Electronic Supplementary Material (ESI) for Nanoscale.

Tuning the reorganization energy of electron transfer in supramolecular ensembles – metalloporphyrin, oligophenylenevinylenes, and fullerene – and the impact on electron transfer kinetics

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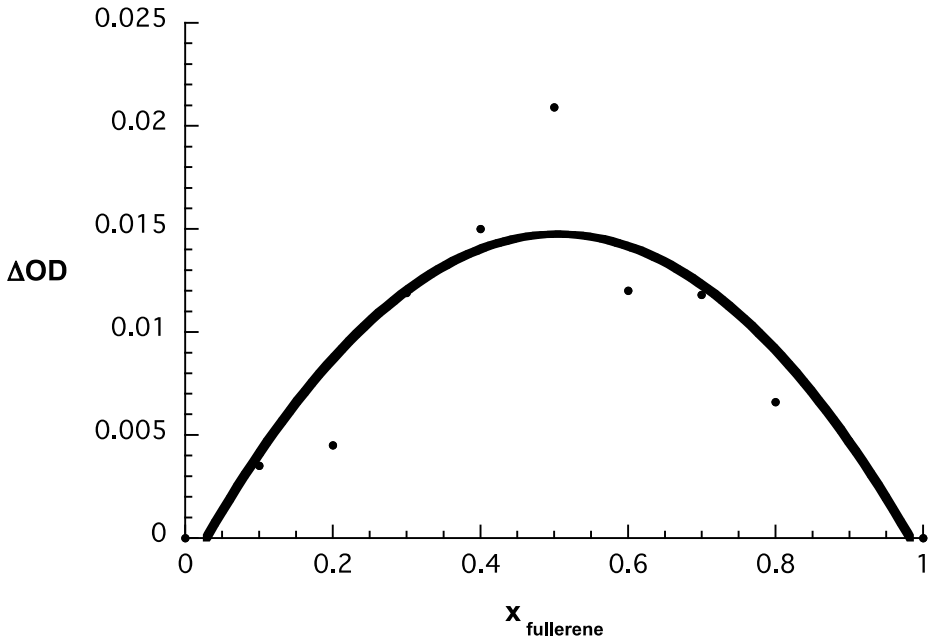
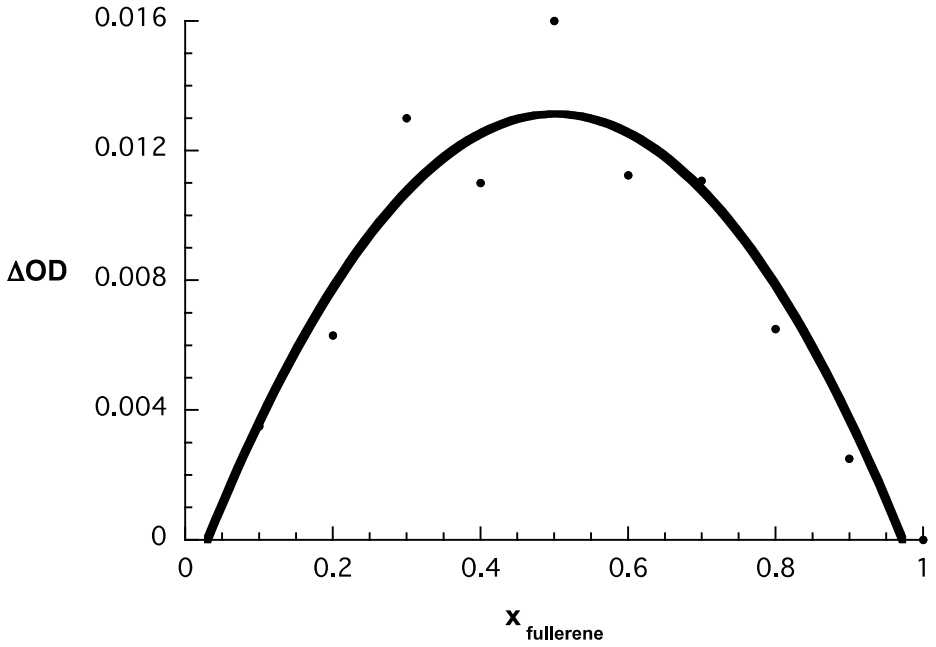
Supporting Information

Supplementary Figures





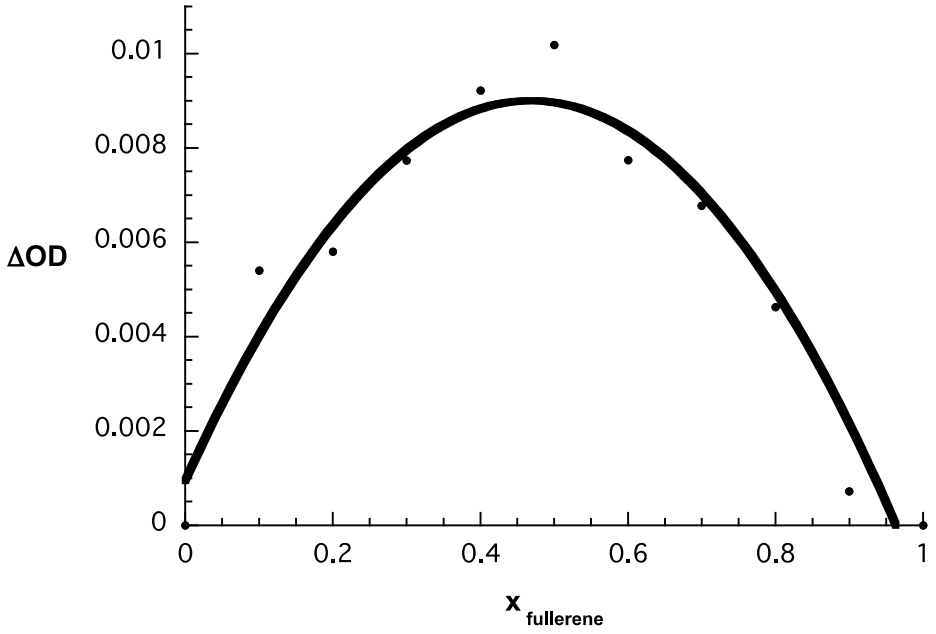


Figure S1: Job's plot analysis of **C_{60}-PPV1-pyr•ZnP** – upper part – **C_{60}-PPV3-pyr•ZnP** – central part – and **C_{60}-pyr•ZnP** – lower part – corresponding to the mutual interactions in toluene.

