Electronic supplementary materials *Mendeleev Commun.*, 2020, **30**, 683–685

Novel small oligothiophene molecules with phenylene and naphthalene cores as promising absorber materials for organic solar cells

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Materials and instrumentation

All solvents and reagents were purchased from Sigma-Aldrich or Acros Organics and used as received or purified according to standard procedures.

Compounds 2,2'-(2,5-bis((2-octyldodecyl)oxy)-1,4-phenylene)dithiophene [S1], 2,2'-(1,5-bis((2-octyldodecyl)oxy)naphthalene-2,6-diyl)dithiophene [S2], *N*-hexyl rhodanine [S3] and 5'-bromo-[2,2'-bithiophene]-5-carbaldehyde [S4] were obtained as described.

Absorption spectra were measured on Avantes AvaSpec-2048 optical fiber spectrometer. The optical spectra of thin films were recorded using 2-channel AvaSpec-2048-2 optical fiber spectrometer integrated inside the glove box. The ^{1}H and ^{13}C NMR spectra were obtained using Bruker AVANCE 500 instrument. Mass spectra were obtained using electrospray/APCI combined ionization technique on GC-MS LCMS-2020 instrument. Elemental analysis was performed using Vario Microcube instrument.

Synthesis

{[2,5-Bis(2-hexyldecyloxy)-1,4-phenylene]bis(thiophene-5,2-diyl}bis(trimethylstannane) ***2a*** was prepared as reported previously [S5].

^{1}H NMR (CDCl$_3$, 500 MHz, δ): 7.61 (d, *J*=3.37 Hz, 2H), 7.21 (s, 2H), 7.16 (d, *J*=3.37 Hz, 2H), 3.93 (d, *J*=5.42 Hz, 4H), 1.83 (m, 2H), 1.3-1.2 (m, 64H), 0.85 (t, 12H), 0.37 (s, 18H) ppm.

{[1,5-Bis(2-hexyldecyloxy)naphthalene-2,6-diyl]bis(thiophene-5,2-diyl}bis(trimethylstannane ***2b*** was synthesized following the procedure given for compound **2a** using 2,2'-[1,5-bis(2-octyldodecyloxy)naphthalene-2,6-diyl]dithiophene (1 g, 1.13 mmol) *n*-BuLi (2.5 M in hexane, 0.62 g, 2.26 mmol, 2.0 eq.) and trimethyltin chloride (0.477 g, 2.26 mmol, 2.0 eq.) Yield =84%.

^{1}H NMR (CDCl$_3$, 500 MHz, δ): 7.96 (d, *J*=8.73 Hz, 2H), 7.77 (d, *J*=8.83 Hz, 2H), 7.72 (d, *J*=3.41 Hz, 2H), 7.26 (d, *J*=3.41 Hz, 2H), 3.76 (d, *J*=6.32 Hz, 4H), 2.04 (m, 2H), 1.3-1.2 (m, 64H), 0.9-0.8 (m, 12H), 0.4 (s, 18H) ppm. ^{13}C NMR (CDCl$_3$, 126 MHz, δ): 151.60, 145.34, 138.60, 135.19, 129.62, 127.23, 127.19, 123.62, 118.83, 77.33, 39.28, 31.96, 31.28, 30.13, 29.76, 29.73, 29.70, 29.40, 26.97, 22.72, 14.13, -8.24 ppm. ESI-MS, found: 1209.6 ([M-H]$^-$); calculated, m/z: 1210.58 Chemical analysis (%) for $C_{64}H_{108}O_2S_2Sn_2$: C, 63.47; H, 8.99; O, 2.64; S, 5.29; Sn, 19.60; found C, 63.43; H, 9.00; S, 5.32.

5'',5''''-[2,5-Bis(2-octyldodecyloxy)-1,4-phenylene]bis([2,2':5',2''-terthiophene]-5-carbaldehyde) ***3a***. Compound **2a** (1.0 g, 0.86 mmol) and 5'-bromo-[2,2'-bithiophene]-5-carbaldehyde (0.47 g, 1.72 mmol) were placed under argon in a two-necked flask equipped with a reflux condenser. Then toluene (50 ml) and tetrakis(triphenylphosphine)palladium(0) (10 mg) were added. The mixture was refluxed for 24 h, then the solvent was removed under reduced pressure. The formed precipitate was collected by filtration and washed three times with methanol (3 x 100 m). The yield of the red crystalline powder of **3a** was 90%.

^{1}H NMR (CDCl$_3$, 500 MHz, δ): 9.84 (s, 2H), 7.65 (d, *J*=3.97 Hz, 2H), 7.46 (d, *J*=3.97 Hz, 2H), 7.27 (d, *J*=3.87 Hz, 2H), 7.22 (d, *J*=1.42 Hz, 2H), 7.21 (s, 2H), 7.20 (d, *J*=3.87 Hz, 2H), 7.13 (d, *J*=3.87 Hz, 2H), 3.99 (d, *J*=5.49 Hz, 4H), 1.92 (m, 2H), 1.4-1.2 (m, 64H), 0.84 (t, 12H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz, δ): 182.35, 149.47, 146.98, 141.56, 139.68, 139.23, 137.32, 136.33, 134.26, 127.02, 126.12, 124.25, 124.15, 123.91, 122.68, 111.83, 72.56, 38.32, 31.94, 31.66, 30.13, 29.76, 29.73, 29.70, 29.39, 27.09, 22.69, 14.11 ppm. ESI-MS, found: 1217.6 ($[M-H]^-$); calculated, m/z: 1218.58 Chemical analysis (%) for $C_{72}H_{98}O_4S_6$: C, 70.89; H, 8.10; O, 5.25; S, 15.77; found C, 71.95; H, 8.03; S, 15.78.

