Supporting Information

Planar-chiral building blocks for metal-organic frameworks

Murat Cakici, Zhi-Gang Gu, Martin Nieger, Jochen Bürck, Lars Heinke and Stefan Bräse

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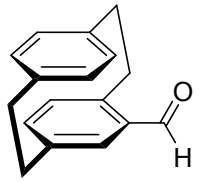
General. The starting materials, solvents and reagents were purchased from Acros, ABCR, Alfa Aesar or Sigma-Aldrich and used without further purification. All reactions involving moisture sensitive reactants were executed under argon atmosphere using oven dried or flame dried glassware. TLC: MERCK ready-to-use plates with silica gel 60 (F254). Column chromatography: MERCK silica gel 60 (0.04–0.063 mm). ^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a *Bruker* Avance 400 [400 MHz (^{1}H) and 100 MHz (^{13}C)] and a *Bruker* Avance DRX 500 [500 MHz (^{1}H) and 125 MHz (^{13}C)] spectrometer. All spectra are referenced to tetramethylsilane (TMS) as the internal standard ($\delta = 0$ ppm) by using the signals of the residual protons of $CHCl_3$ [7.26 ppm (^{1}H) or 77.0 ppm (^{13}C)] in $CDCl_3$. Multiplicities of signals are described as follows: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublets of doublets. Coupling constants (*J*) are given in Hertz (Hz). Mass spectra (EI and HRMS) were measured on a Finnigan MAT 90 spectrometer or on an Agilent GC-MS (GC 6890N, MS 5975B VL MSD) (GC-MS). IR (infrared spectroscopy) spectra were recorded on a FT-IR *Bruker* IFS 88 or a *Bruker* Alpha T spectrometer. IR spectra were recorded using the DRIFT technique (diffused reflectance infrared Fourier transform-spectroscopy) or ATR Diamond (attenuated total reflection) for solids. IR spectra of oils were determined as KBr plates, prepared inside an argon atmosphere. The deposit of the absorption band was given in wave numbers $\tilde{\nu}$ in cm^{-1}.

Experimental Procedures

***rac*-4-Formyl[2.2]paracyclophane:**

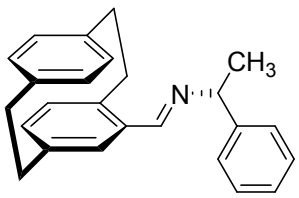


(*rac*)

[2.2]Paracyclophane (1.124 g, 5.4 mmol) was dissolved in CH_2Cl_2 (50 mL) and cooled to 0 °C. Titanium(IV)chloride (1.184 mL, 10.8 mmol) and dichloromethoxymethane (0.516 mL, 5.7 mmol) were added subsequently. The mixture was stirred at room temperature for 6 h, poured into water (50 mL), and stirred for another 2 h. The two phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (50 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. *rac*-4-Formyl[2.2]paracyclophane

(1.26 g, 99%) was obtained as a colorless solid. M.p. 159-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.95 (s, 1H), 7.02 (d, *J* = 1.9 Hz, 1H), 6.73 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.59 (d, *J* = 7.8 Hz, 1H), 6.56 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.50 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.43 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.38 (dd, *J* = 7.9, 1.8 Hz, 1H), 4.10 (ddd, *J* = 11.8, 9.6, 1.5 Hz, 1H), 3.29-3.14 (m, 3H), 3.13-2.91 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 191.8, 143.1, 140.6, 139.4, 139.4, 138.0, 136.5, 136.3, 136.0, 133.2, 132.8, 132.3, 132.1, 35.2, 35.1, 34.9, 33.5; IR (KBr cm^{-1}) 2926, 2853, 1680, 1590, 1555, 1410, 1228, 1143.

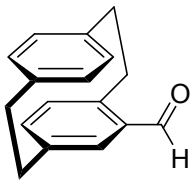
(S_p,*R*)-[*N*-1-(Phenylethyl)]-4-[2.2]paracyclophanylmethaneimine:[1]



(S_p,*R*)

rac-4-Formyl[2.2]paracyclophane (2.36 g, 10.0 mmol) and (*R*)-Phenylethylamine (1.21 g, 10.0 mmol) were dissolved in toluene (80 mL) and refluxed for 16 h. The solvent was evaporated and the crude product (mixture of diastereoisomers) recrystallized twice (25 mL, then 15 mL) from hexane giving 0.713 g (21%) of a white crystalline product (*de*: >99%, calculated by ^{1}H NMR considering the resonance at 8.36 (S_p,*R*) and 8.34 (R_p,*R*) ppm). M.p. 138-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.36 (s, 1H), 7.53 (d, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.32–7.24 (m, 1H), 7.15–6.95 (m, 1H), 6.59 (d, *J* = 7.5 Hz, 1H), 6.52–6.46 (m, 3H), 6.40 (d, *J* = 7.4 Hz, 1H), 6.28 (d, *J* = 7.4 Hz, 1H), 4.59 (m, 1H), 4.00–3.80 (m, 1H), 3.31–2.96 (m, 5H), 2.95-2.76 (m, 2H), 1.68 (d, *J* = 6.6 Hz, 3H); IR (KBr cm^{-1}) 3085, 3027, 2965, 2923, 2850, 1638, 1430, 1408, 1121.

(S_p)-4-Formyl[2.2]paracyclophane:

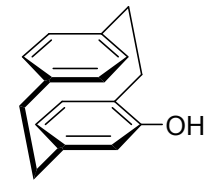


(S_p)

(S_p,*R*)-[*N*-1-(Phenylethyl)]-4-[2.2]paracyclophanylmethaneimine (1.00 g, 2.95 mmol) was hydrolysed and separated by column chromatography on SiO_2 (eluent: CH_2Cl_2). (S_p)-4-Formyl[2.2]paracyclophane (662 mg, 2.80 mmol, 95%) was obtained as a white solid. HPLC (Chiralcel OD-H column, *n*-hexane/*i*PrOH = 98:02, flow rate = 1 mL min^{-1}, λ = 254 nm): t_R = 15.9 (*S*), 20.6 min (*R*); >99%*ee*.

Analytical data agree with *rac*-4-Formyl[2.2]paracyclophane and literature.[1]

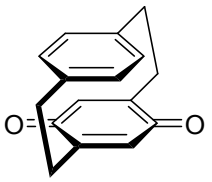
(S_p)-4-Hydroxy[2.2]paracyclophane:



(S_p)

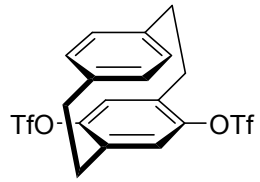
(S_p)-4-Formyl[2.2]paracyclophane (625 mg, 2.64 mmol) was dissolved in 25 mL of CH_2Cl_2/MeOH (1:1). Then concd H_2SO_4 (10 drops) and H_2O_2 (0.391 mL, 31% in water) were subsequently added, and the solution was stirred for 16 h. The solvent was evaporated under reduced pressure, and the residue was taken up in CH_2Cl_2 (25mL) and water (25 mL). The two phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (25 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent: hexane/EtOAc, 9:1) to afford (S_p)-4-hydroxy[2.2]paracyclophane (480 mg, 2.14 mmol 81%) as a pale yellow solid. M.p. 224-226 ^oC; ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.01 (dd, J = 7.8, 1.7 Hz, 1H), 6.56 (dd, J = 7.8, 1.7 Hz, 1H), 6.45 (dd, J = 7.8, 1.7 Hz, 1H), 6.40 (dd, J = 7.8, 1.7 Hz, 1H), 6.39 (d, J = 7.8 Hz, 1H), 6.26 (dd, J = 7.8, 1.7 Hz, 1H), 5.54 (d, J = 1.7 Hz, 1H), 4.46 (bs, 1H), 3.37–3.30 (m, 1H), 3.15-2.87 (m, 6H), 2.70-2.63 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.6, 141.9, 139.5, 138.8, 135.4, 133.5, 132.7, 131.8, 127.9, 125.4, 125.0, 122.5, 35.2, 34.8, 33.8, 31.0; IR (KBr cm^{-1}) 3468, 2926, 2851, 1648, 1600, 1564, 1498, 1417, 1218, 1141, 1087.

(S_p)-[2.2]Paracyclophane-4,7-quinone: (Sp)-[2.2]Paracyclophane-4,7-quinone was synthesized from (S_P)-4-hydroxy[2.2]paracyclophane by the procedure reported in the literature.[2] M.p. >200 °C (dec.); R_f (CH_2Cl_2) = 0.37. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.85 (d, J = 7.9 Hz, 2H), 6.73 (d, J = 7.9 Hz, 2H), 5.82 (s, 2H), 3.28–3.20 (m, 2 H), 3.17–3.01 (m, 4 H), 2.36–2.26 (m, 2H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 187.4, 149.2, 139.0, 134.8, 133.5, 131.5, 33.5, 28.9 ppm. IR (KBr): $\tilde{\nu}$ = 2930, 2858, 1649, 1597, 1413, 1351, 1233, 1115, 1093 cm^{-1}. [α]20 = +224.0 (c = 0.185, benzene) {ref.[3] $[\alpha]_{20}$ = +211(c = 0.185, benzene)}. HPLC (Chiralcel AS-H column, n-hexane/iPrOH = 90:10, flow rate = 1 mL min^{-1}, λ = 254 nm): t_R = 17.4 (S), 18.6 min (R); >99%*ee*.



