Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Campestarenes: A Family of Novel Shape-Persistent Schiff Base Macrocycles With Five-fold Symmetry

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General experimental

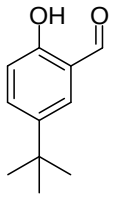
General procedures. All reactions were carried out under air unless otherwise stated. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under nitrogen. Acetonitrile, methanol, and triethylamine were purged with nitrogen gas and dried over molecular sieves before use. Deuterated solvents were obtained from Cambridge Isotope Laboratories, Inc. All reagents were used as received unless otherwise stated.

Equipment. 300 MHz ^{1}H and 75.5 MHz ^{13}C NMR spectra were recorded on a Bruker AV-300 spectrometer. 400 MHz ^{1}H and 100.6 MHz ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer. Mass spectra and elemental analyses were obtained at the UBC Microanalytical Services Laboratory. Matrix assisted laser desorption/ionization (MALDI) mass spectra were obtained on a Bruker Biflex IV time-of-flight (TOF) mass spectrometer equipped with a MALDI ion source. Electrospray ionization (ESI) mass spectra were obtained on a Bruker Esquire-LC ion trap mass spectrometer equipped with an electrospray ion source. High-resolution electrospray ionization (HR-ESI) mass spectra were obtained on a Micromass LCT time-of-flight (TOF) mass spectrometer equipped with an electrospray ion source. Samples for both ESI and HR-ESI were analyzed in methanol, methanol / dimethyl sulfoxide mixture or methanol / methylene chloride mixtures at 1 μM. Gramicidin S, Rifampicin, and Erythromycin were used as the references for HR-ESI. Electron Impact (EI) mass spectra were recorded on a Kratos MS-50 double focusing sector mass spectrometer equipped with an EI ion source. Elemental analyses were obtained on a Carlo Erba Elemental Analyzer EA 1108. Melting points were obtained on a Fisher-John's melting point apparatus. IR spectra were obtained using a Thermo Scientific Nicolet 6700 FT-IR spectrometer equipped with a diamond attenuated total reflectance (ATR) attachment. UV-vis spectra were obtained in DMSO (ca. 1 x 10^{-6} M) on a Varian Cary 5000 UV-vis/near-IR spectrophotometer using a 1 cm quartz cuvette.

General procedure for the synthesis of the 5-alkyl-2-hydroxybenzaldehydes

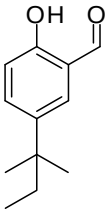
Et_3N (2 eq.) was added dropwise to a solution of *p*-alkylphenol (1 eq.), $MgCl_2$ (2 eq.) and $(CH_2O)_n$ (2.2 eq.) in dry THF (ca. 50 mL for 10 mmol of the *p*-alkylphenol) under a nitrogen atmosphere. After heating at reflux for 24 h, dilute HCl was added at RT until the precipitate dissolved. Most of the THF was removed by rotary evaporation, then the aqueous phase was extracted with CH_2Cl_2 (3 x 25 mL). The combined organic phases were dried over $MgSO_4$, filtered, then concentrated under reduced pressure. Silica gel flash column chromatography (eluent: CH_2Cl_2) of the residue gave the compound.

5-*tert*-butyl-2-hydroxybenzaldehyde



This compound is commercially available (Aldrich), but can be synthesized following the general procedure.

5-(1,1-dimethylpropyl)-2-hydroxybenzaldehyde



This compound is known,[1] but we synthesized it following the general procedure starting with *p*-isoamylphenol (1 eq., 12.2 mmol, 2.0 g). Isolated as a pale yellow oil in 66% yield (1.534 g, 8.05 mmol).

See *Figures S1* and *S2* for NMR spectra.

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ 10.87 (s, 1H, O*H*), 9.90 (s, 1H, C*H*=O), 7.52 (dd, $^{4}J_{H\text{-}H}$ 2.7, $^{3}J_{H\text{-}H}$ 8.7 Hz, 1H, aromatic C*H*), 7.46 (d, $^{4}J_{H\text{-}H}$ 2.7 Hz, 1H, aromatic C*H*), 6.95 (d, $^{3}J_{H\text{-}H}$ 8.7 Hz, 1H, aromatic C*H*), 1.65 (q, $^{3}J_{H\text{-}H}$ 7.4 Hz, 2H, CH_2), 1.30 (s, 6H, CH_3), 0.70 (t, $^{3}J_{H\text{-}H}$ 7.4 Hz, 3H, CH_3);

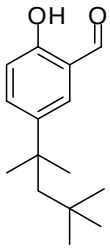
^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ 196.4 (*C*H=O), 159.1 (*C*-OH), 140.5 (aromatic quaternary *C*), 134.6, 130.2 (aromatic *C*H), 119.8 (aromatic quaternary *C*), 116.8 (aromatic *C*H), 36.8 (quaternary *C*), 36.3 (*C*H_2), 27.9, 8.7 (*C*H_3);

MS: *m/z* : 191.4 $[M\text{-}H]^-$;

IR: *v* = 2963, 2876, 1652, 1590, 1482, 1376, 1279, 1222, 1183, 1166, 834, 774, 722 cm^{-1};

Anal. Calc'd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.37; H, 8.38.

5-(1,1,3,3-tetramethylbutyl)-2-hydroxybenzaldehyde



This compound has been prepared previously by a different method.[2] We prepared it using the general procedure above starting with *p*-1,1,3,3-tetramethylbutylphenol (1 eq., 9.7 mmol, 2.0 g) and obtained the compound as a pale yellow oily solid (1.77 g, 7.6 mmol, 78% yield).

See *Figures S3* and *S4* for NMR spectra.

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ 10.88 (s, 1H, O*H*), 9.90 (s, 1H, C*H*=O), 7.58 (dd, $^{4}J_{H\text{-}H}$ 2.7, $^{3}J_{H\text{-}H}$ 8.7 Hz, 1H, aromatic C*H*), 7.50 (d, $^{4}J_{H\text{-}H}$ 2.7 Hz, 1H, aromatic C*H*), 6.93 (d, $^{3}J_{H\text{-}H}$ 8.7 Hz, 1H, aromatic C*H*), 1.74 (s, 2H, CH_2), 1.39 (s, 6H, CH_3), 0.74 (s, 9H, CH_3);

^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ 196.5 (*C*H=O), 159.2 (*C*-OH), 141.4 (aromatic quaternary *C*), 135.1, 130.2 (aromatic *C*H), 119.8 (aromatic quaternary *C*), 116.7 (aromatic *C*H), 56.4 (*C*H_2), 37.7, 32.1 (quaternary *C*), 31.6, 31.2 (*C*H_3);

MS: *m/z* : 233.5 $[M\text{-}H]^-$;

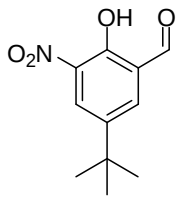
IR: ν = 2953, 2895, 1650, 1620, 1586, 1484, 1386, 1376, 1284, 1230, 1188, 841, 831, 730 cm^{-1};

Anal. Calc'd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.86; H, 9.18.

General procedure for the synthesis of the 5-alkyl-3-nitro-2-hydroxybenzaldehydes

Nitric acid (fuming or 70%) was added slowly to a solution of the alkylsalicylaldehyde in glacial AcOH. After stirring at RT for 1-2 h, water was added to the reaction and the precipitate was collected by filtration to give the compound. When no solid appeared, the crude reaction mixture was extracted with CH_2Cl_2, washed with diluted K_2CO_3, dried over $MgSO_4$, and concentrated under reduced pressure.

5-*tert*-butyl-2-hydroxy-3-nitrobenzaldehyde (2a)



This compound is known,[3] but we synthesized it following the general procedure. Full experimental details are provided for this example to indicate the quantities of reagents used.

See *Figures S5* and *S6* for NMR spectra.

Fuming HNO_3 (750 μL) was added slowly to a solution of *tert*-butylsalicylaldehyde (1 eq., 16.9 mmol, 3.0 g) in AcOH (30 mL). After stirring for 2 h at RT, water (ca. 30 mL) was added and the precipitate was collected by filtration. Recrystallization from EtOH/H_2O gave the compound as a bright yellow solid (2.29 g, 10.3 mmol, 61%).

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 11.22 (s, 1H, O*H*), 10.38 (s, 1H, C*H*=O), 8.32 (d, $^4J_{H\text{-}H}$ 2.1 Hz, 1H, aromatic C*H*), 8.13 (d, $^4J_{H\text{-}H}$ 2,1 Hz, 1H, aromatic C*H*), 1.35 (s, 9H, CH_3);

^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ 189.4 (*C*H=O), 154.4 (*C*-OH), 143.4, 134.7 (aromatic quaternary *C*), 134.2, 127.9 (aromatic *C*H), 124.9 (aromatic quaternary *C*), 34.5 (quaternary *C*), 30.9 (*C*H_3);

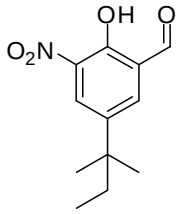
MS: *m/z* : 222.4 $[M\text{-}H]^-$;

IR: ν = 3251, 2958, 2886, 1674, 1616, 1530, 1407, 1253, 1145, 1111, 948, 726, 696 cm^{-1};

Anal. Calc'd for $C_{11}H_{13}NO_4$: C, 59.19; H, 5.87; N, 6.27. Found: C, 59.08; H, 5.84; N, 6.22.

m.p. 88-90 ºC.

2-hydroxy-3-nitro-5-*tert*-pentylbenzaldehyde (2b)



This compound was prepared following the general procedure described above using 2 mL of 70% nitric acid and *p*-iso-amylsalicylaldehyde (1 eq., 5.2 mmol, 1.0 g). The product was purified by flash column chromatography on silica gel (eluent: CH_2Cl_2) to give the compound as a yellow oil (1.07 g, 4.5 mmol, 87%).

See *Figures S7* and *S8* for NMR spectra.

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ 11.25 (s, 1H, O*H*), 10.43 (s, 1H, C*H*=O), 8.29 (d, $^4J_{H\text{-}H}$ 2.4 Hz, 1H, aromatic C*H*), 8.09 (d, $^4J_{H\text{-}H}$ 2.4 Hz, 1H, aromatic C*H*), 1.68 (q, $^3J_{H\text{-}H}$ 7.5 Hz, 2H, CH_2), 1.33 (s, 6H, CH_3), 0.71 (t, $^3J_{H\text{-}H}$ 7.5 Hz, 3H, CH_3);

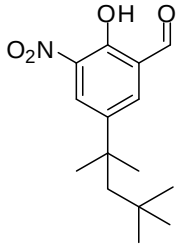
^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ 189.6 (*C*H=O), 153.9 (*C*-OH), 141.5, 134.6 (aromatic quaternary *C*), 134.6, 128.2 (aromatic *C*H), 124.4 (aromatic quaternary *C*), 37.4 (quaternary *C*), 36.0 (*C*H_2), 27.5, 8.5 (*C*H_3);

MS: *m/z* : 260.3 $[M+Na]^+$;

IR: *v* = 2965, 2876, 1693, 1665, 1621, 1590, 1530, 1463, 1344, 1261, 1158, 1107, 963, 926, 767, 724 cm^{-1};

Anal. Calc'd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.47; H, 6.18; N, 5.93.

5-(1,1,3,3-tetramethylbutyl)-3-nitro-2-hydroxybenzaldehyde (2c)



HNO_3 70% (1 mL) in AcOH (5mL) was added slowly to a solution of *p*-1,1,3,3-tetramethylbutylsalicylaldehyde (1 eq., 4.3 mmol, 1.0 g) in AcOH (5 mL). After stirring at RT for 2 h, water was added and the aqueous phase was extracted with CH_2Cl_2 (3×20mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. After flash column chromatography on silica gel (eluent: CH_2Cl_2), the compound was obtained as a yellow oil (1.03 g, 3.7 mmol, 86%).

See *Figures S9* and *S10* for NMR spectra.

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ 11.24 (s, 1H, O*H*), 10.44 (s, 1H, C*H*=O), 8.34 (d, $^4J_{H\text{-}H}$ 2.7 Hz, 1H, aromatic C*H*), 8.14 (d, $^4J_{H\text{-}H}$ 2.7 Hz, 1H, aromatic C*H*), 1.78 (s, 2H, CH_2), 1.41 (s, 6H, CH_3), 0.75 (s, 9H, CH_3);

^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ 189.7 (*C*H=O), 153.5 (*C*-OH), 143.0 (aromatic quaternary *C*), 135.0 (aromatic *C*H), 134.9 (aromatic quaternary *C*), 128.6 (aromatic *C*H), 124.9 (aromatic quaternary *C*), 56.5 (*C*H_2), 38.5, 32.5 (quaternary *C*), 32.0, 31.3 (*C*H_3);

MS: *m/z* : 278.5 $[M-H]^-$;

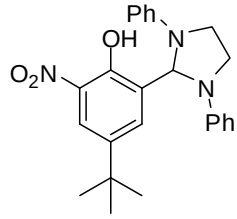
IR: ν = 2955, 2871, 1693, 1665, 1620, 1532, 1466, 1366, 1343, 1302, 1257, 1222, 925 cm^{-1};

TOF HRMS ESI Calc'd for $C_{15}H_{20}NO_4$: 278.1392. Found: 278.1398 (+2.0 ppm).

General procedure for the synthesis of the 4-alkyl-2-(1,3-diphenylimidazolidin-2-yl)-6-nitrophenol

A solution of the alkylnitrosalicylaldehyde (1 eq.) and N,N-diphenylethylenediamine (1 eq.) in EtOH was refluxed for 2-48 h. The solution was then concentrated, the solid was isolated by filtration and washed with EtOH. When no solid appeared, the reaction mixture was evaporated to dryness and the product was obtained as an oil.

4-*tert*-butyl-2-(1,3-diphenylimidazolidin-2-yl)-6-nitrophenol (3a)



5-*tert*-Butyl-3-nitrosalicylaldehyde **2a** (1 eq., 0.448 mmol, 100 mg) and N,N-diphenylethylenediamine (1 eq., 0.448 mmol, 95 mg) were dissolved in EtOH (20 mL). After refluxing for 48 h, the solution was concentrated to 5 mL, the solid was isolated by filtration and washed with EtOH. Compound **3a** was obtained as an orange powder in 81% yield (151 mg, 0.363 mmol).

See *Figures S11* and *S12* for NMR spectra.

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ 11.27 (s, 1H, O*H*), 7.96 (d, $^4J_{H\text{-}H}$ 2.1 Hz, 1H, aromatic C*H*), 7.71 (d, $^4J_{H\text{-}H}$ 2.1 Hz, 1H, aromatic C*H*), 7.21 (t, $^3J_{H\text{-}H}$ 5.6 Hz, 4H, aromatic C*H*), 6.80-6.74 (m, 6H, aromatic C*H*), 6.48 (s, 1H, C*H*), 4.04 (dd, $^2J_{H\text{-}H}$ 6.8, $^3J_{H\text{-}H}$ 4.1 Hz, 2H, CH_2), 3.82 (dd, $^2J_{H\text{-}H}$ 6.8, $^3J_{H\text{-}H}$ 4.1 Hz, 2H, CH_2), 1.23 (s, 9H, CH_3);

^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ 151.0 (*C*-OH), 145.5, 143.4 (aromatic quaternary *C*), 135.2 (aromatic *C*H), 133.5, 132.3 (aromatic quaternary *C*), 129.4, 121.7, 118.2, 113.5 (aromatic *C*H), 71.5 (*C*H), 47.0 (*C*H_2), 34.4 (quaternary *C*), 31.2 (*C*H_3);

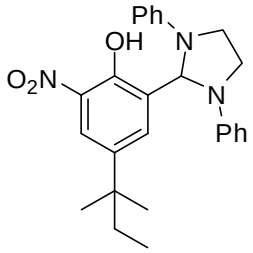
MS: *m/z* : 440.3 $[M+Na]^+$, 416.3 $[M-H]^-$;

IR: ν = 2957, 2837, 1622, 1595, 1537, 1503, 1475, 1363, 1329, 1262, 1200, 1161, 1109, 999, 922, 870, 745, 691 cm^{-1};

Anal. Calc'd for $C_{25}H_{27}N_3O_3$: C, 71.92; H, 6.52; N, 10.06. Found: C, 71.66; H, 6.45; N, 10.08.

m.p. 135-137 ºC.

2-(1,3-diphenylimidazolidin-2-yl)-6-nitro-4-*tert*-pentylphenol (3b)



5-*tert*-Pentyl-3-nitrosalicylaldehyde **2b** (1 eq., 1.58 mmol, 375 mg) and N,N-diphenylethylenediamine (1 eq., 1.58 mmol, 336 mg) were dissolved in EtOH (20 mL). After refluxing for 1h, the solution was concentrated to dryness under reduced pressure. Compound **3b** was obtained as a red oil which slowly solidified in quantitative yield (680 mg, 1.58 mmol).

See *Figures S13* and *S14* for NMR spectra.

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ 11.27 (s, 1H, O*H*), 7.91 (d, $^{4}J_{H\text{-}H}$ 2.4 Hz, 1H, aromatic C*H*), 7.66 (d, $^{4}J_{H\text{-}H}$ 2.4 Hz, 1H, aromatic C*H*), 7.22 (dd, $^{3}J_{H\text{-}H}$ 7.2, $^{3}J_{H\text{-}H}$ 8.4 Hz, 4H, aromatic C*H*), 6.80-6.73 (m, 6H, aromatic C*H*), 6.49 (s, 1H, C*H*), 4.05 (dd, $^{2}J_{H\text{-}H}$ 8.7, $^{3}J_{H\text{-}H}$ 5.1 Hz, 2H, N-CH_2), 3.82 (dd, $^{2}J_{H\text{-}H}$ 8.7, $^{3}J_{H\text{-}H}$ 5.1 Hz, 2H, N-CH_2), 1.55 (q, $^{3}J_{H\text{-}H}$ 7.5 Hz, 2H, CH_2), 0.53 (t, $^{3}J_{H\text{-}H}$ 7.5 Hz, 3H, CH_3);

^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC): δ 150.7 (*C*-OH), 145.0, 141.1 (aromatic quaternary *C*), 135.7 (aromatic *C*H), 133.2, 131.4 (aromatic quaternary *C*), 128.9, 121.9, 117.7, 113.1 (aromatic *C*H), 71.7 (*C*H), 46.5 (N-*C*H_2), 37.2 (*C*H_2), 36.4 (quaternary *C*), 27.8 (*C*H_3), 8.6 (*C*H_3);

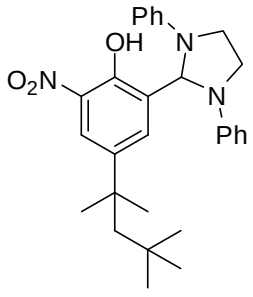
MS: *m/z* : 432.2 $[M+H]^+$, 430.3 $[M-H]^-$;

IR: ν = 2963.1, 2874.1, 1623.6, 1595.3, 1535.8, 1500.4, 1471.3, 1418.6, 1363.3, 1309.9, 1263.5, 1188.8, 1156.9, 1108.6, 1033.6, 1000.2, 907.2, 874.3, 745.7, 689.0 cm^{-1};

TOF HRMS ESI Calc'd for $C_{26}H_{30}N_3O_3$: 432.2287. Found: 432.2291 (+0.9 ppm).

m.p. 77-79 ºC.

2-(1,3-diphenylimidazolidin-2-yl)-6-nitro-4-(2,4,4-trimethylpentan-2-yl)phenol (3c)



5-(1,1,3,3-tetramethylbutyl)-3-nitro-2-hydroxybenzaldehyde **2c** (1 eq., 3.58 mmol, 1.0 g) and N,N-diphenylethylenediamine (1 eq., 3.58 mmol, 760 mg) were dissolved in EtOH (20 mL). After refluxing for 12h, the solution was concentrated to 5 mL, the oily solid was isolated by filtration and washed with MeOH. Compound **3c** was obtained as a red solid in 62% yield (1.05 g, 2.23 mmol).

See *Figures S15* and *S16* for NMR spectra.

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ 11.28 (s, 1H, O*H*), 7.93 (d, $^{4}J_{H\text{-}H}$ 2.0 Hz, 1H, aromatic C*H*), 7.69 (d, $^{4}J_{H\text{-}H}$ 2.0 Hz, 1H, aromatic C*H*), 7.19 (dd, $^{3}J_{H\text{-}H}$ 5.4, $^{3}J_{H\text{-}H}$ 6.3 Hz, 4H, aromatic C*H*), 6.79-6.72 (m, 6H, aromatic C*H*), 6.49 (s, 1H, C*H*), 4.06 (dd, $^{2}J_{H\text{-}H}$ 6.6, $^{3}J_{H\text{-}H}$ 4.2 Hz, 2H, N-CH_2), 3.84 (dd, $^{2}J_{H\text{-}H}$ 6.6, $^{3}J_{H\text{-}H}$ 4.2 Hz, 2H, N-CH_2), 1.61 (s, 2H, CH_2), 1.28 (s, 6H, CH_3), 0.48 (s, 9H, CH_3);

^{13}C NMR (75 MHz, $CDCl_3$, 25ºC): δ 150.6 (*C*-OH), 144.7, 141.6 (aromatic quaternary *C*), 135.8 (aromatic *C*H), 132.8, 131.3 (aromatic quaternary *C*), 128.8, 121.6, 117.4, 112.9 (aromatic *C*H), 71.0 (*C*H), 56.1 (N-*C*H_2), 46.3 (*C*H_2), 37.5 (quaternary *C*), 31.7 (quaternary *C*), 31.3 (*C*H_3), 30.7 (*C*H_3);

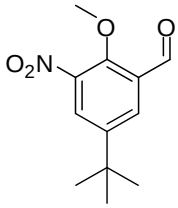
MS: *m/z* : 496.3 $[M+Na]^+$, 472.3 $[M-H]^-$;

IR: *v* = 2953, 1624, 1596, 1534, 1501, 1471, 1420, 1364, 1320, 1249, 1176, 1105, 1034, 1000, 922, 874, 825, 745, 689 cm^{-1};

TOF HRMS ESI Calc'd for $C_{29}H_{36}N_3O_3$: 474.2757. Found: 474.2749 (-1.6 ppm).

m.p. 55-57ºC.

5-*tert*-butyl-2-methoxy-3-nitrobenzaldehyde (4)



Dimethylsulfate (1 eq., 0.897 mmol, 85 μL) was added to 5-*tert*-butyl-3-nitrosalicylaldehyde **2a** (1 eq., 0.897 mmol, 200 mg) and K_2CO_3 (2 eq., 1.79 mmol, 247 mg) in dry toluene (10 mL). After heating to reflux for 4 h, the toluene was removed by rotary evaporation, water was added, and the aqueous phase was extracted with CH_2Cl_2 (3×20 mL). The combined organic fractions were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give the product as a yellow solid (155 mg, 0.655 mmol, 73%).

See *Figures S17* and *S18* for NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$, 25 ºC): δ 10.41 (s, 1H, C*H*=O), 8.11 (d, $^4J_{H-H}$ 2.1 Hz, 1H, aromatic C*H*), 8.09 (d, $^4J_{H-H}$ 2,1 Hz, 1H, aromatic C*H*), 4.07 (s, 3H, OCH_3), 1.37 (s, 9H, CH_3);

^{13}C NMR (100 MHz, $CDCl_3$, 25 ºC): δ 187.8 (*C*H=O), 153.9 (*C*-OCH_3), 148.2, 143.6, 130.5 (aromatic quaternary *C*), 130.0, 127.8 (aromatic *C*H), 65.1 (O*C*H_3), 34.8 (quaternary *C*), 30.8 (*C*H_3);

MS: *m/z* : 260.4 $[M+Na]^+$;

IR: *v* = 2966, 2894, 1693, 1612, 1529, 1482, 1346, 1275, 1235, 1176, 1107, 982, 945, 906, 718 cm^{-1};

Anal. Calc'd for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.80; H, 6.35; N, 5.86.

m.p. 64-65 ºC.

General procedure for the synthesis of campestarenes

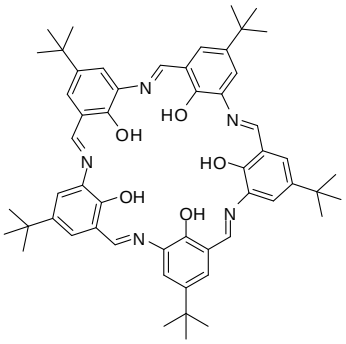
Procedure A:

Sodium dithionite ($Na_2S_2O_4$, 6 eq.) was added to a solution of the nitrosalicylaldehyde **2** (1 eq.) in EtOH and water, and heated to reflux for 2-4 hours under air. After cooling the mixture to RT, the solid was collected by filtration, washed with water and EtOH and dried under vaccum. If the macrocycle did not precipitate, addition of water and concentration of the solution gave a precipitate that could be isolated. Flash column chromatography using neutral alumina (eluent: CH_2Cl_2/MeOH, 10/1) gave the macrocycle as a dark purple powder.

