

SUPPLEMENTARY INFORMATION

Tuning the excited state properties of [2.2]paracyclophane-based antennas to ensure efficient sensitization of lanthanide ions or singlet oxygen generation.

Shiqi Wu,[‡] Laura Abad Galan,^{†,*} Margaux Roux,[†] Francois Riobé,[†] Boris Le Guennic,[≠] Yannick Guyot,[□] Tanguy Le Bahers,[†] Laurent Micouin,[‡] Olivier Maury,^{†,*} Erica Benedetti^{‡,*}.

[†] Univ Lyon, ENS de Lyon, université Claude Bernard Lyon 1, CNRS UMR 5182, Laboratoire de Chimie, F-69342 Lyon, France. E-mail: laura.abad-galan@ens-lyon.fr, olivier.maury@ens-lyon.fr

[‡] Univ Paris, Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques - UMR8601 CNRS, 45 rue des Saints Pères, 75006 Paris, France. E-mail: erica.benedetti@u-paris.fr

[≠] Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) - UMR 6226, F-35000 Rennes, France.

[□] Univ Lyon, Institut Lumière Matière, UMR 5306 CNRS–Université Claude Bernard Lyon 1, 10 rue Ada Byron, 69622 Villeurbanne Cedex, France.

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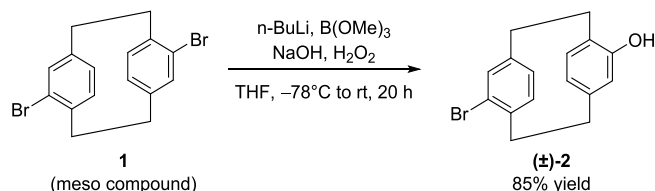
1. General information

All reactions were carried out under inert atmosphere, in oven-dried glassware, using dry solvents unless otherwise specified. All commercially available compounds were purchased from Aldrich Chemical Co., Acros Organics, Alfa Aesar or Carbosynth and used as received. Analytical thin layer chromatography (TLC) was performed on silica gel plates (Merck 60F₂₅₄) visualized either with a UV lamp (254 nm) or by using solutions of *p*-anisaldehyde/sulfuric acid/acetic acid (AcOH) in ethanol (EtOH) or KMnO₄/K₂CO₃/AcOH in water followed by heating. Flash chromatography was performed on silica gel (60-230 mesh) unless otherwise specified. Organic extracts were dried over anhydrous MgSO₄. ¹H NMR and ¹³C NMR spectra were recorded on Bruker Avancell 500 spectrometer, at 500 MHz (H value) or 125 MHz (C value) in CDCl₃ unless otherwise specified. Spectra were referenced to residual chloroform (7.26 ppm, ¹H; 77.0 ppm, ¹³C). Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), and m (multiplet or overlap of nonequivalent resonances), dd (doublet of doublet), td (triplet of doublet), sept (septuplet) and br (broad signal). Coupling constants, *J*, are reported in hertz (Hz). All NMR spectra were obtained at 300K unless otherwise specified. IR spectra were obtained using a spectrum on FT-IR spectrometer (Perkin Elmer). High Resolution mass spectra were recorded on a ThermoFischer Exactive Orbitrap spectrometer.

In the case of the picolinate based derivatives, flash chromatography was performed with analytical-grade solvents using Aldrich silica gel (technical grade, pore size 60 Å, 230-400 mesh particle size). Flexible plates ALUGRAM® Xtra SIL G UV254 from MACHEREY-NAGEL were used for TLC. Compounds were detected by UV irradiation (Bioblock Scientific). NMR spectra were recorded with a Bruker AVANCE III 300 (¹H, 300 MHz and ¹³C, 75MHz) or a Bruker AVANCE DRX500 (¹H, 500 MHz; ¹³C, 125 MHz). Chemical shifts are given in ppm relative to TMS and coupling constants *J* in Hz. High resolution mass spectroscopy measurements were performed at Centre Commun de Spectrométrie de Masse (Villeurbanne, France). Column chromatography was performed using Acros Ogranics (0.035-0.70 mm) silicagel.

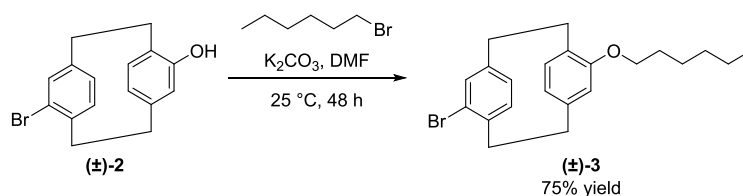
2. Synthetic procedures and characterization data

4-bromo-16-hydroxy[2.2]paracyclophane ((±)-2).



To a solution of **1** (1 eq., 0.7 g, 1.91 mmol) in THF (70 mL) was slowly added the solution of $n\text{-BuLi}$ (2.75 eq., 2.5 M, 2.1 mL, 5.25 mmol) at -78°C . After 30 min, $\text{B}(\text{OMe})_3$ (9.7 eq., 1.92 g, 2.1 mL, 18.5 mmol) was added, the resulting mixture was allowed to warm to r.t and stirred overnight. Subsequently, NaOH_{aq} (0.44 eq., 1 M, 0.841 mL, 0.841 mmol) and aq 30% H_2O_2 (9.69 eq., 2.1 g, 2.1 mL, 18.5 mmol) were added and the mixture was stirred for 1 h. The reaction was quenched by the addition of a sat NH_4Cl aqueous solution. The resulting mixture was extracted with DCM. The combined organic layers were dried over MgSO_4 and concentrated under reduced pressure. Purification of the crude residue by flash chromatography (SiO_2 , eluent: $\text{Cy}/\text{AcOEt} = 15:1$) afforded **(±)-2** (492 mg, 1.62 mmol, 85 %) as an amorphous white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.98 (dd, $J = 7.8, 1.7$ Hz, 1H), 6.81 (dd, $J = 7.7, 1.7$ Hz, 1H), 6.47 (d, $J = 1.5$ Hz, 1H), 6.42 (d, $J = 7.8$ Hz, 1H), 6.35 (d, $J = 7.7$ Hz, 1H), 5.58 (d, $J = 1.6$ Hz, 1H), 4.44 (br, s, 1H), 3.49 (ddd, $J = 13.0, 10.4, 2.2$ Hz, 1H), 3.36 (ddd, $J = 13.3, 10.2, 2.8$ Hz, 1H), 3.14-3.05 (m, 2H), 3.02-2.87 (m, 2H), 2.80 (ddd, $J = 13.3, 10.7, 5.4$ Hz, 1H), 2.68 (ddd, $J = 13.6, 10.7, 5.3$ Hz, 1H) ppm. $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 153.6 (C), 141.5 (C), 141.1 (C), 138.4 (C), 137.5 (CH), 134.5 (CH), 133.8 (CH), 127.7 (CH), 126.5 (C), 124.8 (C), 122.9 (CH), 122.3 (CH), 35.4 (CH_2), 33.2 (CH_2), 32.8 (CH_2), 30.4 (CH_2) ppm. IR (neat): 3351, 2932, 1573, 1417, 1320, 1268, 1093, 1033, 869, 830 cm^{-1} . HRMS (ESI): m/z $[\text{M} - \text{H}]^-$ calcd for $\text{C}_{16}\text{H}_{14}\text{OBr}$: 301.0234; found: 301.0228.

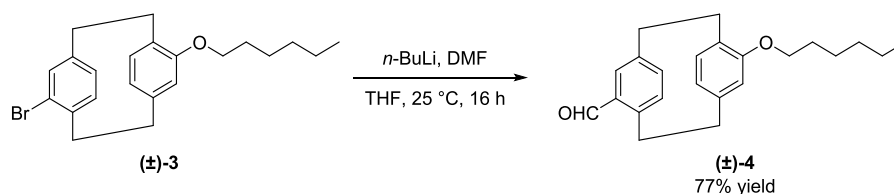
4-bromo-16-hexyloxy[2.2]paracyclophane ((±)-3).



To a solution of **(±)-2** (1 eq., 300 mg, 0.989 mmol) in DMF (18 mL) was added K_2CO_3 (2 eq., 273 mg, 1.98 mmol) and 1-bromohexane (1.5 eq., 244 mg, 0.209 mL, 1.48 mmol). The reaction mixture was stirred for 48 h at r.t under Ar, then poured into water, and extracted with ethyl acetate. The combined organic layer were washed with brine, dried over MgSO_4 , and concentrated *in vacuo* to give a crude mixture.

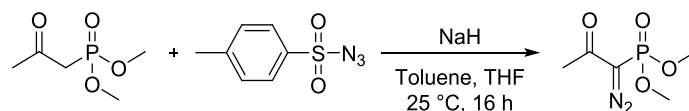
Purification of the crude residue by silica gel column chromatography (eluent: Cy/AcOEt = 500:1) afforded (\pm)-**3** (287 mg, 0.741 mmol, 75 %) as an amorphous white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 6.80 (dd, $J = 7.7, 1.6$ Hz, 1H), 6.73 (dd, $J = 7.8, 1.7$ Hz, 1H), 6.44 (d, $J = 1.7$ Hz, 1H), 6.39 (d, $J = 7.7$ Hz, 1H), 6.37 (d, $J = 7.6$ Hz, 1H), 5.65 (d, $J = 1.6$ Hz, 1H), 3.86 (dt, $J = 9.0, 6.6$ Hz, 1H), 3.68 (dt, $J = 9.0, 6.2$ Hz, 1H), 3.52-3.45 (m, 2H), 3.17-3.10 (m, 1H), 3.07-3.00 (m, 1H), 3.00-2.90 (m, 2H), 2.84-2.76 (m, 1H), 2.64-2.57 (m, 1H), 1.90-1.77 (m, 2H), 1.64-1.52 (m, 2H), 1.44-1.38 (m, 4H), 0.98-0.93 (m, 3H) ppm. $^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 157.3 (C), 142.0 (C), 140.8 (C), 138.2 (C), 137.4 (CH), 133.8 (CH), 133.3 (CH), 127.9 (CH), 126.8 (C), 126.6 (C), 121.9 (CH), 117.3 (CH), 66.9 (CH_2), 35.5 (CH_2), 33.3 (CH_2), 33.2 (CH_2), 31.7 (CH_2), 30.9 (CH_2), 29.5 (CH_2), 26.1 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm. **IR** (neat): 2930, 2854, 1586, 1497, 1415, 1390, 1252, 1147, 1127, 1034, 893, 861, 726 cm^{-1} .

4-hexyloxy-16-formyl[2.2]paracyclophane ((\pm)-4**).**



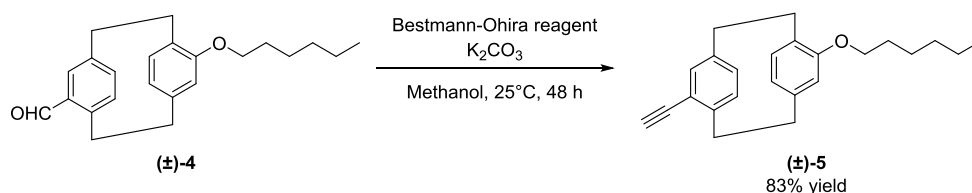
To a flame-dried round-bottomed flask was added (\pm)-**3** (1 eq., 265 mg, 0.684 mmol) and THF (26 mL). The solution was cooled to -78 $^\circ\text{C}$ in a dry ice/acetone bath and $n\text{-BuLi}$ (2 eq., 2.5 M, 0.547 mL, 1.37 mmol) was added dropwise via syringe turning the mixture yellow. The reaction was stirred for 1 h 30 min, then DMF (8 eq., 400 mg, 0.423 mL, 5.47 mmol) was added dropwise via syringe turning the mixture colourless. The solution was allowed to warm to r.t and stirred overnight. The mixture was quenched with a saturated aqueous NH_4Cl solution, and THF was removed under vacuum. The resulting solution was taken up with DCM and washed three times with distilled water. The organic layer was collected, dried over MgSO_4 and concentrated under reduced pressure. The crude product was purified via column chromatography (eluent: Cy/AcOEt = 100:1) to give (\pm)-**4** (178 mg, 0.529 mmol, 77 %) as an amorphous white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 9.90 (s, 1H), 6.97 (dd, $J = 7.7, 2.0$ Hz, 1H), 6.85 (d, $J = 1.9$ Hz, 1H), 6.50 (d, $J = 7.7$ Hz, 1H), 6.34 (d, $J = 7.6$ Hz, 1H), 6.12 (dd, $J = 7.7, 1.7$ Hz, 1H), 5.63 (d, $J = 1.6$ Hz, 1H), 4.10 (ddd, $J = 12.5, 10.3, 1.5$ Hz, 1H), 3.85 (dt, $J = 9.0, 6.5$ Hz, 1H), 3.65 (dt, $J = 9.0, 6.2$ Hz, 1H), 3.51-3.44 (m, 1H), 3.20-3.14 (m, 1H), 3.14-3.09 (m, 2H), 3.01-2.93 (m, 1H), 2.92-2.84 (m, 1H), 2.67-2.60 (m, 1H), 1.89-1.78 (m, 2H), 1.64-1.51 (m, 2H), 1.43-1.38 (m, 4H), 0.98-0.93 (m, 3H) ppm. $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ : 192.2 (CH), 157.2 (C), 142.2 (C), 141.5 (C), 140.8 (C), 137.2 (CH), 136.4 (C), 134.3 (CH), 133.7 (CH), 133.2 (CH), 127.5 (C), 123.5 (CH), 117.1 (CH), 66.9 (CH_2), 34.6 (CH_2), 33.4 (CH_2), 33.3 (CH_2), 31.7 (CH_2), 30.7 (CH_2), 29.5 (CH_2), 26.1 (CH_2), 22.7 (CH_2), 14.1 (CH_3) ppm. **IR** (neat): 2930, 2856, 1690, 1593, 1496, 1416, 1248, 1146, 1120, 1032, 875, 724 cm^{-1} . **HRMS** (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{29}\text{O}_2$: 337.2162; found: 337.2152.

Synthesis of Bestmann-Ohira reagent:



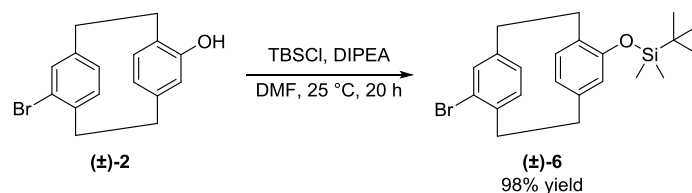
NaH (1.5 eq., 144 mg, 3.6 mmol) was suspended in toluene (6 ml) and THF (1.4 mL) at 0 °C. Dimethyl acetylmethylphosphonate (1 eq., 420 mg, 0.349 mL, 2.4 mmol) previously dissolved in toluene (3.5 mL) was added to the suspension. The mixture was stirred for 1 h at 0 °C. Then *p*-Toluenesulfonyl azide (1 eq., 473 mg, 2.4 mmol) dissolved in toluene (2.5 mL) was added. The reaction was stirred overnight at r.t., then the mixture was filtered over Celite[®], and the filtrate was concentrated under reduced pressure without heating. The desired product (460 mg, 2.39 mmol, quantitative yield) was isolated as a yellow oil and used in the next synthetic steps without any further purification. Spectroscopic data were consistent with the literature data for this compound.¹ ¹H NMR (500 MHz, CDCl₃): δ 3.82 (d, *J* = 11.9 Hz, 6H), 2.24 (s, 3H).

Synthesis of 4-hexyloxy-16-ethynyl[2.2]paracyclophane ((±)-5).



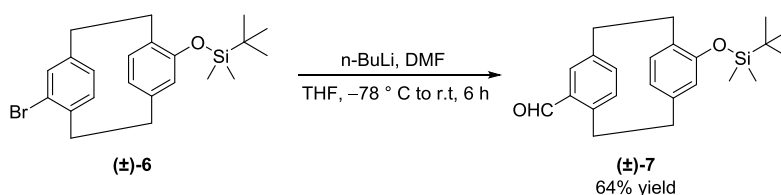
To a solution of (±)-4 (1 eq., 120 mg, 0.357 mmol) and K₂CO₃ (2 eq., 98.6 mg, 0.713 mmol) in MeOH (5.35 mL) was added the Bestmann–Ohira reagent (5 eq., 342 mg, 1.78 mmol) under an argon atmosphere. The resulting solution was stirred at rt for 48 h. The reaction mixture was then diluted with Et₂O, washed with a saturated aqueous solution of NaHCO₃, and dried over MgSO₄. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography over silica gel (eluent: Cy/AcOEt = 250:1) to afford derivative (±)-5 (98 mg, 0.295 mmol, 83 %) as a white amorphous solid. ¹H NMR (500 MHz, CDCl₃): δ 6.75 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.66 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.47 (d, *J* = 1.8 Hz, 1H), 6.40 (d, *J* = 7.9 Hz, 1H), 6.38 (d, *J* = 7.6 Hz, 1H), 5.65 (s, 1H), 3.86 (dt, *J* = 8.9, 6.7 Hz, 1H), 3.67 (dt, *J* = 9.0, 6.1 Hz, 1H), 3.58 (ddd, *J* = 13.2, 10.5, 2.9 Hz, 1H), 3.46 (ddd, *J* = 12.8, 9.9, 2.7 Hz, 1H), 3.25 (s, 1H), 3.19–3.12 (m, 1H), 3.07–2.92 (m, 3H), 2.86–2.78 (m, 1H), 2.63–2.56 (m, 1H), 1.88–1.77 (m, 2H), 1.64–1.53 (m, 2H), 1.45–1.37 (m, 4H), 0.98–0.92 (m, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 157.1 (C), 142.1 (C), 141.2 (C), 140.1 (C), 137.9 (CH), 134.1 (CH), 132.2 (CH), 129.3 (CH), 127.1 (C), 123.6 (C), 122.5 (CH), 117.4 (CH), 84.0 (C), 80.0 (CH), 66.8 (CH₂), 33.9 (CH₂), 33.9 (CH₂), 33.5 (CH₂), 31.7 (CH₂), 31.0 (CH₂), 29.5 (CH₂), 26.1 (CH₂), 22.7 (CH₂), 14.1 (CH₃) ppm. IR (neat): 3309, 2955, 2930, 2856, 1593, 1497, 1416, 1251, 1148, 1114, 1034, 867, 727 cm⁻¹. HRMS (ESI): *m/z* [M+H]⁺ calcd for C₂₄H₂₉O: 333.2213; found: 333.2202.

({11-bromotricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4(16),5,7(15),10,13-hexaen-5-yl}oxy) (tert-butyl)dimethylsilane ((±)-6).



