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Experimental Section

General: Melting points were determined on Mikro-Heiztisch Polytherm A (Hund, Wetzlar) apparatus and are uncorrected. The NMR spectra were measured on Brucker Avance III HD 400, 500 and 600 instruments respectively: the ^{1}H NMR spectra at 400.13 MHz, 499.88 MHz and 600.13 MHz, the ^{13}C NMR spectra at 100.61 MHz, 125.71 MHz and 150.90 MHz in $CDCl_3$ or CD_2Cl_2 as indicated in 5 mm PFG probe with indirect detection. For referencing of ^{1}H NMR spectra the residual solvent signals (δ 7.26 for $CHCl_3$ and δ 5.32 for CH_2Cl_2) were used. In the case of ^{13}C spectra the signals of solvents (δ 77.00 for $CDCl_3$ and δ 53.84 for CD_2Cl_2) were used. The chemical shifts are given in δ-scale, the coupling constants *J* are given in Hz. For the assignment of both the ^{1}H and ^{13}C NMR spectra of key compounds, homonuclear 2D-H,H-COSY, 2D-H,H-ROESY, and heteronuclear 2D-H,C-HSQC, 2D-H,C-HMBC experiments were performed. Chemical shifts in NMR spectra copies were obtained by peak-picking in the MestreNOVA program in the two decimal point format (the third decimal was cut off). Therefore they may differ in some cases by -0.01 ppm from those listed in the characterisation of individual compounds or shown in structure drawings (these values were obtained by the analysis of experimental spectra in the TopSpin program and manualy rounded). The IR spectra were measured in KBr or $CHCl_3$. The EI mass spectra were determined at an ionising voltage of 70 eV, the *m/z* values are given along with their relative intensities (%). The standard 70 eV spectra were recorded in the positive ion mode. The sample was dissolved in chloroform, loaded into a quartz cup of the direct probe and inserted into the ion source. The source temperature was 220 °C. For exact mass measurement, the spectra were internally calibrated using perfluorotri-*n*-butylamine (Heptacosa). The low resolution ESI mass spectra were recorded using a quadrupole orthogonal acceleration time-of-flight tandem mass spectrometer (Q-Tof micro, Waters) and high resolution ESI mass spectra using a hybrid FT mass spectrometer combining a linear ion trap MS and the Orbitrap mass analyzer (LTQ Orbitrap XL, Thermo Fisher Scientific). The conditions were optimised for suitable ionisation in the ESI Orbitrap source (sheat gas flow rate 35 a.u., aux gas flow rate 10 a.u. of nitrogen, source voltage 4.3 kV, capillary voltage 40 V, capillary temperature 275 °C, tube lens voltage 155 V). The samples were dissolved in methanol and applied by direct injection. As a mobile phase was used 80% methanol (flow rate 100 µl/min). APCI MS was measured using LTQ Orbitrap XL hybrid FT mass spectrometer equipped with Ion Max source with APCI probe installed (Thermo Fisher Scientific, San Jose, CA, USA) and

coupled to Rheos 2200 quaternary gradient pump (Flux Instruments, Reinach, Switzerland; the system was controlled by Xcalibur software (Thermo Fisher Scientific). The APCI vaporizer and heated capillary temperatures were set to 400 °C and 200 °C, respectively; the corona discharge current was 5 μA. Nitrogen served both as the sheath and auxiliary gas at a flow rate of 55 and 5 arbitrary units, respectively. Samples were dissolved in methanol for both ESI and APCI measurements. Accurate mass measurements were obtained by the EI, APCI or ESI MS. Optical rotations were measured in CH_2Cl_2 or $CHCl_3$ using an Autopol IV (Rudolph Research Analytical) instrument. The CD spectra were acquired on a J-815 CD spectrometer (Jasco Analytical Instruments, Inc.) in THF (10^{-4} M solutions) using 10 mm quartz sample cell. TLC was performed on Silica gel 60 F_{254}-coated aluminium sheets (Merck) and spots were detected by the solution of $Ce(SO_4)_2.4\ H_2O$ (1%) and $H_3P(Mo_3O_{10})_4$ (2%) in sulphuric acid (10%). The flash chromatography was performed on Silica gel 60 (0.040-0.063 mm, Merck) or on Biotage® KP-C18-HS SNAP cartridges using Isolera One HPFC system (Biotage, Inc.). Biotage Initiator EXP EU (300 W power) was used for reactions carried out in microwave reactor. *N,N*-Diisopropylamine was distilled from calcium hydride under nitrogen; THF was freshly distilled from sodium/benzophenone under nitrogen; benzene and toluene were freshly distilled from sodium under nitrogen. Otherwise, all commercially available solvents, catalysts and reagent grade materials were used as received. CpCo(CO)(fum) (fum = dimethyl fumarate) was synthesised according to the literature procedure.[1] The starting materials **22**, **23**, **31**, **32** and **33** were purchased, the materials (+)-(*R*)-**4a**,[2] (-)-(*S*)-**7**,[3] **11**,[4] **27**,[5] **29**,[6] **30**[7] and **34**[8] were synthesised according to the literature.

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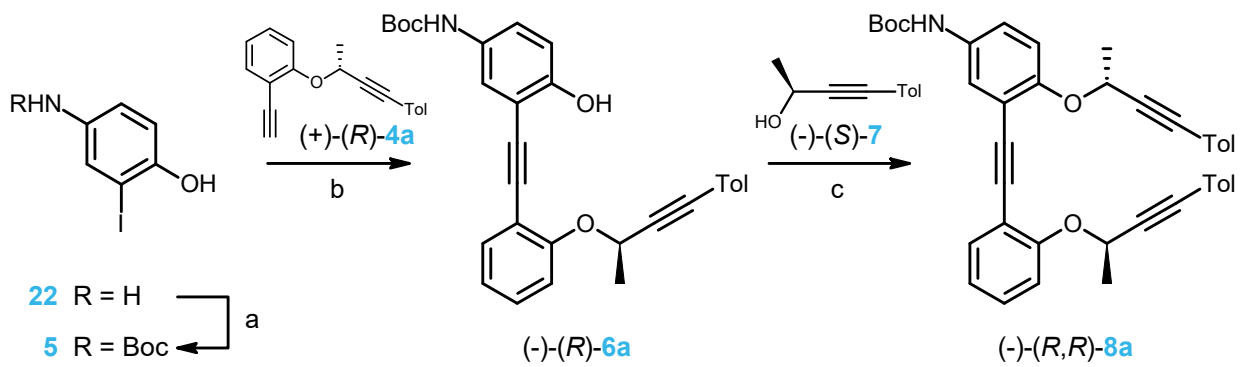
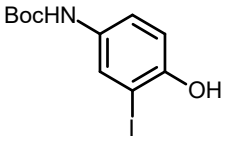
Synthesis of triynes (-)-(*R*,*R*)-8a-b and (-)-(*R*,*R*)-14

Triyne (-)-(*R*,*R*)-8a



(a) Boc_2O (1.1 equiv.), Et_3N (2.0 equiv.), MeOH, rt, 3 h, 96%; (b) (+)-(*R*)-**4a** (1.3 equiv.), $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (4 mol%), *i*-Pr_2NH (2.0 equiv.), toluene, rt, 3 h, 85%; (c) (-)-(*S*)-**7** (1.2 equiv.), PPh_3 (1.2 equiv.), DIAD (1.2 equiv.), benzene, rt, 4 h, 90%.

***tert*-Butyl (4-hydroxy-3-iodophenyl)carbamate 5**



4-Amino-2-iodophenol **22** (3.31 g, 14.1 mmol) was dissolved in methanol (30 ml) and triethylamine (4.00 ml, 28.7 mmol, 2.0 equiv.) was added at room temperature. Then di-*tert*-butyl dicarbonate (3.56 ml, 15.5 mmol, 1.1 equiv.) was slowly added and the solution was stirred at room temperature for 3 h. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 4:1) to afford carbamate **5** (4.55 g, 96%) as an amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (bs, 1H), 7.10 (dd, *J* = 8.8, 2.6, 1H), 6.87 (dd, *J* = 8.8, 0.8, 1H), 6.38 (bs, 1H), 5.38 (bs, 1H), 1.50 (s, 9H).

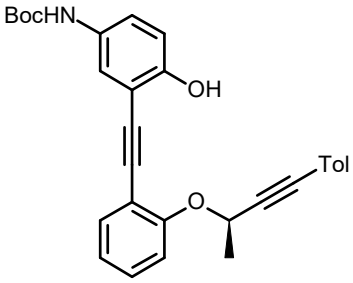
^{13}C NMR (101 MHz, $CDCl_3$): δ 153.00, 151.12, 132.08, 128.73, 121.39, 114.72, 85.21, 80.75, 28.30 (3C).

IR ($CHCl_3$): 3586 w, 3504 m, 3439 m, 3354 w, br, 3091 vw, 2982 m, 2872 w, 2029 w, 1723 s, 1713 s, 1606 w, 1588 m, 1511 vs, 1491 s, 1455 m, 1402 s, 1394 s, 1369 s, 1272 m, 1243 s, sh, 1229 s, 1180 s, sh, 1158 vs, 1124 w, sh, 1056 m, 943 vw, 916 w, 875 w, 815 w, 697 w, 684 w, sh, 567 w, 531 w, 490 w, 461 vw, 446 w cm^{-1}.

ESI MS: 358 ([M+Na]$^+$).

HR ESI MS: calcd for $C_{11}H_{14}O_3NINa$ 357.9911, found 357.9910.

(-)-*tert*-Butyl {4-hydroxy-3-[(2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]-oxy}phenyl)ethynyl]phenyl}carbamate 6a



A Schlenk flask was charged with carbamate **5** (400 mg, 1.19 mmol), $Pd(PPh_3)_2Cl_2$ (17 mg, 0.024 mmol, 2 mol%), CuI (9 mg, 0.05 mmol, 4 mol%) and purged with argon. Then degassed toluene (7 ml) and *N,N*-diisopropylamine (340 µl, 2.43 mmol, 2.0 equiv.) were added. Then alkyne (+)-(*R*)-**4a**[2] (397 mg, 1.53 mmol, 1.3 equiv.) in degassed toluene (5 ml) was added dropwise via cannula to a reaction mixture and the reaction was stirred at room temperature for 3 h. The solvent was evaporated *in vacuo* and the residue was flash chromatographed on silica gel (hexane-ethyl acetate 10:1) to afford phenol carbamate (-)-(*R*)-**6a** (475 mg, 85%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_D$ = -245° (c 0.071, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (bs, 1H), 7.46 (dd, *J* = 7.5, 1.7, 1H), 7.34 (ddd, *J* = 8.4, 7.5, 1.7, 1H), 7.30 – 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 7.17 (dd, *J* = 8.8, 2.7, 1H), 7.10 – 7.07 (m, 2H), 6.99 (td, *J* = 7.5, 1.1, 1H), 6.92 (d, *J* = 8.8, 1H), 6.48 (s, 1H), 6.32 (s, 1H), 5.18 (q, *J* = 6.5, 1H), 2.32 (s, 3H), 1.86 (d, *J* = 6.5, 3H), 1.52 (s, 9H).

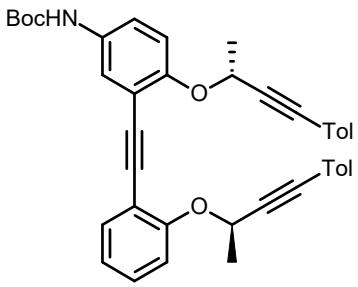
^{13}C NMR (101 MHz, $CDCl_3$): δ 157.80, 153.54, 153.03, 138.75, 131.86, 131.63 (2C), 130.69, 129.77, 128.97 (2C), 121.65, 121.18, 120.62, 119.06, 114.61, 113.38, 112.46, 110.06, 93.62, 88.22, 86.76, 86.60, 80.41, 65.29, 28.35 (3C), 22.35, 21.46.

IR (KBr): 3446 m, 3056 w, 3030 w, 2870 w, 1724 m, 1702 m, 1594 m, 1392 w, 1368 m, 1280 w , 1162 s, 1122 m, 1020 w, 817 m, 751 m cm^{-1}.

ESI MS: 490 ([M+Na]$^+$).

HR ESI MS: calcd for $C_{30}H_{29}O_4NNa$ 490.1989, found 490.1988.

(-)-*tert*-Butyl (4-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}-3-[(2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}phenyl)ethynyl]phenyl)carbamate 8a



To a solution of (-)-(*R*)-**6a** (350 mg, 0.749 mmol), (-)-(S)-**7**[3] (144 mg, 0.899 mmol, 1.2 equiv.), triphenylphosphine (236 mg, 0.899 mmol, 1.2 equiv.) in dry benzene (5 ml), diisopropyl azodicarboxylate (177 µl, 0.899 mmol, 1.2 equiv.) was added dropwise under argon. The reaction mixture was stirred at room temperature for 4 h, the solvent was evaporated *in vacuo* and the crude mixture was purified by flash chromatography on silica gel (hexane-diethyl ether 40:1) to afford the desired triyne (-)-(*R,R*)-**8a** (411 mg, 90%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_{D}$ = -109° (c 0.450, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (dd, *J* = 7.6, 1.7, 1H), 7.44 (d, *J* = 2.7, 1H), 7.36 (bd, *J* = 7.7, 1H), 7.31 – 7.26 (m, 5H), 7.20 (dd, *J* = 8.3, 1.1, 1H), 7.15 (d, *J* = 8.9, 1H), 7.10 – 7.06 (m, 4H), 6.98 (td, *J* = 7.5, 1.2, 1H), 6.34 (s, 1H), 5.20 (q, *J* = 6.5, 1H), 5.19 (q, *J* = 6.5, 1H), 2.32 (s, 6H), 1.82 (d, *J* = 6.5, 3H), 1.80 (d, *J* = 6.5, 3H), 1.52 (s, 9H).

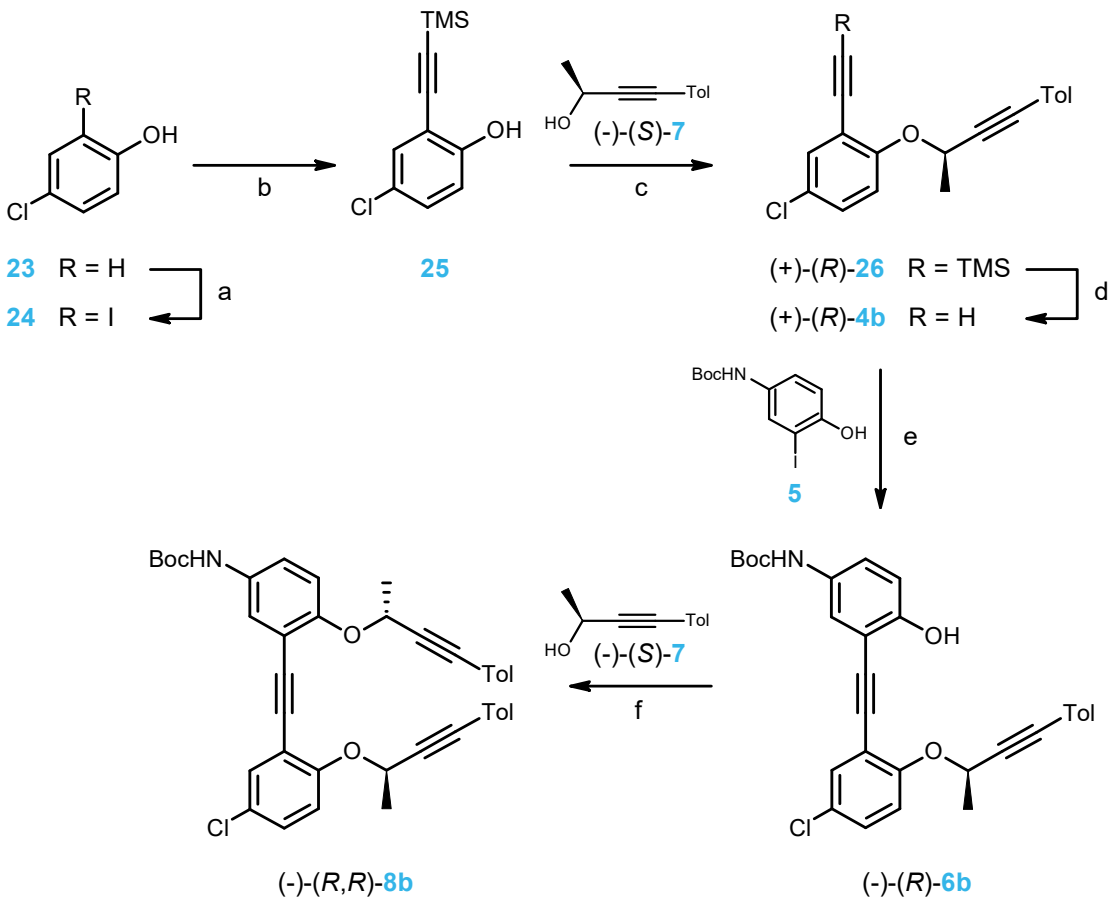
^{13}C NMR (101 MHz, $CDCl_3$): δ 158.16, 154.13, 152.85, 138.49, 138.44, 133.59, 132.60, 131.58 (4C), 129.34, 128.94 (2C), 128.92 (2C), 123.61, 121.59, 119.99, 119.43, 119.42, 117.87, 115.94, 115.63, 114.53, 90.28, 89.65, 87.78, 87.66, 86.05 (2C), 80.47, 66.99, 66.09, 28.33 (3C), 22.49, 22.47, 21.45 (2C).

IR (KBr): 3404 w, 3337 w, br, 3080 vw, sh, 3053 vw, 3028 w, 2982 m, 2924 m, 2233 w, 2206 vw, sh, 1726 s, 1701 s, br, 1609 m, 1594 m, 1585 m, sh, 1574 m, 1520 s, sh, 1508 vs, 1498 vs, 1486 s, 1447 s, 1412 m, 1392 m, 1367 s, 1328 s, 1260 s, 1242 s, 1159 vs, 1123 s, 1106 m, sh, 1084 s, 1033 s, 1019 s, 943 m, 923 m, sh, 834 w, 816 s, 749 s, 709 w, 663 vw, 646 vw, 537 w cm^{-1}.

ESI MS: 632 ($[M+Na]^+$).

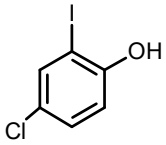
HR ESI MS: calcd for $C_{41}H_{39}O_4NNa$ 632.2771, found 632.2772.

Triyne (-)-(*R*,*R*)-8b



(a) KI (3.0 equiv.), I_2 (1.0 equiv.), aq. NH_3, 0 °C, 2 h, 64%; (b) TMS-C≡CH (1.6 equiv.), $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (4 mol%), *i*-Pr_2NH (1.2 equiv.), toluene, rt, 3 h, 94%; (c) (-)-(*S*)-**7** (1.1 equiv.), PPh_3 (1.1 equiv.), DIAD (1.1 equiv.), benzene, rt, 3 h, 91%; (d) K_2CO_3 (2.0 equiv.), MeOH, rt, 2 h, 93%; (e) (+)-(*R*)-**4b** (1.2 equiv.), $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (4 mol%), *i*-Pr_2NH (1.2 equiv.), toluene, rt, 3 h, 81%; (f) (-)-(*S*)-**7** (1.2 equiv.), PPh_3 (1.2 equiv.), DIAD (1.2 equiv.), benzene, rt, 3 h, 77%.

4-Chloro-2-iodophenol 24

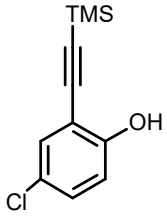


A solution of KI (15.5 g, 93.4 mmol, 3.0 equiv.) and I_2 (7.90 g, 31.1 mmol, 1.0 equiv.) in distilled water (30 ml) was added dropwise into a solution of 4-chlorophenol **23** (4.00 g, 31.1 mmol) in aqueous ammonia (20 ml) precooled to 0°C. The reaction mixture was stirred at 0 °C for 2 h, then acidified with 1N HCl and extracted with ethyl acetate (3 x 50 ml). The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on

silica gel (hexane-dichloromethane 3:1) to afford iodophenol **24** (5.1 g, 64%) as a pale pink solid.

NMR spectra were in agreement with the published ones.[9]

4-Chloro-2-[(trimethylsilyl)ethynyl]phenol 25



A Schlenk flask was charged with iodophenol **24** (3.50 g, 13.8 mmol), $Pd(PPh_3)_2Cl_2$ (193 mg, 0.275 mmol, 2 mol%) and CuI (114 mg, 0.599 mmol, 4 mol%) and purged with argon. The degassed toluene (20 ml) and *N,N*-diisopropylamine (2.30 ml, 16.4 mmol, 1.2 equiv.) were added. Then ethynyltrimethylsilane (3.00 ml, 21.7 mmol, 1.6 equiv.) in degassed toluene (5 ml) was added dropwise via cannula to a reaction mixture and the reaction was stirred at room temperature for 3 h. The solvent was evaporated *in vacuo* and the residue was flash chromatographed on silica gel (hexane-ethyl acetate 10:1) to afford phenol **25** (2.9 g, 94%) as an oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (bd, *J* = 2.6, 1H), 7.19 (dd, *J* = 8.8, 2.6, 1H), 6.87 (bd, *J* = 8.8, 1H), 5.78 (s, 1H), 0.28 (s, 9H).

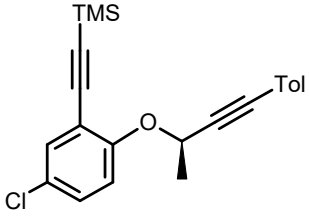
^{13}C NMR (101 MHz, $CDCl_3$): δ 155.66, 130.88, 130.62, 124.84, 115.86, 110.93, 103.72, 97.50, -0.15 (3C).

IR ($CHCl_3$): 3515 w, 3076 vw, 2963 w, 2901 w, 2156 w, 2146 w, 1568 w, 1480 vs, 1413 w, 1400 vw, 1253 s, 1170 w, 1152 vw, sh, 1111 w, 1085 w, 942 vw, 847 vs, 821 m, 702 w, 645 m, 480 w cm^{-1}.

EI MS: 224 ($M^{+\bullet}$, 47), 211 (69), 209 (100), 193 (35), 149 (6), 104 (4), 73 (6).

HR EI MS: calcd for $C_{11}H_{13}{}^{35}ClOSi$ 224.0424, found 224.0423.

(+)-[(5-Chloro-2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}phenyl)ethynyl](trimethyl)silane 26



To a solution of phenol **25** (0.854 g, 3.80 mmol), triphenylphosphine (1.10 g, 4.18 mmol, 1.1 equiv.), alcohol (-)-(*S*)-**7**[3] (0.670 g, 4.18 mmol, 1.1 equiv.) in dry benzene (4.5 ml), diisopropyl azodicarboxylate (825

[9] B. Schmidt, M. Riemer, M. Karras, *J. Org. Chem.* **2013**, *78*, 8680-8688.

µl, 4.18 mmol, 1.1 equiv.) was added dropwise under argon. The reaction mixture was stirred at room temperature for 3 h, then the solvent was evaporated *in vacuo*. The residue was chromatographed on silica gel (hexane) to afford diyne (+)-(*R*)-**26** (1.28 g, 91%) as a pale yellow oil.

Optical rotation: $[\alpha]^{20}_{D}$ = +19.5° (c 0.410, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (bd, *J* = 2.7, 1H), 7.29 – 7.26 (m, 2H), 7.22 (dd, *J* = 8.8, 2.7, 1H), 7.13 – 7.07 (m, 3H), 5.08 (q, *J* = 6.5, 1H), 2.34 (s, 3H), 1.77 (d, *J* = 6.5, 3H), 0.26 (s, 9H).

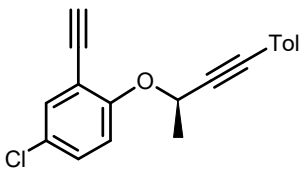
^{13}C NMR (101 MHz, $CDCl_3$): δ 157.46, 138.74, 132.97, 131.55 (2C), 129.44, 129.01 (2C), 126.38, 119.13, 117.29, 115.79, 100.19, 99.73, 86.99, 86.53, 66.50, 22.24, 21.47, -0.12 (3C).

IR ($CHCl_3$): 3083 vw, 3053 vw, 2962 w, 2900 w, 2235 w, 2160 w, 1608 vw, 1591 w, 1567 vw, 1510 m, 1483 s, 1465 m, 1407 vw, 1396 w, 1375 w, 1331 m, 1266 m, sh, 1251 vs, 1237 w, sh, 1120 w, 1113 w, 1095 w, sh, 1084 m, 1035 w, 1020 w, 946 w, 872 m, 846 vs, 819 s, 808 w, 708 vw, 700 vw, 683 vw, 646 w, 483 w cm^{-1}.

ESI MS: 367 ($[M+H]^+$).

HR ESI MS: calcd for $C_{22}H_{24}O^{35}ClSi$ 367.1280, found 367.1280.

(+)-4-Chloro-2-ethynyl-1-{[(2*R*)-4-(4-methylphenyl)but-3-yn-2-yl]oxy}benzene 4b



To a solution of the protected diyne (+)-(*R*)-**26** (546 mg, 1.49 mmol) in methanol (10 ml), anhydrous potassium carbonate (416 mg, 3.01 mmol, 2.0 equiv.) was added in one portion. The reaction mixture was stirred at room temperature for 2 h. Then a saturated ammonium chloride solution (20 ml) was added, the solution was extracted with diethyl ether (3 x 30 ml) and the combined organic layers were dried over anhydrous $MgSO_4$. The solvents were removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 50:1) to give diyne (+)-(*R*)-**4b** (407 mg, 93%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_{D}$ = +44° (c 0.361, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (bd, *J* = 2.6, 1H), 7.29 – 7.25 (m, 3H), 7.13 (d, *J* = 8.9, 1H), 7.11 – 7.09 (m, 2H), 5.08 (q, *J* = 6.6, 1H), 3.31 (s, 1H), 2.34 (s, 3H), 1.78 (d, *J* = 6.6, 3H).

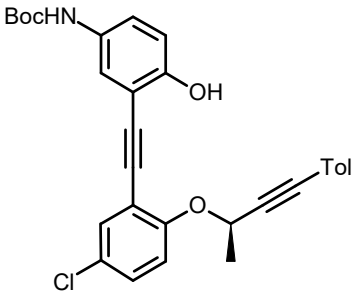
^{13}C NMR (101 MHz, $CDCl_3$): δ 157.51, 138.81, 133.44, 131.57 (2C), 129.78, 129.02 (2C), 126.06, 119.04, 116.28, 114.29, 86.74, 86.62, 82.32, 78.67, 66.12, 22.26, 21.47.

IR ($CHCl_3$): 3306 m, 3083 vw, 3054 vw, 2236 w, 2111 vw, 1607 vw, 1593 w, 1570 vw, 1511 s, 1484 vs, 1462 m, 1409 vw, sh, 1395 m, 1376 w, 1331 m, 1267 vw, sh, 1247 s, 1181 m, 1133 s, 1121 w, 1108 w, 1084 m, 1036 m, 1020 w, 885 w, 819 s, 809 m, 709 vw, 659 m, 621 m, 545 w, 478 vw cm^{-1}.

APCI MS: 295 ($[M+H]^+$).

HR APCI MS: calcd for $C_{19}H_{16}O^{35}Cl$ 295.0884, found 295.0889.

(-)-*tert*-Butyl {3-[(5-chloro-2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}phenyl)-ethynyl]-4-hydroxyphenyl}carbamate 6b



A Schlenk flask was charged with iodide **5** (613 mg, 1.83 mmol), $Pd(PPh_3)_2Cl_2$ (30 mg, 0.043 mmol, 2 mol%), CuI (14 mg, 0.074 mmol, 4 mol%) and purged with argon. Then degassed toluene (30 ml) and *N,N*-diisopropylamine (300 µl, 2.14 mmol, 1.2 equiv.) were added. Then alkyne (+)-(*R*)-**4b** (648 mg, 2.20 mmol, 1.2 equiv.) in degassed toluene (5 ml) was added dropwise to a reaction mixture via cannula and the reaction was stirred at room temperature for 3 h. The solvent was evaporated *in vacuo* and the residue was flash chromatographed on silica gel (hexane-ethyl acetate 10:1) to afford phenol carbamate (-)-(*R*)-**6b** (743 mg, 81%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_D$ = -227° (c 0.288, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (bs, 1H), 7.42 (d, *J* = 2.6, 1H), 7.29 – 7.27 (m, 3H), 7.20 (dd, *J* = 8.8, 2.6, 1H), 7.16 (d, *J* = 8.9, 1H), 7.10 – 7.08 (m, 2H), 6.92 (d, *J* = 8.8, 1H), 6.37 (bs, 1H), 6.33 (bs, 1H), 5.14 (q, *J* = 6.6, 1H), 2.33 (s, 3H), 1.85 (d, *J* = 6.6, 3H), 1.52 (s, 9H).

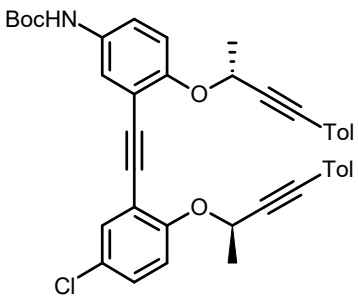
^{13}C NMR (101 MHz, $CDCl_3$): δ 156.37, 153.64, 153.01, 138.94, 131.63 (2C), 131.21, 130.81, 129.46, 129.02 (2C), 126.05, 122.04, 120.79, 118.82, 114.78, 114.62, 114.09, 109.52, 92.20, 89.34, 87.02, 86.25, 80.49, 65.74 (3C), 28.35, 22.28, 21.48.

IR ($CHCl_3$): 3442 m, 2983 m, 2872 w, 2236 w, 2216 vw, 1723 s, 1624 w, 1610 m, 1589 w, 1567 w, 1522 s, 1511 s, 1496 s, 1431 m, 1418 m, 1394 m, 1369 m, 1331 m, 1285 m, 1250 m, 1159 vs, 1121 m, 1086 m, 1055 m, 1020 m, 988 vw, 819 m, 808 m, 542 w cm^{-1}.

ESI MS: 524 ([M+Na]$^+$).

HR ESI MS: calcd for $C_{30}H_{28}O_4N^{35}ClNa$ 524.1599, found 524.1600.

(-)-*tert*-Butyl (3-[(5-chloro-2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}-phenyl)-ethynyl]-4-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}phenyl)-carbamate 8b



To a solution of phenol (-)-(*R*)-**6b** (380 mg, 0.758 mmol), (-)-(*S*)-**7**[3] (145 mg, 0.905 mmol, 1.2 equiv.), triphenylphosphine (236 mg, 0.901 mmol, 1.2 equiv.) in benzene (5 ml), diisopropyl azodicarboxylate (180 µl, 0.914 mmol, 1.2 equiv.) was added dropwise under argon. The reaction mixture was stirred at room temperature for 3 h, the solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 40:1) to afford triyne (-)-(*R,R*)-**8b** (376 mg, 77%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_D$ = -119° (c 0.294, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 2.6, 1H), 7.45 (bd, *J* = 2.7, 1H), 7.36 (bd, *J* = 8.1, 1H), 7.28 – 7.25 (m, 4H), 7.23 (dd, *J* = 8.8, 2.6, 1H), 7.16 – 7.12 (m, 2H), 7.10 – 7.06 (m, 4H), 6.34 (bs, 1H), 5.16 (q, *J* = 6.5, 1H), 5.15 (q, *J* = 6.5, 1H), 2.33 (s, 3H), 2.32 (s, 3H), 1.81 (d, *J* = 6.5, 3H), 1.79 (d, *J* = 6.5, 3H), 1.52 (s, 9H).

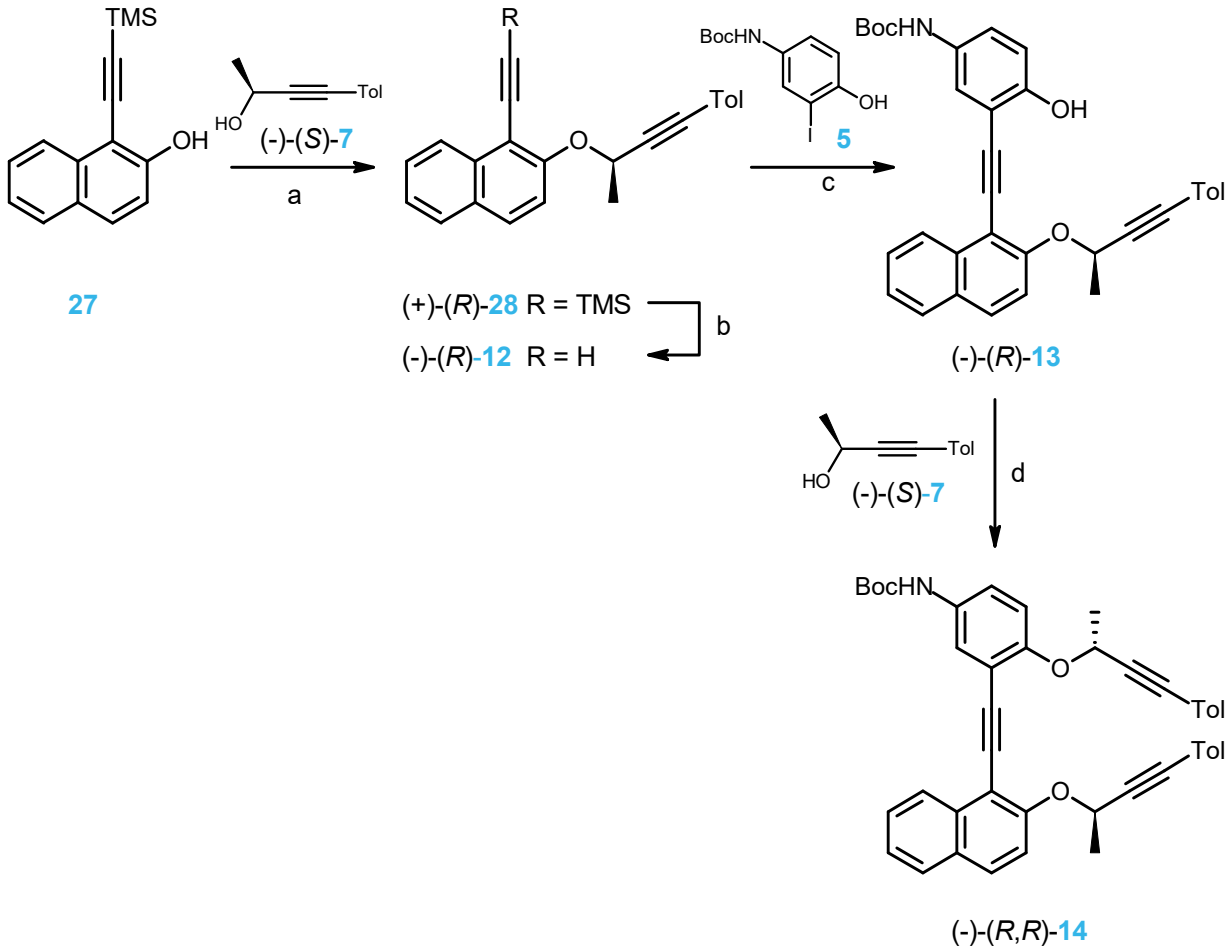
^{13}C NMR (101 MHz, $CDCl_3$): δ 156.76, 154.23, 152.83, 138.67, 138.50, 132.88, 132.51, 131.59 (2C), 131.58 (2C), 129.08, 128.99 (2C), 128.94 (2C), 126.40, 123.68, 120.41, 119.35, 119.19, 117.42, 117.15, 116.18, 114.94, 90.83, 88.83, 87.60, 87.15, 86.44, 86.16, 80.54, 66.85, 66.45, 28.33 (3C), 22.47, 22.43, 21.46, 21.45.

IR ($CHCl_3$): 3440 w, 2985 m, 2871 w, 2235 w, 2217 vw, 1724 s, 1609 m, 1585 w, 1567 w, 1517 s, 1510 s, 1499 s, 1421 m, 1392 m, 1369 m, 1330 m, 1281 m, 1246 m, 1159 vs, 1086 m, 1056 w, 1020 m, 819 m, 708 vw, 541 w cm^{-1}.

ESI MS: 666 ([M+Na]$^+$).

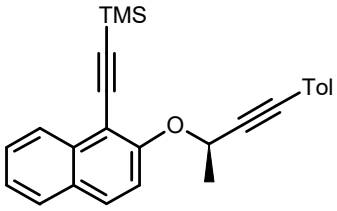
HR ESI MS: calcd for $C_{41}H_{38}O_4N^{35}ClNa$ 666.2382, found 666.2383.

Triyne (-)-(*R*,*R*)-14



(a) (-)-(*S*)-**7** (1.2 equiv.), PPh_3 (1.2 equiv.), DIAD (1.2 equiv.), benzene, rt, 2.5 h, 92%; (b) K_2CO_3 (2.0 equiv.), MeOH, rt, 3 h, 98%; (c) (-)-(*R*)-**12** (1.2 equiv.), $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (5 mol%), *i*-Pr_2NH (2.0 equiv.), benzene, 45 °C, 4.5 h, 83%; (d) (-)-(*S*)-**7** (1.2 equiv.), PPh_3 (1.2 equiv.), DIAD (1.2 equiv.), benzene, rt, 2.5 h, 88%.

(+)-Trimethyl[(2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}naphthalen-1-yl)ethynyl]silane 28



To a solution of naphthol **27**[5] (340 mg, 1.41 mmol), (-)-(*S*)-**7**[3] (276 mg, 1.73 mmol, 1.2 equiv.), triphenylphosphine (445 mg, 1.70 mmol, 1.2 equiv.) in benzene (6 ml), diisopropyl azodicarboxylate (340 µl, 1.72 mmol, 1.2 equiv.) was added dropwise under argon. The

reaction mixture was stirred at room temperature for 2.5 h, the solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-diethyl ether 50:1) to afford the protected diyne (+)-(*R*)-**28** (496 mg, 92%) as a colorless oil.

Optical rotation: $[\alpha]^{20}_{D}$ = +8.5° (c 0.307, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (dd, *J* = 8.3, 0.8, 1H), 7.81 – 7.77 (m, 2H), 7.56 (ddd, *J* = 8.3, 6.9, 1.3, 1H), 7.48 (d, *J* = 9.0, 1H), 7.41 (ddd, *J* = 8.1, 6.9, 1.2, 1H), 7.30 – 7.27 (m, 2H), 7.12 – 7.07 (m, 2H), 5.33 (q, *J* = 6.5, 1H), 2.33 (s, 3H), 1.84 (d, *J* = 6.6, 3H), 0.36 (s, 9H).

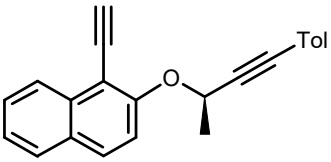
^{13}C NMR (101 MHz, $CDCl_3$): δ 158.25, 138.54, 134.54, 131.55 (2C), 129.77, 129.36, 128.96 (2C), 128.00, 127.10, 125.60, 124.68, 119.40, 118.35, 109.48, 104.54, 99.25, 87.79, 86.31, 67.45, 22.51, 21.43, 0.18 (3C).

IR ($CHCl_3$): 3062 w, 3034 w, 2900 w, 2246 w, sh, 2226 w, 2146 m, 1622 w, 1589 m, 1572 w, 1510 s, 1464 m, 1434 w, 1408 vw, 1376 m, 1328 m, 1271 s, 1250 vs, 1233 m, sh, 1180 w, 1149 w, 1119 m, 1085 s, 1042 m, 1030 m, 1021 m, 910 m, 846 vs, 819 s, 700 w, 543 w cm^{-1}.

ESI MS: 405 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{26}H_{26}ONaSi$ 405.1645, found 405.1645.

(-)-1-Ethynyl-2-{[(2*R*)-4-(4-methylphenyl)but-3-yn-2-yl]oxy}naphthalene 12



To a solution of the protected diyne (+)-(*R*)-**28** (496 mg, 1.30 mmol) in methanol (7 ml), anhydrous potassium carbonate (358 mg, 2.60 mmol, 2.0 equiv.) was added in one portion. The reaction mixture was stirred at room temperature for 3 h. Then it was diluted with a saturated ammonium chloride solution (20 ml), extracted with diethyl ether (3 x 15 ml) and the combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel (hexane-diethyl ether 50:1) to give diyne (-)-(*R*)-**12** (394 mg, 98%) as a colorless oil.

Optical rotation: $[\alpha]^{20}_{D}$ = -42.5° (c 0.374, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, *J* = 8.4, 1H), 7.83 (d, *J* = 9.0, 1H), 7.79 (d, *J* = 8.2, 1H), 7.55 (ddd, *J* = 8.3, 6.9, 1.3, 1H), 7.51 (d, *J* = 9.1, 1H), 7.41 (ddd, *J* = 8.1, 6.9, 1.2, 1H), 7.27 – 7.25 (m, 2H), 7.09 – 7.07 (m, 2H), 5.30 (q, *J* = 6.6, 1H), 3.72 (s, 1H), 2.32 (s, 3H), 1.85 (d, *J* = 6.6, 3H).

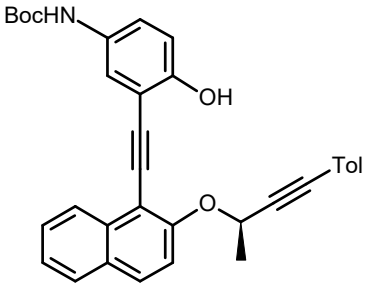
^{13}C NMR (101 MHz, $CDCl_3$): δ 158.36, 138.61, 134.75, 131.56 (2C), 130.09, 129.11, 128.96 (2C), 128.03, 127.26, 125.39, 124.63, 119.30, 117.17, 107.72, 87.56, 86.61, 86.42, 78.10, 66.99, 22.51, 21.42.

IR ($CHCl_3$): 3307 s, 3063 w, 3033 w, 2247 w, sh, 2226 w, 2100 w, 1623 m, 1590 s, 1572 w, sh, 1510 vs, 1465 s, 1434 w, 1408 vw, 1374 m, 1329 s, 1270 vs, 1248 vs, 1231 s, 1180 w, 1148 m, 1120 m, 1085 s, 1040 s, 1027 m, 1020 m, 911 w, 867 w, 819 s, 655 m, 608 m, 537 vw cm^{-1}.

ESI MS: 311 ($[M+H]^+$).

HR ESI MS: calcd for $C_{23}H_{19}O$ 311.1430, found 311.1430.

(-)-*tert*-Butyl {4-hydroxy-3-[(2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}naphthalen-1-yl)ethynyl]phenyl}carbamate 13



A Schlenk flask was charged with iodide **5** (355 mg, 1.06 mmol), $Pd(PPh_3)_2Cl_2$ (15 mg, 0.021 mmol, 2 mol%) and CuI (10 mg, 0.053 mmol, 5 mol%) and purged with argon. Then degassed benzene (4 ml) and *N,N*-diisopropylamine (300 µl, 2.14 mmol, 2.0 equiv.) were added and the mixture was heated at 45 °C. Then alkyne (-)-(*R*)-**12** (392 mg, 1.26 mmol, 1.2 equiv.) in degassed benzene (5 ml) was added dropwise to the reaction mixture and the reaction was stirred at 45 °C for 4.5 h. The solvent was evaporated *in vacuo* and the residue was flash chromatographed on silica gel (hexane-ethyl acetate 20:1) to afford phenol carmabate (-)-(*R*)-**13** (458 mg, 83%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_D$ = -305° (c 0.277, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 – 8.30 (m, 1H), 7.85 (d, *J* = 9.1, 1H), 7.83 – 7.80 (m, 1H) 7.68 (bs, 1H), 7.62 – 7.57 (m, 1H), 7.56 (d, *J* = 9.1, 1H), 7.45 – 7.41 (m, 1H), 7.29 – 7.26 (m, 2H), 7.15 (dd, *J* = 8.9, 2.7, 1H), 7.09 – 7.05 (m, 2H), 6.97 (dd, *J* = 8.8, 0.8, 1H), 6.67 (d, *J* = 0.8, 1H), 6.39 (bs, 1H), 5.36 (q, *J* = 6.5, 1H), 2.31 (s, 3H), 1.92 (d, *J* = 6.5, 3H), 1.55 (s, 9H).

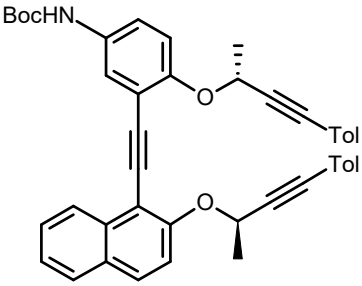
^{13}C NMR (101 MHz, $CDCl_3$): δ 156.93, 153.41, 153.07, 138.76, 133.29, 131.61 (2C), 130.75, 129.97, 128.95 (2C), 128.71, 128.03, 127.44, 125.39, 124.66, 121.47, 120.51, 118.96, 114.77, 114.65, 110.40, 106.95, 93.35, 92.11, 86.92, 86.81, 80.41, 66.04, 28.37 (3C), 22.47, 21.44.

IR (KBr): 3436 m, vbr, 3058 vw, 3030 vw, 2980 w, 2870 w, 2244 vw, sh, 2225 vw, 1725 m, sh, 1699 s, 1685 s, 1622 m, 1587 m, 1526 m, sh, 1510 s, 1495 s, sh, 1467 m, 1418 vw, 1392 m, 1369 s, 1329 m, 1285 m, 1268 s, 1247 vs, 1162 vs, 1117 m, 1083 m, 1038 m, 1026 m, sh, 1020 m, sh, 816 s, 708 vw, 666 w cm^{-1}.

ESI MS: 540 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{34}H_{31}O_4NNa$ 540.2145, found 540.2146.

(-)-*tert*-Butyl (4-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}-3-[(2-{[(1*R*)-1-methyl-3-(4-methylphenyl)prop-2-yn-1-yl]oxy}naphthalen-1-yl)ethynyl]phenyl)carbamate 14



To a solution of phenol (-)-(*R*)-**13** (410 mg, 0.793 mmol), (-)-(*S*)-**7**[3] (152 mg, 0.949 mmol, 1.2 equiv.), triphenylphosphine (249 mg, 0.950 mmol, 1.2 equiv.) in benzene (5 ml), diisopropyl azodicarboxylate (190 µl, 0.965 mmol, 1.2 equiv.) was added dropwise under argon. The reaction mixture was left stirring at room temperature for 2.5 h, the solvent was evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 50:1) to afford triyne (-)-(*R,R*)-**14** (460 mg, 88%) as an amorphous solid.

Optical rotation: $[\alpha]^{20}_D$ = -110° (c 0.526, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (bd, *J* = 8.4, 1H), 7.82 – 7.78 (m, 2H), 7.55 (ddd, *J* = 8.3, 6.8, 1.3, 1H), 7.50 (d, *J* = 9.0, 2H), 7.43 (bd, *J* = 2.7, 1H), 7.41 (ddd, *J* = 8.1, 6.9, 1.3, 1H), 7.30 – 7.26 (m, 4H), 7.21 (d, *J* = 9.0, 1H), 7.09 – 7.05 (m, 4H), 6.35 (bs, 1H), 5.41 (q, *J* = 6.5, 1H), 5.24 (q, *J* = 6.5, 1H), 2.32 (s, 6H), 1.89 (d, *J* = 6.5, 3H), 1.88 (d, *J* = 6.5, 3H), 1.53 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.19, 154.22, 152.90, 138.50 (2C), 134.57, 132.23, 131.61 (2C), 131.56 (2C), 129.51, 129.42, 128.96 (2C), 128.93 (2C), 127.88, 126.96, 126.12, 124.68, 123.40, 120.23, 119.40, 119.33, 118.30, 116.21, 115.13, 109.87, 95.39, 88.46, 87.94, 87.61, 86.19 (2C), 80.46, 67.52, 66.22, 28.35 (3C), 22.64, 22.58, 21.44 (2C).

IR (KBr): 3410 m, 3342 w, br, 3055 w, 2983 m, 2231 w, 1725 s, 1707 m, 1700 m, 1622 w, sh, 1609 m, 1588 m, 1570 vw, 1523 s, br, sh, 1510 vs, 1498 vs, 1466 m, 1434 w, 1392 w, 1368 m, 1328 m, 1282 m, sh, 1268 s, 1246 s, 1158 vs, 1125 s, 1084 s, 1038 s, 1030 m, sh, 1019 m, 944 w, 816 s, 667 w, 536 vw cm^{-1}.

ESI MS: 682 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{45}H_{41}O_4NNa$ 682.2928, found 682.2929.

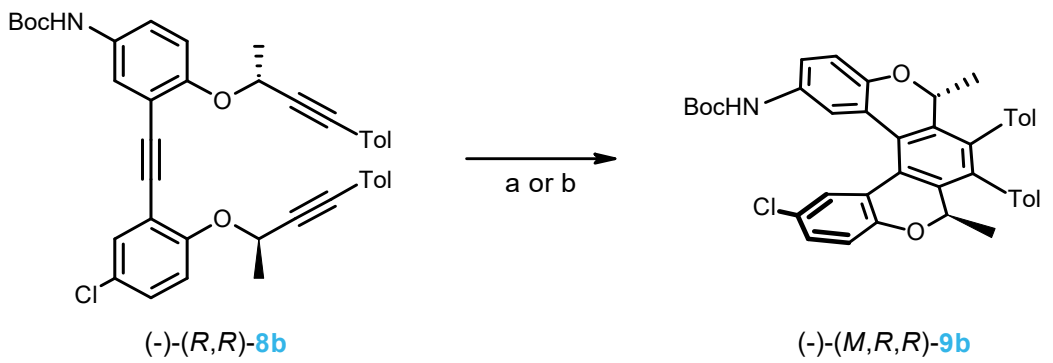
Synthesis of oxahelicene amines (-)-(*M*,*R*,*R*)-9b, (-)-(*M*,*R*,*R*)-10a-g and (-)-(*M*,*R*,*R*)-16

General procedure A *([2+2+2] cycloisomerisation using cobalt catalyst)*: A microwave vial was charged with triyne (-)-(*R*,*R*)-**8a**,**b** or (-)-(*R*,*R*)-**14** (1.0 equiv.) and CpCo(CO)(fum) (30 - 50 mol%) under argon. Tetrahydrofuran (5 ml) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (125 µl) were added and the reaction mixture was heated at 140 °C in a microwave reactor for 15 min. Then the solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel to furnish the desired cyclic product (-)-(*M*,*R*,*R*)-**9a**,**b** or (-)-(*M*,*R*,*R*)-**15**.

General procedure B *(Suzuki-Miyaura coupling of chlorohelicenes)*: To a solution of the oxa[5]helicene amine derivative (-)-(*M*,*R*,*R*)-**9b** (1.0 equiv.), pinacol boronate (2.5 equiv.) or boronic acid (2.1 – 3.3 equiv.) and XPhos Pd G2 (5 – 8 mol%) in tetrahydrofuran (2 – 2.8 ml), 0.5 M K_3PO_4 aqueous solution (1.1 – 2.5 equiv.) was added at room temperature. Then argon was bubbled through this biphasic mixture for 15 min. After this period, the reaction vessel was sealed and the mixture was heated at 100 °C and stirred for 1 - 6 h. The reaction mixture was poured into water (20ml) and extracted with dichloromethane (3 × 10 ml). The combined organic layers were dried over anhydrous $MgSO_4$, the solvents were removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-acetone 20:1) and then on C-18 reversed-phase silica gel (methanol) to afford the desired product (-)-(*M*,*R*,*R*)-**19b-g**.

General procedure C *(deprotection of BOC group)*: Trifluoroacetic acid (15 - 33 equiv.) was added to the solution of BOC-protected oxahelicene amine (-)-(*M*,*R*,*R*)-**9a**, (-)-(*M*,*R*,*R*)-**19b-g** or (-)-(*M*,*R*,*R*)-**15** (1.0 equiv.) in dichloromethane (3 – 10 ml) at room temperature and the reaction mixture was stirred for 3 – 16 h. After that, it was poured into a saturated solution of $NaHCO_3$ (20 ml) and the product was extracted with dichloromethane (3 × 10 ml). The combined organic layers were dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo* to provide the desired oxahelicene amine (-)-(*M*,*R*,*R*)-**10a-g** or (-)-(*M*,*R*,*R*)-**16** which was used without further purification or purified by chromatography.

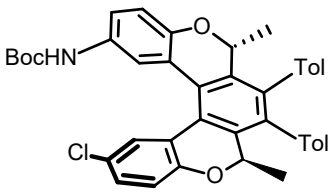
Oxa[5]helicene amine derivative (-)-(*M*,*R*,*R*)-9b



(-)-(*R*,*R*)-**8b** (-)-(*M*,*R*,*R*)-**9b**

(a) CpCo(CO)(fum) (50 mol%), [bdmim]BF_4, microwave reactor, THF, 140 °C, 15 min., 74%; (b) $Ni(PPh_3)_2(CO)_2$ (36 mol%), toluene, 110 °C, 15 min, 70%.

(-)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-12-chloro-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5 dihydrobenzo-[1,2-*c*:4,3-*c'*]dichromen-9-yl]carbamate 9b



The oxa[5]helicene amine derivative (-)-(*M,R,R*)-**9b** was prepared according to the *General procedure A* from triyne (-)-(*R,R*)-**8b** (100 mg, 0.156 mmol), CpCo(CO)(fum) (23 mg, 0.078 mmol, 50 mol%) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (125 µl) in tetrahydrofuran (5 ml). The purification by flash chromatography on silica gel (hexane-ethyl acetate 49:1) gave the oxa[5]helicene amine derivative (-)-(*M,R,R*)-**9b** (74 mg, 74%) as a yellowish solid.

Using $Ni(PPh_3)_2(CO)_2$: A microwave vial was charged with triyne (-)-(*R,R*)-**8b** (50 mg, 0.078 mmol), $Ni(PPh_3)_2(CO)_2$ (18 mg, 0.028 mmol, 36 mol%) and toluene (5 ml) and argon was bubbled through the reaction mixture for 15 min. Then it was heated at 110 °C under stirring for 15 min. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane-ethyl acetate 10:1) to obtain the oxa[5]helicene amine derivative (-)-(*M,R,R*)-**9b** (35 mg, 70%) as a pale yellow solid.

M.p.: 171-174 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -671° (c 0.250, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 – 7.40 (m, 2H), 7.20 (bd, *J* = 2.6, 1H), 7.14 – 7.05 (m, 5H), 6.98 (d, *J* = 8.7, 1H), 6.94 (d, *J* = 8.5, 1H), 6.89 – 6.84 (m, 2H), 6.66 – 6.63 (m, 2H), 6.18 (bs, 1H), 5.23 (q, *J* = 6.7, 1H), 5.22 (q, *J* = 6.7, 1H), 2.26 (s, 6H), 1.48 (s, 9H), 0.95 (d, *J* = 6.7, 3H), 0.93 (d, *J* = 6.7, 3H).

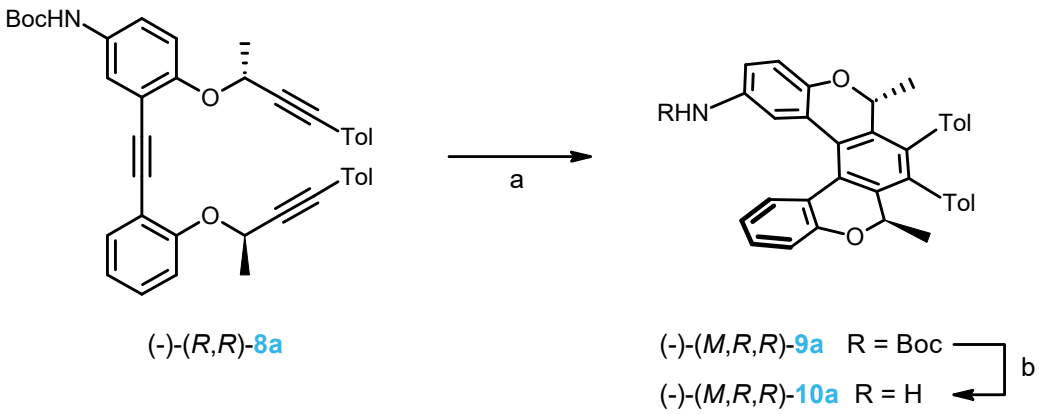
^{13}C NMR (101 MHz, $CDCl_3$): δ 153.01, 152.03, 149.33, 139.33, 138.85, 137.84, 137.38, 136.18 (2C), 134.58 (2C), 131.70, 130.60, 130.53, 128.95, 128.94, 128.82, 128.79, 128.62, 128.59, 128.43, 128.41, 125.76, 125.14, 124.55, 124.00, 122.85, 121.23, 120.40, 119.59 (2C), 80.30, 73.15, 72.85, 28.30 (3C), 21.17 (2C), 18.34, 18.26.

IR ($CHCl_3$): 3439 w, 2983 m, 2871 w, 1723 m, 1616 w, 1594 w, 1517 s, 1481 m, 1454 w, sh, 1431 m, 1408 w, 1393 m, 1368 m, 1328 w, 1260 m, 1257 m, sh, 1159 s, 1102 m, 1089 w, 1061 m, 1022 w, 855 m, 821 m, 696 w, 584 w, 469 m cm^{-1}.

ESI MS: 666 ($[M+Na]^+$).

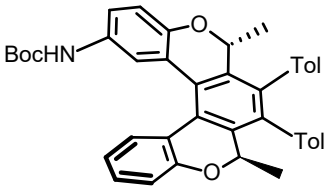
HR ESI MS: calcd for $C_{41}H_{38}O_4N^{35}ClNa$ 666.2381, found 666.2383.

Oxa[5]helicene amine (-)-(*M*,*R*,*R*)-10a



(a) CpCo(CO)(fum) (30 mol%), [bdmim]BF_4, microwave reactor, THF, 140 °C, 15 min., 82%; (b) TFA (15 equiv.), CH_2Cl_2, rt, 16 h, 78%.

(-)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo-[1,2-*c*:4,3-*c'*]dichromen-9-yl]carbamate 9a



The oxa[5]helicene amine derivative (-)-(*M,R,R*)-**9a** was prepared according to the *General procedure A* from triyne (-)-(*R,R*)-**8a** (107 mg, 0.176 mmol), CpCo(CO)(fum) (15 mg, 0.052 mmol, 30 mol%) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (125 µl) in tetrahydrofuran (5 ml). The purification by flash chromatography on silica gel (hexane-ethyl acetate 100:1) gave the oxa[5]helicene amine derivative (-)-(*M,R,R*)-**9a** as a yellow solid (88 mg, 82%).

M.p.: 159-162 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -546° (c 0.286, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (bs, 1H), 7.47 (dd, *J* = 7.9, 1.6, 1H), 7.18 (ddd, *J* = 8.1, 7.3, 1.6, 1H), 7.14 – 7.10 (m, 2H), 7.09 – 7.06 (m, 2H), 7.01 (dd, *J* = 8.1, 1.3, 2H), 6.97 (d, *J* = 8.7, 1H), 6.86 (m, 2H), 6.80 (ddd, *J* = 7.9, 7.3, 1.3, 1H), 6.65 (m, 2H), 6.08 (s, 1H), 5.24 (q, *J* = 6.7, 1H), 5.22 (q, *J* = 6.7, 1H), 2.26 (s, 6H), 1.47 (s, 9H), 0.93 (d, *J* = 6.7, 6H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 153.50, 153.03, 149.25, 139.21, 139.02, 137.32, 137.19, 136.06 (2C), 134.77 (2C), 131.54, 130.65 (2C), 129.22, 129.13, 129.01 (2C), 128.57 (2C), 128.37 (2C),

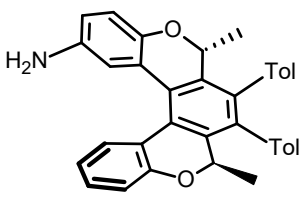
125.21, 124.87, 123.56, 123.21, 120.84, 120.58, 119.67, 119.49, 119.21, 80.31, 72.92, 72.89, 28.31 (3C), 21.16 (2C), 18.32, 18.29.

IR ($CHCl_3$): 3438 w, 3081 vw, 3050 w, sh, 2983 m, 1722 s, 1616 w, 1604 w, 1594 vw, 1583 w, 1550 w, sh, 1517 vs, 1495 s, 1485 m, 1420 m, 1393 m, 1381 m, 1368 s, 1309 w, sh, 1298 w, 1272 w, 1185 w, sh, 1159 vs, 1123 w, 1112 w, 1106 w, 1063 s, 1022 w, 1011 w, 945 w, 918 w, 836 m, 518 w, 461 w cm^{-1}.

ESI MS: 632 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{41}H_{39}O_4NNa$ 632.2771, found 632.2772.

(-)-(*M*)-(2*R*,5*R*)-2,5-Dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-amine 10a



Oxa[5]helicene amine (-)-(*M,R,R*)-**10a** was prepared according to the *General procedure C* from the oxa[5]helicene amine derivative (-)-(*M,R,R*)-**9a** (178 mg, 0.292 mmol), trifluoroacetic acid (340 µl, 4.40 mmol, 15 equiv.) in dichloromethane (5 ml) for 16 h. The purification by flash chromatography on C-18 reversed-phase silica gel (methanol) gave oxa[5]helicene amine (-)-(*M,R,R*)-**10a** (117 mg, 78%) as a yellowish solid.

M.p.: 161-165 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -629° (c 0.133, $CHCl_3$).

UV/Vis (THF): λ_{max} (log ε) = 237 (4.32), 261 (4.28), 316 (3.79), 373 (3.49) nm.

^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.51 (dd, *J* = 7.9, 1.6, 1H), 7.18 (ddd, *J* = 8.0, 7.7, 1.6, 1H), 7.15 – 7.10 (m, 4H), 6.99 (dd, *J* = 8.0, 1.2, 1H), 6.91 (m, 2H), 6.82 (ddd, *J* = 7.9, 7.7, 1.2, 1H), 6.80 (d, *J* = 8.4, 1H), 6.72 (m, 2H), 6.71 (d, *J* = 2.8, 1H), 6.54 (dd, *J* = 8.4, 2.8, 1H), 5.17 (q, *J* = 6.7, 1H), 5.09 (q, *J* = 6.7, 1H), 3.31 (s, 2H), 2.27 (s, 6H), 0.92 (d, *J* = 6.7, 3H), 0.90 (d, *J* = 6.7, 3H).

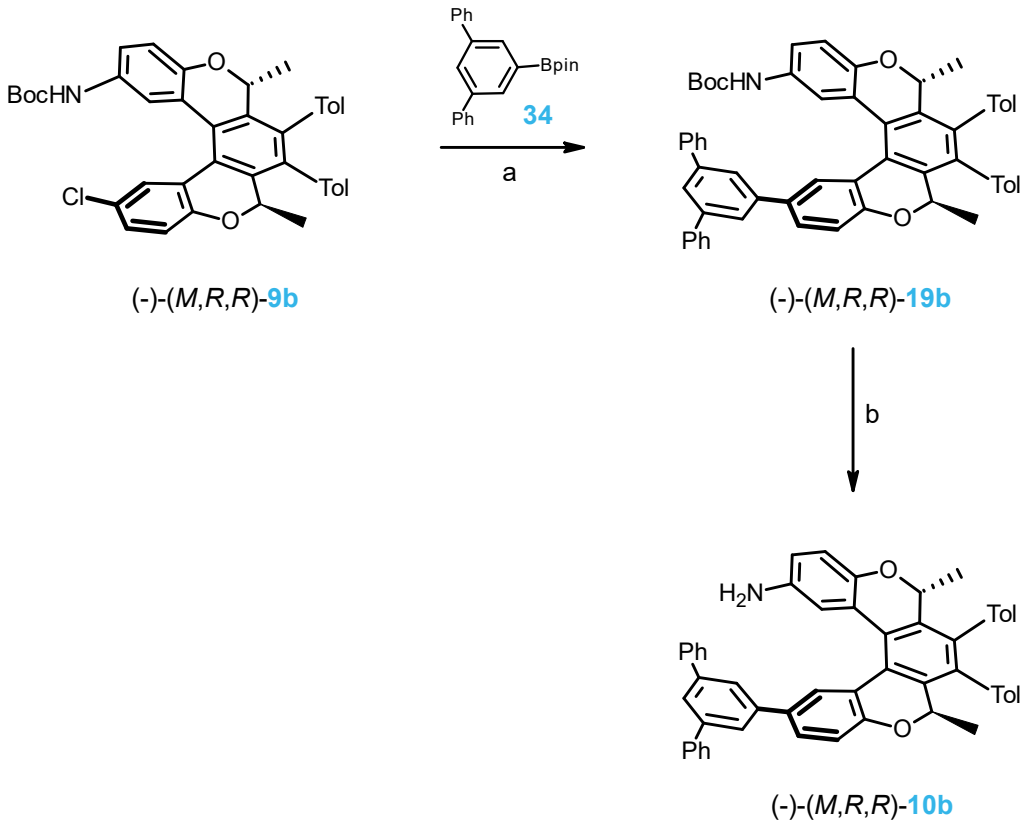
^{13}C NMR (151 MHz, CD_2Cl_2): δ 153.93, 146.17, 140.74, 139.97, 139.41, 137.56, 137.44, 136.64, 136.62, 135.55, 135.51, 131.25, 131.22, 129.76, 129.66, 129.61, 129.46, 128.84, 128.83, 128.82, 128.81, 125.94, 125.52, 124.34, 123.88, 121.06, 119.93, 119.48, 116.66, 115.89, 73.28, 72.98, 21.27 (2C), 18.53, 18.37.

