Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

First asymmetric synthesis of planar chiral [2.2]metacyclophanes

*Marco Blangetti, Helge Müller-Bunz and Donal F. O'Shea**

Centre for Synthesis and Chemical Biology, School of Chemistry and Chemical Biology,

University College Dublin, Belfield, Dublin 4, Ireland

donal.f.oshea@ucd.ie

Table of Contents

Experimental details, synthesis and analysis of compounds **8a-c**, **9a-c**	S2-S7
Enantioselective *ortho*-lithiation of compounds **9a-c**	S8-S9
Synthesis and Analysis of compounds **11a-k**	S10-S23
^{1}H, ^{31}P and ^{13}C NMR spectra of **8a-c**, **9a-c** and **11a-k**	S24-S44
Synthesis and Analysis of compound **9a**-D_1	S45
^{1}H, ^{2}H and ^{13}C NMR spectra of **9a**-D_1	S46-S47
Racemization Plots Data for Compounds **11a-c**	S48-51
References	S52
X-Ray structural data for **(R_p)-11a** and *rac*-**11d**	S53-S64

Experimental details

General Methods: All reactions involving air-sensitive reagents were performed under nitrogen in oven-dried glassware using syringe-septum cap technique. All solvents were purified and degassed before use. Chromatographic separations were carried out under pressure on Merck silica gel 60 using flash-column techniques. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel coated aluminum plates (60 Merck F254) with UV light (254 nm) as visualizing agent. Unless specified, all reagents were used as received without further purifications. TMP(H) was distilled from CaH_2 prior to use. THF and diethyl ether were obtained from a solvent purification system. Heptane was distilled under nitrogen from CaH_2 prior to use. BuLi was purchased as a 2.5 M solution in hexanes, *s*BuLi as a 1.4 M solution in cyclohexanes. KO*t*Bu was purchased as a 1 M solution in THF. The exact concentration of the organolithium solutions were determined by titration with diphenylacetic acid in THF prior to use.[1] (-)-Sparteine and PMDTA were stored over potassium hydroxide. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded at room temperature on 400 MHz or 500 MHz spectrometers and calibrated using residual undeuterated solvent as an internal reference. ^{2}H NMR (92.07 MHz) spectra were obtained in DCM using residual CD_2Cl_2 as an internal standard. Optical rotations were measured at 589 nm. Enantiomeric ratios were determined by analytical chiral HPLC analyses on Daicel Chiralpak columns (250 x 4.6 mm ID) using heptane/ethanol as solvent mixtures. Racemates were obtained using *s*BuLi/PMDTA or by racemization of an enantioenriched sample in NMP at 453 K.

Synthesis and analysis of compounds **8a-c** and **9a-c**.

***N,N*-Diisopropyl-3,5-dimethylbenzamide**.[2] A solution of 3,5-dimethylbenzoic acid (3.00 g, 20 mmol) in thionyl chloride (14.5 mL, 200 mmol) was refluxed for 24 h. The excess thionyl chloride was distilled off by azeotropic distillation with toluene. The residue was dissolved in dry THF (50 mL), diisopropyl amine (14.0 mL, 100 mmol) added dropwise and stirred for 30 minutes at room temperature. The reaction mixture was filtered and the filtrate dried under reduced pressure. Dichloromethane (40 mL) was added and washed with HCl (2 M, 3 x 20 mL), dried over sodium sulfate and concentrated to dryness. Filtration over a short silica plug eluting with 1:1 cyclohexane:ethyl acetate gave a yellow solid (R_f = 0.50, 3.49 g, 75 %), mp 79-81 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (s, 1H), 6.90 (s, 2H), 4.05-3.32 (br, 2H), 2.31 (s, 6H), 1.72-0.92 (br, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 138.9, 138.0, 130.0, 123.1, 50.7, 45.7, 21.2, 20.7. ESI-HRMS $[M+H]^+$: 234.1868, $C_{15}H_{24}NO$ requires 234.1858.

1-Methoxy-3-methyl-5-(3-methylphenethyl)benzene (8a).[3] A solution of *m*-xylene (1.06 g, 10.0 mmol) and 1-methoxy-3,5-dimethylbenzene (0.71 mL, 5.00 mmol) in THF (50 mL) at -78 °C was treated dropwise with BuLi (2.26 M, 7.30 mL, 16.5 mmol) and stirred for 5 min. KO*t*Bu (1.0 M in THF, 16.5 mL, 16.5 mmol) was added dropwise followed by 2,2,6,6-tetramethylpiperidine (2.78 mL, 15.0 mmol). The reaction mixture was stirred for 15 min at -78 °C, 1,2-dibromoethane (2.14 mL, 25.0 mmol) added and stirred for a further 5 min. The reaction mixture was warmed to rt and the solvent was removed under reduced pressure. Diethyl ether (30 mL) was added to the residue, washed with HCl (2 M, 3 x 10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with 98:2 pentane:diethyl ether gave **8a** as a colourless oil (R_f = 0.65, 481 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.5 Hz, 1H), 7.05–6.98 (m, 3H), 6.63 (s, 1H), 6.56 (d, *J* = 7.5 Hz, 2H), 3.76 (s, 3H), 2.85 (br s, 4H), 2.33 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 143.4, 141.9, 139.3, 137.9, 129.2, 128.2, 126.6,

125.4, 121.8, 112.2, 111.1, 55.1, 38.1, 37.9, 21.5, 21.4; ESI-HRMS $[M+H]^+$: 241.1595, $C_{17}H_{21}O$ requires 241.1592.

***N,N*-Diisopropyl-3-methyl-5-(3-methylphenethyl)benzamide (8b)**. A solution of *m*-xylene (1.06 g, 10.0 mmol) and *N,N*-diisopropyl-3,5-dimethylbenzamide (1.16 g, 5.0 mmol) in THF (50 mL) at -78 °C was treated dropwise with BuLi (2.50 M, 8.0 mL, 20.0 mmol) and stirred for 5 min. A solution of KO*t*Bu (1.0 M in THF, 20.0 mL, 20.0 mmol) in THF (25 mL) was added dropwise followed by 2,2,6,6-tetramethylpiperidine (3.37 mL, 20.0 mmol). The reaction mixture was stirred for 15 min at -78 °C, 1,2-dibromoethane (2.14 mL, 25.0 mmol) added and stirred for a further 5 min. The reaction mixture was warmed to rt and the solvent was removed under reduced pressure. Ethyl acetate (30 mL) was added to the residue, washed with HCl (2 M, 3 x 20 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with 60:40 pentane:diethyl ether gave **8b** as a colorless oil (R_f = 0.65, 491 mg, 30%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (t, *J* = 7.8 Hz, 1H), 7.01-6.90 (m, 6H), 3.97-3.37 (br, 2H), 2.86 (s, 4H), 2.32 (s, 3H) superimposed to 2.31 (s, 3H), 1.65-0.96 (br, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 142.0, 141.6, 139.0, 138.1, 137.8, 129.5, 129.2, 128.2, 126.6, 125.4, 123.8, 122.5, 37.8, 37.7, 21.4, 21.3, 20.7. (Note: *i*-Pr tertiary C not observed). ESI-HRMS $[M+H]^+$: 338.2480, $C_{23}H_{32}NO$ requires 338.2484.

1,2-Bis(3-methoxy-5-methylphenyl)ethane (8c).[3] A solution of 1-methoxy-3,5-dimethylbenzene (204 mg, 1.50 mmol) in THF (15 mL) at -78 °C was treated dropwise with BuLi (2.40 M, 0.69 mL, 1.65 mmol) and stirred for 5 min. KO*t*Bu (1.0 M in THF, 1.65 mL, 1.65 mmol) was added dropwise followed by 2,2,6,6-tetramethylpiperidine (0.25 mL, 1.50 mmol). The reaction mixture was stirred for 15 min at -78 °C, 1,2-dibromoethane (0.39 mL, 4.50 mmol) added and stirred for a further 5 min. The reaction mixture was warmed to rt and the solvent was removed under reduced pressure.

Diethyl ether (30 mL) was added to the residue, washed with HCl (2 M, 3 x 10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with 98:2 cyclohexane:ethyl acetate gave **8c** as a colourless solid (R_f = 0.50, 186 mg, 92%), mp 80-81 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.65 (s, 2H), 6.58–6.57 (m, 4H), 3.78 (s, 6H), 2.85 (s, 4H), 2.32 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.69, 143.30, 139.28, 121.75, 112.19, 111.11, 55.11, 37.94, 21.50; ESI-HRMS $[M+Na]^+$: 293.1510, $C_{18}H_{22}O_2Na$ requires 293.1517.

5-Methoxy[2.2]metacyclophane (9a).[3,4] A solution of 1-methoxy-3-methyl-5-(3-methylphenethyl)benzene **8a** (481 mg, 2.00 mmol) in THF (30 mL) at -78 °C was treated dropwise with BuLi (2.26 M, 2.50 mL, 5.00 mmol) and stirred for 5 min. KO*t*Bu (1.0 M in THF, 5.00 mL, 5.00 mmol) was added dropwise followed by 2,2,6,6-tetramethylpiperidine (0.67 mL, 4.00 mmol). The reaction mixture was stirred for 30 min during which time the temperature was raised to -60 °C. 1,2-Dibromoethane (0.51 mL, 15.0 mmol) was added, the reaction mixture was warmed to rt and the solvent was removed under reduced pressure. Diethyl ether (30 mL) was added to the residue, washed with HCl (2 M, 3 x 10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with 99:1 cyclohexane:diethyl ether gave **9a** as a colourless solid (R_f = 0.55, 200 mg, 42%), mp 83-85 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.4 Hz, 1H), 7.03 (dd, *J* = 7.4, 1.4 Hz, 2H), 6.64 (d, *J* = 0.9 Hz, 2H), 4.38 (s, 1H), 3.98 (s, 1H), 3.84 (s, 3H), 3.05 (m, 4H), 2.12 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 140.4, 138.9, 136.2, 129.9, 128.5, 125.3, 110.8, 55.3, 41.1, 40.9; EI-HRMS $[M]^+$: 238.1359, $C_{17}H_{18}O$ requires 238.1358.

***N*,*N*-Diisopropyl[2.2]metacylophane-5-carboxamide (9b)**. A solution of *N*,*N*-diisopropyl-3-methyl-5-(3-methylphenethyl)benzamide **8b** (472 mg, 1.40 mmol) in THF (30 mL) at -78 °C was treated dropwise with BuLi (2.50 M, 1.40 mL, 5.60 mmol) and stirred for 5 min. A solution of KO*t*Bu (1.0 M in THF, 5.60 mL, 5.60 mmol) was added dropwise followed by 2,2,6,6-

tetramethylpiperidine (0.95 mL, 5.60 mmol). The reaction mixture was stirred for 30 min during which time the temperature was raised to -60 °C. 1,2-Dibromoethane (0.72 mL, 8.40 mmol) was added, the reaction mixture was warmed to rt and the solvent was removed under reduced pressure. Ethyl acetate (30 mL) was added to the residue, washed with HCl (2 M, 3 x 10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with 3:2 pentane:diethyl ether gave **9b** as a colourless solid (R_f = 0.65, 144 mg, 31%), mp 65-67 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 1.3 Hz, 3H), 7.04 (d, *J* = 1.5 Hz, 1H), 4.39 (s, 1H), 4.24 (s, 1H), 3.92-3.41 (br, 2H), 3.15-3.03 (m, 4H), 2.19-2.05 (m, 4H), 1.74-0.93 (br, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 139.6, 138.7, 138.6, 137.0, 136.8, 129.0, 125.4, 122.9, 40.9, 40.5, 20.7. (Note: *i*-Pr tertiary C not observed). ESI-HRMS $[M+H]^+$: 336.2314, $C_{23}H_{30}NO$ requires 336.2327.

5,13-Dimethoxy[2.2]metacyclophane (9c).[3,5] A solution of 1,2-bis(3-methoxy-5-methylphenyl)ethane **8c** (354 mg, 1.31 mmol) in THF (30 mL) at -78 °C was treated dropwise with BuLi (2.50 M, 1.31 mL, 3.28 mmol) and stirred for 5 min. KO*t*Bu (1.0 M in THF, 3.28 mL, 3.28 mmol) was added dropwise followed by 2,2,6,6-tetramethylpiperidine (0.44 mL, 2.62 mmol). The reaction mixture was stirred for 30 min during which time the temperature was raised to -60 °C. 1,2-Dibromoethane (0.34 mL, 3.93 mmol) was added, the reaction mixture was warmed to rt and the solvent was removed under reduced pressure. Diethyl ether (30 mL) was added to the residue, washed with HCl (2 M, 3 x 10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with 94:6 pentane:ethyl acetate gave **9c** as a colourless solid (R_f = 0.70, 123 mg, 35%), mp 166-169 °C (lit.[6] mp 168-170 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.62 (s, 4H), 4.08 (s, 2H), 3.83 (s, 6H), 3.06–2.96 (m, 4H), 2.18–2.08 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 140.4, 129.5, 110.8, 55.3, 41.0; EI-HRMS $[M]^+$: 268.1460, $C_{18}H_{20}O_2$ requires 268.1463.

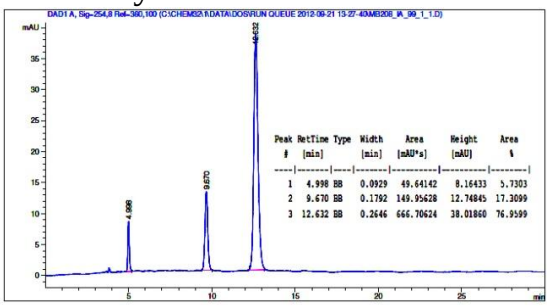
Enantioselective *o*-lithiation of [2.2]metacyclophanes **9a-c**

General procedure. A solution of [2.2]metacyclophane **9** (0.10 mmol) in dry diethyl ether or dry heptane was treated with (-)-sparteine (46 µL, 0.20 mmol) and the mixture was stirred for 5 min. After cooling to the specified temperature, BuLi (2.50 M, 80 µL, 0.20 mmol) or *s*BuLi (1.40 M, 150 µL, 0.20 mmol) were added dropwise and the reaction mixture stirred for the required time. The reaction mixture was cooled to -78 °C and ethyl chloroformate (30 µL, 0.30 mmol) added dropwise. The reaction mixture was stirred for the specified time and the solvent was removed under reduced pressure. Ethyl acetate (10 mL) was added to the residue, washed with HCl (2 M, 2 x 10 mL), dried over sodium sulfate and concentrated to dryness. The crude products were purified by silica gel chromatography followed by chiral HPLC analyses (Chiralpak IA 250 x 4.6 mm ID, 254nm UV detector, room temperature).

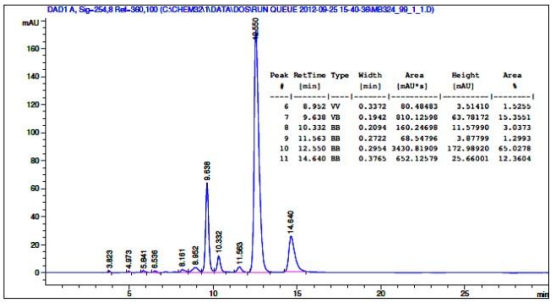
Tabulated results:

Entry	Cyclophane	RLi	T (°C)	solvent	product	yield (%)	e.r.
1	**9a**	BuLi	-78	ether	**11a**	-	-
2	**9a**	BuLi	rt	ether	**11a**	15	72:18
3	**9a**	*s*BuLi	rt	ether	**11a**	51	81:19
4	**9a**	*s*BuLi	-78	ether	**11a**	18	82:18
5	**9a**	*s*BuLi	-60	ether	**11a**	43	89:11
6	**9a**	*s*BuLi	-40	ether	**11a**	65	91:9
7	**9a**	*s*BuLi	-20	ether	**11a**	58	85:15
8	**9a**	*s*BuLi	0	heptane	**11a**	-	-
9	**9b**	BuLi	-40	ether	**11b**	-	-
10	**9b**	*s*BuLi	0	heptane	**11b**	-	-
11	**9b**	*s*BuLi	-40	ether	**11b**	73	74:26
12	**9b**	*s*BuLi	-78	ether	**11b**	76	85:15
13	**9c**	BuLi	-78	ether	**11c**	-	-
14	**9c**	*s*BuLi	-40	ether	**11c**	46	91:9

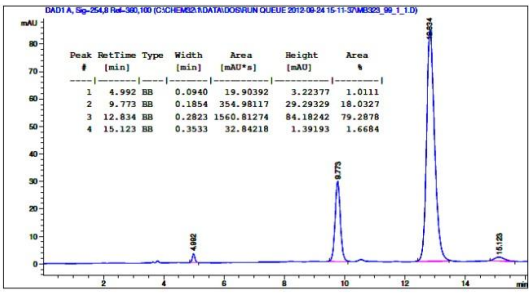
HPLC Analysis for Table 2



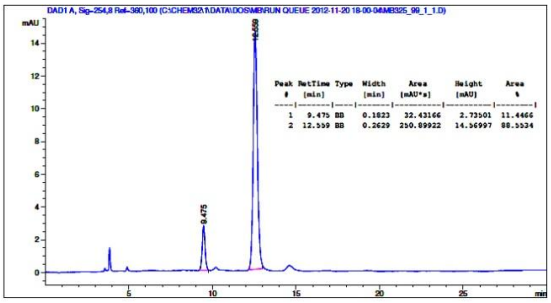
Entry 2. **11a**



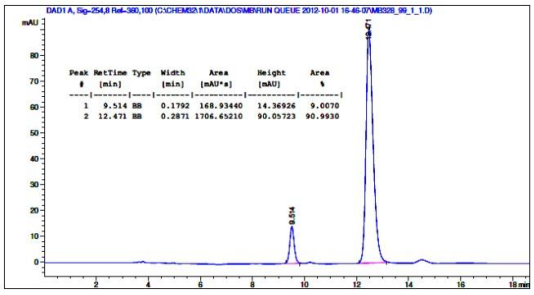
Entry 3. **11a**



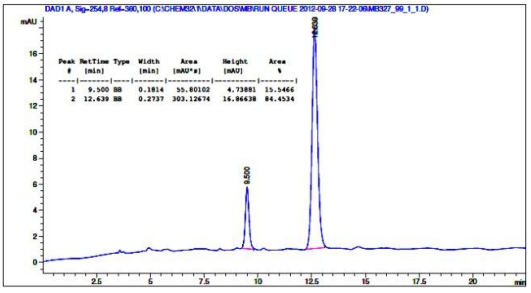
Entry 4. **11a**



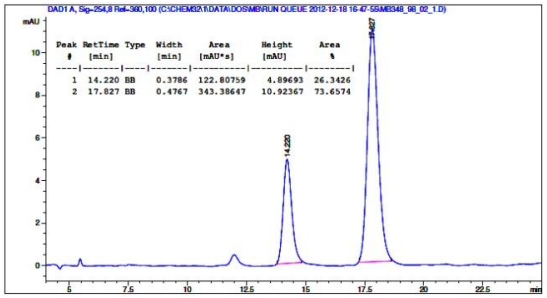
Entry 5. **11a**



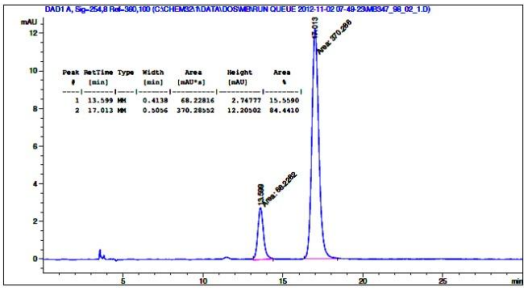
Entry 6. **11a**



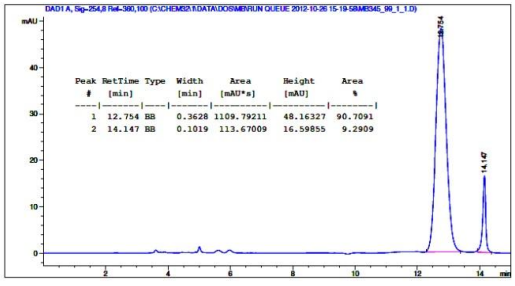
Entry 7. **11a**



Entry 11. **11b**



Entry 12. **11b**



Entry 14. **11c**

11a: Eluent: 1% ethanol in heptane, flow rate: 1.0 ml/min. Retention times: 9.7 min (minor isomer) and 12.8 min (major isomer).

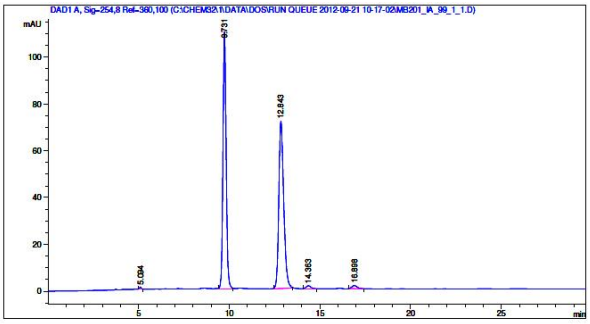
11b: Eluent: 2% ethanol in heptane, flow rate: 1.0 ml/min). Retention times: 13.6 min (minor isomer) and 17.0 min (major isomer).

11c: Eluent: 1% ethanol in heptane, flow rate: 1.0 ml/min. Retention times: 12.7 min (major isomer) and 14.1 min (minor isomer).

Synthesis and analysis of compounds **11a-k**

(R_p)-(-)-5-Methoxy[2.2]metacylophane-4-carboxylic acid ethyl ester (11a). A solution of 5-methoxy[2.2]metacyclophane **9a** (23.8 mg, 0.10 mmol) in dry diethyl ether (1 mL) was treated with (-)-sparteine (46 µL, 0.20 mmol) and the mixture was stirred for 5 min. After cooling to -40 °C, *s*BuLi (150 µL, 0.20 mmol) was added dropwise and the reaction mixture stirred at -40 °C for 4 h. The reaction mixture was cooled to -78 °C and ethyl chloroformate (30 µL, 0.30 mmol) added dropwise. The reaction mixture was stirred at room temperature for 1 h and the solvent was removed under reduced pressure. Ethyl acetate (10 mL) was added to the residue, washed with HCl (2 M, 2 x 10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with 70:30 pentane:diethyl ether gave **11a** as a colourless solid (R_f = 0.60, 20 mg, 65%), mp 70-72 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 2H), 6.66 (s, 1H), 4.53 (s, 1H), 4.50-4.36 (m, 2H), 3.94 (s, 1H), 3.86 (s, 3H), 3.15 (dt, *J* = 12.5, 3.5 Hz, 1H), 3.11 (dt, *J* = 5.8, 3.1 Hz, 1H), 3.08-3.00 (m, 2H), 2.38 (td, *J* = 12.2, 3.5 Hz, 1H), 2.20-2.04 (m, 2H), 1.95 (td, *J* = 12.4, 3.6 Hz, 1H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.5, 157.3, 141.3, 139.0, 138.6, 137.0, 136.3, 129.9, 128.8, 125.6, 125.3, 120.8, 108.5, 61.1, 56.1, 41.3, 40.6, 39.8, 38.7, 14.4. EI-HRMS $[M]^+$: 310.1555, $C_{20}H_{22}O_3$ requires 310.1569. $[\alpha]_D^{20}$= -20.3 (c 0.4, $CHCl_3$, 82% ee). Enantiomeric excess was determined by analytical chiral HPLC (Chiralpak IA 250 x 4.6 mm ID, 254nm UV detector, room temperature, eluent: 1% ethanol in heptane, flow rate: 1.0 ml/min). Retention times: 9.7 min (minor isomer) and 12.8 min (major isomer).

HPLC of *racemic* **11a**



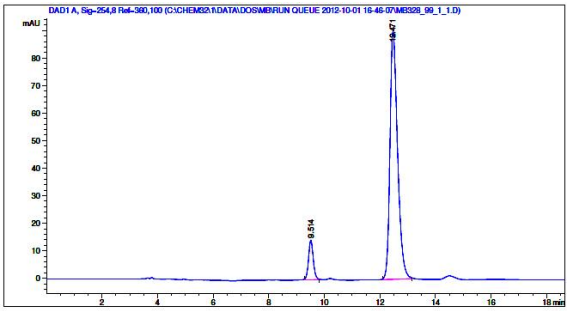
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.094	BB	0.0958	6.18696	1.00515	0.2265
2	9.731	BB	0.1851	1326.16968	109.61888	48.5556
3	12.843	BB	0.2905	1348.18811	71.34035	49.3617
4	14.363	BB	0.2797	23.06743	1.27126	0.8446
5	16.898	BB	0.3177	27.62957	1.33345	1.0116

HPLC of **11a**



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,8 Ref=360,100

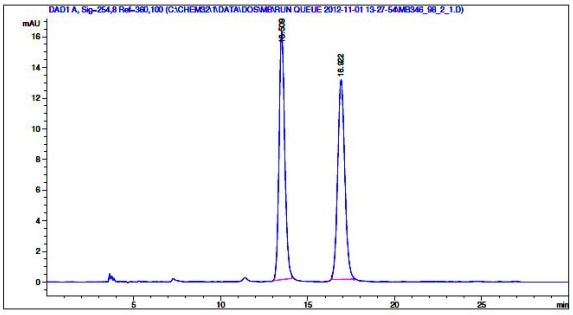
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.514	BB	0.1792	168.93440	14.36926	9.0070
2	12.471	BB	0.2871	1706.65210	90.05723	90.9930

Totals : 1875.58650 104.42649

(R_p)-(-)-5-(*N*,*N*-Diisopropylcarbamoyl)[2.2]metacylophane-4-carboxylic acid ethyl ester (11b). A solution of *N*,*N*-diisopropyl[2.2]metacylophane-5-carboxamide **9b** (33.5 mg, 0.10 mmol) in dry diethyl ether (1 mL) was treated with (-)-sparteine (46 µL, 0.20 mmol) and the mixture was stirred for 5 min. After cooling to -78 °C, *s*BuLi (150 µL, 0.20 mmol) was added dropwise and the reaction mixture stirred at -78 °C for 4 h. Ethyl chloroformate (30 µL, 0.30 mmol) was added dropwise, the reaction mixture was stirred at room temperature for 1 h and the solvent was removed under reduced pressure. Ethyl acetate (10 mL) was added to the residue, washed with HCl (2 M, 2 x 10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with 3:2 pentane:diethyl ether gave **11b** as a colourless solid (R_f = 0.50, 31 mg, 76%), mp 120-121 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 6.96 (s, 1H), 4.60-4.48 (br, 1H), 4.44 (dt, *J* = 17.0, 7.2 Hz, 1H), 4.31 (dt, *J* = 17.5, 7.0 Hz, 1H), 4.24 (s, 1H), 3.77-3.62 (m, 1H), 3.61-3.43 (m, 2H), 3.18-3.05 (m, 3H), 2.60-2.40 (br, 1H), 2.22-2.06 (m, 2H), 1.91 (td, *J* = 12.0, 3.1 Hz, 1H), 1.56 (d, *J* = 6.4 Hz, 6H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.20-1.05 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 167.9, 139.5, 139.2, 138.1, 137.3, 129.3, 126.8, 125.7, 125.3, 122.7, 61.2, 51.1, 45.6, 40.9, 39.8, 39.1, 20.4, 14.3.

ESI-HRMS $[M+H]^+$: 408.2546, $C_{26}H_{34}NO_3$ requires 408.2539. $[\alpha]_D^{20}$= -33.2 (c 0.6, $CHCl_3$, 69% ee). Enantiomeric excess was determined by analytical chiral HPLC (Chiralpak IA 250 x 4.6 mm ID, 254nm UV detector, room temperature, eluent: 2% ethanol in heptane, flow rate: 1.0 ml/min). Retention times: 13.6 min (minor isomer) and 17.0 min (major isomer).

HPLC chart of *racemic* **11b**



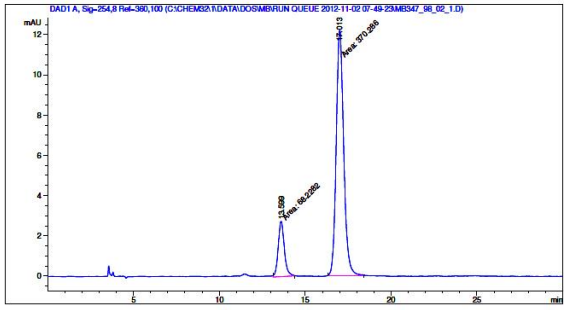
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.509	BB	0.3493	368.43286	16.20470	49.9976
2	16.922	BB	0.4357	368.46783	13.03800	50.0024
Totals :				736.90070	29.24271	

HPLC chart of **11b**



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

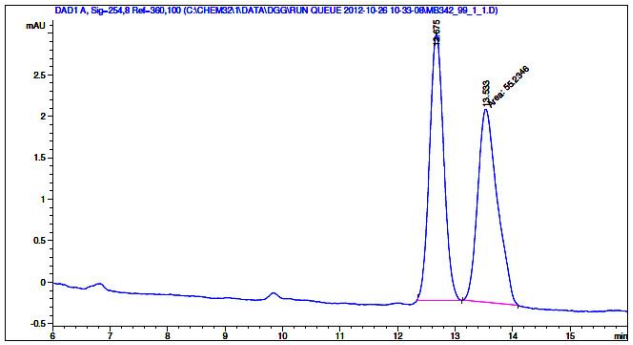
Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.599	MM	0.4138	68.22816	2.74777	15.5590
2	17.013	MM	0.5056	370.28552	12.20502	84.4410
Totals :				438.51368	14.95279	

(R_p)-(-)-5,13-Dimethoxy[2.2]metacylophane-4-carboxylic acid ethyl ester (11c). A solution of 5,13-dimethoxy[2.2]metacyclophane **9c** (26.8 mg, 0.10 mmol) in dry diethyl ether (4 mL) was treated with (-)-sparteine (46 µL, 0.20 mmol) and the mixture was stirred for 5 min. After cooling to -40°C, *s*BuLi (150 µL, 0.20 mmol) was added dropwise and the reaction mixture stirred at -40 °C for 4 h. The reaction mixture was cooled to -78 °C and ethyl chloroformate (30 µL, 0.30 mmol) added dropwise. The reaction mixture was stirred at room temperature for 1 h and the solvent was removed under reduced pressure. Ethyl acetate (10 mL) was added to the residue, washed with HCl (2 M, 2 x 10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with 99.5:0.5 DCM:MeOH gave **11c** as a colourless solid (R_f = 0.50, 16 mg, 46%), mp 74-78 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.64 (s, 1H), 6.62 (s, 2H), 4.50-4.36 (m, 2H), 4.22 (s, 1H), 4.05 (s, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 3.13 (dt, *J* = 12.4, 3.4 Hz, 1H), 3.07-3.02

(m, 2H), 2.98 (dt, *J* = 12.2, 3.5 Hz, 1H), 2.36 (td, *J* = 12.2, 3.4 Hz, 1H), 2.18-2.10 (m, 2H), 2.01 (td, *J* = 12.3, 3.5 Hz, 1H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 160.7, 157.1, 141.3, 140.5, 140.1, 137.0, 129.6, 120.7, 110.9, 110.8, 108.4, 61.1, 56.0, 55.3, 41.2, 40.7, 39.9, 38.6, 14.3. ESI-HRMS $[M+H]^+$: 341.1765, $C_{21}H_{25}O_4$ requires 341.1753. $[\alpha]_D^{20}$= -12.5 (c 0.3, $CHCl_3$, 82% ee). Enantiomeric excess was determined by analytical chiral HPLC (Chiralpak IA 250 x 4.6 mm ID, 254nm UV detector, room temperature, eluent: 1% ethanol in heptane, flow rate: 1.0 ml/min). Retention times: 12.7 min (major isomer) and 14.1 min (minor isomer).

