Electronic Supporting Information

for

Azahelicene-fused Blatter radicals: Chiral paramagnetic NIR absorbers

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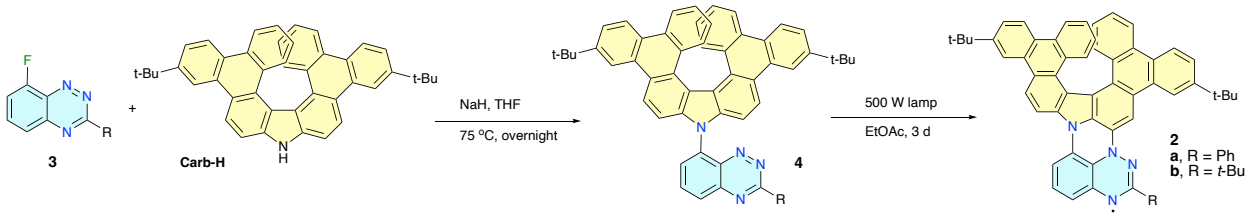
1. Synthetic details

Products were purified by flash chromatography on silica gel (230–400 mesh, Merck). NMR spectra were recorded in $CDCl_3$/DMSO 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_2Cl_2 at concentrations ranging from 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. Passivated SiO_2 was prepared by suspension in 2% solution of Et_3N in CH_2Cl_2 and then evaporation till dryness.

Preparation of Radicals 2



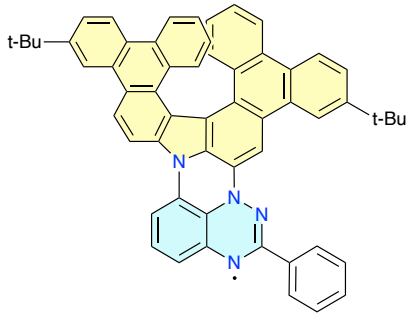
Scheme S1. Preparation of radicals **2**.

Preparation of radicals 2. General procedure.

A solution of 0.1 mmol of precursor **4** in dry EtOAc (195 mL) was placed in a 500 mL RB flask fitted with a reflux condenser. 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 (40% CH_2Cl_2/pet. ether) and the irradiation was stopped after 3 d. The solvent was evaporated, the residue was adsorbed onto ~ 1.0 g of passivated silica, and the unreacted starting material **4** followed by product **2,** was separated using a silica gel column passivated with Et_3N (pet. ether/CH_2Cl_2, gradient 15%). The radical **2** was purified further

by dissolving in minimum amounts of CH_2Cl_2 and then precipitating the radical by the addition of MeCN.

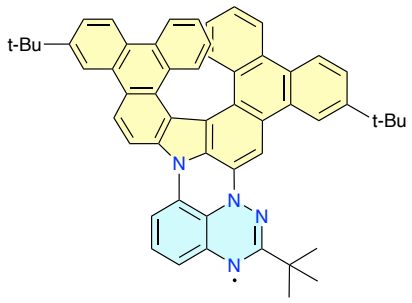
Radical 2a.



Starting from **4a** (150 mg, 0.19 mmol). Irradiation time: 3 d. Chromatographed on passivated silica (pet. ether/CH_2Cl_2, 3:2) to give the title radical **2a** as a dark green solid.

Yield = 30 mg (20%). Mp 335-340 °C (CH_3CN); UV-vis (CH_2Cl_2), λ_{max} (log ε) 828 (3.93), 742.5 (3.61), 564.5 (4.02), 443 (4.12), 382 (4.25), 361 (4.31), 261 (5.00) nm; IR *v* 2918, 1575, 1488, 1388, 1359, 1248, 1027, 764, 697 cm^{-1}; ESI(+)-MS *m/z* 784 (100, $[M+H]^+$); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd. for $C_{57}H_{44}N_4$: 784.3566, found: 784.3530. Anal. Calcd for $C_{57}H_{43}N_4$: C, 87.32; H, 5.53; N, 7.15. Found: C, 87.19; H, 5.76; N, 7.07.

Radical 2b.



Starting from **4b** (150 mg, 0.196 mmol). Irradiation time: 3 d. Chromatographed on passivated silica (pet. ether/CH_2Cl_2, 3:2) to give radical **2b** as a dark green solid.

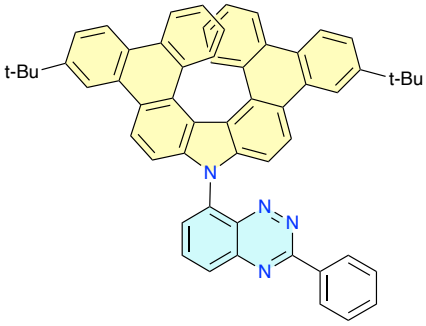
Yield = 27 mg (18%). Mp 192–195 °C (CH_3CN); UV-vis (CH_2Cl_2), λ_{max} (log ε) 814.5 (3.79), 731.5 (3.49), 611 (3.92), 561.5 (3.92), 437.5 (3.93), 380.5 (4.11), 321 (4.56), 260 (4.87) nm; IR *v* 2952, 1579, 1480, 1398, 1358, 1203, 946, 876, 777, 762, 728, 709, 660 cm^{-1}; ESI(+)-MS *m/z* 764 (100, $[M+H]^+$); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd. for $C_{55}H_{48}N_4$: 764.3879, found: 764.3851. Anal. Calcd for $C_{55}H_{47}N_4$: C, 86.47; H, 6.20; N, 7.33. Found: C, 86.48; H, 6.25; N, 7.36. In addition, 104 mg (69%) of the starting material **4b** was recovered.

Preparation of precursors 4. General procedure.

3,11-Di-*tert*-butyl-7*H*-diphenanthro[9,10-*c*:9',10'-*g*]carbazole (**Carb-H**, 0.20 mmol, 1.0 equiv.) and 60% NaH (0.39 mmol, 1.95 equiv.) was dissolved in dry THF. The yellow reaction mixture was stirred for 2 hr at 75 °C, and 8-fluoro-3-phenylbenzo[*e*][1,2,4]triazine (**3a**) or 3-(*tert*-butyl)-8-fluorobenzo[*e*][1,2,4]triazine (**3b**, 0.22 mmol, 1.1 equiv.) in dry THF was added. The reaction

mixture was stirred at 75 °C overnight. Water was added and the mixture was extracted with CH_2Cl_2, washed with brine, and dried ($MgSO_4$). Solvents were evaporated and the crude product **4** was purified by column chromatography followed by recrystallization.

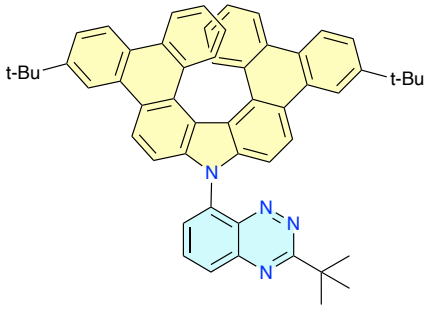
3,11-Di-*tert*-butyl-7-(3-phenylbenzo[*e*][1,2,4]triazin-8-yl)-7*H*-diphenanthro[9,10-*c*:9',10'-*g*]carbazole (4a)



Following the general procedure, **4a** (82 mg, 52%) was obtained starting from 117.4 mg (0.20 mmol) of 3,11-di-*tert*-butyl-7*H*-diphenanthro[9,10-*c*:9',10'-*g*]carbazole (**Carb-H, X=tBu**), 60% NaH (15.5 mg with mineral oil, 0.39 mmol, 1.95 equiv.) and 49.6 mg (0.22 mmol) of 8-fluoro-3-phenylbenzo[*e*][1,2,4]triazine[2] (**3a**).

Mp 185-188 °C (CH_2Cl_2/hexane 1:4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (dd, J_1 = 6.2 Hz, J_2 = 2.4 Hz, 2H), 8.76 (dd, J_1 = 9.0 Hz, J_2 = 6.0 Hz, 2H), 8.69 (dd, J_1 = 8.8 Hz, J_2 = 1.9 Hz, 2H), 8.66 (dd, J_1 = 8.7 Hz, J_2 = 2.2 Hz, 2H), 8.45 (dd, J_1 = 8.6 Hz, J_2 = 1.9 Hz, 1H), 8.43 (dd, J_1 = 8.3 Hz, J_2 = 3.8 Hz, 2H), 8.35 (t, J = 7.9 Hz, 1H), 8.29 (dd, J_1 = 8.7 Hz, J_2 = 1.4 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 8.3 Hz, 2H), 7.61-7.59 (m, 3H), 7.54 (d, J = 8.8 Hz, 1H), 7.51 (d, J = 8.7 Hz, 1H), 7.23 (t, J = 7.4 Hz, 2H), 6.38 (td, J_1 = 7.3 Hz, J_2 = 2.2 Hz, 2H), 1.55 (s, 18H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.5, 149.84, 149.76, 143.4, 142.6, 142.5, 142.4, 136.1, 135.8, 135.2, 132.1, 131.0, 130.6, 130.5, 130.4, 130.3, 129.22, 129.19, 128.7, 128.6, 128.4, 128.1, 127.9, 127.4, 127.3, 127.0, 126.9, 125.3, 125.2, 124.4, 124.3, 124.2, 123.2, 123.1, 121.7, 121.6, 121.5, 119.7, 119.6, 119.5, 110.3, 110.2, 35.3, 31.7; UV-vis (CH_2Cl_2), λ_{max} (log ε) 463 (2.99), 411 (3.94), 381.5 (4.07), 327 (4.63), 280 (4.89) nm; IR ν 2959, 1610, 1565, 1506, 1391, 1325, 1261, 1029, 799, 765, 750, 706, 655 cm^{-1}; APCI (-)-MS *m/z* 784 (100, $[M]^+$); HRMS (APCI-TOF) *m/z* $[M]^+$ calcd. for $C_{57}H_{44}N_4$: 784.3566, found: 784.3554. Anal. Calcd for $C_{57}H_{44}N_4$: C, 87.21; H, 5.65; N, 7.14. Found: C, 87.05; H, 5.59; N, 7.26.

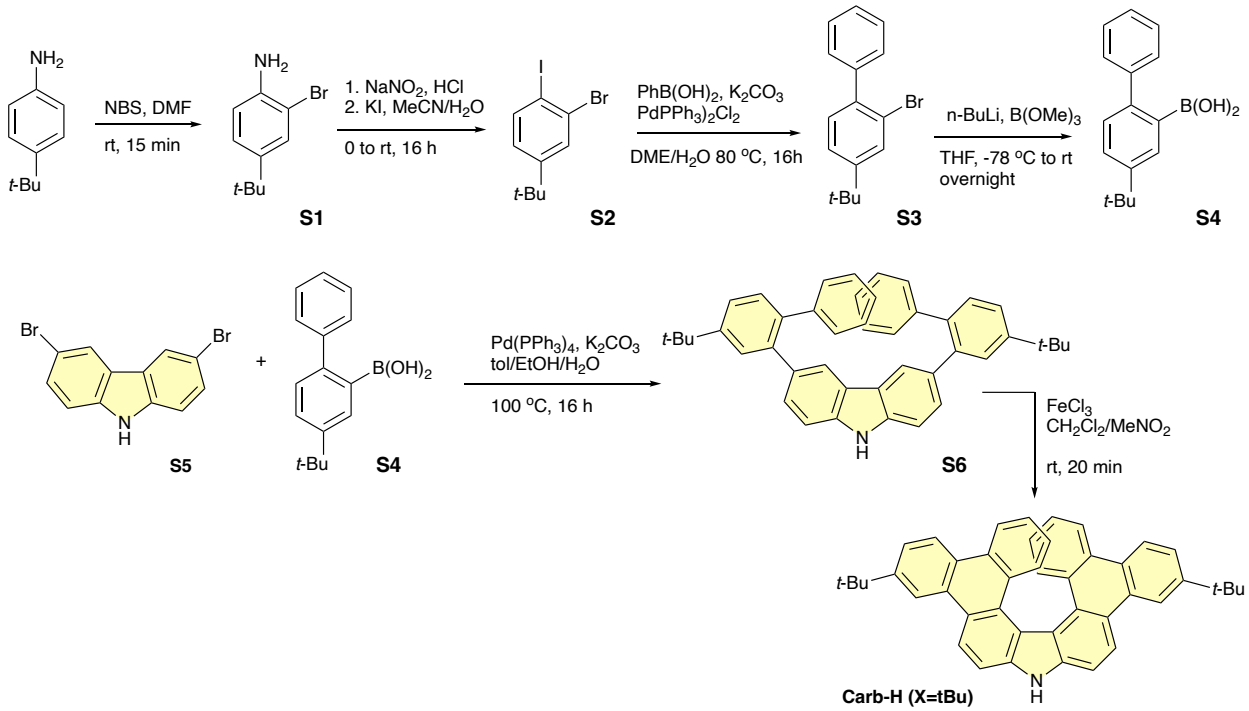
3,11-Di-*tert*-butyl-7-(3-(*tert*-butyl)benzo[*e*][1,2,4]triazin-8-yl)-7*H*-diphenanthro[9,10-*c*:9',10'-*g*]carbazole (4b).



Following the general procedure, **4b** (145 mg, 55%) was obtained starting from 200.0 mg (0.35 mmol) of 3,11-di-*tert*-butyl-7*H*-diphenanthro[9,10-*c*:9',10'-*g*]carbazole (**Carb-H, X=tBu**), 27.6 mg (with mineral oil, 0.69 mmol) of 60% NaH and 78 mg (0.38 mmol) of 3-(*tert*-butyl)-8-fluorobenzo[*e*][1,2,4]triazine (**3b**).

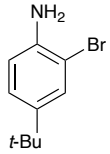
Mp 180-183 °C (CH_2Cl_2/hexane 1:4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 8.9 Hz, 1H), 8.73 (d, J = 8.9 Hz, 1H), 8.69 (dd, J_1 = 5.4, J_2 = 1.9 Hz, 2H), 8.65 (dd, J_1 = 8.8 Hz, J_2 = 1.7 Hz, 2H), 8.44-8.37 (m, 3H), 8.32-8.25 (m, 3H), 7.90 (t, J = 8.7 Hz, 2H), 7.75 (dt, J_1 = 8.6 Hz, J_2 = 1.8 Hz, 2H), 7.49 (d, J = 6.9 Hz, 1H), 7.47 (d, J = 6.8 Hz, 1H), 7.24-7.19 (m, 2H), 6.38 (t, J = 6.9 Hz, 1H), 1.67 (s, 9H), 1.55 (s, 18H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 173.2, 149.8, 149.7, 142.82, 142.63, 142.5, 142.0, 135.8, 135.2, 130.9, 130.6, 130.5, 130.4, 130.3, 128.64, 128.55, 128.4, 128.1, 127.9, 127.4, 127.3, 127.0, 126.9, 125.3, 125.1, 124.4, 124.3, 124.1, 123.2, 123.1, 121.7, 121.6, 121.4, 119.7, 119.5, 119.4, 110.3, 110.2, 39.5, 35.3, 31.7, 29.8; UV-vis (CH_2Cl_2), λ_{max} (log ε) 451 (2.965), 409 (3.87), 371 (4.07), 329 (4.60), 280 (4.77) nm; IR ν 2956, 1610, 1568, 1505, 1485, 1393, 1263, 1158, 785, 765, 731, 722, 656 cm^{-1}; APCI (+)-MS *m/z* 765 (100, $[M+H]^+$); HRMS (APCI-TOF) *m/z* $[M+H]^+$ calcd. for $C_{55}H_{49}N_4$: 765.3957, found: 765.3935. Anal. Calcd for $C_{55}H_{48}N_4$: C, 86.35; H, 6.32; N, 7.32. Found: C, 86.32; H, 6.29; N, 7.30.

Preparation of azahelicene Carb-H (X=tBu)



Scheme S2. Preparation of **Carb-H (X=tBu)**.

Synthesis of 2-bromo-4-(*tert*-butyl)aniline (S1).[3, 4]

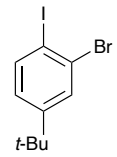


4-*tert*-Butylaniline (5.40 mL, 33.5 mmol, 1 equiv.) was dissolved in dry DMF (50 mL) and a solution of *N*-bromosuccinimide (NBS, 6.31 g, 35.2 mmol, 1.05 equiv.) in dry DMF (30 mL) was added to the above solution dropwise over 30 min. The progress of the reaction was monitored by thin-layer chromatography (TLC, hexane/EtOAc, 9:1) which indicated that the starting material was consumed after 15 min. The reaction mixture was poured into an aq. $NaHSO_3$ (5%, 90 mL) and the organic layer was separated using EtOAc (90 mL). The organic layer was washed with brine (90 mL), dried (Na_2SO_4) and EtOAc was removed under reduced pressure using a rotatory evaporator. After purification using column chromatography (SiO_2, hexane), product **S1** was obtained as a light-brown liquid.

Yield = 7.51 g (98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 2.0 Hz, 1H), 7.14 (dd, J_1 = 8.4 Hz, J_2 = 2.2 Hz, 1H), 6.73 (d, J = 8.3 Hz, 1H), 3.91 (br. s, 2H), 1.28 (m, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.0, 141.6, 129.4, 125.5, 115.7, 109.5, 34.1, 31.5; ESI(+)-MS *m/z* 228 and 230

(1:1, 100, $[M + H]^+$); HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{10}H_{15}BrN$: 228.0388, found: 228.0388. Anal. Calcd. for $C_{10}H_{14}BrN$: C, 52.65; H, 6.19; N, 6.14. Found: C, 52.47; H, 6.23; N, 6.21.

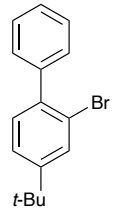
Synthesis of 2-bromo-4-(*tert*-butyl)-1-iodobenzene (S2).[3, 4]



2-Bromo-4-(*tert*-butyl)aniline (**S1**, 5.00 g, 21.93 mmol, 1 equiv.) was dissolved in MeCN (65 mL) and aq. HCl (conc. 12 mL in 40 mL of water) was added dropwise with stirring. The reaction mixture was cooled to 0 °C and a solution of $NaNO_2$ (1.93 g, 27.95 mmol, 1.27 equiv.) in water was added dropwise for over 20 min. The reaction mixture was stirred at 0 °C for 1 hr and then a solution of KI (5.79 g, 35 mmol, 1.6 equiv.) in water (35 mL) was added to the reaction mixture dropwise. The reaction mixture was stirred for 16 hr and the progress of the reaction was monitored by TLC. The reaction mixture was extracted using CH_2Cl_2 (3×90 mL). The combined organic layers were washed with sat. aq. solution of $Na_2S_2O_3$ (125 mL), rinsed with brine (3×100 mL), dried ($MgSO_4$) and finally evaporated. The crude product was purified using column chromatography (SiO_2, hexane) giving compound **S2** as a colourless liquid.

Yield = 7.30 g (98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.3 Hz, 1H), 7.63 (d, J = 2.3 Hz, 1H), 7.02 (dd, J_1 = 8.4 Hz, J_2 = 2.3 Hz, 1H), 1.29 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.4, 139.9, 130.1, 129.6, 126.0, 97.3, 34.7, 31.1; APCI (+)-MS *m/z* 338 and 340 (1:1, 18, $[M]^+$), 213 and 215 (1:1, 100); HRMS (APCI-TOF) *m/z* $[M]^+$ calcd for $C_{10}H_{12}BrI$ 337.9167, found 337.9162. Anal. Calcd for $C_{10}H_{12}BrI$: C, 35.43; H, 3.57; Found: C, 35.29; H, 3.48.

Synthesis of 2-bromo-4-(*tert*-butyl)biphenyl (S3).[5-7]

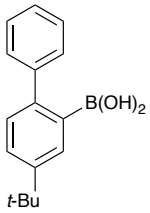


2-Bromo-4-(*tert*-butyl)-1-iodobenzene (**S2**, 10.17 g, 29.99 mmol, 1 equiv.), K_2CO_3 (10.4 g, 75.25 mmol, 2.5 equiv.), phenylboronic acid (4.40 g, 36.09 mmol, 1.2 equiv.) and $(PPh_3)_2PdCl_2$ (316 mg, 0.45 mmol, 0.015 equiv.) were added to a round-bottomed flask with a rubber septum under inert conditions. Water (15 mL) and freshly distilled dimethoxyethane (DME, 85 mL) were added under argon gas. The reaction mixture was stirred at 80 °C for 16 hr, cooled to ambient temperature, and DME was evaporated. Water and CH_2Cl_2 (90 mL) were added and the organic layer was separated. The combined organic layer

was washed with brine (90 mL) and dried ($MgSO_4$). The crude product was purified using column chromatography (SiO_2, pentane) giving intermediate **S3** as a colourless liquid.

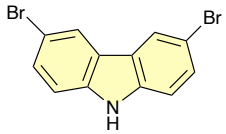
Yield = 7.00 g (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 2.0 Hz, 1H), 7.50–7.45 (m, 5H), 7.45 (dt, J_1 = 7.9 Hz, J_2 = 1.6 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 1.43 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.3, 141.1, 139.7, 131.0, 130.3, 129.6, 128.0, 127.5, 124.7, 122.6, 34.7, 31.4. APCI (+)-MS *m/z* 288 and 290 (1:1, 100, $[M]^+$), 273 and 275 (1:1, 50%); HRMS (APCI-TOF) *m/z* $[M]^+$ calcd for $C_{16}H_{17}Br$: 288.0514, found: 288.0504. Anal. Calcd for $C_{16}H_{17}Br$: C, 66.45; H, 5.92. Found: C, 66.41; H, 5.90.

Synthesis of 4-(*tert*-butyl)biphenyl-2-ylboronic acid (S4).[6, 7]



n-BuLi (1.6 M in hexane, 0.67 mL, 1.66 mmol, 1.2 equiv.) was added dropwise to a solution of 2-bromo-4-(*tert*-butyl)biphenyl (**S3**, 400 mg, 1.38 mmol, 1.0 equiv.) in anhydrous THF at -78 ° C under N_2 in an oven-dried round-bottomed flask. The reaction mixture was stirred at -78 ° C for 1 hr. $B(OMe)_3$ (1.6 mL, 13.6 mmol, 10 equiv.) was slowly added to the reaction mixture and the resulting mixture was allowed to warm to rt and stirred overnight. The reaction mixture was quenched with distilled water and treated with 1.0 M HCl. The product was extracted into EtOAc. The combined organic layer was washed with brine and dried (Na_2SO_4). The crude 4-*tert*-butylbiphenyl-2-ylboronic acid (**S4**) was obtained as a white powder and used without further purification.

Synthesis of 3,6-dibromo-9*H*-carbazole (S5).[8]

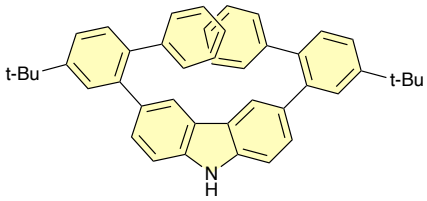


9*H*-Carbazole (7.50 g, 44.85 mmol, 1.0 equiv.) was dissolved in a 250 mL round-bottomed flask in dry DMF (20 mL). The resulting solution was degassed and stirred at 0 °C for 30 min and a degassed solution of NBS (16.00 g, 89.0 mmol, 1.98 equiv.) in dry DMF (30 mL) was added at 0 °C. The reaction mixture was stirred at 0 °C for 10 min, brought to rt and stirred for 12 hr. TLC analysis determined the completion of the reaction. The resulting reaction mixture was poured into water (50 mL) and the white precipitate was filtered off. The precipitate was dissolved in CH_2Cl_2, washed with water to remove water-soluble impurities, dried ($MgSO_4$) filtered, and concentrated under reduced

pressure. The crude white product was recrystallized (EtOH) to yield 3,6-dibromo-9*H*-carbazole (**S5**) as a white solid.