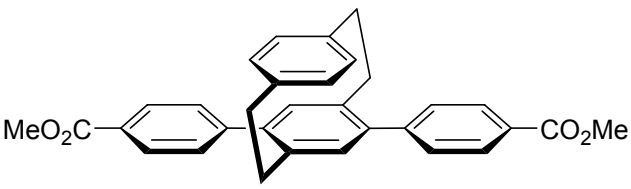
(S_P)

(S_P)-[2.2]Paracyclophane-4,7-bistriflate: Hydrazine hydrate (0.102 mL, 2.10 mmol) was added to a solution of (S_P)-[2.2]-paracyclophane-4,7-quinone (200 mg, 0.84 mmol) in anhydrous EtOH (25 mL). The reaction mixture was heated at reflux for 2 h, the solvent and the excess amount of hydrazine hydrate were distilled off in vacuo, and the flask was filled with argon. The crude [2.2]paracyclophane-4,7-hydroquinone was dissolved in dry dichloromethane (20 mL) under an atmosphere of nitrogen at room temperature followed by the addition of DMAP (615 mg, 5.04 mmol). Trifluoromethanesulfonic anhydride (triflic anhydride; 0.564 mL, 3.36 mmol) in dry dichloromethane (4 mL) was then added dropwise at 0 °C. The colour of the solution changed from yellow to orange and white fumes evolved. The reaction mixture was allowed to stir at room temperature for 2 h. Water (10 mL) was then added, and the reaction mixture was extracted with dichloromethane (3x25 mL). The combined organic phase was washed with brine and dried with $MgSO_4$. The residue after rotary evaporation was purified by column chromatography (silica gel; hexane/ethyl acetate, 90:10). Unconsumed quinone was re-isolated (60 mg, 0.25 mmol, 30%). (S_P)-[2.2]Paracyclophane-4,7-bistriflate (200 mg, 0.40 mmol, 68% with respect to consumed quinone) was obtained and recrystallized (hexane) to give colorless crystals. M.p. 99–100 °C; R_f (hexane/EtOAc = 90:10) = 0.79. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.93 (dd, J = 8.0, 1.6 Hz, 2 H), 6.50 (dd, J = 8.0, 1.6 Hz, 2 H), 6.32 (s, 2 H), 3.42–3.36 (m, 2 H), 3.24–3.13 (m, 4 H), 2.83–2.75 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.4, 139.1, 135.5, 133.1, 130.6, 130.3, 118.8 (q, J = 320.8 Hz, 1 C), 34.0, 31.3 ppm. IR (ATR): $\tilde{\nu}$ = 2931, 2857, 1489, 1412, 1202, 1135, 1106, 1094, 1033 cm^{-1}. HRMS: calcd. for $C_{18}H_{14}F_6O_6S_2$ 504.0136; found 504.0138. $[\alpha]_{20}$ = +17.5 (c = 1, DCM). HPLC (Chiralcel OD-H column, n-hexane/iPrOH = 90:10, flow rate = 1 mLmin^{-1}, λ = 220 nm): t_R = 6.7 (R), 8.8 min (S); >99%*ee*.



(S_P)

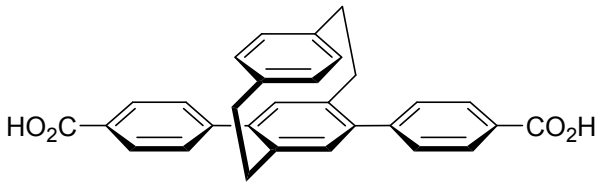
4,7-bis(4-methoxycarboxyphenyl)[2.2]paracyclophane (1-Me):[4] (S_P)-[2.2]Paracyclophane-4,7-bistriflate (150 mg 0.300 mmol), powdered K_3PO_4 (191 mg, 0.900 mmol), and 4-methoxycarbonylphenylboronic acid (216 mg, 1.20 mmol) were added to a 10-mL,



(S_P)

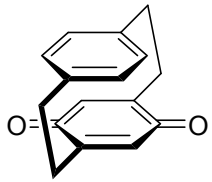
two-necked flask that had been purged with argon. A solution of $Pd(PPh_3)_4$ (21 mg, 0.018 mmol) in dry dioxane (6 mL) was added, and the reaction mixture was stirred under an atmosphere of argon at 100 °C for 2 d. The reaction mixture was cooled and filtered through a short pad of Celite. The filtrate was concentrated under reduced pressure to remove the solvents. The crude product was purified by column chromatography (silica gel; hexane/EtOAc = 90:10) to give diaryl paracyclophane. Recrystallization (hexane) gave colorless crystals. Yield 88%; m.p. 219–220 °C; R_f (hexane/EtOAc = 90:10) = 0.39. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, J = 8.1 Hz, 4 H), 7.62 (d, J = 8.1 Hz, 4 H), 6.73 (s, 2 H), 6.70 (d, J = 7.9 Hz, 2 H), 6.66 (d, J = 7.9 Hz, 2 H), 3.98 (s, 6 H), 3.57–3.52 (m, 2 H), 3.05–2.83 (m, 4 H), 2.64–2.58 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 145.1, 140.5, 139.4, 137.5, 135.2, 131.9, 129.9, 129.7, 129.5, 128.7, 52.1, 34.5, 34.1 ppm. IR (ATR): $\tilde{\nu}$ = 2945, 1705, 1602, 1431, 1276, 1262, 1180, 1101, 1014 cm–1. HRMS: calcd. for $C_{32}H_{28}O_4$ 476.1988; found 476.1989. $[\alpha]_{20}$ = +403.0 (c = 1, DCM). HPLC (Chiralcel OD-H column, *n*-hexane/*i*PrOH = 90:10, flow rate = 1 mLmin^{-1}, λ = 365 nm): t_R = 14.5 (*S*), 25.5 min (*R*); >99%*ee*.

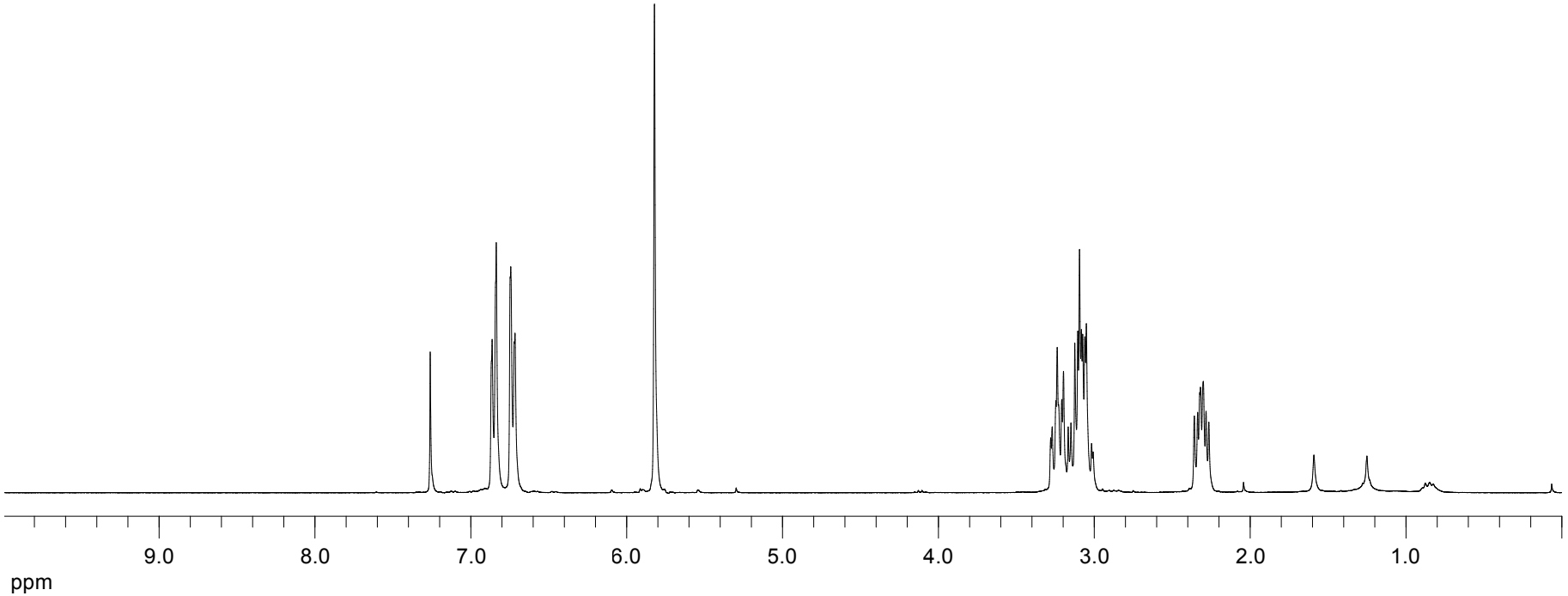
Paracyclophane dicarboxylic acid 1-H: To a solution of 4,7-bis(4-methoxycarboxyphenyl)[2.2]paracyclophane (300 mg, 0,63 mmol) in THF (10 mL) was added aq. 1 M KOH (6.3 mL) and the reaction mixture was refluxed for 16 h. After cooling to room temperature, the THF was removed *in vacuo* and the solution was acidified with 1 M HCl (aq.). The resulting precipitate was separated by filtration, washed with water and dried under vacuum to give desired product **1-H** (266 mg, 0.59 mmol). Yield: 94%; mp: >300 °C (dec.); ^{1}H NMR: (400 MHz, DMSO-d_6): δ = 12.97 (bs, 2H), 8.08 (d, J = 8.2 Hz, 4H), 7.68 (d, J = 8.2 Hz, 4H), 6.81 (s, 2H), 6.75 (dd, J = 7.8, 1.6 Hz, 2H), 6.60 (dd, J = 7.8, 1.6 Hz, 2H), 3.50-3.40 (m, 2H), 3.00-2.89 (m, 4H), 2.49-2.40 (m, 2H) ppm. ^{13}C NMR: (100 MHz, DMSO-d_6): δ = 167.1, 144.2, 139.9, 138.8, 137.0, 134.8, 131.8, 129.6, 129.3, 129.1, 33.9, 33.3 ppm. $[\alpha]_{20}$ = +412.0 (c = 0.75, DMSO)

