Accepted Manuscript

Exploration of 9-bromo[7]helicene reactivity

Jaroslav õ² dnÎ , Petr Vel¾jek, Martin Jakubec, Jan SÎ kora, Vladim¾C¾kva, Jan Storch

PII: S0040-4020(13)00774-6

DOI: 10.1016/j.tet.2013.05.039

Reference: TET 24377

To appear in: *Tetrahedron*

Received Date: 29 December 2012

Revised Date: 30 April 2013

Accepted Date: 13 May 2013

Please cite this article as: õ² dnÎ J, Vel¾jek P, Jakubec M, SÎ kora J, C¾kva V, Storch J, Exploration of 9-bromo[7]helicene reactivity, *Tetrahedron* (2013), doi: 10.1016/j.tet.2013.05.039.

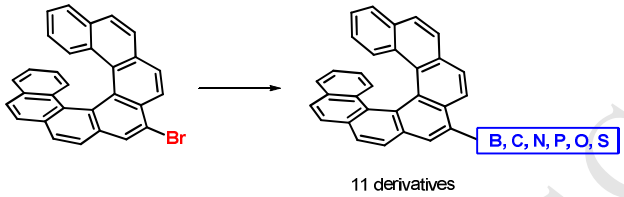
Graphical Abstract

To create your abstract, type over the instructions in the template box below.
Fonts or abstract dimensions should not be changed or altered.

Exploration of 9-bromo[7]helicene reactivity

Leave this area blank for abstract info.

Jaroslav Žádný, Petr Velíšek, Martin Jakubec, Jan Sýkora, Vladimír Církva and Jan Storch*
Institute of Chemical Process Fundamentals, v.v.i., AS CR, Rozvojová 2/135, Prague 6, 165 02



Tetrahedron
journal homepage: www.elsevier.com

Exploration of 9-bromo[7]helicene reactivity

Jaroslav Žádný[a], Petr Velíšek[a], Martin Jakubec[a], Jan Sýkora[a], Vladimír Církva[a] and Jan Storch[a,*]

[a] *Institute of Chemical Process Fundamentals, v.v.i., AS CR, Rozvojová 2/135, Prague 6, 165 02*

ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

Keywords:
Helicene
Palladium Cross-coupling
Microwave-assisted Synthesis

ABSTRACT

Exploration of 9-bromo[7]helicene reactivity mainly in Pd-catalysed reactions is reported. Palladium catalysed carbon – carbon and carbon – heteroatom coupling reactions provide a large portfolio of racemic helicenes bearing different functional groups in good to excellent yields. Many of the reactions were performed in the microwave reactor keeping reaction time to a minimum compared with conventional synthetic methods.

1. Introduction

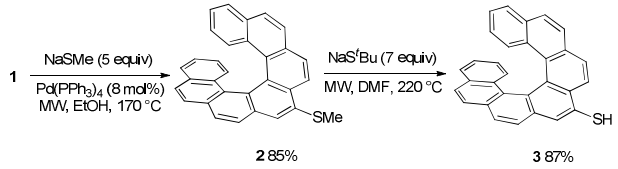
[n]Helicenes, a class of intriguing compounds with fully conjugated aromatic system and a non-planar topology, have attracted considerable attention due to their unique properties and potential applications.[1] Among them they are promising as chiral catalysts[2] and ligands[3] in asymmetric syntheses. They have been employed in various areas of chemical sciences, including supramolecular chemistry[4] and molecular recognition.[5] [7]Helicene is a particularly interesting [n]helicene with complete one full turn of the helix and high optical stability (racemization barrier is 40.5 kcal·mol^{-1}).[6] It has been shown that [7]helicene can act as a "molecular tweezer" for a silver cation,[7] computational studies for other metallic cations have been published.[8] Its deposition onto metal surfaces were also investigated.[9] In comparison to [5]- and [6]helicene, the heptaderivative has been scarcely explored maybe due to its lower synthetic availability.

In this article, we describe the synthesis and characterization of eleven novel racemic [7]helicenes with versatile functionality enabling further derivatization. Starting material 9-bromo[7]helicene **1** is commercially available and the bromine atom serves as a good starting point for introducing different functional groups. The reactivity of **1** is quite unexplored in helicene chemistry and such a similar complex study of bromine helicene derivative was performed only on their [5]helicene analogues.[10] We have focused on palladium catalyzed microwave-assisted transformations with emphasis on keeping reaction time to a minimum compared with conventional and known synthetic methods and up-to-date protocols.

2. Results and Discussion

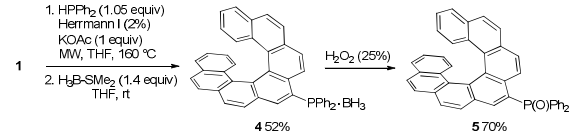
Aiming for metal surface modification by helicenes we prepared sulfur containing structures (Scheme 1). We improved a published Pd catalyzed C-S coupling reaction[10] in the sense of time consumption. Employing microwave assisted chemistry we succeed in reduction of the reaction time from 14 hours to 30 minutes. This also brings an advantage in avoiding the use of the high boiling solvents (such as DMSO) that are problematic to remove from the product. Using an excess of sodium methylthiolate in the presence of $Pd(PPh_3)_4$ in ethanol at 170 °C for 30 min provided the corresponding 9-(methylsulfanyl)[7]helicene **2** in 85% yield after recrystallization from DCM/EtOH. Moreover it was confirmed that this protocol can be used for preparation of other thioethers. Subsequent treatment of **2** with an excess of *t*-BuSNa in DMF under microwave conditions gave 9-sulfanyl[7]helicene **3** in good yield, however rapid decomposition occurred within an hour. This procedure for obtaining the desired thio-helicenes seems to be the easiest despite the fact that thiols can be synthesized directly form **1** analogously to Yi and coworkers.[11]

* Corresponding author. Tel.: +420-220-390-272; fax: +420 220 920 661; e-mail: storchj@icpf.cas.cz



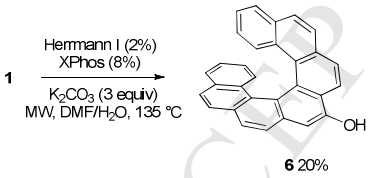
Scheme 1. Introducing of thio group

Helicenes are potentially interesting chiral frameworks for building new chiral phosphines. Thus we decided to explore synthetic routes to the novel [7]helicenyl diphenylphosphine **4**. Being inspired by the methodology of Kappe,[12] **1** was converted to diphenylphosphine on reaction with Ph_2PH, KOAc and a catalytic amount of Herrmann I catalyst (*trans*-bis(acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II))[13] in a microwave initiator (Scheme 2). After conversion into borane complex the crude reaction mixture was purified by flash chromatography on a silica gel yielding desired product **4**. Compound **4** is stable in a solid state towards oxidation under air atmosphere for days. The free phosphine can be quantitatively converted to corresponding phosphinoxide **5** by washing with 25% H_2O_2.



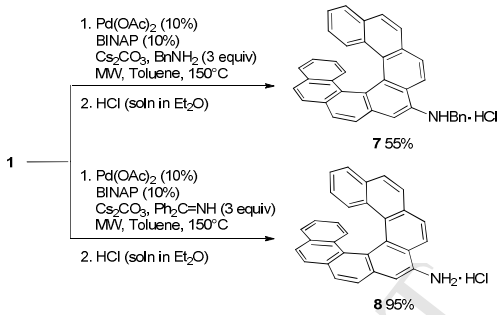
Scheme 2. Introducing of phosphine group

Another interesting functionality is a hydroxyl group. Microwave conditions were used to transfer the oxygen atom into the structure of [7]helicene again. Using a catalytic system consisting of Herrmann I,[13] XPhos and K_2CO_3 in an inert pre-bubbled DMF/H_2O (9:1) mixture led to the 9-hydroxyl[7]helicene **6** as yellow solid in 20% yield after a chromatographic separation (Scheme 3). An easier way to reach the desired hydroxyl containing compound is described below (Scheme 6). However, the product decomposes during an hour, as observed by NMR.



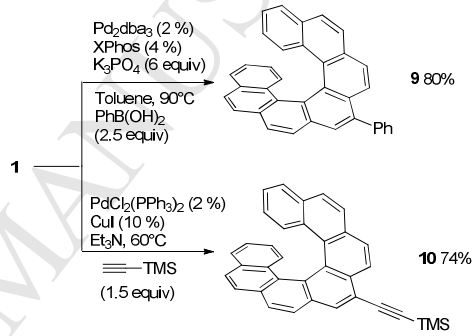
Scheme 3. Pd-catalyzed hydroxylation

Aromatic amines are important intermediates of great interest. One of the most powerful methods for preparing a variety of arylamines from aryl halides and amines catalyzed by palladium complexes was discovered by Buchwald and Hartwig.[15] We applied their chemistry to the preparation of helicene amines (Scheme 4). Accordingly, on treatment of **1** with benzylamine or benzophenone imine under the standard reaction conditions, derivatives **7** and **8** were prepared in good or high yield and isolated as hydrochlorides.



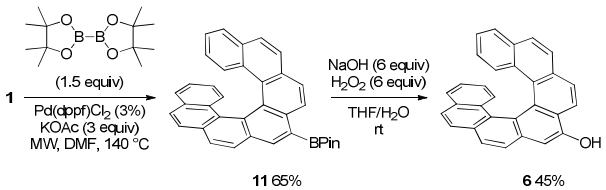
Scheme 4. Buchwald–Hartwig amination

The reactivity of **1** was also tested in relatively unexplored cross-coupling reactions (Scheme 5). We employed Sonogashira conditions with trimethylsilylacetylene in the presence of $Pd(PPh_3)_2Cl_2$, CuI, and triethylamine. This provided high yield of 9-(trimethylsilylethynyl)[7]helicene **10**. Similarly, a Pd-catalyzed Miyaura-Suzuki coupling with phenylboronic acid in the presence of Pd_2dba_3, XPhos and K_3PO_4 as a base led to 9-phenyl[7]helicene **9** in 80% yield.



Scheme 5. C-C couplings

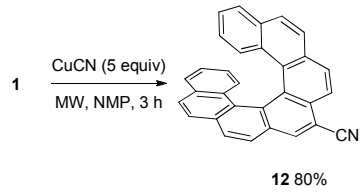
Aryl boronate esters are of great importance in organic synthesis, in particular as a substrate for their ability to form C-C bonds through Suzuki-Miyaura coupling. The cross-coupling reaction of aryl boronic acids esters with aryl halides or aryl triflates has become one of the most widely applied methods for constructing unsymmetrical biaryl systems. Miyaura reported the preparation of aryl boronates from aryl halide and bis(pinacolato)diboron (Pin_2B_2) using palladium catalysis.[14] In the course of our studies, we investigated the borylation reaction of Pin_2B_2 with **1** under the standard conditions ($Pd(dppf)Cl_2$, KOAc, DMF) and helicenyl boronate **11** was obtained in good yield (Scheme 6). Moreover, this derivative can act as a starting material for other reactions. Being inspired by Marder et al.[16] we transformed **11** into **6** giving a better yield (45%) compared with direct Pd-catalysed C-O coupling reaction.



Scheme 6. Borylation and subsequnt hydroxylation

Besides palladium catalyzed cross coupling reactions we also tried to transform **1** into the 9-cyano[7]helicene by Rosenmund-von Braun reaction with CuCN in 1-methyl-2-pyrrolidinone

under MW conditions (Scheme 7). Microwave assisted reaction again brings a significant reduction of a reaction time and **12** was obtained in an excellent yield of 80% after recrystalization from DCM/EtOH mixture.



12 80%

Scheme 7. Cu(I)-mediated cyanation

3. Conclusion

In summary, efficient protocols for microwave assisted palladium- and copper-catalyzed transformations starting from commercially available 9-bromo[7]helicene were developed leading to a novel portfolio of B, C, N, P, O, S substituted [7]helicenes potentially applicable in many fields of chemistry, physics and material science, opening promising and larger use of helicenes.

4. Experimental Section

4.1. General

^{1}H and $^{13}C\{^{1}H\}$ spectra were recorded using a 500 MHz instrument. Chemical shifts are reported in ppm (δ) relative to TMS, referenced to signal $CDCl_3$ (δ = 7.26 ppm and δ = 77.00 ppm respectively); CD_2Cl_2 (δ = 5.32 ppm and δ = 54.00 ppm respectively); CD_3OD (δ = 3.31 ppm and δ = 49.00 ppm respectively); DMSO-d_6 (δ = 2.50, 3.33 ppm and δ = 39.52 ppm respectively). Electron impact (EI) mass spectra were determined at an ionising voltage of 70 eV. TLC was performed on Silica gel 60 F254-coated aluminium sheets and compounds were visualized by UV light (254 nm). Column chromatography was performed on HPFC Biotage system with pre-packed flash silica gel columns. Microwave experiments were performed on Anton Paar Monowave 300 equipped with simultaneous temperature measurement with IR and fiberoptic sensor and Biotage Initiator Microwave Synthesizer. Commercially available reagent grade materials were used as received. THF and Et_2O were freshly distilled from sodium/benzophenone under an atmosphere of nitrogen. 9-Bromo[7]helicene was purchased from Lach-ner s.r.o., Czech Republic.