Yield = 11.6 g (80%). Mp 200-205 °C (EtOH); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.62 (brs, 1H), 8.43 (s, 2H), 7.52 and 7.48 AB (d, J = 8.8 Hz, 4H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 139.3, 129.2, 123.9, 123.8, 113.7, 111.5; ESI(-)-MS *m/z* 322, 324 and 326 (1:2:1, 100, [M]$^{+}$); HRMS (ESI-TOF) *m/z* [M - H]$^{+}$ calcd for $C_{12}H_6Br_2N$: 321.8867, found: 321.8873. Anal. Calcd for $C_{12}H_7Br_2N$: C, 44.35; H, 2.17; N, 4.31. Found: C, 44.32; H, 2.19; N, 4.32.

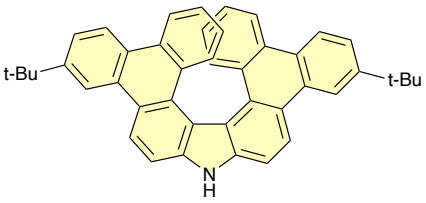
Synthesis of 3,6-bis(4-(*tert*-butyl)biphenyl-2-yl)-9*H*-carbazole (S6). [6, 7]



A solution of 3,6-dibromo-9*H*-carbazole (**S5**, 1.10 g, 3.4 mmol, 1.0 equiv.), 4-(*tert*-butyl)biphenyl-2-ylboronic acid (**S4**, 2.00 g, 7.85 mmol, 2.3 equiv.), $Pd(PPh_3)_4$ (197 mg, 170 µmol, 0.05 equiv.) and K_2CO_3 (1.70 g, 8.5 mmol, 2.5 equiv.) in a toluene/EtOH/H_2O, 2:1:1 (40 mL of toluene, 20 mL of EtOH and 20 mL of water) mixture was degassed and refluxed at 100 °C for 16 hr. The completion of the reaction was monitored by thin-layer chromatography (TLC). The reaction mixture was concentrated under reduced pressure *via* a rotavap, the resulting mixture was quenched with H_2O and extracted with CH_2Cl_2 (90 mL). The combined organic layer was washed with brine (90 mL) and dried ($MgSO_4$). The product was purified using column chromatography (SiO_2, 20% EtOAc in hexane), and 3,6-bis(4-(*tert*-butyl)biphenyl-2-yl)-9*H*-carbazole (**S6**) was obtained as a white solid.

Yield = 1.60 g (81%). Mp 240-242 °C (EtOAc/hexane 1:5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.56 (d, J = 2.1 Hz, 2H), 7.48 (dd, J_1 = 8.1 Hz, J_2 = 2.1 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.21–7.13 (m, 12H), 7.08 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 2H), 1.44 (s, 18H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.5, 141.9, 140.9, 138.6, 137.9, 133.8, 130.4, 130.1, 128.5, 128.4, 127.9, 126.2, 124.3, 123.5, 121.5, 110.0, 34.8, 31.6; APCI (+)-MS *m/z* 584 (63, [M+H]$^{+}$), 472 (43), 279 (100); HRMS (APCI-TOF) *m/z* [M+H]$^{+}$ calcd. for $C_{44}H_{42}N$: 584.3317, found: 584.3320. Anal. Calcd for $C_{44}H_{41}N$: C, 90.52; H,7.08; N, 2.40. Found: C, 90.31; H, 7.12; N, 2.45.

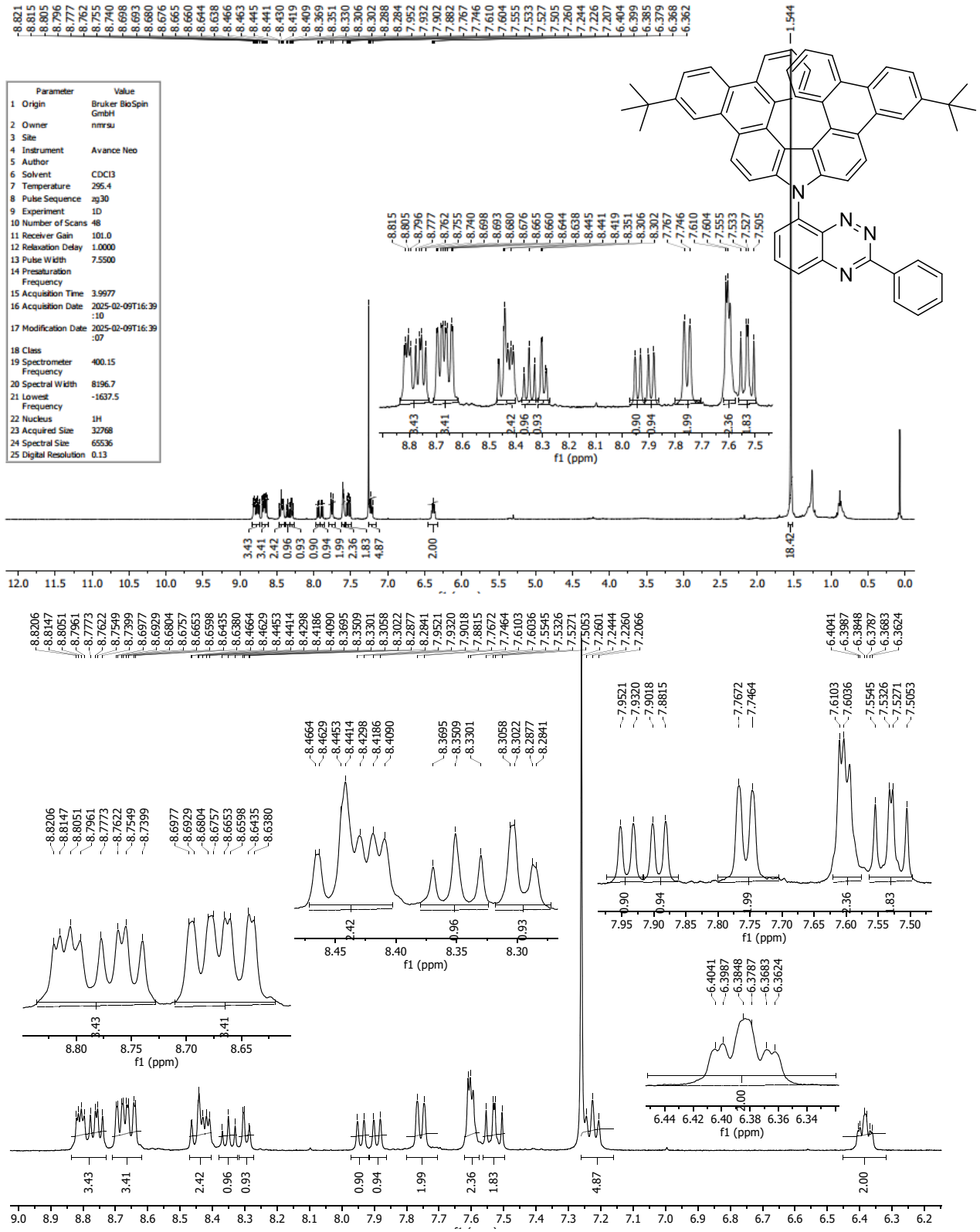
Synthesis of 3,11-di-*tert*-butyl-7*H*-diphenanthro[9,10-*c*:9',10'-*g*]carbazole (Carb-H). [6, 7]



3,6-Bis(4-(*tert*-butyl)biphenyl-2-yl)-9*H*-carbazole (**S6**, 200 mg, 0.343 mmol, 1 equiv.) was dissolved in dry CH_2Cl_2 (60 mL) and the reaction mixture was stirred under the N_2 atmosphere. $FeCl_3$ (334 mg, 2.058 mmol, 6 equiv.) was dissolved in dry $MeNO_2$ (4 mL) and the solution was added to the reaction mixture dropwise over 20 min. Reaction progress was monitored with TLC. After 20 min the reaction mixture was poured into a mixture of aq. $NaHCO_3$ and CH_2Cl_2, the organic layer was separated, washed with water, and dried (Na_2SO_4). The reaction mixture was purified by column chromatography using hexane/THF (95:5) to obtain 3,11-di-*tert*-butyl-7*H*-diphenanthro[9,10-*c*:9',10'-*g*]carbazole as a yellow solid.

Yield = 73.6 mg (37%). Mp > 350 °C (Hexane/THF 19:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.85 (d, J = 8.8 Hz, 2H), 8.75 (s, 2H), 8.65 (d, J = 8.6 Hz, 2H), 8.41 (d, J = 8.2 Hz, 2H), 7.90 (d, J = 8.6 Hz, 2H), 7.76 (apparent d, J = 8.3 Hz, 4H), 7.20 (t, J = 7.6 Hz, 2H), 6.32 (t, J = 7.6 Hz, 2H), 1.59 (s, 18H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.8, 139.5, 130.4, 128.5, 128.2, 128.1, 127.2, 126.9, 124.6, 124.2, 124.1, 123.2, 121.6, 121.5, 119.5, 118.9, 111.1, 35.4, 31.8; ESI(-)-MS *m/z* 578 (100, $[M - H]^+$); HRMS (ESI-TOF) *m/z* $[M-H]^+$ calcd for $C_{44}H_{36}N$: 578.2848, found: 578.2852. Anal. Calcd for $C_{44}H_{37}N$: C, 91.15; H, 6.43; N, 2.42. Found: C, 90.89; H, 6.57; N, 2.55.

2. NMR spectra



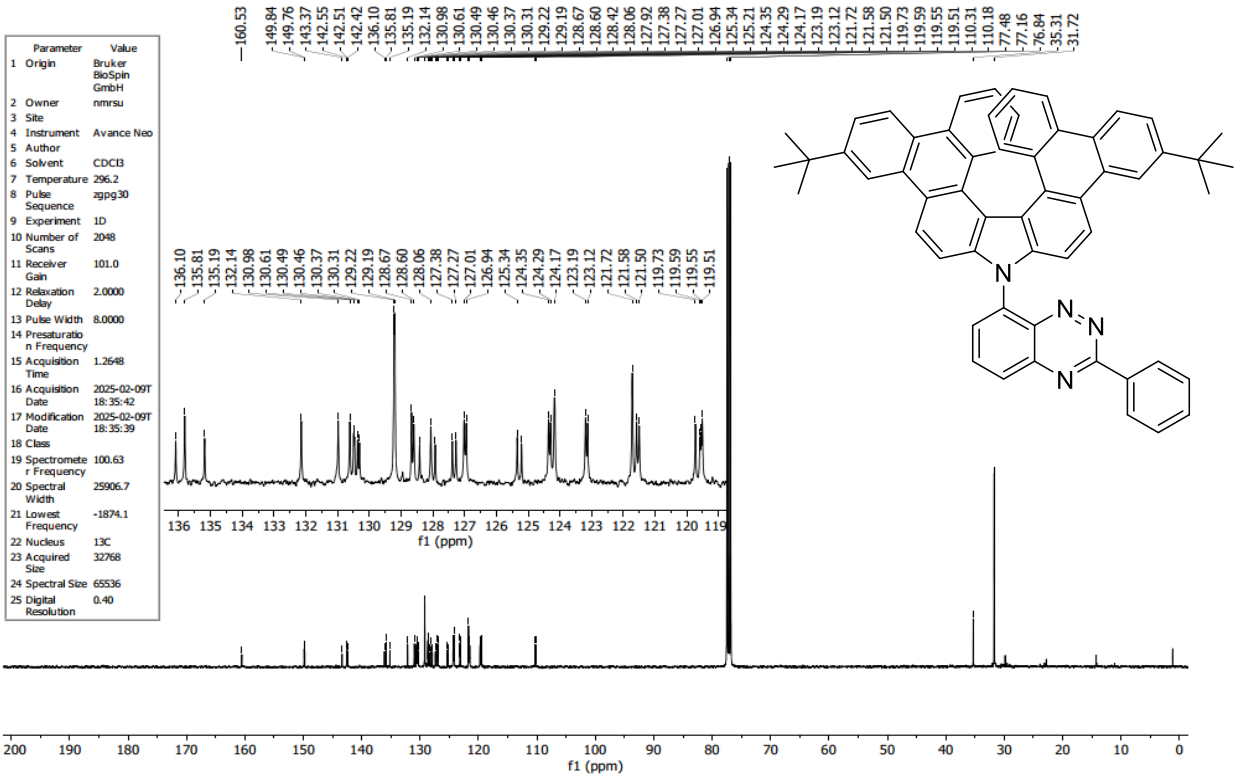
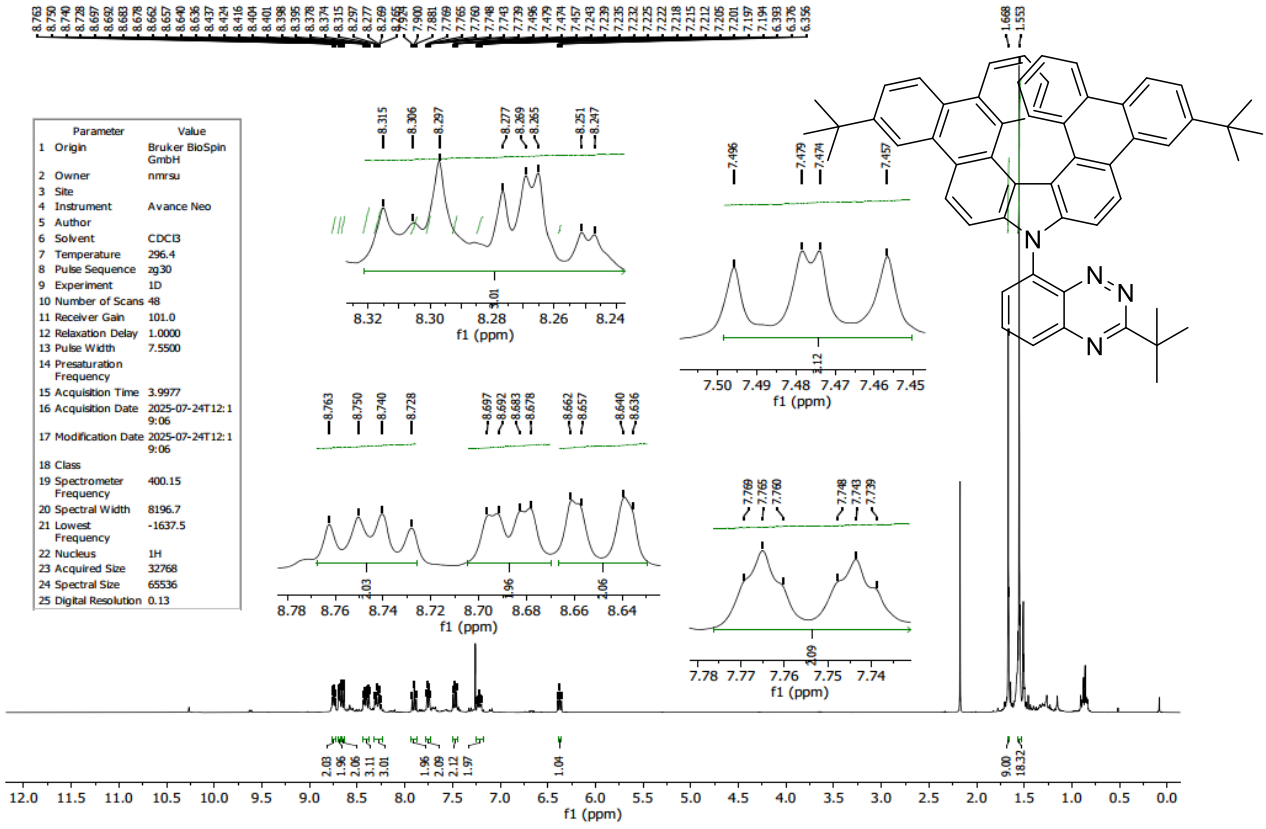


Figure S1. ^{1}H (full and aromatic region) and $^{13}C\{^{1}H\}$ NMR of **4a** recorded in $CDCl_3$ at 400 and 101 MHz, respectively.



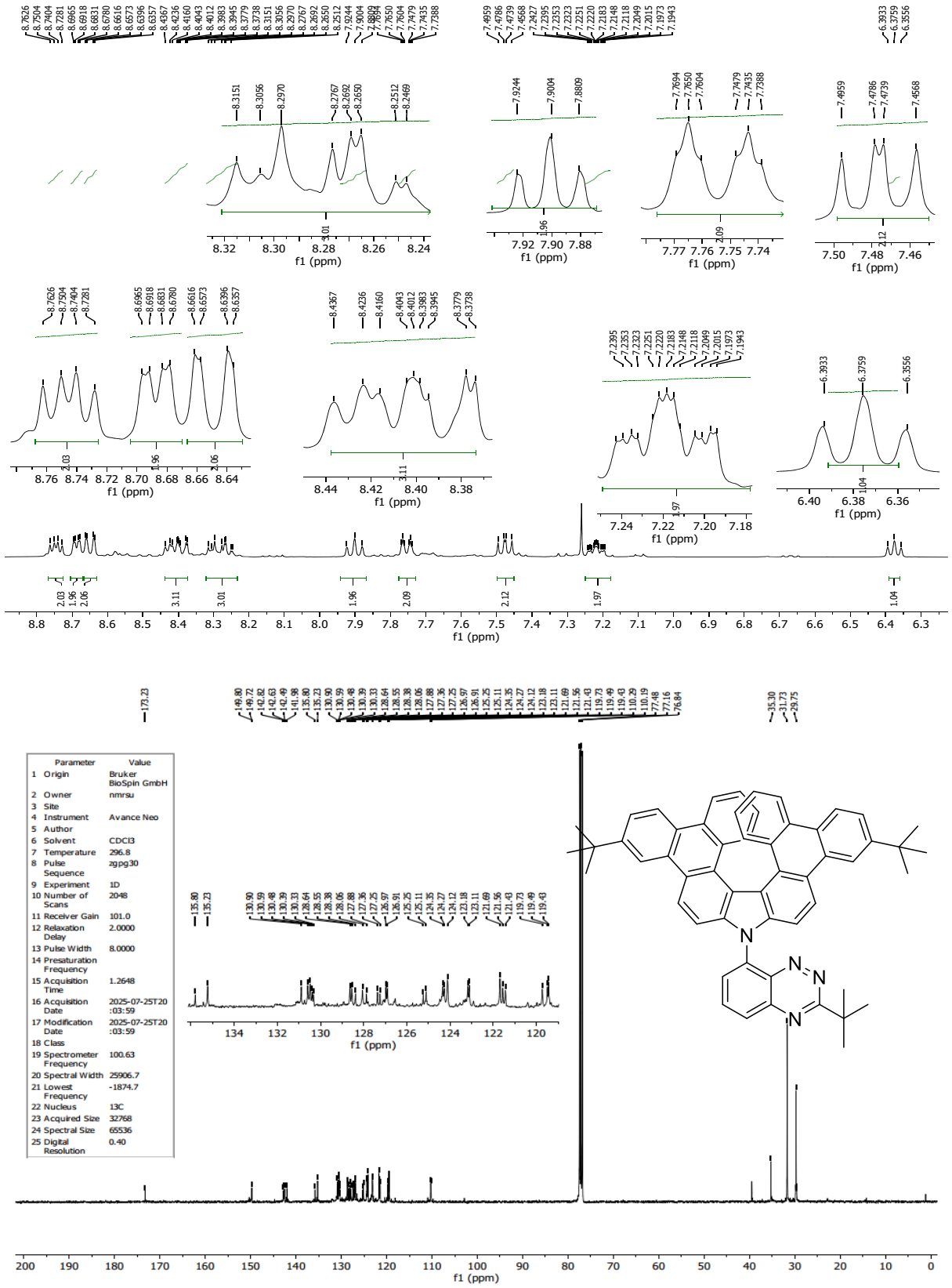


Figure S2. ^{1}H and $^{13}C\{^{1}H\}$ NMR of **4b** recorded in $CDCl_3$ at 400 and 101 MHz, respectively.

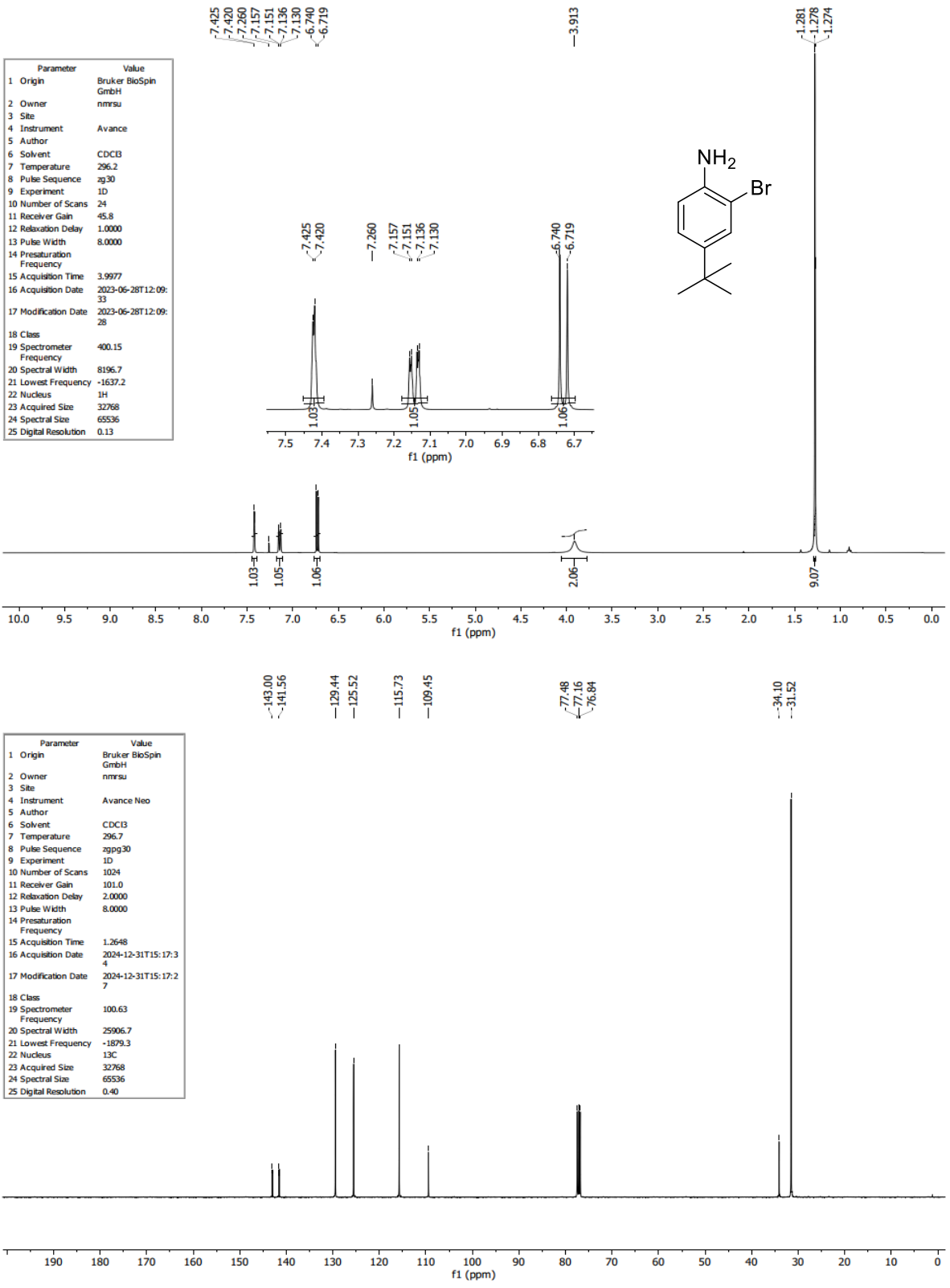


Figure S3. ^{1}H and $^{13}C\{^{1}H\}$ NMR of **S1** recorded in $CDCl_3$ at 400 and 101 MHz, respectively.

