Efficient synthesis of benzo fused tetrathia[7]helicene

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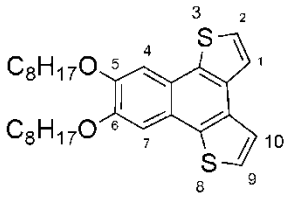
1. General experimental procedure

NMR spectra were acquired on commercial instruments (Bruker Avance 300 MHz and Bruker AMX 400 MHz) and chemical shifts (δ) are reported in parts per million (ppm) referenced to tetramethylsilane (^{1}H) or the internal (NMR) solvent signal (^{13}C). Mass spectra were run using a HP5989A apparatus (EI,70 eV ionization energy) with Apollo 300 data system, a Micromass Quattro II apparatus (ESI) with MASSLYNX data system or a Thermo Finnigan LCQ Advantage apparatus (ESI/APCI). Exact mass measurements were acquired on a Kratos MS50TC instrument (performed in the EI mode at a resolution of 10000). Melting points (not corrected) were determined using a Reichert Thermovar apparatus. UV-Vis spectra were taken on a Perkin-Elmer Lambda 40 spectrometer. For column chromatography, 70-230 mesh silica 60 (E. M. Merck) was used as the stationary phase. Chemicals received from commercial sources were used without further purification. Solvents used in reactions were freshly distilled over sodium/benzophenone, or were otherwise used as received. Thiophene was stirred over CaH_2 under argon for 12 hours, distilled and stored over 4 Å molecular sieves. $ZnCl_2$ was dried overnight in an oven at 260 °C and cooled under vacuum before use.

2. Experimental and characterization data

Building block 5 and helicene 1-3



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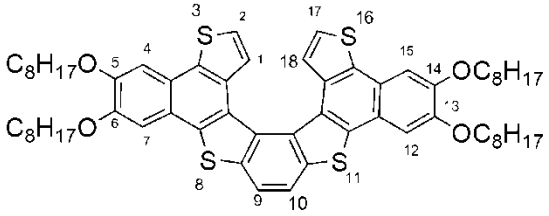

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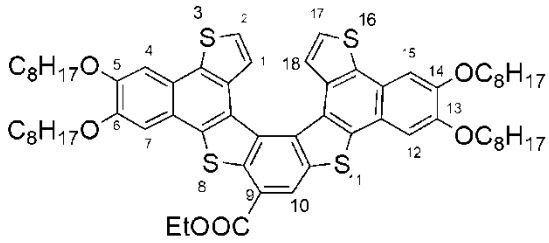

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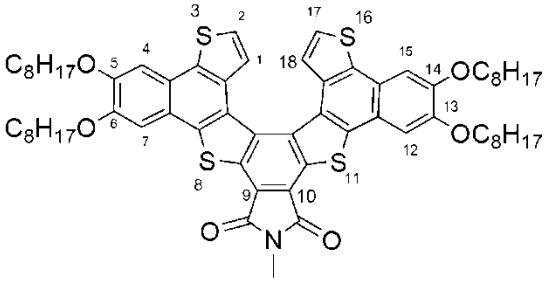

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Synthesis of 1,2-dibromo-4,5-bis(octyloxy)benzene

To a solution of 4,5-dibromocatechol (3.0 g, 11.1 mmol) in 2-butanone (150 mL) was added potassium carbonate (6.65 g, 48.1 mmol) and the reaction mixture was stirred for 30 min at room temperature. Then, 1-bromooctane (4.8 mL, 27.7 mmol) was added and the reaction mixture was refluxed for 12 hours. The solid residue from the reaction mixture was filtered off, and the filtrate was evaporated to dryness. The crude product was then redissolved in diethyl ether, washed with water and brine, dried over anhydrous $MgSO_4$ and evaporated. The excess of 1-bromooctane was removed by recrystallization from EtOH to give 1,2-dibromo-4,5-bis(octyloxy)benzene (4.3g, 78%) as a white solid. mp: 40-47 °C; MS (EI) *m/z* 492 [M^+]; HRMS (EI) calcd for $C_{22}H_{36}Br_2O_2$: 492.1062; found: *m/z* 492.1073; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (s, 2H, ArH), 3.93 (t, J = 6.6 Hz, 4H, OCH_2), 1.79 (quintet, 4H, CH_2), 1.42 (m, 4H, CH_2),

1.29 (m, 16H, CH_2), 0.88 (t, J = 6.4 Hz, 6H, CH_3), ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.1, 118.0, 114.7 (C, CH), 69.6 (OCH_2), 31.9, 29.4/29.3/29.1, 26.0, 22.7 (CH_2), 14.2 (CH_3).

Synthesis of 1,2-bis(octyloxy)-4,5-bis(2-thienyl)-benzene 4

To a solution of thiophene (8.3 mL, 103.6 mmol) in dry DME (150mL) was added *n*-BuLi (41.4 mL, 2.5 M, 103.6 mmol) in hexanes at 0 °C. The cooling bath was removed and the reaction was allowed to stir for 3 h at rt. Freshly dried $ZnCl_2$ (14.6 g, 107.6 mmol) was put in a flask under argon, after which dry DME (50 mL) was added, followed by the addition of the 2-thienyllithium solution via cannula. The mixture was stirred at rt for 1 h. A solution of $(Ph_3P)_4Pd$ (1.15 g, 1.01 mmol) and 1,2-dibromo-4,5-bis(octyloxy)benzene (5.0 g,10.1 mmol) was dissolved in dry DME (150 mL) and was added via cannula to the 2-thienylzinc chloride solution and the mixture was heated under reflux for 12 h, then allowed to cool to rt and quenched with 3 M HCl. The reaction mixture was extracted using petroleum ether, and the combined organic layers were dried over $MgSO_4$ and evaporated to yield a dark brown oil. Purification by column chromatography using CH_2Cl_2/petroleum ether (20:80) afforded compound **4** (4.45 g, 87 %) as a white solid. mp: 58-59 °C; MS (EI) *m/z* 498 [M^+] ; HRMS (EI) calcd for $C_{30}H_{42}O_2S_2$: 498.2626 ; found: *m/z* 498.2625; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, 2H, 4.6 Hz, 2-thiophene), 6.99 (s, 2H, ArH), 6.94-6.92 (t, 2H, J = 3.6 Hz, 3.5Hz 3-thiophene), 6.83 (d, J = 2.7 Hz, 2H, 4-thiophene), 4.0 (t, 4H, J = 6.6Hz OCH_2), 1.88-1.79 (m, 4H, CH_2), 1.47-1.42 (m, 4H, CH_2), 1.31-1.28 (m, 16H, CH_2), 0.88 (t, 6H, J = 6.2Hz CH_3) ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.7, 143.0, 126.9/126.8/126.4/125.5, 116.2 (C, CH), 69.5 (OCH_2), 31.9, 29.5/29.4/29.3, 26.1, 22.8 (CH_2), 14.2 (CH_3).

Synthesis of 5,6-bis(octyloxy)naphtho[1,2-*b*:4,3-*b'*]dithiophene 5

A solution of compound **4** (2.0 g, 4.0 mmol) in toluene (500 mL) with iodine (1.0 g, 4.0 mmol) and excess propylene oxide was irradiated at rt using a UV lamp. After 10 h of irradiation, reaction mixture was washed with $Na_2S_2O_3$, water and brine, dried over anhydrous $MgSO_4$ and evaporated to afford a brown residue. Purification by column chromatography using EtOAc/petroleum ether (20:80) as eluent gave compound **5** (1.64 g, 82 %) as a pale yellow solid. mp: 111-113 °C; MS (EI) *m/z* 496 [M^+] ; HRMS (EI) calcd for $C_{30}H_{40}O_2S_2$: 496.2469; found: *m/z* 496.2470; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (d, 2H, J = 5.2 Hz, ArH), 7.49 (d, 2H, J = 5.2 Hz, ArH), 7.44 (s, 2H, ArH), 4.16 (t, 2H, J = 6.6 Hz, OCH_2), 1.94 (quintet, 4H, J = 6.6 Hz, CH_2), 1.54 (quintet, 4H, J = 6.3 Hz, CH_2), 1.39-1.26 (m, 16H, CH_2), 0.90-0.87 (m, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.5,134.8, 132.1, 124.1/123.2/121.8, 106.3 (C, CH), 69.3 (OCH_2), 31.9, 29.5/29.4/29.3/26.2/22.8 (CH_2), 14.2 (CH_3).

Synthesis of 5,6-bis(octyloxy)naphtho[1,2-*b*:4,3-*b'*]dithiophene-2-carboxaldehyde 6

$POCl_3$ (0.59 mL, 6.5 mmol) was added dropwise to a solution of DMF (0.50 mL, 6.5 mmol) in dichloroethane (16 mL) at 0 °C, and the reaction mixture was stirred for 15 min at this temperature. The Vilsmeier salt thus formed was added dropwise to a solution of compound **5** (0.50 g, 1.0 mmol) in dichloroethane (15 mL) at 0 °C. The reaction mixture was then heated under reflux for 15 h, cooled to room temperature and quenched with 1 M KOAc solution. CH_2Cl_2 was added and the two layers separated, organic layer was washed with saturated $NaHCO_3$ solution, brine and dried over $MgSO_4$ and evaporated to dryness. Purification by column chromatography using EtOAc/Petroleum ether (30:70) as eluent gave aldehyde **6** (0.380 g, 71 %) as a yellow solid. mp 139-140 °C; MS (ESI+) *m/z* 524 [MH^+]; HRMS (APCI+) calcd for $C_{31}H_{40}O_3S_2$: 524.2419 ; found: *m/z* 525.2488 [M+H]$^+$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.11 (s, 1H, CHO), 8.33 (s, 1H, ArH), 7.71 (d, 1H, J = 5.2 Hz, ArH), 7.54 (d, 1H, J = 5.2 Hz, ArH), 7.43 (s, 1H, ArH), 7.38 (s, 1H, ArH), 4.18 (t, 4H, J = 6.7 Hz, OCH_2), 1.94 (quintet, 4H, J = 6.4 Hz, CH_2), 1.58-1.53 (m, 4H, CH_2), 1.39-1.31 (m, 16H, CH_2), 0.87 (t, 6H, J = 6.3Hz CH_3). ^{13}C

NMR (75 MHz, $CDCl_3$) δ 183.8 (CO), 151.2, 149.7, 140.8, 135.6, 132.7, 131.5, 125.1, 123.8, 122.9, 120.9, 106.4, 105.9 (C, CH), 69.3 (OCH_2), 31.9, 29.4, 26.2, 22.8 (CH_2), 14.2 (CH_3).

Synthesis of 5,6-bis(octyloxy)naphto[1,2-*b*:4,3-*b'*]dithiophene-2-methanol 6a

To a stirred solution of aldehyde **6** (0.50 g, 0.97 mmol) in THF (15 mL) and MeOH (5 mL) was added sodium borohydride (0.180 g, 4.7 mmol), and the reaction mixture was heated to 50 ^oC for 30 min. The reaction mixture was quenched with water and diluted with diethyl ether, the organic layer was separated, washed with brine and dried over anhydrous $MgSO_4$ and evaporated to dryness to give 5,6-bis(octyloxy)naphtho[1,2-*b*:4,3-*b'*]dithiophene-2-methanol (0.470 g, 93 %) as a white solid. The compound obtained was used without further purification. mp: 154-155 °C; MS (ESI+) *m/z* 526; HRMS (APCI+) calcd for $C_{31}H_{42}O_3S_2$: 526.2575; found: *m/z* 509.2539 [M-H_2O]; ^1H NMR (300 MHz, $CDCl_3$) δ 7.64 (d, 1H, *J* = 5.28 Hz, ArH), 7.59 (s, 1H, ArH), 7.46 (d, 1H, *J* = 5.2 Hz, ArH), 7.41 (s, 1H, ArH), 7.36 (s, 2H, ArH), 5.02 (s, 2H, C**H_2**OH), 4.20-4.14 (m, 4H, OCH_2), 1.96-1.89 (m, 4H, CH_2), 1.55-1.43 (m, 4H, CH_2), 1.35-1.25 (m, 16H, CH_2), 0.88 (t, 6H, CH_3).^{13}C NMR (75 MHz, $CDCl_3$) δ 149.59, 149.55, 142.7, 134.9, 132.0, 131.7, 124.2, 123.0, 121.8, 121.7, 106.3, 106.1 (C, CH), 69.3 (OCH_2), 61.0 (**C**H_2OH), 32.1, 31.9, 29.5, 29.4, 29.3, 26.2, 22.8 (CH_2), 14.2 (CH_3).

