Supporting Information

First Report of CDCA-Substituted Dyes Improving the Dye Monolayer Quality in Dye-Sensitized Solar Cells

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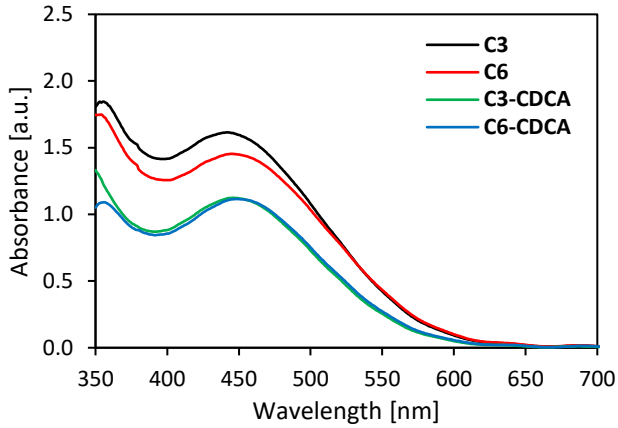


Figure S1. Absorption spectra of the four dyes on TiO_2 films (2.5 µm thickness).

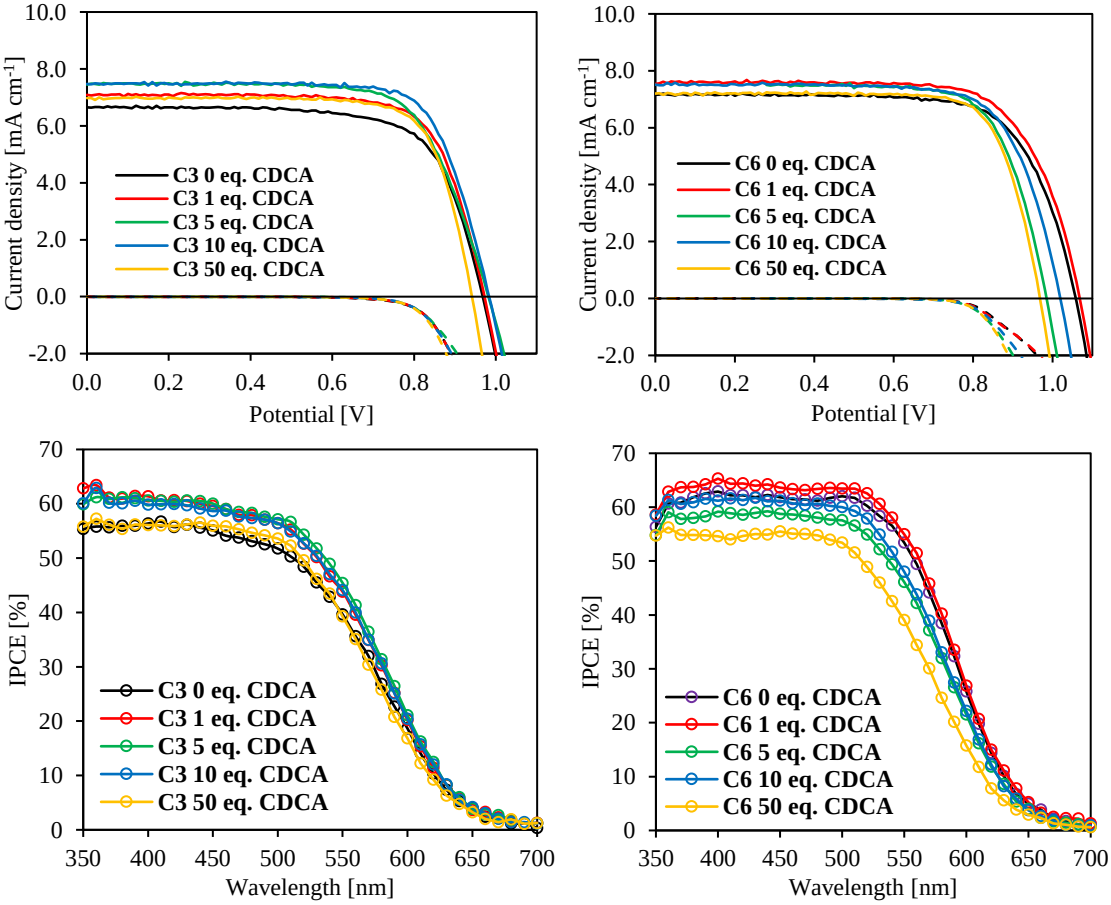


Figure S2. Photovoltaic performance of optimization process of dyes **C3** and **C6** with different amounts of chenodeoxycholic acid (0, 1, 5, 10 and 50 eq. of CDCA).

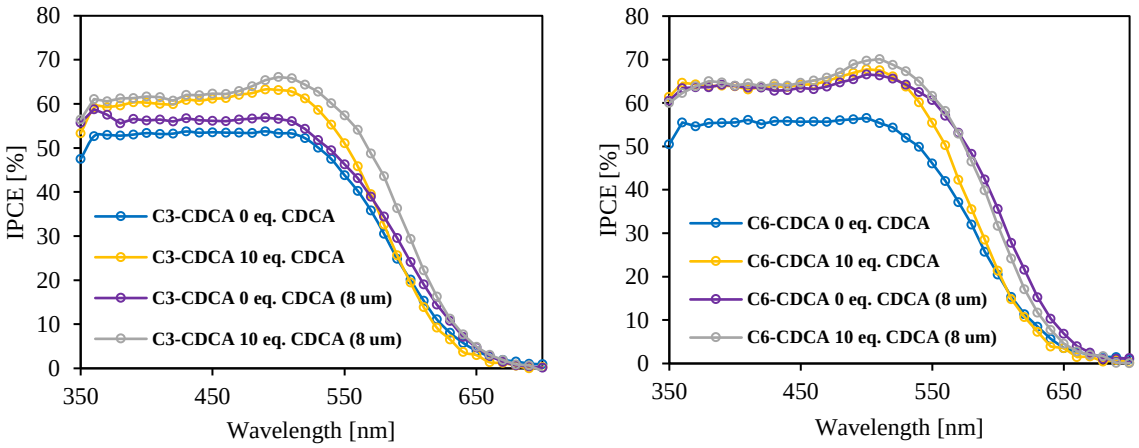


Figure S3. Photocurrent action spectra of the dyes with CDCA substituents, with different additional CDCA concentrations and thickness of TiO_2.

Table S1. Dye loading experiments for a selection of staining solutions and film TiO_2 film thicknesses.

Dye	ε [M^{-1} cm^{-1}] [a]	CDCA [eq.]	TiO_2 [µm]	Dye loading[b] [10^{-8} mol cm^{-2}]
C_3	34700	10	4 + 2	8.52 ± 0.33
C_6	36300	10	4 + 2	6.86 ± 0.03
C_3-CDCA	31200	0	4 + 2	6.17 ± 0.07
		0	8 + 4	10.65 ± 0.12
		10	4 + 2	4.66 ± 0.19
		10	8 + 4	7.70 ± 0.49
C_6-CDCA	33500	0	4 + 2	5.48 ± 0.11
		0	8 + 4	9.51 ± 0.20
		10	4 + 2	4.21 ± 0.21
		10	8 + 4	6.54 ± 0.19

[a] Average extinction coefficient from two solutions of dye in 40 mM TBAOH in stabilized THF.

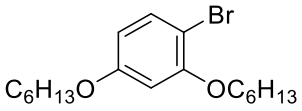
[b] Average of two stained electrodes separately desorbed.

Synthesis details

Materials and reagents: All reactions were carried out under nitrogen atmosphere, and all synthesis reagents were acquired from Sigma Aldrich.

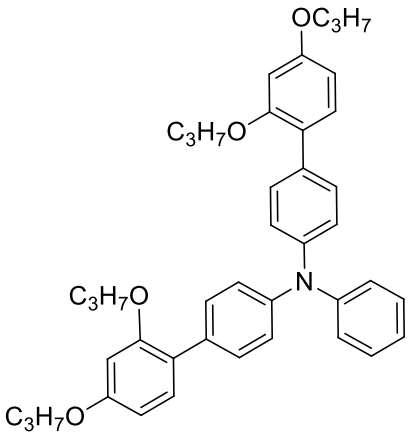
Analytical instruments: NMR spectroscopy (^{1}H and ^{13}C) was recorded on 400 and 600 MHz Bruker instruments, and all chemical shifts are reported relative to the respective solvent signals. Mass determination was performed on a Waters "Synapt G2-S" QTOF instrument in positive and negative modes. UV-vis spectra were recorded on a Hitachi U-1900 instrument using quarts cuvettes for the solution samples, while fluorescence spectroscopy was recorded on an Edinburgh instruments FS5 Spectrofluorometer. Infrared spectra were recorded on a Bruker Alpha FT-IR spectrometer with an ATR module.

Synthesis of 1-bromo-2,4-bis(hexyloxy)benzene (1)[46]



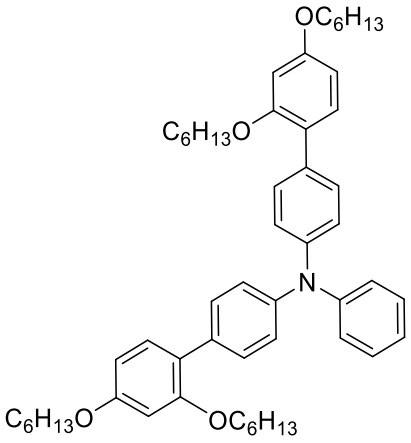
4-Bromoresorcinol (3.00 g, 15.9 mmol) and KOH (2.42 g, 43.1 mmol) were dissolved in DMSO (20 mL), before 1-bromohexane (6.7 mL, 47.7 mmol) was added. The resulting mixture was stirred at room temperature overnight. The product was extracted from DMSO using pentane (4 × 40 mL), the combined pentane phases were washed with water (4 × 40 mL), before drying with brine solution (40 mL) and ultimately dried over anhydrous Na_2SO_4. The pentane phase was then filtered, and the solvents were removed *in vacuo*. The crude product was purified by silica gel column chromatography (dichloromethane/*n*-pentane, 1:4, R_f = 0.27). Compound **1** was isolated as a clear oil (5.29 g, 14.8 mmol, 93%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.39 (d, *J* = 8.7 Hz, 1H), 6.62 (d, *J* = 2.6 Hz, 1H), 6.46 (dd, *J* = 8.7, 2.7 Hz, 1H), 4.01 (t, *J* = 6.4 Hz, 2H), 3.94 (t, *J* = 6.5 Hz, 2H), 1.74-1.64 (m, 4H), 1.47-1.35 (m, 4H), 1.34-1.26 (m, 8H), 0.89-0.85 (m, 6H).

Synthesis of *N*-(2',4'-dipropoxy-[1,1'-biphenyl]-4-yl)-*N*-phenyl-2',4'-dipropoxy-[1,1'-biphenyl]-4-amine (2)



4-Bromo-*N*-(4-bromophenyl)-*N*-phenylaniline (1.00 g, 0.992 mmol), (2,4-dipropoxyphenyl)boronic acid (1.48 g, 5.55 mmol), $Pd(OAc)_2$ (22 mg, 0.098 mmol), SPhos (81 mg, 0.197 mmol) and K_2CO_3 (1.37 g, 9.9 mmol) were mixed. 1,4-Dioxane (8 mL) and water (8 mL) were degassed and added under nitrogen. The reaction mixture was heated to 80 °C and left stirring for 20 hours before cooling to room temperature. Water (40 mL) was added and the aqueous phase extracted by ethyl acetate (3 × 40 mL). The combined organic phases were dried with brine (40 mL) and over anhydrous Na_2SO_4, filtered and the solvents were removed *in vacuo*. The crude product was purified by silica gel column chromatography (CH_2Cl_2, R_f = 0.67) to obtain compound **2** as a clear oil (1.45 g, 2.12 mmol, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46-7.40 (m, 4H), 7.30-7.22 (m, 4H), 7.20-7.16 (m, 2H), 7.15-7.10 (m, 4H), 7.00 (t, *J* = 6.6 Hz, 1H), 6.57-6.51 (m, 4H), 3.98-3.87 (m, 8H), 1.88-1.72 (m, 8H), 1.05 (t, *J* = 7.3 Hz, 6H), 0.98 (t, *J* = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.5 (2C), 157.0 (2C), 148.0, 146.0 (2C), 132.7 (2C), 130.8 (2C), 130.1 (4C), 129.1 (2C), 124.2 (2C), 123.5 (4C), 123.1 (2C), 122.4, 105.4 (2C), 100.5 (2C), 70.0 (2C), 69.6 (2C), 22.7 (2C), 22.6 (2C), 10.8 (2C), 10.6 (2C); IR (neat, cm^{-1}) ν: 2963 (w), 2935 (w), 2875 (w), 1602 (m), 1491 (s), 1468 (m), 1243 (s), 1180 (s), 1132 (m), 908 (w), 731 (w); HRMS (ASAP+, *m/z*): HRMS (ASAP+, *m/z*): found 630.3574 (calcd. $C_{42}H_{48}NO_4$ 630.3583, $[M+H]^+$).

Synthesis of *N*-(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)-2',4'-bis(hexyloxy)-*N*-phenyl-[1,1'-biphenyl]-4-amine (3)

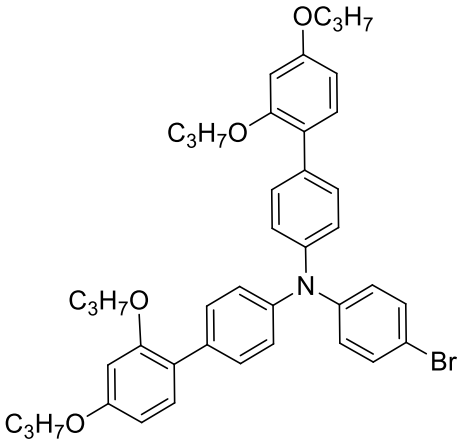


Compound **1** (1.98 g, 5.54 mmol), $PdCl_2(CH_3CN)_2$ (43 mg, 0.17 mmol) and SPhos (136 mg, 0.33 mmol) were added to a two-neck round-bottom flask before it was evacuated, and a N_2-atmosphere established. Dry 1,4-dioxane (15 mL) was used to dissolve the compounds and the reaction mixture was stirred at rt. before 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.7 mL, 11.7 mmol) and dry triethyl amine (2.4 mL, 17.2 mmol) were added. The reaction mixture was heated to 110 °C and left stirring for 90 minutes before cooling to room temperature. The reaction mixture was filtered through Celite using ethyl acetate as eluent, the solvents were removed *in vacuo*. The crude mixture obtained was a yellow oil and was used without further purification.

The aforementioned crude product was added to a single neck round-bottom flask along with 4-bromo-*N*-(4-bromophenyl)-*N*-phenylaniline (0.90 g, 2.23 mmol), $Pd(OAc)_2$ (24 mg, 0.11 mmol), SPhos (81 mg, 0.20 mmol) and K_2CO_3 (1.23 g, 8.90 mmol). 1,4-Dioxane (8 mL) and

water (8 mL) were degassed and added under nitrogen. The reaction mixture was heated to 80 °C and stirred for 24 hours before cooling to room temperature. Water (50 mL) was added and the aqueous phase extracted by dichloromethane (3 × 50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and the solvents were removed *in vacuo*. The crude product was purified by silica gel column chromatography (dichloromethane/*n*-pentane, 1:4, R_f = 0.19) and recrystallized from acetonitrile to yield compound **3** as a white solid (1.11 g, 1.38 mmol, 62%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.40 (m, 4H), 7.28-7.22 (m, 4H), 7.20-7.16 (m, 2H), 7.15-7.10 (m, 4H), 7.00 (t, *J* = 6.8 Hz, 1H), 6.56-6.51 (m, 4H), 4.00-3.92 (m, 8H), 1.84-1.69 (m, 8H), 1.52-1.44 (m, 4H), 1.44-1.23 (m, 20H), 0.91 (t, *J* = 7.1 Hz, 6H), 0.86 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.5 (2C), 157.0 (2C), 148.0, 146.0 (2C), 132.7 (2C), 130.8 (2C), 130.1 (4C), 129.1 (2C), 124.2 (2C), 123.5 (4C), 123.1 (2C), 122.4, 105.3 (2C), 100.4 (2C), 68.4 (2C), 68.1 (2C), 31.6 (2C), 31.5 (2C), 29.3 (2C), 29.1 (2C), 25.78 (2C), 25.76 (2C), 22.63 (2C), 22.57 (2C), 14.1 (2C), 14.0 (2C). IR (neat, cm^{-1}) ν: 2927 (m), 2857 (m), 1603 (m), 1491 (s), 1467 (m), 1271 (s), 1178 (s), 1134 (m), 1045 (m), 835 (m). HRMS (ASAP+, *m/z*): HRMS (ASAP+, *m/z*): found 798.5456 (calcd. $C_{54}H_{72}NO_4$ 798.5461, $[M+H]^+$).

