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Electronic Supplementary Information

Catechol-Derived Propargyl Diol Cyclizations with Malonyl Dichloride: Substituent Effects on the Formation of Macrocyclic Esters and their Hydrochlorinated Adducts

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CONTENTS

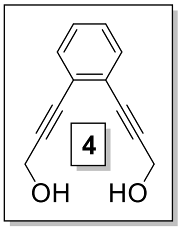
I. Synthetic Methods and Characterization Data

- The following compounds are known and were prepared by applying literature protocols. Known compounds were only characterized by ^{1}H and ^{13}C NMR and their spectroscopic data were checked for consistency with the literature:

4,[S1] **6**,[S2] **10**,[S3] **12**,[S4] **13** (via *Method A*),[S4] **15**,[S5] **20**,[S6] **21**,[S7] **24**,[S7,S8] **25**,[S8] **28**[S1]

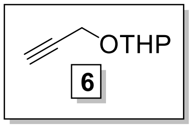
Full characterization data were recorded for all new compounds.

- 3,3'-(1,2-Phenylene)bis(prop-2-yn-1-ol) (**4**)


4

Dibromide **1** or diiodide **2** (4 mmol, 1 equiv) were transferred to a round-bottom flask, along with Pd(PPh$_3$)$_4$ (0.092 g, 0.08 mmol, 0.02 equiv) and CuI (0.023 g, 0.12 mmol, 0.03 equiv). The flask was sealed and set under nitrogen atmosphere, followed by addition of Et$_3$N (60 mL) and propargyl alcohol (0.7 mL, 12 mmol, 3 equiv). The mixture was stirred at r.t. for 3 h and it was subsequently diluted with ethyl acetate and washed twice with water. The organic layer was dried over Na$_2$SO$_4$. After filtration to remove the drying agent, the solution was dried under vacuum. The sample was redissolved in DCM and applied to a silica column for flash chromatography. Elution took place with hexane-ethyl acetate (2:1), to afford diol **4** (0.624 g, 3.35 mmol, 84% from **1**; 0.685 g, 3.68 mmol, 92% from **2**), as a white powder. ^{1}H NMR (CDCl$_3$): δ_H (ppm) 4.52 (s, 4H), 7.23 (dd, 2H, J_1=5.8 Hz, J_2=3.5 Hz), 7.38 (dd, 2H, J_1=5.8 Hz, J_2=3.5 Hz). ^{13}C NMR (CDCl$_3$): δ_C (ppm) 51.3, 84.1, 91.7, 125.3, 128.0, 131.3.

- 2-(Prop-2-yn-1-yloxy)tetrahydro-2*H*-pyran (**6**)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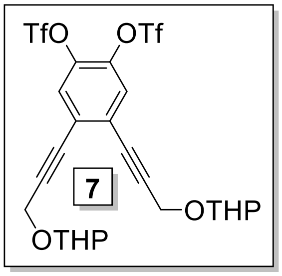
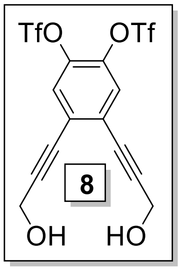
A round-bottom flask containing propargyl alcohol (0.6 mL, 10 mmol, 1 equiv) and *p*-TSA (0.02 g, 0.1 mmol, 0.01 equiv) was set under nitrogen atmosphere. Anhydrous DCM (24 mL) was added, followed by slow addition of 3,4-dihydro-2*H*-pyran (0.90 mL, 10 mmol, 1 equiv), and the resulting mixture was stirred at r.t. for 24 h. After the reaction was quenched with saturated aqueous NaHCO$_3$, extraction took place and the phases were separated. The aqueous phase was back-extracted with fresh DCM and the combined organic layers were dried over MgSO$_4$. After filtration to remove the drying agent, the solvent was removed under vacuum to afford THP-protected propargyl alcohol **6** (1.39 g, 9.9 mmol, 99%), as a yellow oil. ^{1}H NMR (CDCl$_3$): δ_H (ppm) 1.50-1.58 (m, 2H), 1.58-1.68 (m, 2H), 1.69-1.77 (app. tt, 1H, J_1=11.7 Hz, J_2=3.5 Hz), 1.77-1.89 (m, 1H), 2.41 (t, 1H, J=2.4 Hz), 3.53 (m, 1H), 3.83 (ddd, 1H, J_1=10.3 Hz, J_2=8.6 Hz, J_3=3.0 Hz), 4.23 (dd, 1H, J_1= 15.8 Hz, J_2=2.4 Hz), 4.29 (dd, 1H, J_1= 15.8 Hz, J_2=2.4 Hz), 4.82 (t, 1H, J=3.5 Hz). ^{13}C NMR (CDCl$_3$): δ_C (ppm) 19.0, 25.3, 30.2, 54.0, 62.0, 74.0, 79.7, 96.8.

- 4,5-Bis(3-((tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-yn-1-yl)-1,2-phenylene bis(trifluoromethanesulfonate) (**7**)



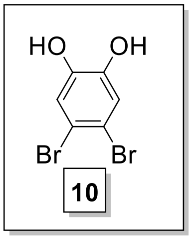
A round-bottom flask containing diiodide **5** (0.41 g, 0.65 mmol, 1 equiv) was set under nitrogen atmosphere and anhydrous THF (2 mL) was added. Subsequently, THP-protected propargyl alcohol **6** (0.46 g, 3.3 mmol, 5 equiv) and triethylamine (0.27 mL, 2.0 mmol, 3 equiv) were added to the solution, followed by $Pd(PPh_3)_2Cl_2$ (0.028 g, 0.04 mmol, 0.06 equiv) and CuI (0.015 g, 0.08 mmol, 0.12 equiv), and the reaction mixture was refluxed at 60 °C for 2 h. It was then allowed to cool down to r.t. and diluted with ethyl acetate. The mixture was transferred to a separatory funnel and washed two times with water. The organic layer was dried over Na_2SO_4 and, after removal of the drying agent, the solvent was evaporated under vacuum. The crude residue was redissolved in DCM and applied on a silica column for flash chromatography. Elution took place using hexane-ethyl acetate (4:1), leading to the isolation of compound **7** (0.29 g, 0.48 mmol, 74%), as a pale-yellow oil. The product appeared to be unstable upon storage and was thus directly subjected to the next reaction (THP deprotection), after performing ^1H and ^{13}C NMR, to verify its formation and purity. ^1H NMR ($CDCl_3$): δ_H (ppm) 1.59-1.63 (m, 4H), 1.63-1.67 (m, 4H), 1.73-1.89 (m, 4H), 3.57 (m, 2H), 3.87 (m, 2H), 4.51 (d, 2H, J=16.2 Hz), 4.55 (d, 2H, J=16.2 Hz), 4.91 (t, 2H, J=3.4 Hz), 7.51 (s, 2H). ^{13}C NMR ($CDCl_3$): δ_C (ppm) 18.9, 25.3, 30.2, 54.4, 62.0, 81.4, 93.6, 96.9, 118.5 (CF_3, q, J=320.0 Hz), 126.7, 127.3, 139.4. ^{19}F NMR ($CDCl_3$): δ_F (ppm) -72.9.

- 4,5-Bis(3-hydroxyprop-1-yn-1-yl)-1,2-phenylene bis(trifluoromethanesulfonate) (**8**)



A three-necked round-bottom flask was equipped with a gas inlet, fitted with a vertical condenser and set under nitrogen atmosphere. Compound **7** (0.37 g, 0.57 mmol, 1 equiv) was treated with pyridinium *p*-toluenesulfonate (0.32 g, 1.3 mmol, 2.3 equiv) in 15 mL of a 2:1 mixture of anhydrous solvents DCM-MeOH. The mixture was stirred at 50 °C for 3.5 h. Upon completion of the reaction, the mixture was allowed to cool down to r.t., diluted with DCM (50 mL) and transferred to a separatory funnel, where it was washed with a saturated $NaHCO_3$ solution and with water. The combined aqueous layer was back-extracted with DCM (2 x 50 mL). The combined organic layers were dried over Na_2SO_4 and, upon removal of the drying agent, the solvent was evaporated under vacuum. The crude product was redissolved in EtOAc, applied on a silica column for flash chromatography and eluted with EtOAc to give diol **8** (0.25 g, 0.5 mmol, 88%), as a orange-yellow wax. Recrystallization of the product was achieved via slow diffusion of pentane in a concentrated solution of compound **8** in DCM, which afforded **8** in the form of orange-yellow crystals. ^1H NMR ($CDCl_3$): δ_H (ppm) 4.55 (s, 4H), 7.48 (s, 2H). ^{13}C NMR ($CDCl_3$): δ_C (ppm) 51.5, 81.7, 95.8, 118.5 (CF_3, q, J=321.0 Hz), 125.9, 127.3, 139.5. FT-IR: wavenumber (cm^{-1}) 3267 (br), 2913 (w), 2856 (w), 2227 (w), 1494 (m), 1434 (s), 1394 (w), 1361 (w), 1315 (w), 1247 (m), 1223 (s), 1209 (s), 1179 (m), 1130 (m), 1078 (m), 1039 (m), 972 (w), 912 (m), 865 (m), 801 (m), 763 (m), 748 (w). MS (MALDI-TOF), m/z: calcd for $C_{14}H_8F_6O_8S_2$: 481.96; found: 504.99 [M+Na$^+$], 520.95 [M+K$^+$] (HCCA matrix). m.p. 109-111 ºC. ^{19}F NMR ($CDCl_3$): δ_F (ppm) -72.8.

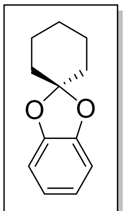
- 4,5-Dibromobenzene-1,2-diol (**10**)



10

Catechol **9** (9.91 g, 90 mmol, 1 equiv) was suspended in dry CCl_4 (100 mL) under air and the mixture was cooled down to 0 ºC. Molecular bromine (9.2 mL, 180 mmol, 2 equiv), dissolved in CCl_4 (25 mL), was added dropwise from a dropping funnel under stirring. Escaping HBr gas was sequestered by using a trap containing aqueous NaOH solution. After the addition of Br_2, the resulting mixture was further stirred at r.t. for 16 h. The solid formed in the reaction was subsequently filtered, washed with cold CCl_4 and dried under vacuum to afford compound **10** (21.97 g, 82 mmol, 91%), as a pale grey powder. ^{1}H NMR (DMSO-d$_6$): δ_H (ppm) 7.59 (s, 2H). ^{13}C NMR (DMSO-d$_6$): δ_C (ppm) 122.9, 130.1, 156.4.

- Spiro[benzo[*d*][1,3]dioxole-2,1'-cyclohexane] (**12**)

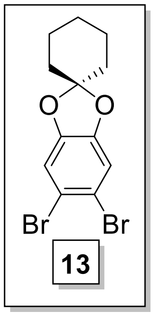


12

A round-bottom flask was loaded with catechol **9** (4.95 g, 45 mmol, 1 equiv) and *p*-TSA (0.428 g, 2.25 mmol, 0.05 equiv), fitted with a Dean-Stark apparatus and vertical condenser, and set under nitrogen atmosphere. Dry toluene (140 mL) was syringed in, followed by cyclohexanone (4.7 mL, 45 mmol, 1 equiv). The reaction mixture was heated under reflux for 24 h, with azeotropic removal of the produced water. After cooling to r.t., the solution was washed, first with a saturated solution of $NaHCO_3$ and then with water, three times. The organic layer was dried over Na_2SO_4 and, after removal of the drying agent, the solvent was evaporated under vacuum. The crude residue was redissolved in DCM and applied to a silica column for flash chromatography. Elution took place using a DCM-ethyl acetate (95:5) solvent system. This led to isolation of compound **12** (7.42 g, 39 mmol, 87%), as a pale yellow powder. ^{1}H NMR ($CDCl_3$): δ_H (ppm) 1.50 (m, 2H), 1.74 (m, 4H), 1.91 (m, 4H), 6.72-6.78 (m, 4H, 2 signals overlapping). ^{13}C NMR ($CDCl_3$): δ_C (ppm) 23.2, 24.6, 35.2, 108.4, 118.2, 120.9, 147.3.

- 5,6-Dibromospiro[benzo[*d*][1,3]dioxole-2,1'-cyclohexane] (**13**)

<u>Method A:</u> A round-bottom flask was loaded with catechol **10** (5.09 g, 19 mmol, 1 equiv) and *p*-TSA (0.181 g, 0.95 mmol, 0.05 equiv), fitted with a Dean-Stark apparatus and vertical condenser, and set under nitrogen atmosphere. Dry toluene (55 mL) was syringed in, followed by cyclohexanone (2.0 mL, 19 mmol, 1 equiv). The reaction mixture was heated under reflux for 24 h, with azeotropic removal of the produced water. After cooling to r.t., the solution was washed, first with a saturated solution of $NaHCO_3$ and then with water, three times. The organic layer was

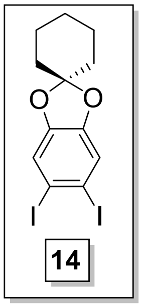


13

dried over Na_2SO_4 and, after removal of the drying agent, the solvent was evaporated under vacuum. The crude residue was redissolved in DCM and applied to a silica column for flash chromatography. Elution took place using a DCM-ethyl acetate (95:5) solvent system. This led to isolation of compound **13** (4.98 g, 14.3 mmol, 75%), as a pale yellow powder. Recrystallization of the product from EtOH-water (10:1) afforded **13** in the form of pale yellow crystals. ^1H NMR ($CDCl_3$): δ_H (ppm) 1.49 (m, 2H), 1.71 (m, 4H), 1.88 (m, 4H), 6.97 (s, 2H). ^{13}C NMR ($CDCl_3$): δ_C (ppm) 23.0, 24.4, 35.1, 113.0, 114.4, 121.1, 147.9.

<u>Method B:</u> In a two-neck round-bottom flask equipped with a gas inlet, cyclohexylidene-protected catechol (0.50 g, 2.6 mmol, 1 equiv) (**12**) was dissolved in DMF (5 mL) at r.t., under a nitrogen atmosphere. *N*-bromosuccinimide (0.98 g, 5.5 mmol, 2.1 equiv) was then added to the reaction mixture and the resulting solution was stirred in darkness for 48 h. Subsequently, the reaction was quenched by addition of water to the flask. The content was then transferred to a separatory funnel and extracted three times with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and, after removal of the drying agent, the solvent was evaporated under vacuum. The solid residue was recrystallized from EtOH-water (10:1) to give compound **13** (0.8 g, 2.25 mmol, 87%), as pale-yellow crystals. The spectroscopic data of compound **13** were identical to those obtained with *Method A*.[S4]

- 5,6-Diiodospiro[benzo[*d*][1,3]dioxole-2,1'-cyclohexane] (**14**)



14

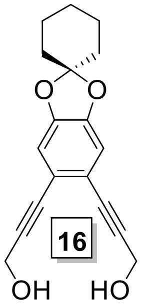
<u>Method C:</u> In a round-bottom flask equipped with a gas inlet, cyclohexylidene-protected catechol (**12**) (1.92 g, 0.01 mmol, 1 equiv) was dissolved in acetonitrile (51 mL), followed by addition of *N*-iodosuccinimide (6.81 g, 0.03 mmol, 3 equiv) and trifluoroacetic acid (1.5 mL), in this order, under a nitrogen atmosphere. The resulting solution was stirred at r.t. overnight. Subsequently, the solvent was removed under high vacuum and the crude mixture was re-suspended in diethyl ether and applied to a silica column for flash chromatography. Elution took place with diethyl ether to afford compound **14** (4.19 g, 0.95 mmol, 94%), as a white powder. Recrystallization of the product was achieved via slow diffusion of pentane in a concentrated solution of compound **14** in DCM, which afforded **14** in the form of white crystals. ^1H NMR ($CDCl_3$): δ_H (ppm) 1.48 (app. quint., 2H, J=5.8 Hz), 1.70 (app. quint., 4H, J=6.0 Hz), 1.87 (app. t, 4H, J=6.2 Hz), 7.22 (s, 2H). ^{13}C NMR ($CDCl_3$): δ_C (ppm) 23.0, 24.4, 35.1, 95.2, 118.6, 120.9, 148.8. FT-IR: wavenumber (cm^{-1}) 2941 (m), 2923 (w), 2849 (w), 1476 (s), 1364 (m), 1345 (m), 1320 (w), 1276 (m), 1255 (w), 1226 (s), 1187 (m), 1134 (m), 1060 (s), 971 (m), 908 (w), 899 (w), 886 (m), 869 (m), 852 (m), 836 (m), 816 (m), 767 (m), 738 (w), 705 (w). MS (MALDI-TOF), m/z: calcd for $C_{12}H_{12}I_2O_2$: 441.89; found: 379.11 [M-cyclohexylidene+H_2O+$2H^+$] (HCCA matrix). m.p. 156-158 ºC.

- *Tert*-butyldimethyl(prop-2-yn-1-yloxy)silane (**15**)

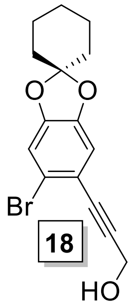
15

A two-neck round-bottom flask containing propargyl alcohol **3** (5.3 mL, 89 mmol, 1 equiv) was set under nitrogen atmosphere and anhydrous DCM (30 mL) was added. The solution was cooled to 0 ºC and the flask was charged with TBDMSCl (16.2 mL, 93.5 mmol, 1.05 equiv), followed by imidazole (12.12 g, 178 mmol, 2 equiv), dissolved in DCM (5 mL). The resulting mixture was stirred at 0 ºC for 1 h and it was subsequently quenched with water. After extraction, the organic layer was collected, dried over Na_2SO_4 and, after removal of the drying agent, the solvent was evaporated under vacuum. The crude residue was redissolved in DCM and applied to a silica column for flash chromatography. Elution took place using hexane-ethyl acetate (10:1), leading to the isolation of TBDMS-protected propargyl alcohol **15** (15.0 g, 88 mmol, 99%), as a colorless oil. ^{1}H NMR ($CDCl_3$): δ_H (ppm) 0.13 (s, 6H), 0.91 (s, 9H), 2.39 (t, 1H, J=2.4 Hz), 4.31 (d, 2H, J=2.4 Hz). ^{13}C NMR ($CDCl_3$): δ_C (ppm) -5.2, 18.3, 25.8, 51.5, 72.8, 82.4.

- 3,3'-(Spiro[benzo[*d*][1,3]dioxole-2,1'-cyclohexane]-5,6-diyl)bis(prop-2-yn-1-ol) (**16**) and 3-(5-Bromospiro[benzo[*d*][1,3]dioxole-2,1'-cyclohexan]-6-yl)prop-2-yn-1-ol (**18**)



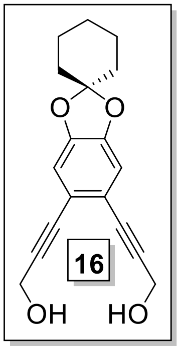
16



18

In a three-neck round-bottom flask fitted with a vertical condenser and equipped with a gas inlet, dibromide **13** (0.50 g, 1.4 mmol, 1 equiv) was dissolved in 15 mL of a 1:1 mixture of DMF-^{n}BuNH$_2$, under nitrogen atmosphere. The flask was then charged with propargyl alcohol **3** (0.25 mL, 4.3 mmol, 3 equiv), followed by $Pd(PPh_3)_4$ (0.033 g, 0.03 mmol, 0.02 equiv) and CuI (0.008 g, 0.04 mmol, 0.03 equiv), and the mixture was refluxed overnight. After cooling down to r.t., the mixture was diluted with ethyl acetate and washed twice with water. The organic layer was dried over Na_2SO_4. Upon filtration, the solution was concentrated under vacuum. The sample was redissolved in DCM and applied to a silica column for flash chromatography. Elution took place with hexane-ethyl acetate (2:1), to afford compound **16** (0.082 g, 0.27 mmol, 38%), as a white powder, and compound **18** (0.044 g, 0.14 mmol, 19%), as an orange oil. Recrystallization of compound **16** was achieved via slow diffusion of pentane in a concentrated solution of the compound in DCM, which afforded **16** in the form of white crystals. Compound **18**: ^{1}H NMR ($CDCl_3$): δ_H (ppm) 1.47 (app. quint., 2H, J=4.3 Hz), 1.70 (app. quint., 4H, J=5.0 Hz), 1.87 (app. t, 4H, J=5.7 Hz), 3.91 (s, 2H), 4.50 (s, 4H), 6.72 (s, 2H). ^{13}C NMR ($CDCl_3$): δ_C (ppm) 23.0, 24.3, 35.1, 51.4, 84.4, 89.8, 110.9, 118.9, 120.3, 147.6. FT-IR: wavenumber (cm^{-1}) 3548 (w), 3252 (br), 2942 (m), 2853 (m), 2232 (w), 1610 (w), 1596 (w), 1493 (s), 1448 (m), 1362 (m), 1345 (m), 1286 (m), 1260 (m), 1236 (m), 1196 (s), 1131 (m), 1061 (s), 1006 (s), 975 (s), 951 (m), 908 (m), 866 (s), 846 (s), 822 (m), 768 (m). MS (MALDI-TOF), m/z: calcd for $C_{18}H_{18}O_4$: 298.12; found: 298.14 [M$^+$], 321.13 [M+Na$^+$] (HCCA matrix). m.p. 131-133 ºC. Compound **18**: ^{1}H NMR ($CDCl_3$): δ_H (ppm) 1.49 (app. quint., 2H, J=5.7 Hz), 1.71 (app. quint., 4H, J=5.9 Hz), 1.88 (app. t, 4H, J=6.1 Hz), 4.51 (s, 2H), 6.81 (s, 1H), 6.92 (s, 1H). ^{13}C NMR ($CDCl_3$): δ_C (ppm) 23.0, 24.4, 35.1, 51.7, 84.6, 89.8, 112.3, 112.4, 116.4, 116.9, 120.8, 146.9, 148.8. FT-IR: wavenumber (cm^{-1}) 3331 (br), 2936 (m), 2863 (w), 2223 (w), 1702 (w), 1478 (s), 1449 (m), 1406 (w), 1366 (m), 1339 (m), 1280 (m), 1244 (m), 1224 (m), 1196 (m), 1177 (m), 1137 (m), 1061 (m), 1031 (m), 1001 (m), 971 (m), 909 (m), 896 (m), 847 (m), 822 (w), 770 (w). MS (MALDI-TOF), m/z: calcd for $C_{15}H_{15}BrO_3$: 322.02; found: 339.1 [$M+H_2O-H^+$] (HCCA matrix).

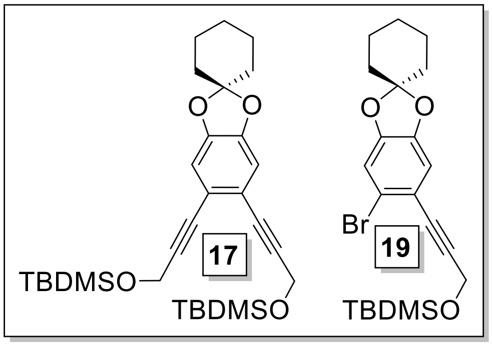
- 3,3'-(Spiro[benzo[*d*][1,3]dioxole-2,1'-cyclohexane]-5,6-diyl)bis(prop-2-yn-1-ol) (**16**)



16

In a three-neck round-bottom flask fitted with a vertical condenser and equipped with a gas inlet, diiodide **14** (0.50 g, 1.1 mmol, 1 equiv) was suspended in ^{n}BuNH$_2$ (16 mL), under nitrogen atmosphere. Propargyl alcohol **3** (0.20 mL, 3.4 mmol, 3 equiv), $Pd(PPh_3)_4$ (0.030 g, 0.022 mmol, 0.02 equiv) and CuI (0.008 g, 0.04 mmol, 0.04 equiv) were added to the flask, and the mixture was allowed to stir at r.t. overnight. Subsequently, ethyl acetate was added and the resulting solution was washed twice with water. The organic layer was dried over Na_2SO_4 and, after removal of the drying agent, the solvent was evaporated under vacuum. The crude residue was redissolved in DCM and applied to a silica column for flash chromatography. Elution took place using ethyl acetate-hexane (2:1) to afford compound **16 (**0.29 g, 0.9 mmol, 84%), as a white powder. Recrystallization of the product was achieved via slow diffusion of pentane in a concentrated solution of compound **16** in DCM, which afforded **16** in the form of white crystals. Spectroscopic and other characterization data of compound **16** produced from this reaction were identical to those obtained in the previous reaction for compound **16**.

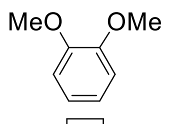
- 5,6-Bis(3-((*tert*-butyldimethylsilyl)oxy)prop-1-yn-1-yl)spiro[benzo[*d*][1,3]dioxole-2,1'-cyclohexane] (**17**) and ((3-(5-Bromospiro[benzo[*d*][1,3]dioxole-2,1'-cyclohexan]-6-yl)prop-2-yn-1-yl)oxy)(*tert*-butyl)dimethylsilane (**19**)



17 **19**

In a three-neck round-bottom flask fitted with a vertical condenser and equipped with a gas inlet, dibromide **13** (0.50 g, 1.4 mmol, 1 equiv) was dissolved in 15 mL of a 1:1 mixture of DMF-^{n}BuNH$_2$, under nitrogen atmosphere. The flask was then charged with TBDMS-protected propargyl alcohol **15** (0.007 g, 4.3 mmol, 3 equiv), followed by $Pd(PPh_3)_4$ (0.033 g, 0.03 mmol, 0.02 equiv) and CuI (0.008 g, 0.04 mmol, 0.03 equiv), and the mixture was refluxed overnight. After cooling down to r.t., the mixture was diluted with ethyl acetate and washed twice with water. The organic layer was dried over Na_2SO_4. Upon filtration, the solution was concentrated under vacuum. The sample was redissolved in DCM and applied to a silica column for flash chromatography. Elution took place with hexane-DCM (1:1), to afford compound **17** (0.070 g, 0.14 mmol, 19%), as a yellow wax, and compound **19** (0.240 g, 0.55 mmol, 38%), as a pale yellow oil. Compound **17**: ^{1}H NMR (CDCl$_3$): δ_H (ppm) 0.16 (s, 12H), 0.93 (s, 18H), 1.49 (app. quint., 2H, J=5.7 Hz), 1.71 (app. quint., 4H, J=6.0 Hz), 1.88 (app. t, 4H, J=6.3 Hz), 4.54 (s, 4H), 6.76 (s, 2H). ^{13}C NMR (CDCl$_3$): δ_C (ppm) -5.0, 18.3, 23.1, 24.4, 25.9, 35.1, 52.4, 83.6, 89.8, 111.6, 118.9, 120.2, 147.5. FT-IR: wavenumber (cm^{-1}) 2951 (w), 2928 (m), 2885 (w), 2856 (m), 1471 (m), 1461 (w), 1361 (w), 1252 (m), 1209 (w), 1134 (w), 1072 (s), 1047 (m), 1019 (w), 1004 (m), 938 (w), 899 (w), 830 (s), 813 (m), 771 (s), 718 (w). MS (MALDI-TOF), m/z: calcd for $C_{30}H_{46}O_4Si_2$: 526.29; found: 462.07 [M-cyclohexylidene+NH_4^+] (HCCA matrix). m.p. 59-61 ºC. Compound **19**: ^{1}H NMR (CDCl$_3$): δ_H (ppm) 0.17 (s, 6H), 0.93 (s, 9H), 1.48 (app. quint., 2H, J=5.7 Hz), 1.70 (app. quint., 4H, J=6.0 Hz), 1.87 (app. t, 4H, J=6.3 Hz), 4.55 (s, 2H), 6.80 (s, 1H), 6.90 (s, 1H). ^{13}C NMR (CDCl$_3$): δ_C (ppm) -5.0, 18.3, 23.0, 24.3, 25.8, 35.1, 52.2, 83.6, 90.4, 112.3, 112.3, 116.7, 116.8, 120.6, 146.8, 148.5. FT-IR: wavenumber (cm^{-1}) 2946 (m), 2855 (w), 2235 (w), 1759 (w), 1732 (m), 1612 (w), 1481 (s), 1449 (m), 1432 (w), 1408 (w), 1389 (w), 1368 (m), 1339 (w), 1296 (w), 1282 (m), 1252 (s), 1223 (m), 1197 (m), 1177 (w), 1137 (m), 1081 (m), 1057 (m), 1008 (m), 996 (w), 971 (m), 928 (w), 909 (w), 890 (m), 869 (w), 834 (s), 777 (m). MS (MALDI-TOF), m/z: calcd for $C_{21}H_{29}BrO_3Si$: 436.11; found: 477.16 [M+K$^+$+2H$^+$] (HCCA matrix).

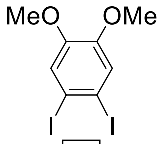
- 1,2-Dimethoxybenzene (**20**)



20

A round-bottom flask was loaded with catechol **9** (3.97 g, 36 mmol, 1 equiv) and K_2CO_3 (12.44 g, 90 mmol, 2.5 equiv), fitted with a vertical condenser and set under nitrogen atmosphere. Dry acetone (175 mL) was syringed in, and the mixture was stirred at r.t. for 10 min. Subsequently, iodomethane (6.4 mL, 72 mmol, 2 equiv) was added, and the resulting mixture was stirred for 1.5 h at r.t., then heated overnight at 60 ºC. The mixture was subsequently cooled down to r.t. and filtered under vacuum to remove K_2CO_3. The filtrate was dried exhaustively under reduced pressure to afford compound **20** (4.89 g, 35.4 mmol, 98%), as a pale yellow oil. This compound was directly employed in the next reaction, after performing ^{1}H and ^{13}C NMR, that verified its formation and purity. ^{1}H NMR (CDCl$_3$): δ_H (ppm) 3.89 (s, 6H), 6.91 (m, 4H, 2 signals overlapping). ^{13}C NMR (CDCl$_3$): δ_C (ppm) 55.8, 111.3, 120.8, 149.0.

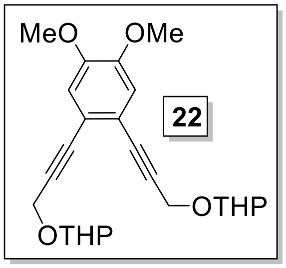
- 1,2-Diiodo-4,5-dimethoxybenzene (**21**)



21

In a three-neck round-bottom flask, fitted with an air condenser and equipped with a gas inlet, orthoperiodic acid (1.64 g, 7.2 mmol, 0.4 equiv) was dissolved in dry methanol (10 mL) under a nitrogen atmosphere. While the solution was being stirred at r.t., molecular iodine (3.66 g, 14.4 mmol, 0.8 equiv) was added. The resulting mixture was stirred vigorously for 10 more minutes after the addition of I_2. Subsequently, compound **20** (2.45 g, 18 mmol, 1 equiv) was added in a single portion and the reaction mixture was heated at 70 °C for 5 h, resulting in the formation of a white solid. At this point, the hot solution was directly poured into a dilute aqueous solution of $Na_2S_2O_5$ and the mixture was allowed to cool down to r.t. The solid residue was collected by filtration on a sintered funnel and washed quickly with two 10 mL portions of cold methanol. Drying of the solid under vacuum furnished compound **21** (6.04 g, 15.5 mmol, 86%), as a white powder. This compound was directly employed in the next reaction, after performing ^{1}H and ^{13}C NMR, that verified its formation and purity. ^{1}H NMR ($CDCl_3$): δ_H (ppm) 3.84 (s, 6H), 7.24 (s, 2H). ^{13}C NMR ($CDCl_3$): δ_C (ppm) 56.1, 96.0, 121.6, 149.6.

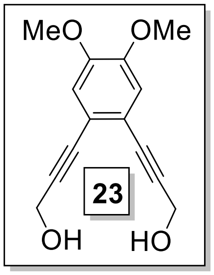
- 2,2'-(((4,5-Dimethoxy-1,2-phenylene)bis(prop-2-yne-3,1-diyl))bis(oxy))bis(tetrahydro-2*H*-pyran) (**22**)



22

In a round-bottom flask, Et_3N (8 mL) was added to a mixture of diiodide **21** (1.00 g, 2.6 mmol, 1 equiv) and THP-protected propargyl alcohol **6** (0.80 g, 5.7 mmol, 2.2 equiv) in THF (16 mL) at r.t., under a nitrogen atmosphere. $Pd(PPh_3)_4$ (0.30 g, 0.26 mmol, 0.1 equiv) was then added, followed by CuI (0.10 g, 0.52 mmol, 0.2 equiv) and the reaction mixture was stirred at 60 ºC for 2 h. The resulting mixture was allowed to cool down to r.t., diluted with ethyl acetate and washed twice with water. The organic layer was dried over Na_2SO_4, filtered and the solvent removed under vacuum. The crude sample was redissolved in DCM, applied to a silica column for flash chromatography and eluted with DCM-EtOAc (95:5), to afford compound **22** (0.480 g, 1.2 mmol, 45%), as a white wax. The product appeared to be unstable upon storage and was thus directly subjected to the next reaction (THP deprotection), after performing ^{1}H NMR, to verify its formation and purity. ^{1}H NMR ($CDCl_3$): δ_H (ppm) 1.49-1.69 (m, 8H), 1.71-1.79 (m, 2H), 1.79-1.89 (m, 2H), 3.55 (m, 2H), 3.85 (s, 6H), 3.87 (m, 2H), 4.48 (d, 2H, J=15.8 Hz), 4.54 (d, 2H, J=15.8 Hz), 4.94 (t, 2H, J=3.4 Hz), 6.90 (s, 2H).