4.2. Procedure for the transformation of 1

*4.2.1. 9-(Methylsulfanyl)[7]helicene (**2**).* A 20 mL microwave vial was charged with **1** (176.6 mg, 0.386 mmol), tetrakis(triphenylphosphine)palladium (35.7 mg, 0.031 mmol, 8 mol %) and sodium thiomethylate (90%, 150.3 mg, 1.678 mmol, 5.0 eq). Absolute ethanol (15 mL) was added and the vial was capped with a PTFE septa. The inert gas was bubbled through the solution for 10 min via needle. The reactor was placed then into the microwave initiator and was reacted at 170 °C for 30 min. The solvent was evaporated at the reduced pressure and the compound was extracted by ether (30 mL). The organic layer was washed three times with water (50 mL) and brine. Aqueous phase was washed by ether and organic fractions were collected and dry over NaSO4. The sulfate was filtered off and the solvent was evaporated to dryness. The crude material was dissolved in an aliquot of DCM and EtOH was added to form a yellow precipitate. The mother liquor was filtered off and the product was washed with EtOH. Recrystallization gives 9-(methylsulfanyl)[7]helicene (2) (121.3 mg, 85 %) as a yellow powder with mp 221 – 223 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.80 (s, 3H), 6.40 (m, 2H), 6.90 (m, 2H), 7.06 (d, J=8.5, 1H), 7.10 (d, J=8.4, 1H), 7.29 (d, J=8.0, 2H), 7.46 (d, J=8.5, 1H), 7.49 (d, J=8.5, 1H), 7.69 (d, J=8.5, 1H), 7.73 (d, J=8.4, 1H), 7.88 (s, 1H), 7.91 (d, J=8.2, 1H), 7.94 (d, J=8.2, 1H), 7.98 (d, J=8.5, 1H), 8.50 (d, J=8.5, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 16.72 (q), 122.5 (d), 123.6 (d), 123.7 (d), 123.7 (s), 123.8 (d), 124.2 (d), 124.6 (d), 124.9 (d), 124.9 (d), 125.4 (d), 125.6 (d), 126.0 (d), 126.5 (d), 126.6 (d), 126.8 (s), 127.0 (d), 127.4 (d), 127.6 (d), 127.9 (d), 128.4 (s), 128.4 (s), 129.3 (s), 129.6 (s), 130.5 (s), 130.5 (s), 130.7 (s), 131.7 (s), 131.7 (s), 131.7 (s), 134.5 ppm. IR ($CHCl_3$): 3052 m, 2924 w, 2861 vw, 2831 vw, 1618 vw, 1603 w, 1595 w, 1569 w, 1553 vw, 1520 vw, 1508 w, 1497 w, 1470 w, 1457 vw, 1439 w, 1420 w, 1388 w, 1382 w, 1376 w, 1362 vw, 1339 vw, 1317 w, 1284 w, 1264 w, 1239 w, 1183 vw, 1176 vw, 1153 w, 1136 w, 1125 w, 1109 vw, 1070 vw, 1036 w, 979 w, 969 w, 960 w, 952 w, 915 w, 891 w, 867 w, 860 m, 846 w, 829 vs, 818 w, 714 w, 706 vw, 694 vw, 682 vw, 648 w, 633 m, 624 w, 610 m, 592 vw, 578 vw, 561 w, 542 vw, 537 vw, 523 m, 513 w, 489 w, 476 w, 472 w, 463 vw, 456 vw, 434 vw cm^{-1}. EI MS: 424 ($M^{+\bullet}$, 100), 409 (13), 376 (24), 350 (16), 337 (5), 187 (13), 181 (5). HR EI MS: calculated for $C_{31}H_{20}S$ 424.1286, found 424.1295.

*4,2,2. 9-Sulfanyl[7]helicene (**3**).* Method A: An oven-dried Schlenk flask was charged with **1** (193.9 mg, 0.424 mmol), sodium thiosulfate (263.0 mg, 1.060 mmol, 2.5 eq), cesium carbonate (276.3 mg, 0.848 mmol, 2.0 eq), Pd(dba)2 (4.9 mg, 8.5 µmol, 0.02 eq) and Xphos (8.1 mg, 17.0 µmol, 0.04 eq). The tube was evacuated and backfilled with argon three times before the solvent mixture (tBuOH/toluene = 4 : 6) was added. The mixture was stirred until homodisperse at rt. An aliquot (15 µL) of water was added via syringe. Then the tube was stirred at 80 °C for 24 h. The solid substance was separated from the reaction mixture and was washed with ether. Zn dust (0.5 g) and HCl (10%, 5 mL) was added to the solid substance with cooling by ice-water. After stirring for 1 h, the mixture was extracted with ethyl acetate. The organic layer was washed with H_2O and brine and dried over Na_2SO_4. Removal of solvent in vacuo provided 9-sulfanyl[7]helicene (3) (76.5 mg, 44%) with a satisfactory purity as a yellow powder.

Method B: A 20 mL microwave vial was charged with **2** (63.4 mg, 0.149 mmol) and sodium 2-methyl-2-propanethiolate (90%, 130.3 mg, 1.045 mmol, 7.0 eq). The vial was sealed with PTFE septa and evacuated and backfield with argon for three times before the anhydrous DMF (15 mL) was added. The inert gas was bubbled through the reaction mixture for 20 min in order to remove the oxygen. The mixture was heated to 220 °C for 320 min in a microwave initiator. The tube was cooled to 0 °C and HCl (3 M, 2 mL) was added at once. The crude pale yellow product was extracted between toluene and HCl. Organic layer was dried over Na_2SO_4 and filtered. After removal of solvent the crude product was collected and filtration on a short silica gel pad was performed using toluene as a solvent to give 9-sulfanyl[7]helicene (3) (53.3 mg, 87 %) with a satisfactory purity as a yellow powder with mp 177 – 180 °C. The colour change is caused by the decomposition of the compound. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.88 (s, 1H), 6.37 – 6.45 (m, 2H), 6.91 (m, 2H), 7.04 (d, J=8.5, 1H), 7.08 (d, J=8.6, 1H), 7.29 (d, J=8.0, 2H), 7.47 (d, J=8.4, 1H), 7.50 (d, J=8.5, 1H), 7.69 (d, J=8.5, 1H), 7.74 (d, J=8.5, 1H), 7.88 (d, J=8.2, 1H), 7.91 (d, J=8.2, 1H), 8.00 (d, J=8.5, 1H), 8.13 (s, 1H), 8.42 (d, J=8.4, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 123.5 (d), 123.7 (d), 123.8 (d), 124.1 (d), 124.6 (d), 124.7 (s), 125.0 (d), 125.0 (d), 125.4 (d), 125.6 (d), 125.8 (d), 126.3 (s), 126.3 (s), 126.59 (d), 126.6 (d), 127.3 (d), 127.7 (d),

127.8 (d), 128.1 (d), 128.27 (s), 128.28 (s), 129.0 (d), 129.2 (s), 129.4 (s), 130.70 (s), 130.72 (s), 131.1 (s), 131.5 (s), 131.7 (s), 131.74 (s) ppm. ESI MS: 409 ([M-H]$^-$). HR ESI MS: calculated for $C_{30}H_{17}S$ 409.10564, found 409.10569

*4.2.3. Borane 9-(diphenylphosphanyl)[7]helicene complex (**4**).* A 20 mL microwave vial was charged with **1** (176.8 mg, 0.387 mmol), KOAc (37.9 mg, 0.387 mmol, 1.0 eq), trans-di(μ-acetato)bis[ortho-(di-orthotolylphosphino)benzyl]dipalladium(II) (Herrmann I) (7.2 mg, 0.008 mmol, 2 mol%) and diphenylphosphine (95%, 74 μL, 79.6 mg, 0.406 mmol, 1.05 eq) and closed with PTFE septa in glovebox. Freshly distilled and degassed THF (15 mL) was added under inert atmosphere. The vial was placed into a microwave initiator and reacted for 50 min at 130 °C. A solution of borane dimethyl sulfide complex (2.0 M, 270 μL in THF, 0.540 mmol, 1.4 eq) was added dropwise and stirred at room temperature overnight. The crude reaction mixture was filtered via silica gel pad eluted by THF. The volatile compounds were removed at reduced pressure and the residue was purified by a flash chromatography (petrolethere – ethylacetate = 8 : 1) on a silica gel to give borane 9-(diphenylphosphanyl)[7]helicene complex (4) (115.0 mg, 52%) as a pale yellow powder with mp 212 – 216 °C. $_1$H NMR (500 MHz, $CDCl_3$): δ 6.42 (m, 2H), 6.92 (m, 2H), 7.02 (d, J = 8.5 Hz, 1H), 7.06 (d, J = 8.6 Hz, 1H), 7.29 (m, 2H), 7.57 – 7.43 (m, 7H), 7.62 – 7.58 (m, 1H), 7.64 (d, J = 8.5 Hz, 1H), 7.69 (d, J = 8.5 Hz, 1H), 7.75 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 8.3 Hz, 1H), 7.85 – 7.78 (m, 5H), 7.90 (d, J = 8.2 Hz, 1H), 8.33 (d, J = 8.5 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 123.85 (d), 123.87 (s), 124.0 (d), 124.2 (d), 124.3 (s), 124.4 (d), 125.0 (d), 125.2 (d), 125.3 (d), 125.5 (d), 125.9 (d, J = 7.7 Hz), 126.1 (s, J = 7.5 Hz), 126.6 (d), 126.7 (d), 126.8 (d), 127.2 (d), 127.3 (s, J = 2.3 Hz), 127.93 (d), 127.94 (s), 128.0 (d, J < 1.0 Hz), 128.4 (d), 128.4 (s), 128.9 (d), 129.0 (d), 129.01 (d), 129.1 (d), 129.2 (s), 129.22 (s, J = 17.7 Hz), 129.3 (s), 129.5 (s, J = 21.3 Hz), 130.1 (s, J = 11.7 Hz), 130.6 (s, J < 0.5 Hz), 131.3 (s, J = 9.8 Hz), 131.4 (d, J = 1.7 Hz), 131.4 (d, J = 1.5 Hz), 131.6 (s), 131.7 (s), 132.0 (s, J < 0.5 Hz), 133.4 (d), 133.5 (d), 133.6 (d), 133.7 (d), 136.0 (d, J = 7.8 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 22.02 (bs) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ –35.3 (bs) ppm. IR ($CHCl_3$): 3079 w, 3055 w, 2408 m, sh, 2392 m, 2351 w, 1618 w, 1603 w, 1596 w, 1573 vw, 1569 vw, 1554 vw, 1521 w, 1509 vw, 1497 w, 1485 w, 1456 w, 1438 s, 1421 vw, 1390 vw, 1384 vw, 1375 vw, 1365 w, 1353 w, 1331 vw, 1320 w, 1285 w, 1265 w, 1243 w, 1230 vw, 1189 w, 1155 w, 1137 w, 1126 w, 1106 m, 1062 m, 1036 w, 1029 w, 1000 w, 978 w, 962 vw, 952 w, 915 w, 897 w, 868 w, 848 w, 832 vs, 713 vw, 694 m, 648 w, 637 w, 621 w, 610 m, 592 w, 561 w, 546 vw, 536 w, 523 m, 516 w, 498 w, 494 w, 486 w, 472 w, 455 w, 440 w cm^{-1}. APCI MS: 563 ([M+H-BH_3]$^+$), 599 ([M+Na]$^+$). HR APCI MS: calculated for $C_{42}H_{28}P$ 563.19231, found 563.19109.

*4.2.4. (9-[7]Helicenyl)diphenylphosphine oxide (**5**).* A 5 mL microwave vial was charged with **1** (40.6 mg, 0.089 mmol), KOAc (8.7 mg, 0.089 mmol, 1.0 eq), trans-di(μ-acetato)bis[ortho-(di-ortho-tolylphosphino)benzyl]dipalladium(II) (Herrmann I) (1.6 mg, 0.002 mmol, 2 mol%) and diphenylphosphine (95%, 17 μL, 18.3 mg, 0.093 mmol, 1.05 eq) and closed with PTFE septa in glovebox. Freshly distilled and degassed THF (3 mL) was added under inert atmosphere. The vial was placed into a microwave initiator and reacted for 30 min at 160 °C. The solvent was removed at reduced pressure and the residue was dissolved in DCM (20 mL) and washed with H_2O_2 (30%, 20 mL) in a separation funnel. The organic layer was then washed with saturated $NaHCO_3$, H_2O and brine and dried over Na_2SO_4. After filtration the solvent was evaporated and the crude product was purified by flash chromatography (20 to 30 % acetone in hexane) to give (9 [7]helicenyl)diphenylphosphine oxide (5) in two steps (36.0 mg, 70%) as a yellow oil which solidified upon standing. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.42 (m, 2H), 6.91 (m, 2H), 7.01 (d, J=8.4, 1H), 7.04 (d, J=8.4, 1H), 7.29 (m, 2H), 7.46 – 7.53 (m, 4H), 7.53 – 7.60 (m, 3H), 7.64 (m, 1H), 7.66 (d, J=8.5, 1H), 7.69 (d, J=8.5, 1H), 7.78 (d, J=8.2, 1H), 7.81 – 7.88 (m, 6H), 7.90 (d, J=8.2, 1H), 8.76 (dd, J=8.5, 1.0, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 123.8 (d), 124.1 (d), 124.2 (d), 124.4 (d), 125.0 (d), 125.3 (d), 125.39 (d), 125.40 (d), 125.8 (d, J = 5.5 Hz), 126.0 (s, J = 8.7 Hz), 126.6 (d), 126.7 (d), 127.0 (d), 127.4 (s), 127.7 (s, J = 2.7 Hz), 127.9 (d), 127.96 (d), 127.97 (d), 128.3 (s, J = 1.0 Hz), 128.5 (d), 128.6 (d), 128.7 (d), 128.73 (d), 128.8 (d), 129.2 (s), 129.3 (s), 129.4 (s), 129.6 (s), 130.64 (s), 131.6 (s, J = 8.3 Hz), 131.64 (s), 131.67 (s), 132.0 (d, J = 2.8 Hz), 132.1 (d, J = 2.8 Hz), 132.12 (d), 132.14 (s), 132.2 (d), 132.3 (d), 132.4 (d), 132.6 (s), 133.4 (s), 135.4 (d, J = 11.7 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 33.65 (s) ppm. IR ($CHCl_3$): 3079 w, 3054 w, 2986 m, 2929 m, 2856 w, 1618 vw, 1602 w, 1596 w, 1592 w, 1569 vw, 1521 w, 1508 vw, 1497 w, 1484 w, 1456 vw, 1438 s, 1421 vw, 1390 w, 1376 w, 1365 w, 1355 w, 1334 vw, 1320 w, 1310 w, 1285 w, 1263 w, 1243 w, 1185 m, sh, 1171 s, 1136 w, 1119 m, 1101 m, 1086 w, sh, 1071 w, 1057 vw, 1036 w, 1028 w, 999 w, 982 w, 962 w, 953 w, 916 w, 899 w, 888 vw, 868 w, 849 w, 832 vs, 822 w, 812 vw, 713 w, 696 s, 663 w, 649 w, 636 w, 626 w, 617 vw, 611 w, 597 m, 570 m, 563 m, 551 s, 531 m, 519 s, 504 w, 472 w, 464 w, 460 w cm^{-1}. APCI MS: 579 ([M+H]$^+$). HR APCI MS: calculated for $C_{42}H_{28}OP$ 579.18723, found 579.18707.

*4.2.5. 9-Hydroxyl[7]helicene (**6**).* Method A: A 2 mL microwave vial was charged with **1** (228.7 mg, 0.500 mmol), Herrmann I (9.4 mg, 0.010 mmol, 2 mol%), XPhos (0.8 mg, 0.040 mmol, 4 mol%) and potassium carbonate (207.3 mg, 1.500 mmol, 3.0 eq). The vial was capped with PTFE septa and solvent mixtrure (DMF : H2O = 9 : 1, 5 mL) was added. The inert gas was bubbled through the reaction mixture for 10 min in order to remove the oxygen. It was reacted in a microwave initiator for 2 hours at 150 °C. HCl (2 M, 20 mL) was added and the reaction mixture was extracted into EtOAc (20 mL). The organic layer was washed with $NaHCO_3$ and water, dried over Na_2SO_4 and filtered. The solvents were removed at the reduced pressure and the crude product was purified by flash chromatography (hexane – acetone = 9 : 1) on silica gel to give 9-hydroxyl[7]helicene (6) (39.0 mg, 20%) as a yellow powder, which turned brown after decomposition.