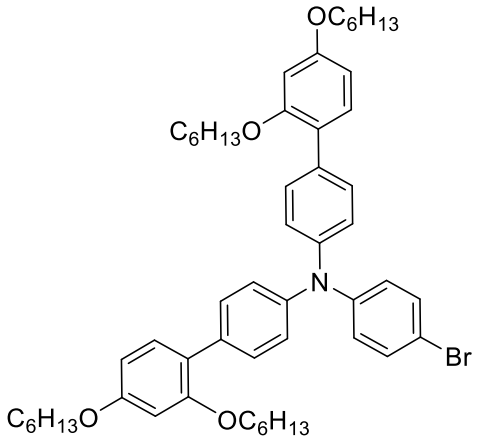
Synthesis of *N*-(4-bromophenyl)-*N*-(2',4'-dipropoxy-[1,1'-biphenyl]-4-yl)-2',4'-dipropoxy-[1,1'-biphenyl]-4-amine (4)



Compound **2** (0.65 g, 1.03 mmol) and NBS (0.19 g, 1.08 mmol) were added to a round-bottom flask under dark conditions. Dichloromethane (20 mL) was degassed and added under nitrogen at 0 °C. The reaction mixture was then allowed to warm to rt. while stirring for 5 hours. Water (40 mL) was added and the aqueous phase was extracted using dichloromethane (3 × 20 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and the solvents were removed *in vacuo*. The crude product was purified by silica gel column chromatography (dichloromethane, R_f = 0.74). Compound **4** was isolated as a clear oil (0.60 g, 0.85 mmol, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.41 (m, 4H), 7.36-7.31 (m, 2H), 7.27-7.23 (m, 2H), 7.14-7.09 (m, 4H), 7.07-7.02 (m, 2H), 6.56-6.51 (m, 4H), 3.97-3.89 (m, 8H), 1.88-1.73 (m, 8H), 1.05 (t, *J* = 7.0 Hz, 6H), 0.99 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.6 (2C), 157.0 (2C), 147.2, 145.5 (2C), 133.3 (2C), 132.0 (2C), 130.9 (2C), 130.3 (4C), 125.2 (2C), 123.7 (4C), 122.9 (2C), 114.4, 105.4 (2C), 100.4 (2C), 70.0 (2C), 69.6 (2C), 22.7 (2C), 22.6 (2C), 10.7 (2C), 10.6 (2C); IR (neat, cm^{-1}) ν: 2962 (w), 2934 (w),

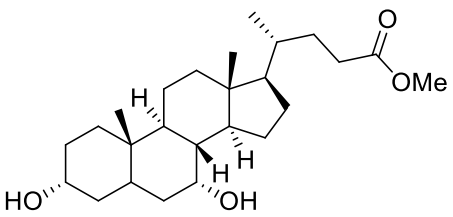
2874 (w), 1605 (m), 1580 (m), 1485 (s), 1269 (s), 1180 (s), 1133 (m), 1002 (m), 795 (m), 731 (m); HRMS (ASAP+, *m/z*): HRMS (ASAP+, *m/z*): found 708.2681 (calcd. $C_{42}H_{47}NO_4Br$ 708.2688, $[M+H]^+$).

Synthesis of *N*-(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)-N-(4-bromophenyl)-2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-amine (5)[47]



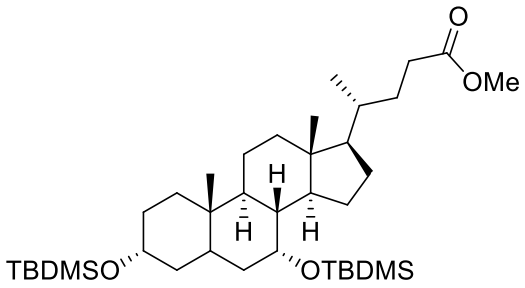
Compound **3** (1.00 g, 1.25 mmol) and NBS (0.22 g, 1.25 mmol) were added to a round-bottom flask under dark conditions. Dichloromethane (25 mL) was degassed and added under nitrogen at 0 °C. The reaction mixture was then allowed to warm to room temperature while stirring for 15 hours. Water (40 mL) was added and the aqueous phase was extracted using dichloromethane (3 × 30 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and the solvents were removed *in vacuo*. The crude product was purified by silica gel column chromatography (dichloromethane, R_f = 0.8). Compound **5** was isolated as a clear oil (0.99 g, 1.12 mmol, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46-7.41 (m, 4H), 7.35-7.30 (m, 2H), 7.27-7.23 (m, 2H), 7.14-7.08 (m, 4H), 7.06-7.02 (m, 2H), 6.56-6.51 (m, 4H), 4.00-3.92 (m, 8H), 1.84-1.70 (m, 8H), 1.52-1.44 (m, 4H), 1.44-1.25 (m, 20H), 0.91 (t, *J* = 6.5 Hz, 6H), 0.87 (t, *J* = 6.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.6 (2C), 157.0 (2C), 147.2, 145.5 (2C), 133.3 (2C), 132.0 (2C), 130.8 (2C), 130.3 (4C), 125.1 (2C), 123.7 (4C), 122.9 (2C), 114.4, 105.3 (2C), 100.3 (2C), 68.4 (2C), 68.1 (2C), 31.6 (2C), 31.5 (2C), 29.3 (2C), 29.1 (2C), 25.78 (2C), 25.76 (2C), 22.64 (2C), 22.58 (2C), 14.1 (2C), 14.0 (2C); IR (neat, cm^{-1}) ν: 2928 (m), 2858 (m), 1606 (m), 1581 (m), 1487 (s), 1468 (m), 1281 (m), 1180 (m), 1135 (w); HRMS (ASAP+, *m/z*): HRMS (ASAP+, *m/z*): found 876.4559 (calcd. $C_{54}H_{71}NO_4Br$ 876.4566, $[M+H]^+$).

Synthesis of methyl (4*S*)-4-((3*S*,7*S*,8*S*,9*R*,10*R*,13*S*,14*R*,17*S*)-3,7-dihydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate (6)[48]



Chenodeoxycholic acid (10.0 g, 25.5 mmol) was dissolved in methanol (300 mL), and while stirring, conc. H_2SO_4 (1.5 mL) was added slowly. Then, the reaction mixture was stirred at room temperature for 1 hour. The reaction mixture was poured into aqueous $NaHCO_3$ solution (0.5 M, 150 mL) and extracted with ethyl acetate (3 × 150 mL). Upon removal of the solvents *in vacuo*, compound **6** was obtained as white solid (10.1 g, 24.7 mmol, 97%), mp 69-73 °C (lit.[48] 85.2-86.0 °C). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 4.31 (d, J = 4.7 Hz, 1H), 4.11 (d, J = 3.7 Hz, 1H), 3.64-3.60 (m, 1H), 3.57 (s, 3H), 3.23-3.13 (m, 1H), 2.37-2.27 (m, 1H), 2.25-2.13 (m, 2H), 1.93-1.61 (m, 7H), 1.50-0.95 (m, 16H), 0.88 (d, J = 6.5 Hz, 3H), 0.83 (s, 3H), 0.60 (s, 3H); HRMS (ESI+, *m/z*): found 371.2946 (calcd. $C_{25}H_{42}O_4Na$ 429.2981, $[M+Na]^+$).

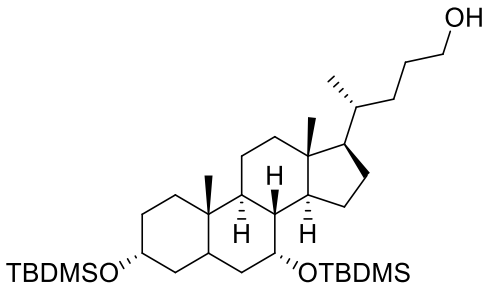
Synthesis of methyl (4*S*)-4-((3*S*,7*S*,8*S*,9*R*,10*R*,13*S*,14*R*,17*S*)-3,7-bis((tert-butyldimethylsilyl)oxy)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate (7)



Compound **6** (6.00 g, 14.8 mmol), 2,6-lutidine (17.2 mL, 148 mmol) and dichloromethane (216 mL) were added to a flask at 0 °C under nitrogen atmosphere. *tert*-Butyl dimethylsilyltrifluoromethanesulphonate (10.2 mL, 44.3 mmol) was added and the reaction was stirred for 22 hours. The reaction mixture was quenched in aqueous $NaHSO_4$ solution (1 M, 150 mL) and the water phase was extracted with CH_2Cl_2 (3 × 150 mL). The combined organic phases were washed with aqueous $NaHSO_4$ solution (1 M, 3 × 100 mL) and brine (100 mL), then dried over anhydrous Na_2SO_4. Compound **7** was obtained as a clear oil (9.30 g, 14.6 mmol, 99%) upon the removal of the solvents *in vacuo*. The material contained a *tert*-butyl trimethylsilyl containing impurity of unknown structure. ^{1}H NMR (400 MHz, acetone-d_6) δ: 3.89-3.89 (m, 1H), 3.60 (s, 3H), 3.53-3.45 (m, 1H), 2.39-2.29 (m, 2H), 2.26-2.18 (m, 1H), 2.03-1.01 (m, 20H), 0.97-0.92 (m, 15H), 0.90-0.87 (m, 12H), 0.69 (s, 3H), 0.15 (s, 3H), 0.10 (s, 3H), 0.053 (s, 3H), 0.046 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ: 174.5, 73.3, 70.6, 56.9, 51.5, 51.0, 43.2, 42.7, 41.6, 41.4, 40.6, 36.3, 36.2, 35.8, 35.3, 33.3, 31.89, 31.86,

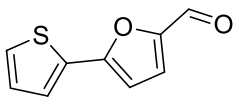
31.5, 28.7, 26.6 (3C), 26.2 (3C), 24.6, 23.3, 21.3, 19.0, 18.7, 18.6, 12.3, -1.9, -4.37, -4.40, -5.4; IR (neat, cm^{-1}) ν: 2952 (m), 2929 (m), 2855 (m), 1739 (m), 1462 (m), 1436 (m), 1373 (m), 1263 (s), 1252 (s), 1088 (s), 1026 (s), 834 (s), 770 (s), 736 (s), 701 (s); HRMS (ASAP+, *m/z*): found 657.4713 (calcd. $C_{37}H_{70}O_4NaSi_2$ 657.4710, $[M+Na]^+$).

Synthesis of (4*S*)-4-((3*S*,7*S*,8*S*,9*R*,10*R*,13*S*,14*R*,17*S*)-3,7-bis((tert-butyldimethylsilyl)oxy)-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentan-1-ol (8)[49]



Compound **7** (9.00 g, 14.2 mmol) was dissolved in THF (210 mL) under nitrogen atmosphere at 0 °C. Lithium aluminium hydride in THF solution (2 M, 21.2 mL, 42.5 mmol) was added, and the reaction was stirred for 19 hours while reaching room temperature, before work-up by a modified Fieser work-up procedure. Addition of water (1.6 mL) causing vigorous bubbling, then aqueous NaOH (4 M, 1.6 mL) was added which formed a white granulate. Water (5 mL) was added and the reaction mixture was stirred for 10 minutes, before addition of anhydrous Na_2SO_4 and 10 minutes stirring before removal of solids by filtration. The solvents were removed *in vacuo* to yield compound **8** as a white solid (8.43 g, 13.9 mmol, 98%), mp 116-117 °C (lit. not reported). ^{1}H NMR (400 MHz, acetone-d_6) δ: 3.89-3.88 (m, 1H), 3.52-3.46 (m, 3H), 3.36 (t, J = 5.4 Hz, 0.5H*), 2.39-2.29 (m, 1H), 2.01-1.01 (m, 24H), 0.96-0.93 (m, 15H), 0.88 (s, 10H), 0.69 (s, 3H), 0.15 (s, 3H), 0.10 (s, 3H), 0.052 (s, 3H), 0.045 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ: 72.3, 69.6, 62.0, 61.9, 56.3, 50.0, 42.1, 41.7, 40.6, 40.4, 39.7, 35.7, 35.2, 34.8, 34.3, 32.4, 32.0, 30.9, 27.8, 25.6 (3C), 25.2 (3C), 23.6, 22.3, 20.3, 18.2, 18.0, 17.6, 11.3, -2.9, -5.38, -5.42, -6.4; IR (neat, cm^{-1}) ν: 3324 (w (br), OH), 2928 (s), 2855 (s), 1462 (m), 1373 (m), 1251 (s), 1091 (s), 1026 (s), 930 (s), 834 (s), 770 (s); HRMS (ESI+, *m/z*): found 629.4751 (calcd. $C_{36}H_{70}O_3NaSi_2$ 629.4761, $[M+Na]^+$). * Exchange of protons observed for OH.

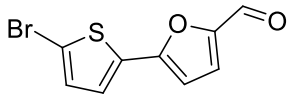
Synthesis of 5-(thiophen-2-yl)furan-2-carbaldehyde (12)[50]



2-Bromothiophene (842 mg, 5.16 mmol), (5-formylfuran-2-yl)boronic acid (1.08 g, 7.75 mmol), $PdCl_2$(dppf) (113 mg, 0.155 mmol) and K_2CO_3 (2.86 g, 20.7 mmol) were mixed, and degassed water (18 mL) and degassed 1,4-dioxane (18 mL) were added under nitrogen

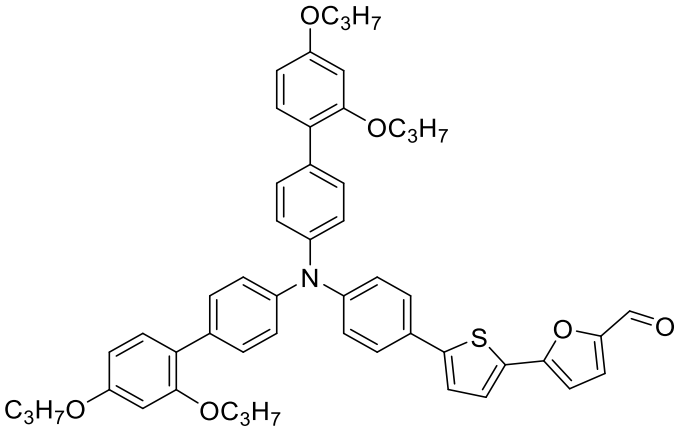
atmosphere. The reaction was heated to 80 ºC and stirred for 24 hours. Upon cooling to room temperature, the solvents were removed from the reaction mixture *in vacuo*, then deionized water (30 mL) and ethyl acetate (30 mL) were added and the phases separated. The aqueous phase was extracted with ethyl acetate (3 × 50 mL) before the combined organic phases were washed with brine (50 mL), dried over anhydrous Na_2SO_4, filtered and the solvents were removed *in vacuo*. The crude product was purified by silica gel column chromatography (*n*-pentane/ethyl acetate 1:1, R_f = 0.60) to yield compound **12** as a yellow oil (445 mg, 2.502 mmol, 48%). ^{1}H NMR (400 MHz, acetone-d_6) δ: 9.63 (s, 1H), 7.67 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.64 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.52 (d, *J* = 3.7 Hz, 1H), 7.20 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.98 (d, *J* = 3.7 Hz, 1H); HRMS (ASAP+, *m/z*): found 179.0164 (calcd. $C_9H_7O_2S$ 179.0167, $[M+H]^+$).

Synthesis of 5-(5-bromothiophen-2-yl)furan-2-carbaldehyde (13)[51]



Compound **12** (203 mg, 1.139 mmol) was dissolved in a mixture of chloroform (6 mL) and glacial acetic acid (6 mL) under nitrogen atmosphere at 0 °C. *N*-Bromosuccinimide (NBS) (250 mg, 1.405 mmol) was added and the reaction was stirred under darkness, at 0 °C for 17 hours. Due to incomplete conversion, another portion of NBS (71 mg, 0.399 mmol) was added and the reaction stirred for another 2 hours before water (10 mL) was added and the aqueous phase was extracted by chloroform (3 × 30 mL). The combined organic phases were washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Purification by silica gel column chromatography (*n*-pentane/ethyl acetate 1:1, R_f = 0.57) gave compound **13** as a light brown solid (173 mg, 0.673 mmol, 59%), mp 90-91 °C (lit.[51] 91-92 °C). ^{1}H NMR (400 MHz, acetone-d_6) δ: 9.64 (s, 1H), 7.52 (d, *J* = 3.8 Hz, 1H), 7.46 (d, *J* = 4.0 Hz, 1H), 7.27 (d, *J* = 4.0 Hz, 1H), 7.01 (d, *J* = 3.8 Hz, 1H); HRMS (ASAP+, *m/z*): found 256.9269 (calcd. $C_9H_6O_2S^{79}Br$ 256.9272, $[M+H]^+$).

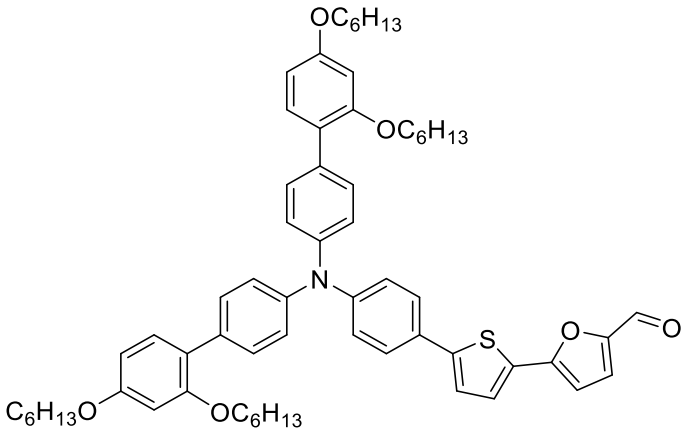
Synthesis of 5-(5-(4-(bis(2',4'-dipropoxy-[1,1'-biphenyl]-4-yl)amino)phenyl)thiophen-2-yl)furan-2-carbaldehyde (16)



Compound **4** (373 mg, 0.53 mmol), $PdCl_2(CH_3CN)_2$ (4 mg, 16 µmol) and SPhos (13 mg, 32 µmol) were added to a Schlenk-tube before it was evacuated, and N_2-atmosphere established. Dry 1,4-dioxane (1.5 mL) was used to dissolve the compounds and the reaction mixture was stirred at rt. before 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (160 µL, 1.11 mmol) and dry triethyl amine (230 µL, 1.65 mmol) were added. The reaction mixture was heated to 110 °C and left stirring for 60 minutes before cooling to room temperature. The reaction mixture was filtered through Celite using ethyl acetate as eluent, the solvents were removed *in vacuo*. The crude mixture obtained was a yellow oil and was reacted without further purification.