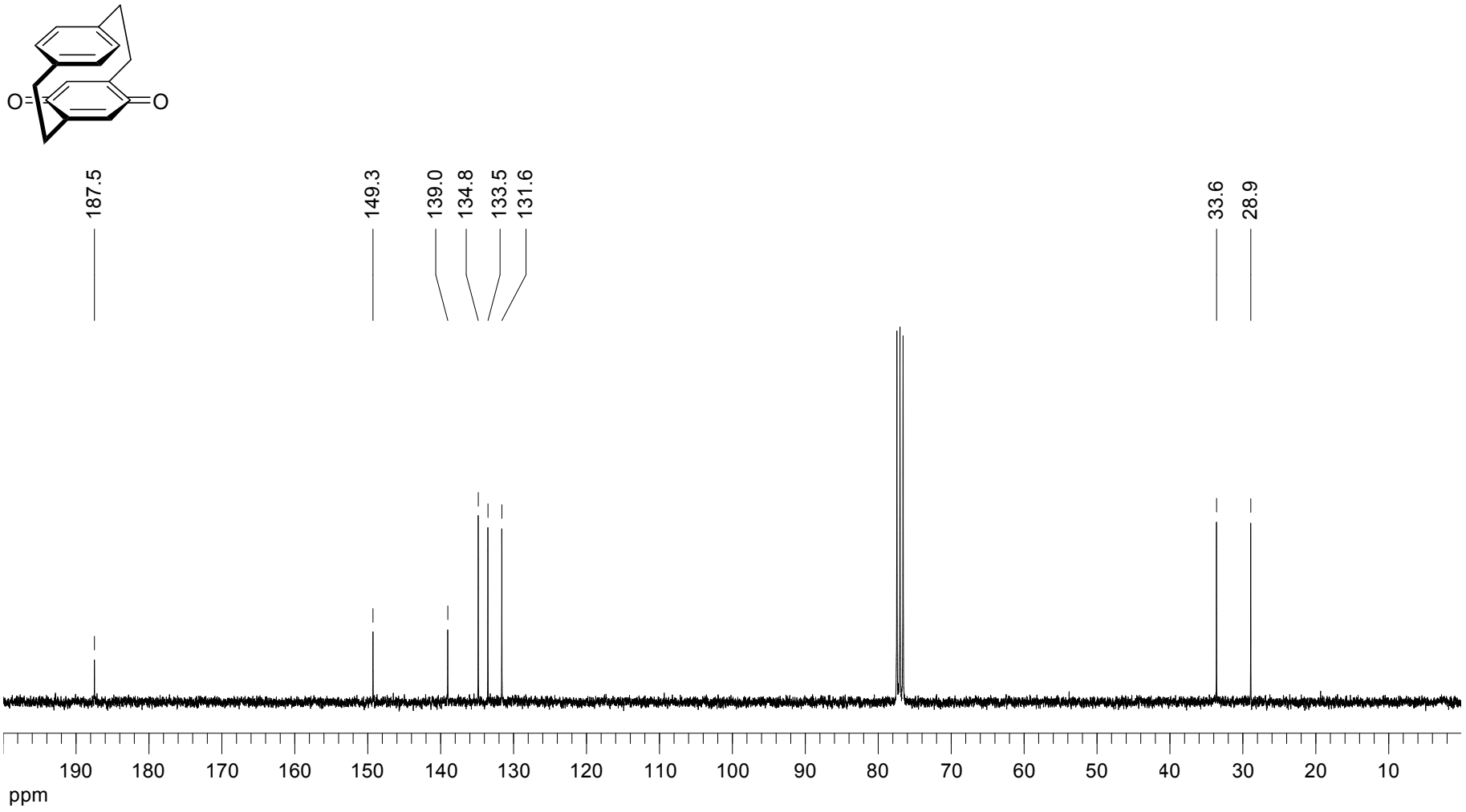


(***S*****P**)

