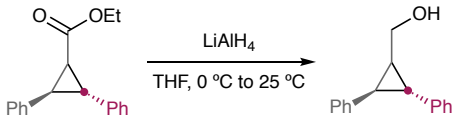
Ethyl (*exo*)-2,3-diphenylcyclopropane-1-carboxylate (1)

A dry two-necked 100 mL round-bottomed flask with a magnetic stirring bar was charged with (*E*)-1,2-diphenylethene (6.56 g, 36.4 mmol, 1.5 equiv) and $CuSO_4$ (232 mg, 1.46 mmol, 6 mol%), under Ar atmosphere. Both solids were dissolved in anhydrous toluene (30 mL, 0.8 M), and the resulting solution was heated to 75 ºC. After that, ethyl 2-diazoacetate (3 mL, 24.2 mmol, 1 equiv, 85% w/w commercial solution with CH_2Cl_2) was added by automatic syringe pump over 8 h (*ca.* 0.4 mL/h), while stirring at 75 ºC. After stirring for s total time of 18 hours, the reaction was allowed to cool down to room temperatrue and the solvent was removed in vacuum. CombiFlash chromatography in SiO_2, using a gradient from cyclohexane to cyclohexane/EtOAc 8:2 as eluent, giving ethyl (*exo*)-2,3-diphenylcyclopropane-1-carboxylate **1** (2.6 g, 24.2 mmol, 40 % yield) as a yellow oil. Characterization data matched the reported ones for this product.[2]

^{1}H NMR (500 MHz, $CDCl_3$) 7.30 – 7.20 (m, 6H), 7.19 – 7.13 (m, 4H), 3.88 (qd, J = 7.1, 1.8 Hz, 2H), 3.14 (dd, J = 7.0, 5.2 Hz, 1H), 2.85 (dd, J = 9.5, 7.1 Hz, 1H), 2.34 (dd, J = 9.6, 5.2 Hz, 1H), 0.96 (t, J = 7.2 Hz, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.1, 139.8, 136.3, 129.3, 128.7, 128.2, 127.0, 126.8, 126.8, 60.6, 34.6, 31.4, 29.4, 14.2 ppm.

(*exo*)-(2,3-Diphenylcyclopropyl)methanol (S1)

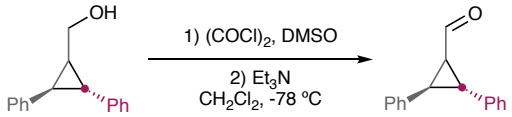


A two-necked 250 mL round-bottomed flask with a magnetic stirring bar was charged, under Ar, with $LiAlH_4$ (534 mg, 14.1 mmol, 1.5 equiv), and it was suspended in anhydrous THF (40 mL, 0.2 M). After cooling down the suspension to 0 ºC in an ice-water bath, a solution of ethyl (*exo*)-2,3-diphenylcyclopropane-1-carboxylate (**1**) (2.5 g, 9.4 mmol, 1 equiv) in 7 mL of anhydrous THF was added dropwise over 5 min, and then the cooling bath was removed. The resulting suspension was stirred for 16 h while coming to room temperature, when no starting material was observed by TLC. The reaction was cooled down again to 0 ºC in an ice-water bath, and was quenched by careful addition of water, and then aqueous (10%) HCl. The aqueous phase was extracted twice with Et_2O, and the combined organic fractions were washed with water once, with brine once, dried over anhydrous Na_2SO_4 and concentrated in vacuum giving (*exo*)-(2,3-diphenylcyclopropyl)methanol (**S1**) (*ca.* quantitative yield, 2.1 g) as a yellow oil, used on the next step without further purification. Characterization data matched the reported ones for this product.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (dtd, J = 11.0, 6.8, 1.8 Hz, 6H), 7.18 – 7.09 (m, 4H), 3.58 (dd, J = 11.7, 6.2 Hz, 1H), 3.41 (dd, J = 11.7, 8.2 Hz, 1H), 2.55 (dd, J = 9.2, 5.6 Hz, 1H), 2.34 (t, J = 5.4 Hz, 1H), 1.83 (dddd, J = 9.3, 8.2, 6.2, 5.2 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 137.7, 128.9, 128.6, 126.7, 126.4, 126.2, 62.3, 31.8, 31.4, 26.5 ppm.

(*exo*)-2,3-Diphenylcyclopropane-1-carbaldehyde (2)

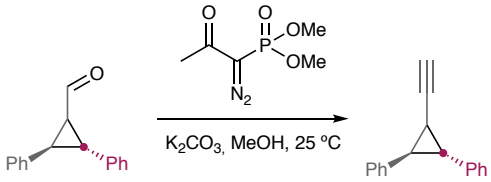


A dry 500 mL round-bottomed flask was charged under argon with a solution of dimethylsulfoxide (2.0 mL, 27.6 mL, 3.1 equiv) in dichloromethane (130 mL). After cooling this solution to -78 ºC, oxalyl chloride (1.6 mL, 18.72 mmol, 2.1 equiv) was added dropwise. After 30 min, a solution of ((*exo*)-2,3-diphenylcyclopropyl)methanol (**S1**) (2.0 g, 8.92 mmol, 1 equiv) in dichloromethane (20 mL) was added. The mixture was stirred for 1h at -78 ºC. After that, triethylamine (5 mL, 35.7 mmol, 4 equiv) was added to the mixture and it was maintained for 15 min at -78 ºC then it was allowed to warm to room temperature. The mixture was diluted with dichloromethane and water was added, and the mixture was extracted three times with dichloromethane. Combined organic fractions were washed with water and with brine, dried over Na_2SO_4 and concentrated under vacuum giving (*exo*)-2,3-diphenylcyclopropane-1-carbaldehyde (**2**) (*ca.* quantitative yield, 1.9 g) as an orange oil, used on the next step without further purification. Characterization data matched the reported ones for this product.[2]

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (d, *J* = 6.3 Hz, 1H), 7.39 – 7.24 (m, 6H), 7.24 – 7.12 (m, 4H), 3.29 (dd, *J* = 6.9, 4.8 Hz, 1H), 3.12 (dd, *J* = 9.4, 6.7 Hz, 1H), 2.41 (ddd, *J* = 9.2, 6.3, 4.8 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.2, 138.5, 135.5, 129.3, 128.9, 128.8, 127.6, 127.2, 126.8, 39.9, 35.1, 29.9 ppm.

((*exo*)-3-Ethynylcyclopropane-1,2-diyl)dibenzene (3)



A modified reported procedure was followed.[3] A 250 mL round-bottomed flask was charged under air with a suspension of crude (*exo*)-2,3-diphenylcyclopropane-1-carbaldehyde (**2**) (1.9 g, 8.55 mmol, 1 equiv) and potassium carbonate (3.5 g, 25.6 mmol, 3 equiv) in HPLC-grade MeOH (71 mL, 0.12 M). Dimethyl (1-diazo-2-oxopropyl)phosphonate (neat, 3.0 g, 15.6 mmol, 1.8 equiv) was added, and the resulting mixture was stirred for 1 h. After confirming complete conversion of (**2**), water was added, and the mixture was extracted three times with diethyl ether. Combined organic fractions were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. CombiFlash chromatography in SiO_2, using a gradient from cyclohexane to cyclohexane/EtOAc 97:3 as eluent gave (*exo*)-(3-ethynylcyclopropane-1,2-diyl)dibenzene (**3**) (1.4 g, 8.55 mmol, 78% overall yield over 3 steps) as a pale yellow solid.

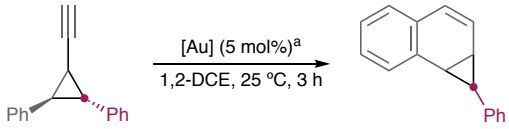
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.21 (m, 6H), 7.21 – 7.11 (m, 4H), 2.63 – 2.52 (m, 2H), 2.05 (ddd, *J* = 8.8, 5.5, 2.2 Hz, 1H), 1.87 (d, *J* = 2.2 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 137.1, 128.7, 128.5, 128.2, 126.8, 126.8, 126.4, 82.4, 69.7, 32.9, 32.7, 19.2 ppm.

HRMS (ESI Pos): calc. for $C_{17}H_{15}$ $[M+H]^+$: 219.1168; found: 219.1179.

MP 88–90 ºC.

(*exo*)-1-Phenyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (4)



Under air, a 100 mL round-bottomed flask equipped with a magnetic stirring bar was charged (*exo*)-(3-ethynylcyclopropane-1,2-diyl)dibenzene (**3**) (510 mg, 2.3 mmol, 1 equiv) and it was dissolved in HPLC-grade 1,2-DCE (23.4 mL, 0.1 M), before [(JohnPhos)Au(MeCN)]SbF_6 (5 mol%) was added. The resulting mixture was further stirred at room temperature for 3 h. After confirming complete conversion of (**3**), the resulting mixture was concentrated in vacuum and the crude product was purified by CombiFlash chromatography in SiO_2, using cyclohexane as eluent gave (*exo*)-1-phenyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (**4**) as a white solid.

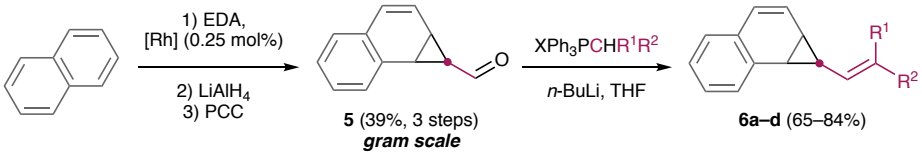
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 3H), 7.24 – 7.15 (m, 4H), 7.10 – 7.01 (m, 2H), 6.44 – 6.31 (m, 2H), 2.80 (dd, *J* = 7.9, 4.5 Hz, 1H), 2.39 (dtd, *J* = 7.9, 4.3, 1.0 Hz, 1H), 1.28 (t, *J* = 4.3 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.8, 134.6, 130.8, 128.6, 128.4, 127.9, 127.9, 127.5, 126.3, 125.7, 125.4, 124.4, 32.5, 29.4, 26.9 ppm.

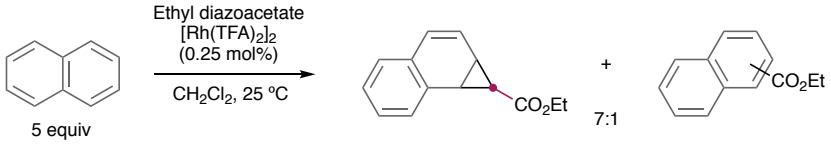
HRMS (APCI Pos): calc. for $C_{17}H_{15}$ $[M+H]^+$: 219.1168; found: 219.1172.

MP 74–77 ºC.

3. Preparation of Vinyl Cyclopropyl Dihydronaphthalenes (6a–d)



Ethyl (*exo*)-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene-1-carboxylate (S2)



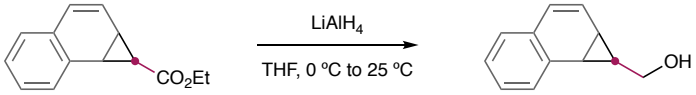
A two-necked 250 mL round-bottomed flask with a magnetic stirring bar was charged with naphthalene (25.9 g, 202 mmol, 5 equiv) and $Rh_2(TFA)_4$ (60 mg, 0.101 mmol, 0.25 mol%), under Ar atmosphere. Both solids were dissolved in anhydrous CH_2Cl_2 (67 mL, 0.6 M), and the resulting dark green solution was degassed by bubbling Ar through over 15 min. After that, ethyl 2-diazoacetate (5 mL, 40.4 mmol, 1 equiv, 85% w/w commercial solution with CH_2Cl_2) was added by automatic syringe pump over 18 h (0.3 mL/h), while stirring at 25 ºC. After stirring for one additional hour, the solvent was removed in vacuum, and the crude mixture was adsorbed into SiO_2, and then submitted to purification by CombiFlash column chromatography in SiO_2, eluting first with cyclohexane to remove excess naphthalene, and then with a slow gradient of cyclohexane/EtOAc from 95:5 to 85:15, giving ethyl (*exo*)-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene-1-carboxylate (**S2**) (4.5 g, 20.8 mmol, 52%) as a colorless oil. Alternatively, the purification can be carried out more rapidly, giving a 7:1 mixture (77% of combined yield, based on ethyl diazoacetate) of the desired product and the formal insertion products (naphthalenes), which can be used in the next steps as is, and purified in later step of the synthetic route. Characterization data matched the reported ones for this product.[4]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 1H), 7.24 – 7.18 (m, 2H), 7.13 – 7.11 (m, 1H), 6.39 (d, J = 9.6 Hz, 1H), 6.29 (ddd, J = 9.6, 5.0, 0.7 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.07 (dd, J = 8.3, 4.0 Hz, 1H), 2.66 – 2.59 (m, 1H), 1.27 (t, J = 7.1 Hz, 3H), 0.84 (t, J = 3.9 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 133.0, 131.1, 129.1, 128.3, 128.0, 127.1, 126.3, 126.3, 61.3, 30.8, 27.9, 23.2, 14.7 ppm.

HRMS (ESI Positive): calculated for $C_{14}H_{15}O_2$ $[M+H]^+$: 215.1067; found: 215.1069.

(*exo*)-(1a,7b-Dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)methanol (S3)



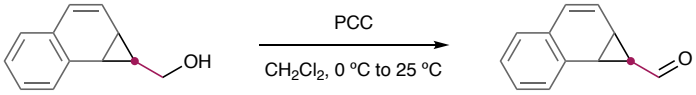
A two-necked 250 mL round-bottomed flask with a magnetic stirring bar was charged under Ar, with $LiAlH_4$ (1.08 g, 28.4 mmol, 1.5 equiv), and it was suspended in anhydrous THF (50 mL, 0.12 M). After cooling down the suspension to 0 ºC in an ice-water bath, a solution of ethyl (*exo*)-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene-1-carboxylate (**S2**) (4.05 g, 18.9 mmol, 1 equiv) in 6 mL of anhydrous THF was added dropwise over 5 min, and then the cooling bath was removed. The resulting suspension was stirred for 14 h while coming to room temperature, when no starting material was observed by TLC. The reaction was cooled down again to 0 ºC in an ice-water bath, and was quenched by careful addition of water, and then aqueous (10%) HCl. The aqueous phase was extracted twice with Et_2O, and the combined organic fractions were washed with water once, with brine once, dried over anhydrous Na_2SO_4 and concentrated in vacuum. Fast filtration through SiO_2 washing with EtOAc gave (*exo*)-(1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)methanol (**S3**) (*ca.* quantitative yield, 3.3 g) as a colorless oil, used on the next step without further purification.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.16 (dtd, *J* = 18.2, 7.3, 1.5 Hz, 2H), 7.08 (dd, *J* = 7.4, 1.7 Hz, 1H), 6.29 – 6.23 (m, 2H), 3.82 (dt, *J* = 11.7, 6.0 Hz, 1H), 3.70 (ddd, *J* = 11.6, 7.0, 5.1 Hz, 1H), 2.35 (dd, *J* = 7.9, 4.4 Hz, 1H), 1.93 (dtd, *J* = 8.0, 4.0, 1.6 Hz, 1H), 0.42 (tt, *J* = 6.8, 4.2 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 134.3, 131.1, 128.3, 128.0, 127.6, 127.6, 126.3, 124.5, 66.5, 25.9, 24.4, 23.1 ppm.

HRMS (APCI Positive): calculated for $C_{12}H_{11}$ $[M\text{-}OH]^+$: 155.0855; found: 155.0852.

(*exo*)-1a,7b-Dihydro-1*H*-cyclopropa[*a*]naphthalene-1-carbaldehyde (5)



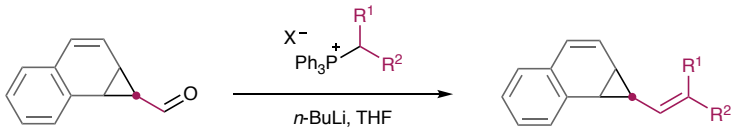
A 500 mL round-bottomed flask was charged under air with a solution of crude (*exo*)-(1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)methanol (**S3**) (3.3 g, 17 mmol, 1 equiv) in HPLC-grade CH_2Cl_2 (140 mL, 0.12 M). After cooling this solution to 0 ºC in an ice-water bath, was added pyridinium chlorochromate (7.34 g, 34 mmol, 2 equiv) in a single portion, and the resulting brown mixture was stirred while coming to room temperature for 14 h, when no starting material was observed by TLC. The mixture was filtered through Celite, concentrated in vacuum and then purified by CombiFlash chromatography in SiO_2 (95:5 to 9:1 cyclohexane/EtOAc gradient) to give (*exo*)-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene-1-carbaldehyde (**5**) (1.6 g, 9.4 mmol, 38% overall yield over 3 steps) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (d, *J* = 3.3 Hz, 1H), 7.45 – 7.41 (m, 1H), 7.29 – 7.26 (m, 2H), 7.22 – 7.18 (m, 1H), 6.50 (d, *J* = 9.6 Hz, 1H), 6.35 (ddd, *J* = 9.5, 5.1, 0.8 Hz, 1H), 3.29 (ddd, *J* = 8.4, 3.8, 0.7 Hz, 1H), 2.87 (dddd, *J* = 8.5, 5.1, 3.6, 0.6 Hz, 1H), 1.20 (q, *J* = 3.6 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 132.3, 130.9, 128.6, 128.2, 127.9, 127.1, 126.6, 125.8, 32.7, 31.2, 29.8 ppm.

HRMS (APCI Positive): calculated for $C_{12}H_{11}O$ $[M+H]^+$: 171.0804; found: 171.0806.

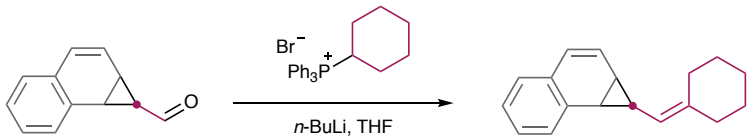
Wittig Reaction of Aldehyde (5) to Give Vinyl Cyclopropanes (6a–d)



An alkyl phosphonium halide (1.3 equiv) was dried in high vacuum at 60 ºC for 4 h, and after cooling it was suspended, under Ar, in anhydrous THF (0.2 M). The suspension was cooled down to 0 ºC in an ice-water bath, and to this mixture was added dropwise a commercial solution of *n*-BuLi (2.5 M in hexanes, 1.4 equiv). After the addition, the mixture was stirred in the ice-water bath for 30 min, before (*exo*)-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene-1-carbaldehyde (**5**) (1 equiv) was added as a solution in anhydrous THF (*ca.* 1 M). The mixture was stirred while coming to room temperature for 16–20 h. The reaction was quenched by the addition of aqueous NH_4Cl, and the aqueous phase was extracted twice with Et_2O. Combined organic fractions were washed with water once, with brine once, dried over anhydrous Na_2SO_4 and concentrated in vacuum. The products were purified by flash chromatography in SiO_2 or preparative TLC using pentane or cyclohexane as eluent.

3.1 Characterization Data for the Different Vinyl Cyclopropanes (6a–d)

(*exo*)-1-(Cyclohexylidenemethyl)-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (6a)



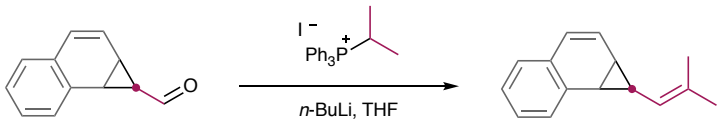
The title compound (colorless oil, 136 mg, 65%) was prepared by Wittig reaction of aldehyde (**5**) (150 mg, 0.88 mmol, 1.0 equiv) using cyclohexyltriphenylphosphonium bromide (487 mg, 1.15 mmol, 1.3 equiv) after purification by CombiFlash chromatography in SiO_2 using cyclohexane as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.14 (dtd, *J* = 17.9, 7.3, 1.5 Hz, 2H), 7.06 (dd, *J* = 7.3, 1.6 Hz, 1H), 6.27 (dd, *J* = 9.6, 4.9 Hz, 1H), 6.21 (d, *J* = 9.6 Hz, 1H), 4.73 (dd, *J* = 9.1, 1.3 Hz, 1H), 2.34 (dd, *J* = 7.7, 4.3 Hz, 1H), 2.15 – 2.08 (m, 4H), 1.91 (dt, *J* = 8.1, 4.4 Hz, 1H), 1.53 (dd, *J* = 6.7, 3.5 Hz, 4H), 1.50 – 1.46 (m, 2H), 0.88 (ddd, *J* = 9.3, 4.9, 3.3 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.3, 134.9, 131.2, 128.4, 128.3, 127.8, 127.5, 126.1, 124.1, 122.9, 37.4, 30.0, 29.6, 28.9, 27.9, 27.2, 26.9, 21.9 ppm.

HRMS (APCI Positive): calculated for $C_{18}H_{21}$ $[M+H]^+$: 237.1638; found: 237.1635.

(*exo*)-1-(2-Methylprop-1-en-1-yl)-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (6b)



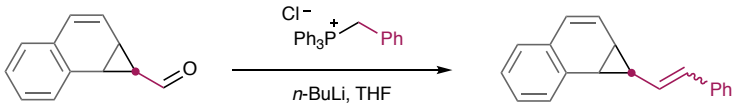
The title compound (colorless oil, 97 mg, 84%) was prepared by Wittig reaction of aldehyde (**5**) (100 mg, 0.59 mmol, 1.0 equiv) using isopropyltriphenylphosphonium iodide (330 mg, 0.76 mmol, 1.3 equiv) after purification by CombiFlash chromatography in SiO_2 using cyclohexane as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 7.1, 1.6 Hz, 1H), 7.14 (dtd, *J* = 16.5, 7.3, 1.6 Hz, 2H), 7.06 (dd, *J* = 7.3, 1.7 Hz, 1H), 6.29 – 6.20 (m, 2H), 4.80 (dp, *J* = 9.1, 1.4 Hz, 1H), 2.36 (dd, *J* = 7.7, 4.4 Hz, 1H), 1.92 (dddd, *J* = 7.6, 4.7, 3.8, 0.7 Hz, 1H), 1.74 (d, *J* = 1.4 Hz, 3H), 1.64 (d, *J* = 1.3 Hz, 3H), 0.85 (dt, *J* = 9.0, 4.1 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 134.9, 133.1, 131.2, 128.4, 128.2, 127.8, 127.5, 126.1, 126.1, 124.1, 29.8, 26.7, 26.2, 22.7, 18.7 ppm.

HRMS (APCI Positive): calculated for $C_{15}H_{17}$ $[M+H]^+$: 197.1325; found: 197.1320.

(*exo*)-1-(Styryl)-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (6c) and (6d)



The title compound (white viscous oil, 196 mg, 68%, 2:1 *E*:*Z*) was prepared by Wittig reaction of aldehyde (**5**) (200 mg, 1.17 mmol, 1.0 equiv) using benzyltriphenylphosphonium chloride (548 mg, 1.41 mmol, 1.2 equiv) after purification by CombiFlash chromatography in SiO_2 using cyclohexane as eluent. Preparative TLC in SiO_2 using pentane as eluent allowed isolating each diastereoisomer separately (**6c** = *E*, bottom fraction, **6d** = *Z*, top fraction).

(*exo*)-1-((*E*)-Styryl)-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (6c)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 7.1, 1.7 Hz, 1H), 7.34 – 7.27 (m, 4H), 7.21 – 7.15 (m, 3H), 7.10 (dd, *J* = 7.3, 1.7 Hz, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.32 – 6.28 (m, 2H), 5.99 (dd, *J* = 15.7, 9.1 Hz, 1H), 2.61 (dd, *J* = 7.9, 4.3 Hz, 1H), 2.20 (dtd, *J* = 7.0, 3.7, 2.4 Hz, 1H), 0.98 (dt, *J* = 9.3, 4.0 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8, 134.2, 132.5, 131.1, 129.1, 128.9, 128.4, 128.0, 127.7, 127.5, 127.1, 126.4, 126.0, 124.7, 31.2, 27.4, 26.8 ppm.

HRMS (APCI Positive): calculated for $C_{19}H_{17}$ $[M+H]^+$: 245.1325; found: 245.1321.

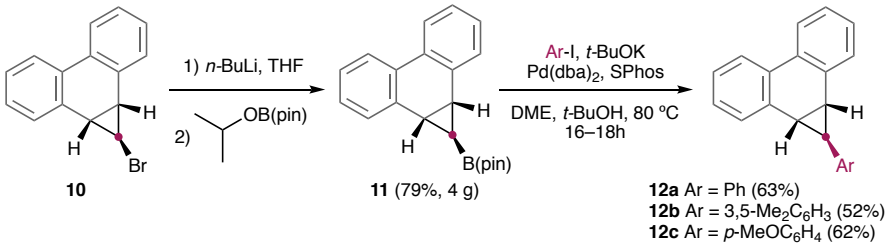
(*exo*)-1-((*Z*)-Styryl)-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (6d)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.25 – 7.21 (m, 2H), 7.18 (td, *J* = 7.4, 1.6 Hz, 1H), 7.14 (td, *J* = 7.3, 1.6 Hz, 2H), 7.07 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.47 (d, *J* = 11.4 Hz, 1H), 6.37 – 6.23 (m, 2H), 5.37 (dd, *J* = 11.5, 9.6 Hz, 1H), 2.56 (dd, *J* = 7.8, 4.3 Hz, 1H), 2.15 – 2.11 (m, 1H), 1.21 (dtd, *J* = 9.5, 4.1, 1.1 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 137.7, 134.1, 134.1, 131.1, 129.5, 128.9, 128.5, 128.5, 128.0, 127.6, 127.2, 126.9, 126.4, 124.9, 31.1, 27.9, 23.7 ppm.

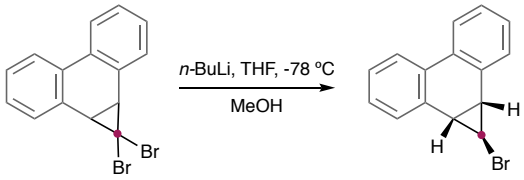
HRMS (APCI Positive): calculated for $C_{19}H_{17}$ $[M+H]^+$: 245.1325; found: 245.1321.

4. Preparation of Aryl Cyclopropyl Dihydrophenanthrenes (12a–c)



10 **11** (79%, 4 g) **12a** Ar = Ph (63%); **12b** Ar = 3,5-$Me_2C_6H_3$ (52%); **12c** Ar = *p*-$MeOC_6H_4$ (62%)

1-Bromo-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (10)



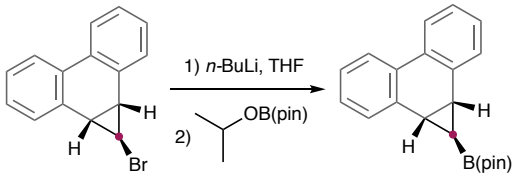
1,1-Dibromo-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene was prepared in multigram scale by the treatment of phenanthrene with $CHBr_3$ and aqueous NaOH in CH_2Cl_2/EtOH (40:1), in the presence of 1 mol% of benzyltriethylammonium chloride, according to a reported procedure.[5]

A two-necked 50 mL round-bottomed flask with a magnetic stirring bar was charged under Ar, with 1,1-dibromo-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (3.5 g, 10.0 mmol, 1 equiv), and it was suspended in anhydrous THF (40 mL, 0.25 M). After cooling down the suspension to -78 ºC, *n*-BuLi (4.4 mL, 2.5 M in hexane, 11.0 mmol, 1.1 equiv) was slowly added and the reaction was stirred for 1 h. Then, methanol (0.8 mL, 20.0 mmol, 2.0 equiv) was added and the reaction was allowed to warm to room temperature. The reaction was further quenched by the addition of water. The aqueous phase was extracted twice with CH_2Cl_2, and the combined organic fractions were washed with brine once, dried over anhydrous Na_2SO_4 and concentrated in vacuum. The crude product was purified by CombiFlash chromatography in SiO_2 using cyclohexane to give 1-bromo-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (**10**) (1.7 g, 10.0 mmol, 63% yield) as a white solid. Characterization data matched the reported ones for this product.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 2H), 7.52 – 7.46 (m, 2H), 7.35 – 7.26 (m, 4H), 3.01 (d, J = 3.1 Hz, 2H), 2.42 (t, J = 3.1 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 131.9, 129.8, 129.3, 128.1, 127.2, 123.3, 29.9, 27.7 ppm.

2-(1a,9b-Dihydro-1*H*-cyclopropa[*l*]phenanthren-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11)



A two-necked 500 mL round-bottomed flask with a magnetic stirring bar was charged under Ar, with 1-bromo-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (4.0 g, 14.8 mmol, 1 equiv), and it was suspended in anhydrous THF (184 mL, 0.08 M). After cooling down the suspension to -78 ºC, *n*-BuLi (8.85 mL, 2.5 M in hexanes, 22.1 mmol, 1.5 equiv) was slowly added and the reaction was stirred for 1 h. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.5 mL, 22.1 mmol, 1.5 equiv) was added at -78 ºC. The reaction was stirred for 2 h while warming to room temperature. The reaction was quenched by the addition of a saturated solution of ammonium chloride. The aqueous phase was extracted twice with diethyl ether, and the combined organic fractions were washed with brine once, dried over anhydrous Na_2SO_4 and concentrated in vacuum, giving a pale yellow solid. The product was purified by trituration and washing with MeOH (3x10 mL), which was then removed by filtration to give pure 2-(1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthren-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11**) (3.7 g, 14.75 mmol, 79% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2H), 7.46 – 7.42 (m, 2H), 7.28 – 7.18 (m, 4H), 2.77 (d, J = 5.3 Hz, 2H), 1.27 (s, 12H), -0.59 (t, J = 5.3 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 136.6, 129.5, 129.3, 127.6, 126.2, 123.3, 83.5, 26.2, 24.9 ppm.

HRMS (APCI Positive): calculated for $C_{21}H_{24}BO_2$ $[M+H]^+$: 318.1900; found: 318.1903.

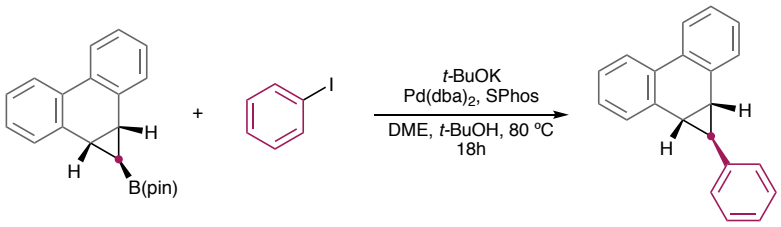
MP 163–168 ºC.

Palladium-Catalyzed Suzuki Cross-Coupling for the Synthesis of Aryl Cyclopropyl Dihydrophenanthrenes

This procedure was adapted from a previously reported one.[7] A microwave vial was charged with $Pd(dba)_2$ (5 mol%), 2-di-cyclohexylphosphino-2',6'-dimethoxybiphenyl (10 mol%), bornonic ester (**11**) (1 equiv), and an aryl iodide (3 equiv). The vial was introduced in an Ar-filled glovebox and *t*-BuOK (4 equiv) was added. The vial was sealed with its cap, and taken out of the glovebox before DME and *t*-BuOH (0.06 M, DME/*t*-BuOH 3:1) were added through the septum of the cap. The mixture was stirred at 80 ºC for 16–18 h. After cooling, the reaction mixture was diluted with water, and extracted three times with EtOAc. The combined organic fractions were washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography in SiO_2.

4.1 Characterization Data for (12a–c)

1-Phenyl-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (12a)



The title compound (white solid, 161 mg, 62%) was prepared by palladium-catalyzed Suzuki-Miyaura cross-coupling of boronic ester (**11**) (300 mg, 0.94 mmol, 1.0 equiv) with iodobenzene (577 mg, 2.83 mmol, 3 equiv), after purification by CombiFlash chromatography in SiO_2 using cyclohexane as eluent.

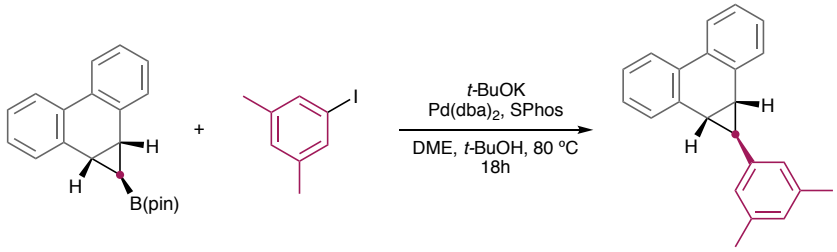
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, J = 7.8, 1.4 Hz, 2H), 7.42 (dd, J = 7.3, 1.7 Hz, 2H), 7.34 – 7.23 (m, 6H), 7.22 – 7.18 (m, 1H), 7.10 – 7.06 (m, 2H), 2.92 (d, J = 4.3 Hz, 2H), 1.40 (t, J = 4.3 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.3, 135.1, 129.5, 129.4, 128.6, 128.0, 126.6, 125.8, 125.5, 123.4, 31.5, 30.6 ppm.

HRMS (APCI Positive): calculated for $C_{21}H_{17}$ $[M+H]^+$: 269.1325; found: 269.1318.

MP 132–134 ºC.

1-(3,5-Dimethylphenyl)-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (12b)



The title compound (white solid, 144 mg, 52%) was prepared by palladium-catalyzed Suzuki-Miyaura cross-coupling of boronic ester (**11**) (300 mg, 0.94 mmol, 1.0 equiv) using 1-iodo-3,5-dimethylbenzene (656 mg, 2.83 mmol, 3 equiv) after purification by CombiFlash chromatography in SiO_2 using cyclohexane as eluent.

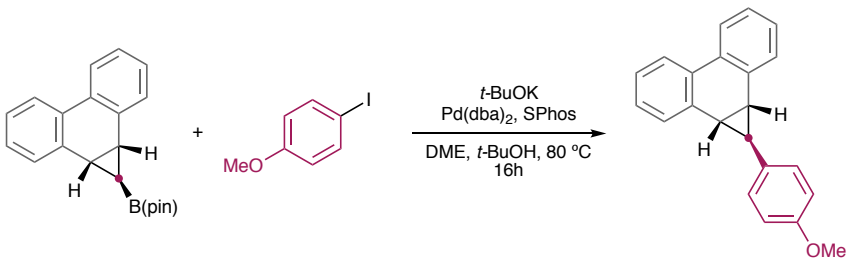
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (dd, J = 7.6, 1.6 Hz, 2H), 7.43 (dd, J = 7.4, 1.7 Hz, 2H), 7.34 – 7.23 (m, 4H), 6.87 (s, 1H), 6.72 (s, 1H), 2.92 (d, J = 4.3 Hz, 2H), 2.33 (s, 6H), 1.36 (t, J = 4.3 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.2, 138.2, 135.3, 129.5, 129.4, 127.9, 127.6, 126.6, 123.4, 123.3, 31.4, 30.6, 21.5 ppm.

HRMS (APCI Positive): calculated for $C_{23}H_{21}$ $[M+H]^+$: 297.1638; found: 297.1634.

MP 126–127 ºC.

1-(4-Methoxyphenyl)-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (12c)



The title compound (white solid, 174 mg, 62%) was prepared by palladium-catalyzed Suzuki-Miyaura cross-coupling of boronic ester (**11**) (300 mg, 0.94 mmol, 1.0 equiv) using 4-iodoanisole (662 mg, 2.83 mmol, 3 equiv) after purification by CombiFlash chromatography in SiO_2 using cyclohexane/EtOAc 97:3 as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, J = 7.7, 1.5 Hz, 2H), 7.43 (dd, J = 7.4, 1.6 Hz, 2H), 7.32 – 7.24 (m, 4H), 7.06 – 7.01 (m, 2H), 6.90 – 6.86 (m, 2H), 3.82 (s, 3H), 2.85 (d, J = 4.3 Hz, 2H), 1.38 (t, J = 4.3 Hz, 1H) ppm.

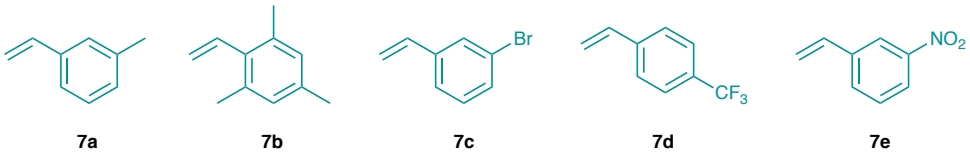
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 135.3, 134.0, 129.5, 129.4, 127.9, 126.5, 126.5, 123.4, 114.2, 55.5, 30.9, 29.9 ppm.

HRMS (APCI Positive): calculated for $C_{22}H_{19}O$ $[M+H]^+$: 299.1430; found: 299.1424.

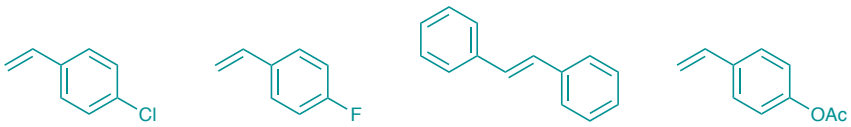
MP 145–147 ºC.

5. List of Substrates

All the alkenes (**7**) employed in this work were commercially available, used as received from commercial sources, and are listed below.

