Electronic Supplementary Information

For

# π-Curved Blatter radicals: Blatter helicenes

Hemant K. Singh,[a] Agnieszka Bodzioch,[a] Anna Pietrzak,[b] and Piotr Kaszyński [a,c]

[a] *Organic Materials Research Group, Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland*
[b] *Faculty of Chemistry, Łódź University of Technology, 90-924 Łódź, Poland*
[c] *Faculty of Chemistry, University of Łódź, 91-403 Łódź, Poland*

**Table of contents**      **Page**

## 1. Additional synthetic details

Products were purified by flash chromatography on silica gel (230–400 mesh, Merck). NMR spectra were recorded in CDCl$_3$ on AV III 500 MHz Bruker NMR or AV 400 Neo spectrometers. Chemical shifts are reported in δ ppm relative to solvent peak ($^1$H NMR: δ 7.26 ppm and $^{13}$C NMR: δ 77.16 ppm for CDCl$_3$).[1] High-resolution mass spectrometry (HRMS) measurements were performed using a G2-Si Waters Synapt HDMS instrument fitted with an atmospheric pressure ionization electrospray source. Melting points were determined on a MEL-TEMP® apparatus and are uncorrected. UV-vis spectra were recorded in spectroscopic grade CH$_2$Cl$_2$ at concentrations in a rage of 2–10 x 10$^{-5}$ M. Molar extinction coefficients ε were obtained by fitting the maximum absorbance against concentration in agreement with Beer's law. More details are provided in the SI. Passivated SiO$_2$ was prepared by suspension in 2% solution of Et$_3$N in CH$_2$Cl$_2$ and then evaporation till dryness.

**Photochemical preparation of helicene radicals 1[n]. General procedure**
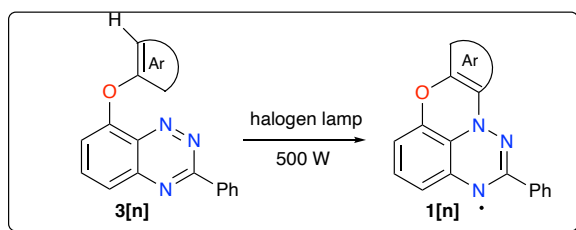


A solution (0.8–1.6 mM) of precursor **3[n]** in dry CH$_2$Cl$_2$ or AcOEt (100-400 mL) was placed in a 500 mL RB flask fitted with a reflux condenser (details in Table S1). The solution was stirred and irradiated with a 500 W halogen lamp, which was set 30 cm from the flask. The irradiation warmed up the reaction mixture to 30–35 °C. Progress of the reaction was monitored by TLC (20% CH$_2$Cl$_2$/pet. ether) and the irradiation was stopped after 1–4 days. The solvent was evaporated, the residue was adsorbed onto ~ 1.0 g of passivated silica and the unreacted starting material **3[n]** followed by product **1[n]** were separated using a silica gel column passivated with Et$_3$N (pet. ether/CH$_2$Cl$_2$, gradient 0-100%). The radical **1[n]** was recrystallized from toluene. Representative results are collected in Table S1.

**Table S1**. Results for photocyclization of **3[n]** in a Pyrex rb flask with a 500 W halogen lamp.

| helicene | scale 3[n] | solvent | conc. | yield 1[n] | time | recovered 3[n] |
|---|---|---|---|---|---|---|
| **1[3]** [a] | 60 mg | $CH_2Cl_2$ | 1.0 mM | 24 mg (40%) | 3 d | 25 mg (42%) |
| [b] | 60 mg | AcOEt | 1.0 mM | 54 mg (90%) | 3d | not present |
| **1[4]** [a] | 43 mg | $CH_2Cl_2$ | 1.0 mM | 15 mg (34%) | 3d | not isolated |
| **1[5]** | 110 mg | $CH_2Cl_2$ | 1.35 mM | 11 mg (10%) | 1 d | 75 mg (68%) |
|  | 109 mg | $CH_2Cl_2$ | 1.35 mM | 24 mg (22%) | 3 d | 53 mg (49%) |
|  | 260 mg | $CH_2Cl_2$ | 1.63 mM | 37 mg (14%) | 4 d | 124 mg (48%) |
|  | 110 mg | AcOEt | 1.35 mM | 32 mg (29%) | 3 d | 50 mg (45%) |
| **1[6]** | 70 mg | $CH_2Cl_2$ | 0.78 mM | 18 mg (26%) | 3 d | 26 mg (37%) |
|  | 250 mg | $CH_2Cl_2$ | 1.44 mM | 33 mg (14%) | 3 d | 170 mg (68%) |
|  | 105 mg | $CH_2Cl_2$ | 2.33 mM | 9.5 mg (9%) | 3 d | 53 mg (50%) |
|  | 100 mg | AcOEt | 1.35 mM | 28 mg (28%) | 3 d | 52 mg (52%) |
| **1[7]** | 130 mg | $CH_2Cl_2$ | 1.30 mM | 40 mg (31%) | 3 d | 59 mg (45%) |
|  | 100 mg | AcOEt | 1.35 mM | 50 mg (50%) | 3 d | 45 mg (45%) |

[a] Ref.[2]  [b] Ref.[3]

*Helicene 1[5]*. Following the general procedure, radical **1[5]** (57 mg, 22% yield in $CH_2Cl_2$) was obtained as a black solid starting from 260 mg (0.652 mmol) of **3[5]**. Mp 261–262 °C (toluene). IR ν 3053, 1594, 1484, 1385, 1300, 1130, 834, 777, 690 cm$^{-1}$. UV-vis ($CH_2Cl_2$) $\lambda_{max}$ (*log* ε) 261 (4.70), 287 (4.49), 300.5 (4.47), 367 (3.94), 386.5 (4.20), 423 (3.93), 547 (3.77), 640 (3.465), 709 (3.55) nm. ESI(+)-TOF *m/z* 422 (30, [M + Na]$^+$), 399 (80, [M + H]$^+$); HRMS (ESI(+)-TOF) *m/z* [M + H]$^+$ calcd for $C_{27}H_{17}N_3O$ 399.1372, found 399.1359. Anal. Calcd for $C_{27}H_{16}N_3O$: C, 81.39; H, 4.05; N, 10.55. Found: C, 81.43; H, 4.15; N, 10.62.

*Helicene 1[6]*. Following the general procedure, radical **1[6]** (33 mg, 14% yield in $CH_2Cl_2$) was obtained as a black solid starting from 250 mg (0.557 mmol) of **3[6]**. Mp 121–123 °C (toluene). IR ν 3046, 1587, 1495, 1350, 1264, 1171, 835, 784, 687 cm$^{-1}$. UV-vis ($CH_2Cl_2$) $\lambda_{max}$ (*log* ε) 284 (4.67), 398 (3.86), 465 (3.38), 565 (3.53), 656.5 (3.21), 727.5 (3.29) nm. ESI(+)-TOF *m/z* 449 (100, [M+H]$^+$); HRMS (ESI(+)-TOF) *m/z* [M+H]$^+$ calcd for $C_{31}H_{19}N_3O$ 449.1528, found 449.1512. Anal. Calcd for $C_{31}H_{18}N_3O$: C, 83.02; H, 4.05; N, 9.37. Found: C, 82.84; H, 3.88; N, 9.32.
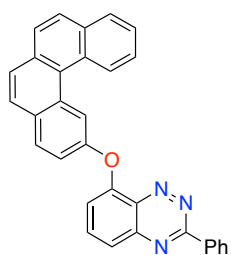
***Helicene 1[7].*** Following the general procedure, radical **1[7]** (50 mg, 50% yield in $CH_2Cl_2$) was obtained as a black solid starting from 100 mg (0.2 mmol) of **3[7]**. Mp 255–257 °C (toluene). IR ν 3041, 1584, 1481, 1346, 1262, 1150, 841, 776, 689 cm$^{-1}$. UV-vis ($CH_2Cl_2$) $\lambda_{max}$ (*log* ε) 265 (4.60), 308.5 (4.57), 395 (3.65), 434 (3.65), 451 (3.62), 482 (3.51), 534 (3.55), 570 (3.66), 659 (3.32), 731 (3.41) nm. ESI(+)-TOF *m/z* 499 (100, [M + H]$^+$); HRMS (ESI(+)-TOF) *m/z* [M + H]$^+$ calcd for $C_{35}H_{21}N_3O$ 499.1685, found 499.1673. Anal. Calcd for $C_{35}H_{20}N_3O$: C, 84.32; H, 4.04; N, 8.43. Found: C, 84.09; H, 4.12; N, 8.34.

**Preparation of precursors 3[n]**. General procedure.[3] To a stirred solution of the appropriate phenol **5[n]** (1.1 mmol) in DMSO (4 mL) 60% NaH (2.2 mmol) was added in one portion. After 15 min 8-fluoro-3-phenylbenzo[*e*][1,2,4]triazine[4] (**4**, 1.0 mmol) was added and the reaction mixture was stirred overnight under Ar atmosphere at 100 ºC. After cooling, the mixture was diluted with AcOEt (30 mL) and organic layer was washed with water (3×25 mL) and brine (25 mL). The combined organic layer was dried ($Na_2SO_4$) and the solvent was evaporated. The solid residue was absorbed onto $SiO_2$ and separated by column chromatography ($SiO_2$, petroleum ether/AcOEt, 2:1) giving **3[n]** as a yellow solid.
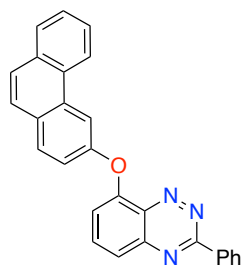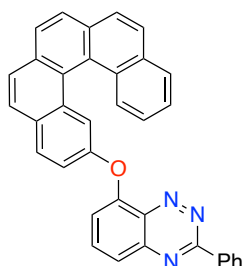


**8-(Phenanthren-3-yloxy)-3-phenylbenzo[*e*][1,2,4]triazine (3[5])**. Following the general procedure, **3[5]** (606 mg, 96%) was obtained starting from 338 mg (1.74 mmol) of phenanthren-3-ol[5] (**5[5]**) and 356 mg (1.58 mmol) of 8-fluoro-3-phenylbenzo[*e*][1,2,4]triazine (**4**).[4] Mp 180-182 ºC (pet. ether/AcOEt, 2:1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.82-8.80 (m, 2H), 8.55-8.52 (m, 2H), 8.00 (d, *J* = 8.6 Hz, 1H), 7.93-7.91 (m, 1H), 7.83-7.80 (m, 2H), 7.78 (d, *J* = 4.0 Hz, 2H), 7.65-7.61 (m, 5H), 7.53 (dd, $J_1$ = 8.6 Hz, $J_2$ = 2.3 Hz, 1H), 7.10 (dd, $J_1$ = 6.4 Hz, $J_2$ = 2.5 Hz, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 160.3, 155.5, 154.4, 142.3, 140.2, 136.0, 135.6, 132.4, 132.1, 131.8, 130.9, 129.9, 129.6, 129.11, 129.05, 128.8, 127.3, 126.83, 128.80, 126.5, 123.0, 122.8, 120.3, 114.2, 113.8. ESI(+)-TOF *m/z* 400 (100, [M+H]$^+$); HRMS (ESI(+)-TOF) *m/z* [M+H]$^+$ calcd for $C_{27}H_{18}N_3O$ 400.1450, found 400.1446. Anal. Calcd for $C_{27}H_{17}N_3O$: C, 81.19; H, 4.29; N, 10.52. Found: C, 81.20; H, 4.24; N, 10.50.

**8-(Benzo[c]phenanthren-2-yloxy)-3-phenylbenzo[e][1,2,4]-triazine (3[6])**. Following the general procedure, **3[6]** (596 mg, 64%) was obtained starting from 556 mg (2.28 mmol) of benzo[c]phenanthren-2-ol[6] (**5[6]**) and 466 mg (2.07 mmol) of 8-fluoro-3-phenylbenzo[e][1,2,4]triazine (**4**).[4] Mp 224-225 °C (pet. ether/AcOEt, 4:1); ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.98-8.95 (m, 2H), 8.83-8.80 (m, 2H), 8.14 (d, $J$ = 8.7 Hz, 1H), 8.00-7.98 (m, 1H), 7.96 (d, $J$ = 8.5 Hz, 1H), 7.92 (d, $J$ = 8.6 Hz, 1H), 7.86 (d, J = 4.8 Hz, 1H), 7.85 (d, $J$ = 4.8 Hz, 1H), 7.80 (d, J = 4.4 Hz, 2H), 7.64-7.55 (m, 6H), 7.02 (t, $J$ = 4.5 Hz, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 160.3, 155.4, 154.2, 142.3, 140.1, 135.9, 135.5, 133.4, 131.7, 131.52, 131.48, 131.0, 130.8, 130.2, 129.02, 128.95, 128.6, 128.3, 128.1, 127.3, 127.1, 126.82, 126.78, 126.7, 126.5, 126.1, 122.7, 119.6, 118.4, 114.2. ESI(+)-TOF $m/z$ 450 (100, [M+H]$^+$); HRMS (ESI(+)-TOF) $m/z$ [M+H]$^+$ calcd for C$_{31}$H$_{20}$N$_3$O: 450.1606, found: 450.1601. Anal. Calcd for C$_{31}$H$_{19}$N$_3$O: C, 82.83; H, 4.26; N, 9.35. Found: C, 82.79; H, 4.28; N, 9.36.

**8-(Dibenzo[c,g]phenanthren-9-yloxy)-3-phenylbenzo[e][1,2,4]-triazine (3[7])**. Following the general procedure, **3[7]** (200 mg, 60%) was obtained starting from 215 mg (0.73 mmol) of dibenzo[c,g]phenanthren-9-ol (**5[7]**)[7] and 150 mg (0.67 mmol) of 8-fluoro-3-phenylbenzo[e][1,2,4]triazine (**4**).[4] Mp 221-223 °C (pet ether/CH$_2$Cl$_2$, 2:3); 1H NMR (400 MHz, CDCl3) δ 8.79-8.77 (m, 2H), 8.44 (d, $J$ = 8.4 Hz, 1H), 8.10 (s, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.96 (d, $J$ = 8.4 Hz, 1H), 7.87 (d, J = 8.4 Hz, 3H), 7.79 (s, 2H), 7.76-7.67 (m, 3H), 7.62-7.59 (m, 3H), 7.55-7.52 (m, 1H), 7.23 (t, $J$ = 7.6 Hz, 1H), 7.05 (d, $J$ = 7.2 Hz, 1H), 6.94 (t, $J$ = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 160.1, 154.3, 154.0, 142.2, 140.4, 135.65, 135.61, 132.8, 132.6, 132.24, 132,19, 131.8, 130.4, 130.2, 129.9, 129.12, 128.99, 128.7, 127.8, 127.72, 127.68, 127.3, 127.2, 127.0, 126.6, 126.25, 126.20, 125.9, 124.4, 123.5, 120.1, 117.4, 116.9. ESI(+)-TOF $m/z$ 500 (100, [M + H]$^+$); HRMS (ESI(+)-TOF) $m/z$ [M + H]$^+$ calcd for C$_{35}$H$_{22}$N$_3$O 500.1763, found 500.1754. Anal. Calcd for C$_{35}$H$_{21}$N$_3$O: C, 84.15; H, 4.24; N, 8.41. Found: C, 84.19; H, 4.28; N, 8.43.

**Preparation of phenols 5[n]. General procedure.** To a solution of the appropriate methoxyarene (~ 3.5 mmol) in dry CH$_2$Cl$_2$ (50 mL) at 0 °C was added dropwise a solution of BBr$_3$ in CH$_2$Cl$_2$ (1.0 M). The resulting mixture was stirred overnight, allowing the solution to warm to room temperature. The solution was then cooled to 0 °C, the reaction was quenched

with water (20 mL) and the solvent was removed under reduced pressure. The aqueous suspension was extracted with AcOEt (3 x 20 mL), the collected organic layers were washed with brine and dried ($Na_2SO_4$). After evaporation of solvent the residue was purified by column chromatography ($SiO_2$, pet. ether/AcOEt, 1:1) giving appropriate phenol **5[n]**.
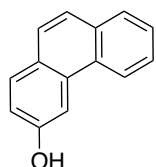
**Phenanthren-3-ol (5[5])**.[5] Following the general procedure, **5[5]** (630 mg, 96% yield) was obtained starting from 704 mg (3.38 mmol) of 3-methoxyphenanthrene (**S3**). Mp 117-119 °C (MeOH)). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta$ 8.54 (d, $J$= 8.1 Hz, 1H), 8.04 (d, $J$= 2.4 Hz, 1H), 7.87 (dd, $J_1$ = 7.1 Hz, $J_2$ = 2.1 Hz, 1H), 7.80 (d, $J$ = 8.6 Hz, 1H), 7.67 (d, $J$ = 8.8 Hz, 1H), 7.64-7.57 (m, 3H), 7.17 (dd, $J_1$ = 8.6 Hz, $J_2$ = 2.5 Hz, 1H), 5.09 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta$ 154.4, 132.5, 132.0, 130.4, 129.6, 128.7, 126.9, 126.7, 126.3, 124.7, 122.9, 116.8, 107.0. ESI(-)-TOF $m/z$ 193 (100, [M-H]−); HRMS (ESI(-)-TOF) $m/z$ [M-H]− calcd for $C_{14}H_9O$ 193.0653, found 193.0658. Anal. Calcd for $C_{14}H_{10}O$: C, 86.57; H, 5.19. Found: C, 86.29; H, 5.22.
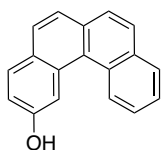
**Benzo[c]phenanthrene-2-ol (5[6])**.[6] Following the general procedure, **5[6]** (899 mg, 97%) was obtained starting from 980 mg (3.8 mmol) of 2-methoxybenzo[c]phenanthrene (**N5**). Mp 108-109 °C (EtOH; lit.[6] 112-115 °C). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta$ 9.13 (d, $J$ =8.4 Hz, 1H), 8.56 (d, $J$= 1.9 Hz, 1H), 8.01 (d, $J$ = 7.9 Hz, 1H), 7.94 (d, $J$ = 8.6 Hz, 1H), 7.89 (d, $J$ = 8.9 Hz, 1H), 7.84 (d, $J$ = 8.5 Hz, 1H), 7.80 (d, $J$ = 8.5 Hz, 1H), 7.70 (d, $J$ = 8.5 Hz, 1H), 7.68 (td, $J_1$ = 8.5 Hz, $J_2$ = 1.5 Hz, 1H), 7.61 (td, $J_1$ = 7.9 Hz, $J_2$ = 1.1 Hz, 1H), 7.23 (dd, $J_1$ = 8.6 Hz, $J_2$ = 2.4 Hz, 1H), 5.05 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta$ 154.3, 133.4, 131.8, 131.7, 130.6, 130.5, 128.8, 127.8, 127.4, 127.1, 126.4, 126.3, 125.8, 124.8, 116.4, 111.7. ESI(-)-TOF $m/z$ 243 (100, [M-H]−); HRMS (ESI(-)-TOF) $m/z$ [M-H]− calcd for $C_{18}H_{11}O$ 243.0810, found 243.0818. Anal. Calcd for $C_{18}H_{12}O$: C, 88.50; H, 4.95. Found: C, 88.45; H, 4.98.
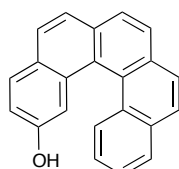
**Dibenzo[c,g]phenanthrene-9-ol (5[7])**.[7] Following the general procedure, **5[7]** (615 mg, 95%) was obtained starting from 678 mg (2.2 mmol) of 9-methoxydibenzo[c,g]phenanthrene (**M4**). Mp 188-190 °C (pet ether/EtOAc, 9:1; lit.[7] 188-191 °C). ^{1}H NMR (400 MHz, $CDCl_3$) $\delta$ 8.56 (d, $J$ = 8.8 Hz, 1H), 7.96-7.85 (m, 8H), 7.76 (d, $J$ = 8.4 Hz, 1H), 7.53 (t, $J$ = 7.2 Hz, 1H), 7.33 (t, $J$ = 8.4 Hz, 1H), 7.15 (dd, $J_1$ = 8.4 Hz, $J_2$ = 2.0 Hz, 1H), 4.86 (bs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) $\delta$ 152.7, 132.9, 132.8, 132.26, 132.21, 130.4, 129.9, 129.4, 128.1, 127.8, 127.49, 127.45, 127.41, 127.3,

126.6, 126,4, 126.1, 124.4, 124.3, 117.0, 112.6. ESI(-)-TOF *m/z* 293 (100, [M-H]⁻); HRMS (ESI(-)-TOF) *m/z* [M-H]⁻ calcd for $C_{22}H_{13}O$ 293.0966, found 293.0974. Anal. Calcd for $C_{22}H_{14}O$: C, 89.77; H, 4.79. Found: C, 89.71; H, 4.75.
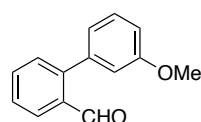
• **Synthesis of methoxyarenes precursors to phenols 5[n]**

***Precursor to phenol 5[5]***

a) 3-Methoxyphenanthrene (**S3**) was synthesized according to a literature procedure,[5] shown in the Scheme S1.
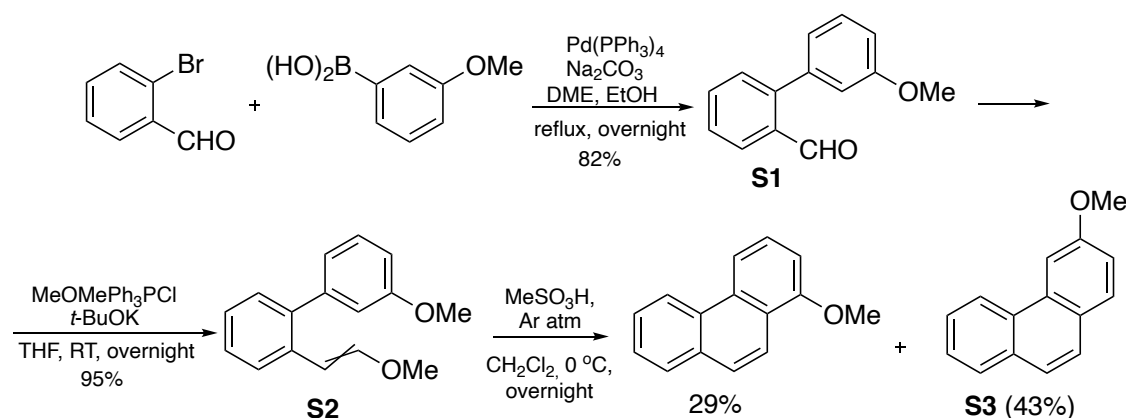


**Scheme S1**. Synthesis of 3-methoxyphenanthrene (**S3**).



**3'-Methoxybiphenyl-2-carboxyaldehyde (S1).**[5] Following a literature procedure,[5] to a solution of 2-bromobenzaldehyde (4.08 g, 22.1 mmol) in dry dimethoxymethane (60 mL) under Ar was added Pd(PPh₃)₄ (0.504 g, 0.44 mmol). The resulting solution was stirred at room temperature, then a solution of 3-methoxyphenylboronic acid (4.02 g, 26.4 mmol) in EtOH (40 mL) was added. After 20 min, a solution of Na₂CO₃ (7.0 g, 66.0 mmol) in H₂O (30 mL) was added and the mixture was refluxed overnight. The solution was cooled and concentrated under reduced pressure. The residue was extracted with CH₂Cl₂ (3 x 50 mL), then combined organic layers were washed with H₂O (50 mL), brine (50 mL) and dried (Na₂SO₄). After evaporation of the solvent the residue was purified by column chromatography (SiO₂, pet. ether/AcOEt, 10:1) giving 3.97 g (82% yield) of product as a colorless oil: ¹H NMR (500 MHz, CDCl₃) δ 10.0 (s, 1H), 8.02 (dd, $J_1$ = 7.8 Hz, $J_2$ = 1.0 Hz, 1H), 7.64 (td, $J_1$ = 7.6 Hz, $J_2$ = 1.4 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 6.99 (dd, $J_1$ = 8.4 Hz, $J_2$ = 2.0 Hz, 1H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 2.0 Hz, 1H), 3.85 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 192.6, 159.6, 146.0, 139.3, 133.9, 133.7, 130.7, 129.6, 128.0, 127.6, 122.9, 115.8, 113.8, 55.5; HRMS (TOF-AP⁺) *m/z* (100, [M]⁺) calcd for $C_{14}H_{12}O_2$ 212.0837, found 212.0836.
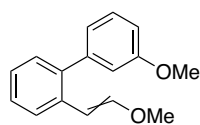
**3'-Methoxy-2-(2-methoxyvinyl)biphenyl (S2).**[5] Following a literature procedure,[5] to a solution of methyltriphenylphosphonium chloride (5.2 g, 15.15 mmol) in dry THF (50 mL) under Ar was added dropwise 1M solution of $t$-BuOK in dry THF (15.2 mL, 15.15 mmol) at room temperature for 1h. Then, the solution of 3'-methoxybiphenyl-2-carboxyaldehyde (**S1**, 1.34 g, 6.06 mmol) in dry THF (50 mL) was added dropwise and resulting mixture was stirred overnight. The solvent was evaporated to dryness and the crude product was purified by column chromatography ($SiO_2$, pet. ether/AcOEt, 0-10%) giving 1.39 g (95% yield) of (S2) as a mixture of the $E$- and $Z$-isomers (5:4 $E/Z$) as a yellowish oil; $E$-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) $\delta$ 7.41 (d, $J$ = 7.6 Hz, 1H), 7.20-7.33 (m, 4H), 6.88-6.98 (m, 4H), 5.80 (d, $J$ = 12.9 Hz, 1H), 3.83 (s, 3H), 3.55 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta$ 159.4, 148.0, 143.3, 139.9, 134.2, 130.2, 129.1, 127.7, 126.0, 125.0, 122.4, 115.3, 112.7, 104.5, 56.6, 55.4; $Z$-isomer: ^{1}H NMR (500 MHz, $CDCl_3$) $\delta$ 8.11 (d, $J$ = 7.9 Hz, 1H), 7.20-7.33 (m, 4H), 6.88-6.98 (m, 3H), 6.07 (d, $J$ = 7.2 Hz, 1H), 5.20 (d, $J$ = 7.2 Hz, 1H), 3.83 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta$ 159.3, 149.0, 143.0, 140.3, 133.3, 129.7, 129.3, 129.1, 127.4, 125.7, 122.3, 115.4, 112.6, 103.8, 60.7, 55.4; HRMS (TOF-AP[+]) $m/z$ (100, [M][+]) calcd for $C_{16}H_{16}O_2$: 240.1150, found: 240.1145.
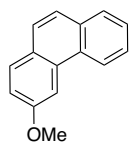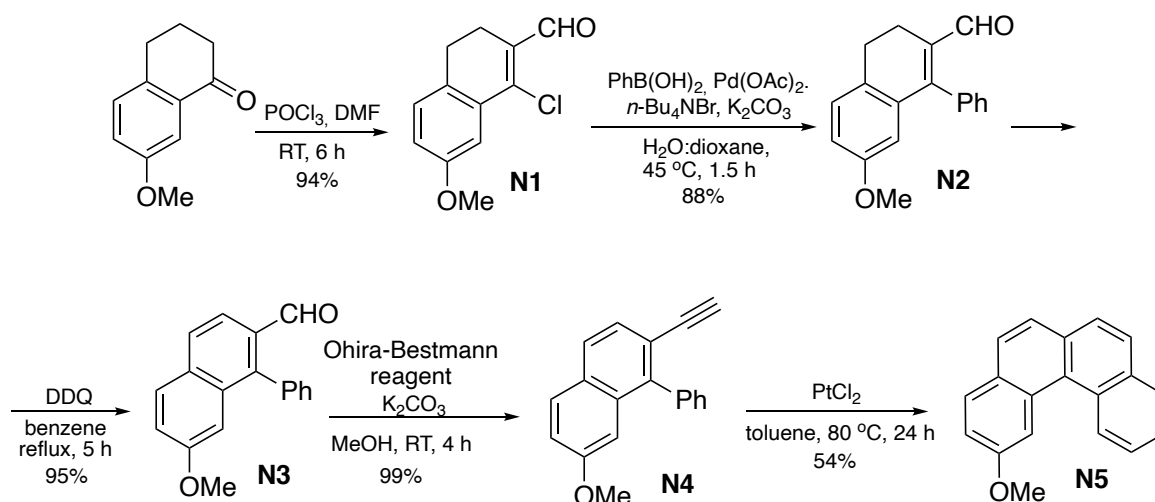
**3-Methoxyphenanthrene (S3).** Following a literature procedure,[5] to a solution of 3'-methoxy-2-(2-methoxyvinyl)biphenyl (**S2**, 1.98 g, 8.25 mmol) in $CH_2Cl_2$ (100 mL) was added MeSO$_3$H (0.45 mL) under Ar at 0 °C. The resulting solution was stirred until TLC showed absence of starting material. Then, a saturated solution of NaHCO$_3$ (30 mL) was added and stirring was continued for 15 min. Layers were separated and the water phase was washed with $CH_2Cl_2$ (2 × 30 mL). Combined organic layers were dried (Na$_2$SO$_4$), solvent was evaporated and the residue was separated by column chromatography (pet. ether/ $CH_2Cl_2$, 0-20 %) giving 1-methoxyphenanthrene (507 mg, 29% yield) as a first fraction and desired 3-methoxyphenanthrene (738 mg, 43% yield) as a second fraction. Analytically pure 3-methoxyphenanthrene (**S3**) was obtained by recrystallization from MeOH. Mp 55-56 °C (MeOH). ^{1}H NMR (500 MHz, $CDCl_3$) $\delta$ 8.62 (d, $J$ = 8.2 Hz, 1H), 8.07 (d, $J$ = 2.3 Hz, 1H), 7.90 (d, $J$ = 7.9 Hz, 1H), 7.82 (d, $J$ = 8.7 Hz, 1H), 7.70 (d, $J$ = 8.7 Hz, 1H), 7.66-7.58 (m, 3H), 7.27 (dd, $J_1$ = 8.5 Hz, $J_2$ = 2.4 Hz, 1H), 4.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) $\delta$ 158.6, 132.5, 131.7, 130.1, 129.9, 128.7, 126.8, 126.75, 126.70, 126.2, 124.7, 122.8, 116.8, 104.1, 55.6. Anal. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.48; H, 5.72.
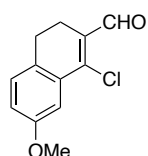
## Precursor to phenol 5[6]