^{1}H NMR and ^{13}C NMR spectra of products



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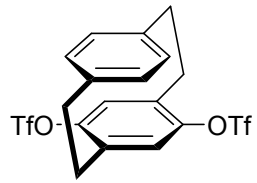
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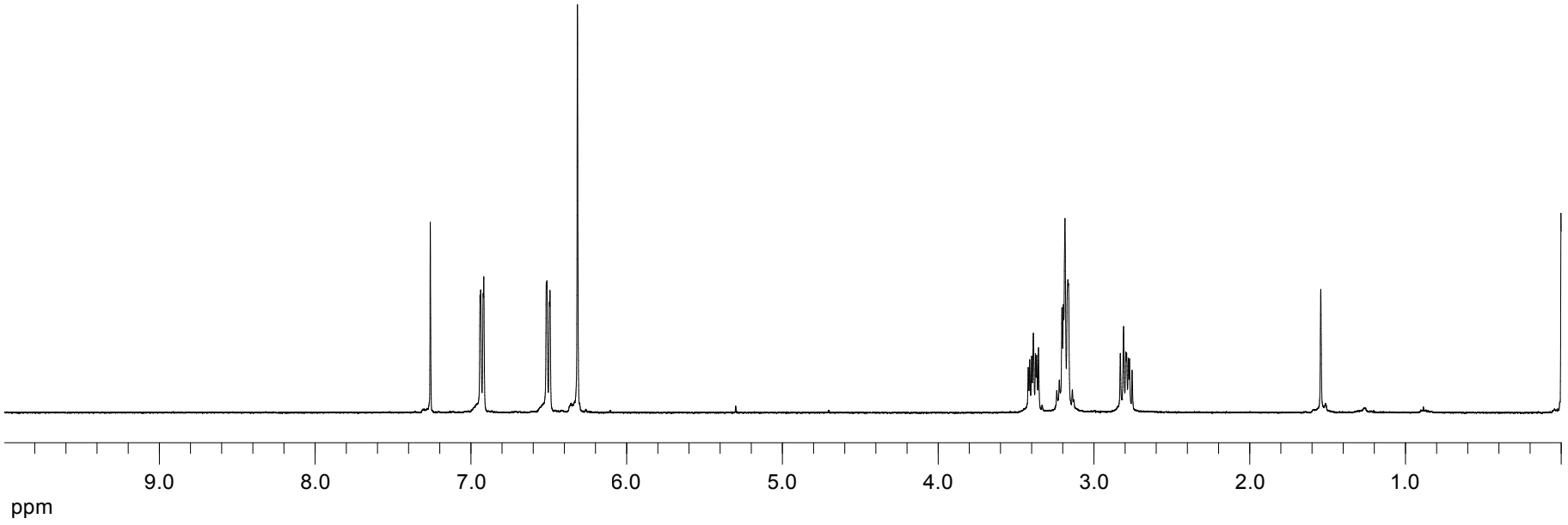
OTf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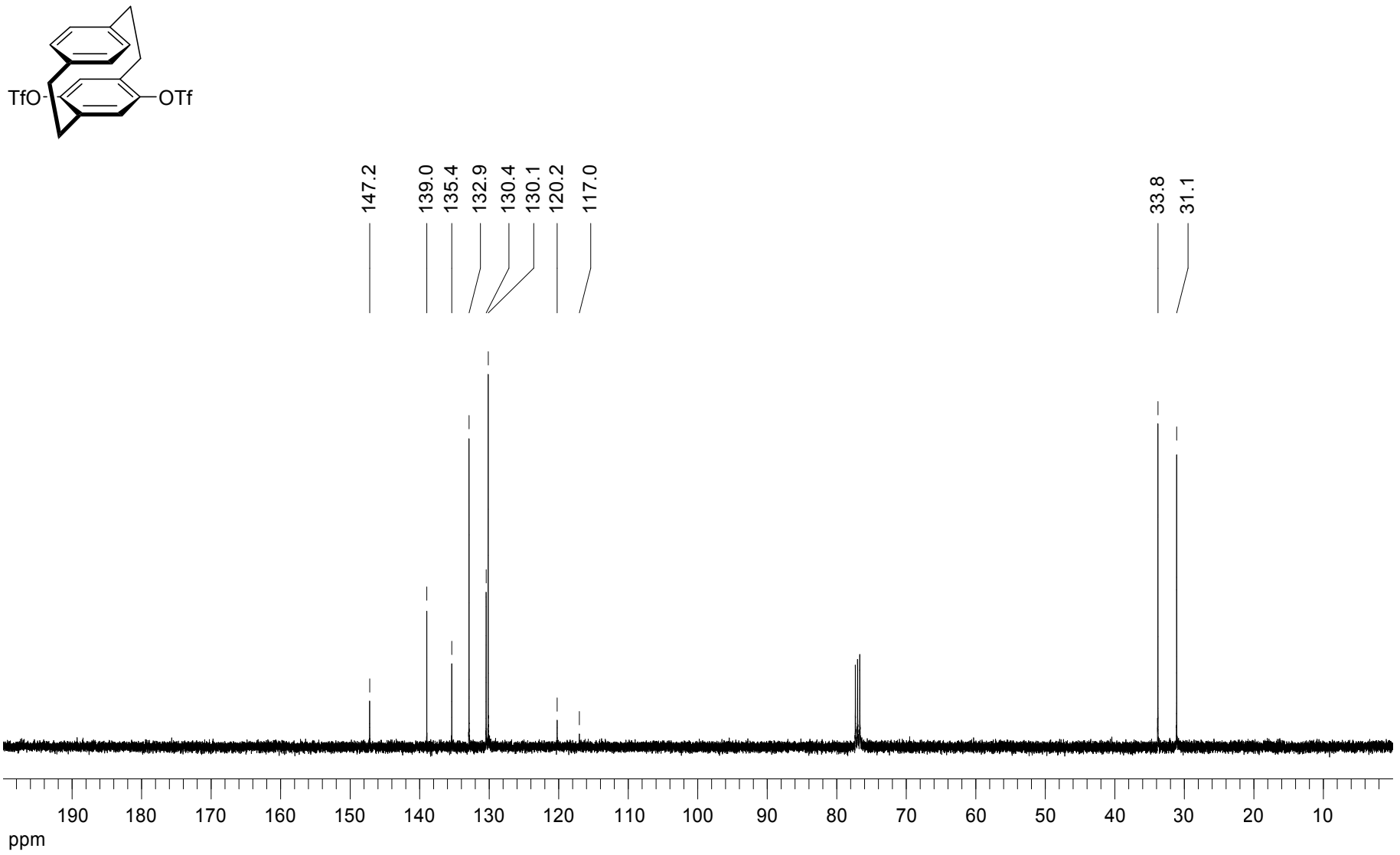