IR (KBr): 3444 m, 3368 m, 3080 vw, sh, 3020 m, 2978 m, sh, 2957 s, 1619 m, 1605 m, 1583 m, 1570 vw, 1546 vw, 1517 s, 1493 s, 1485 s, 1450 s, 1404 w, 1379 vw, 1301 m, 1277 m, 1213 vs, 1183 m, 1150 m, 1124 m, 1111 m, 1033 m, 1022 m, 967 w, 956 w, 944 w, 916 w, 821 m, 791 w, 759 m cm^{-1}.

ESI MS: 510 ($[M+H]^+$).

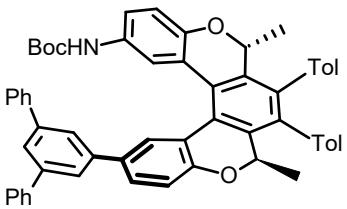
HR ESI MS: calcd for $C_{36}H_{32}O_2N$ 510.2428, found 510.2427.

Oxa[5]helicene amine (-)-(*M*,*R*,*R*)-10b



(a) **34** (2.6 equiv.), XPhos Pd G2 (7 mol%), aq. K_3PO_4 (1.1 equiv.), THF, 100 °C, 6 h, 79%; (b) TFA (33 equiv.), CH_2Cl_2, rt, 3 h, 97%.

(-)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-12-(1,1':3',1''-terphenyl-5'-yl)-2,5-dihydrobenzo[1,2-c:4,3-c']dichromen-9-yl]carbamate 19b



The oxa[5]helicene amine derivative (-)-(*M,R,R*)-**19b** was prepared according to the *General procedure B* from the chloro derivative (-)-(*M,R,R*)-**9b** (145 mg, 0.225 mmol), 2-([1,1':3',1''-terphenyl]-5'-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane acid **34** (205 mg, 0.575 mmol, 2.6 equiv.), XPhos Pd G2 (13 mg, 0.017 mmol, 7 mol%) and K_3PO_4 (0.5 M in water, 0.50 ml, 0.25 mmol, 1.1 equiv.) in tetrahydrofuran (2.8 ml) at 100 °C for 6 h. The purification by flash chromatography on silica gel (hexane-acetone 20:1) and then on C-18 reversed-phase silica gel (methanol) gave the product (-)-(*M,R,R*)-**19b** (149 mg, 79%) as a white solid.

M.p.: 185-190 °C (methanol).

Optical rotation: $[\alpha]^{20}_{D}$ = -596° (c 0.311, $CHCl_3$).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.85 (bd, *J* = 2.3, 1H), 7.73 (t, *J* = 1.7, 1H), 7.65 – 7.62 (m, 4H), 7.55 (dd, *J* = 8.4, 2.3, 1H), 7.52 – 7.47 (m, 7H), 7.43 – 7.37 (m, 3H), 7.18 – 7.10 (m, 5H), 6.99 (d, *J* = 8.8, 1H), 6.94 – 6.91 (m, 2H), 6.74 (dt, *J* = 7.9, 2.0, 2H), 6.26 (bs, 1H), 5.24 (q, *J* = 6.7, 1H), 5.17 (q, *J* = 6.7, 1H), 2.28 (s, 3H), 2.27 (s, 3H), 1.30 (s, 9H), 1.00 (d, *J* = 6.7, 3H), 0.95 (d, *J* = 6.7, 3H).

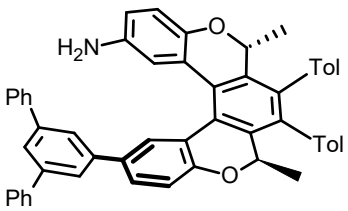
^{13}C NMR (101 MHz, CD_2Cl_2): δ 153.78, 152.95, 149.61, 142.56 (2C), 142.45, 141.29, 139.96, 139.50, 137.81, 136.73, 136.72, 135.35, 135.32, 134.10, 132.55, 131.17 (2C), 129.57, 129.56, 129.24 (4C), 128.88, 128.87, 128.85 (2C), 128.63, 128.43, 127.94 (2C), 127.60 (4C), 125.48, 125.43, 124.79, 124.76 (2C), 124.17, 123.70, 120.50, 120.05, 119.95, 118.98, 80.44, 73.52, 73.29, 28.25 (3C), 21.28 (2C), 18.70, 18.49, one C was not identified.

IR ($CHCl_3$): 3434 w, 3060 w, 2983 m, 1722 m, 1615 w, 1595 m, 1547 w, sh, 1517 s, 1498 m, 1490 m, 1455 w, 1441 w, 1413 w, 1404 w, sh, 1393 w, 1369 m, 1329 w, 1267 w, sh, 1254 m, 1186 w, sh, 1159 s, 1108 w, 1089 w, 1076 vw, 1021 w, 955 w, 916 w, 899 w, 822 m, 809 w, 614 w, 534 w cm^{-1}.

ESI MS: 860 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{59}H_{51}O_4NNa$ 860.3710, found 860.3716.

(-)-(*M*)-(2*R*,5*R*)-2,5-Dimethyl-3,4-bis(4-methylphenyl)-12-(1,1':3',1''-terphenyl-5'-yl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-amine 10b



The oxa[5]helicene amine (-)-(*M,R,R*)-**10b** was prepared according to the *General procedure C* from the oxa[5]helicene amine derivative (-)-(*M,R,R*)-**19b** (115 mg, 0.14 mmol) and trifluoroacetic acid (350 µl, 4.6 mmol, 33 equiv.) in dichloromethane (3 ml) for 3 h. The purification by flash chromatography on silica gel (hexane-ethyl acetate 10:1) gave oxa[5]helicene amine (-)-(*M,R,R*)-**10b** (98 mg, 97%) as a yellowish solid.

M.p.: 169-171 °C (hexane – ethyl acetate).

Optical rotation: $[\alpha]^{20}_{D}$ = -578° (c 0.346, CH_2Cl_2).

UV/Vis (THF): λ_{max} (log ε) = 262 (4.93), 345 (3.87) nm.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.99 (bd, *J* = 2.2, 1H), 7.76 (t, *J* = 1.7, 1H), 7.70 – 7.67 (m, 4H), 7.63 (d, *J* = 1.7, 2H), 7.55 (dd, *J* = 8.3, 2.2, 1H), 7.52 – 7.47 (m, 4H), 7.43 – 7.38 (m, 2H), 7.17 – 7.10 (m, 5H), 6.94 – 6.91 (m, 3H), 6.89 (bd, *J* = 8.4, 1H), 6.76 – 6.73 (m, 2H), 6.55 (dd, *J* = 8.5, 2.7, 1H), 5.23 (q, *J* = 6.7, 1H), 5.12 (q, *J* = 6.7, 1H), 3.28 (bs, 2H), 2.28 (s, 3H), 2.27 (s, 3H), 1.00 (d, *J* = 6.7, 3H), 0.94 (d, *J* = 6.7, 3H).

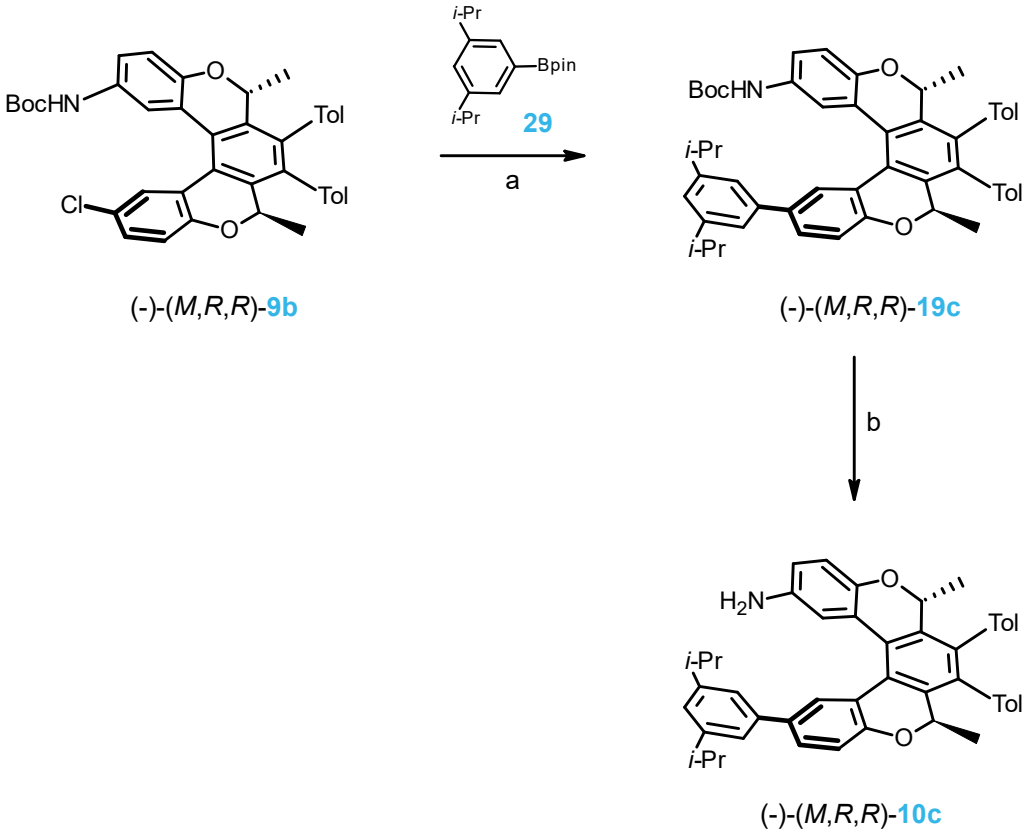
^{13}C NMR (101 MHz, CD_2Cl_2): δ 153.73, 146.41, 142.47, 142.41 (2C), 141.31 (2C), 140.64, 140.13, 139.29, 137.79, 137.51, 136.67, 136.63, 135.48, 135.46, 133.91, 131.23, 131.17, 129.64, 129.58, 129.13 (4C), 128.85 (3C), 128.81, 128.80, 128.37, 127.92 (2C), 127.67 (4C), 126.02, 125.35, 124.83 (2C), 124.66, 124.45, 123.85, 120.15, 119.82, 117.31, 115.78, 73.53, 72.98, 21.28 (2C), 18.72, 18.38.

IR ($CHCl_3$): 3453 w, 3383 w, 3060 w, sh, 3024 m, 1797 s, 1619 m, 1595 m, 1518 m, 1497 s, 1426 m, 1441 m, 1413 m, 1405 w, sh, 1306 w, sh, 1267 m, 1249 m, 1183 w, 1109 m, 1086 m, 1076 m, 1030 m, 1021 m, 1009 m, 957 w, 816 m, 614 m, 534 m cm^{-1}.

ESI MS: 738 ($[M+H]^+$).

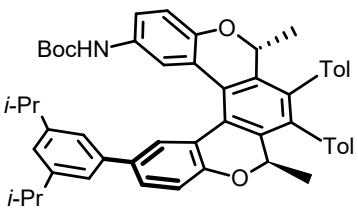
HR ESI MS: calcd for $C_{54}H_{44}O_2N$ 738.3367, found 738.3367.

Oxa[5]helicene amine (-)-(*M*,*R*,*R*)-10c



(a) **29** (2.5 equiv.), XPhos Pd G2 (8 mol%), aq. K_3PO_4 (2.5 equiv.), THF, 100 °C, 2 h, 89%; (b) TFA (25 equiv.), CH_2Cl_2, rt, 16 h, 98%.

(-)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-12-[3,5-bis(1-methylethyl)phenyl]-2,5-dimethyl-3,4-bis(4-methyl-phenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-yl]carbamate 19c



The oxa[5]helicene amine derivative (-)-(*M,R,R*)-**19c** was prepared according to the *General procedure B* from the chloro derivative (-)-(*M,R,R*)-**9b** (120 mg, 0.187 mmol), 1,3-diisopropyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborlan-2-yl)benzene **29**[6] (131 mg, 0.455 mmol, 2.5 equiv.), XPhos Pd G2 (11 mg, 0.014 mmol, 8 mol%) and K_3PO_4 (0.5 M in water, 0.95 ml, 0.48 mmol, 2.5 equiv.) in tetrahydrofuran (2.5 ml) at 100 °C for 2 h. The purification by flash chromatography on silica gel (hexane-acetone 20:1) and then on C-18 reversed-phase silica gel (methanol) gave the product (-)-(*M,R,R*)-**19c** (128 mg, 89%) as a white solid.

M.p.: 161-166 °C (methanol).

Optical rotation: $[\alpha]^{20}_{D}$ = -657° (c 0.304, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (bs, 1H), 7.72 (bd, *J* = 2.2, 1H), 7.42 (dd, *J* = 8.3, 2.2, 1H), 7.20 – 7.03 (m, 7H), 6.99 – 6.97 (m, 3H), 6.90 – 6.80 (m, 2H), 6.67 – 6.65 (m, 2H), 6.15 (s, 1H), 5.28 (q, *J* = 6.7, 1H), 5.23 (q, *J* = 6.7, 1H), 2.86 (sept, *J* = 6.9, 2H), 2.27 (s, 3H), 2.26 (s, 3H), 1.40 (s, 9H), 1.24 (d, *J* = 7.0, 6H), 1.22 (d, *J* = 7.0, 6H), 0.97 (d, *J* = 6.7, 3H), 0.95 (d, *J* = 6.7, 3H).

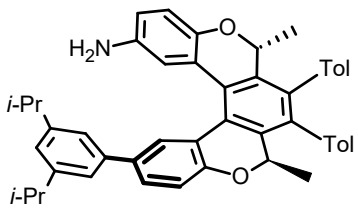
^{13}C NMR (101 MHz, $CDCl_3$): δ 152.85, 152.79, 149.33, 149.31 (2C), 140.81, 139.35, 138.95, 137.30, 137.24, 136.07 (2C), 134.78, 134.75, 134.47, 131.86, 130.71, 130.64, 129.04, 129.02, 128.59, 128.58, 128.38, 128.37, 128.24, 127.90, 125.23, 124.90, 123.77, 123.48, 123.06, 122.25 (2C), 120.48, 119.67, 119.36, 119.15, 80.27, 73.10, 72.96, 34.29 (2C), 28.21 (3C), 24.03 (4C), 21.18 (2C), 18.52, 18.31.

IR ($CHCl_3$): 3433 w, 3086 vw, 3050 w, sh, 2979 m, 2964 m, 2890 vw, 2870 w, 1722 s, 1615 w, 1597 w, 1549 w, sh, 1517 vs, 1467 m, 1455 m, sh, 1427 m, 1404 w, 1393 w, 1384 w, 1369 m, 1301 w, 1184 m, sh, 1159 vs, 1112 w, 1107 w, 1101 w, 1022 w, 956 vw, 946 vw, 887 w, 824 m, 809 w, 714 w, 694 vw cm^{-1}.

ESI MS: 792 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{53}H_{55}O_4NNa$ 792.4023, found 792.4026.

(-)-(*M*)-(2*R*,5*R*)-12-[3,5-bis(1-Methylethyl)phenyl]-2,5-dimethyl-3,4-bis(4-methyl-phenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-amine 10c



Oxa[5]helicene amine (-)-(*M,R,R*)-**10c** was prepared according to the *General procedure C* from the oxa[5]helicene derivative (-)-(*M,R,R*)-**19c** (104 mg, 0.135 mmol) and trifluoroacetic acid (260 µl, 3.40 mmol, 25 equiv.) in dichloromethane (10 ml) for 16 h. Evaporation of solvent provided the desired oxa[5]helicene amine (-)-(*M,R,R*)-**10c** (89 mg, 98%) as a yellowish solid, which was used without further purification.

M.p.: 148-153 °C (dichloromethane).

Optical rotation: $[\alpha]^{20}_{D}$ = -668° (c 0.112, CH_2Cl_2).

UV/Vis (THF): λ_{max} (log ε) = 258 (4.90), 340 (4.02) nm.

^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.82 (d, *J* = 2.3, 1H), 7.44 (dd, *J* = 8.3, 2.3, 1H), 7.16 – 7.10 (m, 4H), 7.08 (d, *J* = 1.7, 2H), 7.05 (d, *J* = 8.3, 1H), 6.99 (t, *J* = 1.7, 1H), 6.92 (m, 2H), 6.86 (bd, *J* = 8.6, 1H), 6.85 (bd, *J* = 2.6, 1H), 6.75 – 6.73 (m, 2H), 6.61 (dd, *J* = 8.6, 2.6, 1H), 5.20 (q, *J* = 6.7, 1H), 5.11 (q, *J* = 6.7, 1H), 3.34 (bs, 2H), 2.87 (sept, *J* = 6.9, 2H), 2.28 (s, 3H), 2.27 (s, 3H), 1.25 (d, *J* = 6.9, 6H), 1.23 (d, *J* = 6.9, 6H), 0.97 (d, *J* = 6.7, 3H), 0.93 (d, *J* = 6.7, 3H).

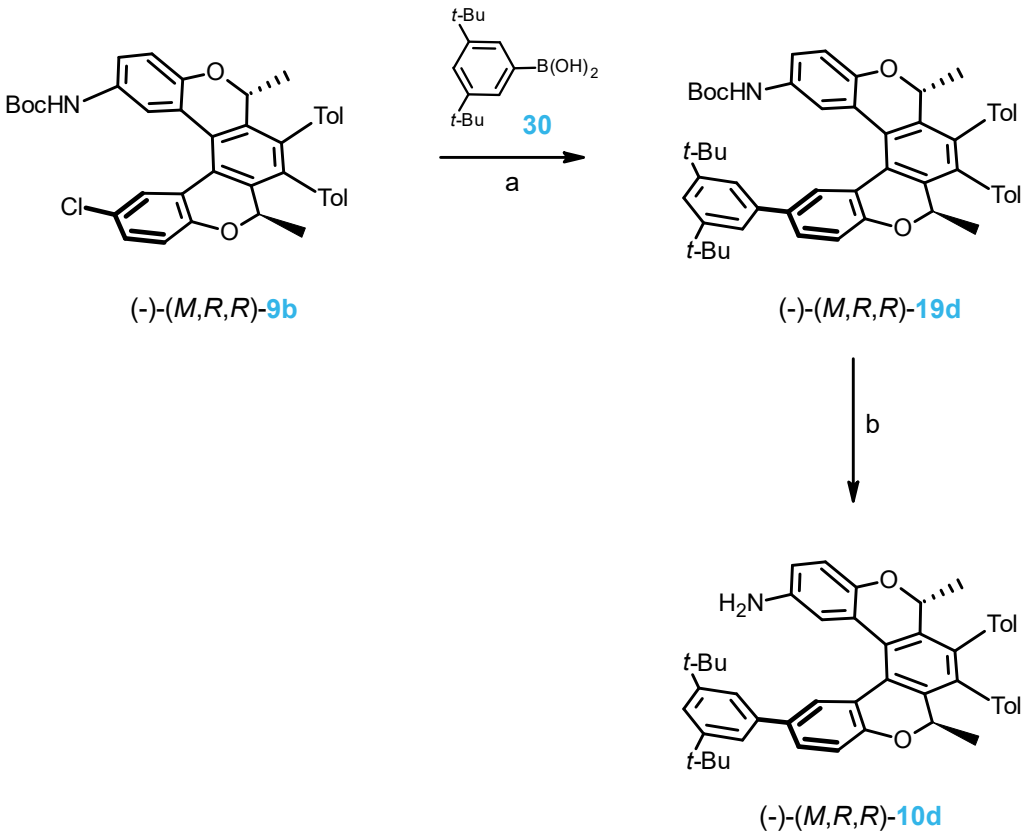
^{13}C NMR (151 MHz, CD_2Cl_2): δ 153.22, 149.77 (2C), 146.30, 141.09, 140.77, 140.05, 139.25, 137.61, 137.41, 136.64, 136.61, 135.51, 135.49, 134.55, 131.24, 131.19, 129.65, 129.60, 128.84, 128.83, 128.80, 128.795, 128.67, 128.05, 126.00, 125.50, 124.48, 123.78, 123.62, 122.60 (2C), 120.13, 119.50, 116.94, 115.80, 73.46, 72.98, 34.74 (2C), 24.25 (4C), 21.273, 21.268, 18.68, 18.36.

IR ($CHCl_3$): 3425 w, 3385 w, 2963 m, 2928 w, 2871 w, 1616 w, 1604 vw, sh, 1583 w, 1544 w, 1496 m, sh, 1490 m, 1458 m, 1428 m, 1366 m, 1330 w, 1299 w, 1149 m, 1112 vw, 1088 w, 1063 m, 895 w, 875 w, 841 w, 815 w, 567 w, 524 vw, 449 vw cm^{-1}.

ESI MS: 670 ($[M+H]^+$).

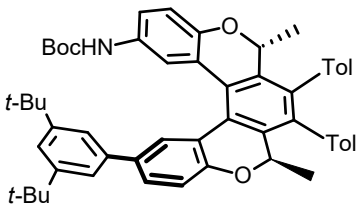
HR ESI MS: calcd for $C_{48}H_{48}O_2N$ 670.3680, found 670.3681.

Oxa[5]helicene amine (-)-(*M*,*R*,*R*)-10d



(a) **30** (3.3 equiv.), XPhos Pd G2 (5 mol%), aq. K_3PO_4 (2.5 equiv.), THF, 100 °C, 6 h, 82%; (b) TFA (26 equiv.), CH_2Cl_2, rt, 16 h, 85%.

(-)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-12-(3,5-di-*tert*-butylphenyl)-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-yl]carbamate 19d



The oxa[5]helicene amine derivative (-)-(*M,R,R*)-**19d** was prepared according to the *General procedure B* from the chloro derivative (-)-(*M,R,R*)-**9b** (100 mg, 0.156 mmol), 3,5-di-*tert*-butylphenyl boronic acid **30**[7] (119 mg, 0.509 mmol, 3.3 equiv.), XPhos Pd G2 (6.7 mg, 0.0085 mmol, 5 mol%) and K_3PO_4 (0.5 M in water, 0.78 ml, 0.39 mmol, 2.5 equiv.) in tetrahydrofuran (2.5 ml) at 100 °C for 6 h. The purification by flash chromatography on silica gel (hexane-acetone 20:1) and then on C-18 reversed-phase silica gel (methanol) gave the product (-)-(*M,R,R*)-**19d** (102 mg, 82%) as a white solid.

M.p.: 142-145 °C (methanol).

Optical rotation: $[\alpha]^{20}_{D}$ = -647° (c 0.359, $CHCl_3$).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80 (bs, 1H), 7.70 (d, *J* = 2.2, 1H), 7.44 (dd, *J* = 8.3, 2.2, 1H), 7.33 (t, *J* = 1.8, 1H), 7.16 – 7.08 (m, 5H), 7.12 (d, *J* = 1.8, 2H), 7.08 (d, *J* = 8.3, 1H), 7.02 (d, *J* = 8.9, 1H), 6.87 (m, 2H), 6.66 (m, 2H), 6.13 (bs, 1H), 5.29 (q, *J* = 6.7, 1H), 5.23 (q, *J* = 6.7, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 1.40 (s, 9H), 1.31 (s, 18H), 0.97 (d, *J* = 6.7, 3H), 0.94 (d, *J* = 6.7, 3H).

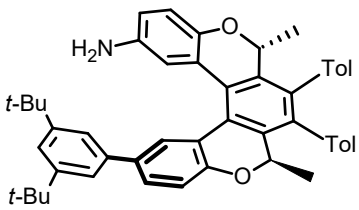
^{13}C NMR (151 MHz, $CDCl_3$): δ 152.81 (2C), 151.07 (2C), 149.25, 140.18, 139.33, 139.07, 137.29, 137.24, 136.08 (2C), 135.07, 134.80 (2C), 131.78, 130.73, 130.68, 129.06 (2C), 128.59 (2C), 128.38 (2C), 128.26, 128.04, 125.30, 124.93, 123.77, 123.22, 121.20 (2C), 120.78, 120.58, 119.60, 119.48, 119.07, 80.28, 73.12, 72.96, 34.93 (2C), 31.45 (6C), 28.22 (3C), 21.17 (2C), 18.50, 18.34.

IR ($CHCl_3$): 3435 w, 3028 w, 2967 s, 2906 m, sh, 2868 m, 1723 s, 1607 w, sh, 1594 m, 1570 vw, sh, 1523 s, sh, 1517 vs, 1489 s, 1478 m, sh, 1403 w, 1381 w, sh, 1368 s, 1365 vw, sh, 1255 m, 1249 m, 1183 w, sh, 1159 vs, 1127 m, 1022 vw, 1008 m, 877 m, 856 w, 843 w, 825 m, 715 w, 469 w cm^{-1}.

ESI MS: 820 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{55}H_{59}O_4NNa$ 820.4336, found 820.4342.

(-)-(*M*)-(2*R*,5*R*)-12-(3,5-di-*tert*-Butylphenyl)-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-amine 10d



Oxa[5]helicene amine (-)-(*M,R,R*)-**10d** was prepared according to the *General procedure C* from the oxa[5]helicene amine derivative (-)-(*M,R,R*)-**19d** (98 mg, 0.13 mmol) and trifluoroacetic acid (240 µl, 3.1 mmol, 26 equiv.) in dichloromethane (10 ml) for 16 h. Evaporation of solvent provided oxa[5]helicene amine (-)-(*M,R,R*)-**10d** (73 mg, 85%) as a light orange solid, which was used without further purification.

M.p.: 168-172 °C (hexane – ethyl acetate).

Optical rotation: $[\alpha]^{20}_{D}$ = -669° (c 0.345, CH_2Cl_2).

UV/Vis (THF): λ_{max} (log ε) = 257 (5.01), 343 (4.16) nm.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.80 (bd, *J* = 2.2, 1H), 7.46 (dd, *J* = 8.3, 2.3, 1H), 7.34 (t, *J* = 1.7, 1H), 7.21 (d, *J* = 1.8, 2H), 7.19 – 7.09 (m, 4H), 7.07 (d, *J* = 8.3, 1H), 6.93 – 6.90 (m, 2H), 6.88 – 6.82 (m, 2H), 6.76 – 6.71 (m, 2H), 6.57 (dd, *J* = 8.5, 2.7, 1H), 5.21 (q, *J* = 6.7, 1H), 5.11 (q, *J* = 6.7, 1H), 3.30 (bs, 2H), 2.28 (s, 3H), 2.27 (s, 3H), 1.32 (s, 18H), 0.97 (d, *J* = 6.7, 3H), 0.93 (d, *J* = 6.7, 3H).

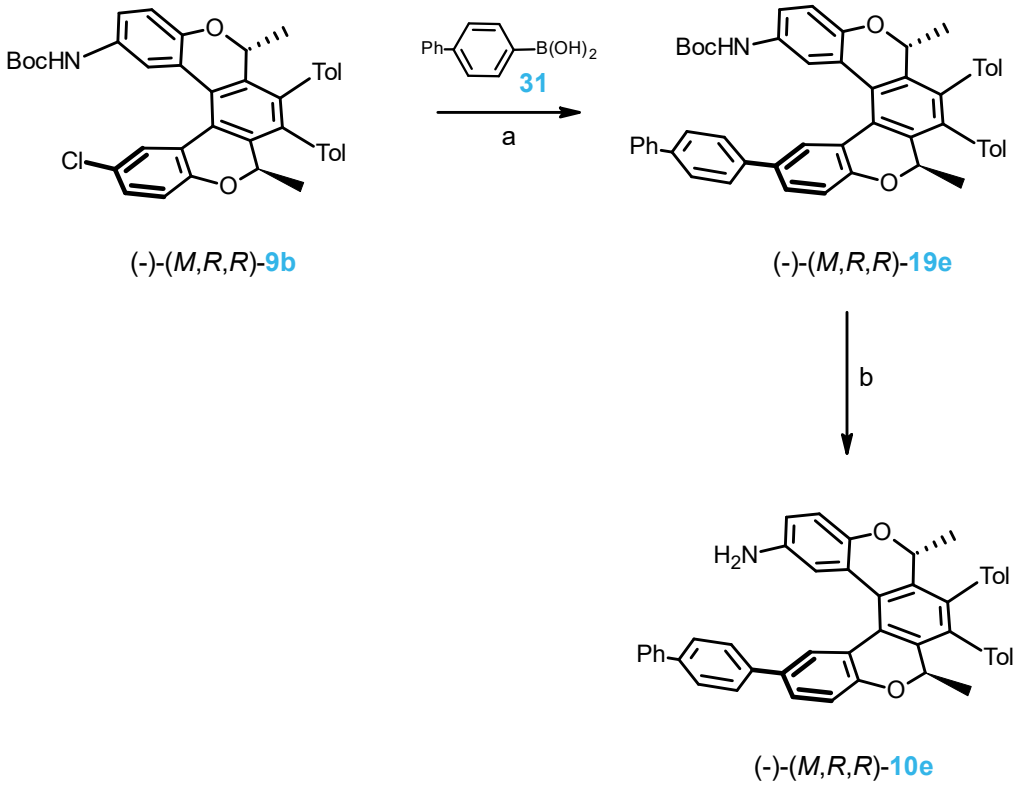
^{13}C NMR (101 MHz, CD_2Cl_2): δ 153.21, 151.50 (2C), 146.19, 140.60, 140.48, 140.00, 139.33, 137.58, 137.37, 136.63, 136.59, 135.53, 135.48, 135.10, 131.24, 131.21, 129.64, 129.61, 128.83 (2C), 128.80, 128.79, 128.65, 128.19, 126.03, 125.56, 124.47, 123.75, 121.47 (2C), 121.14, 120.02, 119.59, 117.15, 115.74, 73.47, 72.97, 35.27 (2C), 31.63 (6C), 21.28 (2C), 18.65, 18.40.

IR ($CHCl_3$): 3471 w, 3386 w, 2966 s, 2868 w, 1619 m, 1605 vw, 1594 m, 1583 w, sh, 1548 w, 1496 m, 1489 s, 1475 m, sh, 1432 m, sh, 1405 vw, sh, 1396 vw, 1365 m, 1149 m, 1128 m, 1061 m, 1010 m, 878 m, 855 w, 835 w, 819 m cm^{-1}.

ESI MS: 698 ($[M+H]^+$).

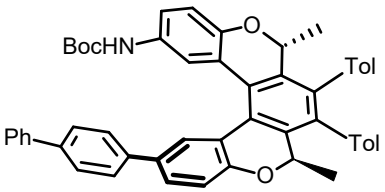
HR ESI MS: calcd for $C_{50}H_{52}O_2N$ 698.3993, found 698.3993.

Oxa[5]helicene amine (-)-(*M*,*R*,*R*)-10e



(a) **31** (2.3 equiv.), XPhos Pd G2 (5 mol%), aq. K_3PO_4 (2.5 equiv.), THF, 100 °C, 1 h, 87%; (b) TFA (26 equiv.), CH_2Cl_2, rt, 16 h, 78%.

(-)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-12-biphenyl-4-yl-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydro-benzo[1,2-*c*:4,3-*c'*]dichromen-9-yl]carbamate 19e



The oxa[5]helicene amine derivative (-)-(*M,R,R*)-**19e** was prepared according to the *General procedure B* from the chloro derivative (-)-(*M,R,R*)-**9b** (99 mg, 0.15 mmol), 4-biphenylboronic acid **31** (71 mg, 0.36 mmol, 2.3 equiv.), XPhos Pd G2 (5.7 mg, 0.0072 mmol, 5 mol%) and K_3PO_4 (0.5 M in water, 0.78 ml, 0.39 mmol, 2.5 equiv.) in tetrahydrofuran (2.5 ml) at 100 °C for 1 h. The purification by flash chromatography on silica gel (hexane-acetone 20:1) gave the product (-)-(*M,R,R*)-**19e** (103 mg, 87%) as a white solid.

M.p.: 170-176 °C (hexane – acetone).

Optical rotation: $[\alpha]^{20}_D$ = -674° (c 0.252, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, *J* = 2.2, 1H), 7.63 (bs, 1H), 7.61 (m, 2H), 7.57 (m, 2H), 7.47 (dd, *J* = 8.2, 2.2, 1H), 7.43 (m, 2H), 7.37 (m, 2H), 7.33 (tt, *J* = 7.4, 1.2, 1H), 7.21 (bd, *J* = 2.3, 1H), 7.14 (m, 2H), 7.095 (d, *J* = 8.2, 1H), 7.09 (m, 2H), 7.04 (d, *J* = 8.7, 1H), 6.87 (m, 2H), 6.67 (m, 2H), 6.10 (bs, 1H), 5.29 (q, *J* = 6.7, 1H), 5.24 (q, *J* = 6.7, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 1.37 (s, 9H), 0.99 (d, *J* = 6.7, 3H), 0.96 (d, *J* = 6.7, 3H).

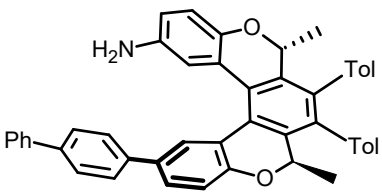
^{13}C NMR (126 MHz, $CDCl_3$): δ 153.13, 152.93, 149.39, 140.61, 139.58, 139.37, 139.34, 138.92, 137.38 (2C), 136.12, 136.11, 134.75, 134.72, 133.16, 131.79, 130.68, 130.63, 129.03, 129.00, 128.71 (2C), 128.60 (2C), 128.41, 128.39, 127.92, 127.74, 127.37 (2C), 127.16, 126.89 (2C), 126.69 (2C), 125.12, 124.96, 123.61, 123.18, 120.81, 119.84, 119.50, 119.46, 80.18, 73.14, 72.96, 28.22 (3C), 21.18 (2C), 18.53, 18.30.

IR ($CHCl_3$): 3436 w, 3028 w, 2983 m, 2868 w, 1722 s, 1601 w, 1524 s, sh, 1517 vs, 1491 w, sh, 1449 m, 1435 m, 1380 w, sh, 1368 m, 1357 vw, sh, 1256 m, 1159 vs, 1151 w, sh, 1128 vw, 1062 m, 1004 m, 910 w, 857 w, 840 w, 469 w cm^{-1}.

ESI MS: 784 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{53}H_{47}O_4NNa$ 784.3397, found 784.3402.

(-)-(*M*)-(2*R*,5*R*)-12-Biphenyl-4-yl-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-amine 10e



Oxa[5]helicene amine (-)-(*M,R,R*)-**10e** was prepared according to the *General procedure C* from the oxa[5]helicene derivative (-)-(*M,R,R*)-**19e** (94 mg, 0.12 mmol) and trifluoroacetic acid (240 µl, 3.1 mmol, 26 equiv.) in dichloromethane (10 ml) for 16 h. The purification by flash chromatography on silica gel (hexane-ethyl acetate 4:1) gave oxa[5]helicene amine (-)-(*M,R,R*)-**10e** (64 mg, 78%) as a yellowish solid.

M.p.: 279-283 °C (hexane – ethyl acetate).

Optical rotation: $[\alpha]^{20}_D$ = -742° (c 0.122, CH_2Cl_2).

UV/Vis (THF): λ_{max} (log ε) = 271 (4.69), 300 (4.44) nm.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.88 (bd, *J* = 2.3, 1H), 7.66 – 7.58 (m, 4H), 7.51 – 7.42 (m, 5H), 7.37 – 7.31 (m, 1H), 7.18 – 7.10 (m, 4H), 7.08 (bd, *J* = 8.4, 1H), 6.94 – 6.91 (m, 2H), 6.87 (d, *J* =

8.6, 1H), 6.86 (d, *J* = 2.7, 1H), 6.76 – 6.72 (m, 2H), 6.63 (dd, *J* = 8.6, 2.7, 1H), 5.22 (q, *J* = 6.7, 1H), 5.12 (q, *J* = 6.7, 1H), 3.32 (s, 2H), 2.28 (s, 3H), 2.27 (s, 3H), 0.99 (d, *J* = 6.7, 3H), 0.94 (d, *J* = 6.7, 3H).

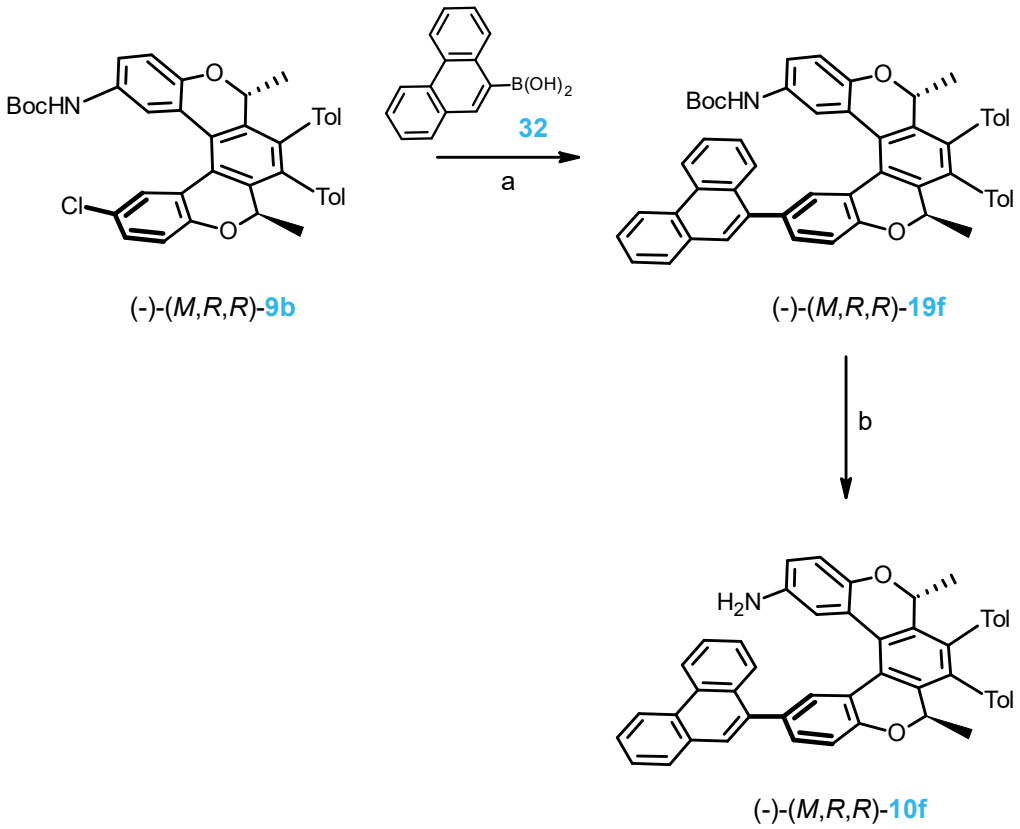
^{13}C NMR (101 MHz, CD_2Cl_2): δ 153.60, 146.31, 140.95 (2C), 140.20, 140.08, 139.67, 139.25, 137.74, 137.48, 136.67, 136.64, 135.48, 135.45, 133.33, 131.23, 131.17, 129.63, 129.58, 129.18 (2C), 128.86, 128.84, 128.81 (2C), 128.49, 128.00, 127.65, 127.59 (2C), 127.24 (2C), 127.19 (2C), 126.01, 125.36, 124.36, 123.81, 120.27, 119.74, 116.76, 115.76, 73.53, 72.99, 21.28 (2C), 18.71, 18.36.

IR ($CHCl_3$): 3386 w, 2985 w, 2927 w, 1619 w, 1599 w, 1547 w, 1518 w, 1495 w, sh, 1482 m, 1475 w, 1435 m, 1403 w, sh, 1331 w, 1270 w, 1150 w, 1128 w, 1107 w, 1063 w, 1005 w, 873 w, 853 w, 840 w, 699 m, 582 w, 503 w cm^{-1}.

ESI MS: 662 ($[M+H]^+$).

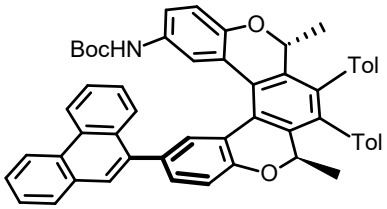
HR ESI MS: calcd for $C_{48}H_{40}O_2N$ 662.3054, found 662.3054.

Oxa[5]helicene amine (-)-(*M*,*R*,*R*)-10f



a) **32** (2.2 equiv.), XPhos Pd G2 (7 mol%), aq. K_3PO_4 (2.5 equiv.), THF, 100 °C, 3.5 h, 89%; (b) TFA (15 equiv.), CH_2Cl_2, rt, 16 h, 76%.

(-)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-12-phenanthren-9-yl-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-yl]carbamate 19f



The oxa[5]helicene amine derivative (-)-(*M,R,R*)-**19f** was prepared according to the *General procedure B* from the chloro derivative (-)-(*M,R,R*)-**9b** (50 mg, 0.078 mmol), 9-phenanthrenylboronic acid **32** (37 mg, 0.17 mmol, 2.2 equiv.), XPhos Pd G2 (4.0 mg, 0.0051 mmol, 7 mol%) and K_3PO_4 (0.5 M in water, 0.40 ml, 0.20 mmol, 2.5 equiv.) in tetrahydrofuran (2 ml) at 100 °C for 3.5 h. The purification by flash chromatography on silica gel (hexane-acetone 20:1) and then on C-18 reversed-phase silica gel (methanol) gave the product (-)-(*M,R,R*)-**19f** (54 mg, 89%) as a white solid.

M.p.: 197-202 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -422° (c 0.303, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (bd, *J* = 8.2, 1H), 8.67 (bd, *J* = 8.2, 1H), 7.91 – 7.89 (m, 1H), 7.84 – 7.82 (m, 1H), 7.68 – 7.51 (m, 6H), 7.50 (bs,1H), 7.35 (dd, *J* = 8.2, 2.1, 1H), 7.31 (bs, 1H), 7.20 – 7.14 (m, 2H), 7.12 – 7.06 (m, 3H), 6.91 – 6.85 (m, 3H), 6.71 – 6.64 (m, 2H), 6.26 (s, 1H), 5.36 (q, *J* = 6.7, 1H), 5.20 (q, *J* = 6.7, 1H), 2.28 (s, 3H), 2.26 (s, 3H), 1.48 (s, 9H), 1.08 (d, *J* = 6.7, 3H), 0.92 (d, *J* = 6.7, 3H).

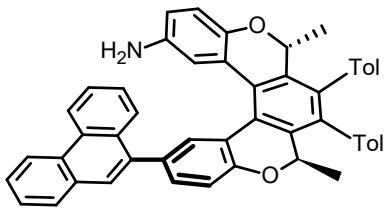
^{13}C NMR (101 MHz, $CDCl_3$): δ 152.94, 152.86, 149.14, 139.42, 139.10, 138.21, 137.33, 137.32, 136.12, 136.09, 134.76, 134.71, 133.48, 131.80, 131.63, 131.10, 130.95, 130.69, 130.65, 130.57, 130.53, 129.76, 129.03, 129.02, 128.64, 128.62, 128.59, 128.42, 128.38, 127.34, 126.82, 126.51, 126.43 (2C), 126.29, 125.15, 125.08, 123.65, 123.51, 122.94, 122.35, 119.81, 119.03, 118.79, 80.41, 73.22, 72.89, 28.34 (3C), 21.20, 21.17, 18.55, 18.28, one CH was not identified.

IR ($CHCl_3$): 3435 w, 2982 w, 2869 w, 1721 m, 1616 w, 1602 w, 1544 vw, sh, 1523 m, sh, 1517 m, 1496 w, 1451 w, 1435 w, 1410 w, 1393 vw, 1369 vw, 1302 w, 1279 vw, sh, 1253 m, 1184 vw, sh, 1159 m, 1150 m, sh, 1095 vw, 1061 m, 1012 w, 949 w, sh, 872 vw, 814 vw, 709 vw, sh, 590 vw, 532 w, 505 w cm^{-1}.

ESI MS: 808 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{55}H_{47}O_4NNa$ 808.3397, found 808.3399.

(-)-(*M*)-(2*R*,5*R*)-2,5-Dimethyl-3,4-bis(4-methylphenyl)-12-phenanthren-9-yl-2,5-dihydrobenzo-[1,2-*c*:4,3-*c'*]dichromen-9-amine 10f



Oxa[5]helicene amine (-)-(*M,R,R*)-**10f** was prepared according to the *General procedure C* from the oxa[5]helicene amine derivative (-)-(*M,R,R*)-**19f** (103 mg, 0.131 mmol) and trifluoroacetic acid (150 µl, 1.96 mmol, 15 equiv.) in dichloromethane (5 ml) for 16 h. The purification by flash chromatography on C-18 reversed-phase silica gel (methanol) provided oxa[5]helicene amine (-)-(*M,R,R*)-**10f** (68 mg, 76%) as a yellowish solid.

M.p.: 216-218 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -358° (c 0.322, CH_2Cl_2).

UV/Vis (THF): λ_{max} (log ε) = 253 (4.83), 302 (4.21) nm.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.77 – 8.69 (m, 1H), 8.73 – 8.67 (m, 1H), 7.99 (bd, *J* = 7.8, 1H), 7.91 – 7.89 (m, 1H), 7.76 (d, *J* = 2.1, 1H), 7.74 (bs, 1H), 7.69 – 7.59 (m, 3H), 7.55 (ddd, *J* = 8.2, 6.9, 1.2, 1H), 7.38 (dd, *J* = 8.2, 2.1, 1H), 7.21 – 7.08 (m, 5H), 6.97 (bd, *J* = 2.7, 1H), 6.95 – 6.90 (m, 2H), 6.78 – 6.72 (m, 3H), 6.57 (d, *J* = 8.0, 1H), 5.28 (q, *J* = 6.7, 1H), 5.09 (q, *J* = 6.7, 1H), 3.45 (s, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 1.07 (d, *J* = 6.7, 3H), 0.91 (d, *J* = 6.7, 3H).

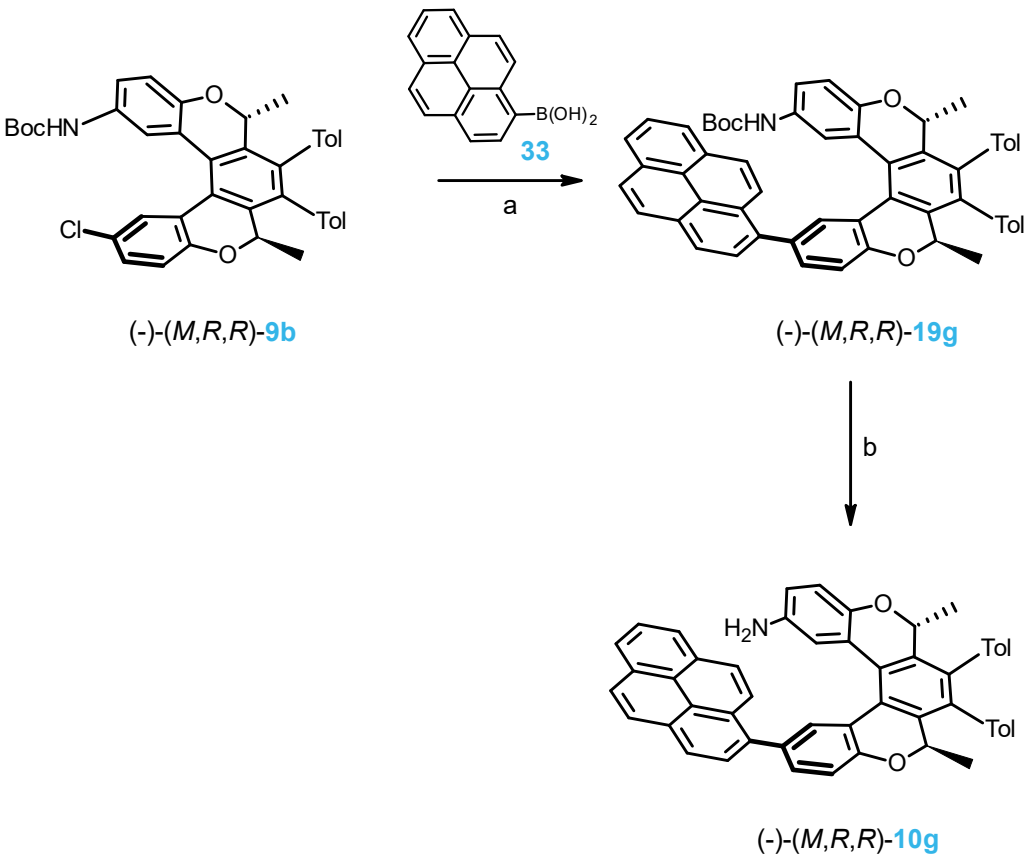
^{13}C NMR (101 MHz, CD_2Cl_2): δ 153.32, 146.18, 140.87, 140.13, 139.46, 138.69, 137.68, 137.47, 136.67, 136.61, 135.48, 135.47, 133.81, 132.25, 131.44, 131.26, 131.23 (2C), 131.19, 130.90, 130.10, 129.64, 129.60, 128.91, 128.87 (2C), 128.80, 128.79, 127.99, 127.18, 127.11, 126.81, 126.80, 126.72, 126.05, 125.45, 124.48, 124.10, 123.28, 122.78, 120.27, 118.97, 116.68, 115.73, 73.60, 72.95, 21.29, 21.27, 18.69, 18.35.

IR ($CHCl_3$): 3458 w, 3379 w, 2984 m, 1619 m, 1605 m, sh, 1589 w, sh, 1548 w, sh, 1527 w, sh, 1518 s, 1494 s, 1462 m, sh, 1450 m, 1434 m, 1405 w, 1385 m, sh, 1275 m, 1244 m, 1183 m, 1150 m, 1112 m, 1022 w, sh, 1014 m, 836 m, 821 m, 534 w cm^{-1}.

ESI MS: 686 ($[M+H]^+$).

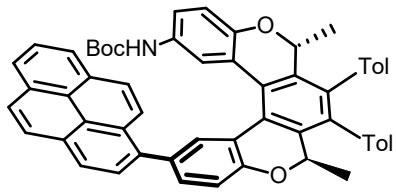
HR ESI MS: calcd for $C_{50}H_{40}O_2N$ 686.3054, found 686.3055.

Oxa[5]helicene amine (-)-(*M*,*R*,*R*)-10g



(a) **33** (2.1 equiv.), XPhos Pd G2 (8 mol%), aq. K_3PO_4 (2.5 equiv.), THF, 100 °C, 3 h, 82%; (b) TFA (33 equiv.), CH_2Cl_2, rt, 16 h, 86%.

(-)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-12-pyren-1-yl-2,5-dihydro-benzo[1,2-*c*:4,3-*c'*]dichromen-9-yl]carbamate 19g



The oxa[5]helicene amine derivative (-)-(*M,R,R*)-**19g** was prepared according to the *General procedure B* from the chloro derivative (-)-(*M,R,R*)-**9b** (100 mg, 0.156 mmol), 1-pyrenylboronic acid **33** (77 mg, 0.31 mmol, 2.1 equiv.), XPhos Pd G2 (9.1 mg, 0.012 mmol, 8 mol%) and K_3PO_4 (0.5 M in water, 0.76 ml, 0.38 mmol, 2.5 equiv.) in tetrahydrofuran (2.5 ml) at 100 °C for 3 h. The purification by flash chromatography on silica gel (hexane-acetone 20:1) and then on C-18 reversed-phase silica gel (methanol) gave the product (-)-(*M,R,R*)-**19g** (103 mg, 82%) as a pale yellow solid.

M.p.: 180-188 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -481° (c 0.272, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (dd, *J* = 7.6, 1.1, 1H), 8.15 (dd, *J* = 7.7, 1.1, 1H), 8.13 (d, *J* = 7.8, 1H), 8.12 (d, *J* = 9.2, 1H), 8.065 (d, *J* = 9.0, 1H), 8.045 (d, *J* = 9.0, 1H), 8.015 (d, *J* = 9.2, 1H), 8.00 (t, *J* = 7.6, 1H), 7.77 (d, *J* = 7.8, 1H), 7.73 (d, *J* = 2.1, 1H), 7.46 (bs, 1H), 7.43 (dd, *J* = 8.2, 2.1, 1H), 7.33 (bs, 1H), 7.21 (d, *J* = 8.2, 1H), 7.185 (m, 1H), 7.12 (m, 2H), 7.07 (m, 1H), 6.895 (m, 1H), 6.87 (m, 1H), 6.86 (d, *J* = 8.7, 1H), 6.69 (m, 1H), 6.66 (m, 1H), 6.19 (bs, 1H), 5.37 (q, *J* = 6.7, 1H), 5.20 (q, *J* = 6.7, 1H), 2.29 (s, 3H), 2.26 (s, 3H), 1.47 (s, 9H), 1.10 (d, *J* = 6.7, 3H), 0.91 (d, *J* = 6.7, 3H).

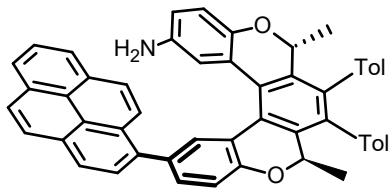
^{13}C NMR (126 MHz, $CDCl_3$): δ 152.97 (2C), 149.22, 139.41, 139.18, 137.36, 137.35, 136.14, 136.10, 134.76, 134.71, 134.00, 131.64, 131.52, 131.46, 130.96, 130.93, 130.70, 130.67, 130.32, 129.05, 129.01, 128.66, 128.60, 128.43, 128.39, 128.33, 127.46, 127.42, 127.38, 127.31, 127.19, 125.90, 125.18, 125.13, 125.02, 125.00, 124.92, 124.89, 124.72 (2C), 123.60, 123.56, 120.75, 119.76, 119.52, 118.95, 80.22, 73.26, 72.91, 28.35 (3C), 21.20, 21.17, 18.57, 18.28.

IR ($CHCl_3$): 3437 w, 2983 m, 2869 w, 1721 s, 1615 w, 1606 vw, 1587 w, 1552 w, sh, 1517 s, 1496 m, 1484 m, 1447 vw, 1416 w, 1407 w, 1393 w, 1368 m, 1299 w, 1159 s, 1123 w, 1112 vw, 1089 vw, 1060 m, 1022 w, 1003 m, 912 w, 825 w, 873 m, 712 w, 642 w, 505 w, 465 w cm^{-1}.

ESI MS: 832 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{57}H_{47}O_4NNa$ 832.3397, found 832.3403.

(-)-(*M*)-(2*R*,5*R*)-2,5-Dimethyl-3,4-bis(4-methylphenyl)-12-pyren-1-yl-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-amine 10g



Oxa[5]helicene amine (-)-(*M,R,R*)-**10g** was prepared according to the *General procedure C* from the oxa[5]helicene derivative (-)-(*M,R,R*)-**19g** (95 mg, 0.12 mmol) and trifluoroacetic acid (290 µl, 3.8 mmol, 33 equiv.) in dichloromethane (10 ml) for 16 h. The purification by flash chromatography on silica gel (hexane-ethyl acetate 4:1) gave oxa[5]helicene amine (-)-(*M,R,R*)-**10g** (71.5 mg, 86%) as a yellowish solid.

M.p.: 181-185 °C (hexane – ethyl acetate).

Optical rotation: $[\alpha]^{20}_D$ = -459° (c 0.155, CH_2Cl_2).

UV/Vis (THF): λ_{max} (log ε) = 237 (4.79), 268 (4.70), 278 (4.71), 346 (4.54) nm.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.21 – 8.16 (m, 4H), 8.09 (bs, 2H), 8.04 – 7.96 (m, 3H), 7.80 (d, *J* = 2.1, 1H), 7.45 (dd, *J* = 8.1, 2.1, 1H), 7.20 (d, *J* = 8.1, 1H), 7.20 – 7.09 (m, 4H), 6.97 (d, *J* = 2.7, 1H), 6.95 – 6.90 (m, 2H), 6.78 – 6.72 (m, 2H), 6.70 (bd, *J* = 8.5, 1H), 6.47 (dd, *J* = 8.5, 2.7, 1H), 5.30 (q, *J* = 6.6, 1H), 5.08 (q, *J* = 6.6, 1H), 3.39 (s, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 1.09 (d, *J* = 6.6, 3H), 0.90 (d, *J* = 6.6, 3H).

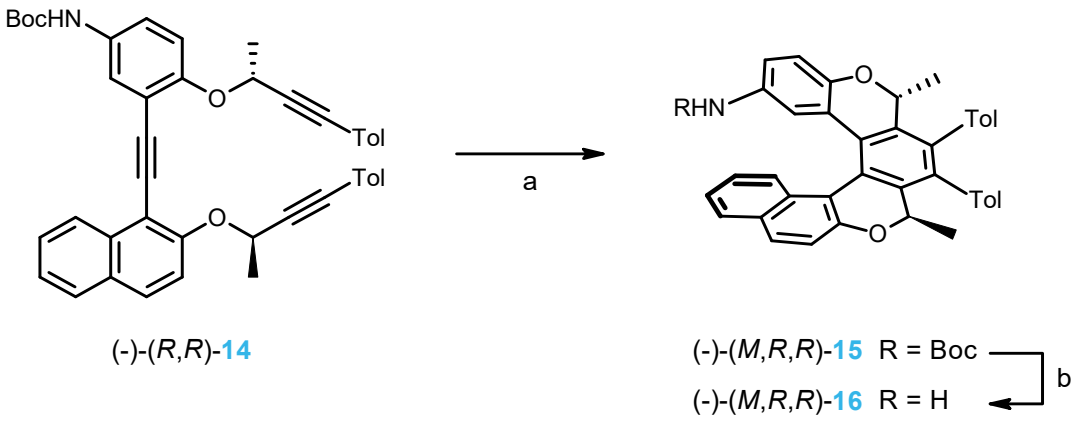
^{13}C NMR (101 MHz, CD_2Cl_2): δ 153.40, 146.10, 140.88, 140.11, 139.55, 137.99, 137.72, 137.48, 136.69, 136.62, 135.48, 135.47, 134.26, 131.87, 131.80, 131.59, 131.38, 131.27, 131.20, 130.73, 129.63, 129.62, 128.88 (2C), 128.81, 128.80, 128.78, 128.19, 127.77, 127.59, 127.56, 126.38, 126.11, 125.65, 125.46, 125.39, 125.22, 125.21, 125.13, 124.97, 124.37, 124.17, 120.17, 119.23, 116.68, 115.69, 73.65, 72.94, 21.30, 21.27, 18.71, 18.35.

IR ($CHCl_3$): 3468 w, 3383 w, 1619 w, 1603 vw, sh, 1596 vw, sh, 1583 vw, 1544 w, 1518 m, 1494 m, 1484 m, 1456 m, 1431 m, 1367 m, 1333 vw, 1262 m, 1184 w, 1150 m, 1128 w, 1062 m, 1009 vw, sh, 880 w, 850 m, 843 vw, 836 vw, sh, 819 m cm^{-1}.

ESI MS: 710 ($[M+H]^+$).

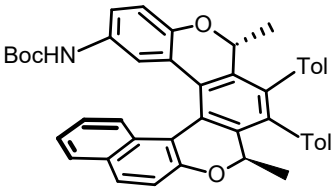
HR ESI MS: calcd for $C_{52}H_{40}O_2N$ 710.3054, found.710.3055.

Oxa[6]helicene amine (-)-(*M*,*R*,*R*)-16



(a) CpCo(CO)(fum) (40 mol%), [bdmim]BF_4, microwave reactor, THF, 140 °C, 15 min., 63%; (b) TFA (15 equiv.), CH_2Cl_2, rt, 16 h, 77%.

(-)-(*M*)-*tert*-Butyl [(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[*f*]benzo-[1,2-*c*:4,3-*c'*]dichromen-14-yl]carbamate 15



The oxa[6]helicene amine derivative (-)-(*M,R,R*)-**15** was prepared according to the *General procedure A* from triyne (-)-(*R,R*)-**14** (116 mg, 0.176 mmol), CpCo(CO)(fum) (21 mg, 0.071 mmol, 40 mol%) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate (125 µl) in tetrahydrofuran (5 ml). The purification by flash chromatography on silica gel (hexane-ethyl acetate 95:5) and then on C-18 reversed-phase silica gel (methanol) gave the cyclic product (-)-(*M,R,R*)-**15** (73 mg, 63%) as a yellow solid.

M.p.: 168-171 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -611° (c 0.340, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.7, 1H), 7.67 (bd, *J* = 8.0, 1H), 7.48 (bd, *J* = 8.6, 1H), 7.28 (d, *J* = 8.7, 1H), 7.18 – 7.14 (m, 4H), 7.095 (m, 2H), 6.95 (ddd, *J* = 8.6, 6.8, 1.3, 1H), 6.90 (m, 2H), 6.87 (d, *J* = 8.6, 1H), 6.77 (m, 1H), 6.75 (m, 1H), 6.14 (d, *J* = 2.6, 1H), 5.34 (vbs, 1H), 5.32 (q, *J* = 6.7, 1H), 5.27 (q, *J* = 6.7, 1H), 2.28 (s, 6H), 1.39 (s, 9H), 1.00 (d, *J* = 6.7, 3H), 0.99 (d, *J* = 6.7, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): 152.81, 152.69, 148.54, 139.58, 138.58, 137.12, 136.70, 136.10, 136.05, 134.94, 134.92, 131.45, 130.86, 130.50, 130.12, 129.86, 129.39, 129.17, 128.99, 128.60,

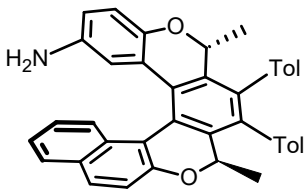
128.48, 128.44, 128.34, 127.47, 125.68, 125.54, 125.25, 124.20, 123.81, 123.58, 120.10, 119.70, 119.10, 118.50, 117.85, 79.89, 73.37, 72.97, 28.24 (3C), 21.19 (2C), 18.64, 17.74.

IR (KBr): 3492 s, sh, 3437 vs, br, 3280 m, sh, 2978 w, 2927 w, 1732 m, 1716 m, 1620 m, 1593 w, 1542 w, sh, 1523 w, sh, 1517 m, 1391 m, sh, 1382 m, 1253 m, 1243 m, 1161 s, 1153 m, sh, 1076 w, 1049 w, 920 w, sh, 843 w, 813 w, 770 w, br, sh, 589 w, 534 w, 470 w cm^{-1}.

ESI MS: 682 ($[M+Na]^+$).

HR ESI MS: calcd for $C_{45}H_{41}O_4NNa$ 682.2928, found 682.2930.

(-)-(*M*)-(2*R*,5*R*)-2,5-Dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[*f*]benzo-[1,2-*c*:4,3-*c'*]-dichromen-14-amine 16



Oxa[6]helicene amine (-)-(*M,R,R*)-**16** was prepared according to the *General procedure C* from the oxa[6]helicene amine derivative (-)-(*M,R,R*)-**15** (157 mg, 0.238 mmol) and trifluoroacetic acid (280 µl, 3.66 mmol, 15 equiv.) in dichloromethane (6 ml) for 16 h. The purification by flash chromatography on silica gel (hexane-ethyl acetate 7:1) gave oxa[6]helicene amine (-)-(*M,R,R*)-**16** (103 mg, 77%) as a pale orange solid.

M.p.: 152-157 °C (methanol).

Optical rotation: $[\alpha]^{20}_D$ = -687° (c 0.186, $CHCl_3$).

UV/Vis (THF): λ_{max} (log ε) = 244 (4.76), 291 (4.18), 320 (3.99), 358 (4.13) nm.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.78 (d, *J* = 8.7, 1H), 7.72 – 7.70 (m, 1H), 7.54 – 7.51 (m, 1H), 7.28 (d, *J* = 8.7, 1H), 7.21 – 7.17 (m, 2H), 7.16 – 7.12 (m, 3H), 7.00 (ddd, *J* = 8.4, 6.8, 1.4, 1H), 6.97 – 6.94 (m, 2H), 6.85 – 6.81 (m, 2H), 6.71 (d, *J* = 8.4, 1H), 6.25 (dd, *J* = 8.4, 2.7, 1H), 5.77 (d, *J* = 2.7, 1H), 5.26 (q, *J* = 6.7, 1H), 5.16 (q, *J* = 6.7, 1H), 2.69 (bs, 2H), 2.29 (s, 6H), 0.98 (d, *J* = 6.7, 3H), 0.96 (d, *J* = 6.7, 3H).

^{13}C NMR (101 MHz, CD_2Cl_2): δ 153.14, 145.52, 140.75, 140.14, 139.36, 137.27, 137.08, 136.69, 136.61, 135.66, 135.60, 131.42, 131.07, 130.44, 130.34, 130.04, 129.73, 129.57, 128.87 (2C), 128.80, 128.73, 128.01, 126.82, 125.94, 125.56, 125.11, 124.09, 123.81, 120.09, 119.09, 118.68, 115.74, 115.12, 73.83, 72.95, 21.29 (2C), 18.72, 17.92.

IR (KBr): 3436 s, 3362 m, sh, 3049 w, 2980 w, 1619 s, 1591 m, 1516 s, 1491 s, 1430 m, sh, 1404 vw, 1382 m, 1365 m, 1183 w, 1110 w, 1022 w, 1014 m, 842 m, 810 s, 711 w cm^{-1}.

ESI MS: 560 ($[M+H]^+$).

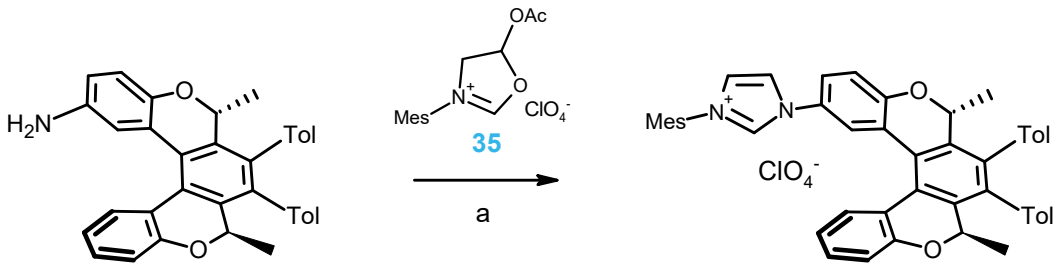
HR ESI MS: calcd for $C_{40}H_{34}O_2N$ 560.2584, found 560.2585.