<u>b) 2-Methoxybenzo[*c*]phenanthrene (**N5**)</u> was synthesized according to a modified literature procedure,[6] as shown in Scheme S2.



**Scheme S2**. Synthesis of 2-Methoxybenzo[*c*]phenanthrene (**N5**).

**1-Chloro-7-methoxy-3,4-dihydronaphthalene-2-carbaldehyde** (**N1**).[6] Following a literature procedure,[6] POCl$_3$ (4.52 mL, 48 mmol) was added dropwise to DMF (4.65 mL, 60.0 mmol) at 0 °C. The mixture was warmed to room temperature and stirred for 15 min, next cooled to 0 °C and then 7-methoxy-1-tetralone (5.45 g, 30.0 mmol) in dry DMF (15mL) was added dropwise. The mixture was again warmed to room temperature and stirred overnight. The reaction mixture was poured into ice, quenched with sat. NaHSO$_3$, then extracted with Et$_2$O (3 × 50 mL) and washed with H$_2$O, and brine. The combined organic layer was dried (Na$_2$SO$_4$), filtered and solvent was evaporated. The residue was purified by column chromatography (SiO$_2$, pet. ether/AcOEt, 10:1) giving 6.52 g (94% yield) of product **N1** as a yellow solid. Mp 54-55 °C (EtOH); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 10.38 (s, 1H), 7.40 (d, $J$ = 2.6 Hz, 1H), 7.13 (d, $J$ = 8.3 Hz, 1H), 6.91 (dd, $J_1$ = 8.2 Hz, $J_2$ = 2.6Hz, 1H), 3.85 (s, 3H), 2.77 (t, $J$ = 7.5 Hz, 2H), 2.61 (t, $J$ = 7.5 Hz, 2H) ; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 190.8, 158.7, 145.9, 133.0, 132.5, 131.2, 128.7, 117.0, 111.9, 55.6, 26.2, 22.1; MS (TOF-AP$^+$) *m/z* 223 (100, [M+1]$^+$); HRMS (ESI(+)-TOF) *m/z* [M+1]$^+$ calcd for C$_{12}$H$_{12}$O$_2$Cl 223.0526, found 223.0522. Anal. Calcd for C$_{12}$H$_{11}$O$_2$Cl: C, 64.73; H, 4.98. Found: C, 64.51; H, 5.09.
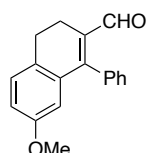
**7-Methoxy-1-phenyl-3,4-dihydronaphthalene-2-carbaldehyde** (**N2**).[6] Following a literature procedure,[6] a suspension of aldehyde **N1** (3.33 g, 14.9 mmol), phenylboronic acid (2.0 g, 16.4 mmol), *n*-Bu$_4$NBr (9.6 g, 29.8 mmol),

Pd(OAc)$_2$ (67 mg, 0.298 mmol), and K$_2$CO$_3$ (5.14 g, 37.3 mmol) in degassed mixture of H$_2$O (30 mL) and 1,4-dioxane (10 mL) was stirred at 45 °C for 1.5 h. The rection mixture was cooled to room temperature, diluted with H$_2$O (20 mL) and then extracted with AcOEt (3x100 mL). The combined organic layer was dried (Na$_2$SO$_4$) and filtered. After evaporation of solvent the residue was purified on column chromatography (SiO$_2$, pet. ether/AcOEt, gradient 0-10%) giving 3.46 g (88% yield) of aldehyde **N2** as a yellow solid. Mp 76-78 °C (EtOH; lit.[6] 71-73 °C); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.57 (s, 1H), 7.46-7.44 (m, 3H), 7.29-7.27 (m, 2H), 7.18 (d, $J$ = 8.2 Hz, 1H), 6.85 (dd, $J_1$ = 8.2 Hz, $J_2$ = 2.7 Hz, 1H), 6.43 (d, $J$ = 2.6 Hz, 1H), 3.65 (s, 3H), 2.85 (t, $J$ = 8.5 Hz, 2H), 2.68 (t, $J$ = 8.5 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 193.6, 158.3, 154.5, 136.3, 135.2, 134.9, 130.9, 130.6, 128.65, 128.63, 128.4, 114.94, 114.89, 55.4, 26.8, 20.8; MS (TOF-AP$^+$) $m/z$ 265 (100, [M+1]$^+$); HRMS (TOF-AP$^+$) $m/z$ [M+1]$^+$ calcd for C$_{18}$H$_{17}$O$_2$ 265.1229, found 265.1225. Anal. Calcd for C$_{18}$H$_{16}$O$_2$: C, 81.79; H, 6.10. Found: C, 81.92; H, 6.25.
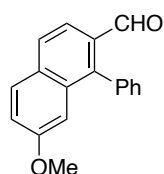


**7-Methoxy-1-phenyl-2-naphthaldehyde (N3).**[6] Following a literature procedure, [6] a suspension of aldehyde **N2** (2.60 g, 9.85 mmol) and DDQ (3.00 g, 12.8 mmol) in benzene (50 mL) was stirred at 80 °C for 5 h. The mixture was cooled to room temperature, filtered through a short pad of Celite and then solvent was evaporated. The residue was washed with 1M NaOH and the aqueous layer was extracted with toluene. The combined organic layer was dried (Na$_2$SO$_4$), filtered and solvent was evaporated. The crude product was purified by column chromatography (SiO$_2$, pet. ether/AcOEt, 10:1) giving 2.46 g (95% yield) of aldehyde **N3** as a yellow solid. Mp 70-72 °C (EtOH, lit.[6] 71-73 °C). $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.87 (s, 1H), 7.93 (d, $J$ = 8.5 Hz, 1H), 7.87 (d, $J$ = 8.6 Hz, 1H), 7.84 (d, $J$ = 8.9 Hz, 1H), 7.56-7.52 (m, 3H), 7.42-7.41 (m, 2H), 7.28 (dd, $J_1$ = 8.9 Hz, $J_2$ = 2.5 Hz, 1H), 6.33 (d, $J$ = 2.5 Hz, 1H), 3.70 (s, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 193.2, 158.4, 145.3, 135.6, 133.9, 131.7, 131.1, 129.8, 128.5, 128.2, 121.2, 120.2, 106.3, 55.3; MS (TOF-AP$^+$) $m/z$ 263 (100, [M+1]$^+$); HRMS (TOF-AP$^+$) $m/z$ [M+H]$^+$ calcd for C$_{18}$H$_{15}$O$_2$ 263.1072, found 263.1060. Anal. Calcd for C$_{18}$H$_{14}$O$_2$: C, 82.42; H, 5.38. Found: C, 82.41; H, 5.36.
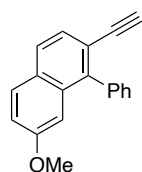


**2-Ethynyl-7-methoxy-1-phenylnaphthalene (N4).**[6] Following a adopted literature procedure,[8] a dried flask equipped with a magnetic stirring bar was loaded with the aldehyde **N3** (1.08 g, 4.12 mmol), pre-dried K$_2$CO$_3$ (1.70g, 12.4 mmol) and dissolved in dry methanol (40 mL). Then, the Ohira–Bestmann reagent

(2.37 g, 12.4 mmol) was added and the mixture stirred at room temperature for 4 h. The reaction mixture was next diluted with Et$_2$O, washed with aq. NaHCO$_3$ solution, dried (Na$_2$SO$_4$). After evaporation of solvent, the residue was passed through short column chromatography (SiO$_2$, pet. ether/AcOEt, 3:1) giving 1.05 g (99% yield) of alkyne **N4** as an oil. ^{1}H NMR (500 MHz, CDCl$_3$) $\delta$ 7.77 (d, $J$ = 8.9 Hz, 1H), 7.74 (d, $J$ = 8.4 Hz, 1H), 7.53-7.50 (m, 3 H), 7.47-7.43 (m, 3H), 7.17 (dd, $J_1$ = 8.9 Hz, $J_2$ = 2.5 Hz, 1H), 6.87 (d, $J$ = 2.4 Hz, 1H), 3.69 (s, 3H), 2.99 (s, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) $\delta$ 158.2, 142.5, 138.9, 133.4, 130.4, 129.6, 129.0, 128.3, 127.7, 127.3, 127.0, 119.4, 119.1, 105.4, 83.8, 80.7, 55.3; MS (TOF-AP[+]) $m/z$ 258 [100, M[+]] HRMS (TOF-AP[+]) $m/z$ [M]$^+$ calcd for C$_{19}$H$_{14}$O 258.1045, found 258.1037.
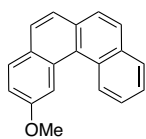


**2-Methoxybenzo[*c*]phenanthrene (N5).**[6] A solution of 2-ethenyl-7-methoxy-1-phenylnaphthalene (452 mg, 1.75 mmol) and PtCl$_2$ (46.6 mg, 0.175 mmol) in dry toluene (15 mL) was stirred at 80 °C for 24 h under N$_2$ atmosphere. Then, the reaction mixture was filtered through a short plug of silica gel (pet. eter/CH$_2$Cl$_2$, 2:1). The filtrate was concentrated under vacuum and the residue was purified by column chromatography (SiO$_2$, pet. ether/AcOEt, 20:1) giving 245 mg (54% yield) of 2-methoxybenzo[*c*]phenanthrene (**N5**) as a white solid. Mp 68-70 °C (EtOH). ^{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 9.20 (d, $J$ = 8.5 Hz, 1H), 8.60 (d, $J$ = 2.4 Hz, 1H), 8.02 (dd, $J_1$ = 7.8 Hz, $J_2$ = 1.5 Hz, 1H), 7.95 (d, $J$ = 8.8 Hz, 1H), 7.89 (d, $J$ = 8.5 Hz, 1H), 7.85 (d, $J$ = 8.4 Hz, 1H), 7.81 (d, $J$ = 8.5 Hz, 1H), 7.71 (d, $J$ = 8.5 Hz, 1H), 7.68-7.60 (m, 2H), 7.30 (dd, $J_1$ = 8.8 Hz, $J_2$ = 2.5 Hz, 1H), 4.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) $\delta$ 158.3, 133.4, 131.6, 130.6, 130.0, 128.7, 128.5, 127.5, 127.2, 127.1, 127.0, 126.6, 126.0, 125.7, 124.6, 116.4, 109.1, 55.6; MS (ESI(+)-TOF) $m/z$ 258 [100, M[+]] HRMS (ESI(+)-TOF) $m/z$ [M]$^+$ calcd for C$_{19}$H$_{14}$O 258.1045, found 258.1045. Anal. Calcd for C$_{19}$H$_{14}$O: C, 88.34; H, 5.46. Found: C, 88.63; H, 5.07.

***Precursor to phenol 5[7]***

<u>c) 9-Methoxydibenzo[*c,g*]phenanthrene (**M4**)</u> was synthesized according to a modified literature procedure, as shown in Scheme S3.
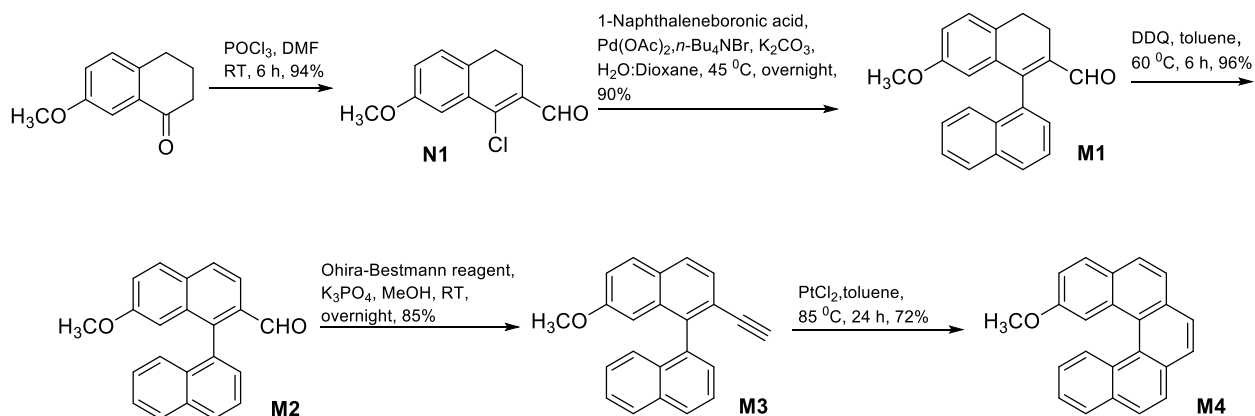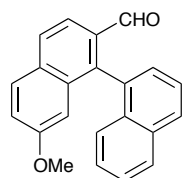
**Scheme S3**. 9-Methoxydibenzo[*c,g*]phenanthrene (**M4**).
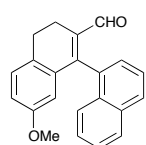
**7-Methoxy-3,4-dihydro-[1,1'-binaphthalene]-2-carbaldehyde (M1).**[7] Following a literature procedure,[7] a suspension of aldehyde **N1** (690 mg, 3.1 mmol), 1-naphthaleneboronic acid (580 mg, 3.4 mmol), *n*-Bu$_4$NBr (990 mg, 3.1 mmol), Pd(OAc)$_2$ (34 mg, 0.16 mmol), and K$_2$CO$_3$ (850 mg, 6.2 mmol) in degassed mixture of H$_2$O) (6 mL) and 1,4-dioxane (2 mL) was stirred at 45 °C for overnight. The rection mixture was cooled to room temperature, diluted with H$_2$O (20 mL) and then extracted with AcOEt (3x10 mL). The combined organic layer was dried (Na$_2$SO$_4$) and filtered. After evaporation of solvent the residue was purified on column chromatography (SiO$_2$, petroleum ether/AcOEt, gradient 0-6%) giving 877 mg (90%) of aldehyde **M1** as a pale yellow solid. Mp 104-106 °C (petroleum ether/AcOEt; lit.[7] 100-103 °C); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.39 (s, 1H), 7.96 (dd, $J_1$ = 12.4 Hz, $J_2$ = 8.4 Hz, 2H), 7.59-7.47 (m, 3H), 7.43-7.37 (m, 2H), 7.24 (d, $J$ = 8.4 Hz, 1H), 6.83 (dd, $J_1$ = 8.4 Hz, $J_2$ = 1.6 Hz, 1H), 6.22 (d, $J$ = 2.4 Hz, 1H), 3.51 (s, 3H), 3.01-2.84 (m, 3H), 2.73-2.65 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 193.3, 158.4, 153.1, 136.4, 136.3, 133.6, 132.82, 132.72, 130.4, 129.1, 128.69, 128.54, 126.9, 126.5, 126.0, 125.2, 114.8, 114.6, 55.3, 26.9, 20.7; ESI(+)-TOF *m/z* 315 (100, [M + H]$^+$); HRMS (ESI(+)-TOF) *m/z* [M + H]$^+$ calcd for C$_{22}$H$_{19}$O$_2$ 315.1385, found 315.1390. Anal. Calcd for C$_{22}$H$_{18}$O$_2$: C, 84.05; H, 5.77. Found: C, 84.07; H, 5.78.

**7-Methoxy-[1,1'-binaphthalene]-2-carbaldehyde (M2).**[7] Following a literature procedure,[7] a suspension of aldehyde **M1** (810 mg, 2.58 mmol) and DDQ (725 mg, 3.19 mmol) in toluene (15 mL) was stirred at 60 °C for 6 h. The mixture was cooled to room temperature, filtered through a short pad of Celite. The mixture was washed with 1M NaOH and the aqueous layer was extracted with toluene. The combined organic layer was dried (Na$_2$SO$_4$), filtered and solvent was evaporated. The

crude product was purified by column chromatography (SiO$_2$, petroleum ether/AcOEt, 19:1) giving 774 mg (96% yield) of aldehyde **M2** as a white solid. Mp 72-75 °C (pet ether/AcOEt, lit.[7] 75-76 °C); ^{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 9.67 (s, 1H), 8.06-8.03 (m, 2H), 8.00 (t, $J$ = 7.6 Hz, 2H), 7.91 (d, $J$ = 9.2 Hz, 1H), 7.68 (t, $J$ = 7.2 Hz, 1H), 7.55-7.51 (m, 2H), 7.37-7.33 (m, 1H), 7.30-7.26 (m, 2H), 6.66 (d, $J$ = 2.4 Hz, 1H), 3.51 (s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) $\delta$ 192.9, 158.4, 143.6, 134.5, 133.52, 133.47, 133.3, 132.7, 131.8, 129.8, 129.3, 129.1, 128.5, 126.9, 126.5, 126.3, 125.3, 121.3, 120.2, 106.3, 55.2; ESI(+)-TOF $m/z$ 313 (100, [M + H]$^+$); HRMS (ESI(+)-TOF) $m/z$ [M + H]$^+$ calcd for C$_{22}$H$_{17}$O$_2$ 313.1229, found 313.1225. Anal. Calcd for C$_{22}$H$_{16}$O$_2$: C, 84.59; H, 5.16. Found: C, 84.62; H, 5.20.
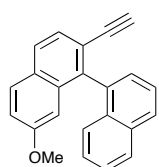
**2-Ethynyl-7-methoxy-1,1'-binaphthyl (M3).**[7] Following a literature procedure,[7] a dried flask equipped with a magnetic stirring bar was loaded with the aldehyde **M2** (770 mg, 2.47 mmol), pre-dried K$_3$PO$_4$ (682 mg, 3.21 mmol) and dissolved in dry methanol (25 mL). Then, the Ohira Bestmann reagent (1.42 g, 7.4 mmol) in methanol (8 mL) was added and the mixture stirred at room temperature for overnight. The reaction mixture was next diluted with Et$_2$O, washed with aq. NaHCO$_3$ solution, dried (Na$_2$SO$_4$). After evaporation of solvent, the residue was passed through short column chromatography (SiO$_2$, pet ether/AcOEt, 19:1) giving 647 mg (85%) of alkyne **M3** as a white solid. Mp 84-87 °C (pet ether/AcOEt, lit.[7] 87-89 °C); ^{1}H NMR (500 MHz, CDCl$_3$) $\delta$ 7.99 (m, 2H), 7.85 (dd, $J_1$ = 8.4 Hz, $J_2$ = 6.8 Hz, 2H), 7.65-7.58 (m, 2H), 7.51-7.46 (m, 2H), 7.32 (dd, $J_1$ = 4.8 Hz, $J_2$ = 1.2 Hz, 2H), 7.17 (dd, $J_1$ = 9.2 Hz, $J_2$ = 2.8 Hz, 1H), 6.53 (d, $J$ = 2.4 Hz, 1H), 3.47 (s, 3H), 2.79 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) $\delta$ 158.2, 140.8, 136.8, 134.2, 133.7, 132.5, 129.6, 128.8, 128.31, 128.28, 128.1, 127.6, 126.9, 126.2, 125.9, 125.6, 120.8, 119.2, 105.6, 83.5, 80.9, 55.2; MS (TOF-AP$^+$) $m/z$ 309 (100, [M + H]$^+$); HRMS (TOF-AP$^+$) $m/z$ [M+H]$^+$ calcd for C$_{23}$H$_{17}$O 309.1279, found 309.1266. Anal. Calcd for C$_{23}$H$_{16}$O: C, 89.58; H, 5.23. Found: C, 89.31; H, 5.52.
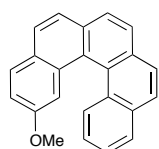
**9-Methoxydibenzo[c,g]phenanthrene (M4).**[7] Following a literature procedure, a solution of 2-ethynyl-7-methoxy-1,1'-binaphthalene (647 mg, 2.10 mmol) and PtCl$_2$ (56 mg, 0.21 mmol) in dry toluene (11 mL) was stirred at 85 °C for 24 h under N$_2$ atmosphere. Then, the reaction mixture was filtered through a short pad of Celite. The filtrate was concentrated under vacuum and the residue was purified by column chromatography (SiO$_2$, petroleum ether/AcOEt, 20:1) giving 466 mg (72%) of **M4** as a pale yellow solid. Mp 119-121 °C (hexane, lit.[7] 144-145 °C). ^{1}H NMR (400 MHz, CDCl$_3$) $\delta$ 8.49

(d, $J$ = 8.4 Hz, 1H), 7.98-7.85 (m, 8H), 7.79 (d, $J$ = 8.8 Hz, 1H), 7.54-7.50 (m, 1H), 7.36-7.32 (m, 1H), 7.19 (dd, $J_1$ = 8.8 Hz, $J_2$ = 2.8 Hz, 1H), 3.50 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.7, 132.9, 132.8, 132.3, 132.0, 130.4, 129.8, 129.5, 128.1, 127.8, 127.6, 127.4, 127.32, 127.30, 127.2, 126.6, 126.4, 126.3, 124.25, 124.23, 118.2, 109.3, 55.0; MS (TOF-AP$^+$) *m/z* 277 (100, [M - OCH$_3$]$^+$), 309 (20, [M + H]$^+$); HRMS (TOF-AP$^+$) *m/z* [M + H]$^+$ calcd for C$_{23}$H$_{17}$O 309.1279, found 309.1280. Anal. Calcd for C$_{23}$H$_{16}$O: C, 89.58; H, 5.23. Found: C, 89.37; H, 5.38.