The crude product from the borylation, compound **13** (57 mg, 0.22 mmol), $Pd(OAc)_2$ (2.4 mg, 11 µmol), SPhos (9 mg, 22 µmol) and K_2CO_3 (122 mg, 0.88 mmol) were mixed. 1,4-Dioxane (4 mL) and water (4 mL) were degassed and added under nitrogen atmosphere. The reaction mixture was heated to 80 °C and left stirring for 16 hours before cooling to room temperature. Water (40 mL) was added and the aqueous phase extracted by dichloromethane (3 × 40 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and the solvents were removed *in vacuo*. The crude product was purified by silica gel column chromatography (*n*-pentane/dichloromethane, 1:4, R_f = 0.13) to obtain compound **16** as a red solid (72 mg, 89 µmol, 41%), mp 82-84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.60 (s, 1H), 7.52-7.45 (m, 7H), 7.29 (d, J = 3.7 Hz, 1H), 7.28-7.26 (m, 2H), 7.22 (d, J = 4.2 Hz, 1H), 7.20-7.15 (m, 6H), 6.66 (d, J = 4.2 Hz, 1H), 6.57-6.53 (m, 4H), 3.99-3.91 (m, 8H), 1.88-1.74 (m, 8H), 1.06 (t, J = 7.0 Hz, 6H), 1.00 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.7, 159.6 (2C), 157.0 (2C), 155.0, 151.4, 148.2 (2C), 147.0, 145.4 (2C), 133.3 (2C), 130.9 (2C), 130.3 (4C), 129.3, 127.4, 126.8, 126.6 (2C), 124.2 (5C), 123.1 (2C), 123.0, 122.9, 107.2, 105.4 (2C), 100.5 (2C), 70.0 (2C), 69.6 (2C), 22.7 (2C), 22.6 (2C), 10.7 (2C), 10.6 (2C); IR (neat, cm^{-1}) ν: 2964 (m), 2876 (m), 1672 (m), 1600 (m), 1517 (s), 1273 (s), 1135 (s), 833 (m); HRMS (ASAP+, *m/z*): found 806.3521 (calcd. $C_{51}H_{52}NO_6S$ 806.3515, $[M+H]^+$).

Synthesis of 5-(5-(4-(bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amino)phenyl)thiophen-2-yl)furan-2-carbaldehyde (17)

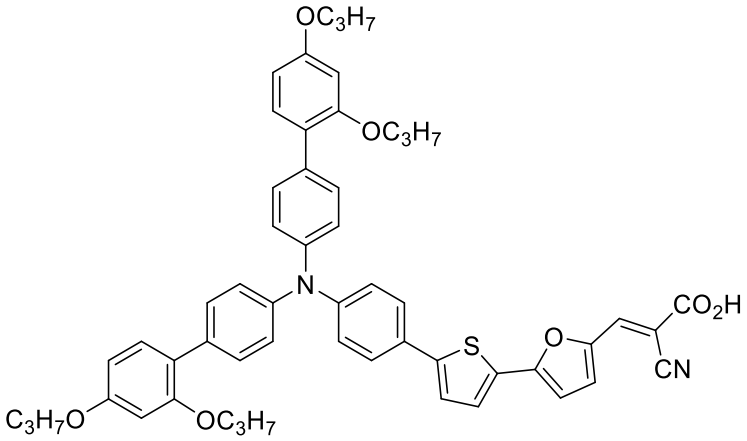


Compound **5** (312 mg, 0.36 mmol), $PdCl_2(CH_3CN)_2$ (3 mg, 12 µmol) and SPhos (9 mg, 22 µmol) were added to a Schlenk-tube before it was evacuated, and N_2-atmosphere established. Dry 1,4-dioxane (1 mL) was used to dissolve the compounds and the reaction mixture was

stirred at rt. before 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (110 µL, 0.75 mmol) and dry triethyl amine (150 µL, 1.10 mmol) were added. The reaction mixture was heated to 110 °C and left stirring for 60 minutes before cooling to room temperature. The reaction mixture was filtered through Celite using ethyl acetate as eluent, the solvents were removed *in vacuo*. The crude mixture obtained was a yellow oil and was reacted without further purification.

The crude product from the borylation, compound **13** (57 mg, 0.222 mmol), $Pd(OAc)_2$ (2.5 mg, 0.011 mmol), SPhos (9.1 mg, 0.022 mmol) and K_2CO_3 (188 mg, 1.36 mmol) were mixed. 1,4-Dioxane (4 mL) and water (4 mL) were degassed and added under nitrogen atmosphere. The reaction mixture was heated to 80 °C and left stirring for 17 hours before cooling to room temperature. Water (40 mL) was added and the aqueous phase extracted by ethyl acetate (3 × 40 mL). The combined organic phases were dried with brine (40 mL) and over anhydrous Na_2SO_4, filtered and the solvents were removed *in vacuo*. The crude product was purified by silica gel column chromatography (CH_2Cl_2, R_f = 0.39) to obtain compound **17** as a red resin (135 mg, 0.138 mmol, 62%). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.60 (s, 1H), 7.50-7.44 (m, 7H), 7.29 (d, J = 3.8 Hz, 1H), 7.27-7.25 (m, 2H), 7.22 (d, J = 3.9 Hz, 1H), 7.18-7.15 (m, 6H), 6.66 (d, J = 3.8 Hz, 1H), 6.56-6.53 (m, 4H), 4.00-3.95 (m, 8H), 1.83-1.72 (m, 8H), 1.51-1.45 (m, 4H), 1.44-1.39 (m, 4H), 1.38-1.34 (m, 8H), 1.32-1.28 (m, 8H), 0.92 (t, J = 7.8 Hz, 6H), 0.87 (t, J = 7.3 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ: 176.7, 159.6 (2C), 157.0 (2C), 155.0, 151.4, 148.3 (2C), 147.0, 145.3 (2C), 133.6 (2C), 130.9 (2C), 130.3 (4C), 129.3, 127.4, 126.7, 126.6 (2C), 124.2 (5C), 123.1 (2C), 122.92, 122.88, 107.2, 105.3 (2C), 100.4 (2C), 68.4 (2C), 68.1 (2C), 31.6 (2C), 31.5 (2C), 29,3 (2C), 29.1 (2C), 25.78 (2C), 22.76 (2C), 22.63 (2C), 22.58 (2C), 14.0 (4C); IR (neat, cm^{-1}) ν: 2952 (m), 2858 (m), 1674 (m), 1601 (m), 1491 (s), 1287 (s), 1182 (s), 833 (m); HRMS (ASAP+, *m/z*): found 974.5391 (calcd. $C_{63}H_{76}NO_6S$ 974.5393, $[M+H]^+$).

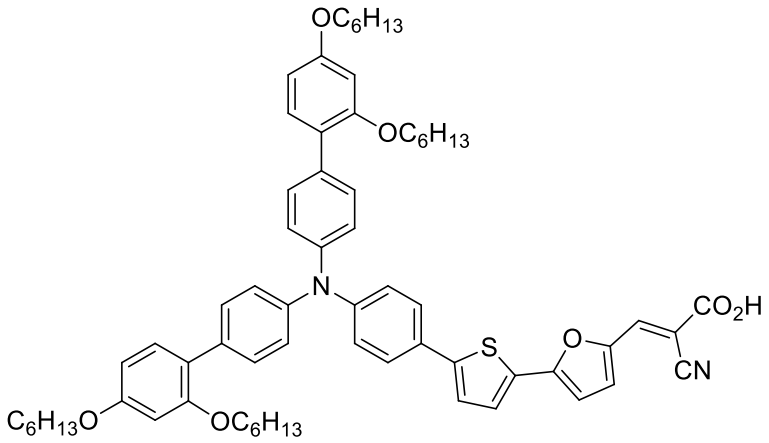
Synthesis of (*E*)-3-(5-(5-(4-(bis(2',4'-dipropoxy-[1,1'-biphenyl]-4-yl)amino)phenyl)thiophen-2-yl)furan-2-yl)-2-cyanoacrylic acid (Dye C_3)



Compound **16** (59 mg, 73 µmol) and cyanoacetic acid (125 mg, 1.46 mmol) were dissolved in degassed acetonitrile (17 mL) under nitrogen atmosphere. Piperidine (87 µL, 75 mg, 0.88

mmol) was added and the reaction was heated to 80 °C for 1 hour before cooling to room temperature and quenched in HCl (4 M, 30 mL). Dichloromethane (50 mL) was added and the organic phase was washed with water (4 × 100 mL), then dried over anhydrous Na_2SO_4, filtered and the solvents were removed *in vacuo*. The crude product was purified by silica gel column chromatography (gradient: 0-15% MeOH in CH_2Cl_2), the dye-containing fractions were washed with HCl (1 M, 2 × 30 mL) to obtain sensitizer **C3** as a dark solid (58 mg, 66 µmol, 91%), mp 125-127 °C (dec. 178 °C). ^{1}H NMR (600 MHz, CD_2Cl_2) δ: 8.00-7.96 (m, 1H), 7.58-7.51 (m, 3H), 7.50-7.46 (m, 4H), 7.42-7.36 (m, 1H), 7.30-7.22 (m, 3H), 7.19-7.11 (m, 6H), 6.81-6.75 (m, 1H), 6.58-6.52 (m, 4H), 3.97-3.91 (m, 8H), 1.84-1.75 (m, 8H), 1.05 (t, *J* = 7.5 Hz, 6H), 1.00 (t, *J* = 7.4 Hz, 6H) ($CO_2\underline{H}$ proton missing); ^{13}C NMR (150 MHz, CD_2Cl_2) δ: 168.1, 160.3 (2C), 157.6 (2C), 156.6, 148.9, 148.4, 147.9, 145.9 (2C), 138.9, 134.4 (2C), 131.4 (4C), 130.9 (4C), 129.6, 129.1, 127.2 (2C), 124.8 (4C), 124.0, 123.4 (2C), 123.2 (2C), 116.3, 109.8, 106.1 (2C), 100.8 (2C), 95.1, 70.6 (2C), 70.2 (2C), 23.2 (2C), 23.1 (2C), 11.1 (2C), 10.9 (2C); IR (neat, cm^{-1}) ν: 3030 (m), 2963 (m), 2932 (m), 2874 (m), 2218 (w), 1687 (w), 1601 (m), 1555 (m), 1474 (s), 1267 (m), 1181 (s), 1025 (m), 793 (m); HRMS (TOF MS ES+, *m/z*): found 873.3561 (calcd. $C_{54}H_{53}N_2O_7S$ 873.3573, $[M+H]^+$).

Synthesis of (*E*)-3-(5-(5-(4-(bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amino)phenyl)thiophen-2-yl)furan-2-yl)-2-cyanoacrylic acid (Dye C_6)



Compound **17** (110 mg, 0.11 mmol) and cyanoacetic acid (192 mg, 2.26 mmol) were dissolved in degassed acetonitrile (26 mL) under nitrogen atmosphere. Piperidine (134 µL, 115 mg, 1.35 mmol) was added and the reaction was heated to 80 °C for 1 hour before cooling to room temperature and quenched in HCl (4 M, 50 mL). Dichloromethane (100 mL) was added and the organic phase was washed with water (4 × 100 mL), then dried over anhydrous Na_2SO_4, filtered and the solvents were removed *in vacuo*. The crude product was purified by silica gel column chromatography (gradient: 0-20% MeOH in CH_2Cl_2), the dye-containing fractions were washed with HCl (1 M, 2 × 20 mL) to obtain sensitizer **C_6** as a dark solid (96 mg, 92 µmol, 82%), mp 97-99 °C (dec. 142 °C). ^{1}H NMR (600 MHz, CD_2Cl_2) δ: 8.00-7.97 (m, 1H), 7.60-7.58 (m, 1H), 7.57-7.52 (m, 2H), 7.50-7.46 (m, 4H), 7.44-7.37 (m, 1H), 7.33-7.22 (m, 4H), 7.21-7.10 (m, 5H), 6.82-6.79 (m, 1H), 6.57-6.53 (m, 4H), 4.00-3.96 (m, 8H), 1.82-1.73 (m, 8H), 1.51-1.46 (m, 4H), 1.45-1.41 (m, 4H), 1.38-1.34 (m, 8H), 1.33-1.29 (m, 8H), 0.92 (t, J = 7.1 Hz, 6H), 0.88 (t, J = 7.0 Hz, 6H) ($CO_2\underline{H}$ proton missing); ^{13}C NMR (150 MHz, CD_2Cl_2) δ: 168.0, 160.4 (2C), 157.6 (2C), 156.7, 149.1, 148.6, 147.9, 145.8 (2C), 139.0, 134.5 (2C), 131.3 (4C), 130.9 (4C), 129.6, 129.2, 127.2 (2C), 124.9 (4C), 124.0, 123.3 (2C), 123.1 (2C), 116.2, 109.8, 106.0 (2C), 100.8 (2C), 95.0, 69.0 (2C), 68.7 (2C), 32.2 (2C), 32.1 (2C), 29.9 (2C), 29.7 (2C), 26.4 (2C), 26.3 (2C), 23.21 (2C), 23.17 (2C), 14.40 (2C), 10.38 (2C); IR (neat, cm^{-1}) ν: 3400 (br), 3031 (w), 2926 (m), 2856 (m), 222 (w), 1685 (m), 1599 (s), 1492 (s), 1418 (s), 1286 (s), 1025 (s), 792 (m), 705 (m); HRMS (ASAP+, *m/z*): found 997.5543 (calcd. $C_{65}H_{77}N_2O_5S$ 997.5553, $[M\text{-}CO_2+H]^+$).

NMR

Compound 1

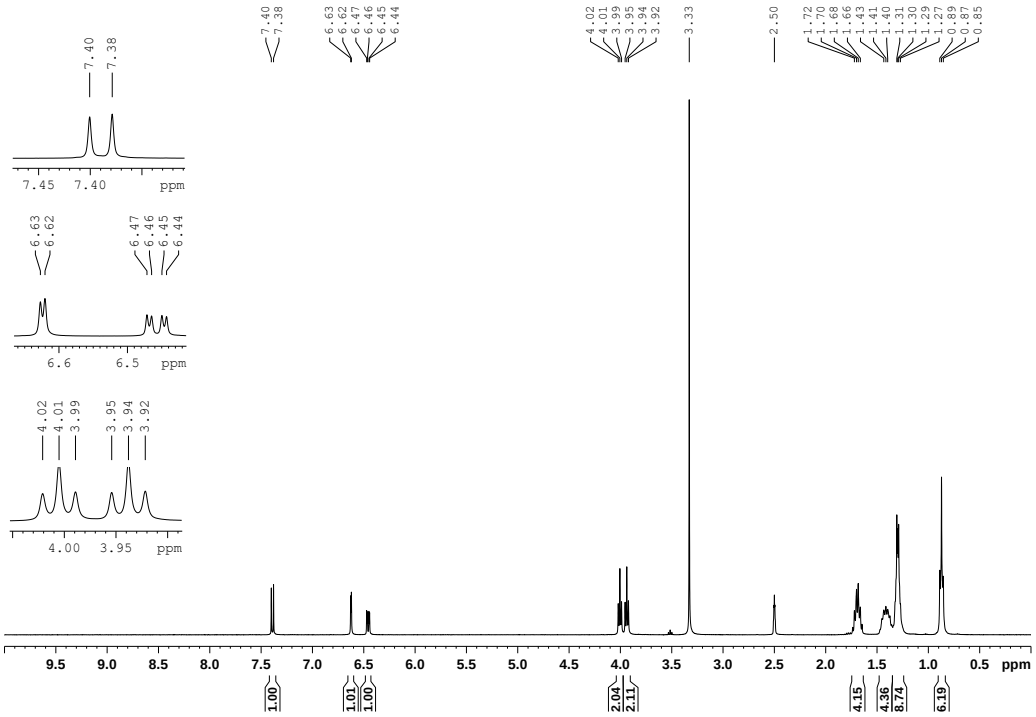


Figure S4. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum for compound **1**.

Compound 2

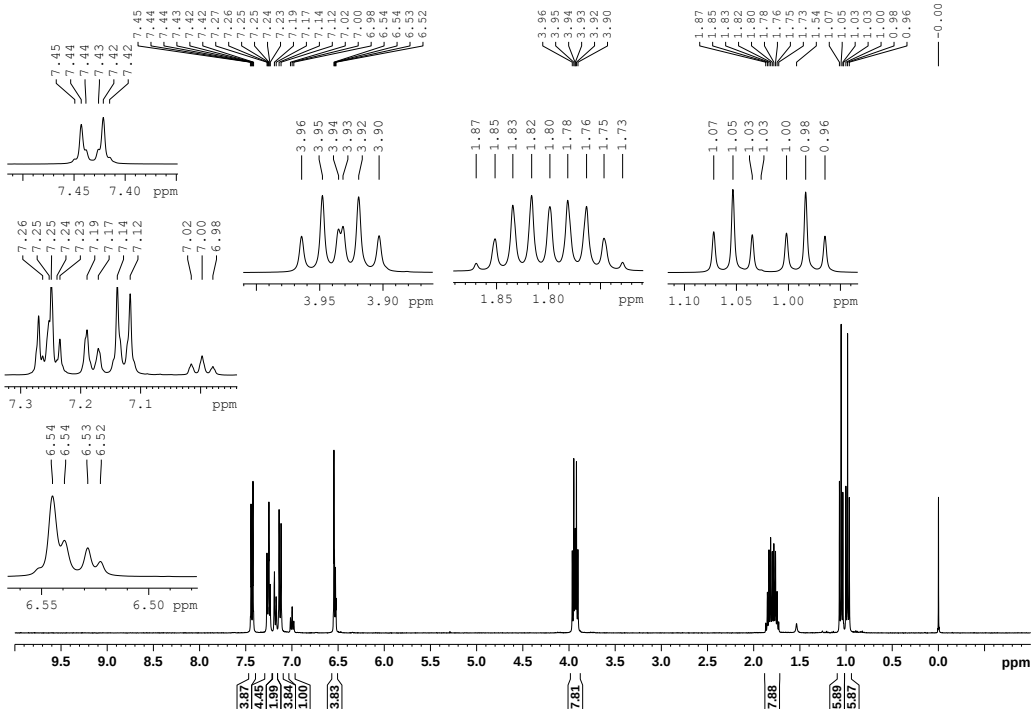


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for compound **2**.