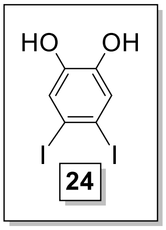
- 3,3'-(4,5-Dimethoxy-1,2-phenylene)bis(prop-2-yn-1-ol) (**23**)



23

A three-neck round-bottom flask equipped with a gas inlet and a vertical condenser, set under nitrogen atmosphere, was loaded with 0.40 g of compound **22** (1.0 mmol, 1 equiv) and 15 mL of a 2:1 mixture of anhydrous solvents DCM-EtOH. Pyridinium *p*-toluenesulfonate (0.570 g, 2.3 mmol, 2.3 equiv) was then added and the reaction mixture was stirred at 55 ºC overnight. After the completion of the reaction, the mixture was allowed to cool down to r.t. and was diluted with ethyl acetate and washed with a saturated solution of $NaHCO_3$ and then with water. The organic phase was dried over Na_2SO_4. After filtration and solvent evaporation under vacuum, the crude sample was redissolved in DCM and applied to a silica column for flash chromatography. Elution took place with EtOAc-hexane (8.5:1.5) and afforded diol **23** (0.210 g, 0.8 mmol, 81%), as a white powder. ^{1}H NMR (CDCl$_3$): δ_H (ppm) 3.87 (s, 6H), 4.54 (s, 4H), 6.89 (s, 2H). ^{13}C NMR (CDCl$_3$): δ_C (ppm) 51.7, 56.0, 84.5, 90.1, 113.7, 118.2, 149.1. FT-IR: wavenumber (cm^{-1}) 3295 (br), 3190 (br), 2952 (w), 2932 (w), 2906 (w), 2850 (w), 2827 (w), 2221 (w), 1735 (w), 1601 (w), 1508 (m), 1460 (m), 1445 (m), 1396 (w), 1348 (m), 1267 (m), 1217 (s), 1151 (m), 1018 (s), 968 (m), 890 (w), 860 (m), 850 (m), 791 (w), 704 (w). MS (MALDI-TOF), m/z: calcd for $C_{14}H_{14}O_4$: 246.09; found: 269.11 [M+Na$^+$] (HCCA matrix). m.p. 169-171 ºC.

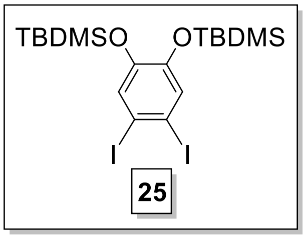
- 4,5-Diiodobenzene-1,2-diol (**24**)



24

A round-bottom flask was loaded with compound **21** (1.17 g, 3 mmol, 1 equiv), fitted with an addition funnel and set under nitrogen atmosphere. Dry DCM (22 mL) was added and the resulting solution was cooled to 0 °C. Subsequently, BBr$_3$ (7.5 mL of a 1.0 M solution in DCM, 7.5 mmol, 2.5 equiv) was added dropwise, over a period of 20 min. The resulting mixture was stirred at 0 °C for 4 h and then quenched with water (15 mL) and extracted. The aqueous layer was extracted two more times with DCM. The combined organic layer was dried over MgSO$_4$ and passed through a SiO$_2$ pad, before evaporating the solvent under vacuum to furnish compound **24** (1.07 g, 2.97 mmol, 99%), as a white solid. This compound was directly employed in the next reaction, after performing ^{1}H and ^{13}C NMR, that verified its formation and purity. ^{1}H NMR (CDCl$_3$): δ_H (ppm) 7.17 (s, 2H). ^{13}C NMR (CDCl$_3$): δ_C (ppm) 95.8, 125.5, 144.4.

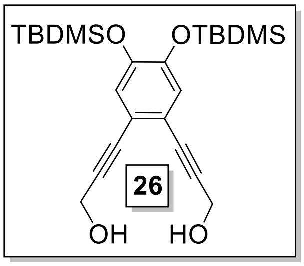
- ((4,5-Diiodo-1,2-phenylene)bis(oxy))bis(*tert*-butyldimethylsilane) (**25**)



25

A round-bottom flask was loaded with compound **24** (1.07 g, 3 mmol, 1 equiv) and set under nitrogen atmosphere. Dry DMF (10 mL) was added to dissolve the solid, followed by dropwise addition of a solution of imidazole (0.817 g, 12 mmol, 4 equiv) and TBDMSCl (0.90 g, 6 mmol, 2 equiv) in dry DMF (5 mL), under stirring. The resulting mixture was allowed to stir for an additional 48 h. After this time, it was poured into water, extracted with ether and the organic layer dried over MgSO$_4$. The drying agent was then removed by filtration and the solvent was evaporated under vacuum. The crude residue was redissolved in hexane and applied to a silica column for flash chromatography. Elution took place using hexane, leading to the isolation of compound **25** (1.22 g, 2.07 mmol, 69%), as a white powder. ^{1}H NMR (CDCl$_3$): δ_H (ppm) 0.19 (s, 12H), 0.96 (s, 18H), 7.27 (s, 2H). ^{13}C NMR (CDCl$_3$): δ_C (ppm) -4.3, 18.4, 25.8, 96.3, 131.2, 147.9.

- 3,3'-(4,5-Bis((*tert*-butyldimethylsilyl)oxy)-1,2-phenylene)bis(prop-2-yn-1-ol) (**26**)

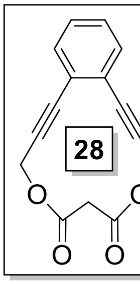


26

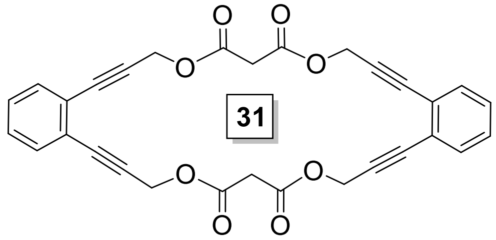
Diiodide **25** (0.44 g, 0.74 mmol, 1 equiv) was transferred to a round-bottom flask, which was set under nitrogen atmosphere. THF (5 mL) was added, followed by propargyl alcohol **3** (0.22 mL, 3.7 mmol, 5 equiv), Et_3N (2.5 mL), $Pd(PPh_3)_4$ (0.086 g, 0.07 mmol, 0.1 equiv) and CuI (0.027 g, 0.14 mmol, 0.2 equiv). The mixture was stirred at 60 °C for 24 h. It was then diluted with ethyl acetate, transferred to a separatory funnel and washed twice with water. The organic phase was dried over Na_2SO_4 and, after filtration, the solvent was evaporated under vacuum. The crude sample was redissolved in DCM and applied to a silica column for flash chromatography. Elution took place with hexane-EtOAc (1:1), to afford compound **26** (0.160 g, 0.35 mmol, 47%), as a yellow wax. ^1H NMR ($CDCl_3$): δ_H (ppm) 0.20 (s, 12H), 0.97 (s, 18H), 4.52 (s, 4H), 6.86 (s, 2H). ^{13}C NMR ($CDCl_3$): δ_C (ppm) -4.1, 18.4, 25.8, 51.8, 84.5, 89.9, 118.7, 123.7, 147.6. FT-IR: wavenumber (cm^{-1}) 3300 (br), 2953 (w), 2929 (m), 2886 (w), 2857 (m), 1591 (w), 1538 (m), 1498 (s), 1472 (m), 1399 (m), 1333 (s), 1253 (m), 1207 (s), 1167 (m), 1025 (m), 981 (w), 929 (m), 896 (m), 829 (s), 779 (s), 707 (w). MS (MALDI-TOF), m/z: calcd for $C_{24}H_{38}O_4Si_2$: 446.23; found: 469.23 [$M+Na^+$] (HCCA matrix). m.p. 49-51 °C.

- *Cyclo*-monomalonic ester (**28**) and *cyclo*-bismalonic ester (**31**) of diol **4**

Synthesis of compound **28** via literature method is known.[S1] Synthesis via an alternative procedure is described herein.



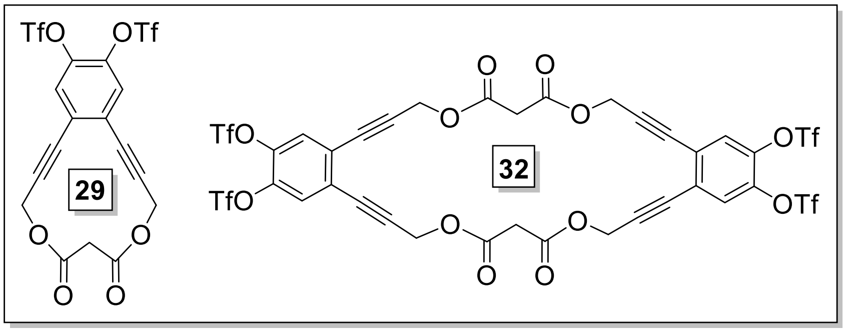
28



31

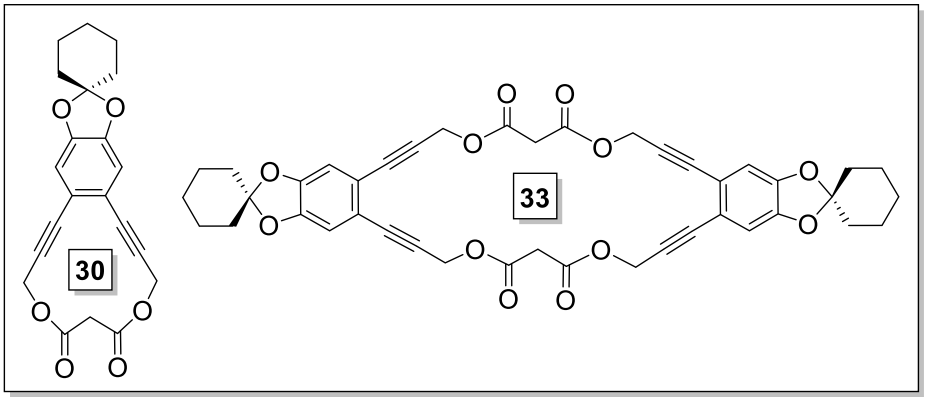
In a three-neck round-bottom flask equipped with a gas inlet and fitted with a dropping funnel, propargyl diol **4** (0.184 g, 1 mmol, 1 equiv) was dissolved in DCM (95 mL), under nitrogen atmosphere. Subsequently, pyridine (0.20 mL, 2 mmol, 2.0 equiv) was added to the solution, followed by dropwise addition of a solution of malonyl dichloride (**27**) (0.05 mL, 2 mmol, 2 equiv) in DCM (50 mL), over a period of 2 h. After stirring overnight at r.t., the mixture was concentrated and passed through a short column of SiO_2, then washed out with DCM, to remove polymers and pyridine salts. The obtained solution was dried under vacuum and the crude mixture obtained was redissolved in DCM and applied to silica gel for column chromatography. Elution took place with DCM-EtOAc (99:1), to afford *cyclo*-monomalonic ester **28** (0.140 g, 0.55 mmol, 55%) and *cyclo*-bismalonic ester **31** (0.015 g, 0.03 mmol, 3%), both in the form of white powder. Separate recrystallizations of these macrolactones via slow diffusion of pentane in a concentrated solution of each compound in DCM, afforded *cyclo*-monomalonic ester **28** and *cyclo*-bismalonic ester **31** in the form of white crystals. Compound **28**: ^{1}H NMR (CDCl$_3$): δ_H (ppm) 3.43 (s, 2H), 5.03 (s, 4H), 7.24 (dd, 2H, J_1=5.6 Hz, J_2=3.4 Hz), 7.34 (dd, 2H, J_1=5.6 Hz, J_2=3.4 Hz). ^{13}C NMR (CDCl$_3$): δ_C (ppm) 41.9, 53.2, 85.6, 87.1, 124.8, 128.1, 130.1, 164.7. Compound **31**: ^{1}H NMR (CDCl$_3$): δ_H (ppm) 3.59 (s, 4H), 5.05 (s, 8H), 7.26 (m, 4H), 7.41 (m, 4H). ^{13}C NMR (CDCl$_3$): δ_C (ppm) 41.0, 53.9, 85.1, 86.5, 125.1, 128.5, 131.9, 165.6. FT-IR: wavenumber (cm^{-1}) 3062 (w), 3005 (w), 2948 (w), 2237 (w), 1725 (s), 1477 (w), 1442 (w), 1424 (w), 1371 (w), 1325 (m), 1277 (m), 1184 (m), 1141 (m), 1045 (w), 1011 (m), 985 (m), 966 (m), 943 (m), 905 (m), 829 (w), 754 (m), 670 (w), 657 (w), 625 (w), 573 (m), 543 (w), 523 (w), 498 (w), 444 (m). MS (MALDI-TOF), m/z: calcd for $C_{30}H_{20}O_8$: 508.12; found: 531.15 [M+Na$^+$], 547.11 [M+K$^+$] (HCCA matrix). m.p. 196-198 ºC.

- C*yclo*-monomalonic ester (**29**) and *cyclo*-bismalonic ester (**32**) of diol **8**



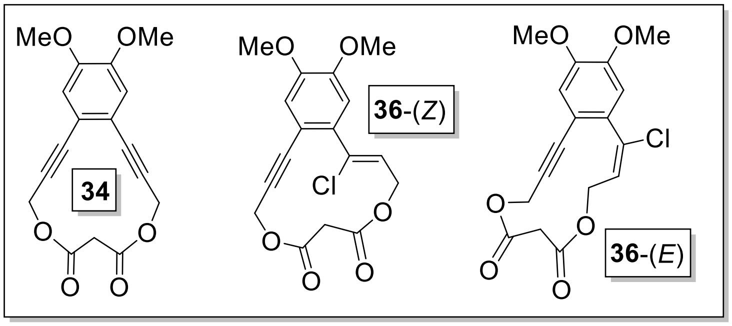
In a three-neck round-bottom flask equipped with a gas inlet and fitted with a dropping funnel, propargyl diol **8** (0.240 g, 0.5 mmol, 1 equiv) was dissolved in DCM (40 mL), under nitrogen atmosphere. Subsequently, pyridine (0.1 mL, 1 mmol, 2 equiv) was added to the solution, followed by dropwise addition of a solution of malonyl dichloride (**27**) (0.10 mL, 1 mmol, 2 equiv) in DCM (20 mL), over a period of 2 h. After stirring overnight at r.t., the mixture was concentrated and passed through a short column of SiO$_2$, then washed out with DCM, to remove polymers and pyridine salts. The obtained solution was dried under vacuum and the crude mixture obtained was redissolved in DCM and applied to silica gel for column chromatography. Elution took place with DCM, to afford *cyclo*-monomalonic ester **29** (0.077 g, 0.14 mmol, 28%) and *cyclo*-bismalonic ester **32** (0.033 g, 0.03 mmol, 6%), both in the form of white powder. Separate recrystallizations of these macrolactones via slow diffusion of pentane in a concentrated solution of each compound in DCM, afforded *cyclo*-monomalonic ester **29** and *cyclo*-bismalonic ester **32** in the form of white crystals. Compound **29**: ^{1}H NMR (CDCl$_3$): δ_H (ppm) 3.48 (s, 2H), 5.06 (s, 4H), 7.45 (s, 2H). ^{13}C NMR (CDCl$_3$): δ_C (ppm) 41.9, 52.8, 82.7, 91.5, 118.5 (CF$_3$, q, J=321.5 Hz), 125.2, 126.8, 139.7, 164.5. ^{19}F NMR (CDCl$_3$): δ_F (ppm) -72.9. FT-IR: wavenumber (cm^{-1}) 3107 (w), 3048 (w), 3014 (w), 2955 (w), 1769 (w), 1741 (s), 1560 (w), 1491 (m), 1425 (s), 1399 (m), 1362 (w), 1283 (w), 1249 (m), 1213 (s), 1180 (m), 1125 (s), 1088 (m), 1022 (w), 1005 (m), 928 (m), 908 (m), 892 (m), 870 (m), 839 (w), 816 (m), 767 (m), 751 (m), 718 (w). MS (MALDI-TOF), m/z: calcd for $C_{17}H_8F_6O_{10}S_2$: 549.95; found: 604.98 [M+Na$^+$+CH$_3$OH] (HCCA matrix). m.p. 234 ºC (decomp.). Compound **32**: ^{1}H NMR (CDCl$_3$): δ_H (ppm) 3.60 (s, 4H), 5.06 (s, 8H), 7.50 (s, 4H). ^{13}C NMR (CDCl$_3$): δ_C (ppm) 40.9, 53.4, 82.1, 90.7, 118.5 (CF$_3$, q, J=321.4 Hz), 126.7, 126.9, 139.8, 165.4. ^{19}F NMR (CDCl$_3$): δ_F (ppm) -72.9. FT-IR: wavenumber (cm^{-1}) 3117 (w), 3054 (w), 2955 (w), 2920 (w), 2850 (w), 1755 (m), 1728 (m), 1567 (w), 1493 (m), 1428 (m), 1378 (w), 1333 (w), 1308 (w), 1279 (w), 1247 (m), 1190 (m), 1134 (m), 1091 (m), 1018 (m), 959 (w), 906 (m), 875 (m), 814 (m), 753 (w), 718 (w). MS (MALDI-TOF), m/z: calcd for $C_{34}H_{16}F_{12}O_{20}S_4$: 1099.90; found: 1122.80 [$M+Na^+$] (HCCA matrix). m.p. 189 ºC (decomp.).

- *Cyclo*-monomalonic ester (**30**) and *cyclo*-bismalonic ester (**33**) of diol **16**



In a three-neck round-bottom flask equipped with a gas inlet and fitted with a dropping funnel, propargyl diol **16** (0.420 g, 1.4 mmol, 1 equiv) was dissolved in DCM (110 mL), under nitrogen atmosphere. Pyridine (0.23 mL, 2.8 mmol, 2.0 equiv) was then added to the solution, followed by dropwise addition of a solution of malonyl dichloride (**27**) (0.28 mL, 2.8 mmol, 2 equiv) in DCM (60 mL), over a period of 2 h. After stirring overnight at r.t., the mixture was concentrated and passed through a short column of SiO_2, then washed out with DCM, to remove polymers and pyridine salts. The obtained solution was dried under vacuum and the crude mixture obtained was redissolved in DCM and applied to silica gel for column chromatography. Elution took place with DCM-EtOAc (98:2), to afford *cyclo*-monomalonic ester **30** (0.168 g, 0.46 mmol, 33%) and *cyclo*-bismalonic ester **33** (0.080 g, 0.11 mmol, 8%), both in the form of white powder. Separate recrystallizations of these macrolactones via slow diffusion of pentane in a concentrated solution of each compound in DCM, afforded *cyclo*-monomalonic ester **30** and *cyclo*-bismalonic ester **33** in the form of white crystals. Compound **30**: ^1H NMR ($CDCl_3$): δ_H (ppm) 1.49 (app. quint., 2H, J=5.5 Hz), 1.71 (app. quint., 4H, J=5.7 Hz), 1.88 (app. t, 4H, J=5.9 Hz), 3.44 (s, 2H), 5.03 (s, 4H), 6.70 (s, 2H).^{13}C NMR ($CDCl_3$): δ_C (ppm) 23.0, 24.4, 35.1, 42.0, 53.4, 85.1, 85.9, 110.0, 118.5, 120.5, 147.7, 164.8. FT-IR: wavenumber (cm^{-1}) 2945 (w), 2852 (w), 2235 (w), 1759 (m), 1731 (s), 1490 (s), 1448 (w), 1432 (w), 1406 (w), 1389 (w), 1369 (m), 1338 (w), 1285 (m), 1256 (s), 1233 (m), 1197 (s), 1137 (m), 1080 (w), 1055 (s), 1008 (m), 969 (m), 928 (m), 910 (w), 890 (s), 869 (m), 850 (m), 846 (m), 824 (w), 771 (w). MS (MALDI-TOF), m/z: calcd for $C_{21}H_{18}O_6$: 366.11; found: 411.25 [$M-H^++2Na^+$] (HCCA matrix). m.p. 166-168 ºC. Compound **33**: ^1H NMR ($CDCl_3$): δ_H (ppm) 1.49 (app. quint., 4H, J=5.5 Hz), 1.71 (app. quint., 8H, J=5.7 Hz), 1.88 (app. t, 8H, J=5.9 Hz), 3.56 (s, 4H), 5.02 (s, 8H), 6.74 (s, 4H). ^{13}C NMR ($CDCl_3$): δ_C (ppm) 23.0, 24.4, 35.1, 41.1, 54.1, 84.8, 85.4, 111.4, 118.9, 120.6, 148.0, 165.7. FT-IR: wavenumber (cm^{-1}) 2942 (w), 2865 (w), 2237 (w), 1763 (m), 1735 (m), 1607 (w), 1538 (w), 1491 (m), 1424 (w), 1368 (m), 1329 (m), 1260 (m), 1197 (m), 1140 (s), 1057 (m), 1022 (w), 998 (m), 975 (m), 902 (w), 850 (m), 771 (w), 736 (w), 705 (w), 609 (w), 581 (w), 553 (w), 526 (w), 487 (w), 447 (w), 410 (m). MS (MALDI-TOF), m/z: calcd for $C_{42}H_{36}O_{12}$: 732.22; found: 771.14 [$M+K^+$] (HCCA matrix). m.p. 256 ºC (decomp.).

- *Cyclo*-monomalonic ester (**34**) and hydrochlorinated *cyclo*-monomalonic esters (**36**-(*Z*) and **36**-(*E*)) of diol **23**

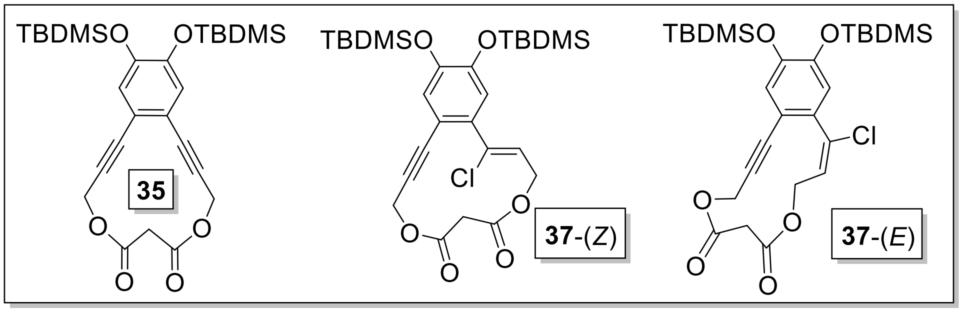


In a three-neck round-bottom flask equipped with a gas inlet and fitted with a dropping funnel, propargyl diol **23** (0.340 g, 1.4 mmol, 1 equiv) was dissolved in DCM (55 mL), under nitrogen atmosphere. Subsequently, pyridine (0.25 mL, 2.8 mmol, 2 equiv) was added to the solution, followed by dropwise addition of a solution of malonyl dichloride (**27**) (0.28 mL, 2.8 mmol, 2 equiv) in DCM (30 mL), over a period of 2 h. After stirring overnight at r.t., the mixture was concentrated and passed through a short column of SiO_2, then washed out with DCM, to remove polymers and pyridine salts. The obtained solution was dried under vacuum and the crude mixture obtained was redissolved in DCM and applied to silica gel for column chromatography. Elution took place with hexane-EtOAc-DCM (4:3:2), to afford *cyclo*-monomalonic ester **34** (0.180 g, 0.57 mmol, 41%), hydrochlorinated *cyclo*-monomalonic ester **36**-(*Z*) (0.105 g, 0.3 mmol, 22%) and hydrochlorinated *cyclo*-monomalonic ester **36**-(*E*) (0.011 g, 0.03 mmol, 2%), in the form of white powders. Separate attempts for recrystallization of the three isolated macrolactones, **34**, **36**-(*Z*) and **36**-(*E*), via slow diffusion of pentane in a concentrated solution of each compound in DCM, yielded white crystals only for *cyclo*-monomalonic ester **34**. Compound **34**: ^{1}H NMR ($CDCl_3$): δ_H (ppm) 3.46 (s, 2H), 3.86 (s, 6H), 5.05 (s, 4H), 6.83 (s, 2H). ^{13}C NMR ($CDCl_3$): δ_C (ppm) 42.1, 53.4, 56.0, 85.6, 85.8, 112.6, 118.0, 149.1, 164.8. FT-IR: wavenumber (cm^{-1}) 2996 (w), 2958 (w), 2922 (w), 2853 (w), 2240 (w), 1732 (m), 1599 (w), 1560 (w), 1525 (w), 1505 (w), 1467 (w), 1438 (w), 1404 (w), 1361 (w), 1293 (w), 1257 (w), 1210 (w), 1186 (w), 1151 (m), 1017 (w), 978 (w), 849 (w), 797 (w). MS (MALDI-TOF), m/z: calcd for $C_{17}H_{14}O_6$: 314.08; found: 379.13 [$M+2Na^++H_2O+H^+$] (HCCA matrix). m.p. 234 ºC (decomp.). Compound **36-(*Z*)**: ^{1}H NMR ($CDCl_3$): δ_H (ppm) 3.42 (s, 2H), 3.88 (s, 3H), 3.90 (s, 3H), 5.02 (s, 2H), 5.05 (d, 2H, J=7.0 Hz), 6.23 (t, 1H, J=7.0 Hz), 6.86 (s, 1H), 6.96 (s, 1H). ^{13}C NMR ($CDCl_3$): δ_C (ppm) 41.9, 53.1, 56.0, 56.1, 61.2, 85.5, 85.8, 111.5, 112.8, 113.5, 124.8, 133.4, 134.1, 149.1, 149.3, 165.2, 165.5. FT-IR: wavenumber (cm^{-1}) 2996 (w), 2958 (w), 2922 (w), 2852 (w), 1755 (m), 1725 (m), 1659 (w), 1599 (w), 1560 (w), 1511 (m), 1454 (w), 1399 (w), 1375 (w), 1351 (m), 1303 (m), 1260 (m), 1224 (w), 1210 (m), 1193 (w), 1150 (m), 1137 (m), 1095 (w), 1022 (m), 1012 (m), 989 (m), 971 (m), 946 (m), 876 (w), 852 (m), 809 (w), 781 (m). MS (MALDI-TOF), m/z: calcd for $C_{17}H_{15}ClO_6$: 350.06; found: 379.14 [$M+Li^++Na^+$] (HCCA matrix). m.p. 168-170 ºC. Compound **36-(*E*)**: ^{1}H NMR ($CDCl_3$): δ_H (ppm) 3.36 (s, 1H, J=5.2 Hz), 3.47 (s, 1H, J=5.2 Hz), 3.89(0) (s, 3H), 3.89(5) (s, 3H), 3.91 (t, 1H, J=11.6 Hz), 4.73 (d, 1H, J=15.3

Hz), 4.88 (dd, 1H, J_1=11.6 Hz, J_2=5.5 Hz), 5.24 (d, 1H, J=15.3 Hz), 6.34 (dd, 1H, J_1=11.6 Hz, J_2=5.5 Hz), 6.75 (s, 1H), 6.94 (s, 1H). ^{13}C NMR ($CDCl_3$): δ_C (ppm) 42.3, 53.5, 56.0, 56.1, 61.9, 84.7, 85.3, 111.6, 113.4, 114.3, 124.3, 132.1, 137.7, 149.3, 149.9, 165.4, 165.9. FT-IR: wavenumber (cm^{-1}) 2994 (w), 2959 (w), 2920 (w), 2852 (w), 1754 (m), 1726 (m), 1659 (w), 1599 (w), 1560 (w), 1511 (m), 1455 (w), 1399 (w), 1375 (w), 1351 (m), 1303 (m), 1260 (m), 1223 (w), 1210 (m), 1193 (w), 1150 (m), 1136 (m), 1095 (w), 1022 (m), 1011 (m), 989 (m), 971 (m), 948 (m), 876 (w), 850 (m), 810 (w), 780 (m). MS (MALDI-TOF), m/z: calcd for $C_{17}H_{15}ClO_6$: 350.06; found: 379.14 [M+Li$^+$+Na$^+$] (HCCA matrix). m.p. N/D.

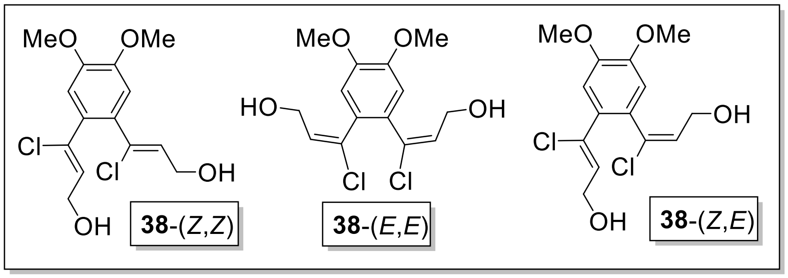
When the same reaction was repeated in the absence of pyridine, keeping everything else unchanged, 0.141 g of *cyclo*-monomalonic ester **34** were isolated (0.45 mmol, 32%).