HPLC chart of *racemic* **11c**



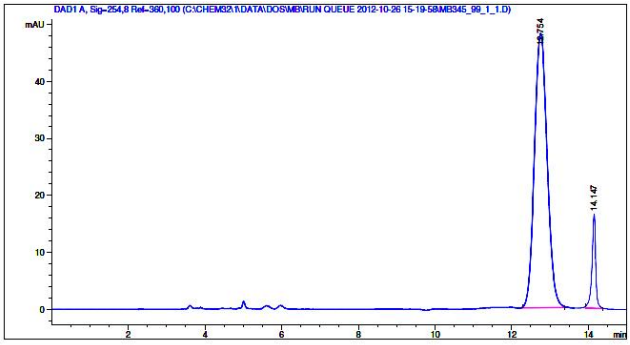
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.675	BB	0.2638	54.95518	3.20832	49.8732
2	13.533	MM	0.3950	55.23459	2.33072	50.1268
Totals :				110.18977	5.53904	

HPLC chart of **11c**



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

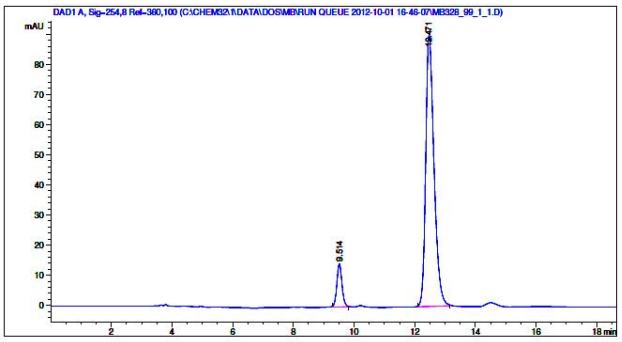
Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.754	BB	0.3628	1109.79211	48.16327	90.7091
2	14.147	BB	0.1019	113.67009	16.59855	9.2909
Totals :				1223.46220	64.76181	

(R_p)-(-)-5-Methoxy[2.2]metacylophane-4-carboxylic acid (11d). A solution of (R_p)-5-methoxy[2.2]metacylophane-4-carboxylic acid ethyl ester **11a** (50.0 mg, 0.16 mmol, 91:9 e.r.) in 2-propanol (3 mL) was treated with KOH (20% in 2-propanol, 6 mL) and the mixture was heated at 80 °C for 30 min. After cooling to room temperature, the reaction mixture was quenched with HCl (2 M, 20 mL), ethyl acetate (10 mL) was added, washed with water (2 x 20 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with ethyl acetate gave **11d** as a colourless solid (R_f = 0.50, 40 mg, 88%), mp 162-164 °C. ^{1}H NMR (500

MHz, CD_3OD) δ 7.27 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 2H), 4.49 (s, 1H), 3.94 (s, 1H), 3.88 (s, 3H), 3.25 (dt, *J* = 12.5, 3.5 Hz, 1H), 3.16-3.09 (m, 2H), 3.04 (dt, *J* = 12.3, 3.5 Hz, 1H), 2.34 (td, J = 12.2, 3.5 Hz, 1H), 2.20-2.12 (m, 1H), 2.10-2.03 (m, 1H), 1.94 (td, *J* = 12.3, 3.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 158.3, 143.4, 141.3, 139.4, 138.0, 135.8, 131.9, 129.1, 125.8, 125.2, 116.4, 108.7, 56.6, 41.3, 40.6, 40.1, 39.4. ESI-HRMS $[M-H]^-$: 281.1168, $C_{18}H_{17}O_3$ requires 281.1178. $[\alpha]_D^{20}$= -5.3 (c 0.3, MeOH, 82% ee). Enantiomeric excess was determined after esterification followed by analytical chiral HPLC analysis. A solution of 5-methoxy[2,2]metacylophane-4-carboxylic acid (40 mg, 0.14 mmol) in ethanol (10 mL) was treated with 12 M HCl (three drops) and heated under reflux for 1 h. The solvent was removed under reduced pressure and ethyl acetate (20 mL) was added. The organic layer was washed with saturated $NaHCO_3$ and water, dried over sodium sulfate and concentrated to dryness. Purification over a short silica plug (70:30 pentane:diethyl ether) gave the corresponding ethyl ester **11a** which was analyzed by chiral HPLC (Chiralpak IA 250 x 4.6 mm ID, 254nm UV detector, room temperature, eluent: 1% ethanol in heptane, flow rate: 1.0 ml/min). Retention times: 9.7 min (minor isomer) and 12.8 min (major isomer).

HPLC chart of **11a** *before* hydrolysis



Area Percent Report

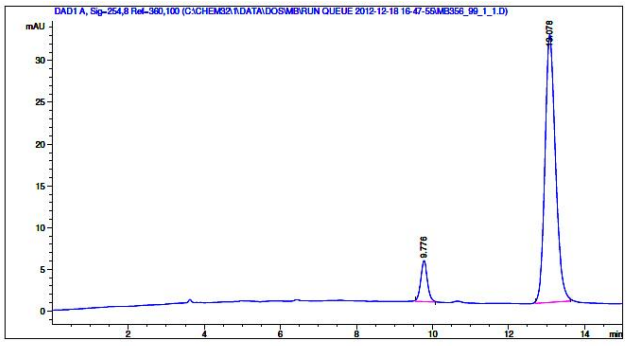
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.514	BB	0.1792	168.93440	14.36926	9.0070
2	12.471	BB	0.2871	1706.65210	90.05723	90.9930

Totals : 1875.58650 104.42649

HPLC chart of **11a** *after* hydrolysis *and* re-esterification.



Area Percent Report

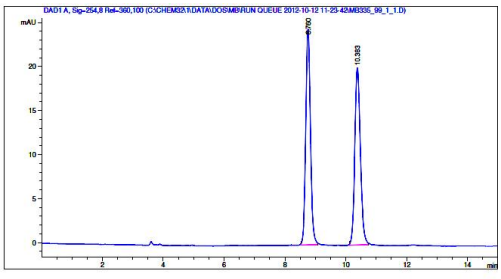
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.776	BB	0.1853	59.27991	4.89419	8.7532
2	13.078	BB	0.2948	617.95917	32.07657	91.2468

(R_p)-(+)-5-Methoxy[2.2]metacylophane-4-carbaldehyde (11e). A solution of 5-methoxy[2.2]metacyclophane **9a** (23.8 mg, 0.10 mmol) in dry diethyl ether (1 mL) was treated with (-)-sparteine (46 µL, 0.20 mmol) and the mixture was stirred for 5 min. After cooling to -40°C, *s*BuLi (150 µL, 0.20 mmol) was added dropwise and the reaction mixture stirred at -40 °C for 4 h. The reaction mixture was cooled to -78 °C and DMF (24 µL, 0.30 mmol) added dropwise. The reaction mixture was stirred at room temperature for 2 h and the solvent was removed under reduced pressure. Ethyl acetate (10 mL) was added to the residue, washed with HCl (2 M, 2 x 10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with 70:30 pentane:diethyl ether gave **11e** as a colourless solid (R_f = 0.80, 18 mg, 68%), mp 88-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.64 (s, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.69 (s, 1H), 4.45-4.35 (m, 2H), 3.99 (s, 1H), 3.93 (s, 3H), 3.20-3.03 (m, 3H), 2.22-2.02 (m, 4H), 1.69 (td, *J* = 11.7, 3.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 164.2, 146.8, 142.2, 139.4, 137.8, 135.3, 131.8, 129.0, 125.8, 125.1, 120.4, 108.4, 55.9, 41.6, 40.6, 40.2, 38.0. ESI-HRMS $[M+H]^+$: 267.1379, $C_{18}H_{19}O_2$ requires 267.1385. $[\alpha]_D^{20}$= +97.2 (c 0.4, $CHCl_3$, 82% ee). Enantiomeric excess was determined by analytical chiral HPLC (Chiralpak IA 250 x 4.6 mm ID, 254nm UV detector, room temperature, eluent: 1% ethanol in heptane, flow rate: 1.0 ml/min). Retention times: 8.6 min (minor isomer) and 10.3 min (major).

HPLC chart of *racemic* **11e**



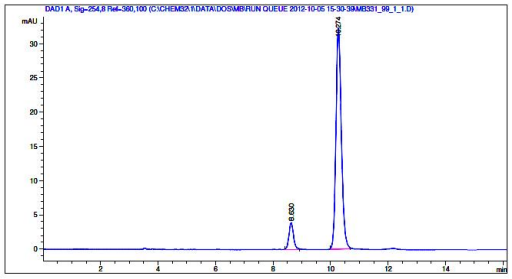
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.760	BB	0.1617	260.15094	24.54319	50.3743
2	10.383	BB	0.1945	256.28528	20.12814	49.6257

HPLC chart of **11e**



Area Percent Report

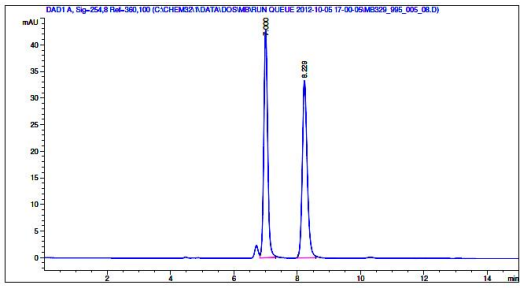
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.630	BB	0.1677	42.58598	3.89077	9.1525
2	10.274	BB	0.2006	422.70691	32.32074	90.8475

(R_p)-(-)-4-Iodo-5-methoxy[2.2]metacylophane (11f). A solution of 5-methoxy[2.2]metacyclophane **9a** (23.8 mg, 0.10 mmol) in dry diethyl ether (1 mL) was treated with (-)-sparteine (46 µL, 0.20 mmol) and the mixture was stirred for 5 min. After cooling to -40°C, *s*BuLi (150 µL, 0.20 mmol) was added dropwise and the reaction mixture stirred at -40 °C for 4 h. The reaction mixture was cooled to -78 °C and a solution of iodine (76 mg, 0.30 mmol) in diethyl ether (1 mL) added dropwise. The reaction mixture was stirred at room temperature for 2 h and the solvent was removed under reduced pressure. Ethyl acetate (10 mL) was added to the residue, washed with HCl (2 M, 2 x 10 mL), sodium thiosulfate (2 x 15 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with 95:5 pentane:diethyl ether gave **11f** as a colourless solid (R_f = 0.70, 22 mg, 59%), mp 56-60 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 7.4, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.56 (d, *J* = 1.5 Hz, 1H), 4.38 (s, 1H), 4.06 (d, *J* = 1.5 Hz, 1H), 3.92 (s, 3H), 3.59 (dt, *J* = 12.4, 3.5 Hz, 1H), 3.10 (dt, *J* = 11.4, 3.3 Hz, 1H), 3.05 (dt, *J* = 11.9, 3.2 Hz, 1H), 3.00 (dt, *J* = 12.4, 3.5 Hz, 1H), 2.27 (td, *J* = 12.3, 3.3 Hz, 1H), 2.18-2.02 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 142.8, 140.1, 138.7, 138.5, 135.9, 130.4, 128.9, 125.8, 125.3, 108.4, 87.3, 56.6, 45.8, 40.7, 40.7, 38.3. $[\alpha]_D^{20}$= −2.4 (c 0.4, $CHCl_3$, 85% ee). Enantiomeric excess was determined by analytical chiral HPLC (Chiralpak IA 250 x 4.6 mm ID, 254nm UV detector, room temperature, eluent: 0.5% ethanol in heptane, flow rate: 0.8 ml/min). Retention times: 7.0 min (minor isomer) and 8.2 min (major isomer).

HPLC chart of *racemic* **11f**



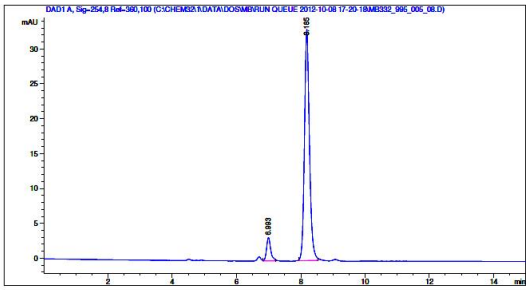
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.000	VB	0.1275	358.79871	42.91515	49.8336
2	8.229	BB	0.1664	361.19470	33.33778	50.1664

HPLC chart of **11f**



Area Percent Report

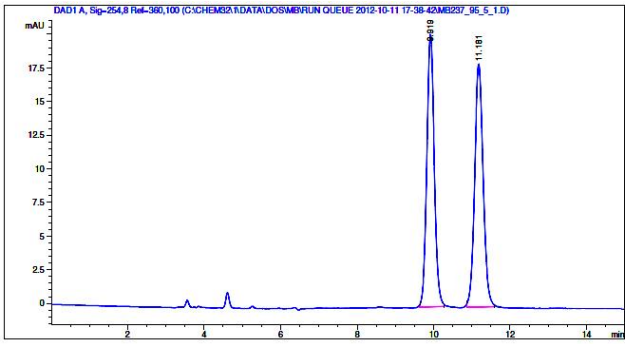
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.993	VB	0.1326	29.48874	3.35470	7.5657
2	8.185	BB	0.1666	360.28149	33.19736	92.4343

(R_p)-(-)-5-Methoxy[2.2]metacylophane-4-phosphonic acid diethyl ester (11g). A solution of 5-methoxy[2.2]metacyclophane **9a** (23.8 mg, 0.10 mmol) in dry diethyl ether (1 mL) was treated with (-)-sparteine (46 µL, 0.20 mmol) and the mixture was stirred for 5 min. After cooling to -40°C, *s*BuLi (150 µL, 0.20 mmol) was added dropwise and the reaction mixture stirred at -40 °C for 4 h. The reaction mixture was cooled to -78 °C and diethyl chlorophosphate (43 µL, 0.30 mmol) added dropwise. The reaction mixture was stirred at room temperature for 4 h and the solvent was removed under reduced pressure. Ethyl acetate (10 mL) was added to the residue, washed with HCl (2 M, 2 x 10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with ethyl acetate gave **11g** as a colourless solid (R_f = 0.50, 22 mg, 58%), mp 113-116 °C. ^{1}H NMR (500 MHz, CD_3OD) δ 7.18 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 2H), 6.79 (dd, *J* = 5.6, 0.7 Hz, 1H), 4.30 (s, 1H), 4.27-4.22 (m, 1H), 4.12-3.97 (m, 4H), 3.95 (d, *J* = 4.2 Hz, 1H), 3.81 (s, 3H), 3.08-3.02 (m, 3H), 2.99 (dt, *J* = 12.5, 3.6 Hz, 1H), 2.17-2.05 (m, 2H), 1.97-1.89 (m, 1H), 1.67 (td, *J* = 12.2, 2.9 Hz, 1H), 1.28-1.21 (m, 6H). ^{13}C NMR (100 MHz, CD_3OD) δ 163.6 (d, *J* = 3.1 Hz), 145.7 (d, *J* = 2.6 Hz), 145.0 (d, *J* = 9.7 Hz), 139.0, 138.1, 134.9, 131.5 (d, *J* = 16.2 Hz), 128.8, 125.2, 124.9, 110.9, 108.9 (d, *J* = 9.8 Hz), 61.9 (d, *J* = 6.0 Hz), 61.8 (d, *J* = 5.9 Hz), 55.3, 40.7 (d, *J* = 0.8 Hz), 40.4 (d, *J* = 1.1 Hz), 40.1 (d, *J* = 0.9 Hz), 39.7 (d, *J* = 2.5 Hz), 15.3 (d, *J* = 6.8 Hz), 15.2 (d, *J* = 6.7 Hz). ^{31}P NMR (162 MHz, CD_3OD) δ 19.6 (s). ESI-HRMS $[M+Na]^+$: 397.1557, $C_{21}H_{27}O_4PNa$ requires 397.1545. $[\alpha]_D^{20}$= −3.9 (c 0.4, $CHCl_3$, 86% ee). Enantiomeric excess was determined by analytical chiral HPLC (Chiralpak IA 250 x 4.6 mm ID, 254nm UV detector, room temperature, eluent: 5% ethanol in heptane, flow rate: 1.0 ml/min). Retention times: 9.9 min (minor isomer) and 11.2 min (major isomer).

HPLC chart of *racemic* **11g**



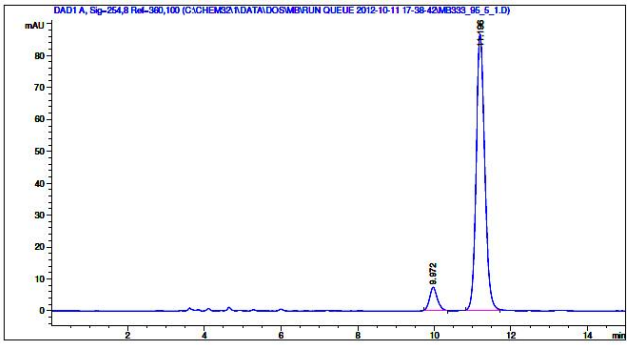
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.919	BB	0.2070	272.82547	20.26728	49.5678
2	11.181	BB	0.2353	277.58316	18.06306	50.4322

HPLC chart of **11g**



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

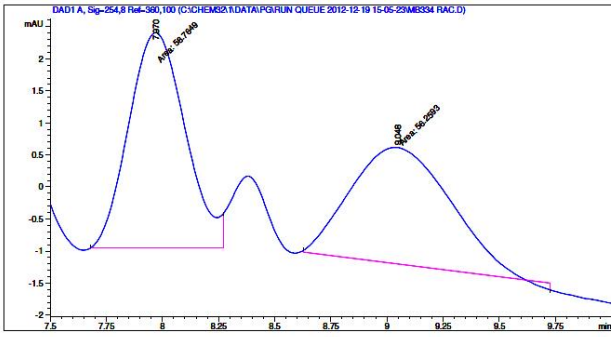
Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.972	BB	0.2153	106.18696	7.40441	7.3450
2	11.196	BB	0.2384	1339.52466	86.62981	92.6550

(R_p)-(-)-Diphenyl(5-methoxy[2.2]metacylophan-4-yl)phosphine oxide (11h). A solution of 5-methoxy[2.2]metacyclophane **9a** (23.8 mg, 0.10 mmol) in dry diethyl ether (1 mL) was treated with (-)-sparteine (46 µL, 0.20 mmol) and the mixture was stirred for 5 min. After cooling to -40°C, *s*BuLi (150 µL, 0.20 mmol) was added dropwise and the reaction mixture stirred at -40 °C for 4 h. The reaction mixture was cooled to -78 °C and chlorodiphenylphosphine (55 µL, 0.30 mmol) added dropwise. The reaction mixture was stirred at room temperature for 4 h and the solvent was removed under reduced pressure. Ethyl acetate (10 mL) was added to the residue, washed with HCl (2 M, 2 x 10 mL), dried over sodium sulfate and concentrated to dryness. Purification by short-pad silica gel chromatography eluting with DCM gave **11h** as a colourless solid (R_f = 0.40, 30 mg, 69%), mp 196-198 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.78 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.67 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.65 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.53-7.42 (m, 4H), 7.42-7.36 (m, 2H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.08-7.02 (m, 2H), 6.60-6.57 (m, 1H), 4.92 (dt, *J* = 12.1, 3.3 Hz, 1H), 4.47 (s, 1H), 4.13 (d, *J* = 1.7 Hz, 1H), 3.24 (s, 3H), 3.15 (dt, *J* = 12.1, 3.5 Hz, 1H), 3.08 (dq, *J* = 11.4, 3.8 Hz, 2H), 2.25-2.15 (m, 2H), 2.08 (td, *J* = 12.0, 3.7 Hz, 1H), 1.80 (td, *J* = 12.1, 3.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8 (d, *J* = 4.7 Hz), 147.8 (d, *J* = 6.1 Hz), 144.9

(d, *J* = 2.1 Hz), 139.7, 137.9, 136.9, 135.9, 135.8, 135.2, 134.8, 133.1 (d, *J* = 11.2 Hz), 131.4 (d, *J* = 10.2 Hz), 131.1 (d, *J* = 10.3 Hz), 131.0 (d, *J* = 2.8 Hz), 130.7 (d, *J* = 2.9 Hz), 129.0, 128.1 (d, *J* = 12.5 Hz), 127.9 (d, *J* = 12.5 Hz), 125.7, 125.0, 115.2, 114.1, 109.1 (d, *J* = 6.6 Hz), 55.1, 41.1, 41.0, 40.6, 39.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.0 (s). ESI-HRMS $[M+H]^+$: 439.1815, $C_{29}H_{28}O_2P$ requires 439.1827. $[\alpha]_D^{20}$= -14.2 (c 0.6, $CHCl_3$, 89% ee). Enantiomeric excess was determined by analytical chiral HPLC (Chiralpak IA 250 x 4.6 mm ID, 254nm UV detector, room temperature, eluent: 20% ethanol in heptane, flow rate: 0.8 ml/min). Retention times: 7.8 min (minor isomer) and 8.9 min (major isomer).

HPLC chart of *racemic* **11h***



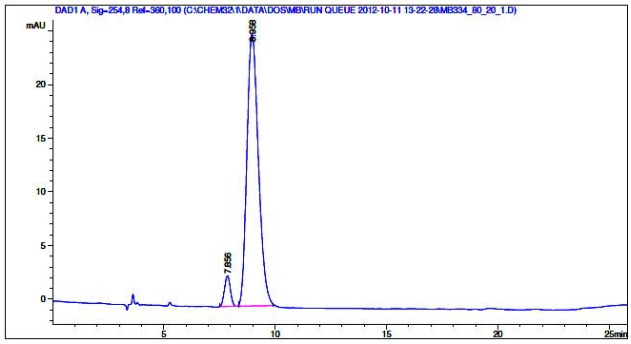
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.970	MM	0.2918	58.76494	3.35668	51.0892
2	9.048	MM	0.5155	56.25933	1.81906	48.9108

HPLC chart of **11h**



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,8 Ref=360,100

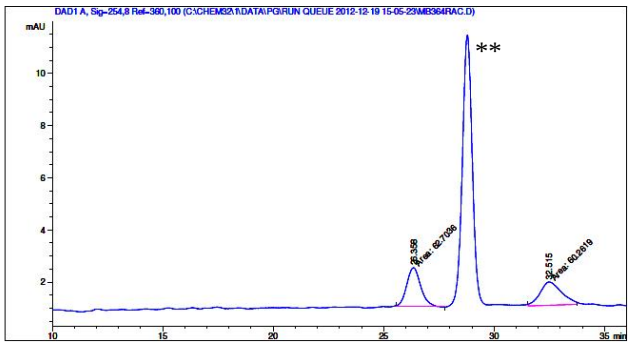
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.856	BB	0.2910	52.73690	2.86195	5.4968
2	8.958	BB	0.5512	906.68085	25.35197	94.5032

* obtained by racemization of **11h** in NMP (453 K)

(R_p)-(+)-*N*,*N*-Diisopropyl-4-formyl-[2.2]metacylophane-5-carboxamide (11i). A solution of *N*,*N*-diisopropyl[2.2]metacylophane-5-carboxamide **9b** (33.5 mg, 0.10 mmol) in dry diethyl ether (1 mL) was treated with (-)-sparteine (46 µL, 0.20 mmol) and the mixture was stirred for 5 min. After cooling to -78 °C, *s*BuLi (150 µL, 0.20 mmol) was added dropwise and the reaction mixture stirred at -78 °C for 4 h. DMF (24 µL, 0.30 mmol) was added dropwise, the reaction mixture was stirred at room temperature for 2 h and the solvent was removed under reduced pressure. Ethyl acetate (10

mL) was added to the residue, washed with HCl (2 M, 2 x 10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with 3:2 pentane:ethyl acetate gave **11i** as a colourless solid (R_f = 0.60, 19 mg, 59%), mp 101-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.12-7.00 (m, 3H), 4.42-4.26 (m, 3H), 3.57-3.45 (m, 2H), 3.24-3.10 (m, 3H), 2.21-2.06 (m, 3H), 1.85 (td, *J* = 12.0, 3.0 Hz, 1H), 1.60 (dd, *J* = 6.8, 2.8 Hz, 6H), 1.08 (d, *J* = 5.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.0, 169.4, 138.7, 138.6, 137.8, 136.0, 129.5, 127.5, 125.8, 125.4, 123.5, 51.2, 46.0, 41.1, 40.3, 37.6, 20.6, 20.5, 20.4, 20.2. ESI-HRMS $[M+H]^+$: 364.2284, $C_{24}H_{30}NO_2$ requires 364.2277. $[\alpha]_D^{20}$= +30.3 (c 0.4, $CHCl_3$, 68% ee). Enantiomeric excess was determined by analytical chiral HPLC (Chiralpak IA 250 x 4.6 mm ID, 254nm UV detector, room temperature, eluent: 2% ethanol in heptane, flow rate: 1.0 ml/min). Retention times: 26.5 min (major isomer) and 33.3 min (minor isomer).

HPLC chart of *racemic* **11i***



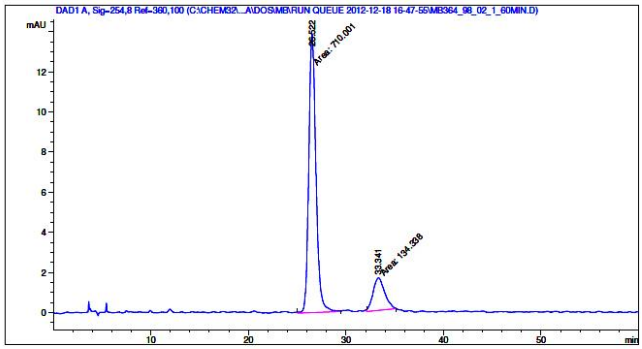
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.358	MM	0.7165	62.70362	1.45848	50.9928
2	32.515	MM	1.1295	60.26192	8.89231e-1	49.0072
Totals :				122.96554	2.34771	

HPLC chart of **11i**



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

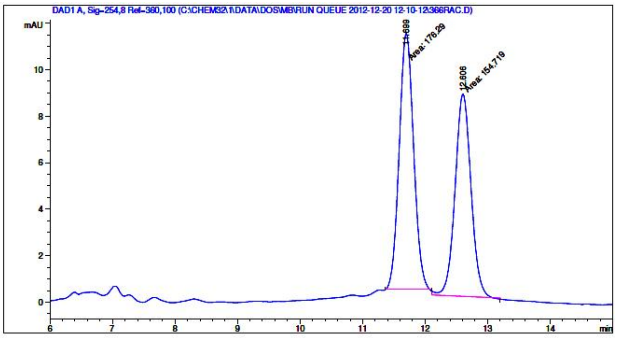
Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.522	MM	0.8531	710.00061	13.87142	84.0895
2	33.341	MM	1.3806	134.33829	1.62175	15.9105

* obtained by racemization of **11i** in NMP (453 K)
** by-product due to decomposition of starting material at 453K

(R_p)-(-)-5,13-Dimethoxy[2.2]metacylophane-4-phosphonic acid diethyl ester (11j). A solution of 5,13-dimethoxy[2.2]metacyclophane **9c** (26.8 mg, 0.10 mmol) in dry diethyl ether (4 mL) was treated with (-)-sparteine (46 µL, 0.20 mmol) and the mixture was stirred for 5 min. After cooling to -40 °C, *s*BuLi (150 µL, 0.20 mmol) was added dropwise and the reaction mixture stirred at -40 °C for 4 h. The reaction mixture was cooled to -78 °C and diethyl chlorophosphate (43 µL, 0.30 mmol) added dropwise. The reaction mixture was stirred at room temperature for 4 h and the solvent was removed under reduced pressure. Ethyl acetate (10 mL) was added to the residue, washed with HCl (2 M, 2 x 10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with ethyl acetate gave **11j** as a colourless solid (R_f = 0.40, 16 mg, 40%), mp 130-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (d, *J* = 5.3 Hz, 1H), 6.61 (d, *J* = 11.1 Hz, 2H), 4.48 (dt, *J* = 11.8, 3.3 Hz, 1H), 4.25-4.02 (m, 6H), 3.88 (s, 3H), 3.82 (s, 3H), 3.10-3.00 (m, 3H), 2.26 (td, *J* = 12.3, 3.1 Hz, 1H), 2.20-2.04 (m, 2H), 1.83 (dd, *J* = 12.0, 9.2 Hz, 1H), 1.38-1.27 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0 (d, *J* = 2.9 Hz), 160.8, 145.8 (d, *J* = 9.9 Hz), 144.7 (d, *J* = 2.6 Hz), 141.1, 139.5, 131.6 (d, *J* = 16.0 Hz), 128.8, 110.7, 108.9 (d, *J* = 9.7 Hz), 61.68-61.51 (m), 56.4, 55.3, 41.1 (d, *J* = 0.6 Hz), 41.0 (d, *J* = 0.8 Hz), 40.6, 40.1 (d, *J* = 2.5 Hz), 16.5 (d, *J* = 6.6 Hz), 16.3 (d, *J* = 6.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.7 (s). ESI-HRMS $[M+Na]^+$: 427.1663, $C_{22}H_{29}O_5NaP$ requires 427.1650. $[\alpha]_D^{20}$= -6.2 (c 0.3, $CHCl_3$, 79% ee). Enantiomeric excess was determined by analytical chiral HPLC (Chiralpak IA 250 x 4.6 mm ID, 254nm UV detector, room temperature, eluent: 5% ethanol in heptane, flow rate: 1.0 ml/min). Retention times: 11.8 min (major isomer) and 12.7 min (minor isomer).