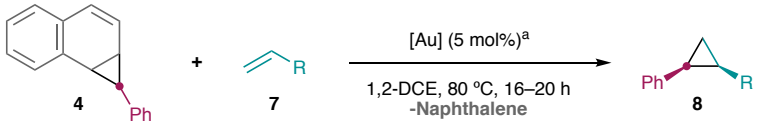


7a **7b** **7c** **7d** **7e**



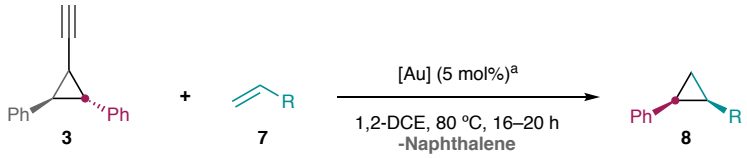
7f **7g** **7h** **7i**

6. General Procedure A for the Decarbenation of Phenyl Cyclopropyl Dihydronaphthalene (4)



A microwave vial equipped with a Teflon-coated magnetic stirring bar was charged, under air, with the corresponding cyclopropyl dihydronaphthalene (**4**) (1.0 equiv) and the corresponding alkene (**7**) (6 equiv). Both reagents were dissolved in HPLC-grade 1,2-DCE (0.15 M), before [(JohnPhos)Au(MeCN)]SbF_6 (5 mol%) was added. The vial was closed with the cap and then stirred at 80 ºC for 16–20 hours, until complete consumption of the starting material (**4**), which was confirmed by TLC and GC-MS. The resulting mixture was concentrated in vacuum and the crude product was purified by flash column chromatography or preparative TLC on SiO_2. The configuration of the products was assigned by direct comparson or analogy with reported substrates, based on X-ray or nOe analysis.[8]

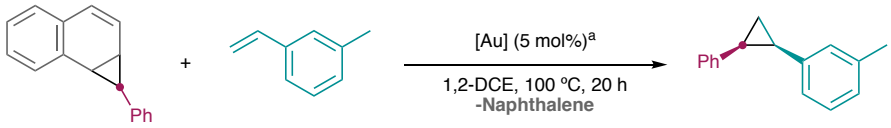
6.1 General Procedure A' for the One-pot Hydroarylation–Decarbenation–Cyclopropanation Sequence



A microwave vial equipped with a Teflon-coated magnetic stirring bar was charged, under air, with the corresponding (*exo*)-(3-ethynylcyclopropane-1,2-diyl)dibenzene (**3**) (1.0 equiv) and the corresponding alkene (**7**) (6 equiv). Both reagents were dissolved in HPLC-grade 1,2-DCE (0.15 M), before [(JohnPhos)Au(MeCN)]SbF_6 (5 mol%) was added. The vial was closed with the cap and then stirred at 80 ºC for 21 hours, until complete consumption of the starting material (**3**), which was confirmed by TLC and GC-MS. The resulting mixture was concentrated in vacuum and the crude product was purified by preparative TLC on SiO_2, using pentane as eluent.

6.2 Characterization Data for the Different Phenyl Cyclopropanes

(*cis*)-1-Methyl-3-(2-phenylcyclopropyl)benzene (8a)



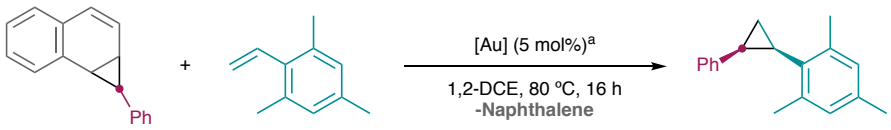
The title compound (colorless oil, 15 mg, 68% yield, 5:1 d.r.) was obtained following General Procedure **A** from (*exo*)-1-phenyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (**4**) (23 mg, 0.105 mmol) and 1-methyl-3-vinylbenzene (75 mg, 0.64 mmol, 6 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (4.1 mg, 5 mol%) after purification by preparative TLC on SiO_2 using pentane as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.04 (m, 3H), 7.00 – 6.94 (m, 3H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.81 (s, 1H), 6.75 – 6.67 (m, 1H), 2.47 (ddd, *J* = 8.8, 6.3, 4.0 Hz, 2H), 2.20 (s, 3H), 1.46 (td, *J* = 8.6, 5.3 Hz, 1H), 1.36 (td, *J* = 6.3, 5.3 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 138.4, 137.2, 130.0, 129.1, 127.7, 127.6, 126.5, 125.9, 125.7, 24.4, 24.4, 21.5, 11.6 ppm.

HRMS (APCI Positive): calculated for $C_{16}H_{17}$ $[M+H]^+$: 209.1325; found: 209.1319.

(*cis*)-1,3,5-Trimethyl-2-(2-phenylcyclopropyl)benzene (8b)



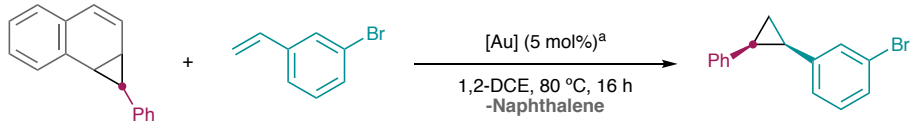
The title compound (colorless oil, 14 mg, 55% yield, 6:1 d.r.) was obtained following General Procedure **A** from (*exo*)-1-phenyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (**4**) (23 mg, 0.105 mmol) and 1,3,5-trimethyl-2-vinylbenzene (92 mg, 0.64 mmol, 6 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (4.1 mg, 5 mol%) after purification by preparative TLC on SiO_2 using pentane as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 – 6.99 (m, 3H), 6.72 (s, 2H), 6.67 – 6.62 (m, 2H), 2.41 – 2.34 (m, 2H), 2.34 – 2.25 (m, 2H), 2.25 – 2.11 (m, 9H), 1.74 (td, *J* = 8.9, 5.4 Hz, 1H), 1.14 (dt, *J* = 7.6, 5.6 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 135.7, 130.9, 128.9, 127.5, 126.5, 125.1, 23.6, 23.1, 20.9, 20.8, 17.9 ppm.

HRMS (APCI Positive): calculated for $C_{18}H_{21}$ $[M+H]^+$: 237.1638; found: 237.1633.

(*cis*)-1-Bromo-3-(2-phenylcyclopropyl)benzene (8c)



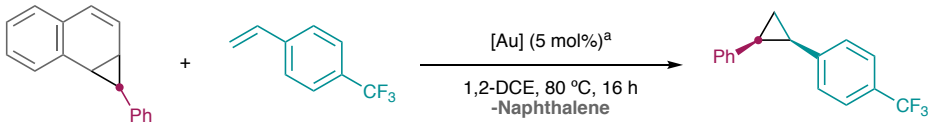
The title compound (colorless oil, 18 mg, 63% yield, 11:1 d.r.) was obtained following General Procedure **A** from (*exo*)-1-phenyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (**4**) (23 mg, 0.105 mmol) and 1-bromo-3-vinylbenzene (116 mg, 0.64 mmol, 6 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (4.1 mg, 5 mol%) after purification by preparative TLC on SiO_2 using pentane as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.09 (m, 4H), 7.10 – 7.06 (m, 1H), 6.98 – 6.94 (m, 2H), 6.91 (d, J = 7.8 Hz, 1H), 6.81 – 6.76 (m, 1H), 2.52 (td, J = 8.9, 6.4 Hz, 1H), 2.43 (td, J = 8.9, 6.2 Hz, 1H), 1.48 (td, J = 8.7, 5.6 Hz, 1H), 1.37 (q, J = 6.1 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 137.8, 132.2, 129.2, 129.2, 128.8, 127.9, 127.5, 126.0, 121.9, 24.76, 23.9, 11.5 ppm.

HRMS (APCI Positive): calculated for $C_{15}H_{14}Br$ $[M+H]^+$: 273.0273; found: 273.0263.

(*cis*)-1-(2-Phenylcyclopropyl)-4-(trifluoromethyl)benzene (8d)



The title compound (colorless oil, 14 mg, 51% yield, 10:1 d.r.) was obtained following General Procedure **A** from (*exo*)-1-phenyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (**4**) (23 mg, 0.105 mmol) and 1-(trifluoromethyl)-4-vinylbenzene (109 mg, 0.64 mmol, 6 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (4.1 mg, 5 mol%) after purification by preparative TLC on SiO_2 using pentane as eluent.

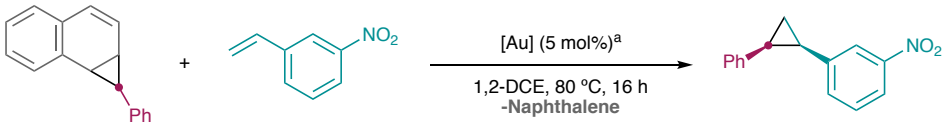
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, J = 8.1 Hz, 2H), 7.16 – 7.04 (m, 3H), 7.02 – 6.93 (m, 4H), 2.59 (td, J = 8.9, 6.4 Hz, 1H), 2.50 (td, J = 8.9, 6.2 Hz, 1H), 1.58 – 1.52 (m, 1H), 1.42 (td, J = 6.4, 5.5 Hz, 1H) ppm.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.39 ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1 (q, J = 1.2 Hz), 137.5, 129.3, 128.9, 128.0, 127.7, 126.1, 125.5, 124.6 (q, J = 3.8 Hz), 123.4, 121.2, 77.4, 25.1, 24.0, 11.9 ppm.

HRMS (APCI Positive): calculated for $C_{16}H_{14}F_3$ $[M+H]^+$: 263.1042; found: 263.1033.

(*cis*)-1-Nitro-3-(2-phenylcyclopropyl)benzene (8e)



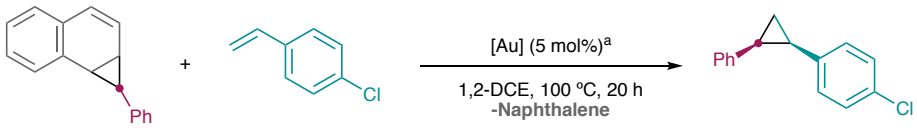
The title compound (viscous white oil, 11 mg, 41% yield, 8:1 d.r.) was obtained following General Procedure **A** from (*exo*)-1-phenyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (**4**) (23 mg, 0.105 mmol) and 1-nitro-3-vinylbenzene (94 mg, 0.64 mmol, 6 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (4.1 mg, 5 mol%) after purification by preparative TLC on SiO_2 using pentane/Et_2O 97:3 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dt, *J* = 7.6, 2.0 Hz, 1H), 7.84 – 7.78 (m, 1H), 7.25 – 7.15 (m, 2H), 7.14 – 7.09 (m, 2H), 7.08 – 7.03 (m, 1H), 6.99 – 6.93 (m, 2H), 2.63 (td, *J* = 8.9, 6.4 Hz, 1H), 2.55 (td, *J* = 8.9, 6.2 Hz, 1H), 1.61 – 1.55 (m, 1H), 1.50 (q, *J* = 6.2 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 137.0, 134.9, 129.3, 128.5, 128.2, 126.4, 123.7, 120.9, 25.2, 23.8, 11.5 ppm.

HRMS (APCI Pos): calculated for $C_{15}H_{12}NO_2$ $[M–H]^+$: 238.0863; found: 238.0857.

(*cis*)-1-Chloro-4-(2-phenylcyclopropyl)benzene (8f)



The title compound (colorless oil, 16 mg, 66% yield, 11:1 d.r.) was obtained following General Procedure **A** from (*exo*)-1-phenyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (**4**) (23 mg, 0.105 mmol) and 1-chloro-4-vinylbenzene (88 mg, 0.64 mmol, 6 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (4.1 mg, 5 mol%) after purification by preparative TLC on SiO_2 using pentane as eluent.

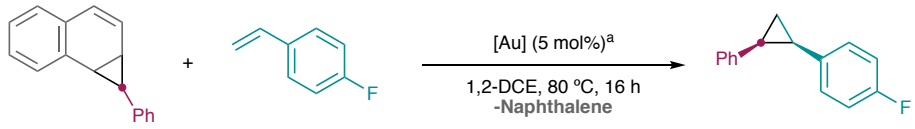
Alternatively, the title compound (colorless oil, 12 mg, 57% yield, 12:1 d.r.) was obtained following General Procedure **A'** from (*exo*)-(3-ethynylcyclopropane-1,2-diyl)dibenzene (**3**) (20 mg, 0.092 mmol) and 1-chloro-4-vinylbenzene (76 mg, 0.64 mmol, 6 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (3.5 mg, 5 mol%) after purification by preparative TLC on SiO_2 using pentane as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15 – 7.10 (m, 2H), 7.09 – 7.03 (m, 3H), 6.98 – 6.90 (m, 2H), 6.90 – 6.82 (m, 2H), 2.50 (td, *J* = 8.9, 6.3 Hz, 1H), 2.43 (td, *J* = 8.9, 6.3 Hz, 1H), 1.48 (td, *J* = 8.6, 5.5 Hz, 1H), 1.34 (td, *J* = 6.3, 5.5 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.0, 137.1, 130.3, 129.1, 127.9, 127.9, 125.9, 24.6, 23.8, 11.5 ppm.

HRMS (APCI Positive): calculated for $C_{15}H_{14}Cl$ $[M+H]^+$: 229.0760; found: 229.0768.

(*cis*)-1-Fluoro-4-(2-phenylcyclopropyl)benzene (8g)



The title compound (colorless oil, 17 mg, 76% yield, 12:1 d.r.) was obtained following General Procedure **A** from (*exo*)-1-phenyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (**4**) (23 mg, 0.105 mmol) and 1-fluoro-4-vinylbenzene (77 mg, 0.64 mmol, 6 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (4.1 mg, 5 mol%) after purification by preparative TLC on SiO_2 using pentane as eluent.

Alternatively, the title compound (colorless oil, 12 mg, 62% yield, 12:1 d.r.) was obtained following General Procedure **A'** from (*exo*)-(3-ethynylcyclopropane-1,2-diyl)dibenzene (**3**) (20 mg, 0.092 mmol) and 1-fluoro-4-vinylbenzene (67 mg, 0.55 mmol, 6 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (3.5 mg, 5 mol%) after purification by preparative TLC on SiO_2 using pentane as eluent.

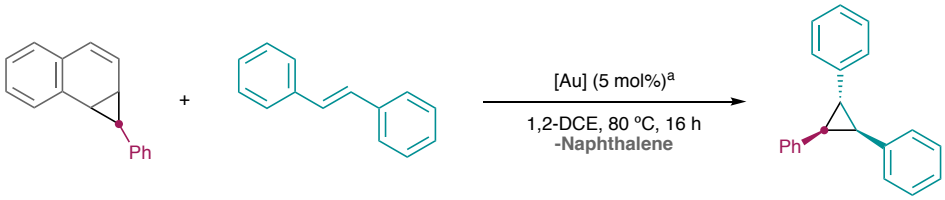
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.02 (m, 3H), 6.95 – 6.86 (m, 4H), 6.83 – 6.74 (m, 2H), 2.46 (ddd, *J* = 8.5, 6.3, 2.0 Hz, 2H), 1.47 (td, *J* = 8.6, 5.5 Hz, 1H), 1.33 (td, *J* = 6.2, 5.4 Hz, 1H) ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.70 ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1 (d, *J* = 243.5 Hz), 138.1, 133.9 (d, *J* = 3.0 Hz), 130.4 (d, *J* = 7.9 Hz), 128.8, 127.7, 125.6, 114.4 (d, *J* = 21.3 Hz), 24.0, 23.6, 11.4 ppm.

HRMS (APCI Positive): calculated for $C_{15}H_{14}F$ $[M+H]^+$: 213.1074; found: 213.1069.

(*exo*)-1,2,3-Triphenylcyclopropane (8h)



The title compound (colorless oil, 20 mg, together with a 20% of product of phenyl cyclopropanation of (**4**), (**S4**), 80% corrected yield) was obtained following General Procedure **A** from (*exo*)-1-phenyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (**4**) (23 mg, 0.105 mmol) and (*E*)-1,2-diphenylethene (114 mg, 0.64 mmol, 6 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (4.1 mg, 5 mol%) after purification by CombiFlash chromatography in SiO_2 using cyclohexane as eluent.

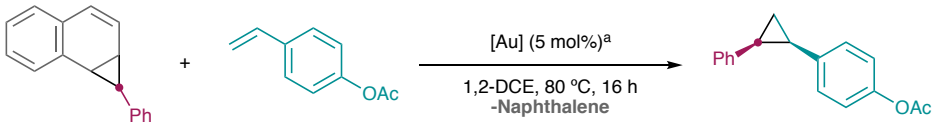
Alternatively, the title compound (colorless oil, 17 mg, together with a 20% of product of phenyl cyclopropanation of (**4**), (**S4**), 71% corrected yield) was obtained following General Procedure **A'** from (*exo*)-(3-ethynylcyclopropane-1,2-diyl)dibenzene (**3**) (20 mg, 0.092 mmol) and (*E*)-1,2-diphenylethene (99 mg, 0.55 mmol, 6 equiv) using

[(JohnPhos)Au(MeCN)]SbF_6 (3.5 mg, 5 mol%) after purification by preparative TLC on SiO_2 using pentane as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 4H), 7.31 – 7.27 (m, 1H), 7.22 – 7.12 (m, 6H), 7.10 – 7.04 (m, 4H), 2.94 – 2.86 (m, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 137.7, 129.0, 128.6, 127.9, 126.5, 126.1, 126.0, 34.5, 30.7 ppm.

(*cis*)-4-(2-Phenylcyclopropyl)phenyl acetate (8i)



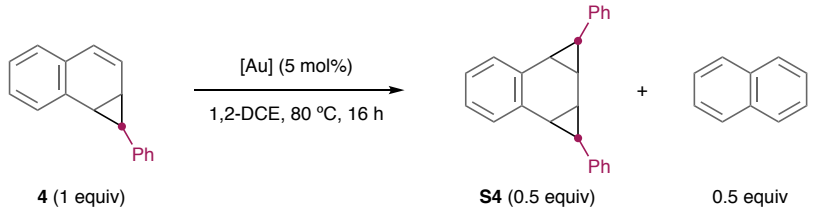
The title compound (visous colorless oil, 21 mg, 54% yield, 10:1 d.r.) was obtained following General Procedure **A** from (*exo*)-1-phenyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (**4**) (32.7 mg, 0.150 mmol) and 4-vinylphenyl acetate (73 mg, 0.45 mmol, 3 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (4.1 mg, 5 mol%) after purification by preparative TLC on SiO_2 using pentane/Et_2O 9:1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.07 (m, 3H), 6.99 – 6.94 (m, 4H), 6.88 – 6.82 (m, 2H), 2.50 (ddd, J = 9.0, 6.3, 2.9 Hz, 2H), 2.25 (s, 3H), 1.51 (td, J = 8.6, 5.4 Hz, 1H), 1.40 – 1.33 (m, 1H) ppm.

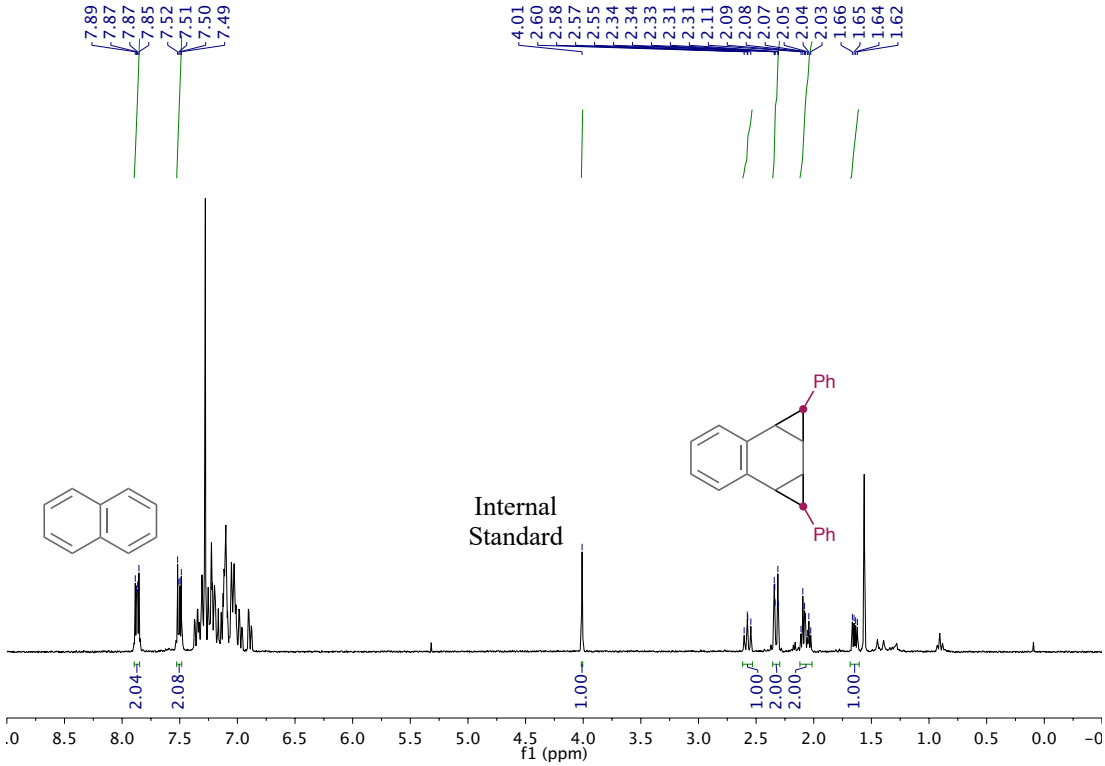
^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 148.6, 138.1, 136.0, 129.9, 128.9, 127.7, 125.7, 120.7, 24.2, 23.8, 21.1, 11.7 ppm.

HRMS (ESI Pos): calculated for $C_{17}H_{16}NaO_2$ $[M+Na]^+$: 275.1043; found: 275.1056.

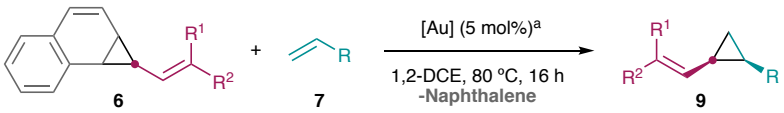
Formation of biscyclopropane (S4) byproduct by heating (4) with [Au]



Dissolving (**4**) in 1,2-DCE, adding 5 mol% of [(JohnPhos)Au(MeCN)]SbF_6 and heating at 80 ºC for 16 h gives quantitative release of 0.5 equiv of naphthalene and 0.5 equiv of bisphenylcyclopropyl product (**S4**), which is unreactive towards retro-cyclopropanation under the reaction conditions. Characterization data for (**S4**) matched the reported ones.[9]



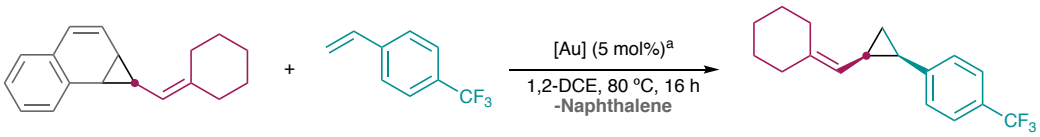
7. General Procedure B for the Decarbenation of Vinyl Cyclopropyl Dihydronaphthalenes (6a–d)



A microwave vial equipped with a Teflon-coated magnetic stirring bar was charged, under air, with the corresponding cyclopropyl dihydronaphthalene (**6**) (1.0 equiv) and the corresponding alkene (**7**) (6 equiv). Both reagents were dissolved in HPLC-grade 1,2-DCE (0.15 M), before [(JohnPhos)Au(MeCN)]SbF_6 (5 mol%) was added. The vial was closed with the cap and then stirred at 80 ºC for 16–20 hours, until complete consumption of the starting (**6**), which was confirmed by TLC and GC-MS. The resulting mixture was concentrated in vacuum and the crude product was purified by flash column chromatography or preparative TLC on SiO_2. The configuration of the products was assigned by direct comparson or analogy with reported substrates, based on X-ray or nOe analysis [10]

8.1. Characterization Data for the Different Vinyl Cyclopropanes

(*cis*)-1-(2-(Cyclohexylidenemethyl)cyclopropyl)-4-(trifluoromethyl)benzene (9a)



The title compound (colorless oil, 16 mg, 54% yield, 5:1 d.r.) was obtained following General Procedure **B** from (*exo*)-1-(cyclohexylidenemethyl)-1a,7b-dihydro-1*H*-cyclopropa[*a*]-naphthalene (**6a**) (25 mg, 0.106 mmol) and 1-(trifluoromethyl)-4-vinylbenzene (109 mg, 0.64 mmol, 6 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (4.1 mg, 5 mol%) after purification by preparative TLC on SiO_2 using pentane as eluent.

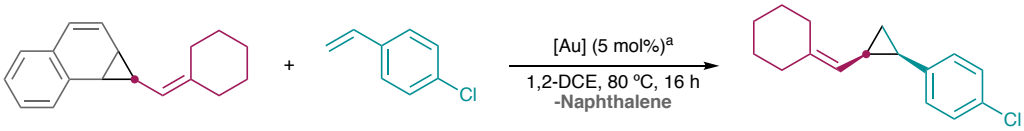
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.28 – 7.24 (m, 2H), 4.45 (dt, J = 8.1, 1.2 Hz, 1H), 2.33 – 2.26 (m, 1H), 2.22 (ddd, J = 6.8, 4.8, 1.2 Hz, 2H), 2.03 – 1.97 (m, 1H), 1.94 (t, J = 5.8 Hz, 2H), 1.53 – 1.29 (m, 7H), 0.94 – 0.91 (m, 1H) ppm.

^{19}F NMR (471 MHz, $CDCl_3$) δ -62.30 ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 129.1, 125.7, 124.7, 124.7, 124.6, 124.6, 123.2, 118.9, 36.8, 29.3, 28.5, 27.6, 26.7, 22.9, 17.9, 13.3 ppm.

HRMS (APCI Pos): calculated for $C_{17}H_{20}F_3$ $[M+H]^+$: 281.1512; found: 281.1504.

(*cis*)-1-(2-(Cyclohexylidenemethyl)cyclopropyl)-4-chlorobenzene (9b)



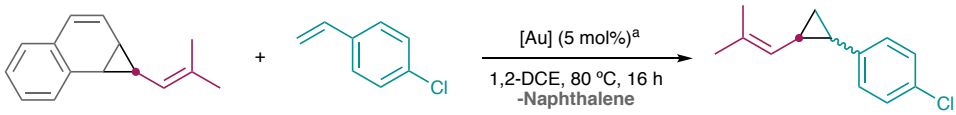
The title compound (colorless oil, 19 mg, 73% yield, 2:1 d.r.) was obtained following General Procedure **B** from (*exo*)-1-(cyclohexylidenemethyl)-1a,7b-dihydro-1*H*-cyclopropa[*a*]-naphthalene (**6a**) (25 mg, 0.106 mmol) and 1-chloro-4-vinylbenzene (88 mg, 0.64 mmol, 6 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (4.1 mg, 5 mol%) after purification by preparative TLC on SiO_2 using pentane as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.20 (m, 2H), 7.13 – 7.07 (m, 2H), 4.41 (dt, *J* = 8.4, 1.2 Hz, 1H), 2.26 – 2.19 (m, 3H), 1.96 – 1.90 (m, 3H), 1.58 – 1.51 (m, 4H), 1.43 – 1.36 (m, 1H), 1.31 – 1.25 (m, 2H), 0.83 (td, *J* = 6.0, 5.0 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 138.1, 130.3, 127.9, 123.5, 119.4, 36.9, 29.3, 28.6, 27.7, 26.8, 22.3, 17.4, 12.9 ppm.

HRMS (APCI Positive): calculated for $C_{16}H_{20}Cl$ $[M+H]^+$: 247.1248; found: 247.1243.

1-Chloro-4-(2-(2-methylprop-1-en-1-yl)cyclopropyl)benzene (9c)



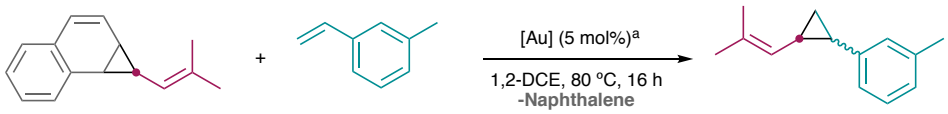
The title compound (colorless oil, 15 mg, 65% yield, 1:1 d.r.) was obtained following General Procedure **B** from (*exo*)-1-(2-methylprop-1-en-1-yl)-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (**6b**) (22 mg, 0.112 mmol) and 1-chloro-4-vinylbenzene (93 mg, 0.67 mmol, 6 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (4.3 mg, 5 mol%) after purification by preparative TLC on SiO_2 using pentane as eluent.

^{1}H NMR (500 MHz, $CDCl_3$, *cis*/*trans* 1:1 mixture, unassigned) δ 7.23 – 7.18 (m, 4H), 7.09 – 7.05 (m, 2H), 7.01 – 6.95 (m, 2H), 4.71 (dp, *J* = 8.8, 1.4 Hz, 1H), 4.42 (dp, *J* = 8.7, 1.4 Hz, 1H), 2.20 (td, *J* = 8.6, 6.2 Hz, 1H), 1.87 (td, *J* = 8.7, 5.7 Hz, 1H), 1.80 – 1.75 (m, 1H), 1.69 (d, *J* = 1.4 Hz, 6H), 1.68 (d, *J* = 1.3 Hz, 3H), 1.67 – 1.62 (m, 1H), 1.55 (d, *J* = 1.4 Hz, 3H), 1.23 – 1.21 (m, 1H), 1.12 (dt, *J* = 8.6, 5.2 Hz, 1H), 0.96 (ddd, *J* = 8.5, 5.7, 4.9 Hz, 1H), 0.79 (td, *J* = 6.0, 5.0 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, *cis*/*trans* 1:1 mixture, unassigned) δ 141.9, 138.4, 130.6, 128.7, 128.3, 127.3, 127.2, 123.0, 25.9, 25.8, 24.7, 23.7, 22.6, 18.8, 18.7, 18.6, 17.5, 12.9 ppm.

HRMS (APCI Positive): calculated for $C_{13}H_{16}Cl$ $[M+H]^+$: 207.0935; found: 207.0937.

(*cis*)-1-Methyl-3-(2-(2-methylprop-1-en-1-yl)cyclopropyl)benzene (9d)



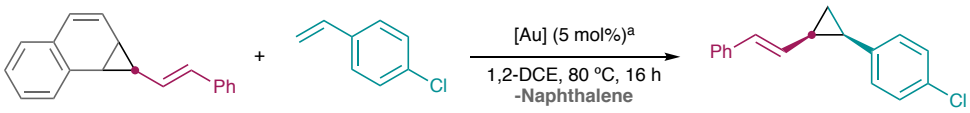
The title compound (colorless oil, 12 mg, 58% yield, the yield was confirmed/corrected by NMR with the addition of 1 equiv of Ph_2CH_2 as internal standard, 1:1 d.r.) was obtained following General Procedure **B** from (*exo*)-1-(2-methylprop-1-en-1-yl)-1a,7b-dihydro-1*H*-cyclopropa[*a*]-naphthalene (**6b**) (22 mg, 0.112 mmol) and 1-methyl-3-vinylbenzene (79 mg, 0.67 mmol, 6 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (4.3 mg, 5 mol%) after purification by preparative TLC on SiO_2 using pentane as eluent. Characterization data matched the reported ones for this compound.[10]

^{1}H NMR (400 MHz, $CDCl_3$, *cis* isomer) δ 7.18 (t, *J* = 7.5 Hz, 1H), 7.04 – 6.96 (m, 4H), 4.55 (dt, *J* = 8.9, 1.3 Hz, 1H), 2.36 (s, 3H), 2.26 (td, *J* = 8.6, 6.5 Hz, 1H), 1.89 (qd, *J* = 8.8, 5.8 Hz, 1H), 1.74 (d, *J* = 1.0 Hz, 4H), 1.61 – 1.60 (m, 4H), 1.25 (td, *J* = 8.5, 4.9 Hz, 1H), 0.90 – 0.85 (m, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, *cis* isomer) δ 139.3, 137.3, 132.6, 129.9, 127.7, 126.4, 125.9, 123.1, 25.6, 22.7, 21.5, 18.3, 18.3, 12.3 ppm.

GC-MS (EI): calculated for $C_{14}H_{18}$ $[M]^+$: 186.1; found: 186.1.

(*cis*)-1-Chloro-4-(2-((*E*)-styryl)cyclopropyl)benzene (9e)



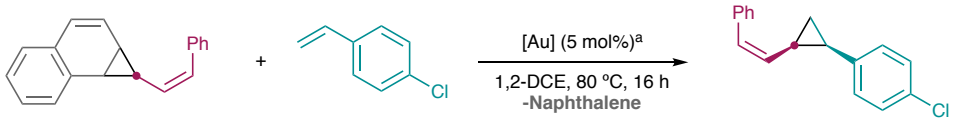
The title compound (colorless oil, 10 mg, 50% yield, 20:1 d.r.) was obtained following General Procedure **B** from (*E*)-1-styryl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (**6c**) (18 mg, 0.106 mmol) and 1-chloro-4-vinylbenzene (62 mg, 0.45 mmol, 6 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (2.9 mg, 5 mol%) after purification by preparative TLC on SiO_2 using pentane as eluent. Characterization data matched the reported ones for this compound.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 - 7.32 (m, 9H), 6.56 (d, J=15.8 Hz, 1H), 5.52 (dd, J=15.8, 9.4 Hz, 1H), 2.38 - 2.49 (m, 1H), 2.01 - 2.13 (m, 1H), 1.37 - 1.46 (m, 1H), 1.08 - 1.19 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.6, 137.4, 131.9, 130.7, 130.1, 130.0, 128.6, 128.3, 126.9 , 125.8 , 23.3 , 22.8 , 12.8 ppm.

GC-MS (EI): calculated for $C_{17}H_{16}Cl$ $[M+H]^+$: 255.1; found: 255.1.

(*cis*)-1-Chloro-4-(2-((*Z*)-styryl)cyclopropyl)benzene (9f)



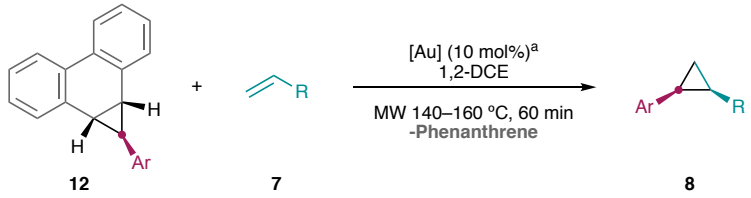
The title compound (colorless oil, 13 mg, 68% yield, 8:1 d.r.) was obtained following General Procedure **B** from (*Z*)-1-styryl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (**6d**) (18 mg, 0.075 mmol) and 1-chloro-4-vinylbenzene (63 mg, 0.45 mmol, 6 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (2.9 mg, 5 mol%) after purification by preparative TLC on SiO_2 using pentane as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 2H), 7.34 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.28 – 7.19 (m, 4H), 7.18 – 7.14 (m, 2H), 6.33 (d, *J* = 11.5 Hz, 1H), 4.91 (dd, *J* = 11.5, 9.7 Hz, 1H), 2.38 (td, *J* = 8.6, 6.3 Hz, 1H), 2.28 (dtdd, *J* = 9.8, 8.6, 5.7, 1.1 Hz, 1H), 1.39 (td, *J* = 8.4, 5.1 Hz, 1H), 1.05 (dt, *J* = 6.4, 5.4 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 138.0, 137.5, 132.2, 131.6, 130.8, 130.0, 129.1, 128.6, 128.6, 126.9, 24.1, 19.4, 14.2 ppm.

HRMS (APCI Positive): calculated for $C_{17}H_{16}Cl$ $[M+H]^+$: 255.0935; found: 255.0923.

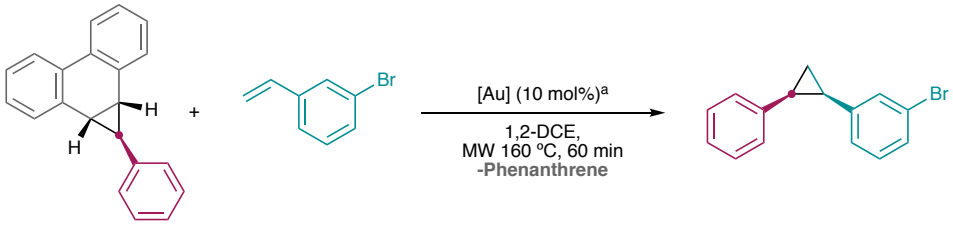
8. General Procedure C for the Decarbenation of Aryl Cyclopropyl Dihydrophenanthrenes



A microwave vial equipped with a Teflon-coated magnetic stirring bar was charged, under air, with the corresponding aryl cyclopropyl dihydrophenanthrene (**12**) (1.0 equiv) and the corresponding alkene (**7**) (2 equiv). Both reagents were dissolved in HPLC-grade 1,2-DCE (0.15 M), before [(JohnPhos)Au(MeCN)]SbF_6 (10 mol%) was added. The vial was closed with the cap and then stirred at 140–160 ºC for 60 min in a microwave reactor. The resulting mixture was concentrated in vacuum and the crude product was purified by flash column chromatography or preparative TLC on SiO_2. The configuration of the products was assigned by direct comparson or analogy with reported substrates, based on X-ray, ^{1}H NMR, or nOe analysis [8]

8.1 Characterization Data for the Different Aryl Cyclopropanes

(*cis*)-1-Bromo-3-(2-phenylcyclopropyl)benzene (8c)



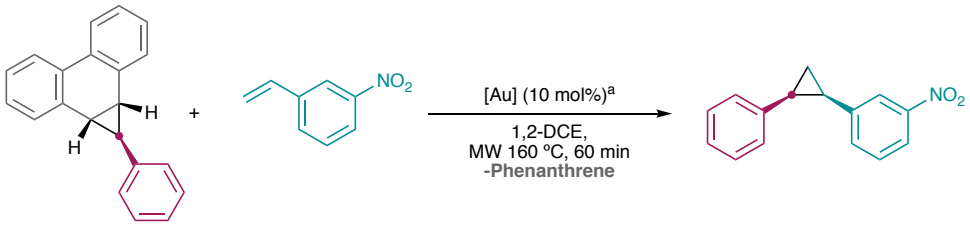
The title compound (colorless oil, 19 mg, 60% yield, 6:1 d.r.) was obtained following General Procedure **C** from *exo*-1-phenyl-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (**12a**) (30 mg, 0.11 mmol) and 1-bromo-3-vinylbenzene (41 mg, 0.22 mmol, 2 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (8.6 mg, 10 mol%) after purification by preparative TLC on SiO_2 using pentane as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 – 7.09 (m, 4H), 7.10 – 7.06 (m, 1H), 6.98 – 6.94 (m, 2H), 6.91 (d, J = 7.8 Hz, 1H), 6.81 – 6.76 (m, 1H), 2.52 (td, J = 8.9, 6.4 Hz, 1H), 2.43 (td, J = 8.9, 6.2 Hz, 1H), 1.48 (td, J = 8.7, 5.6 Hz, 1H), 1.37 (q, J = 6.1 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 137.8, 132.2, 129.2, 129.2, 128.8, 127.9, 127.5, 126.0, 121.9, 24.76, 23.9, 11.5 ppm.

HRMS (APCI Positive): calculated for $C_{15}H_{14}Br$ $[M+H]^+$: 273.0273; found: 273.0263.