Procedure B:

The macrocycles can be prepared by a different approach that avoids Na^+ in the preparation.
A solution of protected nitrosalicylaldehyde **3** (1 eq.) and Pd/C 10% (10% in mass, cat.) in dry THF was stirred for 12 h under an H_2 atmosphere, then filtered through a short Celite® pad and concentrated under reduced pressure. The crude product was then dissolved in EtOH and heated at reflux for 2-4 h, then concentrated under reduced pressure. Flash column chromatography using neutral alumina (eluent: CH_2Cl_2/MeOH, 10/1) gave the macrocycle as a dark purple powder.

4-*tert*-Butyl-Campestarene (1a)



The macrocycle was obtained with the general procedure A, using nitrosalicylaldehyde **2a** (1 eq., 4.48 mmol, 1.0 g). The product was isolated as a purple powder in nearly quantitative yield (910 mg).

See *Figure S19* for NMR spectrum, and *Figures S23-S25* for MALDI-TOF spectra.

^{1}H NMR (300 MHz, DMSO-d_6, 25 ºC): δ 17.10 (d, $^3J_{H\text{-}H}$ 6.0 Hz, 5H, O*H* monomer), 17.04 (d, $^3J_{H\text{-}H}$ 11.4 Hz, 10H, O*H* dimer), 9.45 (d, $^3J_{H\text{-}H}$ 6.0 Hz, 5H, C*H*=N monomer), 8.42 (d, $^3J_{H\text{-}H}$ 11.4 Hz, 10H, C*H*=N dimer), 8.03 (d, $^4J_{H\text{-}H}$ 1.4 Hz, 5H, aromatic C*H* monomer), 7.58 (d, $^4J_{H\text{-}H}$ 1.4 Hz, 10H, aromatic C*H* dimer), 7.52 (d, $^5J_{H\text{-}H}$ 1,4 Hz, 5H, aromatic C*H* monomer), 7.02 (d, $^5J_{H\text{-}H}$ 1,4 Hz, 10H, aromatic C*H* dimer), 1.49 (s, 90H, CH_3 dimer), 1.39 (s, 45H, CH_3 monomer);

The compound is not soluble enough to obtain a ^{13}C NMR spectrum, even after 10,000 scans.

MALDI-TOF-MS: *m/z*: 898.6 $[M+Na]^+$, 1773.8 $[M_2+Na]^+$, 2673.0 $[M_3\text{-}H+2Na]^+$;

TOF HRMS ESI calc'd for $C_{55}H_{66}N_5O_5$: 876.5064. Found: 876.5078 (+1.6 ppm);

IR: ν = 3390, 2953, 2866, 1615, 1521, 1479, 1390, 1364, 1222, 1153, 1013, 940, 860, 784 cm^{-1};

UV-vis (DMSO) λ_{max} (ε) = 296 (90 x 10^3), 406 (68 x 10^3), 523 (50 x 10^3), 556 (48 x 10^3) nm (L mol^{-1} cm^{-1}).

Anal. Calc'd for $C_{55}H_{65}N_5O_5 \cdot 2H_2O$: C, 72.42; H, 7.62; N, 7.68. Found: C, 72.85; H, 7.51; N, 7.83.

m.p. >300ºC.

The same macrocycle was prepared from compound **3a** using the general procedure B. A solution of protected nitrosalicylaldehyde **3a** (1 eq., 1.20 mmol, 500 mg) and Pd/C 10% (cat., 10 mg) in dry THF (20 mL) was stirred for 12 h under an H_2 atmosphere, then filtered through a short Celite® pad and concentrated under reduced pressure. The crude product was then dissolved in EtOH (20 mL) and heated at reflux for 2 h, then concentrated under reduced pressure. Flash column chromatography using neutral alumina (eluent: CH_2Cl_2/MeOH, 10/1) gave the macrocycle **1a** as a dark red powder (195 mg, 0.22 mmol, 93%).

When the reaction was performed in the presence of LiCl (5 eq. per eq. of **3a**), the mass spectrum showed only the 5-fold symmetric macrocycle – no evidence for other size rings.

See *Figures S31-S32* MALDI-TOF spectra.

MALDI-TOF-MS: *m/z*: 876.7 $[M+H]^+$, 882.7 $[M+Li]^+$, 914.7 $[M+K]^+$.

When the reaction was performed in the presence of NaCl (5 eq. per eq. of **3a**), the mass spectrum showed only the 5-fold symmetric macrocycle.

See *Figures S33-S34* MALDI-TOF spectra.

MALDI-TOF-MS: *m/z*: 898.7 $[M+Na]^+$, 914.7 $[M+K]^+$.

When the reaction was performed in the presence of KBr (5 eq. per eq. of **3a**), the mass spectrum showed only the 5-fold symmetric macrocycle.

See *Figures S35-S36* MALDI-TOF spectra.

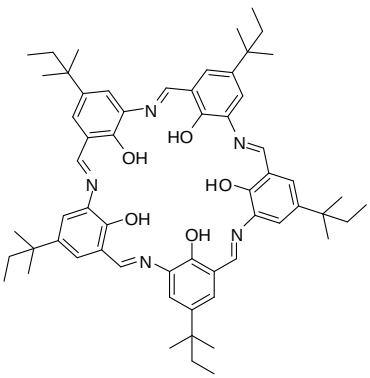
MALDI-TOF-MS: *m/z*: 914.6 $[M+K]^+$.

When the reaction was performed in the presence of CsCl (5 eq. per eq. of **3a**), the mass spectrum showed only the 5-fold symmetric macrocycle.

See *Figures S37-S38* MALDI-TOF spectra.

MALDI-TOF-MS: *m/z*: 1008.6 $[M+Cs]^+$.

4-(1,1-dimethylpropyl)-Campestarene (1b)



The macrocycle was obtained with the general procedure A, using nitrosalicylaldehyde **2b** (1 eq., 2.11 mmol, 500 mg). The product was isolated as a dark purple powder (350 mg, 0.37 mmol, 88%).

The macrocycle was obtained with the general procedure B, using the protected aldehyde **3b** (1 eq., 0.695mmol, 300 mg). The product was isolated as a dark purple powder (130 mg, 0.138 mmol, 99%).

See *Figure S20* for NMR spectrum, and *Figures S26-S28* for MALDI-TOF spectra.

^{1}H NMR (300 MHz, DMSO-d_6, 25 ºC): δ 17.10 (d, $^3J_{H-H}$ 4.8 Hz, 5H, O*H* monomer), 17.04 (d, $^3J_{H-H}$ 9.2 Hz, 10H, O*H* dimer), 9.43 (d, $^3J_{H-H}$ 4.8 Hz, 5H, C*H*=N monomer), 8.42 (d, $^3J_{H-H}$ 9.2 Hz, 10H, C*H*=N dimer), 7.95 (s, 5H, aromatic C*H* monomer), 7.49 (s, 10H, aromatic C*H* dimer), 7.45 (s, 5H, aromatic C*H* monomer), 6.96 (s, 10H, aromatic C*H* dimer), 1.73 (m, 30H, CH_2 monomer and dimer), 1.37 (s, 60H, CH_3 dimer), 1.35 (s, 30H, CH_3 monomer), 0.81 (t, $^3J_{H-H}$ 7.2 Hz, 30H, CH_3 dimer), 0.73 (t, $^3J_{H-H}$ 7.2 Hz, 15H, CH_3 monomer);

The compound is not soluble enough to obtain a ^{13}C NMR spectrum even after 10,000 scans.

MALDI-TOF-MS: *m/z*: 968.8 $[M+Na]^+$, 1915.1 $[M_2+Na]^+$, 2884.8 $[M_3-H+2Na]^+$;

TOF HRMS ESI calc'd for $C_{60}H_{76}N_5O_5$: 946.5846. Found: 946.5832 (-1.5 ppm);

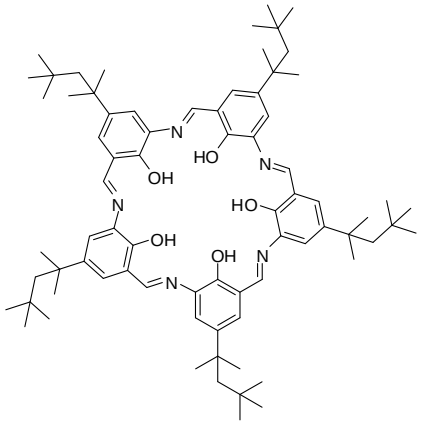
UV-vis (DMSO) λ_{max} (ε) = 314 (41 x 10^3), 408 (33 x 10^3), 525 (22 x 10^3), 558 (24 x 10^3) nm (L mol^{-1} cm^{-1}).

IR: ν = 3400, 2961, 2874, 1614, 1520, 1463, 1236, 1163, 1022, 946, 858, 783, 628 cm^{-1};

Anal. Calc'd for $C_{60}H_{75}N_5O_5 \cdot 2H_2O$: C, 73.36; H, 8.11; N, 7.13. Found: C, 73.71; H, 8.07; N, 7.16.

m.p. >300ºC.

4-(1,1,3,3-tetramethylbutyl)-Campestarene (1c)



The macrocycle was obtained with the general procedure A, using nitrosalicylaldehyde **2c** (1 eq., 2.01 mmol, 560 mg). The product was isolated as a dark purple powder (326 mg, 0.28 mmol, 70%).

The macrocycle was obtained with the general procedure B, using the protected aldehyde **3c** (1 eq., 1.27 mmol, 600 mg). The product was isolated as a dark purple powder (290 mg, 0.251 mmol, 99%).

See *Figures S21-S22* for NMR spectra, and *Figures S29-S30* for MALDI-TOF spectra.

^{1}H NMR (400 MHz, DMSO-d_6, 25 ºC): δ 17.08 (d, $^3J_{H-H}$ 5.5 Hz, 5H, O*H* monomer), 16.97 (d, $^3J_{H-H}$ 11.2 Hz, 10H, O*H* dimer), 9.44 (d, $^3J_{H-H}$ 5.5 Hz, 5H, C*H*=N monomer), 8.42 (d, $^3J_{H-H}$ 11.2 Hz, 10H, C*H*=N dimer), 8.02 (s, 5H, aromatic C*H* monomer), 7.55 (s, 10H, aromatic C*H* dimer), 7.49 (s, 5H,

aromatic C*H* monomer), 7.01 (s, 10H, aromatic C*H* dimer), 1.82 (s, 10H, CH_2 monomer), 1.63 (s, 20H, CH_2 dimer), 1.60 (s, 60H, CH_3 dimer), 1.45 (s, 30H, CH_3 monomer), 0.80 (s, 45H, CH_3 monomer), 0.77 (s, 90H, CH_3 dimer);

^{13}C NMR (75 MHz, DMSO-d_6, 25 ºC): δ 161.2 (*C*-OH), 155.4(*C*H=N), 136.5, 130.9 (aromatic quaternary *C*), 127.9, 118.3 (aromatic *C*H), 117.6 (aromatic quaternary *C*), 56,0 (*C*H_2), 38.0, 32.2 (quaternary *C*), 31.7, 31.3 (*C*H_3);

MALDI-TOF-MS: *m/z*: 1156.8 $[M+H]^+$, 1178.9 $[M+Na]^+$, 2335.1 $[M_2+Na]^+$;

TOF HRMS ESI calc'd for $C_{75}H_{106}N_5O_5$: 1156.8194. Found: 1156.8207 (+1.1 ppm);

UV-vis (DMSO) λ_{max} (ε) = 312 (26 x 10^3), 413 (21 x 10^3), 524 (18 x 10^3), 558 (13 x 10^3) nm (L mol^{-1} cm^{-1}).

IR: *v* = 2950, 1616, 1520, 1471, 1365, 1237, 1185, 1023, 785 cm^{-1};

Anal. Calc'd for $C_{75}H_{105}N_5O_5 \cdot 3H_2O$: C, 74.40; H, 9.24; N, 5.78. Found: C, 74.36; H, 8.77; N, 5.75.

m.p. >300ºC.

NMR spectra

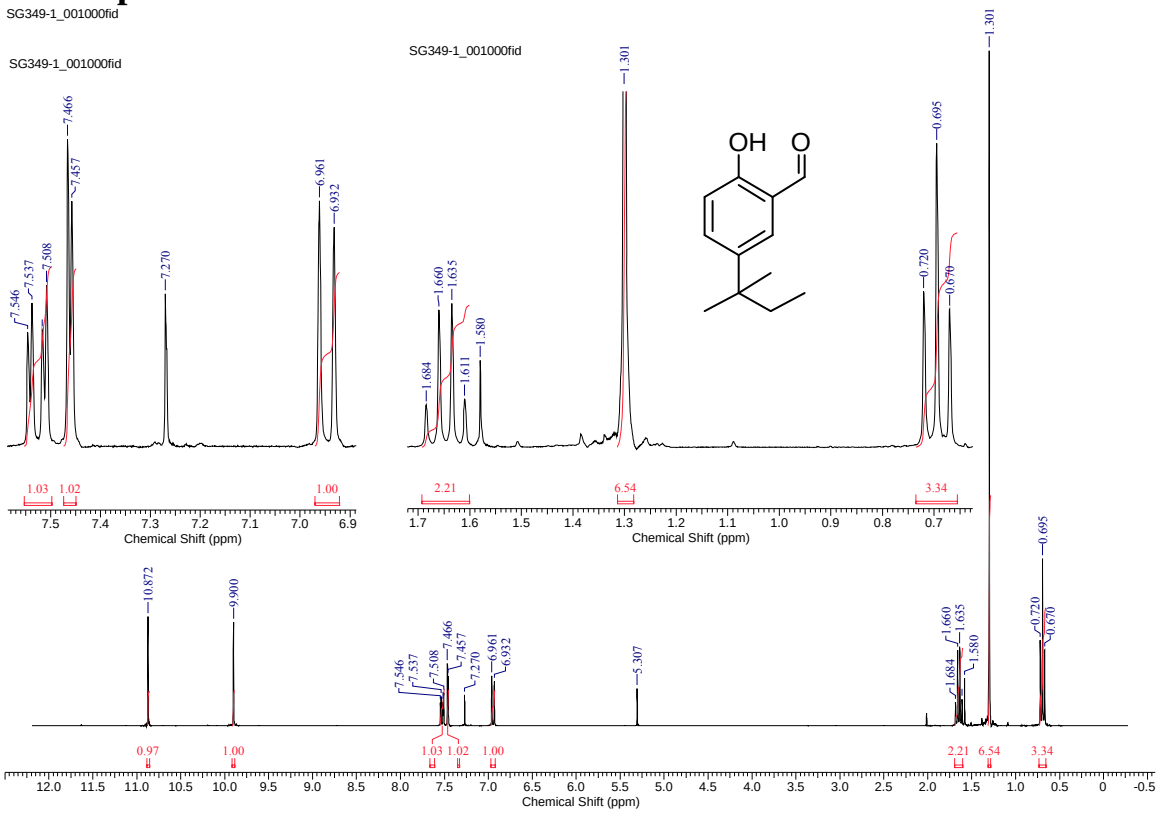


Figure S1: ^{1}H NMR spectrum of 5-(1,1-dimethylethyl) -2-hydroxybenzaldehyde in $CDCl_3$

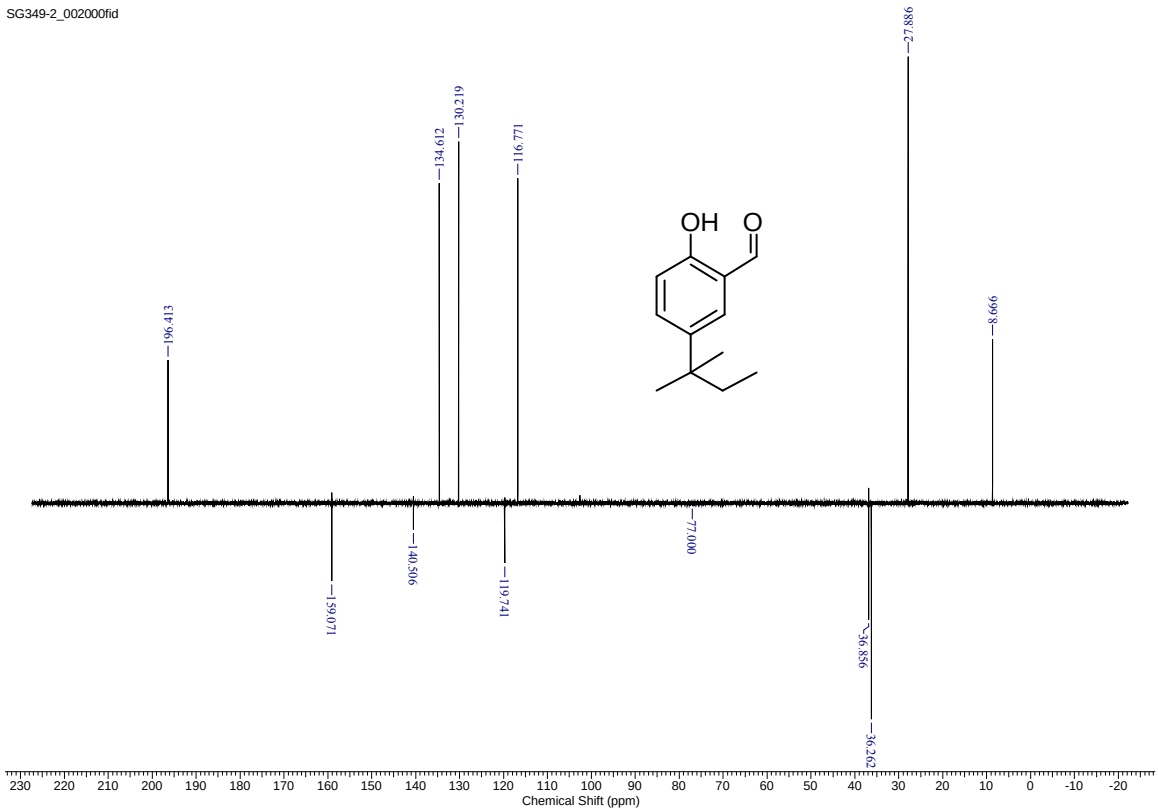


Figure S2: ^{13}C NMR spectrum of 5-(1,1-dimethylethyl) -2-hydroxybenzaldehyde in $CDCl_3$

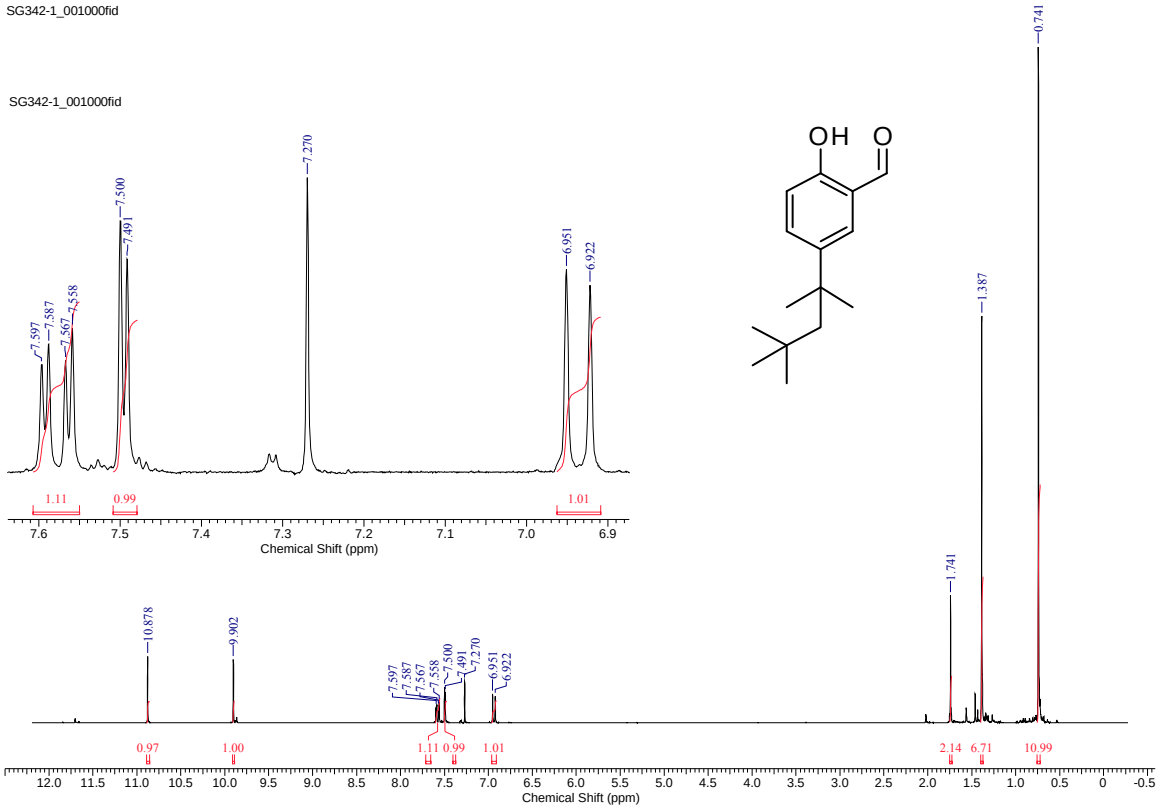


Figure S3: ^{1}H NMR spectrum of 5-(1,1,3,3-tetramethylbutyl)-2-hydroxybenzaldehyde in $CDCl_3$

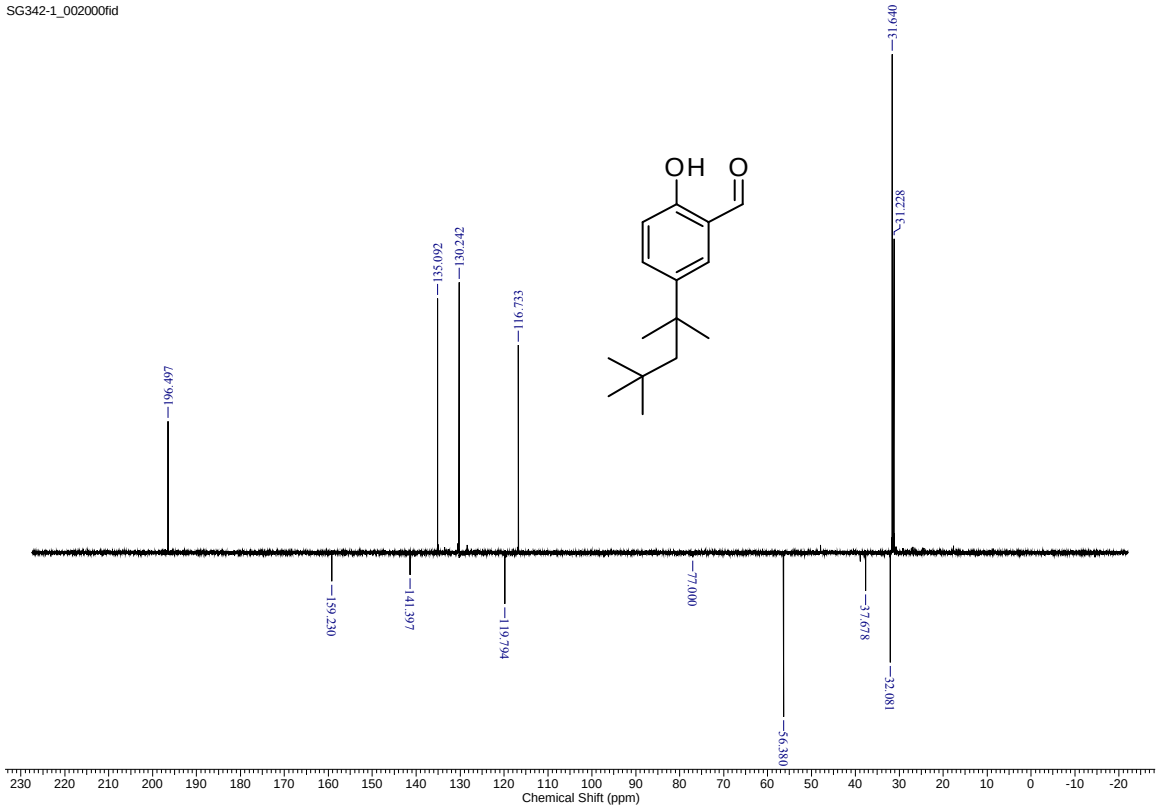


Figure S4: ^{13}C NMR spectrum of 5-(1,1,3,3-tetramethylbutyl)-2-hydroxybenzaldehyde in $CDCl_3$