Synthesis of oxahelicene imidazolium salts (-)-(*M,R,R*)-1, (-)-(*M,R,R*),(*M,R,R*)-2 and (-)-(*M,R,R*),(*M,R,R*)-3a-g

General procedure D *(preparation of symmetrical imidazolium chlorides*[10]*)*: The reaction was performed in an open vessel under ambient atmosphere. A solution of glyoxal (40 wt% in H_2O, 0.5 – 0.6 equiv.), formaldehyde (37 wt% in H_2O, 0.6 – 0.8 equiv.) and acetic acid (0.5 ml) was heated at 40 - 55 °C for 5 min before it was added to a solution of oxahelicene amine (-)-(*M,R,R*)-10a-g or (-)-(*M,R,R*)-16 (1.0 equiv.) in acetic acid (0.5 ml), which was also pre-heated at 40-55 °C for 5 min. The resulting mixture was stirred at 40 - 55 °C for 25 min - 3.7 h. Then the reaction mixture was cooled down to room temperature. Dichloromethane (10 ml) was added and the organic layer was successively washed with water (10 ml), brine (3 × 10 ml) and dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel to afford the desired imidazolium chloride (-)-(*M,R,R*),(*M,R,R*)-3a-g or (-)-(*M,R,R*),(*M,R,R*)-2.

[10] P. Queval, C. Jahier, M. Rouen, I. Artur, J.-C. Legeay, L. Falivene, L. Toupet, C. Crévisy, L. Cavallo, O. Baslé, M. Mauduit, *Angew. Chem. Int. Ed.* **2013**, *52*, 14103-14107.

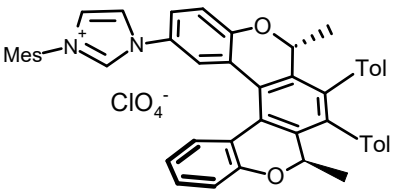
Imidazolium perchlorate (-)-(*M,R,R*)-1



(-)-(*M*,*R*,*R*)-10a (-)-(*M*,*R*,*R*)-1

(a) 11 (1.9 equiv.), $HClO_4$ (3.6 equiv.), toluene, rt, 4 h, then $HClO_4$ (3.6 equiv.), 80 °C, 16 h, 38%.

(-)-(*M*)-1-[(2*R*,5*R*)-2,5-Dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-yl]-3-(2,4,6-trimethylphenyl)-1*H*-imidazol-3-ium perchlorate 1



A suspension of oxazolinium perchlorate **35** (freshly prepared from *N*-mesityl-*N*-(2-oxoethyl)formamide **11** (38 mg, 0.19 mmol, 1.9 equiv.), acetic anhydride (180 µl) and $HClO_4$ (70 wt%, 30 µl, 0.35 mmol, 3.6 equiv.) according to the literature procedure[4]) in toluene (1.5 ml) was reacted with oxa[5]helicene amine (-)-(*M,R,R*)-**10a** (49 mg, 0.10 mmol) at room temperature for 4 h and then $HClO_4$ (70 wt%, 30 µl, 0.35 mmol, 3.6 equiv.) was added. The mixture was stirred at 80 °C for 16 h, then the solvent was removed *in vacuo*. The crude product was flash chromatographed on silica gel (dichloromethane-acetonitrile 20:1 then dichloromethane-methanol 20: 1) to provide (-)-(*M,R,R*)-**1** (29 mg, 38%) as a brown solid.

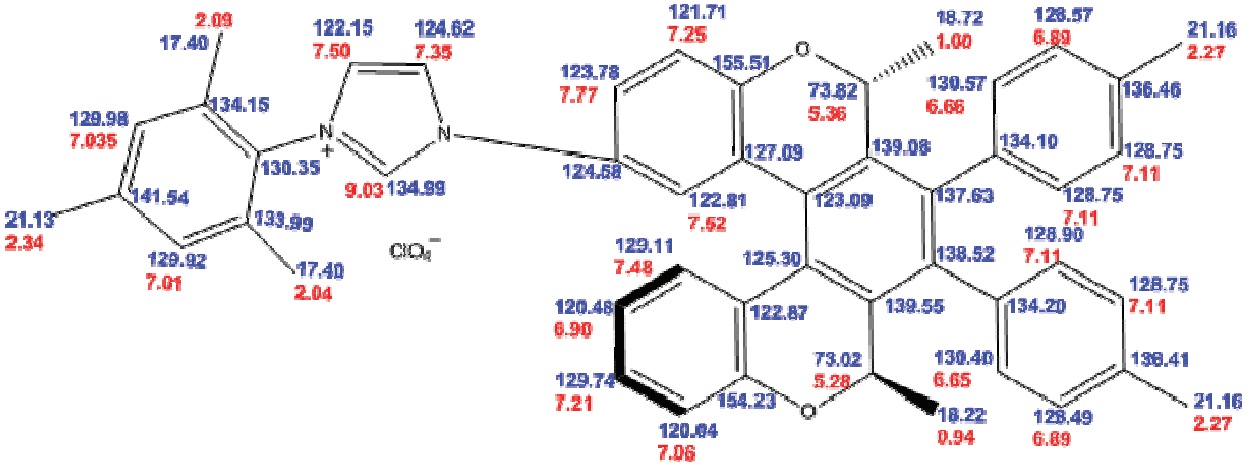
M.p.: 206-209 °C (dichloromethane – methanol).

Optical rotation: $[\alpha]^{20}_{D}$ = -452° (c 0.215, $CHCl_3$).

UV/Vis (THF): λ_{max} (log ε) = 263 (4.55), 337 (4.04) nm.

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.03 (t, *J* = 1.6, 1H), 7.77 (dd, *J* = 8.7, 2.8, 1H), 7.52 (d, *J* = 2.8, 1H), 7.50 (dd, *J* = 1.8, 1.6, 1H), 7.48 (dd, *J* = 7.8, 1.6, 1H), 7.35 (dd, *J* = 1.8, 1.6, 1H), 7.25 (d, *J* = 8.7, 1H), 7.21 (ddd, *J* = 8.1, 7.3, 1.6, 1H), 7.11 (m, 4H), 7.06 (dd, *J* = 8.1, 1.2, 1H), 7.035 (bs, 1H), 7.01 (bs, 1H), 6.90 (ddd, *J* = 7.8, 7.3, 1.2, 1H), 6.89 (m, 2H), 6.66 (m, 1H), 6.65 (m, 1H), 5.36 (q, *J* = 6.7, 1H), 5.28 (q, *J* = 6.7, 1H), 2.34 (s, 3H), 2.27 (s, 6H), 2.09 (s, 3H), 2.04 (s, 3H), 1.00 (d, *J* = 6.7, 3H), 0.94 (d, *J* = 6.7, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 155.51, 154.23, 141.54, 139.55, 139.08, 138.52, 137.63, 136.46, 136.41, 134.99, 134.20, 134.15, 134.10, 133.99, 130.57, 130.40, 130.35, 129.98, 129.92, 129.74, 129.11, 128.80, 128.75 (3C), 128.57, 128.49, 127.09, 125.30, 124.62, 124.58, 123.78, 123.09, 122.87, 122.81, 122.15, 121.71, 120.48, 120.04, 73.82, 73.02, 21.16 (2C), 21.13, 18.72, 18.22, 17.40.

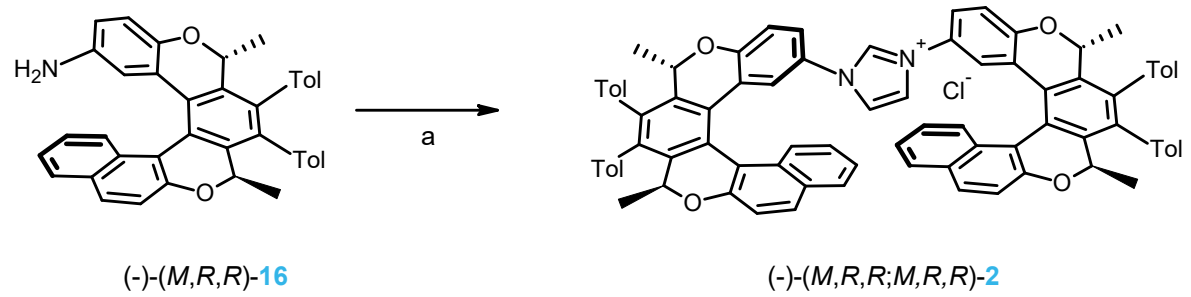


IR ($CHCl_3$): 3164 w, 3140 w, 3053 w, sh, 2983 m, 1612 w, sh, 1603 w, 1593 vw, 1583 w, 1541 m, 1518 m, 1495 m, sh, 1485 m, 1448 m, 1425 m, 1404 vw, 1379 m, sh, 1369 m, 1183 w, 1147 s, 1127 s, 1106 vs, 1099 vs, 1033 m, 1022 m, 981 w, 947 vw, 886 w, 855 m, 838 m, 819 w, 635 m, 627 m, 576 w, 534 w, 521 w, 461 w cm^{-1}.

ESI MS: 679 ($[M]^+$).

HR ESI MS: calcd for $C_{48}H_{43}O_2N_2$ 679.3319, found 679.3317.

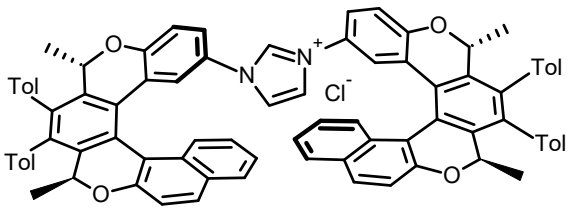
Imidazolium chloride (-)-(*M,R,R*),(*M,R,R*)-2



(-)-(*M*,*R*,*R*)-16 (-)-(*M*,*R*,*R*;*M*,*R*,*R*)-2

(a) aq. glyoxal (0.5 equiv.), aq. formaldehyde (0.6 equiv.), AcOH, 55 °C, 35 min, 78%.

(-)-(*M*,*M*)-1,3-Bis[(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[*f*]benzo-[1,2-*c*:4,3-*c'*]dichromen-14-yl]-1*H*-imidazol-3-ium chloride 2



Imidazolium chloride (-)-(*M,R,R*),(*M,R,R*)-2 was synthesised according to the *General procedure D* from oxa[6]helicene amine (-)-(*M,R,R*)-16 (47 mg, 0.084 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 5.0 µl, 0.044 mmol, 0.5 equiv.), formaldehyde (37 wt% in H_2O, 4.0 µl, 0.054 mmol, 0.6 equiv.) in acetic acid (0.5 ml) at 55 °C for 35 min. The purification by flash chromatography on silica gel (dichloromethane-methanol 20:1) provided (-)-(*M,R,R*),(*M,R,R*)-2 (39 mg, 78%) as a pale white solid.

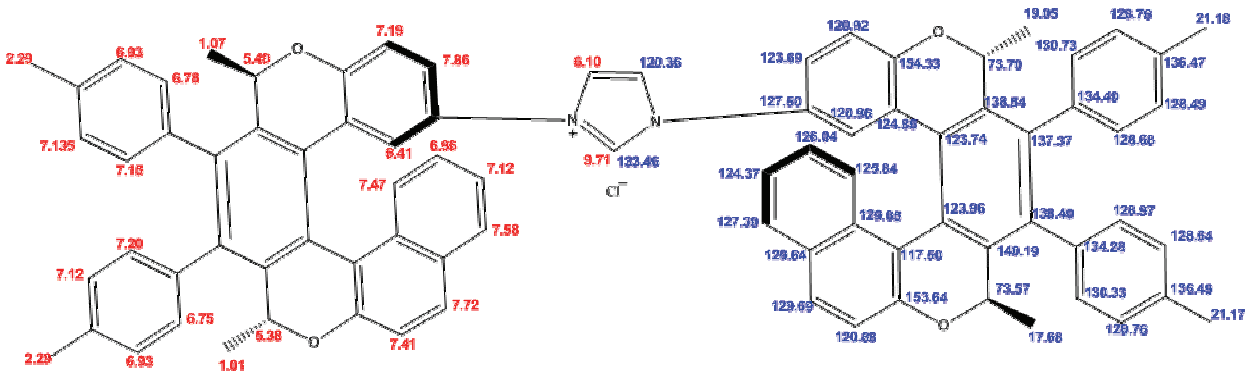
M.p.: 288-294 °C (dichloromethane – methanol).

Optical rotation: $[\alpha]^{20}_D$ = -669° (c 0.247 $CHCl_3$).

UV/Vis (THF): λ_{max} (log ε) = 241 (4.77), 259 (5.69), 351 (4.09) nm.

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.71 (t, *J* = 1.6, 1H), 7.86 (dd, *J* = 8.7, 2.8, 2H), 7.72 (d, *J* = 8.6, 2H), 7.58 (bdd, *J* = 8.2, 1.2, 2H), 7.47 (dd, *J* = 8.6, 1.0, 2H), 7.41 (d, *J* = 8.6, 2H), 7.20 (m, 2H), 7.19 (d, *J* = 8.7, 2H), 7.15 (m, 2H), 7.135 (m, 2H), 7.12 (m, 2H), 7.12 (ddd, *J* = 8.2, 6.8, 1.0, 2H), 6.96 (ddd, *J* = 8.6, 6.8, 1.2, 2H), 6.93 (m, 4H), 6.78 (m, 2H), 6.75 (m, 2H), 6.41 (d, *J* = 2.8, 2H), 6.10 (d, *J* = 1.6, 2H), 5.40 (q, *J* = 6.7, 2H), 5.38 (q, *J* = 6.7, 2H), 2.29 (s, 12H), 1.07 (d, *J* = 6.7, 6H), 1.01 (d, *J* = 6.7, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 154.33, 153.64, 140.19, 138.54, 138.40, 137.37, 136.49, 136.47, 134.40, 134.28, 133.46, 130.73, 130.33, 129.69, 129.64, 129.05, 128.97, 128.76 (2C), 128.68, 128.64, 128.49, 127.50, 127.30, 126.04, 125.84, 124.86, 124.37, 123.96, 123.74, 123.69, 120.96, 120.92, 120.88, 120.36, 117.50, 73.70, 73.57, 21.18, 21.17, 19.05, 17.68.

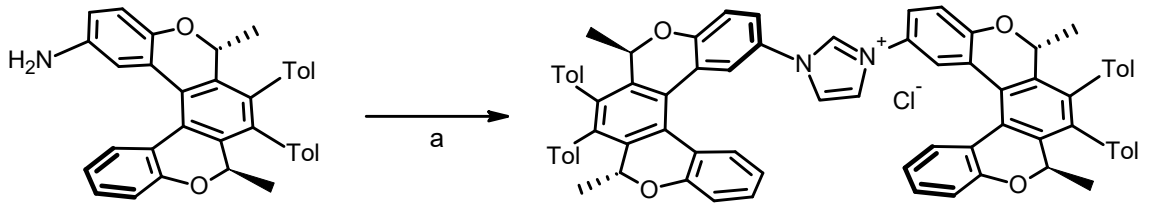


IR (KBr): 3140 w, 3050 w, 2982 m, 1618 vs, 1592 s, 1549 s, 1516 s, 1487 s, 1404 w, 1382 s, 1263 w, 1183 m, 1150 s, 1111 m, 1018 m, 981 w, 885 w, 837 m, 817 m cm^{-1}.

ESI MS: 1154 ($[M]^+$).

HR ESI MS: calcd for $C_{83}H_{65}O_4N_2$ 1153.4939, found 1153.4940.

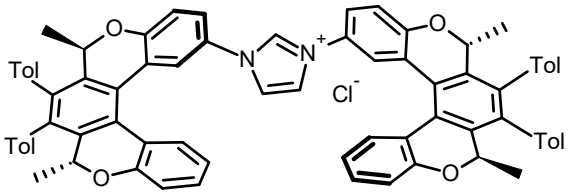
Imidazolium chloride (-)-(*M,R,R*),(*M,R,R*)-3a



(-)-(*M,R,R*)-10a (-)-(*M,R,R*),(*M,R,R*)-3a

(a) aq. glyoxal (0.5 equiv.), aq. formaldehyde (0.7 equiv.), AcOH, 40 °C, 25 min, 66%.

(-)-(*M,M*)-1,3-bis[(2*R*,5*R*)-2,5-Dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo-[1,2-*c*:4,3-*c'*]dichromen-9-yl]-1*H*-imidazol-3-ium chloride 3a



Imidazolium chloride (-)-(*M,R,R*),(*M,R,R*)-3a was synthesised according to the *General procedure D* from oxa[5]helicene amine (-)-(*M,R,R*)-10a (100 mg, 0.20 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 11 µl, 0.096 mmol, 0.5 equiv.), formaldehyde (37 wt% in H_2O, 10 µl, 0.13 mmol, 0.7 equiv.) in acetic acid (0.5 ml) at 40 °C for 25 min. The purification by flash chromatography on silica gel (dichloromethane-methanol 20:1) provided (-)-(*M,R,R*),(*M,R,R*)-3a (70 mg, 66%) as a pale white solid.

M.p.: 238-242 °C (dichloromethane – methanol).

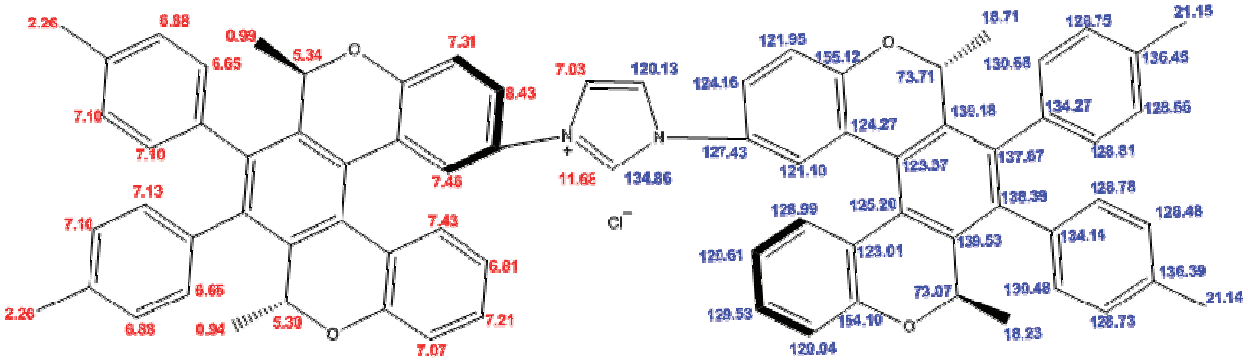
Optical rotation: $[\alpha]^{20}_{D}$ = -601° (c 0.091, $CHCl_3$).

UV/Vis (THF): λ_{max} (log ε) = 270 (4.95), 336 (4.44) nm.

^{1}H NMR (600 MHz, $CDCl_3$): δ 11.68 (t, *J* = 1.6, 1H), 8.43 (dd, *J* = 8.8, 2.8, 2H), 7.46 (d, *J* = 2.8, 2H), 7.43 (dd, *J* = 7.9, 1.6, 2H), 7.31 (d, *J* = 8.8, 2H), 7.21 (ddd, *J* = 8.0, 7.3, 1.6, 2H), 7.13 (m, 2H), 7.11 – 7.09 (m, 6H), 7.07 (dd, *J* = 8.0, 1.3, 2H), 7.03 (d, *J* = 1.6, 2H), 6.88 (m, 4H), 6.81 (ddd, *J* = 7.9, 7.3, 1.3, 2H), 6.66 – 6.64 (m, 4H), 5.34 (q, *J* = 6.7, 2H), 5.30 (q, *J* = 6.7, 2H), 2.26 (bs, 12H), 0.99 (d, *J* = 6.7, 6H), 0.94 (d, *J* = 6.7, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 155.12, 154.10, 139.53, 139.18, 138.39, 137.67, 136.45, 136.39, 134.86, 134.27, 134.14, 130.55, 130.48, 129.53, 128.99, 128.81, 128.78, 128.75, 128.73, 128.56,

128.48, 127.43, 125.20, 124.27, 124.16, 123.37, 123.01, 121.95, 121.10, 120.61, 120.13, 120.04, 73.71, 73.07, 21.15, 21.14, 18.71, 18.23.

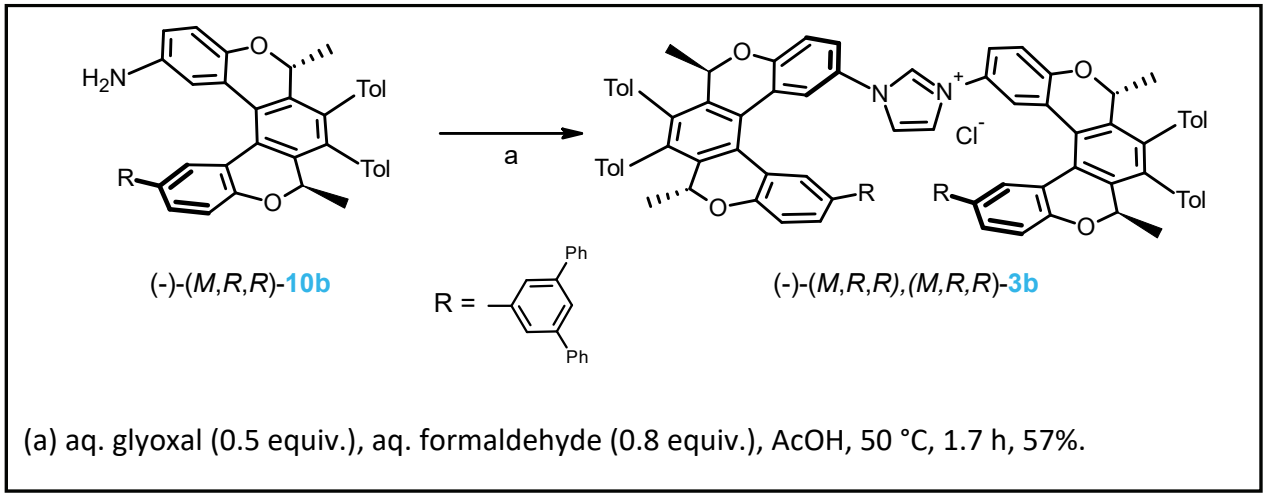


IR (KBr): 3145 w, 3050 m, 2980 m, 1603 m, 1583 m, 1517 s, 1485 s, 1446 s, 1405 w, 1183 w, 1149 m, 1111 m, 1022 m, 980 w, 886 w, 837 m, 761 m cm^{-1}.

ESI MS: 1053 ($[M]^+$).

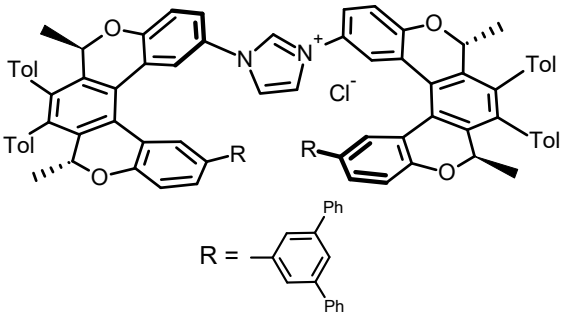
HR ESI MS: calcd for $C_{75}H_{61}O_4N_2$ 1053.4626, found 1053.4626.

Imidazolium chloride (-)-(*M,R,R*),(*M,R,R*)-3b



(a) aq. glyoxal (0.5 equiv.), aq. formaldehyde (0.8 equiv.), AcOH, 50 °C, 1.7 h, 57%.

1,3-Bis[(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-12-(1,1':3',1''-terphenyl-5'-yl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-yl]-1*H*-imidazol-3-ium chloride 3b



Imidazolium chloride (-)-(*M,R,R*),(*M,R,R*)-**3b** was synthesised according to the *General procedure D* from oxa[5]helicene amine (-)-(*M,R,R*)-**10b** (72 mg, 0.098 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 6.0 µl, 0.052 mmol, 0.5 equiv.), formaldehyde (37 wt% in H_2O, 6.0 µl, 0.081 mmol, 0.8 equiv.) in acetic acid (0.5 ml) at 50 °C for 1.7 h. The purification by flash chromatography on silica gel (dichloromethane-methanol 20:1) provided (-)-(*M,R,R*),(*M,R,R*)-**3b** (43 mg, 57%) as a pale white solid.

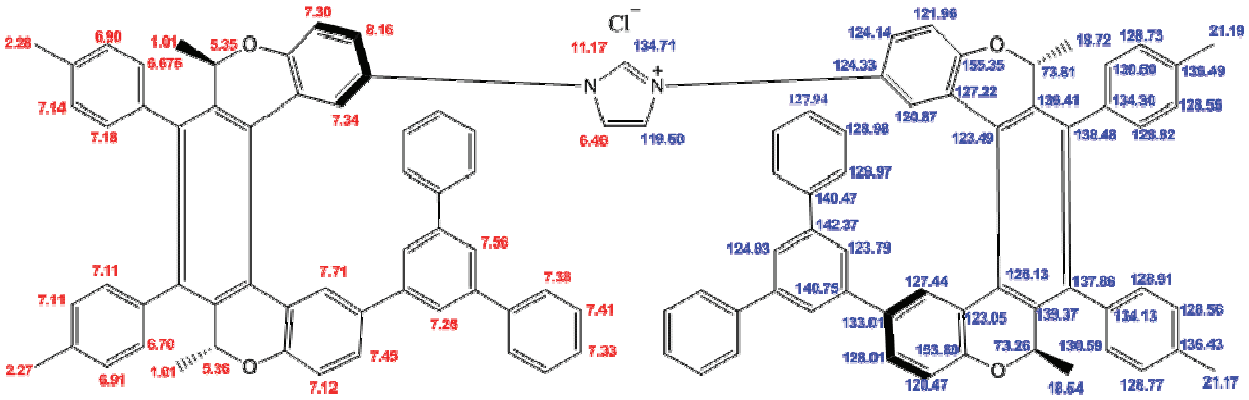
M.p.: 278-284 °C (dichloromethane – methanol).

Optical rotation: $[\alpha]^{20}_{D}$ = -716° (c 0.313, $CHCl_3$).

UV/Vis (THF): λ_{max} (log ε) = 265 (5.17), 342 (4.30) nm.

^{1}H NMR (600 MHz, $CDCl_3$): δ 11.17 (bs, 1H), 8.16 (bdd, *J* = 8.8, 2.5, 2H), 7.71 (d, *J* = 2.3, 2H), 7.56 (t, *J* = 1.7, 2H), 7.45 (dd, *J* = 8.3, 2.3, 2H), 7.43 – 7.38 (m, 16H), 7.35 – 7.32 (m, 6H), 7.30 (d, *J* = 8.8, 2H), 7.25 (d, *J* = 1.7, 4H), 7.18 (m, 2H), 7.14 – 7.11 (m, 6H), 7.12 (d, *J* = 8.3, 2H), 6.91 – 6.89 (m, 4H), 6.70 (m, 2H), 6.675 (m, 2H), 6.46 (d, *J* = 1.5, 2H), 5.36 (q, *J* = 6.7, 2H), 5.35 (q, *J* = 6.7, 2H), 2.28 (s, 6H), 2.27 (s, 6H), 1.01 (d, *J* = 6.7, 12H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 155.35, 153.80, 142.37, 140.75, 140.47, 139.41, 139.37, 138.48, 137.86, 136.49, 136.43, 134.71, 134.30, 134.13, 133.01, 130.59, 130.50, 128.98, 128.91, 128.82, 128.77, 128.73, 128.56 (2C), 128.01, 127.94, 127.44, 127.22, 126.97, 125.13, 124.83, 124.33, 124.14, 123.79, 123.49, 123.05, 121.96, 120.87, 120.47, 119.50, 73.81, 73.26, 21.19, 21.17, 18.72, 18.54.

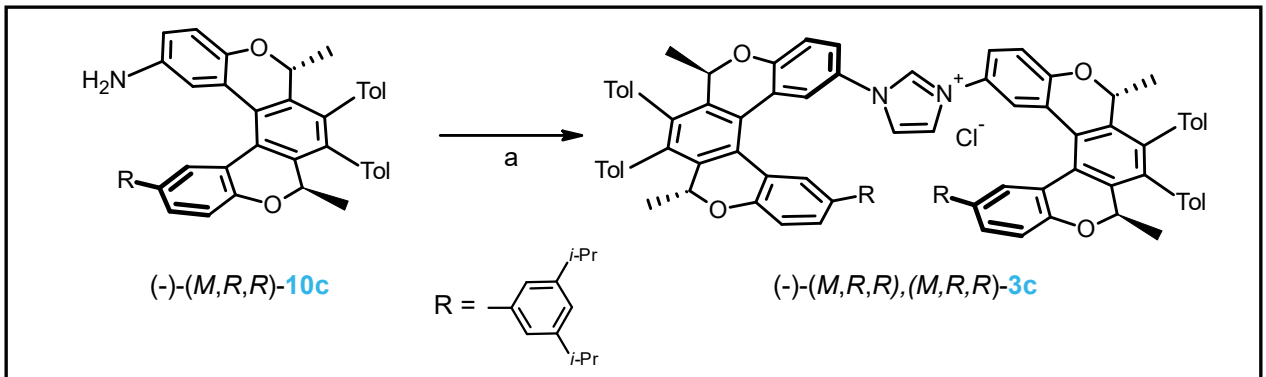


IR ($CHCl_3$): 3060 w, sh, 1595 s, 1547 m, 1518 s, 1497 s, 1489 s, 1441 m, 1426 m, 1414 m, 1405 w, sh, 1274 m, 1261 m, sh, 1250 m, 1184 w, 1148 m, 1109 m, 1085 m, 1073 w, sh, 1030 w, 1021 m, 957 w, sh, 881 m, 879 m, 839 m, 823 m, 719 m, 614 w, 534 w cm^{-1}.

ESI MS: 1509 ($[M]^+$).

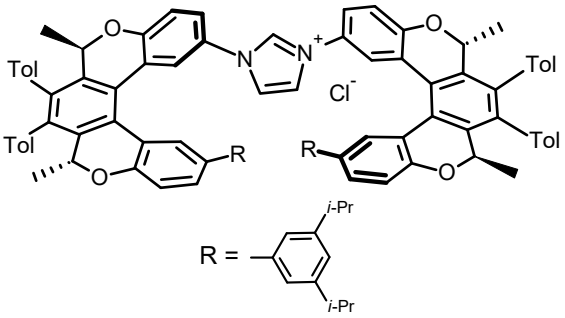
HR ESI MS: calcd for $C_{111}H_{85}O_4N_2$ 1509.6504, found 1509.6509.

Imidazolium chloride (-)-(*M,R,R*),(*M,R,R*)-3c



(a) aq. glyoxal (0.5 equiv.), aq. formaldehyde (0.6 equiv.), AcOH, 45 °C, 40 min, 64%.

(-)-(*M,M*)-1,3-Bis[(2*R*,5*R*)-12-[3,5-bis(1-methylethyl)phenyl]-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-yl]-1*H*-imidazol-3-ium chloride 3c



Imidazolium chloride (-)-(*M,R,R*),(*M,R,R*)-**3c** was synthesised according to the *General procedure D* from oxa[5]helicene amine (-)-(*M,R,R*)-**10c** (77 mg, 0.115 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 7.0 µl, 0.061 mmol, 0.5 equiv.), formaldehyde (37 wt% in H_2O, 5.0 µl, 0.067 mmol, 0.6 equiv.) in acetic acid (0.5 ml) at 45 °C for 40 min. The purification by flash chromatography on silica gel (dichloromethane-methanol 20:1) provided (-)-(*M,R,R*),(*M,R,R*)-**3c** (52 mg, 64%) as pale white solid.

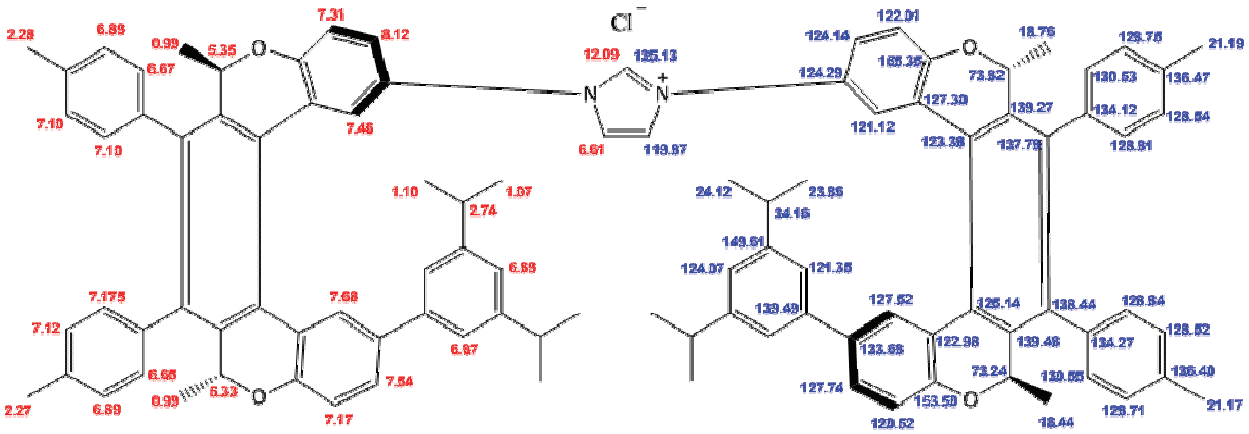
M.p.: 256-262 °C (dichloromethane – methanol).

Optical rotation: $[\alpha]^{20}_{D}$ = -806° (c 0.275, $CHCl_3$).

UV/Vis (THF): λ_{max} (log ε) = 264 (4.99), 342 (4.29) nm.

^{1}H NMR (600 MHz, $CDCl_3$): δ 12.09 (s, 1H), 8.12 (bdd, *J* = 8.7, 2.7, 2H), 7.68 (d, *J* = 2.3, 2H), 7.54 (dd, *J* = 8.3, 2.3, 2H), 7.46 (d, *J* = 2.7, 2H), 7.31 (d, *J* = 8.7, 2H), 7.175 (m, 2H), 7.17 (d, *J* = 8.3, 2H), 7.12 (m, 2H), 7.10 (m, 4H), 6.90 – 6.88 (m, 6H), 6.87 (d, *J* = 1.7, 4H), 6.67 (m, 2H), 6.65 (m, 2H), 6.61 (d, *J* = 1.3, 2H), 5.35 (q, *J* = 6.7, 2H), 5.33 (q, *J* = 6.7, 2H), 2.74 (sept, *J* = 6.9, 4H), 2.28 (s, 6H), 2.27 (s, 6H), 1.10 (d, *J* = 6.7, 12H), 1.07 (d, *J* = 6.7, 12H), 0.99 (d, *J* = 6.7, 12H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 155.35, 153.50, 149.61, 139.49, 139.48, 139.27, 138.44, 137.78, 136.47, 136.40, 135.13, 134.27, 134.12, 133.68, 130.55, 130.53, 128.84, 128.81, 128.75, 128.71, 128.54, 128.52, 127.74, 127.52, 127,30, 125.14, 124.29, 124.14, 124.07, 123.38, 122.98, 122.01, 121.35, 121.12, 120.52, 119.87, 73.82, 73.24, 34.16, 24.12, 23.86, 21.19, 21.17, 18.76, 18.44.

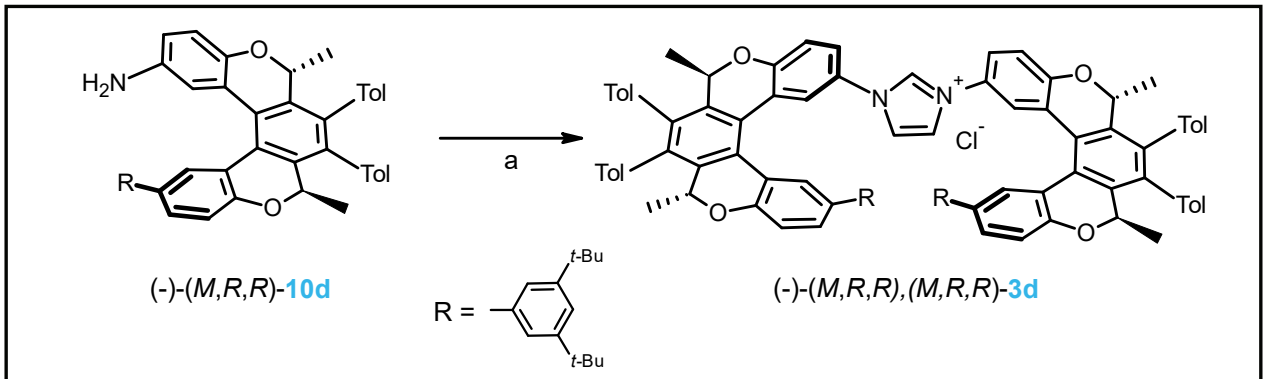


IR ($CHCl_3$): 3049 w, sh, 2962 m, 2928 w, 1598 w, 1545 w, 1518 w, 1457 w, sh, 1428 w, 1384 w, 1369 vw, 1343 w, sh, 1260 w, 1148 w, 1132 w, 1108 w, 1090 w, 1067 m, 876 w, 839 w, 823 w, 569 w, 525 w, 467 w cm^{-1}.

ESI MS: 1374 ($[M]^+$).

HR ESI MS: calcd for $C_{99}H_{93}O_4N_2$ 1373.7130, found 1373.7130.

Imidazolium chloride (-)-(*M,R,R*),(*M,R,R*)-3d

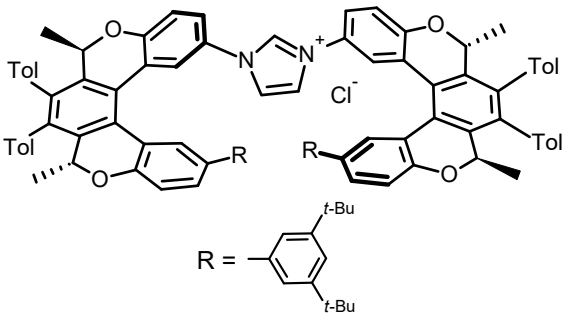


(-)-(*M,R,R*)-10d

(-)-(*M,R,R*),(*M,R,R*)-3d

(a) aq. glyoxal (0.6 equiv.), aq. formaldehyde (0.8 equiv.), AcOH, 45 °C, 50 min, 82%.

(-)-(*M,M*)-1,3-Bis[(2*R*,5*R*)-12-(3,5-di-*tert*-butylphenyl)-2,5-dimethyl-3,4-bis(4-methyl-phenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-yl]-1*H*-imidazol-3-ium chloride 3d



Imidazolium chloride (-)-(*M,R,R*),(*M,R,R*)-**3d** was synthesised according to the *General procedure D* from oxa[5]helicene amine (-)-(*M,R,R*)-**10d** (50 mg, 0.072 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 5.0 µl, 0.044 mmol, 0.6 equiv.), formaldehyde (37 wt% in H_2O, 4.0 µl, 0.054 mmol, 0.8 equiv.) in acetic acid (0.5 ml) at 45 °C for 50 min. The purification by flash chromatography on silica gel (dichloromethane-methanol 20:1) provided (-)-(*M,R,R*),(*M,R,R*)-**3d** (43 mg, 82%) as a pale white solid.

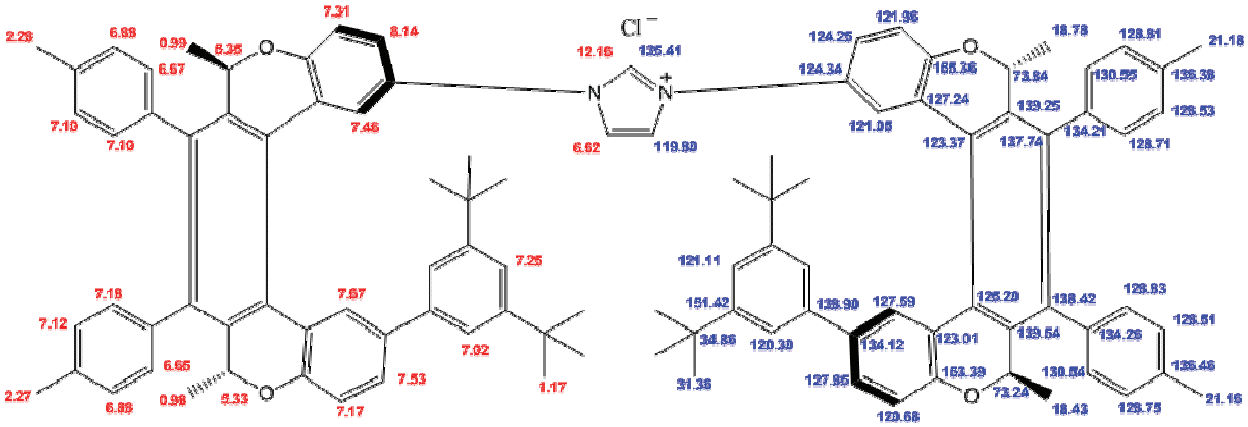
M.p.: 256-259 °C (dichloromethane – methanol).

Optical rotation: $[\alpha]^{20}_{D}$ = -808° (c 0.258, $CHCl_3$).

UV/Vis (THF): λ_{max} (log ε) = 263 (5.02), 343 (4.33) nm.

^{1}H NMR (600 MHz, $CDCl_3$): δ 12.16 (s, 1H), 8.14 (dd, *J* = 8.7, 2.6, 2H), 7.67 (d, *J* = 2.3, 2H), 7.53 (dd, *J* = 8.3, 2.3, 2H), 7.46 (d, *J* = 2.6, 2H), 7.31 (d, *J* = 8.7, 2H), 7.25 (t, *J* = 1.8, 2H), 7.18 (m, 2H), 7.17 (d, *J* = 8.3, 2H), 7.12 (m, 2H), 7.10 (m, 4H), 7.02 (d, *J* = 1.8, 4H), 6.89 – 6.86 (m, 4H), 6.67 (m, 2H), 6.65 (m, 2H), 6.62 (d, *J* = 0.9, 2H), 5.35 (q, *J* = 6.7, 2H), 5.33 (q, *J* = 6.7, 2H), 2.28 (s, 6H), 2.27 (s, 6H), 1.17 (s, 36H), 0.99 (d, *J* = 6.7, 6H), 0.98 (d, *J* = 6.7, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 155.36, 153.39, 151.42, 139.54, 139.25, 138.90, 138.42, 137.74, 136.46, 136.38, 135.41, 134.26, 134.21, 134.12, 130.55, 130.54, 128.83, 128.81, 128.75, 128.71, 128.53, 128.51, 127.85, 127.59, 127.24, 125.20, 124.34, 124.25, 123.37, 123.01, 121.96, 121.11, 121.05, 120.68, 120.30, 119.80, 73.84, 73.24, 34.86, 31.36, 21.18, 21.16, 18.78, 18.43.

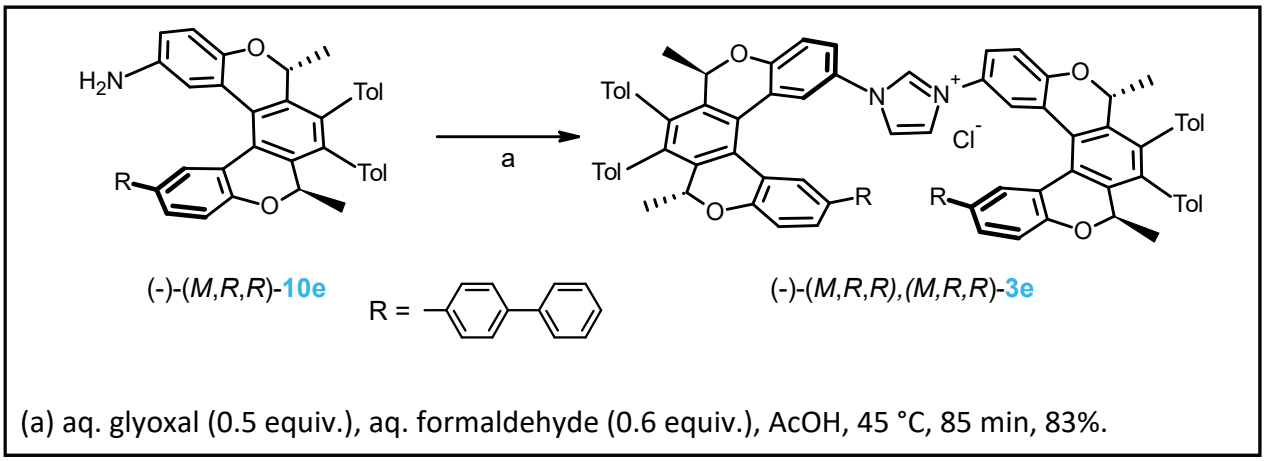


IR ($CHCl_3$): 3052 w, sh, 2966 vs, 2871 w, 1545 w, 1518 m, 1445 w, 1425 m, 1405 w, sh, 1395 w, 1368 m, 1343 w, 1330 w, sh, 1260 m, 1184 w, 1131 w, 1091 w, 1067 s, 1058 m, 838 m, 824 m, 808 m, 715 vw cm^{-1}.

ESI MS: 1430 ($[M]^+$).

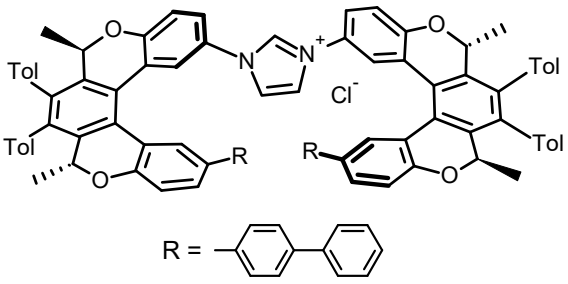
HR ESI MS: calcd for $C_{103}H_{101}O_4N_2$ 1429.7756, found 1429.7755.

Imidazolium chloride (-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-3e



(a) aq. glyoxal (0.5 equiv.), aq. formaldehyde (0.6 equiv.), AcOH, 45 °C, 85 min, 83%.

(-)-(*M*,*M*)-1,3-Bis[(2*R*,5*R*)-12-biphenyl-4-yl-2,5-dimethyl-3,4-bis(4-methylphenyl)-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-yl]-1*H*-imidazol-3-ium chloride 3e



Imidazolium chloride (-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3e** was synthesised according to the *General procedure D* from oxa[5]helicene amine (-)-(*M*,*R*,*R*)-**10e** (57 mg, 0.086 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 5.0 µl, 0.044 mmol, 0.5 equiv.), formaldehyde (37 wt% in H_2O, 4.0 µl, 0.054 mmol, 0.6 equiv.) in acetic acid (0.5 ml) at 45 °C for 85 min. The purification by flash chromatography on silica gel (dichloromethane-methanol 20:1) provided (-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3e** (50 mg, 83%) as a pale white solid.

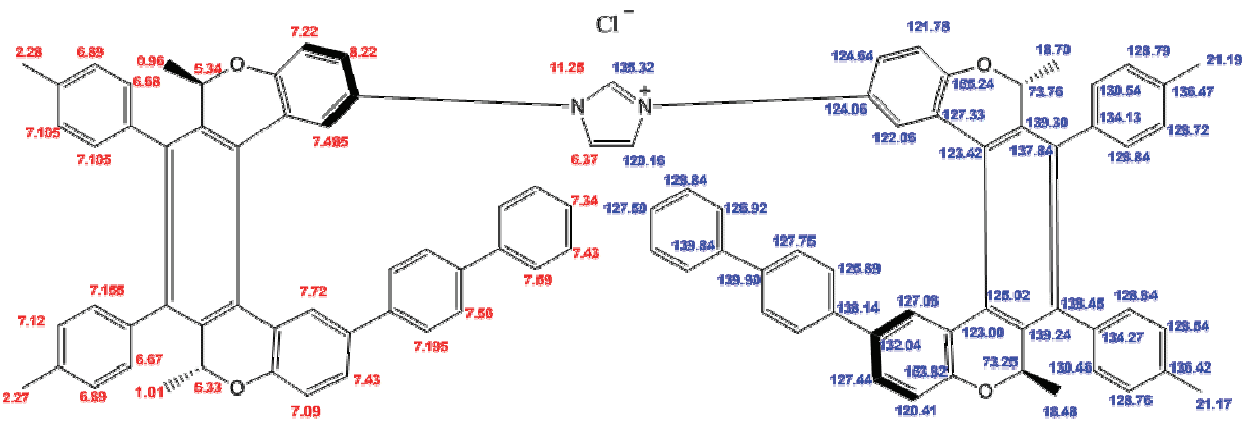
M.p.: 294-295 °C (dichloromethane – methanol).

Optical rotation: $[\alpha]^{20}_{D}$ = -825° (c 0.273, $CHCl_3$).

UV/Vis (THF): λ_{max} (log ε) = 274 (5.13), 300 (4.89), 350 (4.33) nm.

^{1}H NMR (600 MHz, $CDCl_3$): δ 11.25 (s, 1H), 8.22 (dd, *J* = 8.8, 2.6, 2H), 7.72 (d, *J* = 2.3, 2H), 7.59 (m, 4H), 7.50 (m, 4H), 7.485 (d, *J* = 2.6, 2H), 7.44 – 7.42 (m, 6H), 7.34 (tt, *J* = 7.4, 1.2, 2H), 7.22 (d, *J* = 8.8, 2H), 7.195 (m, 4H), 7.155 (m, 2H), 7.12 (m, 2H), 7.105 (m, 4H), 7.09 (d, *J* = 8.3, 2H), 6.89 (m, 4H), 6.68 (m, 2H), 6.67 (m, 2H), 6.37 (d, *J* = 1.6, 2H), 5.34 (q, *J* = 6.7, 2H), 5.33 (q, *J* = 6.7, 2H), 2.28 (s, 6H), 2.27 (s, 6H), 1.01 (d, *J* = 6.7, 6H), 0.96 (d, *J* = 6.7, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 155.24, 153.82, 139.90, 139.84, 139.30, 139.24, 138.45, 138.14, 137.84, 136.47, 136.42, 135.32, 134.27, 134.13, 132.04, 130.54, 130.46, 128.84 (3C), 128.79, 128.76, 128.72, 128.54, 127.75, 127.50, 127.44, 127.33, 127.08, 126.92, 125.89, 125.02, 124.64, 124.06, 123.42, 123.00, 122.06, 121.78, 120.41, 120.16, 73.76, 73.25, 21.19, 21.17, 18.70, 18.48.

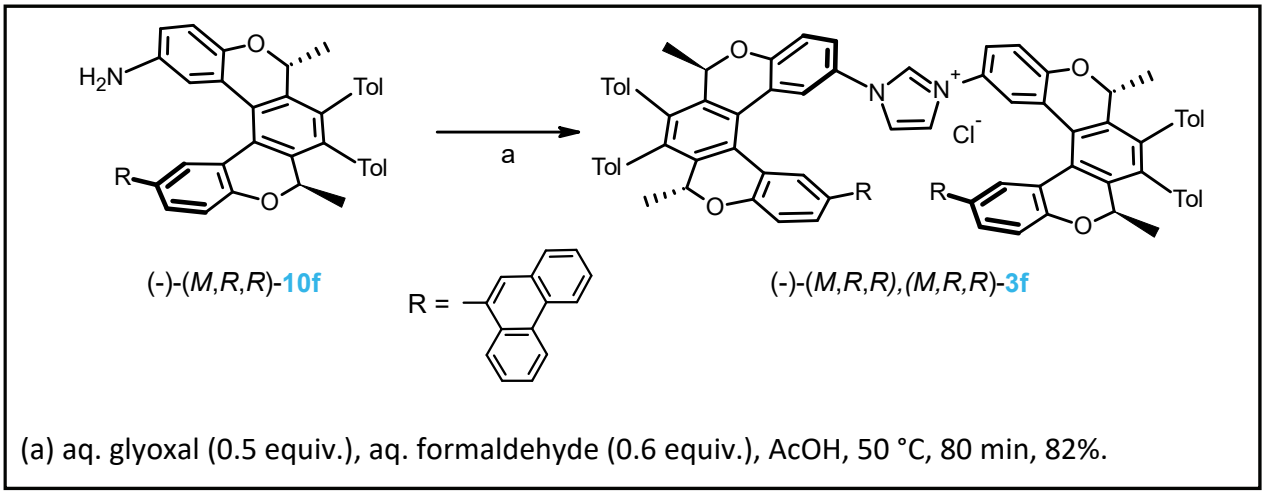


IR ($CHCl_3$): 3052 w, sh, 1602 w, 1585 vw, 1544 w, 1518 m, 1482 s, 1448 w, sh, 1435 m, 1401 w, 1369 m, 1341 vw, 1330 vw, 1132 w, 1109 w, 1090 w, 1065 w, 1006 w, 943 vw, 838 m, 699 m, 508 w cm^{-1}.

ESI MS: 1358 ($[M]^+$).

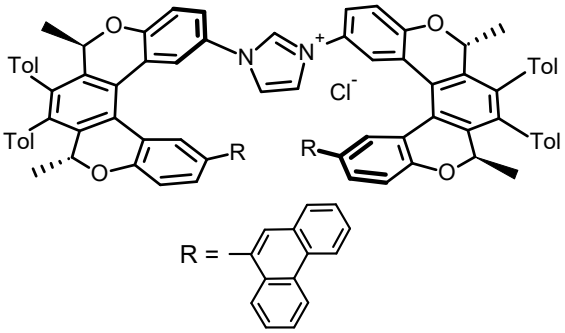
HR ESI MS: calcd for $C_{99}H_{77}O_4N_2$ 1357.5878, found 1357.5886.

Imidazolium chloride (-)-(*M,R,R*),(*M,R,R*)-3f



(a) aq. glyoxal (0.5 equiv.), aq. formaldehyde (0.6 equiv.), AcOH, 50 °C, 80 min, 82%.

(-)-(*M,M*)-1,3-Bis[(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-12-phenanthren-9-yl-2,5-dihydrobenzo[1,2-*c*:4,3-*c'*]dichromen-9-yl]-1*H*-imidazol-3-ium chloride 3f



Imidazolium chloride (-)-(*M,R,R*),(*M,R,R*)-3f was synthesised according to the *General procedure D* from oxa[5]helicene amine (-)-(*M,R,R*)-10f (58 mg, 0.085 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 5.0 µl, 0.044 mmol, 0.5 equiv.), formaldehyde (37 wt% in H_2O, 4.0 µl, 0.054 mmol, 0.6 equiv.) in acetic acid (0.5 ml) at 50 °C for 80 min. The purification by flash chromatography on silica gel (dichloromethane-methanol 20:1) provided (-)-(*M,R,R*),(*M,R,R*)-3f (50 mg, 82%) as a pale white solid.

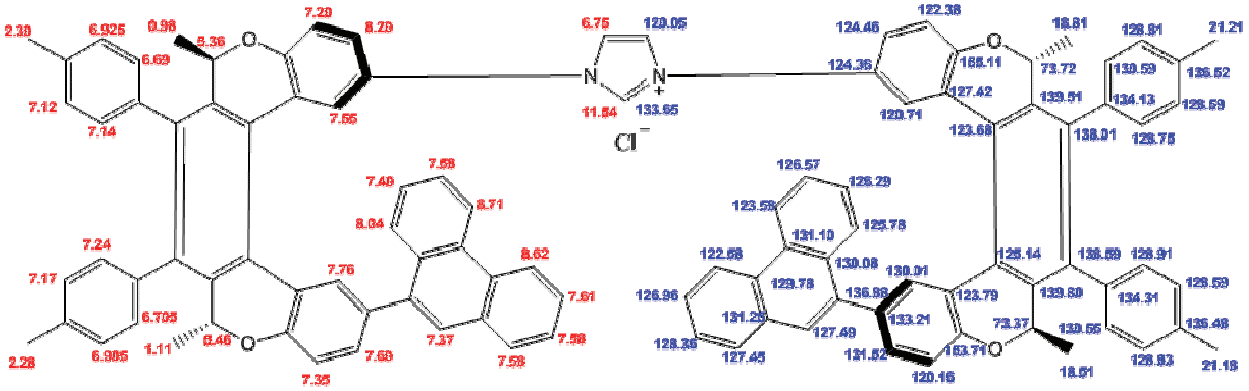
M.p.: 313-319 °C (dichloromethane – methanol).

Optical rotation: $[\alpha]^{20}_{D}$ = -799° (c 0.301, $CHCl_3$).

UV/Vis (THF): λ_{max} (log ε) = 259 (5.11), 300 (4.65), 338 (4.35) nm.

^{1}H NMR (600 MHz, $CDCl_3$): δ 11.54 (s, 1H), 8.71 (d, *J* = 8.3, 2H), 8.62 (d, *J* = 8.3, 2H), 8.20 (bs, 2H), 8.04 (d, *J* = 7.8, 2H), 7.76 (d, *J* = 1.9, 2H), 7.61 – 7.55 (m, 12H), 7.35 (d, *J* = 8.0, 2H), 7.40 (dd, *J* = 7.2, 7.2, 2H), 7.37 (bs, 2H), 7.24 (m, 2H), 7.20 (vbs, 2H), 7.17 (m, 2H), 7.14 (m, 2H), 7.12 (m, 2H), 6.925 (m, 2H), 6.905 (m, 2H), 6.75 (bs, 2H), 6.705 (m, 2H), 6.69 (m, 2H), 5.46 (q, *J* = 6.7, 2H), 5.36 (bq, *J* = 6.7, 2H), 2.30 (s, 6H), 2.28 (s, 6H), 1.11 (d, *J* = 6.7, 6H), 0.98 (bd, *J* = 6.7, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 155.11, 153.71, 139.80, 139.51, 138.59, 138.01, 136.88, 136.52, 136.48, 134.31, 134.13, 133.65, 133.21, 131.52, 131.25, 131.10, 130.59, 130.55, 130.08, 130.01, 129.78, 128.91, 128.83, 128.81, 128.75, 128.59 (2C), 128.36, 127.49, 127.45, 127.42, 126.96, 126.57, 126.29, 125.78, 125.14, 124.46, 124.36, 123.79, 123.68, 123.58, 122.58, 122.38, 120.71, 120.16, 120.05, 73.72, 73.37, 21.21, 21.18, 18.81, 18.51.

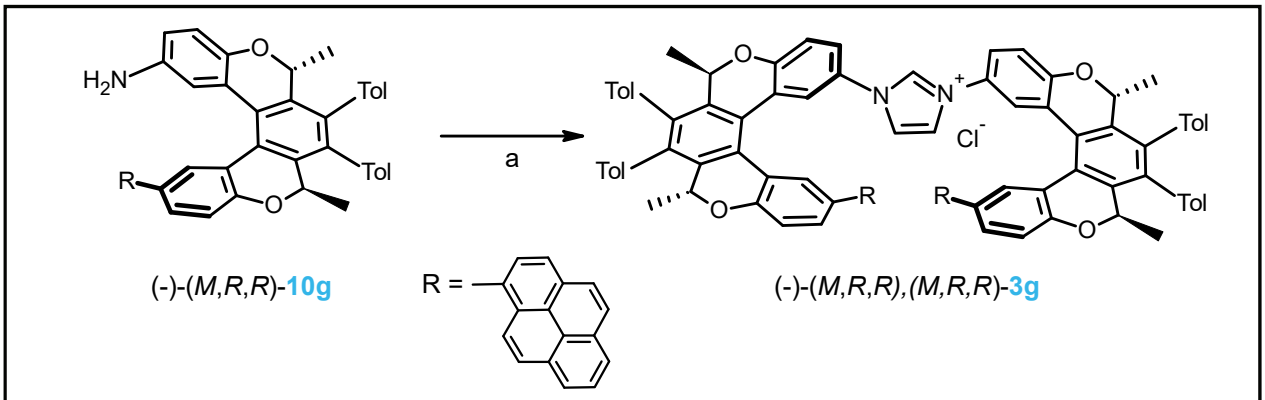


IR ($CHCl_3$): 3083 w, 3046 w, 1603 w, 1543 m, 1526 vw, 1517 s, 1451 w, 1432 m, 1402 w, 1344 w, 1308 vw, 1261 m, 1243 m, sh, 1184 w, 1169 w, sh, 1150 s, 1129 m, 1089 m, 1088 m, 1066 s, 1037 w, sh, 947 vw, 868 m, 839 m, 830 m, 808 m, 501 w cm^{-1}.

ESI MS: 1406 ($[M]^+$).

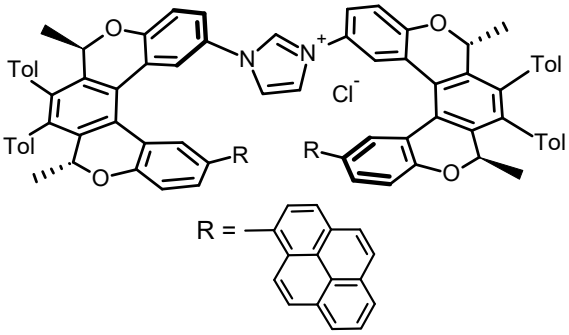
HR ESI MS: calcd for $C_{103}H_{77}O_4N_2$ 1405.5878, found 1405.5876.

Imidazolium chloride (-)-(*M,R,R*),(*M,R,R*)-3g



(a) aq. glyoxal (0.5 equiv.), aq. formaldehyde (0.6 equiv.), AcOH, 55 °C, 3.7 h, 61%.

(-)-(*M,M*)-1,3-Bis[(2*R*,5*R*)-2,5-dimethyl-3,4-bis(4-methylphenyl)-12-pyren-1-yl-2,5-dihydro-benzo[1,2-*c*:4,3-*c'*]dichromen-9-yl]-1*H*-imidazol-3-ium chloride 3g



Imidazolium chloride (-)-(*M,R,R*),(*M,R,R*)-**3g** was synthesised according to the *General procedure D* from oxa[5]helicene amine (-)-(*M,R,R*)-**10g** (63 mg, 0.089 mmol) in acetic acid (0.5 ml), glyoxal (40 wt% in H_2O, 5.0 µl, 0.044 mmol, 0.5 equiv.), formaldehyde (37 wt% in H_2O, 4.0 µl, 0.054 mmol, 0.6 equiv.) in acetic acid (0.5 ml) at 55 °C for 3.7 h. The purification by flash chromatography on silica gel (dichloromethane-methanol 20:1) provided (-)-(*M,R,R*),(*M,R,R*)-**3g** (40 mg, 61%) as a pale white solid.

M.p.: 319-325 °C (dichloromethane – methanol).

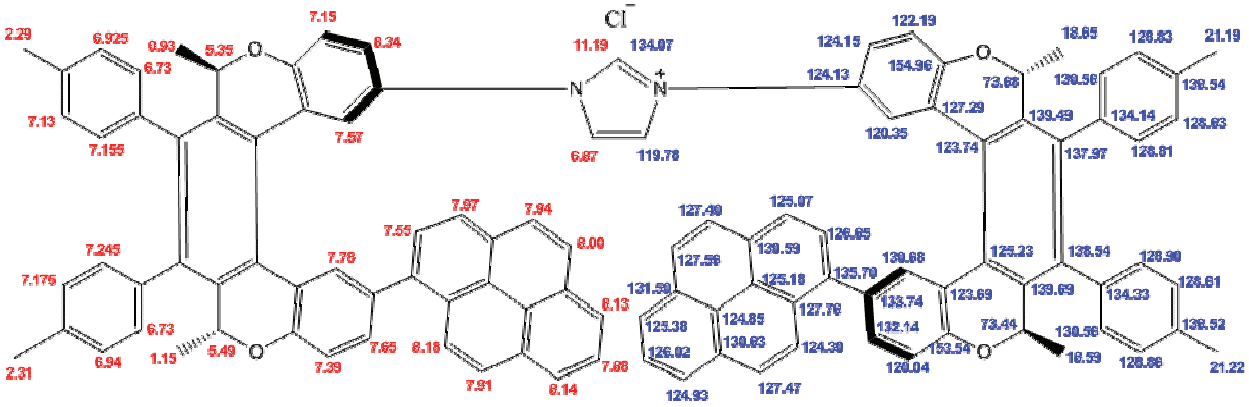
Optical rotation: $[\alpha]^{20}_{D}$ = -952° (c 0.353, $CHCl_3$).

UV/Vis (THF): λ_{max} (log ε) = 237 (5.11), 270 (5.09), 278 (5.08), 346 (4.88) nm.

^{1}H NMR (600 MHz, $CDCl_3$): δ 11.19 (s, 1H), 8.34 (bd, *J* = 7.6, 2H), 8.18 (d, *J* = 9.2, 2H), 8.14 (dd, *J* = 7.6, 1.1, 2H), 8.13 (dd, *J* = 7.6, 1.1, 2H), 8.00 (d, *J* = 9.0, 2H), 7.97 (d, *J* = 7.9, 2H), 7.94 (d, *J* = 9.0, 2H), 7.91 (d, *J* = 9.2, 2H), 7.88 (t, *J* = 7.6, 2H), 7.78 (d, *J* = 2.2, 2H), 7.65 (dd, *J* = 8.2, 2.2, 2H), 7.57 (bs, 2H), 7.55 (d, *J* = 7.9, 2H), 7.39 (d, *J* = 8.2, 2H), 7.245 (m, 2H), 7.175 (m, 2H), 7.155 (m, 2H), 7.15 (vbs, 2H), 7.13 (m, 2H), 6.94 (m, 2H), 6.925 (m, 2H), 6.87 (bs, 2H), 6.73 (m, 4H), 5.49

(q, *J* = 6.7, 2H), 5.35 (q, *J* = 6.7, 2H), 2.31 (s, 6H), 2.29 (s, 6H), 1.15 (d, *J* = 6.7, 6H), 0.93 (d, *J* = 6.7, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 154.96, 153.54, 139.69, 139.49, 138.54, 137.97, 136.54, 136.52, 135.70, 134.33, 134.14, 134.07, 133.74, 132.14, 131.50, 130.68, 130.63, 130.59, 130.56 (2C), 128.90, 128.86, 128.83, 128.81, 128.63, 128.61, 127.76, 127.56, 127.47, 127.40, 127.29, 126.65, 126.02, 125.38, 125.23, 125.18, 125.07, 124.93, 124.85, 124.30, 124.15, 124.13, 123.74, 123.69, 122.19, 120.35, 120.04, 119.78, 73.68, 73.44, 21.22, 21.19, 18.65, 18.59.