(*cis*)-1-Nitro-3-(2-phenylcyclopropyl)benzene (8e)



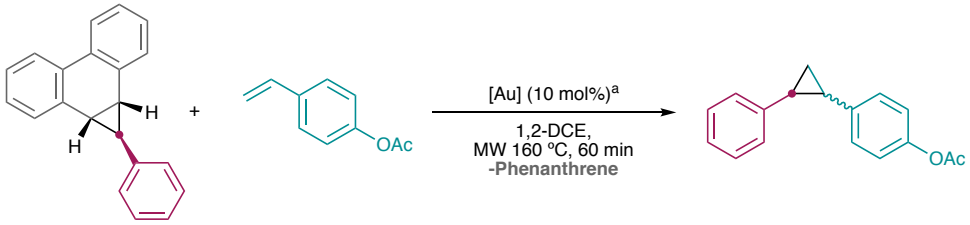
The title compound (colorless oil, 14 mg, 52% yield, the yield was confirmed/corrected by NMR with the addition of 1 equiv of Ph_2CH_2 as internal standard, 7:1 d.r.) was obtained following General Procedure **C** from *exo*-1-phenyl-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (**12a**) (30 mg, 0.11 mmol) and 1-nitro-3-vinylbenzene (33 mg, 0.22 mmol, 2 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (8.6 mg, 10 mol%) after purification by preparative TLC on SiO_2 using pentane/Et_2O 97:3 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dt, *J* = 7.6, 2.0 Hz, 1H), 7.84 – 7.78 (m, 1H), 7.25 – 7.15 (m, 2H), 7.14 – 7.09 (m, 2H), 7.08 – 7.03 (m, 1H), 6.99 – 6.93 (m, 2H), 2.63 (td, *J* = 8.9, 6.4 Hz, 1H), 2.55 (td, *J* = 8.9, 6.2 Hz, 1H), 1.61 – 1.55 (m, 1H), 1.50 (q, *J* = 6.2 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 137.0, 134.9, 129.3, 128.5, 128.2, 126.4, 123.7, 120.9, 25.2, 23.8, 11.5 ppm.

HRMS (APCI Pos): calculated for $C_{15}H_{12}NO_2$ $[M–H]^+$: 238.0863; found: 238.0857.

(*cis*)-4-(2-Phenylcyclopropyl)phenyl acetate (8i)



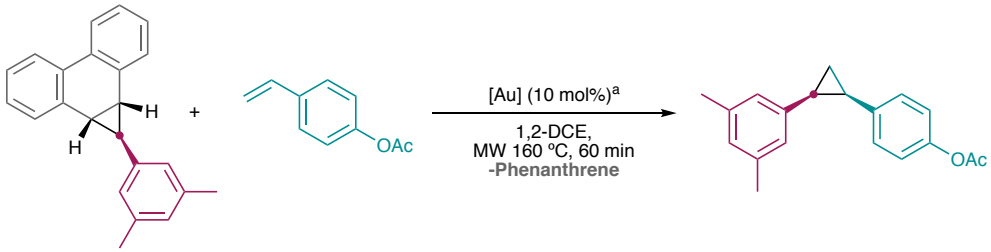
The title compound (colorless oil, 10 mg, 36% yield, 1:1 d.r.) was obtained following General Procedure C from *exo*-1-phenyl-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (**12a**) (30 mg, 0.11 mmol) and 4-vinylphenyl acetate (36 mg, 0.22 mmol, 2 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (8.6 mg, 10 mol%) after purification by preparative TLC on SiO_2 using pentane/Et_2O 9:1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$, *cis* isomer) δ 7.17 – 7.07 (m, 3H), 6.99 – 6.94 (m, 4H), 6.88 – 6.82 (m, 2H), 2.50 (ddd, *J* = 9.0, 6.3, 2.9 Hz, 2H), 2.25 (s, 3H), 1.51 (td, *J* = 8.6, 5.4 Hz, 1H), 1.40 – 1.33 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$, *cis* isomer) δ 169.4, 148.6, 138.1, 136.1, 129.9, 128.9, 127.7, 125.7, 120.7, 24.2, 23.8, 21.1, 11.7 ppm.

HRMS (ESI Pos): calculated for $C_{17}H_{16}NaO_2$ $[M+Na]^+$: 275.1043; found: 275.1056.

(*cis*)-4-(2-(3,5-Dimethylphenyl)cyclopropyl)phenyl acetate (8j)



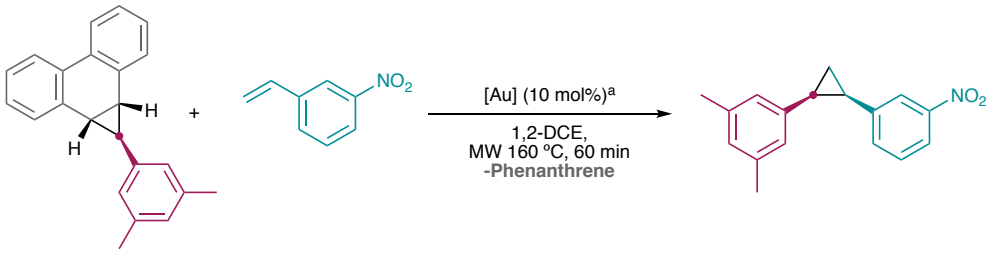
The title compound (viscous colorless oil, 14 mg, 59% yield, 3:1 d.r.) was obtained following General Procedure **C** from *exo*-1-(3,5-dimethylphenyl)-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (**12b**) (25 mg, 0.084 mmol) and 4-vinylphenyl acetate (27 mg, 0.17 mmol, 2 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (6.5 mg, 10 mol%) after purification by preparative TLC on SiO_2 using pentane/Et_2O 97:3 as eluent.

^{1}H NMR (500 MHz, $CDCl_3$, *cis* isomer) δ 6.95 – 6.92 (m, 2H), 6.83 – 6.80 (m, 2H), 6.67 (s, 1H), 6.51 (d, J = 0.9 Hz, 2H), 2.43 – 2.35 (m, 2H), 2.22 (s, 3H), 2.13 (d, J = 0.7 Hz, 6H), 1.44 – 1.41 (m, 1H), 1.28 – 1.25 (m, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$, 3:1 *cis*/*trans*, unassigned) δ 169.8, 148.9, 138.4, 137.4, 136.7, 130.3, 127.7, 127.1, 123.9, 121.7, 120.9, 24.4, 24.0, 21.6, 21.5, 21.5, 12.2 ppm.

HRMS (APCI Positive): calculated for $C_{19}H_{21}O_2$ $[M+H]^+$: 281.1536; found: 281.1536.

(*cis*)-1,3-Dimethyl-5-(2-(3-nitrophenyl)cyclopropyl)benzene (8k)



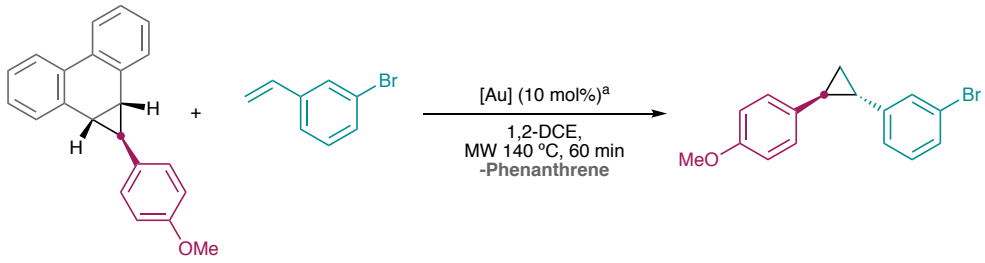
The title compound (colorless oil, 15 mg, 55% yield, 12:1 d.r.) was obtained following General Procedure **C** from *exo*-1-(3,5-dimethylphenyl)-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (**12b**) (30 mg, 0.101 mmol) and 1-nitro-3-vinylbenzene (30 mg, 0.20 mmol, 2 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (7.8 mg, 10 mol%) after purification by preparative TLC on SiO_2 using pentane/Et_2O 97:3 as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dt, J = 7.3, 2.1 Hz, 1H), 7.85 – 7.81 (m, 1H), 7.26 – 7.17 (m, 2H), 6.69 (s, 1H), 6.59 (s, 2H), 2.53 (dtd, J = 28.1, 9.0, 6.3 Hz, 2H), 2.14 (s, 6H), 1.53 (td, J = 8.6, 5.7 Hz, 1H), 1.46 (q, J = 6.2 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.4, 137.5, 136.7, 134.9, 128.4, 128.0, 127.1, 123.6, 120.7, 25.2, 23.8, 21.3, 11.6 ppm.

HRMS (APCI Positive): calculated for $C_{17}H_{16}NO_2$ $[M+H]^+$: 266.1176; found: 266.1173.

(*trans*)-1-Bromo-3-(2-(4-methoxyphenyl)cyclopropyl)benzene (8l)



The title compound (colorless oil, 29 mg, 94% yield, 15:1 d.r.) was obtained following General Procedure **C** from *exo*-1-(4-methoxyphenyl)-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (**12c**) (30 mg, 0.101 mmol) and 1-bromo-3-vinylbenzene (37 mg, 0.20 mmol, 2 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (7.8 mg, 10 mol%) after purification by preparative TLC on SiO_2 using pentane/Et_2O 98:2 as eluent.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (ddd, *J* = 7.9, 2.0, 1.1 Hz, 1H), 7.27 (t, *J* = 1.9 Hz, 1H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.10 – 7.04 (m, 3H), 6.89 – 6.82 (m, 2H), 3.80 (s, 3H), 2.13 (ddd, *J* = 8.8, 6.1, 4.5 Hz, 1H), 2.05 (ddd, *J* = 8.6, 5.9, 4.5 Hz, 1H), 1.40 (dddd, *J* = 14.0, 8.8, 6.0, 5.4 Hz, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 145.4, 134.1, 130.0, 128.9, 128.8, 127.1, 124.7, 122.7, 114.1, 55.5, 27.7, 27.2, 17.9 ppm.

HRMS (APCI Pos): calculated for $C_{16}H_{16}{}^{79}BrO$ $[M+H]^+$: 303.0379; found: 303.0366.

(*trans*)-1-(2-(4-Methoxyphenyl)cyclopropyl)-3-nitrobenzene (8m)

The title compound (pale yellow solid, 21 mg, 87% yield, 10:1 d.r.) was obtained following General Procedure **C** from *exo*-1-(4-methoxyphenyl)-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (**12c**) (30 mg, 0.089 mmol) and 1-nitro-3-vinylbenzene (27 mg, 0.18 mmol, 2 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (6.9 mg, 10 mol%) after purification by CombiFlash chromatography on SiO_2 using a cyclohexane/EtOAc gradient from 99:1 to 9:1. Characterization data matched previously reported ones.[8a]

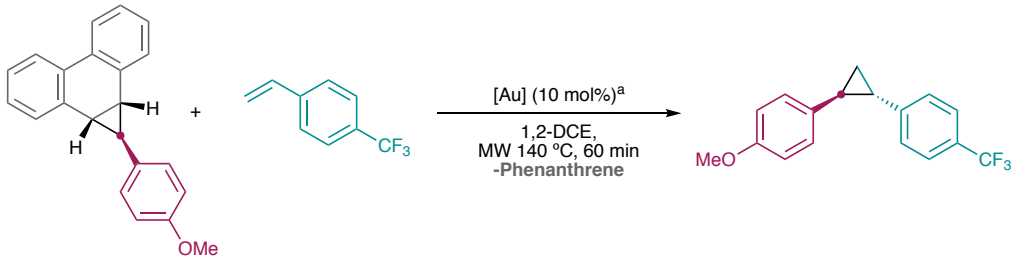
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (ddd, *J* = 7.6, 2.3, 1.5 Hz, 1H), 7.96 (t, *J* = 2.0 Hz, 1H), 7.51 – 7.38 (m, 2H), 7.13 – 7.05 (m, 2H), 6.89 – 6.82 (m, 2H), 3.80 (s, 3H), 2.20 (dddd, *J* = 13.0, 8.6, 6.0, 4.5 Hz, 2H), 1.49 (ddt, *J* = 20.1, 8.8, 5.6 Hz, 2H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 148.7, 145.2, 133.5, 132.3, 129.3, 127.1, 120.8, 120.4, 114.1, 55.5, 28.2, 27.1, 18.4 ppm.

MP 92–94 °C.

HRMS (APCI Pos): calculated for $C_{16}H_{15}NO_3$ $[M]^+$: 269.1046; found: 269.1052.

(*trans*)-1-Methoxy-4-(2-(4-(trifluoromethyl)phenyl)cyclopropyl)benzene (8n)



The title compound (colorless oil, 21 mg, 88% yield, 14:1 d.r.) was obtained following General Procedure **C** from *exo*-1-(4-methoxyphenyl)-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (**12c**) (24 mg, 0.080 mmol) and 1-(trifluoromethyl)-4-vinylbenzene (28 mg, 0.16 mmol, 2 equiv) using [(JohnPhos)Au(MeCN)]SbF_6 (6.2 mg, 10 mol%) after purification by preparative TLC on SiO_2 using pentane/diethyl ether 97:3 as eluent. Characterization data matched previously reported ones.[8a]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.27 – 7.16 (m, 2H), 7.12 – 7.06 (m, 2H), 6.89 – 6.83 (m, 2H), 3.80 (s, 3H), 2.16 (dddd, *J* = 24.3, 8.6, 5.9, 4.5 Hz, 2H), 1.46 (ddt, *J* = 20.0, 8.8, 5.7 Hz, 2H) ppm.

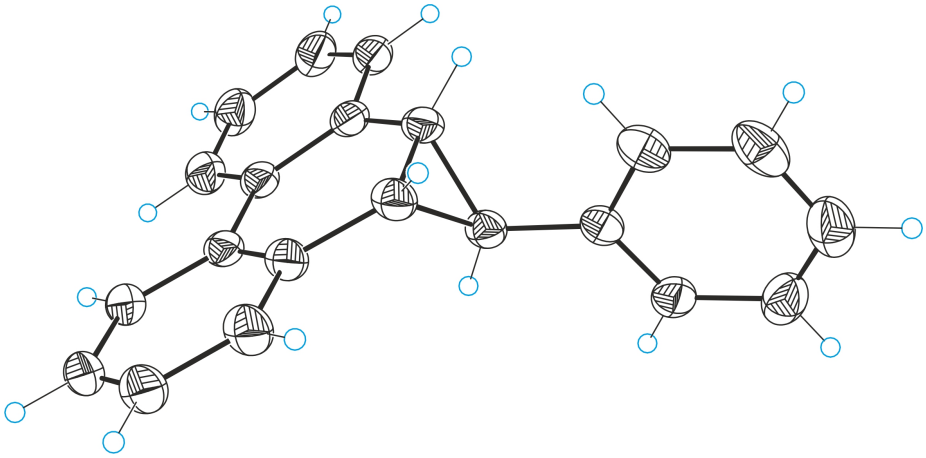
^{19}F NMR (471 MHz, $CDCl_3$) δ -62.33 ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 147.4, 134.10, 128.2 (q, *J* = 32.9 Hz), 127.3, 126.2, 125.7 (q, *J* = 3.8 Hz), 124.9 (q, *J* = 271.3 Hz), 114.3, 55.7, 28.4, 27.7, 18.6 ppm.

9. Crystal Data and Structure Refinement

9.1 *exo*-1-Phenyl-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (12a)

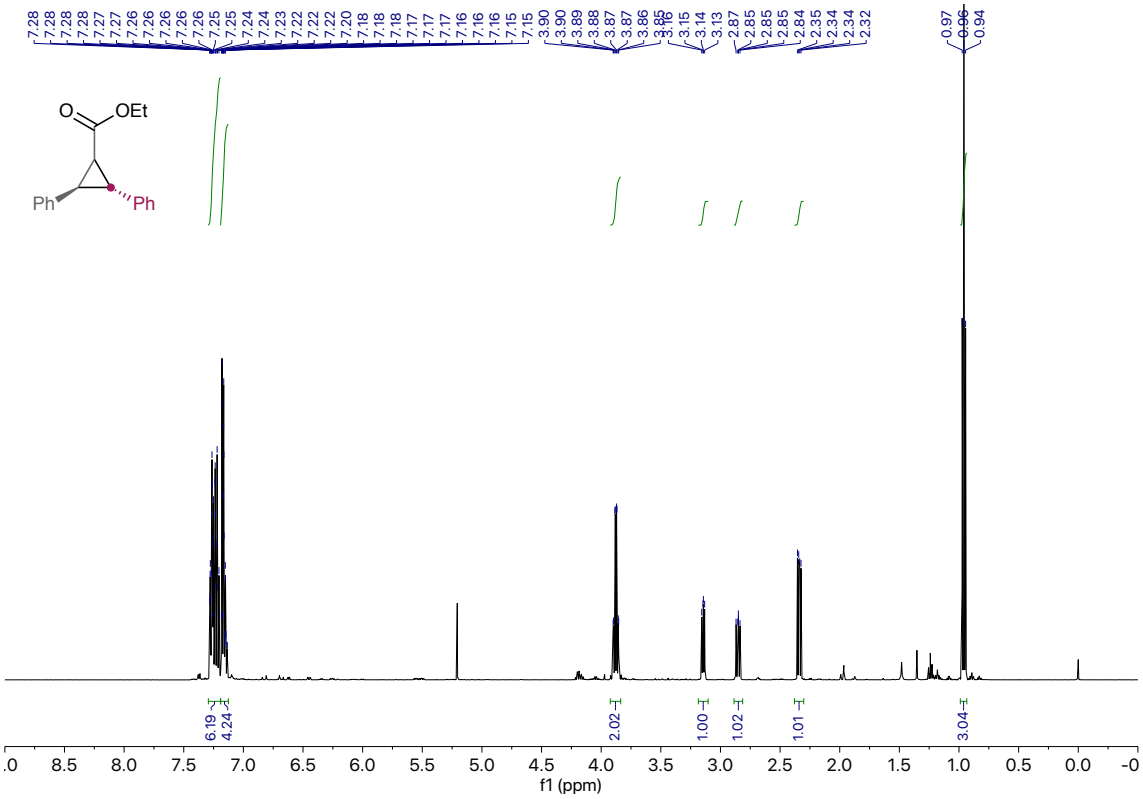
Suitable crystals for X-ray diffraction were obtained by slow evaporation from cyclohexane. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC 1897077 contains the crystal structure information of this compound and can be obtained free of charge via http://www.ccdc.cam.ac.uk.

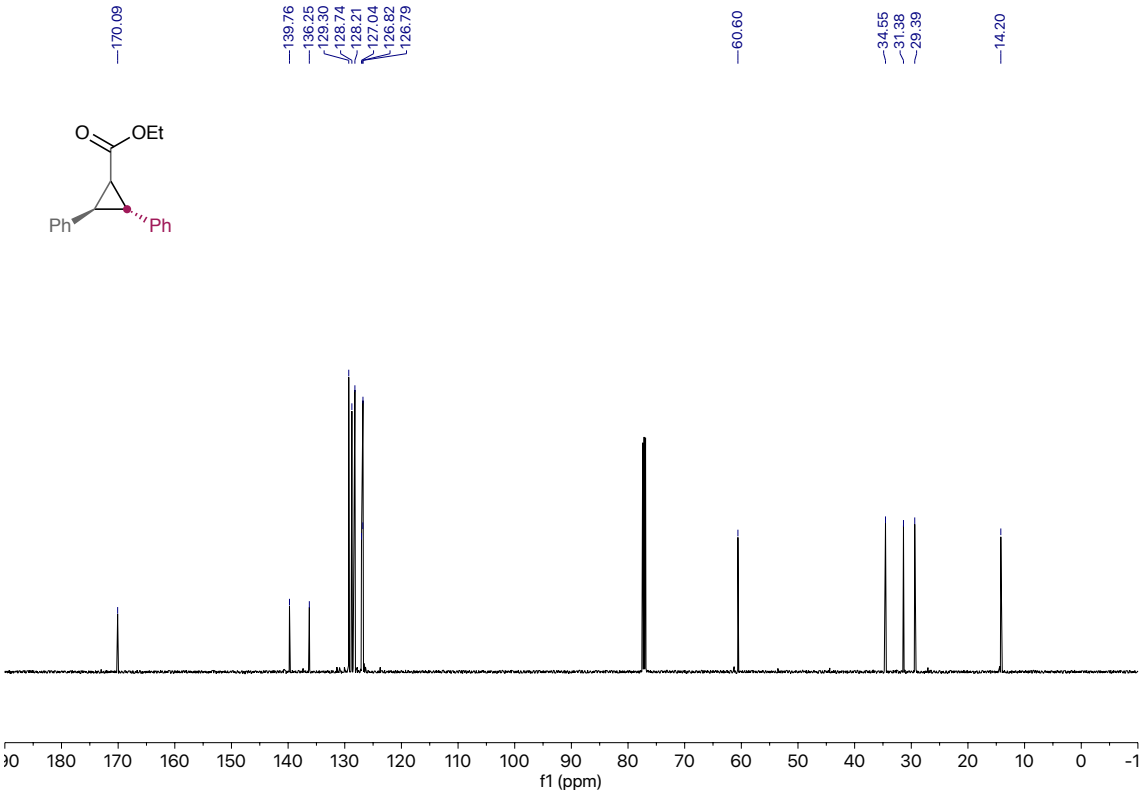


Identification code	BHB1-231
Empirical formula	C21 H16
Formula weight	268.34
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pna2(1)
Unit cell dimensions	a = 12.6579(7)Å a= 90°. b = 19.8384(11)Å b = 90°. c = 5.6765(3)Å g = 90°.
Volume	1425.44(13) Å3
Z	4
Density (calculated)	1.250 Mg/m3
Absorption coefficient	0.071 mm-1
F(000)	568
Crystal size	0.40 x 0.25 x 0.15 mm3
Theta range for data collection	1.908 to 31.184°.
Index ranges	-18<=h<=13,-28<=k<=28,-8<=l<=8
Reflections collected	21744
Independent reflections	4210[R(int) = 0.0272]
Completeness to theta =31.184°	94.5%
Absorption correction	Empirical
Max. and min. transmission	0.989 and 0.761
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	4210/ 1/ 190
Goodness-of-fit on F2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0407, wR2 = 0.1078
R indices (all data)	R1 = 0.0475, wR2 = 0.1152
Flack parameter	x =2.9(10)
Largest diff. peak and hole	0.224 and -0.261 e.Å-3

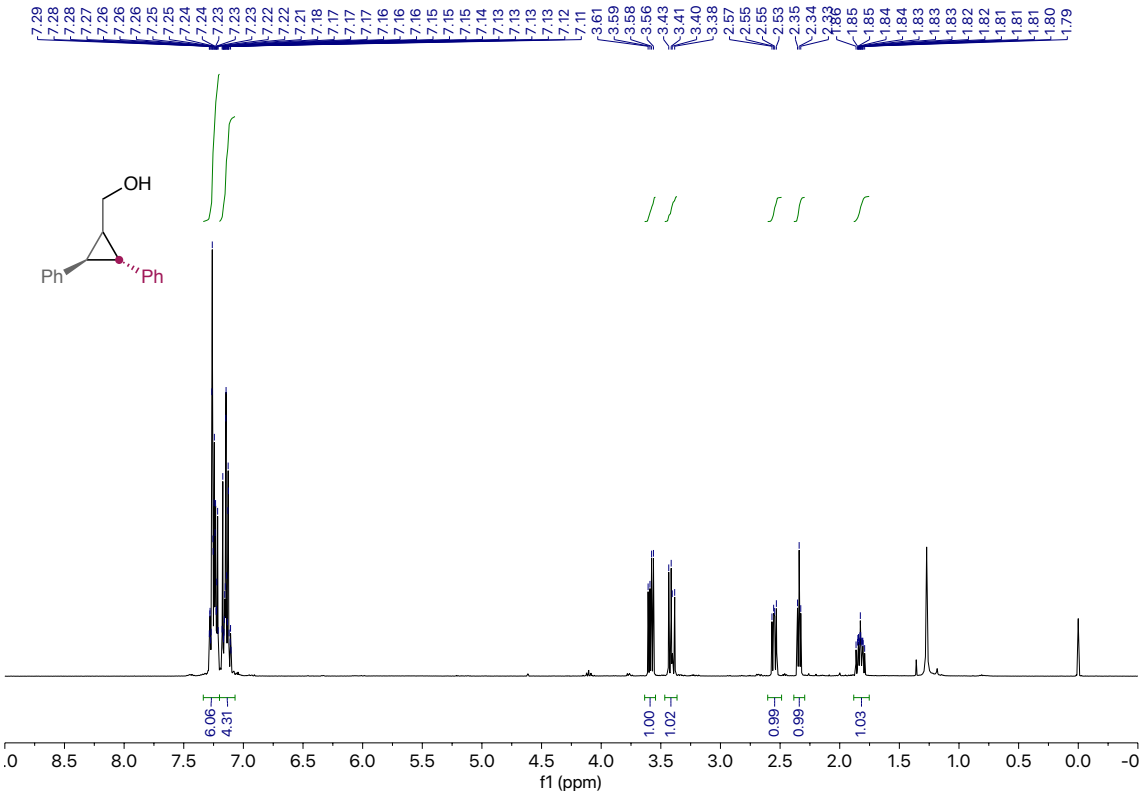
10. NMR Spectra

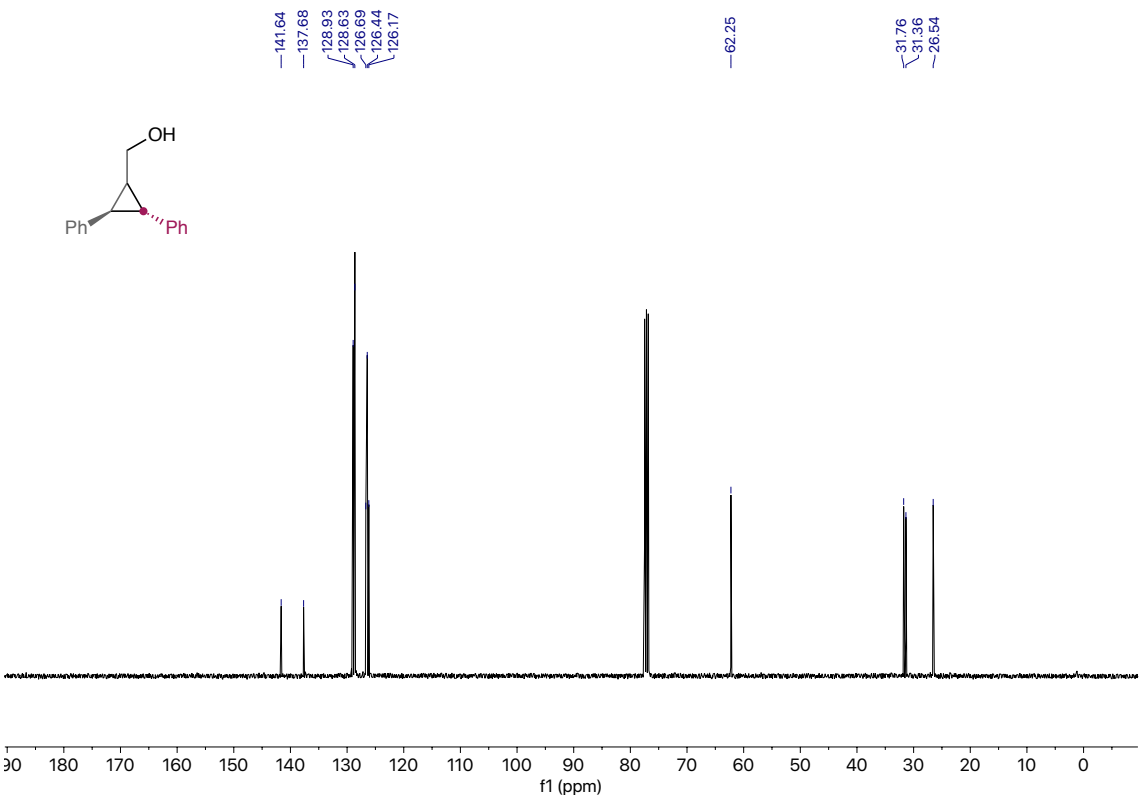
Ethyl (*exo*)-2,3-diphenylcyclopropane-1-carboxylate (1)



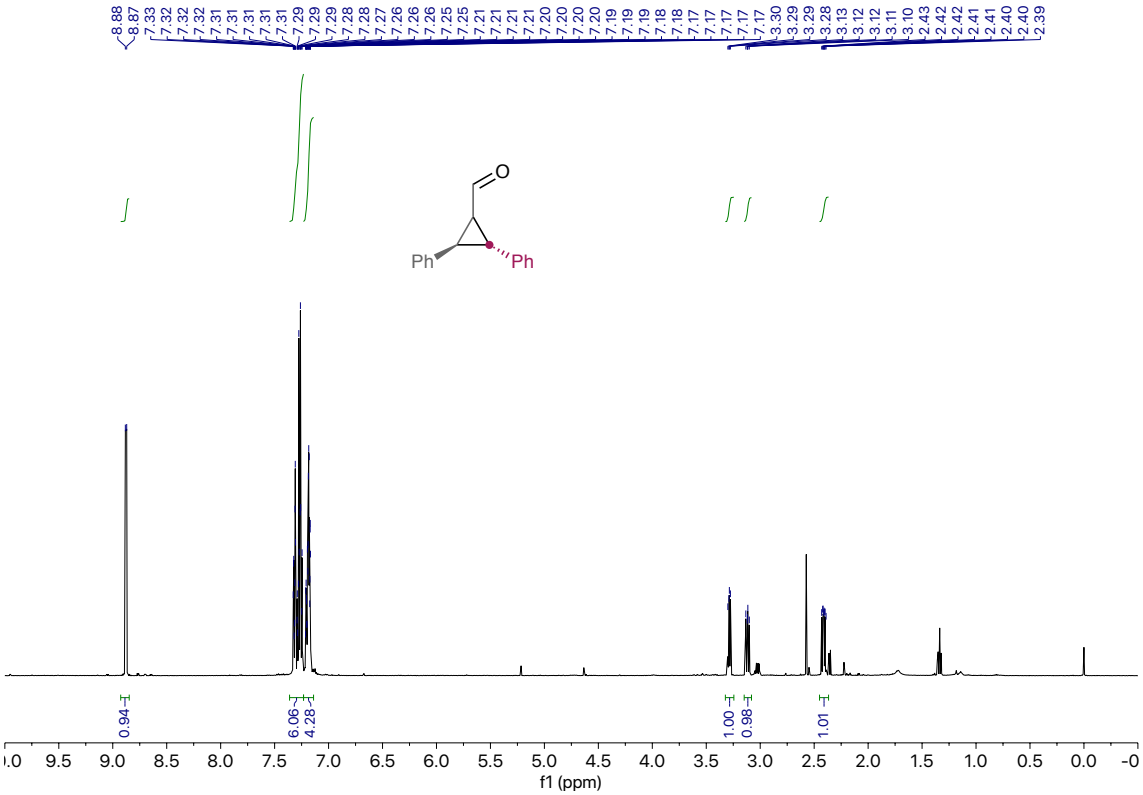


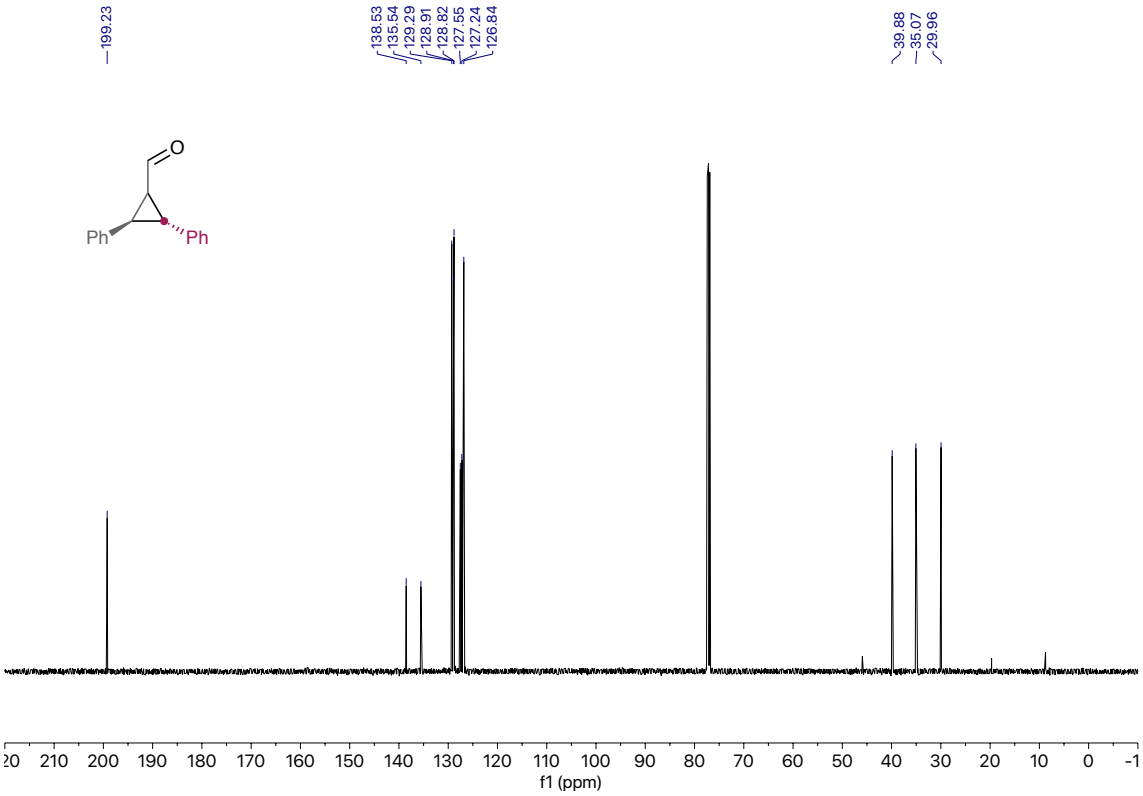
(*exo*)-(2,3-Diphenylcyclopropyl)methanol (S1)



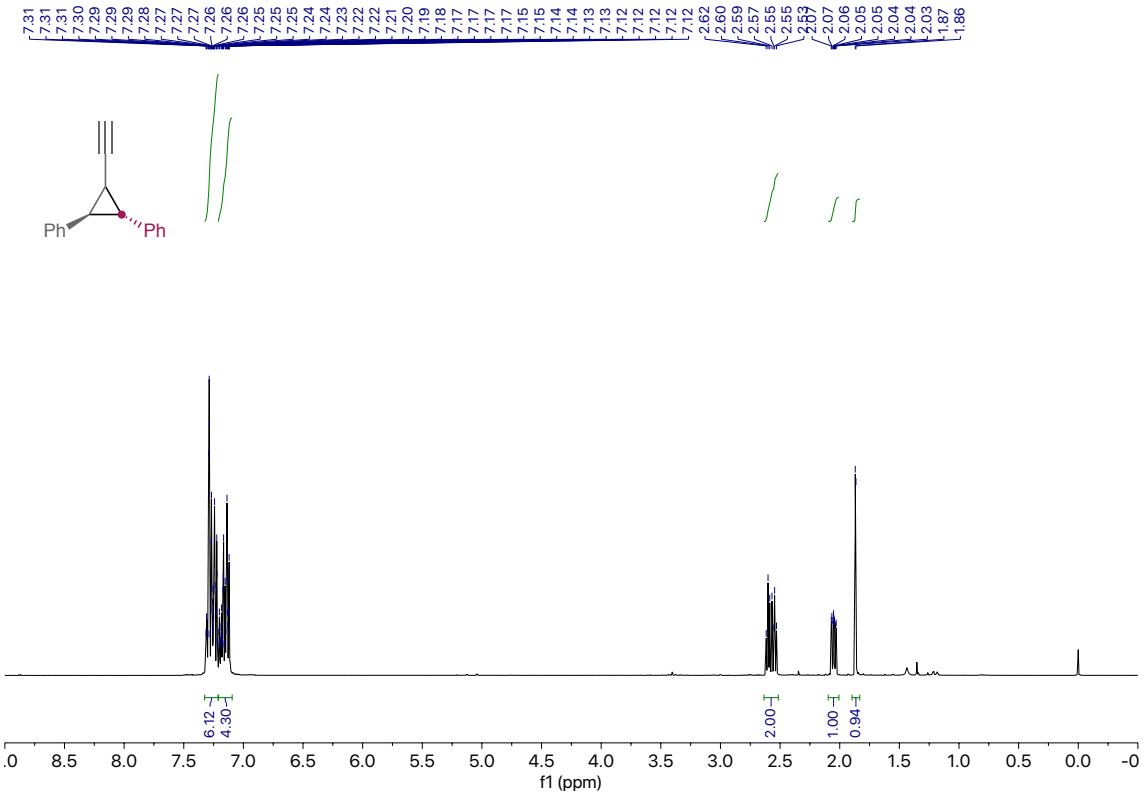


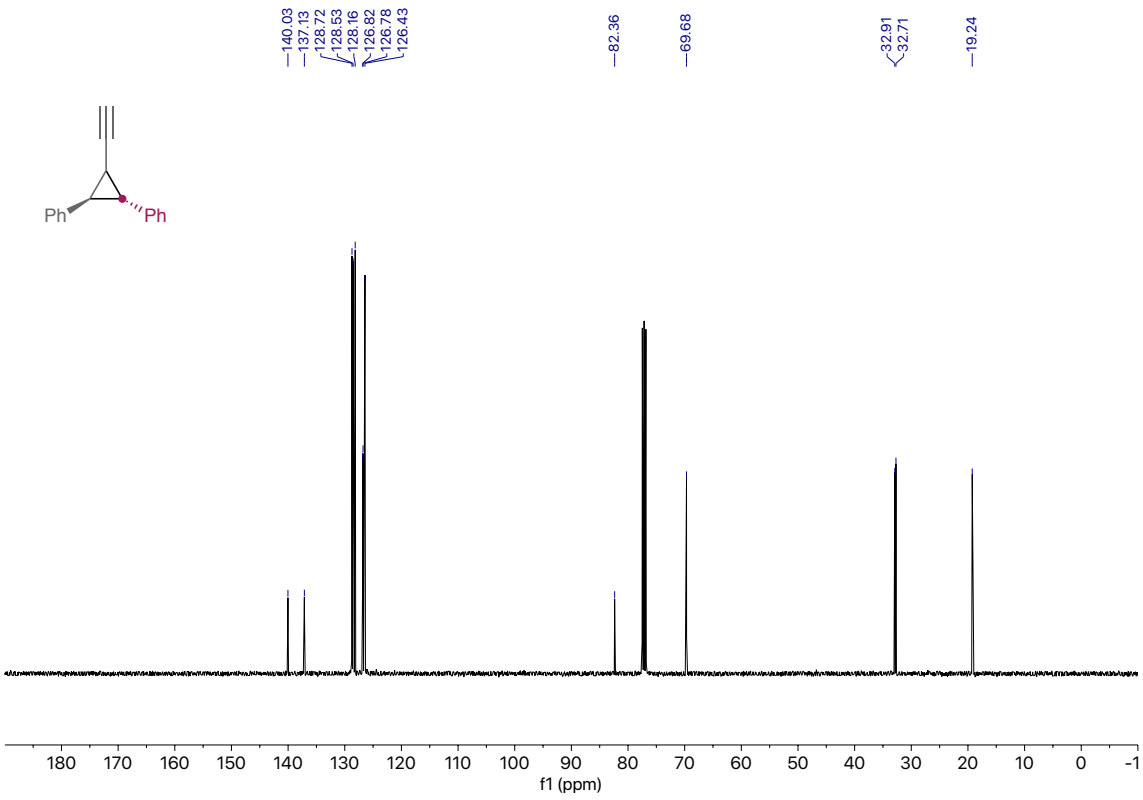
(*exo*)-2,3-Diphenylcyclopropane-1-carbaldehyde (2)



