Total synthesis of Helioxanthin, Retrohelioxanthin, and analogs via Photo-Dehydro-Diels-Alder reaction as key step

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Supporting Information

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1. General Information

The reagents and solvents were purchased in the highest available purity from commercial suppliers. All reagents were used without additional purification and the solvents were distilled prior to utilization. Dry glassware and a nitrogen atmosphere were used for the reactions. Reactions were monitored by TLC plates from Merck. The flash column chromatography (FSC) to clean the crude products was performed on silica gel from VWR (40−63 μm). The specific solvent mixtures are listed in the experimental details. Routine NMR spectra were recorded on the 400 MHz spectrometers (Bruker Avance) with appropriate deuterated solvents. As internal standards, the solvent peaks of $CDCl_3$ and MeOH were used. If the conzentration of the sample was too low the spectra were recorded on the 500/600 MHz spectrometer (Bruker Avance). Chemical sifts are reported in ppm and the coupling constants are given in hertz (s^{-1}). Mass spectra were recorded with GC-EI-Q-TOF 7250 A, Agilent, Waldbronn, Germany or LC-ESI-Q-TOF maXis, Bruker Daltonics GmbH & Co KG Bremen, Germany. All photoreactions were performed under flow conditions using an annular continuous-flow reactor developed in our group. A low-pressure mercury discharge lamp from PHILIPS was used as ultraviolet B (UVB) light source (PL-L 36 W, 41.7 cm × 3,9 cm × 1.8 cm, base 2G11). For more information about the flow reactor, see previous publication.[1] Infrared (IR) spectra were measured with the FT-IR spectrometer Spectrum Two from *PerkingElmer*. The samples were measured with an Attenuated Total Reflection (ATR) sample holder.

1 Experimental procedures and characterization

1.1 General Procedure 1 (GP1) for the synthesis of the diester with Steglich esterification

The corresponding alcohol, acid and dimethylaminopyridin (DMAP) were dissolved in dry dichloromethane (DCM). Then diisopropylcarbodiimide (DIC) was added to the reaction. This reaction mixture was stirred for 3 days at room temperature. After completion the reaction was quenched with water and 1 M HCl. After that the aqueous phase was extracted several times with DCM. The combined organic phase was washed with brine and dried with $MgSO_4$. Then the solvent was removed and the crude product was purified by flash chromatography on silica gel.

1.2 General Procedure 2 (GP2) for the synthesis of the PDDA reactant with a Sonogashira cross coupling

The flask were loaded with the reactant, palladium catalyst and copper iodide and dissolved in trimethylamine (TEA). Then the triethyl orthopropiolate was added and the mixture was stirred at the specified temperature until the whole educt was converted. After completion the TEA was removed and the residual was acidified with 1 M HCl and stirred for at least four hours. The aqueous phase was extracted several times with EA several times. The combined organic phase was washed with brine and dried with $MgSO_4$. Then the solvent was removed and the crude product was purified by flash chromatography on silica gel.

1.3 General Procedure 3 (GP3) for the cleavage of the Ethylpropiolate

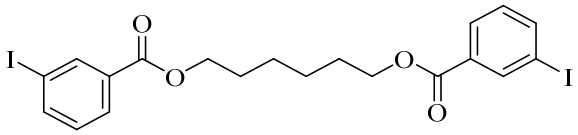
The reactant was dissolved in 45 mL/g of methanol. Then an aqueous sodium hydroxide solution 25 mL/g, 1 M was added and stirred till full consumption of the educt. This aqueous solution was extracted with DCM and then acidified with a 1 M HCl. Thereafter the phase was extracted with EA, this organic phase was washed with brine and dried with $MgSO_4$. Then the solvent was removed and the product can be used in the next steps without further purification.

1.4 General Procedure 4 (GP4) for the PDDA reaction

The PDDA reactant was dissolved in DCM. Then the mixture was pumped by using a HPLC pump through a photo reactor and irradiated with UVB-light. When the reaction was finished the reactor was

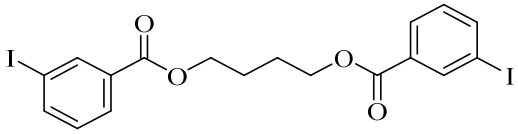
washed with an additional volume of DCM and after the solvent was removed, the product was purified by flash chromatography on silica gel.

1.5 Hexane-1,6-diyl bis(3-iodobenzoate) (4a)



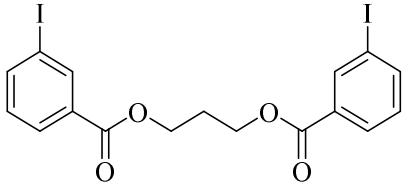
According the **GP1** Hexane-1,6-diol (476.5 mg, 4.0 mmol, 1.0 eq.), 3-Iodobenzoic acid **3a** (2.0 g, 8.1 mmol, 2.0 eq.) and DMAP (49.3 mg, 403.2 µmol, 0.1 eq.) were dissolved in 30 mL dry DCM. Then DIC (1.87 mL, 12.1 mmol, 3.0 eq.) was added. The crude product was purified by flash chromatography on silica gel with DCM. The product **4a** was isolated (1.57 g, 67 %) as a withe solid. Mp. 78.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (t, J = 1.3 Hz, 2H), 7.99 (dt, J = 7.9, 1.3 Hz, 2H), 7.88 (dt, J = 7.9, 1.3 Hz, 2H), 7.18 (t, J = 7.9 Hz, 2H), 4.35 – 4.31 (m, 4H), 1.85 – 1.77 (m, 4H), 1.54 – 1.51 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 141.8, 138.6, 132.4, 130.2, 128.9, 93.9, 65.4, 28.7, 25.9. HRMS (ESI) $[M+H]^+$ calculated for $C_{20}H_{21}I_2O_4$ 578.9524, found 578.9509. IR (ATR, cm^{-1}) 2939, 2856, 1703, 1564, 1481, 1417, 1277, 1263, 1128, 969, 738, 704.

1.6 Butane-1,4-diyl bis(3-iodobenzoate) (4b)



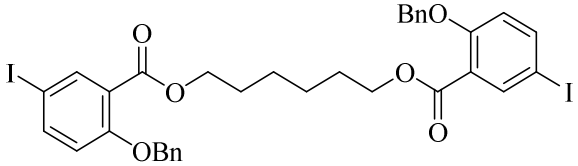
According the **GP1** Butane-1,4-diol (89.0 µL, 1.0 mmol, 1.0 eq.), 3-Iodobenzoic acid **3a** (500.0 mg, 2.0 mmol, 2.0 eq.) and DMAP (24.6 mg, 101.0 µmol, 0.1 eq.) were dissolved in 10 mL dry DCM. Then DIC (473.5 µL, 3.0 mmol, 3.0 eq.) was added. The crude product was purified by flash chromatography on silica gel with DCM. The product **4b** was isolated (289.0 mg, 52 %) as a withe solid. Mp. 129.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (t, J = 1.4 Hz, 2H), 8.00 (dt, J = 7.8, 1.4 Hz, 2H), 7.89 (dt, J = 7.9, 1.4 Hz, 2H), 7.18 (t, J = 7.8 Hz, 2H), 4.42 – 4.38 (m, 4H), 1.96 – 1.92 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 142.0, 138.6, 132.2, 130.2, 128.9, 94.0, 64.9, 25.6. HRMS (ESI) $[M+H]^+$ calculated for $C_{18}H_{17}I_2O_4$ 550.9211, found 550.9194. IR (ATR, cm^{-1}) 2960, 1695, 1563, 1419, 1277, 1263, 1242, 1124, 965, 741, 702.

1.7 Propane-1,3-diyl bis(3-iodobenzoate) (4c)



According the **GP1** Propane-1,3-diol (146.0 µL, 2.0 mmol, 1.0 eq.), 3-Iodobenzoic acid **3a** (1.0 g, 4.0 mmol, 2.0 eq.) and DMAP (24.6 mg, 201.6 µmol, 0.1 eq.) were dissolved in 20 mL dry DCM. Then DIC (1.3 mL, 8.1 mmol, 4.0 eq.) was added. The crude product was purified by flash chromatography on silica gel with DCM. The product **4c** was isolated (673.0 mg, 62 %) as a withe solid. Mp. 59.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (t, J = 1.7 Hz, 2H), 7.98 (dt, J = 7.8, 1.4 Hz, 2H), 7.87 (dt, J = 7.9, 1.5 Hz, 2H), 7.16 (t, J = 7.9 Hz, 2H), 4.49 (t, J = 6.2 Hz, 4H), 2.26 (p, J = 6.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.1, 142.0, 138.6, 132.0, 130.2, 128.9, 94.0, 62.3, 28.3. HRMS (ESI) $[M+H]^+$ calculated for $C_{17}H_{15}I_2O_4$ 536.9054, found 536.9069. IR (ATR, cm^{-1}) 2981, 2904, 1710, 1564, 1416, 1271, 1254, 1123, 1107, 1094, 743, 701.

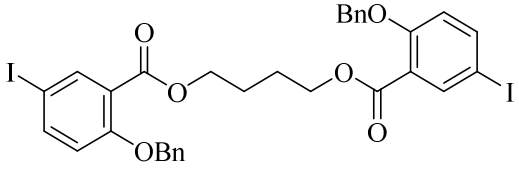
1.8 Hexane-1,6-diyl bis(2-(benzyloxy)-5-iodobenzoate) (4d)



According the **GP1** Hexane-1,6-diol (166.9 mg, 1.4 mmol, 1.0 eq.), 2-(Benzyloxy)-5-iodobenzoic acid **3b** (1.0 g, 2.8 mmol, 2.0 eq.) and DMAP (17.3 mg, 141.2 µmol, 0.1 eq.) were dissolved in 20 mL dry DCM. Then DIC (656.0 µL, 4.2 mmol, 4.0 eq.) was added. The crude product was purified by flash

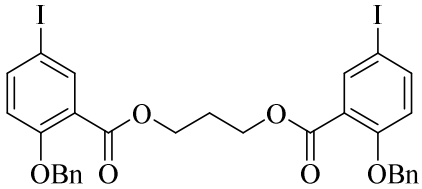
chromatography on silica gel with DCM. The product **4d** was isolated (786.0 mg, 70 %) as a withe solid. Mp. 90.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 2.3 Hz, 2H), 7.67 (dd, J = 8.8, 2.4 Hz, 2H), 7.46 – 7.42 (m, 4H), 7.38 – 7.34 (m, 4H), 7.32 – 7.27 (m, 2H), 6.77 (d, J = 8.7 Hz, 2H), 5.13 (s, 4H), 4.28 – 4.24 (m, 4H), 1.67 (s, 4H), 1.39 – 1.34 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 158.0, 141.8, 140.2, 136.3, 128.7, 128.2, 127.2, 123.5, 116.1, 82.4, 70.9, 65.4, 28.6, 25.8. HRMS (ESI) $[M+H]^+$ calculated for $C_{34}H_{33}I_2O_6$ 791.0361, found 791.0348. IR (ATR, cm^{-1}) 2949, 1719, 1699, 1481, 1453, 1290, 1280, 1252, 1228, 1077, 737.

1.9 Butane-1,4-diyl bis(2-(benzyloxy)-5-iodobenzoate) (4e)



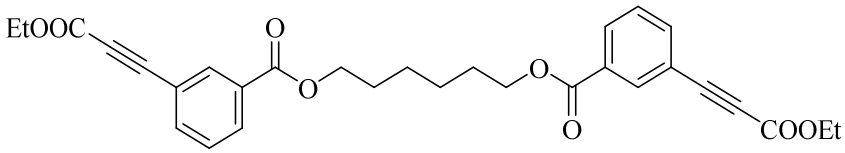
According the **GP1** Butane-1,4-diol (125.0 µL, 1.4 mmol, 1.0 eq.), 2-(Benzyloxy)-5-iodobenzoic acid **3b** (1.0 g, 2.8 mmol, 2.0 eq.) and DMAP (17.3 mg, 141.2 µmol, 0.1 eq.) were dissolved in 20 mL dry DCM. Then DIC (656.0 µL, 4.2 mmol, 4.0 eq.) was added. The crude product was purified by flash chromatography on silica gel with DCM. The product **4e** was isolated (802.0 mg, 75 %) as a withe solid. Mp. 130.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 2.3 Hz, 2H), 7.68 (dd, J = 8.8, 2.3 Hz, 2H), 7.44 – 7.41 (m, 4H), 7.38 – 7.33 (m, 4H), 7.31 – 7.27 (m, 2H), 6.77 (d, J = 8.8 Hz, 2H), 5.11 (s, 4H), 4.26 – 4.22 (m, 4H), 1.75 – 1.70 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 158.0, 141.9, 140.2, 136.2, 128.7, 128.3, 127.3, 123.2, 116.0, 82.4, 70.9, 64.9, 25.4. HRMS (ESI) $[M+H]^+$ calculated for $C_{32}H_{29}I_2O_6$ 763.0048, found 763.0058. IR (ATR, cm^{-1}) 2922, 2866, 1690, 1400, 1290, 1278, 1245, 1227, 1209, 1158, 1016, 816.

1.10 Propane-1,3-diyl bis(2-(benzyloxy)-5-iodobenzoate) (4f)



According the **GP1** Propane-1,3-diol (102.0 µL, 1.4 mmol, 1.0 eq.), 2-(Benzyloxy)-5-iodobenzoic acid **3b** (1.0 g, 2.8 mmol, 2.0 eq.) and DMAP (17.3 mg, 141.2 µmol, 0.1 eq.) were dissolved in 20 mL dry DCM. Then DIC (656.0 µL, 4.2 mmol, 4.0 eq.) was added. The crude product was purified by flash chromatography on silica gel with DCM. The product **4f** was isolated (569.0 mg, 54 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 2.4 Hz, 2H), 7.68 (dd, J = 8.8, 2.4 Hz, 2H), 7.44 – 7.41 (m, 4H), 7.37 – 7.33 (m, 4H), 7.31 – 7.27 (m, 2H), 6.77 (d, J = 8.8 Hz, 2H), 5.12 (s, 4H), 4.34 – 4.31 (m, 4H), 2.08 – 2.02 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 158.0, 142.0, 140.3, 136.2, 128.8, 128.2, 127.3, 123.0, 116.0, 82.3, 70.9, 62.0, 28.1. HRMS (ESI) $[M+H]^+$ calculated for $C_{31}H_{27}I_2O_6$ 748.9891, found 748.9874. IR (ATR, cm^{-1}) 3029, 2932, 1723, 1700, 1481, 1452, 1289, 1277, 1225, 1155, 1077, 696.

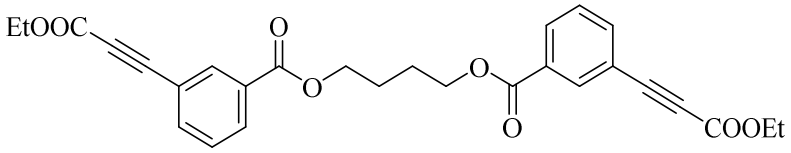
1.11 Hexane-1,6-diyl bis(3-(3-ethoxy-3-oxoprop-1-yn-1-yl)benzoate) (5a)



According the **GP2 4a** (700.0 mg, 1.2 mmol, 1.0 eq.), CuI (18.5 mg, 96.9 µmol, 0.08 eq.), $Pd(P(Ph)_3)_2Cl_2$ (68.0 mg, 96.9 µmol, 0.08 eq.) in 30 mL TEA. Then triethyl orthopropiolate (834.0 mg, 4.8 mmol, 4.0 eq.) was added and the reaction was stirred at r.t. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **5a** was isolated (559.0 mg, 89 %) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (t, J = 1.5 Hz, 2H), 8.10 (dt, J = 7.8, 1.5 Hz, 2H), 7.75 (dt, J = 7.8, 1.5 Hz, 2H), 7.46 (t, J = 7.8 Hz, 2H), 4.37 – 4.33 (m, 4H), 4.33 – 4.28 (m, 4H), 1.85 – 1.78 (m, 4H), 1.53 (p, J = 3.7 Hz, 4H), 1.38 – 1.34 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 153.9, 136.9, 134.1, 131.6, 131.2, 128.9, 120.2, 84.8, 81.4, 65.5, 62.4, 28.7, 25.9, 14.2. HRMS (ESI) $[M+H]^+$ calculated for

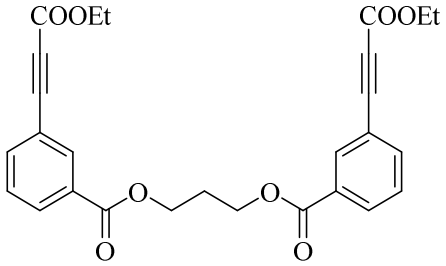
$C_{30}H_{31}O_8$ 519.2013, found 519.2021. IR (ATR, cm^{-1}) 2935, 2219, 1709, 1295, 1250, 1182, 1165, 1105, 1082, 1023, 750.

1.12 Butane-1,4-diyl bis(3-(3-ethoxy-3-oxoprop-1-yn-1-yl)benzoate) (5b)



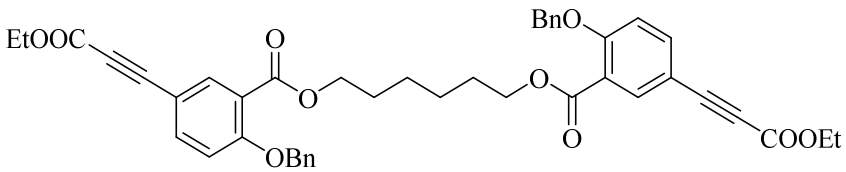
According the **GP2 4b** (320.0 mg, 1.2 mmol, 1.0 eq.), CuI (17.7 mg, 92.7 µmol, 0.08 eq.), $Pd(P(Ph)_3)_2Cl_2$ (65.1 mg, 92.7 µmol, 0.08 eq.) in 15 mL TEA. Then triethyl orthopropiolate (798.5 mg, 4.6 mmol, 4.0 eq.) was added and the reaction was stirred at r.t. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **5b** was isolated (224.0 mg, 78 %) as a yellow solid. Mp. 89.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.17 (m, 2H), 8.09 – 8.05 (m, 2H), 7.73 – 7.69 (m, 2H), 7.46 – 7.41 (m, 2H), 4.41 – 4.36 (m, 4H), 4.30 – 4.24 (m, 4H), 1.95 – 1.90 (m, 4H), 1.34 – 1.30 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 153.8, 136.9, 134.0, 131.5, 130.9, 128.9, 120.2, 84.6, 81.3, 64.9, 62.3, 25.5, 14.1. HRMS (ESI) $[M+H]^+$ calculated for $C_{28}H_{27}O_8$ 491.1700, found 491.1719. IR (ATR, cm^{-1}) 2963, 2216, 1721, 1702, 1292, 1257, 1241, 1185, 1111, 1024, 974.

1.13 Propane-1,3-diyl bis(3-(3-ethoxy-3-oxoprop-1-yn-1-yl)benzoate) (5c)



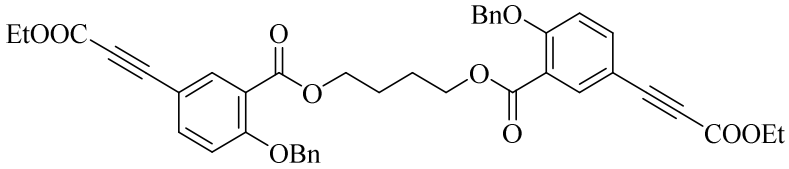
According the **GP2 4c** (600.0 mg, 1.1 mmol, 1.0 eq.), CuI (17.1 mg, 89.5 µmol, 0.08 eq.), $Pd(P(Ph)_3)_2Cl_2$ (62.8 mg, 89.5 µmol, 0.08 eq.) in 30 mL TEA. Then triethyl orthopropiolate (771.0 mg, 4.5 mmol, 4.0 eq.) was added and the reaction was stirred at r.t. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **5b** was isolated (526.0 mg, 99 %) as a yellow solid. Mp. 62.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (td, J = 1.4, 0.6 Hz, 2H), 8.09 (dt, J = 7.8, 1.4 Hz, 2H), 7.75 (dt, J = 7.8, 1.4 Hz, 2H), 7.45 (td, J = 7.8, 0.6 Hz, 2H), 4.51 (t, J = 6.2 Hz, 4H), 4.31 (q, J = 7.2 Hz, 4H), 2.28 (p, J = 6.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 153.9, 137.1, 134.1, 131.6, 130.8, 129.0, 120.3, 84.6, 81.5, 62.4, 62.3, 28.3, 14.2. HRMS (ESI) $[M+H]^+$ calculated for $C_{27}H_{25}O_8$ 477.1544, found 477.1562. IR (ATR, cm^{-1}) 2988, 2219, 1722, 1700, 1296, 1257, 1186, 1167, 1109, 1021, 748.

1.14 Hexane-1,6-diyl bis(2-(benzyloxy)-5-(3-ethoxy-3-oxoprop-1-yn-1-yl)benzoate) (5d)



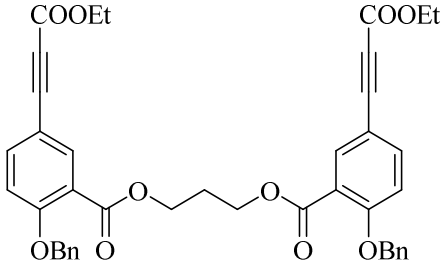
According the **GP2 4d** (700.0 mg, 885.6 µmol, 1.0 eq.), CuI (13.5 mg, 70.9 µmol, 0.08 eq.), $Pd(P(Ph)_3)_2Cl_2$ (49.7 mg, 70.9 µmol, 0.08 eq.) in 30 mL TEA. Then triethyl orthopropiolate (610.1 mg, 3.5 mmol, 4.0 eq.) was added and the reaction was stirred at r.t. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **5d** was isolated (459.0 mg, 71 %) as a brown solid. Mp. 98.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 2.2 Hz, 2H), 7.64 (dd, J = 8.7, 2.2 Hz, 2H), 7.47 – 7.44 (m, 4H), 7.40 – 7.35 (m, 4H), 7.33 – 7.28 (m, 2H), 7.00 (d, J = 8.7 Hz, 2H), 5.20 (s, 4H), 4.31 – 4.26 (m, 8H), 1.71 – 1.65 (m, 4H), 1.39 – 1.33 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 153.9, 137.1, 134.1, 131.6, 130.8, 129.0, 120.3, 84.6, 81.5, 62.4, 62.3, 28.3, 14.2. HRMS (ESI) $[M+H]^+$ calculated for $C_{44}H_{43}O_{10}$ 731.2851 found 731.2874. IR (ATR, cm^{-1}) 2967, 2210, 1696, 1602, 1500, 1316, 1290, 1255, 1231, 1186, 1156, 1012.

1.15 Butane-1,4-diyl bis(2-(benzyloxy)-5-(3-ethoxy-3-oxoprop-1-yn-1-yl)benzoate) (5e)



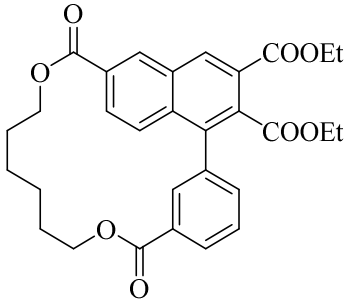
According the **GP2 4e** (490.0 mg, 642.7 µmol, 1.0 eq.), CuI (9.8 mg, 51.4 µmol, 0.08 eq.), $Pd(P(Ph)_3)_2Cl_2$ (36.1 mg, 51.4 µmol, 0.08 eq.) in 20 mL TEA. Then triethyl orthopropiolate (442.8 mg, 2.6 mmol, 4.0 eq.) was added and the reaction was stirred at r.t. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **5e** was isolated (451.0 mg, 100 %) as a brown solid. Mp. 124.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 2.2 Hz, 2H), 7.64 (dd, J = 8.7, 2.2 Hz, 2H), 7.45 – 7.43 (m, 4H), 7.39 – 7.35 (m, 4H), 7.32 – 7.28 (m, 2H), 7.00 (d, J = 8.7 Hz, 2H), 5.18 (s, 4H), 4.32 – 4.24 (m, 8H), 1.75 – 1.72 (m, 4H), 1.37 – 1.33 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 159.8, 154.2, 138.1, 137.0, 135.9, 128.8, 128.4, 127.3, 121.5, 113.8, 111.7, 85.4, 80.7, 70.9, 64.9, 62.2, 25.4, 14.3. HRMS (ESI) $[M+H]^+$ calculated for $C_{42}H_{39}O_{10}$ 703.2538 found 703.2576. IR (ATR, cm^{-1}) 2963, 2213, 1709, 1697, 1603, 1494, 1306, 1278, 1249, 1235, 1178, 1156.

1.16 Propane-1,3-diyl bis(2-(benzyloxy)-5-(3-ethoxy-3-oxoprop-1-yn-1-yl)benzoate) (5f)



According the **GP2 4f** (500.0 mg, 668.1 µmol, 1.0 eq.), CuI (10.2 mg, 53.5 µmol, 0.08 eq.), $Pd(P(Ph)_3)_2Cl_2$ (37.5 mg, 53.5 µmol, 0.08 eq.) in 20 mL TEA. Then triethyl orthopropiolate (460.3 mg, 2.7 mmol, 4.0 eq.) was added and the reaction was stirred at r.t. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **5f** was isolated (360.0 mg, 78 %) as a yellow solid. Mp. 119.0 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 2.2 Hz, 2H), 7.64 (dd, J = 8.7, 2.2 Hz, 2H), 7.45 – 7.42 (m, 4H), 7.38 – 7.34 (m, 4H), 7.32 – 7.28 (m, 2H), 6.99 (d, J = 8.7 Hz, 2H), 5.18 (s, 4H), 4.35 – 4.26 (m, 8H), 2.09 – 2.03 (m, 2H), 1.35 (t, J = 7.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.0, 159.8, 154.2, 138.2, 137.1, 135.8, 128.8, 128.4, 127.3, 121.2, 113.8, 111.7, 85.4, 80.7, 70.9, 62.2, 62.0, 28.1, 14.2. HRMS (ESI) $[M+H]^+$ calculated for $C_{41}H_{37}O_{10}$ 689.2381 found 689.2363. IR (ATR, cm^{-1}) 2974, 2209, 1693, 1599, 1491, 1310, 1278, 1245, 1223, 1182, 1155.

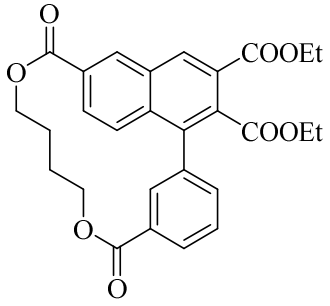
1.17 Diethyl 3,12-dioxo-4,11-dioxa-1(1,6)-naphthalena-2(1,3)-benzenacyclododecaphane-1^2,1^3-dicarboxylate (6a)



According the **GP4 5a** (259.0 mg, 499.5 µmol, 4.0 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 2 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **6a** was isolated (90.0 mg, 35 %) as a withe solid. Mp. 201.9 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 8.55

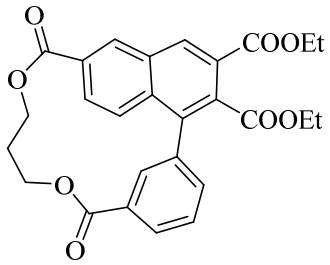
(s, 1H), 8.06 – 7.99 (m, 3H), 7.68 (s, 1H), 7.61 – 7.55 (m, 2H), 4.47 – 4.41 (m, 3H), 4.25 – 4.16 (m, 5H), 1.82 – 1.67 (m, 4H), 1.61 – 1.54 (m, 2H), 1.52 – 1.40 (m, 5H), 1.13 – 1.07 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 166.5, 166.4, 165.5, 137.5, 137.3, 137.0, 136.4, 132.8, 132.6, 132.3, 132.0, 130.4, 130.1, 129.8, 129.0, 128.8, 128.8, 127.8, 126.1, 67.5, 66.3, 61.9, 61.8, 30.4, 29.8, 28.9, 28.4, 14.3, 13.9. HRMS (ESI) $[M+H]^+$ calculated for $C_{30}H_{31}O_8$ 519.2013 found 519.2032. IR (ATR, cm^{-1}) 2956, 1725, 1710, 1292, 1260, 1232, 1188, 1156, 1130, 1110, 1073, 747. For crystallographic data see chapter 3.

1.18 Diethyl 3,10-dioxo-4,9-dioxa-1(1,6)-naphthalena-2(1,3)-benzenacyclodecaphane-1²,1³-dicarboxylate (6b)



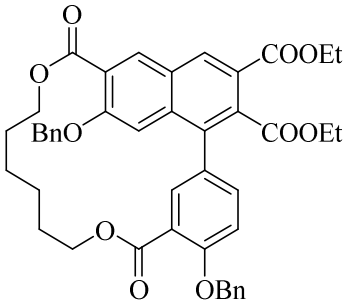
According the **GP4 5b** (150.0 mg, 305.8 µmol, 4.0 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 2 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **6b** was isolated (30.0 mg, 20 %) as a withe solid. Mp. 231.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.20 – 8.16 (m, 1H), 8.11 – 8.07 (m, 1H), 8.01 – 7.97 (m, 1H), 7.64 – 7.59 (m, 2H), 7.46 – 7.40 (m, 2H), 4.49 – 4.43 (m, 2H), 4.31 – 4.26 (m, 2H), 4.20 – 4.15 (m, 1H), 4.13 – 4.05 (m, 1H), 3.90 – 3.83 (m, 1H), 3.56 – 3.48 (m, 1H), 2.00 – 1.91 (m, 1H), 1.85 – 1.76 (m, 2H), 1.47 – 1.42 (m, 3H), 1.21 – 1.12 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 168.1, 165.5, 165.4, 139.6, 138.4, 138.3, 137.0, 132.8, 132.3, 132.1, 131.3, 130.6, 129.6, 129.5, 129.0, 128.7, 127.6, 126.8, 126.0, 70.0, 64.2, 62.1, 62.0, 26.6, 24.2, 14.4, 14.1. HRMS (ESI) $[M+H]^+$ calculated for $C_{28}H_{27}O_8$ 491.1700 found 491.1704. IR (ATR, cm^{-1}) 2969, 1728, 1461, 1381, 1328, 1292, 1259, 1180, 1135, 1074, 1024.

1.19 Diethyl 3,9-dioxo-4,8-dioxa-1(1,6)-naphthalena-2(1,3)-benzenacyclononaphane-1²,1³-dicarboxylate (6c)



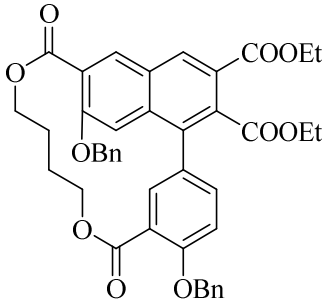
According the **GP4 5c** (316.0 mg, 663.2 µmol, 4.0 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 2 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **6c** was isolated (174.0 mg, 55 %) as a dark solid. Mp. 209.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.06 – 8.02 (m, 1H), 7.99 (s, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.52 (t, J = 7.7 Hz, 1H), 7.38 (d, J = 8.9 Hz, 1H), 7.16 (d, J = 8.9 Hz, 1H), 6.97 (s, 1H), 4.79 – 4.71 (m, 1H), 4.42 – 4.35 (m, 2H), 4.23 (q, J = 7.1 Hz, 2H), 3.91 – 3.82 (m, 1H), 3.54 – 3.45 (m, 1H), 3.43 – 3.34 (m, 1H), 2.23 – 2.14 (m, 1H), 2.08 – 1.99 (m, 1H), 1.40 – 1.35 (m, 3H), 1.16 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 167.4, 165.3, 164.3, 142.0, 140.0, 139.2, 137.5, 132.9, 131.6, 131.5, 130.6, 130.4, 129.2, 128.8, 128.6, 127.9, 127.0, 126.8, 123.6, 68.6, 61.9, 61.8, 59.9, 30.5, 14.2, 13.9. HRMS (ESI) $[M+H]^+$ calculated for $C_{27}H_{25}O_8$ 477.1544 found 477.1563. IR (ATR, cm^{-1}) 2967, 1722, 1303, 1288, 1256, 1224, 1180, 1119, 1101, 1071, 1025, 1009. For crystallographic data see chapter 3.

1.20 Diethyl 1^{7},2^{4}-bis(benzyloxy)-3,12-dioxo-4,11-dioxa-1(1,6)-naphthalena-2(1,3)-benzenacyclododecaphane-1^{2},1^{3}-dicarboxylate (6d)



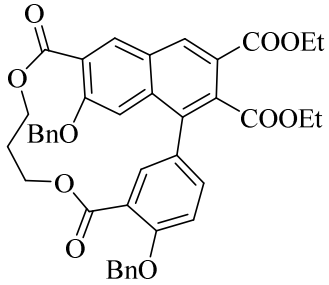
According the **GP4 5d** (400.0 mg, 547.3 µmol, 4.0 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 1 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **6d** was isolated (223.0 mg, 56 %) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.02 (s, 1H), 7.88 – 7.84 (m, 1H), 7.78 – 7.76 (m, 1H), 7.62 – 7.59 (m, 2H), 7.44 – 7.40 (m, 2H), 7.35 – 7.30 (m, 2H), 7.30 – 7.27 (m, 4H), 7.20 – 7.17 (m, 1H), 7.05 (s, 1H), 5.37 (d, J = 12.3 Hz, 1H), 5.32 (d, J = 12.3 Hz, 1H), 4.97 (d, J = 11.8 Hz, 1H), 4.93 (d, J = 11.5 Hz, 1H), 4.45 – 4.42 (m, 1H), 4.41 – 4.39 (m, 1H), 4.22 – 4.15 (m, 4H), 4.04 – 3.95 (m, 2H), 3.75 – 3.65 (m, 1H), 1.76 – 1.70 (m, 1H), 1.53 – 1.47 (m, 2H), 1.43 – 1.40 (m, 3H), 1.28 – 1.22 (m, 4H), 1.09 – 1.05 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 167.9, 165.5, 164.4, 158.7, 155.5, 138.3, 137.9, 136.5, 135.6, 135.5, 134.5, 132.7, 131.3, 129.3, 128.8, 128.7, 128.4, 128.3, 128.1, 127.9, 127.2, 126.9, 126.1, 124.0, 119.3, 113.6, 108.0, 70.8, 70.5, 68.6, 65.7, 61.8, 61.7, 59.2, 29.9, 28.6, 28.1, 27.2, 15.0, 14.4, 14.0.. HRMS (ESI) $[M+H]^+$ calculated for $C_{44}H_{43}O_{10}$ 731.2851 found 731.2819. IR (ATR, cm^{-1}) 2928, 1723, 1624, 1500, 1377, 1279, 1220, 1205, 1135, 1076, 1056, 1017.

1.21 Diethyl 1^{7},2^{4}-bis(benzyloxy)-3,10-dioxo-4,9-dioxa-1(1,6)-naphthalena-2(1,3)-benzenacyclodecaphane-1^{2},1^{3}-dicarboxylate (6e)



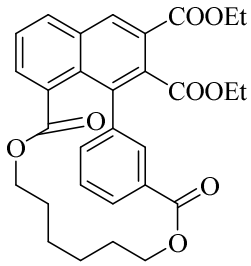
According the **GP4 5e** (52.0 mg, 74.0 µmol, 4 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 1 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **6e** was isolated (8.0 mg, 15 %) as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.99 – 7.95 (m, 1H), 7.86 (s, 1H), 7.61 – 7.57 (m, 2H), 7.44 – 7.38 (m, 3H), 7.36 – 7.27 (m, 5H), 7.25 – 7.21 (m, 2H), 7.17 – 7.13 (m, 1H), 6.90 (s, 1H), 5.37 – 5.30 (m, 2H), 4.95 – 4.80 (m, 2H), 4.46 – 4.40 (m, 3H), 4.25 (tq, J = 7.2, 3.2 Hz, 2H), 3.85 – 3.77 (m, 1H), 3.69 – 3.62 (m, 1H), 3.41 – 3.29 (m, 1H), 1.84 – 1.73 (m, 2H), 1.44 – 1.40 (m, 3H), 1.17 – 1.12 (m, 3H), 0.97 – 0.90 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 167.4, 166.6, 165.4, 157.9, 157.5, 136.7, 136.3, 136.3, 135.1, 134.5, 134.3, 133.6, 132.8, 131.5, 128.8, 128.8, 128.7, 128.4, 128.3, 127.9, 127.8, 127.1, 127.1, 123.1, 120.1, 120.1, 115.7, 113.5, 71.5, 70.6, 65.7, 64.9, 61.7, 61.4, 26.2, 24.1, 14.4, 13.9. HRMS (ESI) $[M+H]^+$ calculated for $C_{42}H_{39}O_{10}$ 703.2538 found 703.2513. IR (ATR, cm^{-1}) 2960, 1718, 1617, 1501, 1449, 1378, 1218, 1176, 1085, 1063, 1019, 732.

1.22 Diethyl 1⁷,2⁴-bis(benzyloxy)-3,9-dioxo-4,8-dioxa-1(1,6)-naphthalena-2(1,3)-benzenacyclononaphane-1²,1³-dicarboxylate (6f)



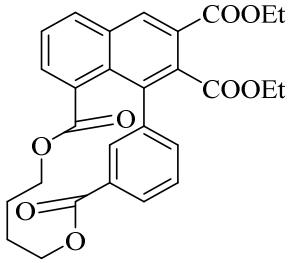
According the **GP4 5f** (300.0 mg, 435.6 µmol, 4.0 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 1 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **6f** was isolated (237.0 mg, 79 %) as a red oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.81 (s, 1H), 7.57 – 7.52 (m, 2H), 7.40 – 7.36 (m, 2H), 7.32 – 7.27 (m, 4H), 7.25 – 7.22 (m, 2H), 7.10 (d, J = 8.5 Hz, 1H), 6.99 (s, 1H), 6.75 (s, 1H), 5.34 – 5.26 (m, 2H), 4.87 (s, 2H), 4.49 – 4.38 (m, 3H), 4.29 – 4.22 (m, 2H), 3.85 – 3.76 (m, 1H), 3.59 – 3.47 (m, 2H), 2.13 – 2.04 (m, 2H), 1.43 – 1.38 (m, 3H), 1.22 – 1.15 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 167.9, 165.5, 163.0, 157.8, 154.1, 144.1, 141.8, 137.4, 136.2, 134.7, 133.0, 131.9, 130.1, 129.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.0, 127.4, 127.4, 126.8, 126.8, 124.9, 123.2, 118.9, 112.7, 110.2, 70.6, 70.3, 68.1, 61.7, 61.7, 60.4, 29.4, 14.3, 14.0. HRMS (ESI) $[M+H]^+$ calculated for $C_{41}H_{37}O_{10}$ 689.2381 found 689.2379. IR (ATR, cm^{-1}) 2977, 1722, 1614, 1375, 1261, 1218, 1201, 1175, 1132, 1081, 1064, 1016.

1.23 Diethyl 3,12-dioxo-4,11-dioxa-1(1,8)-naphthalena-2(1,3)-benzenacyclododecaphane-1²,1³-dicarboxylate (7a)



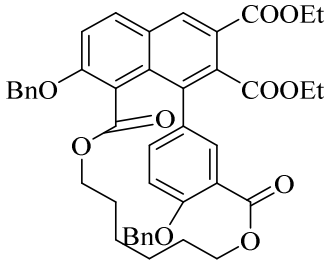
According the **GP4 5a** (259.0 mg, 499.5 µmol, 4.0 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 2 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **7a** was isolated (84.0 mg, 32 %) as a yellow solid. Mp. 142.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.13 – 8.06 (m, 2H), 8.04 – 8.01 (m, 1H), 7.70 – 7.65 (m, 1H), 7.62 – 7.57 (m, 1H), 7.56 – 7.44 (m, 2H), 4.70 – 4.59 (m, 1H), 4.44 – 4.38 (m, 2H), 4.32 – 4.26 (m, 1H), 4.04 – 3.94 (m, 2H), 3.81 – 3.70 (m, 1H), 3.07 – 2.89 (m, 1H), 1.98 – 1.88 (m, 1H), 1.82 – 1.72 (m, 2H), 1.56 – 1.47 (m, 2H), 1.46 – 1.37 (m, 5H), 1.22 – 1.14 (m, 1H), 1.00 – 0.92 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 168.3, 166.5, 165.3, 137.5, 136.4, 136.3, 134.4, 133.4, 132.8, 132.5, 132.4, 131.3, 131.2, 130.2, 129.8, 129.5, 128.2, 126.6, 125.3, 66.1, 65.1, 61.9, 61.4, 25.7, 25.3, 24.9, 23.8, 14.3, 13.7. HRMS (ESI) $[M+H]^+$ calculated for $C_{30}H_{31}O_8$ 519.2013 found 519.1995. IR (ATR, cm^{-1}) 2952, 1713, 1255, 1216, 1194, 1173, 1136, 1109, 1073, 1054, 1025. For crystallographic data see chapter 3.

1.24 Diethyl 3,10-dioxo-4,9-dioxa-1(1,8)-naphthalena-2(1,3)-benzenacyclodecaphane-1²,1³-dicarboxylate (7b)



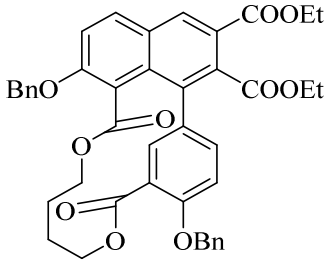
According the **GP4 5b** (500.0 mg, 964.2 µmol, 4.0 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 2 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **7b** was isolated (60.0 mg, 40 %) as a yellow solid. Mp. 196.6 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 8.15 – 8.11 (m, 1H), 8.09 – 8.04 (m, 1H), 8.04 – 7.99 (m, 1H), 7.77 – 7.72 (m, 2H), 7.64 – 7.55 (m, 2H), 4.86 – 4.76 (m, 1H), 4.43 (q, J = 7.1 Hz, 2H), 4.23 – 4.17 (m, 1H), 4.09 – 4.02 (m, 2H), 4.01 – 3.94 (m, 1H), 3.37 – 3.27 (m, 1H), 2.25 – 2.14 (m, 1H), 2.12 – 2.00 (m, 1H), 1.81 – 1.72 (m, 2H), 1.43 (t, J = 7.1 Hz 3H), 1.01 – 0.95 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 168.4, 166.9, 165.5, 138.5, 136.0, 134.8, 134.4, 133.8, 133.1, 132.8, 132.4, 132.3, 130.9, 130.4, 129.9, 129.3, 129.0, 126.4, 125.7, 65.8, 64.4, 62.0, 61.6, 26.8, 24.1, 14.4, 13.8. HRMS (ESI) $[M+H]^+$ calculated for $C_{28}H_{27}O_8$ 491.1700 found 491.1685. IR (ATR, cm^{-1}) 2978, 1716, 1285, 1256, 1219, 1200, 1142, 1176, 1112, 1084, 1055. For crystallographic data see chapter 3.

1.25 Diethyl 1⁷,2⁴-bis(benzyloxy)-3,12-dioxo-4,11-dioxa-1(1,8)-naphthalena-2(1,3)-benzenacyclododecaphane-1²,1³-dicarboxylate (7d)



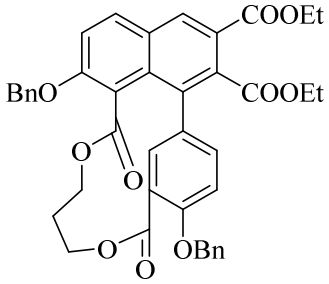
According the **GP4 5d** (400.0 mg, 547.3 µmol, 4.0 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 1 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **7d** was isolated (132.0 mg, 33 %) as a brown solid. Mp. 138.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.05 – 8.01 (m, 1H), 7.87 – 7.84 (m, 1H), 7.55 – 7.51 (m, 2H), 7.42 – 7.38 (m, 4H), 7.35 – 7.28 (m, 6H), 7.06 – 7.02 (m, 1H), 5.32 – 5.28 (m, 1H), 5.21 (d, J = 12.2 Hz, 3H), 4.54 – 4.49 (m, 1H), 4.41 – 4.36 (m, 2H), 4.35 – 4.29 (m, 1H), 3.96 – 3.90 (m, 2H), 3.26 – 3.18 (m, 1H), 2.00 – 1.91 (m, 1H), 1.76 – 1.64 (m, 2H), 1.57 – 1.52 (m, 2H), 1.43 – 1.37 (m, 5H), 1.35 – 1.28 (m, 2H), 1.03 – 0.99 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 167.1, 166.1, 165.4, 158.0, 157.0, 138.1, 136.8, 136.3, 135.5, 134.8, 134.4, 133.3, 132.7, 131.5, 128.7, 128.7, 128.2, 128.2, 127.9, 127.1, 126.9, 122.9, 120.5, 119.8, 115.7, 112.8, 71.3, 70.6, 66.2, 65.6, 61.7, 61.5, 59.2, 25.4, 25.0, 23.6, 15.0, 14.4, 13.9. HRMS (ESI) $[M+H]^+$ calculated for $C_{44}H_{43}O_{10}$ 731.2851 found 731.2815. IR (ATR, cm^{-1}) 2948, 1725, 1609, 1498, 1450, 1367, 1277, 1228, 1178, 1150, 1064.

1.26 Diethyl $1^7,2^4$-bis(benzyloxy)-3,10-dioxo-4,9-dioxa-1(1,8)-naphthalena-2(1,3)-benzenacyclodecaphane-$1^2,1^3$-dicarboxylate (7e)



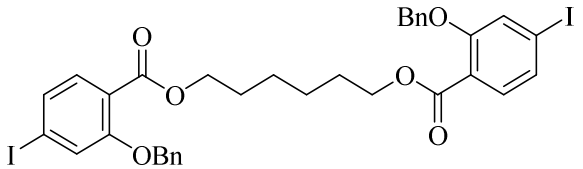
According the **GP4 5e** (52.0 mg, 74.0 µmol, 4.0 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 1 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **7e** was isolated (6.0 mg, 12 %) as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.09 – 8.01 (m, 1H), 7.85 – 7.83 (m, 1H), 7.53 – 7.50 (m, 2H), 7.47 – 7.44 (m, 1H), 7.43 – 7.37 (m, 4H), 7.35 – 7.31 (m, 5H), 7.08 – 7.04 (m, 1H), 5.33 – 5.24 (m, 2H), 5.22 – 5.16 (m, 2H), 4.56 – 4.47 (m, 1H), 4.44 – 4.42 (m, 1H), 4.40 – 4.37 (m, 2H), 3.99 – 3.92 (m, 2H), 3.85 – 3.79 (m, 1H), 3.66 – 3.60 (m, 1H), 1.71 – 1.59 (m, 4H), 1.42 – 1.38 (m, 3H), 0.97 – 0.93 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 167.4, 166.6, 165.4, 157.9, 157.5, 136.7, 136.3, 136.3, 135.1, 134.5, 134.3, 133.6, 132.8, 131.5, 128.8, 128.7, 128.4, 128.3, 127.9, 127.8, 127.1, 127.1, 123.1, 120.1, 120.1, 115.7, 113.5, 71.5, 70.6, 65.7, 64.9, 61.7, 61.4, 26.2, 24.1, 14.4, 13.9. HRMS (ESI) $[M+H]^+$ calculated for $C_{42}H_{39}O_{10}$ 703.2538 found 703.2516. IR (ATR, cm^{-1}) 2939, 1725, 1608, 1498, 1452, 1371, 1243, 1179, 1149, 1072, 1020.

1.27 Diethyl $1^7,2^4$-bis(benzyloxy)-3,9-dioxo-4,8-dioxa-1(1,8)-naphthalena-2(1,3)-benzenacyclononaphane-$1^2,1^3$-dicarboxylate (7f)



According the **GP4 5f** (300.0 mg, 435.6 µmol, 4.0 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 1 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **7f** was isolated (7.0 mg, 2 %) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.97 – 7.90 (m, 1H), 7.57 – 7.54 (m, 2H), 7.43 – 7.38 (m, 3H), 7.34 – 7.29 (m, 5H), 7.23 – 7.20 (m, 2H), 7.13 – 7.10 (m, 1H), 6.93 – 6.91 (m, 1H), 6.62 (s, 1H), 5.38 – 5.29 (m, 2H), 4.89 – 4.81 (m, 2H), 4.56 – 4.50 (m, 1H), 4.47 – 4.42 (m, 2H), 4.25 – 4.20 (m, 2H), 3.88 – 3.81 (m, 1H), 3.61 – 3.55 (m, 1H), 3.52 – 3.45 (m, 1H), 2.13 – 2.08 (m, 1H), 1.44 – 1.40 (m, 3H), 1.20 – 1.16 (m, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 168.0, 166.2, 165.9, 163.1, 157.9, 153.9, 144.0, 141.5, 137.7, 136.2, 134.6, 133.6, 130.5, 130.0, 129.8, 128.9, 128.9, 128.7, 128.2, 128.2, 127.5, 127.0, 124.7, 124.6, 119.1, 112.7, 110.9, 70.8, 70.7, 68.2, 62.4, 62.2, 60.6, 29.6, 14.2, 14.0. HRMS (ESI) $[M+H]^+$ calculated for $C_{41}H_{37}O_{10}$ 689.2381 found 689.2352. IR (ATR, cm^{-1}) 2932, 1726, 1612, 1500, 1375, 1292, 1263, 1202, 11176, 1139, 1071, 1014.

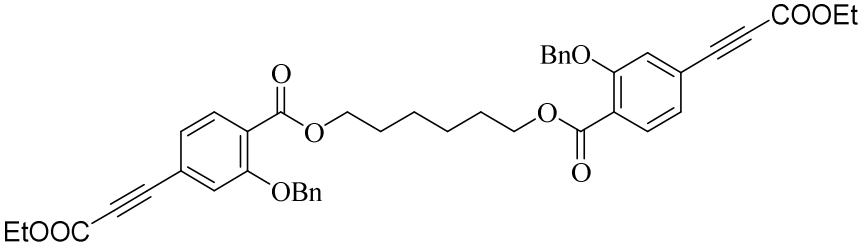
1.28 Hexane-1,6-diyl bis(2-(benzyloxy)-4-iodobenzoate) (9)



According the **GP1** Hexane-1,6-diol (37.7 mg, 319.0 µmol, 1.0 eq.), 2-(Benzyloxy)-4-iodobenzoic acid **8** (226.0 mg, 638.1 µmol, 2.0 eq.) and DMAP (4.0 mg, 31.9 µmol, 0.1 eq.) were dissolved in 10 mL dry DCM. Then DIC (143.5 µL, 957.1 µmol, 3.0 eq.) was added. The crude product was purified by flash

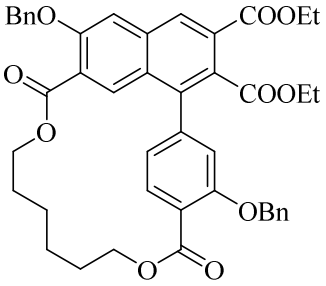
chromatography on silica gel with DCM. The product **9** was isolated (176.0 mg, 70 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 2H), 7.48 – 7.45 (m, 4H), 7.40 – 7.35 (m, 7H), 7.34 – 7.28 (m, 3H), 5.11 (s, 4H), 4.26 – 4.22 (m, 4H), 1.67 – 1.60 (m, 4H), 1.37 – 1.31 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 158.4, 136.2, 133.0, 130.0, 128.7, 128.2, 127.3, 123.2, 120.7, 99.8, 71.0, 65.2, 28.6, 25.8. HRMS (ESI) $[M+H]^+$ calculated for $C_{34}H_{33}I_2O_6$ 791.0361, found 791.0337. IR (ATR, cm^{-1}) 2946, 1681, 1582, 1561, 1406, 1386, 1286, 1240, 1137, 1105, 1022.

1.29 Hexane-1,6-diyl bis(2-(benzyloxy)-4-(3-ethoxy-3-oxoprop-1-yn-1-yl)benzoate) (10)



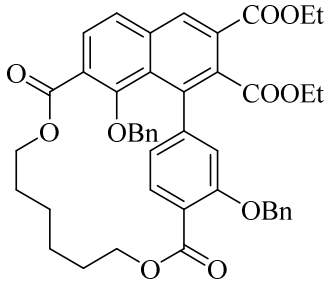
According the **GP2 9** (80.0 mg, 101.2 µmol, 1.0 eq.), CuI (1.5 mg, 8.1 µmol, 0.08 eq.), $Pd(P(Ph)_3)_2Cl_2$ (5.7 mg, 8.1 µmol, 0.08 eq.) in 10 mL TEA. Then triethyl orthopropiolate (69.7 mg, 404.8 µmol, 4.0 eq.) was added and the reaction was stirred at r.t. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **10** was isolated (74.0 mg, 100 %) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.75 (m, 2H), 7.48 – 7.44 (m, 4H), 7.40 – 7.35 (m, 4H), 7.32 – 7.28 (m, 2H), 7.22 – 7.19 (m, 4H), 5.14 (s, 4H), 4.34 – 4.30 (m, 4H), 4.29 – 4.25 (m, 4H), 1.68 – 1.62 (m, 4H), 1.39 – 1.34 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 157.7, 153.9, 136.1, 131.9, 128.7, 128.2, 127.2, 125.1, 124.3, 123.4, 117.6, 84.7, 82.1, 70.9, 65.4, 62.5, 28.6, 25.8, 14.2. HRMS (ESI) $[M+H]^+$ calculated for $C_{44}H_{43}O_{10}$ 731.2851 found 731.2863. IR (ATR, cm^{-1}) 2946, 2220, 1702, 1683, 1582, 1561, 1407, 1386, 1285, 1238, 1137, 1081, 1022.

1.30 Diethyl 1^6,2^3-bis(benzyloxy)-3,12-dioxo-4,11-dioxa-1(1,7)-naphthalena-2(1,4)-benzenacyclododecaphane-1^2,1^3-dicarboxylate (11)



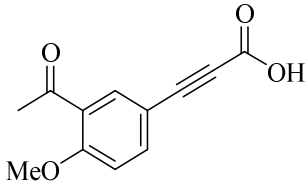
According the **GP4 10** (80.0 mg, 109.5 µmol, 4.0 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 1 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **11** was isolated (17.0 mg, 21 % %) as a clear oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.77 – 7.74 (m, 1H), 7.59 – 7.54 (m, 3H), 7.43 – 7.40 (m, 3H), 7.39 – 7.35 (m, 2H), 7.34 – 7.31 (m, 2H), 7.30 – 7.28 (m, 1H), 7.26 – 7.22 (m, 1H), 7.02 – 6.98 (m, 2H), 5.32 (s, 2H), 5.20 – 5.11 (m, 2H), 4.46 – 4.42 (m, 2H), 4.41 – 4.38 (m, 2H), 4.22 – 4.18 (m, 2H), 4.16 – 4.11 (m, 2H), 1.80 – 1.75 (m, 2H), 1.59 – 1.53 (m, 2H), 1.50 – 1.46 (m, 2H), 1.45 – 1.40 (m, 5H), 1.09 – 1.05 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 167.1, 165.9, 164.2, 156.7, 156.5, 141.0, 138.7, 136.4, 136.3, 135.4, 132.0, 130.0, 129.8, 128.8, 128.6, 128.3, 128.3, 128.1, 128.0, 127.9, 127.0, 126.9, 123.8, 123.1, 122.7, 115.8, 109.6, 70.7, 70.6, 66.9, 66.7, 62.0, 61.7, 30.1, 29.2, 29.2, 28.1, 14.3, 14.0. HRMS (ESI) $[M+H]^+$ calculated for $C_{44}H_{43}O_{10}$ 731.2851 found 731.2891. IR (ATR, cm^{-1}) 2935, 1719, 1440, 1412, 1379, 1271, 1236, 1175, 1132, 1092, 1069, 1020.

1.31 Diethyl 1^8,2^3-bis(benzyloxy)-3,12-dioxo-4,11-dioxa-1(1,7)-naphthalena-2(1,4)-benzenacyclododecaphane-1^2,1^3-dicarboxylate (12)



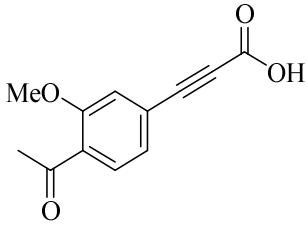
According the **GP4 10** (80.0 mg, 109.5 µmol, 4.0 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 1 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **12** was isolated (15 mg, 19 %) as a clear oil. The analysis data shows a mixture of two conformers from product **12**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 – 8.56 (m, 2H), 7.91 – 7.85 (m, 2H), 7.72 – 7.67 (m, 3H), 7.47 – 7.44 (m, 2H), 7.39 – 7.27 (m, 8H), 7.25 – 7.22 (m, 2H), 7.19 – 7.15 (m, 3H), 7.13 – 7.08 (m, 3H), 7.07 – 7.02 (m, 2H), 6.77 – 6.73 (m, 2H), 6.73 – 6.69 (m, 2H), 6.57 – 6.53 (m, 2H), 4.96 – 4.81 (m, 3H), 4.65 – 4.59 (m, 1H), 4.53 – 4.41 (m, 7H), 4.37 – 4.02 (m, 17H), 1.87 – 1.67 (m, 5H), 1.46 – 1.41 (m, 8H), 1.38 – 1.36 (m, 2H), 1.15 – 1.11 (m, 3H), 1.05 – 1.02 (m, 3H), 0.89 – 0.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 168.1, 167.6, 167.4, 165.8, 165.4, 159.2, 158.7, 157.0, 157.0, 144.8, 143.7, 136.9, 136.8, 136.5, 136.3, 136.3, 135.6, 135.2, 131.8, 131.7, 131.4, 131.3, 131.3, 131.0, 130.9, 129.2, 129.2, 129.0, 128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.6, 127.5, 126.8, 126.7, 126.6, 125.4, 125.0, 124.1, 124.0, 123.8, 122.8, 120.4, 120.0, 115.8, 112.7, 79.6, 79.0, 70.4, 69.8, 67.4, 66.7, 66.6, 62.1, 61.8, 30.3, 30.3, 29.7, 29.5, 29.2, 29.0, 28.3, 28.1, 14.4, 14.0, 13.9. HRMS (ESI) $[M+H]^+$ calculated for $C_{44}H_{43}O_{10}$ 731.2851 found 731.2888. IR (ATR, cm^{-1}) 2925, 1716, 1407, 1369, 1257, 1234, 1191, 1175, 1147, 1127, 1088, 1019.

1.32 3-(3-Acetyl-4-methoxyphenyl)propiolic acid (14a)



According the **GP2** 1-(5-Iodo-2-methoxyphenyl)ethan-1-one **13a** (650.0 mg, 2.4 mmol, 1.0 eq.), CuI (18.0 mg, 94.2 µmol, 0.04 eq.), $Pd(P(Ph)_3)_2Cl_2$ (66.1 mg, 94.2 µmol, 0.04 eq.) in 20 mL TEA. Then triethyl orthopropiolate (811.0 mg, 4.7 mmol, 2.0 eq.) was added and the reaction was stirred at r.t. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The intermediate product was isolated (542.0 mg, 93 %) as a red solid. According the **GP3** the intermediate product (800.0 mg, 3.25 mmol) was converted to Product **14a** (705.0 mg, 99 %) as a yellow solid. Mp. 136.1 °C. ^{1}H NMR (400 MHz, MeOD) δ 7.87 – 7.81 (m, 1H), 7.75 – 7.69 (m, 1H), 7.23 – 7.18 (m, 1H), 3.99 (s, 3H), 2.58 (s, 3H). ^{13}C NMR (101 MHz, MeOD) δ 200.3, 162.0, 139.4, 135.9, 135.2, 129.7, 113.9, 112.9, 86.0, 56.6, 31.8, 22.8. HRMS (ESI) $[M+H]^+$ calculated for $C_{12}H_{11}O_4$ 219.0652 found 219.0648. IR (ATR, cm^{-1}) 2942, 2206, 1707, 1644, 1594, 1493, 1402, 1250, 1234, 1179, 1149, 1016.

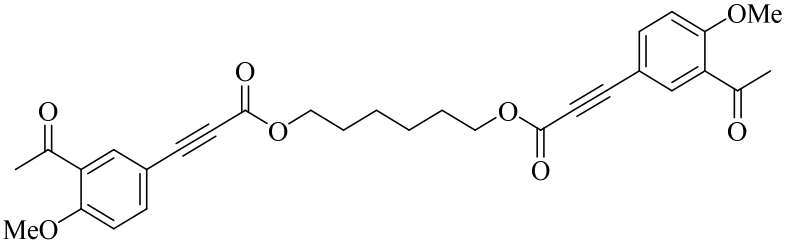
1.33 3-(4-Acetyl-3-methoxyphenyl)propiolic acid (14b)



According the **GP2** 1-(4-Iodo-2-methoxyphenyl)ethan-1-one **13b** (1.0 g, 4.4 mmol, 1.0 eq.), CuI (33.3 mg, 174.6 µmol, 0.04 eq.), $Pd(P(Ph)_3)_2Cl_2$ (122.6 mg, 174.6 µmol, 0.04 eq.) in 20 mL TEA. Then triethyl orthopropiolate (2.26 g, 13.1 mmol, 3.0 eq.) was added and the reaction was stirred at r.t. The crude

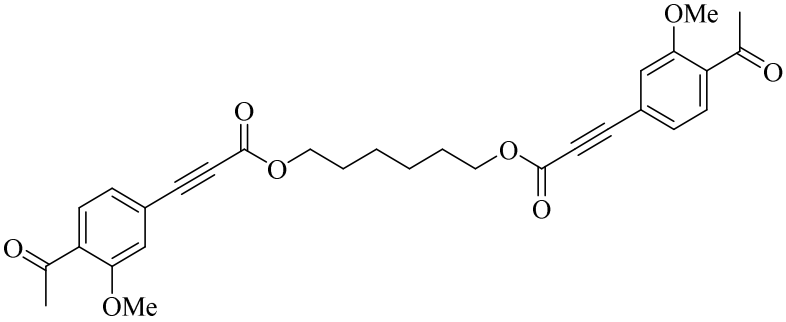
product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The intermediate product was isolated (1.04 g, 97 %) as a yellow solid. According the **GP3** the intermediate product (1.46 g, 5.93 mmol) was converted to Product **14b** (1.29 g, 100 %) as a yellow solid. Mp. 167.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 1H), 7.26 – 7.22 (m, 1H), 7.20 – 7.16 (m, 1H), 3.94 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 158.5, 156.8, 130.8, 130.4, 125.5, 124.1, 116.1, 87.2, 81.5, 56.0, 31.9. HRMS (ESI) $[M+H]^+$ calculated for $C_{12}H_{11}O_4$ 219.0652 found 219.0648. IR (ATR, cm^{-1}) 2908, 2769, 2567, 2220, 1699, 1631, 1594, 1549, 1403, 1265, 1224, 1188, 1167, 1136, 1022.

1.34 Hexane-1,6-diyl bis(3-(3-acetyl-4-methoxyphenyl)propiolate) (15a)



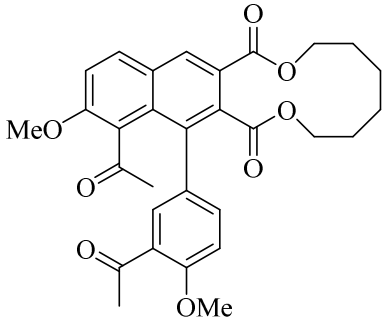
According the **GP1** Hexane-1,6-diol (423.0 mg, 3.6 mmol, 1.0 eq.), **14a** (1.56 g, 7.2 mmol, 2.0 eq.) and DMAP (87.6 mg, 716.8 µmol, 0.2 eq.) were dissolved in 20 mL dry DCM. Then DIC (2.24 mL, 14.3 mmol, 4.0 eq.) was added. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **15a** was isolated (789.0 mg, 42 %) as a yellow solid. Mp. 107.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 2.3 Hz, 2H), 7.69 (dd, J = 8.7, 2.3 Hz, 2H), 6.97 (d, J = 8.7 Hz, 2H), 4.26 – 4.21 (m, 4H), 3.96 (s, 6H), 2.60 (s, 6H), 1.80 – 1.69 (m, 4H), 1.49 – 1.44 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 160.4, 154.3, 138.3, 135.7, 128.7, 112.2, 112.0, 85.7, 80.6, 66.1, 56.0, 31.8, 28.5, 25.7. HRMS (ESI) $[M+H]^+$ calculated for $C_{30}H_{31}O_8$ 519.2013, found 519.2002. IR (ATR, cm^{-1}) 2928, 2212, 1705, 1667, 1598, 1494, 1400, 1246, 1220, 1168, 1146, 1018.

1.35 Hexane-1,6-diyl bis(3-(4-acetyl-3-methoxyphenyl)propiolate) (15b)



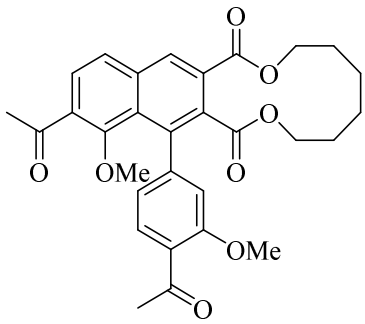
According the **GP1** Hexane-1,6-diol (574.1 mg, 4.9 mmol, 1.0 eq.), **14b** (2.12 g, 9.7 mmol, 2.0 eq.) and DMAP (118.7 mg, 971.6 µmol, 0.2 eq.) were dissolved in 30 mL dry DCM. Then DIC (3.04 mL, 19.4 mmol, 4.0 eq.) was added. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **15b** was isolated (994.0 mg, 39 %) as a withe solid. Mp. 105.9 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.1 Hz, 2H), 7.18 (dd, J = 7.9, 1.4 Hz, 2H), 7.13 (d, J = 1.4 Hz, 2H), 4.23 (t, J = 6.6 Hz, 4H), 3.89 (s, 6H), 2.57 (s, 6H), 1.73 (t, J = 6.7 Hz, 4H), 1.44 (q, J = 3.3 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 160.4, 154.3, 138.3, 135.7, 128.7, 112.2, 112.0, 85.7, 80.6, 66.1, 56.0, 31.8, 28.5, 25.7. HRMS (ESI) $[M+H]^+$ calculated for $C_{30}H_{31}O_8$ 519.2013, found 519.2029. IR (ATR, cm^{-1}) 2949, 2223, 1706, 1665, 1599, 1407, 1358, 1288, 1274, 1232, 1188, 1165, 1031.

1.36 12-Acetyl-11-(3-acetyl-4-methoxyphenyl)-13-methoxy-3,4,5,6,7,8-hexahydronaphtho[2,3-c][1,6]dioxacyclododecine-1,10-dione (16a)



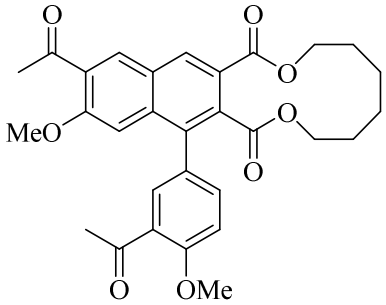
According the **GP4 15a** (120.0 mg, 231.4 µmol, 2 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 2 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **16a** was isolated (51.0 mg, 43 %) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.03 – 7.99 (m, 1H), 7.58 – 7.55 (m, 1H), 7.39 – 7.33 (m, 2H), 7.00 – 6.94 (m, 1H), 4.44 – 4.36 (m, 2H), 4.05 – 4.00 (m, 1H), 3.97 – 3.94 (m, 3H), 3.88 – 3.86 (m, 3H), 3.84 – 3.79 (m, 1H), 2.60 – 2.58 (m, 3H), 1.94 – 1.90 (m, 3H), 1.85 – 1.71 (m, 4H), 1.56 – 1.49 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.4, 198.8, 168.5, 166.1, 159.0, 156.5, 134.9, 134.1, 133.6, 132.8, 132.0, 129.2, 128.4, 127.6, 122.7, 114.4, 110.8, 67.2, 65.5, 56.6, 55.7, 32.8, 31.9, 25.6, 25.5, 25.4, 22.9. HRMS (ESI) $[M+H]^+$ calculated for $C_{30}H_{31}O_8$ 519.2013, found 519.2026. IR (ATR, cm^{-1}) 2949, 2925, 1730, 1701, 1672, 1604, 1493, 1352, 1250, 1207, 1173, 1148, 999.

1.37 13-Acetyl-11-(4-acetyl-3-methoxyphenyl)-12-methoxy-3,4,5,6,7,8-hexahydronaphtho[2,3-c][1,6]dioxacyclododecine-1,10-dione (16b)



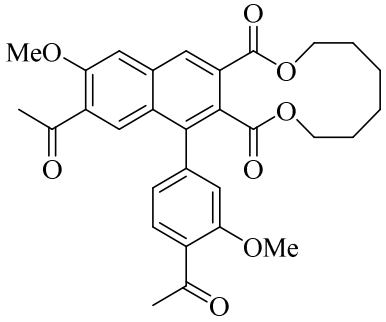
According the **GP4 15b** (170.0 mg, 327.8 µmol, 2 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 2 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **16b** was isolated (82.5 mg, 49 %) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.82 – 7.76 (m, 2H), 7.70 – 7.66 (m, 1H), 7.00 – 6.94 (m, 2H), 4.48 – 4.38 (m, 2H), 4.11 – 4.03 (m, 1H), 3.86 (s, 4H), 3.15 (s, 3H), 2.66 (s, 3H), 2.58 (s, 3H), 1.83 – 1.68 (m, 4H), 1.59 – 1.50 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 199.2, 168.0, 165.9, 157.9, 157.7, 145.7, 136.3, 136.3, 133.3, 133.0, 132.9, 129.1, 128.0, 127.7, 126.8, 126.5, 126.0, 121.7, 113.5, 67.5, 65.7, 64.2, 55.8, 32.1, 30.5, 25.7, 25.6, 25.4, 23.0. HRMS (ESI) $[M+H]^+$ calculated for $C_{30}H_{31}O_8$ 519.2013, found 519.2023. IR (ATR, cm^{-1}) 2939, 1741, 1709, 1688, 1671, 1604, 1350, 1259, 1240, 1206, 1163, 1148.

1.38 14-Acetyl-11-(3-acetyl-4-methoxyphenyl)-13-methoxy-3,4,5,6,7,8-hexahydronaphtho[2,3-c][1,6]dioxacyclododecine-1,10-dione (17a)



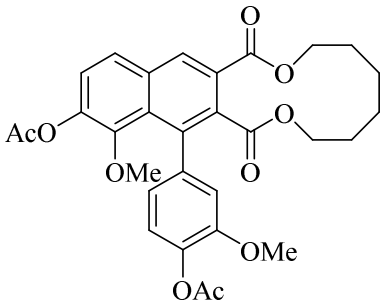
According the **GP4 15a** (120.0 mg, 231.4 µmol, 2 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 2 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **17a** was isolated (45.0 mg, 38 %) as a yellow solid. Mp. 191.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.25 (s, 1H), 7.75 (d, J = 2.3 Hz, 1H), 7.46 (dd, J = 8.6, 2.3 Hz, 1H), 7.08 (d, J = 8.6 Hz, 1H), 6.84 (s, 1H), 4.46 – 4.39 (m, 2H), 4.20 – 4.15 (m, 1H), 3.99 (s, 3H), 3.96 – 3.94 (m, 1H), 3.74 (s, 3H), 2.64 – 2.62 (m, 6H), 1.86 – 1.76 (m, 4H), 1.59 – 1.53 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7, 199.1, 168.6, 166.3, 158.7, 157.8, 137.1, 135.8, 135.5, 133.5, 133.0, 132.4, 132.3, 131.7, 128.8, 127.9, 127.1, 123.7, 111.6, 105.5, 67.0, 65.7, 55.7, 55.6, 32.0, 31.6, 25.6, 25.6, 25.5, 23.1. HRMS (ESI) $[M+H]^+$ calculated for $C_{30}H_{31}O_8$ 519.2013, found 519.2026. IR (ATR, cm^{-1}) 2939, 1724, 1707, 1673, 1608, 1405, 1279, 1247, 1217, 1189, 1158, 1137.

1.39 13-Acetyl-11-(4-acetyl-3-methoxyphenyl)-14-methoxy-3,4,5,6,7,8-hexahydronaphtho[2,3-c][1,6]dioxacyclododecine-1,10-dione (17b)



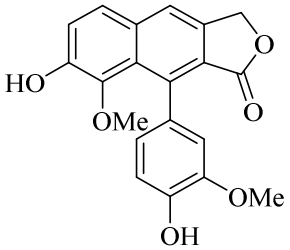
According the **GP4 15b** (170.0 mg, 327.8 µmol, 2 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 2 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **17b** was isolated (53.5 mg, 31 %) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.84 – 7.82 (m, 1H), 7.76 (s, 1H), 7.34 (s, 1H), 6.97 – 6.94 (m, 2H), 4.49 – 4.42 (m, 2H), 4.19 – 4.13 (m, 1H), 4.04 (s, 3H), 3.98 – 3.94 (m, 1H), 3.88 (s, 3H), 2.68 (s, 3H), 2.58 (s, 3H), 1.84 – 1.80 (m, 2H), 1.79 – 1.76 (m, 1H), 1.75 – 1.71 (m, 1H), 1.59 – 1.53 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 199.4, 168.4, 166.6, 158.7, 156.6, 142.2, 139.1, 135.3, 133.5, 130.7, 130.4, 129.2, 129.0, 127.9, 127.8, 127.6, 122.6, 114.0, 107.7, 67.3, 65.7, 56.0, 55.8, 32.1, 31.7, 25.8, 25.7, 25.4, 23.2. HRMS (ESI) $[M+H]^+$ calculated for $C_{30}H_{31}O_8$ 519.2013, found 519.2031. IR (ATR, cm^{-1}) 2938, 1721, 1675, 1604, 1458, 1402, 1356, 1275, 1241, 1165, 1137.

1.40 4-(13-Acetoxy-12-methoxy-1,10-dioxo-1,3,4,5,6,7,8,10-octahydronaphtho[2,3-c][1,6]dioxacyclododecin-11-yl)-2-methoxyphenyl acetate (18)



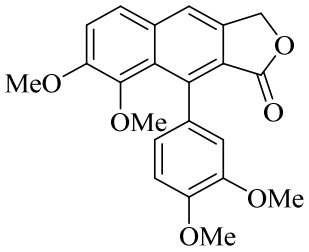
To a solution of **16b** (90.0 mg, 173.6 µmol, 1.0 eq.) in DCM were added 70 % m-chloroperbenzoicacid (107.0 mg, 433.9 µmol, 2.5 eq.) and p-toluenesulfonicacid (33.0 mg, 173.6 µmol, 1.0 eq.). The solution was stirred at reflux for 24 h. After the compilation of the reaction, the organic phase was washed twice with water and dried over $MgSO_4$. Then the solvent was removed and the crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 1:1). The product **18** was isolated (70.0 mg, 73 %) as a withe solid. Mp. 169.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.78 (d, J = 8.9 Hz, 1H), 7.36 (d, J = 8.9 Hz, 1H), 7.00 (d, J = 8.1 Hz, 1H), 6.95 (d, J = 1.9 Hz, 1H), 6.90 (dd, J = 8.0, 1.9 Hz, 1H), 4.44 – 4.40 (m, 2H), 4.00 – 3.94 (m, 2H), 3.78 (s, 3H), 3.23 (s, 3H), 2.34 (s, 3H), 2.33 (s, 3H), 1.81 (s, 2H), 1.78 – 1.73 (m, 2H), 1.57 – 1.54 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 168.9, 168.5, 166.2, 149.7, 148.4, 143.9, 139.0, 138.3, 135.8, 133.1, 132.5, 129.3, 126.0, 124.9, 124.7, 122.1, 121.2, 114.7, 67.5, 65.4, 61.3, 56.2, 25.7, 25.5, 25.5, 23.1, 21.1, 20.9. HRMS (ESI) $[M+H]^+$ calculated for $C_{30}H_{31}O_{10}$ 551.1912, found 551.1887. IR (ATR, cm^{-1}) 2942, 1766, 1732, 1714, 1370, 1257, 1194, 1158, 1140, 1118, 1094, 1031.

1.41 7-Hydroxy-9-(4-hydroxy-3-methoxyphenyl)-8-methoxynaphtho[2,3-c]furan-1(3H)-one (19)



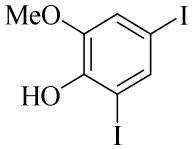
In a round-bottom flask the reactant **18** (120.0 mg, 218.0 µmol, 1.0 eq.) was dissolved in 5 mL THF. Then $LiAlH_4$ (38.3 mg, 959.0 µmol, 4.4 eq.) was added to the mixture. This mixture was stirred until the eductspot disappeared. In the next step the reaction was acidified with 1 M HCl and extracted with EA. The combined organic phases was washed with brine and dried with $MgSO_4$. . Then the solvent was removed and the crude product was purified by flash chromatography on silica gel with PE:EA (5:1 → 1:3). The product **19** was isolated (24.0 mg, 31 %) as a dark solid. Mp. 139.2 °C. ^{1}H NMR (400 MHz, DMSO) δ 9.75 (s, 1H), 8.97 (s, 1H), 7.94 (s, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.37 (d, J = 8.8 Hz, 1H), 6.77 – 6.72 (m, 2H), 6.61 – 6.57 (m, 1H), 5.34 (s, 2H), 3.67 (s, 3H), 3.07 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 169.6, 148.6, 146.3, 145.4, 143.3, 138.7, 138.0, 132.5, 129.6, 128.3, 125.3, 122.8, 121.7, 121.4, 121.4, 114.3, 113.7, 67.8, 60.2, 56.0. HRMS (ESI) $[M+H]^+$ calculated for $C_{20}H_{17}O_6$ 353.1020, found 353.1021. IR (ATR, cm^{-1}) 3366, 2938, 1755, 1733, 1598, 1515, 1447, 1260, 1200, 1160, 1123, 1021.

1.42 9-(3,4-Dimethoxyphenyl)-7,8-dimethoxynaphtho[2,3-c]furan-1(3H)-one (20)



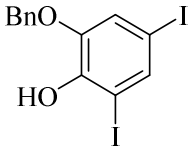
In a round-bottom flask the reactant **19** (10.0 mg, 28.4 µmol, 1.0 eq.) and K_2CO_3 (15.7 mg, 113.5 µmol, 4.0 eq.) was dissolved in 10 mL acetone. Then CH_3I (7.1 µL, 113.5 µmol, 4.0 eq.) was added to the mixture. This mixture was heated to reflux until the reaction was finished. In the next step the solvent was removed and the residue was dissolved in water and extracted with EA. The combined organic phases was washed with brine and dried with $MgSO_4$. Then the solvent was removed and the crude product was purified by flash chromatography on silica gel with PE:EA (5:1 → 1:1). The product **20** was isolated (3.0 mg, 28 %) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.72 (d, J = 9.0 Hz, 1H), 7.49 (d, J = 9.0 Hz, 1H), 6.95 – 6.92 (m, 1H), 6.89 – 6.84 (m, 2H), 5.36 (s, 2H), 3.96 (s, 3H), 3.95 (s, 3H), 3.85 (s, 3H), 3.26 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 150.8, 148.2, 147.8, 146.5, 140.2, 138.0, 133.0, 130.7, 128.6, 124.6, 121.9, 121.0, 120.7, 118.1, 112.6, 109.8, 67.6, 60.9, 56.9, 56.0, 55.9. HRMS (ESI) $[M+H]^+$ calculated for $C_{22}H_{21}O_6$ 381.1333, found 381.1353. IR (ATR, cm^{-1}) 3321, 2960, 2922, 2852, 1763, 1601, 1259, 1209, 1176, 1086, 1019, 798.

1.43 2,4-Diiodo-6-methoxyphenol (22a)



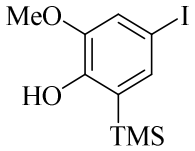
In a round-bottom flask 2-Methoxyphenol **21a** (5.0 g, 40.3 mmol, 1.0 eq.), NaI (13.28 g, 88.6 mmol, 2.2 eq.) and NaOH (2.42 g, 60.4 mmol, 1.5 eq.) was dissolved in 100 mL methanol. The mixture was cooled to 0 °C and a 12 % NaClO solution (45.8 mL, 88.6 mmol, 2.2 eq.) was added dropwise within 30 minutes to the mixture. This mixture was stirred further for 30 minutes at 0 °C. After completion the solvent was removed and the residue was dissolved in water, acidified with 1 M HCl and extracted with DCM. The combined organic phases was washed with brine and dried with $MgSO_4$. Then the solvent was removed and the crude product was purified by flash chromatography on silica gel with DCM. The product **22a** was isolated (13.18 g, 87 %) as a withe solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 1.8 Hz, 1H), 7.08 (d, J = 1.8 Hz, 1H), 6.06 (s, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.7, 146.1, 138.2, 119.9, 82.4, 81.8, 56.6. HRMS (ESI) $[M+H]^+$ calculated for $C_7H_7I_2O_2$ 376.8530, found 376.8520. IR (ATR, cm^{-1}) 3383, 1581, 1476, 1438, 1392, 1337, 1266, 1228, 1189, 1150, 1014.

1.44 2-(Benzyloxy)-4,6-diiodophenol (22b)



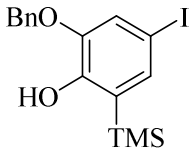
In a round-bottom flask 2-(Benzyloxy)phenol **21b** (5.0 g, 25.0 mmol, 1.0 eq.), NaI (8.23 g, 54.9 mmol, 2.2 eq.) and NaOH (1.5 g, 37.5 mmol, 1.5 eq.) was dissolved in 80 mL methanol. The mixture was cooled to 0 °C and a 12 % NaClO solution (32.3 mL, 62.4 mmol, 2.5 eq.) was added dropwise within 30 minutes to the mixture. This mixture was stirred further for 30 minutes at 0 °C. After completion the solvent was removed and the residue was dissolved in water, acidified with 1 M HCl and extracted with DCM. The combined organic phases was washed with brine and dried with $MgSO_4$. Then the solvent was removed and the crude product was purified by flash chromatography on silica gel with DCM. The product **22b** was isolated (9.18 g, 81 %) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 1.8 Hz, 1H), 7.44 – 7.37 (m, 5H), 7.17 (d, J = 1.8 Hz, 1H), 6.14 (s, 1H), 5.07 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 145.9, 138.6, 135.3, 129.0, 129.0, 128.1, 121.3, 82.5, 81.7, 71.9. HRMS (EI) [M+] calculated for $C_{13}H_{10}I_2O_2$ 451.8765, found 451.8756. IR (ATR, cm^{-1}) 3071, 1583, 1450, 1376, 1265, 1201, 1118, 1010, 831, 736, 695.