IR ($CHCl_3$): 3049 w, sh, 1586 vw, 1545 w, 1517 m, 1445 w, 1431 m, 1416 vw, 1405 w, 1360 m, 1343 w, 1261 m, 1184 m, 1133 w, 1066 m, 840 m, 825 m, 817 w, 808 vw, 709 vw cm^{-1}.

ESI MS: 1454 ($[M]^+$).

HR ESI MS: calcd for $C_{107}H_{77}O_4N_2$ 1453.5878, found 1453.5884.

Ni^0-catalysed enantioselective [2+2+2] cycloisomerisation of triynes 17 and 20

Drying of $Ni(acac)_2$:

The commercially available nickel(II) acetylacetonate was heated in a Schlenk flask under vacuum at 150 °C for 4 h, then it was allowed to cool down to room temperature and flushed with argon. This material was used for catalytic experiments for at least one month without any decrease in reactivity.

Preparation of EtMgCl stock solution:

The commercially available EtMgCl solution (5 ml, 2M in THF) was diluted with of freshly distilled THF (20 ml) to form an approximately 0.4 M solution. The exact concentration was determined before each experiment by titration with iodine.

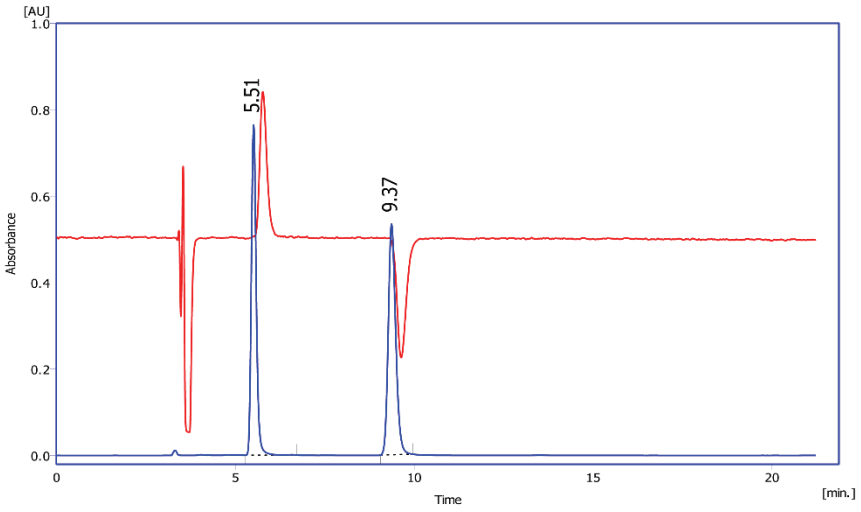
*Representative procedure for [2+2+2] cycloisomerisation of triyne **17** using chiral imidazolium chloride* (-)-(*M,R,R*),(*M,R,R*)-**3a** *as a ligand:*

A dry Schlenk flask was charged with $Ni(acac)_2$ (1.2 mg, 0.0047 mmol, 20 mol%) and imidazolium chloride **3a** (11 mg, 0.010 mmol, 44 mol%) and heated at 80 °C for 1 h under vacuum. After cooling down to room temperature and flushing with argon, the freshly distilled tetrahydrofuran (300 µl) was added followed by ethylmagnesium chloride (0.36 M in THF, 58 µl, 0.021 mmol, 92 mol%). The solution immediately turned black. After 2 min, triyne **17** (10 mg, 0.023 mmol, 1.0 equiv.) in tetrahydrofuran (200 µl) was injected and the reaction mixture was stirred at room temperature for 2 h. The solvent was evaporated and the residue was filtered through a short pad of silica gel (hexane-dichloromethane 7:1) to get the crude enantioenriched helicene (+)-(*P*)-**18** (7.2 mg). HPLC analysis (Chiralpak IA, heptane – chloroform 7:2) showed the conversion >90% and 41% *ee.*

HPLC analyses of dibenzo[6]helicene 18 and dibenzo[7]helicene 21

HPLC analyses were performed on a Chiralpak IA column (250 × 4.6 mm, 5 µm, Chiral Technologies) using an instrument consisting of an isocratic HPLC pump (Knauer Smartline 1000), a variable-wavelength UV detector set at 254 nm (Knauer Smartline 2500), a polarimetric detector (Chiralyser LED 426 nm, IBZ Messtechnik) and a PC workstation with Clarity software (Dataapex). Heptane-chloroform (70:30) was used as a mobile phase at a flow rate of 1.0 ml/min. For analyses, the samples were dissolved in HPLC grade chloroform (ca 1 mg/ml) and filtered through a 0.45 µm PTFE syringe filter before injection (ca 1 µl).

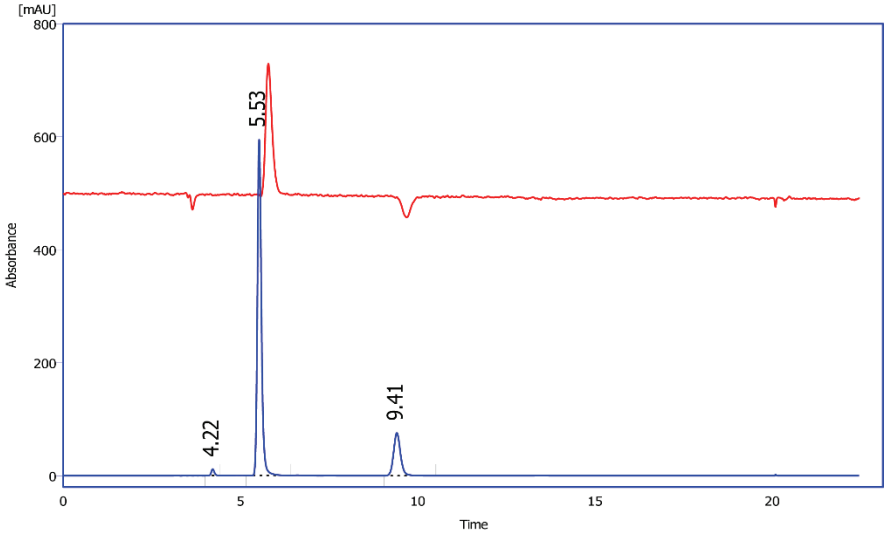
Conversions as well as enantiomeric excesses were determined by integration of the corresponding peaks of the UV-absorption (254 nm) traces in the respective HPLC chromatograms *via* the calibration curve. The authentic samples of the racemic helicenes, required for identification of peaks corresponding to the individual enantiomers, were prepared in our group earlier.



Result Table (Uncal - C:\Clarity_Samal\Data\SAM-[6]dibn_public2 - S 2500: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	5.510	7297.104	764.381	48.68	58.9	0.15	
2	9.367	7692.849	533.652	51.32	41.1	0.22	
	Total	14989.953	1298.033	100.00	100.0		

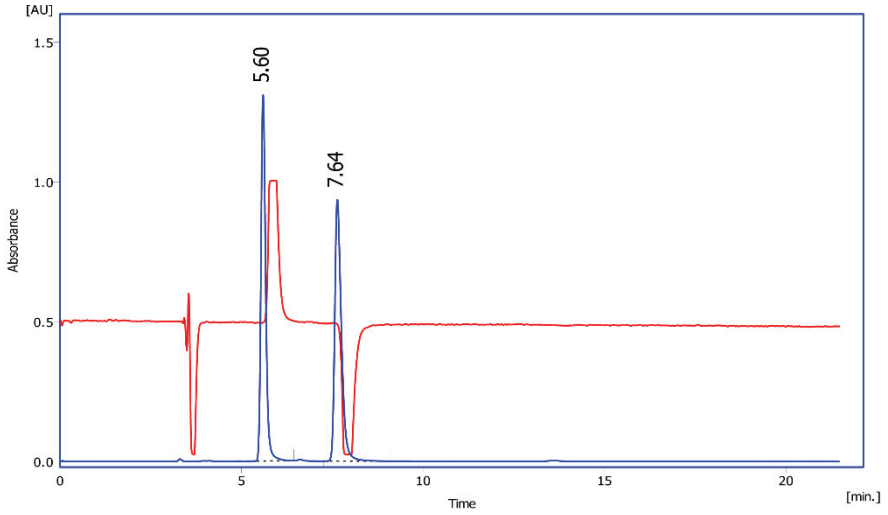
Figure S1: HPLC chromatogram (Chiralpak IA column, heptane – chloroform 7:3) of *rac*-[6]helicene 18 (blue: UV detector, red: downstream polarimetric detector).



Result Table (Uncal - C:\Clarity_Samal\Data\SAM-[6]dibn_public_cat1 - S 2500: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	4.217	68.633	11.354	1.19	1.7	0.09	
2	5.527	4671.710	594.269	81.00	87.2	0.12	
3	9.410	1027.138	75.549	17.81	11.1	0.21	
	Total	5767.481	681.172	100.00	100.0		

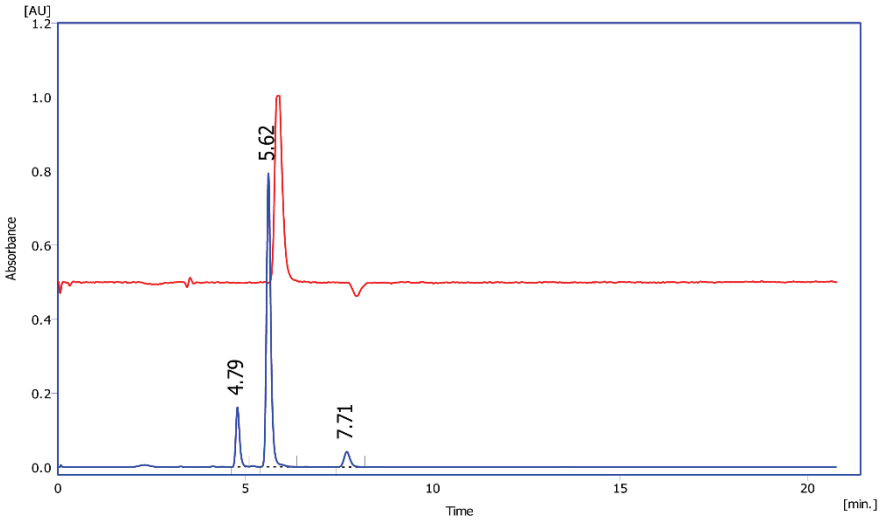
Figure S2: HPLC chromatogram (Chiralpak IA column, heptane – chloroform 7:3) of (*P*)-[6]helicene **18** (64% *ee*) after cyclisation, where (-)-(*M,R,R*),(*M,R,R*)-**3c** was used as the chiral ligand. The peak at 4.22 min corresponds to the starting material (blue: UV detector, red: downstream polarimetric detector).



Result Table (Uncal - C:\Clarity_Samal\Data\SAM-[7]dibn_public2 - S 2500: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	5.597	11801.091	1308.922	49.73	58.3	0.14	
2	7.640	11928.425	934.606	50.27	41.7	0.19	
	Total	23729.516	2243.528	100.00	100.0		

Figure S3: HPLC chromatogram (Chiralpak IA column, heptane – chloroform 7:3) of *rac*-[7]helicene **21** (blue: UV detector, red: downstream polarimetric detector).

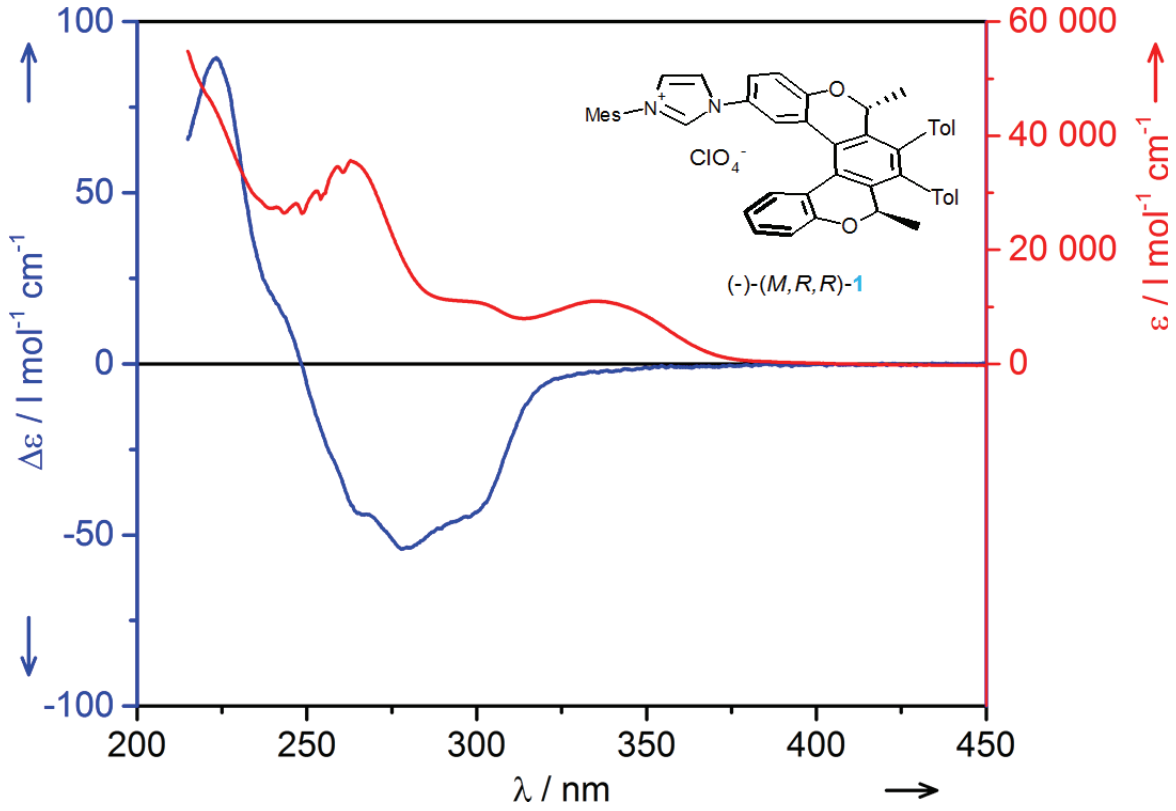


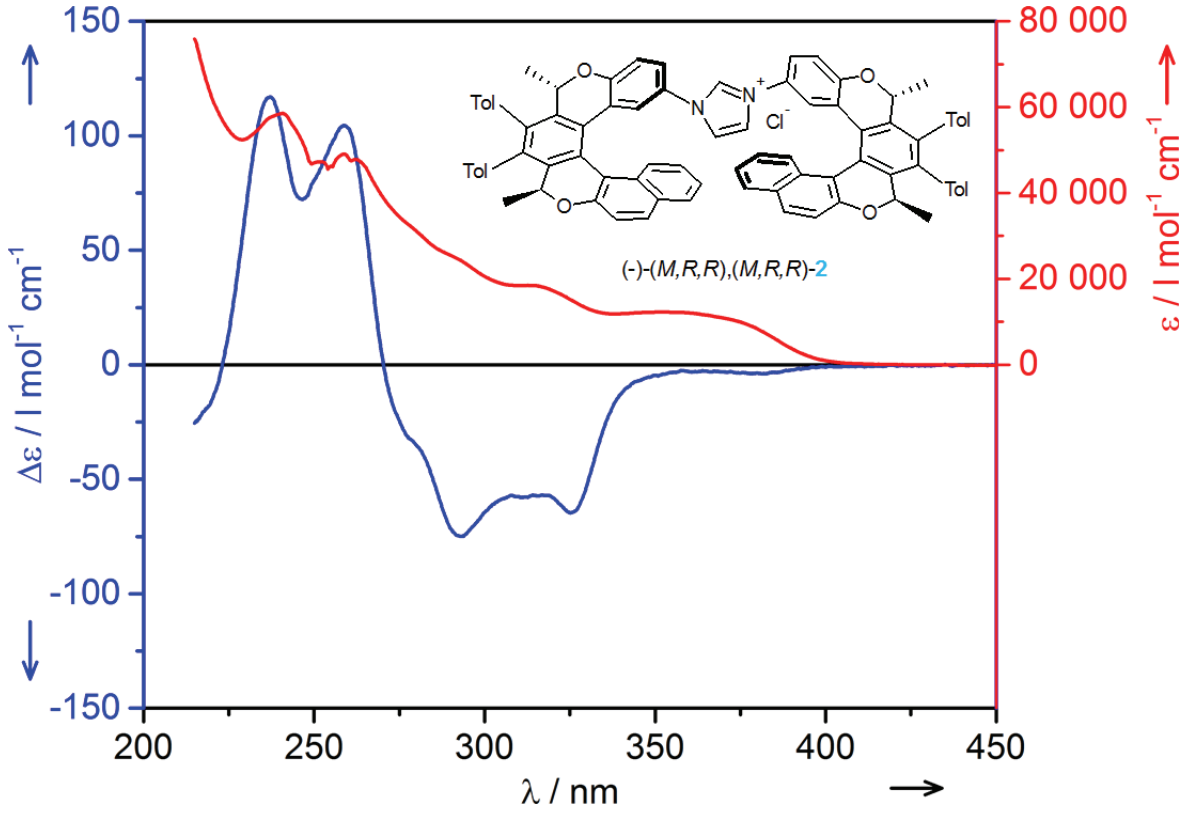
Result Table (Uncal - C:\Clarity_Samal\Data\SAM-[7]dibn_public_cat2 - S 2500: Channel 1)

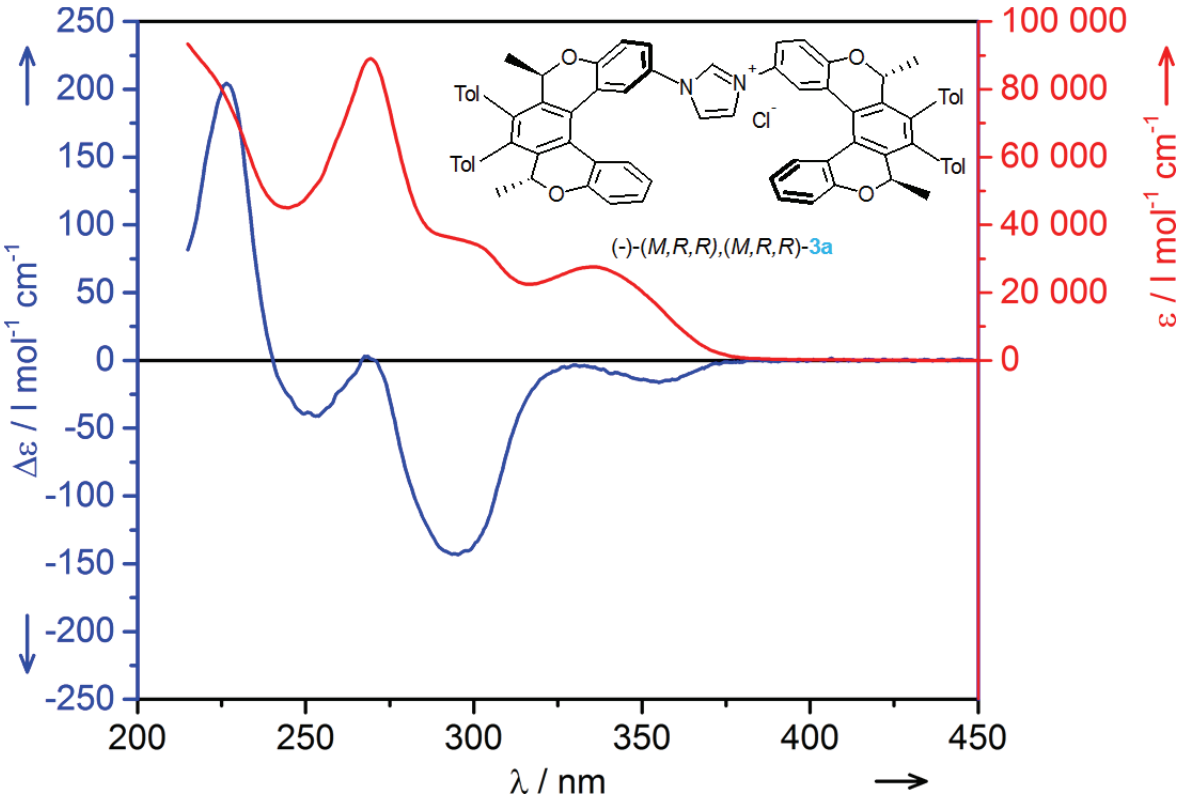
	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]	Compound Name
1	4.790	1125.959	160.856	14.11	16.2	0.11	
2	5.617	6379.459	793.017	79.95	79.7	0.12	
3	7.707	474.256	41.312	5.94	4.2	0.18	
	Total	7979.674	995.184	100.00	100.0		

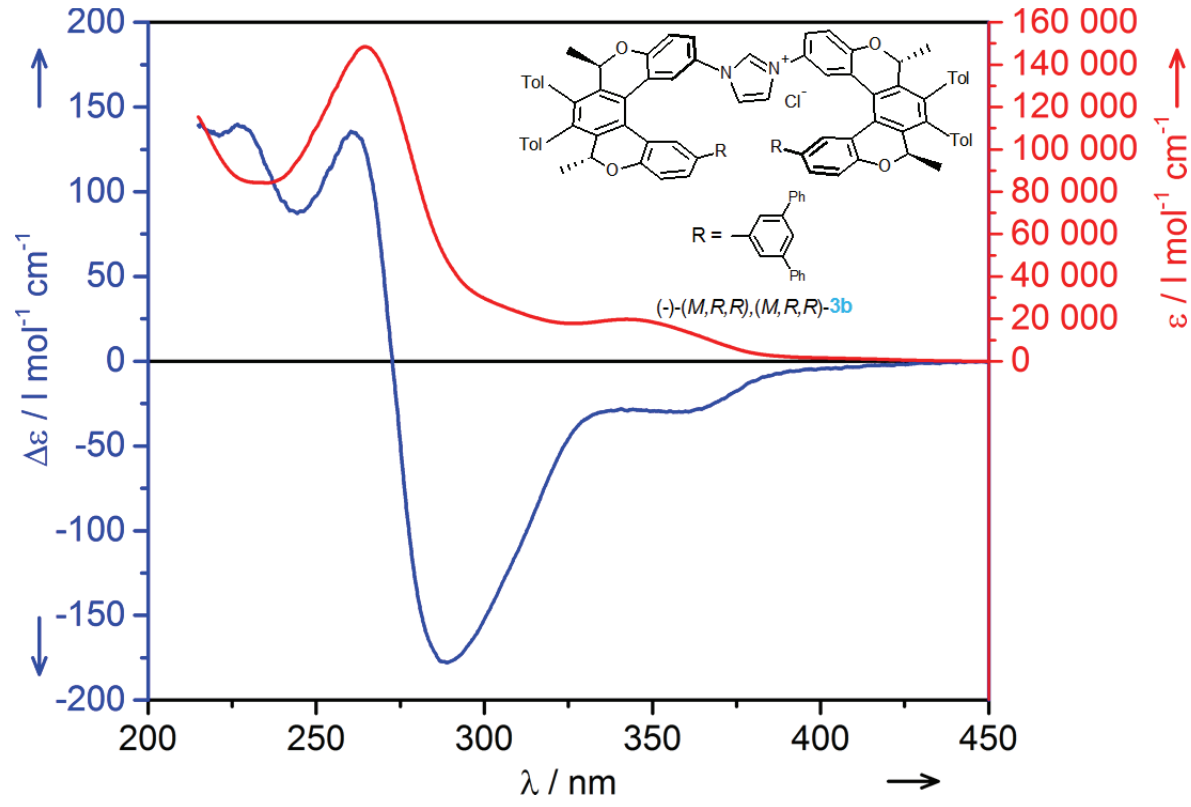
Figure S4: HPLC chromatogram (Chiralpak IA column, heptane – chloroform 7:3) of (*P*)-[7]helicene **21** (86% *ee*) after cyclisation, where (-)-(*M,R,R*),(*M,R,R*)-**3c** was used as the chiral ligand. The peak at 4.79 min corresponds to the starting material (blue: UV detector, red: downstream polarimetric detector).

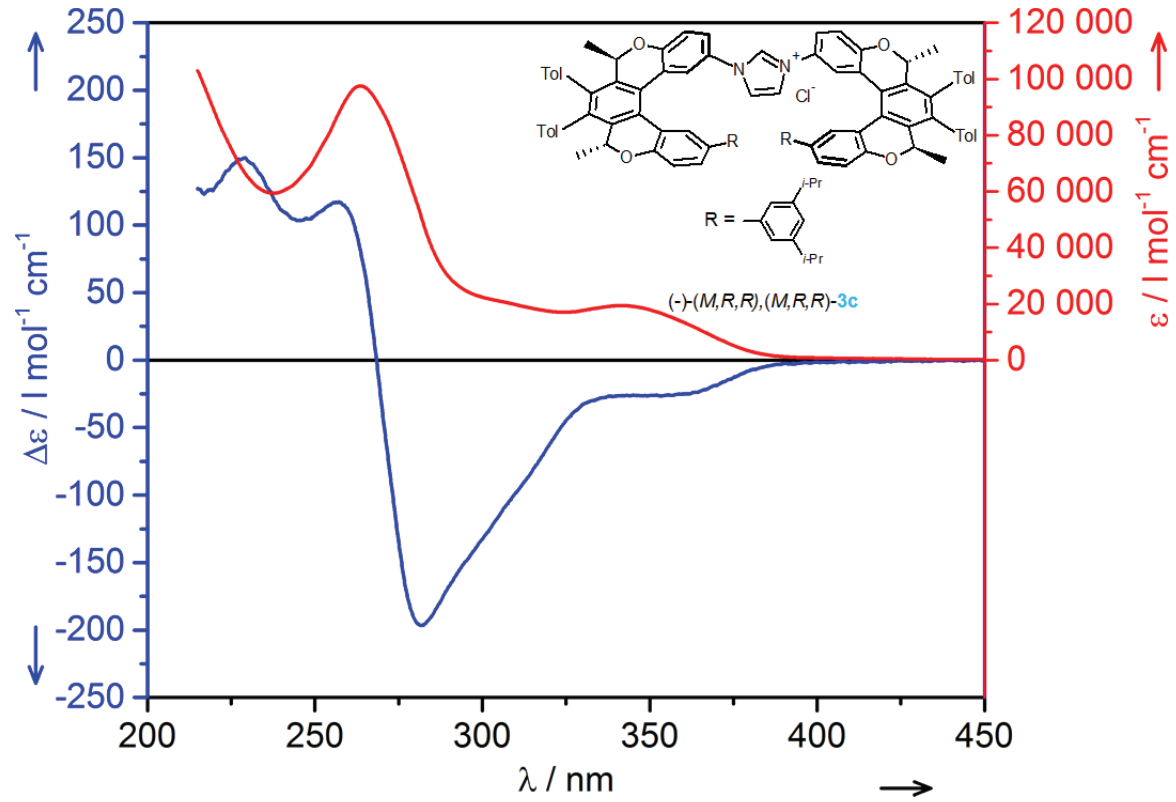
The experimental UV and CD spectra of compounds (-)-(*M*,*R*,*R*)-1, (-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-2, (-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-3a-g, (-)-(*M*,*R*,*R*)-10a-g and (-)-(*M*,*R*,*R*)-16

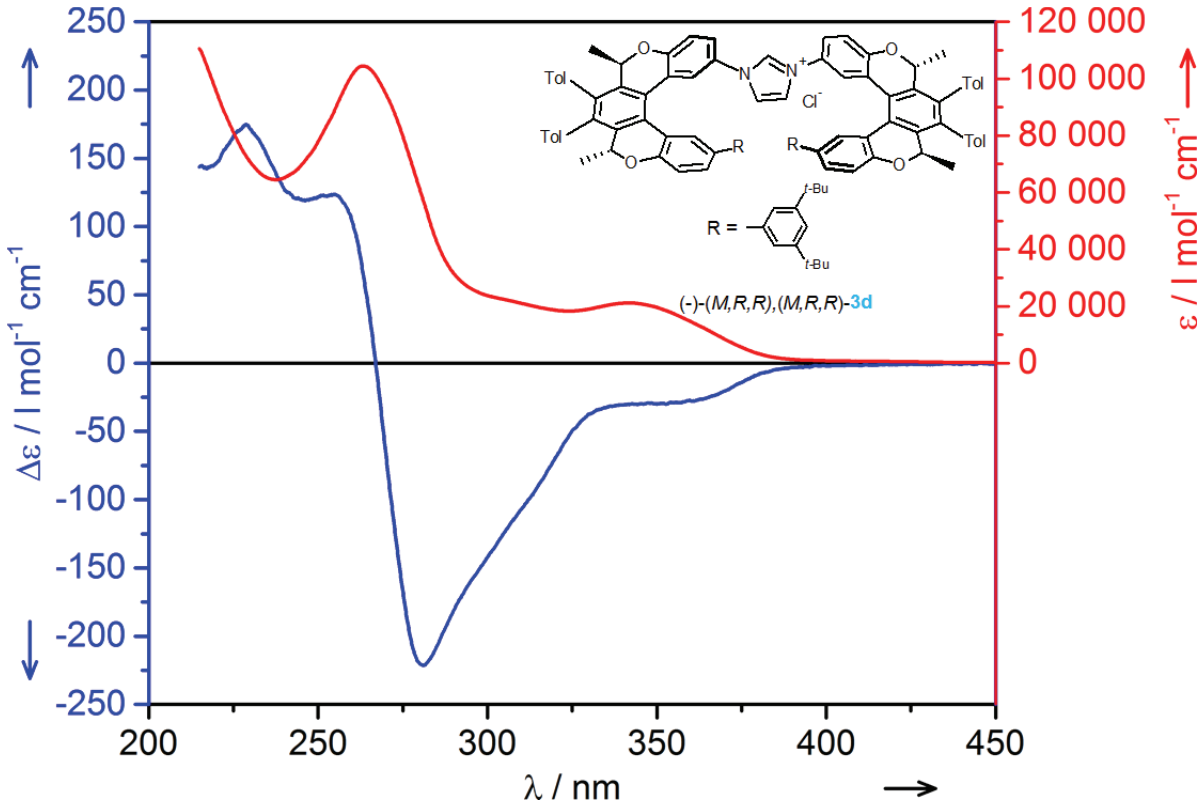


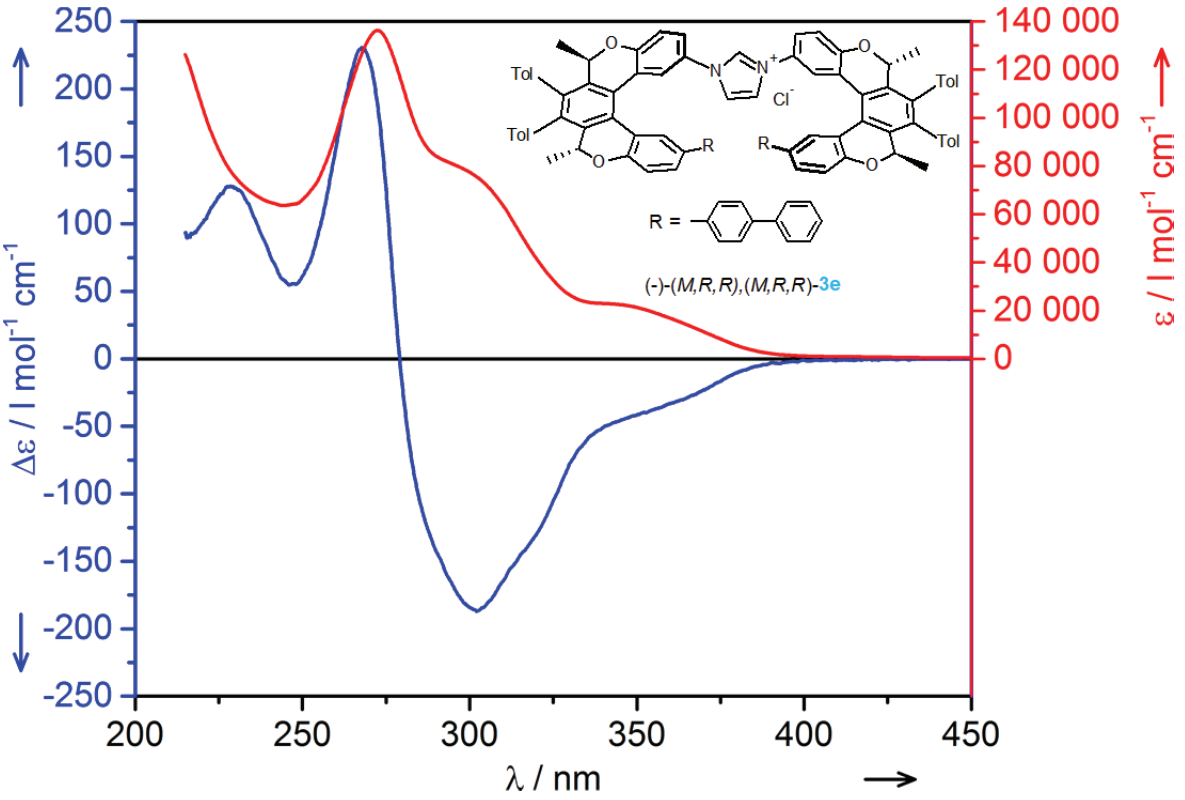


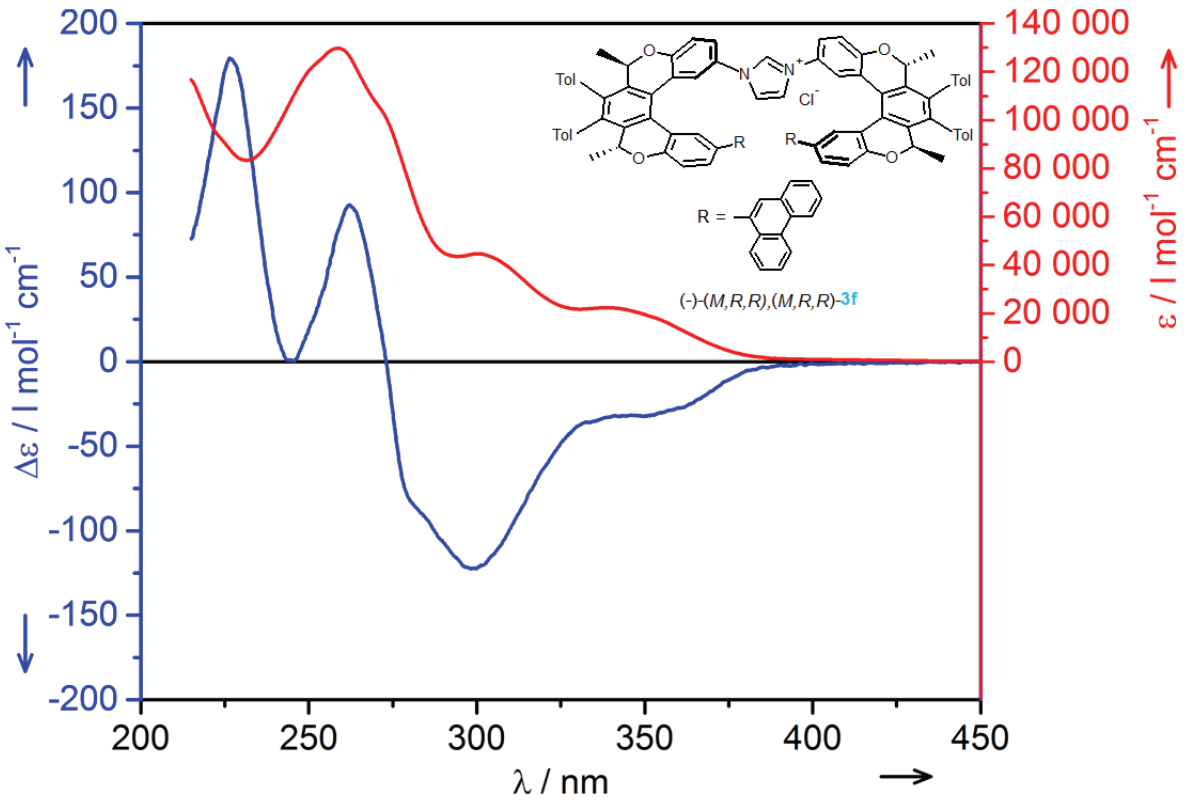

Δε / l mol-1 cm-1
ε / l mol-1 cm-1
λ / nm
Tol
Cl-
(-)-(M,R,R),(M,R,R)-3a

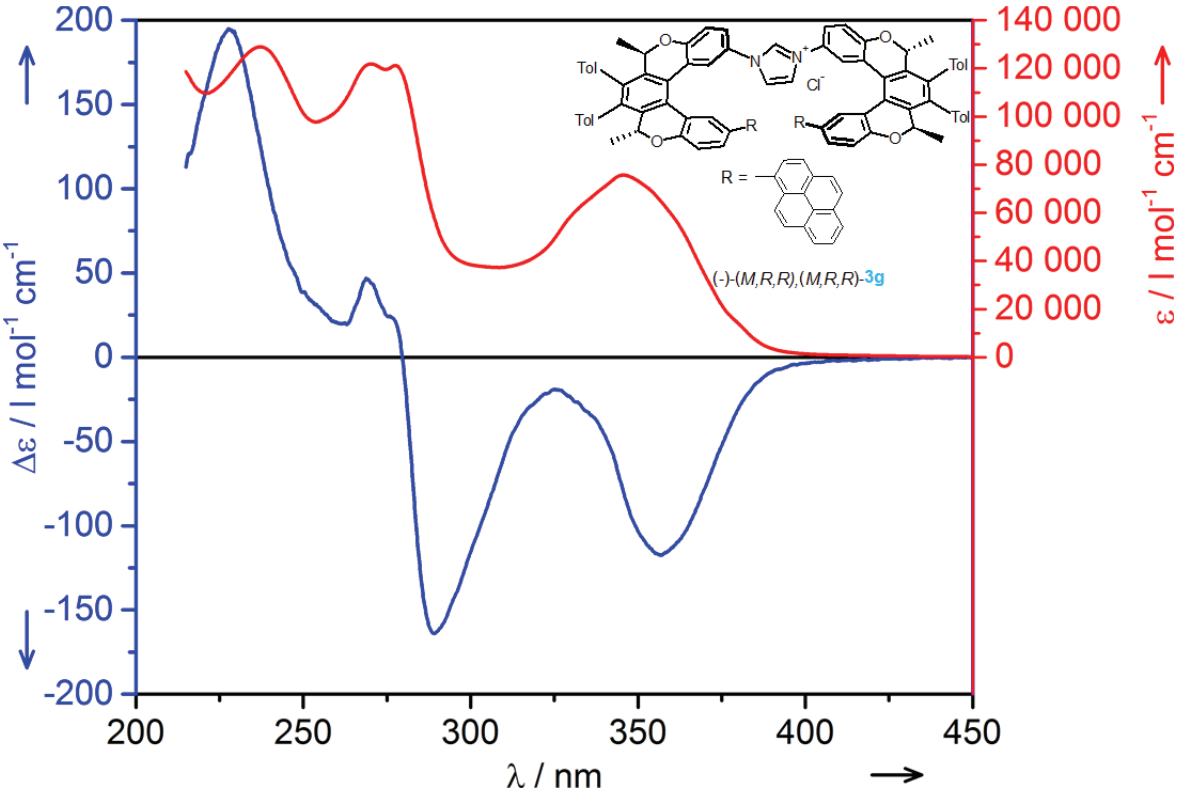

Δε / l mol-1 cm-1
ε / l mol-1 cm-1
λ / nm
Tol
R =
Ph
(-)-(M,R,R),(M,R,R)-3b

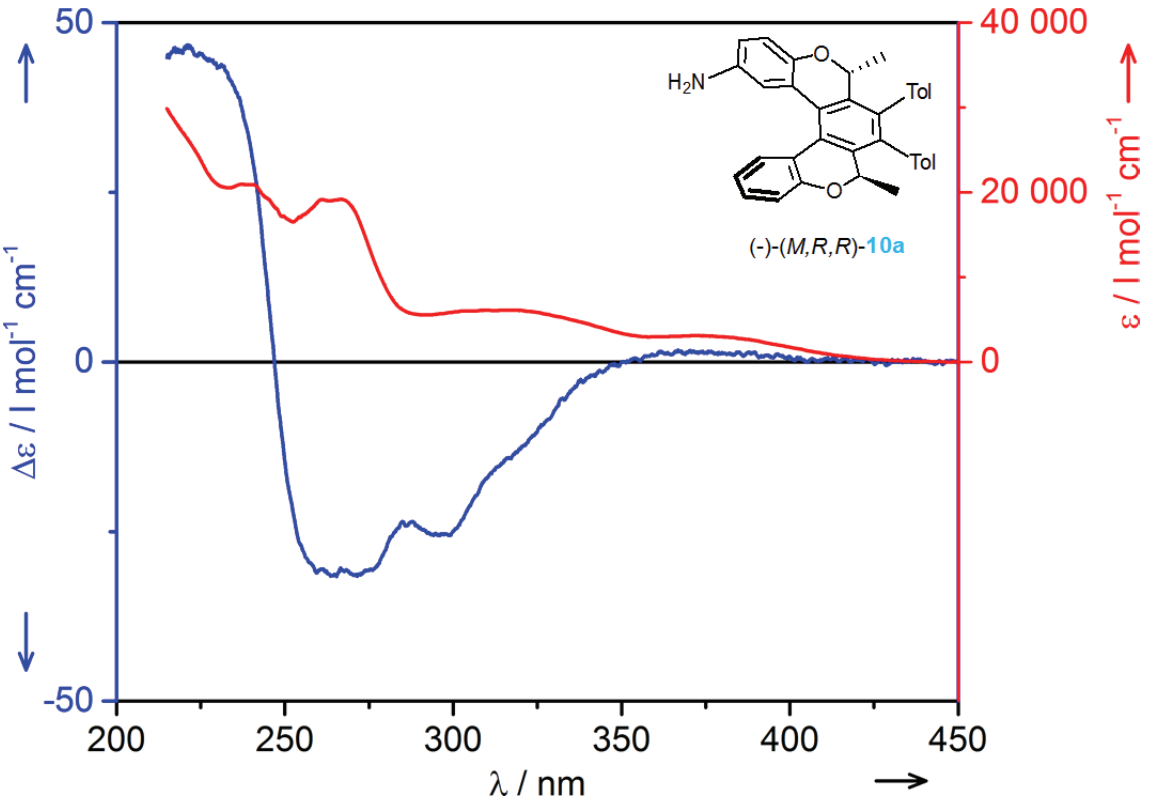

Δε / l mol-1 cm-1
ε / l mol-1 cm-1
λ / nm
(-)-(M,R,R),(M,R,R)-3c
Tol
R =
i-Pr
Cl-

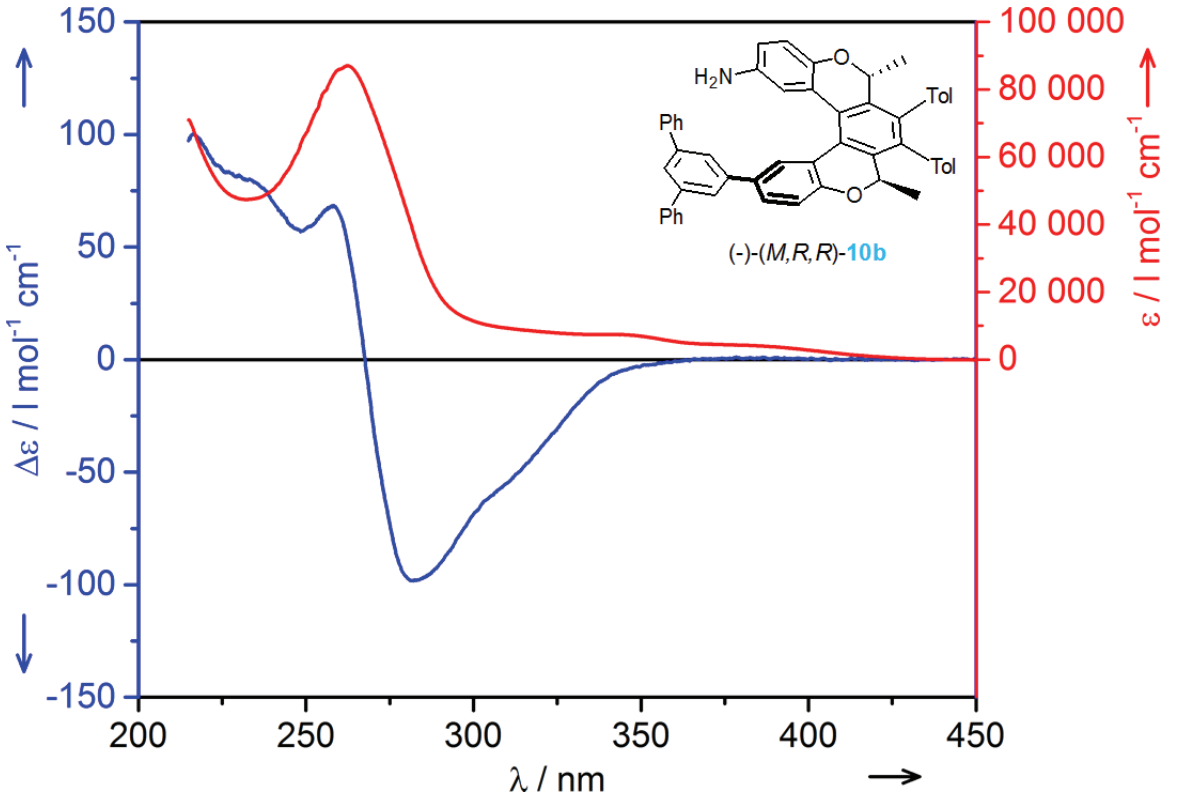

Δε / l mol-1 cm-1
ε / l mol-1 cm-1
λ / nm
(-)-(M,R,R),(M,R,R)-3d
Tol
R =
t-Bu
Cl-

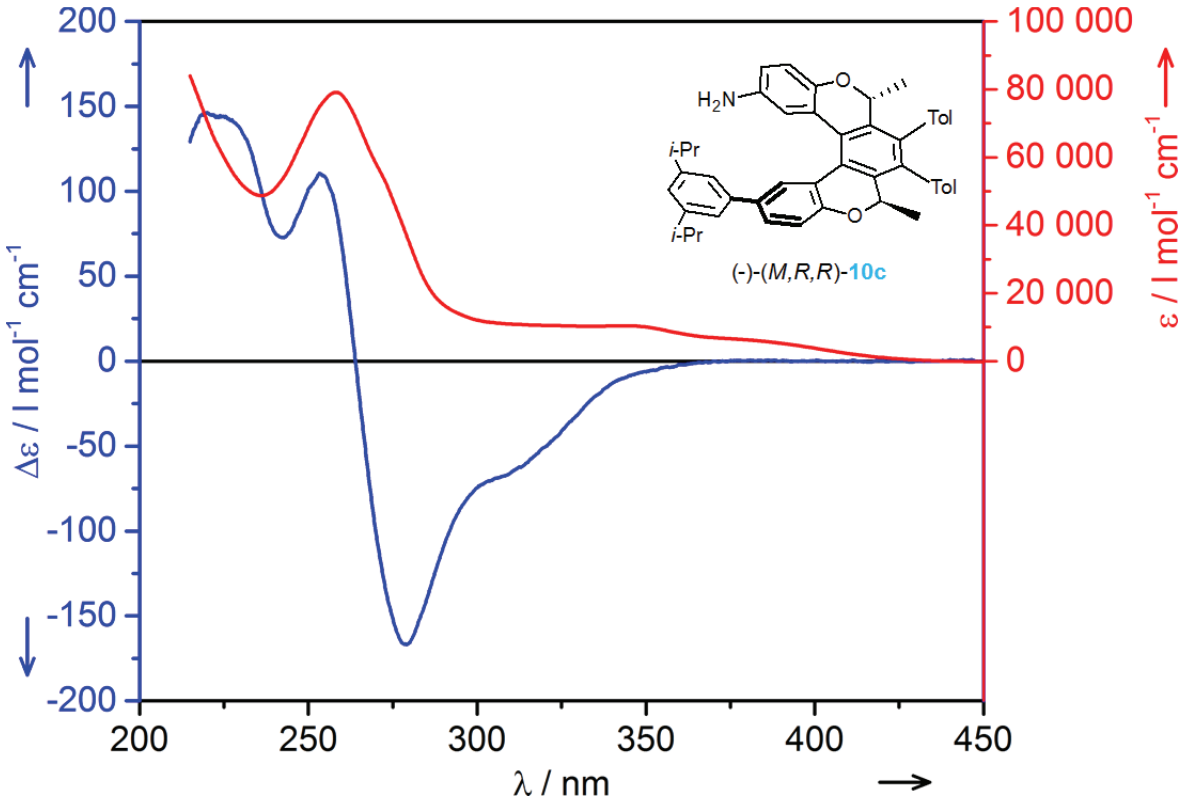

Δε / l mol-1 cm-1
ε / l mol-1 cm-1
λ / nm
Tol
Tol
R
Cl-
R =
(-)-(M,R,R),(M,R,R)-3e

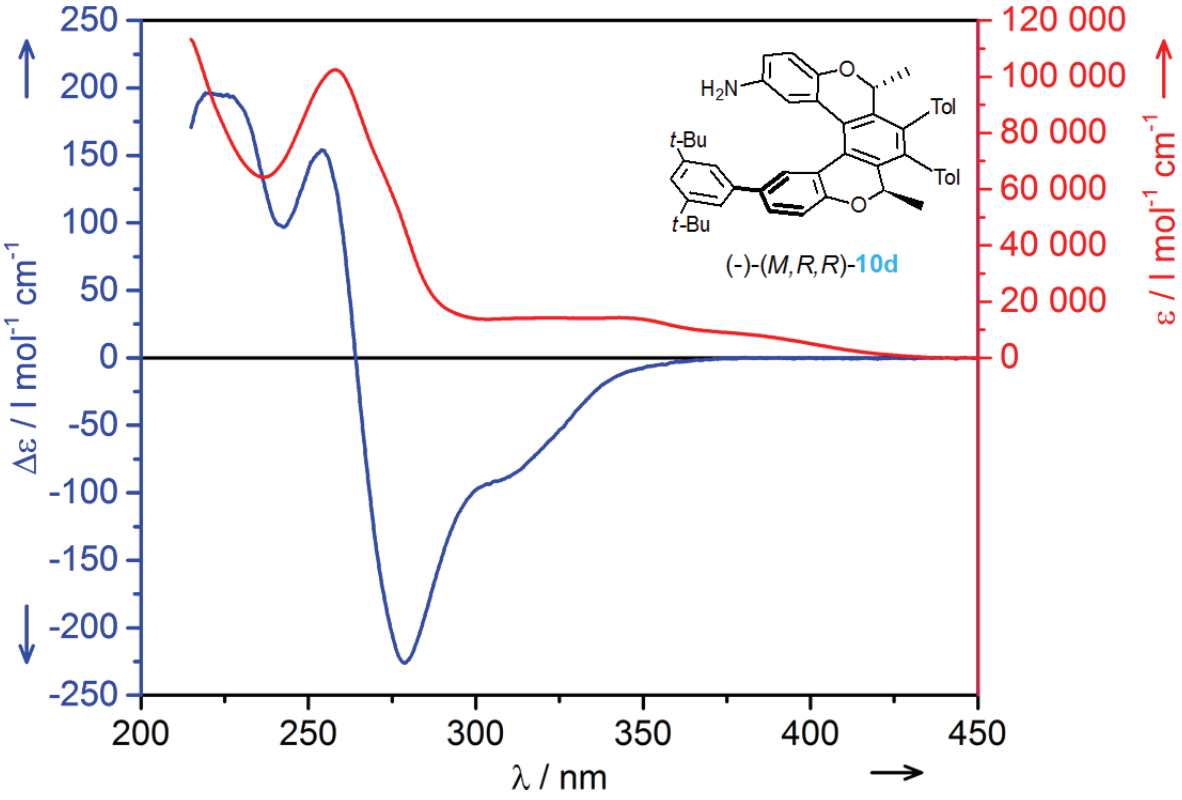

Δε / l mol-1 cm-1
ε / l mol-1 cm-1
λ / nm
Tol
Tol
R
Cl-
R =
(-)-(M,R,R),(M,R,R)-3f

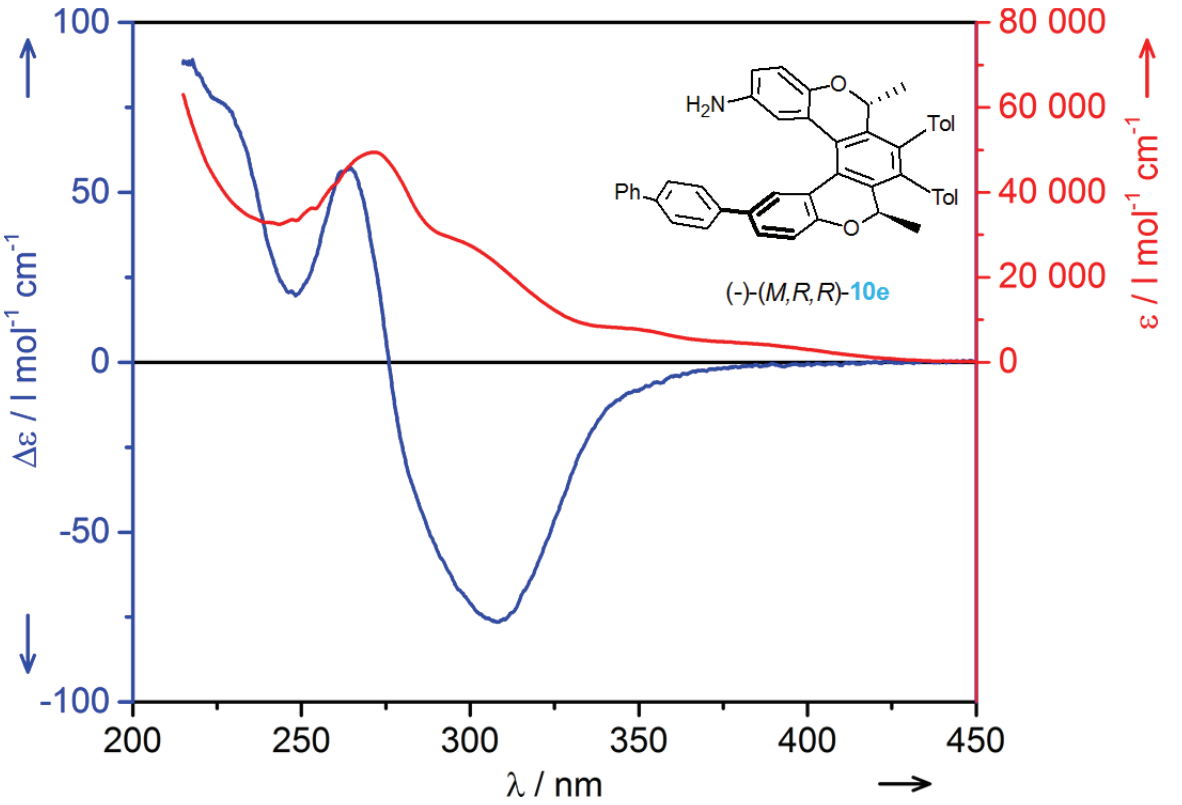

Δε / l mol-1 cm-1
ε / l mol-1 cm-1
λ / nm
(-)-(M,R,R),(M,R,R)-3g
R =

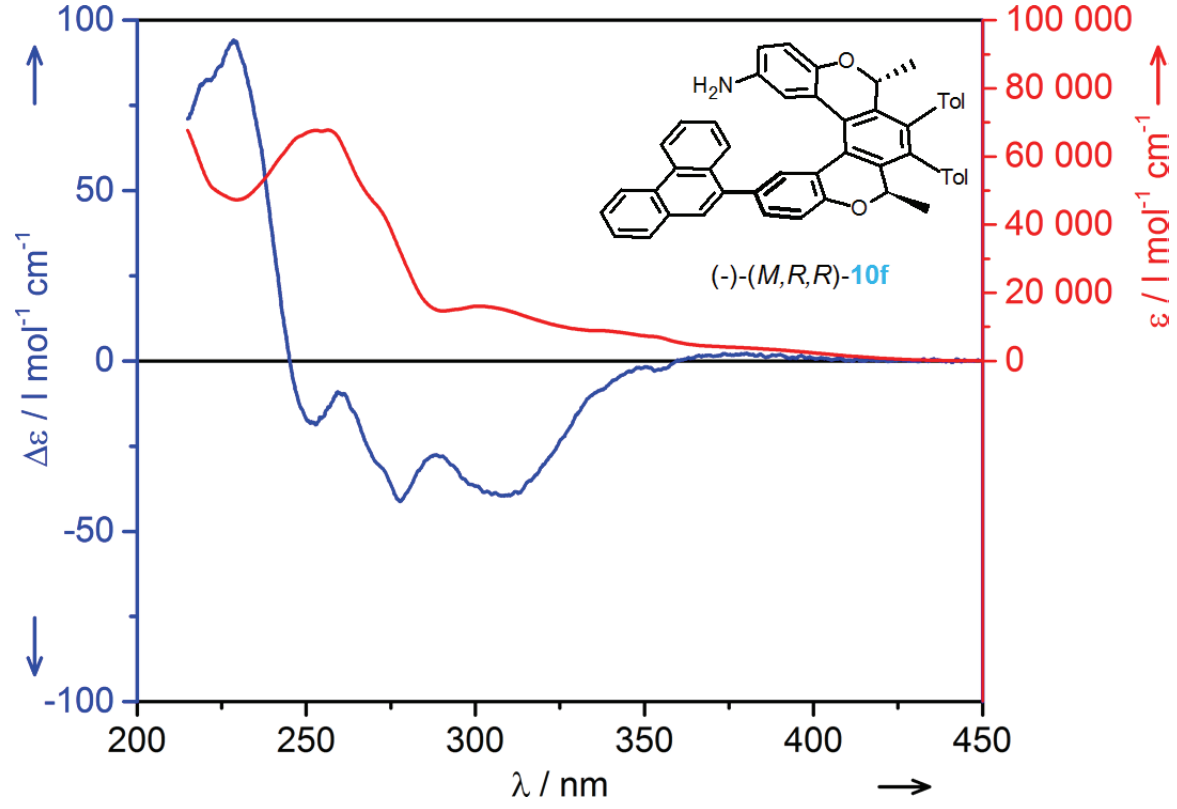

Δε / l mol-1 cm-1
ε / l mol-1 cm-1
λ / nm
(-)-(M,R,R)-10a

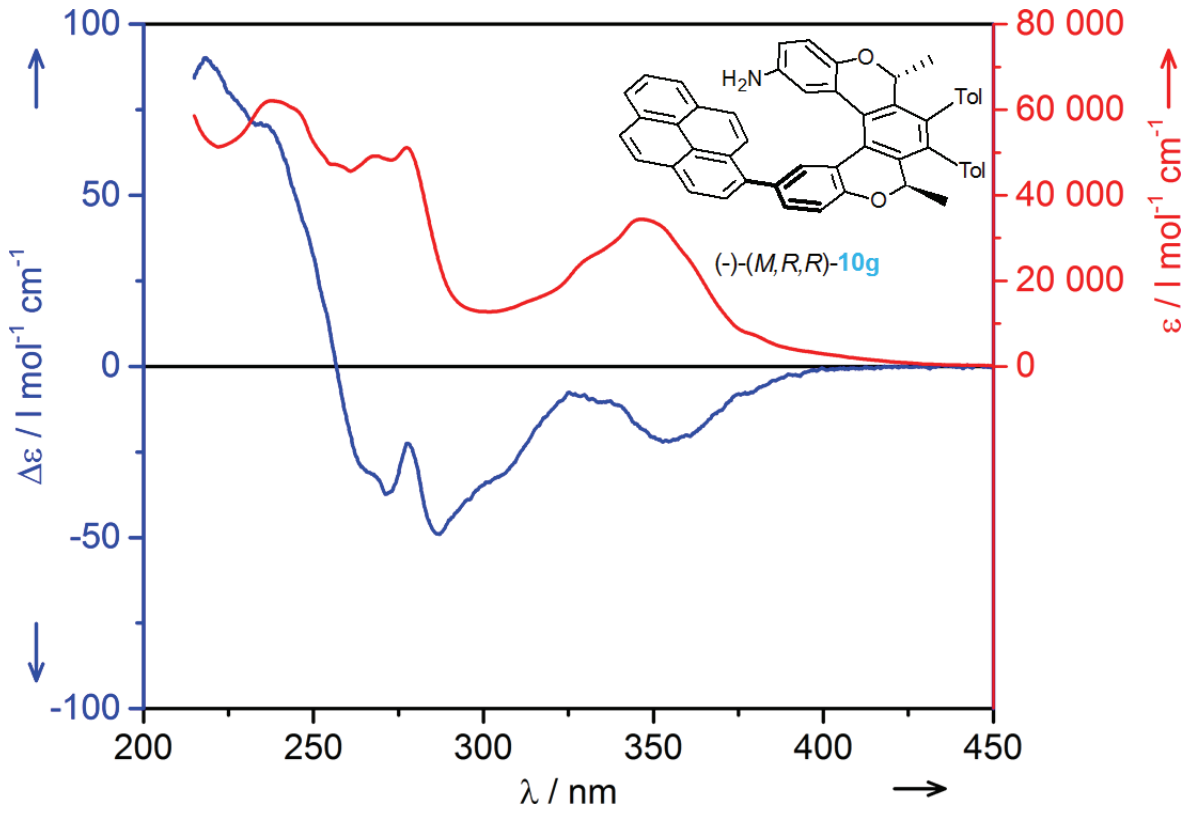

150
100
50
0
-50
-100
-150
Δε / l mol-1 cm-1
100 000
80 000
60 000
40 000
20 000
0
ε / l mol-1 cm-1
200
250
300
350
400
450
λ / nm
H2N
O
Tol
Tol
Ph
Ph
O
(-)-(M,R,R)-10b

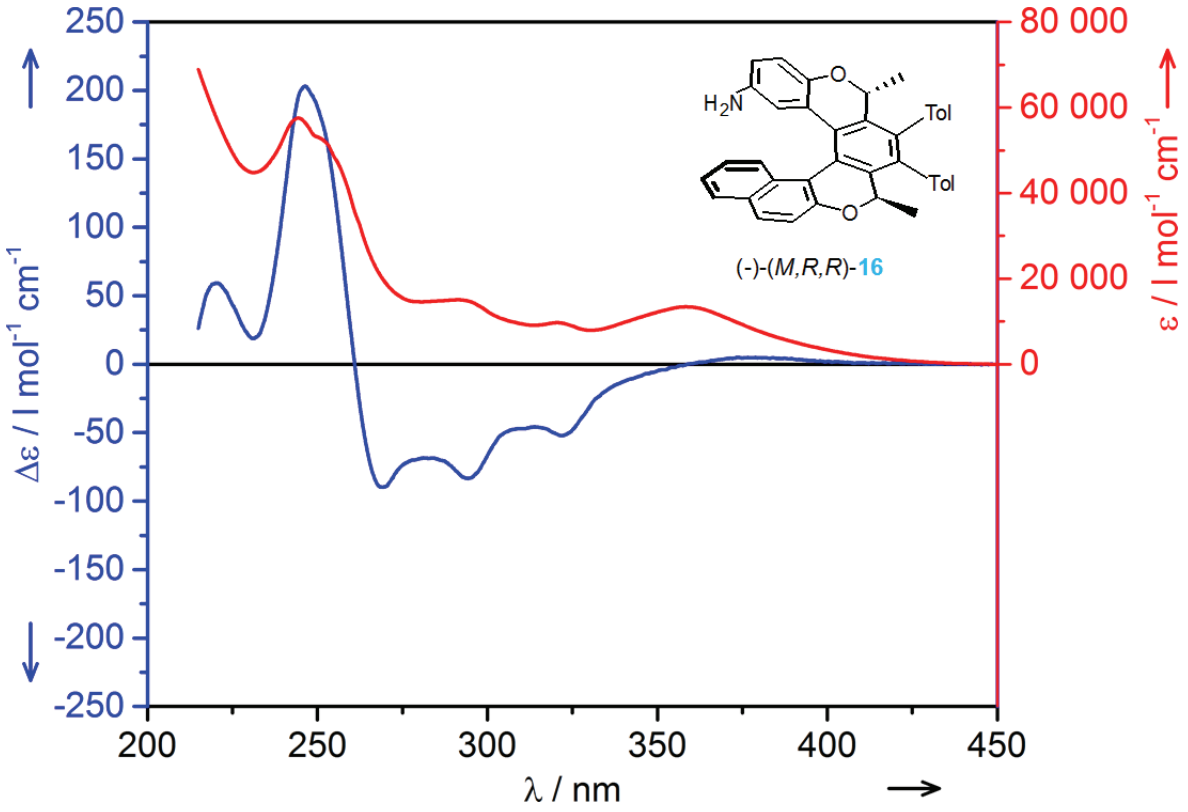

200
150
100
50
0
-50
-100
-150
-200
Δε / l mol-1 cm-1
100 000
80 000
60 000
40 000
20 000
0
ε / l mol-1 cm-1
200
250
300
350
400
450
λ / nm
H2N
O
Tol
Tol
i-Pr
i-Pr
O
(-)-(M,R,R)-10c