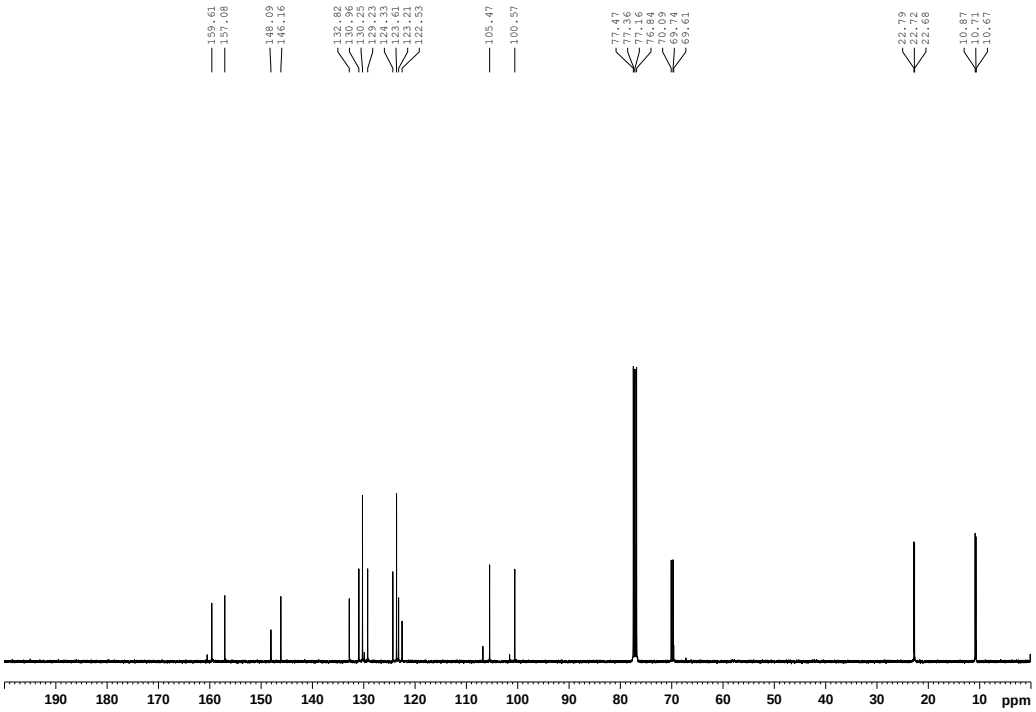


Figure S6. ^{1}H NMR (100 MHz, $CDCl_3$) spectrum for compound **2**.

Compound 3

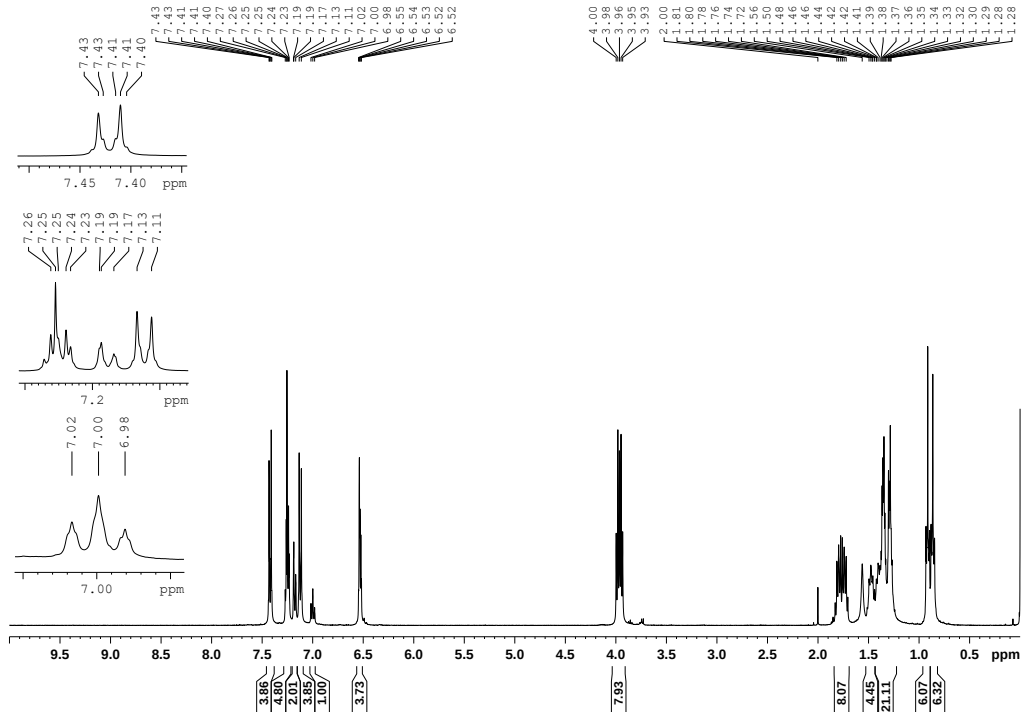


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for compound **3**.

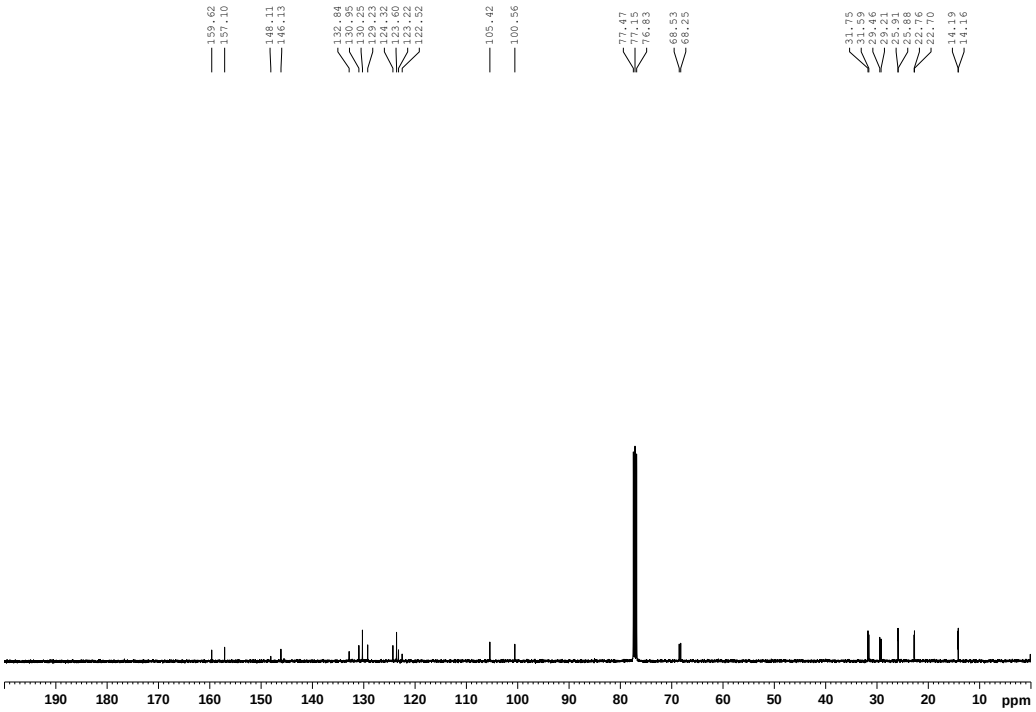


Figure S8. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for compound **3**.

Compound 4

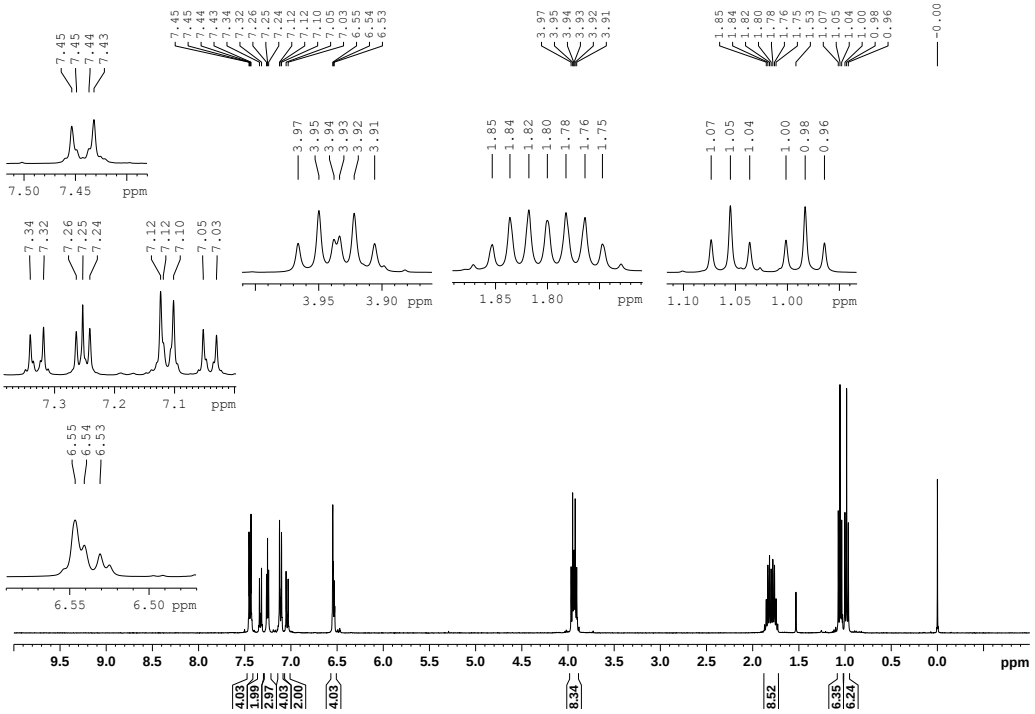


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for compound **4**.

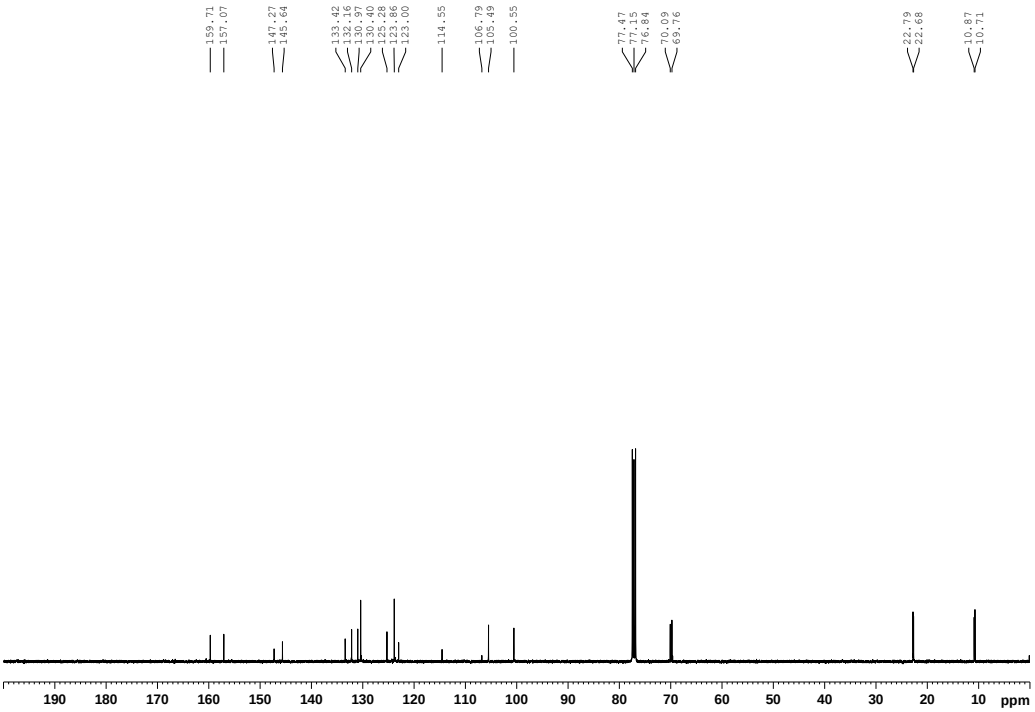


Figure S10. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for compound **4**.

Compound 5

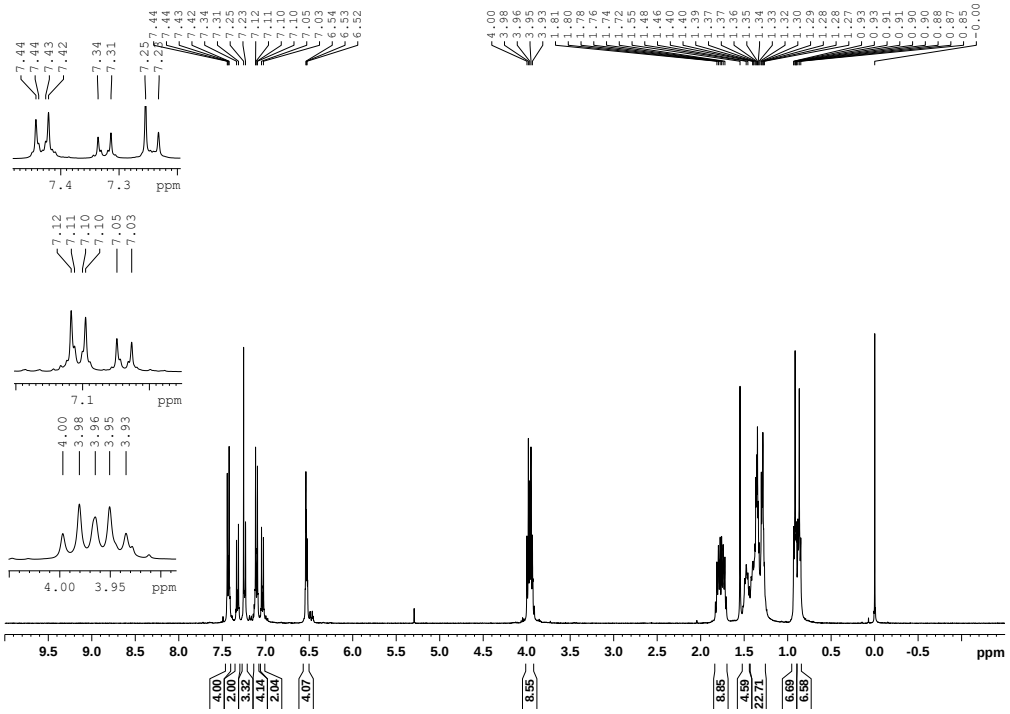


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for compound **5**.

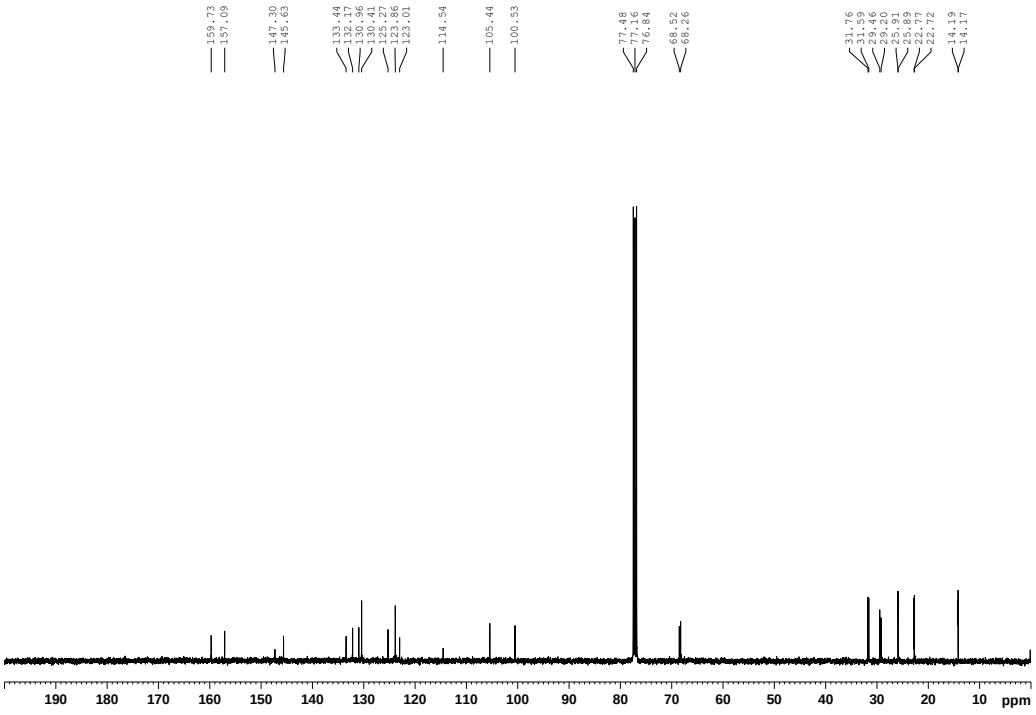


Figure S12. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum for compound **5**.