A 50 mL round bottom flask was charged with (±)-**2** (1 eq., 1 g, 3.3 mmol) and TBSCl (4 eq., 1.99 g, 13.2 mmol) in DMF (30 mL). The flask was evacuated and refilled with argon 3 times, then DIPEA (6 eq., 2.56 g, 3.27 mL, 19.8 mmol) was added. The resulting mixture was stirred at r.t overnight. The reaction was diluted with EtOAc and quenched by H₂O. The two phases were separated and the aqueous layer was extracted with EtOAc. The combined organic phase was dried over MgSO₄ and concentrated under reduced pressure. The crude residue was purified by column chromatography (SiO₂, eluent: Cy/EtOAc = 200:1) to afford (±)-**6** (1.35 g, 3.22 mmol, 98 %) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 6.95 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.81 (dt, *J* = 7.8, 1.7 Hz, 1H), 6.44 (d, *J* = 1.8 Hz, 1H), 6.38 (dd, *J* = 7.7, 1.2 Hz, 1H), 6.36 (dd, *J* = 7.8, 1.2 Hz, 1H), 5.60 (d, *J* = 1.8 Hz, 1H), 3.47 (ddd, *J* = 12.9, 10.7, 2.2 Hz, 1H), 3.37 (ddd, *J* = 13.0, 10.2, 2.6 Hz, 1H), 3.14-3.06 (m, 1H), 3.06-2.99 (m, 1H), 2.94-2.87 (m, 2H), 2.83-2.76 (m, 1H), 2.60-2.53 (m, 1H), 1.08-1.05 (m, 9H), 0.19 (d, *J* = 1.3 Hz, 3H), 0.08 (d, *J* = 1.3 Hz, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 153.7 (C), 141.8 (C), 140.5 (C), 138.3 (C), 137.3 (CH), 133.9 (2CH), 129.5 (C), 128.3 (CH), 126.9 (CH), 126.3 (C), 123.0 (CH), 35.4 (CH₂), 33.4 (CH₂), 32.9 (CH₂), 31.3 (CH₂), 25.8 (3CH₃), 18.2 (C), -4.04 (CH₃), -4.94 (CH₃) ppm. IR (neat): 2955, 2930, 2856, 1589, 1491, 1412, 1264, 1146, 996, 950, 887, 839, 781 cm⁻¹.

14-[(tert-butyl dimethylsilyl)oxy]tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaene-5-carbaldehyde ((±)-7).



A flame-dried 250 mL round-bottomed flask was added (±)-**6** (1 eq., 1.33 g, 3.19 mmol) and THF (120 mL). The solution was cooled to -78 °C in a dry ice/acetone bath, and *n*-BuLi (1.2 eq., 2.5 M, 1.53 mL, 3.82 mmol) was added dropwise via syringe turning the mixture yellow. The reaction was stirred for 1 h at -78 °C, then DMF (8 eq., 1.86 g, 1.97 mL, 25.5 mmol) was added dropwise turning the mixture colourless. The solution was allowed to warm to r.t slowly and stirred for 6 h. The mixture was then quenched with a saturated aqueous NH₄Cl solution, and THF was removed under vacuum. The resulting solution was taken up with DCM and washed

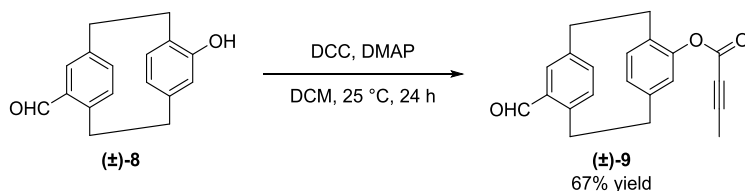
with distilled water three times. The organic layer was collected, dried over MgSO_4 and concentrated under reduced pressure. The crude residue was purified via column chromatography (SiO_2 , eluent: Cy/EtOAc = 50:1) to give (\pm)-**7** (746 mg, 2.04 mmol, 64 %) as a white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 9.92 (s, 1H), 7.20 (dd, $J = 7.7$, 2.0 Hz, 1H), 6.87 (d, $J = 2.0$ Hz, 1H), 6.49 (d, $J = 7.7$ Hz, 1H), 6.32 (d, $J = 7.7$ Hz, 1H), 6.15 (dd, $J = 7.8$, 1.9 Hz, 1H), 5.57 (d, $J = 1.9$ Hz, 1H), 4.12-4.06 (m, 1H), 3.40-3.32 (m, 1H), 3.15-3.04 (m, 3H), 2.98-2.84 (m, 2H), 2.64-2.56 (m, 1H), 1.10-1.03 (m, 9H), 0.19 (s, 3H), 0.07 (s, 3H) ppm. $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ : 192.2 (CH), 153.6 (C), 142.4 (C), 141.1 (C), 140.5 (C), 137.2 (CH), 136.2 (C), 134.8 (CH), 133.9 (CH), 133.6 (CH), 130.2 (C), 126.7 (CH), 124.7 (CH), 34.3 (CH_2), 33.4 (CH_2), 33.1 (CH_2), 31.2 (CH_2), 25.8 (3 CH_3), 18.2 (C), -4.01 (CH_3), -4.93 (CH_3) ppm. **IR** (neat): 2955, 2930, 2857, 1693, 1592, 1560, 1490, 1411, 1263, 1145, 1120, 998, 887, 839, 781 cm^{-1} . **HRMS** (ESI): m/z [$\text{M}+\text{H}$] $^+$ calcd for $\text{C}_{23}\text{H}_{31}\text{O}_2\text{Si}$: 367.2088; found: 367.2078.

4-hydroxy-16-formyl[2.2]paracyclophane ((\pm)-8**).**



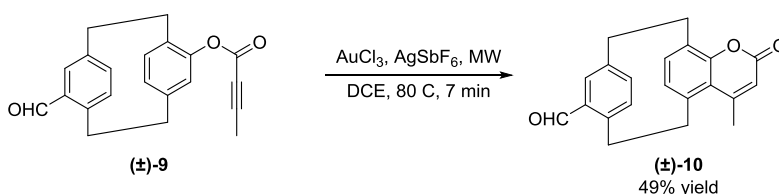
To a stirred solution of (\pm)-**7** (1 eq., 970 mg, 2.65 mmol) in dry DMF (80 mL) was added NaH (1.5 eq., 159 mg, 3.97 mmol) at r.t and the reaction was stirred overnight. After completion, it was quenched by water and diluted with EtOAc. The organic layer was separated, washed with water, dried over MgSO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: Cy/EtOAc = 10:1) to give (\pm)-**8** (597 mg, 2.37 mmol, 89 %). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 9.93(d, $J = 1.1$ Hz, 1H), 7.26-7.23 (m, 1H), 6.89 (t, $J = 1.4$ Hz, 1H), 6.54 (d, $J = 7.7$ Hz, 1H), 6.32 (d, $J = 7.7$ Hz, 1H), 6.14 (dt, $J = 7.8$, 1.5 Hz, 1H), 5.56 (s, 1H), 4.51 (s, 1H), 4.10 (t, $J = 11.8$ Hz, 1H), 3.36 (ddd, $J = 13.4$, 9.8, 3.2 Hz, 1H), 3.18-3.09 (m, 3H), 2.99-2.92 (m, 1H), 2.92- 2.85 (m, 1H), 2.75-2.68 (m, 1H) ppm. $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ : 192.2 (CH), 153.7 (C), 142.5 (C), 141.7 (C), 140.4 (C), 137.3 (CH), 136.3 (C), 134.8 (CH), 134.4 (CH), 133.0 (CH), 125.5 (C), 124.5 (CH), 122.1 (CH), 34.2 (CH_2), 33.3 (CH_2), 33.2 (CH_2), 30.3 (CH_2) ppm. **IR** (neat): 3454, 2927, 2855, 1669, 1589, 1419, 1271, 1223, 1105, 992, 878, 781, 718 cm^{-1} . **HRMS** (ESI): m/z [$\text{M} - \text{H}$] $^-$ calcd for $\text{C}_{17}\text{H}_{15}\text{O}_2$: 251.1076; found: 251.1064.

14-formyltricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl but-2-ynoate ((±)-9).



2-butynoic acid (1.5 eq., 298 mg, 3.55 mmol), DMAP (15 %, 43.4 mg, 0.355 mmol) and (±)-8 (1 eq., 597 mg, 2.37 mmol) were dissolved in dry DCM (35 mL) under Ar atmosphere. Then DCC (1.5 eq., 1 M, 3.55 mL, 3.55 mmol) was added turning the reaction yellow and cloudy. The mixture was stirred at r.t for 24 h, followed by filtration through a plug of silica gel with DCM washing. The crude product was concentrated under reduced pressure and purified by column chromatography (SiO₂, eluent: Cy/EtOAc = 20:1) to yield (±)-9 (502 mg, 1.58 mmol, 67 %) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 9.94 (s, 1H), 7.18 (dd, *J* = 7.8, 2.0 Hz, 1H), 6.95 (d, *J* = 2.0 Hz, 1H), 6.58 (d, *J* = 7.8 Hz, 1H), 6.45 (d, *J* = 7.9 Hz, 1H), 6.38 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.11 (d, *J* = 1.8 Hz, 1H), 4.11 (ddd, *J* = 12.6, 10.8, 1.8 Hz, 1H), 3.23-3.15 (m, 3H), 3.10 (t, *J* = 10.3 Hz, 1H), 3.07-2.99 (m, 1H), 2.96-2.88 (m, 1H), 2.84-2.74 (m, 1H), 2.09 (d, *J* = 0.7 Hz, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃) δ: 192.0 (CH), 151.3 (C), 148.5 (C), 142.7 (C), 141.6 (C), 140.4 (C), 137.0 (CH), 136.6 (C), 135.4 (CH), 134.7 (CH), 134.4 (CH), 131.1 (C), 130.0 (CH), 127.4 (CH), 88.1 (C), 72.2 (C), 34.3 (CH₂), 33.7 (CH₂), 33.1 (CH₂), 30.6 (CH₂), 4.1 (CH₃) ppm. IR (neat): 2933, 2234, 1723, 1686, 1592, 1558, 1492, 1411, 1221, 1114, 1098, 1091, 1043, 884, 783, 741, 719 cm⁻¹. HRMS (ESI): *m/z* [M + Na]⁺ calcd for C₂₁H₁₈O₃Na: 341.1148; found: 341.1139.

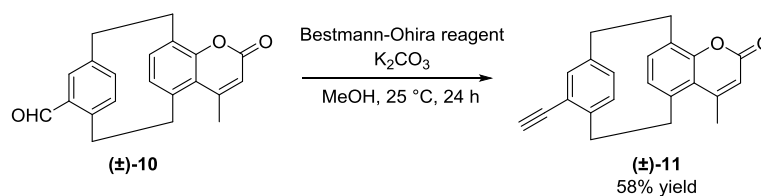
5-methyl-13-oxo-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]jicosa-1(16),4(20),5,7(19),10,14,17 -heptaene-5-carbaldehyde ((±)-10).



A G10 microwave vial was charged with AuCl₃ (8 %, 20 mg, 0.067 mmol) and AgSbF₆ (16 %, 46 mg, 0.13 mmol). The tube was sealed, then evacuated and refilled with argon three times. Then DCE (3 mL) was added and the resulting mixture was stirred at r.t for 5 min. Compound (±)-9 (1 eq., 266 mg, 0.836 mmol) in DCE (9.5 mL) was finally added. The solution was stirred at 80 °C for 7 min under microwave irradiation. After the reaction, the solution was directly charged over silica gel and

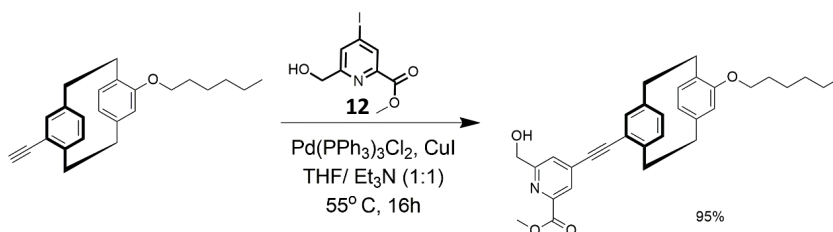
purified by column chromatography (eluent: Pentane/AcOEt = 7:1). Product (\pm)-**10** (130 mg, 0.41 mmol, 49 %) was isolated as an amorphous white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 9.91-9.88 (m, 1H), 7.00-6.97 (m, 1H), 6.80 (dt, $J = 7.9, 1.9$ Hz, 1H), 6.65 (dd, $J = 7.8, 1.6$ Hz, 1H), 6.50 (dd, $J = 7.7, 1.7$ Hz, 1H), 6.31 (dd, $J = 7.9, 1.6$ Hz, 1H), 6.29-6.25 (m, 1H), 4.07 (dd, $J = 13.3, 9.3$ Hz, 1H), 3.75-3.67 (m, 2H), 3.30-3.22 (m, 1H), 3.21-3.14 (m, 1H), 3.12-3.03 (m, 1H), 2.83-2.75 (m, 1H), 2.66-2.58 (m, 1H), 2.53 (t, $J = 1.6$ Hz, 3H) ppm. $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ : 192.0 (CH), 160.4 (C), 153.4 (C), 153.0 (C), 141.1 (C), 141.0 (C), 139.7 (CH), 137.1 (C), 136.7 (CH), 135.4 (CH), 132.3 (CH), 131.8 (CH), 130.5 (C), 128.4 (C), 122.1 (C), 116.3 (CH), 36.2 (CH_2), 34.5 (CH_2), 33.2 (CH_2), 29.8 (CH_2), 22.6 (CH_3) ppm. **IR** (neat): 2931, 1723, 1688, 1573, 1439, 1416, 1356, 1249, 1229, 1192, 1121, 1043, 916, 878, 856, 739, 722 cm^{-1} . **HRMS** (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{19}\text{O}_3$: 319.1329; found: 319.1321.

20-ethynyl-15-methyl-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]jicosa-1(16),4,6,10,14,17,19-heptaen-13-one ((\pm)-11**).**



To a solution of K_2CO_3 (2 eq., 217 mg, 1.57 mmol) in MeOH (9 mL) was added a solution of the Bestmann–Ohira reagent (1.5 eq., 226 mg, 1.18 mmol) in MeOH (4 ml). The resulting mixture was stirred at r.t for 10 min. Then (\pm)-**10** (1 eq., 250 mg, 0.785 mmol) was added under Ar. The reaction stirred overnight at r.t. The mixture was then diluted with Et_2O , washed with 5% aqueous NaHCO_3 solution, and dried over MgSO_4 . The solvent was removed under reduced pressure and the crude residue was purified by column chromatography (SiO_2 , eluent: Cy/EtOAc = 15:1) to afford the desired product (\pm)-**11** (143 mg, 0.455 mmol, 58 %) as an amorphous white solid. $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.05 (d, $J = 7.7$ Hz, 1H), 6.70 (d, $J = 7.7$ Hz, 1H), 6.57 (dd, $J = 7.9, 1.9$ Hz, 1H), 6.55 (d, $J = 1.7$ Hz, 1H), 6.24 (t, $J = 1.2$ Hz, 1H), 6.18 (d, $J = 7.9$ Hz, 1H), 3.68 (ddd, $J = 13.5, 10.5, 2.9$ Hz, 1H), 3.62-3.52 (m, 2H), 3.36-3.27 (m, 2H), 3.19-3.12 (m, 1H), 3.05-2.98 (m, 1H), 2.79-2.71 (m, 1H), 2.57-2.49 (m, 4H) ppm. $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ : 160.7 (C), 153.4 (C), 153.1 (C), 141.3 (C), 140.1 (C), 139.3 (C), 137.3 (CH), 135.6 (CH), 129.8 (CH), 129.6 (CH), 128.2 (CH), 128.1 (CH), 123.8 (C), 122.1 (C), 116.1 (CH), 83.1 (C), 80.9 (CH), 34.8 (CH_2), 34.5 (CH_2), 33.02 (CH_2), 29.8 (CH_2), 22.6 (CH_3) ppm. **IR** (neat): 3285, 2927, 1719, 1574, 1440, 1416, 1356, 1252, 1193, 1043, 915, 856, 774, 731 cm^{-1} . **HRMS** (ESI): m/z $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{22}\text{H}_{18}\text{O}_2\text{Na}$: 337.1199; found: 337.1209.

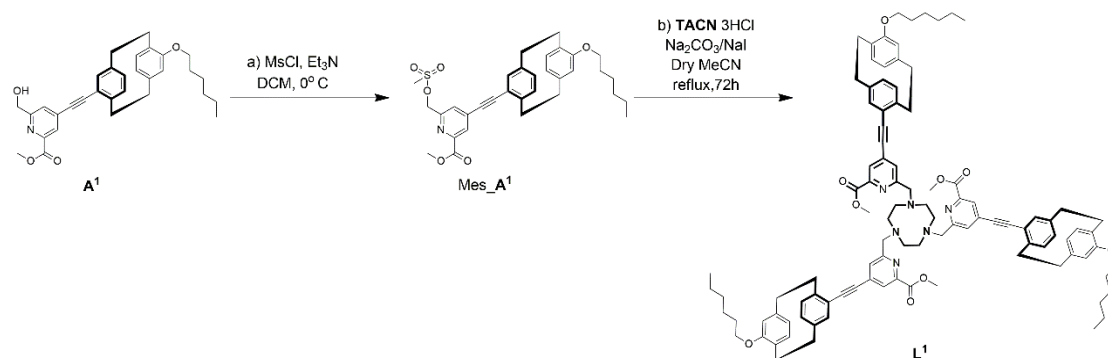
Antenna A¹.



12² (76 mg, 0.26 mmol, 1eq) and (±)-**5** (75 mg, 0.21 mmol, 1.2 eq) were dissolved in a 1:1 THF/Et₃N mixture (10mL) in a Schlenk flask, and the solution was degassed under argon for 30 min. Pd(PPh₃)₂Cl₂ (18 mg, 0.026 mmol, 0.1 eq) and CuI (10 mg, 0.052 mmol, 0.2 eq) were added, the Ar flow was removed and the mixture was stirred overnight at 55 °C. The solvent was evaporated, the residue was dissolved in EtOAc and the mixture was washed with saturated NH₄Cl and brine. The organic layer was collected, dried over Na₂SO₄, filtered and concentrated under reduced pressure. The oily residue was purified by column chromatography on silica gel (eluent = gradient from DCM to DCM:MeOH (97:3) to give a soft yellow solid in 95% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.14 (s, 1H), 7.65 (s, 1H), 6.82 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.62 – 6.33 (m, 4H), 5.68 (s, 1H), 4.90 (d, *J* = 5.1 Hz, 2H), 4.04 (s, 3H), 3.93 – 3.80 (m, 1H), 3.73 – 3.58 (m, 2H), 3.49 (ddd, *J* = 12.6, 9.4, 2.9 Hz, 1H), 3.29 – 2.84 (m, 5H), 2.62 (ddd, *J* = 12.9, 10.1, 6.2 Hz, 1H), 1.92 – 1.74 (m, 2H), 1.50 – 1.33 (m, 4H), 0.95 (t, *J* = 6.8 Hz, 3H). One signal is missing (2H) which is overlapped with the water signal as proved by hsqc experiment.