250
200
150
100
50
0
-50
-100
-150
-200
-250
Δε / l mol-1 cm-1
120 000
100 000
80 000
60 000
40 000
20 000
0
ε / l mol-1 cm-1
200
250
300
350
400
450
λ / nm
H2N
O
Tol
t-Bu
Tol
t-Bu
O
(-)-(M,R,R)-10d

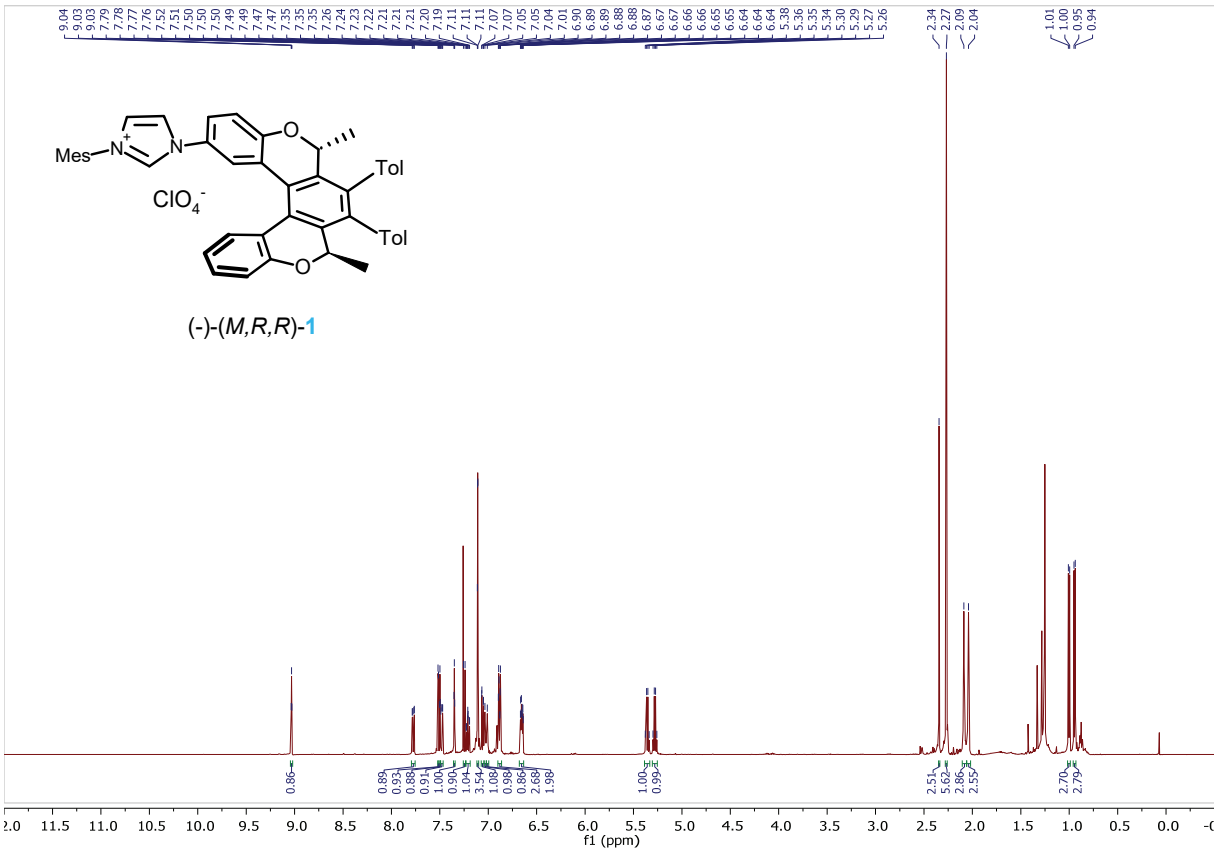

100
50
0
-50
-100
Δε / l mol-1 cm-1
80 000
60 000
40 000
20 000
0
ε / l mol-1 cm-1
200
250
300
350
400
450
λ / nm
H2N
O
Tol
Ph
Tol
O
(-)-(M,R,R)-10e


100
50
0
-50
-100
Δε / l mol-1 cm-1
100 000
80 000
60 000
40 000
20 000
0
ε / l mol-1 cm-1
200
250
300
350
400
450
λ / nm
H2N
O
Tol
Tol
O
(-)-(M,R,R)-10f

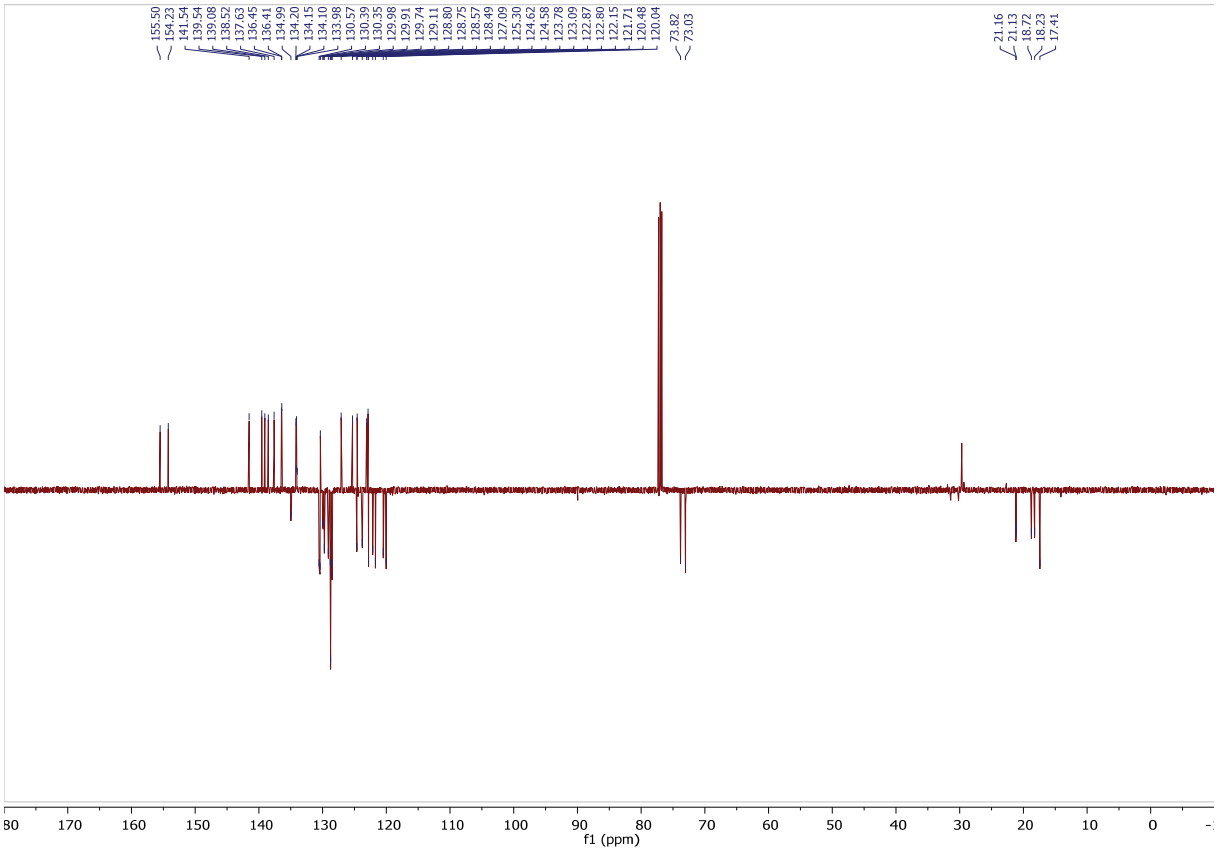

100
50
0
-50
-100
Δε / l mol-1 cm-1
80 000
60 000
40 000
20 000
0
ε / l mol-1 cm-1
200
250
300
350
400
450
λ / nm
H2N
O
Tol
Tol
O
(-)-(M,R,R)-10g

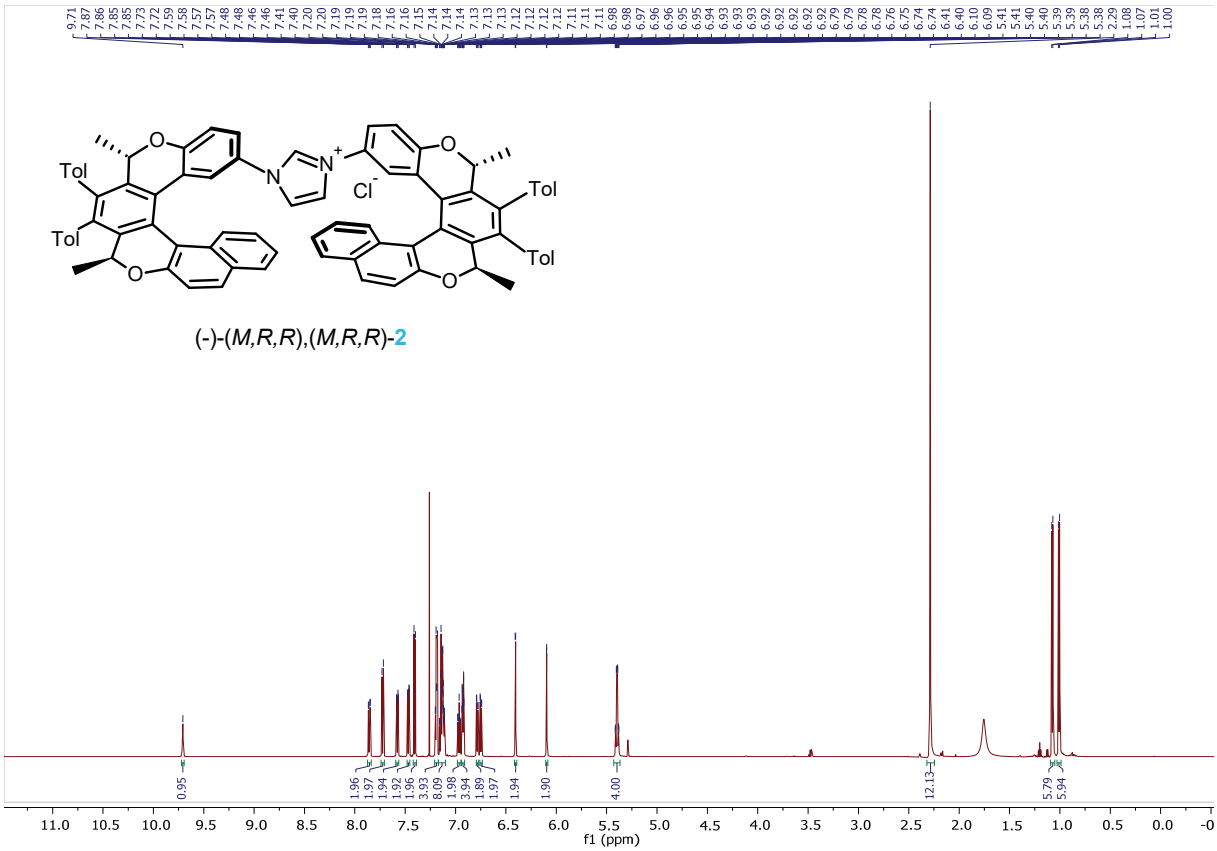

250
200
150
100
50
0
-50
-100
-150
-200
-250
Δε / l mol-1 cm-1
80 000
60 000
40 000
20 000
0
ε / l mol-1 cm-1
200
250
300
350
400
450
λ / nm
H2N
O
Tol
Tol
O
(-)-(M,R,R)-16

^{1}H and ^{13}C NMR spectra of compounds 1, 2, 3a-g, 4b, 5, 6a-b, 8a-b, 9a-b, 10a-g, 12-16, 19b-g, 25, 26 and 28

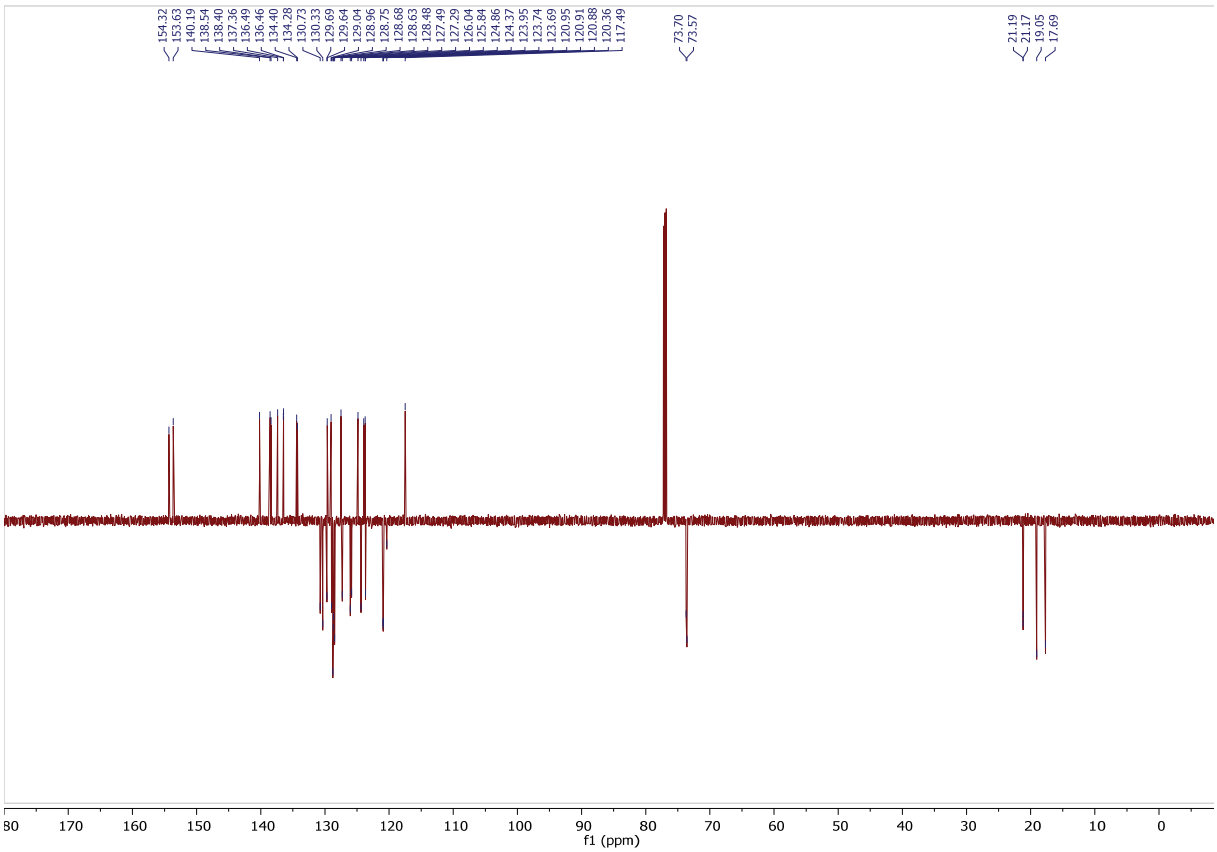


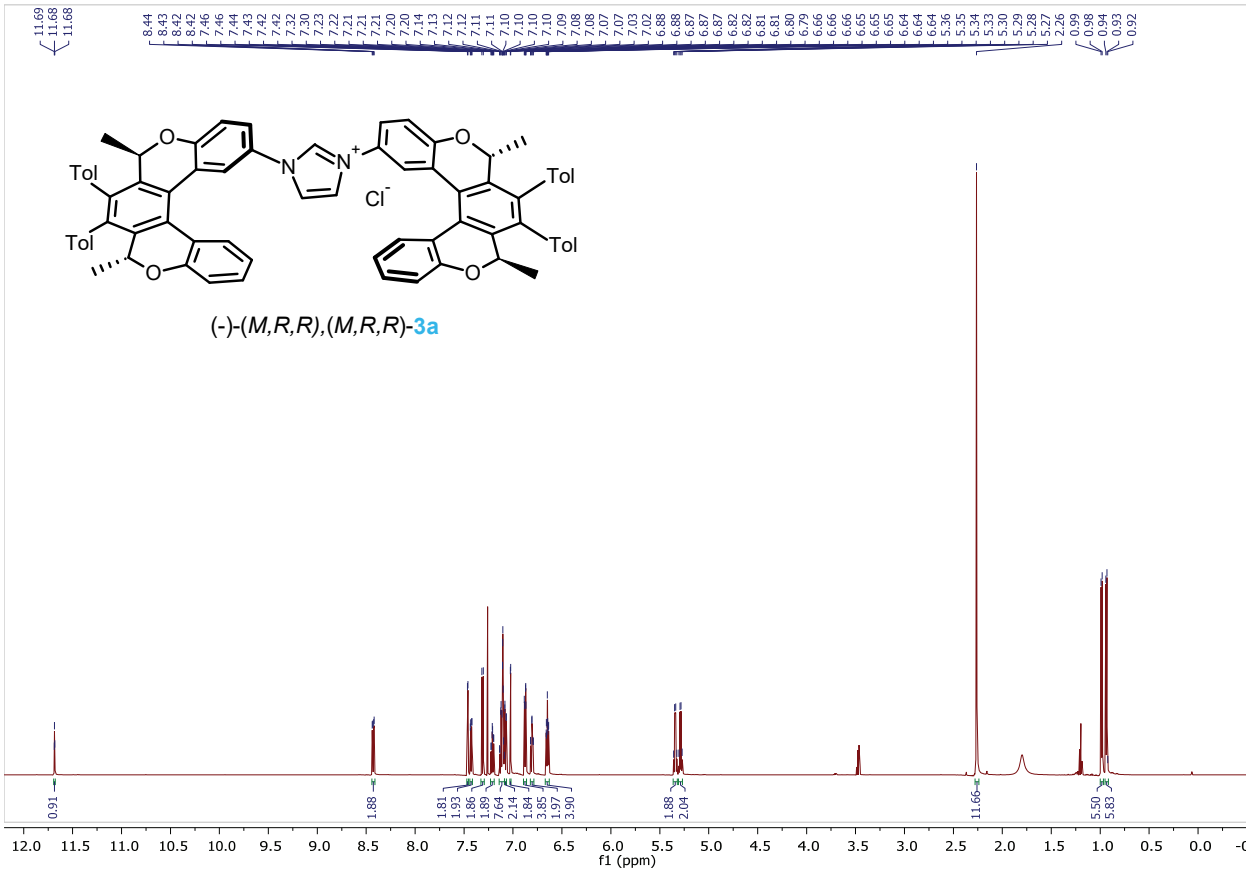
(-)-(*M,R,R*)-1



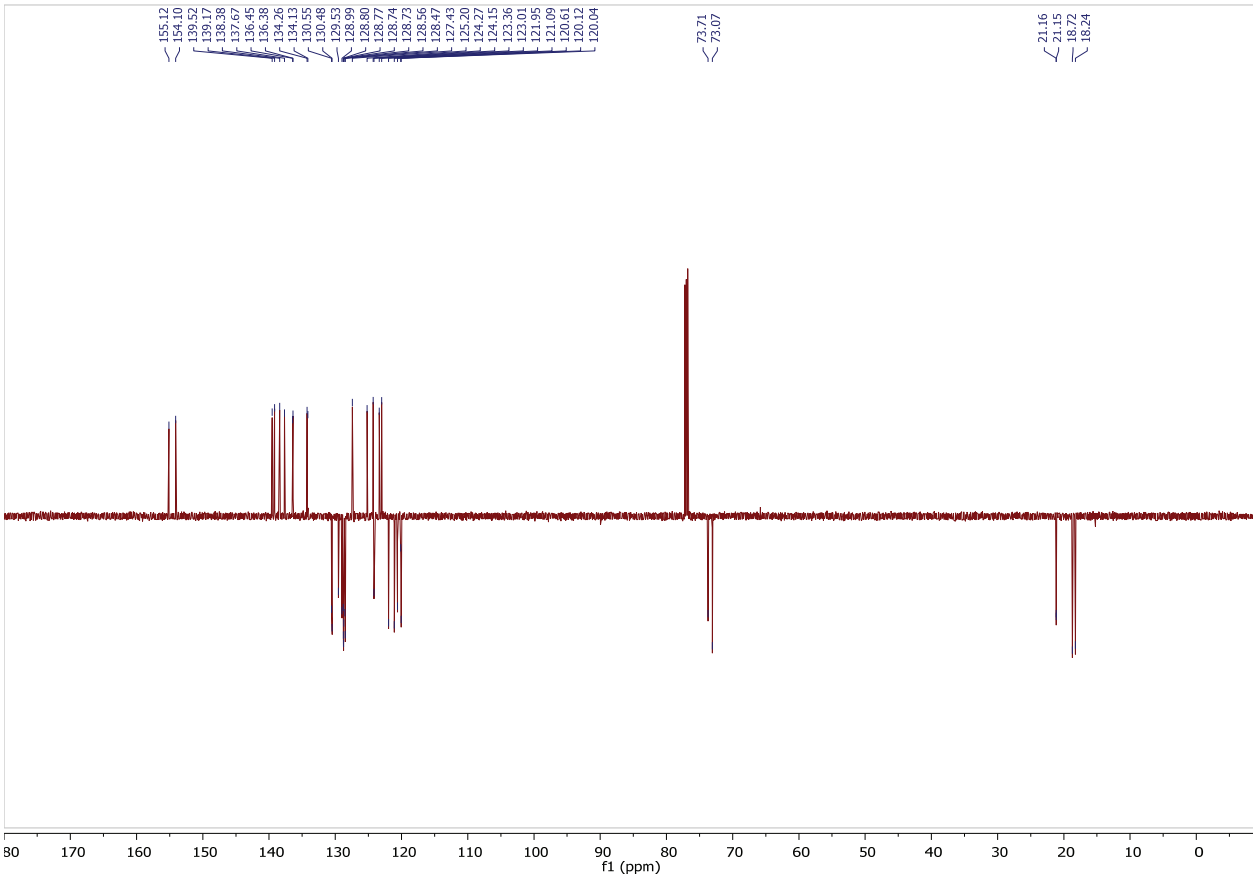


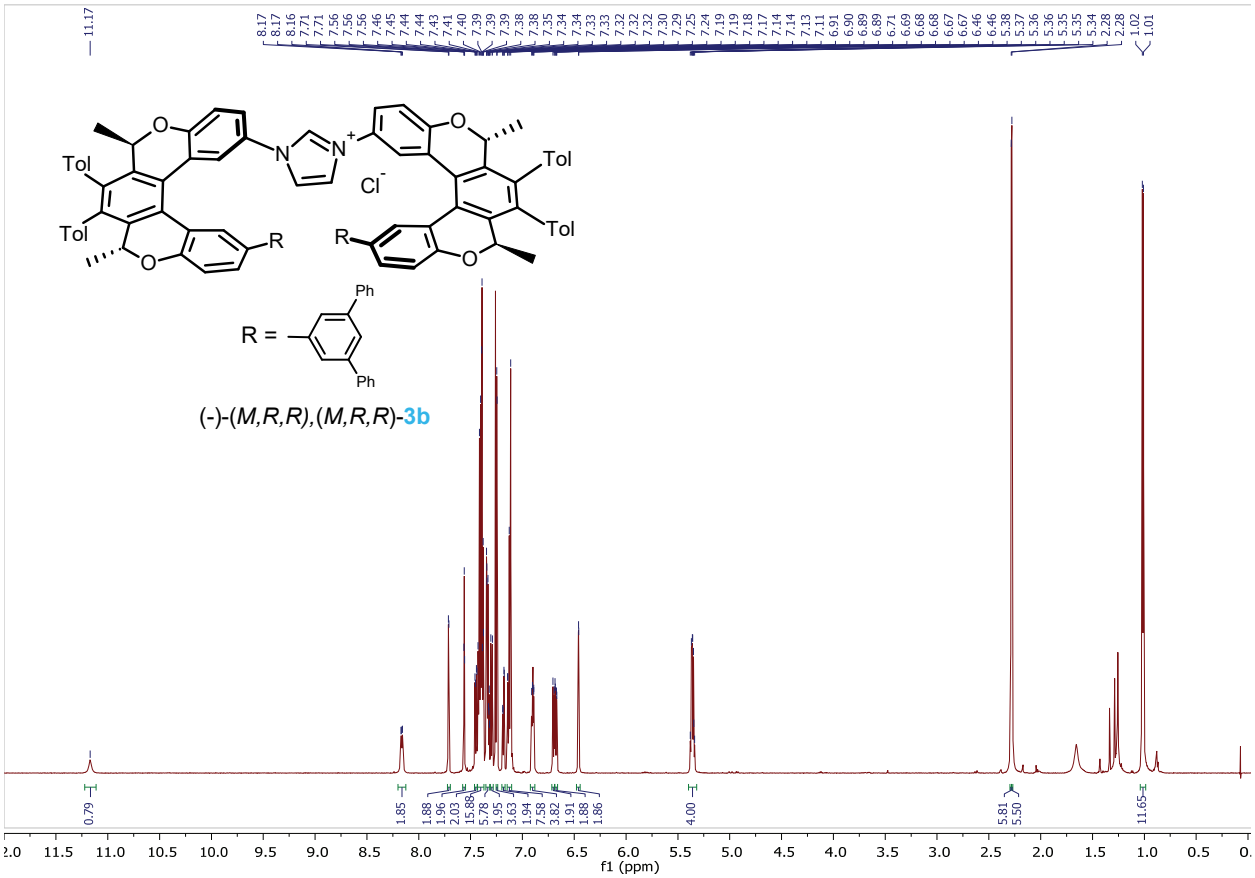
(-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**2**

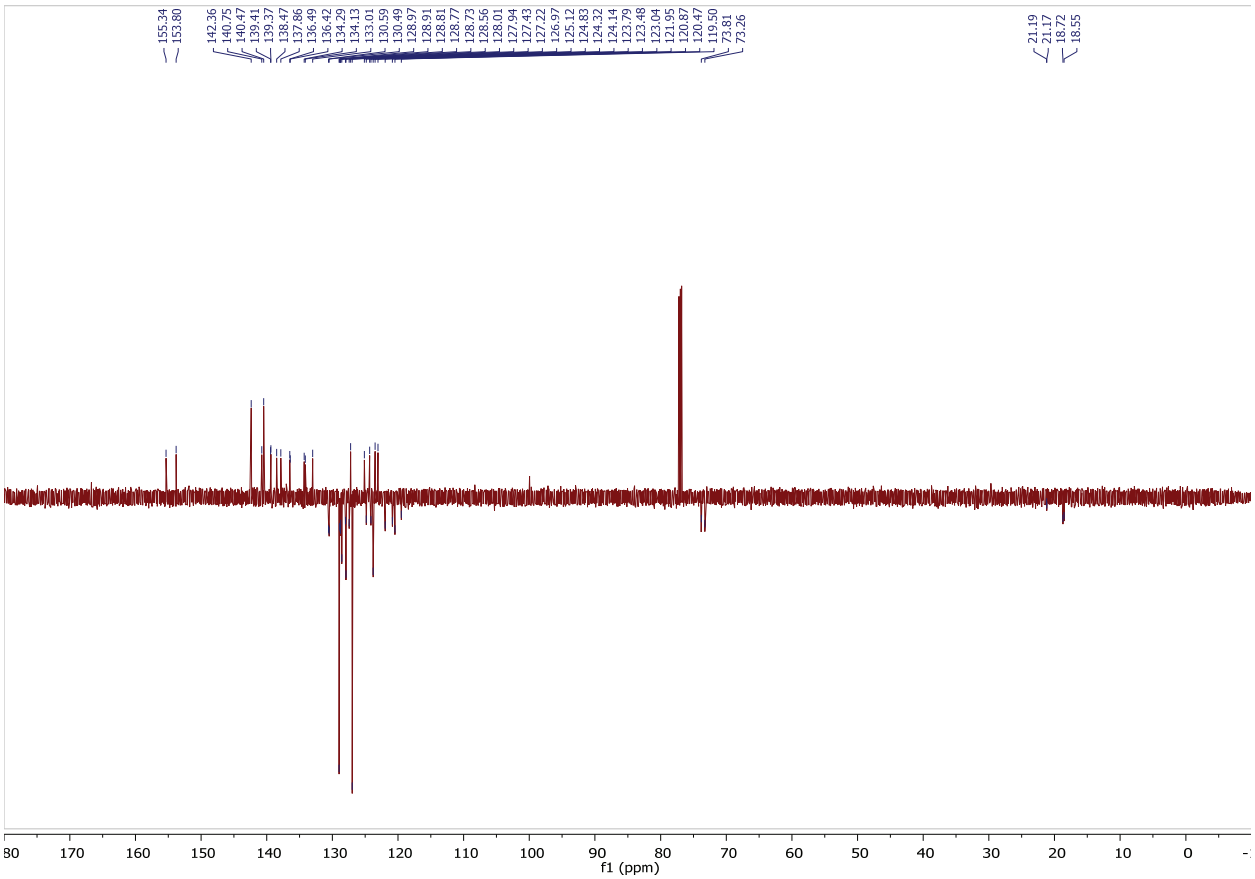


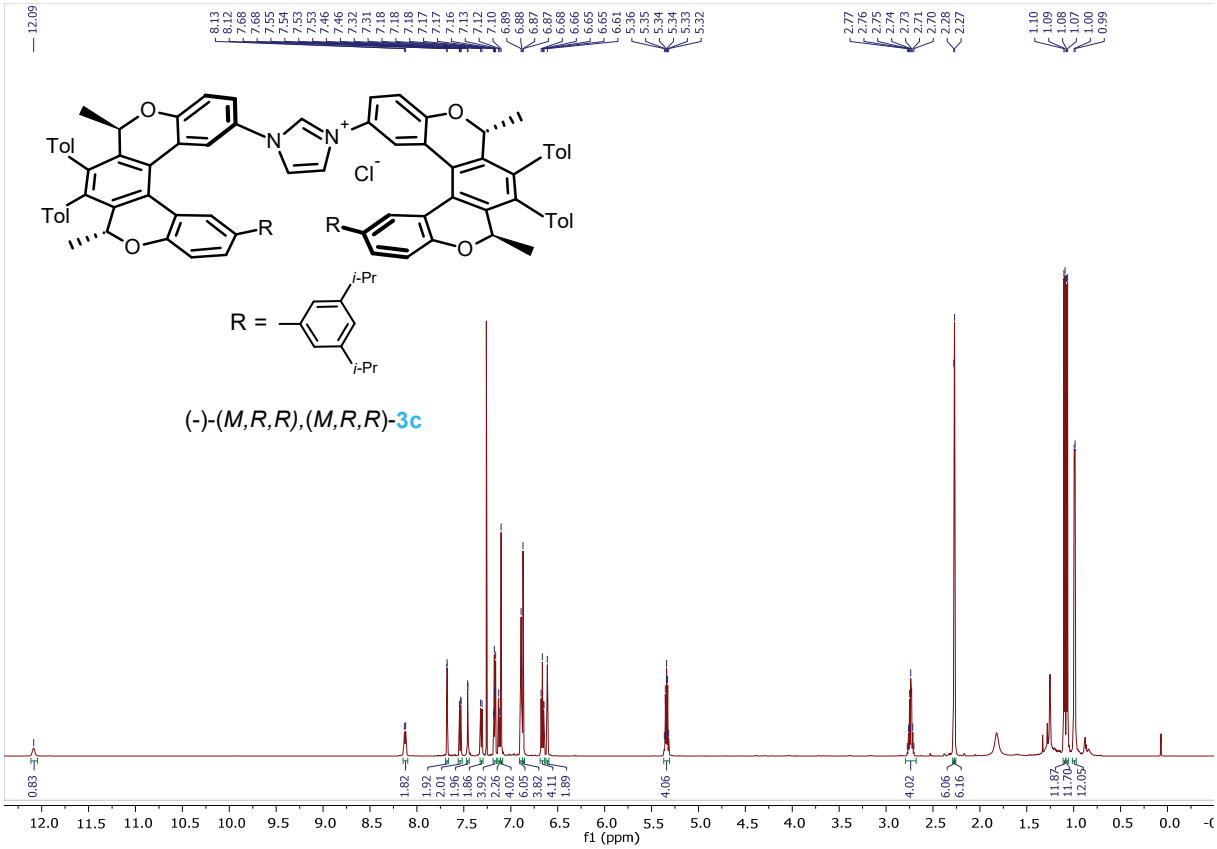


(-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3a**

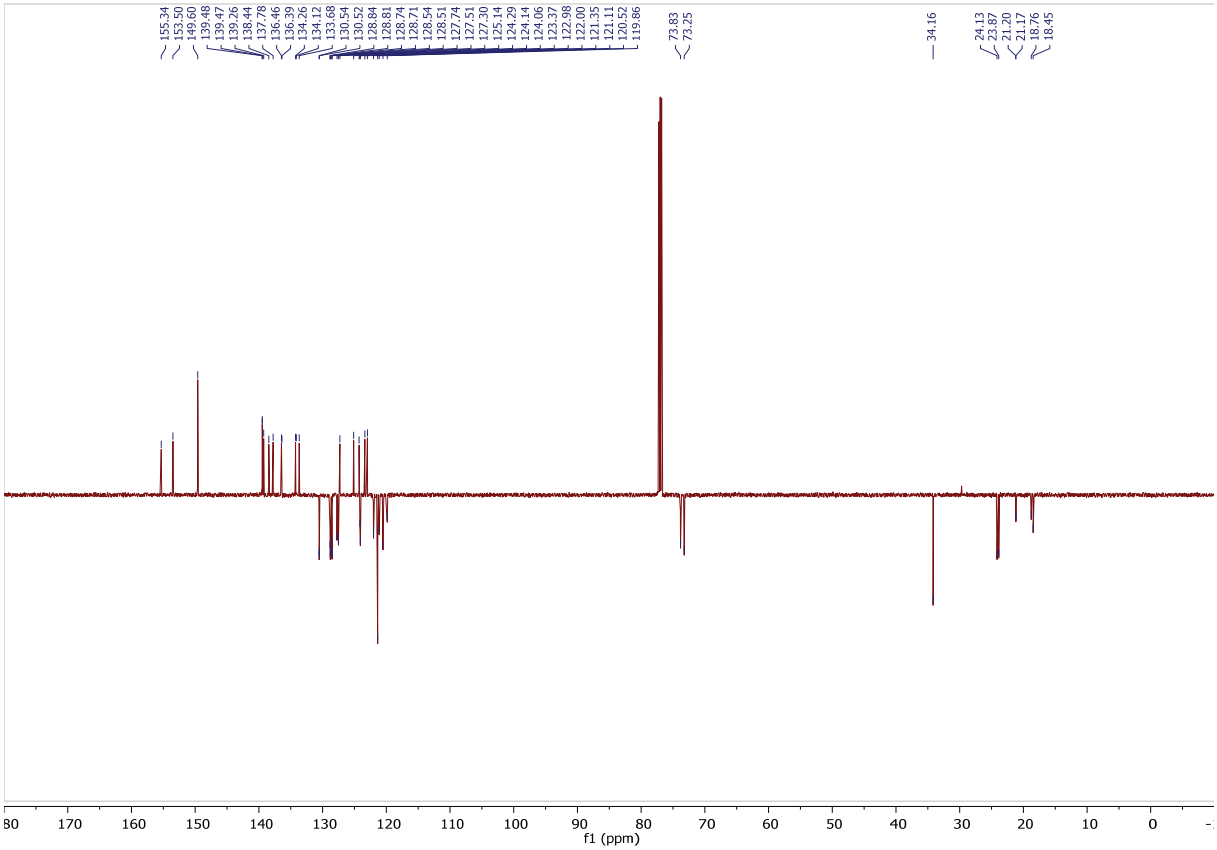


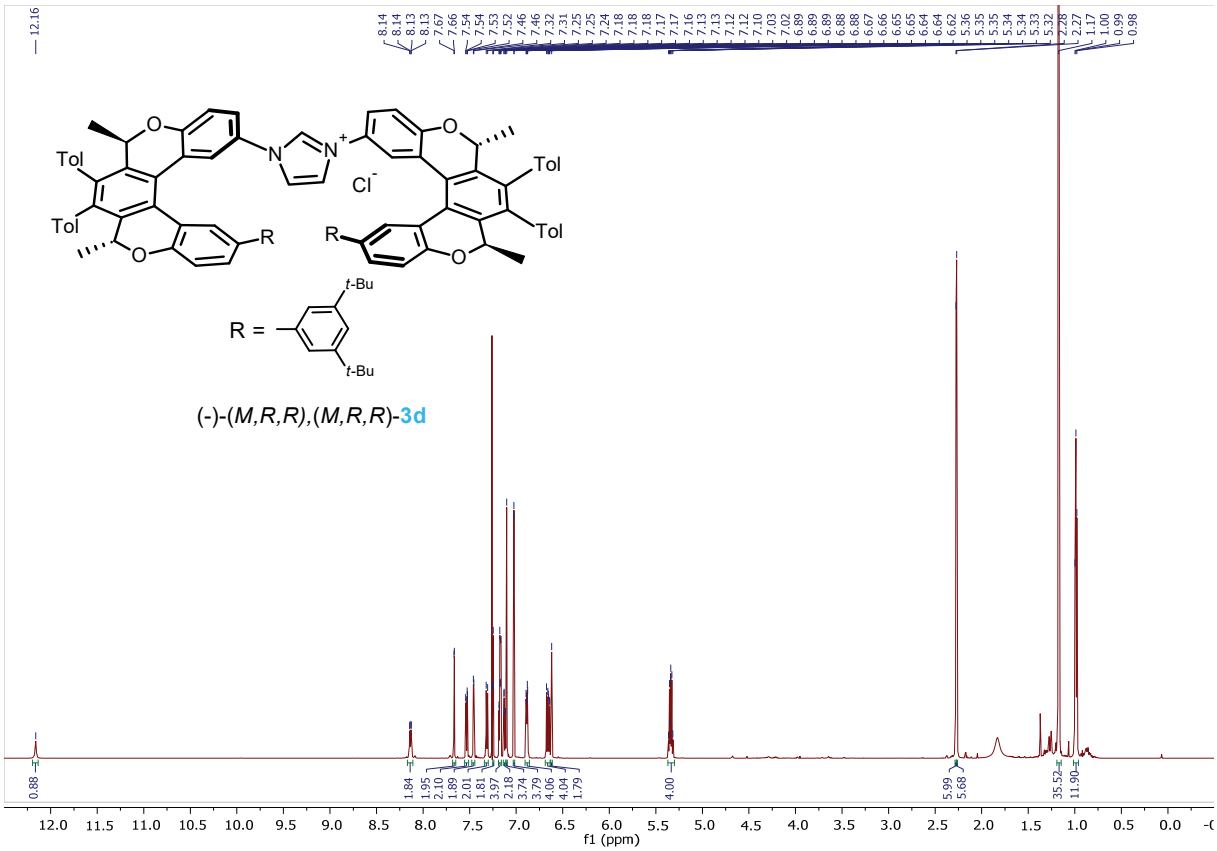

Tol
Tol
R
Cl-
Tol
Tol
R
R =
Ph
Ph
(-)-(M,R,R),(M,R,R)-3b
f1 (ppm)


f1 (ppm)

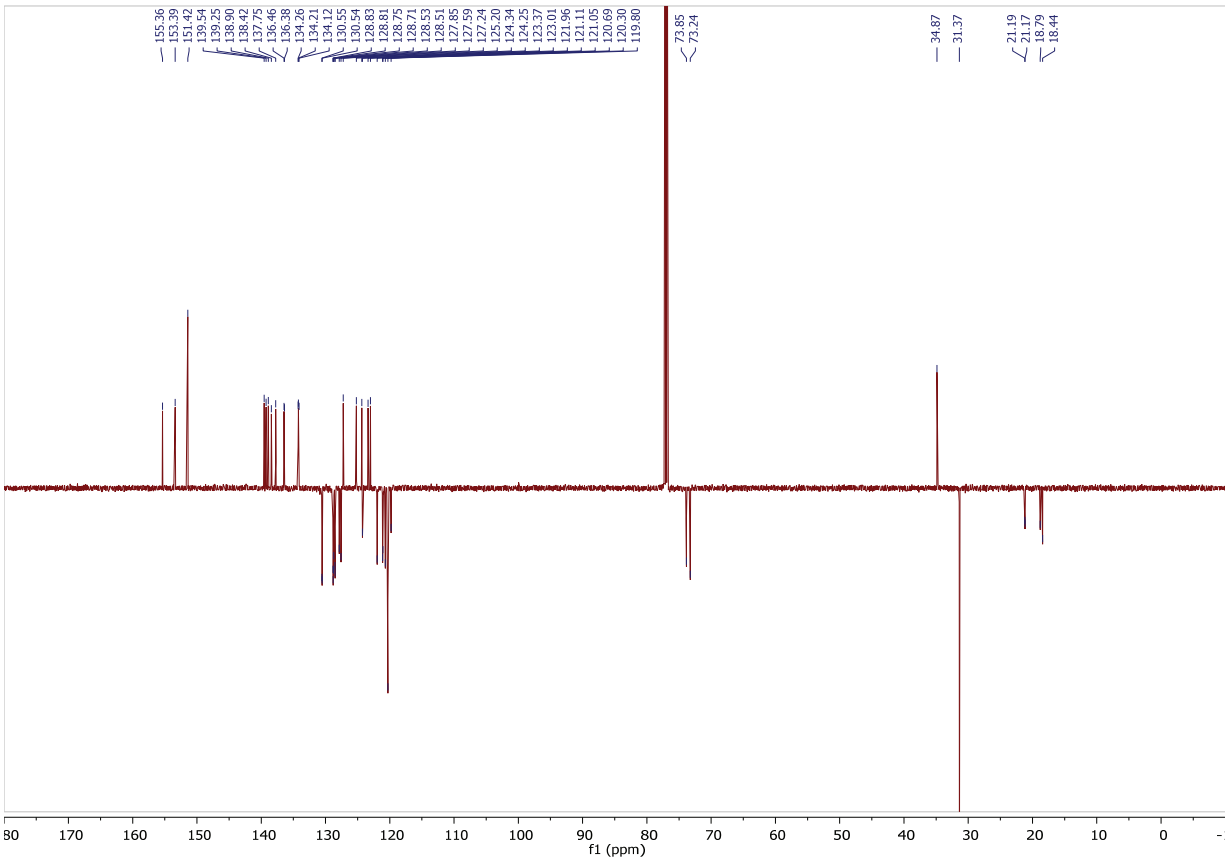


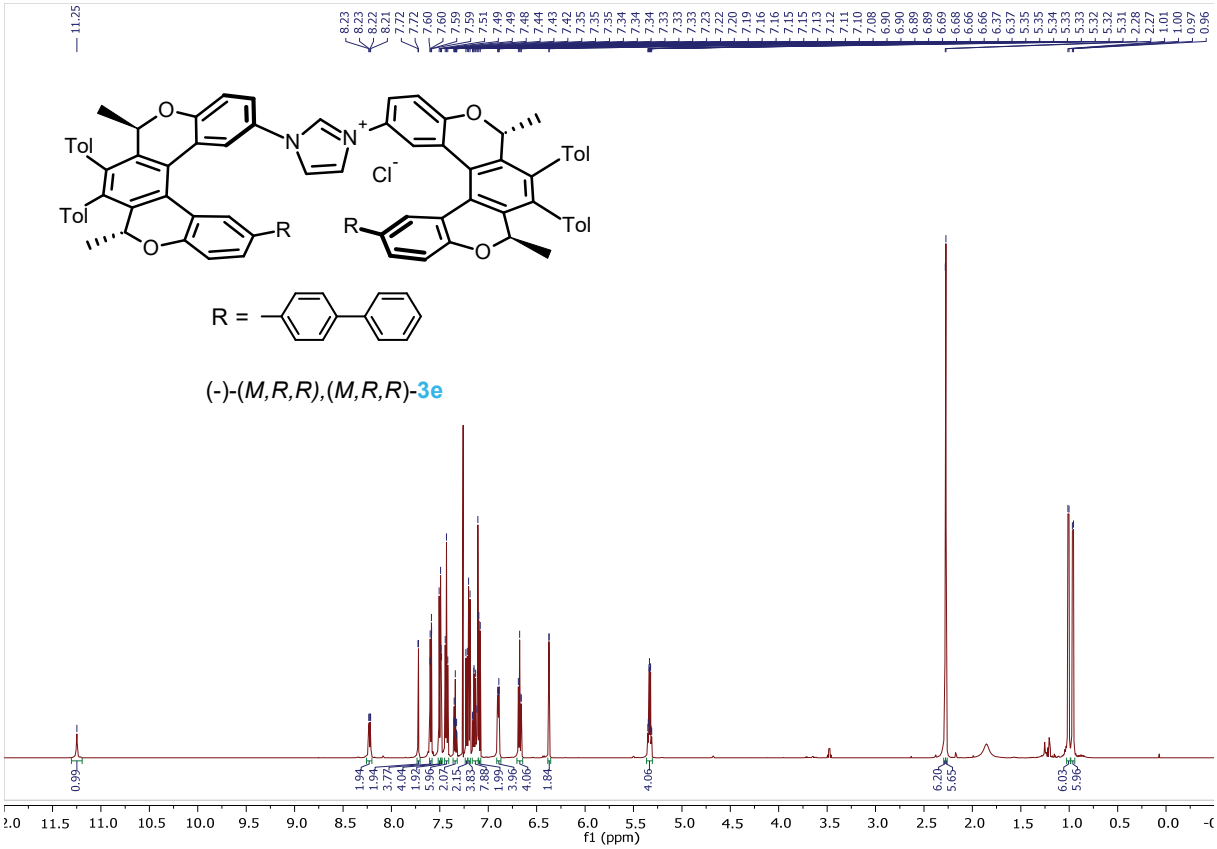
(-)-(*M,R,R),(M,R,R*)-**3c**



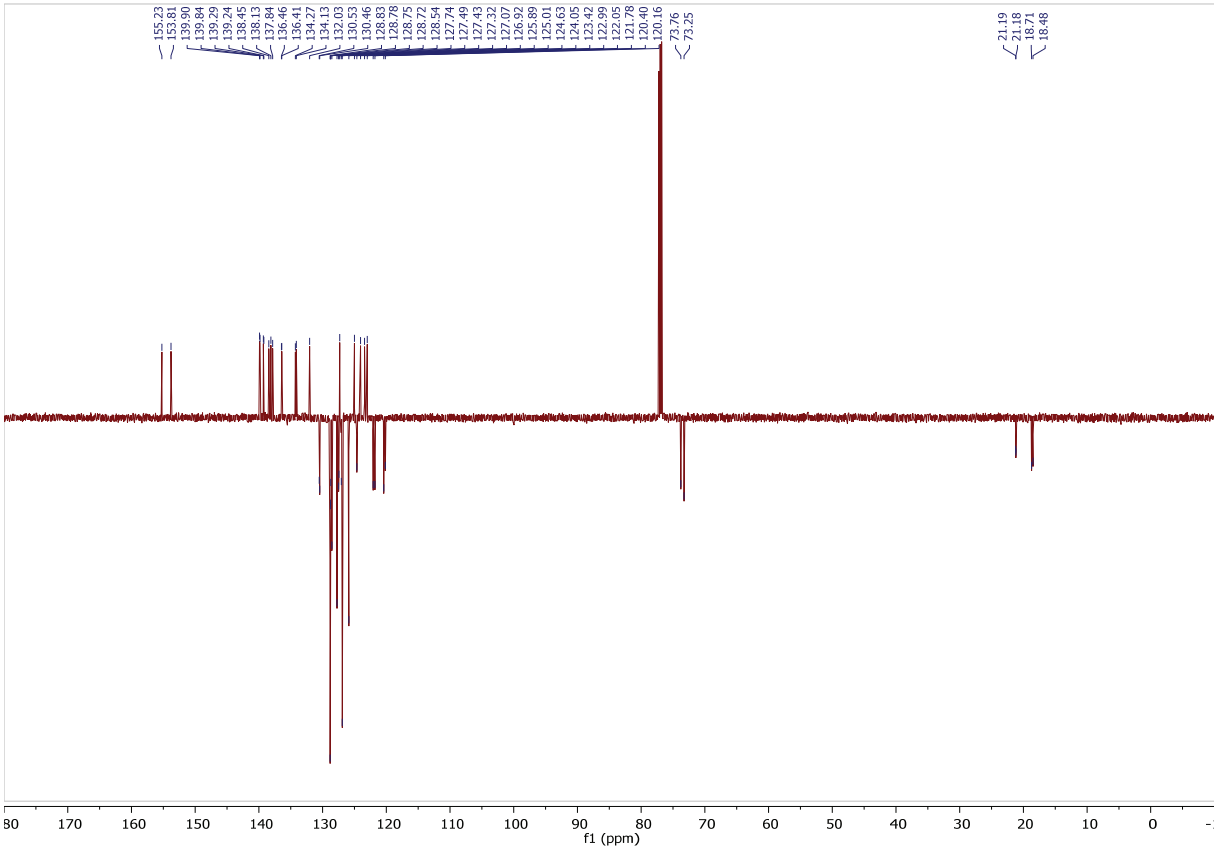


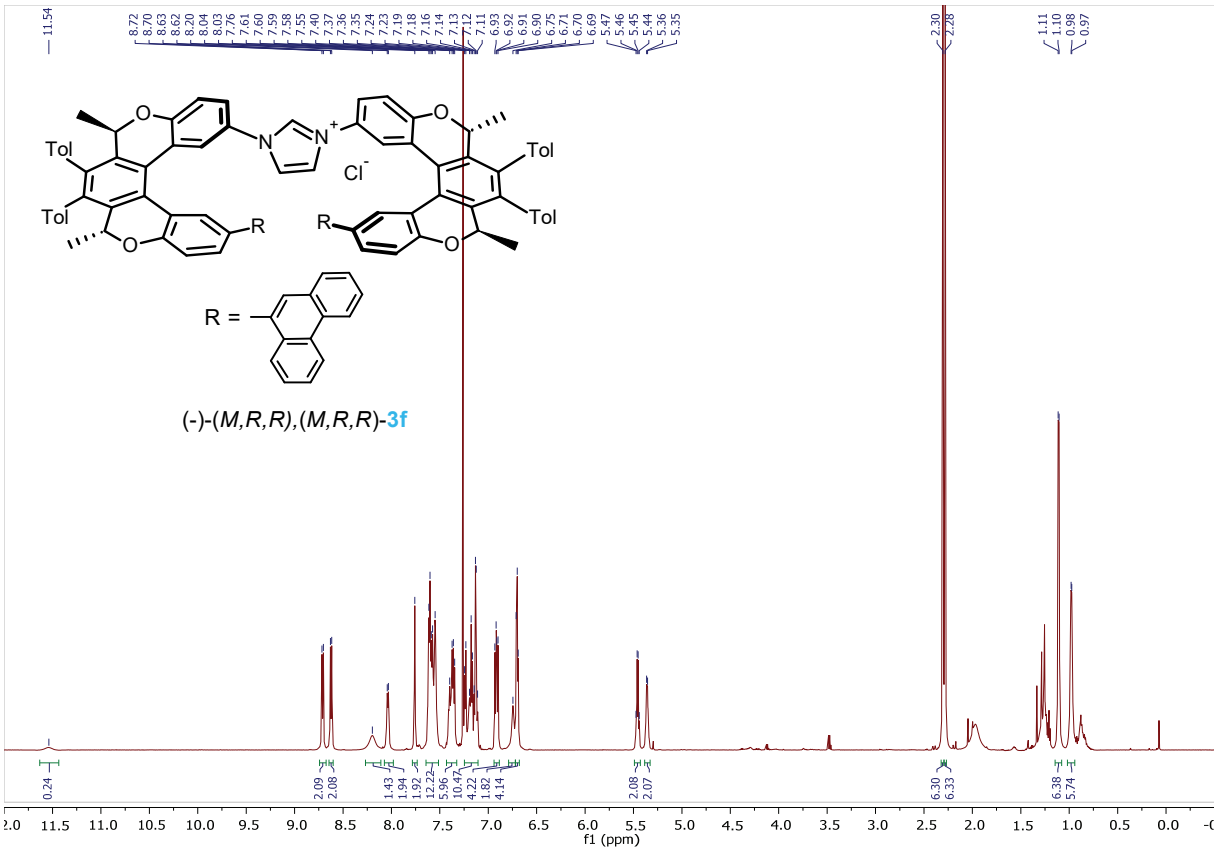
(-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3d**



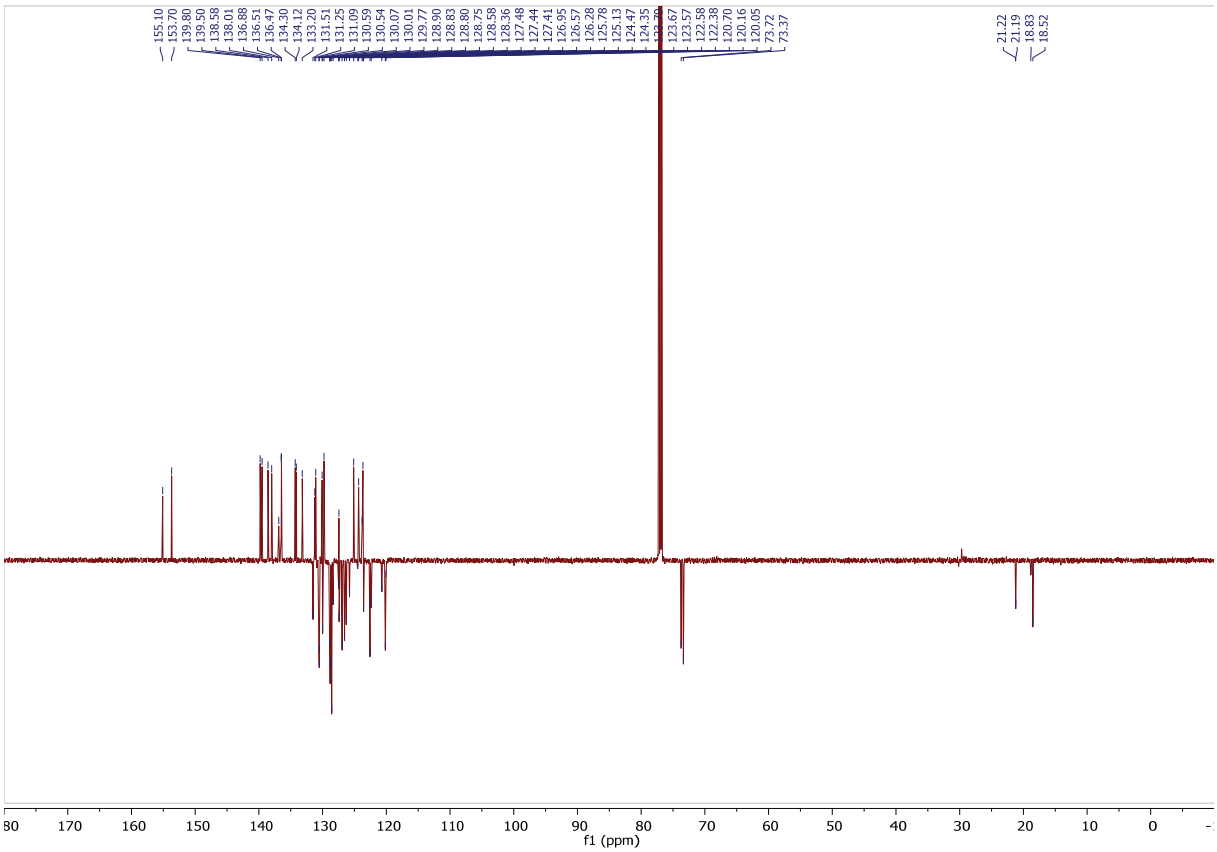


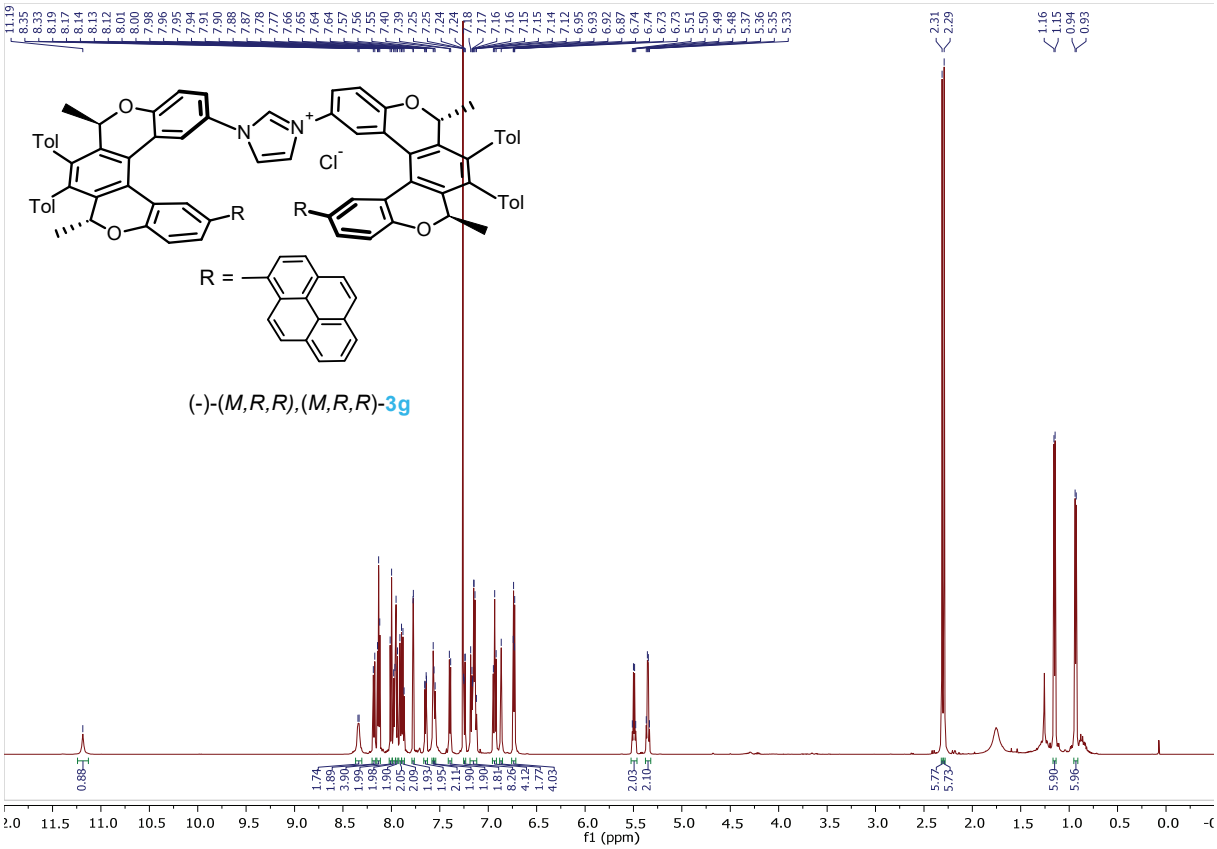
(-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3e**



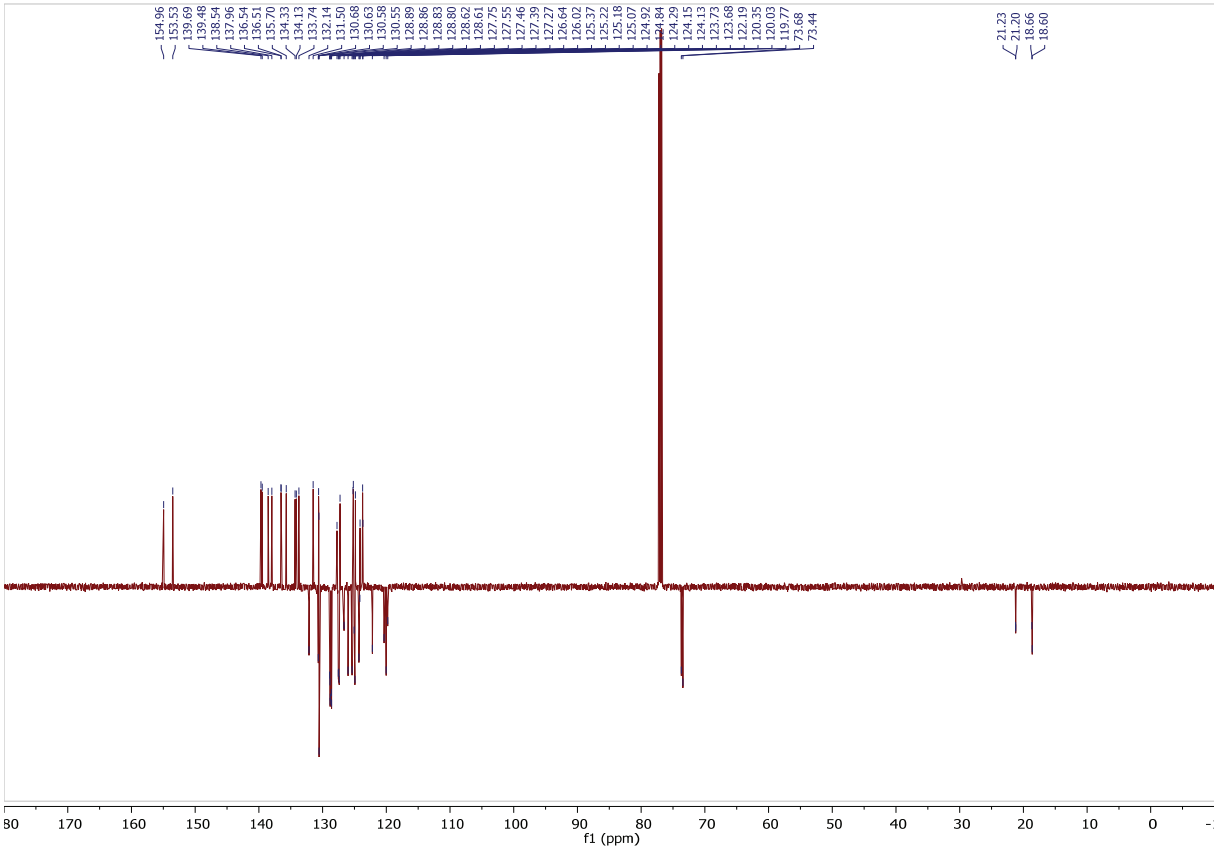


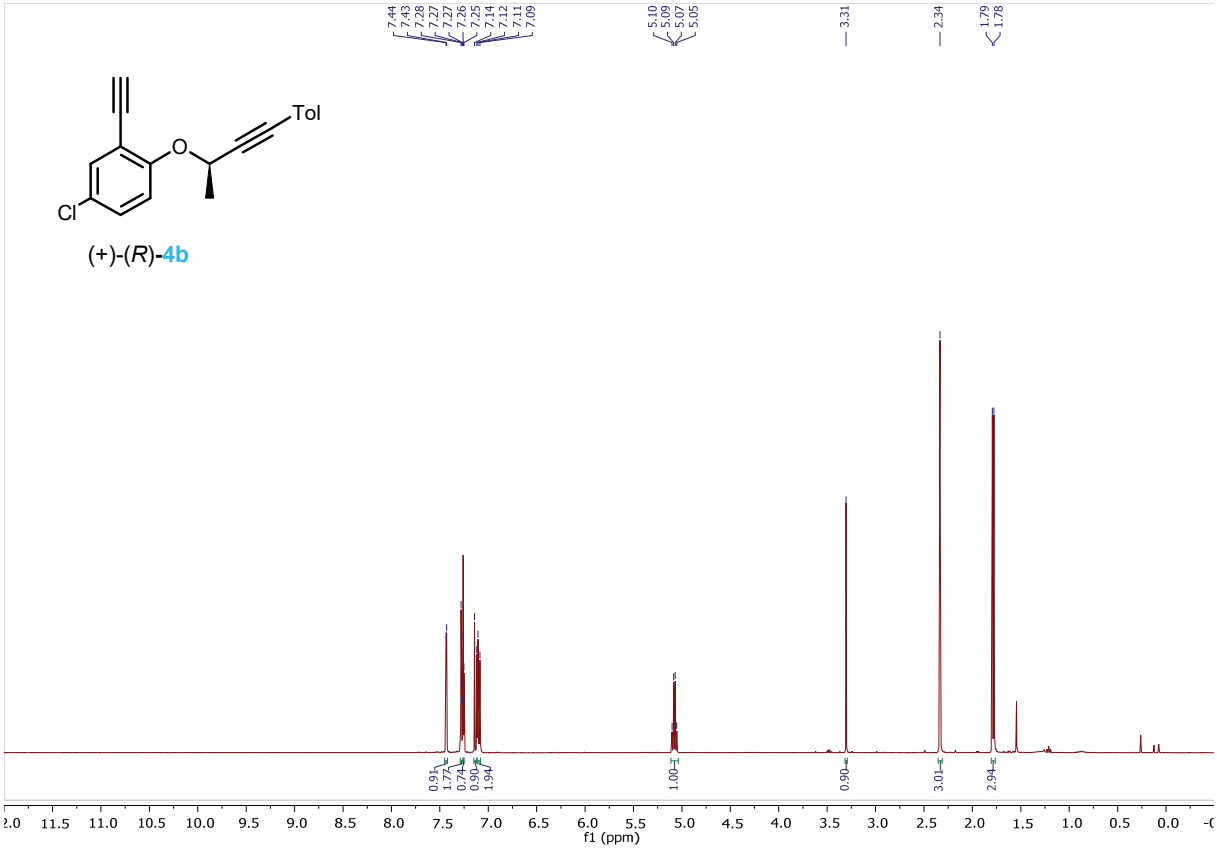
(-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3f**