Compound 6

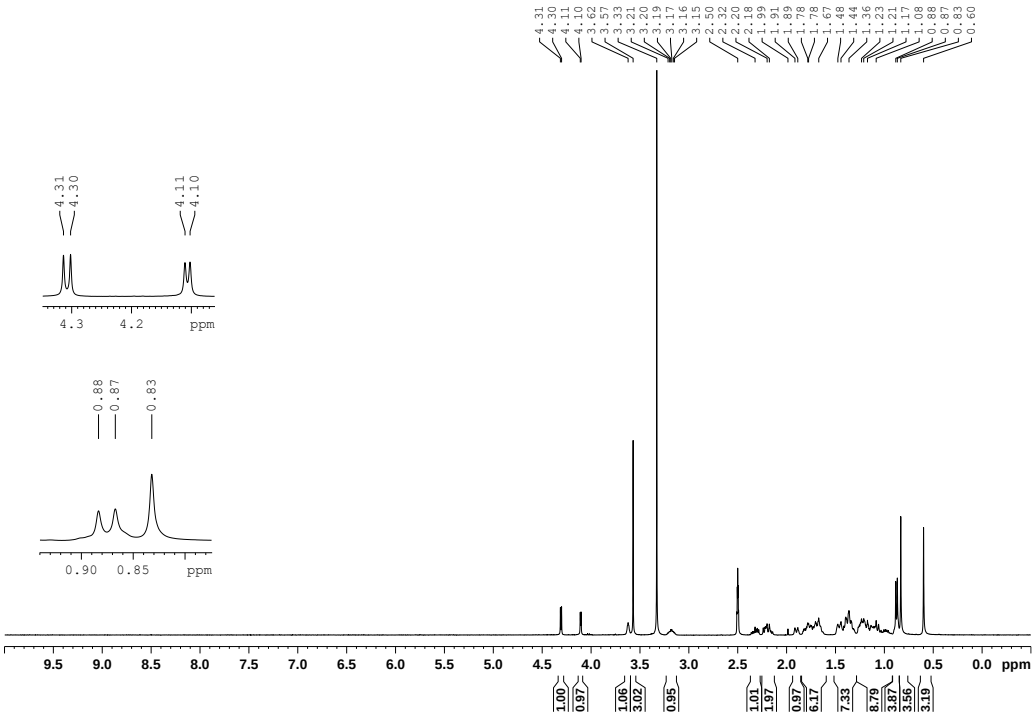


Figure S13. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum for compound **6**.

Compound 7

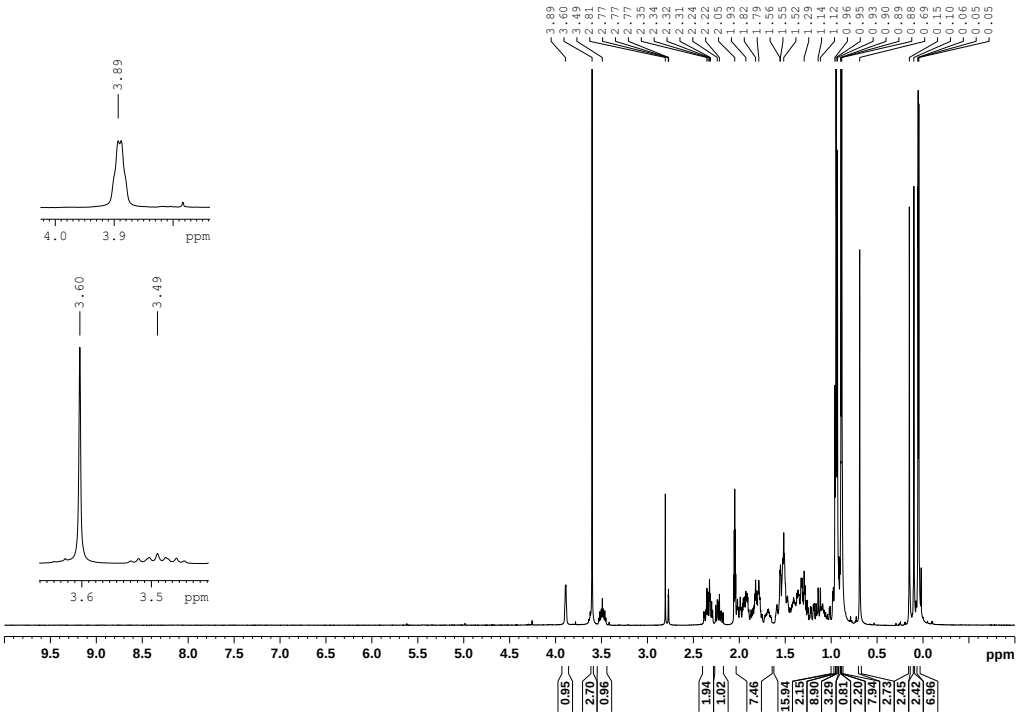


Figure S14. ^{1}H NMR (400 MHz, acetone-d_6) spectrum for compound **7**. The material contained a *tert*-butyl trimethylsilyl containing impurity of unknown structure.

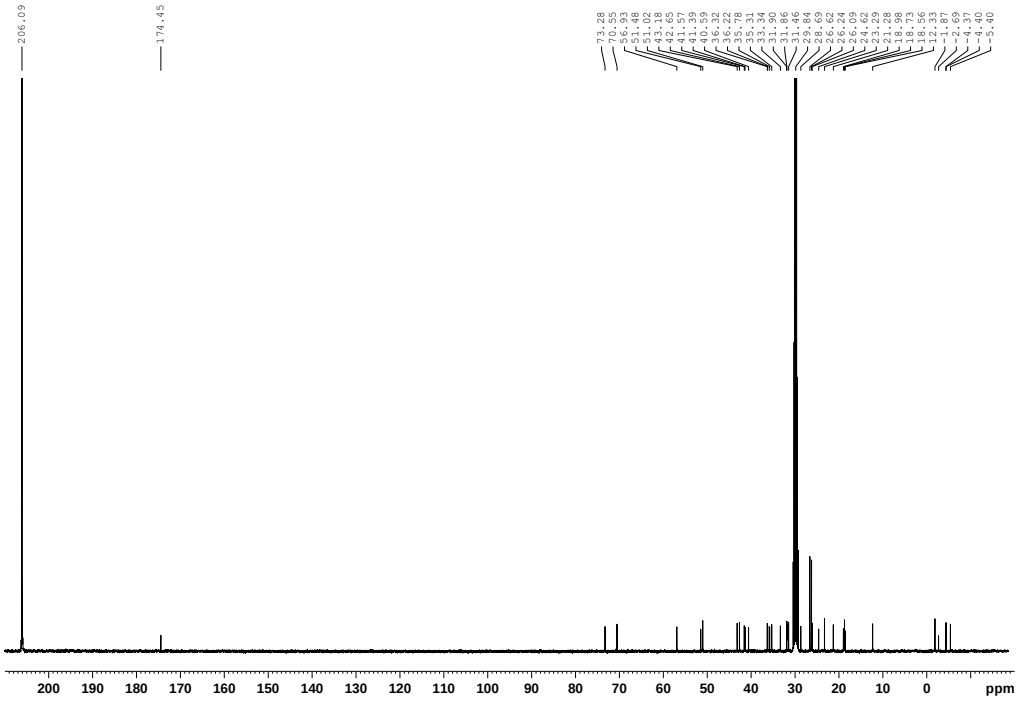


Figure S15. ^{13}C NMR (100 MHz, acetone-d_6) spectrum for compound **7**. (Impurity visible at 26.1 and -2.7 ppm)

Compound 8

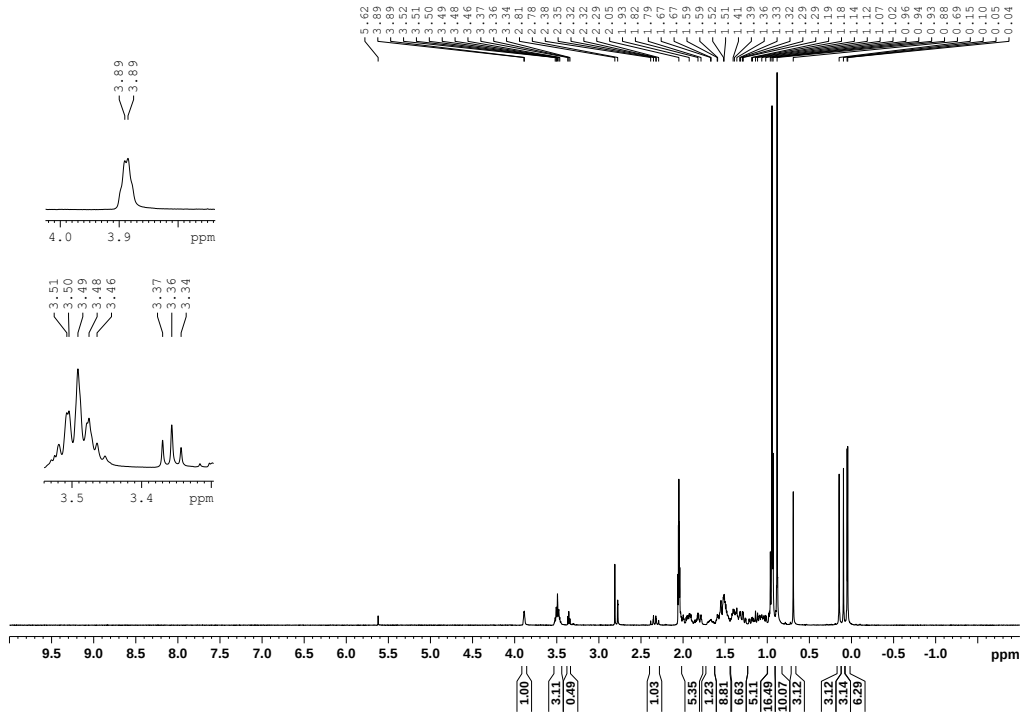


Figure S16. ^{1}H NMR (400 MHz, acetone-d_6) spectrum for compound **8**.

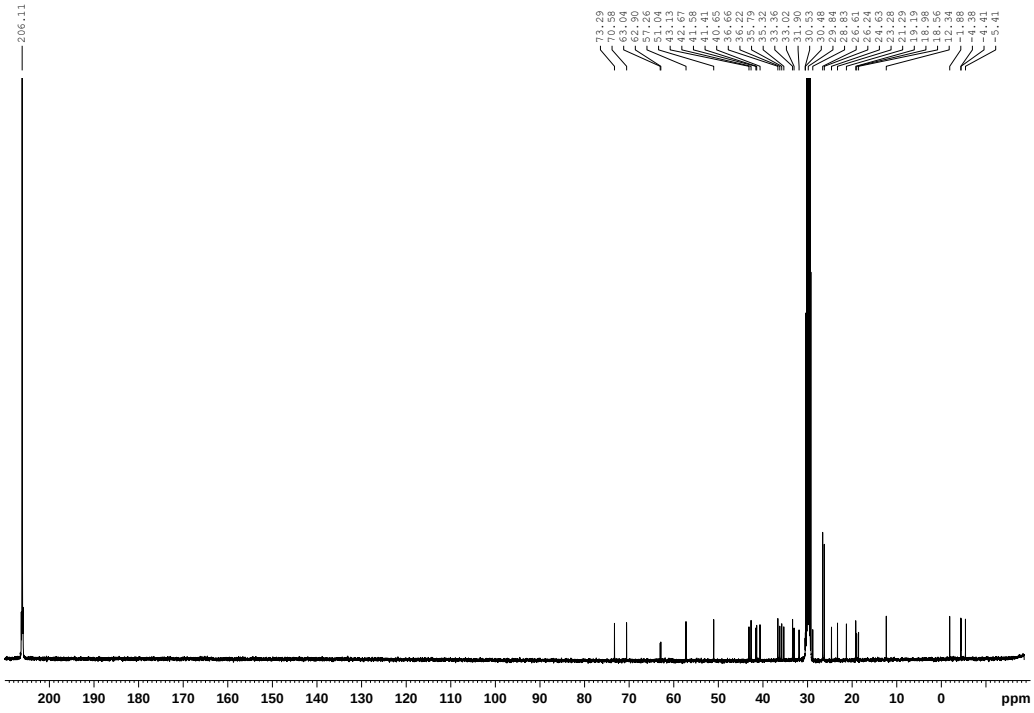


Figure S17. ^{13}C NMR (100 MHz, acetone-d_6) spectrum for compound **8**.

Compound 9

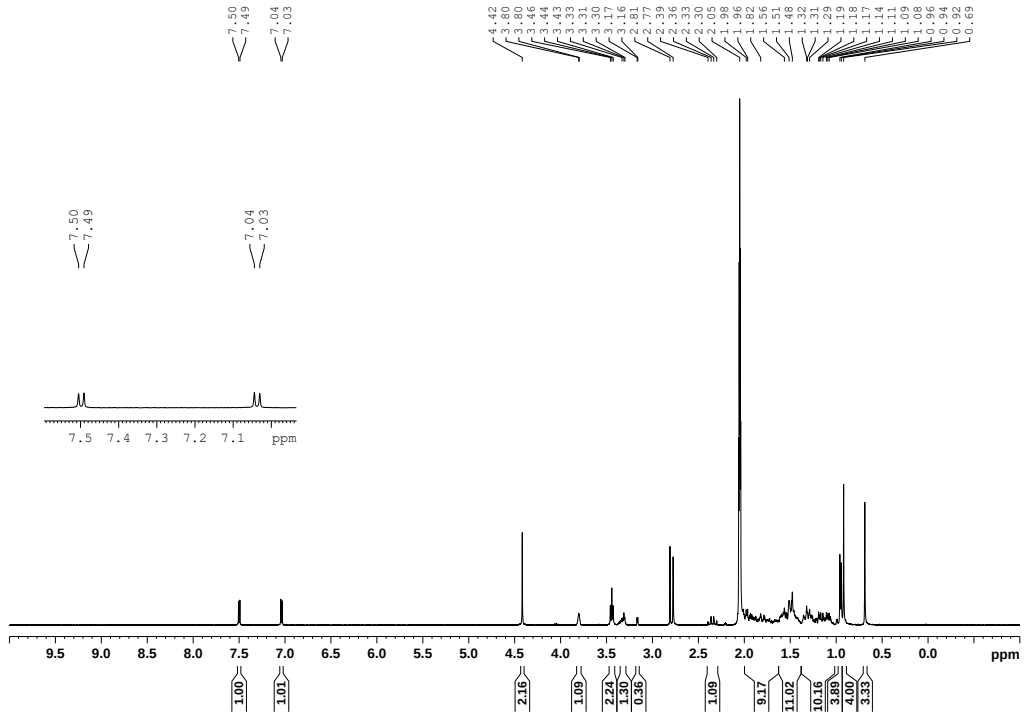


Figure S18. ^{1}H NMR (600 MHz, acetone-d_6) spectrum for compound **9**.

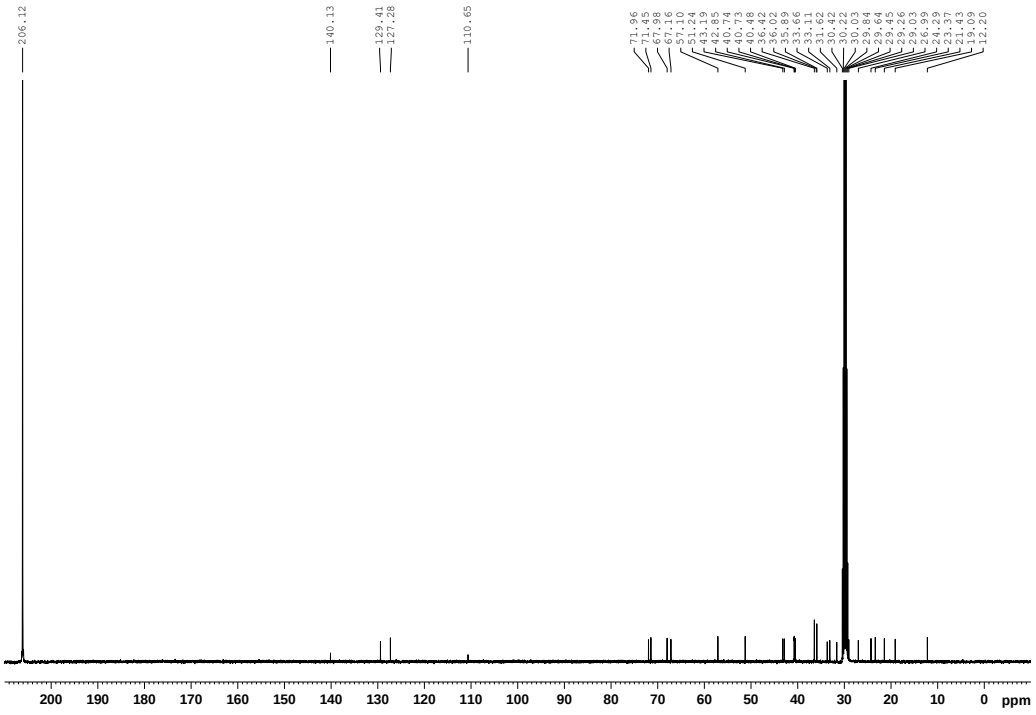


Figure S19. ^{13}C NMR (150 MHz, acetone-d_6) spectrum for compound **9**.