## 2. NMR spectra
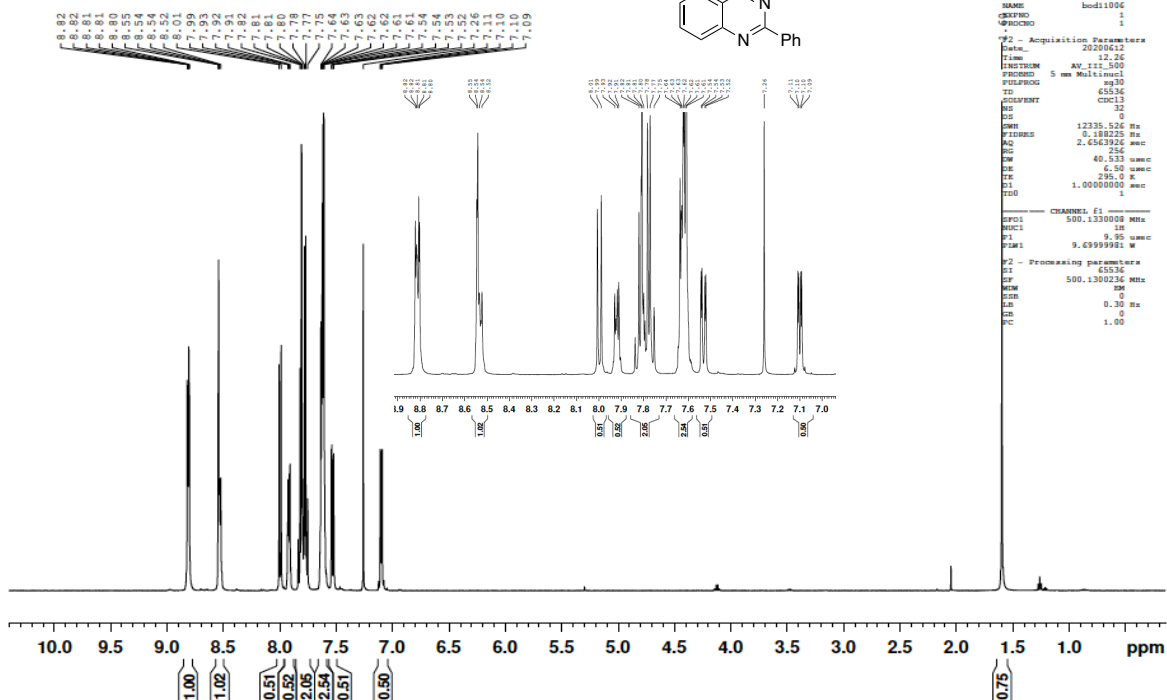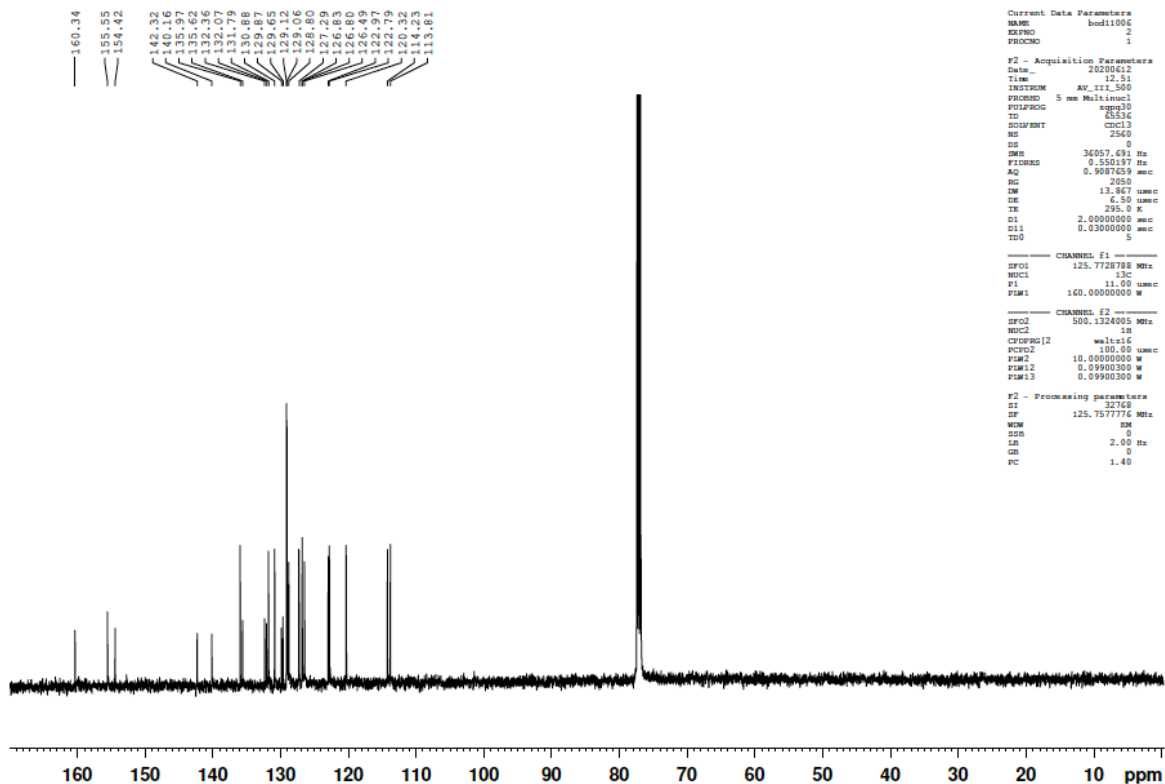


**Figure S1**. $^1$H and $^{13}$C{$^1$H} NMR of **3[5]** recorded in CDCl$_3$ at 500 and 100 MHz, respectively.
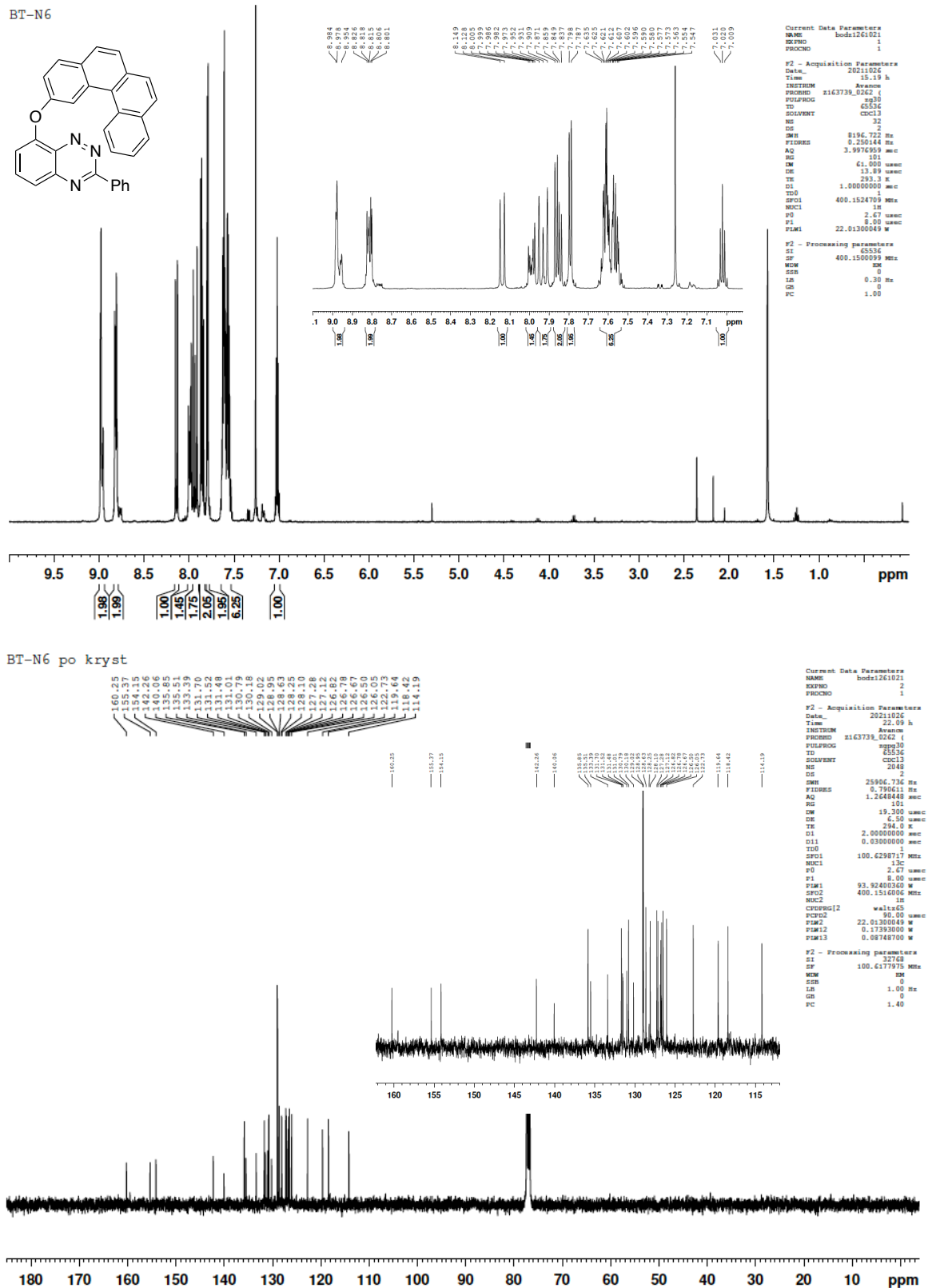
**Figure S2**. $^1$H and $^{13}$C{$^1$H} NMR of **3[6]** recorded in CDCl$_3$ at 400 and 100 MHz, respectively.

**Figure S3**. $^{1}$H and $^{13}$C{$^{1}$H} NMR of **3[7]** recorded in CDCl$_3$ at 400 and 100 MHz, respectively.

S 17

fen-3-OH
1H CDC13



fen-3-OH
13C{1H} CDC13



**Figure S4**. $^1$H and $^{13}$C{$^1$H} NMR of **5[5]** recorded in CDCl$_3$ at 400 and 100 MHz, respectively.

**Figure S5**. $^1$H and $^{13}$C{$^1$H} NMR of **5[6]** recorded in CDCl₃ at 400 and 100 MHz, respectively.
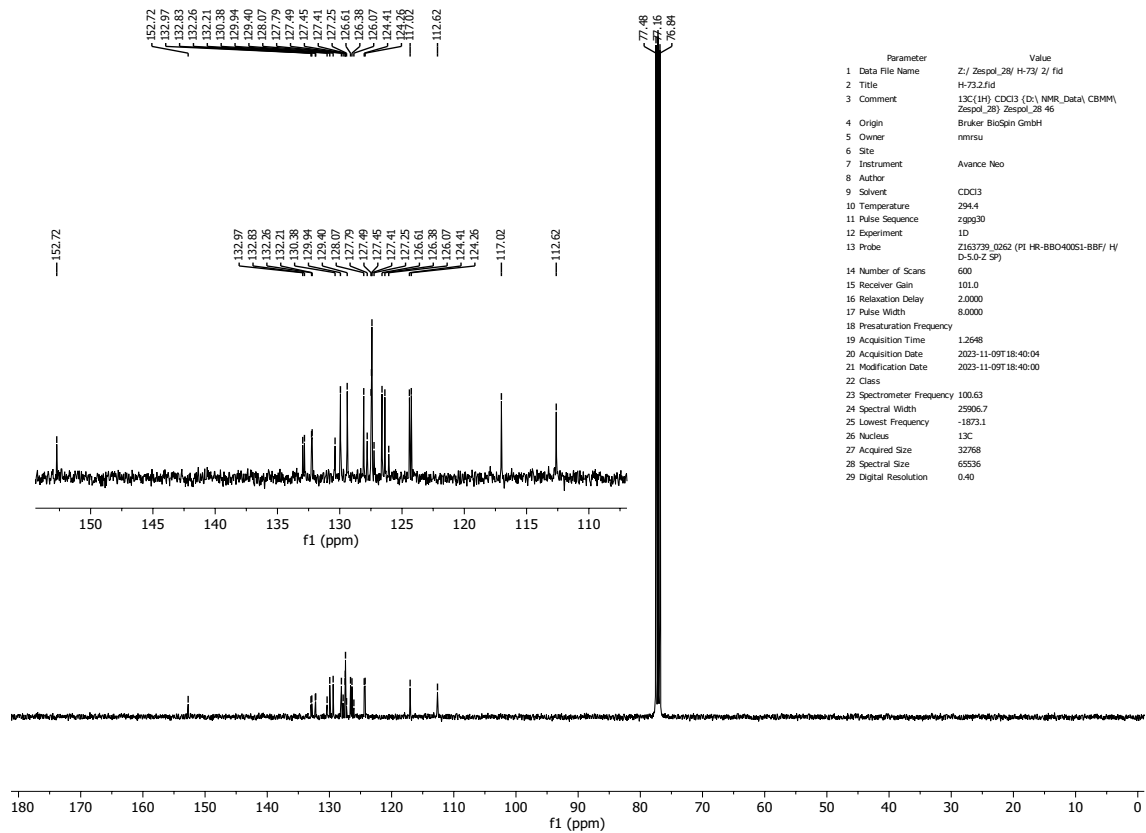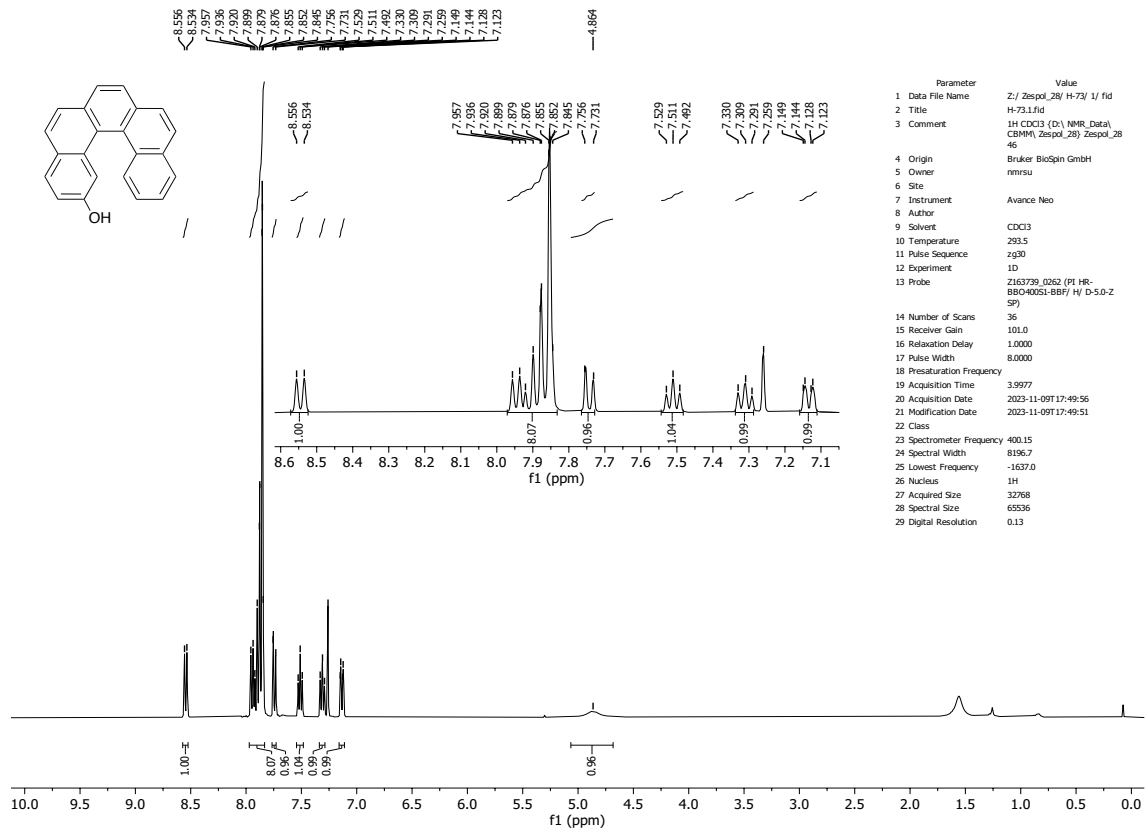
**Figure S6**. ^{1}H and ^{13}C{^{1}H} NMR of **5[7]** recorded in CDCl₃ at 400 and 100 MHz, respectively.
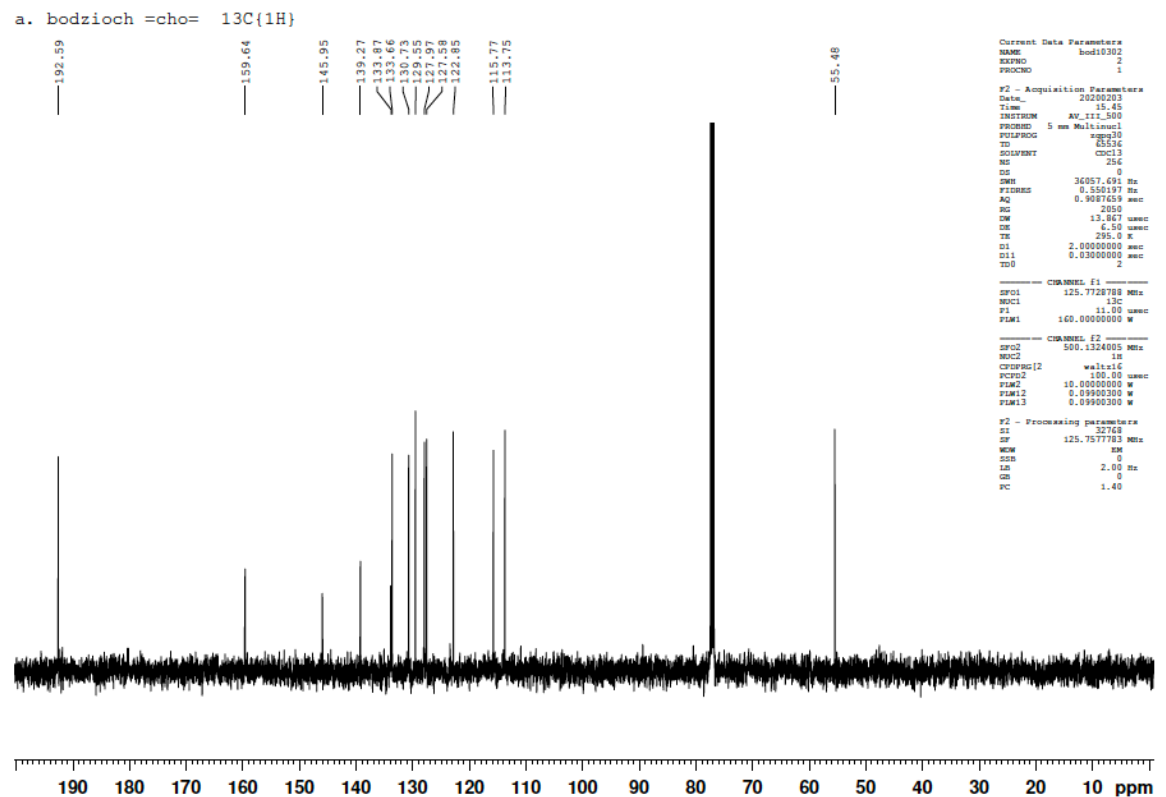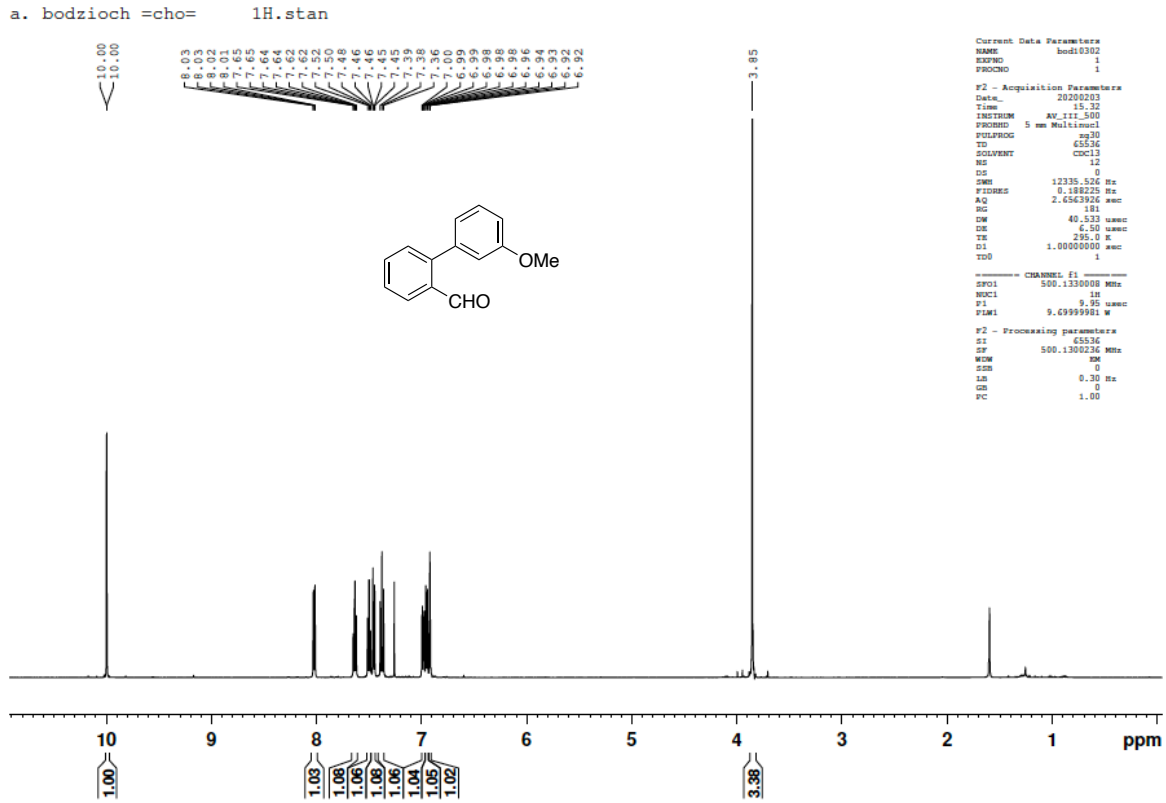
**Figure S7**. $^1$H and $^{13}$C{$^1$H} NMR of **S1** recorded in CDCl$_3$ at 500 and 125 MHz, respectively.
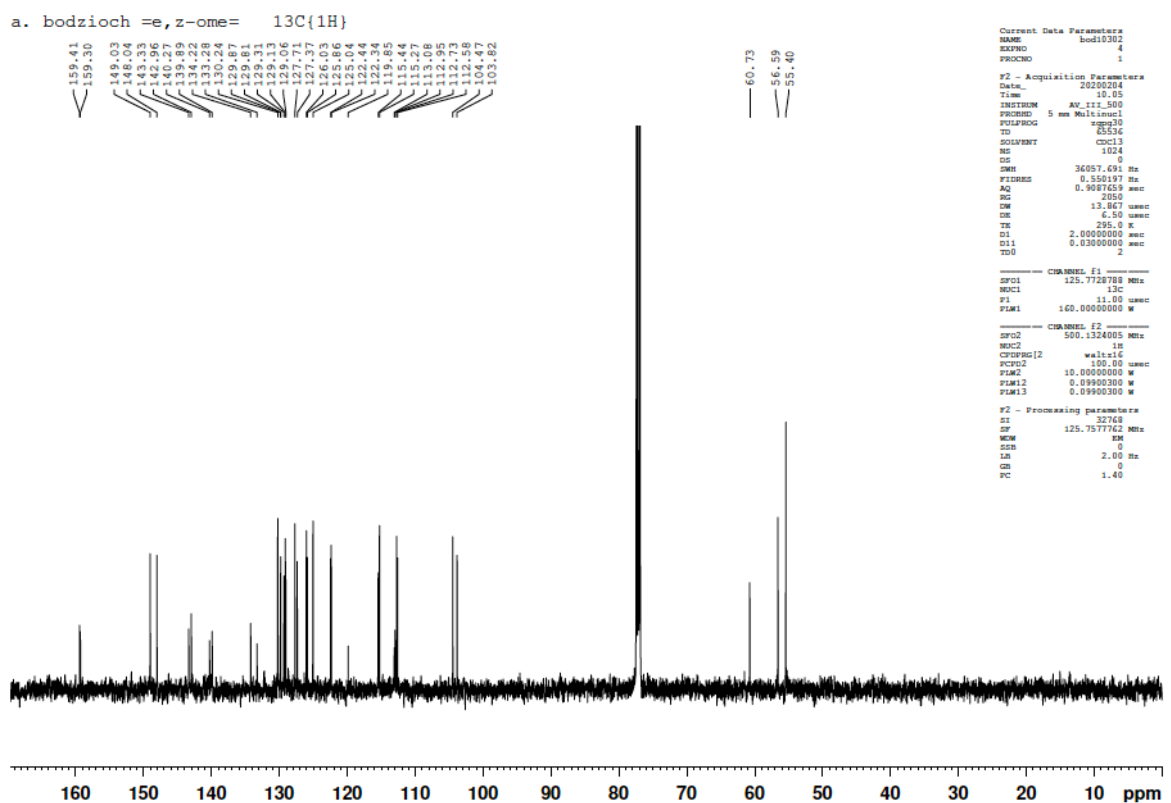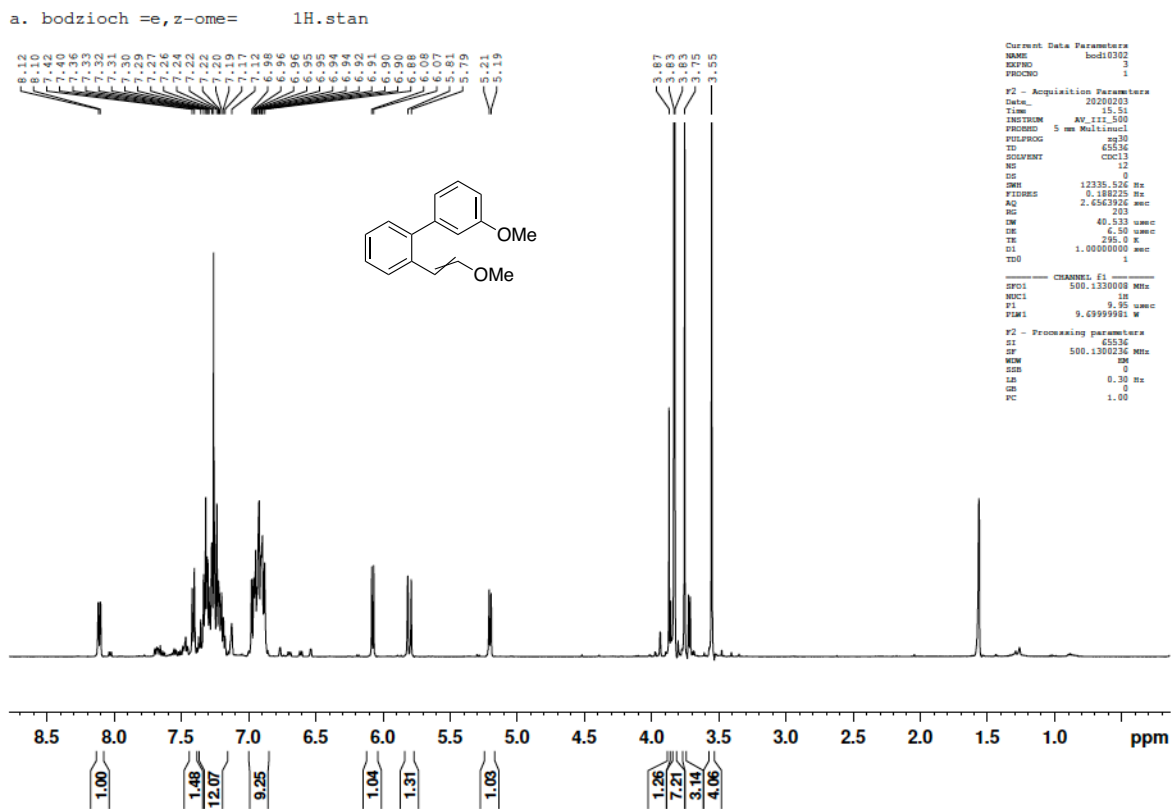
**Figure S8**. $^1$H and $^{13}$C{$^1$H} NMR of **S2** recorded in CDCl$_3$ at 500 and 125 MHz, respectively.