5'',5''''-[1,5-Bis(2-octyldodecyloxy)naphthalene-2,6-diyl]bis([2,2':5',2''-terthiophene]-5-carbaldehyde) ***3b*** was synthesized following the procedure given for compound **3a** using **2b** (1 g, 0.826 mmol) and 5'-bromo-[2,2'-bithiophene]-5-carbaldehyde (0.45 g, 1.65 mmol). Yield =88%

^{1}H NMR ($CDCl_3$, 500 MHz, δ): 9.85 (s, 2H), 7.92 (d, *J*=8.87 Hz, 2H), 7.74 (d, *J*=8.87 Hz, 2H), 7.67 (d, *J*=4.03 Hz, 2H), 7.50 (d, *J*=3.83 Hz, 2H), 7.30 (d, *J*=3.83 Hz, 2H), 7.28 (d, *J*=3.83 Hz, 2H), 7.25 (d, *J*=3.63 Hz, 2H), 7.17 (d, *J*=3.83 Hz, 2H), 3.78 (d, *J*=6.25 Hz, 4H), 2.05 (m, 2H), 1.4-1.2 (m, 64H), 0.9-0.8 (m, 12H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz, δ): 182.35, 151.96, 146.91, 141.62, 139.48, 139.28, 137.31, 136.92, 134.44, 129.69, 127.02, 126.90, 126.48, 124.41, 124.33, 123.98, 123.26, 119.08, 77.89, 39.29, 31.98, 31.97, 31.32, 30.17, 29.79, 29.75, 29.44, 29.42, 26.98, 22.72, 14.14 ppm. ESI-MS, found: 1267.6 ($[M-H]^-$); calculated, m/z: 1268.59 Chemical analysis (%) for $C_{76}H_{100}O_4S_6$: C, 71.88; H, 7.94; O, 5.04; S, 15.15; found C, 71.67; H, 7.99; S, 15.20.

(5Z,5'E)-5,5'-[2,5-Bis(2-octyldodecyloxy)-1,4-phenylene]bis([2,2':5',2''-terthiophene]-5'',5-diyl)bis(methylidene))bis(3-hexyl-2-thioxothiazolidin-4-one) ***4a***. Compound **3a**(1 g, 0.82 mmol), *N*-hexyl rhodanine (0.356 g, 1.64 mmol) and triethylamine (0.166 g, 1.64 mmol) were dissolved in chloroform (20 ml) in a 50 ml round bottom flask equipped with reflux condenser. The mixture was refluxed under argon for 3 h, then cooled down to the room temperature and poured into methanol. The crude product was purified by column chromatography using as eluent mixture of toluene : hexane (1 : 1). Yield = 94%

^{1}H NMR ($CDCl_3$, 500 MHz, δ): 7.78 (s, 2H), 7.45 (d, unresolved doublet, 2H), 7.29 (d, *J*=2.94 Hz, 2H), 7.20 (br, d, unresolved doublet, 2H), 7.20 (s, 2H), 7.17 (d, unresolved doublet, 2H), 7.17 (d, unresolved doublet, 2H), 7.11 (d, unresolved doublet, 2H), 4.06 (t, 4H), 4.00 (d, 4H), 1.99 (m, 2H), 1.68 (m, 4H), 1.65 (m, 4H), 1.53 (m, 4H), 1.4-1.2 (m, 68H), 0.9-0.8 (m, 18H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz, δ): 192.07, 184.59, 182.76, 181.55, 181.22, 167.49, 149.40, 145.18, 139.11, 137.25, 136.43, 135.22, 126.20, 124.86, 124.72, 124.11, 122.57, 120.44, 111.56, 72.51, 44.89, 38.33, 31.97, 31.66, 31.35, 30.17, 29.78, 29.74, 29.44, 27.13, 26.96, 26.47, 22.73, 22.53, 14.17, 14.02 ppm. ESI-MS, found: 1615.7 ($[M-H]^-$); calculated, m/z: 1616.68 Chemical analysis (%) for $C_{90}H_{124}N_2O_4S_{10}$: C, 66.79; H, 7.72; N, 1.73; O, 3.95; S, 19.81; found C, 66.86; H, 7.75; N, 1.75; S, 19.70

(5Z,5'E)-5,5'-[1,5-Bis(2-octyldodecyloxy)naphthalene-2,6-diyl]bis([2,2':5',2''-terthiophene]-5'',5-diyl)bis(methylidene)bis(3-hexyl-2-thioxothiazolidin-4-one) ***4b*** was synthesized following the procedure given for compound **4a** using **3b** (1 g, 0.787 mmol) and *N*-hexyl rhodanine (0.342 g, 1.57 mmol) . Yield =96%