1.45 4-Iodo-2-methoxy-6-(trimethylsilyl)phenol (23a)



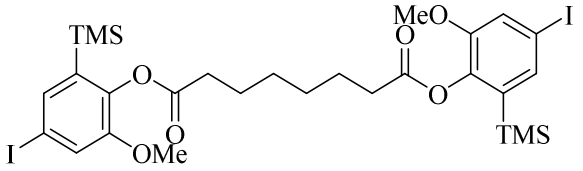
In a round-bottom flask the reactant **22a** (500.0 mg, 1.3 mmol, 1.0 eq.) was dissolved in 10 mL THF. Then hexamethyldisilazane (557.6 µL, 2.7 mmol, 2.0 eq.) was added and the mixture was heated to reflux. After 2 h the mixture was cooled down and the solvent was removed. To the intermediate 10 mL dry THF was added under N_2 atmosphere. Then the mixture was cooled down to -78 °C and a 1.6 M n-BuLi solution (836.8 µL, 1.3 mmol, 1 eq.) was added dropwise and the reaction was stirred for 1 h at -78 °C. Then was waited until the reaction reached room temperature, after that the reaction was quenched with a 1 M HCl and extracted with EA. The combined organic phases was washed with brine and dried with $MgSO_4$. Then the solvent was removed and the crude product was purified by flash chromatography on silica gel with DCM. The product **23a** was isolated (418.0 mg, 97 %) as a yellow solid. Mp. 59.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 2.0 Hz, 1H), 7.11 (d, J = 2.0 Hz, 1H), 5.77 (s, 1H), 3.86 (s, 3H), 0.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 146.7, 135.1, 128.0, 120.5, 81.9, 56.2, -1.1. HRMS (ESI) $[M+H]^+$ calculated for $C_{10}H_{16}IO_2Si$ 322.9959, found 322.9967. IR (ATR, cm^{-1}) 3537, 2956, 1456, 1393, 1331, 1263, 1235, 1201, 1182, 1161, 838, 827.

1.46 2-(Benzyloxy)-4-iodo-6-(trimethylsilyl)phenol (23b)



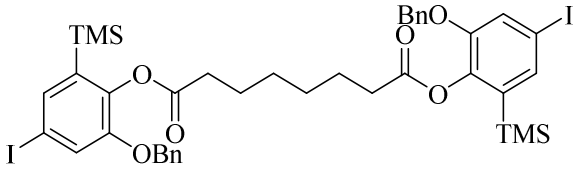
In a round-bottom flask the reactant **22b** (3.5 g, 7.7 mmol, 1.0 eq.) was dissolved in 20 mL THF. Then hexamethyldisilazane (3.25 mL, 15.5 mmol, 2.0 eq.) was added and the mixture was heated to reflux. After 2 h the mixture was cooled down and the solvent was removed. To the intermediate 30 mL dry THF was added under N_2 atmosphere. Then the mixture was cooled down to -78 °C and a 1.6 M n-BuLi solution (4.48 mL, 7.7 mmol, 1 eq.) was added dropwise and the reaction was stirred for 2 h at -78 °C. Then was waited until the reaction reached room temperature, after that the reaction was quenched with a 1 M HCl and extracted with EA. The combined organic phases was washed with brine and dried with $MgSO_4$. Then the solvent was removed and the crude product was purified by flash chromatography on silica gel with DCM. The product **23b** was isolated (2.5 g, 82 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 5H), 7.23 – 7.20 (m, 2H), 5.82 (s, 1H), 5.05 (s, 2H), 0.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 146.7, 135.1, 128.0, 120.5, 81.9, 56.2, -1.1. HRMS (EI) [M+] calculated for $C_{16}H_{19}IO_2Si$ 322.9959, found 322.9967. IR (ATR, cm^{-1}) 353, 2956, 1493, 1452, 1400, 1378, 1266, 1245, 1198, 1021, 836, 737, 694.

1.47 Bis(4-iodo-2-methoxy-6-(trimethylsilyl)phenyl) octanedioate (24a)



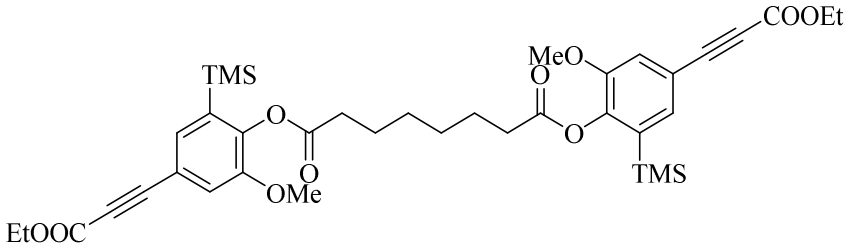
According the **GP1 23a** (3.76 g, 11.7 mmol, 1.0 eq.), octanedioic acid (1.02 g, 5.8 mmol, 0.5 eq.) and DMAP (142.5 mg, 1.2 mmol, 0.1 eq.) were dissolved in 50 mL dry DCM. Then DIC (4.57 mL, 29.2 mmol, 2.5 eq.) was added. The crude product was purified by flash chromatography on silica gel with DCM. The product **24a** was isolated (2.71 g, 59 %) as a withe solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 2.0 Hz, 2H), 7.24 (d, J = 1.9 Hz, 2H), 3.77 (s, 6H), 2.62 – 2.53 (m, 4H), 1.83 – 1.75 (m, 4H), 1.53 – 1.46 (m, 4H), 0.25 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 151.3, 144.5, 136.1, 134.9, 122.7, 91.2, 56.2, 34.2, 28.9, 24.8, -0.8. HRMS (ESI) $[M+H]^+$ calculated for $C_{28}H_{41}I_2O_6Si_2$ 783.0531, found 783.0533. IR (ATR, cm^{-1}) 2939, 1753, 1452, 1436, 1389, 1261, 1247, 1207, 1160, 1186, 1120, 835.

1.48 Bis(2-(benzyloxy)-4-iodo-6-(trimethylsilyl)phenyl) octanedioate (24b)



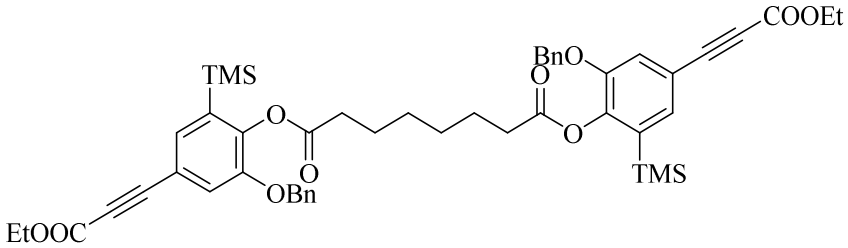
According the **GP1 23b** (1.63 g, 4.1 mmol, 1.0 eq.), octanedioic acid (356.2 mg, 2.0 mmol, 0.5 eq.) and DMAP (50.0 mg, 409.3 µmol, 0.1 eq.) were dissolved in 25 mL dry DCM. Then DIC (2.56 mL, 16.4 mmol, 4.0 eq.) was added. The crude product was purified by flash chromatography on silica gel with DCM. The product **24b** was isolated (899.0 mg, 47 %) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 10H), 7.32 (d, J = 2.1 Hz, 2H), 7.31 (d, J = 2.1 Hz, 2H), 4.98 (s, 4H), 2.46 – 2.38 (m, 4H), 1.59 – 1.52 (m, 4H), 1.26 – 1.17 (m, 4H), 0.25 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 150.5, 144.8, 136.3, 136.1, 135.2, 128.7, 128.4, 127.9, 123.7, 91.0, 71.1, 34.2, 28.9, 24.7, -0.8. HRMS (ESI) $[M+H]^+$ calculated for $C_{40}H_{49}I_2O_6Si_2$ 935.1157, found 935.1133. IR (ATR, cm^{-1}) 2949, 1760, 1547, 1439, 1401, 1373, 1248, 1262, 1205, 1162, 1116, 836.

1.49 Bis(4-(3-ethoxy-3-oxoprop-1-yn-1-yl)-2-methoxy-6-(trimethylsilyl)phenyl) octanedioate (25a)



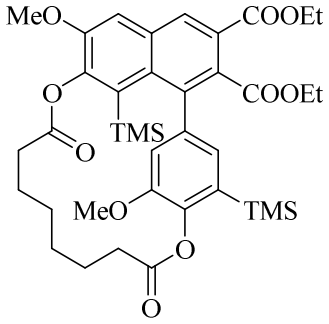
According the **GP2 24a** (2.17 g, 2.8 mmol, 1.0 eq.), CuI (42.2 mg, 221.3 µmol, 0.08 eq.), $Pd(P(Ph)_3)_2Cl_2$ (155.3 mg, 221.3 µmol, 0.08 eq.) in 30 mL TEA. Then triethyl orthopropiolate (1.43 g, 8.3 mmol, 3.0 eq.) was added and the reaction was stirred at r.t. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **25a** was isolated (1.89 g, 95 %) as a red oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 1.8 Hz, 2H), 7.17 (d, J = 1.8 Hz, 2H), 4.31 (q, J = 7.1 Hz, 4H), 3.80 (s, 6H), 2.64 – 2.54 (m, 4H), 1.84 – 1.75 (m, 4H), 1.54 – 1.48 (m, 4H), 1.36 (t, J = 7.1 Hz, 6H), 0.26 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 154.2, 150.5, 146.7, 134.3, 131.8, 117.8, 117.6, 86.2, 80.5, 62.3, 56.1, 34.2, 28.9, 24.8, 14.3, -0.9. HRMS (ESI) $[M+H]^+$ calculated for $C_{38}H_{51}O_{10}Si_2$ 723.3021 found 723.3021. IR (ATR, cm^{-1}) 2953, 2215, 1761, 1705, 1446, 1317, 1245, 1213, 1134, 1113, 864, 837.

1.50 Bis(2-(benzyloxy)-4-(3-ethoxy-3-oxoprop-1-yn-1-yl)-6-(trimethylsilyl)phenyl) octanedioate (25b)



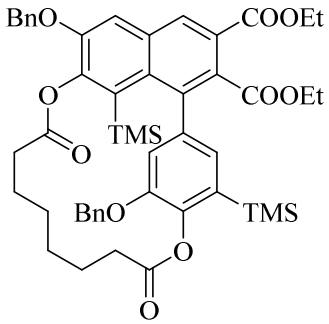
According the **GP2 24b** (100.0 mg, 107.0 µmol, 1.0 eq.), CuI (0.8 mg, 4.3 µmol, 0.04 eq.), $Pd(P(Ph)_3)_2Cl_2$ (3.0 mg, 4.3 µmol, 0.04 eq.) in 10 mL TEA. Then triethyl orthopropiolate (55.3 mg, 320.9 µmol, 3.0 eq.) was added and the reaction was stirred at r.t. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **25b** was isolated (76.0 mg, 81 %) as a yellow solid. Mp. 113.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.35 (m, 6H), 7.34 – 7.30 (m, 4H), 7.24 – 7.21 (m, 2H), 5.01 (s, 4H), 4.30 (q, J = 7.1 Hz, 4H), 2.49 – 2.43 (m, 4H), 1.61 – 1.53 (m, 4H), 1.36 (t, J = 7.1 Hz, 6H), 1.28 – 1.23 (m, 4H), 0.28 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 154.1, 149.6, 147.0, 136.0, 134.3, 132.0, 128.6, 128.3, 127.7, 118.5, 117.7, 86.1, 80.5, 70.9, 62.2, 34.1, 28.8, 24.5, 14.2, -0.9. HRMS (ESI) $[M+H]^+$ calculated for $C_{50}H_{59}O_{10}Si_2$ 875.3641 found 875.3632. IR (ATR, cm^{-1}) 2942, 2214, 1761, 1701, 1382, 1319, 1244, 1212, 1134, 1111, 843, 748.

1.51 Diethyl 1^6,2^3-dimethoxy-4,11-dioxo-1^8,2^5-bis(trimethylsilyl)-3,12-dioxa-1(1,7)-naphthalena-2(1,4)-benzenacyclododecaphane-1^2,1^3-dicarboxylate (26a)



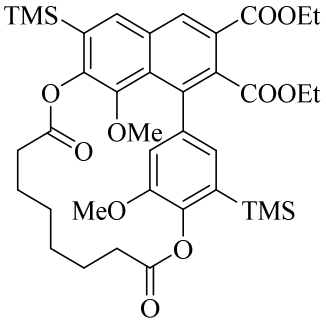
According the **GP4 25a** (1.76 g, 2.4 mmol, 3 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 3 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **26a** was isolated (47.0 mg, 3 %) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.48 (d, J = 2.0 Hz, 1H), 7.12 (s, 1H), 6.08 (d, J = 2.0 Hz, 1H), 4.42 – 4.36 (m, 2H), 4.22 – 4.14 (m, 1H), 4.02 – 3.96 (m, 1H), 3.93 (s, 3H), 3.56 (s, 3H), 2.78 – 2.71 (m, 1H), 2.67 – 2.59 (m, 1H), 2.53 – 2.45 (m, 1H), 2.02 – 1.94 (m, 1H), 1.87 – 1.80 (m, 1H), 1.76 – 1.70 (m, 1H), 1.66 – 1.57 (m, 2H), 1.41 – 1.37 (m, 3H), 1.02 – 0.98 (m, 3H), 0.34 (s, 9H), -0.16 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 172.2, 168.6, 165.8, 151.4, 151.1, 148.9, 146.5, 139.0, 138.1, 137.6, 134.7, 132.6, 130.9, 130.5, 129.9, 127.5, 124.7, 121.0, 108.2, 61.6, 61.4, 56.1, 55.5, 34.4, 31.5, 29.4, 27.7, 27.4, 25.2, 23.9, 14.4, 13.9, 1.7, -0.8. HRMS (ESI) $[M+H]^+$ calculated $C_{38}H_{51}O_{10}Si_2$ 723.3021 found 723.3019. IR (ATR, cm^{-1}) 2946, 1771, 1753, 1718, 1417, 1262, 1238, 1207, 1138, 1109, 1066, 837.

1.52 Diethyl 1^6,2^3-bis(benzyloxy)-4,11-dioxo-1^8,2^5-bis(trimethylsilyl)-3,12-dioxa-1(1,7)-naphthalena-2(1,4)-benzenacyclododecaphane-1^2,1^3-dicarboxylate (26b)



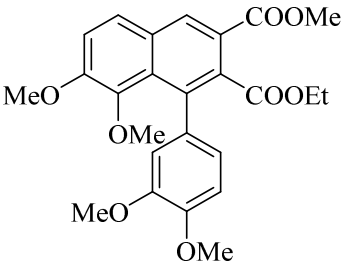
According the **GP4 25b** (250.0 mg, 285.7 µmol, 2 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 3 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **26b** was isolated (44.0 mg, 18 %) as a yellow solid. Mp. 160.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.54 (d, J = 2.0 Hz, 1H), 7.46 – 7.29 (m, 10H), 7.18 (s, 1H), 6.27 (d, J = 2.0 Hz, 1H), 5.29 – 5.21 (m, 2H), 4.99 – 4.92 (m, 1H), 4.69 – 4.62 (m, 1H), 4.44 – 4.37 (m, 2H), 4.24 – 4.16 (m, 1H), 4.04 – 3.96 (m, 1H), 2.80 – 2.72 (m, 1H), 2.72 – 2.62 (m, 1H), 2.50 – 2.42 (m, 1H), 1.84 – 1.74 (m, 2H), 1.69 (s, 1H), 1.67 – 1.58 (m, 2H), 1.42 – 1.38 (m, 3H), 1.10 – 1.05 (m, 2H), 1.04 – 1.00 (m, 3H), 0.96 – 0.73 (m, 2H), 0.37 (s, 9H), -0.13 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 172.1, 168.7, 165.8, 151.8, 150.2, 148.1, 146.8, 139.0, 138.2, 137.9, 136.3, 136.1, 134.9, 132.5, 131.2, 130.6, 130.0, 128.8, 128.4, 128.3, 127.9, 127.9, 127.4, 127.2, 124.7, 122.3, 109.8, 70.7, 69.9, 61.7, 61.5, 34.5, 31.7, 27.5, 27.3, 25.4, 23.2, 14.4, 14.0, 1.8, -0.7. HRMS (ESI) $[M+H]^+$ calculated for $C_{50}H_{59}O_{10}Si_2$ 875.3641 found 875.3652. IR (ATR, cm^{-1}) 2939, 1773, 1723, 1421, 1262, 1246, 1229, 1138, 1153, 1100, 1067, 838.

1.53 Diethyl 1^8,2^3-dimethoxy-4,11-dioxo-1^6,2^5-bis(trimethylsilyl)-3,12-dioxa-1(1,7)-naphthalena-2(1,4)-benzenacyclododecaphane-1^2,1^3-dicarboxylate (27a)



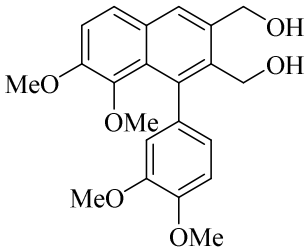
According the **GP4 25a** (1.76 g, 2.4 mmol, 3 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 3 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **27a** was isolated (938.0 mg, 53 %) as a yellow solid. Mp. 161.7 °C. ^{1}H NMR (400 MHz, MeOD) δ 8.73 (s, 1H), 8.06 (s, 1H), 7.27 (d, J = 1.9 Hz, 1H), 6.77 (d, J = 1.9 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 4.22 – 4.17 (m, 1H), 4.09 – 4.03 (m, 1H), 3.73 (s, 3H), 3.05 (s, 3H), 2.74 – 2.66 (m, 1H), 2.53 – 2.37 (m, 2H), 2.03 – 1.94 (m, 1H), 1.77 – 1.67 (m, 2H), 1.66 – 1.58 (m, 2H), 1.40 (t, J = 7.1 Hz, 3H), 1.06 – 1.02 (m, 3H), 0.35 (s, 9H), 0.31 (s, 9H). ^{13}C NMR (101 MHz, MeOD) δ 175.3, 172.9, 170.2, 166.6, 151.1, 150.6, 148.7, 146.8, 139.2, 137.3, 136.2, 134.1, 133.9, 133.8, 133.4, 131.6, 131.0, 126.6, 125.6, 118.3, 63.3, 62.8, 62.6, 56.4, 35.0, 32.3, 29.5, 27.7, 26.5, 24.6, 14.6, 14.2, -0.8, -0.9. HRMS (ESI) $[M+H]^+$ calculated for $C_{38}H_{51}O_{10}Si_2$ 723.3021 found 723.3016. IR (ATR, cm^{-1}) 2928, 1765, 1731, 1709, 1396, 1262, 1249, 1223, 1109, 1092, 838, 822. For crystallographic data see chapter 3.

1.54 2-ethyl 3-methyl 1-(3,4-dimethoxyphenyl)-7,8-dimethoxynaphthalene-2,3-dicarboxylate (28)



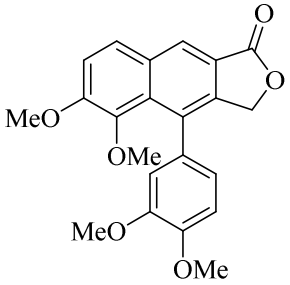
To a solution of **27a** (170.0 mg, 235.1 µmol, 1.0 eq.) in 10 mL dry ethanol, NaOH (282.1 mg, 7.1 mmol, 30.0 eq.) and KF (27.3 mg, 470.3 µmol, 2.0 eq.) were added. Than the mixture was heated to reflux for 24 h. The solvent was removed and the crude residual was dissolved in dry acetonitrile. For the next step CH_3I (439.2 µL, 7.1 mmol, 30.0 eq.) was added and the mixture was heated to reflux for 4 h. After completion the solvent was removed the residuals acidified with 1 M HCl and the aqueous phase was extracted wit EE several times. The combined organic phases was washed with brine and dried over $MgSO_4$. After the solvent was removed the crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **28** was isolated (21.0 mg, 20 %) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.76 (d, J = 9.0 Hz, 1H), 7.39 (d, J = 9.0 Hz, 1H), 6.92 – 6.89 (m, 1H), 6.88 – 6.83 (m, 2H), 4.05 – 3.98 (m, 2H), 3.95 (s, 3H), 3.91 (s, 6H), 3.83 (s, 3H), 3.21 (s, 3H), 1.06 – 1.01 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.0, 166.2, 152.9, 148.0, 147.4, 144.8, 135.4, 133.8, 132.5, 132.4, 129.5, 128.8, 126.6, 122.1, 115.7, 113.7, 109.6, 61.2, 60.7, 56.5, 56.0, 55.9, 52.5, 14.0. HRMS (ESI) $[M+H]^+$ calculated for $C_{25}H_{27}O_8$ 455.1700, found 1705. IR (ATR, cm^{-1}) 2954, 2927, 1718, 1452, 1255, 1232, 1205, 1139, 1103, 1075, 1025.

1.55 (1-(3,4-dimethoxyphenyl)-7,8-dimethoxynaphthalene-2,3-diyl)dimethanol (29)



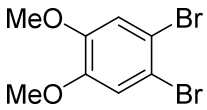
In a dried flask the educt **28** (15.0 mg, 33.0 µmol, 1.0 eq.) was dissolved in 8.25 mL dry THF. Than $LiAlH_4$ (10.0 mg, 264.0 µmol, 8.0 eq.) was added and the reaction was stirred till completion at r.t. After the reaction was finished, the mixture was acidified by 1 M HCl and extracted with DCM. The combined organic phases were washed with brine and dried over $MgSO_4$. After the solvent was removed the crude product was purified by flash chromatography on silica gel with PE:EA (5:1 → 1:1). The product **29** was isolated (4.0 mg, 32 %) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.61 (d, J = 9.0 Hz, 1H), 7.31 (d, J = 9.0 Hz, 1H), 6.90 (d, J = 8.1 Hz, 1H), 6.86 (d, J = 1.9 Hz, 1H), 6.82 (dd, J = 8.0, 1.9 Hz, 1H), 4.97 – 4.84 (m, 2H), 4.59 – 4.47 (m, 2H), 3.94 (s, 3H), 3.92 (s, 3H), 3.83 (s, 3H), 3.22 (s, 3H), 2.49 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 148.0, 147.7, 144.8, 137.5, 136.7, 135.4, 134.8, 129.7, 129.4, 128.0, 124.7, 121.1, 115.3, 112.9, 110.2, 65.3, 63.1, 60.6, 60.2, 56.6, 56.1, 56.0, 32.9, 29.5, 25.8. HRMS (ESI) $[M+H]^+$ calculated for $C_{22}H_{25}O_6$ 385.1646, found 385.1272. IR (ATR, cm^{-1}) 3390, 2931, 1729, 1602, 1510, 1455, 1336, 1227, 1080.

1.56 4-(3,4-dimethoxyphenyl)-5,6-dimethoxynaphtho[2,3-c]furan-1(3H)-one (30)



The educt **29** (4.0 mg, 10.4 µmol, 1.0 eq) was dissolved in 5 mL DCM. Then MnO_2 (54.3 mg, 624.3 µmol, 60.0 eq.) was added to the mixture and all was stirred for 48 h at r.t. After the whole educt was converted, the reaction was filtered over Celite® and washed with DCM. The solvent was removed and the crude product was purified by flash chromatography on silica gel with PE:EA (5:1 → 1:2). The product **30** was isolated (3.0 mg, 76 %) as a withe solid. Mp. 211.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.88 (d, J = 9.1 Hz, 1H), 7.43 (d, J = 9.1 Hz, 1H), 6.95 – 6.92 (m, 1H), 6.89 – 6.84 (m, 2H), 5.18 – 5.04 (m, 2H), 4.00 (s, 3H), 3.96 (s, 3H), 3.86 (s, 3H), 3.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 152.6, 148.5, 148.2, 144.3, 141.2, 132.2, 131.4, 130.6, 130.5, 127.4, 127.1, 121.1, 120.2, 115.3, 112.0, 110.6, 70.1, 60.8, 56.7, 56.1, 56.1. HRMS (ESI) $[M+H]^+$ calculated for $C_{22}H_{21}O_6$ 381.1333, found 381.1330. IR (ATR, cm^{-1}) 2934, 1752, 1604, 1512, 1456, 1275, 1244, 1229, 1133, 1072, 1019. For crystallographic data see chapter 3.

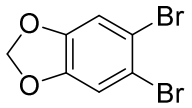
1.57 1,2-Dibromo-4,5-dimethoxybenzene (32a) [6]



The reactant 1,2-Dimethoxybenzene **31a** (1.0 g, 7.2 mmol, 1.0 eq.) was dissolved in 20 mL DCM and cooled with an ice bath to 0 °C. Then a solution of 20 ml DCM and bromine (815.6 µL, 15.9 mmol, 2.2 eq.) was added dropwise over a period of 2.5 h. In the next step the ice bath was removed and the reaction was stirred till full conversion. The organic phase was washed twice with 30 mL of a 20 % sodium thiosulfate solution, then with brine and dried over $MgSO_4$. The solvent was removed and the crude product was purified by flash chromatography on silica gel with DCM. The product **32a** was isolated (2.1 g, 99 %) as a withe solid. Mp. 88.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (s, 2H), 3.86 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.1, 116.1, 114.9, 56.4. HRMS (ESI) $[M+H]^+$ calculated for

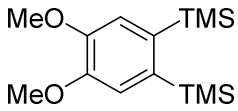
$C_8H_9Br_2O_2$ 294.8964, found 294.8962. IR (ATR, cm^{-1}) 2904, 2831, 1494, 1435, 1420, 1350, 1330, 1246, 1209, 1189, 1175, 1018, 837.

1.58 5,6-Dibromobenzo[d][1,3]dioxole (32b) [7]



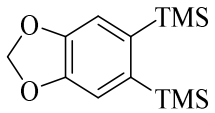
The reactant Benzo[d][1,3]dioxole **31b** (10.0 g, 81.9 mmol, 1.0 eq.) was dissolved in 50 mL DCM and cooled with an ice bath to 0 °C. Then a solution of 50 ml DCM and bromine (8.8 mL, 172.0 mmol, 2.1 eq.) was added dropwise over a period of 2.5 h. In the next step the ice bath was removed and the reaction was stirred till full conversion. The organic phase was washed twice with 30 mL of a 20 % sodium thiosulfate solution, then with brine and dried over $MgSO_4$. The solvent was removed and the crude product was purified by flash chromatography on silica gel with DCM. The product **32b** was isolated (22.9 g, 100 %) as a withe solid. Mp. 82.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 – 6.99 (m, 2H), 6.02 – 5.98 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 115.5, 113.4, 102.5. HRMS (ESI) $[M+H]^+$ calculated for $C_7H_5Br_2O_2$ 278.8651, found 278.8597. IR (ATR, cm^{-1}) 3106, 2904, 1688, 1495, 1479, 1446, 1401, 1355, 1225, 1214, 1192, 1138, 927, 848.

1.59 (4,5-Dimethoxy-1,2-phenylene)bis(trimethylsilane) (33a)



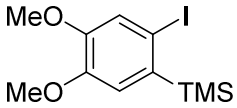
A schlenk flask was loaded with CuCl (1.4 g, 13.7 mmol, 1.0 eq.) and LiCl (4.7 g, 109.8 mmol, 8.0 eq) and all was dried at 200 °C. Then Mg powder (2.7 g, 109.8 mmol, 8.0 eq.) and 50 mL dry THF were added. To this solution chlorotrimethylsilane (27.9 mL, 219.5 mmol, 16.0 eq.) was slowly added. After 5 minutes the mixture was cooled with ice to 0 °C and in the next step the reactant **32a** (4.1 g, 13.7 mmol, 1.0 eq.) was added. After 2 h at 0 °C the ice was removed and the mixture was stirred for additional 24 h at r. t. Then the reaction was slowly quenched with ice and saturated $NaHCO_3$ solution while cooling with an ice bath. The aqueous phase was extracted with PE several times. Then the combined organic phases was washed with brine and dried over $MgSO_4$. The crude product was purified by flash chromatography on silica gel with PE:DCM (1:1). The product **33a** was isolated (1.26 g, 33 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (s, 2H), 3.91 (s, 6H), 0.38 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.3, 138.4, 118.9, 55.7, 2.2. HRMS (ESI) $[M+H]^+$ calculated for $C_{14}H_{27}O_2Si_2$ 283.1544, found 283.1591. IR (ATR, cm^{-1}) 2950, 1556, 1298, 1275, 1254, 1198, 1129, 1043, 857, 830, 754.

1.60 5,6-Bis(trimethylsilyl)benzo[d][1,3]dioxole (33b)



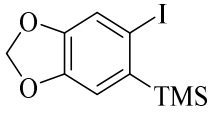
A schlenk flask was loaded with CuCl (707.3 mg, 7.2 mmol, 1.0 eq.) and LiCl (2.42 g, 57.2 mmol, 8.0 eq) and all was dried at 200 °C. Then Mg powder (1.39 g, 57.2 mmol, 8.0 eq.) and 50 mL dry THF were added. To this solution chlorotrimethylsilane (14.5 mL, 114.3 mmol, 16.0 eq.) was slowly added. After 5 minutes the mixture was cooled with ice to 0 °C and in the next step the reactant **32b** (2.0 g, 7.2 mmol, 1.0 eq.) was added. After 2 h at 0 °C the ice was removed and the mixture was stirred for additional 24 h at r. t. Then the reaction was slowly quenched with ice and saturated $NaHCO_3$ solution while cooling with an ice bath. The aqueous phase was extracted with PE several times. Then the combined organic phases was washed with brine and dried over $MgSO_4$. The crude product was purified by flash chromatography on silica gel with PE:DCM (1:1). The product **33b** was isolated (1.17 g, 61 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 2H), 5.92 (s, 2H), 0.35 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 140.1, 127.3, 115.7, 112.9, 108.7, 100.6, 100.5, 2.3. HRMS (ESI) $[M+H]^+$ calculated for $C_{13}H_{23}O_2Si_2$ 267.1231, found 267.1216. IR (ATR, cm^{-1}) 2953, 1475, 1292, 1248, 1217, 1087, 1040, 938, 859, 828, 756.

1.61 (2-Iodo-4,5-dimethoxyphenyl)trimethylsilane (34a)



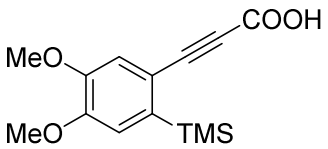
To a solution of **33a** (1.3 g, 4.5 mmol, 1.0 eq.) and N-iodosuccinimide (1.2 g, 5.4 mmol, 1.2 eq.) in 30 mL acetic acid was stirred at r.t. for 4 h. The reaction mixture was poured in water and neutralized with $NaHCO_3$. Than the mixture was extracted with DCM. In the next step the organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by flash chromatography on silica gel with PE:DCM (1:1). The product **34a** was isolated (1.25 g, 83 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 6.89 (s, 1H), 3.86 – 3.85 (m, 6H), 0.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 148.6, 136.6, 123.2, 119.0, 92.7, 56.1, 56.0, -0.2. HRMS (ESI) $[M+H]^+$ calculated for $C_{11}H_{18}IO_2Si$ 337.0115, found 337.0135.

1.62 (6-Iodobenzo[d][1,3]dioxol-5-yl)trimethylsilane (34b)



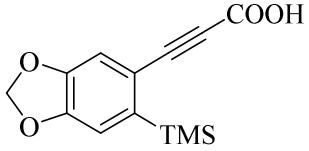
To a solution of **33b** (150.0 mg, 562.9 µmol, 1.0 eq.) and N-iodosuccinimide (126.6 mg, 562.9 µmol, 1.0 eq.) in 30 mL acetic acid was stirred at r.t. for 4 h. The reaction mixture was poured in water and neutralized with $NaHCO_3$. Than the mixture was extracted with DCM. In the next step the organic phase was washed with brine and dried over $MgSO_4$. The crude product was purified by flash chromatography on silica gel with PE:DCM (1:1). The product **34b** was isolated (153.0 mg, 85 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 6.90 (s, 1H), 5.94 (s, 2H), 0.39 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 148.0, 137.8, 120.5, 115.7, 101.4, 92.0, -0.0. HRMS (ESI) $[M+H]^+$ calculated for $C_{10}H_{14}IO_2Si$ 320.9802, found 320.9769. IR (ATR, cm^{-1}) 2956, 2897, 1501, 1465, 1353, 1247, 1233, 1201, 1038, 934, 908, 837, 822.

1.63 3-(4,5-Dimethoxy-2-(trimethylsilyl)phenyl)propiolic acid (35a)



According the **GP2 34a** (10.0 mg, 29.7 µmol, 1.0 eq.), CuI (1.1 mg, 6.0 µmol, 0.2 eq.), $Pd(P(Ph)_3)_2Cl_2$ (4.2 mg, 6.0 µmol, 0.2 eq.) in 5 mL TEA. Then triethyl orthopropiolate (10.2 mg, 59.5 µmol, 2.0 eq.) was added and the reaction was stirred at reflux. After completion the crude intermediate product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The intermediate product was isolated (7.0 mg, 77 %) as a yellow oil. According the **GP3** the intermediate product (110.0 mg, 359.0 µmol) was converted to product **35a** (100.0 mg, 100 %) as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 1H), 6.98 (s, 1H), 3.94 (s, 3H), 3.89 (s, 3H), 0.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 150.9, 149.3, 139.6, 117.3, 116.5, 116.4, 91.4, 81.9, 56.1, 56.0, -0.8. HRMS (ESI) $[M+H]^+$ calculated for $C_{14}H_{19}O_4Si$ 279.1047 found 279.1055. IR (ATR, cm^{-1}) 3259, 2955, 2204, 1702, 1678, 1586, 1553, 1498, 1253, 1165, 1066, 841.

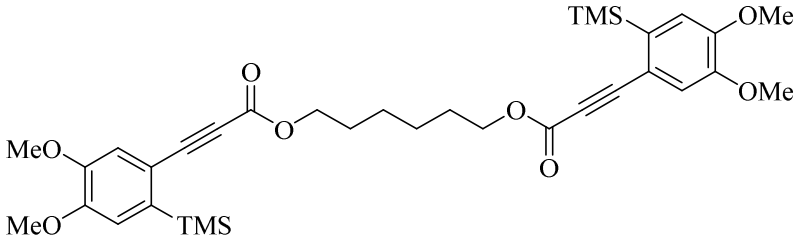
1.64 3-(6-(Trimethylsilyl)benzo[d][1,3]dioxol-5-yl)propiolic acid (35b)



According the **GP2 34b** (588.0 mg, 1.8 mmol, 1.0 eq.), CuI (70.0 mg, 367.3 µmol, 0.2 eq.), $Pd(P(Ph)_3)_2Cl_2$ (257.8 mg, 367.3 µmol, 0.2 eq.) in 20 mL TEA. Then triethyl orthopropiolate (632.5 mg, 3.7 mmol, 2.0 eq.) was added and the reaction was stirred at reflux. After completion the crude intermediate product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The intermediate product was isolated (427.0 mg, 92 %) as a yellow oil. According the **GP3** the intermediate product (105.0 g, 361.6 µmol) was converted to product **35b** (95.0 mg, 100 %) as a brown solid. Mp. 165.4 °C. ^{1}H NMR

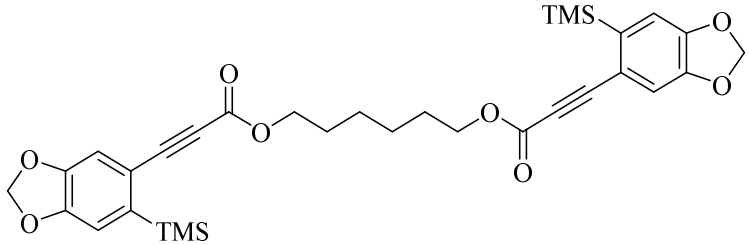
(400 MHz, $CDCl_3$) δ 7.09 (s, 1H), 6.98 (s, 1H), 6.01 (s, 2H), 0.37 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.9, 150.0, 148.2, 142.1, 117.5, 114.6, 114.1, 101.7, 90.9, 81.8, -0.8. HRMS (ESI) $[M+H]^+$ calculated for $C_{13}H_{15}O_4Si$ 263.0734 found 263.0713. IR (ATR, cm^{-1}) 2952, 2920, 2201, 1681, 1658, 1499, 1481, 1287, 1238, 1028, 834.

1.65 Hexane-1,6-diyl bis(3-(4,5-dimethoxy-2-(trimethylsilyl)phenyl)propiolate) (36a)



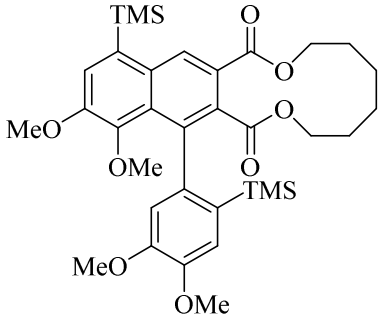
According the **GP1** Hexane-1,6-diol (19.0 mg, 161.7 µmol, 1.0 eq.), **35a** (90.0 mg, 323.3 µmol, 2.0 eq.) and DMAP (4.0 mg, 32.3 µmol, 0.2 eq.) were dissolved in 10 mL dry DCM. Then DIC (60.8 µL, 388.0 mmol, 2.4 eq.) was added. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **36a** was isolated (36.0 mg, 35 %) as a white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.12 (s, 2H), 6.96 (s, 2H), 4.26 – 4.20 (m, 4H), 3.92 (s, 6H), 3.87 (s, 6H), 1.77 – 1.69 (m, 4H), 1.50 – 1.43 (m, 4H), 0.38 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 150.5, 149.2, 138.9, 117.0, 116.9, 116.4, 88.6, 82.6, 65.7, 56.1, 55.9, 28.5, 25.6, -0.9. HRMS (ESI) $[M+H]^+$ calculated for $C_{34}H_{47}O_8Si_2$ 639.2804, found 639.2787. IR (ATR, cm^{-1}) 2948, 2207, 1705, 1585, 1499, 1246, 1211, 1187, 1165, 1069, 843.

1.66 Hexane-1,6-diyl bis(3-(6-(trimethylsilyl)benzo[d][1,3]dioxol-5-yl)propiolate) (36b)



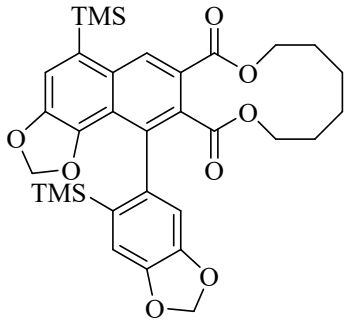
According the **GP1** Hexane-1,6-diol (20.0 mg, 171.5 µmol, 1.0 eq.), **35b** (90.0 mg, 343.1 µmol, 2.0 eq.) and DMAP (4.2 mg, 34.3 µmol, 0.2 eq.) were dissolved in 10 mL dry DCM. Then DIC (64.5 µL, 411.7 mmol, 2.4 eq.) was added. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **36b** was isolated (66.0 mg, 63 %) as a yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.06 (s, 1H), 6.96 (s, 1H), 5.99 (s, 2H), 4.25 – 4.20 (m, 2H), 1.76 – 1.69 (m, 2H), 1.49 – 1.44 (m, 2H), 0.36 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 149.6, 148.1, 141.3, 118.0, 114.3, 113.9, 101.6, 88.2, 82.5, 65.7, 28.5, 25.6, -0.9. HRMS (ESI) $[M+H]^+$ calculated for $C_{32}H_{39}O_8Si_2$ 607.2178, found 607.2186. IR (ATR, cm^{-1}) 2956, 2208, 1693, 1503, 1476, 1335, 1264, 1228, 1169, 1033, 1019, 837.

1.67 11-(4,5-Dimethoxy-2-(trimethylsilyl)phenyl)-12,13-dimethoxy-15-(trimethylsilyl)-3,4,5,6,7,8-hexahydronaphtho[2,3-c][1,6]dioxacyclododecine-1,10-dione (37a)



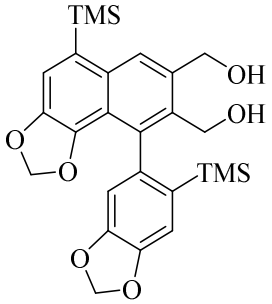
According the **GP4 36a** (30.0 mg, 47.0 µmol, 4 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 2 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **37a** was isolated (30.0 mg, 100 %) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 7.55 (s, 1H), 6.99 (s, 1H), 6.82 (s, 1H), 4.44 – 4.39 (m, 2H), 3.94 (s, 3H), 3.93 (s, 3H), 3.89 – 3.86 (m, 2H), 3.81 (s, 3H), 3.19 (s, 3H), 1.84 – 1.79 (m, 2H), 1.75 – 1.71 (m, 2H), 1.58 – 1.54 (m, 4H), 0.52 (s, 9H), -0.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 166.7, 151.4, 147.3, 146.8, 146.2, 138.8, 137.7, 137.4, 133.3, 132.7, 132.4, 131.8, 131.2, 123.9, 121.9, 116.1, 113.8, 67.2, 64.9, 60.3, 56.8, 56.0, 55.9, 25.8, 25.7, 25.6, 23.0, 0.5, 0.1. HRMS (ESI) $[M+H]^+$ calculated for $C_{34}H_{47}O_8Si_2$ 639.2804, found 639.2833. IR (ATR, cm^{-1}) 2953, 1726, 1580, 1503, 1458, 1255, 1205, 1160, 1070, 840.

1.68 5-(Trimethylsilyl)-17-(6-(trimethylsilyl)benzo[d][1,3]dioxol-5-yl)-9,10,11,12,13,14-hexahydro-[1,3]dioxolo[4',5':5,6]naphtho[2,3-c][1,6]dioxacyclododecine-7,16-dione (37b)



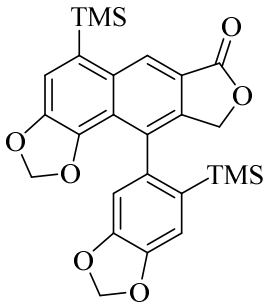
According the **GP4 36b** (60.0 mg, 98.9 µmol, 4 mmol/L, 1.0 eq.) was dissolved in DCM. Then the mixture was pumped through the UVB reactor once with a flowrate of 2 mL/min. The crude product was purified by flash chromatography on silica gel with PE:EA (10:1 → 3:1). The product **37b** was isolated (37.0 mg, 62 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.46 (s, 1H), 6.97 (s, 1H), 6.69 (s, 1H), 6.05 – 5.93 (m, 2H), 5.87 – 5.72 (m, 2H), 4.43 (s, 2H), 4.14 – 3.93 (m, 2H), 1.89 – 1.74 (m, 4H), 1.57 (s, 4H), 0.50 (s, 9H), -0.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 166.7, 146.8, 146.3, 143.4, 137.1, 136.0, 135.9, 133.8, 133.6, 132.7, 131.2, 122.6, 122.1, 118.8, 112.8, 111.3, 101.5, 100.9, 67.1, 65.1, 25.8, 25.6, 23.1, 0.6, 0.1. HRMS (ESI) $[M+H]^+$ calculated for $C_{32}H_{39}O_8Si_2$ 607.2178, found 607.2186. IR (ATR, cm^{-1}) 2953, 2923, 1722, 1477, 1452, 1255, 1232, 1210, 1168, 1152, 834.

1.69 (5-(trimethylsilyl)-9-(6-(trimethylsilyl)benzo[d][1,3]dioxol-5-yl)naphtho[1,2-d][1,3]dioxole-7,8-diyl)dimethanol (38)



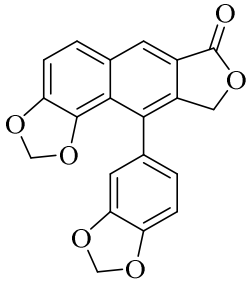
In a roundbottem flask the reactant **37b** (20.0 mg, 33.0 µmol, 1.0 eq.) was dissolved in 10 mL THF. Then $LiAlH_4$ (5.8 mg, 145.0 µmol, 4.4 eq.) was added to the mixture. This mixture was stirred until the eductspot disappeared. In the next step the reaction was acidified with 1 M HCl and extracted with EA. The combined organic phases was washed with brine and dried with $MgSO_4$. The product **38** was isolated (5.0 mg, 31%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.39 (s, 1H), 7.04 (s, 1H), 6.70 (s, 1H), 6.04 – 6.00 (m, 2H), 5.78 – 5.70 (m, 2H), 5.04 (d, J = 12.2 Hz, 1H), 4.81 (d, J = 12.2 Hz, 1H), 4.65 (d, J = 11.8 Hz, 1H), 4.51 (d, J = 11.8 Hz, 1H), 2.04 (s, 2H), 0.47 (s, 9H), -0.30 (s, 9H).

1.70 5-(trimethylsilyl)-10-(6-(trimethylsilyl)benzo[d][1,3]dioxol-5-yl)furo[3',4':6,7]naphtho[1,2-d][1,3]dioxol-7(9H)-one (39)



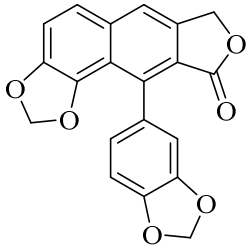
The reactant **38** (5.0 mg, 10.1 µmol, 1.0 eq) was dissolved in 5 mL DCM. Then MnO_2 (52.5 mg, 604.0 µmol, 60.0 eq.) was added to the mixture and all was stirred for 48 h at r.t. After the whole educt was converted, the reaction was filtered over Celite and washed with DCM. The solvent was removed and the crude product was purified by flash chromatography on silica gel with PE:EA (5:1 → 1:2). The product **39** was isolated (2.0 mg, 40 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.51 (s, 1H), 7.07 (s, 1H), 6.68 (s, 1H), 6.05 – 6.02 (m, 2H), 5.89 – 5.83 (m, 2H), 5.12 – 4.99 (m, 2H), 0.52 (s, 9H), -0.27 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 148.1, 147.2, 146.1, 143.2, 140.1, 137.3, 136.9, 134.2, 131.7, 131.6, 127.3, 123.8, 120.5, 118.7, 114.0, 109.8, 101.5, 101.2, 69.6, 0.7, 0.1. HRMS (ESI) $[M+H]^+$ calculated for $C_{26}H_{29}O_6Si_2$ 493.1497, found 493.1515. IR (ATR, cm^{-1}) 2953, 1760, 1624, 1481, 1463, 1360, 1298, 1227, 1075, 1030, 1014, 833.

1.71 Helioxanthin (1)



The reactant **39** (48.0 mg, 97.4 µmol, 1.0 eq) was dissolved in a mixture of 3 mL Chloroform and 3 mL trifluoroacetic acid. This reaction mixture was stirred for 12 h. The organic phase was washed with 2 x 10 mL saturated $NaHCO_3$ and brine. After organic phase was dried over $MgSO_4$ the solvent was removed and the crude product was purified by flash chromatography on silica gel with PE:EA (3:1 → 1:2). The product **1** was isolated (7.0 mg, 21 %) as a yellow solid. Mp. 216.6 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.70 (d, J = 8.7 Hz, 1H), 7.31 (d, J = 8.7 Hz, 1H), 6.91 – 6.87 (m, 1H), 6.82 – 6.77 (m, 2H), 6.08 – 6.04 (m, 2H), 5.98 – 5.93 (m, 2H), 5.26 – 5.14 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 147.6, 147.5, 147.1, 141.9, 139.9, 130.9, 130.6, 129.2, 127.6, 125.6, 122.5, 121.7, 121.2, 111.9, 109.8, 108.1, 101.7, 101.4, 69.7. HRMS (ESI) $[M+H]^+$ calculated for C20H13O6 349.0707, found 349.0713. IR (ATR, cm^{-1}) 2911, 1751, 1502, 1489, 1458, 113, 1271, 1255, 1231, 1069, 1032, 1009.

1.72 Retrohelioxanthin (2)



The reactant **37b** (60.0 mg, 98.9 µmol, 1.0 eq) was dissolved in 5 mL THF. Than potassium trimethylsilanolate (63.4 mg, 494.4 µmol, 5 eq.) was added and the mixture was stirred for 12 h. In the next step the solution was acidified with 1 M HCl and extracted with EE. The combined organic phases was washed with brine. Than the organic phase was dried with $MgSO_4$ and the solvent was removed. The crude product was dissolved in 5 mL dry THF and a 2.0 M boran dimethylsulfide complex (198.5

µL, 396.9 µmol, 4.0 eq.) was added. The solution was stirred for 5 h and acidified with 1 M HCl. This solution was stirred for additional 2 h and extracted with EE. The combined organic phases was washed with brine. Than the organic phase was dried with $MgSO_4$ and the solvent was removed. This intermediat was dissolved in a mixture of 3 mL Chloroform and 3 mL trifluoroacetic acid and stirred for 12 h. The organic phase was washed with 2 x 10 mL saturated $NaHCO_3$ and brine. After the organic phase was dried over $MgSO_4$ the solvent was removed and the crude product was purified by flash chromatography on silica gel with PE:EA (3:1 → 1:2). The product **2** was isolated (10.0 mg, 29 %) as a yellow solid. Mp. 189.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 1.4 Hz, 1H), 7.53 (d, J = 8.6 Hz, 1H), 7.35 (d, J = 8.6 Hz, 1H), 6.89 – 6.86 (m, 1H), 6.83 – 6.79 (m, 2H), 6.07 (d, J = 1.5 Hz, 1H), 6.02 (d, J = 1.5 Hz, 1H), 5.92 – 5.90 (m, 2H), 5.38 – 5.36 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 147.5, 146.8, 145.2, 143.7, 138.1, 137.7, 132.9, 129.2, 123.2, 122.4, 121.2, 121.0, 120.3, 113.8, 110.3, 107.5, 101.7, 101.2, 68.0. HRMS (ESI) $[M+H]^+$ calculated for $C_{20}H_{13}O_6$ 349.0707, found 349.0702. IR (ATR, cm^{-1}) 208, 1744, 11612, 1492, 1454, 1440, 1337, 1310, 1236, 1150, 1037, 1017.

2 Details of X-ray structure analysis

2.1 General details of X-ray structure analysis

The crystal structures of the compounds **6c**, **7a**, **7b**, **27a** and **30** were determined by single crystal structure analysis. Suitable single crystals were selected using a Leica M205C light microscope and separated with oil. X-ray crystal structure analysis was performed on a Stadivari diffractometer (Stoe) with monochromated Mo-Kα radiation (λ = 0.71073 Å). The data correction was performed using the program X-Area.[2] **7a** was refined as a 2-component twin. The structures were solved by direct methods and refined against F2 on all data by full-matrix least-squares using the SHELX suite of programs.[3, 4] In **27a** diffuse electron density in solvent-accessible voids was treated using the SQUEEZE routine in PLATON. A total of 120 electrons per unit cell were found in the voids, corresponding to approximately 0.63 molecules of ethyl acetate per unit cell. All non-hydrogen atoms were refined anisotropically, the hydrogen atoms were placed on calculated positions. Tab. 1 was created using FinalCif.[5] The crystal structures were visualized with Mercury 4.[4] The data (**6c**: CCDC 2536112, **7a**: CCDC 2536080, **7b**: CCCD 2551433, **27a**: CCCD 2536062, **30**: CCCD 2536066) can be obtained free of charge from The Cambridge Crystallographic Data Centre, http://www.ccdc.cam.ac.uk.

2.2 Crystallographic Data

Tab. 1: Crystal data and structure refinement for 6c, 7a, and 7b.

Compound	**6c**	**7a**	**7b**
CCDC number	2536112	2536080	2551433
Empirical formula	$C_{27}H_{24}O_8$	$C_{30}H_{30}O_8$	$C_{28}H_{26}O_8$
Formula weight	476.46	518.54	490.49
Temperature [K]	240	240	210
Crystal system	monoclinic	triclinic	monoclinic
Space group (number)	$P2_1/c$ (14)	$P\overline{1}$ (2)	$P2_1/n$ (14)
a [Å]	12.472(3)	8.1658(16)	15.5758(7)
b [Å]	9.5366(19)	9.840(2)	6.8858(4)
c [Å]	19.493(4)	17.134(3)	22.9327(11)
α [°]	90	92.38(3)	90
β [°]	104.42(3)	90.80(3)	102.990(4)
γ [°]	90	106.06(3)	90
Volume [Å^3]	2245.5(8)	1321.4(5)	2396.6(2)
Z	4	2	4
ρ_{calc} [gcm^{-3}]	1.409	1.303	1.359
μ [mm^{-1}]	0.104	0.093	0.100
F(000)	1000	548	1032
Crystal size [mm^3]	0.100×0.200×0.250	0.025×0.158×0.300	0.500×0.700×0.700
Crystal colour	colorless	colorless	colorless
Crystal shape	block	plate	block
Radiation	MoK_α (λ=0.71073 Å)	MoK_α (λ=0.71073 Å)	Mo K_α (λ=0.71073 Å)
2θ range [°]	6.10 to 66.01 (0.65 Å)	5.76 to 55.00 (0.77 Å)	5.52 to 52.74 (0.80 Å)
Index ranges	−18 ≤ h ≤ 17	−10 ≤ h ≤ 10	−15 ≤ h ≤ 19
	−14 ≤ k ≤ 14	−12 ≤ k ≤ 12	−8 ≤ k ≤ 8
	−29 ≤ l ≤ 26	−22 ≤ l ≤ 22	−28 ≤ l ≤ 28
Reflections collected	38396	41959	25976

Independent reflections	7869 $R_{int} = 0.0562$ $R_{sigma} = 0.0946$	41959 Twin (no R_{int}) R_{sigma} = 0.1054	4890 R_{int} = 0.0405 R_{sigma} = 0.0396
Completeness to θ = 25°	99.6 %	99.4 %	99.6 %
Data / Restraints / Parameters	7869 / 0 / 329	41959 / 0 / 367	4890 / 0 / 327
Absorption correction T_{min}/T_{max} (method)	0.8066 / 0.9947 (sphere)	0.7720 / 1.0000 (sphere)	0.9148 / 0.9781 (sphere)
Goodness-of-fit on F^2	0.795	0.882	0.910
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0416 wR_2 = 0.0874	R_1 = 0.0524 wR_2 = 0.1245	R_1 = 0.0377 wR_2 = 0.0880
Final *R* indexes [all data]	R_1 = 0.1037 wR_2 = 0.0950	R_1 = 0.1387 wR_2 = 0.1513	R_1 = 0.0622 wR_2 = 0.0927
Largest peak/hole [eÅ^{-3}]	0.24/−0.25	0.22/−0.20	0.36/−0.24

Tab. 2: Crystal data and structure refinement for 27a** and **30.

Compound	**27a**	**30**
CCDC number	2536062	2536066
Empirical formula	(C38 H50 O10 Si_2), 0.63(C_4 H_8 O_2)	$C_{22}H_{20}O_6$
Formula weight	778.473	380.38
Temperature [K]	240	210
Crystal system	monoclinic	monoclinic
Space group (number)	$P2_1/c$ (14)	$P2_1/c$ (14)
a [Å]	14.035(3)	10.3663(3)
b [Å]	16.937(3)	16.0340(6)
c [Å]	18.718(4)	10.8288(3)
α [°]	90	90
β [°]	103.84(3)	94.065(2)
γ [°]	90	90
Volume [Å^3]	4320.1(16)	1795.36(10)
Z	4	4
ρ_{calc} [gcm^{-3}]	1.197	1.407
μ [mm^{-1}]	0.131	0.103
F(000)	1544	800
Crystal size [mm^3]	0.500×0.500×0.500	0.100×0.150×0.200
Crystal colour	colorless	yellow
Crystal shape	block	block
Radiation	MoK_α (λ=0.71073 Å)	Mo K_α (λ=0.71073 Å)
2θ range [°]	5.82 to 55.00 (0.77 Å)	5.84 to 64.39 (0.67 Å)
Index ranges	−18 ≤ h ≤ 18 −19 ≤ k ≤ 22 −24 ≤ l ≤ 24	−15 ≤ h ≤ 15 −23 ≤ k ≤ 23 −16 ≤ l ≤ 14
Reflections collected	104172	82545
Independent reflections	9916 R_{int} = 0.0769 R_{sigma} = 0.0428	6061 R_{int} = 0.0467 R_{sigma} = 0.0309
Completeness to θ = 25°	99.7 %	99.7 %
Data / Restraints / Parameters	9916 / 12 / 503	6061 / 0 / 257
Absorption correction T_{min}/T_{max} (method)	0.8015 / 0.9858 (sphere)	0.8988 / 0.9959 (sphere)
Goodness-of-fit on F^2	0.684	1.028
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0499 wR_2 = 0.1542	R_1 = 0.0405 wR_2 = 0.1164
Final *R* indexes [all data]	R_1 = 0.0778 wR_2 = 0.1738	R_1 = 0.0659 wR_2 = 0.1226
Largest peak/hole [eÅ^{-3}]	0.61/−0.24	0.42/−0.19

2.3 Visualizations of the crystal structure and molecule structure

2.3.1 Compound 6c

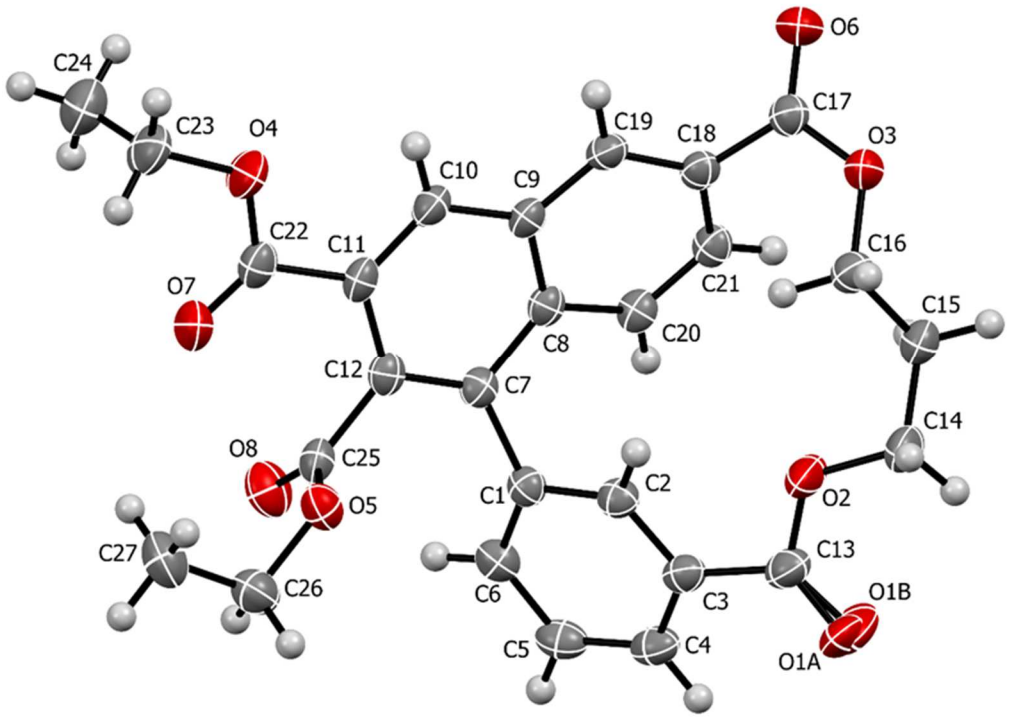


Figure 1: Molecular structure with atom labeling of **6c**. Displacement ellipsoids are shown at the 50% probability level. The O1 atom is disordered over two positions. The occupancy ratio of components A:B is 0.53:0.47.

2.3.2 **Compound 7a**

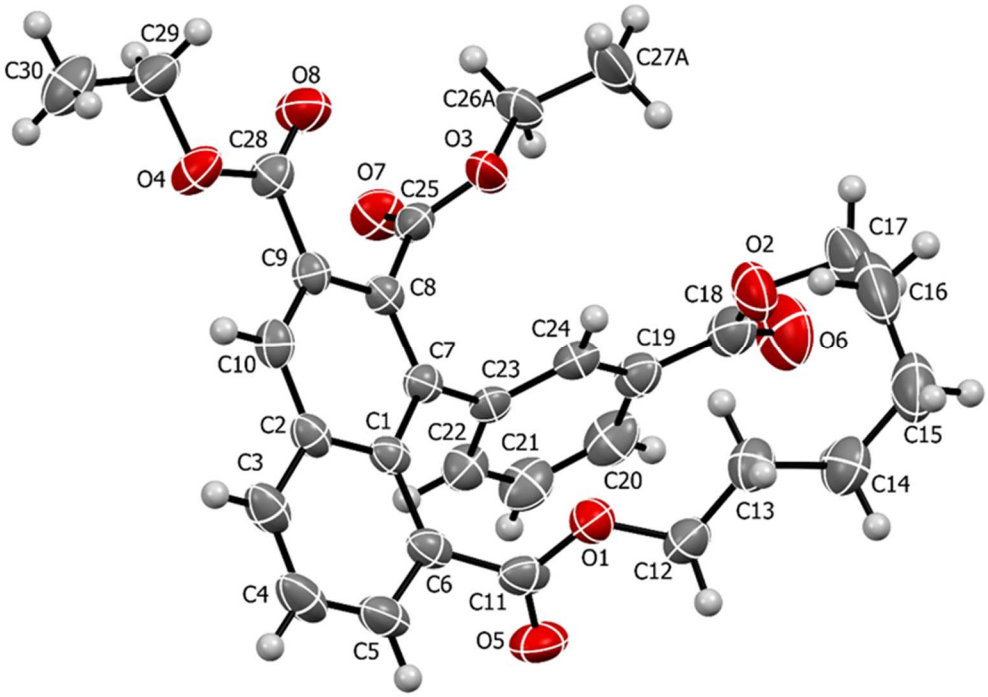


Figure 2: Molecular structure with atom labeling of **7a**. Displacement ellipsoids are shown at the 50% probability level.

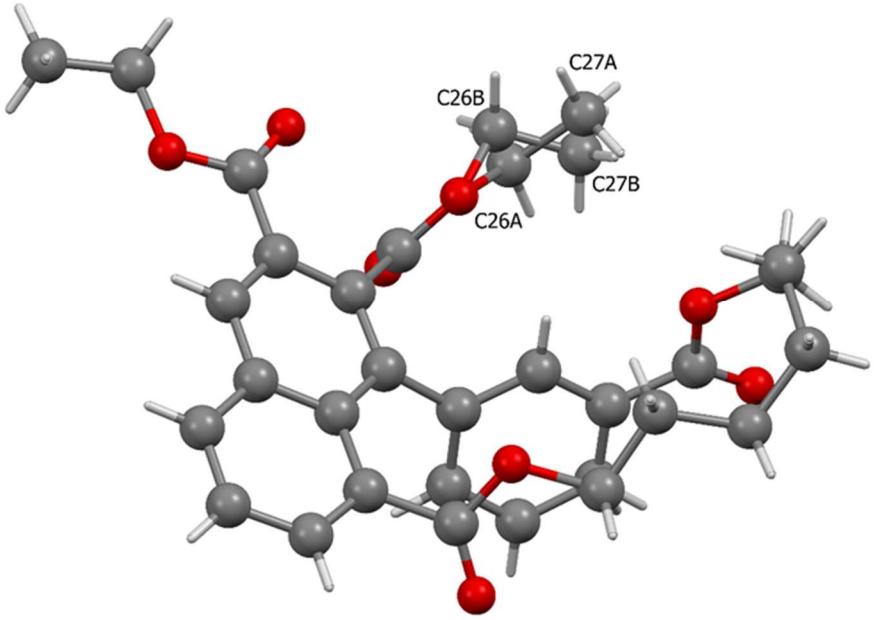


Figure 3: An alkyl group in **7a** is disordered over two positions. The occupancy ratio of components A:B is 0.59:0.41, including the corresponding hydrogen atoms.

2.3.3 **Compound 7b**

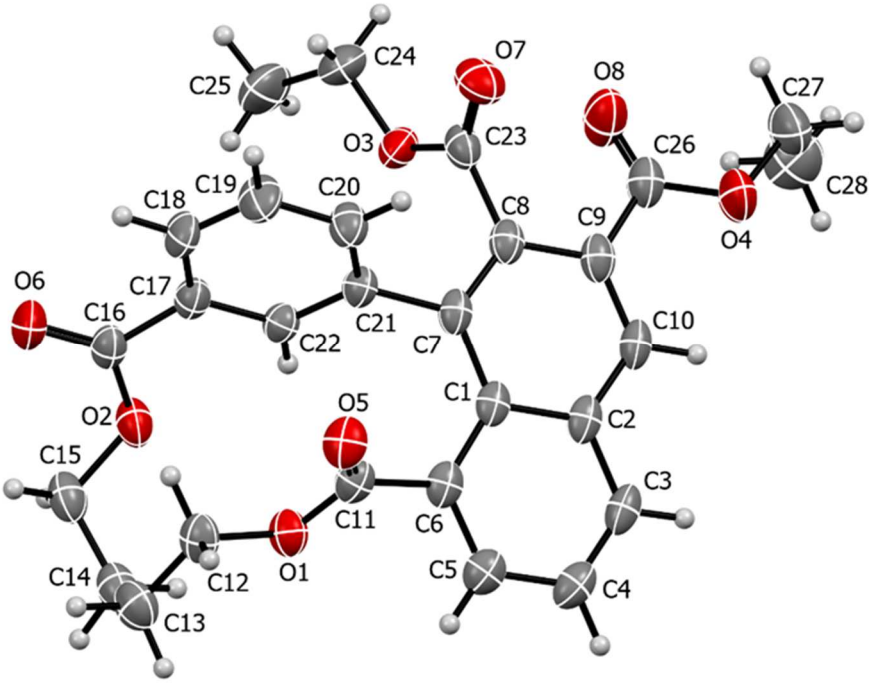


Figure 4: Molecular structure with atom labeling of **7b**. Displacement ellipsoids are shown at the 50% probability level.

2.3.4 **Compound 27a**

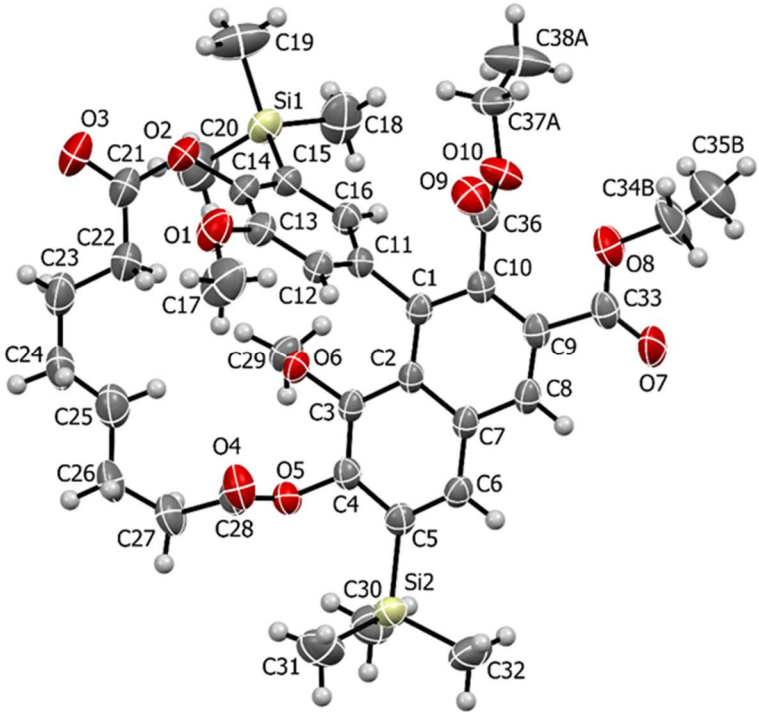


*Figure 5: Molecular structure with atom labeling of **27a**. Displacement ellipsoids are shown at the 50% probability level.*

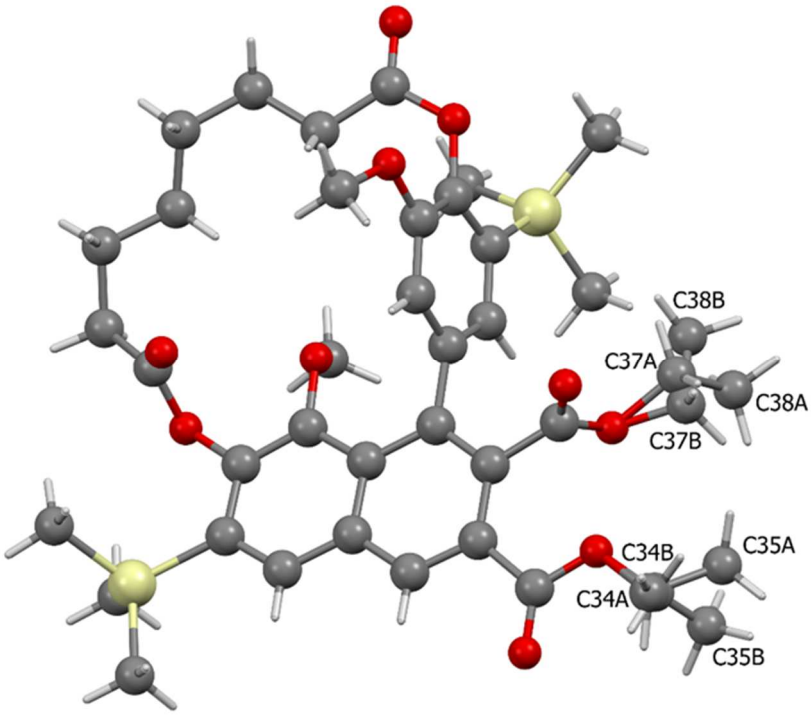


Figure 6: The alkyl groups in **27a** are disordered over two positions. The occupancy ratio of components A:B is 0.26:0.74 for atoms C34/C35 and 0.55:0.45 for atoms C37/C38, including the corresponding hydrogen atoms.

2.3.5 **Compound 30**

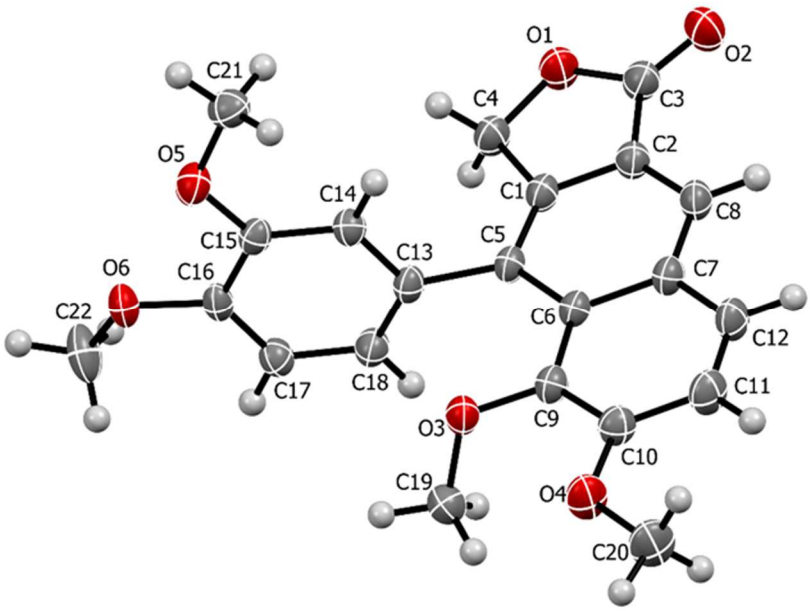
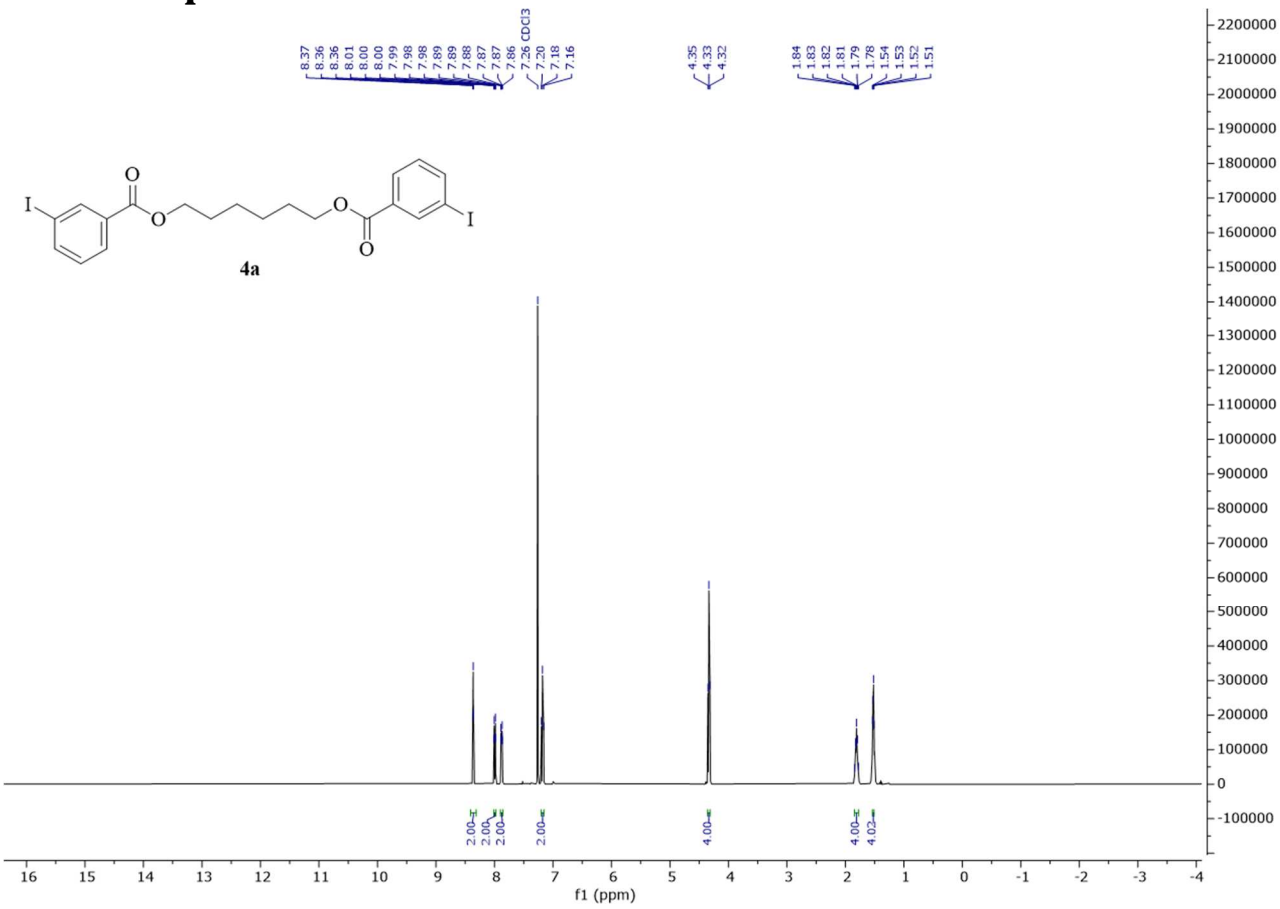
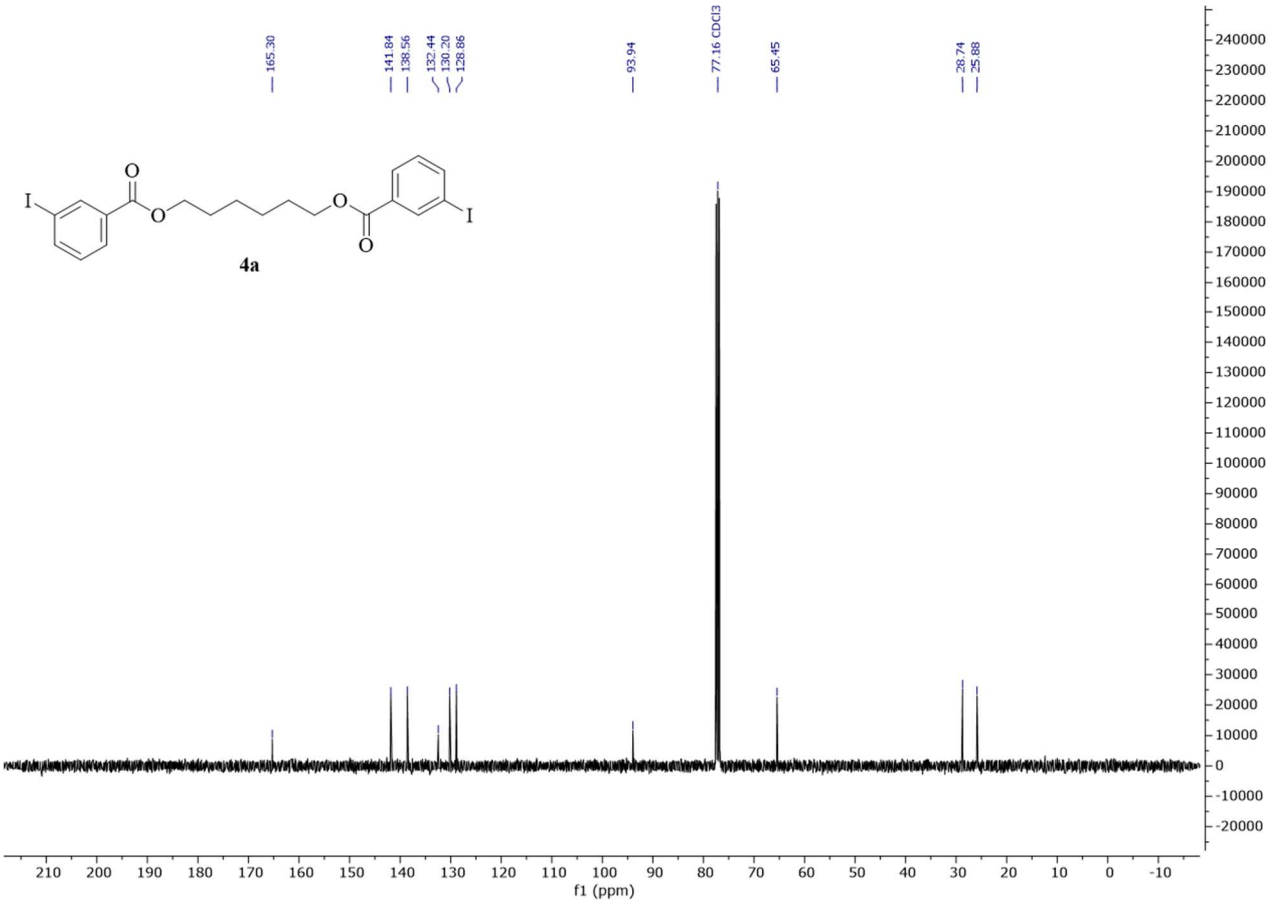
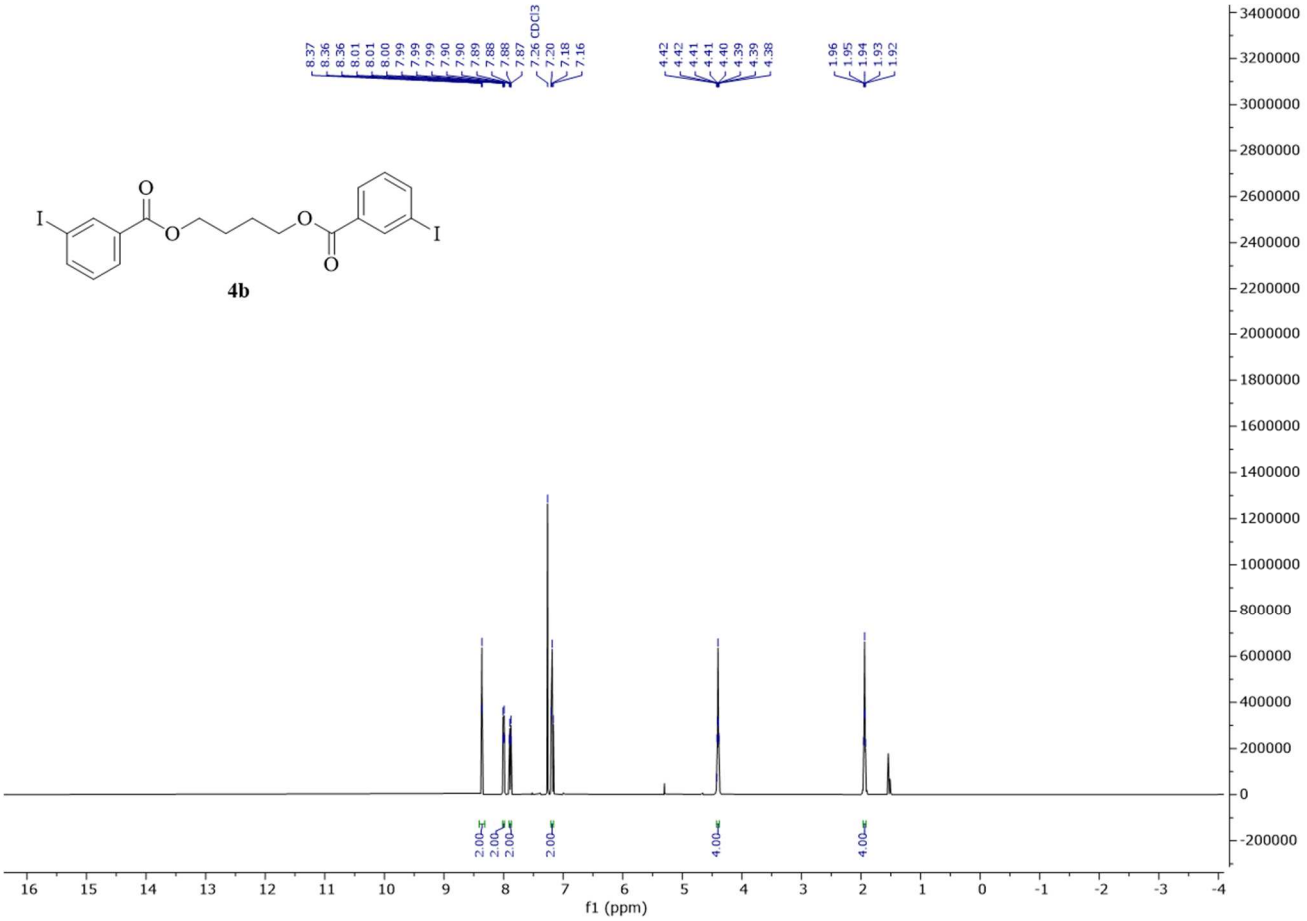


Figure 7: Molecular structure with atom labeling of **30**. Displacement ellipsoids are shown at the 50% probability level.