**Figure S9**. ¹H and ¹³C{¹H} NMR of **S3** recorded in CDCl₃ at 500 and 125 MHz, respectively.
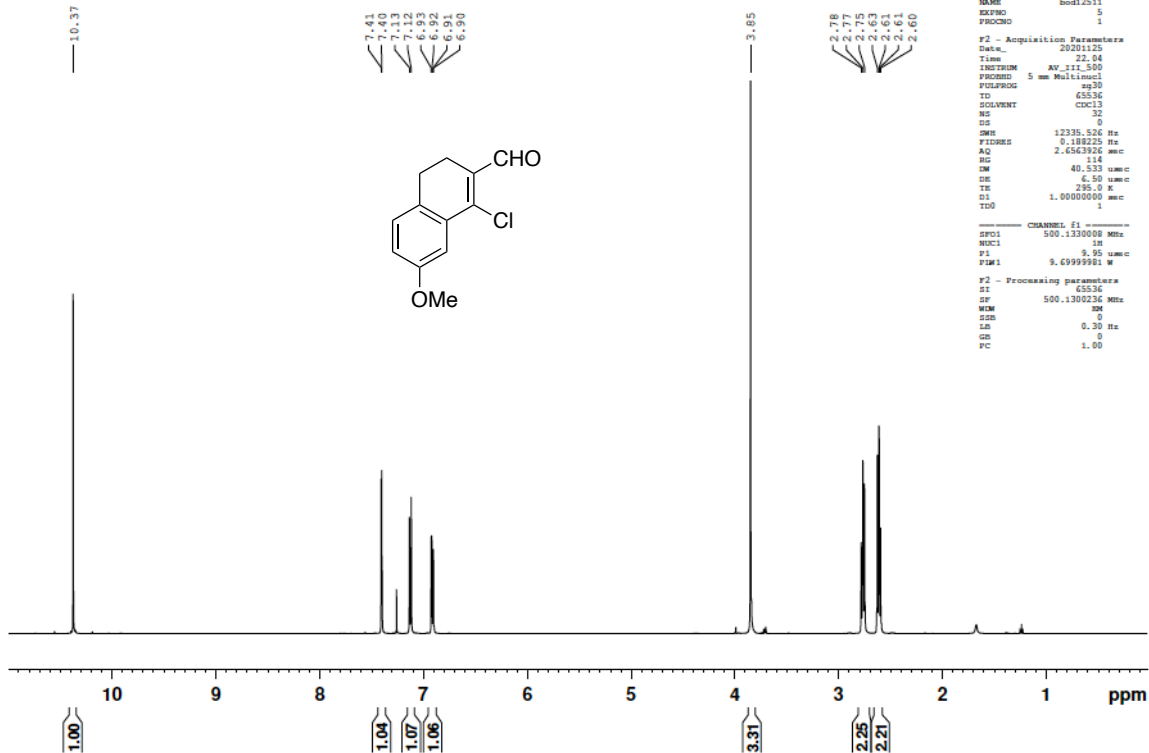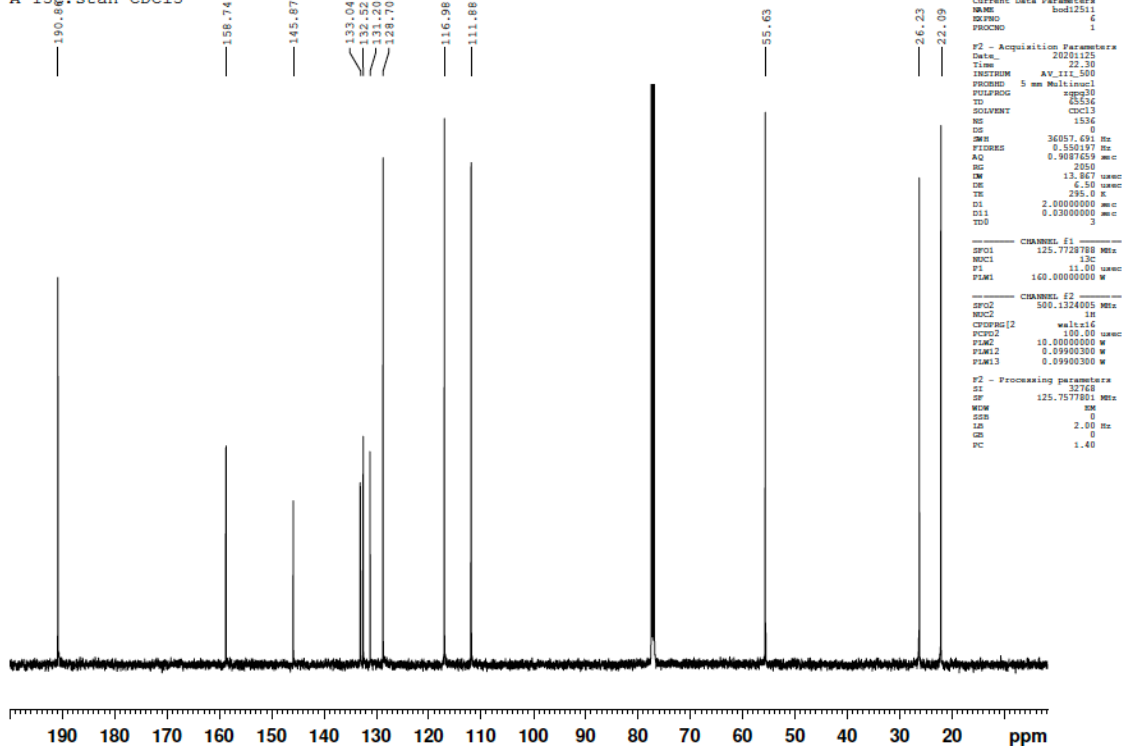
**Figure S10**. $^1H$ and $^{13}C\{^1H\}$ NMR of **N1** recorded in CDCl₃ at 500 and 125 MHz, respectively.
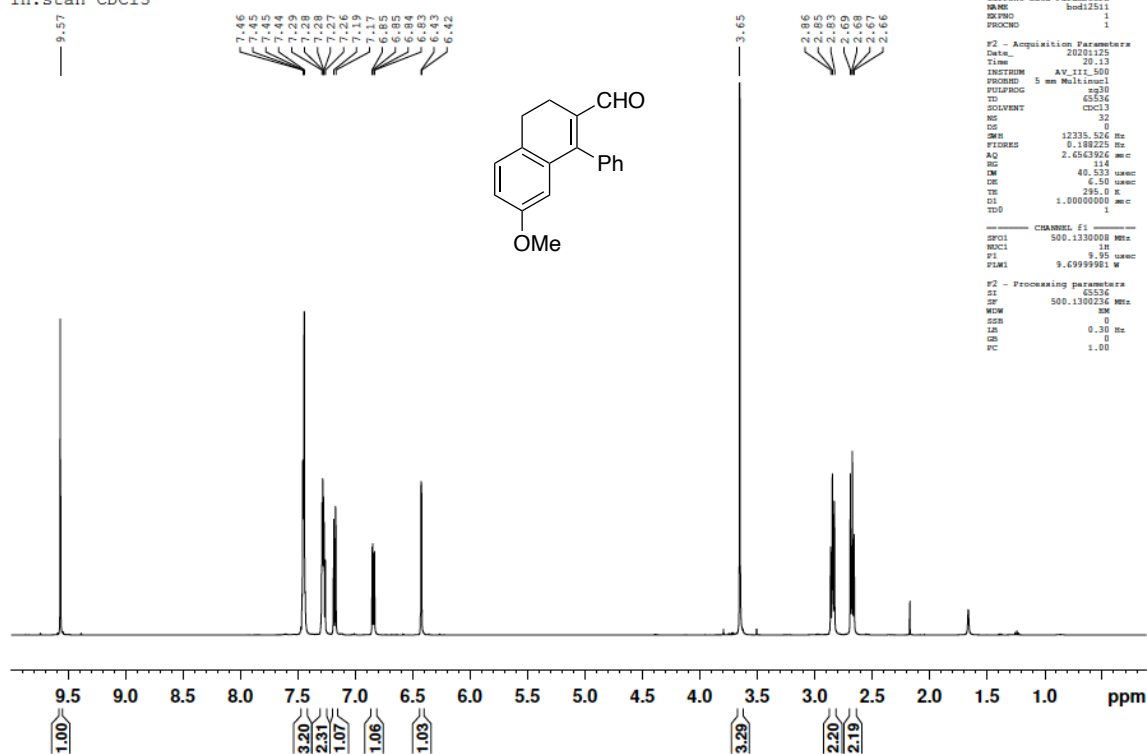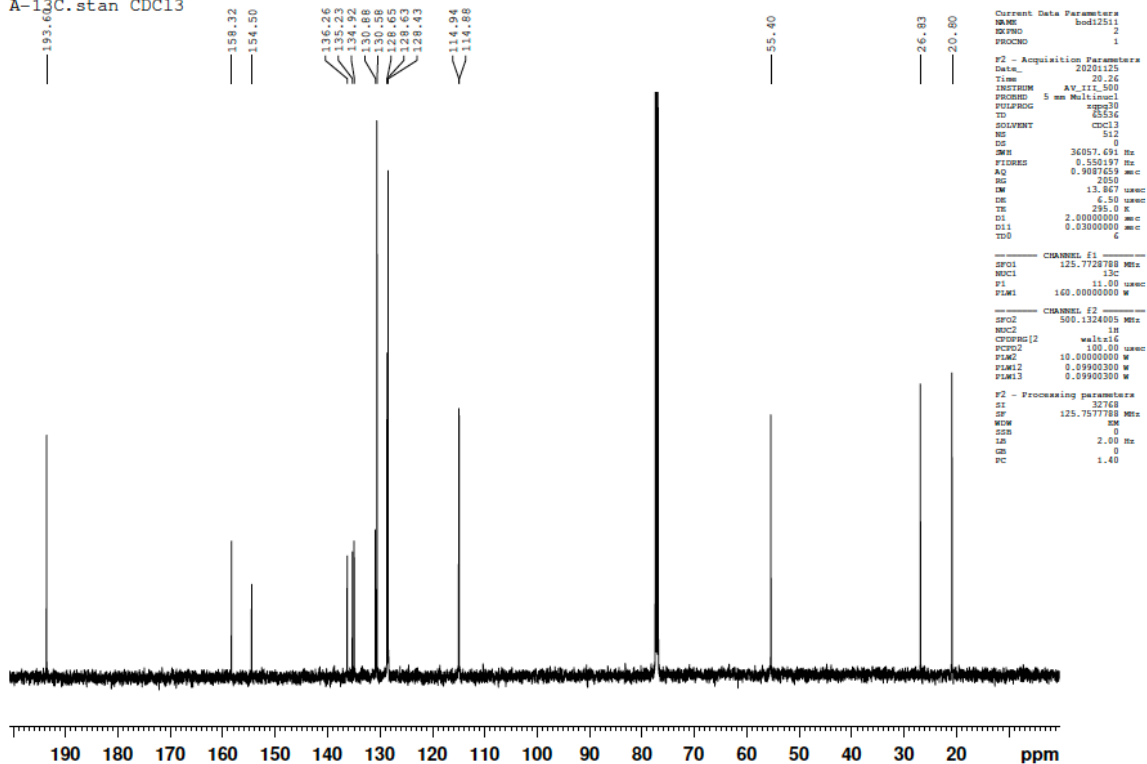
**Figure S11**. $^1$H and $^{13}$C{$^1$H} NMR of **N2** recorded in CDCl$_3$ at 500 and 125 MHz, respectively.
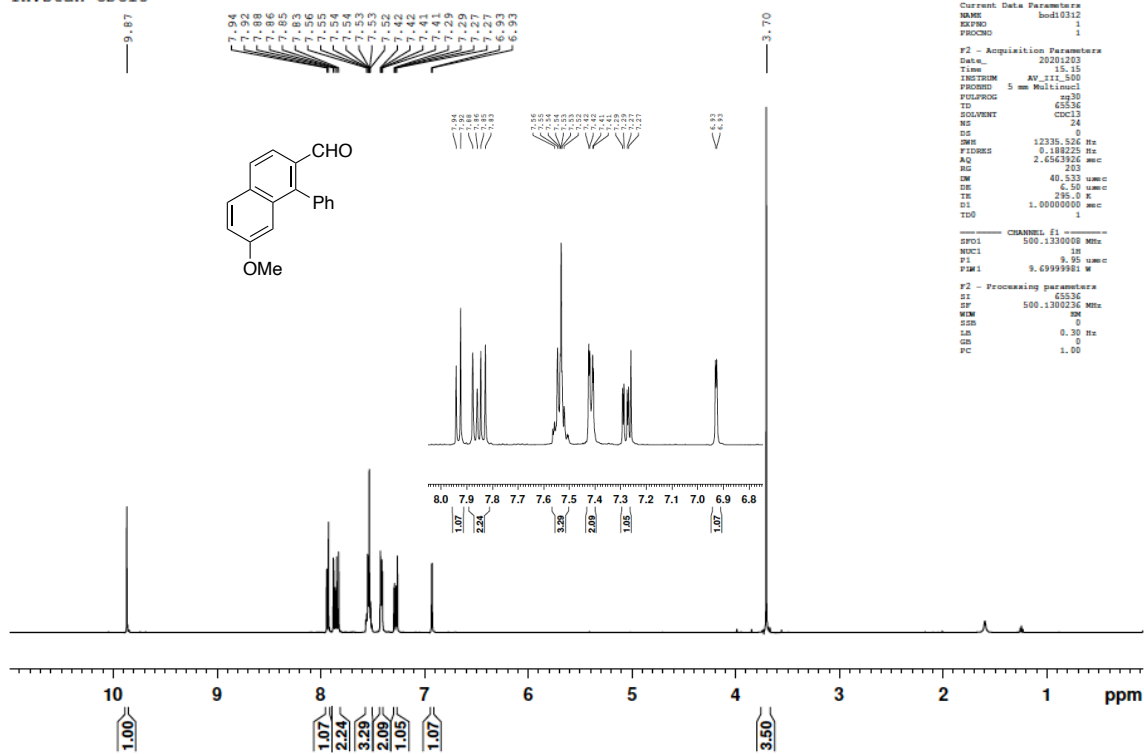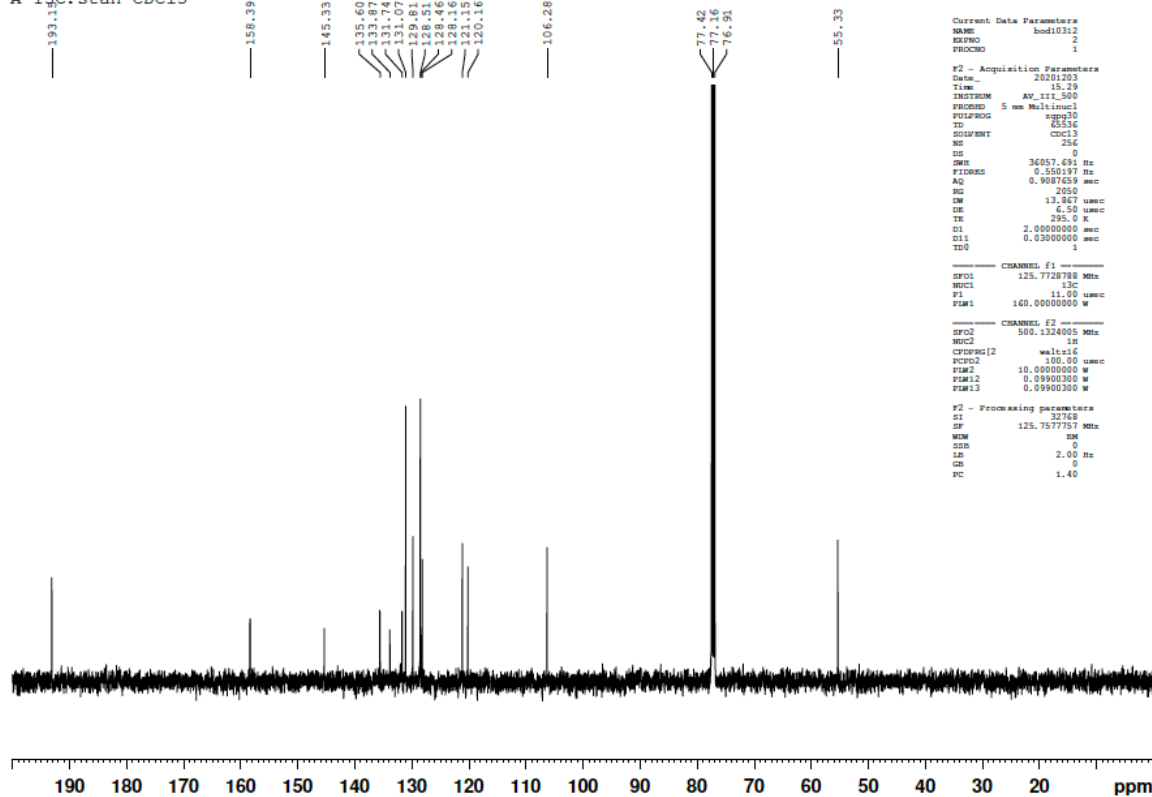
**Figure S12**. ^{1}H and ^{13}C{^{1}H} NMR of **N3** recorded in CDCl₃ at 500 and 125 MHz, respectively.
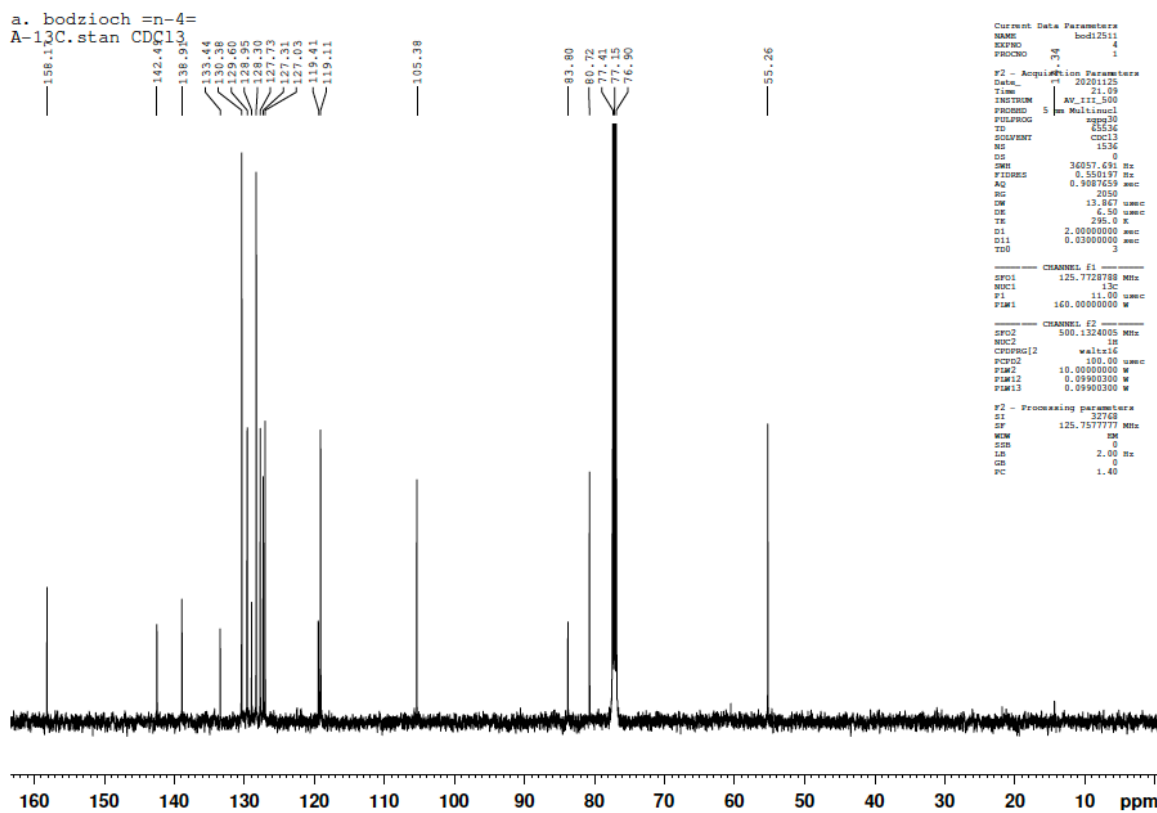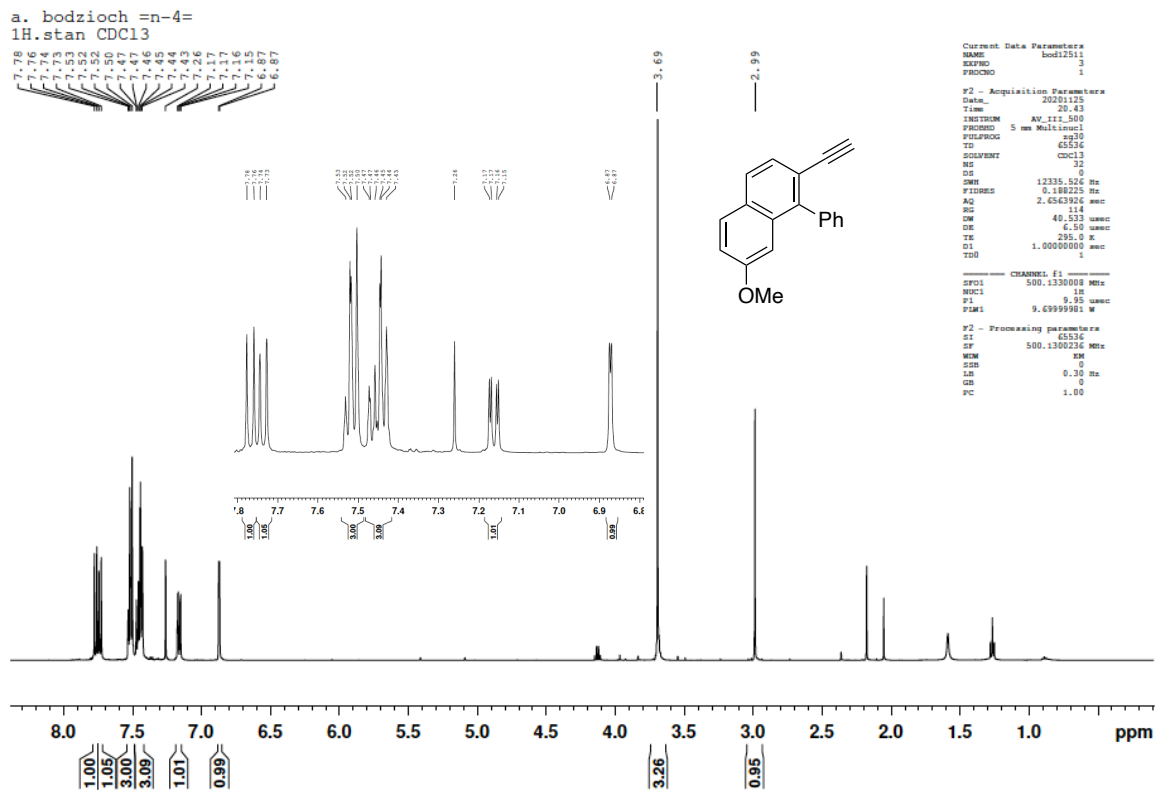
**Figure S13**. $^{1}H$ and $^{13}C\{^{1}H\}$ NMR of **N4** recorded in CDCl$_3$ at 500 and 125 MHz, respectively.