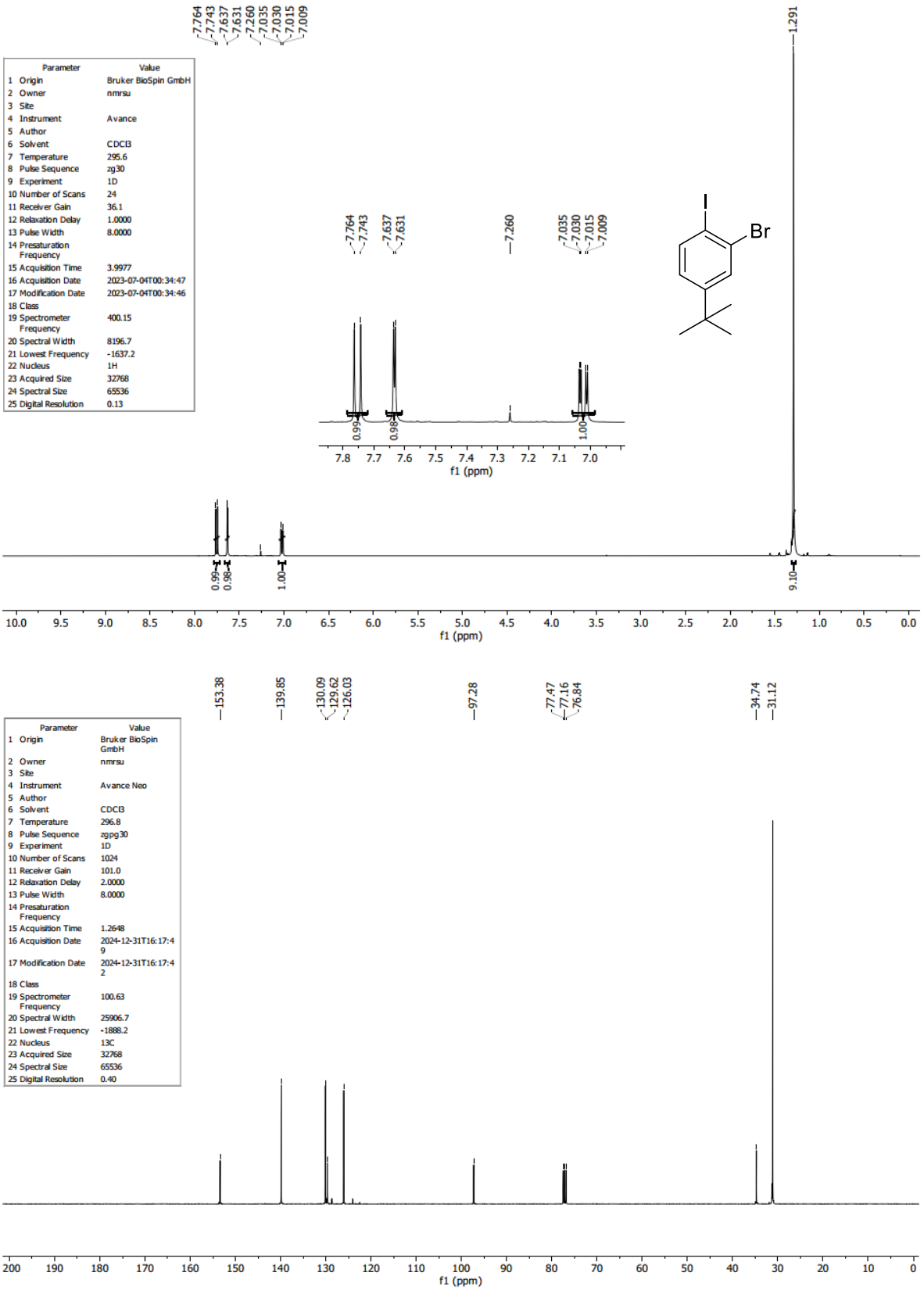


Figure S4. ^{1}H and $^{13}C\{^{1}H\}$ NMR of **S2** recorded in $CDCl_3$ at 400 and 101 MHz, respectively.

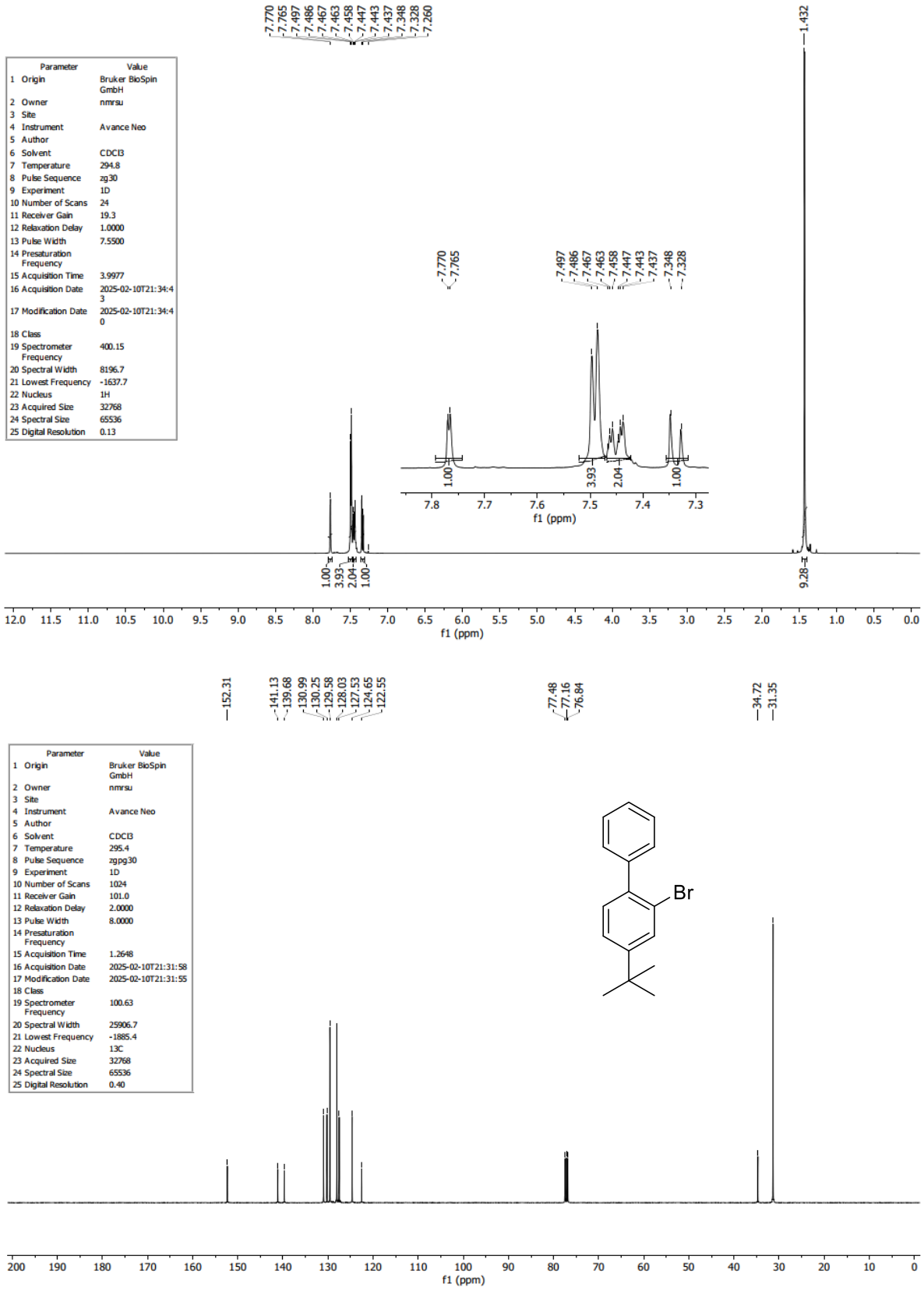


Figure S5. ^{1}H and $^{13}C\{^{1}H\}$ NMR of **S3** recorded in $CDCl_3$ at 400 and 101 MHz, respectively.

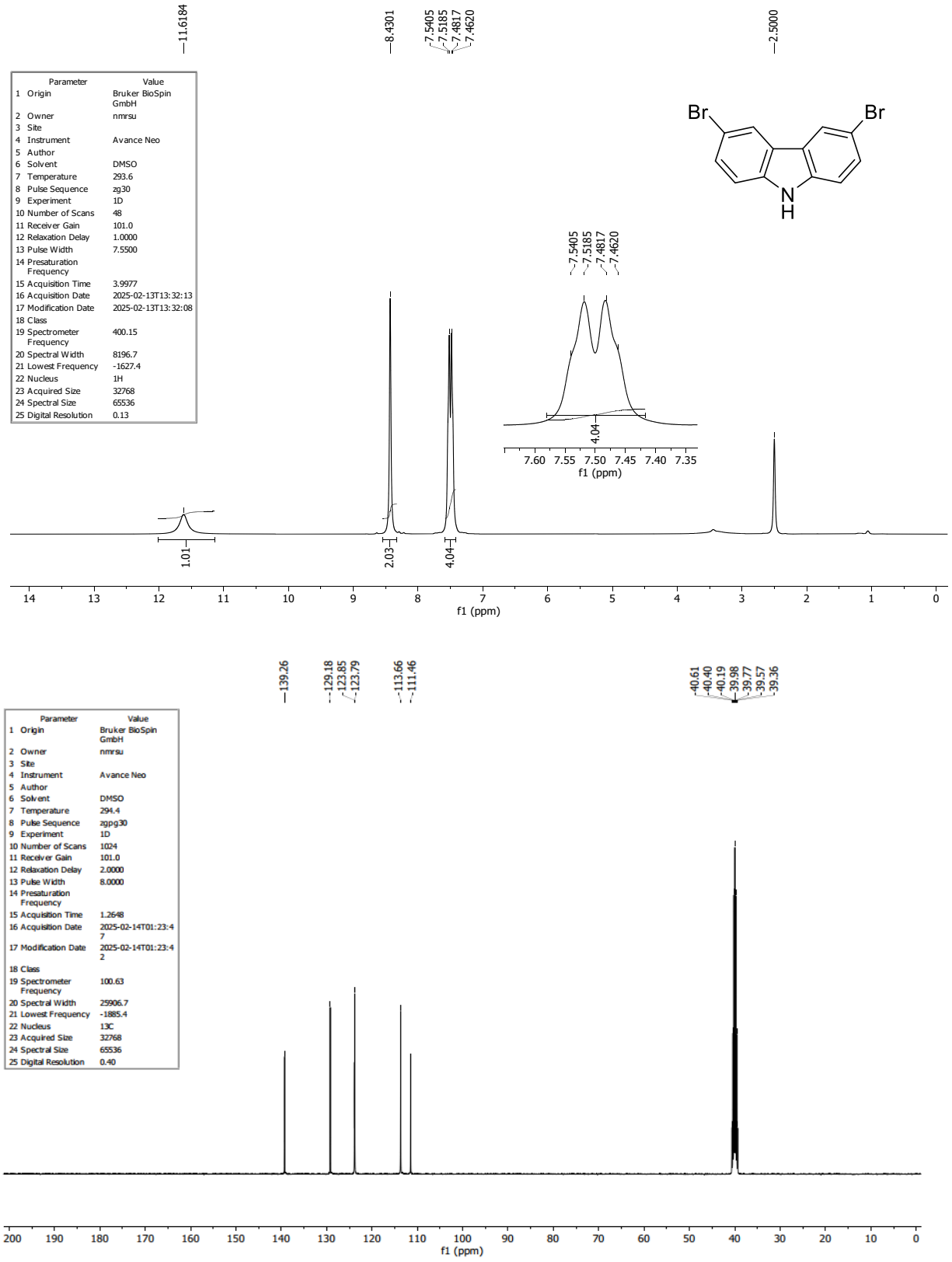


Figure S6. ^{1}H and $^{13}C\{^{1}H\}$ NMR of **S5** recorded in DMSO-d_6 at 400 and 101 MHz, respectively.

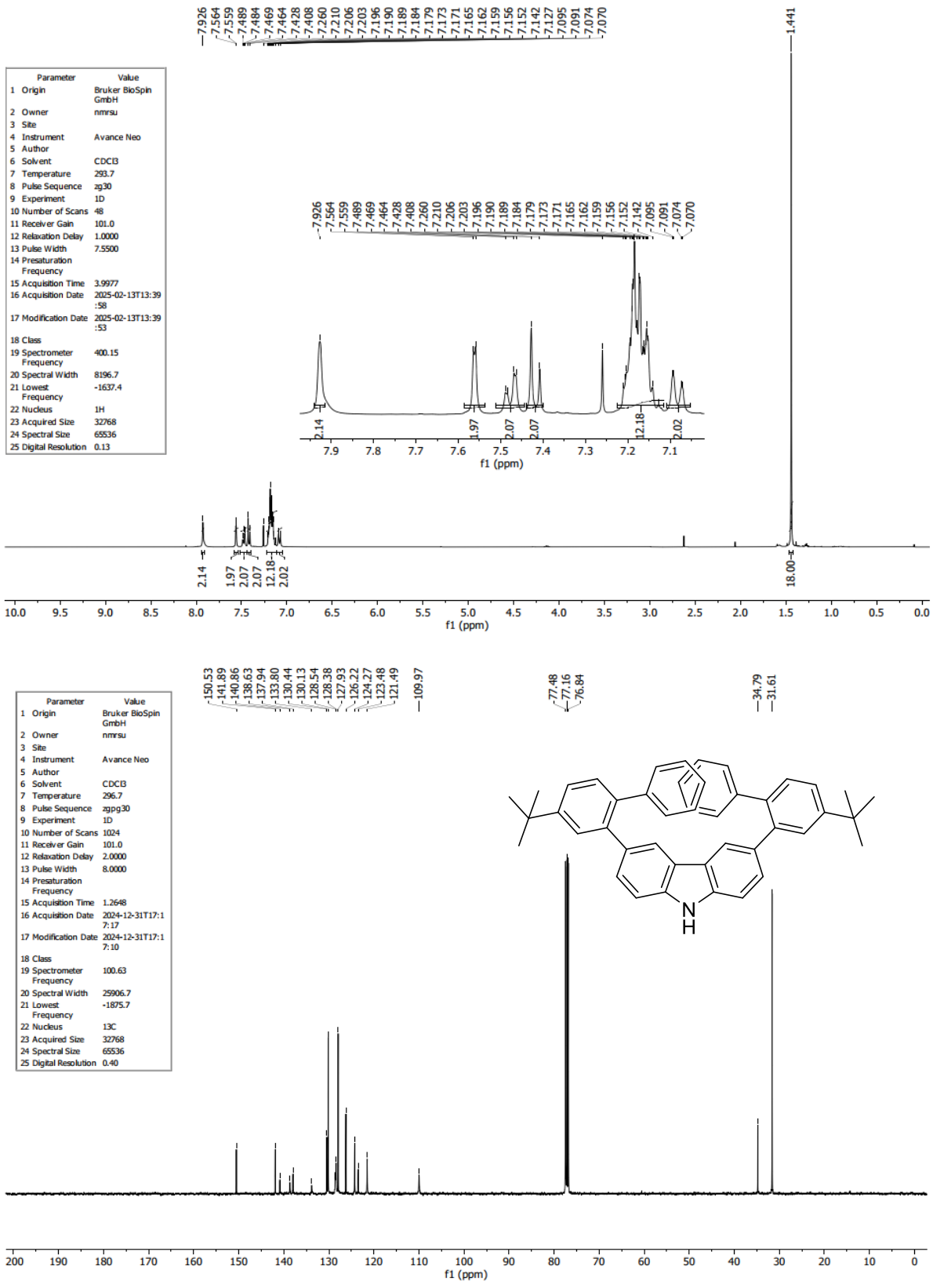


Figure S7. ^{1}H and $^{13}C\{^{1}H\}$ NMR of **S6** recorded in $CDCl_3$ at 400 and 101 MHz, respectively.

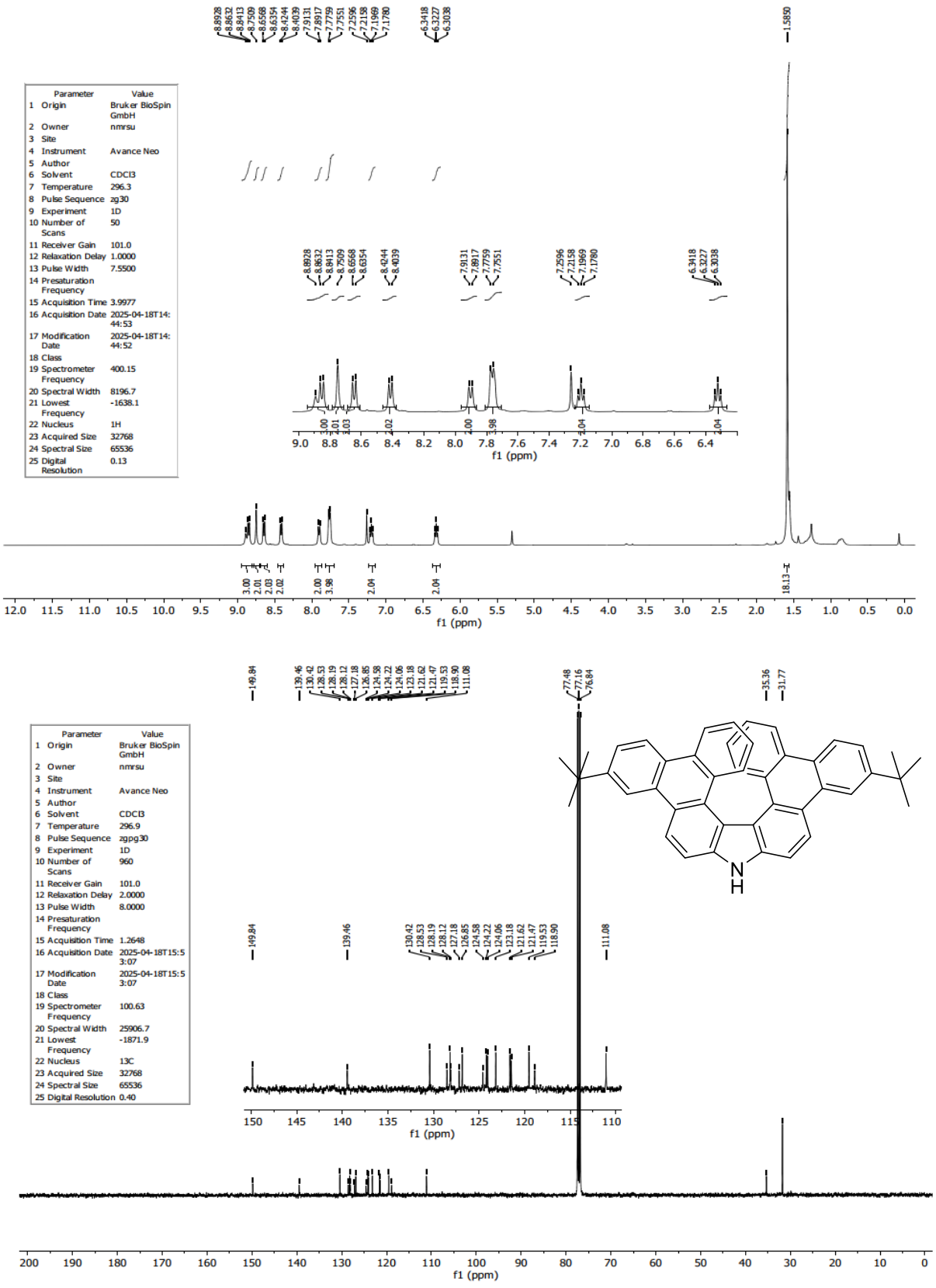


Figure S8. ^{1}H and $^{13}C\{^{1}H\}$ NMR of **Carb-H** recorded in $CDCl_3$ at 400 and 101 MHz, respectively.

2. IR spectra

Solid-state IR spectra of radicals **2** and precursors **4** were recorded using a Thermo Scientific Nicolet 6700 FT-IR spectrometer and are shown in Figures S9–S12.

