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Supporting Information

Benzo-Extended Cyclohepta[*def*]fluorene Derivatives with Very Low-Lying Triplet States

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1. Experimental Section

1.1 General Methods and Materials

Unless otherwise noted, commercially available starting materials, reagents, catalysts, and dry solvents were used without further purification. Reactions were performed using standard vacuum-line and Schlenk techniques. All starting materials were obtained from TCI, Sigma Aldrich, abcr, Alfa Aesar, Acros Organics, or Fluorochem. Catalysts were purchased from Strem. Column chromatography was performed on silica (SiO_2, particle size 0.063-0.200 mm, purchased from VWR). Silica-coated aluminum sheets with a fluorescence indicator (TLC silica gel 60 F254, purchased from Merck KGaA) were used for thin layer chromatography.

NMR data were recorded both on a Bruker AV-II 300 spectrometer operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C and on a Bruker Avance III 500 spectrometer operating at 500 MHz for ^{1}H and at 125 MHz for ^{13}C using standard Bruker pulse programs. The measurements were made at room temperature (296 K; AV-II 300) and at 30 °C (303 K, Avance III 500) if not otherwise stated. Chemical shifts (δ) are reported in ppm. Coupling constants (J) are reported in Hz. Dichloromethane-d_2 ($\delta(^1H) = 5.32$ ppm, $\delta(^{13}C) = 53.8$ ppm) was used as solvent. The following abbreviations are used to describe peak patterns as appropriate: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, and *m* = multiplet. Dichloromethane-d_2 (99.9 atom % D) was purchased from Eurisotop.

High-resolution electrospray ionization mass spectrometry (HR-ESI-MS) was recorded with an Agilent 6538 Ultra High Definition (UHD) Accurate-Mass Q-TOF LC/MC system. Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) MS was recorded on a Bruker Autoflex Speed MALDI-TOF MS (Bruker Daltonics, Bremen, Germany). All of the samples, were prepared by mixing the analyte and the matrix, 1,8-dihydroxyanthracen-9(10H)-one (dithranol, purchased from Fluka Analytical, purity > 98%) or *trans*-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, purchased from Sigma Aldrich, purity > 99%) in the solid state.

UV-visible (UV-vis) spectra were measured on an Agilent Cary 5000 UV-VIS-NIR spectrophotometer by using 10 mm optical-path quartz cell at room temperature.

(1,1':2',1''-terphenyl)-2,6-dicarbaldehyde (**9**)[1], 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)isophthalaldehyde (**10**)[2], 5-Bromochrysene (**13**)[3], (3-bromonaphthalen-2-yl)boronic acid (**21**)[4] were synthesized through multi steps procedures.

1.2 Detailed Synthetic Procedures

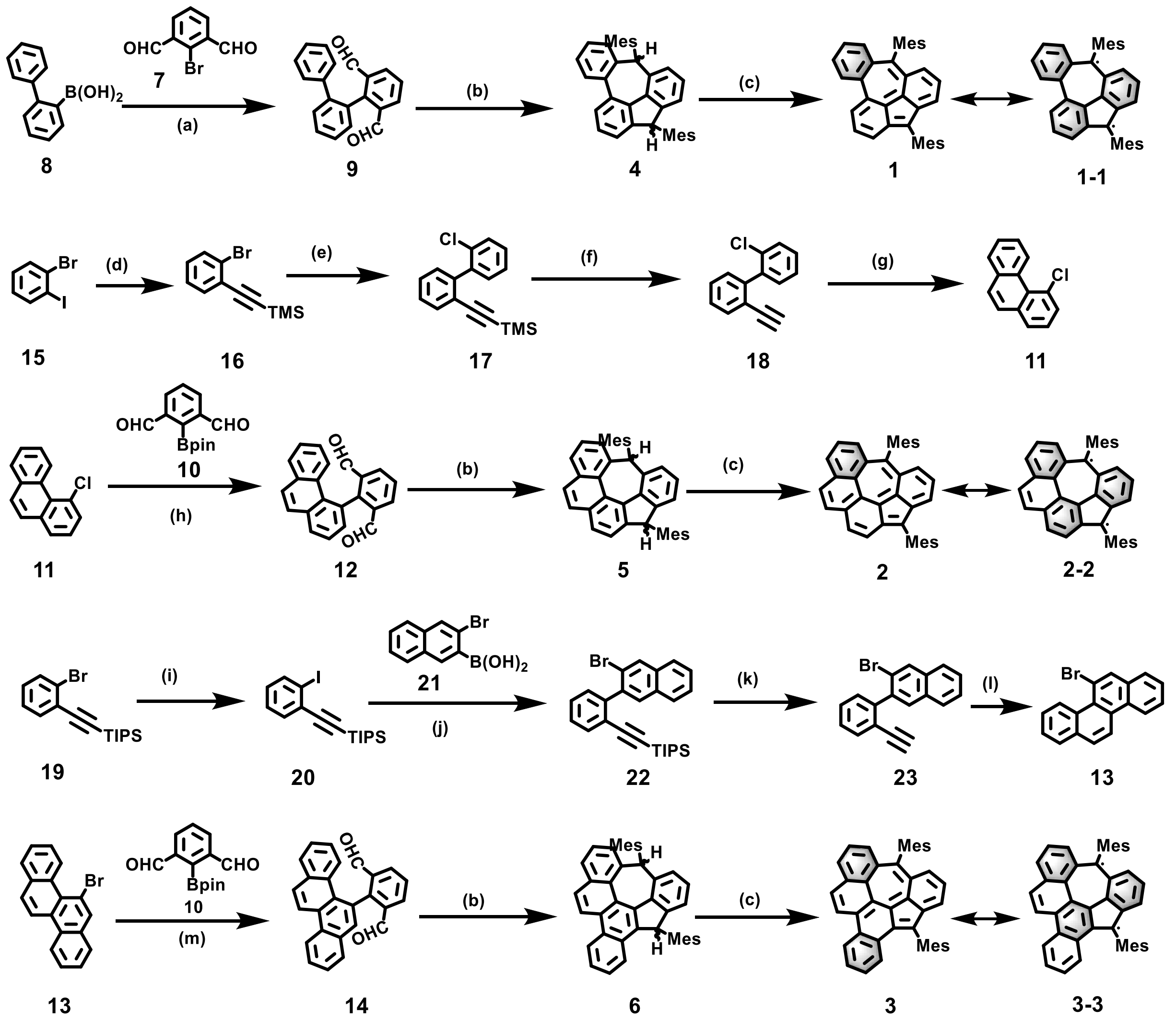
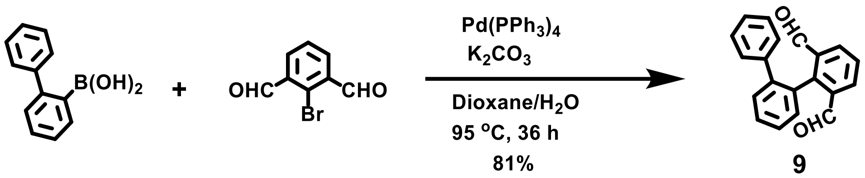


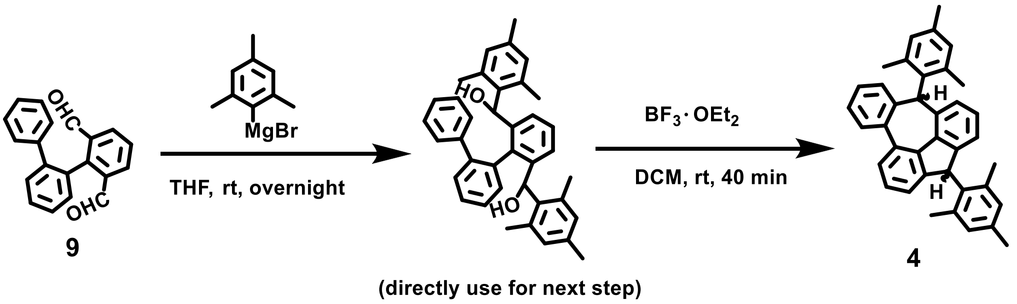
Figure S1. Synthetic route to the diradicaloids 1, 2 and 3. Reagents and conditions: (a) 2-bromoisophthalaldehyde, Pd(PPh$_3$)$_4$/K$_2$CO$_3$, dioxane/H$_2$O, 95 °C, 36 h, 81%; (b) (1) 2-mesitylmagnesium bromide, THF, rt, overnight (2) BF$_3$·OEt$_2$, DCM, rt, 40 min, **4**: 61%, **5**: 72%, **6**: 70%, yield in two steps; (c) 3 eq. DDQ, chlorobenzene for **1** or toluene for **2** and **3**, rt, 30 min; (d) ethynyltrimethylsilane, Pd(PPh$_3$)$_2$Cl$_2$, CuI, THF/Et$_3$N, rt, 3h, 95%; (e) Pd(PPh$_3$)$_4$, K$_2$CO$_3$, Tol/EtOH/H$_2$O, 85 °C, overnight, 90%; (f) K$_2$CO$_3$, MeOH/THF, 40 °C, 1h, 98%; (g) PtCl$_2$, toluene, 110 °C, 24 h, 40%; (h) Pd(OAc)$_2$, SPhos, K$_3$PO$_4$, Tol/EtOH/H$_2$O, 80 °C, 40 h, 34%; (i) n-BuLi, Et$_2$O, -78 to 0 °C, 1.2 h, then ICH$_2$CH$_2$I/Et$_2$O, -78 °C, 3 h, 82%; (j) (3-bromonaphthalen-2-yl)boronic acid **20**, Pd(PPh$_3$)$_4$, K$_2$CO$_3$, THF/Ethanol/H$_2$O, 60 °C, 87%; (k) TBAF, THF, rt, 95%; (l) PtCl$_2$, toluene, 90 °C, 63%; (m) Pd$_2$(dba)$_3$, SPhos, K$_3$PO$_4$, Tol/THF, 100 °C, 36 h, 70%.

Synthesis of (1,1':2',1''-terphenyl)-2,6-dicarbaldehyde (9):



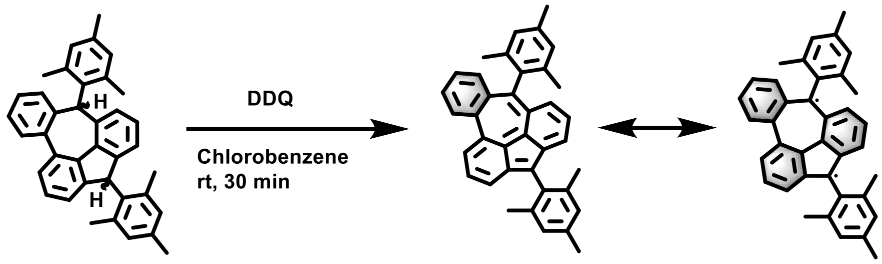
Compound (1,1':2',1''-terphenyl)-2,6-dicarbaldehyde (**9**) was synthesized according to our previous work.[1] A 500 mL round-bottom Schlenk flask was charged with commercially available 2-bromoisophthalaldehyde (6.0 g, 26.76 mmol), commercially available 2-biphenylboronic acid (12.8 g, 61.54 mmol), K_2CO_3 (25.5 g, 184.62 mmol) and $Pd(PPh_3)_4$ (0.6 g, 0.48 mmol) and was evacuated and charged with argon three times. Then degassed 1,4-dioxane (300 mL) and water (30 mL) were added and the reaction mixture was heated at 95 °C for 36 h under argon atmosphere. After cooling to room temperature, the mixture was poured into water and extracted with DCM three times. The organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum. The residue was purified by silica gel column chromatography (ethyl acetate: cyclohexane = 1:20 to 1:10) and washed with ethanol to give compound as a white solid (6.2 g, yield: 81 %). ^{1}H NMR (300 MHz, CD_2Cl_2) δ (ppm) = 9.81 (d, *J* = 0.8 Hz, 2H), 8.07 (d, *J* = 7.7 Hz, 2H), 7.66-7.49 (4H), 7.41 (ddd, *J* = 7.6, 1.5, 0.6 Hz, 1H), 7.18-7.13 (3H), 7.04-6.98 (2H). ^{13}C NMR (75MHz, CD_2Cl_2) δ 191.09, 147.95, 143.26, 140.41, 135.27, 132.95, 132.45, 131.74, 130.80, 130.13, 129.97, 128.83, 128.80, 127.93, 127.73. The spectroscopic data are consistent with those described in literature.[1] HR-ESI-MS (positive mode): calc. for $[M+H]^+$: 287.1067, found for $[M+H]^+$:287.1060 (deviation: -2.4 ppm).

Synthesis of 1,5-dimesityl-1,5-dihydrobenzo[5,6]cyclohepta[1,2,3,4-def]fluorene (mixture of isomers) (4)



A 100 mL round-bottom Schlenk flask was charged with [1,1':2',1''-terphenyl]-2,6-dicarbaldehyde (**9**) (300 mg, 1.05 mmol) and was evacuated and charge with argon three times. Then degassed THF (30 mL) and mesitylmagnesium bromide (1M in diethylether, 8.38 mL, 8.38 mmol) were added and the reaction mixture was stirred at room temperature for overnight under argon atmosphere. Afterwards the reaction mixture was poured into water and extracted with DCM. The organic layer was washed by brine and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum and the residue was directly use for next step without further purify. The residue was dissolved in 20 ml anhydrous DCM and degassed by Argon for 30 min. Then boron trifluoride diethyl etherate (2 mL, 16.2 mmol) was added slowly at 0 °C. Then the ice bath was removed and the mixture was stirred at room temperature for another 40 min. Then the mixture was cooled to 0 °C again and carefully quenched with $NaHCO_3$ solution. Afterwards, the reaction mixture was extracted with DCM. The organic layer was washed by brine and dried over anhydrous MgSO4. The solvent was removed under vacuum and the residue was washed with MeOH to get the pale-yellow powder. R_f: 0.22 (DCM: isohexane = 1:10). The crude product was further purified by recycle-GPC (GPC columns: JAIGEL-2HH + JAIGEL-1HH; column solvent: chloroform; flow rate: 5.0 mL/min; collecting fraction at *t* = 150 min-160 min) to give the title compound as a white solid (mixture of isomers, 312 mg, 61% yield in two steps). Detailed ^{1}H and ^{13}C NMR spectroscopic data of two isomers were reported in **Table S9**. HR-MALDI-TOF (matrix: DCTB): calc. $[M]^+$: 490.2655, found for $[M]^+$: 490.2644 (deviation: -2.2 ppm).

Synthesis of 1,5-dimesitylbenzo[5,6]cyclohepta[1,2,3,4-def]fluorene (1)



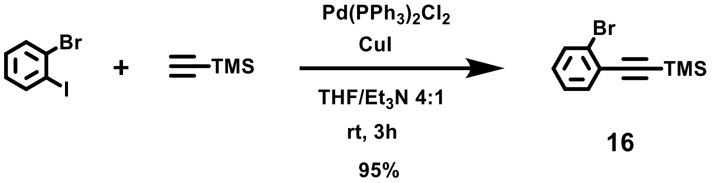
4 **1** **1-1**

To a 10 ml Schlenk tube connected with a vacuum trap (as shown in the following Figure) was charged with compound **4** (20 mg, 0.04 mmmol) and 2.5 mL anhydrous chlorobenzene. The mixture was bubbled with argon for 30 min, then a solution of DDQ (28 mg, 0.12 mmol) in 2.5 mL degassed anhydrous chlorobenzene was added dropwise. After stirring at room temperature for 10 min, start removing the solvent in-situ under reduced pressure (the reaction time was controlled in 30-40 min in total). Then the Schlenk flask was moved to a glove box. The residue was washed with dry, degassed n-heptane to give a dark black solid 20 mg, which was directly use for other characterization. HR-MALDI-TOF (matrix: DCTB): calc. $[M]^+$: 488.2499, found for $[M]^+$: 488.2490 (deviation: -1.8 ppm).

Note: We found that the solvent plays a role in the dehydrogenation to **1**. When anhydrous toluene (from Sigma-Aldrich) was used as the solvent, we mainly got the partially dehydrogenated byproduct of **1** according to the HR MALDI-TOF measurement (the color of the reaction mixture in toluene is reddish). We assumed that the diradicaloid **1** was formed under this reaction condition, but it is easy to abstract hydrogen from the methyl group in toluene due to the high reactivity. Therefore, we changed the solvent to anhydrous chlorobenzene (from Sigma-Aldrich) and the complete dehydrogenation was confirmed by HR-MALDI-TOF measurement (the color of the reaction mixture in chlorobenzene is dark green).

(Figure shows the reaction device: 10 mL Schlenk tube connected with a vacuum trap then connect to a manifold)

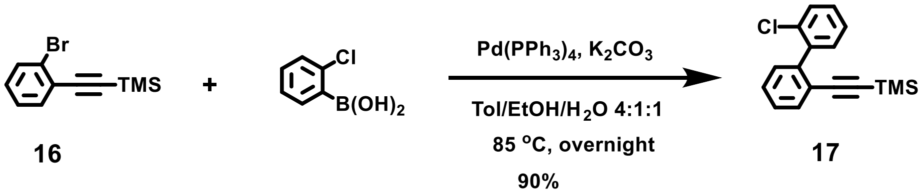
Synthesis of ((2-dromophenyl)ethynyl)trimethylsilane (16)



To an oven-dried 250 mL Schlenk flask was charged with bis(triphenylphosphine)palladium(II) dichloride (1.24 g, 1.77 mmol, 5 mol%) and copper(I) iodide (471.2 mg, 2.47 mmol, 7 mol%), degassed and refilled with argon three times; 80 ml THF after degassed with argon 30 min was added into the flask; then add 4.54 mL 1-bromo-2-iodobenzene (10 g, 35.35 mmol) and 5.38 mL ethynyltrimethylsilane (3.82g, 38.9 mmol) and 20 mL trimethylamine (Et_3N). The reaction mixture was stirred at room temperature for 3 h. These reaction mixture was diluted in 200 mL dichloromethane (DCM) and washed with saturated ammonium chloride solution (3×100 mL) and dried over magnesium sulfate ($MgSO_4$). The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica (Iso-hexane) to afford the compound **16** as a yellow liquid (8.5 g, 95%)

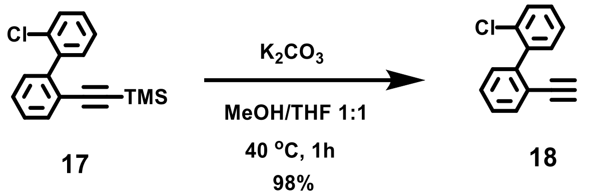
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.52 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.31-7.13 (2H), 0.31 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.73, 132.49, 129.69, 127.01, 125.90, 125.38, 103.17, 99.77, 0.01. HR-ESI-MS (positive mode): calc. for $[M]^+$: 251.9970, found for $[M]^+$:251.9958 (deviation: -4.8 ppm).

Synthesis of ((2'-chloro-[1,1'-biphenyl]-2-yl)ethynyl)trimethylsilane (17)



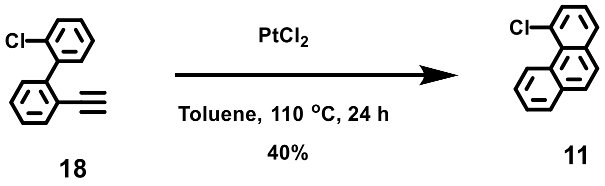
A 200 mL Schlenk flask was charged with (2-chlorophenyl)boronic acid (8.86 g, 56.63 mmol), $Pd(PPh_3)_4$ (1.64 g, 1.42 mmol, 5 mol%) and K_2CO_3 (15.6g, 113.3 mmol) and %) and the flask was deagassed and refilled with argon three times. To the reaction mixture was added a solution of **16** (7.17 g, 28.32 mmol) in toluene (40 mL), 10 mL EtOH and 10 mL H_2O. The reaction mixture was stirred at 85 °C for overight under argon. After cooling to room temperature, the reaction mixture was poured into water, extracted with ethyl acetate. The organic layer dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica (iso-hexane) to give compound **17** as a yellow liquid (7.3 g, 90%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.54 (dd, *J* = 7.3, 2.2 Hz, 1H), 7.46 (m, 1H), 7.41-7.29 (6H), 0.03 (s, 9H). ^{13}C NMR (75MHz, CD_2Cl_2) δ 143.20, 140.06, 133.72, 132.37, 132.08, 130.19, 129.80, 129.46, 128.80, 128.24, 126.87, 123.49, 104.19, 98.53, -0.19. HR-ESI-MS (positive mode): calc. for $[M]^+$: 284.0783, found for $[M]^+$:284.0773 (deviation: -3.5 ppm).

Synthesis of 2-chloro-2'-ethynyl-1,1'-biphenyl (18)



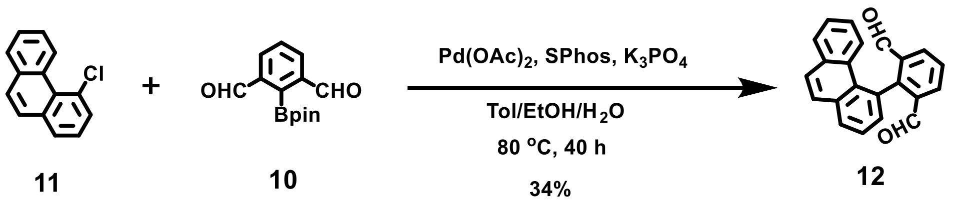
In a 250 mL round-bottom Schlenk flask compound **17** (6.07 g, 21.3 mmol), K_2CO_3 (5.89 g, 42.6 mmol), MeOH (40 mL) and THF (40 mL) were added and degassed with argon for 15 minutes. Then the reaction mixture was stirred at 40 °C for 1 h. After cooling to room temperature, the reaction mixture was passed through a plug of silica with DCM as eluent. The solvent was removed under reduced pressure to yield the target compound **18** as a light-yellow liquid (4.45 g, 98%) then directly use for next step without further purify.

Synthesis of 4-chlorophenanthrene (11)



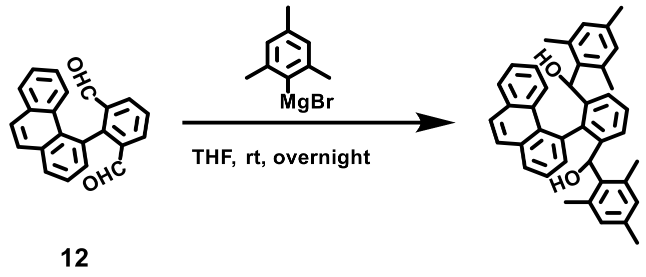
To an oven-dried 200 mL Schlenk flask was charged with **18** (3 g, 14.11 mmol) and platinum chloride (187 mg, 0.71 mmol, 5 mol%) and degassed and anhydrous toluene (100 mL). The reaction mixture was stirred at 110 °C for 24 h. After cooling to room temperature, the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography (Iso-hexane) to afford the compound **11** as a white and waxy solid (1.2 g, 40%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 9.94 (m, 1H), 7.93 (m, 1H), 7.84 (d, J = 9.2 Hz, 1H), 7.80-7.73 (3H), 7.72-7.64 (2H), 7.49 (m, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 135.72, 134.01, 132.05, 131.26, 130.15, 129.19, 128.89, 128.83, 127.80, 127.70, 127.66, 127.53, 126.90, 126.51. HR-ESI-MS (positive mode): calc. for $[M]^+$: 212.0387, found for $[M]^+$:212.0391 (deviation: 1.9 ppm).

Synthesis of 2-(phenanthren-4-yl)isophthalaldehyde (12)



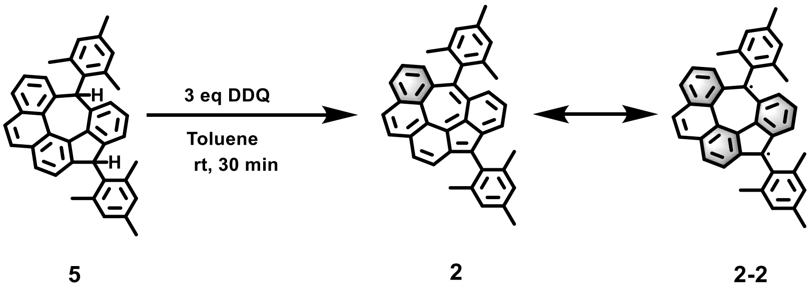
A 100 mL Schlenk flask was charged with **11** (1.45 g, 6.82 mmol), **7** (2.31 g, 8.86 mmol), $Pd(OAc)_2$ (153 mg, 0.68 mmol, 10 mol%) and Sphos (560 mg, 1.36 mmol) and K_3PO_4 (5.79 g, 27.3 m mmol) and the flask was deagassed and refilled with argon three times. Toluene (40 mL), 10 mL EtOH and 10 mL H_2O were added into the reaction mixture after degassed with argon for 30 min. The reaction mixture was stirred at 80 °C for 40 h under argon. After cooling to room temperature, the reaction mixture was poured into water, extracted with ethyl acetate. The organic layer dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica (iso-hexane/DCM 1:1) to give compound **12** as a pale-yellow solid (720 mg, 34%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 9.60 (d, J = 0.8 Hz, 2H), 8.36 (*d*, J = 7.8 Hz, 2H), 8.10 (dd, J = 7.9, 1.5 Hz, 1H), 7.93-7.79 (4H), 7.70 (dd, J = 8.0, 7.2 Hz, 1H), 7.51-7.37 (3H), 7.14 (ddd, J = 8.6, 7.0, 1.5 Hz, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 191.13, 151.32, 135.13, 134.37, 134.07, 133.83, 132.84, 131.07, 130.66, 130.38, 130.22, 129.80, 129.35, 129.06, 128.07, 127.11, 126.94, 126.79, 126.18. HR-ESI-MS (negative mode): calc. for $[M]^-$: 310.0999, found for $[M]^-$:310.0995 (deviation: -1.2 ppm).

Synthesis of 1,5-dimesityl-1,5-dihydroindeno[6,7,1,2-ghij]pleiadene (5)



To a solution of compound **12** (100 mg, 0.32 mmol) in 15 mL of dry THF, mesitylmagnesium bromide (3.22 mL, 1M in diethylether, 3.22 mmol) was added under an argon atmosphere and the mixture was stirred at room temperature for overnight. The reaction mixture was then poured into 50 mL water and extracted by DCM. The organic layer was dried over anhydrous MgSO$_4$ and the solvent was removed under reduced pressure. The residue was redissolved in 20 mL of dry DCM under argon atmosphere and 2 mL of BF$_3$•OEt$_2$ was added at 0 °C. The mixture was stirred for 40 min at room temperature and quenched with water at 0 oC. Then thereaction mixture was washed with NaHCO3 solution (3 x 20 mL) and water (3 x 20 mL). The organic layer was dried over anhydrous MgSO$_4$ and the solvent was removed under reduced pressure. The residue was washed by methanol to give crude product asa white solid. R_f: 0.21 (DCM: iso-hexane = 1:10). This crude product can be further purified by recycle-GPC (GPC columns: JAIGEL-2HH + JAIGEL-1HH; column solvent: chloroform; flow rate: 5.0 mL/min; collecting fraction at *t* = 75 min-80 min) to give compound **5** as a white solid (mixture of isomers, 120 mg, 72% yield in two steps). Detailed ^{1}H and ^{13}C NMR spectroscopic data of two isomers were reported in **Table S10**. HR-MALDI-TOF (matrix: DCTB): calc. [M]$^+$: 514.2655, found for [M]$^+$: 514.2658 (deviation: -0.58 ppm).

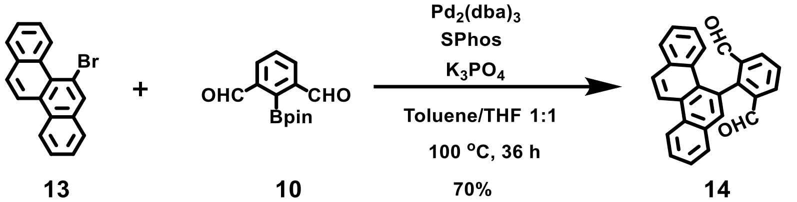
Synthesis of 1,5-dimesitylindeno[6,7,1,2-ghij]pleiadene (2)



A 25 ml Schlenk flask was charged with compound **9** (50 mg, 0.097 mmmol) and 5 mL anhydrous toluene. The mixture was bubbled with argon for 30 min, then a solution of DDQ (66 mg, 0.29 mmol) in 5 mL degassed anhydrous toluene was added dropwise. The reaction was monitored by HR-MALDI-TOF until completion. After stirring at room temperature for about 30 min, the reaction mixture was poured into a Bio-beads SX12 column and eluent with degassed anhydrous toluene under argon (as shown in the following Figure/Left) to remove most of the unreacted DDQ and its reduction side-product. The first brown color fraction was collected in a dry 100 mL single-beck round bottle with bubbling of argon. And the solvent was removed under reduced pressure (as shown in the following Figure/Right). Then the round bottle was transferred to a glove box. The residue was washed with dry, degassed n-heptane to give 20 mg compound **2** as a dark black solid. HR-MALDI-TOF (matrix: DCTB): calc. [M]$^+$: 512.2499, found for [M]$^+$: 512.2508 (deviation: 1.8 ppm).

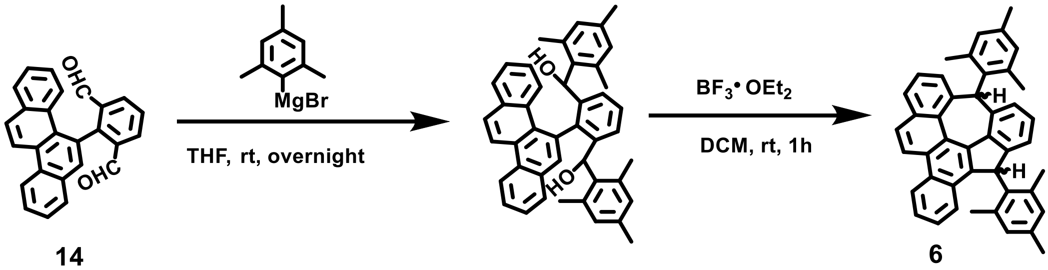
(*Figure shows* operation of Bio-beads SX12 column chromatography then collecting the first fraction then remove the eluent solvent (toluene) by distillation under reduced pressure at room temperature)

Synthesis of 2-(chrysen-5-yl)isophthalaldehyde (14)



A 25 mL seal tube was charged with compound **13** (100 mg, 0.33 mmol), compound **10** (170 mg, 0.65 mmol), $Pd_2(dba)_3$ (30 mg, 0.033 mmol, 10 mol%), Sphos (53.5 mg, 0.13 mmol, 40 mol%) and K_3PO_4 (691 mg, 3.26 mmol) and was evacuated and charged with argon three times. Then degassed toluene (5 mL) and THF (5 mL) was added and the reaction was heated at 100 ^{o}C for 36 h under argon atmosphere. After cooling to room temperature, the mixture was poured into water and extracted with DCM. The organic layer was washed by brine and dried over anhydrous $MgSO_4$. The solvent was removed under vacuum and the residue was purified by silica gel column chromatography (iso-hexene/DCM 1:1) to give compound **14** as a pale-red solid (82 mg, 70%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 9.69 (d, J = 0.8 Hz, 2H), 8.95-8.89 (2H), 8.37 (d, J = 7.7 Hz, 2H), 8.15 (d, J = 9.1 Hz, 1H), 7.99 (ddd, J = 11.2, 7.9, 1.5 Hz, 2H), 7.87-7.80 (3H), 7.73 (ddd, J = 8.0, 7.0, 1.1 Hz, 1H), 7.55-7.47 (2H), 7.16 (ddd, J = 8.7, 7.0, 1.5 Hz, 1H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 191.17, 151.44, 135.35, 134.26, 134.02, 133.84, 131.30, 131.15, 130.59, 130.40, 129.78, 129.70, 129.30, 129.09, 129.03, 128.67, 128.52, 128.07, 127.18, 126.79, 126.73, 123.96, 122.08. HR-ESI-MS (postive mode): calc. for $[M+H]^+$: 361.1223, found for $[M+H]^+$:361.1214 (deviation: -2.4 ppm).

Synthesis of 5,9-dimesityl-5,9-dihydrobenzo[4,5]indeno[6,7,1,2-ghij]pleiadene (6)

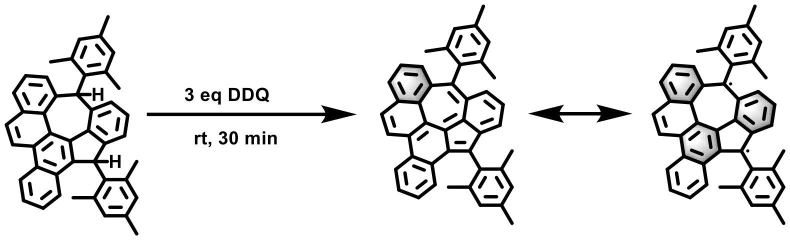


To a solution of compound **14** (95 mg, 0.26 mmol) in 15 mL of dry THF, mesitylmagnesium bromide (2.64 mL, 1M in diethylether, 2.64 mmol) was added under an argon atmosphere and the reaction mixture was stirred at room temperature for overnight. Then the reaction mixture was poured into 50 mL water and extracted by DCM. The organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The residue was redissolved in 20 mL of dry DCM under argon atmosphere and 2 mL of BF_3•OEt_2 was added at 0 ^{o}C. The mixture was stirred for 40 min at room temperature and quenched with water at 0 ^{o}C. Then thereaction mixture was washed with $NaHCO_3$ solution (3x20 mL) and brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure. The residue was washed by methanol to give crude product. R_f: 0.21 (DCM: isohexane = 1:10). This crude product can be further purified by recycle-GPC (GPC columns:

JAIGEL-2HH + JAIGEL-1HH; column solvent: chloroform; flow rate: 5.0 mL/min; collecting fraction at *t* = 75 min-80 min) to give compound **6** as a pale-yellow solid (mixture of isomers, 105 mg, 70% yield in two steps).

Detailed ^{1}H and ^{13}C NMR spectroscopic data of the major isomer were reported in **Table S11**. HR-MALDI-TOF (matrix: DCTB): calc. [M]$^{+}$: 564.2812, found for [M]$^{+}$: 564.2830 (deviation: 3.2 ppm).