- *Cyclo*-monomalonic ester (**35**) and hydrochlorinated *cyclo*-monomalonic esters (**37**-(*Z*) and **37**-(*E*)) of diol **26**



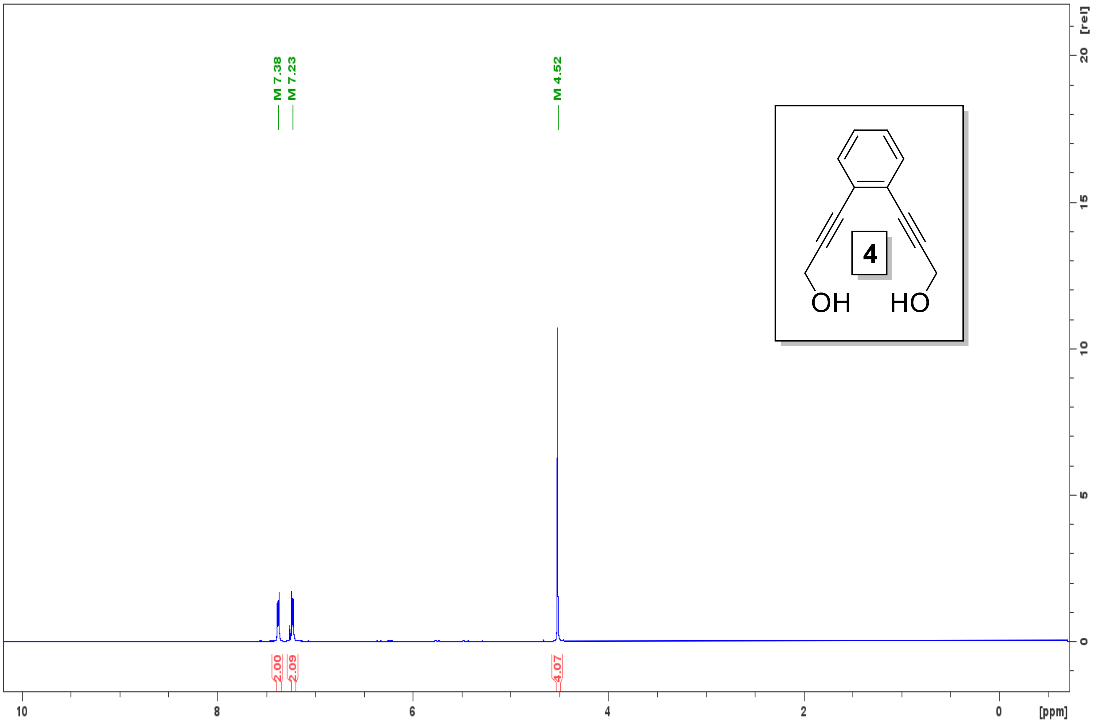
In a three-neck round-bottom flask equipped with a gas inlet and fitted with a dropping funnel, propargyl diol **26** (0.222 g, 0.5 mmol, 1 equiv) was dissolved in DCM (40 mL), under nitrogen atmosphere. Subsequently, pyridine (0.08 mL, 1 mmol, 2 equiv) was added to the solution, followed by dropwise addition of a solution of malonyl dichloride (**27**) (0.10 mL, 1 mmol, 2 equiv) in DCM (20 mL), over a period of 2 h. After stirring overnight at r.t., the mixture was concentrated and passed through a short column of SiO_2, then washed out with DCM, to remove polymers and pyridine salts. The obtained solution was dried under vacuum and the crude mixture obtained was redissolved in DCM and applied to silica gel for column chromatography. Elution took place with hexane-EtOAc (2:1), to afford *cyclo*-monomalonic ester **35** (0.103 g, 0.2 mmol, 40%) and an inseparable 1:5 mixture of hydrochlorinated *cyclo*-monomalonic esters **37**-(*Z*) and **37**-(*E*) (total of 0.077 g, 0.14 mmol, 28% conversion), in the form of white powders. Recrystallization of macrolactone **35** was achieved via slow diffusion of pentane in a concentrated solution of the compound in DCM, which afforded **35** in the form of white crystals. A similar recrystallization effort on the mixture of **37**-(*Z*) and **37**-(*E*) afforded only the major compound **37-**(*E*), in the form of white crystals. Compound **35**: ^{1}H NMR ($CDCl_3$): δ_H (ppm) 0.19 (s, 12H), 0.96 (s, 18H), 3.45 (s, 2H), 5.03 (s, 4H), 6.81 (s, 2H). ^{13}C NMR ($CDCl_3$): δ_C (ppm) -4.2, 18.4, 25.8, 42.1, 53.4, 85.3, 85.6, 118.3, 122.7, 147.6, 164.8. FT-IR: wavenumber (cm^{-1}) 2929 (w), 2856 (w), 2240 (w), 1739 (m), 1589 (w), 1538 (m), 1504 (m), 1477 (w), 1462 (w), 1437 (w), 1401 (m), 1375 (w), 1361 (w), 1303 (m), 1256 (m), 1223 (m), 1171 (m), 1143 (m), 1027 (m), 1004 (m), 982 (w), 955 (w), 938 (m), 902 (m), 889 (w), 862 (w), 830 (m), 806 (m), 777 (m). MS (MALDI-TOF), m/z: calcd for $C_{27}H_{38}O_6Si_2$: 514.22; found: 585.20 $[M+3Na^{+}+2H^{+}]$ (HCCA matrix). m.p. 117-119 ºC. Compound **37-**(*Z*) (assigned as the minor set of peaks in the stereoisomeric 1:5 mixture): ^1H NMR ($CDCl_3$): δ_H (ppm) 0.21 (s, 6H), 0.21 (s, 6H), 0.97 (s, 9H), 0.98 (s, 9H), 3.41 (s, 2H), 5.00 (s, 2H), 5.04 (d, 2H, J=7.0 Hz), 6.22 (t, 1H, J=7.0 Hz), 6.83 (s, 1H), 6.95 (s, 1H). ^{13}C NMR ($CDCl_3$): δ_C (ppm) -4.2, -4.1, 18.3(7), 18.4(0), 25.8, 42.0, 53.2, 61.3, 85.2, 85.7, 113.2, 121.6, 123.6, 124.5, 133.6, 133.8, 147.3, 147.7, 165.2, 165.5. Compound **37-**(*E*) (assigned as the major set of peaks in the stereoisomeric mixture): ^1H NMR ($CDCl_3$): δ_H (ppm) 0.19 (s, 3H), 0.20 (s, 3H), 0.22(2) (s, 3H), 0.22(6) (s, 3H), 0.96 (s, 9H), 0.98 (s, 9H), 3.36 (d, 1H, J=15.2 Hz), 3.44 (d, 1H, J=15.2 Hz), 3.92 (t, 1H, J=11.6 Hz), 4.72 (d, 1H, J=15.4 Hz), 4.87 (dd, 1H, J_1=11.6 Hz, J_2=5.5 Hz), 5.22 (d, 1H, J=15.4 Hz), 6.29 (dd, 1H, J_1=11.6 Hz, J_2=5.5 Hz), 6.73 (s, 1H), 6.90 (s, 1H). ^{13}C NMR ($CDCl_3$): δ_C (ppm) -4.1(3), -4.1(2), 18.3(6), 18.4(4), 25.8, 42.3, 53.5, 61.9, 84.5, 84.9, 113.9, 121.9, 124.0, 124.1, 132.3, 137.6, 147.7, 148.3, 165.4, 165.9. Mixture of stereoisomers **37-**(*Z*) and **37-**(*E*): FT-IR: wavenumber (cm^{-1}) 2952 (w), 2931 (w), 2896 (w), 2859 (w), 2240 (w), 1752 (m), 1732 (s), 1649 (w), 1591 (w), 1546 (w), 1506 (m), 1472 (w), 1432 (w), 1402 (w), 1376 (w), 1359 (w), 1342 (m), 1293 (m), 1253 (m), 1210 (m), 1138 (m), 1094 (w), 1024 (w), 991 (m), 963 (w), 912 (w), 857 (w), 832 (m), 806 (m), 780 (m). MS (MALDI-TOF), m/z: calcd for $C_{27}H_{39}ClO_6Si_2$: 550.20; found: 605.21 $[M+Na^{+}+CH_3OH]$ (HCCA matrix).

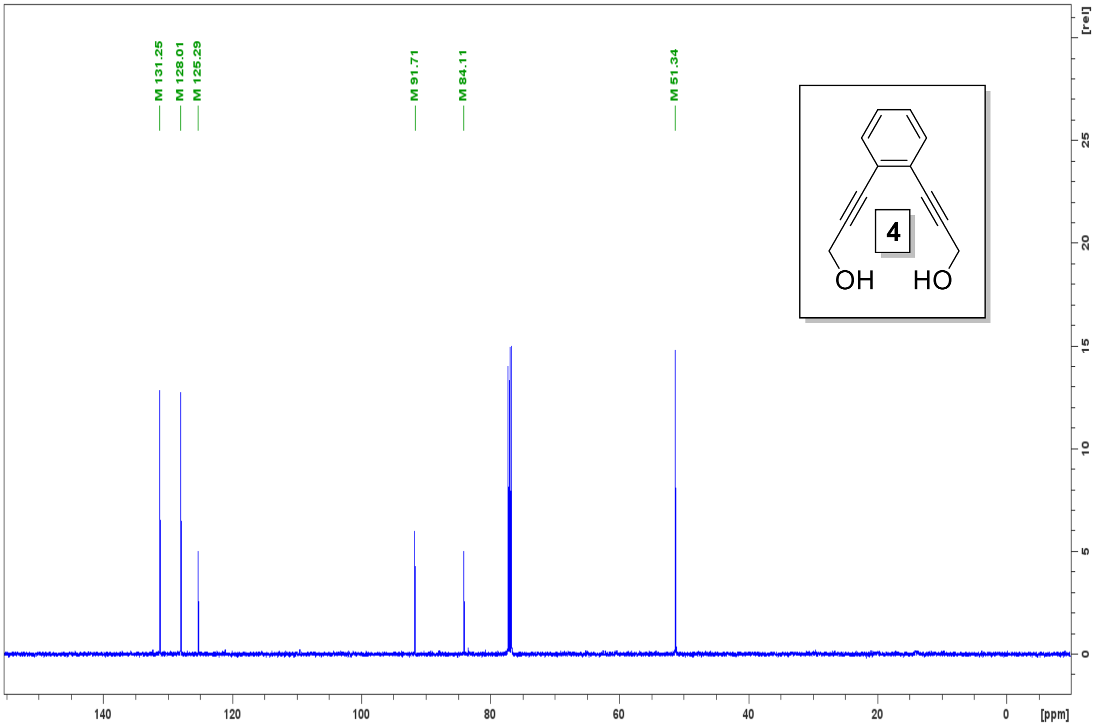
- (2*Z*,2'*Z*)-3,3'-(4,5-dimethoxy-1,2-phenylene)bis(3-chloroprop-2-en-1-ol) (**38-**(*Z*,*Z*)), (2*E*,2'*E*)-3,3'-(4,5-dimethoxy-1,2-phenylene)bis(3-chloroprop-2-en-1-ol) (**38-**(*E*,*E*)) and (*Z*)-3-chloro-3-(2-((*E*)-1-chloro-3-hydroxyprop-1-en-1-yl)-4,5-dimethoxyphenyl)prop-2-en-1-ol (**38-**(*Z*,*E*))

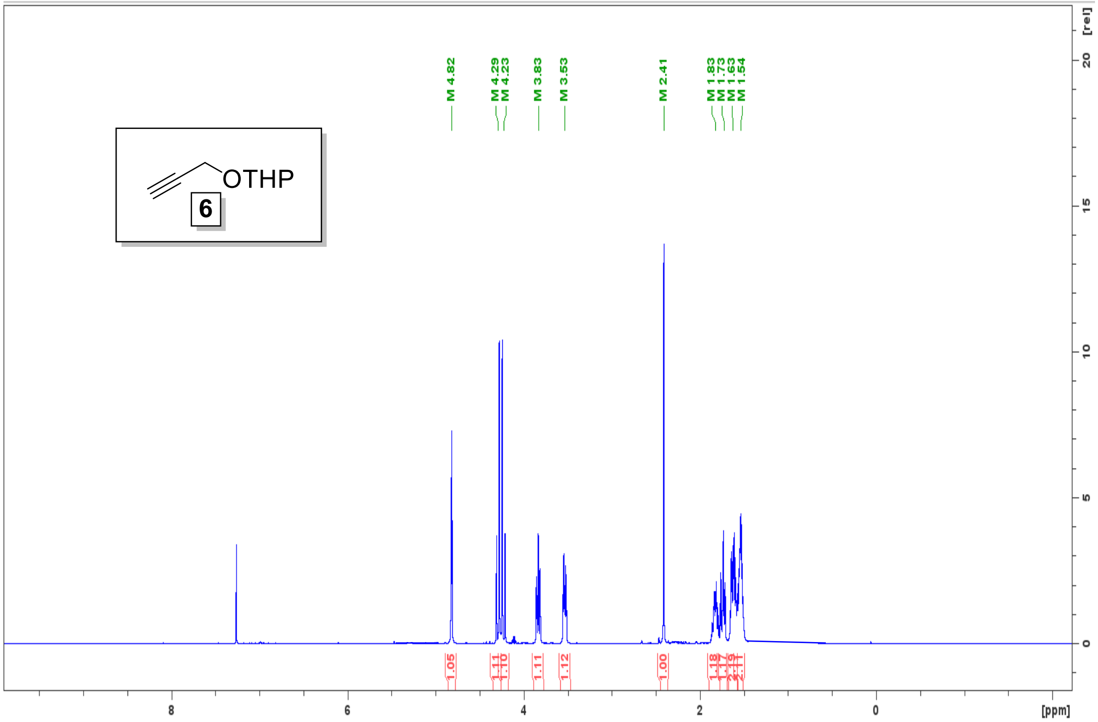


HCl gas was prepared from the dropwise addition of 99.999% wt. sulfuric acid (0.69 mL, 13 mmol) to NaCl granules (1.5 g, 25.6 mmol) at 200 °C and was dried by passing it through an anhydrous $CaCl_2$-filled column, before channeling it in the reaction solution. Diol **23** (0.025 g, 0.1 mmol, 1 equiv) was transferred to a two-neck round-bottom flask, which was fitted with a vertical condenser and set under nitrogen atmosphere. DCM (9.3 mL) was added, followed by the freshly prepared HCl gas, which was bubbled through the solution, via a long needle, for a period of 4 h. After the needle was removed, the solution was allowed to stir at r.t. overnight. The solvent was subsequently evaporated and the crude residue was redissolved in DCM and applied to a silica column for flash chromatography. Elution took place using EtOAc, to afford an inseparable mixture of three bis-hydrochlorination adducts (total of 0.028 g, 0.085 mmol, 94% conversion), in the form of a white powder. In this mixture of three stereoisomers, one was dominant relative to the other two, in 12:1:1 molar ratio. This was the only out of the three stereoisomers, whose NMR peaks could be reported, while significant peak overlap was detected for the two minor stereoisomers. A recrystallization effort on the mixture, involving slow diffusion of pentane in a concentrated solution of the mixture in DCM, only afforded a significant quantity of white crystals belonging to the major component, compound **38-**(*Z,Z*). Compound **38-**(*Z,Z*): ^{1}H NMR ($CDCl_3$): δ_H (ppm) 3.90 (s, 6H), 3.98 (d, 4H, J=7.5 Hz), 6.20 (t, 2H, J=7.5 Hz), 6.74 (s, 2H). ^{13}C NMR ($CDCl_3$): δ_C (ppm) 56.1, 60.2, 112.5, 128.0, 129.9, 130.6, 149.4. FT-IR: wavenumber (cm^{-1}) 3321 (br), 3009 (w), 2962 (w), 2935 (w), 2852 (w), 1657 (w), 1597 (m), 1510 (s), 1460 (m), 1392 (w), 1372 (w), 1351 (m), 1326 (m), 1303 (w), 1259 (s), 1217 (s), 1190 (m), 1111 (s), 1062 (m), 1004 (m), 988 (s), 971 (m), 877 (m), 855 (m), 796 (s), 777 (s), 736 (w). MS (MALDI-TOF), m/z: calcd for $C_{14}H_{16}O_4Cl_2$: 318.04; found: 336.18 [$M+NH_4^+$], 350.16 [$M+CH_3OH$] (HCCA matrix).

II. ^{1}H, ^{13}C and ^{19}F NMR Spectra of Synthesized Compounds



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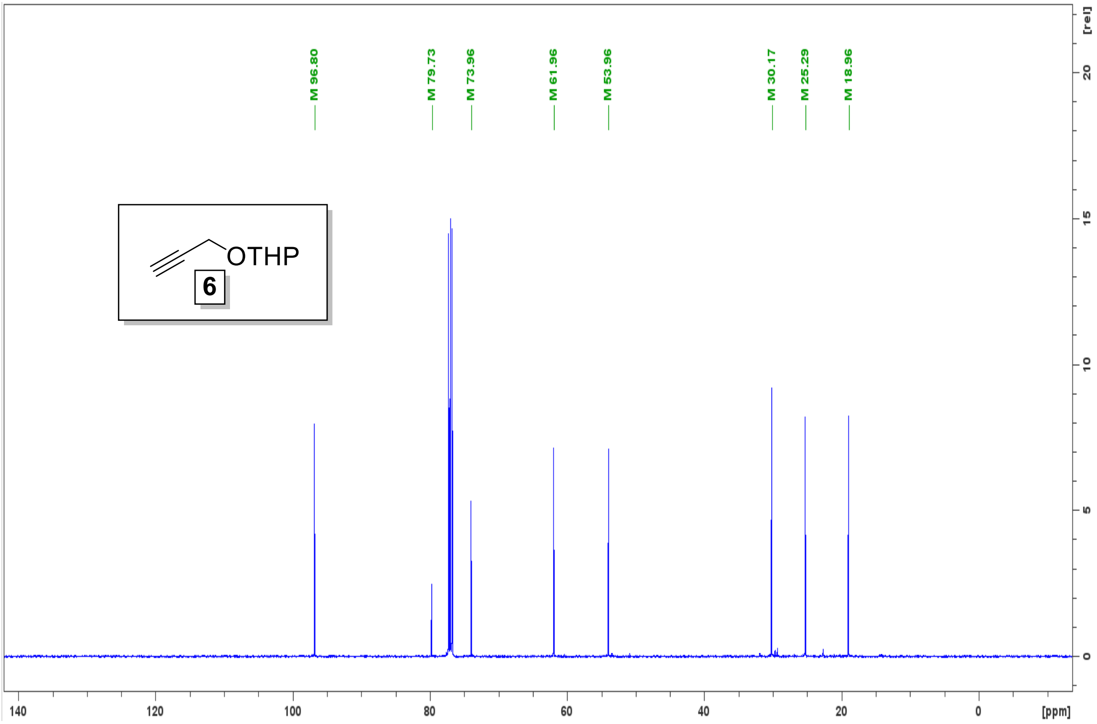
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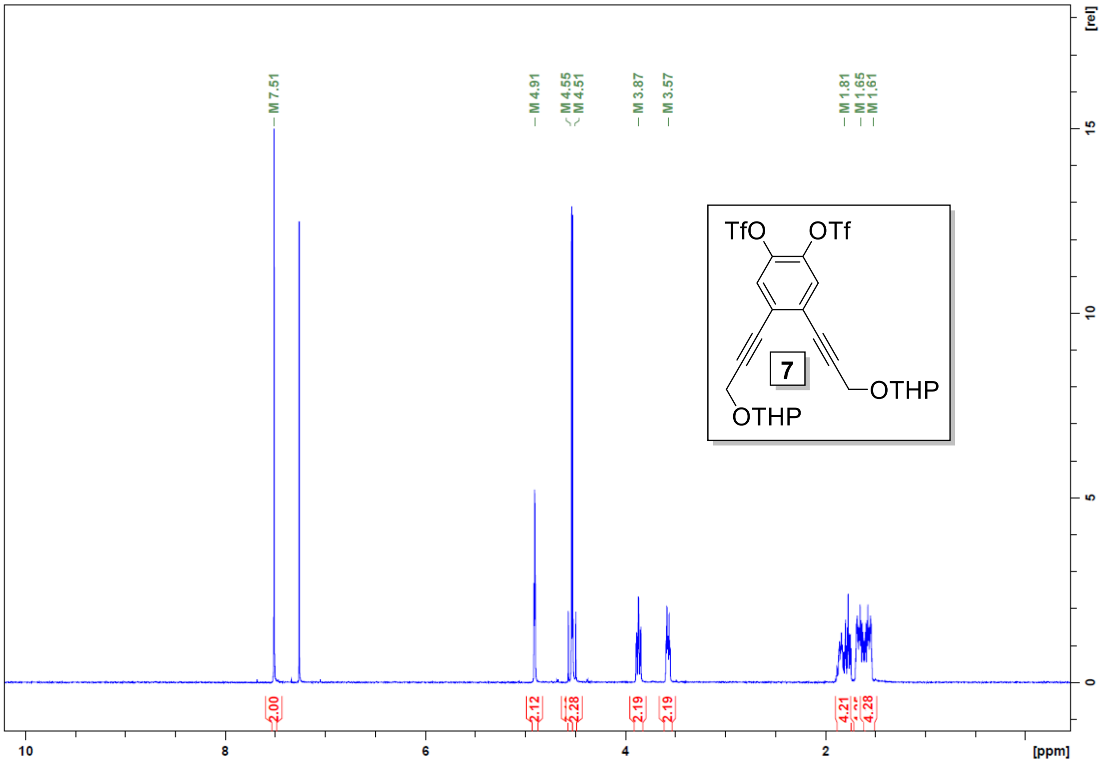
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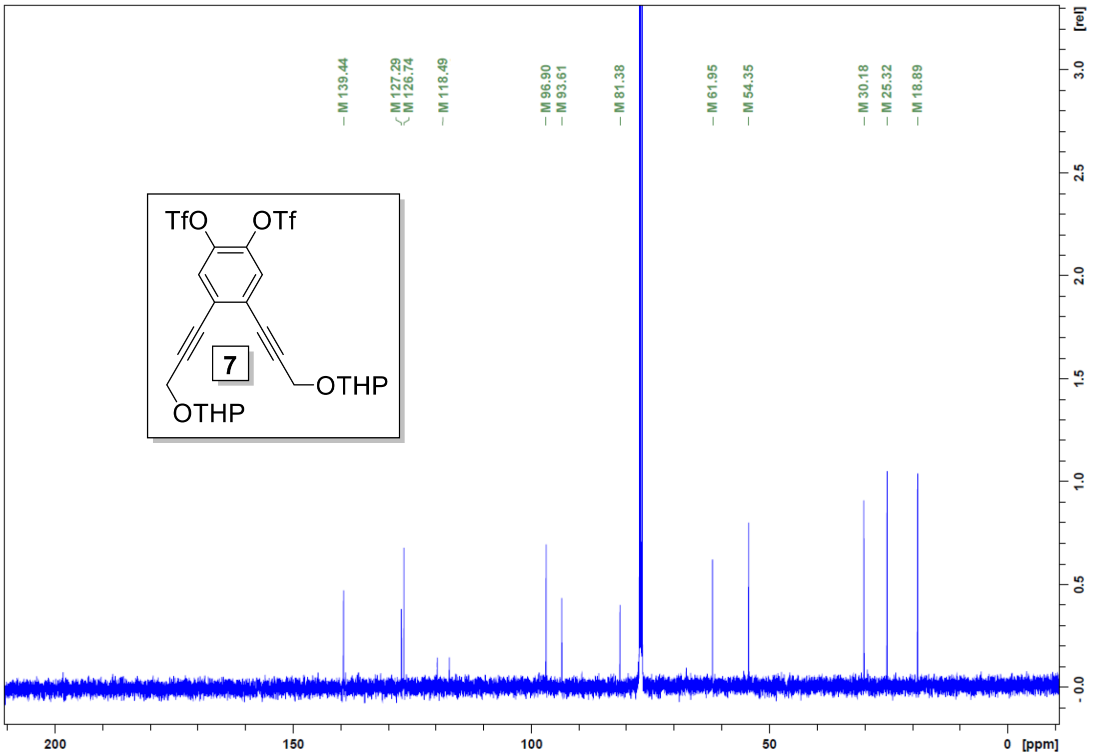
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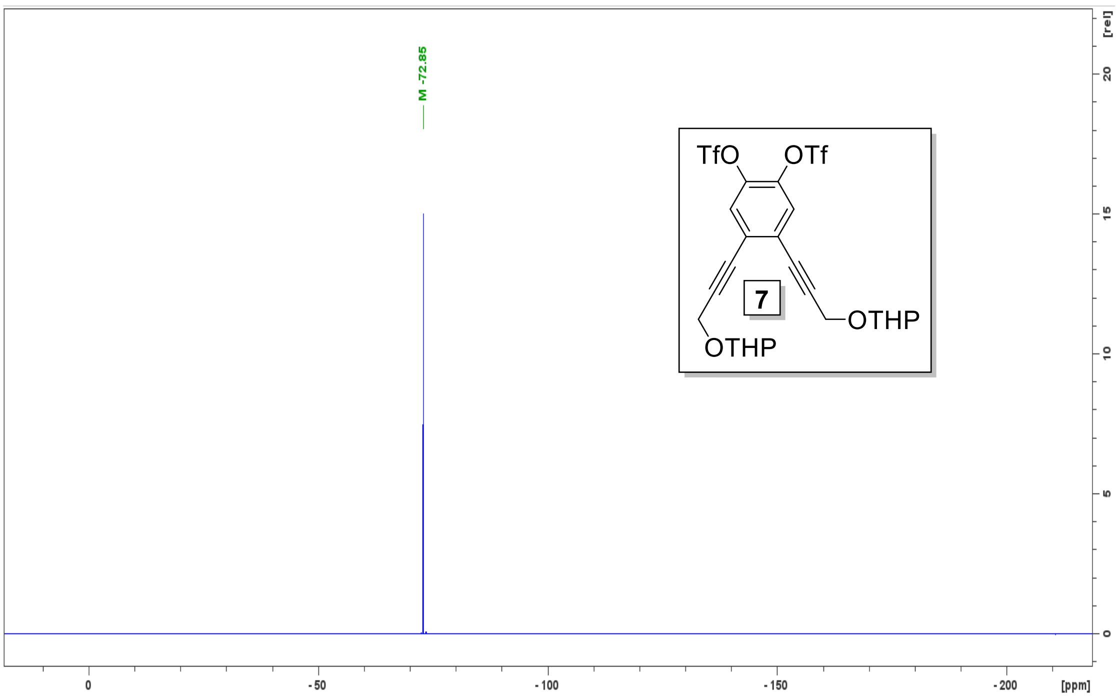
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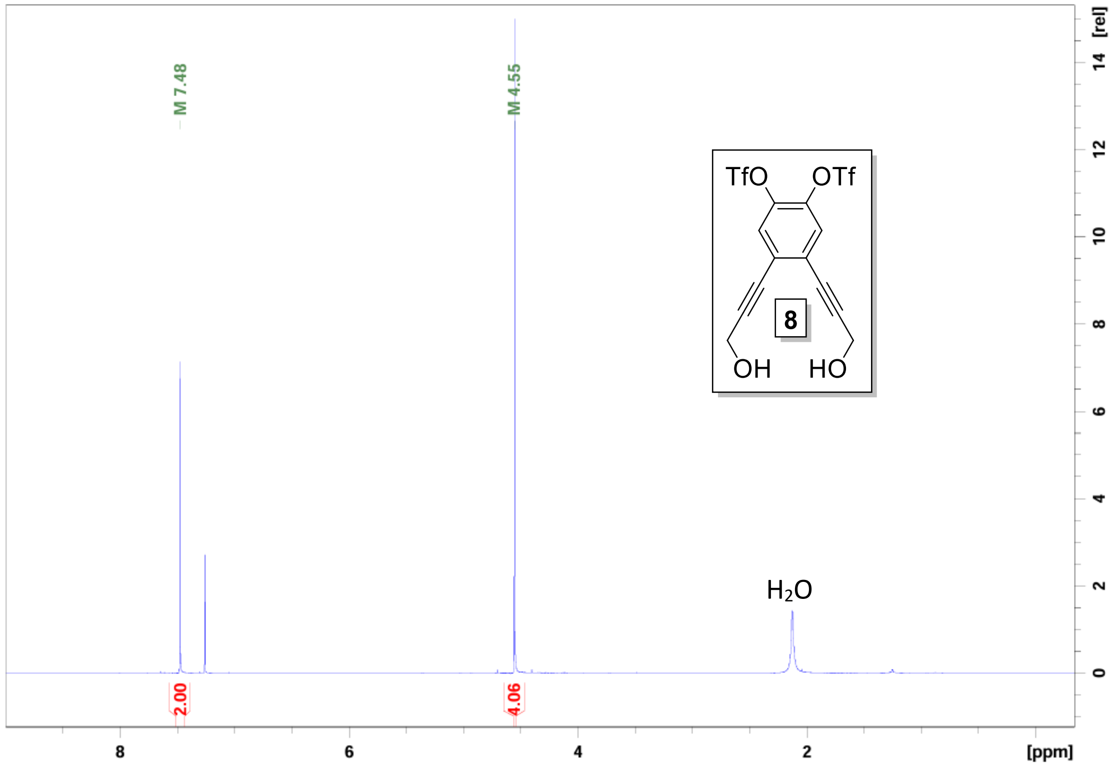
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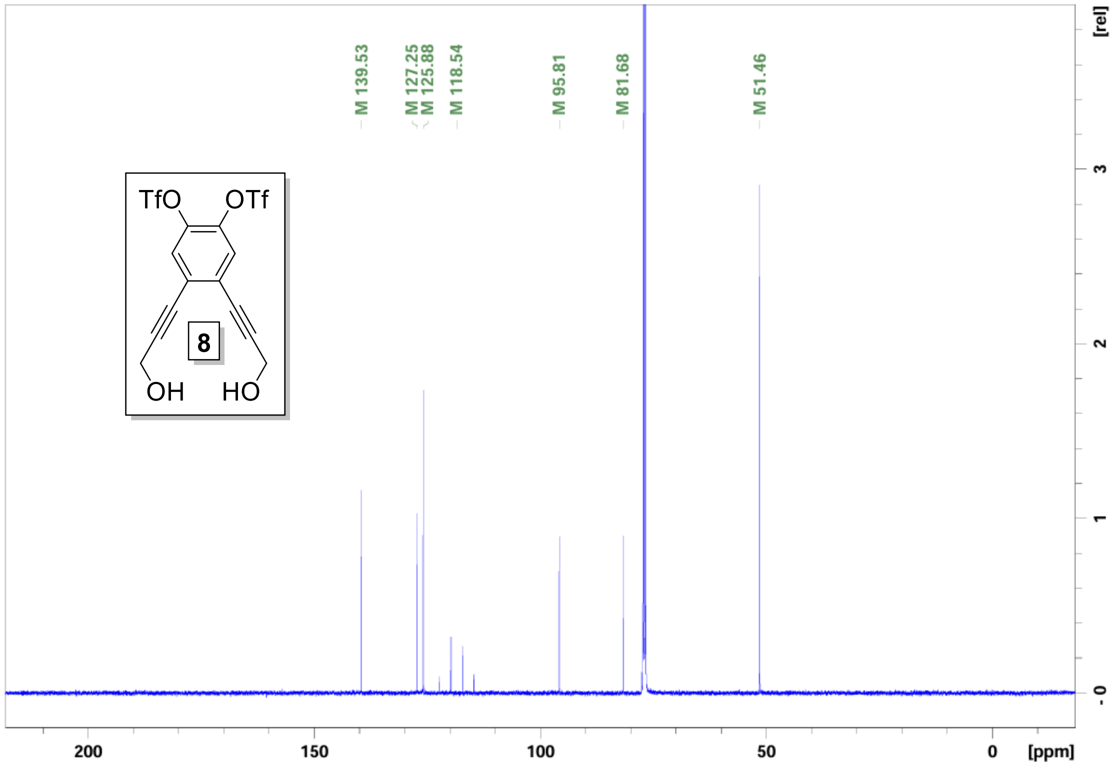
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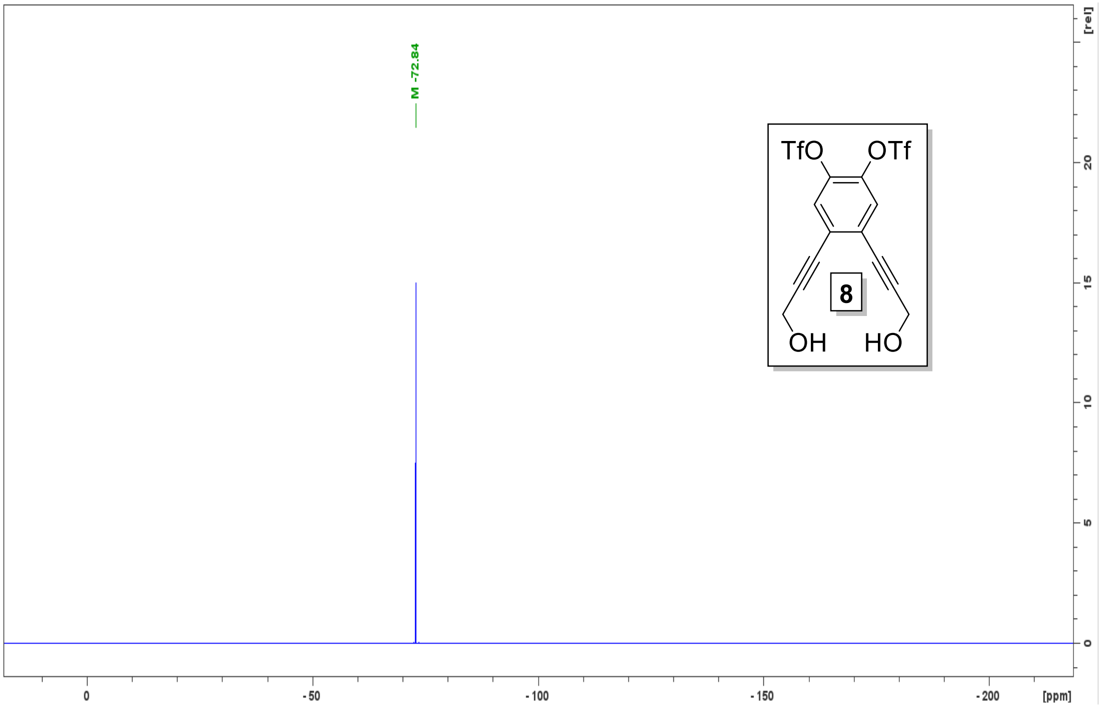
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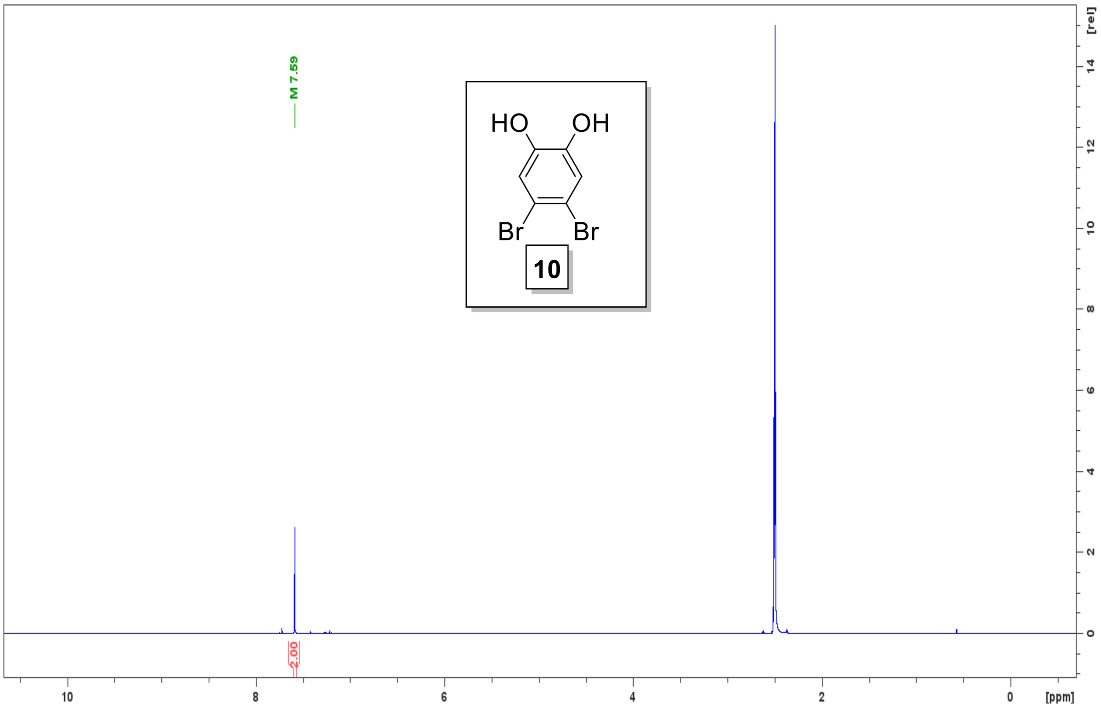
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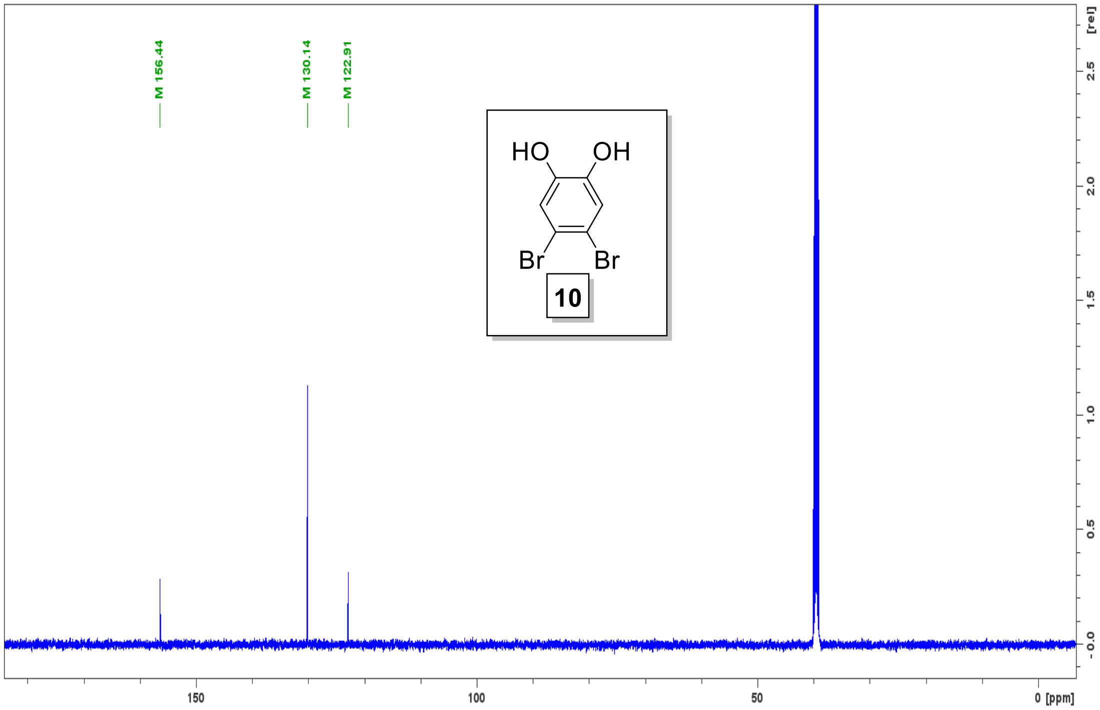
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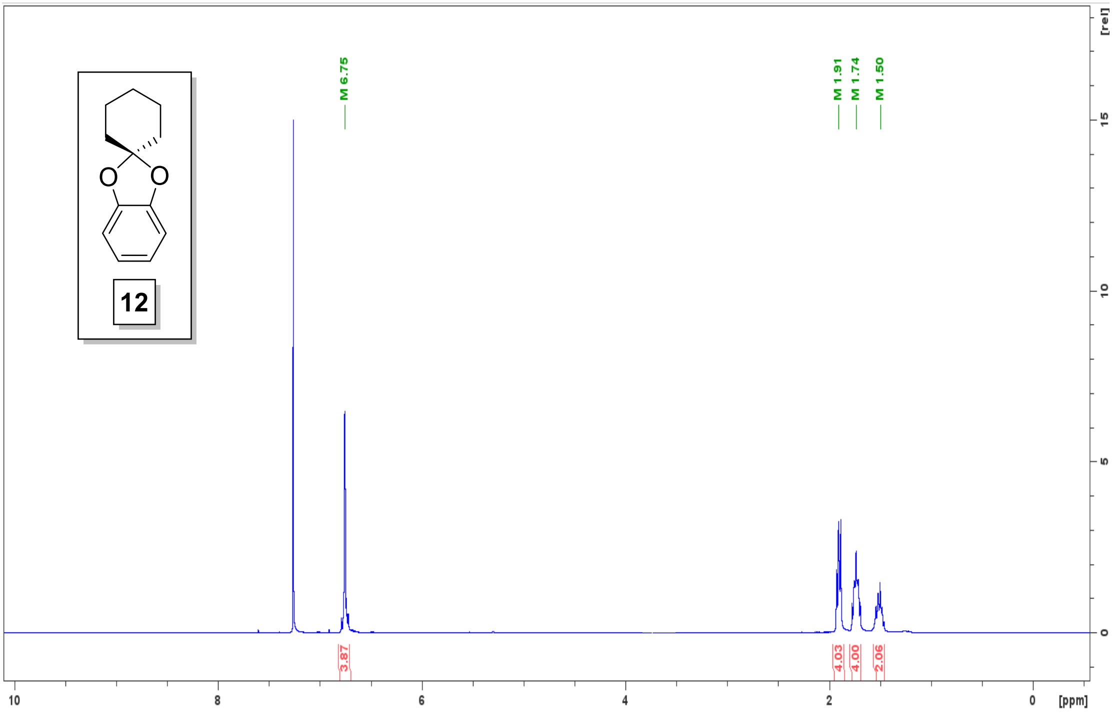
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M 1.74
M 1.50
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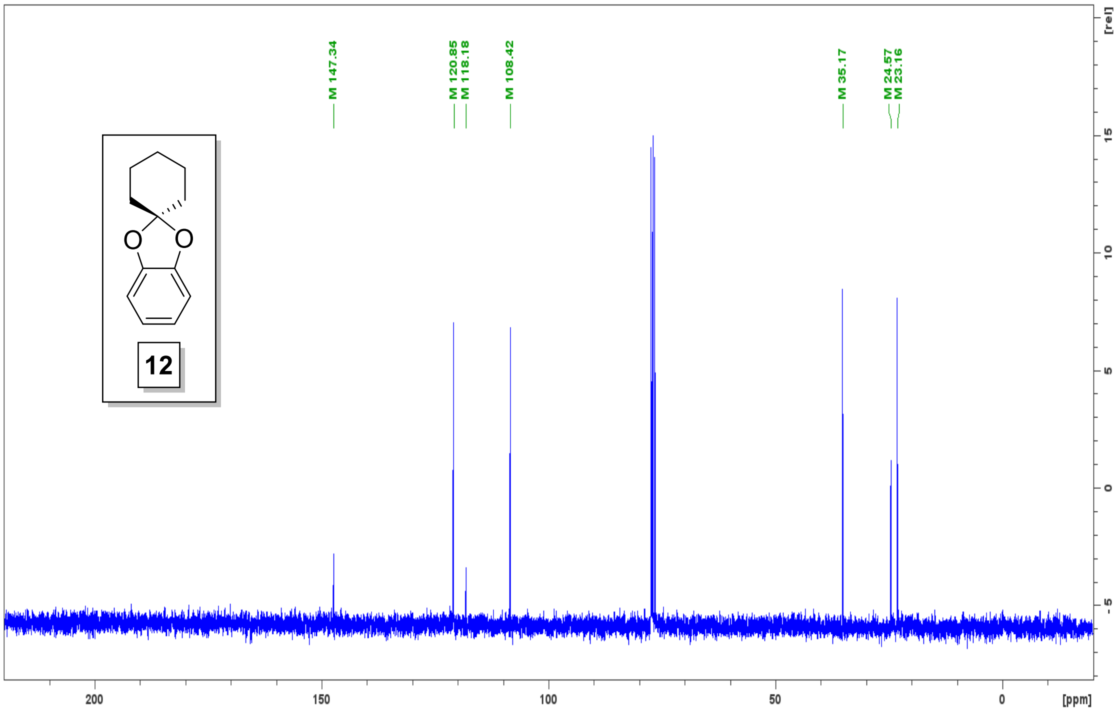
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M 118.18
M 108.42
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M 24.57
M 23.16
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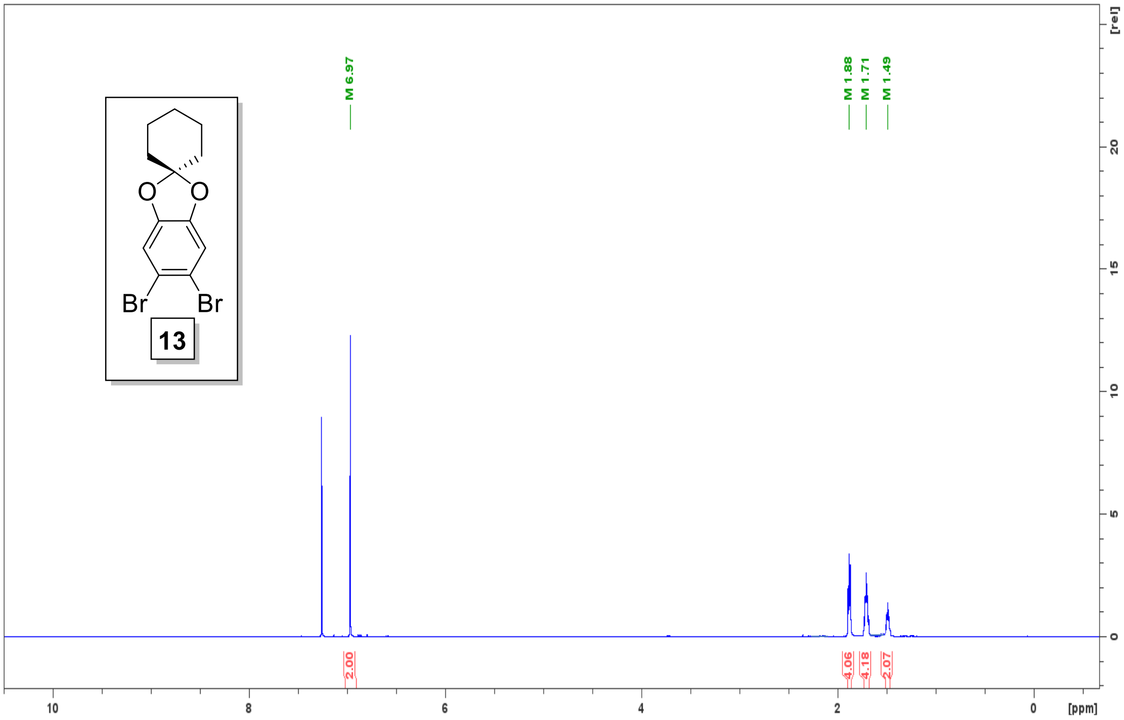