N5 po krystalizacji
1H CDCl3



N5
13C{1H} CDCl3
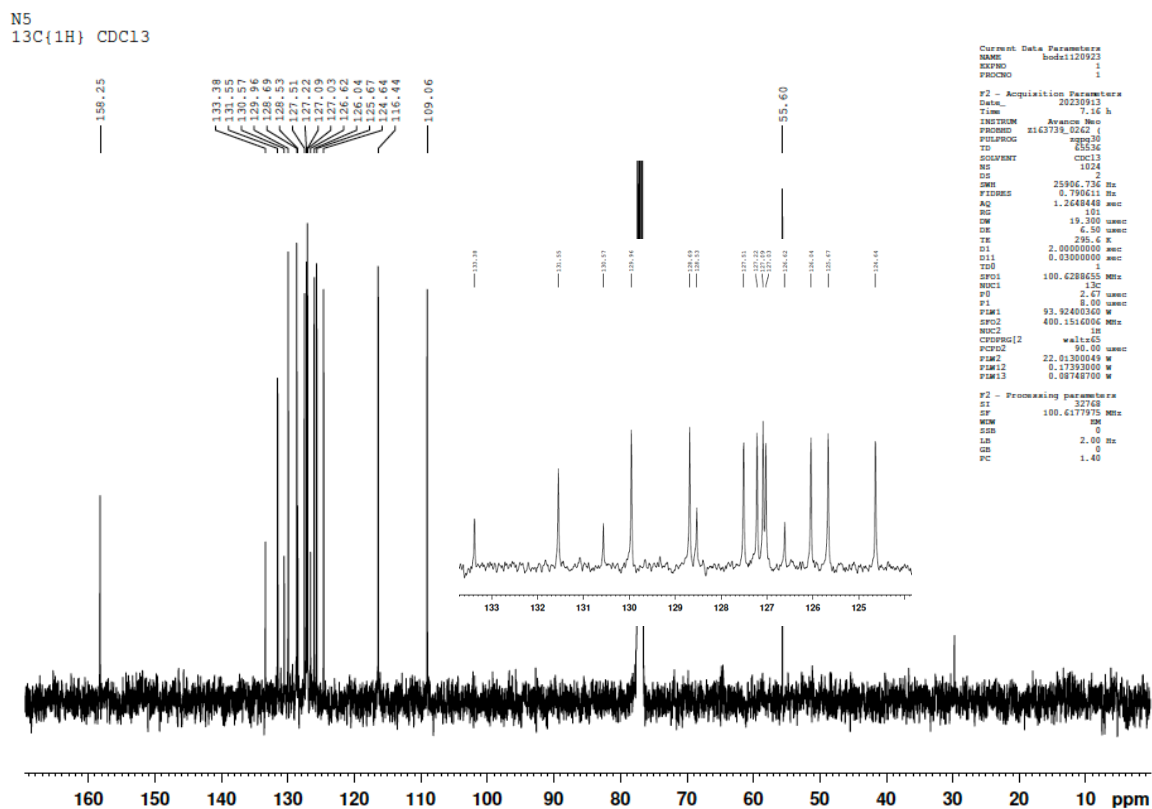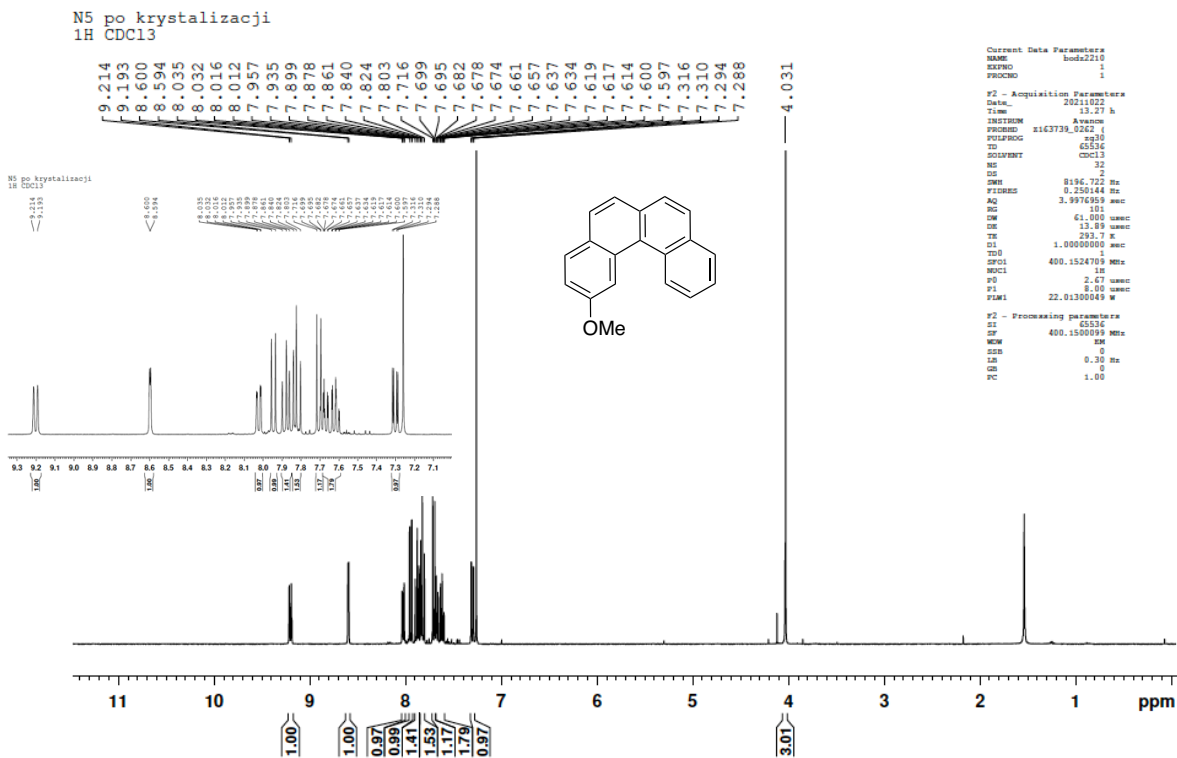


**Figure S14**. $^1$H and $^{13}$C{$^1$H} NMR of **N5** recorded in CDCl$_3$ at 400 and 100 MHz, respectively.
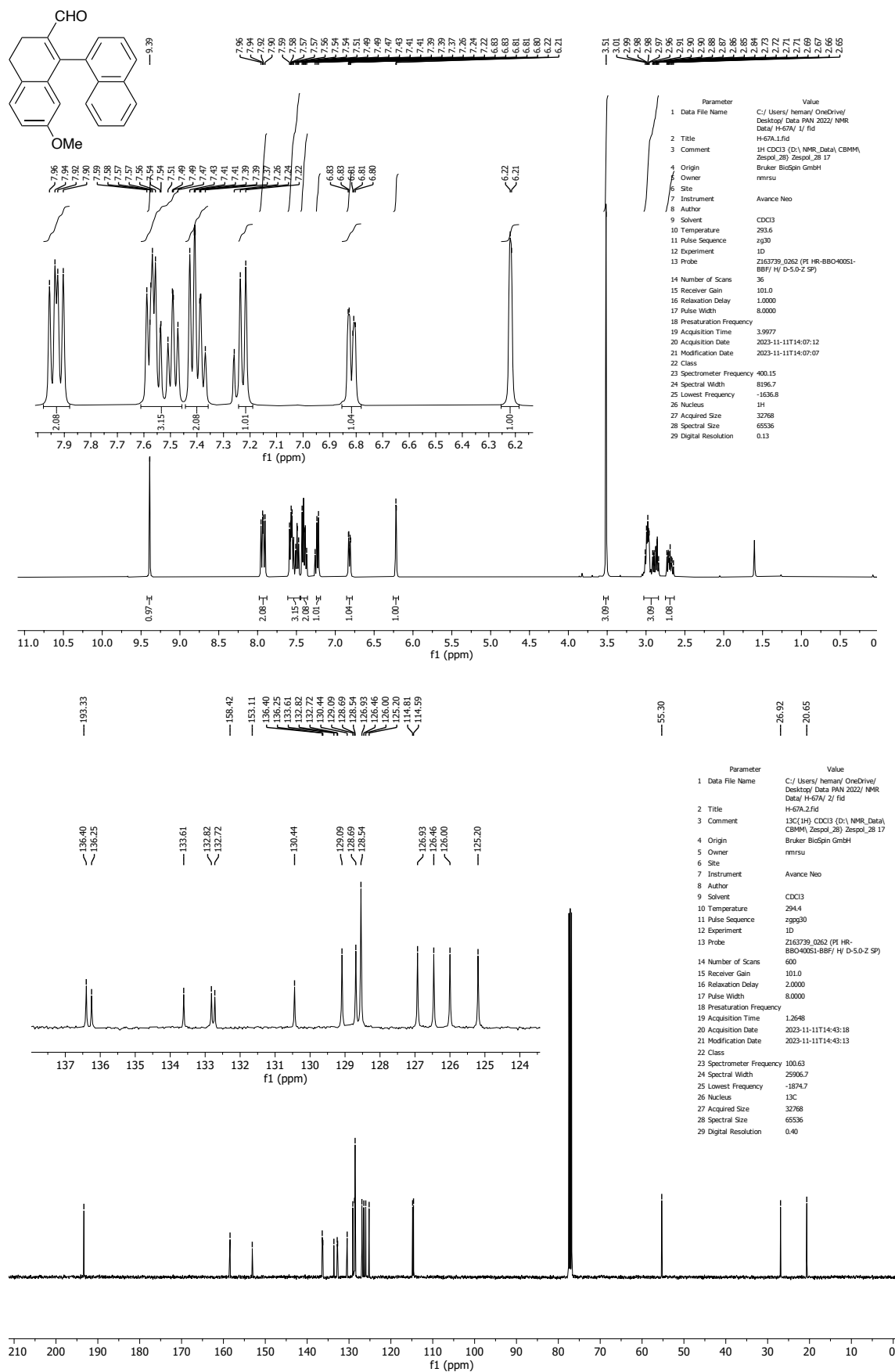
**Figure S15**. $^1$H and $^{13}$C{$^1$H} NMR of **M1** recorded in CDCl$_3$ at 400 and 100 MHz, respectively.

**Figure S16**. $^{1}H$ and $^{13}C\{^{1}H\}$ NMR of **M2** recorded in CDCl₃ at 400 and 100 MHz, respectively.
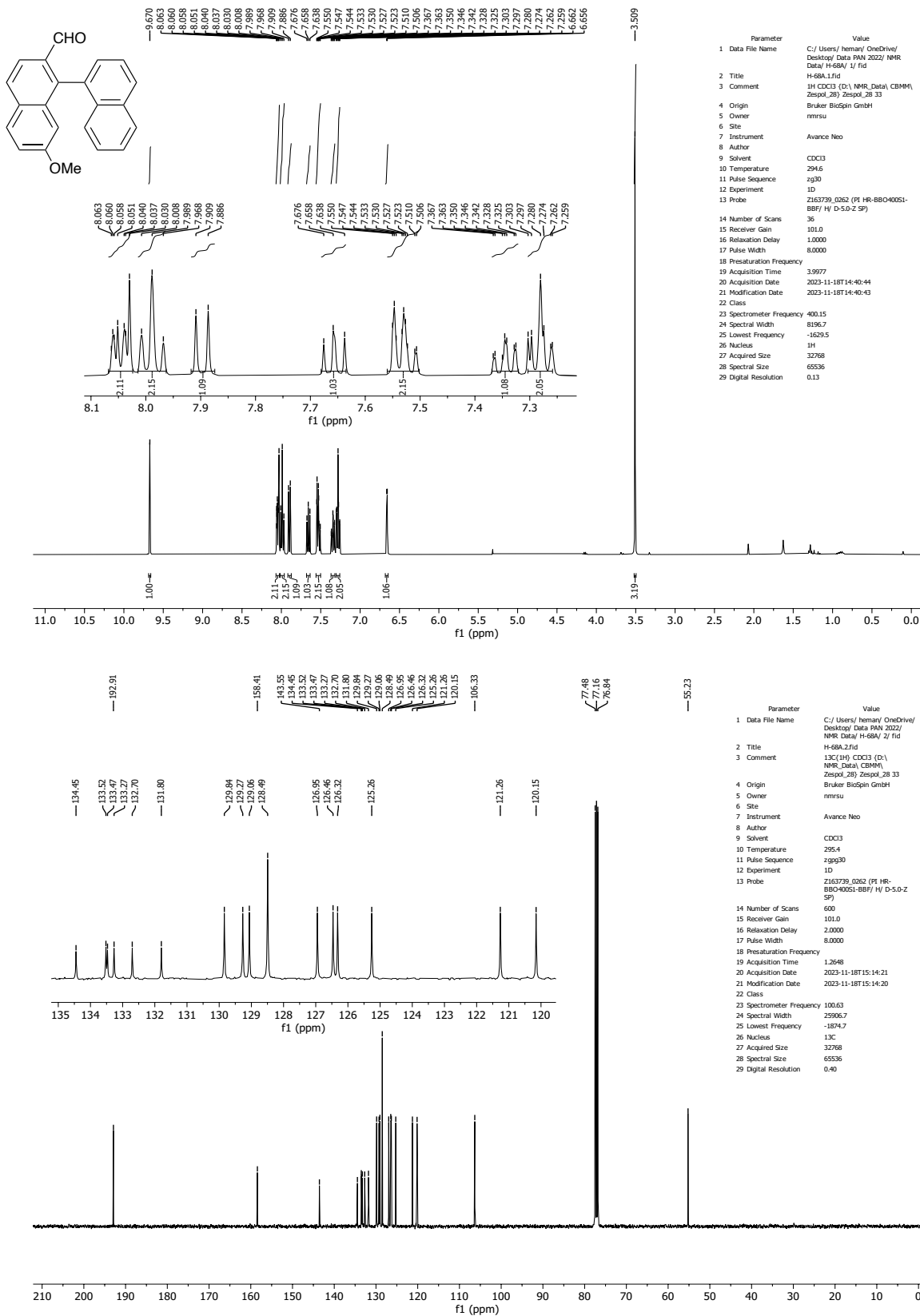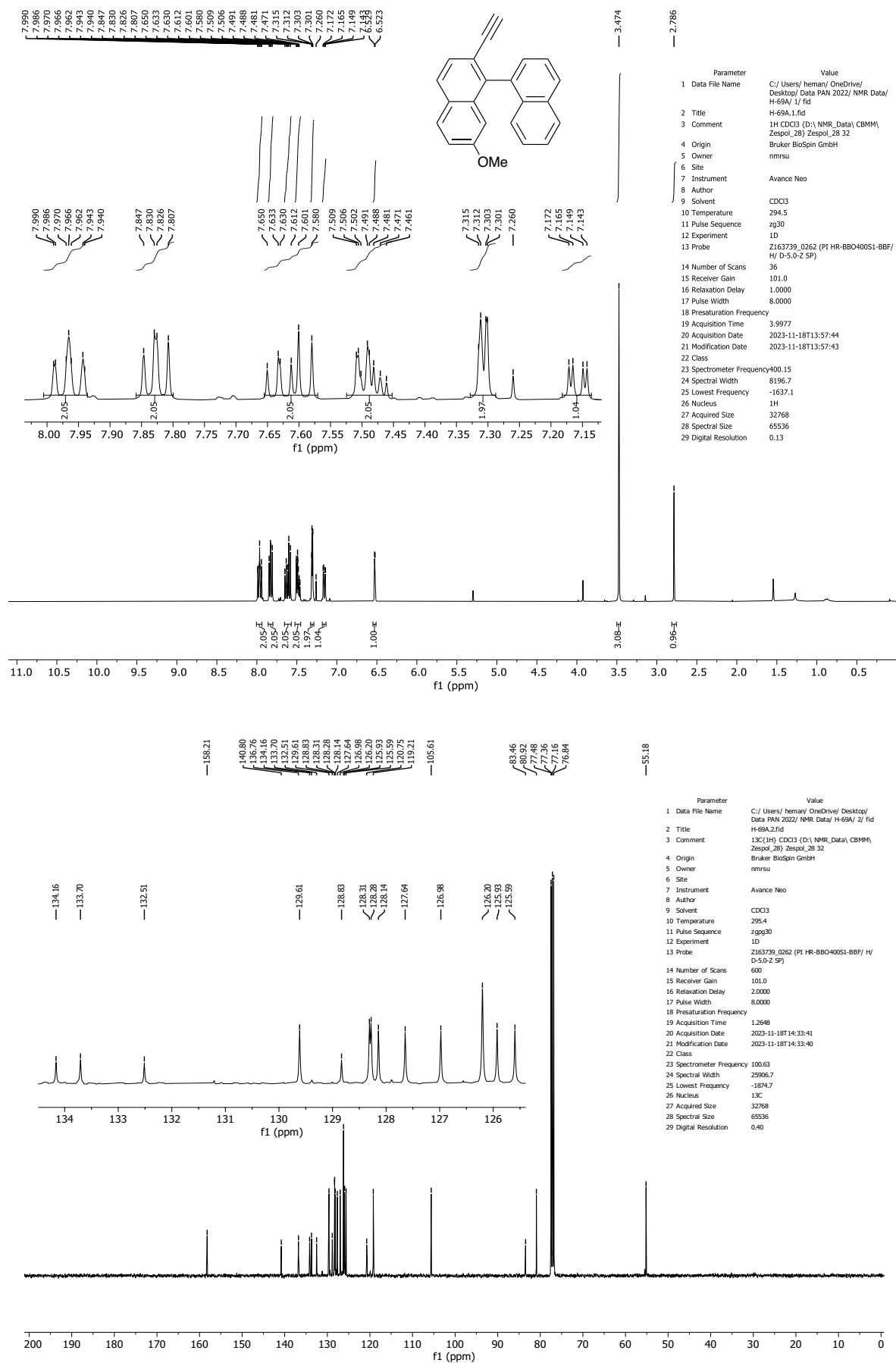
**Figure S17**. $^1$H and $^{13}$C{$^1$H} NMR of **M3** recorded in CDCl$_3$ at 400 and 100 MHz, respectively.

**Figure S18**. $^1H$ and $^{13}C\{^1H\}$ NMR of **M4** recorded in CDCl$_3$ at 400 and 100 MHz, respectively.

### 3.    XRD data collection and refinement

Single-crystal XRD measurements for radicals **1[5]** and **1[7]** and precursor **3[7]** were performed with a Rigaku XtaLAB Synergy, Pilatus 300K diffractometer. The measurement was conducted at 100(2) K using the Cu$K_\alpha$ radiation ($\lambda$ = 1.54184 Å). The data was integrated using CrysAlisPro program.[9] Intensities for absorption were corrected using multi-scan method as in SCALE3 ABSPACK scaling algorithm implemented in CrysAlisPro program.[9] CCDC: Files 2311971, 2312391, and 2339405 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures

#### *Structure solution and refinement*

The structures were solved with the ShelXT[10] structure solution program using Intrinsic Phasing and refined in the ShelXle[11] by the full-matrix least-squares minimization on $F^2$ with the ShelXL[12] refinement package. All non-hydrogen atoms were refined anisotropically, and C–H hydrogens were generated geometrically using the HFIX command as in ShelXL. Hydrogen atoms were refined isotropically and constrained to ride on their parent atoms. The crystal structure of helicene **1[5]** contains a solvent molecule that is disordered around two symmetry elements (3-fold rotoinversion axis and inversion center). The disorder was treated using SQUEEZE procedure[13] resulting in 22 electrons within a single void of a volume ~80 Å$^3$. It suggests the presence of an acetonitrile molecule used as the solvent for crystallization.

The crystal data and structure refinement descriptors are presented in Table S2. Molecular structures, partial packing diagrams, and a molecular overlay for radicals **1[5]** and **1[7]** and precursor **3[7]** are shown in Figures S19 – S24.

**Table S2. Selected structural data for radicals 1[5] and 1[7] and precursor 3[7]**

| | 1[5]<br>CCDC: 2339405 | 1[7]<br>CCDC: 2312391 | 3[7]<br>CCDC: 2311971 |
|---|---|---|---|
| Formula | $C_{27}H_{16}N_3O$ | $C_{35}H_{20}N_3O$ | $C_{35}H_{21}N_3O$ |
| Formula Weight | 398.43 | 498.54 | 499.55 |
| Crystal System | trigonal | monoclinic | monoclinic |
| Space Group | $R\overline{3}$ | $P2_1/c$ | $P2_1/n$ |
| $a$/Å | 43.1890(5) | 21.3059(3) | 15.5452(2) |
| $b$/Å | 43.1890(5) | 11.4684(2) | 4.78961(6) |
| $c$/Å | 5.1711(3) | 9.6844(1) | 32.4950(4) |
| $\alpha$/° | 90 | 90 | 90 |
| $\beta$/° | 90 | 94.6850(1) | 103.488(1) |
| $\gamma$/° | 120 | 90 | 90 |
| Volume/Å$^3$ | 8353.3(5) | 2358.42(6) | 2353.79(5) |
| Z | 18 | 4 | 4 |
| 2θ range for data collection/° | 7.09 to 157.5 | 8.328 to 159.37 | 5.594 to 157.632 |
| Index ranges | $-54 \le h \le 54$, $-52 \le k \le 53$, $-6 \le l \le 5$ | $-27 \le h \le 26$, $-13 \le k \le 14$, $-12 \le l \le 9$ | $-19 \le h \le 18$, $-6 \le k \le 4$, $-38 \le l \le 40$ |
| No. of measured, independent, and observed [$I>2\sigma(I)$] reflections | 28218,3920, 3106 | 44352, 4960,4557 | 28677, 4812, 4426 |
| $R_{int}$ | 0.0380 | 0.0387 | 0.0203 |
| Goodness-of-fit on $F^2$ | 1.029 | 1.026 | 1.040 |
| Final $R$ indexes [$F^2 > 2\sigma(F^2)$] | $R_1 = 0.0375$, $wR_2 = 0.0947$ | $R_1 = 0.0383$, $wR_2 = 0.0991$ | $R_1 = 0.0318$, $wR_2 = 0.0830$ |
| Final $R$ indexes [all data] | $R_1 = 0.0505$, $wR_2 = 0.1022$ | $R_1 = 0.0412$, $wR_2 = 0.1013$ | $R_1 = 0.0347$, $wR_2 = 0.0852$ |
| Data/restraints/parameters | 3920/0/280 | 4960/0/352 | 4812/0/353 |
| Largest diff. peak/hole Å$^{-3}$ | 0.20/-0.18 | 0.20/-024 | 0.23/-0.18 |
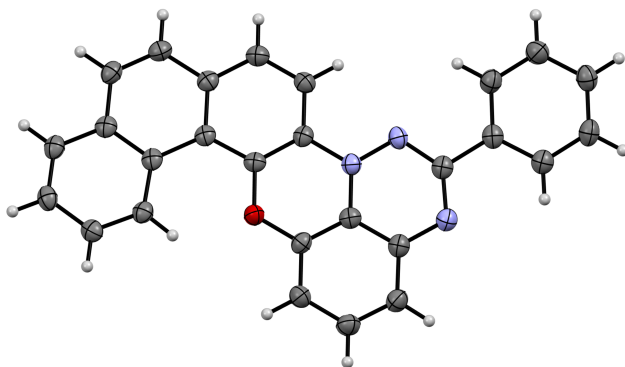


**Figure S19**. Molecular structure of radical **1[5]**. Displacement ellipsoids are drawn at 50% probability level.
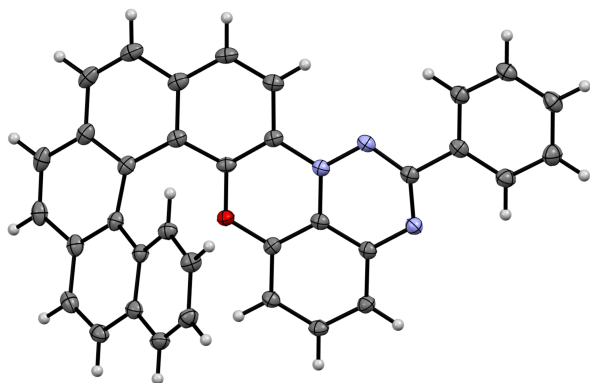
**Figure S20**. Molecular structure of radical **1[7]**. Displacement ellipsoids are drawn at 50% probability level.

The solid-state structure of precursor **3[7]** demonstrates dimensions of the heterocyclic fragment typical for this ring system.[14] The angle between the mean planes of the terminal benzene rings in the [5]helicene fragment in **3[7]** is 56.6° (Figure S21), while the analogous angle in **1[7]** is 48.6°. The former value compares to 45.1° in an *O*-methyl derivative of phenol **5[7]**.[7] The planes of the benzo[*e*][1,2,4]triazine and the benzenoxy ring of the carbohelicene fragment form an angle of 46.1°, which positions the heterocycle nearly orthogonal (89.9°) to the terminal benzene ring of the carbohelicene.
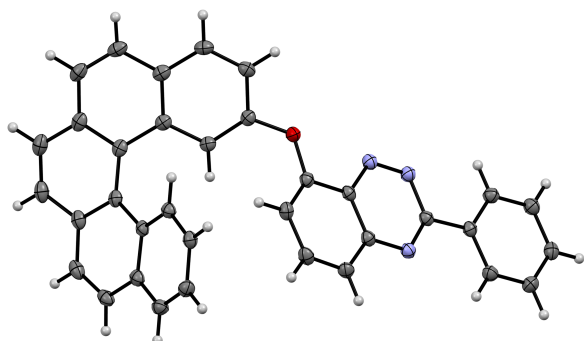


**Figure S21**. Molecular structure of precursor **3[7]**. Displacement ellipsoids are drawn at 50% probability level.

In the crystal structure of radical **1[5]** MeCN solvent molecules form channels extending along the [0 0 1] direction, around which molecules of radical **1[5]** are assembled in six stacks (Figure S22). The stacks are stabilized by π···π interactions defined by C···C contacts of 3.295 Å (0.105 Å inside the vdW separation). Neighboring stacks around the solvent channel are associated through C–H···N interactions with the H···N distance 0.337 Å shorter than the sum of vdW radii. The phenyl rings form a hydrophobic interior of the resulting hexagonal tubes (Figure S22). The

lack of strong electrostatic interactions between radical and solvent molecules gives rise to significant positional disorder of the latter in the crystal.

The structure of helical radical **1[7]** is stabilized by C-H⋯O hydrogen bonds (with the H⋯O distance 0.256 Å inside the vdW separation) forming double chains propagating along the [0 0 1] direction. Adjacent chains are linked by C–H⋯π interactions defined by the H⋯C distance of 2.689Å (0.211 Å inside the VdW separation, Figure S23).
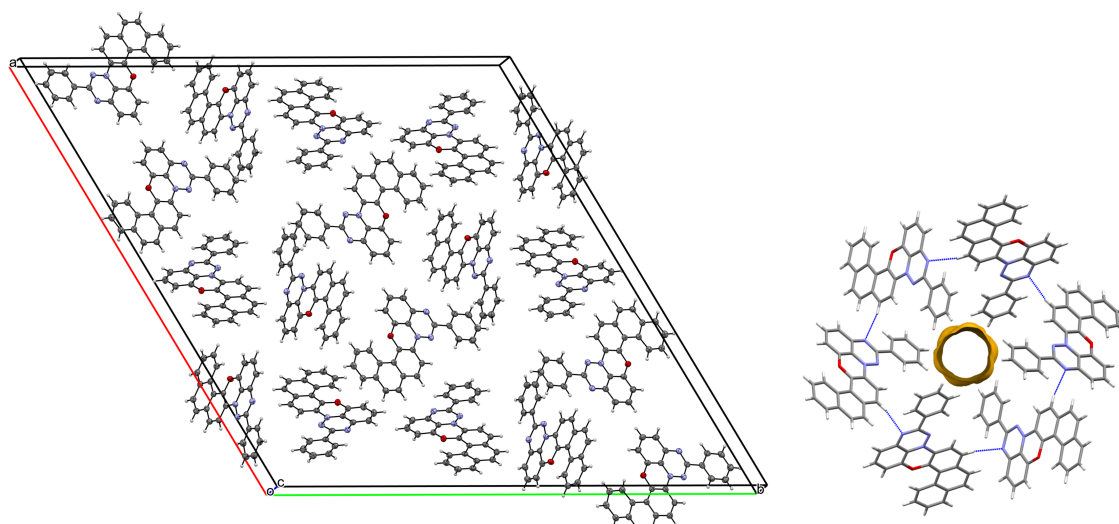


**Figure S22**. Two views of partial packing diagram of radical **1[5]**.
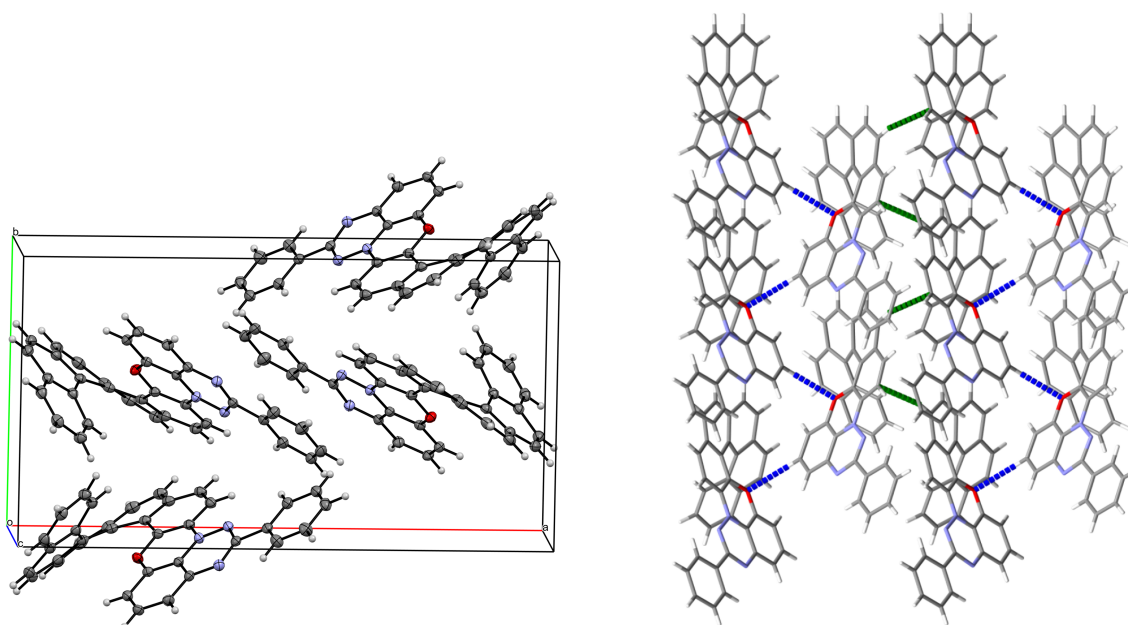


**Figure S23**. Two views of partial packing diagram of radical **1[7]**.
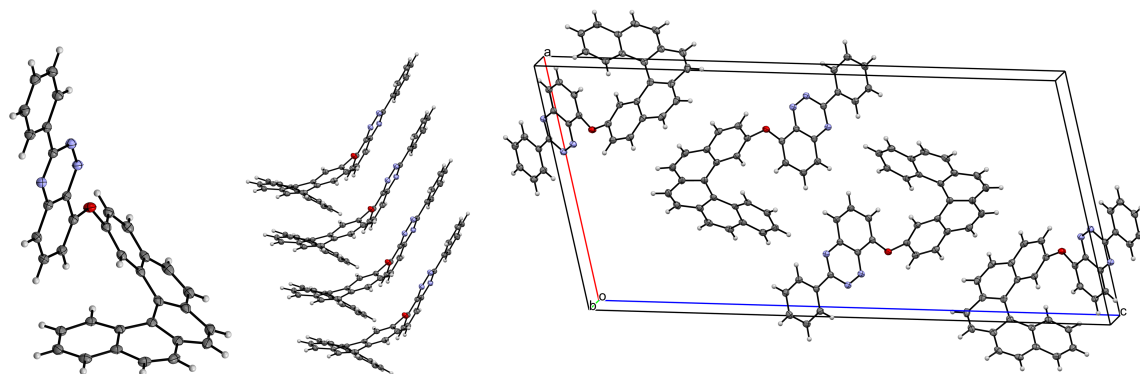
**Figure S24**. Left: XRD molecular structure of precursor **3[7]**. Middle and right: Partial crystal packing of **3[7]**. Atomic displacement ellipsoids are drawn at 50% probability level. Color code: oxygen-red, nitrogen-blue, carbon-black, hydrogen-grey.