Synthesis of 5,9-dimesitylbenzo[4,5]indeno[6,7,1,2-ghij]pleiadene (3)



6 **3** **3-3**

A 25 ml Schlenk flask was charged with compound **6** (50 mg, 0.088 mmmol) and 5 mL anhydrous toluene. The mixture was bubbled with argon for 30 min, then a solution of DDQ (60 mg, 0.26 mmol) in 5 mL degassed anhydrous toluene was added dropwise. The reaction was monitored by HR-MALDI-TOF until completion. After stirring at room temperature for about 30 min, the reaction mixture was poured into a Bio-beads SX12 column and eluent with degassed anhydrous toluene under argon (as shown in the following Figure/Left) to remove most of the unreacted DDQ and its reduction side-product. The first green color fraction was collected in a dry 100 mL single-beck round bottle with bubbling of argon. And the solvent was removed under reduced pressure (as shown in the following Figure/Right). Then the round bottle was transferred to a glove box. The residue was washed with dry, degassed n-heptane to give 18 mg compound **3** as a deep green solid. HR-MALDI-TOF (matrix: DCTB): calc. [M]$^{+}$: 562.2655, found for [M]$^{+}$: 562.2667 (deviation: 2.1 ppm).

(Figure shows operation of Bio-beads SX12 column chromatography then collecting the first fraction then remove the eluent solvent (toluene) by distillation under reduced pressure at room temperature)

2. X-ray Crystallographic Analysis

Single crystal of **4-6** was obtained by slow evaporation of its dichloromethane/methanol solution. Accession codes: The X-ray crystallographic coordinates for structures reported in this article have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposition number CCDC 2111792 (for **4**), 2111790 (for **5**) and 2111791 (for **6**). These data can be obtained free of charge from CCDC via http://www.ccdc.cam.ac.uk/data_request/cif.

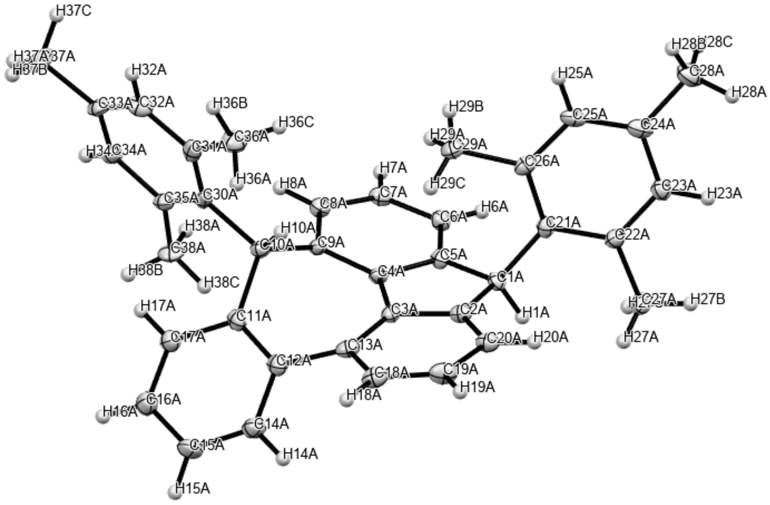


Figure S2. X-ray crystallographic structure of **4** (ORTEP drawing with at the 50% probability level).

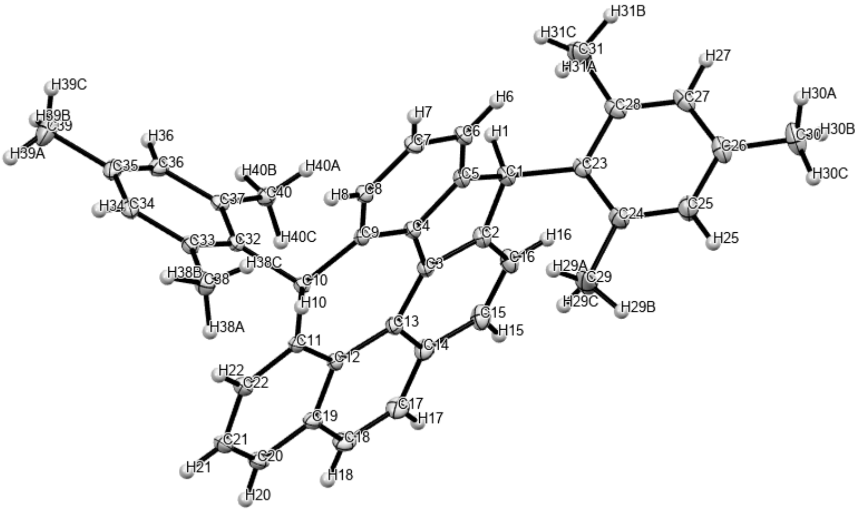


Figure S3. X-ray crystallographic structure of **5** (ORTEP drawing with at the 50% probability level).

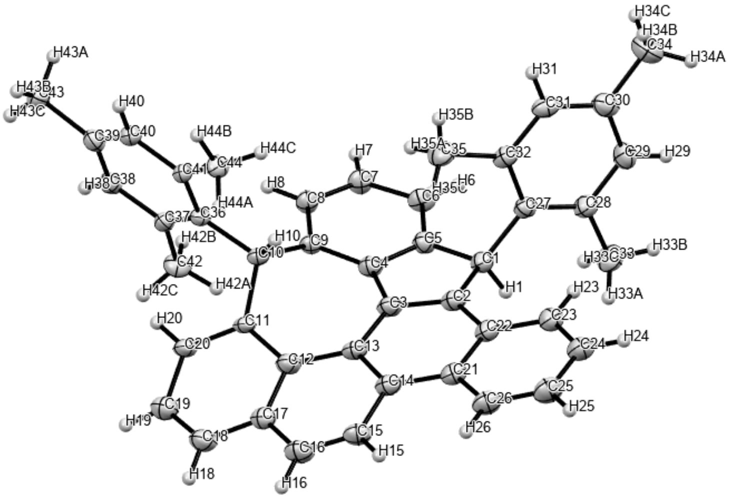


Figure S4. X-ray crystallographic structure of **6** (ORTEP drawing with at the 50% probability level).

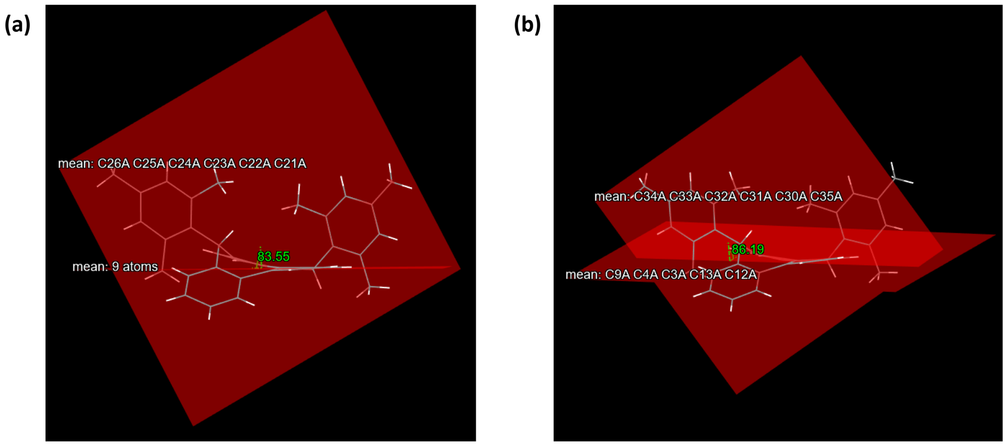


Figure S5. (a) 2,4,6-Trimethylphenyl ring in **4**, attached with the five-membered ring, is rotated out of plane by 83.55°; (b) 2,4,6-Trimethylphenyl ring in **4**, attached with the seven-membered ring, is rotated out of plane by 86.19°.

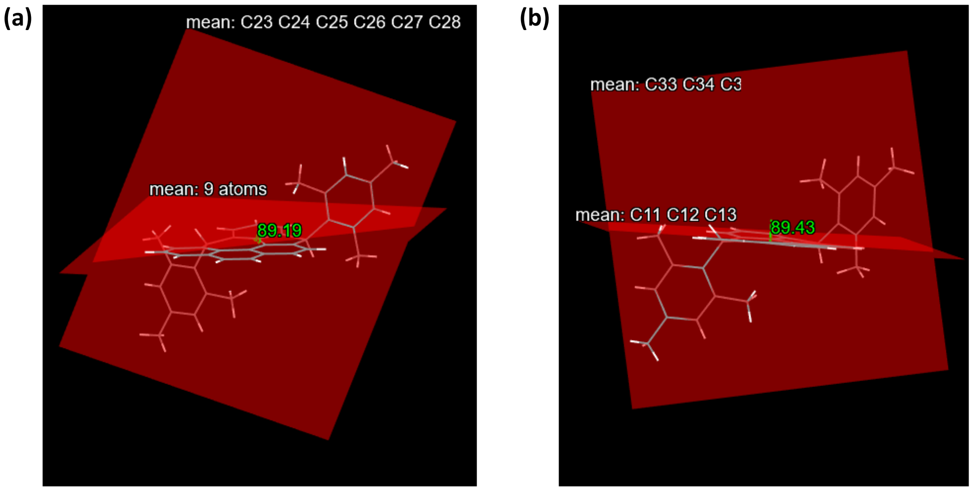


Figure S6. (a) 2,4,6-Trimethylphenyl ring in **5**, attached with the five-membered ring, is rotated out of plane by 89.19°; (b) 2,4,6-Trimethylphenyl ring in **5**, attached with the seven-membered ring, is rotated out of plane by 89.43°.

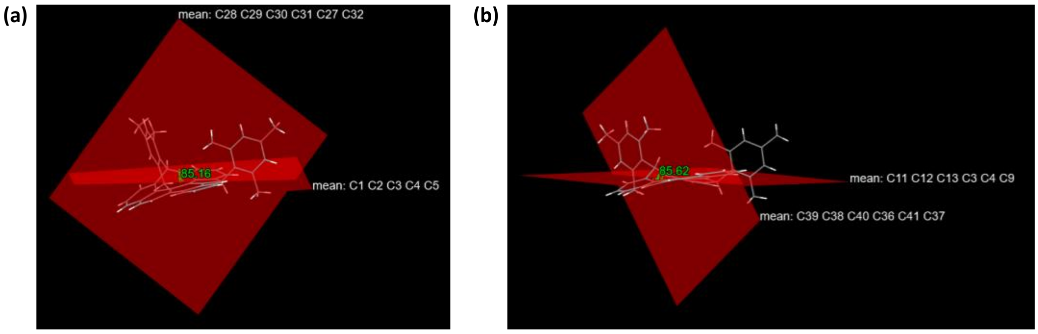


Figure S7. (a) 2,4,6-Trimethylphenyl ring in **6**, attached with the five-membered ring, is rotated out of plane by 85.16°; (b) 2,4,6-Trimethylphenyl ring in **6**, attached with the seven-membered ring, is rotated out of plane by 85.62°.

Table S1. Crystallographic data and details of the structure refinements of **4**, **5** and **6**.

Crystal	**4**	**5**	**6**
Moiety formula	$2C_{38}H_{34}/2CH_2Cl_2$	$C_{40}H_{34}$	$C_{44}H_{36}$
Formula weight	1151.15	514.67	564.73
Crystal size, mm	0.07 × 0.0.08 × 0.1	0.06 × 0.0.08 × 0.1	0.05 × 0.0.05 × 0.1
Crystal system	monoclinicc	triclinic	triclinic
Space group	$P2_1$	$P\bar{1}$	$P\bar{1}$
***a*, Å**	8.8500(18)	8.1200(16)	9.890(2)
***b*, Å**	14.500(3)	12.280(3)	12.050(2)
***c*, Å**	23.750(5)	14.770(3)	12.290(3)
***α*, deg**	90	106.55(3)	84.45(3)
***β*, deg**	99.66(3)	96.00(3)	88.28(3)
***γ*, deg**	90	93.65(3)	88.54(3)
Volume, Å^3	3004.5(11)	1397.3(5)	1456.8(5)
Z	2	2	2
$D_{calcd.}$, g cm^{-3}	1.272	1.223	1.287
F_{000}	1216	548	600
***T*, K**	100(2)	100(2)	100(2)
Radiation (λ, Å)	synchrotron (0.7999)	synchrotron(0.82656)	synchrotron (0.7999)
μ, mm^{-1}	0.336	0.095	0.094
2Θ range (°)	1.958 to 73.306	3.374 to 67.95	3.748 to 73.308
Index ranges	$-13 \leq h \leq 13$, $-20 \leq k \leq 20$, $-31 \leq l \leq 31$	$-10 \leq h \leq 10$, $-16 \leq k \leq 16$, $-19 \leq l \leq 19$	$-14 \leq h \leq 14$, $-17 \leq k \leq 17$, $-16 \leq l \leq 16$
no. of collected reflections	55080	21738	27190
no. of unique ref. (R_{int})	17697 (0.0206)	6363 (0.0217)	7962 (0.0240)
Data/restraints/parameters	17697 / 1 / 751	6363 / 0 / 367	7962 / 0 / 403
R_1, wR_2 [obs $I>2\sigma(I)$]	0.0420, 0.1211	0.0481, 0.1311	0.0615, 0.1664
R_1, wR_2 (all data)	0.0428, 0.1221	0.0490, 0.1322	0.0636, 0.1686
residual peak/hole, e. Å^{-3}	0.447 / -0.700	0.406 / -0.376	0.704 / -0.379
Goodness-of-fit on F^2	1.085	1.042	1.032
CCDC	2111792	2111790	2111791

3. Optical Properties

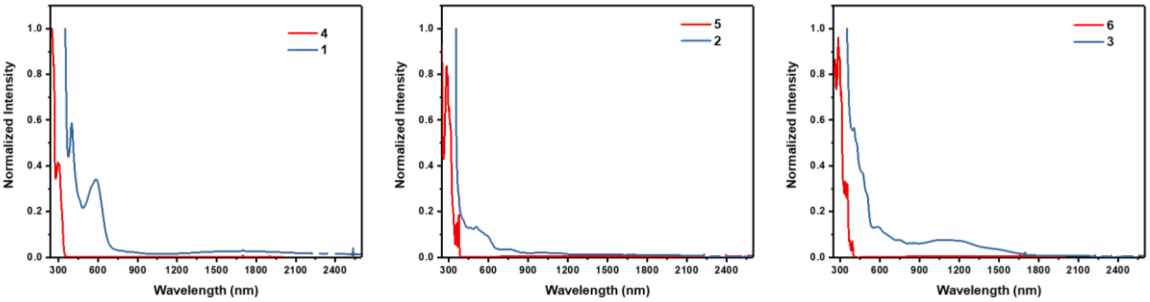


Figure S8. Normalized UV/Vis/NIR absorption spectra of **1**, **2** and **3** compare with their dihydrogen-precursors **4**, **5** and **6**. The spectra were recorded in dry and degassed CH_2Cl_2 at room temperature. The background absorbance at ca. 2250 nm and 2370 nm was deleted which may arise from the overtone of CH vibration of the solvent

Time-depended UV/Vis/NIR absorption spectra of **1-3** were performed to test their stabilities. During the stability test, the solution of **1-3** in dry CH_2Cl_2 was exposed to ambient air and sun light conditions. With the time going on, the solution slowly decomposed with a decrease of the optical density at near-infrared region. By plotting the absorption intensity with ambient light irradiation time, according to the linear regression and extrapolation to % change = 0.50, the half-life time ($t_{1/2}$) of **1-3** was estimated as 11.7 h, 23.8 h and 33.3 h under ambient air and sun light condition, respectively.

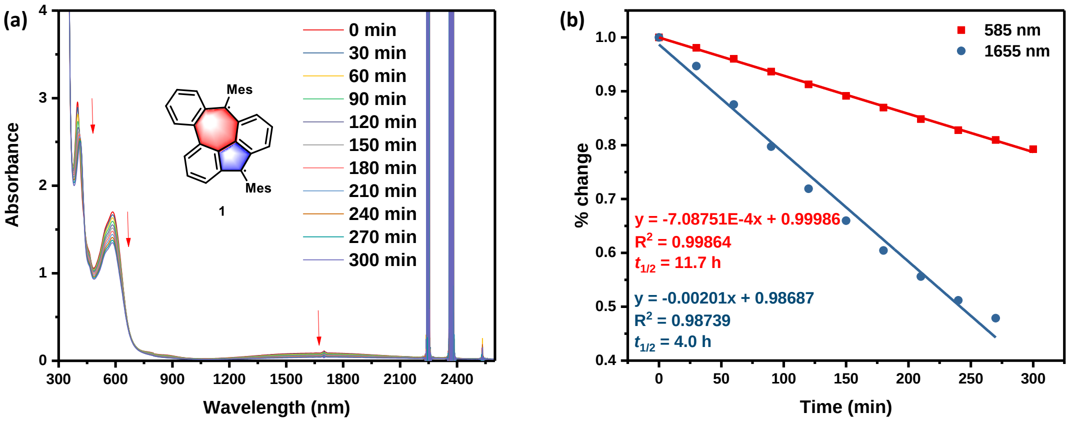


Figure S9. (a) Time-depended UV/Vis/NIR absorption spectra of **1**. The spectra were recorded in dry and degassed CH_2Cl_2 under ambient air and light irradiation. The background absorbance at ca. 2250 nm and 2370 nm may arise from the overtone of CH vibration of the solvent. (b) Changes of the optical density at the absorption maximum at 1655 nm and 585 nm of **1** under ambient condition.

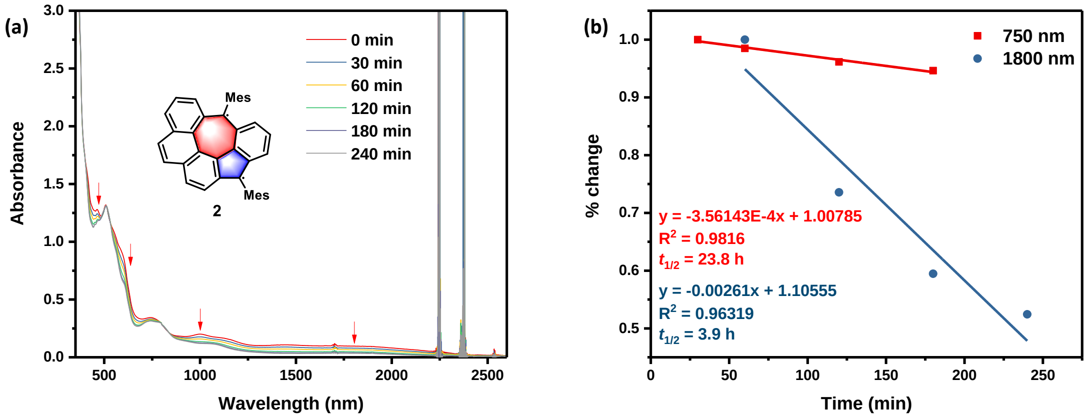


Figure S10. (a) Time-depended UV/Vis/NIR absorption spectra of **2**. The spectra were recorded in dry and degassed CH_2Cl_2 under ambient air and light irradiation. The background absorbance at ca. 2250 nm and 2370 nm may arise from the overtone of CH vibration of the solvent. (b) Changes of the optical density at the absorption maximum at 1800 nm and 750 nm of **2** under ambient condition.

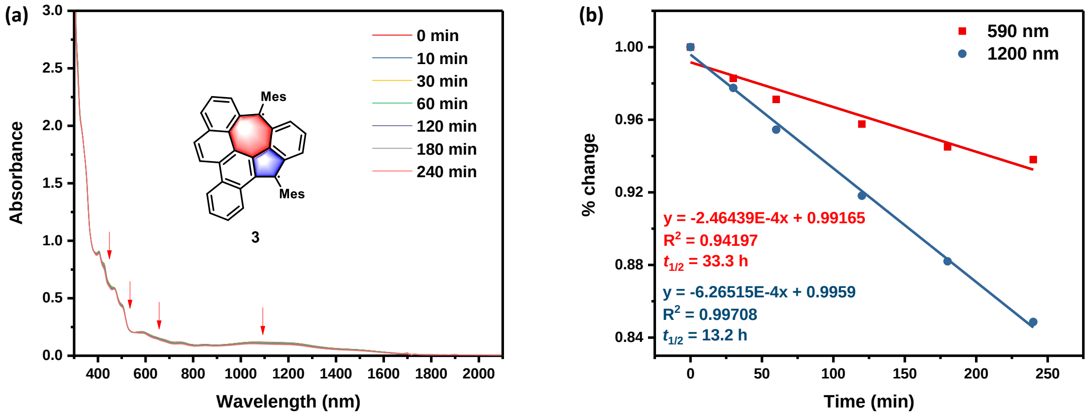


Figure S11. (a) Time-depended UV/Vis/NIR absorption spectra of **3**. The spectra were recorded in dry and degassed CH_2Cl_2 under ambient air and light irradiation. The background absorbance at ca. 2250 nm and 2370 nm may arise from the overtone of CH vibration of the solvent. (b) Changes of the optical density at the absorption maximum at 1200 nm and 590 nm of **3** under ambient condition.

4. EPR Analysis

Unless otherwise noted, commercially available starting materials, reagents, catalysts, and dry solvents were used. Continuous wave (CW) EPR measurements were carried out on a Bruker EMXmicro spectrometer equipped with a Bruker ER4122-SHQE-W1 resonator and an Oxford Instruments ESR900 cryostat. The temperature was varied using an Oxford Instrument ITC503 controller. Typical scans used 50 µW power, 1 G modulation amplitude, 100 kHz modulation frequency, 20 ms time constant. For each temperature we checked that the signal was not saturated by measuring the signal intensity at different powers and observing a linear behaviour. The data was then fit to the Bleaney-Bowers equation to obtain the value of exchange coupling J (or the singlet-triplet energy gap ΔE_{ST}, in which $\Delta E_{\mathrm{ST}} = -J$):

$$\chi_m(T) = \frac{2N_A\mu_B^2 g^2}{k_B T} \times \frac{1}{3 + exp(-J/k_B T)}$$

Where N_A is the Avogadro constant, μ_B the Bohr magneton, g the Landé factor, k_B the Boltzmann constant [5] Indeed, the mass measured includes both the mass of the diamagnetic part of the sample and the singlet biradical subset.

We simulated the solution EPR measurements using the following Hamiltonian:

$$H = \ \mu_B g B S_z + \sum_{i}^{N} a_{iso}^{(i)} S_z I_z,$$

where, μ_B is the Bohr magneton, g the isotropic Landé factor, $a_{iso}^{(i)}$ the isotropic hyperfine coupling of the i-th nucleus, and N the number of coupled nuclei. All simulations were carried out using the Matlab package Easyspin.

Spin-unrestricted Density Functional Theory (DFT) calculations of the spin density and the EPR constants were carried using the software ORCA 4.2.1 at the PBE0/EPR-II level of theory using the optimized geometry structures by DFT at the B3LYP/6-31 G(d) level.

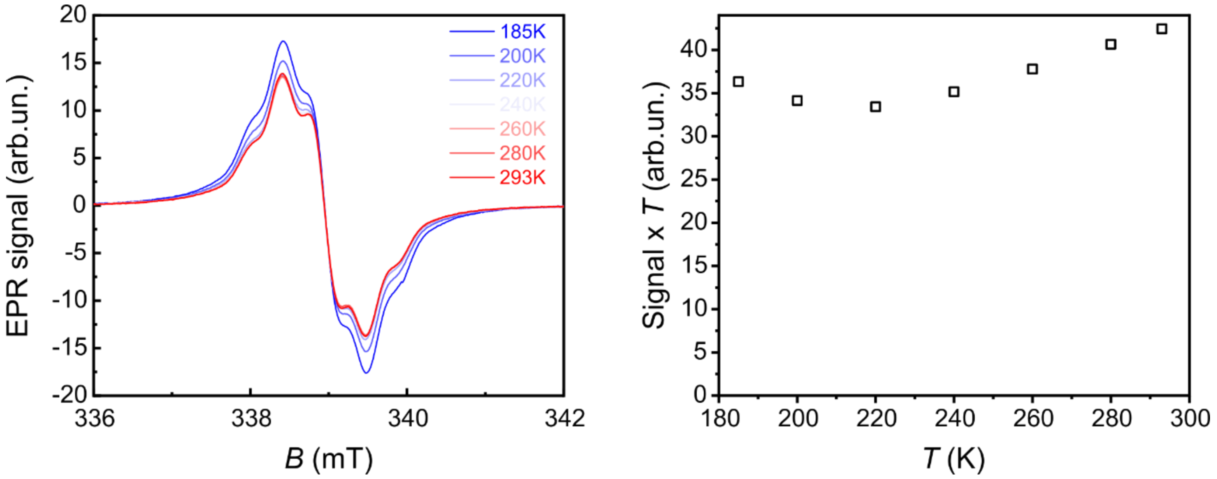


Figure S12. Temperature dependence of the signal for **1** in toluene solution. Integrated signal multiplied by temperature.

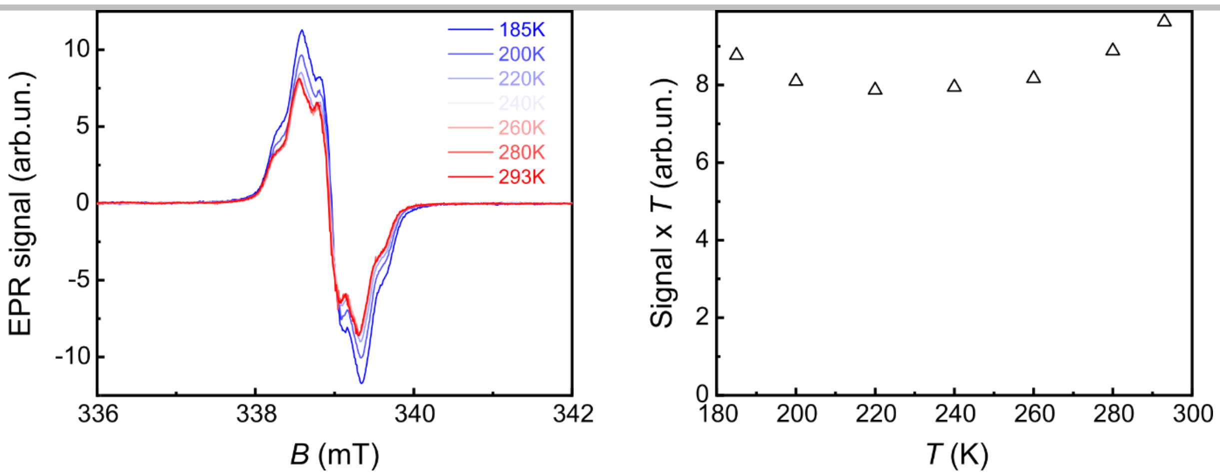


Figure S13. Temperature dependence of the signal for **2** in toluene solution. Integrated signal multiplied by temperature.

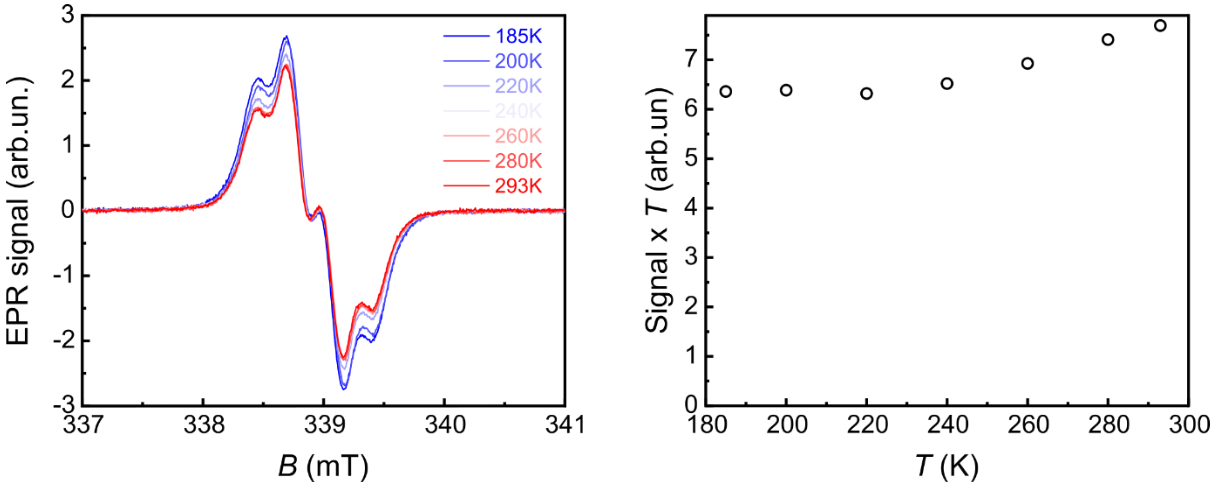


Figure S14. Temperature dependence of the signal for **3** in toluene solution. Integrated signal multiplied by temperature.

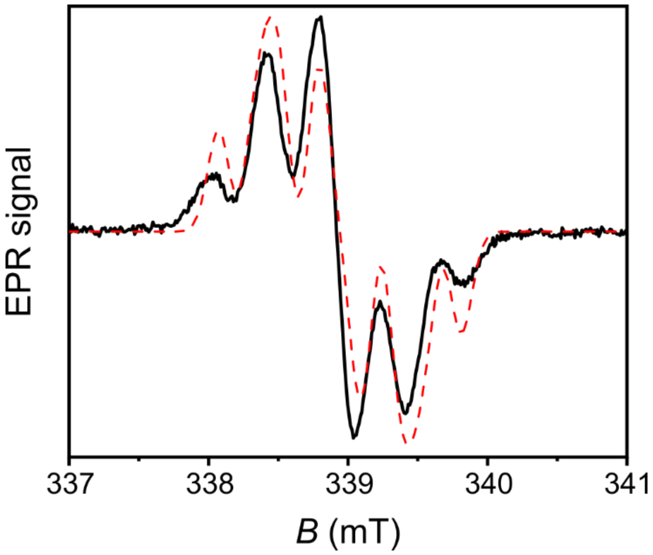


Figure S15. Room temperature continuous wave EPR spectrum of **1** in toluene solution (solid line), and simulation (dashed line).

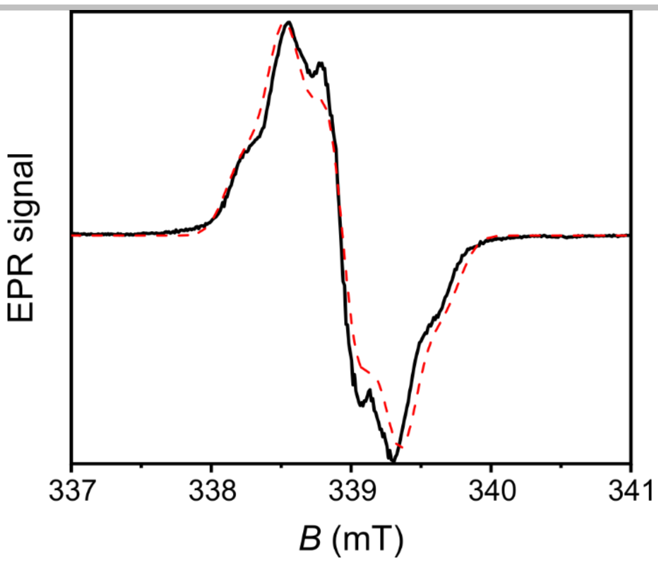


Figure S16. Room temperature continuous wave EPR spectrum of **2** in toluene solution (solid line), and simulation (dashed line).

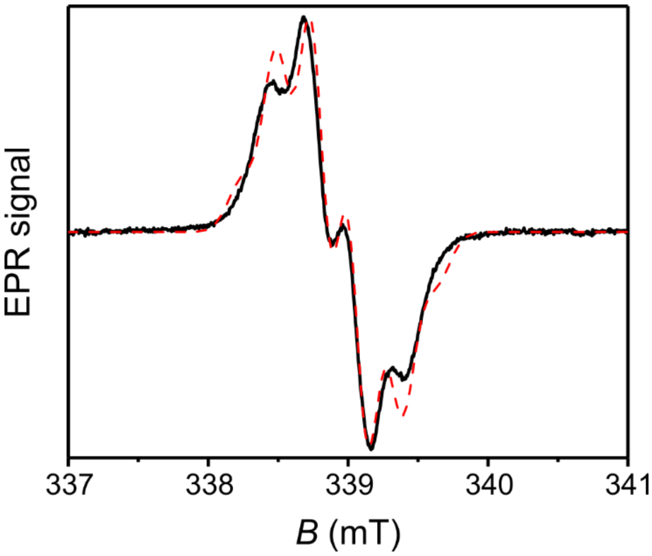
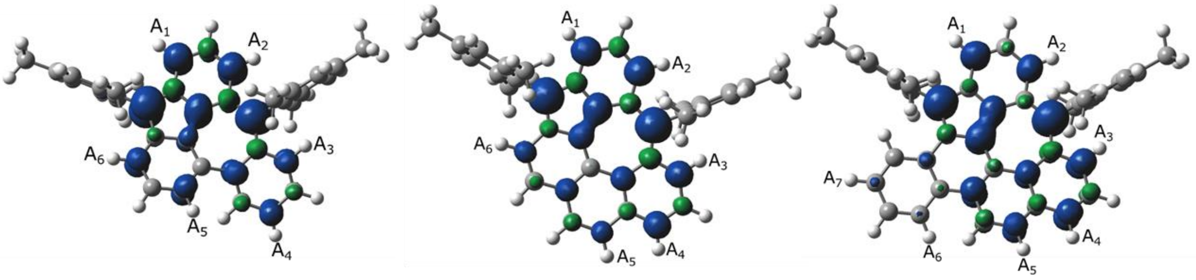


Figure S17. Room temperature continuous wave EPR spectrum of **3** in toluene solution (solid line), and simulation (dashed line).



1 **2** **3**

Figure S18. Spin density surfaces calculated by DFT PBE0/EPR-II in the triplet state, iso value 0.005. Labels indicate the coupled nuclei, EPR parameters are listed in the table.

Table S2. Isotropic EPR parameters for **1**, **2** and **3**, as calculated by DFT and the best fit parameters for the simulations.