Compound 10

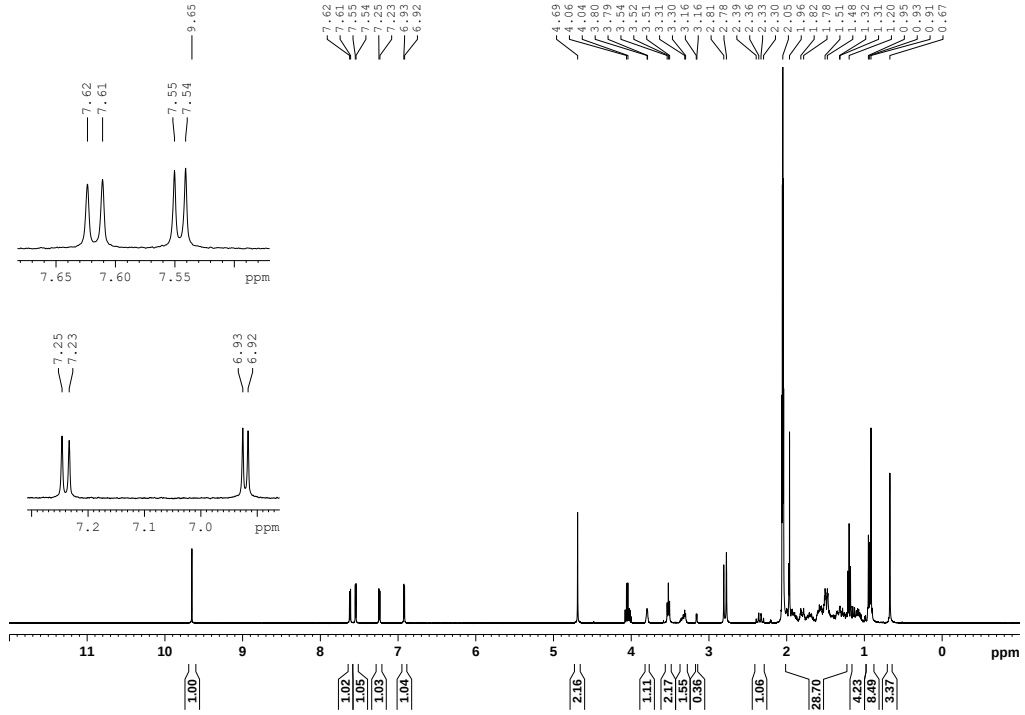


Figure S20. ^{1}H NMR (600 MHz, acetone-d_6) spectrum for compound **10**. The analyzed material contained EtOAc.

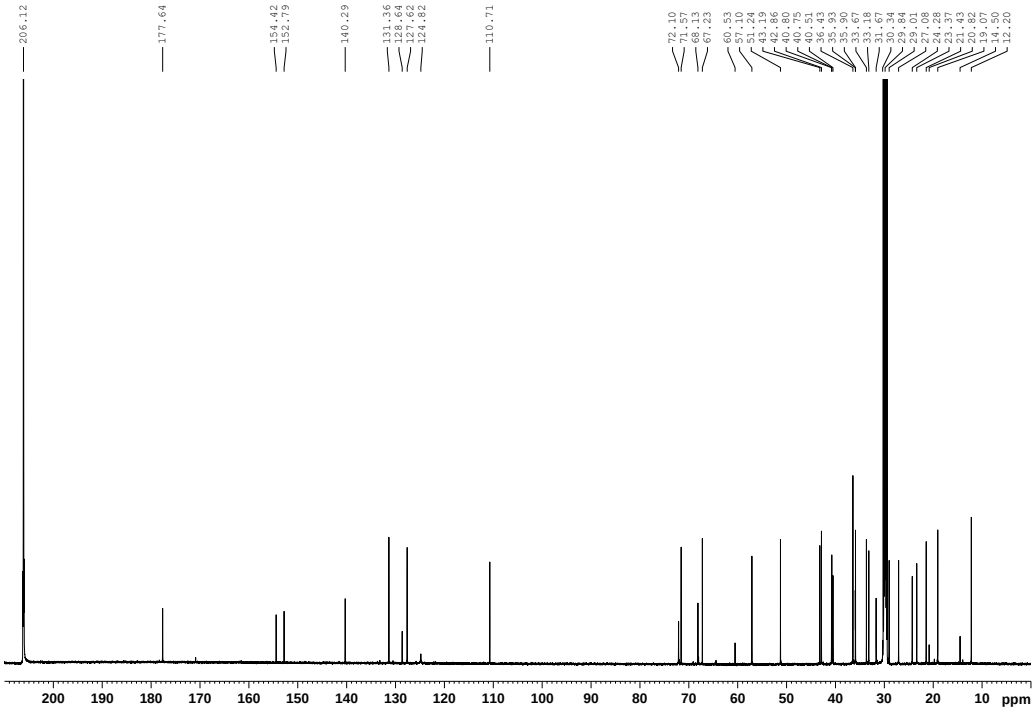


Figure S21. ^{13}C NMR (150 MHz, acetone-d_6) spectrum for compound **10**. The analyzed material contained EtOAc.

Compound 11

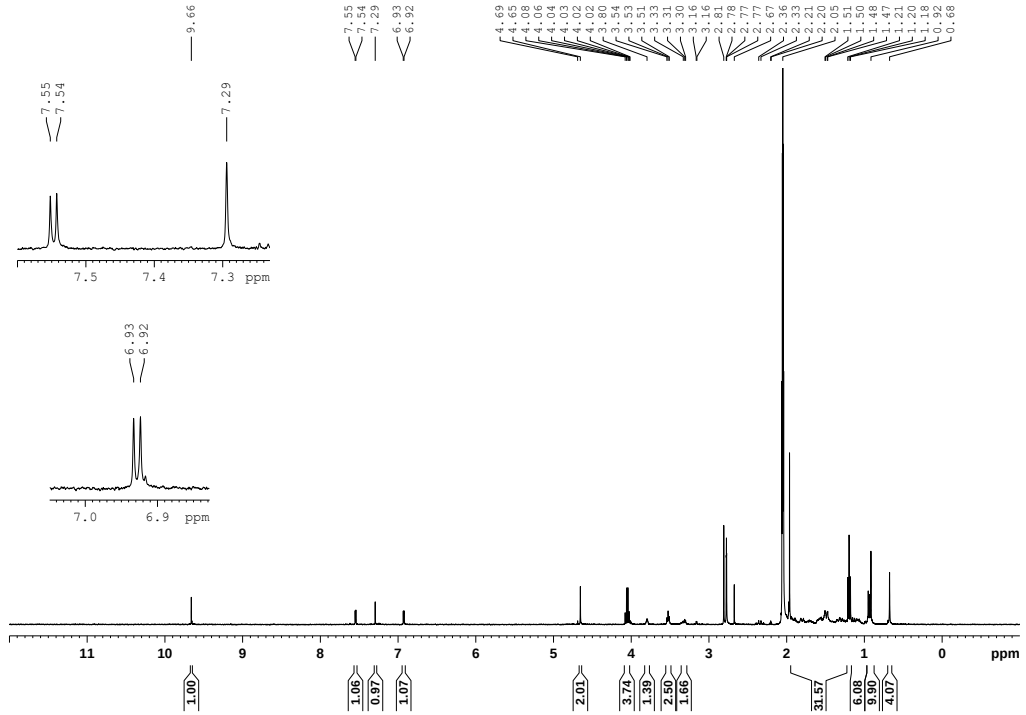


Figure S22. ^{1}H NMR (600 MHz, acetone-d_6) spectrum for compound **11**. The analyzed material contained EtOAc.

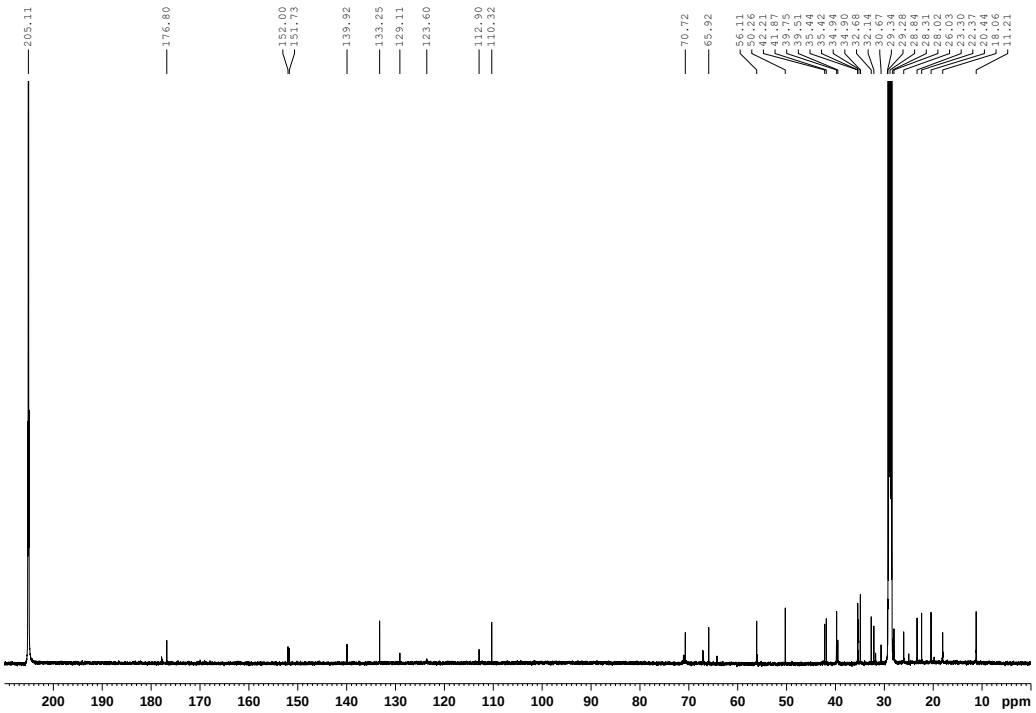


Figure S23. ^{13}C NMR (150 MHz, acetone-d_6) spectrum for compound **11**. The analyzed material contained EtOAc.

Compound 12

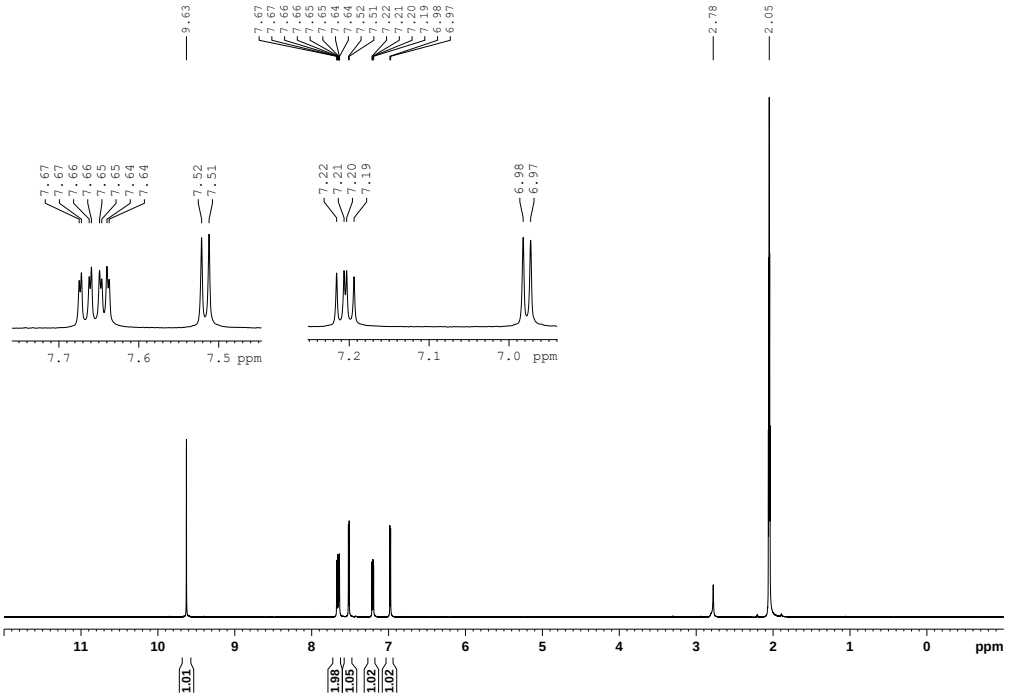


Figure S24. ^{1}H NMR (400 MHz, acetone-d_6) spectrum for compound **12**.

Compound 13

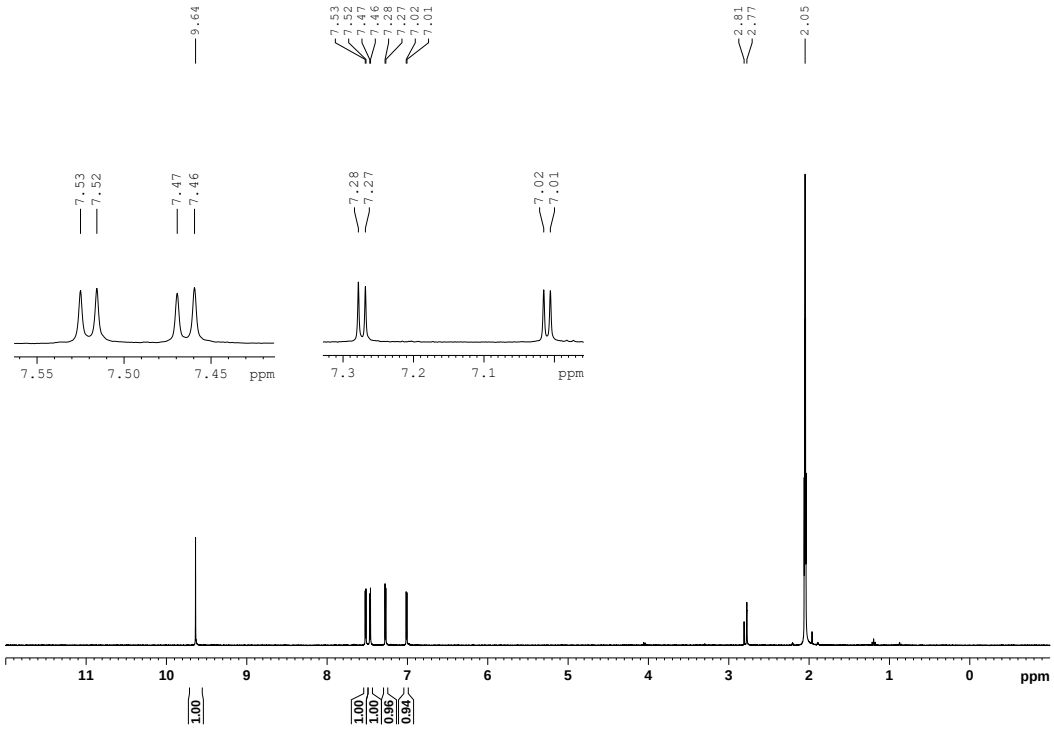


Figure S25. ^{1}H NMR (400 MHz, acetone-d_6) spectrum for compound **13**.

Compound 14

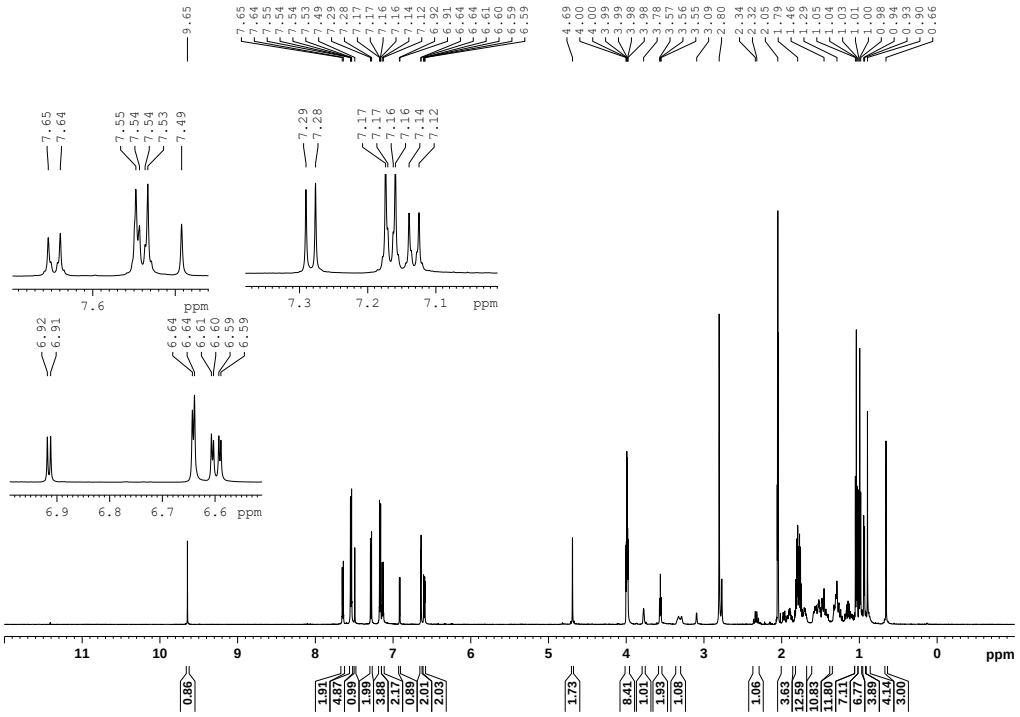


Figure S26. ^{1}H NMR (600 MHz, acetone-d_6) spectrum for compound **14**.

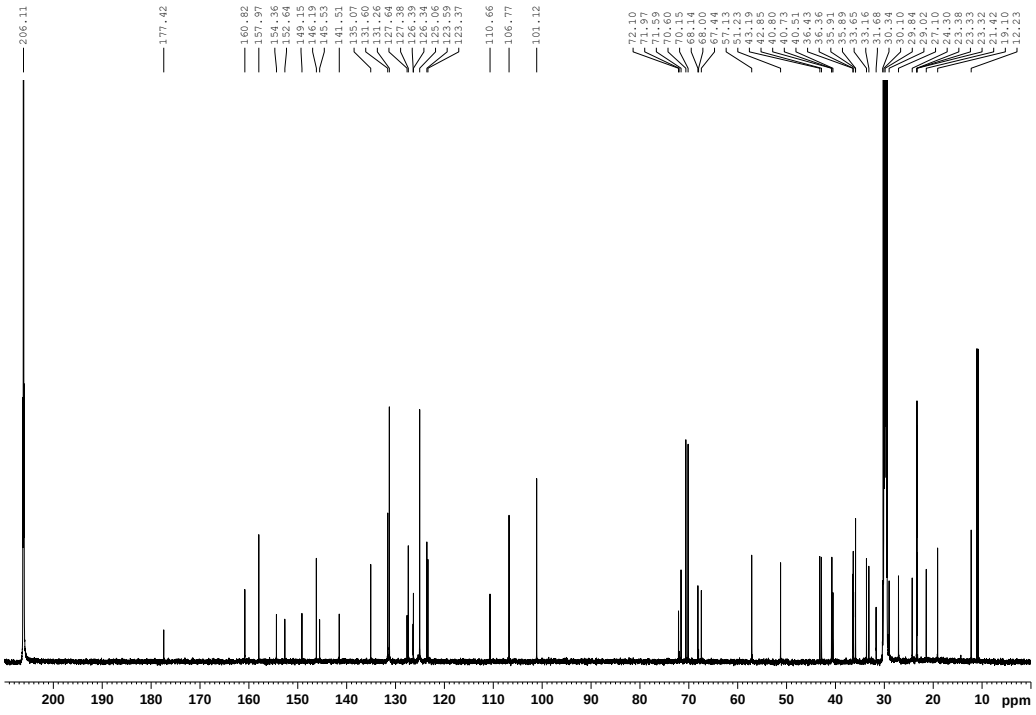


Figure S27. ^{13}C NMR (150 MHz, acetone-d_6) spectrum for compound **14**.