¹³C NMR (101 MHz, CDCl₃) δ 165.3, 160.4, 157.2, 147.3, 142.4, 141.0, 140.5, 137.6, 134.1, 132.5, 130.2, 127.2, 125.7, 125.3, 123.1, 122.7, 117.5, 96.1, 89.2, 66.9, 64.6, 53.1, 34.2, 34.2, 33.6, 31.7, 31.0, 29.5, 26.1, 22.7, 14.1 (1C is missing) HRMS (ESI): *m/z* [M+Na]⁺ calcd for C₃₂H₃₅NNaO₄: 520.2458; , found: 520.2460; *m/z* [M+H] calcd for C₃₂H₃₆NO₄: 498.2639, found: 498.2638.

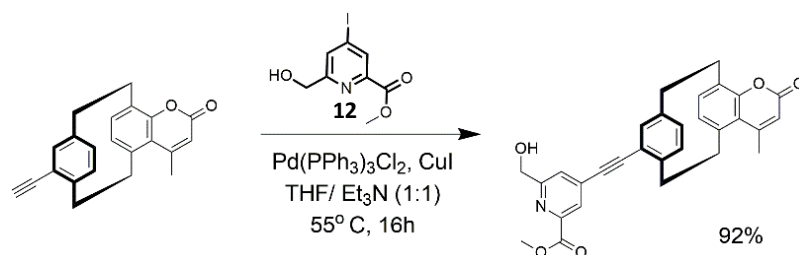
Ligand L¹.



A¹ (100 mg, 0.20 mmol, 1eq) was dissolved in DCM (10 mL) and Et₃N (80 μ L, 0.60 mmol, 3 equiv.). Mesityl chloride (37 mg, 0.32 mmol, 1.6 equiv.) in 2 mL of THF was added, and the mixture was stirred at room temperature. When all the starting material was consumed (monitored by TLC), the solvent was removed under reduced pressure. The residue was then dissolved in CH₂Cl₂ and washed with a saturated aqueous solution of NH₄Cl (3 \times 5 mL) and with brine (3 \times 5 mL). The desired compound **MesA**¹ was obtained in quantitative yields and was used in the next synthetic step without further purification.

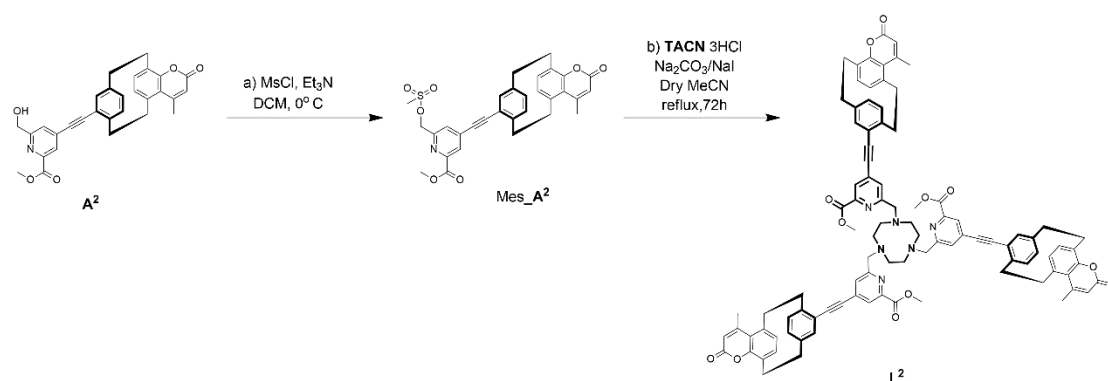
To a solution of **TACN** 3HCl (11 mg, 0.05 mmol, 1eq) in dry MeCN (7 mL), Na₂CO₃ (20 mg, 0.20 mmol, 4 equiv.), and NaI (28 mg, 0.20 mmol, 4 equiv.) were added. 3 cycles of vacuum/argon were applied. To this solution, compound **MesA**¹ (86 mg, 0.15 mmol, 3.1 equiv.) dissolved in dry MeCN (7 mL) was added dropwise, and reaction mixture stir at reflux for 72 h. The solvent was removed under reduce pressure. The obtained residue was dissolved in DCM, and washed with water (3x mL) to remove the residual salts. The organic layer was then dried over MgSO₄, filtered, and concentrated under reduce pressure. The crude product was then purified by silica gel column chromatography (eluent = gradient from DCM to [DCM:NH₃(2M)]:MeOH, 97:3). Compound **L**¹ was isolated as a yellow oil in 55% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (s, 1H), 7.96 (s, 1H), 6.79 (d, J = 7.8 Hz, 1H), 6.64 – 6.33 (m, 4H), 5.63 (s, 1H), 4.05 (s, 2H), 3.99 (s, 3H), 3.84 (dd, J = 15.4, 6.7 Hz, 1H), 3.70 – 3.53 (m, 2H), 3.53 – 3.40 (m, 1H), 3.20 – 2.92 (m, 8H), 2.92 – 2.78 (m, 1H), 2.66 – 2.50 (m, 1H), 1.81 (pt, J = 13.7, 6.6 Hz, 2H), 1.71 – 1.48 (m, 4H), 1.48 – 1.32 (m, 4H), 1.05 – 0.82 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.6, 161.6, 157.2, 147.5, 142.3, 140.9, 140.4, 137.7, 134.0, 133.6, 132.4, 130.0, 127.7, 127.2, 125.3, 123.3, 122.7, 117.4, 95.6, 89.6, 66.9, 64.6, 56.2, 53.0, 34.2, 33.5, 31.7, 30.9, 29.5, 26.1, 22.7, 14.1. **HRMS** (ESI): m/z [M+H]⁺ calcd for C₁₀₂H₁₁₅N₆O₉: 1567.8720, found: 1567.8756; m/z [M+2H]²⁺ calcd for C₁₀₂H₁₁₆N₆O₉ = 784.4396, found: 784.4405.

Antenna A².



12 (75 mg, 0.26 mmol, 1 eq) and (\pm)-**11** (100 mg, 0.32 mmol, 1.25 eq) were dissolved in a 1:1 mixture of THF/Et₃N (10mL) in a Schlenk flask, and the solution was degassed under argon for 30 min. Pd(PPh₃)₂Cl₂ (22 mg, 0.031 mmol, 0.12 eq) and CuI (12 mg, 0.063 mmol, 0.25 eq) were added, the Ar flow was removed and the mixture was stirred overnight at 55 °C. The solvent was evaporated, the residue was dissolved in EtOAc and the mixture was washed with a saturated NH₄Cl solution and brine. The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The oily residue was purified by column chromatography on silica gel (eluent = gradient from DCM to DCM:MeOH (97:3) to afford a soft yellow solid in 92 % yield. **¹H NMR** (300 MHz, CDCl₃) δ 8.18 (s, 1H), 7.70 (s, 1H), 7.00 (d, $J = 7.8$ Hz, 1H), 6.76 (d, $J = 7.7$ Hz, 1H), 6.69 – 6.62 (m, 2H), 6.29 (dd, $J = 4.7, 3.6$ Hz, 2H), 4.95 (d, $J = 5.1$ Hz, 2H), 4.08 (s, 3H), 3.81 – 3.57 (m, 3H), 3.38 – 3.00 (m, 4H), 2.88 – 2.74 (m, 1H), 2.72 – 2.59 (m, 1H), 2.56 (d, $J = 1.0$ Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 165.3, 160.6, 153.5, 153.0, 147.5, 141.5, 140.5, 139.0, 137.1, 135.5, 133.6, 130.0, 129.8, 129.0, 128.4, 127.3, 125.6, 125.3, , 123.3, , 122.2, , 116.2, , 94.8, 89.8, 64.7, 53.1, 35.1, 35.0, 33.3, 29.8, 22.7. **HRMS** (ESI): m/z [M+Na]⁺ calcd for C₃₀H₂₅NNaO₅ 502.1625, found: 502.1623; m/z [M+H] calcd for C₃₀H₂₆NO₅: 480.1805, found: 480.1803.

Ligand L².

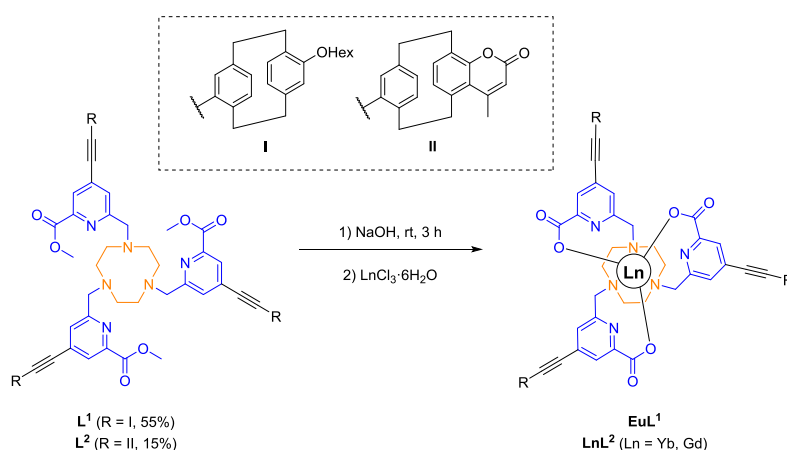


A² (100 mg, 0.21 mmol, 1eq) was dissolved in DCM (10 mL) and Et₃N (50 μ L, 0.630 mmol, 3 equiv.). Mesyl chloride (38 mg, 0.33 mmol, 1.6 equiv.) in 2 mL of THF was added and the mixture was stirred at room temperature. When all the starting material

was consumed (monitored by TLC), the solvent was removed under reduced pressure. The residue was then dissolved in DCM, and washed with a saturated NH_4Cl aqueous solution (3×5 mL) and brine (3×5 mL). The desired compound **MesA**² was obtained in quantitative yields and was used in the next synthetic step without further purification.

To a solution of **TACN** 3HCl (16 mg, 0.07 mmol, 1 eq) in dry MeCN (7 mL), Na_2CO_3 (30 mg, 0.28 mmol, 4 equiv.), and NaI (42 mg, 0.28 mmol, 4 equiv.) were added. Three cycles of vacuum/argon were applied. To this solution, compound **MesA**² (115 mg, 0.21 mmol, 3.1 equiv.) dissolved in dry MeCN (7 mL) was added dropwise, and reaction mixture stirred at reflux for 72 h. The solvent was removed under reduced pressure, and the resulting residue dissolved in DCM, then washed with water (3x mL) to remove the residual salts. The organic layer was collected, dried over MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent = gradient from DCM to DCM:MeOH 97:3). Compound **L**² was isolated as a yellow oil in 15% yield. ¹H NMR (400 MHz, CDCl_3) δ 8.06 (d, $J = 3.2$ Hz, 1H), 7.58 (s, 1H), 6.95 (d, $J = 7.6$ Hz, 1H), 6.74 (d, $J = 7.7$ Hz, 1H), 6.68 – 6.54 (m, 2H), 6.27 (d, $J = 7.7$ Hz, 2H), 4.11 (m, 5H), 3.69 – 3.41 (m, 5H), 3.14 (m, 6H), 2.94 – 2.83 (m, 2H), 2.82 – 2.60 (m, 2H), 2.55 (s, 3H). ¹³C NMR (101 MHz, CDCl_3) δ 165.0, 160.5, 159.7, 153.4, 153.0, 147.9, 141.5, 140.5, 138.9, 137.0, 135.5, 133.7, 130.0, 129.8, 129.1, 128.3, 127.2, 125.9, 123.1, 122.1, 116.2, 95.1, 89.4, 70.6, 60.5, 54.2, 53.6, 51.2, 46.3, 35.1, 34.9, 33.3, 29.8, 22.6. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{96}\text{H}_{85}\text{N}_6\text{O}_{12}$: 1513.6225, found: 1513.6243; m/z $[\text{M}+2\text{H}]^{2+}$ calcd for $\text{C}_{96}\text{H}_{86}\text{N}_6\text{O}_{12}$: 757.3149, found: 757.3146.

Procedure for the synthesis of lanthanide complexes



All complexes were synthesised by first diluting the corresponding ligand (1 eq.) in THF/ H_2O (1:1 mixture, 4 mL). Then, 1M NaOH was added (1.5 mL), and the reaction was heated at 40 °C until complete consumption of the starting material (followed by mass-spectrometry). Then, the pH was adjusted to 6.0 with HCl 0.2 M followed by the addition of the correspondent lanthanide salt $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$ (1.5 eq.). The mixture

was stirred at room temperature for 16 h. THF was then removed by evaporation, and the water layer was extracted with DCM (3 x 5 mL). The organic phase was evaporated, and the resulting solid dried under vacuum to obtain the desired complexes in 92-94% yield.

[EuL¹]. In this case, 10 mg of **L¹** and 3.5 mg of EuCl₃·6H₂O were used for the complexation. The final complex was isolated as a soft yellow solid in 94% yield. **HRMS** (ESI): *m/z* [M+H]⁺ calcd for C₉₉H₁₀₇EuN₆O₉: 838.3650, found: 838.3660; *m/z* [M+2H]²⁺ calcd for C₉₉H₁₀₆EuN₆O₉: 1675.7228, found: 1675.7263.

[YbL²]. In this case, 7 mg of **L²** and 2.7 mg of YbCl₃·6H₂O were used for the complexation. The final complex was isolated as a yellow solid in 92% yield. **HRMS** (ESI): *m/z* [M+Na]⁺ calcd for C₉₃H₇₅N₆NaO₁₂Yb: 1664.4724, found: 1664.4763.

[GdL²]. In this case, 7 mg of **L²** and 2.6 mg of GdCl₃·6H₂O were used for the complexation. The final complex was isolated as a yellow solid in 93% yield. **HRMS** (ESI): *m/z* [M+Na]⁺ calcd for C₉₃H₇₅GdN₆NaO₁₂: 1648.4612, found: 1648.4576; *m/z* [M+2Na]²⁺ calcd for C₉₃H₇₅GdN₆Na₂O: 835.7234, found: 835.7250.

3. Photophysical properties of the pCp chromophores and corresponding antennas

Absorption spectra were recorded on a JASCO V-650 spectrophotometer in diluted solution (ca. 10⁻⁵ or 10⁻⁶ mol L⁻¹), using spectrophotometric grade solvents. Emission spectra were measured using Horiba-Jobin - Yvon Fluorolog-3 fluorimeter. The steady-state luminescence was excited by unpolarised light from a 450 W xenon continuous wave (CW) lamp and detected at an angle of 90° for measurements of dilute solutions (10 mm quartz cuvette) by using a Hamamatsu R928. Near infra-red spectra were recorded using a liquid nitrogen cooled, solid indium/gallium/arsenic detector (850-1600 nm) protected with a RG780 filter. All spectra were corrected for both excitation source light-intensity variation and emission spectral responses. Luminescence quantum yields *Q* were measured in diluted solutions with an absorbance lower than 0.1, by using the following Equation (1):

$$\frac{Q_x}{Q_r} = \left[\frac{A_r(\lambda)}{A_x(\lambda)} \right] \cdot \left[\frac{n_x^2}{n_r^2} \right] \cdot \left[\frac{D_x}{D_r} \right] \quad (1)$$

where *A*(λ) is the absorbance (or optical density) at the excitation wavelength, *n* the refractive index of the solvent and *D* the integrated luminescence intensity. “*r*” and “*x*” stand for reference and sample, respectively. Here, the reference is coumarin-153 in methanol (*Q_r* = 0.45).³ Excitations of reference and sample compounds were performed at the same wavelength. The reported results are the average of 4-5 independent measurements at various absorbances (comprised between 0.01-0.1) for

both sample and reference. The plot of the integrated luminescence intensity vs. absorbance gives a straight line with excellent correlation coefficients and the slope S can be determined for both sample (x) and reference (r). Equation (1) becomes Equation (2).

$$\frac{Q_x}{Q_r} = \left[\frac{S_x}{S_r} \right] \cdot \left[\frac{n_x^2}{n_r^2} \right] \quad (2)$$

For singlet oxygen quantum yield determination ϕ_{Δ} , the principle is exactly the same except that the singlet oxygen luminescence emission band (D) is integrated for both sample (x) and reference (r) compounds. $A(\lambda)$ is the absorbance (or optical density) at the excitation wavelength. In this case it is very important that both experiments are conducted in the same solvent at exactly the same excitation wavelength ($n_x = n_r$). The reported results are the average of 4-5 independent measurements at various absorbances (comprised between 0.01-0.1) for both sample and reference. The plot of the integrated singlet oxygen luminescence intensity vs. absorbance gives straight line with excellent correlation coefficients and the slope S can be determined for both sample (x) and reference (r). In the present case, the reference is phenalenone ($\phi_{\Delta r} = 0.98$ in dichloromethane).⁴

Photophysical data of the OHex substituted chromophore and related antenna

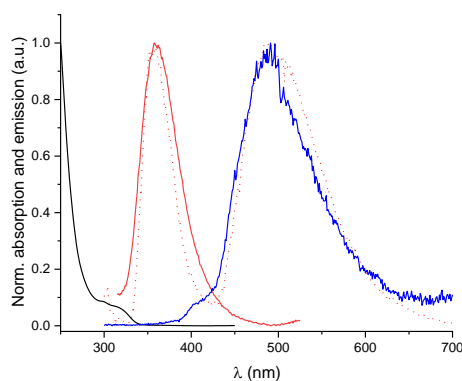


Figure S1. Normalized absorption (black bold), and emission (red bold) of (±)-**5** in dichloromethane at room temperature. 77K emission (red dotted), and phosphorescence spectrum (blue) after application of a 0.1 ms delay.

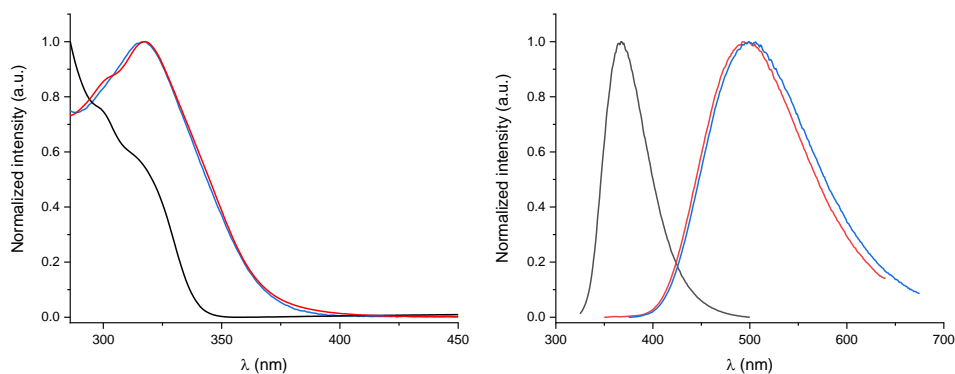


Figure S2. Room temperature absorption (left) and emission (right) spectra of (\pm)-**5** (black trace), **A**¹ (red trace, and **L**¹ (blue trace) in a diluted dichloromethane solution.