HPLC chart of *racemic* **11j**



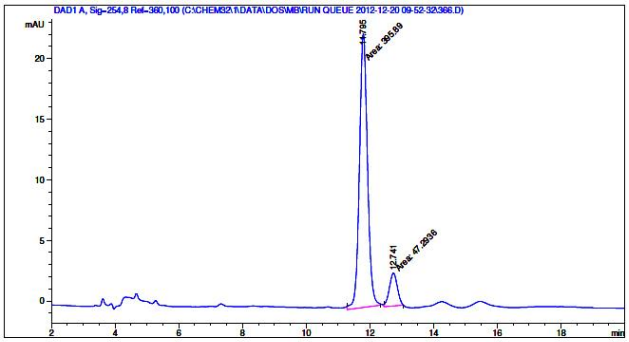
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.699	MM	0.2669	176.28999	11.00942	53.2583
2	12.606	MM	0.2962	154.71931	8.70587	46.7417

HPLC chart of **11j**



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

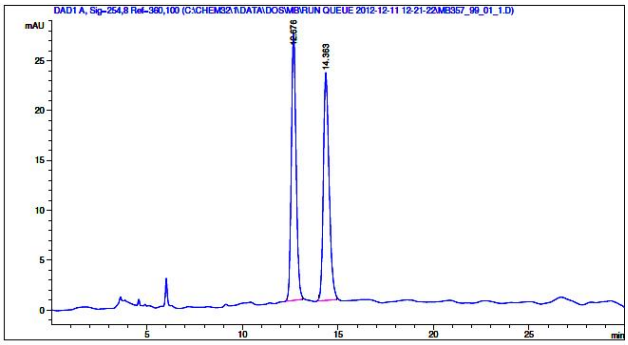
Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.795	MM	0.2916	395.89020	22.62751	89.3287
2	12.741	MM	0.2905	47.29364	2.71353	10.6713

(R_p)-(+)-5,13-Dimethoxy[2.2]metacylophane-4-carbaldehyde (11k). A solution of 5,13-dimethoxy[2.2]metacyclophane **9c** (26.8 mg, 0.10 mmol) in dry diethyl ether (4 mL) was treated with (-)-sparteine (46 µL, 0.20 mmol) and the mixture was stirred for 5 min. After cooling to -40°C, *s*BuLi (150 µL, 0.20 mmol) was added dropwise and the reaction mixture stirred at -40 °C for 4 h. The reaction mixture was cooled to -78 °C and DMF (24 µL, 0.30 mmol) added dropwise. The reaction mixture was stirred at room temperature for 2 h and the solvent was removed under reduced pressure. Ethyl acetate (10 mL) was added to the residue, washed with HCl (2 M, 2 x 10 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with 80:20 pentane:ethyl acetate gave **11k** as a colourless solid (R_f = 0.70, 17 mg, 58%), mp 80-82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.62 (s, 1H), 6.67 (s, 1H), 6.63 (s, 1H), 6.60 (s, 1H), 4.38 (dt, *J* = 11.5, 3.5 Hz, 1H), 4.09 (s, 1H), 4.07 (s, 1H), 3.92 (s, 3H), 3.82 (s, 3H), 3.12-3.00 (m, 3H), 2.20-2.07 (m, 3H), 1.74 (td, *J* = 11.8, 3.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 164.1, 160.8, 146.9, 142.3, 140.9, 139.3, 131.5, 128.6, 120.4, 110.9, 110.8, 108.4, 55.9, 55.3, 41.5, 40.8, 40.4, 37.9. ESI-HRMS $[M+Na]^+$: 319.1301, $C_{19}H_{20}O_3Na$ requires 319.1310.

$[\alpha]_D^{20}$= +69.7 (c 0.3, $CHCl_3$, 82% ee). Enantiomeric excess was determined by analytical chiral HPLC (Chiralpak IA 250 x 4.6 mm ID, 254nm UV detector, room temperature, eluent: 1% ethanol in heptane, flow rate: 1.0 ml/min). Retention times: 12.7 min (minor isomer) and 14.4 min (major isomer).

HPLC chart of *racemic* **11k**



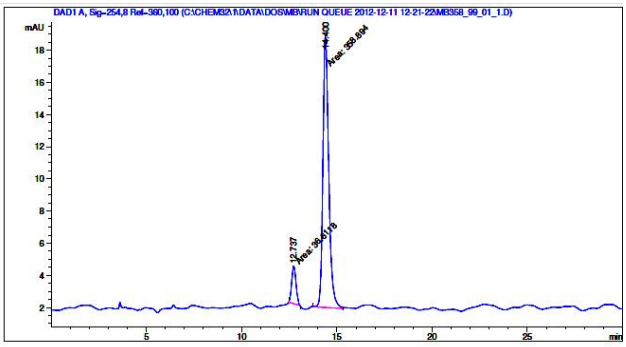
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.676	BB	0.2636	461.48309	26.70400	49.2204
2	14.363	BB	0.3192	476.10104	22.84047	50.7796

HPLC chart of **11k**



Area Percent Report

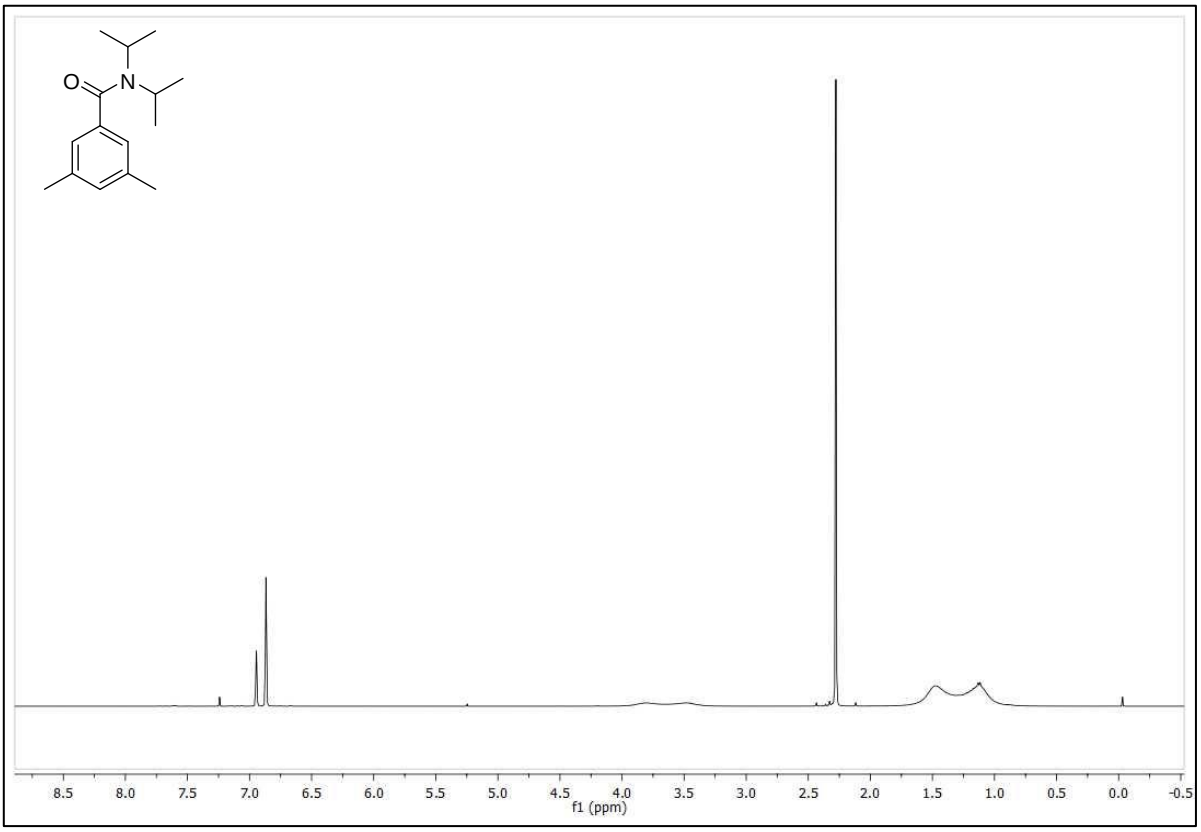
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,8 Ref=360,100

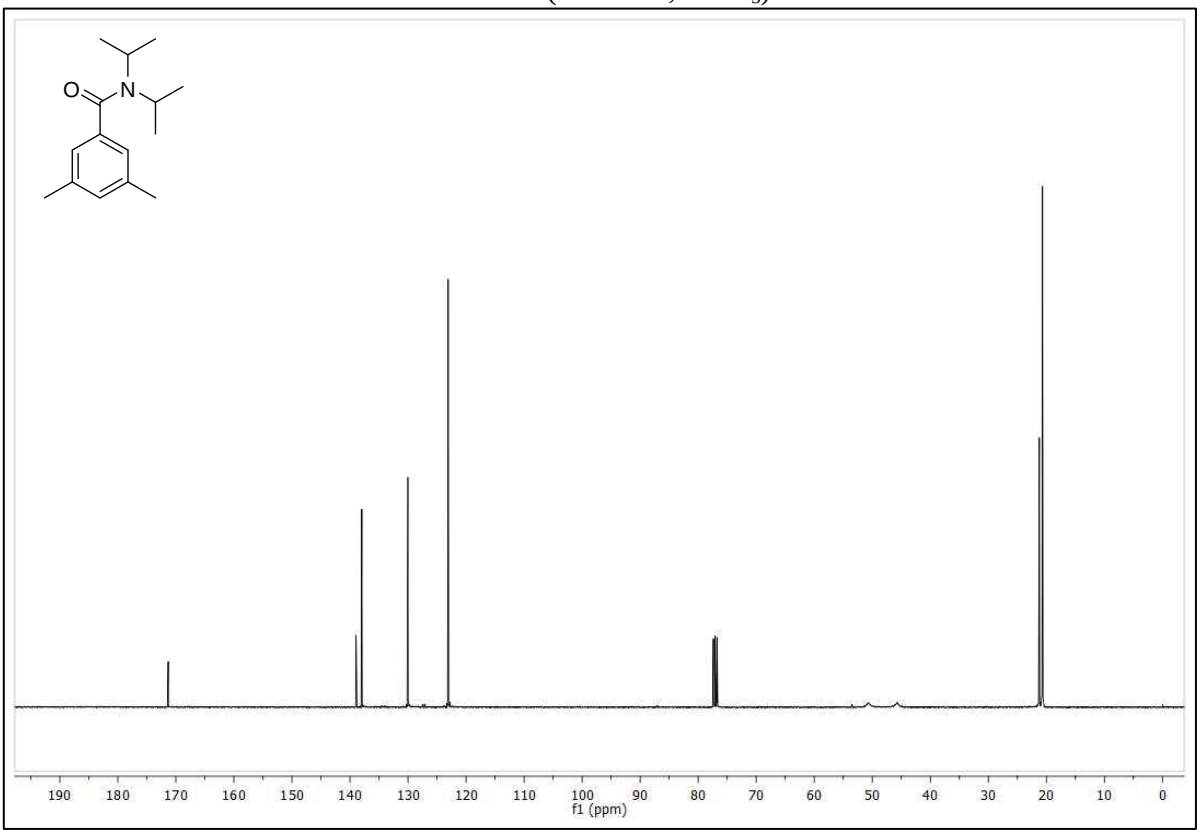
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.737	MM	0.2597	36.61177	2.34934	9.2570
2	14.400	MM	0.3544	358.89392	16.87868	90.7430

N,N-Diisopropyl-3,5-dimethylbenzamide

^{1}H NMR (500 MHz, $CDCl_3$)

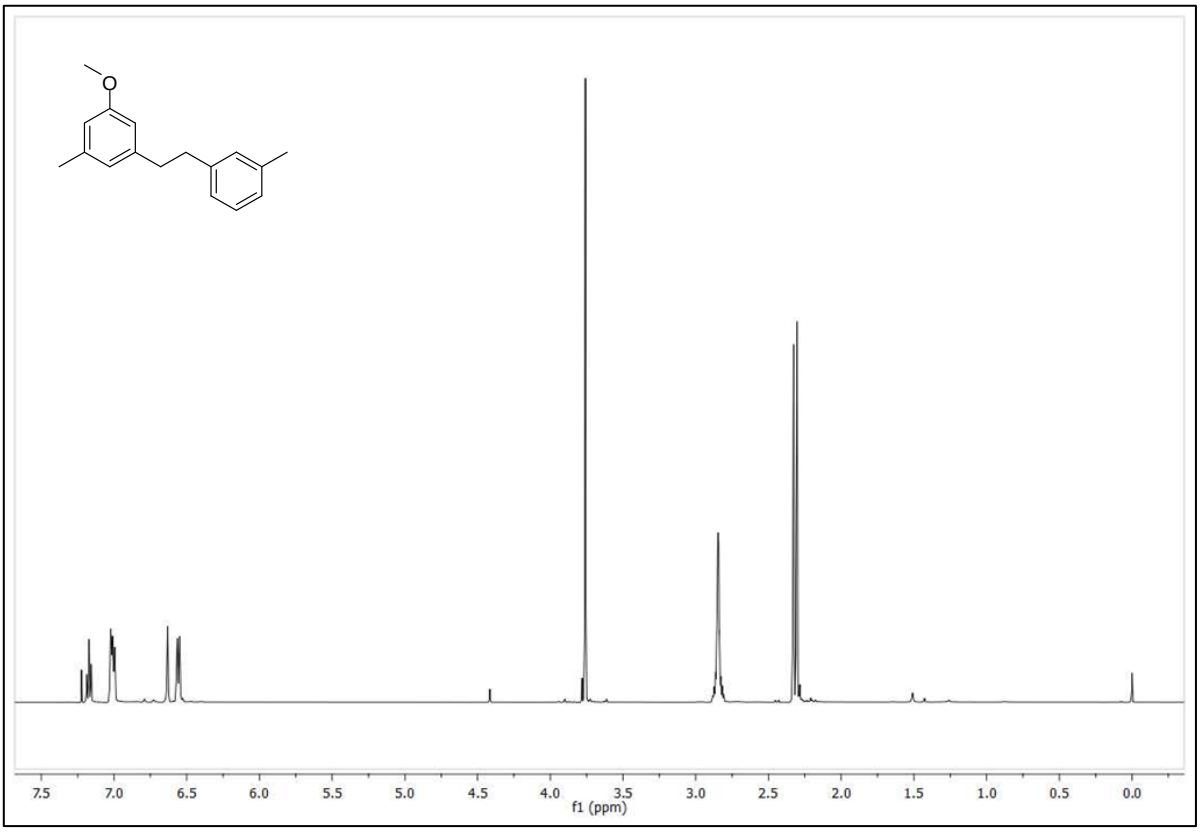


^{13}C NMR (100 MHz, $CDCl_3$)

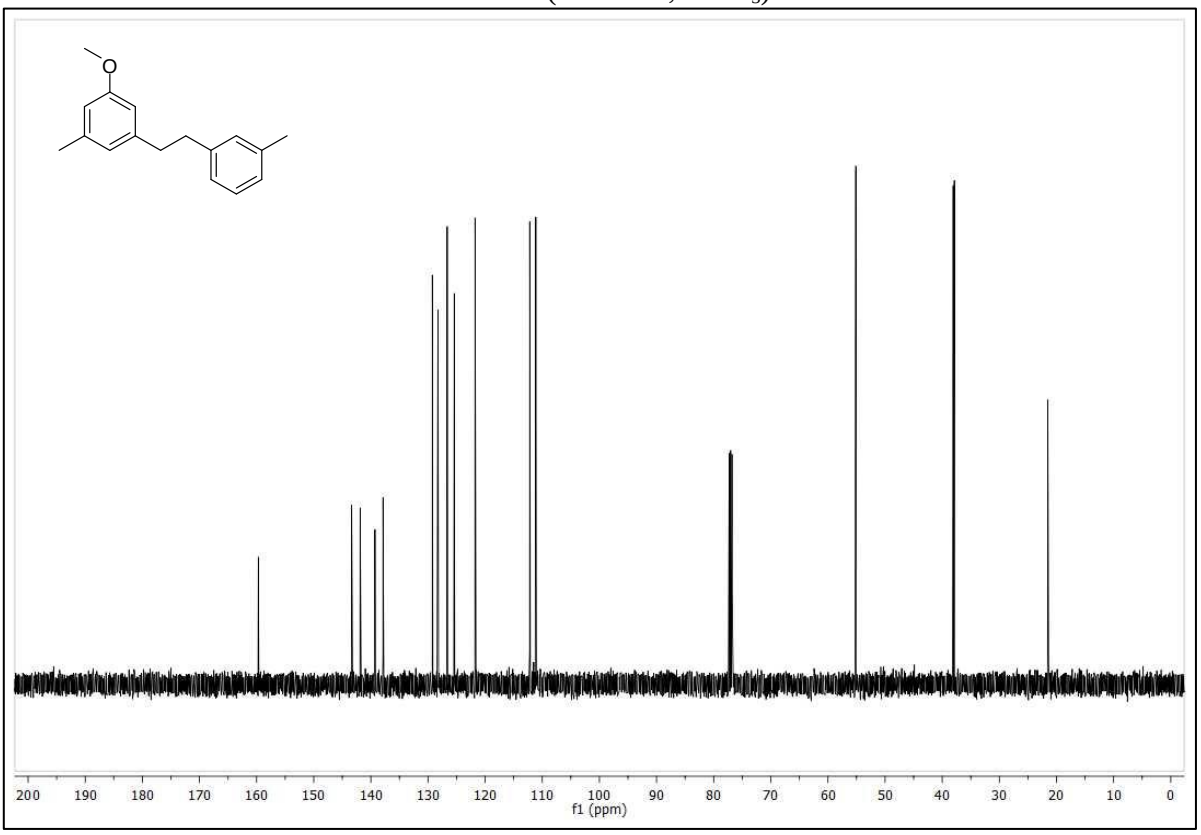


1-Methoxy-3-methyl-5-(3-methylphenethyl)benzene (8a)

^{1}H NMR (500 MHz, $CDCl_3$)

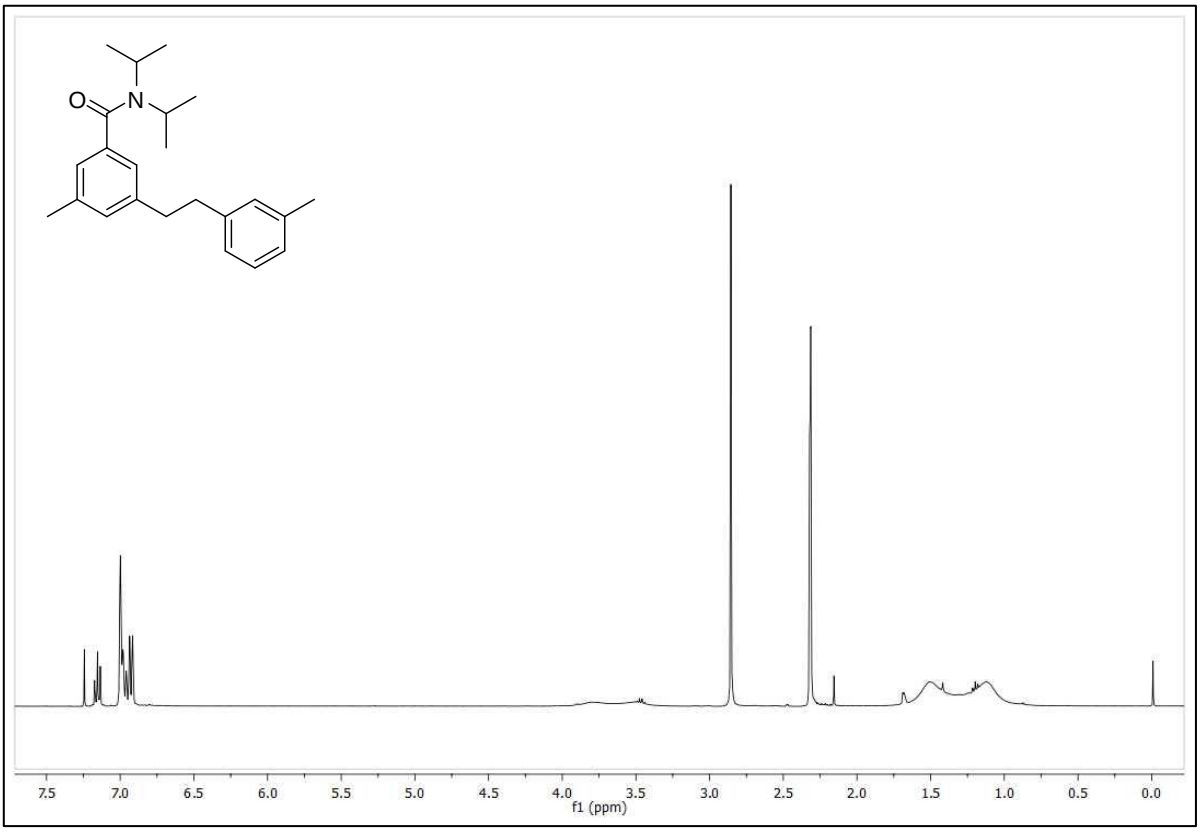


^{13}C NMR (125 MHz, $CDCl_3$)

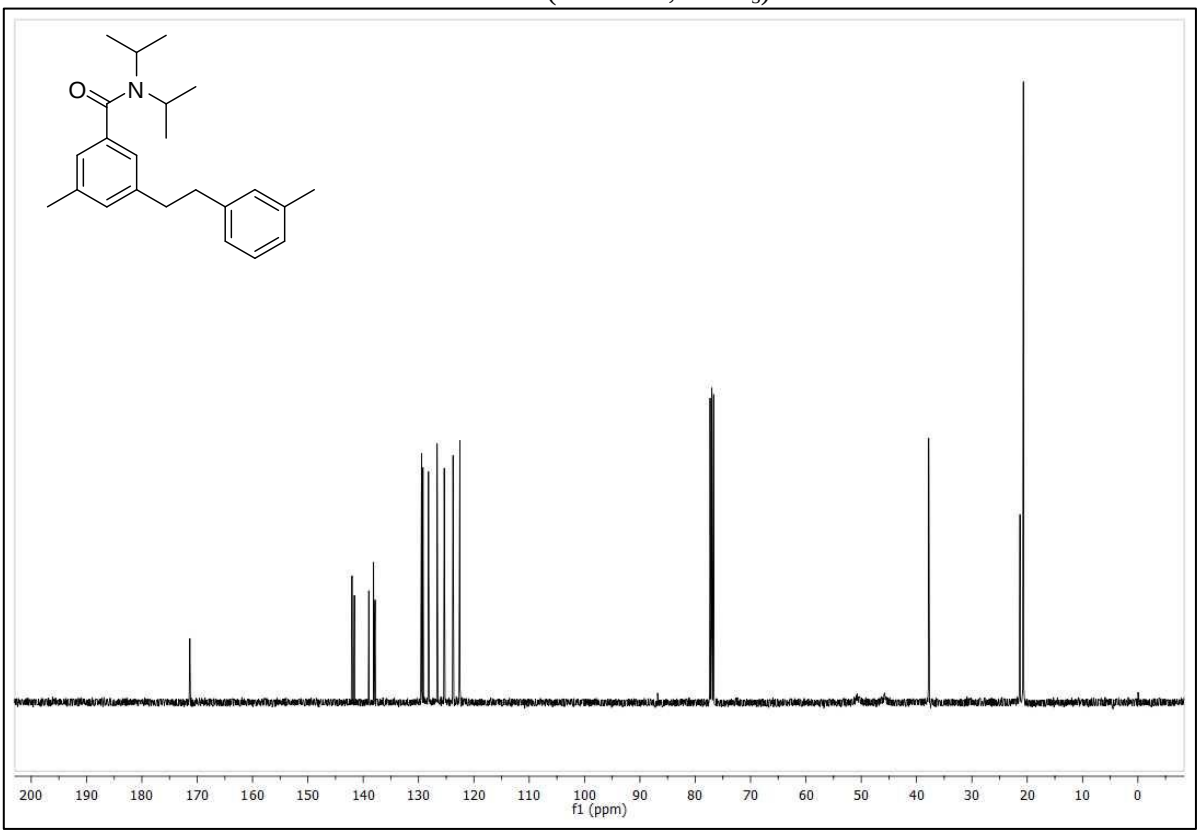


N,N-Diisopropyl-3-methyl-5-(3-methylphenethyl)benzamide (8b)

^{1}H NMR (400 MHz, $CDCl_3$)

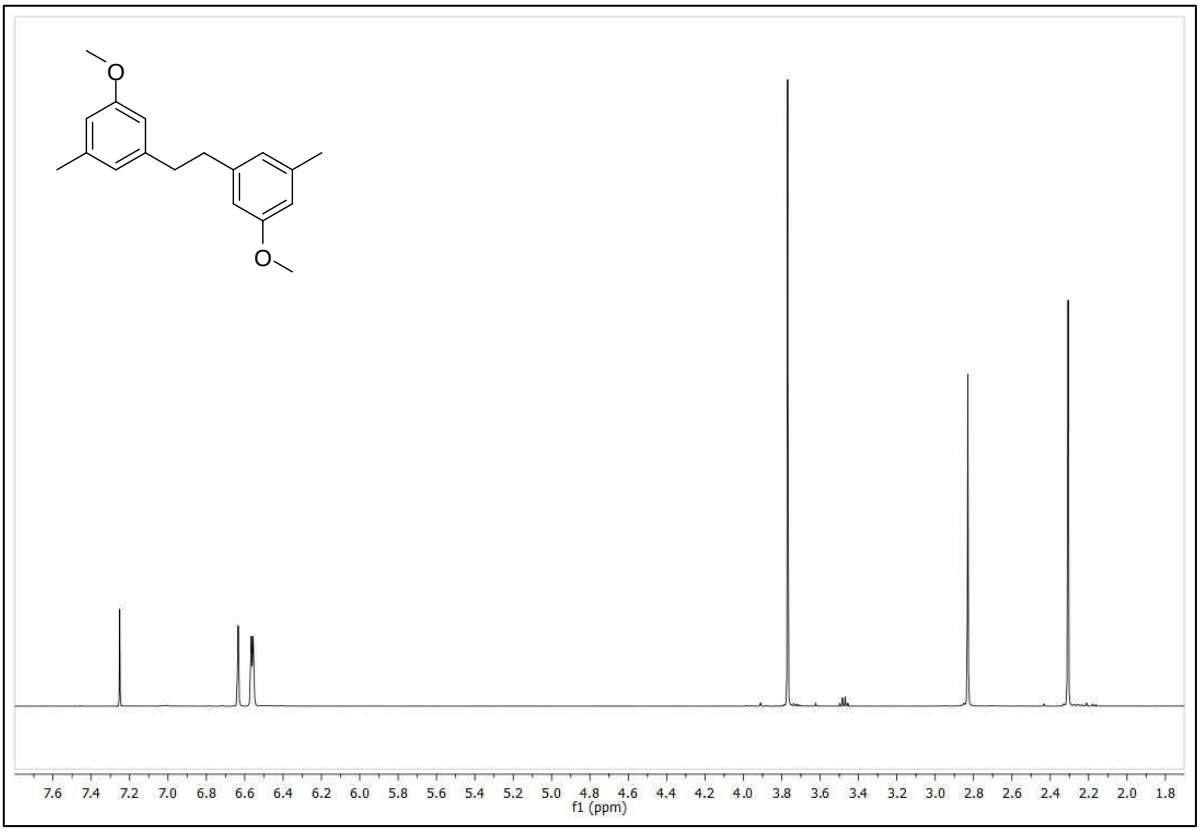


^{13}C NMR (100 MHz, $CDCl_3$)

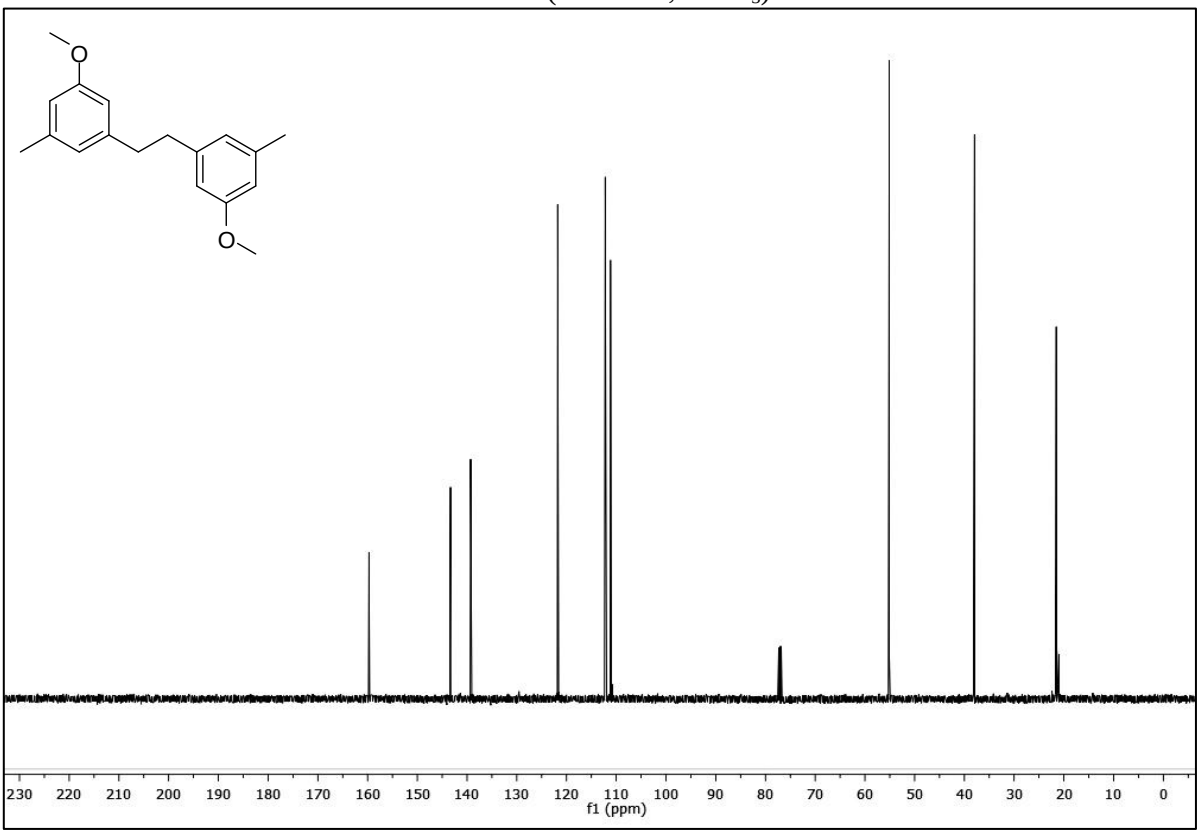


1,2-Bis(3-methoxy-5-methylphenyl)ethane (8c)