Method B: A Schlenk flask was charged with **11** (60.3 mg, 0.120 mmol) and NaOH (28.7 mg, 0.717 mmol, 6.0 eq). The content was dissolved in THF (5 mL) and an aqueous solution of H_2O_2 (30%, 73 μL, 0.717 mmol, 6.0 eq) was added dropwise under argon. The raction was stirred for 30 min at room temperature and extracted with EtOAc (50 mL), washed with water (50 mL), brine (50 mL), dried over anhydrous $MgSO_4$ and filtered. The solvents were removed at the reduced pressure and the crude product was purified by flash chromatography (hexane – acetone = 9 : 1) on silica gel to give 9-hydroxyl[7]helicene (6) (21.1 mg, 45%) as a yellow powder, which turned brown after decomposition. ^{1}H NMR (500 MHz, CD_2Cl_2): δ 5.99 (bs, 1H), 6.39 (m, 2H), 6.90 (m, 2H), 7.12 (d, J=8.6, 1H), 7.16 (d, J=8.6, 1H), 7.31 (m, 2H), 7.37 (s, 1H), 7.46 (d, J=8.5, 1H), 7.53 (d, J=8.5, 1H), 7.73 (d, J=8.5, 1H), 7.78 (d, J=8.5, 1H), 7.86 (d, J=8.2, 1H), 7.90 (d, J=8.2, 1H), 7.99 (d, J=8.4, 1H), 8.44 (d, J=8.4, 1H) ppm. ^{13}C NMR (125 MHz, CD_2Cl_2): δ 108.0 (d), 120.6 (d), 121.4 (s), 123.9 (d), 124.1 (d), 124.7 (d), 125.0 (d), 125.3 (s), 125.4 (d), 125.5 (d), 126.3 (d), 126.34 (d), 126.4 (d), 126.7 (d), 127.08 (d), 127.10 (d), 127.6 (s), 127.65 (d), 128.1 (d), 128.5 (d) 128.7 (s), 129.1 (s), 129.8 (s), 130.12 (s), 130.14 (s),

131.6 (s), 132.3 (s), 132.4 (s), 133.1 (s), 150.8 (s) ppm. APCI MS: 393 ([M-H]$^-$). HR APCI MS: calculated for $C_{30}H_{18}O$ 393.12849, found 393.12784.

*4.2.6. 9-(Benzylamino)[7]helicene hydrochloride (**7**).* A flask was charged with **1** (250.0 mg, 0.547 mmol), Cs_2CO_3 (427.9 mg, 1.313 mmol, 2.4 eq), BINAP (34.1 mg, 0.055 mmol, 0.1 eq) and $Pd(OAc)_2$ (12.3 mg, 0.055 mmol, 10 mol%). The content was dissolved in toluene (18 mL) and benzylamine (178 µL, 1.641 mmol, 3.0 eq) was added. The flask was purged with inert gas and a condenser was connected. It was reacted under reflux for 3 hours under inert gas. The crude reaction mixture was filtered through a pad of silica gel eluting with toluene. The solvent was evaporated at the reduced pressure and the residue was dissolved in diethyl ether (10 mL). A solution of HCl (2.0 M, 0.5 mL, 1.00 mmol, 1.8 eq in ether) was added dropwise to form crystals of product. The solvent was filtered off and the crude product was washed with ether to give 9-(benzylamino)[7]helicene (7) (156.0 mg, 55%) in a satisfactory purity as a yellow powder with mp 144 °C decomp. ^{1}H NMR (500 MHz, CD_3OD): δ 4.86 (m, 4H), 6.36 (m, 2H), 6.88 (m, 2H), 6.95 (d, J=8.5, 1H), 6.98 (d, J=8.5, 1H), 7.29 (m, 2H), 7.32 – 7.41 (m, 3H), 7.46 (d, J=8.6, 1H), 7.50 – 7.57 (m, 3H), 7.72 (d, J=8.5, 1H), 7.80 (d, J=8.5, 1H), 7.88 (d, J=8.3, 1H), 7.94 (d, J=8.2, 1H), 8.09 (d, J=8.6, 1H), 8.26 (d, J=8.5, 1H) ppm. ^{13}C NMR (125 MHz, CD_3OD): δ 52.8 (t), 120.1 (d), 122.9 (s), 124.6 (d), 124.9 (d), 125.1 (d), 125.5 (d), 125.7 (s), 126.0 (d), 126.2 (d), 126.4 (d), 126.8 (d), 127.3 (d), 127.8 (d), 127.9 (d), 127.9 (d), 128.1 (s), 128.7 (d), 129.1 (d), 129.35 (d), 129.40 (d), 129.6 (s), 129.7 (s), 129.8 (d), 129.84 (d), 129.91 (d), 130.4 (s), 130.7 (s), 131.5 (s), 132.2 (s), 133.3 (s), 133.33 (s), 133.4 (s), 137.0 (s) ppm. IR ($CHCl_3$): 3053 m, 2981 m, 2888 m, br, 2713 m, 2637 m, 2584 m, 2559 m, 1740 w, 1681 vw, 1604 m, 1596 m, 1578 s, 1555 w, 1526 m, 1499 m, 1489 m, 1472 w, 1458 m, 1453 m, 1439 m, 1431 m, 1405 w, 1399 w, 1391 w, 1385 w, 1363 w, 1352 w, 1341 w, 1322 w, 1311 vw, 1289 w, 1276 w, 1270 w, 1246 m, 1198 vw, 1180 vw, 1164 w, 1158 w, 1143 vw, 1137 w, 1131 vw, 1128 vw, 1111 w, 1082 w, 1040 w, 1029 w, 1004 w, sh, 992 w, 960 w, 912 w, 892 w, 878 w, 869 w, 844 w, 831 s, 819 w, 716 w, 699 m, 645 w, 629 w, 612 w, 597 vw, 571 w, 564 w, 558 w, 521 m, 505 m, 478 w, 465 w, 410 w cm^{-1}. ESI MS: 484 ([M+H]$^+$). HR APCI MS: calculated for $C_{37}H_{26}N$ 484.20576, found 484.20598.

*4.2.7. 9-(Amino)[7]helicene hydrochloride (**8**).* A flask was charged with **1** (100.0 mg, 0.219 mmol), Cs_2CO_3 (171.0 mg, 0.525 mmol, 2.4 eq), BINAP (13.6 mg, 0.022 mmol, 0.1 eq) and $Pd(OAc)_2$ (4.9 mg, 0.022 mmol, 0.1 eq). The content was dissolved in toluene (15 mL) and benzophenone imine (119.0 mg, 110 µL, 0.657 mmol, 3.0 eq) was added. The flask was purged with inert gas and a condenser was connected. It was reacted under reflux for 5 hours under inert gas. The crude reaction mixture was filtered through a pad of silica gel eluting with toluene. The solvent was evaporated at the reduced pressure and the residue was dissolved in diethyl ether (10 mL). A solution of HCl (2.0 M, 0.2 mL, 0.4 mmol, 1.8 eq in ether) was added dropwise to form crystals of product. The solvent was filtered off and the crude product was washed with ether to give 9-amino[7]helicene (8) (90.0 mg, 95%) in satisfactory purity as a yellow powder with mp 155 °C decomp. Further purification can be achieved by crystallization from EtOH. ^{1}H NMR (500 MHz, DMSO-d_6): δ 4.15 (bs, 2H), 6.39 (m, 2H), 6.89 – 6.98 (m, 4H), 7.40 (m, 2H), 7.61 (d, J = 8.5 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.5 Hz, 1H), 8.11 – 8.21 (m, 3H), 8.23 (d, J = 8.5 Hz, 1H), 8.33 (d, J = 8.5 Hz, 1H) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ 118.7 (d), 120.7 (d), 123.0 (s), 123.2 (d), 123.6 (d), 123.7 (d), 123.8 (d), 125.2 (d), 125.3 (s), 125.33 (d), 125.5 (d), 125.7 (d), 125.73 (s), 126.5 (d), 126.9 (d), 126.92 (d), 127.3 (s), 127.4 (s), 127.44 (d), 128.0 (d), 128.1 (d), 128.4 (s), 128.5 (s), 128.7 (d), 130.5 (s), 130.6 (s), 130.7 (s), 131.4 (s), 131.5 (s) ppm. IR ($CHCl_3$): 3390 w, 3053 s, 3170 w, br, sh, 2854 s, br, 2595 m, br, 2005 vw, br, 1627 w, 1601 w, 1596 w, 1578 w, 1555 vw, 1527 m, 1518 s, 1500 m, 1477 w, 1469 w, 1439 vw, 1430 w, 1422 vw, 1411 vw, 1399 w, 1378 w, 1363 w, 1322 w, 1290 w, 1271 w, 1248 w, 1238 w, 1186 vw, 1178 vw, 1158 w, 1145 w, 1137 w, 1104 vw, 1090 vw, 1080 vw, 1054 m, 1037 m, 1029 m, 1011 w, 977 vw, 960 w, 915 vw, 891 w, 877 w, 853 vw, 830 s, 819 w, 715 w, 704 vw, 695 vw, 687 vw, 648 w, 639 vw, 631 m, 611 w, 605 w, 576 w, 564 vw, 553 vw, 544 vw, 527 w, 521 m, 509 vw, 491 w, 478 w, 463 w, 446 vw, 436 vw cm^{-1}. ESI MS: 394 ([M+H]$^+$). HR ESI MS: calculated for $C_{30}H_{20}N$ 394.15903, found 394.15906.

*4.2.8. 9-Phenyl[7]helicene (**9**).* A Schlenk flask was charged with **1** (150.0 mg, 0.328 mmol), $Pd(dba)_2$ (6.8 mg, 6.6 µmol, 2 mol%), Xphos (6.3 mg, 13.0 µmol, 4 mol%), $PhB(OH)_2$ (120 mg, 0.948 mmol, 3.0 eq) and K_3PO_4 (418 mg, 1.968 mmol, 6.0 eq). The mixture was heated at 90°C for 5 h in toluene (10 mL) and then cooled to room temperature. Crude reaction mixture was filtered through a short pad of silica gel eluting with toluene. The solvents were removed at the reduced pressure and the crude product was purified by crystallization from DCM/EtOH mixture yielding desired product (120.0 mg, 80%) as a yellow powder with mp 219 – 222 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.44 (m, 2H), 6.93 (m, 2H), 7.18 (m, 2H), 7.32 (m, 2H), 7.51 (d, J = 9.0 Hz, 2H), 7.53 – 7.56 (m, 1H), 7.60 (t, J = 7.5, 2H), 7.70 – 7.75 (m, 4H), 7.86 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.98 (s, 1H), 8.01 (d, J = 8.2 Hz, 1H), 8.05 (d, J = 8.5 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 123.6 (d), 123.7 (d), 124.3 (d), 124.5 (d), 124.8 (d), 124.9 (d), 124.94 (d), 125.4 (d), 125.7 (d), 125.8 (s), 126.57 (d), 126.58 (d), 126.8 (d), 127.1 (d), 127.2 (d), 127.45 (d), 127.47 (d), 127.48 (d), 127.8 (d), 128.2 (s), 128.3 (s), 128.4 (d), 129.4 (s), 129.6 (s), 130.4 (s), 130.5 (s), 130.53 (d), 130.8 (s), 131.2 (s), 131.7 (s), 131.71 (s), 138.6 (s), 140.6 (s) ppm. IR ($CHCl_3$): 3084 w, sh, 3052 s, 3034 w, sh, 1620 w, 1600 m, 1574 vw, 1554 vw, 1524 vw, 1497 m, 1473 m, 1459 w, 1442 w, 1423 w, 1389 m, 1364 vw, 1342 vw, 1321 w, 1291 vw, 1278 vw, 1265 vw, 1250 vw, 1238 m, 1192 vw, 1179 vw, 1163 w, 1149 w, 1136 w, 1113 vw, 1073 w, 1030 w, 1000 vw, 968 w, 961 w, 953 w, 949 w, 918 vw, 911 vw, 891 m, 884 m, 868 w, 833 vs, 822 w, 716 m, 707 m, 701 m, 690 vw, 679 vw, 652 m, 643 m, 623 vw, 617 m, 611 s, 595 w, 578 w, 566 w, 533 vw, 523 s, 512 w, 502 w, 496 vw, 472 w, 434 vw, 420 vw cm^{-1}. APCI MS: 455 ([M+H]$^+$). HR APCI MS: calculated for $C_{36}H_{23}$ 455.17943, found 455.17871.

*4.2.9. 9-Trimethylsilylethynyl[7]helicene (**10**).* To a solution of **1** (150.0 mg, 0.328 mmol), $Pd(PPh_3)_2Cl_2$ (46.0 mg, 66 µmol, 0.2 eq) and CuI (6.9 mg, 36 µmol, 0.11 eq) in triethylamine (10 mL) was added trimethylsilylacetylene (64.4 mg, 93 µL, 0.656 mmol, 2.0 eq). The mixture was heated at 60°C for 15 h and then cooled to room temperature. Crude reaction mixture was evaporated to dryness, extracted with DCM and filtered through a short pad of silica gel eluting with DCM. The solvents were removed at reduced pressure and the crude product was purified by crystallization from DCM/MeCN yielding the desired product (115.0 mg, 74%) as a yellow powder with mp 207 – 210 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.42 (s, 9H), 6.40 (m, 2H), 6.91 (m, 2H), 7.05 (d, J = 8.4 Hz, 1H), 7.08 (d, J = 8.5 Hz, 1H), 7.29 (d, J = 7.9 Hz, 2H), 7.49 (d, J = 8.3 Hz, 1H), 7.50 (d, J = 8.2 Hz, 1H), 7.70 (d, J = 8.5 Hz, 1H), 7.74 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.94 (d, J = 8.2 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 8.28 (s, 1H), 8.56 (d, J = 8.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 0.2 (q), 99.9 (s), 103.3 (s), 119.2 (s), 123.7 (d), 123.8 (d), 124.1 (d), 124.4 (d), 124.7 (d), 125.0 (d), 125.1 (d), 125.4 (s), 125.5 (s),

125.55 (d), 125.6 (d), 126.4 (d), 126.58 (d), 126.60 (d), 127.6 (d), 127.7 (d), 127.9 (d), 127.93 (d), 128.17 (s), 128.2 (s), 129.3 (s), 129.4 (s), 130.9 (s), 131.0 (s), 131.4 (s), 131.5 (s), 131.67 (d), 131.7 (s), 131.71 (s) ppm. IR ($CHCl_3$): 3053 m, 2962 m, 2929 w, 2900 w, 2855 vw, 2795 vw, 2147 m, 1620 vw, 1603 w, 1573 vw, 1554 vw, 1520 vw, 1507 vw, 1497 w, 1484 vw, 1474 vw, 1457 vw, 1439 w, 1423 w, 1409 vw, 1388 w, 1380 vw, 1363 vw, 1358 vw, 1341 vw, 1322 w, 1288 w, 1269 m, 1262 m, 1251 s, 1243 m, 1196 vw, 1191 vw, 1177 vw, 1159 w, 1154 w, 1143 vw, 1134 vw, 1120 vw, 1090 w, 1079 w, 1043 m, 1037 w, 1024 m, 978 vw, 961 vw, 949 vw, 938 m, 893 m, 877 s, 852 vs, 847 vs, 837 vs, 832 vs, 820 m, 718 m, 699 w, 689 w, 663 vw, 651 m, 643 m, 629 w, 617 vw, 609 m, 599 vw, 578 vw, 564 vw, 542 w, 533 vw, 522 m, 505 m, 492 w, 470 w, 456 vw, 447 vw, 440 vw, 427 vw, 418 vw, 414 vw cm^{-1}. EI MS: 474 ($M^{+\bullet}$, 100%), 459, 447, 433, 413, 400, 229, 216, 200, 187, 73. HR EI MS: calculated for $C_{35}H_{26}Si$ 474.1804, found 474.1809.