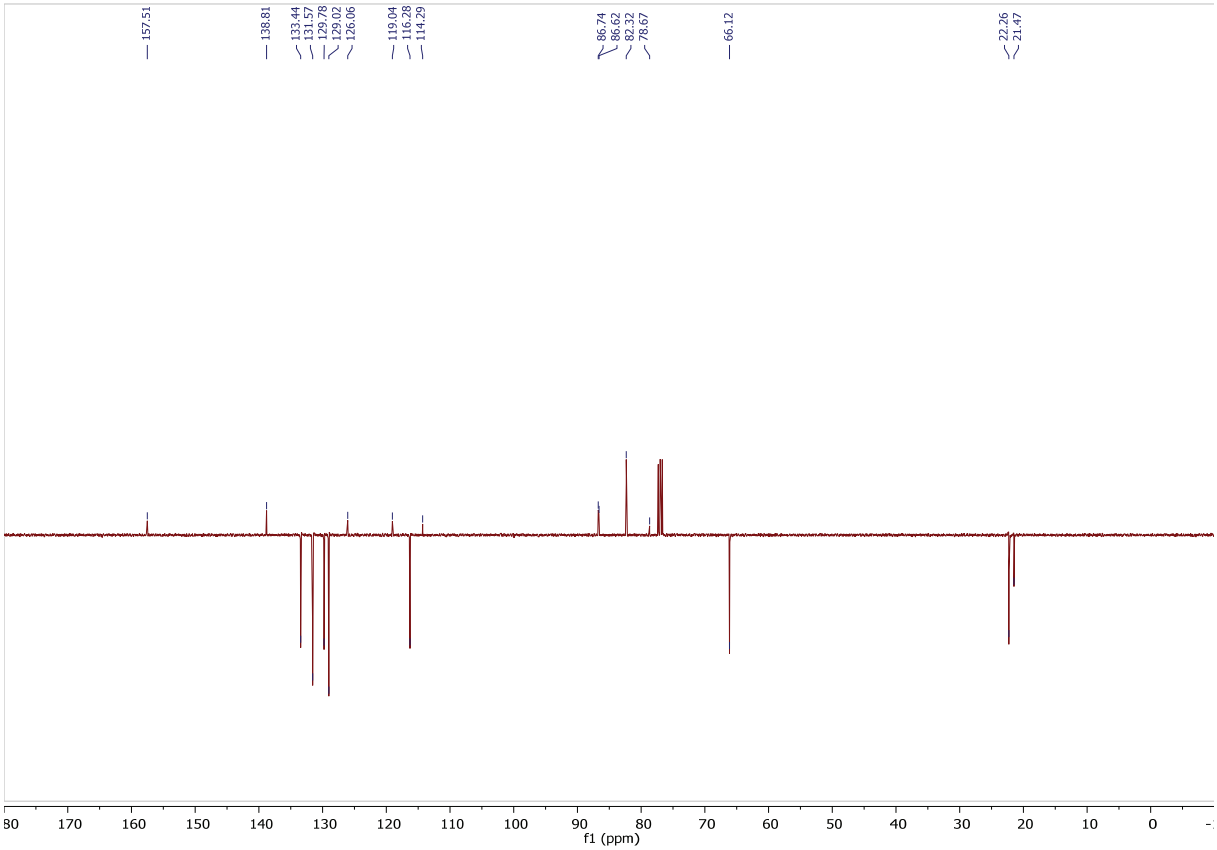


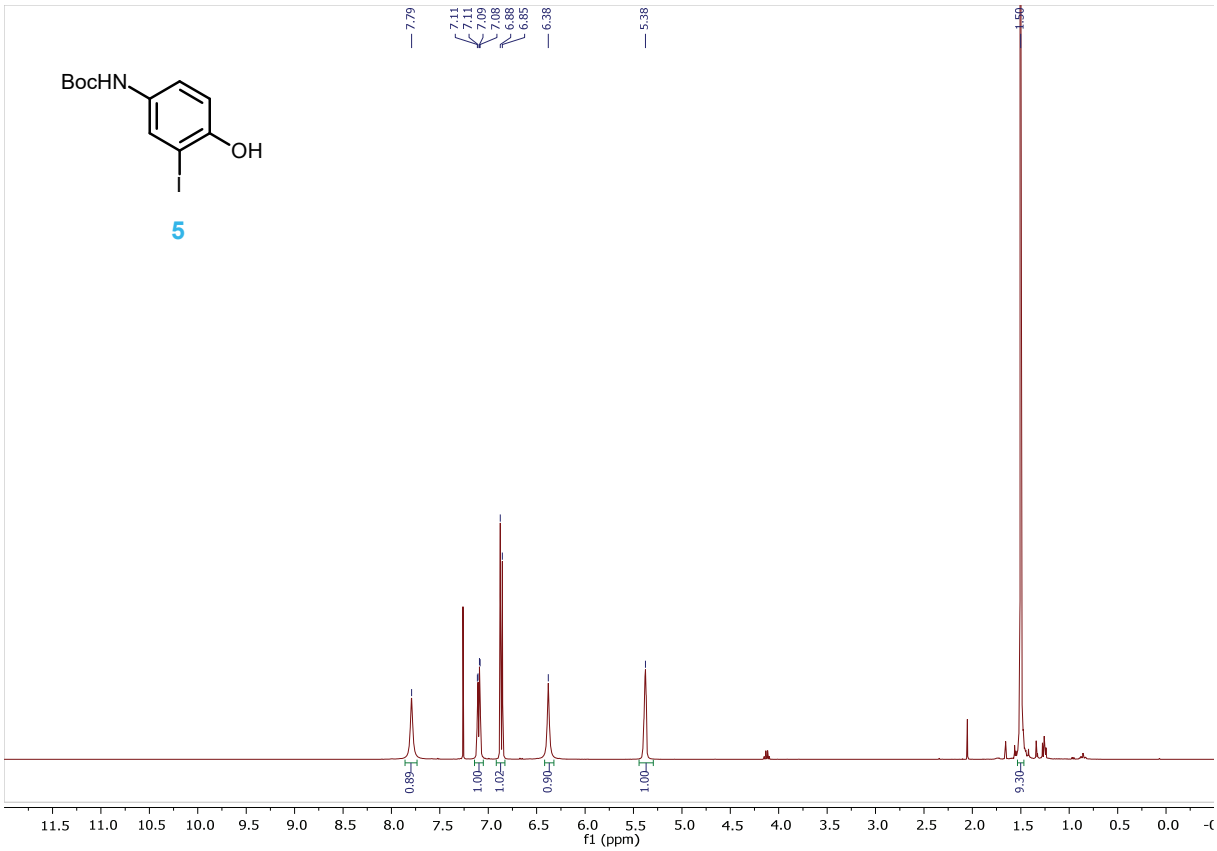
(-)-(*M*,*R*,*R*),(*M*,*R*,*R*)-**3g**



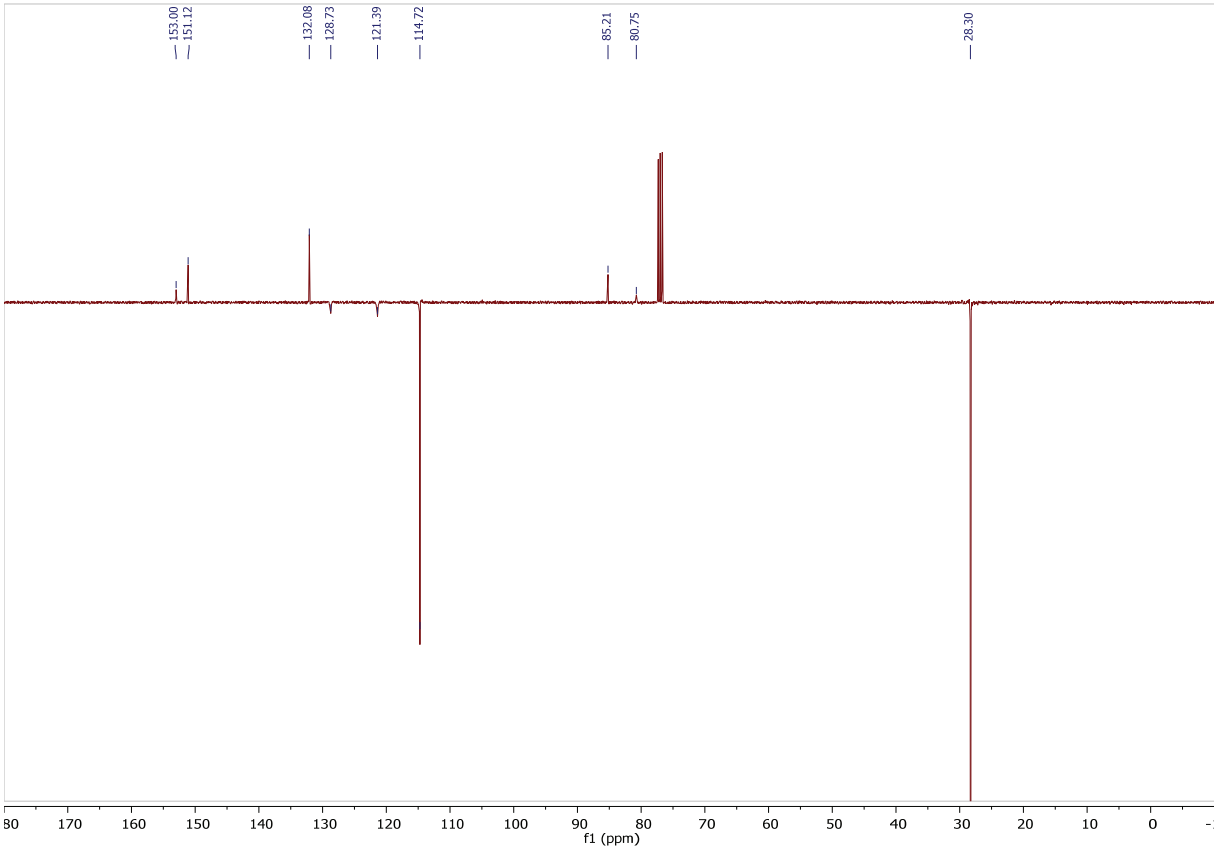

7.44
7.43
7.28
7.27
7.27
7.26
7.25
7.14
7.12
7.11
7.09
5.10
5.09
5.07
5.05
3.31
2.34
1.79
1.78
Tol
O
Cl
0.91
1.77
0.74
0.90
1.94
1.00
0.90
3.01
2.94
f1 (ppm)

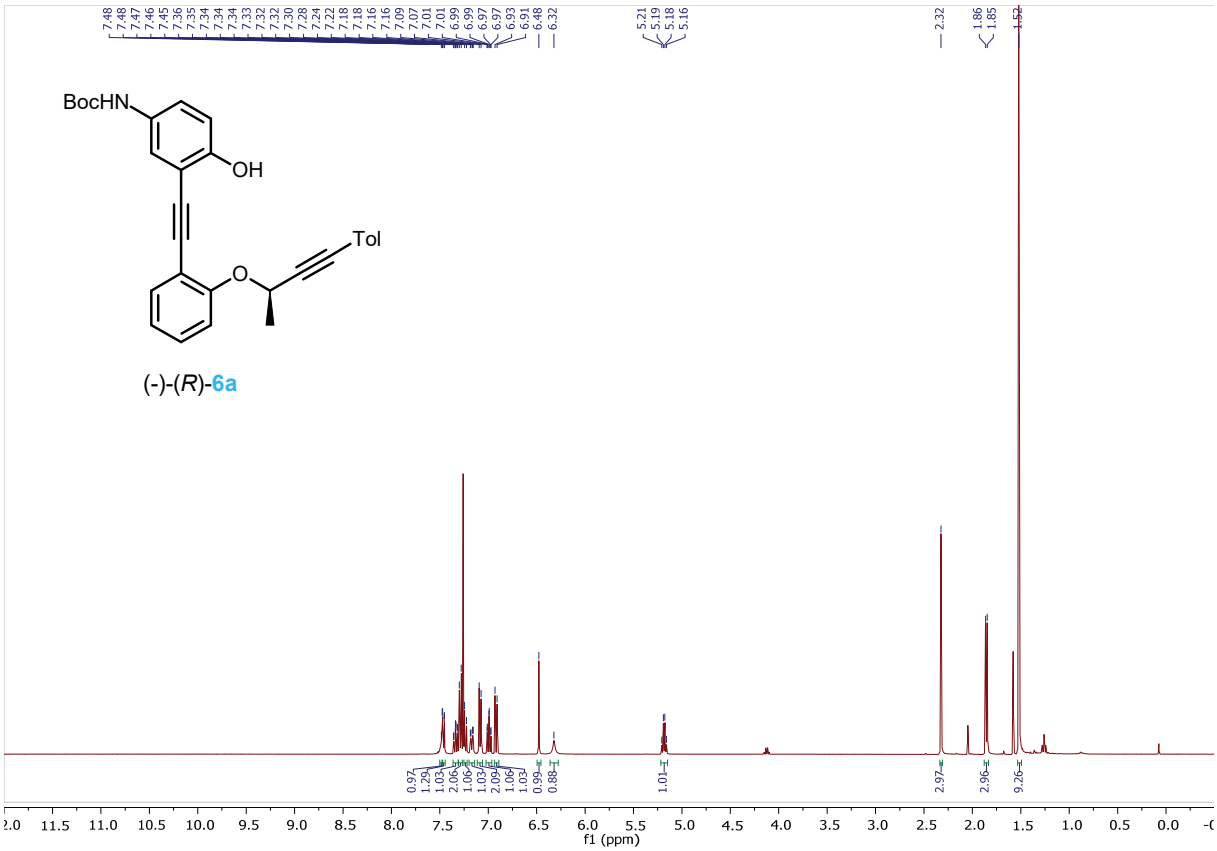
(+)-(*R*)-**4b**

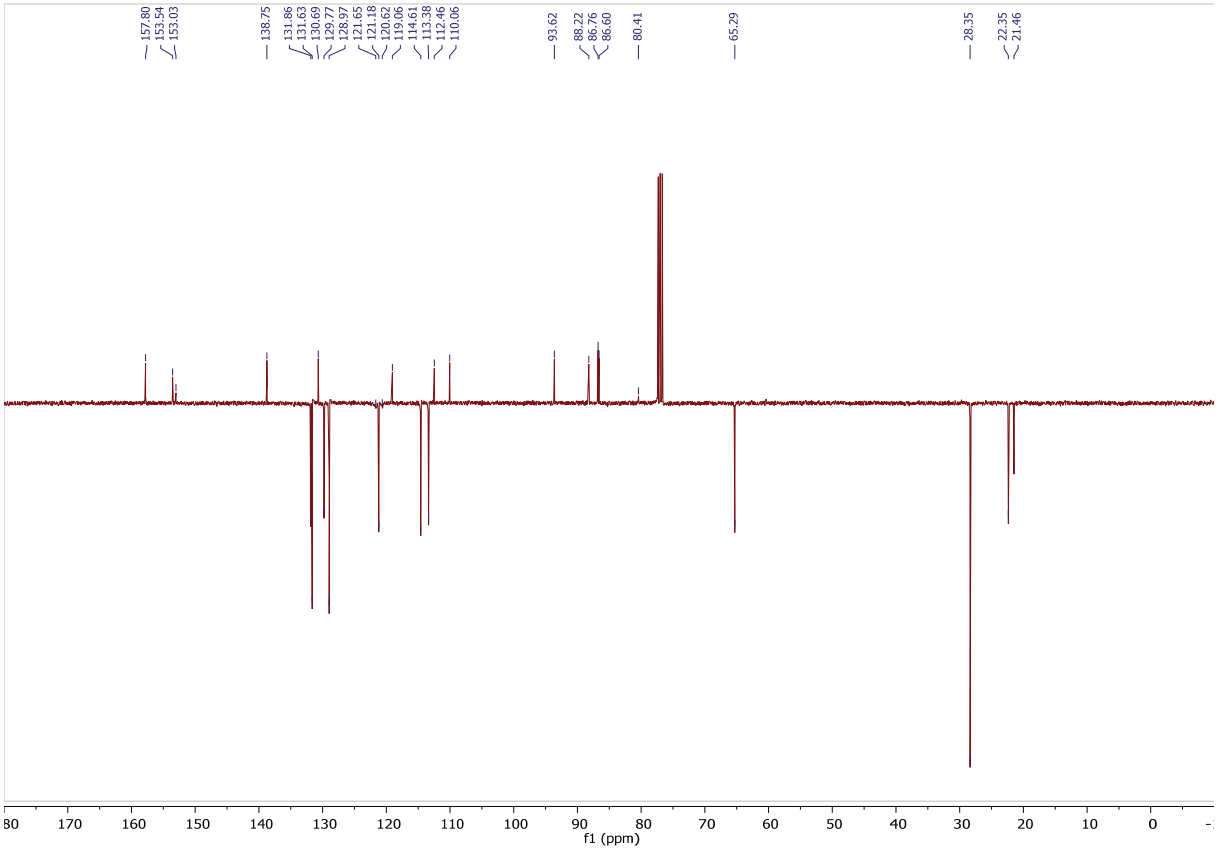

157.51
138.81
133.44
131.57
129.78
129.02
126.06
119.04
116.28
114.29
86.74
86.62
82.32
78.67
66.12
22.26
21.47
f1 (ppm)

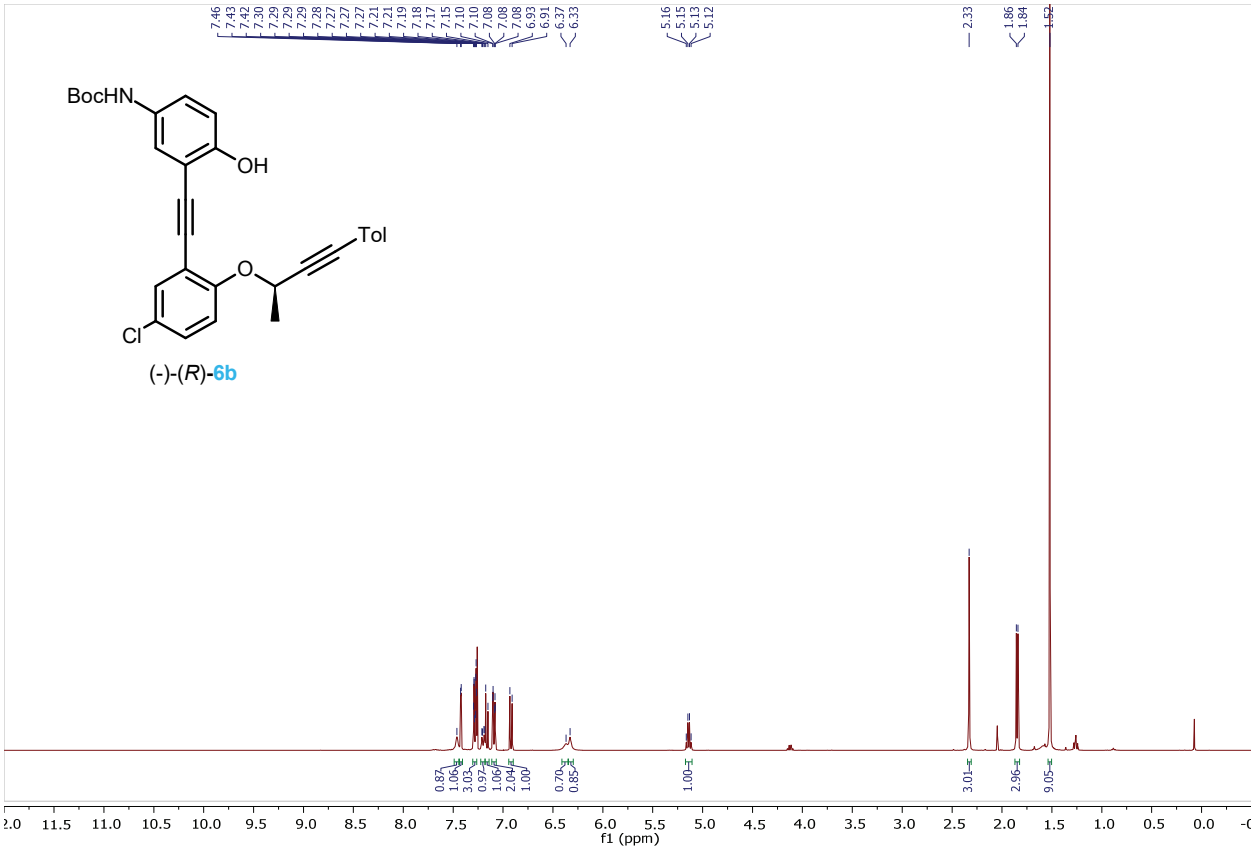

BocHN
OH
I
7.79
7.11
7.11
7.09
7.08
6.88
6.85
6.38
5.38
1.50
0.89
1.00
1.02
0.90
1.00
9.30
f1 (ppm)

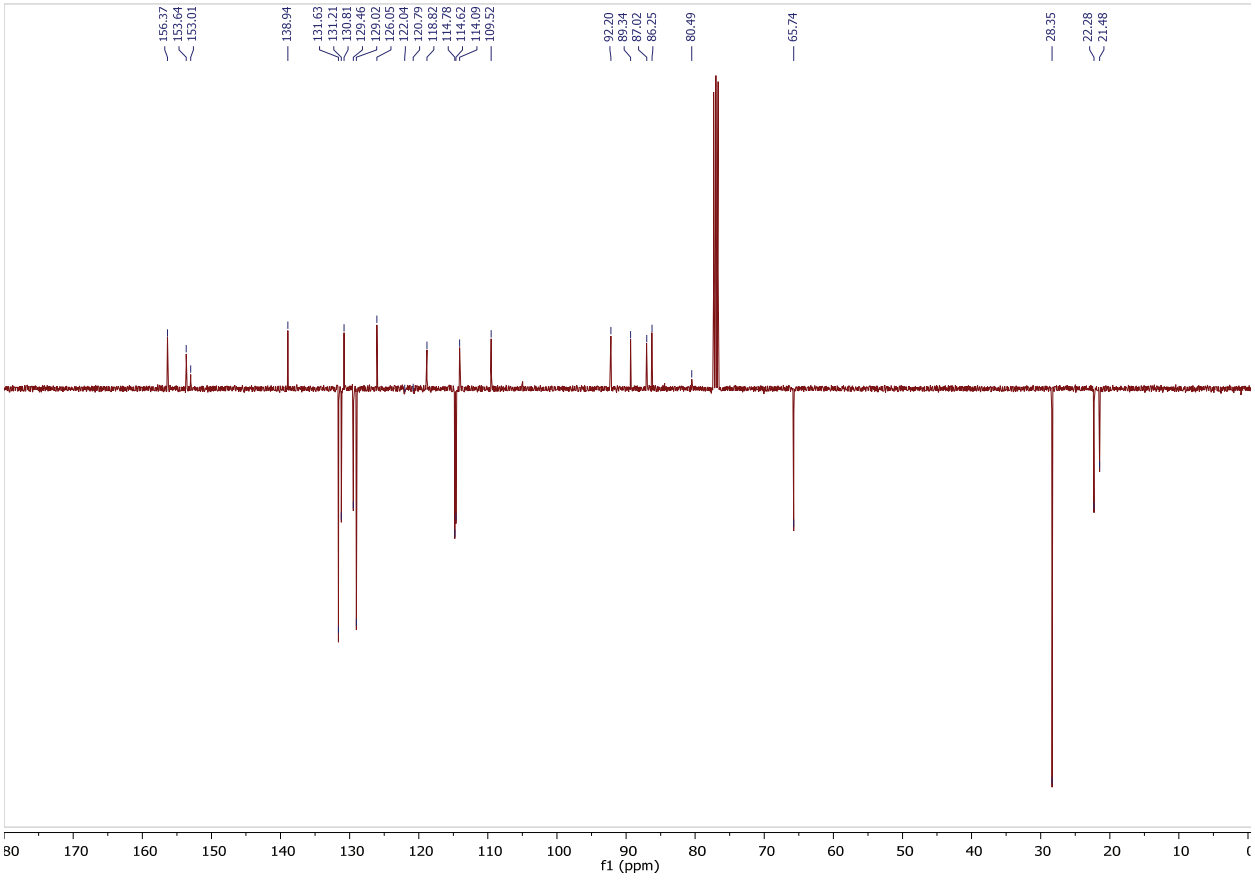
5

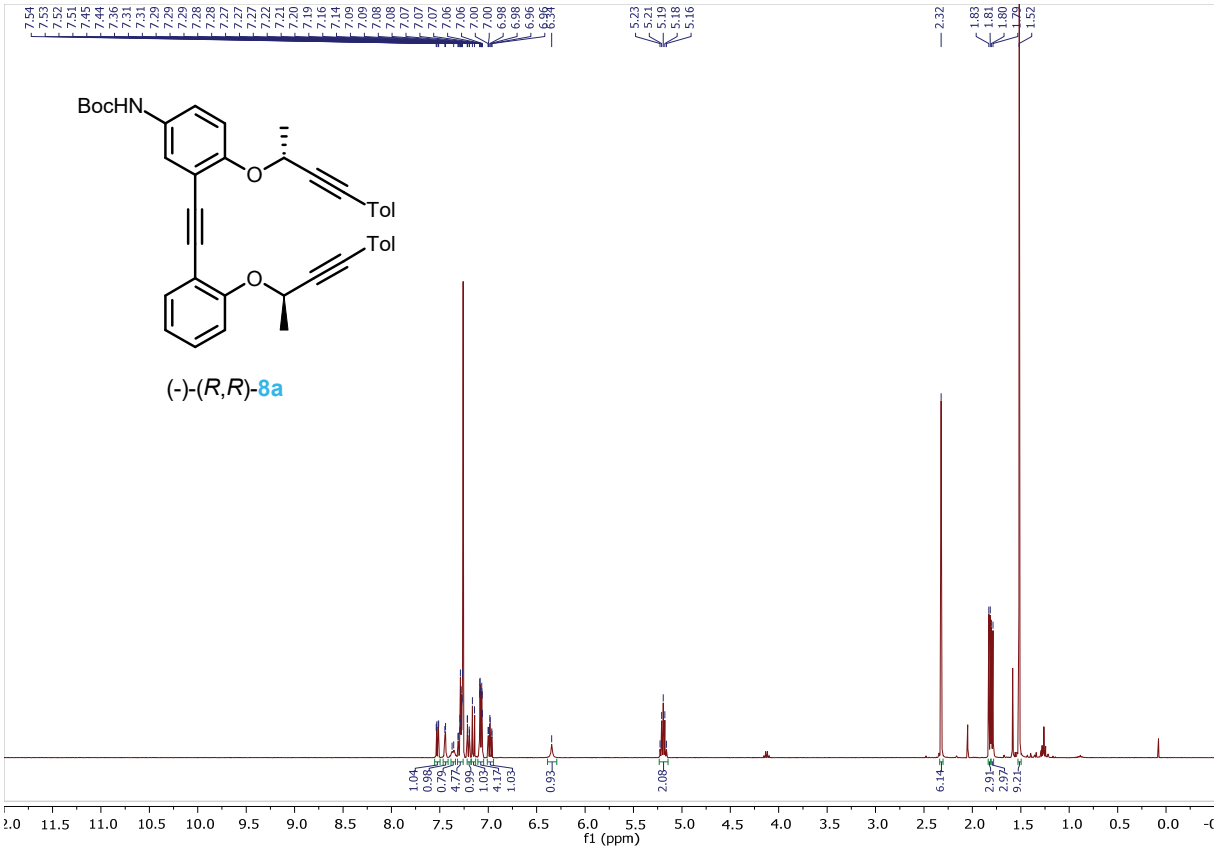

153.00
151.12
132.08
128.73
121.39
114.72
85.21
80.75
28.30
f1 (ppm)


BocHN
OH
Tol
O
(-)-(R)-6a
f1 (ppm)

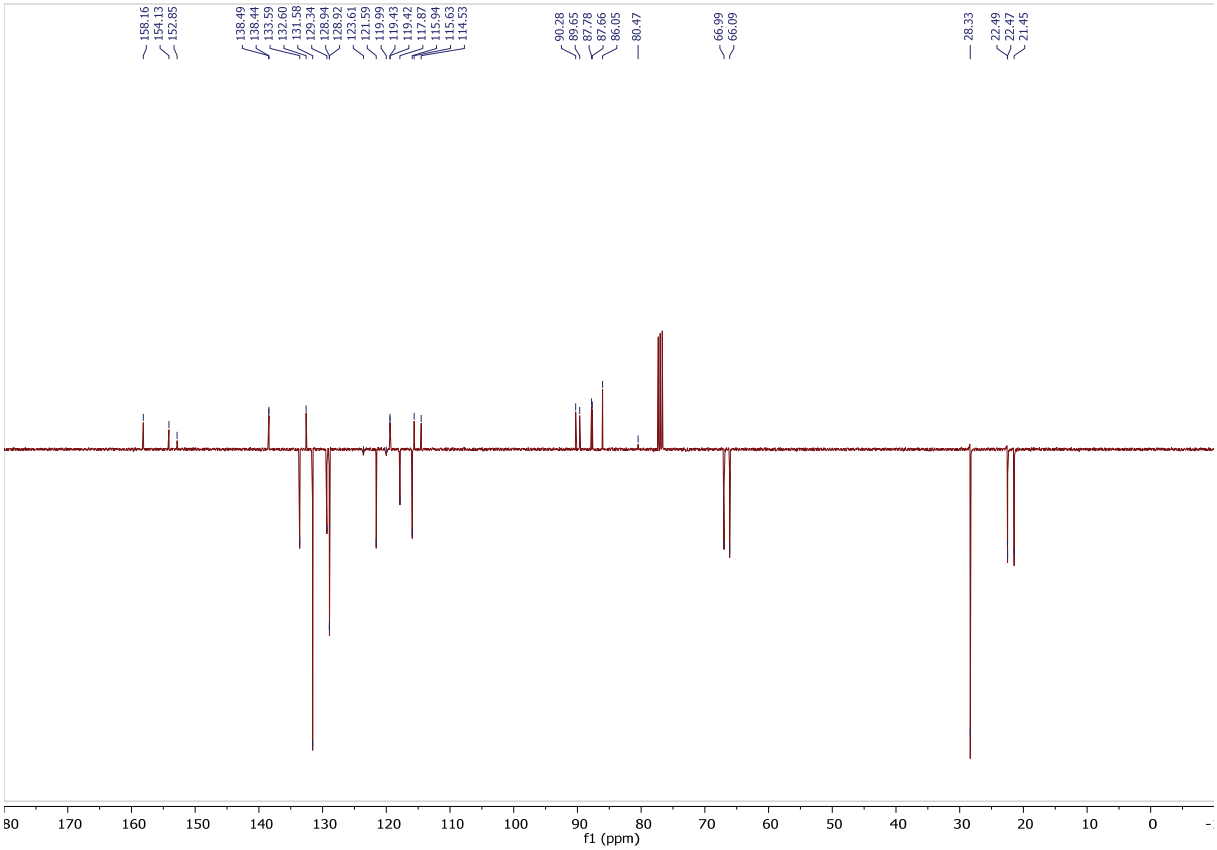

f1 (ppm)

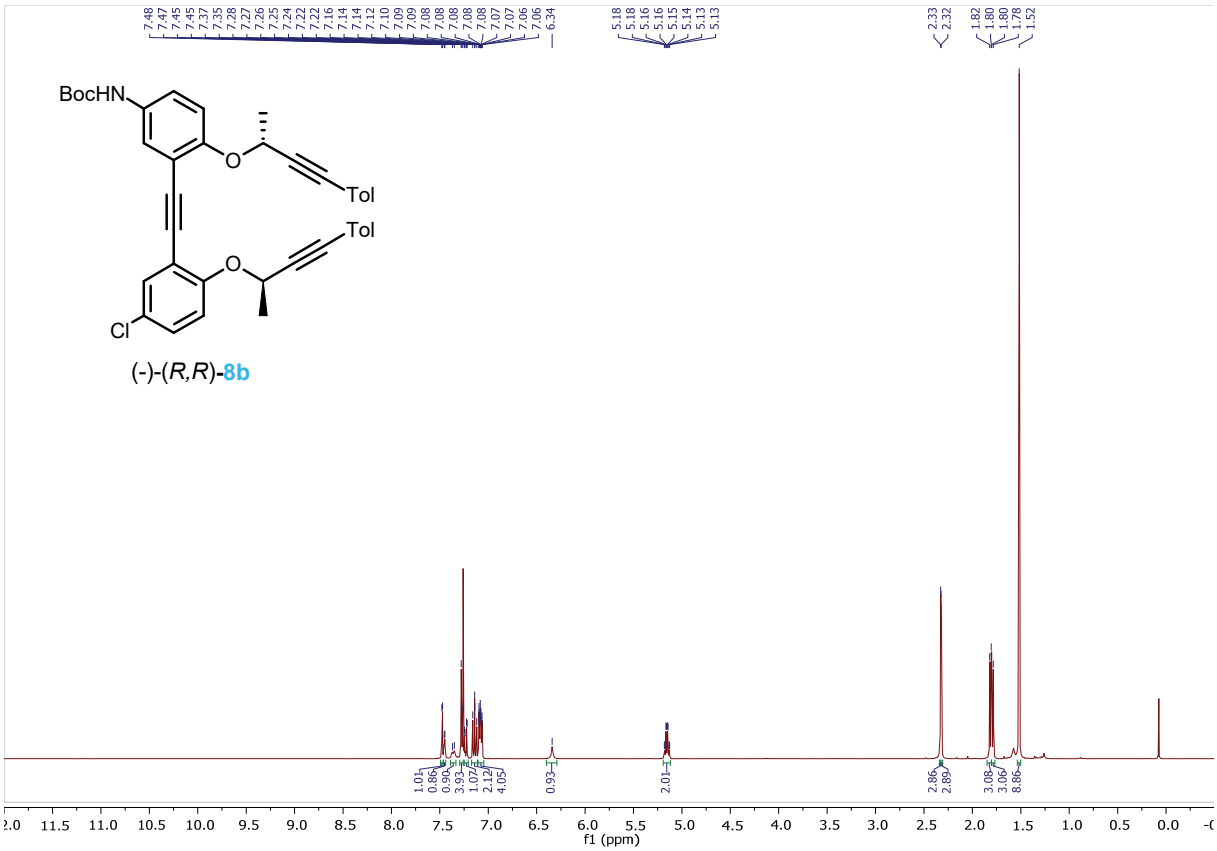

BocHN
OH
Tol
O
Cl
(-)-(R)-6b
f1 (ppm)


f1 (ppm)