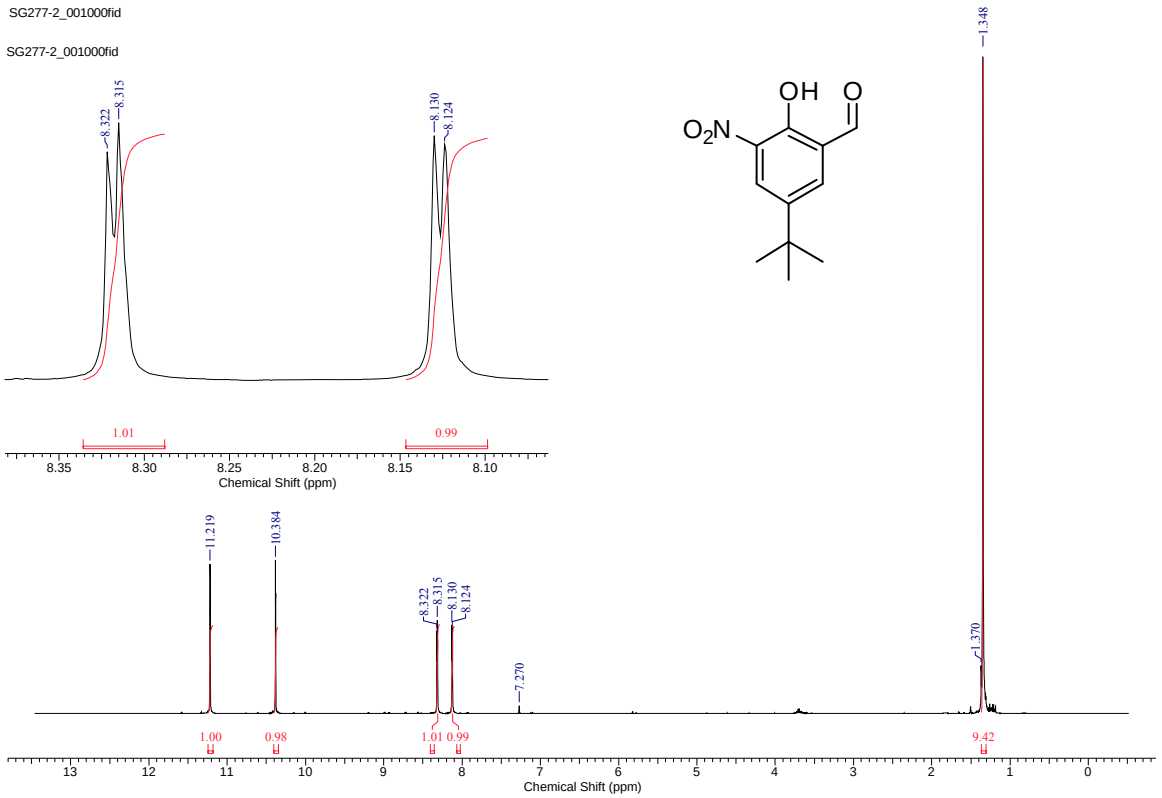


Figure S5: ^{1}H NMR spectrum of 5-*tert*-butyl-2-hydroxy-3-nitrobenzaldehyde (**2a**) in $CDCl_3$

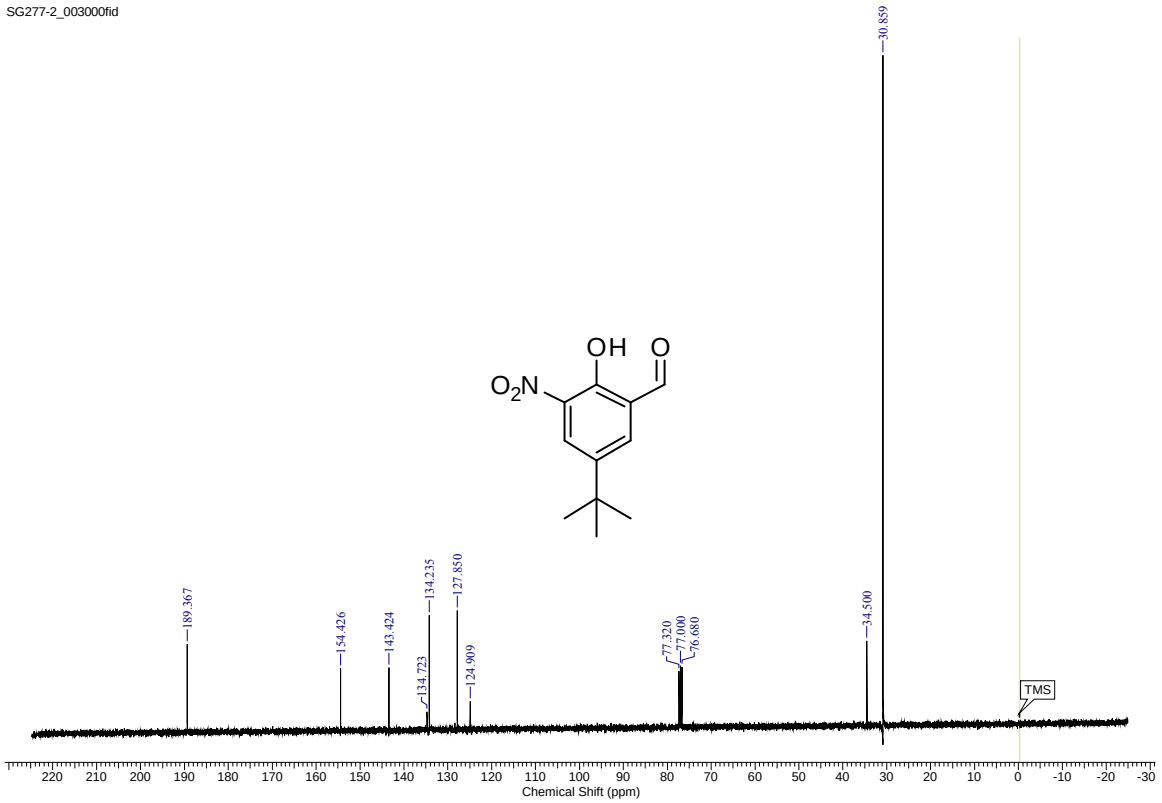


Figure S6: ^{13}C NMR spectrum of 5-*tert*-butyl-2-hydroxy-3-nitrobenzaldehyde (**2a**) in $CDCl_3$

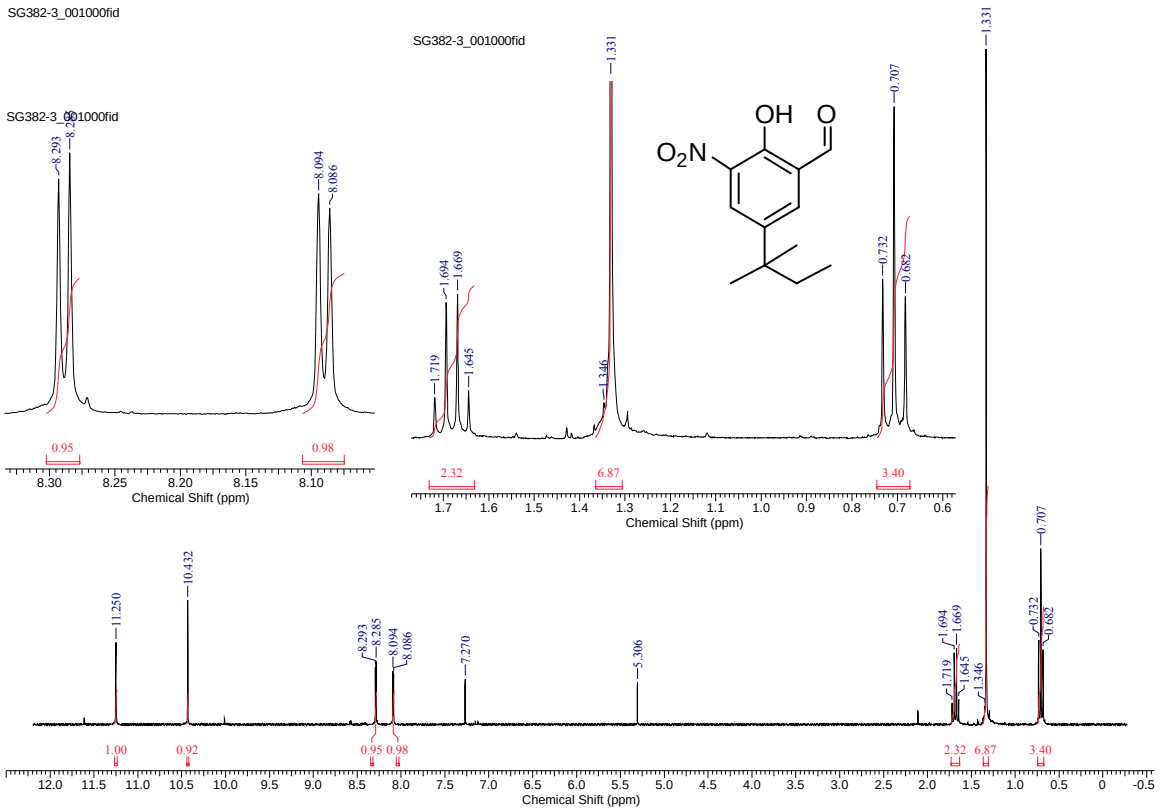


Figure S7: ^{1}H NMR spectrum of 2-hydroxy-3-nitro-5-*tert*-pentylbenzaldehyde (**2b**) in $CDCl_3$

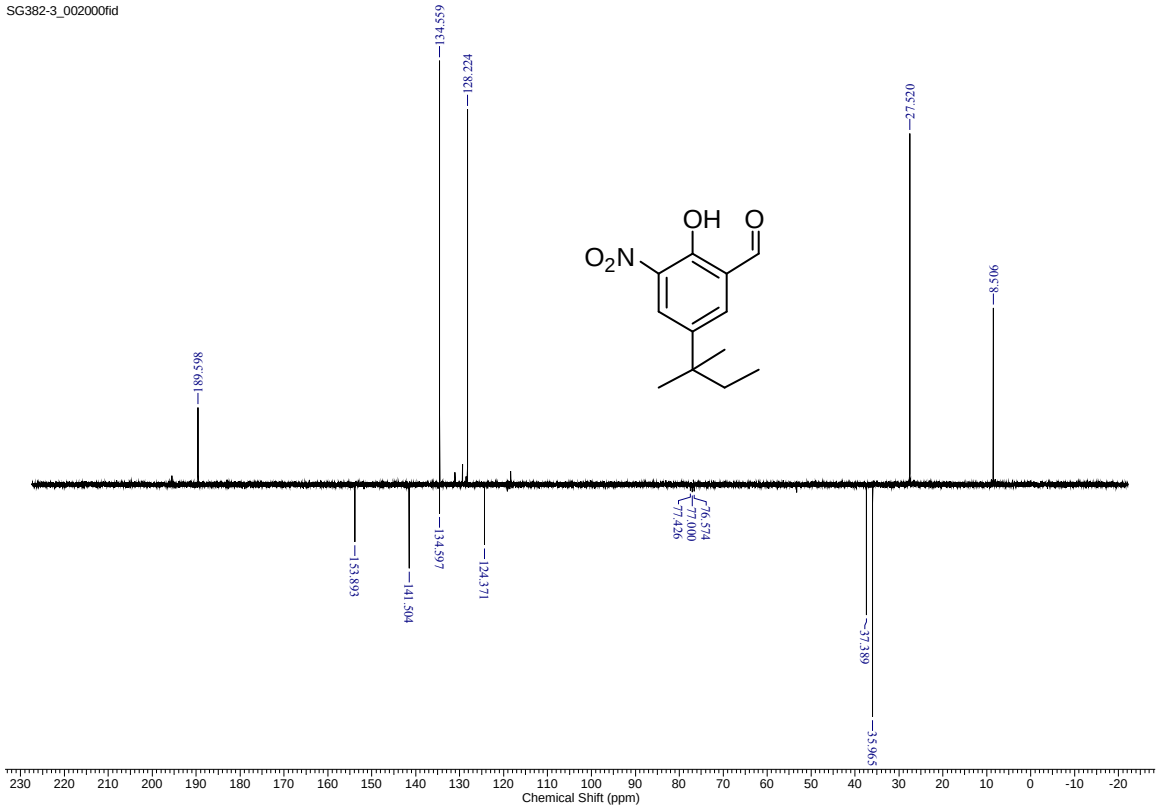


Figure S8: ^{13}C NMR spectrum of 2-hydroxy-3-nitro-5-*tert*-pentylbenzaldehyde (**2b**) in $CDCl_3$

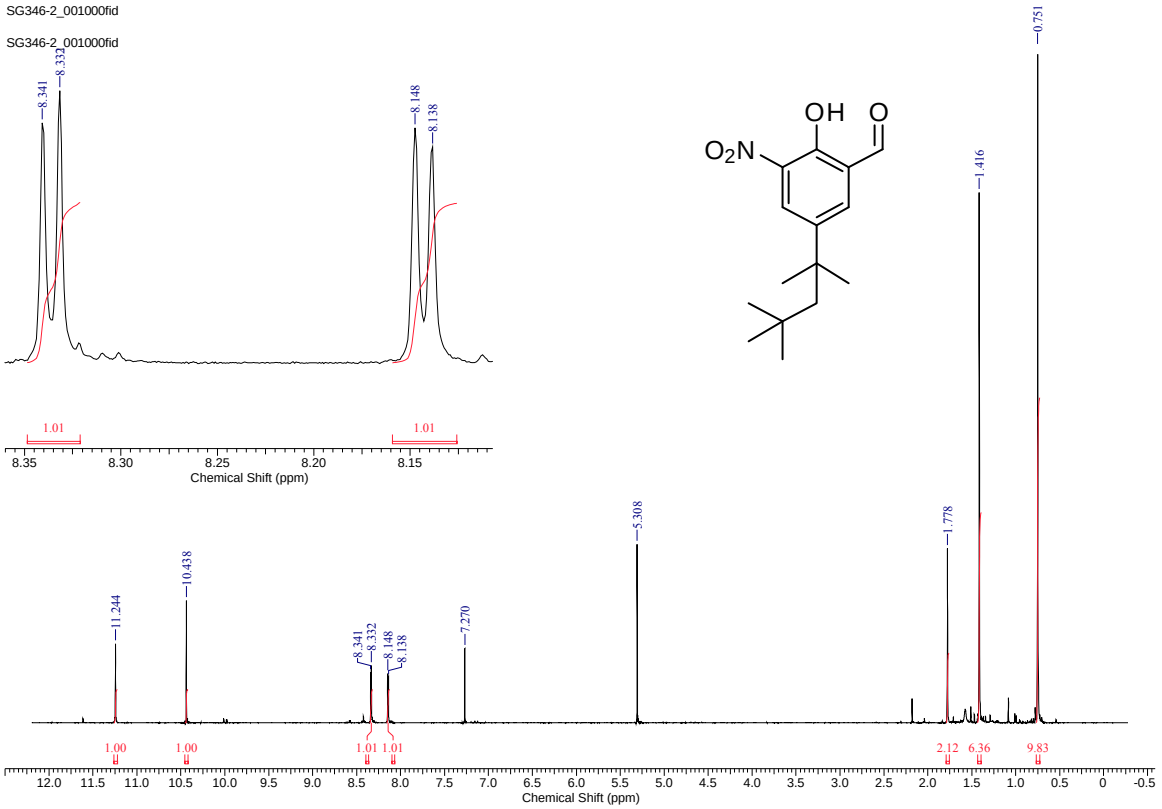


Figure S9: ^{1}H NMR spectrum of 5-(1,1,3,3-tetramethylbutyl)-3-nitro-2-hydroxybenzaldehyde (**2c**) in $CDCl_3$

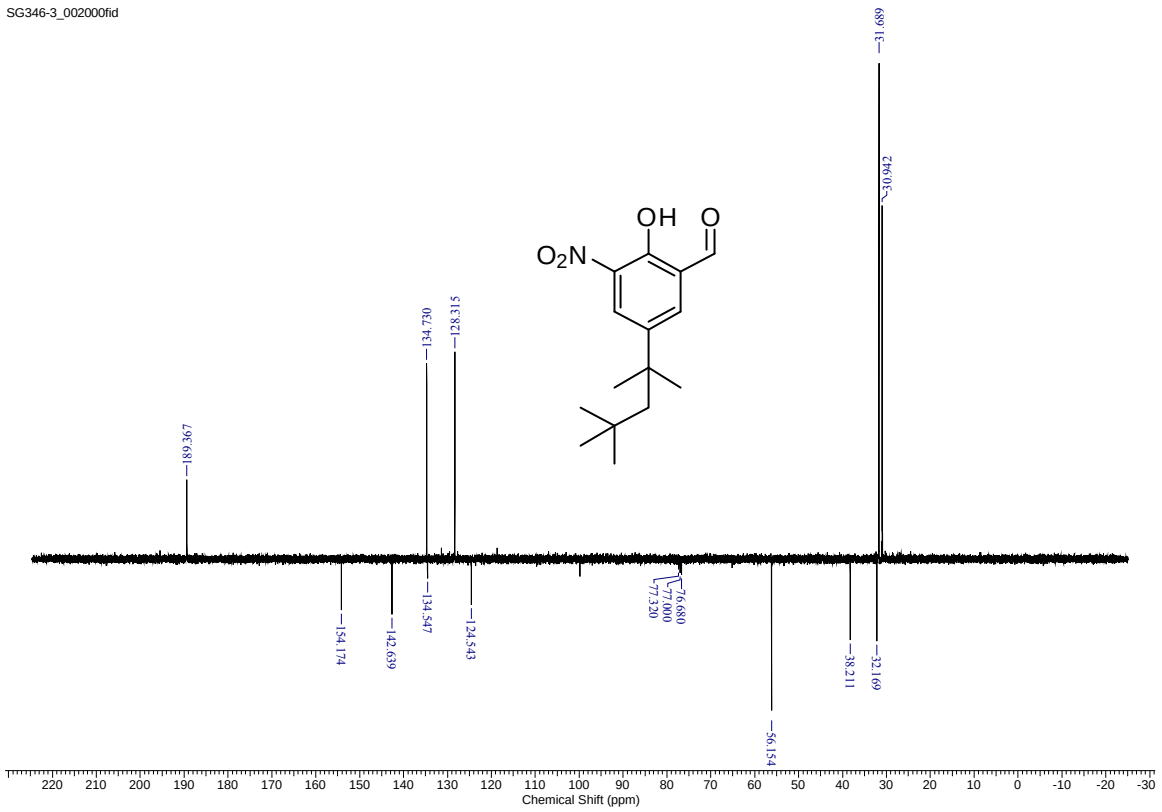


Figure S10: ^{13}C NMR spectrum of 5-(1,1,3,3-tetramethylbutyl)-3-nitro-2-hydroxybenzaldehyde (**2c**) in $CDCl_3$

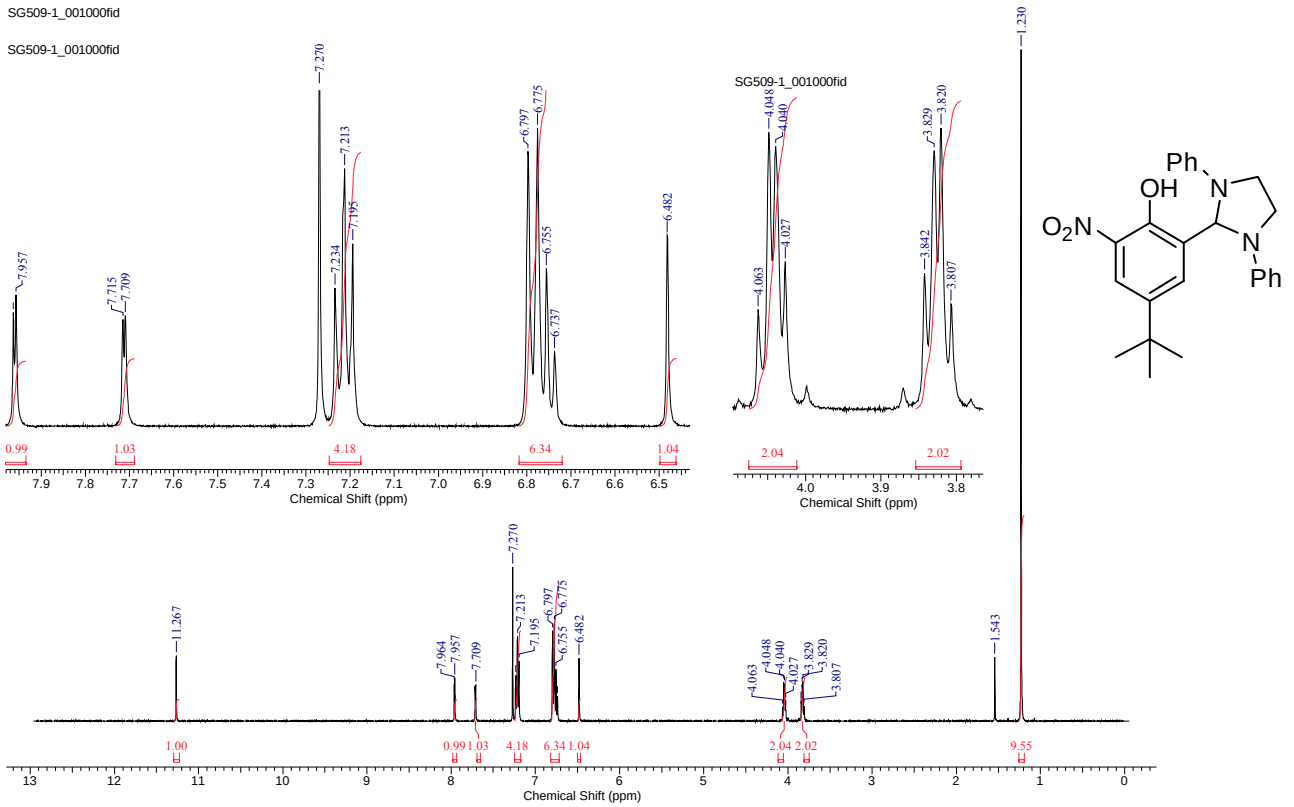


Figure S11: ^{1}H NMR spectrum of 4-*tert*-butyl-2-(1,3-diphenylimidazolidin-2-yl)-6-nitrophenol (**3a**) in $CDCl_3$

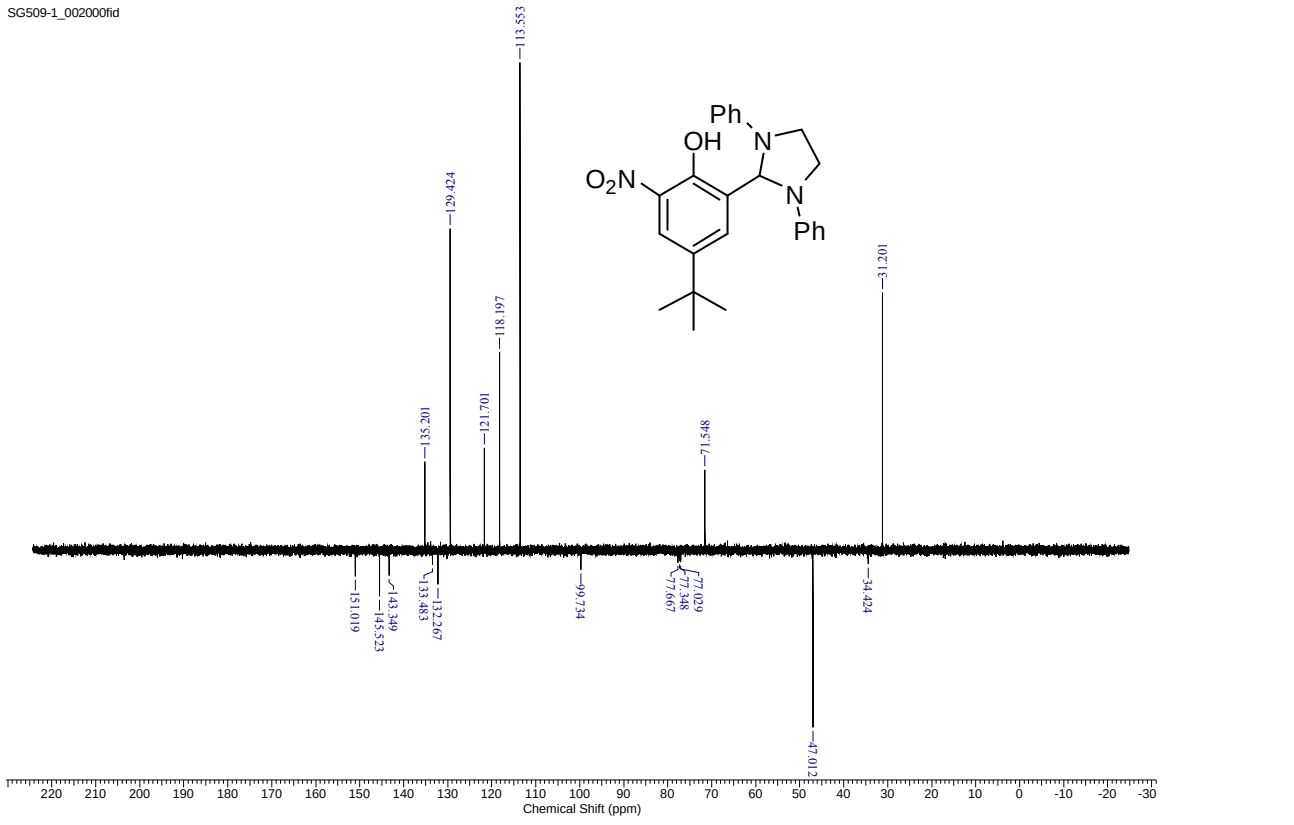


Figure S12: ^{13}C NMR spectrum of 4-*tert*-butyl-2-(1,3-diphenylimidazolidin-2-yl)-6-nitrophenol (**3a**) in $CDCl_3$