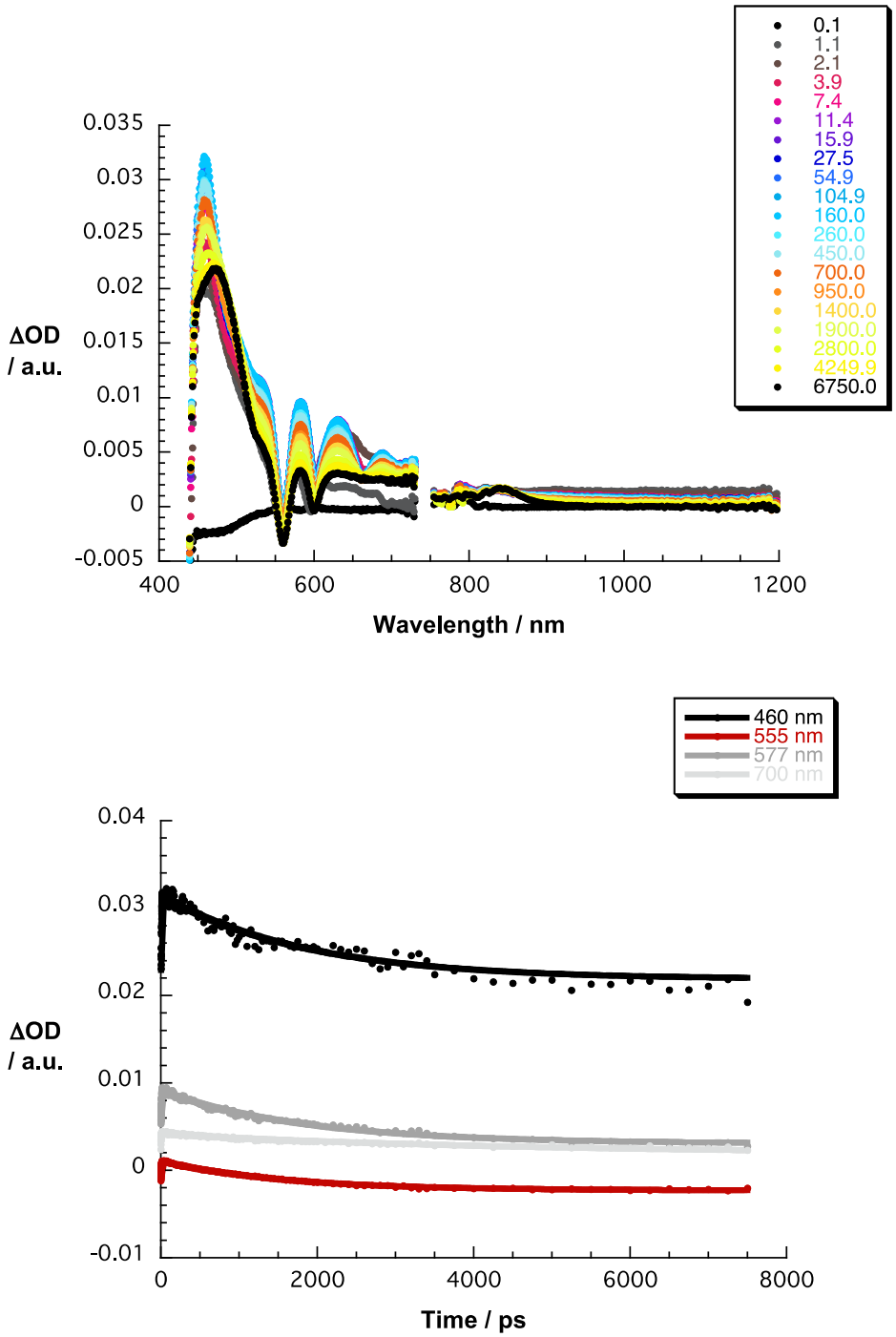
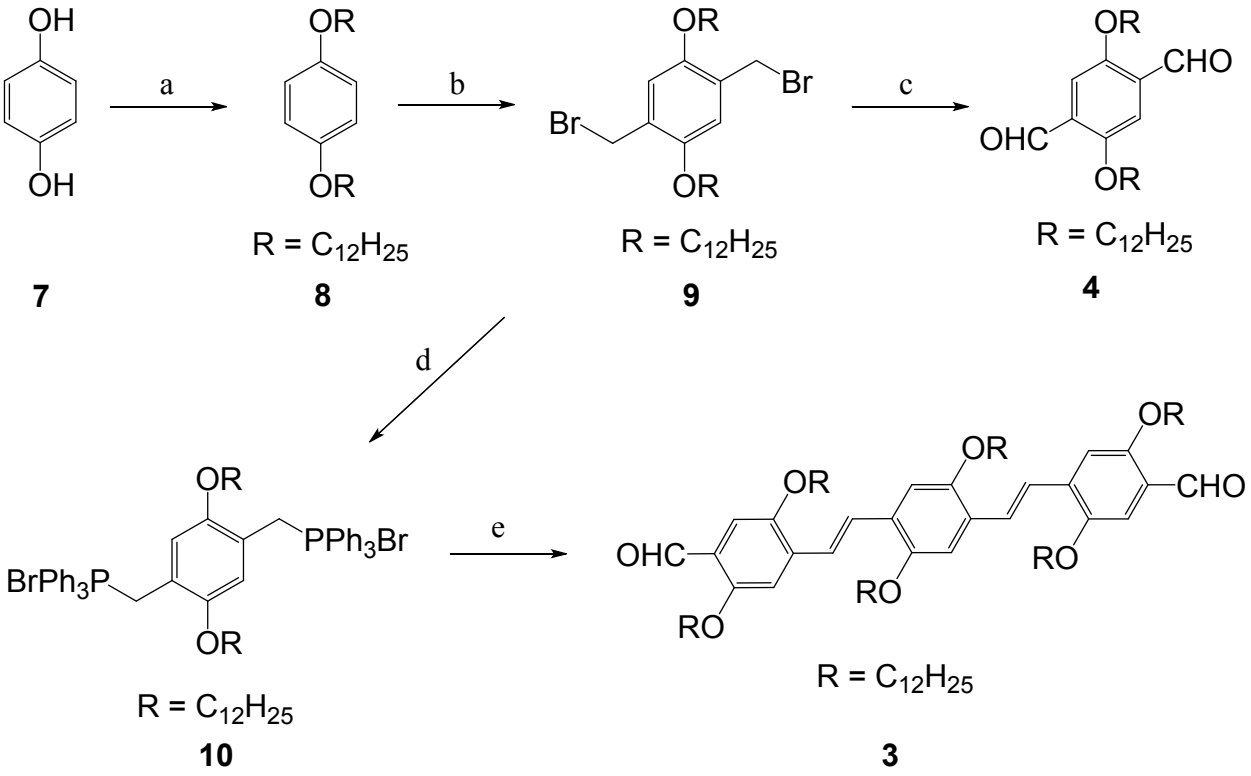


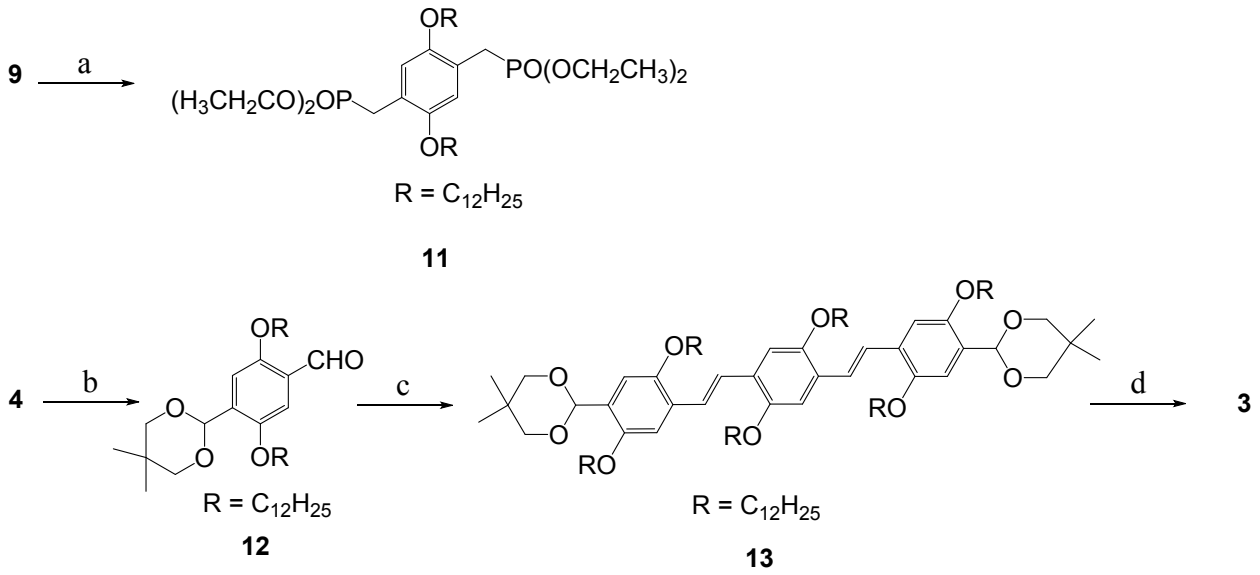
Figure S2: Upper part – differential absorption spectra (visible) obtained upon pump probe excitation (420 nm, 200 nJ) of **ZnTPP** in chlorobenzene with several time delays between 0.1 and 6750 ps at room temperature – see legend for details. Lower part – time-absorption profiles of the spectra in chlorobenzene at 460, 555, 577, and 700 nm monitoring the excited state dynamics.

Synthetic details and characterization



7 **8** **9** **4** **10** **3**

Scheme S1. Reagents and conditions: a) $C_{12}H_{25}Cl$, KOH, EtOH, reflux, 12 h, 93%; b) paraformaldehyde, HBr, 65 °C, 15 h, 98%; c) $NaHCO_3$, DMSO, 115 °C, 0.5 h, 45%, d) PPh_3, toluene, reflux, 3 h; e) (i) **4**, LiOEt, CH_2Cl_2, room temperature, 10 min; (ii) I_2, CH_2Cl_2, room temperature, overnight, 81.2%.



Scheme S2. Reagents and conditions: a) triethylphosphite, 140 °C, 48 h, 85%; b) 2,2- dimethylpropane-1,3-diol,*p*-TsOH (cat.), benzene, reflux, Dean-Stark trap, 24 h, 82.3%; c) (i) **11**, *t*BuOK, THF, 0 °C, 2 h ; (ii) I_2, CH_2Cl_2, H_2O, room temperature, overnight, 80% ; d) CF_3CO_2H, CH_2Cl_2, H_2O, room temperature, 4 h, 93%.

1,4-Bis(dodedyloxy)benzene (8). A suspension of 1,4 hydroquinone **7** (10 g, 90.8 mmol), 1-chlorododecane (63 mL, 272.4 mmol) and KOH (15 g, 267.3 mmol), in ethanol (200mL), under N_2 was heated at reflux overnight. The reaction mixture was cooled to room temperature and the precipitates were filtered and washed with ethanol and water. After being dried under vacuum the precipitates dissolved in hot methanol. Reprecipitation of resulting solution in methanol then gave **8** as a white solid, after being filtered and dried under vacuum (37.7 g, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7 Hz, 6H,), 1.26 (m, 32H), 1.44 (m, 4H), 1.78 (quintet, *J* =7Hz, 4H,) 3.89 (t, *J* = 6.5 Hz, 4H), 6.82 (s, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.36, 115.56, 68.84, 32.06, 29.80, 29.74, 29.73, 29.56, 29.55, 26.20, 22.8, 14.2. HRMS (MALDI-TOF): *m/z* calcd for $C_{30}H_{54}O_2$: 446.4125 $[M]^+$. Found: 446.4117.

2,5-Bis(bromomethyl)-1,4-bis(dodecyloxy)benzene (9). To a suspension of **8** (6 g, 13.43 mmol) and paraformaldehyde (0.806 g, 26.86mmol) in acetic acid (44 mL), HBr (6.0 mL, 33 wt % in acetic acid) was added and the mixture was heated to 65 – 70 °C for 15 h. The resulting solution was cooled to room temperature and water was added (400 mL). The precipitates were filtered, washed with water, dried under vacuum and then dissolved in hot methylene chloride. Reprecipitation of resulting solution in methanol then gave **9** as a white solid after being filtered and dried under vacuum (8.338 g, 98% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, *J* = 6.9 Hz, 6H,), 1.26 (m, 32H), 1.48 (m, 4H), 1.80 (m, 4H,) 3.98 (t, *J* = 6.6 Hz, 4H), 4.52 (s, 4H), 6.84 (s, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 150.84, 127.70, 114.84, 69.20, 32.08, 29.78, 28.90, 26.22, 22.85, 14.28. HRMS (MALDI-TOF): *m/z* calcd for $C_{32}H_{56}Br_2O_2$: 630.2647 $[M]^+$. Found: 630.2653.