3 NMR spectra



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8.00
7.99
7.99
7.99
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7.90
7.89
7.88
7.88
7.87
7.26 CDCl3
7.20
7.18
7.16
4.42
4.42
4.41
4.41
4.40
4.39
4.39
4.38
1.96
1.95
1.94
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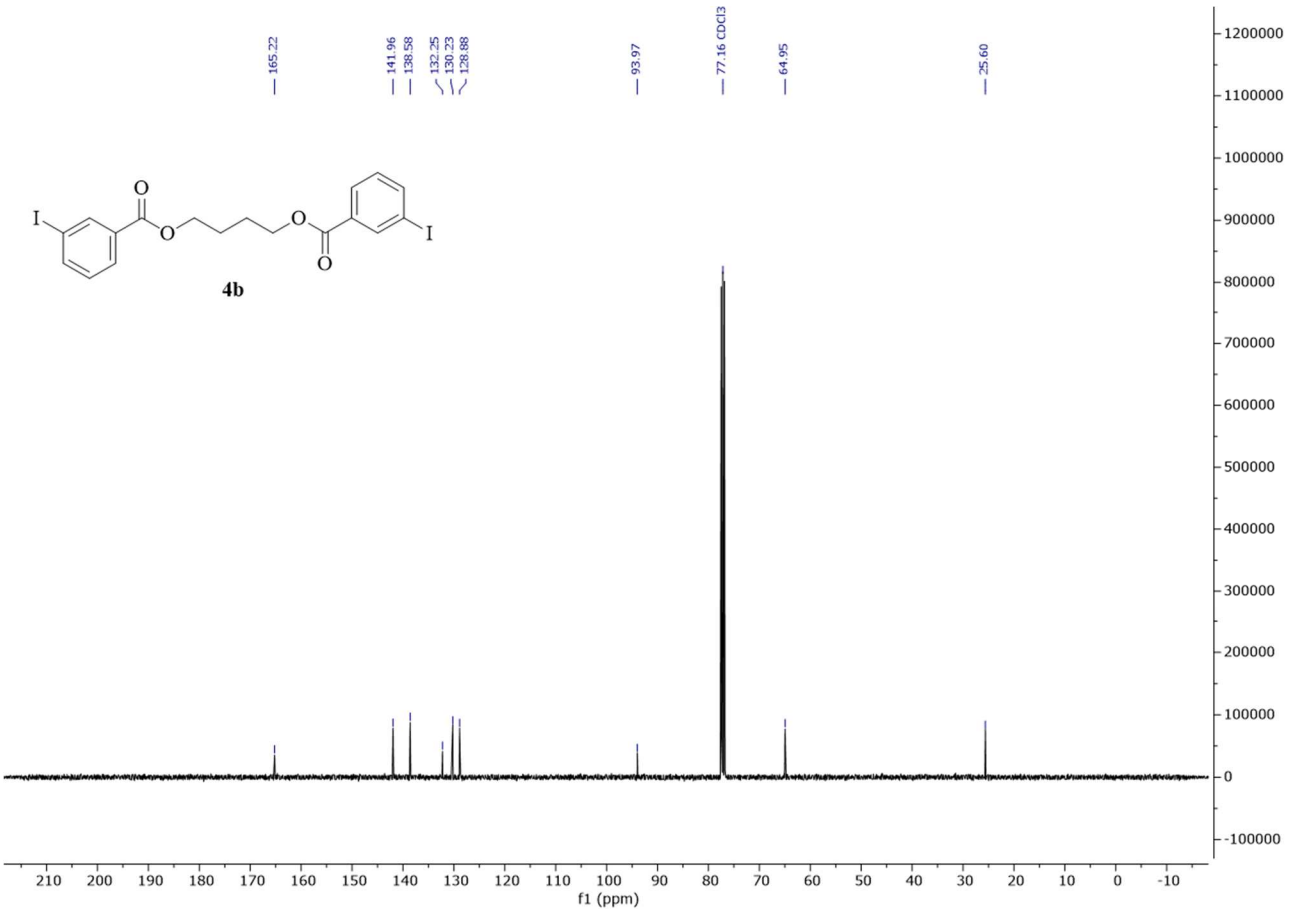
4.00
4.00
f1 (ppm)

4b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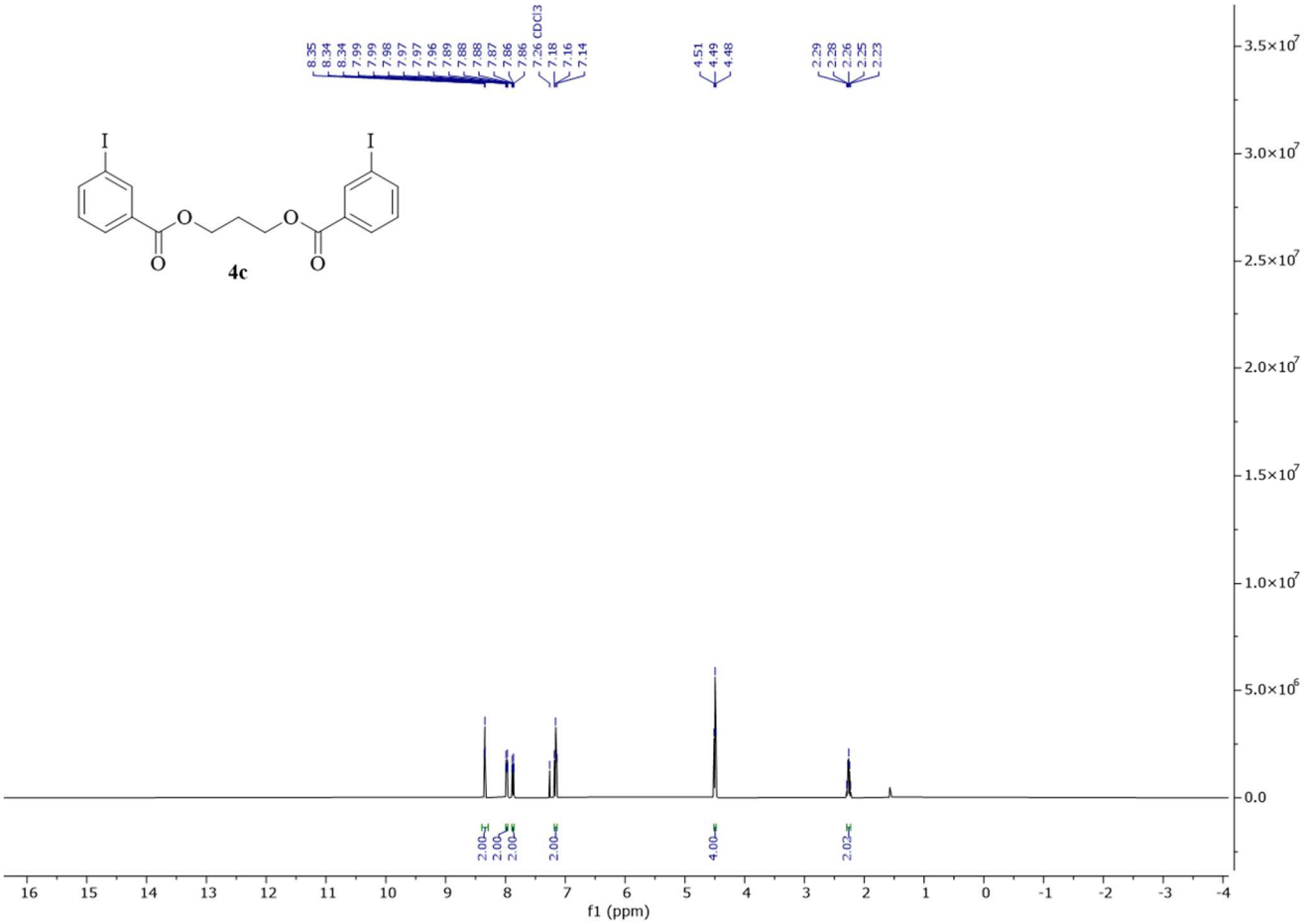
64.95
25.60
f1 (ppm)

4b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7.99
7.98
7.97
7.97
7.96
7.89
7.88
7.88
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7.86
7.86
7.26 CDCl3
7.18
7.16
7.14
4.51
4.49
4.48
2.29
2.28
2.26
2.25
2.23
I
I
O
O
O
O
4c
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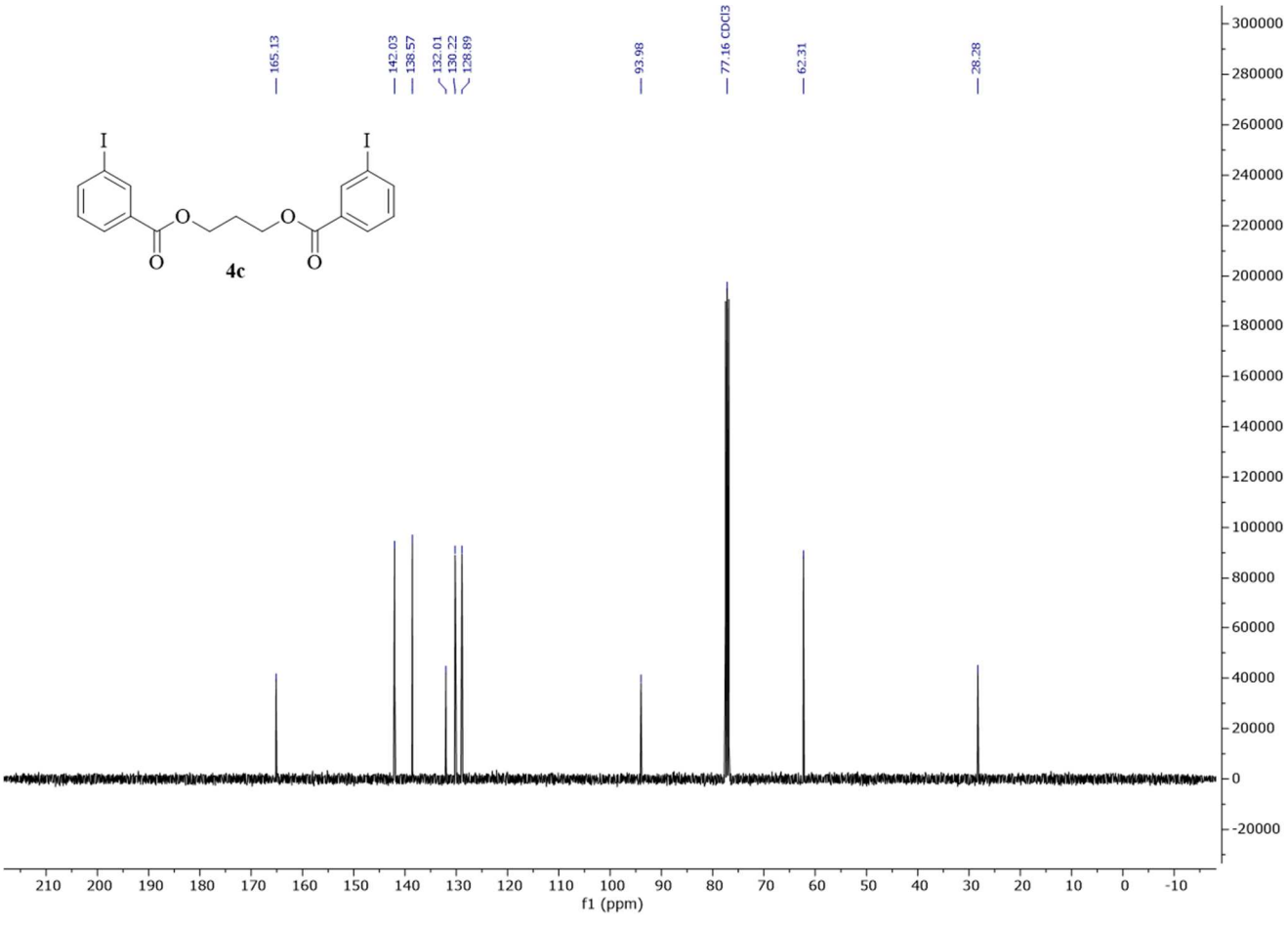
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
2.00
2.00
2.00
2.00
4.00
2.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)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132.01
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62.31
28.28
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O
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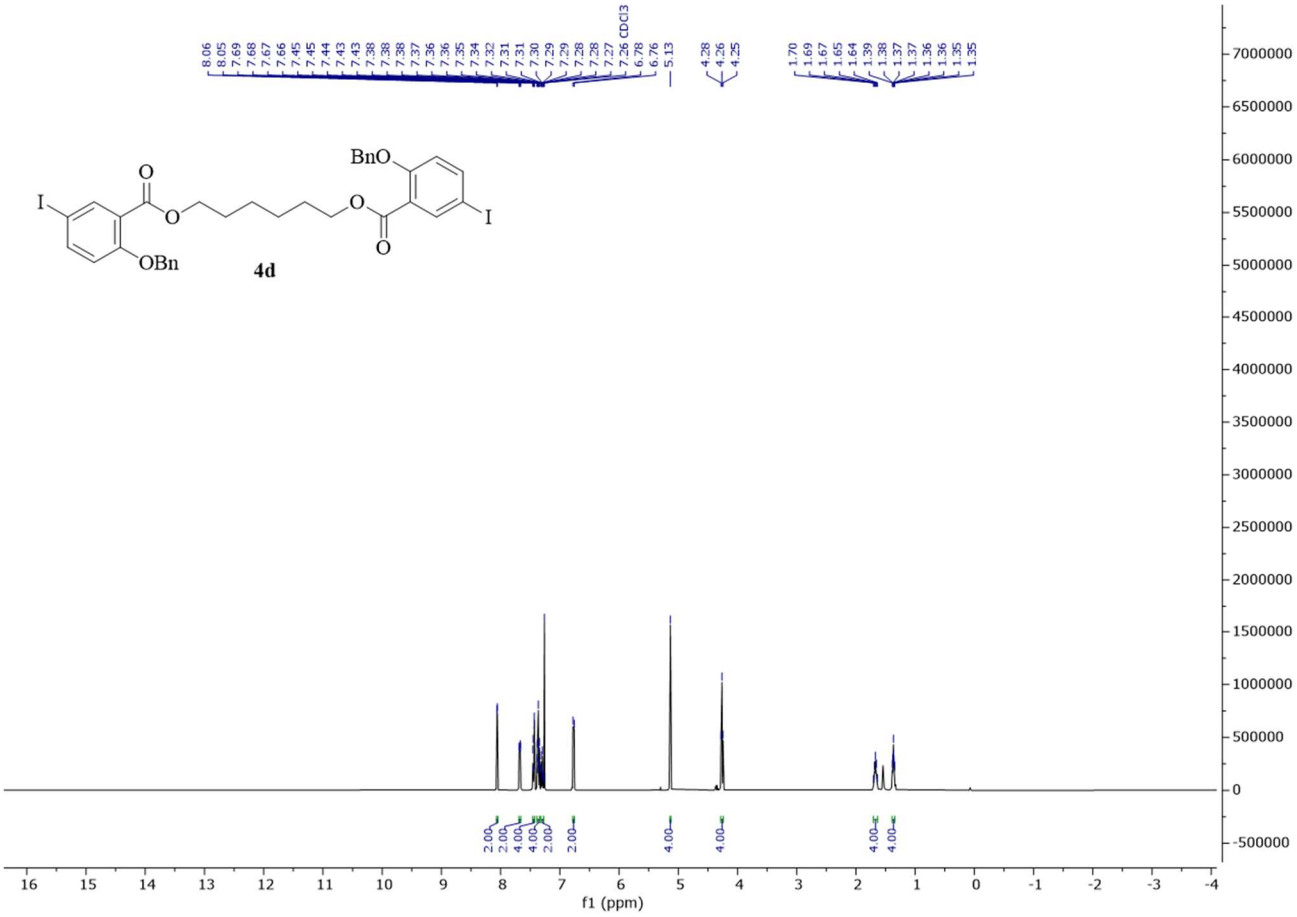
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.38
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7.36
7.35
7.34
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.26 CDCl3
6.78
6.76
5.13
4.28
4.26
4.25
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1.69
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1.65
1.64
1.39
1.38
1.37
1.37
1.36
1.36
1.35
1.35
BnO
O
I
O
O
O
I
OBn
4d
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4.00
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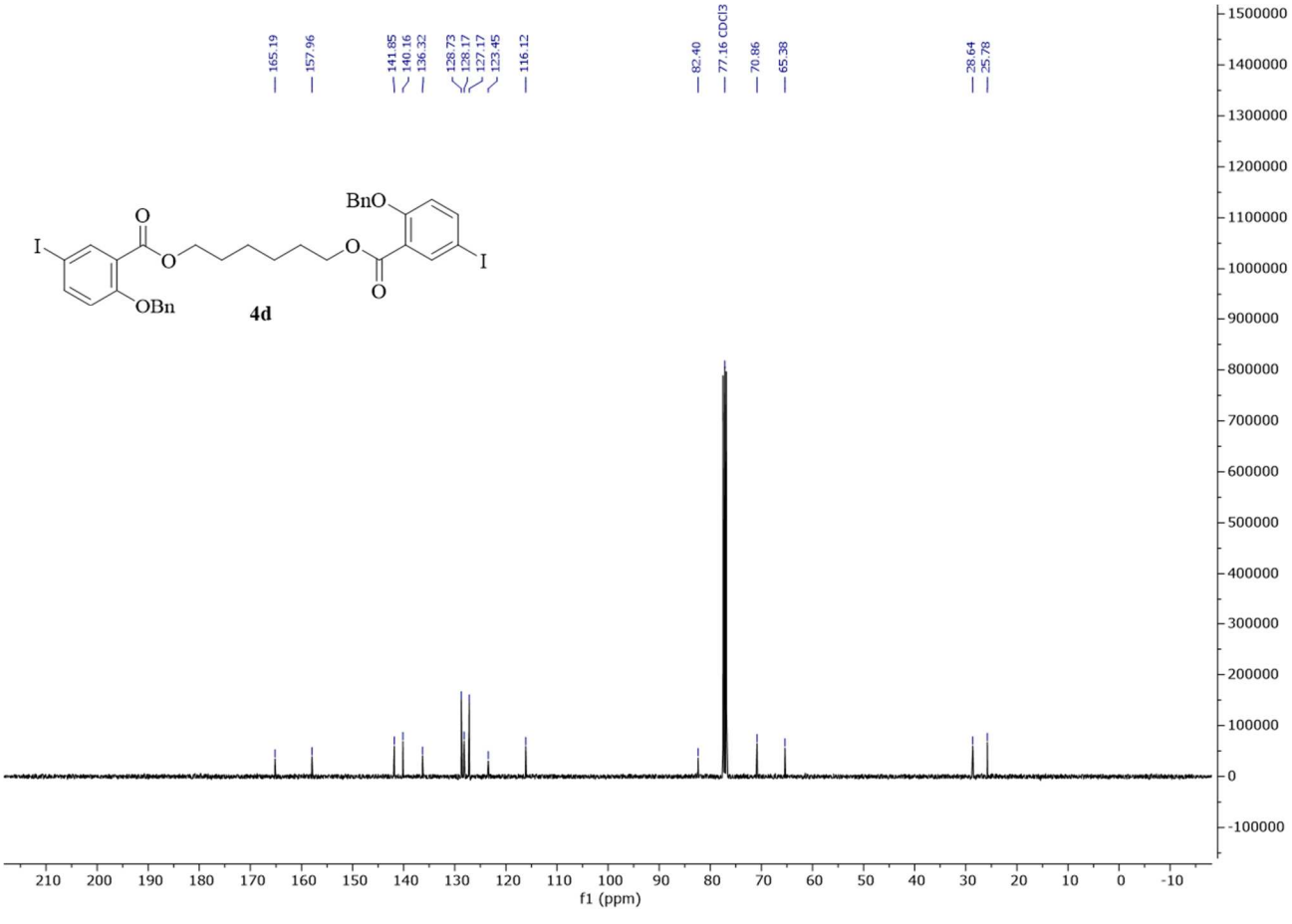
4.00
4.00
4.00
4.00
f1 (ppm)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140.16
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127.17
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116.12
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25.78
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O
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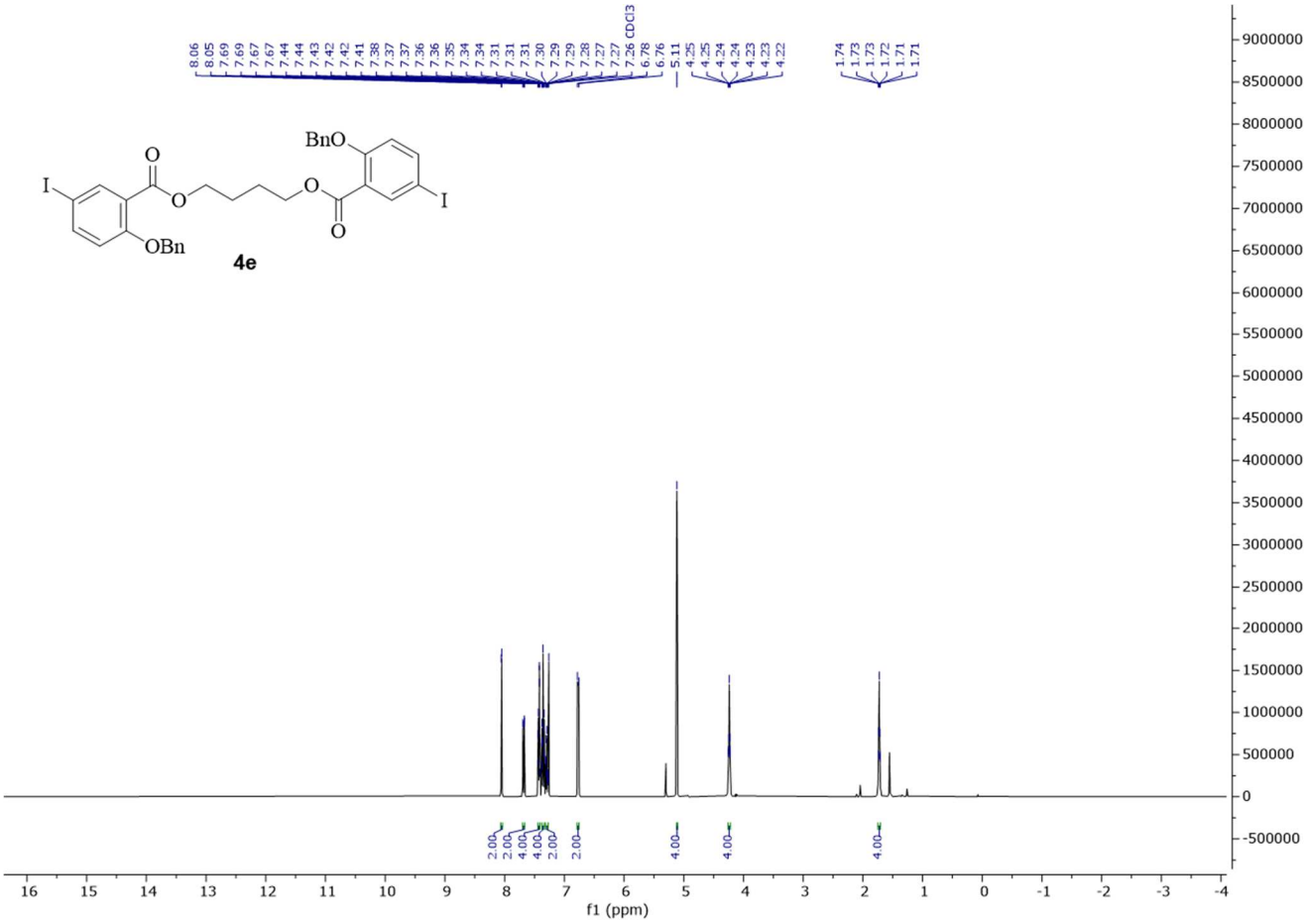
OBn
4d
f1 (ppm)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7.34
7.34
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7.31
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.26 CDCl3
6.78
6.76
5.11
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4.24
4.24
4.23
4.23
4.22
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1.73
1.73
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1.71
1.71
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I
O
O
O
O
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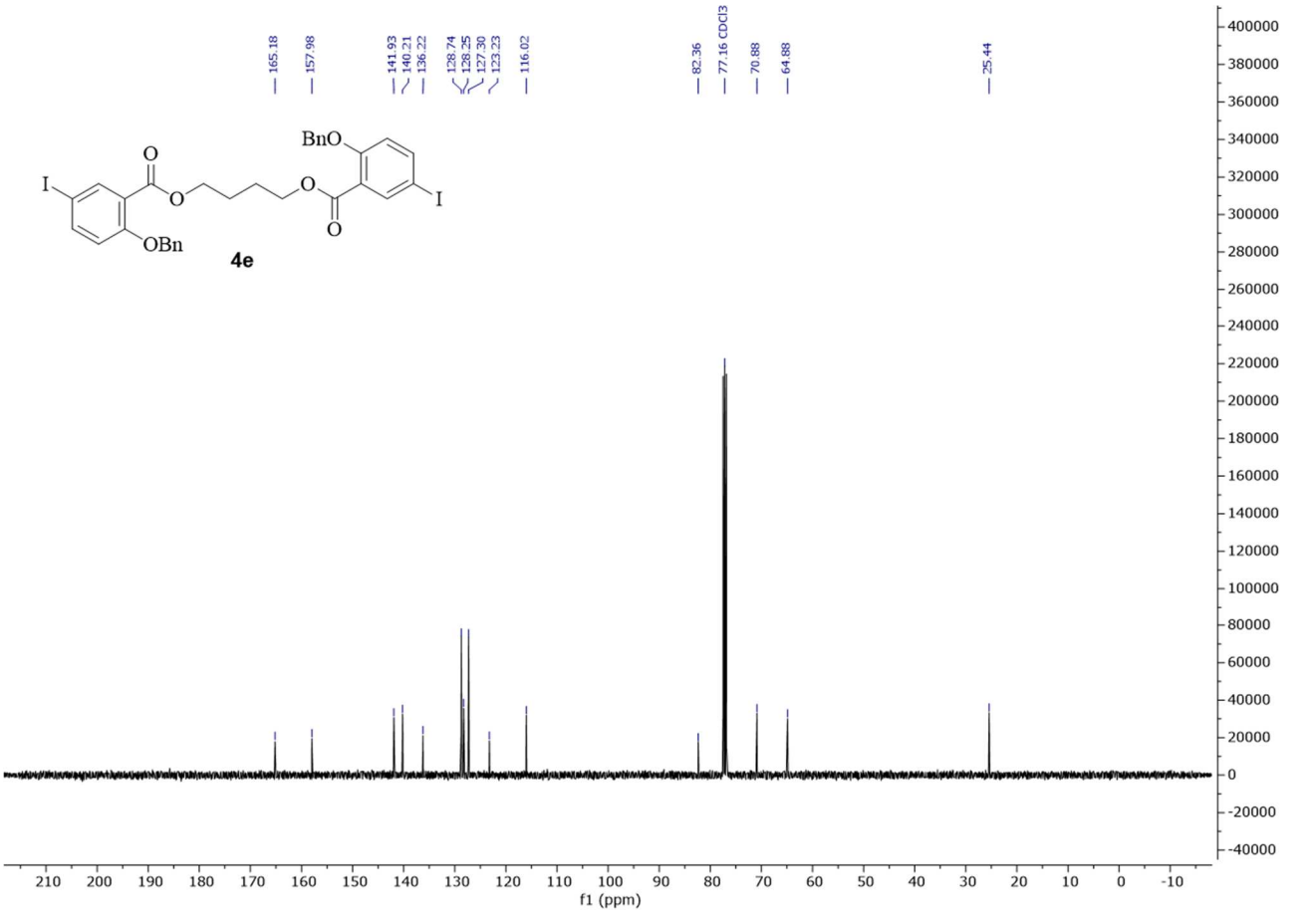
4.00
f1 (ppm)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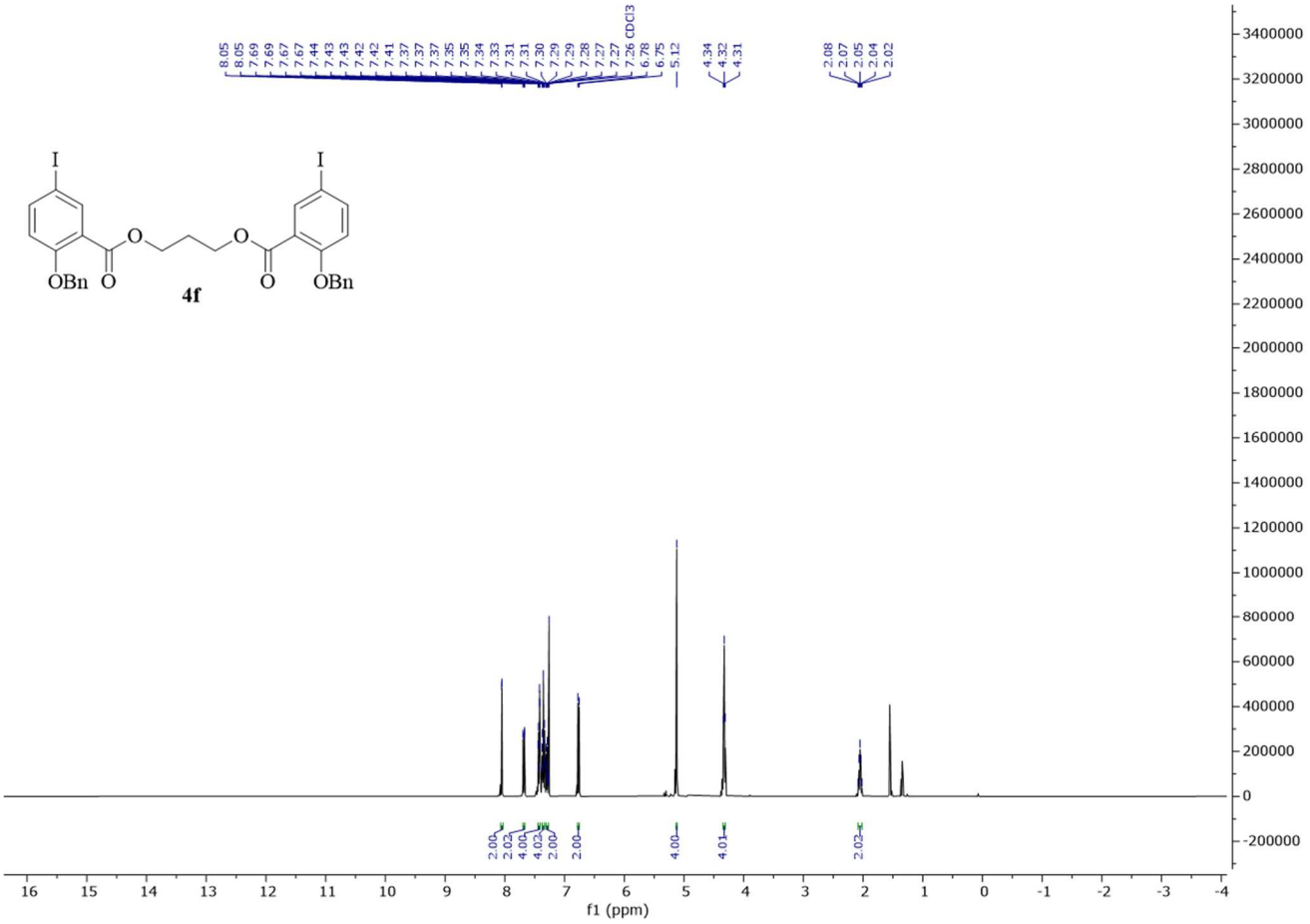
O
O
O
I
OBn
4e
f1 (ppm)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7.29
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7.28
7.27
7.27
7.26 CDCl3
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6.75
5.12
4.34
4.32
4.31
2.08
2.07
2.05
2.04
2.02
I
I
O
O
OBn
O
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OBn
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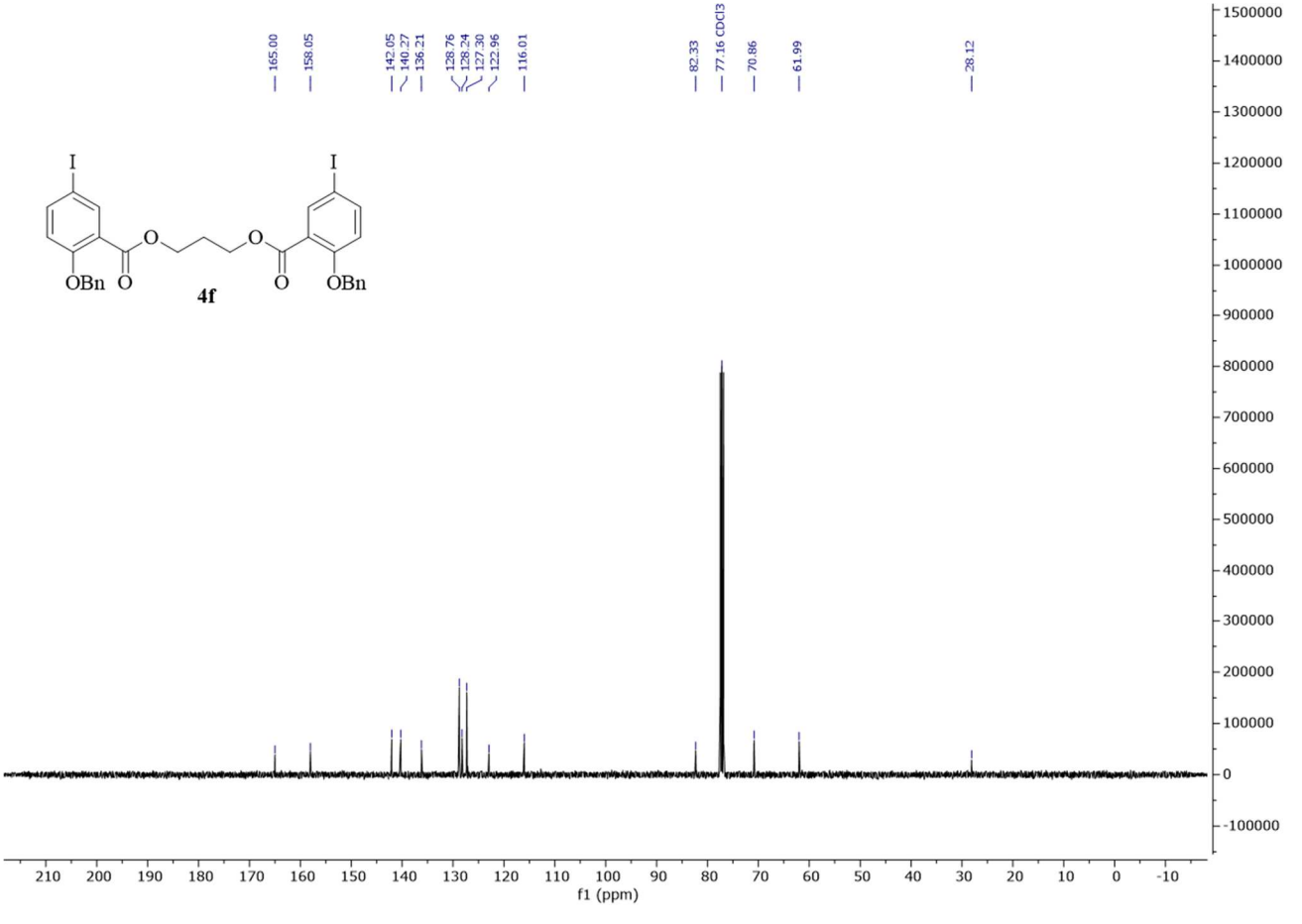
2.02
f1 (ppm)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OBn
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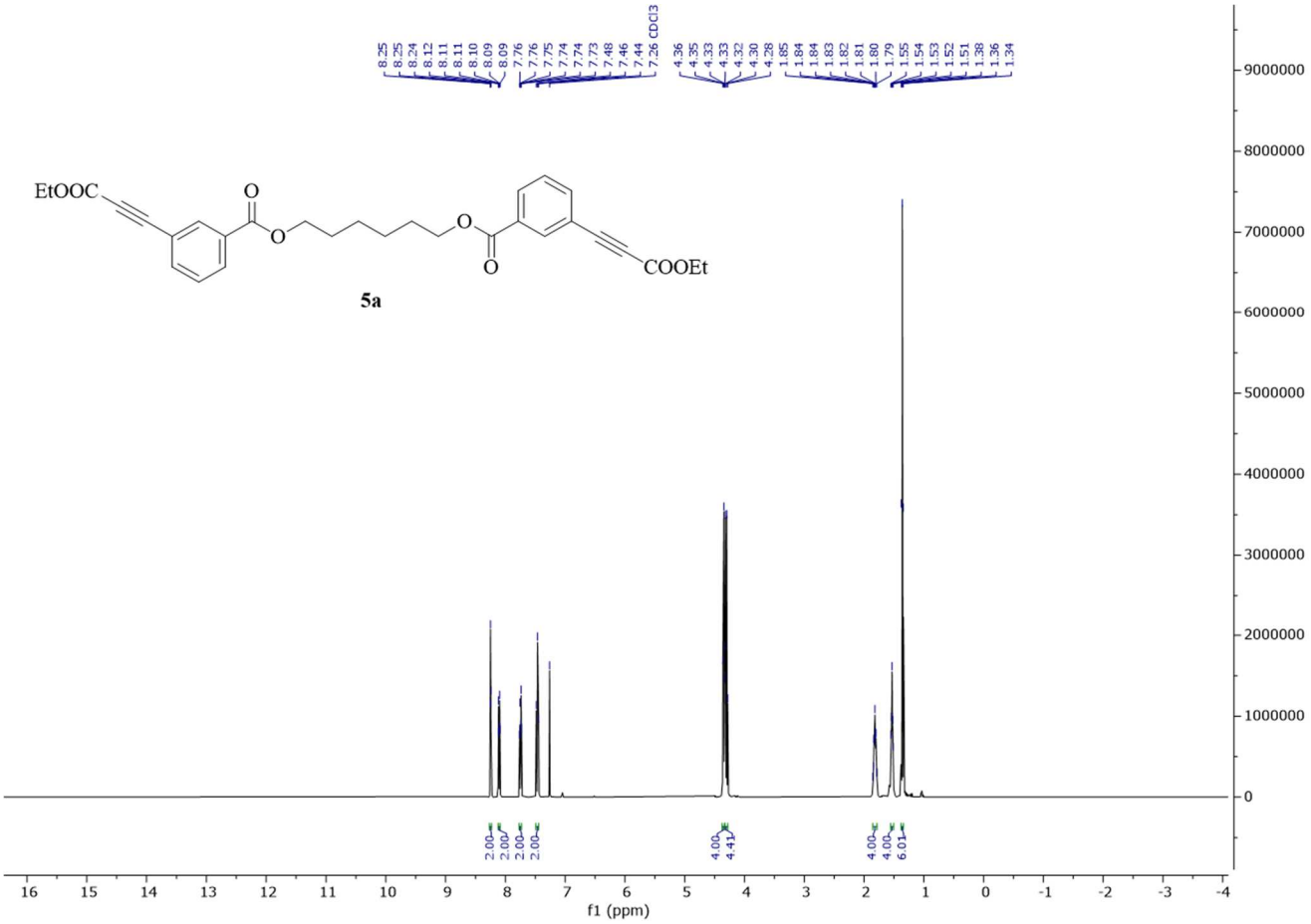
OBn
4f
f1 (ppm)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1.79
1.55
1.54
1.53
1.52
1.51
1.38
1.36
1.34
EtOOC
O
O
O
O
O
COOEt
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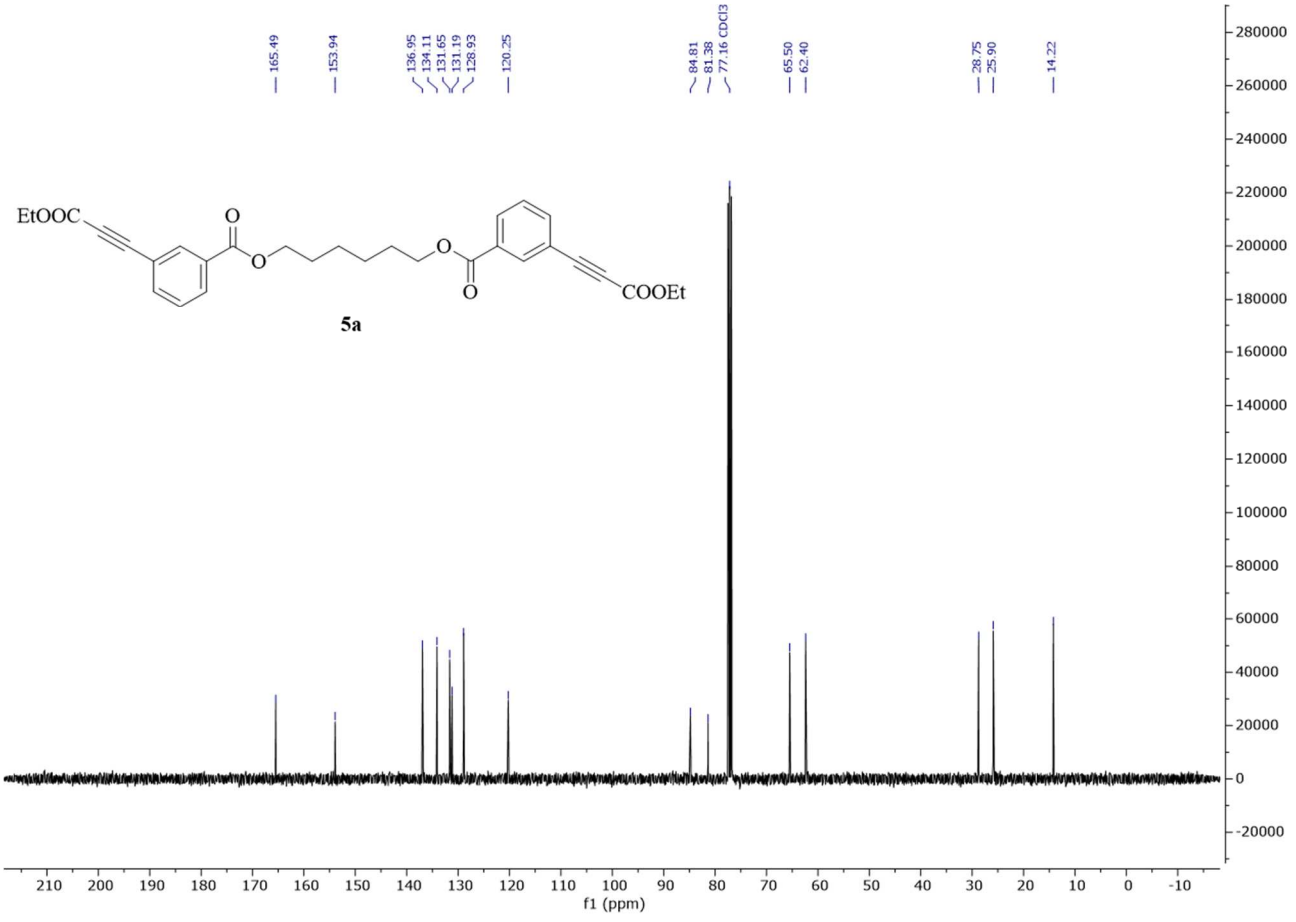
6.01
f1 (ppm)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25.90
14.22
EtOOC
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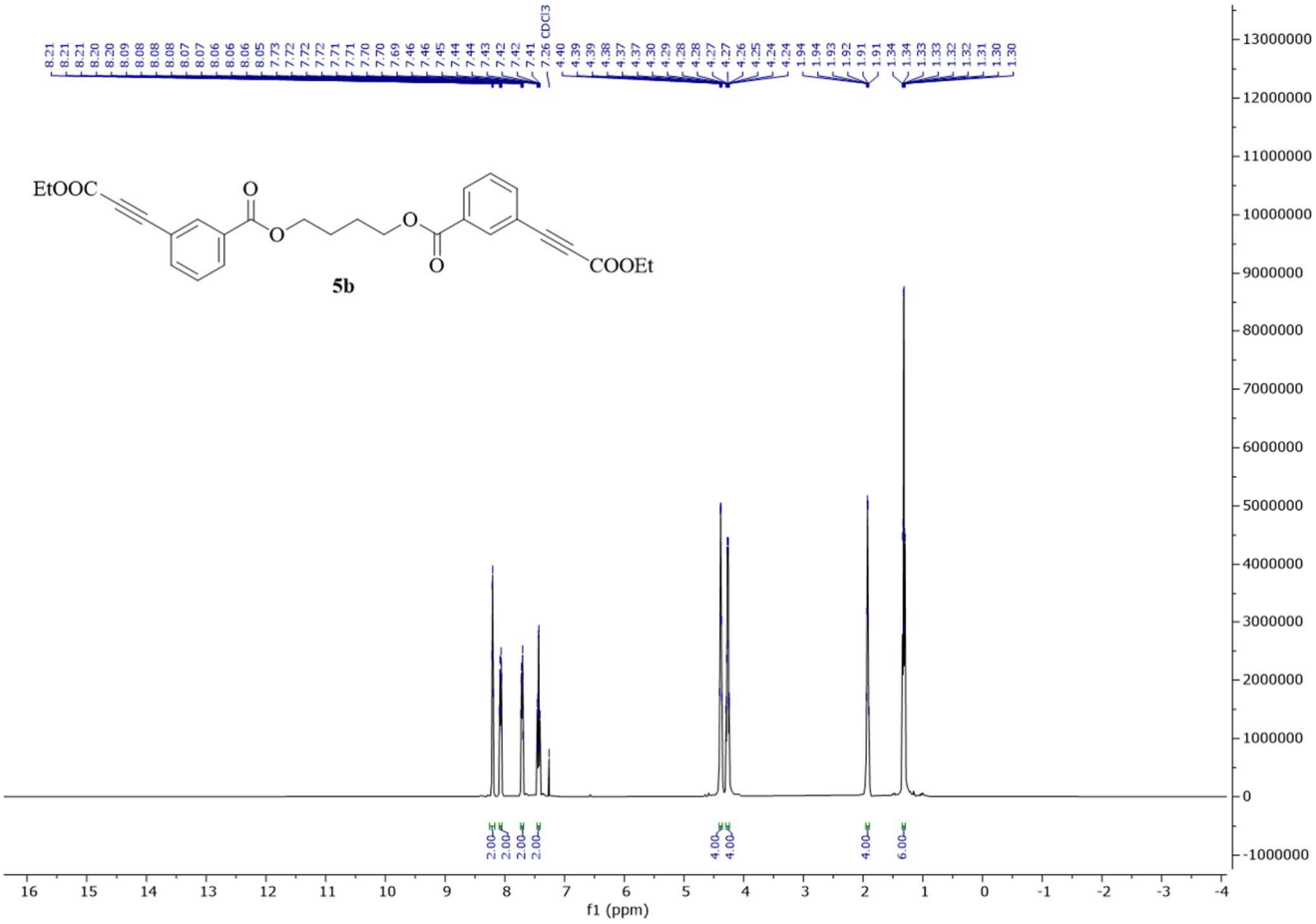
O
O
O
O
COOEt
5a
f1 (ppm)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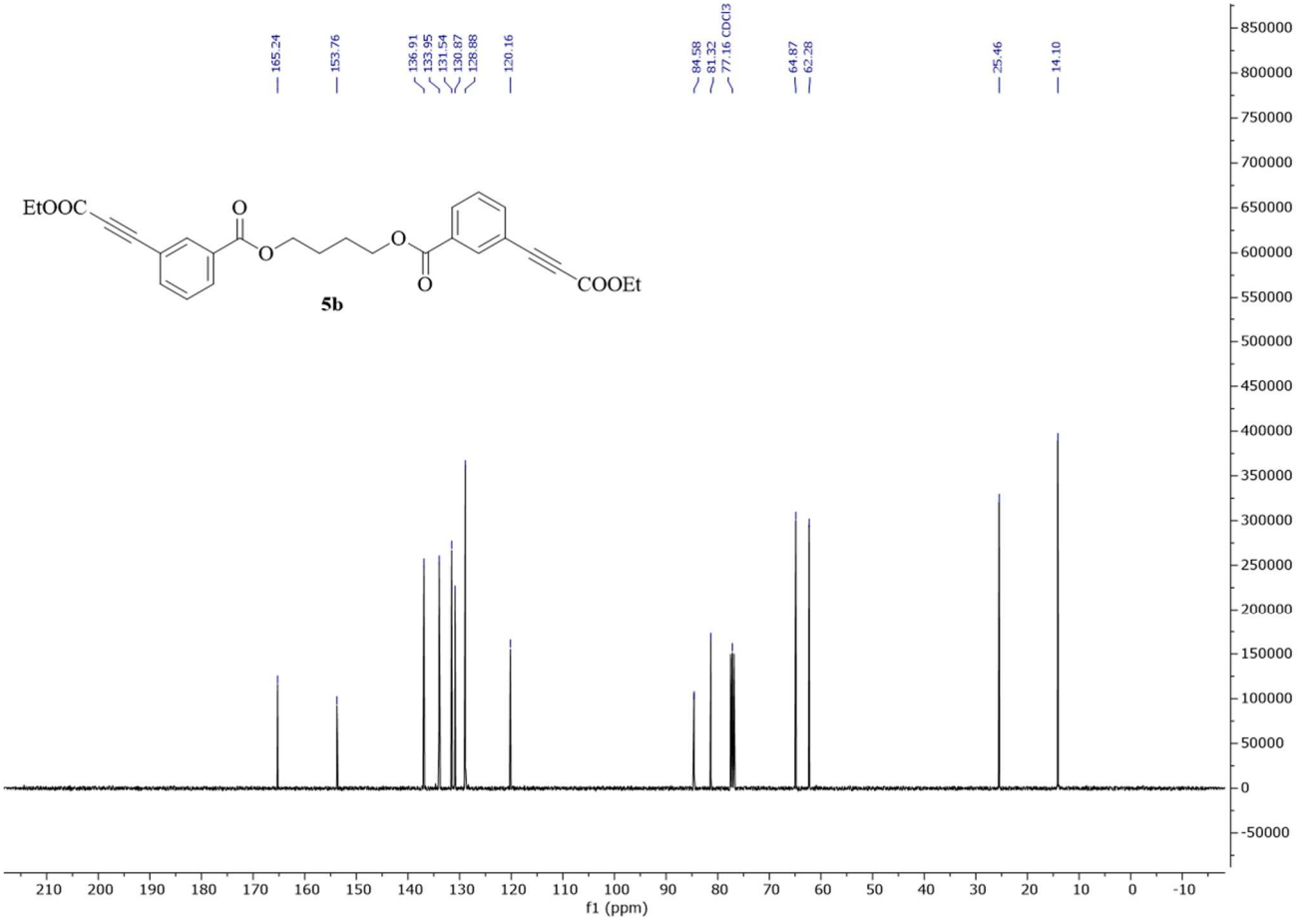
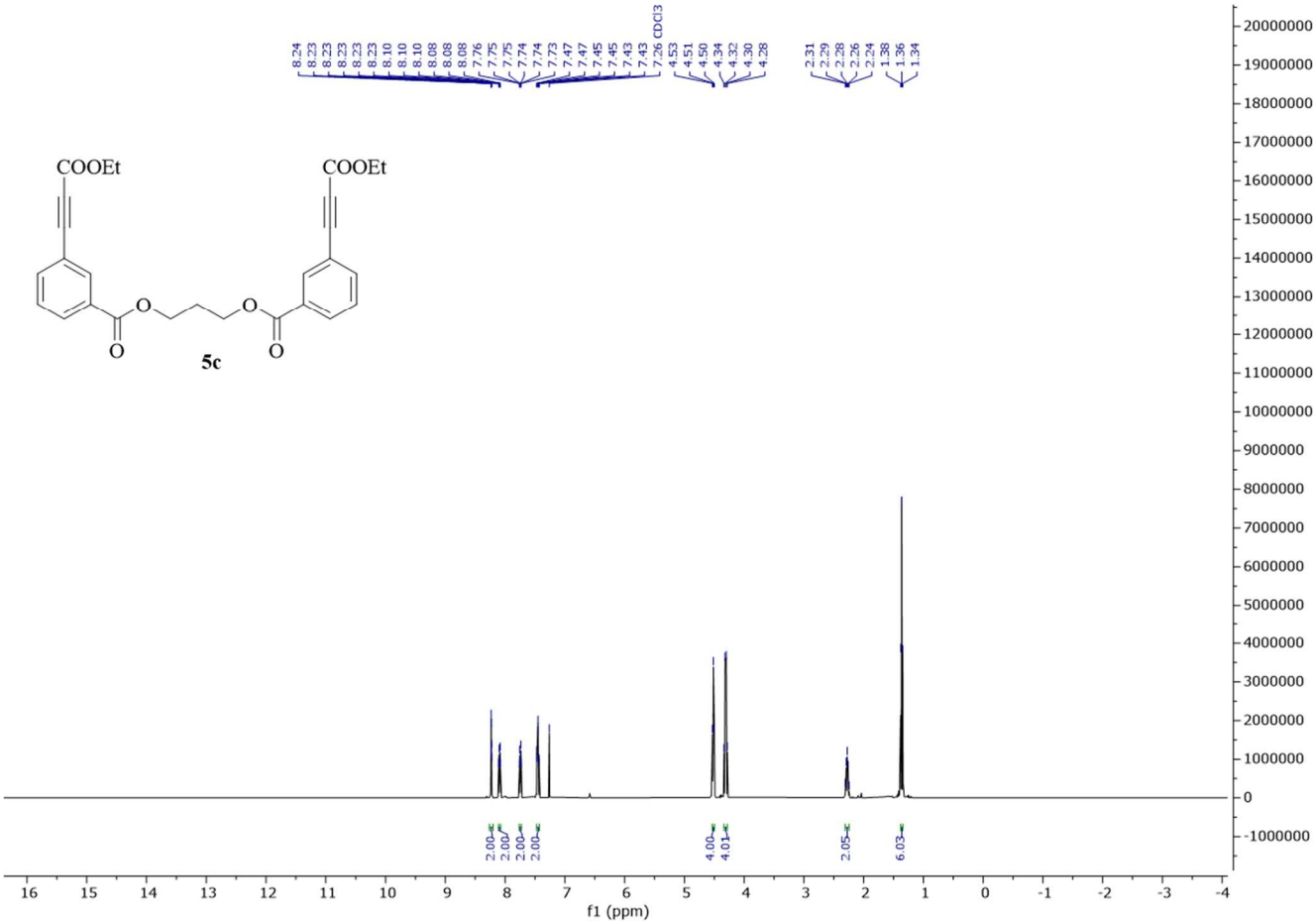
O
O
O
O
COOEt
5b
f1 (ppm)


EtOOC
O
O
O
O
O
COOEt
5b
f1 (ppm)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8.08
8.08
8.08
7.76
7.75
7.75
7.74
7.74
7.73
7.47
7.47
7.45
7.45
7.43
7.43
7.26 CDCl3
4.53
4.51
4.50
4.34
4.32
4.30
4.28
2.31
2.29
2.28
2.26
2.24
1.38
1.36
1.34
COOEt
COOEt
O
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O
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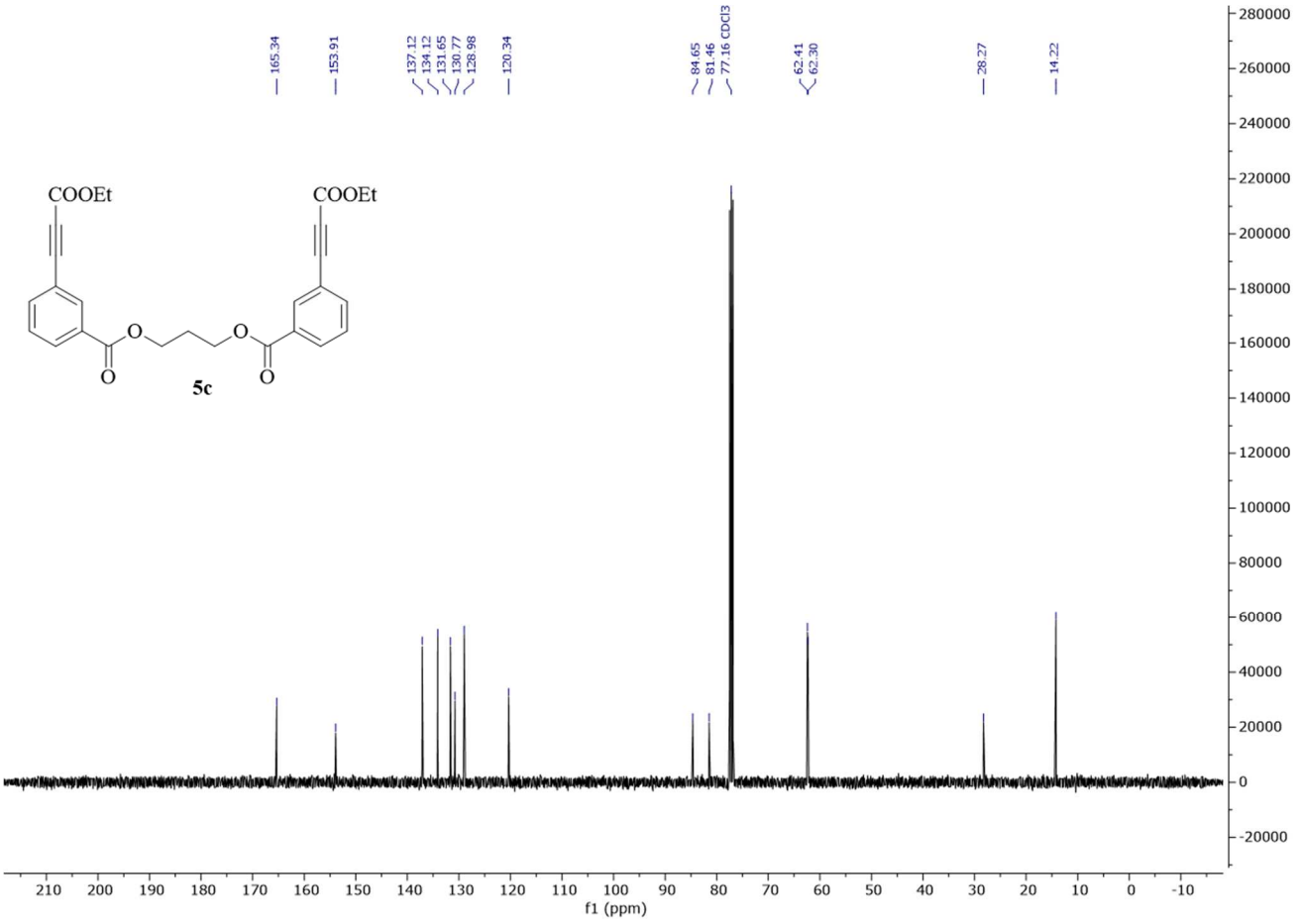
2.00
2.00
2.00
4.00
4.01
2.05
6.03
f1 (ppm)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130.77
128.98
120.34
84.65
81.46
77.16 CDCl3
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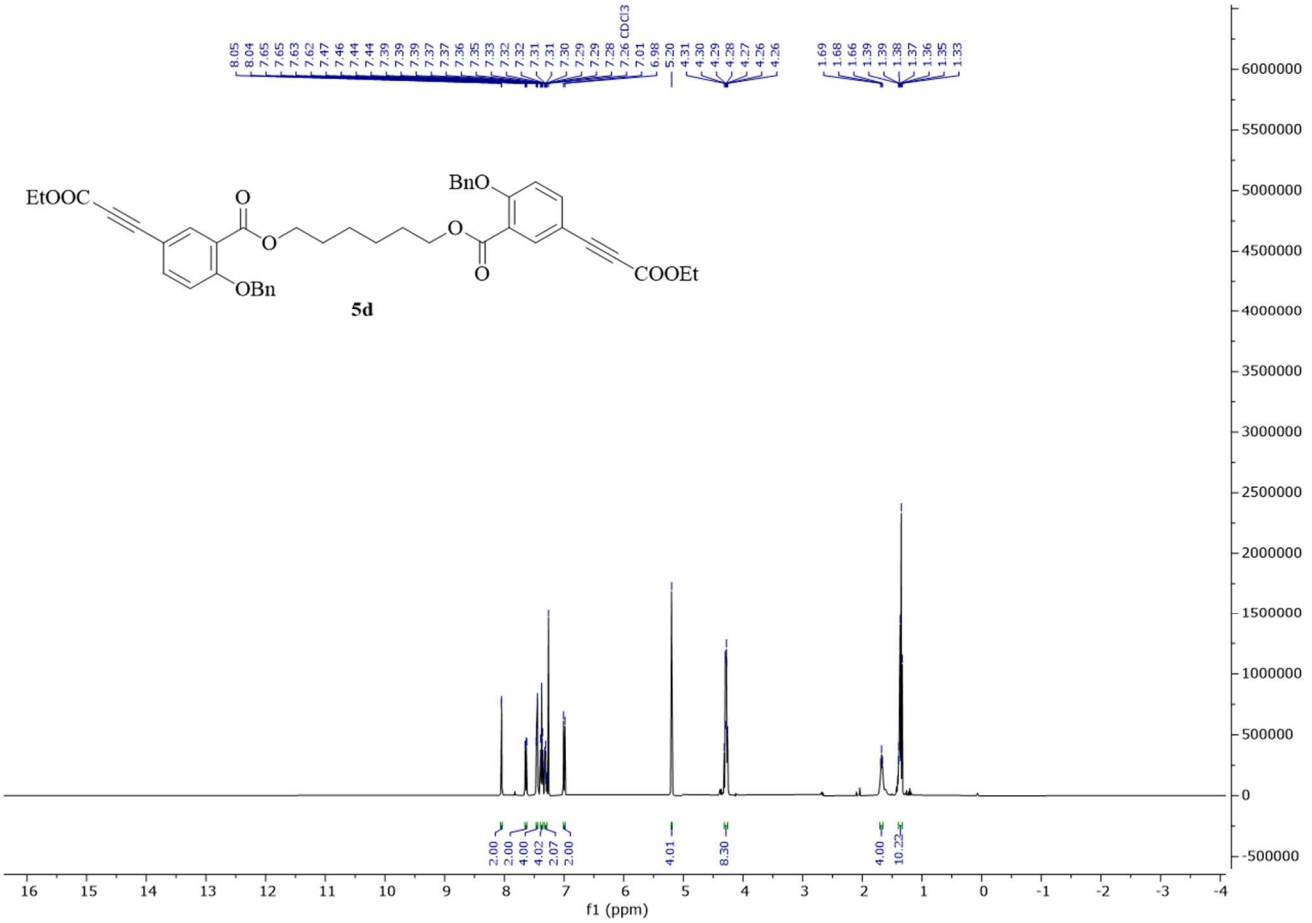
62.30
28.27
14.22
COOEt
COOEt
O
O
O
O
5c
f1 (ppm)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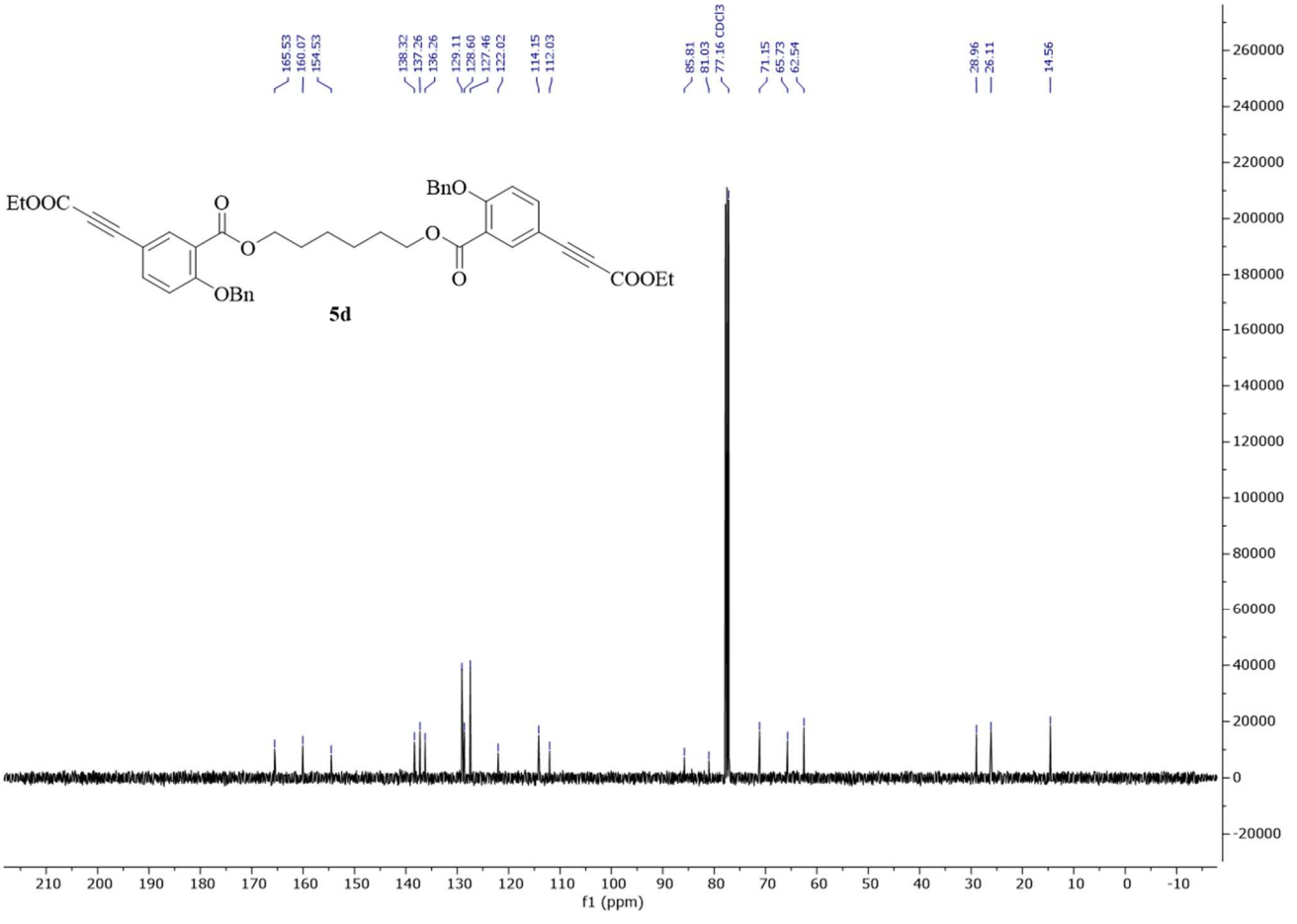
7.39
7.39
7.37
7.37
7.36
7.35
7.33
7.32
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.26 CDCl3
7.01
6.98
5.20
4.31
4.30
4.29
4.28
4.27
4.26
4.26
1.69
1.68
1.66
1.39
1.39
1.38
1.37
1.36
1.35
1.33
EtOOC
BnO
COOEt
OBn
5d
2.00
2.00
4.00
4.02
2.07
2.00
4.01
8.30
4.00
10.22
f1 (ppm)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128.60
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122.02
114.15
112.03
85.81
81.03
77.16 CDCl3
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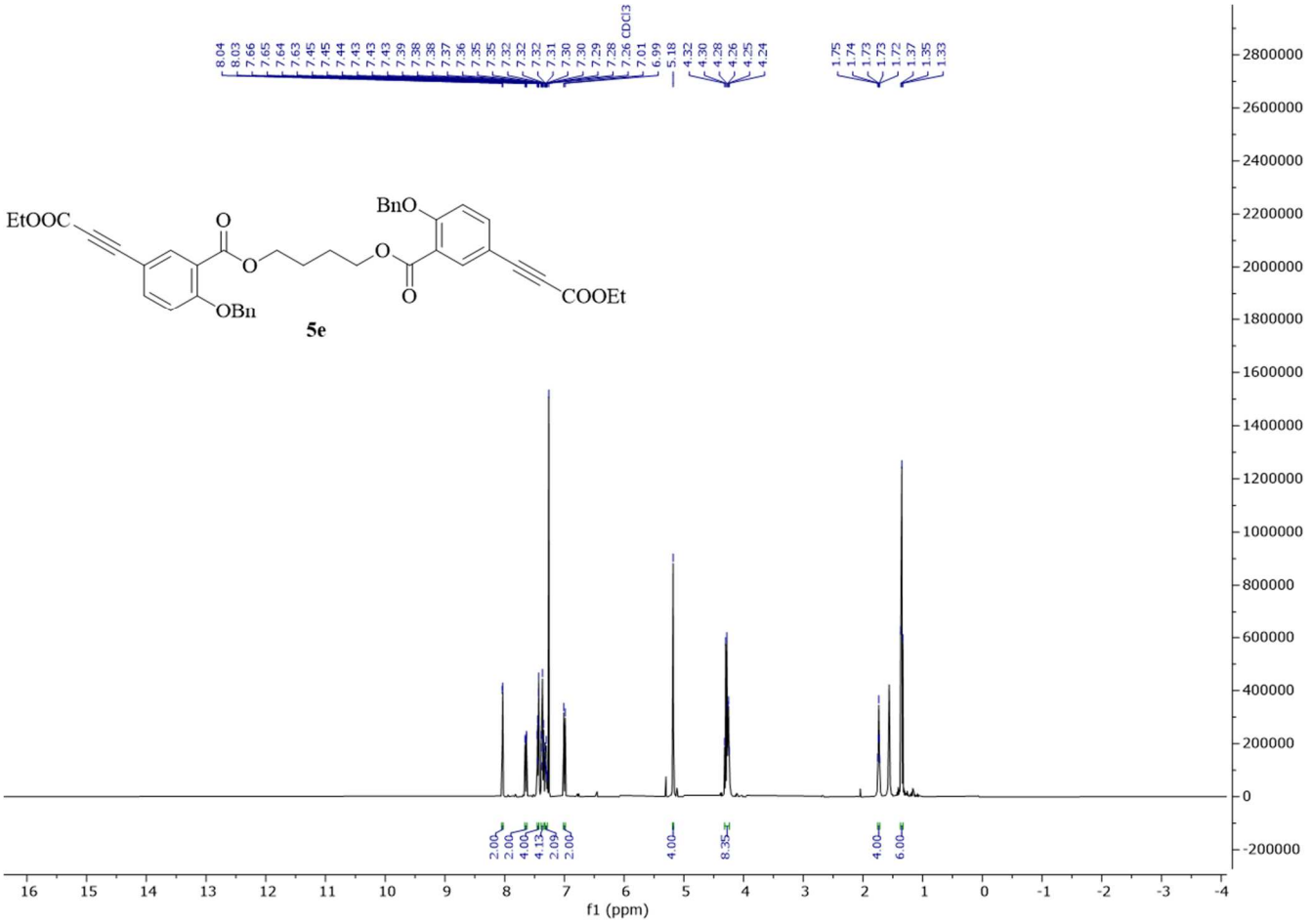
28.96
26.11
14.56
EtOOC
BnO
COOEt
OBn
5d
f1 (ppm)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8.03
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7.63
7.45
7.45
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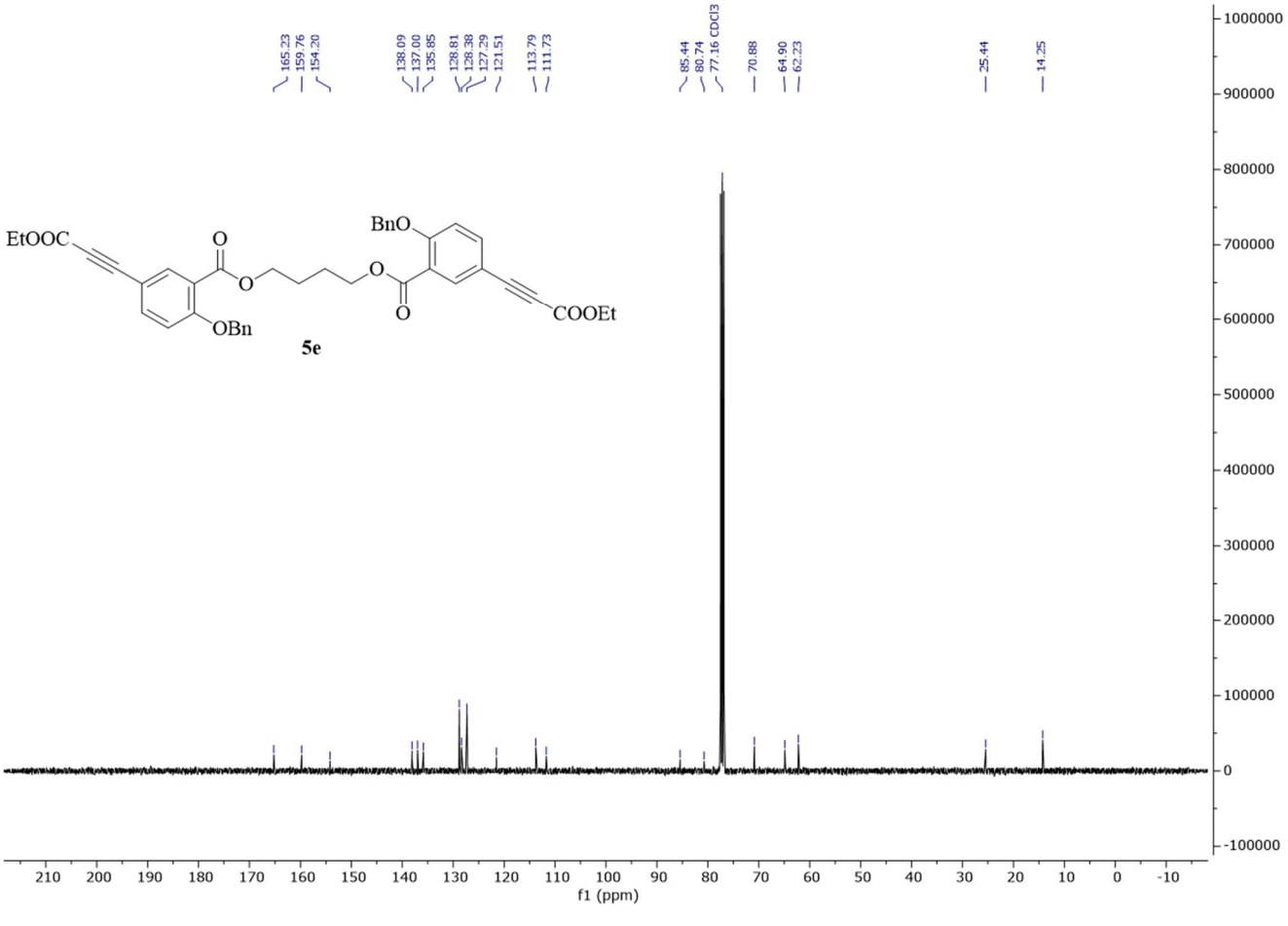
7.43
7.39
7.38
7.38
7.37
7.36
7.35
7.35
7.32
7.32
7.32
7.31
7.30
7.30
7.29
7.28
7.26 CDCl3
7.01
6.99
5.18
4.32
4.30
4.28
4.26
4.25
4.24
1.75
1.74
1.73
1.73
1.72
1.37
1.35
1.33
EtOOC
O
O
O
BnO
O
O
COOEt
OBn
5e
2.00
2.00
4.00
4.13
2.09
2.00
4.00
8.35
4.00
6.00
f1 (ppm)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121.51
113.79
111.73
85.44
80.74
77.16 CDCl3
70.88
64.90
62.23
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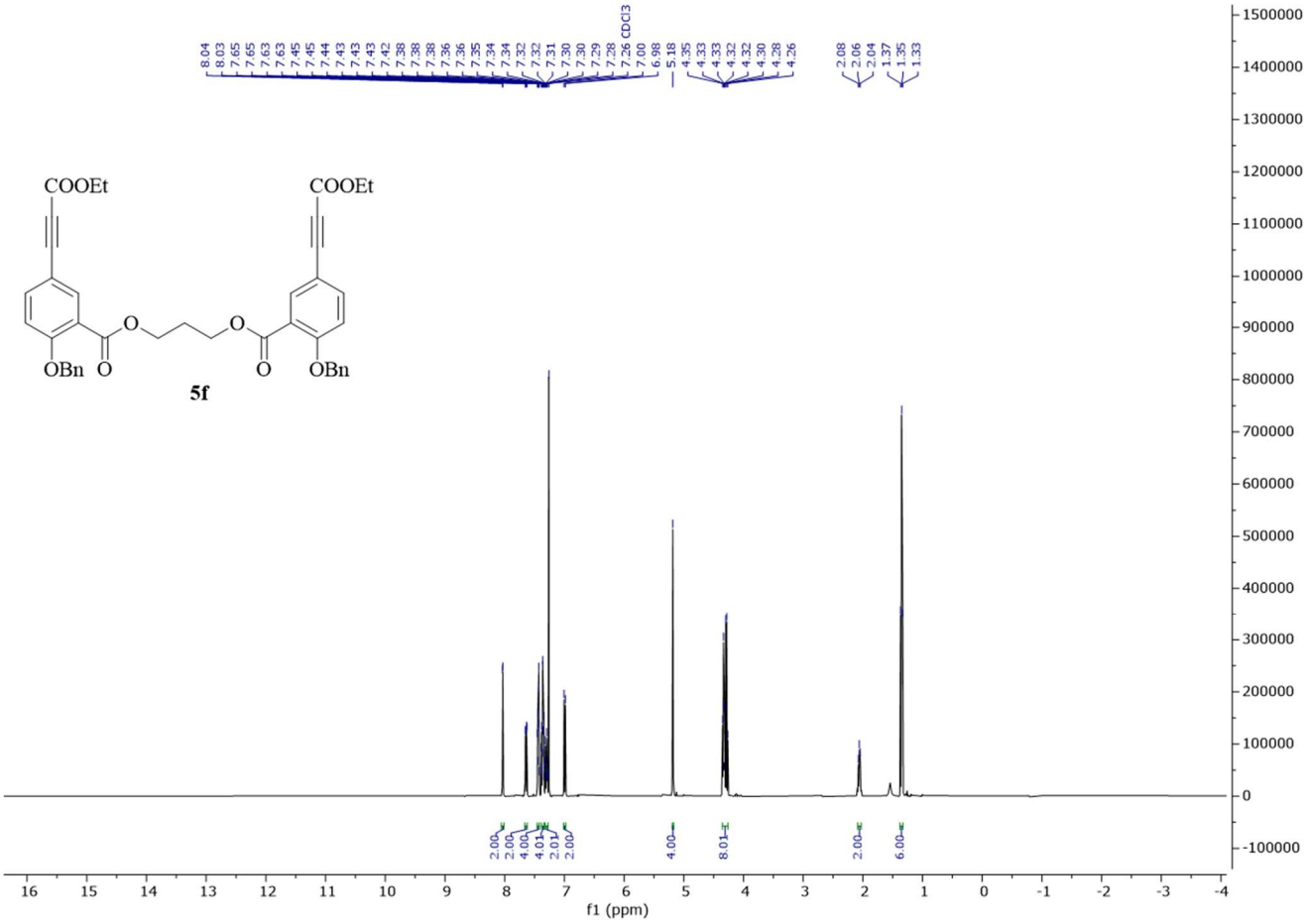
14.25
EtOOC
O
O
O
BnO
O
O
COOEt
OBn
5e
f1 (ppm)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7.63
7.63
7.45
7.45
7.44
7.43
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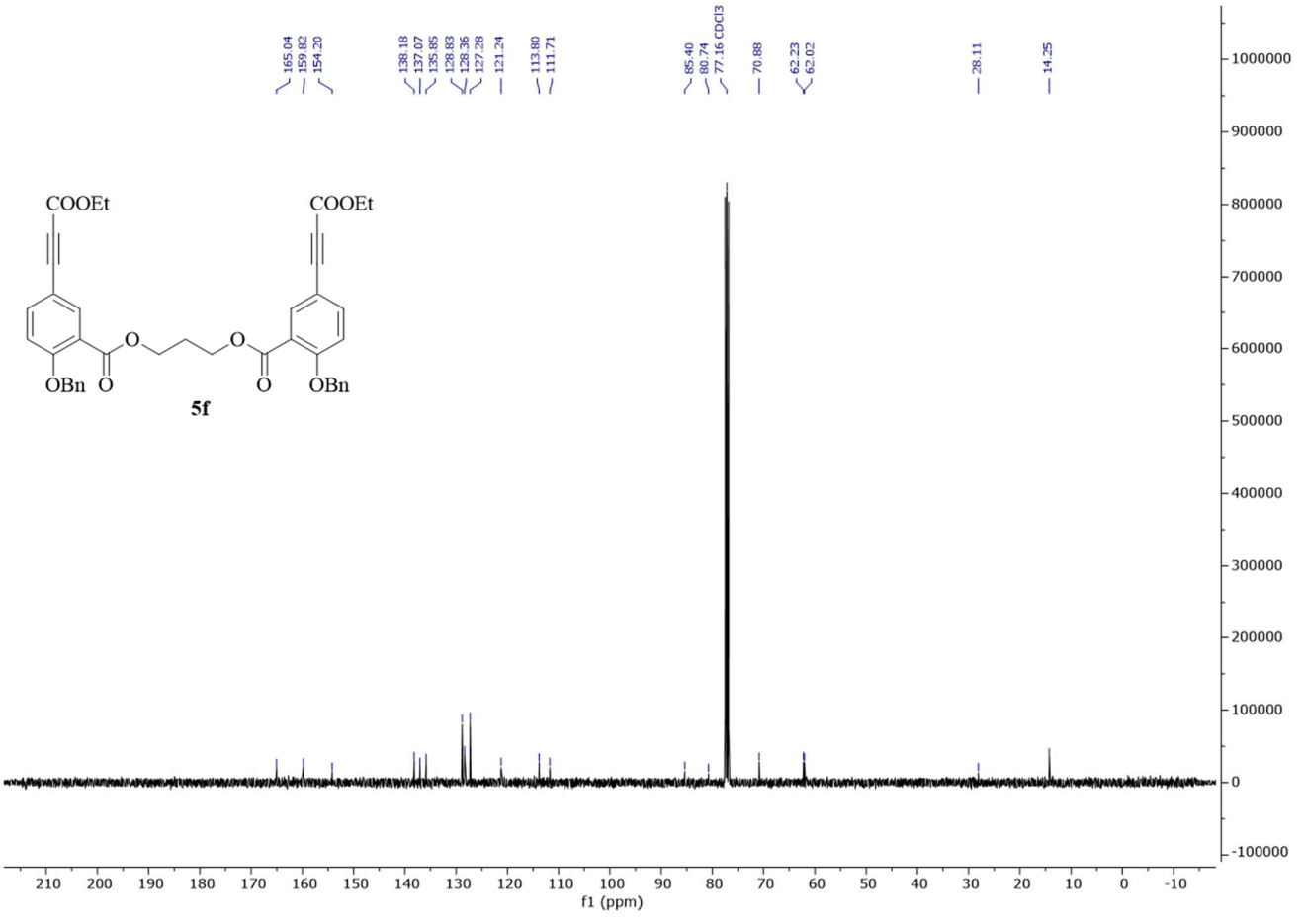
7.38
7.38
7.38
7.36
7.36
7.35
7.34
7.34
7.32
7.32
7.31
7.30
7.30
7.29
7.28
7.26 CDCl3
7.00
6.98
5.18
4.35
4.33
4.33
4.32
4.32
4.30
4.28
4.26
2.08
2.06
2.04
1.37
1.35
1.33
COOEt
COOEt
O
O
O
O
OBn
OBn
5f
2.00
2.00
4.00
4.01
2.01
2.00
4.00
8.01
2.00
6.00
f1 (ppm)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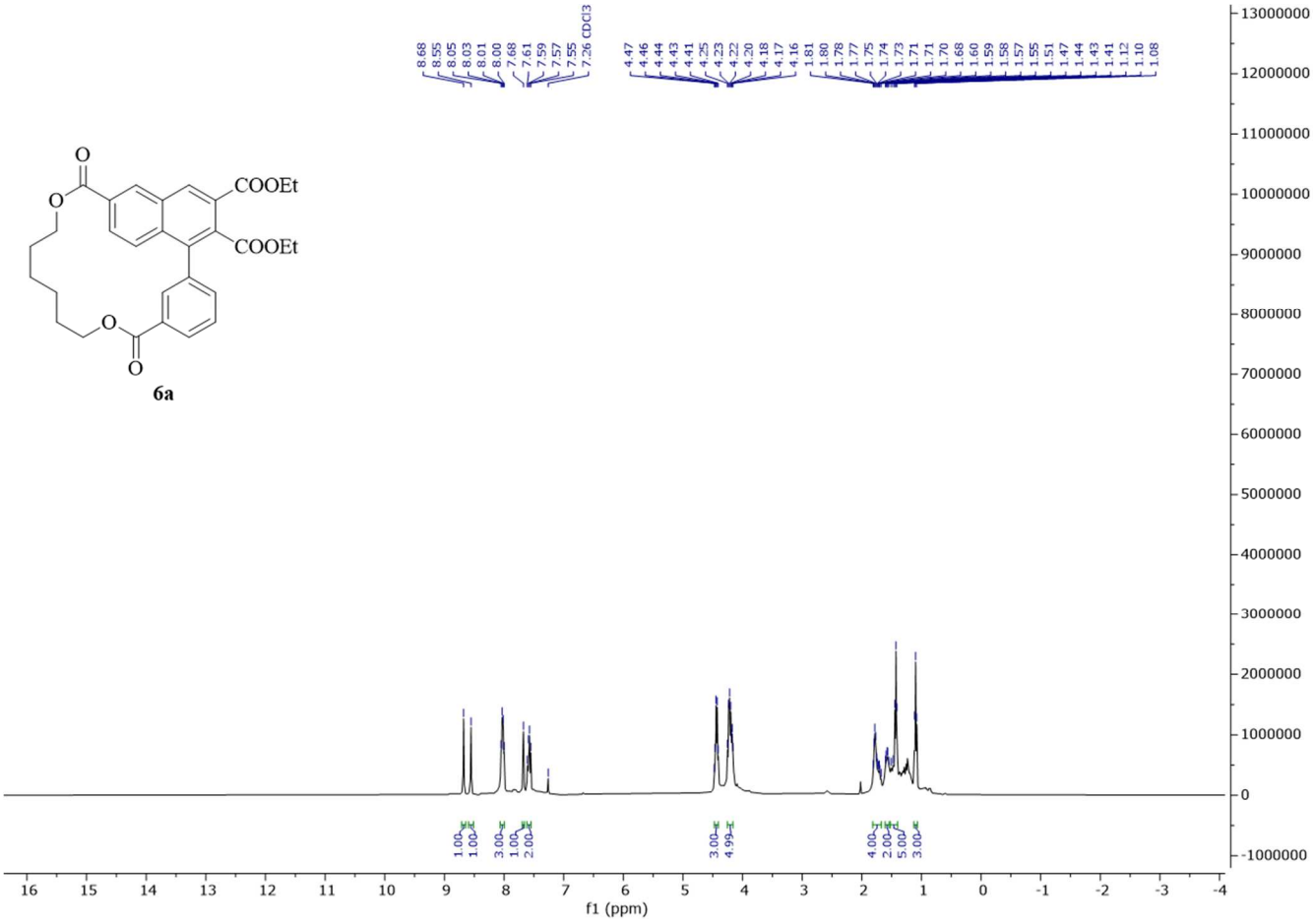
128.83
128.36
127.28
121.24
113.80
111.71
85.40
80.74
77.16 CDCl3
70.88
62.23
62.02
28.11
14.25
COOEt
COOEt
O
O
O
O
OBn
OBn
5f
f1 (ppm)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7.61
7.59
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7.55
7.26 CDCl3
4.47
4.46
4.44
4.43
4.41
4.25
4.23
4.22
4.20
4.18
4.17
4.16
1.81
1.80
1.78
1.77
1.75
1.74
1.73
1.71
1.71
1.70
1.68
1.60
1.59
1.58
1.57
1.55
1.51
1.47
1.44
1.43
1.41
1.12
1.10
1.08
COOEt
COOEt
O
O
O
O
O
1.00
1.00
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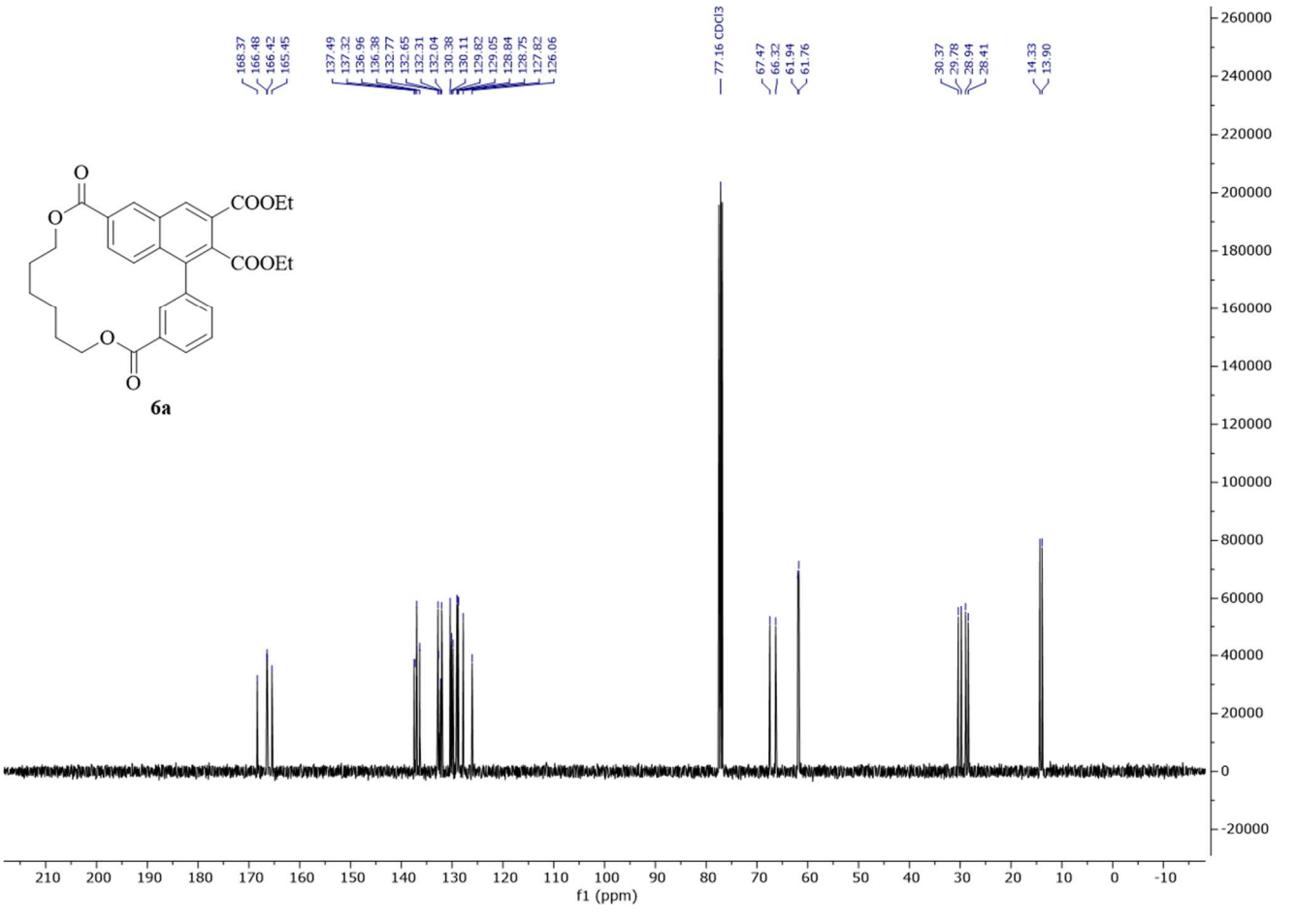
2.00
3.00
4.99
4.00
2.00
5.00
3.00
f1 (ppm)