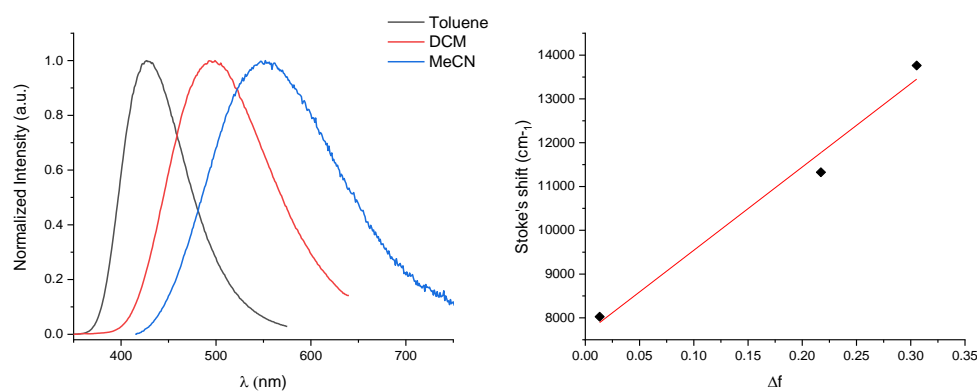


Figure S3. Room temperature emission spectra (left) of **A**¹ in toluene (black trace), dichloromethane (red trace) and acetonitrile (blue trace), and the corresponding Lippert-Mataga plot (right) using Δf as polarity scale.

Photophysical data of the coumarin based pCp chromophore and related antenna

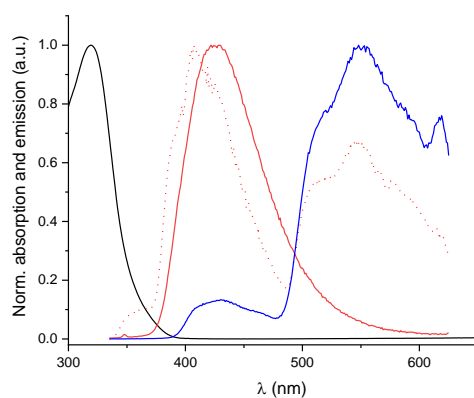


Figure S4. Normalized absorption (black bold), and emission (red bold) of (\pm)-**11** in dichloromethane at room temperature; 77K emission (red dotted), and 77K absorption (black dotted).

phosphorescence spectrum (blue) after application of a 0.1 ms delay.

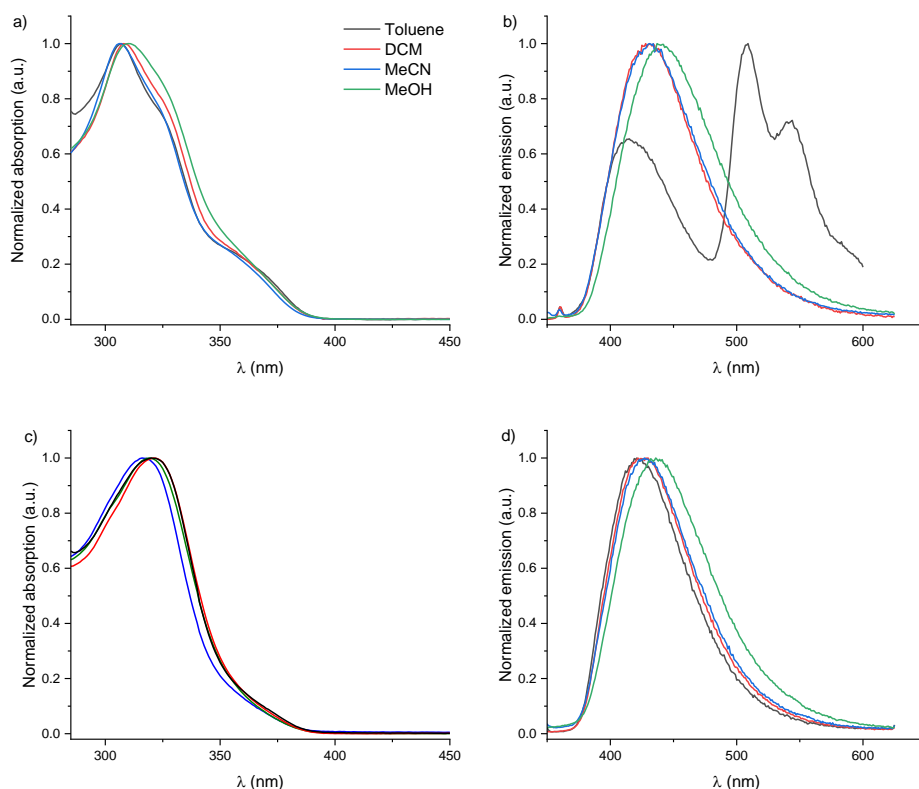


Figure S5. Room temperature absorption (a,c), and emission (b,d) spectra of compounds (\pm)-**11** (top), and **A²** (bottom). The solvents used are toluene (black trace), dichloromethane (red trace), acetonitrile (blue trace), and methanol (green trace).

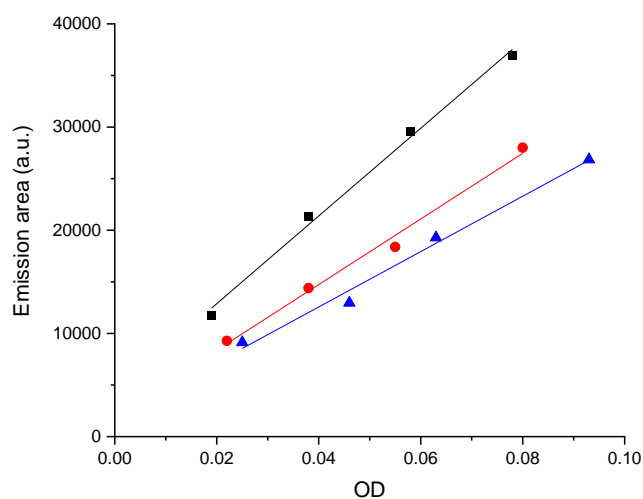


Figure S6. Integrated singlet oxygen emission band area (1,270 nm) vs optical density measured for phenalenone (black square), (\pm)-**11** (red dot), and **A²** (blue triangle) in DCM at room temperature. The lines are the linear regression whose slope is used to calculate the quantum yield efficiency ϕ_{Δ} .

4. Computational details

Molecular calculations were carried out with the Gaussian16 code.⁵ The global hybrid functional CAM-B3LYP was used both for ground state and excited state geometry optimizations.⁶ Structural optimizations and subsequent frequency calculations for both the ground and excited states were performed using an all electron Pople triple zeta basis set with one polarization function on all atoms and one diffuse function of heavier atoms, known as 6-311+G(d,p), for H, C, N and O atoms.⁷ Dichloromethane was considered as solvent using a PCM approach.⁸ The fluorescence energies were obtained by relaxing the first excited state geometry in TD-DFT at the same level of theory.

The Dalton41 program⁹ was used to compute the SOC between the triplet states lower in energy than S_1 and the S_1 state at the S_1 optimized geometry using the quadric-response TD-DFT at the CAM-B3LYP/PCM level with the cc-pVDZ-DK basis set adapted for the Douglas-Kroll calculations.¹⁰ The Spin-Orbit Coupling was computed using the Douglas-Kroll Hamiltonian along with the spin-orbit mean field approach. Dichloromethane was considered as solvent using a PCM approach.

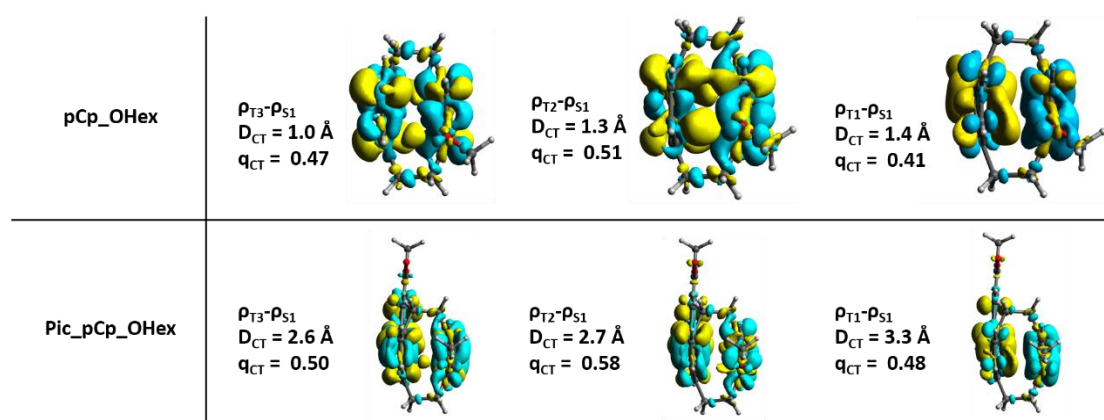


Figure S7. Electron variation density from the S_1 to the calculated T_n states, computed at the S_1 geometry for the OHex derivatives

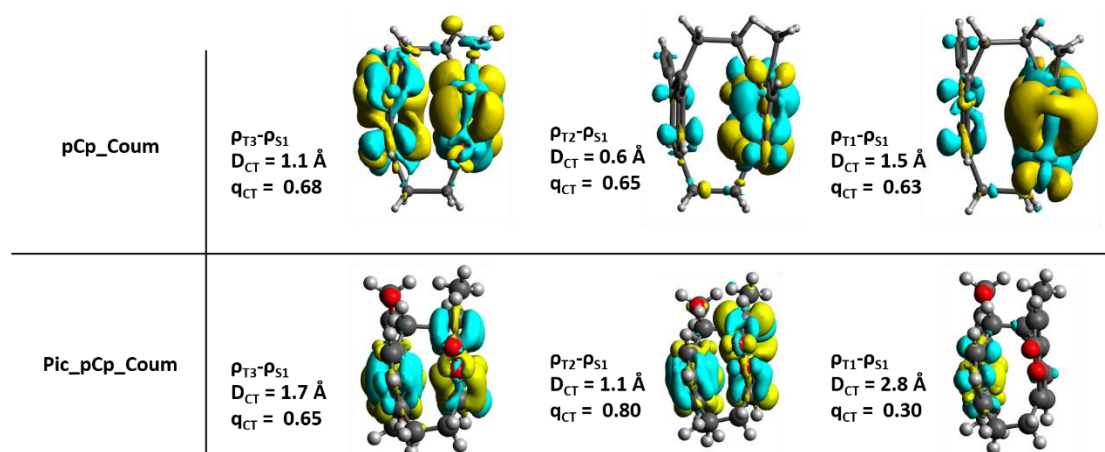


Figure S8. Electron variation density from the S_1 to the calculated T_n states, computed at the S_1 geometry for the coumarin derivatives

5. Photophysical properties of the ligands and related complexes

Europium(III) luminescence lifetimes were measured using the integrated flash-lamp (Horiba Jobin-Yvon, Fluorolog 3), and the luminescence decay was fitted with Origin software. For ytterbium (III) luminescence lifetimes, the sample was excited using a pulsed Nd:YAG laser (SpectraPhysics), operating at 10 Hz. Light emitted at right angles to the excitation beam was focused onto the slits of a monochromator (PTI120), which was used to select the appropriate wavelength. The growth and decay of the luminescence at selected wavelengths was detected using a Ge photodiode (Edinburgh Instruments, EI-P), and recorded using a digital oscilloscope (Tektronix TDS320) before being transferred for analysis. Luminescence lifetimes were obtained by iterative reconvolution of the detector response (obtained by using a scatterer) with exponential components for growth and decay of the metal-centred luminescence.

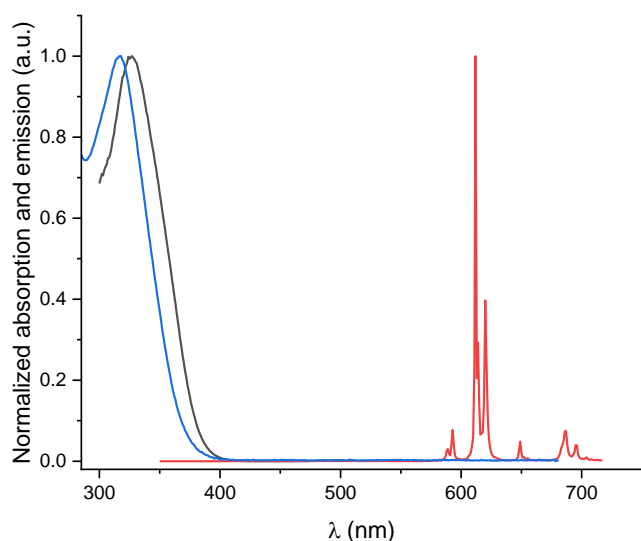


Figure S9. Normalized absorption spectra of the ligand \mathbf{L}^1 (blue trace), and the related complex \mathbf{EuL}^1 (black trace). Normalized emission spectrum of complex \mathbf{EuL}^1 (red trace) upon excitation at $\lambda_{\text{exc}} = 325$ nm. All spectra were recorded in DCM at room temperature.

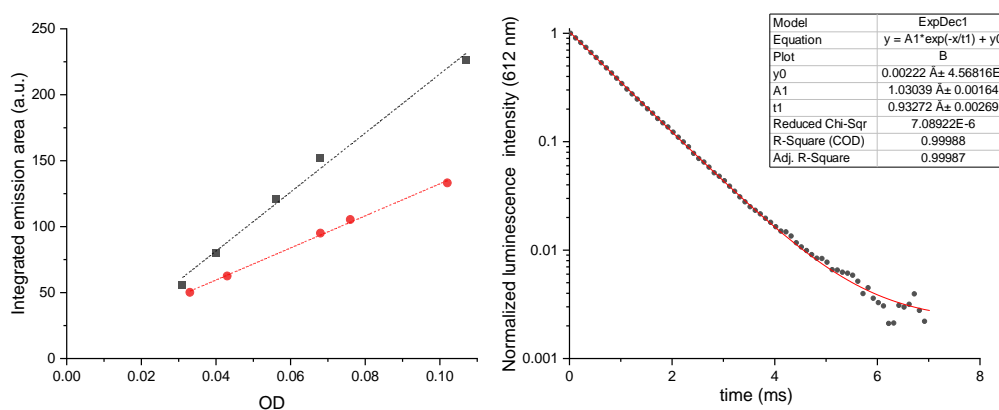


Figure S10. (Left) Integrated emission band area vs optical density measured for \mathbf{EuL}^1 in dichloromethane (red circle), and quinine sulfate (black square) in acidic water at room temperature. The dotted lines are the linear regression whose slope are used to calculate the quantum yield. (Right) Luminescence decay at $\lambda_{\text{em}} = 612$ nm for $[\mathbf{EuL}^1]$ in DCM (log scale). Mono-exponential fit with the corresponding parameters (inset) is plotted in red.

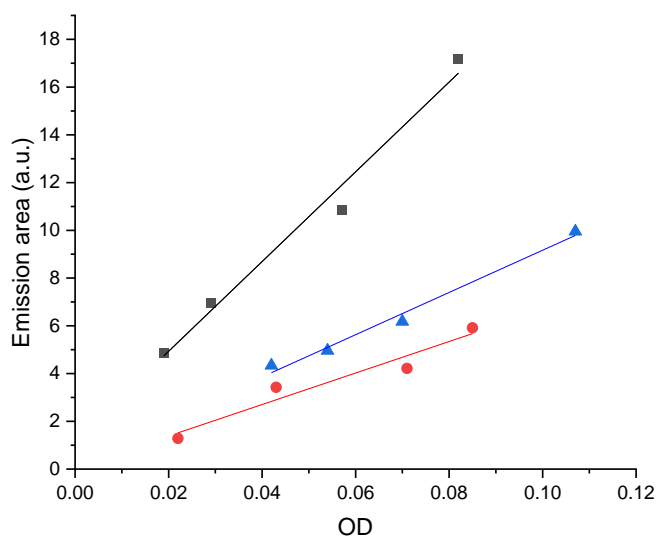


Figure S11. Integrated singlet oxygen emission band area (1,270 nm) vs optical density measured for phenalene (black square), L^2 (red circle) and GdL^2 (blue triangle) in DCM at room temperature. The lines are the linear regression whose slope is used to calculate the quantum yield efficiency ϕ_{Δ} .