^{1}H NMR ($CDCl_3$, 500 MHz, δ): 7.91 (d, *J*=8.84 Hz, 2H), 7.81 (s, 2H), 7.74 (d, *J*=8.94 Hz, 2H), 7.49 (d, *J*=3.48 Hz, 2H), 7.31 (d, *J*=3.97 Hz, 2H), 7.25 (d, 2H), 7.23 (d, unresolved doublet, 2H), 7.22 (d, *J*=3.48 Hz, 2H), 7.16 (d, *J*=3.28 Hz, 2H), 4.09 (t, *J*=15.3 Hz, 4H), 3.78 (d, *J*=6.06 Hz, 4H), 2.05 (m, 2H), 1.69 (m, 4H), 1.59 (m, 4H), 1.47 (m, 4H), 1.4-1.2 (m, 68H), 0.9-0.8 (m, 18H) ppm. ^{13}C NMR ($CDCl_3$, 126 MHz, δ): 192.10, 167.54, 151.92, 145.16, 139.16, 138.91, 137.05, 136.52, 135.27, 134.58, 129.67, 126.90, 126.47, 126.30, 124.92, 124.81, 124.42, 124.30, 123.26, 120.53, 119.09, 77.87, 44.92, 39.28, 31.99, 31.37, 31.31, 30.18, 29.81, 29.76, 29.44, 26.98, 26.47, 22.74, 22.52, 14.16, 14.02 ppm. ESI-MS, found: 1666.7 ($[M-H]^-$); calculated, m/z:

1667.70 Chemical analysis (%) for $C_{94}H_{126}N_2O_4S_{10}$: C, 67.66; H, 7.61; N, 1.68; O, 3.84; S, 19.21; found C, 67.59; H, 7.63; N, 1.70; S, 19.17

Cyclic voltammetry measurements

The cyclic voltammetry measurements were performed for thin films (150-250 nm) deposited on glassy carbon disc electrode (*d*=5 mm, BAS Inc.) by drop casting from 1,2-dichlorobenzene, chlorobenzene, chloroform or their mixtures. The measurements were performed in a three-electrode electrochemical cell using 0.1 M solution of Bu_4NPF_6 in acetonitrile as supporting electrolyte, platinum wire as a counter electrode and a silver wire immersed in 0.01 M solution of $AgNO_3$ in 0.1 M TBAP (MeCN) as a reference Ag/Ag^+ electrode (BAS Inc.). Ferrocene was used as internal reference. The electrolyte solution was purged with argon before the measurements. The voltammograms were recorded using an ELINS P-30SM instrument at room temperature with a potential sweep rate of 50 mV s^{-1}.

Fabrication of photovoltaic devices

The small molecules (15 mg) and $PC_{71}BM$ (15 mg) were dissolved together in $CDCl_3$ (1 ml) while stirring at room temperature for 48 h. The obtained solution was filtered through a PTFE 0.45 mm syringe filter and subjected to spin-coating at 4000-5000 rpm for 150 s on the top of the annealed PEDOT:PSS (Clevios HTL) films deposited on the patterned ITO electrodes. The obtained films were transferred immediately inside the glove box. The top electrode comprising Mg and Al was deposited by thermal evaporation at the pressure below 4×10^{-6} mbar in a vacuum chamber integrated inside the MBraun glove box. The size of the active area in photovoltaic cells was ~0.28 cm^2 as it was defined by a shadow mask.

Characterization of organic solar cells

The current-voltage (*J*-V) characteristics of the devices were obtained in the dark and under the simulated 100 mW cm^{-2} AM1.5 solar irradiation provided by a KHS Steuernagel solar simulator integrated in MBraun glove box. The intensity of the illumination was checked every time before the measurements using a calibrated silicon diode with a known spectral response. The *J*-V curves were recorded in inert atmosphere using a Kethley 2400 source-measurement unit. The active areas of all devices were measured with a good accuracy just after the *J*-V measurements to estimate the short circuit current densities. The obtained J_{SC} values were reconfirmed by integrating the external quantum efficiency (EQE) spectra against standard AM1.5G spectrum. The EQE spectra were measured in inert atmosphere using specially designed setup, LOMO instruments, Russia.

References

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[S5] X. Sun, Z. Zhang, R. Hou, M. Huang, B. Zhao and S. Tan, *Dyes and Pigments*, 2017, **139**, 403.