^{1}H NMR (500 MHz, $CDCl_3$)

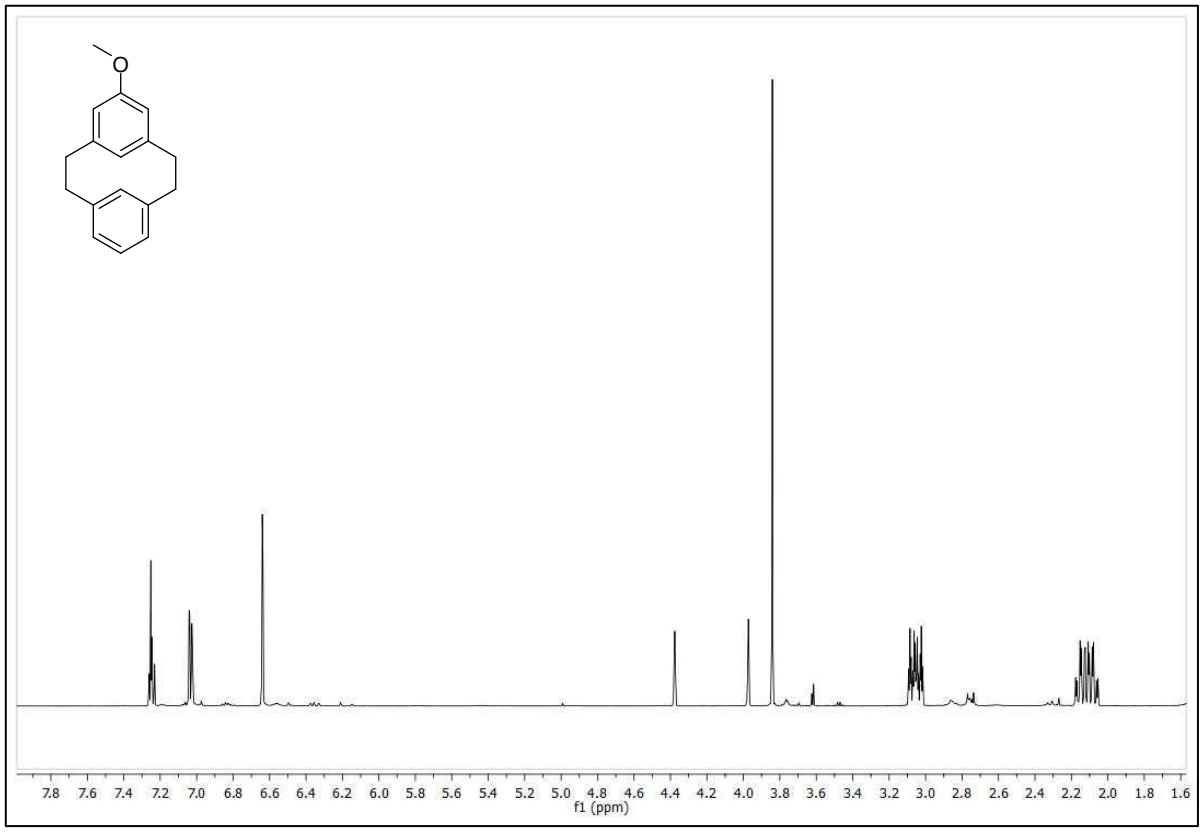


^{13}C NMR (125 MHz, $CDCl_3$)

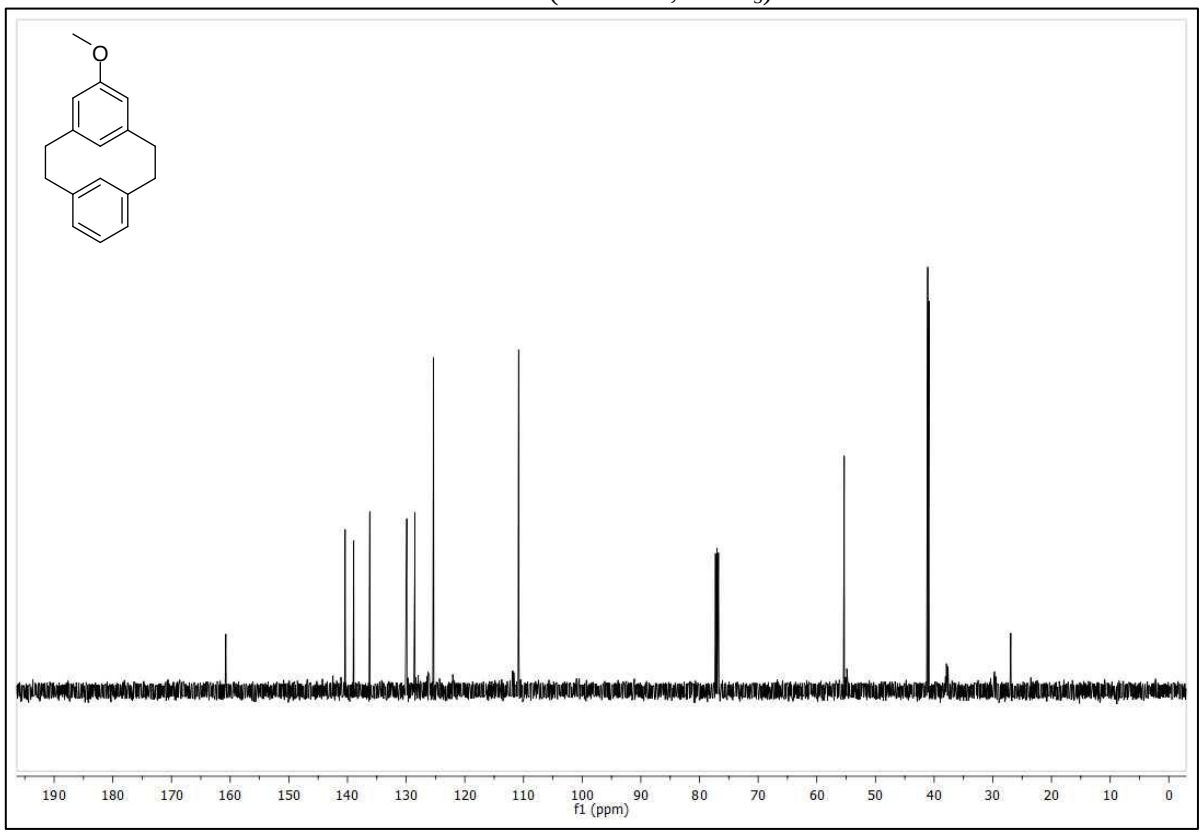


5-Methoxy[2.2]metacyclophane (9a)

^{1}H NMR (500 MHz, $CDCl_3$)

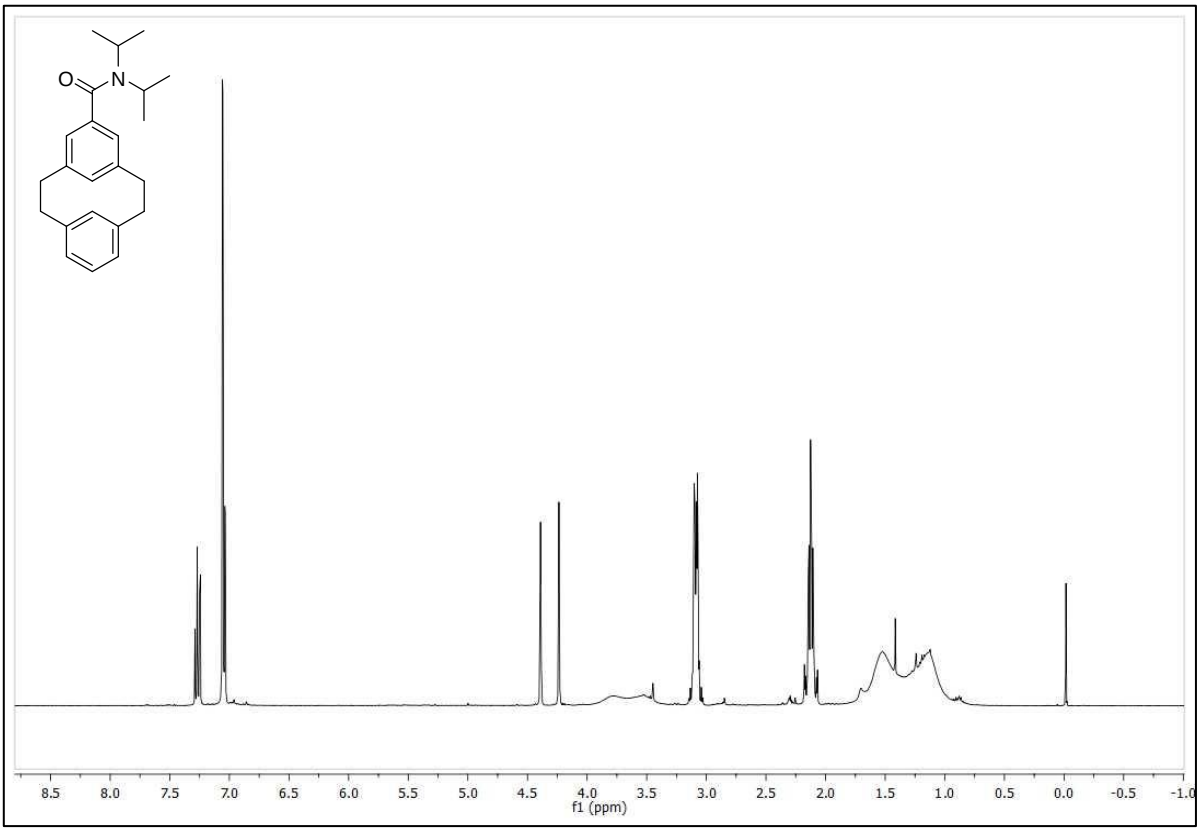


^{13}C NMR (125 MHz, $CDCl_3$)

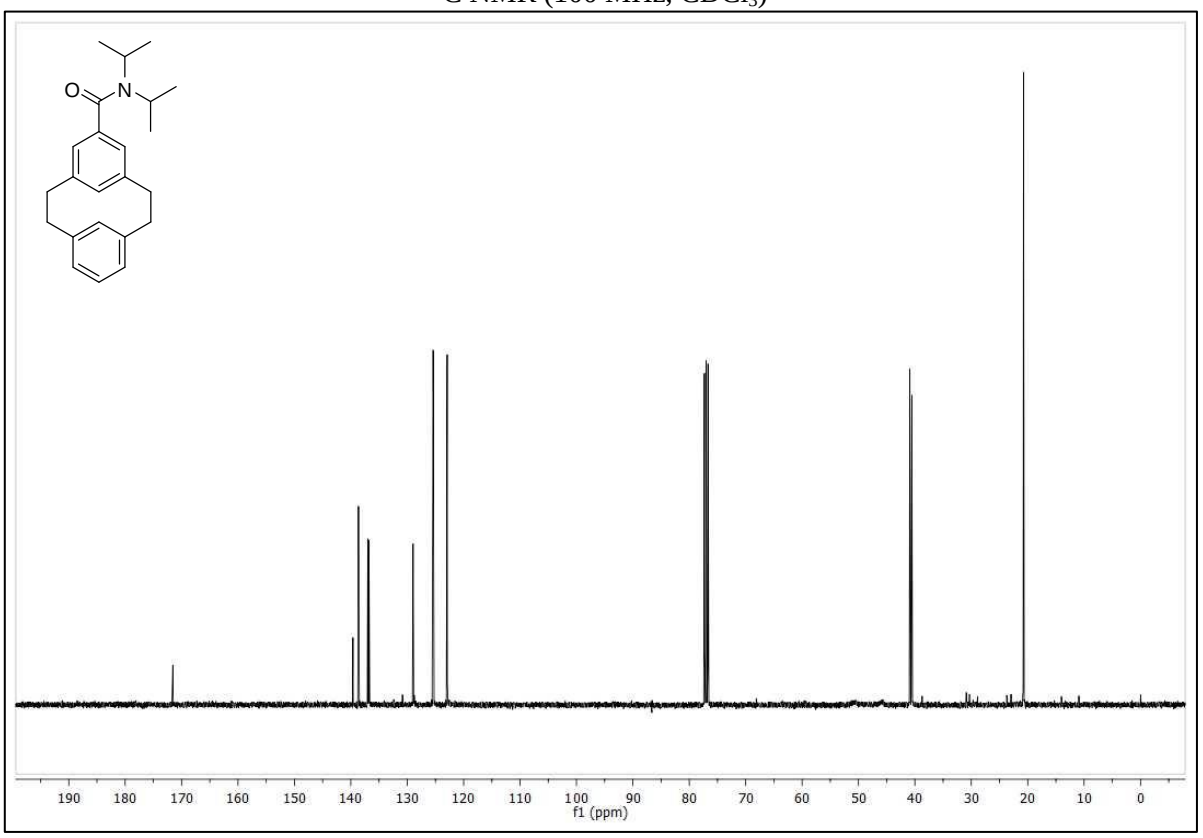


N,*N*-Diisopropyl[2.2]metacylophane-5-carboxamide (9b)

^{1}H NMR (400 MHz, $CDCl_3$)

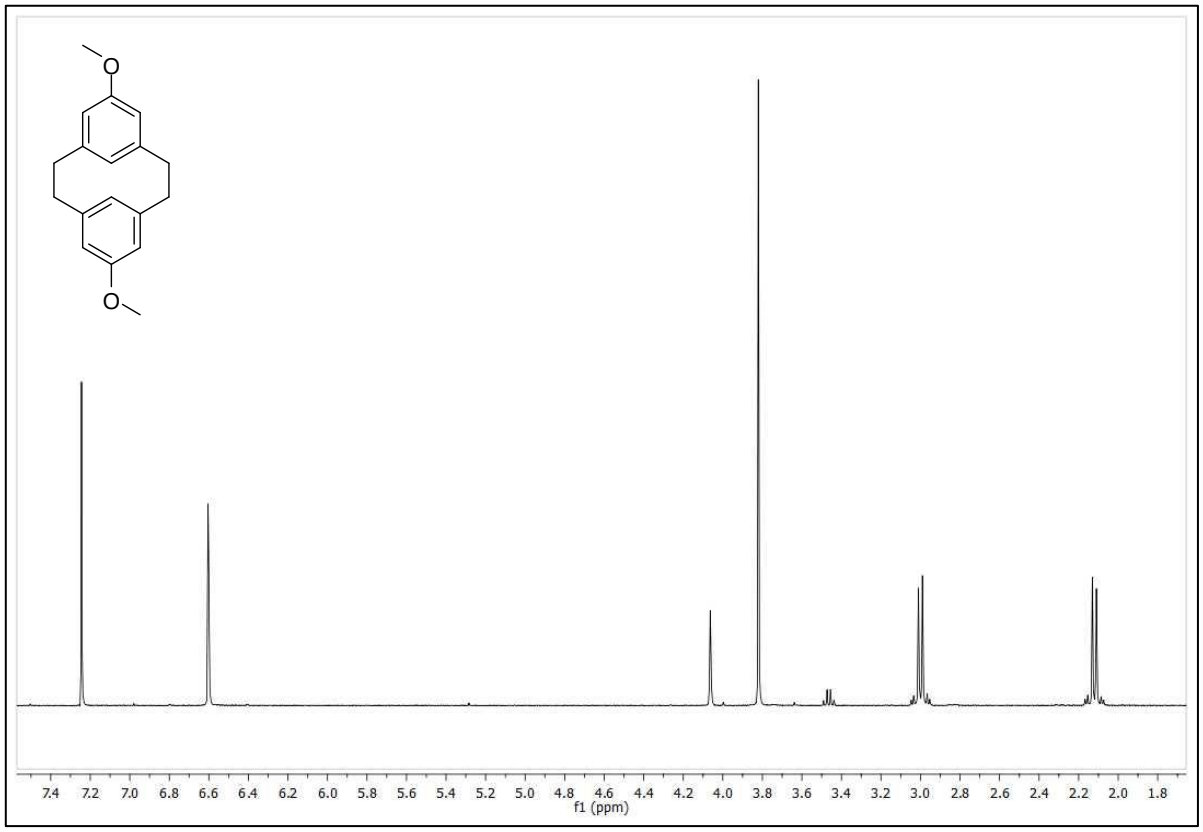


^{13}C NMR (100 MHz, $CDCl_3$)

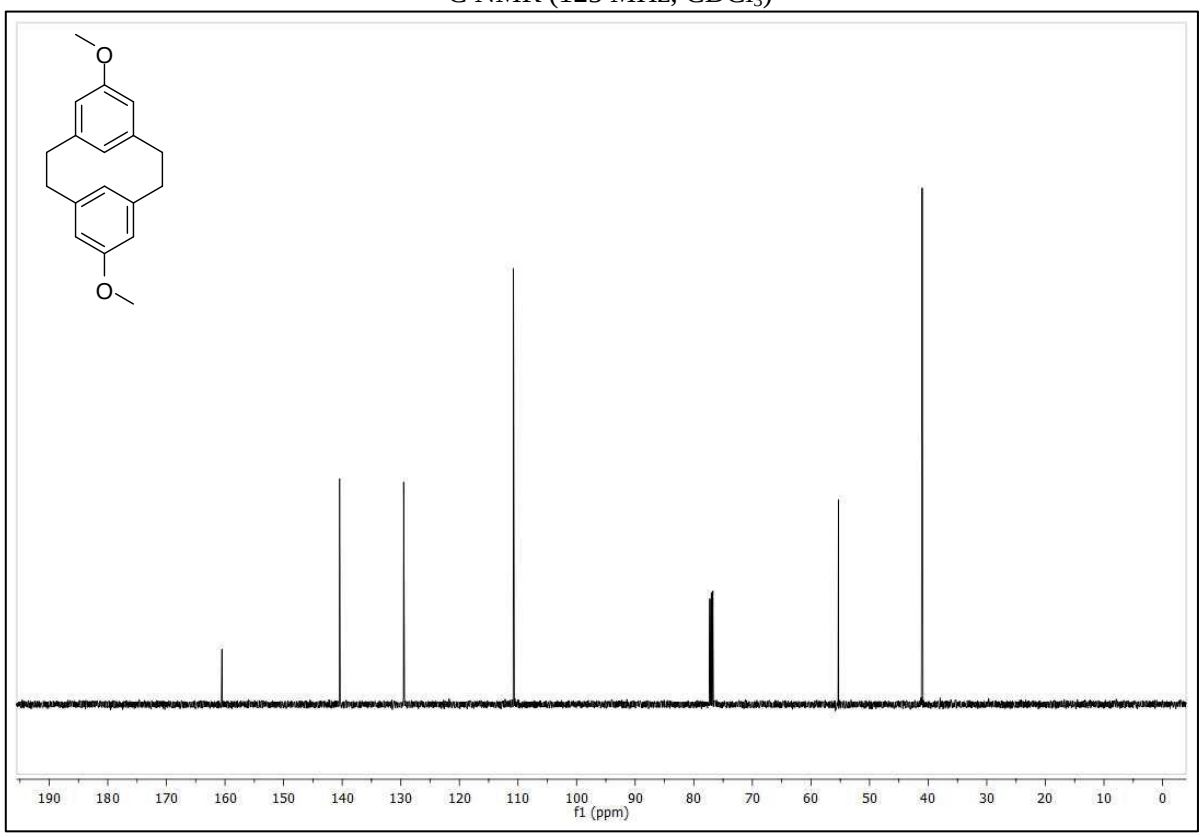


5,13-Dimethoxy[2.2]metacyclophane (9c)

^{1}H NMR (500 MHz, $CDCl_3$)

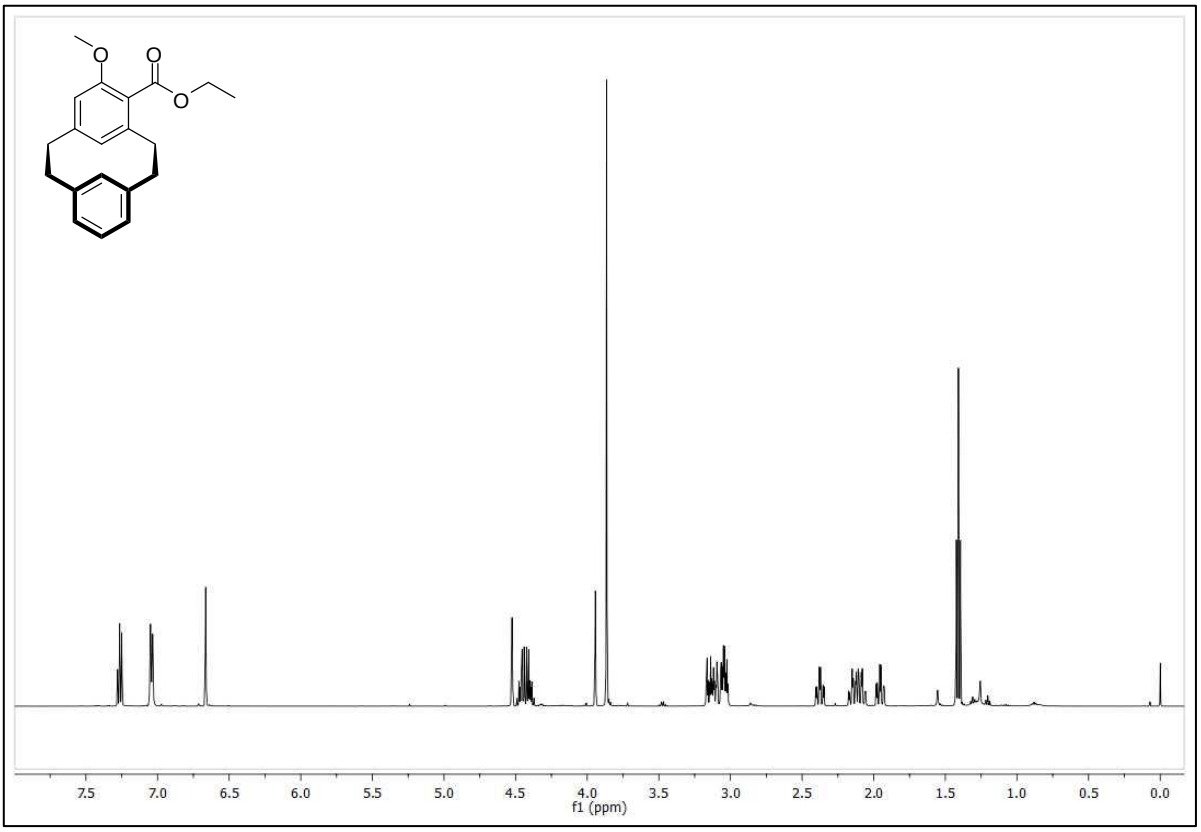


^{13}C NMR (125 MHz, $CDCl_3$)

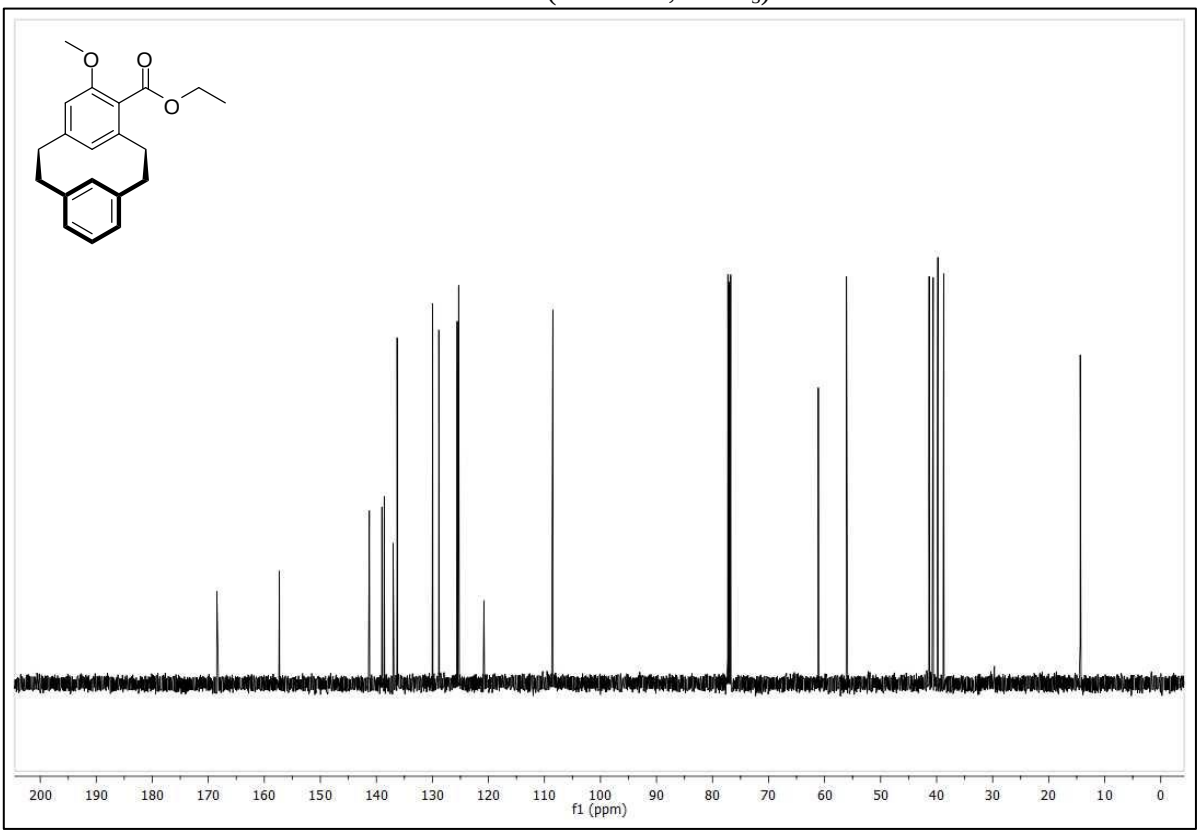


(R_p)-(-)-5-Methoxy[2.2]metacylophane-4-carboxylic acid ethyl ester (11a)

^{1}H NMR (500 MHz, $CDCl_3$)

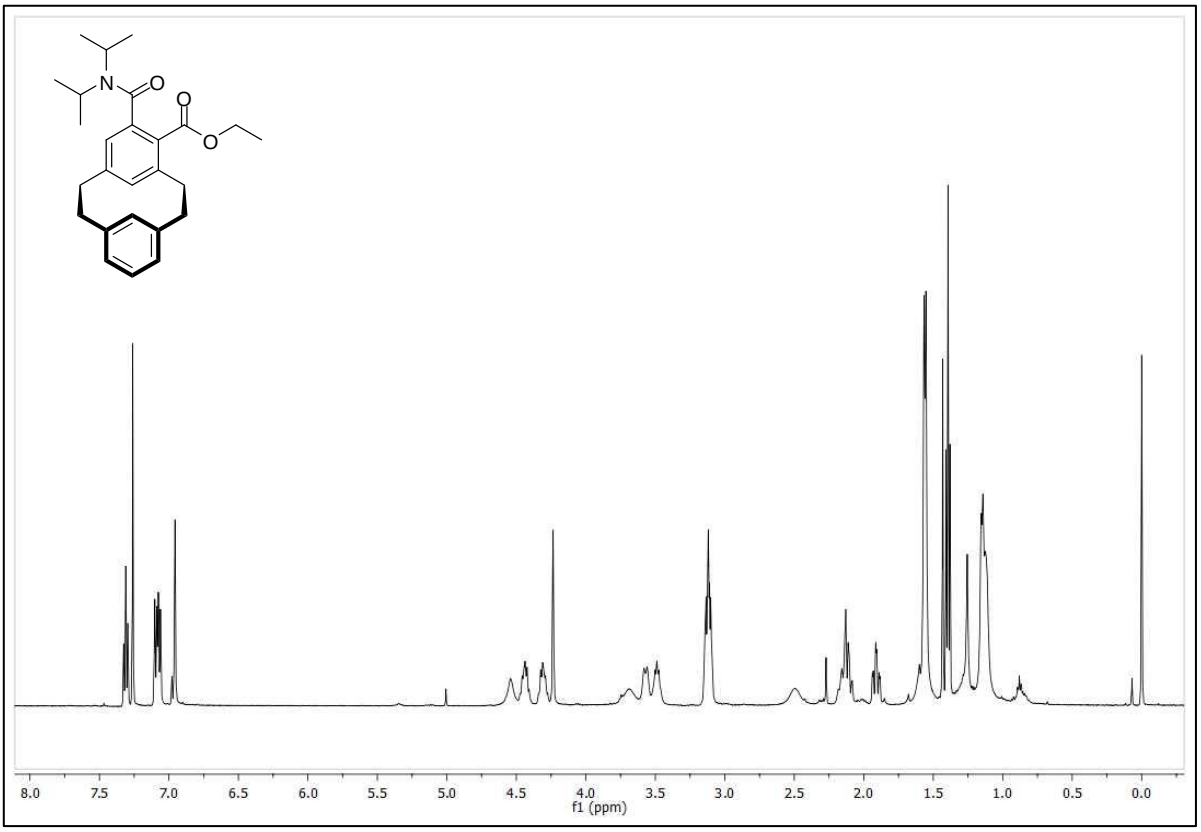


^{13}C NMR (125 MHz, $CDCl_3$)