6a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136.38
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132.04
130.38
130.11
129.82
129.05
128.84
128.75
127.82
126.06
77.16 CDCl3
67.47
66.32
61.94
61.76
30.37
29.78
28.94
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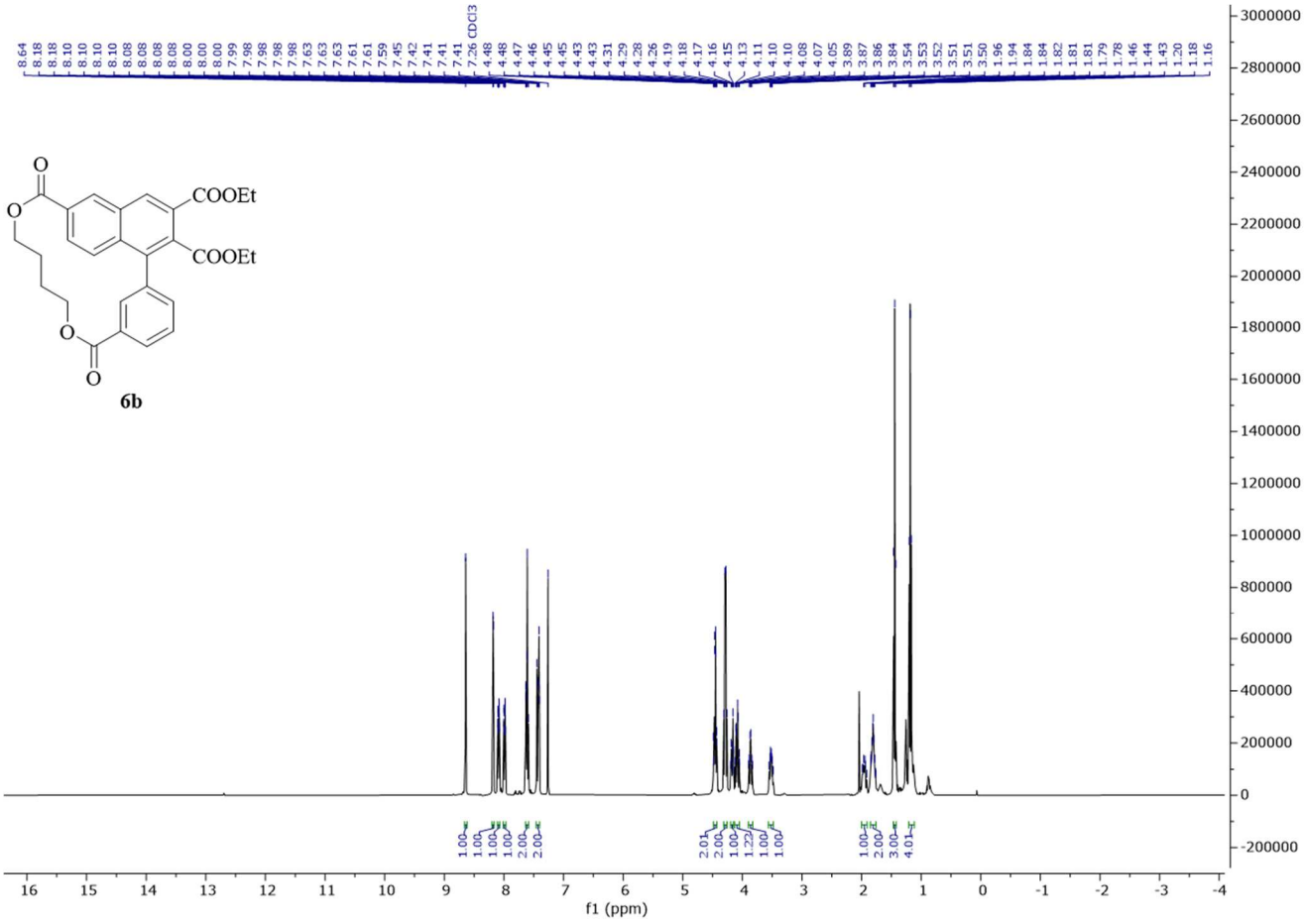
14.33
13.90
COOEt
COOEt
O
O
O
O
O
f1 (ppm)

6a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COOEt
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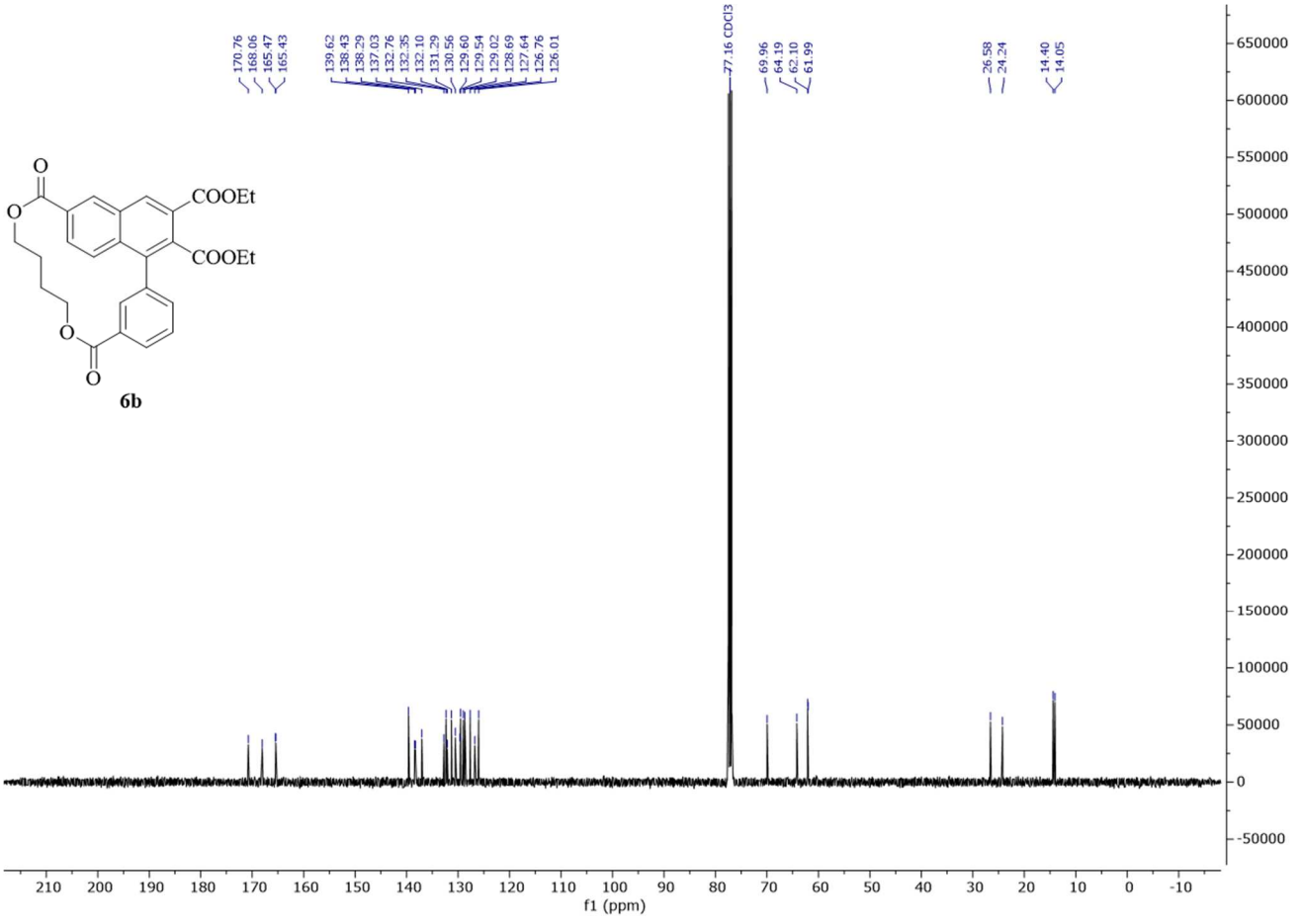
O
O
O
6b
f1 (ppm)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COOEt
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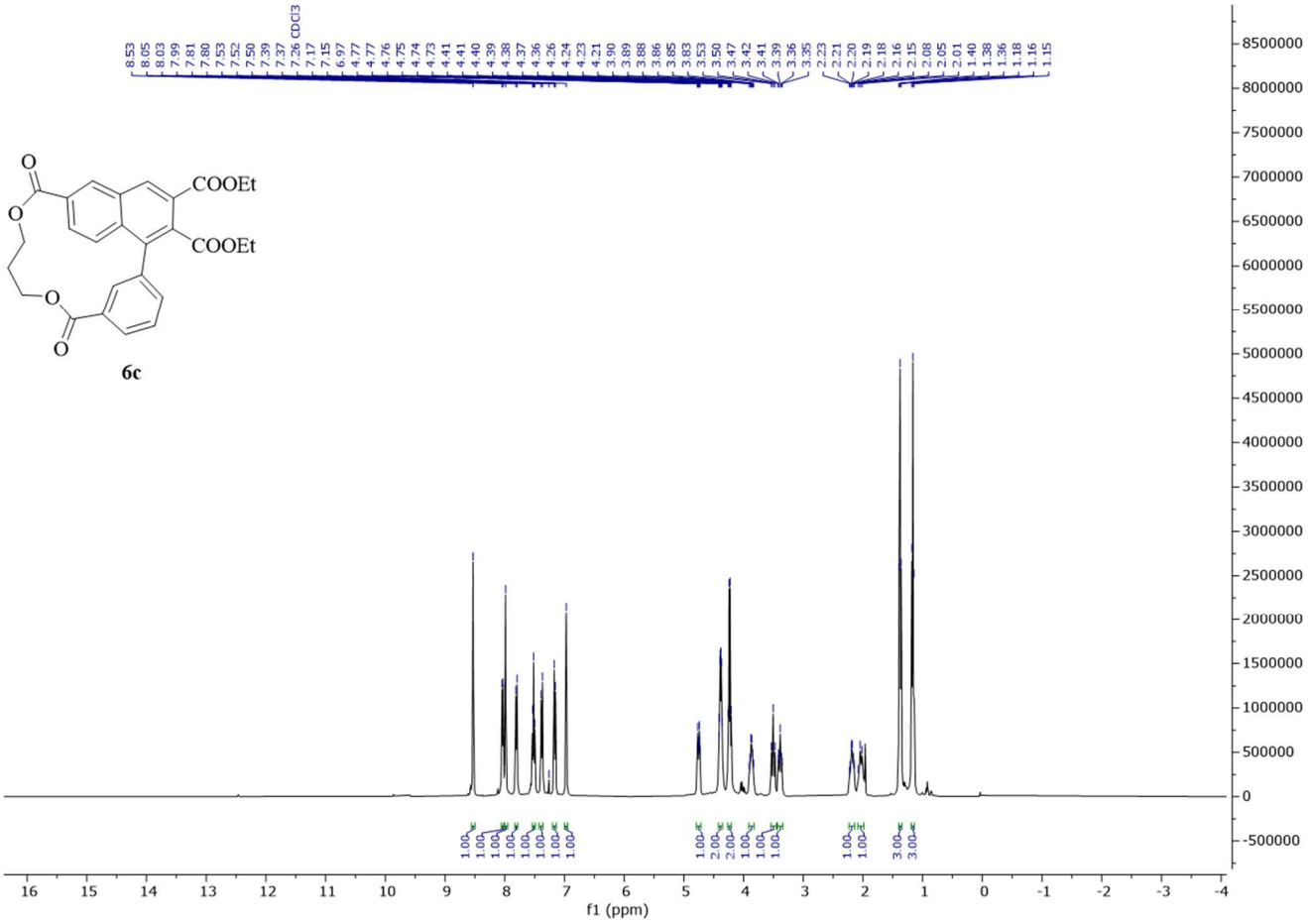
O
O
O
6b
f1 (ppm)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7.37
7.26 CDCl3
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7.15
6.97
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4.77
4.76
4.75
4.74
4.73
4.41
4.41
4.40
4.39
4.38
4.37
4.36
4.26
4.24
4.23
4.21
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3.88
3.86
3.85
3.83
3.53
3.50
3.47
3.42
3.41
3.39
3.36
3.35
2.23
2.21
2.20
2.19
2.18
2.16
2.15
2.08
2.05
2.01
1.40
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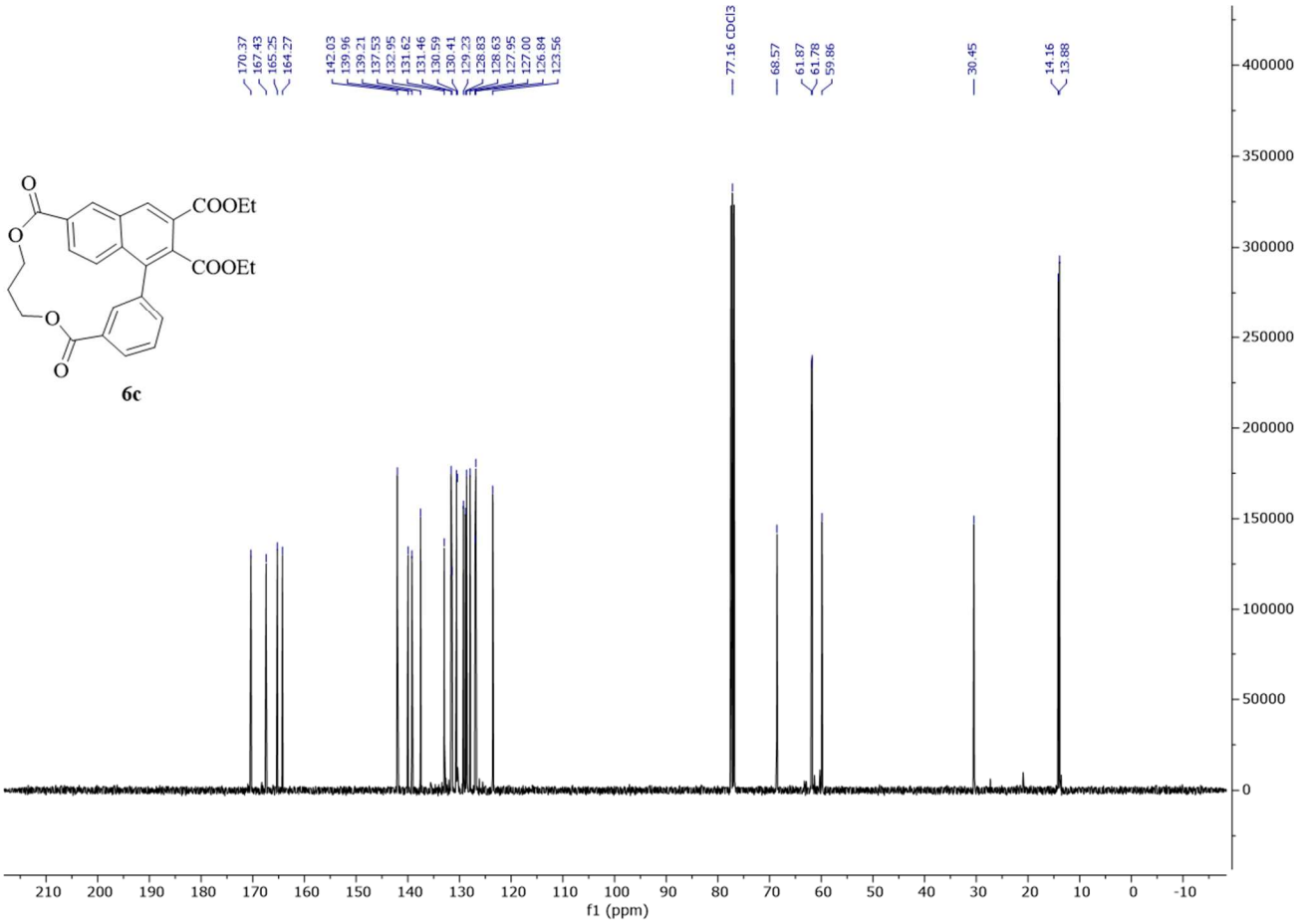
1.16
1.15
COOEt
COOEt
O
O
O
O
O
6c
f1 (ppm)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129.23
128.83
128.63
127.95
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126.84
123.56
77.16 CDCl3
68.57
61.87
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O
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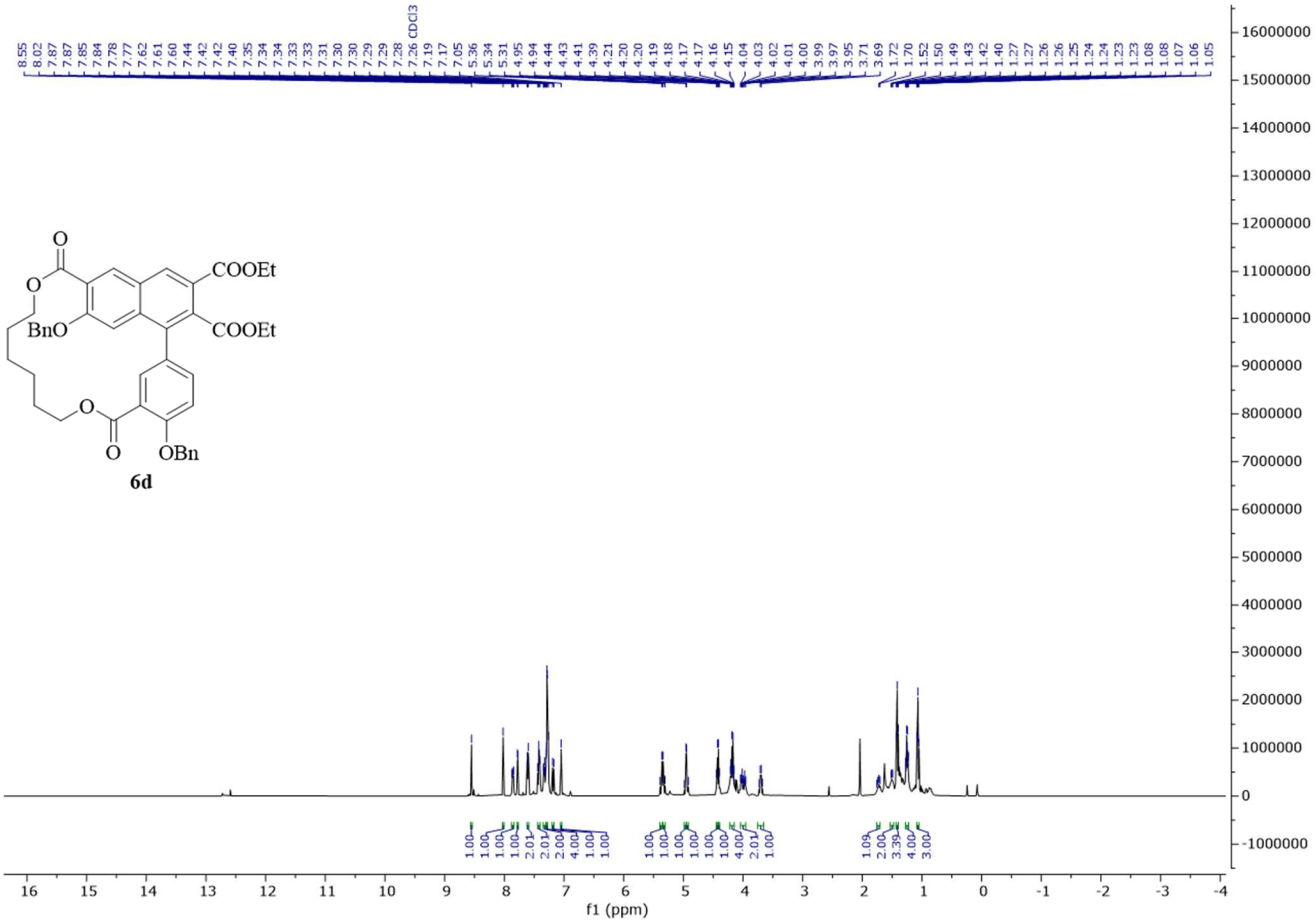
O
6c
f1 (ppm)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7.40
7.35
7.34
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7.30
7.30
7.29
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7.28
7.26 CDCl3
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7.17
7.05
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5.34
5.31
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4.17
4.16
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4.04
4.03
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1.42
1.40
1.27
1.27
1.26
1.26
1.25
1.24
1.24
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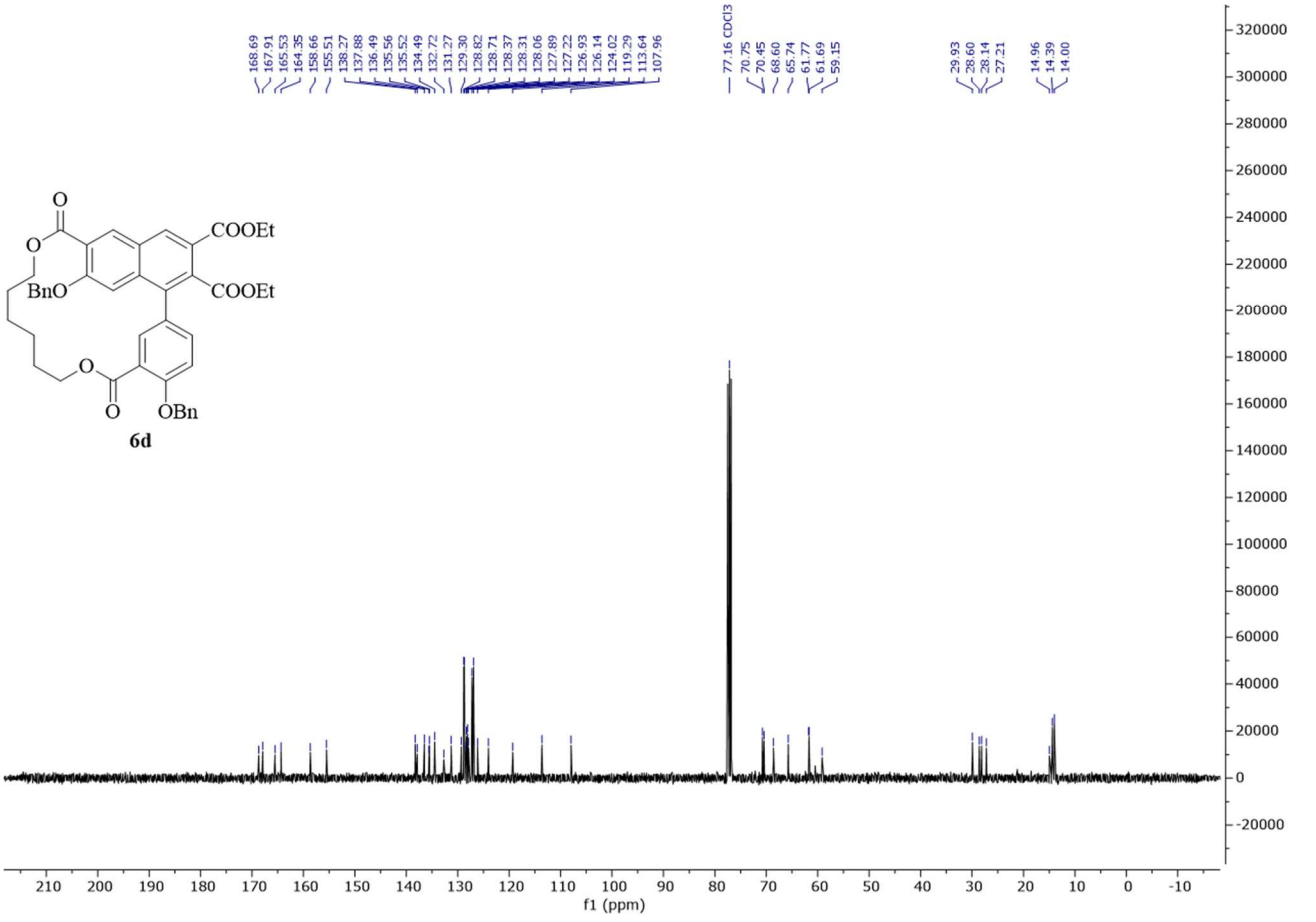
1.08
1.07
1.06
1.05
COOEt
COOEt
BnO
OBn
6d
f1 (ppm)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132.72
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129.30
128.82
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128.37
128.31
128.06
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126.14
124.02
119.29
113.64
107.96
77.16 CDCl3
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70.45
68.60
65.74
61.77
61.69
59.15
29.93
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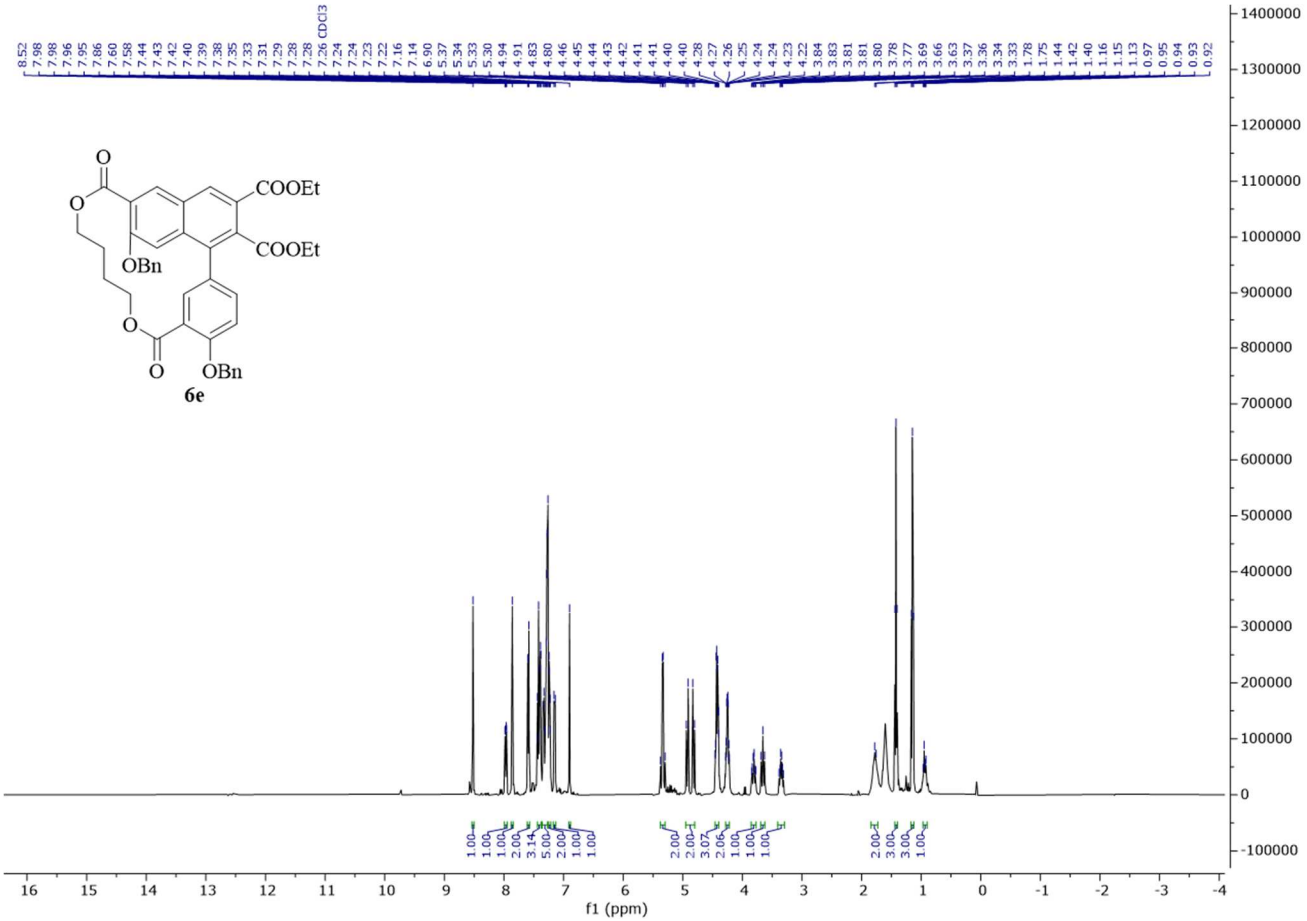
27.21
14.96
14.39
14.00
COOEt
COOEt
BnO
OBn
6d
f1 (ppm)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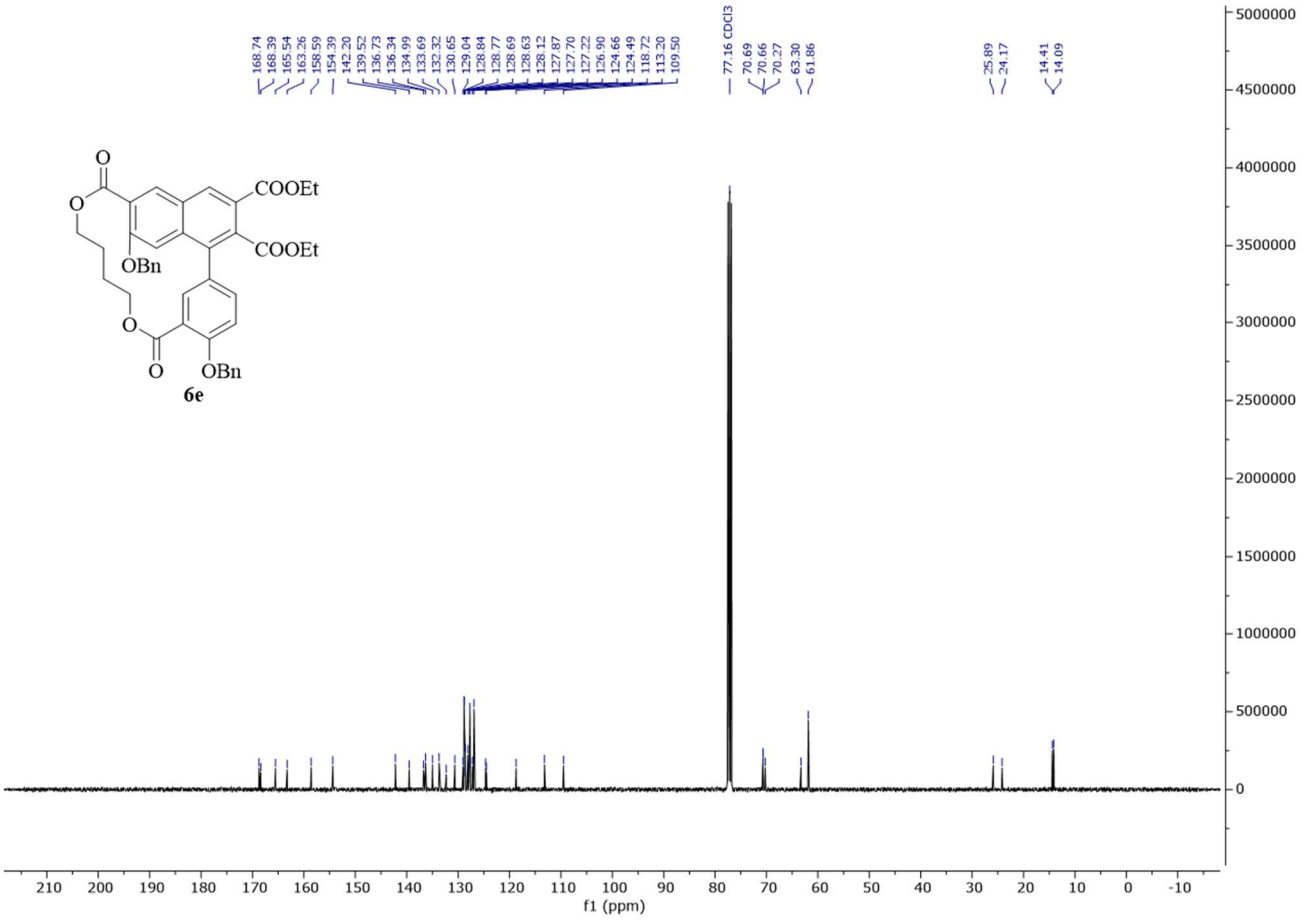
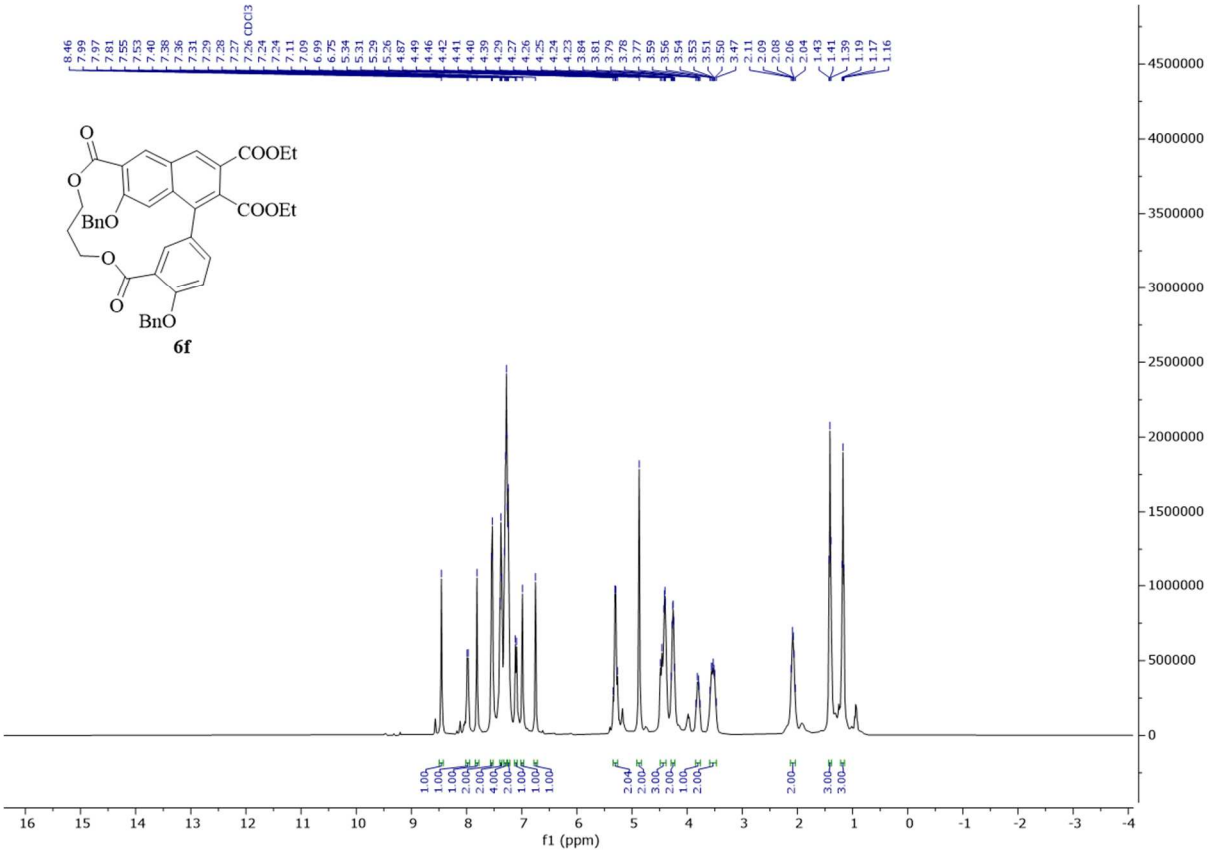
COOEt
OBn
OBn
O
O
O
O
6e
f1 (ppm)


COOEt
COOEt
OBn
OBn
O
O
O
O
6e
f1 (ppm)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7.27
7.26 CDCl3
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3.50
3.47
2.11
2.09
2.08
2.06
2.04
1.43
1.41
1.39
1.19
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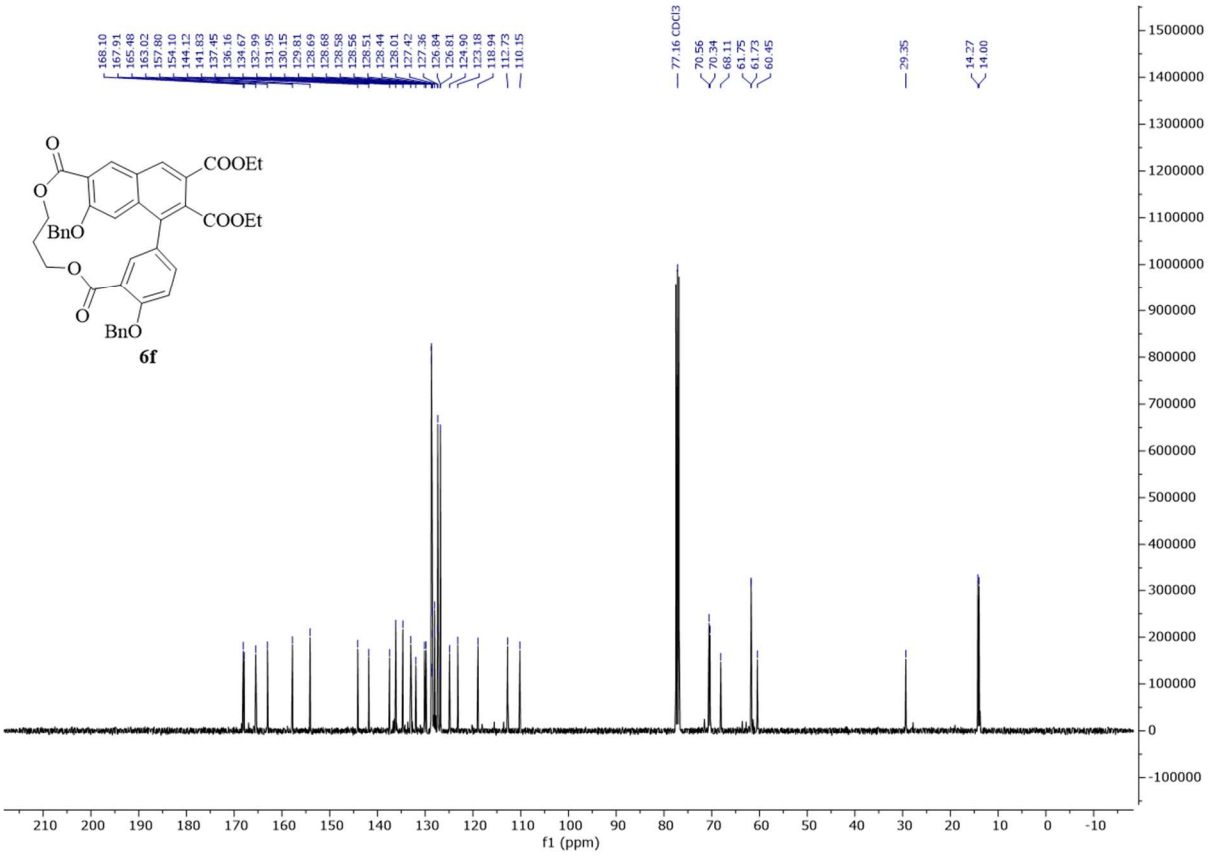
1.16
COOEt
COOEt
BnO
BnO
O
O
O
O
6f
f1 (ppm)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134.67
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131.95
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128.69
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128.44
128.01
127.42
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126.84
126.81
124.90
123.18
118.94
112.73
110.15
77.16 CDCl3
70.56
70.34
68.11
61.75
61.73
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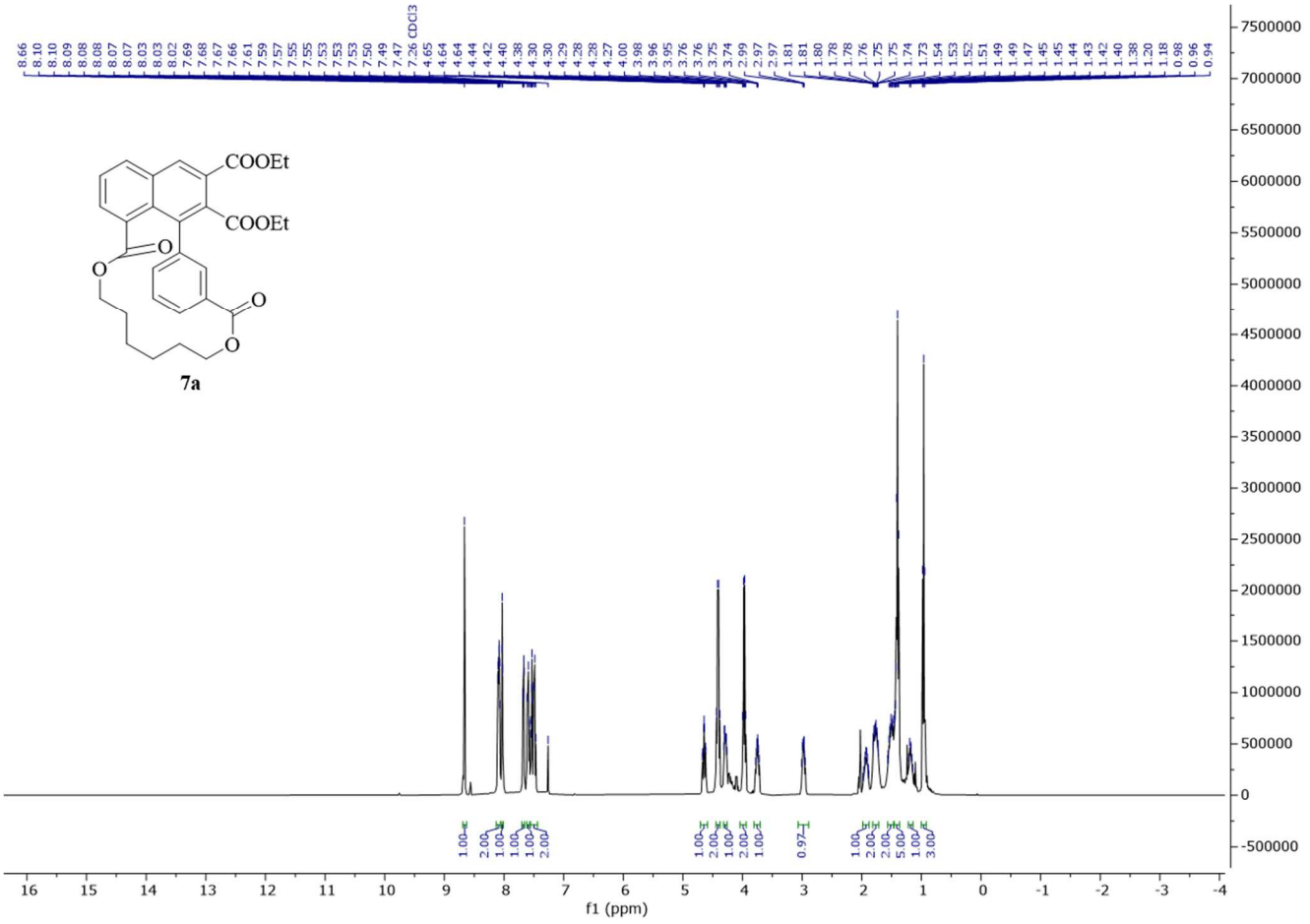
14.00
COOEt
COOEt
BnO
BnO
O
O
O
O
6f
f1 (ppm)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COOEt
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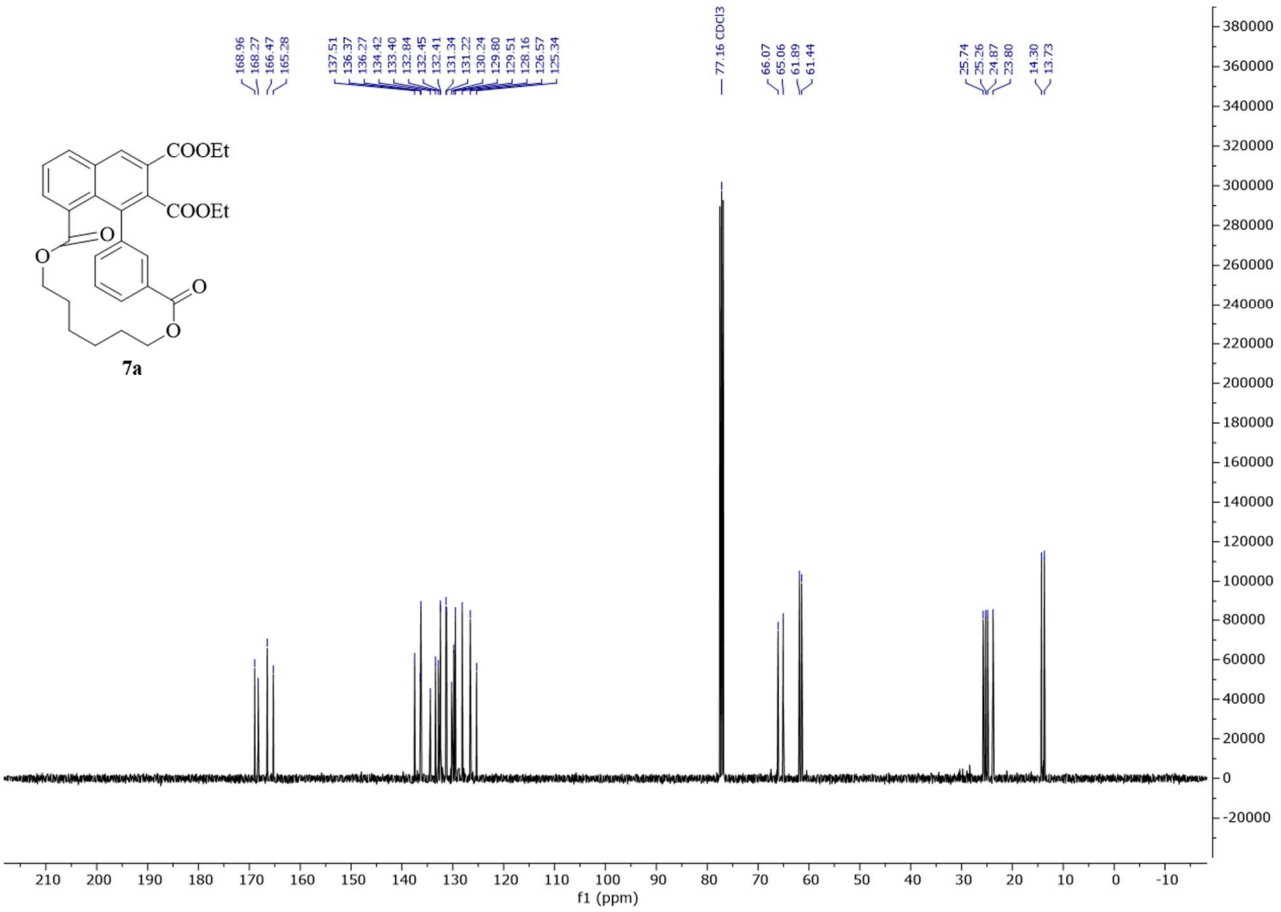
7a
f1 (ppm)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COOEt
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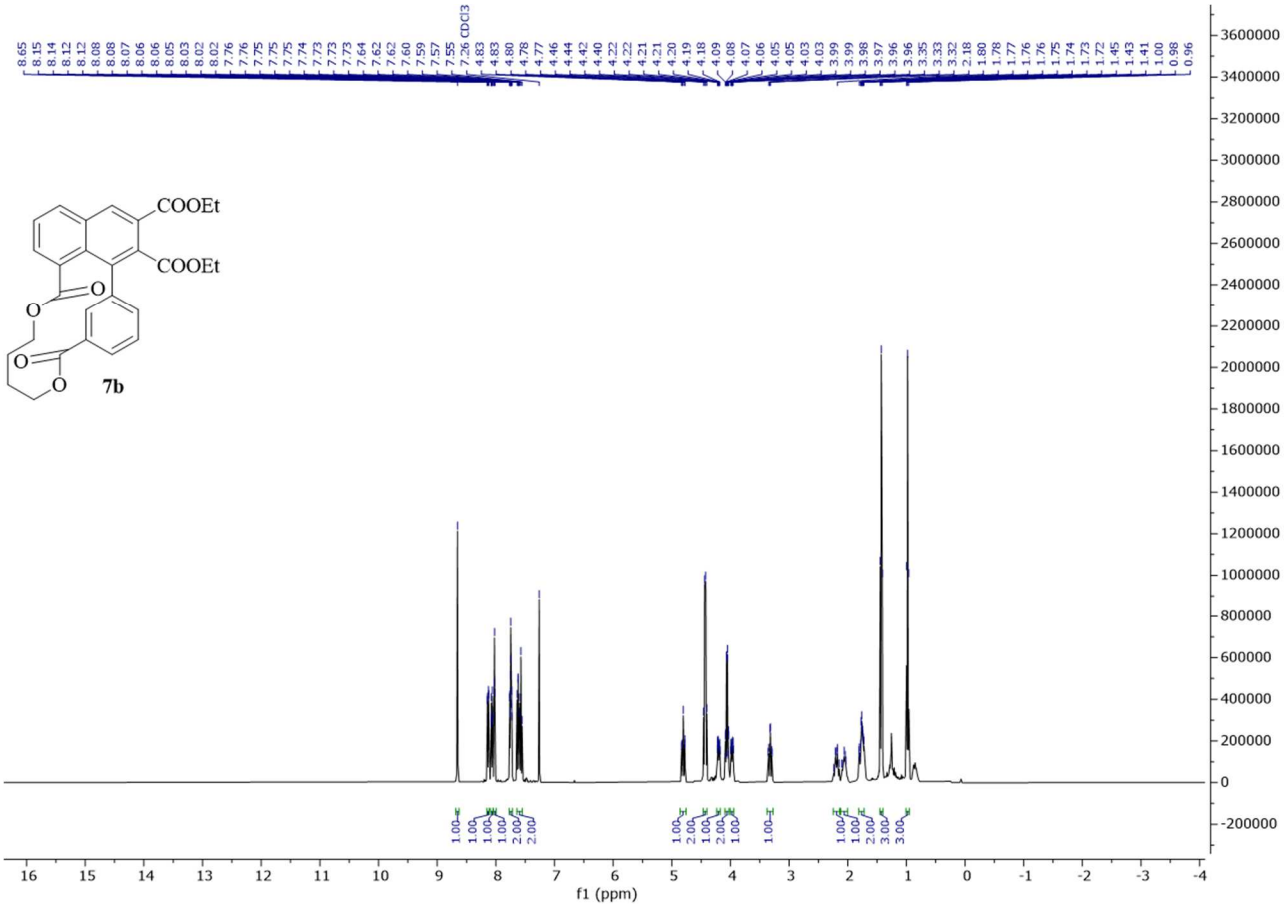
7a
f1 (ppm)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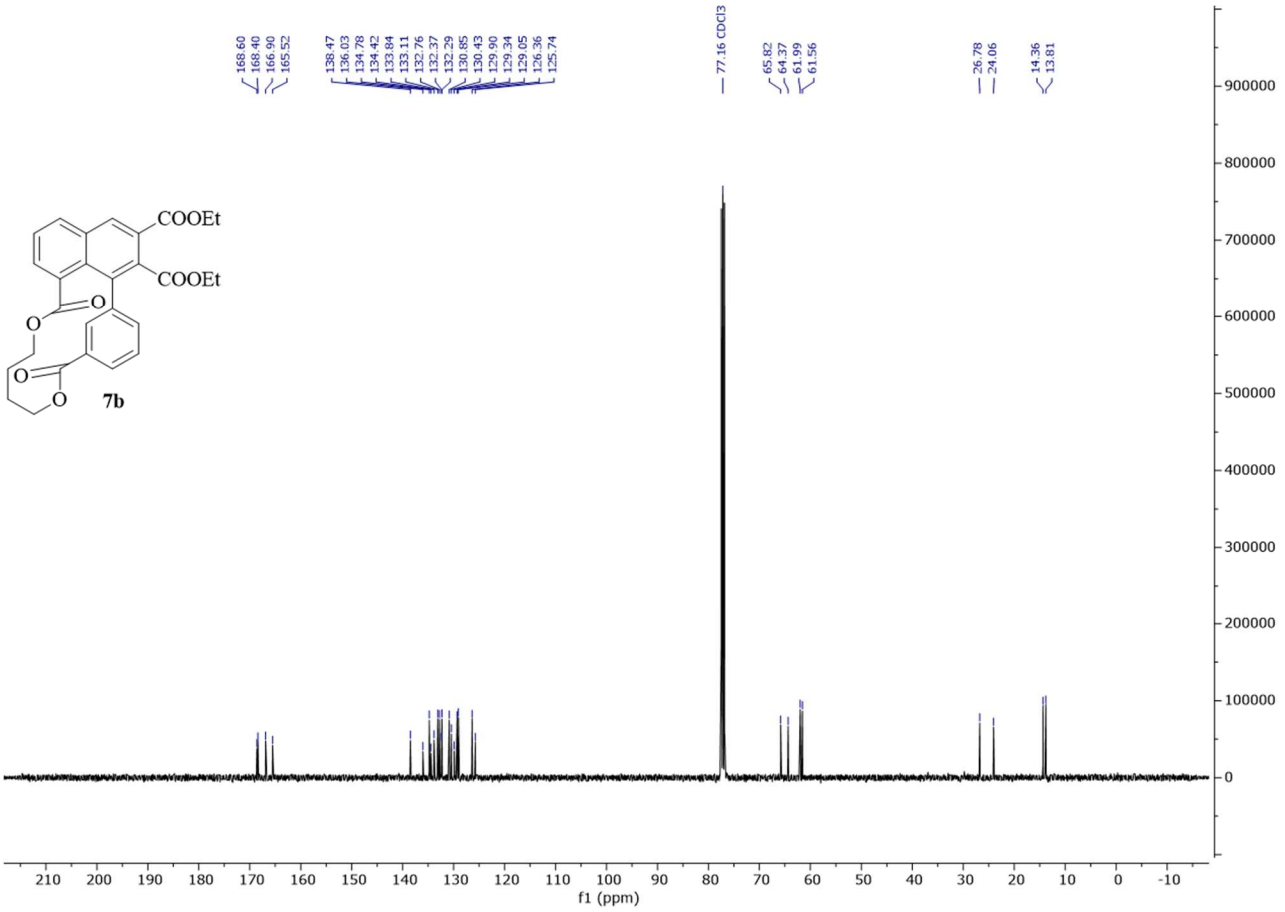
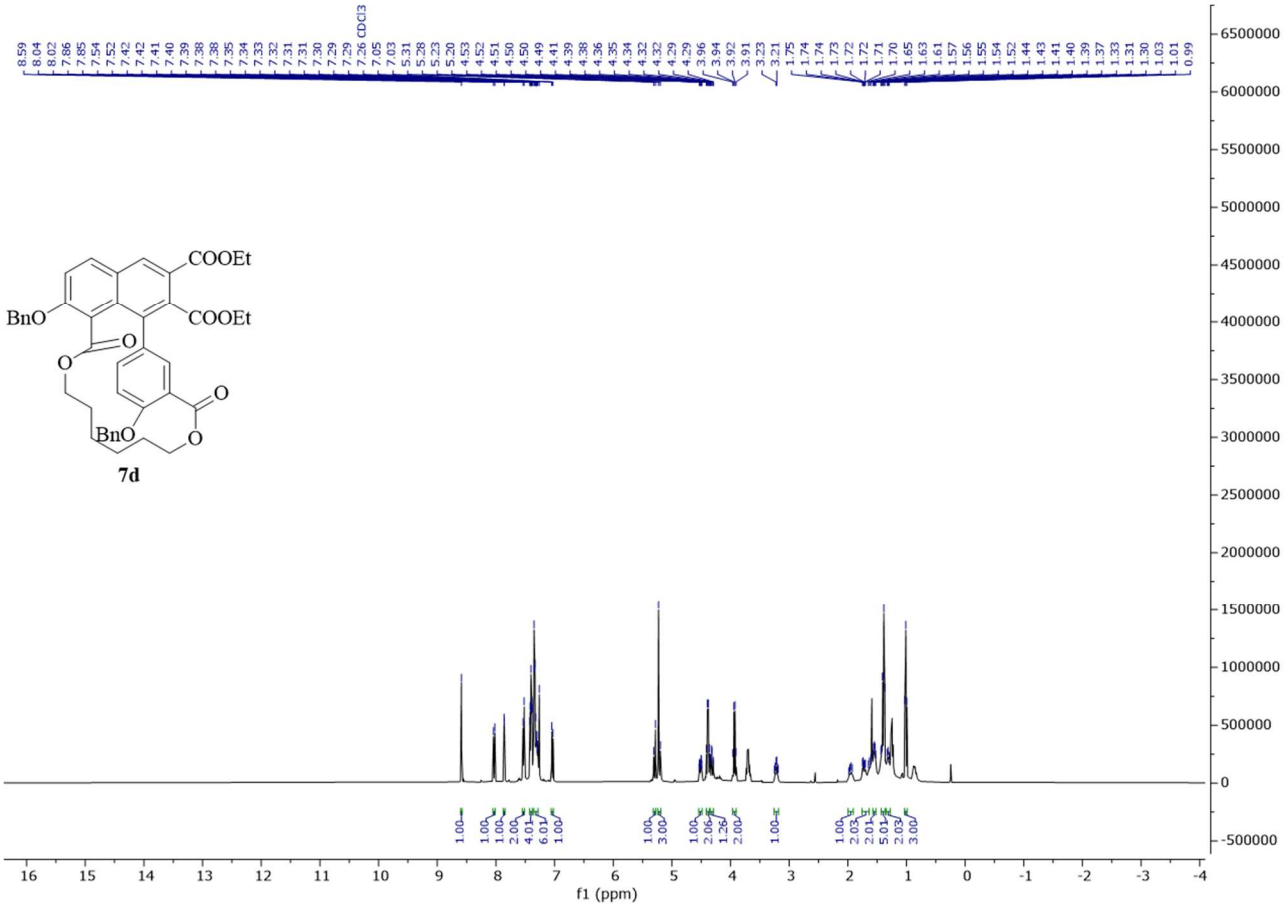
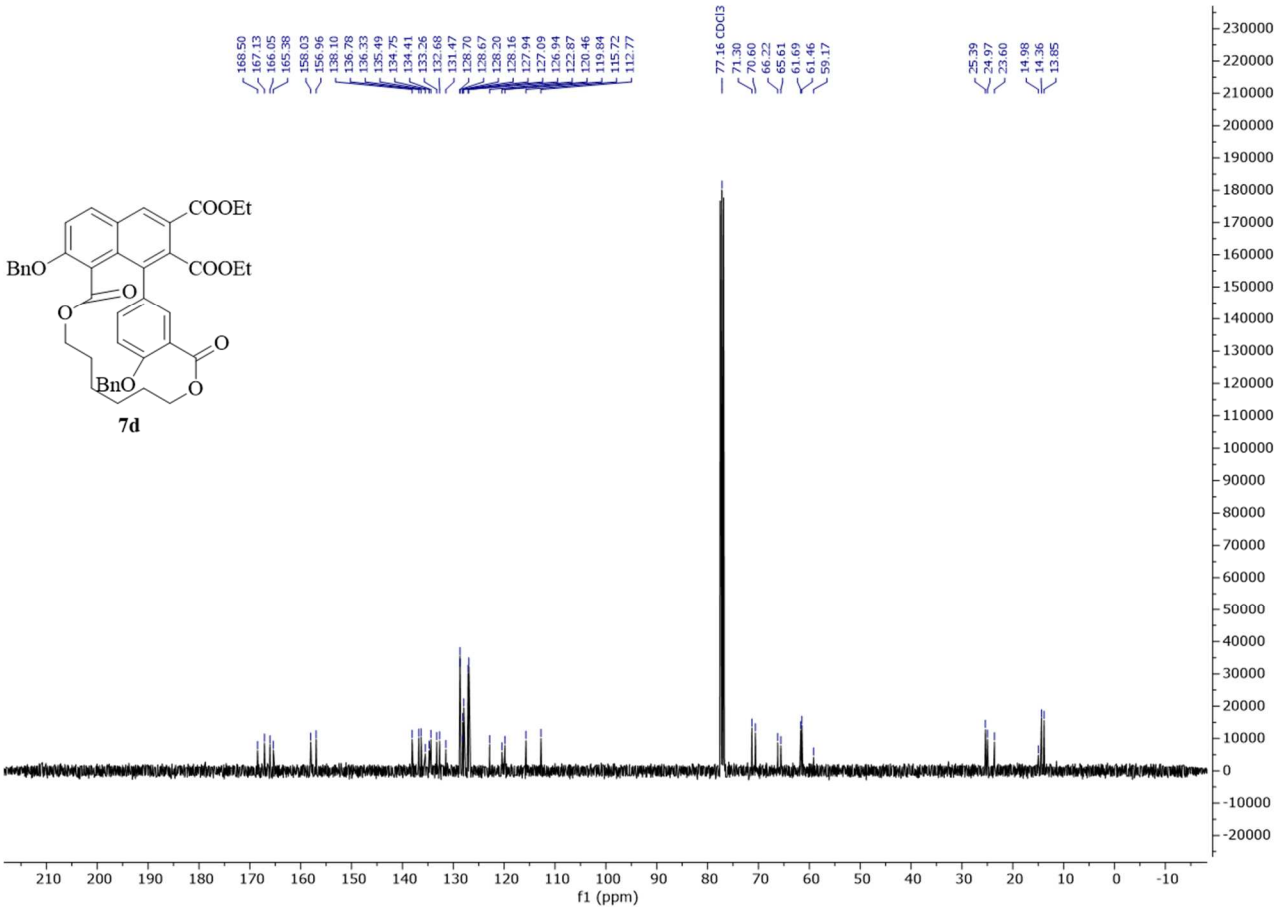
COOEt
O
O
O
O
O
7b
f1 (ppm)


COOEt
COOEt
O
O
O
O
O
7b
f1 (ppm)


COOEt
COOEt
BnO
BnO
O
O
O
O
O
7d
f1 (ppm)


COOEt
COOEt
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BnO
O
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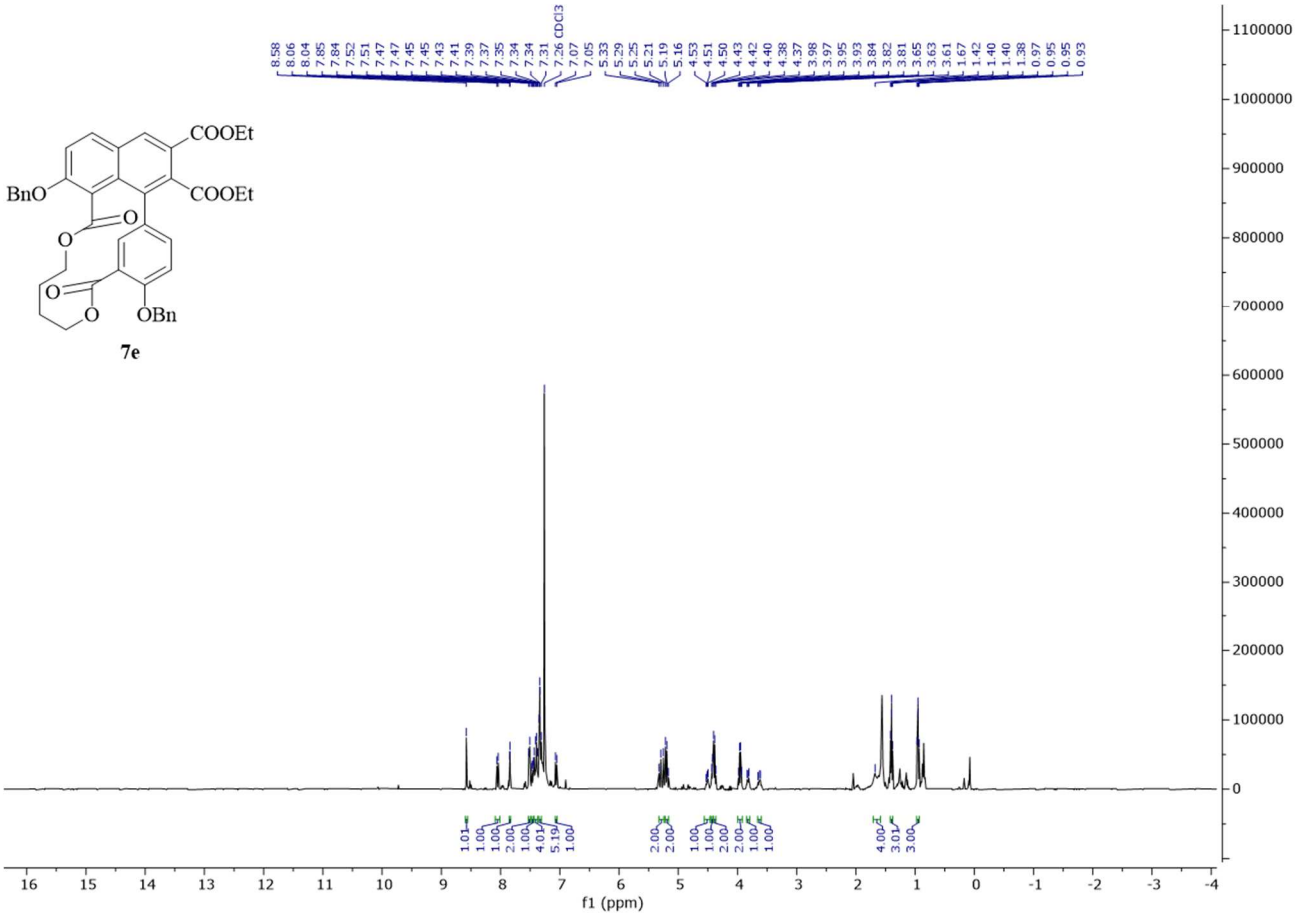
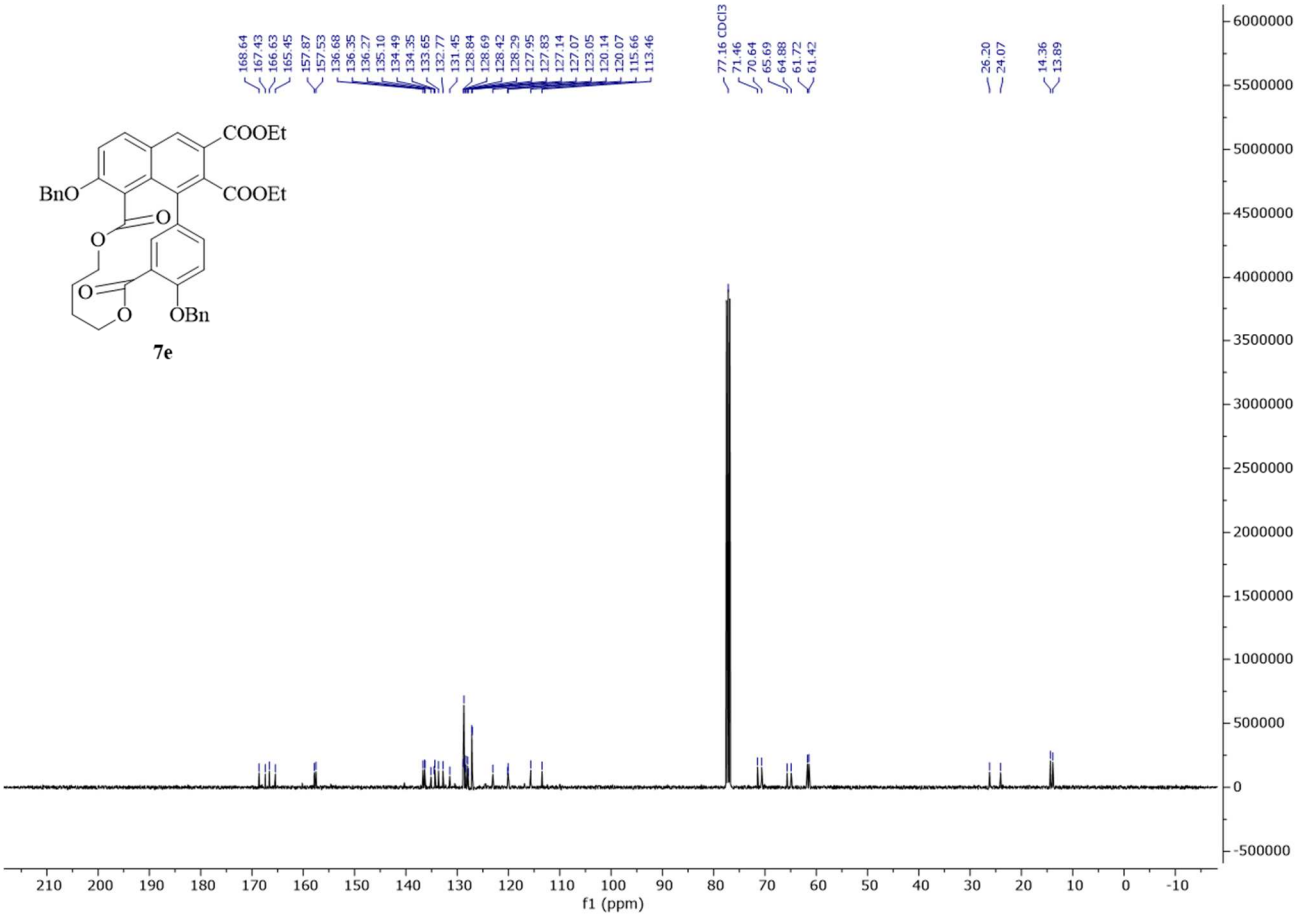
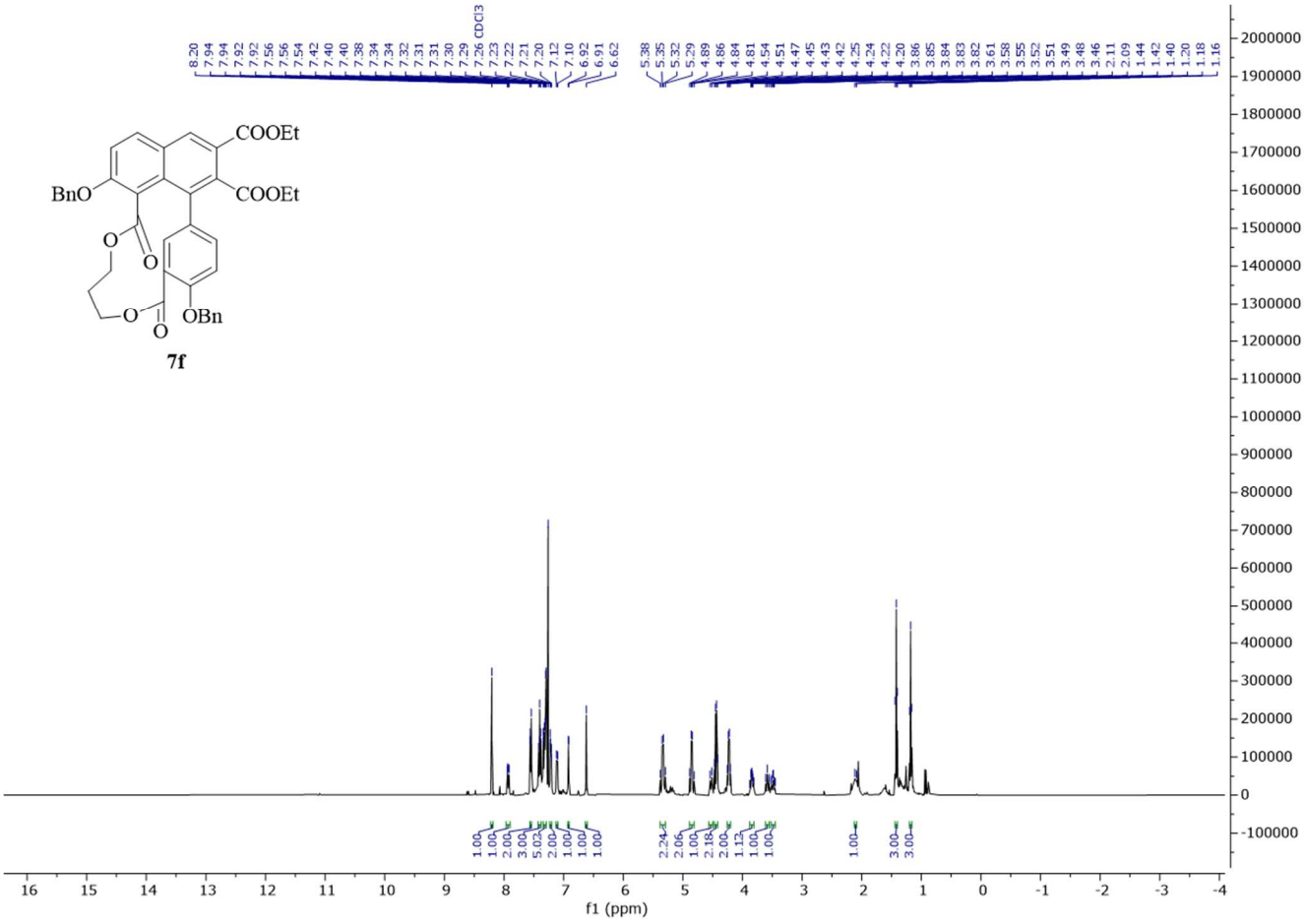
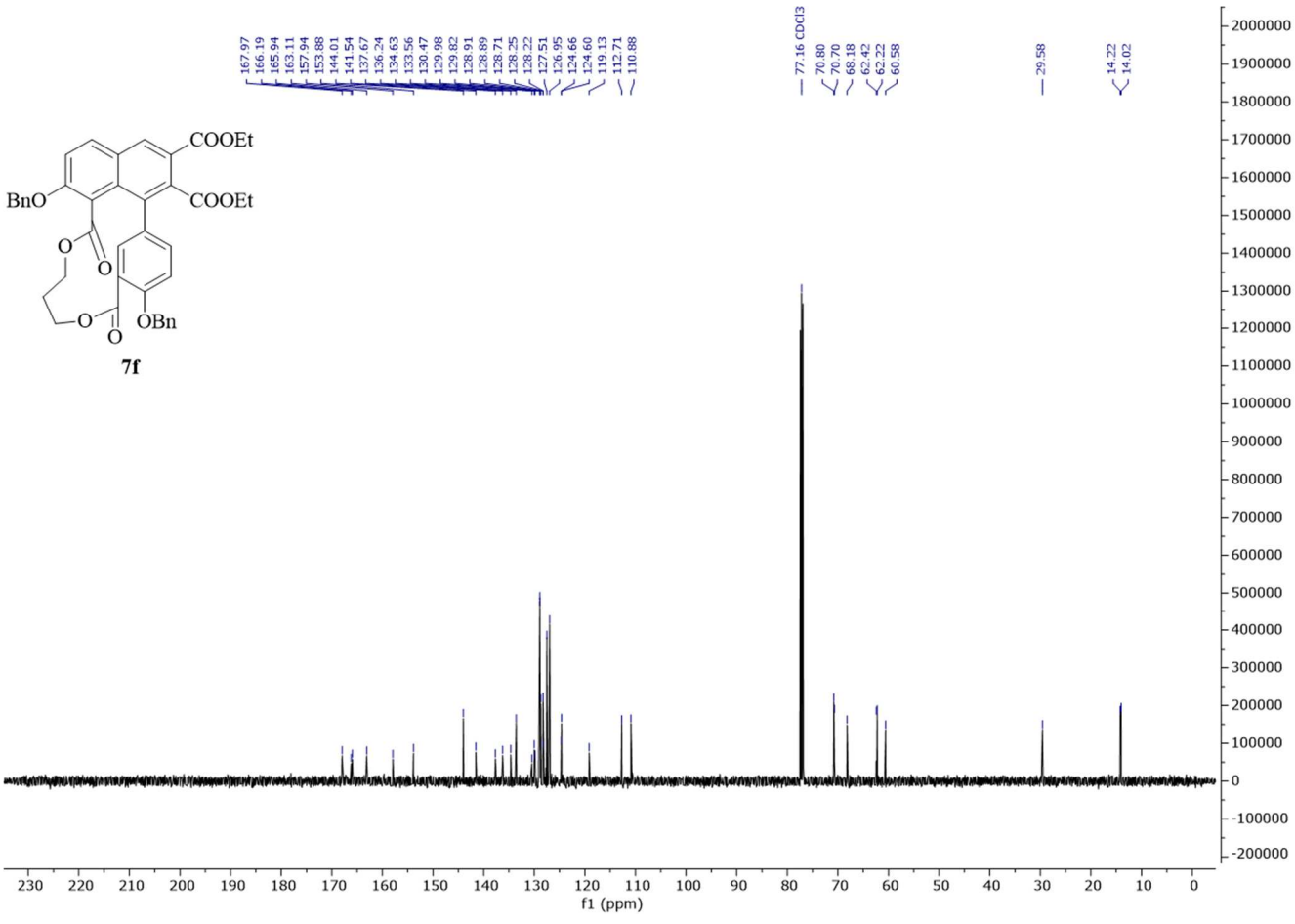
O
O
7d
f1 (ppm)