## 4.     UV-vis spectroscopy

Electronic absorption spectra for radicals **1[n]** were recorded were recorded on a Jasco V770 spectrometer in spectroscopic grade $CH_2Cl_2$ at concentrations in a range $1.5\text{–}10\times10^{-5}$ M and fitted to the Beer–Lambert law. Results are shown in Figures S25–S27.
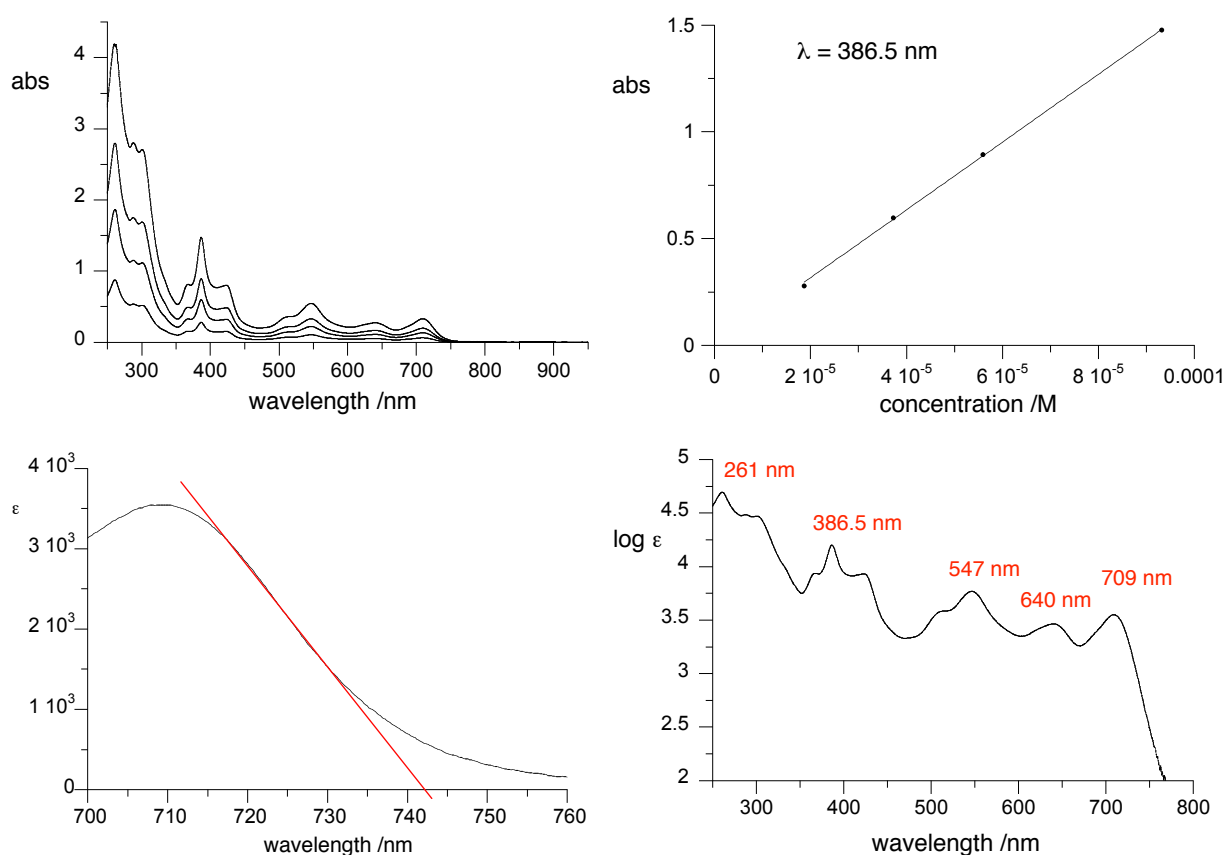


**Figure S25**. Clockwise: electronic absorption spectra for helicene **1[5]** in $CH_2Cl_2$ for four concentrations and determination of molar extinction coefficient $\varepsilon$ at $\lambda = 386.5$ nm (best fit function: $\varepsilon = 15{,}875(88)\times$conc, $r^2 = 0.9996$), molar excitation $log\ (\varepsilon)$, and determination of onset of optical absorption.
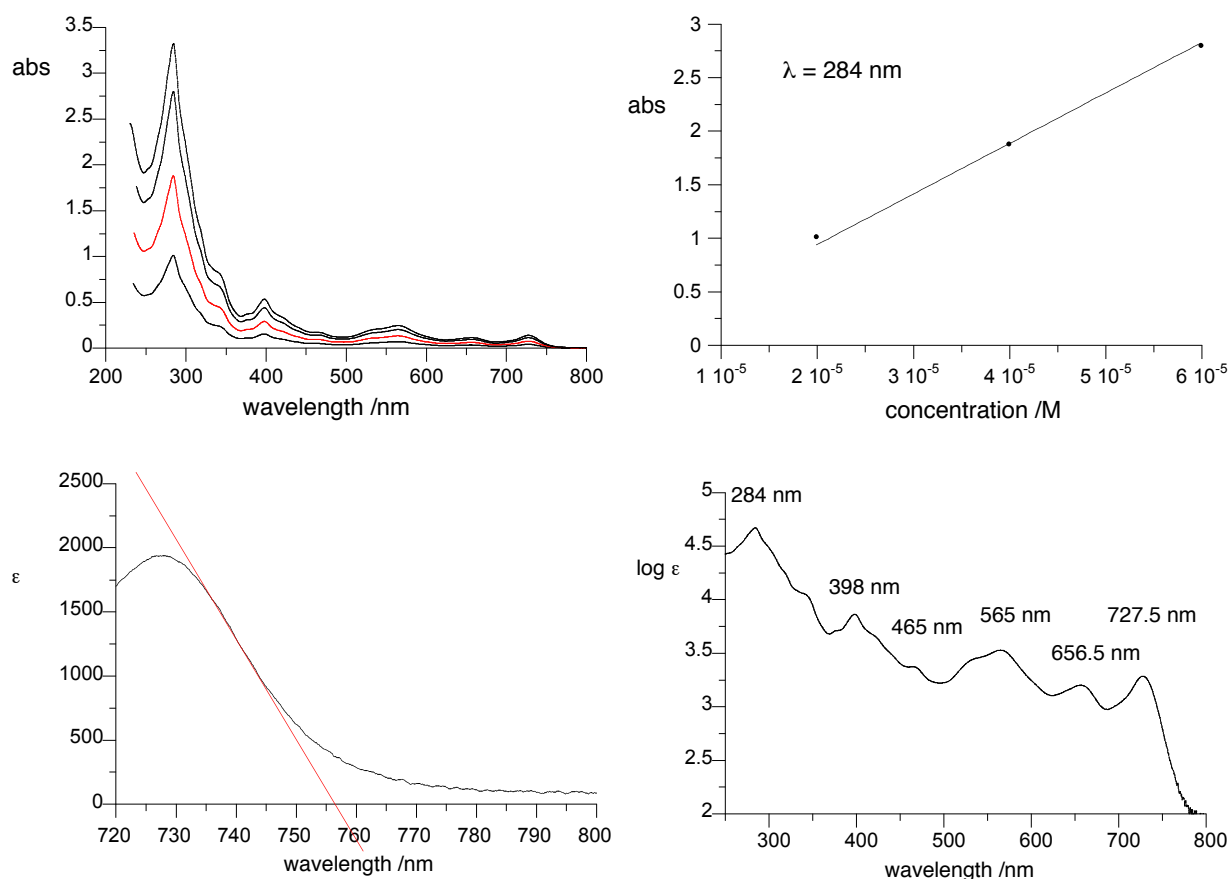
**Figure S26**. Clockwise: electronic absorption spectra for helicene **1[6]** in $CH_2Cl_2$ for four concentrations and determination of molar extinction coefficient $\varepsilon$ at $\lambda = 284$ nm (best fit function: $\varepsilon = 47{,}174(743) \times$conc, $r^2 = 0.996$), and a molar excitation *log* ($\varepsilon$) plot. and determination of onset of optical absorption.
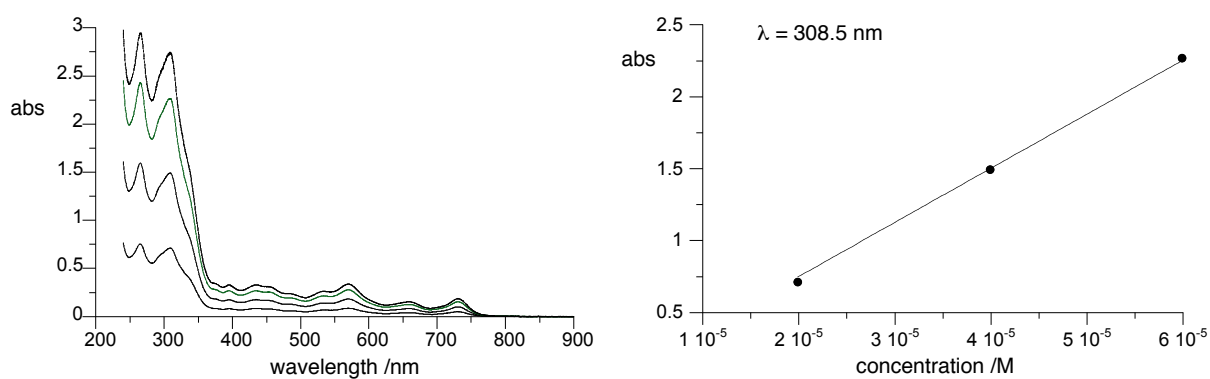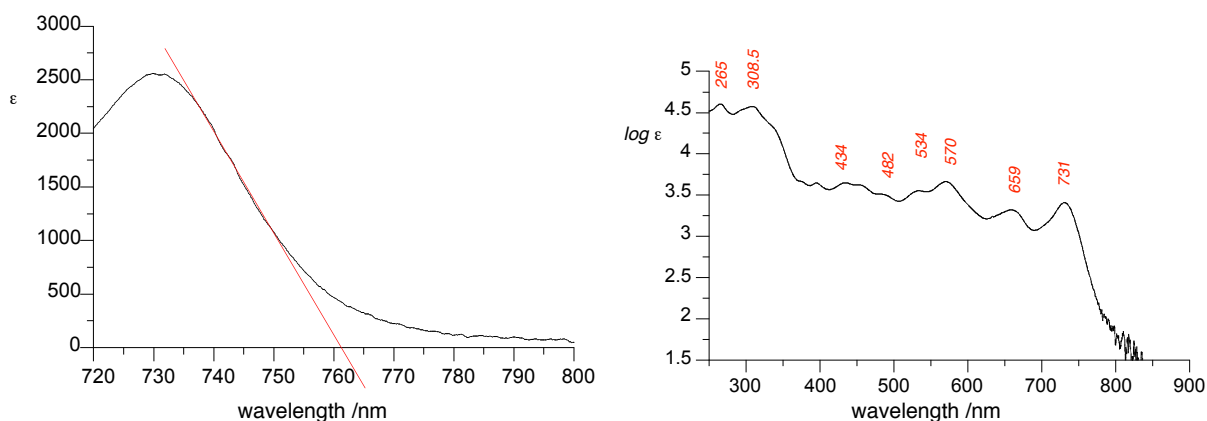
**Figure S27**. Clockwise: electronic absorption spectra for helicene **1[7]** in $CH_2Cl_2$ for four concentrations and determination of molar extinction coefficient $\varepsilon$ at $\lambda = 308.5$ nm (best fit function: $\varepsilon = 37.593(380)\times$conc, $r^2 = 0.999$), molar excitation $log$ ($\varepsilon$) plot, and determination of onset of optical absorption.

## 5.     Chiral HPLC analysis and resolution

Chiral HPLC separation was performed using Phenomenex Lux® 5 µm i-Amylose-3 column (250 × 4.6 mm) and solvent system consisting of hexane (40%), $CH_2Cl_2$ (58.8%) $i$-PrOH (1%) and $Et_3N$ (0.2%). The flow rate was 0.8 mL min$^{-1}$. Example of chromatogram is shown in Figure S28.
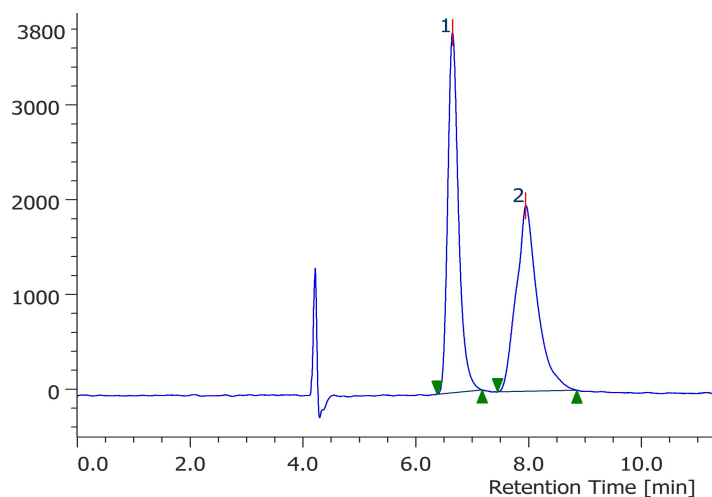


**Figure S28**. Chiral HPLC analysis of racemic radical **rac-1[7]** using Phenomenex Lux® 5 µm i-Amylose-3 column monitored at 365 nm. Hexane/$CH_2Cl_2$ 2:3, containing $i$-PrOH and $Et_3N$.

## 6.  Electronic circular dichroism spectroscopy

Electronic circular dichroism (ECD) spectra of enantiomers **1[7]** were recorded on Jasco J-815 CD spectrometer using solutions obtained directly from HPLC separation (hexane/$CH_2Cl_2$ 2:3, containing *i*-PrOH and $Et_3N$). Results are shown in Figure S29. The notation *first* and *second* refers to the shorter and longer retention times, respectively, of the individual enantiomers.
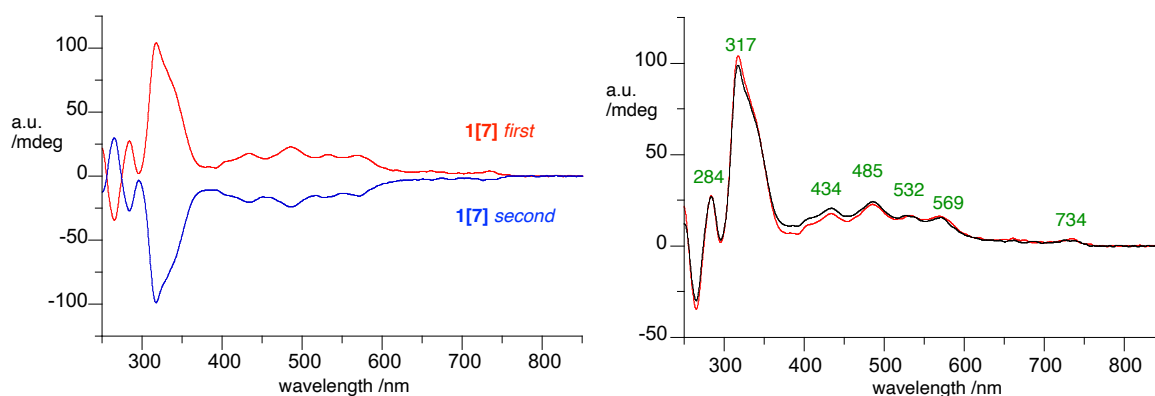


**Figure S29**. Left: Electronic circular dichroism spectra for *the first* (red) and *the second* (black) enantiomers of radical **1[7]** in hexane/$CH_2Cl_2$. Right: overlay of the two spectra with listed maxima.

## 7.  Electrochemical results

Electrochemical characterization of selected radicals was conducted using a Metrohm Autolab PGSTAT128N potentiostat/galvanostat instrument. Helicene radicals **1[n]** were dissolved in dry, spectroscopic grade $CH_2Cl_2$ (concentration 0.5 mM) in the presence of [*n*-$Bu_4N]^+[PF_6]^-$ as an electrolyte (concentration 50 mM) and the resulting solution was degassed by purging with Ar gas for 20 minutes. A three-electrode electrochemical cell was used with glassy carbon disk as the working electrode ($\phi$ 2 mm, alumina polished), Pt wire as the counter electrode and Ag/AgCl wire as the pseudoreference electrode. All samples were measured without internal reference once and afterwards with Fc/Fc$^+$ (0.0 V) as the internal reference couple with a scan rate of 50 mV s$^{-1}$ at *ca.* 20 °C. Cyclic voltammetry (CV) measurements were started from 0.0 V in the oxidative direction and plots are shown in Figures S30–S32.
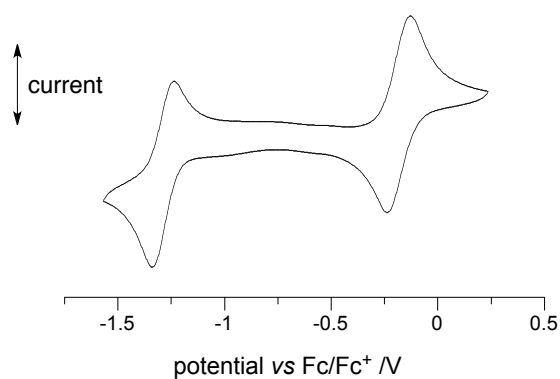
**Figure S30**. Cyclic voltammograms for helicene **1[5]** in $CH_2Cl_2$ referenced to the $Fc/Fc^+$ couple.
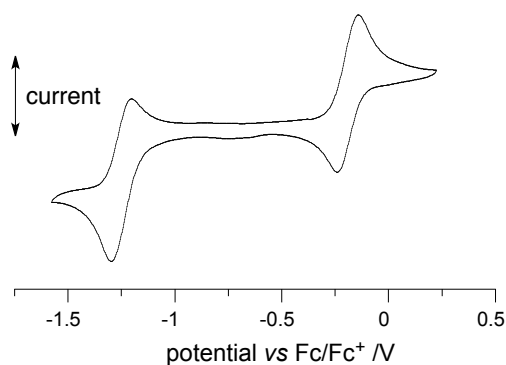


**Figure S31**. Cyclic voltammogram for helicene **1[6]** in $CH_2Cl_2$ referenced to the $Fc/Fc^+$ couple.
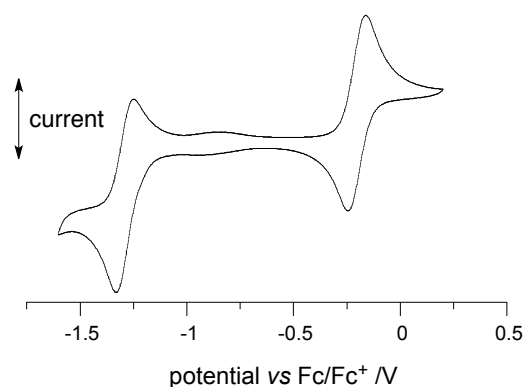


**Figure S32**. Cyclic voltammogram for helicene **1[7]** in $CH_2Cl_2$ referenced to the $Fc/Fc^+$ couple.

## 8. EPR spectroscopy

EPR spectra for helicene-type radicals **1[n]** were recorded on a X-band EMX-Nano EPR spectrometer at room temperature on diluted and degassed solutions in benzene. The microwave power was in a range 3-12 mW (established with the Power Sweep program below the saturation of the signal) with a modulation frequency of 100 kHz, modulation amplitude of

0.5 $G_{pp}$ and spectral width of 100 G. Accurate *g*-values were obtained using TEMPO as EMX-Nano internal standard.

Simulations of the spectra were performed with *Easy Spin* (Matlab) using DFT results (*vide infra*) as the starting point including all nitrogen atoms and up to 8 hydrogen atoms. The resulting *hfcc* values were perturbed several times until a global minimum for the fit was achieved. For the purpose of consistency, original spectra[3, 15] for **1[3]** and **1[4]** were resimmulated. Experimental and simulated spectra are shown in Figures S33–S35 and resulting *hfcc* are listed in Table S3.
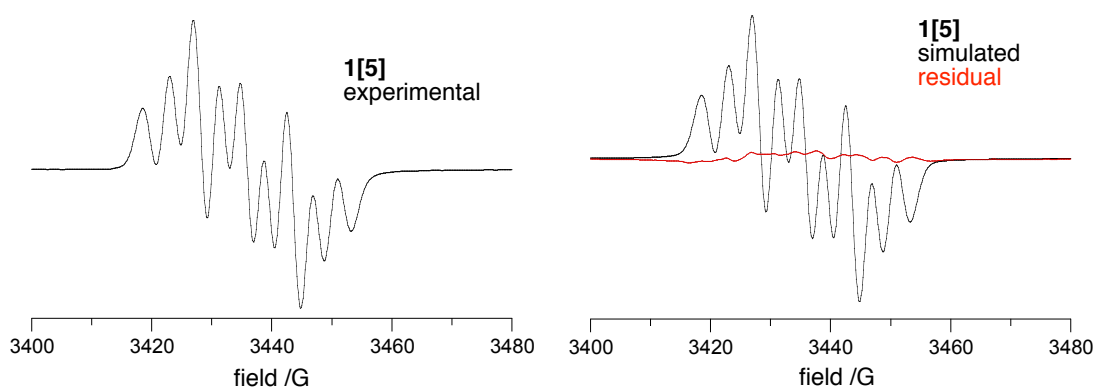


**Figure S33**. Experimental, simulated and difference spectra for helicene **1[5]** in benzene.
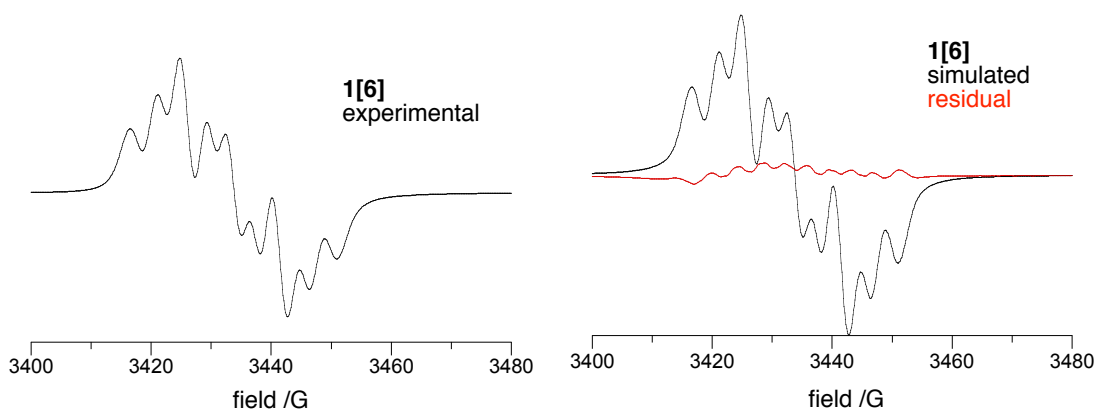


**Figure S34**. Experimental, simulated and difference spectra for helicene **1[6]** in benzene.
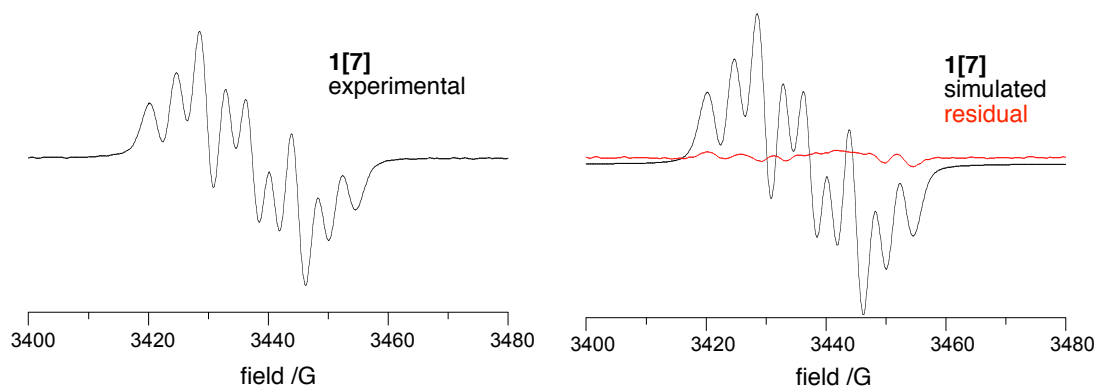


**Figure S35**. Experimental, simulated and difference spectra for helicene **1[7]** in benzene.

**Table S3**. Hyperfine coupling constants (G) for helicenes **1[n]**.

| hfcc /G | 1[3] | 1[4] | 1[5] | 1[6] | 1[7] |
|---------|------|------|------|------|------|
| $a_N$ | 7.52 | 7.60 | 7.50 | 7.38 | 7.36 |
| $a_N$ | 4.35 | 4.16 | 4.09 | 4.06 | 4.05 |
| $a_N$ | 4.35 | 4.20 | 4.30 | 4.28 | 4.26 |
| $a_H$ | 0.93 | 0.96 | 1.36 | 0.83 | 0.65 |
| $a_H$ | 0.60 | 0.99 | 0.70 | 0.87 | 0.66 |
| $a_H$ | 1.94 | 0.84 | 0.88 | 0.78 | 1.06 |
| $a_H$ | 0.45 | 0.39 | 1.29 | 1.15 | 0.41 |
| $a_H$ | 0.70 | 0.51 | 0.97 | 0.46 | 0.34 |
| $a_H$ | 0.43 | -0.52 | 0.00 | 0.51 | 0.35 |
| $a_H$ | 0.33 | 0.36 | 0.38 | 0.42 | 0.44 |
| $a_H$ | 0.35 | 0.29 | 0.01 | 0.34 | 0.29 |
| g | 2.0026 | 2.0028 | 2.0041 | 2.0053 | 2.0032 |

[a] Referenced to TEMPO as the internal standard.