*4.2.10. 9-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-[7]helicene (**11**).* A 20 mL microwave vial was charged with **1** (310.4 mg, 0.679 mmol), bis(pinacolato)diboron (258.5 mg, 1.018 mmol, 1.5 eq), KOAc (199.8 mg, 2.036 mmol, 3.0 eq) and Pd(dppf)Cl_2 (14.9 mg, 0.020 mmol, 3 mol%). The vial was capped with PTFE septa and DMF (15 mL) was added. The inert gas was bubbled through the reaction mixture for 10 min in order to remove the oxygen. It was reacted in a microwave initiator for 45 min at 140 °C. After the reaction the solvent was evaporated at the reduced pressure and the residue was purified by a flash chromatography on a silica gel (2 to 7 % acetone in hexane) to give 9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)[7]helicene (11) (221.8 mg, 65%) as a yellow powder with mp 288 – 293 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.27 (s, 6H), 1.53 (s, 6H), 6.39 (m, 2H), 6.89 (m, 2H), 7.04 (d, J=8.5, 1H), 7.06 (d, J=8.6, 1H), 7.28 (m, 2H), 7.47 (d, J=8.4, 1H), 7.48 (d, J=8.3, 1H), 7.71 (d, J=8.6, 1H), 7.73 (d, J=8.6, 1H), 7.91 (d, J=8.1, 1H), 7.96 (d, J=8.5, 1H), 8.05 (d, J=8.2, 1H), 8.65 (s, 1H), 8.97 (d, J=8.5, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.0 (q), 25.0 (q), 25.05 (q), 25.07 (q), 83.5 (s), 84.0 (s), 123.5 (d), 123.7 (d), 124.3 (d), 124.5 (d), 124.6 (d), 124.8 (s), 124.9 (d), 125.5 (d), 125.6 (d), 126.47 (d), 126.5 (d), 127.0 (d), 127.03 (d), 127.06 (s), 127.09 (d), 127.35 (d), 127.37 (d), 127.7 (d), 128.1 (s), 128.2 (s), 129.3 (s), 129.5 (s), 130.4 (s), 130.7 (s), 131.5 (s), 131.54 (s), 131.6 (s), 134.8 (s), 137.17 (s), 137.2 (d) ppm. ^{11}B NMR (160 MHz, $CDCl_3$): δ 30.6 (bs) ppm. IR ($CHCl_3$): 3051 m, 3002 m, 2983 s, 2931 m, 2869 w, 2857 w, 1618 vw, 1599 w, 1572 w, 1554 vw, 1523 w, 1509 vw, 1496 w, 1478 m, 1470 w, 1458 w, 1440 m, 1428 w, 1403 m, 1392 m, 1381 s, 1373 s, 1350 m, 1316 s, 1298 s, sh, 1285 s, 1260 m, 1241 w, 1172 m, 1143 s, 1124 vs, 1108 m, 1083 vw, 1070 w, 1036 w, 1006 vw, 986 m, 960 m, 949 w, 920 vw, 908 w, 889 vw, 867 w, 847 s, 839 m, 833 m, 824 w, 815 vw, 715 vw, 705 vw, 693 vw, 683 vw, 647 w, 627 w, 618 m, 612 w, 588 vw, 579 w, 563 vw, 553 w, 522 m, 501 vw, 490 vw, 473 w, 417 vw cm^{-1}. APCI MS: 505 ($[M+H]^+$). HR APCI MS: calculated for $C_{36}H_{30}O_2B$ 505.23334, found 505.23356.

*4.2.11. 9-Cyano[7]helicene (**12**).* A 20 mL microwave vial was charged with 1 (152.3 mg, 0.333 mmol) and CuCN (149.1 mg, 1.665 mmol, 5.0 eq). The vial was capped with PTFE septa and NMP (12 mL) was added. The inert gas was bubbled through the reaction mixture for 10 min in order to remove the oxygen. It was reacted in a microwave initiator for 3 hours at 210 °C. After the reaction an aqueous solution of NH_4OH (25%, 50 mL) was added and the product was extracted with EtOAc, dried over $MgSO_4$, filtered and the solvent was evaporated at the reduced pressure. A recrystallization from DCM/EtOH mixture gives 9-cyano[7]helicene (12) (104.5 mg, 80%) as a yellow powder with mp 286 – 292 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.43 (m, 2H), 6.94 (m, 2H), 7.00 (d, J=8.4, 2H), 7.32 (d, J=8.0, 2H), 7.55 (d, J=8.4, 1H), 7.56 (d, J=8.4, 1H), 7.73 (d, J=8.6, 1H), 7.75 (d, J=8.6, 1H), 7.98 (m, 2H), 8.08 (d, J=8.4, 1H), 8.39 (d, J=8.4, 1H), 8.47 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 108.5 (s), 118.2 (s), 123.3 (d), 123.8 (d), 124.0 (d), 124.03 (d), 124.2 (d), 125.4 (d), 125.42 (d), 125.44 (d), 125.5 (d), 126.3 (d), 126.8 (d), 126.82 (d), 127.5 (s), 127.9 (s), 128.1 (s), 128.4 (d), 128.7 (d), 129.0 (s), 129.02 (d), 129.1 (s), 129.3 (d), 129.7 (s), 123.0 (s), 131.3 (s), 131.8 (s), 131.83 (s), 132.5 (s), 133.8 (s), 133.82 (d) ppm. IR ($CHCl_3$): 3053 m, 2224 m, 1620 w, 1603 w, 1598 w, 1573 w, 1553 vw, 1523 w, 1512 vw, 1498 w, 1471 vw, 1461 vw, 1440 w, 1423 w, 1391 w, 1380 w, 1362 m, 1341 w, 1322 w, 1289 w, 1268 w, 1243 w, 1192 w, 1181 w, 1156 w, 1144 vw, 1138 w, 1036 w, 962 w, 954 w, 895 m, 887 w, 868 w, 833 vs, 820 w, 815 w, 718 w, 707 vw, 651 w, 642 m, 633 w, 617 vw, 609 m, 580 vw, 564 w, 554 w, 528 w, 521 m, 509 m, 498 w, 481 vw, 473 w, 465 vw, 454 w, 440 vw, 423 vw, 414 w, 408 vw cm^{-1}. EI MS: 403 (M+•, 100), 388 (18), 376 (34), 362 (18), 349 (6), 325 (13), 228 (24), 211 (15), 185 (17), 149 (10), 129 (8), 111 (11), 102 (17), 83 (18), 71 (23), 57 (33), 43 (37). HR EI MS: calculated for $C_{31}H_{17}N$ 403.1361, found 403.1360.

Acknowledgment

We appreciate the financial support from the Grant Agency of the Czech Republic (Grant No. P207/10/1124), the Technology Agency of the Czech Republic (Grant No. TA01010646) and Ministry of Industry and Trade of the Czech Republic (Grant No. FR-TI3/628).

References and notes

1. (a) Gingras, M. *Chem. Soc. Rev.* **2013**, *42*, 968. (b) Gingras, M.; Félix, G.; Peresutti, R. *Chem. Soc. Rev.* **2013**, *42*, 1007. (c) Gingras, M. *Chem. Soc. Rev.* **2013**, 42, 1051. (d) Shen, Y.; Chen, Ch. F. *Chem Rev.* **2012**, 112, 1463. (e) Stara, I. G.; Stary, I. *Science of Synthesis* **2010**, **45b**, 885. (f) Starý, I.; Stará, I. G. Helicenes in *Strained Hydrocarbons* (Ed.: H. Dodziuk), Wiley-VCH Weinheim, **2009**, ch. 4, 166–176.
2. (a) Chen, J.; Takenaka, N. *Chem. Eur. J.* **2009**, *15*, 7268. (b) Sato, I.; Yamashima, R.; Kadowaki, K.; Yamamoto, J.; Shibata, T.; Soai, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 1096.
3. (a) Álvarez, C. M.; Barbero, H.; García-Escudero, L. A.; Martín-Alvarez, J. M.; Martínez-Pérez, C.; Miguel D. *Inorg. Chem.* **2012**, *51*, 8103. (b) El Abed, R.; Aloui, F.; Genet, J. P.; Ben Hassine, B.; Marinetti, A. *J. Organomet. Chem.* **2007**, *692*, 1156. (c) Reetz, M. T.; Beuttenmüller, E. W.; Goddard, R. *Tetrahedron Lett.* **1997**, *38*, 3211.
4. (a) Nakano, K.; Oyama, H.; Nishimura, Y.; Nakasako, S.; Nozaki, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 695. (b) Stoehr, M.; Boz, S.; Schaer, M.; Manh-Thuong, N.; Pignedoli, C. A.; Passerone, D.; Schweizer, W. B.; Thilgen, C.; Jung, T. A.; Diederich, F. *Angew. Chem. Int. Ed.* **2011**, *50*, 9982. (c) Rybáček, J.; Huerta-Angeles, G.; Kollárovič, A.; Stará, I. G.; Starý, I.; Rahe, P.; Nimmrich, M.; Kühnle, A. *Eur. J. Org. Chem.* **2011**, *5*, 853. (d) Kaseyama, T.; Furumi, S.; Zhang, X.; Tanaka, K.; Takeuchi, M. *Angew. Chem. Int. Ed.* **2011**, *50*, 3684. (e) Lovinger, A. J.; Nuckolls, C.; Katz, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 264. (f) Yamamoto, K.; Ikeda, T.; Kitsuki, T.; Okamoto, Y.; Chikamatsu, H.; Nakazaki, M. *J. Chem. Soc., Perkin Trans. 1* **1990**, 271. (g) Fox, J. M.; Katz, T. J.; Van Elshocht, S.; Verbiest, T.; Kauranen, M.; Persoons, A.; Thongpanchang, T.; Krauss, T.; Brus, L. *J. Am. Chem. Soc.* **1999**, *121*, 3453.
5. (a) Wang, D. Z. G.; Katz, T. J. *J. Org. Chem.* **2005**, *70*, 8497. (b) Xu, Y.; Zhang, Y. X.; Sugiyama, H.; Umano, T.; Osuga, H.; Tanaka, K. *J. Am. Chem. Soc.* **2004**, *126*, 6566. (c) Zhigang; D.; Katz, T. J.; Golen, J.; Rheingold, A. L. *J. Org. Chem.* **2004**, *69*, 7769. (d) Reetz, M. T.; Sostmann, S. *Tetrahedron* **2001**, *57*, 2515. (e) Murguly, E.; McDonald, R.; Branda, N. R. *Org. Lett.* **2000**, *2*, 3169. (f) Weix, D. J.; Drether, S. D.; Katz, T. J. *J. Am. Chem. Soc.* **2000**, *122*, 10027.
6. Martin, R. H.; Marchant M. J. Tetrahedron **1974**, *30*, 347.
7. Fuchter, M. J.; Schaefer J.; Judge, D. K.; Wardzinski, B.; Weimar, M.; Krossing I. *Dalton Trans.*, **2012**, *41*, 8238.

8. (a) Saini, S.; Deb, B. M. *Ind. J. Chem.*, **2007**, *46A*, 9. (b) Johansson, M. P.; Patzschke, M. *Chem. Eur. J.*, **2009**, *15*, 13210.
9. (a) Fasel, F.; Parschau, M.; Ernst, K. H. *Nature* **2006**, *439*, 449. (b) Ernst, K. H.; Kuster, Y.; Fasel, R.; Müller, M.; Ellerbeck, U. *Chirality* **2001**, *13*, 675. (c) Fasel, R.; Cossy, A. Ernst, K. H., Baumberger, F.; Greber, T.; Osterwalder, J. *J. Chem. Phys.* **2001**, *115*, 1020. (d) Ernst, K. H., Neuber, M.; Grunze, M.; Ellerbeck, U. *J. Am. Chem. Soc.* **2001**, *123*, 493. (e) Ernst, K. H., Böhringer, M.; McFadden, C. F.; Hug, P.; Müller, U.; Ellerbeck, U. *Nanotechnology* **1999**, *10*, 355. (f) Katz, T. J.; Sudhakar, A.; Teasley, M. F.; Gilbert, A. M.; Geiger, W. E.; Robben, M. P.;Wuensch, M.; Ward, M. D. *J. Am. Chem. Soc.* **1993**, *115*, 3182. (g) Gilbert, A. M.; Katz, T. J.; Geiger, W. E.; Robben, M. P.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 3199. (h) Sudhakar, A.; Katz, T. J.; Yang, B. W. *J. Am. Chem. Soc.* **1986**, *108*, 2790.
10. (a) Goretta, S.; Tasciotti, C.; Mathieu, S.; Smet, M.; Maes, W.; Chabre, Y.M.; Dehaen, W.; Giasson, R.; Raimundo, J.-M.; Henry, C.R.; Barth, C.; Gingras, M. *Org. Lett.* **2009**, *11*, 3846. (b) Gingras, M.; Collet, Ch. *Synlett* **2005**, *15*, 2337.
11. Yi, J.; Fu, Y.; Xiao, B.; Cui, W.-C.; Guo, Q.-X. *Tetrahedron Lett.* **2011**, *52*, 205.
12. Stadler, A.; Kappe, C.O. *Org. Lett.* **2002**, *4*, 3541.
13. Böhm, V.P.W.; Herrmann, W.A. *Chem. Eur. J.* **2001**, *7*, 4191.
14. Ishiyama, T.; Murata, M.; Miyaura, N. *J. Org. Chem.* **1995**, *60*, 7508.
15. For recent reviews, see: (a) Hartwig, J. F. *Acc. Chem. Res.*, **2008**, *41*, 1534. (b) Surry, D. S.; Buchwald, S. L. *Angew. Chem. Int. Ed.*, **2008**, *47*, 6338. (c) Martin, R.; Buchwald, S. L. *Acc. Chem. Res.*, **2008**, *41*, 1461.
16. Crawford, A. G.; Liu, Z.; Mkhalid, I. A. I.; Thibault, M.-H.; Schwarz, N.; Alcaraz, G.; Steffen, A.; Collings, J. C.; Batsanov, A. S.; Howard, J. A. K.; Marder T. B. *Chem. Eur. J.* **2012**, *18*, 5022.