COOEt
BnO
COOEt
O
O
O
O
OBn
7e
f1 (ppm)

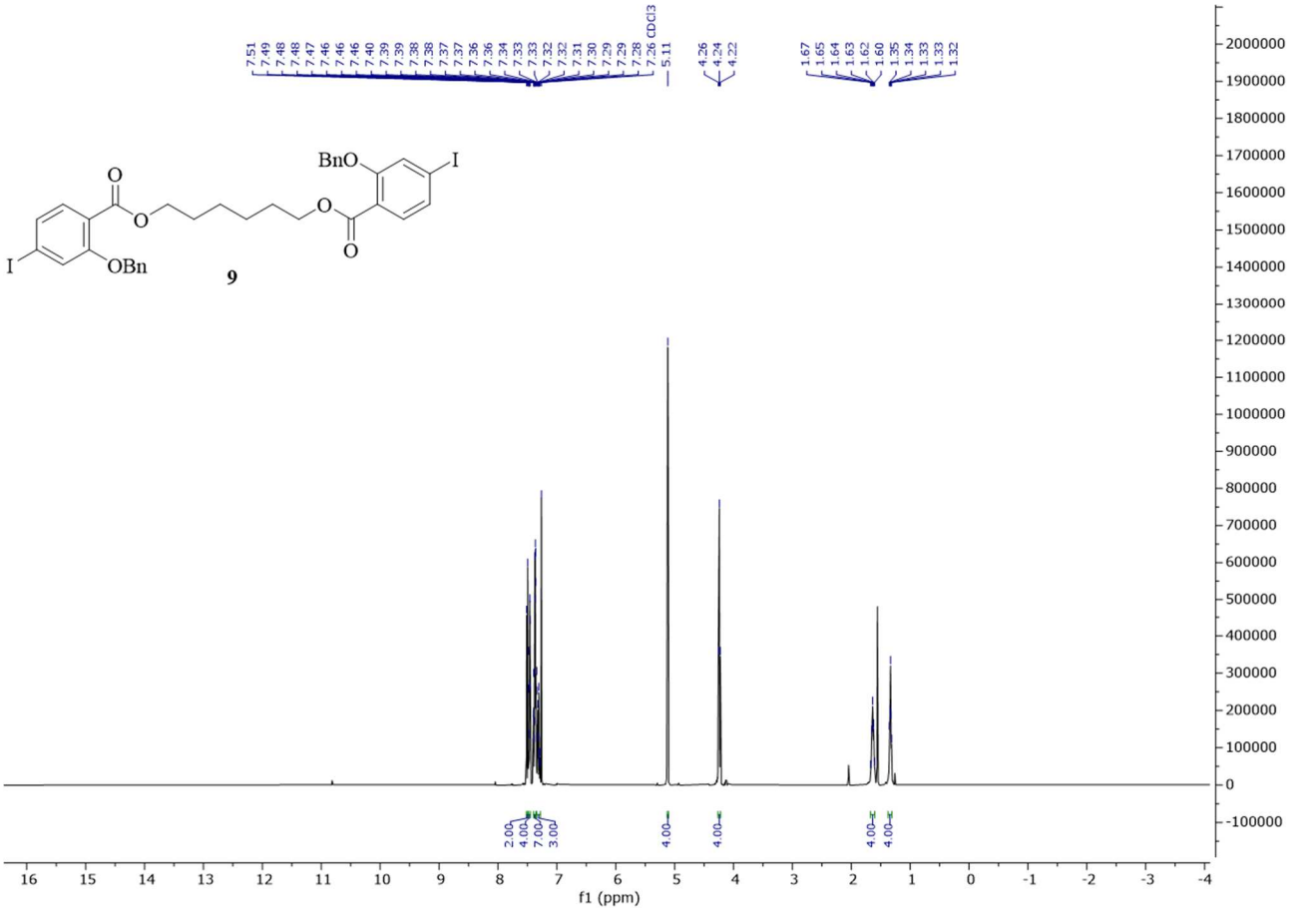

COOEt
BnO
COOEt
O
O
O
O
OBn
7e
f1 (ppm)

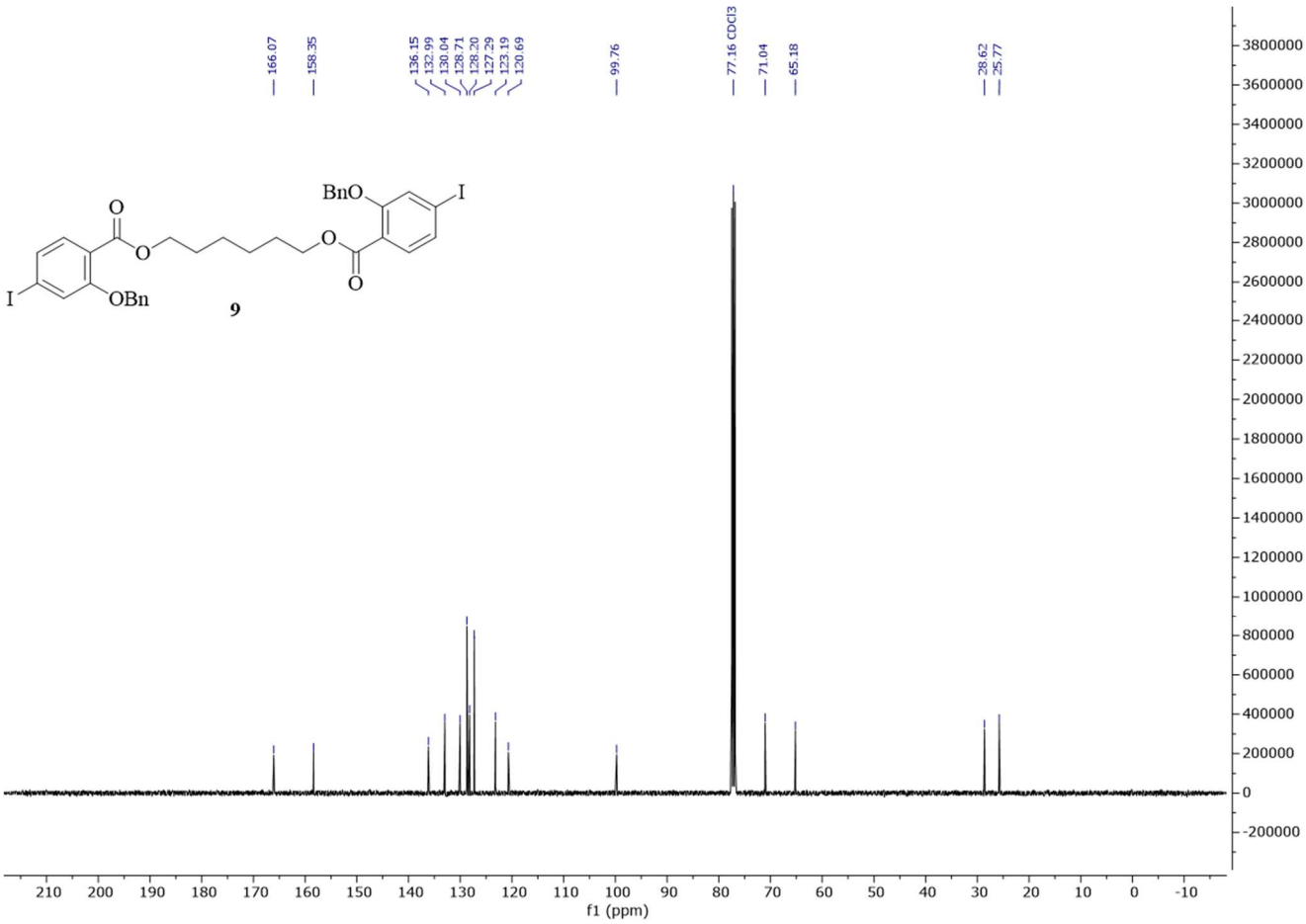

8.20
7.94
7.94
7.92
7.92
7.56
7.56
7.54
7.42
7.40
7.40
7.38
7.34
7.34
7.32
7.31
7.31
7.30
7.29
7.26 CDCl3
7.23
7.22
7.21
7.20
7.12
7.10
6.92
6.91
6.62
5.38
5.35
5.32
5.29
4.89
4.86
4.84
4.81
4.54
4.51
4.47
4.45
4.43
4.42
4.25
4.24
4.22
4.20
3.86
3.85
3.84
3.83
3.82
3.61
3.58
3.55
3.52
3.51
3.49
3.48
3.46
2.11
2.09
1.44
1.42
1.40
1.20
1.18
1.16
COOEt
COOEt
BnO
O
O
O
O
OBn
1.00
1.00
2.00
3.00
5.02
2.00
1.00
1.00
1.00
2.24
2.06
1.00
2.18
2.00
1.12
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

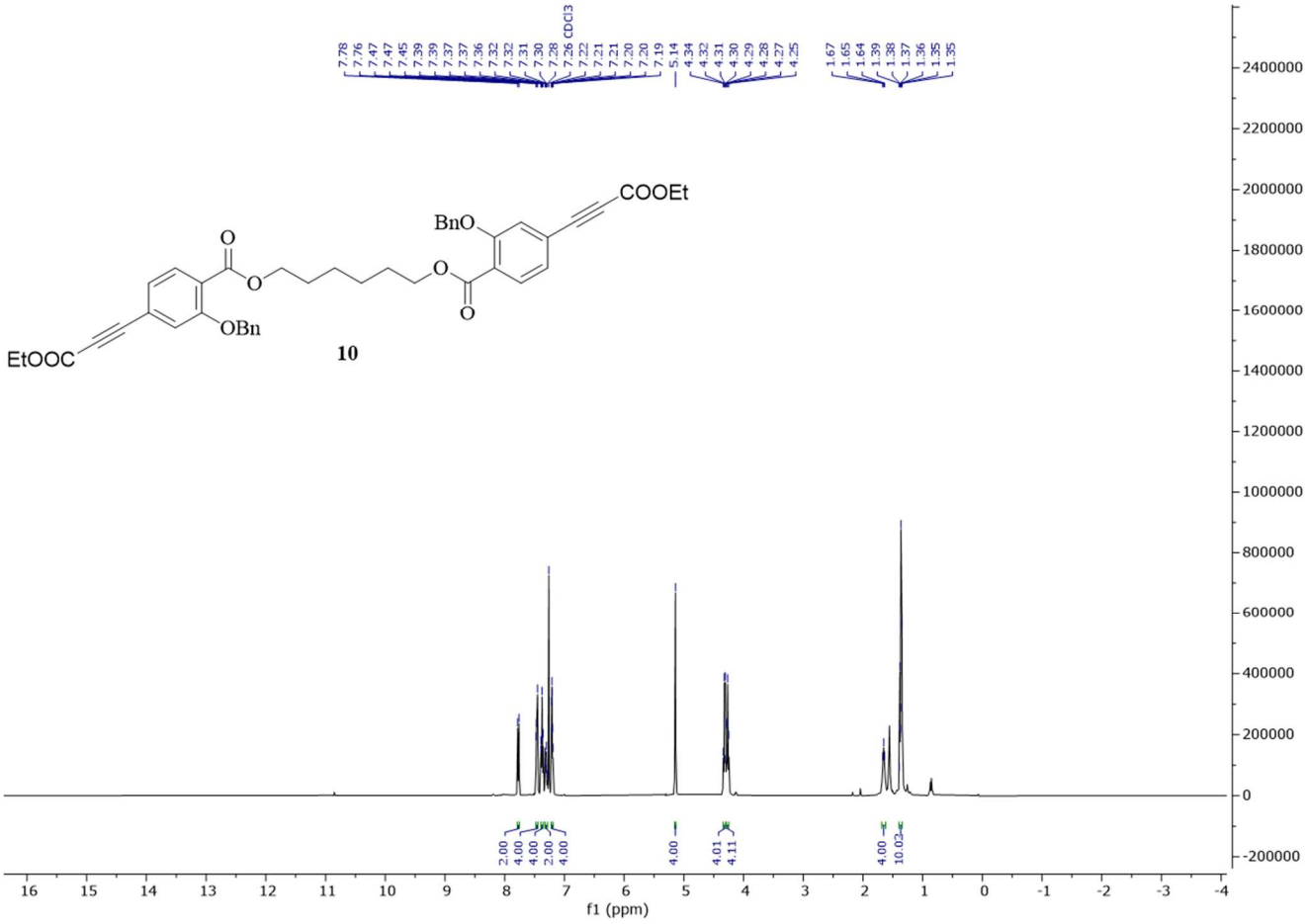
7f

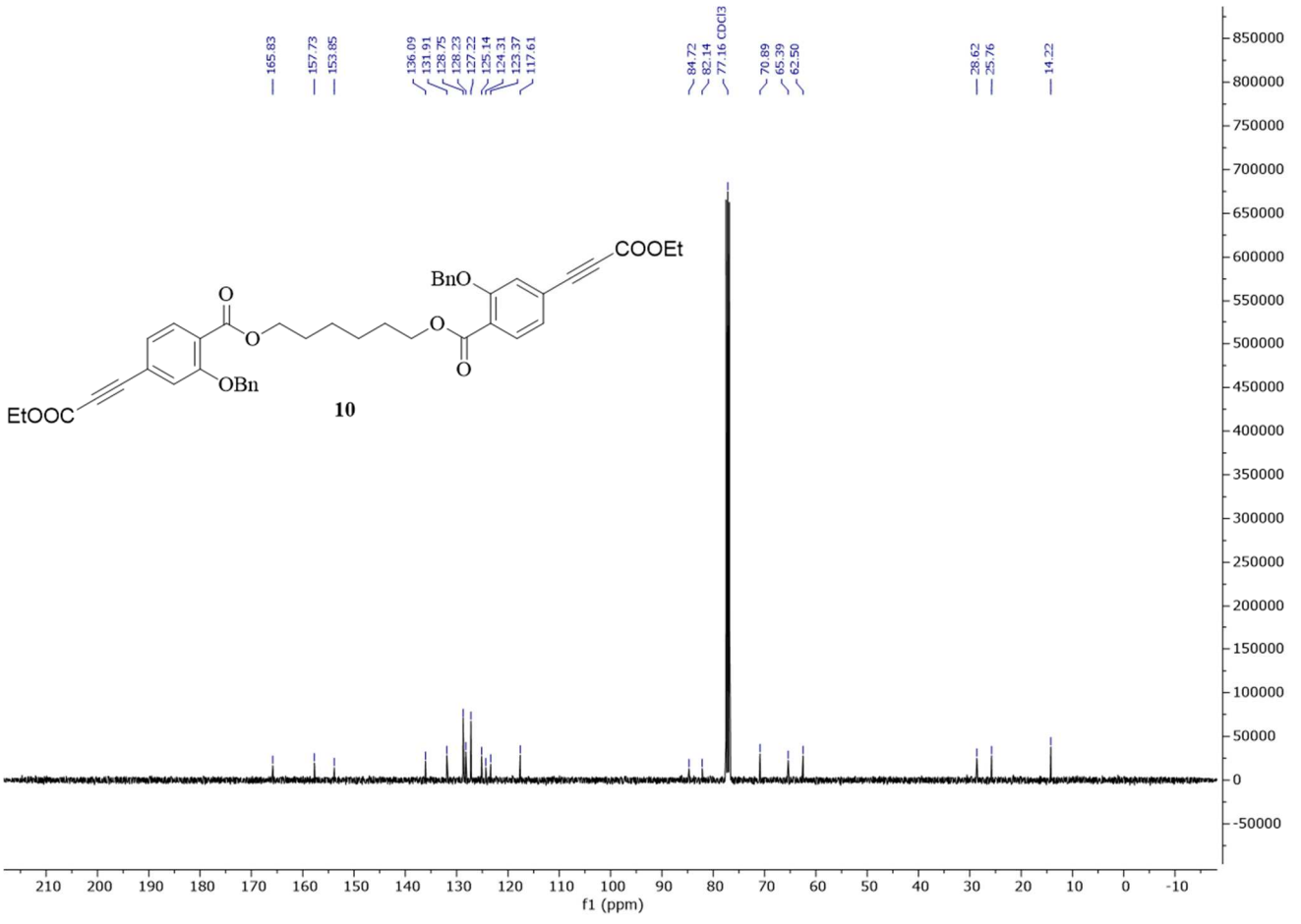

167.97
166.19
165.94
163.11
157.94
153.88
144.01
141.54
137.67
136.24
134.63
133.56
130.47
129.98
129.82
128.91
128.89
128.71
128.25
128.22
127.51
126.95
124.66
124.60
119.13
112.71
110.88
77.16 CDCl3
70.80
70.70
68.18
62.42
62.22
60.58
29.58
14.22
14.02
COOEt
COOEt
BnO
O
O
O
O
OBn
f1 (ppm)

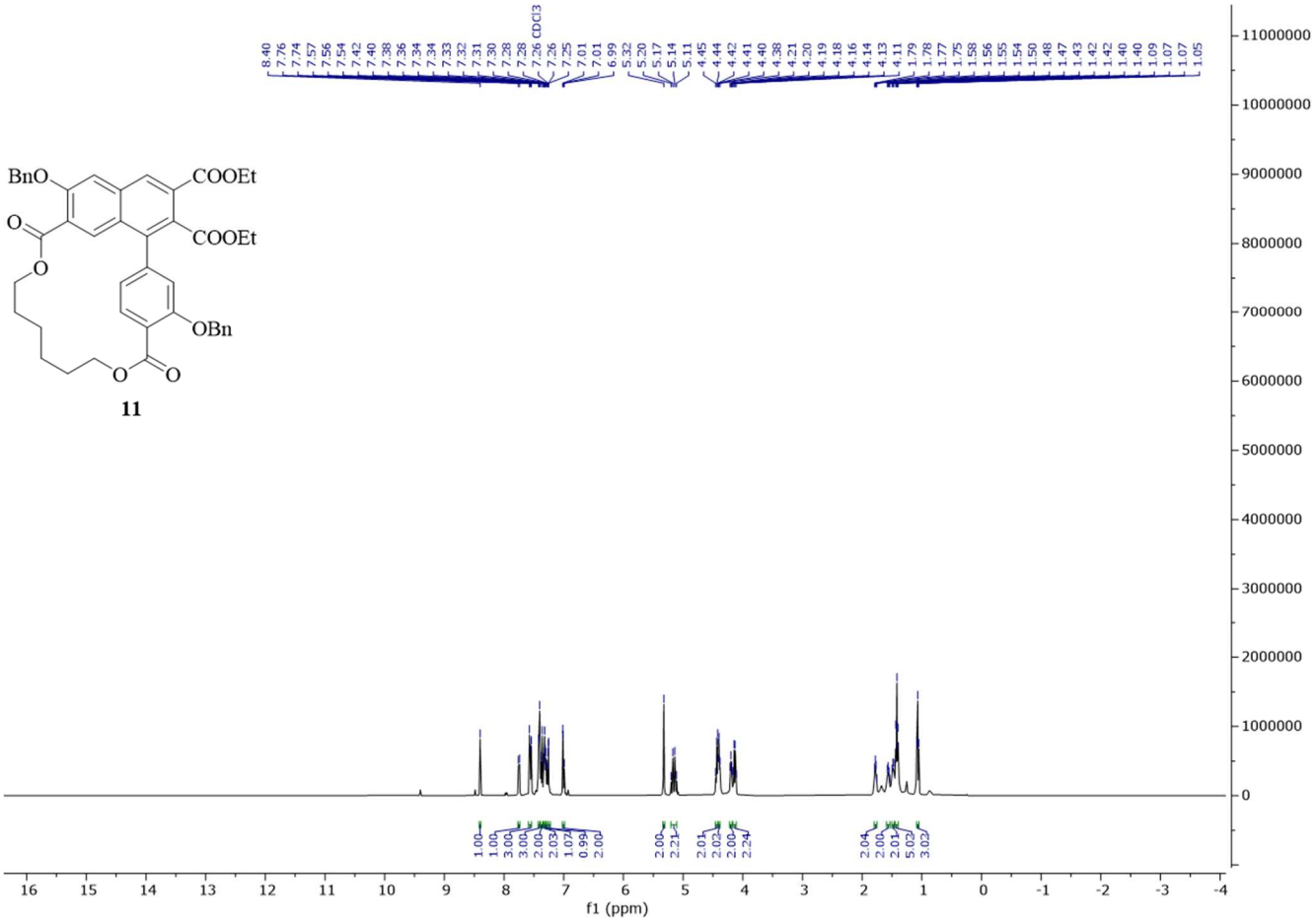
7f

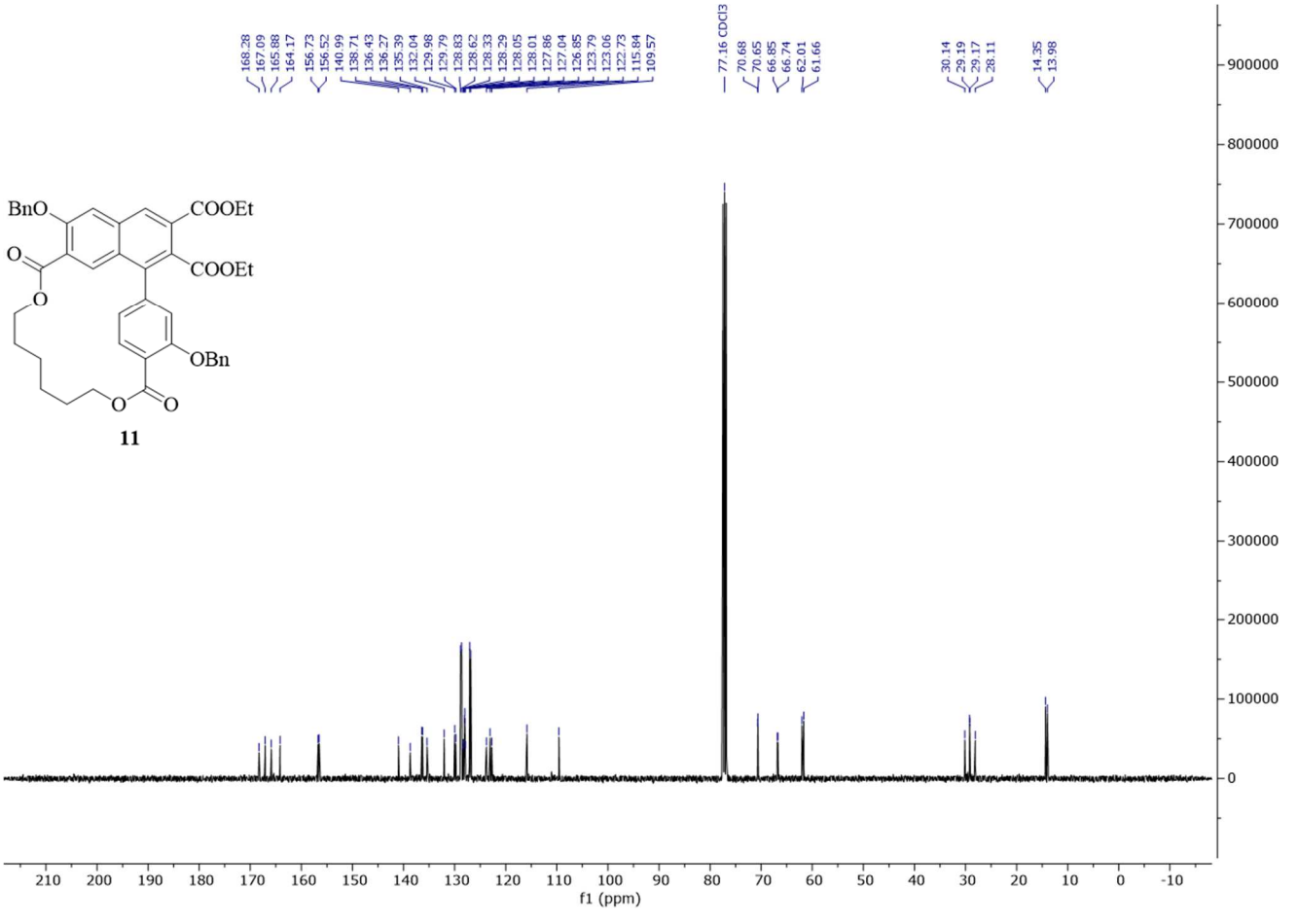

7.51 7.49 7.48 7.48 7.47 7.46 7.46 7.46 7.40 7.39 7.39 7.38 7.38 7.37 7.37 7.36 7.36 7.34 7.33 7.33 7.32 7.32 7.31 7.30 7.29 7.29 7.28 7.26 CDCl3 5.11 4.26 4.24 4.22 1.67 1.65 1.64 1.63 1.62 1.60 1.35 1.34 1.33 1.33 1.32
BnO
I
O
O
O
O
I
OBn
9
2.00 4.00 7.00 3.00 4.00 4.00 4.00 4.00
f1 (ppm)

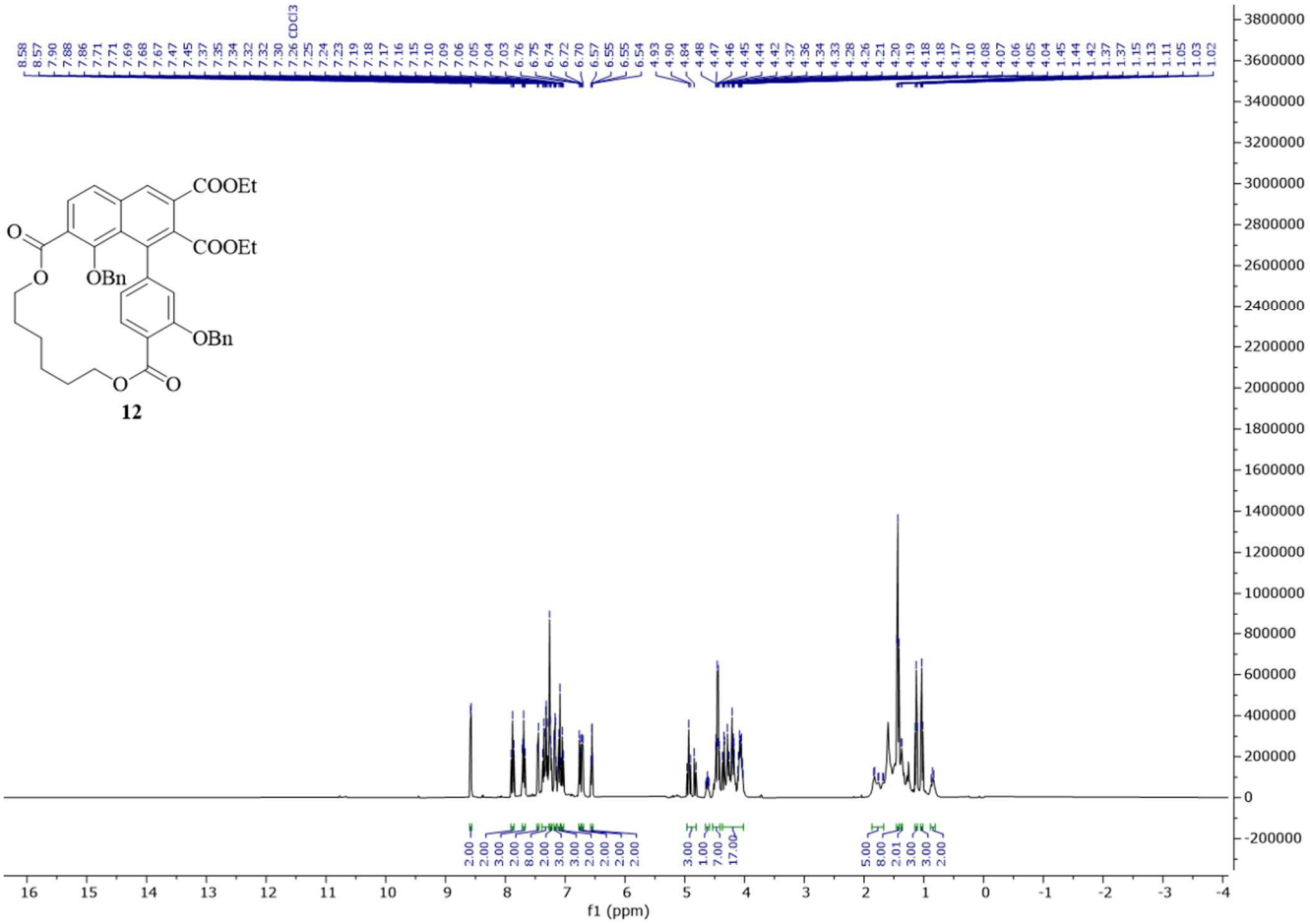

166.07 158.35 136.15 132.99 130.04 128.71 128.20 127.29 123.19 120.69 99.76 77.16 CDCl3 71.04 65.18 28.62 25.77
BnO
I
O
O
O
O
I
OBn
9
f1 (ppm)

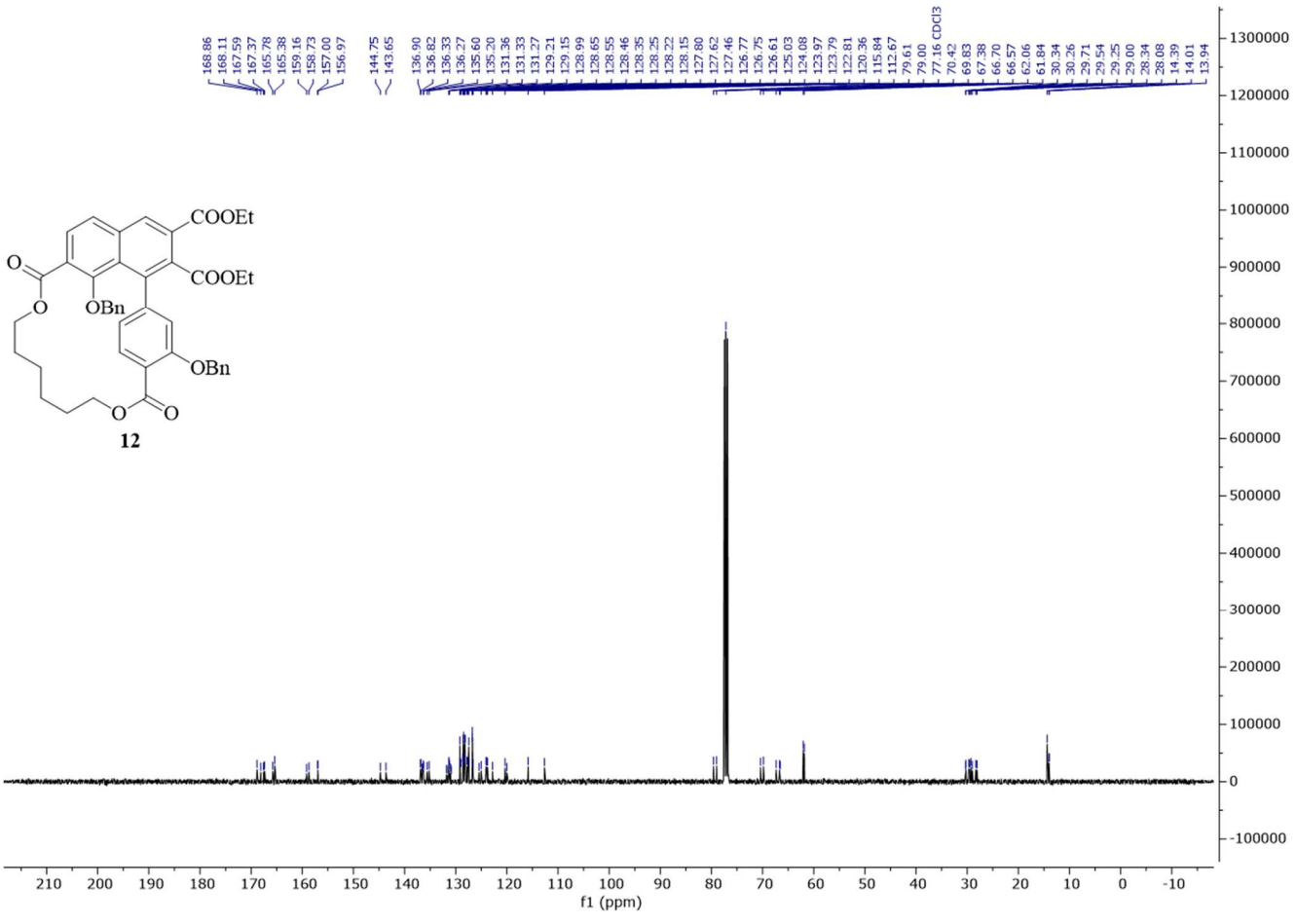

7.78
7.76
7.47
7.47
7.45
7.39
7.39
7.37
7.37
7.36
7.32
7.32
7.31
7.30
7.28 CDCl3
7.22
7.21
7.21
7.20
7.20
7.19
5.14
4.34
4.32
4.31
4.30
4.29
4.28
4.27
4.25
1.67
1.65
1.64
1.39
1.38
1.37
1.36
1.35
1.35
COOEt
BnO
O
O
O
O
OBn
EtOOC
10
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
2.00
4.00
4.00
2.00
4.00
4.00
4.01
4.11
4.00
10.03
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

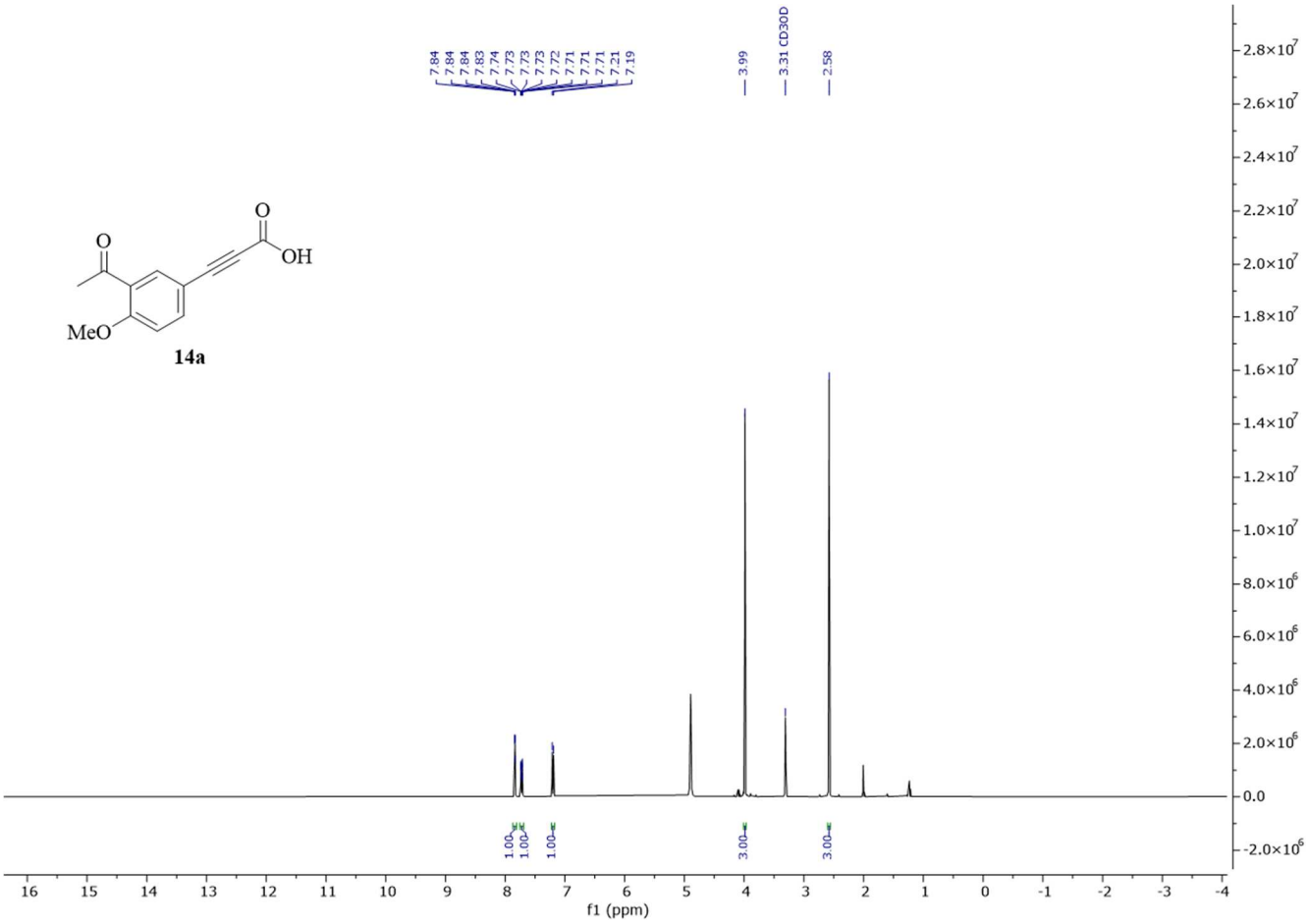

165.83
157.73
153.85
136.09
131.91
128.75
128.23
127.22
125.14
124.31
123.37
117.61
84.72
82.14
77.16 CDCl3
70.89
65.39
62.50
28.62
25.76
14.22
COOEt
BnO
O
O
O
O
OBn
EtOOC
10
850000
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


BnO
COOEt
COOEt
OBn
11
f1 (ppm)

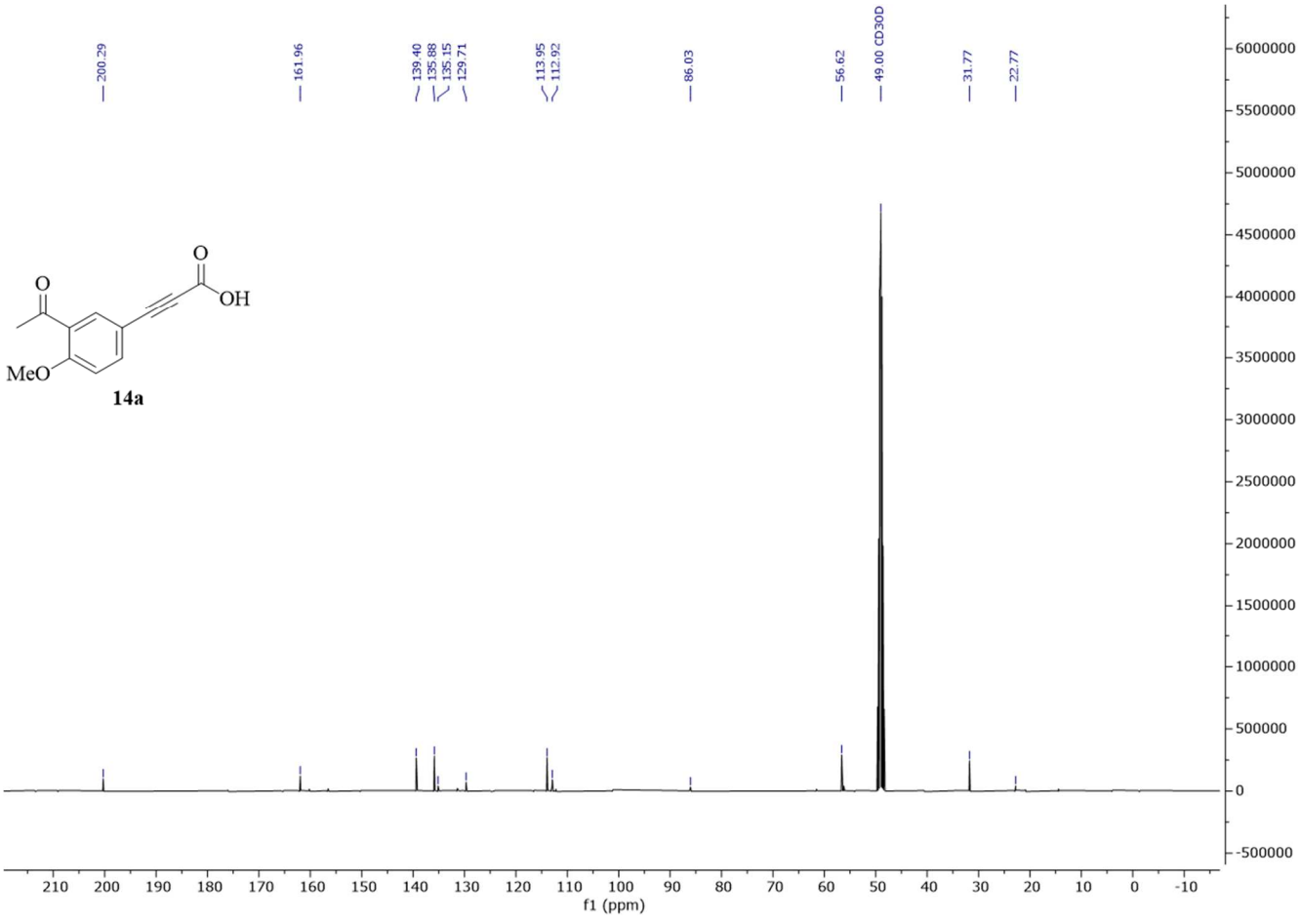

BnO
COOEt
COOEt
OBn
11
f1 (ppm)


COOEt
COOEt
O
O
OBn
OBn
O
O
12
f1 (ppm)

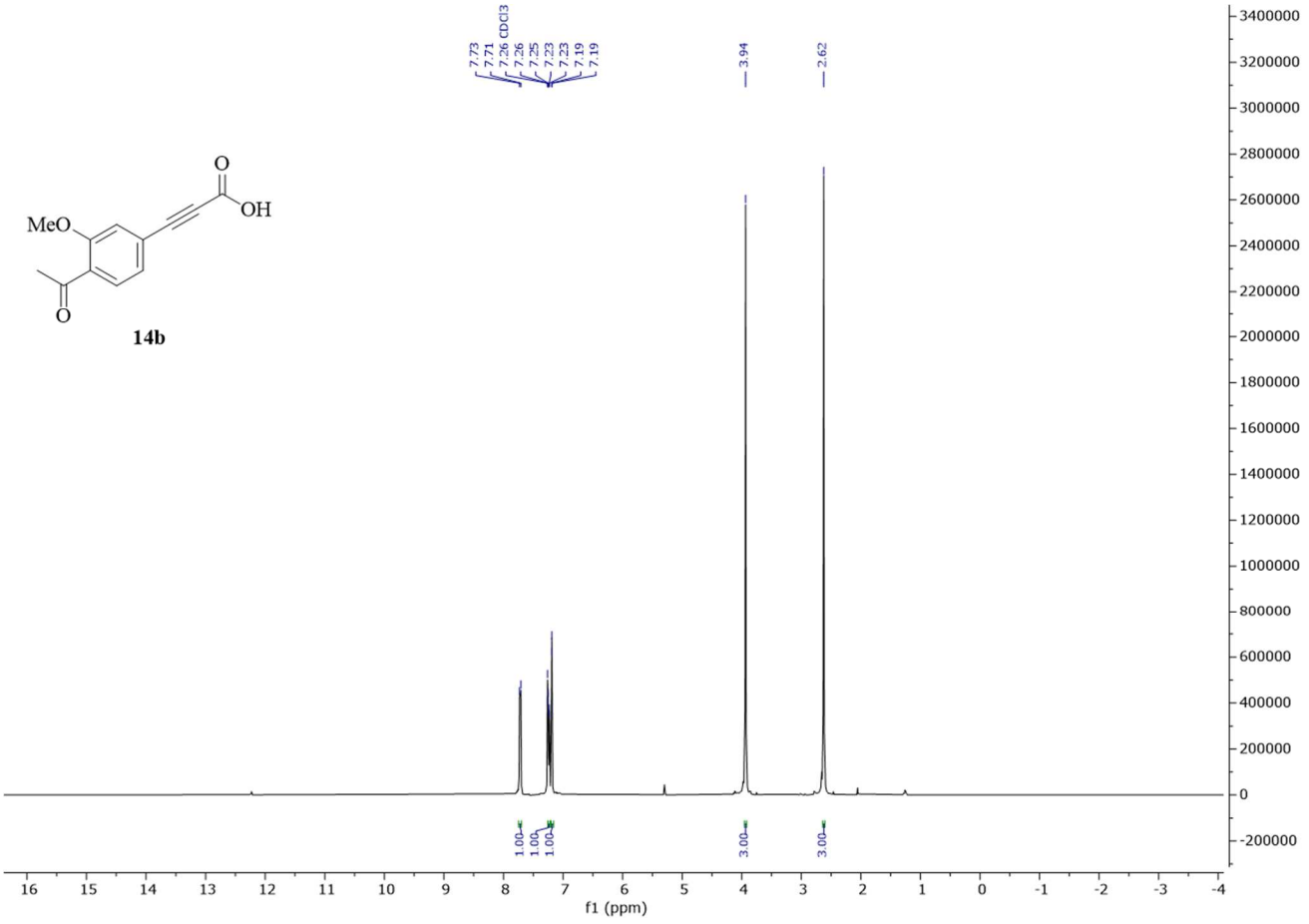

COOEt
COOEt
O
O
OBn
OBn
O
O
12
f1 (ppm)


7.84
7.84
7.84
7.83
7.74
7.73
7.73
7.73
7.72
7.71
7.71
7.71
7.71
7.21
7.19
3.99
3.31 CD3OD
2.58
O
O
OH
MeO
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

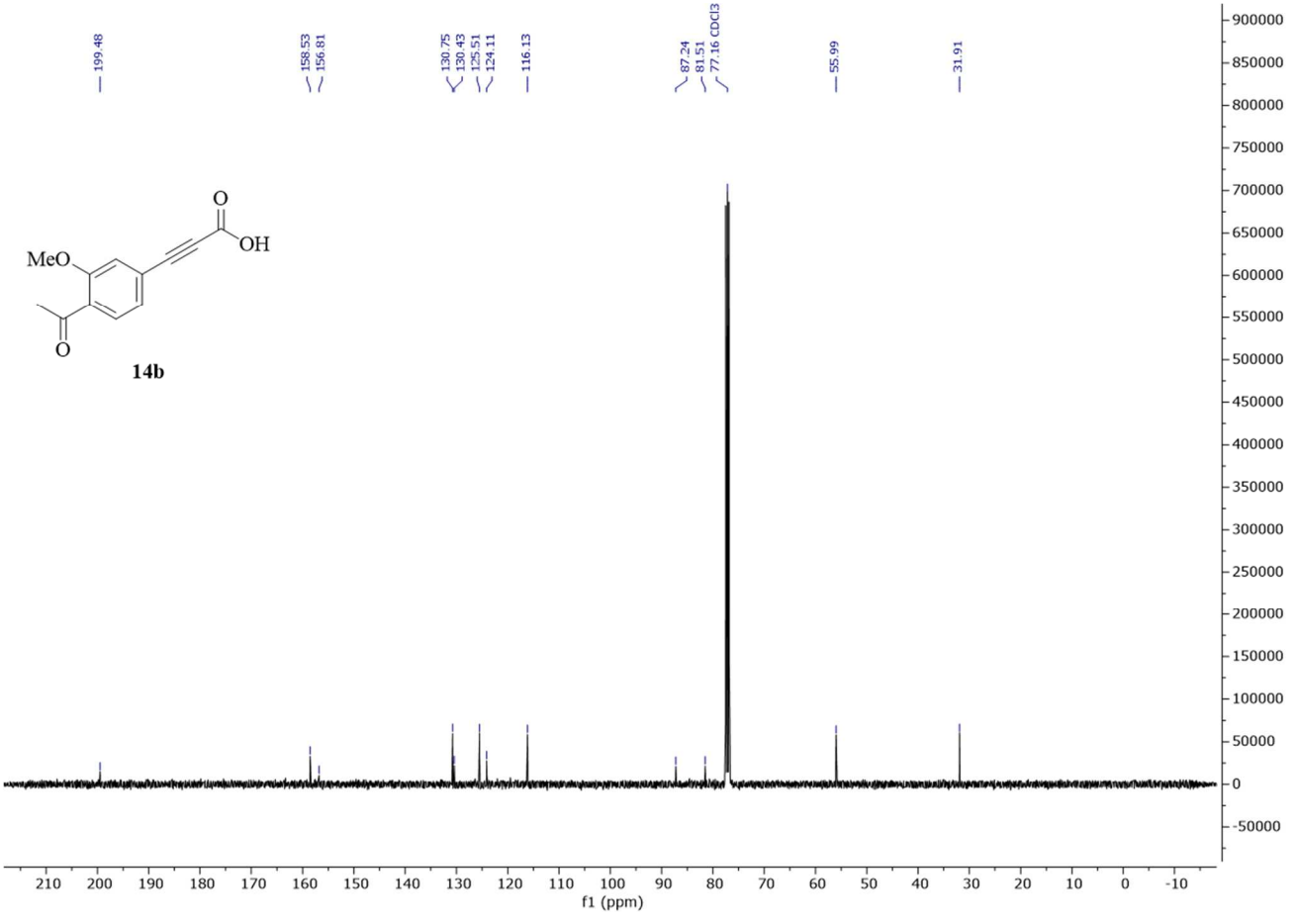
14a


200.29
161.96
139.40
135.88
135.15
129.71
113.95
112.92
86.03
56.62
49.00 CD3OD
31.77
22.77
O
O
OH
MeO
f1 (ppm)

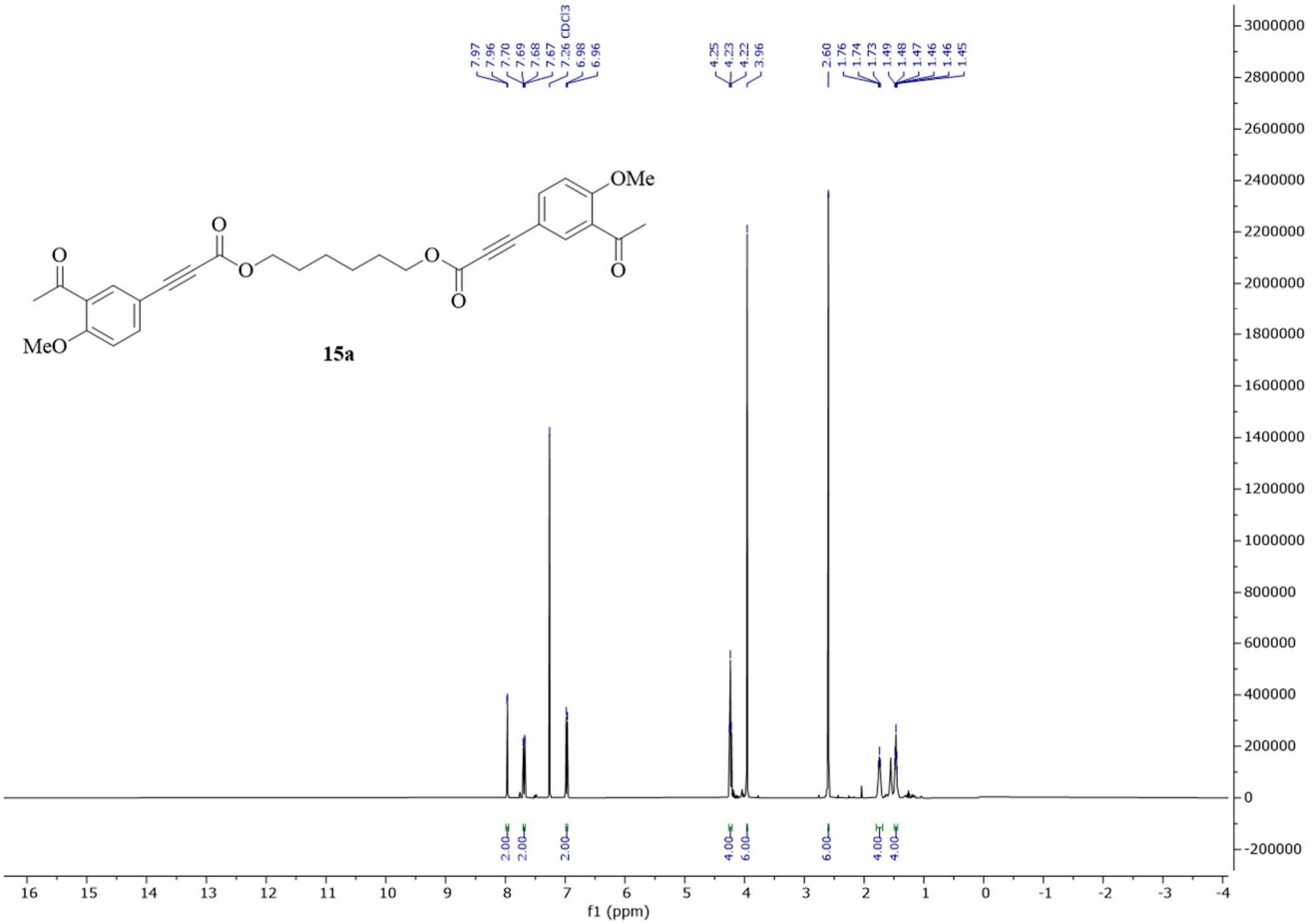
14a

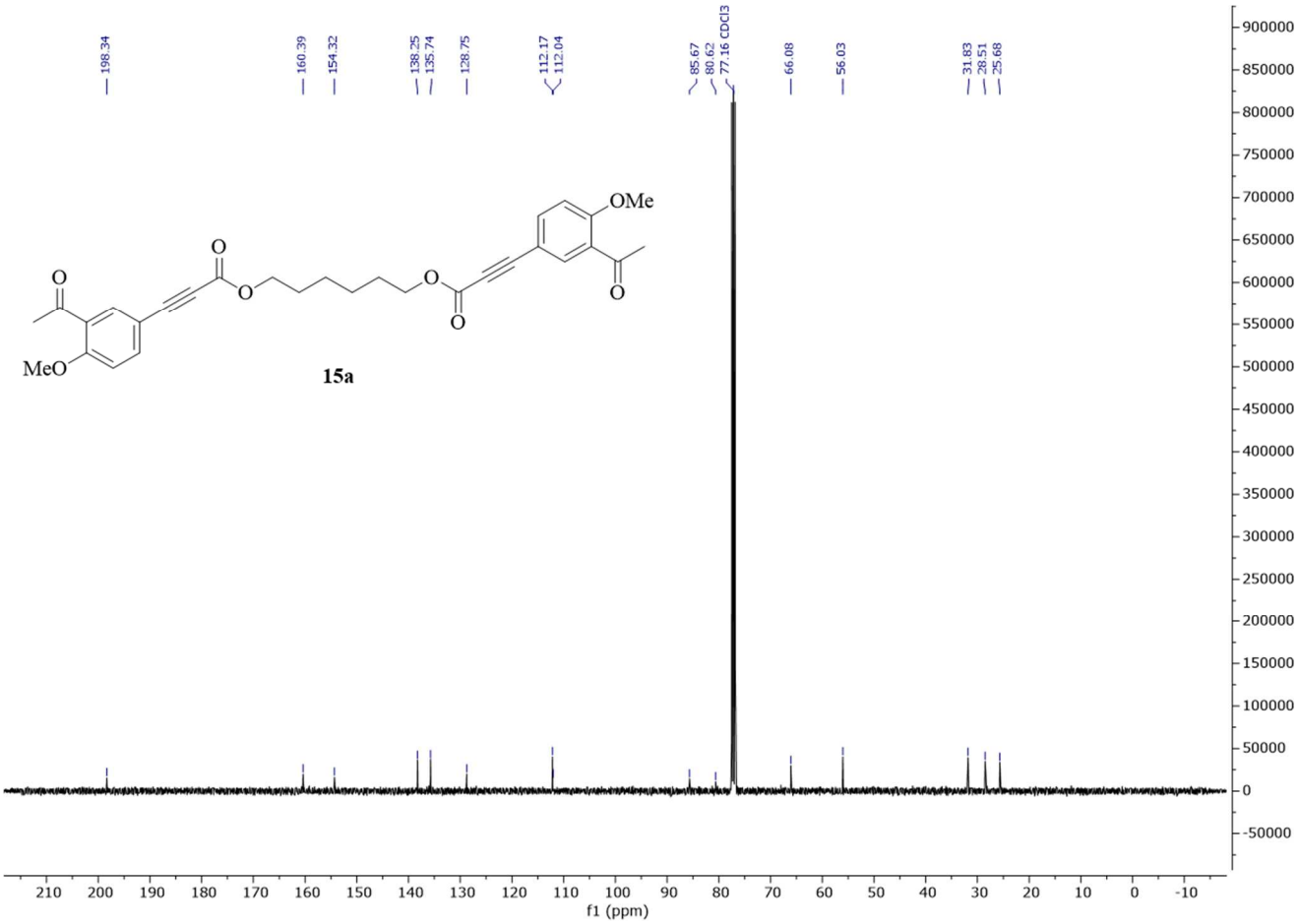

7.73
7.71
7.26 CDCl3
7.26
7.25
7.23
7.23
7.19
7.19
3.94
2.62
MeO
OH
O
O
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

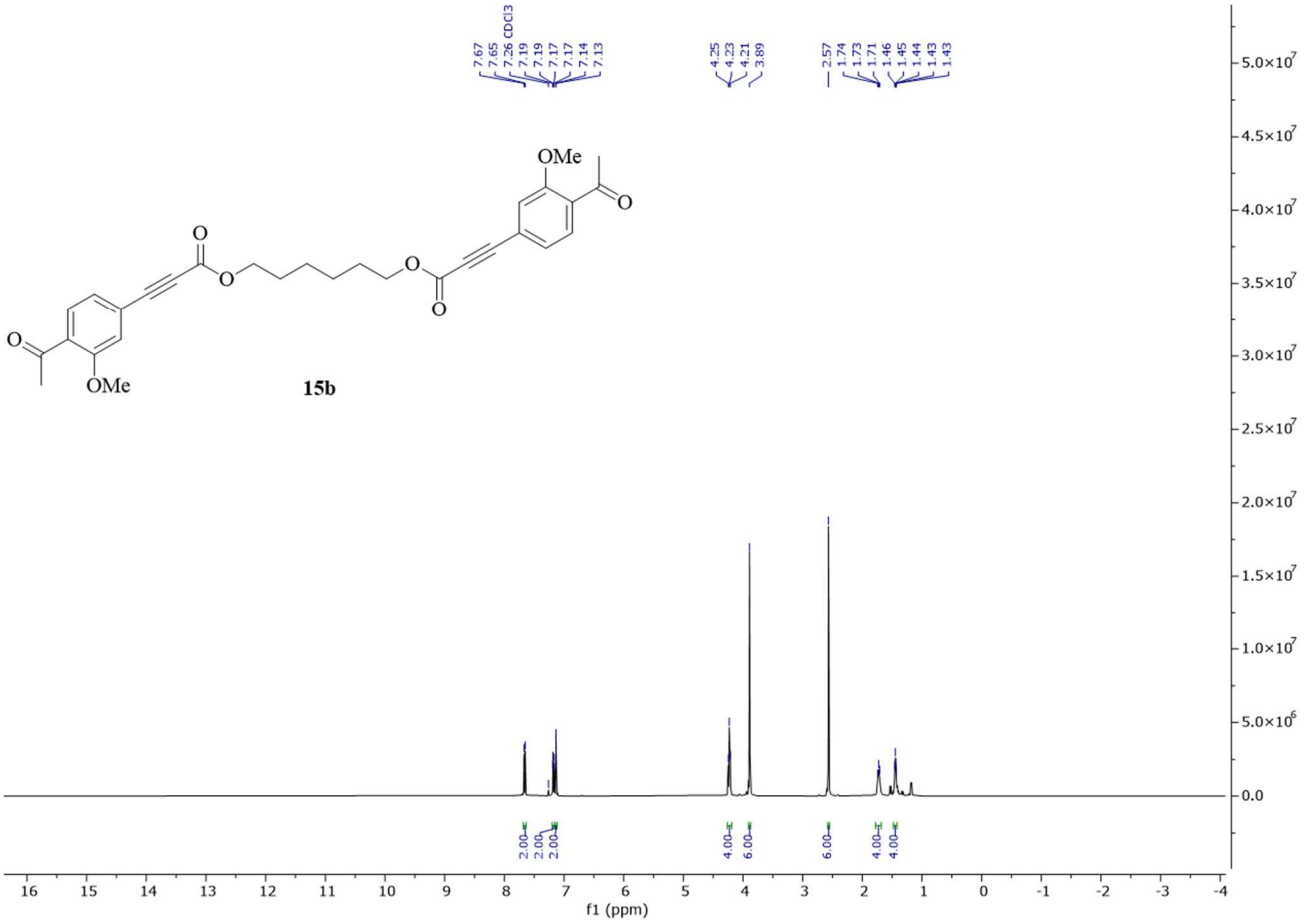
14b

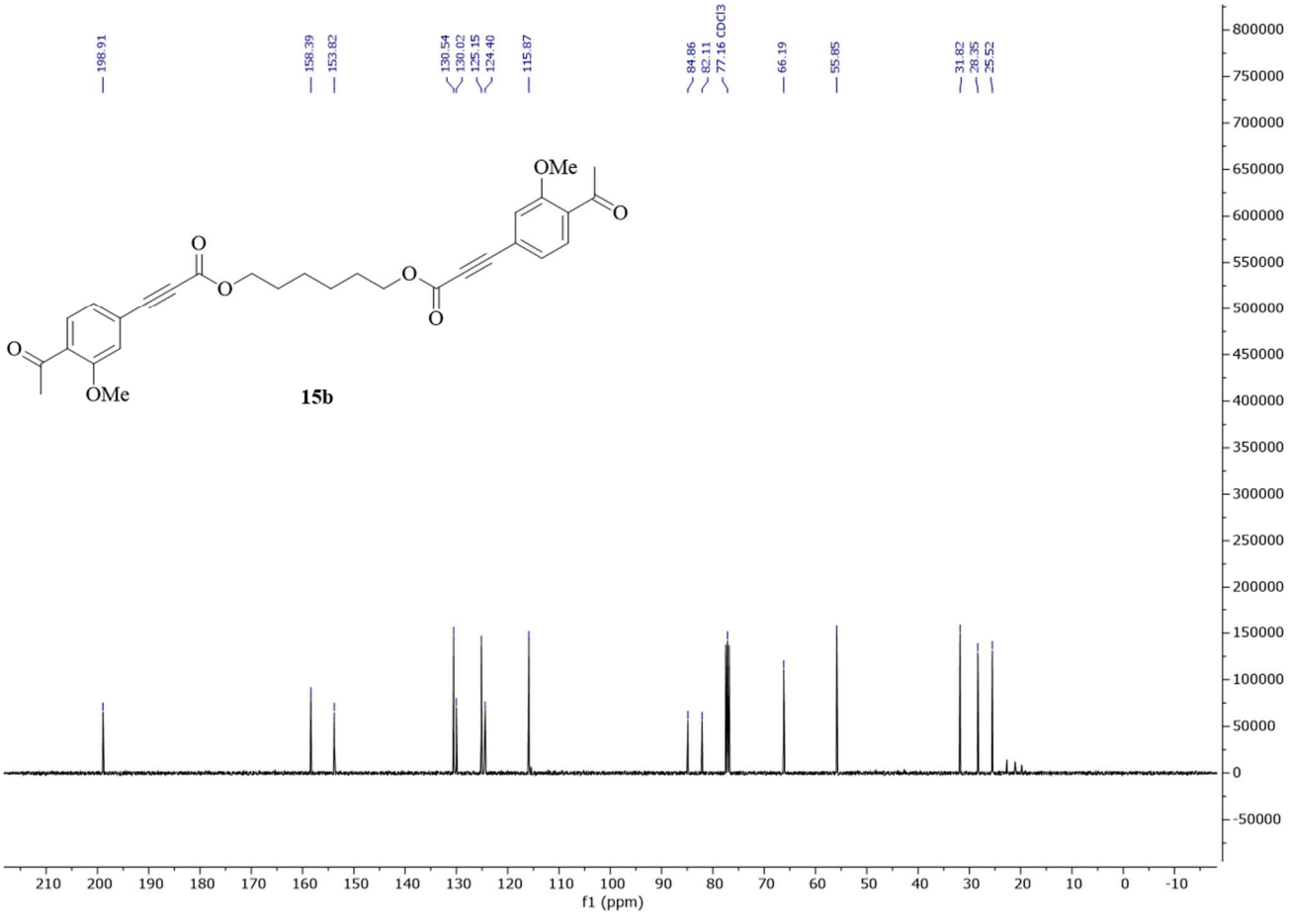

199.48
158.53
156.81
130.75
130.43
125.51
124.11
116.13
87.24
81.51
77.16 CDCl3
55.99
31.91
MeO
OH
O
O
f1 (ppm)

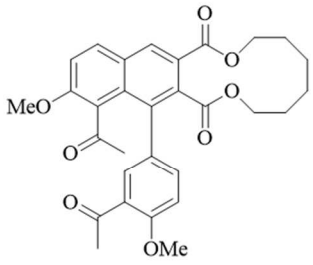
14b


7.97
7.96
7.70
7.69
7.68
7.67
7.26 CDCl3
6.98
6.96
4.25
4.23
4.22
3.96
2.60
1.76
1.74
1.73
1.49
1.48
1.47
1.46
1.46
1.45
OMe
O
O
O
O
O
O
MeO
15a
2.00
2.00
2.00
4.00
6.00
6.00
4.00
4.00
f1 (ppm)


198.34
160.39
154.32
138.25
135.74
128.75
112.17
112.04
85.67
80.62
77.16 CDCl3
66.08
56.03
31.83
28.51
25.68
OMe
O
O
O
O
O
O
MeO
15a
f1 (ppm)

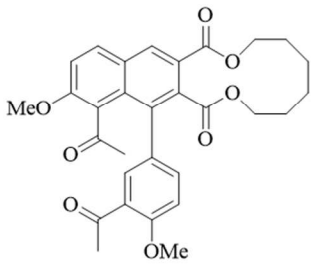

7.67
7.65
7.26 CDCl3
7.19
7.19
7.17
7.17
7.14
7.13
4.25
4.23
4.21
3.89
2.57
1.74
1.73
1.71
1.46
1.45
1.44
1.43
1.43
OMe
O
O
O
O
O
O
O
OMe
15b
2.00
2.00
2.00
4.00
6.00
6.00
4.00
4.00
f1 (ppm)


198.91
158.39
153.82
130.54
130.02
125.15
124.40
115.87
84.86
82.11
77.16 CDCl3
66.19
55.85
31.82
28.35
25.52
OMe
O
O
O
O
O
O
O
OMe
15b
f1 (ppm)


MeO
O
O
O
O
O
O
OMe

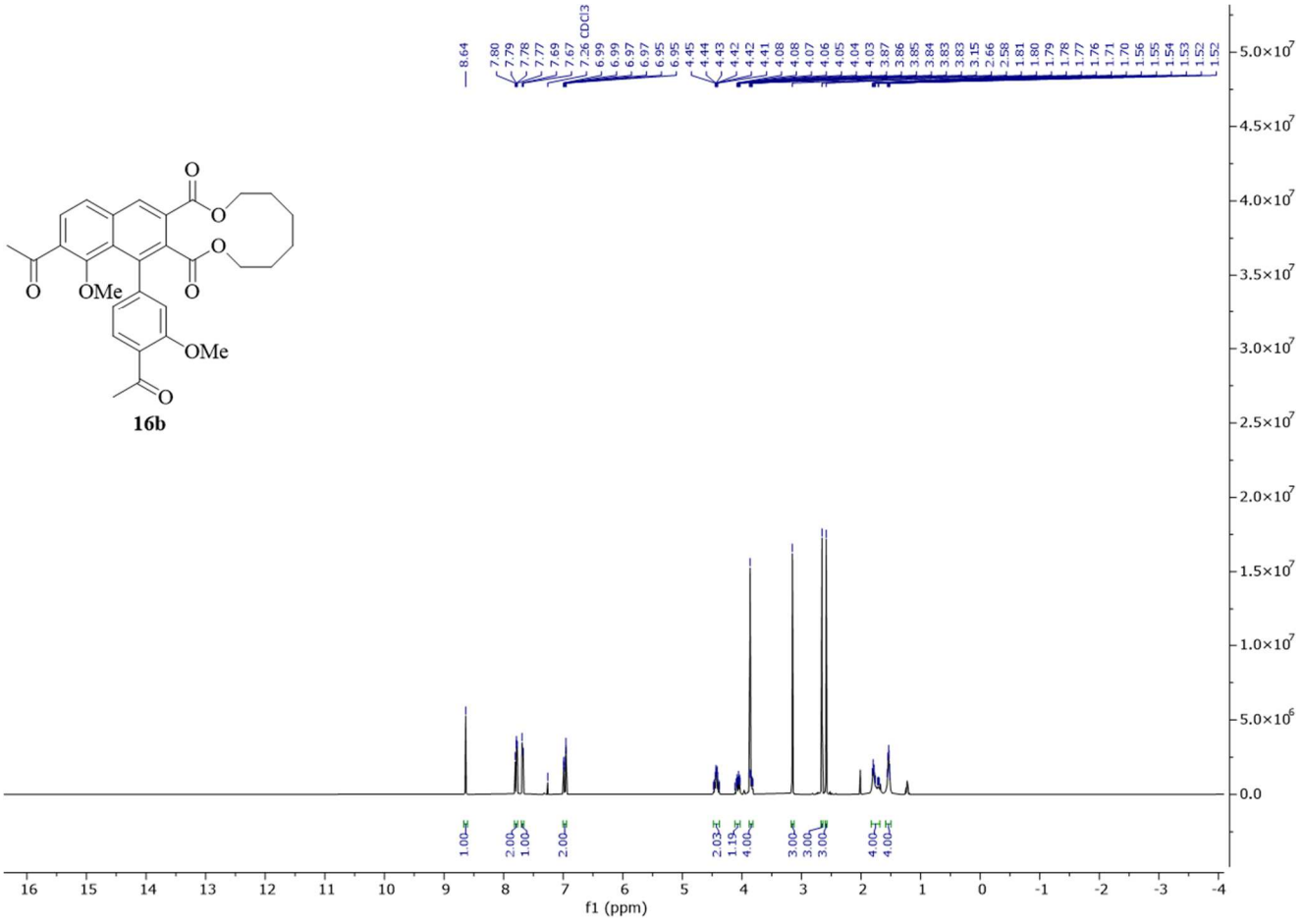
16a

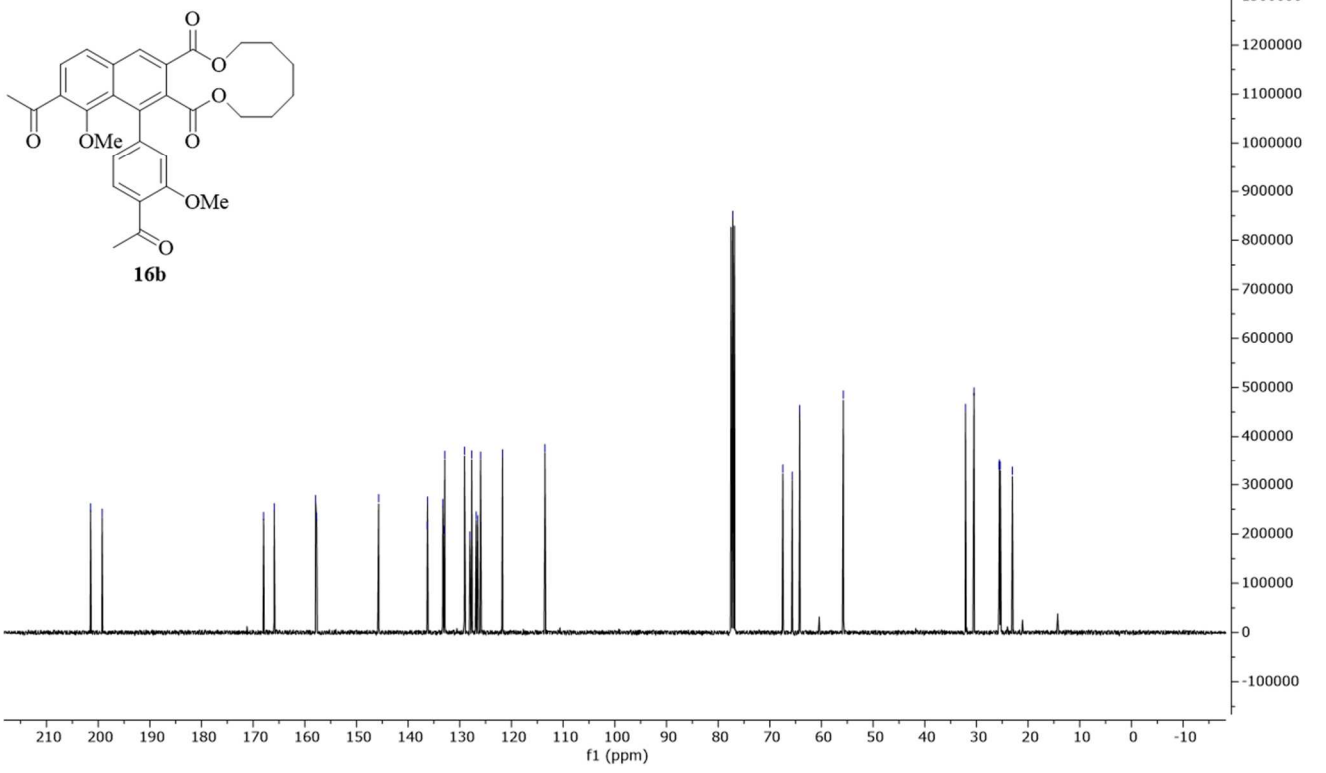
8.64
8.02
8.02
8.00
8.00
7.57
7.57
7.56
7.39
7.38
7.37
7.36
7.34
7.34
7.26 CDCl3
6.98
6.96
4.44
4.42
4.41
4.39
4.38
4.36
4.05
4.04
4.03
4.02
4.02
4.01
4.00
3.96
3.96
3.87
3.87
3.84
3.83
3.82
3.81
3.81
3.79
2.60
2.59
1.92
1.92
1.80
1.79
1.77
1.76
1.76
1.54
1.53
1.52
1.00
1.00
1.00
2.00
1.00
2.02
1.01
3.00
3.00
1.14
3.00
3.00
4.00
4.00
f1 (ppm)

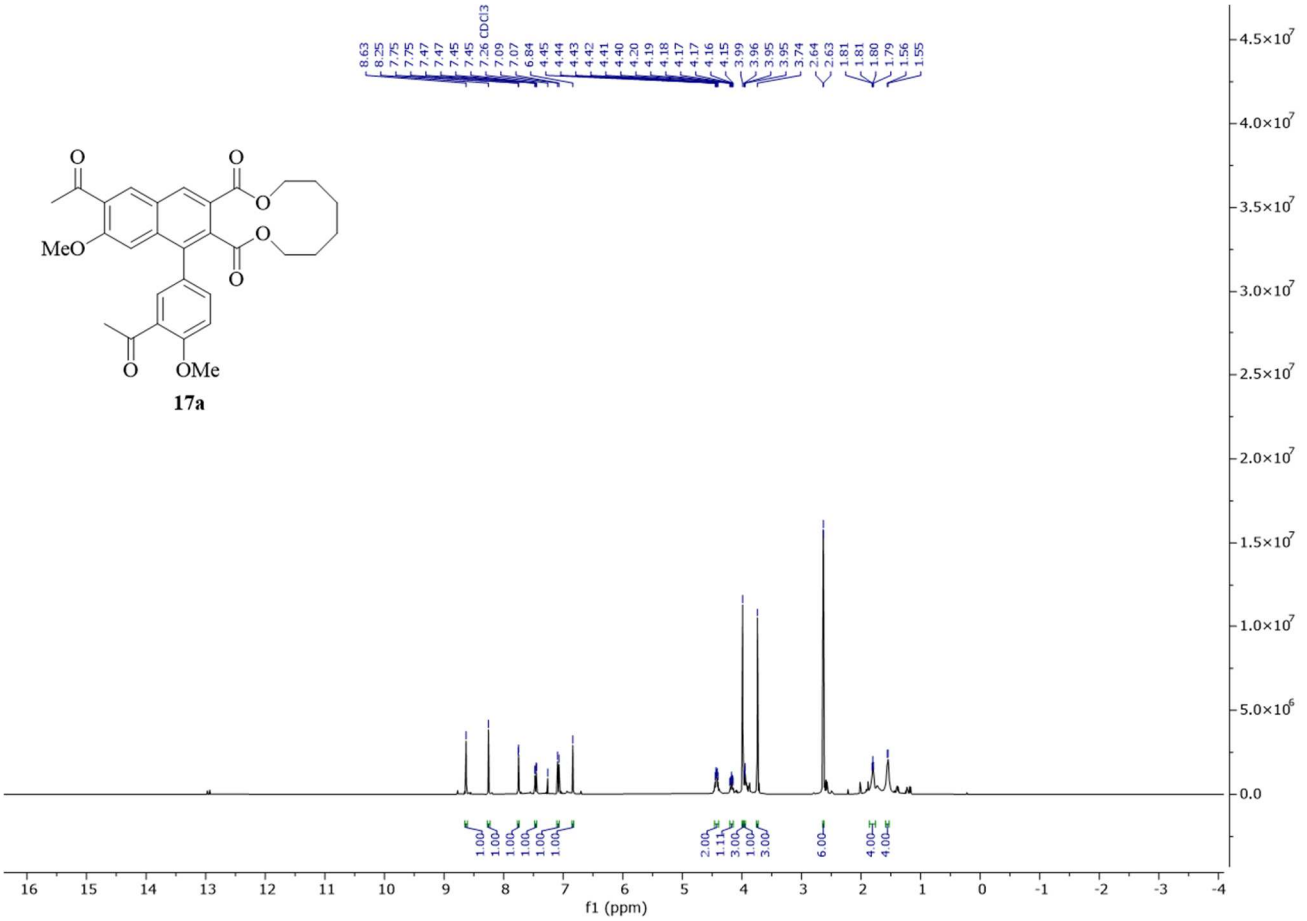

MeO
O
O
O
O
O
O
OMe

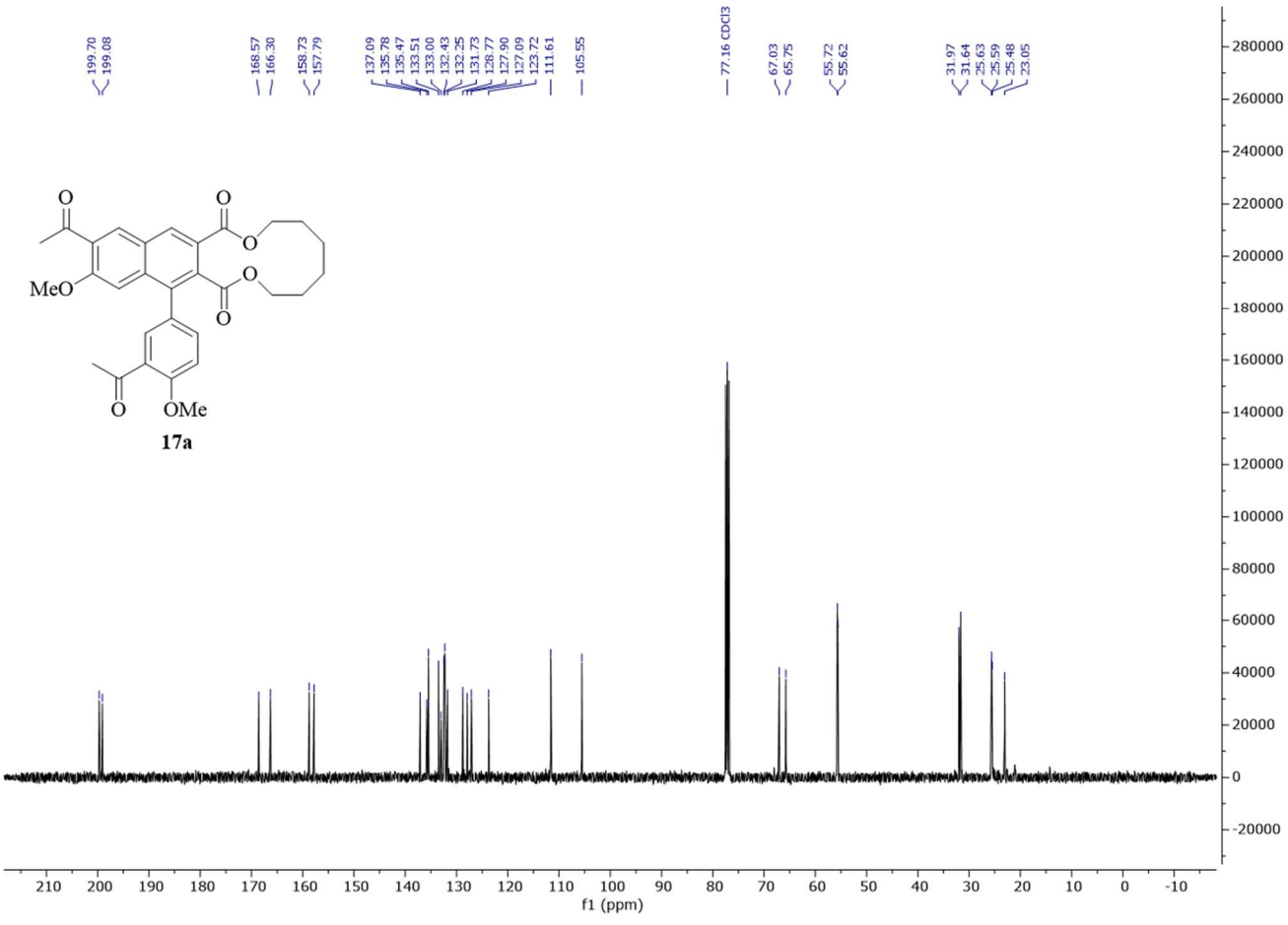
16a

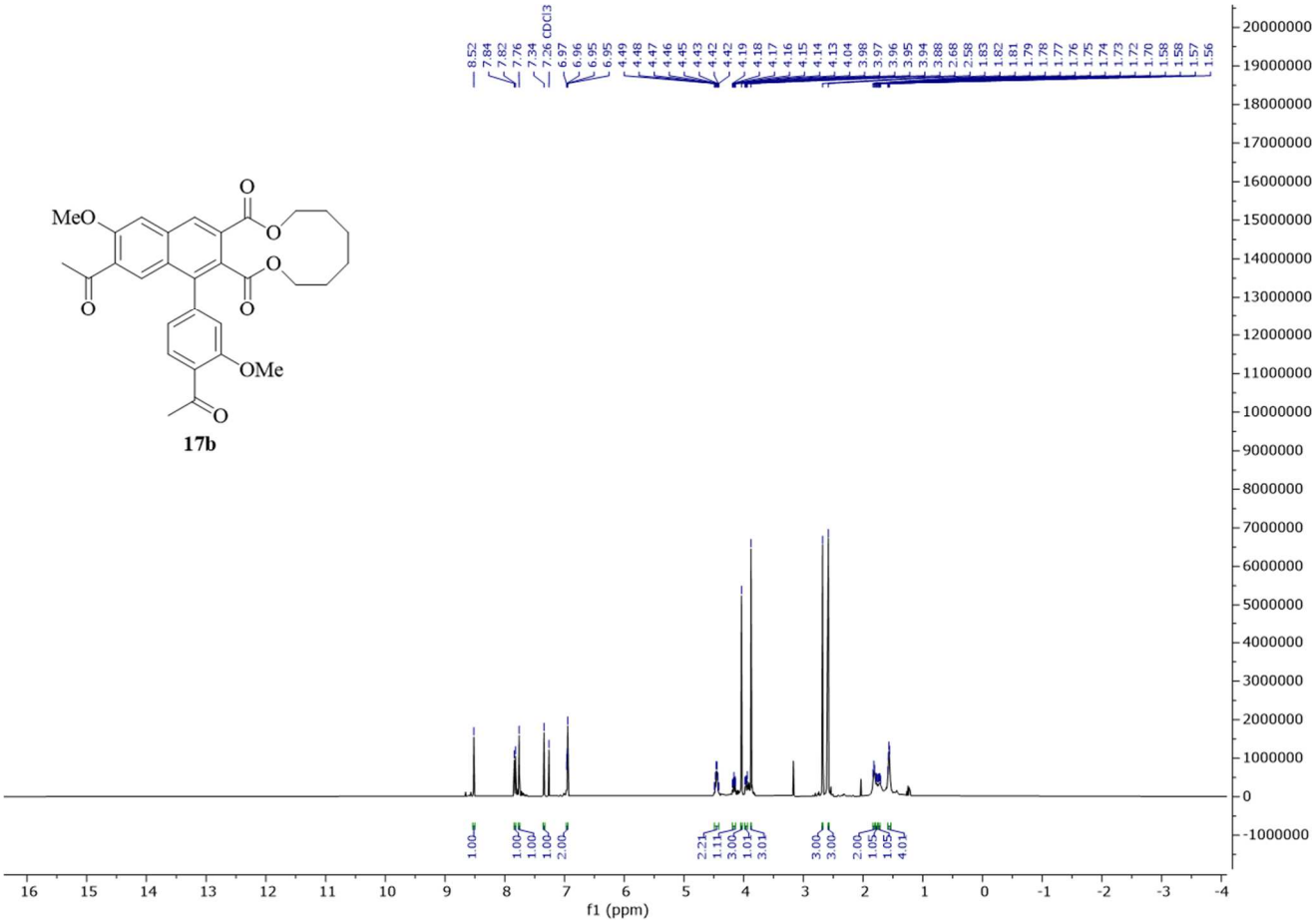
204.39
198.81
168.45
166.10
159.02
156.46
134.90
134.05
133.58
132.79
132.04
129.24
128.40
127.59
122.69
114.36
110.81
77.16 CDCl3
67.22
65.49
56.57
55.72
32.80
31.90
25.56
25.48
25.38
22.87
f1 (ppm)