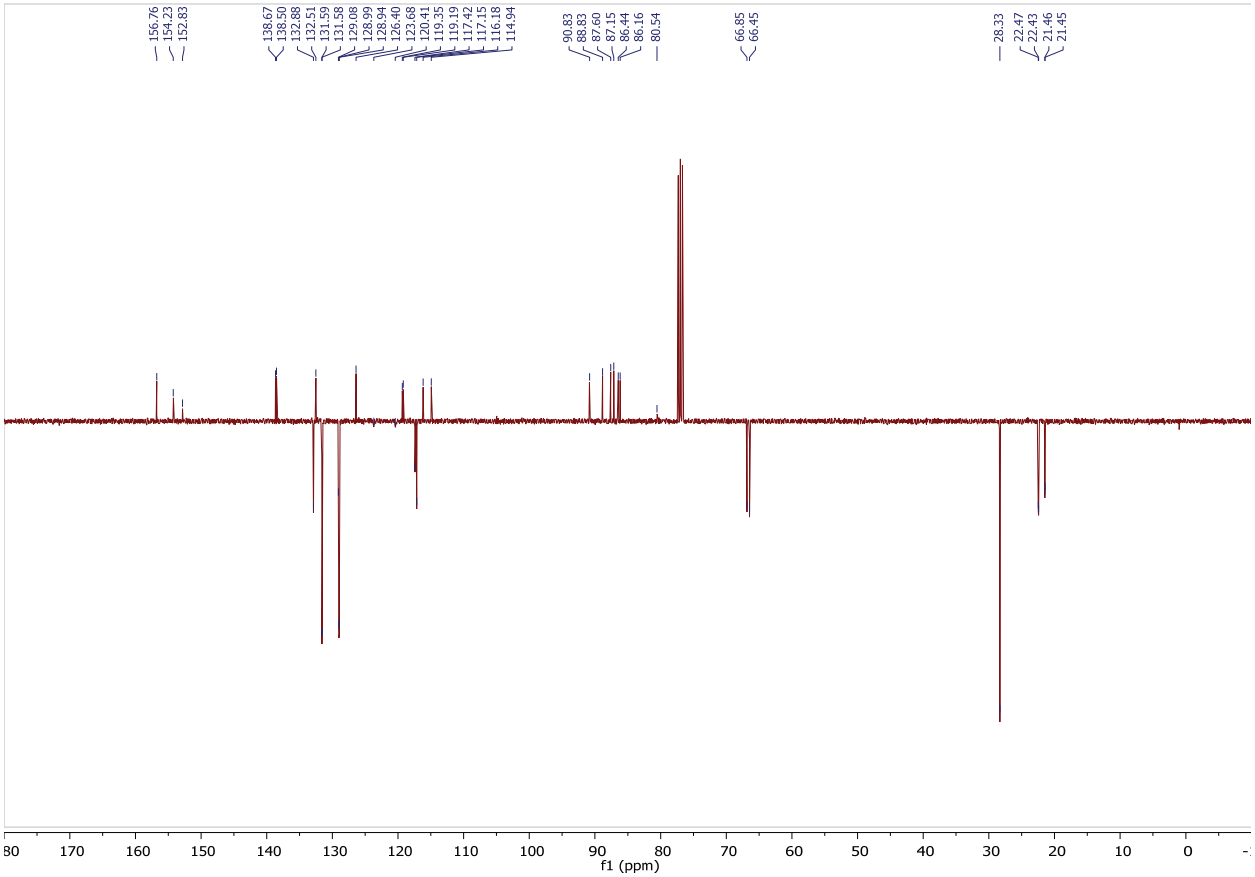


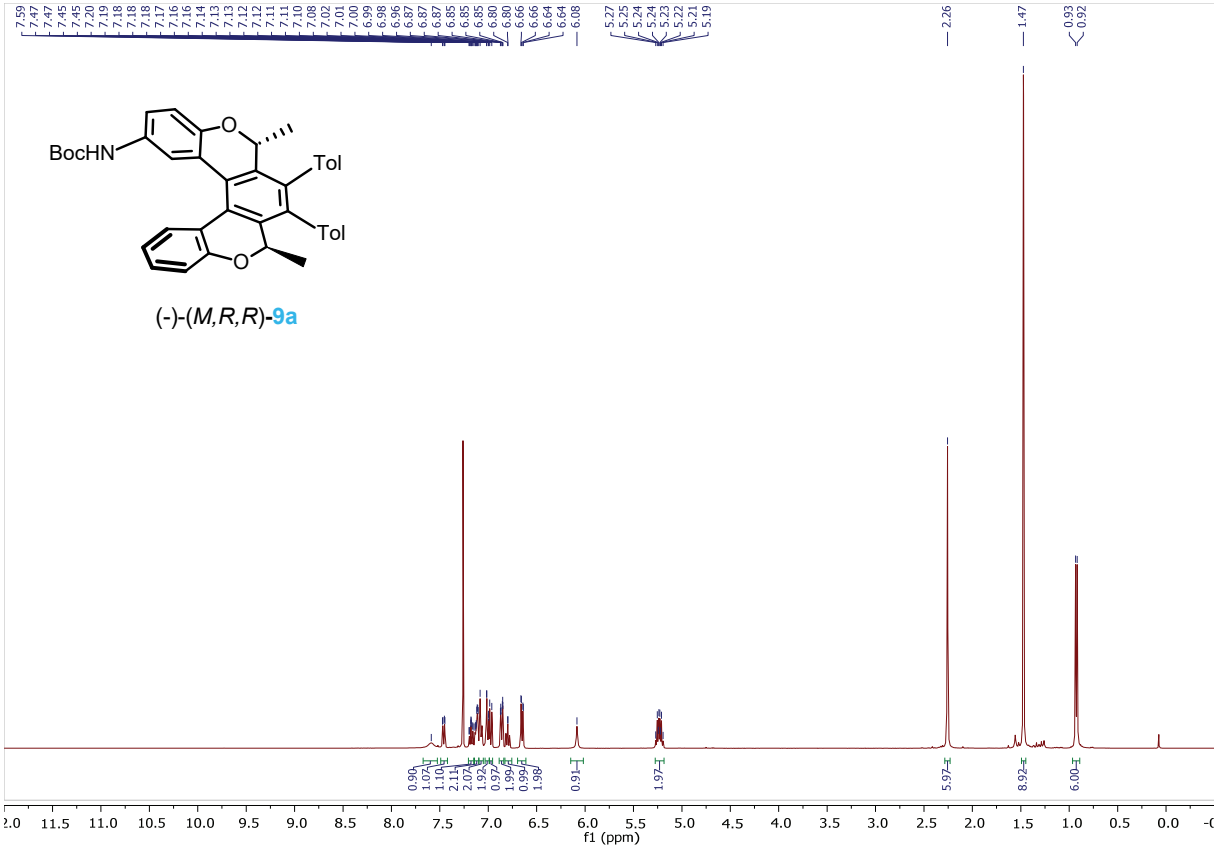
(-)-(*R*,*R*)-**8a**



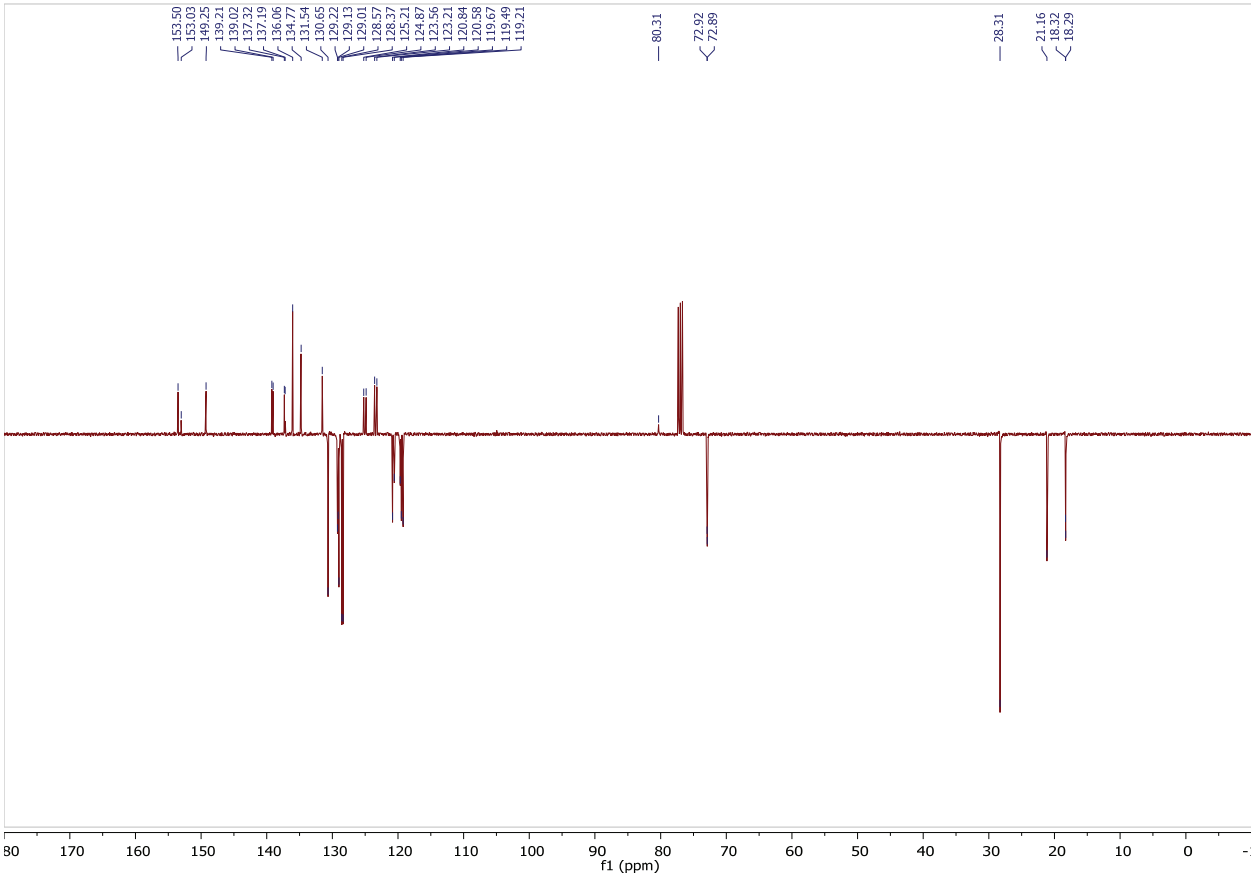


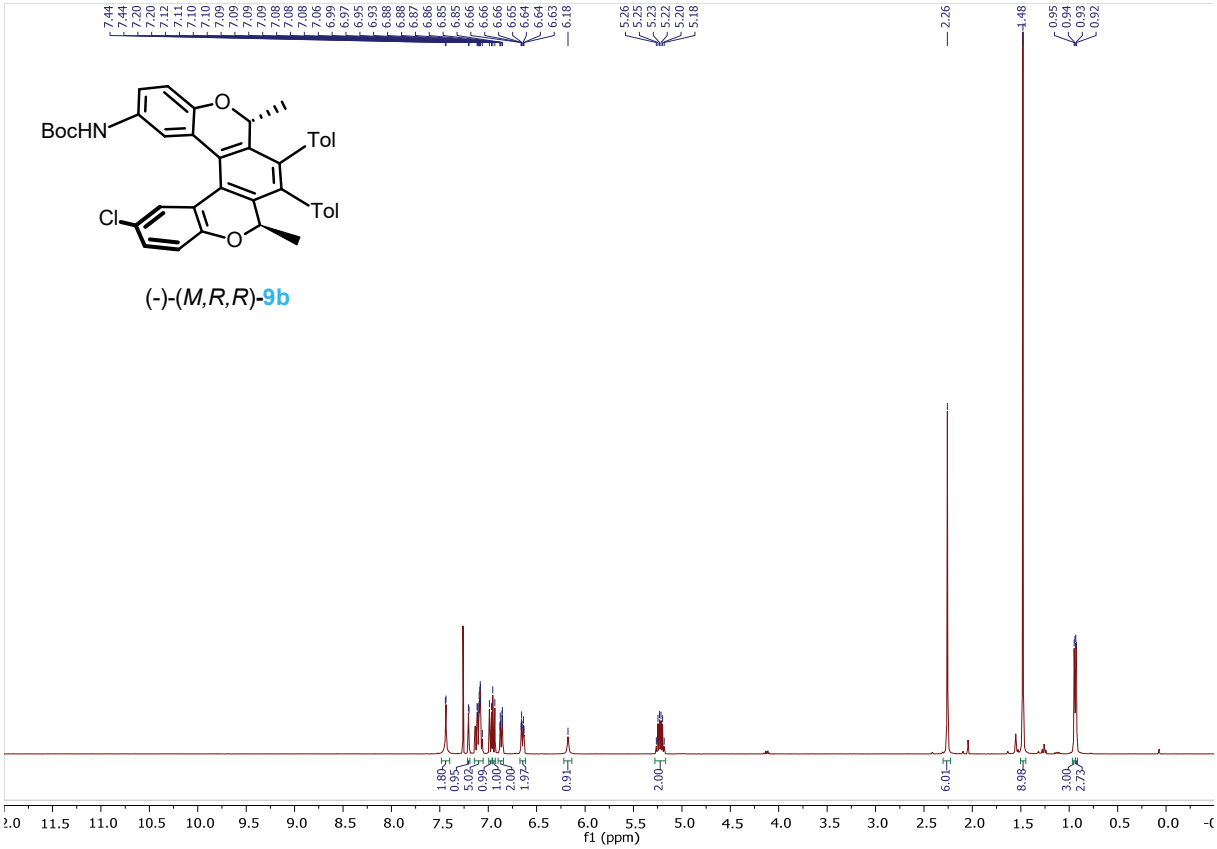
(-)-(*R*,*R*)-**8b**



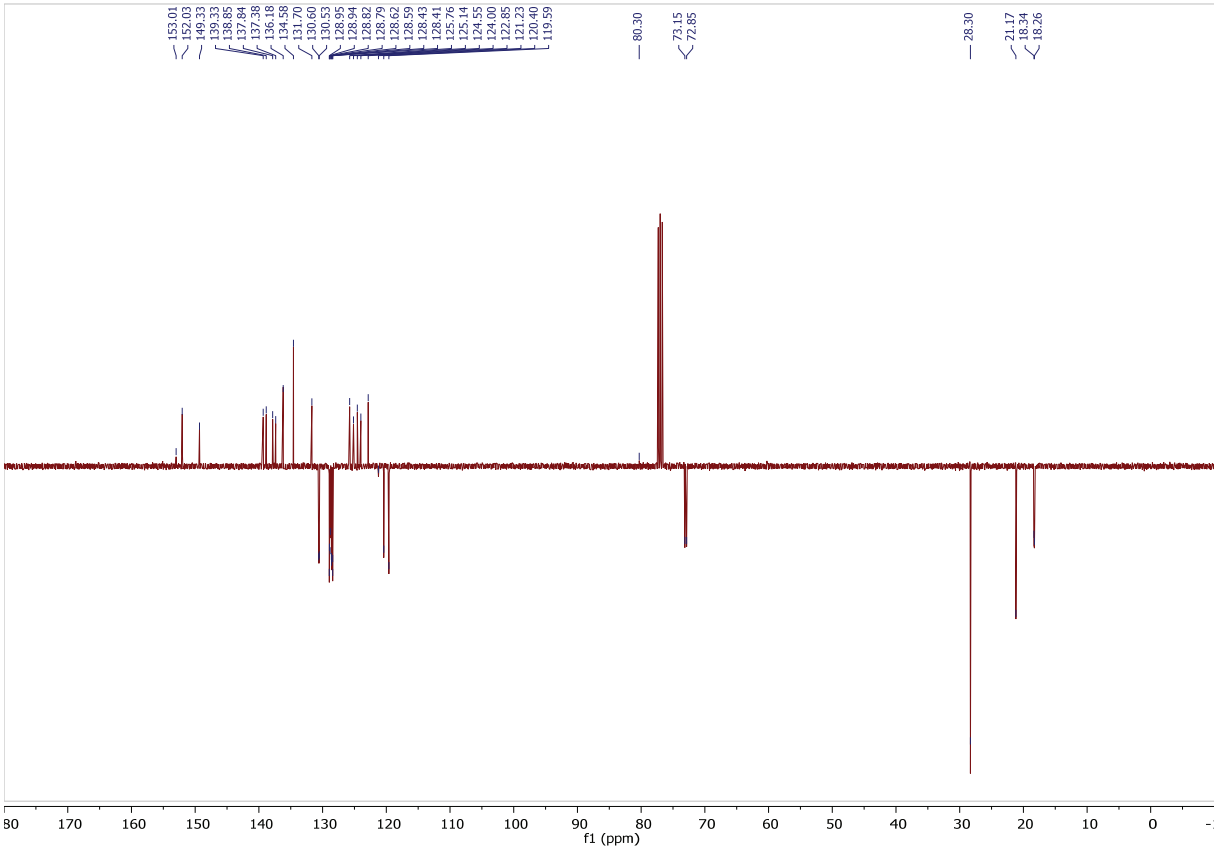


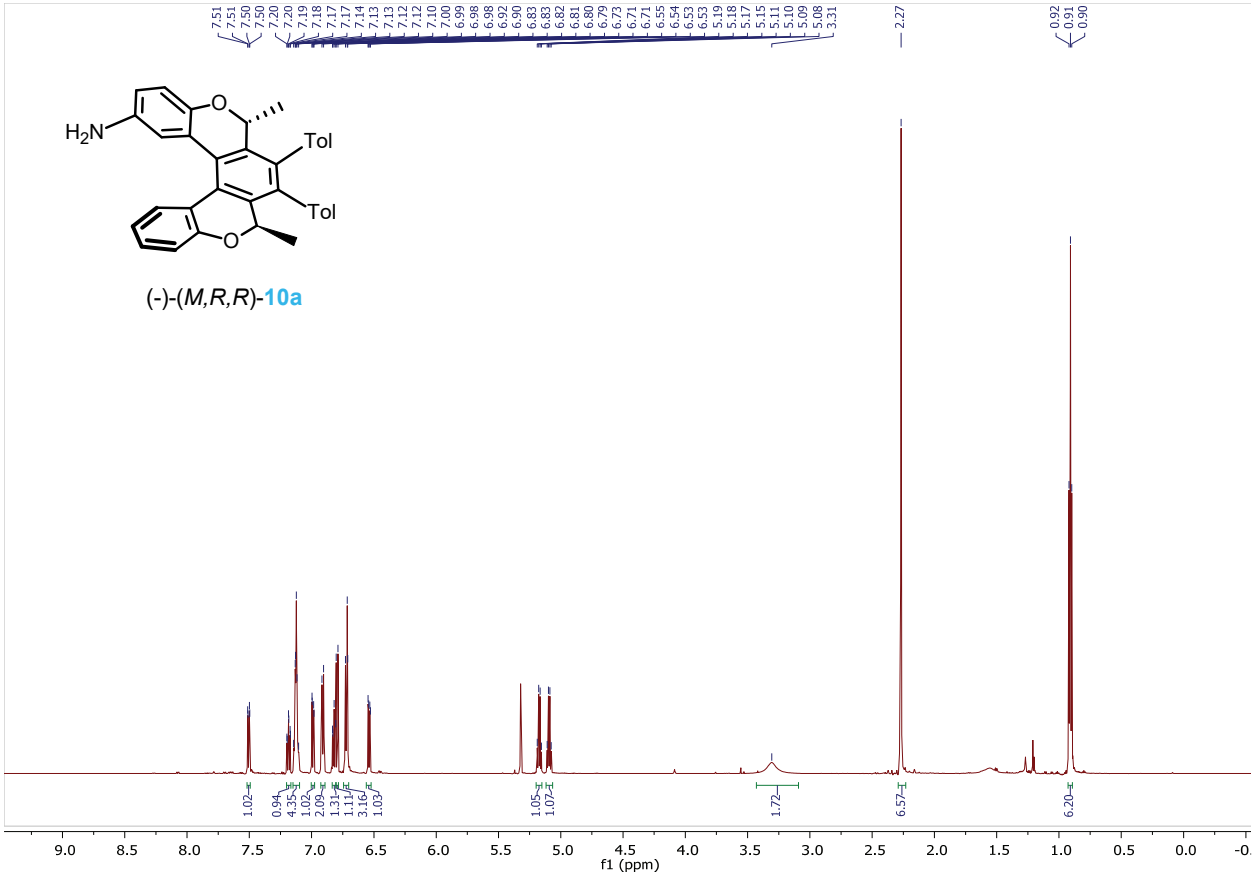
(-)-(*M*,*R*,*R*)-**9a**



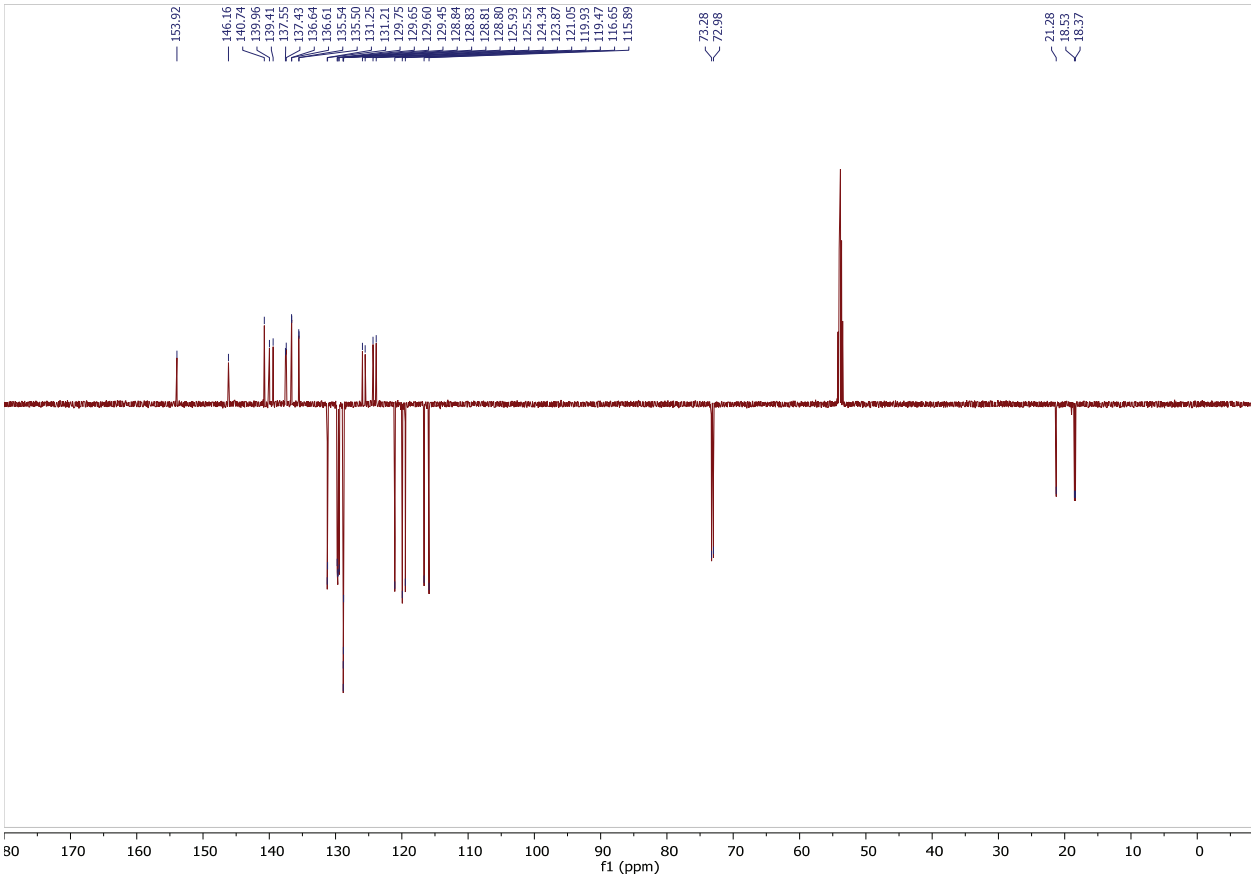


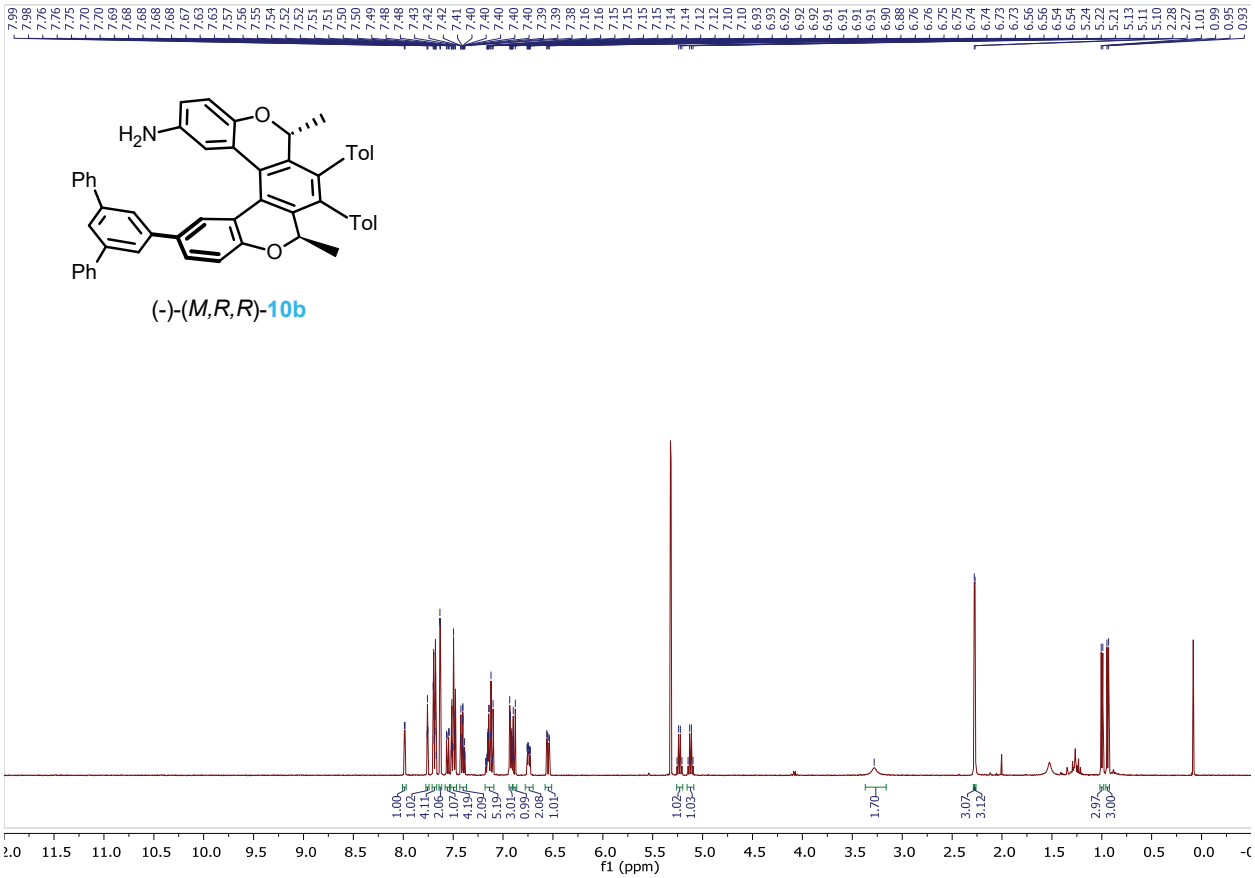
(-)-(*M,R,R*)-**9b**



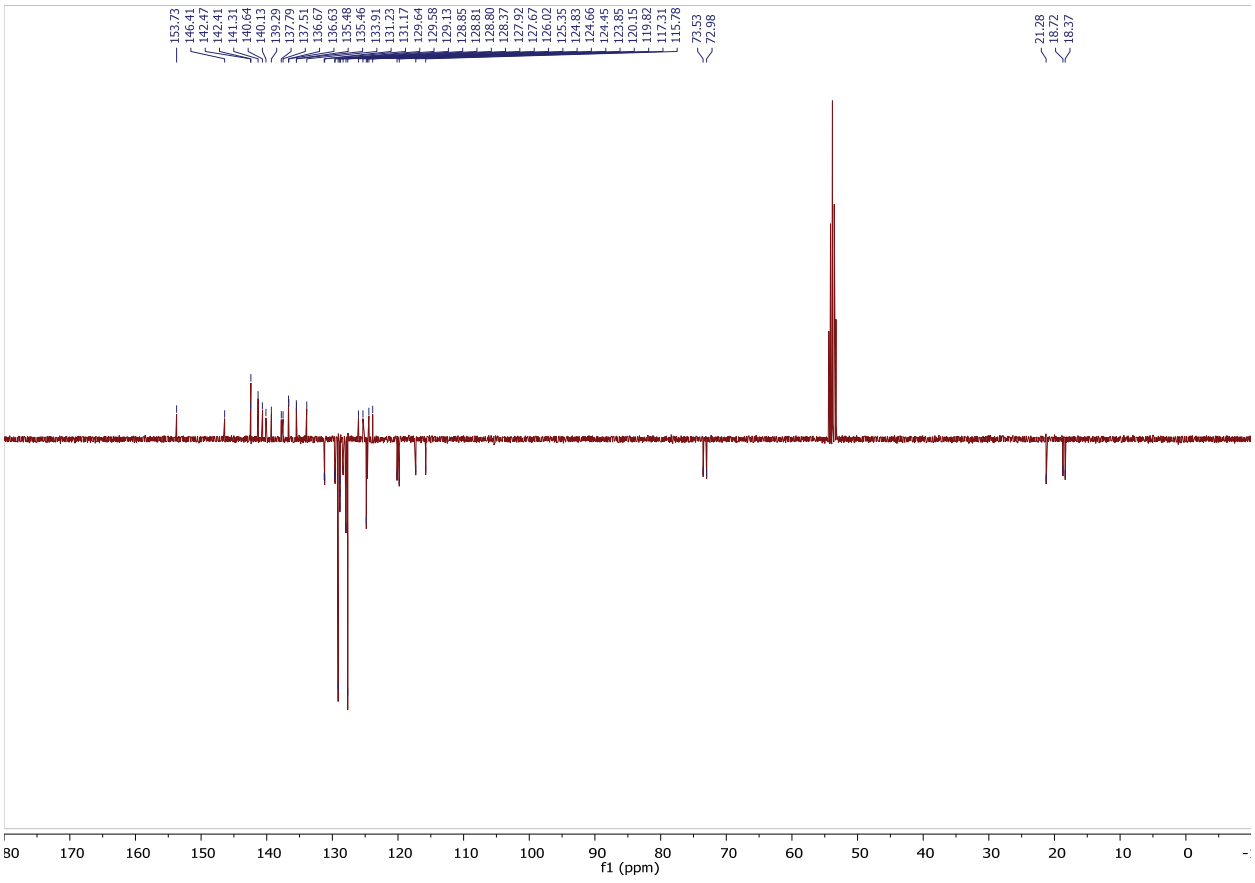


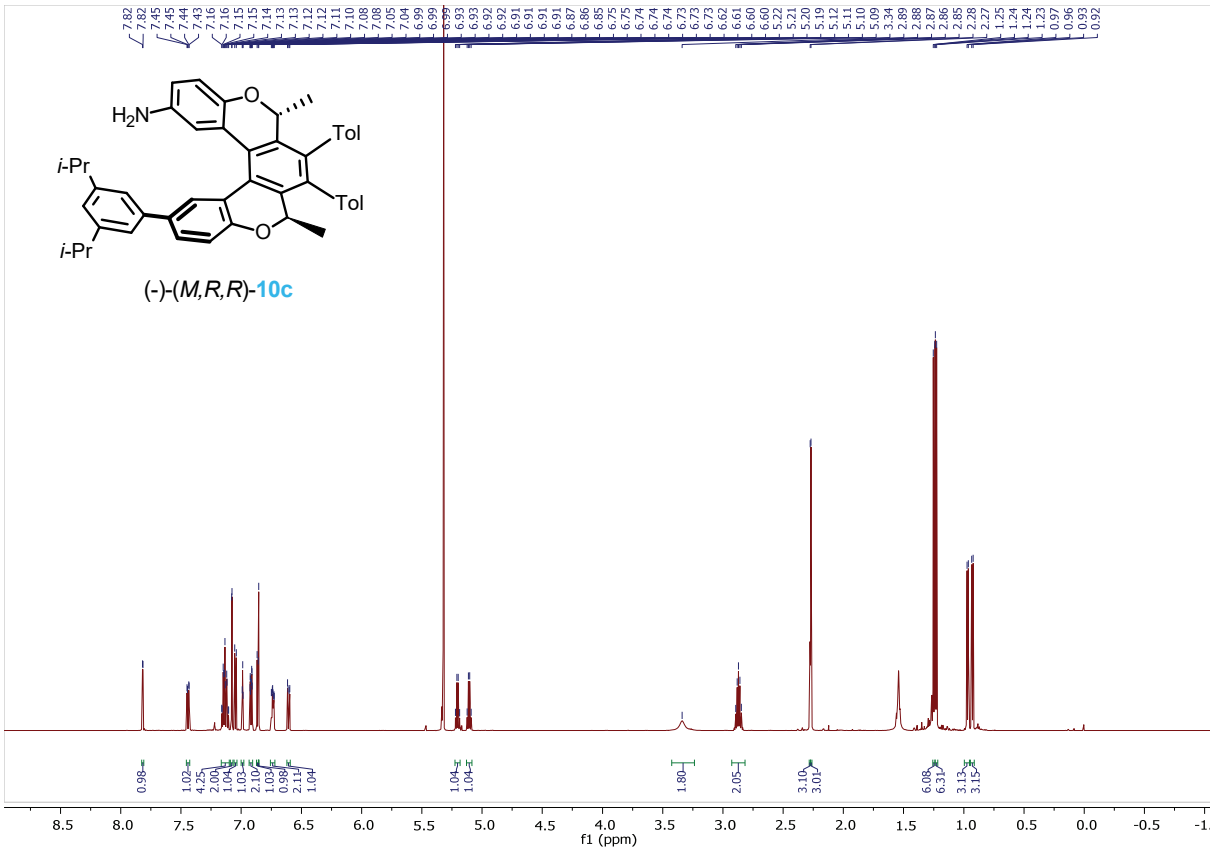
(-)-(*M,R,R*)-**10a**



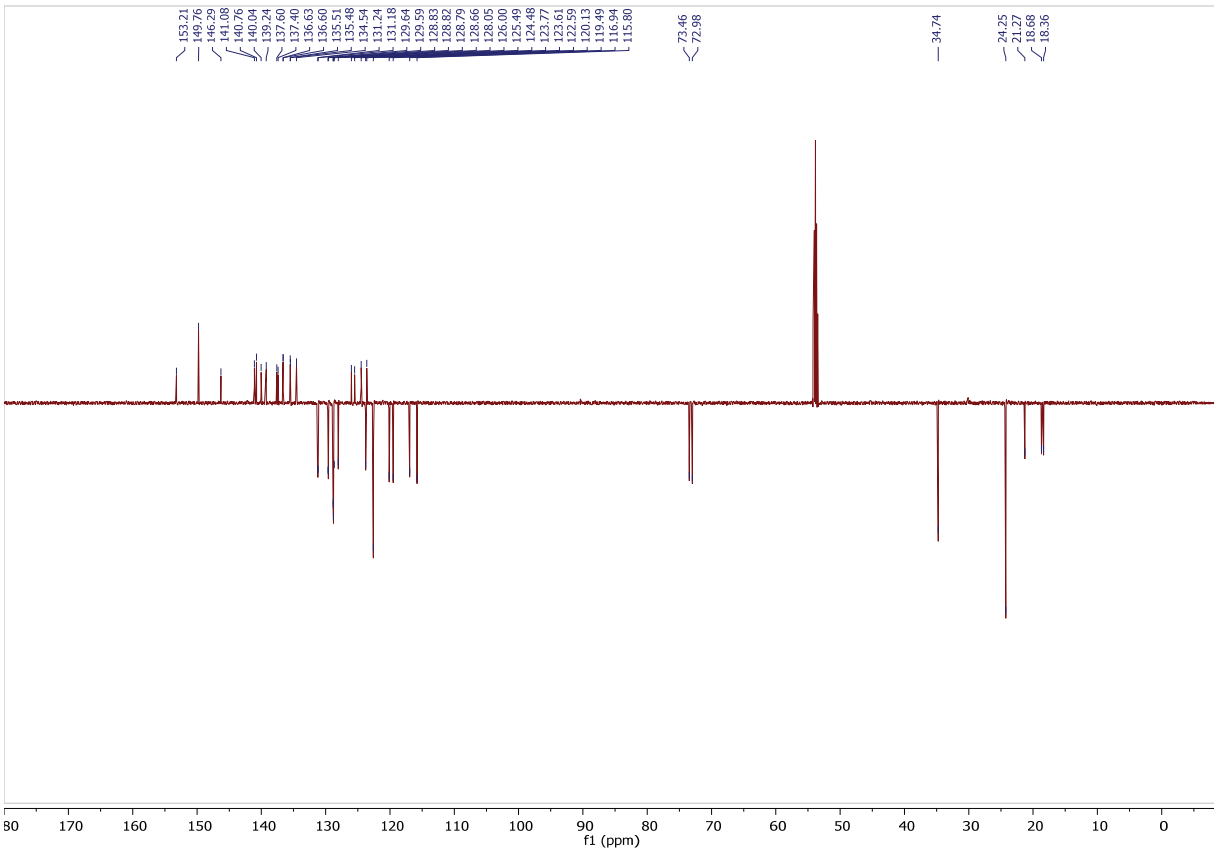


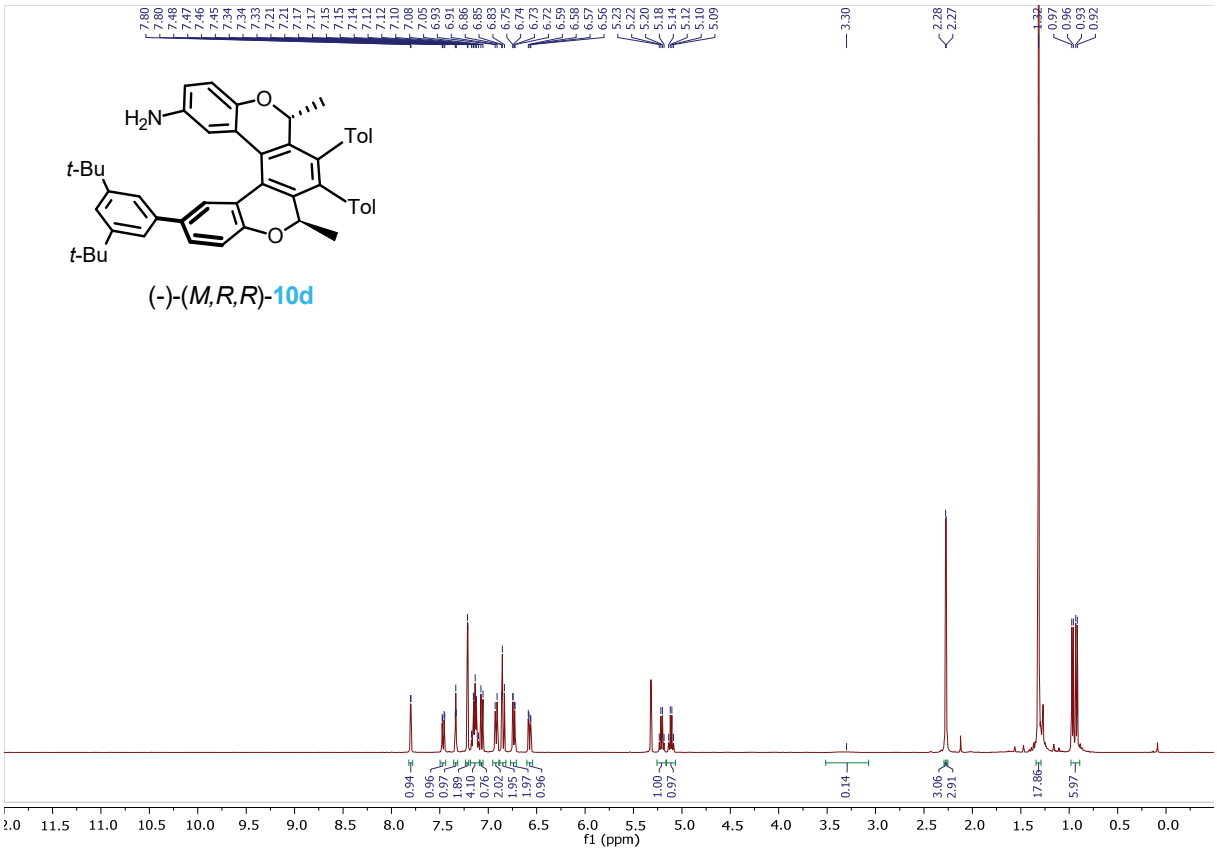
(-)-(*M*,*R*,*R*)-**10b**



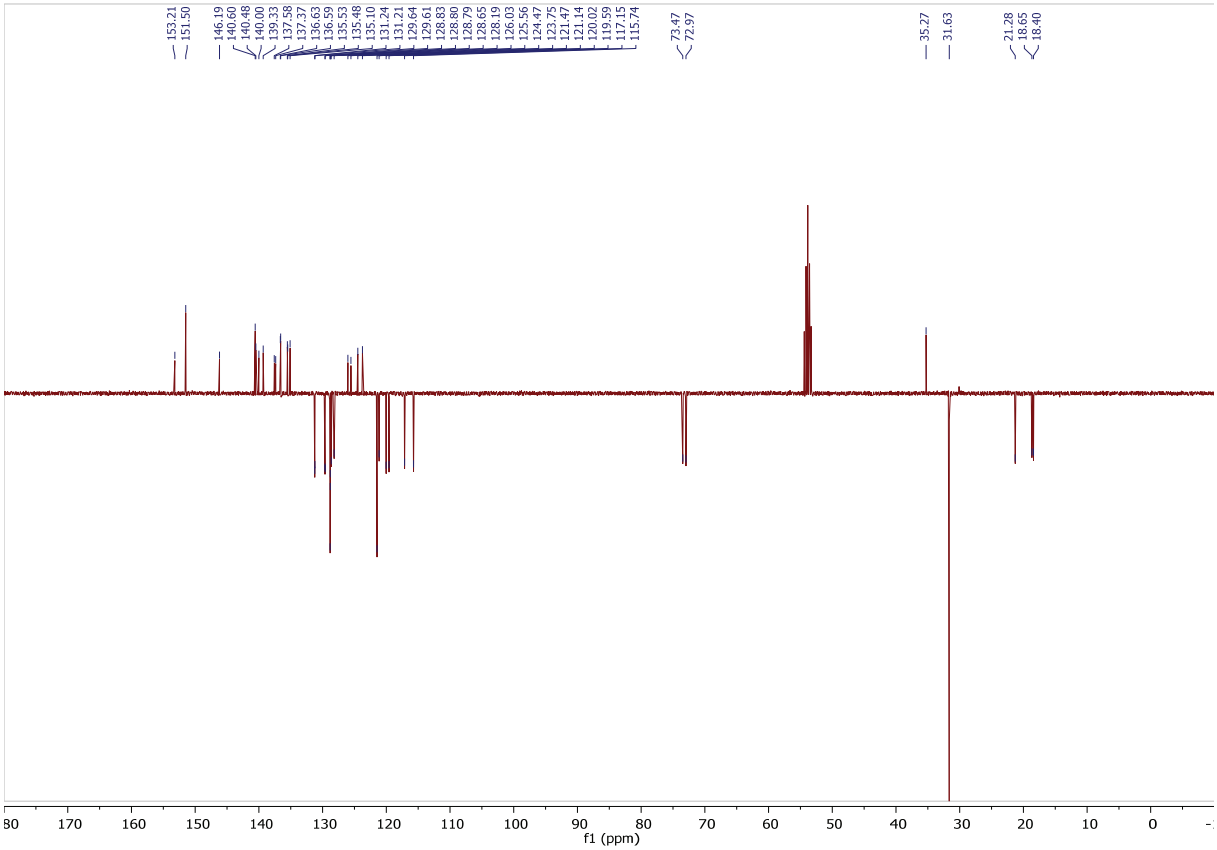


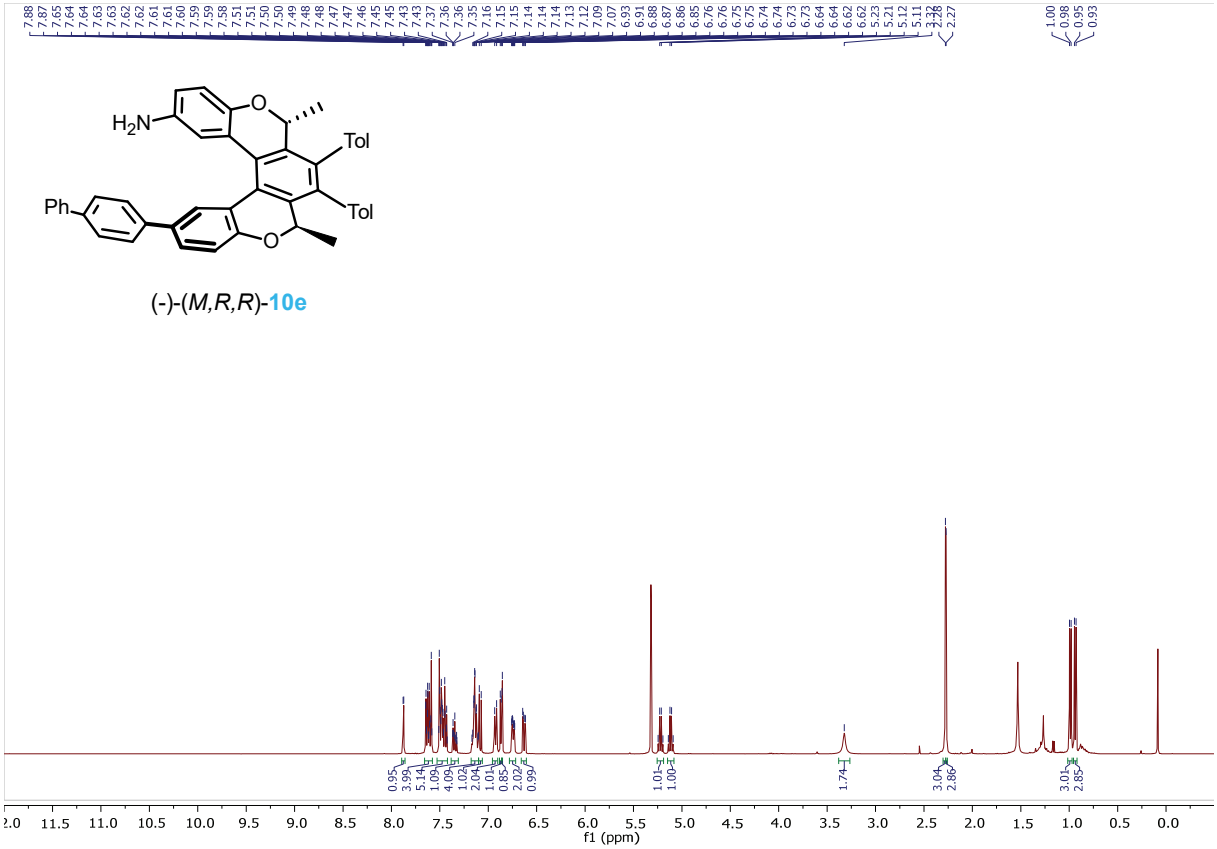
(-)-(*M*,*R*,*R*)-**10c**



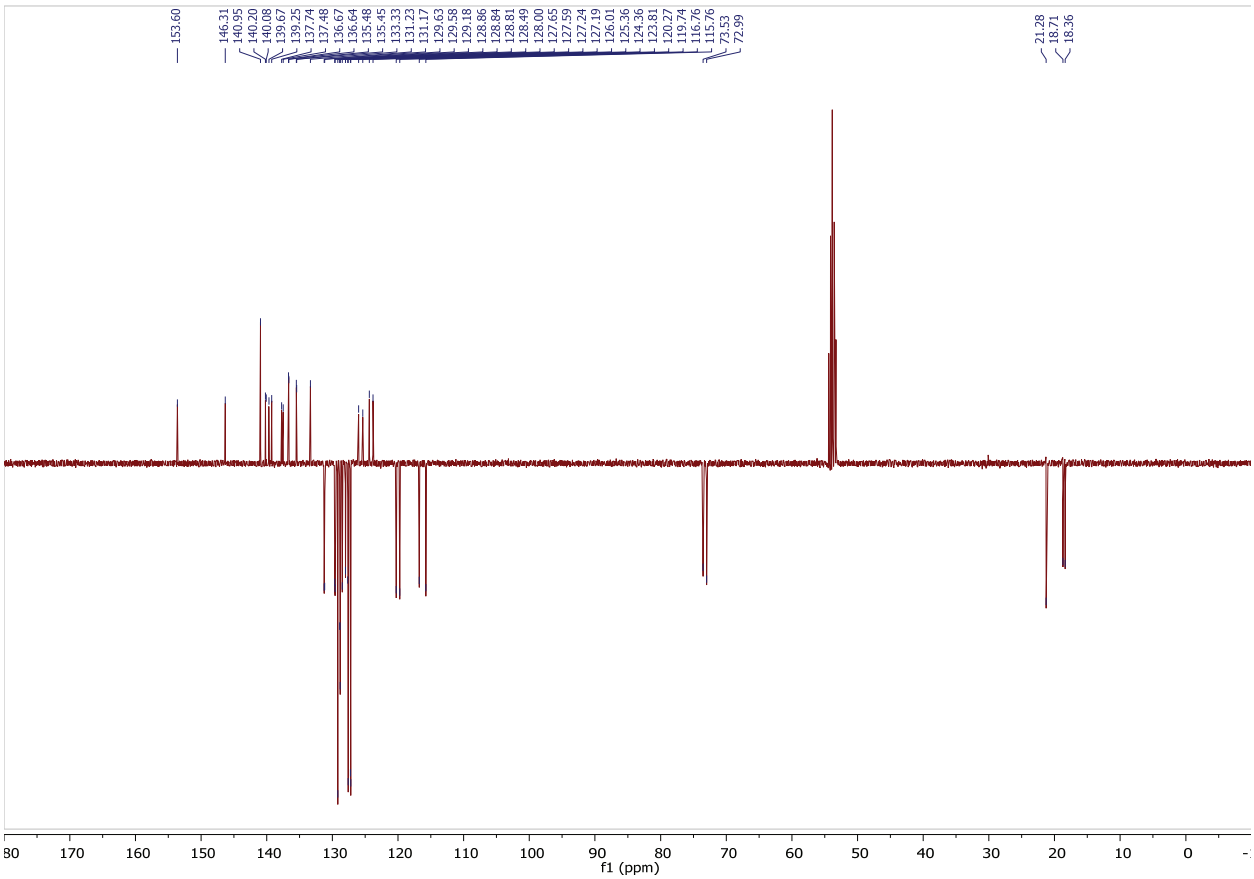


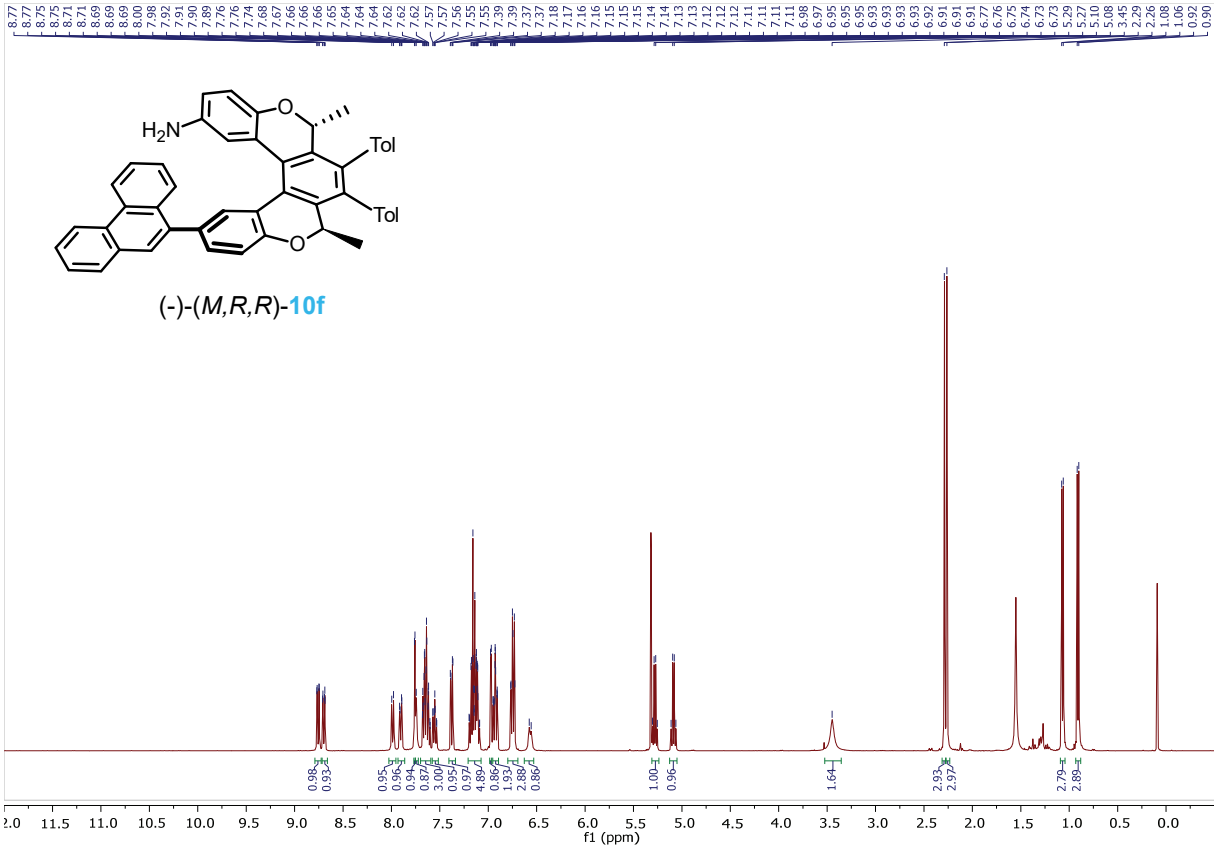
(-)-(*M*,*R*,*R*)-**10d**



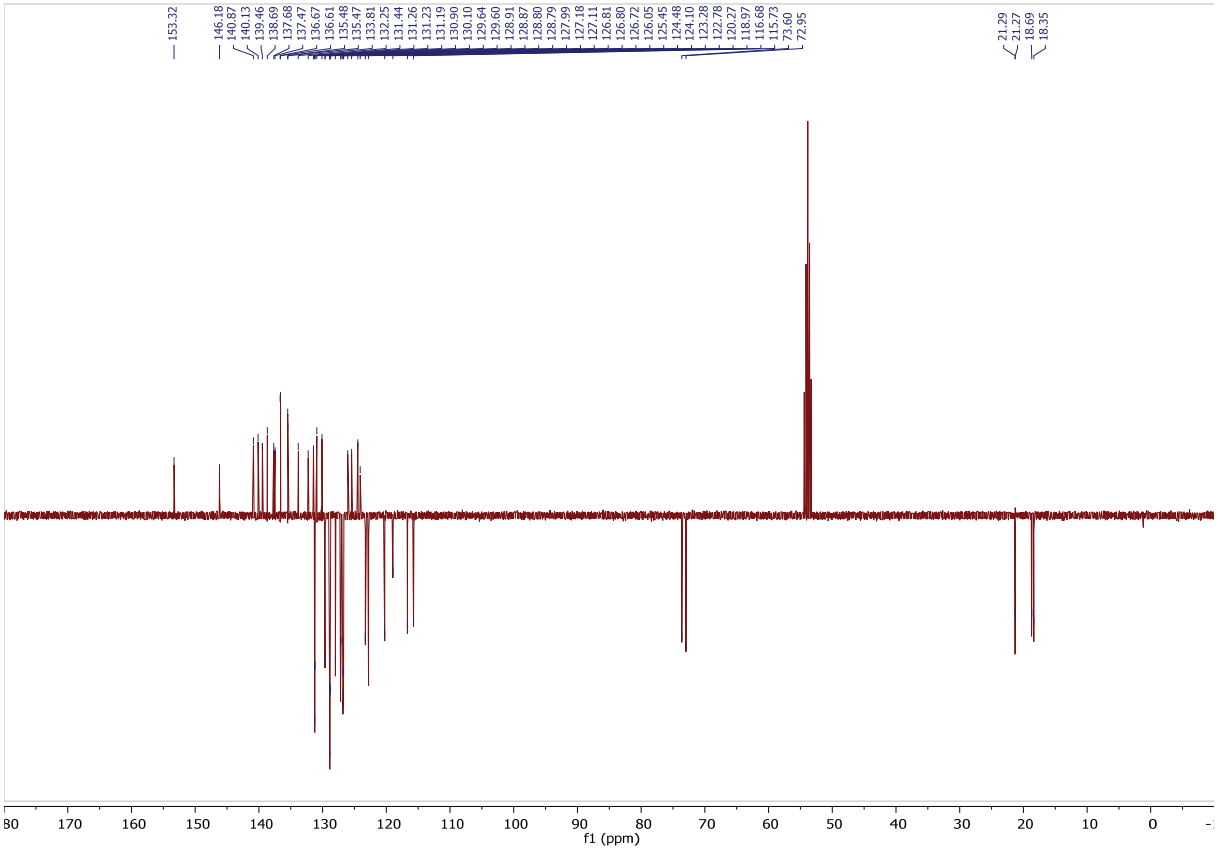


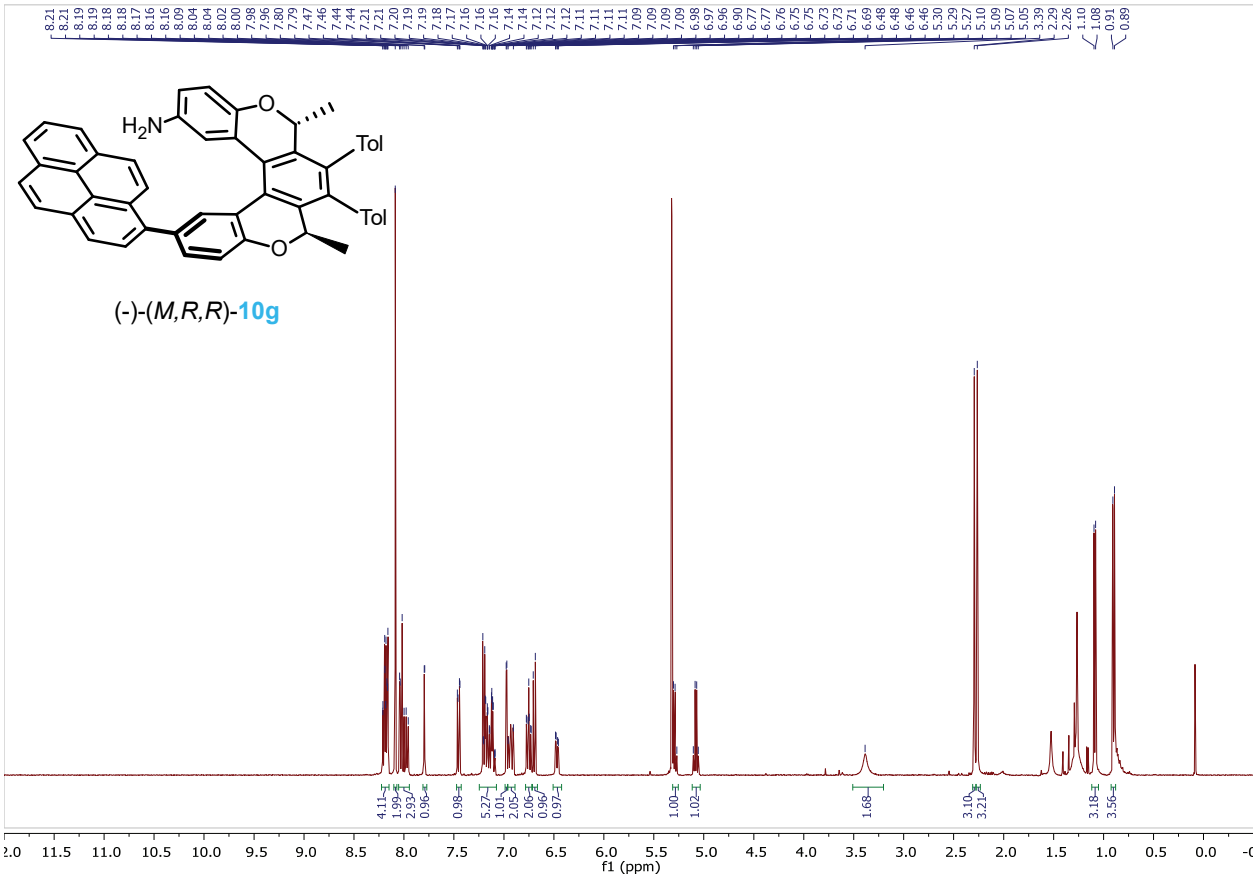
(-)-(*M*,*R*,*R*)-**10e**



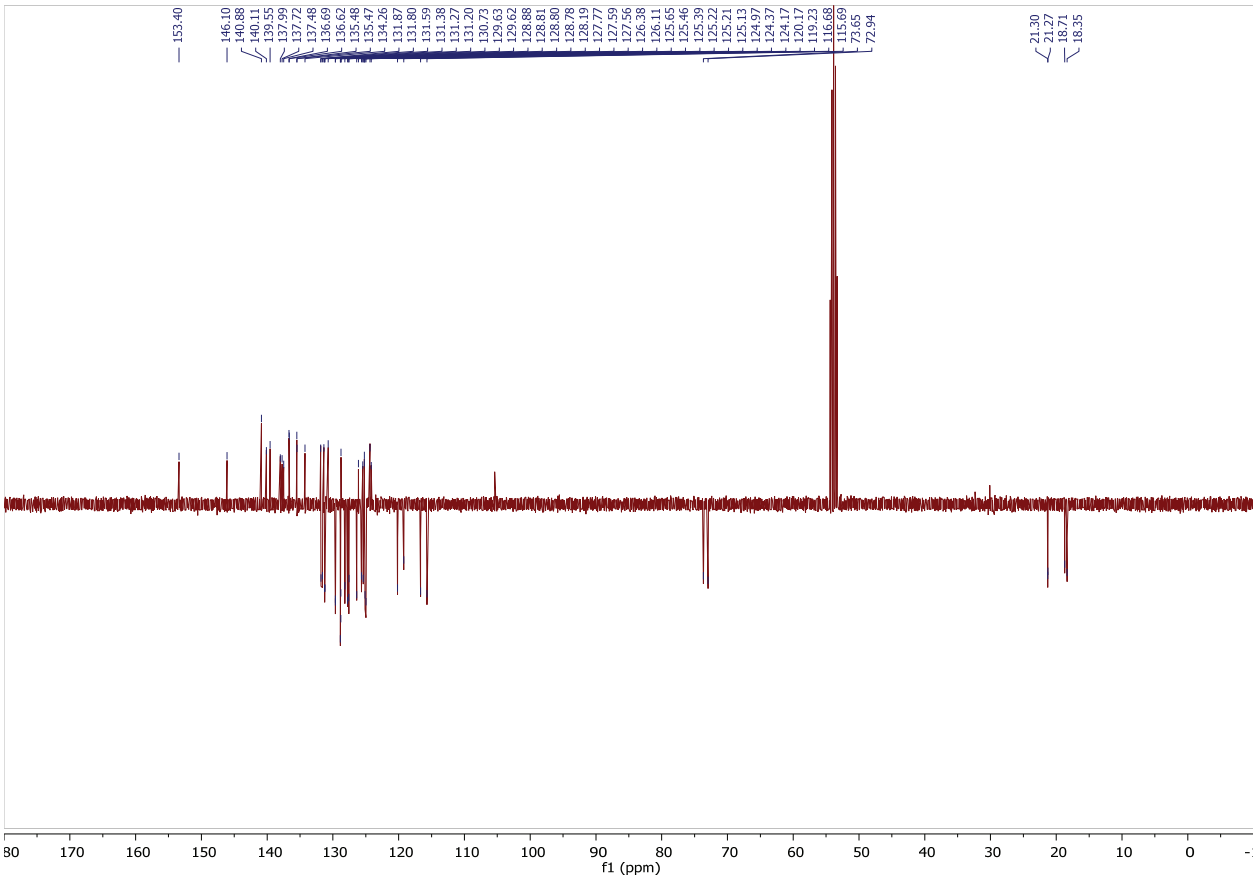


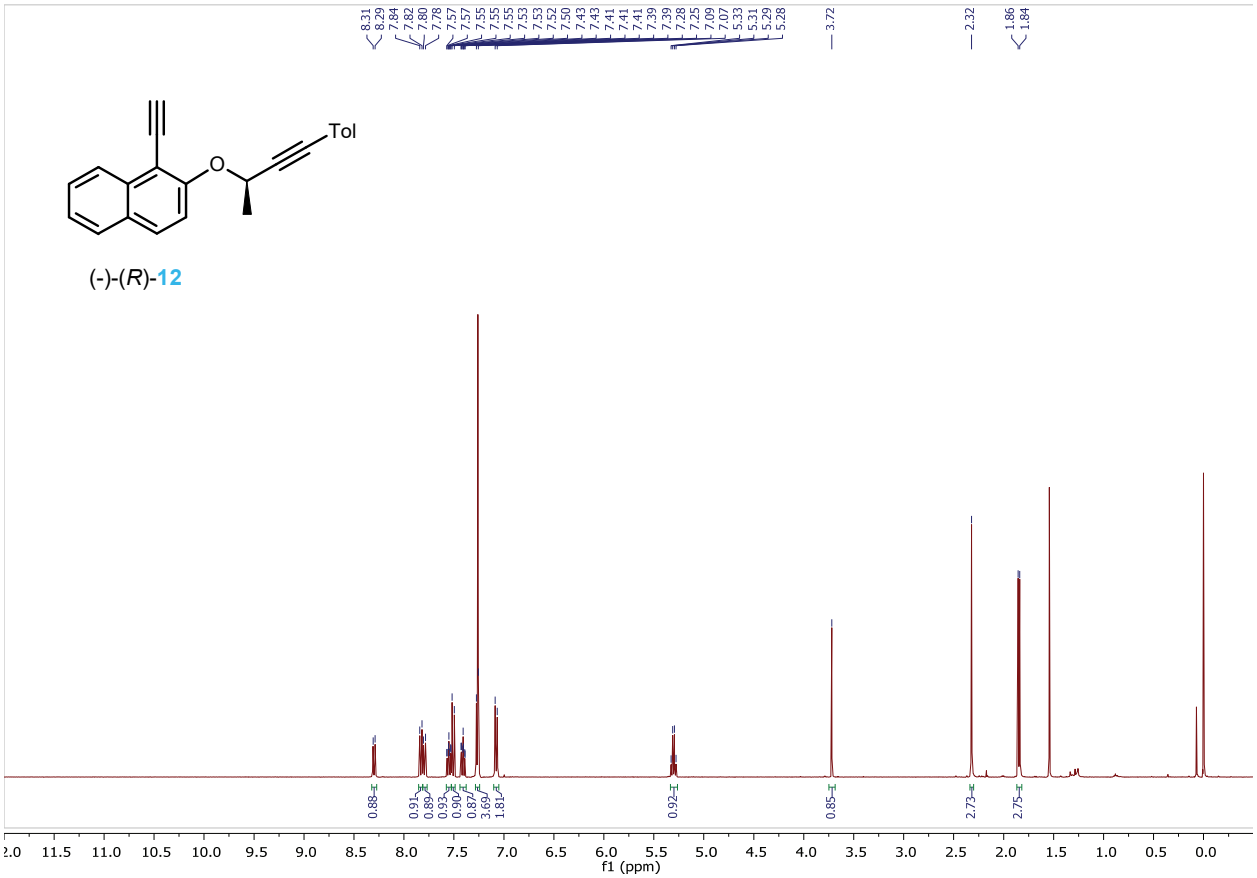
(-)-(*M*,*R*,*R*)-**10f**

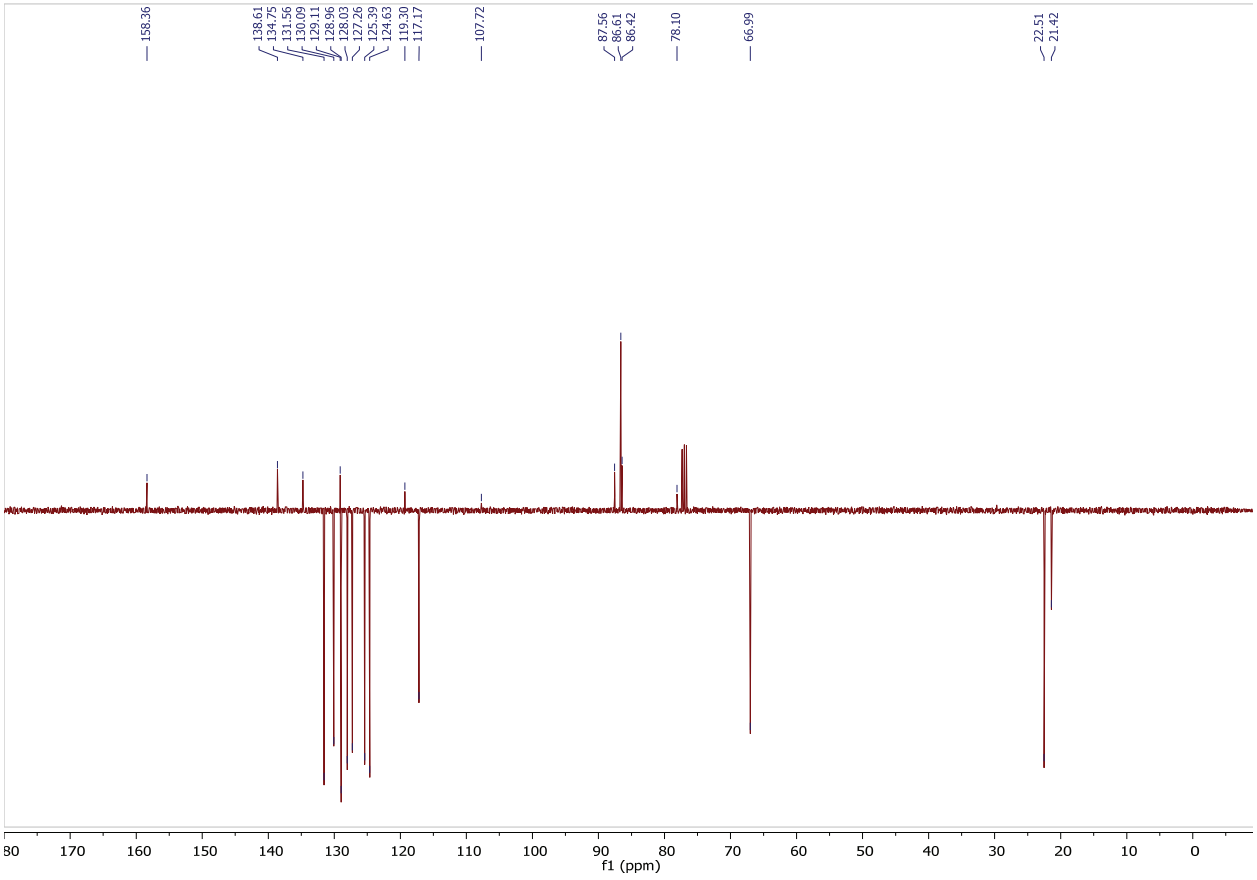


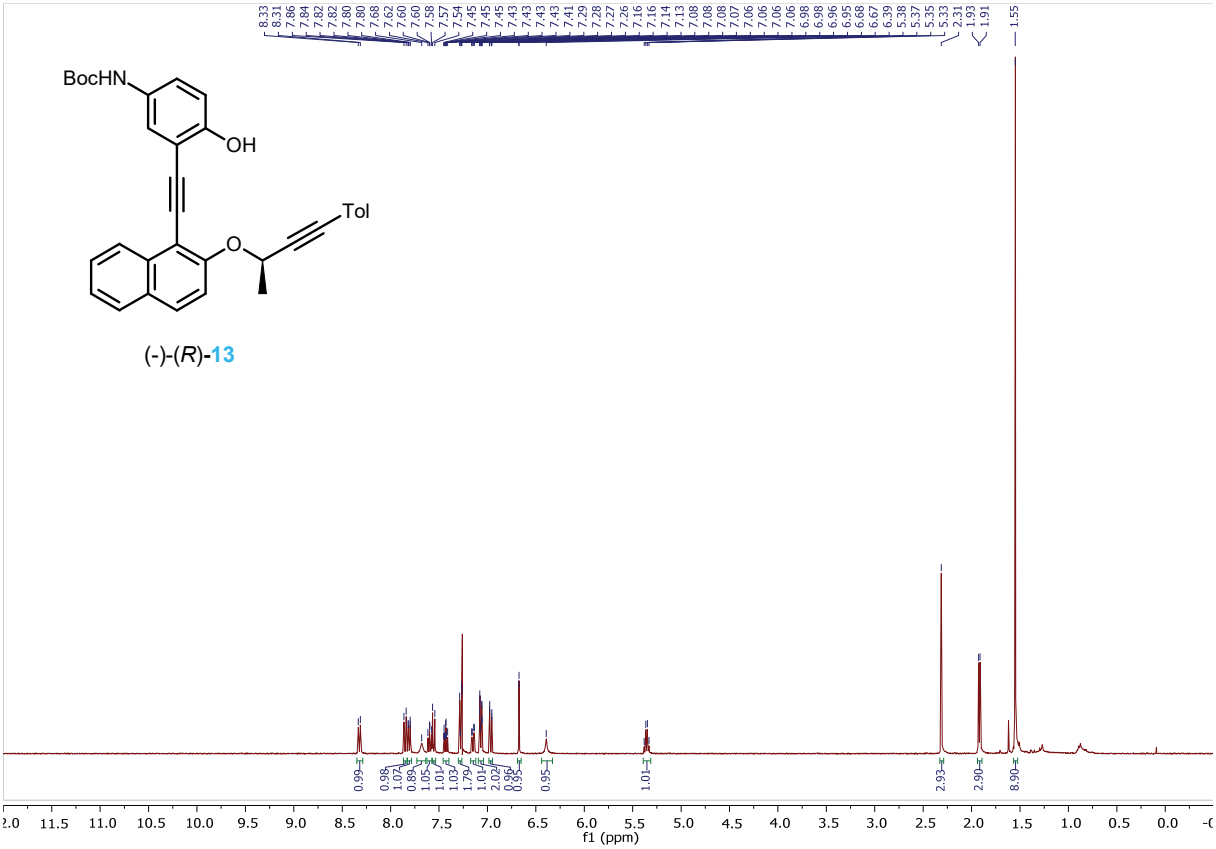


(-)-(*M,R,R*)-**10g**

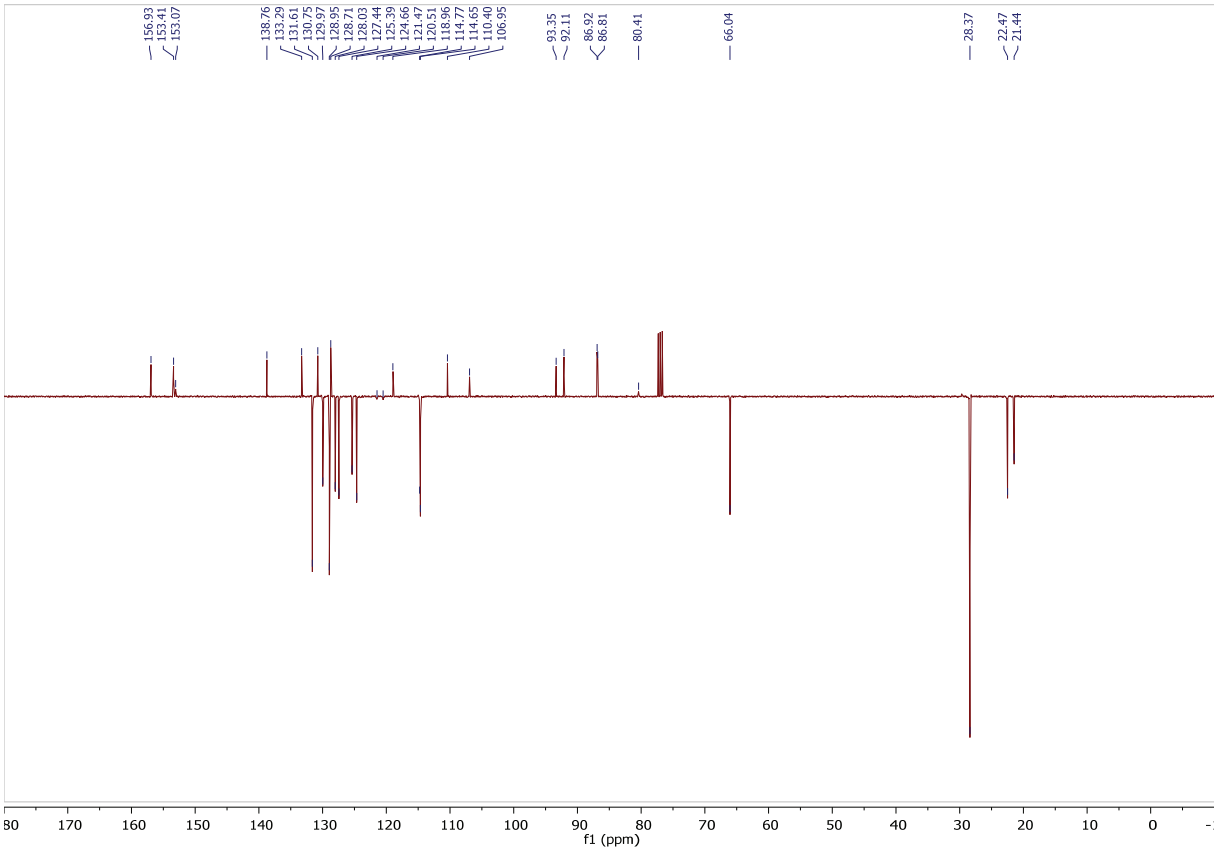


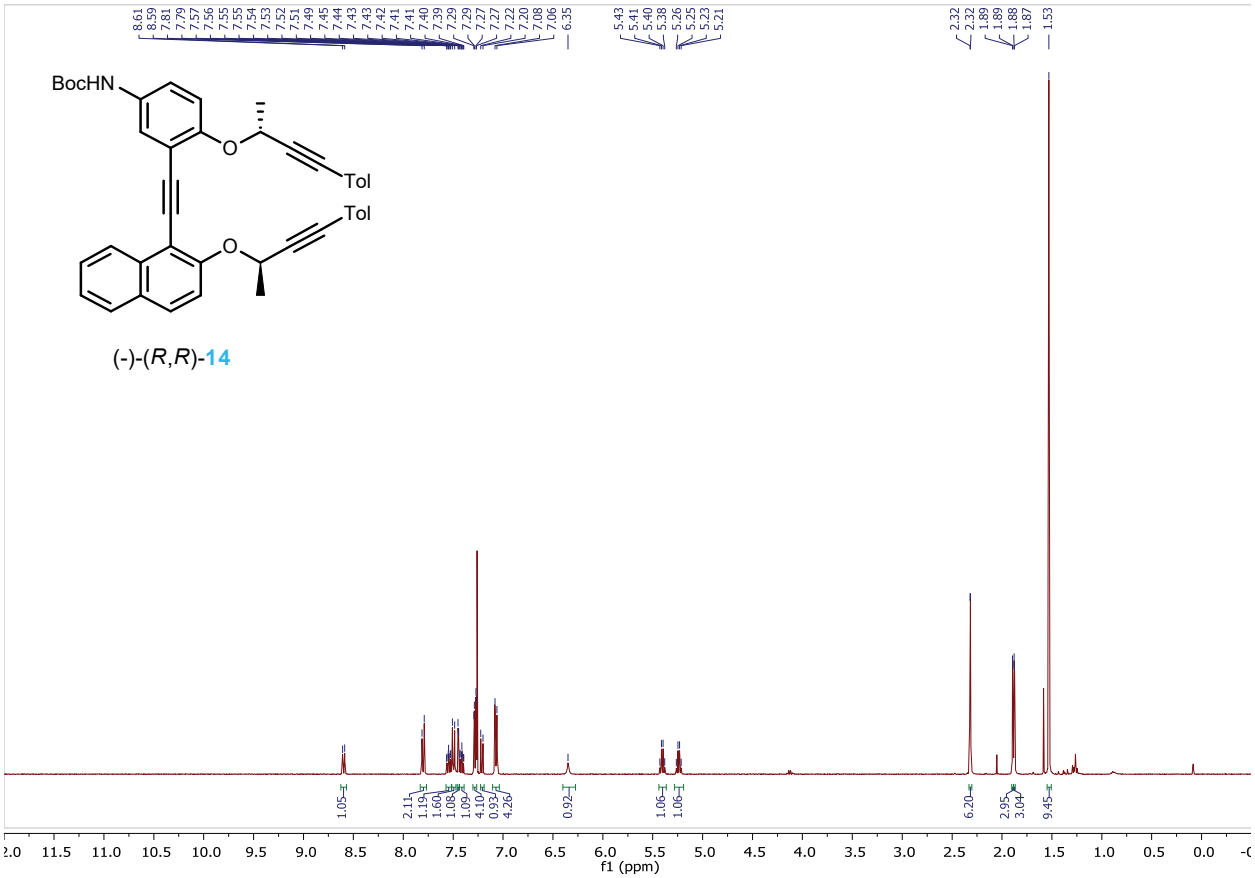

Tol
O
(-)-(R)-12
f1 (ppm)


f1 (ppm)