13
Br
Br
O
O
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M 1.71
M 1.49
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2.07
10
8
6
4
2
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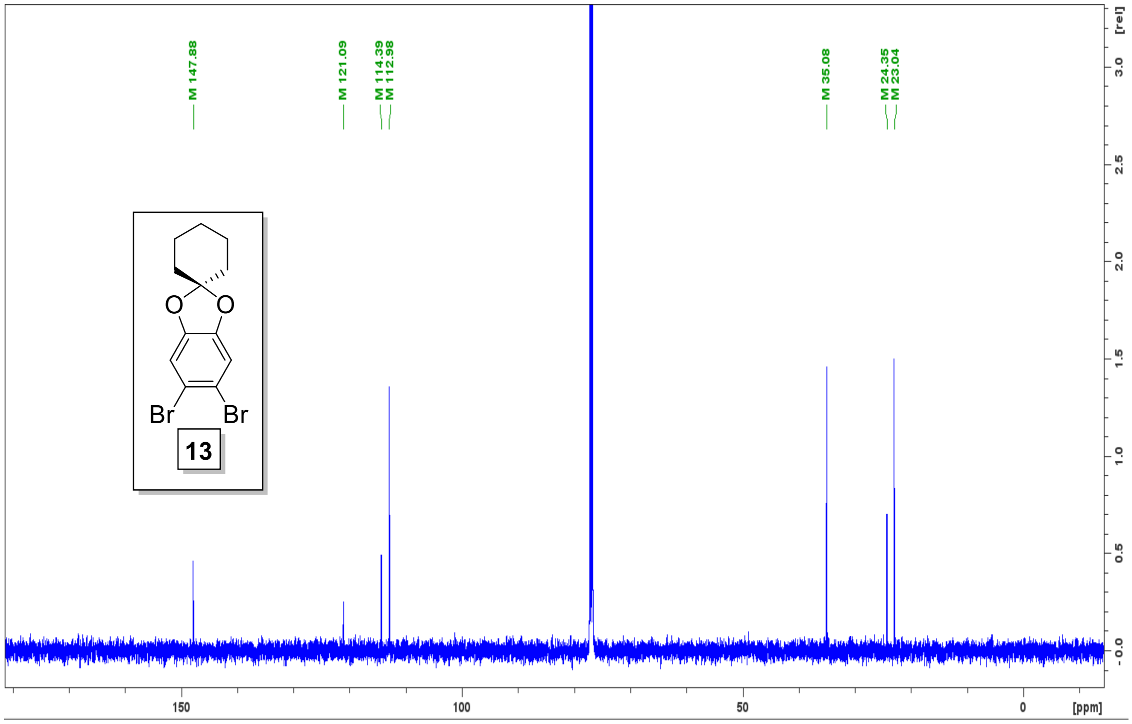
[rel]