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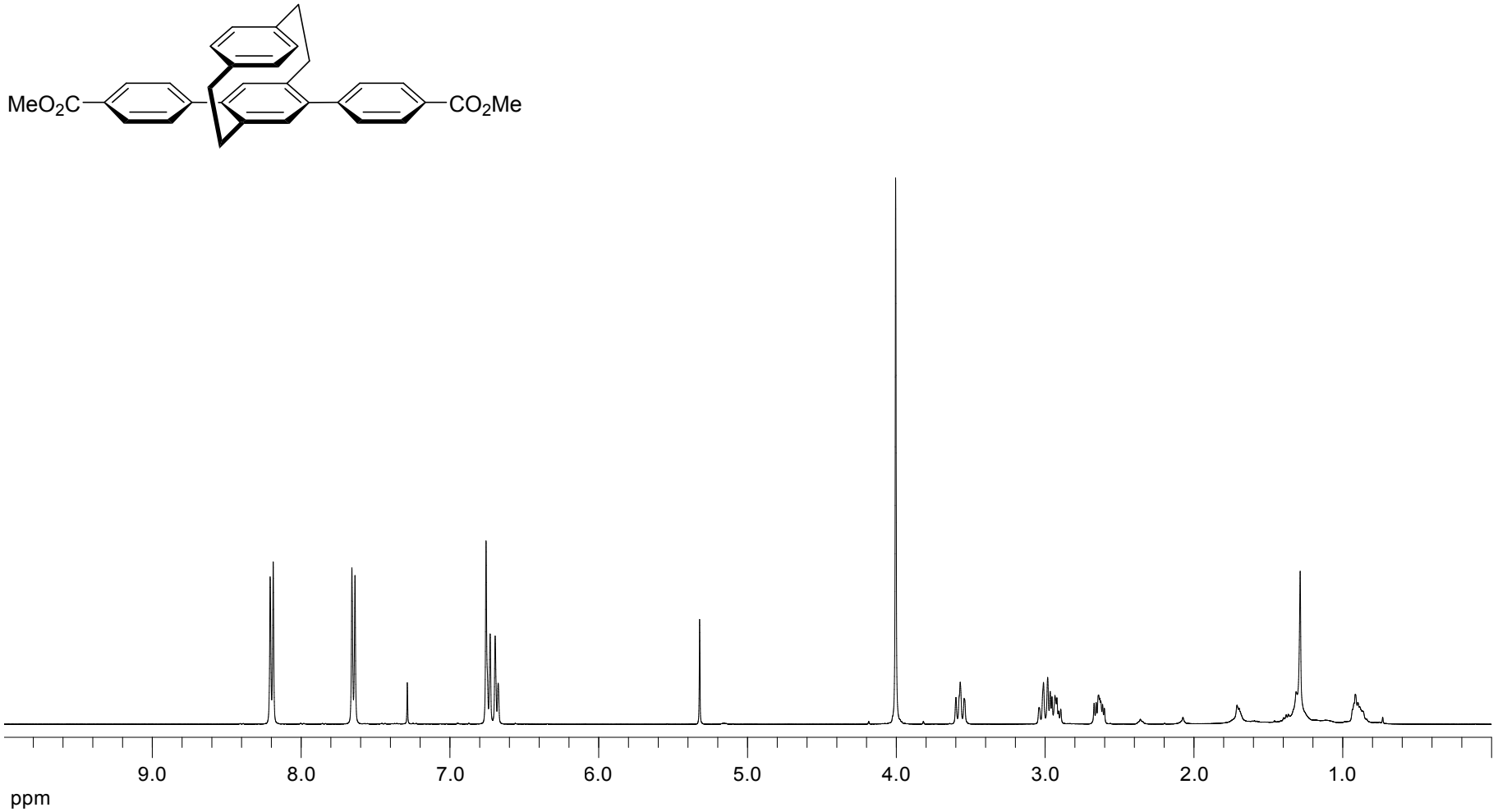
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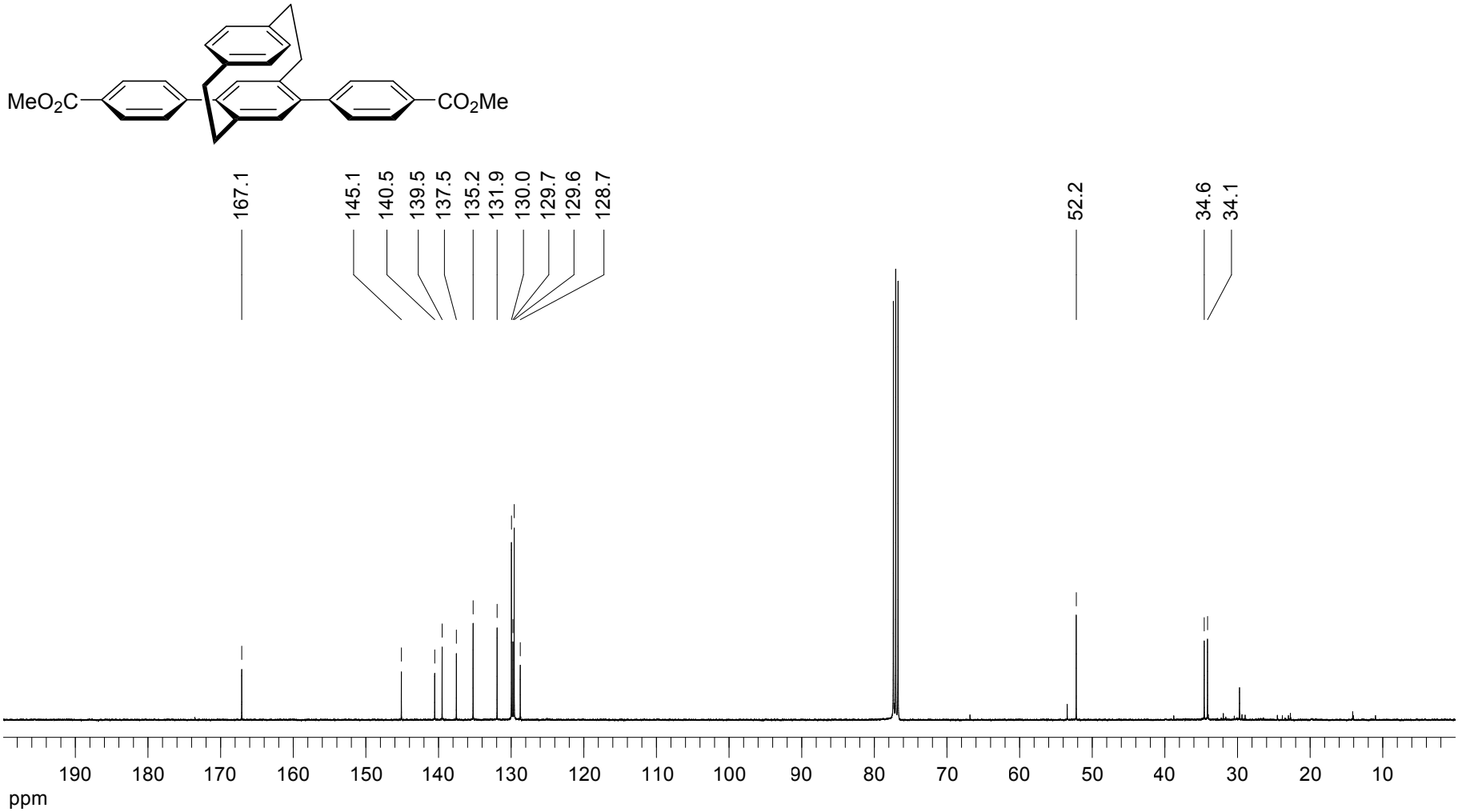
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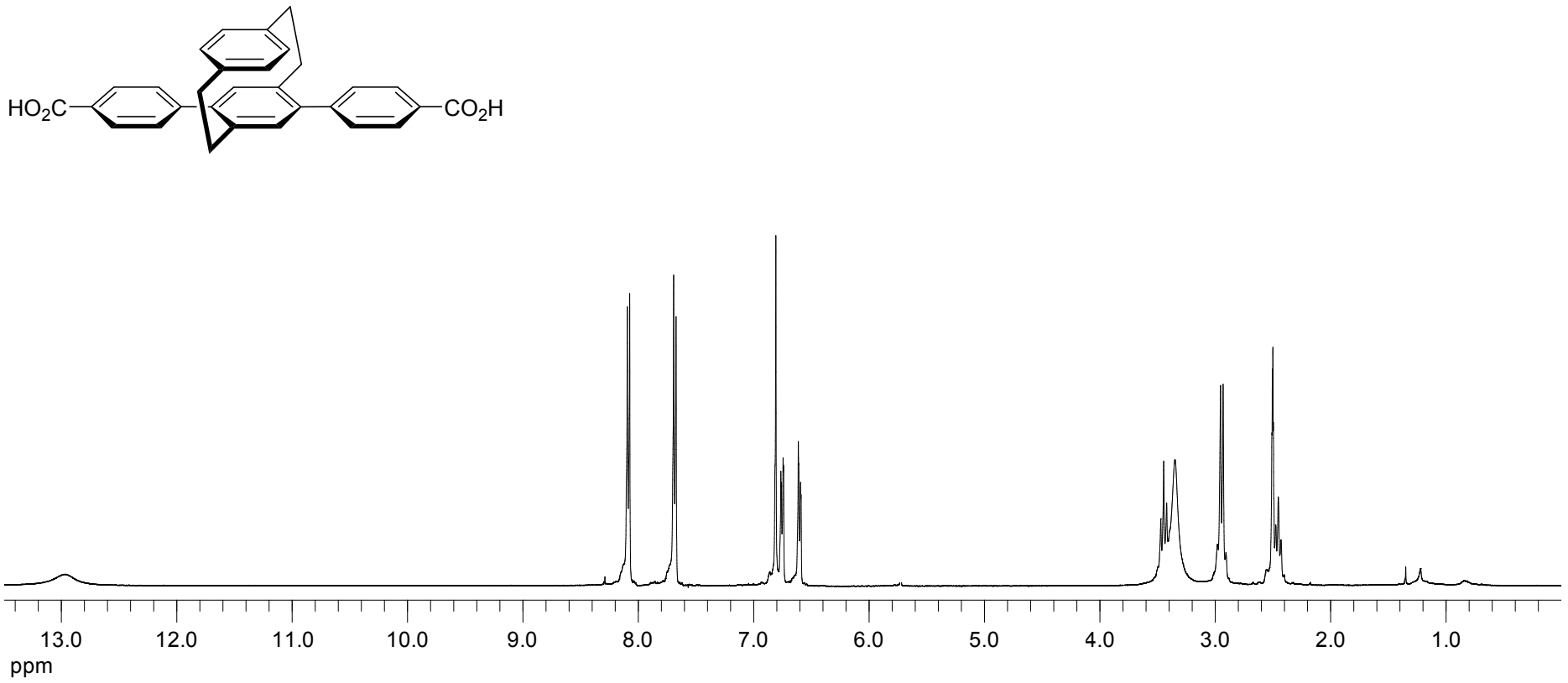