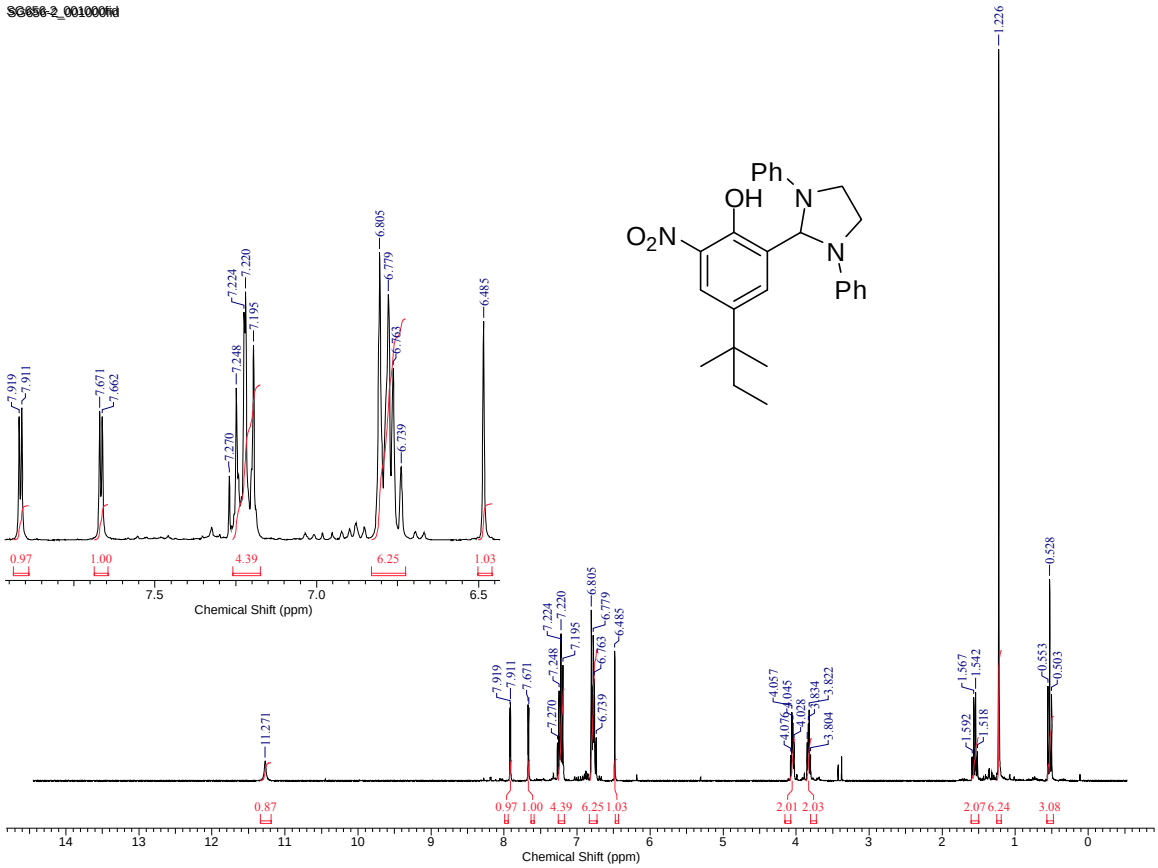


Figure S13: ^{1}H NMR spectrum of 2-(1,3-diphenylimidazolidin-2-yl)-6-nitro-4-*tert*-pentylphenol (**3b**) in $CDCl_3$

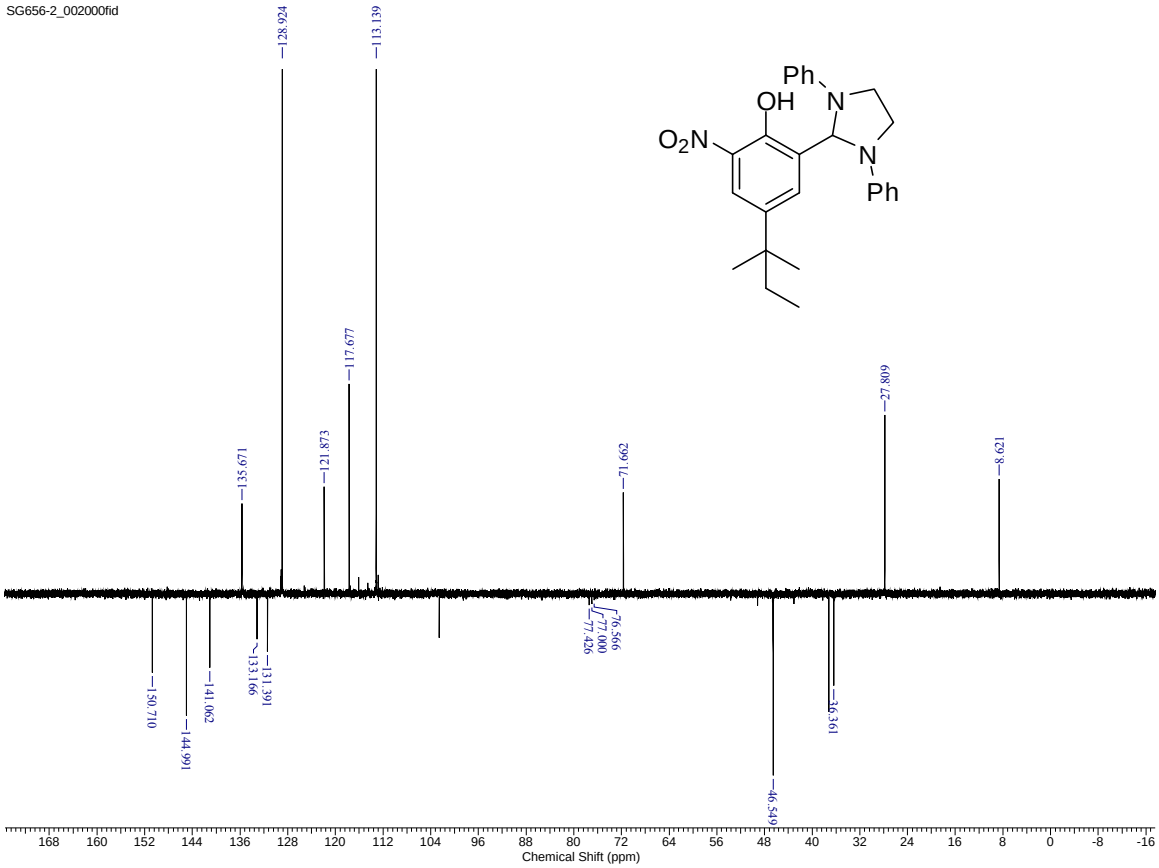


Figure S14: ^{13}C NMR spectrum of 2-(1,3-diphenylimidazolidin-2-yl)-6-nitro-4-*tert*-pentylphenol (**3b**) in $CDCl_3$

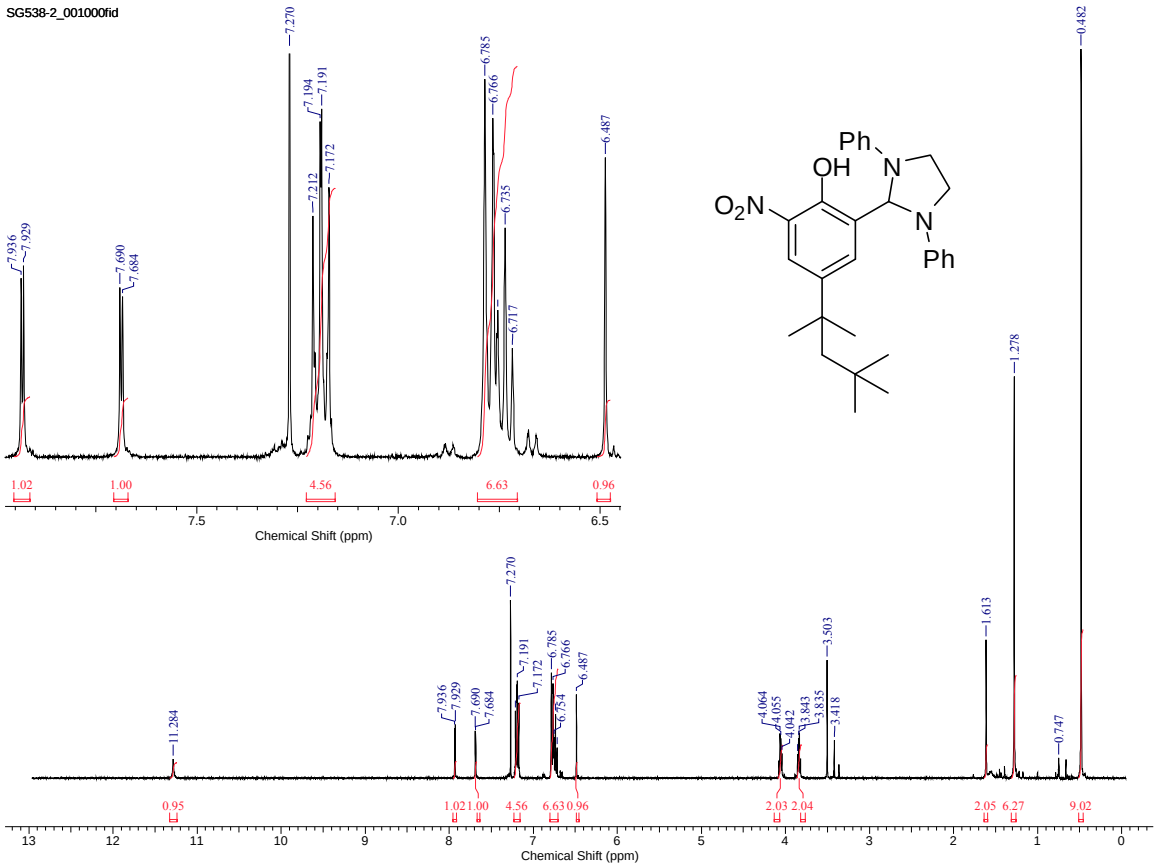


Figure S15: ^{1}H NMR spectrum of 2-(1,3-diphenylimidazolidin-2-yl)-6-nitro-4-(2,4,4-trimethylpentan-2-yl)phenol (**3c**) in $CDCl_3$

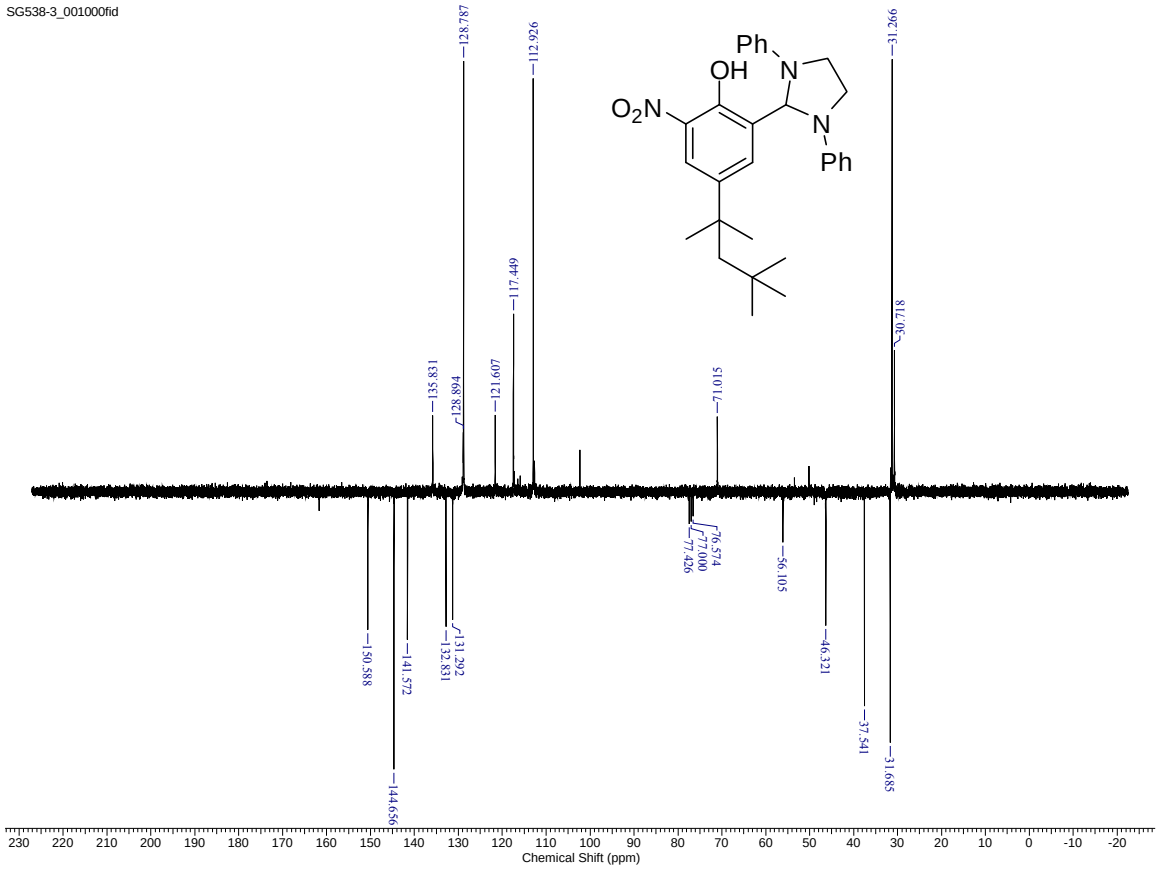


Figure S16: ^{13}C NMR spectrum of 2-(1,3-diphenylimidazolidin-2-yl)-6-nitro-4-(2,4,4-trimethylpentan-2-yl)phenol (**3c**) in $CDCl_3$

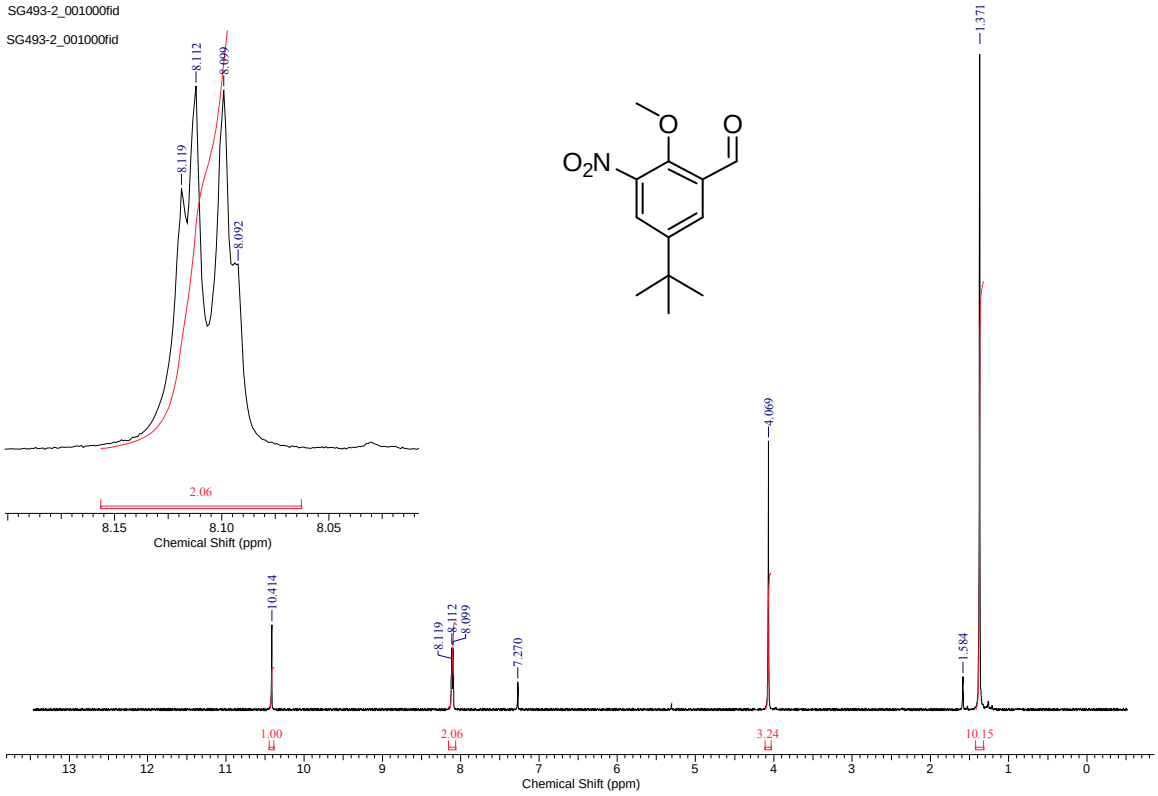


Figure S17: ^{1}H NMR spectrum of 5-*tert*-butyl-2-methoxy-3-nitrobenzaldehyde (**4**) in $CDCl_3$

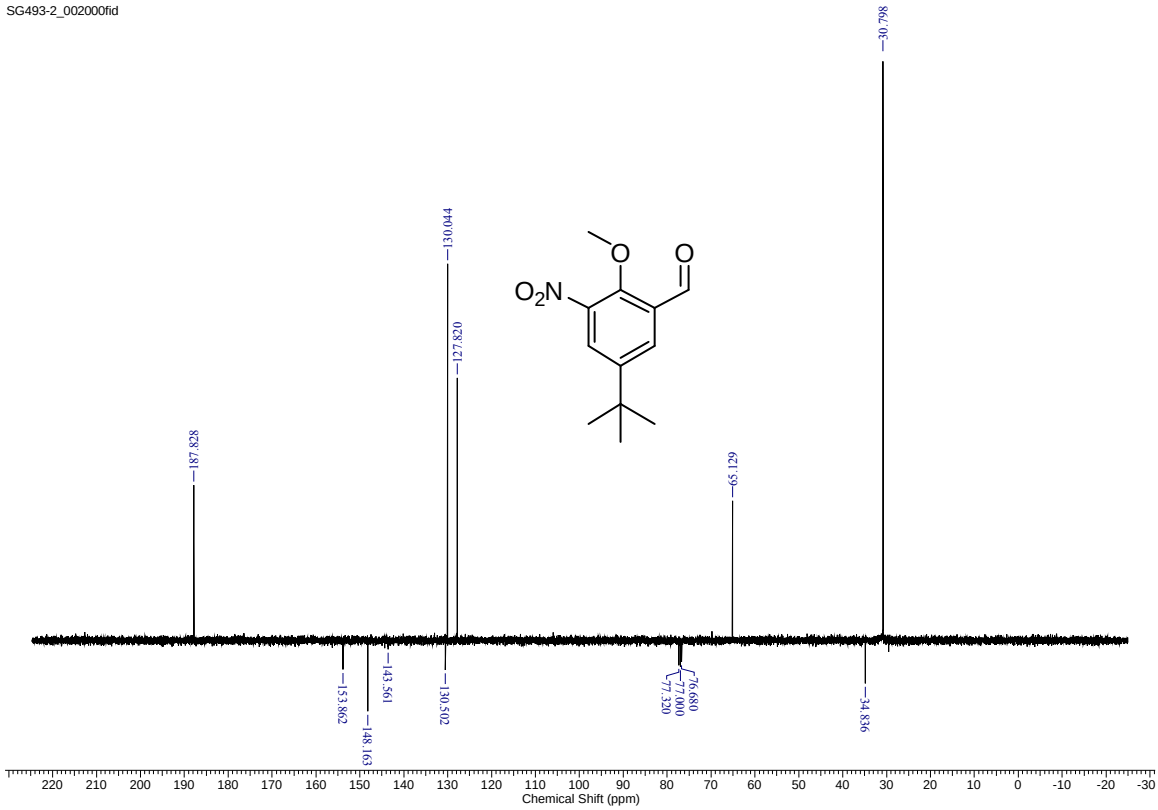


Figure S18: ^{13}C NMR spectrum of 5-*tert*-butyl-2-methoxy-3-nitrobenzaldehyde (**4**) in $CDCl_3$

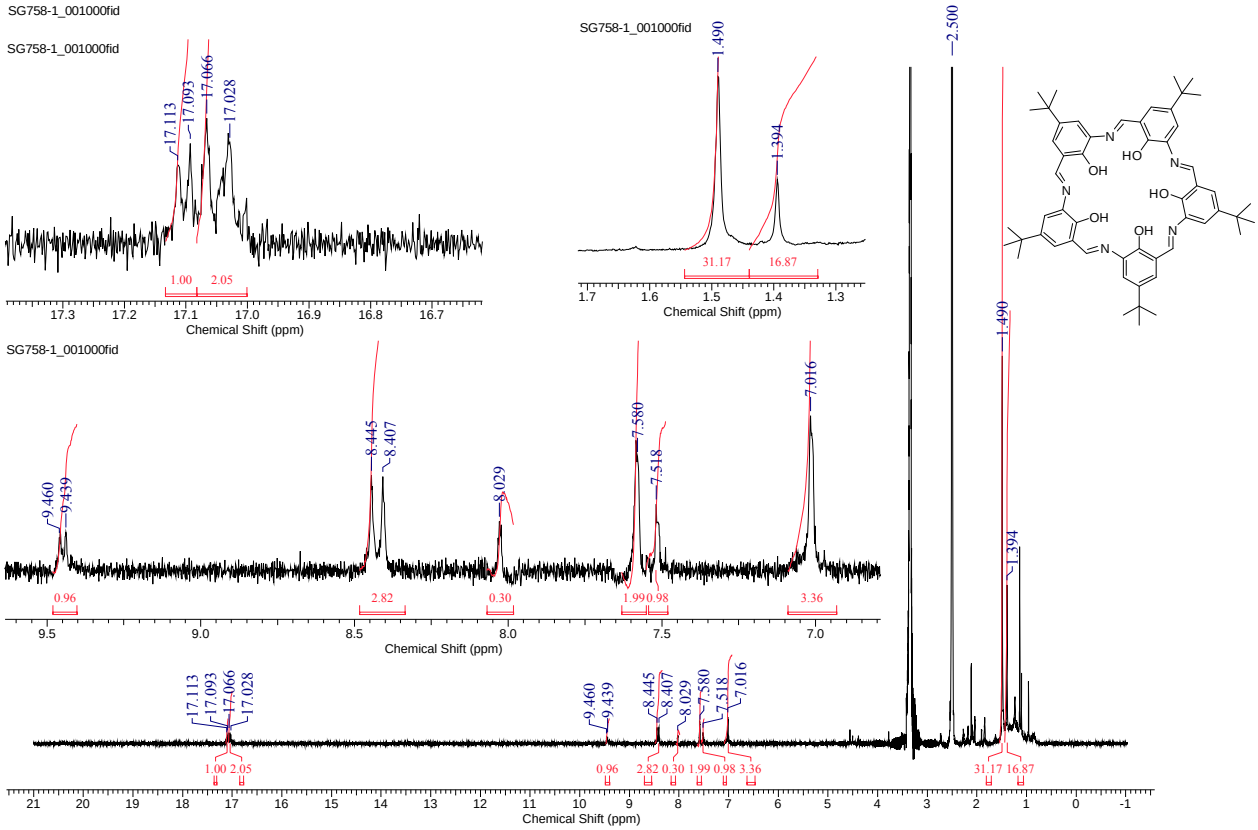


Figure S19: ^{1}H NMR spectrum of 4-*tert*-Butyl-Campestarene (**1a**) in DMSO-d_6