Synthesis of ((5,6-Bis(octyloxy)naphtho[1,2-*b*:4,3-*b'*]dithiophene-2-yl)methyl) triphenylphosphonium bromide 7

To a solution of alcohol **6a** (0.47 g, 0.89 mmol) in acetonitrile (20 mL) was added triphenylphosphine hydrobromide (0.368 g, 1.07 mmol) and the mixture was heated under reflux for 5 h. The solvent was evaporated and the residue was washed with diethyl ether. The obtained powder was dried under vacuum to give phosphonium salt **7** (0.485 g, 63 %) and was used without further purification. mp: 143-146 °C; MS (APCI+) *m/z* 851 (observed 851-Br = 772); HRMS (APCI+) calcd for $C_{49}H_{56}BrO_2PS_2$: 851.9755; found: *m/z* 771.3460 $[M-Br]^+$; ^1H NMR (300 MHz, $CDCl_3$) δ 7.87 (m, 6H, ArH), 7.70 (m, 3H, ArH), 7.64 (m, 6H, ArH), 7.40 (s, 1H, ArH), 7.23 (d, 1H, CH-thiophene, *J* = 4.8 Hz), 7.18 (d, 1H, CH-thiophene, *J* = 4.52 Hz), 7.08 (s, 1H, ArH), 6.80 (s, 1H, ArH), 6.24 (d, 2H, *J* = 13.5Hz), 4.11 (t, 2H, *J* = 6.4Hz, OCH_2), 3.96 (t, 2H, *J* = 6.2Hz, OCH_2), 1.91-1.90 (m, 4H, CH_2), 1.56 (m, 4H, CH_2), 1.38-1.33 (m, 16H, CH_2), 0.91-0.90 (m, 6H, CH_3). ^{13}CNMR (75 MHz, $CDCl_3$) δ 149.2, 149.1, 135.2, 135.1, 134.8, 134.7, 134.4, 132.3, 131.2, 131.1, 130.2, 128.6, 128.0, 127.9, 126.3, 126.2, 123.6, 123.2, 121.4 (CH), 118.6, 117.5 (CH_2), 106.0, 105.7, 69.3, 69.2, (OCH_2), 31.9, 29.6, 26.2, 22.8 (CH_2), 14.2 (CH_3)

Synthesis of 1,2-bis(5,6-bis(octyloxy)naphtho[1,2-*b*:4,3-*b'*]dithiophene-2-yl)ethene 8

To a stirred solution of phosphonium salt **7** (0.23 g, 0.28 mmol) in THF (5 mL) was added *t*-BuOK (0.04 g, 0.36 mmol) at 0 ^oC and the mixture was stirred for 30 min. To the resulting dark orange solution was added a solution of aldehyde **6** (0.15 g, 0.28 mmol) in THF (5 mL) at 0 ^oC and reaction mixture was stirred at rt for 3 h. The solvent was removed under reduced pressure and a mixture of CH_2Cl_2 and MeOH was added to give a precipitate which was collected by filtration and dried in vacuo to give **8** (0.17 g, 58 %) as a yellow solid. Compound **8** was difficult to characterize by ^1H NMR spectroscopy due to its poor solubility. mp: 224-226 ^oC, MS (APCI+) *m/z* 1017; HRMS (APCI+) calcd for $C_{62}H_{80}O_4S_4$: 1017.5562 found: *m/z* 1017.5276.

Synthesis of 5,6,13,14-tetrakis(octyloxy)dibenzotetrathia[7]helicene 1

To a solution of compound **8** (0.15 g, 0.14 mmol, mixture of two isomers) in toluene (500 mL) was added iodine (0.037 g, 0.14 mmol). Argon was bubbled through the solution for 30 min before excess propylene oxide was added to the solution. The reaction mixture was irradiated at rt using a UV lamp. After 20 h of irradiation, the toluene layer was washed with aqueous

$Na_2S_2O_3$, water and brine, dried over anhydrous $MgSO_4$ and evaporated to afford a brown residue. Purification by column chromatography using EtOAc/petroleum ether (10:90) as eluent gave the racemic **helicene 1** (0.024 g, 16 %) as a light yellow solid. mp: 135-137 °C; MS (APCI+) *m/z* 1015; HRMS (APCI+) calcd for $C_{62}H_{78}O_4S_4$: 1015.5403; found: *m/z* 1015.4856; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 2H, ArH), 7.56 (s, 2H, ArH), 7.52 (s, 2H, ArH), 6.94 (d, 2H, *J* = 5.5 Hz, 2-thiophene), 6.87 (d, 2H, *J* = 5.56 Hz, 3-thiophene), 4.28-4.23 (m, 8H, OCH_2), 2.00-1.96 (m, 8H, CH_2), 1.60-1.56 (m, 8H, CH_2), 1.44-1.33 (m, 32H, CH_2), 0.91-0.89 (m, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 149.7, 137.1/135.3/ 134.5/133.4/131.4, 128.4, 126.7, 121.5, 121.4, 119.7, 106.8, 106.0 (C, CH), 69.5, 69.4, 32.0, 29.8/29.5/29.4/29.3/26.2, 22.8 (CH_2), 14.2 (CH_3).

Synthesis of 5,6-bis(octyloxy)naphtho[1,2-*b*:4,3-*b'*]dithiophene-2-oxoethyl acetate 9

To a solution of compound **5** (0.50 g, 1.0 mmol) in dry THF (20 mL), *n*-BuLi (0.52 mL, 2.5 M in hexanes, 1.3 mmol) was added dropwise at -78 °C under nitrogen atmosphere. The mixture was stirred for 1 h at -78 °C. To this yellow suspension was added dropwise a solution of diethyl oxalate (0.46 mL, 3.5 mmol) in dry THF (20 mL) over 15 min at -78 °C. The reaction mixture was stirred at this temperature for 30 min, then at rt for another 30 min and was then quenched with saturated aqueous NH_4Cl (20 mL) and extracted with EtOAc.The organic phases were dried over anhydrous $MgSO_4$ and evaporated under vacuum. The residue was purified by column chromatography (eluent: with a gradient from petroleum ether to ethylacetate) to give first the unreacted starting material **5** (0.072 g, 12 %) and then compound **9** (0.390 g, 65 %) as an orange solid. mp:134-136 °C; MS (APCI+) *m/z* 596; HRMS (APCI+) calcd for $C_{34}H_{44}O_5S_2$: 596.2630; found: *m/z* 597.2716 $[M+H]^+$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H, ArH), 7.71 (d, 1H, *J* = 5.28 Hz, 1H, ArH), 7.52 (d, 1H, *J* = 5.28 Hz, 1H, ArH), 7.41 (s, 1H, ArH), 7.34 (s, 1H, ArH), 4.53 (q, 2H, *J* = 7.23 Hz, COC**H$_2$**), 4.19 (quintet, 4H, OCH_2), 1.96 (quintet, 4H, CH_2), 1.57-1.49 (m, 4H, CH_2), 1.47 (t, 3H, *J* = 7.0 Hz, CH_2**CH$_3$**), 1.42-1.25 (m, 16H, CH_2), 0.92 (t, 3H, *J* = 5.2Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9 (CO), 161.8 (COOR), 151.5/149.8, 142.7, 136.2, 135.9, 133.5, 132.4, 131.8, 125.1, 124.1, 123.1, 120.7, 106.5, 106.0 (C,CH), 69.4 (OCH_2), 63.0 (COO**CH$_2$**), 31.9, 29.5, 29.4, 29.2, 26.2, 22.8 (CH_2), 14.2 (CH_3).

Synthesis of 1-oxoethylacetate-1,2-bis(5,6-bis(octyloxy)naphtho[1,2-*b*:4,3-*b'*]dithiophene-2-yl)ethene 10

To a stirred solution of phosphonium salt **7** (0.297 g, 0.36 mmol) in THF (5 mL) was added *t*-BuOK (0.074 g, 0.66 mmol) at 0 °C and the mixture was stirred for 30 min. To the resulting dark orange solution was added a solution of oxoester **9** (0.200 g, 0.33 mmol) in THF (10 mL) at 0 °C and reaction mixture was stirred at rt for 3 h. THF was removed under reduced pressure and the crude product was purified by column chromatography using EtOAc/petroleum ether (20:80) as the eluent to give compound **10** (0.192 g, 52 % as a 1:1 mixture of *cis:trans* isomers) as an orange solid. mp: 110-112 °C; MS (APCI+) *m/z* 1089; HRMS (APCI+) calcd for $C_{65}H_{84}O_6S_4$: 1089.6189; found: *m/z* 1089.5204; ^{1}H NMR (400 MHz, $CDCl_3$) (mixture of *cis:trans* isomers) δ 8.35 (s, 1H, ArH), 7.87 (s,1H, vinylic protons of *cis* isomer), 7.82 (s, 1H), 7.67 (m, 2H), 7.56 (d, 1H), 7.42 (m, 6H), 6.81 (s, 1H, vinylic protons of *trans* isomer), 4.40-4.35 (m, 2H), 4.23-4.18 (m, 6H), 4.17-4.09 (m, 2H), 3.65-3.62 (m, 2H), 1.97-1.83 (m, 9H), 1.57-1.48 (m, 9H), 1.41-1.23 (m, 50H), 0.91-0.85 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0 (CO), 150.3, 149.7, 149.5, 149.3, 138.6, 137.4, 137.2, 136.0, 135.1, 134.7, 133.6, 132.2, 131.7, 131.6, 130.8, 126.2, 124.4, 123.9, 123.3, 123.0, 122.8, 122.7, 121.9, 120.9, 106.5, 106.0 (C,CH), 69.4 (OCH_2), 61.7, 32.2, 31.9, 29.6-29.2, 26.2, 25.9, 22.8 (CH_2), 14.5, 14.2 (CH_3).

Synthesis of 5,6,13,14-tetrakis(octyloxy)(9-ethoxycarbonyl)dibenzotetrathia[7]helicene 2

To a solution of compound **10** (0.050 g, 0.045 mmol, mixture of two isomers) in toluene (100 mL) was added iodine (0.011 g, 0.045 mmol). Argon was bubbled through the solution for 30 min before excess propylene oxide was added to the solution. The reaction mixture was irradiated at room temperature using a UV lamp. After 20 h of irradiation, the toluene layer was washed with aqueous $Na_2S_2O_3$, water and brine, dried over anhydrous $MgSO_4$ and evaporated to afford an orange residue. Purification by column chromatography using EtOAc/petroleum ether (20:80) as the eluent gave the racemic helicene **2** (0.031 g, 62 %) as light yellow solid and 10 % of trans isomer was recovered. mp: 133-134 °C; MS (APCI+) *m/z* 1087; HRMS (APCI+) calcd for $C_{65}H_{82}O_6S_4$: 1087.6030; found: *m/z* 1087.5071; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1H, ArH), 7.73 (s, 1H, ArH), 7.55 (s, 1H, ArH), 7.51 (s, 2H, ArH), 6.86-6.79 (m, 4H, CH thiophene), 4.62 (q, 2H, *J* = 7 Hz, COO**CH$_2$**), 4.29-4.23 (m, 8H, CH_2), 2.01-1.96 (m, 8H, CH_2), 1.60-1.58 (m, 8H, CH_2), 1.56 (t, 3H, *J* = 7 Hz, CH_2CH_3), 1.54-1.25 (m, 16H, CH_2), 0.92-0.89 (m, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4 (COO), 151.1, 150.6, 149.8, 138.2, 138.0, 137.4, 136.5, 134.8, 134.6, 133.3, 132.3, 127.8, 127.2, 126.6, 126.4, 123.9, 123.4, 122.0, 121.8, 121.6, 121.1, 120.6, 107.0, 106.5, 106.0, 105.9 (C, CH), 69.6, 69.5, 69.4 (OCH_2), 61.8 (COO**C**H_2), 32.0, 29.5, 29.4, 26.2, 22.8 (CH_2), 14.2 (CH_3).