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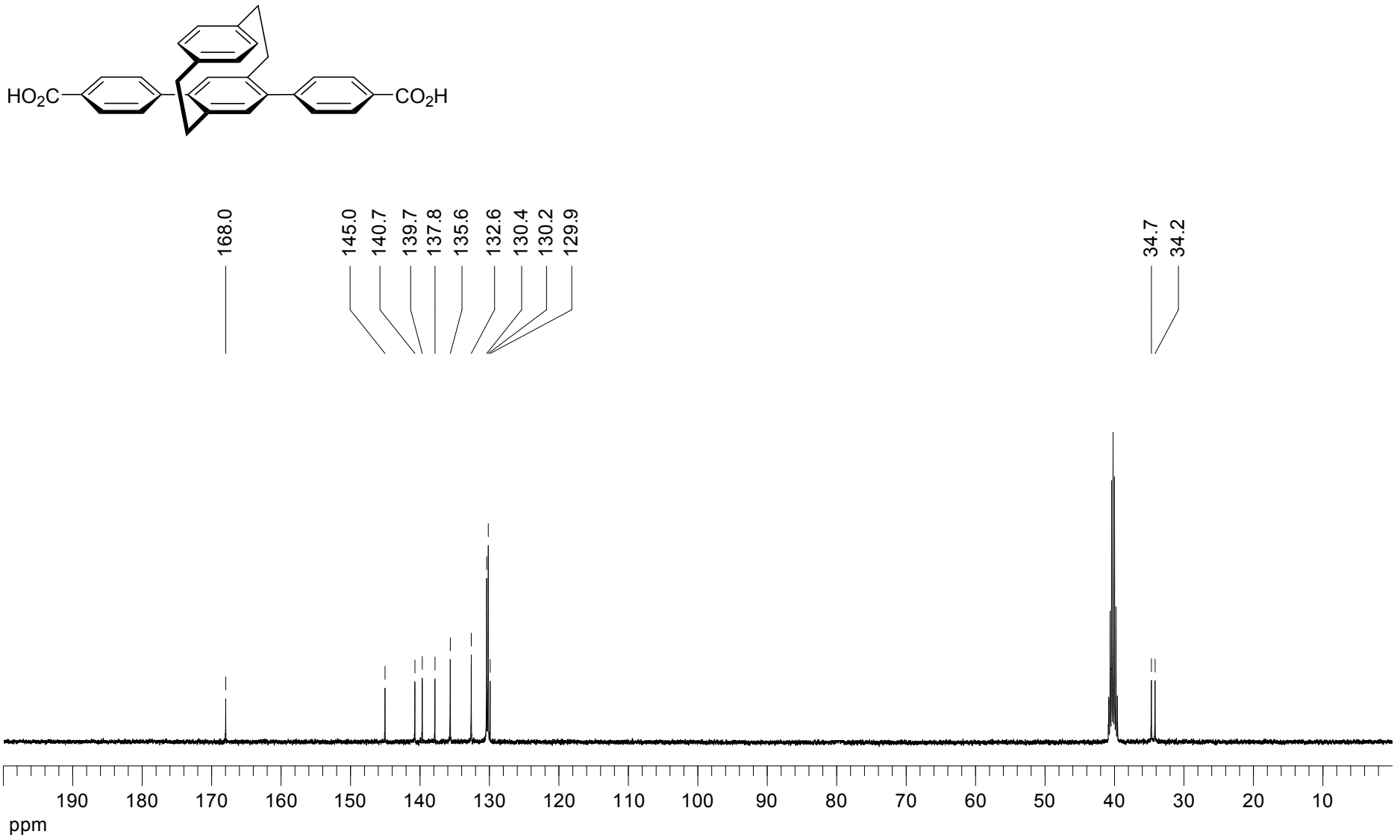
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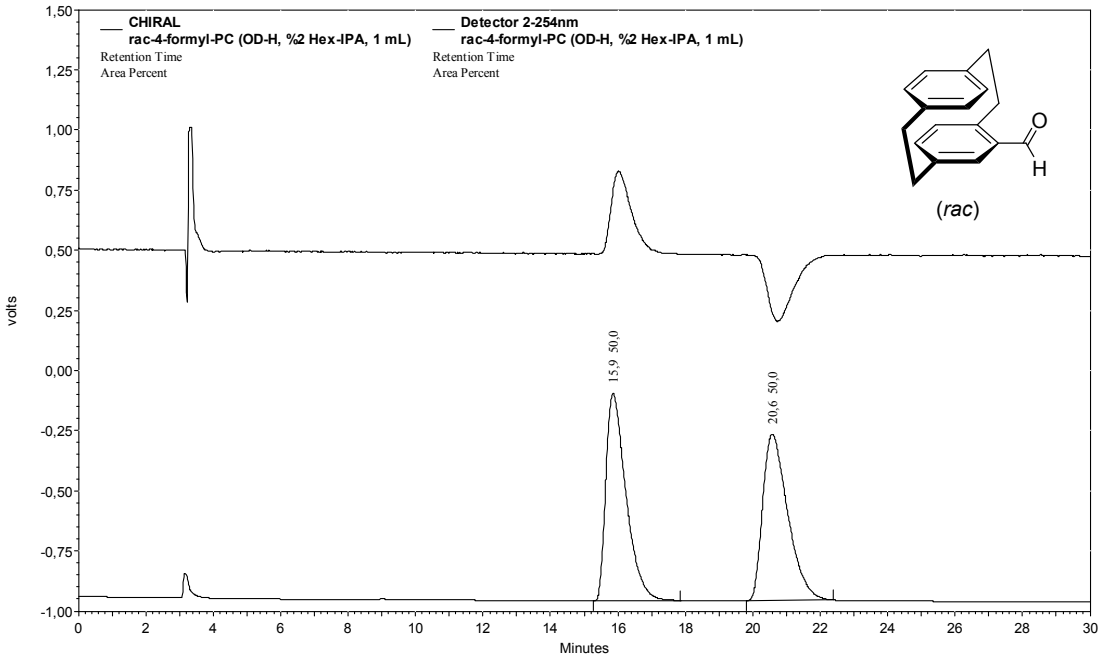
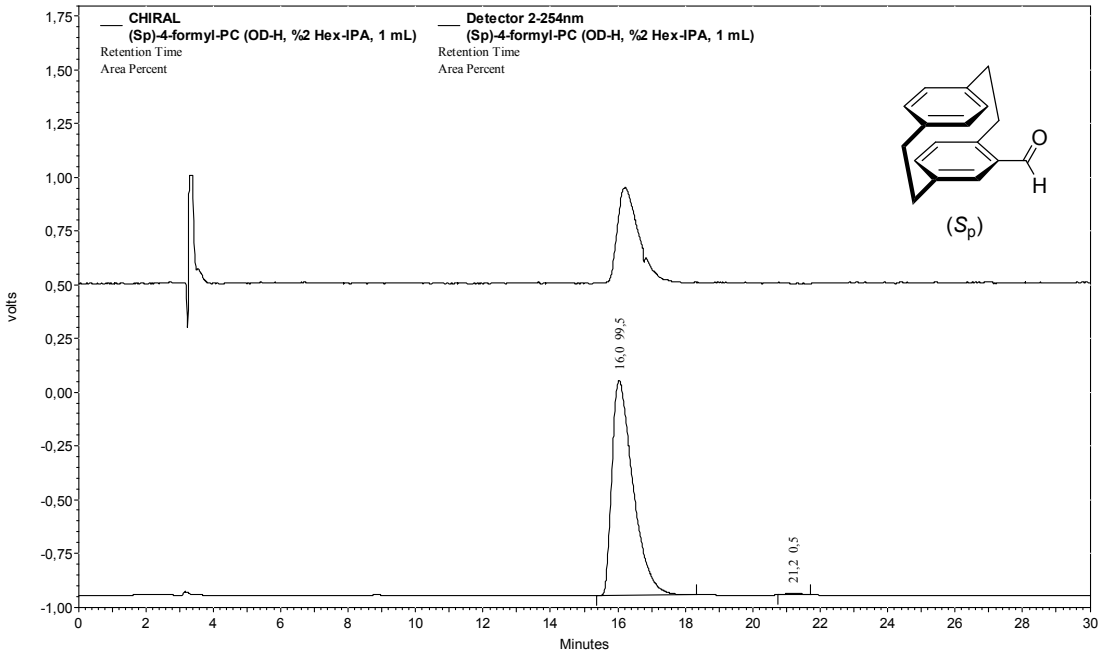
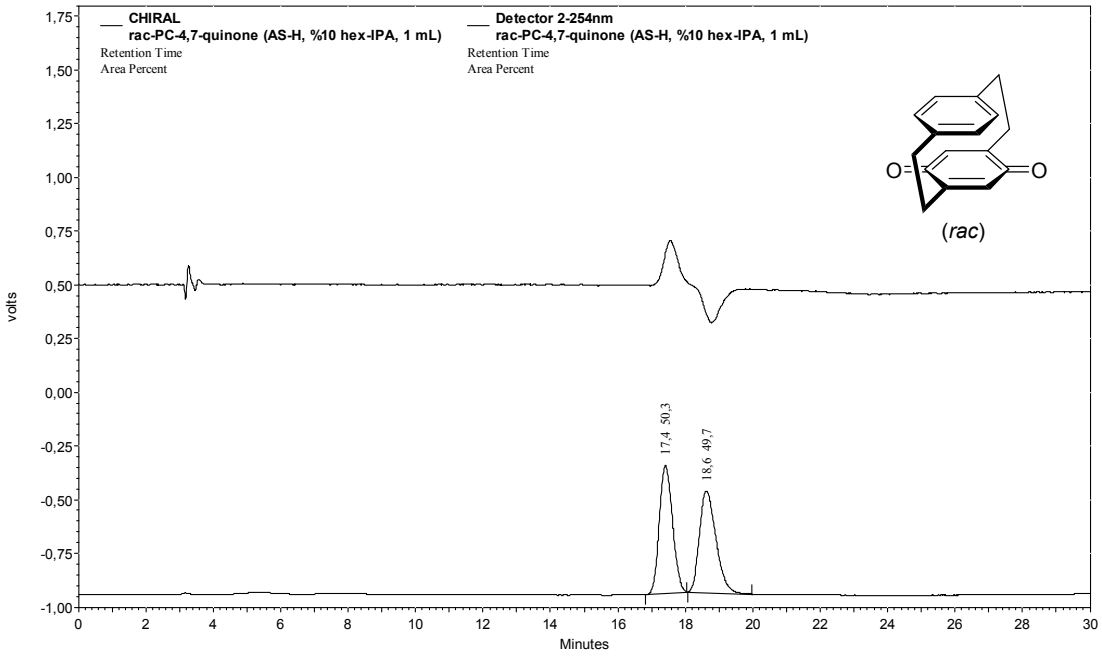
ppm