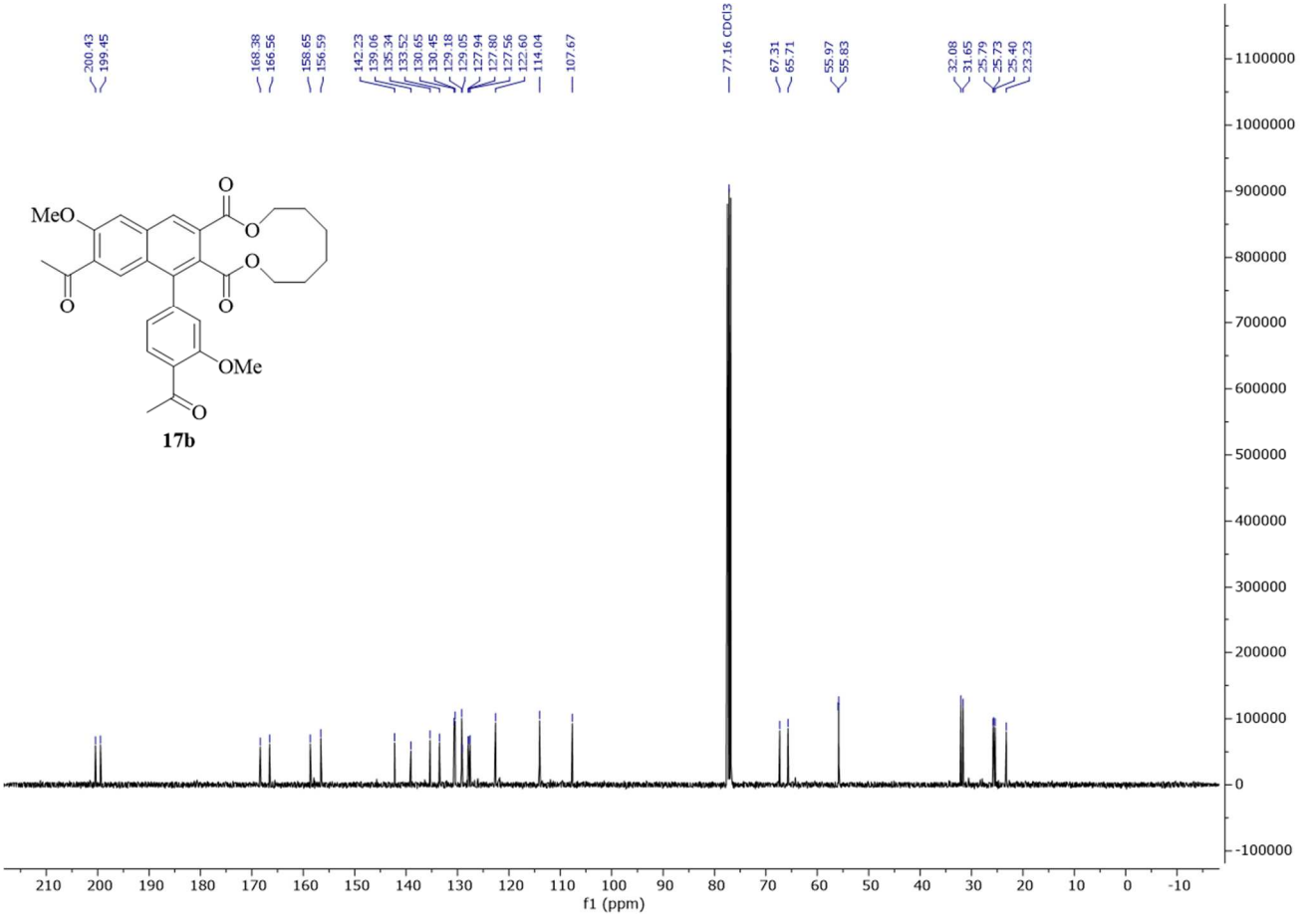

8.64
7.80
7.79
7.78
7.77
7.69
7.67
7.26 CDCl3
6.99
6.99
6.97
6.97
6.95
6.95
4.45
4.44
4.43
4.42
4.42
4.41
4.08
4.08
4.07
4.06
4.05
4.04
4.03
3.87
3.86
3.85
3.84
3.83
3.83
3.15
2.66
2.58
1.81
1.80
1.79
1.78
1.77
1.76
1.71
1.70
1.56
1.55
1.54
1.53
1.52
1.52
5.0×10^7
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
1.00
2.00
1.00
2.00
2.03
1.19
4.00
3.00
3.00
3.00
4.00
4.00
f1 (ppm)

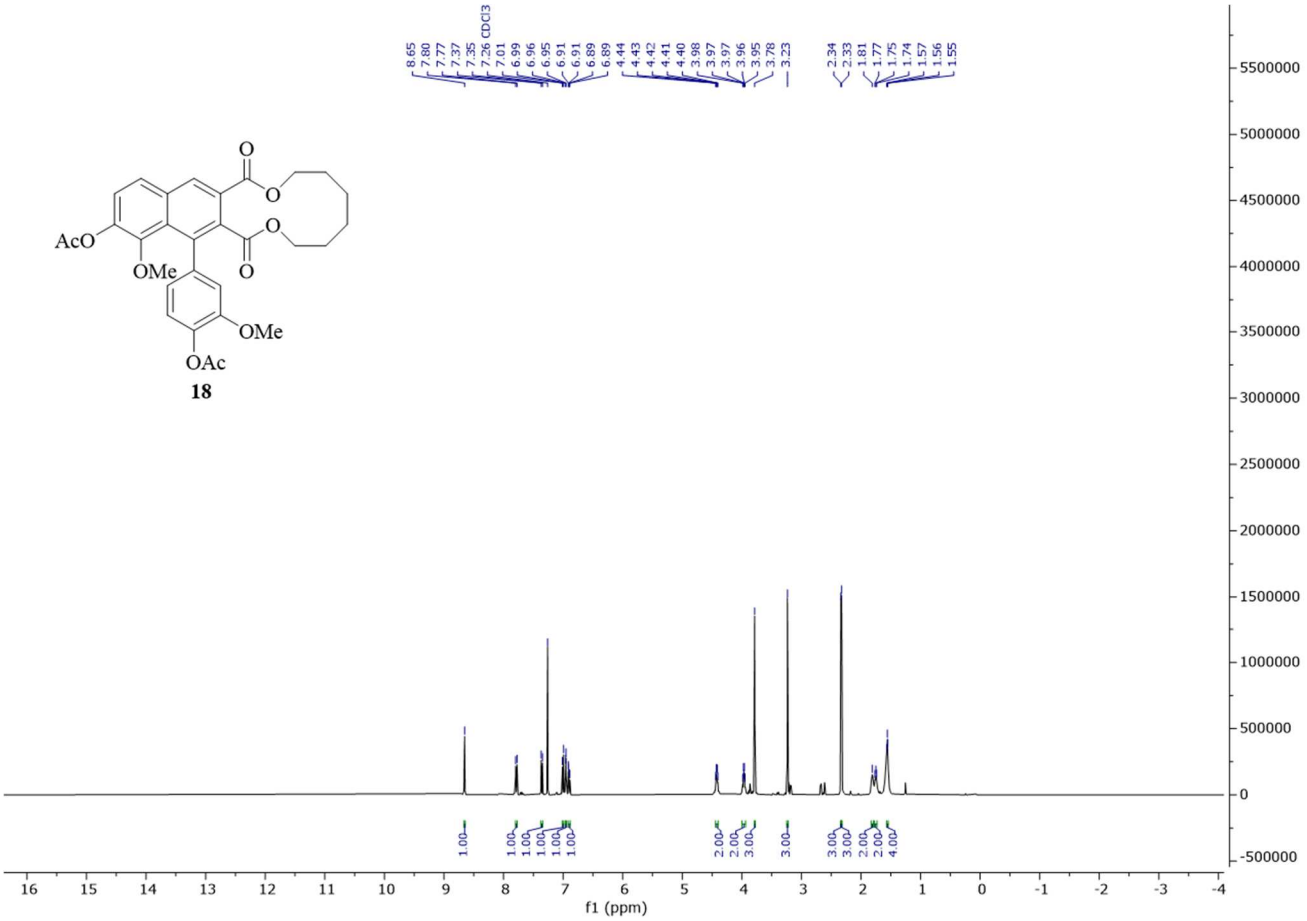

201.46
199.23
167.98
165.93
157.91
157.70
145.71
136.31
136.25
133.30
133.02
132.91
129.10
128.04
127.70
126.83
126.54
125.98
121.73
113.52
77.16 CDCl3
67.47
65.66
64.22
55.77
32.13
30.47
25.65
25.55
25.39
23.03
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
f1 (ppm)

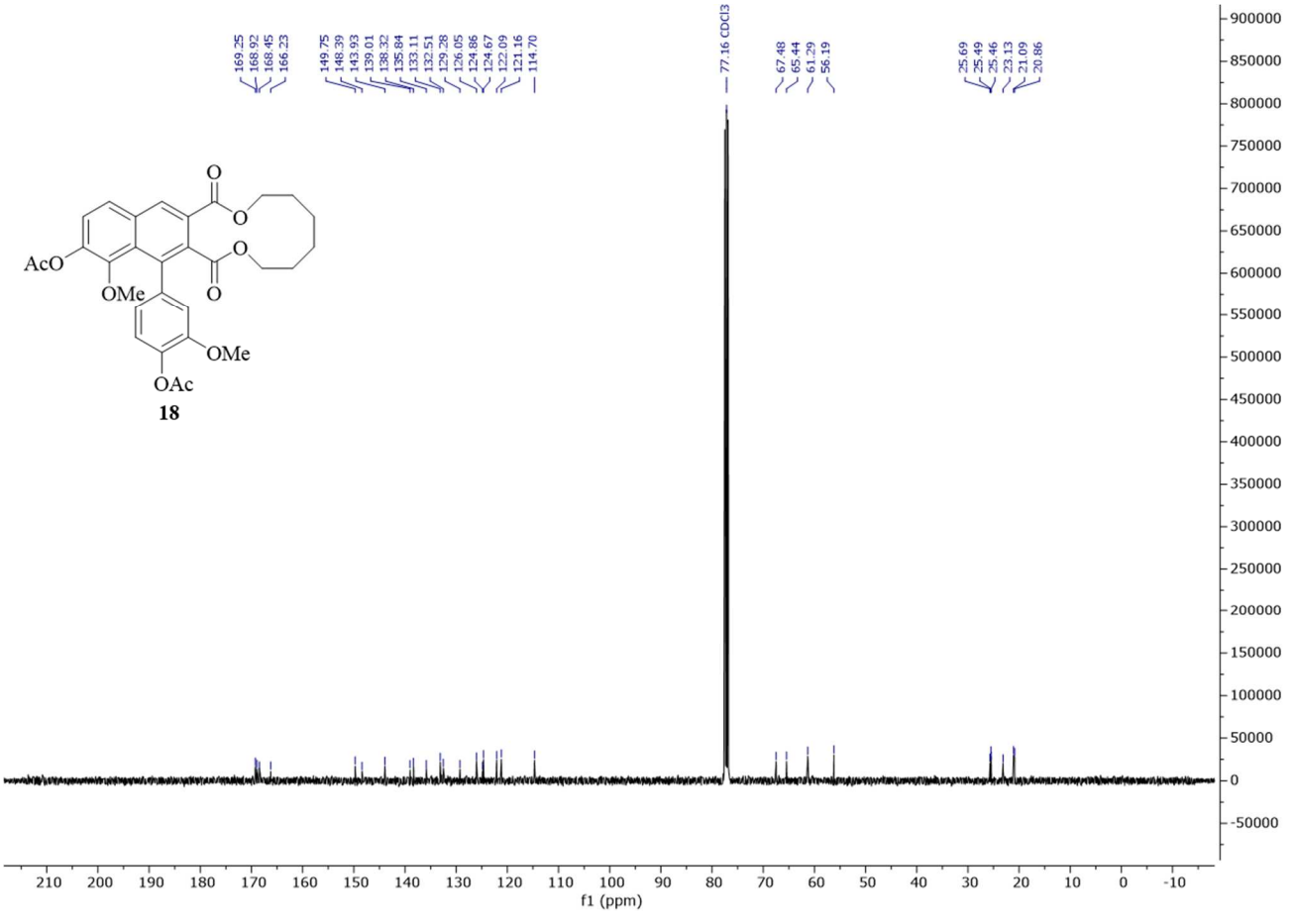

8.63
8.25
7.75
7.75
7.47
7.47
7.45
7.45
7.26 CDCl3
7.09
7.07
6.84
4.45
4.44
4.43
4.42
4.41
4.40
4.20
4.19
4.18
4.17
4.17
4.16
4.15
3.99
3.96
3.95
3.95
3.74
2.64
2.63
1.81
1.81
1.80
1.79
1.56
1.55
MeO
O
OMe
17a
1.00
1.00
1.00
1.00
1.00
1.00
2.00
1.11
3.00
1.00
3.00
6.00
4.00
4.00
f1 (ppm)

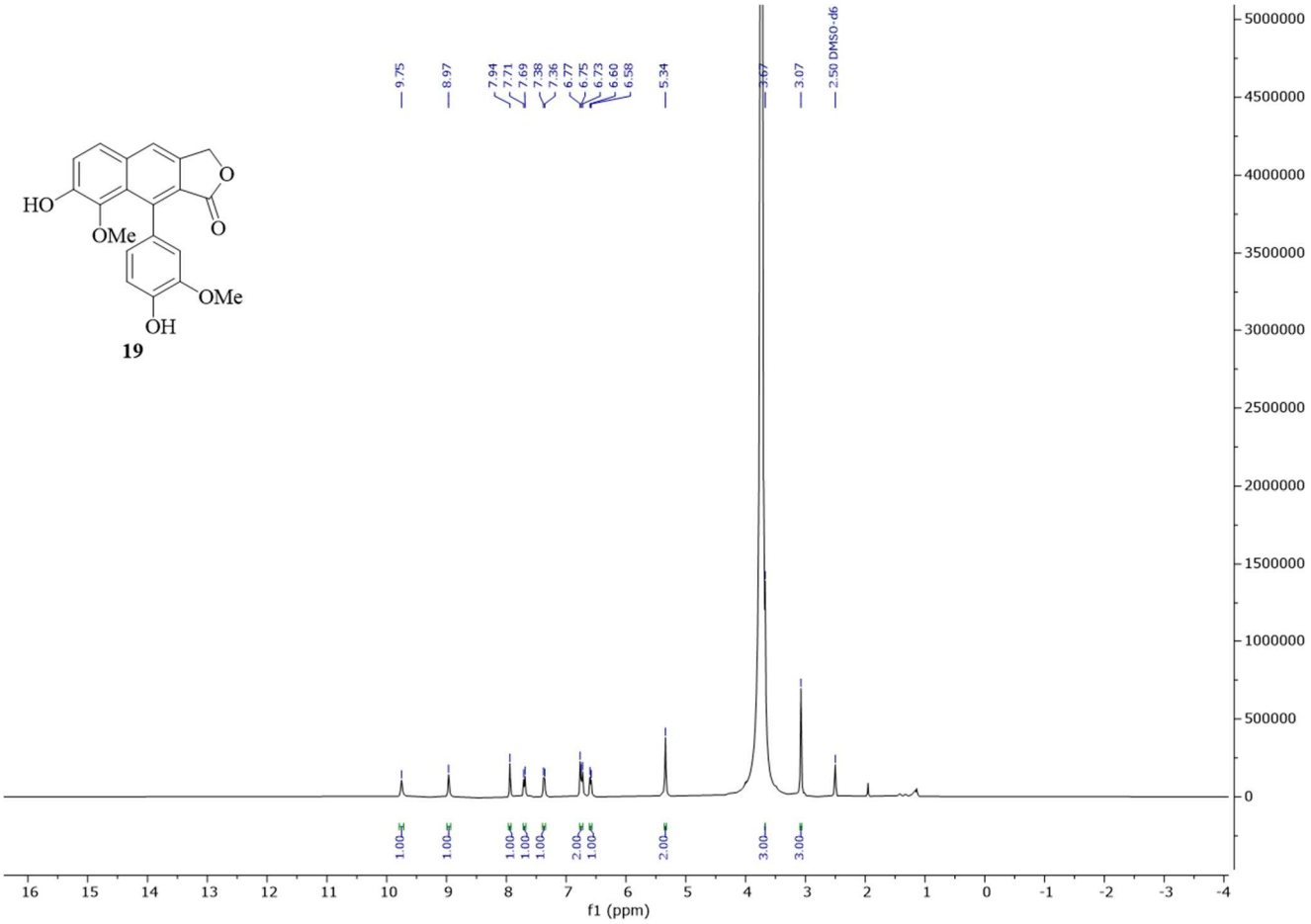

199.70
199.08
168.57
166.30
158.73
157.79
137.09
135.78
135.47
133.51
133.00
132.43
132.25
131.73
128.77
127.90
127.09
123.72
111.61
105.55
77.16 CDCl3
67.03
65.75
55.72
55.62
31.97
31.64
25.63
25.59
25.48
23.05
MeO
O
OMe
17a
f1 (ppm)

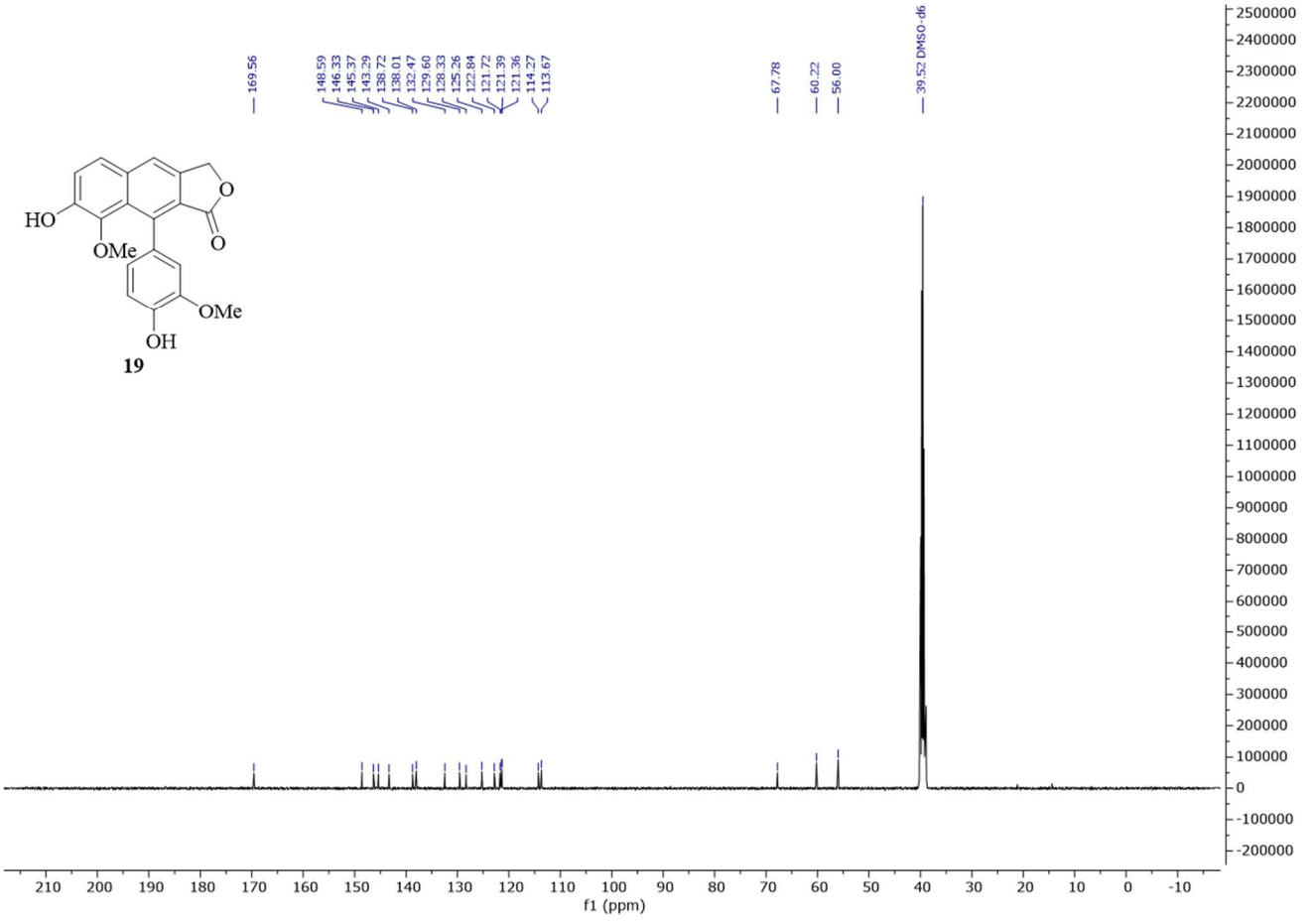

8.52
7.84
7.82
7.76
7.34
7.26 CDCl3
6.97
6.96
6.95
6.95
4.49
4.48
4.47
4.46
4.45
4.43
4.42
4.42
4.19
4.18
4.17
4.16
4.15
4.14
4.13
4.04
3.98
3.97
3.96
3.95
3.94
3.88
2.68
2.58
1.83
1.82
1.81
1.79
1.78
1.77
1.76
1.75
1.74
1.73
1.72
1.70
1.58
1.58
1.57
1.56
MeO
O
O
O
O
O
OMe
O
17b
1.00
1.00
1.00
1.00
2.00
2.21
1.14
3.00
1.01
3.01
3.00
3.00
2.00
1.05
1.05
4.01
f1 (ppm)

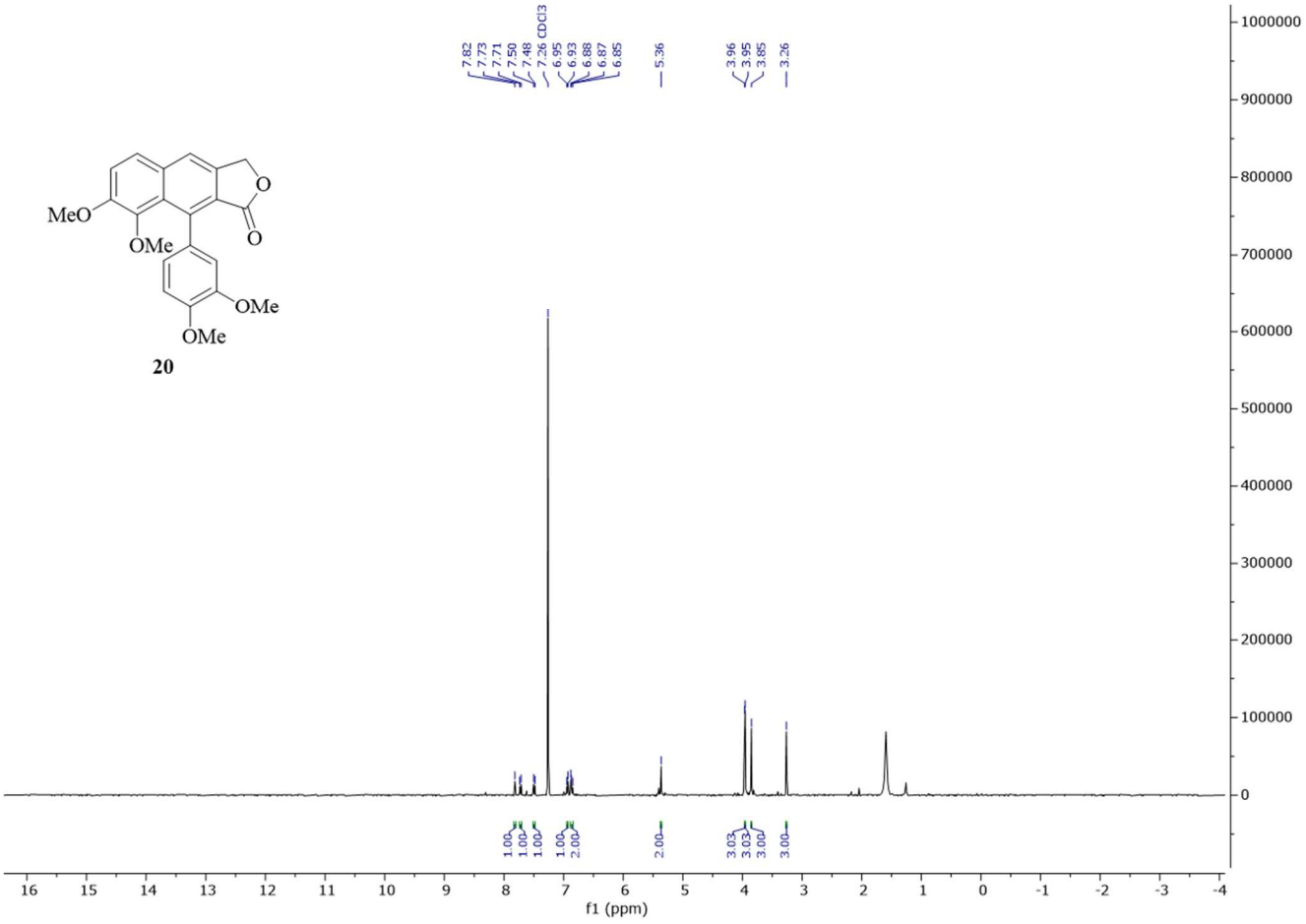

200.43
199.45
168.38
166.56
158.65
156.59
142.23
139.06
135.34
133.52
130.65
130.45
129.18
129.05
127.94
127.80
127.56
122.60
114.04
107.67
77.16 CDCl3
67.31
65.71
55.97
55.83
32.08
31.65
25.79
25.73
25.40
23.23
MeO
O
O
O
O
O
OMe
O
17b
f1 (ppm)


8.65
7.80
7.77
7.37
7.35
7.26 CDCl3
7.01
6.99
6.96
6.95
6.91
6.91
6.89
6.89
4.44
4.43
4.42
4.41
4.40
3.98
3.97
3.97
3.96
3.95
3.78
3.23
2.34
2.33
1.81
1.77
1.75
1.74
1.57
1.56
1.55
AcO
OMe
O
O
O
O
OMe
OAc
18
1.00
1.00
1.00
1.00
1.00
2.00
2.00
3.00
3.00
3.00
3.00
2.00
2.00
4.00
f1 (ppm)

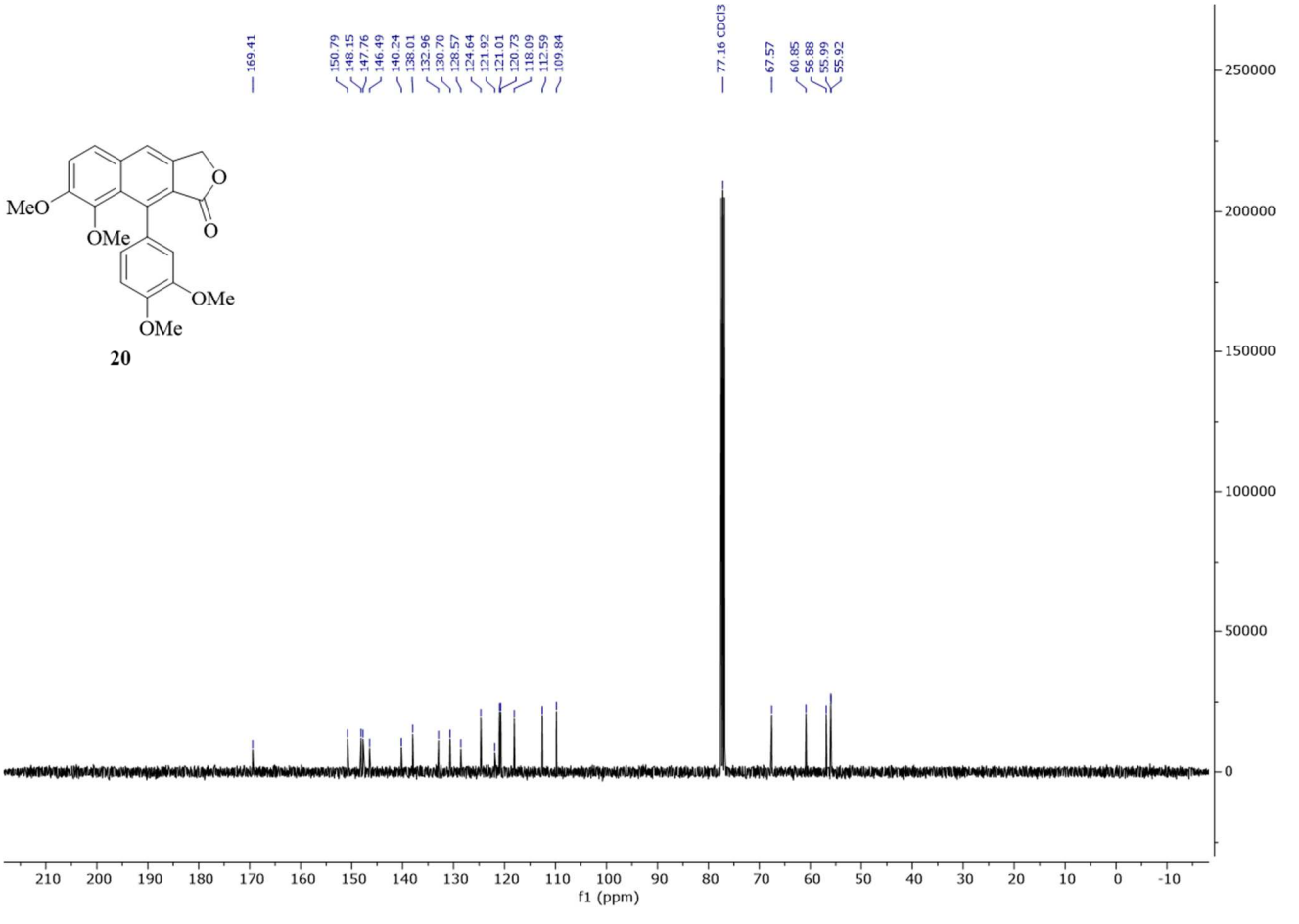

169.25
168.92
168.45
166.23
149.75
148.39
143.93
139.01
138.32
135.84
133.11
132.51
129.28
126.05
124.86
124.67
122.09
121.16
114.70
77.16 CDCl3
67.48
65.44
61.29
56.19
25.69
25.49
25.46
23.13
21.09
20.86
AcO
OMe
O
O
O
O
OMe
OAc
18
f1 (ppm)


9.75
8.97
7.94
7.71
7.69
7.38
7.36
6.77
6.75
6.73
6.60
6.58
5.34
3.67
3.07
2.50 DMSO-d6
HO
OMe
O
O
OMe
OH
19
f1 (ppm)


169.56
148.59
146.33
145.37
143.29
138.72
138.01
132.47
129.60
128.33
125.26
122.84
121.72
121.39
121.36
114.27
113.67
67.78
60.22
56.00
39.52 DMSO-d6
HO
OMe
O
O
OMe
OH
19
f1 (ppm)


7.82
7.73
7.71
7.50
7.48
7.26 CDCl3
6.95
6.93
6.88
6.87
6.85
5.36
3.96
3.95
3.85
3.26
MeO
OMe
OMe
OMe
O
O
1.00
1.00
1.00
1.00
2.00
2.00
3.03
3.03
3.00
3.00
f1 (ppm)

20


169.41
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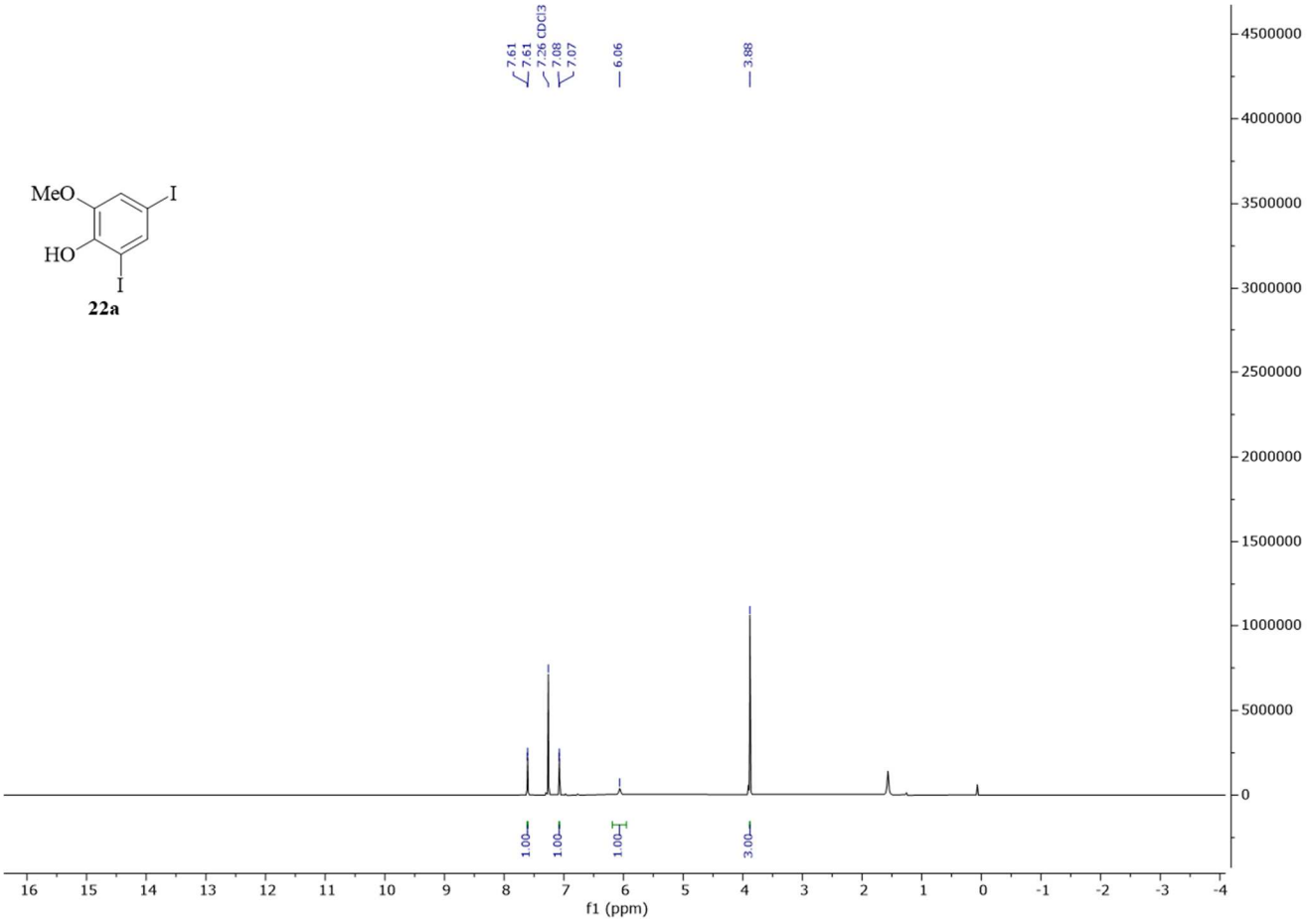
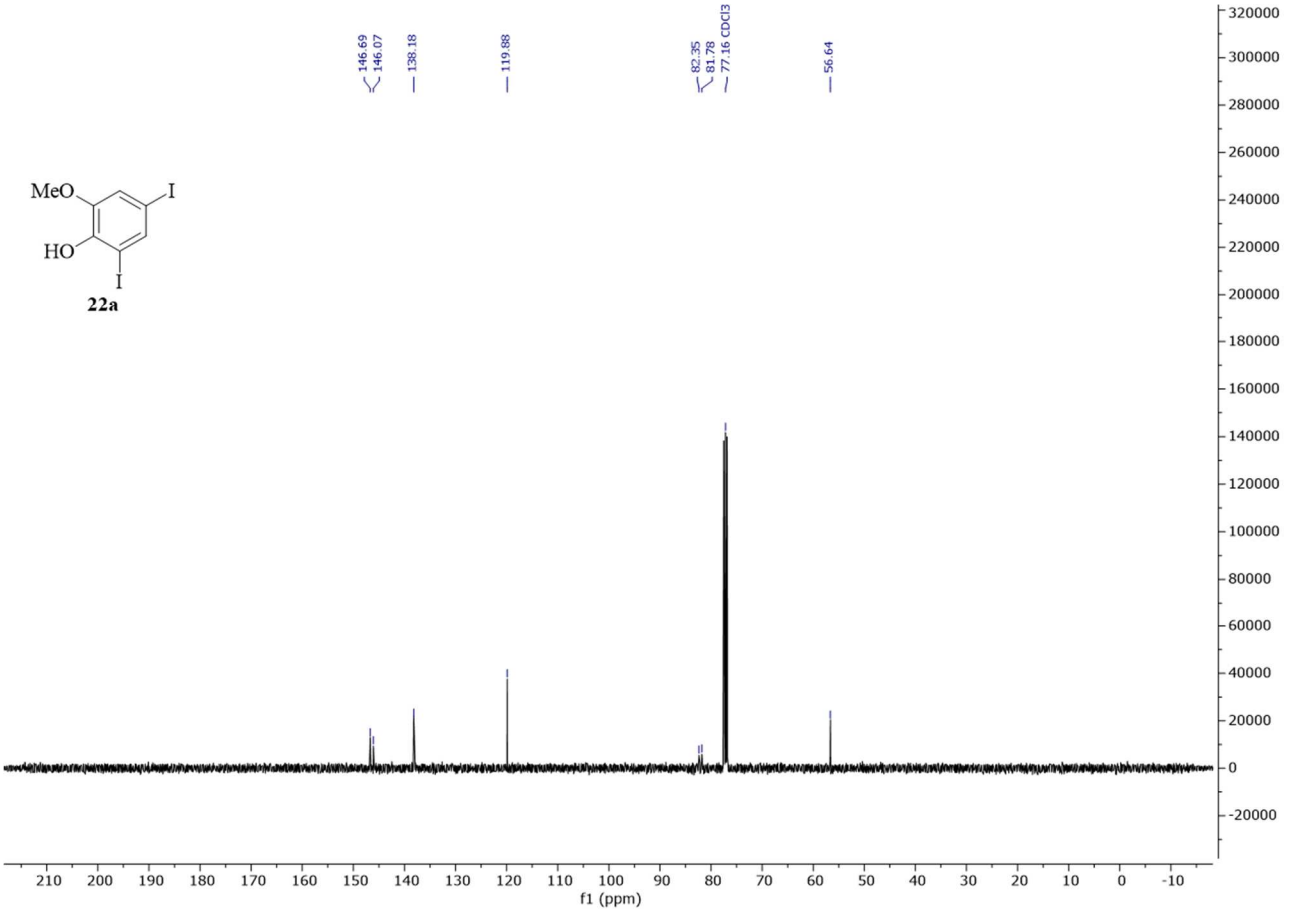
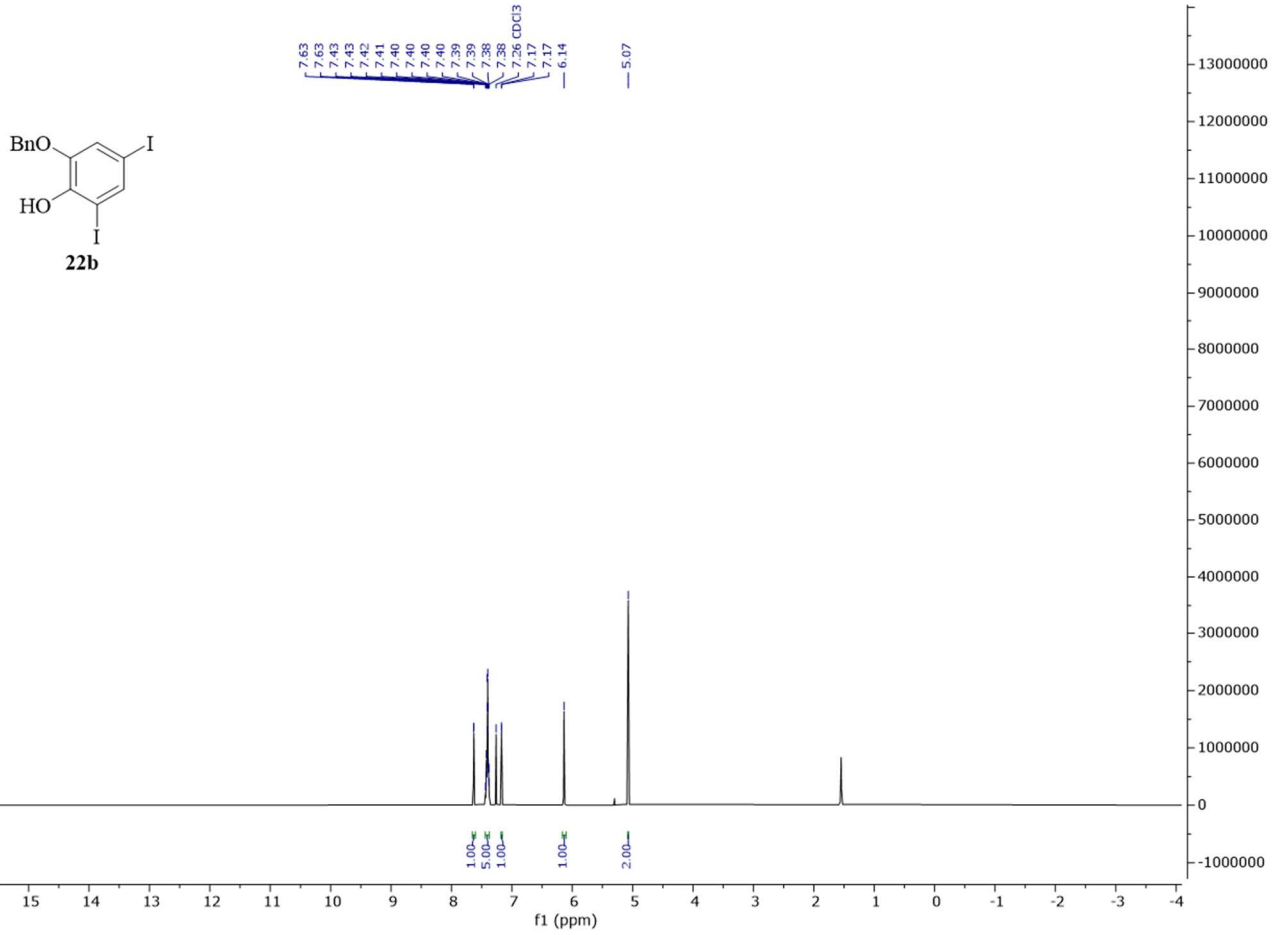
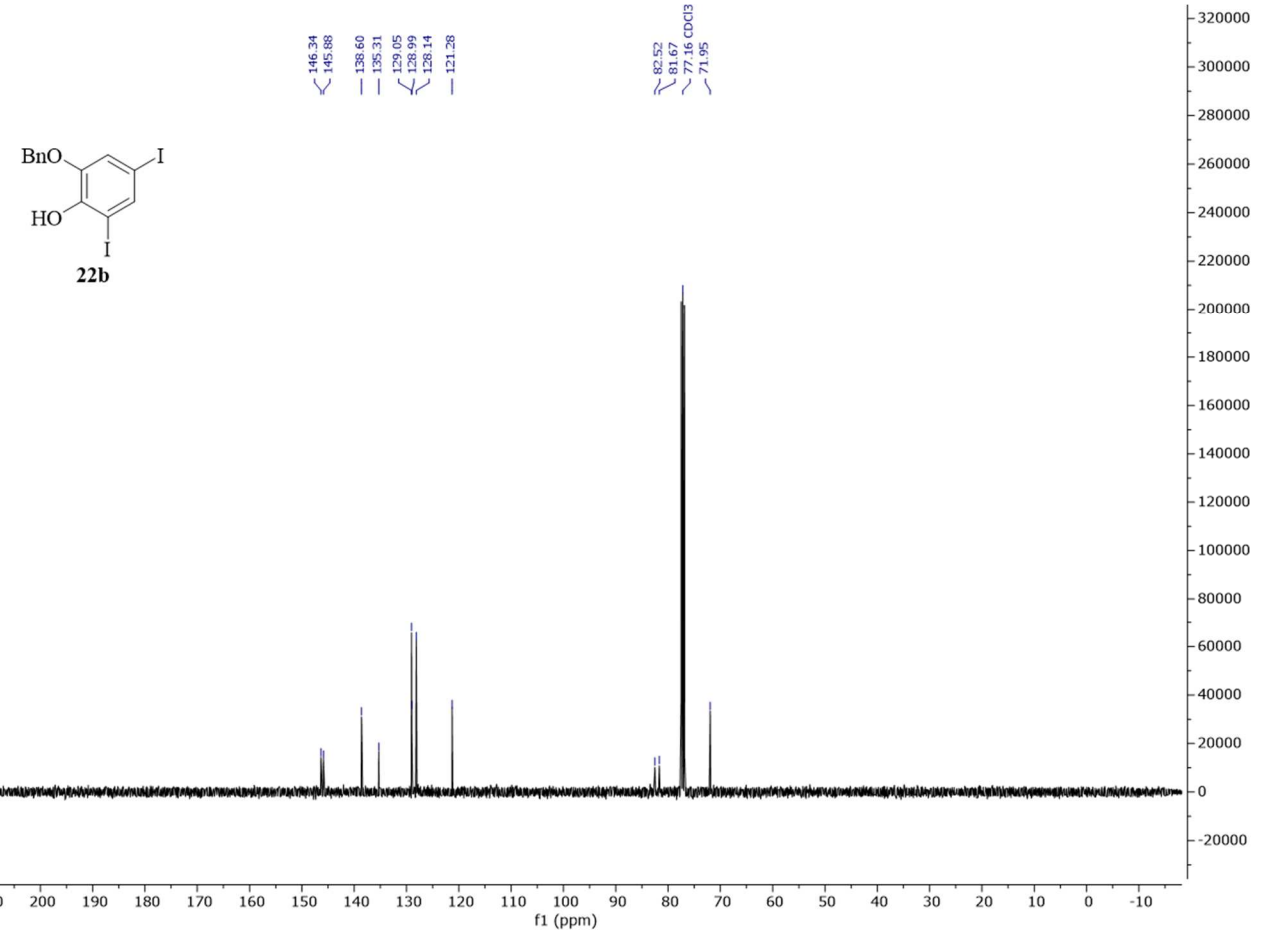
148.15
147.76
146.49
140.24
138.01
132.96
130.70
128.57
124.64
121.92
121.01
120.73
118.09
112.59
109.84
77.16 CDCl3
67.57
60.85
56.88
55.99
55.92
MeO
OMe
OMe
OMe
O
O
f1 (ppm)

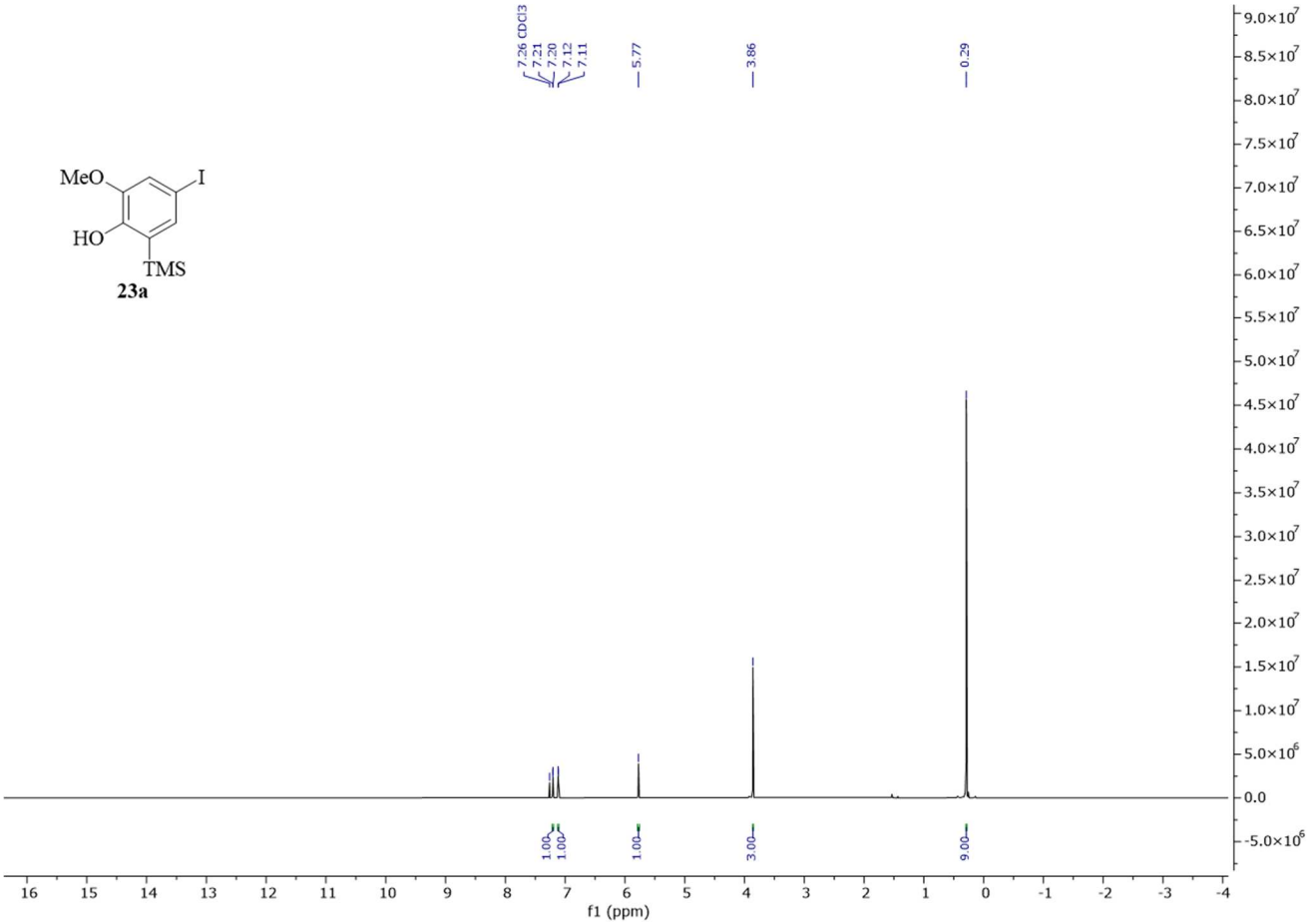
20

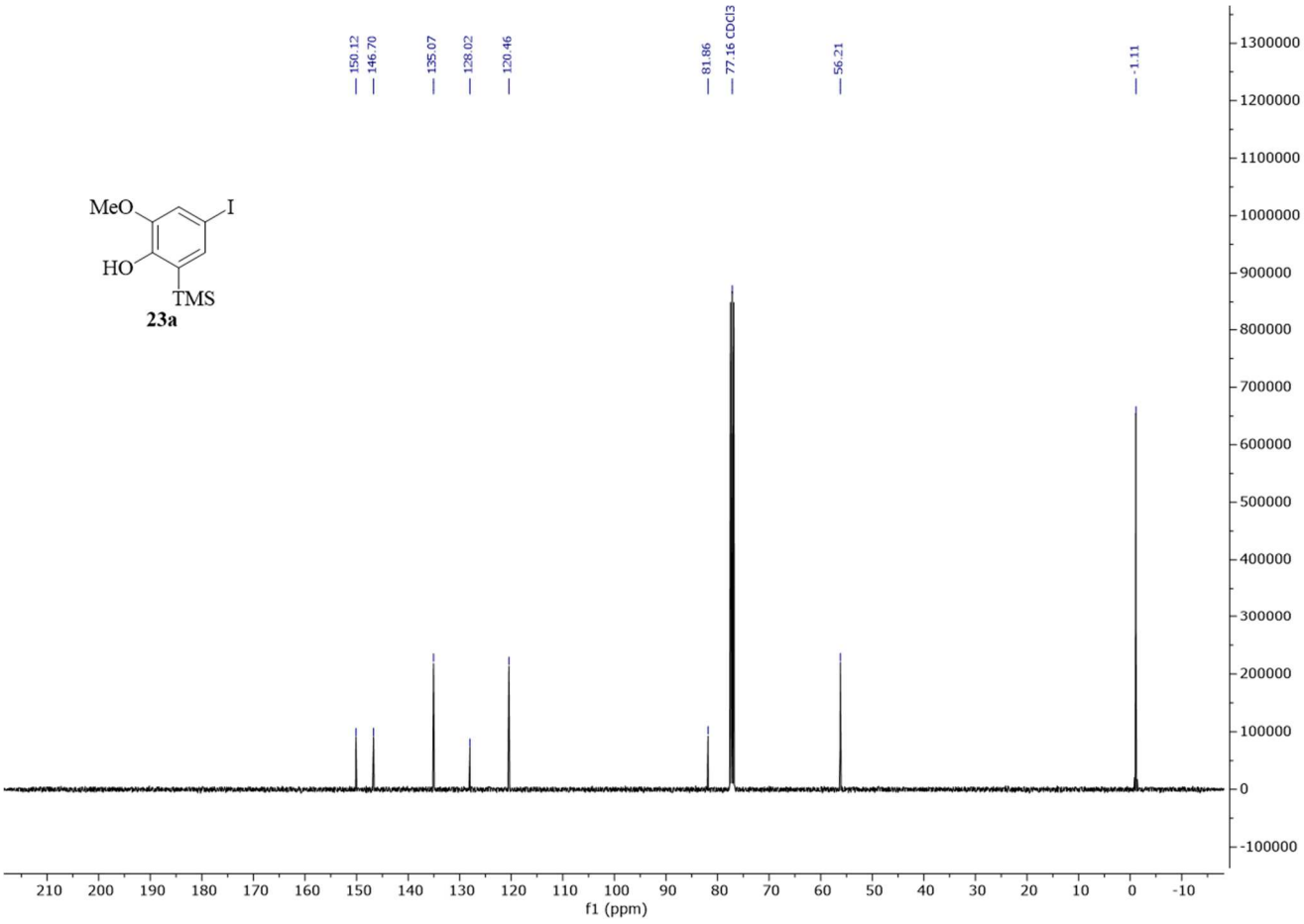

7.61
7.61
7.26 CDCl3
7.08
7.07
6.06
3.88
MeO
HO
I
I
22a
1.00
1.00
1.00
3.00
f1 (ppm)

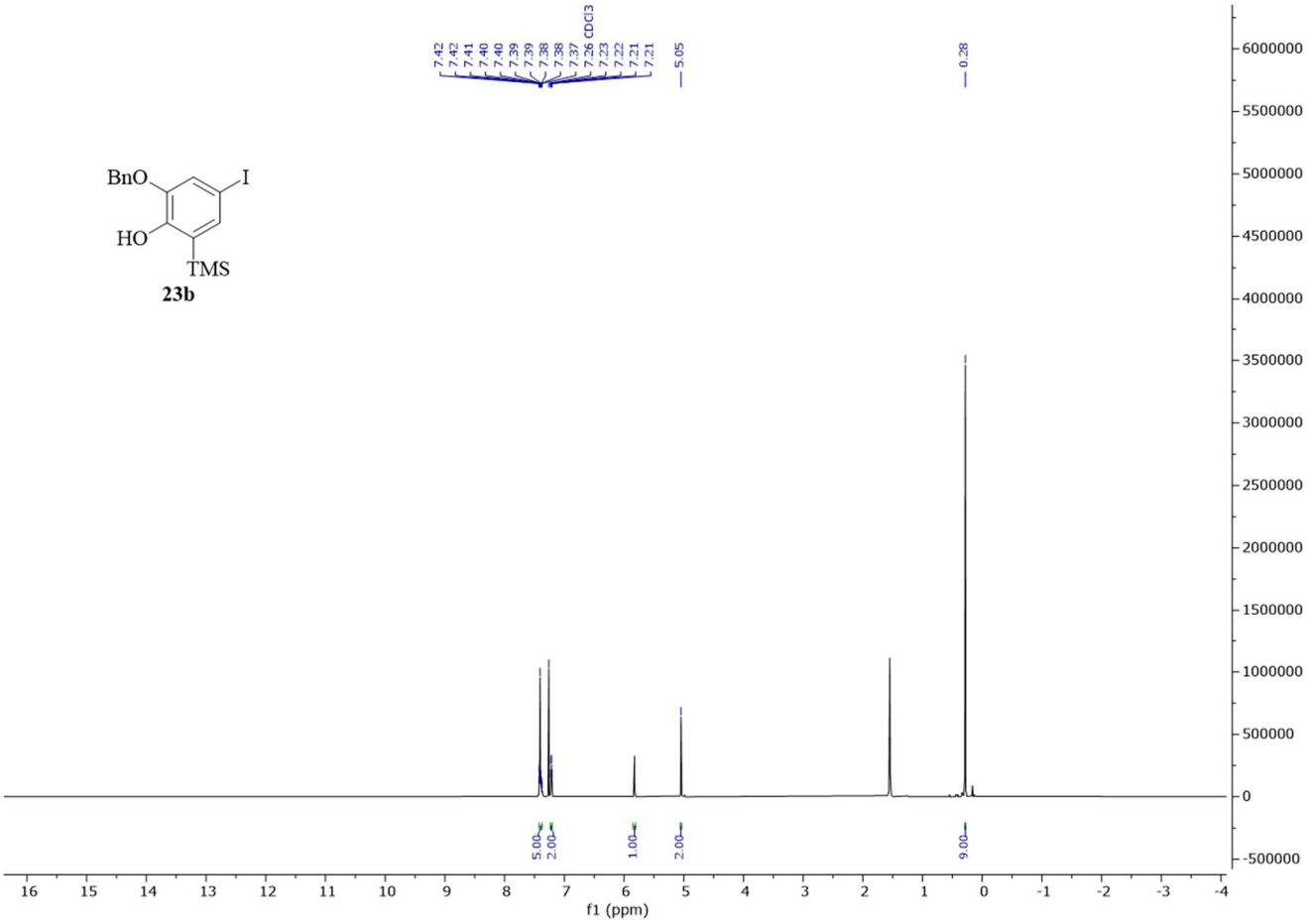

146.69
146.07
138.18
119.88
82.35
81.78
77.16 CDCl3
56.64
MeO
HO
I
I
22a
f1 (ppm)

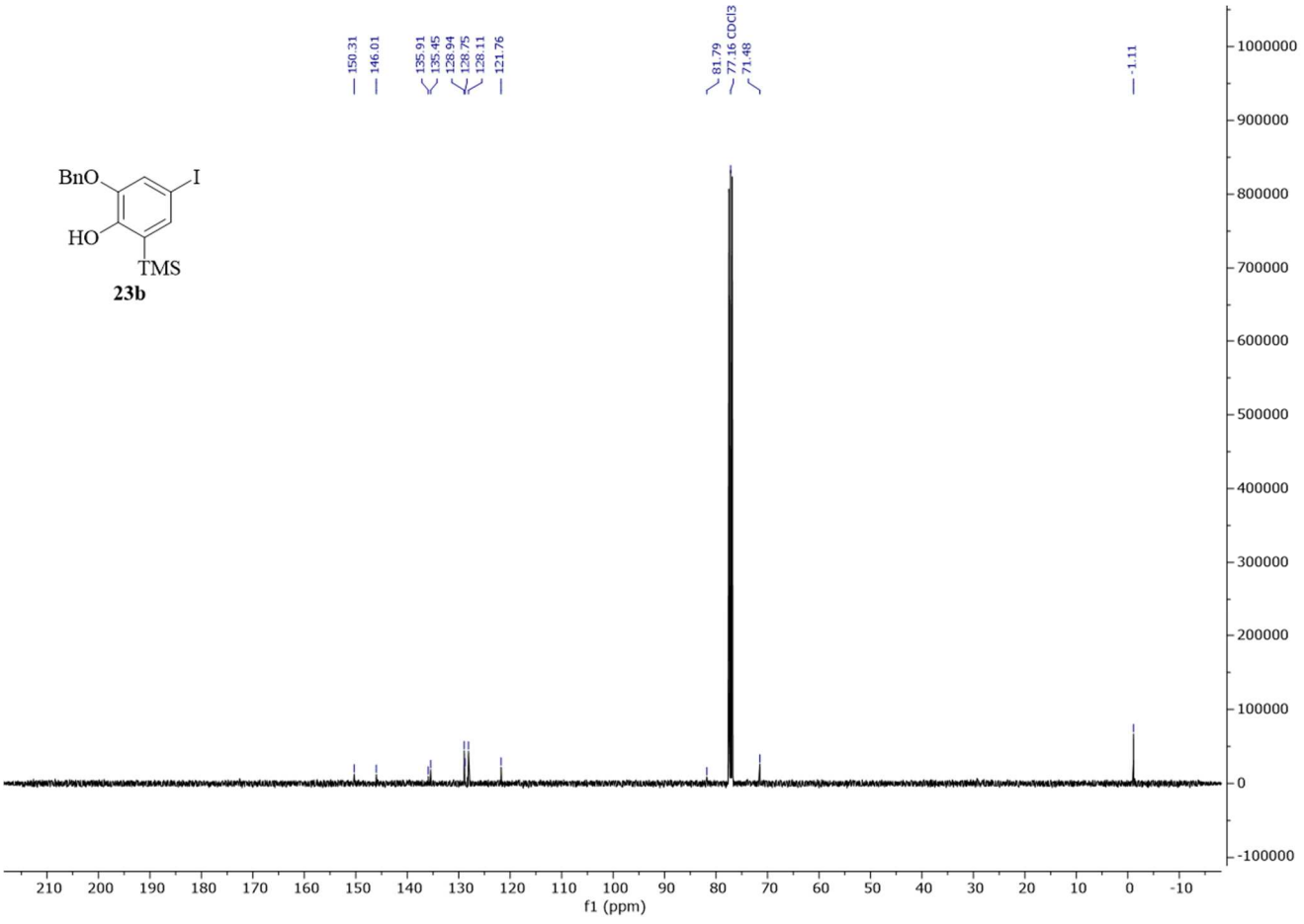

7.63
7.63
7.43
7.43
7.42
7.41
7.40
7.40
7.40
7.40
7.39
7.39
7.38
7.38
7.26 CDCl3
7.17
7.17
6.14
5.07
BnO
I
HO
I
22b
1.00
5.00
1.00
1.00
2.00
f1 (ppm)

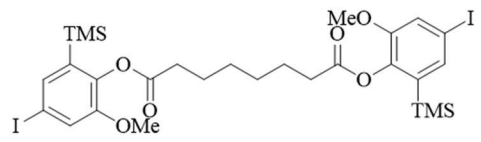

146.34
145.88
138.60
135.31
129.05
128.99
128.14
121.28
82.52
81.67
77.16 CDCl3
71.95
BnO
I
HO
I
22b
f1 (ppm)


7.26 CDCl3
7.21
7.20
7.12
7.11
5.77
3.86
0.29
MeO
I
HO
TMS
23a
1.00
1.00
1.00
3.00
9.00
f1 (ppm)


150.12
146.70
135.07
128.02
120.46
81.86
77.16 CDCl3
56.21
-1.11
MeO
I
HO
TMS
23a
f1 (ppm)

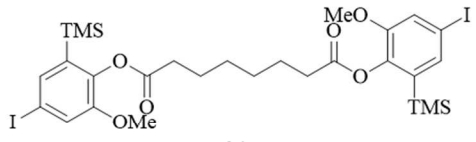

7.42
7.42
7.41
7.40
7.40
7.39
7.39
7.38
7.38
7.37
7.26 CDCl3
7.23
7.22
7.21
7.21
5.05
0.28
BnO
I
HO
TMS
23b
5.00
2.00
1.00
2.00
9.00
f1 (ppm)


150.31
146.01
135.91
135.45
128.94
128.75
128.11
121.76
81.79
77.16 CDCl3
71.48
-1.11
BnO
I
HO
TMS
23b
f1 (ppm)


TMS
MeO
I
O
O
O
O
I
OMe
TMS

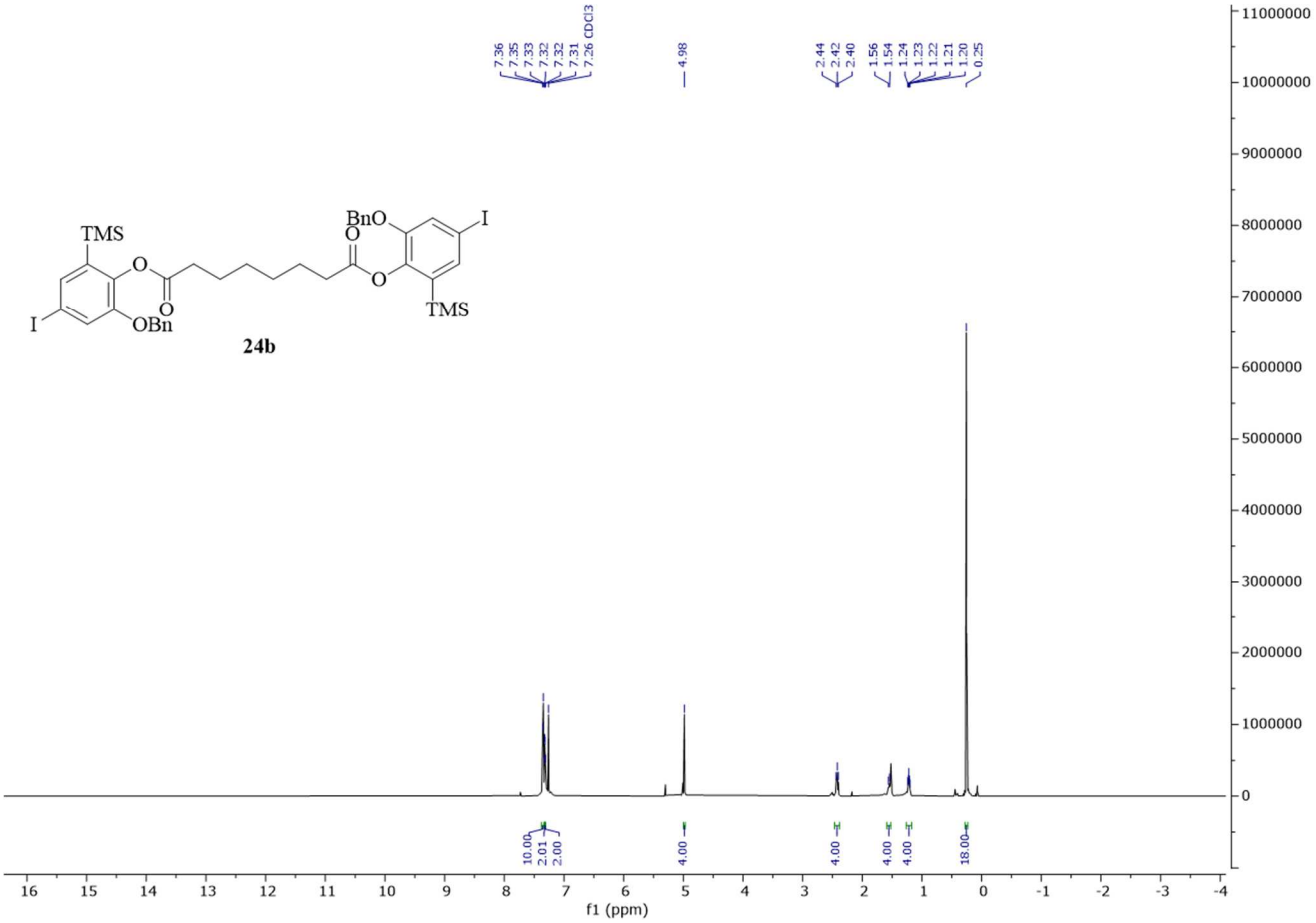
24a

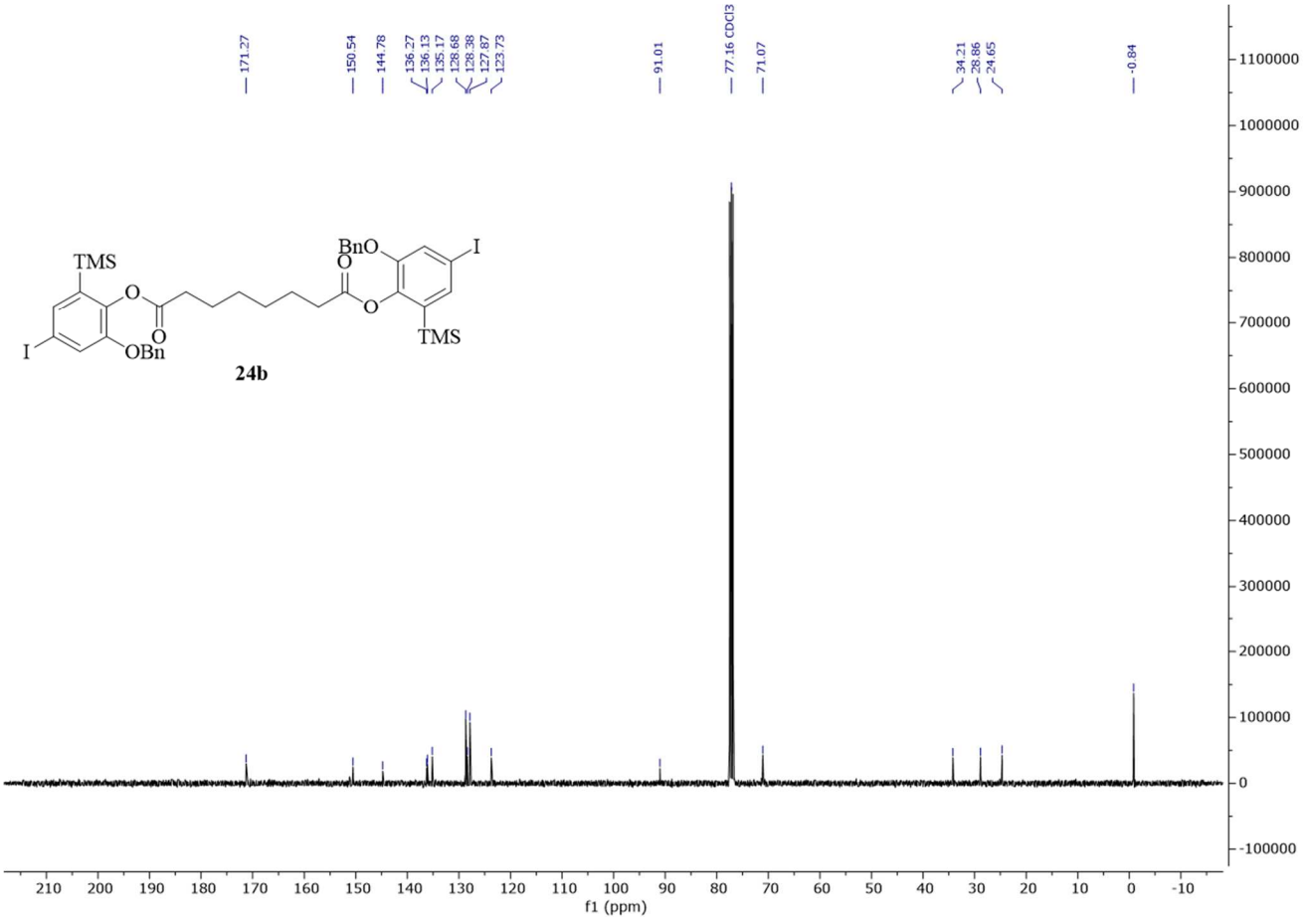
7.30
7.30
7.26 CDCl3
7.24
7.24
3.77
2.59
2.57
2.55
1.80
1.79
1.77
1.52
1.50
1.49
1.48
0.25
2.00
2.00
6.00
4.00
4.00
4.00
17.99
f1 (ppm)

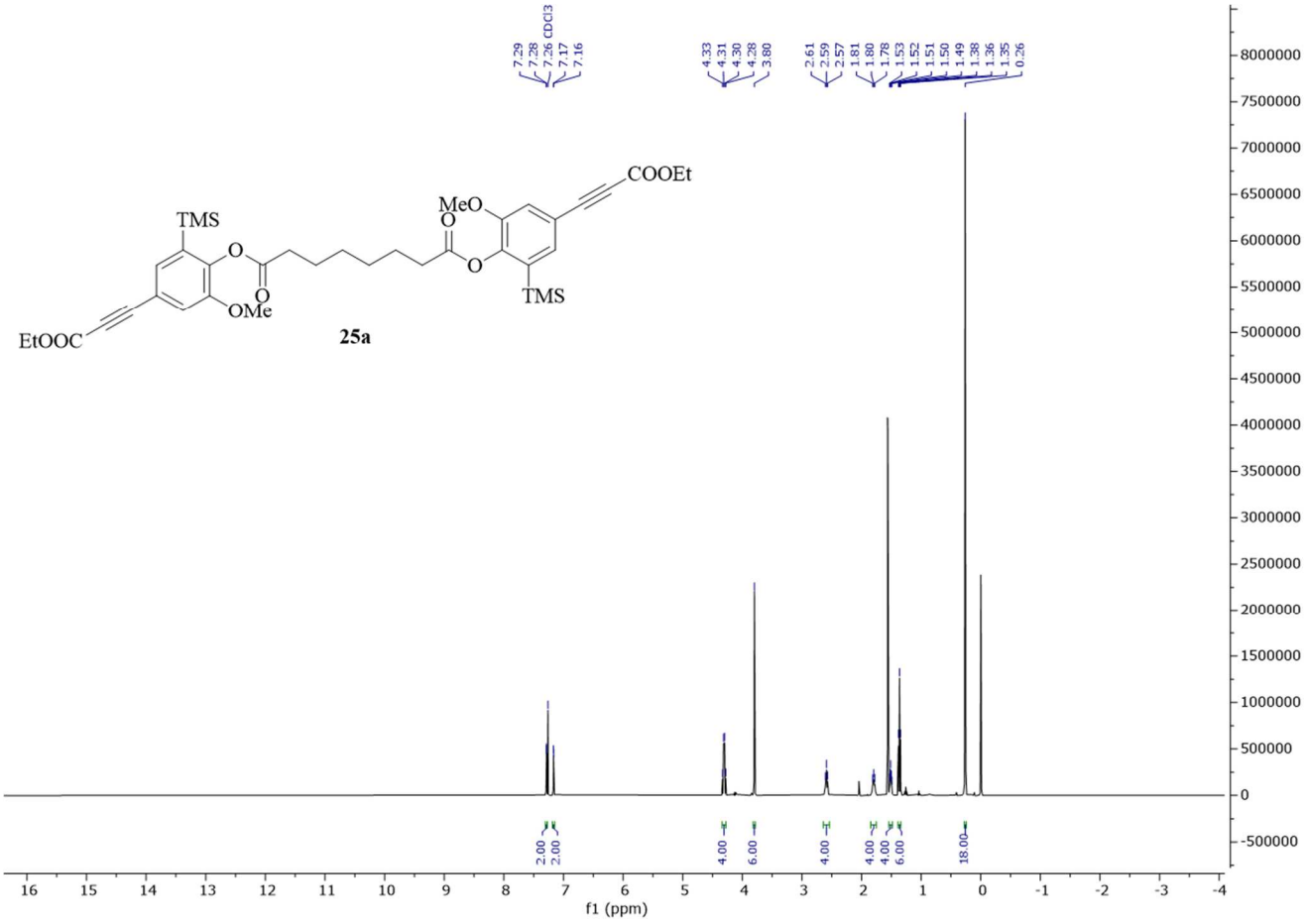

TMS
MeO
I
O
O
O
O
I
OMe
TMS

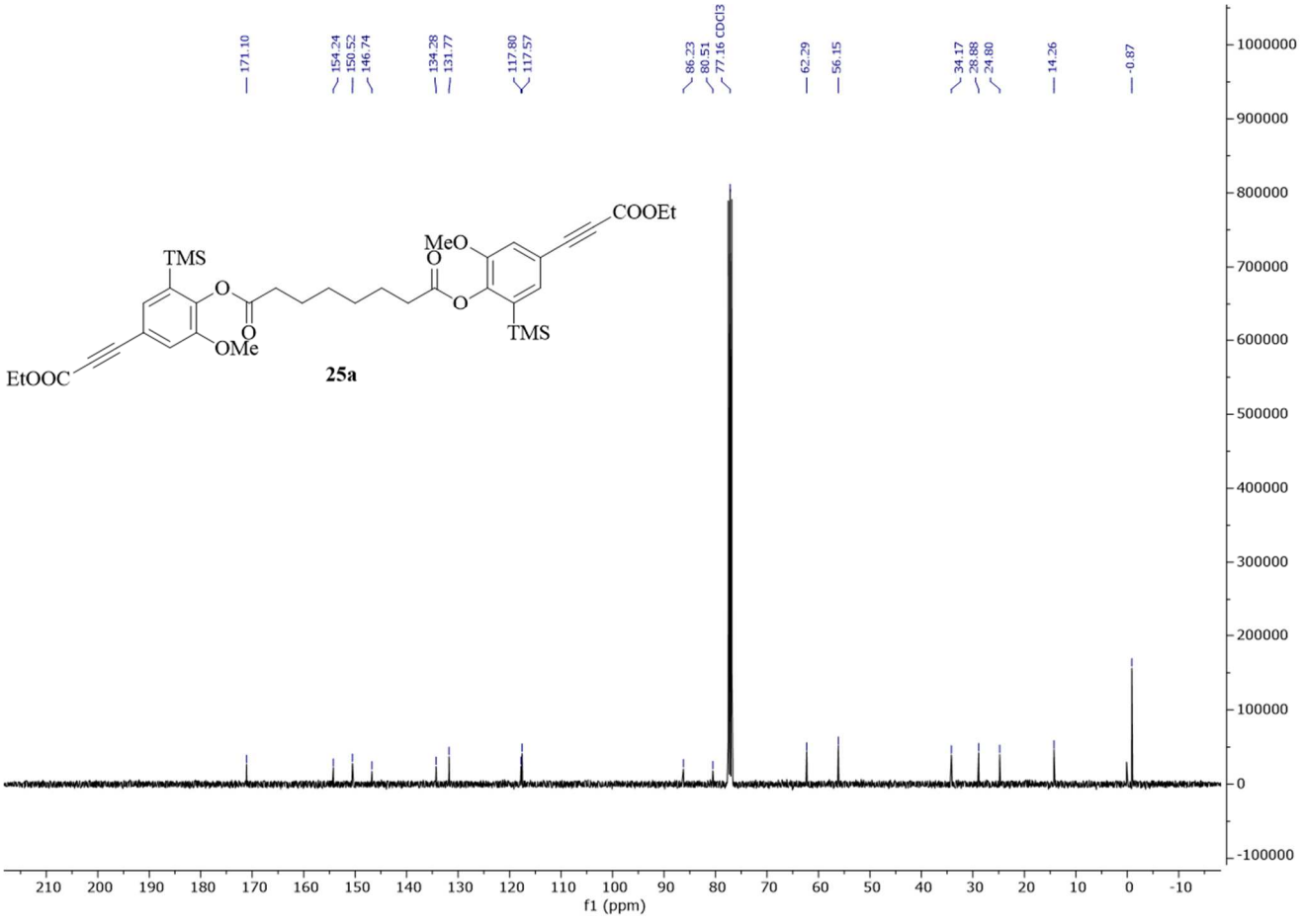
24a

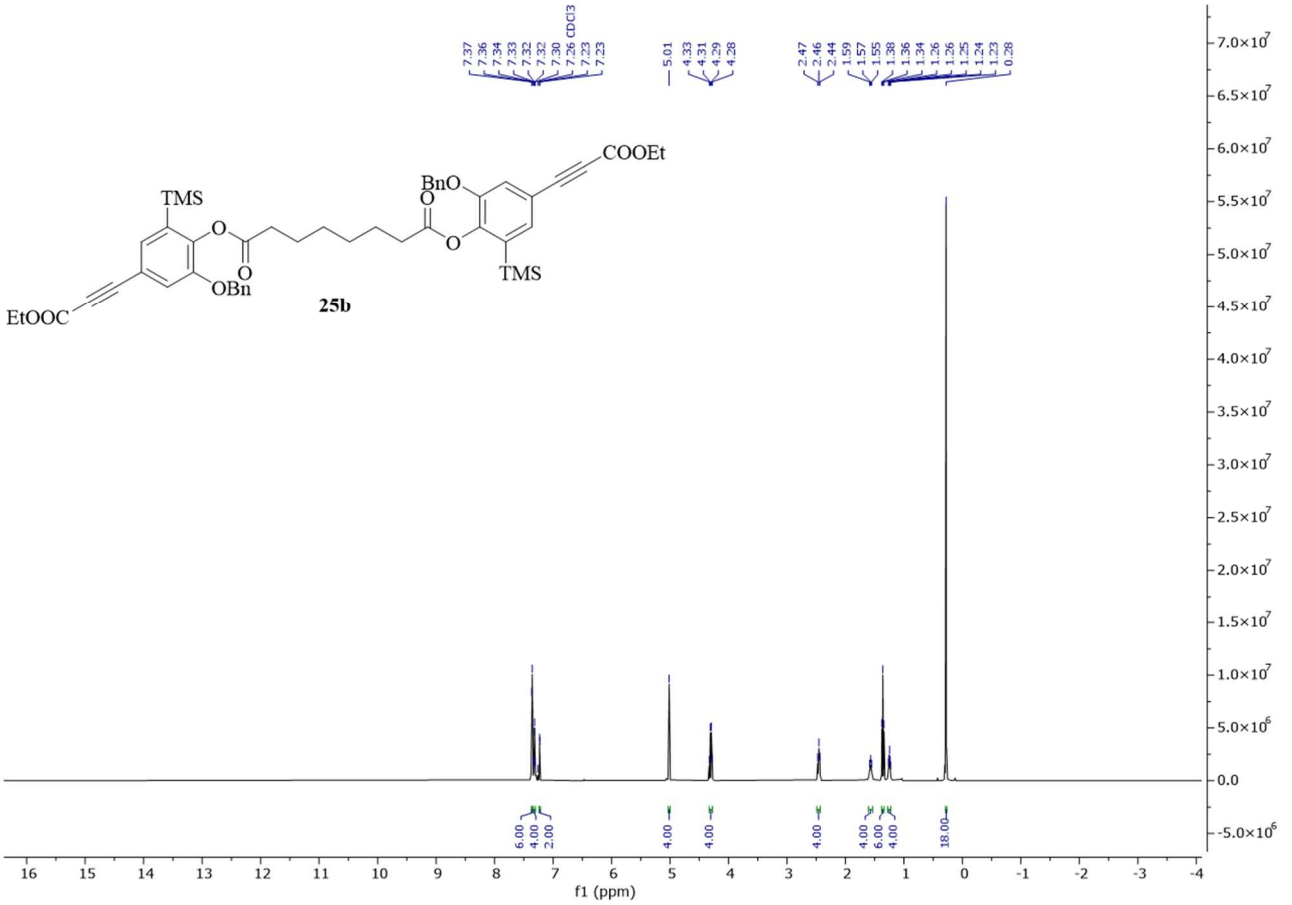
171.29
151.32
144.49
136.13
134.90
122.68
91.16
77.16 CDCl3
56.22
34.19
28.90
24.84
-0.85
f1 (ppm)