## 9. Computational details

### a) geometry optimization and energies for radicals 1[n]

Quantum-mechanical calculations were carried out using Gaussian 16 suite of programs.[16] Geometry optimizations of radicals **1[n]** were undertaken at the UB3LYP/6-311G(d,p) level of theory in $CH_2Cl_2$ dielectric medium (PCM model[17]) requested with the SCRF(Solvent=CH2Cl2) keyword and using tight convergence limits. The nature of the stationary points was verified with frequency calculations.

### b) spin delocalization in radicals 1[n]

Spin delocalization parameter RDV (Radical Delocalization Value) was calculated for radicals **1[n]** according to the formula:[18]

$$RDV = \sum_{i=1}^{n} (\rho_i)^2$$

where spin concentration $\rho_i$ on each heavy atoms $i$ (hydrogen atoms summed up to heavy atoms) is obtained with the UCAM-B3LYP/EPR-II // UB3LYP/6-311G(d,p) method in benzene dielectric medium using the PCM model[17] [keyword: SCRF(Solvent=benzene)].

For the purpose of this work, the inverse is reported: RDV$^{-1}$=1/$RDV$, since now larger values correspond to greater delocalization.

### c) electronic excitation data for radicals 1[n]

Electronic excitation energies in $CH_2Cl_2$ dielectric medium were obtained for radicals **1[n]** at the UB3LYP/6-311G(d,p) // UB3LYP/6-311G(d,p) level of theory using time-dependent DFT method[19] supplied in the Gaussian 16 package.[16] Dielectric medium for calculations was implemented by the PCM model[17] using the SCRF(solvent=CH2Cl2) keyword. Partial output data are shown below.

Calculation indicated that the lowest energy absorption band consist of two close energy excitations. Therefore, for the purpose of comparison with the experimental spectra the position of the lowest energy absorption band was determined as a peak of a composite band obtained in Gauss View software using half-width half-height of 60 meV. A comparison of the experimental and TD-DFT derived lowest energy absorption band is shown in Figure S36.
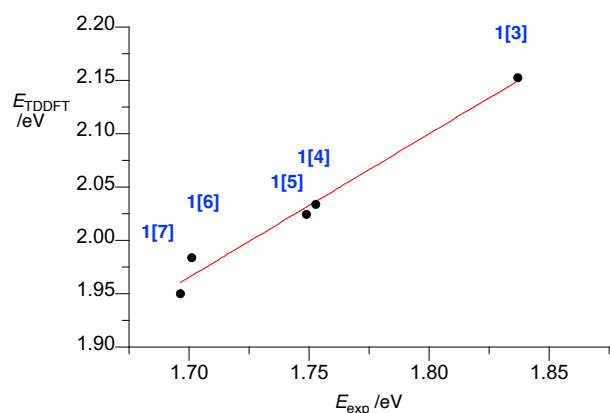


**Figure S36**. A correlation of experimental and TD-DFT derived energy of the lowest absorption band for radicals **1[n]**. Best fit function: $E_{TDDFT}$ = 1.334(11)×$E_{exp}$ –0.3(2), $r^2$ = 0.980.

### d) partial output from TD-DFT calculation for radicals 1[n]

```
UB3LYP/6-311G(d,p)// UB3LYP/6-311G(d,p) TD(NStates=90) in CH2Cl2

1[3]
Excited State   1:   2.045-A'     2.0272 eV  611.60 nm  f=0.0030  <S**2>=0.796
      78A -> 79A        0.96004
      76B -> 78B       -0.11108
      77B -> 78B       -0.14197
 This state for optimization and/or second-order correction.
```

```
Total Energy, E(TD-HF/TD-DFT) =  -970.854411652
Copying the excited state density for this state as the 1-particle RhoCI
density.

Excited State   2:  2.087-A'      2.1535 eV  575.73 nm  f=0.0511  <S**2>=0.838
      78A -> 79A         0.13351
      78A -> 80A        -0.10957
      77B -> 78B         0.96336


Excited State   3:  2.198-A'      2.7448 eV  451.71 nm  f=0.0417  <S**2>=0.958
      77A -> 80A         0.13162
      78A -> 80A         0.94342
      72B -> 78B         0.13039
      77B -> 80B        -0.10603


Excited State   4:  2.048-A"      2.9615 eV  418.65 nm  f=0.0011  <S**2>=0.799
      73B -> 78B         0.98755


Excited State   5:  2.484-A'      3.1496 eV  393.66 nm  f=0.0353  <S**2>=1.293
      75A -> 82A         0.10333
      76A -> 79A         0.14687
      77A -> 79A         0.32426
      78A -> 79A         0.12618
      76B -> 78B         0.84595
      76B -> 79B         0.14736
      77B -> 79B         0.20627


1[4]
Excited State   1:  2.091-A'      1.9573 eV  633.46 nm  f=0.0102  <S**2>=0.844
      90A -> 93A        -0.10158
      91A -> 92A         0.89868
      91A -> 93A         0.11461
      91A -> 94A         0.10436
      90B -> 91B         0.33227
This state for optimization and/or second-order correction.
Total Energy, E(TD-HF/TD-DFT) =  -1124.53396741
Copying the excited state density for this state as the 1-particle RhoCI
density.

Excited State   2:  2.109-A'      2.0425 eV  607.02 nm  f=0.0285  <S**2>=0.862
      91A -> 92A        -0.23695
      91A -> 93A        -0.46992
      90B -> 91B         0.81734


Excited State   3:  2.257-A'      2.2712 eV  545.89 nm  f=0.0937  <S**2>=1.023
      90A -> 92A        -0.14299
      90A -> 93A         0.11947
      91A -> 92A        -0.21552
      91A -> 93A         0.80266
      89B -> 91B        -0.11408
      90B -> 91B         0.41020
      90B -> 92B         0.13301
      90B -> 93B        -0.11709


Excited State   4:  3.141-A'      2.8762 eV  431.07 nm  f=0.0212  <S**2>=2.217
      89A -> 92A        -0.18509
      89A -> 93A         0.17285
      90A -> 92A        -0.33349
      90A -> 93A         0.33332
      91A -> 92A         0.17150
```

```
        91A -> 93A       -0.28049
        91A -> 94A        0.13196
        91A -> 96A       -0.14134
        86B -> 91B       -0.14191
        89B -> 91B       -0.22163
        89B -> 92B        0.21382
        89B -> 93B       -0.16354
        89B -> 94B        0.10548
        90B -> 92B        0.41900
        90B -> 93B       -0.38455

 Excited State   5:   2.401-A'      2.9713 eV  417.28 nm  f=0.0221  <S**2>=1.191
        89A -> 93A        0.10622
        90A -> 92A       -0.20357
        90A -> 93A       -0.12328
        91A -> 92A       -0.14216
        91A -> 94A        0.39300
        89B -> 91B        0.78116
        90B -> 91B        0.12895
        90B -> 92B        0.22060
        90B -> 94B        0.10108

 Excited State   6:   2.050-A"      2.9978 eV  413.59 nm  f=0.0011  <S**2>=0.801
        85B -> 91B        0.98622

 Excited State   7:   2.150-A'      3.0012 eV  413.11 nm  f=0.0487  <S**2>=0.905
        91A -> 94A        0.84325
        86B -> 91B        0.18543
        89B -> 91B       -0.40085


1[5]
 Excited State   1:   2.056-A'      1.9878 eV  623.74 nm  f=0.0134  <S**2>=0.807
       104A ->105A        0.93318
       104A ->107A       -0.13660
       103B ->104B        0.20658
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -1278.20610030
 Copying the excited state density for this state as the 1-particle RhoCI
density.

 Excited State   2:   2.123-A'      2.0313 eV  610.36 nm  f=0.0506  <S**2>=0.877
       104A ->105A       -0.21413
       104A ->106A       -0.30647
       103B ->104B        0.89603

 Excited State   3:   2.299-A'      2.3096 eV  536.82 nm  f=0.1197  <S**2>=1.071
       103A ->106A       -0.16697
       104A ->106A        0.85199
       104A ->108A        0.12053
       102B ->104B        0.18689
       103B ->104B        0.29731
       103B ->106B       -0.17047

 Excited State   4:   2.300-A'      2.5982 eV  477.19 nm  f=0.0012  <S**2>=1.072
       102A ->107A       -0.10412
       103A ->106A       -0.11645
       104A ->105A        0.13692
       104A ->106A       -0.12915
       104A ->107A        0.73772
       102B ->104B        0.54991
```

```
         102B ->106B         0.10739
         102B ->107B         0.10243
         103B ->106B        -0.10610

 Excited State   5:  2.388-A'     2.8388 eV  436.75 nm  f=0.1787  <S**2>=1.176
         102A ->106A         0.12991
         102A ->107A         0.12326
         103A ->106A         0.14724
         104A ->106A         0.26457
         104A ->107A         0.58438
         104A ->108A         0.21153
         101B ->106B         0.10700
         102B ->104B        -0.56483
         102B ->107B        -0.10890
         103B ->105B        -0.10571
         103B ->106B         0.24387

 Excited State   6:  2.253-A'     2.9424 eV  421.37 nm  f=0.0262  <S**2>=1.018
         103A ->105A         0.10353
         103A ->106A         0.14689
         104A ->108A         0.13880
         101B ->104B         0.90236
         102B ->104B         0.15060
         103B ->104B         0.10831
         103B ->105B         0.13800
         103B ->106B         0.10437

1[6]
 Excited State   1:  2.177-A      1.9187 eV  646.19 nm  f=0.0115  <S**2>=0.935
         116A ->118A         0.10413
         117A ->118A         0.72309
         117A ->119A        -0.21872
         117A ->120A         0.20979
         117A ->121A         0.10240
         116B ->117B        -0.54960
         116B ->118B        -0.11497
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -1431.87300351
 Copying the excited state density for this state as the 1-particle RhoCI
density.

 Excited State   2:  2.090-A      2.0059 eV  618.10 nm  f=0.0169  <S**2>=0.842
         117A ->118A        -0.27031
         117A ->119A         0.64563
         117A ->120A        -0.12339
         115B ->117B        -0.16370
         116B ->117B        -0.63976

 Excited State   3:  2.221-A      2.1741 eV  570.27 nm  f=0.1216  <S**2>=0.983
         116A ->118A         0.17350
         117A ->118A         0.48555
         117A ->119A         0.64656
         114B ->117B         0.14381
         115B ->117B         0.11946
         116B ->117B         0.43777
         116B ->118B        -0.15780

 Excited State   4:  2.515-A      2.4839 eV  499.15 nm  f=0.0062  <S**2>=1.331
         115A ->120A         0.14835
         116A ->118A         0.22921
         117A ->118A        -0.29549
```

```
        117A ->120A        0.67178
        114B ->117B        0.30218
        115B ->117B       -0.28985
        115B ->118B        0.13323
        115B ->120B       -0.15328
        116B ->118B       -0.21392

 Excited State   5:   2.600-A      2.5434 eV  487.47 nm  f=0.0140  <S**2>=1.440
        115A ->118A       -0.11099
        116A ->118A        0.30848
        117A ->118A       -0.17477
        117A ->119A       -0.14012
        117A ->120A       -0.21531
        117A ->121A       -0.10472
        114B ->117B        0.22267
        115B ->117B        0.69493
        115B ->118B        0.23762
        116B ->117B       -0.18226
        116B ->118B       -0.27536

 Excited State   6:   2.576-A      2.6369 eV  470.19 nm  f=0.0527  <S**2>=1.409
        115A ->118A        0.10111
        115A ->120A       -0.11764
        116A ->118A       -0.26563
        116A ->120A        0.13130
        117A ->119A        0.20472
        117A ->120A        0.53878
        115B ->117B        0.54119
        115B ->118B       -0.17233
        115B ->120B        0.10563
        116B ->117B       -0.13743
        116B ->118B        0.32659

 Excited State   7:   2.323-A      2.8488 eV  435.22 nm  f=0.1067  <S**2>=1.099
        115A ->118A        0.15610
        116A ->118A       -0.23349
        117A ->120A       -0.26296
        117A ->121A       -0.14115
        114B ->117B        0.83290
        115B ->117B       -0.17261
        115B ->118B       -0.15775
        116B ->117B       -0.10572

1[7]
Excited State   1:   2.176-A      1.9153 eV  647.34 nm  f=0.0139  <S**2>=0.933
        130A ->131A        0.72456
        130A ->133A       -0.30593
        130A ->134A        0.15903
        129B ->130B       -0.52445
        129B ->131B       -0.10275
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -1585.54351062
 Copying the excited state density for this state as the 1-particle RhoCI
density.

 Excited State   2:   2.109-A      1.9899 eV  623.06 nm  f=0.0129  <S**2>=0.862
        130A ->131A        0.28960
        130A ->132A        0.43680
        130A ->133A       -0.46166
        127B ->130B        0.16147
        128B ->130B       -0.10483
```

```
        129B ->130B           0.64768


Excited State    3:  2.244-A      2.1614 eV  573.64 nm  f=0.1237  <S**2>=1.009
        129A ->131A           0.15579
        130A ->131A          -0.44064
        130A ->132A           0.52375
        130A ->133A          -0.40427
        130A ->134A          -0.11597
        125B ->130B           0.10372
        127B ->130B          -0.13147
        128B ->130B           0.18772
        129B ->130B          -0.42271
        129B ->131B           0.13793


Excited State    4:  2.347-A      2.3005 eV  538.95 nm  f=0.0096  <S**2>=1.127
        129A ->132A          -0.18899
        130A ->131A           0.31113
        130A ->132A           0.46316
        130A ->133A           0.61721
        128B ->130B           0.39436
        128B ->132B           0.13140
        129B ->132B           0.13658


Excited State    5:  2.558-A      2.4751 eV  500.93 nm  f=0.0587  <S**2>=1.386
        128A ->132A           0.15856
        128A ->133A           0.10029
        129A ->131A           0.17115
        129A ->132A          -0.16117
        130A ->132A          -0.48947
        130A ->133A          -0.25106
        130A ->134A           0.14432
        127B ->130B          -0.24447
        127B ->131B          -0.18121
        128B ->130B           0.52475
        128B ->132B           0.17376
        129B ->130B           0.17912
        129B ->131B           0.23190
        129B ->132B           0.13491


Excited State    6:  2.223-A      2.6044 eV  476.06 nm  f=0.0107  <S**2>=0.986
        129A ->132A           0.10390
        130A ->132A          -0.11723
        130A ->134A          -0.10601
        127B ->130B           0.81408
        128B ->130B           0.44223
        129B ->132B          -0.11541


Excited State    7:  2.776-A      2.6440 eV  468.93 nm  f=0.0040  <S**2>=1.676
        127A ->131A          -0.15176
        128A ->131A          -0.21914
        128A ->132A          -0.18087
        128A ->133A          -0.12349
        129A ->131A          -0.26544
        129A ->132A           0.14769
        130A ->131A          -0.10898
        127B ->130B          -0.35851
        127B ->131B           0.21472
        128B ->130B           0.52757
        128B ->131B           0.11380
        128B ->132B          -0.20731
        128B ->133B          -0.11146
```

S 49

```
      129B ->130B        0.24577
      129B ->131B       -0.28161
```

## *e) MO energies for radicals 1[n]*

```
                        UB3LYP/6-311G(d,p) in CH2Cl2
1[3]
Alpha  occ. eigenvalues --    -0.30960  -0.28453  -0.27556  -0.27492  -0.26244
Alpha  occ. eigenvalues --    -0.25940  -0.22972  -0.17767
Alpha virt. eigenvalues --    -0.06414  -0.03969  -0.02294  -0.01366  -0.00543
Alpha virt. eigenvalues --     0.01031   0.04223   0.05339   0.05594   0.06289

Beta  occ. eigenvalues --    -0.29761  -0.27911  -0.26929  -0.26878  -0.26242
Beta  occ. eigenvalues --    -0.25337  -0.22055
Beta virt. eigenvalues --    -0.10797  -0.06001  -0.03575  -0.01799  -0.01265
Beta virt. eigenvalues --    -0.00096   0.02106   0.04318   0.05369   0.05616

1[4]
Alpha  occ. eigenvalues --    -0.26761  -0.26436  -0.26168  -0.24937  -0.22425
Alpha  occ. eigenvalues --    -0.17516
Alpha virt. eigenvalues --    -0.06557  -0.05984  -0.03387  -0.01458  -0.00979
Alpha virt. eigenvalues --    -0.00535   0.01910   0.04589   0.05162   0.05326

Beta  occ. eigenvalues --    -0.26440  -0.26223  -0.25770  -0.24489  -0.21479
Beta virt. eigenvalues --    -0.10717  -0.06158  -0.05654  -0.03080  -0.01390
Beta virt. eigenvalues --    -0.00210  -0.00104   0.02386   0.04657   0.05177

1[5]
Alpha  occ. eigenvalues --    -0.29966  -0.28549  -0.27555  -0.26385  -0.26186
Alpha  occ. eigenvalues --    -0.24895  -0.23868  -0.22438  -0.17544
Alpha virt. eigenvalues --    -0.06511  -0.05984  -0.04995  -0.02656  -0.01382
Alpha virt. eigenvalues --    -0.00600   0.00702   0.01331   0.04503   0.04732

Beta  occ. eigenvalues --    -0.29395  -0.28175  -0.26947  -0.26262  -0.25726
Beta  occ. eigenvalues --    -0.24473  -0.23634  -0.21548
Beta virt. eigenvalues --    -0.10926  -0.06138  -0.05736  -0.04517  -0.02324
 Beta virt. eigenvalues --    -0.01336  -0.00158   0.01360   0.01588   0.04562

1[6]
Alpha  occ. eigenvalues --    -0.31933  -0.30858  -0.30214  -0.27864  -0.27528
Alpha  occ. eigenvalues --    -0.27117  -0.26222  -0.25874  -0.23909  -0.23127
Alpha  occ. eigenvalues --    -0.22008  -0.17526
Alpha virt. eigenvalues --    -0.07187  -0.06323  -0.05525  -0.03097  -0.01728

Beta  occ. eigenvalues --    -0.31463  -0.30522  -0.29425  -0.27519  -0.26925
Beta  occ. eigenvalues --    -0.26797  -0.26225  -0.25328  -0.23688  -0.22717
Beta  occ. eigenvalues --    -0.21335
Beta virt. eigenvalues --    -0.10934  -0.06951  -0.06016  -0.05120  -0.02723

1[7]
Alpha  occ. eigenvalues --    -0.28807  -0.27467  -0.26742  -0.26197  -0.26168
Alpha  occ. eigenvalues --    -0.25381  -0.23186  -0.22611  -0.21731  -0.17427
Alpha virt. eigenvalues --    -0.07152  -0.06664  -0.06034  -0.04339  -0.01846

Beta  occ. eigenvalues --    -0.28410  -0.26864  -0.26465  -0.26188  -0.25746
Beta  occ. eigenvalues --    -0.25002  -0.22787  -0.22389  -0.21162
Beta virt. eigenvalues --    -0.10858  -0.06930  -0.06439  -0.05616  -0.04140
```

***f)*** *TD-DFT calculation of electronic circular dichroism (ECD) results for radicals 1[6] and 1[7]*

Results of TD-DFT calculations for **1[6]** and **1[7]** at the UB3LYP/6-311G(d,p)//UB3LYP/6-311G(d,p)

level of theory using TD(NStates=90) in CH2Cl2 dielectric medium are shown in Figures S37 and S38.

```
UV-vis peaks half-width at half-height set at 0.175 eV
Δε, rotatory strengths (R_vel /10⁻⁴⁰ esu²cm²)
```
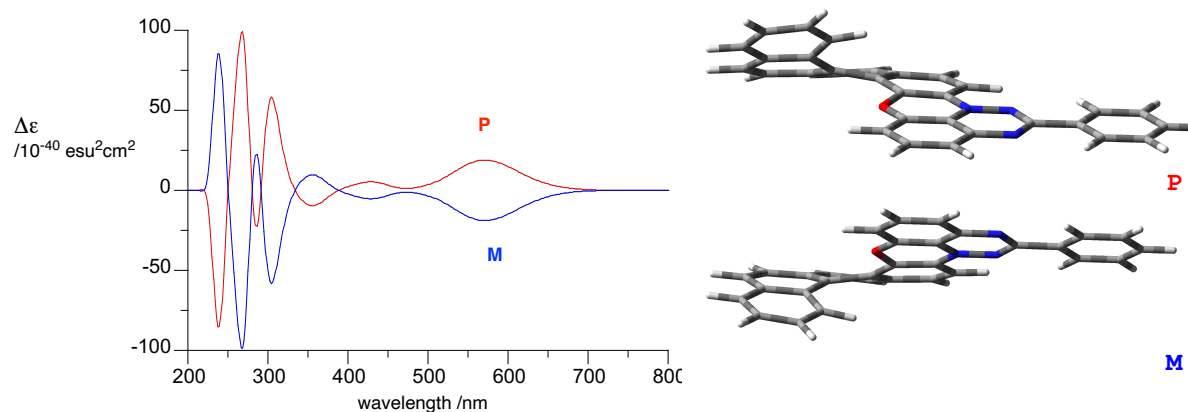


**Figure S37**. Right: Calculated (DFT) electronic circular dichroism spectra for two enantiomers of **1[6]** in $CH_2Cl_2$ dielectric medium. Left: UB3LYP/6-311G(d,p) optimized structures of the two enantiomers.
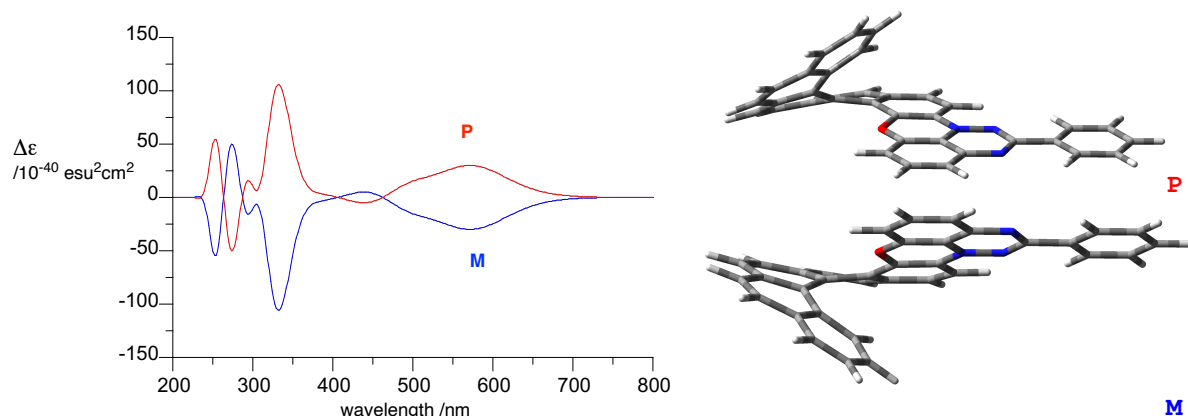


**Figure S38**. Right: Calculated (DFT) electronic circular dichroism spectra for two enantiomers of **1[7]** in $CH_2Cl_2$ dielectric medium. Left: UB3LYP/6-311G(d,p) optimized structures of the two enantiomers.