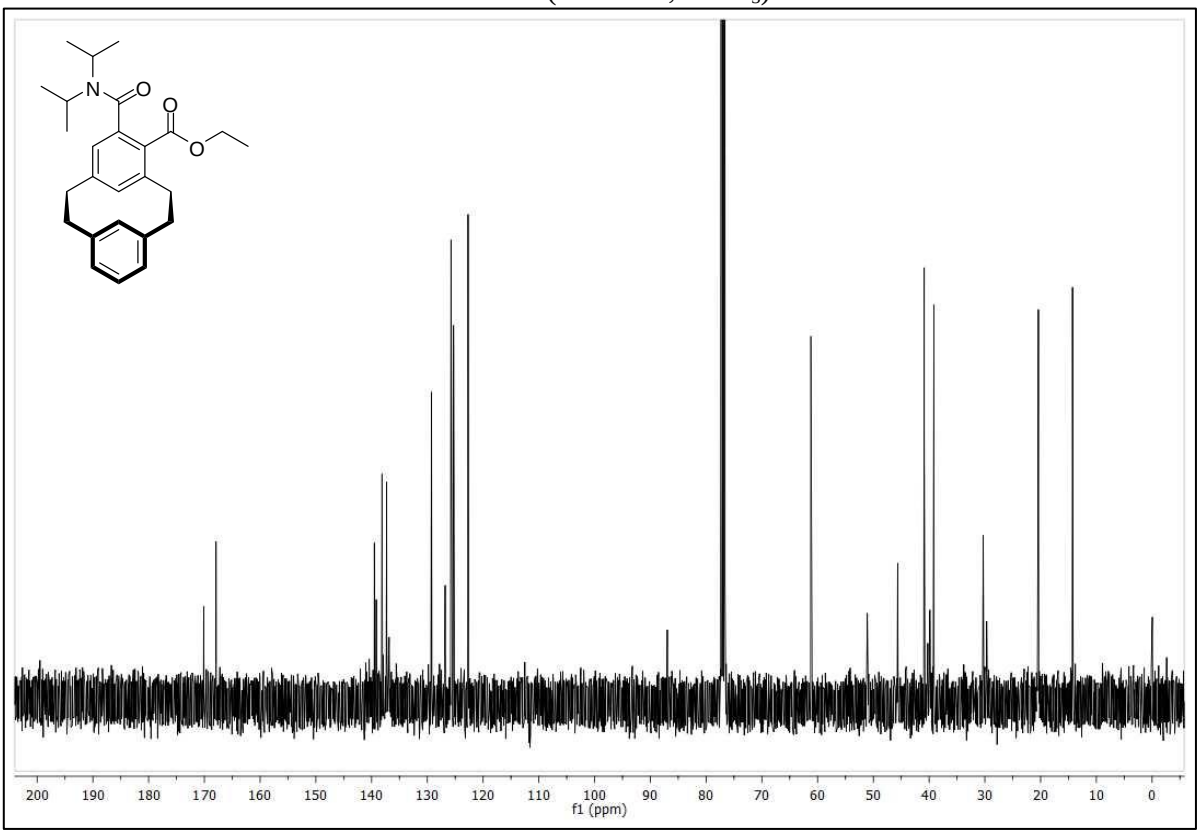


(R_p)-(-)-5-(*N*,*N*-diisopropylcarbamoyl)[2.2]metacylophane-4-carboxylic acid ethyl ester (11b)

^{1}H NMR (500 MHz, $CDCl_3$)

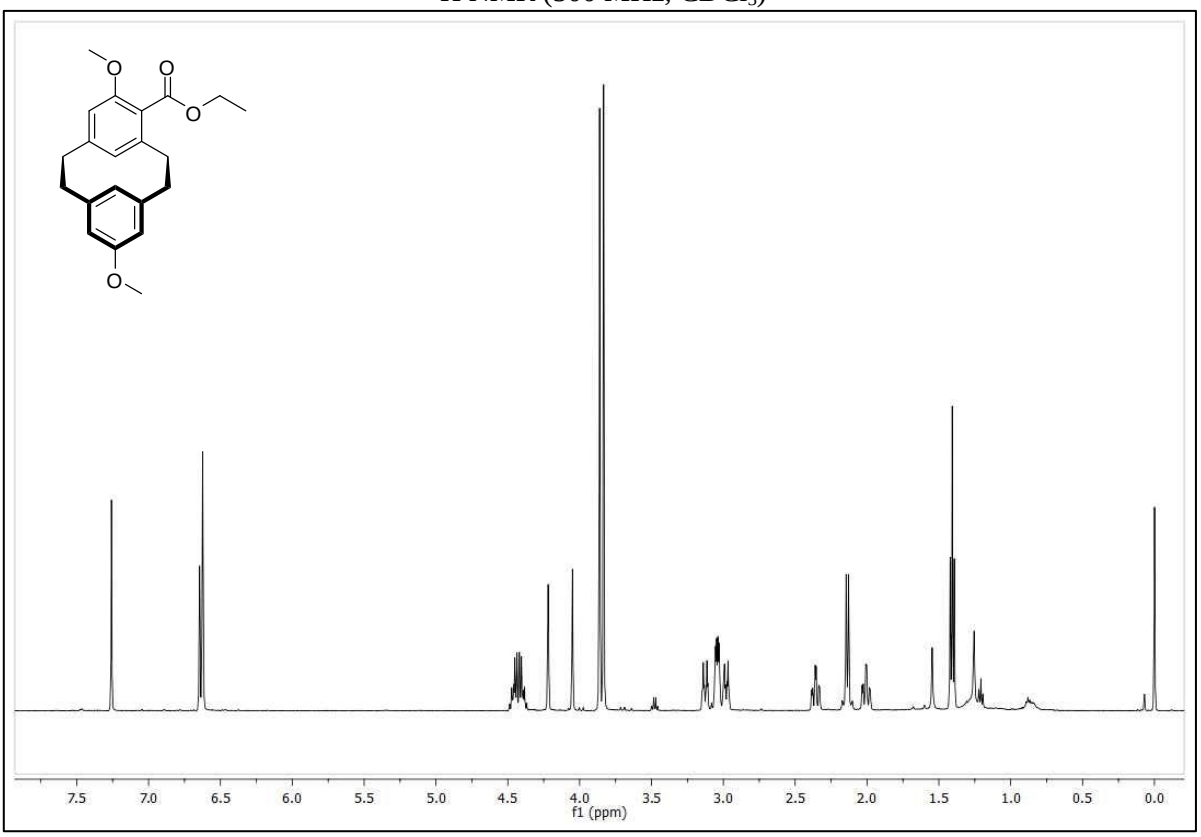


^{13}C NMR (100 MHz, $CDCl_3$)

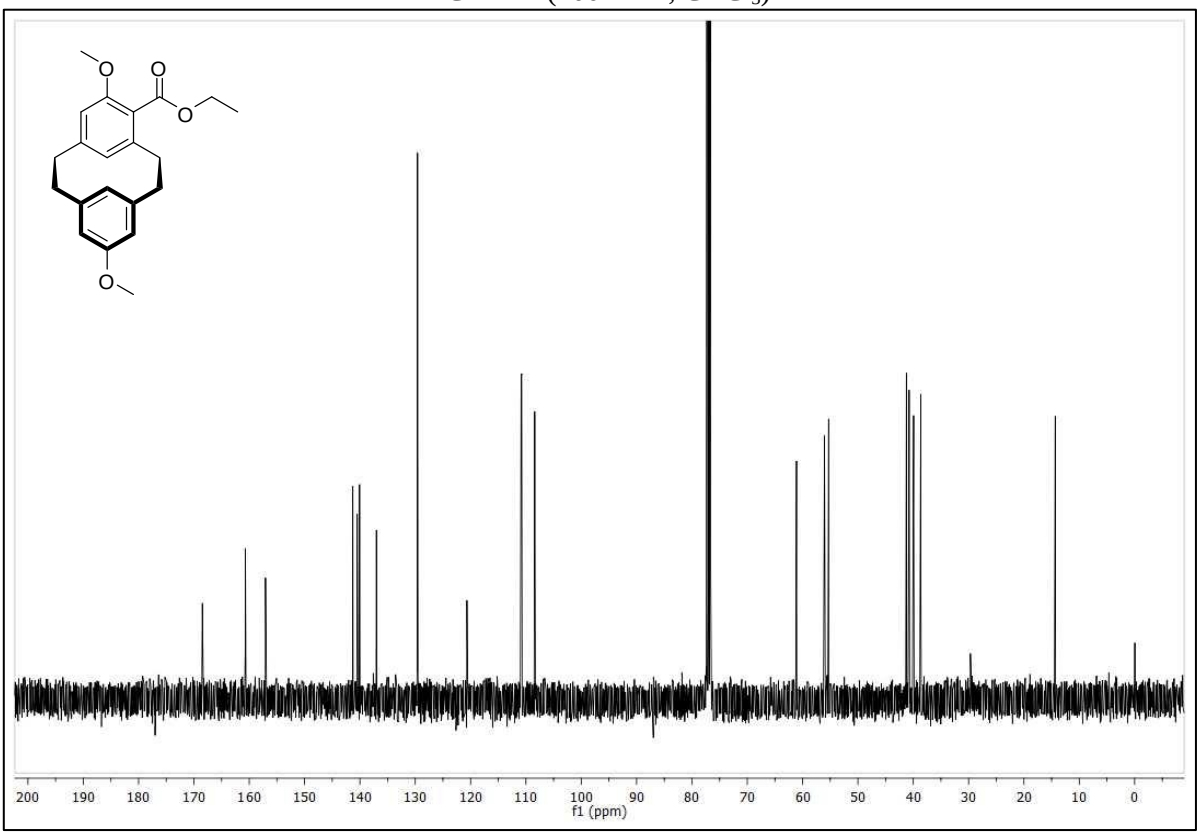


(R_p)-(-)-5,13-Dimethoxy[2.2]metacylophane-4-carboxylic acid ethyl ester (11c)

^{1}H NMR (500 MHz, $CDCl_3$)

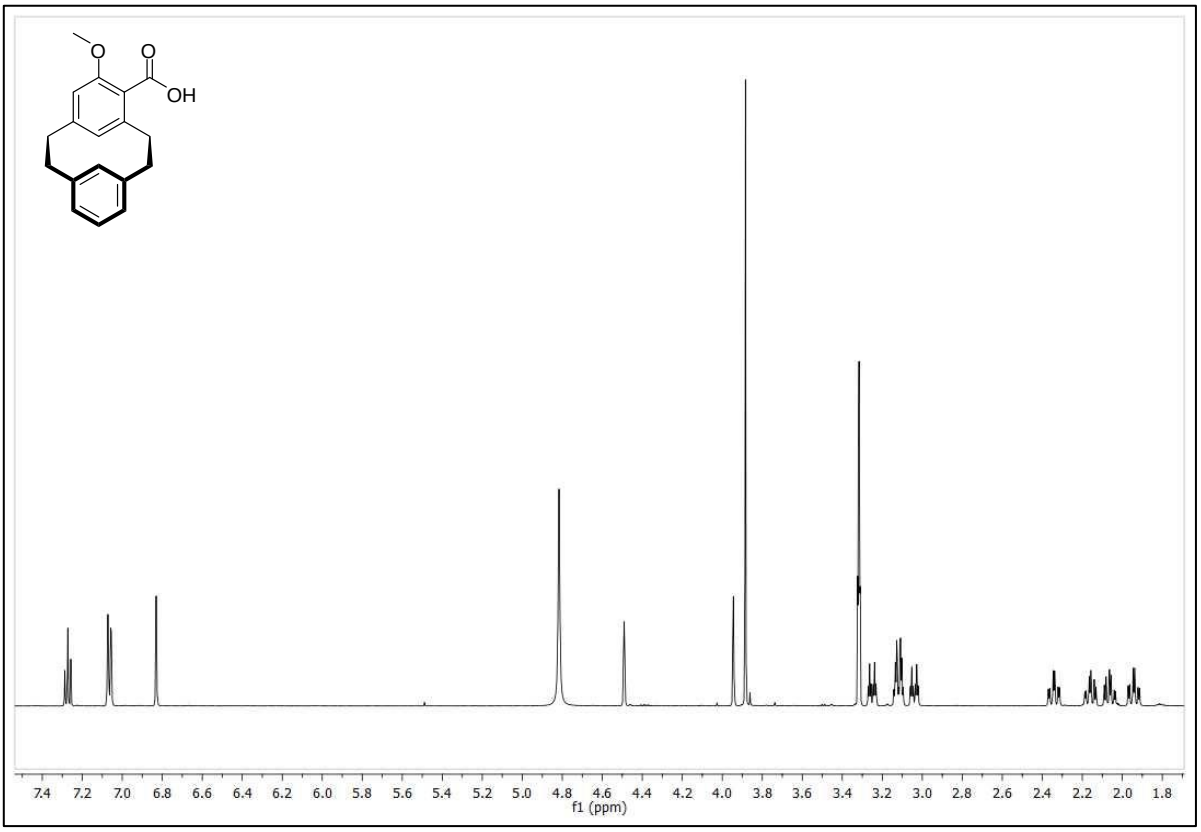


^{13}C NMR (100 MHz, $CDCl_3$)

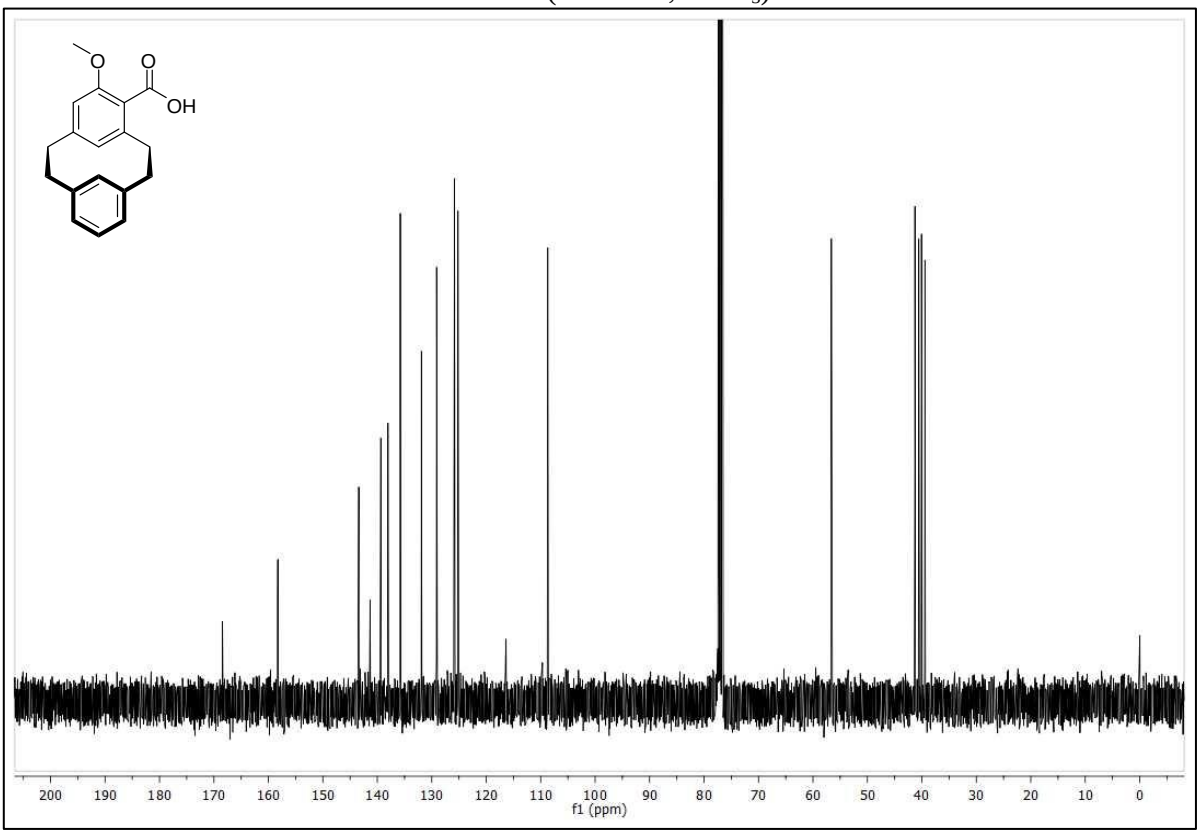


(R_p)-(-)-5-Methoxy[2.2]metacylophane-4-carboxylic acid (11d)

^{1}H NMR (500 MHz, CD_3OD)

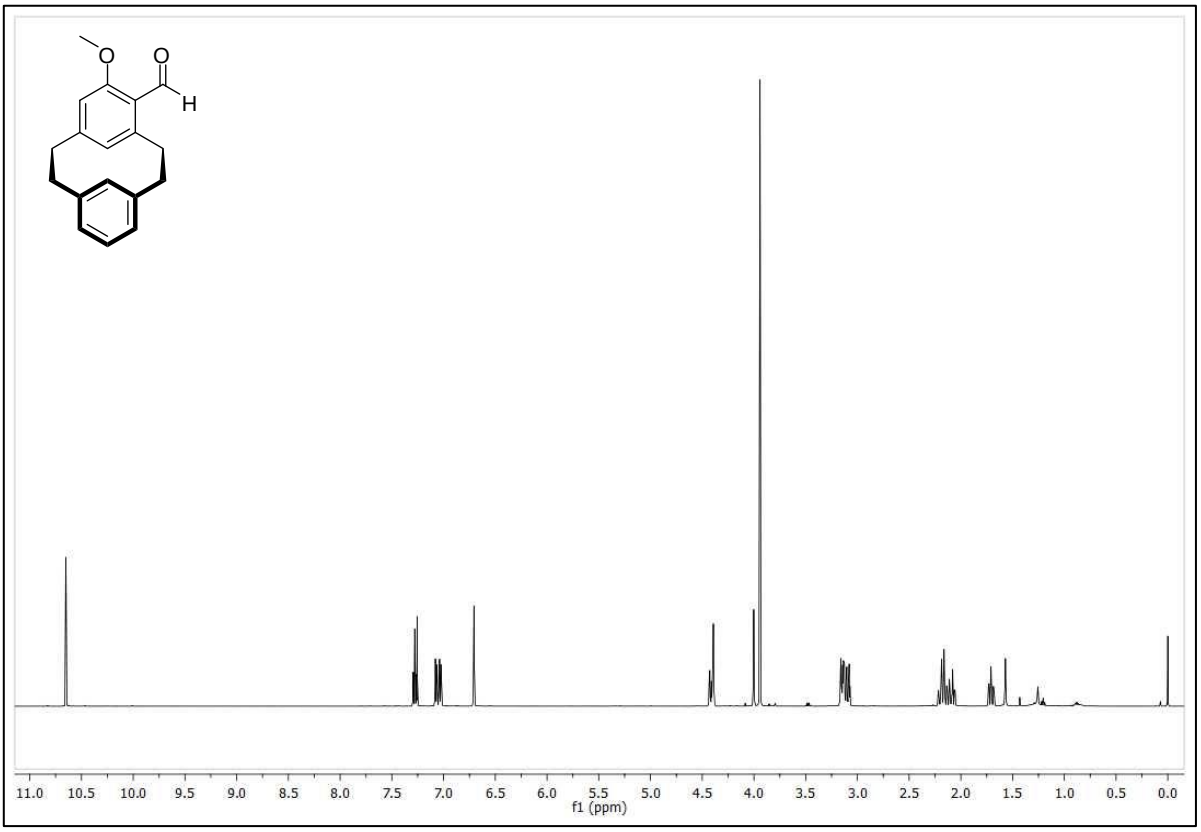


^{13}C NMR (100 MHz, $CDCl_3$)

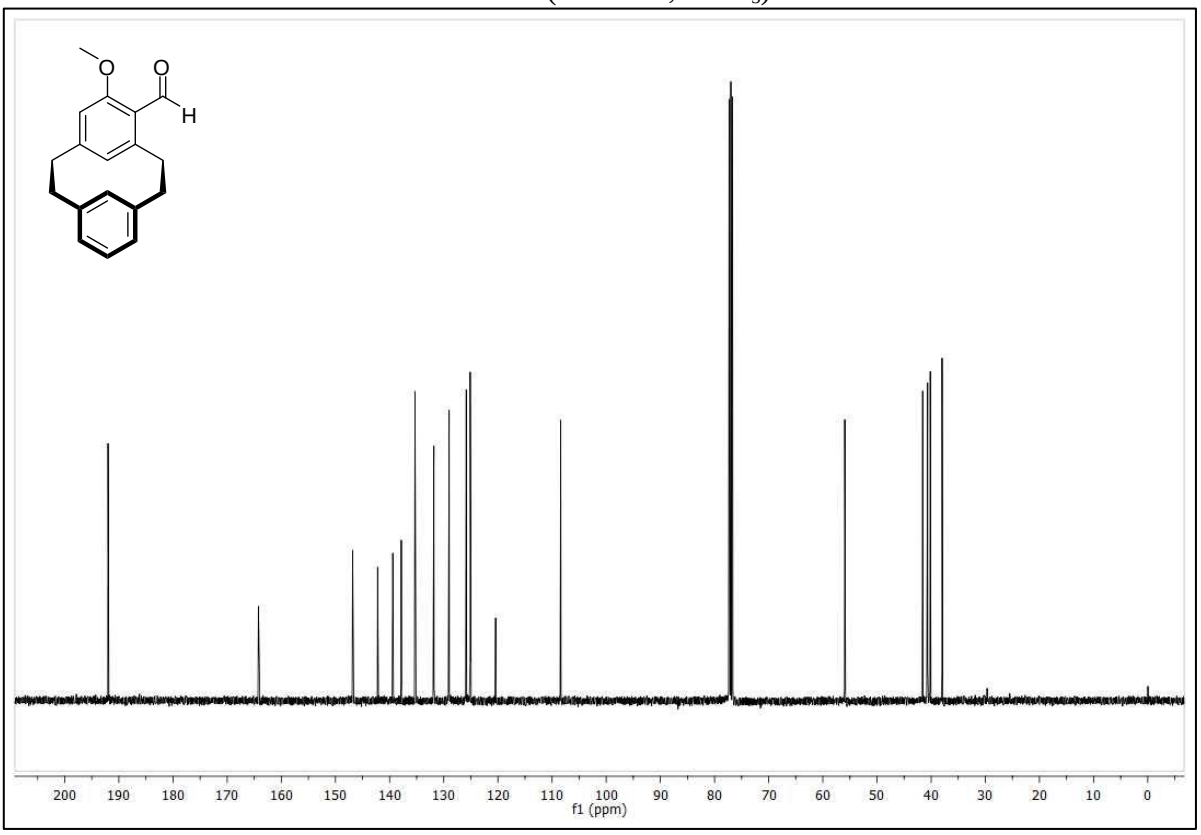


(R_p)-(+)-5-Methoxy[2.2]metacylophane-4-carbaldehyde (11e)

^{1}H NMR (400 MHz, $CDCl_3$)

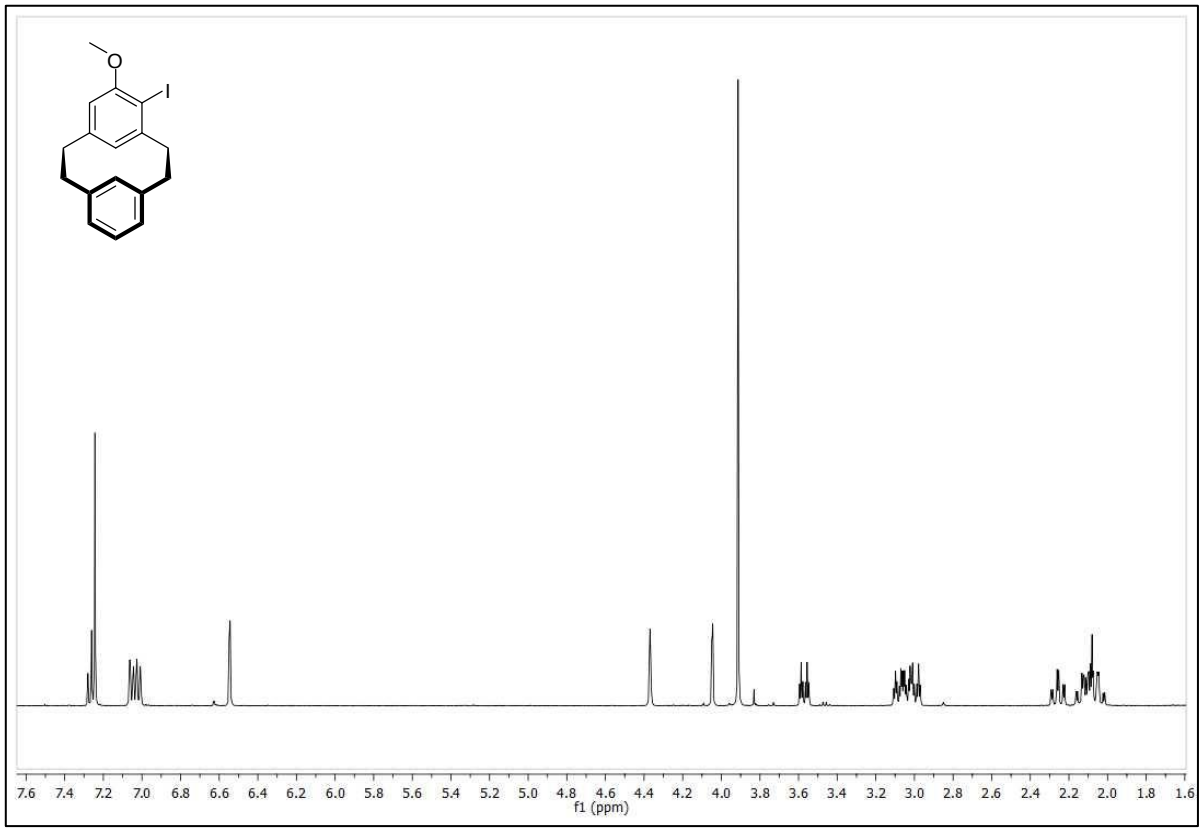


^{13}C NMR (100 MHz, $CDCl_3$)

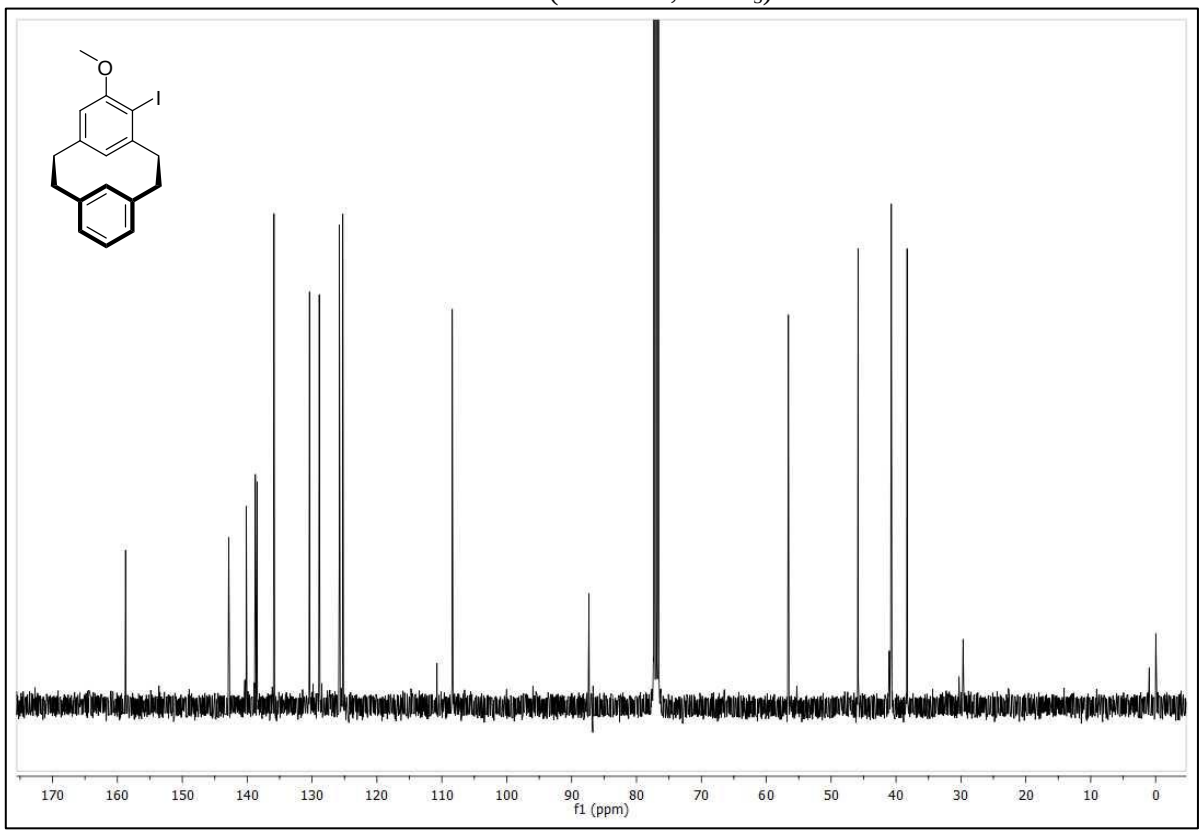


(R_p)-(-)-4-Iodo-5-methoxy[2.2]metacylophane (11f)

^{1}H NMR (500 MHz, $CDCl_3$)