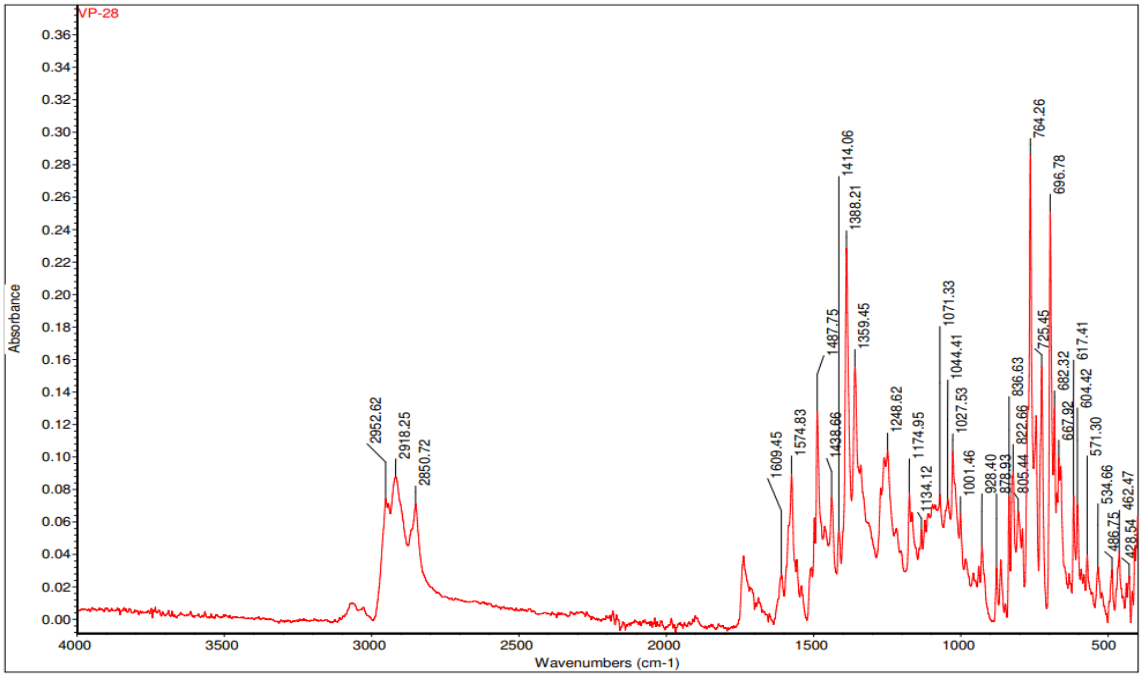


Figure S9. IR spectrum for radical **2a.**

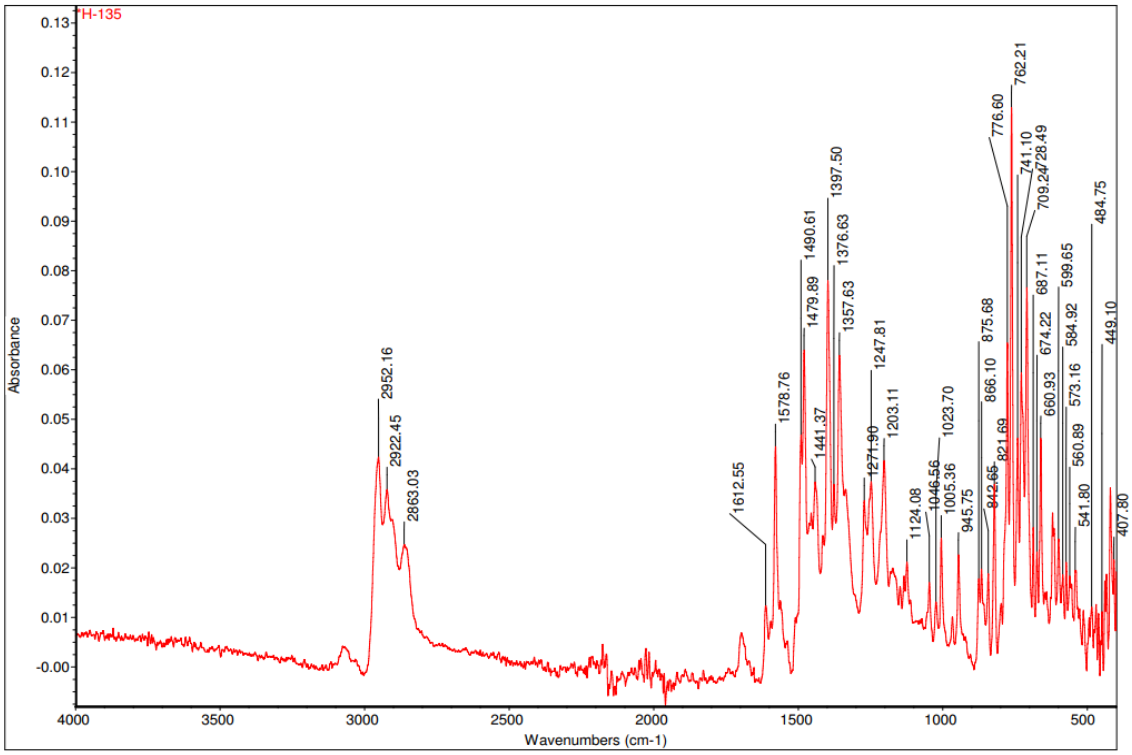


Figure S10. IR spectrum of radical **2b.**

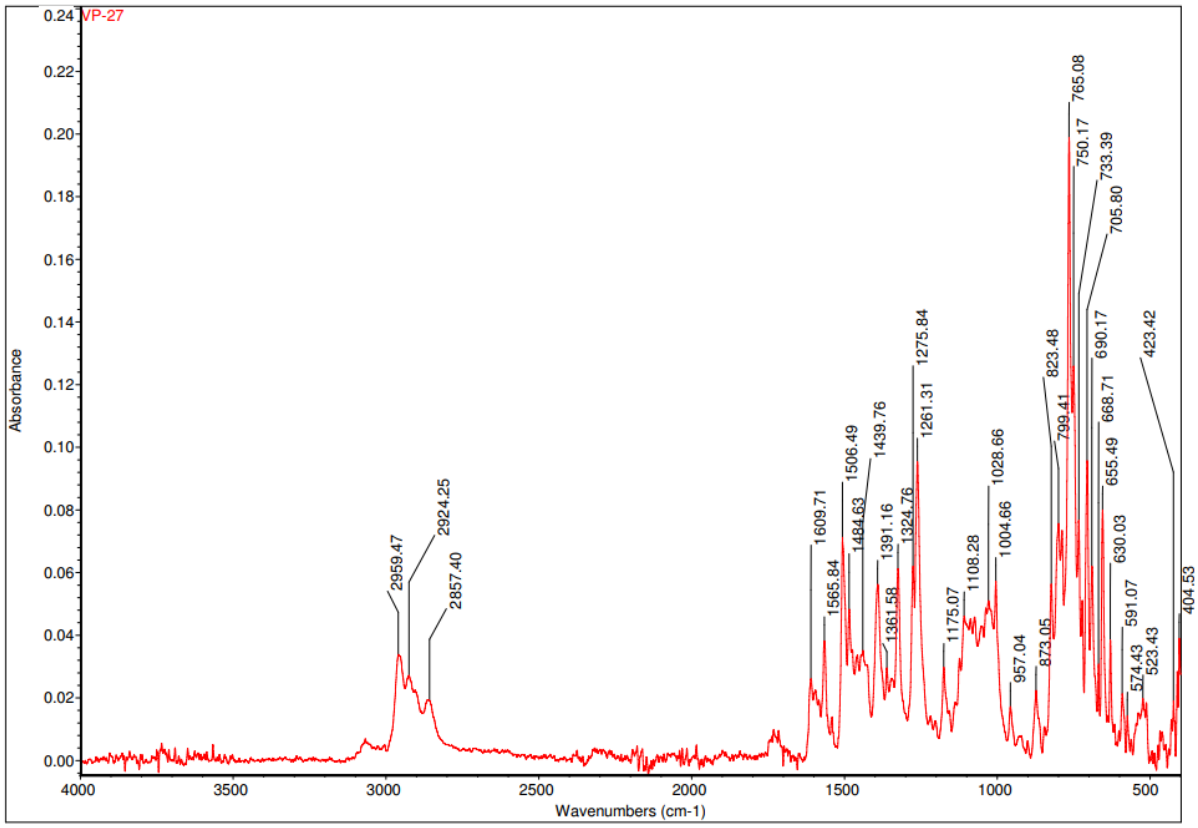


Figure S11. IR spectrum of precursor **4a.**

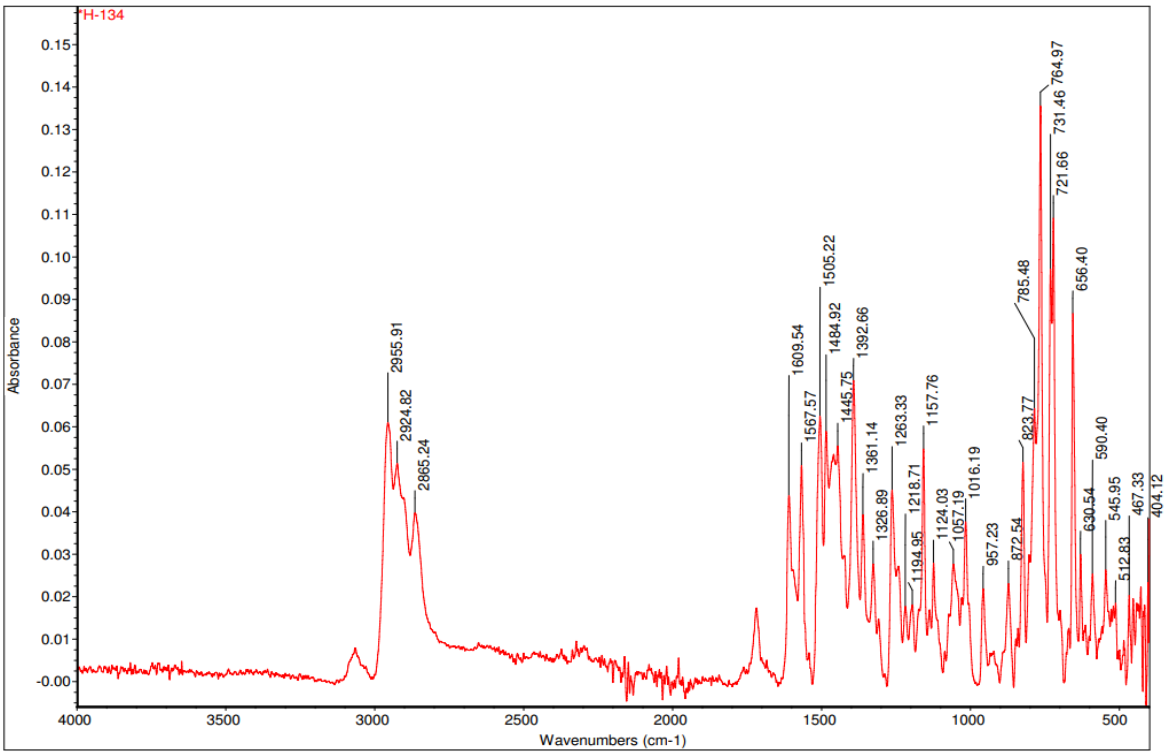


Figure S12. IR spectrum for **4b**.

4. XRD data collection and refinement

A single crystal of radical **2a** suitable for XRD analysis was obtained by slow evaporation of a MeOH/CH_2Cl_2 solution at ambient temperature. XRD measurements of the single-crystal was performed with a Rigaku XtalAB Synergy, Pilatus 300K diffractometer. The measurements were conducted at 100.0(1) K using the CuK_α radiation (λ = 1.54184 Å). The data was integrated using CrysAlisPro program.[9] Intensities for absorption were corrected using gaussian method as in SCALE3 ABSPACK scaling algorithm implemented in CrysAlisPro program.

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.

Crystal packing

Radical **2a** crystallizes in the triclinic *P*-1 space group with one symmetrically independent molecule. Molecules within the crystal assembly in slipped stacks constituted of dimers associated by multiple π···π interactions represented by short (<vdW-0.1Å) C···C and C···N contacts. The dimers associate through CH···π interactions between *tert*-Bu groups and nitrogen and carbon atoms of polycyclic fragments. Resulting stacks extend along [1 -1 0] direction. The dimers are defined by an interplanar distance of 3.33Å between mean planes of benzo[*e*][1,2,4]triazine fragments while the individual dimers are separated by the interplanar distance of 3.99Å. The neighbouring stacks are connected through weak C-H...C and π···π interactions.

The crystal data and structure refinement descriptors are presented in Table S1. Molecular structure and partial packing diagrams for **2a** are shown in Figures S13– S16.

CCDC: File 2483441 contains 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.

Table S1. Selected structural data for 2a

	2a CCDC: 2483441
Formula	$C_{57}H_{43}N_4$
Formula Weight	783.95
Crystal System	triclinic
Space Group	$P\bar{1}$
a/Å	12.5314(7)
b/Å	13.3027(9)
c/Å	14.2917(10)
α/°	68.818(7)
β/°	70.202(6)
γ/°	66.085(6)
Volume/Å^3	1978.5(3)
Z	2
2θ range for data collection/°	6.808 to 157.496
Index ranges	$-12 \leq h \leq 15$, $-15 \leq k \leq 16$, $-16 \leq l \leq 18$
No. of measured, independent, and observed [$I>2\sigma(I)$] reflections	26301, 7791, 4421
*R*int	0.0950
Goodness-of-fit on F^2	1.046
Final *R* indexes [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.0816$, w$R_2 = 0.1872$
Final *R* indexes [all data]	$R_1 = 0.1462$, w$R_2 = 0.2190$
Data/restraints/parameters	7791/0/556
Largest diff. peak/hole Å^{-3}	0.36/-0.31

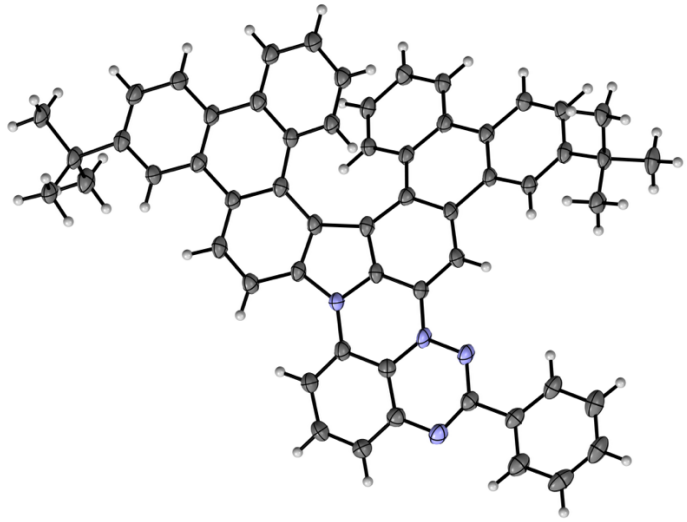


Figure S13. The molecular structure of **2a**. Atomic displacement ellipsoids are drawn at 50% probability level.

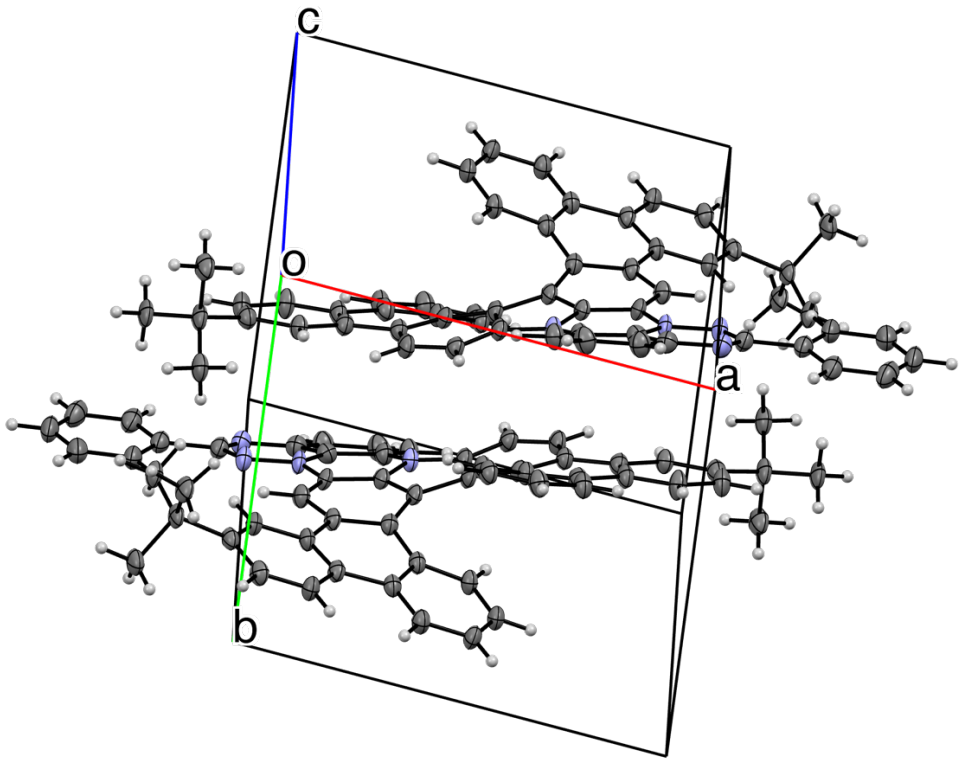


Figure S14. Unit cell for the XRD structure of **2a** showing two enantiomers related by an inversion center. Atomic displacement ellipsoids are drawn at 50% probability level.

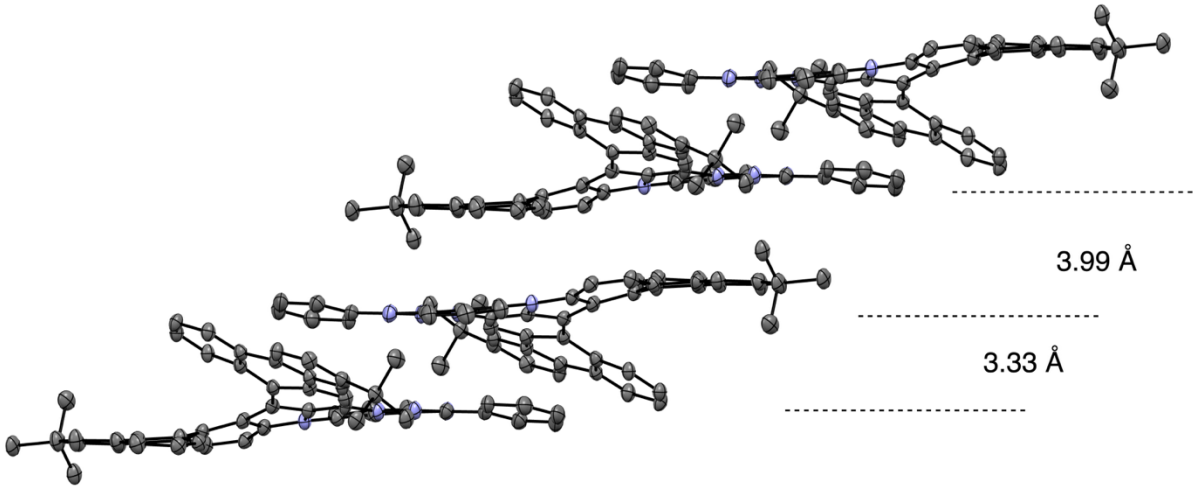


Figure S15. Partial packing diagram for the structure of **2a** with indicated distances between mean planes of the benzo[*e*][1,2,4]triazinyl fragments in neighbouring molecules. Atomic displacement ellipsoids are drawn at 50% probability level.

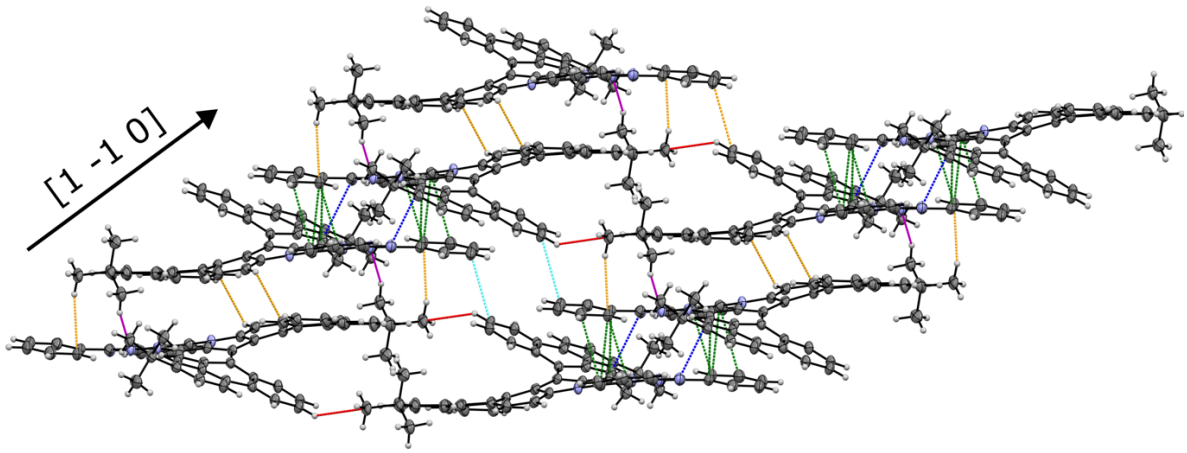


Figure S16. Partial packing diagram for **2a**. Green and blue dotted lines represent π···π interactions formed by contacts of C···C and C···N, respectively. CH···π interactions formed by short contacts of H···C and H···N are represent by orange and magenta dotted lines. Red and cyan dotted lines represent C-H···C and π···π interactions between neighbouring stacks. All showed contacts are shorter than vdW radii of 0.1Å.

5. UV-vis spectroscopy

Electronic absorption spectra for the radicals **2** and their precursors **4** were recorded on a Jasco V770 spectrometer using quartz quvettes with 10 mm optical path in spectroscopic grade CH_2Cl_2 at concentrations in a range 2–10×10^{-5} M and fitted to the Beer–Lambert law. Results are shown in Figures S17–S20.

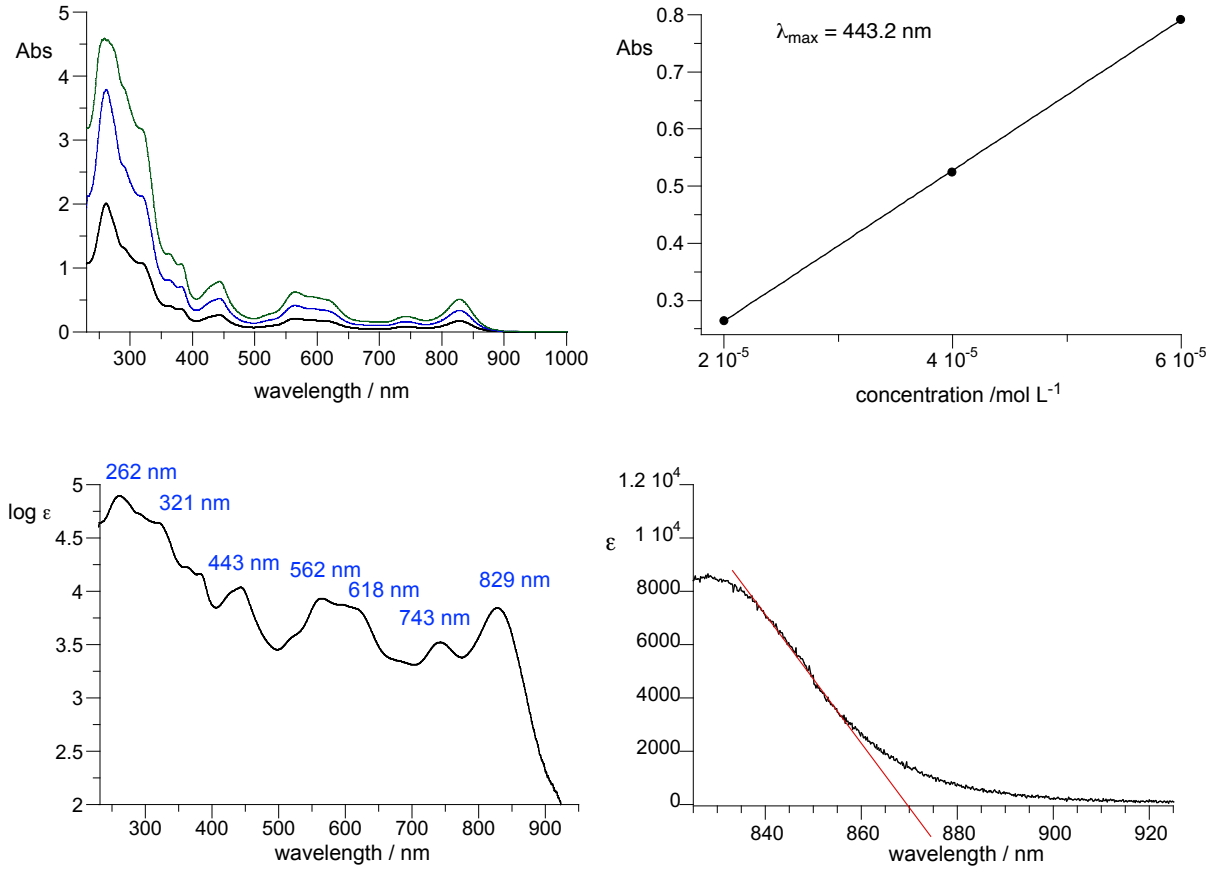


Figure S17. Clockwise: electronic absorption spectra for helicene **2a** in CH_2Cl_2 for three concentrations and determination of molar extinction coefficient ε at λ = 443.2 nm (best fit function: ε = 13,191(23)×conc, r^2 = 0.9999), molar excitation log (ε), and determination of onset of optical absorption.