13
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Br
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O
M 147.88
M 121.09
M 114.39
M 112.98
M 35.08
M 24.35
M 23.04
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1.5
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3.0
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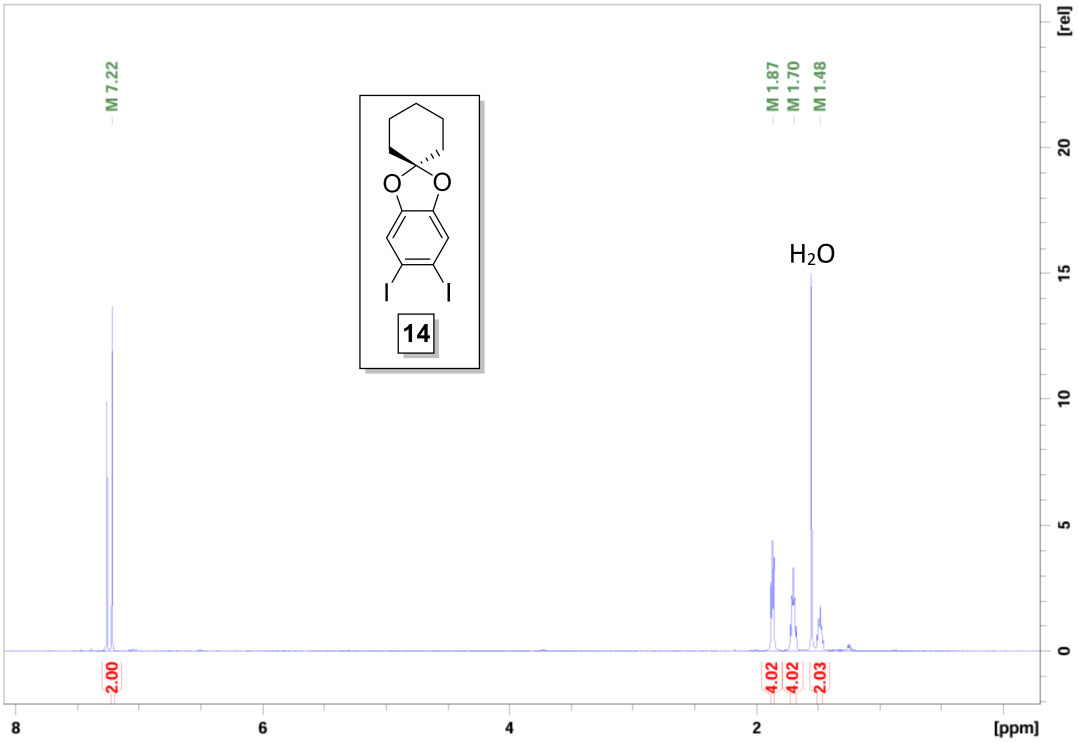
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M 1.70
M 1.48
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4.02
2.03
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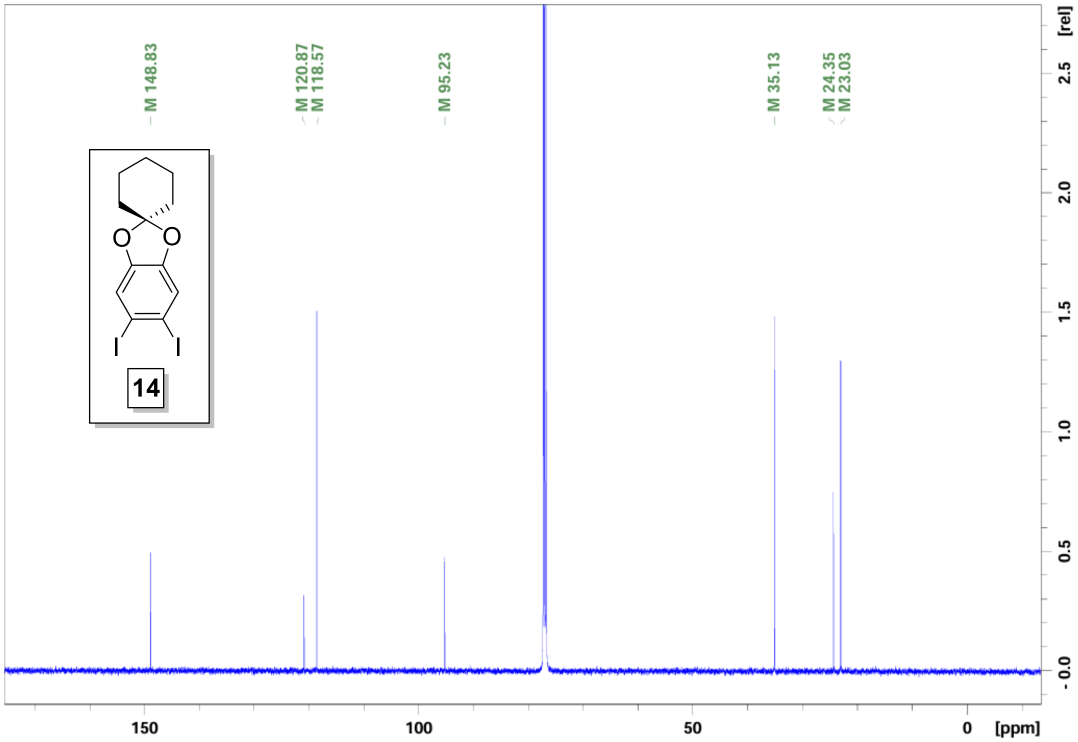
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M 120.87
M 118.57
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M 35.13
M 24.35
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1.5
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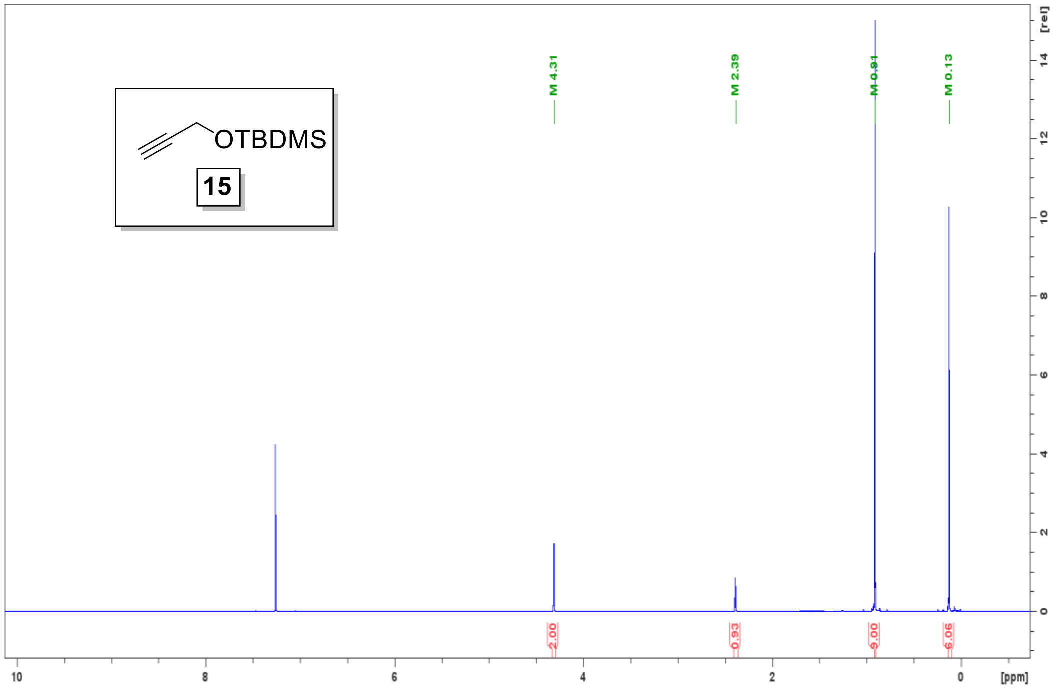
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M 2.39
M 0.91
M 0.13
2.00
0.93
9.00
6.06
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8
6
4
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0
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6
4
2
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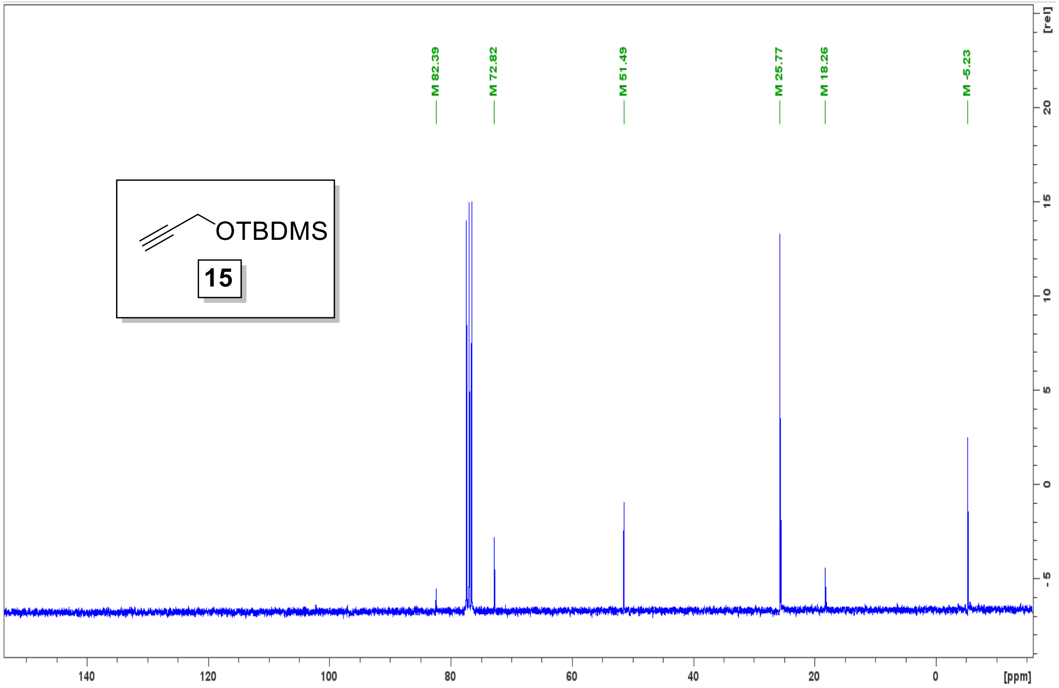
OTBDMS
15
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M 72.82
M 51.49
M 25.77
M 18.26
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120
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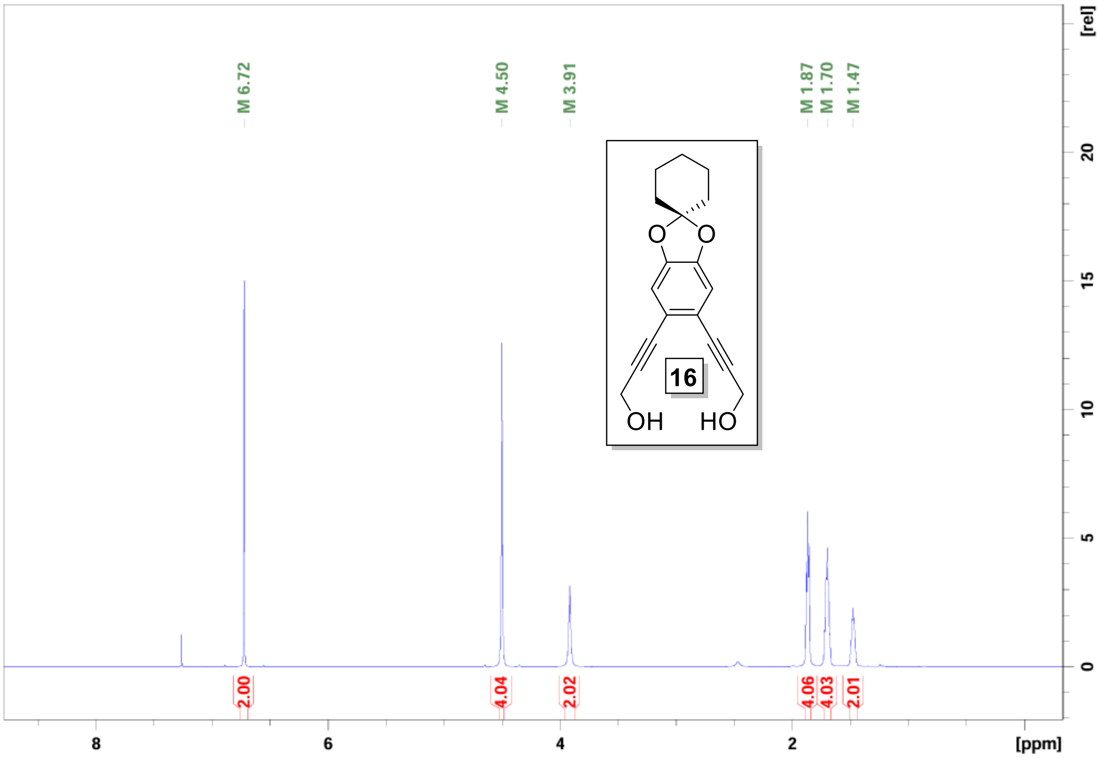
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M 3.91
M 1.87
M 1.70
M 1.47
2.00
4.04
2.02
4.06
4.03
2.01
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HO
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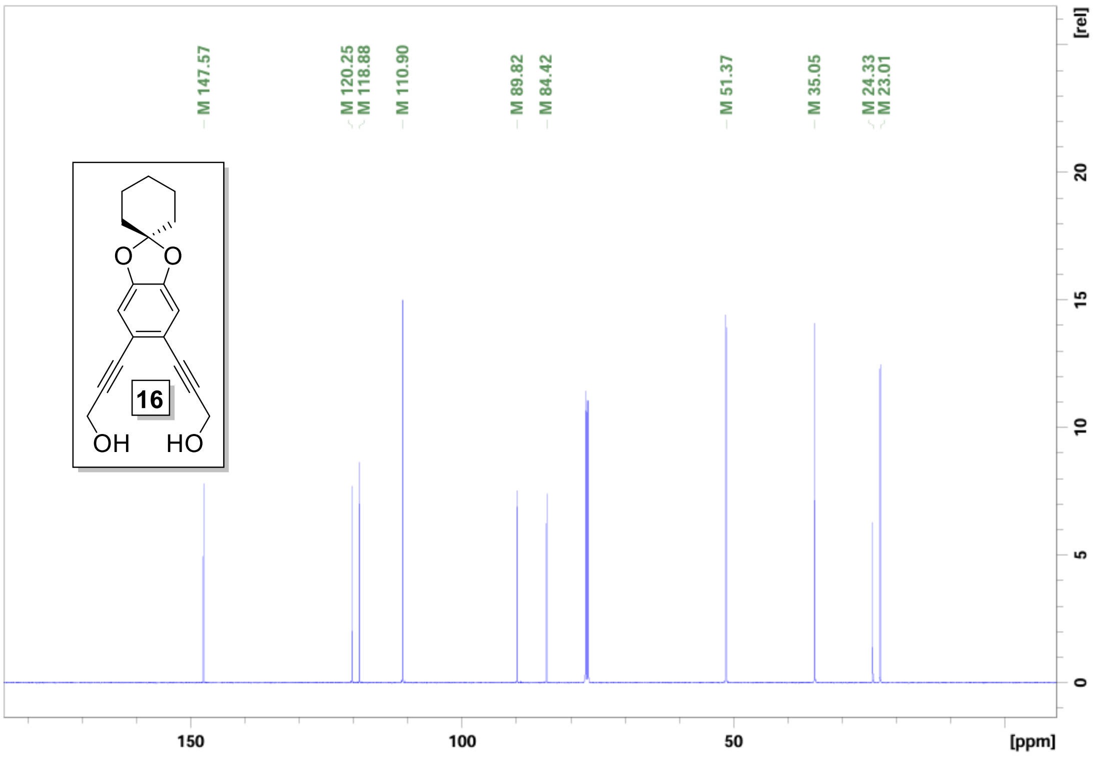
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M 120.25
M 118.88
M 110.90
M 89.82
M 84.42
M 51.37
M 35.05
M 24.33
M 23.01
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OH
HO
O
O
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100
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[ppm]
[rel]
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15
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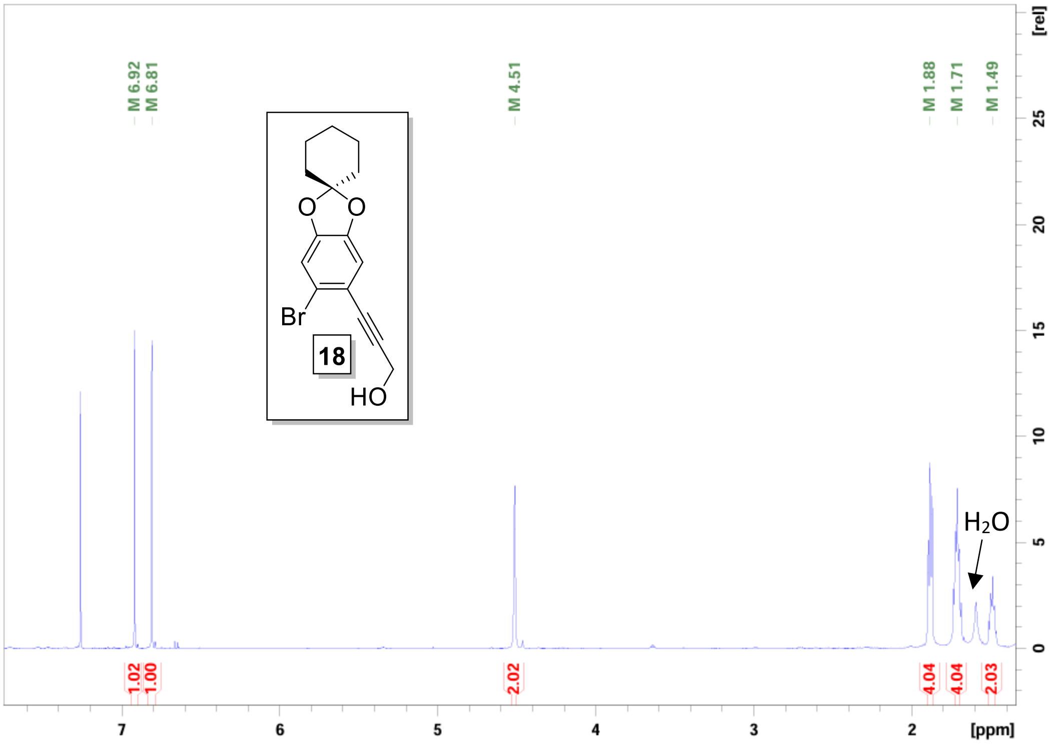
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M 6.81
M 4.51
M 1.88
M 1.71
M 1.49
1.02
1.00
2.02
4.04
4.04
2.03
H2O
Br
18
HO
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O
[rel]
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7
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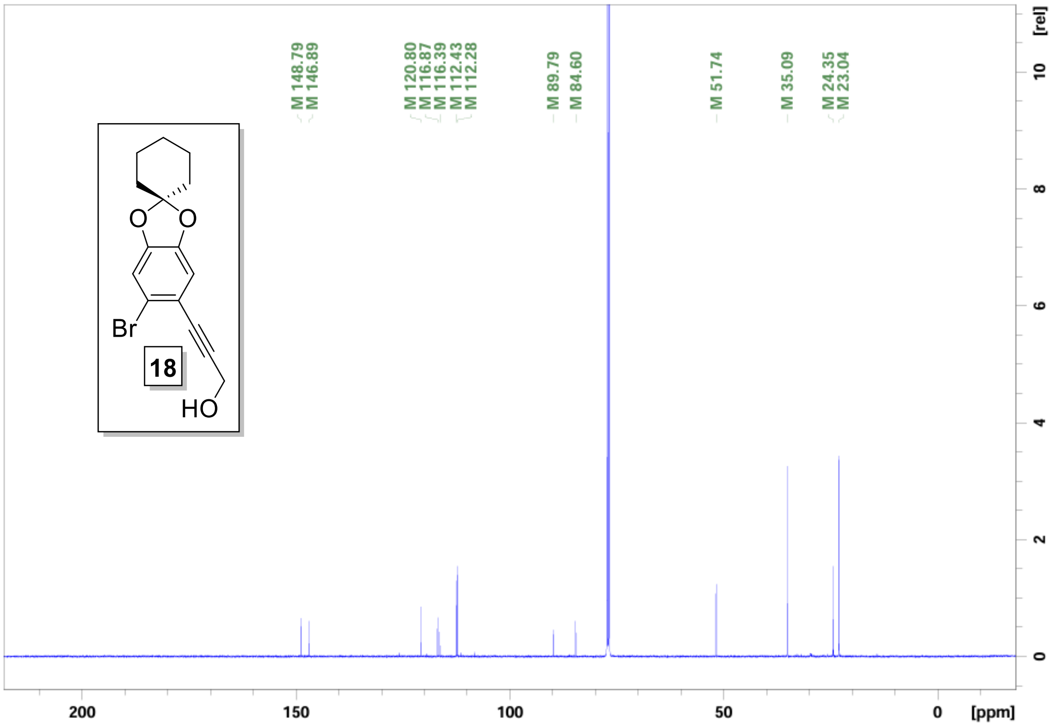
5
4
3
2
[ppm]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M 146.89
M 120.80
M 116.87
M 116.39
M 112.43
M 112.28
M 89.79
M 84.60
M 51.74
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M 24.35
M 23.04
Br
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HO
O
O
[rel]
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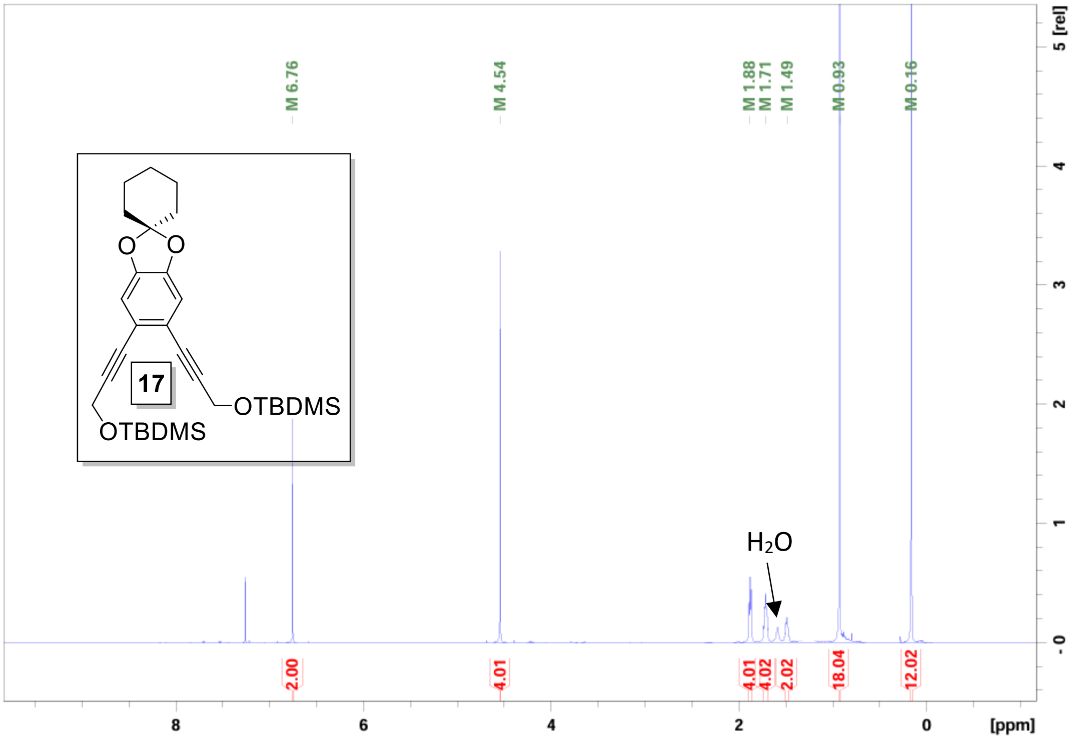
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M 1.88
M 1.71
M 1.49
M 0.93
M 0.16
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4.01
4.01
4.02
2.02
18.04
12.02
H2O
O
O
17
OTBDMS
OTBDMS
8
6
4
2
0
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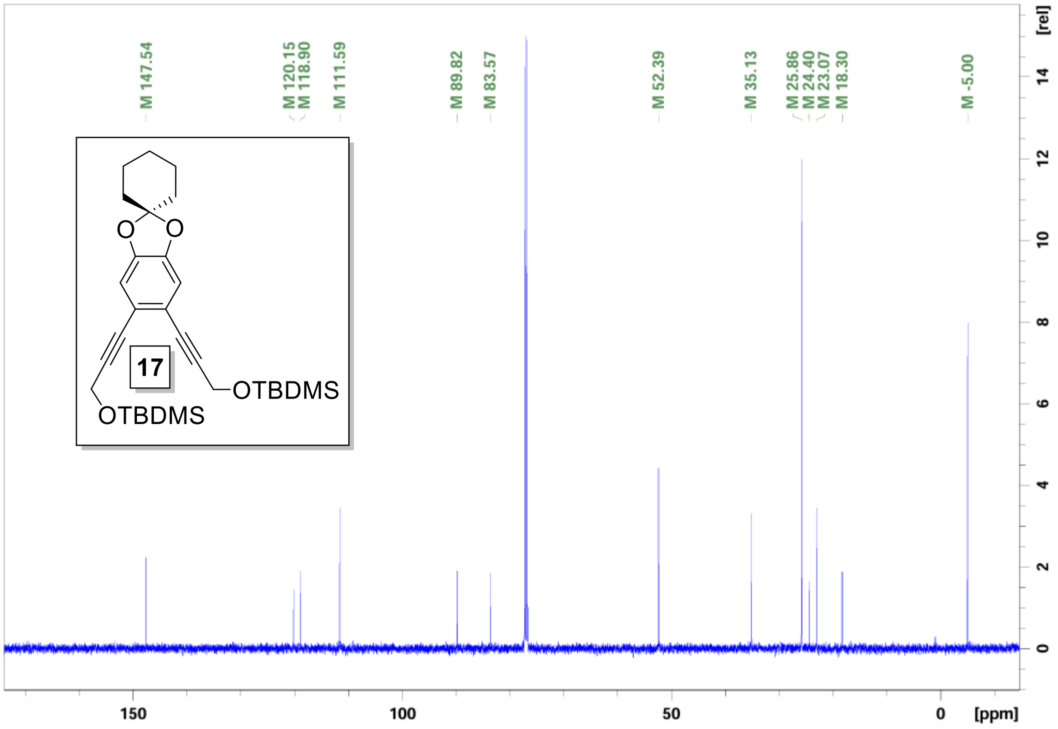
4
3
2
1
0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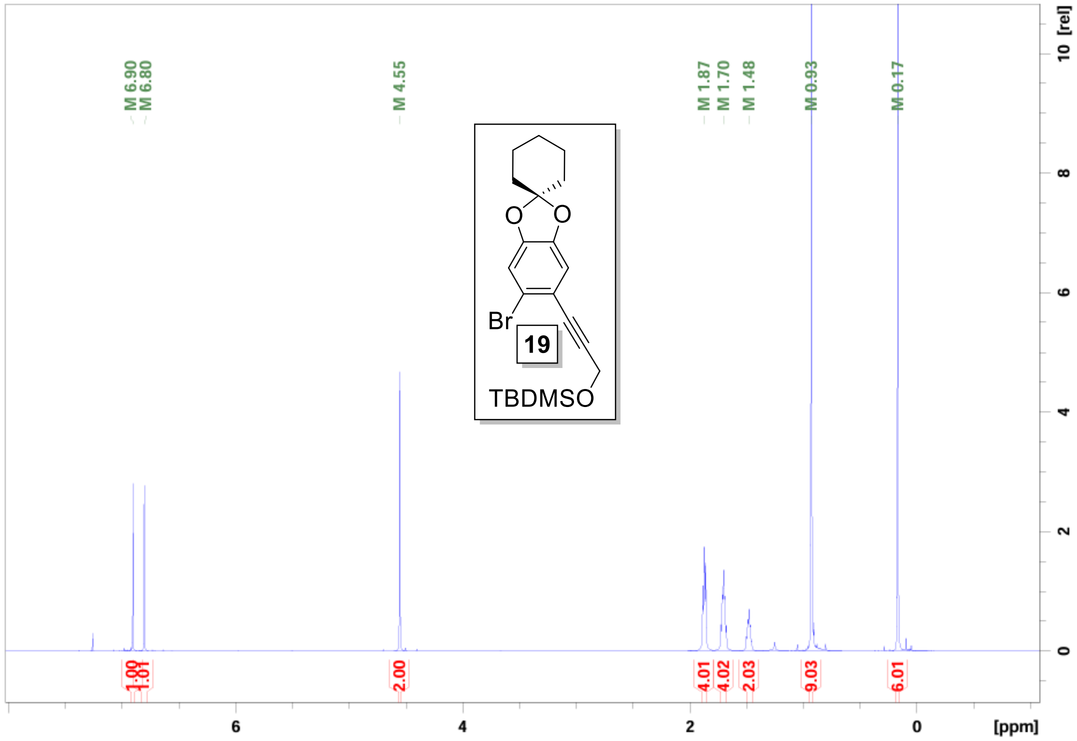
M 120.15
M 118.90
M 111.59
M 89.82
M 83.57
M 52.39
M 35.13
M 25.86
M 24.40
M 23.07
M 18.30
M -5.00
O
O
17
OTBDMS
OTBDMS
150
100
50
0
[ppm]
[rel]
14
12
10
8
6
4
2
0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M 6.80
M 4.55
M 1.87
M 1.70
M 1.48
M 0.93
M 0.17
1.00
1.01
2.00
4.01
4.02
2.03
9.03
6.01
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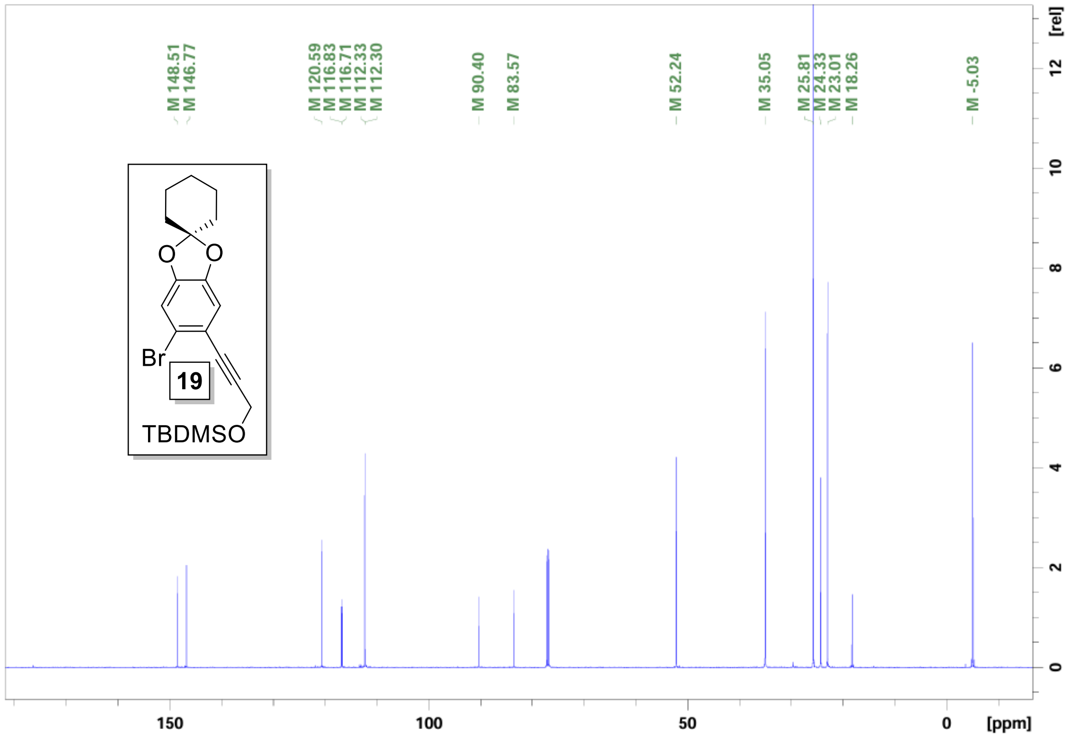
O
Br
19
TBDMSO
10 [rel]
8
6
4
2
0
6
4
2
0
[ppm]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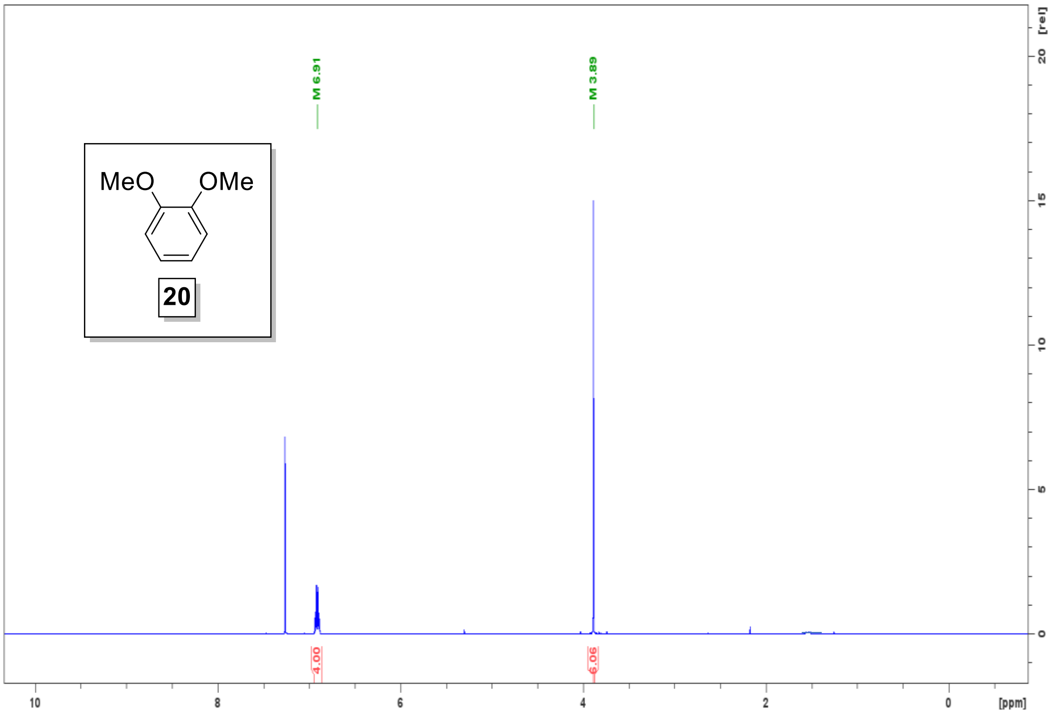
M 146.77
M 120.59
M 116.83
M 116.71
M 112.33
M 112.30
M 90.40
M 83.57
M 52.24
M 35.05
M 25.81
M 24.33
M 23.01
M 18.26
M -5.03
O
O
Br
19
TBDMSO
[rel]
12
10
8
6
4
2
0
150
100
50
0
[ppm]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M 3.89
MeO
OMe
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6.06
10
8
6
4
2
0
[ppm]
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10
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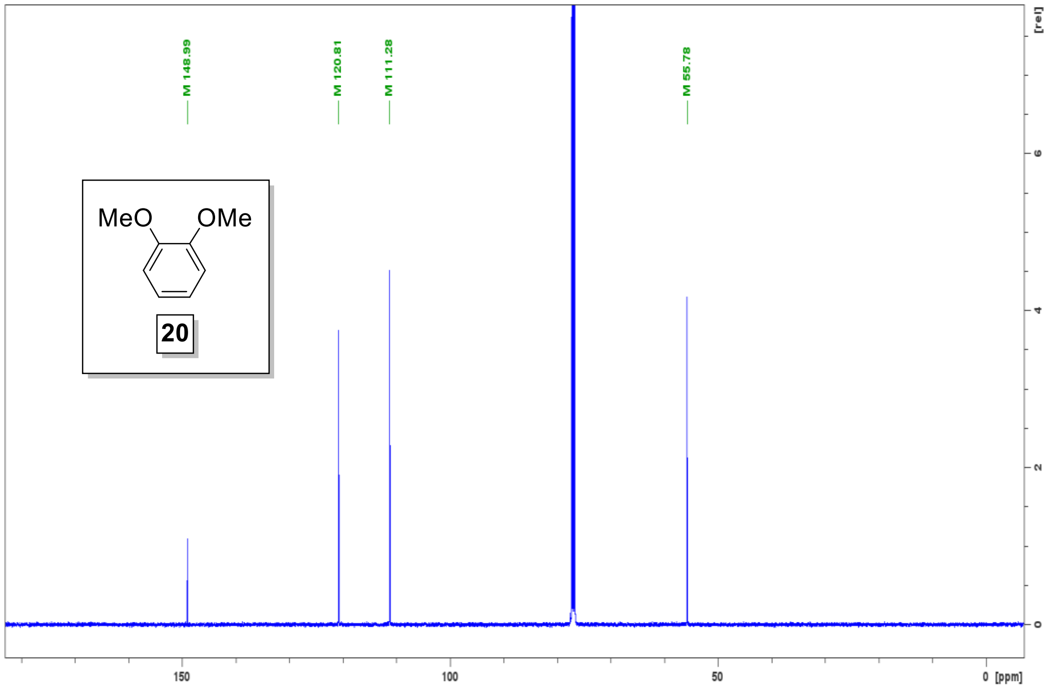
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M 120.81
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OMe
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100
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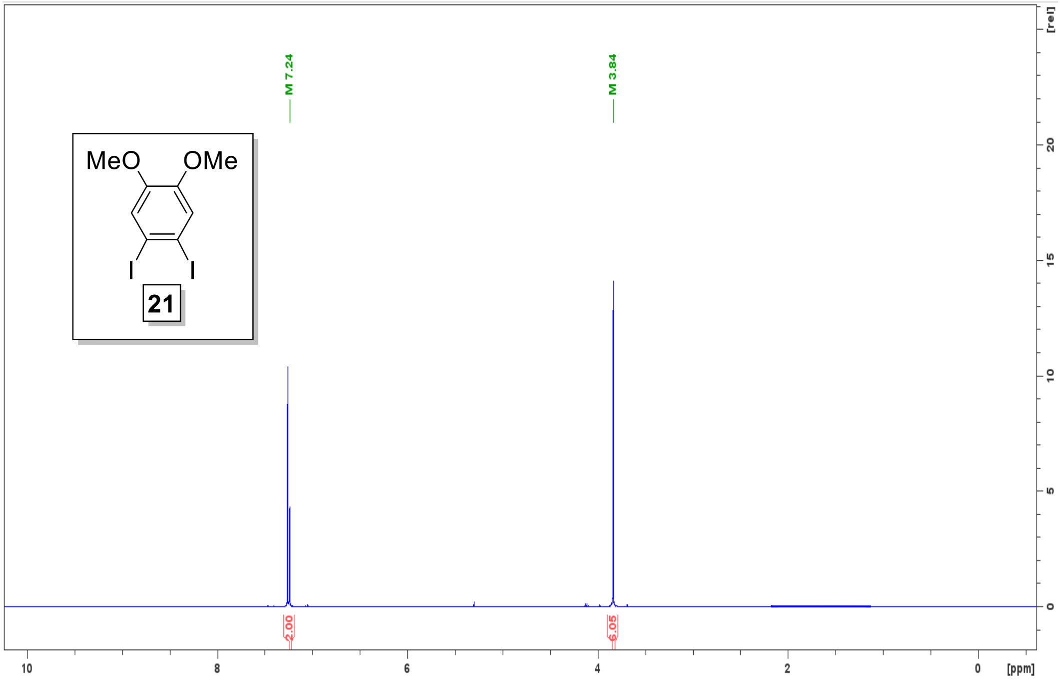
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M 3.84
MeO
OMe
I
I
21
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6.05
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6
4
2
0
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15
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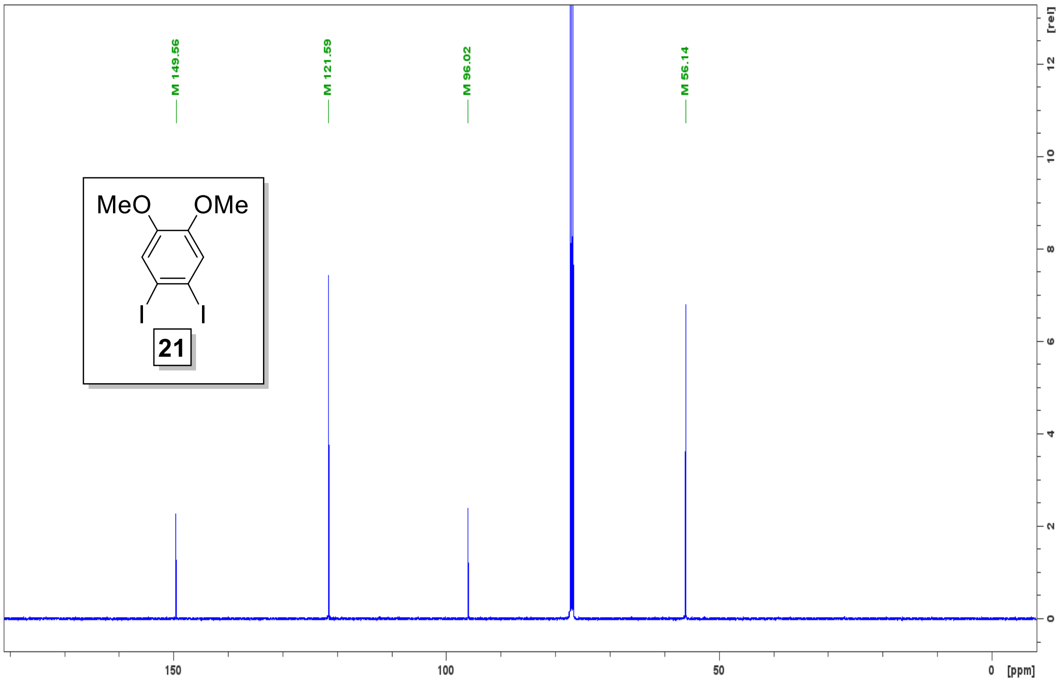
5
0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M 121.59
M 96.02
M 56.14
MeO
OMe
I
I
21
150
100
50
0
[ppm]
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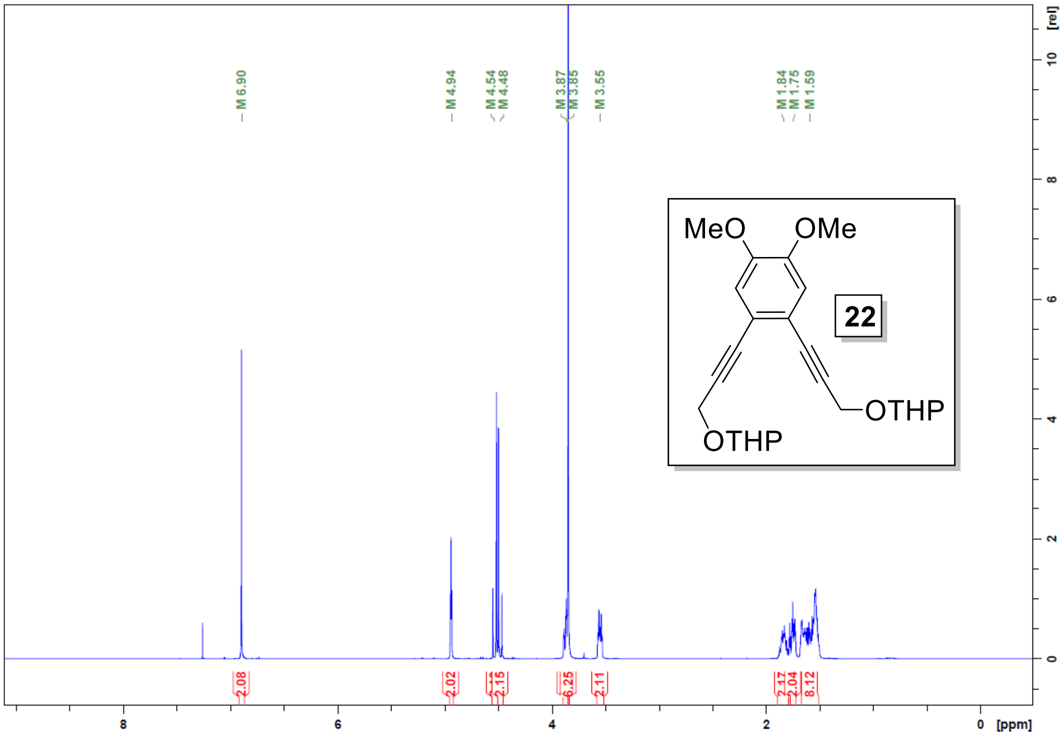
10
8
6
4
2
0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M 4.94
M 4.54
M 4.48
M 3.87
M 3.85
M 3.55
M 1.84
M 1.75
M 1.59
2.08
2.02
2.15
2.15
6.25
2.11
2.17
2.04
8.12
MeO
OMe
22
OTHP
OTHP
[rel]
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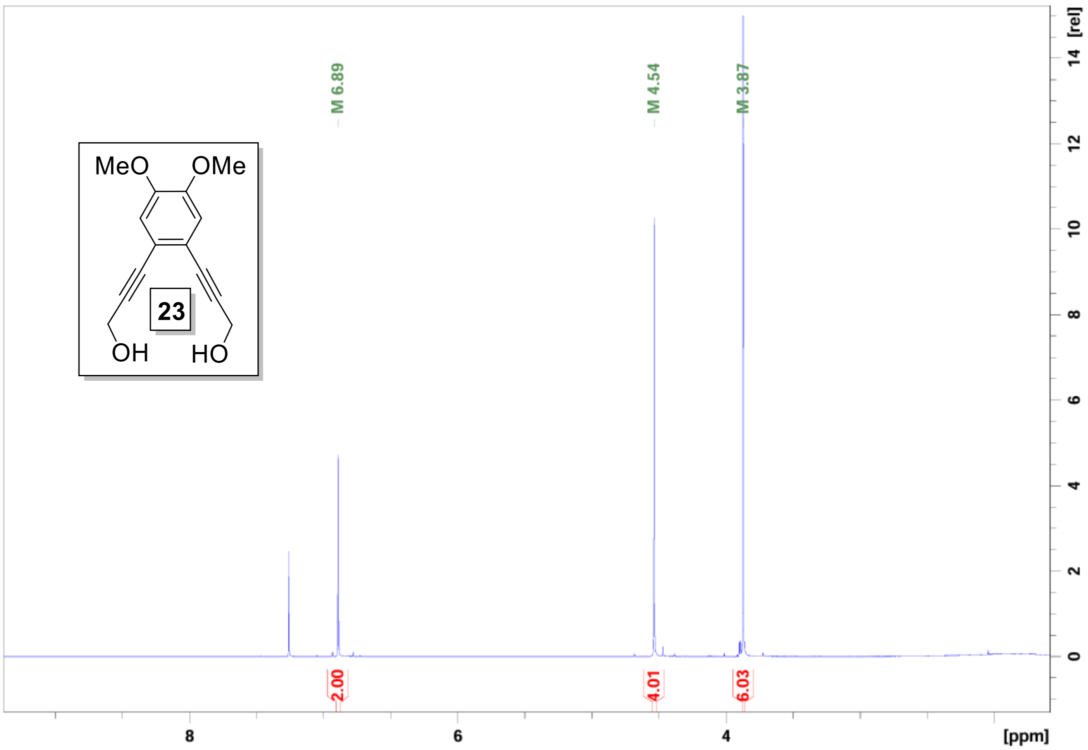
8
6
4
2
0
8
6
4
2
0 [ppm]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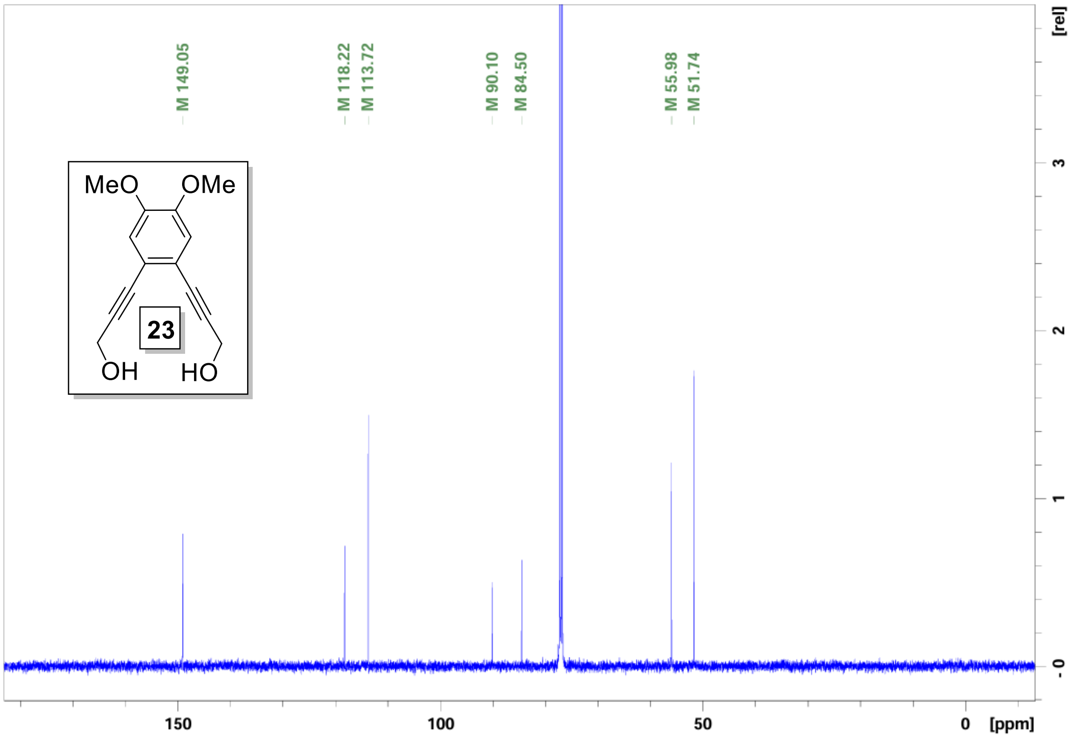
M 4.54
M 3.87
2.00
4.01
6.03
MeO
OMe
OH
HO
23
8
6
4
[ppm]
[rel]
14
12
10
8
6
4
2
0