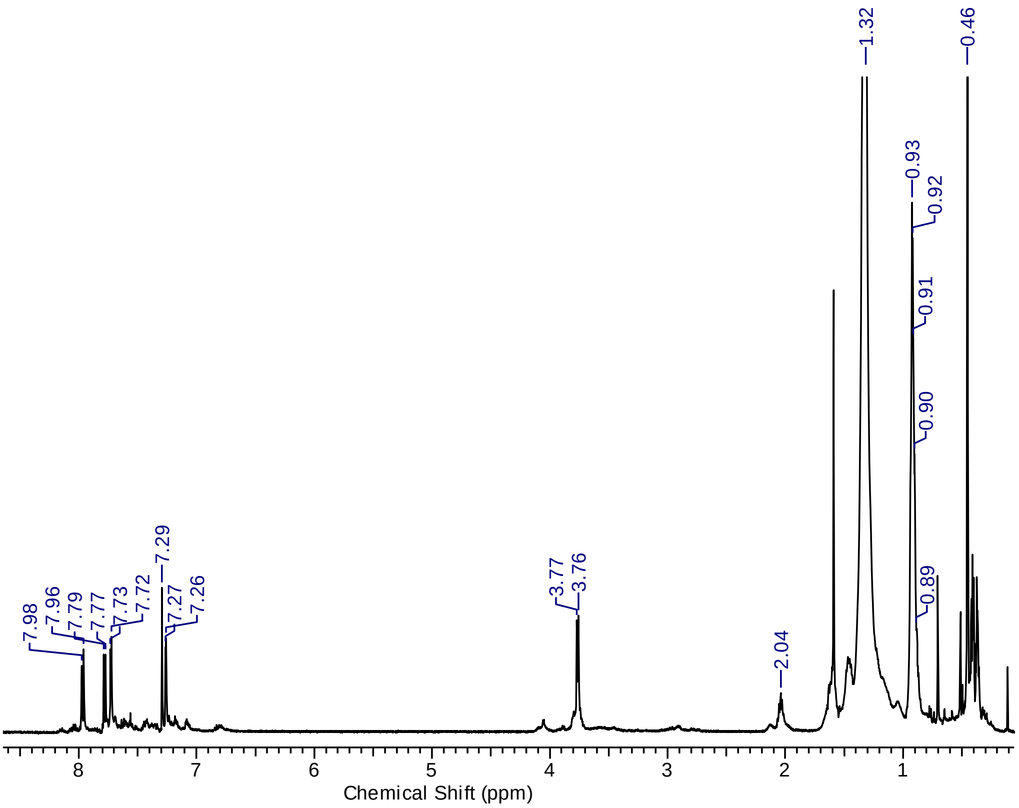

Figure S1. ^{1}H NMR spectrum of compound **2b**

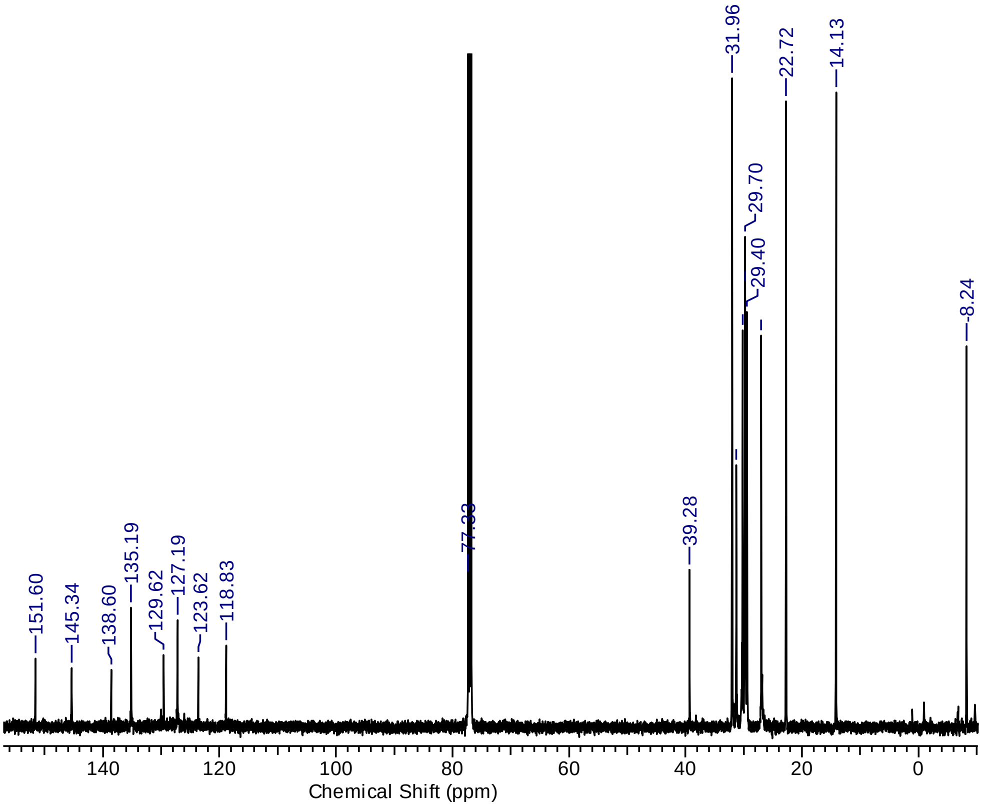

Figure S2. ^{13}C NMR spectrum of compound **2b**