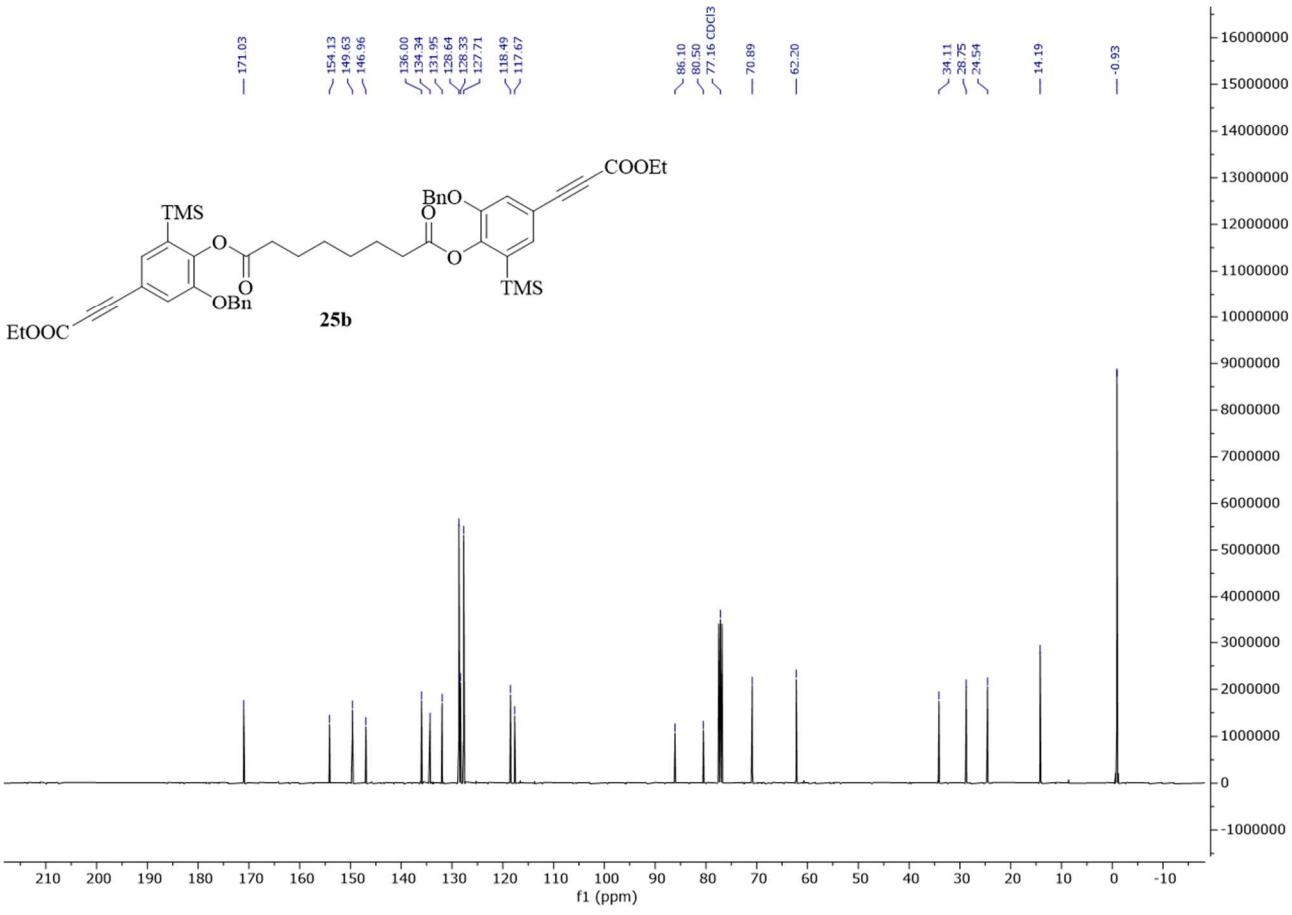

7.36
7.35
7.33
7.32
7.32
7.31
7.26 CDCl3
4.98
2.44
2.42
2.40
1.56
1.54
1.24
1.23
1.22
1.21
1.20
0.25
TMS
BnO
I
O
O
O
O
TMS
I
OBn
24b
10.00
2.01
2.00
4.00
4.00
4.00
4.00
18.00
f1 (ppm)

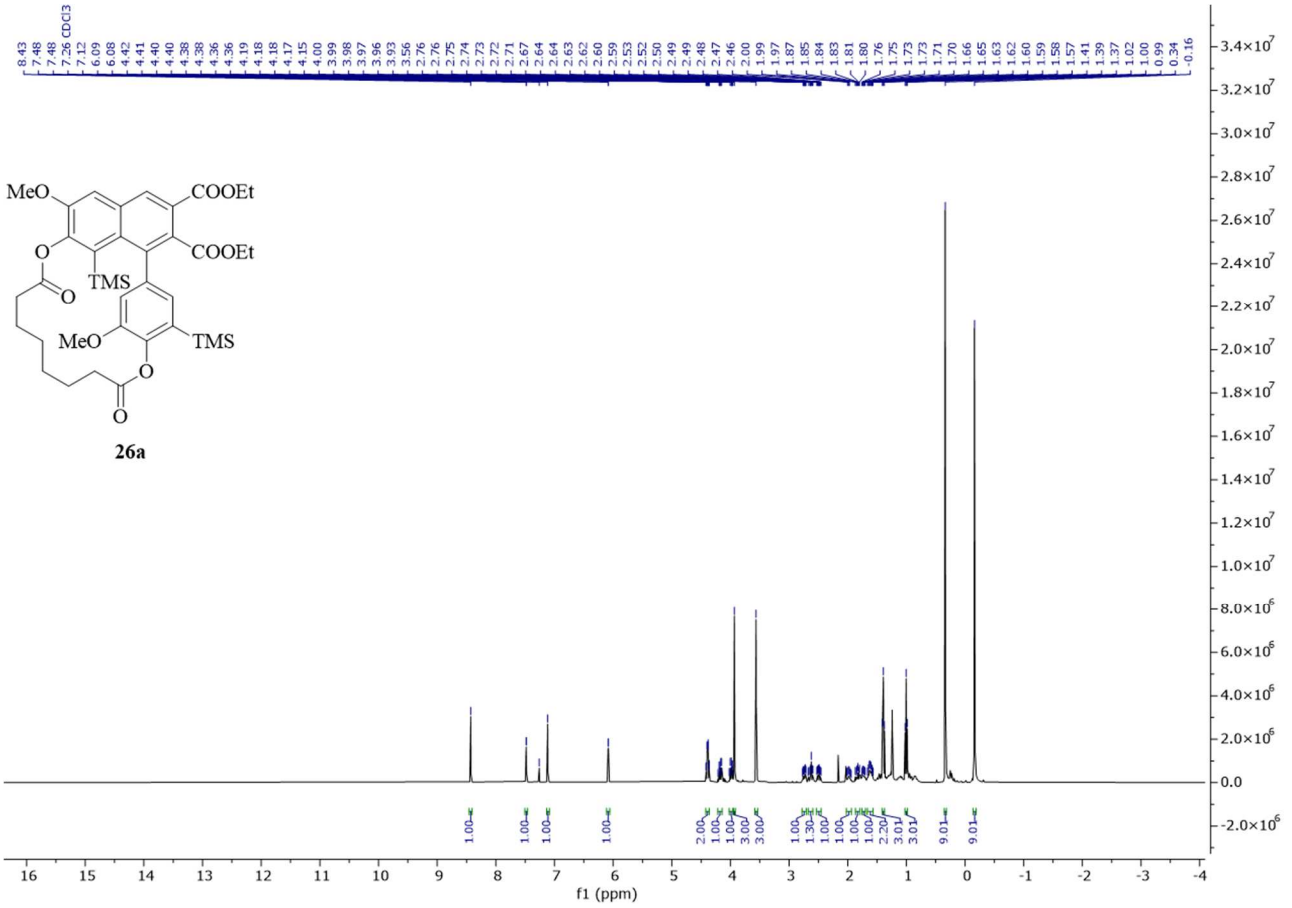

171.27
150.54
144.78
136.27
136.13
135.17
128.68
128.38
127.87
123.73
91.01
77.16 CDCl3
71.07
34.21
28.86
24.65
-0.84
TMS
BnO
I
O
O
O
O
TMS
I
OBn
24b
f1 (ppm)


7.29
7.28
7.26 CDCl3
7.17
7.16
4.33
4.31
4.30
4.28
3.80
2.61
2.59
2.57
1.81
1.80
1.78
1.53
1.52
1.51
1.50
1.49
1.38
1.36
1.35
0.26
TMS
MeO
COOEt
TMS
OMe
EtOOC
25a
2.00
2.00
4.00
6.00
4.00
4.00
4.00
6.00
18.00
f1 (ppm)

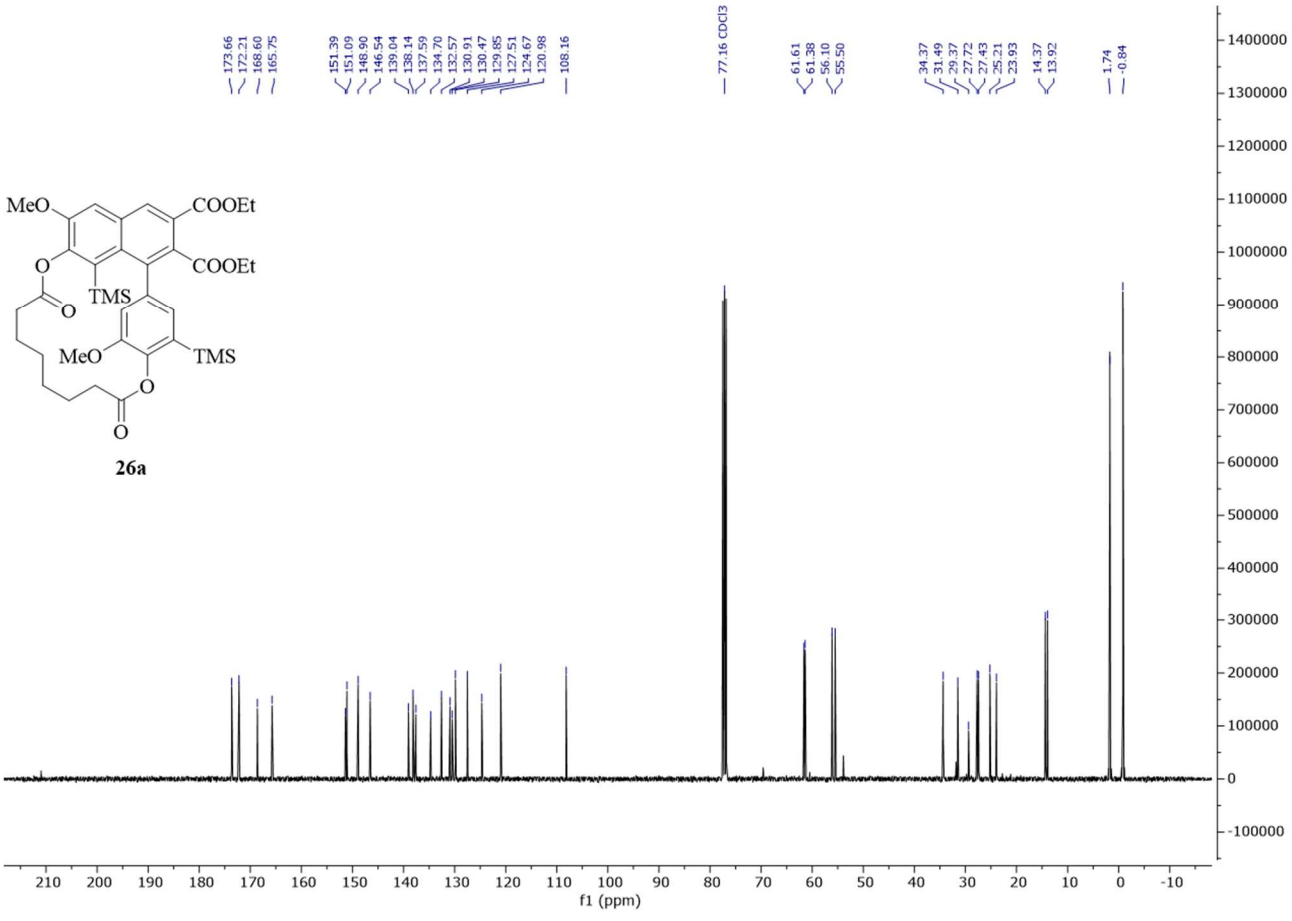

171.10
154.24
150.52
146.74
134.28
131.77
117.80
117.57
86.23
80.51
77.16 CDCl3
62.29
56.15
34.17
28.88
24.80
14.26
-0.87
TMS
MeO
COOEt
TMS
OMe
EtOOC
25a
f1 (ppm)


7.37
7.36
7.34
7.33
7.32
7.32
7.30
7.26 CDCl3
7.23
7.23
5.01
4.33
4.31
4.29
4.28
2.47
2.46
2.44
1.59
1.57
1.55
1.38
1.36
1.34
1.26
1.26
1.25
1.24
1.23
0.28
COOEt
BnO
TMS
OBn
TMS
EtOOC
25b
6.00
4.00
2.00
4.00
4.00
4.00
4.00
6.00
4.00
18.00
f1 (ppm)

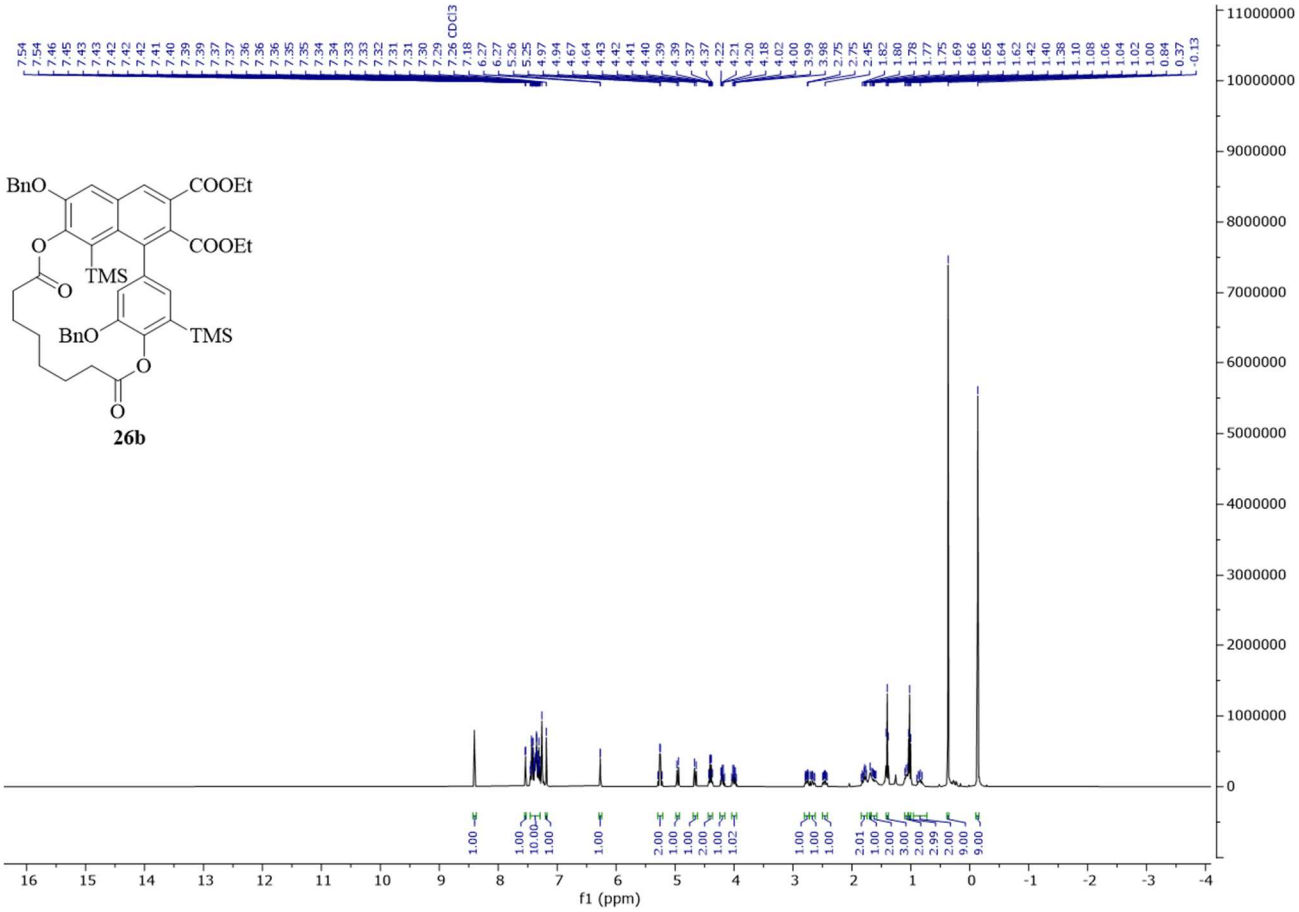

171.03
154.13
149.63
146.96
136.00
134.34
131.95
128.64
128.33
127.71
118.49
117.67
86.10
80.50
77.16 CDCl3
70.89
62.20
34.11
28.75
24.54
14.19
-0.93
COOEt
BnO
TMS
OBn
TMS
EtOOC
25b
f1 (ppm)


MeO
COOEt
COOEt
TMS
MeO
TMS
O
O
O
O

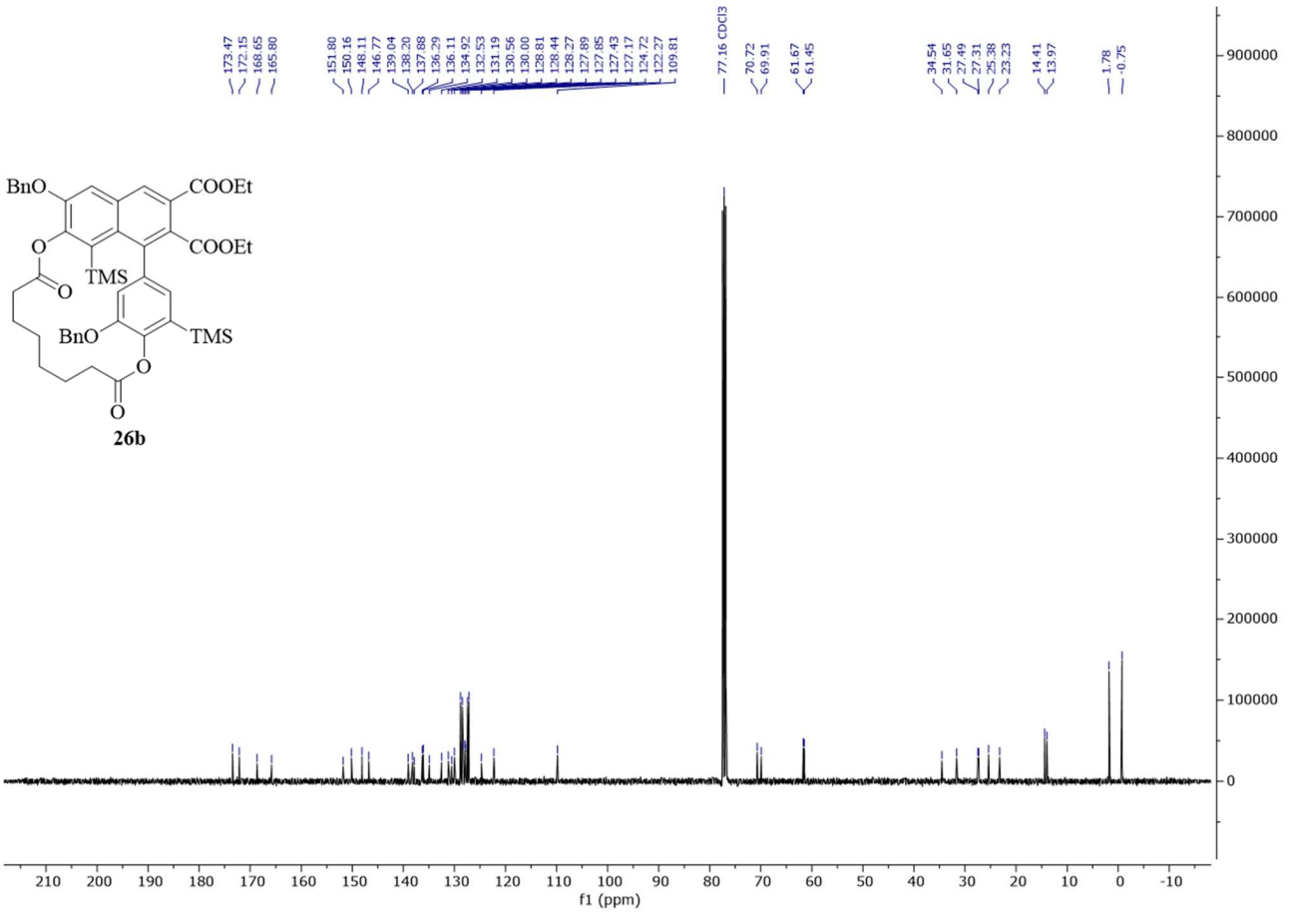
26a


MeO
COOEt
COOEt
TMS
MeO
TMS
O
O
O
O

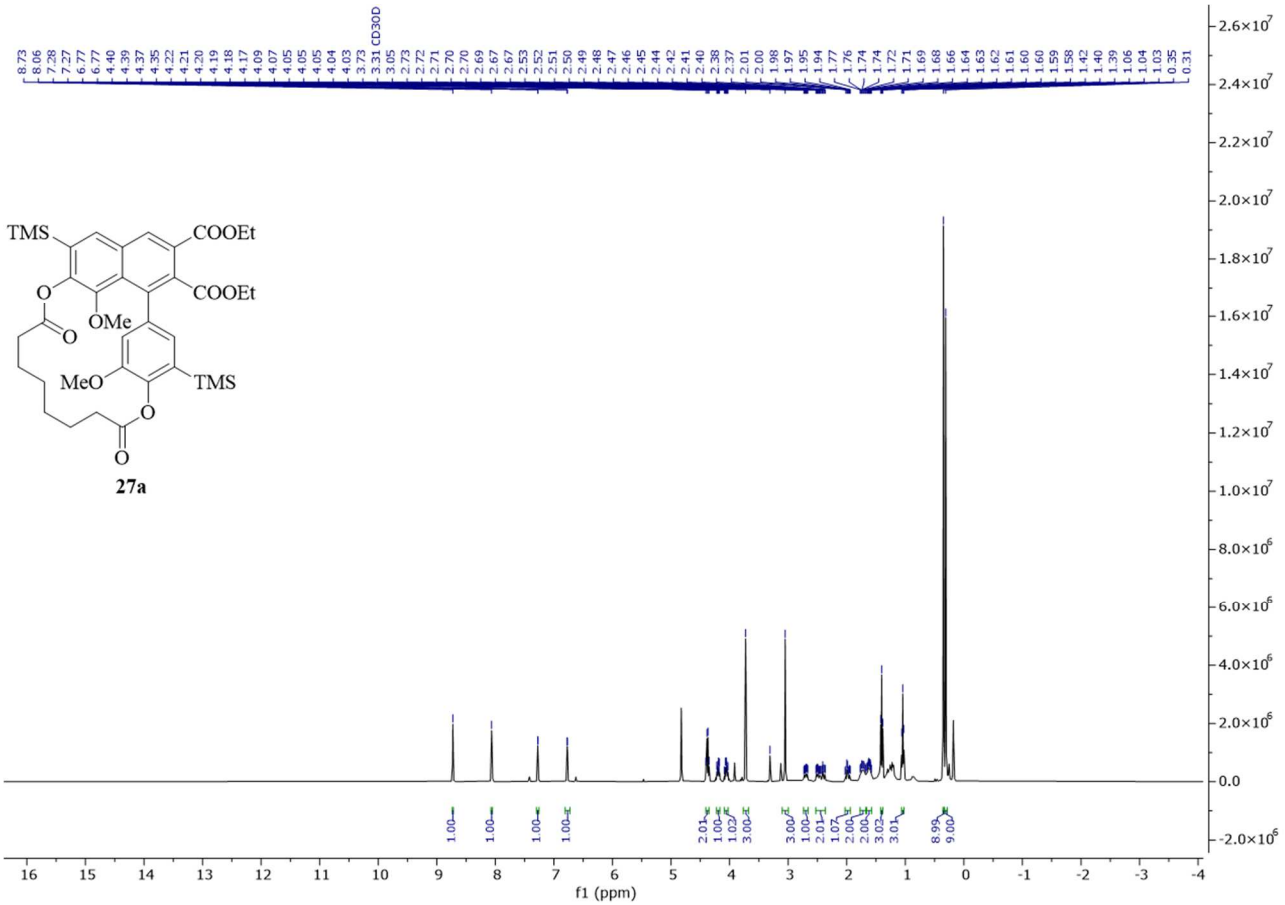
26a

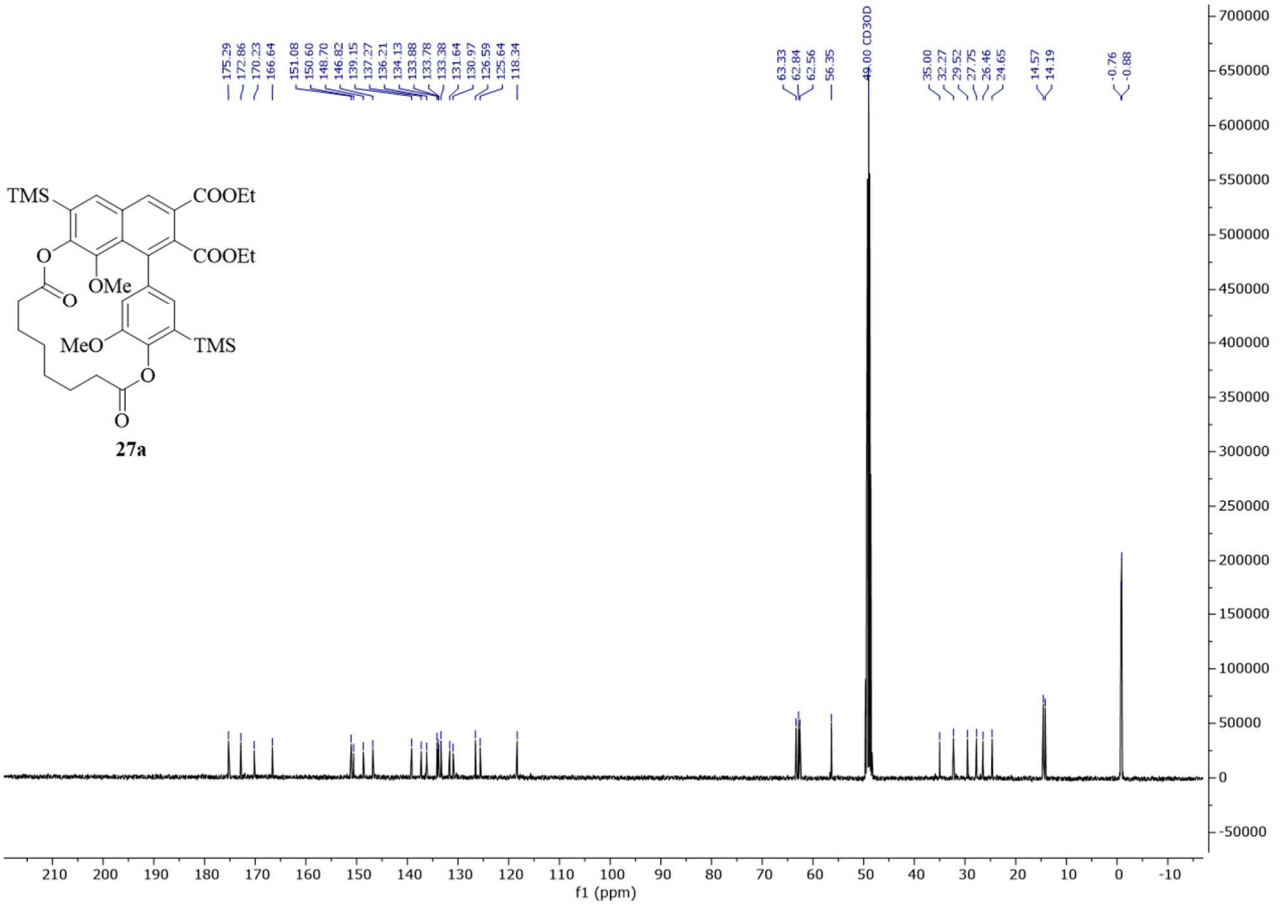

BnO
COOEt
COOEt
TMS
BnO
TMS
O
O
O
O

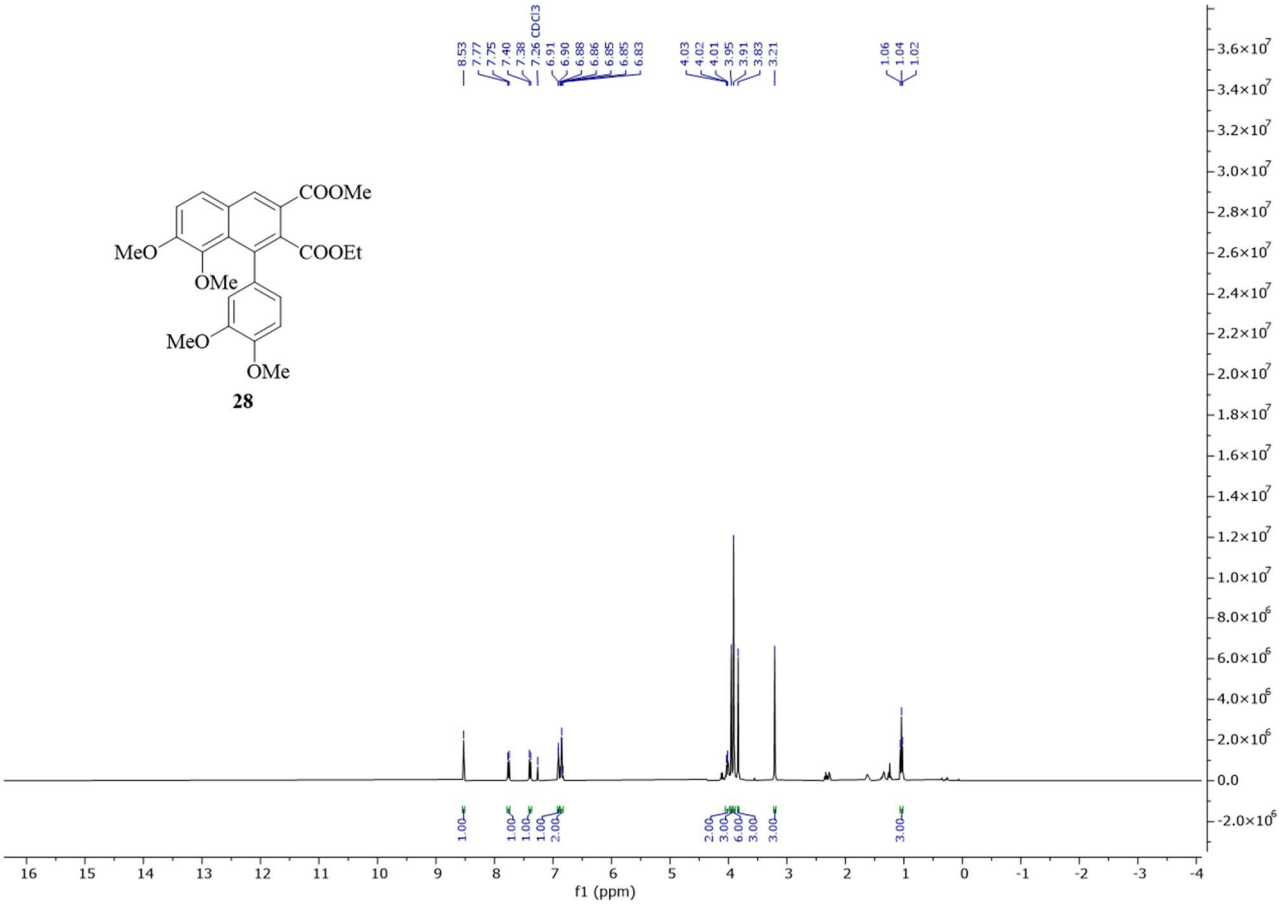
26b

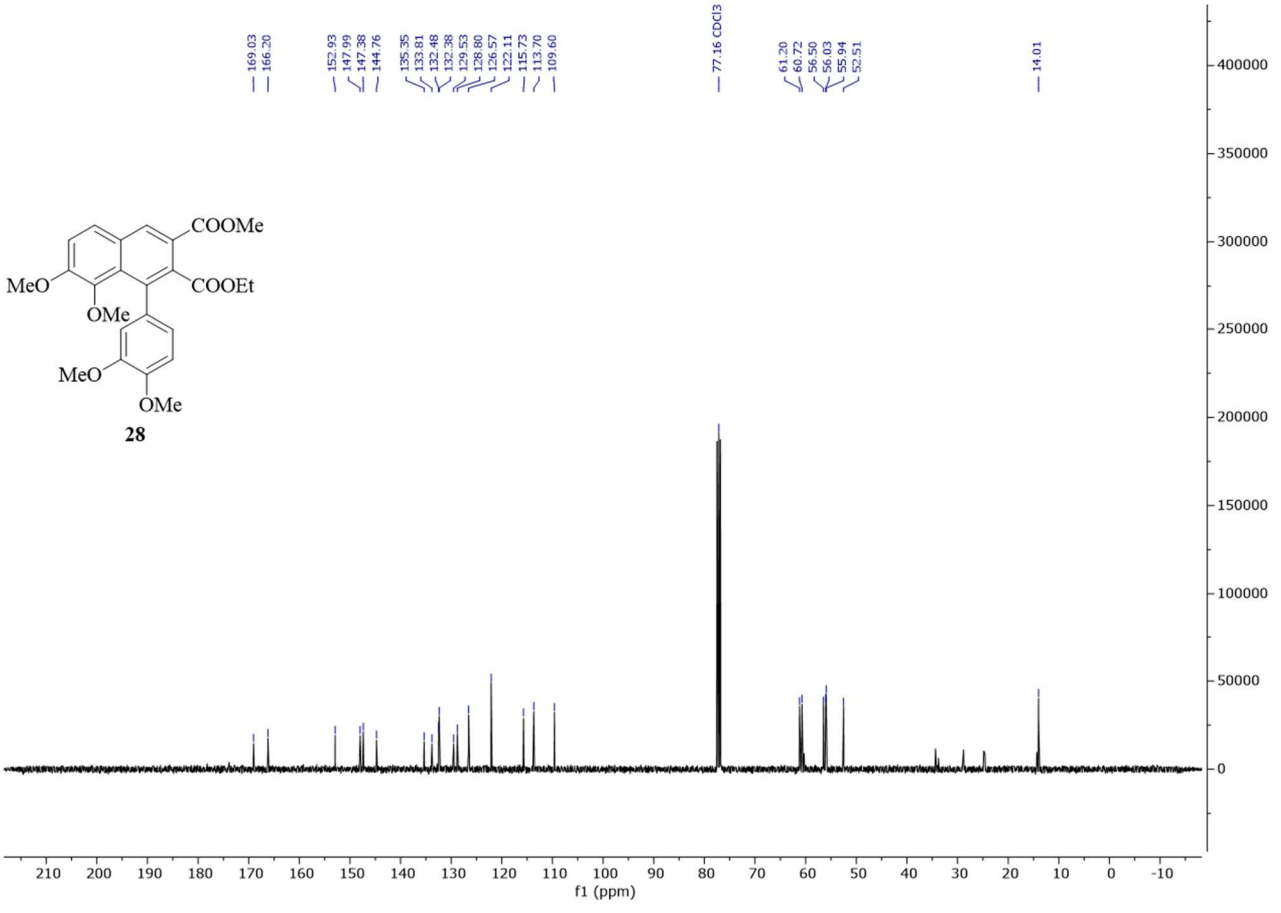

BnO
COOEt
COOEt
TMS
BnO
TMS
O
O
O
O

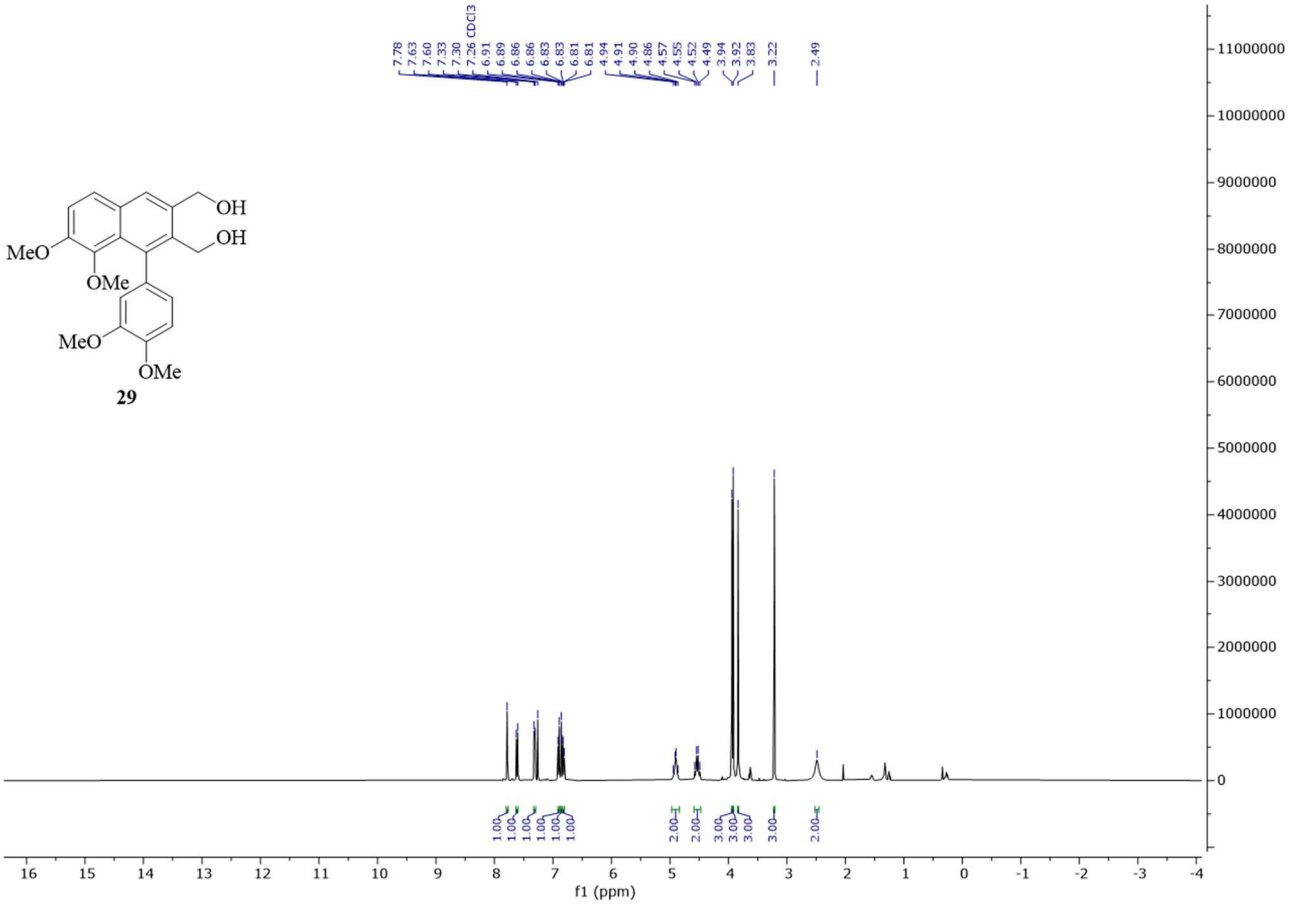
26b


TMS
COOEt
COOEt
OMe
MeO
TMS
27a
f1 (ppm)

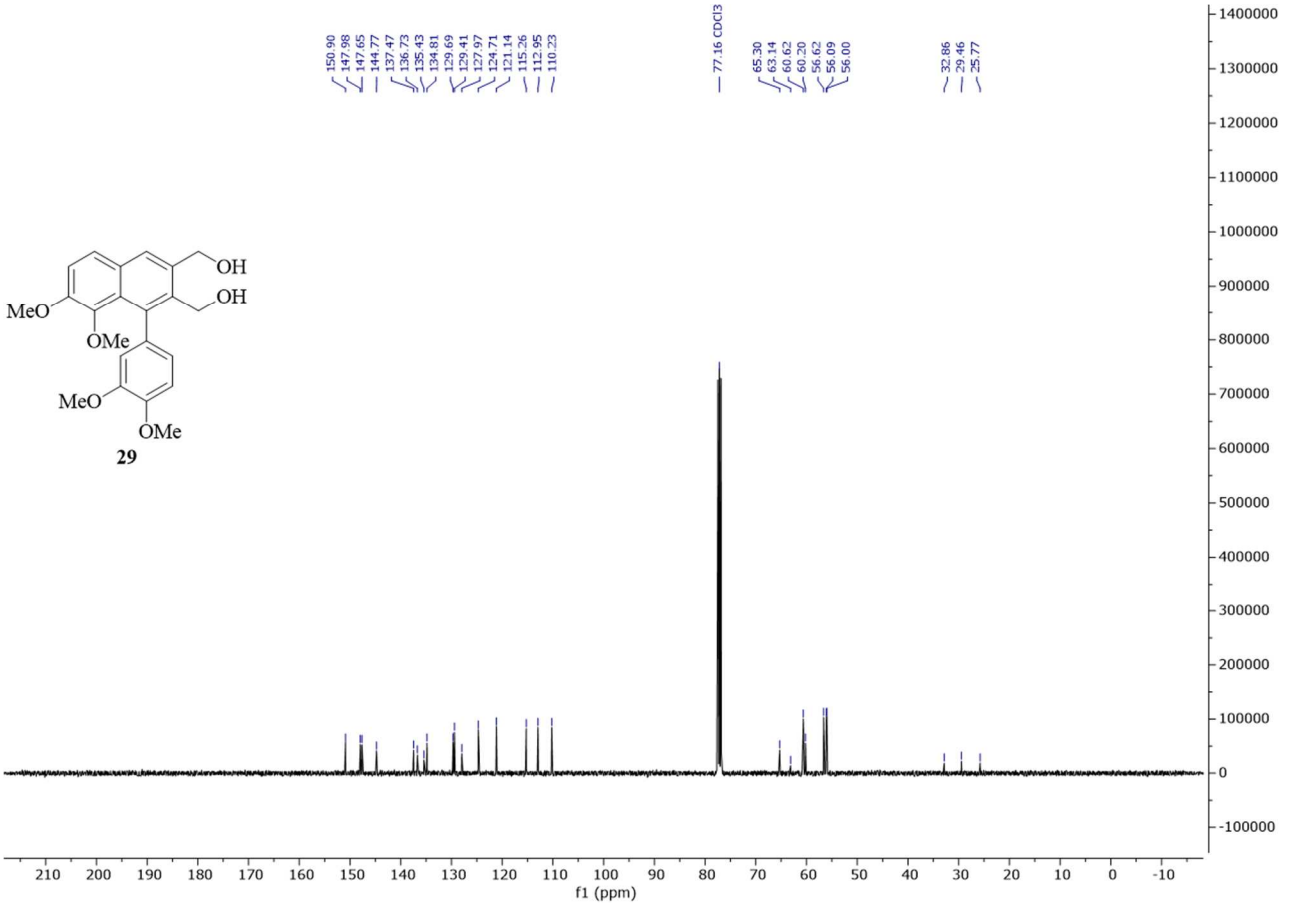

TMS
COOEt
COOEt
OMe
MeO
TMS
27a
f1 (ppm)


8.53
7.77
7.75
7.40
7.38
7.26 CDCl3
6.91
6.90
6.88
6.86
6.85
6.85
6.83
4.03
4.02
4.01
3.95
3.91
3.83
3.21
1.06
1.04
1.02
COOMe
COOEt
MeO
OMe
MeO
OMe
28
f1 (ppm)

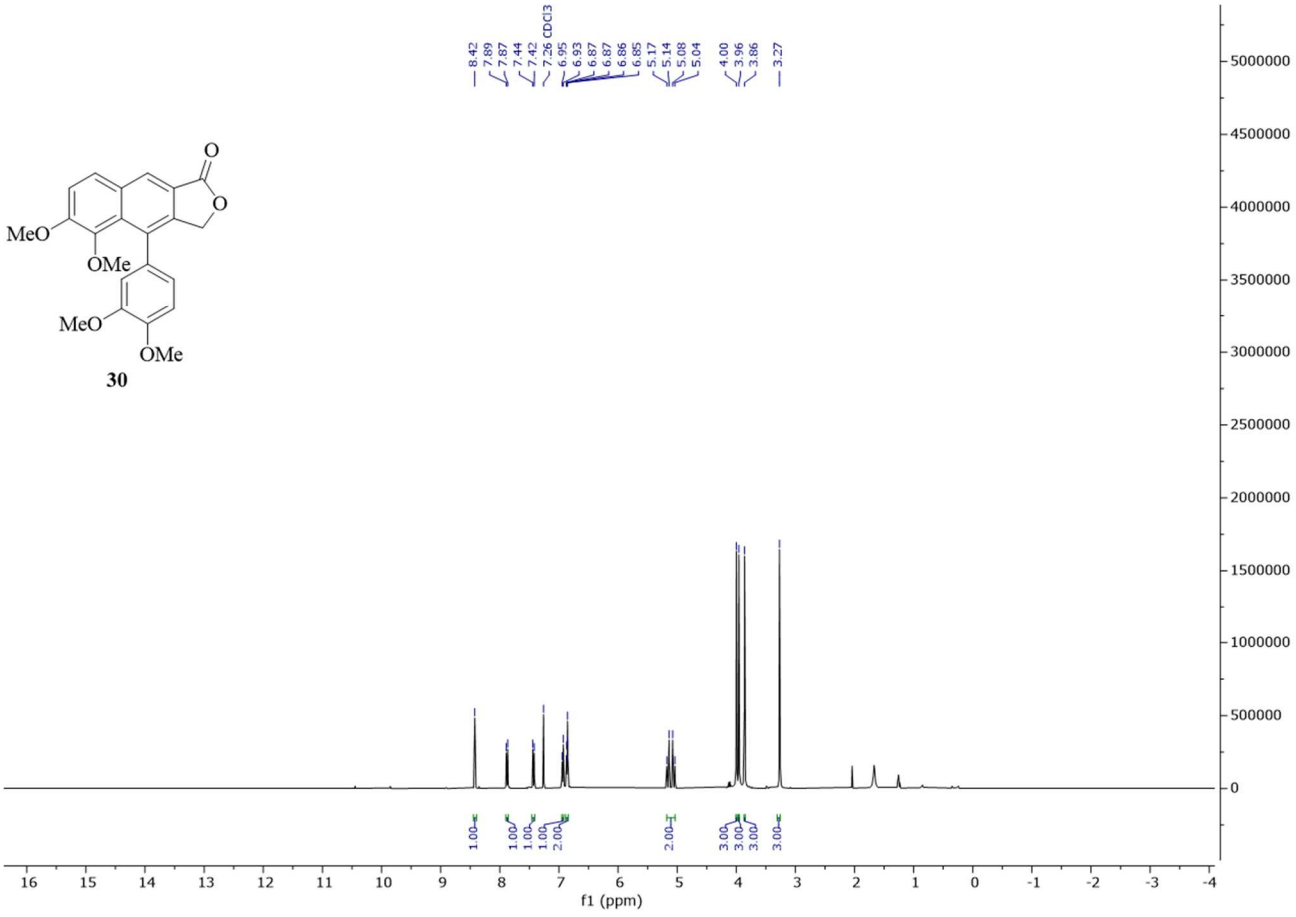

169.03
166.20
152.93
147.99
147.38
144.76
135.35
133.81
132.48
132.38
129.53
128.80
126.57
122.11
115.73
113.70
109.60
77.16 CDCl3
61.20
60.72
56.50
56.03
55.94
52.51
14.01
COOMe
COOEt
MeO
OMe
MeO
OMe
28
f1 (ppm)

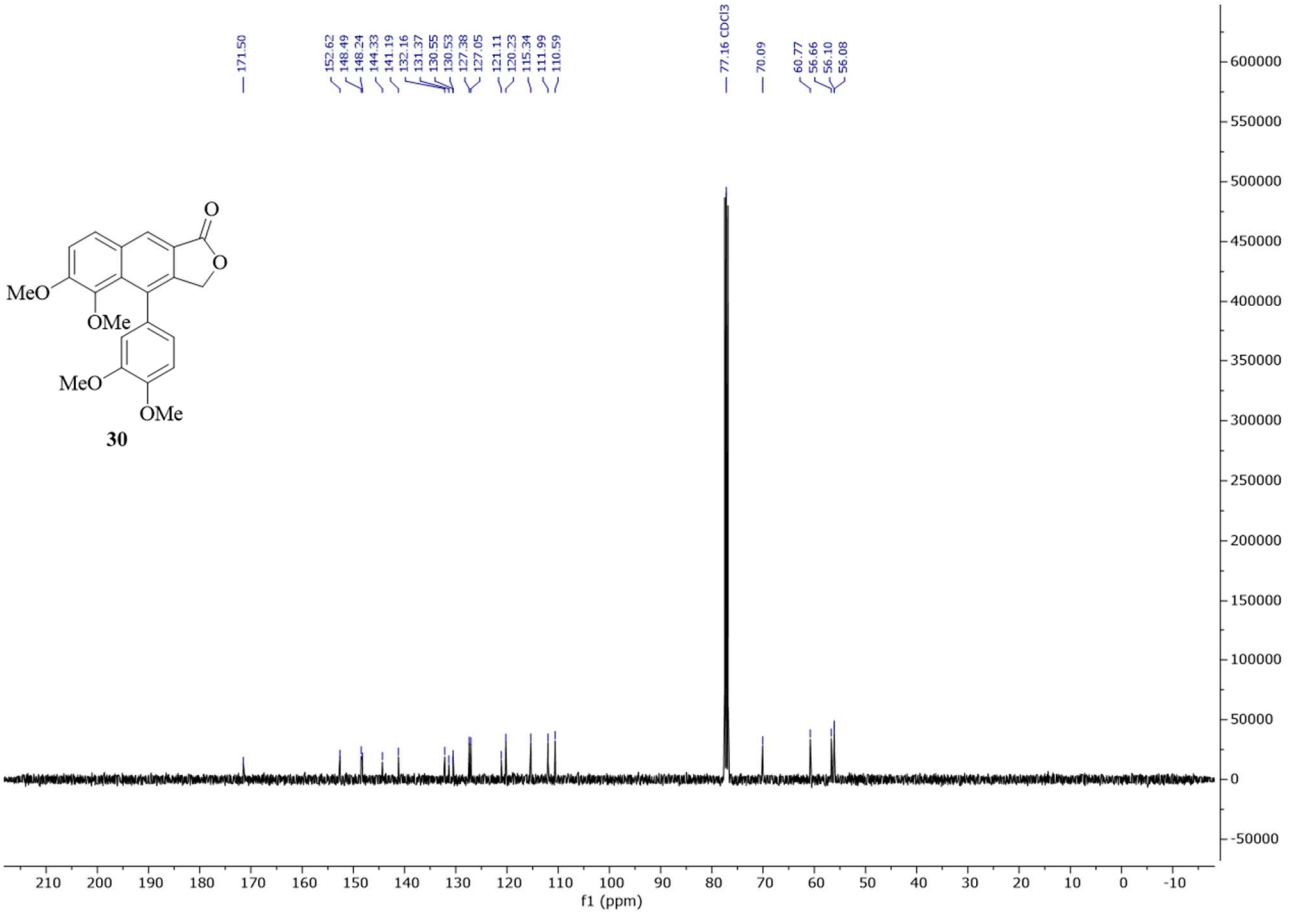

7.78
7.63
7.60
7.33
7.30
7.26 CDCl3
6.91
6.89
6.86
6.86
6.83
6.83
6.81
6.81
4.94
4.91
4.90
4.86
4.57
4.55
4.52
4.49
3.94
3.92
3.83
3.22
2.49
OH
OH
MeO
OMe
MeO
OMe
f1 (ppm)

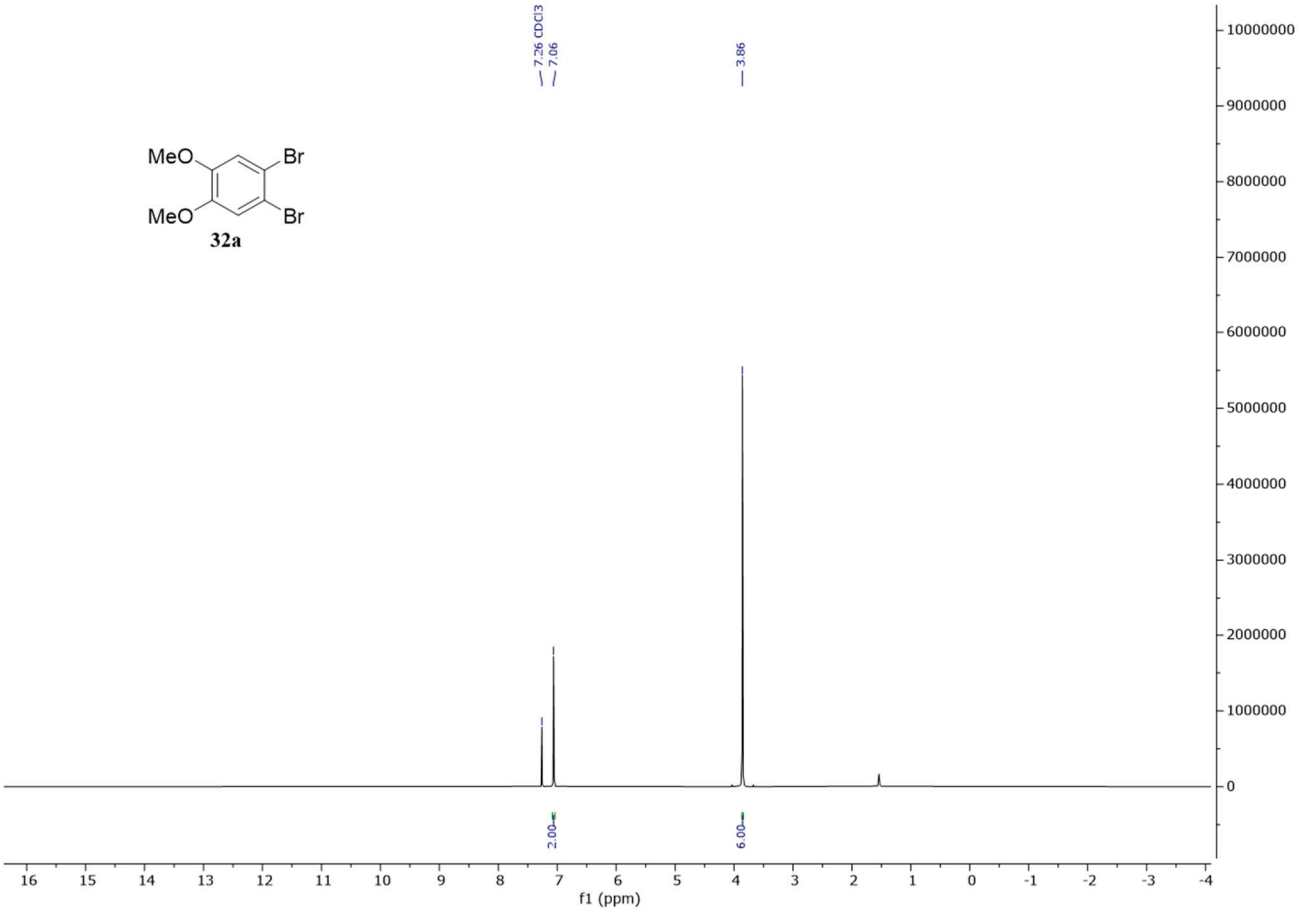
29

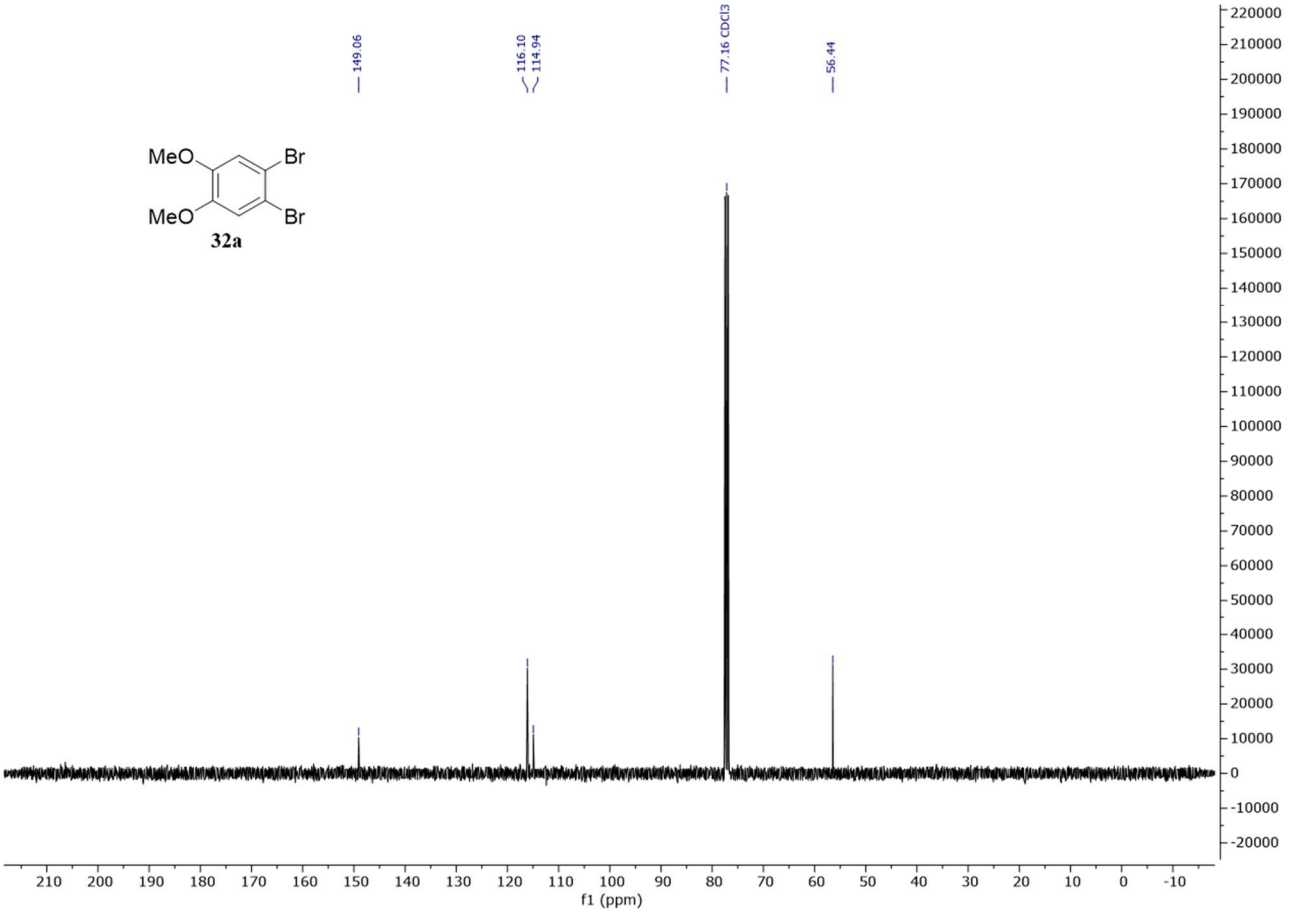

150.90
147.98
147.65
144.77
137.47
136.73
135.43
134.81
129.69
129.41
127.97
124.71
121.14
115.26
112.95
110.23
77.16 CDCl3
65.30
63.14
60.62
60.20
56.62
56.09
56.00
32.86
29.46
25.77
OH
OH
MeO
OMe
MeO
OMe
f1 (ppm)

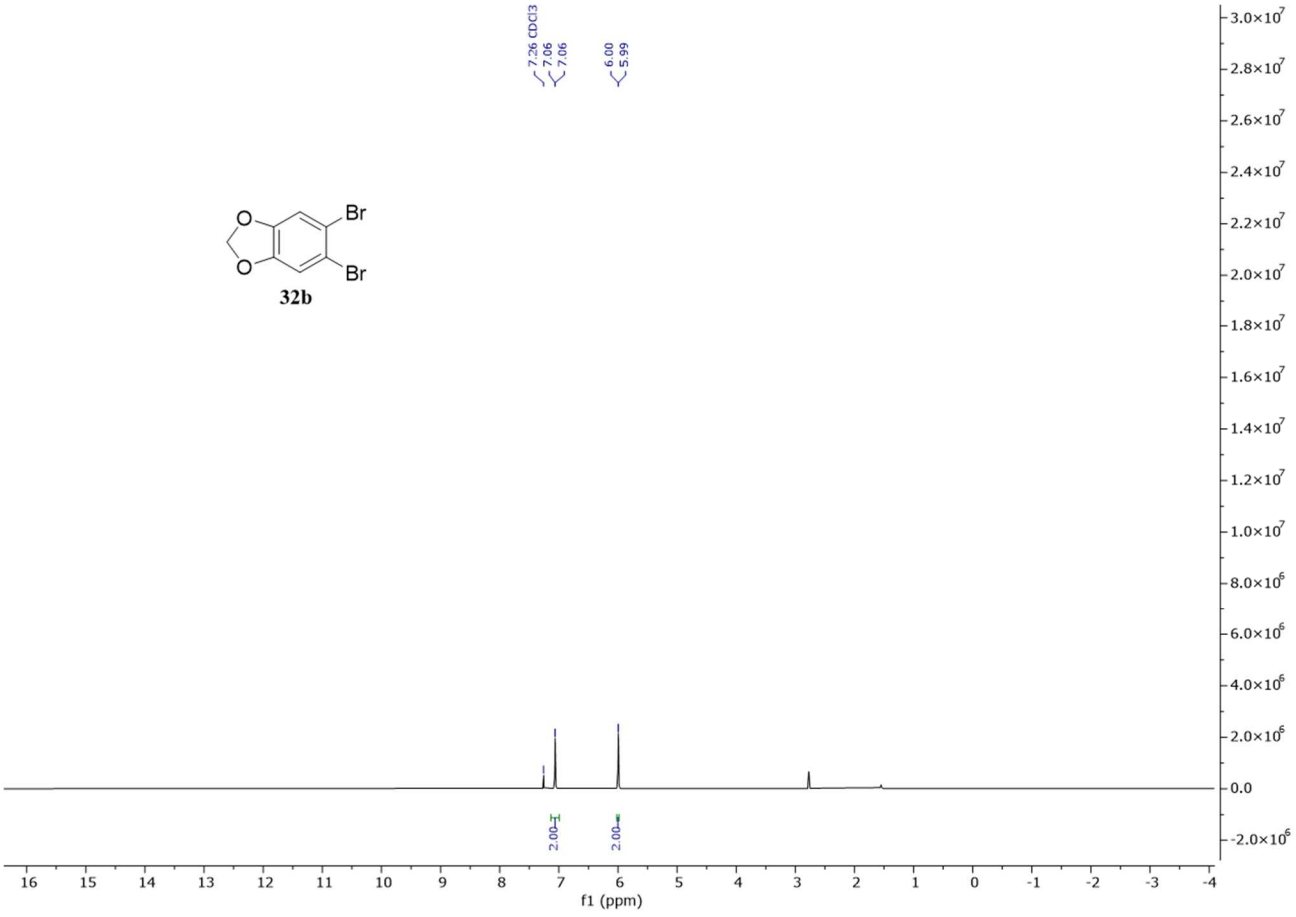
29

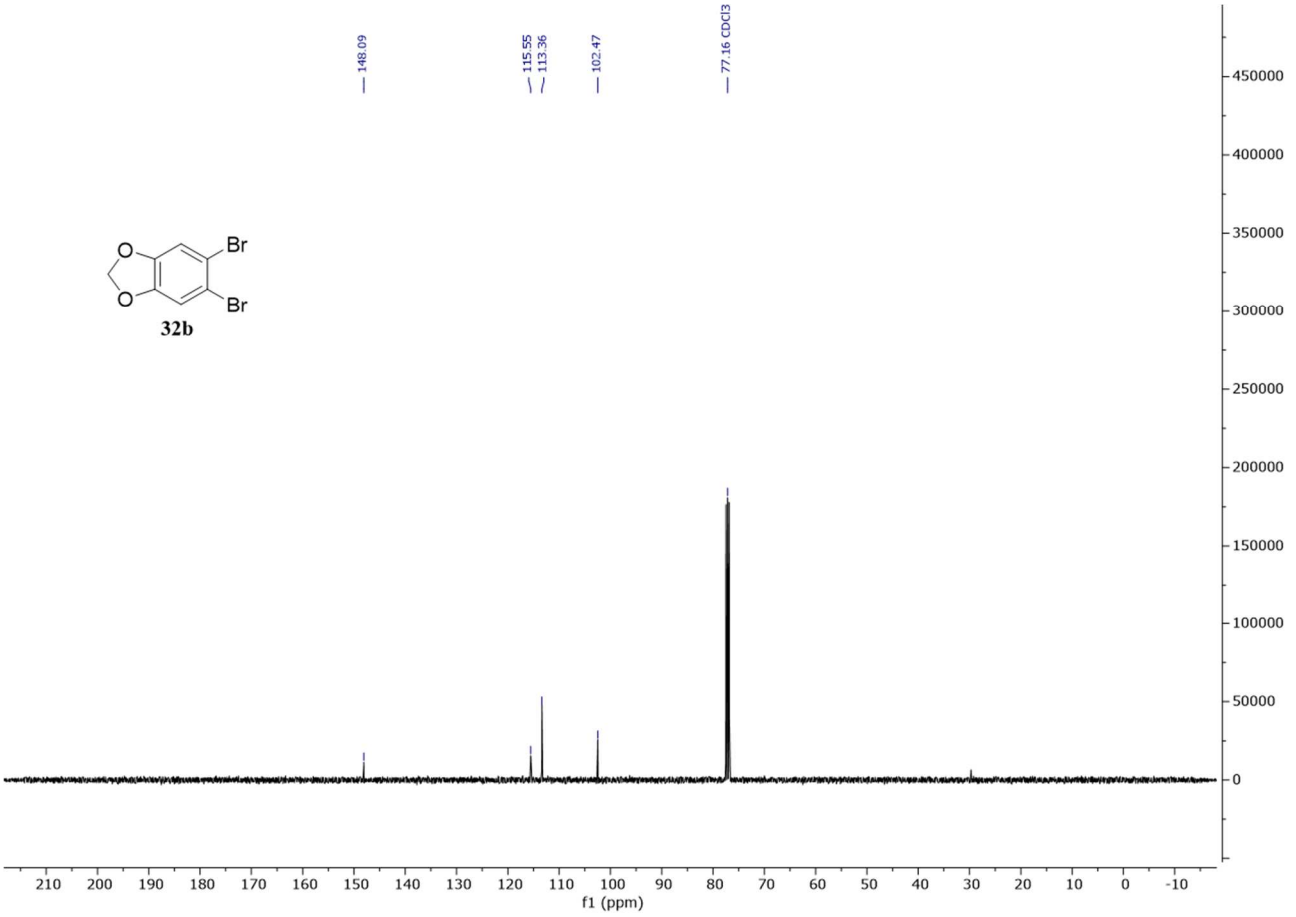

8.42
7.89
7.87
7.44
7.42
7.26 CDCl3
6.95
6.93
6.87
6.87
6.86
6.85
5.17
5.14
5.08
5.04
4.00
3.96
3.86
3.27
MeO
OMe
MeO
OMe
O
O
30
f1 (ppm)

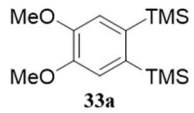

171.50
152.62
148.49
148.24
144.33
141.19
132.16
131.37
130.55
130.53
127.38
127.05
121.11
120.23
115.34
111.99
110.59
77.16 CDCl3
70.09
60.77
56.66
56.10
56.08
MeO
OMe
MeO
OMe
O
O
30
f1 (ppm)


7.26 CDCl3
7.06
3.86
MeO
Br
MeO
Br
32a
2.00
6.00
f1 (ppm)


149.06
116.10
114.94
77.16 CDCl3
56.44
MeO
Br
MeO
Br
32a
f1 (ppm)

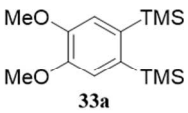

7.26 CDCl3
7.06
7.06
6.00
5.99
Br
Br
32b
2.00
2.00
f1 (ppm)


148.09
115.55
113.36
102.47
77.16 CDCl3
Br
Br
32b
f1 (ppm)


MeO
TMS
MeO
TMS

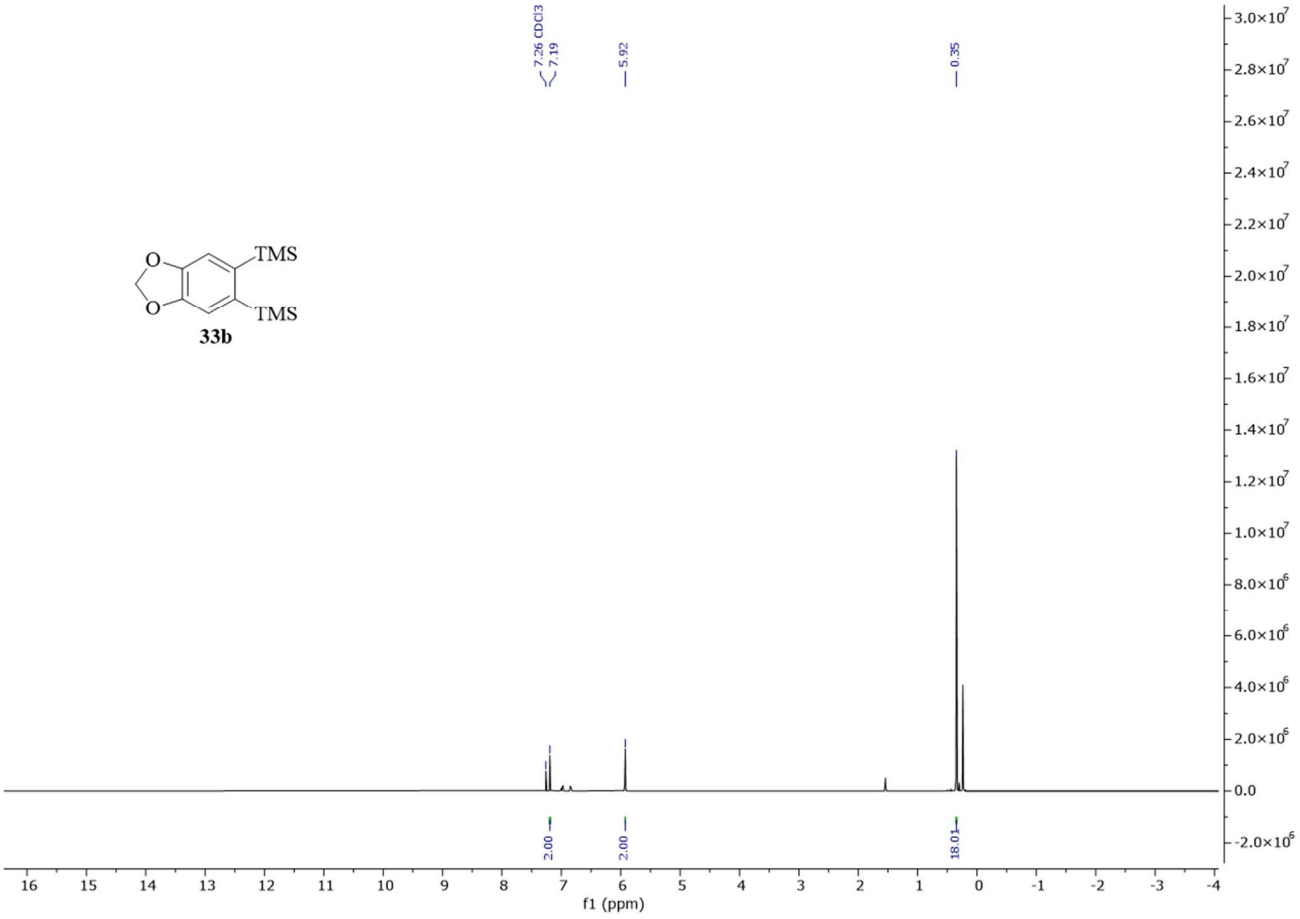
33a

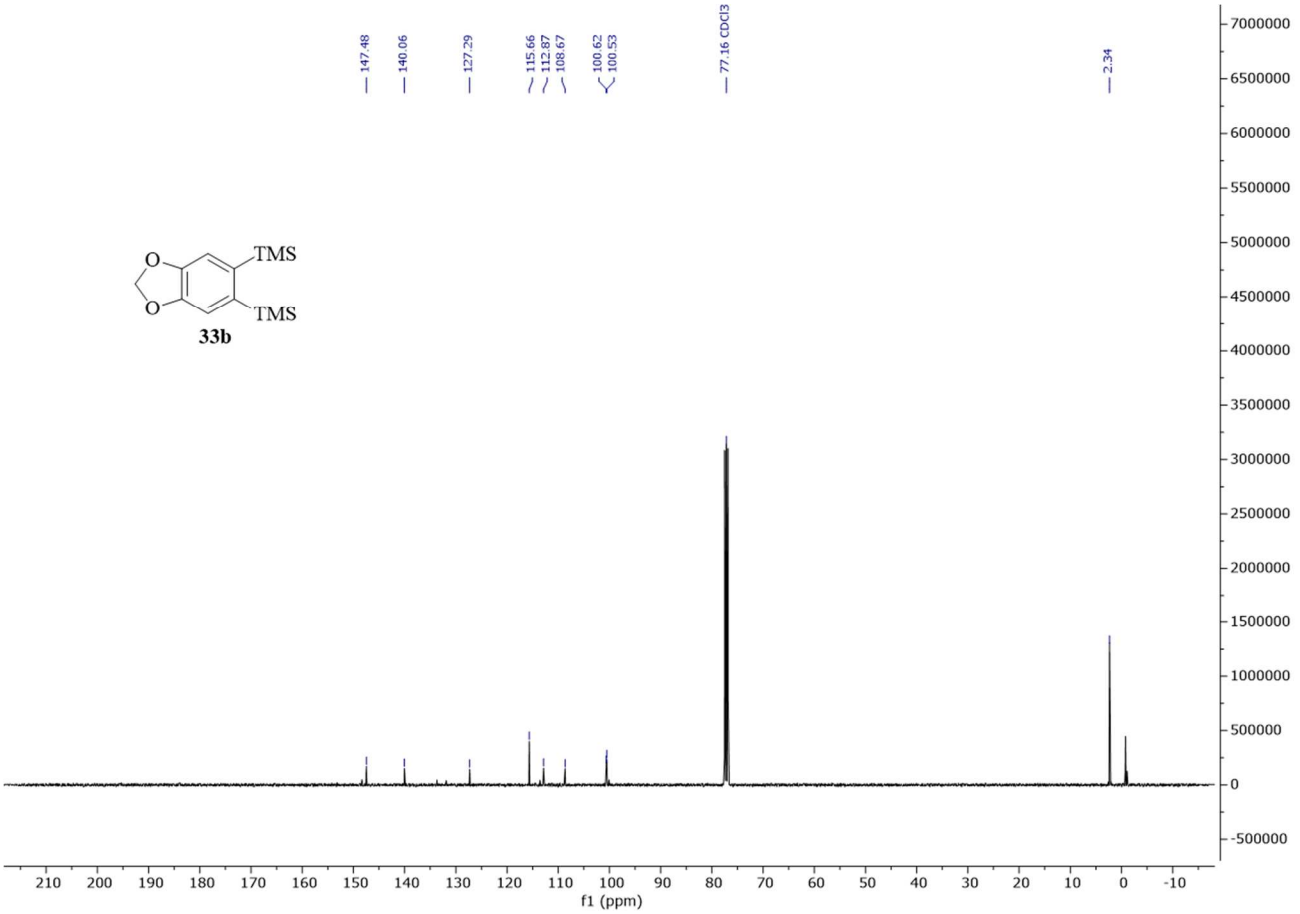
7.26 CDCl3
7.21
3.91
0.38
2.00
6.00
18.00
f1 (ppm)