HPLC chromatograms






CHIRAL
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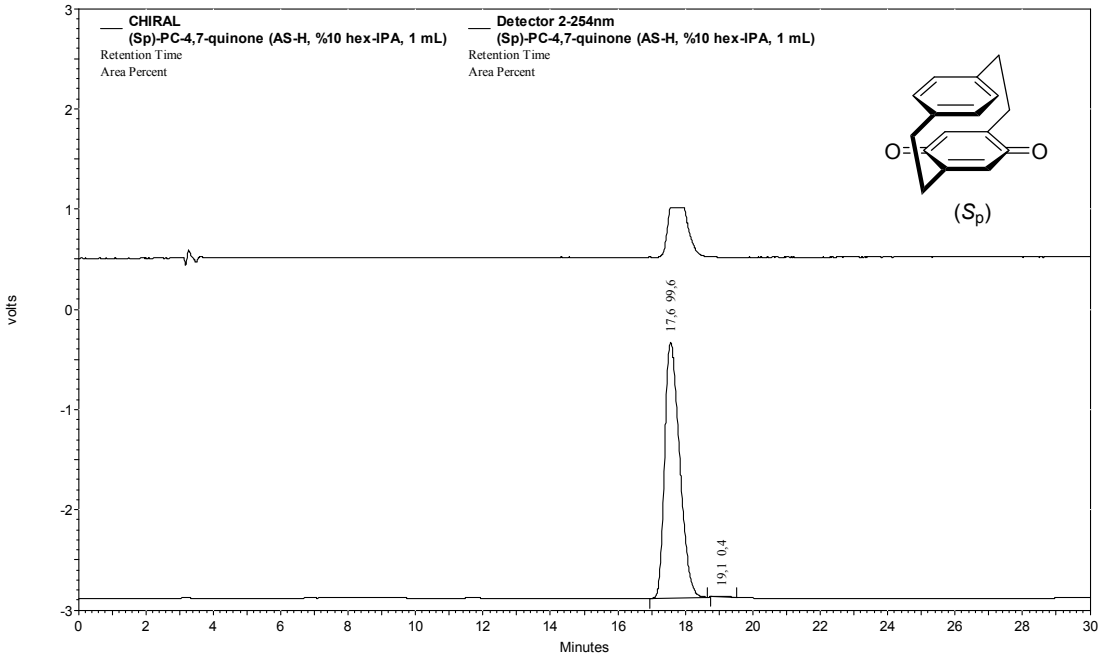
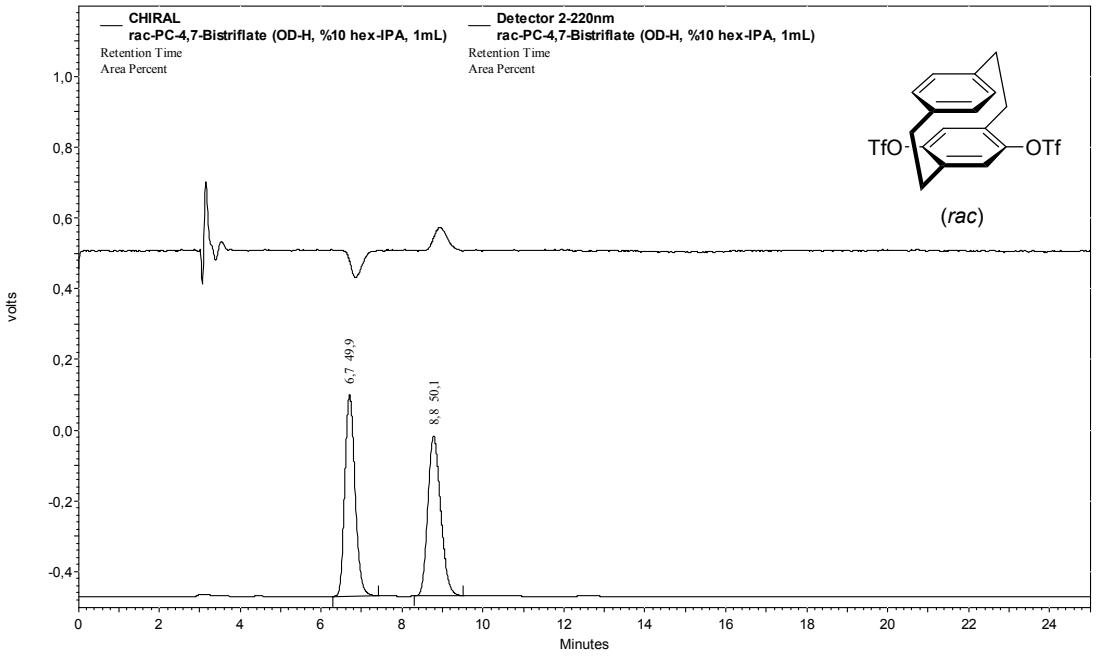
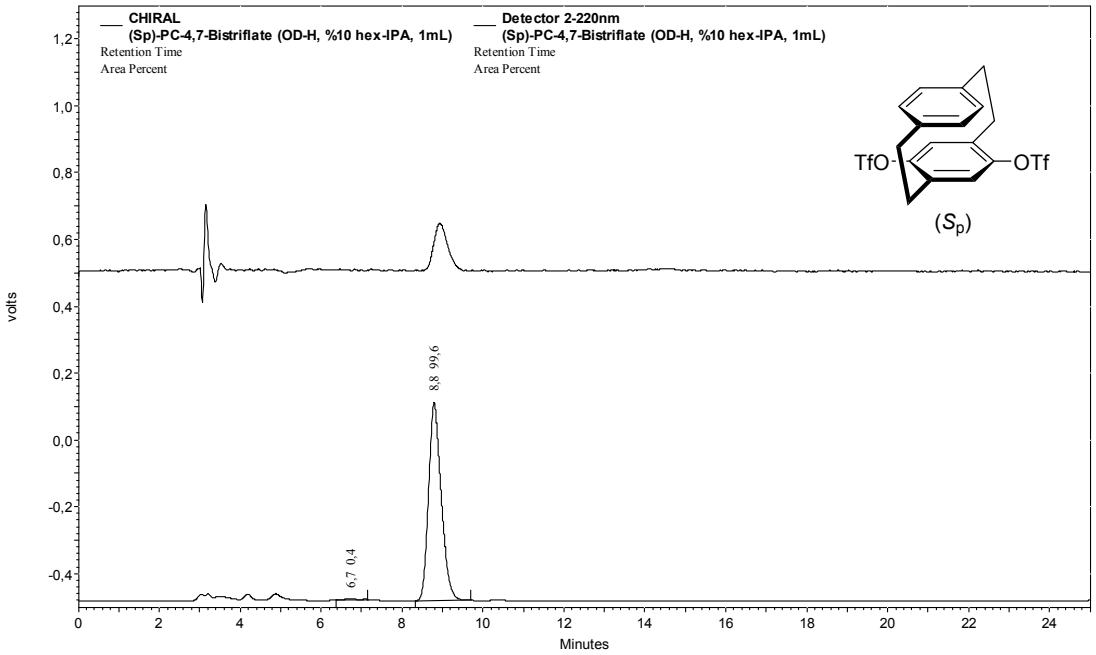
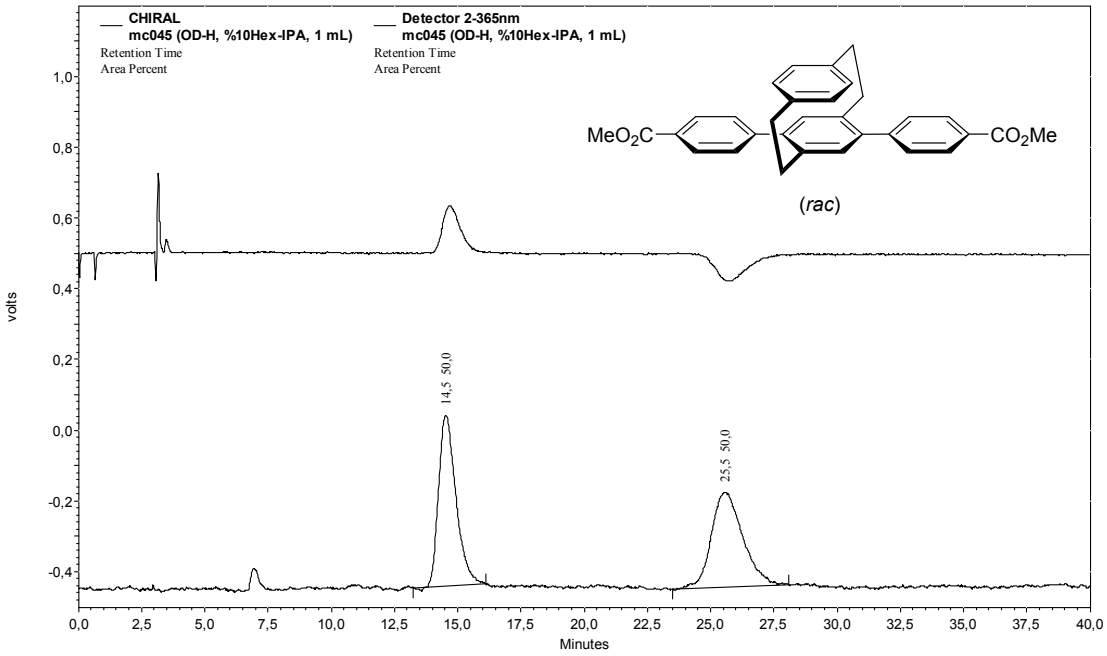
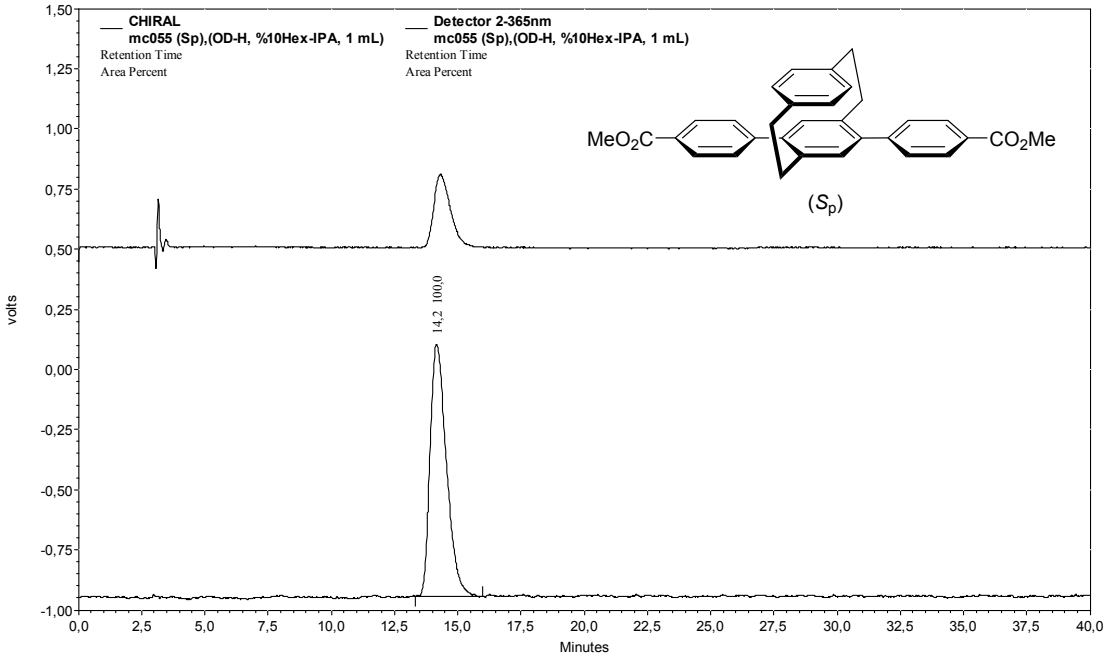
Area Percent
Detector 2-254nm
rac-PC-4,7-quinone (AS-H, %10 hex-IPA, 1 mL)
Retention Time
Area Percent
(rac)
17,4 50,3
18,6 49,7
volts
Minutes