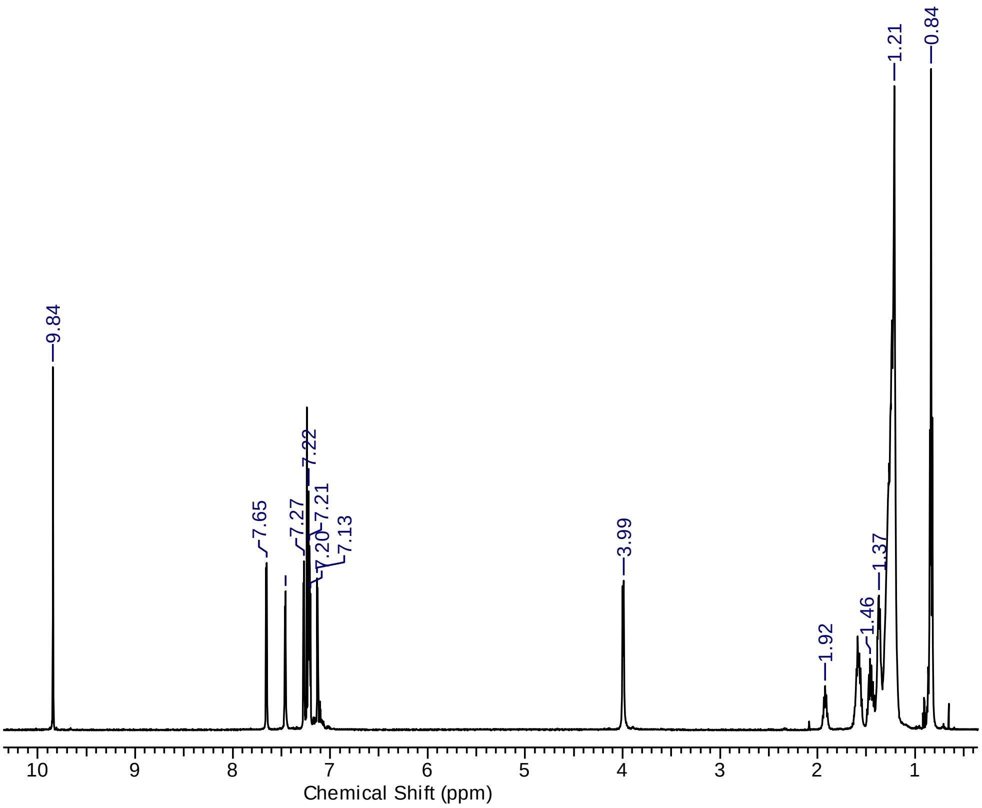

Figure S3. ^{1}H NMR spectrum of compound **3a**

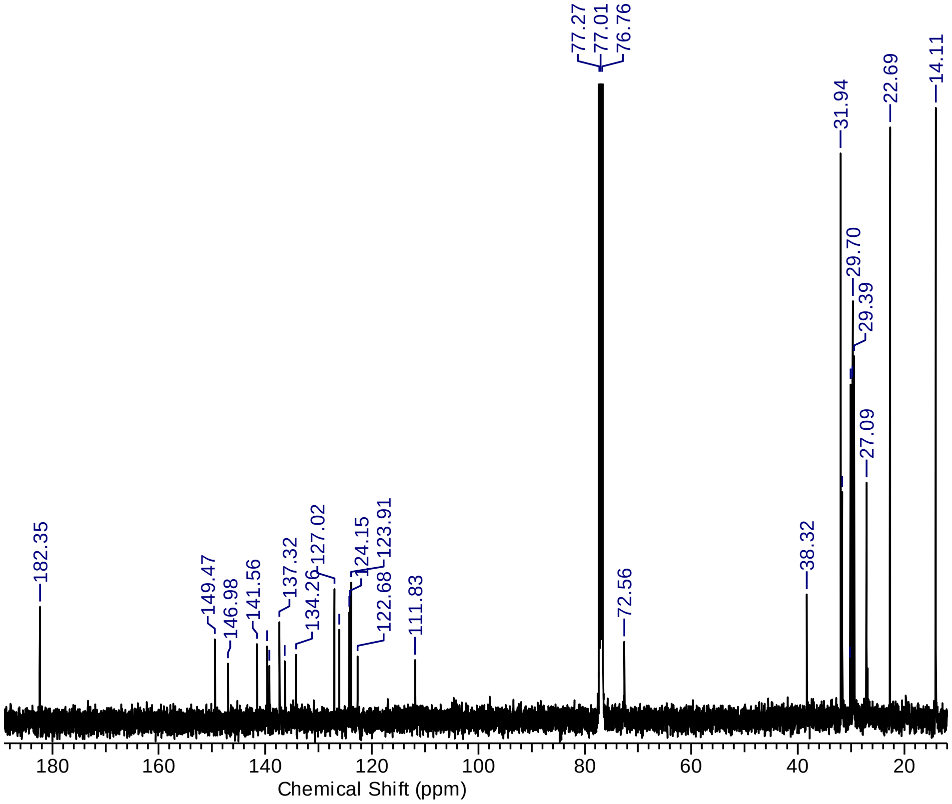

Figure S4. ^{13}C NMR spectrum of compound **3a**