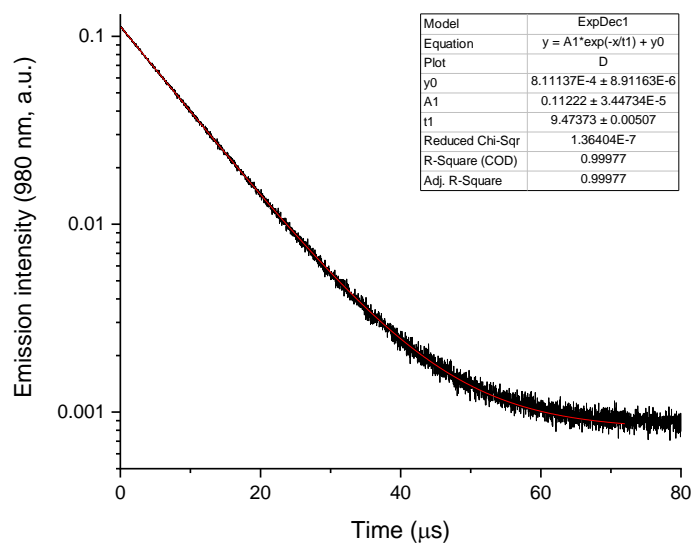
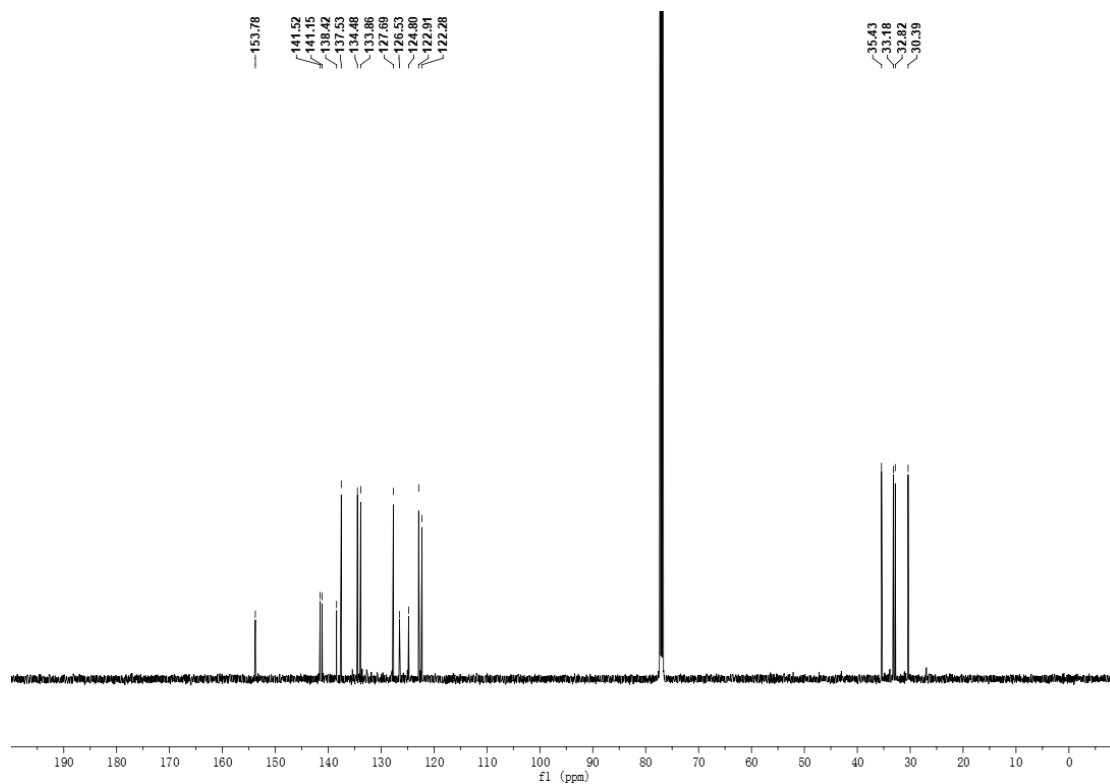
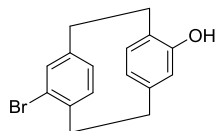
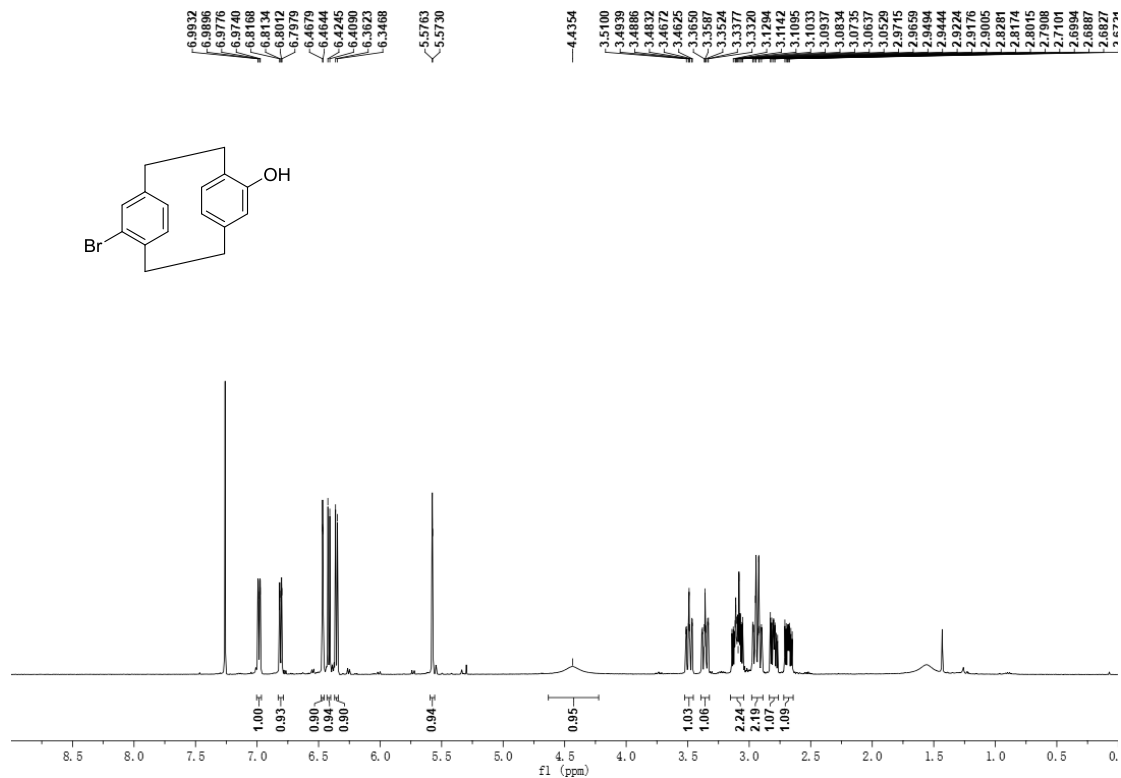


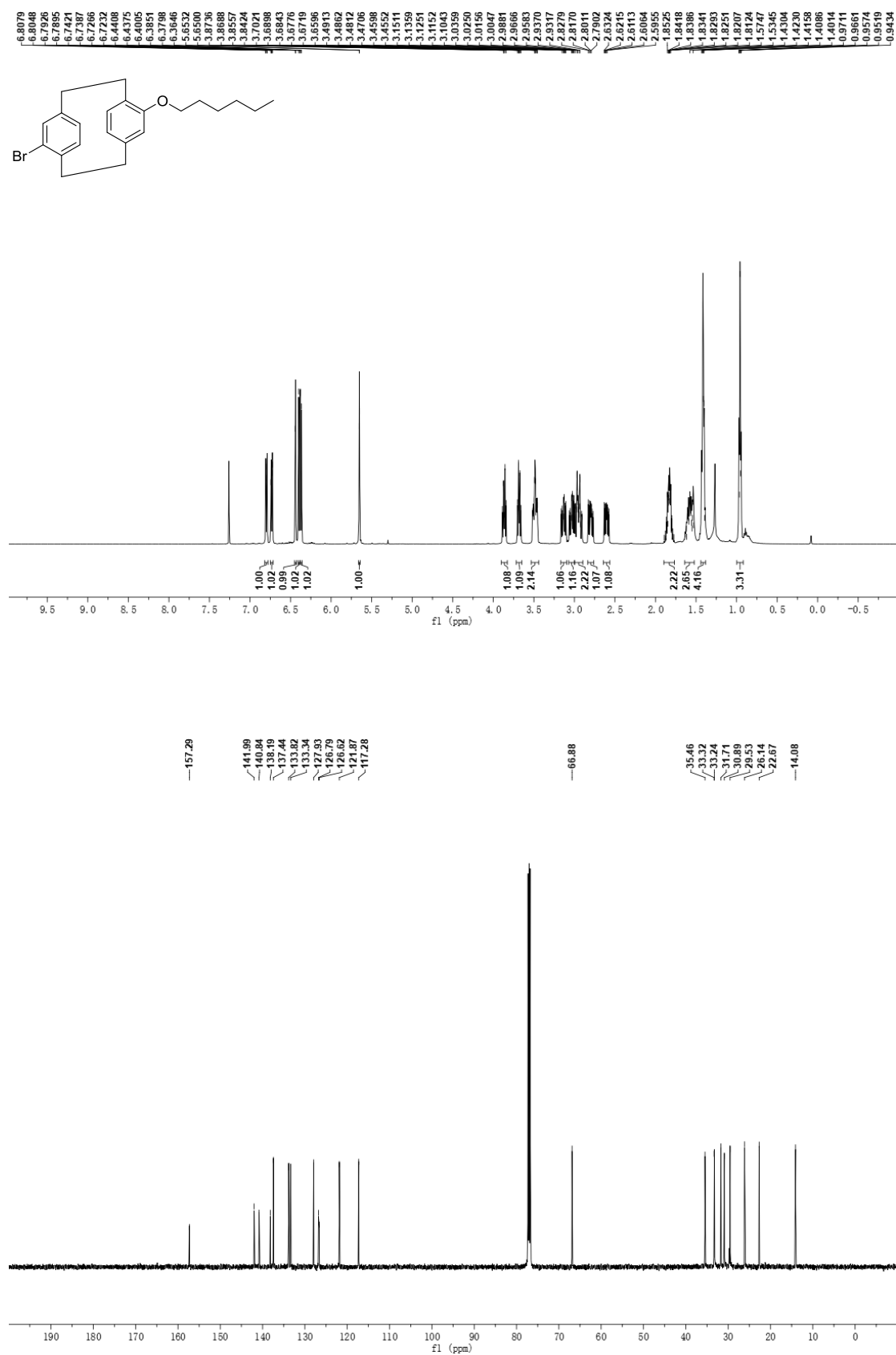
Figure S12. Luminescence decay at $\lambda_{em} = 980$ nm for YbL^2 in DCM (log scale). Mono-exponential fit with the corresponding parameters (inset) is plotted in red.

6. Copies of ^1H and ^{13}C NMR spectra

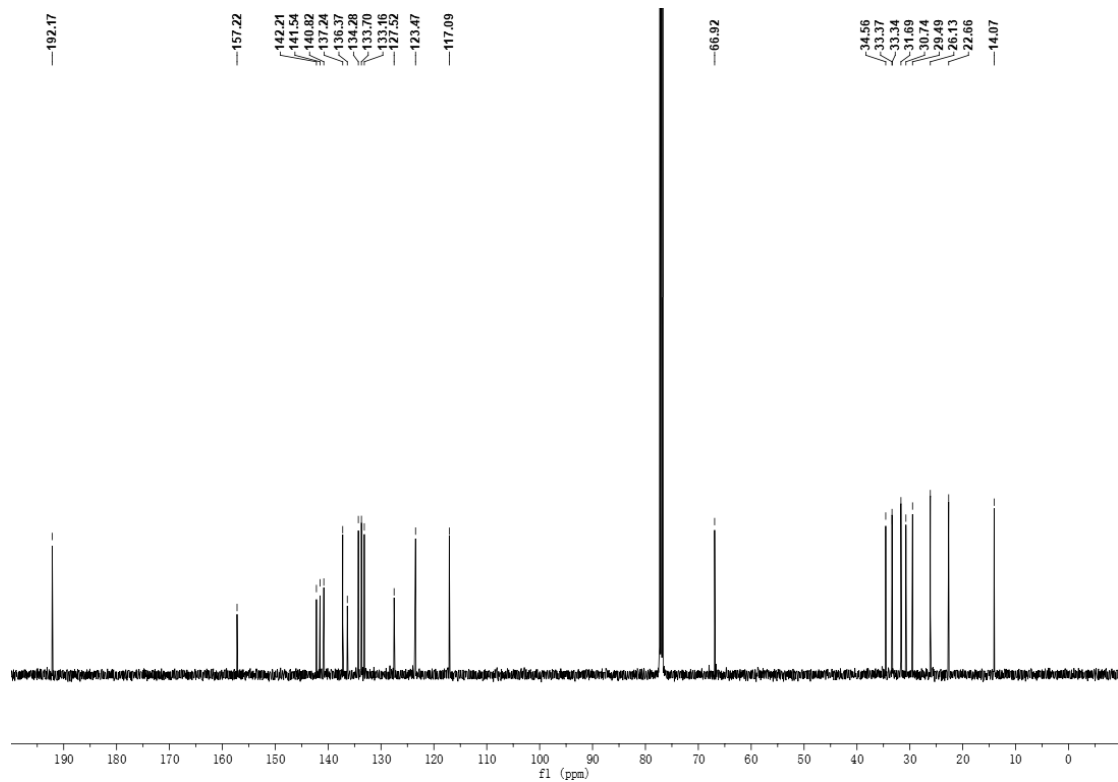
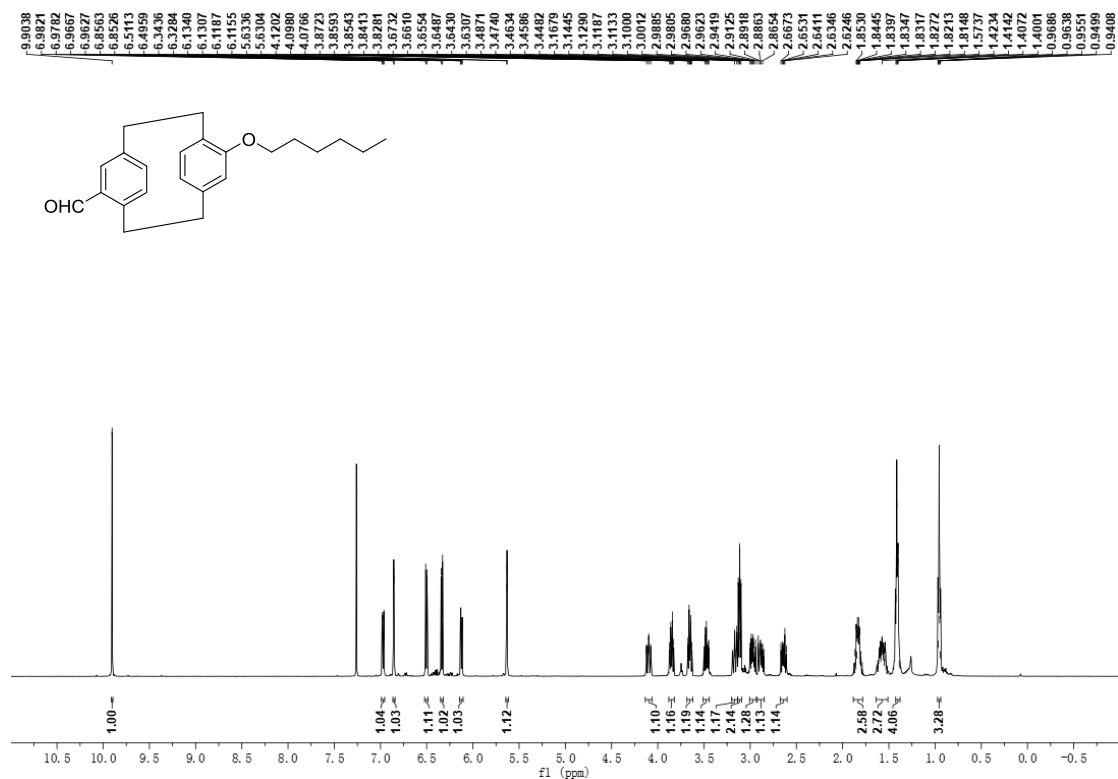
4-Bromo-16-hydroxy[2.2]paracyclophane ((±)-2):



4-Bromo-16-hexyloxy[2.2]paracyclophane ((±)-3):

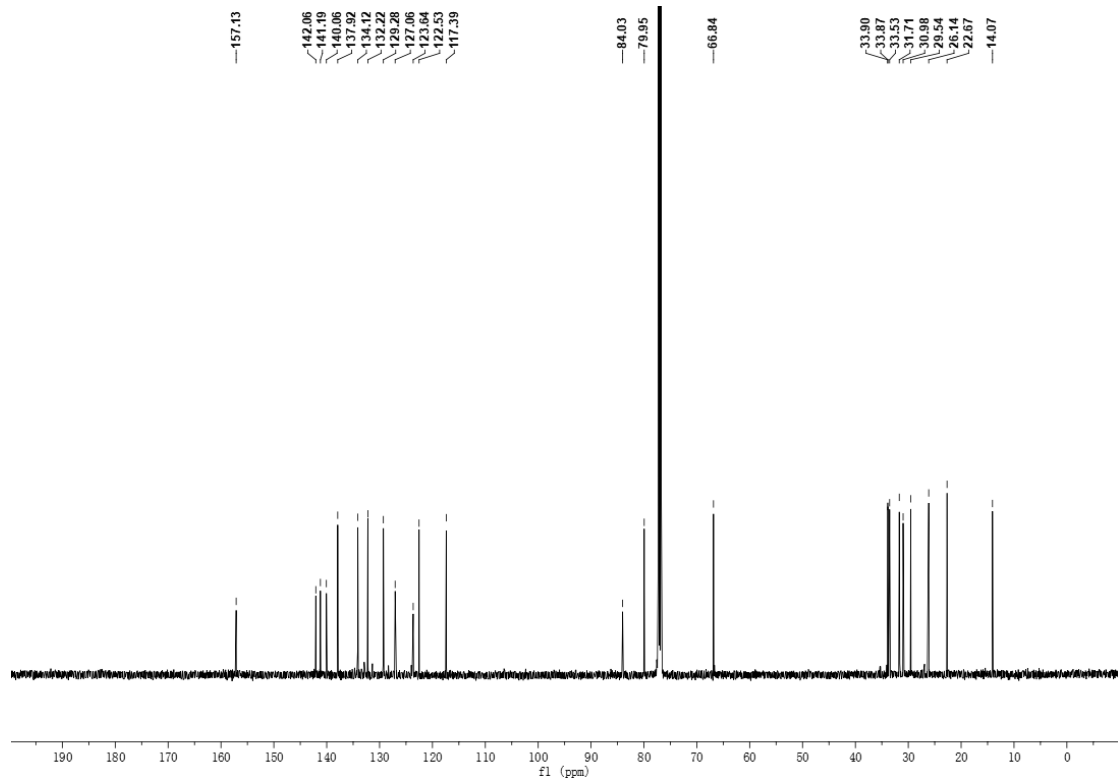
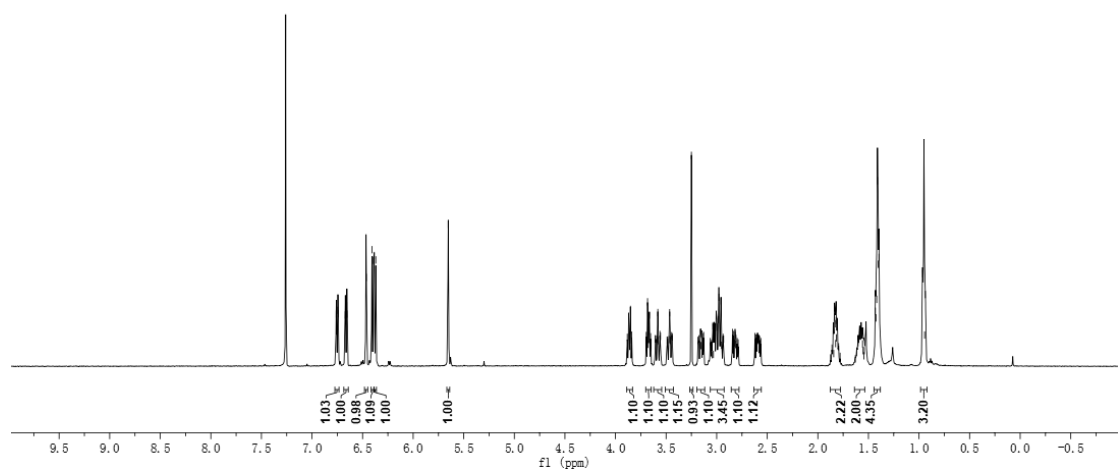
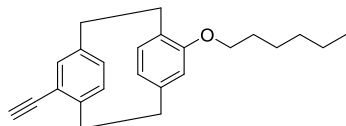