	1		**2**		**3**	
	DFT	Best fit	DFT	Best fit	DFT	Best fit
g	2.0026	2.0026	2.0025	2.0026	2.0025	2.0026
A_1 (MHz)	11.8	11.1	11.3	8.9	10.1	7.6
A_2 (MHz)	11.5	11.6	11.0	8.4	8.1	7.2
A_3 (MHz)	6.6	8.0	8.3	7.6	8.4	7
A_4 (MHz)	6.5	8.5	8.4	7.4	8.2	6.3
A_5 (MHz)	6.6	4.6	4.9	3.2	3.5	5.5
A_6 (MHz)	6.1	1.7	5	3.3	1.1	1.25
A_7 (MHz)	--	--	--	--	1.4	1.4

Since the DDQ radical anion could be also generated during the oxidative dehydrogenation reactions of the dehydro precursors, DDQ radical anion was prepared by treating DDQ with bis(cyclopentadienyl)cobalt (Cp_2Co) in THF in the glovebox and measured its EPR for comparison. Experiment show this EPR spectra are not come from DDQ radical anion, due to the reasonably large difference in g-factor (DDQ radical anion is 2.005 and the samples are 2.0026.

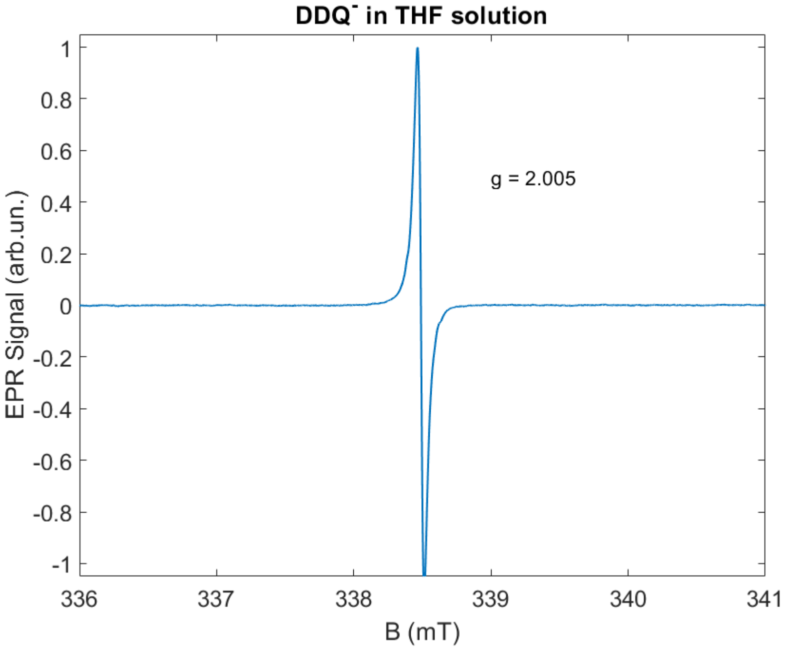


Figure S19. Room temperature EPR spectrum of DDQ radical anion in THF solution. (Prepared through DDQ react with Cp_2Co in THF in the glovebox. We observed changed in colour of the solution. However, N hyperfine coupling was not observed, but the g-factor corresponds to literature[6] and calculations.

5. DFT Calculation

All density functional theory (DFT) calculation was performed using the Gaussian 09 program.[7] The geometry optimization of compound **1**-**3** in the ground state was optimized by the UB3LYP/6-31G(d) and B3LYP/6-31G(d). All geometry optimization was done in the gas phase. Singlet biradical character index (y_0) was estimated using a symmetry-broken UHF/6-31G(d) method after geometry optimization. The following equation showed the calculate method:[8]

$$y = 1 - 2T/(1 + T^2)$$

T is the orbital overlap between the corresponding orbital pairs (HOMO and LUMO), it can be calculated by using the following equation:

$$T = (n_{HOMO}-n_{LUMO})/2$$

Anisotropy of the induced current density (ACID) plots were calculated by Herges's method.[9] Nucleus independent chemical shifts (NICS) values were calculated using the standard gauge invariant atomic orbital (GIAO)[10] method at the level of B3LYP/6-31+G(2d, p) and UB3LYP/6-31+G(2d,p), respectively. All NICS values were averaged by two positions (above and below the plane) of each molecule.

Table S3. Calculation of the biradical character of **1**

E (closed shell state)	E (open shell singlet biradical state)	E (open shell triplet state)	ΔE_{ST} (E open shell singlet biradical state - E open shell triplet state)	y_0 (Biradical yield) UHF/6-31G (d)
-1467.508272 a.u.	-1467.511786 a.u.	-1467.514861 a.u.	1.93 kcal/mol	0.75

Table S4. Calculation of the biradical character of **2**

E (closed shell state)	E (open shell singlet biradical state)	E (open shell triplet state)	ΔE_{ST} (E open shell singlet biradical state - E open shell triplet state)	y_0 (Biradical yield)
-1543.757932 a.u.	-1543.758735 a.u.	-1543.760127 a.u.	0.873 kcal/mol	0.62

Table S5. Calculation of the biradical character of **3**

E (closed shell state)	E (open shell singlet biradical state)	E (open shell triplet state)	ΔE_{ST} (E open shell singlet biradical state - E open shell triplet state)	y_0 (Biradical yield)
-1697.42293 a.u.	-1697.423025 a.u.	-1697.420363 a.u.	-1.67 kcal/mol	0.48

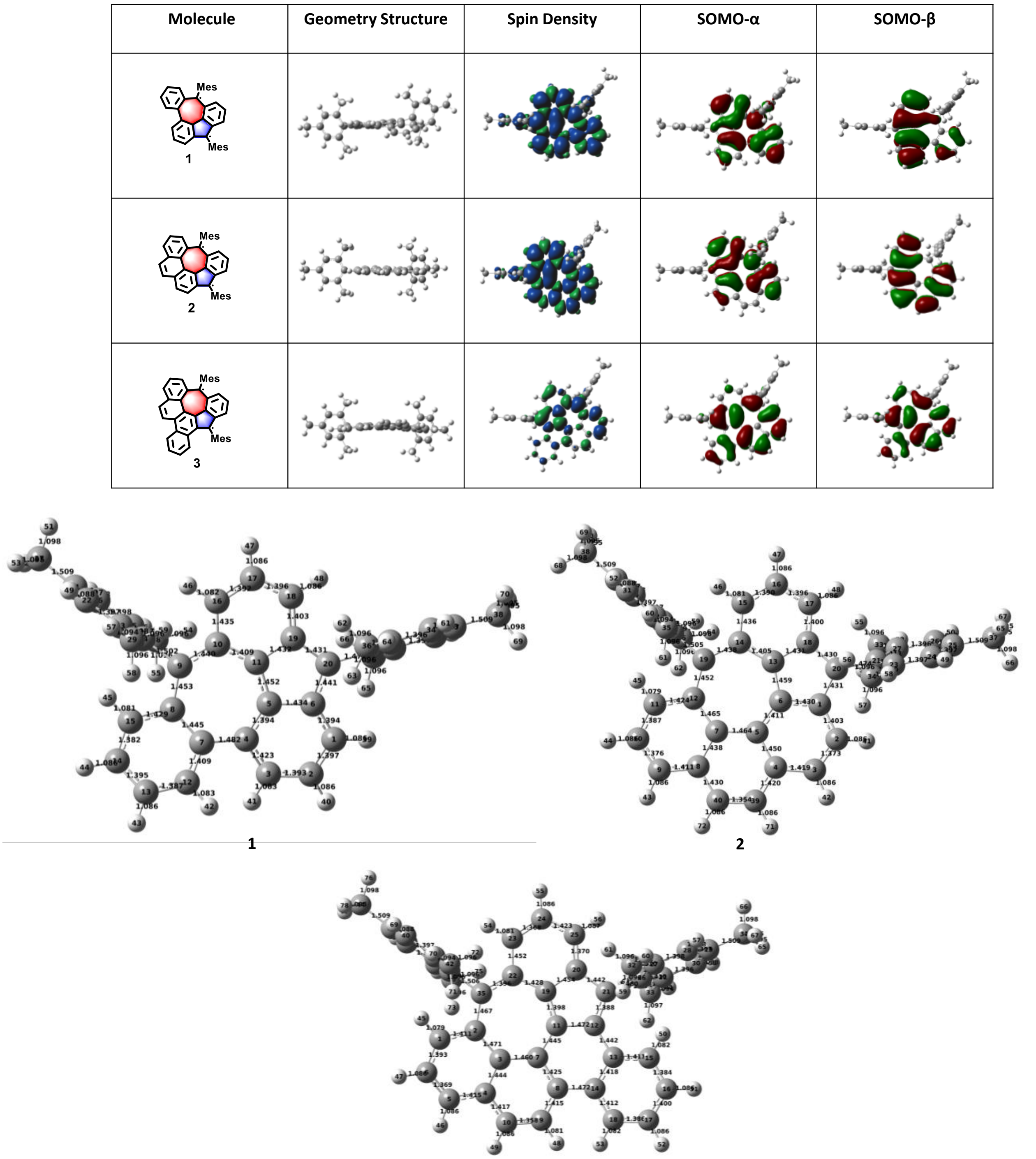


Figure S20. Visualization of optimized geometry structure (side view), spin density and the single occupied molecular orbitals SOMO-α, SOMO-β and bond length plots for **1**, **2** and **3**

As shown in Figure S20, the DFT-optimized structures of **1-3** have a near-planar backbone, respectively. Compared to **3**, the carbon-carbon bond lengths of C8-C9, C9-C10, C19-C20 and C6-C20 in **1** or C12-C19, C14-C19, C18-C20 and C1-C20 in **2** are more closed to the carbon-carbon single bond's length. This result suggests that **1** and **2** show stronger open-shell resonance form, which are consistent with their higher diradical yields (y_0 = 0.75, 0.62 and 0.48 for **1**, **2** and **3**, respectively) that are calculated by the UHF method.

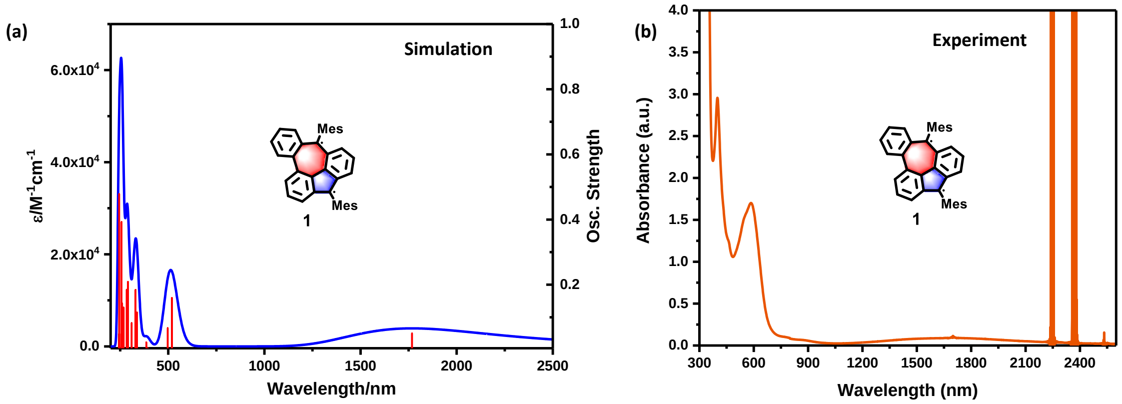


Figure S21. (a) Calculated (UB3LYP/ wb97xd) stick spectrum for **1** showing oscillator strengths; (b) Experimental UV-vis spectra of **1** in dichloromethane.

Table S6. TD-DFT (UB3LYP/ wb97xd) calculated energies, oscillator strength (*f*) and compositions of major electronic transitions of **1**

Energy (eV)	**Wavelength (nm)**	***f***	**Major contributions***
0.7014	1767.67	0.05080	Hb → Lb 50.0%, Ha → La 50.0%
2.3903	518.70	0.15970	Hb-1 → Lb 47.8%, Ha-1 → La 47.8%
2.4964	496.65	0.06710	Hb → Lb+1 47.9%, Ha → La+1 47.9%
3.1527	393.26	0.00460	Hb-4 → Lb 44.5%, Ha-4 → La 44.5%
3.2143	385.73	0.02340	Ha-5 → La 23.7%, Hb-5 → Lb 23.7%, Ha-2 → La 9.7%, Hb-2 → Lb 9.7%, Hb-6 → Lb 7.1%, Ha-6 → La 7.1%
3.6336	341.22	0.00080	Ha-6 → La 35.3%, Hb-6 → Lb 35.3%, Hb-5 → Lb 13.5%, Ha-5 → La 13.5%
3.6739	337.47	0.11490	Hb-2 → Lb 19.4%, Ha-2 → La 19.4%, Ha-7 → La 12.1%, Hb-7 → Lb 12.1%, Ha-5 → La 8.4%, Hb-5 → Lb 8.4%, Ha-6 → La 5.1%, Hb-6 → Lb 5.1%
3.7631	329.47	0.18450	Hb-7 → Lb 25.4%, Ha-7 → La 25.4%, Ha-2 → La 16.2%, Hb-2 → Lb 16.2%
4.0053	309.55	0.08240	Ha → La+2 23.6%, Hb → Lb+2 23.6%, Ha-1 → La+1 11.2%, Hb-1 → Lb+1 11.2%, Ha → La+7 5.4%, Hb → Lb+7 5.4%
4.1420	299.33	0.00170	Hb-3 → Lb 46.4%, Ha-3 → La 46.4%

*Ha: HOMO (α); Hb: HOMO (β); La: LUMO (α); Lb: LUMO (β)

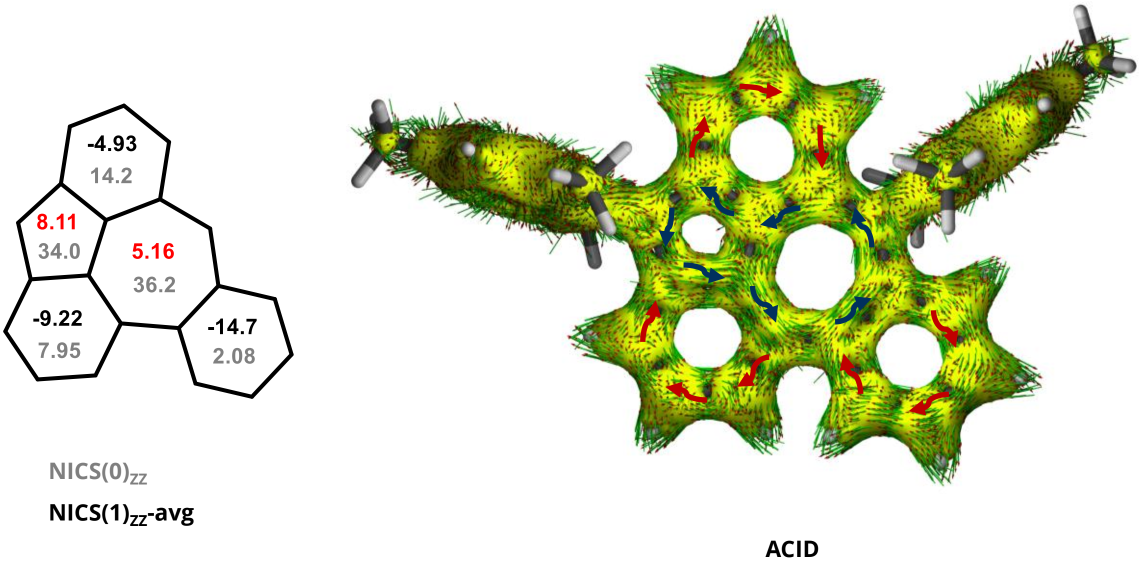


Figure S22. Calculated NICS and ACID plots of **1** at the level of UB3LYP/6–311+G (d, 2p) (D3BJ)

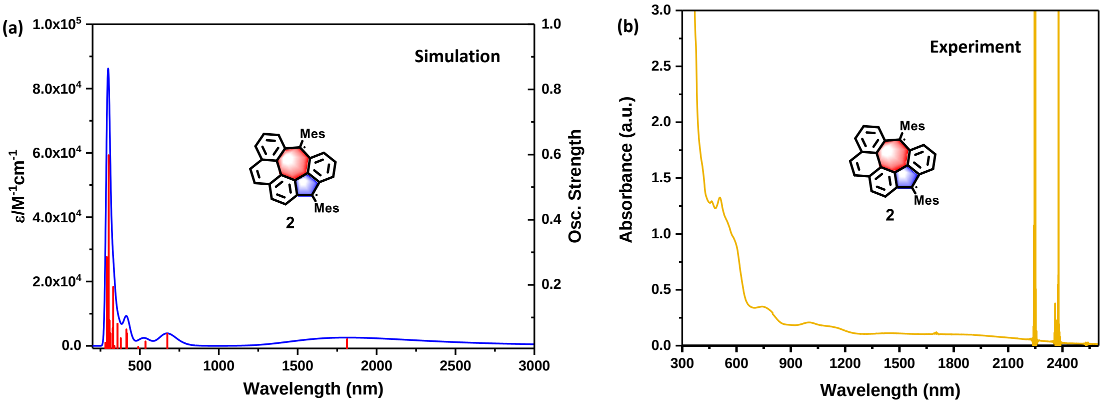


Figure S23. (a) Calculated (UB3LYP/6-31G(d) (D3BJ) stick spectrum for **2** showing oscillator strengths; (b) Experimental UV-vis spectra of **2** in dichloromethane.

Table S7. TD-DFT (UB3LYP/6-31G(d) (D3BJ) calculated energies, oscillator strength (*f*) and compositions of major electronic transitions of **2**

Energy (eV)	Wavelength (nm)	*f*	Major contributions*
0.6838	1813.16	0.03340	Hb → Lb 51.3%, Ha → La 51.3%
1.8417	673.21	0.05030	Hb-1 → Lb 48.9%, Ha-1 → La 48.9%
2.3193	534.58	0.02630	Hb → Lb+1 48.4%, Ha → La+1 48.4%
2.4871	498.51	0.00240	Ha-4 → La 33.6%, Hb-4 → Lb 33.6%, Hb-2 → Lb 16.0%, Ha-2 → La 16.0%
2.5346	489.17	0.01000	Hb-2 → Lb 33.5%, Ha-2 → La 33.5%, Hb-4 → Lb 16.0%, Ha-4 → La 16.0%
2.7298	454.19	0.00110	Hb-3 → Lb 49.5%, Ha-3 → La 49.5%
2.7798	446.02	0.00010	Hb-5 → Lb 49.8%, Ha-5 → La 49.8%
2.9656	418.07	0.05120	Hb-6 → Lb 24.0%, Ha-6 → La 24.0%, Hb → Lb+2 23.1%, Ha → La+2 23.1%
2.9958	413.86	0.06330	Hb-6 → Lb 25.4%, Ha-6 → La 25.4%, Hb → Lb+2 21.2%, Ha → La+2 21.2%
3.2732	378.79	0.03670	Ha-7 → La 42.5%, Hb-7 → Lb 42.5%

*Ha: HOMO (α); Hb: HOMO (β); La: LUMO (α); Lb: LUMO (β)

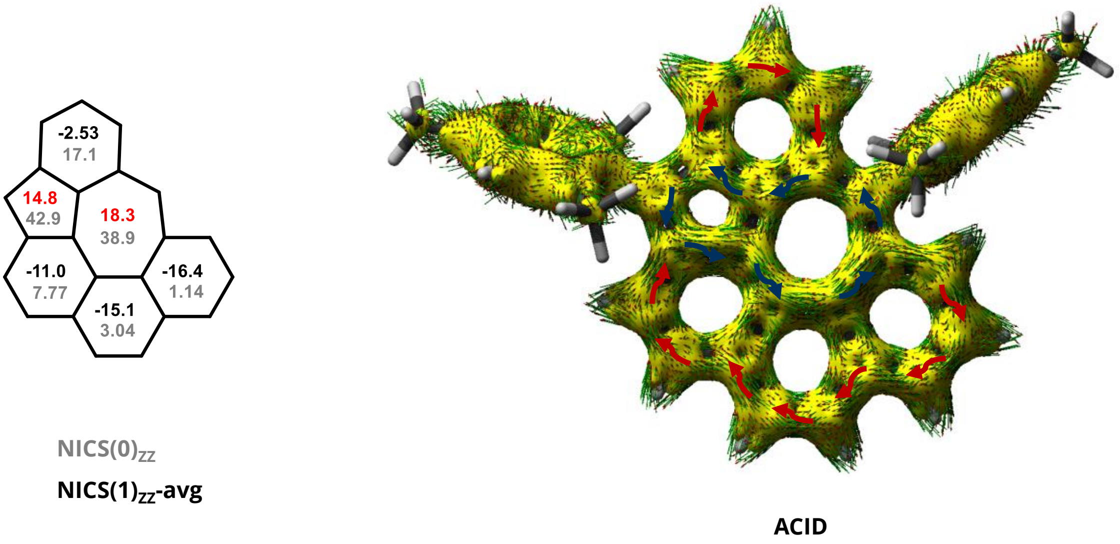


Figure S24. Calculated NICS and ACID plots of **2** at the level of UB3LYP/6–311+G (d, 2p) (D3BJ)

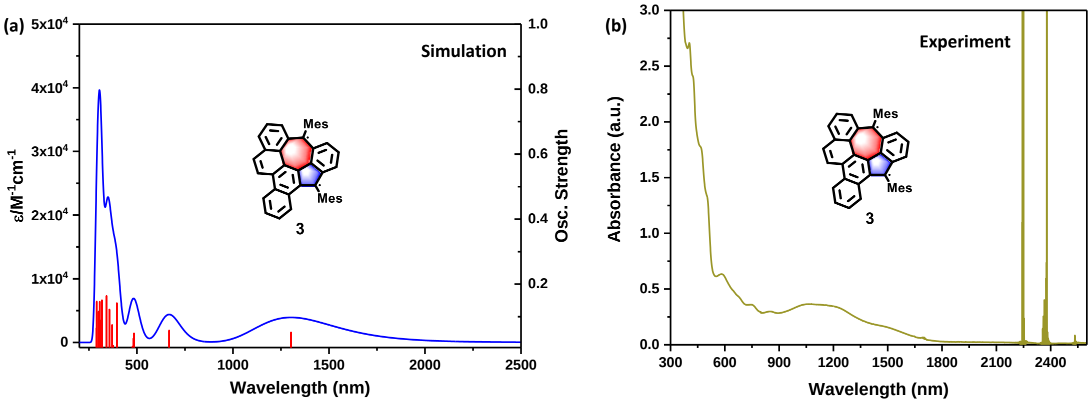
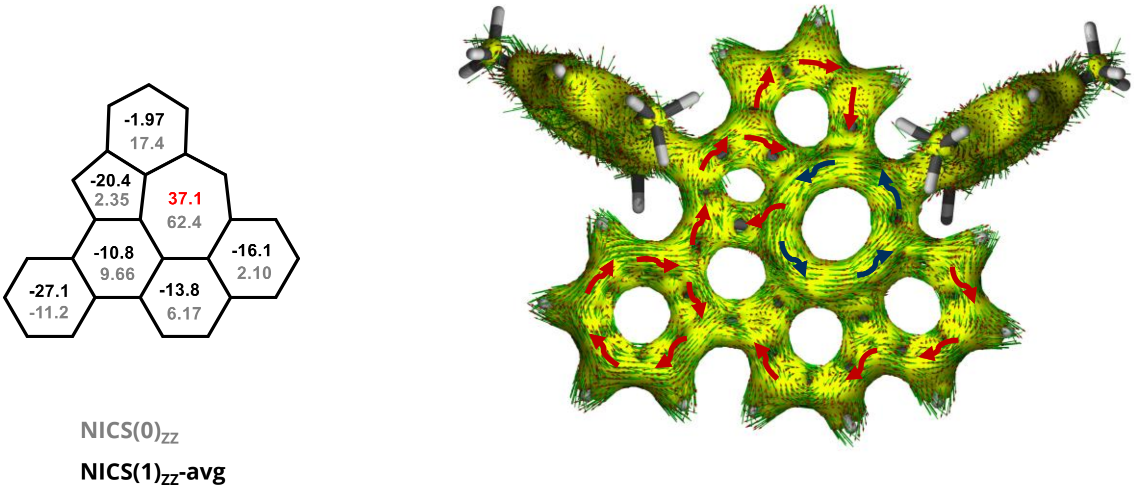


Figure S25. (a) Calculated (UB3LYP/6-31G(d) (D3BJ) stick spectrum for **3** showing oscillator strengths; (b) Experimental UV-vis spectra of **3** in dichloromethane.

Table S8. TD-DFT (UB3LYP/6-31G(d) (D3BJ) calculated energies, oscillator strength (*f*) and compositions of major electronic transitions of **3**

Energy (eV)	**Wavelength (nm)**	***f***	**Major contributions***
0.9519	1302.49	0.05100	Hb → Lb 50.4%, Ha → La 50.4%
1.8567	667.77	0.05700	Hb-1 → Lb 49.2%, Ha-1 → La 49.2%
2.5600	484.31	0.04850	Hb → Lb+1 25.5%, Ha → La+1 25.5%, Ha-3 → La 13.9%, Hb-3 → Lb 13.9%, Ha-4 → La 6.9%, Hb-4 → Lb 6.9%
2.5708	482.28	0.03290	Ha-2 → La 29.1%, Hb-2 → Lb 29.1%, Hb → Lb+1 13.5%, Ha → La+1 13.5%
2.5995	476.95	0.00750	Ha-2 → La 18.1%, Hb-2 → Lb 18.1%, Hb-4 → Lb 11.8%, Ha-4 → La 11.8%, Ha-3 → La 10.5%, Hb-3 → Lb 10.5%, Hb → Lb+1 8.1%, Ha → La+1 8.1%
2.7258	454.85	0.00170	Hb-3 → Lb 22.7%, Ha-3 → La 22.7%, Hb-4 → Lb 22.3%, Ha-4 → La 22.3%
2.8552	434.24	0.00020	Ha-5 → La 44.8%, Hb-5 → Lb 44.8%
2.8735	431.47	0.00020	Hb-6 → Lb 49.1%, Ha-6 → La 49.1%
3.1356	395.41	0.14130	Ha → La+2 39.8%, Hb → Lb+2 39.8%
3.2949	376.29	0.01020	Hb → Lb+3 33.2%, Ha → La+3 33.2%, Ha-7 → La 10.4%, Hb-7 → Lb 10.4%

*Ha: HOMO (α); Hb: HOMO (β); La: LUMO (α); Lb: LUMO (β)



ACID

Figure S26. Calculated NICS and ACID plots of **3** at the level of UB3LYP/6–311+G (d, 2p) (D3BJ)

6. Mass and NMR Spectra

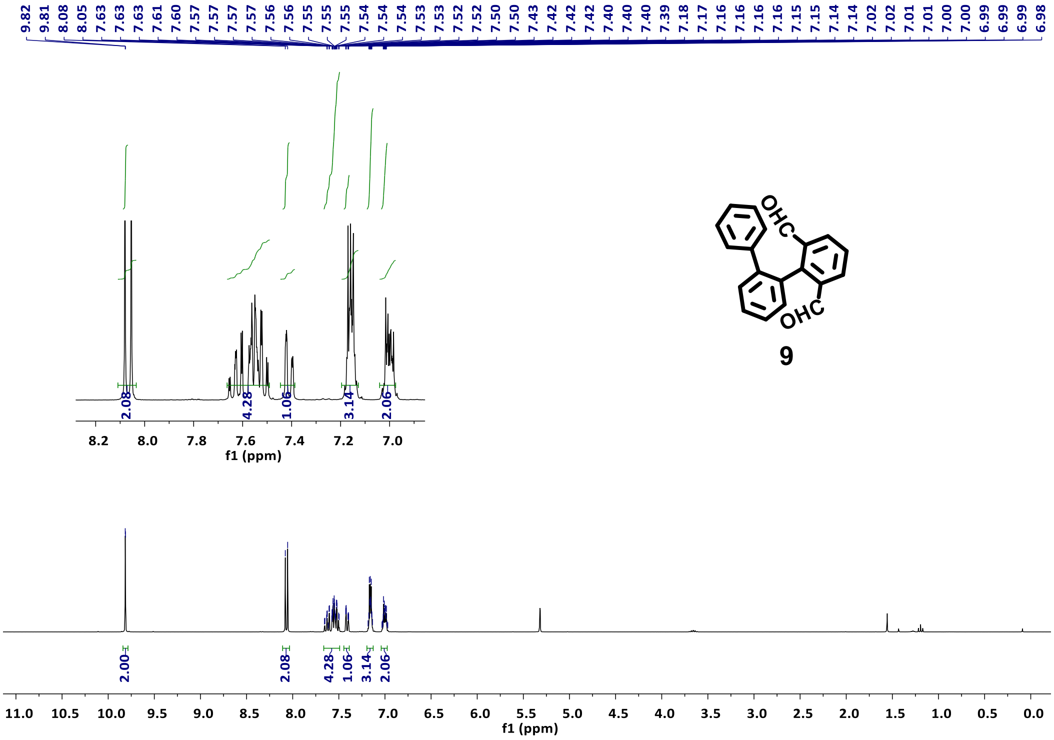


Figure S27. ^{1}H NMR spectrum of **9** dissolved in CD_2Cl_2 300 MHz, 296 K.

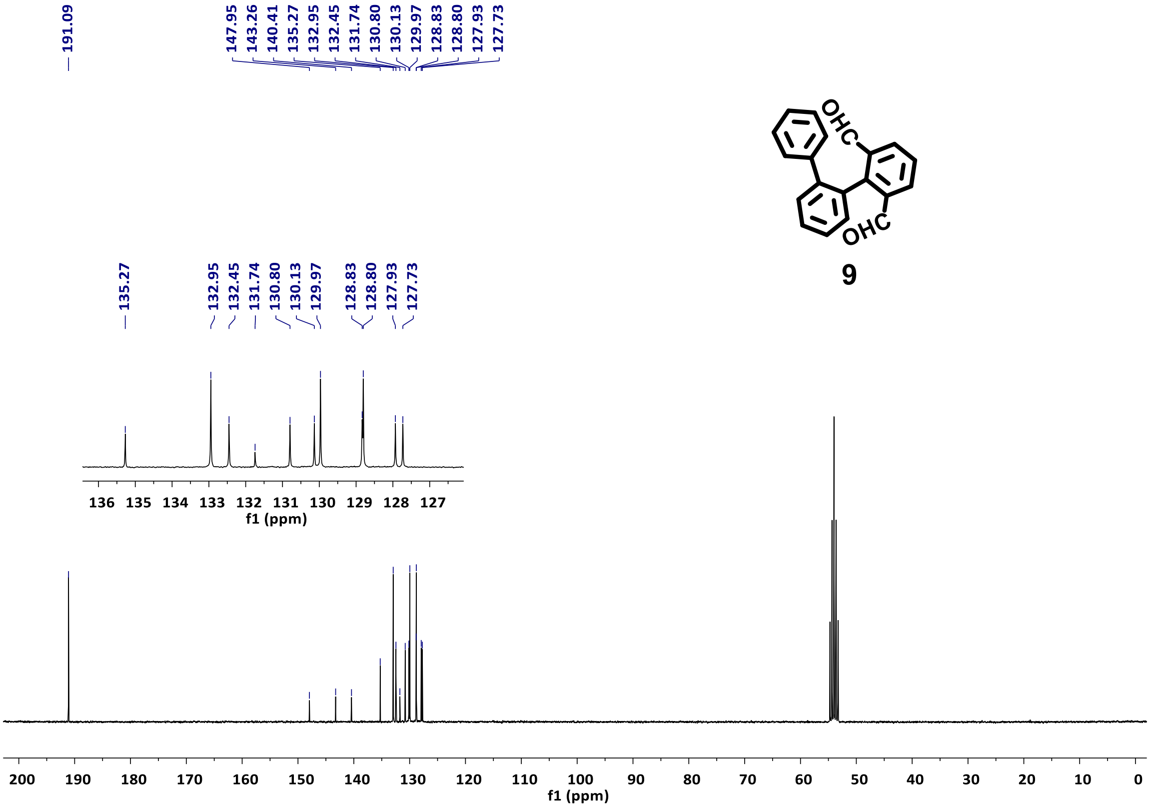
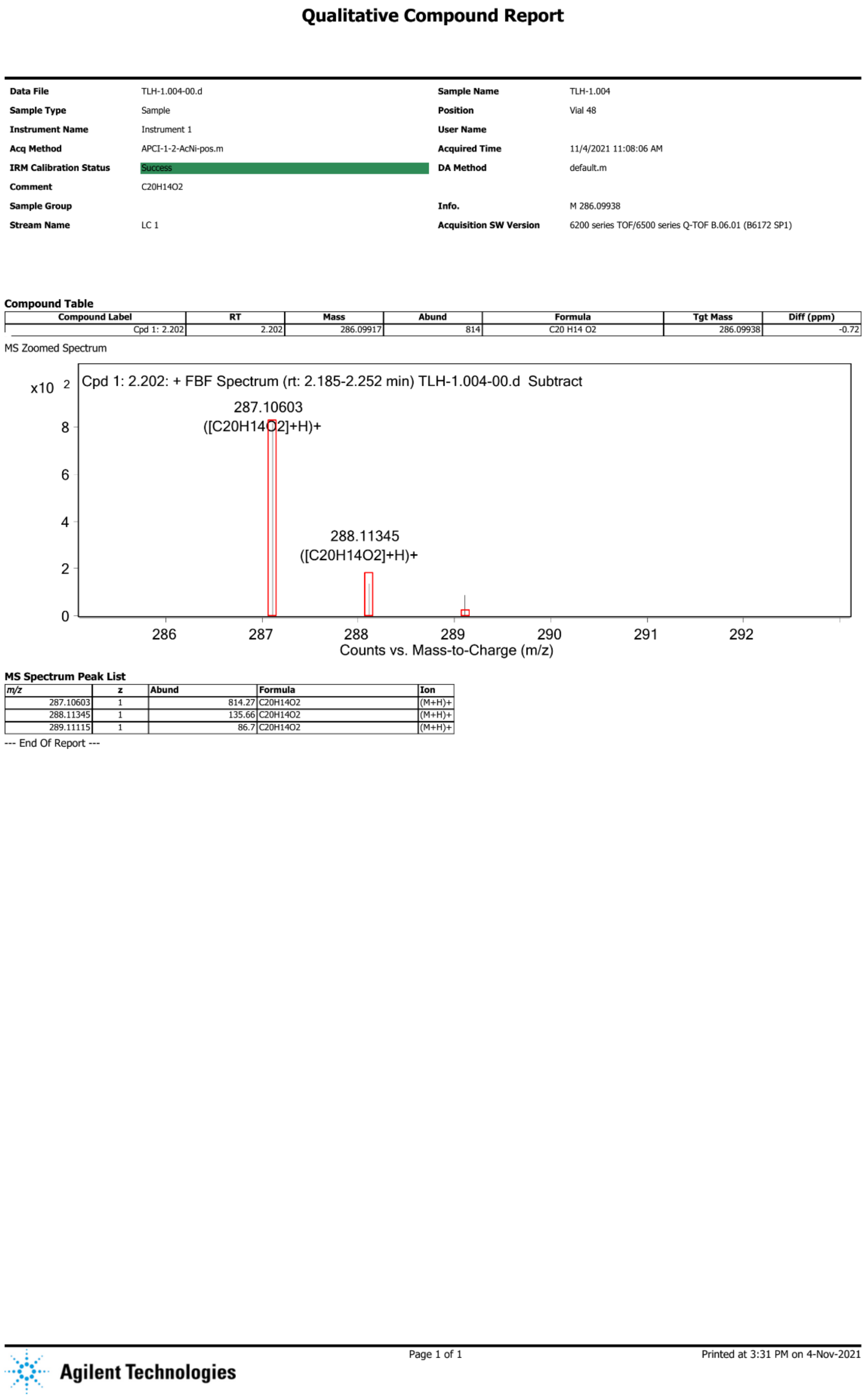


Figure S28. ^{13}C NMR spectrum of **9** dissolved in CD_2Cl_2, 75 MHz, 296 K.