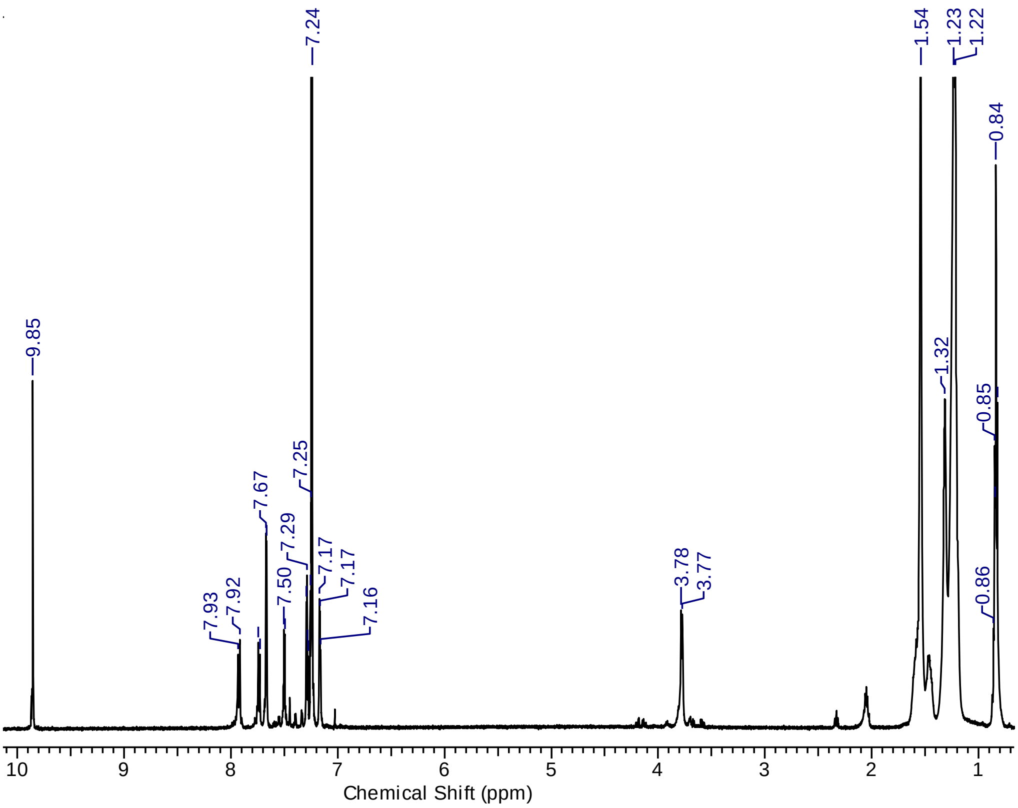

Figure S5. ^{1}H NMR spectrum of compound **3b**

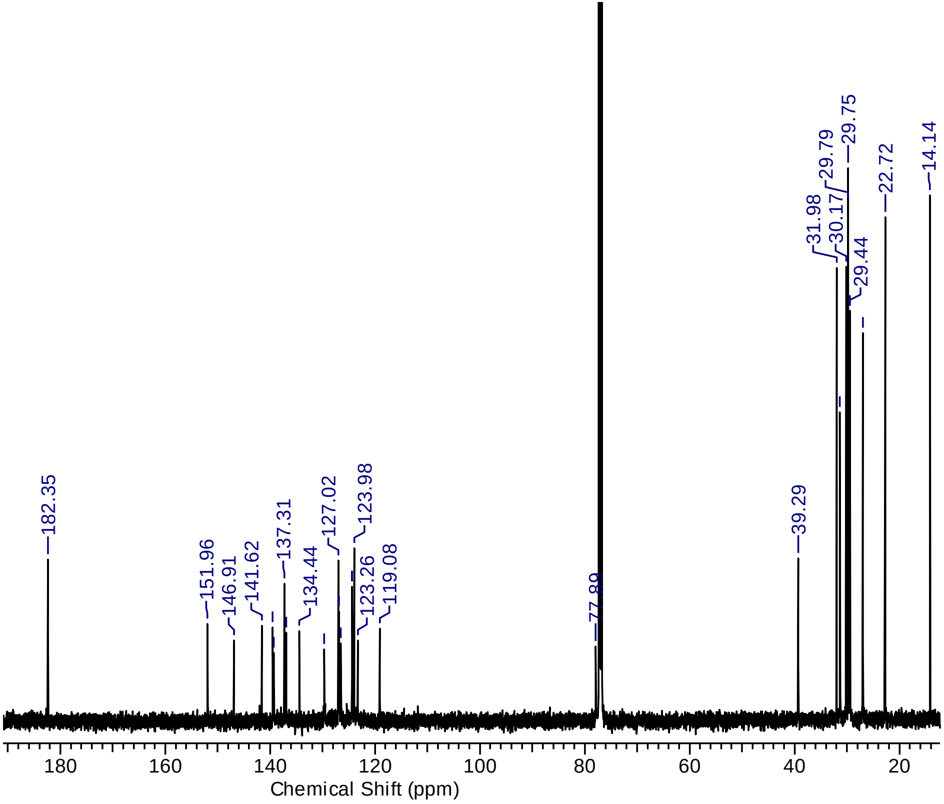

Figure S6. ^{13}C NMR spectrum of compound **3b**