Compound 15

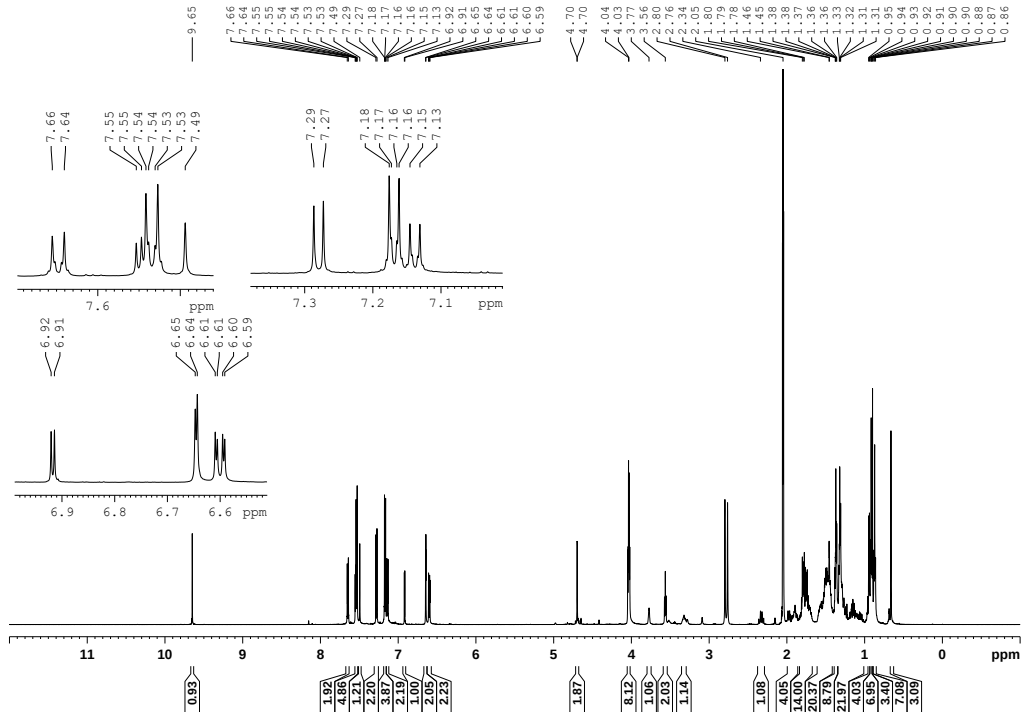


Figure S28. ^{1}H NMR (600 MHz, acetone-d_6) spectrum for compound **15**.

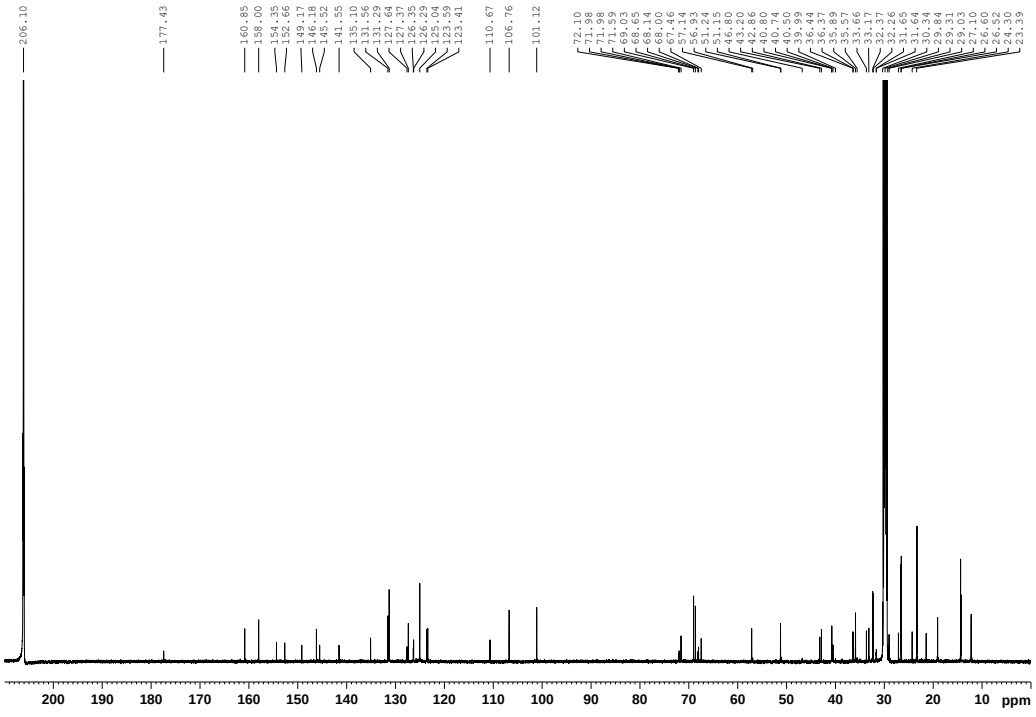


Figure S29. ^{13}C NMR (150 MHz, acetone-d_6) spectrum for compound **15**.

Compound 16

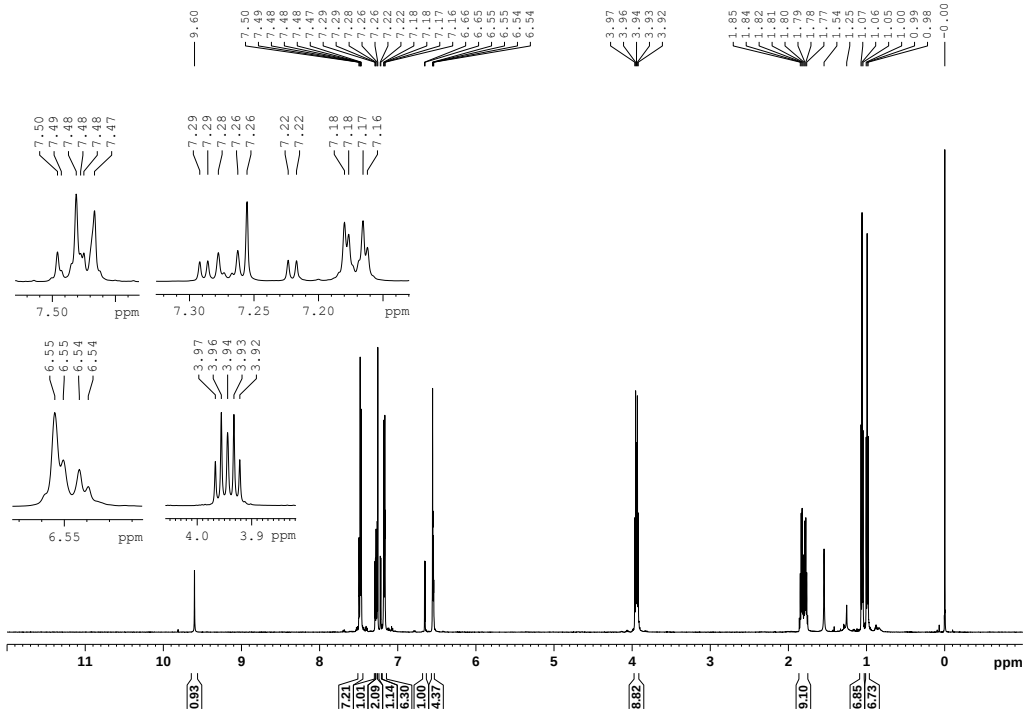


Figure S30. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum for compound **16**.

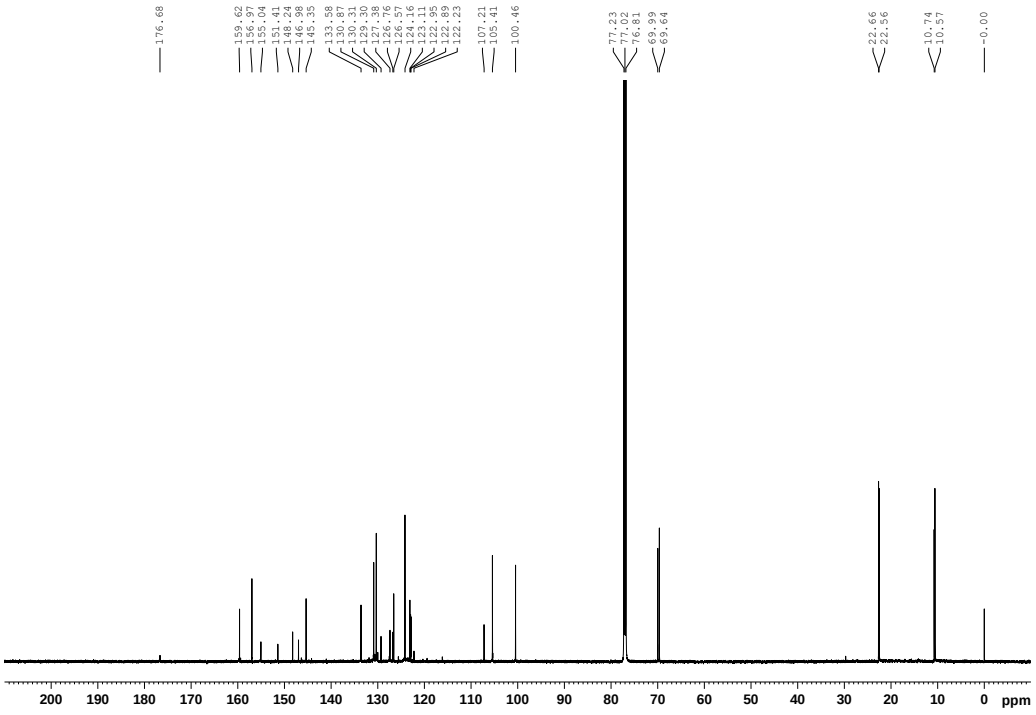


Figure S31. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum for compound **16**.

Compound 17

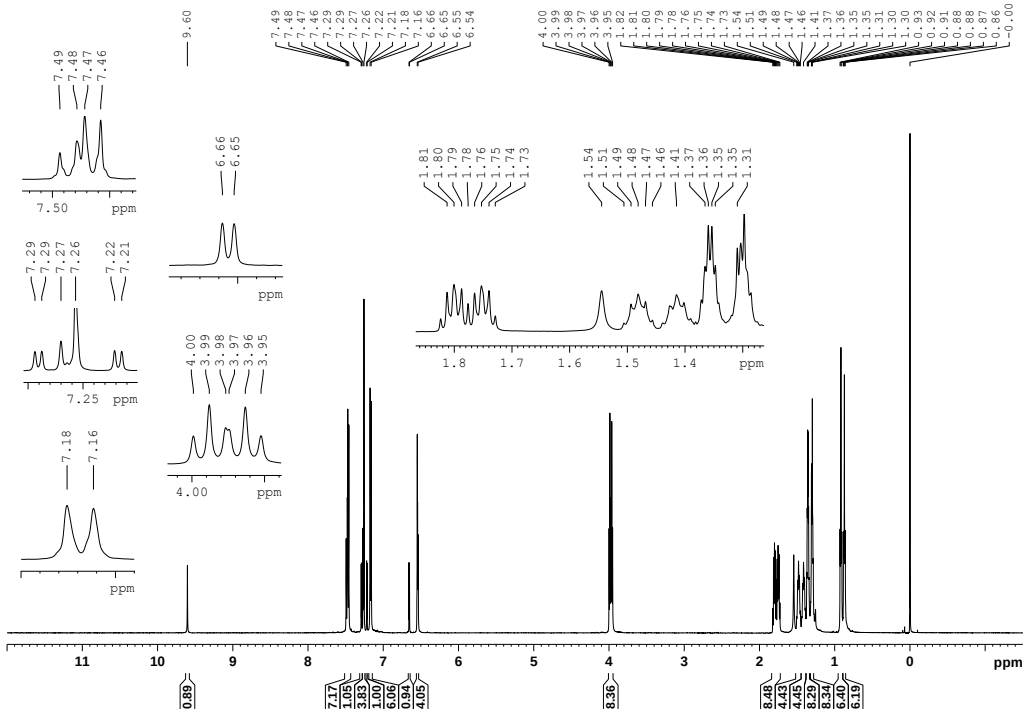


Figure S32. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum for compound **17**.

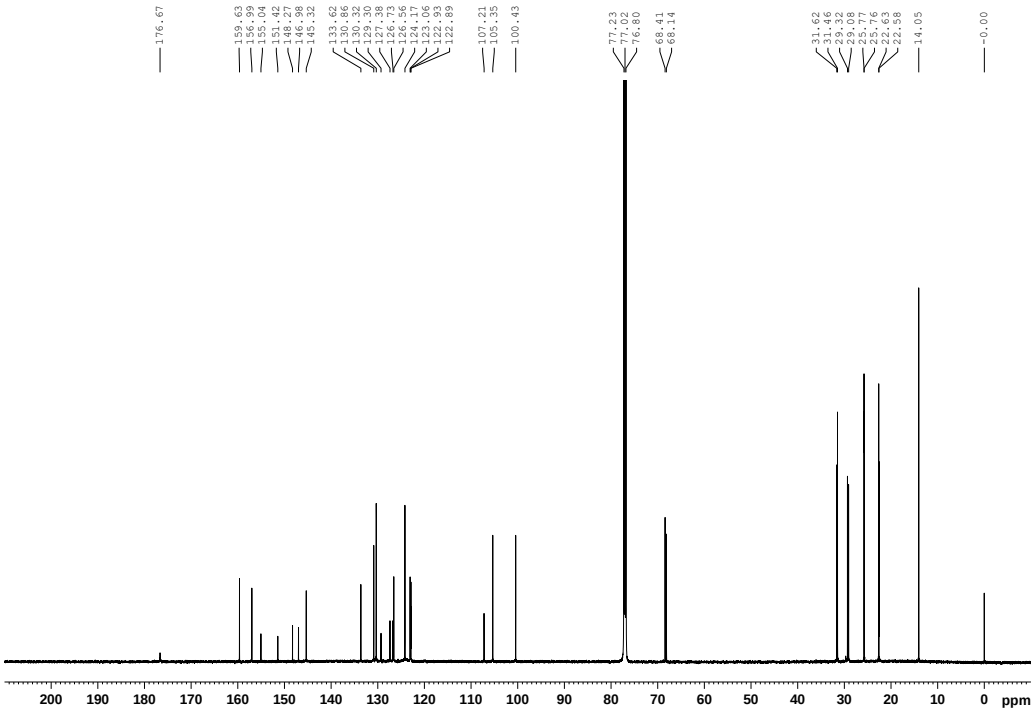


Figure S33. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum for compound **17**.

Sensitizer C_3-CDCA

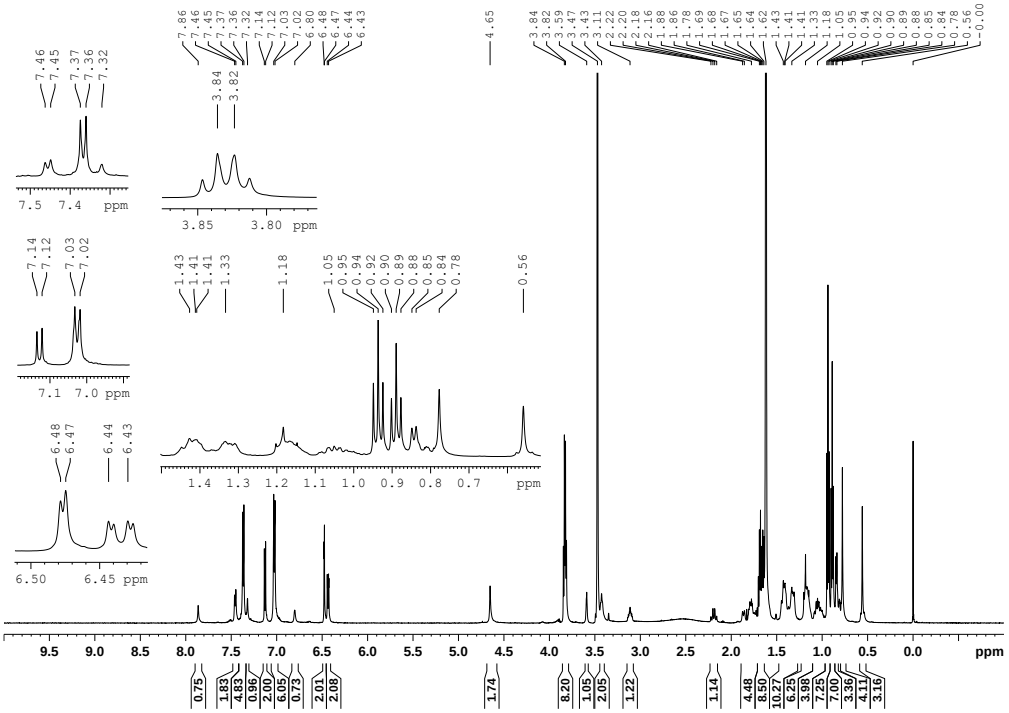


Figure S34. ^{1}H NMR (600 MHz, THF-d_8) spectrum for compound **C_3-CDCA**.