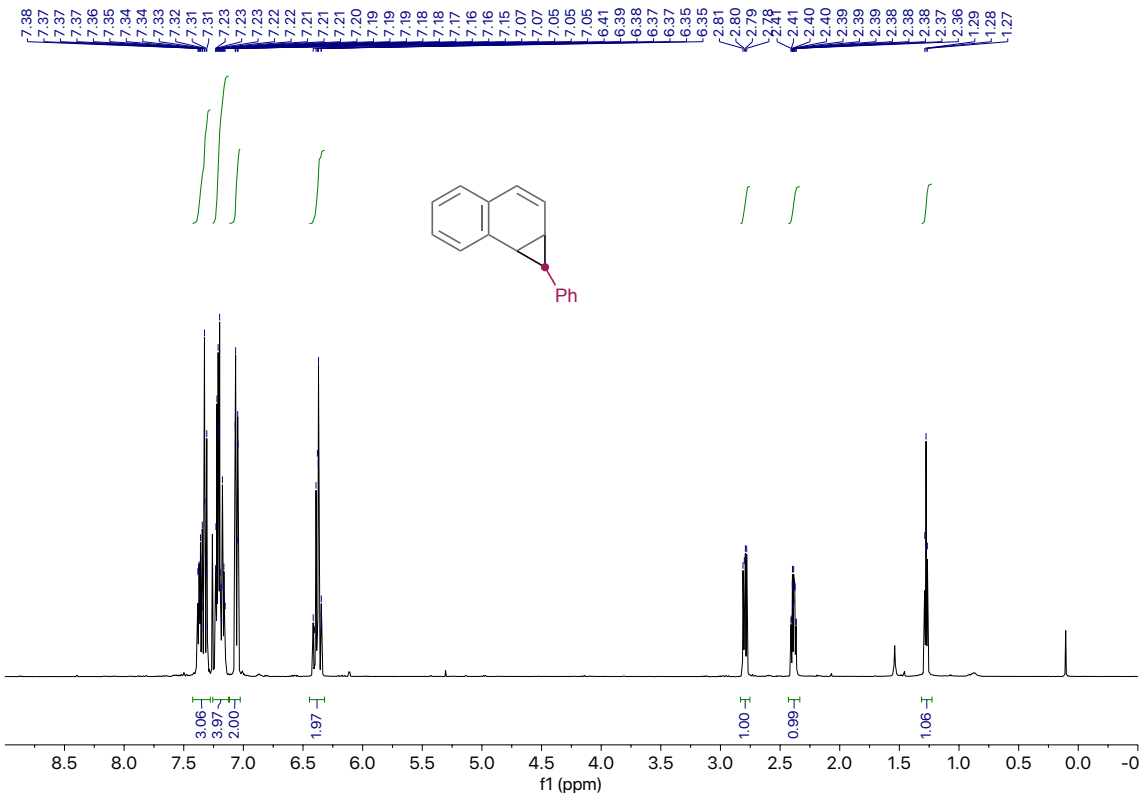


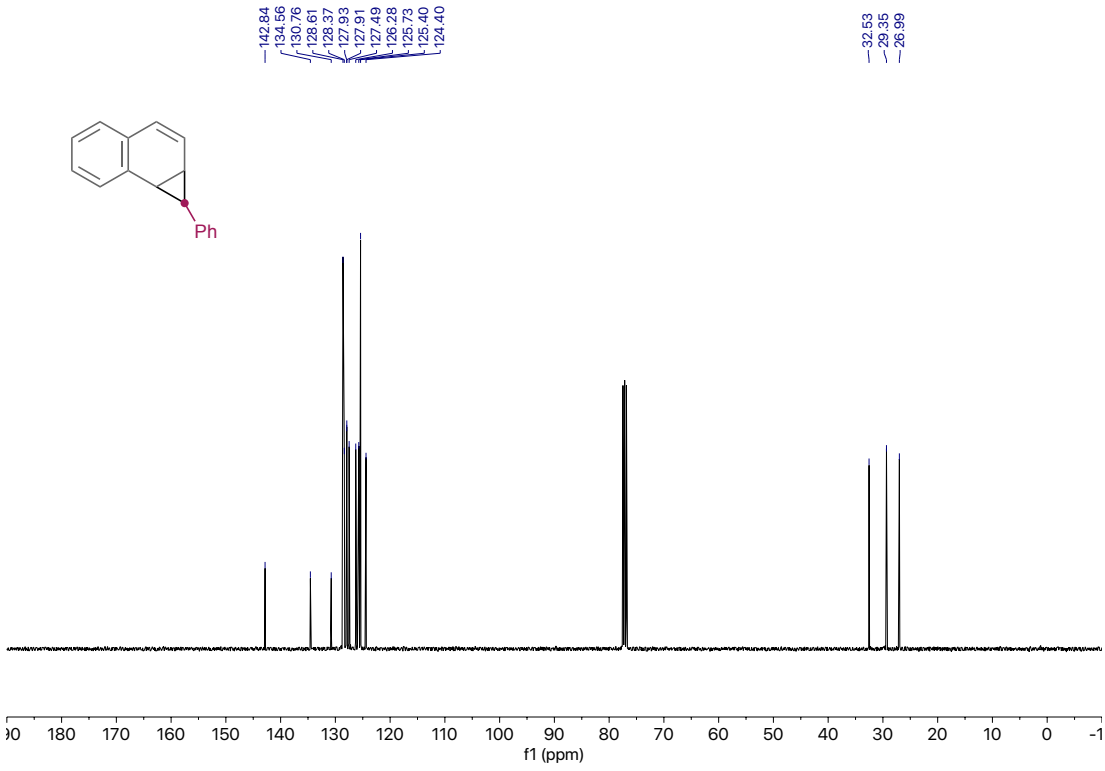
(*exo*)-(3-Ethynylcyclopropane-1,2-diyl)dibenzene (3)



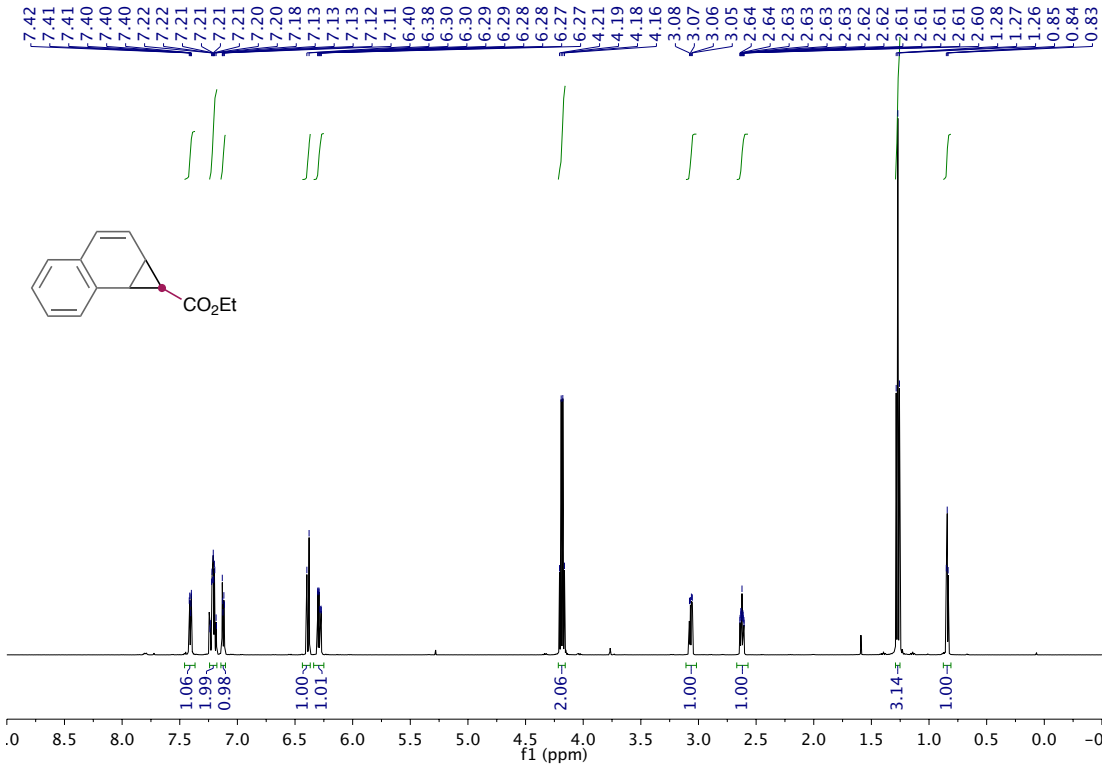


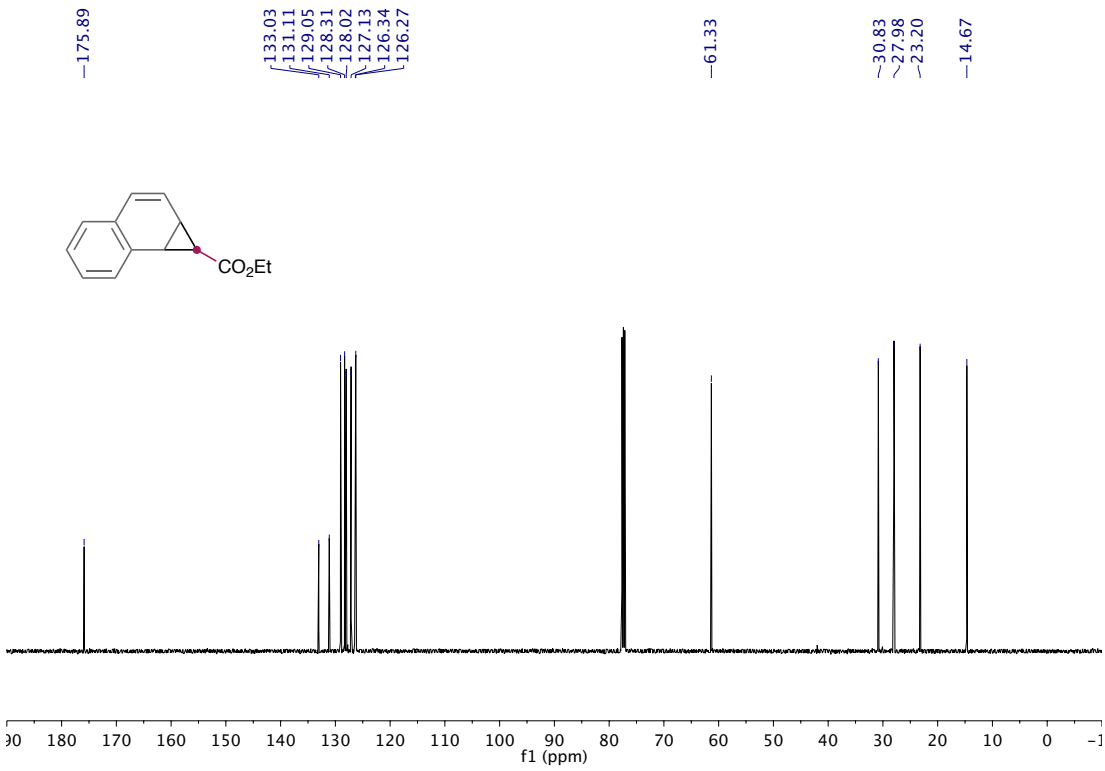
(*exo*)-1-Phenyl-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (4)



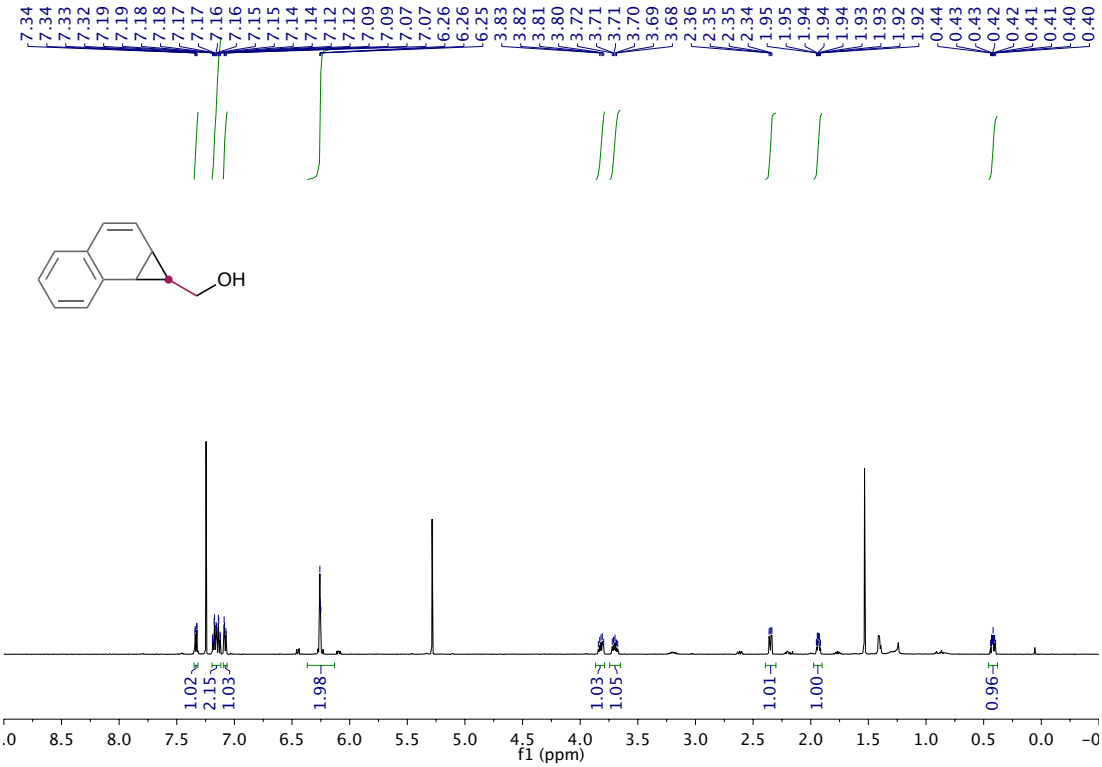


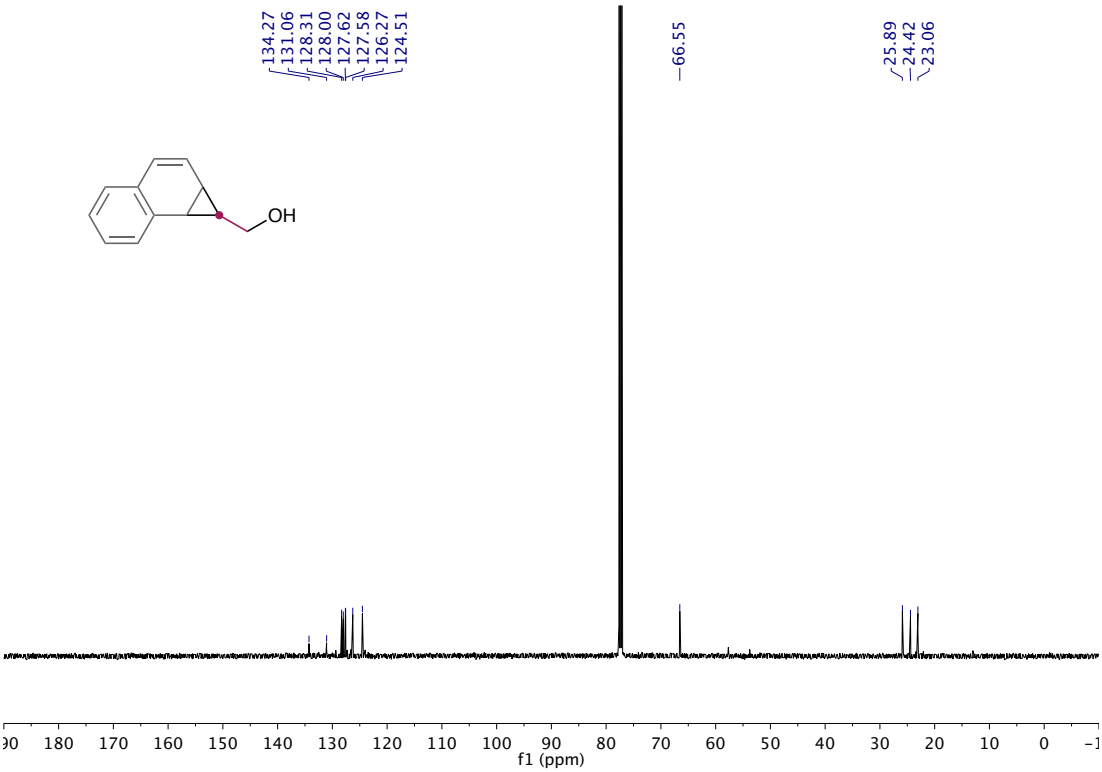
Ethyl (*exo*)-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene-1-carboxylate (S2)



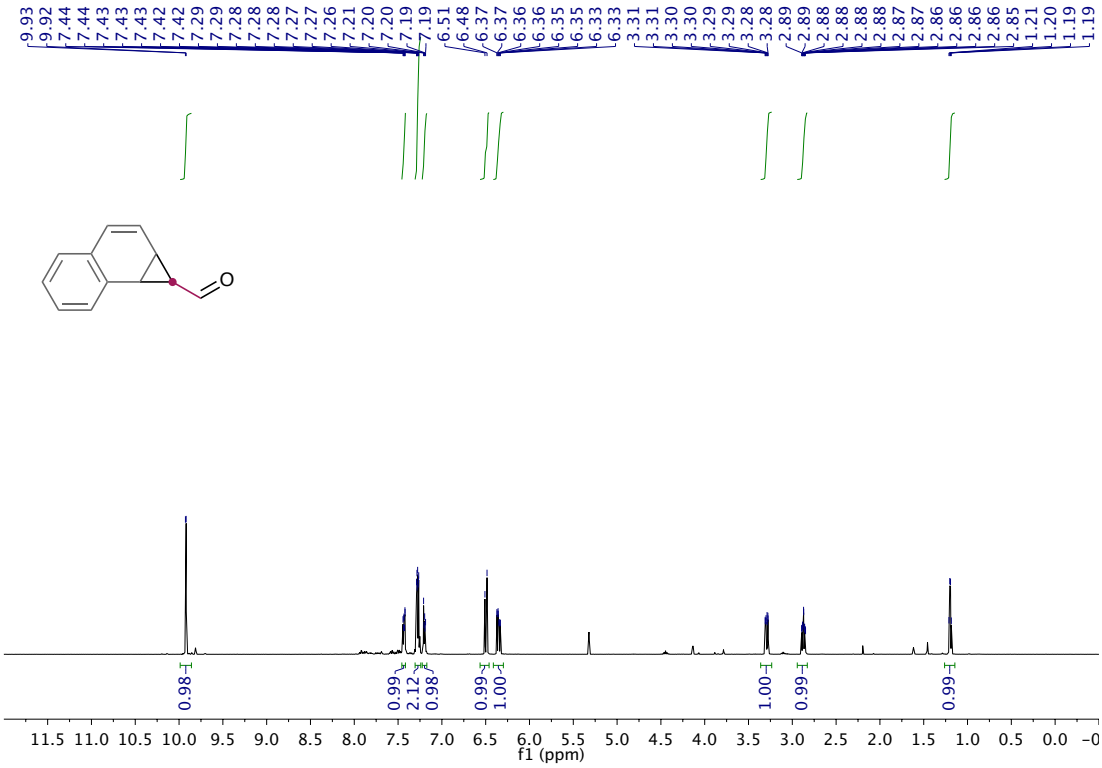


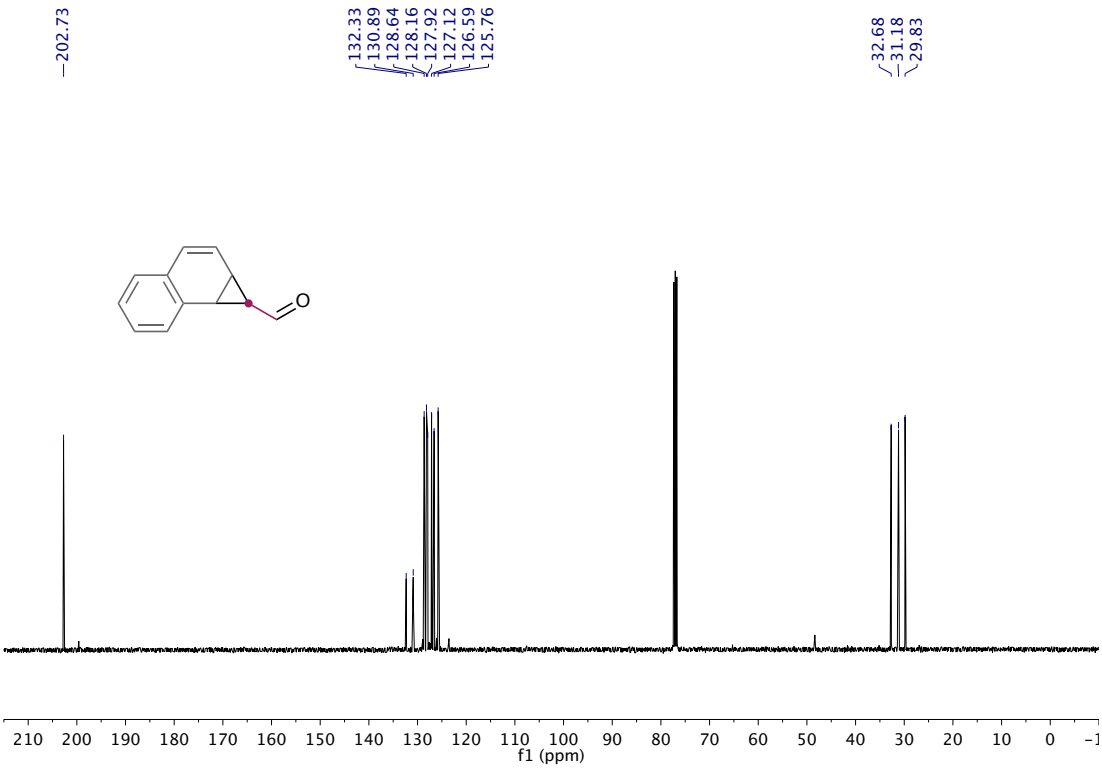
(*exo*)-(1a,7b-Dihydro-1*H*-cyclopropa[*a*]naphthalen-1-yl)methanol (S3)



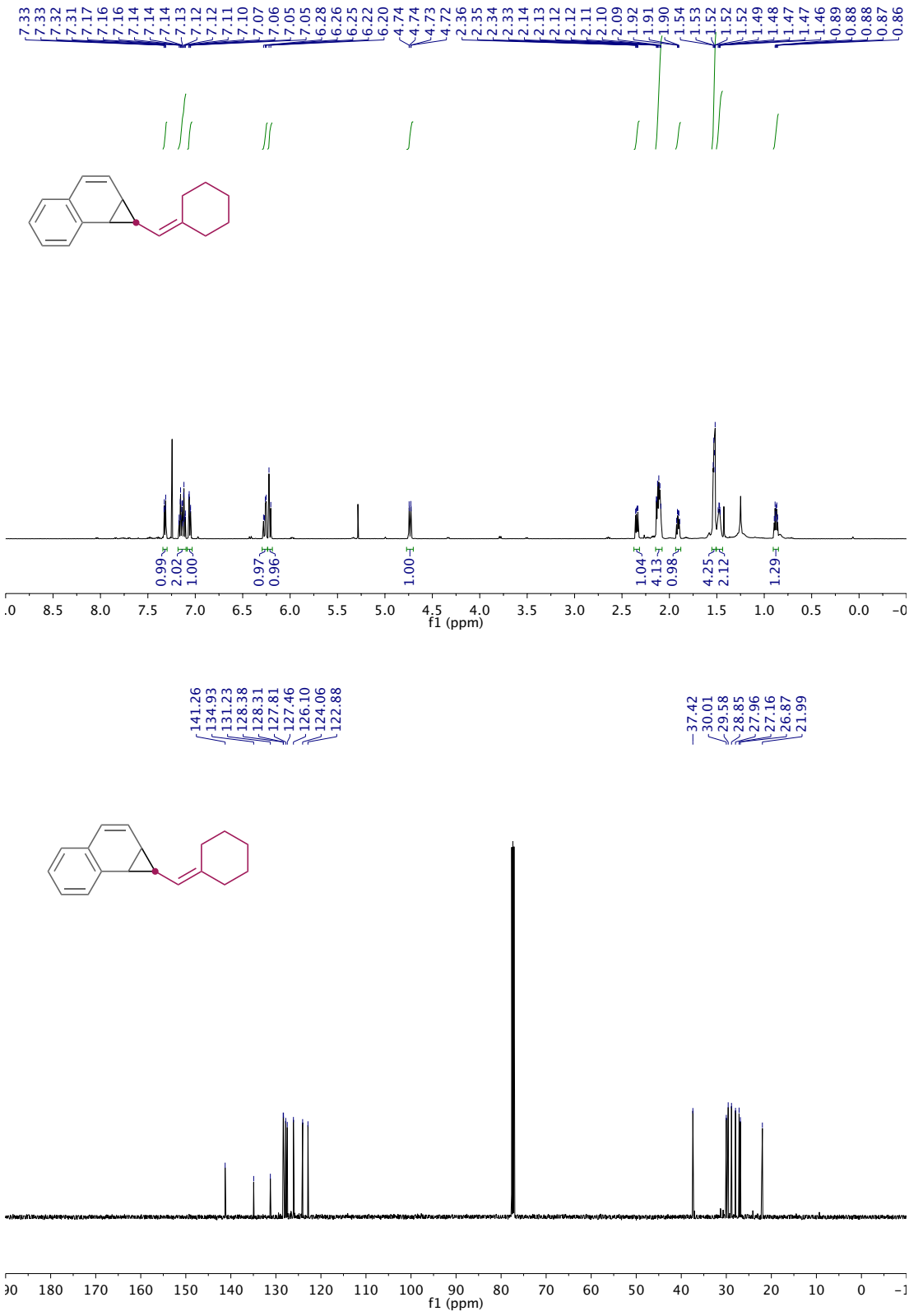


(*exo*)-1a,7b-Dihydro-1*H*-cyclopropa[*a*]naphthalene-1-carbaldehyde (5)

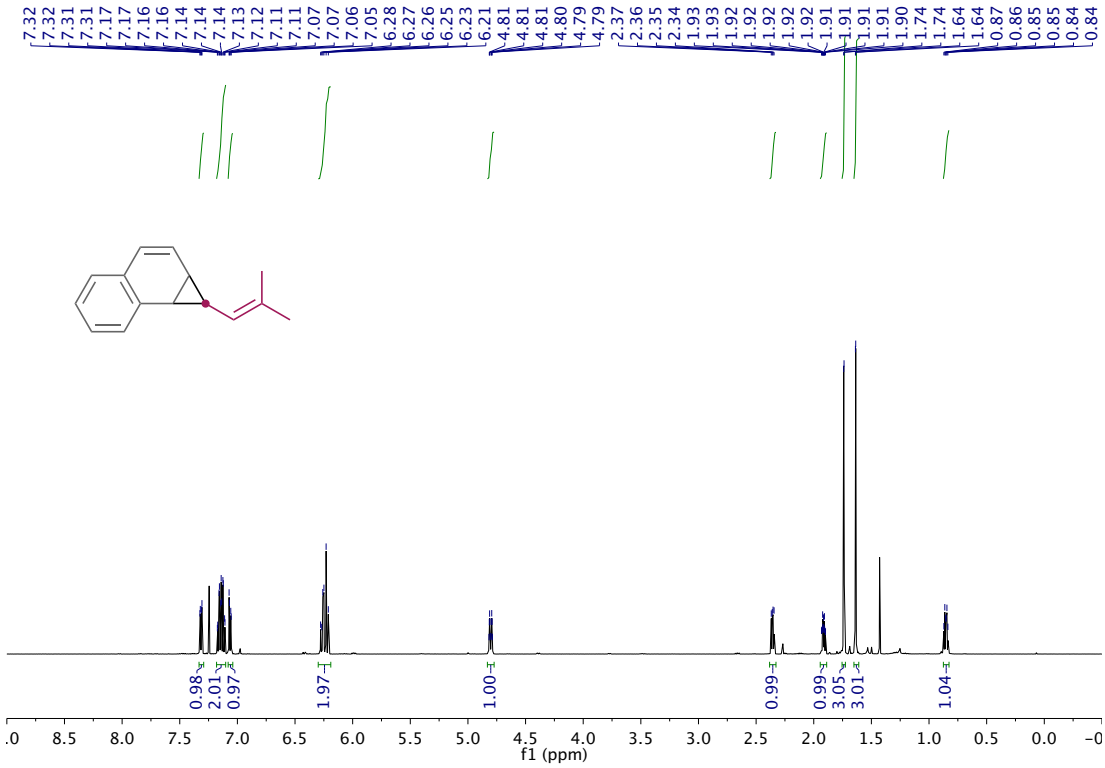


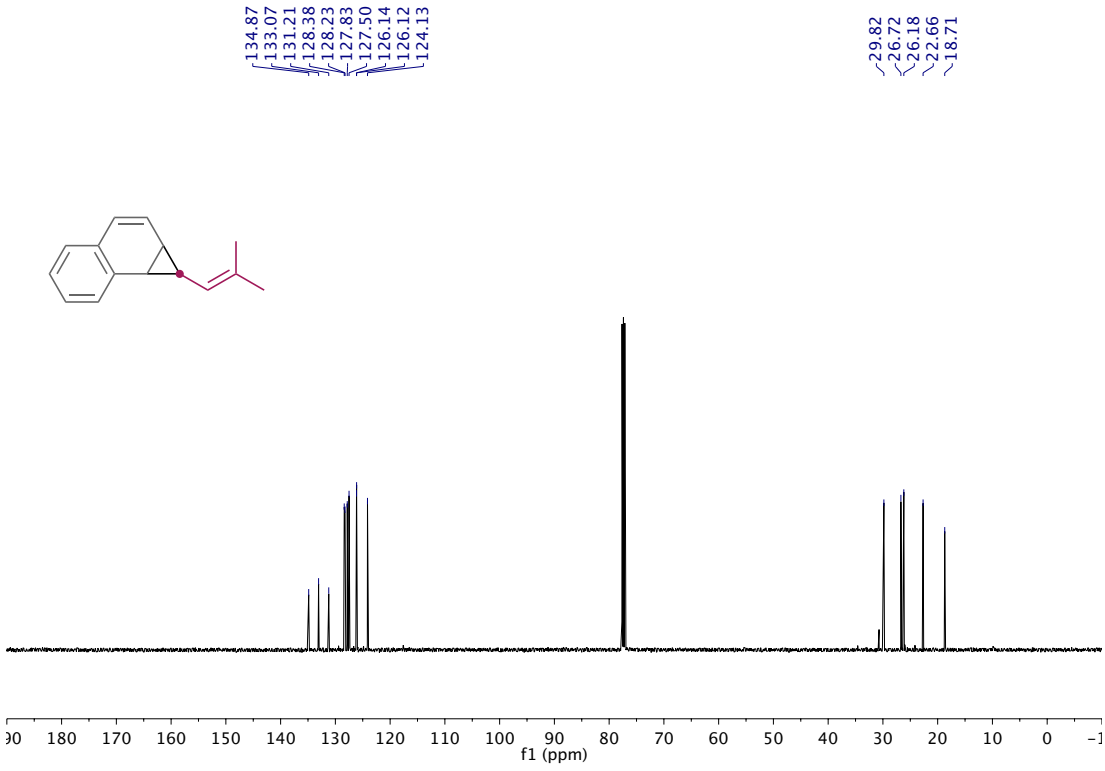


(*exo*)-1-(Cyclohexylidenemethyl)-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (6a)

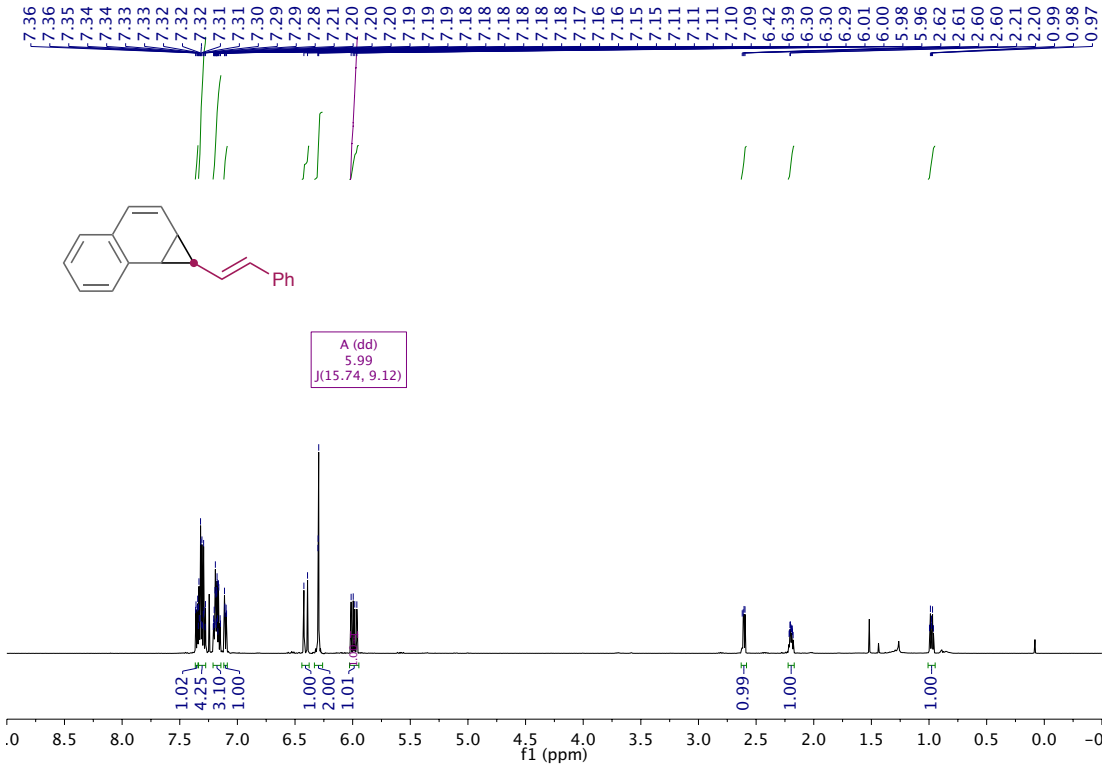


(*exo*)-1-(2-Methylprop-1-en-1-yl)-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (6b)