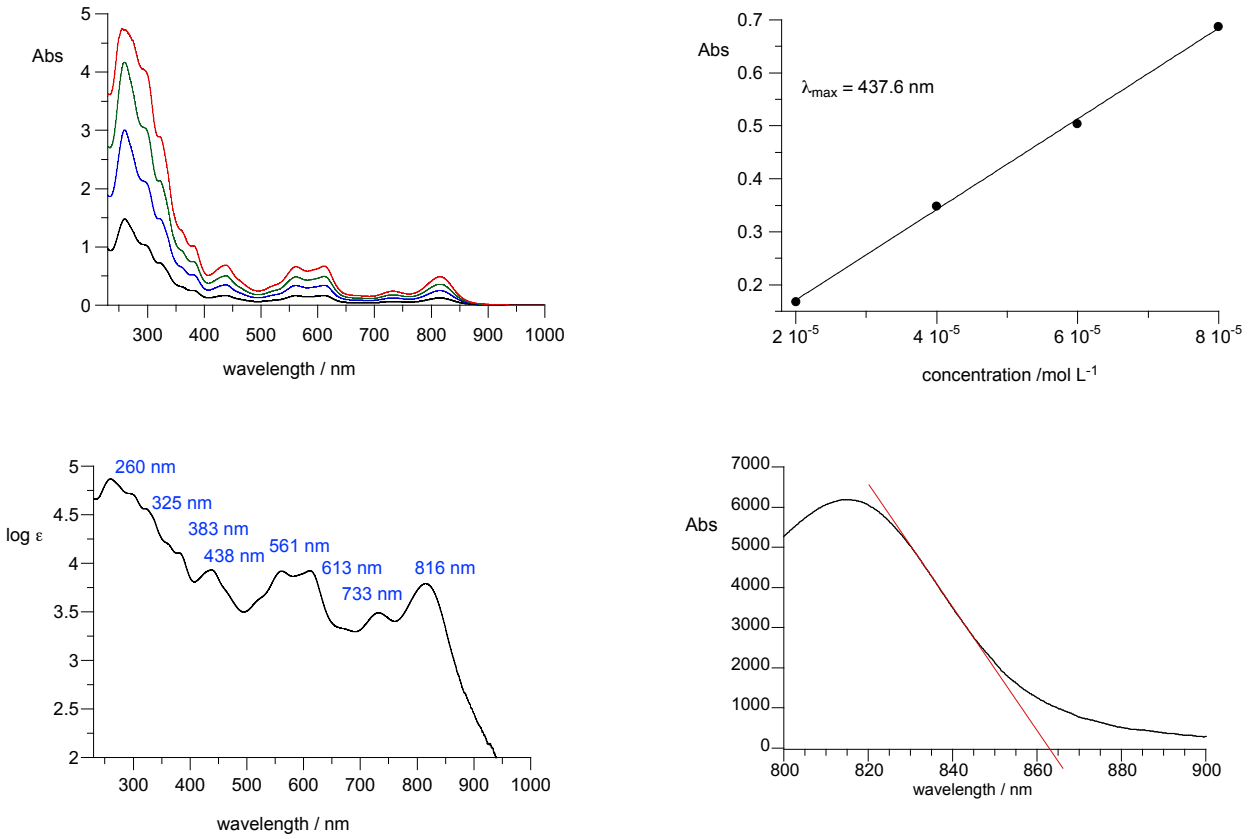
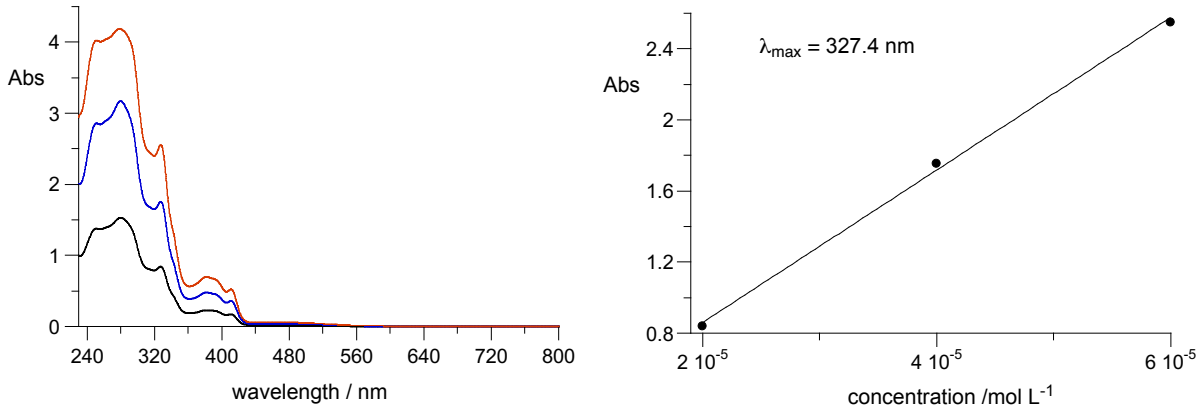


Figure S18. Clockwise: electronic absorption spectra for helicene **2b** in CH_2Cl_2 for four concentrations and determination of molar extinction coefficient ε at λ = 437.6 nm (best fit function: ε = 8,557(62)×conc, r^2 = 0.9991), molar excitation log (ε), and determination of onset of optical absorption.



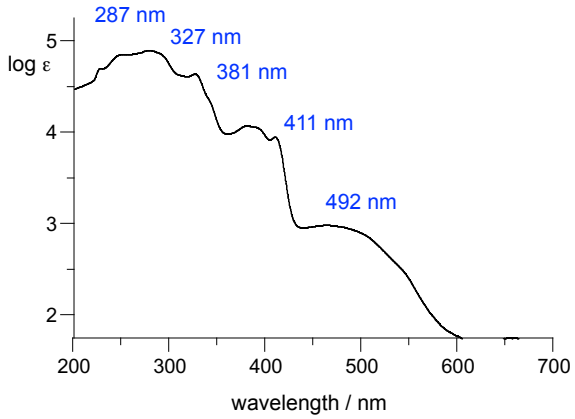


Figure S19. Clockwise: electronic absorption spectra for helicene **4a** in CH_2Cl_2 for three concentrations and determination of molar extinction coefficient ε at λ = 327.4 nm (best fit function: ε = 42,952(458)×conc, r^2 = 0.9984), and molar excitation log (ε).

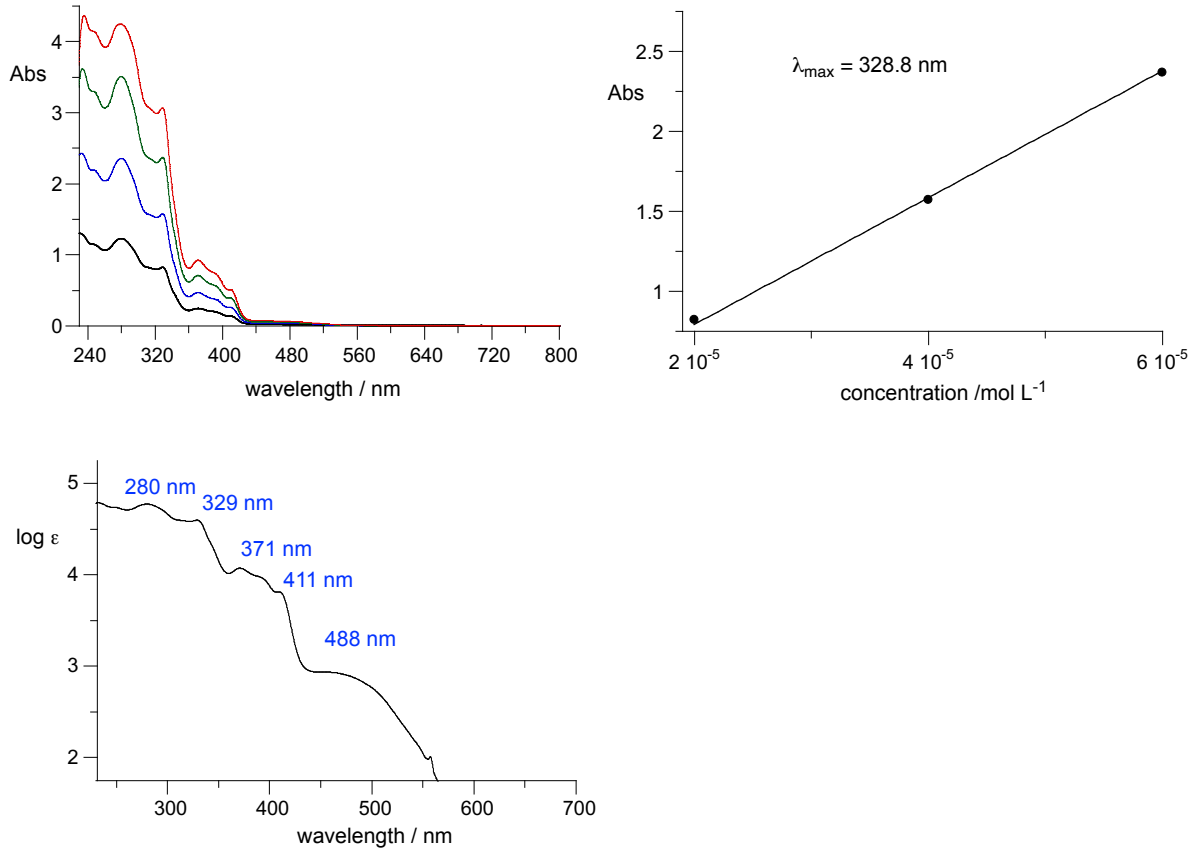


Figure S20. Clockwise: electronic absorption spectra for helicene **4b** in CH_2Cl_2 for four concentrations and determination of molar extinction coefficient ε at λ = 328.8 nm (best fit function: ε = 39,640(308)×conc, r^2 = 0.9991), and molar excitation log (ε).

6. Fluorescence spectroscopy

Qualitative fluorescence spectra of precursor **4a** purified by HPLC methods (*vide infra*) were recorded in DCM (10^{-5} M) using Horiba Duetta spectrophotometer and quartz quvettes with 10 mm optical path by accumulating 100 spectra with both emission and excitation bandwidth of 5 nm, at three excitation wavelengths: 330 nm, 350 nm and 400 nm. Results are shown in Figure S21.

Although the spectra were not quantified, they appeared very weak.

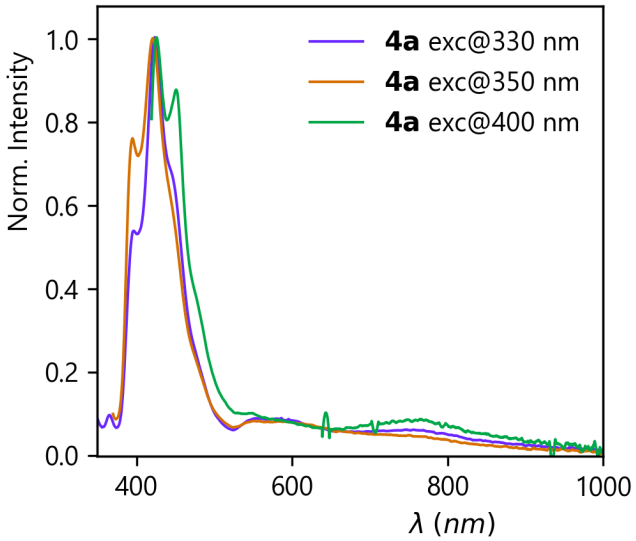


Figure S21. Normalized fluorescence spectra of precursor **4a** in DCM (10^{-5} M) at three different excitation wavelengths.

7. Chiral HPLC analysis and resolution

Analytical chiral HPLC separations were performed on a Knauer Azura system equipped with a binary high-pressure gradient pumping module (700 bar) and a DAD (200 – 800 nm) detector, injecting 5 µL samples (1 mg/mL in toluene, filtered through a 0.23 µm PTFE syringe filter). For semipreparative separations, Interchim Puriflash P5.250 system with a low-pressure quaternary gradient pumping unit (250 bar), a DAD (200 – 800 nm) detector and a 18 mm test tube fraction collector were used. The material was dissolved in toluene (5–20 mg/mL), filtered through a 0.23 µm PTFE syringe filter and injected by means of a 2 mL sample loop. Results are shown in Figures S22–S24.

Radical ***rac*-2a** (R = Ph) was separated under the following conditions (Figure S22):

- *Analytical*: Chiralpak IE column (250 × 4.6 mm ID, 5 µm, DAICEL), isooctane – toluene 2:3, containing diethylamine (0.2%), flow rate 1 mL/min, temperature 23 °C
- *Semipreparative*: Chiralpak IE column (250 × 20 mm ID, 5 µm, DAICEL), isooctane–toluene 2:3, containing diethylamine (0.2%), flow rate 20 mL/min, temperature 23 °C. 1.5 mg of the racemic mixture was injected in 0.5 mL of toluene, affording 0.2 mg of each enantiomer (27% yield of chromatography) in >99% and 96% *ee* for the fast- and slow-eluting enantiomer, respectively.

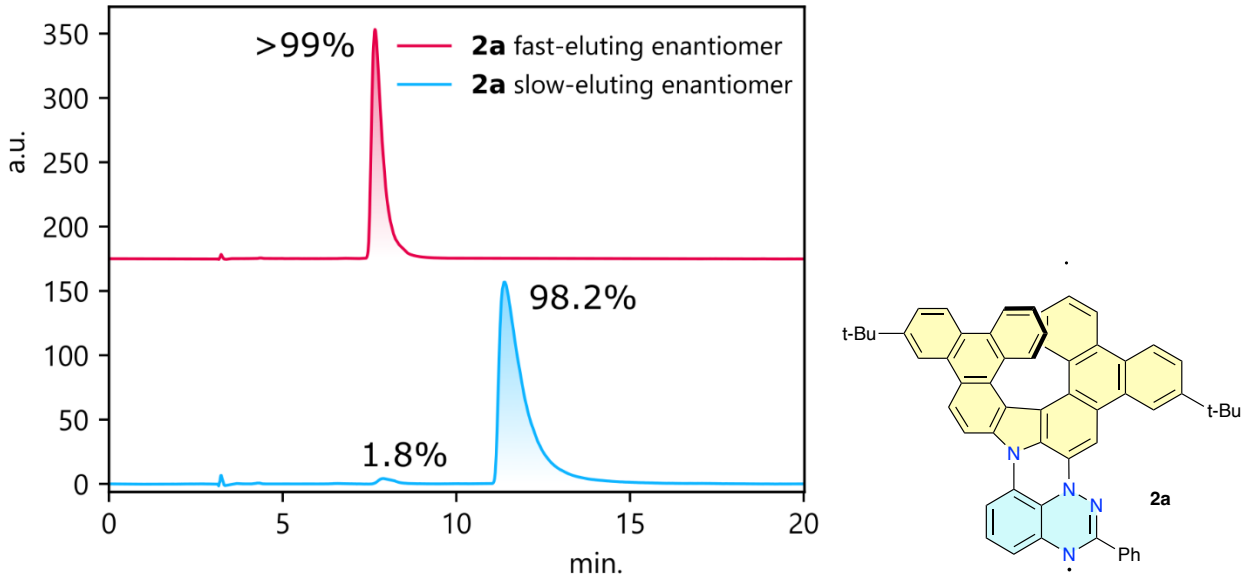


Figure S22. Chiral HPLC analyses of the resolved radical **2a** using Chiralpak IE (250 × 4.6 mm ID, 5 µm, DAICEL), isooctane – toluene 2:3, 0.2% diethylamine, monitored at 360 nm.

Radical ***rac*-2b** (R = *t*-Bu) was separated under the following conditions (Figure S23):

- *Analytical*: Chiralpak IE column (250 × 4.6 mm ID, 5 µm, DAICEL), isooctane–toluene 2:3, containing diethylamine (0.2%), flow rate 1 mL/min, temperature 23 °C
- *Semipreparative*: Chiralpak IE column (250 × 20 mm ID, 5 µm, DAICEL), isooctane–toluene 2:3, containing diethylamine (0.2%), flow rate 20 mL/min, temperature 23 °C. 4 mg of the racemic mixture was injected in 0.5 mL of toluene, affording 1.3 mg of each enantiomer (65%

yield of chromatography) in >99% and 95% *ee* for the fast- and slow-eluting enantiomer, respectively.

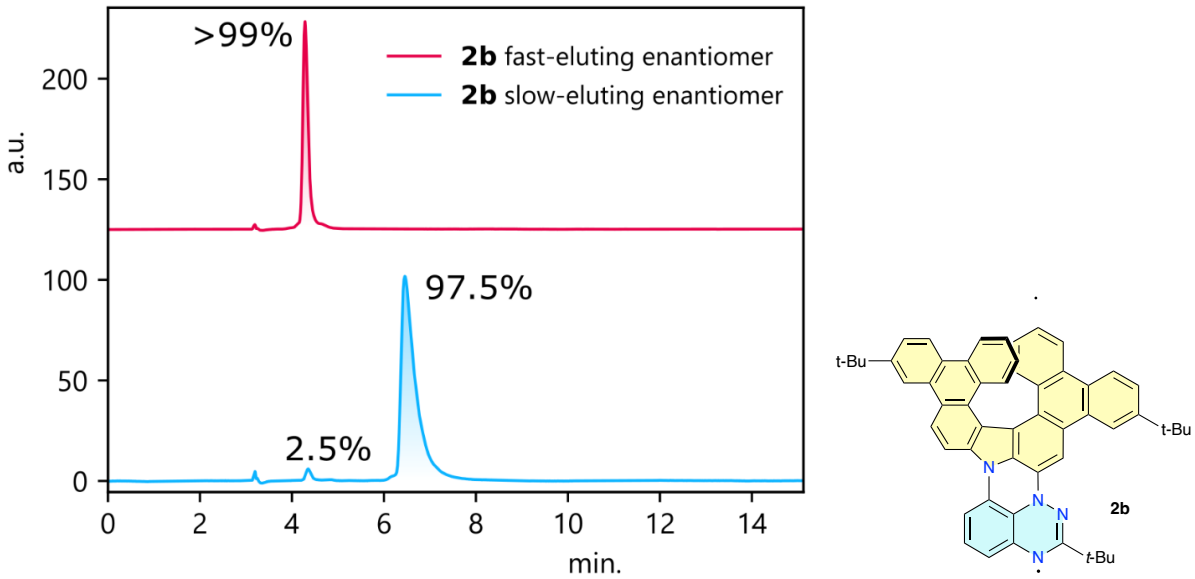


Figure S23. Chiral HPLC analyses of the resolved precursor **2b** using Chiralpak IE column (250 × 4.6 mm ID, 5 µm, DAICEL), isooctane–toluene 2:3, 0.2% diethylamine, monitored at 305 nm.

Precursor ***rac*-4a** (R = Ph) was separated under the following conditions (Figure S24):

- *Analytical*: ChiralArt Amylose-SA column (250 × 4.6 mm ID, 5 µm, YMC), isooctane–toluene 2:3, containing diethylamine (0.2%), flow rate 1 mL/min, temperature 23 °C
- *Semipreparative*: ChiralArt Amylose-SA column (250 × 20 mm ID, 5 µm, YMC), isooctane–toluene 2:3, containing diethylamine (0.2%), flow rate 20 mL/min, temperature 23 °C. 20 mg of the racemic mixture was injected in 1 mL of toluene, affording 7 mg of each enantiomer (70% yield of chromatography) in >99% and 94% *ee* for the fast- and slow-eluting enantiomer, respectively.

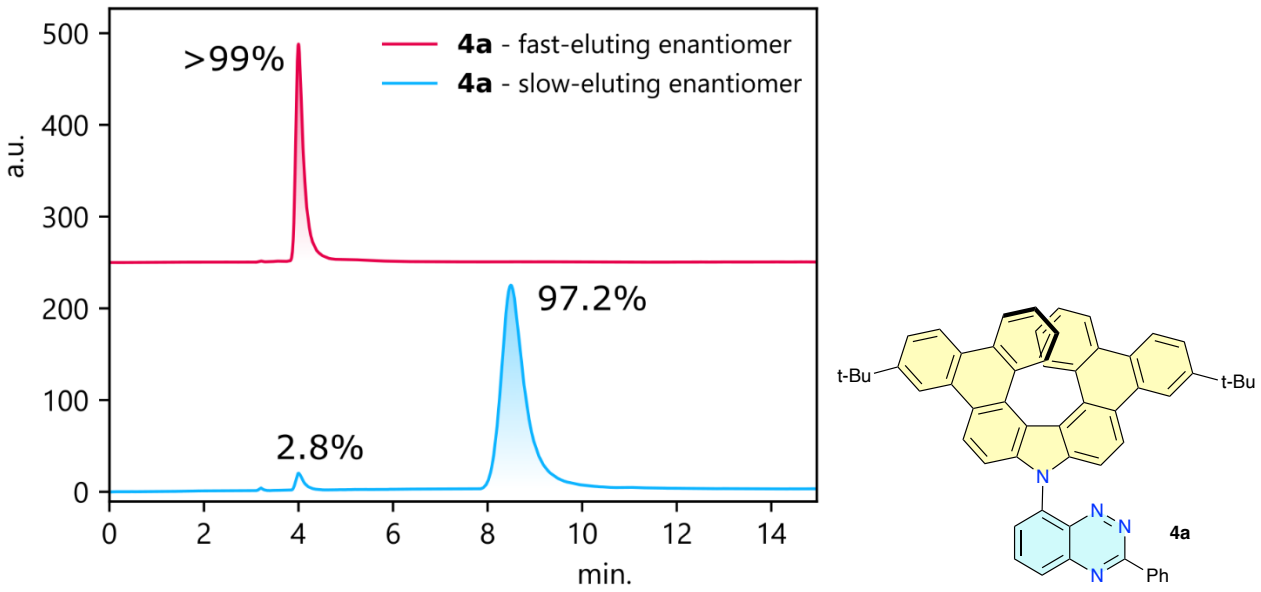


Figure S24. Chiral HPLC analyses of the resolved precursor **4a** using ChiralArt Amylose-SA (250 × 4.6 mm ID, 5 µm, YMC), isooctane – toluene 2:3, 0.2% diethylamine, monitored at 305 nm.

8. Electronic circular dichroism spectroscopy

Electronic circular dichroism (ECD) and absorption (UV-vis) spectra of enantiomers of precursor **4a** and radicals **2a** and **2b** were recorded on Jasco 1500 spectropolarimeter (JASCO International Co. Ltd.) in the spectral range of 230 – 900 nm for **4a** (10^{-4} M in DCM) and 280 – 900 nm for **2a** and **2b** (10^{-4} M in toluene). Measurements were made in quartz cell with a 0.2 cm path length (below 450 nm) and 1.0 cm path length (above 450 nm) using a scanning rate of 20 nm/min, response time of 4 seconds, 1 nm bandwidth, one accumulation and default instrument sensitivity. After a baseline correction, spectra were expressed in terms of differential molar extinction (Δε) and molar extinction (ε), respectively. Results are shown in Figures S25– S27. The notation *first* and *second* refers to the shorter and longer retention times, respectively, of the individual enantiomers.

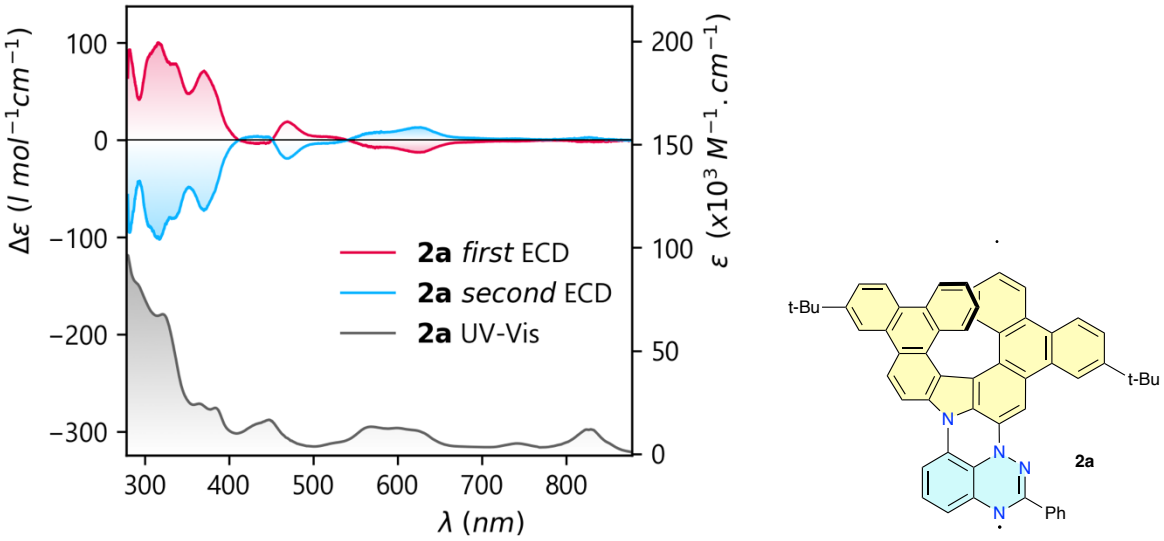


Figure S25. Electronic circular dichroism spectra for *the first* (red) and *the second* (blue) enantiomers of radical **2a** in toluene.