4-Hexyloxy-16-formyl[2.2]paracyclophane ((±)-4):

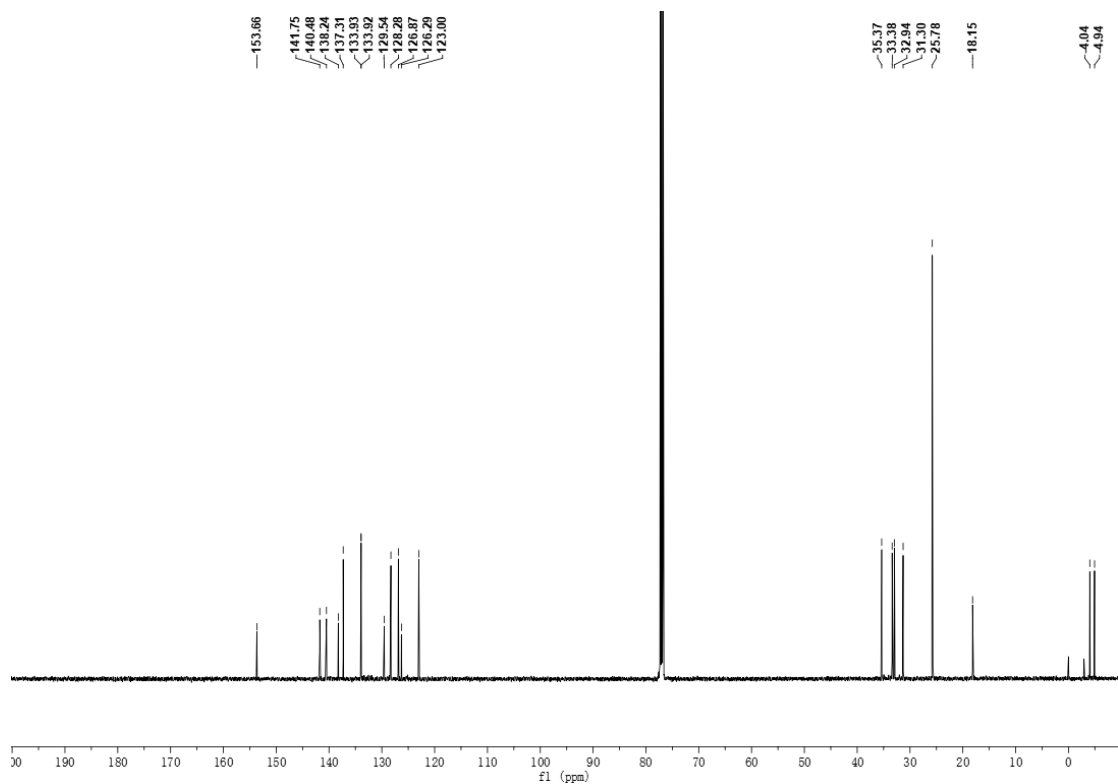
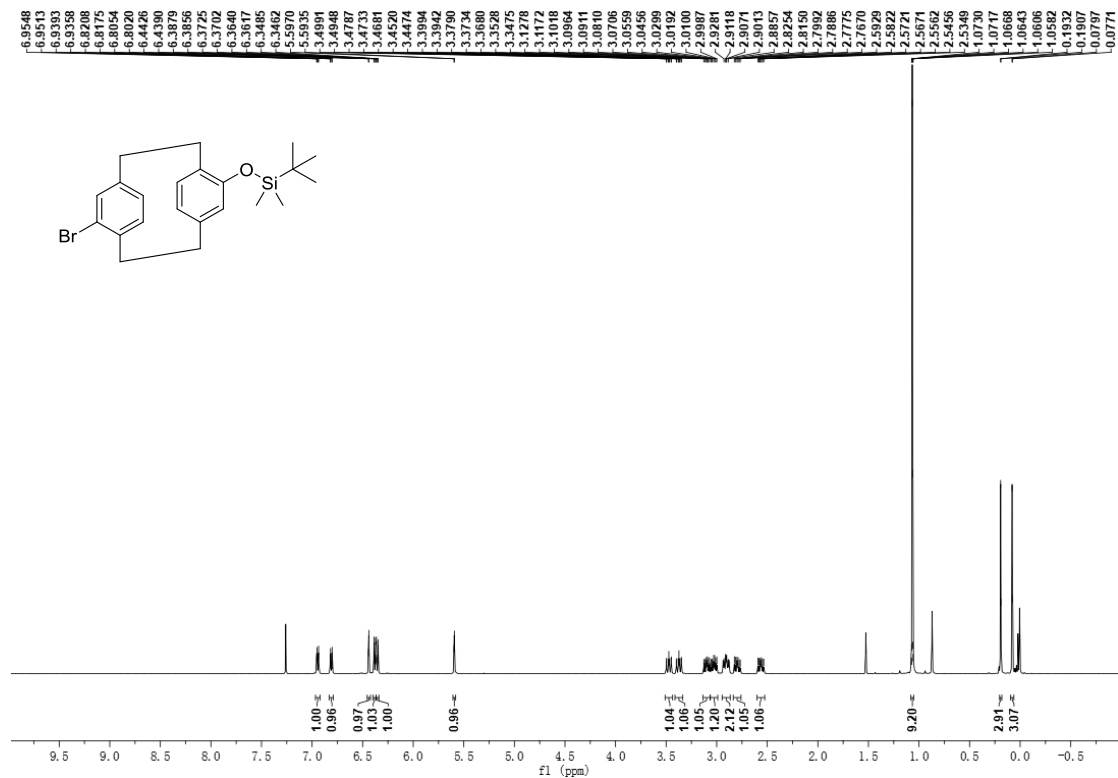


4-Hexyloxy-16-ethynyl[2.2]paracyclophane ((±)-5)

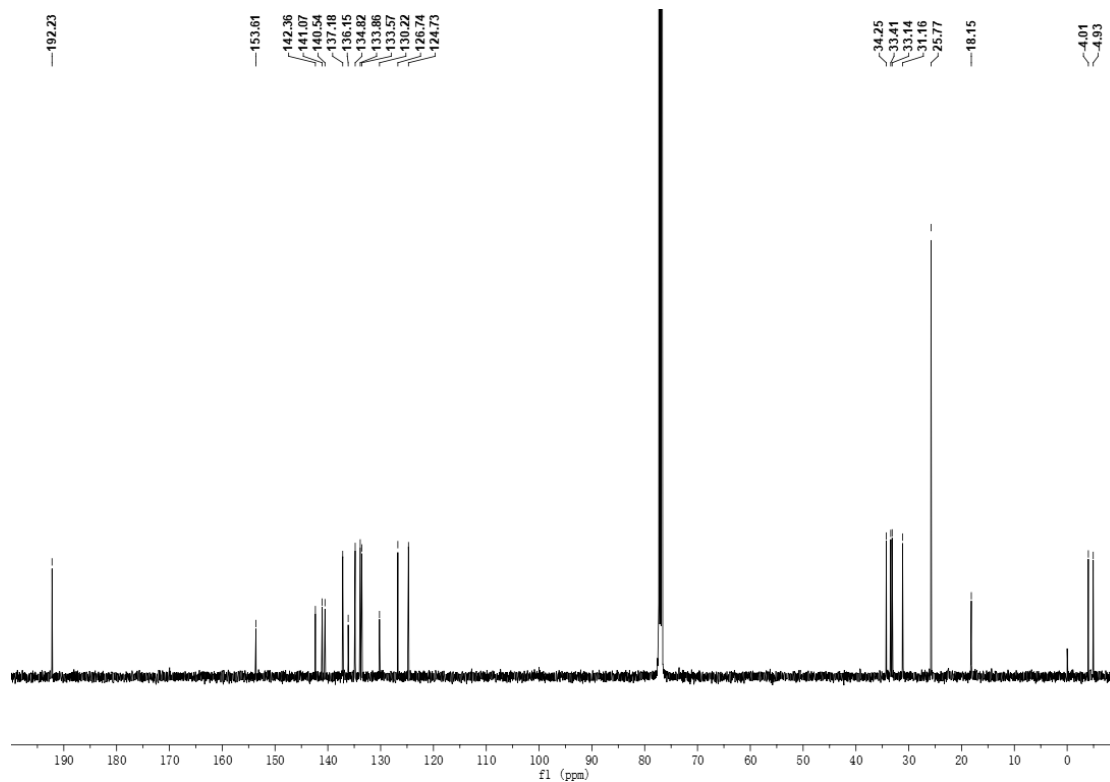
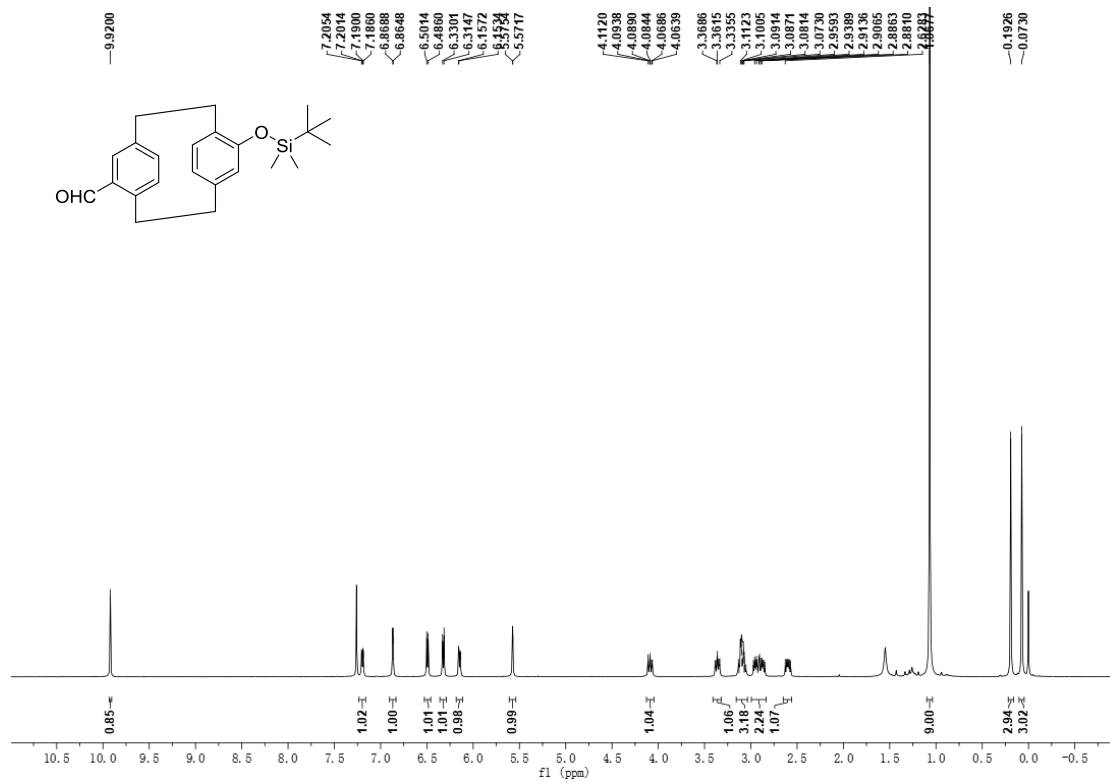
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6.3847
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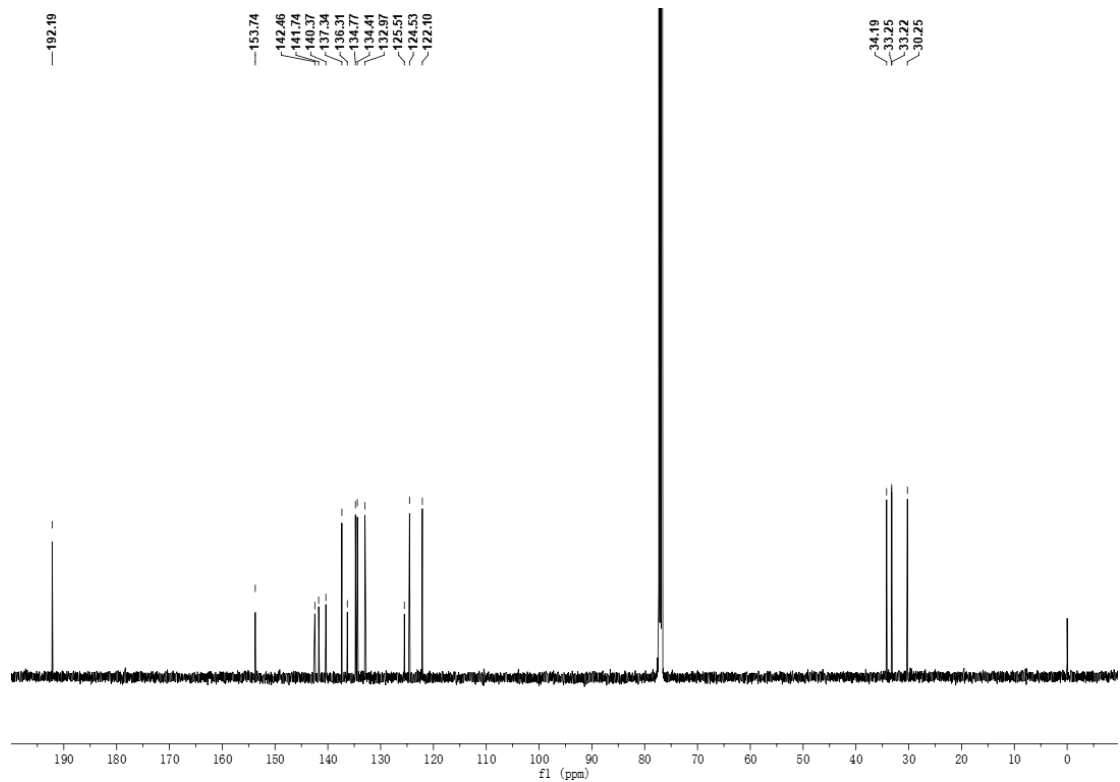
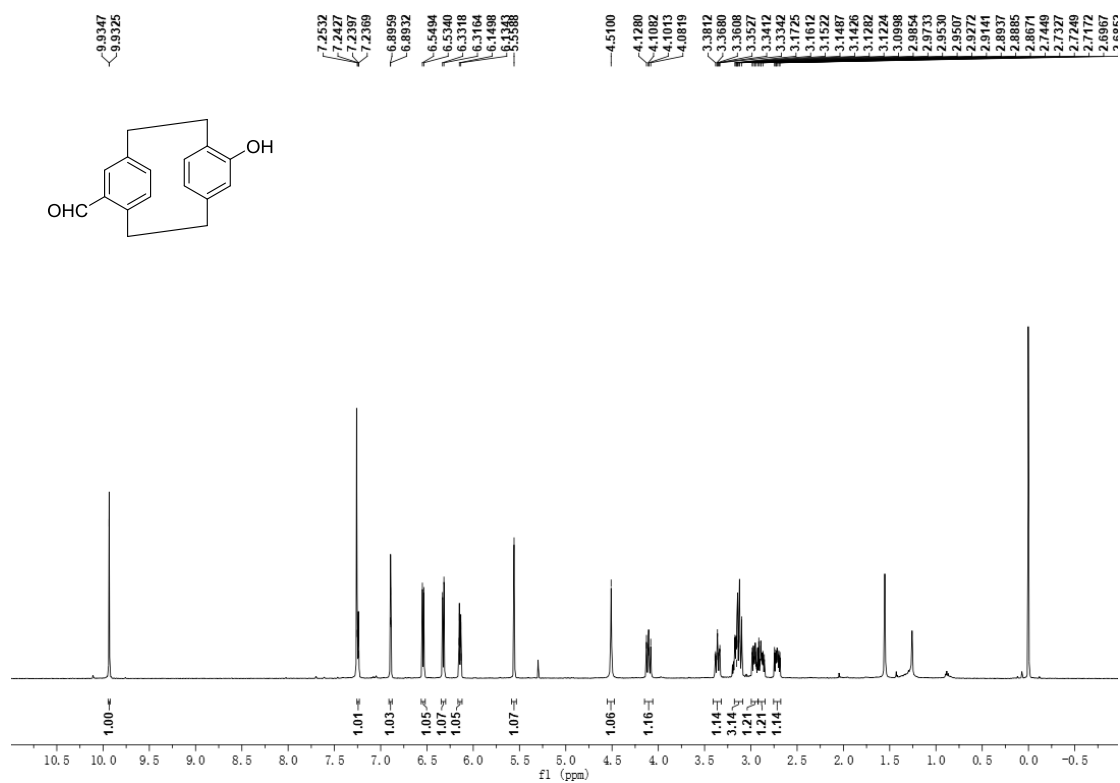
{11-Bromotricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4(16),5,7(15),10,13-hexaen-5-yl}oxy (tert-butyl)dimethylsilane ((±)-7)