Supplementary Material

Supplementary data, NMR spectra of all compounds are available in the online version, at

Exploration of 9-bromo[7]helicene reactivity

Jaroslav Žádný, Petr Velíšek, Martin Jakubec, Jan Sýkora, Vladimír Církva

and Jan Storch*

Institute of Chemical Process Fundamentals, v.v.i., AS CR, Rozvojová 2/135, Prague 6, 165 02

storchj@icpf.cas.cz

Supplementary Information

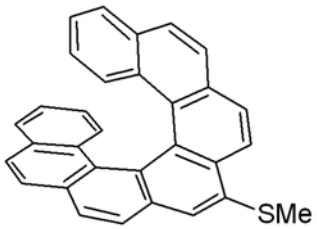
Index

General Considerations

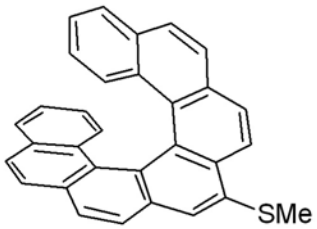
^{1}H and $^{13}C\{^{1}H\}$ spectra were recorded using a 500 MHz instrument. Chemical shifts are reported in ppm (δ) relative to TMS, referenced to signal $CDCl_3$ (δ = 7.26 ppm and δ = 77.00 ppm respectively); CD_2Cl_2 (δ = 5.32 ppm and δ = 54.00 ppm respectively); CD_3OD (δ = 3.31 ppm and δ = 49.00 ppm respectively); DMSO-d_6 (δ = 2.50, 3.33 ppm and δ = 39.52 ppm respectively). Electron impact (EI) mass spectra were determined at an ionising voltage of 70 eV. TLC was performed on Silica gel 60 F254-coated aluminium sheets and compounds were visualized by UV light (254 nm). Column chromatography was performed on HPFC Biotage system with pre-packed flash silica gel columns. Microwave experiments were performed on Anton Paar Monowave 300 equipped with simultaneous temperature measurement with IR and fiberoptic sensor and Biotage Initiator Microwave Synthesizer. Commercially available reagent grade materials were used as received. THF and Et_2O were freshly distilled from sodium/benzophenone under an atmosphere of nitrogen. 9-Bromo[7]helicene was purchased from Lach-ner s.r.o., Czech Republic.

Spectroscopic Data

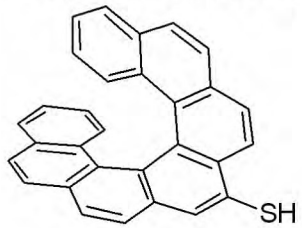
^{1}H NMR (500 MHz, $CDCl_3$)

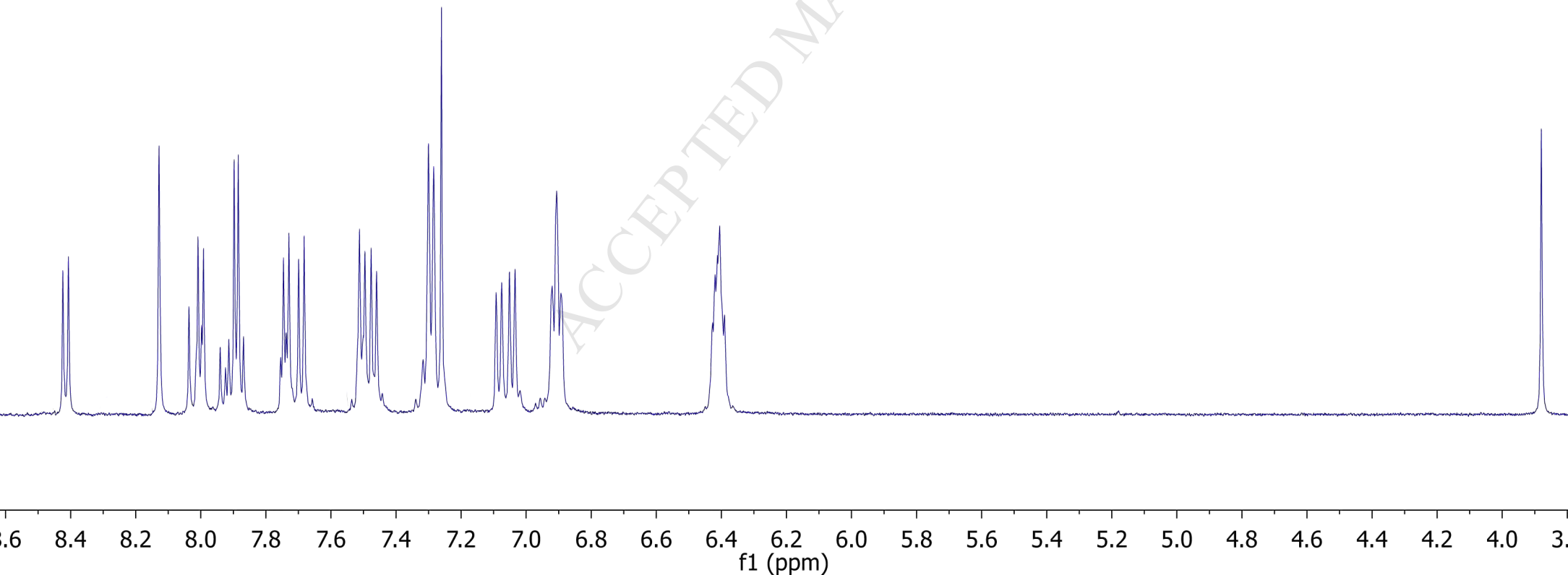


^{13}C NMR (125 MHz, $CDCl_3$)

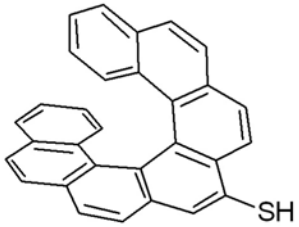


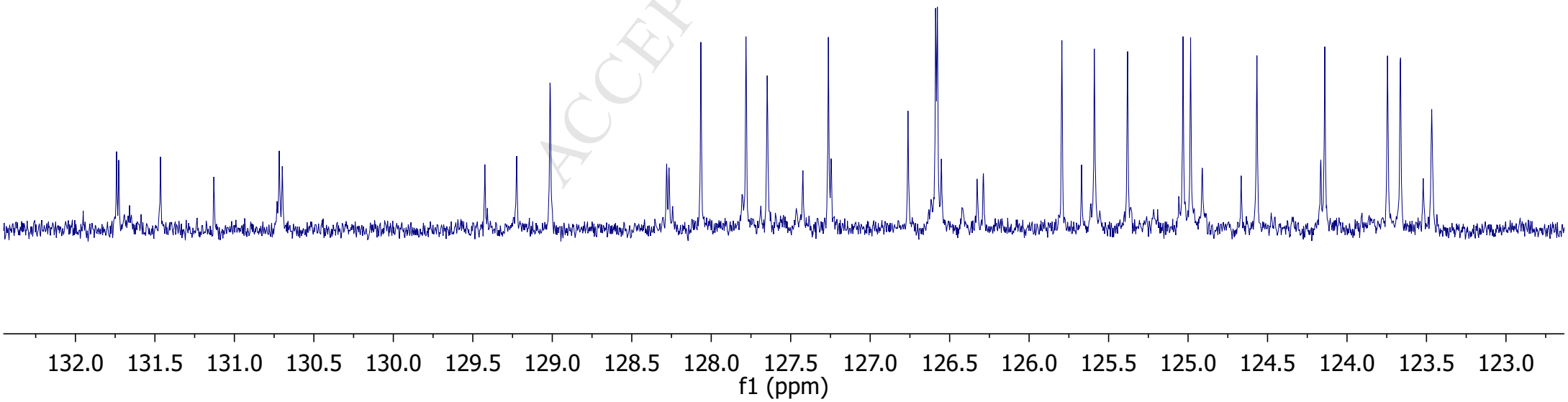
^{1}H NMR (500 MHz, $CDCl_3$)



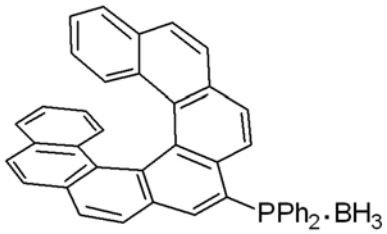


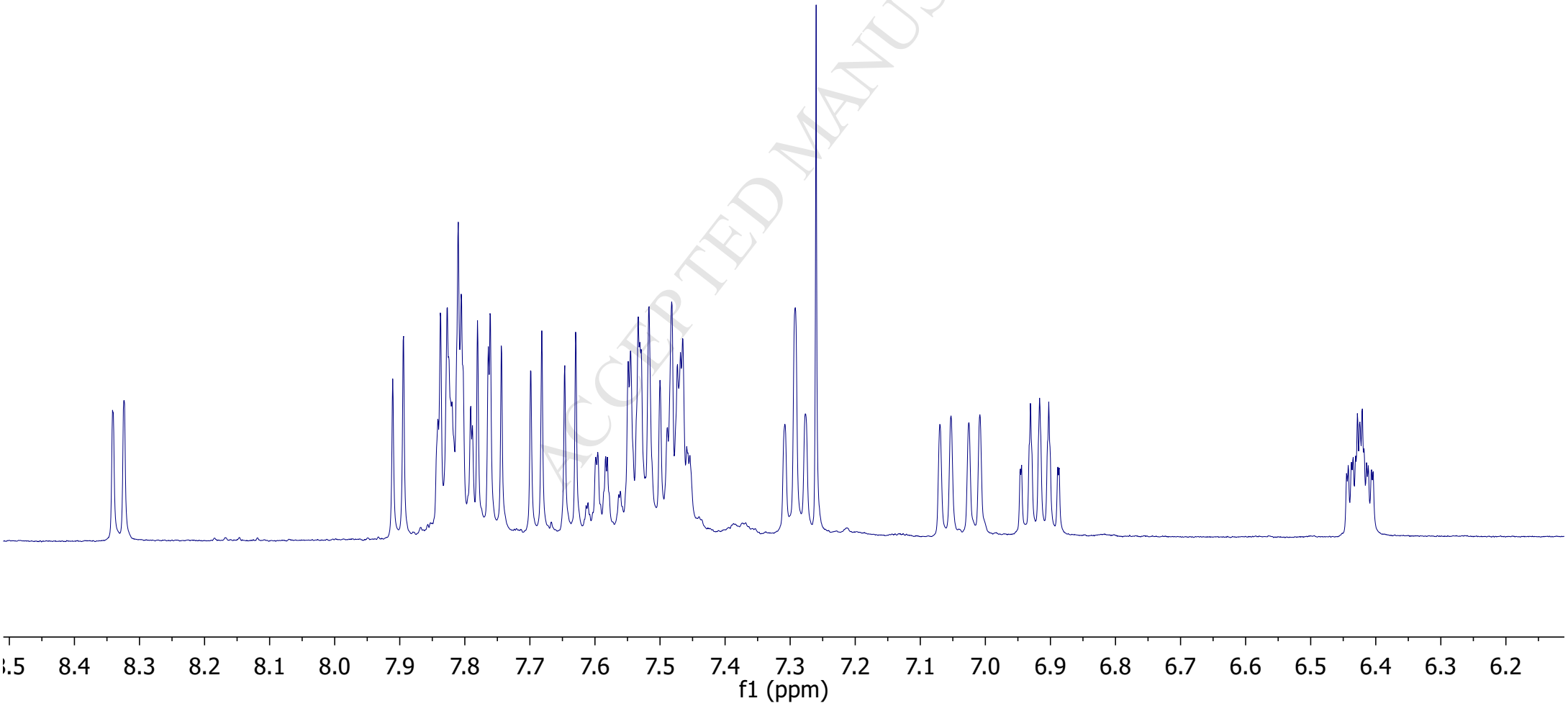
^{13}C NMR (125 MHz, $CDCl_3$)



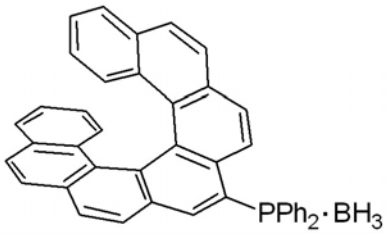


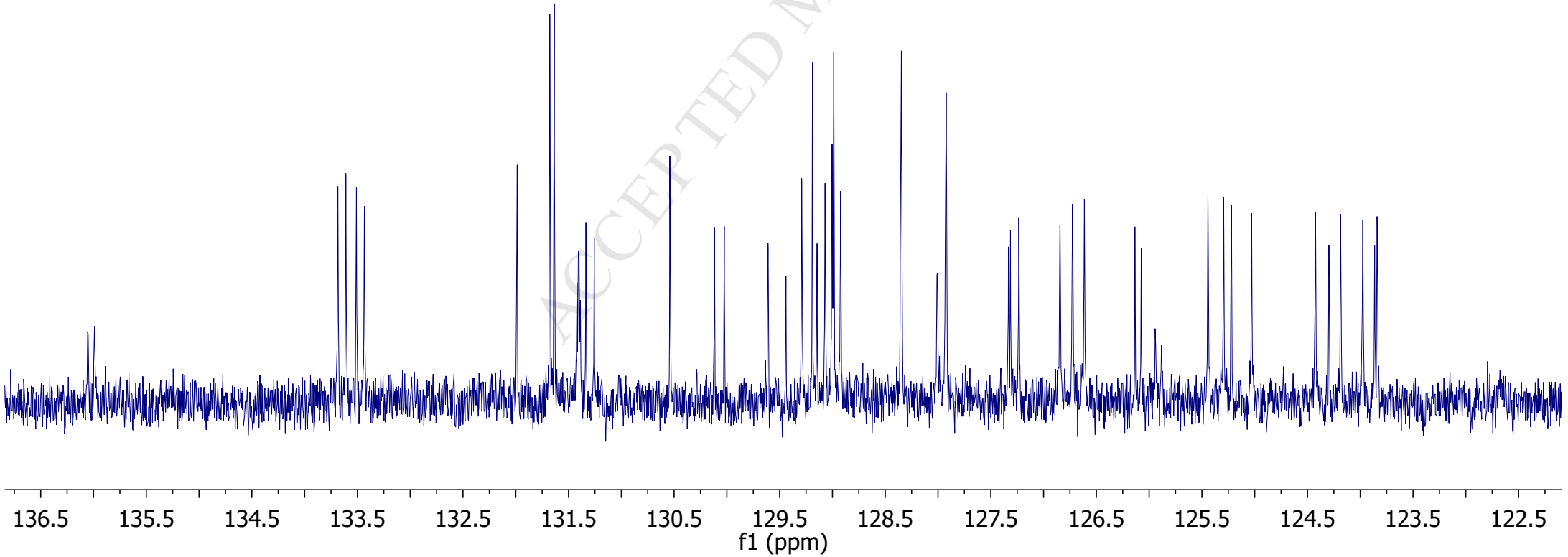
^{1}H NMR (500 MHz, $CDCl_3$)