Qualitative Compound Report

Data File	TLH-1.004-00.d	**Sample Name**	TLH-1.004
Sample Type	Sample	**Position**	Vial 48
Instrument Name	Instrument 1	**User Name**	
Acq Method	APCI-1-2-AcNi-pos.m	**Acquired Time**	11/4/2021 11:08:06 AM
IRM Calibration Status	Success	**DA Method**	default.m
Comment	C20H14O2		
Sample Group		**Info.**	M 286.09938
Stream Name	LC 1	**Acquisition SW Version**	6200 series TOF/6500 series Q-TOF B.06.01 (B6172 SP1)

Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: 2.202	2.202	286.09917	814	C20 H14 O2	286.09938	-0.72

MS Zoomed Spectrum

MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
287.10603	1	814.27	C20H14O2	(M+H)+
288.11345	1	135.66	C20H14O2	(M+H)+
289.11115	1	86.7	C20H14O2	(M+H)+

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Figure S29. Qualitative compound report of HR-ESI-MS (positive mode) for **9**.

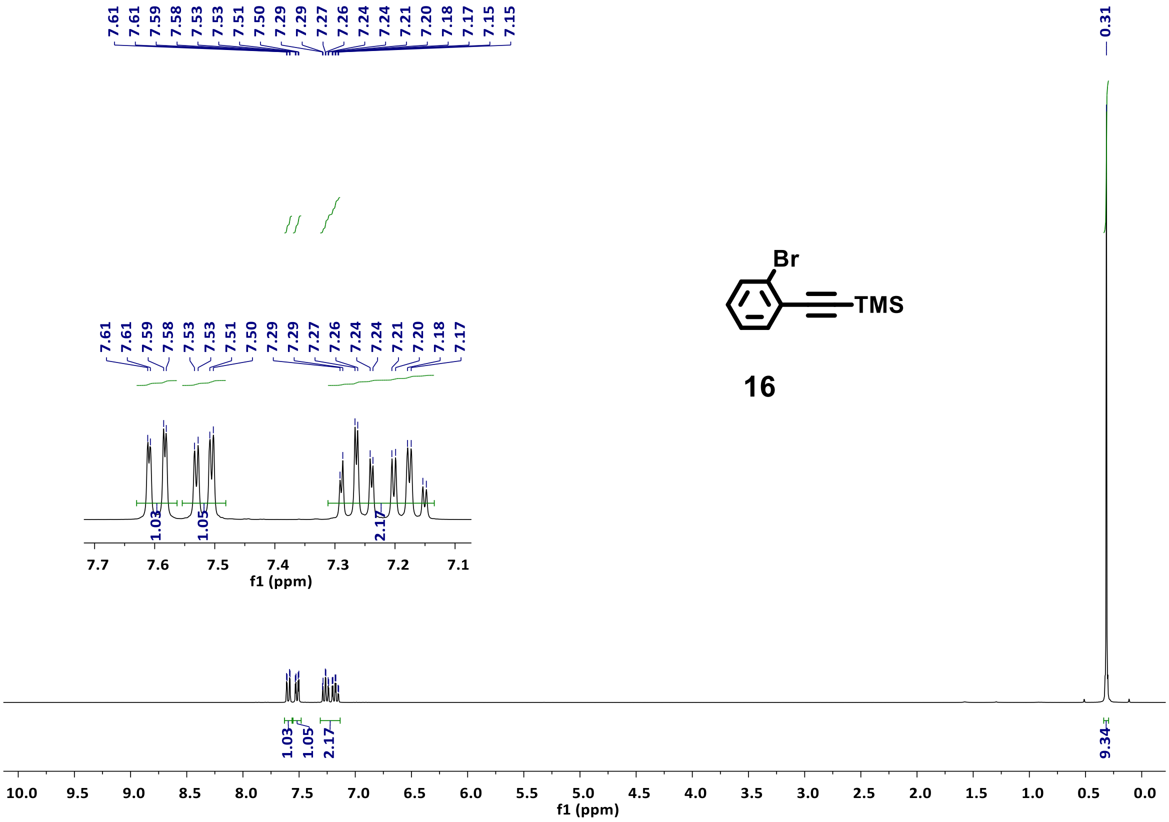


Figure S30. ^{1}H NMR spectrum of **16** dissolved in $CDCl_3$, 300 MHz, 296 K.

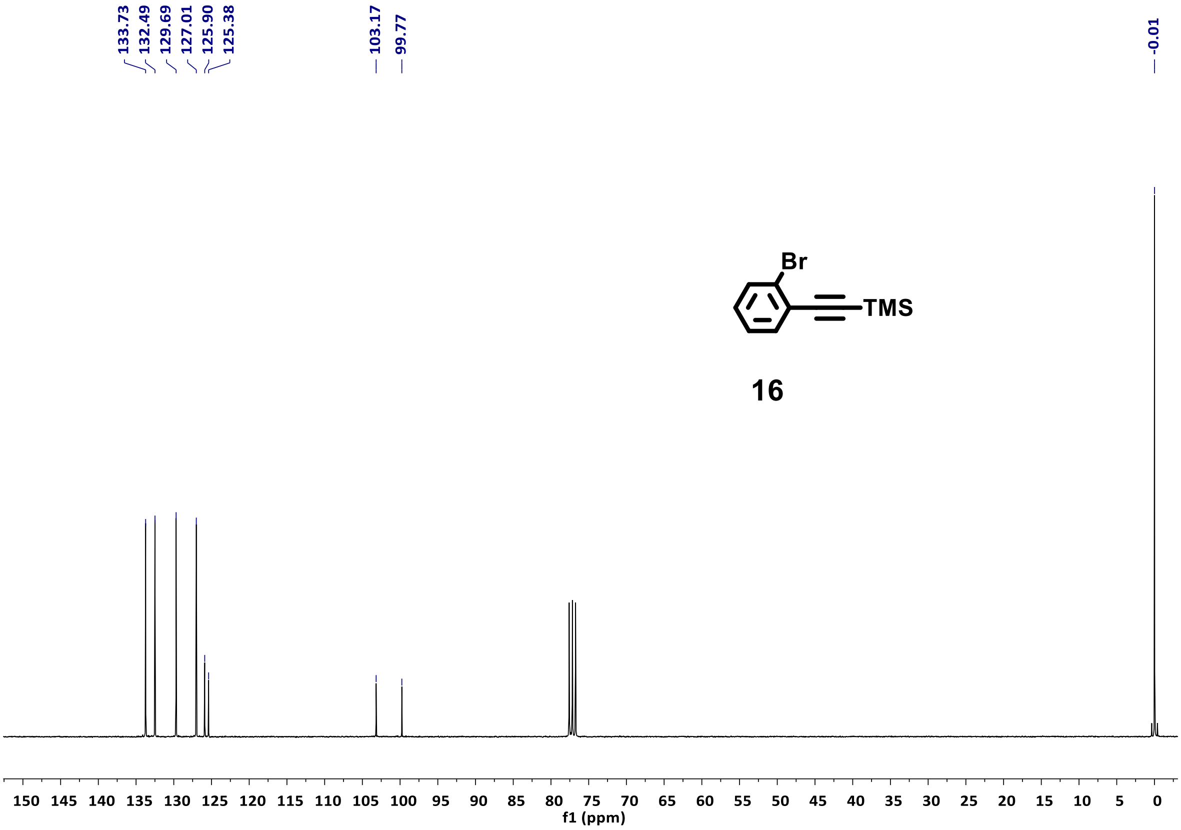


Figure S31. ^{13}C NMR spectrum of **16** dissolved in $CDCl_3$, 75 MHz, 296 K.

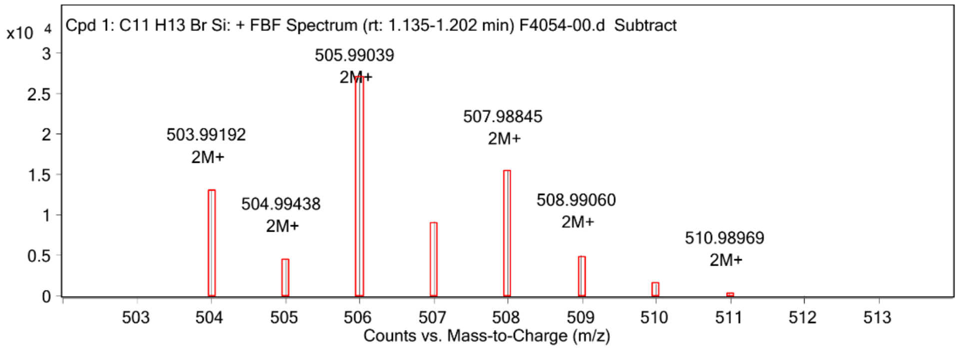
Qualitative Compound Report

Data File	F4054-00.d	**Sample Name**	F4054
Sample Type	Sample	**Position**	Vial 11
Instrument Name	Instrument 1	**User Name**	
Acq Method	APCI-1-2-AcNi-pos.m	**Acquired Time**	5/27/2021 11:01:54 AM
IRM Calibration Status	Success	**DA Method**	default.m
Comment	C11H13BrSi		
Sample Group		**Info.**	M 253.99499
Stream Name	LC 1	**Acquisition SW Version**	6200 series TOF/6500 series Q-TOF B.06.01 (B6172 SP1)

Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C11 H13 Br Si	1.152	251.99578	27003	C11 H13 Br Si	251.99699	-4.79

MS Zoomed Spectrum



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
503.99192	1	13083.74	C11H13BrSi	2M+
504.99438	1	4524.43	C11H13BrSi	2M+
505.99039	1	27003.11	C11H13BrSi	2M+
506.99283	1	9189.4	C11H13BrSi	2M+
507.98845	1	15455.33	C11H13BrSi	2M+
508.9906	1	5036.67	C11H13BrSi	2M+
509.98943	1	1542.61	C11H13BrSi	2M+
510.98969	1	328.24	C11H13BrSi	2M+
511.99613	1	64.11	C11H13BrSi	2M+

--- End Of Report ---

Figure S32. Qualitative compound report of HR-ESI-MS (positive mode) for **16**.

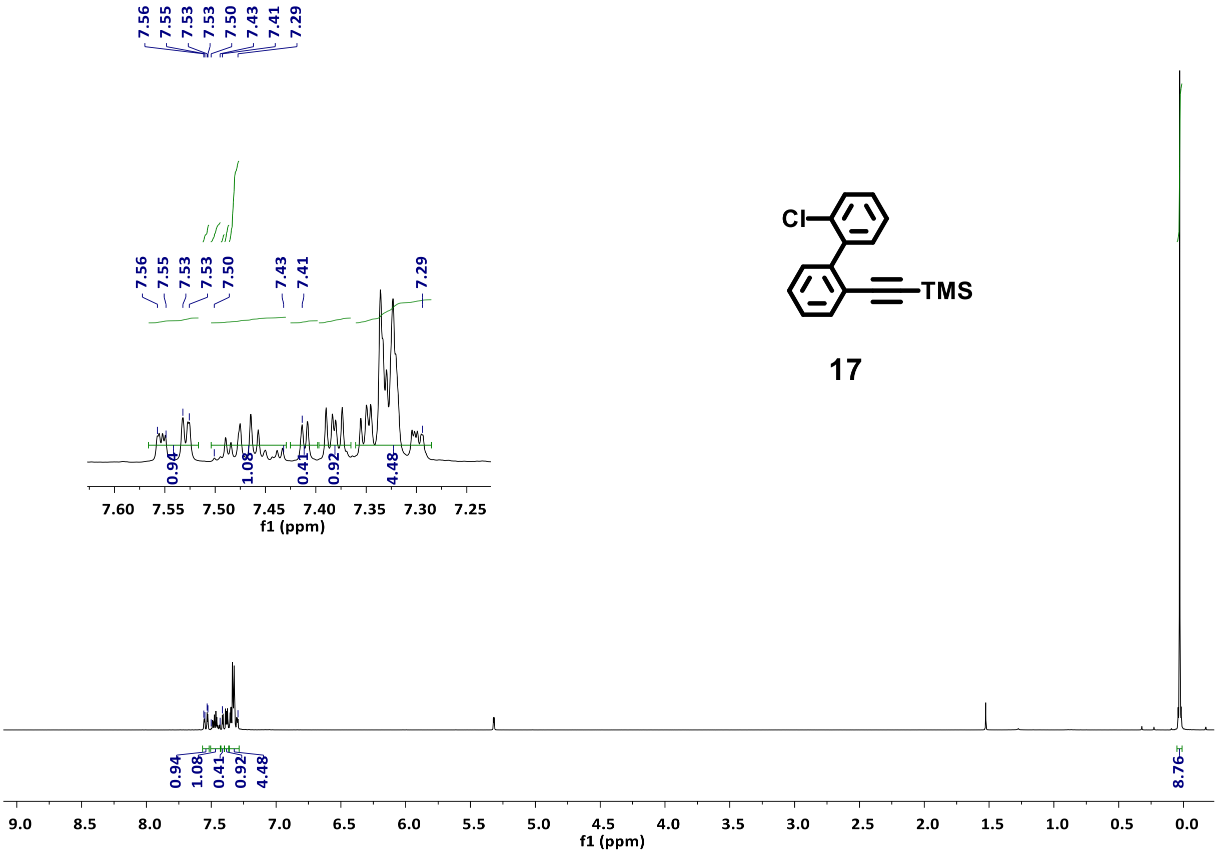


Figure S33. ^{1}H NMR spectrum of **17** dissolved in CD_2Cl_2, 300 MHz, 296 K.

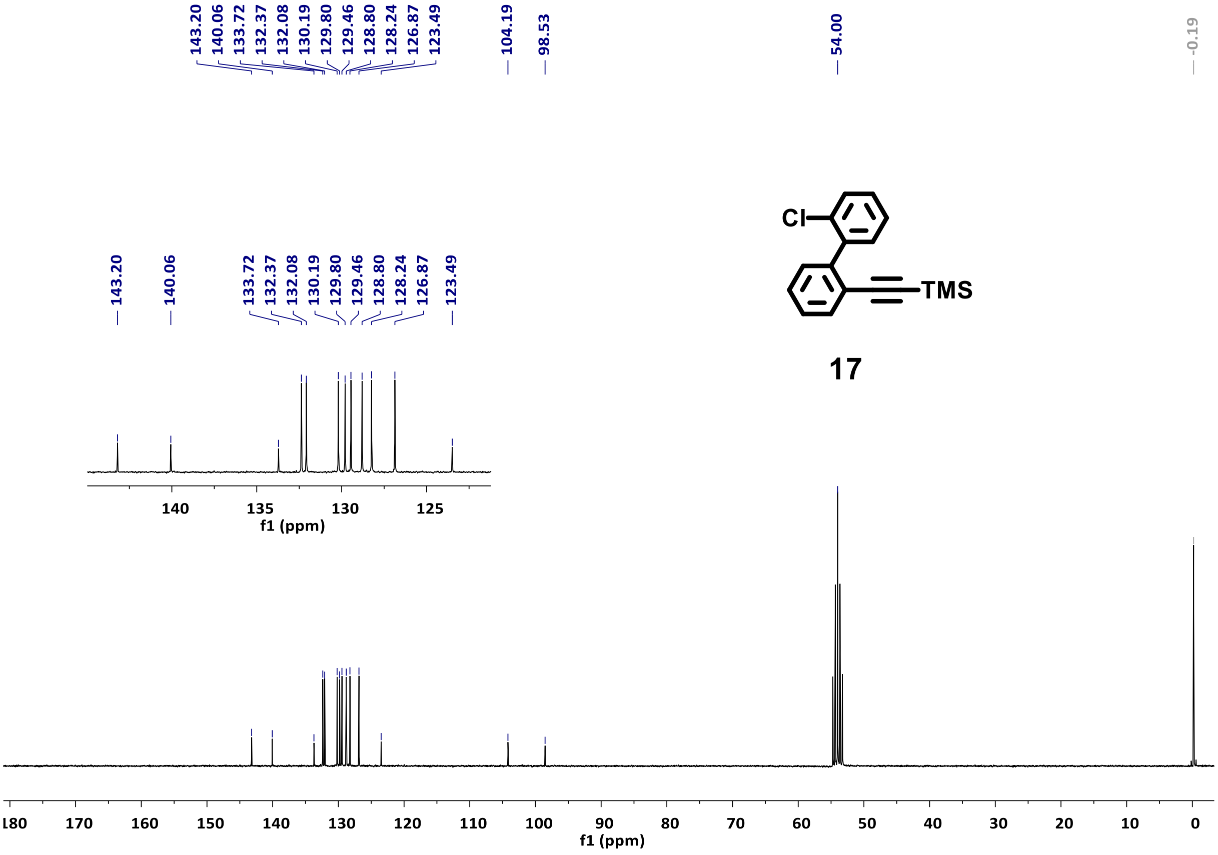


Figure S34. ^{13}C NMR spectrum of **17** dissolved in CD_2Cl_2, 75 MHz, 296 K.

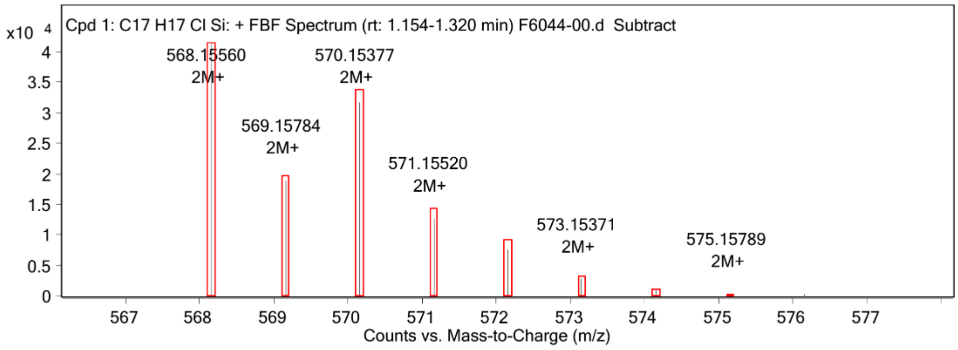
Qualitative Compound Report

Data File	F6044-00.d	**Sample Name**	F6044
Sample Type	Sample	**Position**	Vial 12
Instrument Name	Instrument 1	**User Name**	
Acq Method	APCI-1-2-AcNi-pos.m	**Acquired Time**	5/27/2021 11:05:00 AM
IRM Calibration Status	🟩 Success	**DA Method**	default.m
Comment	C17H17ClSi		
Sample Group		**Info.**	M 284.0788
Stream Name	LC 1	**Acquisition SW Version**	6200 series TOF/6500 series Q-TOF B.06.01 (B6172 SP1)

Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C17 H17 Cl Si	1.187	284.07726	41516	C17 H17 Cl Si	284.0788	-5.43

MS Zoomed Spectrum



MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
568.1556	1	41516.41	C17H17ClSi	2M+
569.15784	1	18825.55	C17H17ClSi	2M+
570.15377	1	31654.14	C17H17ClSi	2M+
571.1552	1	12709.45	C17H17ClSi	2M+
572.15219	1	7606.07	C17H17ClSi	2M+
573.15371	1	2712.66	C17H17ClSi	2M+
574.15317	1	839.67	C17H17ClSi	2M+
575.15789	1	266.19	C17H17ClSi	2M+
576.15399	1	156.25	C17H17ClSi	2M+

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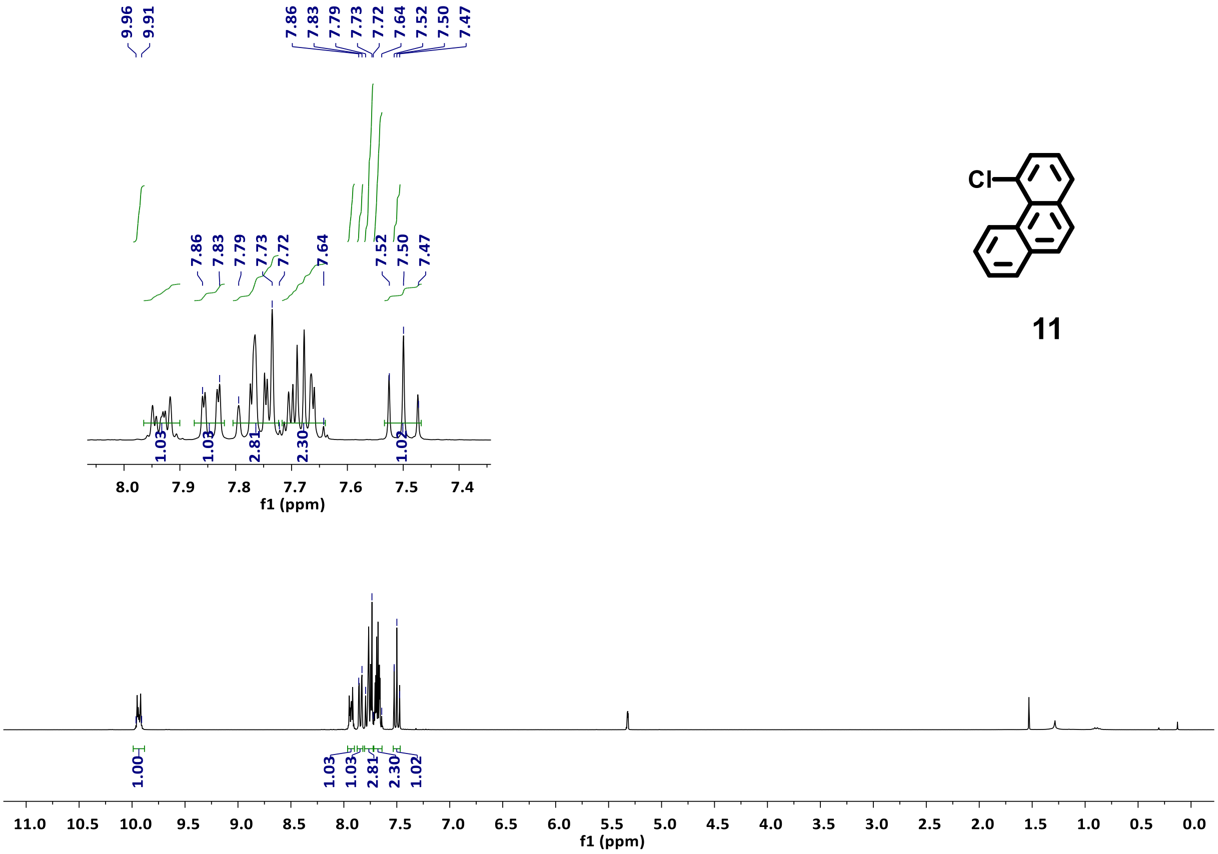
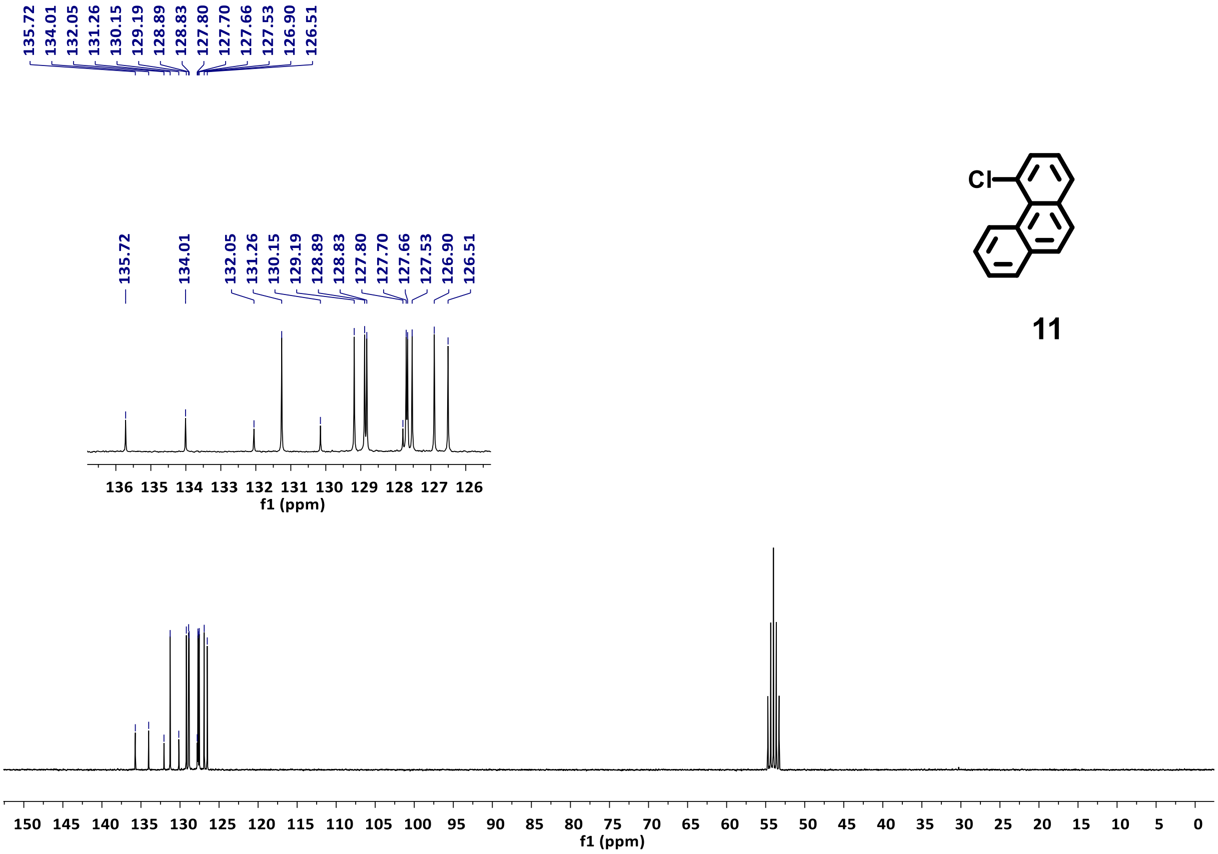
Figure S35. Qualitative compound report of HR-ESI-MS (positive mode) for **17**.



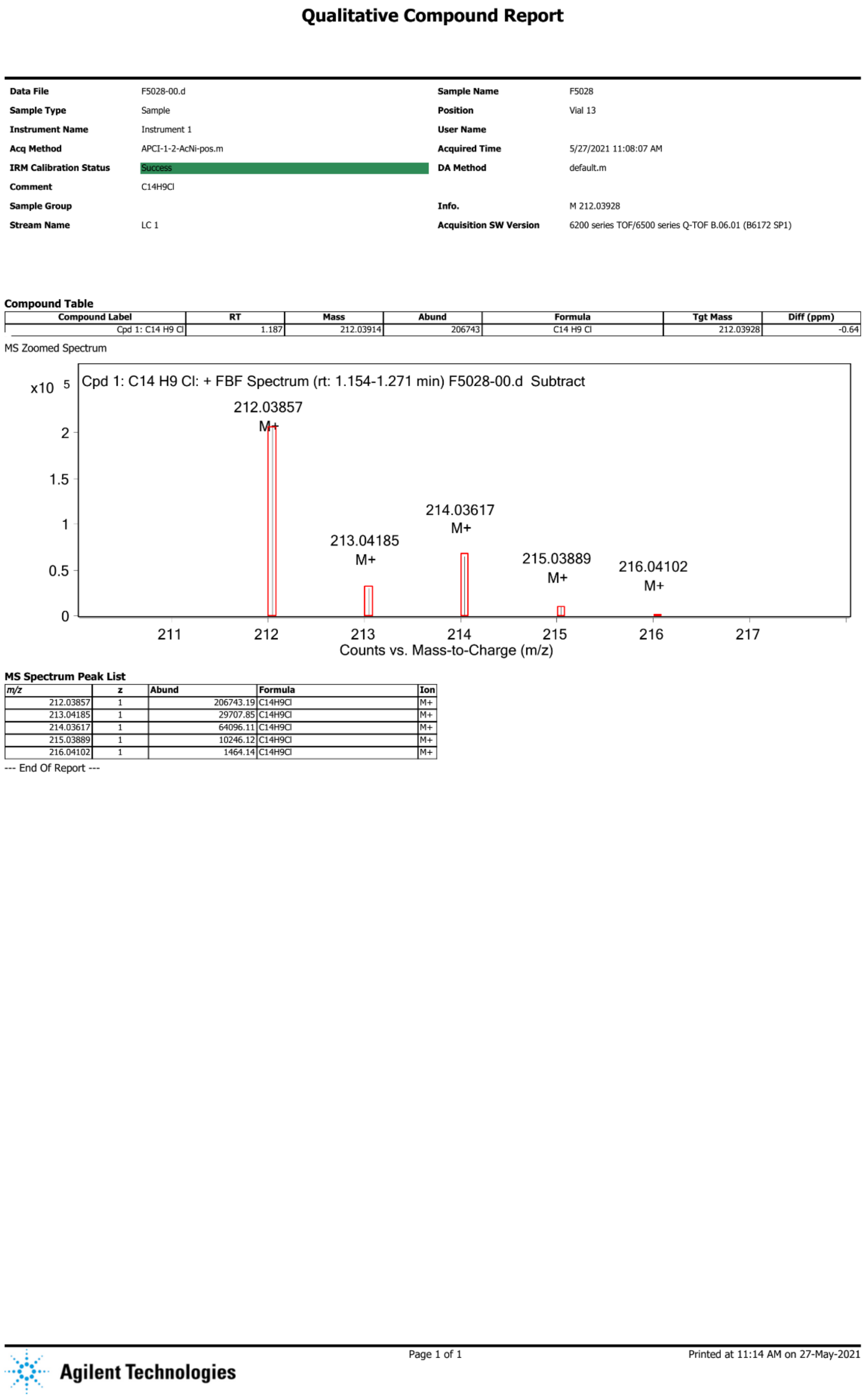
11

Figure S36. ^{1}H NMR spectrum of **11** dissolved in CD_2Cl_2, 300 MHz, 296 K.



11

Figure S37. ^{13}C NMR spectrum of **11** dissolved in CD_2Cl_2, 75 MHz, 296 K.



Qualitative Compound Report

Data File	F5028-00.d	**Sample Name**	F5028
Sample Type	Sample	**Position**	Vial 13
Instrument Name	Instrument 1	**User Name**	
Acq Method	APCI-1-2-AcNi-pos.m	**Acquired Time**	5/27/2021 11:08:07 AM
IRM Calibration Status	Success	**DA Method**	default.m
Comment	C14H9Cl		
Sample Group		**Info.**	M 212.03928
Stream Name	LC 1	**Acquisition SW Version**	6200 series TOF/6500 series Q-TOF B.06.01 (B6172 SP1)

Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: C14 H9 Cl	1.187	212.03914	206743	C14 H9 Cl	212.03928	-0.64

MS Zoomed Spectrum

MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
212.03857	1	206743.19	C14H9Cl	M+
213.04185	1	29707.85	C14H9Cl	M+
214.03617	1	64096.11	C14H9Cl	M+
215.03889	1	10246.12	C14H9Cl	M+
216.04102	1	1464.14	C14H9Cl	M+

--- End Of Report ---

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Figure S38. Qualitative compound report of HR-ESI-MS (positive mode) for **11**.