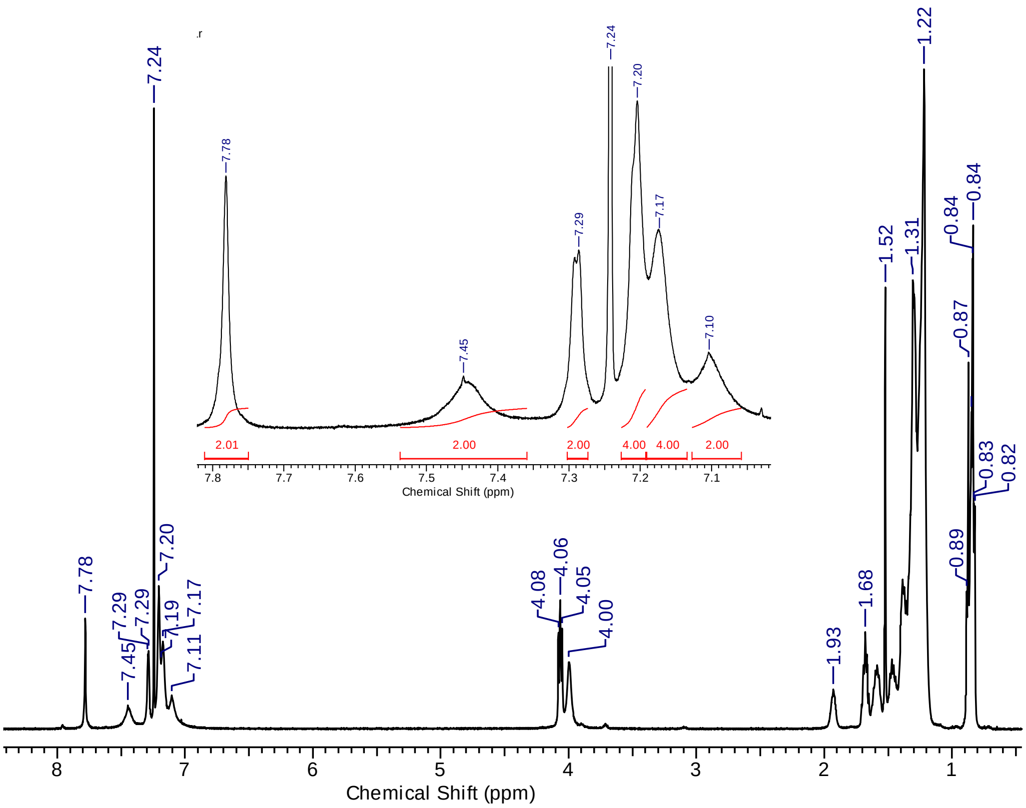

Figure S7. ^{1}H NMR spectrum of compound **4a**

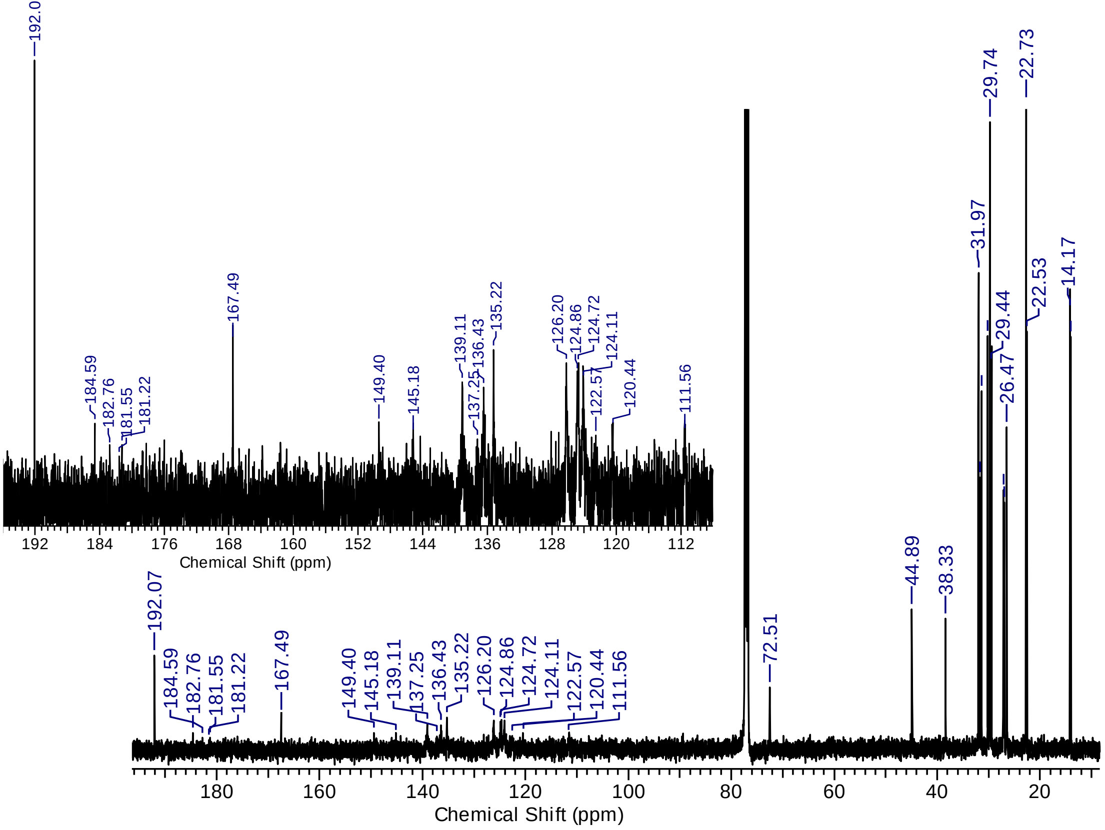

Figure S8. ^{13}C NMR spectrum of compound **4a**