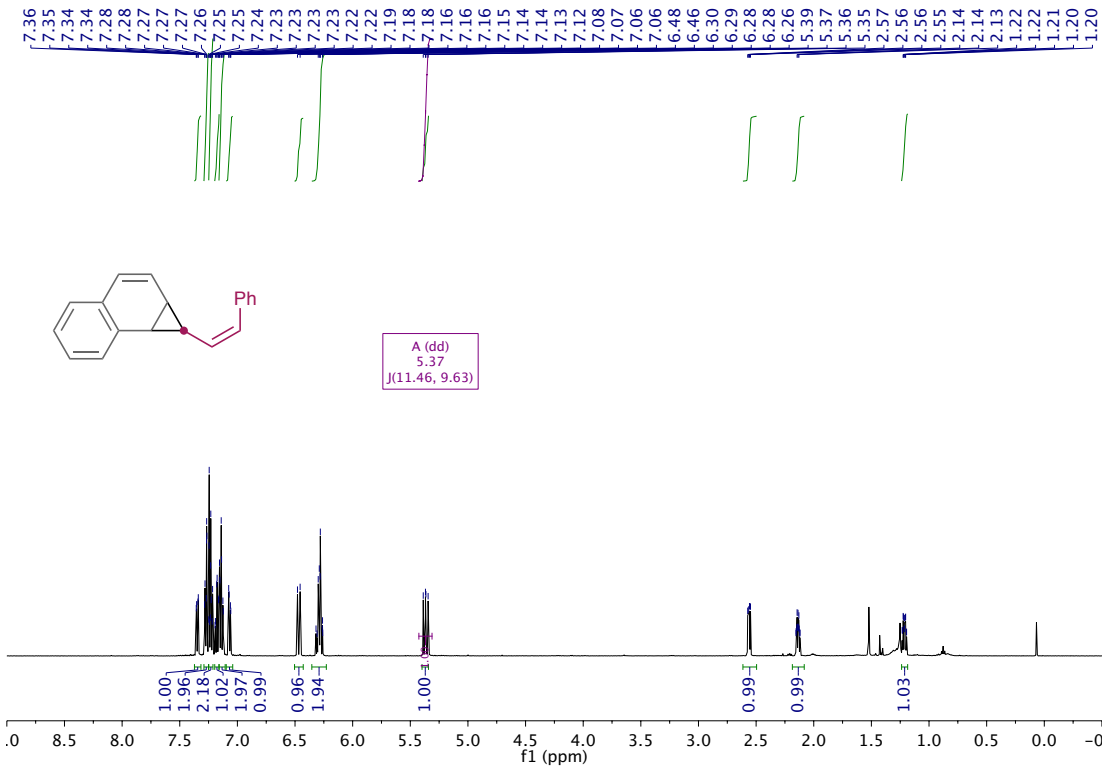




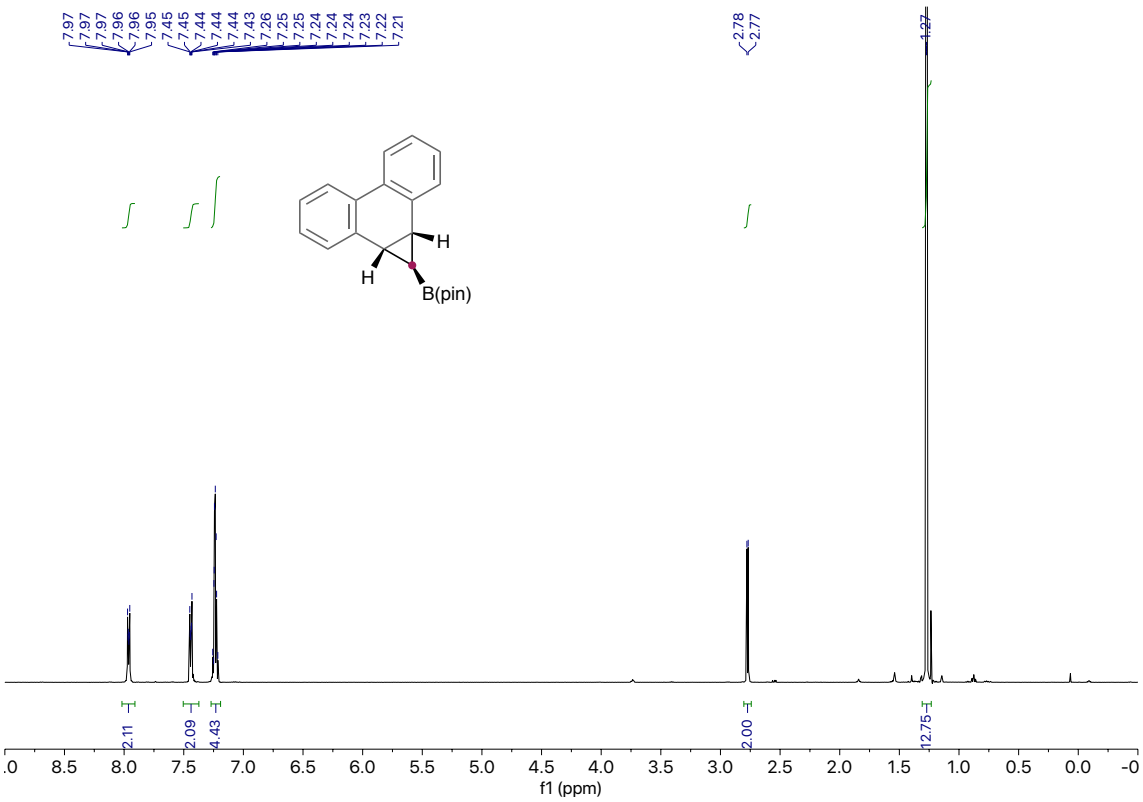
(*exo*)-1-((*E*)-Styryl)-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (6c)

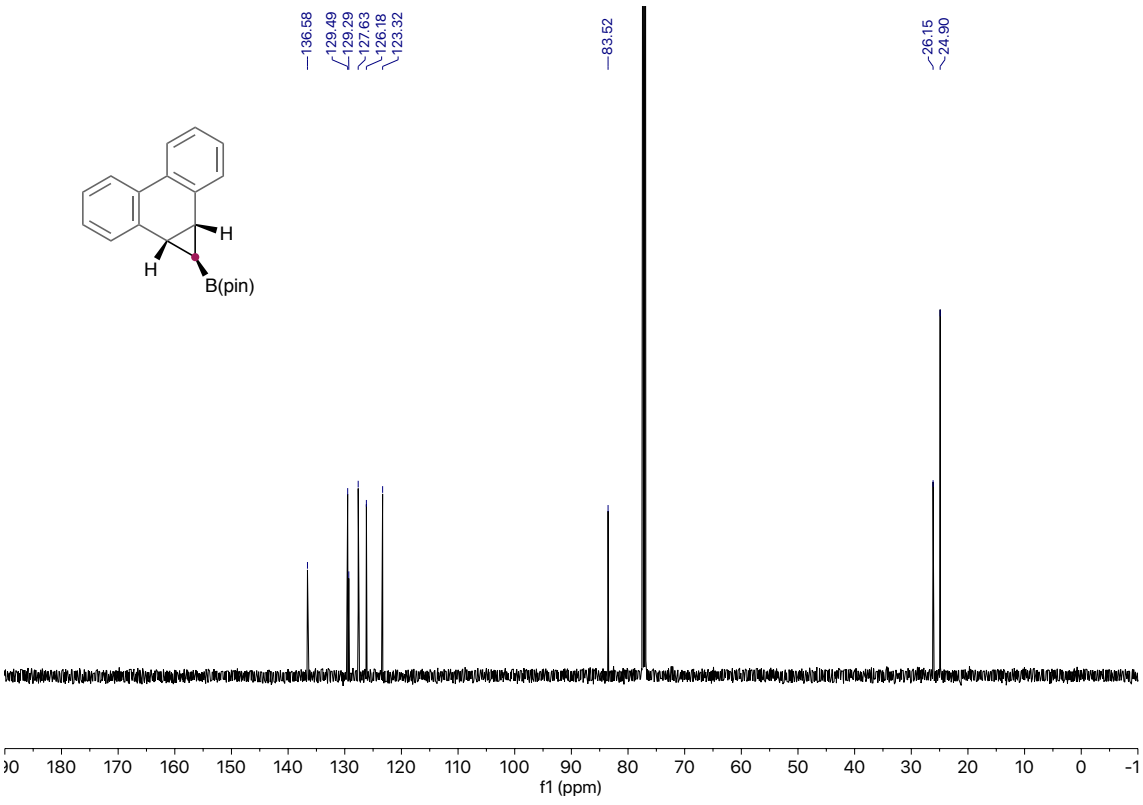


(*exo*)-1-((*Z*)-Styryl)-1a,7b-dihydro-1*H*-cyclopropa[*a*]naphthalene (6d)

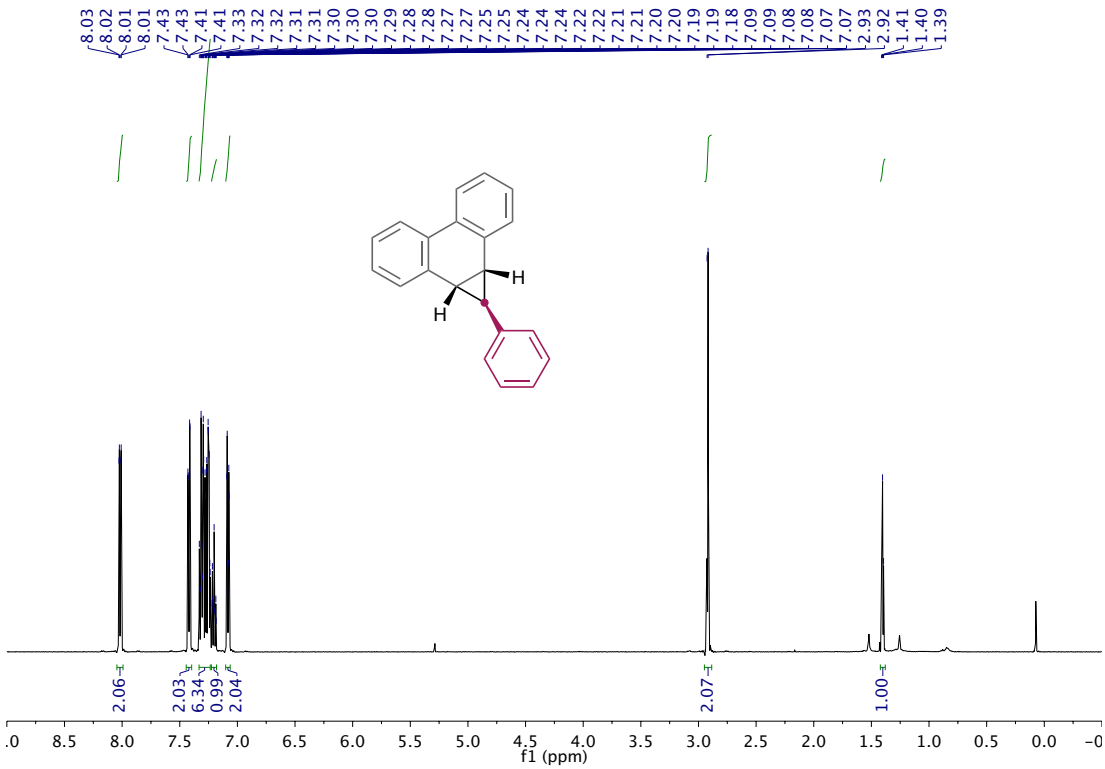


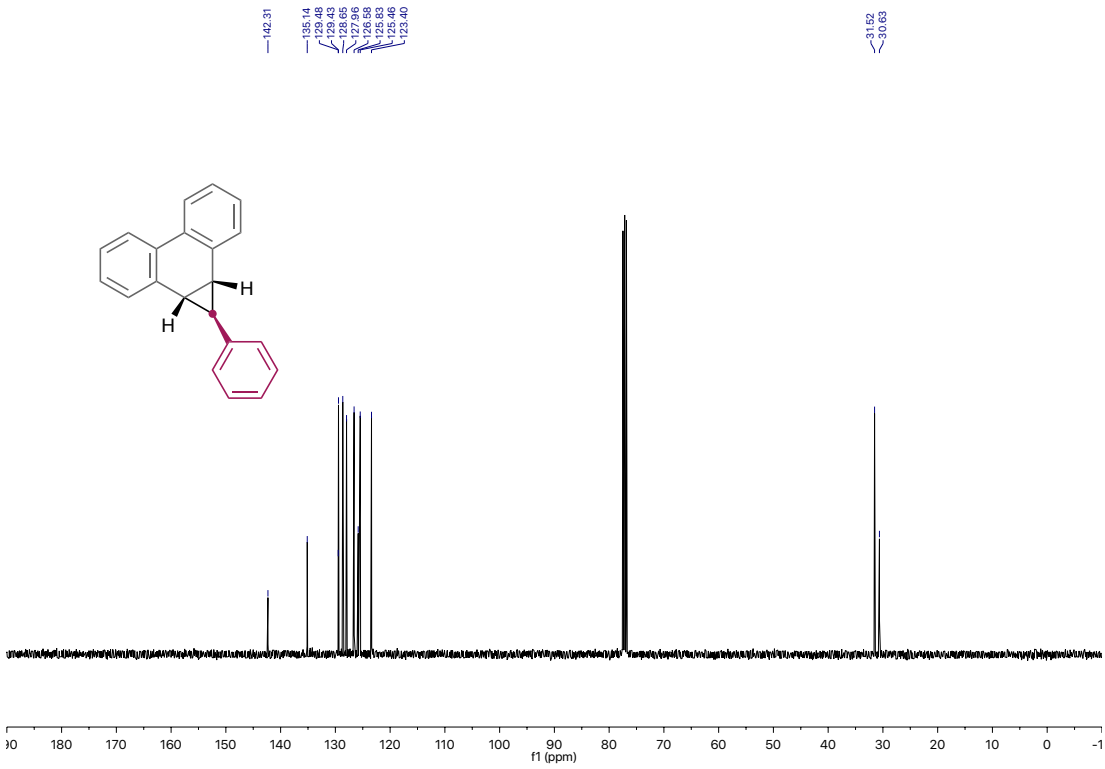
2-(1a,9b-Dihydro-1*H*-cyclopropa[*l*]phenanthren-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11)



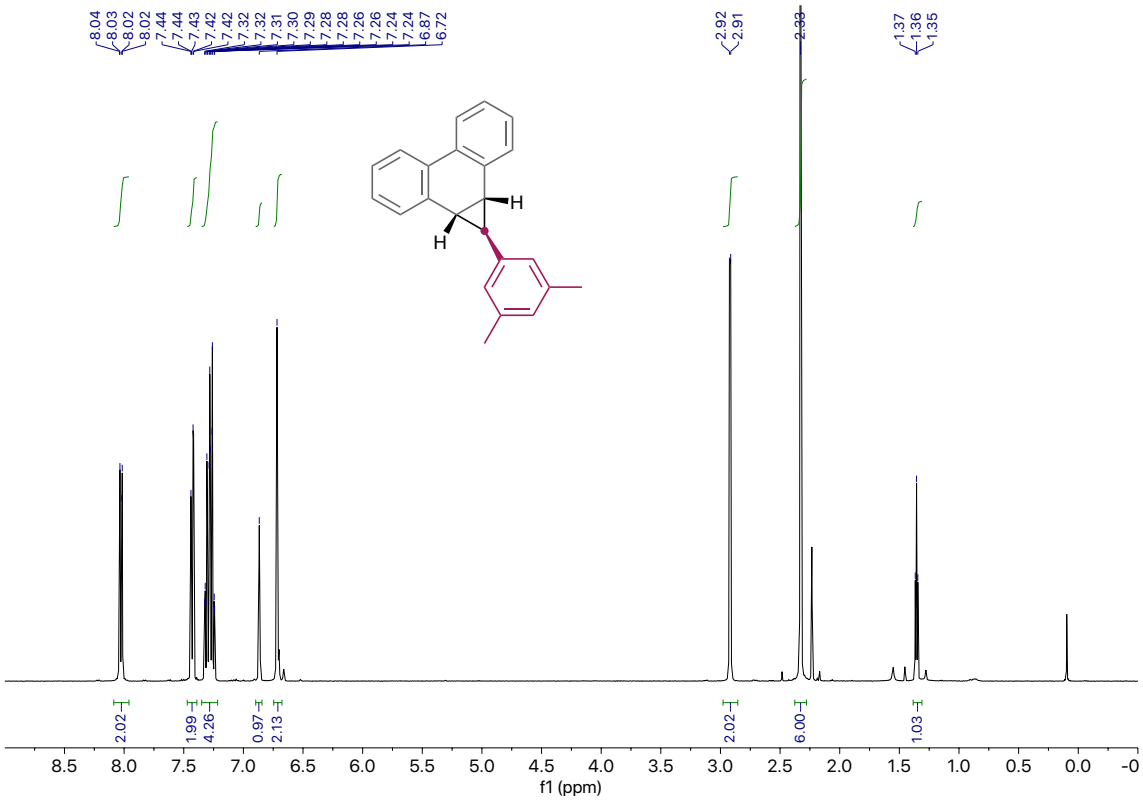


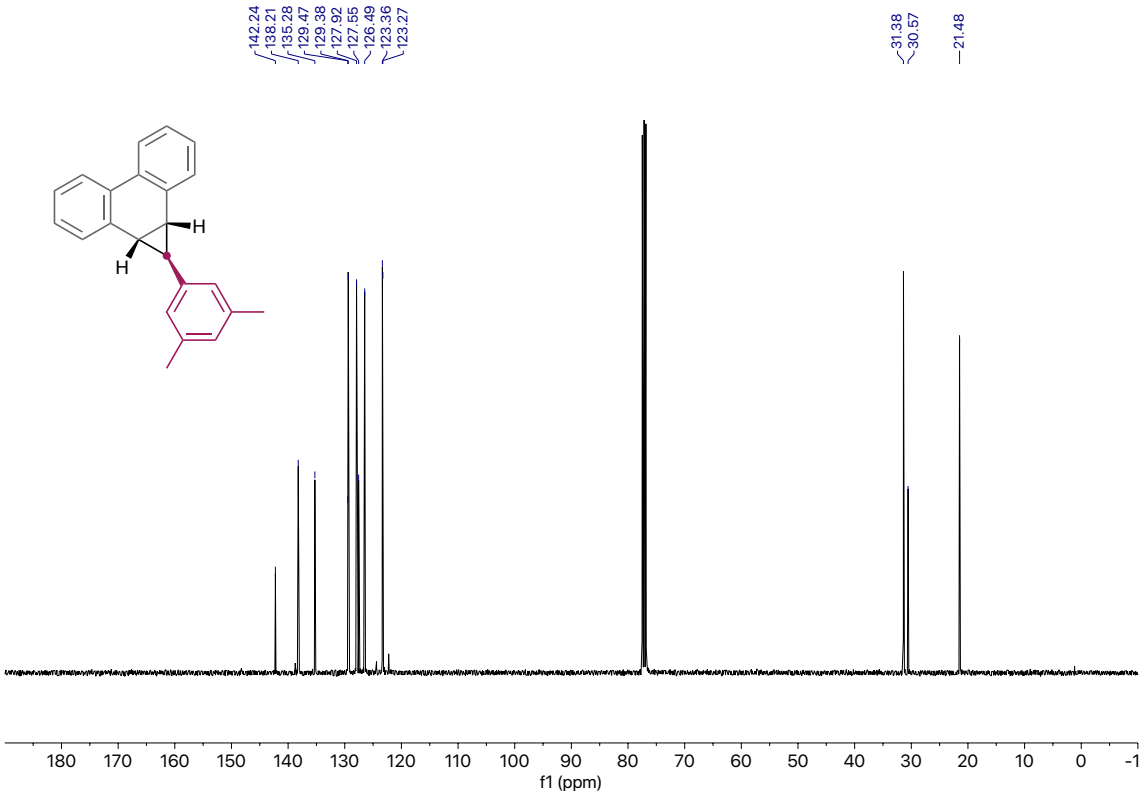
(*exo*)-1-Phenyl-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (12a)



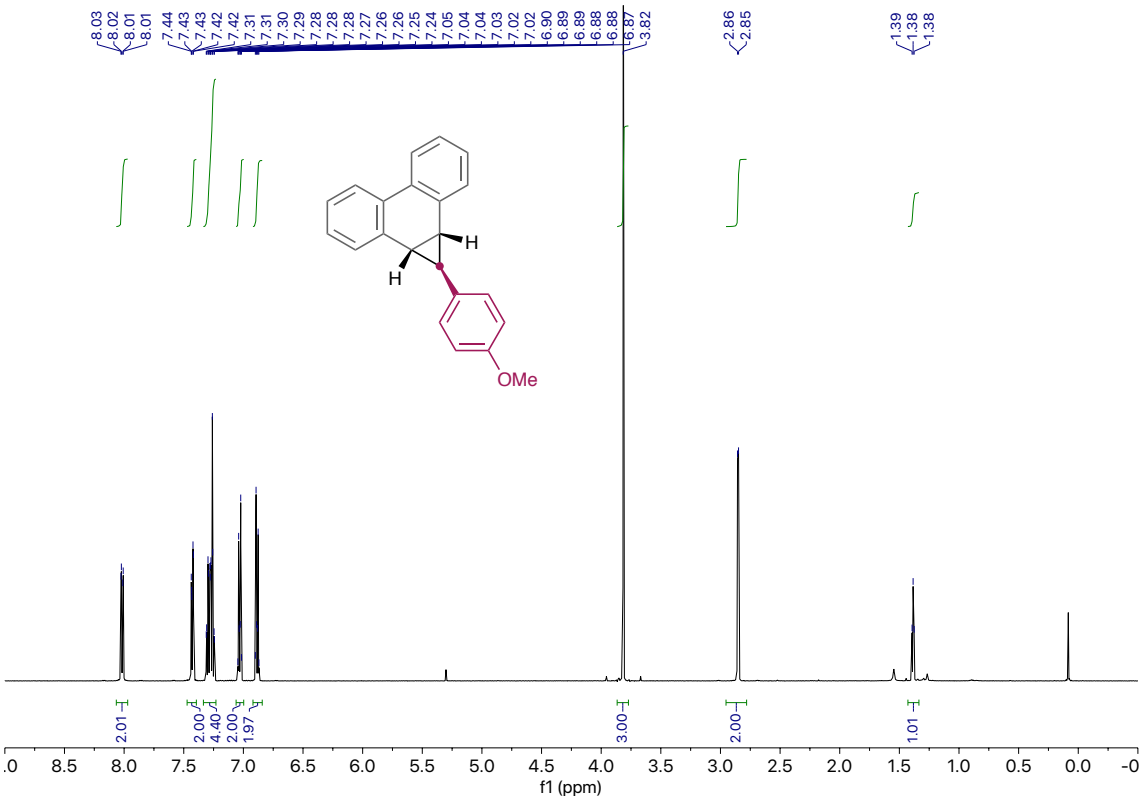


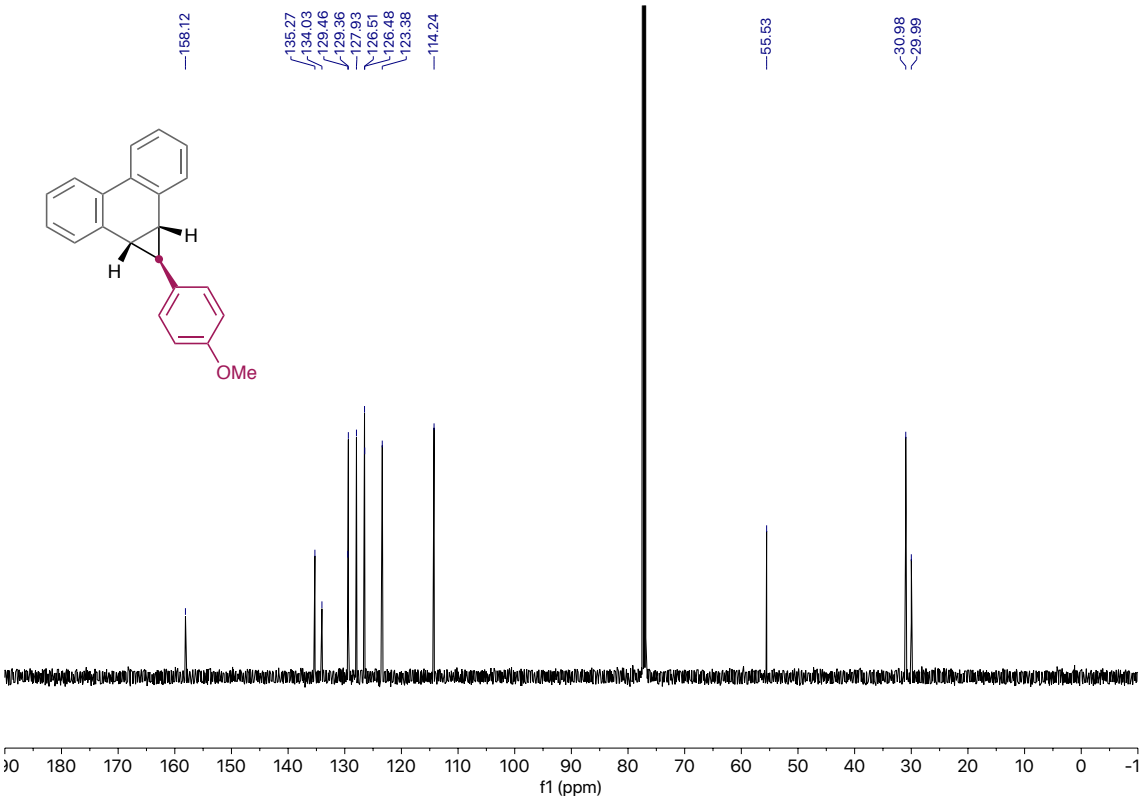
(*exo*)-1-(3,5-Dimethylphenyl)-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (12b)



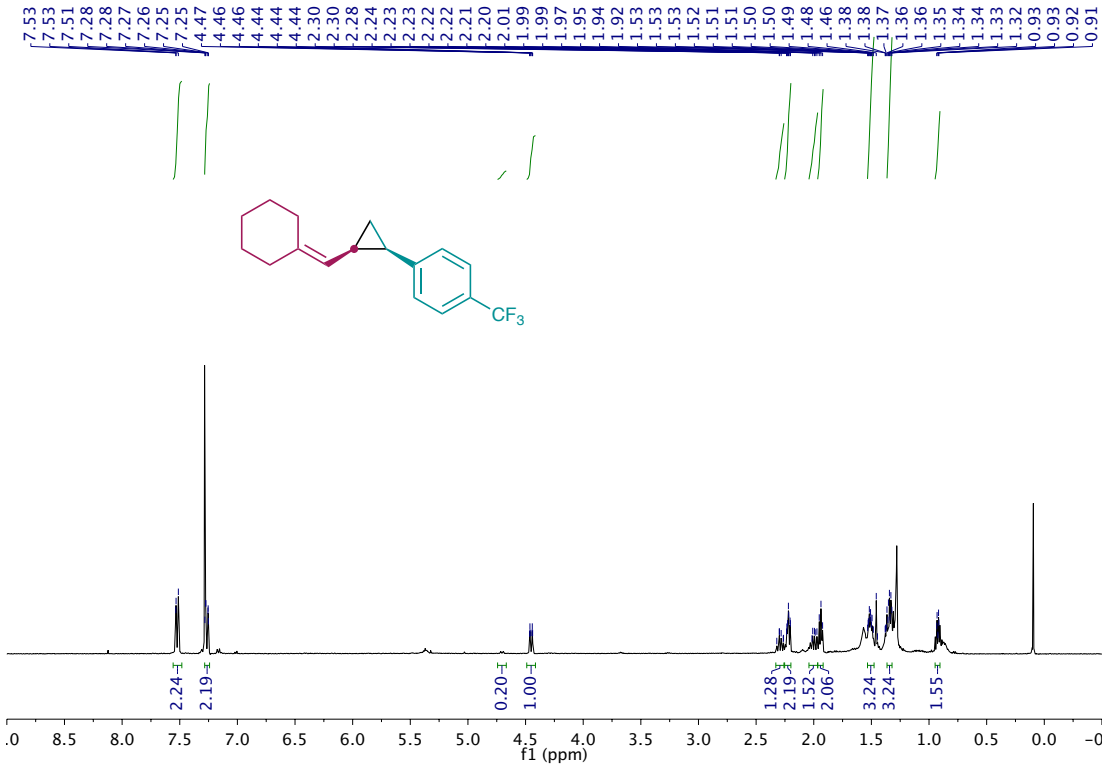


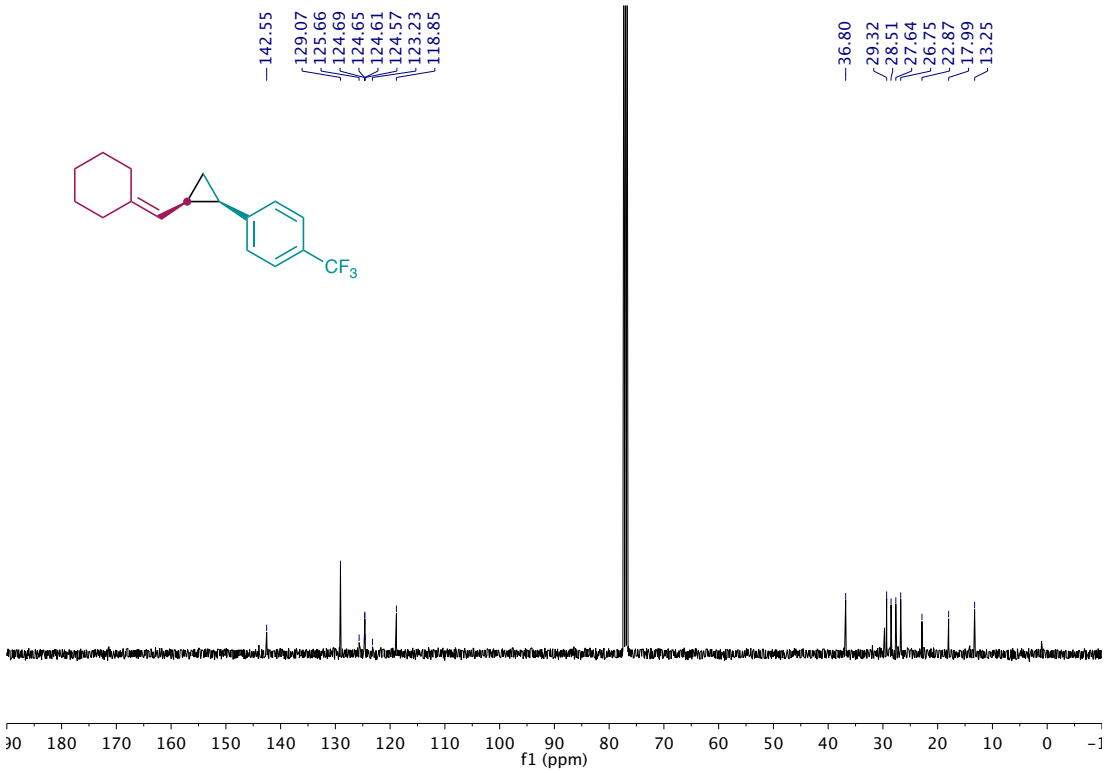
(*exo*)-1-(4-Methoxyphenyl)-1a,9b-dihydro-1*H*-cyclopropa[*l*]phenanthrene (12c)



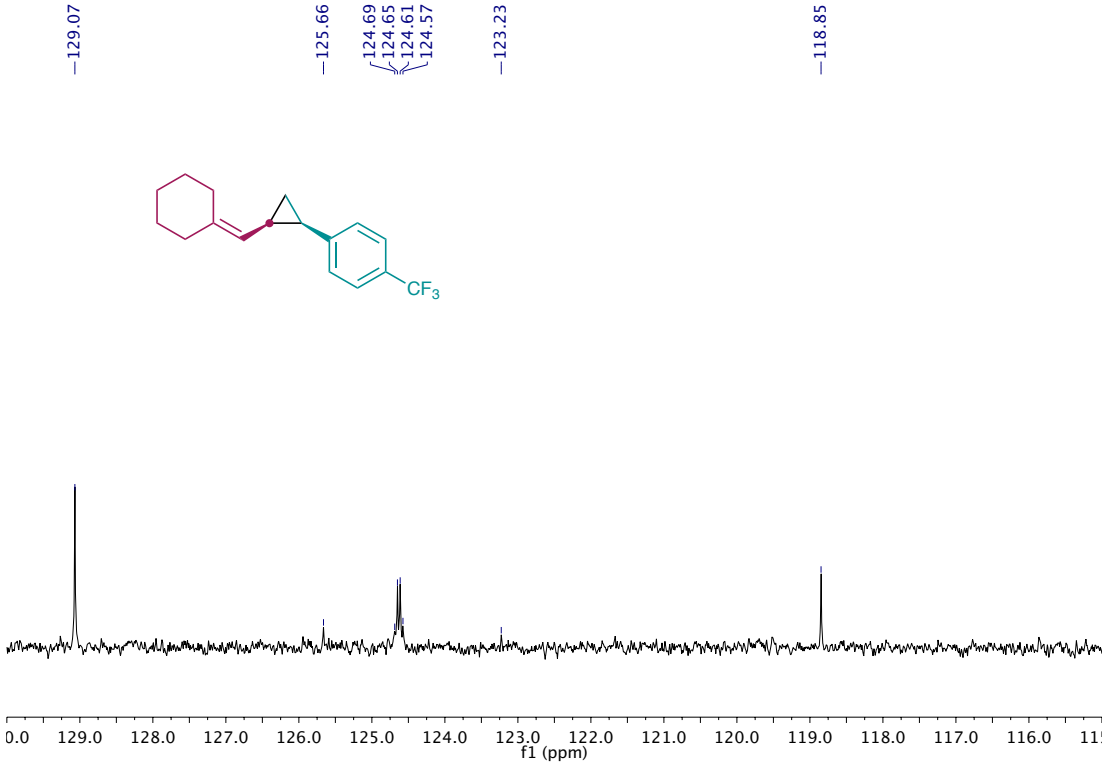


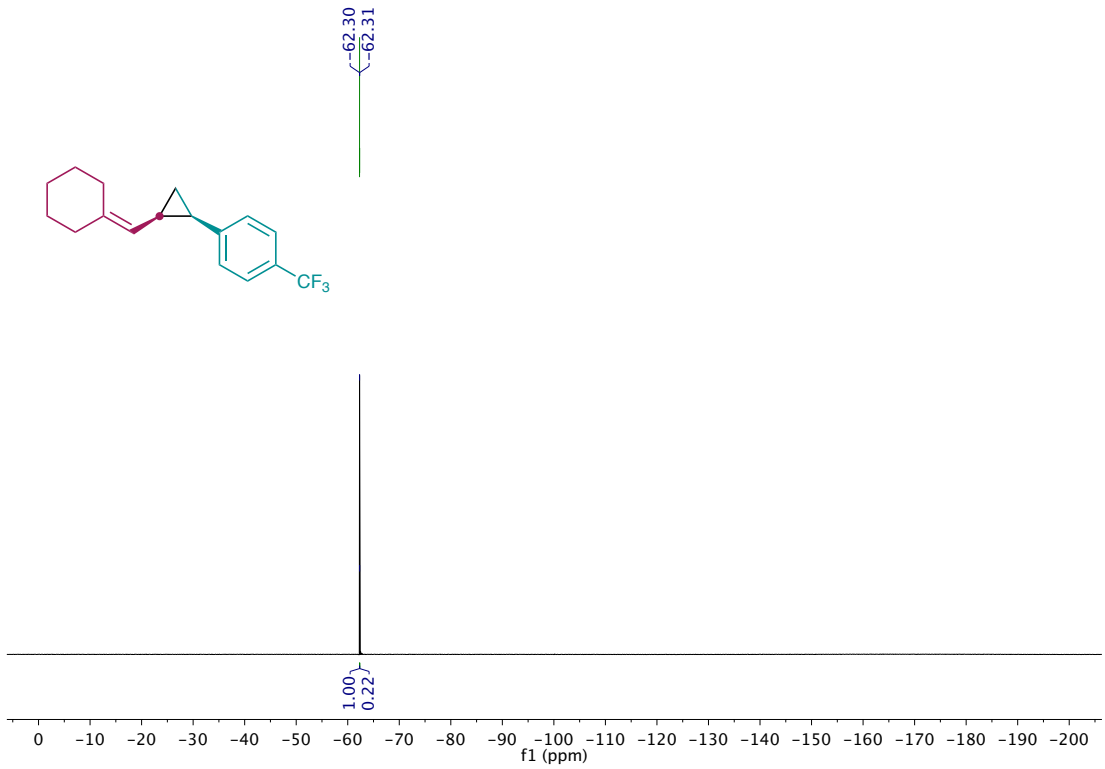
(*cis*)-1-(2-(Cyclohexylidenemethyl)cyclopropyl)-4-(trifluoromethyl)benzene (9a)