M 149.05
M 118.22
M 113.72
M 90.10
M 84.50
M 55.98
M 51.74
MeO
OMe
OH
HO
23
150
100
50
0
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[rel]
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1
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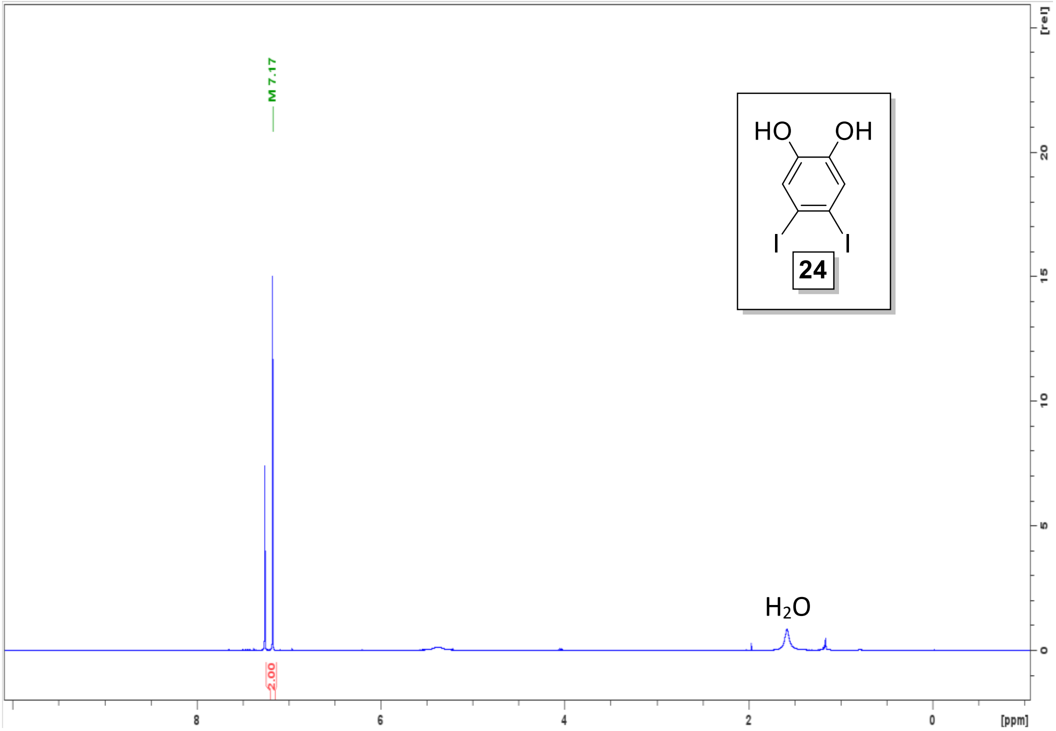
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HO
OH
I
I
24
8
6
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[rel]
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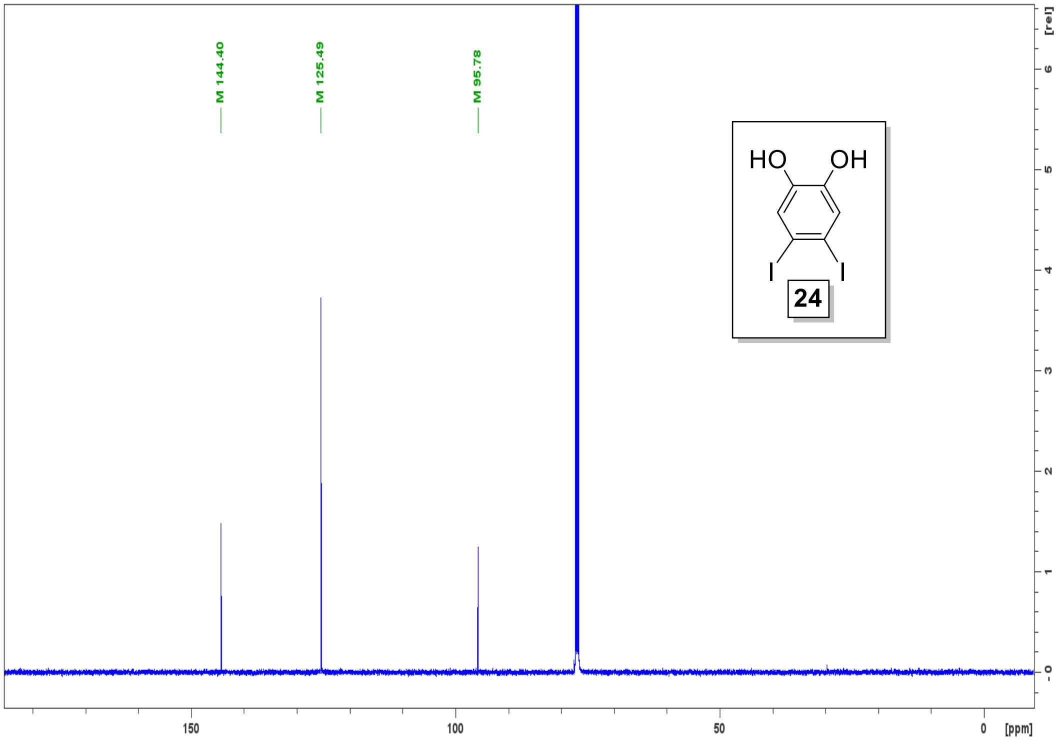
15
10
5
0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M 125.49
M 95.78
HO
OH
I
I
24
150
100
50
0
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[rel]
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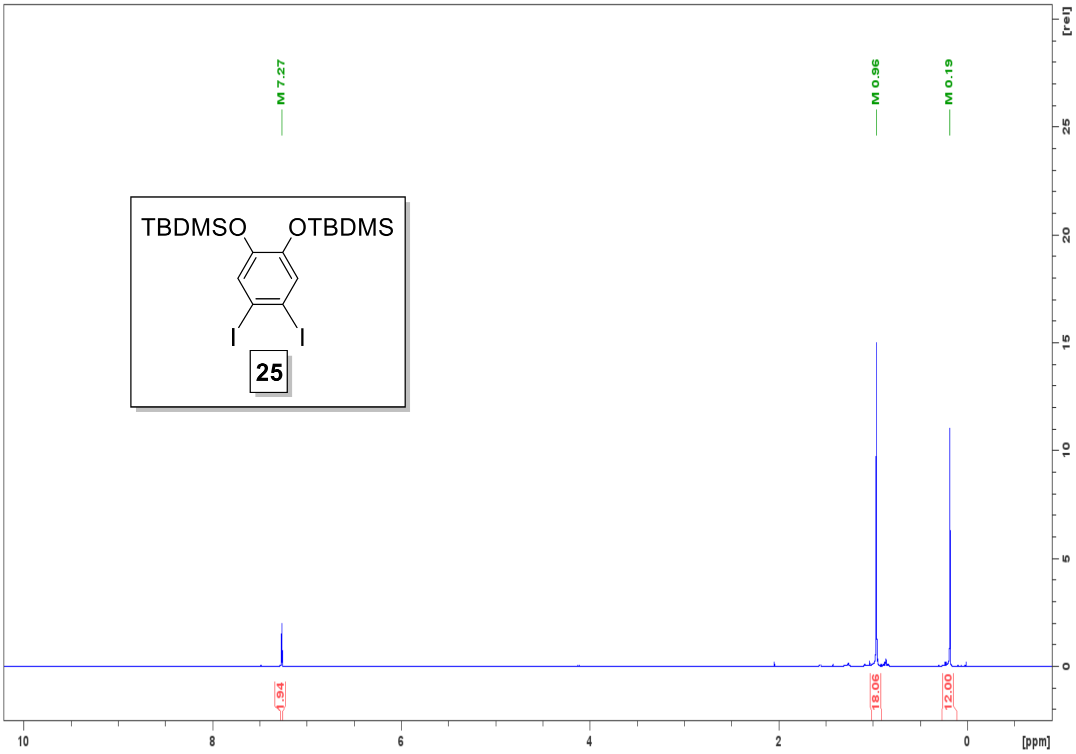
5
4
3
2
1
0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M 0.19
TBDMSO
OTBDMS
I
I
25
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18.06
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10
8
6
4
2
0
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[rel]
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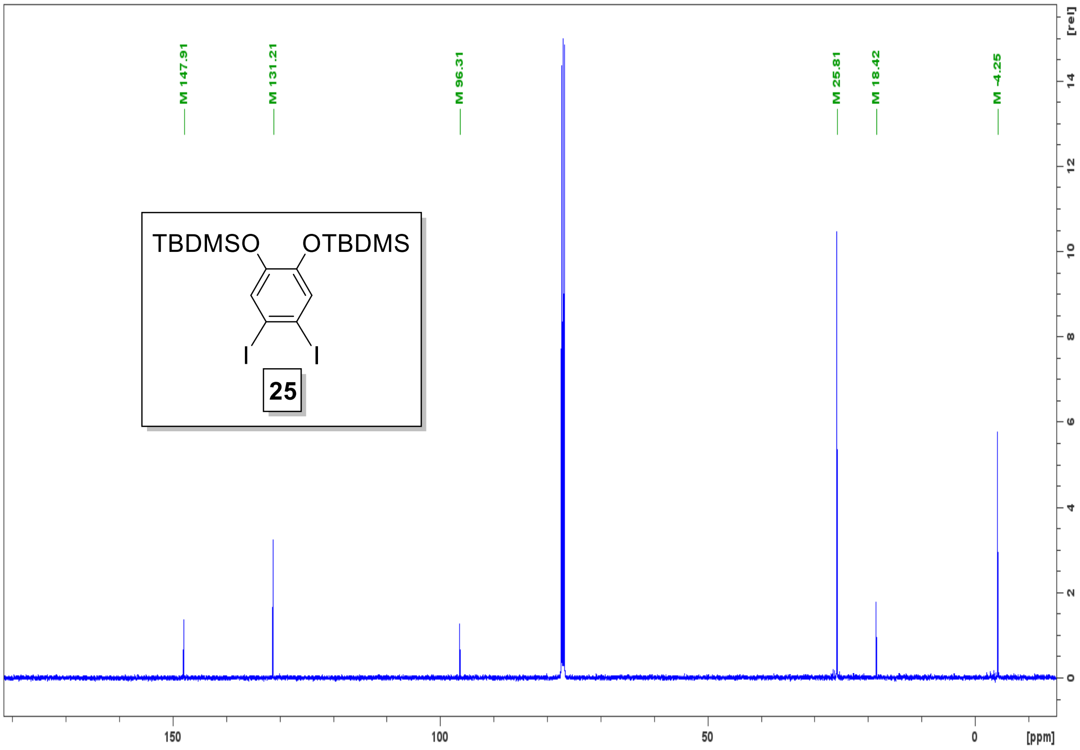
10
15
20
25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M 131.21
M 96.31
M 25.81
M 18.42
M -4.25
TBDMSO
OTBDMS
I
I
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100
50
0
[ppm]
[rel]
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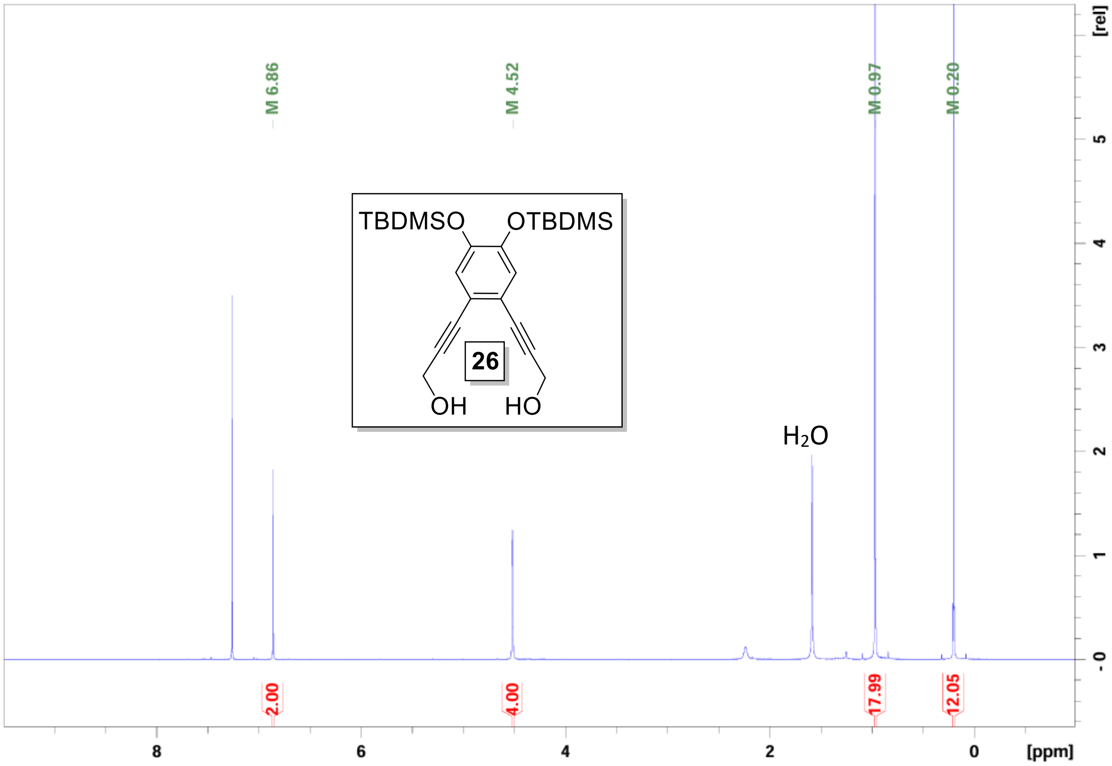
6
8
10
12
14


M 6.86
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M 0.20
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OTBDMS
26
OH
HO
H2O
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17.99
12.05
8
6
4
2
0
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[rel]
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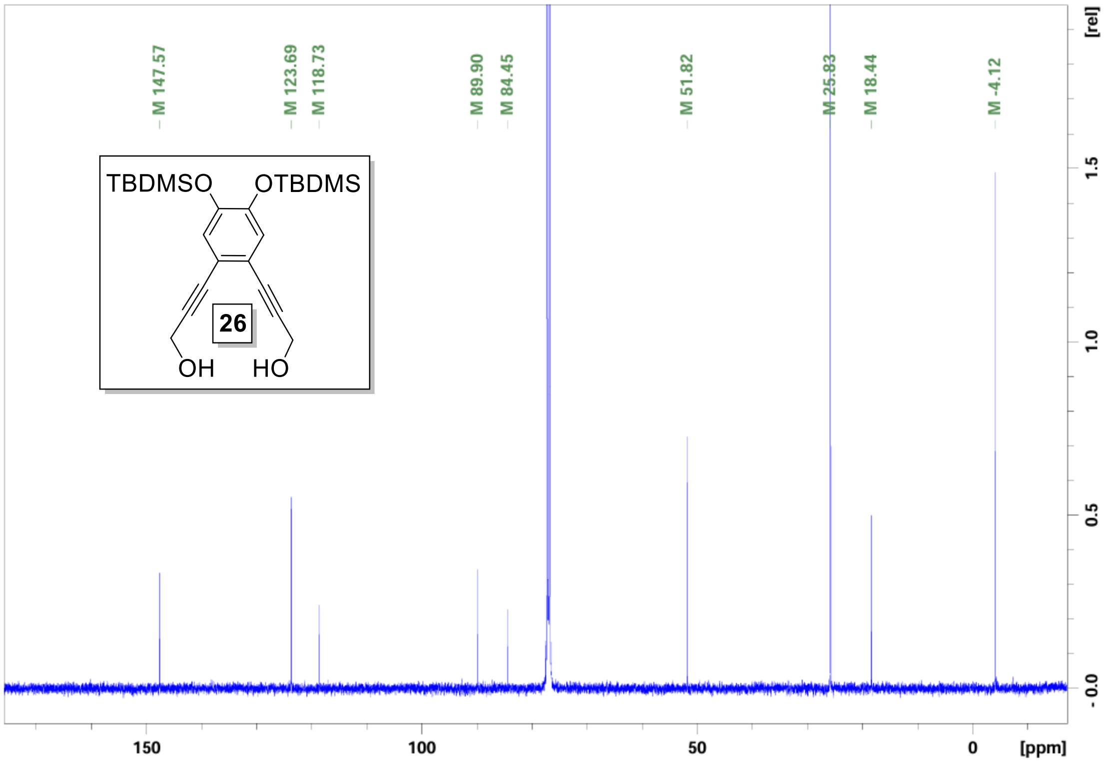
4
3
2
1
0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M 25.83
M 18.44
M -4.12
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OTBDMS
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HO
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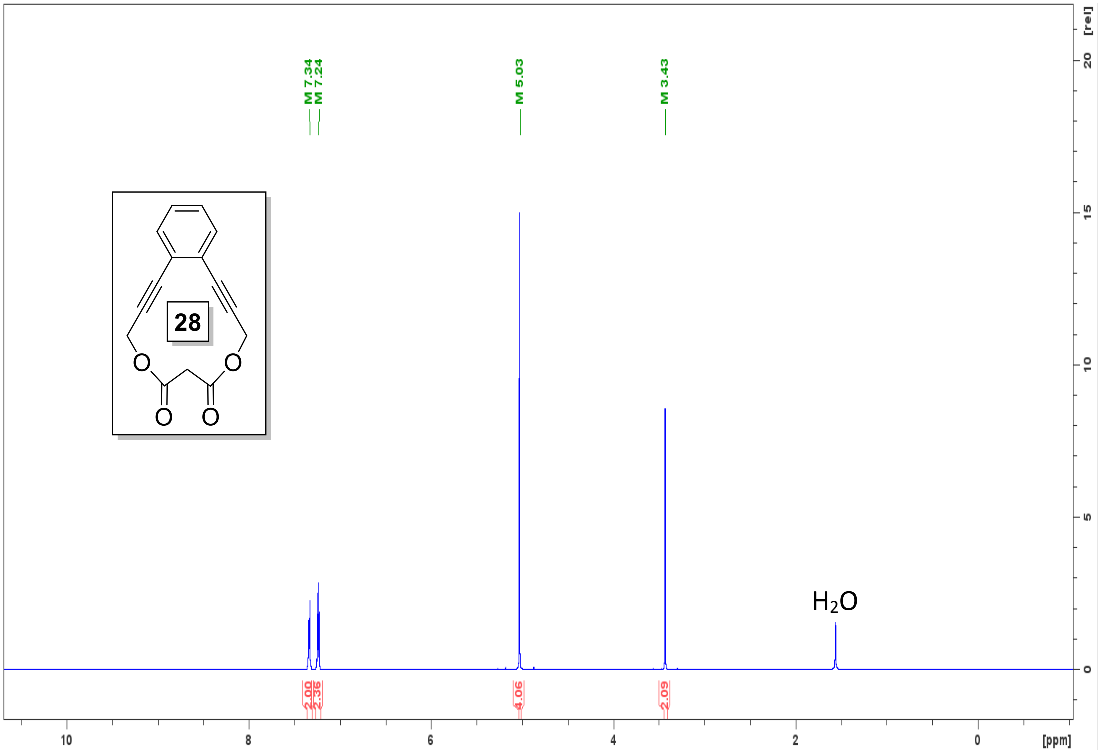
M 7.34
M 7.24
M 5.03
M 3.43
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H₂O
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2.09
10
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6
4
2
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15
10
5
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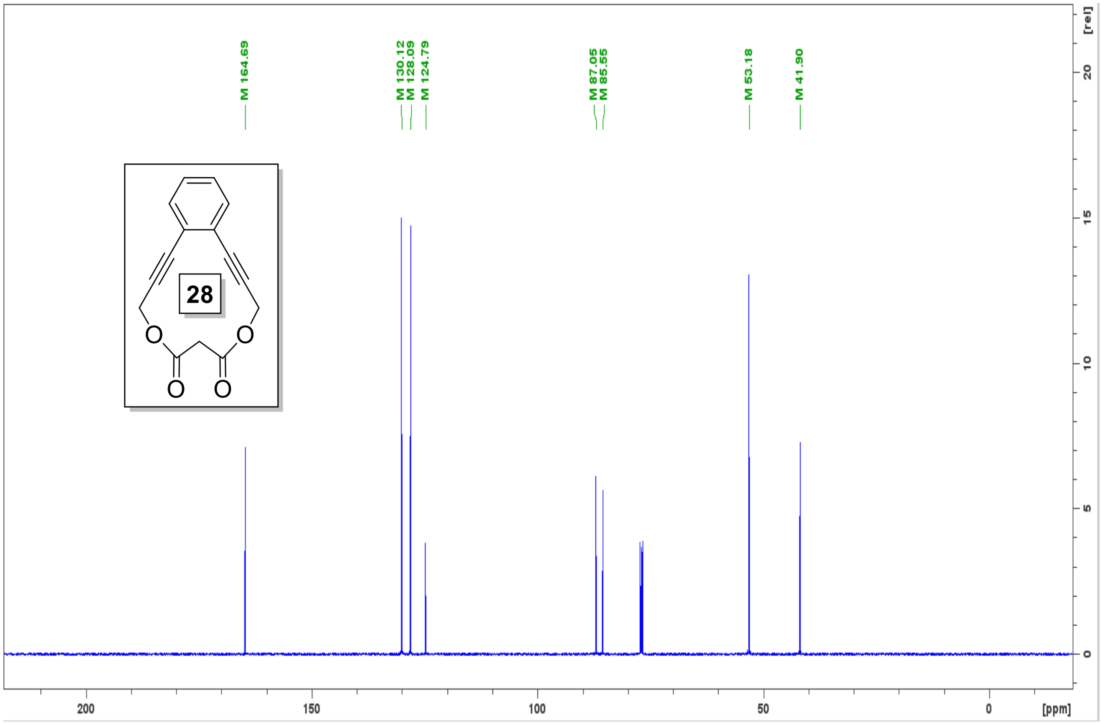
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M 130.12
M 128.09
M 124.79
M 87.05
M 85.55
M 53.18
M 41.90
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[ppm]
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5
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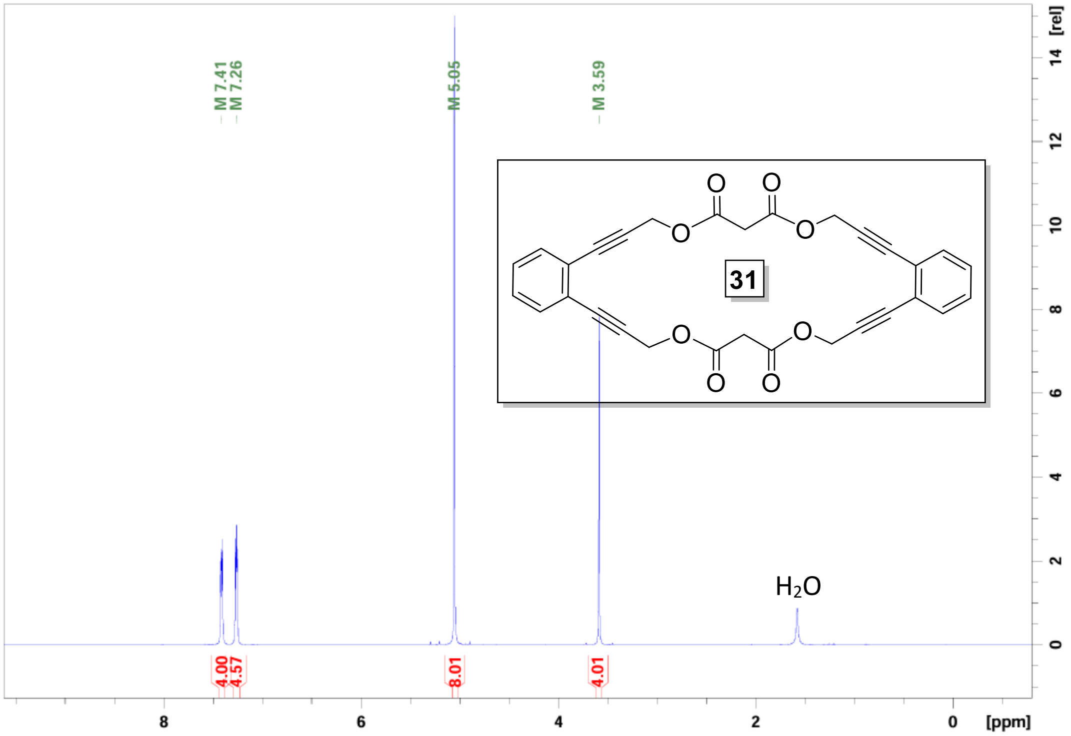
M 7.41
M 7.26
M 5.05
M 3.59
31
H2O
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4.57
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4.01
8
6
4
2
0
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10
8
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4
2
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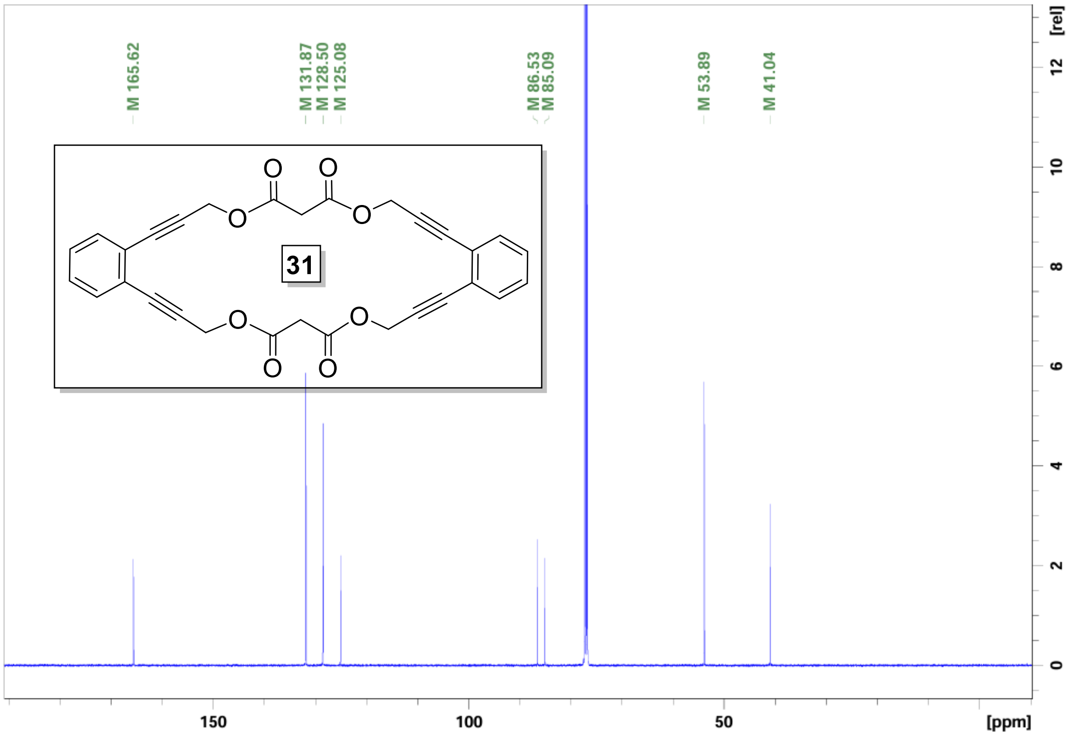
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M 53.89
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6
4
2
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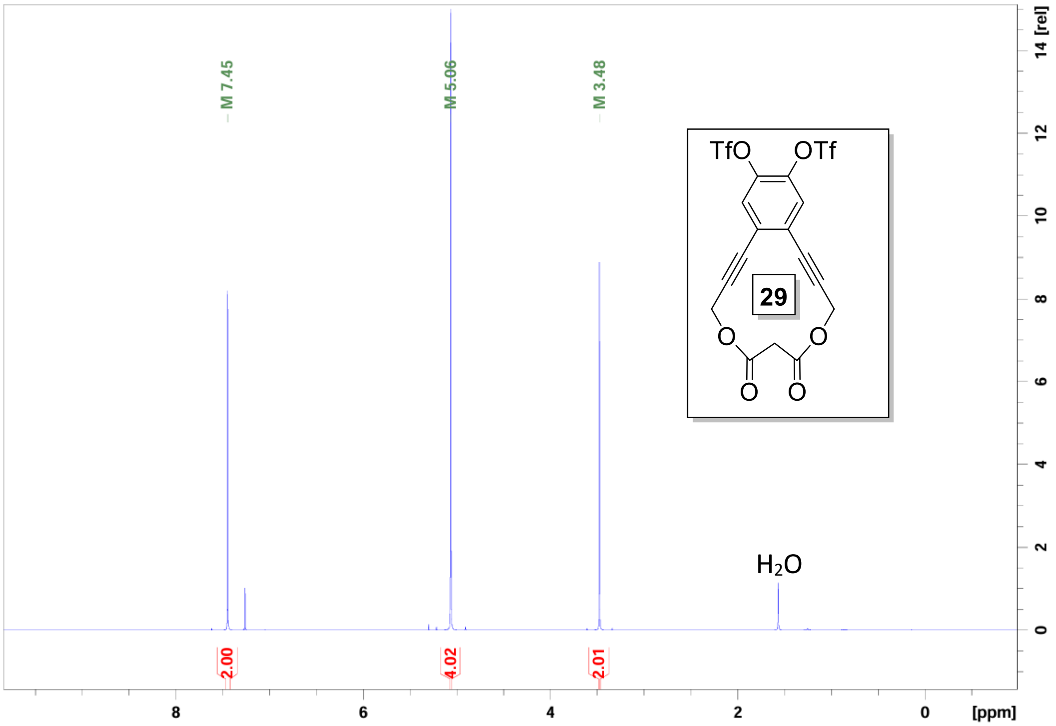
[rel]


M 7.45
M 5.06
M 3.48
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4.02
2.01
H2O
TfO
OTf
29
O
O
O
O
14 [rel]
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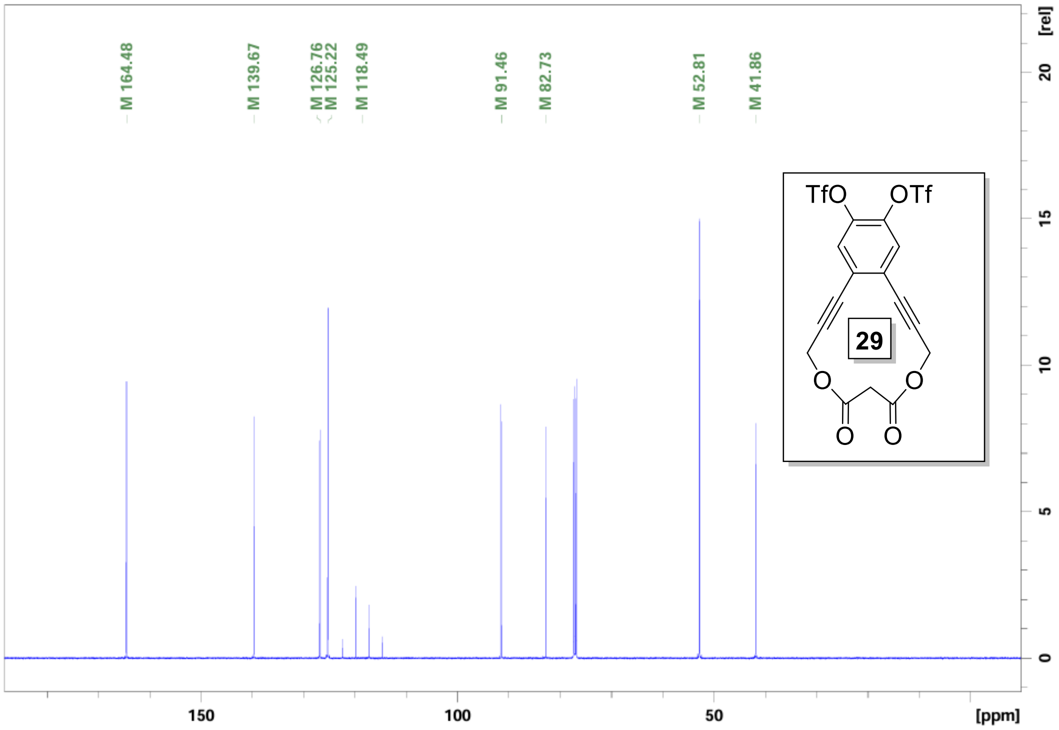
10
8
6
4
2
0
8
6
4
2
0
[ppm]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M 118.49
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M 82.73
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M 41.86
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29
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O
O
O
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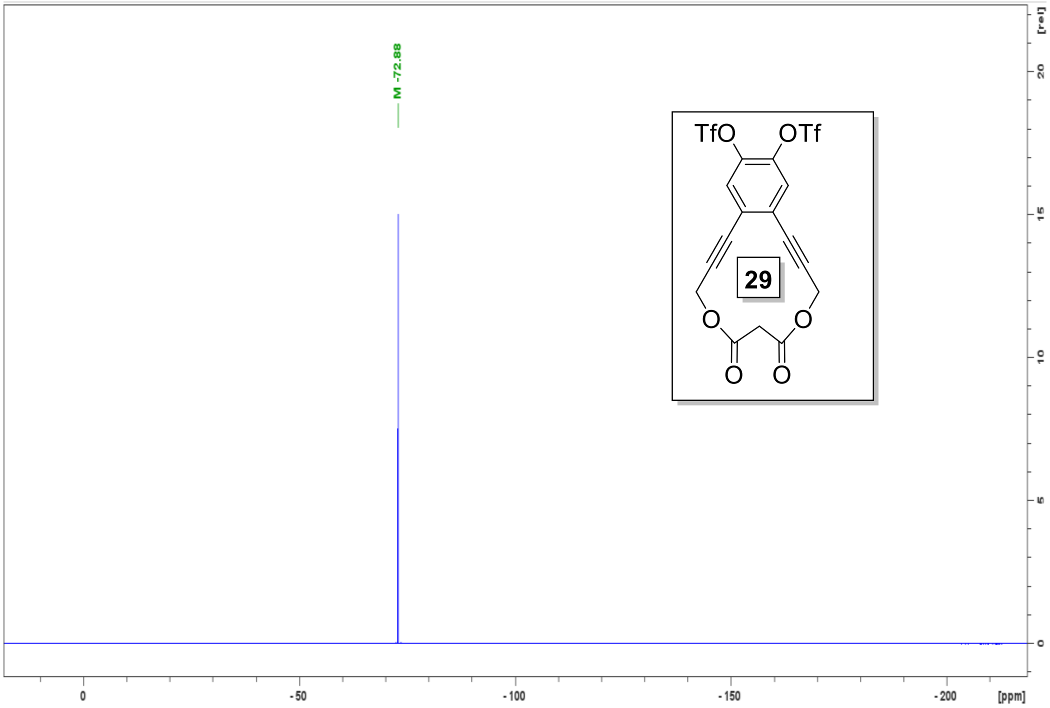
[ppm]