2,5-Bis(dodecyloxy)benzene-1,4-dialdehyde (4). A suspension of **9** (2 g, 3.162 mmol) and $NaHCO_3$ (4 g, 47.43 mmol) in dimethyl sulfoxide (50 mL) was heated at 115 °C for 0.5 h before being poured into water (500 mL). The yellow precipitate was filtered, washed with water and dried under vacuum. The residue was purified by column chromatography (SiO_2, hexanes/CH_2Cl_2, 1:1) to obtain **4** as a yellow fluorescent solid. (0.715 g, 45% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, *J* = 6.9 Hz, 6H,), 1.26 (m, 32H), 1.44 (m, 4H), 1.83 (quintet, *J* = 8.1 Hz, 4H,) 4.10 (t, *J* = 6.3 Hz, 4H), 7.42 (s, 2H), 10.51 (s, 2H). ^{13} C NMR (75 MHz, $CDCl_3$): δ 189.57, 155.38, 129.44, 111.,7 69.40, 32.40, 29.74, 26.15, 22.82, 14.24. HRMS (MALDI-TOF): *m/z* calcd for $C_{32}H_{54}O_4$: 502.4022 $[M]^+$. Found: 502.4030.

2,5-Bis(dodecyloxy)-1,4-bis[(2,5-didecoxy-4-formyl)phenylenevinylene] benzene (3). A suspension of **9** (0.576 g, 1.0 mmol) and triphenylphosphine (0.26 g, 0.99 mmol) in dry toluene, under N_2 was heated at reflux for 3 h. The solvent was then removed under reduced pressure and the resulting residue being dried. Dialdehyde **4** (0.47 g, 0.94 mmol) was then added, and the resulting residue dissolved in dry methylene chloride (24 mL). To this solution lithium ethoxide solution (1.18 mL, 1.0 M in ethanol) was added

dropwise at room temperature. The base should be introduced at such a rate that the transient red-purple color produced upon the addition of base should not persist. The resulting solution was stirred for 10 min more after the completion of base addition. The reaction was quenched by the addition of dilute aqueous HCl. The organic layer was separated, washed with water, dried (Na_2SO_4), filtered and concentrated. The resulting residue contained both *E*- and *Z*-isomers. A solution of the *E*:*Z* isomer mixture and I_2 (500 mg) in methylene chloride (50 mL) was stirred at room temperature overnight. The dark brown solution was then diluted with methylene chloride and washed consecutively with aqueous $Na_2S_2O_3$ solution (1.0 M, 2 x 75 mL). The organic layer was washed with water, dried (Na_2SO_4), filtered and evaporated to dryness. Column chromatography (SiO_2, CH_2Cl_2 / hexane, 6:4) gave **3** as an orange fluorescent solid (0.55 g, 81.2 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85-0.88 (m, 18H), 1.25 (m, 96 H,), 1.48 -1.58 (m, 12H), 1.85 (m, 12H), 4.01-4.12 (m, 12H), 7.15 (s, 2H), 7.20 (s, 2H), 7.33 (s, 2H), 7.50 (AB, *J* = 16.50 Hz, 2H), 7.60 (AB, *J* = 16.50 Hz, 2H), 10.40 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.3, 150.4, 151.5, 150.9, 135.1, 127.6, 127.1, 124.3, 123.4, 110.1, 110.6, 110.3, 69.3, 69.6, 32.1, 29.4, 26.33, 22.84, 14.25.HRMS (MALDI-TOF): *m/z* calcd for $C_{96}H_{162}O_8$: 1443.2270 $[M]^+$. Found: 1443.2262.

{[(2,5-bis(dodecyloxy)-1,4-phenylene]bis(methylene)}bis-tetraethylphosphonate (11). A mixture of **9** (0.6 g, 1.10 mmol) and triethylphosphite (1.9 mL, 11mmol) was heated at 150 °C for 24h. After cooling to room temperature, the excess of triethylphosphite was distilled under reduced pressure at 70 °C. Reprecipitation of resulting glassy product in petroleum ether then gave **11** as a white solid, after being filtered and dried under vacuum (0.69 g, 85%).^{1}HNMR (300 MHz, $CDCl_3$): δ 0.87 (t, *J* = 6.3 Hz, 6H), 1.23 (m, 44H), 1.44 (m, 4H), 1.75 (m, 4H), 3.21 (d, J_{PH} = 20.4 Hz, 2H), 3.90 (t, *J* = 6.6 Hz, 4H), 4.02 (dq, J_{PH} = 7.2 Hz, J_{HH} = 7.2 Hz, 8H), 6.9 (s, 2H).^{13}C NMR (125 MHz, $CDCl_3$): δ 150.53, 119.57, 115.05, 69.15, 62.01, 32.05, 29.82, 29.76, 29.62, 29.60, 29.49, 26.28, 22.83, 16.53, 16.50, 16.48, 14.26. HRMS (MALDI-TOF): *m/z* calcd for $C_{40}H_{76}O_8P_2$: 746.5015 $[M]^+$. Found: 746.5021.

4-[(5,5-dimethyl-1,3-dioxan-2-yl)-2,5-bis(dodecyloxy)]benzaldehyde (12). A solution of **4** (0.11 g, 0.23 mmol), 2,2-dimethylpropane-1,3-diol (0.025 g, 0.26 mmol), and *p*-TsOH (1 mg, 0.0052 mmol) in benzene (6 ml) was refluxed for 48 h using a Dean-Stark trap. After cooling to room temperature, the solution was evaporated to dryness. The resulting residue was taken up in CH_2Cl_2. The organic layer washed with water, dried (Na_2SO_4), filtered and evaporated to dryness. Column chromatography (SiO_2, hexanes/CH_2Cl_2 1:1) gave **12** (0.112 g, 82.3%) as a colorless solid.^{1}HNMR (300 MHz, $CDCl_3$): δ 0.78 (s, 1H), 0.88 (t, *J* = 6.3 Hz, 6H), 1.26 (m, 35H), 1.44 (m, 4H), 1.78 (m, 4H), 3.66 (d, *J* = 10.2 Hz, 2H), 3.76 (d, *J* = 11.1 Hz, 2H), 3.98 (t, *J* = 6.6 Hz, 2H), 4.08 (t, *J* = 6.6 Hz, 2H), 5.73 (s, 1H), 7.30 (s, 1H), 10.46 (s, 1H).^{13}C NMR (125 MHz, $CDCl_3$): δ 189.84, 156.17, 150.25, 134.73, 125.37, 112.19, 110.36, 96.67, 69.26, 32.06, 30.51, 29.05,

29.85, 29.80, 29.75, 29.72, 29.36, 29.30, 26.23, 26.16, 23.37, 22.84, 21.99, 14.27. HRMS (MALDI-TOF): *m/z* calcd for $C_{37}H_{64}O_5$: 588.4754 $[M]^+$. Found: 588.4760.

2,2'-{[(1E,1'E)-(2,5-bis(dodecyloxy)-1,4-phenylene)bis(ethene-2,1-diyl)]bis(2,5-bis(dodecyloxy)-4,1-phenylene)}bis(5,5-dimethyl-1,3-dioxane) (13): *t*-BuONa (0.010 g, 0.09 mmol) was added to a solution of **11** (0.029 g, 0.038 mmol) and **12** (0.056 g, 0.077 mmol) in dry THF under N_2 at 0 °C. The mixture was stirred for 2 h and then the resulting solution evaporated to dryness. The residue was taken up with CH_2Cl_2. The organic layer washed with water, dried (Na_2SO_4), filtered and evaporated to dryness. The resulting residue contained both *E* and *Z* isomers. Isomerization to the all *E*- isomers was achieved following the procedure as described for compound **3**. Column chromatography (SiO_2, CH_2Cl_2 /hexane, 8:2) gave **13** (0.049 g, 80%) as a yellow fluorescent solid.^{1}H NMR (300 MHz, $CDCl_3$): δ 0.80 (s, 1H), 0.87 (m, 18H), 1.28 (m, 102H), 1.52 (m, 12H), 1.80 (m, 12H), 3.67 (d, *J* = 10.8 Hz, 4H), 3.77 (d, *J* = 10.8 Hz, 4H), 4.01 (m, 12H), 5.75 (s, 2H), 7.13 (m, 4H), 7.18 (s, 2H), 7.45 (s, 1H).^{13}C NMR (125 MHz, $CDCl_3$):δ 151.20, 150.48, 128.74, 127.46, 127.13, 123.89, 123.55, 111.65, 110.74, 110.70, 97.28, 78.05, 69.64, 69.52, 32.08, 30.45, 29.89, 29.86, 29.72, 29.64, 29.53, 26.46, 26.39, 26.33, 23.40, 22.84, 22.05, 14.27. HRMS (MALDI-TOF): *m/z*calcd for $C_{106}H_{182}O_{10}$: 1615.3733 $[M]^+$. Found: 1615.3726.