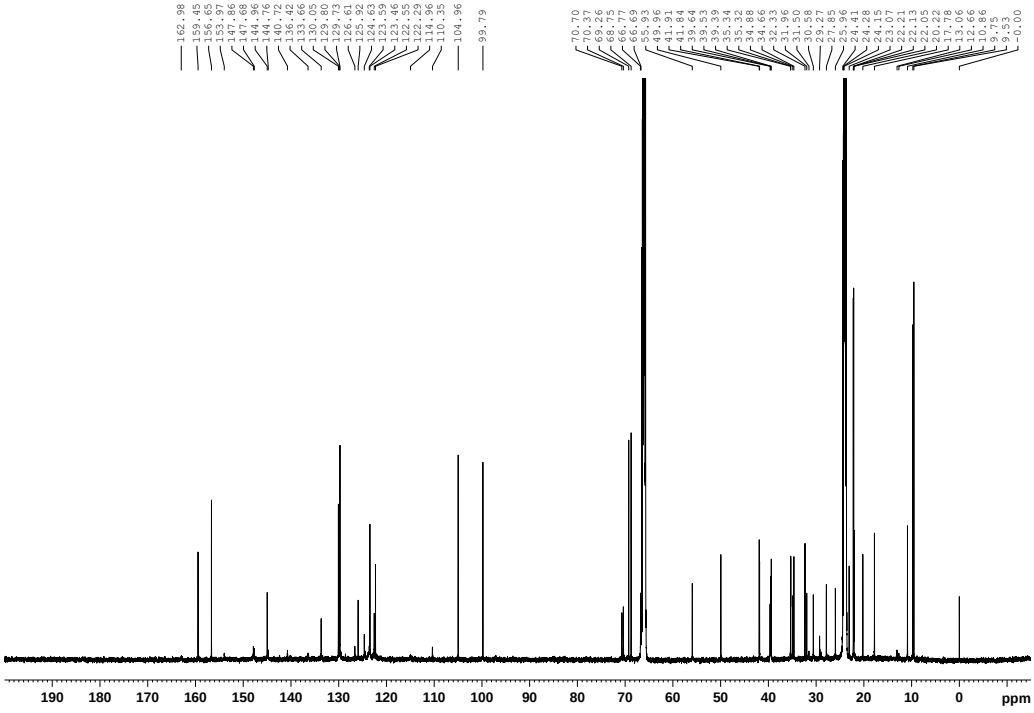


Figure S35. ^{13}C NMR (150 MHz, THF-d_8) spectrum for sensitizer **C_3-CDCA**.

Sensitizer C_6-CDCA

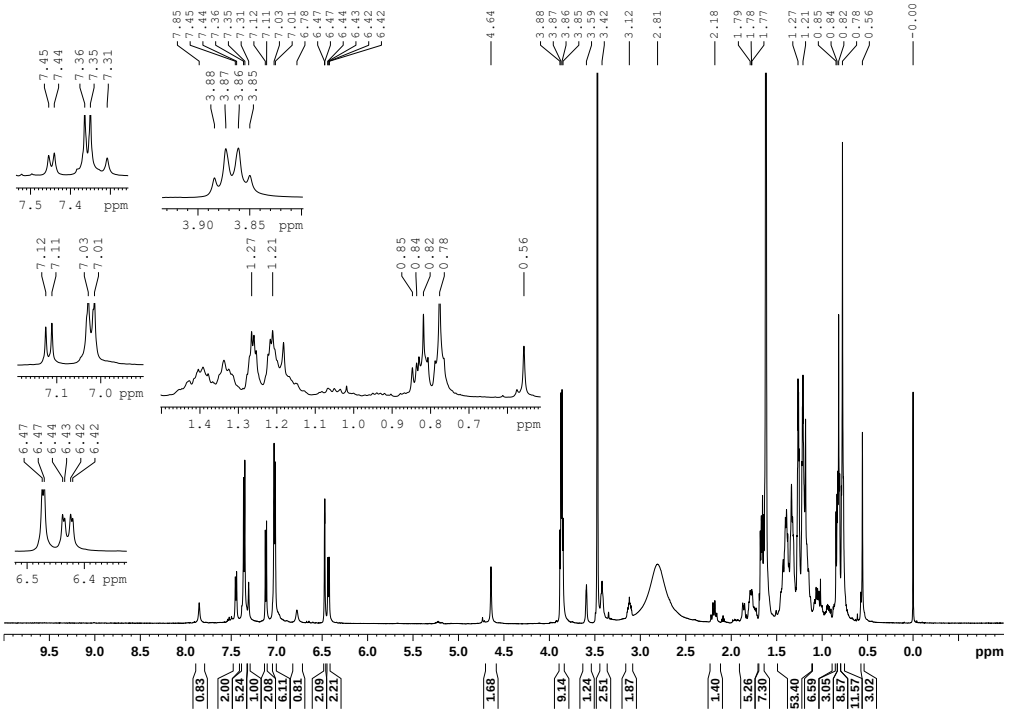


Figure S36. ^{1}H NMR (600 MHz, THF-d_8) spectrum for sensitizer **C_6-CDCA**.

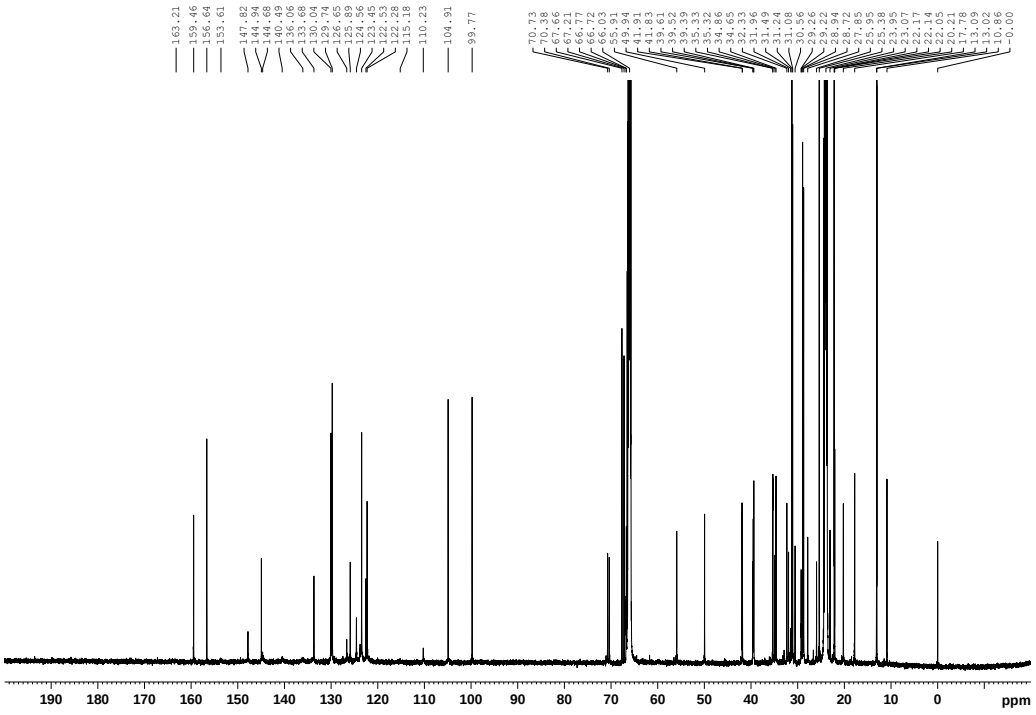


Figure S37. ^{13}C NMR (150 MHz, THF-d_8) spectrum for sensitizer **C_6-CDCA**.

Sensitizer C_3

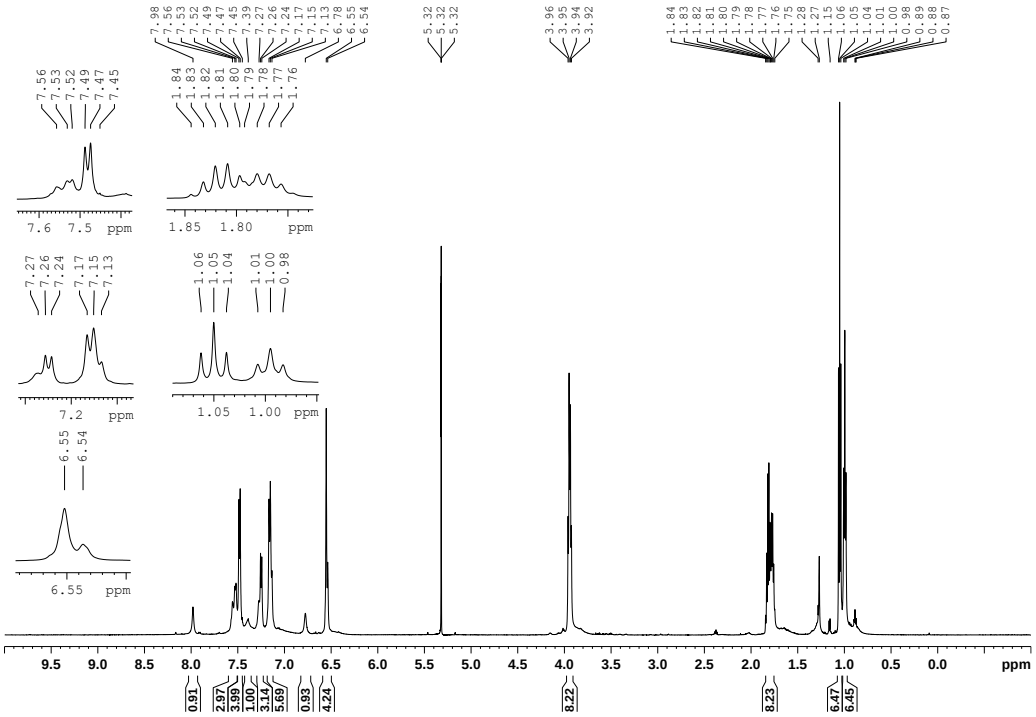


Figure S38. ^{1}H NMR (600 MHz, CD_2Cl_2) spectrum for sensitizer **C_3**.

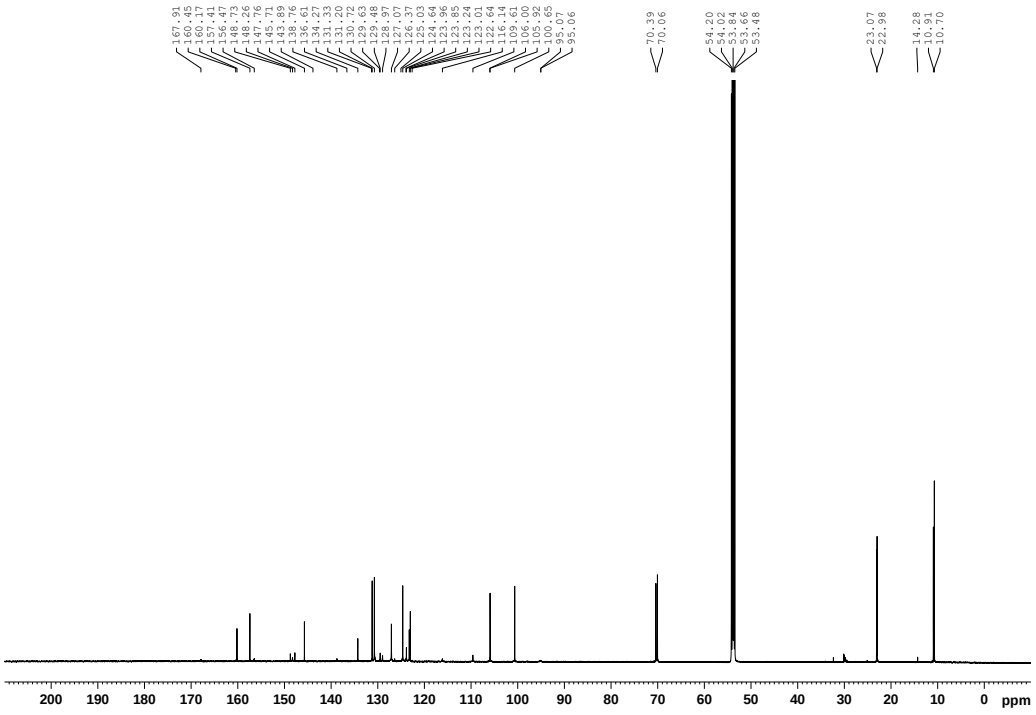


Figure S39. ^{13}C NMR (600 MHz, CD_2Cl_2) spectrum for sensitizer **C_3.**

Sensitizer C_6

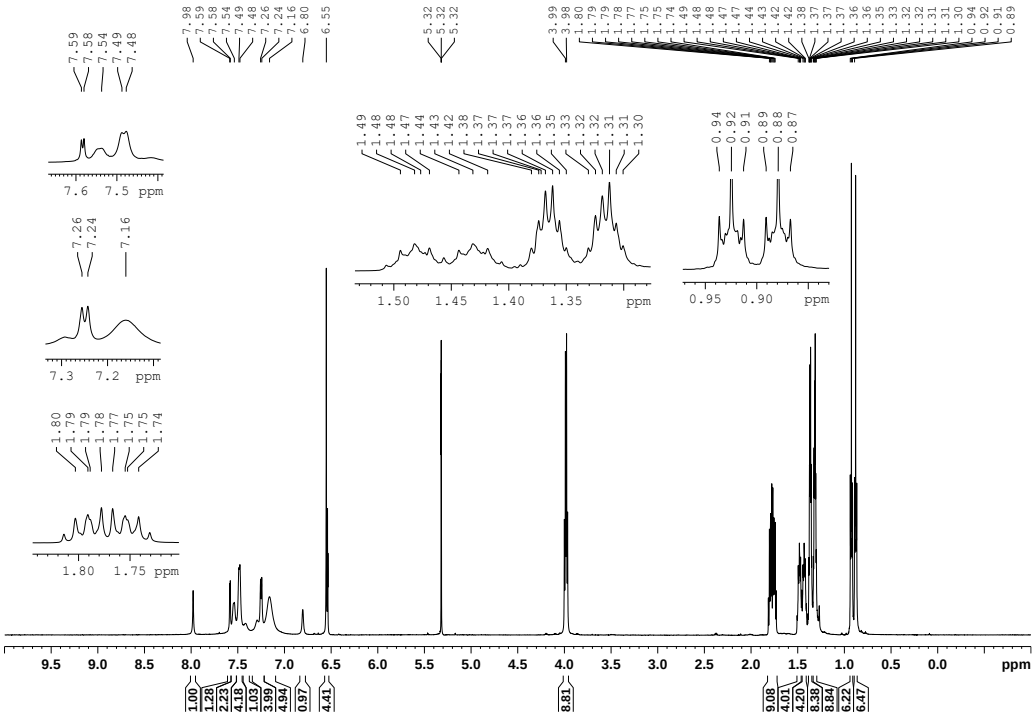


Figure S40. ^{1}H NMR (600 MHz, CD_2Cl_2) spectrum for sensitizer **C_6**.

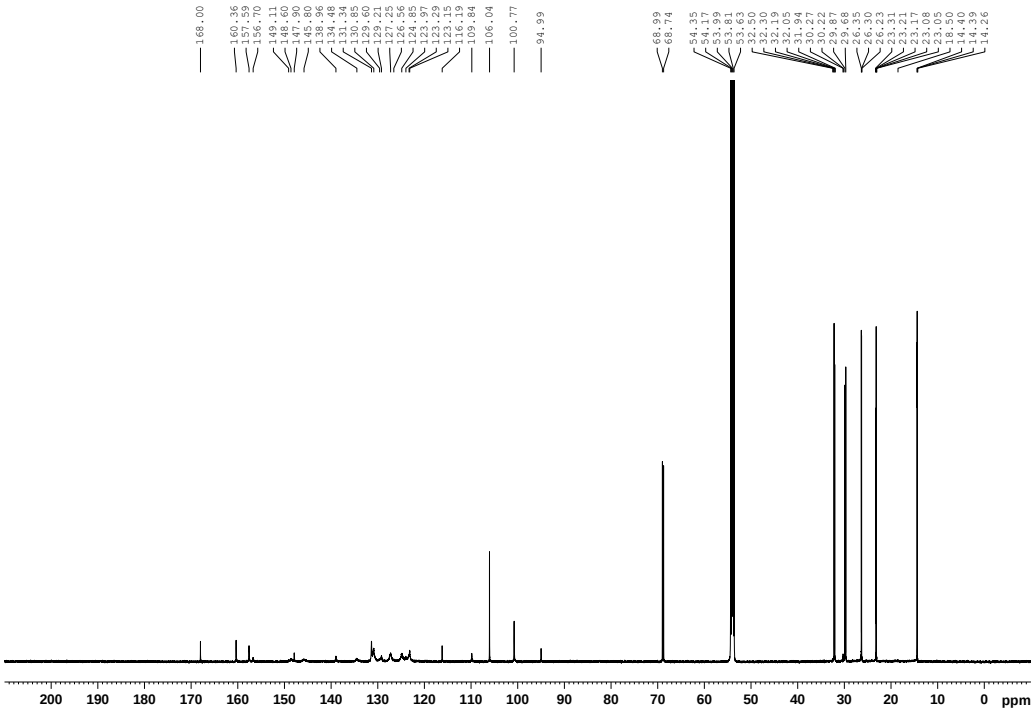


Figure S41. ^{13}C NMR (150 MHz, CD_2Cl_2) spectrum for sensitizer **C_6**.