Synthesis of 1-methyl-3,4-bis(5,6(bis(octyloxy)naphtho[1,2-*b*:3,4-*b'*]dithiophene-2-yl) pyrrole-2,5-dione 12

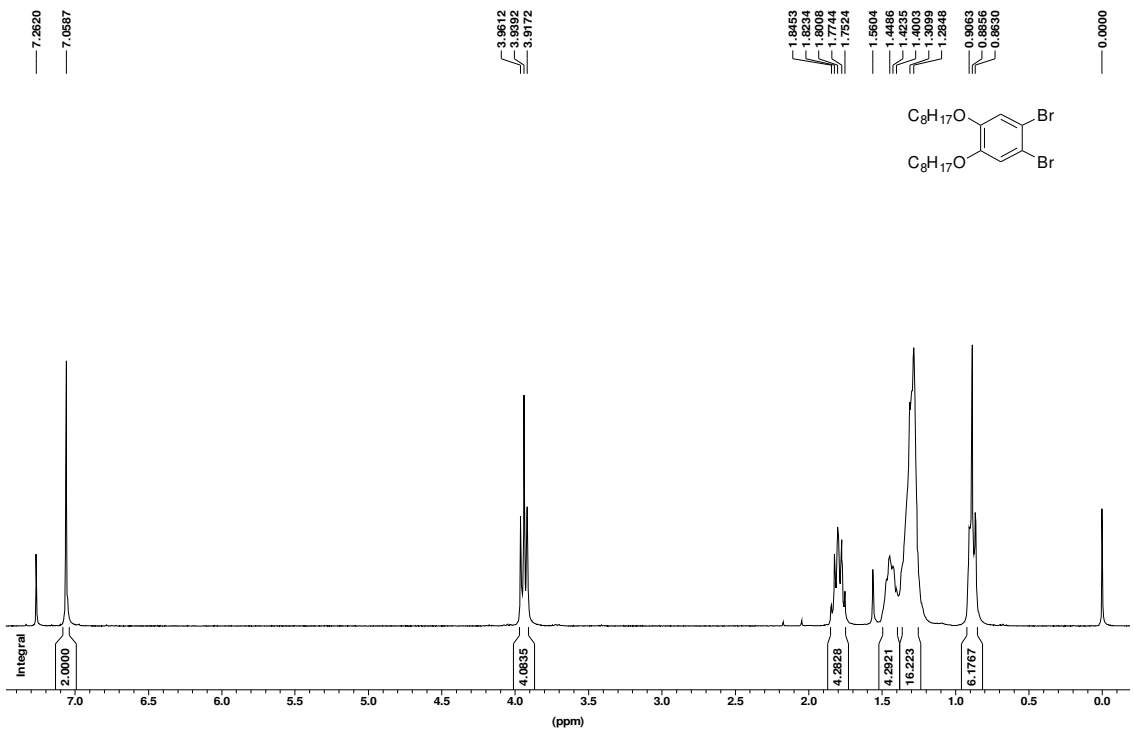
To a solution of compound **5** (1.0 g, 2.0mmol) in dry THF (100 mL) was added *n*-BuLi (0.96 mL, 2.4 mmol, 2.5 M in hexanes) at -78 ^{o}C under argon and the mixture was stirred for 2 h. To this was added tributyltin(IV)chloride (0.71 mL, 2.2 mmol) at -78 ^{o}C. The reaction mixture was stirred at this temperature for 2 h. The mixture was filtered through silica gel to remove inorganic salts. The filtrate was concentrated to give 2-tributyltin(IV)-5,6-bis(octyloxy)naphtho[1,2-*b*:4,3-*b'*]dithiophene (1.59 g, quantitative) as a green oil. This compound was used immediately in the following reaction without further purification.

To a solution of monostannyl compound (1.59 g, 2.0 mmol) and *N*-methyl dibromomaleimide **11** (0.220 g, 0.8 mmol) in toluene (50 mL) was added $Pd(PPh_3)_4$ (0.092 g, 0.08 mmol) under argon and the mixture was refluxed for 12 h. Toluene was removed under reduced pressure and the crude product was purified by column chromatography using EtOAc/petroleum ether (25:75) as eluent to give compound **12** (0.670 g, 74 %) as a violet solid. mp: 184-185 °C; MS (APCI) *m/z* 1100; HRMS (APCI+) calcd for $C_{65}H_{81}NO_6S_4$: 1100.6017; found: *m/z* 1100.5011; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 2H, CH thiophene), 7.55 (d, 2H, *J* = 5.28 Hz, ArH), 7.36 (d, 2H, *J* = 5.28 Hz, ArH), 7.25 (s, 2H, ArH), 7.22 (s, 2H, ArH), 4.13 (t, 4H, *J* = 6.5 Hz, OCH_2), 3.98 (t, 4H, *J* = 6.5 Hz, OCH_2), 3.18 (s, 3H, *N*-Me), 1.95-1.90 (m, 4H, CH_2), 1.88-1.76 (m, 4H, CH_2), 1.66-1.60 (m, 2H, CH_2), 1.58-1.51 (m, 6H, CH_2), 1.40-1.25 (m, 32H, CH_2), 0.94-0.85 (m,12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3 (CON), 150.4, 149.5, 138.3, 135.2, 131.7, 128.0, 127.9, 124.4, 123.2, 122.8, 120.9, 106.2, 105.9 (C, CH), 69.2, 69.2 (OCH_2), 32.0, 29.6, 29.3, 28.1, 26.9, 26.2, 24.6, 22.8 (CH_2), 17.6, 14.1 (CH_3).

Synthesis of 5,6,13,14-tetrakis(octyloxy)(1-methyl-2,5-dioxo pyrolo)dibenzotetrathia[7] helicene 3

To a solution of compound **12** (0.50 g, 0.45 mmol) in toluene (450 mL) was added iodine (0.116 g, 0.45 mmol) and excess propylene oxide (2.0 mL). The reaction mixture was irradiated using a 500 W high intensity lamp. After 1 h of irradiation, the toluene layer was washed with aqueous $Na_2S_2O_3$, water and brine, dried over anhydrous $MgSO_4$ and evaporated to afford a dark orange