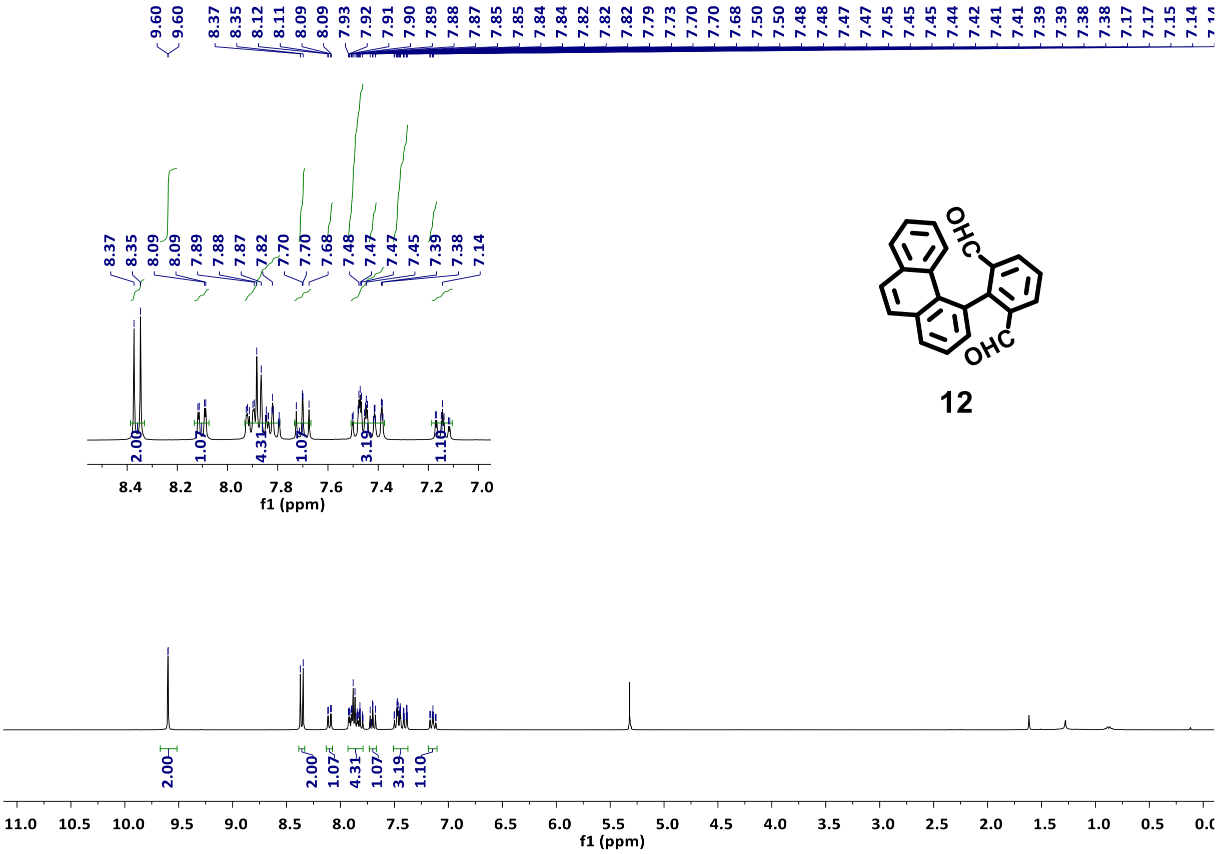


Figure S39. ^{1}H NMR spectrum of **12** dissolved in CD_2Cl_2, 300 MHz, 296 K.

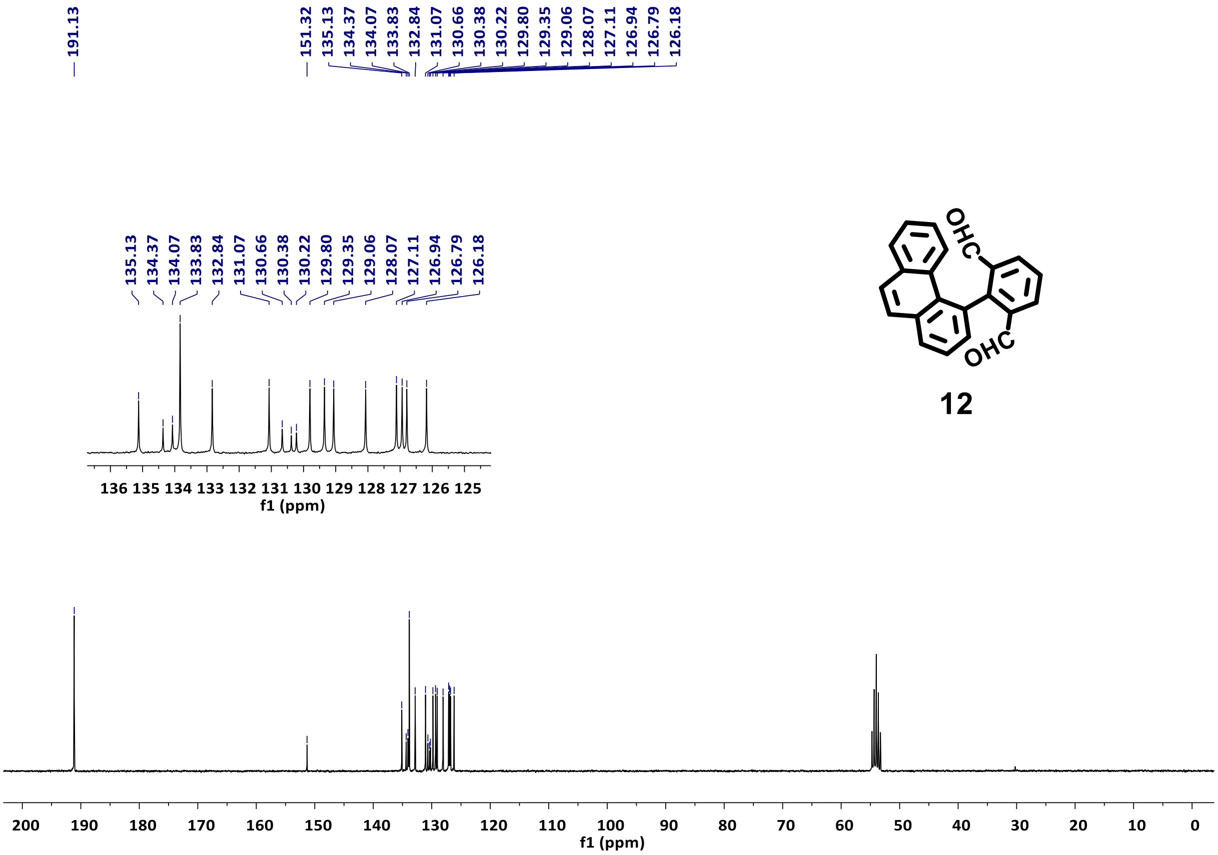
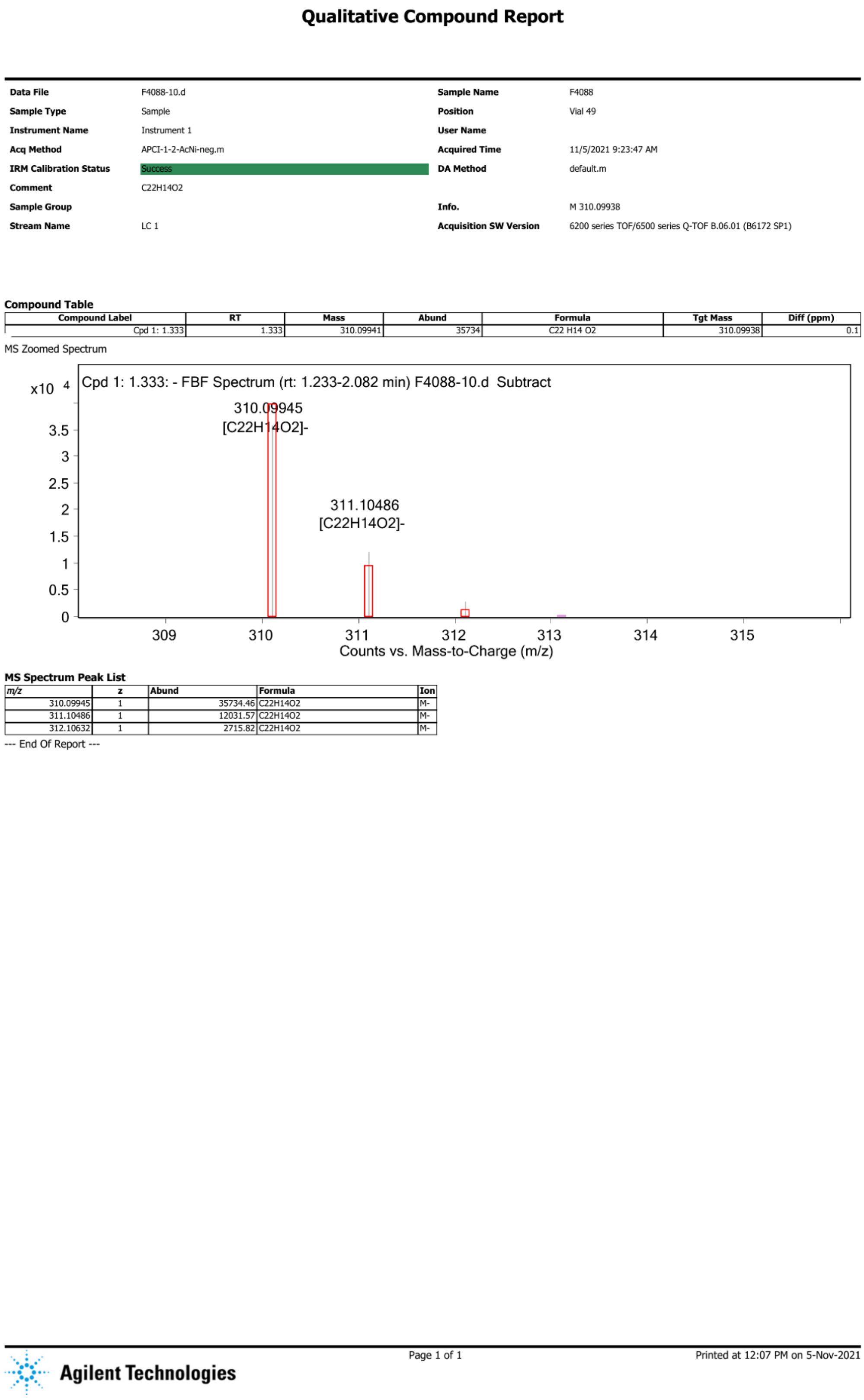


Figure S40. ^{13}C NMR spectrum of **12** dissolved in CD_2Cl_2, 75 MHz, 296 K.



Qualitative Compound Report

Data File	F4088-10.d	**Sample Name**	F4088
Sample Type	Sample	**Position**	Vial 49
Instrument Name	Instrument 1	**User Name**	
Acq Method	APCI-1-2-AcNi-neg.m	**Acquired Time**	11/5/2021 9:23:47 AM
IRM Calibration Status	Success	**DA Method**	default.m
Comment	C22H14O2		
Sample Group		**Info.**	M 310.09938
Stream Name	LC 1	**Acquisition SW Version**	6200 series TOF/6500 series Q-TOF B.06.01 (B6172 SP1)

Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: 1.333	1.333	310.09941	35734	C22 H14 O2	310.09938	0.1

MS Zoomed Spectrum

MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
310.09945	1	35734.46	C22H14O2	M-
311.10486	1	12031.57	C22H14O2	M-
312.10632	1	2715.82	C22H14O2	M-

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Figure **S41**. Qualitative compound report of HR-ESI-MS (negative mode) for **12**.

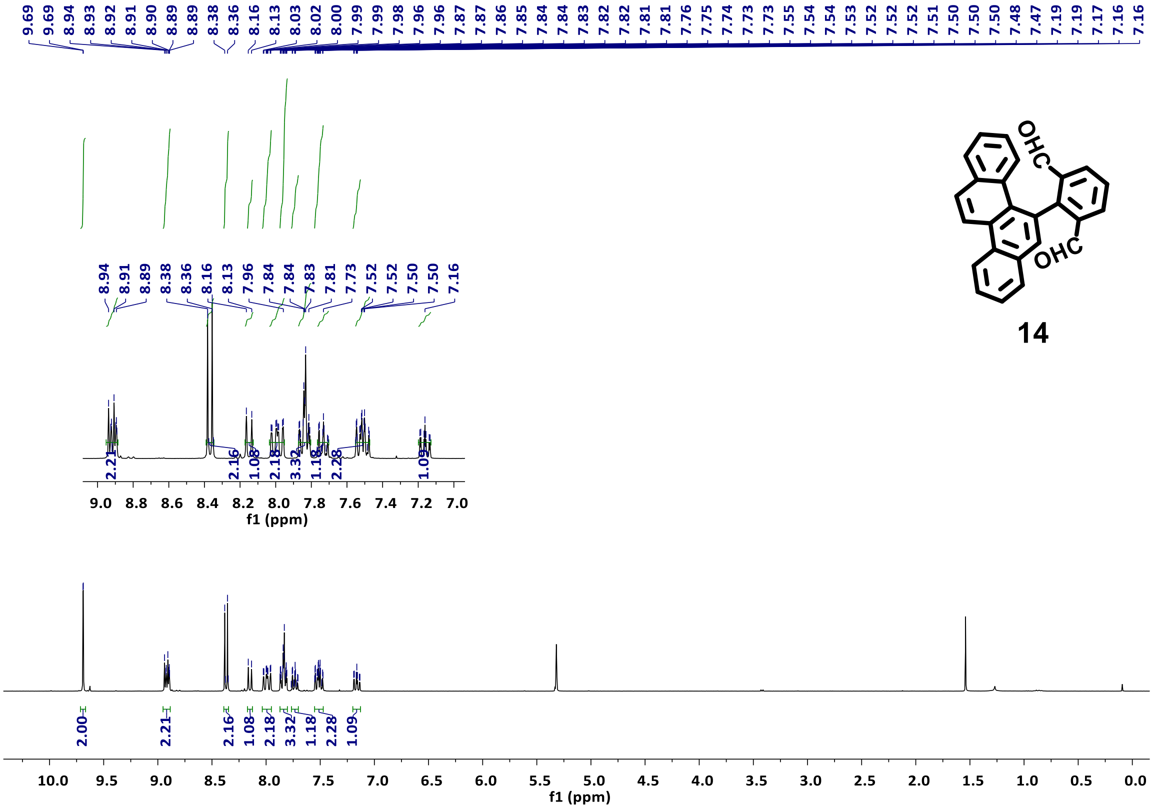


Figure S42. ^{1}H NMR spectrum of **14** dissolved in CD_2Cl_2, 300 MHz, 296 K.

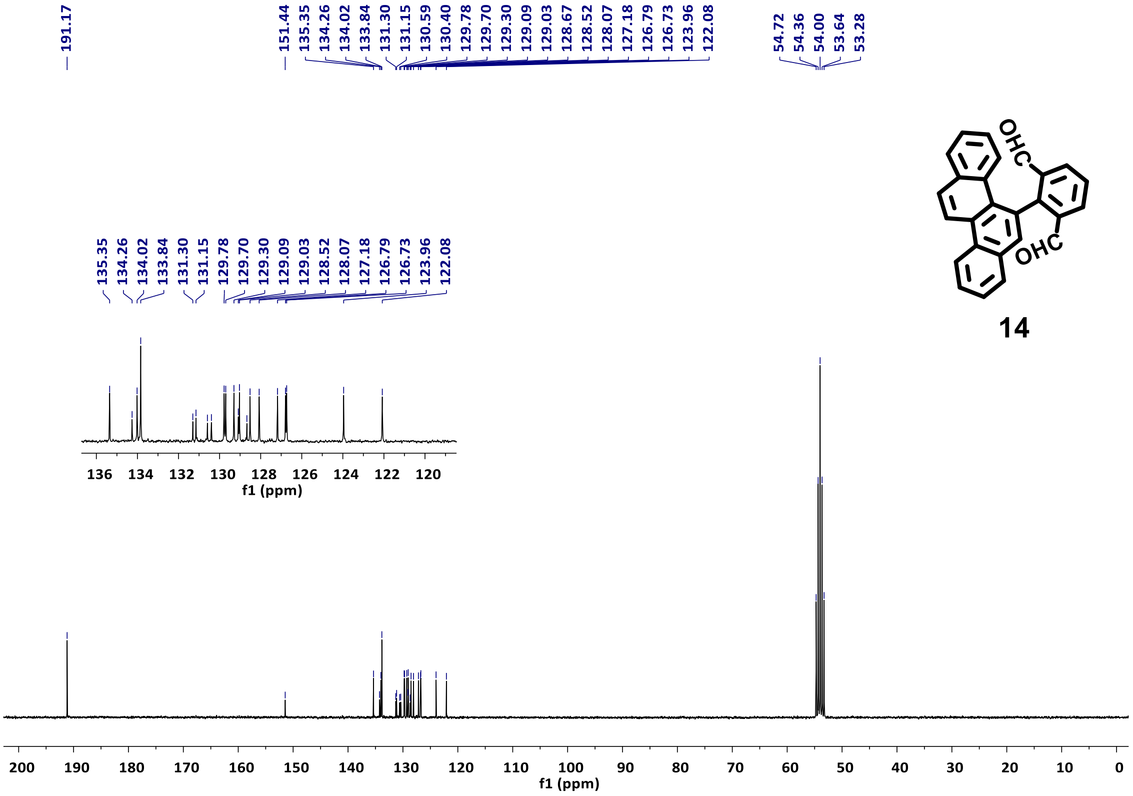
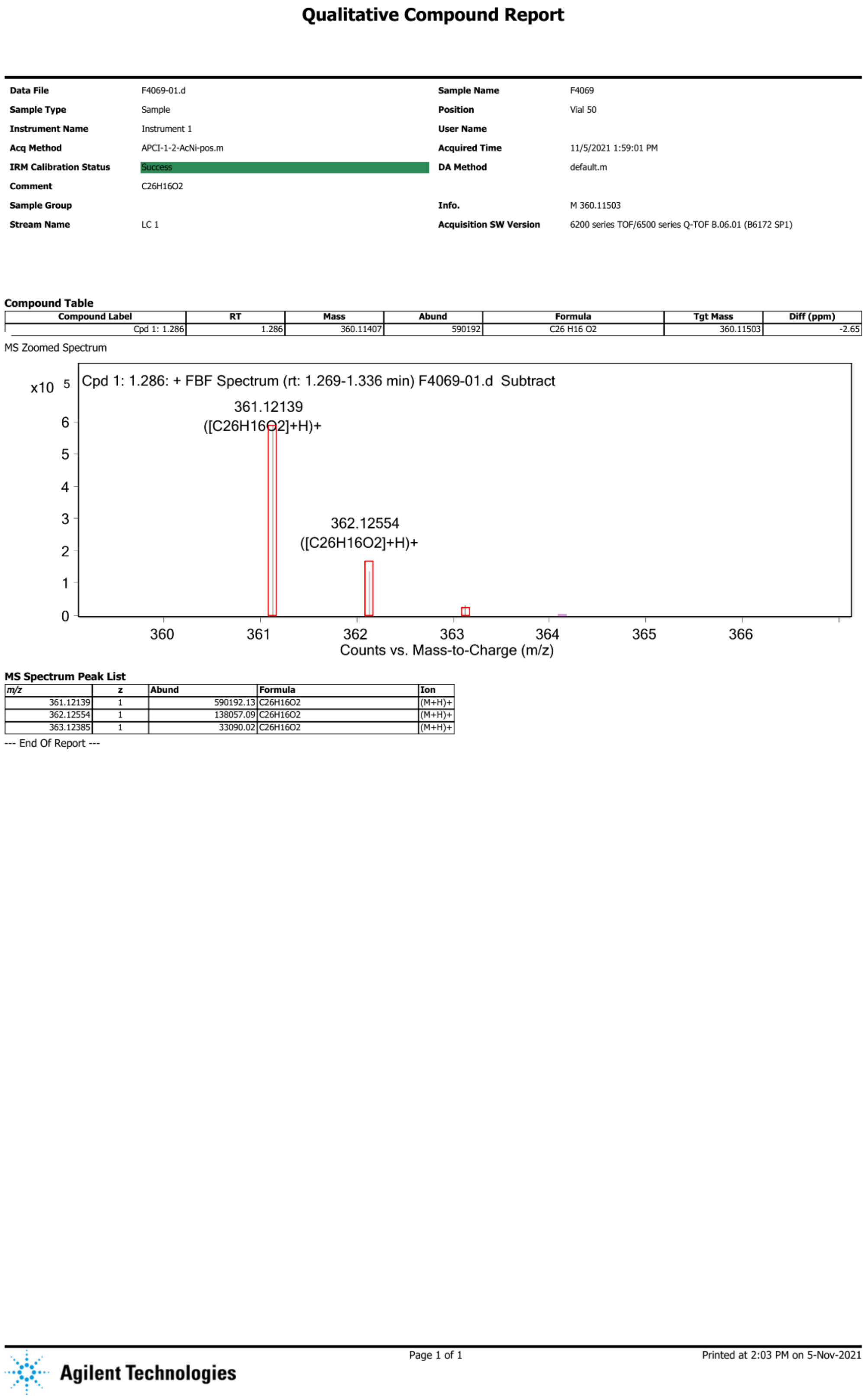


Figure S43. ^{13}C NMR spectrum of **14** dissolved in CD_2Cl_2, 75 MHz, 296 K.



Qualitative Compound Report

Data File	F4069-01.d	**Sample Name**	F4069
Sample Type	Sample	**Position**	Vial 50
Instrument Name	Instrument 1	**User Name**	
Acq Method	APCI-1-2-AcNi-pos.m	**Acquired Time**	11/5/2021 1:59:01 PM
IRM Calibration Status	🟩 Success	**DA Method**	default.m
Comment	C26H16O2		
Sample Group		**Info.**	M 360.11503
Stream Name	LC 1	**Acquisition SW Version**	6200 series TOF/6500 series Q-TOF B.06.01 (B6172 SP1)

Compound Table

Compound Label	RT	Mass	Abund	Formula	Tgt Mass	Diff (ppm)
Cpd 1: 1.286	1.286	360.11407	590192	C26 H16 O2	360.11503	-2.65

MS Zoomed Spectrum

MS Spectrum Peak List

m/z	z	Abund	Formula	Ion
361.12139	1	590192.13	C26H16O2	(M+H)+
362.12554	1	138057.09	C26H16O2	(M+H)+
363.12385	1	33090.02	C26H16O2	(M+H)+

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Figure S44. Qualitative compound report of HR-ESI-MS (positive mode) for **14**.

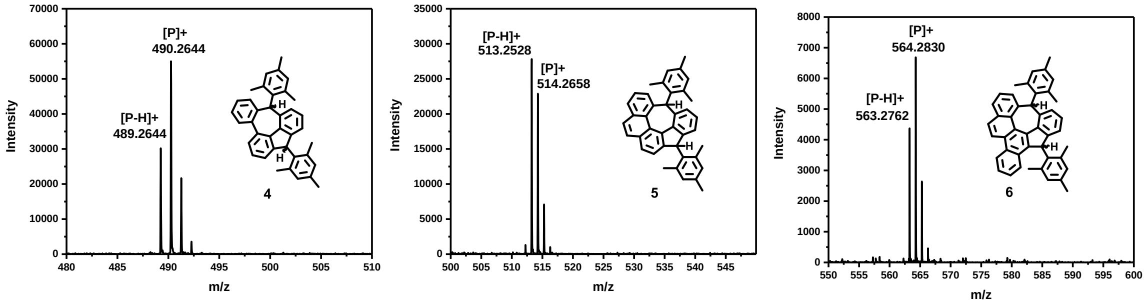


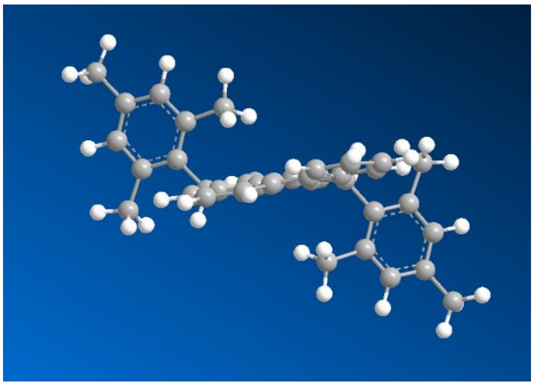
Figure S45. Liquid-state HR-MALDI-TOF-MS spectra of **4**- **6** (matrix: DCTB). Spectra show some [P-H] peaks during MALDI measurements. Structure **4-6** can further be confirmed by their NMR and single crystal analysis.

NMR data and spectra of 4, 5 and 6

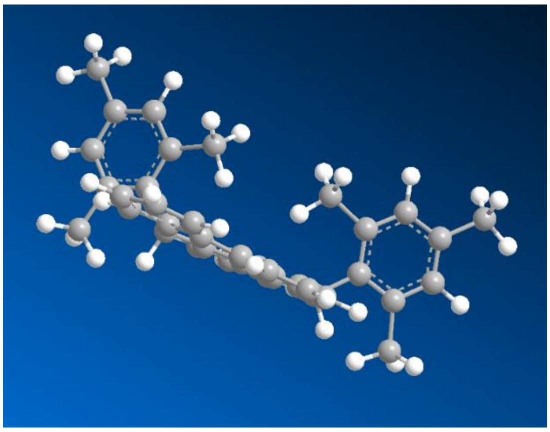
General considerations

The ^{1}H and ^{13}C NMR spectra of **4, 5** and **6** are characterised by signals of up to four isomers. In these compounds, the two methine carbons present stereocenters. The methine carbons are part of a 5-membered and a 7-membered ring, respectively. Thus, four stereo isomers can be distinguished: (5-S, 7-S), (5-S, 7-R), (5-R, 7-S) and (5-R,7-R). The polycyclic structure and the sterically demanding mesityl groups seem to result in four different structures and not in enatiomeric stereoisomers.

MM2 calculations (Chem3D, version 17) for the four stereoisomers of **4** result in the following structures:
lower energy isomers

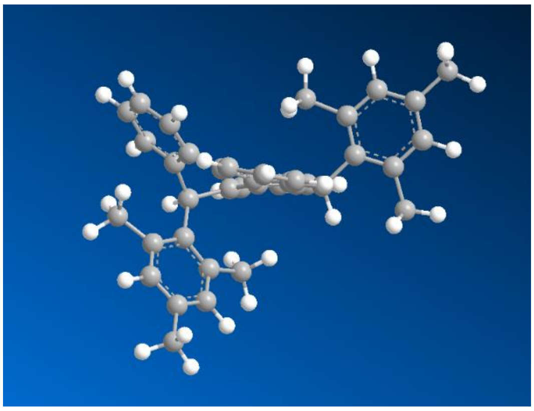


(*5-R; 7-R*) (~ 36.9 kcal/mol)

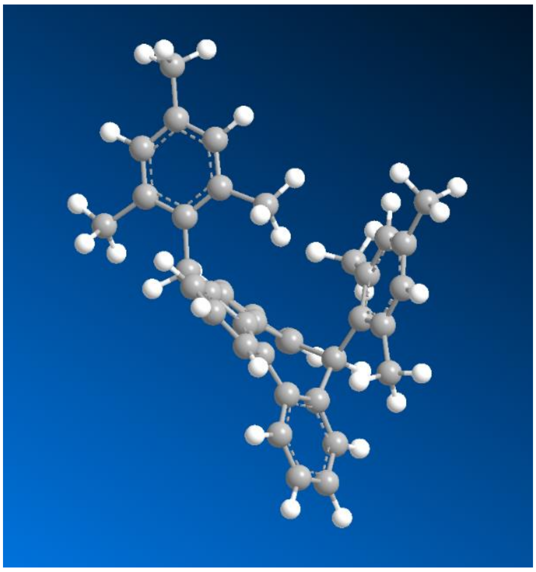


(*5-S; 7-R*) (~ 36.6 kcal/mol)

higher energy isomers



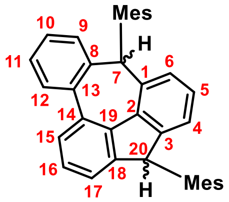
(5-S; 7-S) (~ 42.8 kcal/mol)



(5-R; 7-S) (~ 43.2 kcal/mol)

A detailed investigation is not the aim of the NMR studies, but it is obvious that some structures are sterically very demanding and the different content of isomers in the isomer mixture (two for **4** (55:45) and **5** (75:25); four for **6** (55: 32: 9: 4) might result from steric reasons.
It should be noted that the mesityl moiety bonded to carbon 7 (7-membered ring) can rotate fast on the NMR timescale, which leads to an equivalence of positions 22/22’, 23/23’ and 25/25’, respectively. This does not apply to the mesityl moiety, which is attached to carbon 20 (5-membered ring). Because of slow rotation, these positions result in well separated signals.
Variable-temperature (VT) NMR experiments reveal changes in line width for mesityl signals.

NMR data and spectra of **4**



4

Mes =

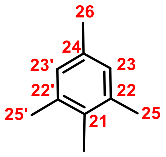


Table S9. NMR data of **4**

	Major isomer (~ 55 mol%)		**Minor isomer (~ 45 mol%)**	
#	^{1}H	^{13}C	^{1}H	^{13}C
1	-	137.7	-	138.2
2	-	140.5	-	141.6
3	-	147.5	-	147.4
4	7.08	121.8	6.98 (d)	122.1
5	7.13	127.9	7.08	127.8
6	6.94 (d)	127.0	6.88 (d)	126.4
7	6.14 (s)	47.7	6.00 (s)	47.2
8	-	140.2	-	139.8
9	7.20	130.3	7.20	129.8
10	7.20	127.8	7.20	127.8
11	7.33	127.1	7.33	127.2
12	7.77 (d)	131.0	7.65 (d)	131.1
13	-	138.0	-	138.8
14	-	136.1	-	136.9
15	7.85 (d)	126.9	7.79 (d)	127.0
16	7.42 (t)	127.7	7.40 (t)	127.3
17	7.21	123.2	7.21	122.7
18	-	146.7	-	148.8
19	-	139.9	-	139.3
20	5.53 (s)	49.9	5.63 (s)	50.0
Mes at carbon 7				
21	-	135.5	-	134.3
22 = 22‘	-	138.5	-	138.7
23 = 23‘	7.07 (s)	130.4	7.09 (s)	130.4
24	-	136.6	-	136.6
25 = 25‘	2.26 (s)	22.5	2.22 (s)	22.6
26	2.38 (s)	20.9	2.40 (s)	20.95
Mes at carbon 20				
21	-	134.1	-	134.4
22	-	138.05	-	138.2
22‘	-	138.0	-	137.8
23	7.05 (s)	129.2	7.04 (s)	129.1
23‘	6.66 (s)	130.7	6.65 (s)6	130.8
24	-	136.5	-	136.5
25	2.70 (s)	21.8	2.68 (s)	21.7
25‘	1.20 (s)	18.9	0.98 (s)	18.4
26	2.28 (s)	20.8	2.28 (s)	20.8

Note: The multiplicity is not reported when signals are overlapped.

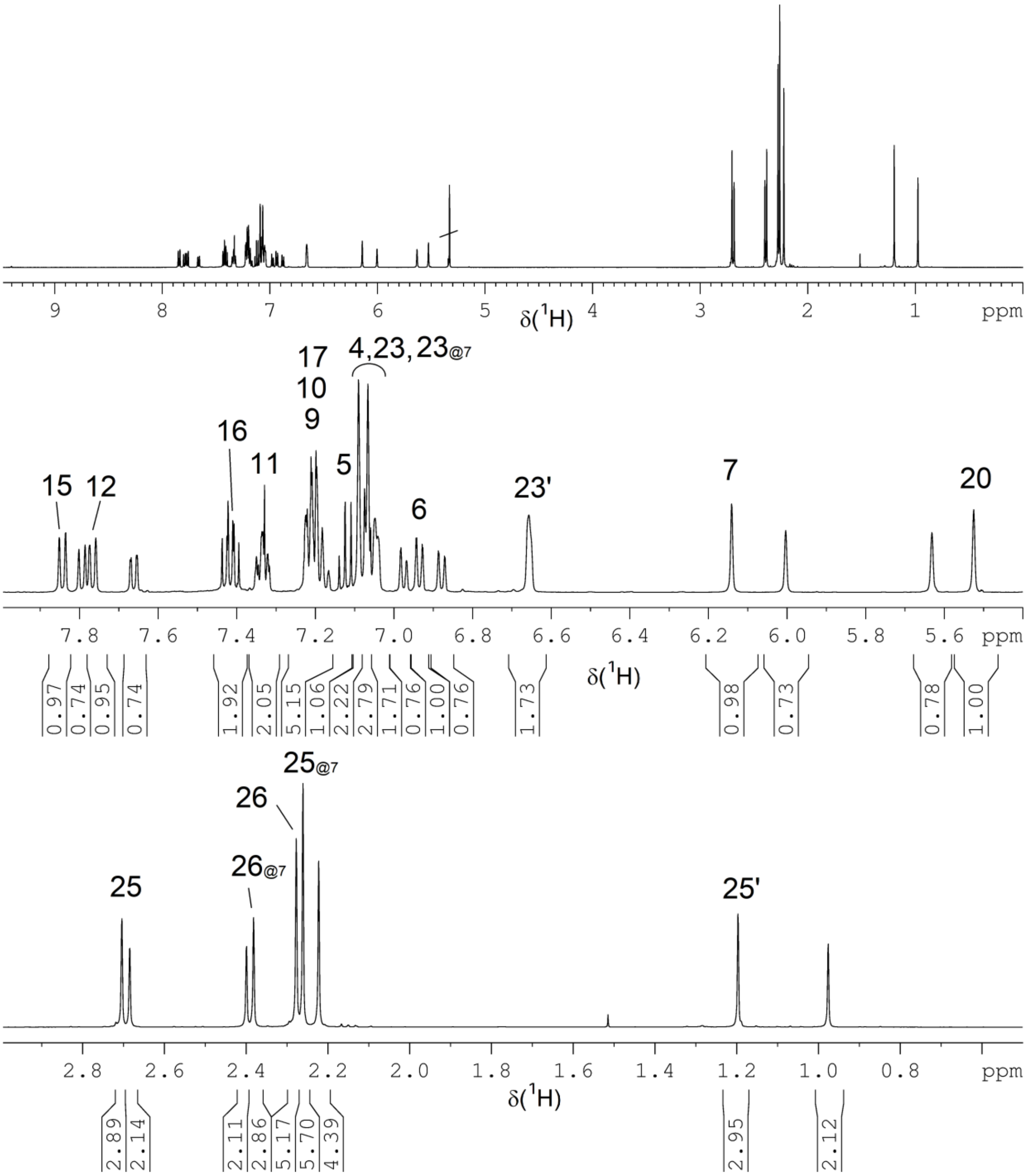


Figure S46. ^{1}H NMR spectrum and selected regions of **4** (CD$_2$Cl$_2$; 500 MHz; 30°C) with signal assignment for the major isomer. Note: The integral values can deviate from the expected ones due to signal overlap with signals of minor isomer. H$_{23/23'}$, H$_{25/25'}$ and H$_{26}$ of the mesityl moiety bonded to CH$_{20}$ are not marked with $_{@20}$.