2,5-Bis(dodecyloxy)-1,4-bis[(2,5-didecoxy-4-formyl)phenylenevinylene] benzene (3). A mixture of **13** (0.030 g, 0.018 mmol) and CF_3CO_2H (0.6 mL) in CH_2Cl_2/H_2O 1:1 (2 mL) was stirred at room temperature for 4 h. The organic layer was washed with water, dried (Na_2SO_4), filtered and evaporated to dryness. Column chromatography (SiO_2, CH_2Cl_2 / hexane, 6:4) gave **6** as an orange fluorescent solid (0.025 g, 93% yield).

^{1}H NMR and ^{13}C NMR for all the new compounds

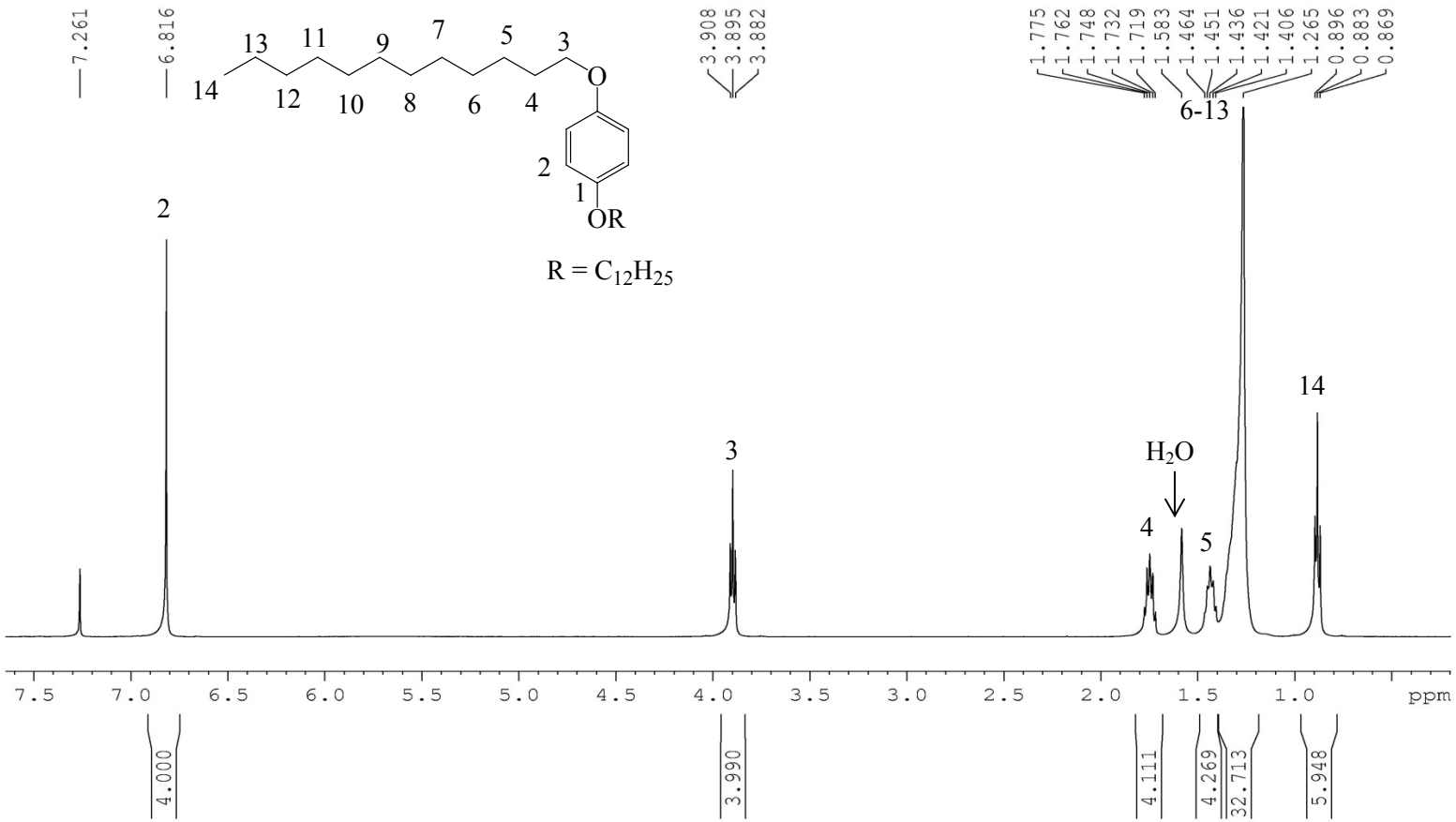


Figure S3a. ^{1}H-NMR spectrum in $CDCl_3$ of compound **8.**

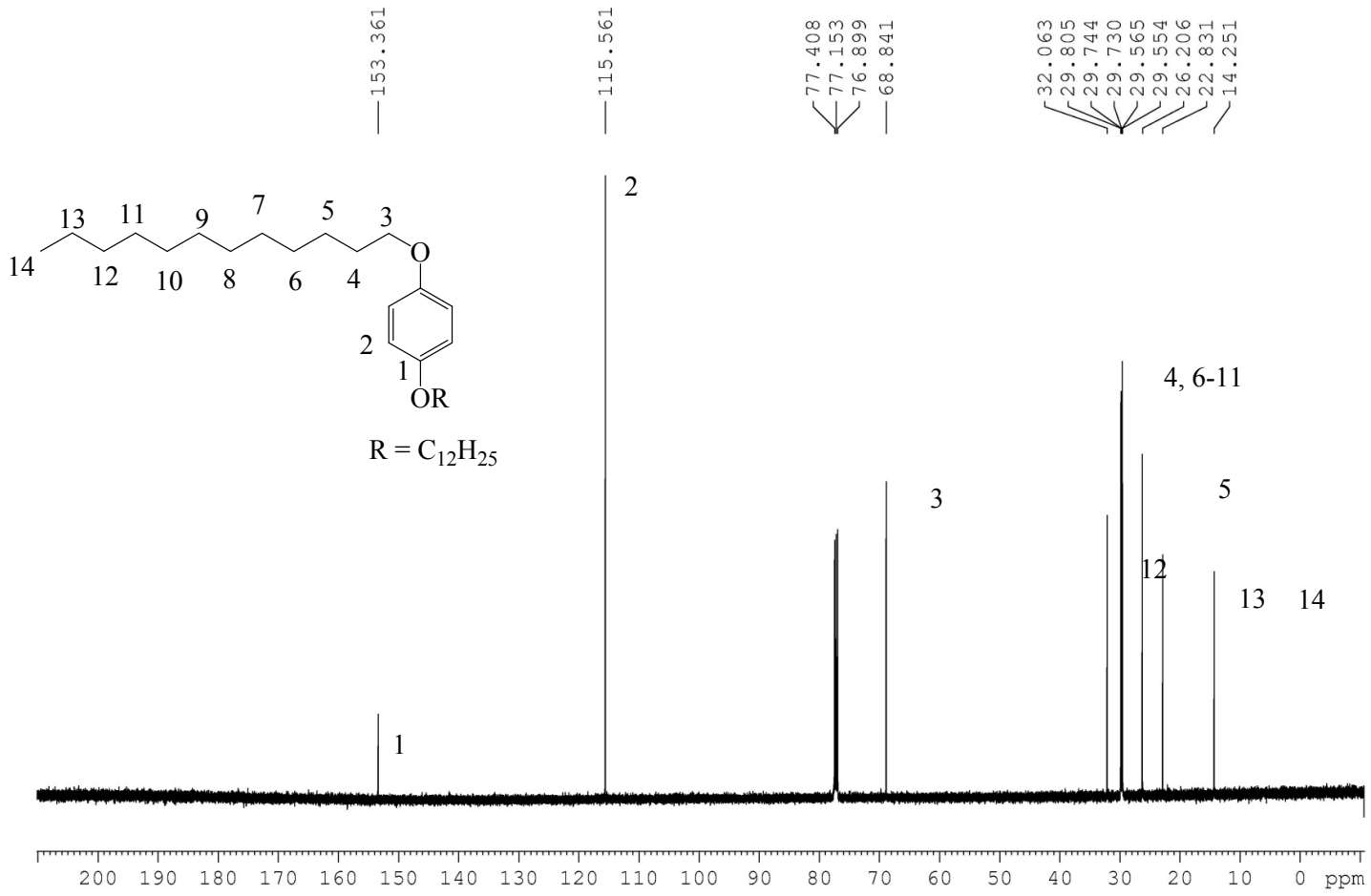


Figure S4b. ^{13}C-NMR spectrum in $CDCl_3$ of compound **8.**