CHIRAL
(Sp)-PC-4,7-quinone (AS-H, %10 hex-IPA, 1 mL)
Retention Time
Area Percent
Detector 2-254nm
(Sp)-PC-4,7-quinone (AS-H, %10 hex-IPA, 1 mL)
Retention Time
Area Percent
(Sp)
17,6 99,6
19,1 0,4
volts
Minutes


CHIRAL
rac-PC-4,7-Bistriflate (OD-H, %10 hex-IPA, 1mL)
Retention Time
Area Percent
Detector 2-220nm
rac-PC-4,7-Bistriflate (OD-H, %10 hex-IPA, 1mL)
Retention Time
Area Percent
TfO
OTf
(rac)
6,7 49,9
8,8 50,1
volts
Minutes


CHIRAL
(Sp)-PC-4,7-Bistriflate (OD-H, %10 hex-IPA, 1mL)
Retention Time
Area Percent
Detector 2-220nm
(Sp)-PC-4,7-Bistriflate (OD-H, %10 hex-IPA, 1mL)
Retention Time
Area Percent
TfO
OTf
(Sp)
6,7 0,4
8,8 99,6
volts
Minutes


CHIRAL
mc045 (OD-H, %10Hex-IPA, 1 mL)
Retention Time
Area Percent
Detector 2-365nm
mc045 (OD-H, %10Hex-IPA, 1 mL)
Retention Time
Area Percent
MeO2C
CO2Me
(rac)
14,5 50,0
25,5 50,0
volts
Minutes


CHIRAL
mc055 (Sp),(OD-H, %10Hex-IPA, 1 mL)
Retention Time
Area Percent
Detector 2-365nm
mc055 (Sp),(OD-H, %10Hex-IPA, 1 mL)
Retention Time
Area Percent
MeO2C
CO2Me
(Sp)
14,2 100,0
volts
Minutes

Crystal Structure Determinations of 4,7-bis(4-methoxycarboxyphenyl)[2.2]paracyclophane

The single-crystal X-ray diffraction study was carried out on a Bruker Smart APEXII diffractometer at 120(2) K (using MoKα radiation (λ = 0.71073 Å). Direct Methods (SHELXS-97)[5] were used for structure solution and refinement was carried out using SHELXL-97 [a)] (full-matrix least-squares on F^2). Hydrogen atoms were localized by difference electron density determination and refined using a riding model. A semi-empirical absorption correction was applied.

colourless crystals, $C_{32}H_{28}O_4$, M = 476.54, crystal size 0.30 x 0.12 x 0.06 mm, T = 120(2) K, monoclinic, space group $P2_1/n$ (No. 14), a = 10.2761(2) Å, b = 15.2040(3) Å, c = 15.2549(3) Å, β = 96.857(1)°, V = 2366.34(8) Å^3, Z = 4, ρ(calc) = 1.338 Mg m^{-3}, F(000) = 1008, μ = 0.087 mm^{-1}, 30513 reflections ($2\theta_{max}$ = 55°), 5416 unique [R_{int} = 0.024], 327 parameters, $R1$ (for 4519 $I > 2\sigma(I)$) = 0.039, *wR2 (all data)* = 0.107, S = 1.05, largest diff. peak and hole 0.301 and -0.214 e Å^{-3}.

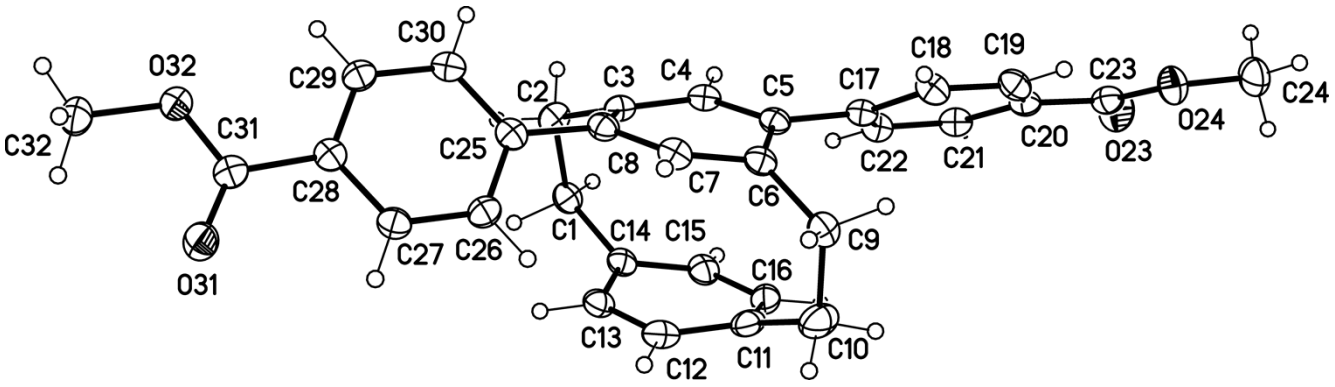


Fig. Xrya-S1. Molecular structure of **4,7-bis(4-methoxycarboxyphenyl)[2.2]paracyclophane** (displacement parameters are drawn at 50% probability level).

Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1042413. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

Scanning Electron Microscopy (SEM) of the SURMOF

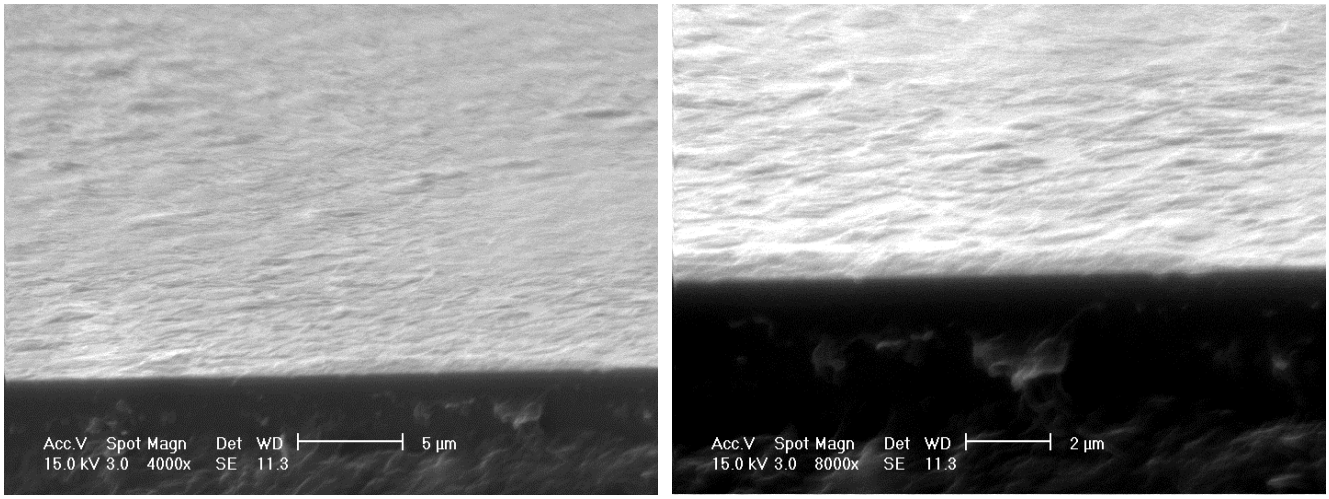


Figure SI-SEM: SEM images of the SURMOF sample (i.e. Zn(PcTPDC) SURMOF on top of the Cu(DMTPDC) SURMOF seeding layer grown on the QCM substrate). The images show side views of the broken sample. The SEM image was recorded with a Scanning Electron Microscope (SEM) Philips XL 30.

References:

[1] a) S. Banfi, A. Manfredi, F. Montanari, G. Pozzi, S. Quici, *J. Mol. Catal. A: Chem.* **1996**, *113*, 77-86; b) C. J. Friedmann, S. Ay, S. Bräse, S. *J. Org. Chem.* **2010**, 75, 4612-4614.

[2] a) D. J. Cram, A. C. Day, *J. Org. Chem.* **1966**, *31*, 1227–1232; b) N. V. Vorontsova, V. I. Rozenberg, E. V. Vorontsov, D. Y. Antonov, Z. A. Starikova, Y. N. Bubnov, *Russ. Chem. Bull. Int. Ed.* **2002**, *51*, 1483–1490.

[3] N. Vorontsova, V. Rozenberg, E. Vorontsov, D. Antonov, Z. Starikova, *Eur. J. Org. Chem.* **2003**, 761–770.

[4] M. Cakici, S. Bräse, *Eur. J. Org. Chem.* **2012**, 6132–6135.

[5] G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112-122.