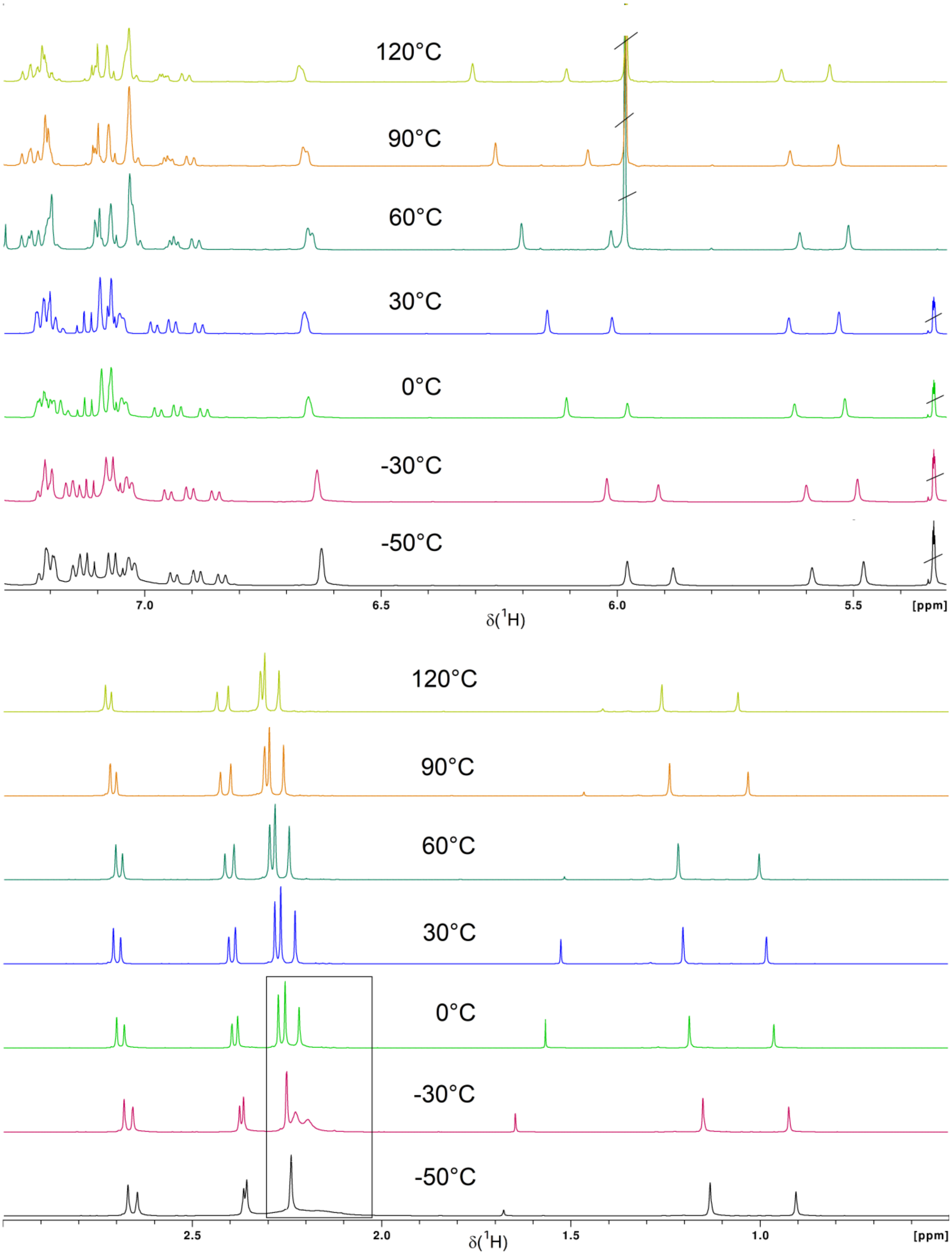


Figure S47. ^{1}H NMR spectra (regions) of **4** at different temperatures (CD_2Cl_2 @ -50 to 30°C; $C_2D_2Cl_2$ @ 60-120 °C; 500 MHz). The box marks signals with changing line width.

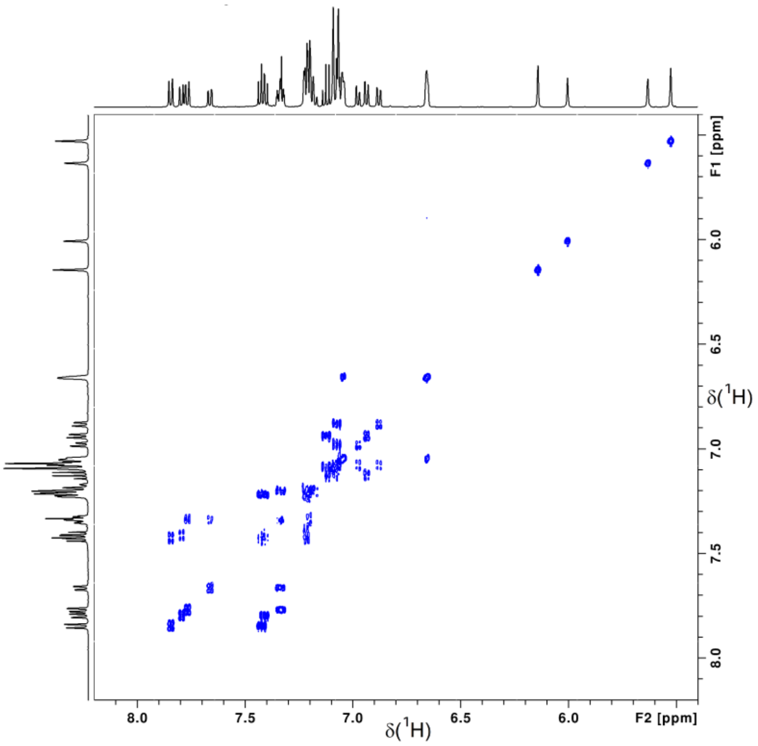


Figure S48. COSY spectrum (region) of **4** (CD_2Cl_2).

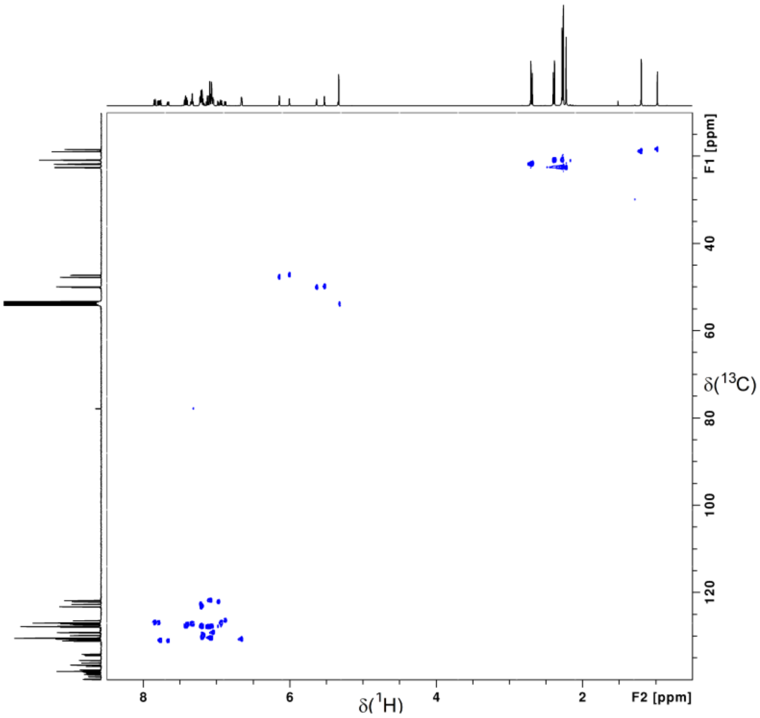


Figure S49. HSQC spectrum of **4** (CD_2Cl_2). The spectra on the F1 and F2 axis are not the projections but the corresponding ^{13}C and ^{1}H NMR spectra showing also quarternary carbons' signals.

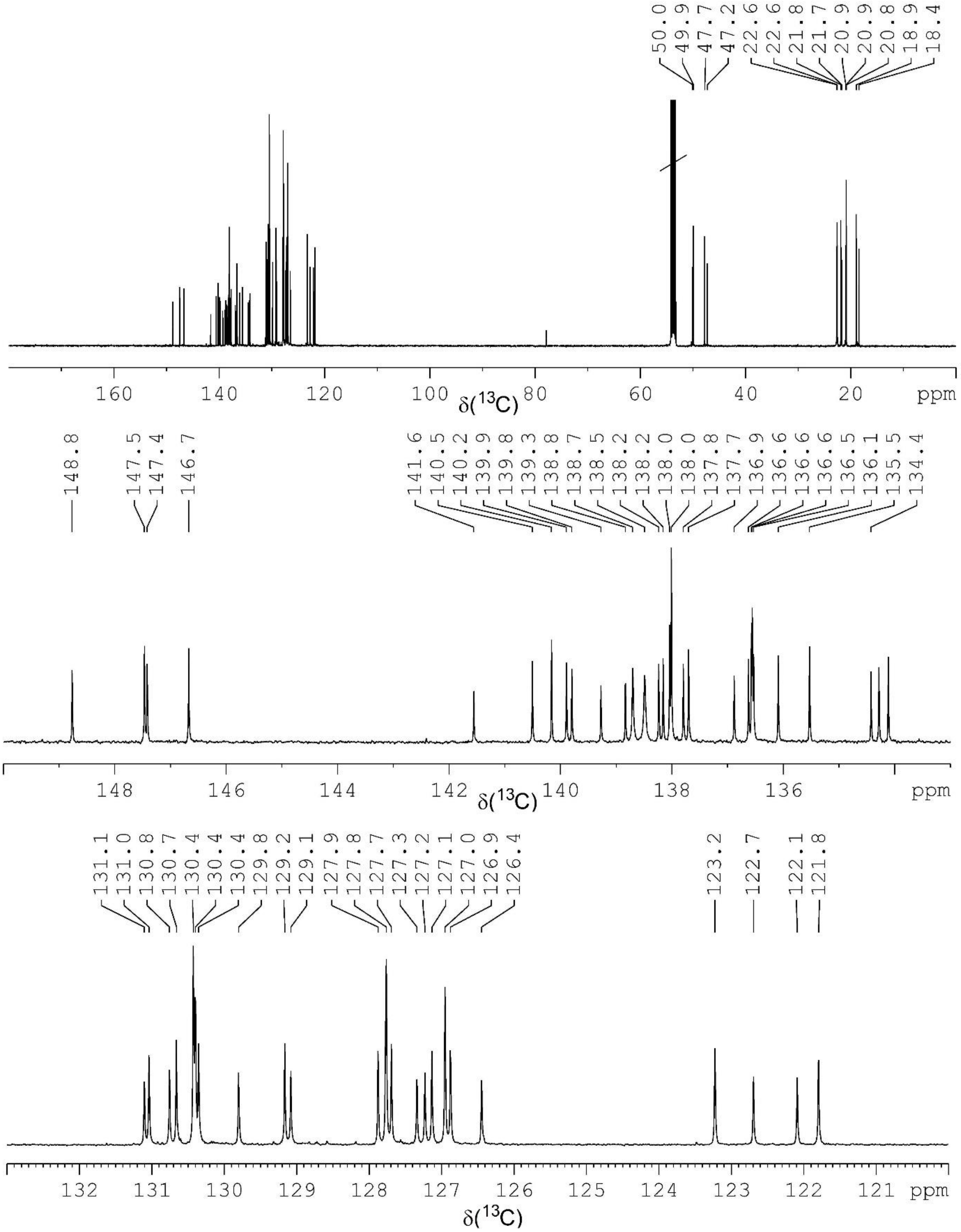
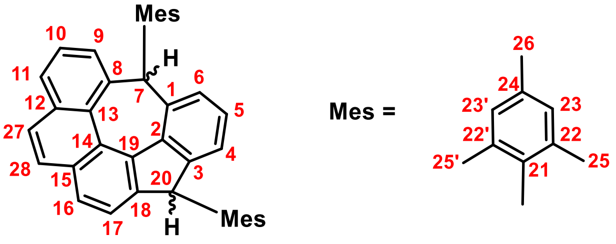


Figure S50. ^{13}C NMR spectrum and selected regions of **4** (CD_2Cl_2; 125 MHz; 30°C).

NMR data and spectra of **5**



5

Table S10. NMR data of **5**

	Major isomer (~ 75 mol%)		**Minor isomer (~ 25 mol%)**	
#	**^{1}H**	**^{13}C**	**^{1}H**	**^{13}C**
1	-	137.2	-	137.3
2	-	140.0 or 140.1	-	139.8 or 140.2
3	-	147.2 *	-	147.2 *
4	7.05 (d)	121.5	7.05 (d)	121.4
5	7.13 (t)	127.4 *	7.13 (t)	127.4 *
6	7.10	128.0	7.10	127.9
7	7.09	50.9	7.09	50.8
8	-	140.0 or 140.1	-	139.8 or 140.2
9	7.60 (d)	132.1	7.60 (d)	132.2
10	7.46	126.8	7.44	126.7
11	7.78	128.9	7.78	128.9
12	-	134.4 *	-	134.4 *
13	-	130.5	-	130.8
14	-	127.8 *	-	127.8 *
15	-	133.5 *	-	133.5 *
16	7.87 (d)	129.5 *	7.86 (d)	129.5 *
17	7.46 (d)	123.2	7.44 (d)	123.1
18	-	147.3 *	-	147.3 *
19	-	138.3	-	138.1
20	5.64	49.9	5.62	49.8
27	7.78	128.3	7.78	128.4
28	7.83 (d)	128.0	7.82 (d)	127.8
Mes at carbon 7				
21	-	144.6	-	145.1
22 = 22‘	-	136.5 (br)	-	136.5 (br)
23 = 23‘	6.90	130.5	6.88	130.4 (br)
24	-	136.1	-	136.0
25 = 25‘	2.33 (br)	21.5	2.33 (br)	21.3 (br)
26	2.27	20.7	2.27	20.7

Mes at carbon 20				
21	-	134.3 *	-	134.3 *
22	-	138.4	-	138.3
22‘	-	137.9	-	137.8
23	7.09	129.2 *	7.09	129.2 *
23‘	6.67	130.8	6.68	130.7
24	-	136.7	-	136.7
25	2.75	21.9 *	2.75	21.9 *
25‘	1.11	18.6	1.10	18.7
26	2.30	20.8	2.30	20.8

Note: The multiplicity is not reported when signals are overlapped. For signals marked * two signals appear for major and minor isomer but separated less than 0.1 ppm.

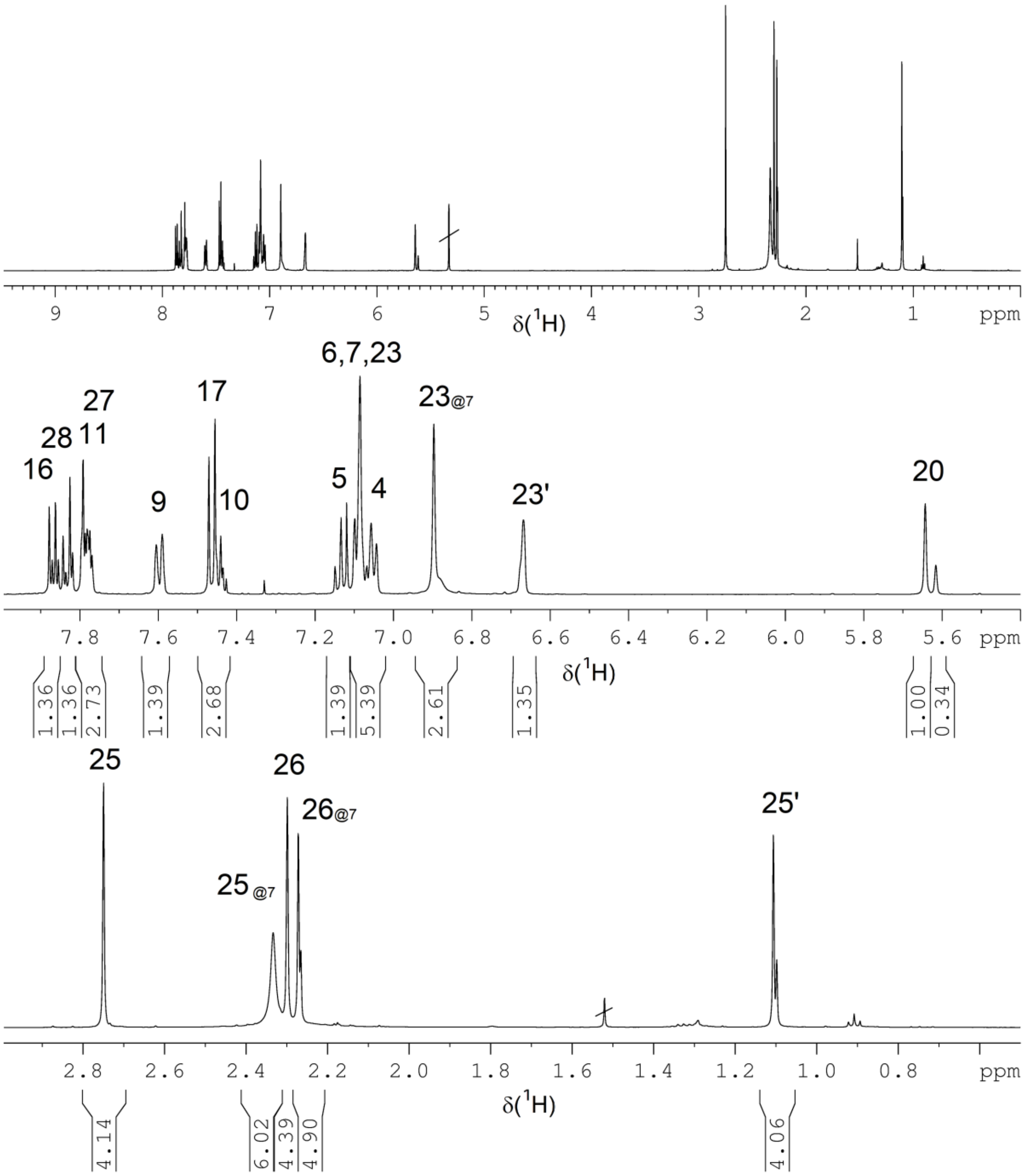


Figure S51. ^{1}H NMR spectrum and selected regions of **5** (CD_2Cl_2; 500 MHz, 30 °C) with signal assignment for the major isomer. Note: The integral values can deviate from the expected ones due to signal overlap with signals of minor isomer. $H_{23/23'}$, $H_{25/25'}$ and H_{26} of the mesityl moiety bonded to CH_{20} are not marked with $_{@20}$.

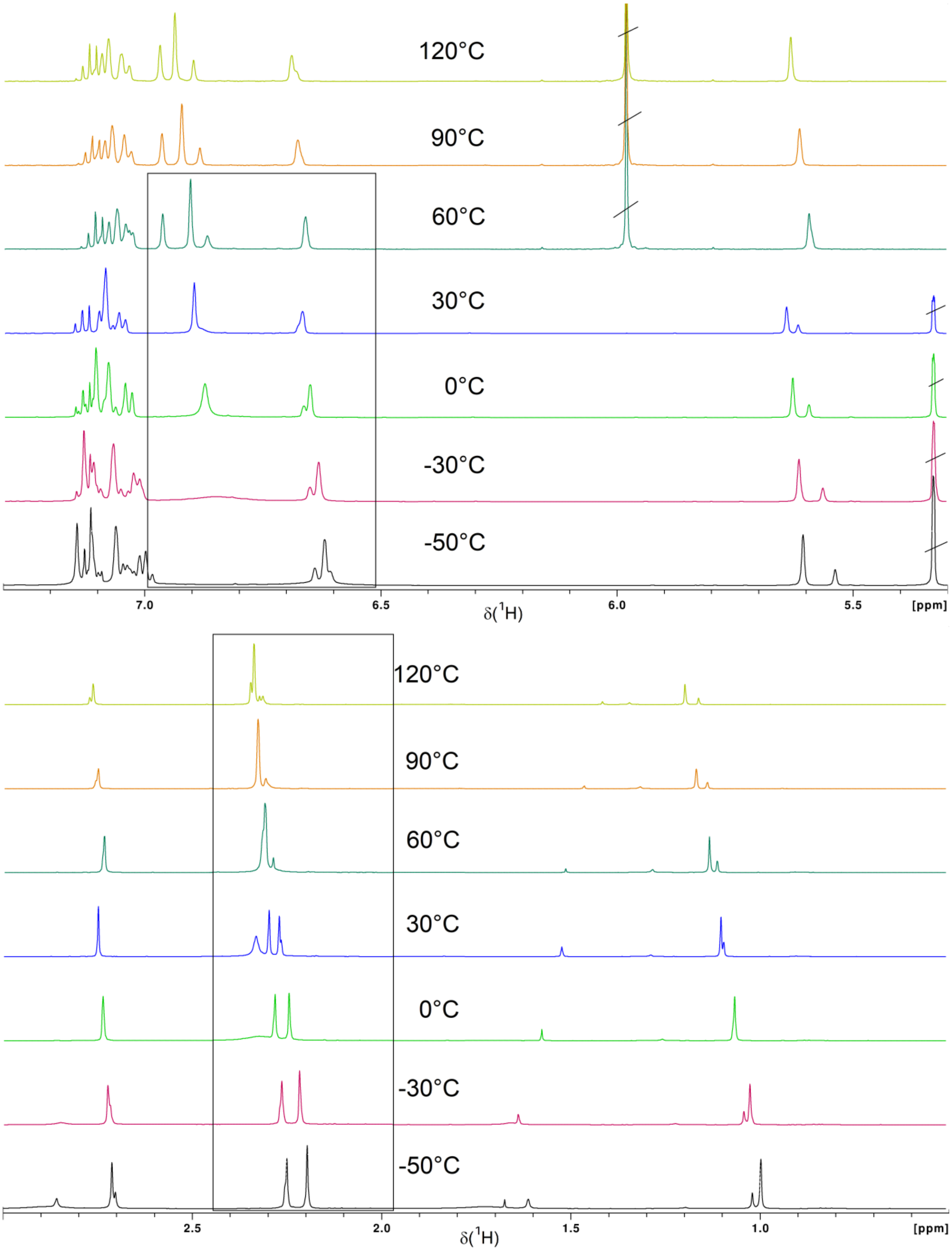


Figure S52. ^{1}H NMR spectra (regions) of **5** at different temperatures (CD_2Cl_2 @ -50 to 30 °C; $C_2D_2Cl_2$ @ 60-120°C; 500 MHz). The box marks signals with changing line width.

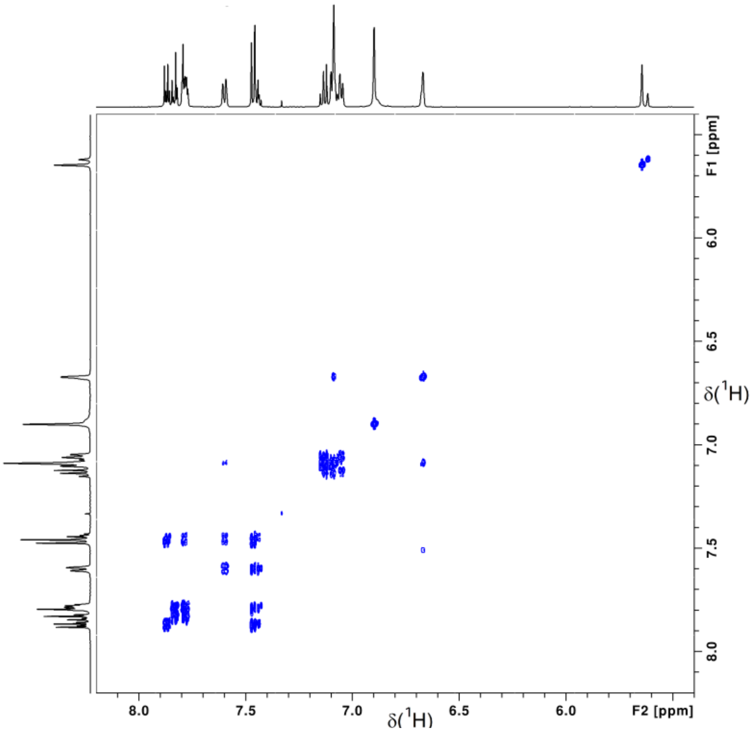


Figure S53. COSY spectrum (region) of **5** (solvent: CD_2Cl_2).

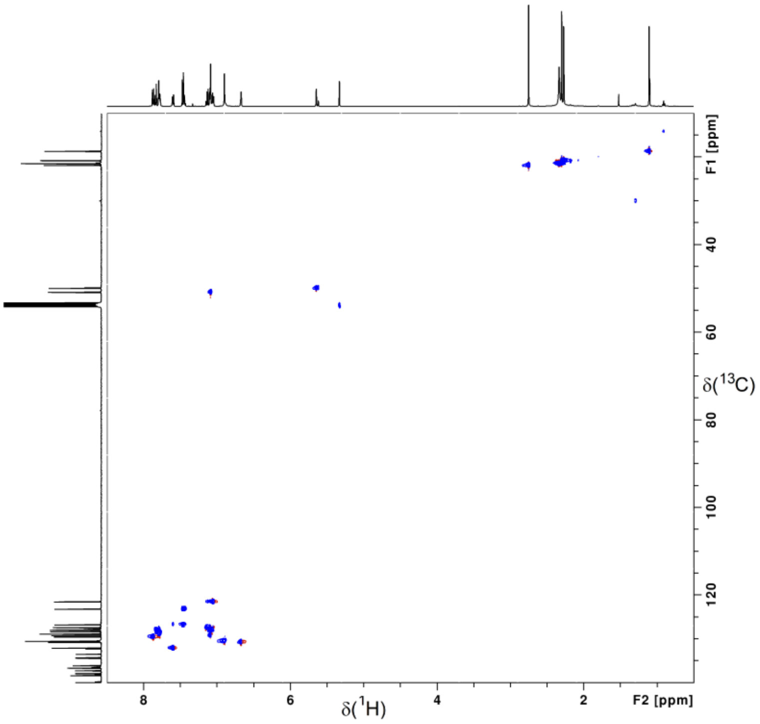


Figure S54. HSQC spectrum of **5** (solvent: CD_2Cl_2). The spectra on the F1 and F2 axis are not the projections but the corresponding ^{13}C and ^{1}H NMR spectra showing also quaternary carbons' signals.

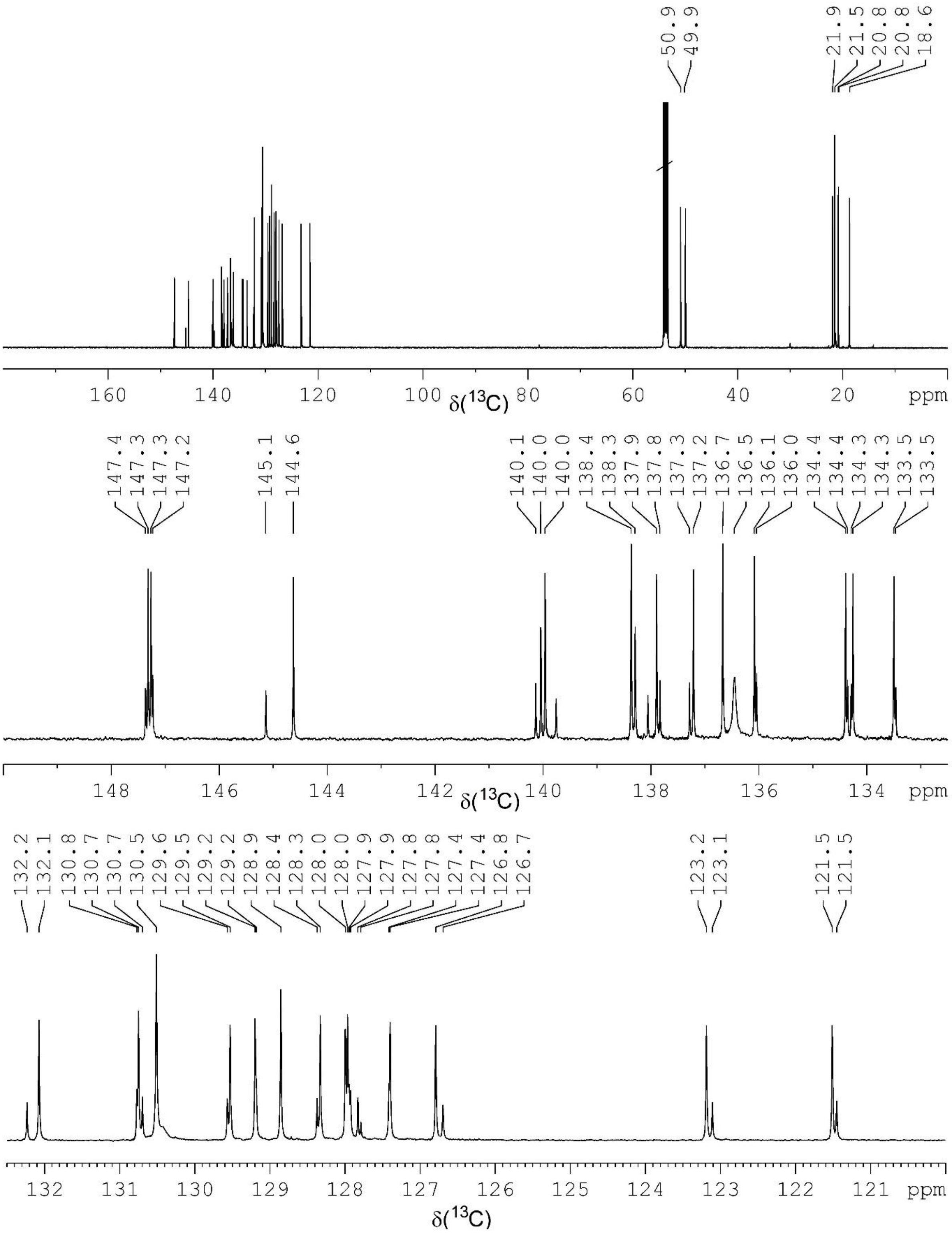
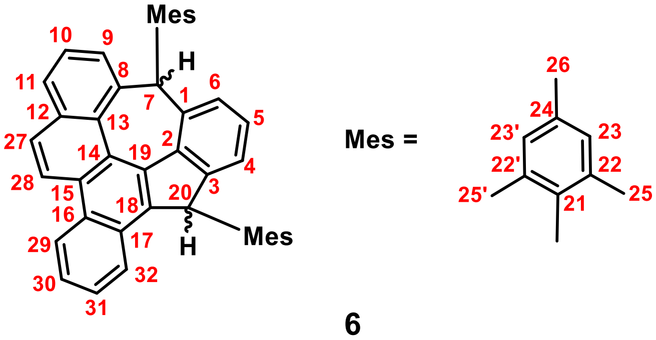


Figure S55. ^{13}C NMR spectrum and selected regions of **5** (CD_2Cl_2; 125 MHz; 30 °C).

NMR data and spectra of **6**



6

Mixture of four isomers in a molar ratio of ~ 55 : 32 : 9 : 4

Table S11. NMR data of **6**

	Major isomer (~ 55 mol%)		**Selected ^{1}H NMR signals of minor isomers**
#	**^{1}H**	**^{13}C**	
1	-	~136.8	
2	-	141.0	
3	-	146.6	
4	7.06 (d)	121.4	
5	7.14 (t)	127.0	
6	7.14	127.8	
7	7.03	50.7	
8	-	139.8	
9	7.72	132.0	
10	7.51	126.5	
11	7.92	129.0	
12	-	134.4	
13	-	131.4	
14	-	130.9 or 127.2	
15	-	130.7	
16	-	130.9 or 127.2	
17	-	129.6	
18	-	144.0	
19	-	~136.8	
20	5.89	49.9	5.87 (32) - 5.66 (9) - 5.64 (4 mol%)
27	8.09	129.1	
28	8.92	122.1	
29	8.89	124.8	
30	7.65	126.7	
31	7.46	127.1	

32	7.75	124.4	
Mes at carbon 7			
21	-	142.9	
22 = 22‘	-	~ 136.8 (br)	
23 = 23‘	6.91	130.6	
24	-	~ 136.8 (br)	
25 = 25‘	2.32	21.8	
26	2.28	20.8	
Mes at carbon 20			
21	-	136.1	
22	-	137.1	
22‘	-	137.6	
23	7.17	129.8	
23‘	6.59	131.0	6.57 (32) – 6.69 (9) – 6.65 (4 mol%)
24	-	~136.8	
25	2.89	22.2	2.91 (32) – 2.73 (9) – 2.77 (4 mol%)
25‘	1.06	18.4	0.98 (32) – 1.14 (9) – 1.02 (4 mol%)
26	2.29	20.9	

n.a. – not assigned

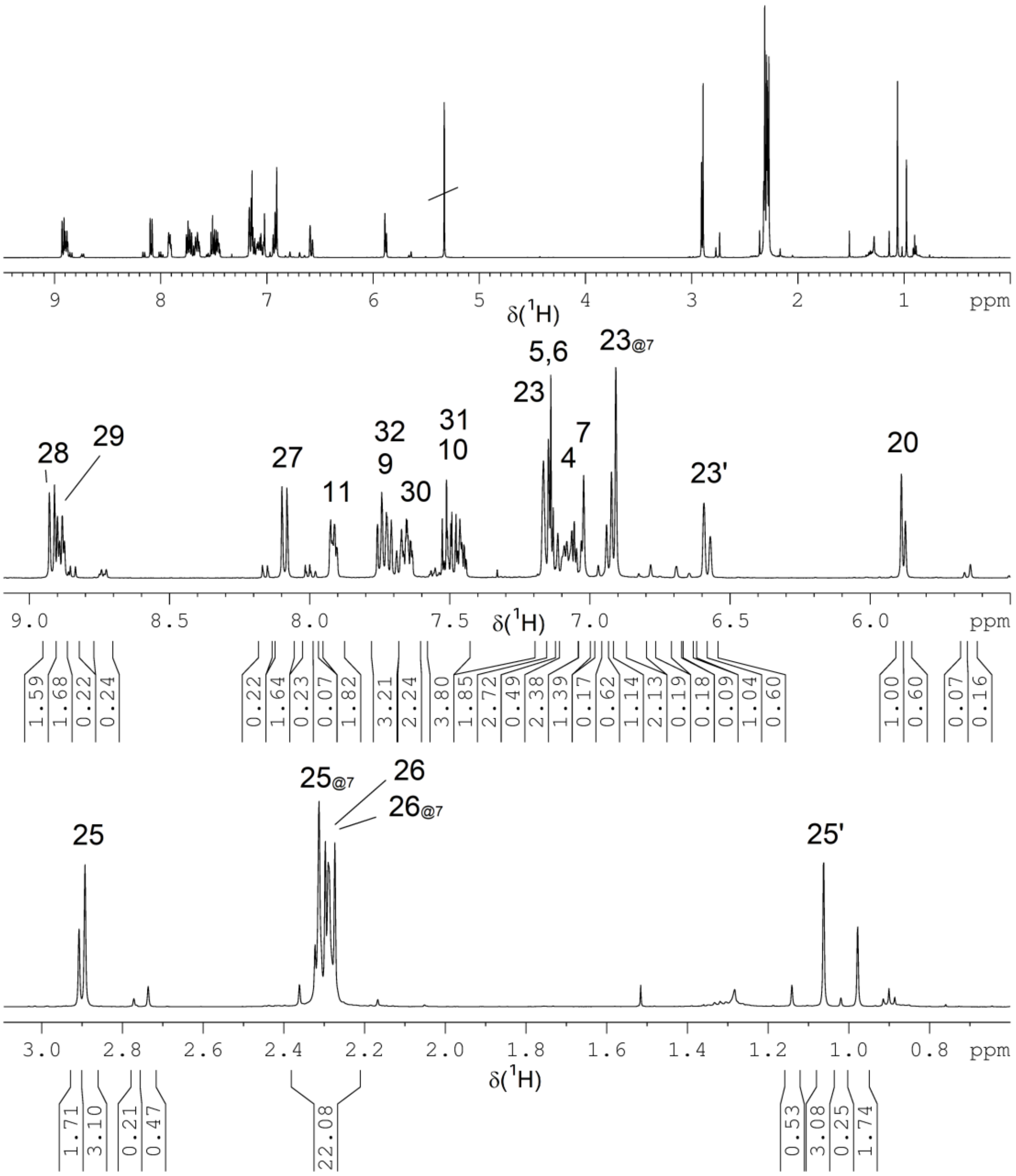


Figure S56. ^{1}H NMR spectrum and selected regions of **6** (CD_2Cl_2; 500 MHz, 30 °C) with signal assignment for the major isomer. Note: The integral values can deviate from the expected ones due to signal overlap with signals of minor isomer. $H_{23/23'}$, $H_{25/25'}$ and H_{26} of the mesityl moiety bonded to CH_{20} are not marked.