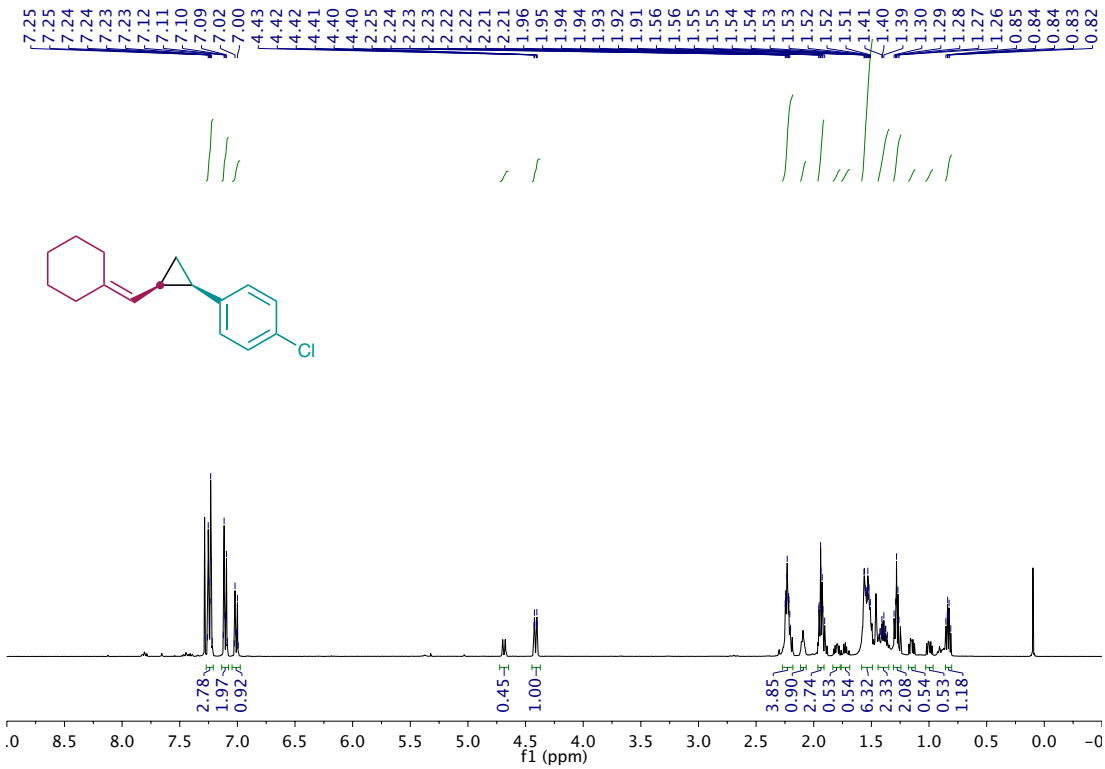


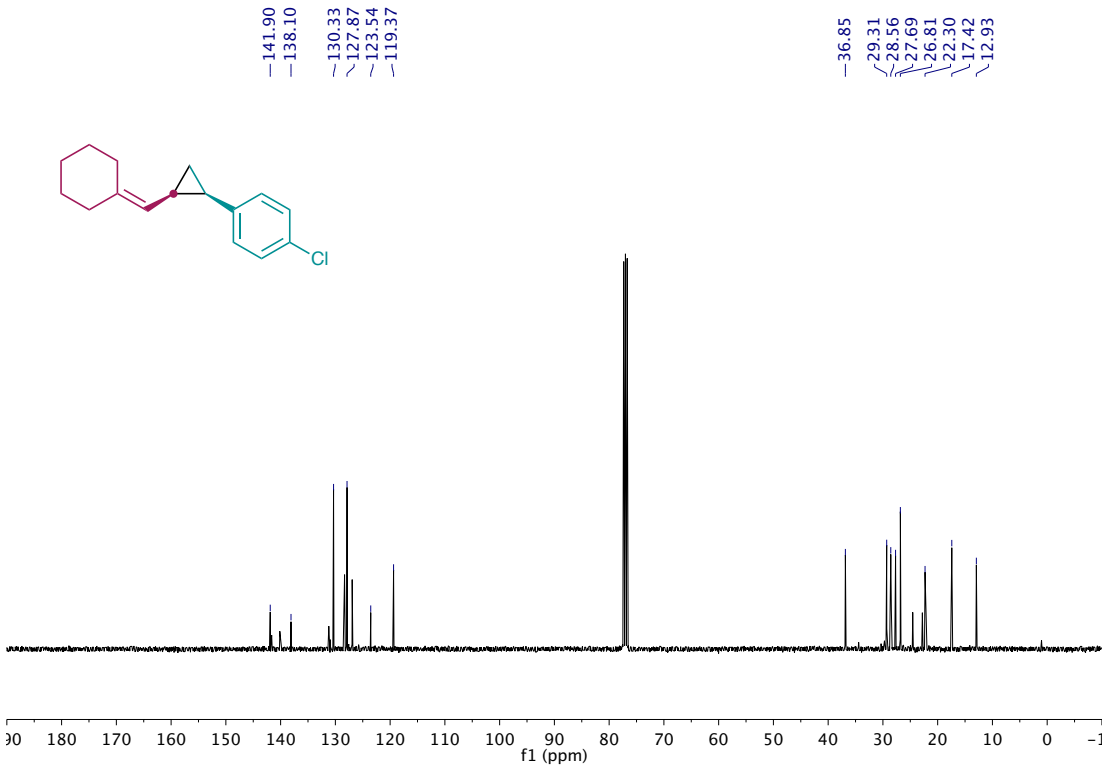
^{13}C detail and ^{19}F



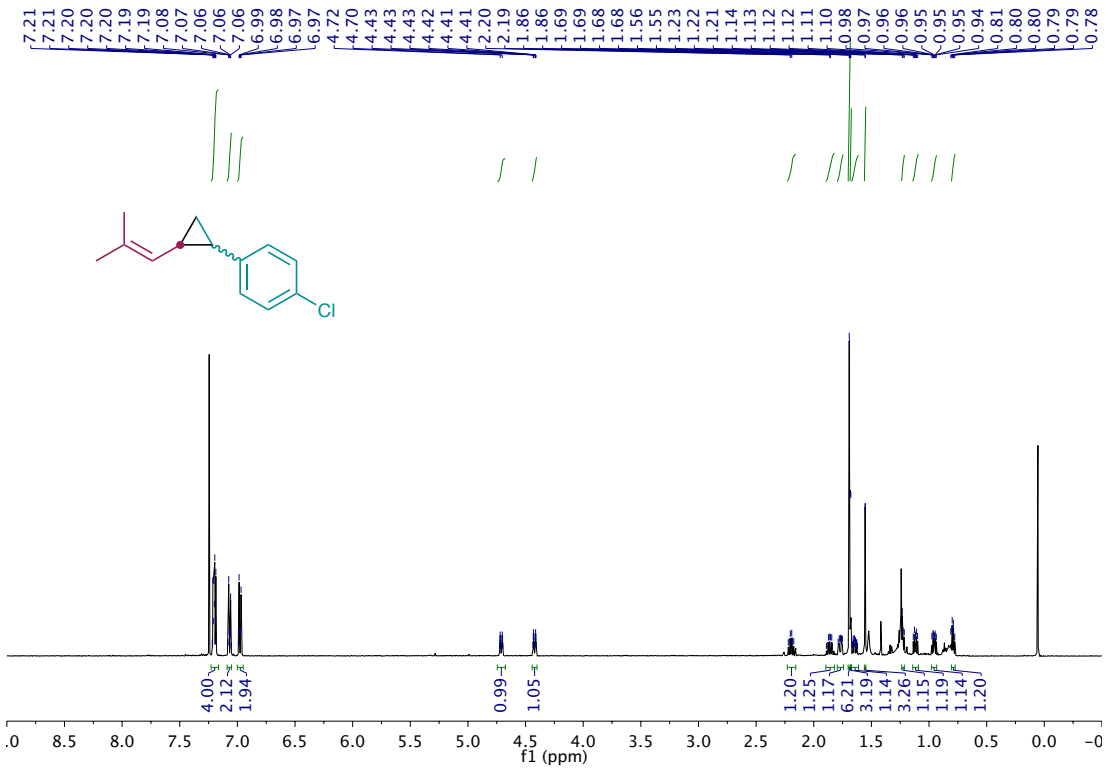


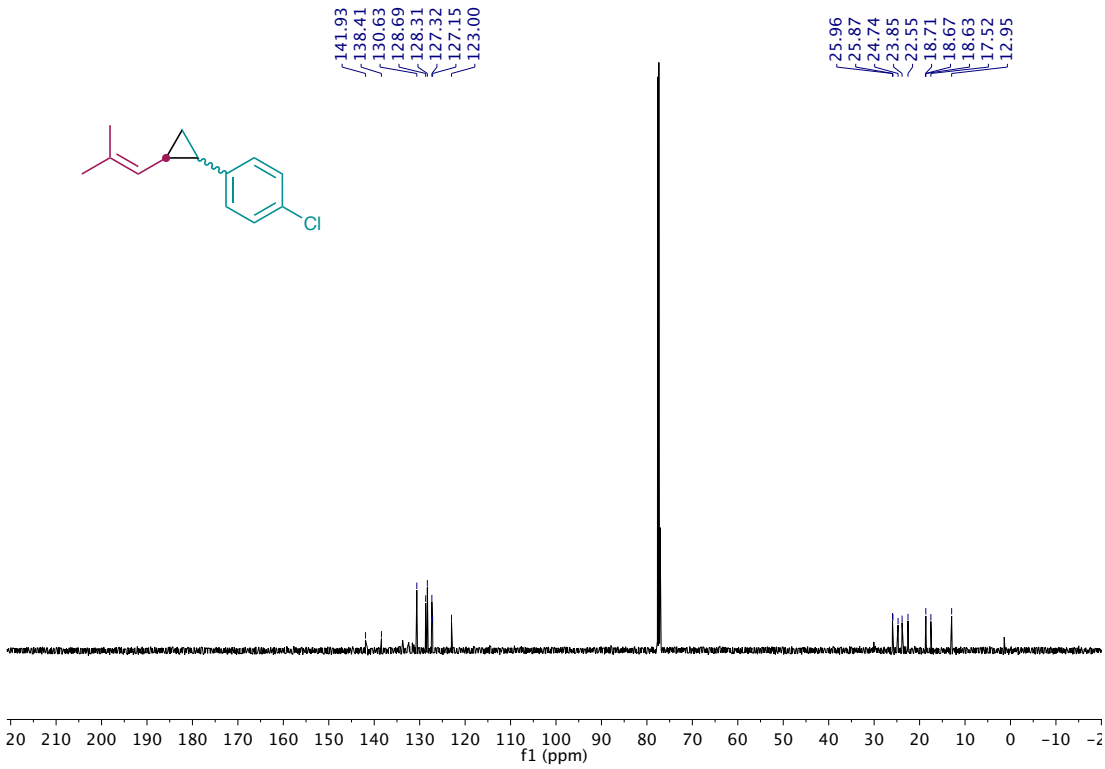
(*cis*)-1(2-(Cyclohexylidenemethyl)cyclopropyl)-4-chlorobenzene (9b)



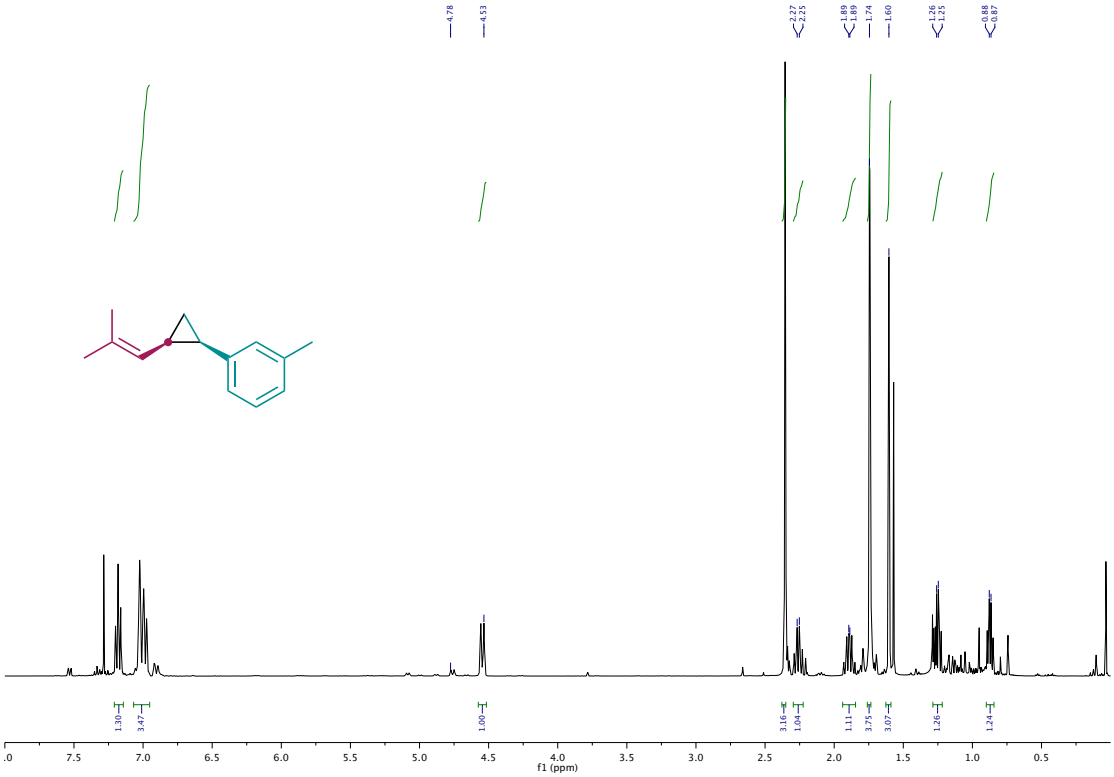


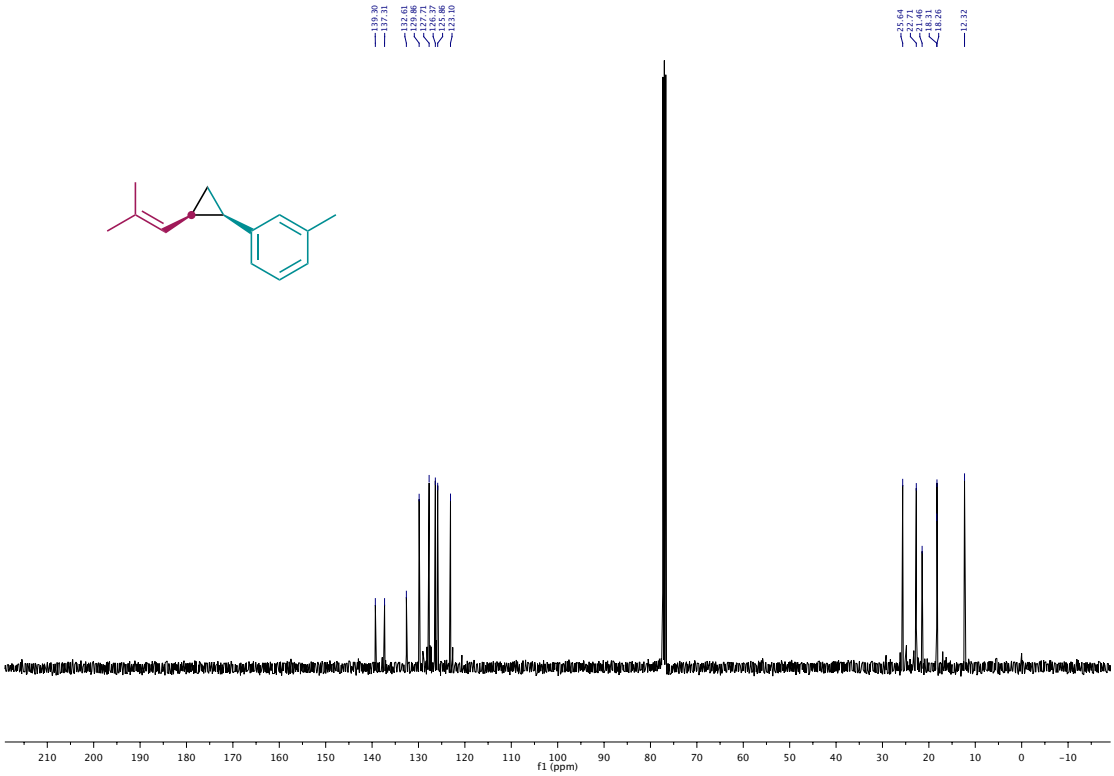
1-Chloro-4-(2-(2-methylprop-1-en-1-yl)cyclopropyl)benzene (9c) (1:1 d.r.)



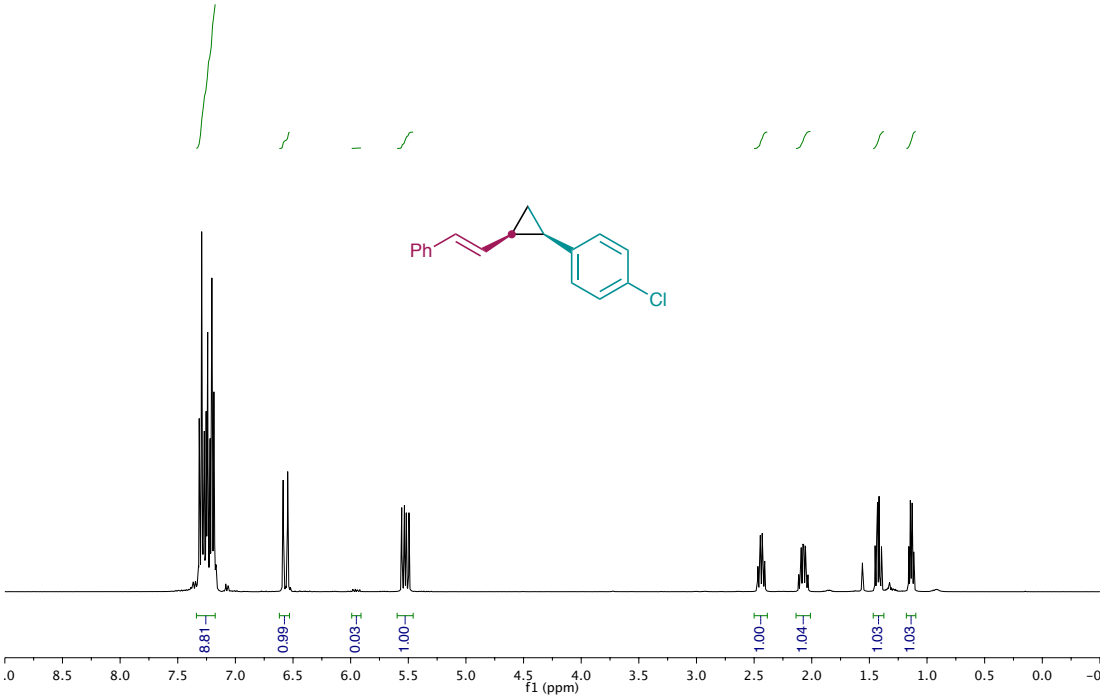


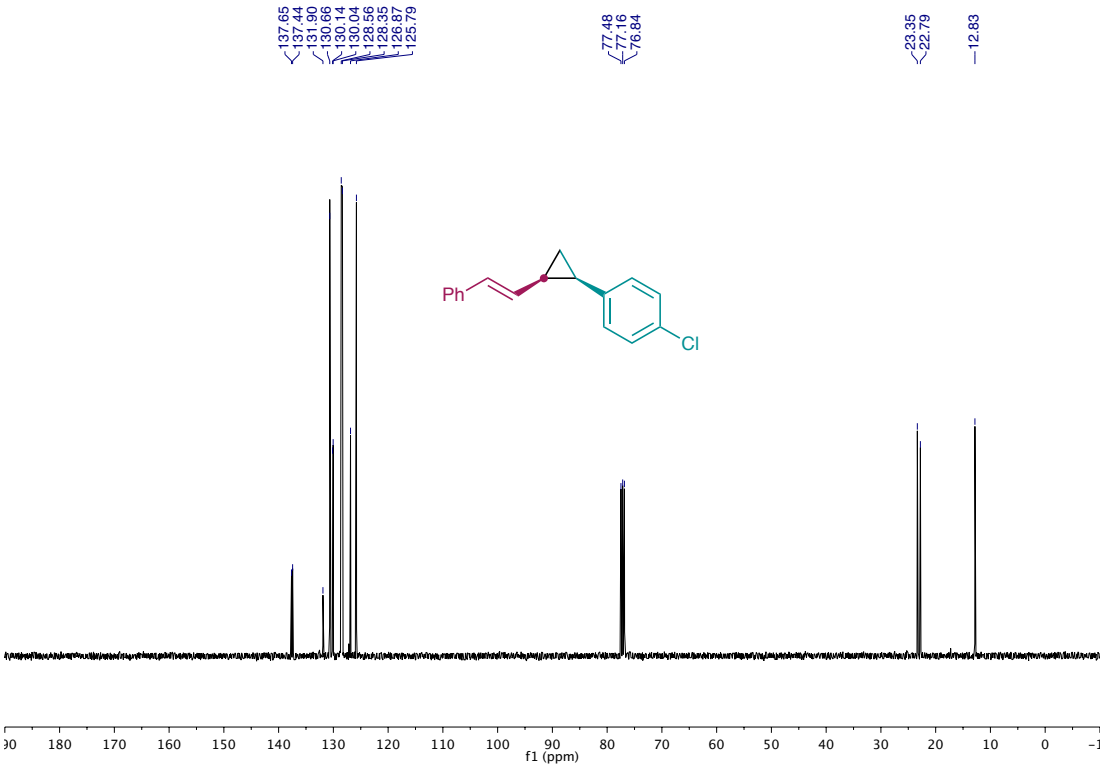
(*cis*)-1-Methyl-4-(2-(2-methylprop-1-en-1-yl)cyclopropyl)benzene (9d)



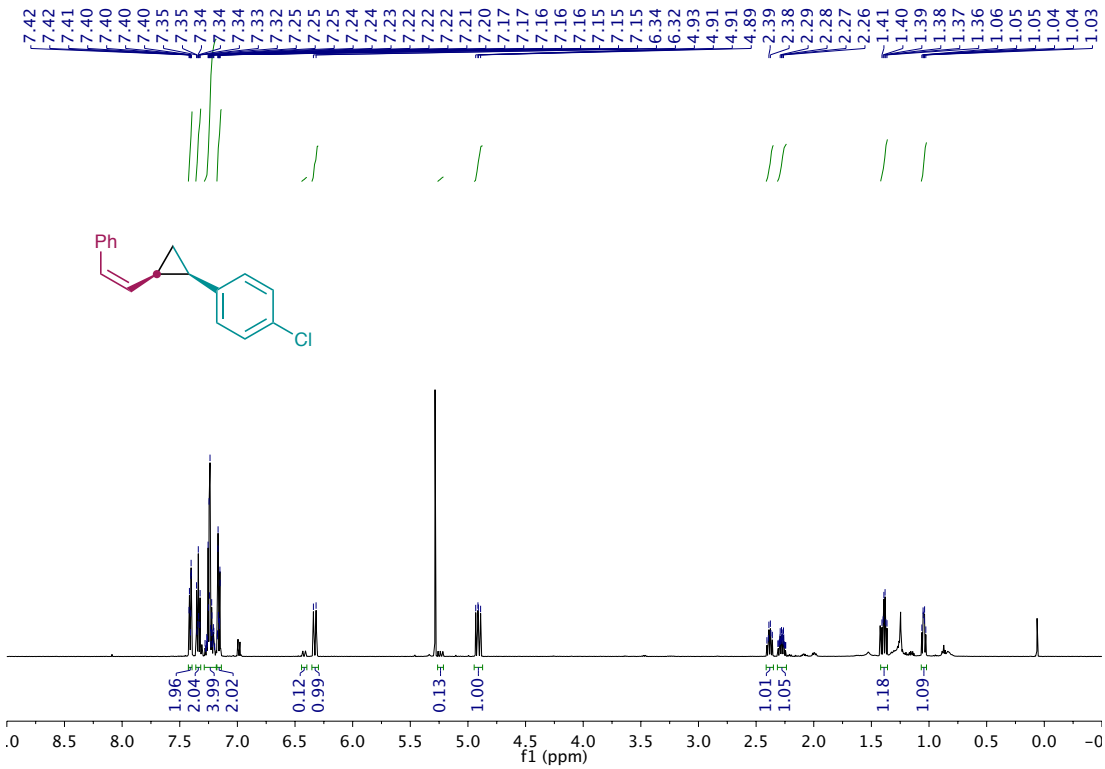


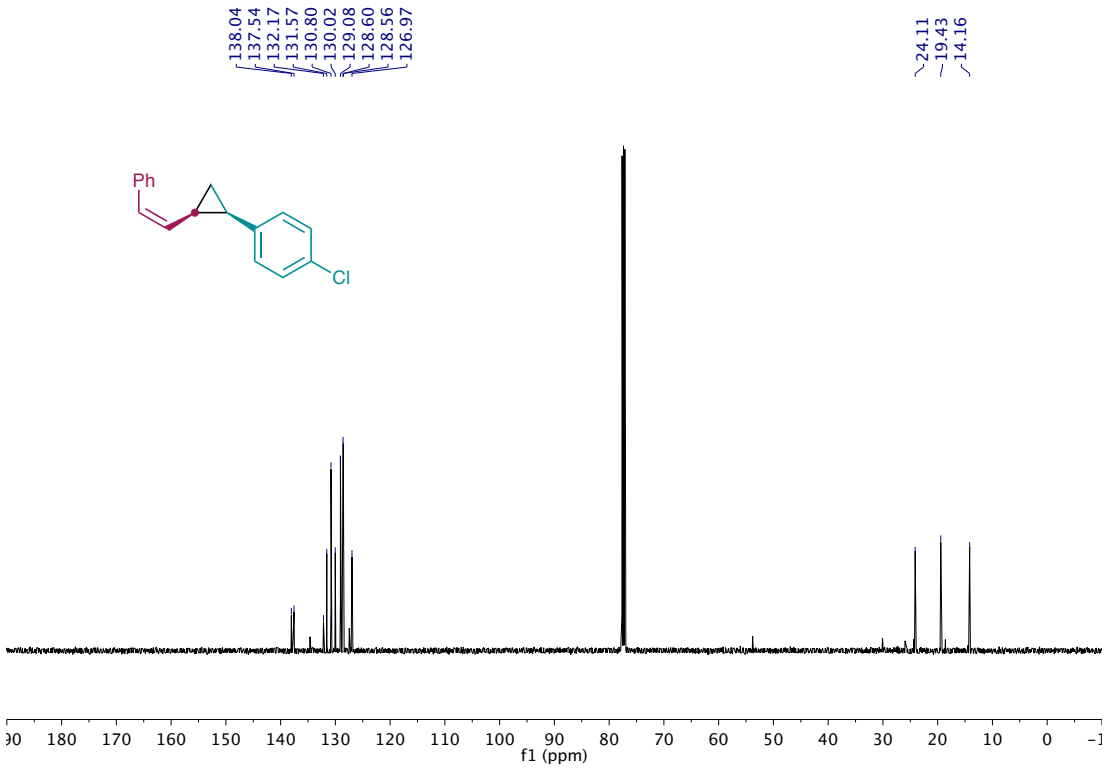
(*cis*)-1-Chloro-4-(2-((*E*)-styryl)cyclopropyl)benzene (9e)



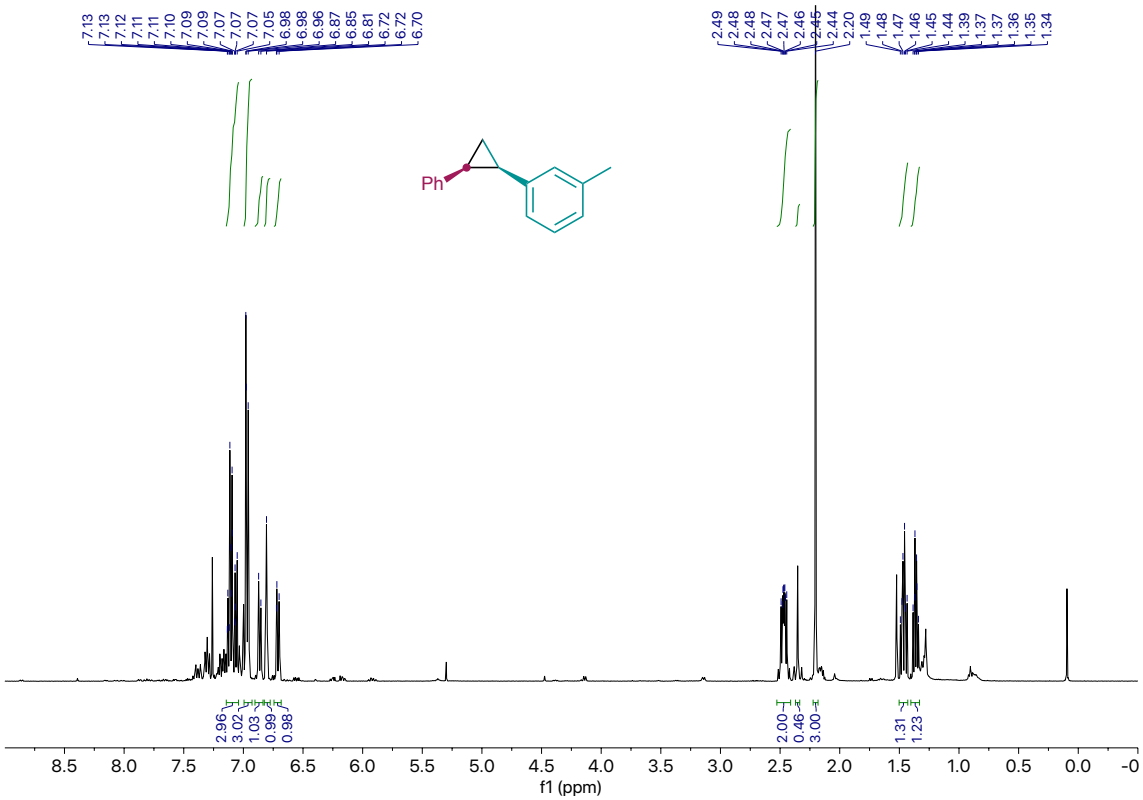


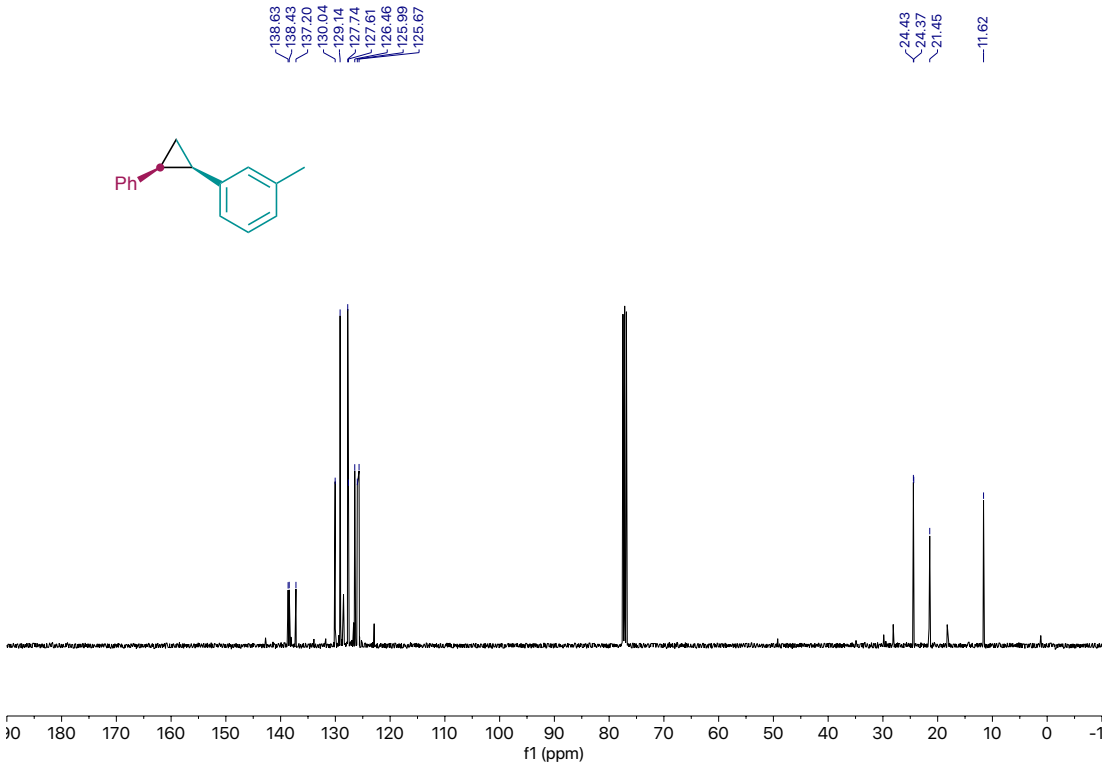
(*cis*)-1-Chloro-4-(2-((*Z*)-styryl)cyclopropyl)benzene (9f)



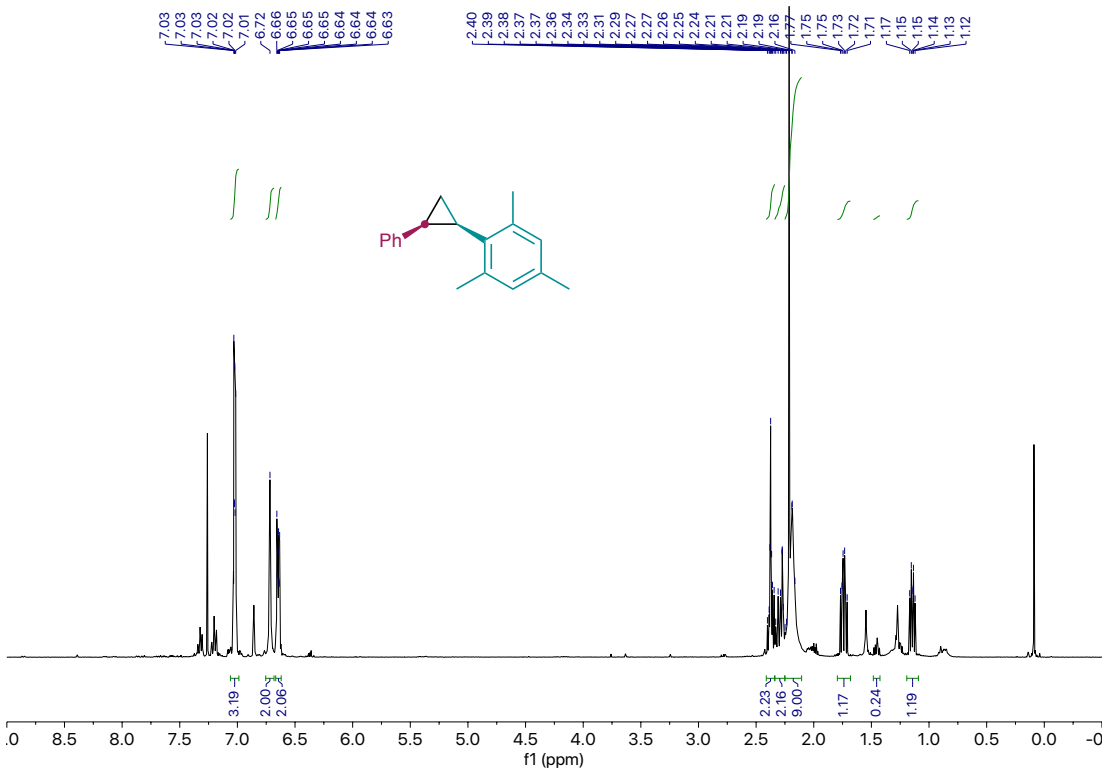


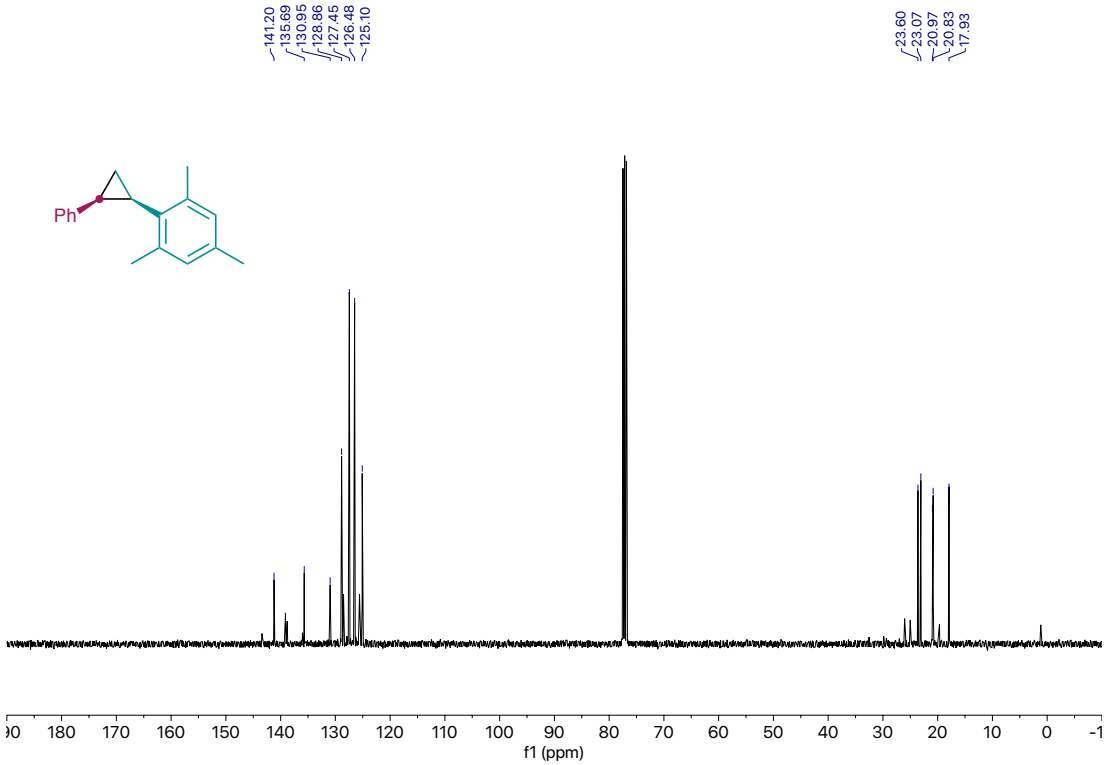
(*cis*)-1-Methyl-3-(2-phenylcyclopropyl)benzene (8a)



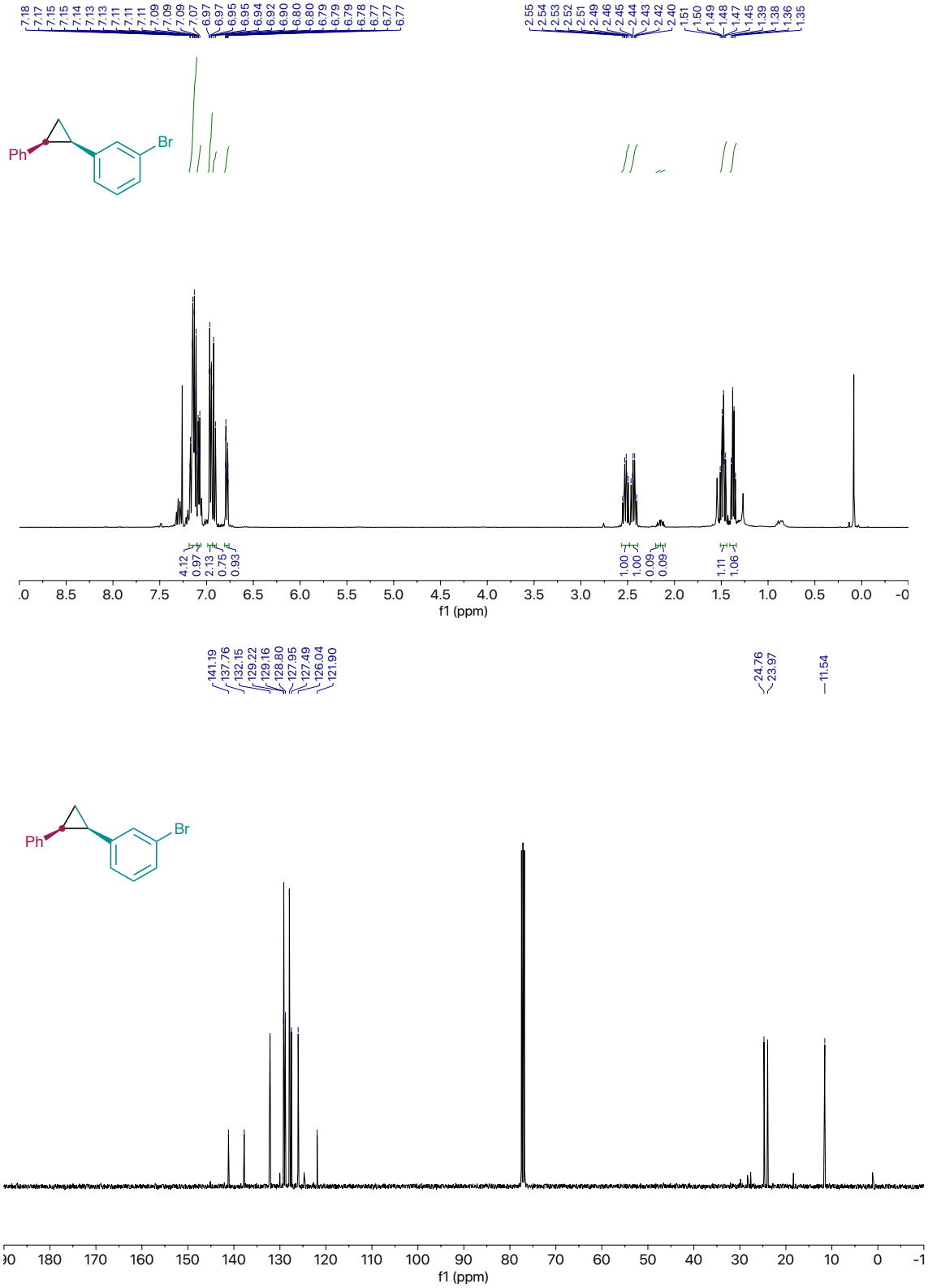


(*cis*)-1,3,5-Trimethyl-2-(2-phenylcyclopropyl)benzene (8b)