M -72.88
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OTf
29
O
O
O
O
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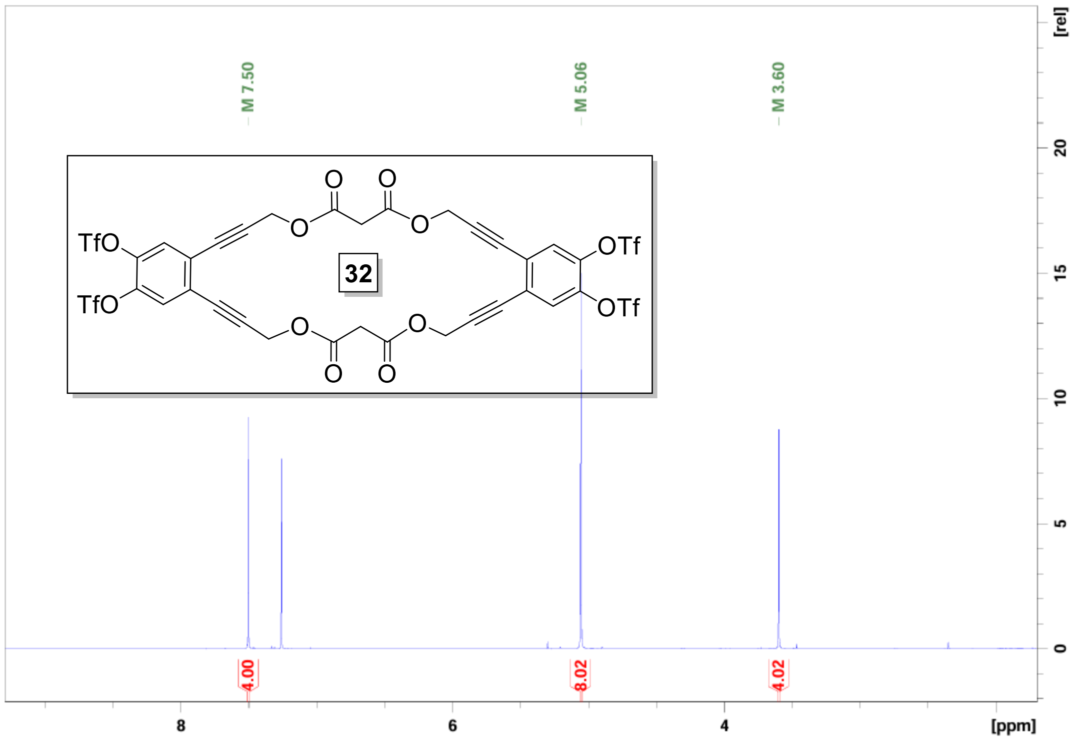
-50
-100
-150
-200
[ppm]
0
5
10
15
20
[rel]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M 5.06
M 3.60
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TfO
OTf
OTf
4.00
8.02
4.02
8
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[rel]
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15
10
5
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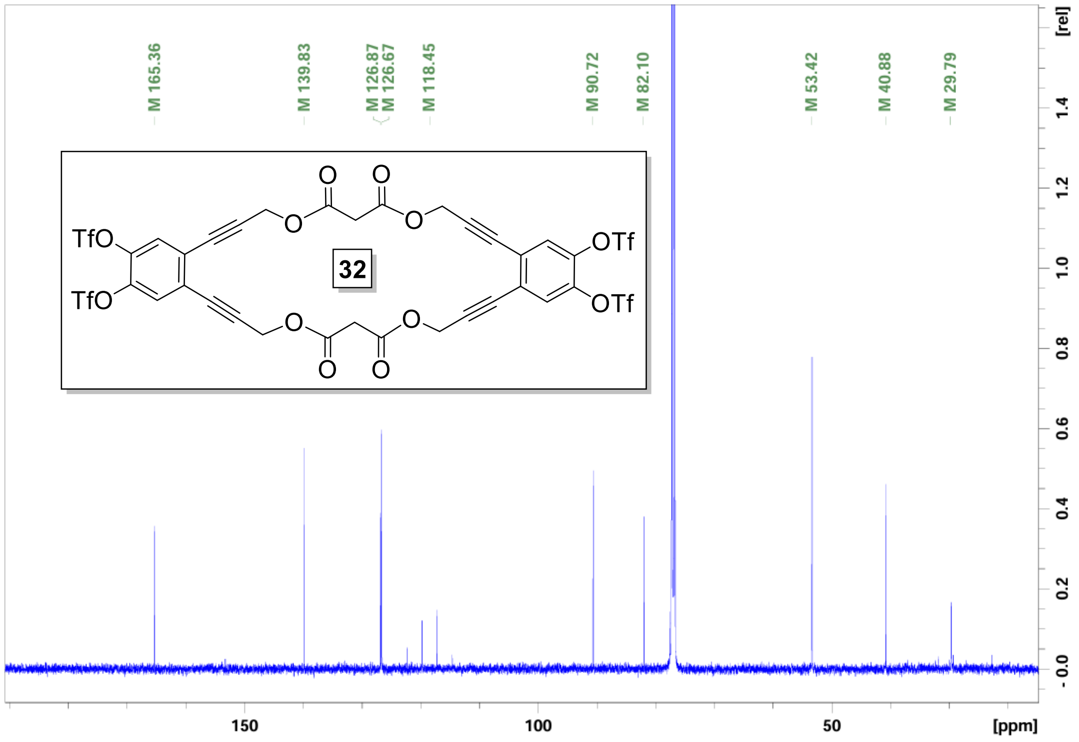
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M 139.83
M 126.87
M 126.67
M 118.45
M 90.72
M 82.10
M 53.42
M 40.88
M 29.79
32
TfO
TfO
OTf
OTf
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100
50
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[rel]
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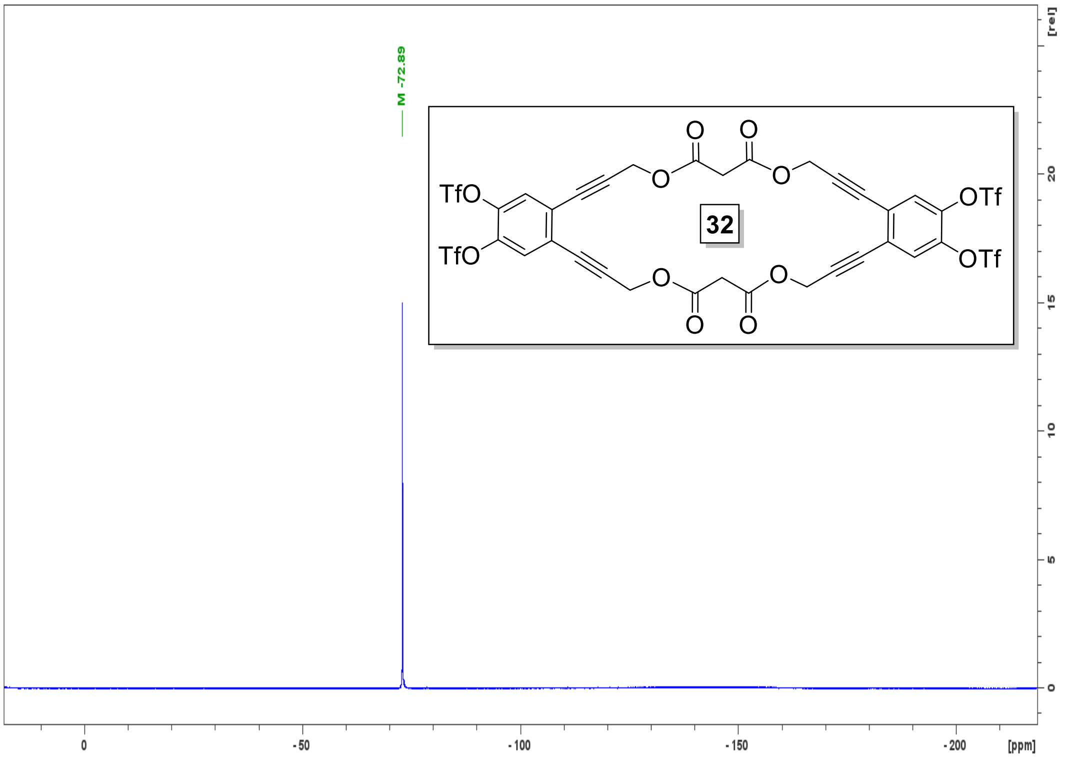
0.2
0.0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[rel]
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15
10
5
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0
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-150
-200
[ppm]
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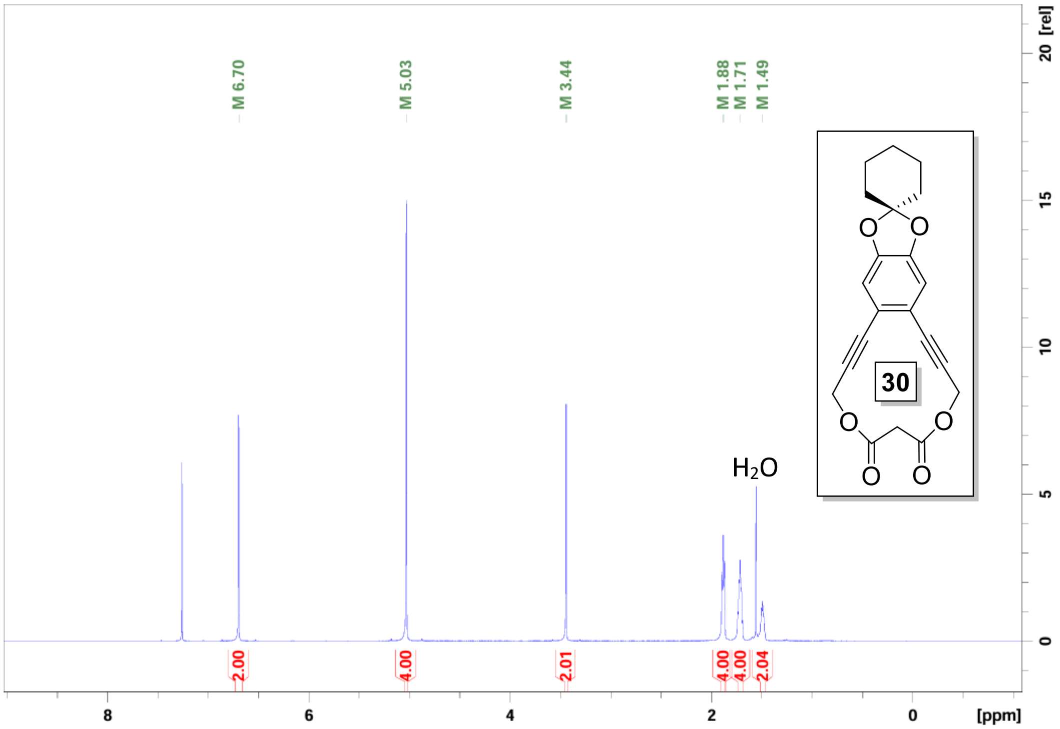
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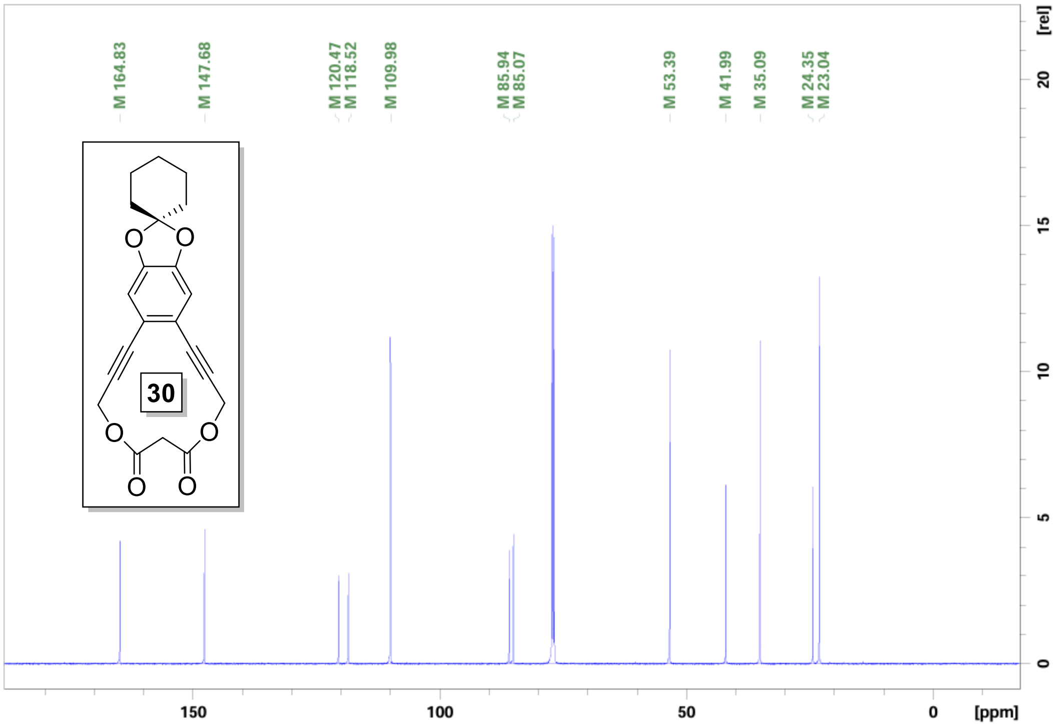
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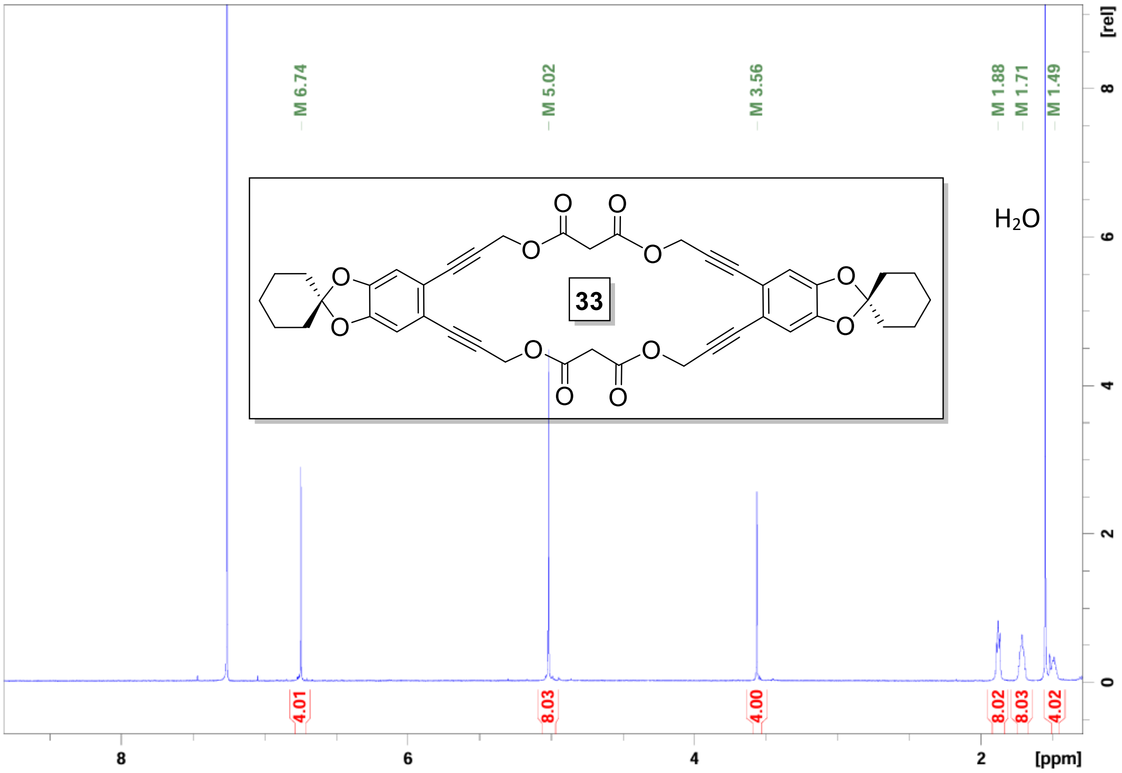
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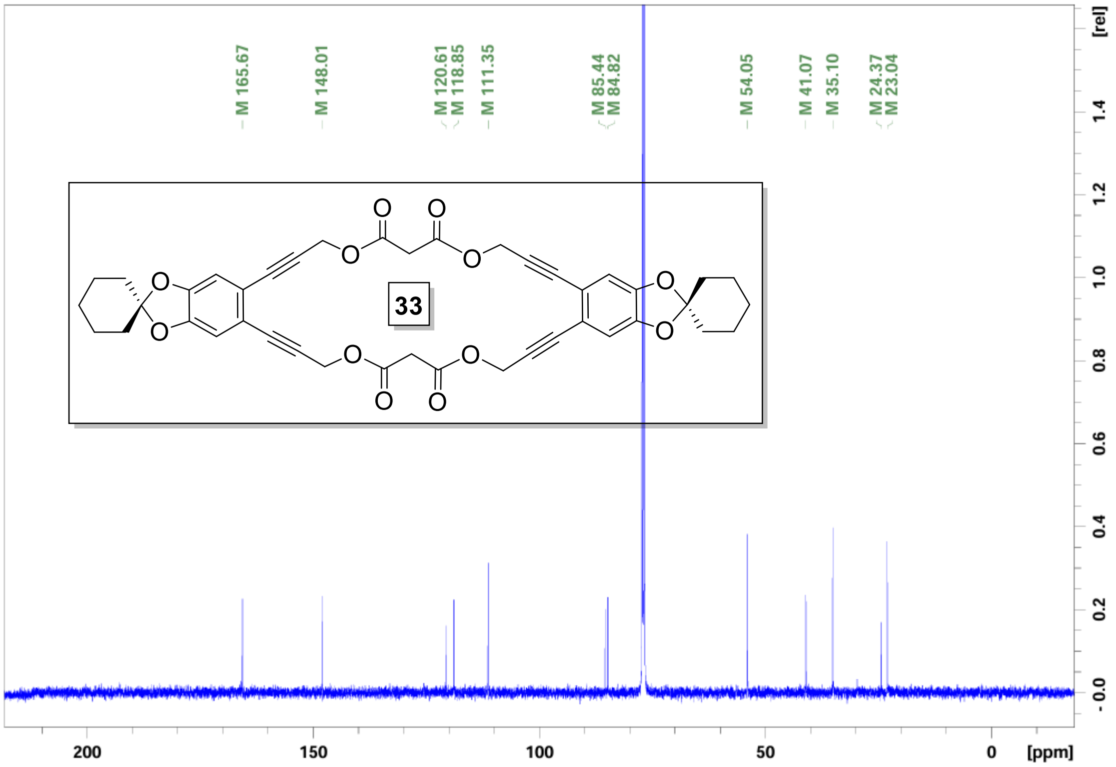
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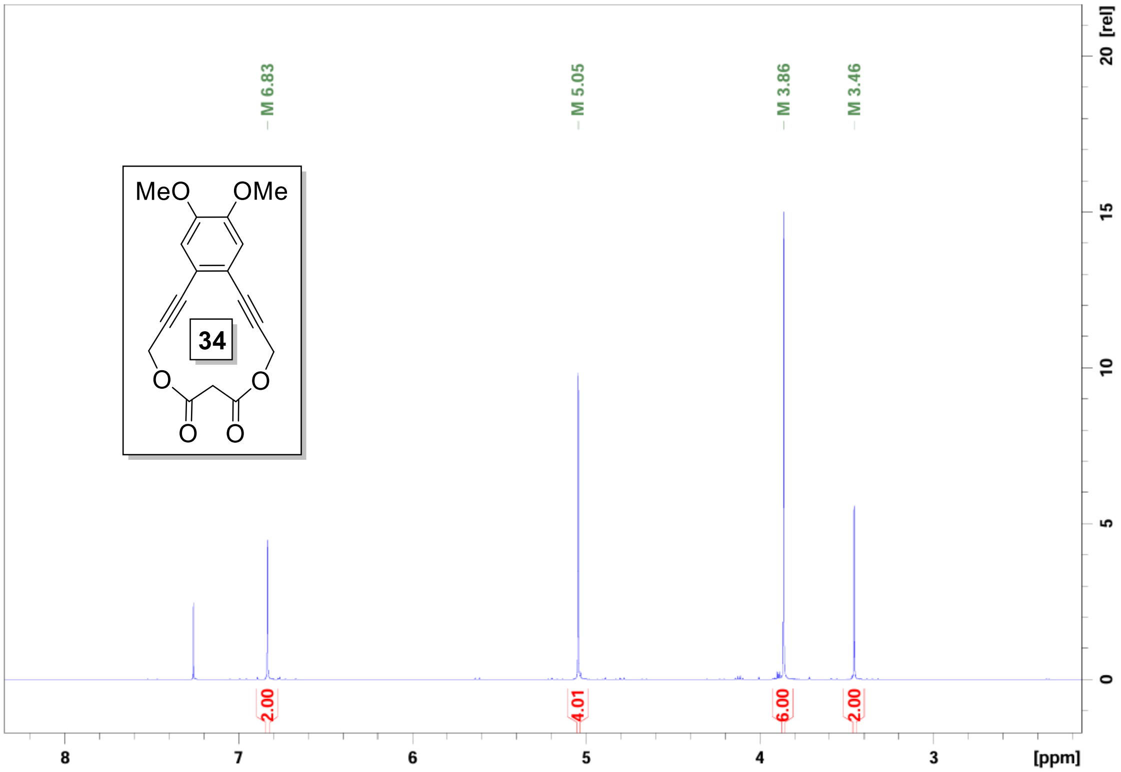
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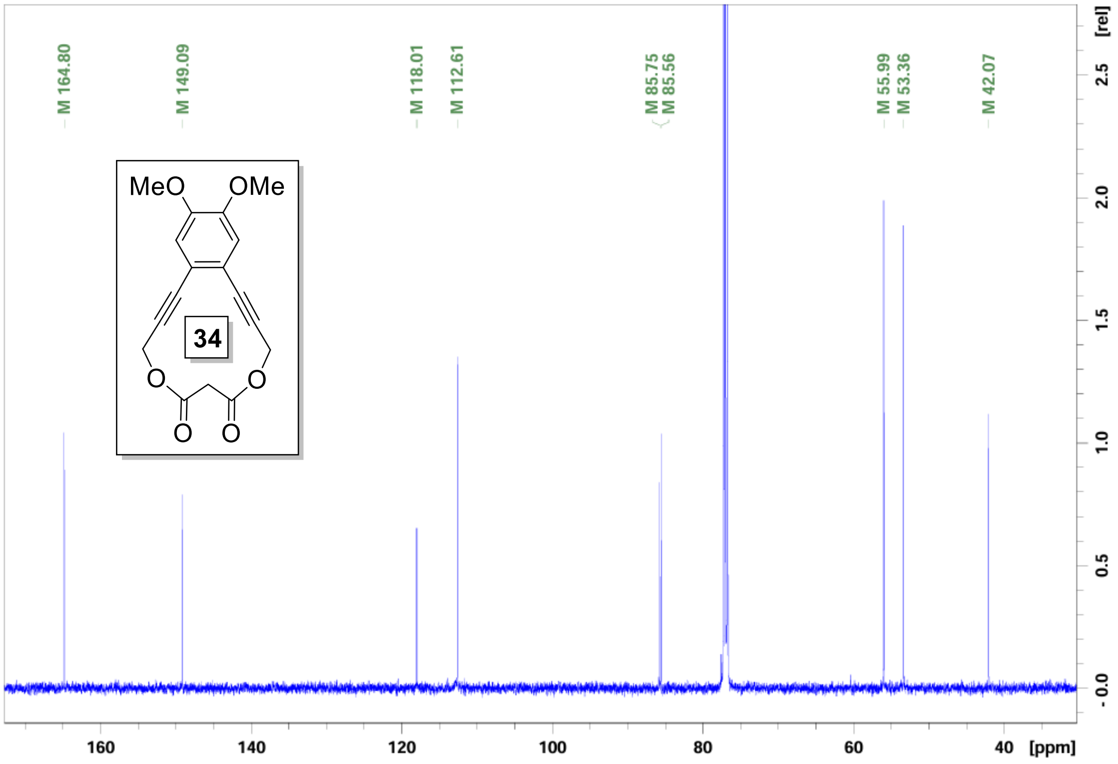
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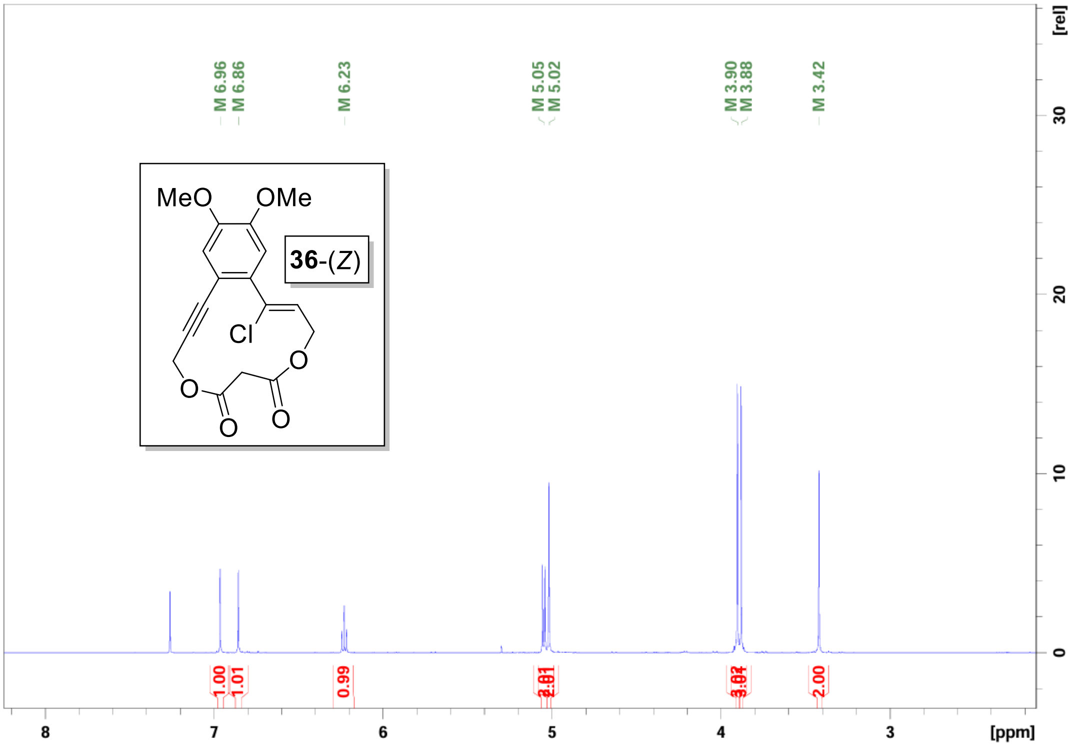
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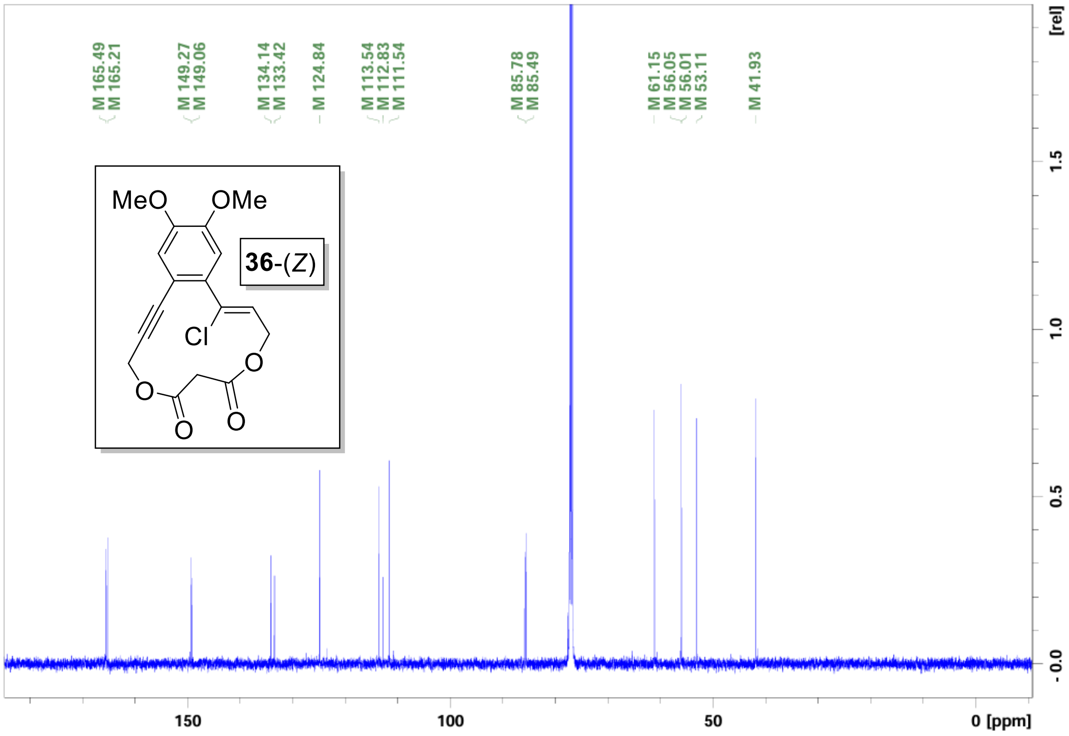
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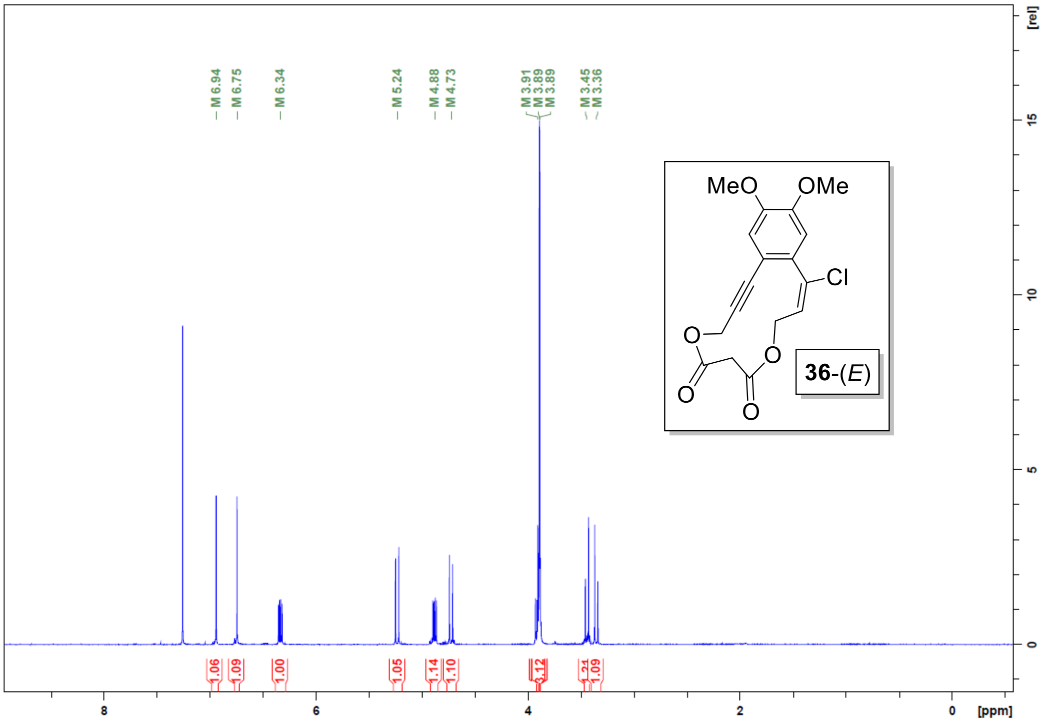
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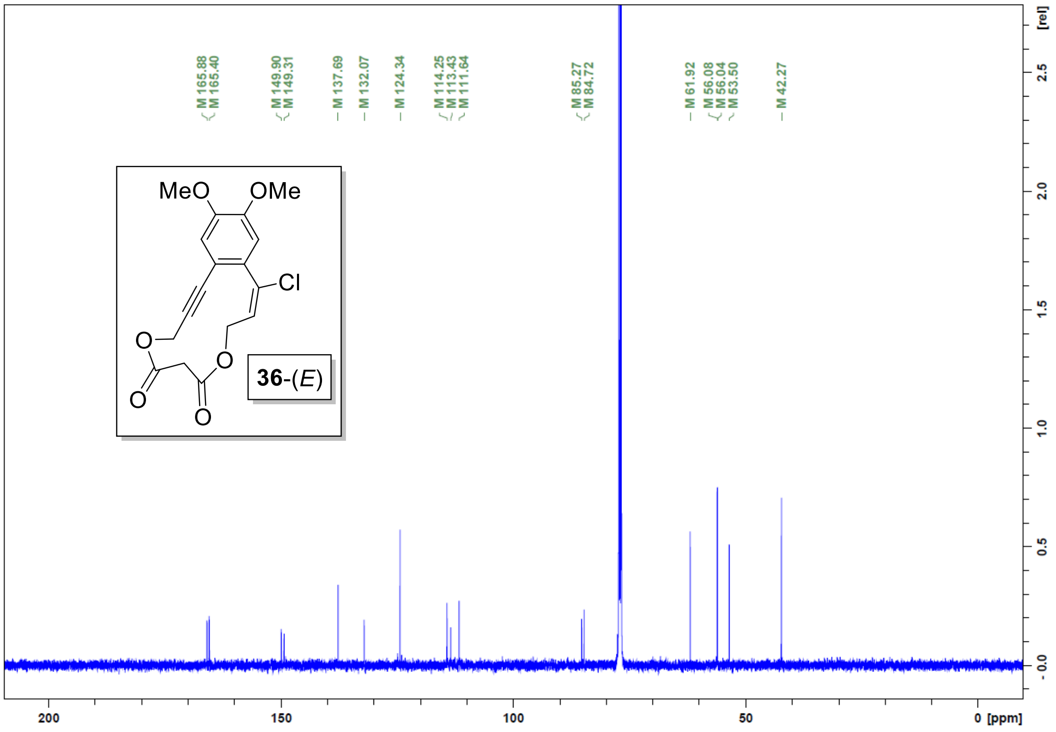
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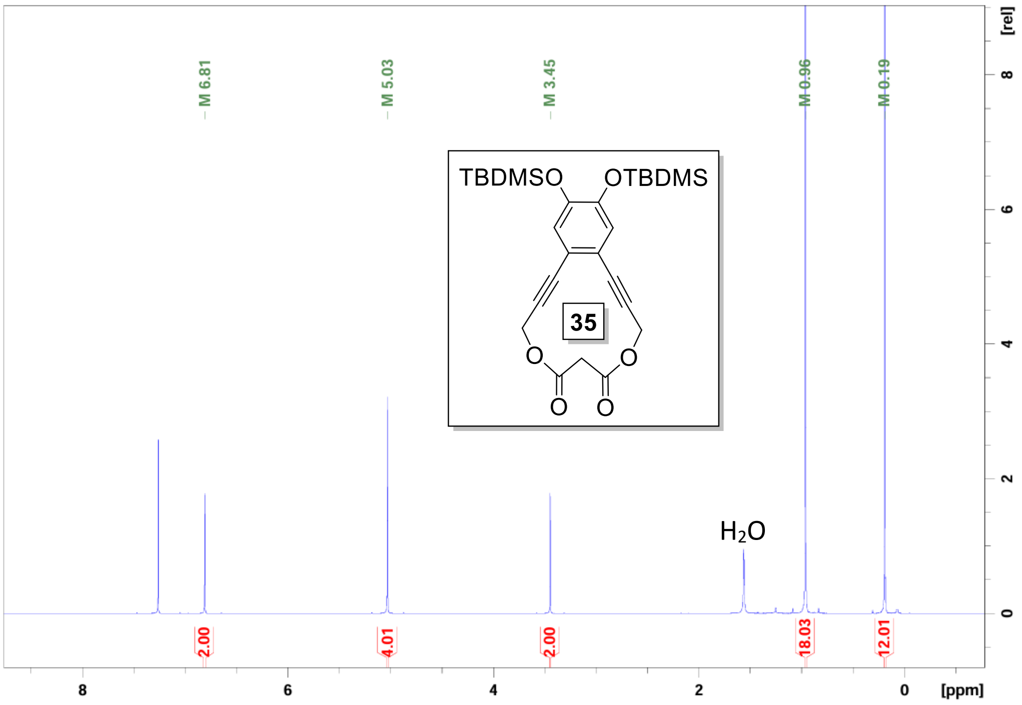
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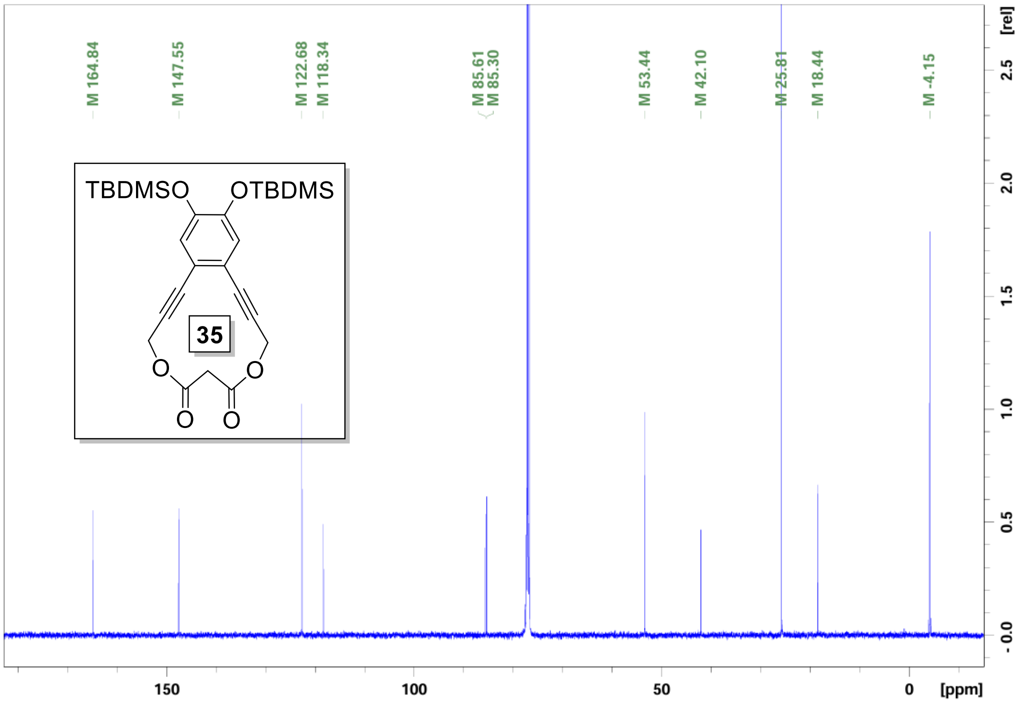
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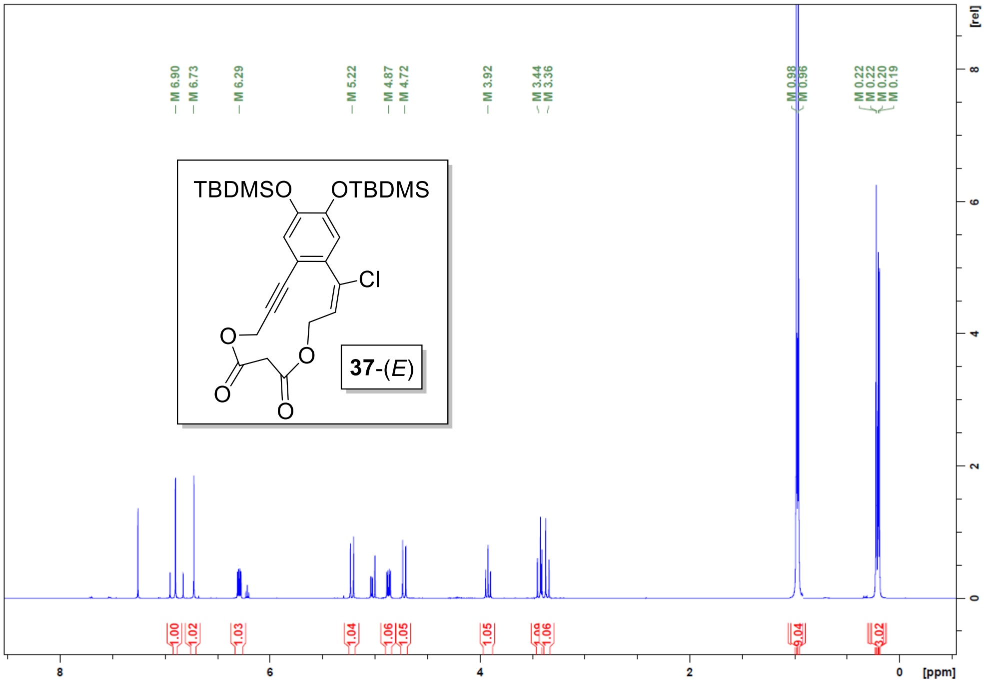
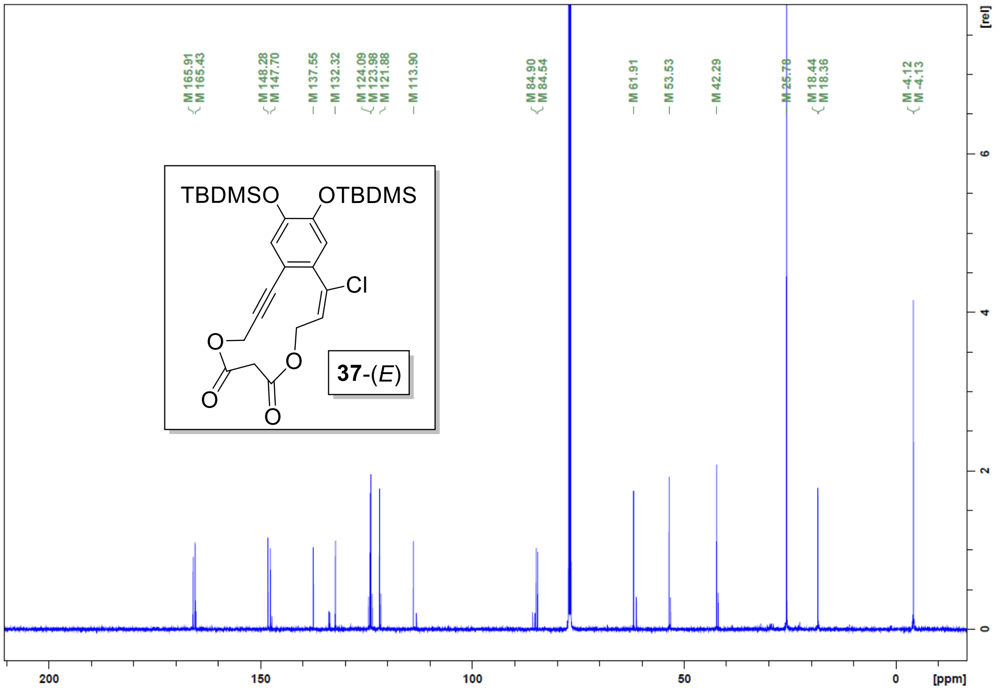
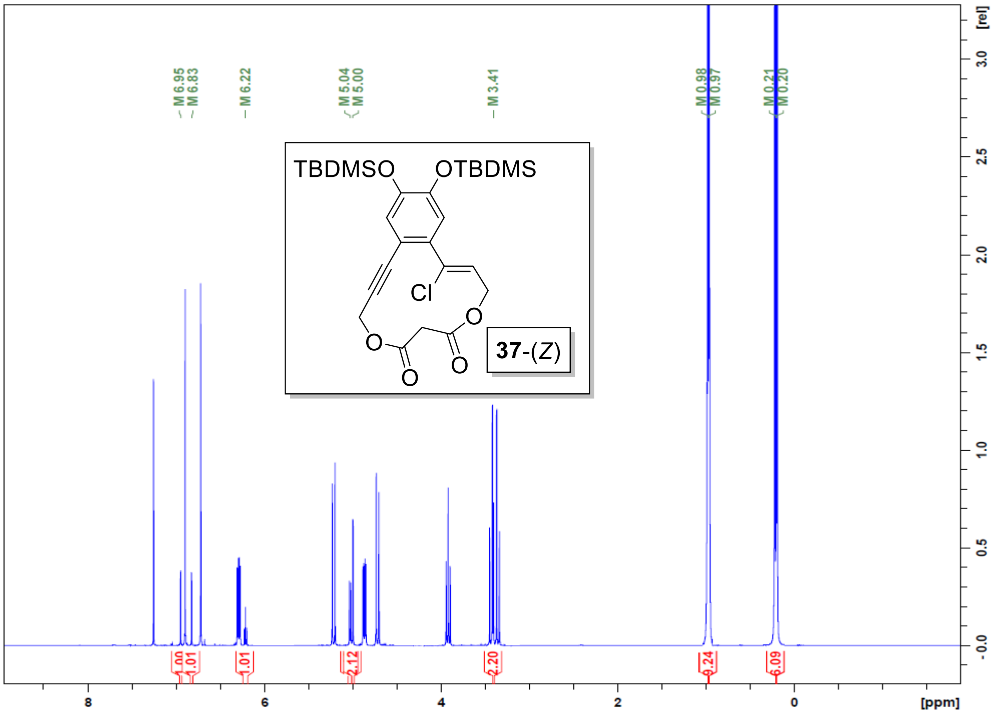