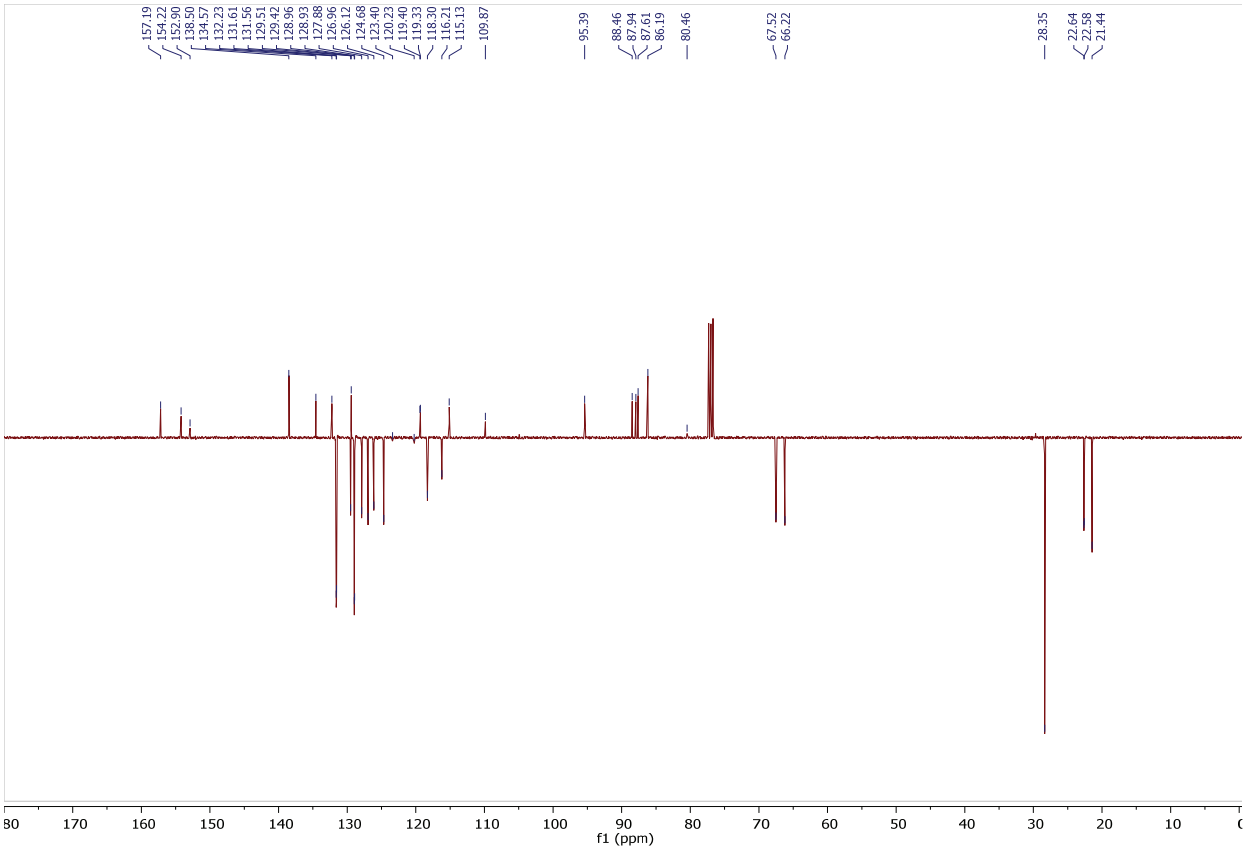


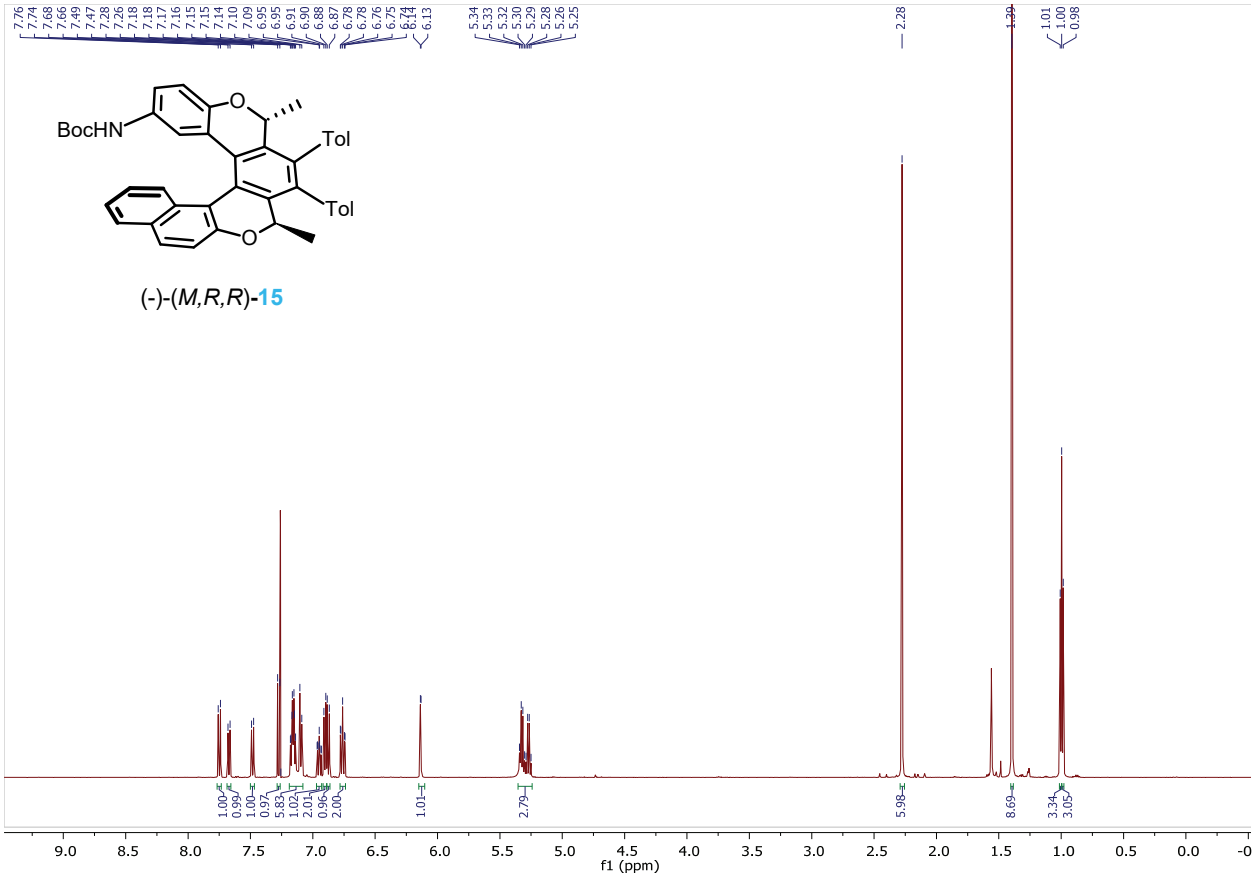
(-)-(*R*)-**13**



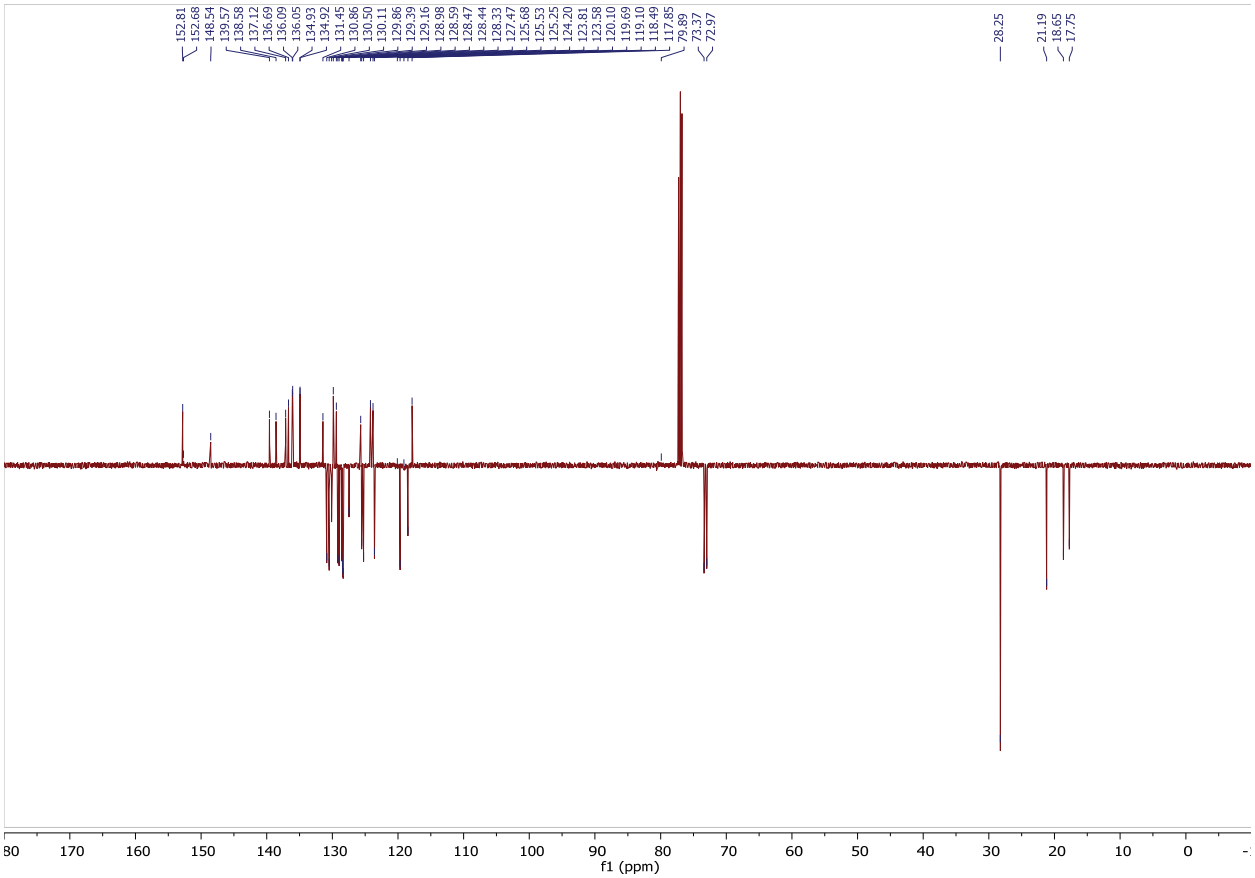


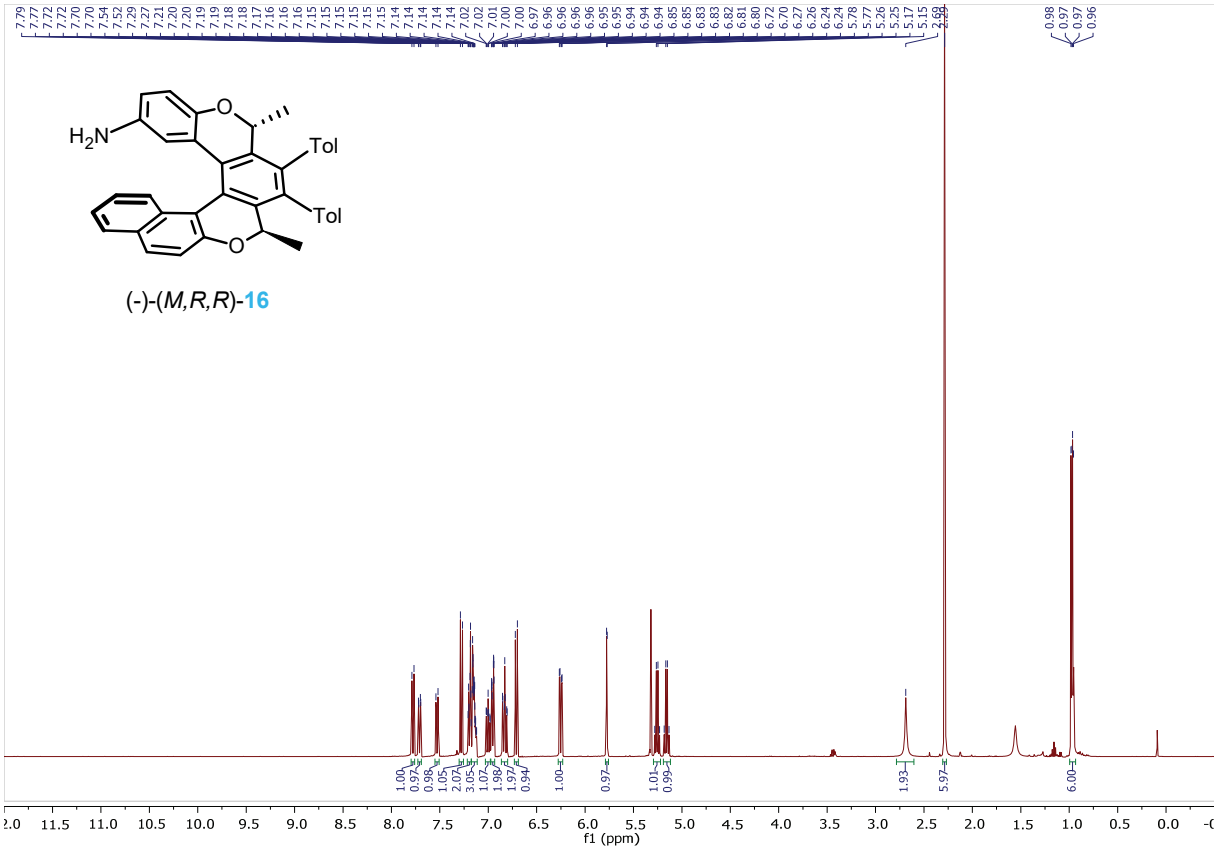
(-)-(*R*,*R*)-**14**



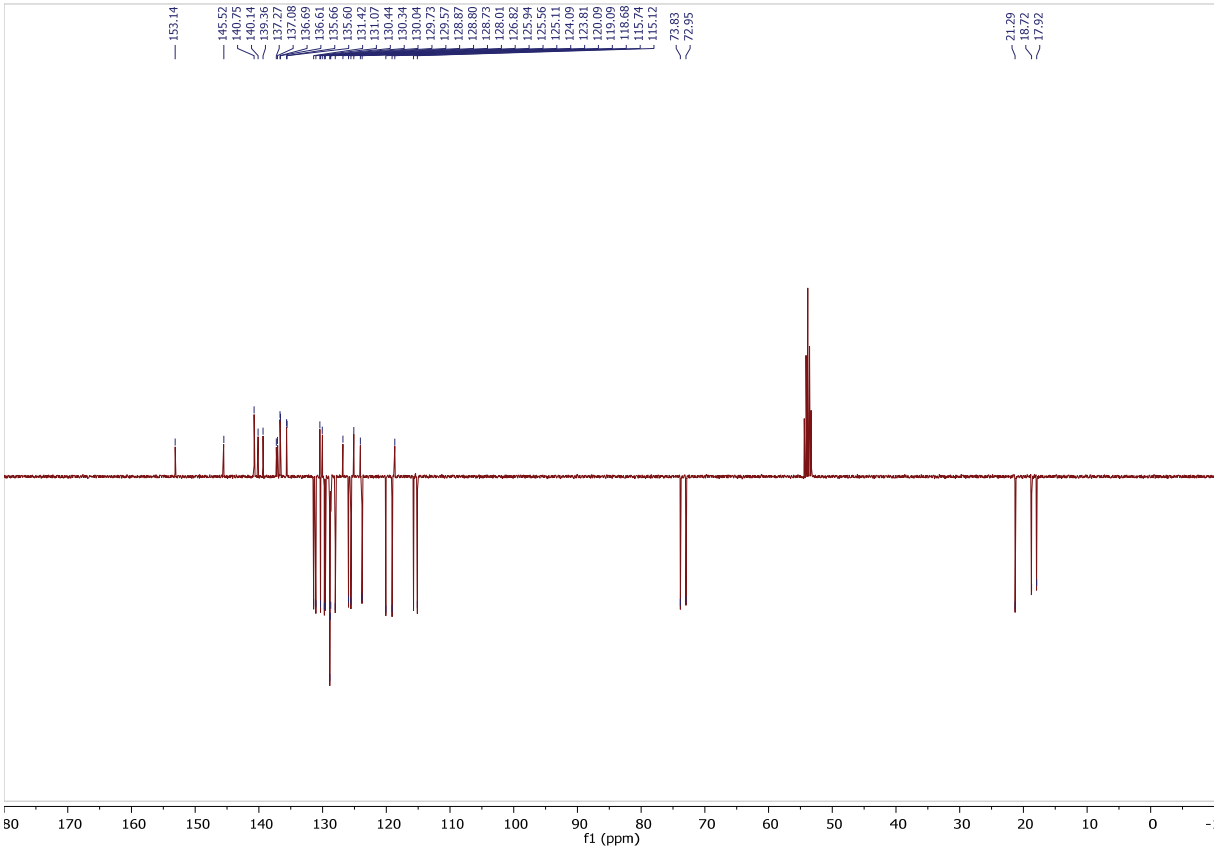


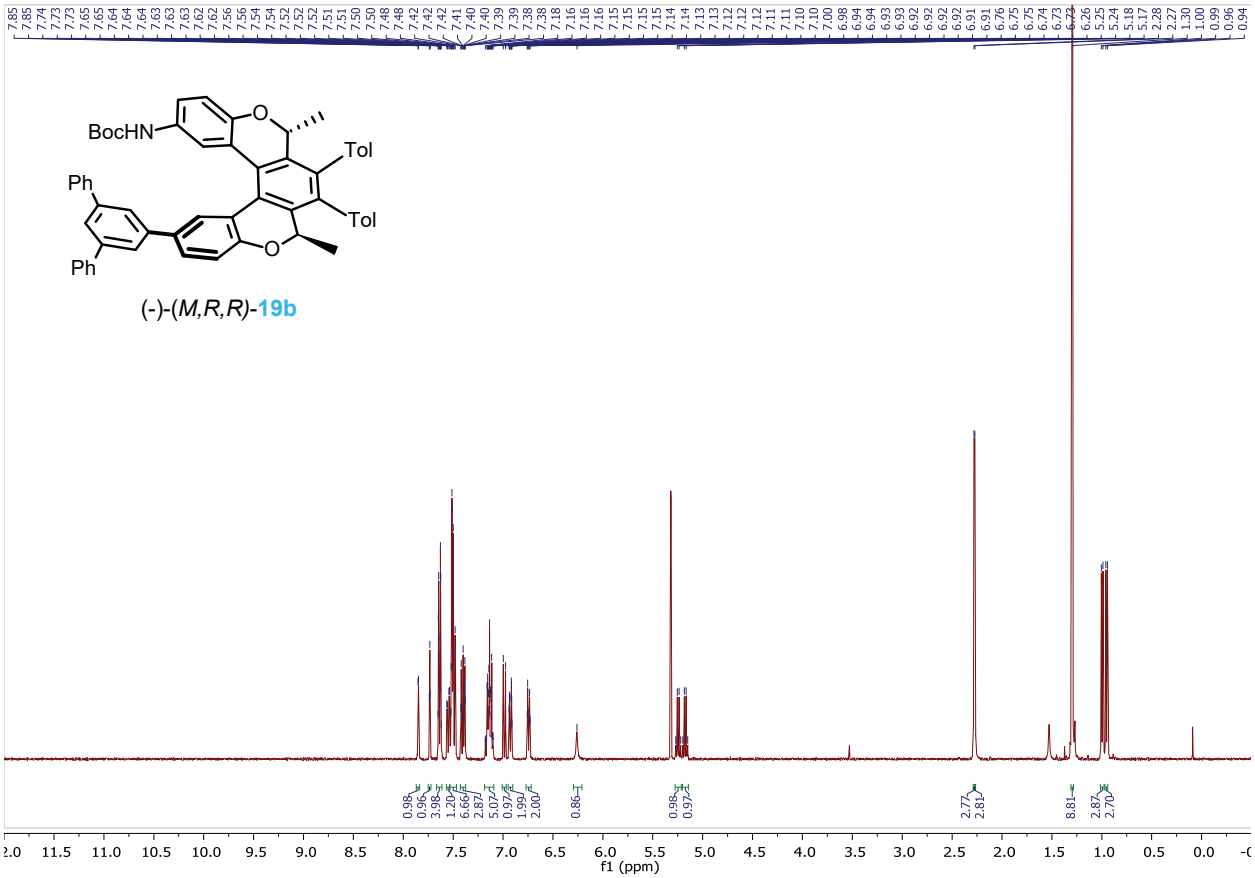
(-)-(*M,R,R*)-**15**



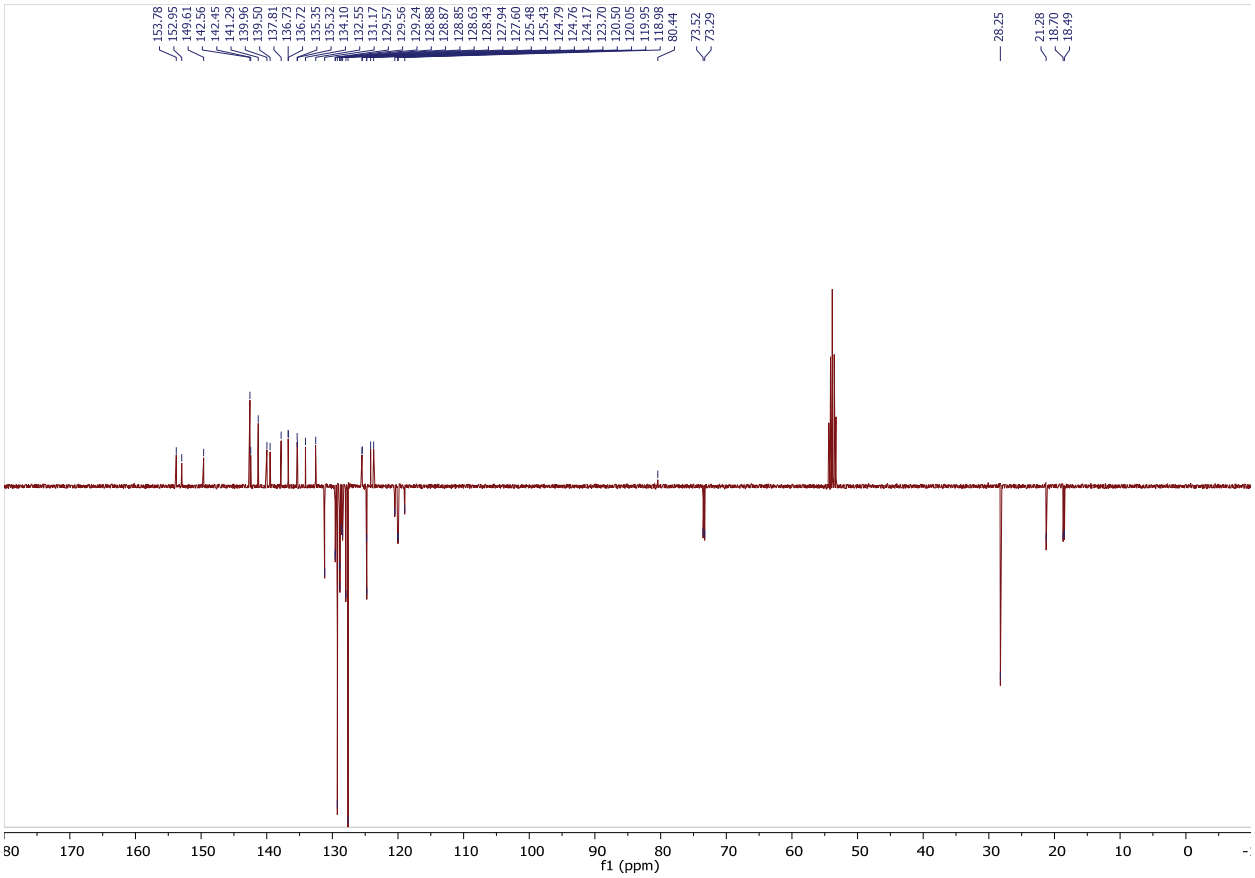


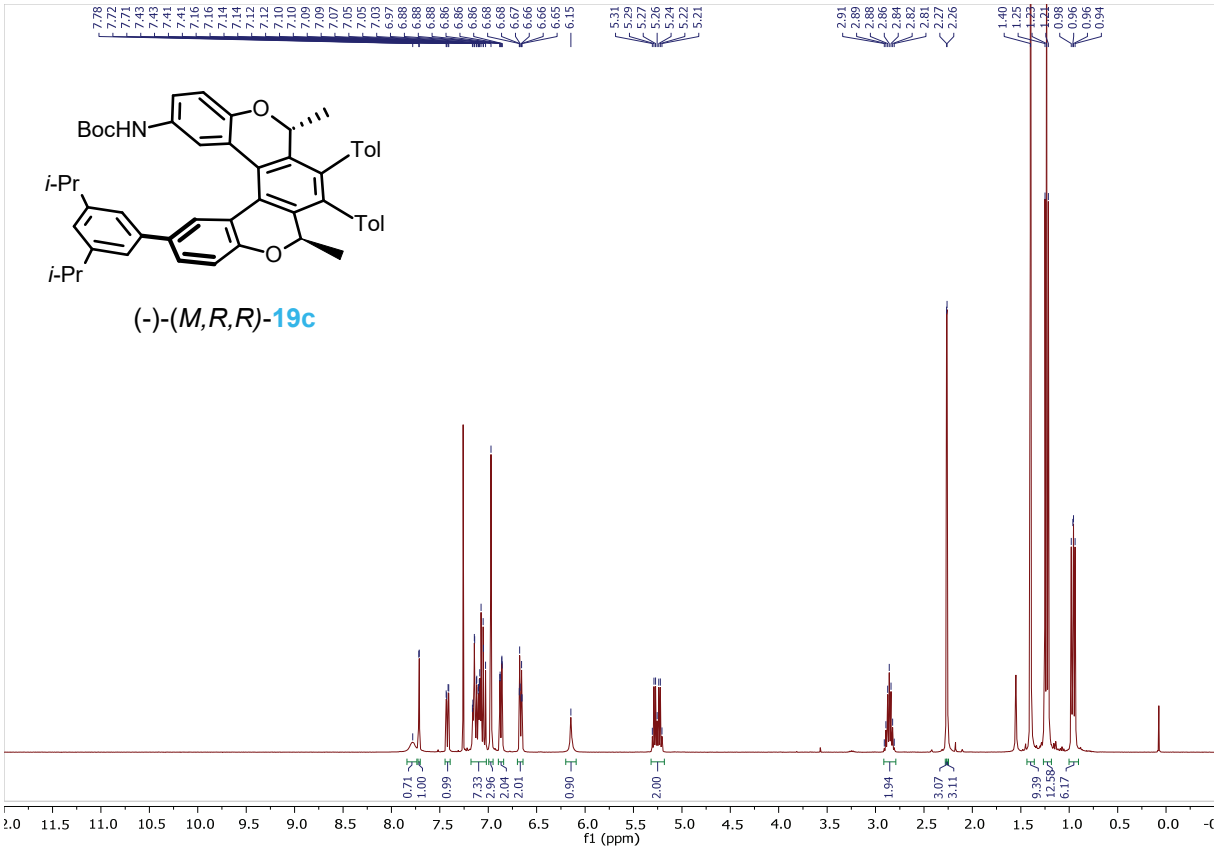
(-)-(*M*,*R*,*R*)-**16**

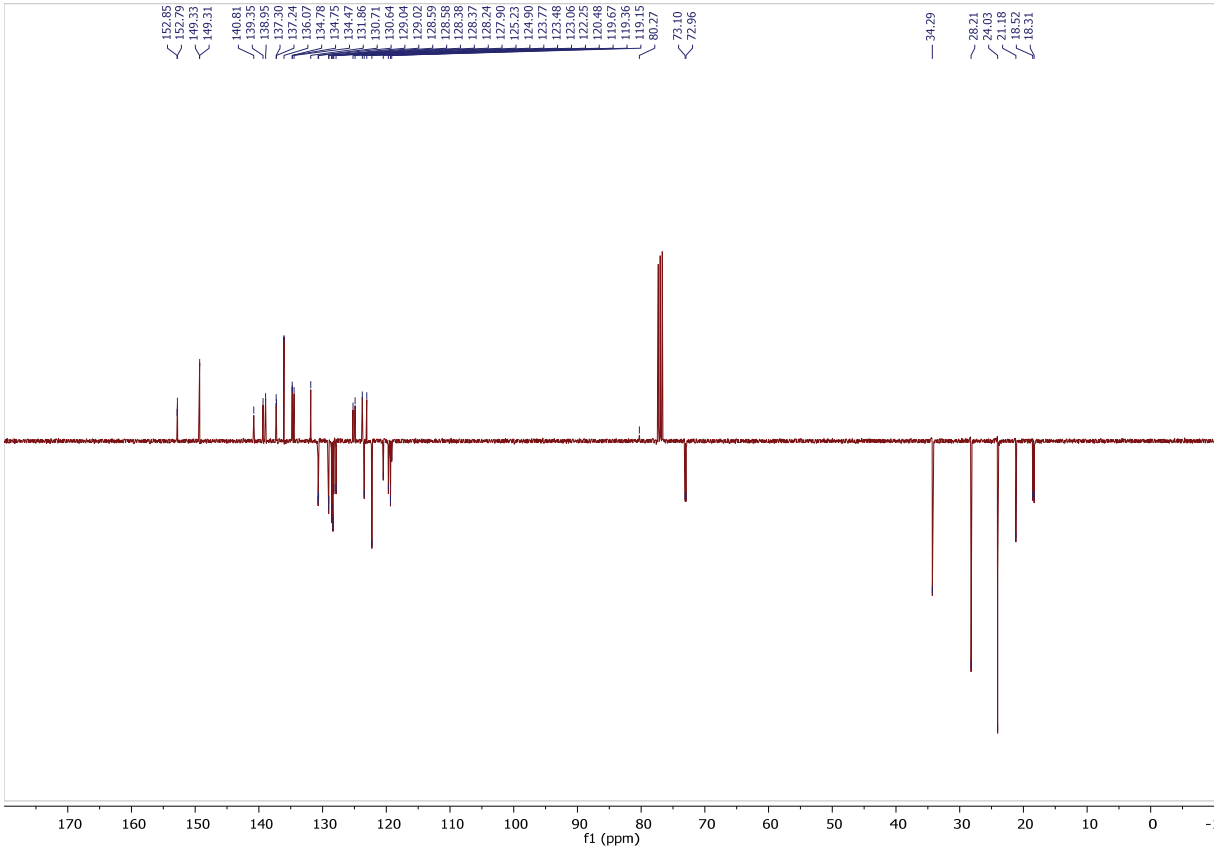


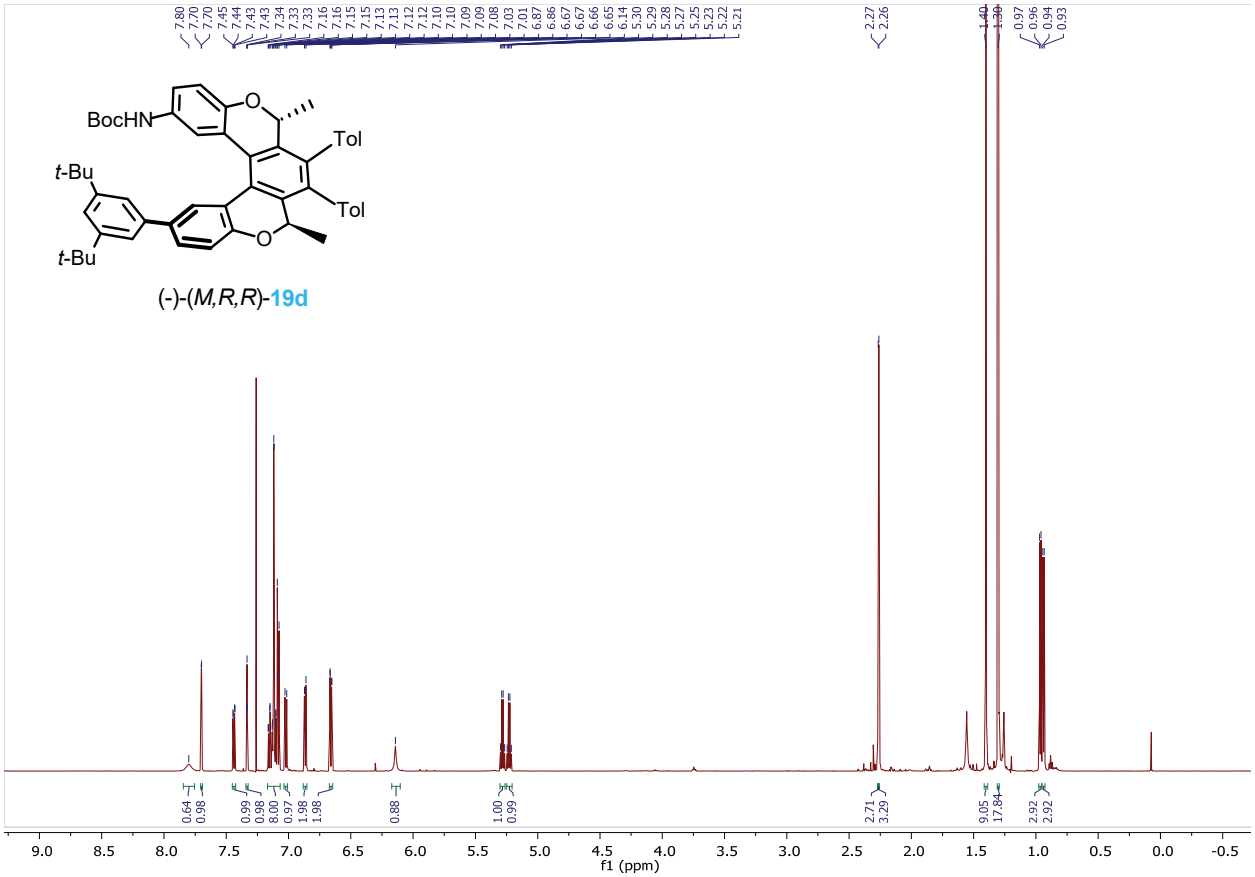


(-)-(*M,R,R*)-**19b**

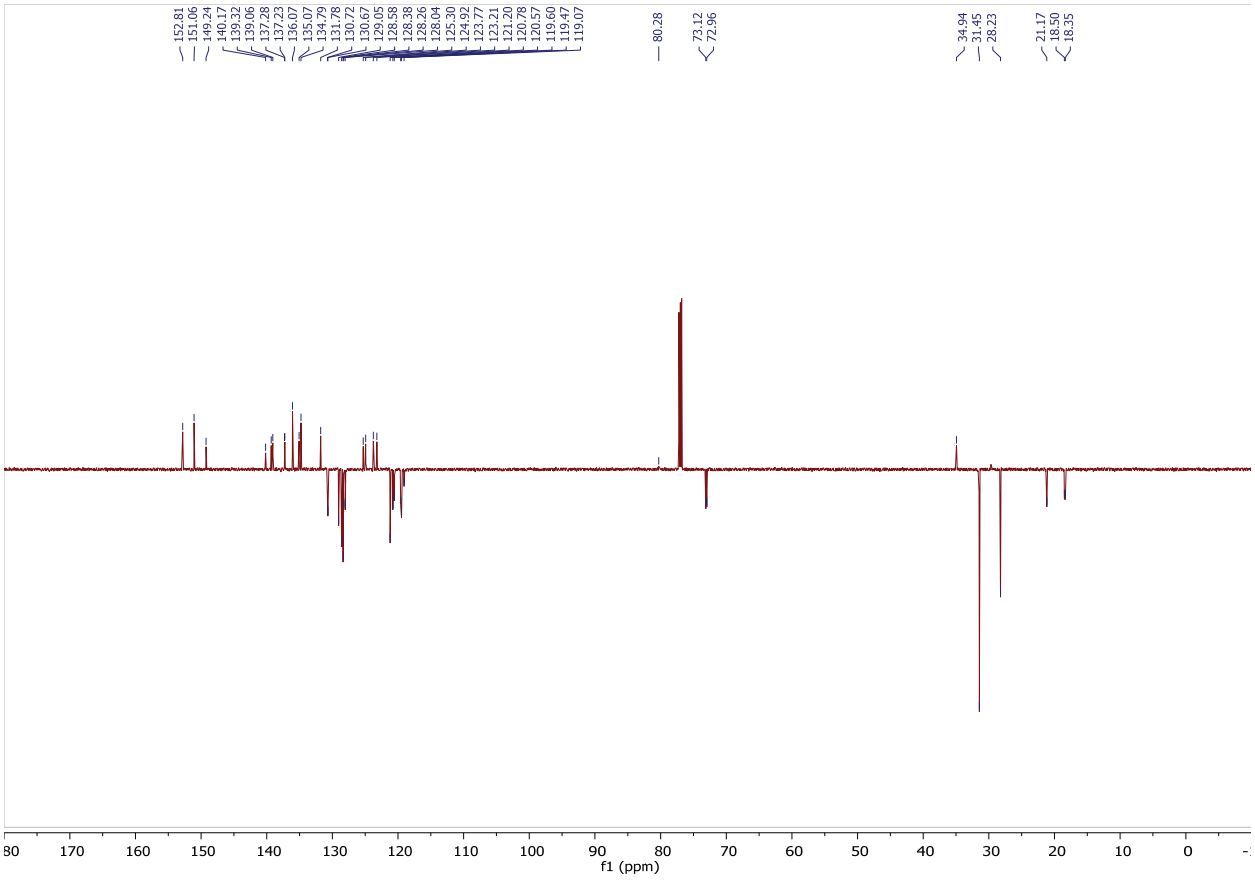


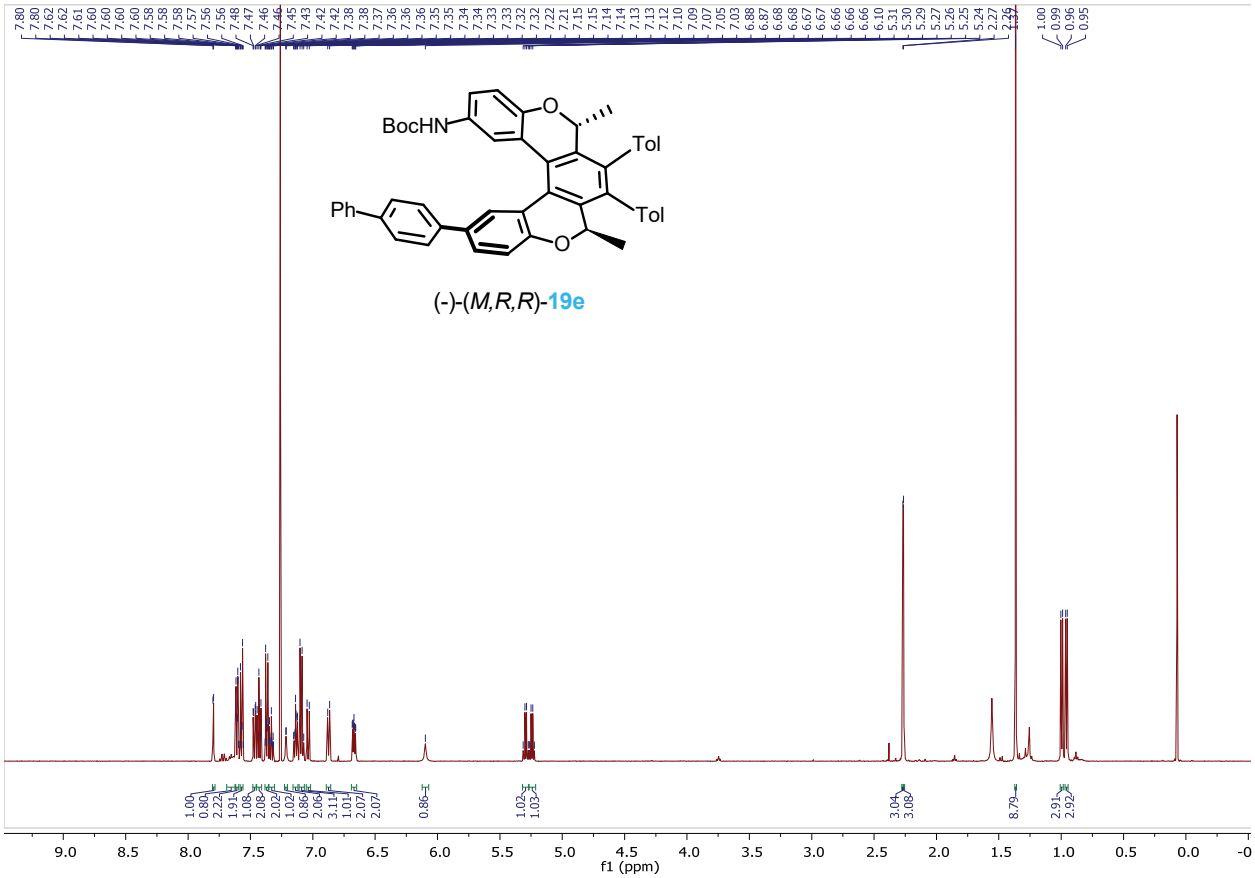

BocHN
O
Tol
i-Pr
Tol
O
i-Pr
(-)-(M,R,R)-19c
f1 (ppm)


f1 (ppm)

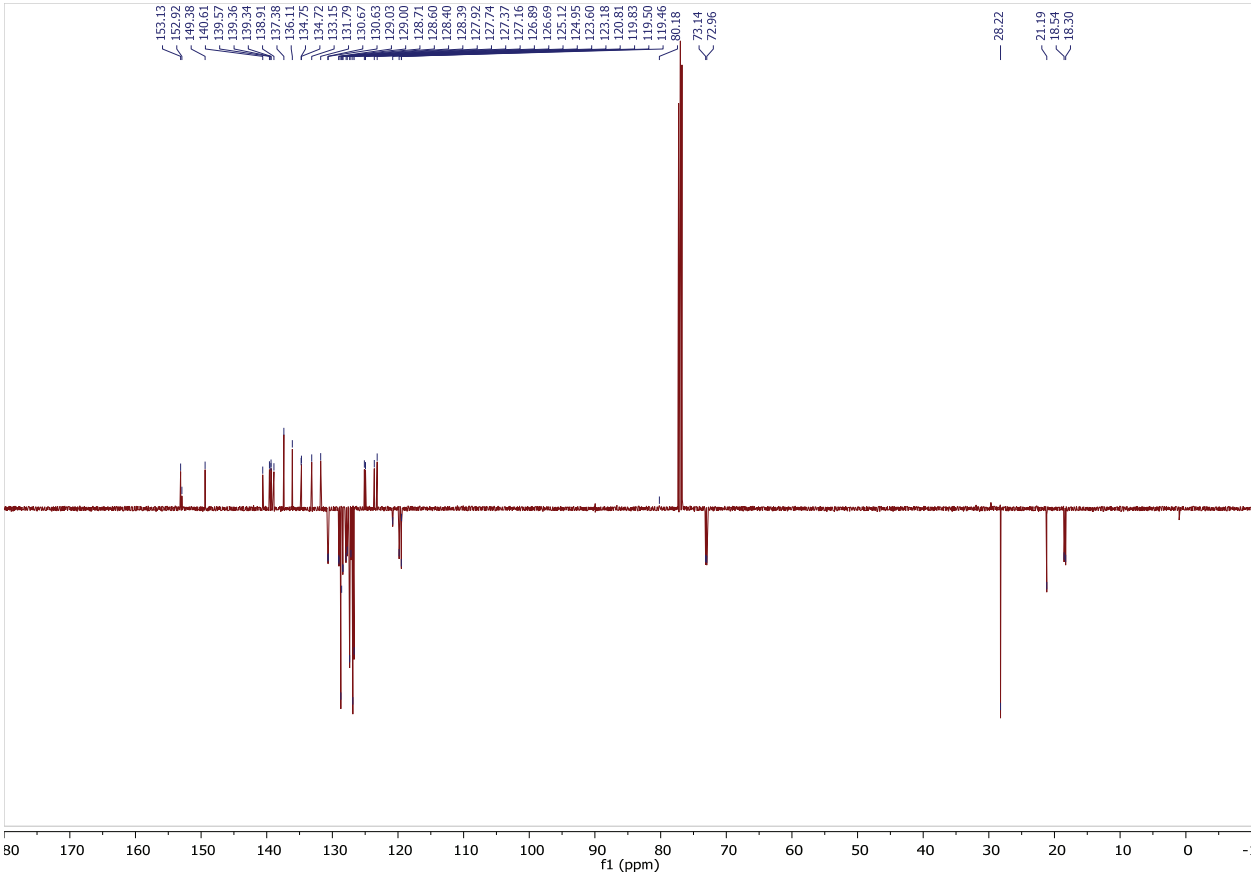


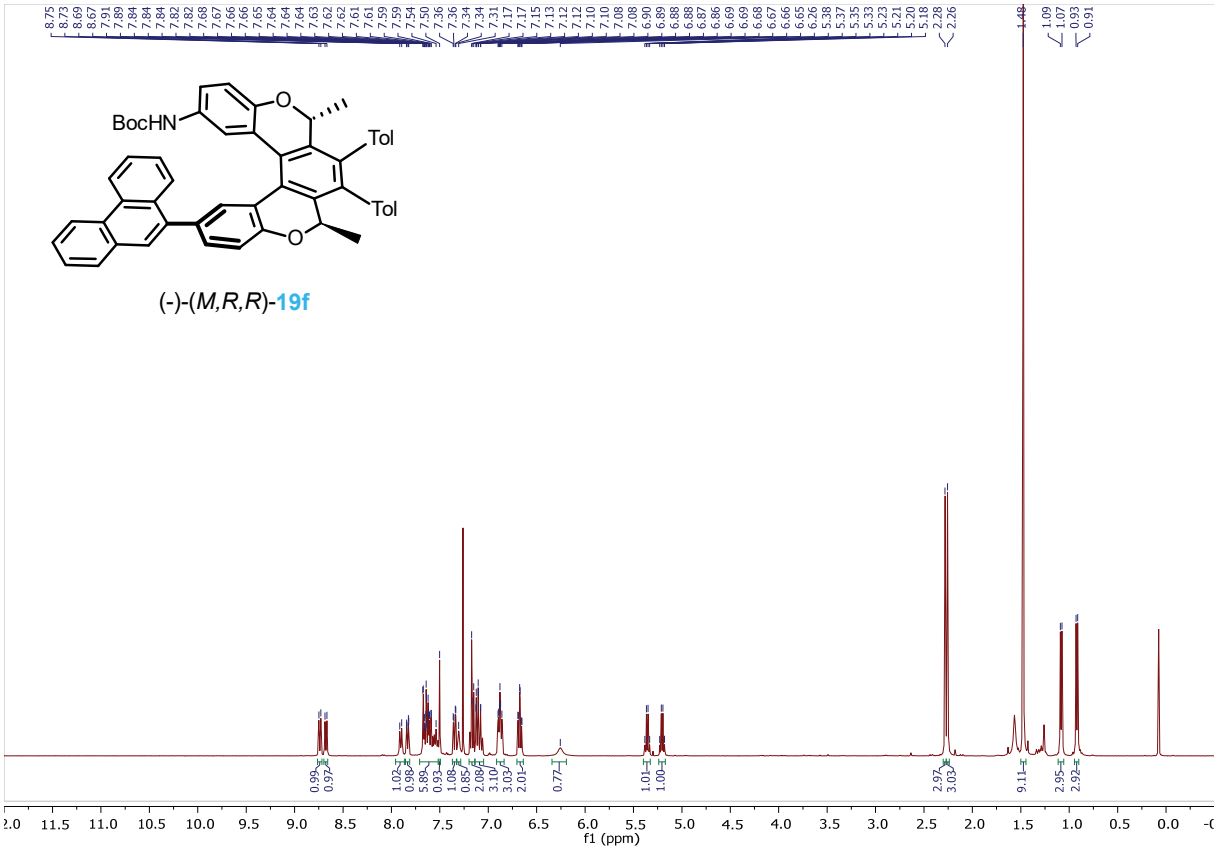
(-)-(*M,R,R*)-**19d**



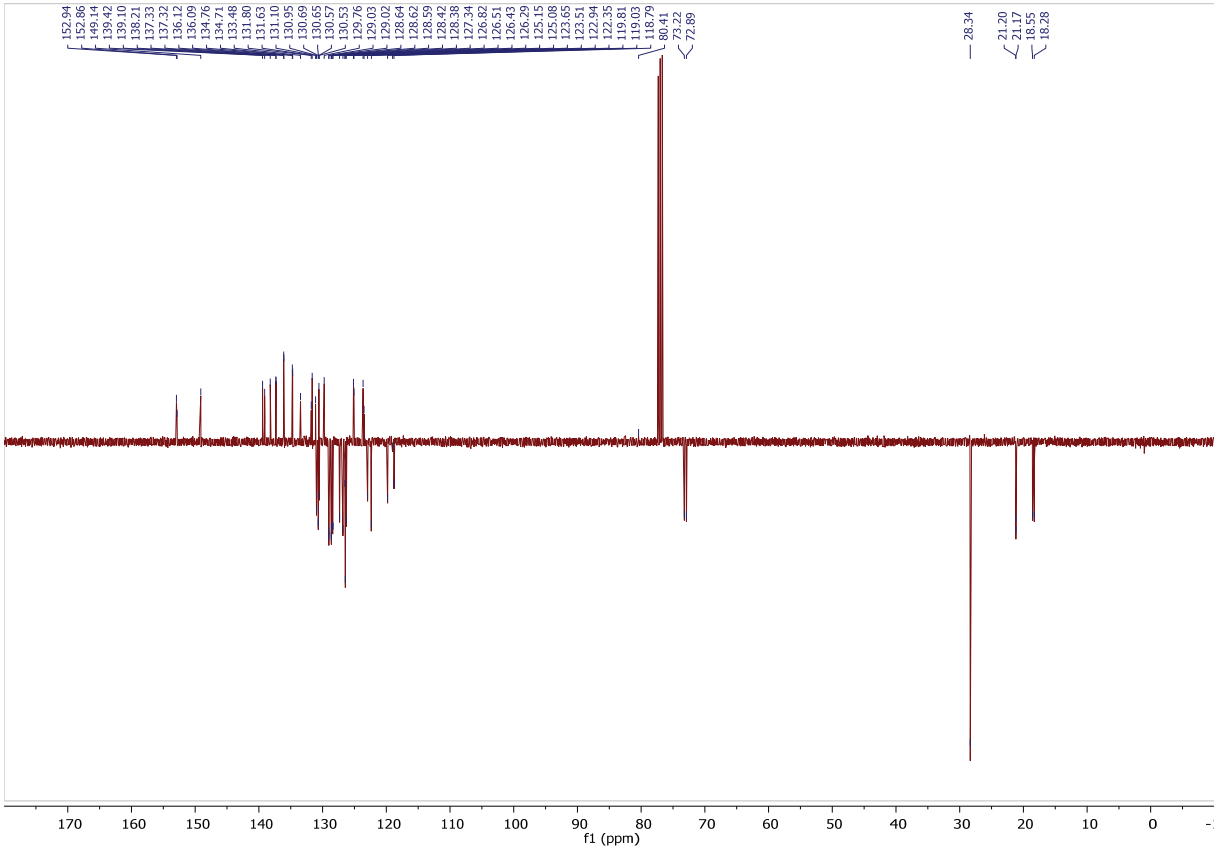


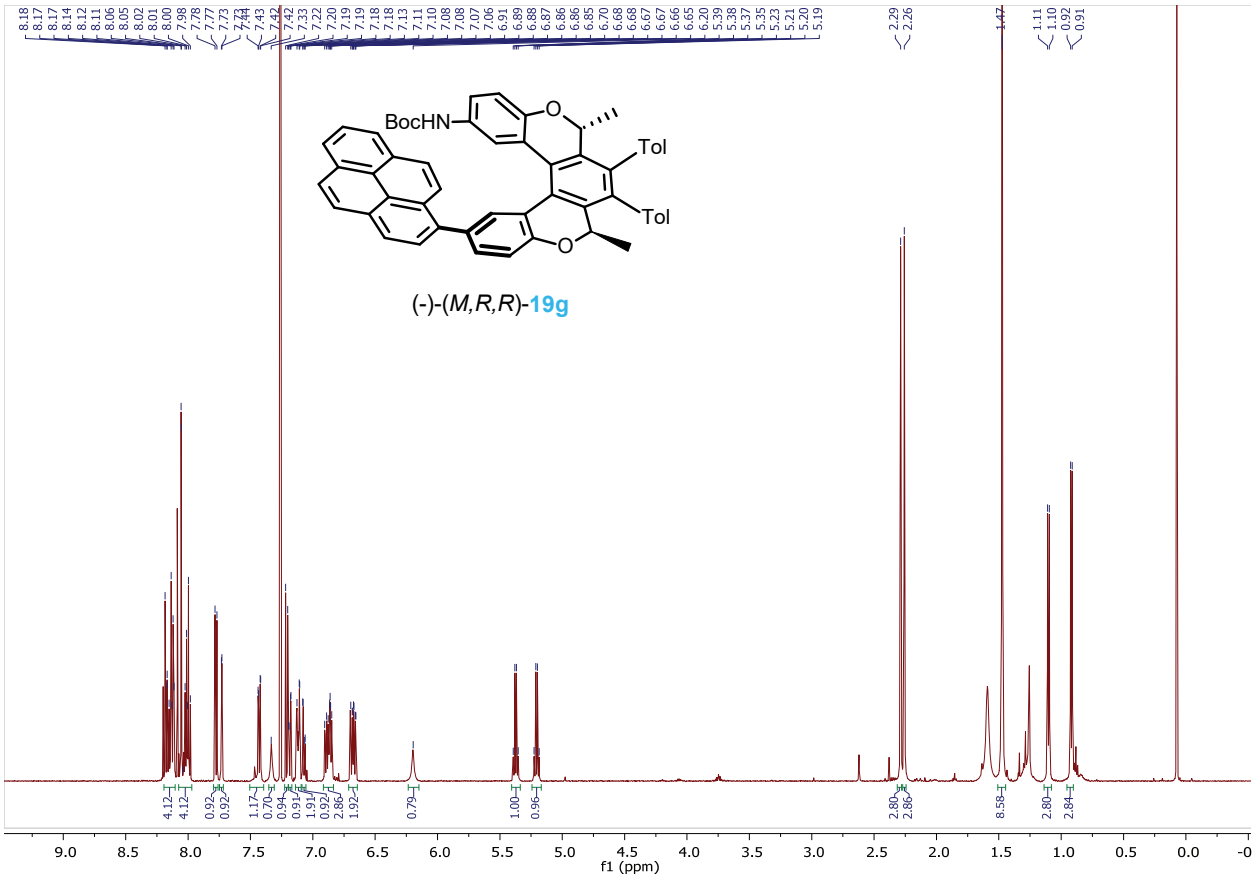
(-)-(*M*,*R*,*R*)-**19e**



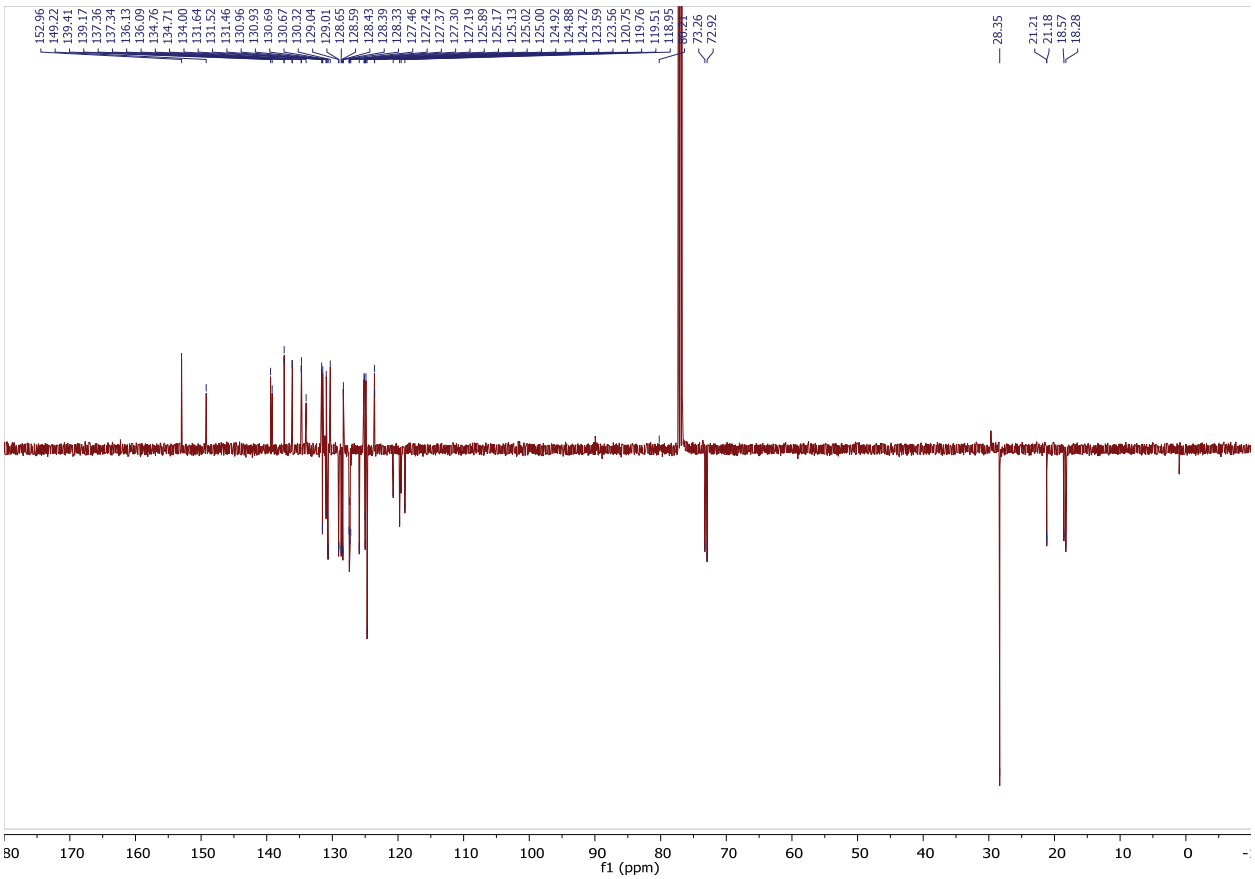


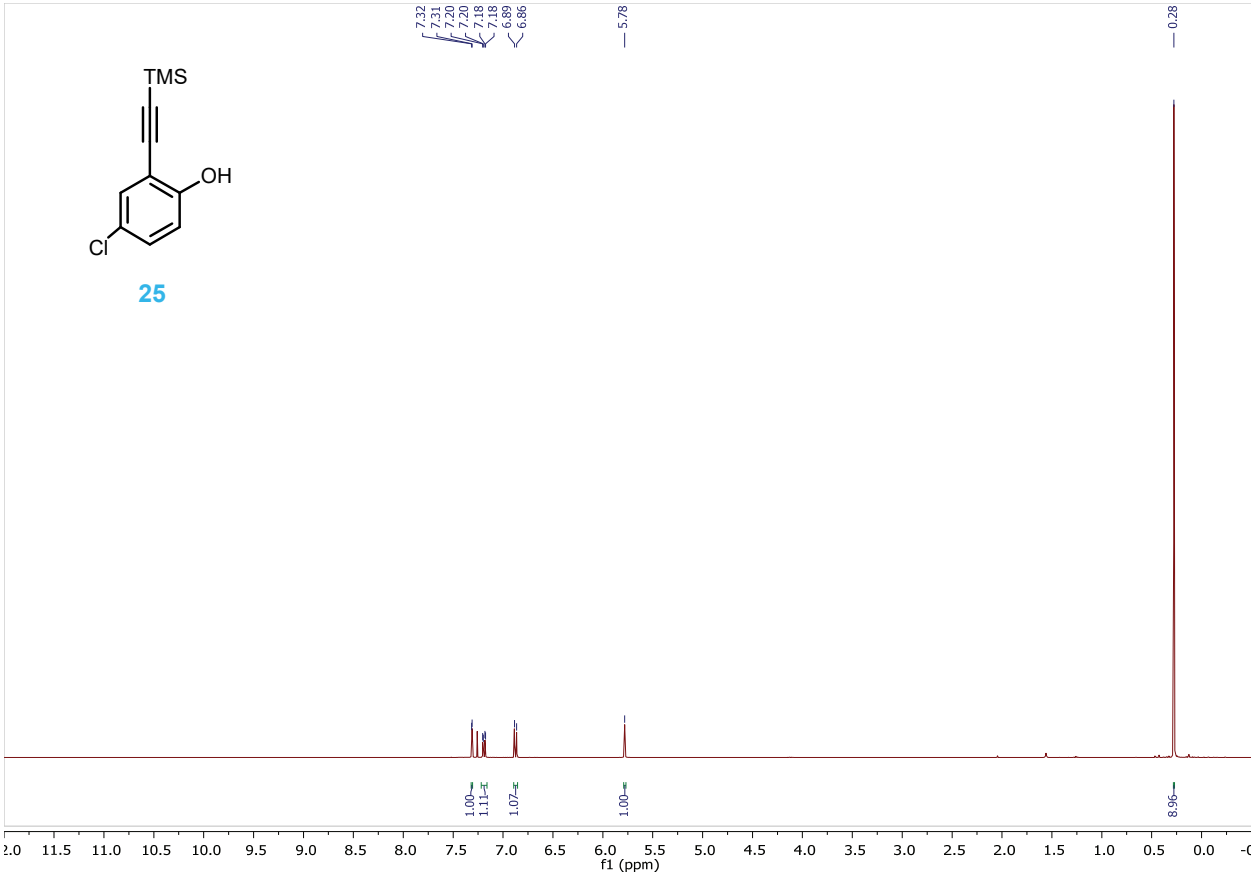
(-)-(*M*,*R*,*R*)-**19f**

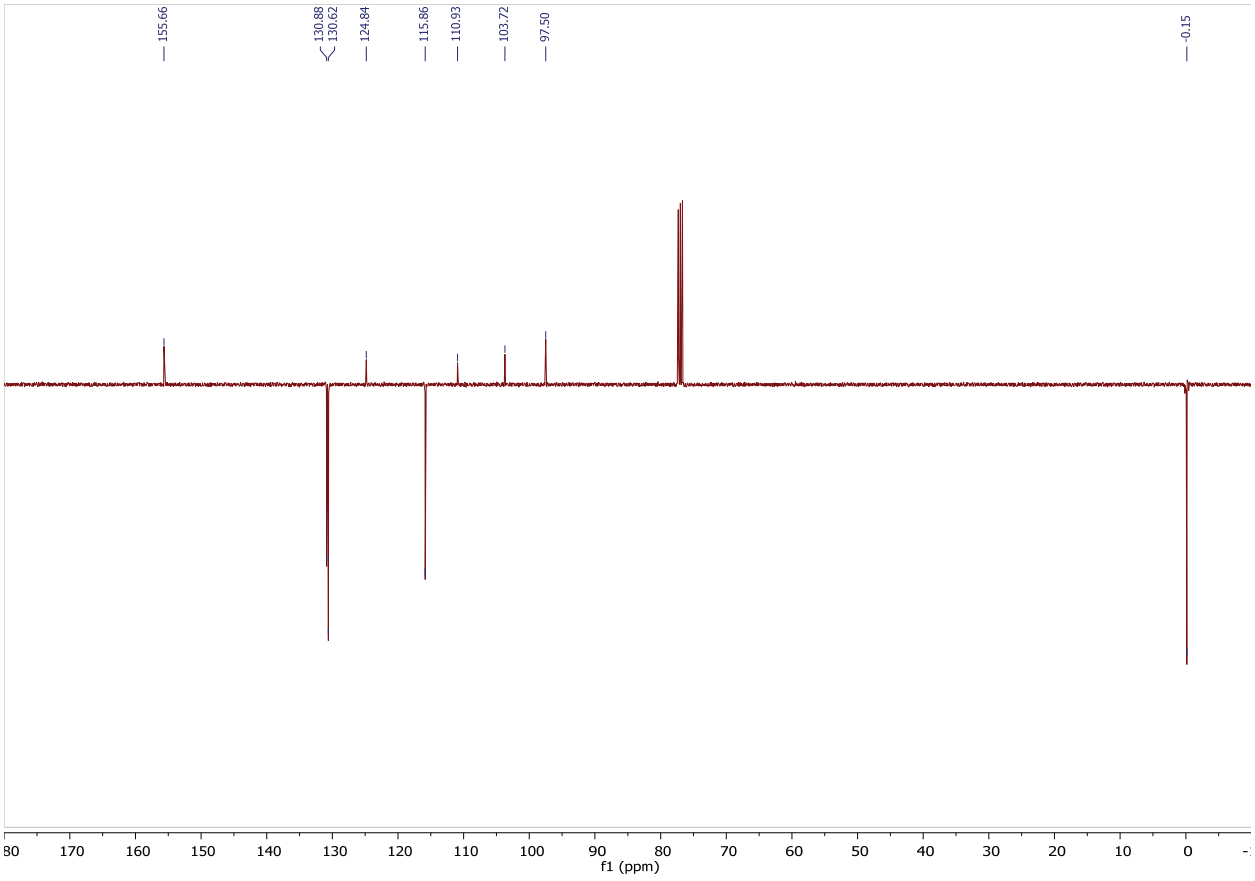


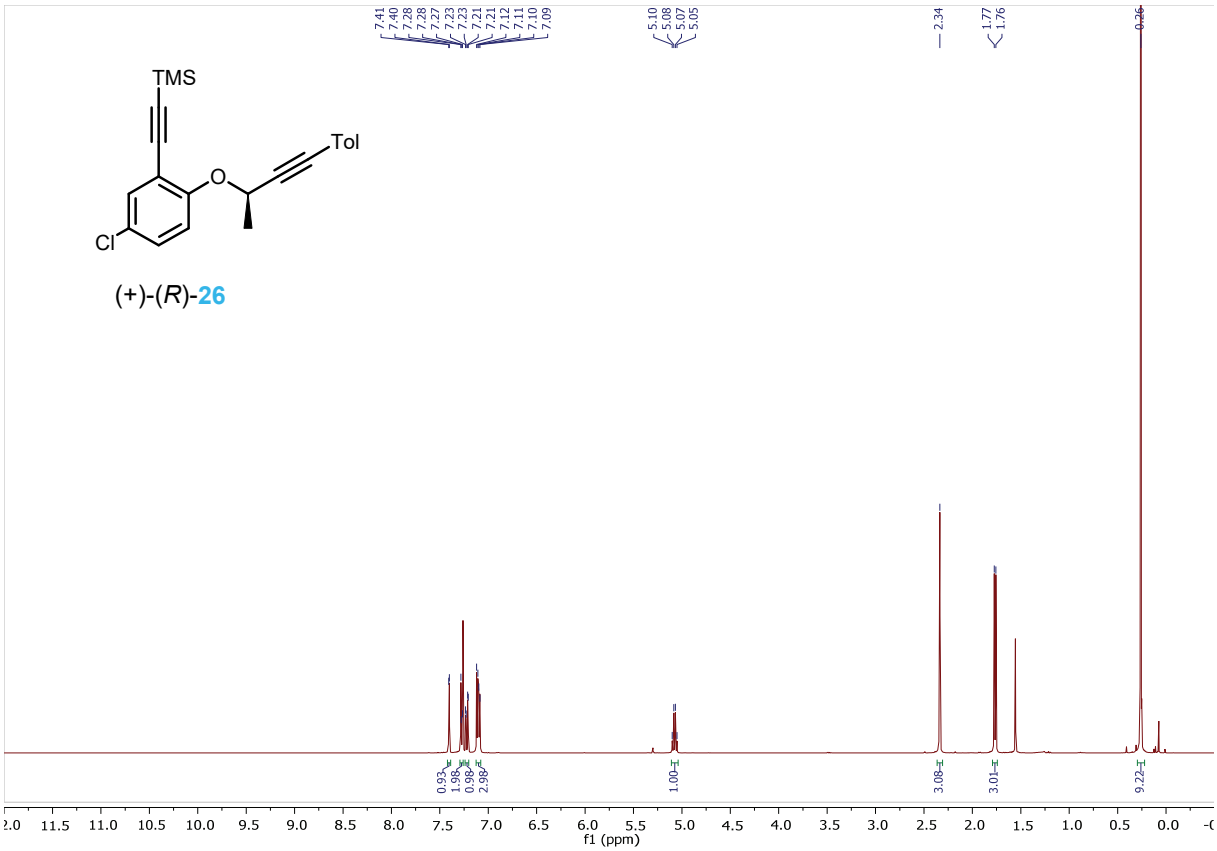


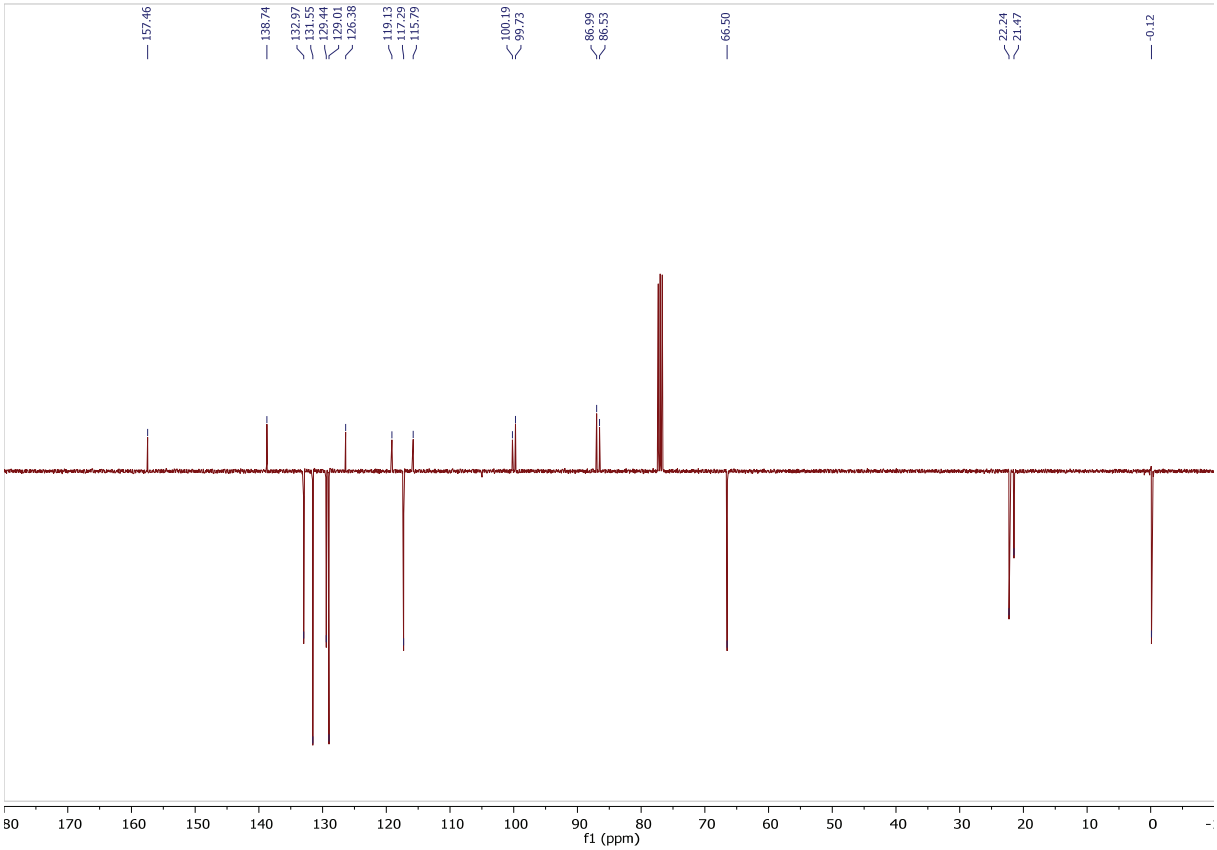
(-)-(*M,R,R*)-**19g**

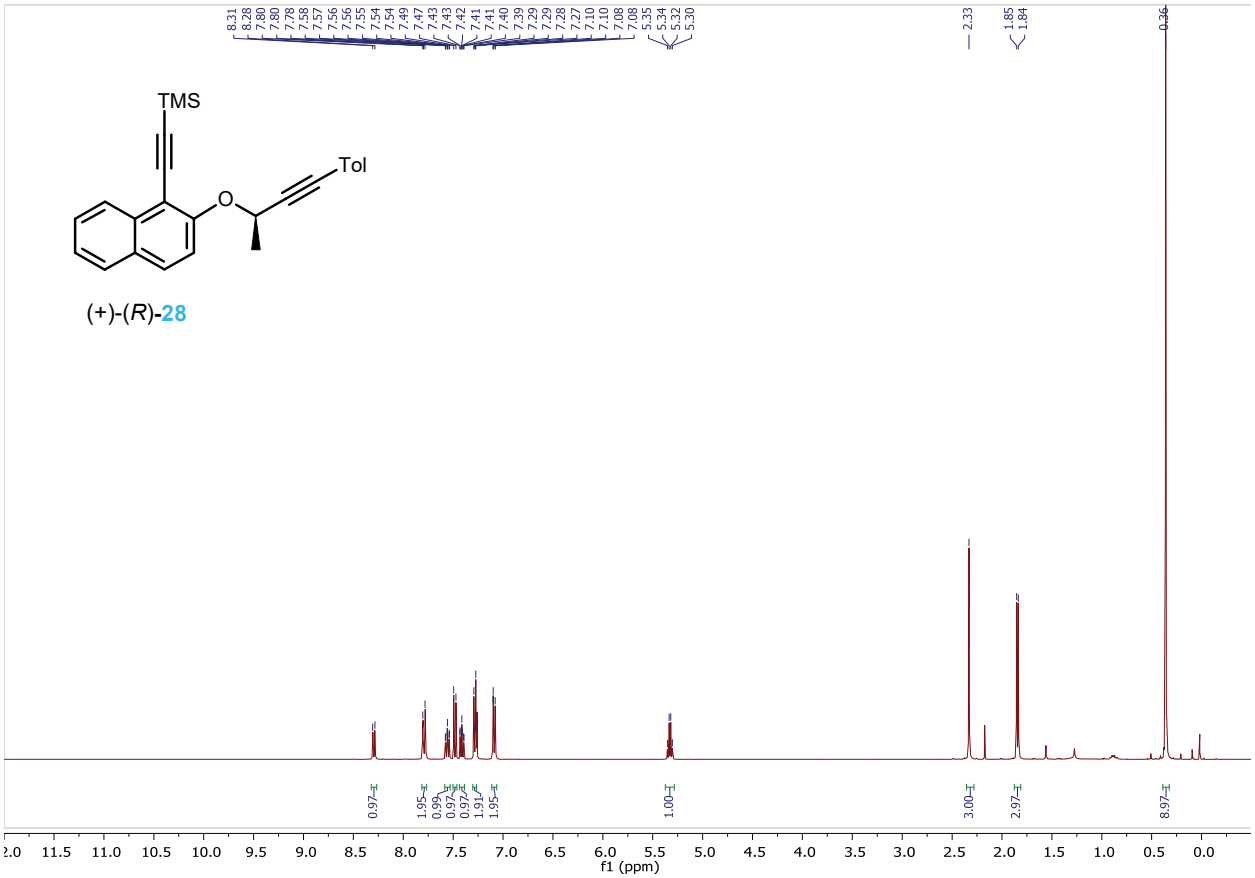


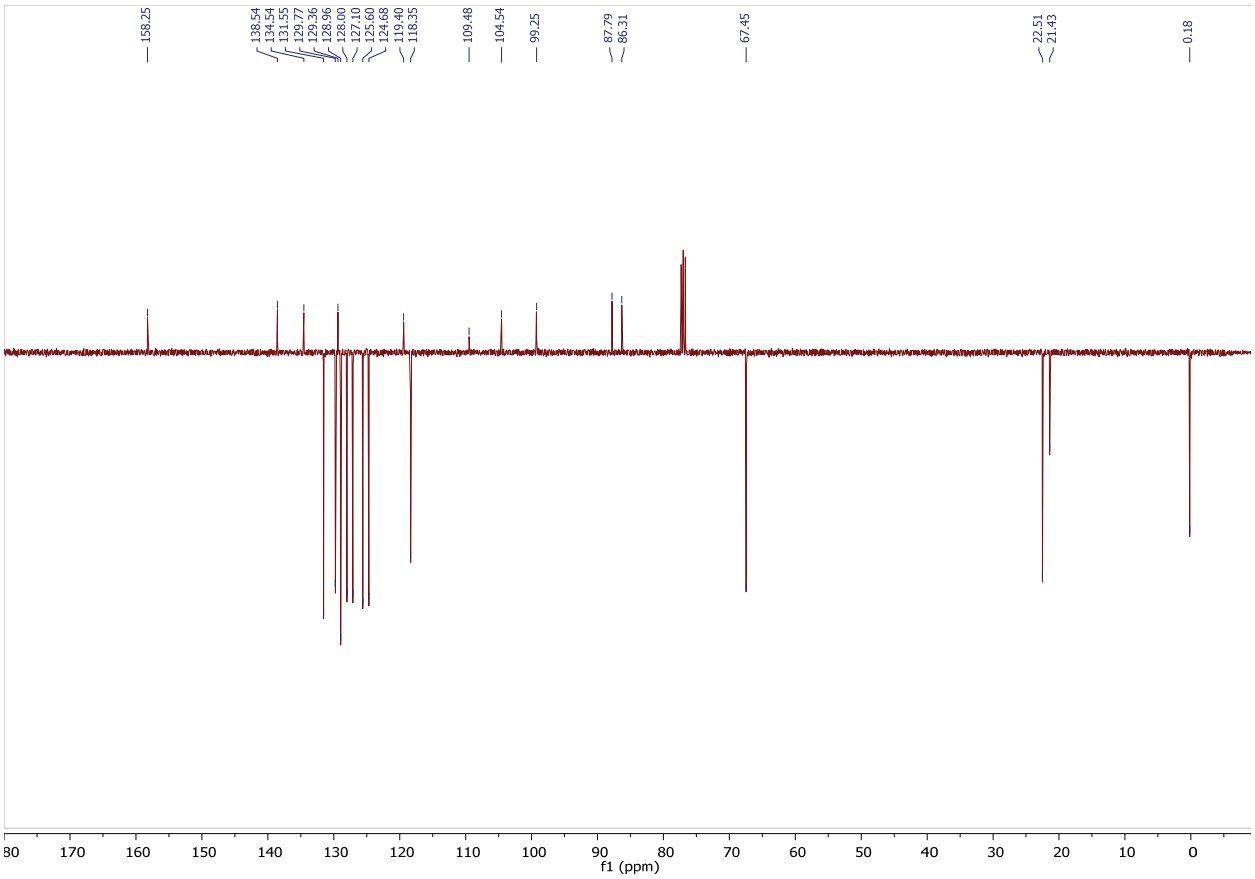

TMS
OH
Cl
25
7.32
7.31
7.20
7.20
7.18
7.18
6.89
6.86
5.78
0.28
1.00
1.11
1.07
1.00
8.96
f1 (ppm)


155.66
130.88
130.62
124.84
115.86
110.93
103.72
97.50
-0.15
f1 (ppm)


TMS
Tol
O
Cl
(+)-(R)-26
7.41
7.40
7.28
7.28
7.27
7.23
7.23
7.21
7.21
7.12
7.11
7.10
7.09
5.10
5.08
5.07
5.05
2.34
1.77
1.76
0.26
0.93
1.98
0.98
2.98
1.00
3.08
3.01
9.22
f1 (ppm)


157.46
138.74
132.97
131.55
129.44
129.01
126.38
119.13
117.29
115.79
100.19
99.73
86.99
86.53
66.50
22.24
21.47
-0.12
f1 (ppm)


TMS
Tol
O
(+)-(R)-28
f1 (ppm)


f1 (ppm)