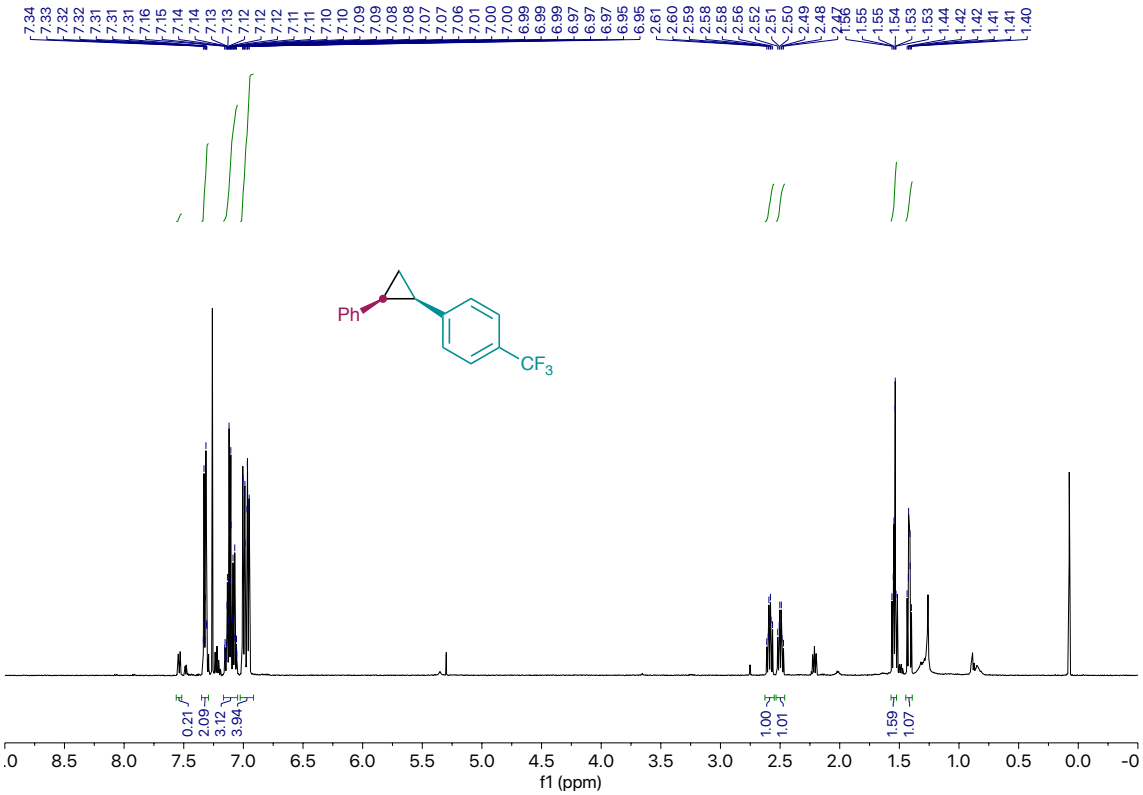


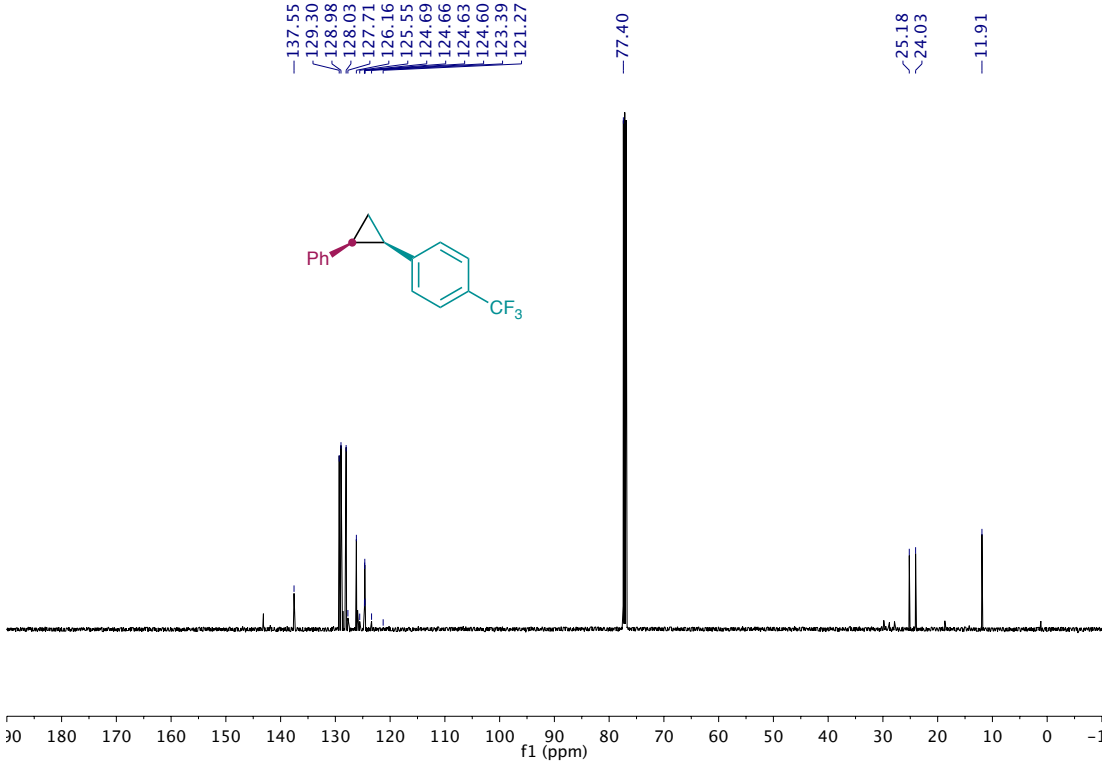


(*cis*)-1-Bromo-3-(2-phenylcyclopropyl)benzene (8c)

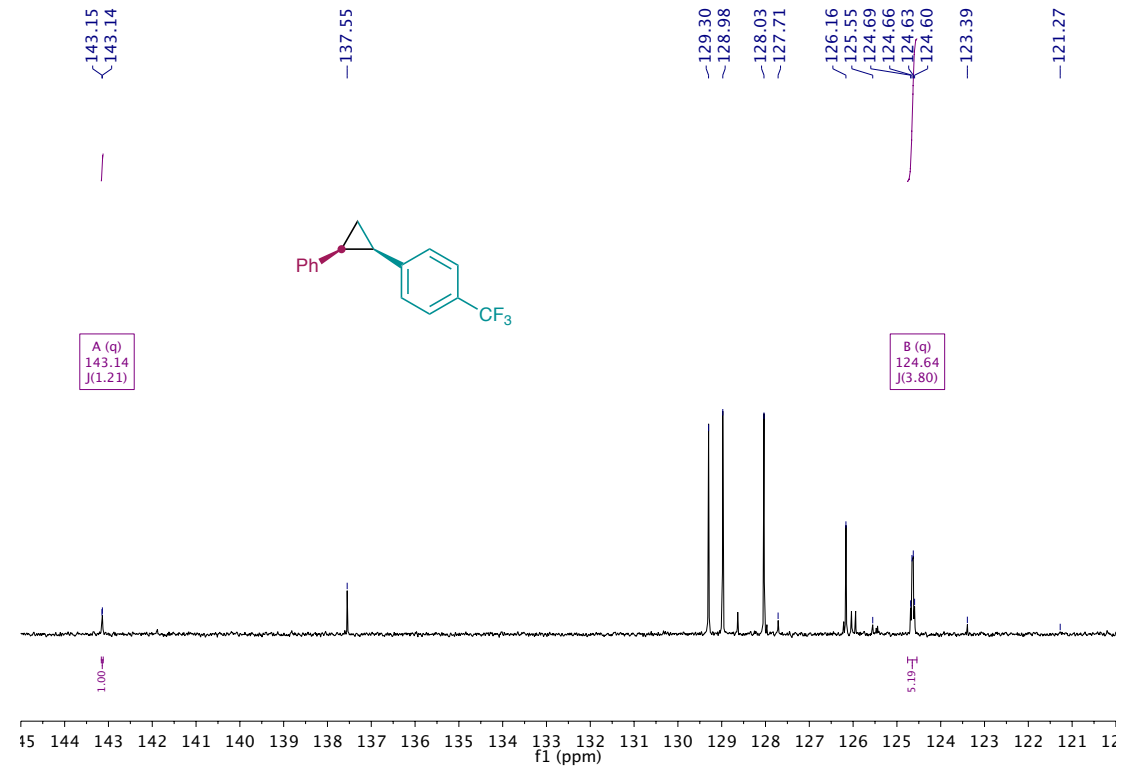


(*cis*)-1-(2-Phenylcyclopropyl)-4-(trifluoromethyl)benzene (8d)

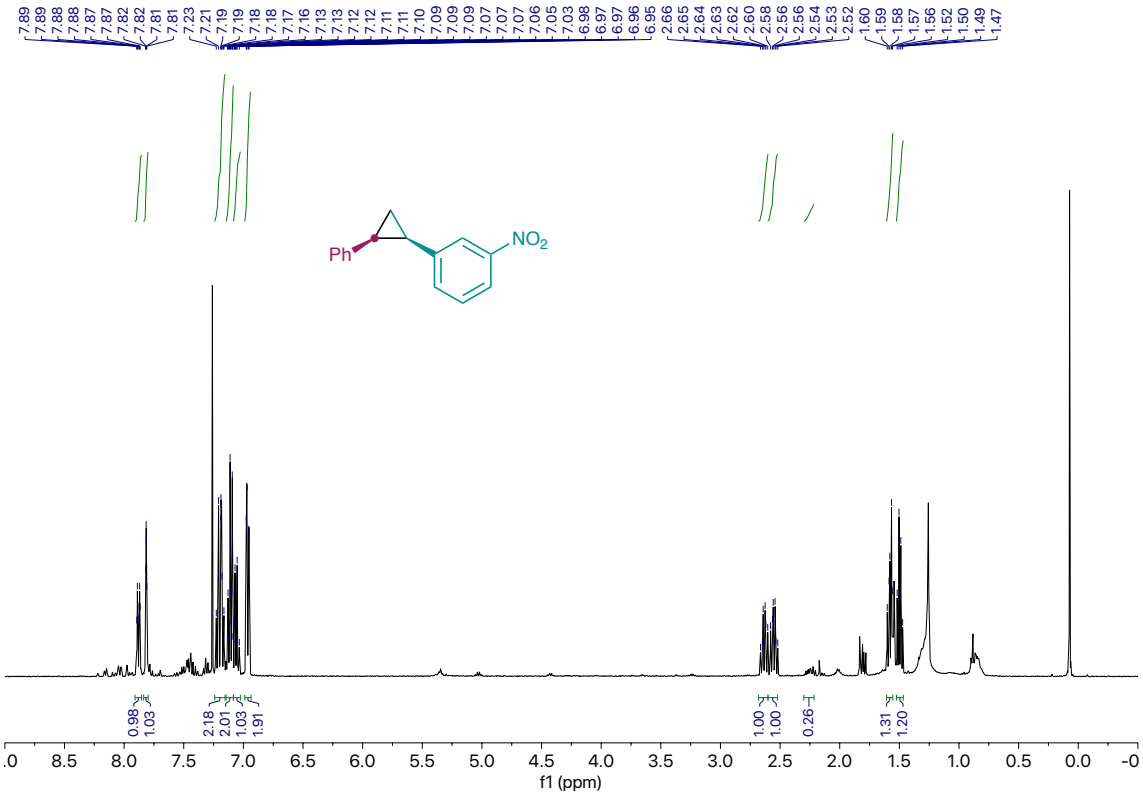


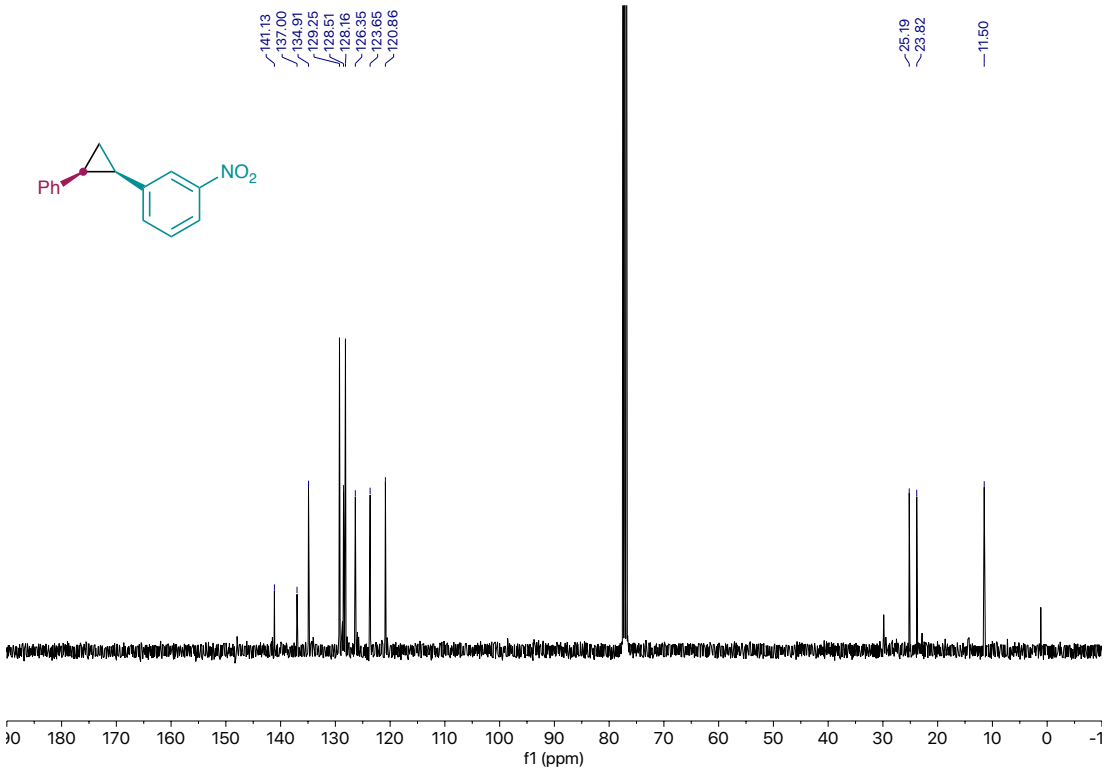


^{13}C detail and ^{19}F

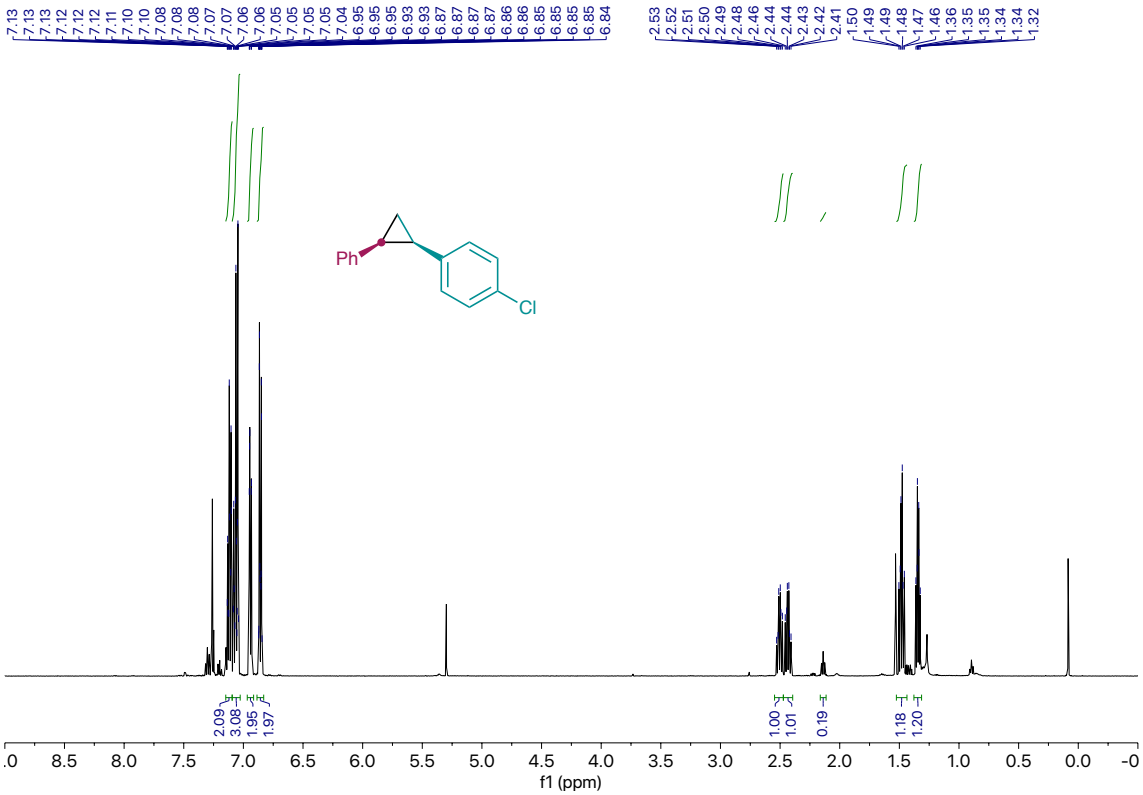


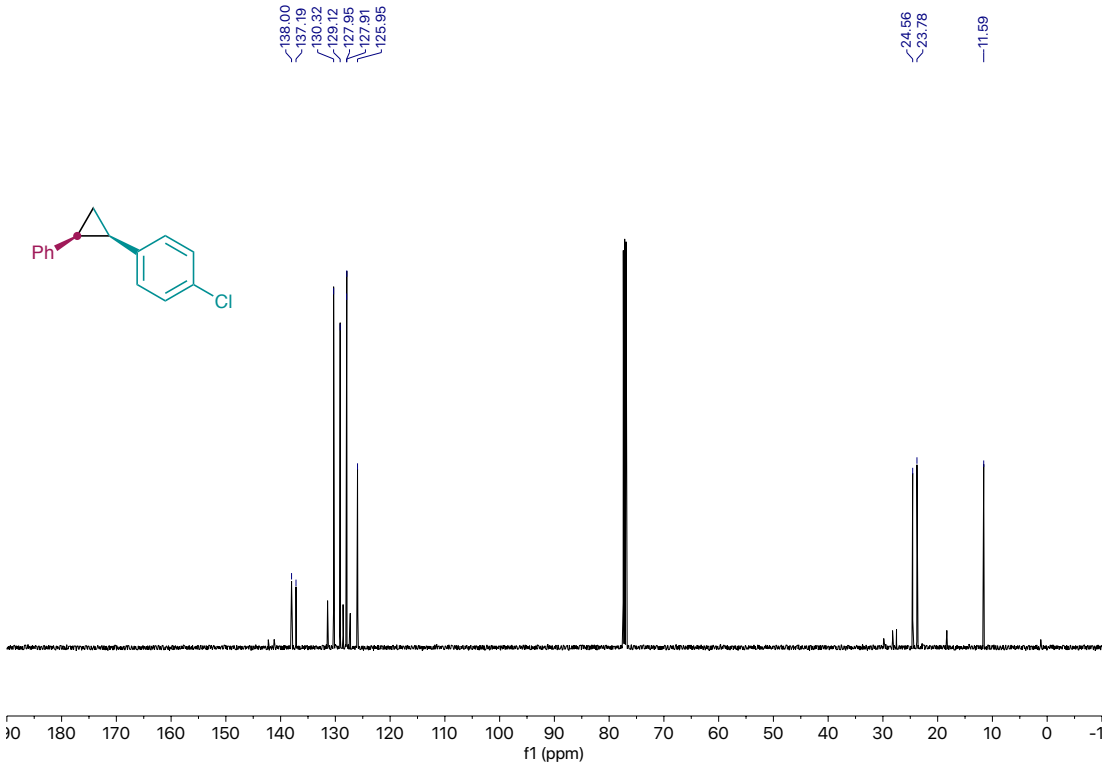
(*cis*)-1-Nitro-3-(2-phenylcyclopropyl)benzene (8e)



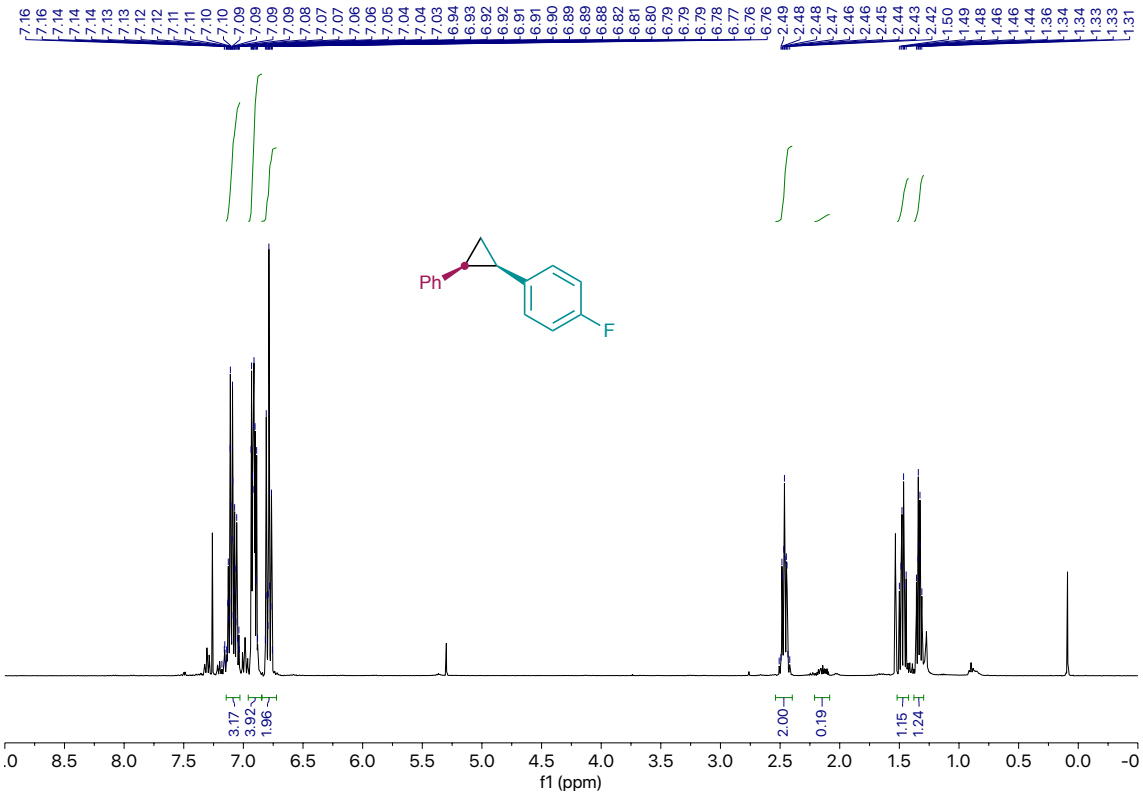


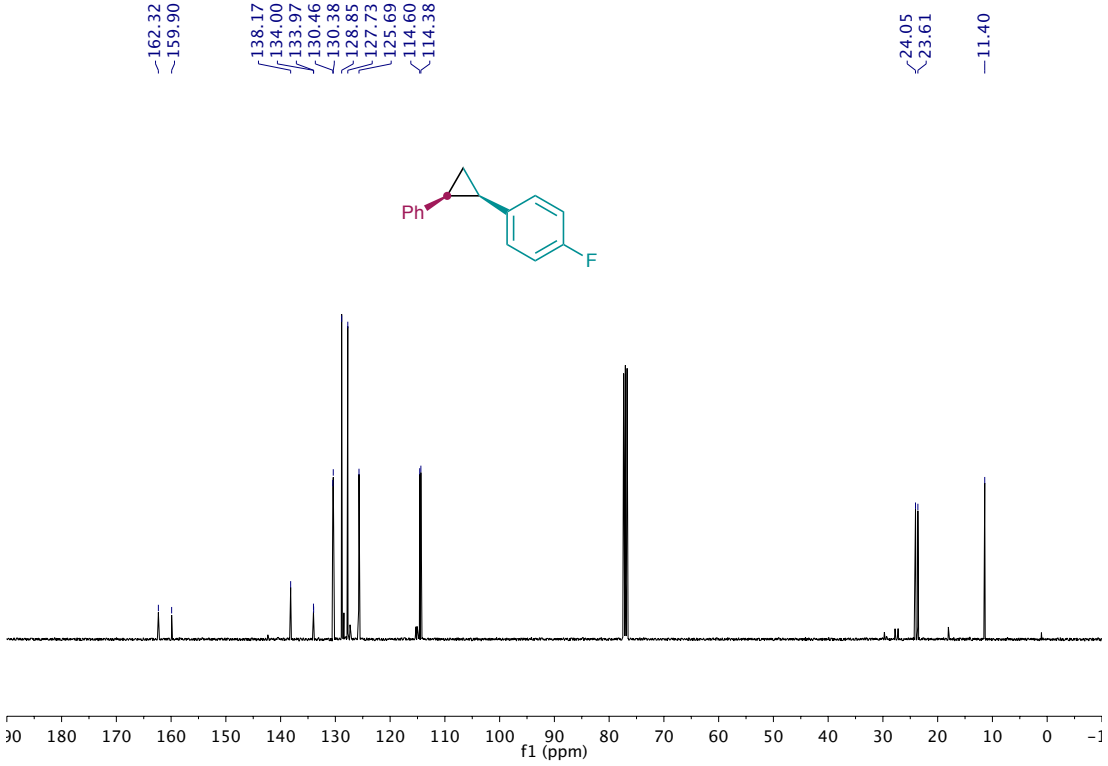
(*cis*)-1-Chloro-4-(2-phenylcyclopropyl)benzene (8f)



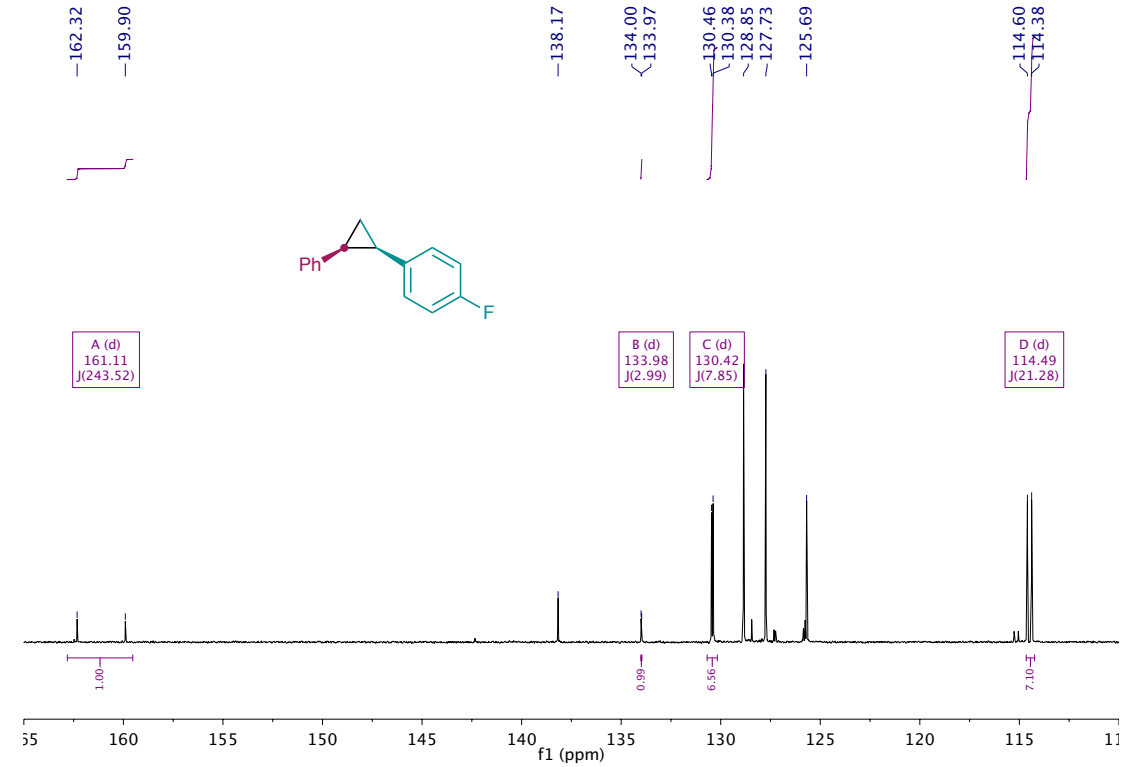


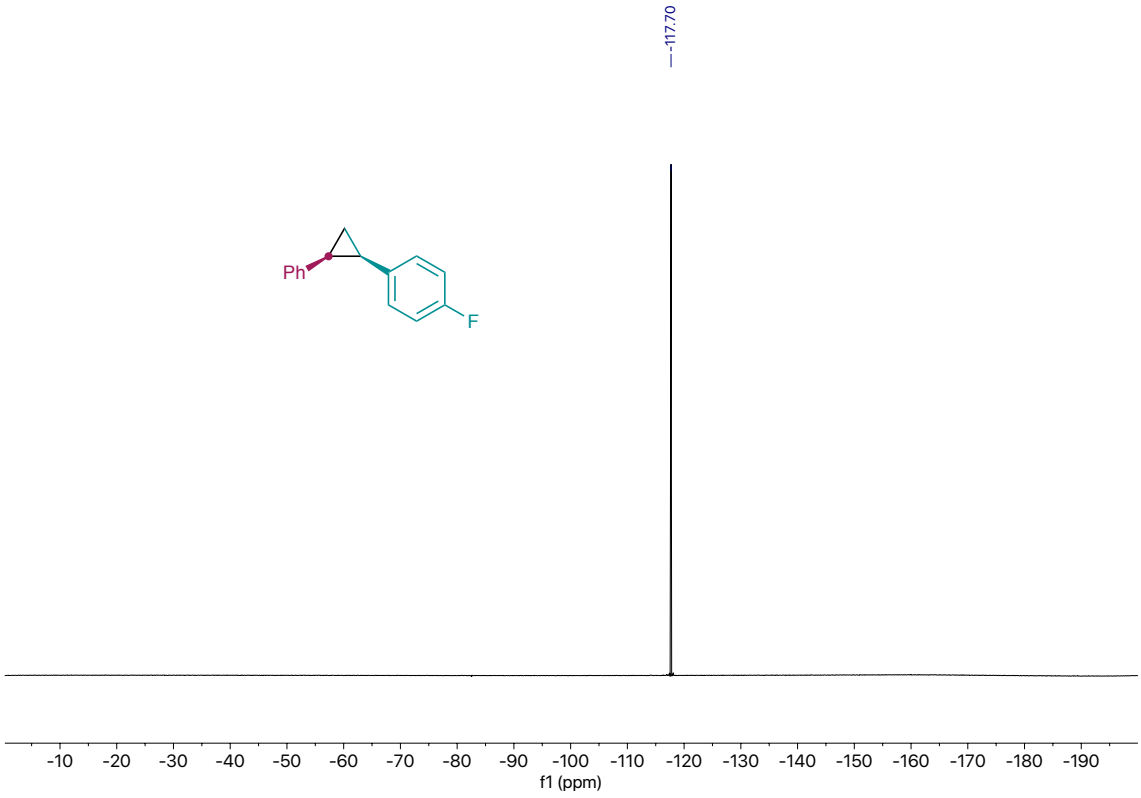
(*cis*)-1-Fluoro-4-(2-phenylcyclopropyl)benzene (8g)



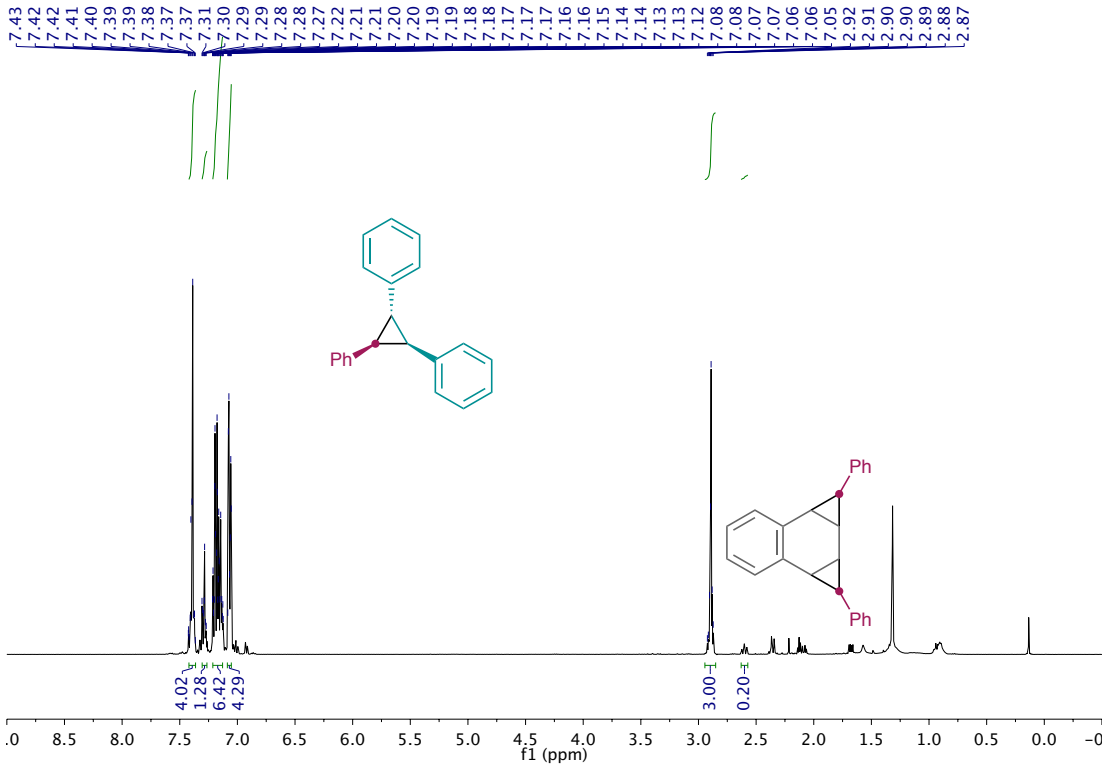


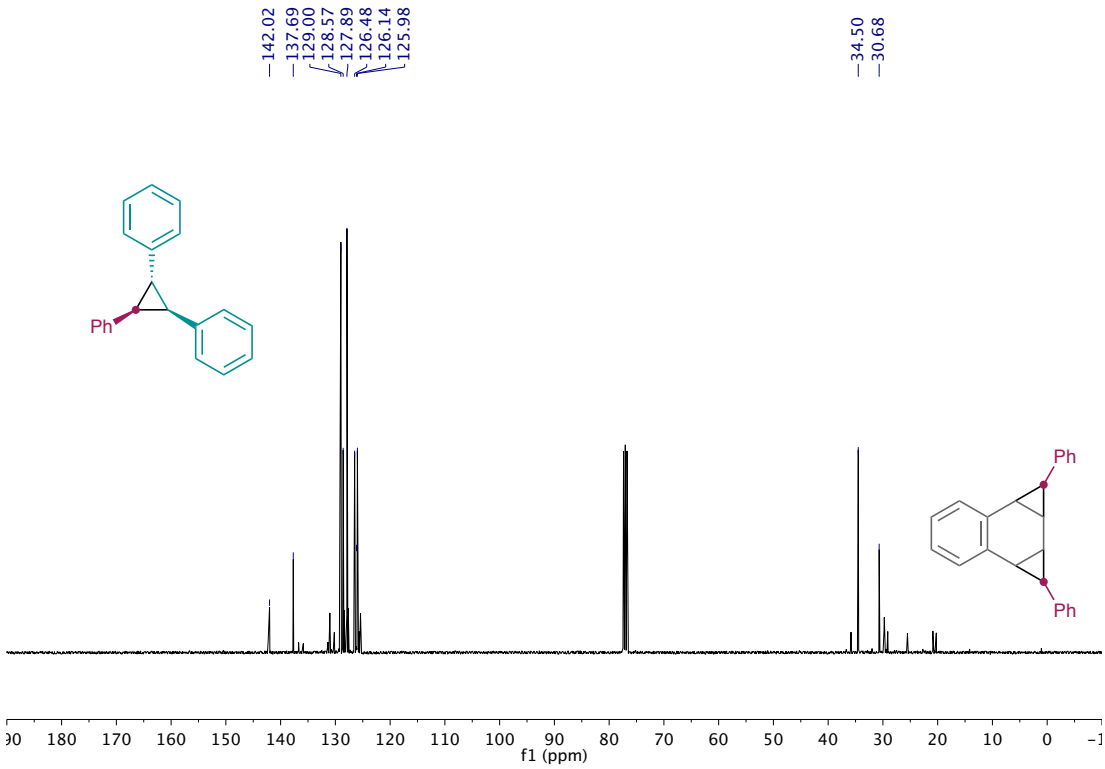
^{13}C detail and ^{19}F



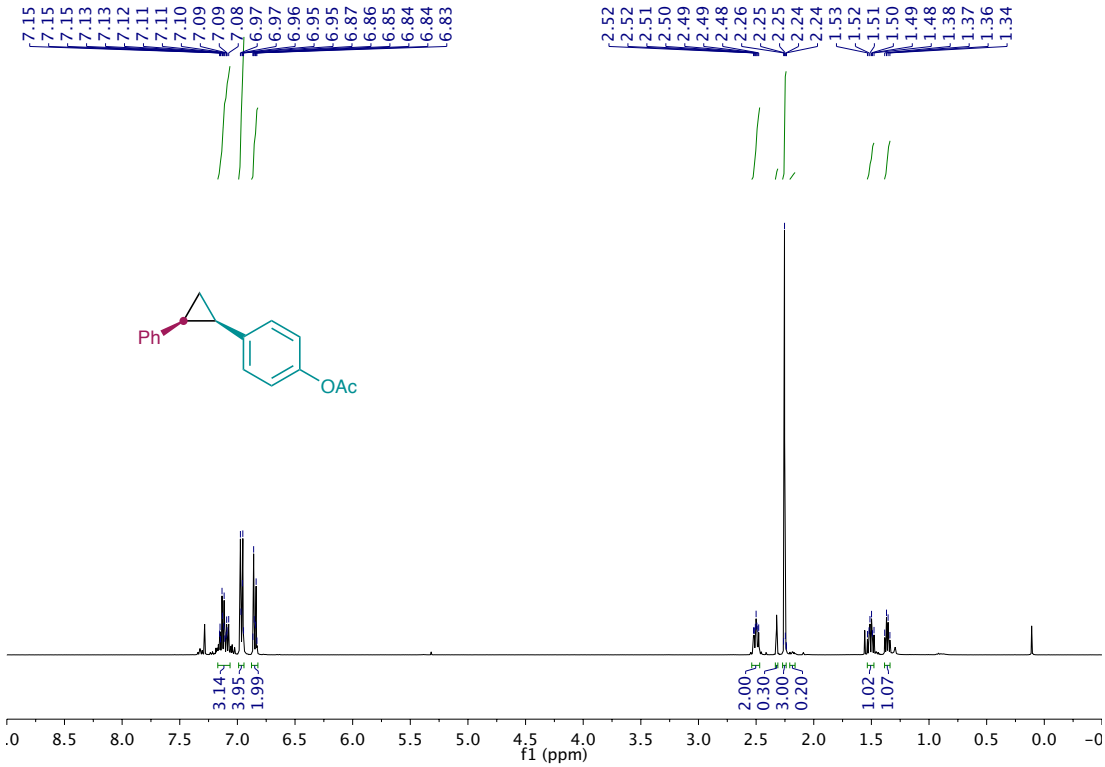


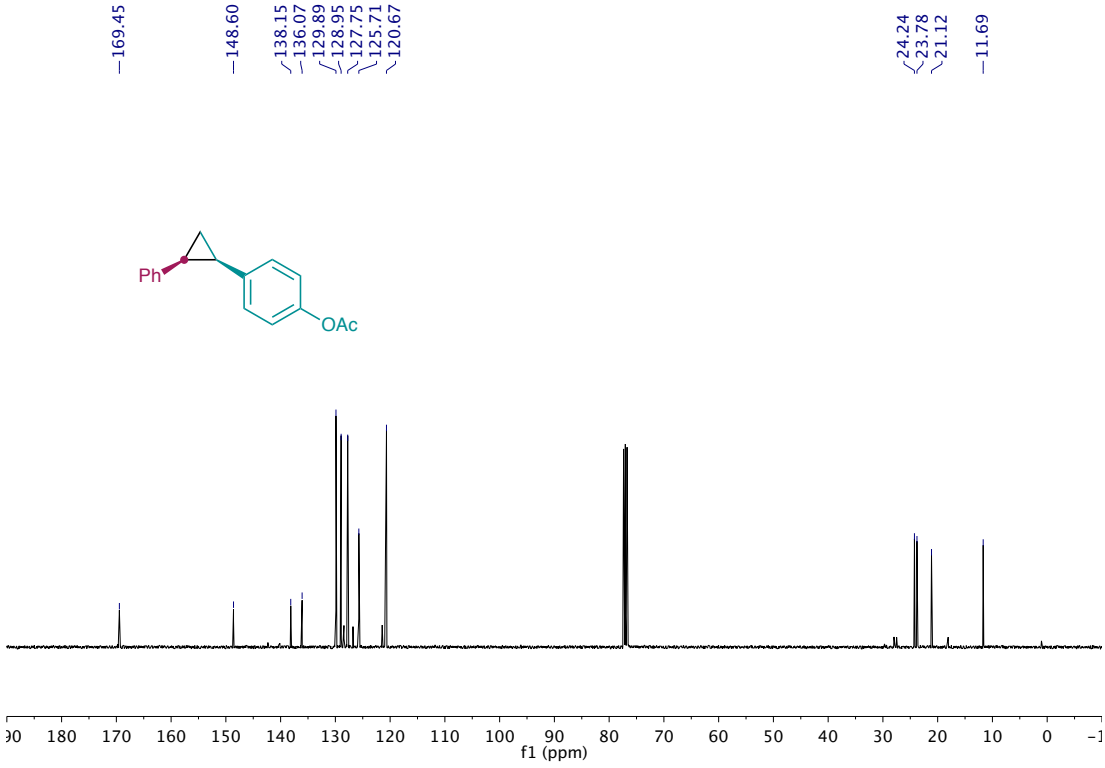
(*exo*)-1,2,3-Triphenylcyclopropane (8h) with 20% of (**S4**)