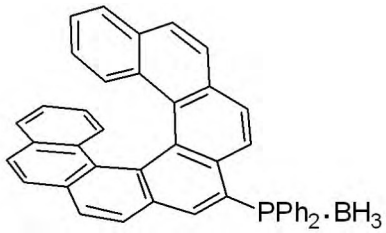


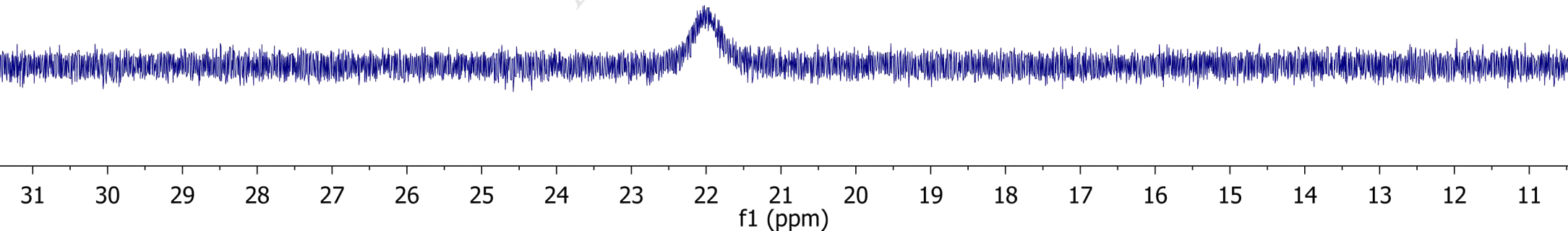
^{13}C NMR (125 MHz, $CDCl_3$)



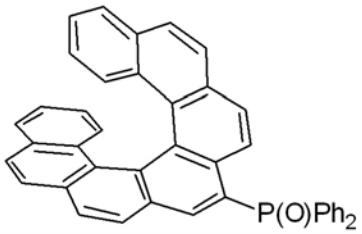


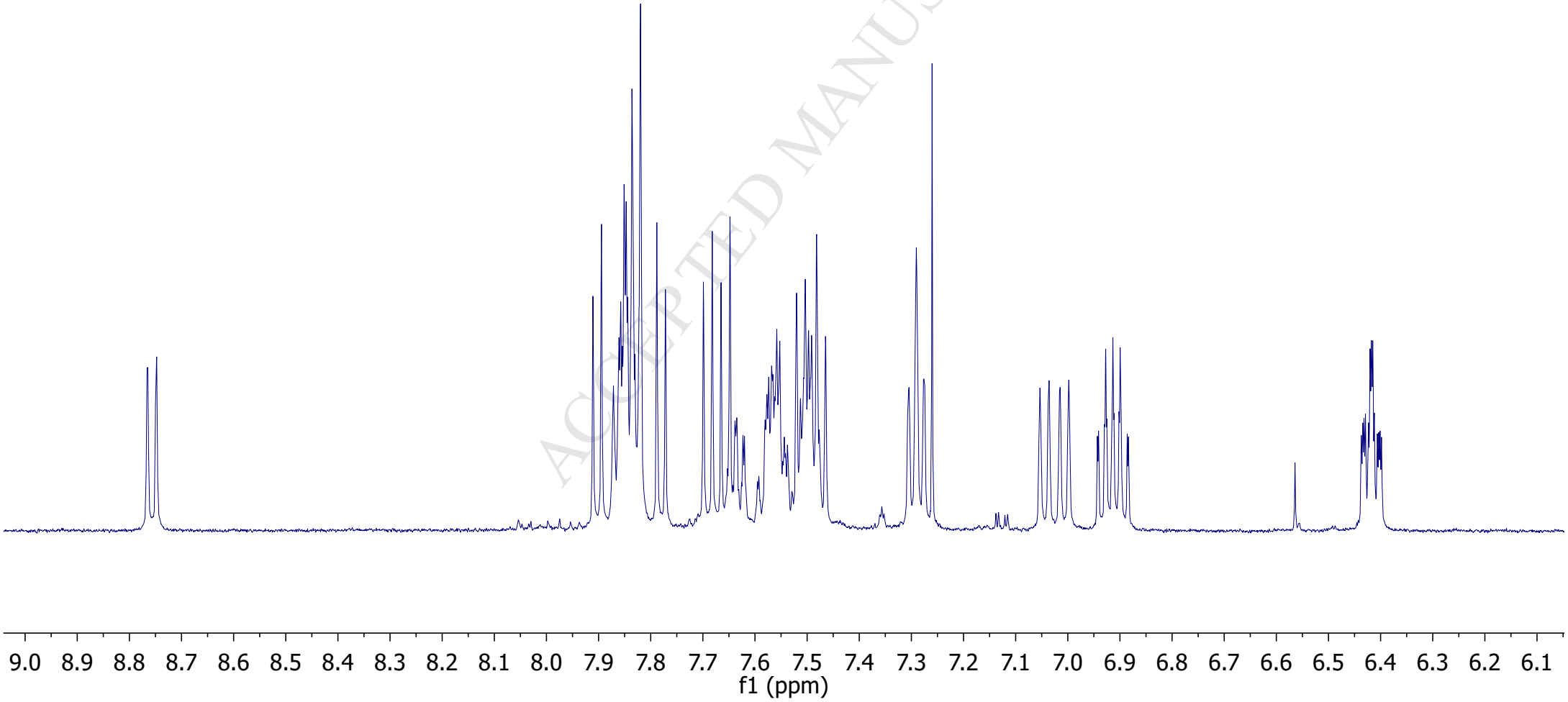
31P NMR (202 MHz, CDCl3)



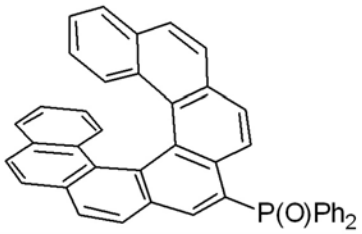


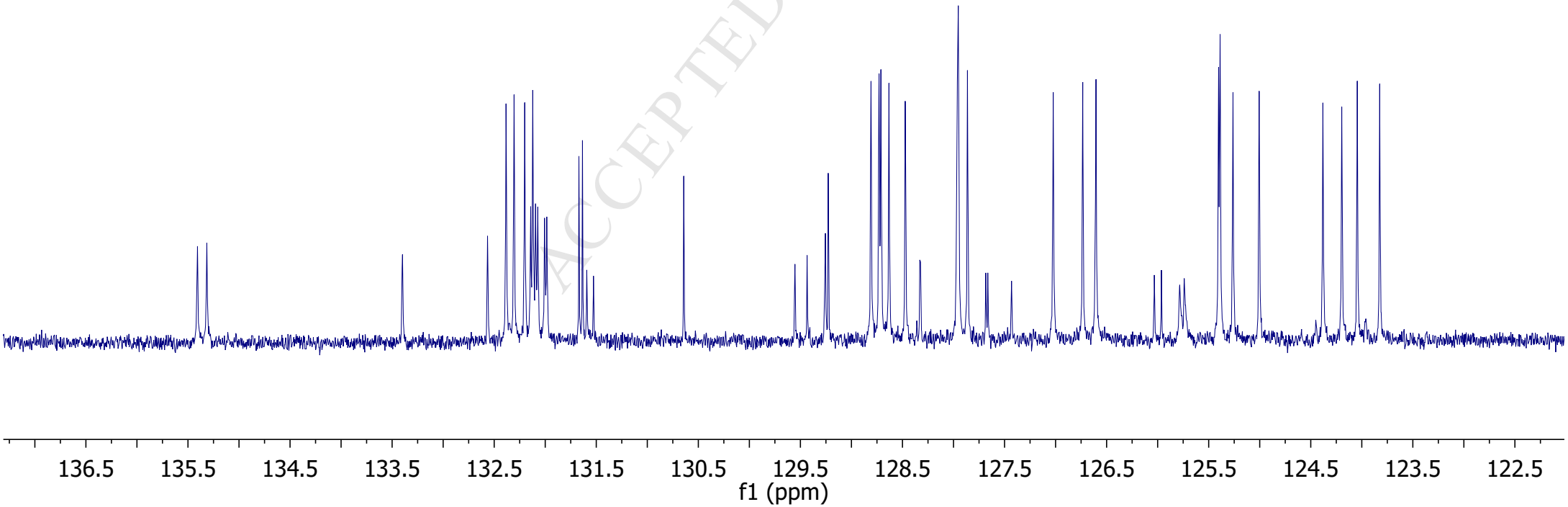
^{1}H NMR (500 MHz, $CDCl_3$)



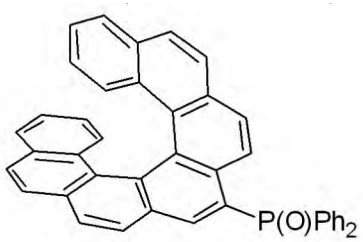


^{13}C NMR (125 MHz, $CDCl_3$)

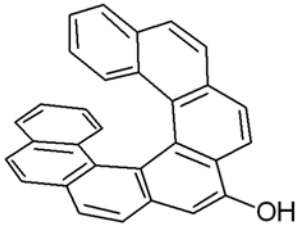


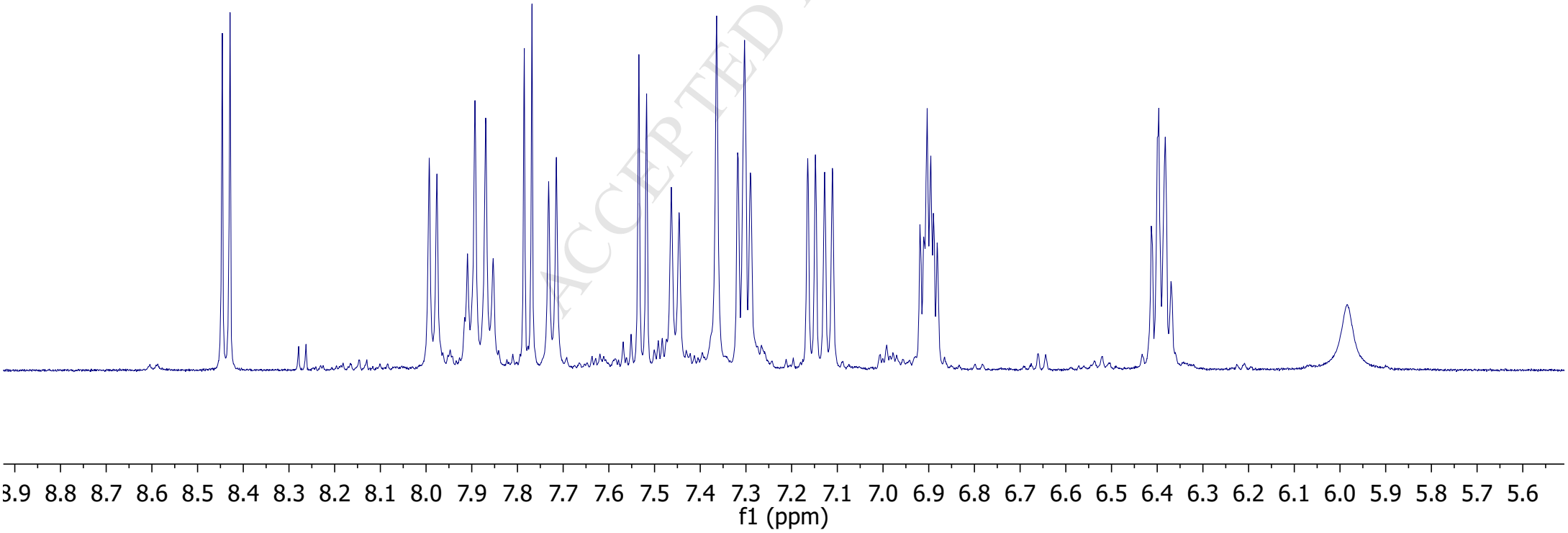


31P NMR (202 MHz, CDCl3)

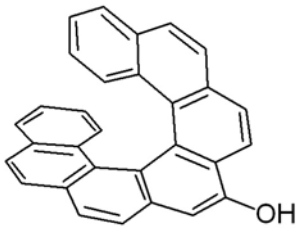


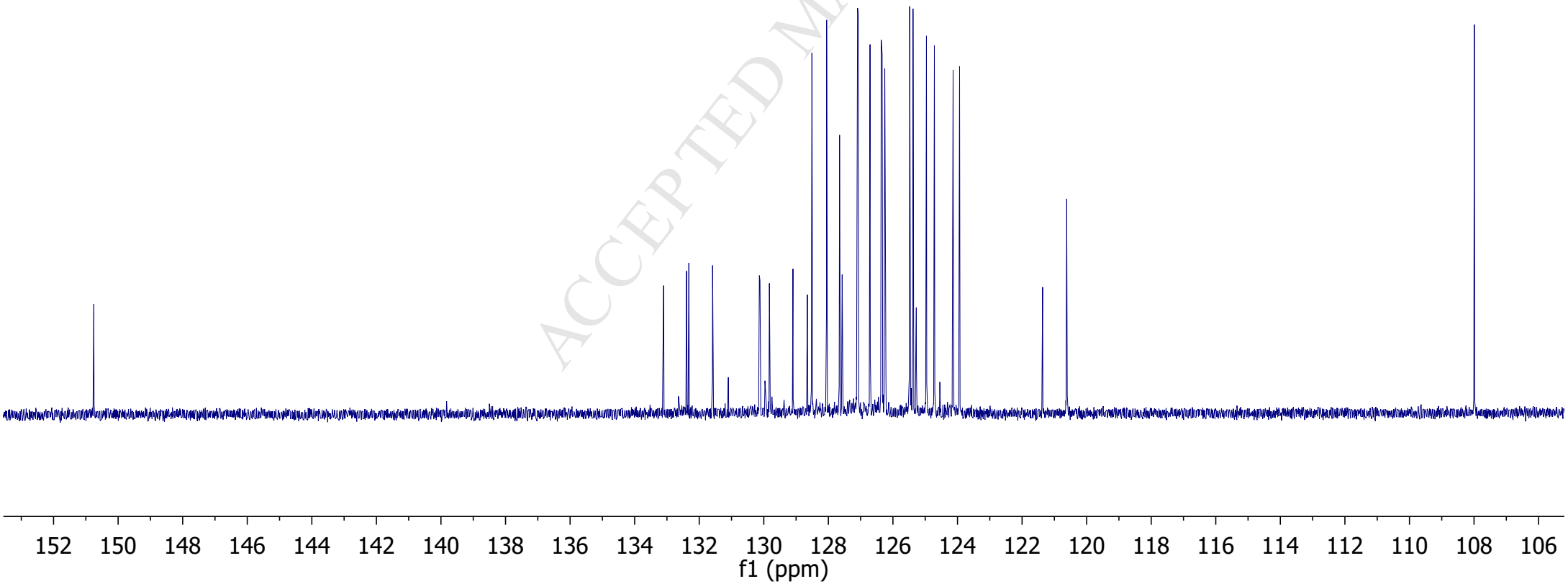
^{1}H NMR (500 MHz, CD_2Cl_2)