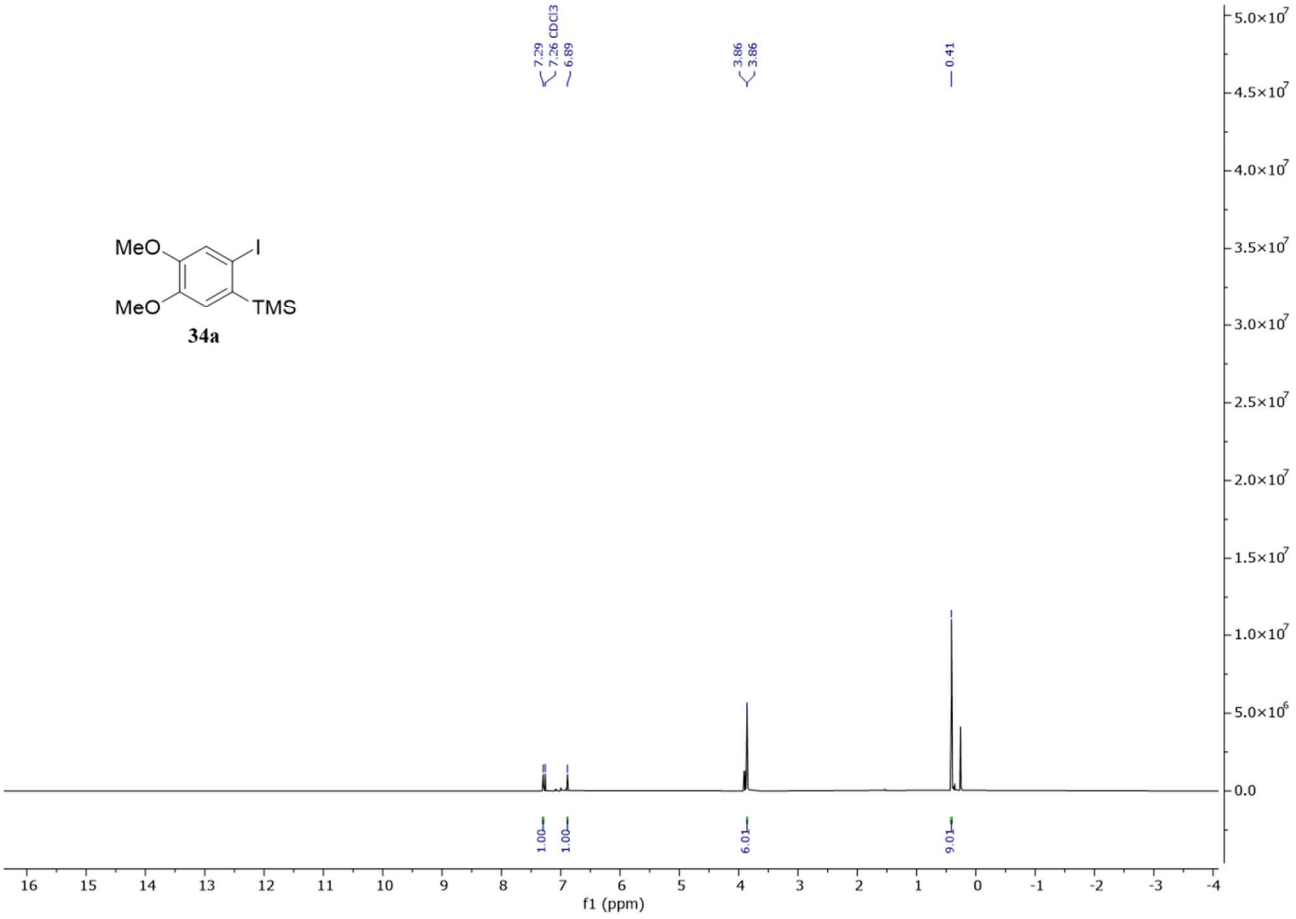

MeO
TMS
MeO
TMS

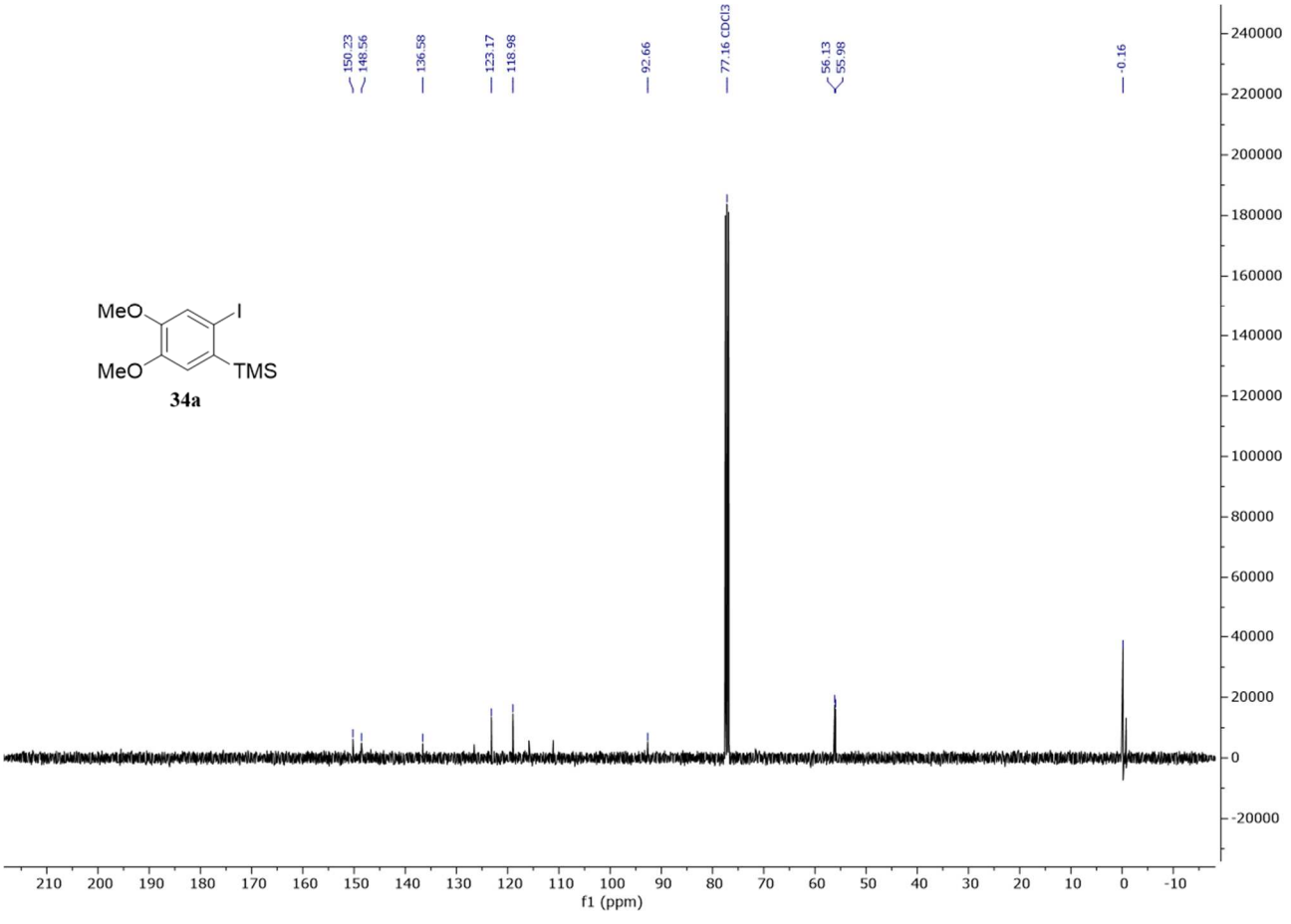
33a

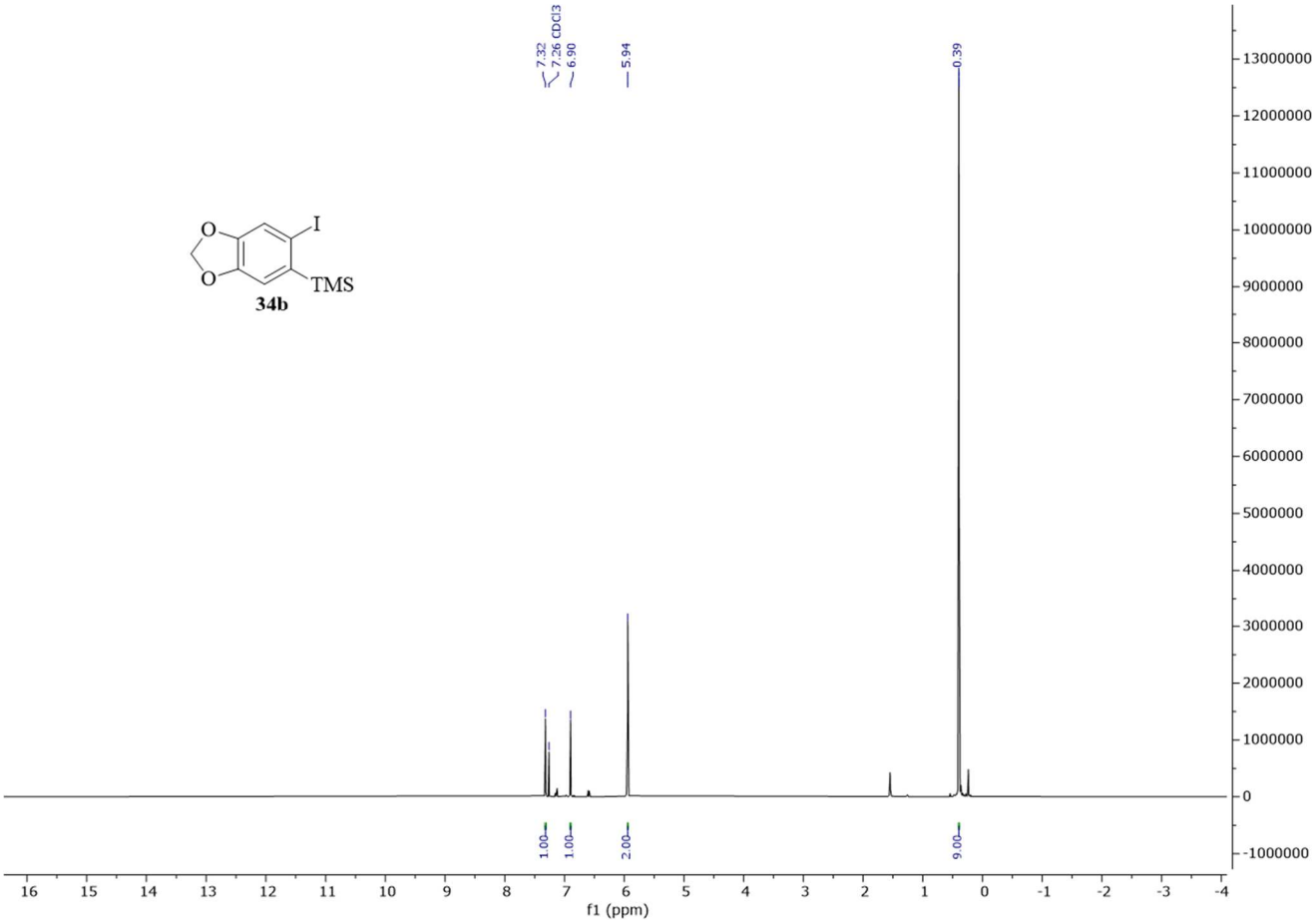
148.30
138.40
118.88
77.16 CDCl3
55.72
2.21
f1 (ppm)


7.26 CDCl3
7.19
5.92
0.35
TMS
TMS
33b
2.00
2.00
18.01
f1 (ppm)


147.48
140.06
127.29
115.66
112.87
108.67
100.62
100.53
77.16 CDCl3
2.34
TMS
TMS
33b
f1 (ppm)

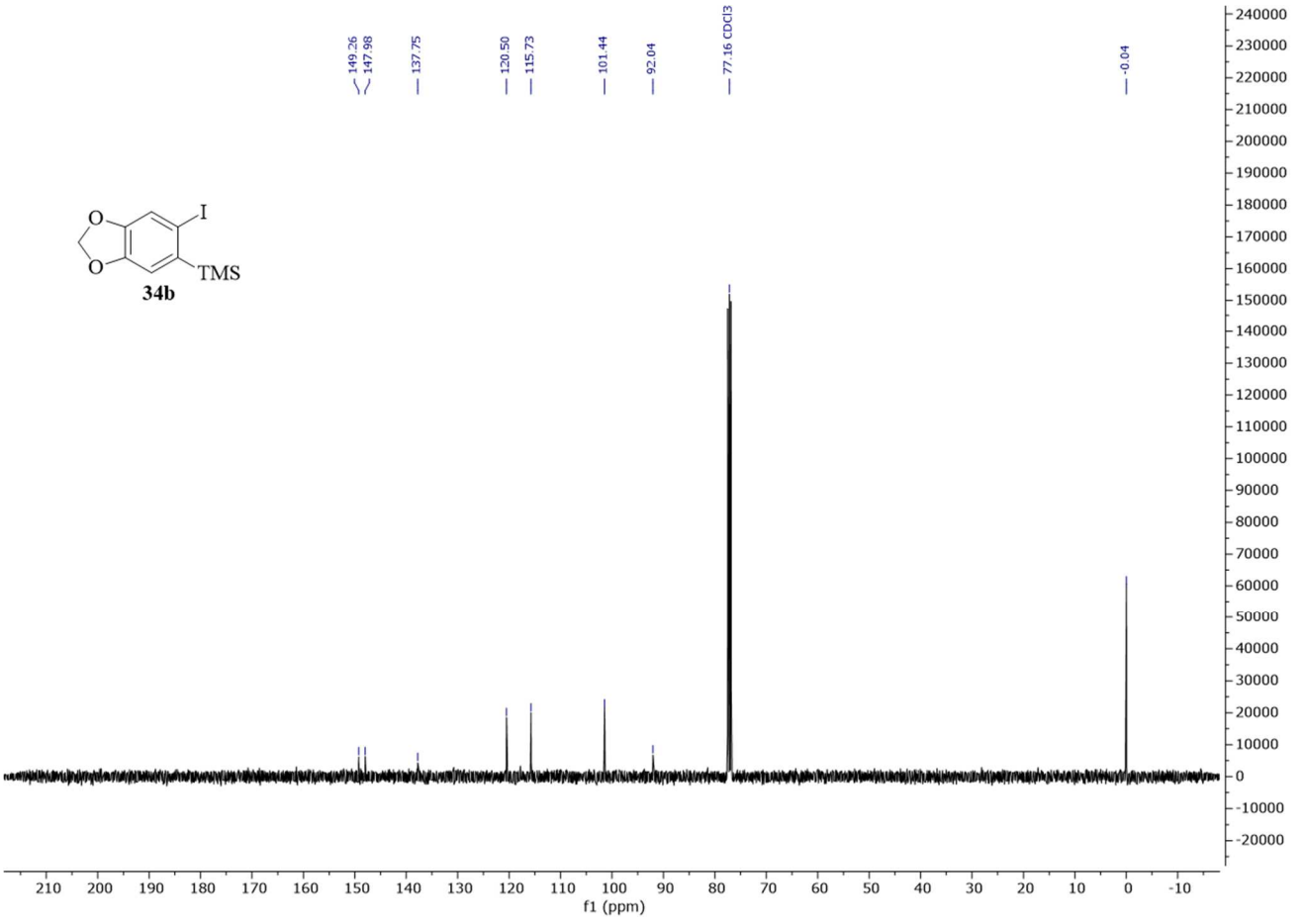

7.29
7.26 CDCl3
6.89
3.86
3.86
0.41
MeO
I
MeO
TMS
34a
1.00
1.00
6.01
9.01
f1 (ppm)


150.23
148.56
136.58
123.17
118.98
92.66
77.16 CDCl3
56.13
55.98
-0.16
MeO
I
MeO
TMS
34a
f1 (ppm)


7.32
7.26 CDCl3
6.90
5.94
0.39
1.00
1.00
2.00
9.00
f1 (ppm)

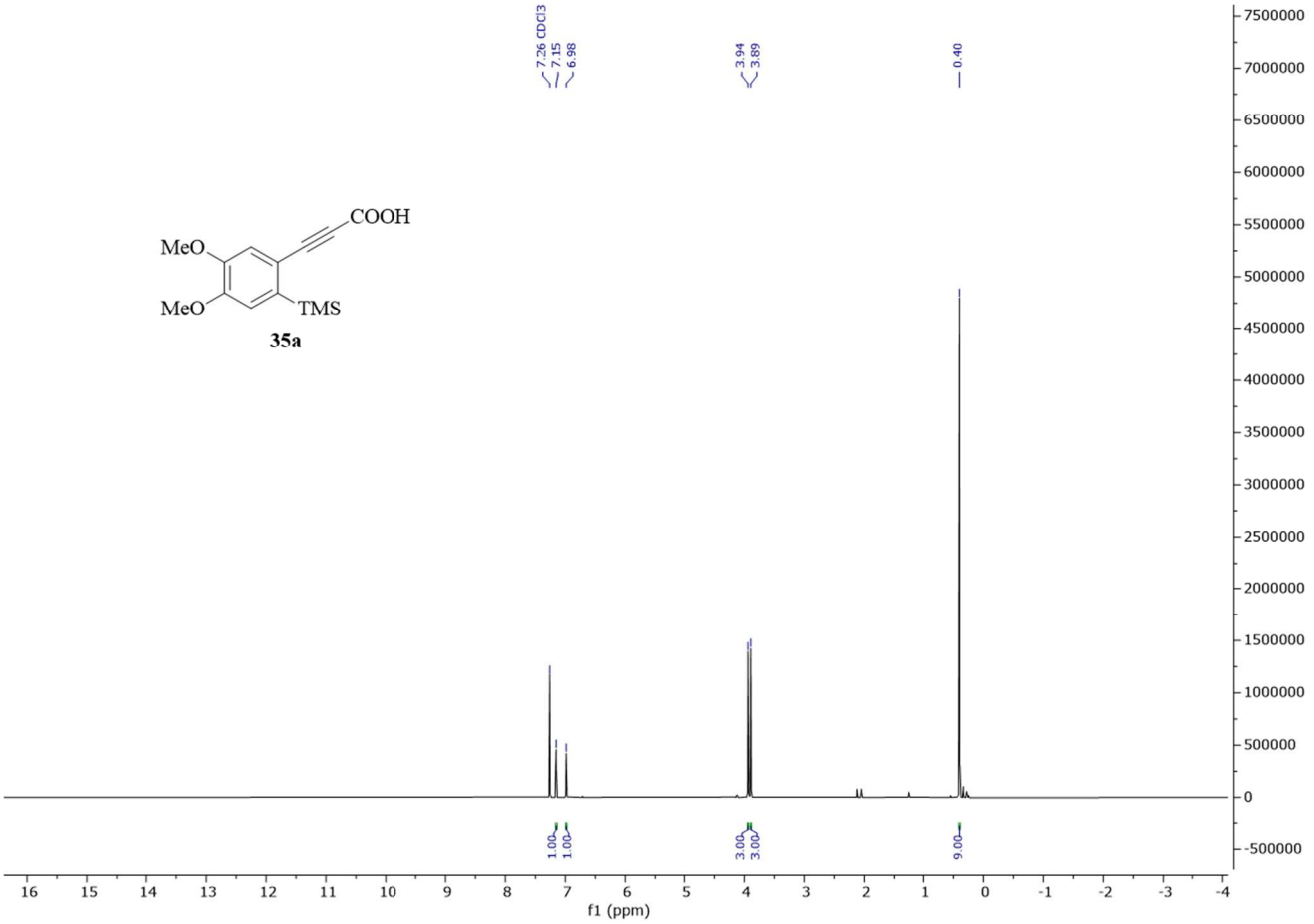
O
O
I
TMS

34b

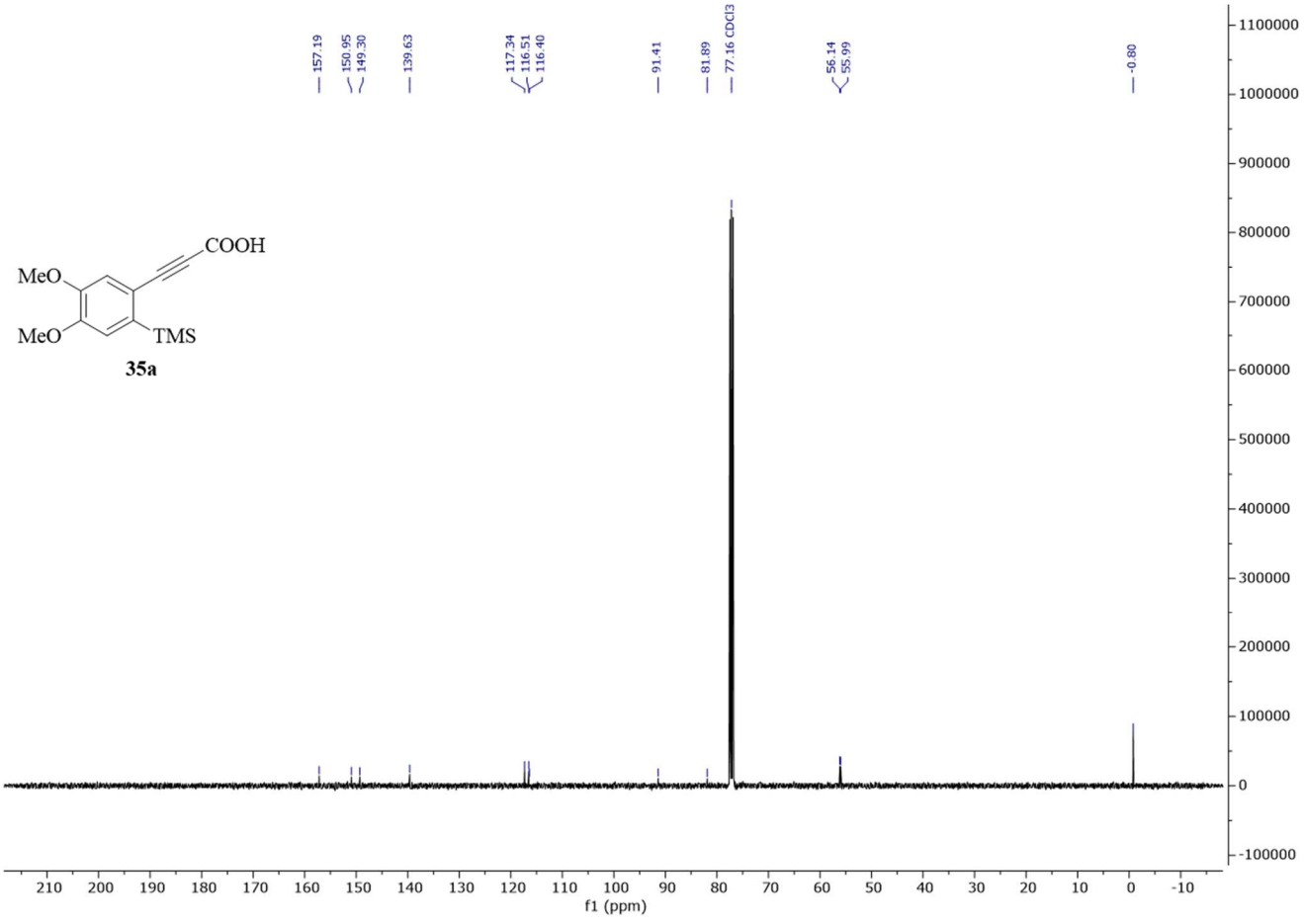

149.26
147.98
137.75
120.50
115.73
101.44
92.04
77.16 CDCl3
-0.04
f1 (ppm)

O
O
I
TMS

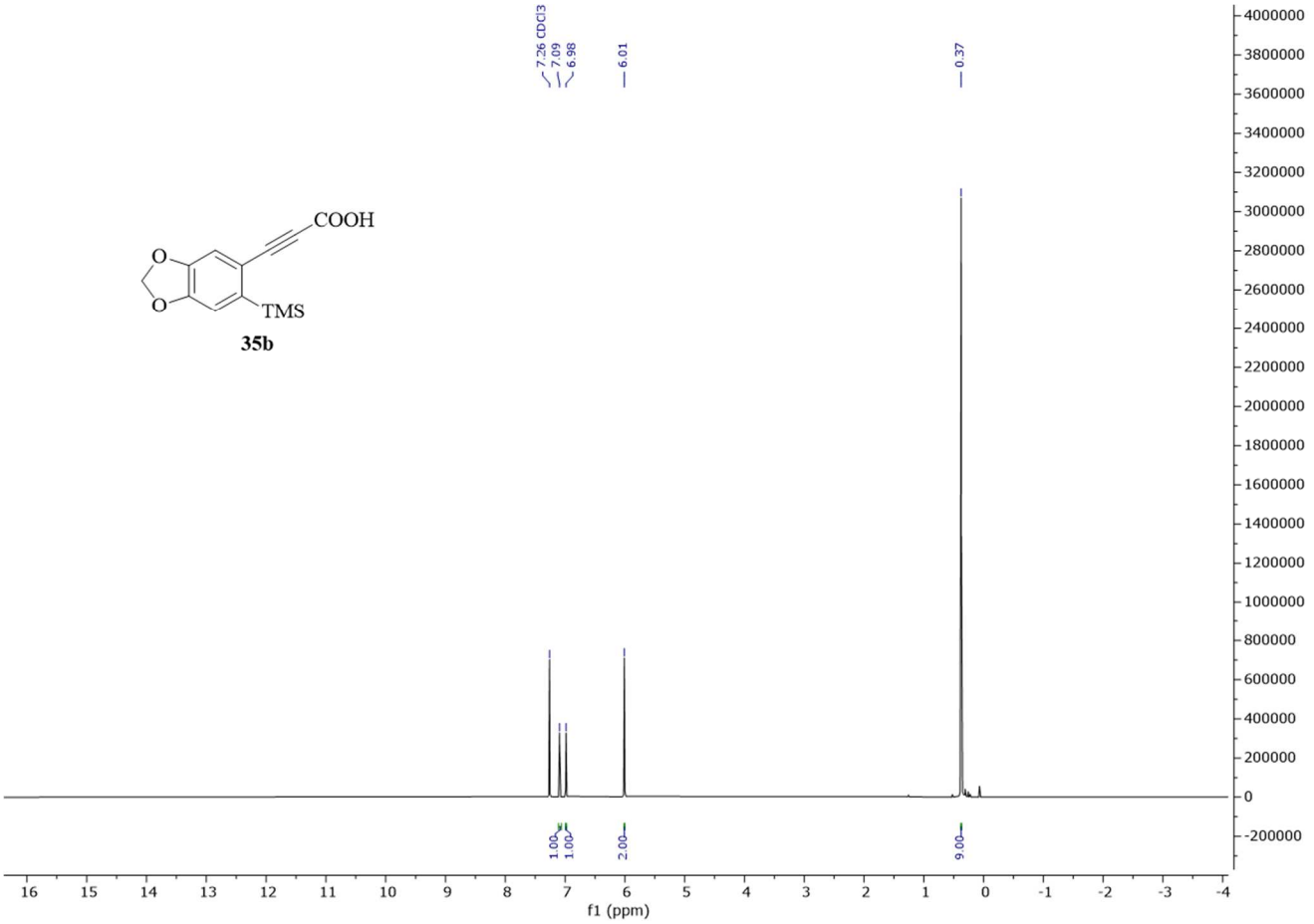
34b

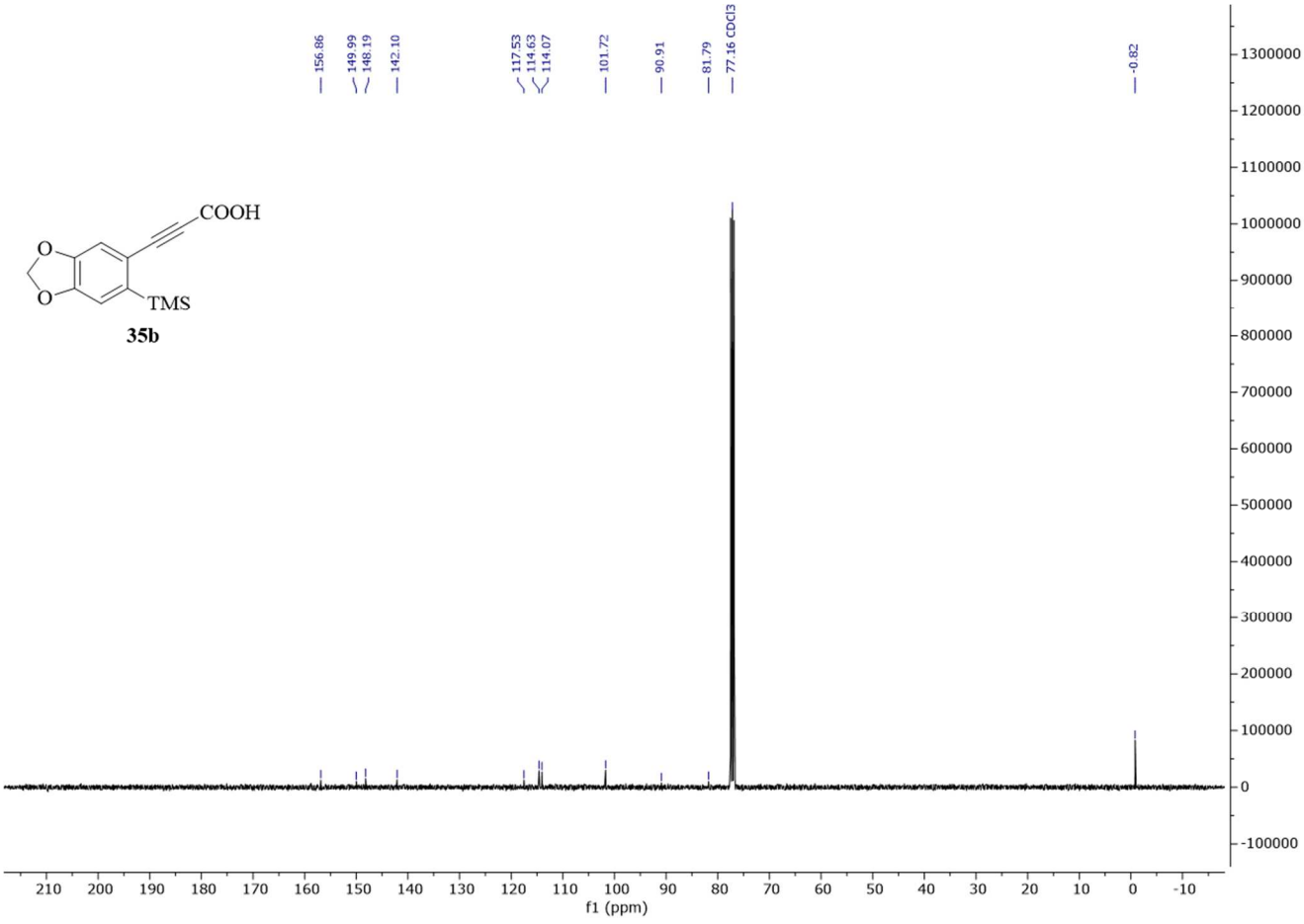

7.26 CDCl3
7.15
6.98
3.94
3.89
0.40
COOH
MeO
MeO
TMS
1.00
1.00
3.00
3.00
9.00
f1 (ppm)

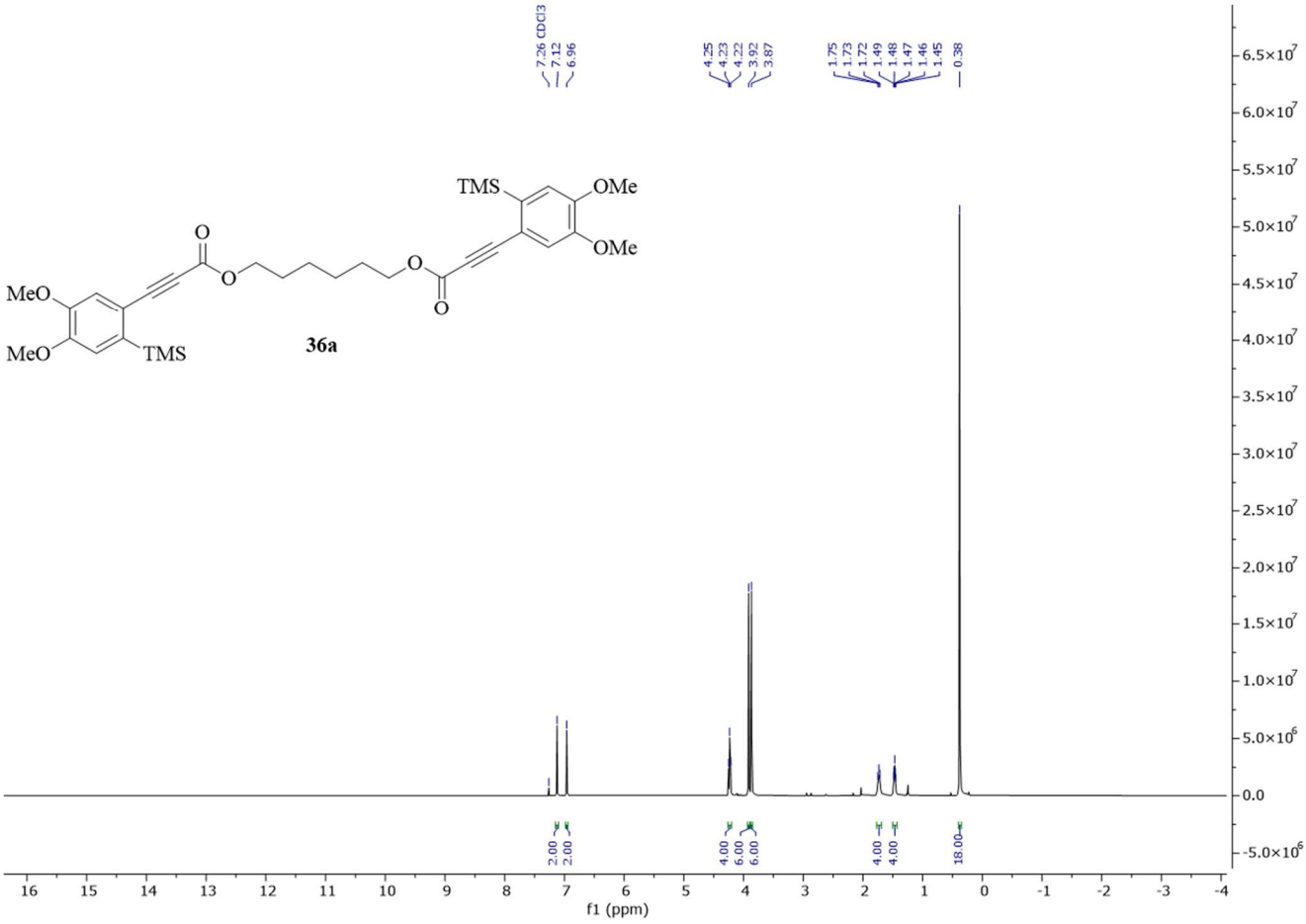
35a


157.19
150.95
149.30
139.63
117.34
116.51
116.40
91.41
81.89
77.16 CDCl3
56.14
55.99
-0.80
COOH
MeO
MeO
TMS
f1 (ppm)

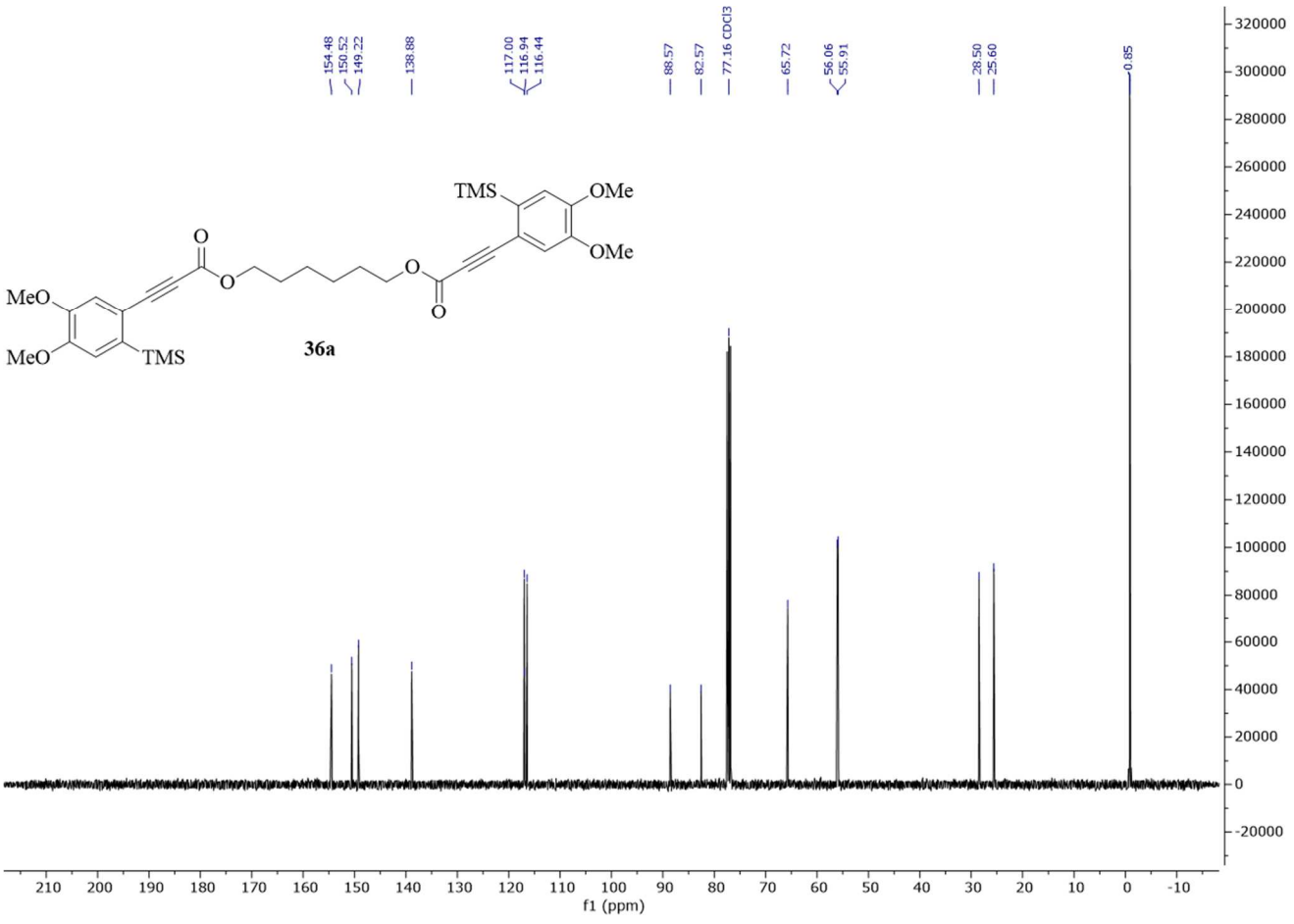
35a


7.26 CDCl3
7.09
6.98
6.01
0.37
COOH
O
O
TMS
35b
1.00
1.00
2.00
9.00
f1 (ppm)

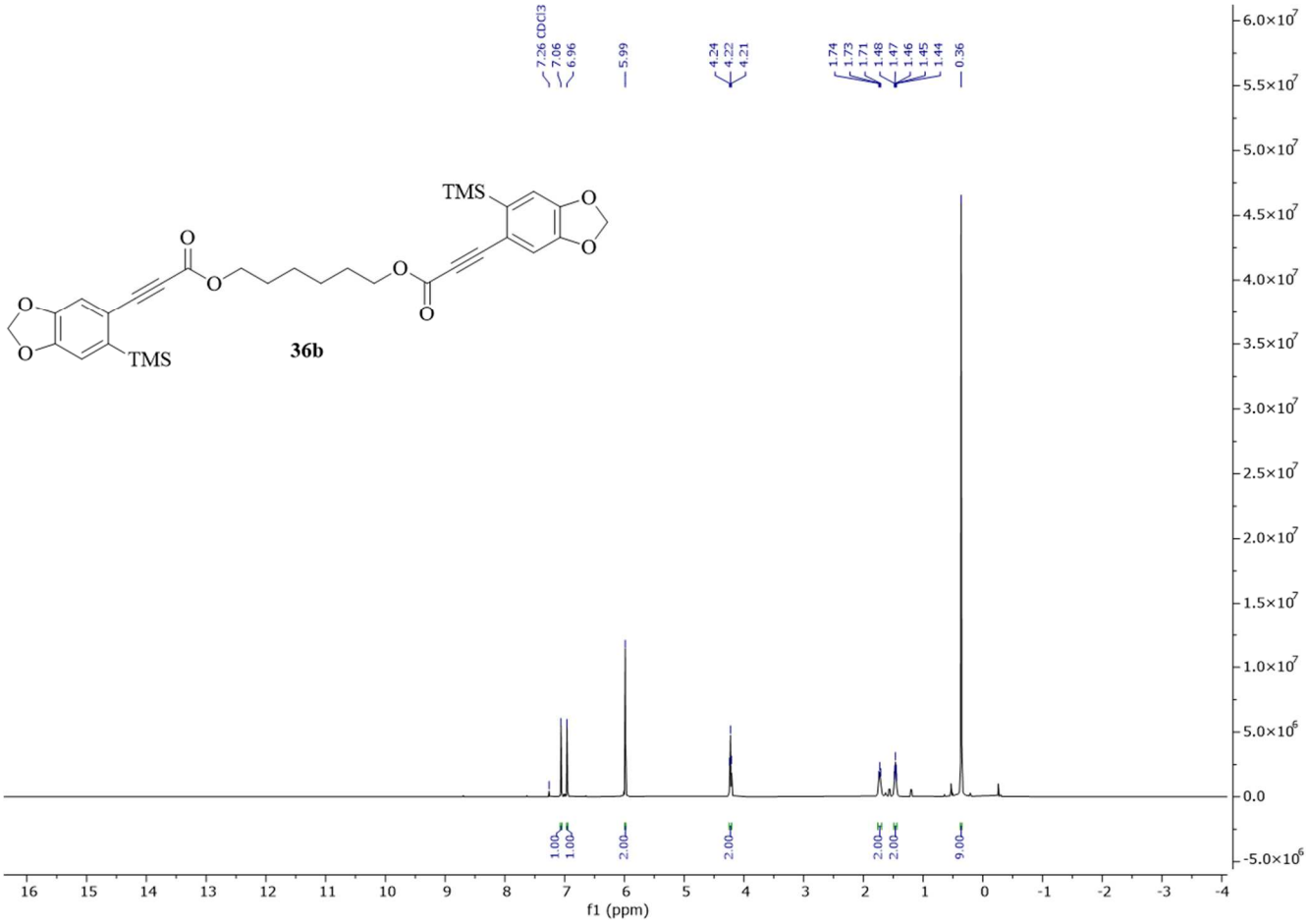

156.86
149.99
148.19
142.10
117.53
114.63
114.07
101.72
90.91
81.79
77.16 CDCl3
-0.82
COOH
O
O
TMS
35b
f1 (ppm)

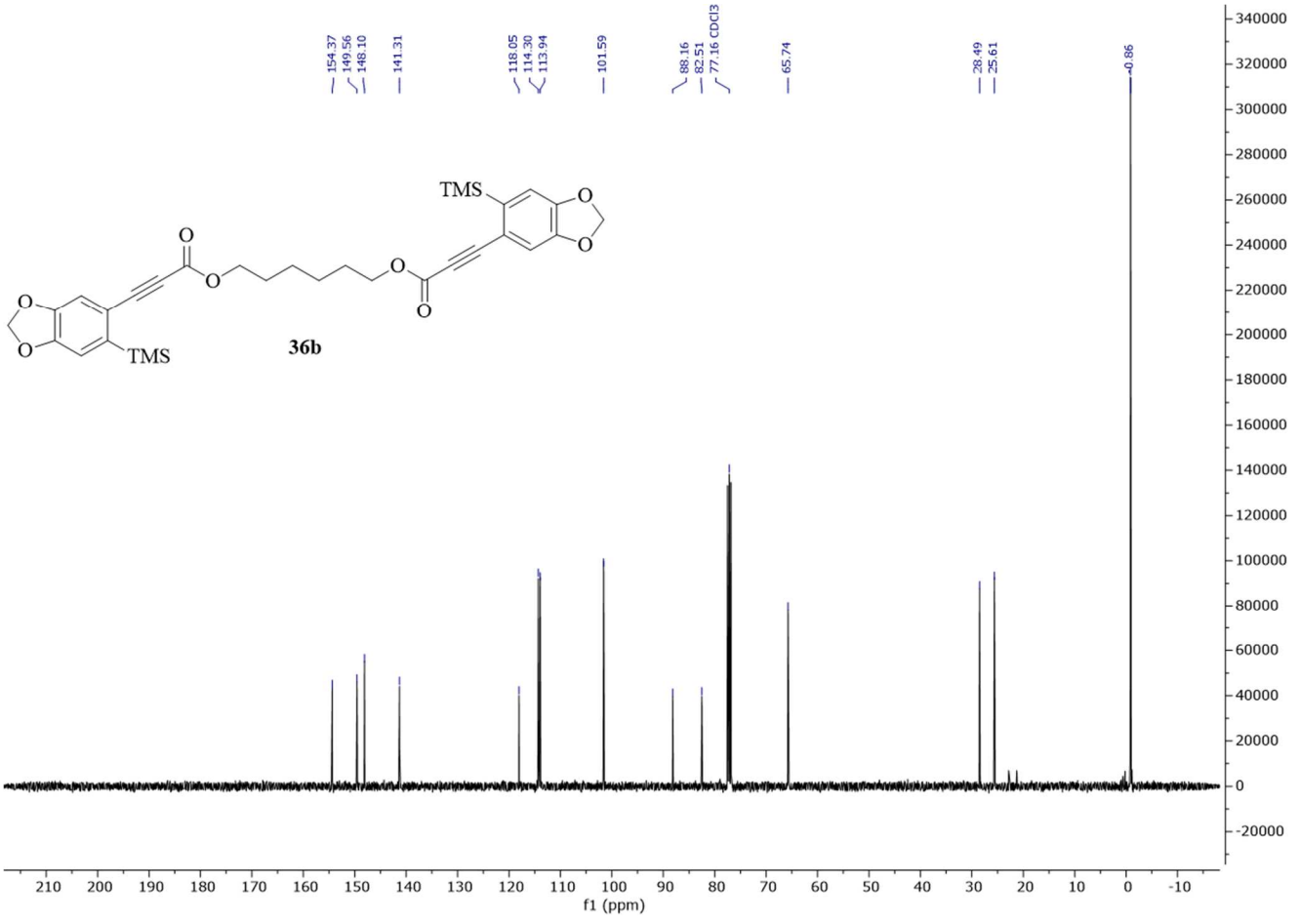

7.26 CDCl3
7.12
6.96
4.25
4.23
4.22
3.92
3.87
1.75
1.73
1.72
1.49
1.48
1.47
1.46
1.45
0.38
TMS
OMe
OMe
MeO
MeO
TMS
O
O
O
O
2.00
2.00
4.00
6.00
6.00
4.00
4.00
18.00
f1 (ppm)

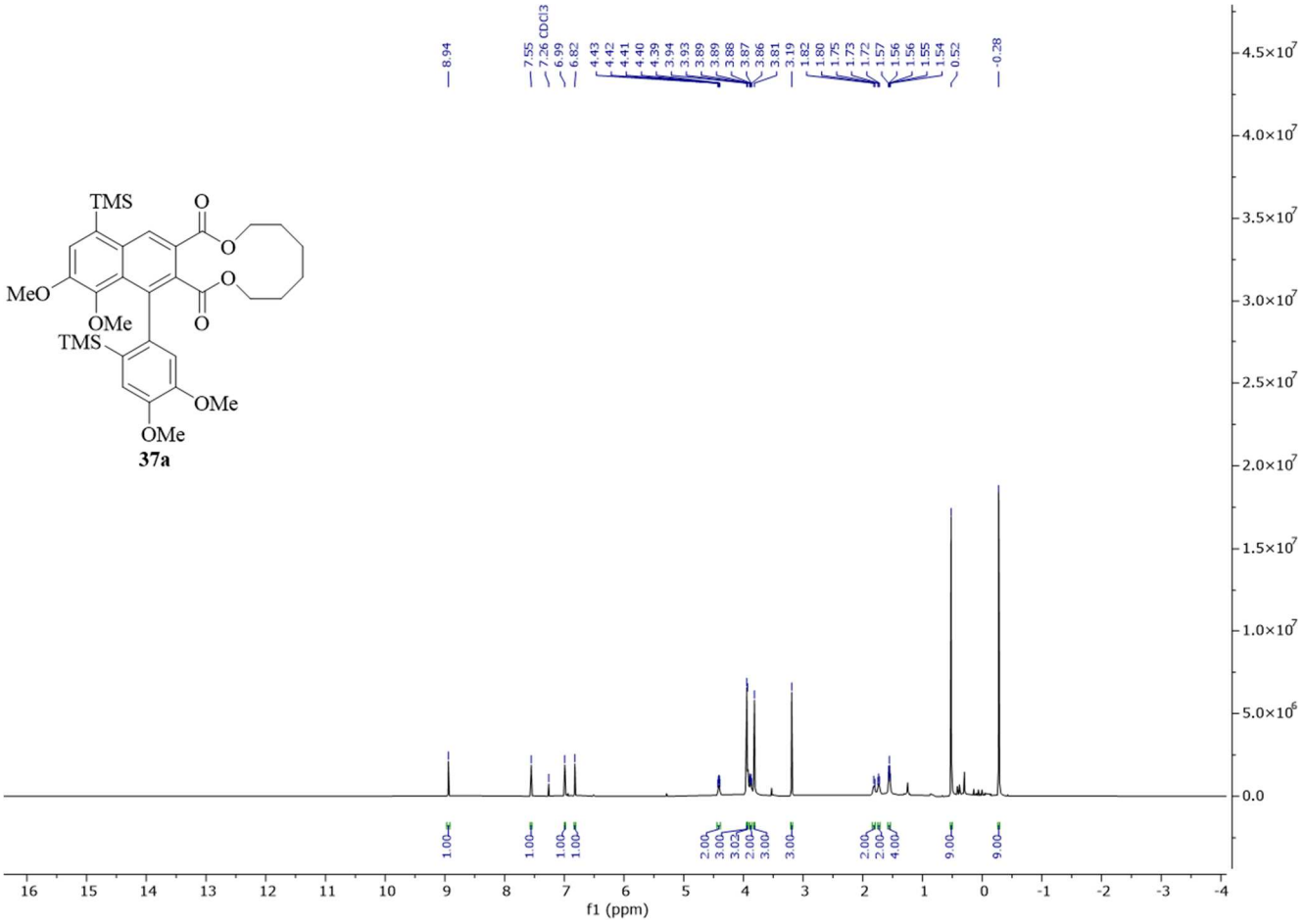
36a


154.48
150.52
149.22
138.88
117.00
116.94
116.44
88.57
82.57
77.16 CDCl3
65.72
56.06
55.91
28.50
25.60
0.85
TMS
OMe
OMe
MeO
MeO
TMS
O
O
O
O
f1 (ppm)

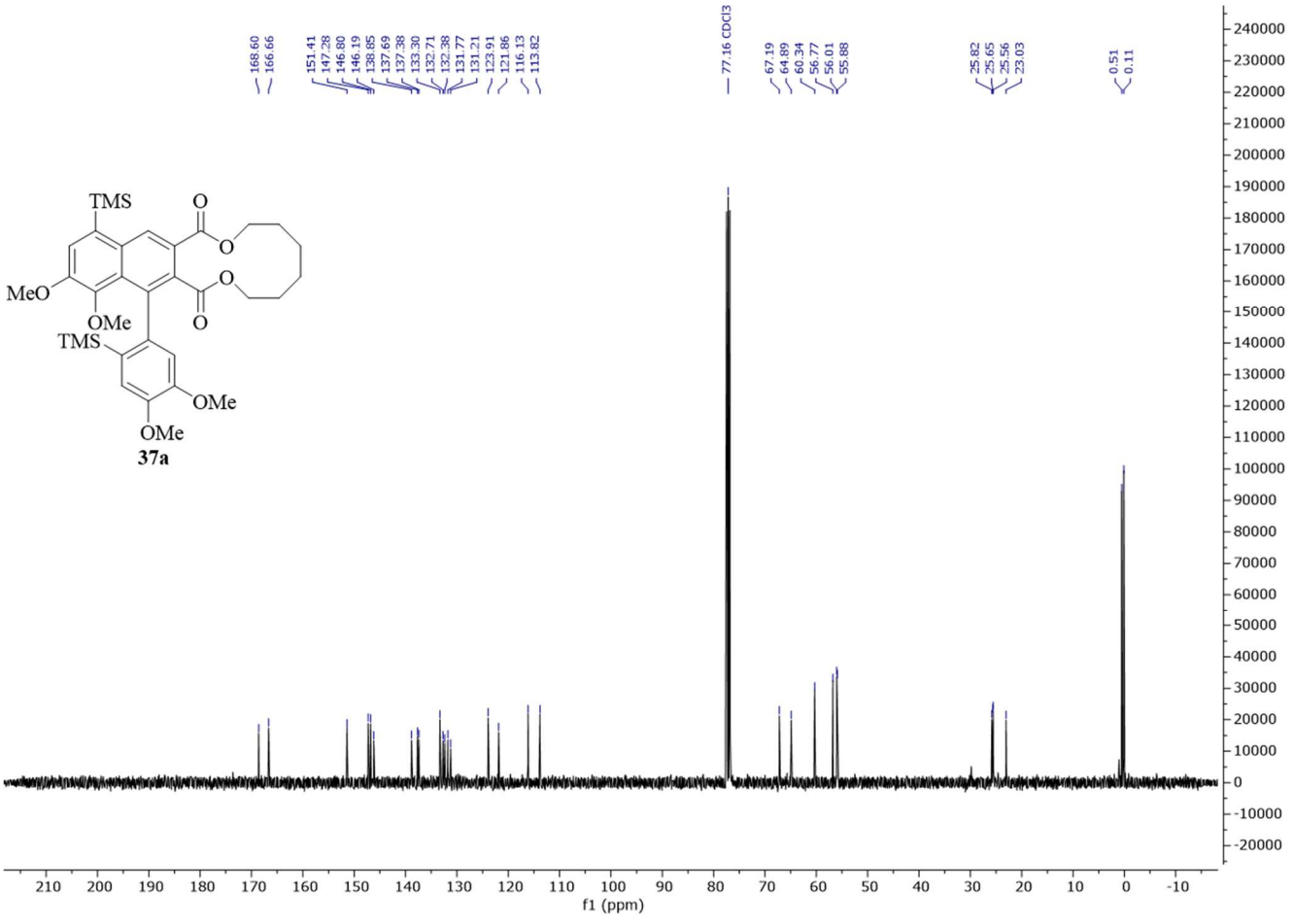
36a


7.26 CDCl3
7.06
6.96
5.99
4.24
4.22
4.21
1.74
1.73
1.71
1.48
1.47
1.46
1.45
1.44
0.36
TMS
TMS
36b
1.00
1.00
2.00
2.00
2.00
2.00
9.00
f1 (ppm)

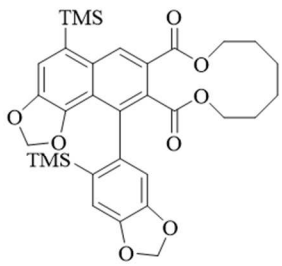

154.37
149.56
148.10
141.31
118.05
114.30
113.94
101.59
88.16
82.51
77.16 CDCl3
65.74
28.49
25.61
0.86
TMS
TMS
36b
f1 (ppm)


8.94
7.55
7.26 CDCl3
6.99
6.82
4.43
4.42
4.41
4.40
4.39
3.94
3.93
3.89
3.89
3.88
3.87
3.86
3.81
3.19
1.82
1.80
1.75
1.73
1.72
1.57
1.56
1.56
1.55
1.54
0.52
-0.28
TMS
O
O
MeO
O
OMe
TMS
O
OMe
OMe
f1 (ppm)

37a

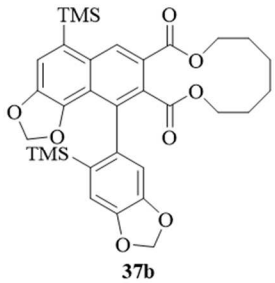

168.60
166.66
151.41
147.28
146.80
146.19
138.85
137.69
137.38
133.30
132.71
132.38
131.77
131.21
123.91
121.86
116.13
113.82
77.16 CDCl3
67.19
64.89
60.34
56.77
56.01
55.88
25.82
25.65
25.56
23.03
0.51
0.11
TMS
O
O
MeO
O
OMe
TMS
O
OMe
OMe
f1 (ppm)

37a


TMS
TMS

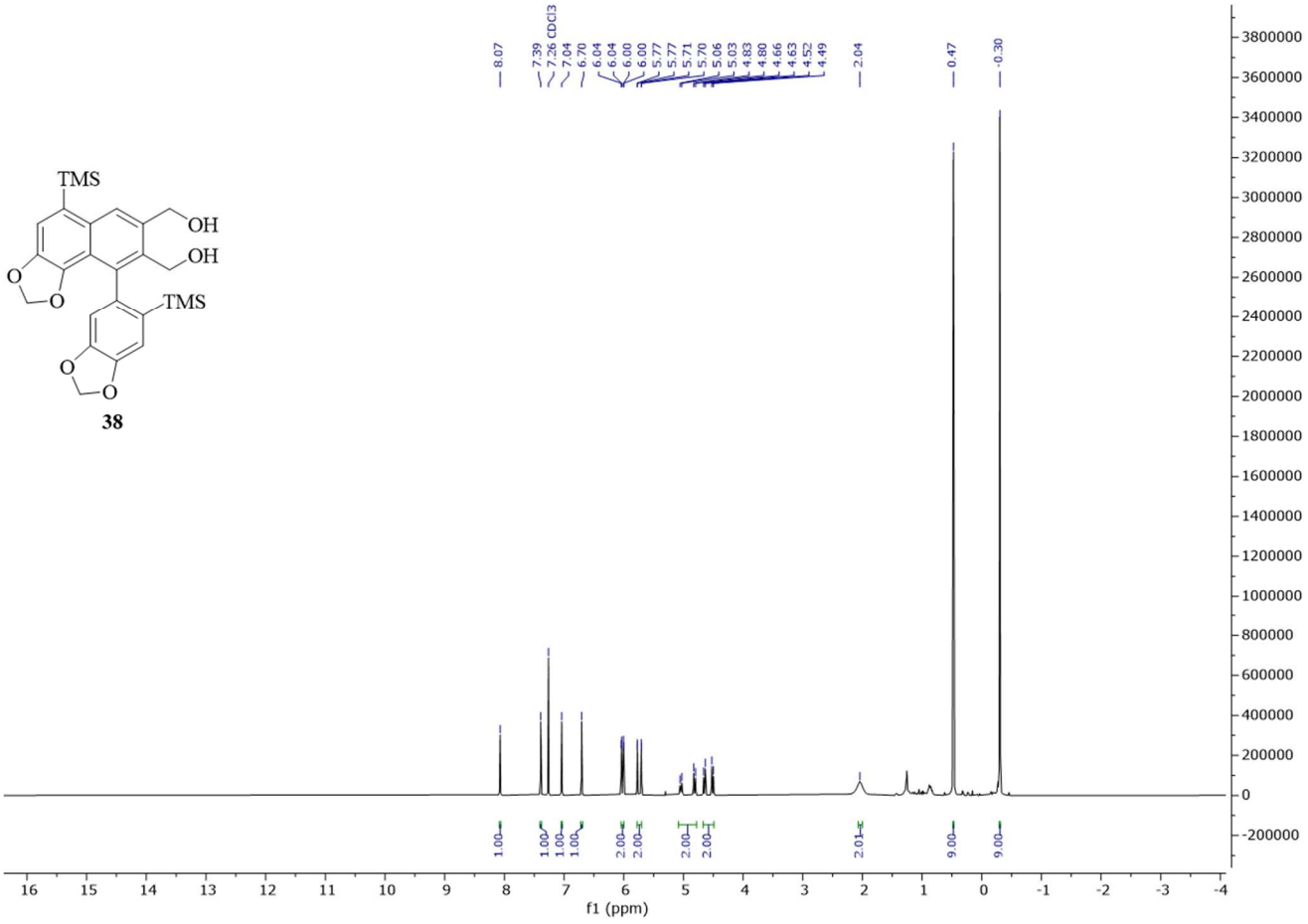
37b

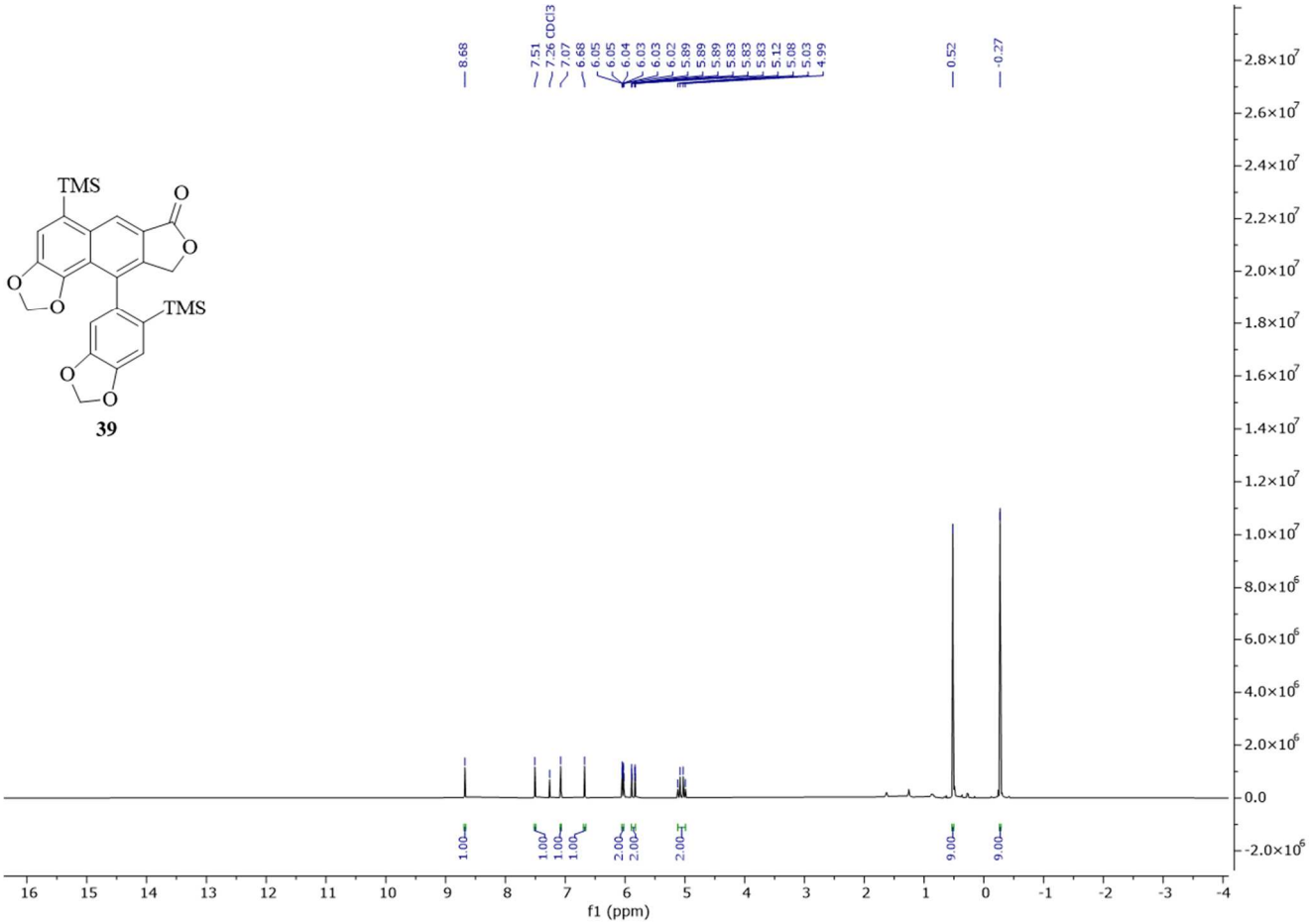
8.95
7.46
7.26 CDCl3
6.97
6.69
6.00
5.98
5.83
5.77
4.43
4.09
3.96
1.83
1.76
1.57
0.50
-0.27
1.00
1.00
1.00
2.00
2.00
2.00
2.00
4.00
4.00
9.00
9.00
f1 (ppm)

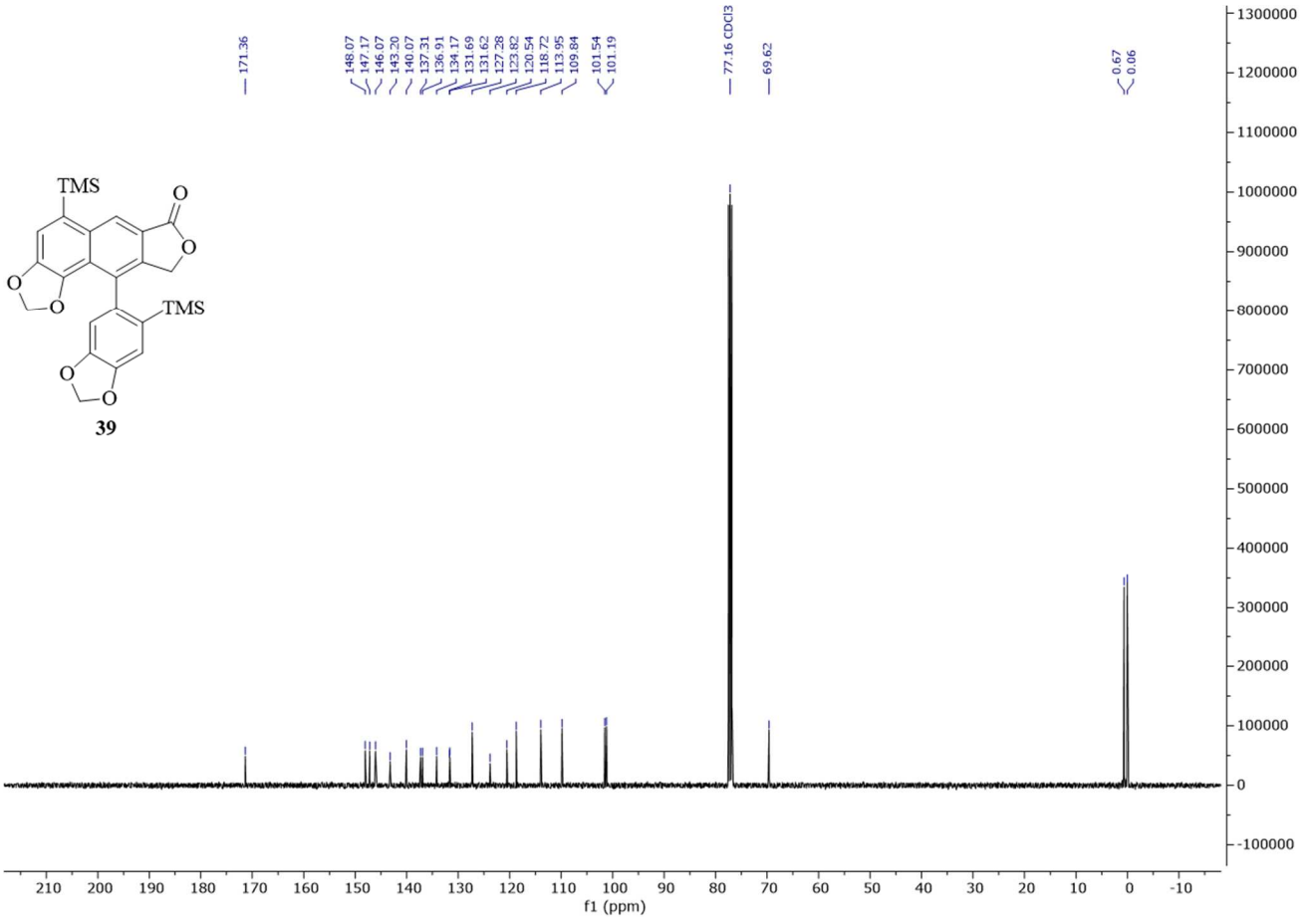

TMS
TMS

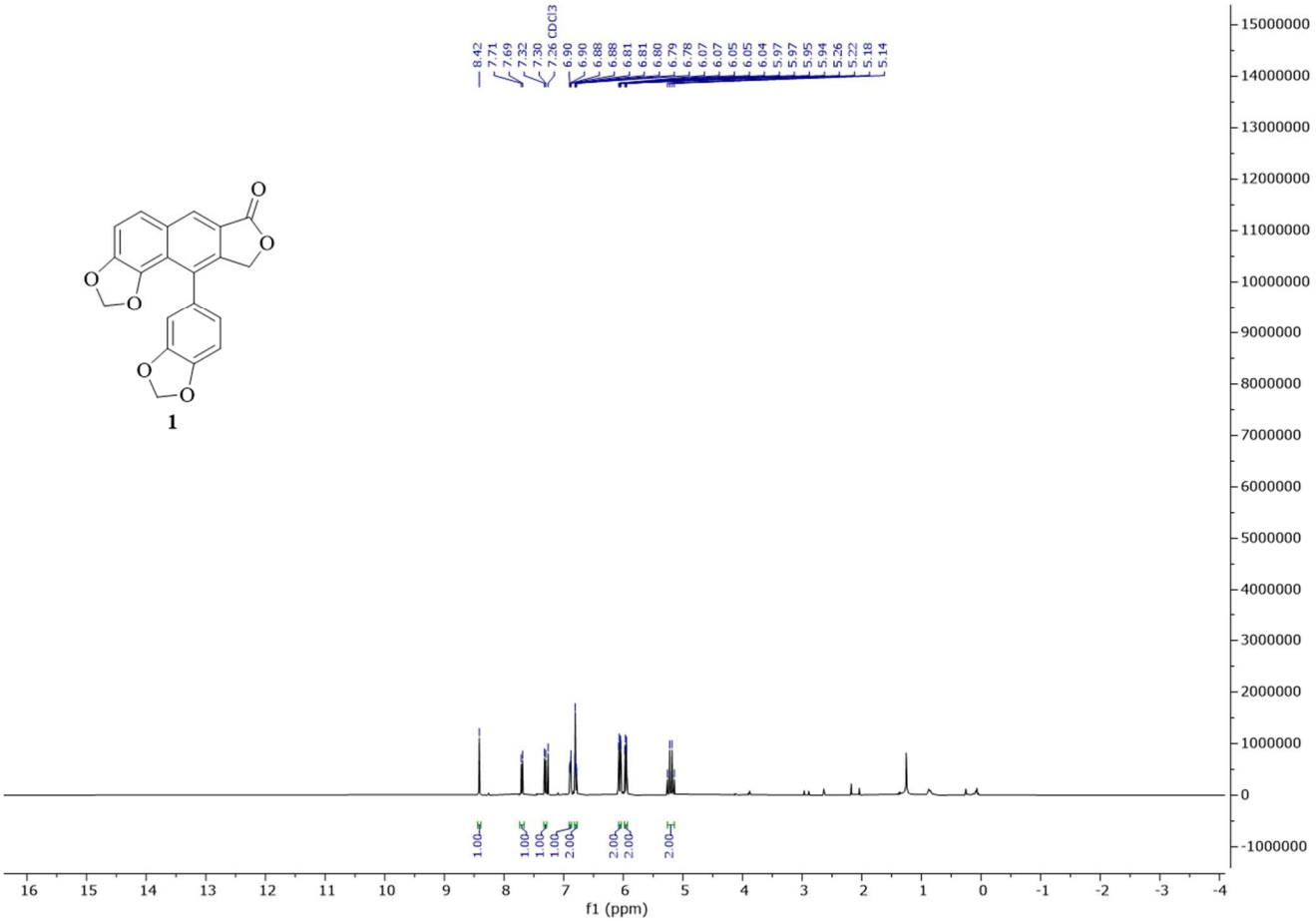
37b

168.24
166.71
146.78
146.29
143.42
137.10
136.05
135.94
133.80
133.55
132.66
131.24
122.56
122.06
118.84
112.79
111.29
101.45
100.85
77.16 CDCl3
67.15
65.14
25.82
25.61
23.13
0.56
0.10
f1 (ppm)

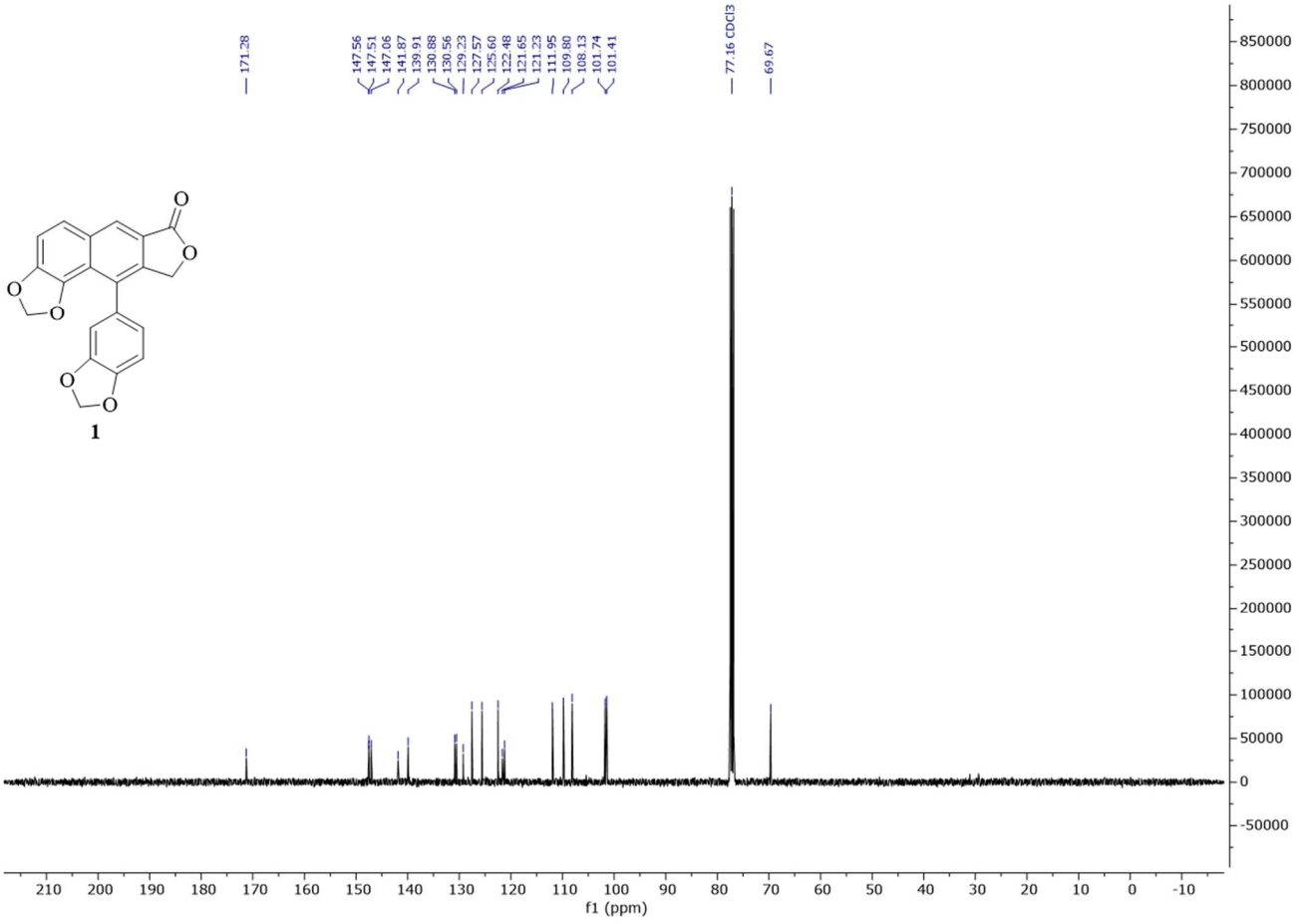

TMS
OH
OH
TMS
O
O
O
O
38
8.07
7.39
7.26 CDCl3
7.04
6.70
6.04
6.04
6.00
6.00
5.77
5.77
5.71
5.70
5.06
5.03
4.83
4.80
4.66
4.63
4.52
4.49
2.04
0.47
-0.30
1.00
1.00
1.00
1.00
2.00
2.00
2.00
2.00
2.01
9.00
9.00
f1 (ppm)


TMS
O
O
O
O
TMS
O
O
39
8.68
7.51
7.26 CDCl3
7.07
6.68
6.05
6.05
6.04
6.03
6.03
6.02
5.89
5.89
5.89
5.83
5.83
5.83
5.12
5.08
5.03
4.99
0.52
-0.27
1.00
1.00
1.00
1.00
2.00
2.00
2.00
9.00
9.00
f1 (ppm)

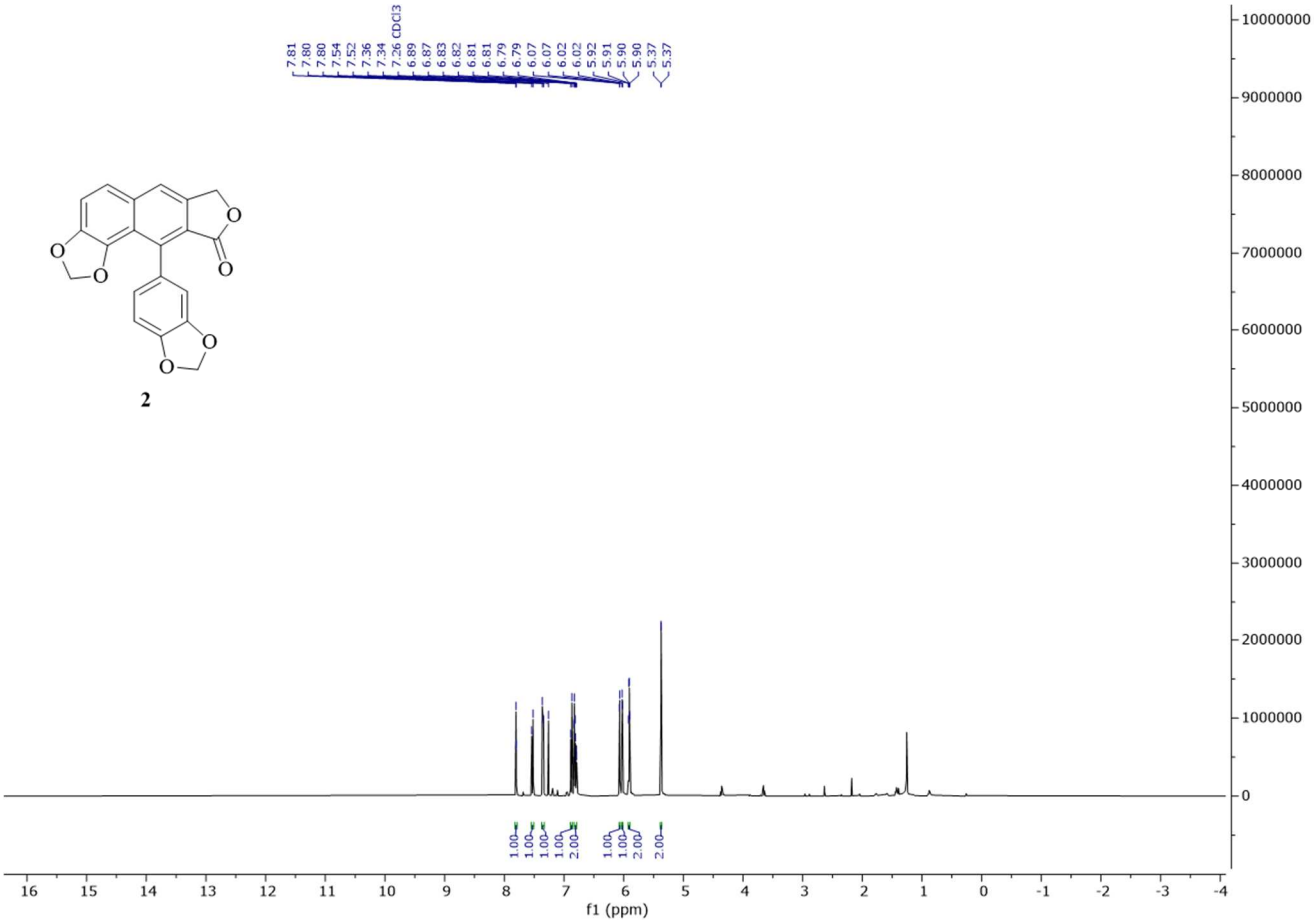

TMS
O
O
O
O
TMS
O
O
39
171.36
148.07
147.17
146.07
143.20
140.07
137.31
136.91
134.17
131.69
131.62
127.28
123.82
120.54
118.72
113.95
109.84
101.54
101.19
77.16 CDCl3
69.62
0.67
0.06
f1 (ppm)


8.42
7.71
7.69
7.32
7.30
7.26 CDCl3
6.90
6.90
6.88
6.88
6.81
6.81
6.80
6.79
6.78
6.07
6.07
6.05
6.05
6.04
5.97
5.97
5.95
5.94
5.26
5.22
5.18
5.14
1.00
1.00
1.00
1.00
2.00
2.00
2.00
2.00
f1 (ppm)

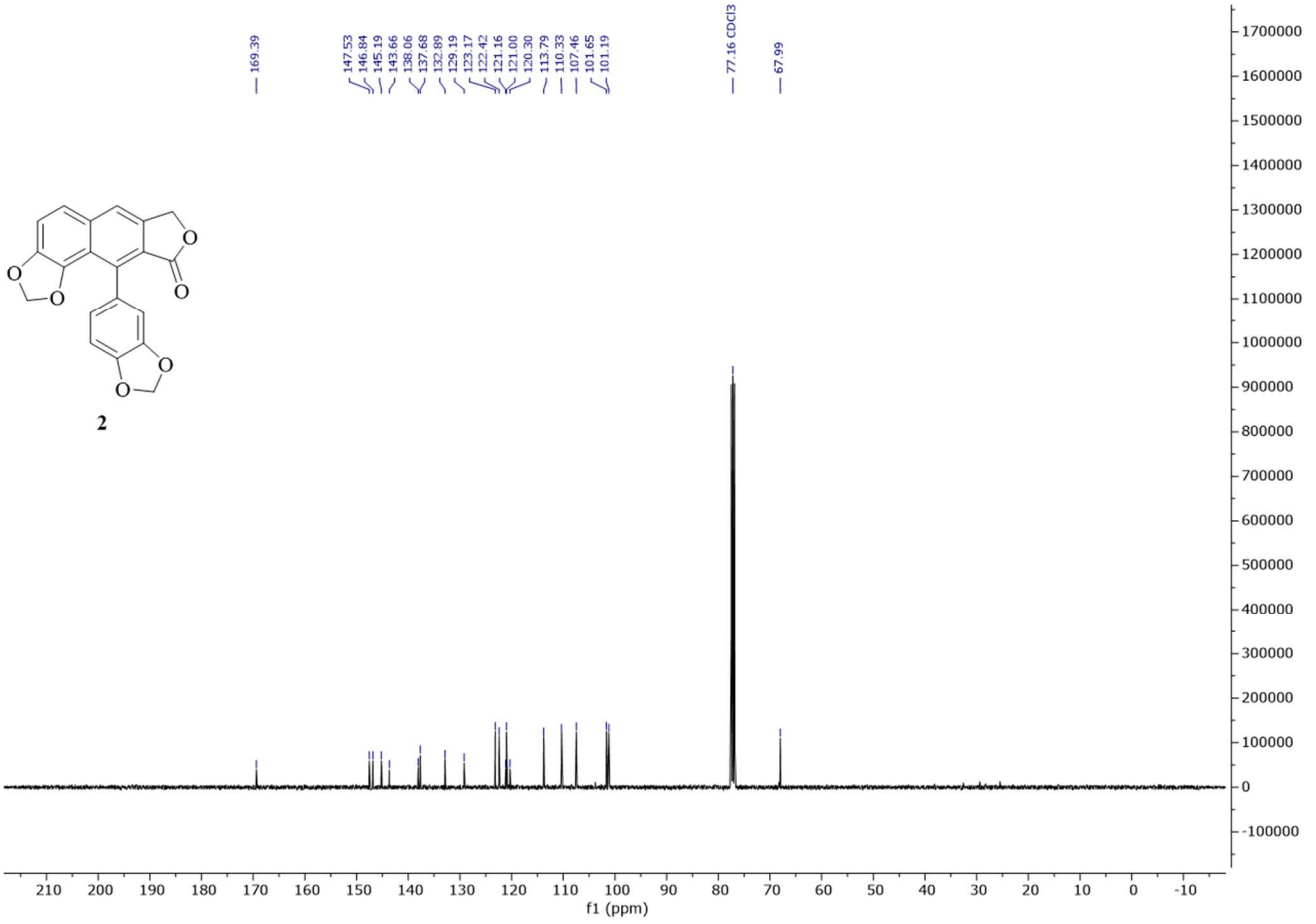
1


171.28
147.56
147.51
147.06
141.87
139.91
130.88
130.56
129.23
127.57
125.60
122.48
121.65
121.23
111.95
109.80
108.13
101.74
101.41
77.16 CDCl3
69.67
f1 (ppm)

1


7.81
7.80
7.80
7.54
7.52
7.36
7.34
7.26 CDCl3
6.89
6.87
6.83
6.82
6.81
6.81
6.79
6.79
6.07
6.07
6.02
6.02
5.92
5.91
5.90
5.90
5.37
5.37
1.00
1.00
1.00
1.00
2.00
1.00
1.00
2.00
2.00
f1 (ppm)

2


169.39
147.53
146.84
145.19
143.66
138.06
137.68
132.89
129.19
123.17
122.42
121.16
121.00
120.30
113.79
110.33
107.46
101.65
101.19
77.16 CDCl3
67.99
f1 (ppm)

2

4 List of illustrations

5 References

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