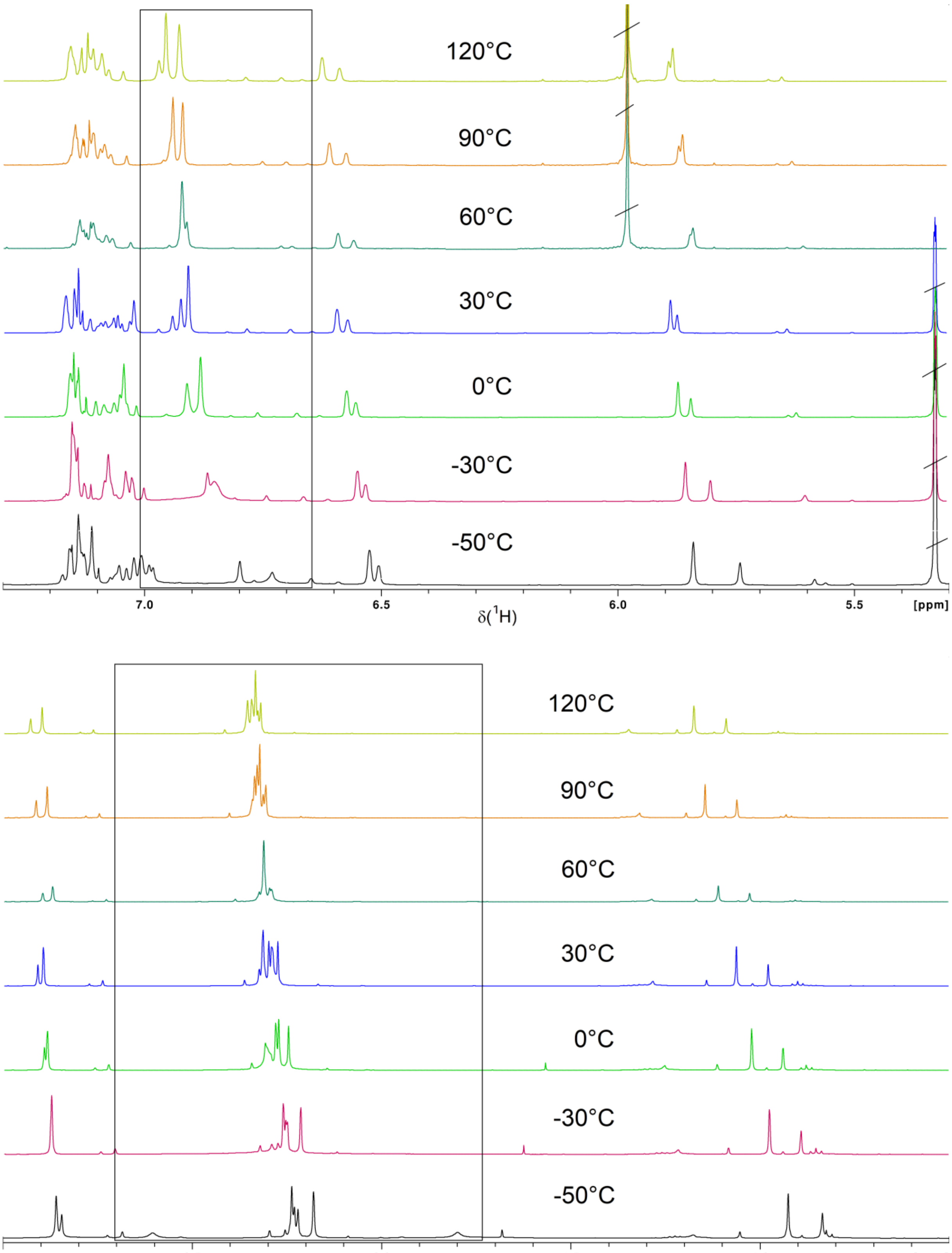


Figure S57. ^{1}H NMR spectra (regions) of **6** at different temperatures (CD_2Cl_2 @ -50 to 30 °C; $C_2D_2Cl_2$ @ 60 – 120 °C; 500 MHz). The box marks signals with changing line width.

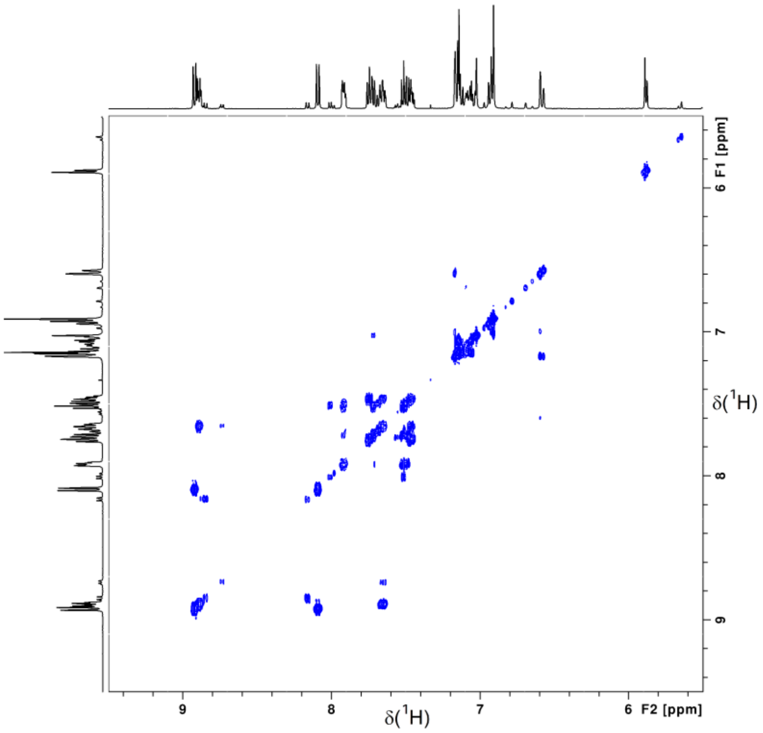


Figure S58. COSY spectrum (region) of **6** (solvent: CD_2Cl_2).

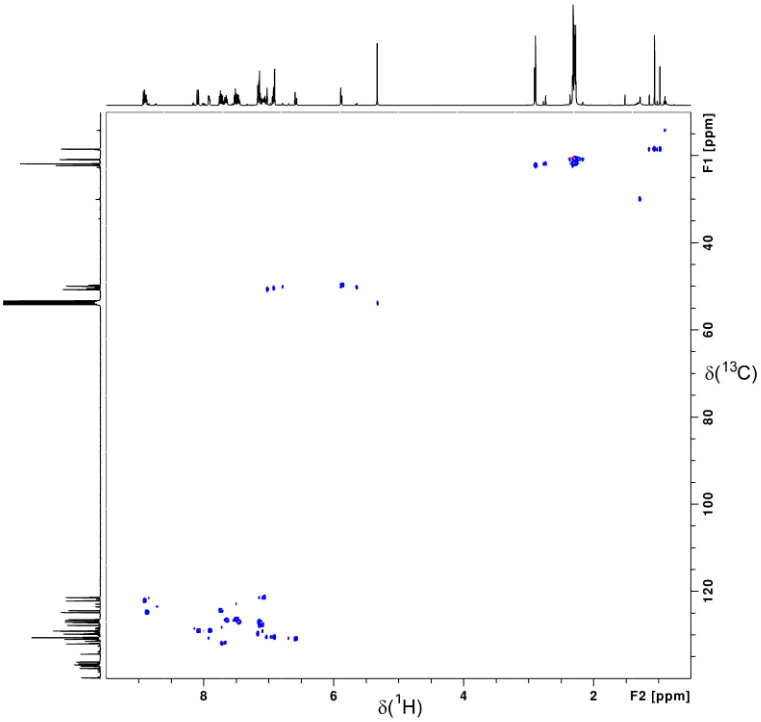


Figure S59. HSQC spectrum of **6** (solvent: CD_2Cl_2). The spectra on the F1 and F2 axis are not the projections but the corresponding ^{13}C and ^{1}H NMR spectra showing also quarternary carbons' signals.

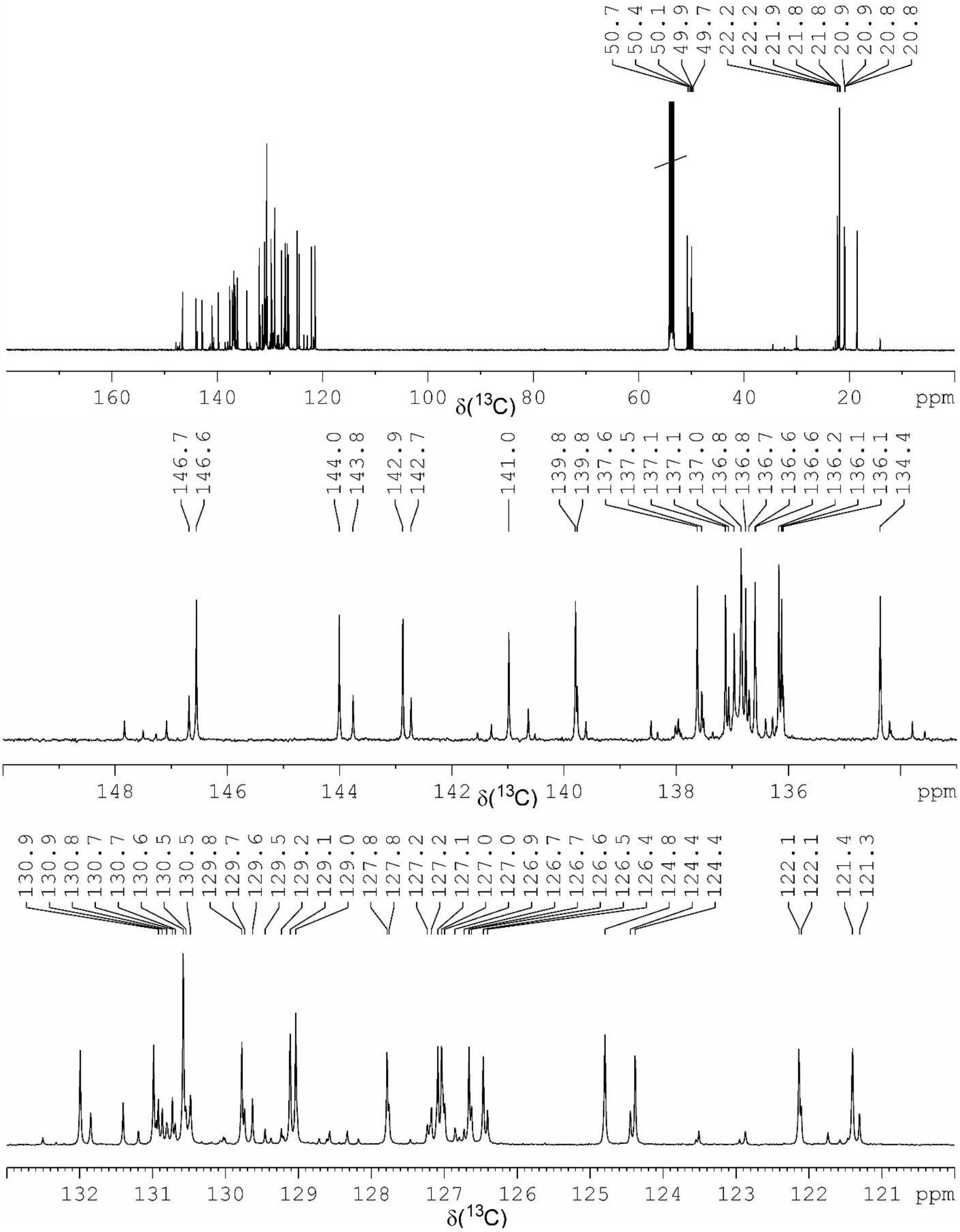


Figure S60. ^{13}C NMR spectrum and selected regions of **6** (CD_2Cl_2; 125 MHz; 30 °C).

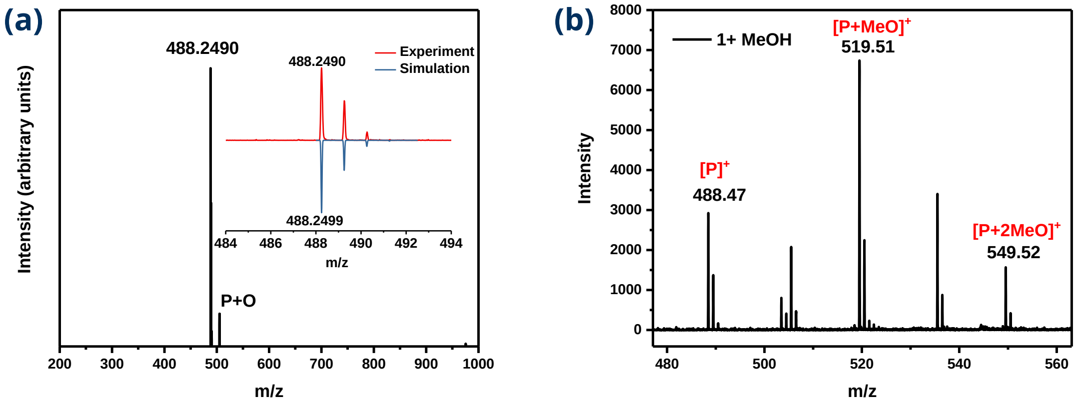


Figure S61. (a) HR-MALDI-TOF mass spectrum of **1**. Inset: experimental (red solid line) and simulated (blue solid line) isotopic distribution patterns of the mass peak. (Minor oxidation peaks were observed due to the oxidation under air during the MALDI operation). (b) MALDI-TOF mass spectrum of **1** in MeOH. (Matrix: DCTB)

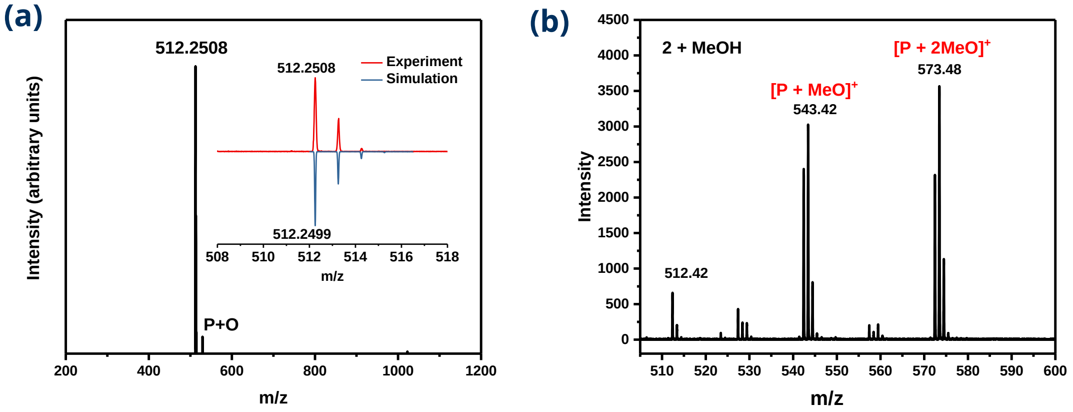


Figure S62. (a) HR-MALDI-TOF mass spectrum of **2**. Inset: experimental (red solid line) and simulated (blue solid line) isotopic distribution patterns of the mass peak. (Minor oxidation peaks were observed due to the oxidation under air during the MALDI operation). (b) MALDI-TOF mass spectrum of **2** in MeOH. (Matrix: DCTB)

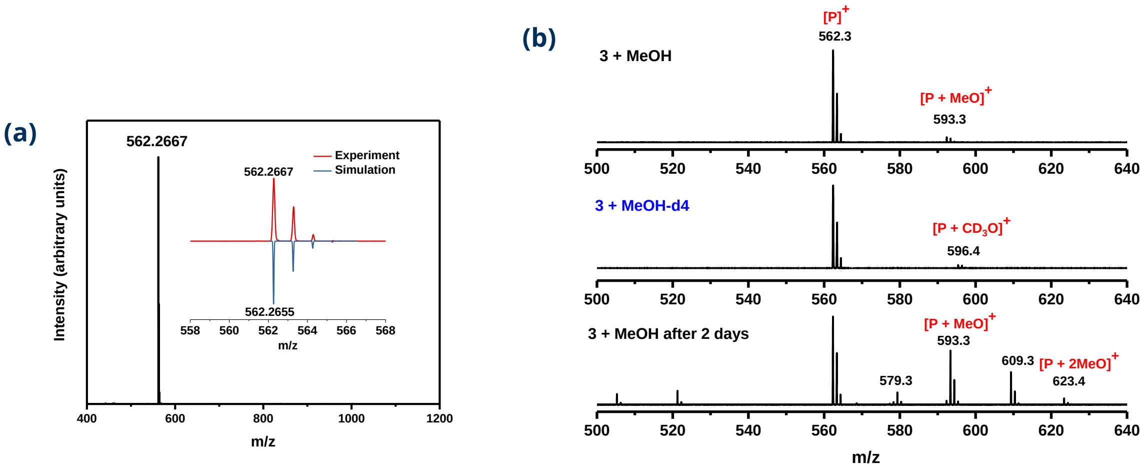


Figure S63. (a) HR-MALDI-TOF mass spectrum of **3**. Inset: experimental (red solid line) and simulated (blue solid line) isotopic distribution patterns of the mass peak. (b) MALDI-TOF mass spectrum of **3** in MeOH and MeOH-d4. (Matrix: DCTB)

In-situ synthesis of 1, 2 and 3 followed by ^{1}H NMR spectroscopy

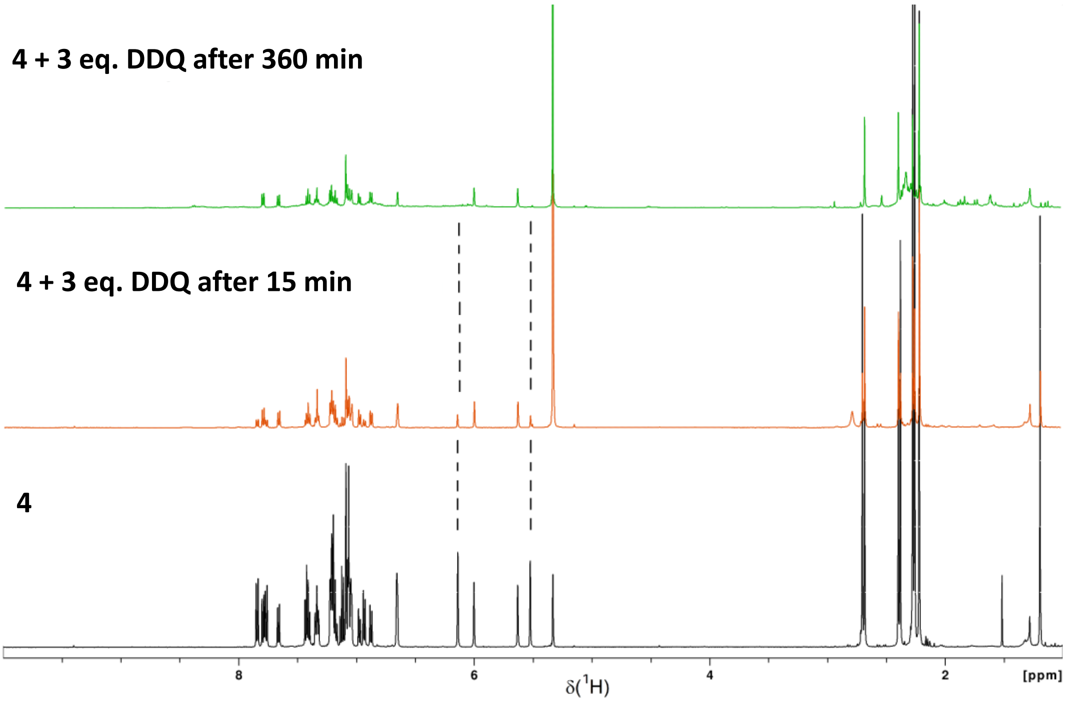


Figure S64. ^{1}H NMR spectra (500 MHz) of precursor **4** and the reaction mixture after addition of 3 eq. DDQ at 30°C in CD_2Cl_2 after 15 min and 6 hours. The reaction proceeds much slower than the reaction of **5** and **6** with 3 eq. DDQ. Moreover, the major isomer (two signals are marked with dashed lines) reacts faster with DDQ to **1** than the minor isomer. Signals of by-products were observed before the reaction was complete. Therefore, no experiments were carried out at low temperatures.

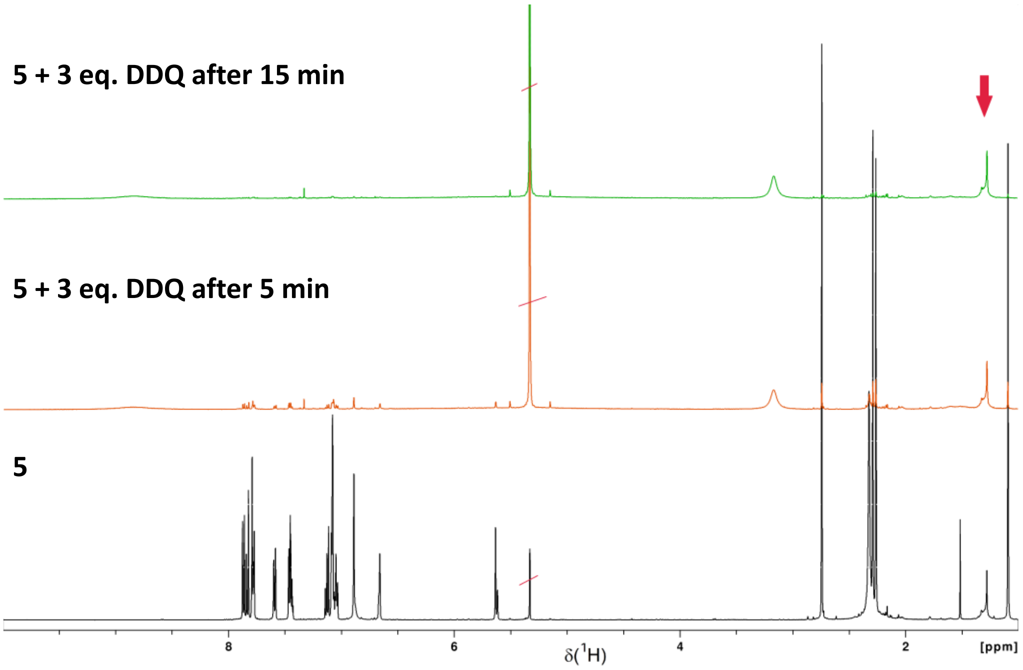


Figure S65. ^{1}H NMR spectra (500 MHz) of precursor **5** and the reaction mixture after addition of 3 eq. DDQ at 30 °C in CD_2Cl_2 after 5 min and 15 min. The signals of **5** have completely disappeared after 15 min and the formed diradical **2** shows very broad lines. The red arrow marks an intensity reference.

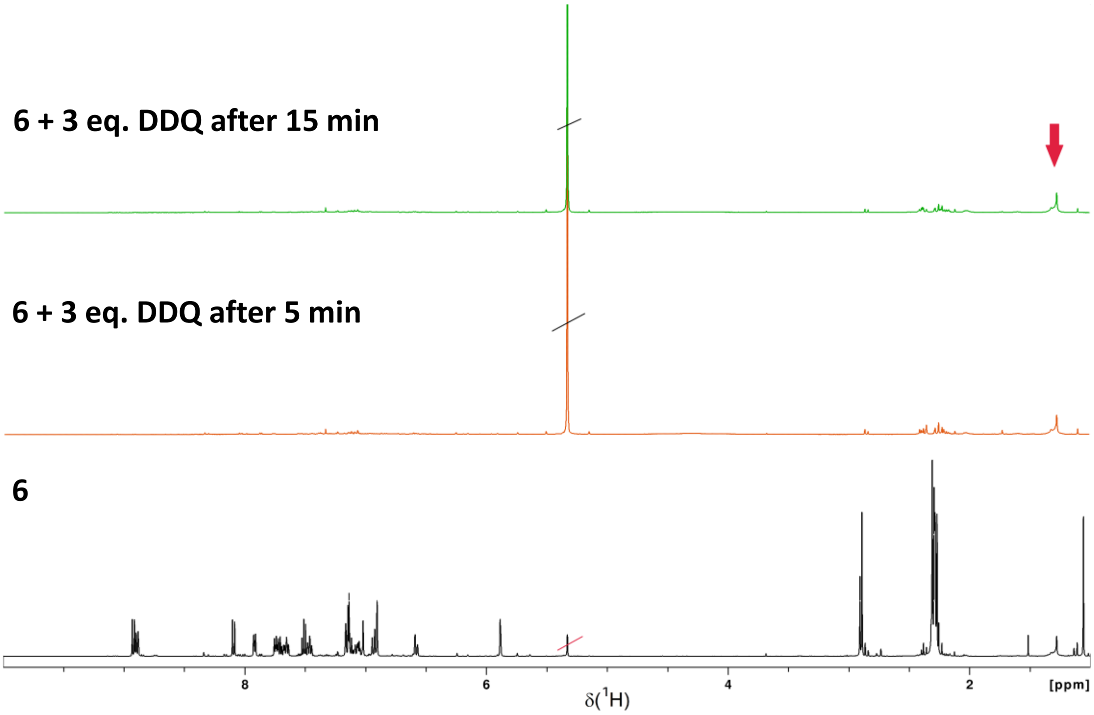


Figure S66. ^{1}H NMR spectra (500 MHz) of precursor **6** and the reaction mixture after addition of 3 eq. DDQ at 30 °C in CD_2Cl_2 after 5 min and 15 min. The signals of **6** have completely disappeared after 5 min and the formed diradical **3** shows very broad lines. The red arrow marks an intensity reference.

Low-temperature ^{1}H NMR measurements on 2 and 3

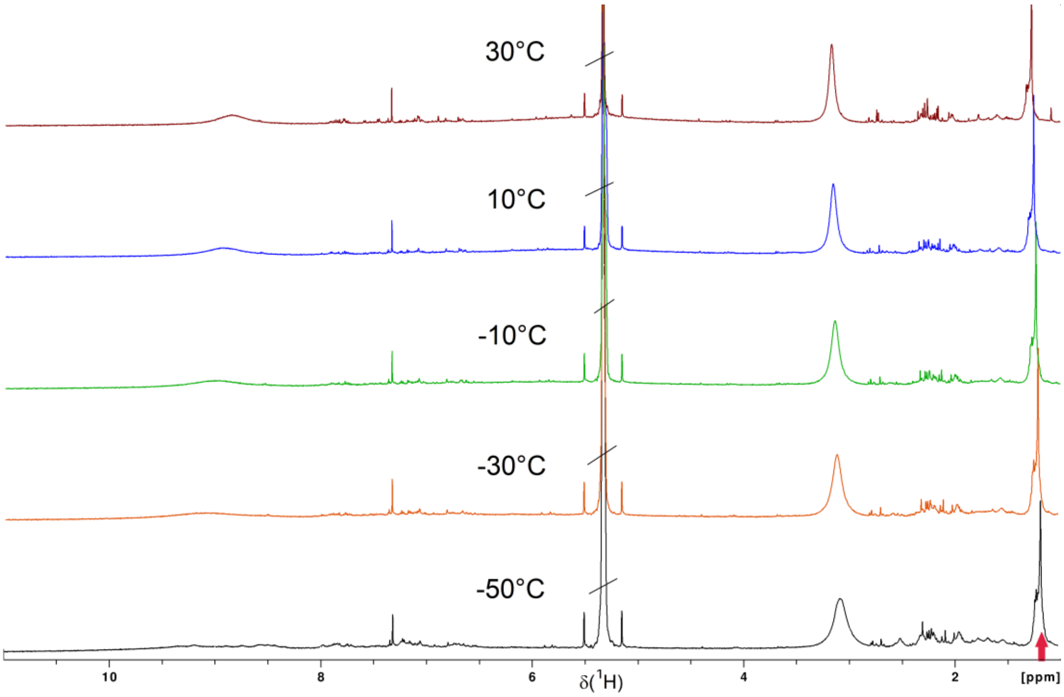


Figure S67. Low-temperature ^{1}H NMR measurements on in situ formed **2** (CD_2Cl_2; 500 MHz). The broad signals show some changes in position and line width but these effects cannot be explained. The red arrow marks an intensity reference.

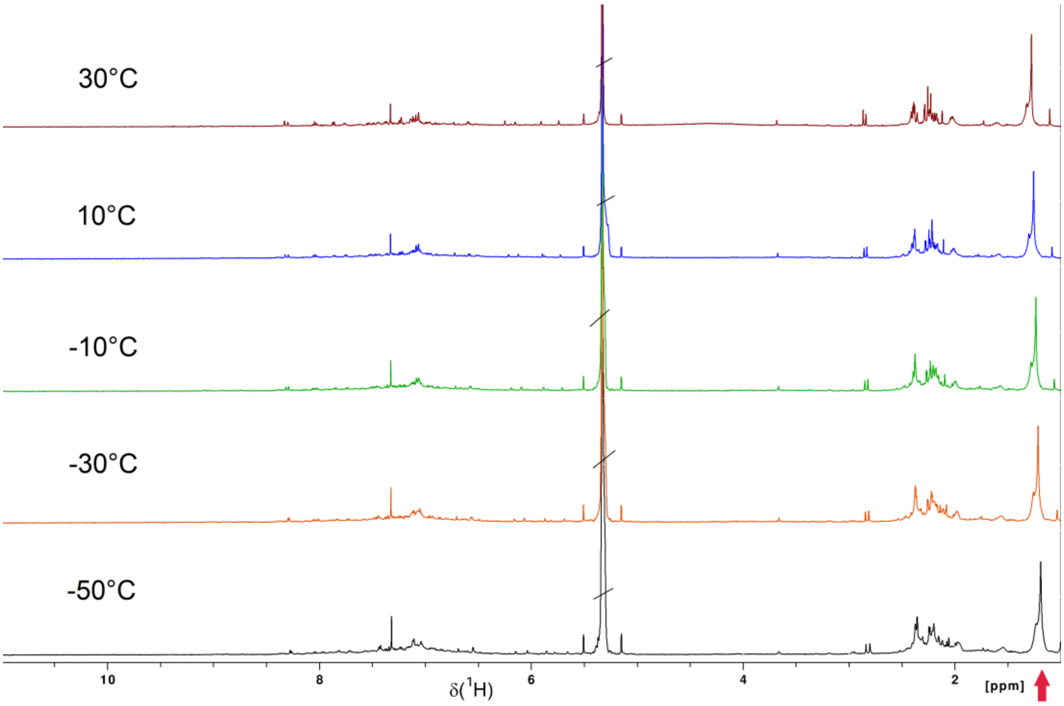


Figure S68. Low-temperature ^{1}H NMR measurements on in situ formed **3** (CD_2Cl_2; 500 MHz). The broad signals show some changes in position and line width but these effects cannot be explained. The red arrow marks an intensity reference.