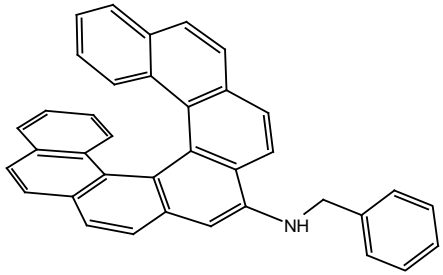


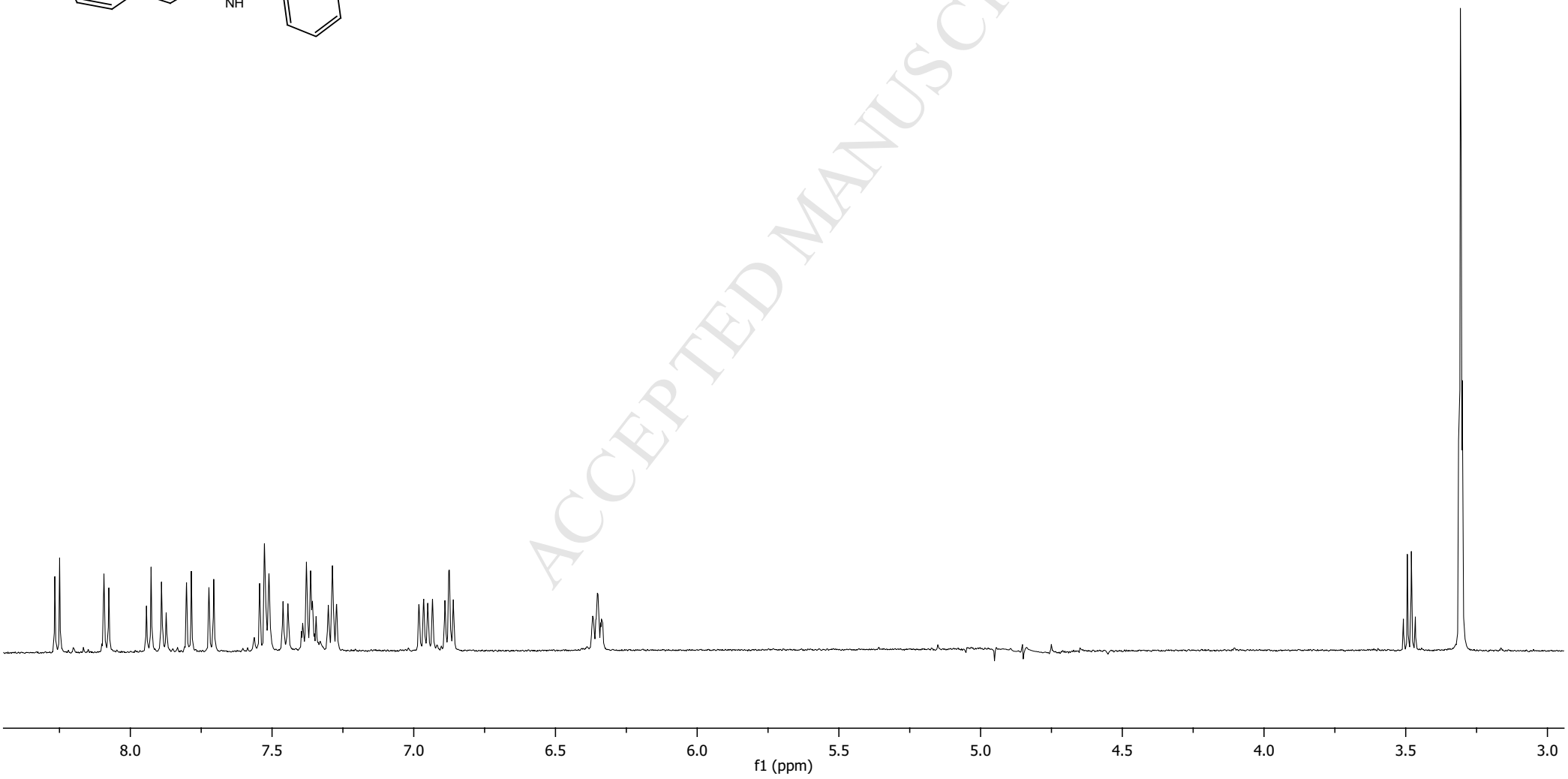
^{13}C NMR (125 MHz, CD_2Cl_2)



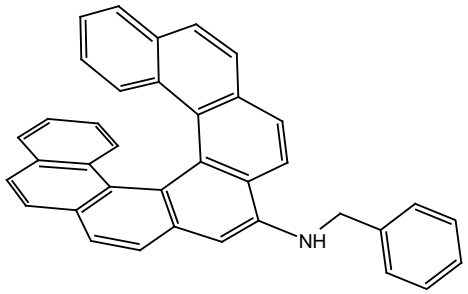


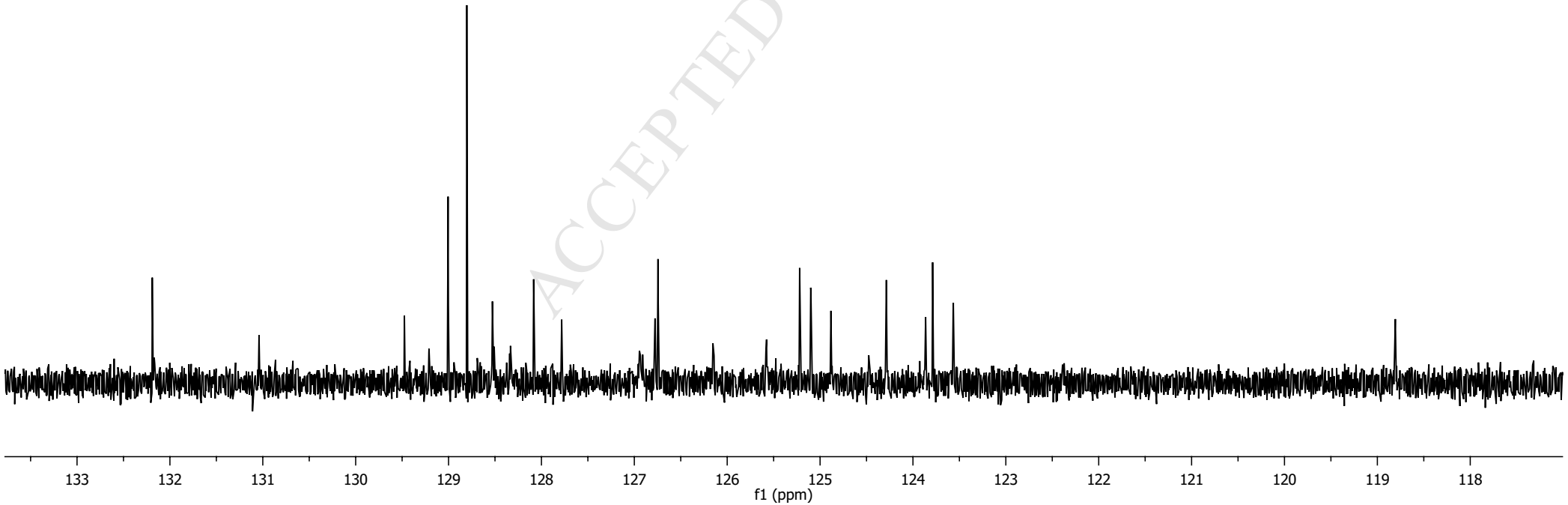
^{1}H NMR (500 MHz, CD_3OD)



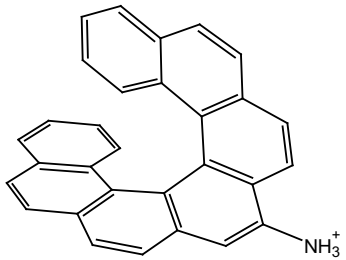


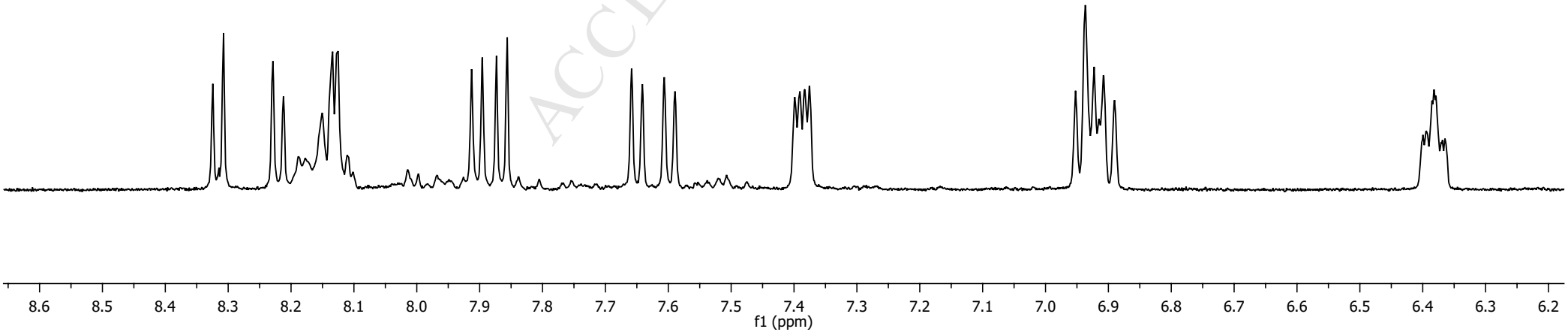
^{13}C NMR (125 MHz, CD_3OD)



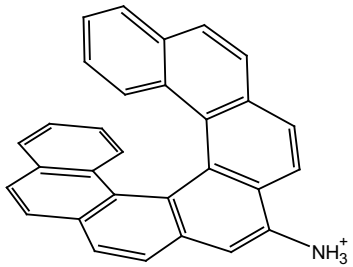


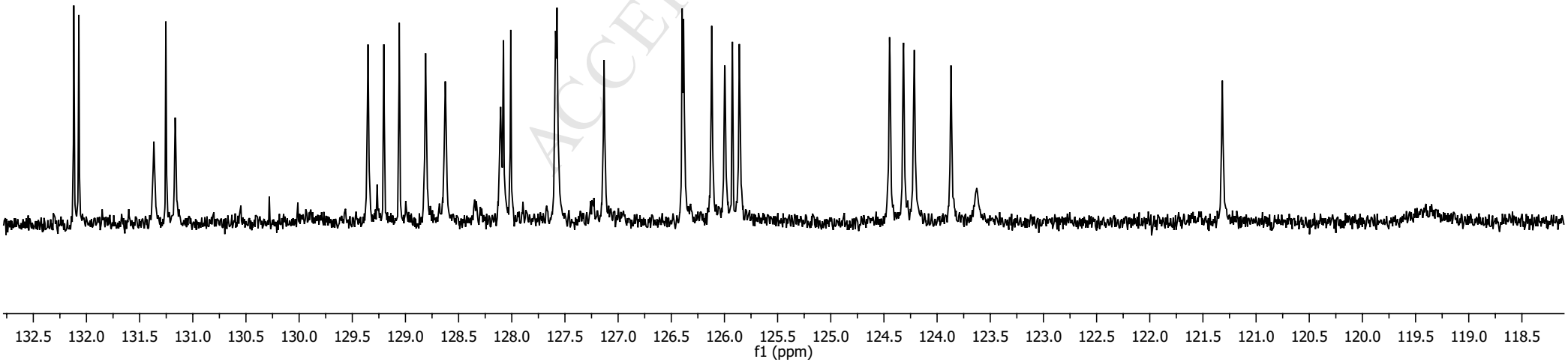
^{1}H NMR (500 MHz, DMSO-d_6)



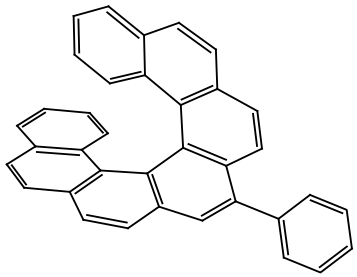


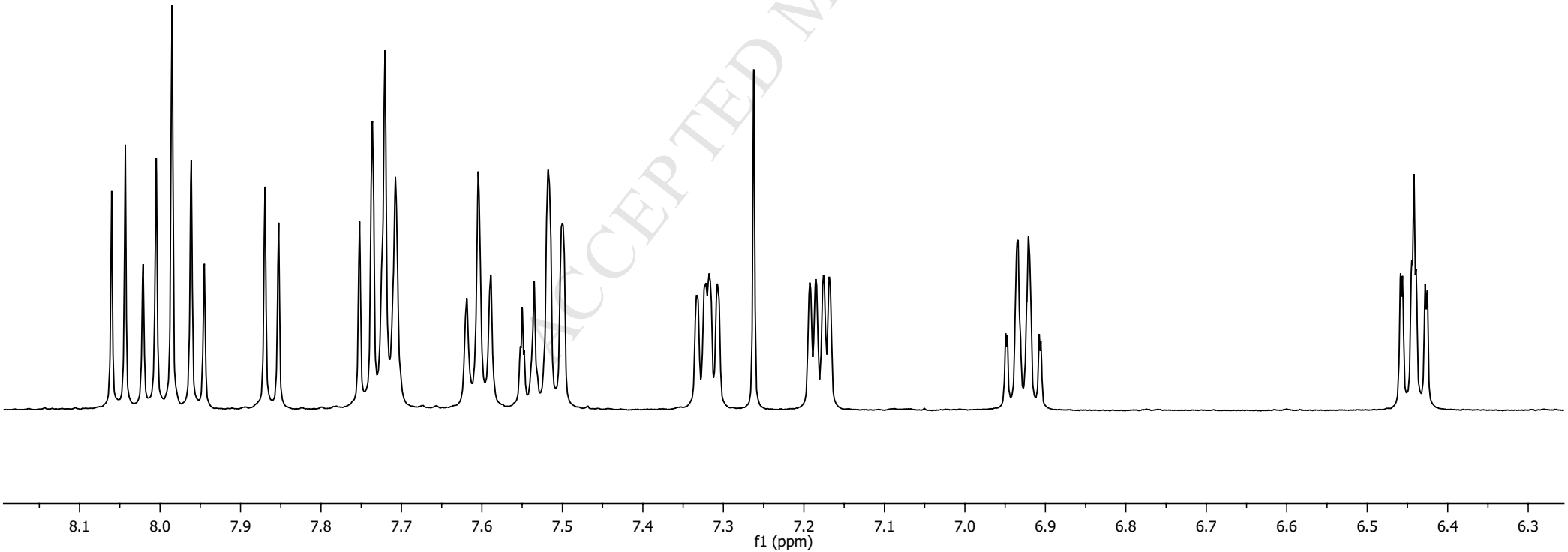
^{13}C NMR (125 MHz, DMSO-d_6)