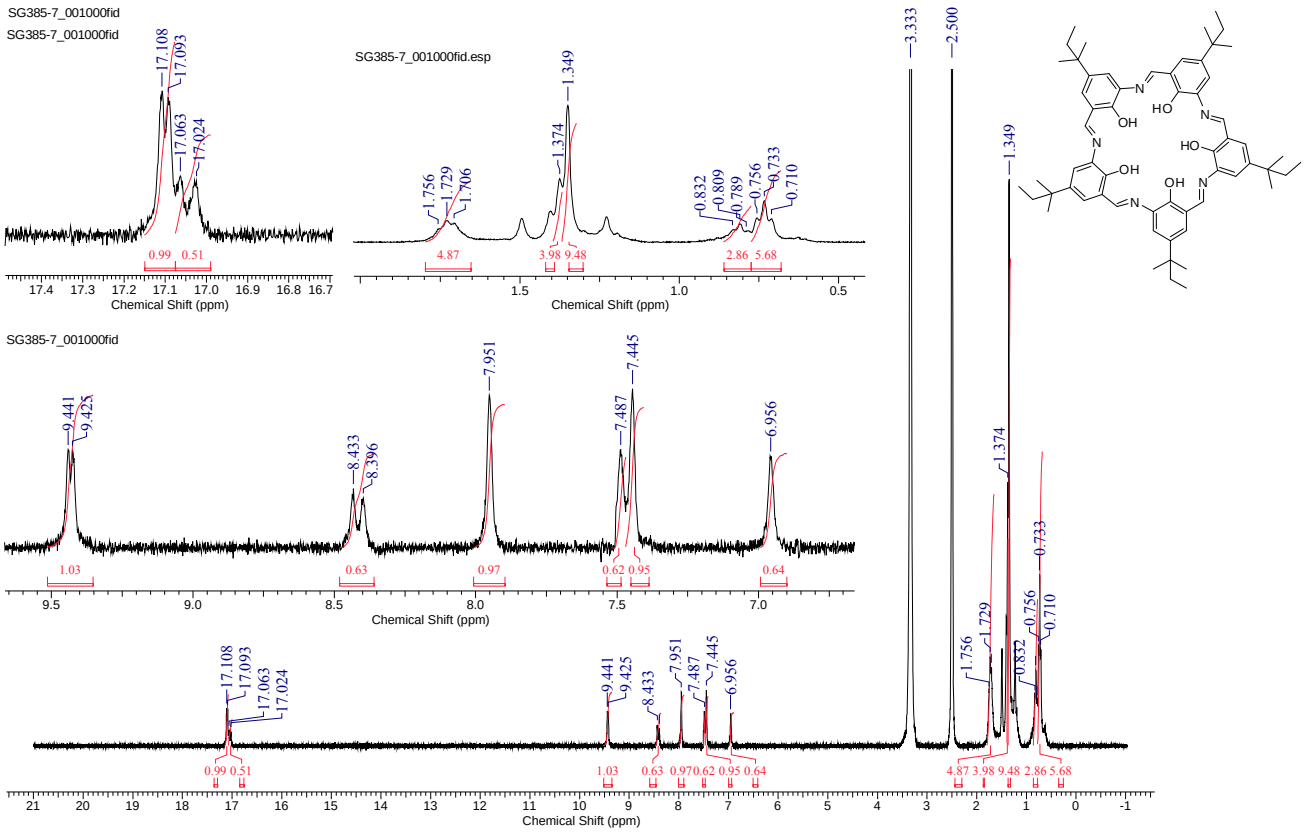


Figure S20: ^{1}H NMR spectrum of 4-(1,1-dimethylpropyl)- Campestarene (**1b**) in DMSO-d_6

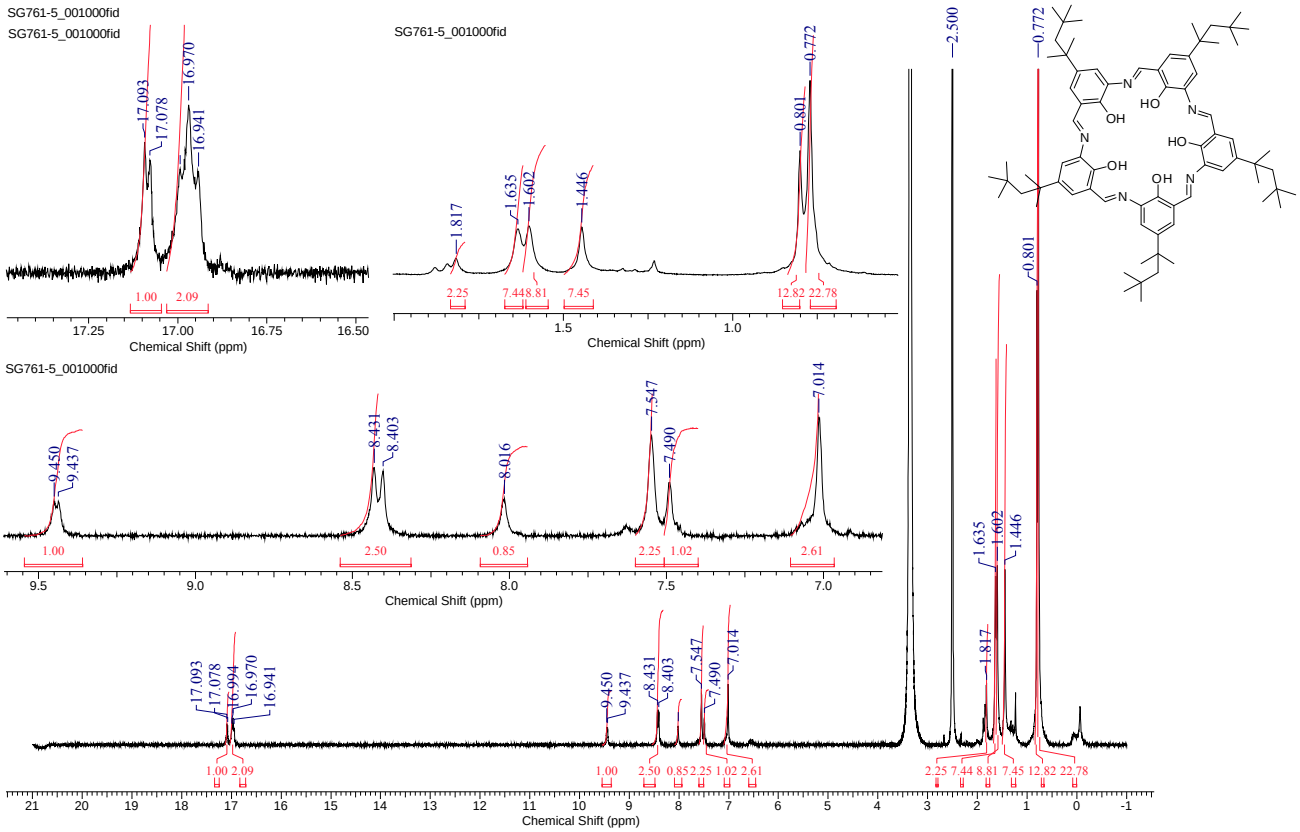


Figure S21: ^{1}H NMR spectrum of 4-(1,1,3,3-tetramethylbutyl)- Campestarene (**1c**) in DMSO-d_6

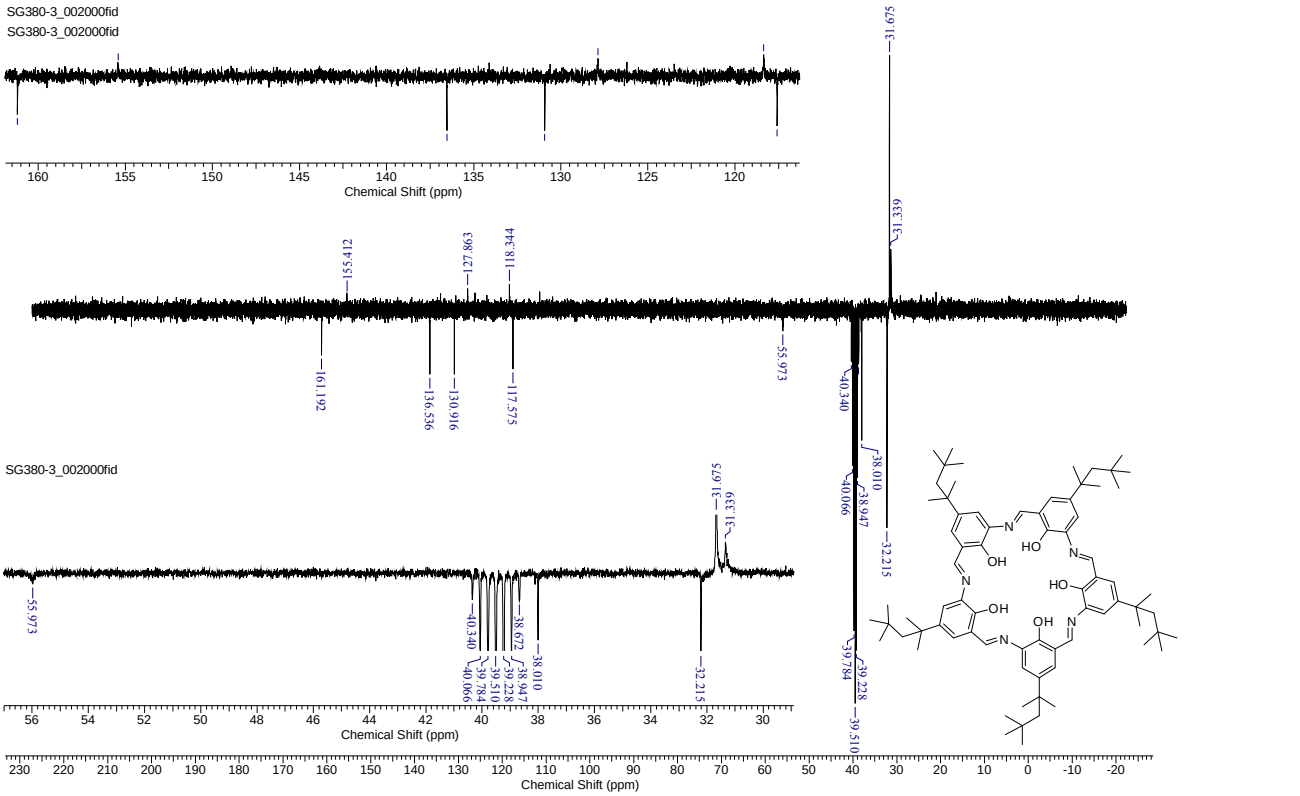


Figure S22: ^{13}C NMR spectrum of 4-(1,1,3,3-tetramethylbutyl)- Campestarene (**1c**) in DMSO-d_6

Mass Spectra of the macrocycles

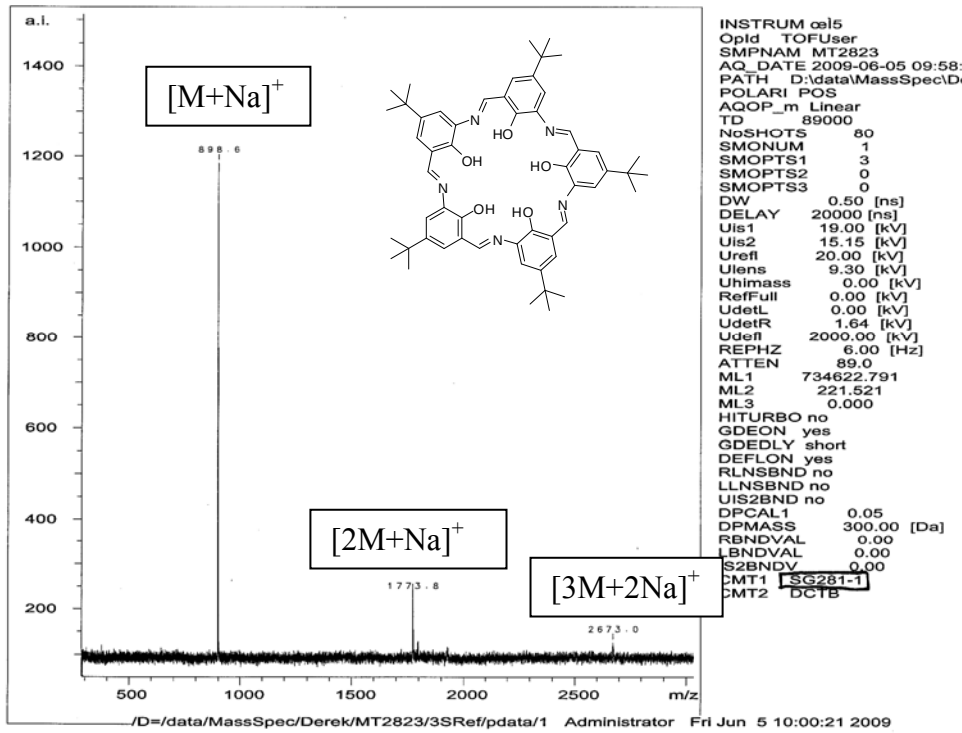


Figure S23: MALDI-TOF spectrum of 4-*tert*-Butyl-Campestarene (**1a**)

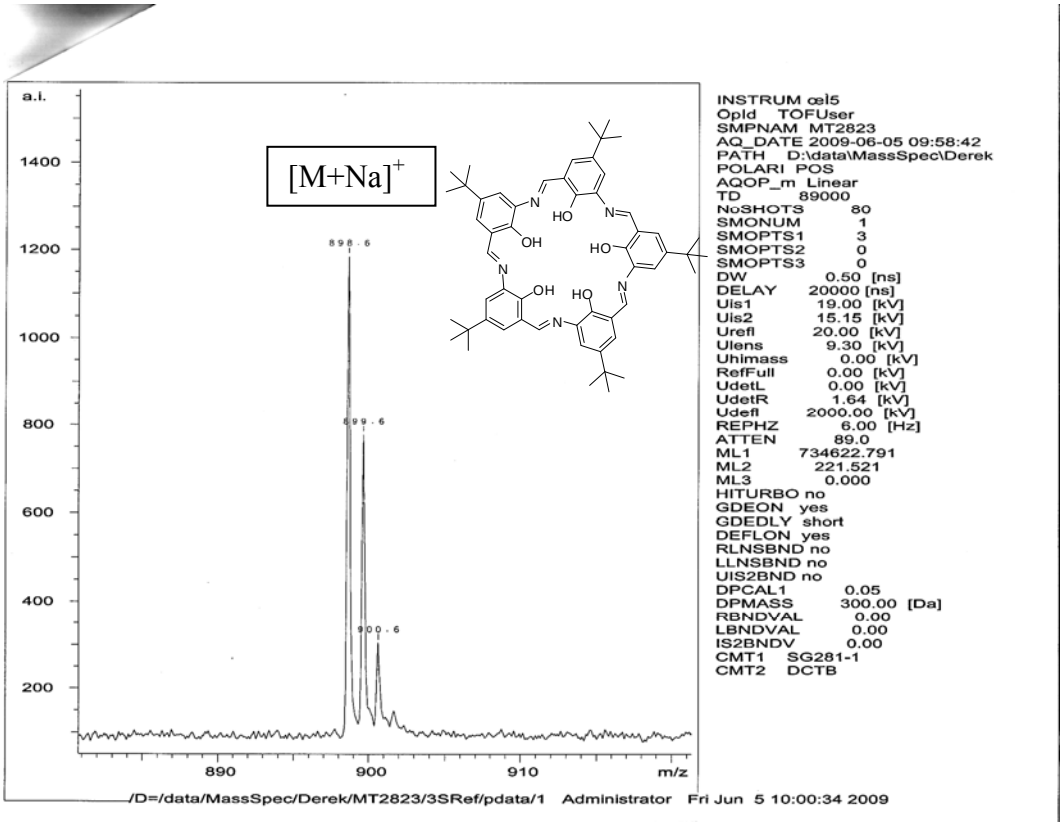


Figure S24: Section of the MALDI-TOF spectrum of 4-*tert*-Butyl-Campestarene (**1a**)

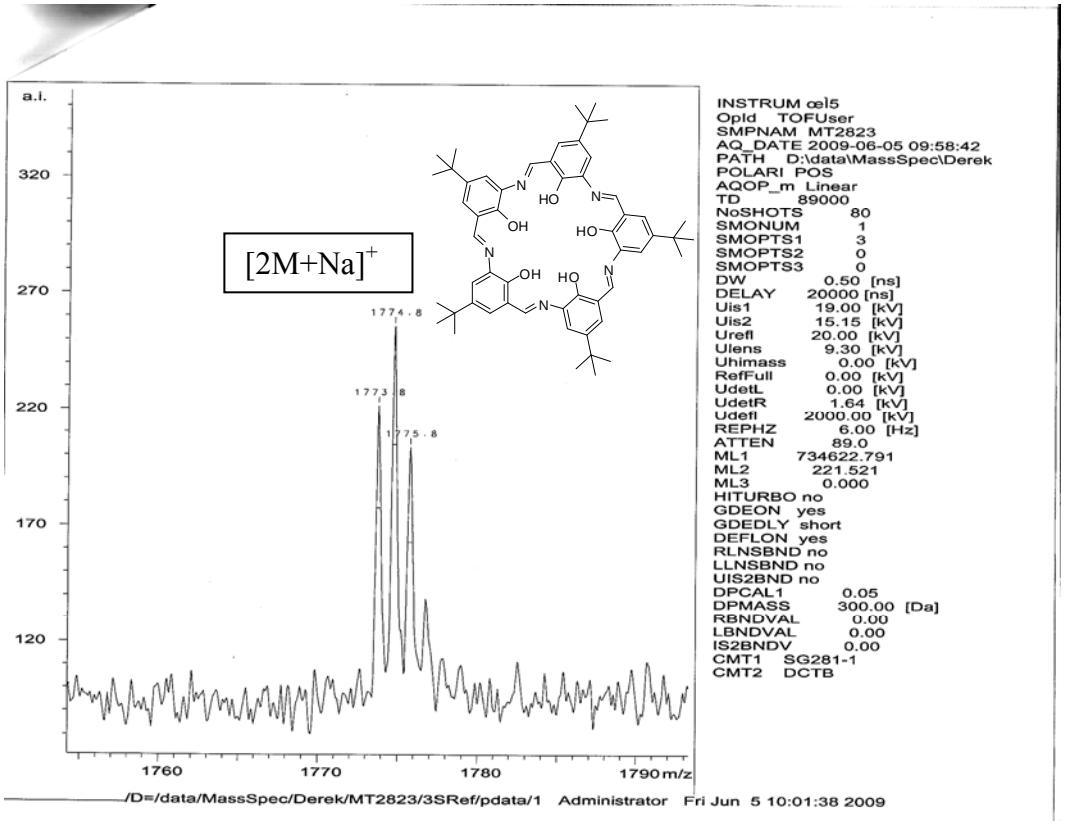


Figure S25: Section of the MALDI-TOF spectrum of 4-*tert*-Butyl-Campestarene (**1a**)

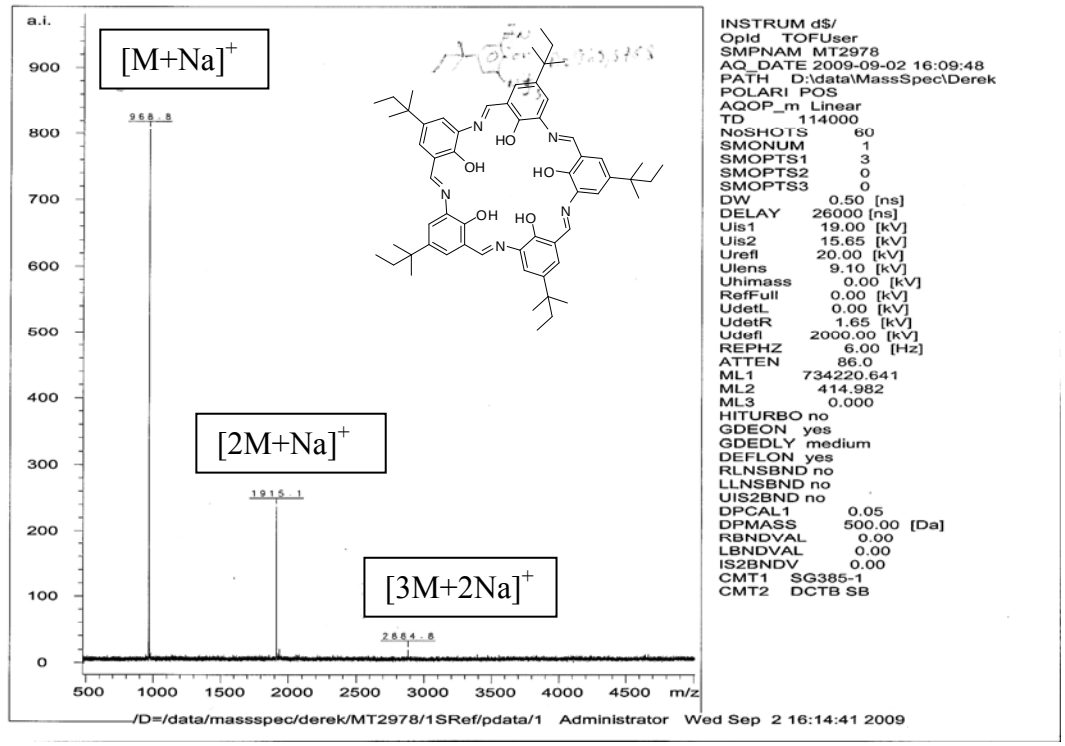


Figure S26: MALDI-TOF spectrum of 4-(1,1-dimethylethyl)-Campestarene (**1b**)

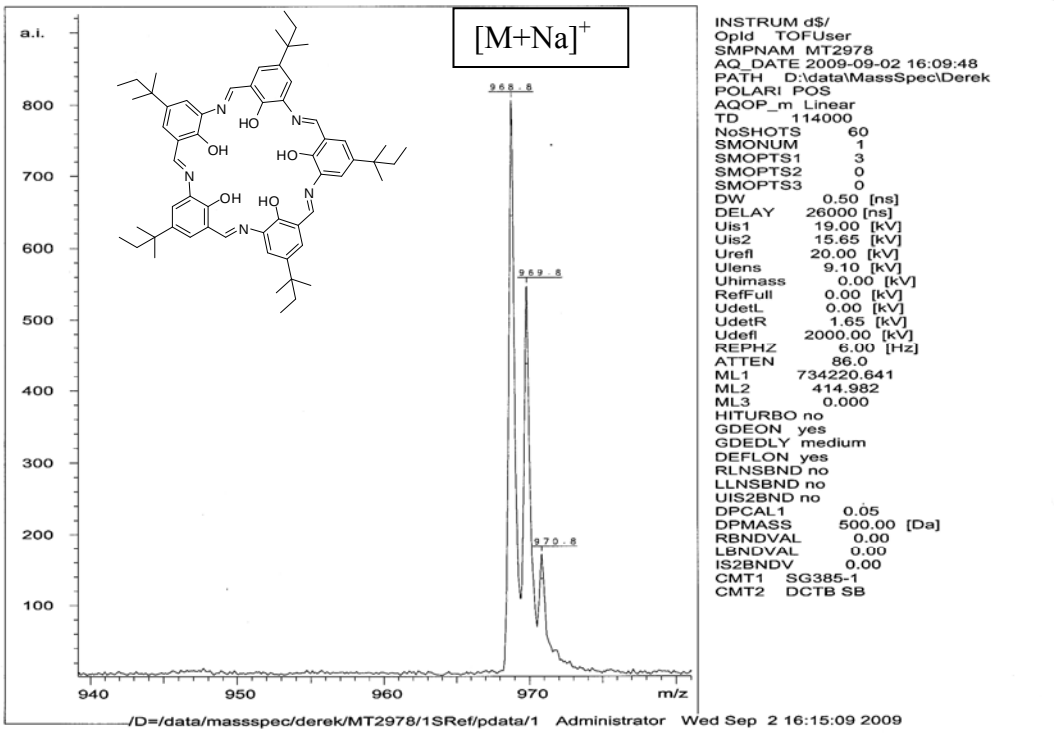


Figure S27: Section of the MALDI-TOF spectrum of 4-(1,1-dimethylethyl)-Campestarene (**1b**)