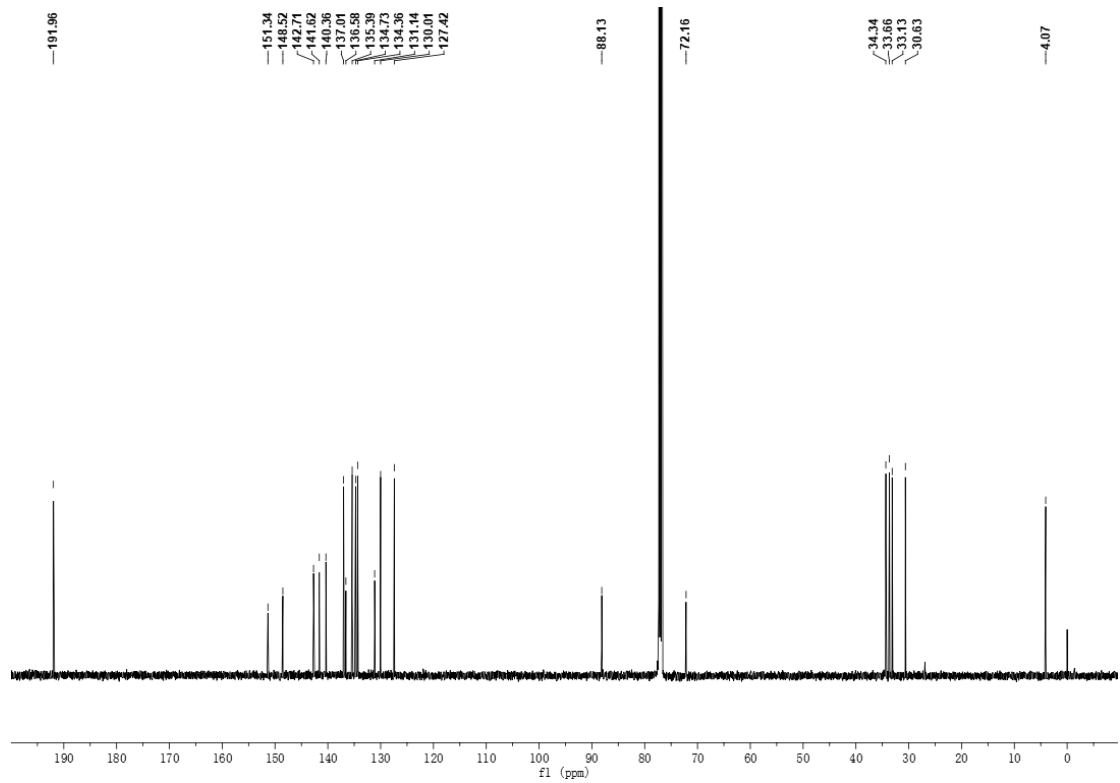
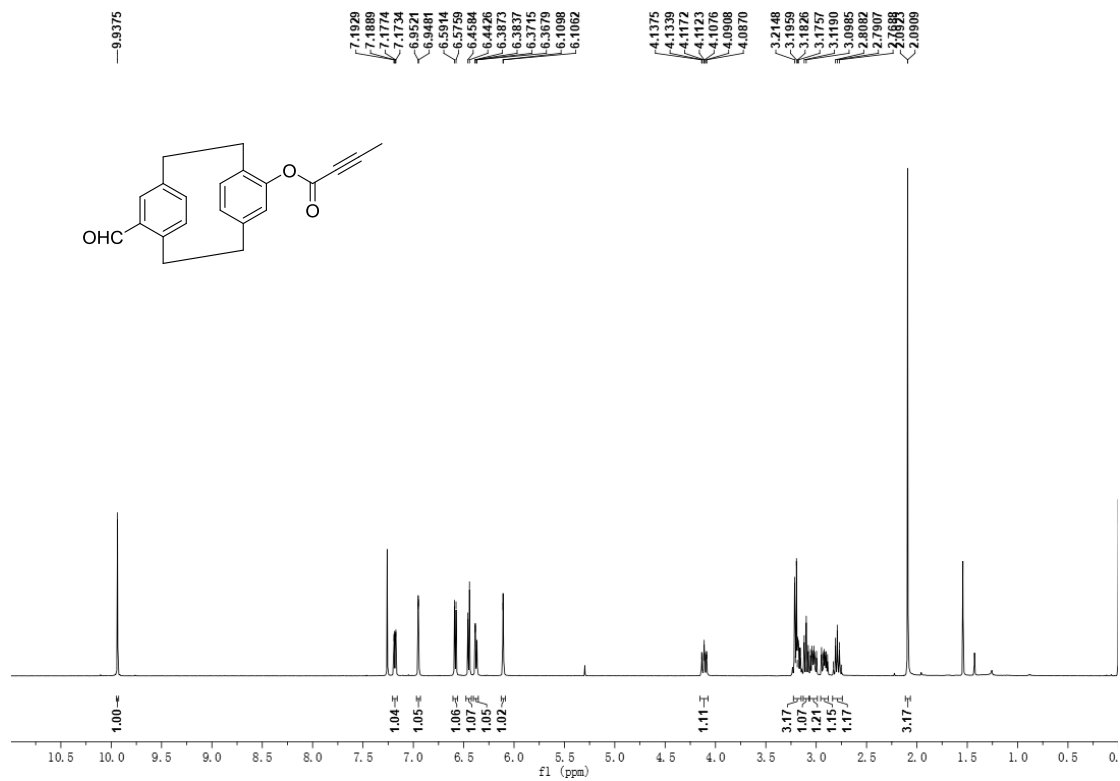
14-[(*Tert*-butyldimethylsilyl)oxy]tricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaene-5-carbaldehyde ((±)-7):



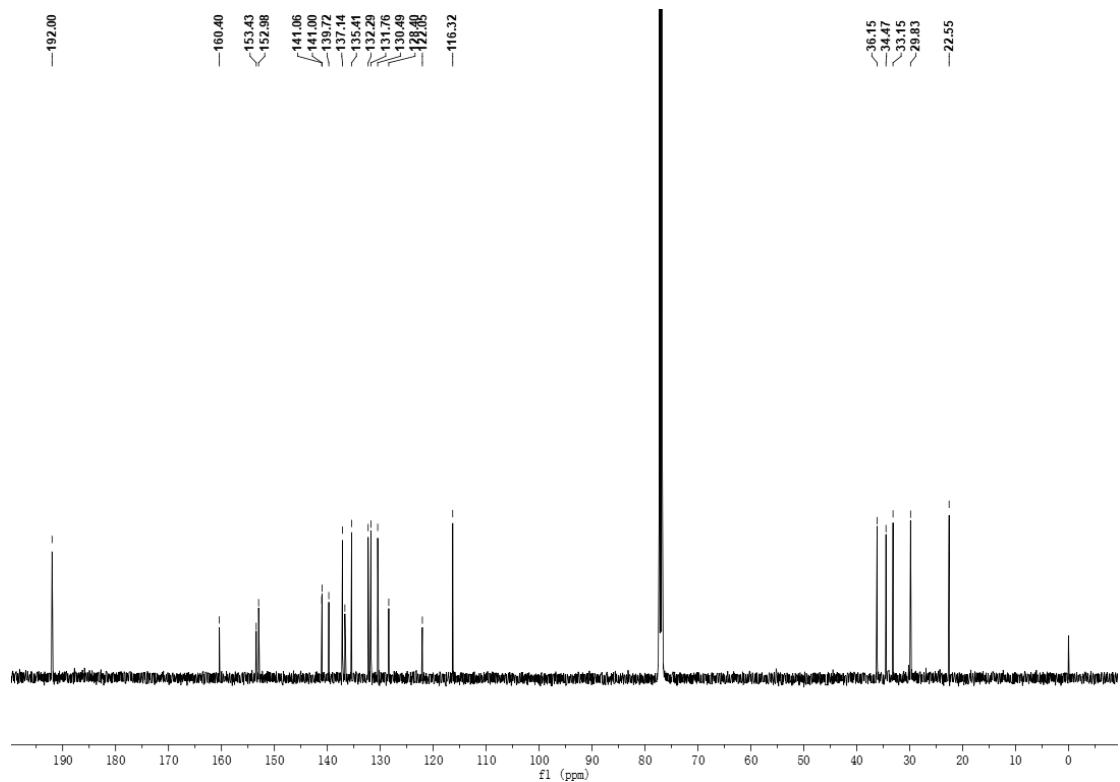
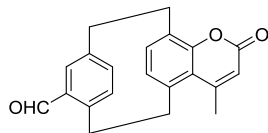
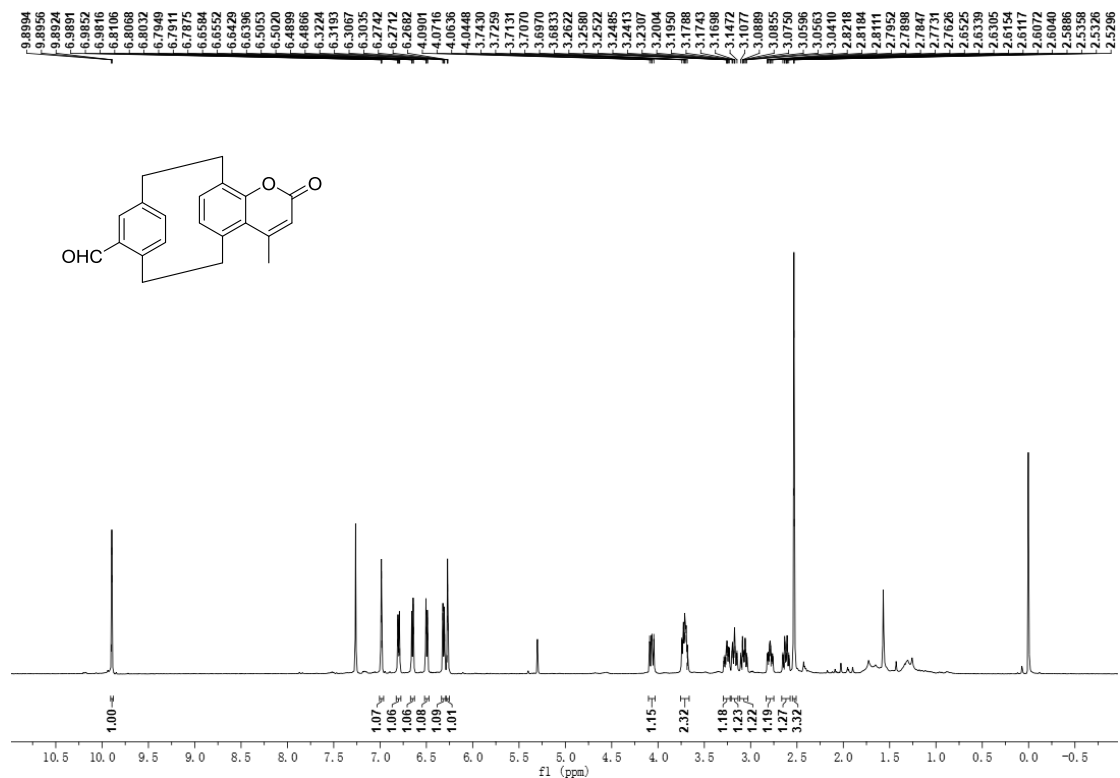
4-Hydroxy-16-formyl[2.2]paracyclophane ((±)-8):



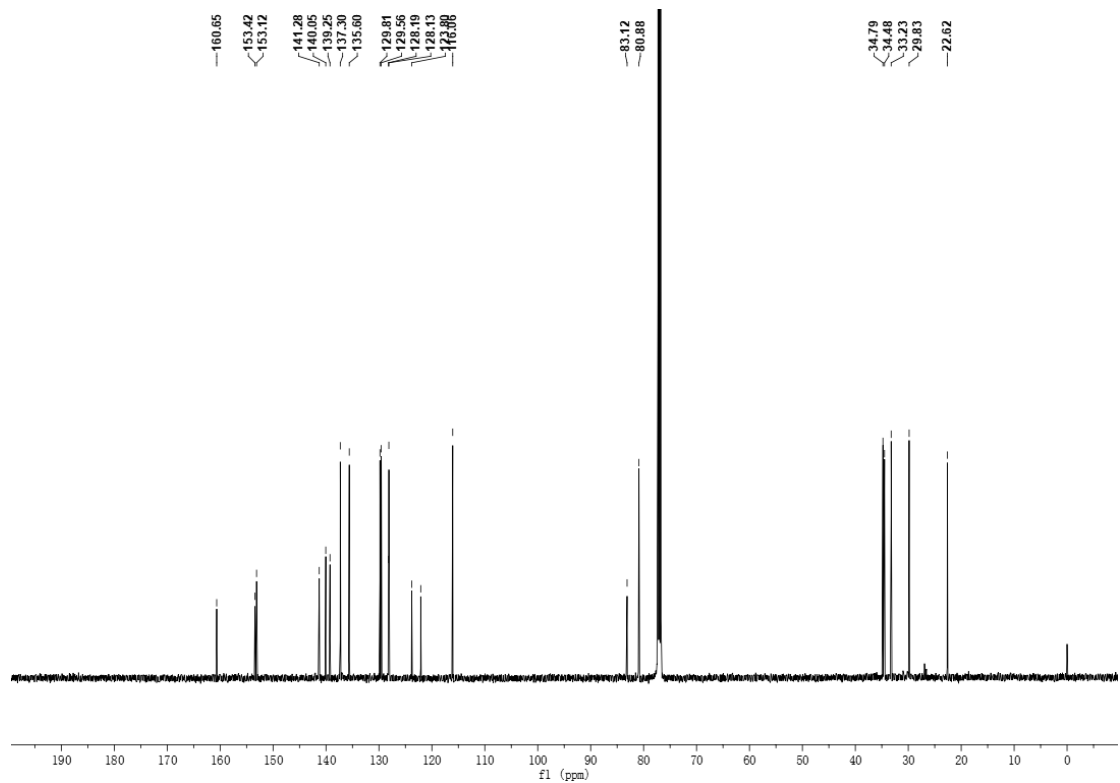
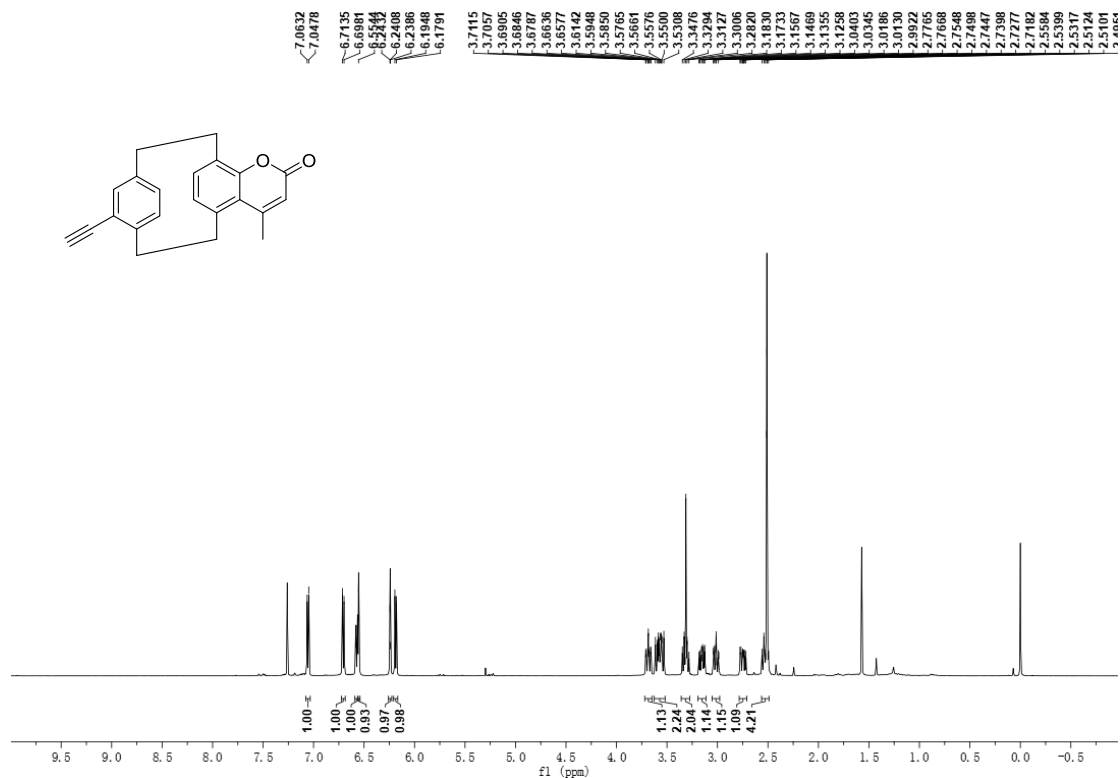
14-Formyltricyclo[8.2.2.2^{4,7}]hexadeca-1(12),4,6,10,13,15-hexaen-5-yl-but-2-ynoate ((±)-9):



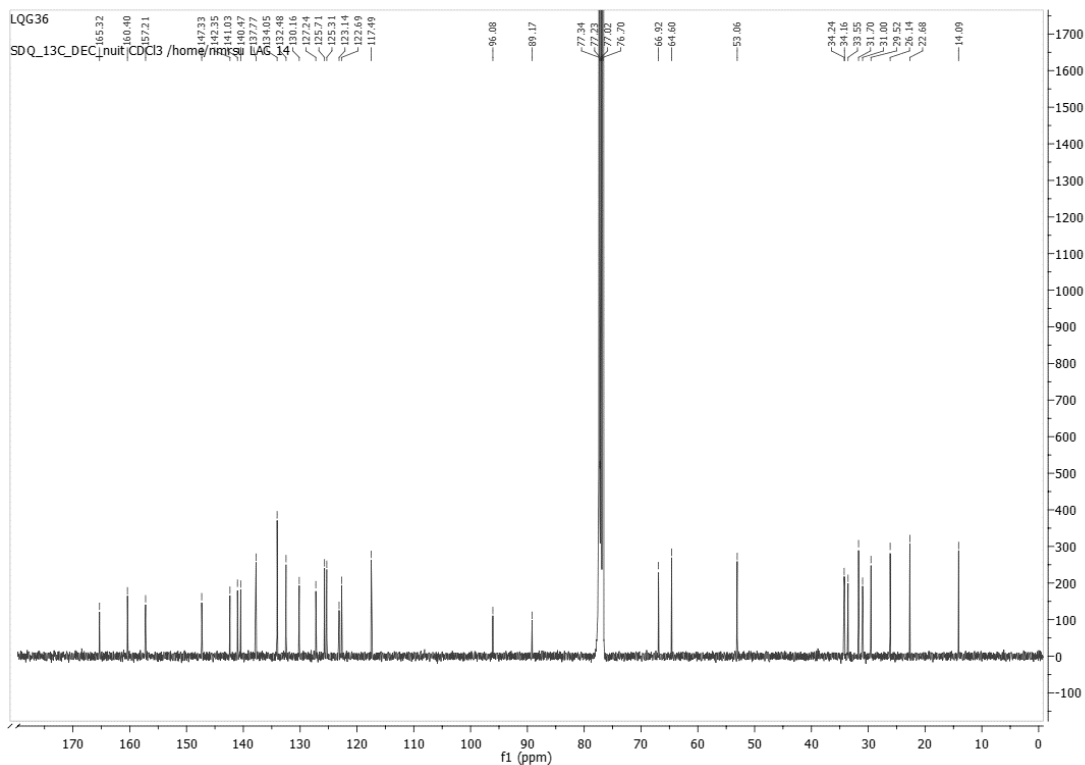
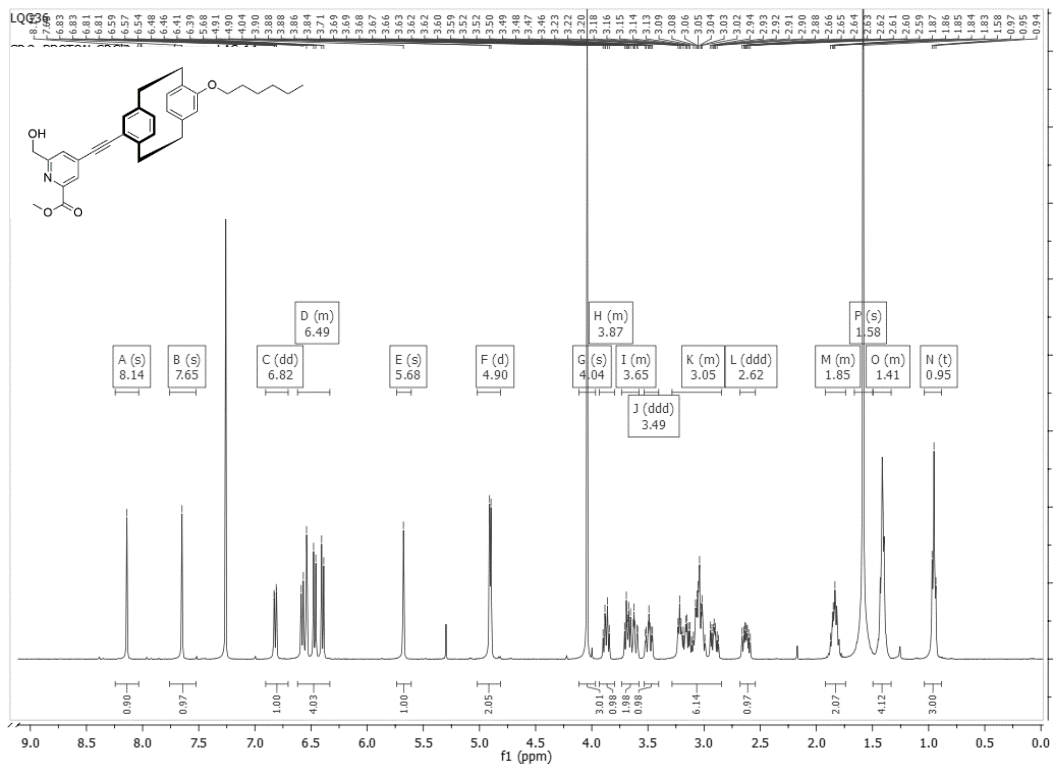
5-Methyl-13-oxo-12-oxatetracyclo[8.6.2.2^{4,7}.0^{11,16}]icosa-1(16),4(20),5,7(19),10,14,17-heptaene-5-carbaldehyde ((±)-10):