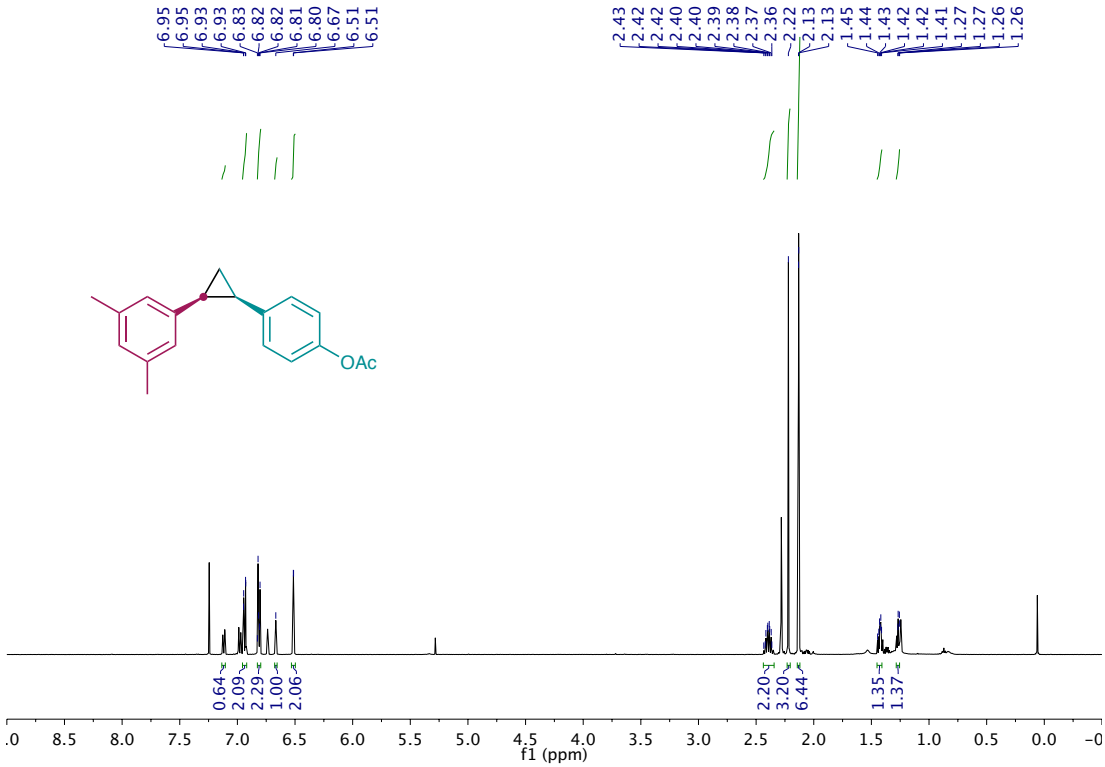


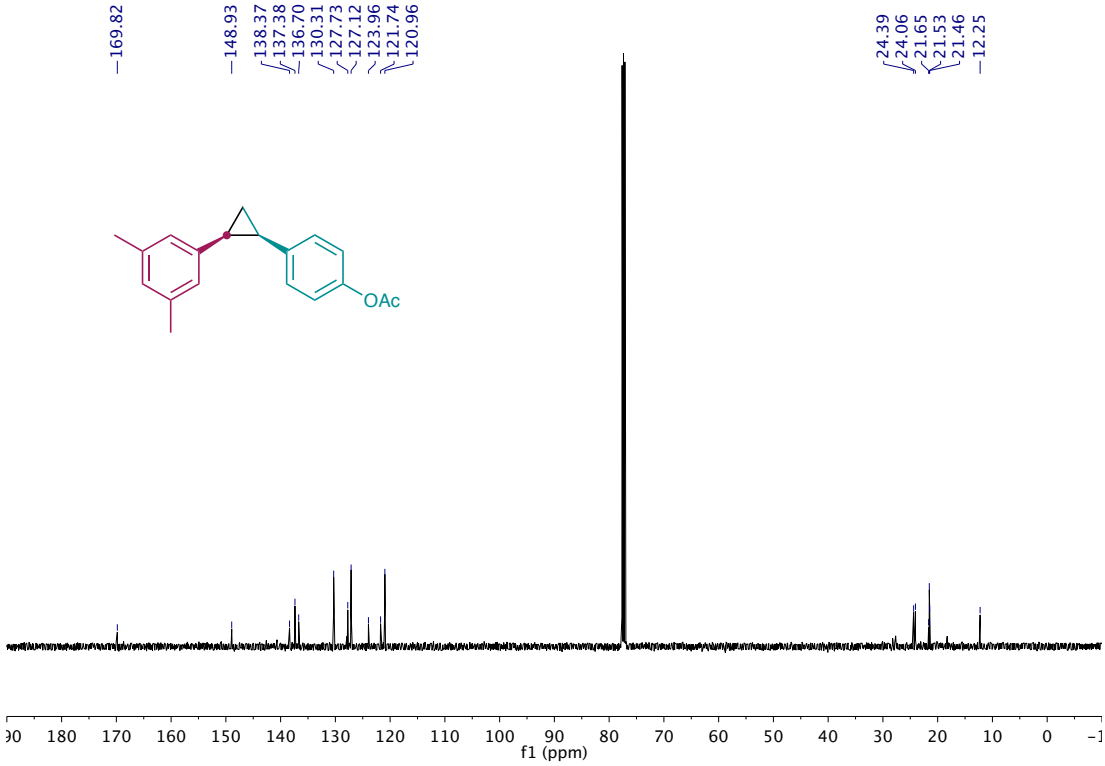
(*cis*)-4-(2-Phenylcyclopropyl)phenyl acetate (8i)



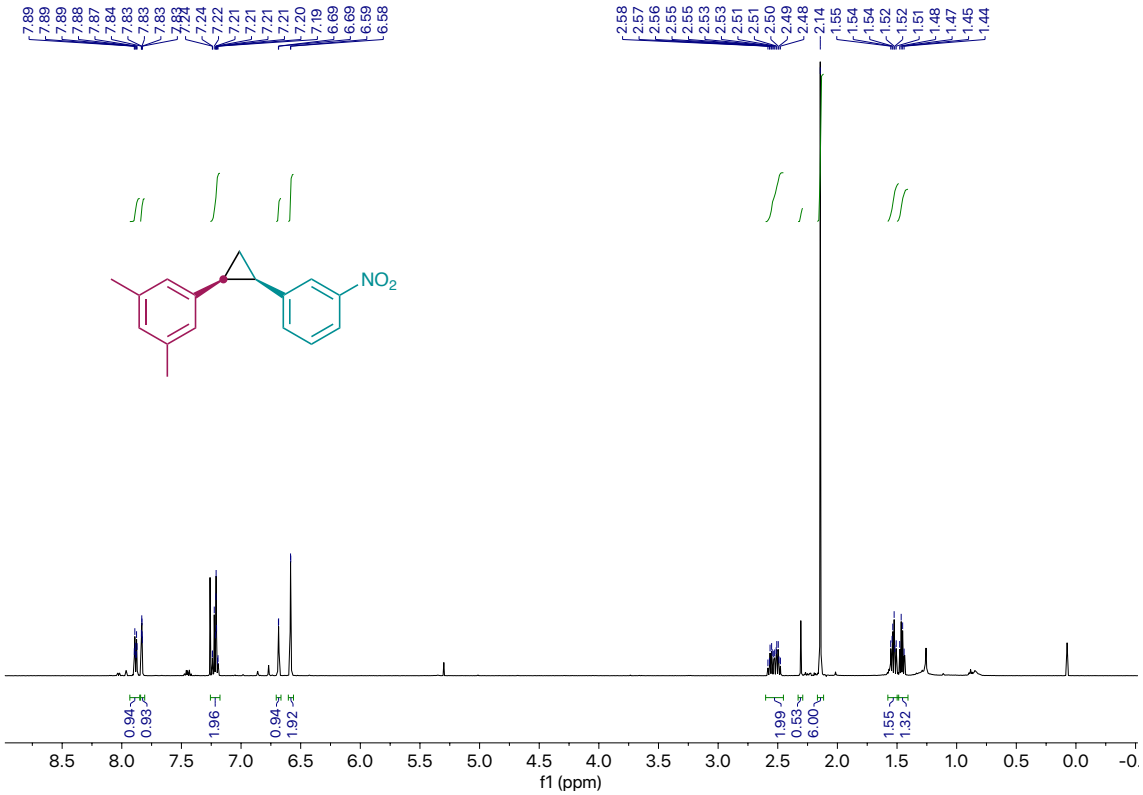


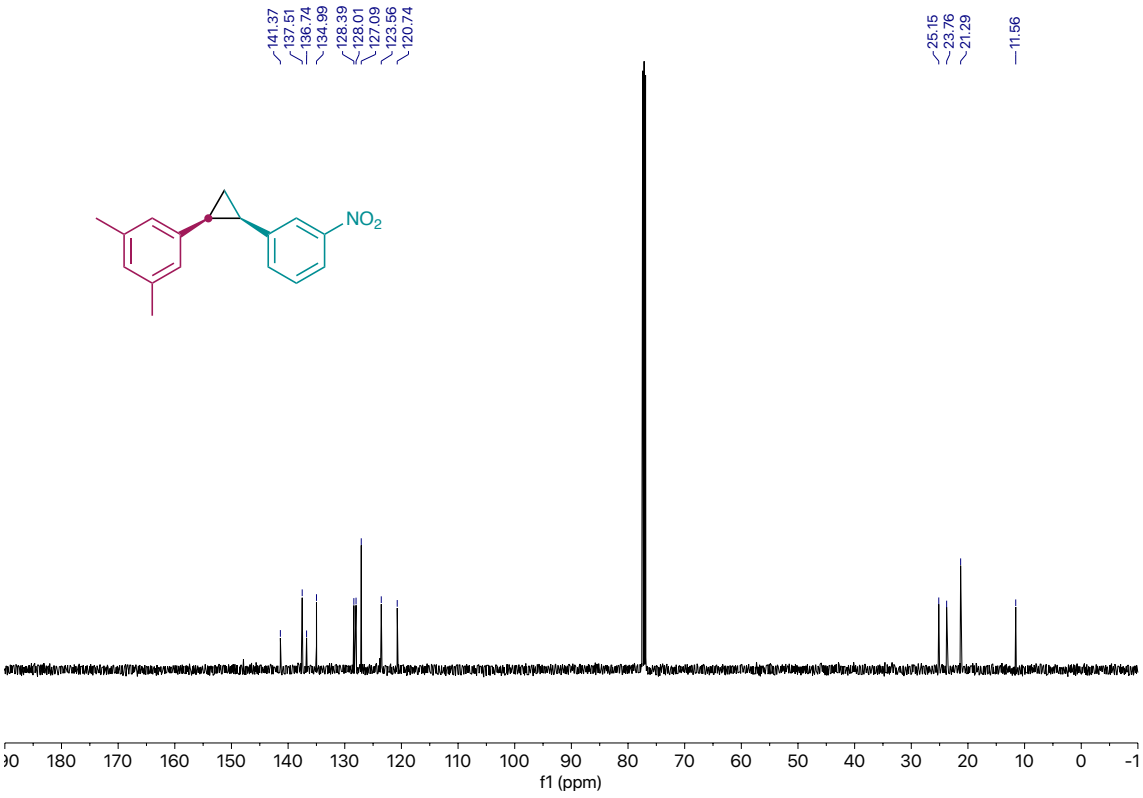
(*cis*)-4-(2-(3,5-Dimethylphenyl)cyclopropyl)phenyl acetate (8j)



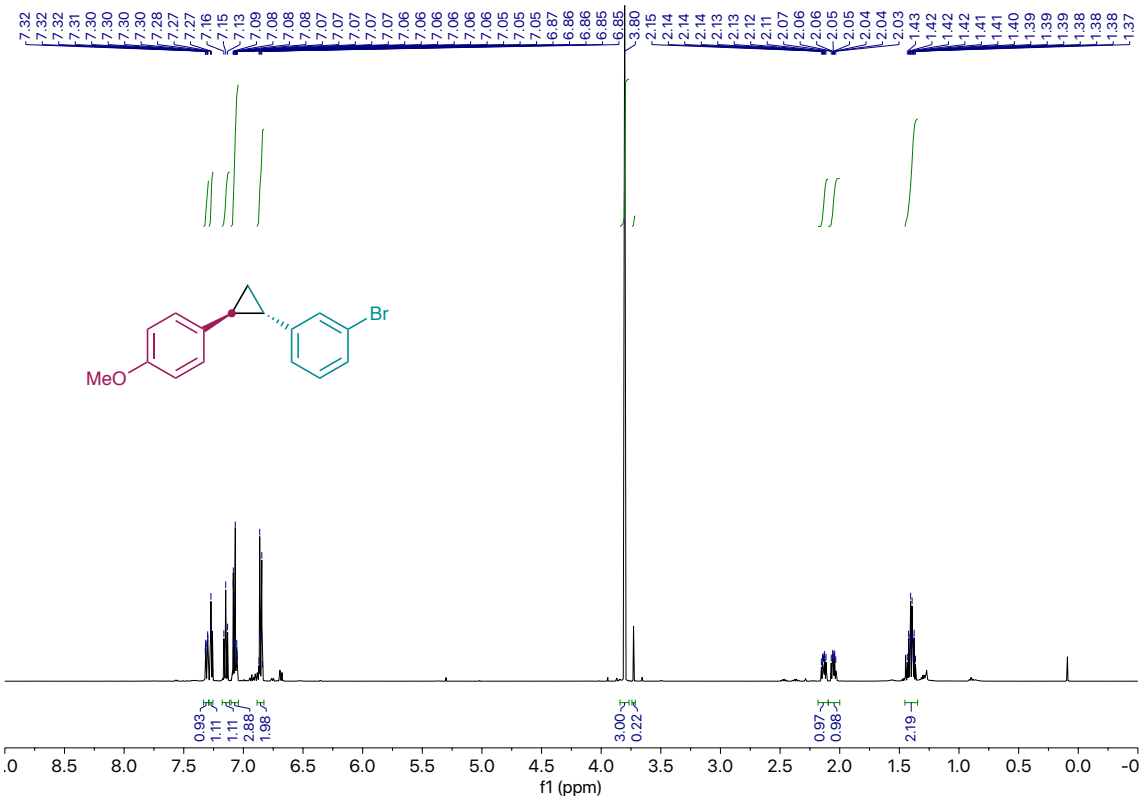


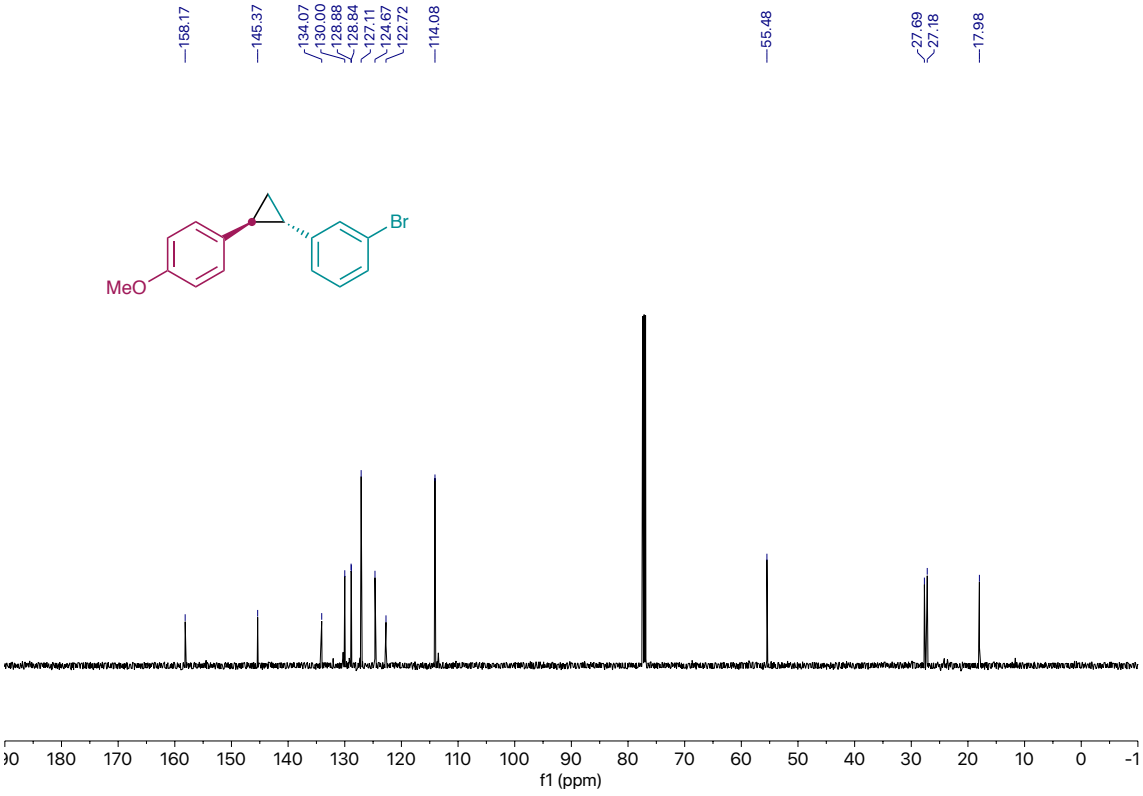
(*cis*)-1,3-Dimethyl-5-(2-(3-nitrophenyl)cyclopropyl)benzene (8k)



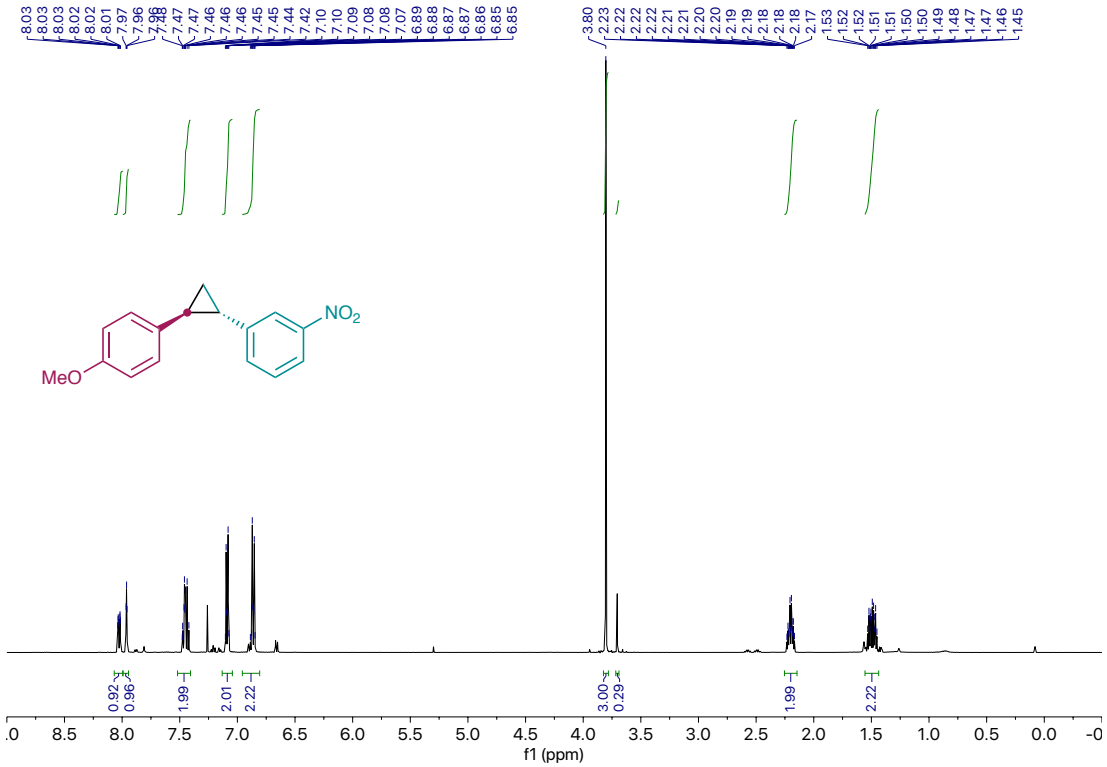


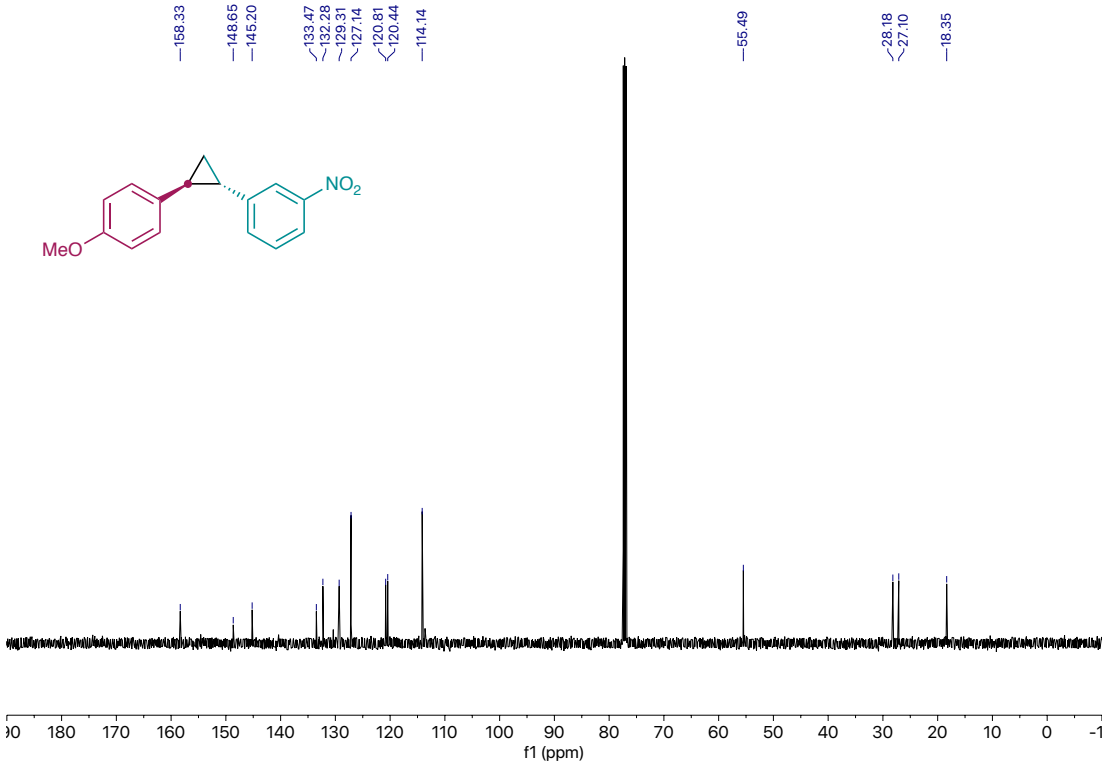
(*trans*)-1-Bromo-3-(2-(4-methoxyphenyl)cyclopropyl)benzene (8l)



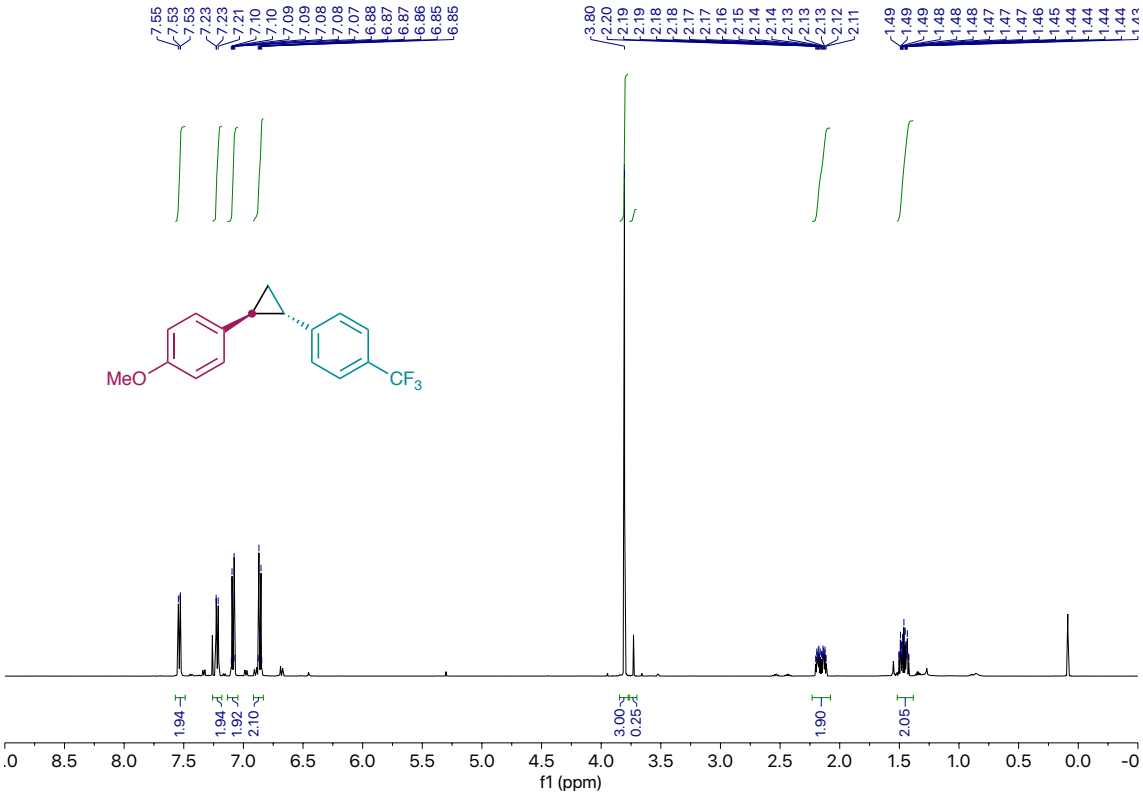


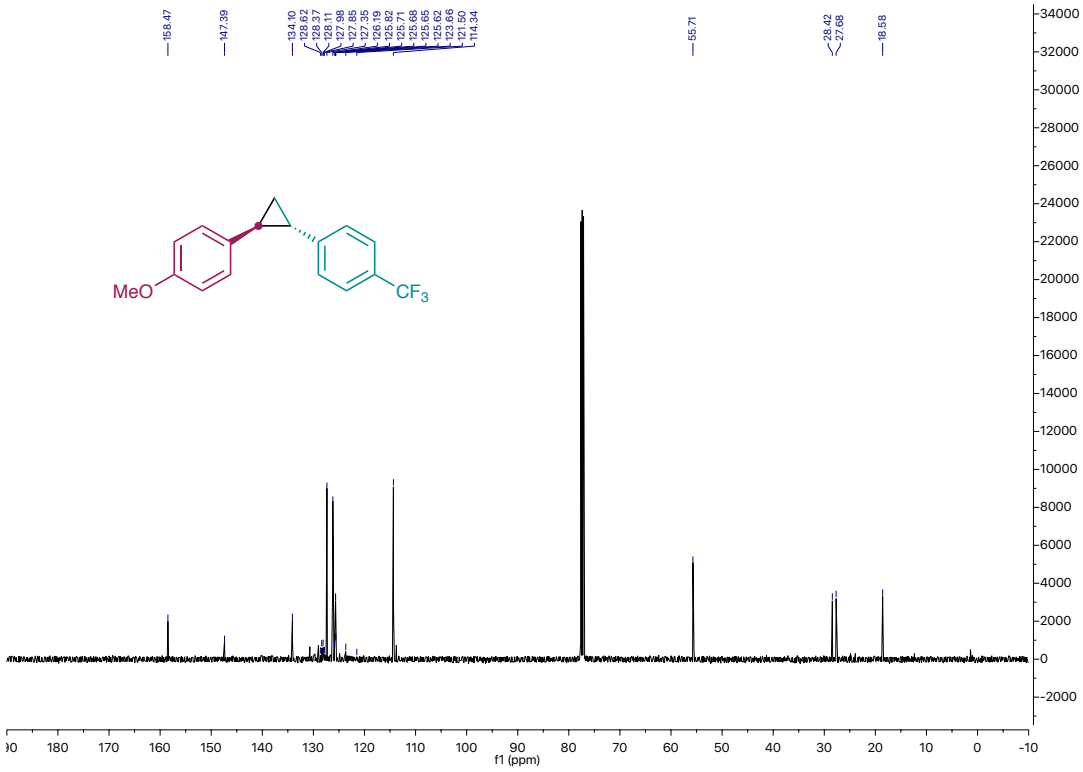
(*trans*)-1-(2-(4-Methoxyphenyl)cyclopropyl)-3-nitrobenzene (8m)



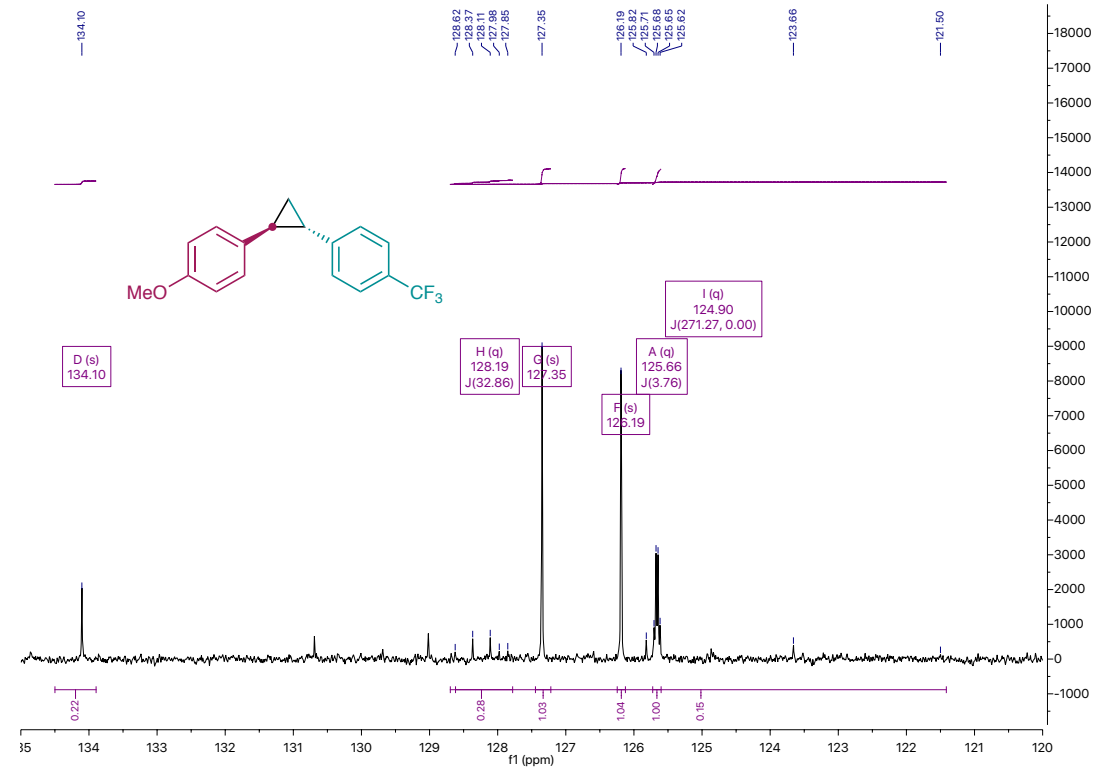


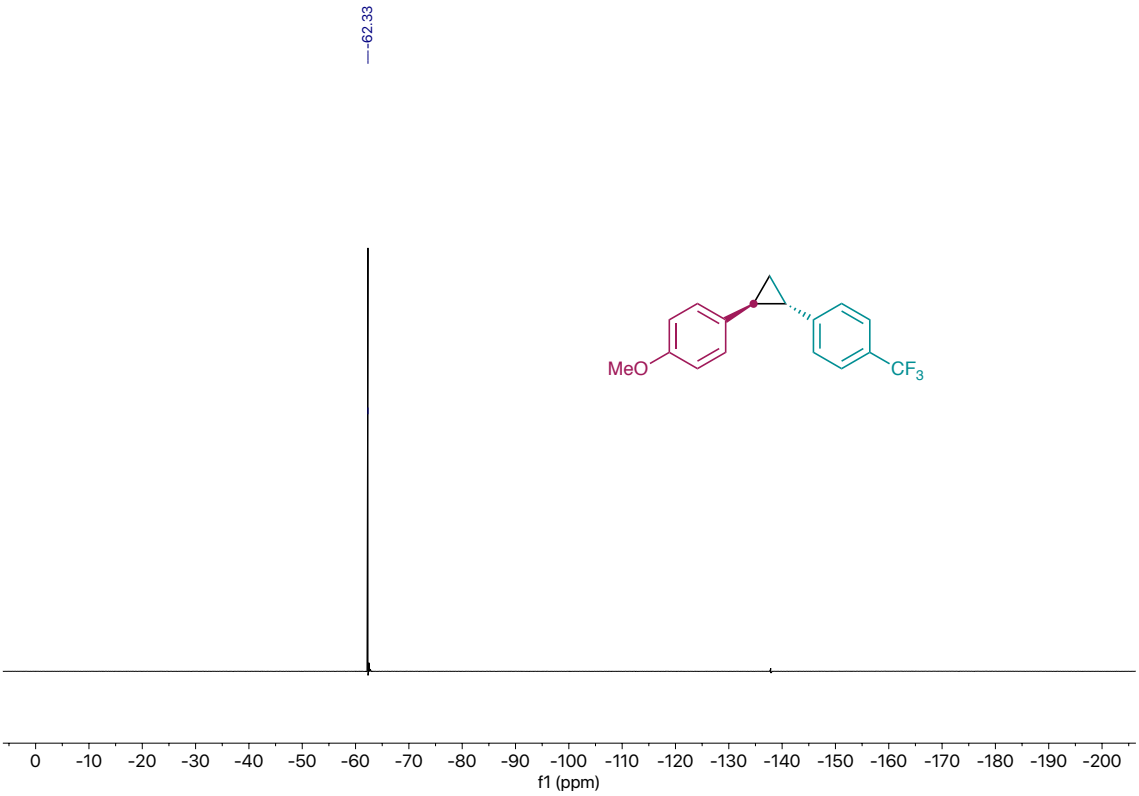
(*trans*)-1-Methoxy-4-(2-(4-(trifluoromethyl)phenyl)cyclopropyl)benzene (8n)





^{13}C detail and ^{19}F





11. References

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