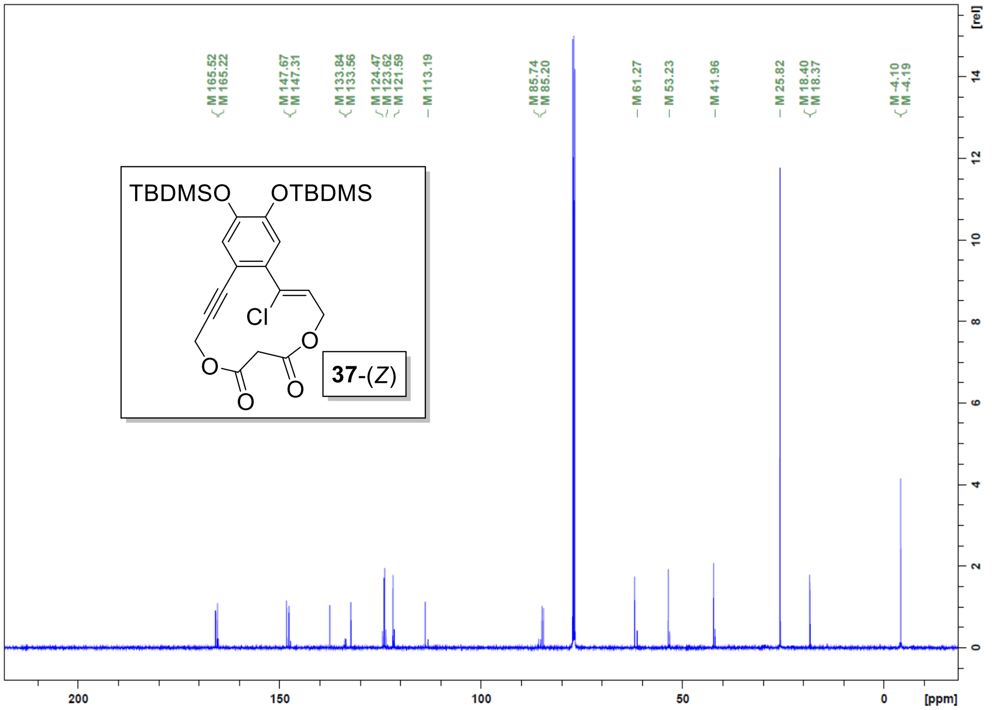
Note: Inseparable mixture. Marked peaks (major set) belong to compound **37**-(*E*). The minor set of peaks (unmarked) belong to stereoisomer **37**-(*Z*).



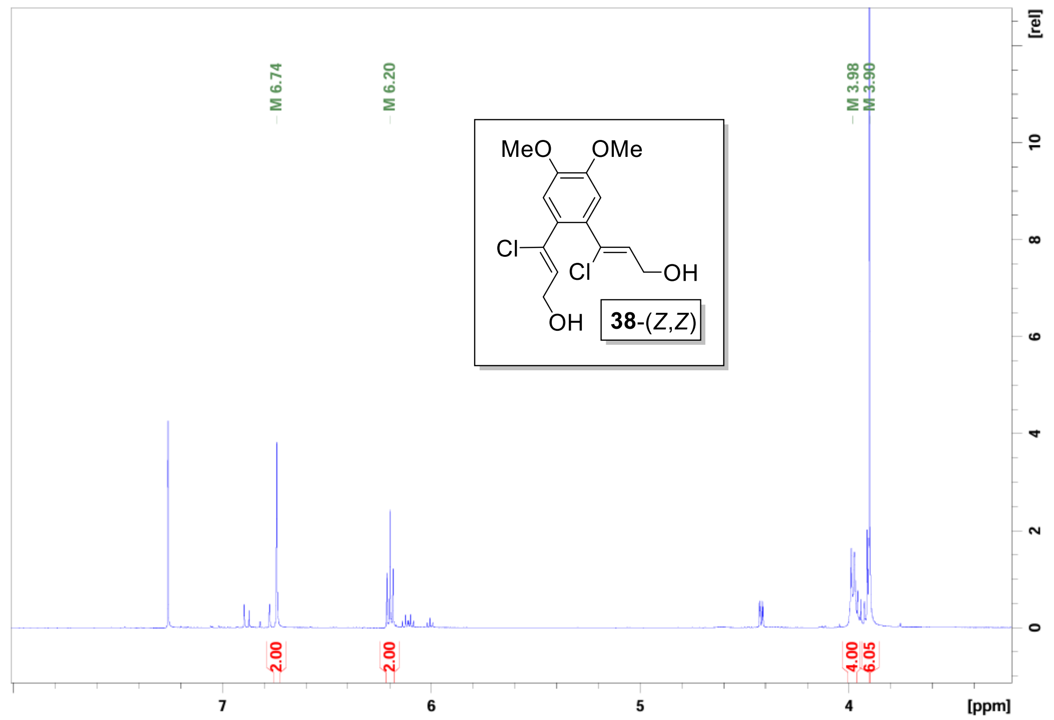
Note: Inseparable mixture. Marked peaks (major set) belong to compound **37**-(*E*). The minor set of peaks (unmarked) belong to stereoisomer **37**-(*Z*).



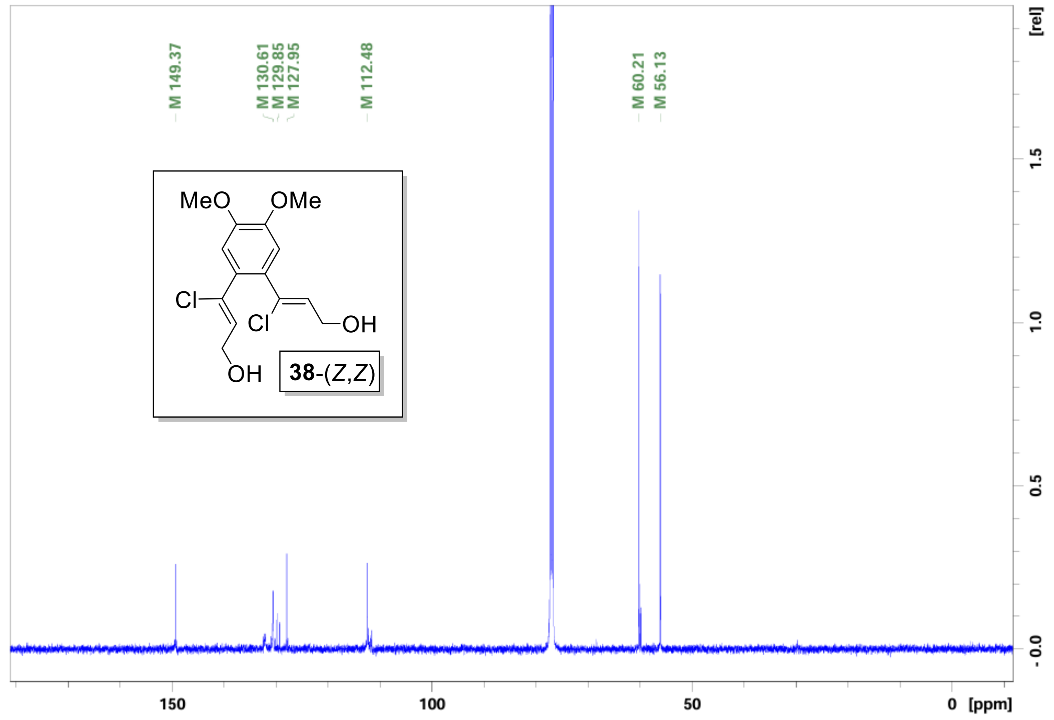
Note: Inseparable mixture. Marked peaks (minor set) belong to compound **37**-(*Z*). The major set of peaks (unmarked) belong to stereoisomer **37**-(*E*).



Note: Inseparable mixture. Marked peaks (minor set) belong to compound **37**-(*Z*). The major set of peaks (unmarked) belong to stereoisomer **37**-(*E*).



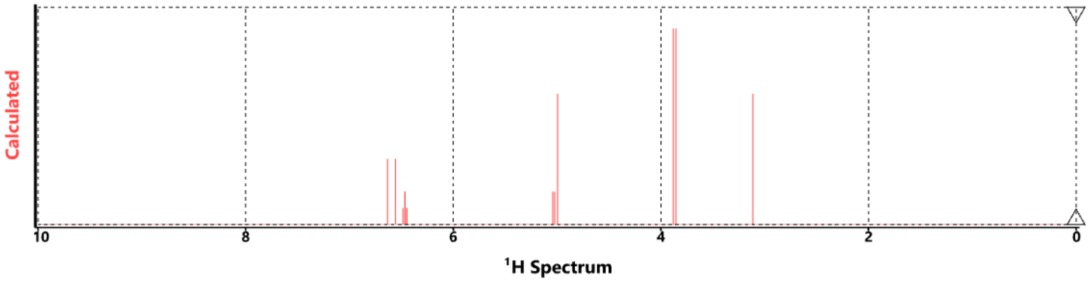
Note: Inseparable mixture. Marked peaks (major set) belong to compound **38**-(*Z*,*Z*). The minor sets of peaks (unmarked) belong to stereoisomers **38**-(*E*,*E*) and **38**-(Z,*E*).



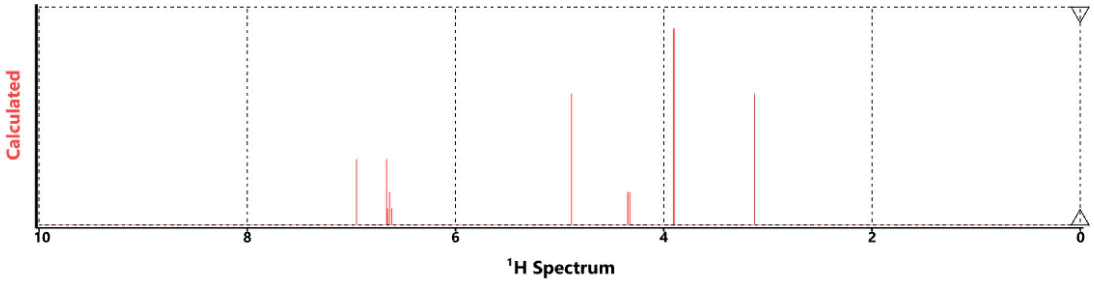
Note: Inseparable mixture. Marked peaks (major set) belong to compound **38**-(*Z*,*Z*). The minor sets of peaks (unmarked) belong to stereoisomers **38**-(*E*,*E*) and **38**-(Z,*E*).

III. ^{1}H NMR Simulations of Compounds 36-(*Z*) and 36-(*E*)

- ^{1}H NMR simulated spectrum of compound **36**-(*Z*):



- ^{1}H NMR simulated spectrum of compound **36**-(*E*):



Notes:

- NMR simulations were carried out in SPARTAN'24, using model ωB97X-D/6-31G*.
- Simulations for **37**-(*E*) and **37**-(*Z*) stereoisomers were not possible due to lacking the appropriate parameters for silicon (Si).

IV. Single-Crystal X-Ray Diffraction Data

Table S1. Selected crystal data for compounds **8**, **14**, **16**, **28**, **29**, **30**, **31**, **32**, **34**, **35**, **37-**(*E*) and **38-**(*Z*,*Z*).

Identification code	**8**	**14**	**16**	**28**	**29**	**30**
Empirical formula (cryst. unit)	$C_{14}H_8F_6O_8S_2$	$C_{12}H_{12}I_2O_2$	$C_{18}H_{18}O_4$	$C_{15}H_{10}O_4$	$C_{17}H_8F_6O_{10}S_2$	$C_{21}H_{18}O_6$
Formula weight (cryst. unit)	482.32	442.03	298.34	254.24	550.35	366.37
Temperature (K)	180.00(10)	100(2)	100(2)	149.99(10)	100(2)	293(2)
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	tetragonal
Space group	-P32"c	P 2_1/c	P 2_1/c	P 2_1/c	-P2ybc	I 41/a
a (Å)	18.7218(4)	9.8726(4)	26.8172(12)	10.2640(3)	14.1102(5)	26.2190(4)
b (Å)	18.7218(4)	10.1182(5)	6.2237(3)	4.6033(2)	5.6464(2)	26.2190(4)
c (Å)	9.4802(2)	12.6876(5)	18.7127(7)	24.6429(8)	25.3583(9)	10.3673(2)
α, b, c (°)	90, 90, 120	90, 93.083(4), 90	90, 99.189(4), 90	90, 90.708(3), 90	90, 93.723(3), 90	90, 90, 90
Volume (Å^3)	2877.69(11)	1265.57(10)	3083.1(2)	1164.25(7)	2016.08(12)	7126.9(3)
Z	6	4	8	4	4	16
ρ_{calc}g/cm^3	1.663	2.320	1.259	1.450	1.813	1.366
μ/mm^{-1}	3.466	38.906	0.737	0.883	3.472	0.836
F(000)	1450.987	824	1216	528	1104	3072
Reflections collected	10336	4618	18806	3574	7425	13591
Independent reflections	1999 [R_{int} = 0.0385]	2492 [R_{int} = 0.0893]	6004 [R_{int} = 0.0842]	1288 [Rint = 0.0319]	3820 [R_{int} = 0.0285]	3501 [R_{int} = 0.0279]
Data/restraints/parameters	1999/0/137	2492/0/145	6004/0/397	1288/0/173	3820/0/317	3501/0/244
Goodness-of-fit on F^2	1.0428	1.169	1.079	1.111	1.086	1.065
Final R index values [I>=2σ (I)]	R_{obs} = 0.0594, wR_{obs} = 0.1743	R_{obs} = 0.1129, wR_{obs} = 0.2600	R_{obs} = 0.0812, wR_{obs} = 0.2318	R_{obs} = 0.0365, wR_{obs} = 0.0842	R_{obs} = 0.0340, wR_{obs} = 0.0893	R_{obs} = 0.0434, wR_{obs} = 0.1116
Final R index values [all data]	R_{all} = 0.0623, wR_{all} = 0.1769	R_{all} = 0.1163, wR_{all} = 0.2712	R_{all} = 0.1083, wR_{all} = 0.2643	R_{all} = 0.0399, wR_{all} = 0.0865	R_{all} = 0.0423, wR_{all} = 0.0952	R_{all} = 0.0524, wR_{all} = 0.1179

$^a R = \Sigma||Fo|-|Fc|| / \Sigma|Fo|$, $wR = \{\Sigma[w(|Fo|^2 - |Fc|^2)^2] / \Sigma[w(|Fo|^4)]\}^{1/2}$ and $^b w=1/[\sigma^2(Fo^2)+(mP)^2+nP]$ where $P=(Fo^2+2Fc^2)/3$ and m and n are constants.

Table S1 (continued). Selected crystal data for compounds **8**, **14**, **16**, **28**, **29**, **30**, **31**, **32**, **34**, **35**, **37-**(*E*) and **38-**(*Z*,*Z*).

Identification code	**31**	**32***	**34**	**35**	**37-**(*E*)	**38-**(*Z*,*Z*)
Empirical formula (cryst. unit)	$C_{30}H_{20}O_8$	$C_{34}H_{16}F_{12}O_{20}S_4$	$C_{17}H_{14}O_6$	$C_{27}H_{38}O_6Si_2$	$C_{27}H_{39}ClO_6Si_2$	$C_{14}H_{16}Cl_2O_4$
Formula weight (cryst. unit)	508.48	1100.70	314.29	514.77	551.22	319.18
Temperature (K)	150.15	293(2)	293(2)	298(2)	100.00(2)	293(2)
Crystal system	triclinic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	P-1	'C2/c'	$P2_12_12_1$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a (Å)	4.9784(3)	44.719(3)	7.2063(3)	6.6012(3)	18.961(3)	11.3695(4)
b (Å)	9.4845(5)	5.5125(6)	8.3188(4)	9.5836(5)	8.0956(10)	7.1981(2)
c (Å)	13.8410(8)	16.5460(10)	24.7645(9)	45.8856(19)	19.913(2)	37.3231(14)
α, b, c (°)	107.549(5), 97.168(5), 99.712(5)	90, 94.745(6), 90	90, 90, 90	90, 90.243(4), 90	90, 97.868(13), 90	90, 95.476(3), 90
Volume (Å^3)	603.37(6)	4064.9(6)	1484.58(11)	2902.8(2)	3027.9(6)	3040.54(18)
Z	1	4	4	4	4	8
ρ_{calc}g/cm^3	1.399	1.851	1.406	1.178	1.209	1.403
μ/mm^{-1}	0.852	3.504	0.906	0.158	2.174	3.938
F(000)	264	2272	656	1104	1176	1344
Reflections collected	3470	12882	5890	20960	24560	10222
Independent reflections	2021 [R_{int} = 0.0348]	3614 [R_{int} = 0.0447]	2580 [R_{int} = 0.0293]	6890 [R_{int} = 0.0899]	6261 [R_{int} = 0.2029]	5412 [R_{int} = 0.0860]
Data/restraints/parameters	2021/0/172	3614/14/344	2580/0/208	6890/0/316	6261/29/329	5412/3/361
Goodness-of-fit on F^2	1.008	1.309	1.054	1.052	1.351	1.041
Final R index values [I>=2σ (I)]	R_{obs} = 0.0408, wR_{obs} = 0.0915	R_{obs} = 0.1063, wR_{obs} = 0.2970	R_{obs} = 0.0359, wR_{obs} = 0.0876	R_{obs} = 0.0679, wR_{obs} = 0.1598	R_{obs} = 0.1885, wR_{obs} = 0.4577	R_{obs} = 0.1071, wR_{obs} = 0.2963
Final R index values [all data]	R_{all} = 0.0656, wR_{all} = 0.1026	R_{all} = 0.1263, wR_{all} = 0.3224	R_{all} = 0.0401, wR_{all} = 0.0918	R_{all} = 0.1294, wR_{all} = 0.2068	R_{all} = 0.2529, wR_{all} = 0.5330	R_{all} = 0.1340, wR_{all} = 0.3363

$^{a}R = \Sigma||Fo|-|Fc|| / \Sigma|Fo|$, $wR = \{\Sigma[w(|Fo|^2 - |Fc|^2)^2] / \Sigma[w(|Fo|^4)]\}^{1/2}$ and $^{b}w=1/[\sigma^2(Fo^2)+(mP)^2+nP]$ where $P=(Fo^2+2Fc^2)/3$ and m and n are constants.

[*Solvent co-crystallizing with the compound]

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