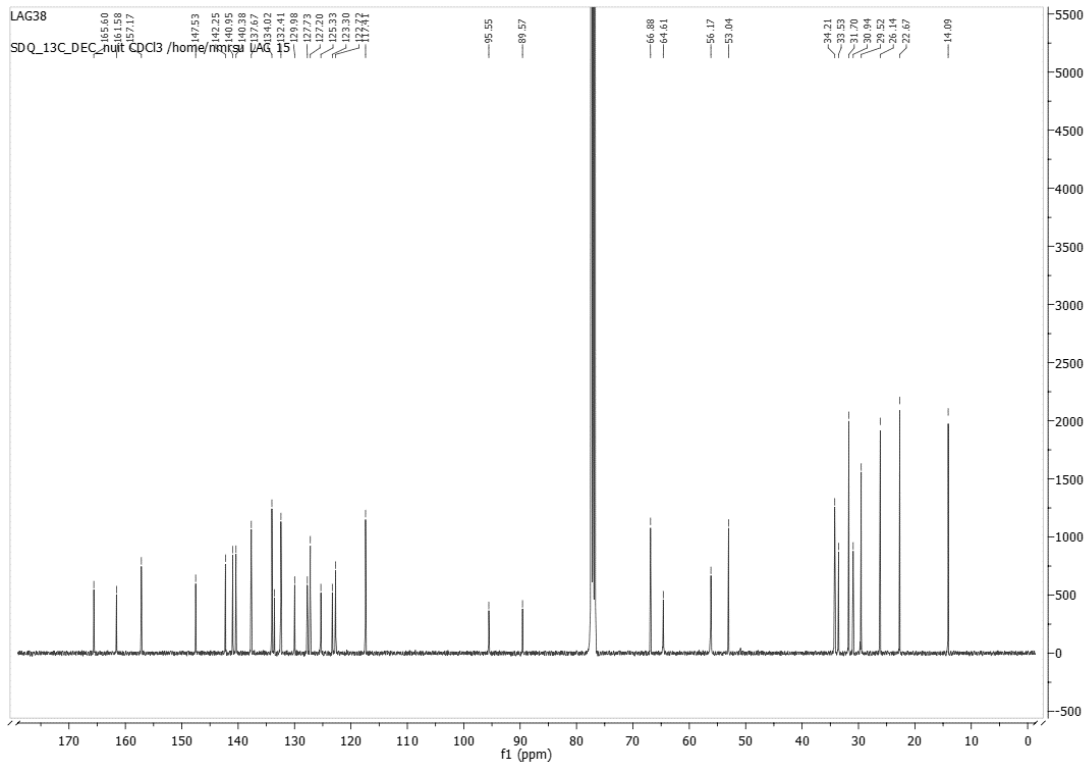
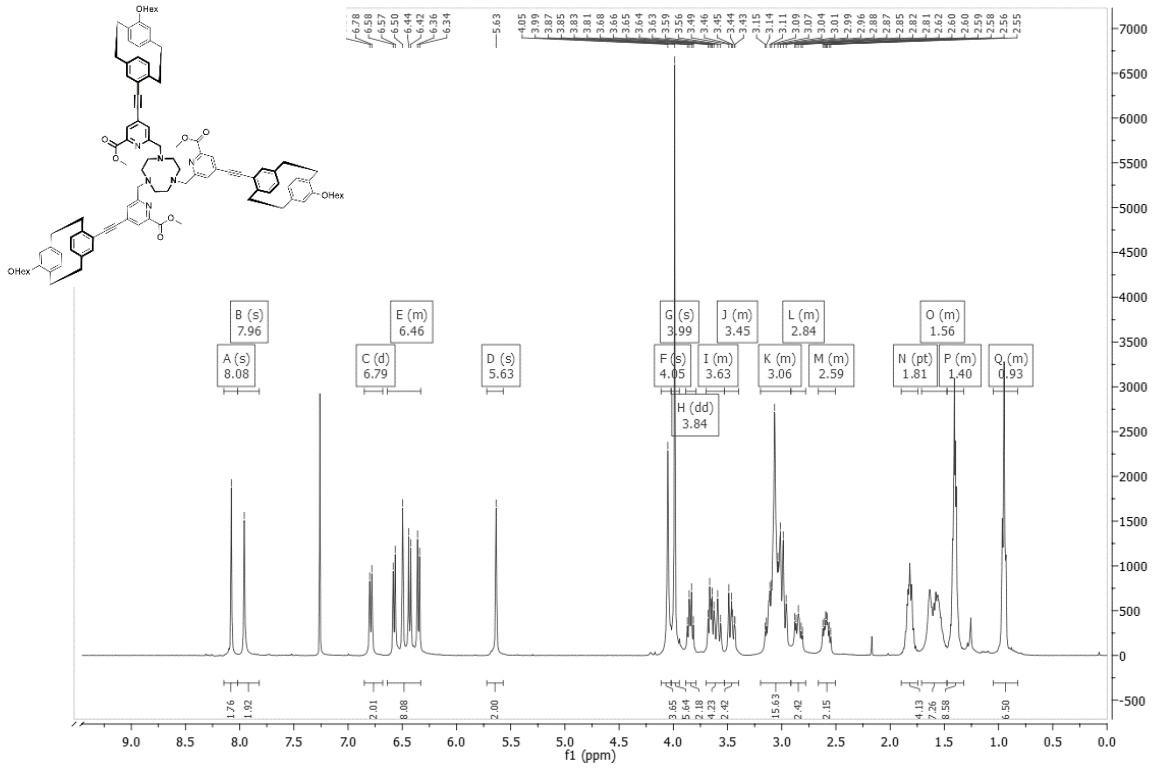
20-Ethynyl-15-methyl-12-oxatetracyclo[8.6.2.2⁴, 7 .0^{11,16}]icosa-1(16),4,6,10,14,17,19-heptaen-13-one ((±)-11):



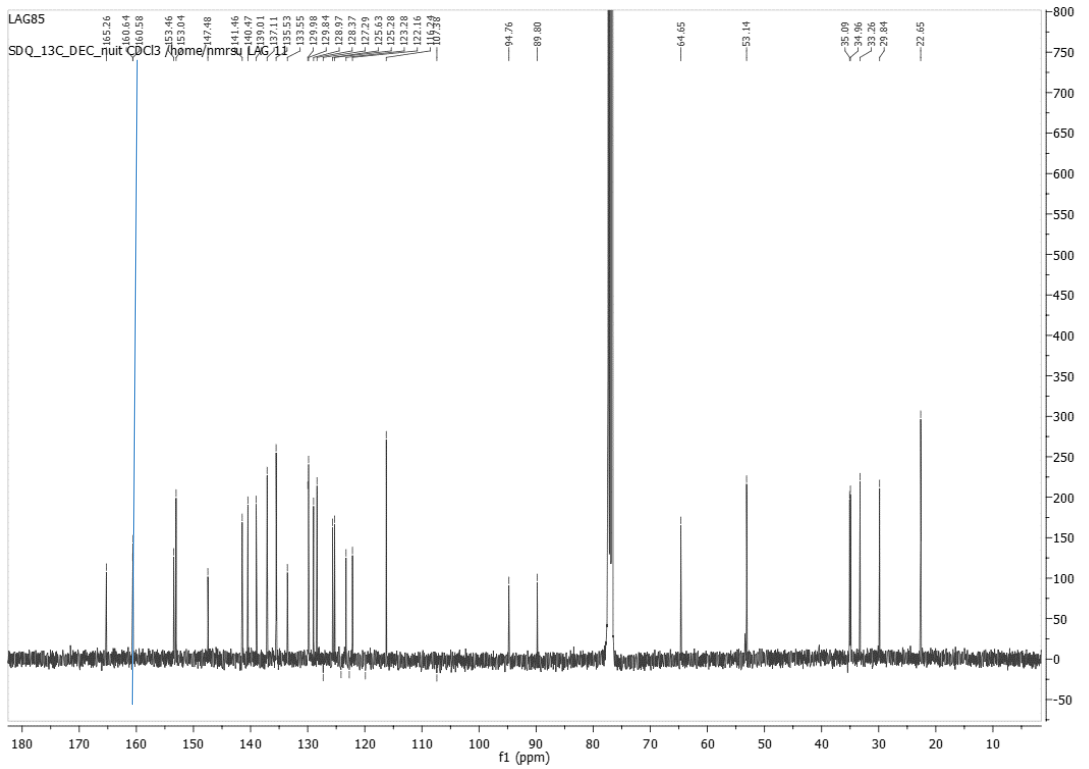
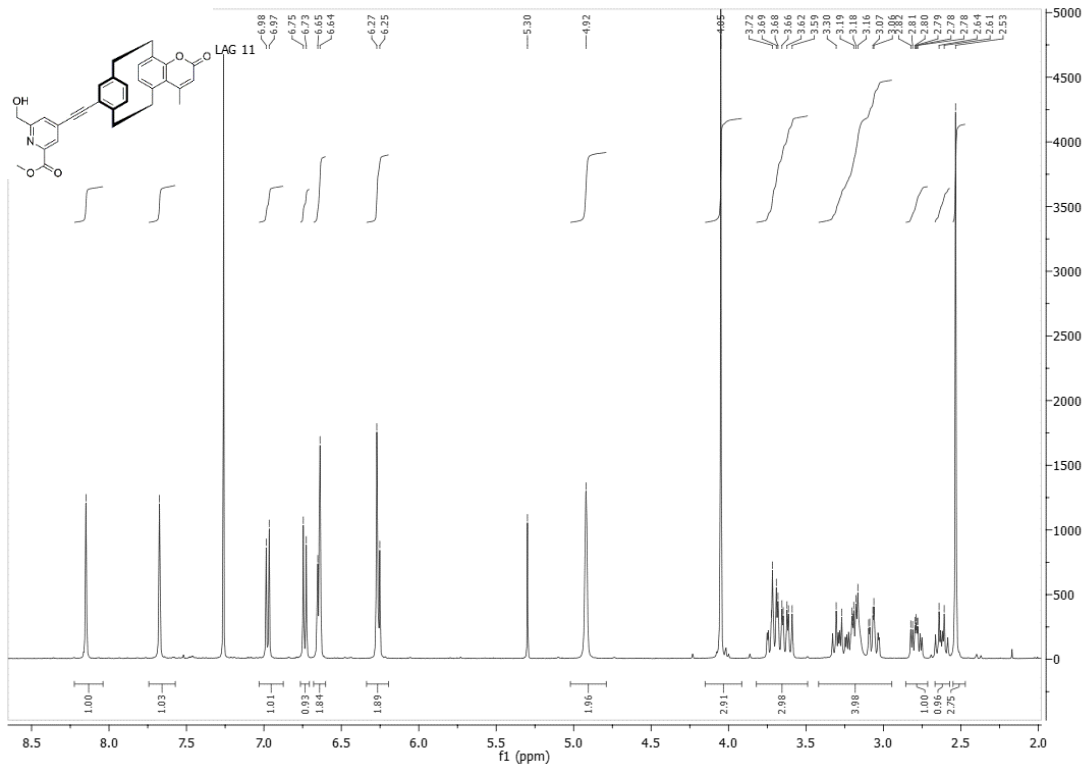
Antenna A¹



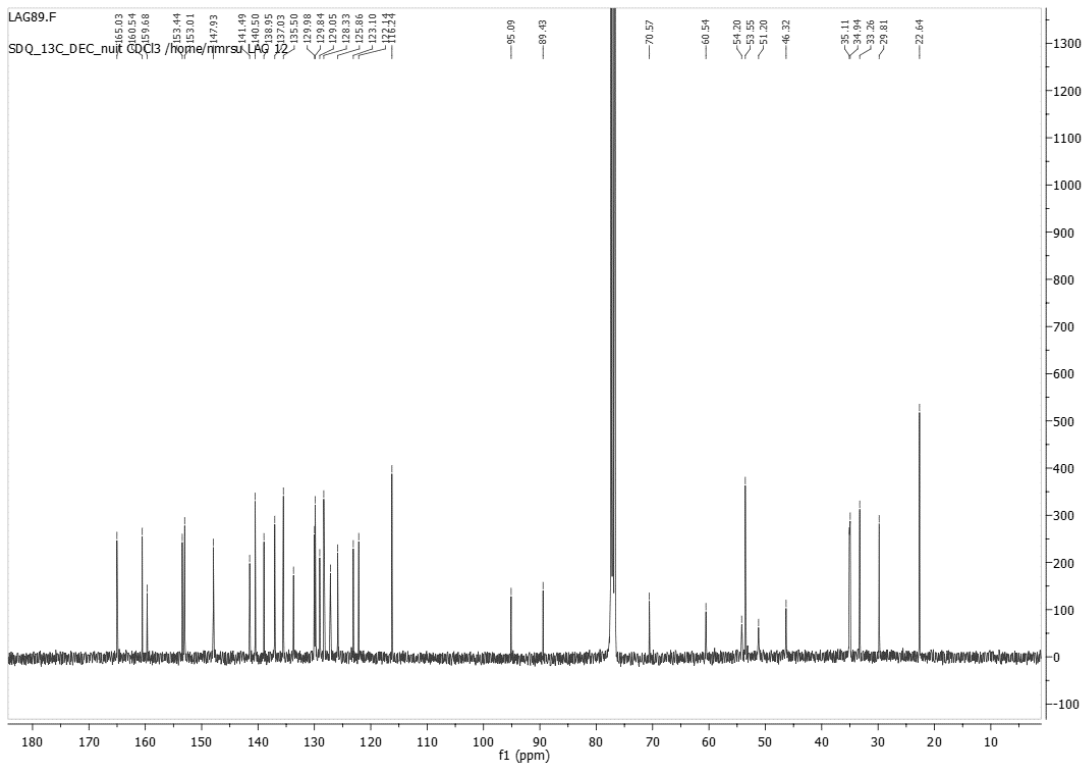
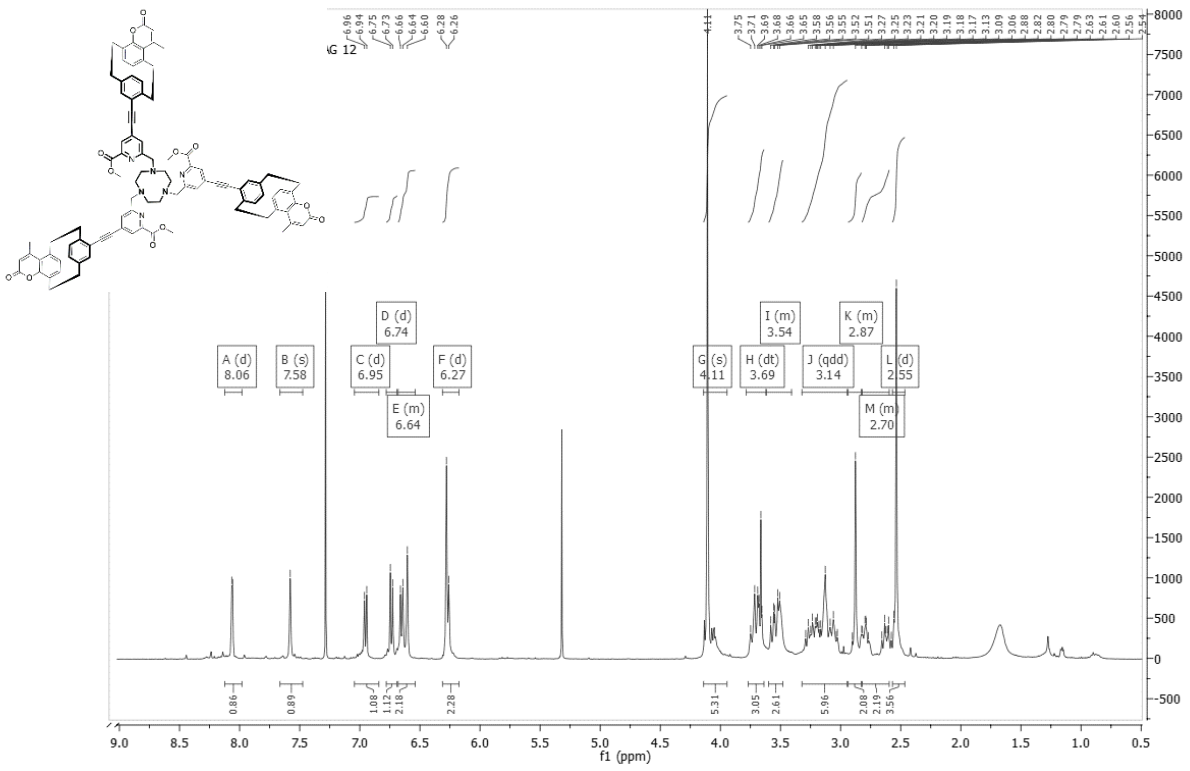
Ligand L¹



Antenna A²



Ligand L²



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gradients in NWChem: estimating scalar relativistic effects using Douglas–Kroll contracted basis sets, *J. Chem. Phys.* **2001**, *114*, 48–53.