residue. Purification by column chromatography using EtOAc/petroleum ether (20:80) as eluent gave the racemic helicene **3** (0.365 g, 73 %) as an orange solid. mp: 162-163 °C; MS (APCI+) *m/z* 1098; HRMS (APCI+) calcd for $C_{65}H_{81}NO_6S_4$: 1098.5859; found: *m/z* 1098.4852; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (s, 2H, ArH), 7.42 (s, 2H, ArH), 6.61 (d, 2H, *J* = 5.56 Hz, ArH), 6.45 (d, 2H, *J* = 5.56 Hz, ArH), 4.26-4.24 (m, 8H, OCH_2), 3.30 (s, 3H, *N*-Me), 2.04-1.97 (m, 8H, CH_2), 1.65-1.58 (m, 8H, CH_2), 1.45-1.35 (m, 32H, CH_2), 0.93-0.89 (m, 12H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4 (CON), 151.3, 149.9, 139.4, 136.1, 134.9, 132.7, 131.1, 126.6, 126.3, 123.9, 122.2, 121.8, 120.9, 106.4, 105.6, (C, CH), 69.5, 69.4 (OCH_2), 32.0, 29.6-29.2, 26.2, 22.8 (CH_2) 14.1 (CH_3).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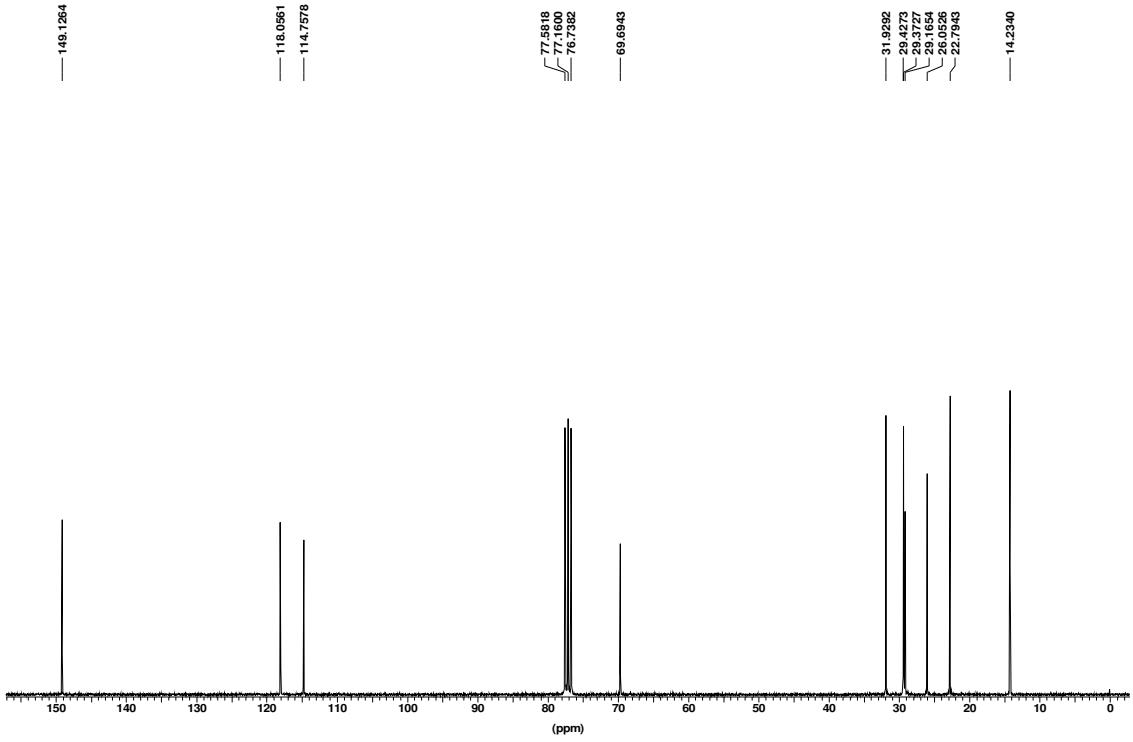
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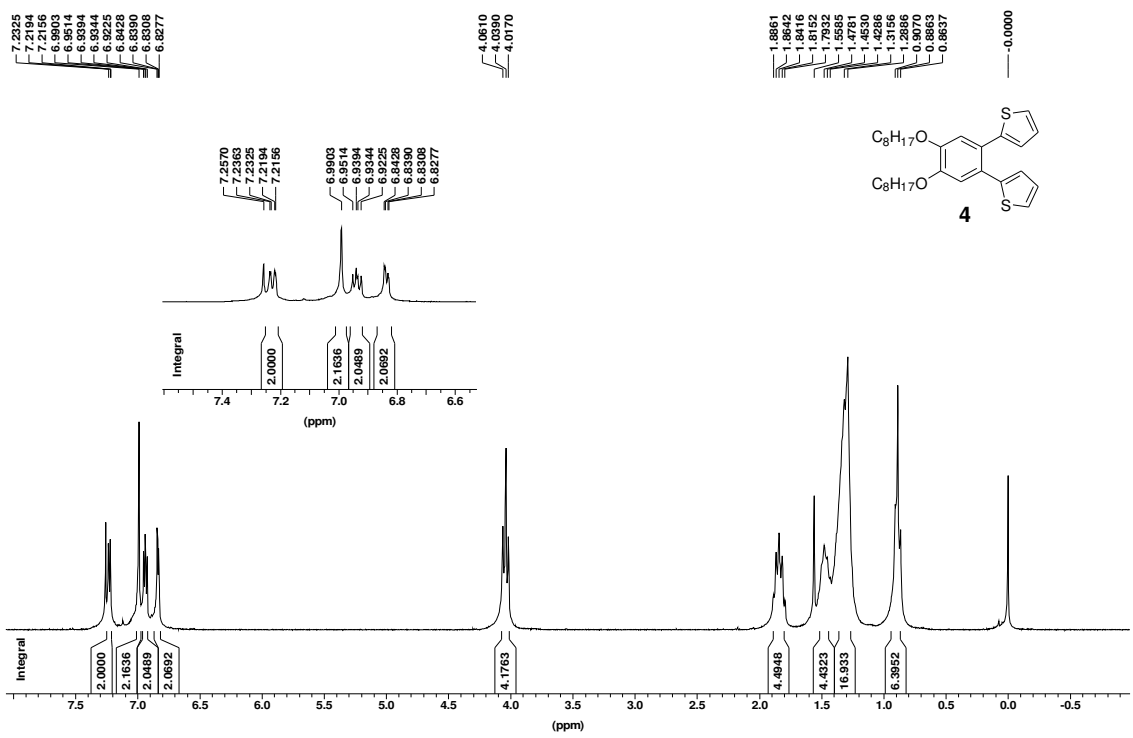
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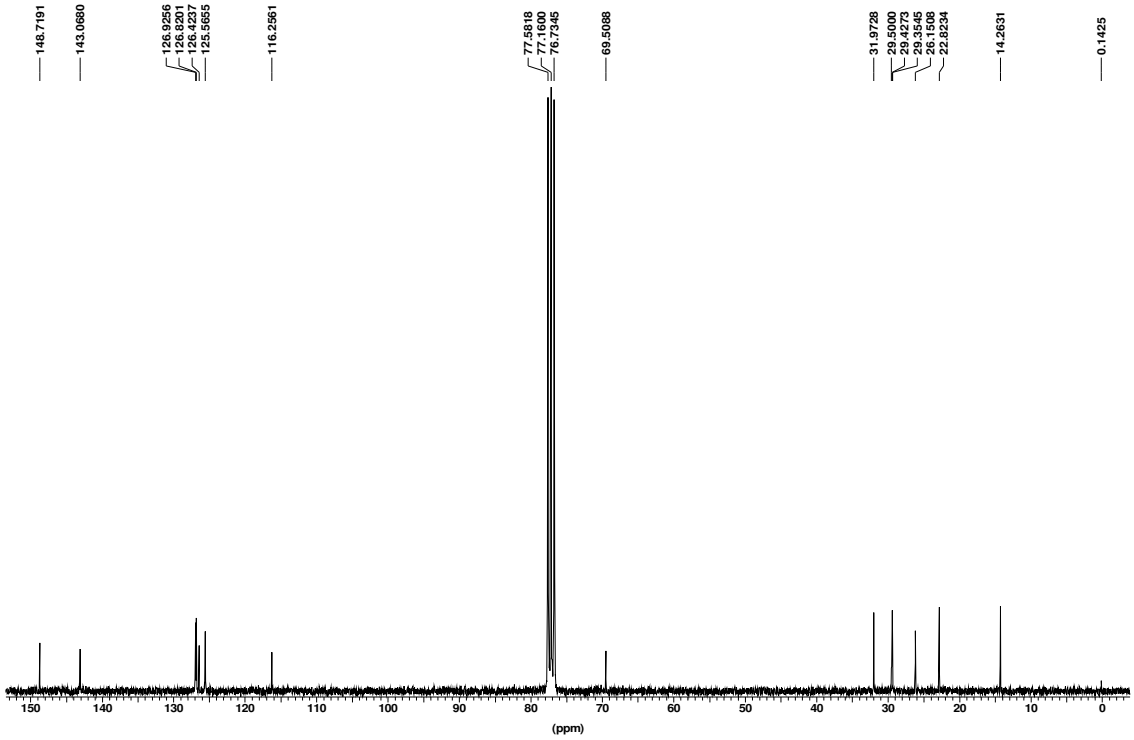