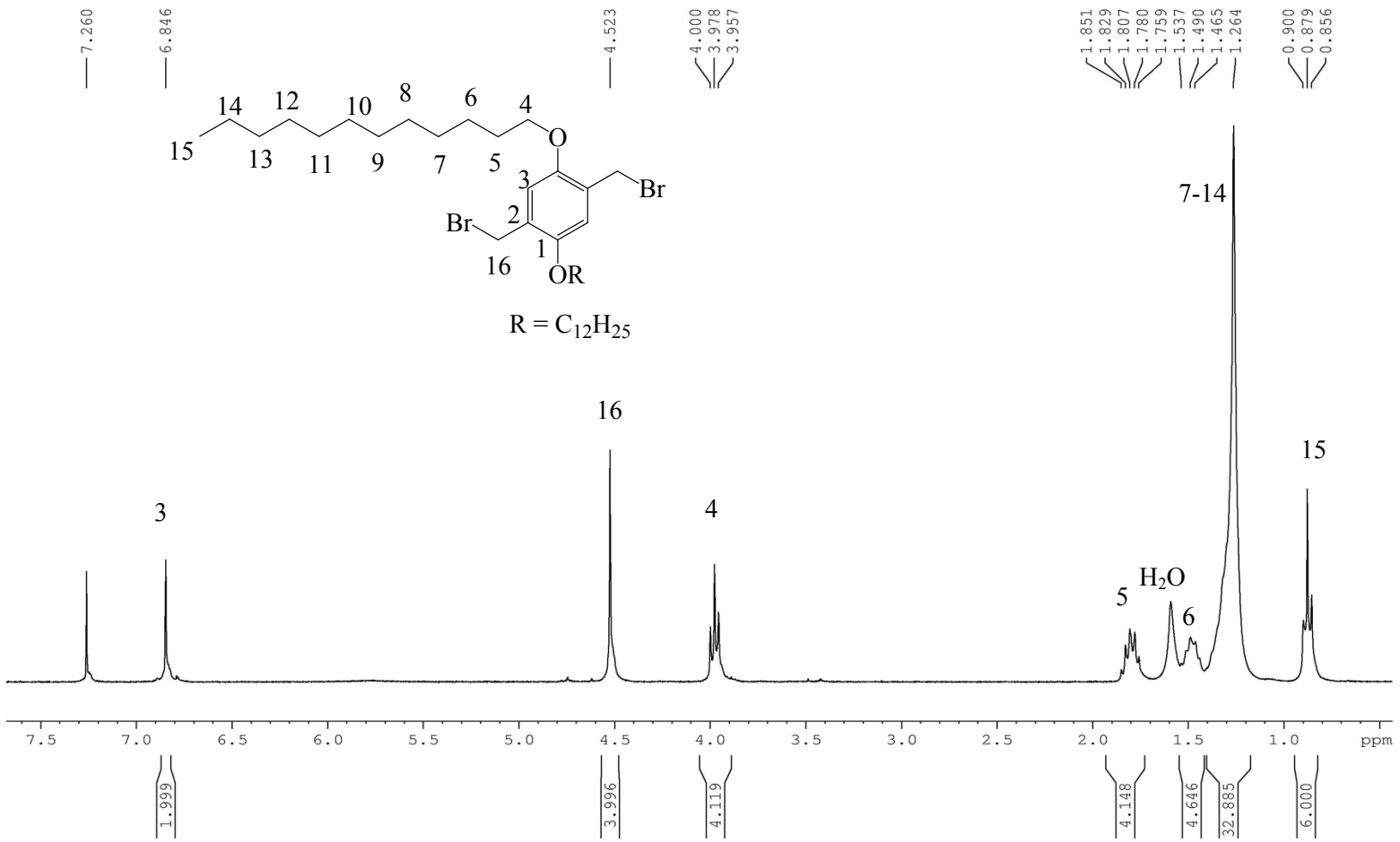


Figure S4a. ^{1}H-NMR spectrum in $CDCl_3$ of compound **9.**

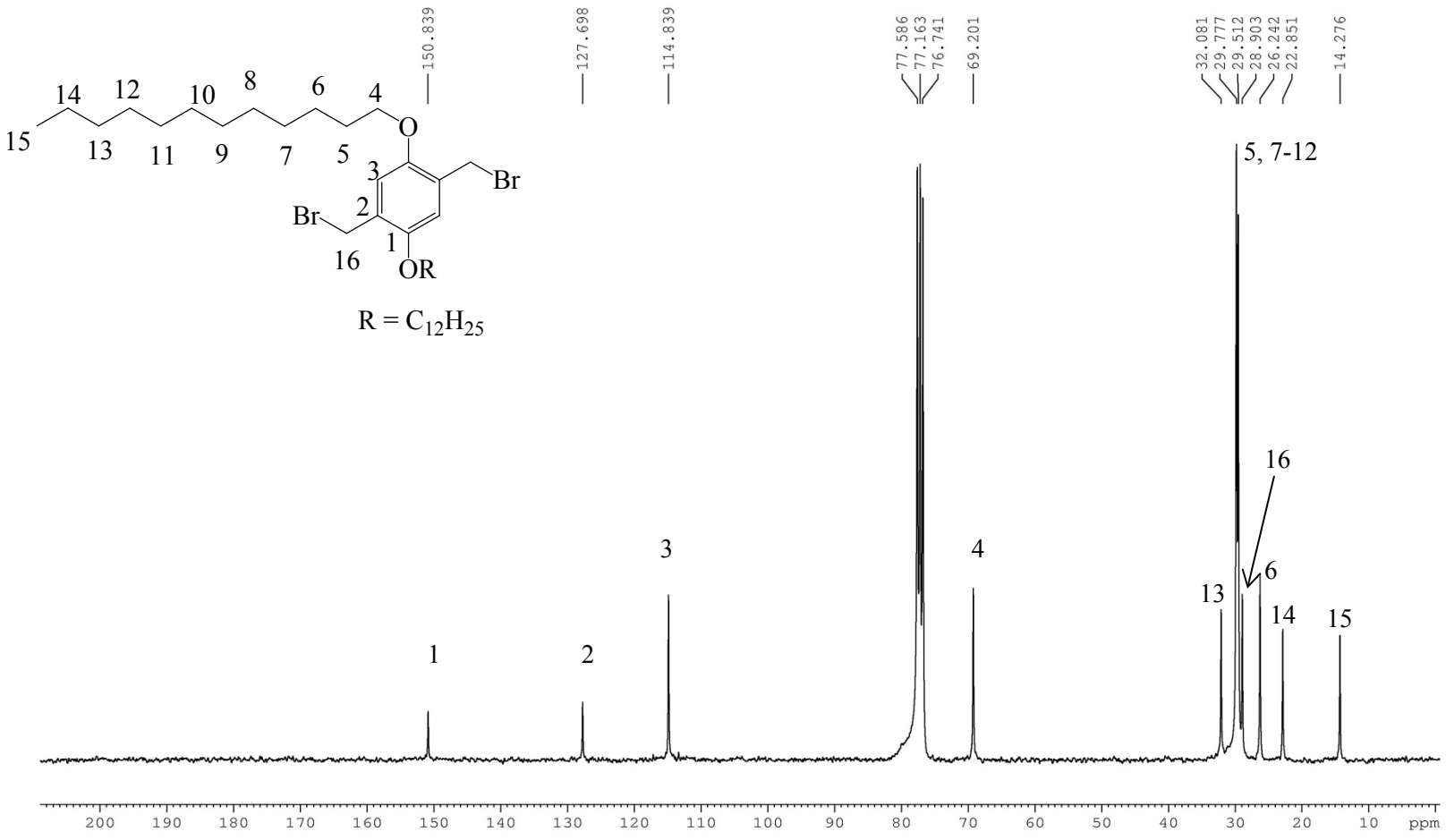


Figure S4b. ^{13}C-NMR spectrum in $CDCl_3$ of compound **9.**

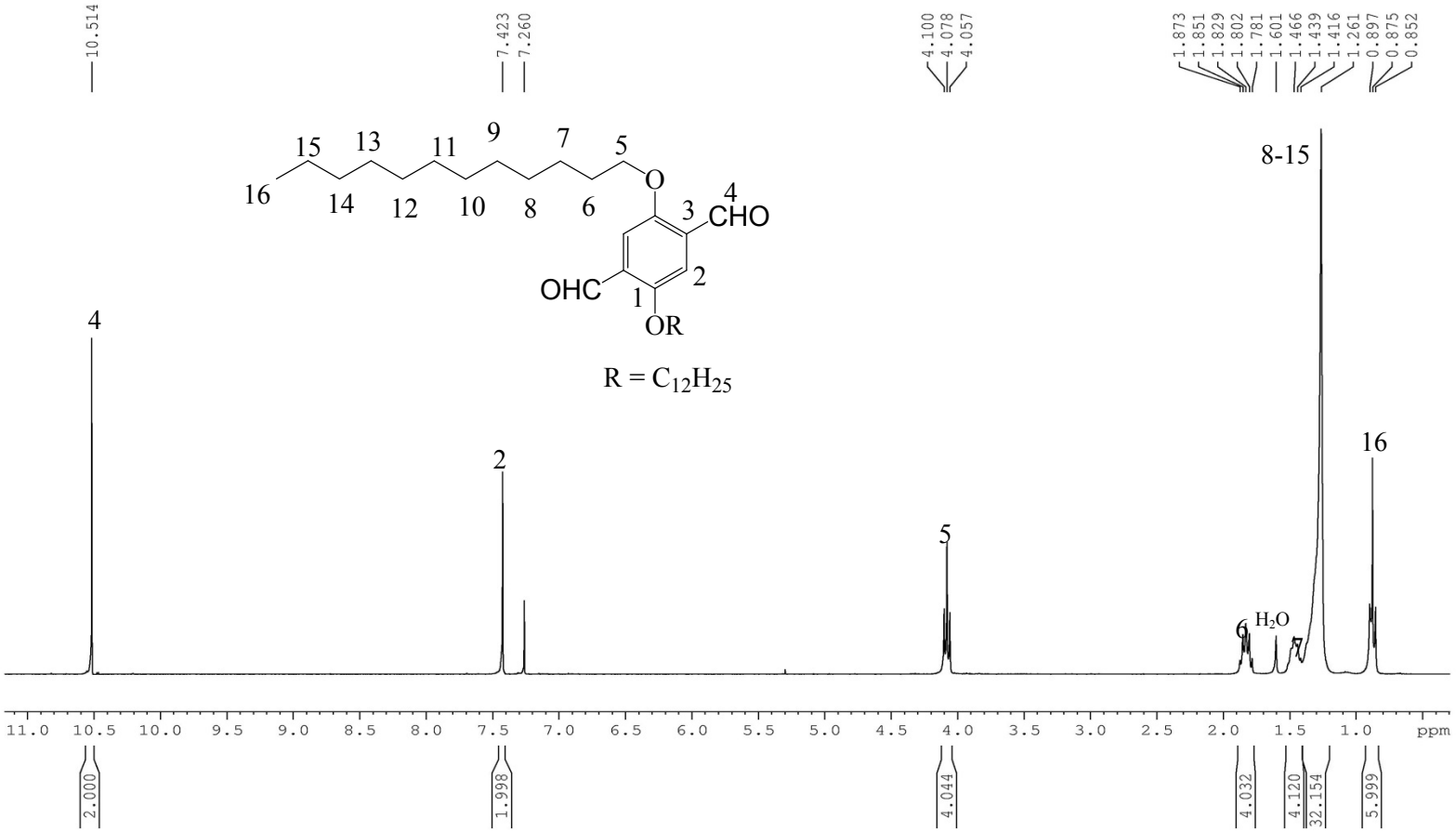


Figure S5a. ^{1}H-NMR spectrum in $CDCl_3$ of compound **4.**

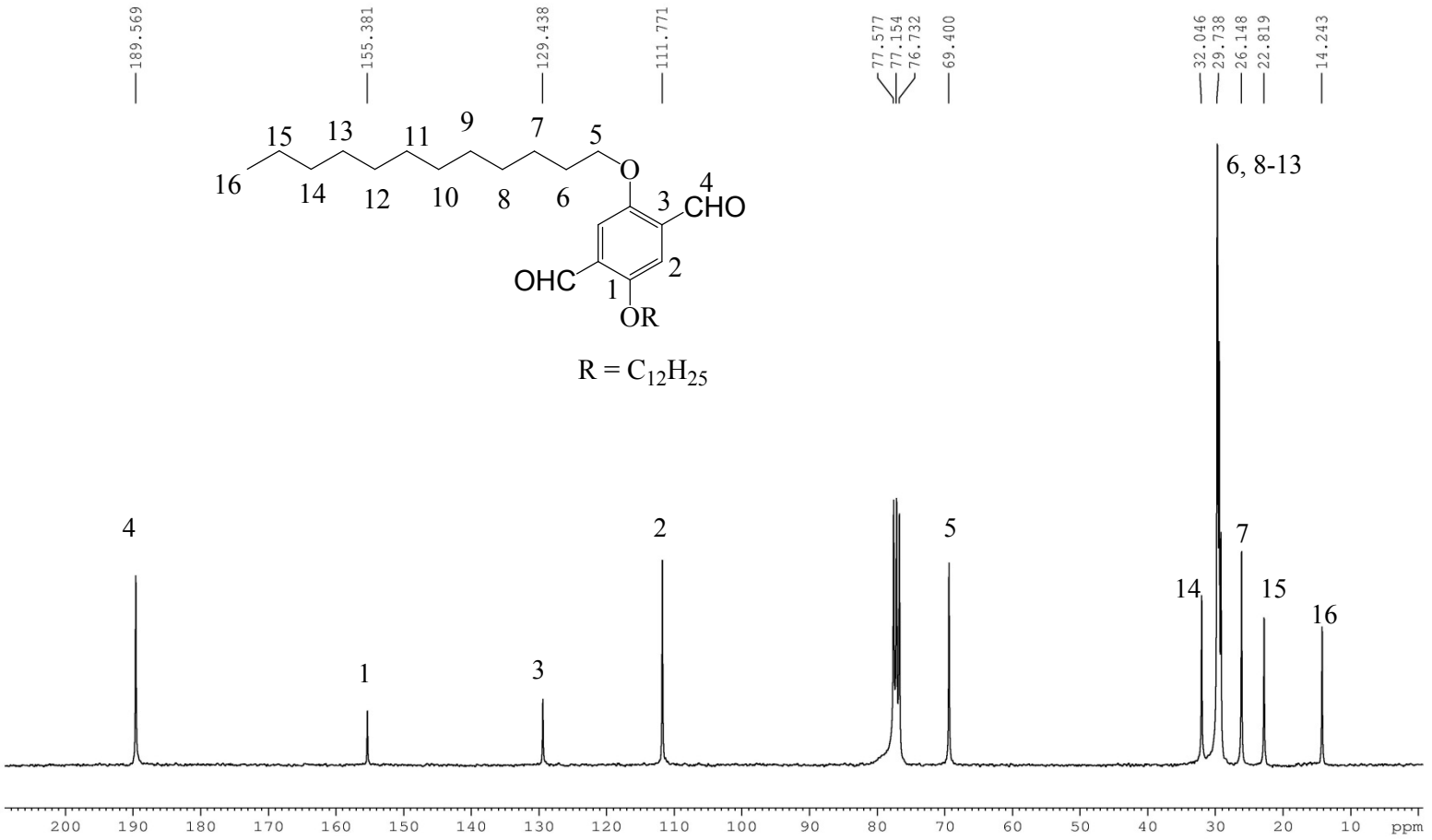