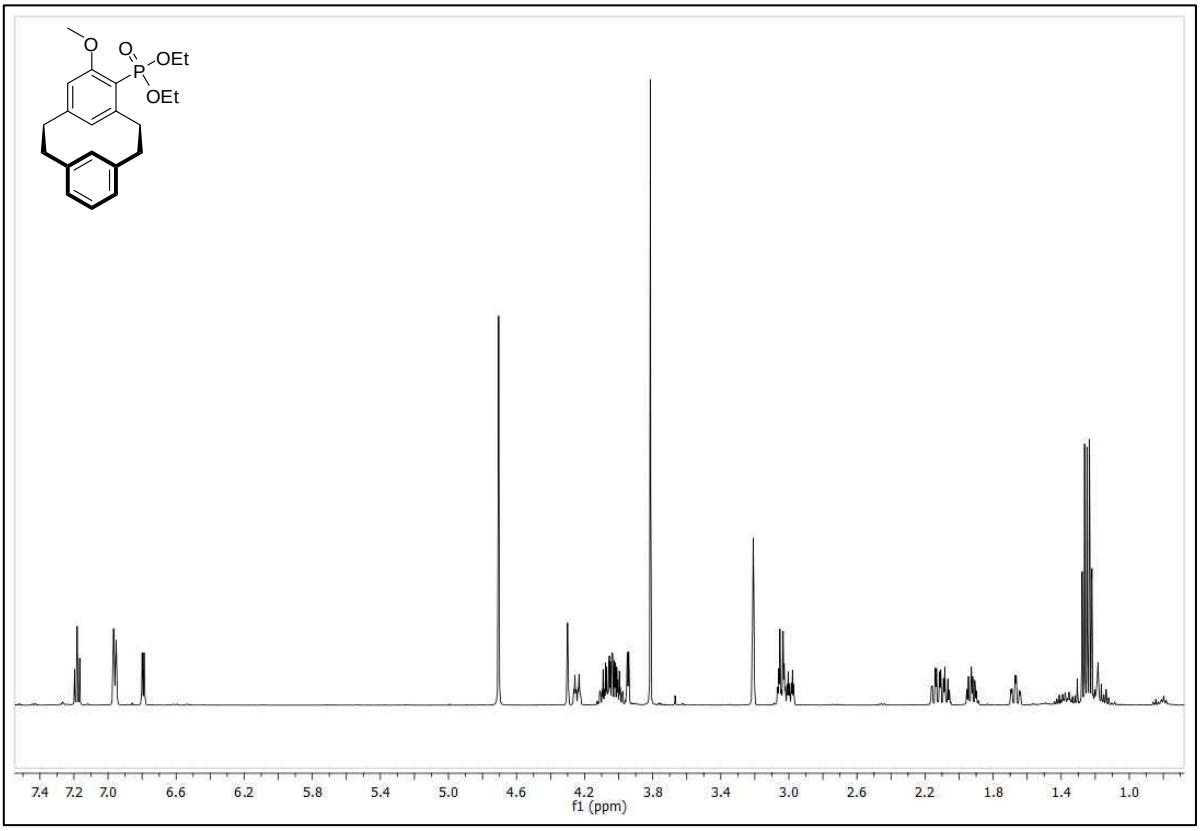


^{13}C NMR (100 MHz, $CDCl_3$)

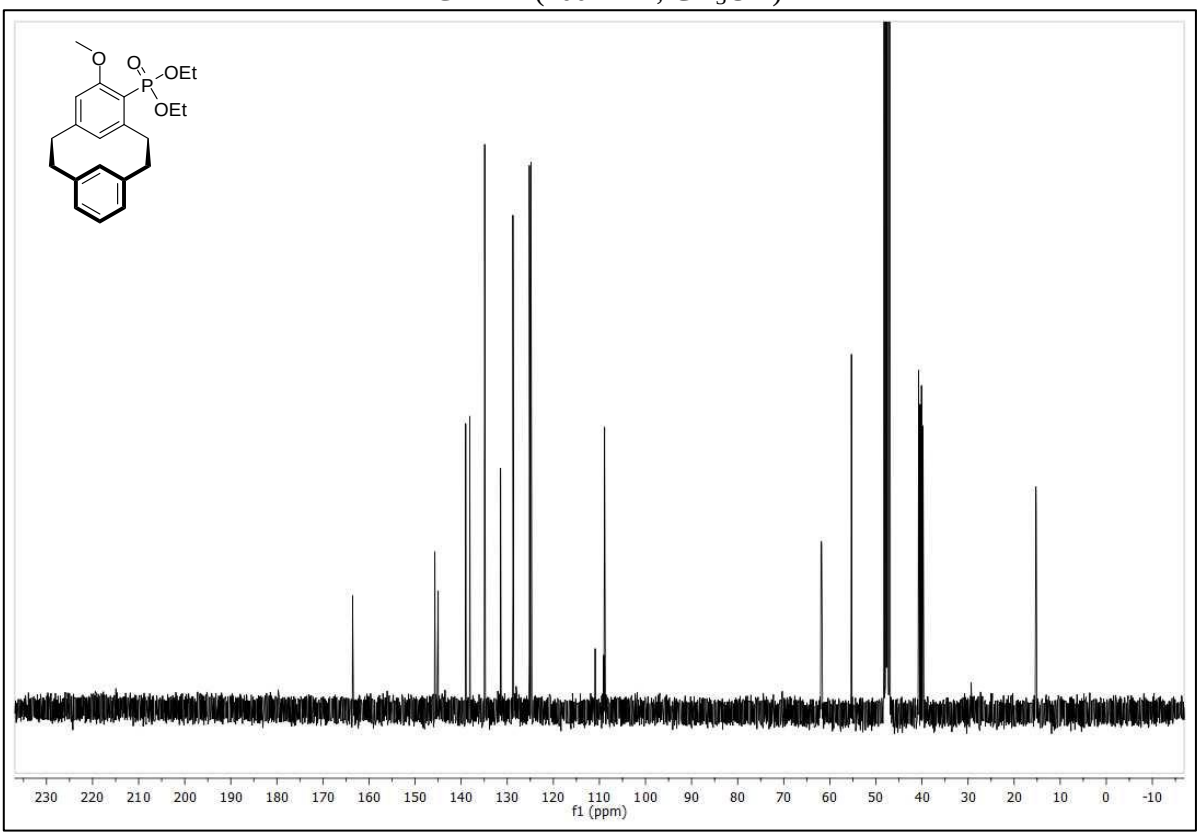


(R_p)-(-)-5-Methoxy[2.2]metacylophane-4-phosphonic acid diethyl ester (11g)

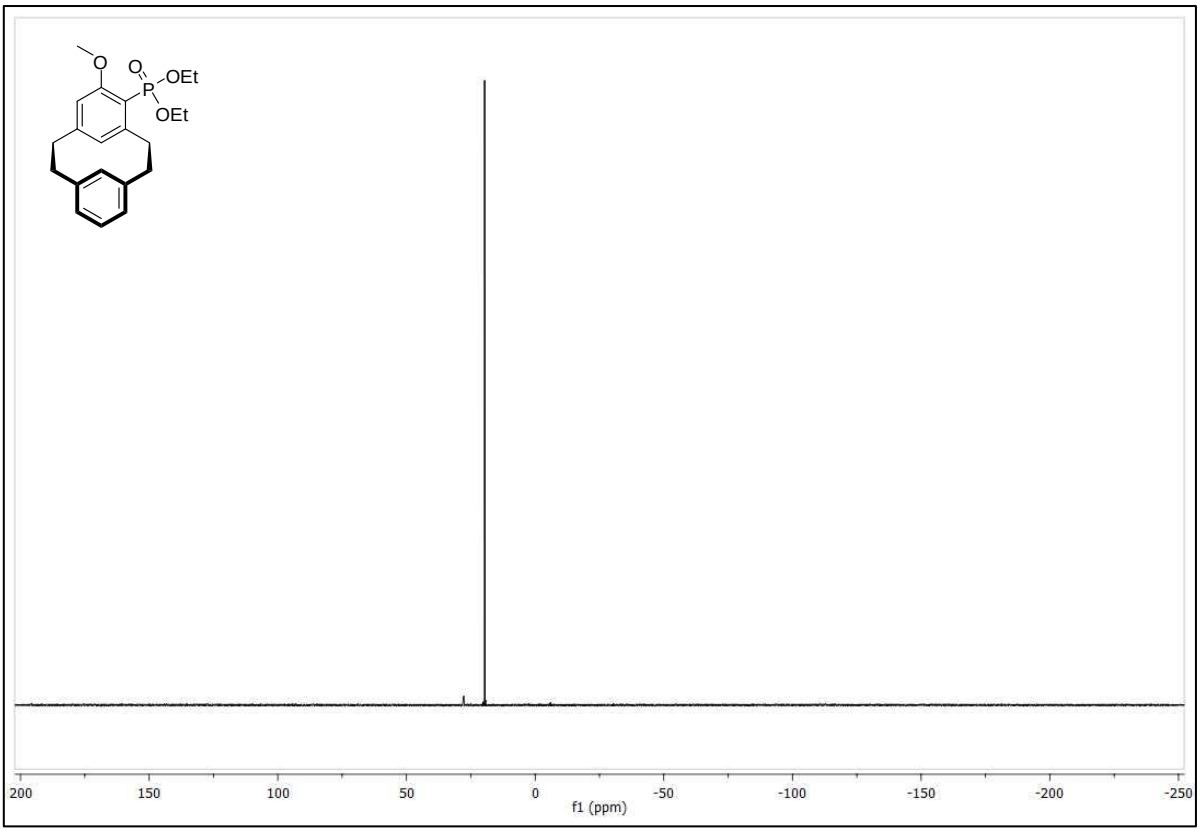
^{1}H NMR (500 MHz, CD_3OD)



^{13}C NMR (100 MHz, CD_3OD)

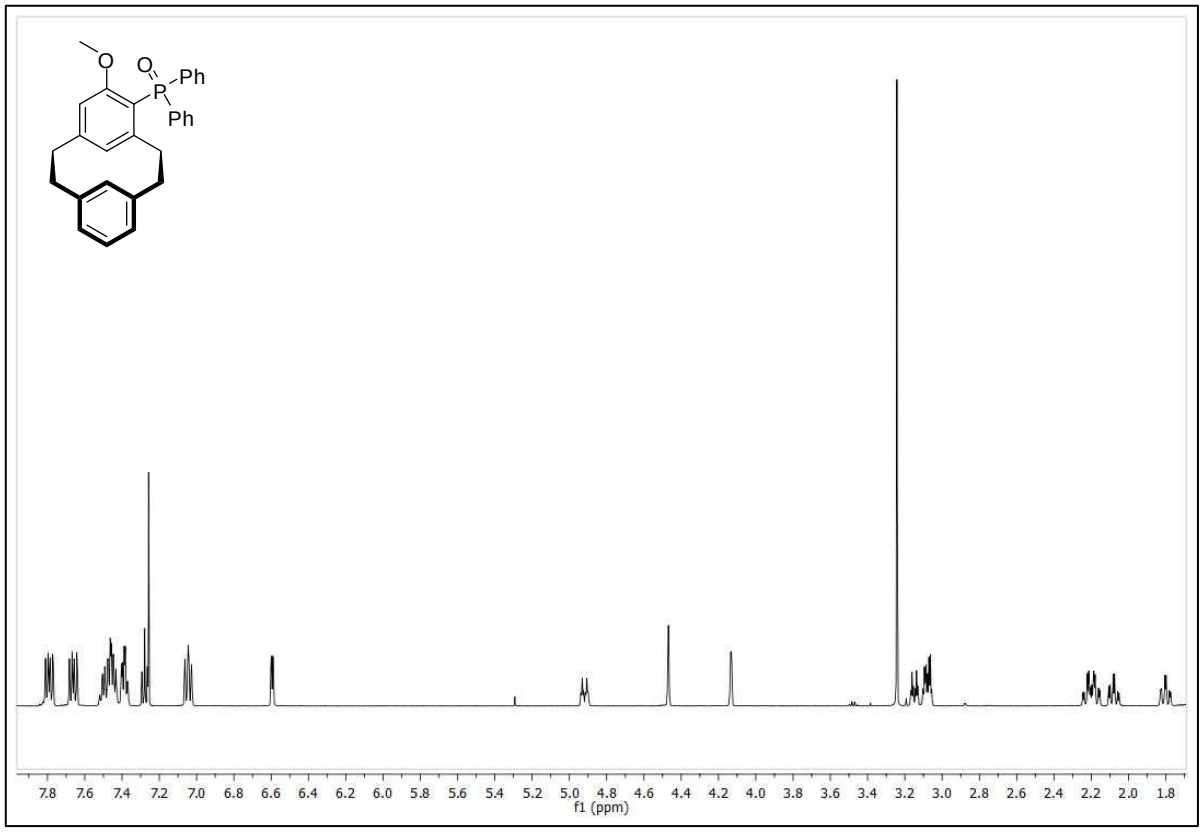


^{31}P NMR (162 MHz, CD_3OD)

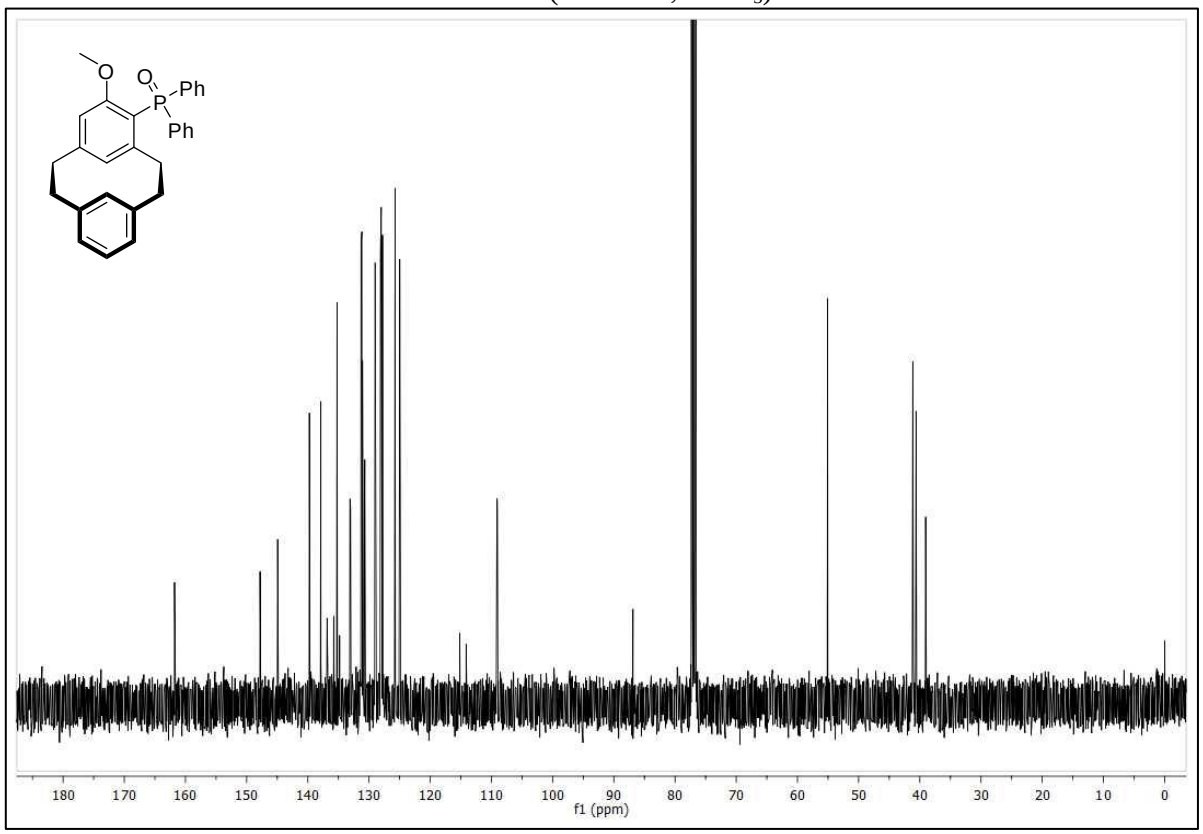


(R_p)-(-)-Diphenyl(5-methoxy[2.2]metacylophan-4-yl)phosphine oxide (11h)

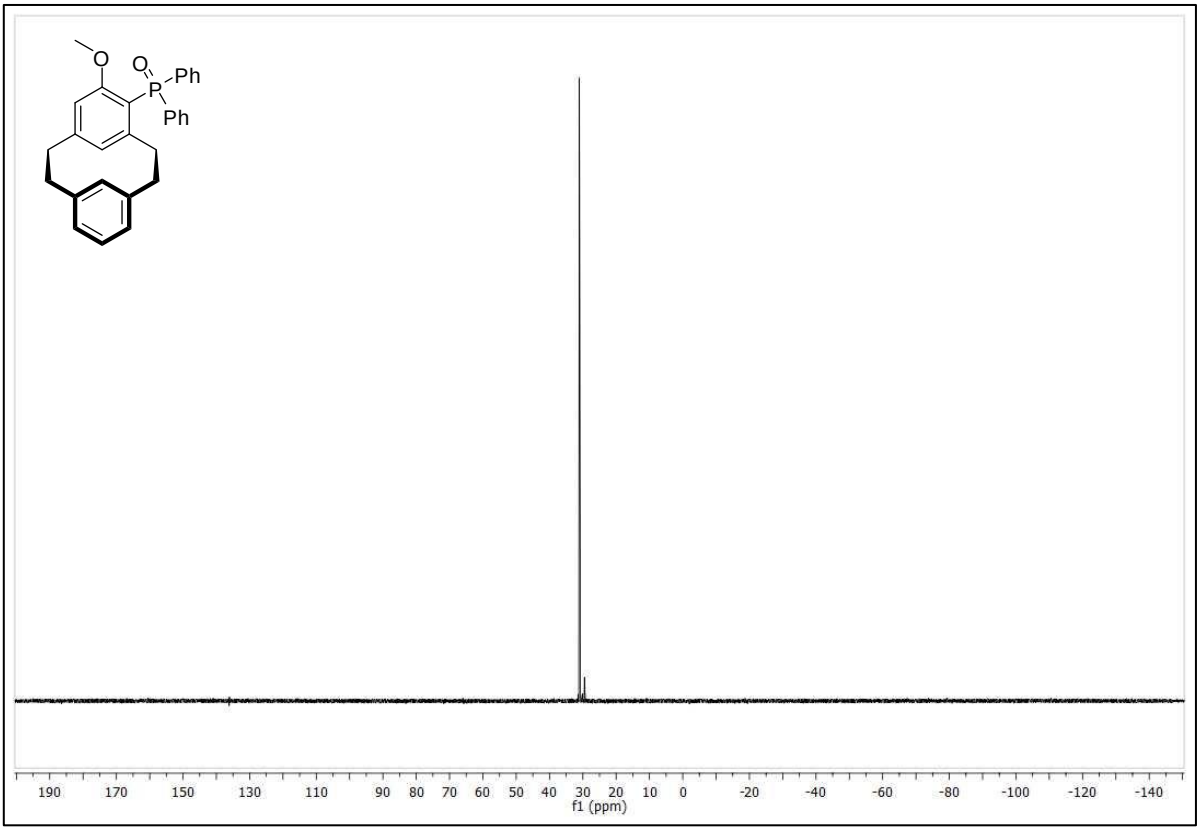
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

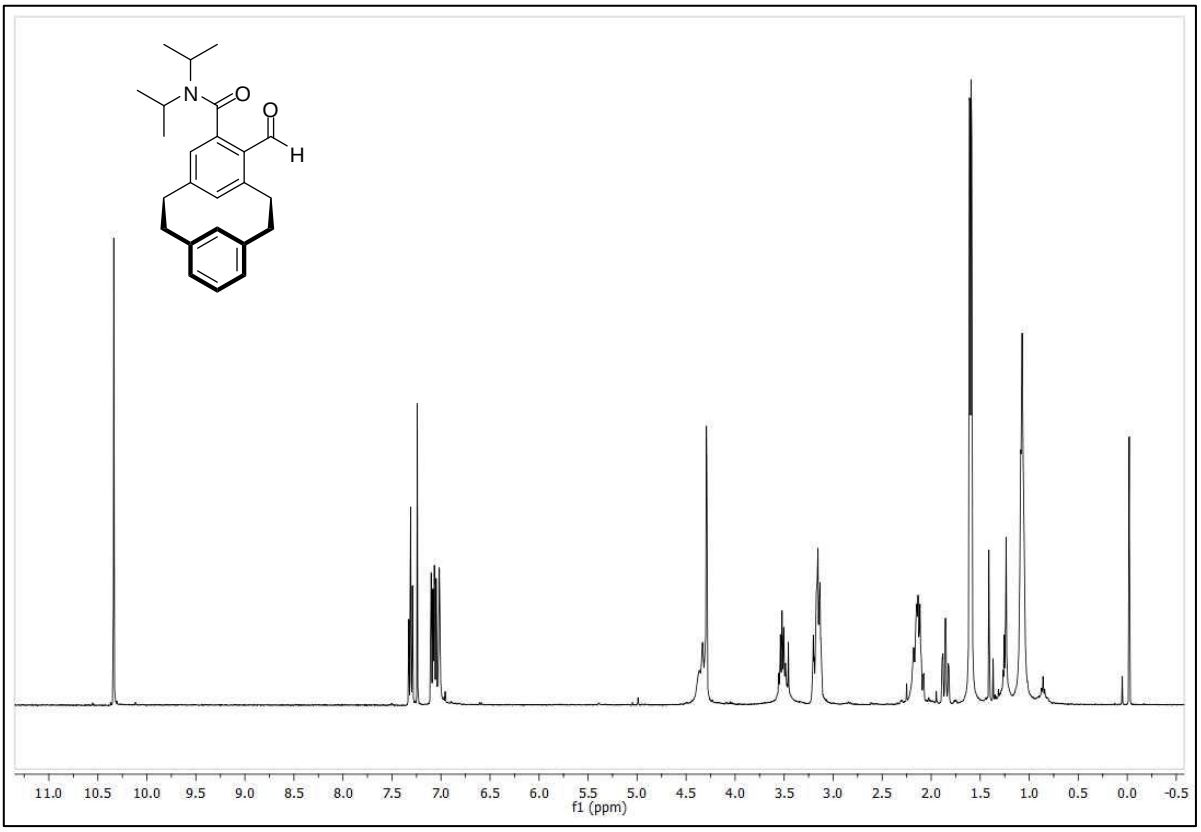


^{31}P NMR (162 MHz, $CDCl_3$)

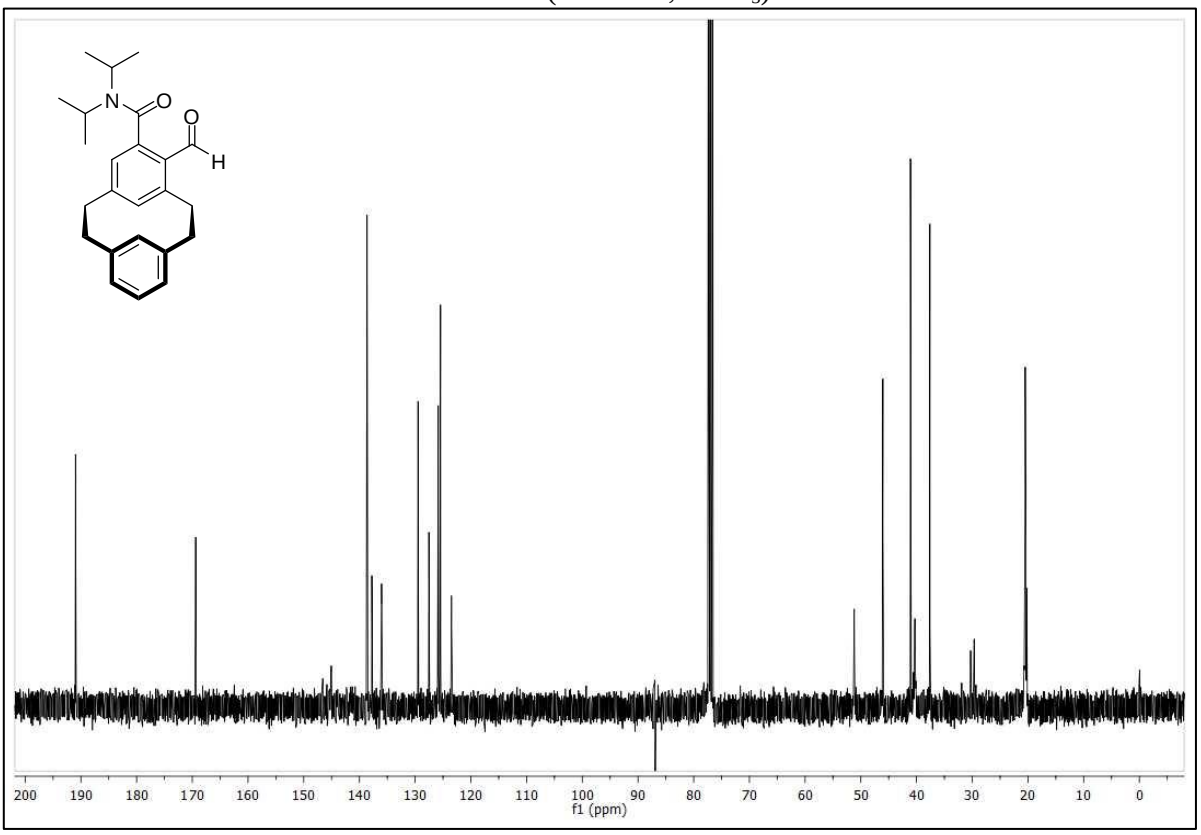


(R_p)-(+)-*N*,*N*-Diisopropyl-4-formyl-[2.2]metacylophane-5-carboxamide (11i)

^{1}H NMR (400 MHz, $CDCl_3$)

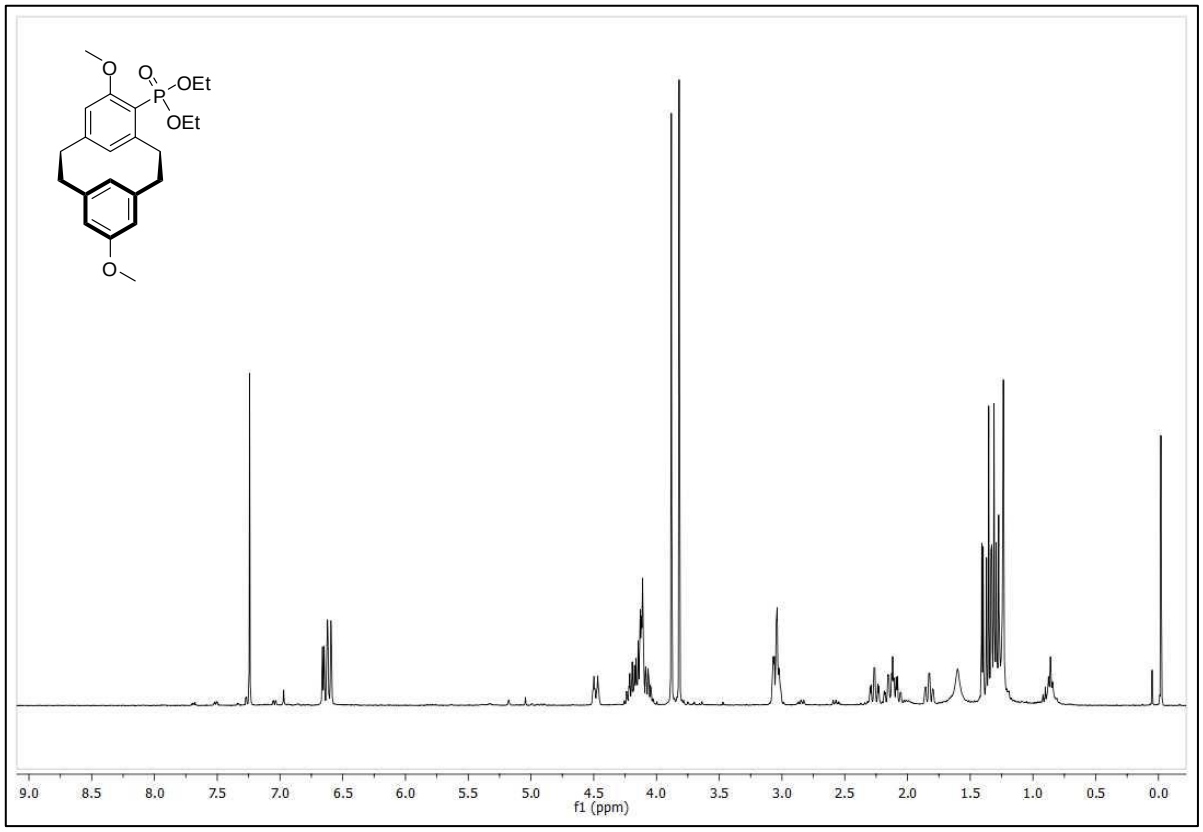


^{13}C NMR (100 MHz, $CDCl_3$)

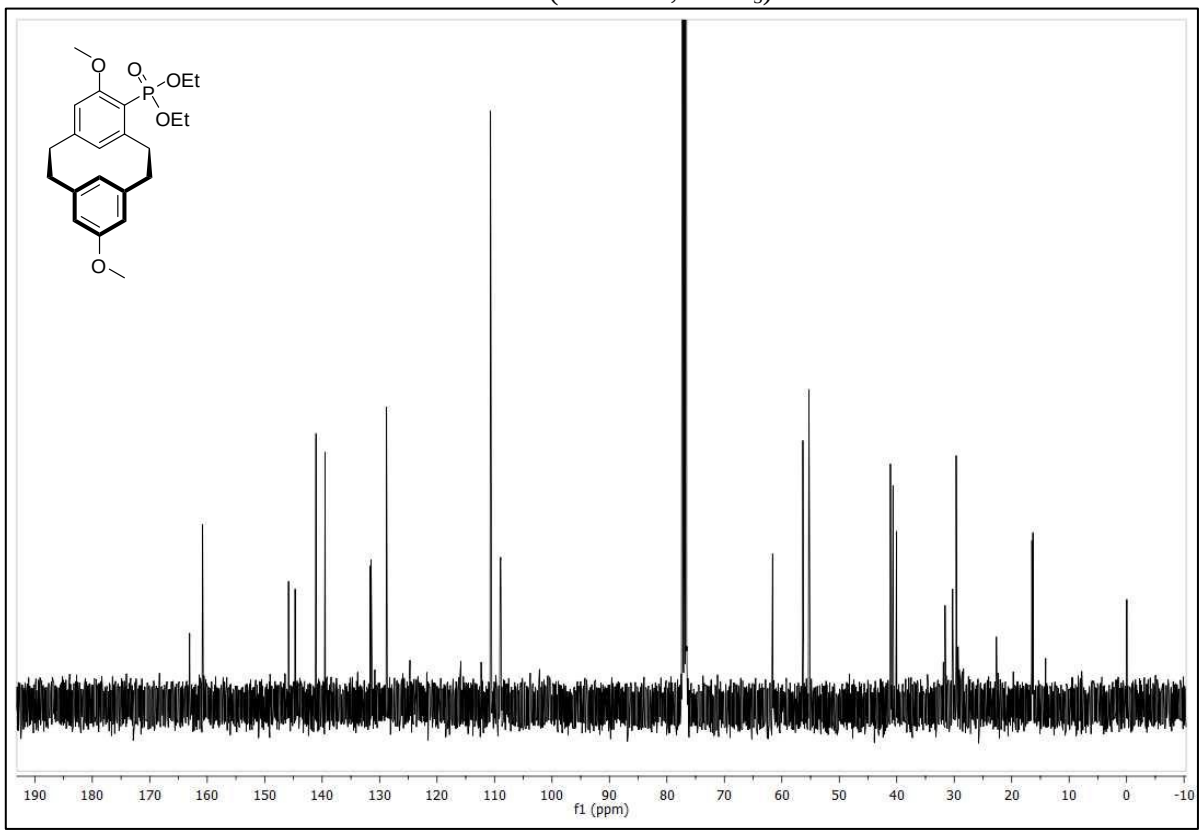


(R_p)-(-)-5,13-Dimethoxy[2.2]metacylophane-4-phosphonic acid diethyl ester (11j)