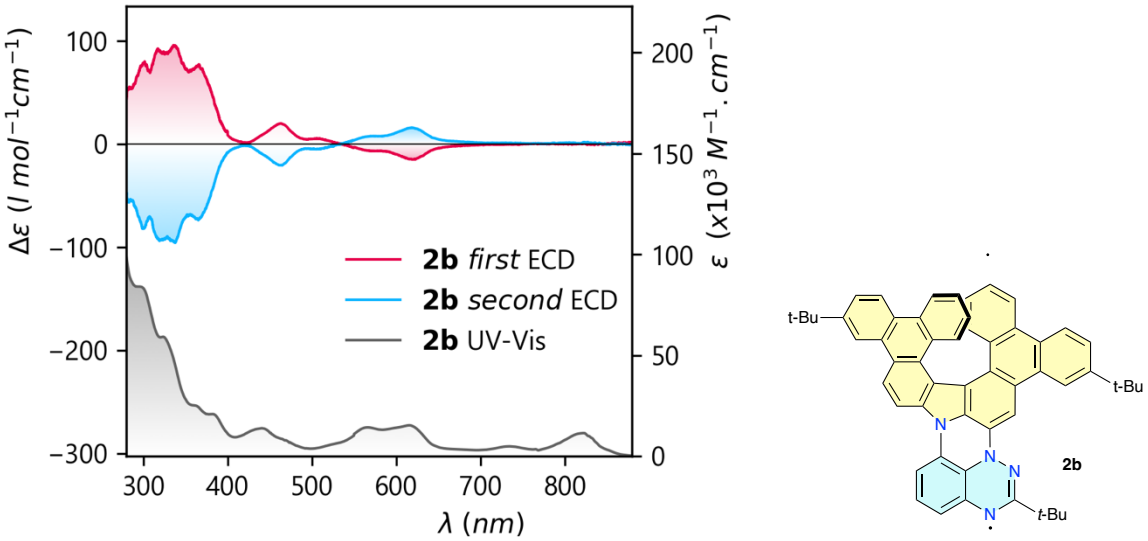


Figure S26. Electronic circular dichroism spectra for *the first* (red) and *the second* (blue) enantiomers of radical **2b** in toluene.

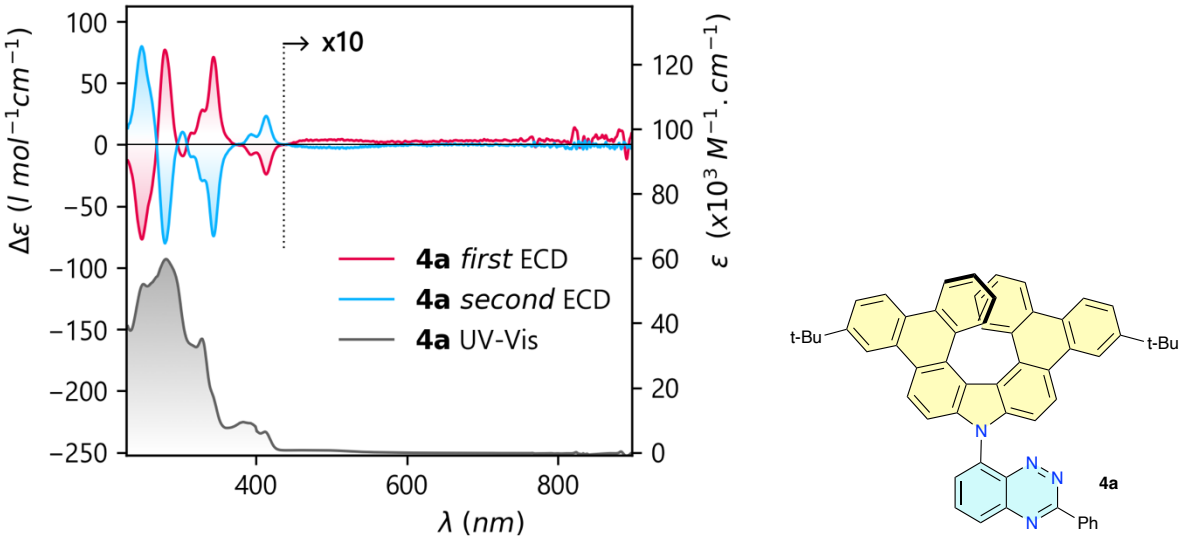


Figure S27. Electronic circular dichroism spectra for *the first* (red) and *the second* (blue) enantiomers of precursor **4a** in CH_2Cl_2.

9. Electrochemical results

Electrochemical radical characterization was conducted using a Metrohm Autolab PGSTAT128N potentiostat/galvanostat instrument. Carbazole radicals **2** were dissolved in dry, spectroscopic grade CH_2Cl_2 (concentration 0.5 mM) in the presence of $[Bu_4N]^+[PF_6]^-$ 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 a glassy carbon disk as the working electrode (ϕ = 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 S28 and S29.

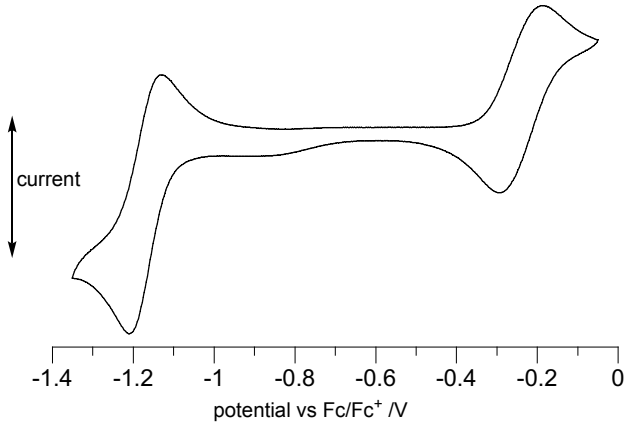


Figure S28. Cyclic voltammogram for helicene **2a** in CH_2Cl_2 referenced to the Fc/Fc^+ couple.

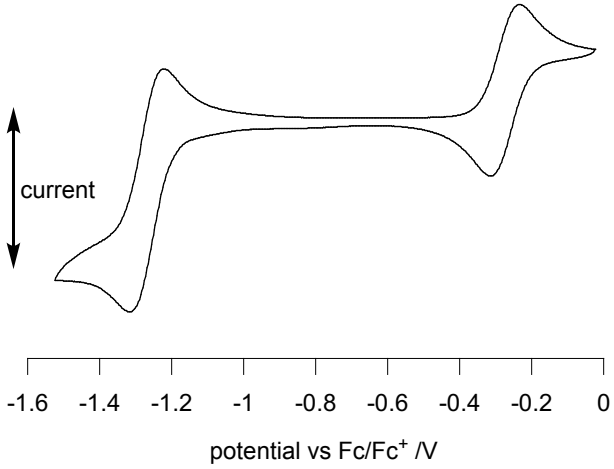


Figure S29. Cyclic voltammogram for helicene **2b** in CH_2Cl_2 referenced to the Fc/Fc^+ couple.

10. EPR spectroscopy

EPR spectra for azahelicene radicals **2a** and **2b** 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 Gpp 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 6 hydrogen atoms. The resulting *hfcc* values were perturbed several times until a global minimum for the fit was achieved.

Experimental and simulated spectra are shown in Figures S30 and S31 and resulting *hfcc* are listed in Table S2.

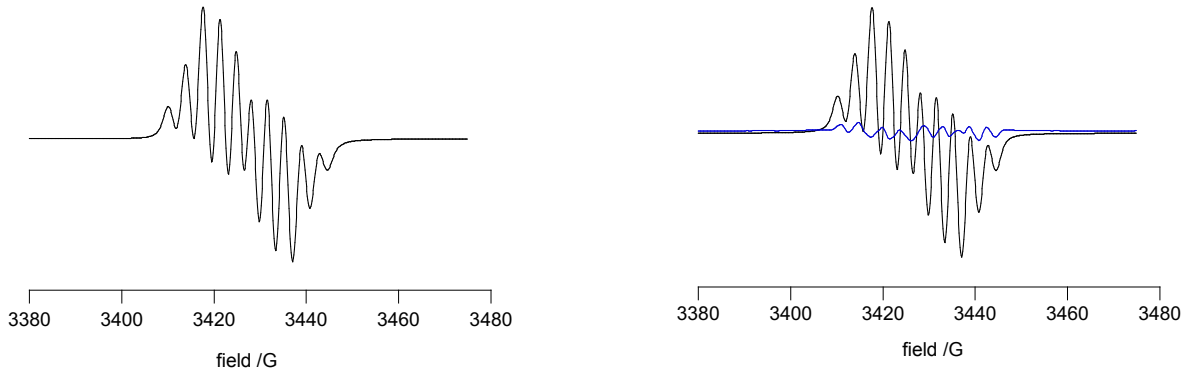


Figure S30. Experimental, recorded in benzene at 20 dB and *ca* 20 °C (left), simulated (right), and difference (blue, right) spectra for **2a.**

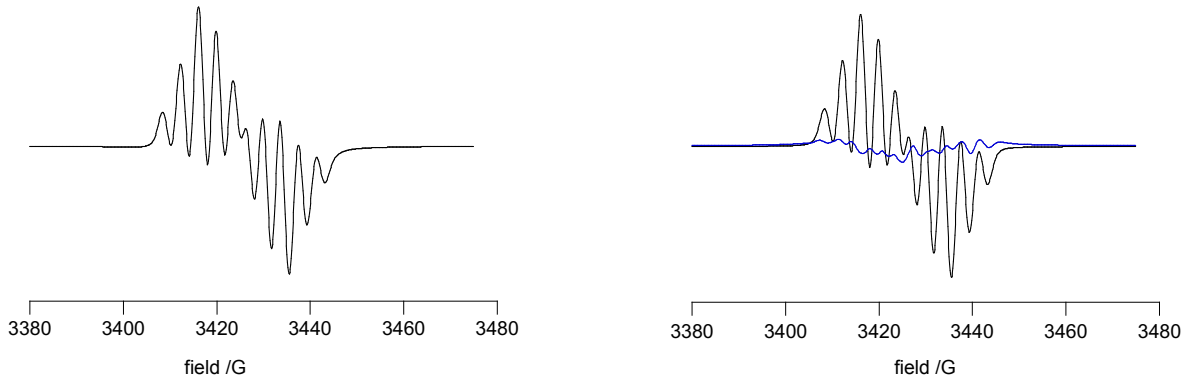


Figure S31. Experimental, recorded in benzene at 20 dB and *ca* 20 °C (left), simulated (right), and difference (blue, right) spectra for **2b**.

Table S2. Hyperfine coupling constants (G) for radicals **1** and **2**.[a]

hfcc /G	**1-H** [b]	**1-tBu** [b]	**2a**	**2b**
a_N	7.08	7.14	6.67	6.57
a_N	4.15	4.00	3.71	4.01
a_N	4.02	4.00	4.05	4.04
a_N	0.35	0.36	0.44	0.47
a_H	2.77	2.79	3.21	3.33
a_H	2.31	2.47	1.07	1.05
a_H	0.34	0.36	0.44	0.36
a_H	0.32	0.35	0.29	0.37
a_H	0.29	0.34	0.49	0.37
a_H	0.29	0.34	0.34	0.33
g	2.0036	2.0044	2.0091	2.0100

[a] Referenced to TEMPO as the internal standard. [b] Taken from ref. [13].

11. Computational details and results

Quantum-mechanical calculations were carried out using Gaussian 16 suite of programs.[14] Geometry optimizations of radicals **1** and **2** and precursors **4** were conducted at the UB3LYP/6-31G(d,p) level of theory in methylene chloride dielectric medium (PCM model[15]) requested with the SCRF(Solvent= CH2Cl2) keyword and using tight convergence limits and without symmetry constrains. Initially, geometries of enantiomers of *P* configuration were optimized. The resulting optimized geometries were used to obtain the *M* enantiomers by mirror inversion of the P enantiomers, which were subsequently independently optimized.

a) mechanistic investigation of photocyclization of 4a

Mechanistic investigation of photocyclization of model **4a'** (in which t-Bu was approximated with Me) was conducted at the CAM-B3LYP/6-311G(d,p) level of theory in EtOAc dielectric medium (PCM model[15]) requested with the SCRF(Solvent=EthylEthanoate) keyword and default convergence limits. Excitation energy calculations of **4a'** were conducted using the TD-DFT method for closed-shell systems. Geometry optimization in the S_1 state was performed using FOpt with default convergent limits and TD=(singlets, root=1, NStates=3) keywords in AcOEt dielectric medium (PCM model[15]).

The triplet state geometry of model precursor **4a'** was obtained using the UCAM-B3LYP/6-311G(d,p) method and starting with the GS geometry of **4a'**. TD-DFT calculations for

closed-shell singlet at the triplet geometry using CAM-B3LYP/6-311G(d,p) method and TD=(triplets, root=1, NStates=12) keyword gave the forbidden S_0–>T_n transitions.

The same method was recently used for obtaining photophysical data for carbazole and dibenzocarbazole analogues.[13] Partial Jablonski diagrams for **4a'** and its carbazole analogues are shown in Figure S32. A comparison of the diagrams demonstrates that in derivative **4a'** and the carbazole analogue the T_1 state has the desired (n,π*) character and is capable of formation of a stable zwitterion, while in the dibenzocarbazole derivative the T_1 state is (π,π*) and photocyclization does not occur.[13] The MOs relevant to these excitations and excited states in model **4a'** are shown in Figure S33.

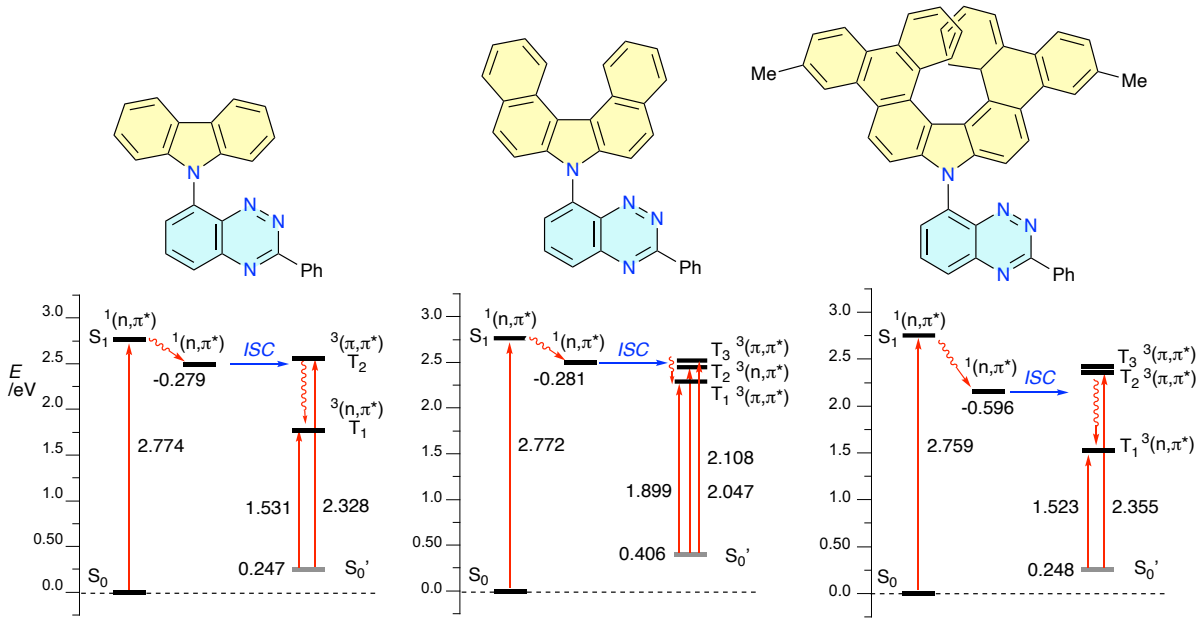


Figure S32. Partial Jablonski diagrams for carbazole, dibenzocarbazole, and model **4a'** precursors.

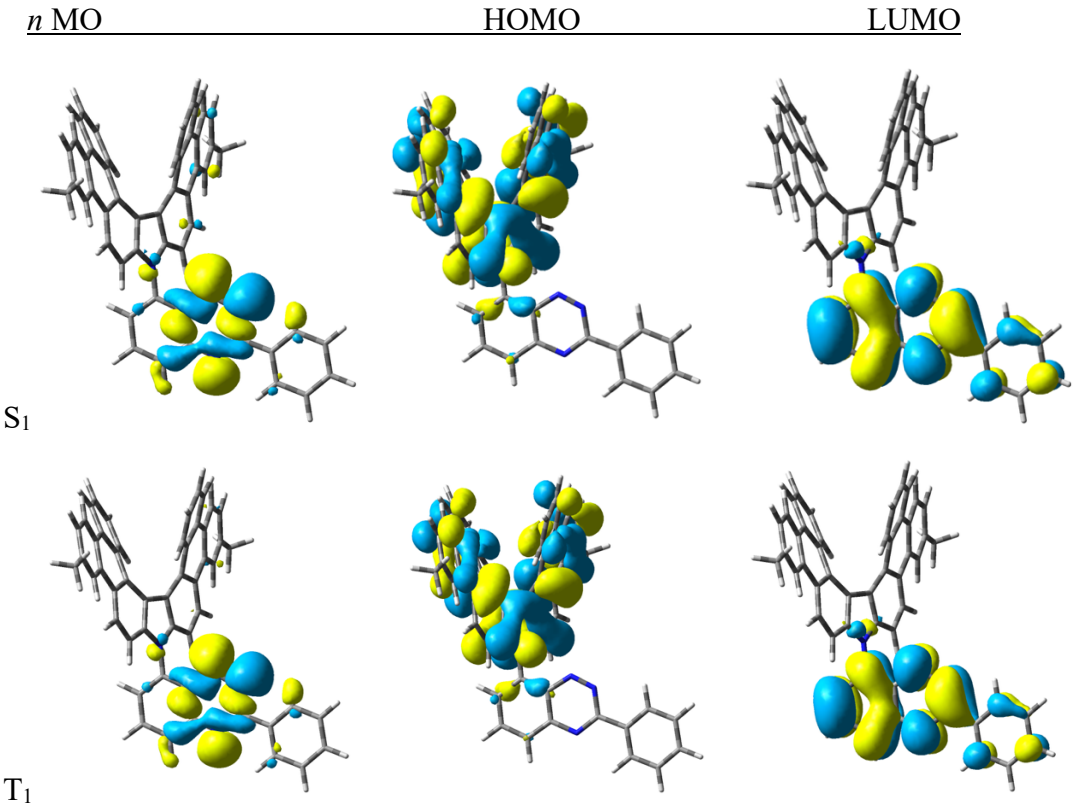


Figure S33. Contours of MOs (n and LUMO) involved in the S1 (top) and T1 (bottom) states and also the HOMO of model **4a'** (CAM-B3LYP/6-311G(d,p) in AcOEt).

b) isotropic Fermi contact coupling constants (hfcc) and spin densities for radicals

Isotropic Fermi contact coupling constants for radicals **1** and **2** were calculated using the UCAM-B3LYP/EPR-II // UB3LYP/6-31G(d,p) method in benzene dielectric medium requested with the SCRF(Solvent=Benzene) keywords (PCM model).[15] The resulting *hfcc* values are shown in Table S3 and spin densities are listed in Table S4. Summarized spin densities of pertinent molecular fragments are listed in Table S5. Graphical maps of DFT spin densities for radicals **1** and **2** are shown in Figure S34.

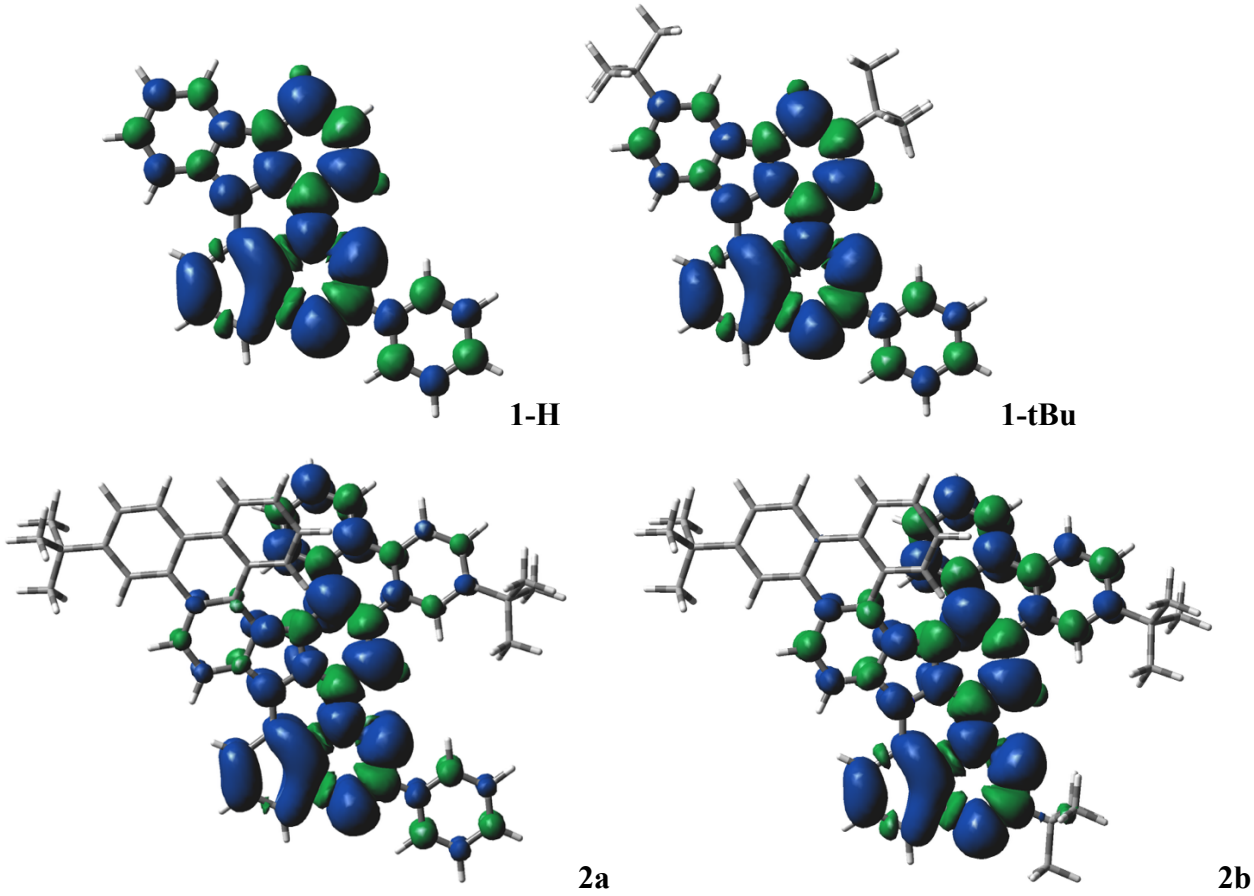
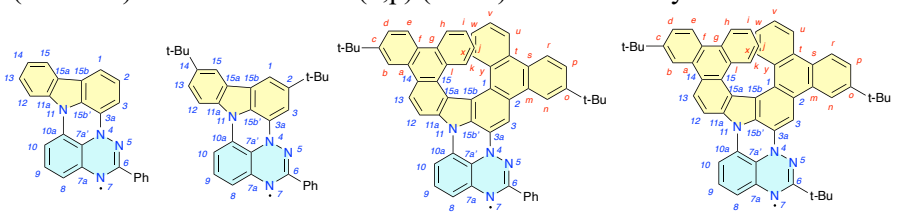


Figure S34. Graphical spin density maps for radicals **1** and **2**; blue: positive spin density; *density* = 0.004.