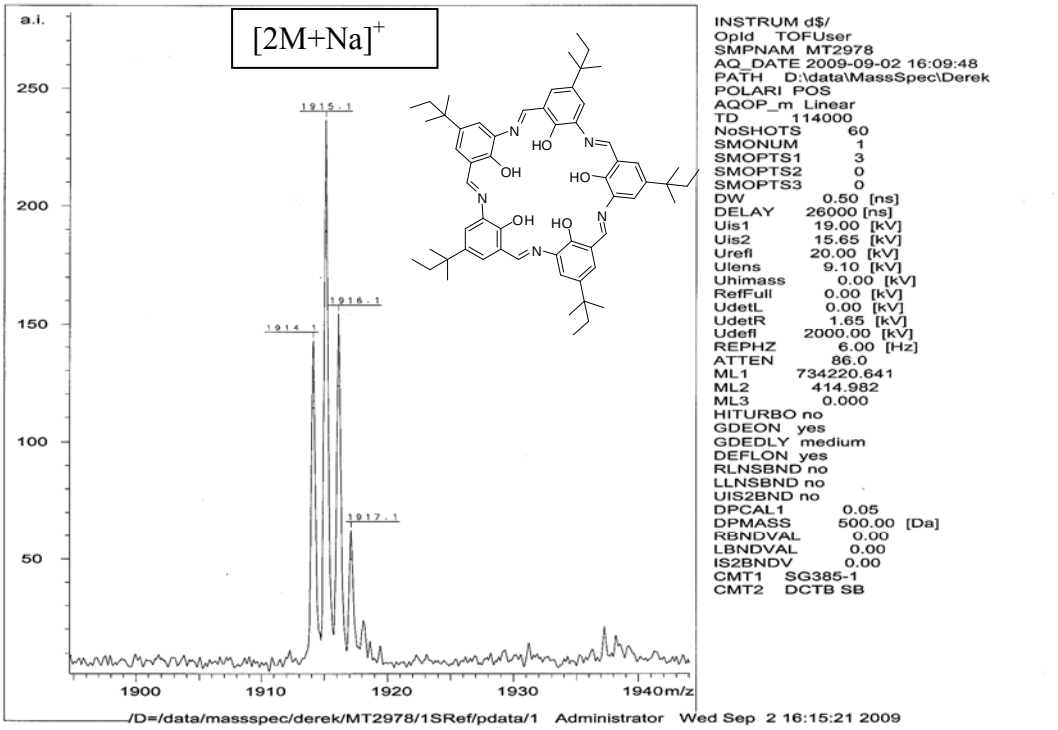


Figure S28: Section of the MALDI-TOF spectrum of 4-(1,1-dimethylethyl)-Campestarene (**1b**)

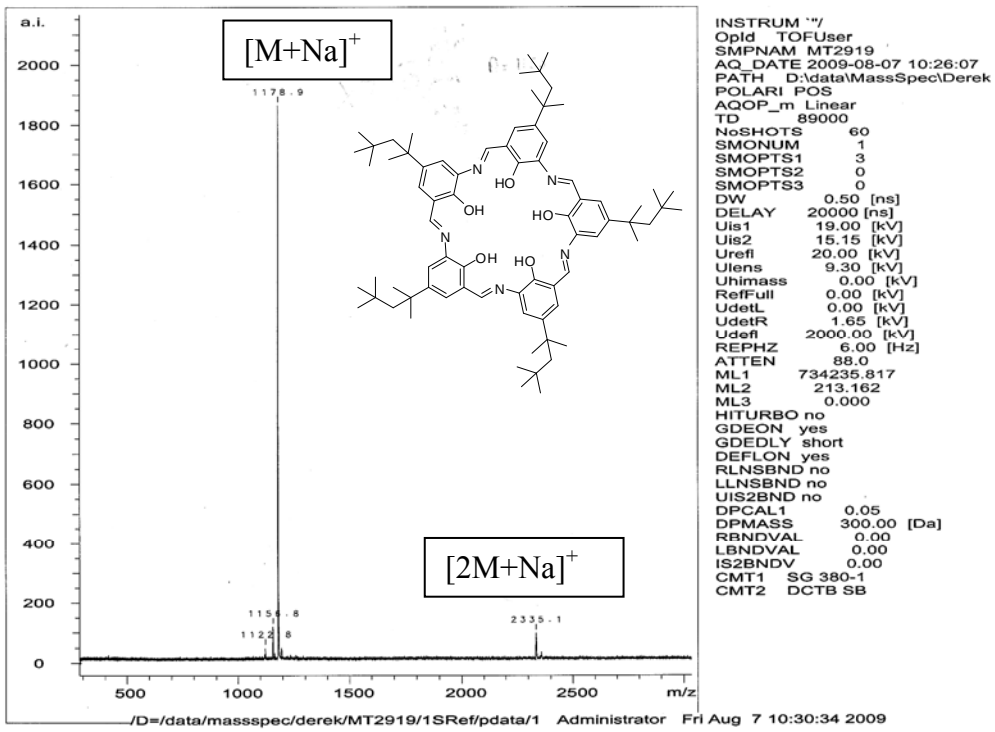


Figure S29: MALDI-TOF spectrum of 4-(1,1,3,3-tetramethylbutyl)-Campestarene (**1c**)

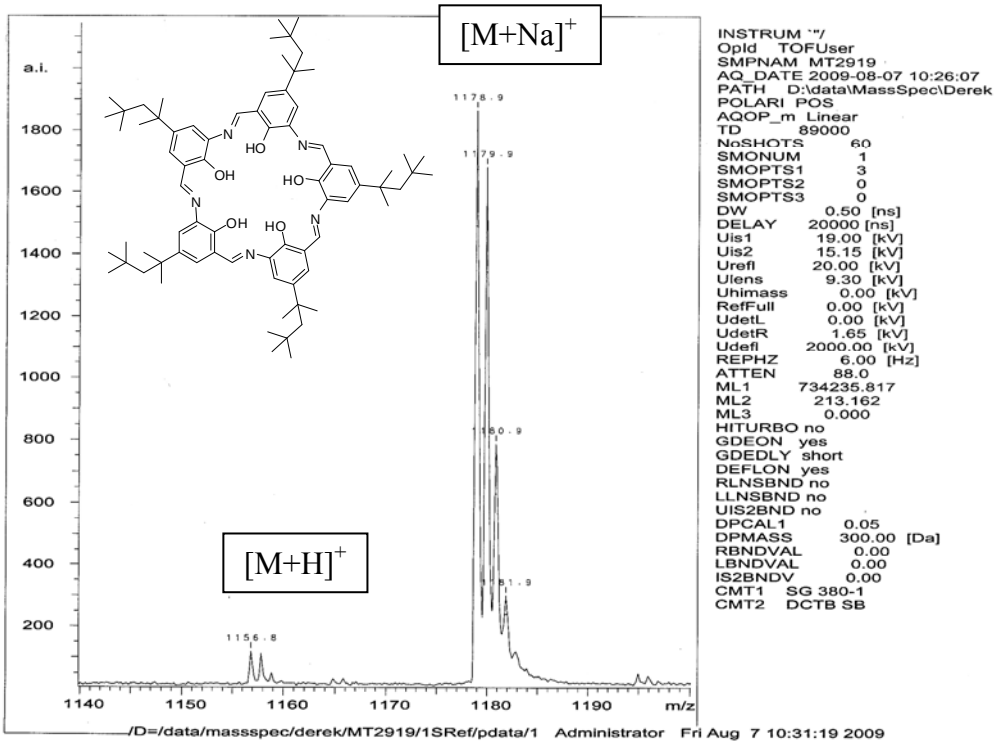


Figure S30: Section of the MALDI-TOF spectrum of 4-(1,1,3,3-tetramethylbutyl)-Campestarene (**1c**)

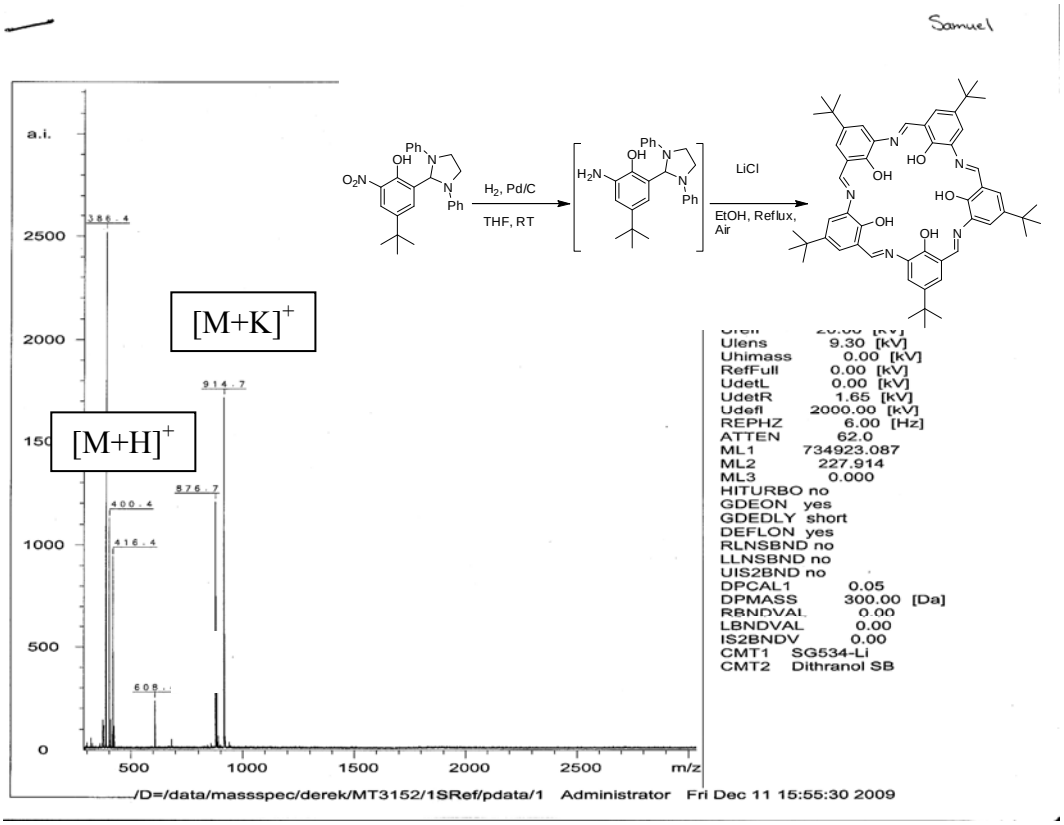


Figure S31: MALDI-TOF spectrum of 4-*tert*-Butyl-Campestarene (**1a**), synthesized from (**3a**) with Lithium salts

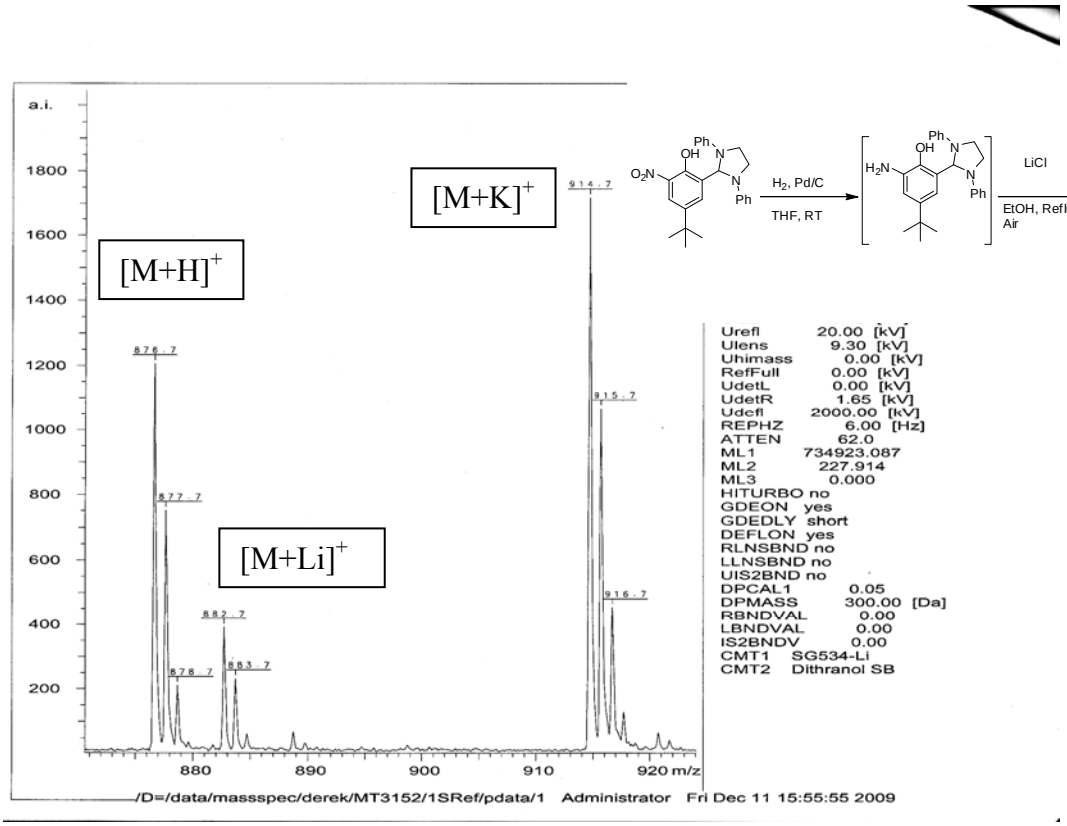


Figure S32: Section of the MALDI-TOF spectrum of 4-*tert*-Butyl-Campestarene (**1a**), synthesized from (**3a**) with Lithium salts

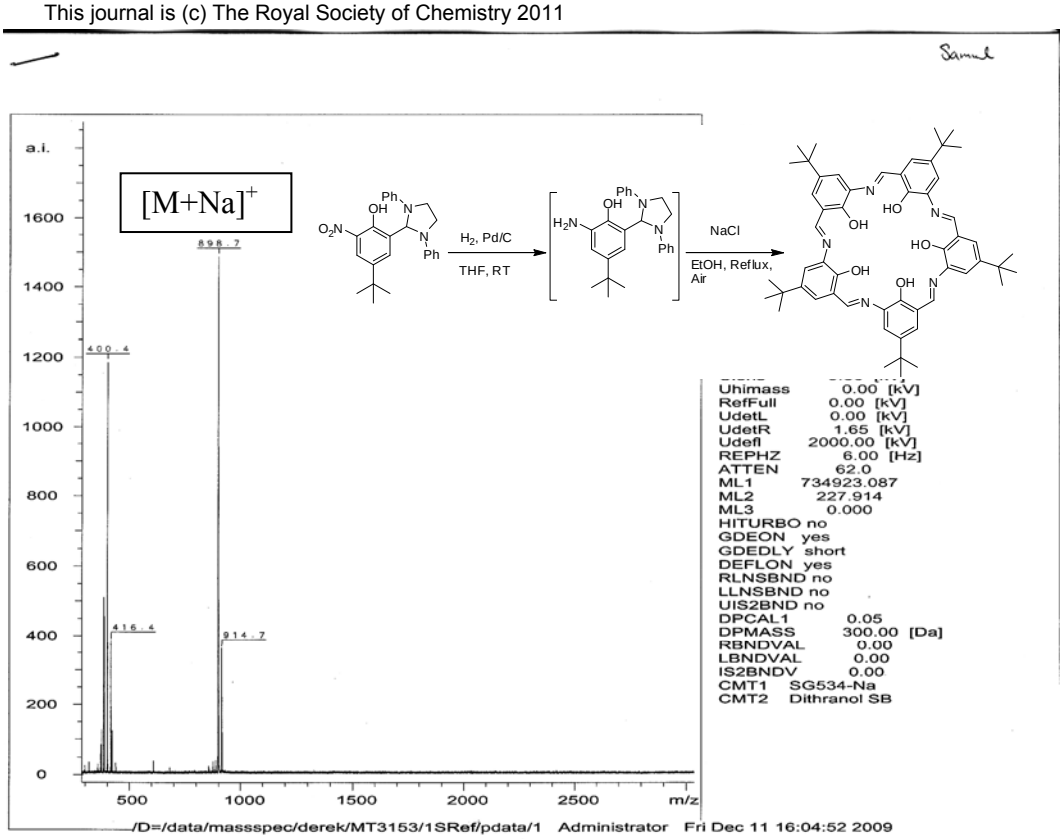


Figure S33: MALDI-TOF spectrum of 4-*tert*-Butyl-Campestarene (**1a**), synthesized from (**3a**) with Sodium salts

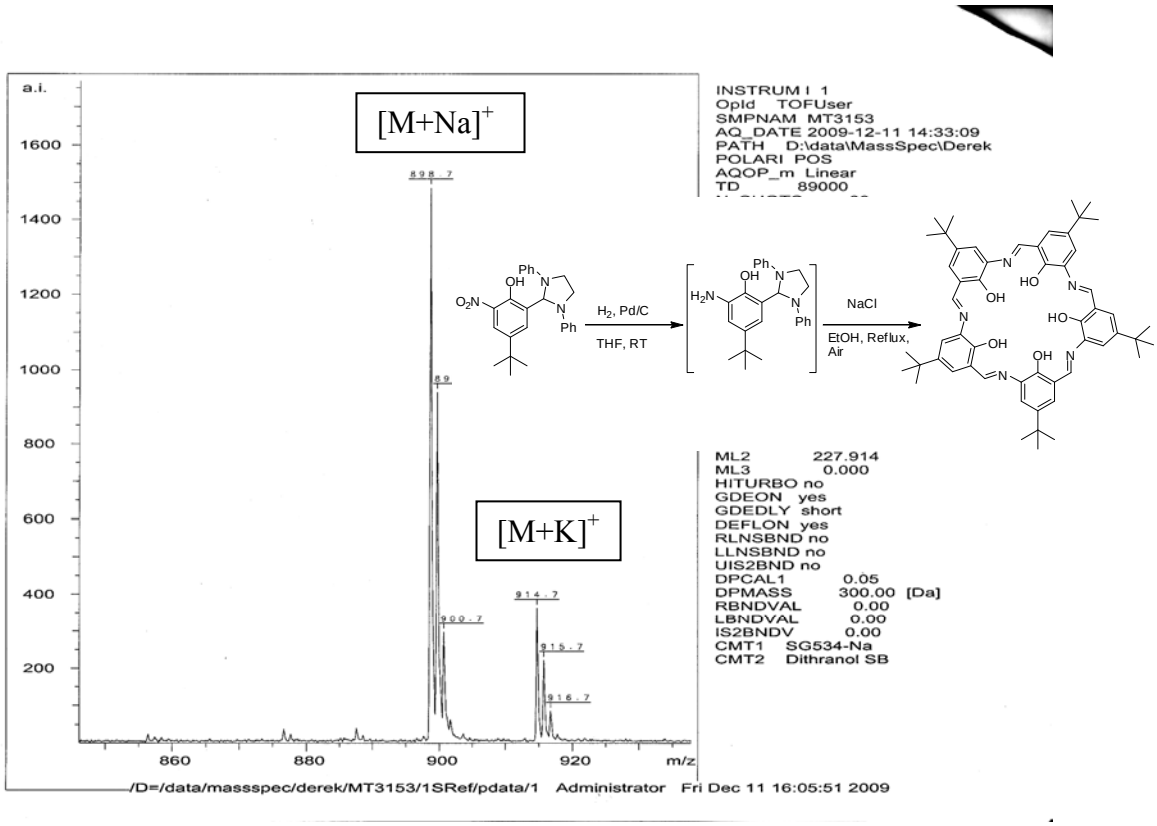


Figure S34: Section of the MALDI-TOF spectrum of 4-*tert*-Butyl-Campestarene (**1a**), synthesized from (**3a**) with Sodium salts

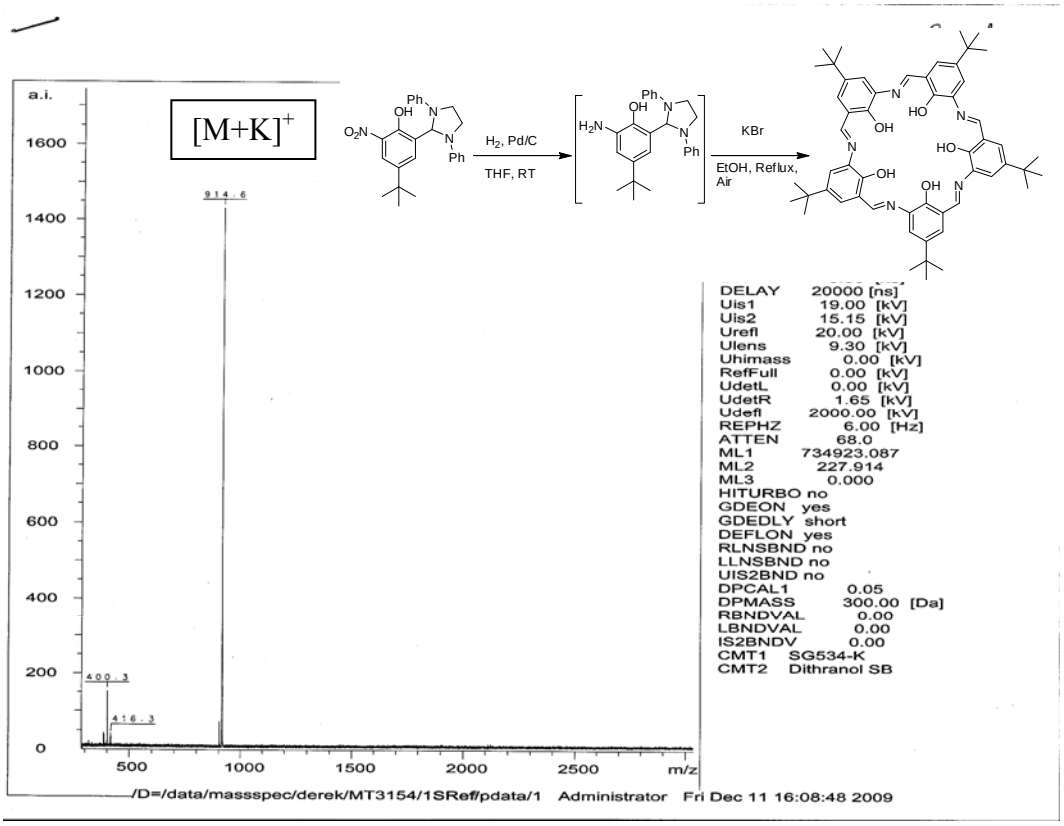


Figure S35: MALDI-TOF spectrum of 4-*tert*-Butyl-Campestarene (**1a**), synthesized from (**3a**) with Potassium salts

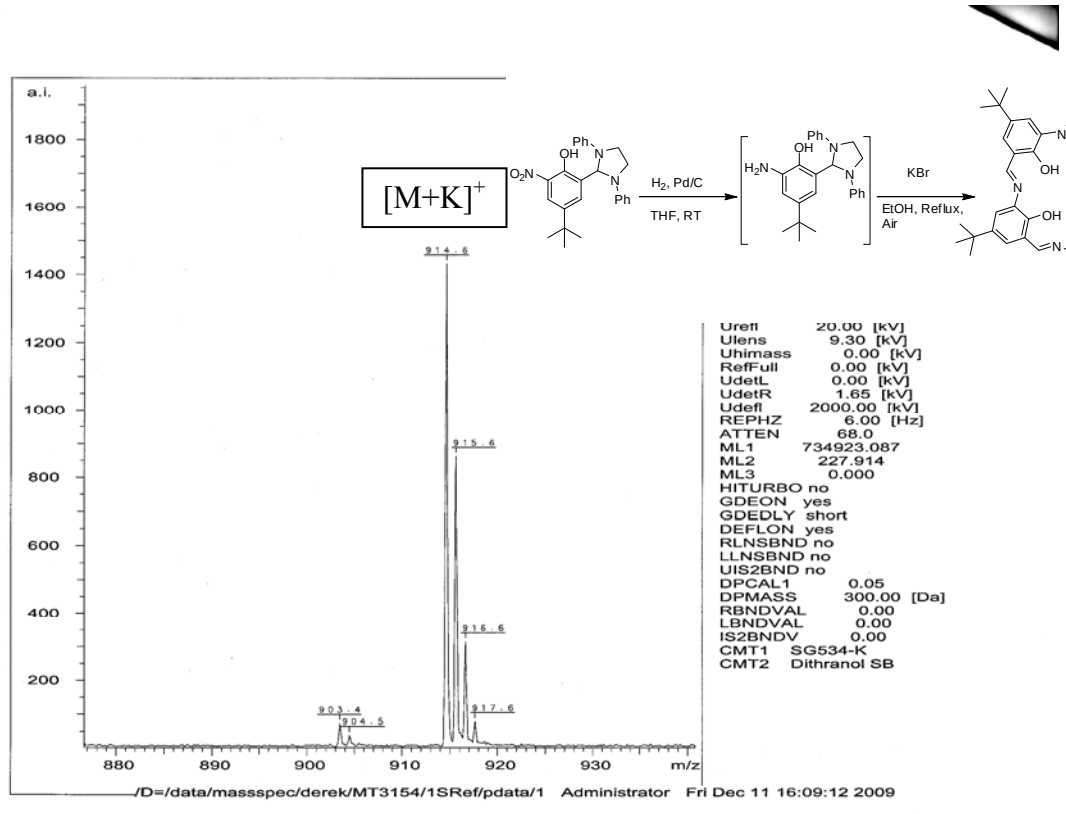


Figure S36: Section of the MALDI-TOF spectrum of 4-*tert*-Butyl-Campestarene (**1a**), synthesized from (**3a**) with Potassium salts