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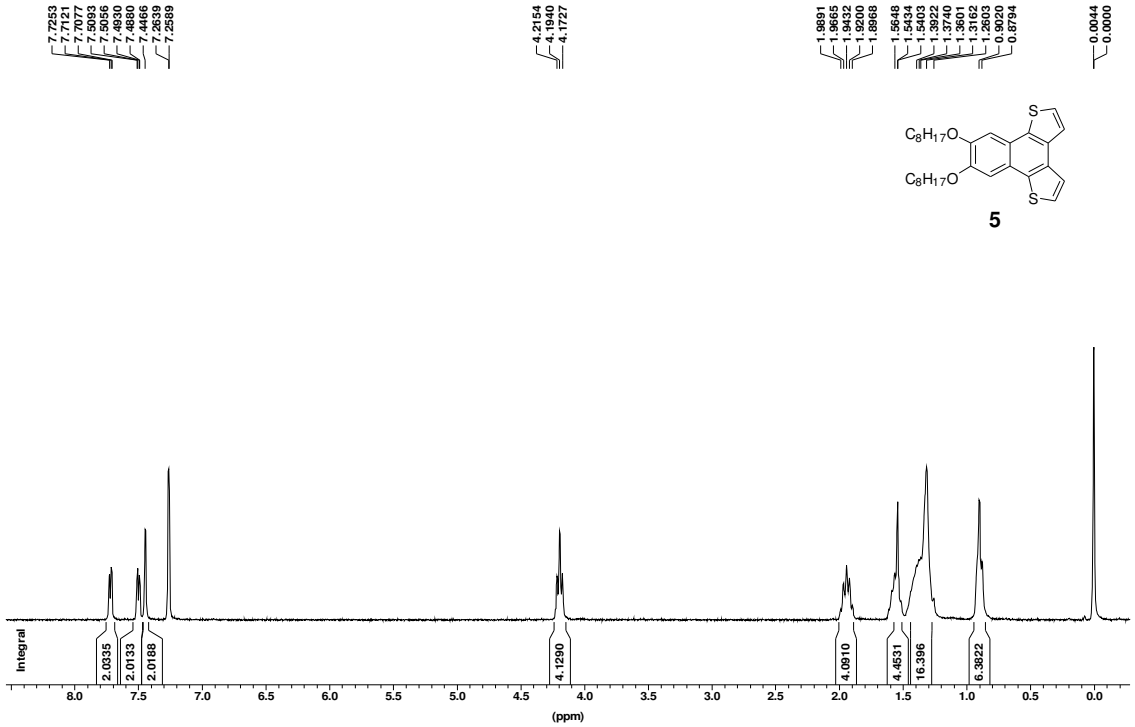
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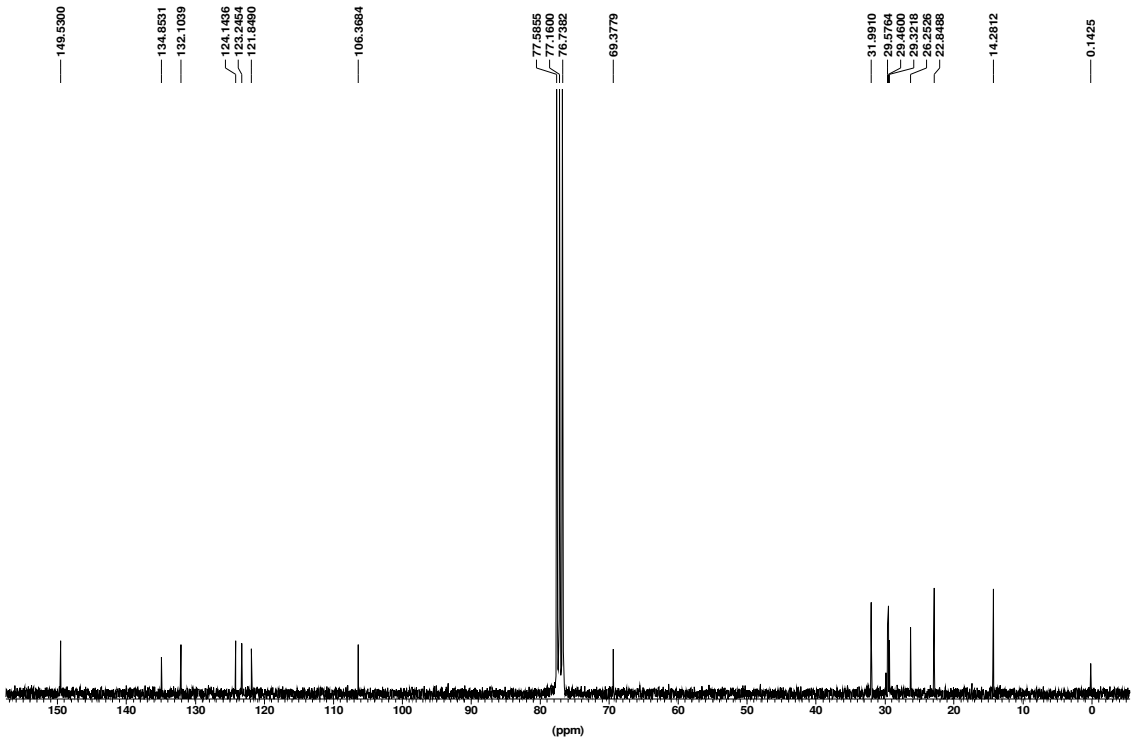
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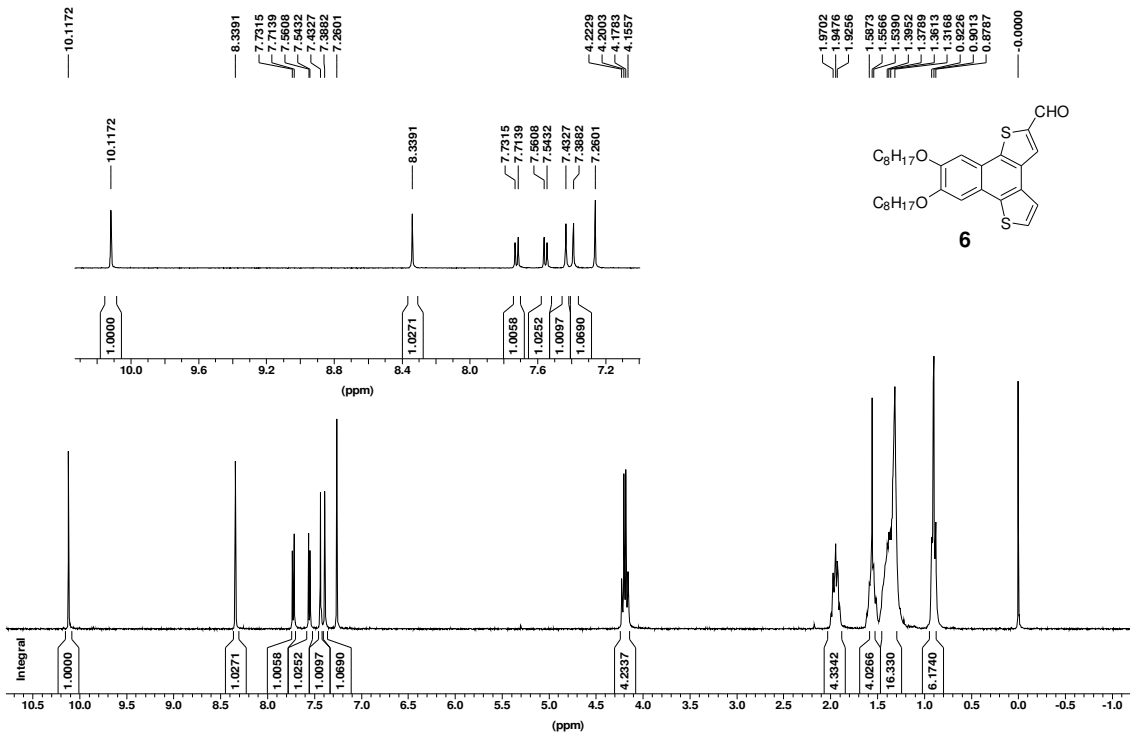
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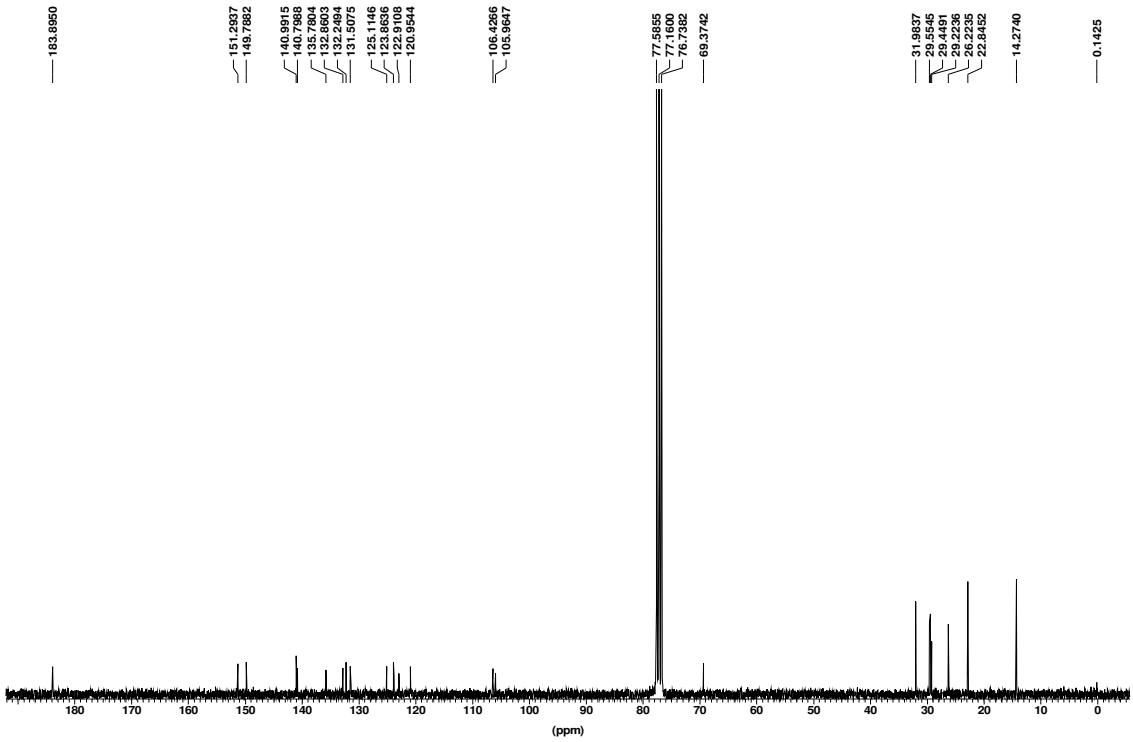
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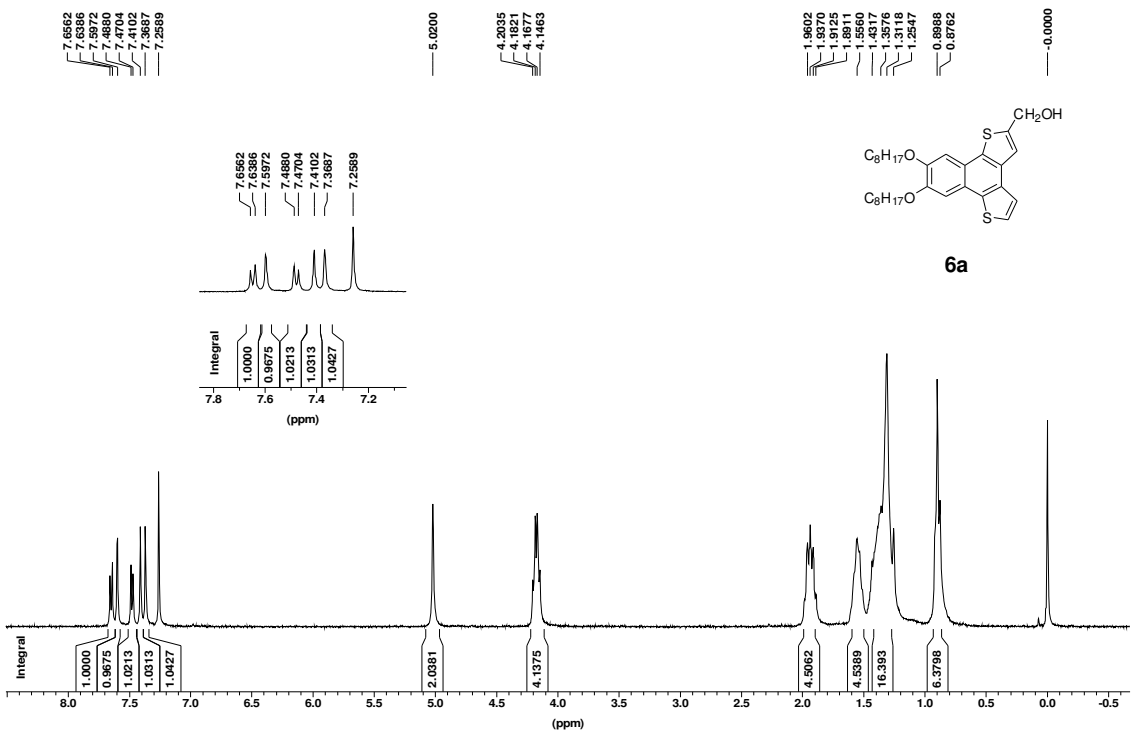
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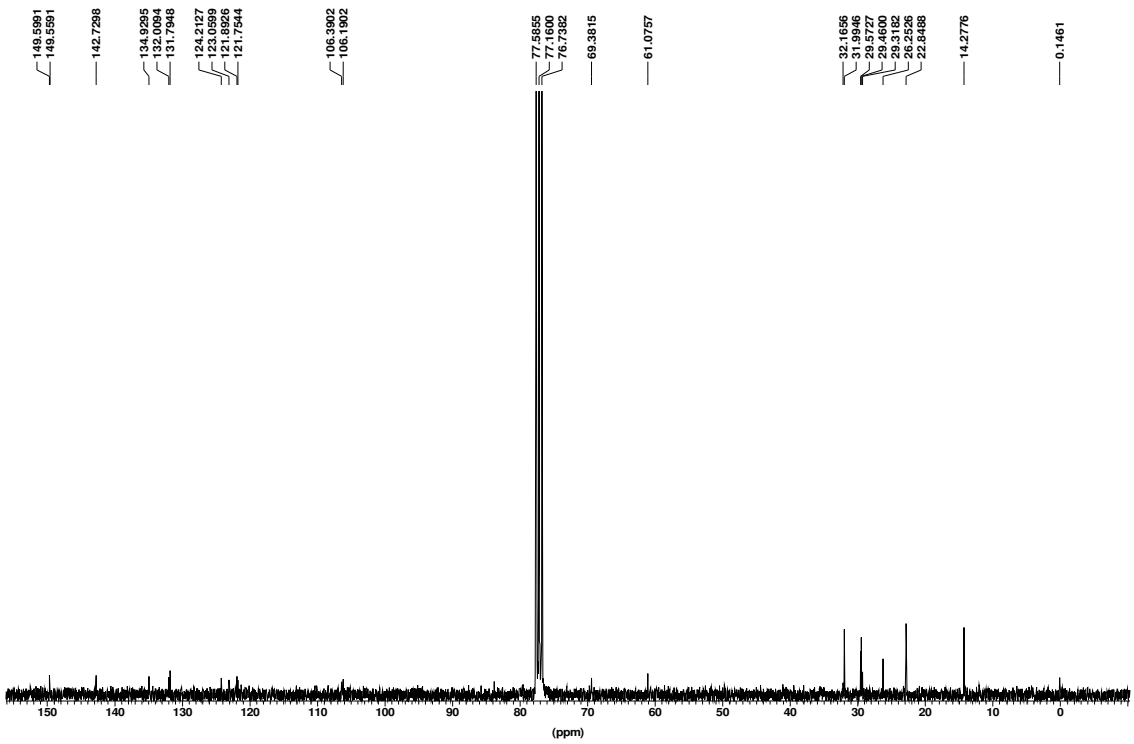
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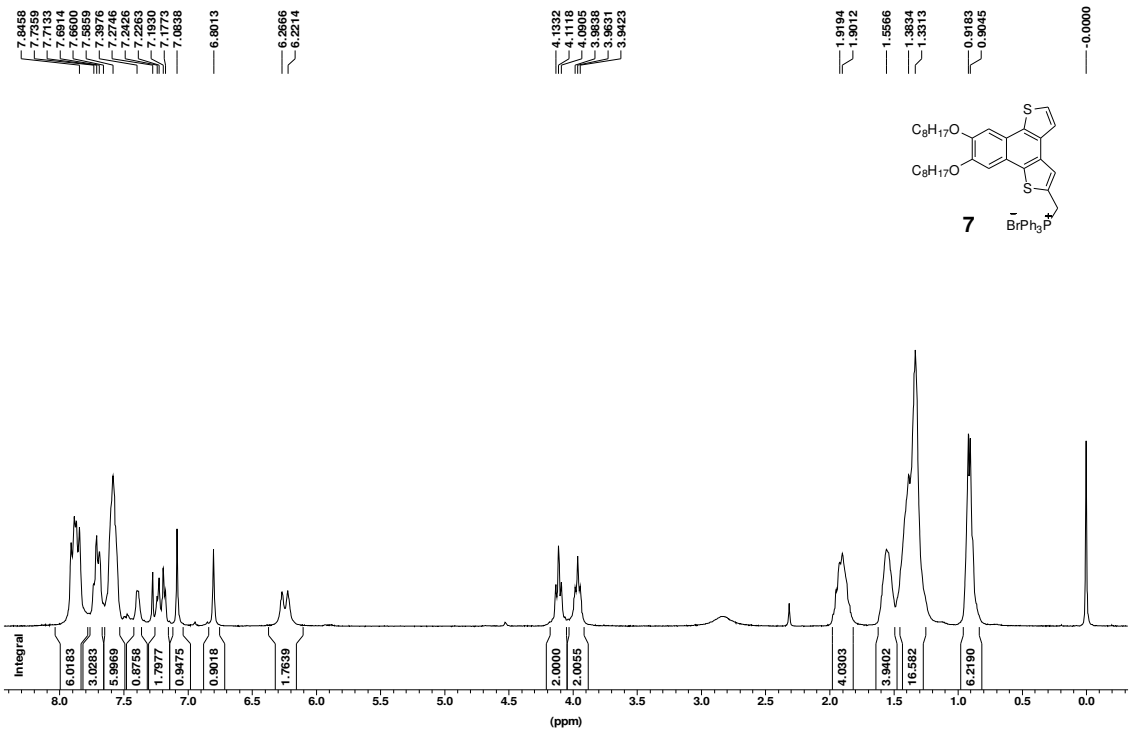
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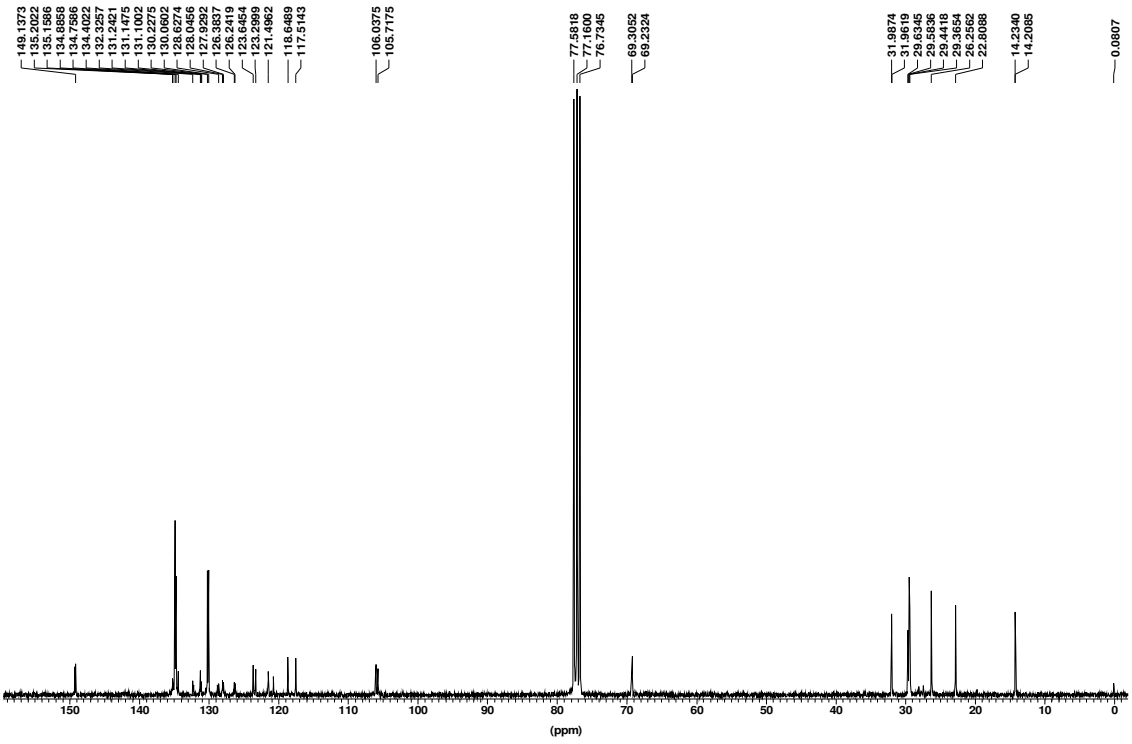
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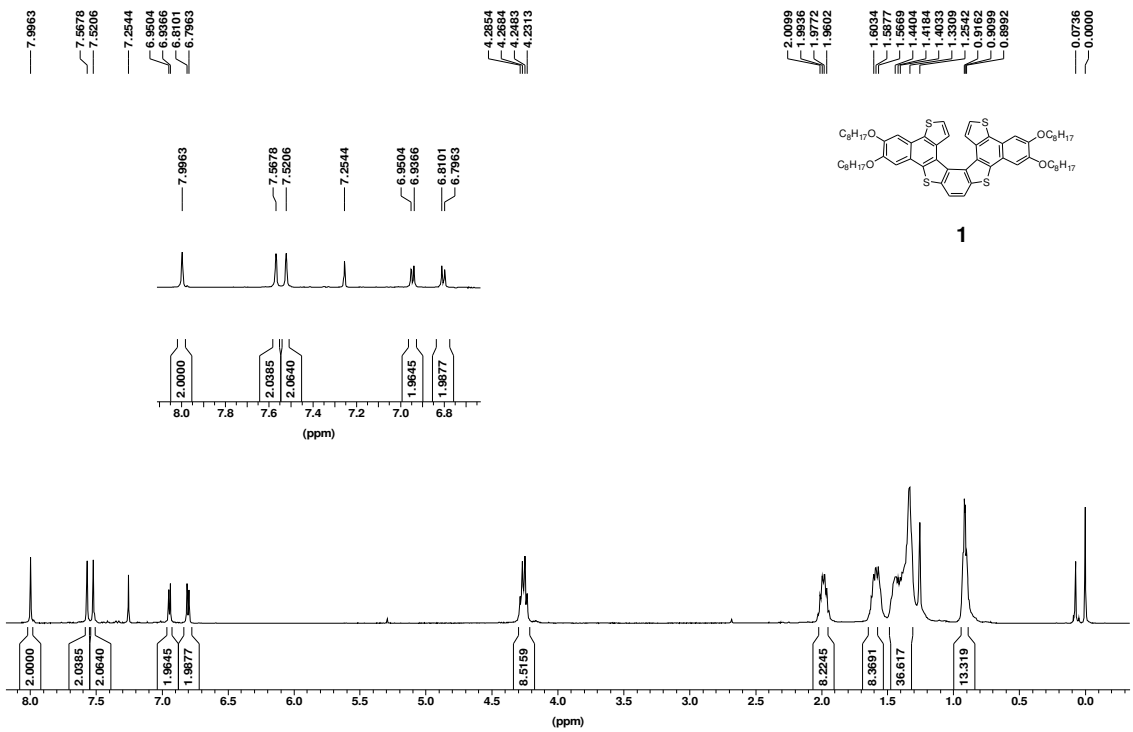
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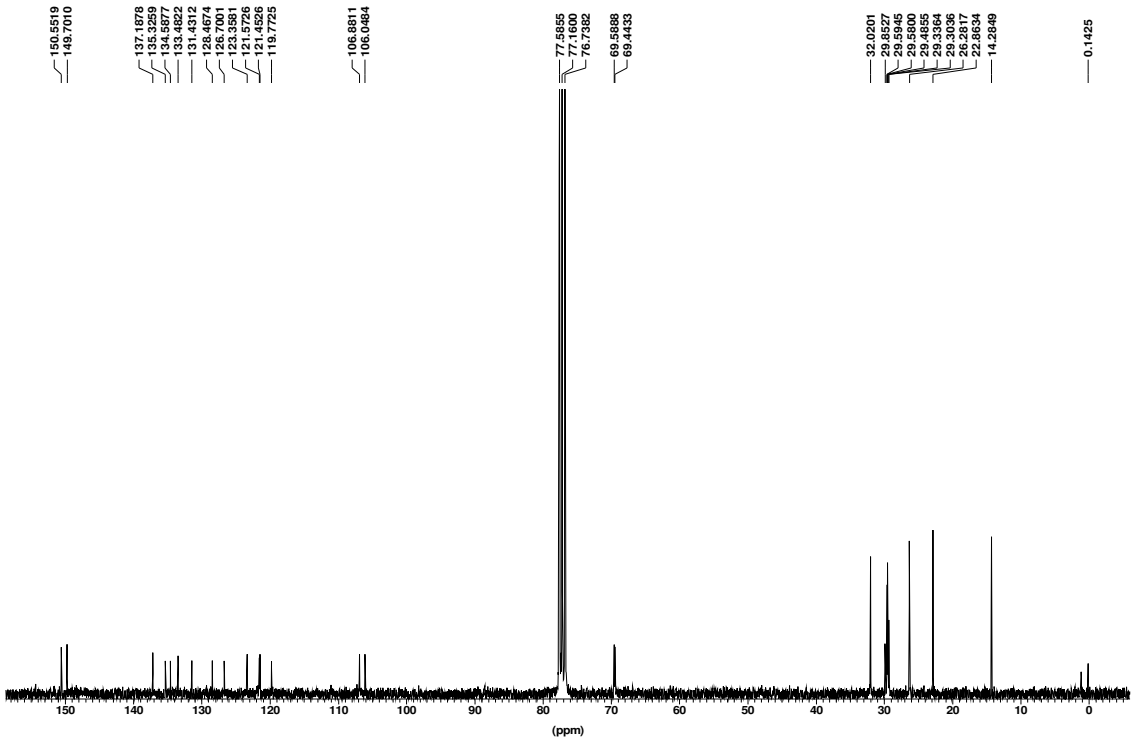
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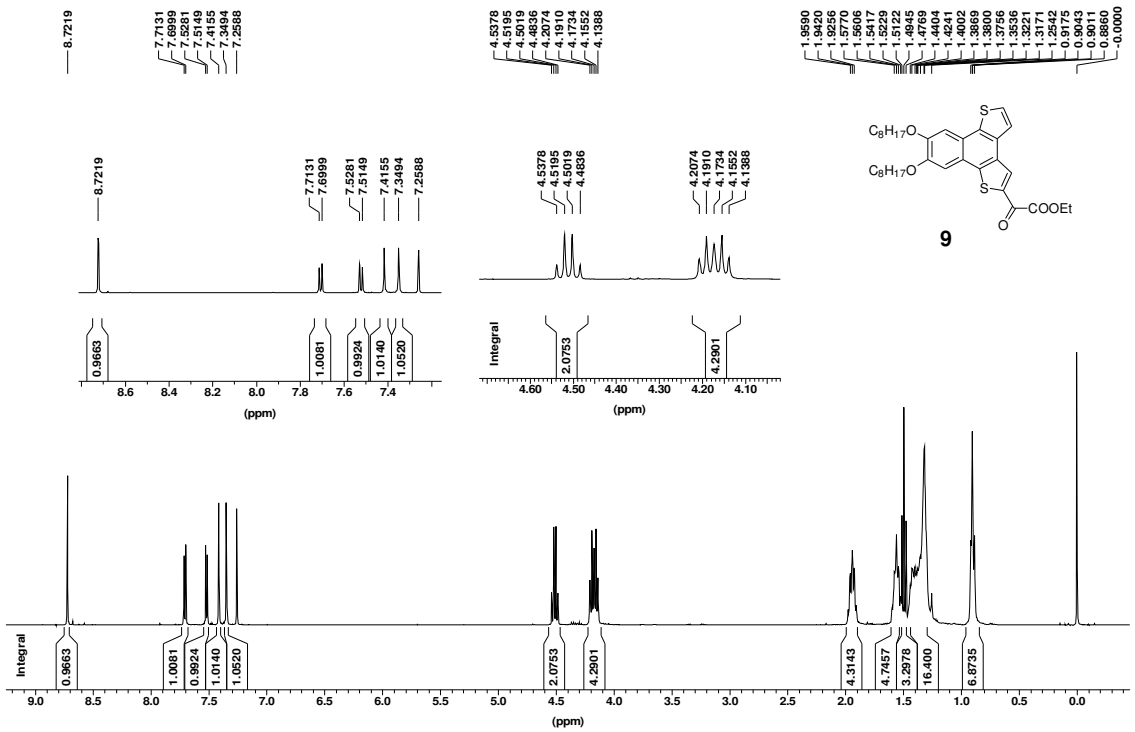