Figure S5b. ^{13}C-NMR spectrum in $CDCl_3$ of compound **4.**

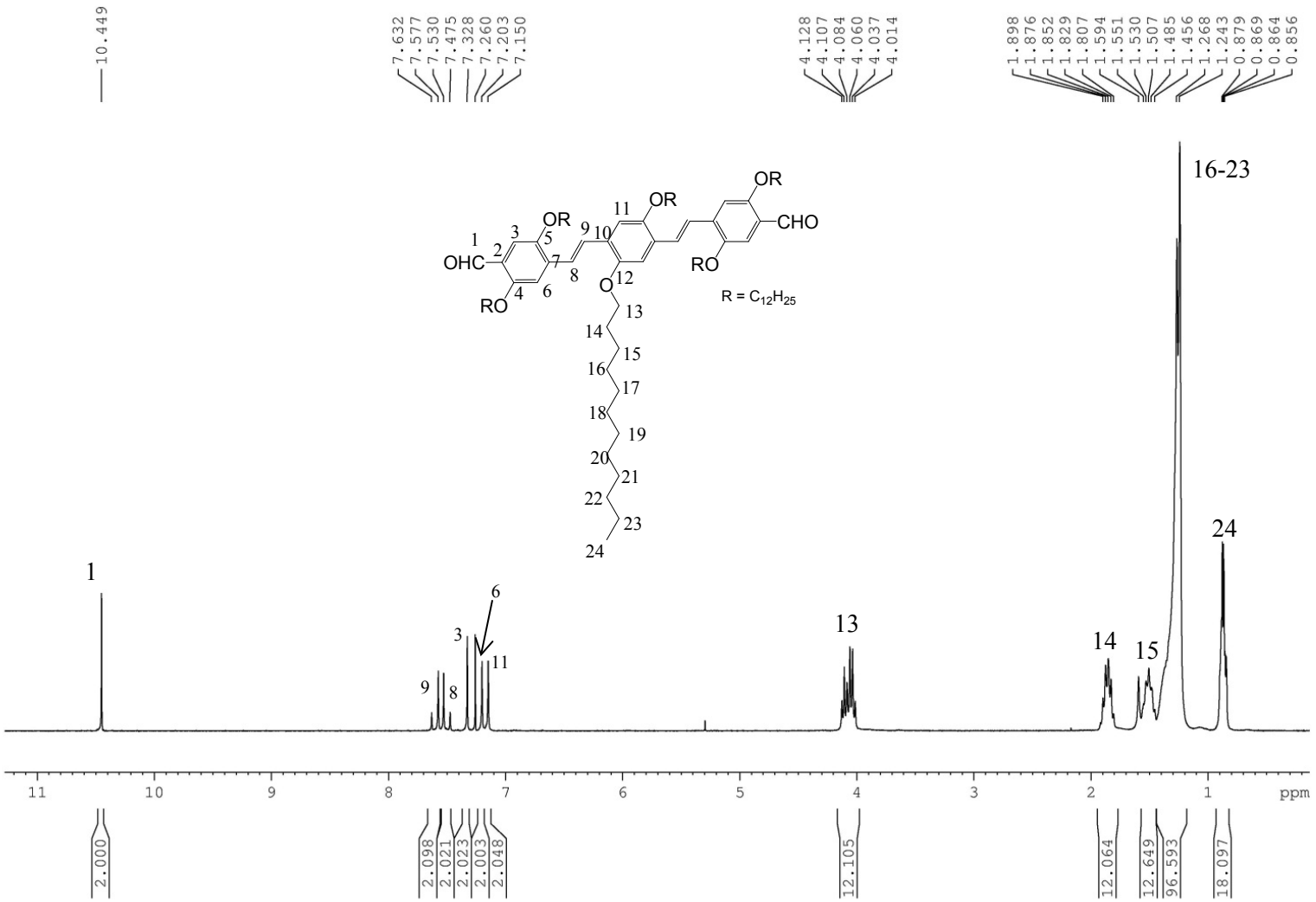


Figure S6a. ^{1}H-NMR spectrum in $CDCl_3$ of compound **3.**

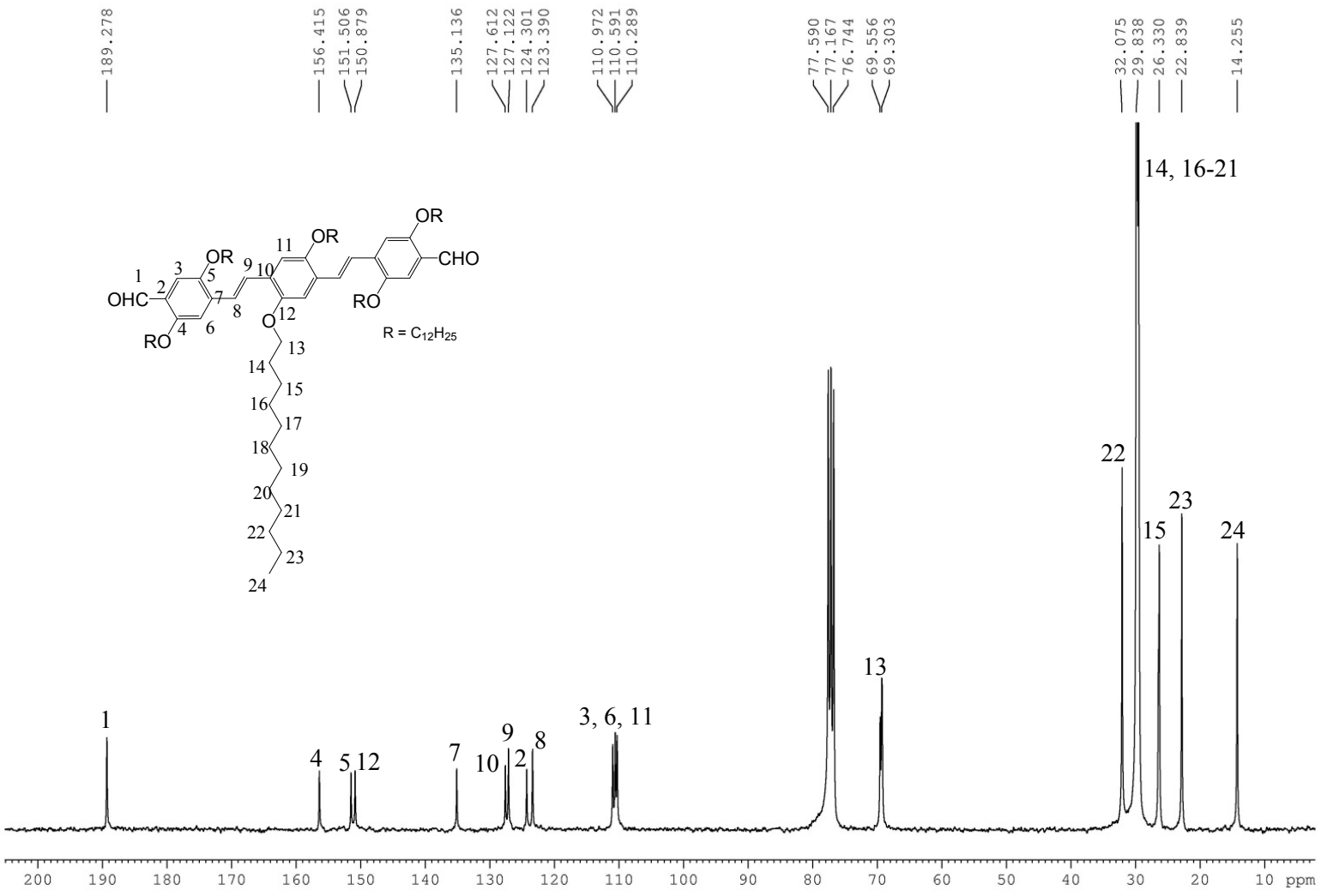


Figure S6b. ^{13}C-NMR spectrum in $CDCl_3$ of compound **3.**

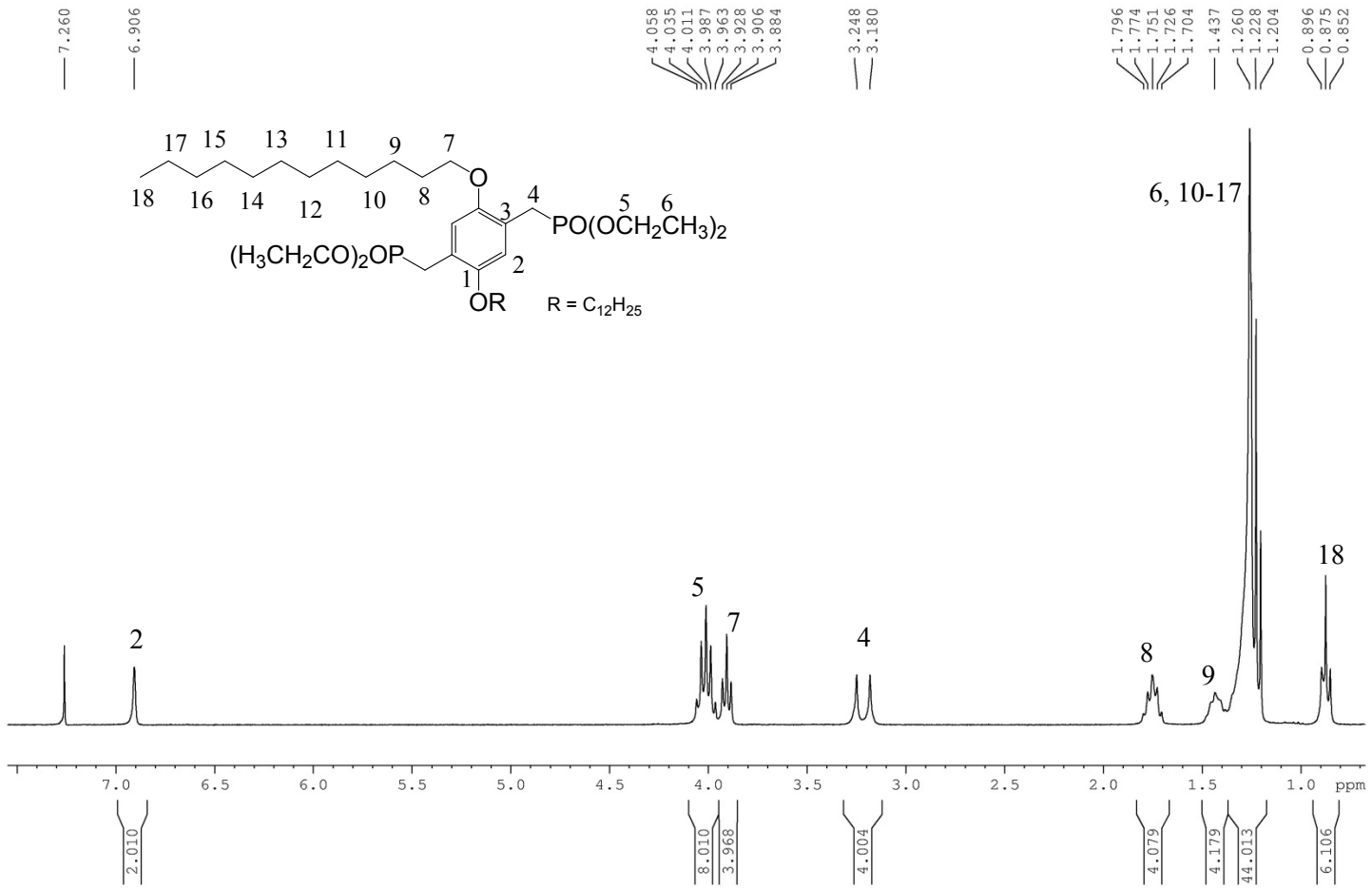


Figure S7a. ^{1}H-NMR spectrum in $CDCl_3$ of compound **11.**