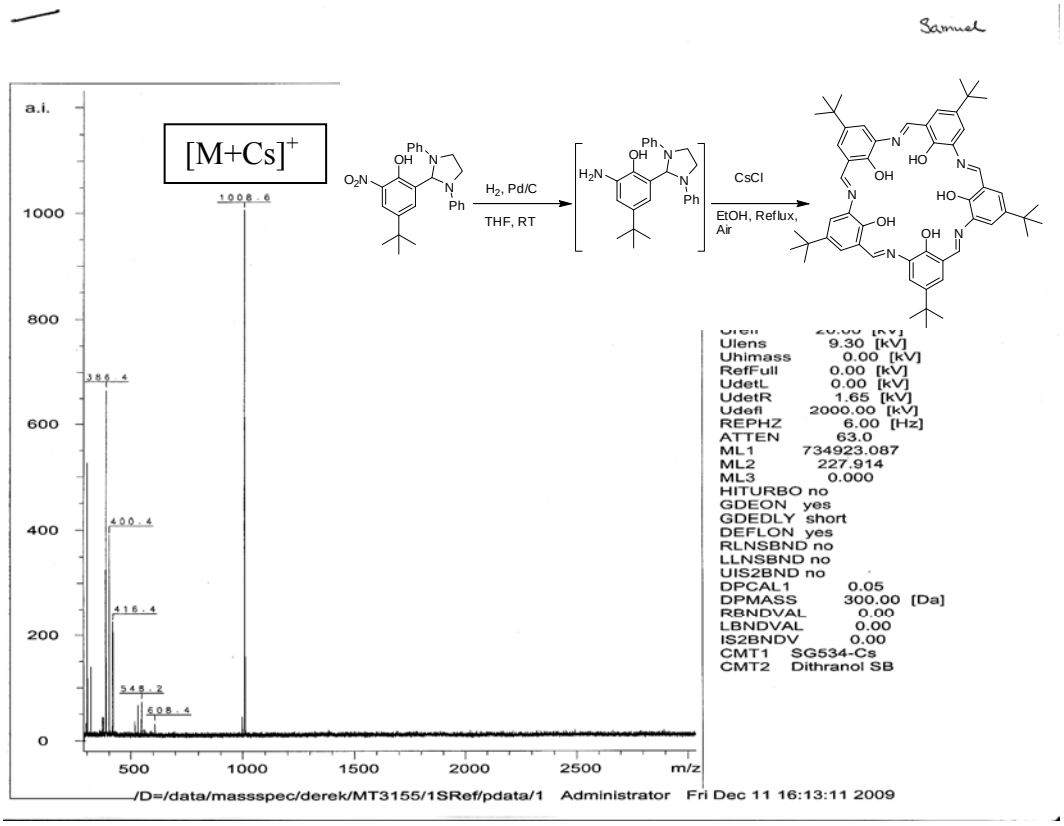


Figure S37: MALDI-TOF spectrum of 4-*tert*-Butyl-Campestarene (**1a**), synthesized from (**3a**) with Cesium salts

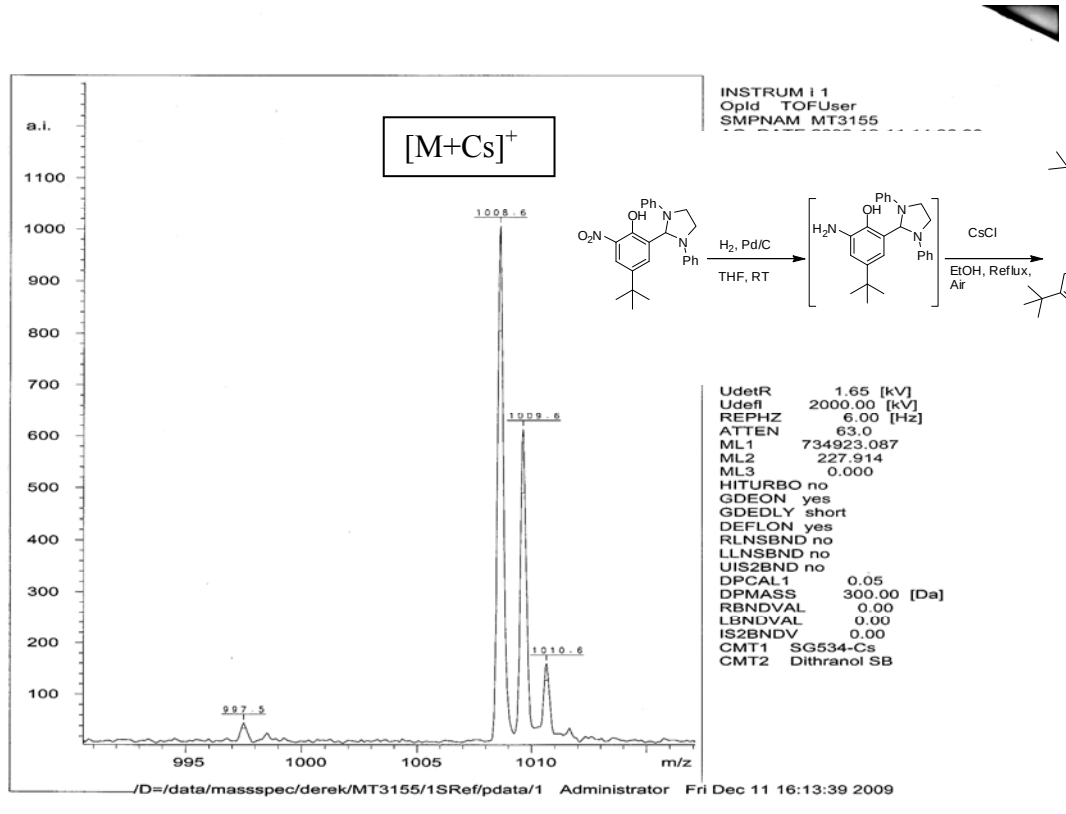


Figure S38: Section of the MALDI-TOF spectrum of 4-*tert*-Butyl-Campestarene (**1a**), synthesized from (**3a**) with Cesium salts

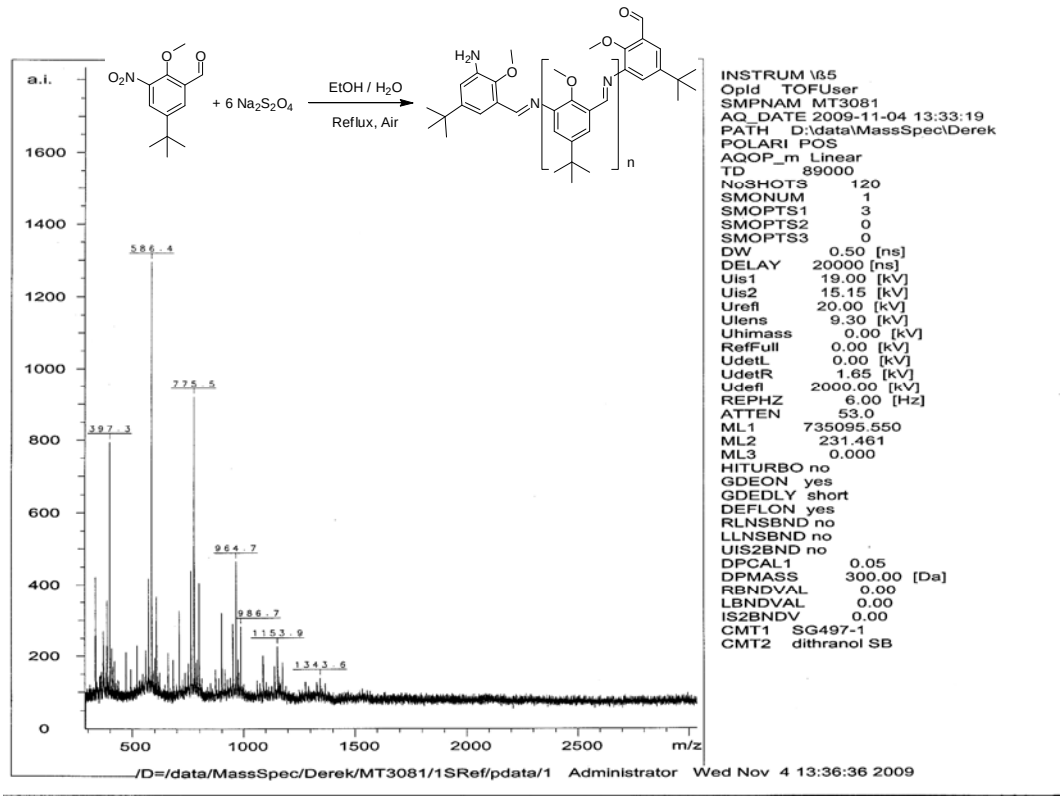


Figure S39: MALDI-TOF spectrum of the crude of the reaction of (**4**) with $Na_2S_2O_4$

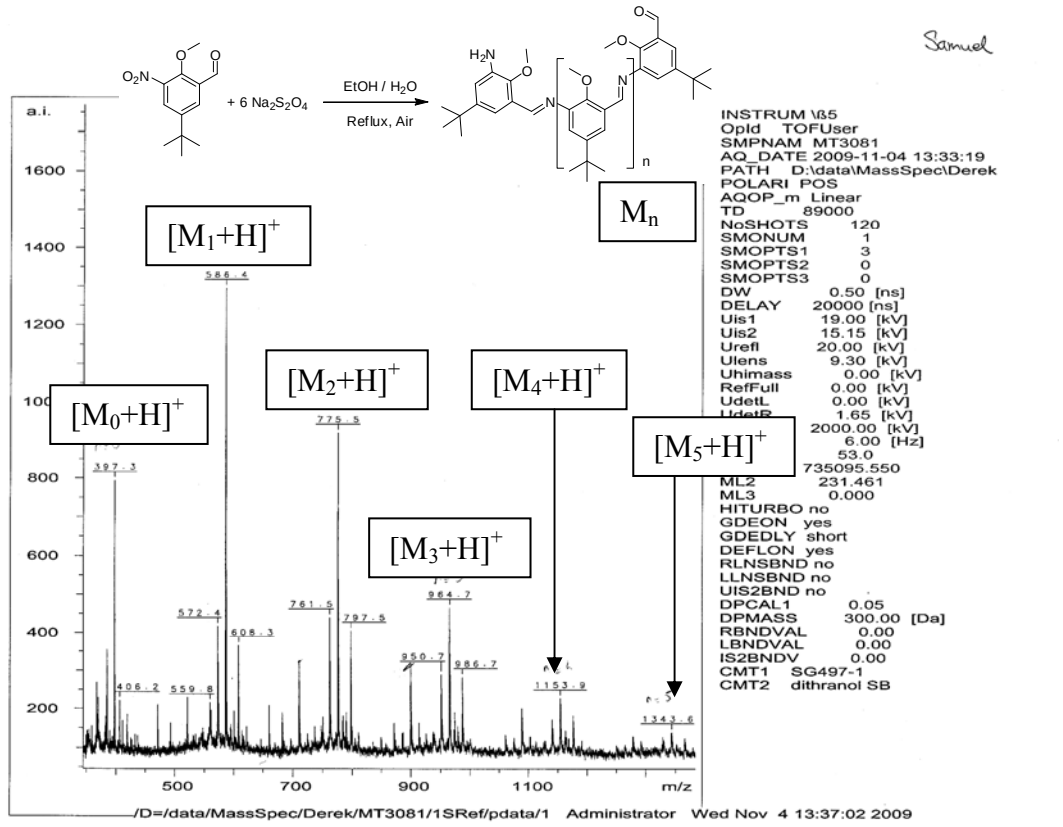


Figure S40: Section of the MALDI-TOF spectrum of the crude of the reaction of (**4**) with $Na_2S_2O_4$

UV-Vis spectra of campestarenes in DMSO

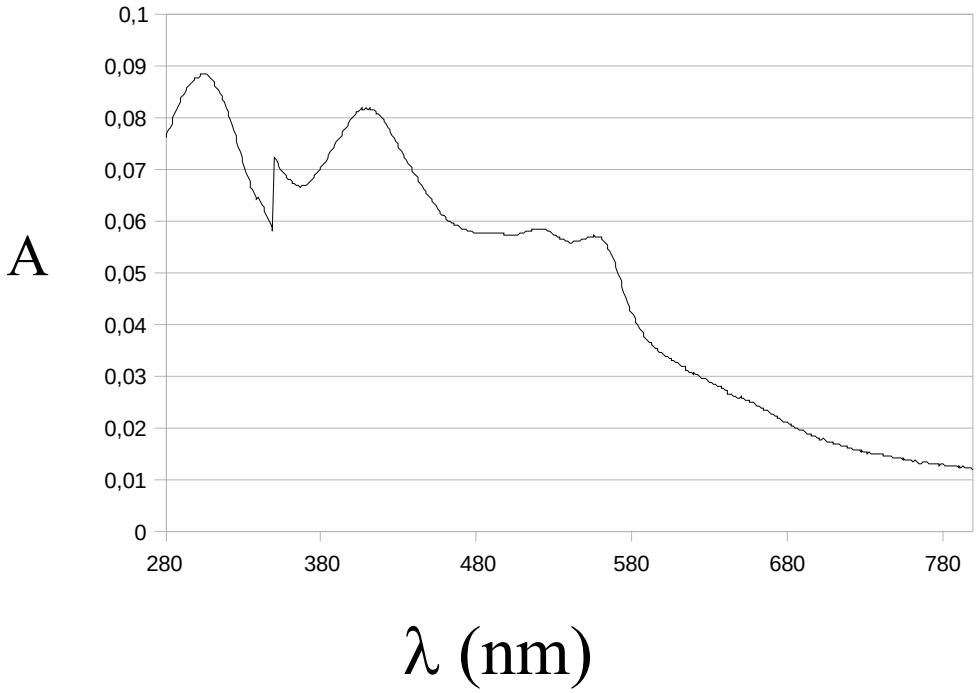


Figure S41: UV-Vis spectrum of 4-*tert*-Butyl-Campestarene (**1a**) (11.10^{-6} $mol.L^{-1}$ in DMSO)

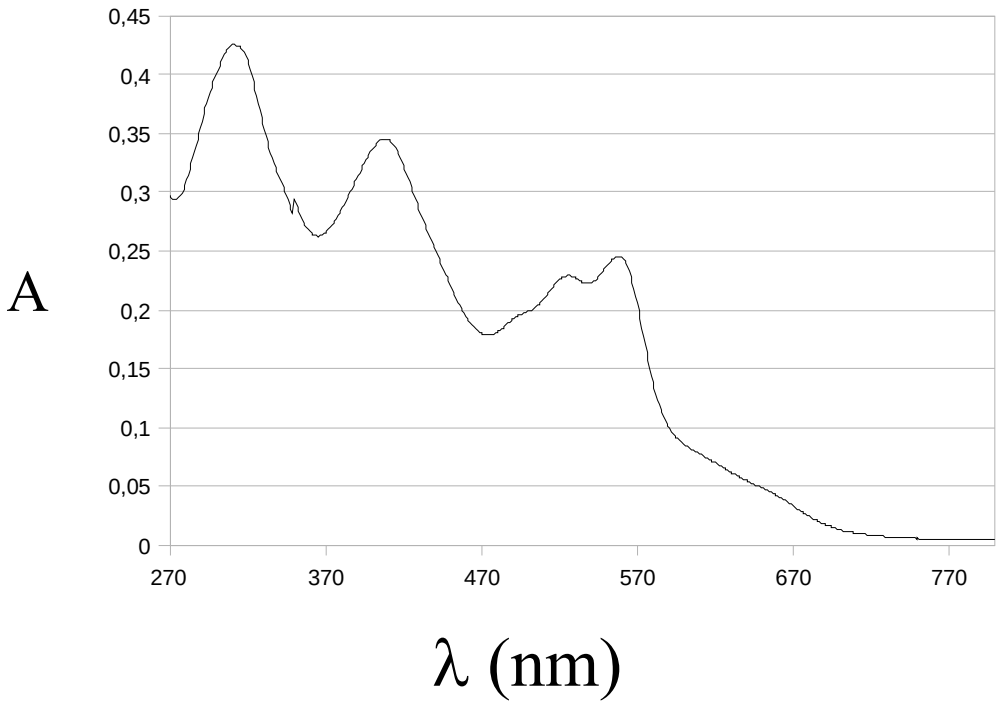


Figure S42: UV-Vis spectrum of 4-(1,1-dimethylpropyl)-Campestarene (**1b**) (11.10^{-6} $mol.L^{-1}$ in DMSO)

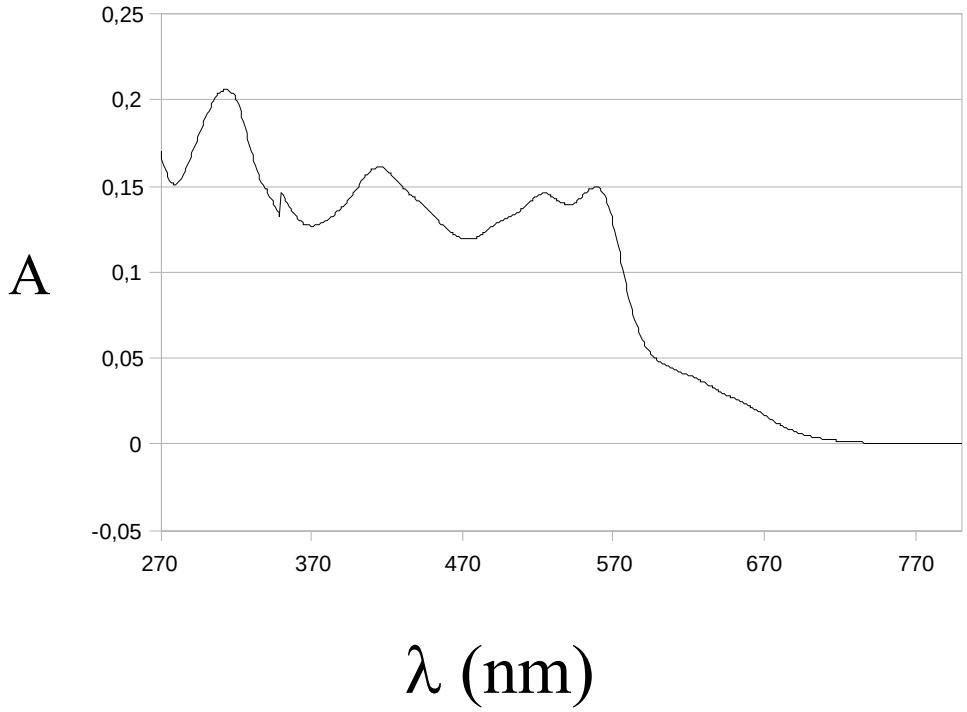


Figure S43: UV-Vis spectrum of 4-(1,1,3,3-tetramethylbutyl)-Campestarene (**1c**) (8.10^{-6} $mol.L^{-1}$ in DMSO)

Computational Methods

All Calculations were carried out on the Orcinus cluster of WestGrid, consisting of Intel Xeon E5450 quad-core processors. Ground state geometry optimization and frequency calculations were carried out using the Gaussian 03' package.[4] B3LYP[5] and 6-31G*[6] basis-set were used for all geometry optimization calculations. Frequency calculations were performed using B3LYP and 6-31G**[7] basis set. Calculations were assumed to occur in the gas phase at 298.15 K and 1.00 atm. The conversion factor for HT/particle to J/mol used was 2.625 x 10^6.

Calculation of Pentacycle **1e** enol-imine

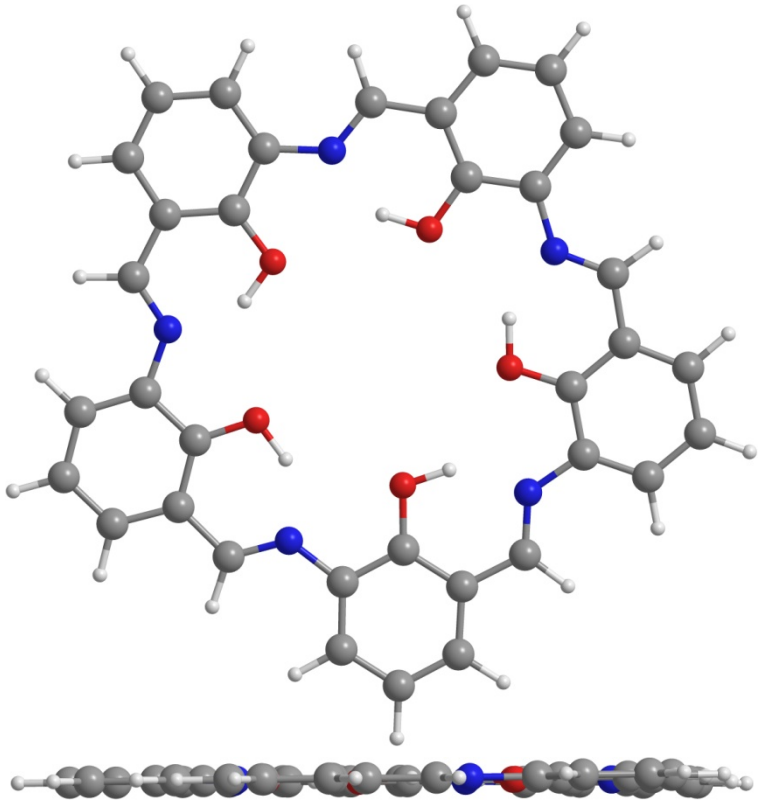


Figure S44: Optimized structure of Pentacycle **1e** enol-imine (B3LYP/6-31G*)

Optimized Cartesian Coordinates for Pentacycle **1e** enol-imine

6	0.645	-4.069	0.009	6	-6.371	-2.68	-0.059
6	0.58	-6.886	0.043	6	-4.71	-0.897	-0.024
6	-0.602	-4.756	0.015	1	-5.606	-4.692	-0.058
6	1.861	-4.813	0.019	1	-7.412	-2.987	-0.080
6	1.799	-6.218	0.036	1	-6.841	-0.583	-0.062
6	-0.612	-6.156	0.034	6	3.283	3.494	-0.011

1	2.729	-6.781	0.045	6	2.199	6.088	-0.021
1	-1.56	-6.685	0.045	6	1.87	3.671	-0.004
1	0.55	-7.972	0.059	6	4.113	4.622	-0.023
8	0.617	-2.739	-0.006	6	3.579	5.913	-0.028
6	3.148	-4.133	0.017	6	1.323	4.988	-0.009
1	4.042	-4.77	0.037	1	5.192	4.492	-0.029
7	3.198	-2.845	-0.003	1	4.24	6.773	-0.037
6	4.339	-2.043	-0.004	1	1.777	7.09	-0.026
6	6.47	-0.21	-0.010	8	-2.416	-1.433	0.011
6	5.668	-2.483	-0.011	1	-1.803	-2.233	0.016
6	4.07	-0.644	-0.001	6	-2.309	4.202	0.018
6	5.153	0.283	-0.004	6	-5.11	3.973	0.045
6	6.73	-1.576	-0.014	6	-3.124	5.34	0.044
1	5.878	-3.549	-0.016	6	-2.914	2.913	0.006
1	7.753	-1.939	-0.020	6	-4.335	2.8	0.020
1	7.293	0.501	-0.013	6	-4.517	5.23	0.056
1	1.568	-2.405	-0.008	1	-2.668	6.326	0.059
7	-1.718	-3.919	0.009	1	-5.131	6.125	0.078
6	-2.958	-4.27	-0.018	1	-6.194	3.881	0.057
1	-3.287	-5.318	-0.043	8	-2.109	1.854	-0.016
8	2.796	-0.261	0.006	1	-2.682	1.024	-0.020
1	2.772	0.747	0.007	6	-4.975	1.493	0.015
6	4.903	1.716	-0.004	1	-6.074	1.483	0.040
1	5.785	2.37	-0.004	7	-4.259	0.422	-0.016
7	3.693	2.161	-0.007	7	-0.914	4.18	0.012
6	-4.003	-3.258	-0.024	6	-0.117	5.193	-0.004
6	-6.044	-1.321	-0.048	1	-0.467	6.234	-0.016
6	-3.671	-1.871	-0.012	8	1.112	2.578	0.007
6	-5.358	-3.632	-0.048	1	0.146	2.867	0.010