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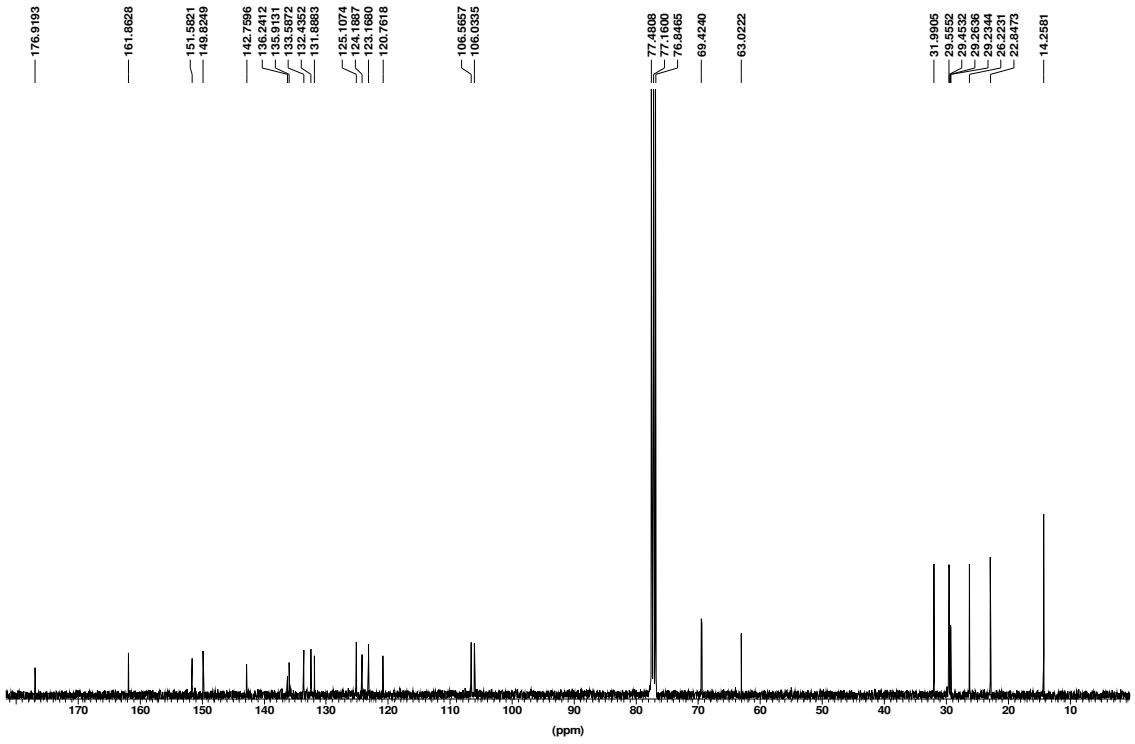
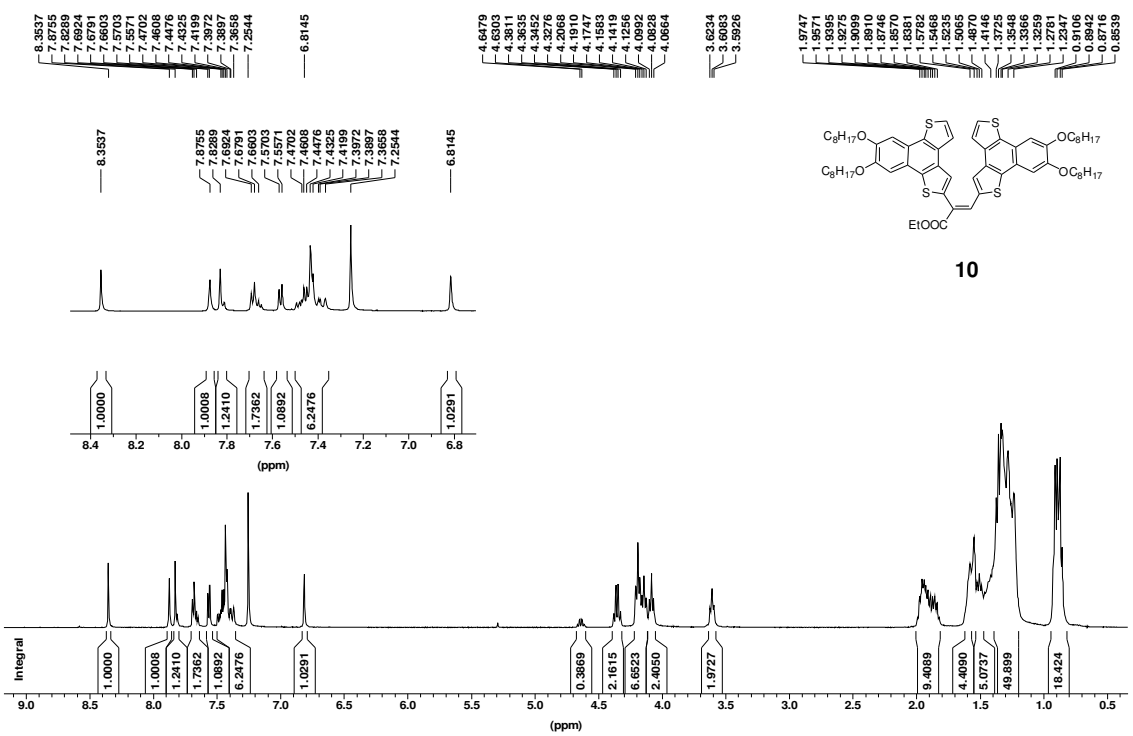
9