7. Appendix

Coordinates of optimized structures:

Singlet Closed Shell of **1** (RB3LYP/6-31G(d) (D3BJ))

C	2.81065200	2.55337800	0.40850300
C	2.04535500	3.66091000	0.67794100
C	0.62589100	3.64893200	0.55406800
C	-0.07318300	2.51927800	0.15165400
C	0.68338000	1.31729000	0.00026700
C	2.15339400	1.33551400	0.09173900
C	-1.50419000	2.58850400	-0.21458800
C	-2.46822900	1.51449100	-0.19784200
C	-2.23660600	0.07210200	-0.08018400
C	-1.01678200	-0.61018500	-0.17099200
C	0.27643500	0.00201800	-0.20119000
C	-1.96373800	3.86751200	-0.59830100
C	-3.29524900	4.16829600	-0.83134100
C	-4.25158500	3.16291700	-0.68691900
C	-3.83367700	1.88045100	-0.38983100
C	-1.02854600	-2.05944700	-0.22837800
C	0.12250400	-2.79619400	-0.33243700
C	1.40461100	-2.17603800	-0.33778400
C	1.49346100	-0.80781900	-0.26399700
C	2.64520400	0.04505100	-0.10384200
C	-5.74598800	-2.38540300	0.47107800
C	-5.25881600	-2.12008300	-0.81163400
C	-4.12669200	-1.32852700	-1.02107800
C	-3.46256900	-0.78197900	0.09386600
C	-3.93665400	-1.03077600	1.39489000
C	-5.07198300	-1.82831900	1.56043900
C	-6.95151900	-3.27007400	0.67478500
C	-3.23047500	-0.44505700	2.59335900
C	-3.62685400	-1.06574400	-2.42080900
C	4.05037300	-0.40523000	-0.05332900
C	4.75804800	-0.40136700	1.16869300
C	6.08633100	-0.83447700	1.19175200
C	6.73771000	-1.27830500	0.03875900
C	6.02031300	-1.28701300	-1.15990700
C	4.69293900	-0.85721800	-1.22650800
C	3.96644200	-0.85710200	-2.55075400
C	4.08583700	0.03177400	2.44948100
C	8.18310800	-1.71131300	0.08141800
H	3.89483600	2.58615400	0.46105300
H	2.52514300	4.59072400	0.97204400
H	0.09327600	4.56642700	0.77531800
H	-1.22804200	4.65047100	-0.72789400
H	-3.58107100	5.17472300	-1.12324300
H	-5.30732800	3.36675800	-0.83775700
H	-4.58274900	1.10428100	-0.32771500

H	-1.98062500	-2.57155500	-0.20164000
H	0.05884700	-3.87902600	-0.38836000
H	2.30570100	-2.78374500	-0.36688200
H	-5.77364300	-2.53826000	-1.67396800
H	-5.43785000	-2.01809400	2.56724500
H	-6.65648000	-4.32166100	0.78778600
H	-7.50560700	-2.98973000	1.57661800
H	-7.63692500	-3.21479000	-0.17731400
H	-2.19124200	-0.78875000	2.64966400
H	-3.19835900	0.64951400	2.54224500
H	-3.73419700	-0.72760600	3.52216700
H	-4.31343800	-1.47941300	-3.16498800
H	-3.52119900	0.00795900	-2.61253500
H	-2.64021100	-1.51516100	-2.58246000
H	6.62292900	-0.83555700	2.13867700
H	6.50983700	-1.62846600	-2.07008300
H	3.19048200	-1.63059500	-2.59240900
H	3.46004500	0.09917400	-2.72032500
H	4.66105000	-1.03560600	-3.37753500
H	3.88829100	1.10981500	2.46368800
H	3.11528200	-0.46155400	2.57061600
H	4.70863200	-0.20870200	3.31680300
H	8.45111300	-2.11450200	1.06386000
H	8.85781400	-0.86804900	-0.11871900
H	8.39376800	-2.47966700	-0.67024600

Singlet Biradical Open Shell of **1** (UB3LYP/6-31G(d) (D3BJ) nosymm guess=(mix,always))

C	2.80407700	2.52882900	0.45295100
C	2.04574400	3.66768000	0.67789200
C	0.64977100	3.65523200	0.51561200
C	-0.05857500	2.50737600	0.10682400
C	0.69065900	1.32622700	-0.00088400
C	2.12842400	1.33755200	0.13847700
C	-1.49833000	2.59898000	-0.24982200
C	-2.46719300	1.52947400	-0.20764500
C	-2.24069000	0.09381600	-0.10282900
C	-1.00106000	-0.61644800	-0.23530200
C	0.27944200	-0.02992500	-0.23295600
C	-1.94515300	3.87709100	-0.63260700
C	-3.28084100	4.19619300	-0.84170900
C	-4.24086500	3.20381600	-0.65373100
C	-3.83330800	1.91648000	-0.35357900
C	-1.02162300	-2.05124500	-0.35428700
C	0.12929400	-2.80770000	-0.45903400
C	1.40345700	-2.20731400	-0.41334900
C	1.47263300	-0.82991100	-0.28820800
C	2.62364600	0.02155100	-0.07385900
C	-5.71172400	-2.40918100	0.48962100

C	-5.27456000	-2.09331400	-0.79978200
C	-4.15819900	-1.28266700	-1.02042100
C	-3.45571200	-0.76788800	0.08678200
C	-3.88065100	-1.07137500	1.39327700
C	-5.00272900	-1.88475800	1.57291800
C	-6.90090000	-3.31331200	0.70515400
C	-3.13493400	-0.51966200	2.58390600
C	-3.71359200	-0.95873100	-2.42580300
C	4.02837000	-0.41832900	-0.02382000
C	4.71959400	-0.44754500	1.20665500
C	6.04956500	-0.87377100	1.22837200
C	6.71661800	-1.27017100	0.06682000
C	6.01311300	-1.24166000	-1.14008000
C	4.68251300	-0.82407600	-1.20716600
C	3.96714000	-0.78219500	-2.53673700
C	4.02734300	-0.06507000	2.49335200
C	8.16444200	-1.69371100	0.11000000
H	3.88658600	2.53966200	0.53847500
H	2.52989300	4.59358900	0.97505200
H	0.10666400	4.56961200	0.72279700
H	-1.20517900	4.65408200	-0.77922000
H	-3.56132500	5.20317400	-1.13576900
H	-5.29907100	3.41961500	-0.76973700
H	-4.59131200	1.15195000	-0.25568700
H	-1.97841800	-2.55639500	-0.36123600
H	0.04704900	-3.88657800	-0.55463800
H	2.30874700	-2.80695900	-0.44470900
H	-5.81701000	-2.48624000	-1.65727600
H	-5.32996000	-2.11389700	2.58501500
H	-6.59357300	-4.36577700	0.76654900
H	-7.42248900	-3.07285000	1.63748200
H	-7.61929400	-3.23253500	-0.11736100
H	-2.08847400	-0.84604500	2.58281800
H	-3.12333800	0.57643700	2.57270900
H	-3.59388700	-0.84679400	3.52158600
H	-4.38436700	-1.40942400	-3.16318500
H	-3.69462500	0.12369100	-2.59669400
H	-2.69928700	-1.32754300	-2.61776300
H	6.57515200	-0.90628800	2.18057300
H	6.51533700	-1.54645600	-2.05598900
H	3.16276000	-1.52452800	-2.59007500
H	3.50090000	0.19519500	-2.70391700
H	4.66137000	-0.97759000	-3.35949900
H	3.80861500	1.00777000	2.53623600
H	3.06721200	-0.58299300	2.59490700
H	4.64776100	-0.31769400	3.35845200
H	8.42547700	-2.12772900	1.08087100
H	8.83316300	-0.83828000	-0.05456000
H	8.38847700	-2.43398000	-0.66533000

Triplet State of **1** (UB3LYP/6-31G(d) (D3BJ)

C	2.80229700	2.51025700	0.46612800
C	2.05197600	3.67005900	0.67723100
C	0.66888900	3.66642100	0.51449500
C	-0.05611900	2.50792000	0.11732100
C	0.68780500	1.33256700	0.02062100
C	2.11427000	1.33649900	0.16278000
C	-1.49938200	2.61220600	-0.20070400
C	-2.46383100	1.53659400	-0.16260300
C	-2.23587600	0.10295100	-0.09013600
C	-1.00141700	-0.62144600	-0.24752700
C	0.28154700	-0.03971000	-0.22652500
C	-1.95873600	3.90011500	-0.54094400
C	-3.29740100	4.21985000	-0.71550800
C	-4.25049400	3.21823900	-0.52963100
C	-3.83501200	1.92684600	-0.26696900
C	-1.02397700	-2.04764100	-0.40171300
C	0.13348500	-2.81276300	-0.51778500
C	1.39968400	-2.22872400	-0.45468200
C	1.46934600	-0.83738300	-0.29117200
C	2.60657200	0.00085200	-0.06324400
C	-5.69468400	-2.42596400	0.46501200
C	-5.27319100	-2.06837600	-0.81876000
C	-4.16190000	-1.24741800	-1.02596500
C	-3.44917100	-0.76407300	0.08856200
C	-3.85722000	-1.11129400	1.38926000
C	-4.97479200	-1.93364000	1.55615900
C	-6.87844000	-3.34070000	0.66550100
C	-3.09775700	-0.59650100	2.58764400
C	-3.73307400	-0.87668900	-2.42452600
C	4.01564000	-0.42691900	-0.03050400
C	4.71216200	-0.47434000	1.19588000
C	6.04665800	-0.88619200	1.20184000
C	6.71210500	-1.24844100	0.02815900
C	6.00222200	-1.20179500	-1.17444400
C	4.66628300	-0.79932000	-1.22612600
C	3.94079500	-0.74217000	-2.54950800
C	4.02012100	-0.12850900	2.49314500
C	8.16484000	-1.65606600	0.05472600
H	3.88446900	2.50974400	0.55712400
H	2.54729800	4.59103500	0.97081200
H	0.13047300	4.58285400	0.72145300
H	-1.22659000	4.68395300	-0.68836700
H	-3.58723500	5.23221500	-0.98017700
H	-5.31164400	3.43369000	-0.61682700
H	-4.58984500	1.15951100	-0.16782500
H	-1.98099200	-2.55172600	-0.42273900
H	0.03996200	-3.88846500	-0.63791300

H	2.30587500	-2.82518100	-0.49785400
H	-5.82380100	-2.43654600	-1.68207300
H	-5.28953600	-2.19593900	2.56419900
H	-6.56726000	-4.39355200	0.69045000
H	-7.39022300	-3.13137100	1.61072500
H	-7.60646900	-3.23676200	-0.14590400
H	-2.05139400	-0.92246700	2.56312200
H	-3.08682400	0.49940800	2.61087100
H	-3.54501200	-0.95369100	3.52006500
H	-4.39354200	-1.32839500	-3.17062100
H	-3.74661400	0.20986700	-2.56860600
H	-2.70915900	-1.21127000	-2.62776200
H	6.57718400	-0.93440600	2.15055400
H	6.50284100	-1.48174700	-2.09903200
H	3.13832600	-1.48644300	-2.60452500
H	3.47095800	0.23592700	-2.70230200
H	4.62938000	-0.92536300	-3.37968600
H	3.78240200	0.93920800	2.55701600
H	3.07047300	-0.66631200	2.59045600
H	4.64954500	-0.38555700	3.35027400
H	8.43588600	-2.10847700	1.01433900
H	8.82259100	-0.78936400	-0.09411200
H	8.39315800	-2.37619400	-0.73805700

Singlet Closed Shell of **2** (RB3LYP/6-31G(d) (D3BJ))

C	-2.17333200	1.11065900	-0.06164600
C	-2.87512700	2.34330100	-0.10988000
C	-2.15630300	3.49676200	-0.13237400
C	-0.71641500	3.52305400	-0.12426300
C	0.06089900	2.32718500	-0.09374400
C	-0.69722300	1.09867100	-0.05786300
C	1.50720600	2.40026200	-0.10685400
C	2.08218900	3.73032600	-0.15362600
C	3.47788900	3.94254100	-0.18825800
C	4.34971500	2.88454200	-0.18137100
C	3.83780600	1.59140800	-0.12688300
C	2.46191000	1.27874700	-0.08101100
C	-0.30125900	-0.23080800	-0.01044500
C	0.98874300	-0.85060000	0.03160400
C	0.99836700	-2.29874700	0.11306800
C	-0.15416900	-3.03869800	0.14798100
C	-1.43310400	-2.41727100	0.10424400
C	-1.51689400	-1.05031400	0.01680300
C	2.20430400	-0.16567700	-0.00133900
C	-2.66464400	-0.18781500	-0.02065800
C	-4.07855100	-0.61559000	0.00156700
C	3.42490500	-1.04799800	0.05482800
C	-4.86864400	-0.39731900	1.15111100
C	-6.20209200	-0.81414000	1.15471800

C	-6.78011600	-1.44492900	0.05051300
C	-5.98377700	-1.65776100	-1.07707200
C	-4.64758900	-1.25206500	-1.12250400
C	3.97654000	-1.55616600	-1.13534800
C	5.09005100	-2.39653000	-1.05768100
C	5.66753300	-2.74368500	0.16641500
C	5.09636100	-2.23052600	1.33394000
C	3.98376700	-1.38625400	1.30077600
C	-3.83563000	-1.47507500	-2.37647900
C	-4.28045300	0.25660100	2.37866300
C	3.38458700	-0.85680700	2.58045200
C	3.37008000	-1.20877600	-2.47281300
C	-8.23180000	-1.85837700	0.06511300
C	6.88987500	-3.62681700	0.22470600
C	-0.09163000	4.79151500	-0.15790700
C	1.26328100	4.89273100	-0.17223700
H	-3.96092400	2.34540000	-0.13175200
H	-2.66382500	4.45745600	-0.16599200
H	3.83932500	4.96654400	-0.22413000
H	5.42405800	3.03844000	-0.21371200
H	4.54858200	0.78053800	-0.11565400
H	1.94944600	-2.81047800	0.14840300
H	-0.09146100	-4.12098500	0.21277900
H	-2.33768900	-3.01885500	0.14444300
H	-6.80270200	-0.64969000	2.04732200
H	-6.41646400	-2.14405100	-1.94934800
H	5.51455100	-2.79128900	-1.97826100
H	5.52537700	-2.49522300	2.29799600
H	-4.47988400	-1.76634200	-3.21188500
H	-3.28933600	-0.56822700	-2.65682700
H	-3.08388100	-2.26200900	-2.24360700
H	-3.32963300	-0.21025900	2.65755900
H	-4.06681900	1.31876800	2.21157600
H	-4.96718000	0.18101000	3.22751800
H	2.35960900	-1.21994000	2.71932400
H	3.97520500	-1.16671800	3.44721400
H	3.33626600	0.23804600	2.57349500
H	3.29727300	-0.12352600	-2.60671600
H	3.97033000	-1.61431500	-3.29222200
H	2.35397500	-1.60986600	-2.56473900
H	-8.56539500	-2.11215500	1.07701700
H	-8.88011600	-1.04913500	-0.29698800
H	-8.40752300	-2.72689500	-0.57853700
H	7.81139400	-3.03063700	0.19222800
H	6.91550100	-4.21380200	1.14869100
H	6.92225000	-4.32130000	-0.62115200
H	-0.71662800	5.68038400	-0.17645000
H	1.75275800	5.86176000	-0.20307700

Singlet Biradical Open Shell of **2** (UB3LYP/6-31G(d) (D3BJ) nosymm guess=(mix,always))

C	-2.16414500	1.11217000	-0.01352500
C	-2.88338800	2.33184000	-0.02729900
C	-2.17521000	3.49488600	-0.02387100
C	-0.74051100	3.52263900	-0.01808200
C	0.04502500	2.32479400	-0.01862300
C	-0.70564300	1.10454200	-0.01575400
C	1.49910900	2.40802300	-0.02527300
C	2.06224600	3.73746900	-0.03197200
C	3.45727100	3.96753500	-0.04688200
C	4.33584300	2.91509400	-0.05674400
C	3.83211200	1.61800100	-0.04574800
C	2.45568500	1.29124700	-0.02647800
C	-0.29875700	-0.24997700	-0.01282300
C	0.98284200	-0.85298400	0.00179200
C	1.00032600	-2.30041200	0.02644300
C	-0.14860100	-3.05370300	0.04037300
C	-1.42535200	-2.44018100	0.02751000
C	-1.49975500	-1.06533700	-0.00893600
C	2.20931300	-0.15196200	-0.00491700
C	-2.65144400	-0.20088800	-0.01208000
C	-4.06322900	-0.62964200	-0.00172700
C	3.42938400	-1.03419600	0.01331600
C	-4.84851500	-0.45329300	1.15798700
C	-6.18105800	-0.87217500	1.14944100
C	-6.76173900	-1.46052700	0.02333700
C	-5.96884500	-1.63006000	-1.11419600
C	-4.63272200	-1.22417800	-1.14820700
C	3.98407400	-1.48902700	-1.19722800
C	5.09469500	-2.33583800	-1.15731700
C	5.66830200	-2.74168600	0.05051800
C	5.09615400	-2.28158500	1.23946900
C	3.98588000	-1.43346300	1.24246100
C	-3.82272500	-1.39818400	-2.41118200
C	-4.25550100	0.15360500	2.40729700
C	3.38608300	-0.95955400	2.54342500
C	3.38256500	-1.07454200	-2.51761500
C	-8.21298500	-1.87516100	0.02627400
C	6.88768900	-3.63075900	0.06996400
C	-0.11824800	4.79452800	-0.01897500
C	1.23511300	4.89732100	-0.02587800
H	-3.96912800	2.32037500	-0.04530700
H	-2.68882900	4.45256700	-0.03191400
H	3.80925800	4.99524400	-0.05196600
H	5.40968500	3.07605700	-0.07112000
H	4.54794800	0.81109700	-0.05053800
H	1.95494400	-2.80718000	0.03696200
H	-0.07509100	-4.13704200	0.06375700

H	-2.33148600	-3.03957700	0.04964100
H	-6.77881600	-0.74286600	2.04954700
H	-6.40394700	-2.08277900	-2.00301800
H	5.52011100	-2.68881300	-2.09441700
H	5.52247700	-2.59217500	2.19105300
H	-4.46531400	-1.68058000	-3.25067800
H	-3.29719600	-0.47327000	-2.67243600
H	-3.05444800	-2.17212400	-2.30095500
H	-3.30815800	-0.32930800	2.67071800
H	-4.03550900	1.21945700	2.27695400
H	-4.94232800	0.05253100	3.25319400
H	2.35355500	-1.31031400	2.65608900
H	3.96407300	-1.32350300	3.39779100
H	3.35681500	0.13503200	2.59114600
H	3.34151100	0.01680900	-2.60969100
H	3.96660900	-1.46653600	-3.35530100
H	2.35418800	-1.44083600	-2.61840700
H	-8.54459300	-2.16368900	1.02936700
H	-8.86172600	-1.05394600	-0.30673300
H	-8.38929300	-2.72089400	-0.64676300
H	7.81157000	-3.03735900	0.05904200
H	6.91347900	-4.25476200	0.96940900
H	6.91552600	-4.29076900	-0.80332100
H	-0.74538300	5.68195000	-0.01651700
H	1.72125900	5.86866300	-0.02904200

Triplet State of **2** (UB3LYP/6-31G(d) (D3BJ)

C	-2.14269600	1.12267500	-0.04604000
C	-2.88014200	2.31506000	-0.10845500
C	-2.18131900	3.49610400	-0.15108600
C	-0.76310600	3.52641600	-0.14170000
C	0.03256600	2.31564700	-0.09104700
C	-0.71299000	1.11907600	-0.04543900
C	1.49364400	2.41045400	-0.09016500
C	2.04643500	3.73755000	-0.13905200
C	3.43552100	3.98248100	-0.14205400
C	4.32101200	2.93001100	-0.09616400
C	3.82534500	1.63595800	-0.04803500
C	2.44284600	1.29577200	-0.04244400
C	-0.30423900	-0.28058200	0.00113500
C	0.97113800	-0.86826500	0.02995600
C	0.99189100	-2.30359200	0.08342900
C	-0.16400500	-3.07561800	0.11414000
C	-1.42673900	-2.48157000	0.08964500
C	-1.48777000	-1.08414800	0.02406700
C	2.20836600	-0.13661000	0.01085800
C	-2.62907400	-0.22238600	-0.00361000
C	-4.04290800	-0.63754900	0.01058500

C	3.42550200	-1.02022200	0.05215600
C	-4.82771800	-0.42840400	1.16439500
C	-6.16391100	-0.83444600	1.15808400
C	-6.74636300	-1.43603500	0.03974800
C	-5.95112100	-1.63644800	-1.09140600
C	-4.60994700	-1.24920200	-1.12751700
C	3.98663000	-1.50029200	-1.14581600
C	5.08963000	-2.35591000	-1.08576700
C	5.65036900	-2.74868300	0.13246300
C	5.07281100	-2.26627800	1.30993200
C	3.96941300	-1.40928100	1.29037400
C	-3.79189500	-1.46059000	-2.37935500
C	-4.22850300	0.19153700	2.40450900
C	3.36244900	-0.90957200	2.57819000
C	3.39848800	-1.09806300	-2.47583100
C	-8.20189500	-1.83458100	0.04396700
C	6.86178200	-3.64806200	0.17458700
C	-0.13757900	4.80036600	-0.18882000
C	1.21330700	4.89854700	-0.18734000
H	-3.96562100	2.28850900	-0.12618800
H	-2.70593100	4.44634000	-0.19750600
H	3.78238500	5.01096300	-0.18050600
H	5.39429700	3.09632200	-0.09701200
H	4.54397900	0.83168300	-0.01254400
H	1.94773200	-2.80825000	0.10471800
H	-0.07271400	-4.15707900	0.16077400
H	-2.33776900	-3.07112200	0.12545800
H	-6.76298400	-0.68385600	2.05378000
H	-6.38727400	-2.10222100	-1.97271000
H	5.51914700	-2.72687500	-2.01417800
H	5.48902800	-2.56662600	2.26940700
H	-4.42408300	-1.80012300	-3.20517200
H	-3.29223900	-0.53516700	-2.68698000
H	-3.00318600	-2.20608200	-2.22780400
H	-3.29775600	-0.31167500	2.68916600
H	-3.97884700	1.24755100	2.25119500
H	-4.92430700	0.12855000	3.24642400
H	2.31616400	-1.22365600	2.67070100
H	3.91071700	-1.28982000	3.44523000
H	3.37007500	0.18573600	2.62131200
H	3.41011200	-0.00915100	-2.60143200
H	3.95721900	-1.54379200	-3.30413800
H	2.35256000	-1.41596500	-2.55870800
H	-8.54378700	-2.08985200	1.05243500
H	-8.83821400	-1.01604200	-0.31805200
H	-8.38255100	-2.69745600	-0.60561200
H	7.79151700	-3.06384400	0.15759500
H	6.87733700	-4.25586600	1.08537800
H	6.88807800	-4.32441000	-0.68628100

H	-0.76471200	5.68678200	-0.22619000
H	1.70028800	5.86891900	-0.22303600

Singlet Closed Shell of **3** (RB3LYP/6-31G(d) (D3BJ))

C	-3.98538800	1.71774400	-0.43418000
C	-2.67085200	1.26738700	-0.19954800
C	-1.61303300	2.27953900	-0.05617600
C	-2.06892900	3.64911100	0.00669500
C	-3.42534700	4.01044100	-0.16915700
C	-4.37107300	3.05718900	-0.43459900
C	-0.17077300	2.06942800	-0.01025300
C	0.71421800	3.18063900	0.07390700
C	0.18489400	4.47982200	0.26308300
C	-1.15367200	4.70734600	0.23110400
C	0.44917300	0.76145800	-0.05172400
C	1.91859800	0.60413400	-0.06509000
C	2.78037400	1.75938100	-0.12476700
C	2.17583700	3.03968600	-0.04872400
C	4.17931300	1.64976400	-0.26891200
C	4.98393800	2.77441300	-0.33098900
C	4.39713900	4.04304500	-0.26786400
C	3.02250200	4.16620800	-0.13726400
C	-0.10435400	-0.51160600	-0.00329700
C	0.99974300	-1.46500700	0.03170500
C	2.24475100	-0.74107000	-0.01939800
C	-1.45357200	-0.99187300	0.05249600
C	-1.61881200	-2.42897200	0.20020200
C	-0.55995400	-3.29173500	0.23851700
C	0.77966300	-2.81036400	0.14930900
C	3.56041700	-1.41889100	0.02766100
C	4.08771900	-2.01644900	-1.13455300
C	5.31782200	-2.67631100	-1.06499500
C	6.03782900	-2.76438700	0.12871100
C	5.49978300	-2.16365100	1.27045000
C	4.27389500	-1.49577400	1.24152800
C	3.34846200	-1.91373300	-2.44676800
C	3.73224800	-0.83558000	2.48500900
C	7.34954500	-3.50864400	0.19079000
C	-2.58485000	-0.19301300	-0.05607800
C	-3.89968100	-0.92489800	0.00248200
C	-4.57336800	-1.04589200	1.23205500
C	-5.78172200	-1.74538500	1.27331800
C	-6.33902000	-2.32332800	0.12943400
C	-5.65357200	-2.18429700	-1.08002800
C	-4.43885400	-1.49860600	-1.16368200
C	-3.71942800	-1.37441600	-2.48489900
C	-3.99947800	-0.43385000	2.48606900
C	-7.63188400	-3.09822200	0.20406900

H	-4.75781800	0.98120600	-0.59114200
H	-3.68480300	5.06413100	-0.11645200
H	-5.40852300	3.32179500	-0.61521900
H	0.84860500	5.31572000	0.43718200
H	-1.54794000	5.71289400	0.34603300
H	4.62598700	0.66716700	-0.34179800
H	6.05919400	2.66811500	-0.44225200
H	5.01141700	4.93668300	-0.33384600
H	2.60705600	5.16557100	-0.13195300
H	-2.62166800	-2.82521500	0.27545600
H	-0.73820000	-4.35764000	0.34453000
H	1.61868700	-3.50024100	0.18915200
H	5.72599200	-3.12705900	-1.96741500
H	6.04913400	-2.21598400	2.20838000
H	3.13094100	-0.86848700	-2.69415900
H	3.93440500	-2.34710800	-3.26300700
H	2.38338600	-2.43173000	-2.40734500
H	3.72077400	0.25562700	2.37663400
H	2.69989500	-1.14389800	2.68259300
H	4.34211600	-1.08344300	3.35914500
H	8.02777500	-3.06382400	0.92682300
H	7.19880600	-4.55712800	0.48085700
H	7.85518500	-3.50976000	-0.78052100
H	-6.30113400	-1.83949500	2.22461200
H	-6.07351800	-2.62047500	-1.98389300
H	-4.34306400	-1.74032100	-3.30565400
H	-3.45017400	-0.33359700	-2.69668600
H	-2.78671400	-1.95074600	-2.48526200
H	-3.89262900	0.65222900	2.38386300
H	-4.64143800	-0.63338500	3.34877500
H	-3.00177900	-0.83234400	2.70308100
H	-7.44751600	-4.15569400	0.43537100
H	-8.28937200	-2.70500600	0.98647200
H	-8.17453900	-3.06324300	-0.74625400

Singlet Biradical Open Shell of **3** (UB3LYP/6-31G(d) (D3BJ) nosymm guess=(mix,always))

C	-3.99667800	1.73777500	-0.29105200
C	-2.67567600	1.27463400	-0.11356400
C	-1.61364700	2.28056900	0.04579700
C	-2.06450500	3.64706500	0.16485000
C	-3.42456300	4.01815600	0.04218700
C	-4.38024000	3.07562200	-0.22598200
C	-0.16952100	2.06691500	0.05985200
C	0.71922700	3.17648100	0.15805200
C	0.19605500	4.47036800	0.39256000
C	-1.14268800	4.69802300	0.39794900
C	0.45002700	0.76329500	-0.01686500
C	1.91388500	0.60576700	-0.03461600

C	2.77981800	1.75805300	-0.07971100
C	2.17769600	3.03798000	0.01449100
C	4.17801800	1.64897900	-0.23245300
C	4.98214900	2.77411100	-0.28952100
C	4.39667900	4.04303900	-0.21367200
C	3.02346700	4.16573500	-0.07199000
C	-0.10763100	-0.51879400	-0.00374400
C	0.99280500	-1.46940200	0.00770500
C	2.23867200	-0.74324300	-0.01990900
C	-1.45291200	-0.99649000	0.02425900
C	-1.62059400	-2.43619000	0.10903700
C	-0.56194300	-3.30304900	0.13007300
C	0.77590900	-2.82083200	0.07565800
C	3.55394200	-1.42183400	0.00923100
C	4.07867900	-1.99267200	-1.16746100
C	5.30880400	-2.65395000	-1.11482200
C	6.03063300	-2.76953500	0.07544400
C	5.49470500	-2.19483200	1.23152500
C	4.26916900	-1.52595100	1.21996100
C	3.33771700	-1.85873800	-2.47589400
C	3.72946400	-0.89377900	2.47877800
C	7.34219500	-3.51533900	0.11842800
C	-2.58915300	-0.18844600	-0.05144500
C	-3.90044100	-0.92884500	-0.04767100
C	-4.57703500	-1.14377100	1.16737700
C	-5.78060300	-1.85267000	1.15406300
C	-6.32970800	-2.35125800	-0.03040200
C	-5.64130000	-2.12093200	-1.22416600
C	-4.43179400	-1.42173100	-1.25366900
C	-3.70869300	-1.19676300	-2.55928200
C	-4.01046300	-0.62001200	2.46396000
C	-7.61678900	-3.13920000	-0.01642200
H	-4.77445000	1.00934600	-0.45851300
H	-3.67894200	5.06990600	0.13871800
H	-5.42251400	3.34706700	-0.36378500
H	0.86469100	5.29997000	0.57756200
H	-1.53353300	5.69935700	0.55405200
H	4.62445200	0.66731500	-0.31735200
H	6.05667800	2.66834100	-0.40823100
H	5.01117700	4.93658200	-0.27836800
H	2.60710200	5.16471000	-0.05767300
H	-2.62424200	-2.83480000	0.15447100
H	-0.74389000	-4.37177700	0.19291700
H	1.61605500	-3.50989200	0.09774000
H	5.71550900	-3.08374200	-2.02803100
H	6.04552900	-2.26870300	2.16711000
H	3.12055100	-0.80780400	-2.69842800
H	3.92253700	-2.27278400	-3.30285100
H	2.37259000	-2.37731600	-2.44756800

H	3.71716000	0.19955100	2.39463400
H	2.69774500	-1.20725300	2.67173200
H	4.34114000	-1.16052800	3.34601700
H	8.02252200	-3.08628300	0.86183800
H	7.19165600	-4.56956500	0.38691900
H	7.84523000	-3.49630900	-0.85402500
H	-6.30250700	-2.01835100	2.09418600
H	-6.05465700	-2.49479900	-2.15850300
H	-4.31602000	-1.53003000	-3.40577700
H	-3.46932900	-0.13738800	-2.70512600
H	-2.75904300	-1.74400200	-2.58674800
H	-3.89827100	0.46993300	2.43586800
H	-4.65954700	-0.87450100	3.30670100
H	-3.01605900	-1.03703500	2.66074700
H	-7.42505800	-4.20924800	0.13849700
H	-8.27961600	-2.80847500	0.79003800
H	-8.15694400	-3.03969800	-0.96361400

Triplet State of **3** (UB3LYP/6-31G(d) (D3BJ)

C	-3.99701800	1.80695600	0.00425600
C	-2.66033900	1.31097800	0.05145000
C	-1.58647600	2.31109200	0.11125100
C	-2.00393000	3.68327700	0.23318700
C	-3.35863300	4.08149300	0.25393600
C	-4.35290300	3.14214300	0.10856800
C	-0.14372800	2.07090200	0.02245200
C	0.76937200	3.18992900	-0.01471500
C	0.27827200	4.49910700	0.19531600
C	-1.05356600	4.73382000	0.32538900
C	0.46720900	0.78788000	-0.00532300
C	1.88406200	0.61417400	-0.07340100
C	2.77292600	1.72233500	-0.26157800
C	2.19850700	3.02217600	-0.24583800
C	4.16208900	1.57447200	-0.48302800
C	4.97058100	2.67525900	-0.68568600
C	4.40976400	3.96299500	-0.69139300
C	3.05444200	4.12656300	-0.48089400
C	-0.11735800	-0.54836400	0.11352000
C	0.95561600	-1.48354900	0.15501900
C	2.19508400	-0.76787000	0.03995100
C	-1.44813500	-0.99114000	0.16024200
C	-1.63591500	-2.40823400	0.28852300
C	-0.57863500	-3.30567200	0.35788600
C	0.74234800	-2.85798800	0.28898000
C	3.51061600	-1.43910800	0.08815200
C	3.98476200	-2.13672500	-1.04048700
C	5.22067800	-2.78413000	-0.96650500
C	5.99170800	-2.76731000	0.19836000

C	5.50058300	-2.07092900	1.30647600
C	4.27314200	-1.40708000	1.27334500
C	3.18681100	-2.15037000	-2.32191100
C	3.77891300	-0.64506500	2.47794200
C	7.30791200	-3.50244300	0.26775600
C	-2.59657800	-0.13098200	0.05822700
C	-3.89968300	-0.87786300	-0.02945000
C	-4.61116400	-1.20587700	1.14013800
C	-5.79917600	-1.93289300	1.03204200
C	-6.29796900	-2.34744700	-0.20606400
C	-5.57588700	-2.01067900	-1.35367600
C	-4.38235900	-1.28692200	-1.28600600
C	-3.62174500	-0.94188100	-2.54275300
C	-4.09570200	-0.77332600	2.49051100
C	-7.56644200	-3.16031000	-0.29798000
H	-4.79567800	1.08813000	-0.09553200
H	-3.58703800	5.13814100	0.35733800
H	-5.40077100	3.42623300	0.08343100
H	0.96632400	5.32959300	0.27474500
H	-1.42113200	5.74410000	0.48082400
H	4.59193200	0.58250500	-0.50854000
H	6.03459600	2.54070900	-0.85830900
H	5.03519800	4.83170500	-0.87552500
H	2.64924500	5.12900500	-0.53411200
H	-2.64438600	-2.79488100	0.33369400
H	-0.79086000	-4.36594400	0.46156100
H	1.58356500	-3.54279100	0.33470100
H	5.59161700	-3.31075100	-1.84333700
H	6.08861500	-2.04319200	2.22152300
H	2.95431600	-1.13155600	-2.65307900
H	3.73831300	-2.65311900	-3.12186900
H	2.22802200	-2.66509300	-2.19245500
H	3.77099600	0.43438200	2.28457100
H	2.75305600	-0.92941200	2.73665800
H	4.41750300	-0.82819800	3.34718700
H	8.01208900	-2.99996900	0.93933200
H	7.17181600	-4.52450500	0.64559300
H	7.77517800	-3.58030600	-0.71942400
H	-6.34804900	-2.18189600	1.93801300
H	-5.94931800	-2.31974900	-2.32785200
H	-4.14247100	-1.31063600	-3.43145000
H	-3.49393900	0.14196700	-2.64549500
H	-2.61681300	-1.37980600	-2.52917400
H	-4.02315800	0.31858500	2.55635800
H	-4.75366300	-1.12078800	3.29252900
H	-3.09087000	-1.17028500	2.67615700
H	-7.35494200	-4.23580100	-0.23063100
H	-8.25896100	-2.91470400	0.51405000
H	-8.08265300	-2.99005300	-1.24858600

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