Zero-point energy for Pentacycle **1e** enol-imine

B3LYP/6-31G* = -1998.65385395 HT/particle
B3LYP/6-31G** = -1998.71455482 HT/particle

Relevant thermal parameters calculated using B3LYP/6-31G** for Pentacycle **1e** enol-imine

Sum of electronic and zero-point Energies: -1998.182192 HT/particle
Sum of electronic and thermal Energies: -1998.147069 HT/particle
Sum of electronic and thermal Enthalpies: -1998.146125 HT/particle

Sum of electronic and thermal Free Energies: -1998.249701 HT/particle

$H° = -5.245686 \times 10^6$ kJ mol^{-1}
$G° = -5.245958 \times 10^6$ kJ mol^{-1}
$S° = 912.0095$ J mol^{-1} K^{-1}

Calculation of Pentacycle **1e** keto-enamine

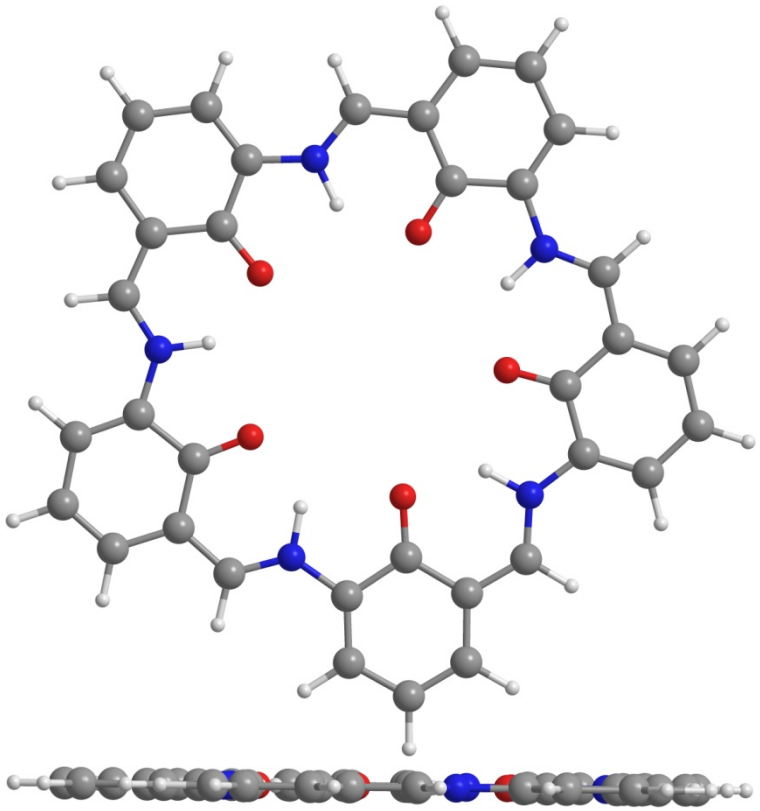


Figure S45: Optimized structure of Pentacycle **1e** keto-enamine (B3LYP/6-31G*)

Optimized Cartesian Coordinates for Pentacycle **1e** keto-enamine

6	2.047	-6.195	-0.001	6	1.139	5.072	0.000
1	2.996	-6.727	-0.001	6	1.724	3.736	-0.001
6	0.863	-6.898	-0.001	8	1.045	2.681	0.001
1	0.869	-7.984	-0.001	6	-0.265	5.214	0.000
6	-0.379	-6.213	0.000	1	-0.696	6.214	0.000
1	-1.298	-6.795	0.000	7	-1.101	4.188	0.000
6	-0.422	-4.836	0.000	1	-0.649	3.249	0.000
6	2.061	-4.773	-0.001	6	-2.501	4.161	0.000
6	0.802	-4.035	-0.001	6	-3.345	5.249	0.000
8	0.73	-2.783	0.002	1	-2.944	6.26	0.000

6	3.279	-4.064	0.000	6	-4.753	5.074	0.000
1	4.216	-4.619	0.000	1	-5.396	5.948	0.000
7	3.354	-2.742	0.000	6	-5.298	3.809	0.000
1	2.436	-2.248	0.000	1	-6.378	3.681	0.000
6	4.47	-1.896	0.000	6	-3.021	2.794	0.000
6	5.793	-2.28	0.000	6	-4.472	2.65	0.000
1	6.064	-3.333	0.000	8	-2.226	1.822	0.000
6	6.829	-1.309	0.001	6	-5.041	1.36	0.000
1	7.862	-1.639	0.001	1	-6.125	1.259	0.000
6	6.525	0.034	0.001	7	-4.324	0.247	0.000
1	7.324	0.773	0.001	1	-3.292	0.385	0.000
6	5.176	0.485	0.000	6	-4.731	-1.093	0.000
6	4.086	-0.485	0.000	6	-6.027	-1.56	0.001
8	2.873	-0.167	0.000	1	-6.865	-0.867	0.001
6	4.877	1.863	0.000	6	-6.294	-2.954	0.001
1	5.694	2.582	0.001	1	-7.324	-3.295	0.001
7	3.643	2.341	0.000	6	-5.259	-3.862	0.001
1	2.889	1.621	0.000	1	-5.471	-4.929	0.001
6	3.184	3.665	0.000	6	-3.591	-2.009	0.000
6	3.958	4.804	0.000	6	-3.903	-3.434	0.000
1	5.044	4.735	0.000	8	-2.422	-1.554	-0.001
6	3.356	6.089	0.000	6	-2.851	-4.373	0.000
1	3.989	6.97	0.000	1	-3.09	-5.436	0.000
6	1.985	6.215	0.000	7	-1.571	-4.035	-0.001
1	1.529	7.203	-0.001	1	-1.384	-3.01	-0.001

Zero-point energy for Pentacycle **1e** keto-enamine

B3LYP/6-31G* = -1998.66248443 HT/particle
B3LYP/6-31G** = -1998.71228014 HT/particle

Relevant thermal parameters calculated using B3LYP/6-31G** for Pentacycle **1e** keto-enamine

Sum of electronic and zero-point Energies: -1998.176617 HT/particle
Sum of electronic and thermal Energies: -1998.141594 HT/particle
Sum of electronic and thermal Enthalpies: -1998.140649 HT/particle
Sum of electronic and thermal Free Energies: -1998.243296 HT/particle

$H° = -5.245671 \times 10^6$ kJ mol^{-1}
$G° = -5.245941 \times 10^6$ kJ mol^{-1}

$S° = 903.8294\ J\ mol^{-1}\ K^{-1}$

Calculation of Hexacycle enol-imine

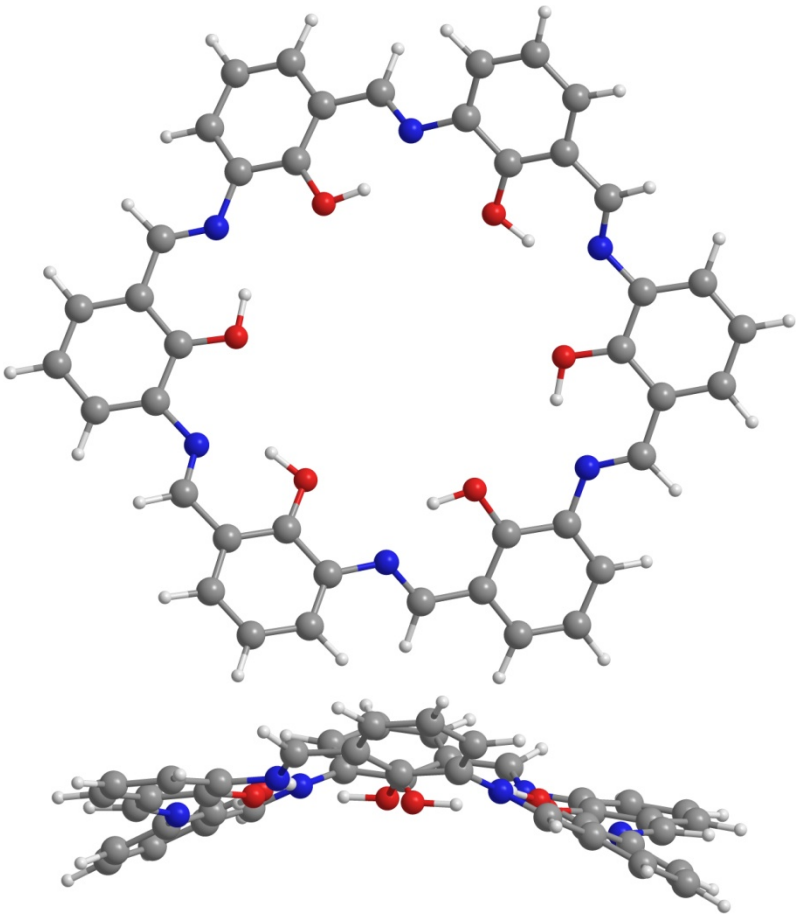


Figure S46: Optimized structure of Hexacycle enol-imine (B3LYP/6-31G*)

Optimized Cartesian Coordinates for Hexacycle enol-imine

6	2.469	4.24	0.527	6	2.498	-4.237	-0.469
6	3.137	6.718	1.708	6	4.59	-4.994	-1.452
6	1.49	5.261	0.653	6	4.046	-6.26	-1.684
6	3.791	4.486	0.991	6	1.948	-5.529	-0.694
6	4.098	5.727	1.580	1	5.601	-4.78	-1.786
6	1.838	6.478	1.246	1	4.641	-7.026	-2.172
1	5.111	5.895	1.942	1	2.301	-7.502	-1.476
1	1.068	7.231	1.384	8	-1.797	3.248	0.086
1	3.38	7.666	2.178	1	-0.867	3.584	0.249
8	2.105	3.088	-0.038	8	1.797	-3.248	0.086
6	4.82	3.468	0.882	1	0.867	-3.584	0.249
1	5.791	3.709	1.335	7	-4.318	2.684	-0.591
7	4.596	2.339	0.299	6	-5.57	2.398	-0.472

6	5.571	1.345	0.148	1	-6.352	3.168	-0.517
6	7.401	-0.76	-0.207	6	-6.022	1.036	-0.253
6	6.952	1.575	0.155	6	-6.952	-1.575	0.155
6	5.09	0.027	-0.080	1	-5.09	-0.027	-0.080
6	6.022	-1.036	-0.253	1	-7.401	0.76	-0.207
6	7.867	0.533	-0.015	1	-7.867	-0.533	-0.015
1	7.318	2.592	0.269	1	-5.571	-1.345	0.148
1	8.933	0.74	-0.010	1	-8.101	1.581	-0.343
1	8.101	-1.581	-0.343	1	-8.933	-0.74	-0.010
1	2.904	2.483	-0.048	1	-7.318	-2.592	0.269
7	0.189	4.952	0.231	6	-1.49	-5.261	0.653
6	-0.578	5.832	-0.317	6	-4.098	-5.727	1.580
1	-0.22	6.847	-0.535	6	-1.838	-6.478	1.246
8	3.771	-0.167	-0.104	6	-2.469	-4.24	0.527
1	3.603	-1.14	-0.281	6	-3.791	-4.486	0.991
6	5.57	-2.398	-0.472	6	-3.137	-6.718	1.708
1	6.352	-3.168	-0.517	1	-1.068	-7.231	1.384
7	4.318	-2.684	-0.591	1	-3.38	-7.666	2.178
6	-1.948	5.529	-0.694	1	-5.111	-5.895	1.942
6	-4.59	4.994	-1.452	8	-2.105	-3.088	-0.038
6	-2.498	4.237	-0.469	1	-2.904	-2.483	-0.048
6	-2.738	6.522	-1.300	8	-3.771	0.167	-0.104
6	-4.046	6.26	-1.684	1	-3.603	1.14	-0.281
6	-3.847	3.98	-0.835	6	-4.82	-3.468	0.882
1	-2.301	7.502	-1.476	1	-5.791	-3.709	1.335
1	-4.641	7.026	-2.172	7	-4.596	-2.339	0.299
1	-5.601	4.78	-1.786	7	-0.189	-4.952	0.231
6	3.847	-3.98	-0.835	6	0.578	-5.832	-0.317
6	2.738	-6.522	-1.300	1	0.22	-6.847	-0.535

Zero-point energy for Hexacycle enol-imine

B3LYP/6-31G* = -2398.38986681 HT/particle
B3LYP/6-31G** = -2398.46217273 HT/particle

Relevant thermal parameters calculated using B3LYP/6-31G** for Hexacycle enol-imine

Sum of electronic and zero-point Energies: -2397.820286 HT/particle
Sum of electronic and thermal Energies: -2397.778045 HT/particle
Sum of electronic and thermal Enthalpies: -2397.777101 HT/particle

Sum of electronic and thermal Free Energies: -2397.895598 HT/particle

$H° = -6.294828 \times 10^6$ kJ mol^{-1}
$G° = -6.295139 \times 10^6$ kJ mol^{-1}
$S° = 1043.392$ J mol^{-1} K^{-1}

Calculation of Hexacycle keto-enamine

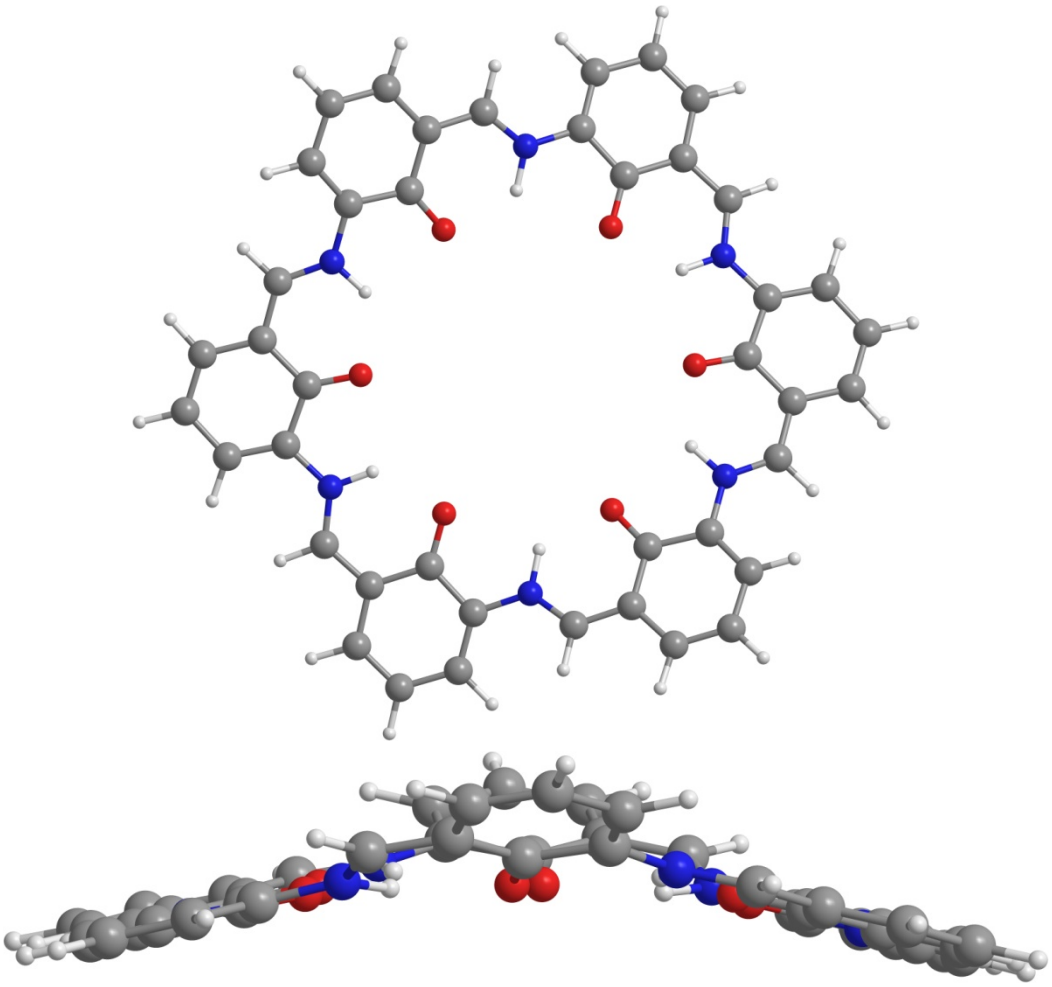


Figure S47: Optimized structure of Hexacycle keto-enamine (B3LYP/6-31G*)

Optimized Cartesian Coordinates for Hexacycle keto-enamine

6	-3.909	-3.132	-0.318	6	-1.649	7.382	1.566
6	-5.674	-5.352	-0.833	6	0.163	5.934	0.820
6	-3.46	-4.521	-0.242	1	-3.635	6.534	1.479
6	-5.321	-2.947	-0.645	1	-2.003	8.32	1.980
6	-6.162	-4.07	-0.892	1	0.411	7.955	1.560
6	-4.309	-5.571	-0.515	8	0.403	-3.724	0.096
1	-7.208	-3.893	-1.136	8	-0.403	3.724	0.097

1	-3.934	-6.592	-0.510	7	3.056	-4.115	0.380
1	-6.316	-6.201	-1.041	6	4.353	-4.233	0.136
8	-3.118	-2.184	-0.106	1	4.758	-5.242	0.173
6	-5.869	-1.657	-0.703	6	5.223	-3.176	-0.172
1	-6.928	-1.563	-0.933	6	7.039	-1.104	-0.749
1	-5.207	-0.529	-0.490	6	4.725	-1.804	-0.208
6	-5.724	0.777	-0.499	6	6.593	-3.458	-0.438
6	-6.593	3.458	-0.438	6	7.482	-2.451	-0.724
6	-7.039	1.104	-0.749	6	5.724	-0.777	-0.499
6	-4.725	1.804	-0.208	1	6.928	-4.493	-0.409
6	-5.223	3.176	-0.172	1	8.525	-2.671	-0.926
6	-7.482	2.451	-0.723	1	7.769	-0.329	-0.971
1	-7.769	0.329	-0.971	6	3.46	4.521	-0.242
1	-8.525	2.671	-0.926	6	6.162	4.07	-0.891
1	-6.928	4.493	-0.408	6	4.309	5.571	-0.515
7	-2.108	-4.675	0.104	6	3.909	3.132	-0.318
6	-1.535	-5.775	0.570	6	5.321	2.947	-0.645
1	-2.198	-6.615	0.767	6	5.674	5.352	-0.833
8	-3.527	1.498	-0.002	1	3.934	6.592	-0.510
6	-4.353	4.233	0.136	1	6.316	6.201	-1.040
1	-4.758	5.242	0.173	1	7.208	3.893	-1.136
7	-3.056	4.115	0.380	8	3.118	2.184	-0.106
6	-0.163	-5.934	0.820	8	3.527	-1.498	-0.002
6	2.583	-6.357	1.266	6	5.869	1.657	-0.703
6	0.765	-4.846	0.521	1	6.928	1.563	-0.933
6	0.311	-7.172	1.339	7	5.207	0.529	-0.490
6	1.649	-7.382	1.566	7	2.108	4.675	0.104
6	2.178	-5.152	0.738	6	1.535	5.775	0.569
1	-0.411	-7.955	1.560	1	2.198	6.615	0.767
1	2.003	-8.32	1.980	1	-4.199	-0.621	-0.278
1	3.635	-6.534	1.479	1	-2.652	3.172	0.254
6	-2.178	5.152	0.738	1	-1.495	-3.848	0.010
6	-0.311	7.172	1.339	1	1.495	3.848	0.010
6	-0.765	4.846	0.521	1	4.199	0.621	-0.278
6	-2.583	6.357	1.266	1	2.652	-3.172	0.254

Zero-point energy for Hexacycle keto-enamine

B3LYP/6-31G* = -2398.34078744 HT/particle
B3LYP/6-31G** = -2398.45593025 HT/particle

Relevant thermal parameters calculated using B3LYP/6-31G** for Hexacycle keto-enamine

Sum of electronic and zero-point Energies: -2397.811150 HT/particle
Sum of electronic and thermal Energies: -2397.768357 HT/particle
Sum of electronic and thermal Enthalpies: -2397.767413 HT/particle
Sum of electronic and thermal Free Energies: -2397.888294 HT/particle

$H° = -6.294802 \times 10^6$ kJ mol^{-1}
$G° = -6.295119 \times 10^6$ kJ mol^{-1}
$S° = 1064.383$ J mol^{-1} K^{-1}

Calculated Thermodynamic and Equilibrium Data

$K_1 = 2.0 \times 10^9$

(1) 5 Hexacycle Enol-imine $\rightleftharpoons$ 6 Pentacycle Enol-imine

$\Delta H° = 22.984$ kJ mol^{-1}
$\Delta S° = 255.10$ J mol^{-1} K^{-1}
$\Delta G° = -53.073$ kJ mol^{-1}
$K = 1.9960 \times 10^9 = 2.0 \times 10^9$

$K_2 = 1.1 \times 10^{-3}$

(2) Pentacycle Enol-imine $\rightleftharpoons$ Pentacycle Keto-imine

$\Delta H° = 14.376$ kJ mol^{-1}
$\Delta S° = -8.1801$ J mol^{-1} K^{-1}
$\Delta G° = 16.815$ kJ mol^{-1}
$K = 0.0011328$

$K_3 = 2.3 \times 10^3$

(3) Hexacycle Keto-imine $\rightleftharpoons$ Hexacycle Enol-imine

$\Delta H° = -25.434$ kJ mol^{-1}
$\Delta S° = -20.992$ J mol^{-1} K^{-1}
$\Delta G° = -19.175$ kJ mol^{-1}
$K = 2287.4 = 2.3 \times 10^3$

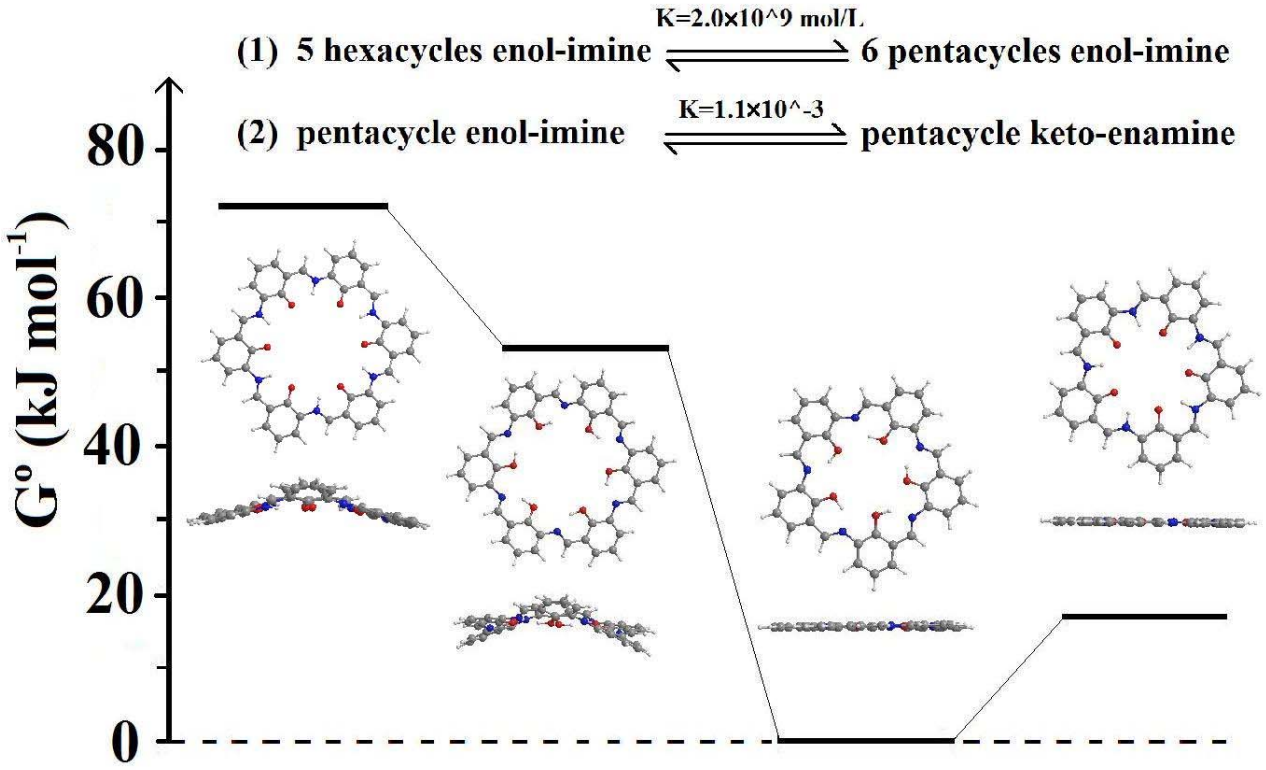


Figure S48: Gibbs free energy and predicted structure of the different macrocycles (B3LYP/6-31G*)

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