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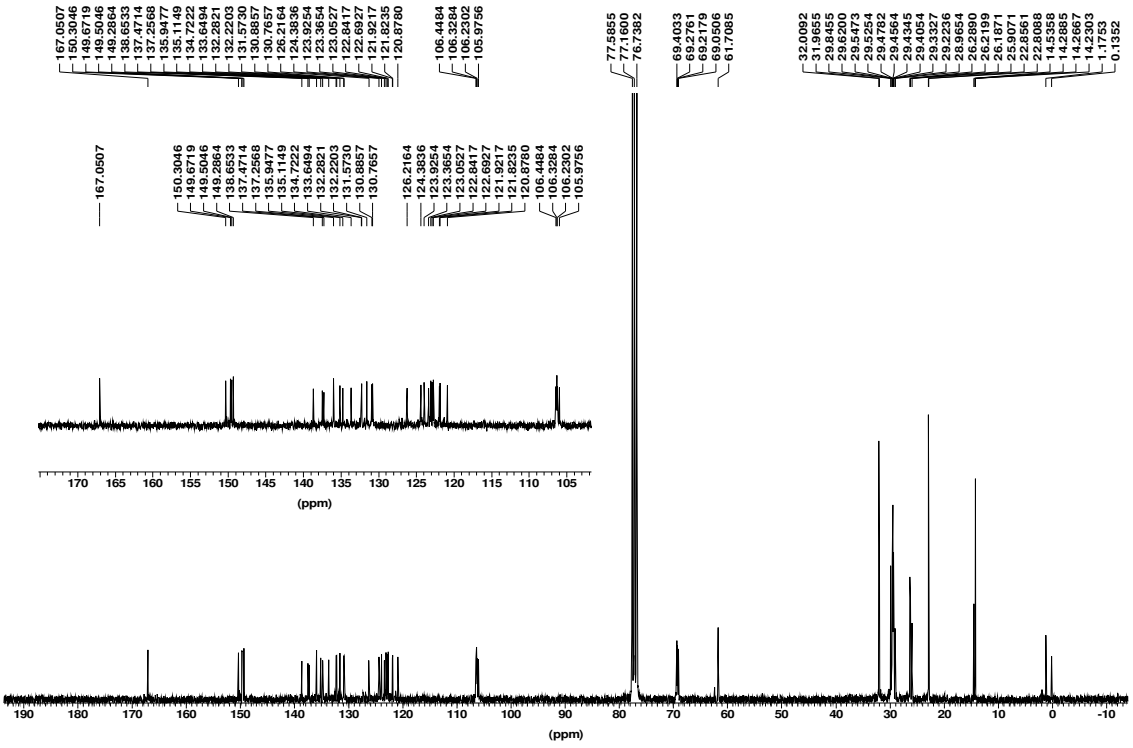
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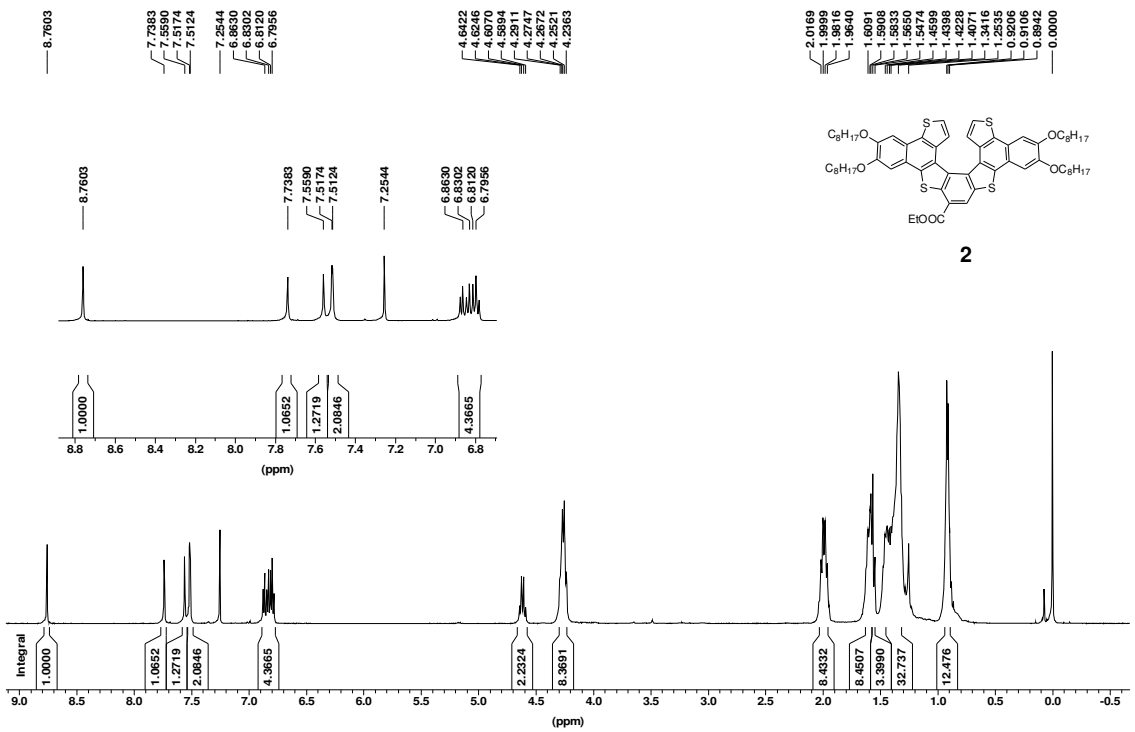
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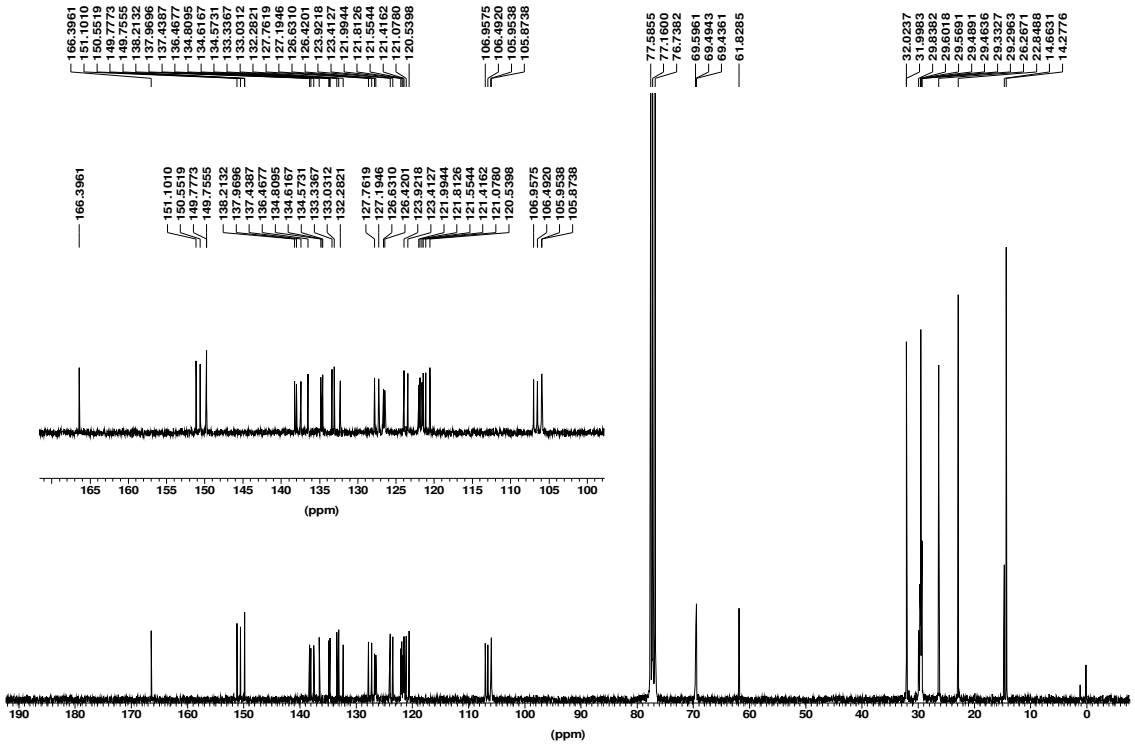
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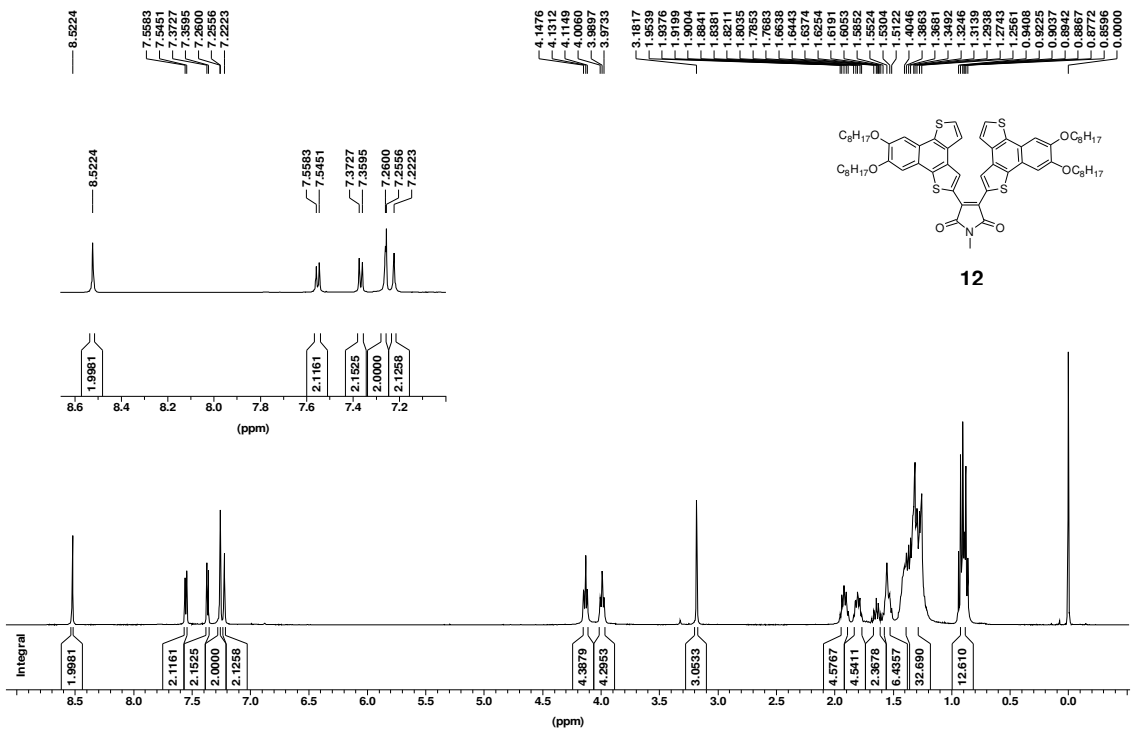
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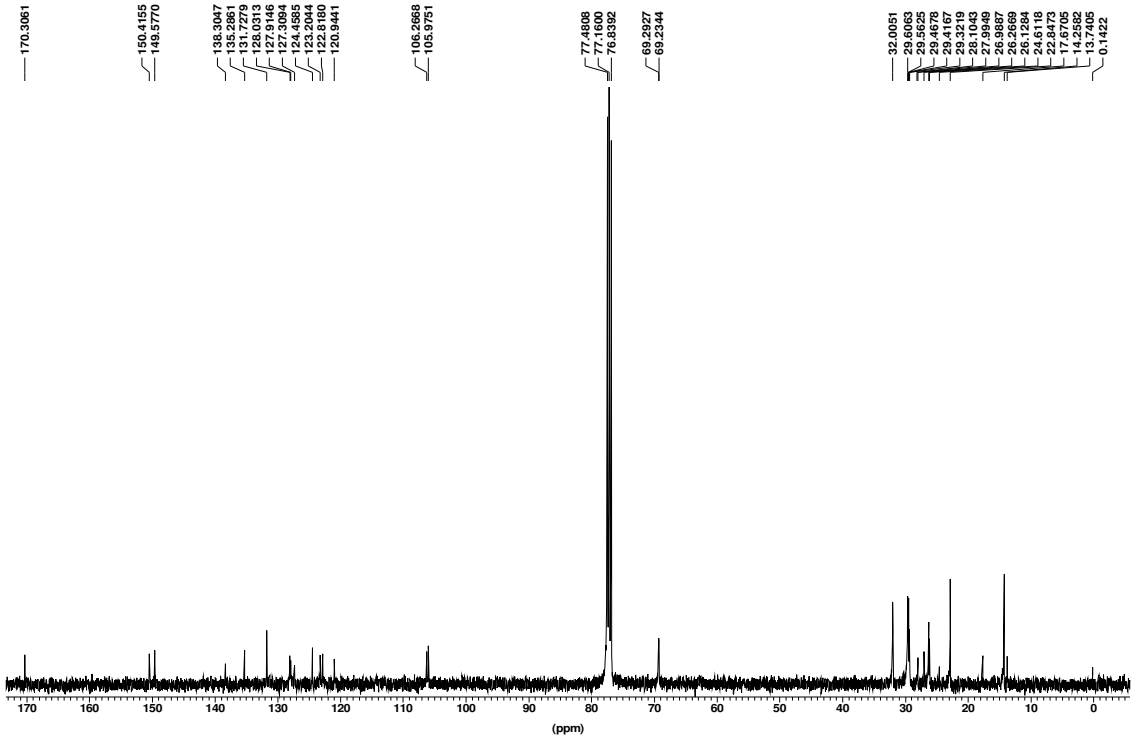
1.8035
1.7853
1.7683
1.6638
1.6443
1.6374
1.6254
1.6191
1.6053
1.5852
1.5524
1.5304
1.5122
1.4046
1.3863
1.3681
1.3492
1.3246
1.3139
1.2938
1.2743
1.2561
0.9408
0.9225
0.9037
0.8942
0.8867
0.8772
0.8596
0.0000
Integral
1.9981
2.1161
2.1525
2.0000
2.1258
4.3879
4.2953
3.0533
4.5767
4.5411
2.3678
6.4357
32.690
12.610
(ppm)