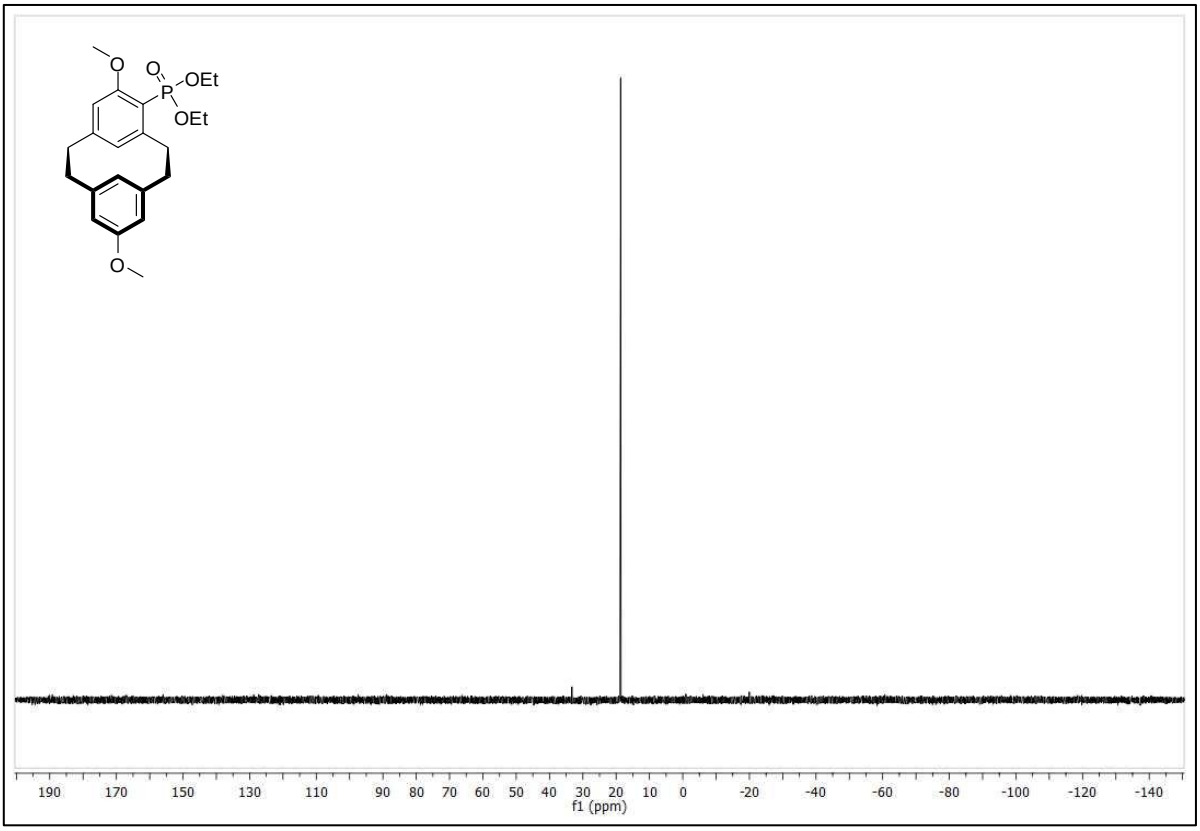
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

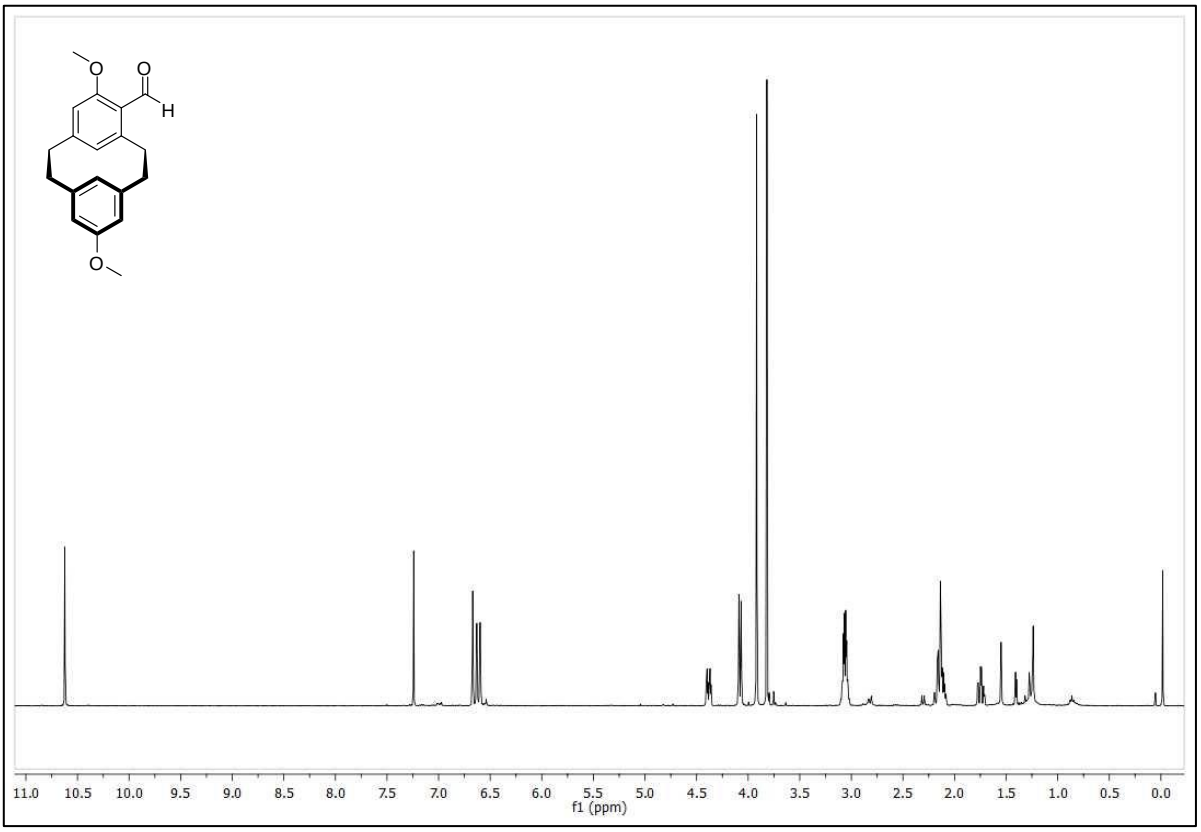


^{31}P NMR (162 MHz, $CDCl_3$)

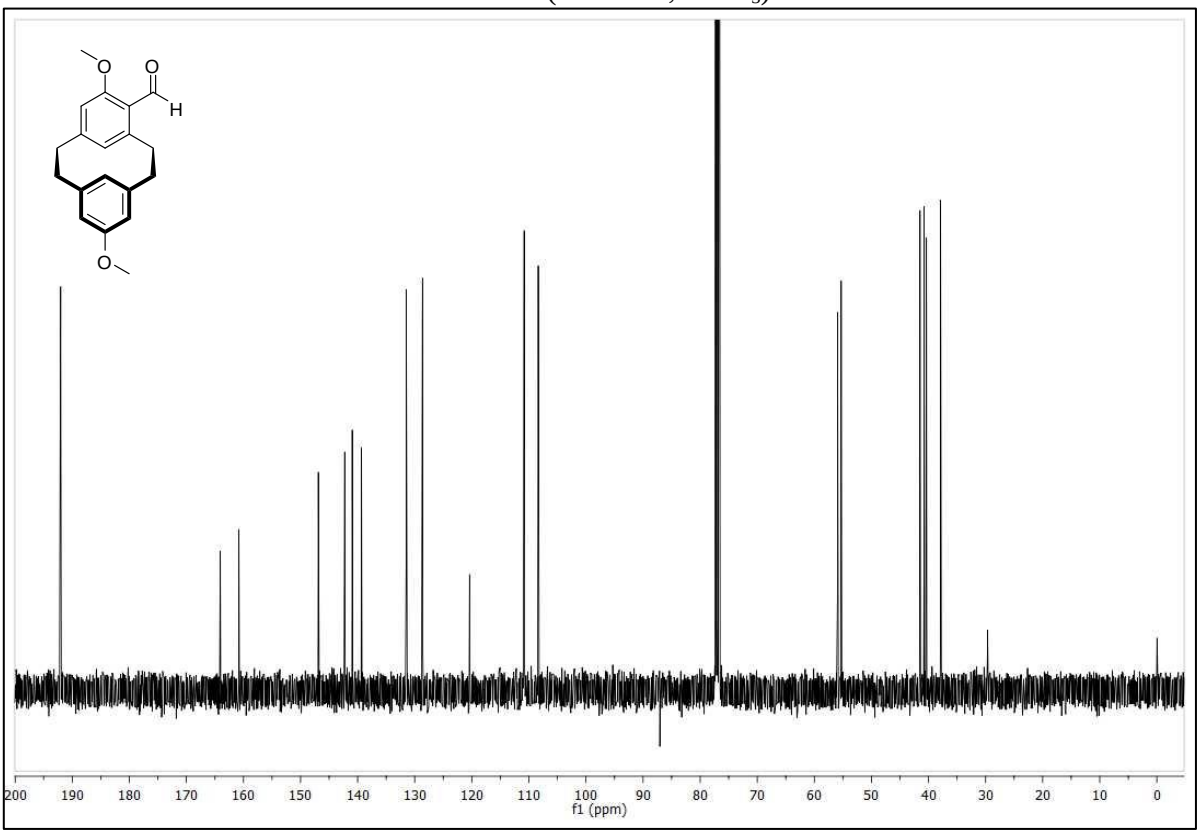


(R_p)-(+)-5,13-Dimethoxy[2.2]metacylophane-4-carbaldehyde (11k)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

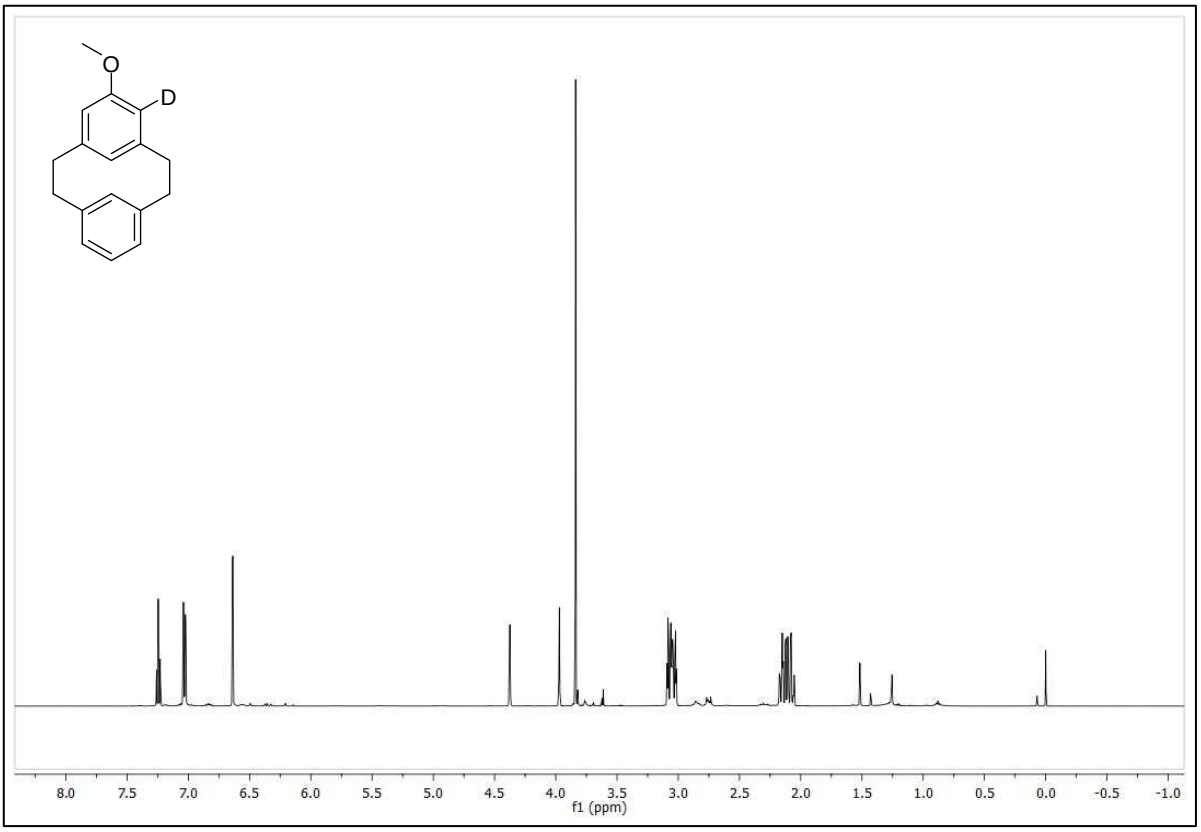


Synthesis and analysis of compound **9a**-D_1

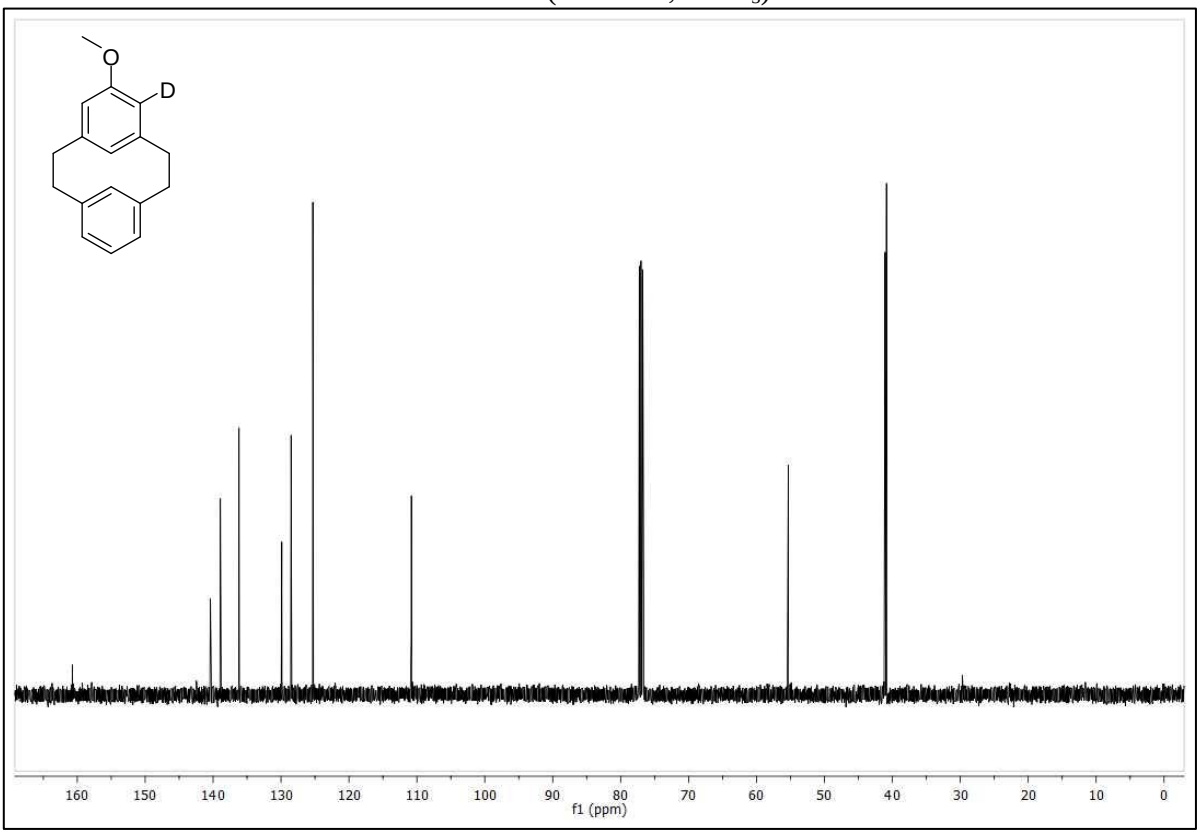
4-Deuterio-5-methoxy[2.2]metacylophane (9a-D_1). A solution of 5-methoxy[2.2]metacylophane **9a** (25 mg, 0.11 mmol) in THF (10 mL) at -78 °C was treated dropwise with BuLi (2.50 M, 0.46 mL, 0.12 mmol) and stirred for 5 min. KO*t*Bu (1.0 M in THF, 0.12 mL, 0.12 mmol) was added dropwise, the reaction mixture was stirred for 15 min at -78 °C and CD_3OD (33 µL) added. The reaction mixture was warmed under N_2 to rt and the solvent removed under reduced pressure. Ethyl acetate (20 mL) was added to the residue, washed with HCl (2 M, 3 x 10 mL), dried over sodium sulfate and concentrated to dryness to give **9a**-D_1 as a colourless solid (23 mg, 88%, 75% D incorporation). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 7.3 Hz, 2H), 6.64 (s, 1H), 4.37 (s, 1H), 3.97 (s, 1H), 3.84 (s, *J* = 7.6 Hz, 3H), 3.13-2.98 (m, 4H), 2.19-2.04 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.8, 140.5, 140.5, 140.5, 139.1, 136.4, 130.0, 128.7, 125.5, 111.0, 110.9, 55.5, 41.3, 41.2, 41.0. ^{2}H NMR (92.07 MHz, CH_2Cl_2) δ 6.66 (s). EI-HRMS $[M]^+$: 239.1422, $C_{17}H_{17}DO$ requires 239.1420.

4-Deuterio-5-methoxy[2.2]metacylophane (9a-D_1)

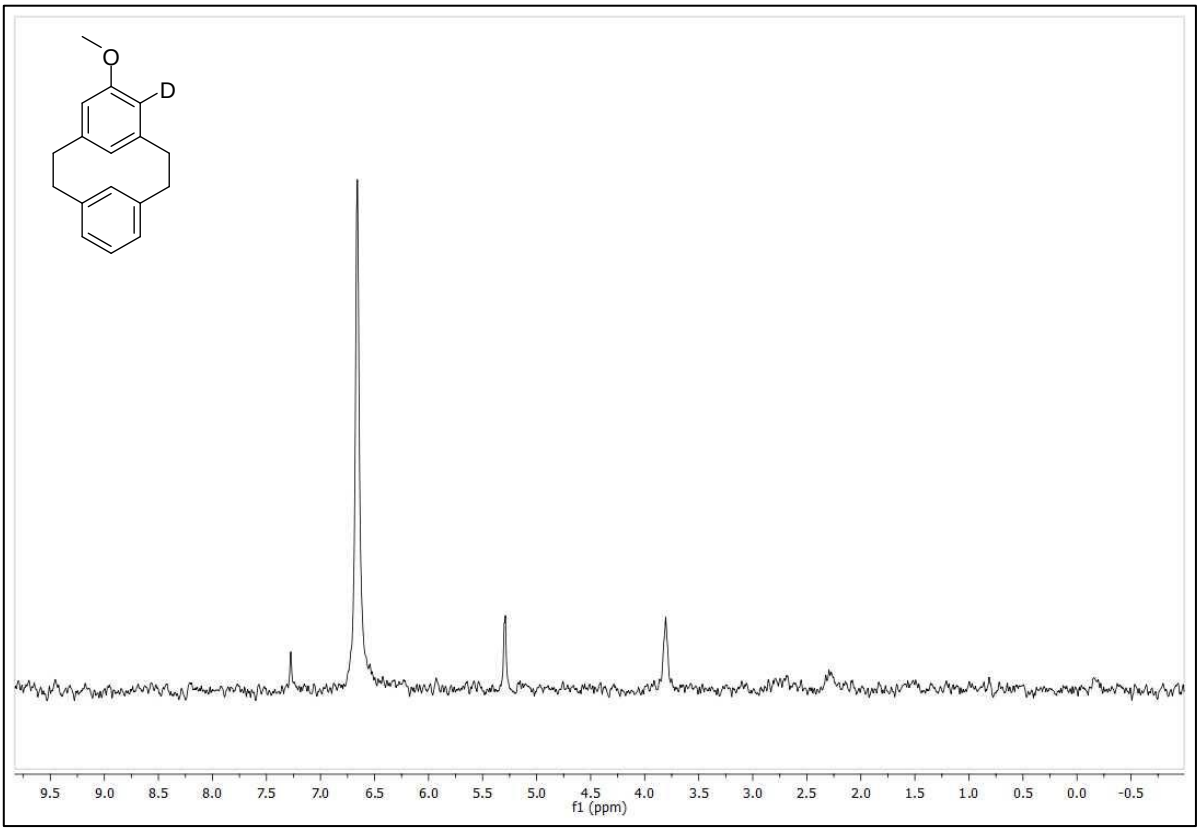
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



^{2}H NMR (92.07 MHz, CH_2Cl_2)



Racemization Plots Data for Compounds **11a-c**

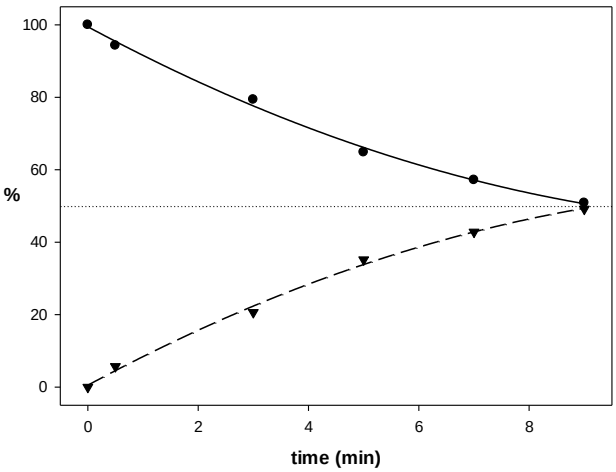
General procedure for the racemization of [2.2]metacyclophanes 11a-c. In a round-bottom flask equipped with a reflux condenser, a sample of enantioenriched [2.2]metacyclophane **11a-c** (0.5 mg) was dissolved in *N*-methyl-2-pyrrolidone (1 mL) and heated at 453 K. At a specified time interval, a sample (approx vol. 100 µL) was taken and rapidly cooled to room temperature with an ice bath. Heptane (approx. vol. 0.5 mL) was added and, after a short micro extraction, the upper heptane layer was isolated and submitted for HPLC analysis.

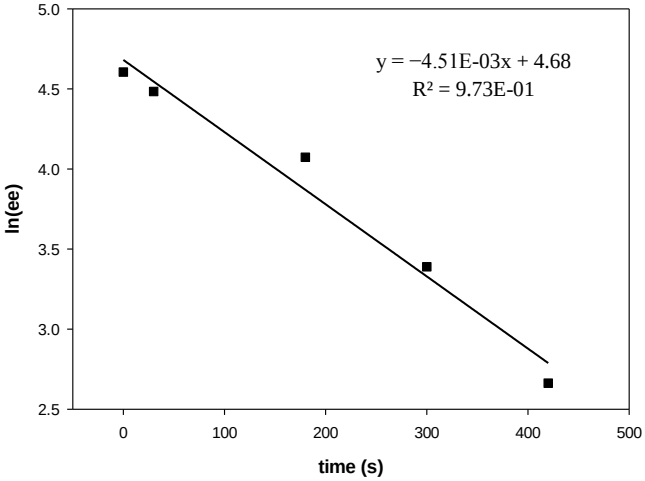
Determination of rate constant and racemization barriers. The inversion barriers (ΔG^{*}) were calculated on the basis of the absolute rate equation[7,8] assuming a unitary transmission coefficient. The rate constants were determined *via* a first-order integrated law plot considering the racemization of an optical antipode as a reversible first order reaction, where the forward and reverse reaction-rate constants k_f and k_r are identical:

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} B$$

and $k_f = k_r = k_i$ (inversion constant).

(R_p)-(-)-5-Methoxy[2.2]metacylophane-4-carboxylic acid ethyl ester (**11a**)





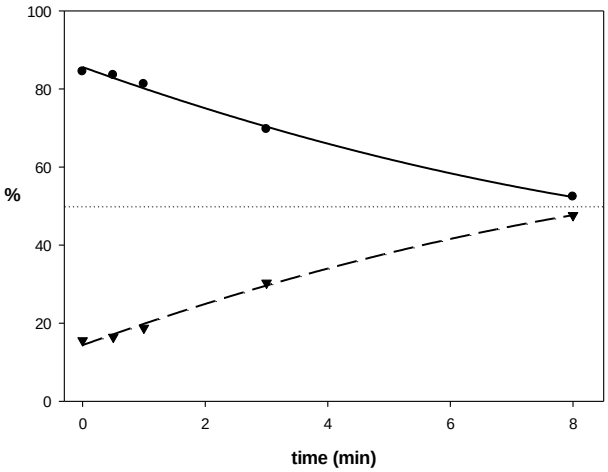
T = 453.0 K

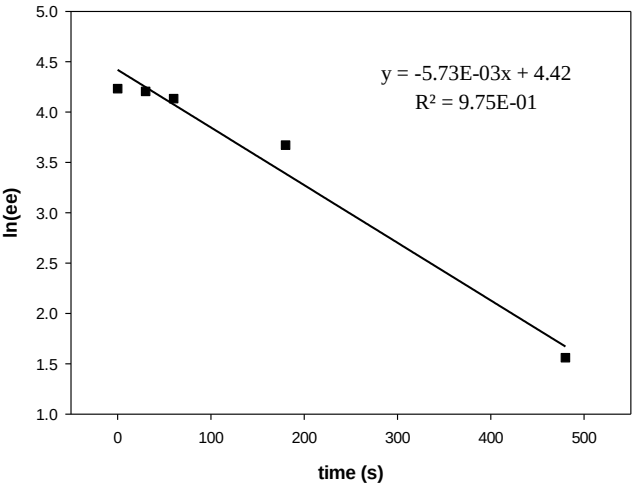
k' (x 10^5) = 450 s^{-1}

k_i (x 10^5) = 225 s^{-1}

ΔG^*_{453} = 141.6 kJ/mol (33.8 kcal/mol)

(R_p)-(-)-5-(*N*,*N*-diisopropylcarbamoyl)[2.2]metacylophane-4-carboxylic acid ethyl ester (**11b**)





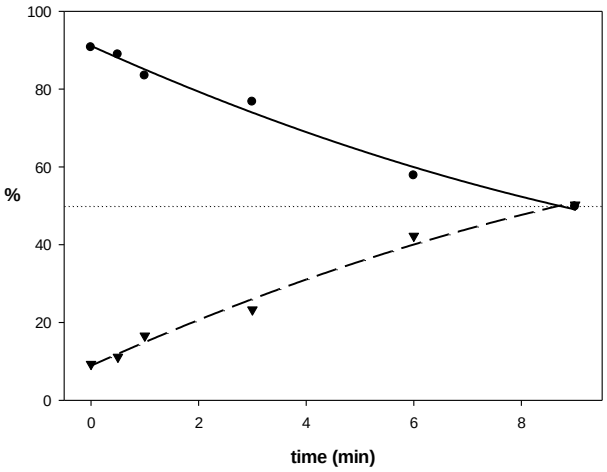
T = 453.0 K

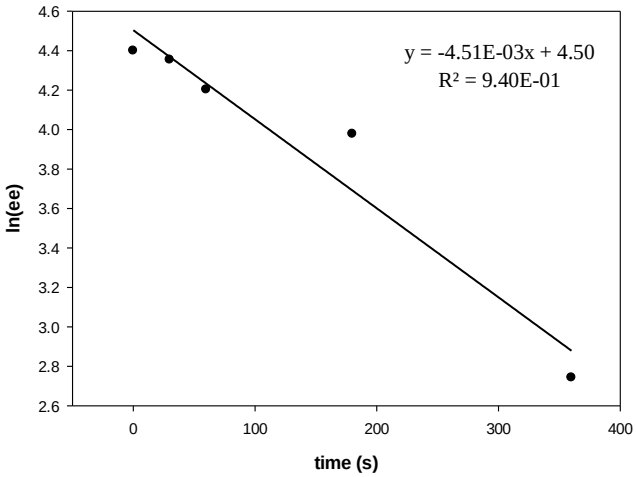
k' (x 10^5) = 572 s^{-1}

k_i (x 10^5) = 286 s^{-1}

ΔG^*_{453} = 134.5 kJ/mol (32.1 kcal/mol)

(R_p)-(-)-5,13-Dimethoxy[2.2]metacylophane-4-carboxylic acid ethyl ester (**11c**)





T = 453.0 K

k' (x 10^5) = 451 s^{-1}

k_i (x 10^5) = 225.5 s^{-1}

ΔG^*_{453} = 135.4 kJ/mol (32.4 kcal/mol)

References

1. W. G. Kofron and L. M. Baclawski, *J. Org. Chem.* 1976, **41**, 1879.
2. G. G. Pagani, G. G. Caccialanza and P. P. Borgna, *Farmaco Sci.* 1973, **28**, 835.
3. M. Blangetti, P. Fleming and D. F. O'Shea, *Beilstein J. Org. Chem.* 2011, **7**, 1249.
4. S. A. Sherrod and R. L. Da Costa, *Tetrahedron Lett.* 1973, **23**, 2083.
5. G. J. Bodwell, T. J. Houghton, J. Kennedy and M. R. Mannion, *Angew. Chem., Int. Ed.* 1996, **35**, 2121.
6. T. Sato, K. Torizuka, R. Komaki and H. Atobe, *J. Chem. Soc, Perkin Trans. 2* 1980, **4**, 561.
7. (a) S. Glasstone, K. J. Laidler and H. Eyring, *The theory of rate processes*, McGraw-Hill Book Co., New York, N.Y., 1941. (b) F. W. Cagle Jr and H. Eyring, *J. Am. Chem. Soc.* 1951, **73**, 5628.
8. C. Glotzmann, E. Langer, H. Lehner and K. Schlogl, *Monatsh. Chem.* 1974, **105**, 907.