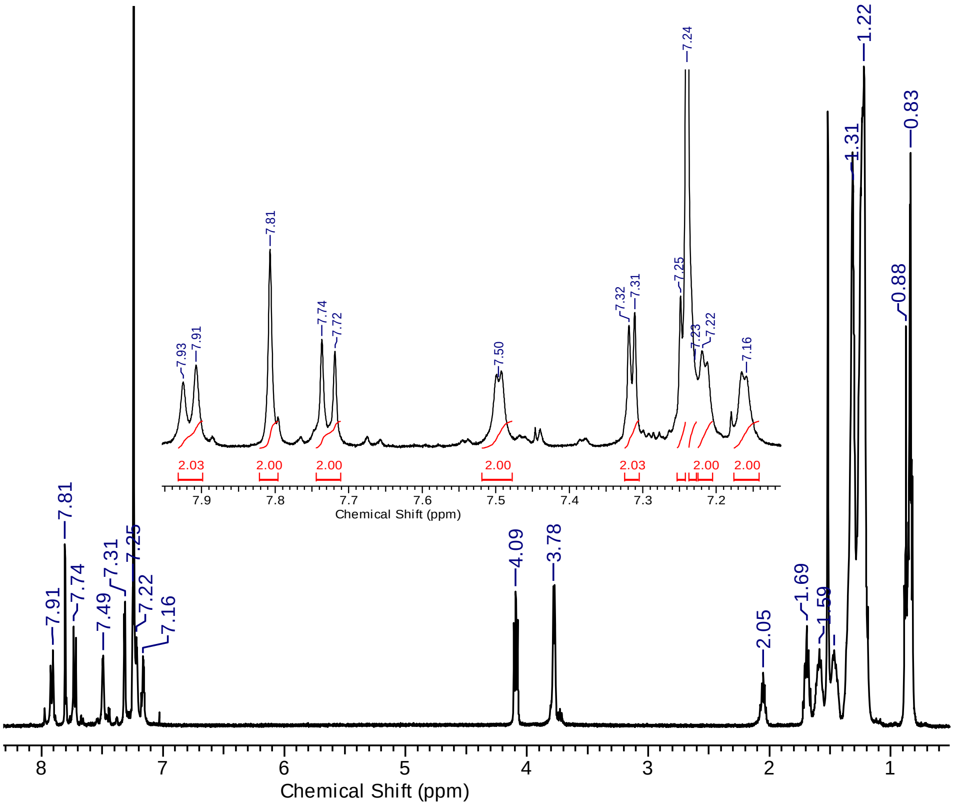

Figure S9. ^{1}H NMR spectrum of compound **4b**

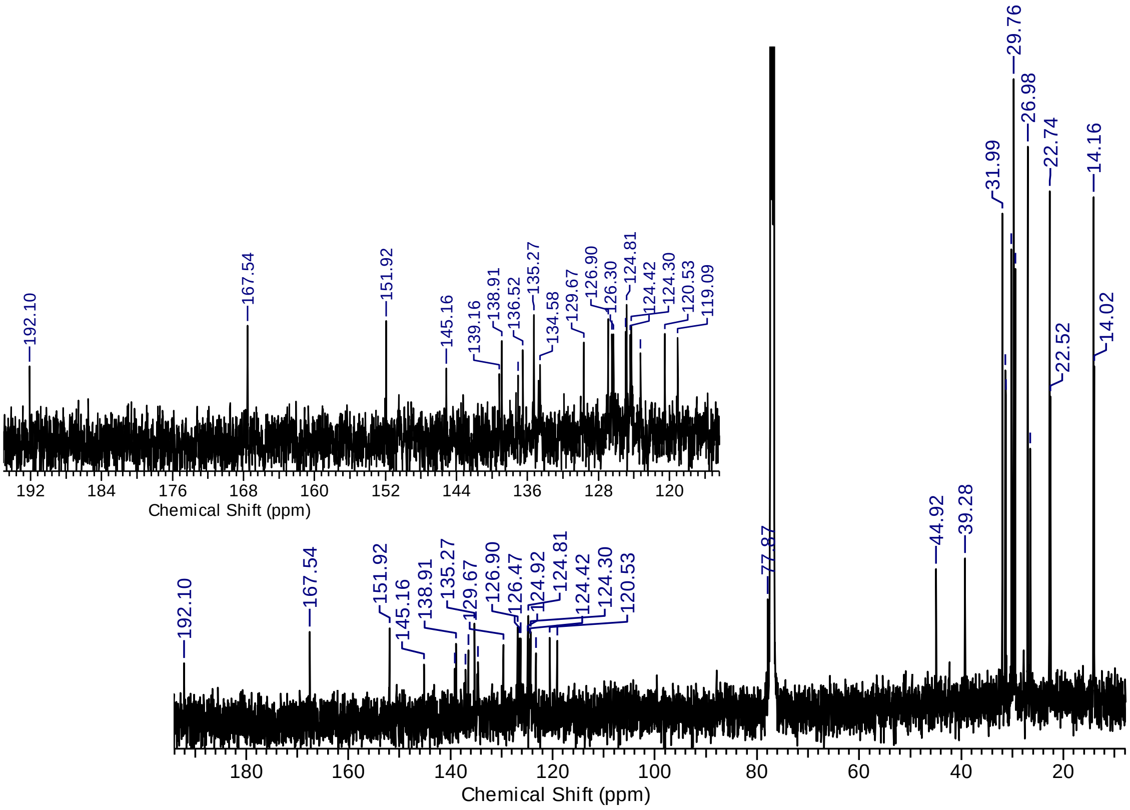

Figure S10. ^{13}C NMR spectrum of compound **4b**