12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122.8180
120.9441
106.2668
105.9751
77.4808
77.1600
76.8392
69.2927
69.2344
32.0051
29.8063
29.5625
29.4670
29.4157
29.3219
28.1043
27.9949
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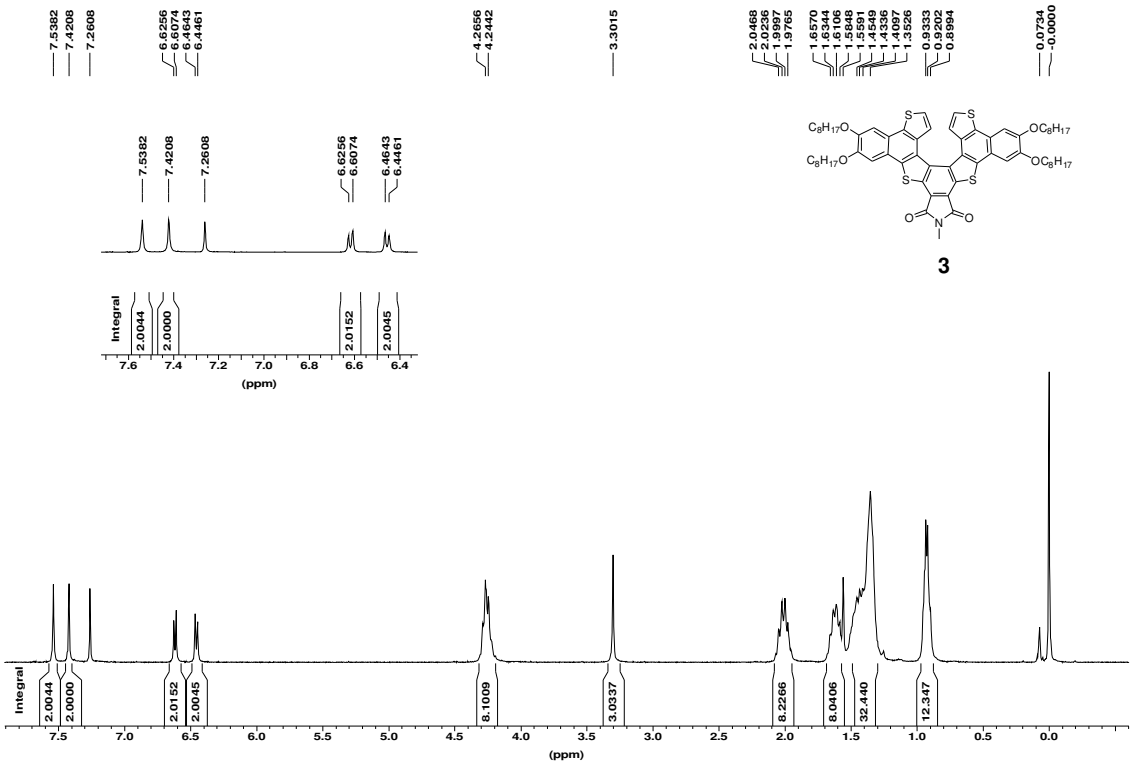
14.2582
13.7405
0.1422
(ppm)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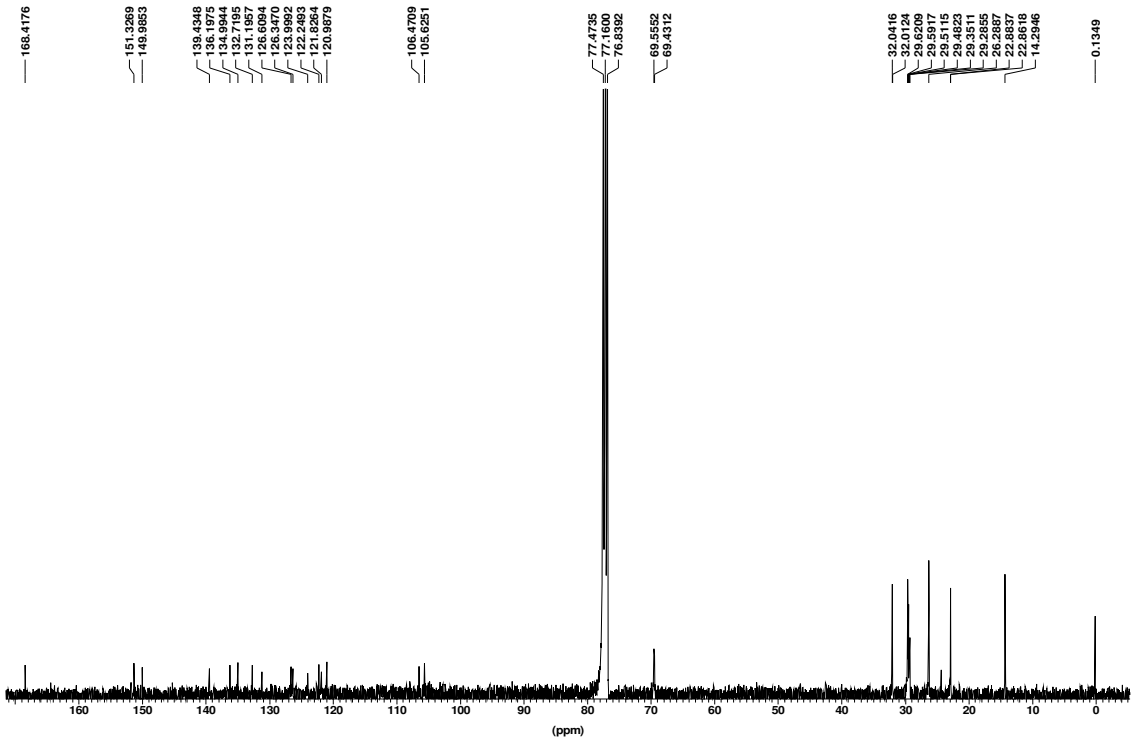
7.4208
7.2608
6.6256
6.6074
6.4643
6.4461
4.2656
4.2442
3.3015
2.0466
2.0236
1.9997
1.9765
1.6570
1.6544
1.6106
1.5848
1.5591
1.4549
1.4336
1.4097
1.3525
0.9333
0.9202
0.8994
0.0734
-0.0000
Integral
2.0044
2.0000
2.0152
2.0045
8.1009
3.0337
8.2266
8.0406
32.440
12.347
(ppm)

3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126.6004
126.3470
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122.2483
121.8264
120.9879
106.4709
105.6251
77.4735
77.1600
76.8392
69.5552
69.4312
32.0416
32.0124
29.6209
29.5917
29.5115
29.4823
29.3511
29.2855
26.2887
22.8837
22.8618
14.2946
0.1349
(ppm)