Table S3. DFT calculated hyperfine coupling constants (G) in radicals **1** and **2** in benzene at the UCAM-B3LYP/EPR-II (Benzene) // UB3LYP/6-31G(d,p) (DCM) level of theory.[a]



hfcc /G	**1-H**	**1-tBu**	**2a**	**2b**
$a_{N(4)}$	5.836	5.935	5.569	5.484
$a_{N(5)}$	3.658	3.598	3.663	4.058
$a_{N(7)}$	4.018	3.994	3.942	3.790
$a_{N(11)}$	0.382	0.405	0.142	0.101
$a_{H(1)}$	-3.014	-2.986	–	–
$a_{H(2)}$	1.227	–	–	–
$a_{H(3)}$	-3.240	-3.244	-3.962	-3.994
$a_{H(8)}$	-0.469	-0.405	-0.578	-0.474
$a_{H(9)}$	-0.775	-0.824	-0.758	-0.831
$a_{H(10)}$	-0.694	-0.613	-0.831	-0.677
$a_{H(12)}$	-0.324	-0.323	-0.256	0.238
$a_{H(13)}$	0.313	0.343	0.350	0.331
$a_{H(14)}$	-0.345	–	–	–
$a_{H(15)}$	0.313	0.286	–	–
$a_{H(b)}$	–	–	-0.071	-0.068
$a_{H(d)}$	–	–	-0.068	-0.065
$a_{H(e)}$	–	–	0.044	0.042
$a_{H(h)}$	–	–	-0.018	-0.015
$a_{H(i)}$	–	–	0.033	0.029
$a_{H(j)}$	–	–	-0.023	-0.021
$a_{H(k)}$	–	–	0.025	0.023
$a_{H(n)}$	–	–	0.356	0.359
$a_{H(p)}$	–	–	0.377	0.378
$a_{H(r)}$	–	–	-0.312	-0.312
$a_{H(u)}$	–	–	0.578	0.578
$a_{H(v)}$	–	–	-0.939	-0.938
$a_{H(w)}$	–	–	0.569	0.569
$a_{H(x)}$	–	–	-0.927	-0.926
$a_{H(6\text{-}o)\ avg}$	0.526	0.516	0.536	–
$a_{H(6\text{-}m)\ avg}$	-0.309	-0.304	-0.313	–
$a_{H(6\text{-}p)}$	0.442	0.433	0.453	–

[a] For comparative purposes, the numbering of the systems is according to radical **1a**.

Table S4. DFT calculated spin densities of radicals **1** and **2** in benzene at the UCAM-B3LYP/EPR-II//UB3LYP/6-31G(d,p) level of theory.[a]

Spin density	1-H	1-tBu	2a	2b
$\rho_{C(1)}$	0.113	0.113	0.128	0.127
$\rho_{C(2)}$	-0.056	-0.057	-0.066	-0.065
$\rho_{C(3)}$	0.118	0.119	0.143	0.145
$\rho_{C(3a)}$	-0.082	-0.080	-0.090	-0.091
$\rho_{N(4)}$	0.273	0.277	0.261	0.259
$\rho_{N(5)}$	0.272	0.268	0.274	0.292
$\rho_{C(6)}$	-0.096	-0.095	-0.098	-0.106
$\rho_{N(7)}$	0.285	0.283	0.280	0.269
$\rho_{C(7a)}$	0.004	0.005	0.004	0.008
$\rho_{C(7b)}$	0.069	0.069	0.061	0.048
$\rho_{C(8)}$	0.004	0.002	0.009	0.005
$\rho_{C(9)}$	0.023	0.025	0.021	0.024
$\rho_{C(10)}$	0.019	0.016	0.026	0.020
$\rho_{C(10a)}$	0.018	0.020	0.018	0.023
$\rho_{N(11)}$	0.024	0.025	0.013	0.012
$\rho_{C(11a)}$	-0.012	-0.013	-0.013	-0.012
$\rho_{C(12)}$	0.0125	0.012	0.010	0.009
$\rho_{C(13)}$	-0.013	-0.013	-0.012	-0.011
$\rho_{C(14)}$	0.014	0.014	0.010	0.009
$\rho_{C(15)}$	-0.012	-0.011	-0.011	-0.010
$\rho_{C(15a)}$	0.017	0.018	0.021	0.021
$\rho_{C(15a')}$	-0.034	-0.034	-0.044	-0.043
$\rho_{C(a)}$	0.051	0.049	0.043	0.042
$\rho_{X(b)}$	–	–	-0.003	-0.002
$\rho_{C(c)}$	–	–	0.003	0.002
$\rho_{C(d)}$	–	–	-0.002	-0.002
$\rho_{C(e)}$	–	–	0.003	0.003
$\rho_{C(f)}$	–	–	-0.002	-0.002
$\rho_{C(g)}$	–	–	0.003	0.003
$\rho_{C(h)}$	–	–	-0.001	-0.001
$\rho_{C(i)}$	–	–	0.001	0.001
$\rho_{C(j)}$	–	–	-0.001	-0.001
$\rho_{C(k)}$	–	–	0.001	0.001
$\rho_{C(l)}$	–	–	-0.001	-0.001
$\rho_{C(m)}$	–	–	0.001	0.001
$\rho_{C(n)}$	–	–	0.025	0.024

$\rho_{C(o)}$	–	–	-0.014	-0.014
$\rho_{C(p)}$	–	–	0.013	0.013
$\rho_{C(r)}$	–	–	-0.015	-0.015
$\rho_{C(s)}$	–	–	0.013	0.013
$\rho_{C(t)}$	–	–	-0.021	-0.021
$\rho_{C(u)}$	–	–	0.038	0.038
$\rho_{C(v)}$	–	–	-0.025	-0.025
$\rho_{C(w)}$	–	–	0.036	0.036
$\rho_{C(x)}$	–	–	-0.023	-0.023
$\rho_{C(y)}$	–	–	0.035	0.035
$\rho_{C(u)}$	–	–	-0.039	-0.038
ρ_{6Ph} *or* ρ_{6tBu}	-0.012	-0.012	-0.012	0.001
ρ_{2tBu} *or* $\rho_{o\text{-}tBu}$	–	0.000	0.001	0.000
ρ_{14tBu} *or* $\rho_{c\text{-}tBu}$	–	0.001	0.000	0.000

[a] For comparative purposes, the numbering of the systems is according to radical **1a**.

Table S5. DFT calculated total spin densities of key fragments in radicals **1** and **2** in benzene at the UCAM-B3LYP/EPR-II//UB3LYP/6-31G(d,p) level of theory.[a]

Spin density	1-H	1-tBu	2a	2b
$\rho_{Triazine}$	0.807	0.807	0.782	0.771
$\rho_{BenzTriaz}$	0.871	0.869	0.856	0.843
ρ_{Carbaz}	0.141	0.143	0.157	0.156
$\rho_{Phenanth}$	–	–	0.085	0.084
ρ_{6Ph} *or* ρ_{6tBu}	-0.012	-0.012	-0.012	0.001
ρ_{2tBu} *or* $\rho_{o\text{-}tBu}$	–	0.000	0.001	0.000
ρ_{14tBu} *or* $\rho_{c\text{-}tBu}$	–	0.001	0.000	0.000

[a] For comparative purposes, the numbering of the systems is according to radical **1a**.

c) spin delocalization in radicals in benzene dielectric medium

Spin delocalization parameter RDV (Radical Delocalization Value)[16] was calculated according to the formula (eq S1):

$$RDV = \sum_{i=1}^{n} (\rho_i)^2 \qquad \text{eq S1}$$

where spin concentration ρ_i on heavy atoms *i* (hydrogen atoms summed up to heavy atoms) is obtained with the UCAM-B3LYP/EPR-II // UB3LYP/6-31G(d,p) method in benzene dielectric

mediums using the PCM model.[15] For the purpose of this work, an inverse is reported: RDV^{-1} = 1/*RDV,* since now larger values corresponds to greater delocalization. Results are shown in Table S6.

Table S6. Radical delocalization value (RDV^{-1}) for radicals **1** and **2**.

Radical	RDV^{-1} (in benzene)
1-H	3.483
1-tBu	3.502
2a	3.343
2b	3.302

d) electronic excitations

Electronic excitation energies in CH_2Cl_2 dielectric medium were obtained at the UB3LYP/6-31G(d,p) level of theory using the time-dependent TD-DFT method[17] supplied in the Gaussian 16 package. Solvation models in calculations were implemented with the PCM model[15] using the SCRF(solvent=CH_2Cl_2) keyword. Four lowest excitation energies, classified as $\pi \rightarrow \pi^*$ transitions are listed in Table S7.

Energies of MOs involved in the low energy transitions in radicals **1** and **2** are listed in Table S8. The contours of the HOMO and LUMO orbitals for **2a** are shown in Fig. 6 in the main text.

A correlation of experimental low energy maxima, λ_{max}, and TD-DFT derived excitation energies are shown in Figure S35, while Figure S36 demonstrates a correlation of experimental oxidation potential, $E_{1/2}^{0/1}$, with DFT-derived energy of the E_{HOMO}.

Table S7. Electronic transition energies and oscillator strength values with the indicated main electronic transition obtained at the UB3LYP/6-31G(d,p) level of theory in CH_2Cl_2 dielectric medium.

Radical	$D_0 \rightarrow D_1$, (π,π*) β-HOMO→β-LUMO /nm (*f*)	$D_0 \rightarrow D_2$, (π,π*) α-HOMO→α-LUMO /nm (*f*)	$D_0 \rightarrow D_3$, (π,π*) α-HOMO→α-LUMO+1 β-HOMO-1→ β-LUMO /nm (*f*)	$D_0 \rightarrow D_4$, (π,π*) α-HOMO→α-LUMO+2 β-HOMO-1→ β-LUMO /nm (*f*)
1-H	645 (0.081), 94%	619 (0.009), 91%,	486 (0.044), 46% 32%	458 (0.011), 65% 29%
1-tBu	659 (0.096), 95%	623 (0.009), 92%	493 (0.021), 21% 67%	460 (0.030), 57% 16%
2a	722 (0.092), 83%	598 (0.122), 20% [b]	606 (0.034), 24% 52%	568 (0.167), 0% 24% [e]
2b	705 (0.071), 77% [a]	598 (0.122), 29% [c]	567 (0.149), 1% 38% [d]	539 (0.0003), 0% 0% [f]

[a] 15% α-HOMO→α-LUMO. [b] 59% α-HOMO→α-LUMO+1. [c] 59% β-HOMO-1→β-LUMO. [d] 44% α-HOMO→α-LUMO. [e] 52% α-HOMO→α-LUMO. [f] 70% α-HOMO→α-LUMO+1.

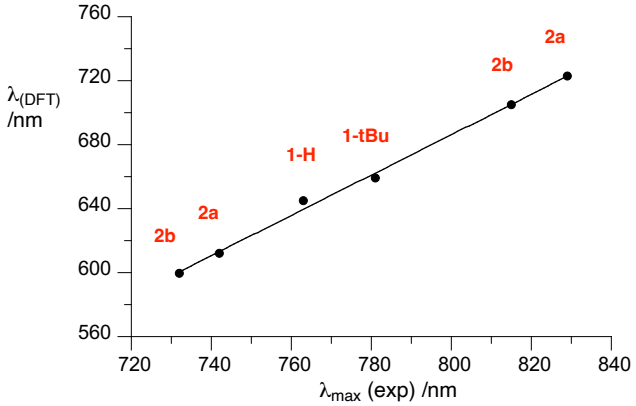


Figure S35. A correlation of experimental low energy absorption maxima and TD-DFT derived excitation energies. Best fit function: $\lambda_{(DFT)} = 1.27(4) \times \lambda_{max} - 330(30)$ nm, $r^2 = 0.996$.

Table S8. Energies of MO involved in low energy transitions obtained from the UB3LYP/6-31G(d,p) method in CH_2Cl_2 dielectric medium.

Radical	α-HOMO-1 π /eV	α-HOMO π /eV	α-LUMO π* /eV	α-LUMO+1 π* /eV	β-HOMO-1 π /eV	β-HOMO π /eV	β-LUMO π* /eV
1-H	-5.706	-4.491	-1.459	-1.051	-6.181	-5.452	-2.715
1-tBu	-5.601	-4.444	-1.434	-0.968	-6.024	-5.349	-2.677
2a	-5.521	-4.512	-1.751	-1.500	-5.596	-5.311	-2.879
2b	-5.510	-4.456	-1.716	-1.219	-5.582	-5.299	-2.803

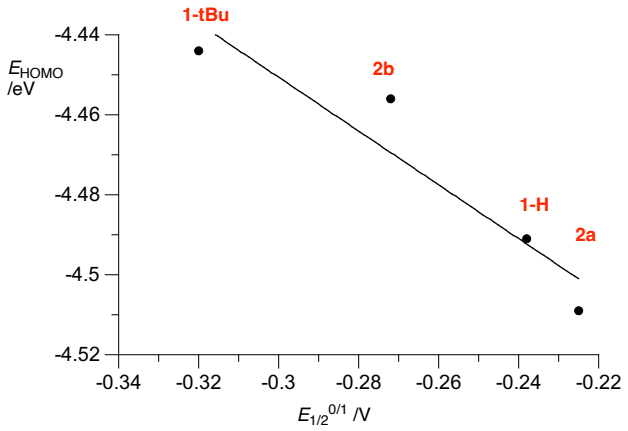


Figure S36. A correlation of oxidation potential, $E_{1/2}^{0/1}$, with E_{HOMO}.

e) partial output data from TD-DFT calculations for radicals 1 and 2

Method: UB3LYP/6-31G(d,p)// UB3LYP/6-31G(d,p)

Keywords: TD(nstates=120, root=1) SCRF(solvent=CH2CL2) SCF=tight

1-H

```
Excited State   1:  2.089-A      1.9236 eV  644.55 nm  f=0.0807  <S**2>=0.841
     97A -> 99A       -0.14189                    α-HOMO -> α-LUMO+1
     96B -> 97B        0.97059                    β-HOMO -> β-LUMO
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -1180.66293526
 Copying the excited state density for this state as the 1-particle RhoCI
density.

 Excited State   2:  2.042-A   2.0022 eV  619.23 nm  f=0.0093  <S**2>=0.793
     96A -> 98A       -0.13197
     97A -> 98A        0.95638                    α-HOMO -> α-LUMO
     97A -> 99A       -0.12479
     94B -> 97B       -0.11643

 Excited State   3:  2.246-A   2.5526 eV  485.73 nm  f=0.0441  <S**2>=1.011
     95A -> 99A        0.10928
     97A -> 98A        0.11589
     97A -> 99A        0.67864                    α-HOMO -> α-LUMO+1
     97A ->100A        0.29326
     95B -> 97B       -0.56981                    β-HOMO-1 -> β-LUMO
     96B -> 97B        0.11964

 Excited State   4:  2.133-A  2.7091 eV  457.67 nm  f=0.0111  <S**2>=0.887
     97A ->100A        0.80612                    α-HOMO -> α-LUMO+2
     95B -> 97B        0.53394

 Excited State   5:  2.303-A   2.8146 eV  440.51 nm  f=0.0494  <S**2>=1.076
```

```
     95A -> 99A       -0.14494
     96A -> 99A        0.10465
     97A -> 99A        0.61915
     97A ->100A       -0.43295
     95B -> 97B        0.53537
     96B -> 98B       -0.15748
```

1-tBu

```
Excited State   1:  2.085-A      1.8821 eV  658.75 nm  f=0.0958  <S**2>=0.837
    129A ->131A        0.13179
    128B ->129B        0.97366                  β-HOMO -> β-LUMO
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -1495.19555529
 Copying the excited state density for this state as the 1-particle RhoCI
density.

 Excited State   2:  2.043-A    1.9898 eV  623.10 nm  f=0.0091  <S**2>=0.793
    128A ->130A       -0.14491
    129A ->130A        0.95774                  α-HOMO -> α-LUMO
    129A ->131A        0.10162
    126B ->129B       -0.11035

 Excited State   3:  2.218-A   2.5154 eV  492.90 nm  f=0.0210  <S**2>=0.980
    127A ->131A        0.14064
    129A ->131A        0.46015
    129A ->132A       -0.14146
    127B ->129B        0.81908                  β-HOMO-1 -> β-LUMO
    127B ->131B        0.10933

 Excited State   4:  2.186-A   2.6970 eV  459.71 nm  f=0.0304  <S**2>=0.945
    129A ->130A        0.10057
    129A ->131A       -0.42297
    129A ->132A        0.75722                  α-HOMO -> α-LUMO+2
    122B ->129B        0.10556
    127B ->129B        0.40576

 Excited State   5:  2.282-A  2.7968 eV  443.31 nm  f=0.0532  <S**2>=1.051
    128A ->131A        0.11012
    129A ->131A        0.67069
    129A ->132A        0.56764
    126B ->129B       -0.11242
    127B ->129B       -0.28647
    128B ->130B        0.19843

 Excited State   6:  2.047-A   2.9736 eV  416.95 nm  f=0.0011  <S**2>=0.798
    123B ->129B        0.98371
```

2a

```
Excited State   1:  2.123-A      1.7153 eV  722.79 nm  f=0.0916  <S**2>=0.877
    207A -> 208A      -0.31241
    204B -> 207B      -0.12253
    206B -> 207B       0.91361                  β-HOMO -> β-LUMO
```

```
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -2417.06428299
 Copying the excited state density for this state as the 1-particle RhoCI
density.

 Excited State   2:  2.060-A   2.0065 eV  617.91 nm  f=0.0471  <S**2>=0.811
    206A -> 209A      -0.14881
    207A -> 208A       0.44322
    207A -> 209A       0.77132                 α-HOMO -> α-LUMO+1
    205B -> 207B       0.32560
    206B -> 207B       0.15681

 Excited State   3:  2.219-A   2.0459 eV  606.01 nm  f=0.0337  <S**2>=0.981
    205A -> 208A       0.11337
    207A -> 208A       0.25523
    207A -> 209A      -0.48840
    201B -> 207B       0.12909
    202B -> 207B      -0.13536
    205B -> 207B       0.72059                 β-HOMO-1 -> β-LUMO
    206B -> 207B       0.21795

 Excited State   4:  2.315-A   2.1823 eV  568.12 nm  f=0.1666  <S**2>=1.089
    206A -> 208A       0.13955
    207A -> 208A       0.72315
    207A -> 209A      -0.23653
    201B -> 207B       0.13524
    205B -> 207B      -0.49359
    206B -> 207B       0.19619
    206B -> 208B      -0.14657
```

2b

```
Excited State   1:  2.141-A      1.7589 eV  704.89 nm  f=0.0706  <S**2>=0.896
    203A -> 204A      -0.39150
    200B -> 203B      -0.12203
    201B -> 203B      -0.11456
    202B -> 203B       0.87890                 β-HOMO -> β-LUMO
 This state for optimization and/or second-order correction.
 Total Energy, E(TD-HF/TD-DFT) =  -2343.26530148
 Copying the excited state density for this state as the 1-particle RhoCI
density.

 Excited State   2:  2.208-A   2.0721 eV  598.34 nm  f=0.1221  <S**2>=0.969
    203A -> 204A       0.53874                 α-HOMO -> α-LUMO
    197B -> 203B       0.12303
    198B -> 203B      -0.12105
    201B -> 203B       0.68550                 β-HOMO-1 -> β-LUMO
    202B -> 203B       0.36427

 Excited State   3:  2.325-A   2.1877 eV  566.73 nm  f=0.1489  <S**2>=1.101
    201A -> 204A      -0.10810
    202A -> 204A       0.13197
    203A -> 204A       0.66053
    203A -> 205A      -0.11036
    198B -> 203B       0.10991
    201B -> 203B      -0.61787
    201B -> 204B      -0.11722
```

```
    202B -> 203B        0.20133
    202B -> 204B       -0.12151

 Excited State   4:  2.189-A  2.3014 eV  538.72 nm  f=0.0003  <S**2>=0.947
    202A -> 208A       -0.13759
    203A -> 204A        0.12971
    203A -> 205A        0.83534                    α-HOMO -> α-LUMO+1
    203A -> 208A        0.42552
```

f) TD-DFT *calculation of electronic circular dichroism (ECD) results for radicals 2 and precursor 4a*

Results of TD-DFT calculations for **2a**, **2b** and **4a** at the UB3LYP/6-31G(d,p)//UB3LYP/6-31G(d,p) level of theory using TD(NStates=100) in CH_2Cl_2 dielectric medium are shown in Figures S37–S39.

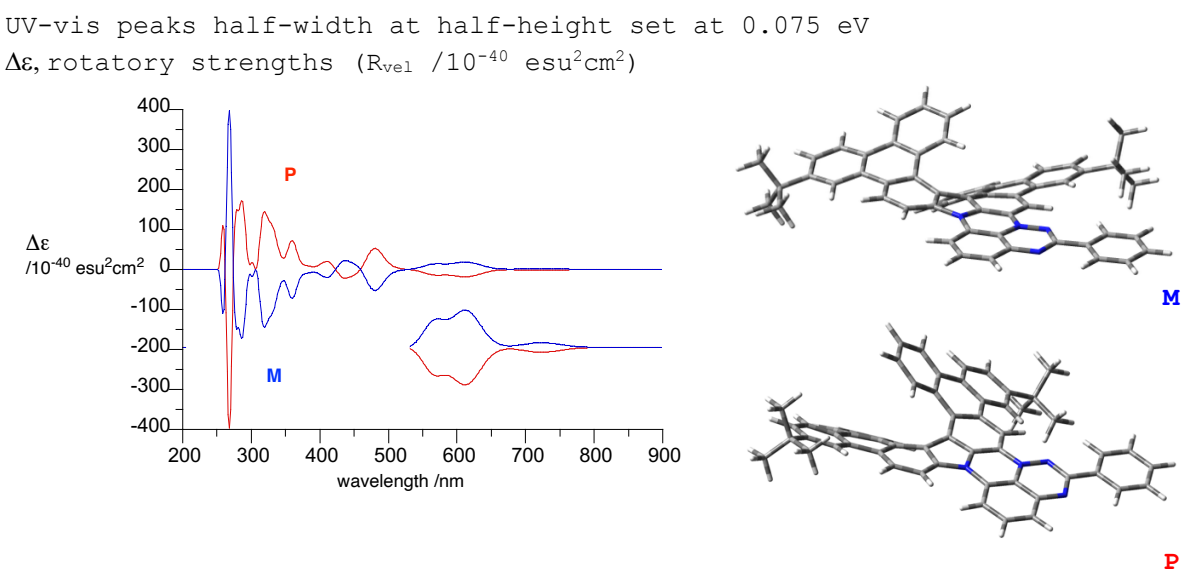


Figure S37. Right: Calculated (DFT) electronic circular dichroism spectra for two enantiomers of **2a** in CH_2Cl_2 dielectric medium. Left: UB3LYP/6-31G(d,p) optimized structures of the two enantiomers. The inset shows magnified low energy region of the spectrum.