X-Ray Structural Data for **(R_p)-11a**

Table 1. Crystal data and structure refinement for **(R_p)-11a**

Identification code	**(R_p)-11a**
Empirical formula	C_{20} H_{22} O_3
Formula weight	310.38
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P2_1$ (#4)
Unit cell dimensions	a = 8.15436(7) Å α= 90°.
	b = 8.76221(7) Å β= 107.081(1)°.
	c = 12.1310(1) Å γ = 90°.
Volume	828.530(12) $Å^3$
Z	2
Density (calculated)	1.244 Mg/m^3
Absorption coefficient	0.658 mm^{-1}
F(000)	332
Crystal size	0.3840 x 0.2026 x 0.1554 mm^3
Theta range for data collection	3.81 to 76.63°.
Index ranges	–10<=h<=10, –10<=k<=11, –13<=l<=15
Reflections collected	16971
Independent reflections	3445 [R(int) = 0.0231]
Completeness to theta = 76.63°	99.4 %
Absorption correction	Analytical
Max. and min. transmission	0.926 and 0.842
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	3445 / 1 / 210
Goodness–of–fit on F^2	1.067
Final R indices [I>2sigma(I)]	R1 = 0.0269, wR2 = 0.0728
R indices (all data)	R1 = 0.0273, wR2 = 0.0732
Absolute structure parameter	0.06(13)
Largest diff. peak and hole	0.193 and –0.172 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **(R_p)-11a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
C(1)	3351(1)	8565(1)	1417(1)	17(1)
C(7)	1898(1)	7468(1)	962(1)	18(1)
O(1)	2069(1)	6125(1)	816(1)	32(1)
O(2)	395(1)	8182(1)	734(1)	21(1)
C(8)	–1139(1)	7283(1)	190(1)	23(1)
C(9)	–1502(2)	7313(1)	–1101(1)	24(1)
C(2)	4097(1)	9240(1)	629(1)	17(1)
O(3)	3311(1)	8898(1)	–503(1)	20(1)
C(10)	4022(2)	9571(1)	–1337(1)	24(1)
C(3)	5560(1)	10145(1)	1020(1)	18(1)

C(4)	6183(1)	10496(1)	2195(1)	17(1)
C(5)	5291(1)	9975(1)	2939(1)	17(1)
C(6)	3968(1)	8908(1)	2588(1)	17(1)
C(11)	7962(1)	11149(1)	2695(1)	19(1)
C(12)	9311(1)	9837(1)	3114(1)	21(1)
C(13)	3520(1)	7945(1)	3492(1)	21(1)
C(14)	4882(2)	6637(1)	3908(1)	23(1)
C(15)	8868(1)	8897(1)	4030(1)	20(1)
C(16)	9405(1)	9339(1)	5187(1)	24(1)
C(17)	8622(2)	8726(2)	5963(1)	27(1)
C(18)	7217(2)	7758(1)	5583(1)	25(1)
C(19)	6652(1)	7300(1)	4431(1)	21(1)
C(20)	7583(1)	7791(1)	3692(1)	20(1)

Table 3. Bond lengths [Å] and angles [°] for **(R_p)-11a**.

C(1)–C(6)	1.3938(14)
C(1)–C(2)	1.4056(14)
C(1)–C(7)	1.4989(14)
C(7)–O(1)	1.2043(14)
C(7)–O(2)	1.3312(13)
O(2)–C(8)	1.4615(12)
C(8)–C(9)	1.5056(16)
C(8)–H(8A)	0.9900
C(8)–H(8B)	0.9900
C(9)–H(9A)	0.9800
C(9)–H(9B)	0.9800
C(9)–H(9C)	0.9800
C(2)–O(3)	1.3670(13)
C(2)–C(3)	1.3946(15)
O(3)–C(10)	1.4332(13)
C(10)–H(10A)	0.9800
C(10)–H(10B)	0.9800
C(10)–H(10C)	0.9800
C(3)–C(4)	1.3997(14)
C(3)–H(3)	0.9500
C(4)–C(5)	1.3913(15)
C(4)–C(11)	1.5109(14)
C(5)–C(6)	1.3965(14)
C(5)–H(5)	0.9500
C(6)–C(13)	1.5107(14)
C(11)–C(12)	1.5687(15)
C(11)–H(11A)	0.9900
C(11)–H(11B)	0.9900
C(12)–C(15)	1.5101(15)
C(12)–H(12A)	0.9900
C(12)–H(12B)	0.9900
C(13)–C(14)	1.5724(15)
C(13)–H(13A)	0.9900
C(13)–H(13B)	0.9900
C(14)–C(19)	1.5118(15)
C(14)–H(14A)	0.9900
C(14)–H(14B)	0.9900
C(15)–C(16)	1.3966(16)
C(15)–C(20)	1.3972(15)
C(16)–C(17)	1.3909(18)
C(16)–H(16)	0.9500
C(17)–C(18)	1.3912(18)

C(17)–H(17)	0.9500
C(18)–C(19)	1.3958(16)
C(18)–H(18)	0.9500
C(19)–C(20)	1.4015(16)
C(20)–H(20)	0.9500

C(6)–C(1)–C(2)	120.23(9)
C(6)–C(1)–C(7)	121.54(9)
C(2)–C(1)–C(7)	118.22(9)
O(1)–C(7)–O(2)	124.59(10)
O(1)–C(7)–C(1)	124.61(10)
O(2)–C(7)–C(1)	110.79(9)
C(7)–O(2)–C(8)	117.03(9)
O(2)–C(8)–C(9)	109.92(9)
O(2)–C(8)–H(8A)	109.7
C(9)–C(8)–H(8A)	109.7
O(2)–C(8)–H(8B)	109.7
C(9)–C(8)–H(8B)	109.7
H(8A)–C(8)–H(8B)	108.2
C(8)–C(9)–H(9A)	109.5
C(8)–C(9)–H(9B)	109.5
H(9A)–C(9)–H(9B)	109.5
C(8)–C(9)–H(9C)	109.5
H(9A)–C(9)–H(9C)	109.5
H(9B)–C(9)–H(9C)	109.5
O(3)–C(2)–C(3)	124.64(9)
O(3)–C(2)–C(1)	114.92(9)
C(3)–C(2)–C(1)	120.41(9)
C(2)–O(3)–C(10)	116.83(8)
O(3)–C(10)–H(10A)	109.5
O(3)–C(10)–H(10B)	109.5
H(10A)–C(10)–H(10B)	109.5
O(3)–C(10)–H(10C)	109.5
H(10A)–C(10)–H(10C)	109.5
H(10B)–C(10)–H(10C)	109.5
C(2)–C(3)–C(4)	119.30(10)
C(2)–C(3)–H(3)	120.4
C(4)–C(3)–H(3)	120.4
C(5)–C(4)–C(3)	119.09(10)
C(5)–C(4)–C(11)	119.15(9)
C(3)–C(4)–C(11)	120.65(9)
C(4)–C(5)–C(6)	121.74(9)
C(4)–C(5)–H(5)	119.1
C(6)–C(5)–H(5)	119.1
C(1)–C(6)–C(5)	118.06(9)
C(1)–C(6)–C(13)	121.82(9)
C(5)–C(6)–C(13)	118.88(9)
C(4)–C(11)–C(12)	110.63(9)
C(4)–C(11)–H(11A)	109.5
C(12)–C(11)–H(11A)	109.5
C(4)–C(11)–H(11B)	109.5
C(12)–C(11)–H(11B)	109.5
H(11A)–C(11)–H(11B)	108.1
C(15)–C(12)–C(11)	109.97(8)
C(15)–C(12)–H(12A)	109.7
C(11)–C(12)–H(12A)	109.7
C(15)–C(12)–H(12B)	109.7
C(11)–C(12)–H(12B)	109.7
H(12A)–C(12)–H(12B)	108.2
C(6)–C(13)–C(14)	109.95(8)

C(6)–C(13)–H(13A)	109.7
C(14)–C(13)–H(13A)	109.7
C(6)–C(13)–H(13B)	109.7
C(14)–C(13)–H(13B)	109.7
H(13A)–C(13)–H(13B)	108.2
C(19)–C(14)–C(13)	110.61(9)
C(19)–C(14)–H(14A)	109.5
C(13)–C(14)–H(14A)	109.5
C(19)–C(14)–H(14B)	109.5
C(13)–C(14)–H(14B)	109.5
H(14A)–C(14)–H(14B)	108.1
C(16)–C(15)–C(20)	118.27(10)
C(16)–C(15)–C(12)	121.09(10)
C(20)–C(15)–C(12)	118.90(9)
C(17)–C(16)–C(15)	120.18(11)
C(17)–C(16)–H(16)	119.9
C(15)–C(16)–H(16)	119.9
C(16)–C(17)–C(18)	120.52(11)
C(16)–C(17)–H(17)	119.7
C(18)–C(17)–H(17)	119.7
C(17)–C(18)–C(19)	120.32(11)
C(17)–C(18)–H(18)	119.8
C(19)–C(18)–H(18)	119.8
C(18)–C(19)–C(20)	118.06(11)
C(18)–C(19)–C(14)	121.59(10)
C(20)–C(19)–C(14)	118.69(10)
C(15)–C(20)–C(19)	121.73(10)
C(15)–C(20)–H(20)	119.1
C(19)–C(20)–H(20)	119.1

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **(R_p)-11a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	14(1)	15(1)	20(1)	1(1)	4(1)	1(1)
C(7)	18(1)	19(1)	18(1)	1(1)	7(1)	0(1)
O(1)	23(1)	18(1)	51(1)	–1(1)	7(1)	0(1)
O(2)	15(1)	21(1)	26(1)	–4(1)	4(1)	0(1)
C(8)	14(1)	28(1)	25(1)	–3(1)	5(1)	–4(1)
C(9)	23(1)	25(1)	24(1)	–5(1)	6(1)	–4(1)
C(2)	18(1)	16(1)	16(1)	0(1)	4(1)	3(1)
O(3)	22(1)	23(1)	15(1)	–1(1)	5(1)	–4(1)
C(10)	28(1)	27(1)	16(1)	1(1)	7(1)	–5(1)
C(3)	18(1)	17(1)	18(1)	3(1)	6(1)	1(1)
C(4)	17(1)	14(1)	20(1)	2(1)	4(1)	1(1)
C(5)	18(1)	18(1)	16(1)	0(1)	4(1)	3(1)
C(6)	16(1)	19(1)	18(1)	2(1)	6(1)	3(1)
C(11)	18(1)	19(1)	21(1)	0(1)	4(1)	–2(1)
C(12)	16(1)	23(1)	23(1)	–1(1)	5(1)	0(1)
C(13)	20(1)	25(1)	19(1)	2(1)	7(1)	–2(1)
C(14)	26(1)	21(1)	22(1)	6(1)	8(1)	–1(1)
C(15)	17(1)	19(1)	22(1)	2(1)	3(1)	4(1)
C(16)	20(1)	26(1)	23(1)	1(1)	0(1)	1(1)

C(17)	29(1)	30(1)	18(1)	3(1)	1(1)	3(1)
C(18)	27(1)	27(1)	20(1)	7(1)	6(1)	3(1)
C(19)	24(1)	17(1)	22(1)	5(1)	6(1)	3(1)
C(20)	21(1)	17(1)	21(1)	1(1)	4(1)	4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **(R_p)-11a**.

Atom	x	y	z	U(eq)
H(8A)	–2131	7707	401	27
H(8B)	–965	6216	469	27
H(9A)	–1514	8373	–1362	36
H(9B)	–2621	6843	–1464	36
H(9C)	–608	6744	–1316	36
H(10A)	4091	10681	–1229	35
H(10B)	3287	9335	–2115	35
H(10C)	5173	9159	–1238	35
H(3)	6128	10520	495	21
H(5)	5590	10356	3706	21
H(11A)	7979	11824	3352	23
H(11B)	8269	11768	2102	23
H(12A)	9319	9177	2454	25
H(12B)	10471	10282	3431	25
H(13A)	2365	7494	3165	25
H(13B)	3497	8592	4156	25
H(14A)	4567	5998	4488	28
H(14B)	4885	5978	3246	28
H(16)	10307	10059	5445	29
H(17)	9050	8972	6759	33
H(18)	6639	7406	6110	30
H(20)	7334	7362	2942	24

Table 6. Torsion angles [°] for **(R_p)-11a**.

C(6)–C(1)–C(7)–O(1)	–93.35(14)
C(2)–C(1)–C(7)–O(1)	86.10(14)
C(6)–C(1)–C(7)–O(2)	87.13(12)
C(2)–C(1)–C(7)–O(2)	–93.42(11)
O(1)–C(7)–O(2)–C(8)	–4.66(16)
C(1)–C(7)–O(2)–C(8)	174.86(8)
C(7)–O(2)–C(8)–C(9)	–87.12(12)
C(6)–C(1)–C(2)–O(3)	–175.76(9)
C(7)–C(1)–C(2)–O(3)	4.78(14)
C(6)–C(1)–C(2)–C(3)	6.00(15)
C(7)–C(1)–C(2)–C(3)	–173.47(9)
C(3)–C(2)–O(3)–C(10)	–2.29(15)
C(1)–C(2)–O(3)–C(10)	179.54(9)
O(3)–C(2)–C(3)–C(4)	175.85(10)
C(1)–C(2)–C(3)–C(4)	–6.08(15)
C(2)–C(3)–C(4)–C(5)	–2.21(15)
C(2)–C(3)–C(4)–C(11)	165.67(9)
C(3)–C(4)–C(5)–C(6)	10.92(15)
C(11)–C(4)–C(5)–C(6)	–157.14(10)
C(2)–C(1)–C(6)–C(5)	2.40(15)
C(7)–C(1)–C(6)–C(5)	–178.15(9)
C(2)–C(1)–C(6)–C(13)	–164.77(10)
C(7)–C(1)–C(6)–C(13)	14.68(15)

C(4)–C(5)–C(6)–C(1)	–10.95(15)
C(4)–C(5)–C(6)–C(13)	156.60(10)
C(5)–C(4)–C(11)–C(12)	77.88(12)
C(3)–C(4)–C(11)–C(12)	–89.99(12)
C(4)–C(11)–C(12)–C(15)	–59.92(11)
C(1)–C(6)–C(13)–C(14)	90.00(11)
C(5)–C(6)–C(13)–C(14)	–77.07(12)
C(6)–C(13)–C(14)–C(19)	60.33(12)
C(11)–C(12)–C(15)–C(16)	–84.97(12)
C(11)–C(12)–C(15)–C(20)	79.74(12)
C(20)–C(15)–C(16)–C(17)	–2.43(16)
C(12)–C(15)–C(16)–C(17)	162.37(10)
C(15)–C(16)–C(17)–C(18)	–4.78(18)
C(16)–C(17)–C(18)–C(19)	4.65(18)
C(17)–C(18)–C(19)–C(20)	2.66(17)
C(17)–C(18)–C(19)–C(14)	–162.43(11)
C(13)–C(14)–C(19)–C(18)	84.39(12)
C(13)–C(14)–C(19)–C(20)	–80.61(13)
C(16)–C(15)–C(20)–C(19)	10.01(16)
C(12)–C(15)–C(20)–C(19)	–155.13(10)
C(18)–C(19)–C(20)–C(15)	–10.12(16)
C(14)–C(19)–C(20)–C(15)	155.41(10)

Symmetry transformations used to generate equivalent atoms:

X-Ray Structural Data for *rac*-**11d**

Table 1. Crystal data and structure refinement for *rac*-**11d**

Identification code	***rac*-11d**
Empirical formula	$C_{18}H_{18}O_3$
Formula weight	282.32
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P2_1/c$ (#14)
Unit cell dimensions	a = 13.4948(2) Å α= 90°.
	b = 14.0951(2) Å β= 96.909(2)°.
	c = 7.5300(1) Å γ = 90°.
Volume	1421.88(3) $Å^3$
Z	4
Density (calculated)	1.319 Mg/m^3
Absorption coefficient	0.715 mm^{-1}
F(000)	600
Crystal size	0.2158 x 0.1231 x 0.0393 mm^3
Theta range for data collection	3.30 to 76.47°.
Index ranges	–16<=h<=17, –17<=k<=17, –9<=l<=9
Reflections collected	22791 [a)]
Independent reflections	2970 [R(int) = 0.0327] [a)]
Completeness to theta = 76.47°	99.8 % [a)]
Absorption correction	Analytical
Max. and min. transmission	0.975 and 0.890
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	2970 / 0 / 194
Goodness–of–fit on F^2	1.002
Final R indices [I>2sigma(I)]	R1 = 0.0353, wR2 = 0.0955
R indices (all data)	R1 = 0.0454, wR2 = 0.0999
Largest diff. peak and hole	0.253 and –0.223 e.$Å^{-3}$

[a)] This crystal is a non–merohedral twin. The refinement was done on an HKLF5 file. This prevents merging of equivalent reflections, so the number of unique reflections and the internal R-value cannot be determined.

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for *rac*-**11d**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
C(1)	1579(1)	5579(1)	6747(1)	17(1)
C(7)	746(1)	5172(1)	7650(1)	19(1)
O(1)	839(1)	5151(1)	9341(1)	21(1)
O(2)	–33(1)	4868(1)	6721(1)	26(1)
C(2)	1400(1)	6458(1)	5891(1)	16(1)
O(3)	515(1)	6869(1)	6168(1)	20(1)
C(8)	326(1)	7816(1)	5536(1)	23(1)
C(3)	2074(1)	6816(1)	4800(1)	18(1)
C(4)	2960(1)	6323(1)	4661(1)	18(1)
C(5)	3182(1)	5514(1)	5693(1)	19(1)

C(6)	2465(1)	5088(1)	6638(1)	18(1)
C(9)	3571(1)	6532(1)	3147(1)	22(1)
C(10)	3240(1)	5879(1)	1489(1)	23(1)
C(11)	2569(1)	4050(1)	7114(1)	22(1)
C(12)	2198(1)	3419(1)	5445(1)	24(1)
C(13)	3351(1)	4845(1)	1991(1)	23(1)
C(14)	2616(1)	4417(1)	2885(1)	22(1)
C(15)	2823(1)	3616(1)	3957(1)	23(1)
C(16)	3732(1)	3151(1)	3891(1)	27(1)
C(17)	4428(1)	3508(1)	2843(2)	29(1)
C(18)	4255(1)	4367(1)	1955(1)	28(1)

Table 3. Bond lengths [Å] and angles [°] for *rac*-**11d**.

C(1)–C(6)	1.3930(12)
C(1)–C(2)	1.4037(12)
C(1)–C(7)	1.4962(11)
C(7)–O(1)	1.2646(11)
C(7)–O(2)	1.2650(12)
O(1)–H(1O1)	0.8400
O(2)–H(1O2)	0.8400
C(2)–O(3)	1.3664(10)
C(2)–C(3)	1.3915(12)
O(3)–C(8)	1.4300(10)
C(8)–H(8A)	0.9800
C(8)–H(8B)	0.9800
C(8)–H(8C)	0.9800
C(3)–C(4)	1.3975(12)
C(3)–H(3)	0.9500
C(4)–C(5)	1.3911(13)
C(4)–C(9)	1.5141(11)
C(5)–C(6)	1.4030(12)
C(5)–H(5)	0.9500
C(6)–C(11)	1.5085(12)
C(9)–C(10)	1.5725(14)
C(9)–H(9A)	0.9900
C(9)–H(9B)	0.9900
C(10)–C(13)	1.5077(14)
C(10)–H(10A)	0.9900
C(10)–H(10B)	0.9900
C(11)–C(12)	1.5712(13)
C(11)–H(11A)	0.9900
C(11)–H(11B)	0.9900
C(12)–C(15)	1.5080(14)
C(12)–H(12A)	0.9900
C(12)–H(12B)	0.9900
C(13)–C(18)	1.3973(13)
C(13)–C(14)	1.4008(14)
C(14)–C(15)	1.3959(14)
C(14)–H(14)	0.9500
C(15)–C(16)	1.3965(13)
C(16)–C(17)	1.3918(16)
C(16)–H(16)	0.9500
C(17)–C(18)	1.3897(16)
C(17)–H(17)	0.9500
C(18)–H(18)	0.9500
C(6)–C(1)–C(2)	120.83(8)

C(6)–C(1)–C(7)	122.25(8)
C(2)–C(1)–C(7)	116.76(8)
O(1)–C(7)–O(2)	121.58(8)
O(1)–C(7)–C(1)	118.52(8)
O(2)–C(7)–C(1)	119.89(8)
C(7)–O(1)–H(1O1)	109.5
C(7)–O(2)–H(1O2)	109.5
O(3)–C(2)–C(3)	125.59(8)
O(3)–C(2)–C(1)	114.13(8)
C(3)–C(2)–C(1)	120.20(8)
C(2)–O(3)–C(8)	117.96(7)
O(3)–C(8)–H(8A)	109.5
O(3)–C(8)–H(8B)	109.5
H(8A)–C(8)–H(8B)	109.5
O(3)–C(8)–H(8C)	109.5
H(8A)–C(8)–H(8C)	109.5
H(8B)–C(8)–H(8C)	109.5
C(2)–C(3)–C(4)	119.28(8)
C(2)–C(3)–H(3)	120.4
C(4)–C(3)–H(3)	120.4
C(5)–C(4)–C(3)	119.63(8)
C(5)–C(4)–C(9)	118.71(8)
C(3)–C(4)–C(9)	120.46(8)
C(4)–C(5)–C(6)	121.26(8)
C(4)–C(5)–H(5)	119.4
C(6)–C(5)–H(5)	119.4
C(1)–C(6)–C(5)	117.79(8)
C(1)–C(6)–C(11)	121.58(8)
C(5)–C(6)–C(11)	119.07(8)
C(4)–C(9)–C(10)	110.80(7)
C(4)–C(9)–H(9A)	109.5
C(10)–C(9)–H(9A)	109.5
C(4)–C(9)–H(9B)	109.5
C(10)–C(9)–H(9B)	109.5
H(9A)–C(9)–H(9B)	108.1
C(13)–C(10)–C(9)	110.93(8)
C(13)–C(10)–H(10A)	109.5
C(9)–C(10)–H(10A)	109.5
C(13)–C(10)–H(10B)	109.5
C(9)–C(10)–H(10B)	109.5
H(10A)–C(10)–H(10B)	108.0
C(6)–C(11)–C(12)	110.33(8)
C(6)–C(11)–H(11A)	109.6
C(12)–C(11)–H(11A)	109.6
C(6)–C(11)–H(11B)	109.6
C(12)–C(11)–H(11B)	109.6
H(11A)–C(11)–H(11B)	108.1
C(15)–C(12)–C(11)	109.70(8)
C(15)–C(12)–H(12A)	109.7
C(11)–C(12)–H(12A)	109.7
C(15)–C(12)–H(12B)	109.7
C(11)–C(12)–H(12B)	109.7
H(12A)–C(12)–H(12B)	108.2
C(18)–C(13)–C(14)	118.14(10)
C(18)–C(13)–C(10)	121.45(9)
C(14)–C(13)–C(10)	118.84(9)
C(15)–C(14)–C(13)	121.50(9)
C(15)–C(14)–H(14)	119.2
C(13)–C(14)–H(14)	119.2
C(14)–C(15)–C(16)	118.34(9)

C(14)–C(15)–C(12)	119.15(9)
C(16)–C(15)–C(12)	120.84(9)
C(17)–C(16)–C(15)	120.38(10)
C(17)–C(16)–H(16)	119.8
C(15)–C(16)–H(16)	119.8
C(18)–C(17)–C(16)	120.16(9)
C(18)–C(17)–H(17)	119.9
C(16)–C(17)–H(17)	119.9
C(17)–C(18)–C(13)	120.49(10)
C(17)–C(18)–H(18)	119.8
C(13)–C(18)–H(18)	119.8

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for ***rac*-11d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	20(1)	18(1)	13(1)	–1(1)	3(1)	–3(1)
C(7)	23(1)	16(1)	18(1)	2(1)	7(1)	1(1)
O(1)	23(1)	26(1)	13(1)	0(1)	5(1)	–4(1)
O(2)	24(1)	39(1)	16(1)	2(1)	4(1)	–12(1)
C(2)	19(1)	17(1)	14(1)	–3(1)	3(1)	–1(1)
O(3)	24(1)	17(1)	21(1)	2(1)	9(1)	2(1)
C(8)	30(1)	18(1)	23(1)	2(1)	5(1)	4(1)
C(3)	23(1)	16(1)	14(1)	0(1)	2(1)	–4(1)
C(4)	19(1)	21(1)	16(1)	–1(1)	3(1)	–6(1)
C(5)	16(1)	24(1)	17(1)	–1(1)	1(1)	–2(1)
C(6)	20(1)	19(1)	14(1)	1(1)	1(1)	–1(1)
C(9)	20(1)	28(1)	21(1)	3(1)	7(1)	–5(1)
C(10)	22(1)	32(1)	17(1)	3(1)	6(1)	1(1)
C(11)	24(1)	21(1)	21(1)	4(1)	3(1)	2(1)
C(12)	25(1)	18(1)	28(1)	2(1)	1(1)	0(1)
C(13)	22(1)	31(1)	15(1)	–3(1)	1(1)	2(1)
C(14)	19(1)	26(1)	19(1)	–3(1)	–1(1)	2(1)
C(15)	23(1)	23(1)	22(1)	–5(1)	–1(1)	0(1)
C(16)	28(1)	24(1)	26(1)	–7(1)	–4(1)	6(1)
C(17)	25(1)	35(1)	28(1)	–10(1)	–1(1)	10(1)
C(18)	23(1)	39(1)	21(1)	–6(1)	4(1)	4(1)

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for ***rac*-11d**.

Atom	x	y	z	U(eq)
H(1O1) [a]	286	5021	9687	31
H(1O2) [a]	34	4915	5630	39
H(8A)	874	8230	6033	35
H(8B)	–302	8043	5915	35
H(8C)	278	7824	4227	35
H(3)	1934	7389	4156	21
H(5)	3831	5246	5758	23
H(9A)	4287	6426	3559	27
H(9B)	3483	7206	2790	27
H(10A)	2535	6012	1033	28
H(10B)	3654	6022	523	28
H(11A)	2171	3905	8103	26

H(11B)	3277	3904	7526	26
H(12A)	2250	2740	5780	28
H(12B)	1489	3562	5036	28
H(14)	1962	4677	2760	26
H(16)	3875	2587	4565	32
H(17)	5023	3163	2734	35
H(18)	4756	4631	1318	33

[a] s.o.f. = 0.5 (s.o.f.: **s**ite **o**ccupation **f**actor)

Table 6. Torsion angles [°] for *rac*-**11d**.

C(6)–C(1)–C(7)–O(1)	75.25(11)
C(2)–C(1)–C(7)–O(1)	–109.27(10)
C(6)–C(1)–C(7)–O(2)	–105.42(11)
C(2)–C(1)–C(7)–O(2)	70.06(11)
C(6)–C(1)–C(2)–O(3)	–177.87(8)
C(7)–C(1)–C(2)–O(3)	6.58(11)
C(6)–C(1)–C(2)–C(3)	5.17(13)
C(7)–C(1)–C(2)–C(3)	–170.38(8)
C(3)–C(2)–O(3)–C(8)	–10.90(12)
C(1)–C(2)–O(3)–C(8)	172.33(7)
O(3)–C(2)–C(3)–C(4)	179.20(8)
C(1)–C(2)–C(3)–C(4)	–4.21(12)
C(2)–C(3)–C(4)–C(5)	–3.77(13)
C(2)–C(3)–C(4)–C(9)	163.54(8)
C(3)–C(4)–C(5)–C(6)	11.09(13)
C(9)–C(4)–C(5)–C(6)	–156.44(8)
C(2)–C(1)–C(6)–C(5)	1.87(12)
C(7)–C(1)–C(6)–C(5)	177.17(8)
C(2)–C(1)–C(6)–C(11)	–163.71(8)
C(7)–C(1)–C(6)–C(11)	11.59(13)
C(4)–C(5)–C(6)–C(1)	–10.02(13)
C(4)–C(5)–C(6)–C(11)	155.94(9)
C(5)–C(4)–C(9)–C(10)	76.90(10)
C(3)–C(4)–C(9)–C(10)	–90.52(10)
C(4)–C(9)–C(10)–C(13)	–58.40(10)
C(1)–C(6)–C(11)–C(12)	86.60(10)
C(5)–C(6)–C(11)–C(12)	–78.80(10)
C(6)–C(11)–C(12)–C(15)	61.04(10)
C(9)–C(10)–C(13)–C(18)	–86.17(10)
C(9)–C(10)–C(13)–C(14)	79.31(10)
C(18)–C(13)–C(14)–C(15)	10.25(14)
C(10)–C(13)–C(14)–C(15)	–155.71(9)
C(13)–C(14)–C(15)–C(16)	–10.55(14)
C(13)–C(14)–C(15)–C(12)	154.87(9)
C(11)–C(12)–C(15)–C(14)	–80.39(10)
C(11)–C(12)–C(15)–C(16)	84.65(11)
C(14)–C(15)–C(16)–C(17)	2.97(14)
C(12)–C(15)–C(16)–C(17)	–162.19(9)
C(15)–C(16)–C(17)–C(18)	4.64(15)
C(16)–C(17)–C(18)–C(13)	–4.94(15)
C(14)–C(13)–C(18)–C(17)	–2.37(14)
C(10)–C(13)–C(18)–C(17)	163.20(9)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for *rac*-**11d** [Å and °].

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O(2)–H(1O2)...O(2)#1	0.84	1.80	2.6305(14)	171.9
O(1)–H(1O1)...O(1)#2	0.84	1.78	2.6139(13)	172.4

Symmetry transformations used to generate equivalent atoms:

#1 –x,–y+1,–z+1 #2 –x,–y+1,–z+2