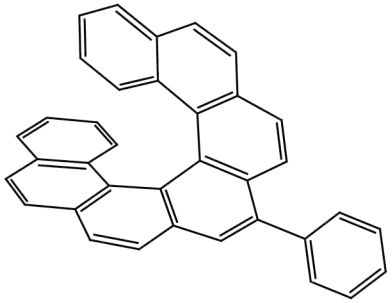


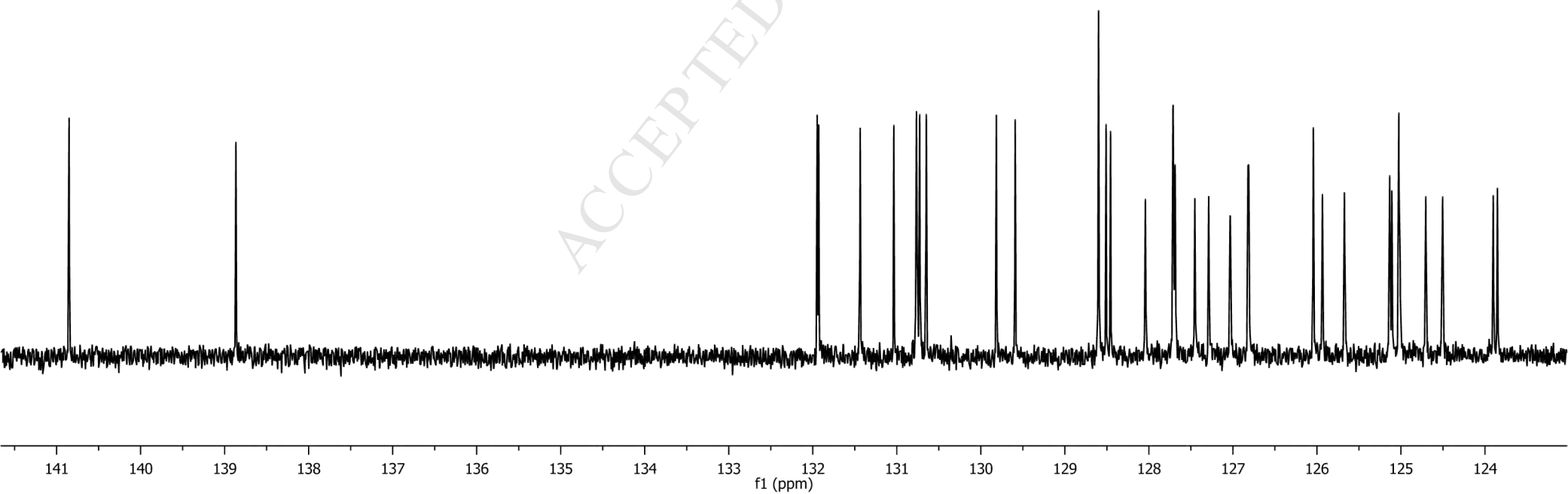
^{1}H NMR (500 MHz, $CDCl_3$)



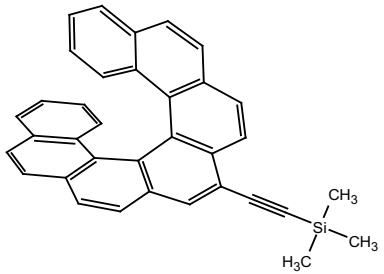


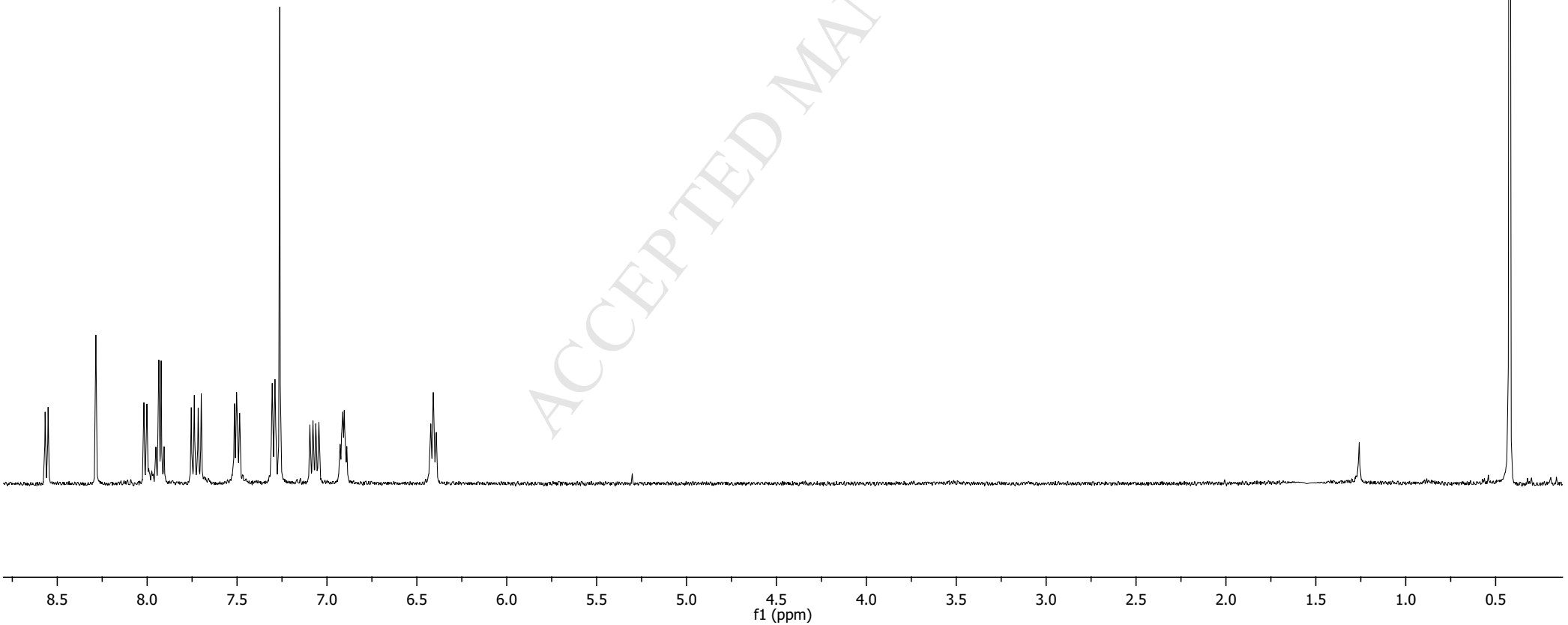
13C NMR (125 MHz, CDCl3)



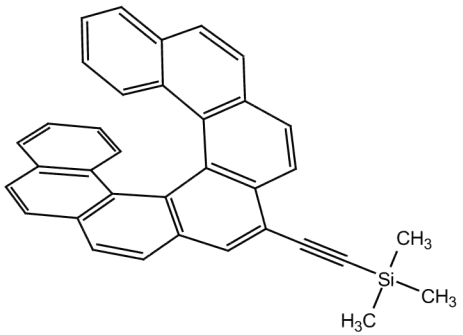


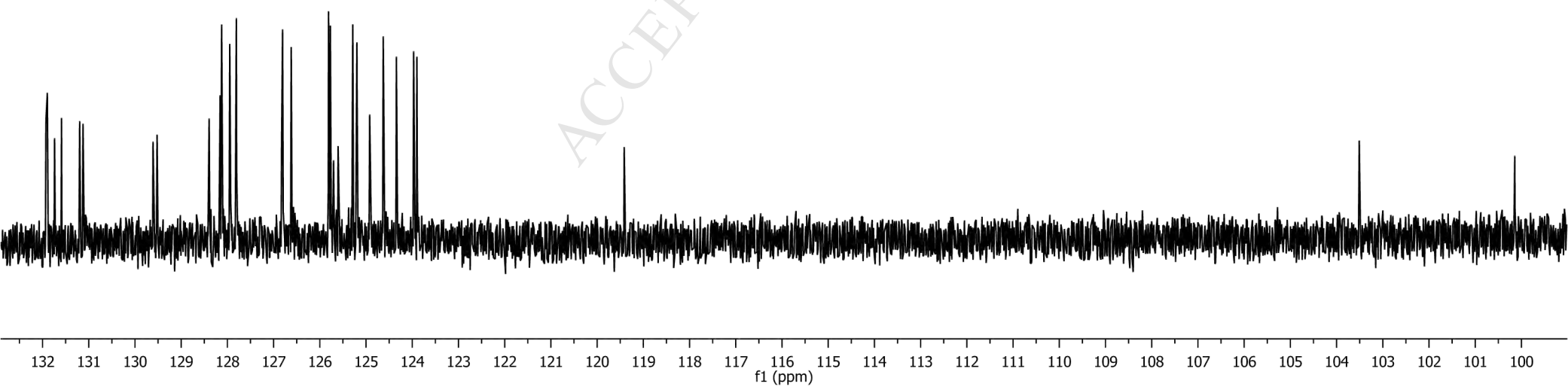
^{1}H NMR (500 MHz, $CDCl_3$)



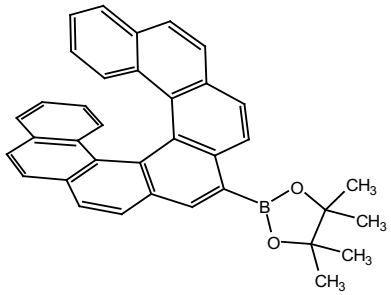


13C NMR (125 MHz, CDCl3)

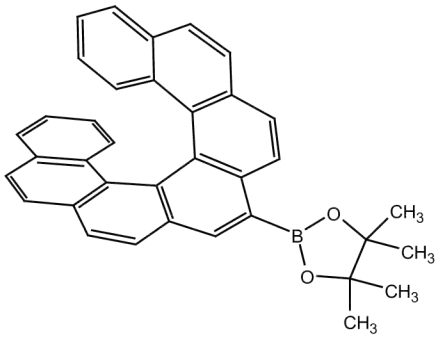




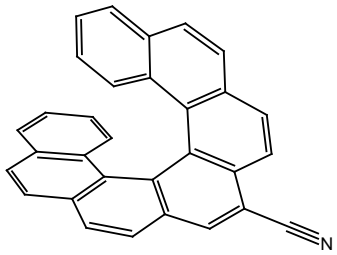
^{1}H NMR (500 MHz, $CDCl_3$)

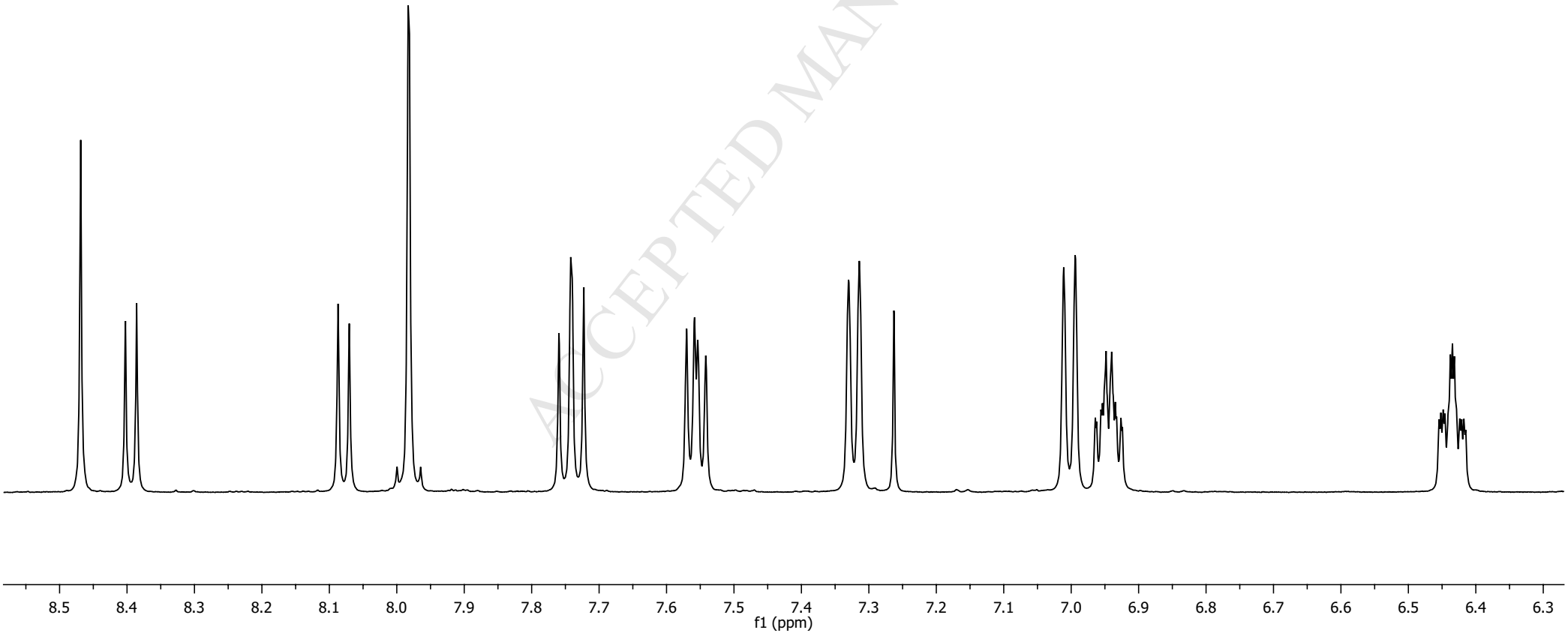


13C NMR (125 MHz, CDCl3)



^{1}H NMR (500 MHz, $CDCl_3$)





^{13}C NMR (125 MHz, $CDCl_3$)