## 10. Archive for DFT calculations

**1[3]**
```
1\1\GINC-LOCALHOST\FOpt\UB3LYP\6-311G(d,p)\C19H12N3O1(2)\PIOTR\07-Aug-
2024\0\\#P UB3LYP/6-311G(d,p) FOpt=tight freq(noraman) SCF=Direct #P G
eom=(NoDistance,NoAngle) fcheck\\Parent C(8)-O-Ph(N1) benzotrazinyl (p
henazinoBT), Cs\\0,2\N,-0.2278877873,0.,-0.7084263176\N,1.6321910991,0
.,1.3128825056\C,0.3129880577,0.,1.5111857835\N,-0.6503075981,0.,0.576
8055176\C,2.8786535524,0.,-2.6902290381\C,1.5291389331,0.,-2.380349485
6\C,1.1219316219,0.,-1.0442236245\C,2.0578378588,0.,0.0125543531\C,3.4
247554582,0.,-0.3201118186\C,3.816972262,0.,-1.6491147022\C,-1.1822310
988,0.,-1.7398126194\C,-0.7290760417,0.,-3.0714973973\C,-1.6371943064,
0.,-4.1201994823\C,-3.0046875126,0.,-3.8560366366\C,-3.459870238,0.,-2
```

.5383765587\C,-2.5557251842,0.,-1.4827298838\C,-0.1683642447,0.,2.9196
786726\C,-1.5360822218,0.,3.2244211726\C,-1.9623219845,0.,4.5480071083
\C,-1.0314057238,0.,5.5858369247\C,0.3306622795,0.,5.2903077622\C,0.76
0909599,0.,3.9678089319\O,0.6085245667,0.,-3.4016442722\H,4.1444535006
,0.,0.4880729973\H,-1.2511252521,0.,-5.131839092\H,-4.5225909432,0.,-2
.328713281\H,-2.8831618771,0.,-0.4536580141\H,-2.2565015446,0.,2.41782
91393\H,-3.0235523825,0.,4.77073054\H,1.0603303916,0.,6.0923893601\H,1
.8146738821,0.,3.72378903\H,4.8719986175,0.,-1.8962881704\H,3.17977092
88,0.,-3.7297147051\H,-3.7085837296,0.,-4.6792968653\H,-1.3657459375,0
.,6.617402166\\Version=ES64L-G16RevC.01\State=2-A"\HF=-970.9224068\S2=
0.765181\S2-1=0.\S2A=0.750177\RMSD=6.549e-09\RMSF=4.240e-06\Dipole=-0.
3140391,0.,-0.7901217\Quadrupole=6.2148761,-11.0265678,4.8116917,0.,-0
.4622123,0.\PG=CS [SG(C19H12N3O1)]\\

**1[4]**

1\1\GINC-LOCALHOST\FOpt\UB3LYP\6-311G(d,p)\C23H14N3O1(2)\PIOTR\27-Jul-
2024\0\\#P UB3LYP/6-311G(d,p) FOpt=tight freq(noraman) SCF=Direct #P G
eom=(NoDistance,NoAngle) fcheck SCRF(Solvent=CH2Cl2)\\benzotrazinyl 1,
2-naphthyl, Cs, Smiles\\0,2\N,0.1360787742,-0.1732928935,0.\N,1.470078
6957,-2.579376815,0.\C,0.1407303001,-2.4582983309,0.\N,-0.5749400497,-
1.3247903862,0.\C,3.6195139616,1.026907499,0.\C,2.2346733602,1.0364571
264,0.\C,1.527472918,-0.1669211033,0.\C,2.1901588663,-1.4126311102,0.\
C,3.596574715,-1.406536373,0.\C,4.2886020228,-0.2044366529,0.\C,-0.544
7192359,1.0538984021,0.\C,0.1953693831,2.2294397141,0.\C,-0.4411620144
,3.4963909334,0.\C,-1.8711663155,3.5394103616,0.\C,-1.9607180393,1.110
402639,0.\C,-0.6643740691,-3.7124427496,0.\C,-2.0662901119,-3.67998793
34,0.\C,-2.7993780121,-4.8625573522,0.\C,-2.1461798709,-6.0951623121,0
.\C,-0.752339903,-6.1361747225,0.\C,-0.0163806121,-4.9550600471,0.\O,1
.5720654166,2.2416815271,0.\H,4.113728359,-2.3574324306,0.\H,-2.507161
1261,0.1791790193,0.\H,-2.5741074111,-2.7250273833,0.\H,-3.8828284371,
-4.8223342211,0.\H,-0.2369127296,-7.0900143053,0.\H,1.0649085526,-4.97
72109182,0.\H,5.3719138371,-0.2104331548,0.\H,4.1575727056,1.965869564
6,0.\H,-2.7190897672,-7.0156090553,0.\C,0.2925022529,4.7118294854,0.\C
,-0.3667795771,5.9184122106,0.\C,-2.5124550821,4.8027136952,0.\C,-1.77
97186384,5.9669777393,0.\C,-2.6009754505,2.3199954643,0.\H,0.200492086
6,6.8419337252,0.\H,-2.2835851561,6.926481403,0.\H,1.3736184112,4.6752
417587,0.\H,-3.5964857216,4.8350803838,0.\H,-3.6841187879,2.3567933784
,0.\\Version=ES64L-G16RevC.01\State=2-A"\HF=-1124.6058951\S2=0.765927\
S2-1=0.\S2A=0.750207\RMSD=7.163e-09\RMSF=1.315e-06\Dipole=-0.1991871,1
.4390989,0.\Quadrupole=9.1165202,6.0167656,-15.1332858,1.1490935,0.,0.
\PG=CS [SG(C23H14N3O1)]\\

**1[5]**

1\1\GINC-LOCALHOST\FOpt\UB3LYP\6-311G(d,p)\C27H16N3O1(2)\PIOTR\30-Jul-
2024\0\\#P UB3LYP/6-311G(d,p) FOpt=tight SCF=Direct SCRF(Solvent=CH2CL
2) #P Geom=(NoDistance,NoAngle) fcheck freq(noraman)\\[5]helicene, Cs
isomerised via Smiles rearr\\0,2\O,1.4965615712,1.3025364014,0.\N,-2.1
98945109,-0.56955949,0.\C,-4.5872428134,-0.4939075499,0.\N,-0.99905463
58,0.0589568935,0.\C,-5.782092744,0.2385777345,0.\N,-3.3103382448,1.55
72054621,0.\C,-7.0112021734,-0.414032096,0.\C,-7.0666070409,-1.8073797
099,0.\C,-5.8821968914,-2.5442696395,0.\C,-4.6518007774,-1.8946648529,
0.\C,-3.2803793458,0.2227005745,0.\C,-0.9018233928,1.442821531,0.\C,-2
.0965217726,2.1932135472,0.\C,0.1740966594,-0.7149059224,0.\C,1.421490
6635,-0.0734507535,0.\C,0.3479999354,2.0562933595,0.\C,0.0947099984,-2
.1172693774,0.\C,1.2506712673,-2.8520448294,0.\C,2.5193160286,-2.23331
8383,0.\C,2.6401513692,-0.8058321849,0.\C,-1.9869719498,3.5952556335,0
.\C,0.4425898857,3.438300716,0.\C,-0.7366293381,4.1959933588,0.\C,3.68
53959156,-3.0600766868,0.\C,3.9867679371,-0.2196842278,0.\C,5.11391642
78,-1.1031907854,0.\C,4.9284449435,-2.5221172845,0.\C,4.2701199722,1.1
698467023,0.\C,5.5663850534,1.6512052674,0.\C,6.6605155203,0.774666806
4,0.\C,6.4274324462,-0.5829011533,0.\H,-5.7299982301,1.3189322205,0.\H

,-7.9271214379,0.1660913915,0.\H,-8.0244592861,-2.3152736803,0.\H,-5.9
169906603,-3.6278928814,0.\H,-3.7343446414,-2.4674143593,0.\H,-0.87967
43794,-2.5809958435,0.\H,1.2013653709,-3.9344209683,0.\H,-2.8965468459
,4.1821120633,0.\H,1.4166061458,3.9095373256,0.\H,-0.6623442109,5.2767
476707,0.\H,3.5464449219,-4.1352785193,0.\H,5.8069607385,-3.1578480431
,0.\H,7.6736584307,1.1597671419,0.\H,7.2566189892,-1.2821162521,0.\H,5
.7313512506,2.7227398566,0.\H,3.4642944784,1.8798838156,0.\\Version=ES
64L-G16RevC.01\State=2-A"\HF=-1278.2791488\S2=0.765874\S2-1=0.\S2A=0.7
5021\RMSD=3.691e-09\RMSF=3.357e-06\Dipole=1.3144464,-0.1980755,0.\Quad
rupole=4.5997758,11.9545776,-16.5543534,2.4902042,0.,0.\PG=CS [SG(C27H
16N3O1)]\\

**1[6]-M**

1\1\GINC-LOCALHOST\FOpt\UB3LYP\6-311G(d,p)\C31H18N3O1(2)\PIOTR\31-Jul-
2024\0\\#P UB3LYP/6-311G(d,p) FOpt=tight SCF=Direct SCRF(Solvent=CH2CL
2) #P Geom=(NoDistance,NoAngle) fcheck\\[6]helicene isomerised via Smi
les rearr, M enantiomer\\0,2\O,-0.8750148894,-0.3434853845,0.965766724
3\N,3.042632529,0.6571381119,0.0320589026\C,5.3679495532,0.1202375902,
-0.095027592\N,1.7684139709,0.3115468842,0.3321727845\C,6.4229893212,-
0.7777435144,0.1164840893\N,3.7915676305,-1.5112187727,0.7356647\C,7.7
299225343,-0.4202002,-0.2008147058\C,8.0038438981,0.8386751118,-0.7344
210399\C,6.9595723521,1.7382515445,-0.9492180457\C,5.651841017,1.38380
86796,-0.6327362075\C,3.9749981089,-0.2812558312,0.2510855322\C,1.4509
884127,-0.9397284912,0.8452585008\C,2.5028334692,-1.8577203566,1.04851
42462\C,0.7404648351,1.24258352,0.1161711781\C,-0.5821014935,0.8660782
675,0.3769428734\C,0.1308470823,-1.2567288332,1.1615862682\C,1.0331036
559,2.5502781311,-0.3171677684\C,0.0214155851,3.4716826521,-0.39489477
04\C,-1.3204477175,3.1170516028,-0.1248132307\C,-1.6657182352,1.751330
0227,0.1375834418\C,2.1766027632,-3.1180886644,1.5804852457\C,-0.17639
92936,-2.5012704953,1.6867907875\C,0.8595286341,-3.4227656142,1.892179
7848\C,-2.3185845513,4.1278613556,-0.0140788696\C,-3.0742791127,1.4001
143455,0.2656677961\C,-3.9808595218,2.4512003013,0.5457246337\C,-3.574
7594196,3.8134195985,0.4035228968\C,-3.6307036256,0.0778385323,0.04531
52099\C,-4.9782904099,-0.1861271447,0.4453883498\C,-5.7897274463,0.878
0401975,0.9411812704\C,-5.327413442,2.1569190939,0.9237170019\C,-2.957
1392955,-0.9431284667,-0.6723683136\C,-3.5304703112,-2.1788357237,-0.8
807464874\C,-4.814068526,-2.4671991086,-0.3771583196\C,-5.5269458824,-
1.4783959882,0.2613234695\H,6.2012398746,-1.7523147532,0.5299771197\H,
8.5357828668,-1.1253751676,-0.0311579883\H,9.0222017214,1.1167647761,-
0.9815184078\H,7.1642858685,2.7185024065,-1.3647472222\H,4.8431617797,
2.0819164931,-0.8015494053\H,2.0611609617,2.8108283118,-0.5174290882\H
,0.2482704337,4.5032654519,-0.6371528726\H,2.9753762724,-3.8309413287,
1.7403637256\H,-1.2039478619,-2.7368173896,1.9296732247\H,0.6188553606
,-4.395724371,2.3034159874\H,-2.0348346953,5.1573291394,-0.2006517214\
H,-4.3090585348,4.5911770642,0.581124338\H,-6.8034230331,0.6586879229,
1.2581714772\H,-5.973667304,2.9824259305,1.2010700607\H,-5.2496817205,
-3.4482945519,-0.5274404231\H,-6.5399885031,-1.6634521633,0.6023919364
\H,-2.9926507556,-2.9295738236,-1.448454115\H,-1.9893097404,-0.7394165
304,-1.1064805428\\Version=ES64L-G16RevC.01\State=2-A\HF=-1431.9435142
\S2=0.766473\S2-1=0.\S2A=0.750228\RMSD=2.499e-09\RMSF=8.094e-07\Dipole
=-1.3487091,0.4966875,-0.0181556\Quadrupole=3.5926448,10.6665606,-14.2
592054,3.1473505,-5.5344043,-3.629379\PG=C01 [X(C31H18N3O1)]\\@

**1[6]-P**

1\1\GINC-LOCALHOST\FOpt\UB3LYP\6-311G(d,p)\C31H18N3O1(2)\PIOTR\30-Jul-
2024\0\\#P UB3LYP/6-311G(d,p) FOpt=tight SCF=Direct SCRF(Solvent=CH2CL
2) #P Geom=(NoDistance,NoAngle) fcheck freq(noraman)\\[6]helicene isom
erised via Smiles rearr, P isomer\\0,2\O,-0.8750160473,-0.3434867383,-
0.9657662644\N,3.0426307128,0.657139871,-0.0320590158\C,5.3679482397,0
.1202413497,0.0950267334\N,1.7684123875,0.3115476296,-0.3321727193\C,6
.4229887545,-0.7777387298,-0.1164855743\N,3.7915675571,-1.5112160972,-

0.7356657826\C,7.7299217282,-0.4201943806,0.2008130414\C,8.0038421035,0.8386809582,0.7344198193\C,6.9595698098,1.7382563735,0.9492174505\C,5.6518387117,1.3838124731,0.6327357923\C,3.974997067,-0.2812531713,-0.2510862085\C,1.4509878097,-0.939727838,-0.8452588172\C,2.5028336267,-1.8577187018,-1.0485151497\C,0.7404624833,1.242583282,-0.116170531\C,-0.5821035759,0.8660769588,-0.3769420462\C,0.130846683,-1.2567292278,-1.1615863849\C,1.0331002559,2.5502779943,0.3171688178\C,0.0214113919,3.471681596,0.3948963952\C,-1.320451663,3.1170494619,0.1248150492\C,-1.6657210403,1.7513276726,-0.1375820345\C,2.1766039047,-3.1180871022,-1.5804865332\C,-0.1763987214,-2.5012709682,-1.686791287\C,0.8595299697,-3.4227650986,-1.8921808695\C,-2.318589414,4.1278583753,0.014081293\C,-3.074281639,1.4001108005,-0.2656661775\C,-3.9808630415,2.4511960587,-0.5457224173\C,-3.5747641055,3.8134156623,-0.4035202856\C,-3.6307049338,0.0778344173,-0.0453139355\C,-4.9782915818,-0.1861323024,-0.4453868463\C,-5.7897296751,0.8780345039,-0.9411791873\C,-5.3274167933,2.1569138013,-0.923714568\C,-2.9571395313,-0.9431322477,0.6723690568\C,-3.5304694081,-2.1788400852,0.8807469221\C,-4.8140674901,-2.4672044189,0.3771589592\C,-5.5269458715,-1.4784016959,-0.2613223008\H,6.2012400728,-1.7523099985,-0.5299789444\H,8.5357826465,-1.1253685615,0.0311558369\H,9.0221997406,1.1167714287,0.9815170475\H,7.1642825564,2.7185072484,1.364746976\H,4.8431588947,2.0819194975,0.8015494761\H,2.0611573803,2.8108290087,0.5174299846\H,0.2482653898,4.5032645081,0.6371548156\H,2.9753780038,-3.8309390042,-1.7403654646\H,-1.2039471399,-2.7368186799,-1.9296735649\H,0.6188574556,-4.3957239169,-2.3034173711\H,-2.0348404205,5.1573263417,0.2006544489\H,-4.3090639485,4.5911725452,-0.5811212694\H,-6.8034251449,0.6586814508,-1.2581692294\H,-5.9736714495,2.9824201686,-1.2010671734\H,-5.2496797841,-3.4483003002,0.5274408132\H,-6.5399884113,-1.6634586404,-0.6023905906\H,-2.9926490544,-2.9295779165,1.4484541487\H,-1.9893100511,-0.7394196158,1.1064811266\\Version=ES64L-G16RevC.01\State=2-A\HF=-1431.9435142\S2=0.766473\S2-1=0.\S2A=0.750228\RMSD=2.501e-09\RMSF=8.094e-07\Dipole=-1.3487095,0.4966863,0.0181561\Quadrupole=3.5926419,10.6665633,-14.2592052,3.1473431,5.5343979,3.6293924\PG=C01 [X(C31H18N3O1)]]\\@

**1[7]-M**

1\1\GINC-LOCALHOST\FOpt\UB3LYP\6-311G(d,p)\C35H20N3O1(2)\PIOTR\01-Aug-2024\0\\#P UB3LYP/6-311G(d,p) FOpt=tight SCF=Direct SCRF(Solvent=CH2CL2) #P Geom=(NoDistance,NoAngle) fcheck\\[7]helicene isomerised via Smiles rearr, M enantiomer\\0,2\O,-0.906994406,-0.36555003,0.7567180553\N,3.0444258874,0.6641192623,0.0166353144\C,5.374875919,0.1374158606,-0.017314394\N,1.7597661047,0.3101882675,0.2562486536\C,6.4241094802,-0.7595661785,0.2247463248\N,3.7694198751,-1.5157901937,0.7096293081\C,7.7422265972,-0.3900157076,-0.0255696933\C,8.033441586,0.8802408648,-0.5216905752\C,6.9952000993,1.7792057356,-0.7661238838\C,5.6763728257,1.412682825,-0.5165271273\C,3.9694774368,-0.2760848869,0.2578533969\C,1.4242191407,-0.9517970094,0.7299150712\C,2.4690928076,-1.8717187039,0.9588788727\C,0.7397912038,1.2458833393,0.0235411779\C,-0.5893369349,0.8679190193,0.2420763136\C,0.092235832,-1.2792832132,0.9786862779\C,1.0444049639,2.5567911163,-0.3912047402\C,0.0346449265,3.4780486643,-0.4970348877\C,-1.3129534248,3.1240790257,-0.2566375831\C,-1.6636032195,1.7591703381,-0.0062921681\C,2.1240809996,-3.1438706352,1.4487941012\C,-0.2332763048,-2.5352432793,1.4636763709\C,0.795317069,-3.4585480128,1.6945435099\C,-2.3115688289,4.1367488196,-0.1540366174\C,-3.0738913305,1.4035332733,0.1299650022\C,-3.9593428541,2.463910796,0.4691869314\C,-3.5580477625,3.8244670921,0.2903029968\C,-3.6438198808,0.0839315913,-0.0346696277\C,-4.8905031804,-0.1818667332,0.5939987432\C,-5.6653032685,0.8834868298,1.1284724958\C,-5.2558158692,2.17525701,0.9759324676\C,-3.0994001881,-0.958131941,-0.8954610528\C,-3.6417412862,-2.2773017357,-0.8269022155\C,-4.7684898387,-2.5393745233,0.0133017599\C,-5.399826738,-1.5180919389,0.6486876\C,-2.1296823184,-0.7084639643,-1.8970291163\C,-1.655686216,-1.712469838,-2.7149540618\C,-2.1283347935,-3.0307064845,-

2.57493758\C,-3.1135762681,-3.299268589,-1.6518030832\H,6.1893387351,-
1.7426866621,0.6095834988\H,8.5432591603,-1.0947489482,0.1672386057\H,
9.0605178412,1.1676499581,-0.7165476479\H,7.2133053818,2.768483321,-1.
1524513654\H,4.8724984236,2.1105944079,-0.7075536463\H,2.0775528723,2.
8184523678,-0.5617439433\H,0.2678730735,4.5098887359,-0.7319355248\H,2
.9174891117,-3.85811327,1.62815052\H,-1.2700983396,-2.7789000018,1.653
1248091\H,0.5398082362,-4.4409166967,2.073205839\H,-2.0300805358,5.165
0107479,-0.350305976\H,-4.2872697371,4.6028826078,0.4853171055\H,-6.61
96110828,0.6539498743,1.5894310549\H,-5.8928191771,3.0007947939,1.2730
532261\H,-5.1515845954,-3.5523134412,0.0728617839\H,-6.3121016661,-1.6
944200357,1.2081481181\H,-1.7641934668,0.2977337403,-2.0458978438\H,-0
.921378094,-1.4799314286,-3.4778473459\H,-1.7407850647,-3.819087063,-3
.2098343781\H,-3.5254719191,-4.29906014,-1.5636862273\\Version=ES64L-G
16RevC.01\State=2-A\HF=-1585.613896\S2=0.766278\S2-1=0.\S2A=0.750223\R
MSD=6.871e-09\RMSF=8.894e-07\Dipole=-1.4169831,0.4636165,-0.026486\Qua
drupole=0.7611551,12.6822541,-13.4434091,3.6280597,-8.9411863,-2.88537
74\PG=C01 [X(C35H20N3O1)]\\@

**1[7]-P**
1\1\GINC-LOCALHOST\FOpt\UB3LYP\6-311G(d,p)\C35H20N3O1(2)\PIOTR\31-Jul-
2024\0\\#P UB3LYP/6-311G(d,p) FOpt=tight SCF=Direct SCRF(Solvent=CH2CL
2) #P Geom=(NoDistance,NoAngle) fcheck\\[7]helicene isomerised via Smi
les rearr\\0,2\O,-0.9069941947,-0.3655511175,-0.7567171712\N,3.0444254
714,0.6641220601,-0.0166363871\C,5.3748760295,0.137420905,0.0173123038
\N,1.7597659305,0.3101898464,-0.2562492132\C,6.4241102942,-0.759560368
3,-0.2247482011\N,3.7694212576,-1.5157866868,-0.7096307299\C,7.7422271
573,-0.3900086511,0.0255673184\C,8.0334411887,0.880248428,0.5216874611
\C,6.9951990005,1.7792125516,0.7661205333\C,5.6763719756,1.4126883889,
0.5165242911\C,3.9694778223,-0.2760811885,-0.2578549042\C,1.4242199591
,-0.9517957967,-0.7299153421\C,2.4690944116,-1.87171649,-0.9588796064\
C,0.739790231,1.2458839544,-0.0235413369\C,-0.589337656,0.8679183061,-
0.242075723\C,0.0922368415,-1.2792833375,-0.9786858335\C,1.0444029243,
2.5567920839,0.3912042491\C,0.0346420381,3.478048652,0.4970348218\C,-1
.3129560934,3.1240776603,0.2566382953\C,-1.6636046899,1.7591685989,0.0
062932303\C,2.124083599,-3.1438687983,-1.4487945504\C,-0.233274311,-2.
5352437679,-1.4636756484\C,0.7953198521,-3.4585475063,-1.6945432419\C,
-2.3115725486,4.136746463,0.1540377603\C,-3.0738925268,1.4035301311,-0
.129963128\C,-3.9593452807,2.4639067501,-0.469184674\C,-3.5580514211,3
.8244634619,-0.2903011234\C,-3.6438196879,0.0839279014,0.0346719485\C,
-4.8905030964,-0.1818717044,-0.5939956708\C,-5.6653045324,0.8834810475
,-1.1284690838\C,-5.2558183051,2.1752516435,-0.9759294325\C,-3.0993984
857,-0.9581350213,0.8954631719\C,-3.6417383553,-2.2773053489,0.8269047
905\C,-4.768487137,-2.539379315,-0.0132985108\C,-5.3998253905,-1.51809
74107,-0.6486840935\C,-2.1296802808,-0.7084660052,1.8970306583\C,-1.65
56827487,-1.7124713398,2.7149554401\C,-2.1283301386,-3.0307084522,2.57
49393699\C,-3.1135718814,-3.2992716035,1.6518054674\H,6.1893402963,-1.
7426812521,-0.6095848062\H,8.5432602662,-1.0947413228,-0.1672407869\H,
9.0605172472,1.167658491,0.7165441422\H,7.2133035324,2.7684905329,1.15
24474244\H,4.8724970315,2.1105993995,0.7075506246\H,2.0775506642,2.818
4543744,0.5617428747\H,0.267869303,4.5098889806,0.7319351958\H,2.91749
2316,-3.858110671,-1.6281513205\H,-1.2700962034,-2.7789015325,-1.65312
35257\H,0.5398117893,-4.4409164726,-2.0732053498\H,-2.0300851533,5.165
0086904,0.3503068377\H,-4.2872742669,4.6028782408,-0.4853149181\H,-6.6
196123968,0.6539431146,-1.5894270527\H,-5.8928225963,3.0007887712,-1.2
730499072\H,-5.1515809466,-3.5523186093,-0.0728582015\H,-6.3121004724,
-1.6944264468,-1.2081440636\H,-1.7641923072,0.2977320697,2.0458990692\
H,-0.9213744128,-1.4799321402,3.4778482761\H,-1.7407792891,-3.81908858
52,3.2098360341\H,-3.5254666236,-4.2990635566,1.5636889487\\Version=ES
64L-G16RevC.01\State=2-A\HF=-1585.613896\S2=0.766278\S2-1=0.\S2A=0.750
223\RMSD=6.972e-09\RMSF=8.892e-07\Dipole=-1.4169836,0.463615,0.0264867
\Quadrupole=0.7611578,12.6822641,-13.4434219,3.628048,8.9411771,2.8853

```
793\PG=C01 [X(C35H20N3O1)]\\@
```

## 11.    References

1.    G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.

2.    G. A. Zissimou, P. Bartos, A. Pietrzak and P. Kaszyński, *J. Org. Chem.*, 2022, **87**, 4829–4837.

3.    P. Bartos, V. G. Young, Jr. and P. Kaszyński, *Org. Lett.*, 2020, **22**, 3835–3840.

4.    P. Kaszyński, C. P. Constantinides and V. G. Young, Jr., *Angew. Chem., Int. Ed.* , 2016, **55**, 11149−11152.

5.    A. Wu, Y. Duan, D. Xu, T. M. Penning and R. G. Harvey, *Tetrahedron*, 2010, **66**, 2111–2118.

6.    M. Sako, Y. Takeuchi, T. Tsujihara, J. Kodera, T. Kawano, S. Takizawa and H. Sasai, *J. Am. Chem. Soc.*, 2016, **138**, 11481–11484.

7.    K. Usui, K. Yamamoto, T. Shimizu, M. Okazumi, B. Mei, Y. Demizu, M. Kurihara and H. Suemune, *J. Org. Chem.*, 2015, **80**, 6502−6508.

8.    T. Hartung, R. Machleid, M. Simon, C. Golz and M. Alcarazo, *Angew. Chem. Int. Ed.* , 2020, **59**, 5660 –5664.

9.    C. P. RigakuOD, Rigaku Oxford Diffraction Ltd, 2018, Yarnton, Oxfordshire, England.

10.    G. M. Sheldrick, *Acta Cryst., Sect.*, 2015, **A71**, 3-8.

11.    C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Cryst.*, 2011, **44**, 1281–1284.

12.    G. M. Sheldrick, *Acta Cryst., Sect.*, 2015, **C71**, 3-8.

13.    A. L. Spek, *Acta Cryst. C*, 2015, **C71**, 9–18.

14.    A. Bodzioch, D. Pomikło, M. Celeda, A. Pietrzak and P. Kaszyński, *J. Org. Chem.*, 2019, **84**, 6377−6394.

15.    P. Bartos, B. Anand, A. Pietrzak and P. Kaszyński, *Org. Lett.*, 2020, **22**, 180–184.

16.    Gaussian 16, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E.

N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT. 2016,.

17. M. Cossi, G. Scalmani, N. Rega and V. Barone, *J. Chem. Phys.*, 2002, **117**, 43–54.

18. F. De Vleeschouwer, A. Chankisjijev, W. Yang, P. Geerlings and F. De Proft, *J. Org. Chem.*, 2013, **78**, 3151–3158.

19. R. E. Stratmann, G. E. Scuseria and M. J. Frisch, *J. Chem. Phys.*, 1998, **109**, 8218-8224.