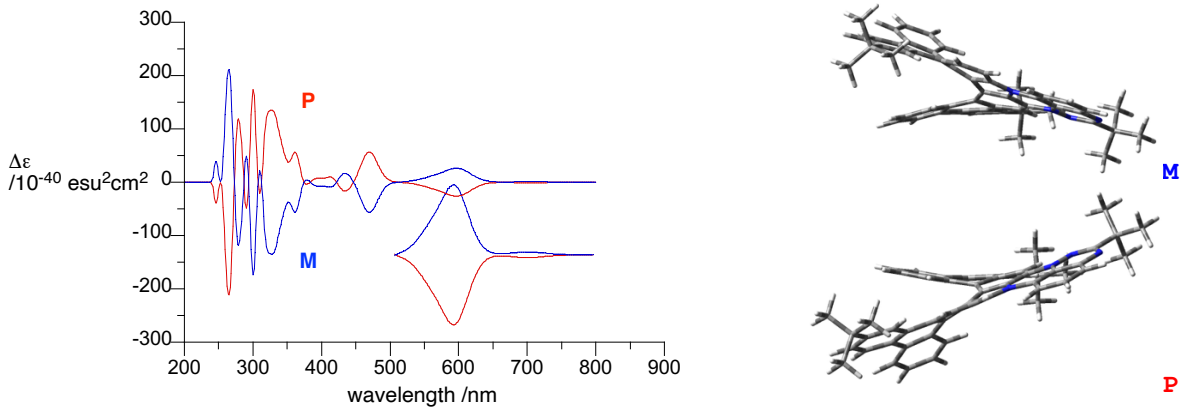


Figure S38. Right: Calculated (DFT) electronic circular dichroism spectra for two enantiomers of **2b** in CH_2Cl_2 dielectric medium. Left: UB3LYP/6-31G(d,p) optimized structures of the two enantiomers. The inset shows magnified low energy region of the spectrum.

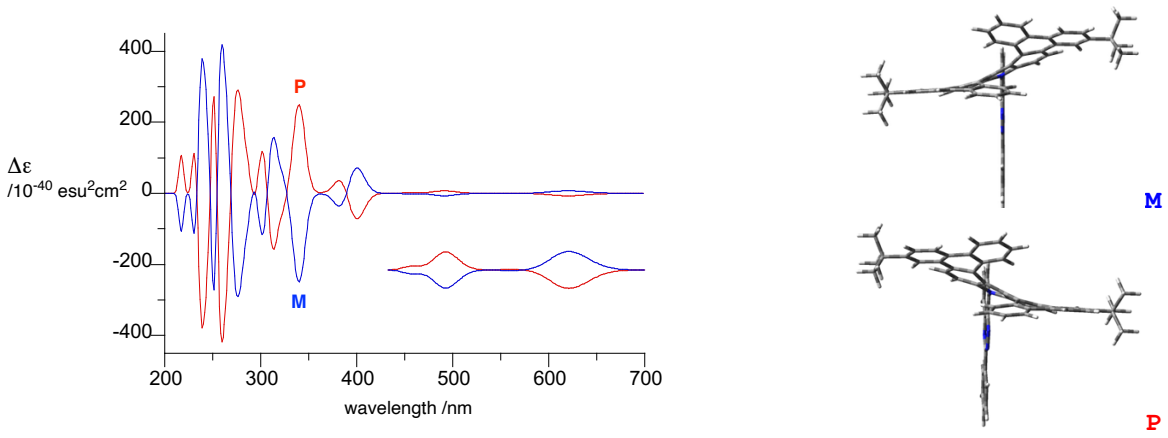


Figure S39. Right: Calculated (DFT) electronic circular dichroism spectra for two enantiomers of **4a** in CH_2Cl_2 dielectric medium. Left: UB3LYP/6-31G(d,p) optimized structures of the two enantiomers. The inset shows magnified low energy region of the spectrum.

12. Archive for DFT calculations

1-H

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\\#P UB3LYP/6-31G(d,p) Fopt(tight) geom=(noangle,nodistance) #P SCF=di
rect fcheck SCRF(Solvent=CH2Cl2)\\benzotrazinyl carbazole radical\\0,2
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1-tBu

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rect fcheck SCRF(Solvent=CH2Cl2)\\benzotrazinyl di-tBu-carbazole\\0,2\
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2a

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.1687992615,2.0201218053,2.7558158776\H,5.0784554191,3.4530752704,-2.7
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9109095,-2.7802037094\H,1.6322643944,1.1685042089,-1.6806154969\H,2.51
60363246,0.5822368526,1.6636144524\H,1.8186560535,5.4680950233,1.80126
6925\H,-1.7302895266,7.1477887623,-0.103700425\H,9.0642102557,-1.2627
357153,0.080766351\H,7.6450844399,0.5553841355,-0.6461487415\H,5.64081
69092,-3.7992812603,0.4931293114\H,0.3740660764,6.236041903,0.66019904
59\H,-3.3044468083,3.1939763875,-0.5537030963\C,8.3918432476,-3.833825
4119,0.7889061735\C,-4.0318971693,5.8434306505,-0.8604193088\C,-1.4319
520815,-3.1925212135,0.1420637607\C,-2.7645220042,-2.7061347998,0.0999
551954\C,-1.2380039476,-4.5685575214,0.273574721\C,-3.8758894276,-3.58
68087024,0.1323090745\C,-2.335801277,-5.4386043062,0.3161729967\H,-0.2
470868015,-4.9793570614,0.370933004\C,-3.6358729087,-4.96964127,0.2349
435262\H,-2.1499446301,-6.5029382051,0.416578616\C,-5.3070065745,-1.78
87761142,-0.022171528\H,-4.4893990237,-5.6374138668,0.2591639691\N,-3.
0616699613,-1.3410214615,0.0463632058\N,-4.3333549785,-0.8673806217,-0
.0292672602\N,-5.1615138285,-3.11265616,0.0669717037\C,-6.6926027697,-
1.25050523,-0.1182855553\C,-6.9333918031,0.1264274598,-0.252885097\C,-
7.7849787846,-2.1308287489,-0.0760231823\C,-8.237609818,0.6090349444,-
0.3423551527\H,-6.0944943053,0.8112790887,-0.2886356388\C,-9.088153394
7,-1.6448276337,-0.1649060197\H,-7.5951452939,-3.19259229,0.0270521359
\C,-9.3198180908,-0.2737335973,-0.2983102157\H,-8.4095769681,1.6761873
243,-0.4470647841\H,-9.9239387202,-2.3374056522,-0.1300147917\H,-10.33
55195084,0.1043637958,-0.3678999146\C,7.6317039717,-5.1378736581,1.094
4684953\H,6.9030673087,-5.006744679,1.9011941213\H,7.1042024797,-5.518
348821,0.2136057903\H,8.3404025698,-5.9086124613,1.4134736682\C,9.4335
157011,-4.1300647214,-0.3167324216\H,10.0384230352,-3.2500657148,-0.55

4093078\H,10.1144403367,-4.9244220967,0.0082476054\H,8.9429332127,-4.4
593871669,-1.2386508123\C,9.1260432563,-3.3890869745,2.0766251614\H,9.
8021133632,-4.1801598565,2.4193860991\H,9.7241575181,-2.4875394513,1.9
149194053\H,8.4130368641,-3.179772896,2.8809058236\C,-5.0919119341,4.7
76027494,-1.1904482107\H,-4.7620869764,4.1065010493,-1.9915633409\H,-5
.3437269002,4.1676880627,-0.3154191727\H,-6.0110199939,5.2651615093,-1
.5280833822\C,-4.6063912878,6.7713073051,0.2369711756\H,-3.9155099911,
7.5808784012,0.4898685066\H,-5.5422870953,7.2268306872,-0.1049104189\H
,-4.8167013846,6.2100706106,1.1533754182\C,-3.7642085316,6.6708763288,
-2.1405018147\H,-4.6951370156,7.1224979981,-2.500664497\H,-3.049790967
,7.4797569253,-1.9616379179\H,-3.3629151407,6.0378512853,-2.9387943788
\\Version=ES64L-G16RevB.01\State=2-A\HF=-2417.1273209\S2=0.76837\S2-1=
0.\S2A=0.750279\RMSD=1.165e-09\RMSF=1.421e-07\Dipole=1.2924005,-0.1971
767,0.0239826\Quadrupole=4.9397129,18.7746632,-23.7143761,-14.0570359,
6.4968552,-5.9893697\PG=C01 [X(C57H43N4)]\\@

2b

1\1\GINC-LOCALHOST\FOpt\UB3LYP\6-31G(d,p)\C55H47N4(2)\PK\24-Jul-2025\0
\\#P UB3LYP/6-31G(d,p) Fopt(tight) geom=(noangle,nodistance) #P SCF=di
rect fcheck SCRF(Solvent=CH2Cl2)\\Chiral di(phenanthro)carbazole-di-t-
Bu-BT-tBu fused M config\\0,2\C,-2.0412872158,-1.1173674855,0.12796182
91\C,-0.6476546186,-1.2357687781,0.0861249029\C,0.2301715621,-0.147427
8446,0.121927768\C,-0.3293070805,1.1333875928,0.4761534041\C,-1.742604
6082,1.2851966102,0.3526146728\C,-2.5814540532,0.1563928608,0.18988345
29\C,1.5482664377,-0.7237603436,-0.1663253322\C,1.3842317468,-2.142122
4277,-0.1646373324\N,0.023009314,-2.4397174293,-0.0370357434\C,2.48003
87132,-3.008089057,-0.287379076\C,3.7415842363,-2.4540816854,-0.342857
4609\C,3.9546723067,-1.0577433497,-0.4272798895\C,2.833396259,-0.18818
49933,-0.5088683279\C,5.3100195588,-0.4977342302,-0.4307117515\C,5.503
7415596,0.8736380374,-0.7248849194\C,0.4301557595,2.2198141047,1.08571
33909\C,-0.1569872262,3.5087371134,1.2356004148\C,-1.5204459355,3.7381
210833,0.7661843766\C,-2.3233360844,2.6333928348,0.390607899\C,3.04856
21703,1.1496815912,-1.0673517563\C,4.3671137522,1.6758932222,-1.170866
4409\C,4.5488275014,2.9423303269,-1.7679679741\C,1.9894008642,1.880921
9206,-1.6497193559\C,1.6999657927,1.9907693116,1.6647976021\C,0.581114
5114,4.5200114309,1.8876931118\C,1.8419395135,4.2792628205,2.407452908
9\C,2.3980414339,2.9955805049,2.3105635734\C,2.1944851668,3.114221285,
-2.2438911869\C,3.4841880325,3.6613929378,-2.2846197701\C,-2.094486417
9,5.0266076691,0.707132947\C,-3.6618511945,2.8662161499,-0.0051794002\
C,-4.2299055175,4.1336410469,-0.0464475734\C,-3.4053412284,5.220931798
8,0.3181119492\C,6.809837147,1.398009866,-0.6193430928\C,7.8836640241,
0.6044582512,-0.2647892088\C,6.4298420712,-1.2839477257,-0.0703216644\
C,7.7183933068,-0.7701701229,0.0147784653\H,-3.6559632147,0.2514121784
,0.1741751238\H,4.5870570823,-3.1285148659,-0.392070514\H,2.3764348526
,-4.0804410611,-0.3361538793\H,2.3811142641,5.0749666505,2.9125449593\
H,3.366909954,2.7824322239,2.7517569663\H,3.656730596,4.6282983309,-2.
7476247841\H,5.547803521,3.3512226354,-1.8640103002\H,1.3583176348,3.6
450802754,-2.6885735584\H,0.9958761515,1.454635414,-1.6596127877\H,2.1
239249433,0.9966191909,1.6302001203\H,0.1432406536,5.5022419019,2.0212
776762\H,-3.7942800365,6.233810072,0.2862486945\H,8.8664484175,1.05980
84136,-0.1938617911\H,6.9854039649,2.4517414197,-0.8037313742\H,6.2696
36861,-2.3220051537,0.1843333647\H,-1.49631845,5.8955946633,0.95616222
13\H,-4.2590557765,2.0233682621,-0.3221078205\C,8.9361775686,-1.621717
7654,0.4147103601\C,-5.6834716811,4.3873414589,-0.4830348138\C,-0.7141
37553,-3.641836694,0.0137162783\C,-2.1295017386,-3.5311706791,0.032766
3278\C,-0.1544425633,-4.9194952029,0.0595666502\C,-2.960831547,-4.6781
179844,0.043818684\C,-0.9764512856,-6.0541665993,0.0800168422\H,0.9133
672162,-5.0532673637,0.1050282502\C,-2.357010136,-5.9482196288,0.06042

23897\H,-0.5087024686,-7.0327159649,0.1132112305\C,-4.8314748294,-3.33
35470329,0.0345346914\H,-2.9997779173,-6.8210608877,0.0686973475\N,-2.
7836628515,-2.2972813083,0.0610040435\N,-4.1410787797,-2.1834844604,0.
0500051333\N,-4.3328072427,-4.5656276479,0.0410914828\C,8.5657762627,-
3.0926492052,0.6810493237\H,7.8570662657,-3.1919835792,1.5097708675\H,
8.129842692,-3.5698491876,-0.2027821604\H,9.4662778257,-3.6540965145,0
.9492130286\C,9.9795985605,-1.585870934,-0.7277657874\H,10.3166910851,
-0.5672379848,-0.940887744\H,10.8601054674,-2.1777810815,-0.4545722097
\H,9.5635627481,-2.0023944534,-1.6510722749\C,9.5685549008,-1.04167027
18,1.7025619501\H,10.4440317957,-1.6325397076,1.9937588271\H,9.8962139
309,-0.0069209948,1.5662305913\H,8.8542537629,-1.0616055794,2.53227940
43\C,-6.4250953484,3.0881671251,-0.8490527124\H,-5.9527848244,2.571493
2358,-1.6910132001\H,-6.4736344889,2.3939910095,-0.0036882004\H,-7.453
0061308,3.3237068062,-1.1422163807\C,-6.4497411536,5.0714720916,0.6745
715493\H,-5.9951226162,6.025579318,0.9570004713\H,-7.4851590763,5.2708
711025,0.3771489645\H,-6.4687152866,4.4319024533,1.5631631428\C,-5.694
3028148,5.3153565978,-1.7214022461\H,-6.724620988,5.5123319783,-2.0375
524595\H,-5.2205420458,6.2792207801,-1.5135510431\H,-5.1639559582,4.85
38195497,-2.5609032307\C,-6.3567330246,-3.1501639405,0.0129685586\C,-6
.7862911629,-2.3588074106,1.2695249661\C,-6.7475521364,-2.3557545114,-
1.2543064773\C,-7.073100849,-4.5104962751,0.0010472894\H,-6.5223840448
,-2.9000521954,2.1844813631\H,-6.3060209146,-1.3779837176,1.3031651208
\H,-7.8717350101,-2.2127167633,1.2651663782\H,-6.4590093813,-2.8964119
054,-2.1621836239\H,-7.8321685294,-2.2060309935,-1.2811905794\H,-6.263
1544966,-1.3764344052,-1.2721456758\H,-8.1560300212,-4.3487110977,-0.0
160783974\H,-6.7989569963,-5.1009655333,-0.8770170637\H,-6.8268610396,
-5.1010645036,0.8872719739\\Version=ES64L-G16RevB.01\State=2-A\HF=-234
3.3299402\S2=0.767456\S2-1=0.\S2A=0.750252\RMSD=7.773e-09\RMSF=2.079e-
07\Dipole=1.2341451,0.0589079,-0.0219779\Quadrupole=9.9202064,9.546782
9,-19.4669894,-15.98639,5.6857262,-1.8587485\PG=C01 [X(C55H47N4)]\\@

4a'

1\1\GINC-LOCALHOST\FOpt\RCAM-B3LYP\6-311G(d,p)\C51H32N4\PIOTR\01-Feb-2
025\0\\#P CAM-B3LYP/6-311G(d,p) FOpt SCF=Direct guess=check #P Geom=(N
oDistance,NoAngle) fcheck SCRF(Solvent=EthylEthanoate)\\Chiral di(phen
anthro)carbazole-dimethyl-at C8 of BT in AcOEt\\0,1\C,1.4549691417,1.8
423597869,-1.451375787\C,0.7772633339,0.6503735277,-1.198839198\C,-0.5
03232709,0.6011860796,-0.6223107994\C,-1.0170486704,1.8100500022,-0.06
1376941\C,-0.4200031975,3.0242398162,-0.4515072813\C,0.8170381315,3.00
99338263,-1.1344794624\C,-0.9253700664,-0.8010997058,-0.7079144268\C,0
.2020785959,-1.511731346,-1.1560465837\N,1.2076682047,-0.6272233483,-1
.4911610842\C,0.253488751,-2.9040926203,-1.2111985075\C,-0.849202666,-
3.5932900525,-0.7860805506\C,-2.0502062151,-2.9383831127,-0.4333683588
\C,-2.1377496655,-1.5360451577,-0.5335222673\C,-3.2018566953,-3.702243
8761,0.0547608207\C,-4.439628423,-3.0644526907,0.2414046764\C,-2.02760
78817,1.8543476878,0.9954324038\C,-2.6359619856,3.0761306124,1.3459918
82\C,-2.2378771276,4.3027659628,0.6625571369\C,-1.098577365,4.29002210
24,-0.1596719664\C,-3.4719648388,-0.9375961456,-0.5904908945\C,-4.6030
613413,-1.6838800521,-0.2031778875\C,-5.8744392541,-1.0980463236,-0.32
21148845\C,-3.6720998822,0.3295831705,-1.1637787951\C,-2.304958699,0.7
202738685,1.7772328995\C,-3.5645409357,3.091979398,2.4002846661\C,-3.8
588091043,1.955381673,3.1174454108\C,-3.2041070482,0.7611988084,2.8166
757451\C,-4.9269325882,0.8785069917,-1.2860705587\C,-6.0395424383,0.16
5867913,-0.8397808777\C,-2.9292430188,5.5143513258,0.8348889912\C,-0.6
827406536,5.4982327755,-0.7505083088\C,-1.3548189289,6.6870047731,-0.5
622324456\C,-2.5026299804,6.6770554324,0.2421795389\C,-5.4945358109,-3
.7974647032,0.8119967031\C,-5.3468775263,-5.1165542127,1.1632239359\C,

-3.081409762,-5.0561120147,0.4212122892\C,-4.1254949419,-5.7745008821,
0.9634341311\H,1.3105089309,3.9419631524,-1.3672913732\H,-0.8050258748
,-4.6723402882,-0.7768529315\H,1.1441018117,-3.4186753534,-1.546684703
8\H,-4.5713633569,1.9990330941,3.9323674503\H,-3.3912132728,-0.1293591
33,3.40414381\H,-7.0328634523,0.5891283606,-0.9283153005\H,-6.75302548
13,-1.6591924112,-0.036010114\H,-5.0471091938,1.8558487673,-1.73732709
\H,-2.8233980452,0.8776696458,-1.5426980512\H,-1.7796356672,-0.2006314
17,1.5765058803\H,-4.0362783185,4.0216322431,2.6865257243\H,-3.0623415
521,7.5939867091,0.3910822442\H,-6.1791397646,-5.651825283,1.607057439
2\H,-6.4458912185,-3.3174089581,0.9957869034\H,-2.1306349789,-5.558955
8589,0.3091024939\H,-3.8273370916,5.5404577937,1.4366371589\H,0.178246
6166,5.5060828625,-1.4048623292\C,-3.9662271228,-7.2187495566,1.353064
9945\H,-2.9520016935,-7.5722796008,1.1654890225\H,-4.1855990191,-7.366
050828,2.4133964377\H,-4.6546660168,-7.853891705,0.7897671041\C,-0.891
1128981,7.9626960742,-1.2108291549\H,-0.0102961712,7.7966308195,-1.831
6580745\H,-1.6744605329,8.3904493374,-1.8413449132\H,-0.6366139811,8.7
134680514,-0.4583556723\C,2.4812500392,-0.9793796403,-1.9989333994\C,3
.6294205823,-0.8916990565,-1.1604326951\C,2.6291116477,-1.4240707446,-
3.2802991721\C,4.89758609,-1.2426039062,-1.6665055871\C,3.9043135996,-
1.7917769137,-3.7779610292\H,1.7598137776,-1.4908944711,-3.9217067109\
C,5.0197865492,-1.7015783633,-3.0000331417\H,3.9828711426,-2.141013258
1,-4.7996345081\C,5.769600742,-0.7248619321,0.3571421721\H,6.002485222
1,-1.9691617877,-3.3653568033\N,3.4978792364,-0.4838901426,0.123093586
2\N,4.5414066695,-0.4030708503,0.86879908\N,5.976983215,-1.1422116619,
-0.8685189764\C,6.9174256077,-0.5839632131,1.2801962178\C,6.7319215069
,-0.1313503937,2.5868935414\C,8.203444661,-0.9042678764,0.8434884431\C
,7.8170057986,-0.0025994512,3.4399156626\H,5.7353240642,0.1169411896,2
.9236112894\C,9.2843999994,-0.7742880774,1.6992432634\H,8.3417486662,-
1.2543668032,-0.1704029657\C,9.094208783,-0.3230694404,2.9997350449\H,
7.6640340873,0.3498440476,4.4526191361\H,10.2790141575,-1.0254712058,1
.3514521628\H,9.9405997732,-0.2215266626,3.6683724483\H,2.4354809891,1
.8434108073,-1.9089323777\\Version=ES64L-G16RevC.01\State=1-A\HF=-2181
.0522147\RMSD=9.977e-09\RMSF=1.799e-06\Dipole=1.3349707,-0.6662712,-1.
4895478\Quadrupole=7.2892185,2.4476113,-9.7368299,-5.3200128,-16.50615
23,0.1068885\PG=C01 [X(C51H32N4)]\\@

4a′-S_1

1\1\GINC-LOCALHOST\FOpt\RCAM-B3LYP TD-FC\6-311G(d,p)\C51H32N4\PIOTR\04
-Feb-2025\0\\#P CAM-B3LYP/6-311G(d,p) Fopt TD=(singlets,root=1, NState
s=3) SCF=tight #P Geom=(NoDistance,NoAngle) SCRF(Solvent=EthylEthanoat
e)\\Chiral di(phenanthro)carbazole-dimethyl-at C8 of BT in AcOEt\\0,1\
C,1.4743208184,1.7792968078,-1.3967140981\C,0.7805583682,0.5936369589,
-1.1559944749\C,-0.5061261468,0.5573801299,-0.5906829156\C,-1.01053407
26,1.769452451,-0.0276644666\C,-0.3945724636,2.9783644828,-0.405204893
3\C,0.8477123668,2.9526066275,-1.0785712722\C,-0.9454163809,-0.8383795
8,-0.691392895\C,0.1780037306,-1.5601963186,-1.1322646073\N,1.19977797
04,-0.6878292775,-1.4487978769\C,0.2127906567,-2.9530849342,-1.1941830
508\C,-0.903087631,-3.630759128,-0.7856167173\C,-2.1001314121,-2.96288
0022,-0.4427244293\C,-2.1688646634,-1.5590611744,-0.5348546044\C,-3.26
7054165,-3.7150359059,0.0267880979\C,-4.4986483728,-3.0624853672,0.203
5120641\C,-2.0325172569,1.8205555128,1.018003947\C,-2.6277855737,3.048
3557672,1.3706350864\C,-2.2062006157,4.2739123649,0.6995751756\C,-1.05
9621198,4.2510310627,-0.1122261044\C,-3.4944225895,-0.94321109,-0.6038
483209\C,-4.6393597697,-1.6773599943,-0.2344359286\C,-5.9016907969,-1.
0744080659,-0.364556998\C,-3.67151676,0.3298619288,-1.1717452574\C,-2.
3368985009,0.6847600788,1.787306019\C,-3.5685478951,3.0698815011,2.413
9513365\C,-3.8898459029,1.9320647435,3.1173822387\C,-3.2494747177,0.73

06028191,2.8148470457\C,-4.9176599681,0.8955569682,-1.3053364986\C,-6.
0444585976,0.1945791215,-0.876378202\C,-2.883608551,5.4933294352,0.872
4679187\C,-0.6233954987,5.4570558772,-0.6928327748\C,-1.2821654609,6.6
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4a′-T_1

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b-2025\0\\#P UCAM-B3LYP/6-311G(d,p) FOpt SCF=Direct freq(noraman) gues
s=check #P Geom=(NoDistance,NoAngle) SCRF(Solvent=EthylEthanoate)\\Chi
ral di(phenanthro)carbazole-dimethyl-at C8 of BT in T state in AcOEt\\
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