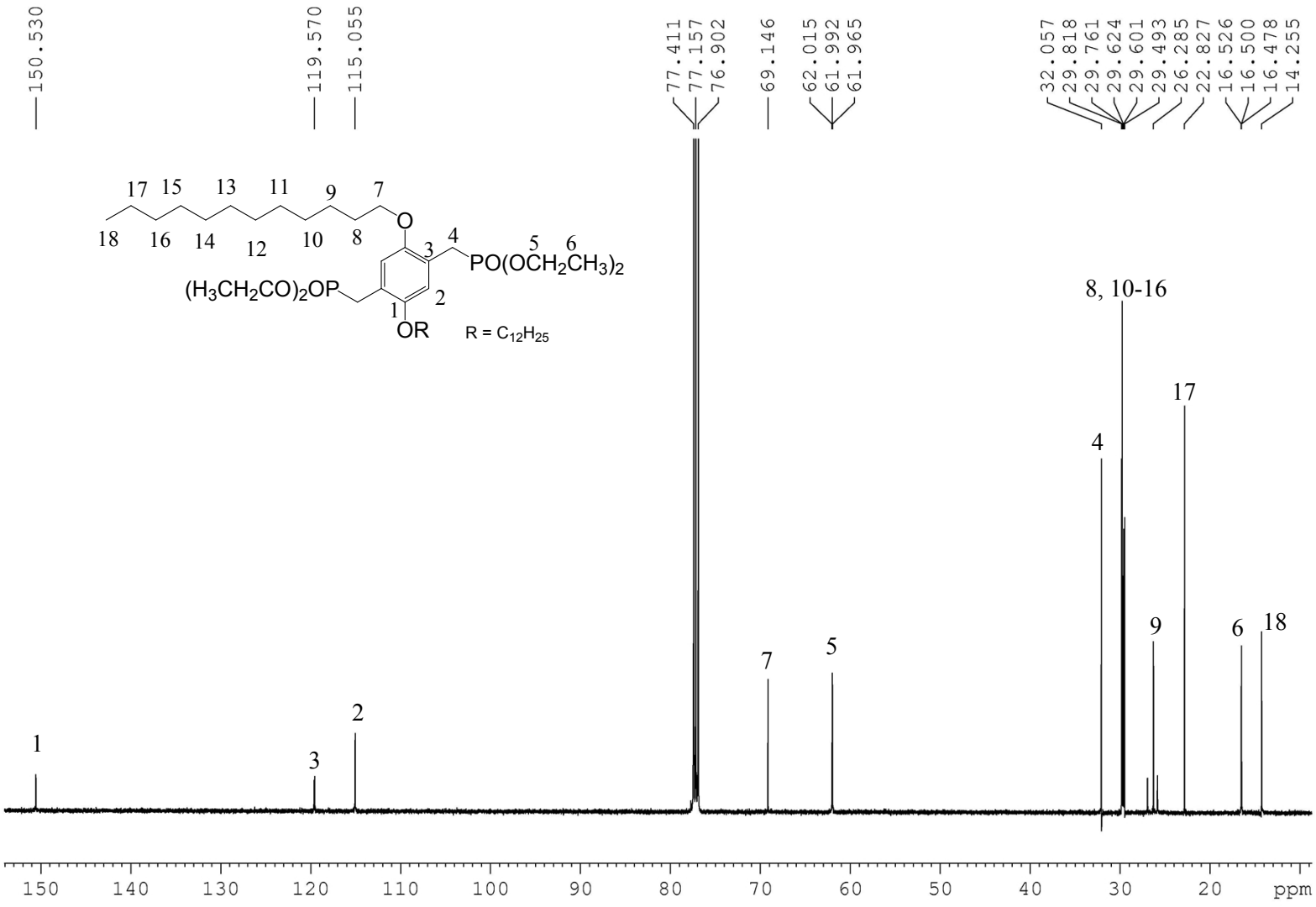


Figure S7b. ^{13}C-NMR spectrum in $CDCl_3$ of compound **11.**

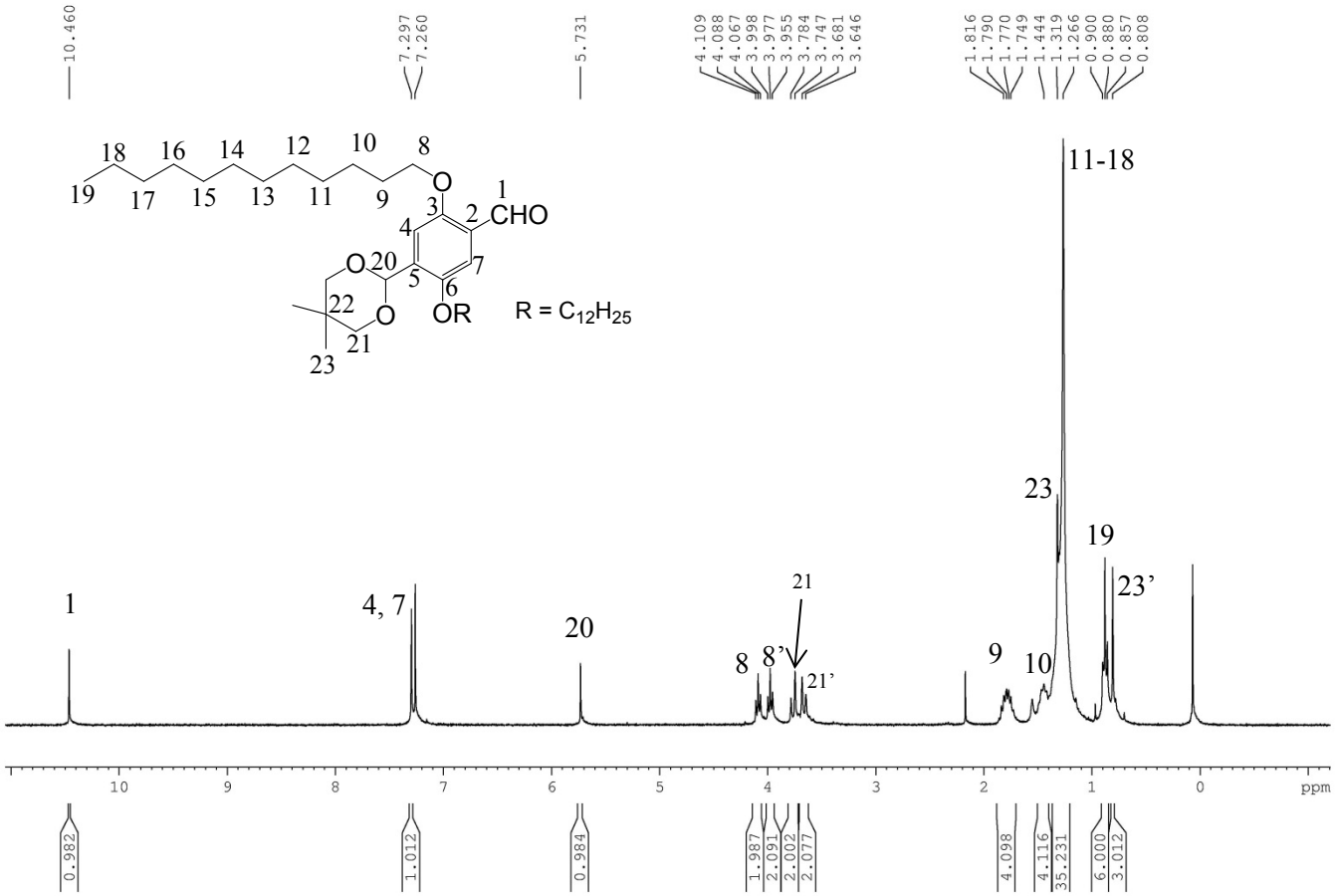


Figure S8a. ^{1}H-NMR spectrum in $CDCl_3$ of compound **12.**

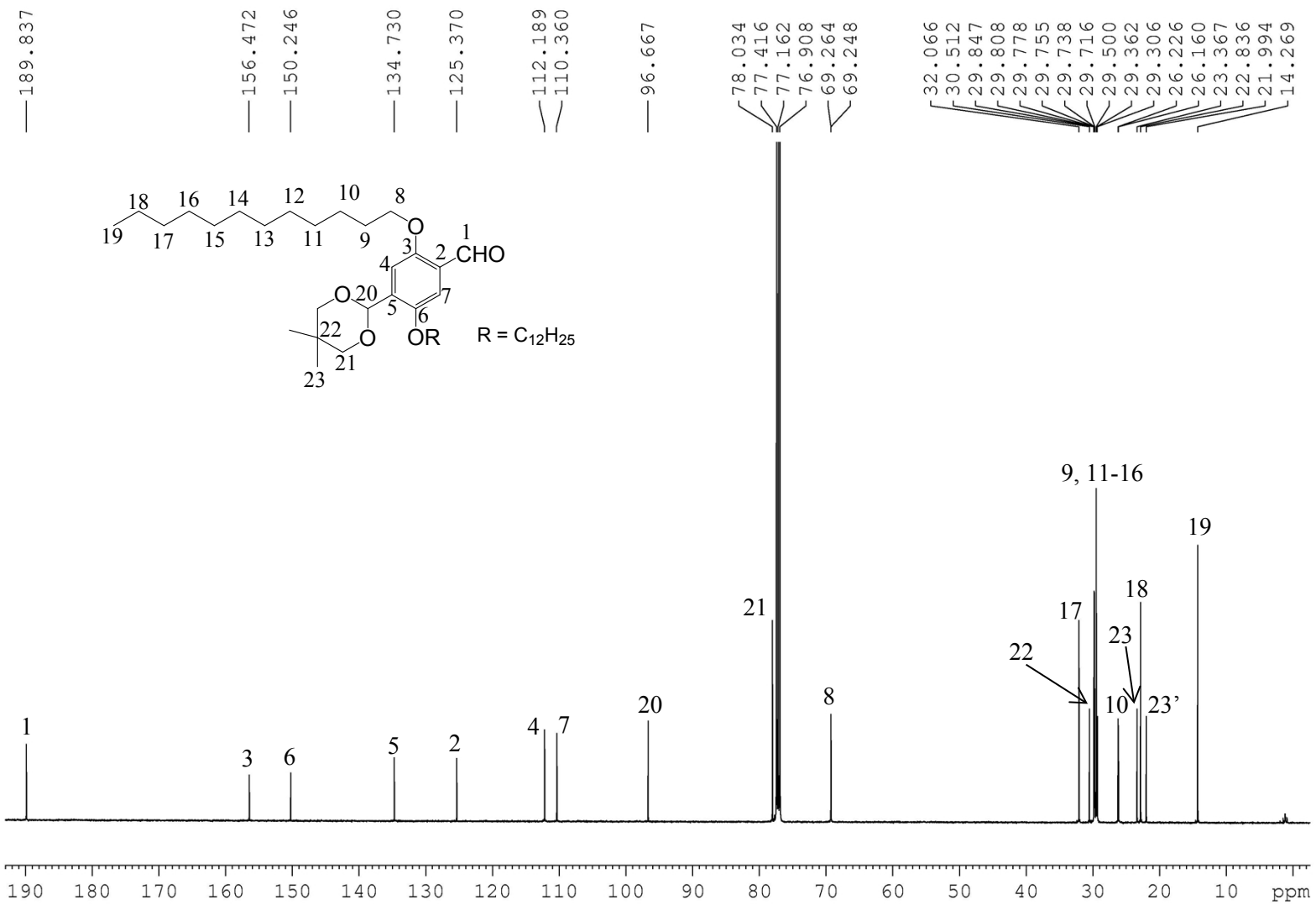


Figure S8b. ^{13}C-NMR spectrum in $CDCl_3$ of compound **12.**

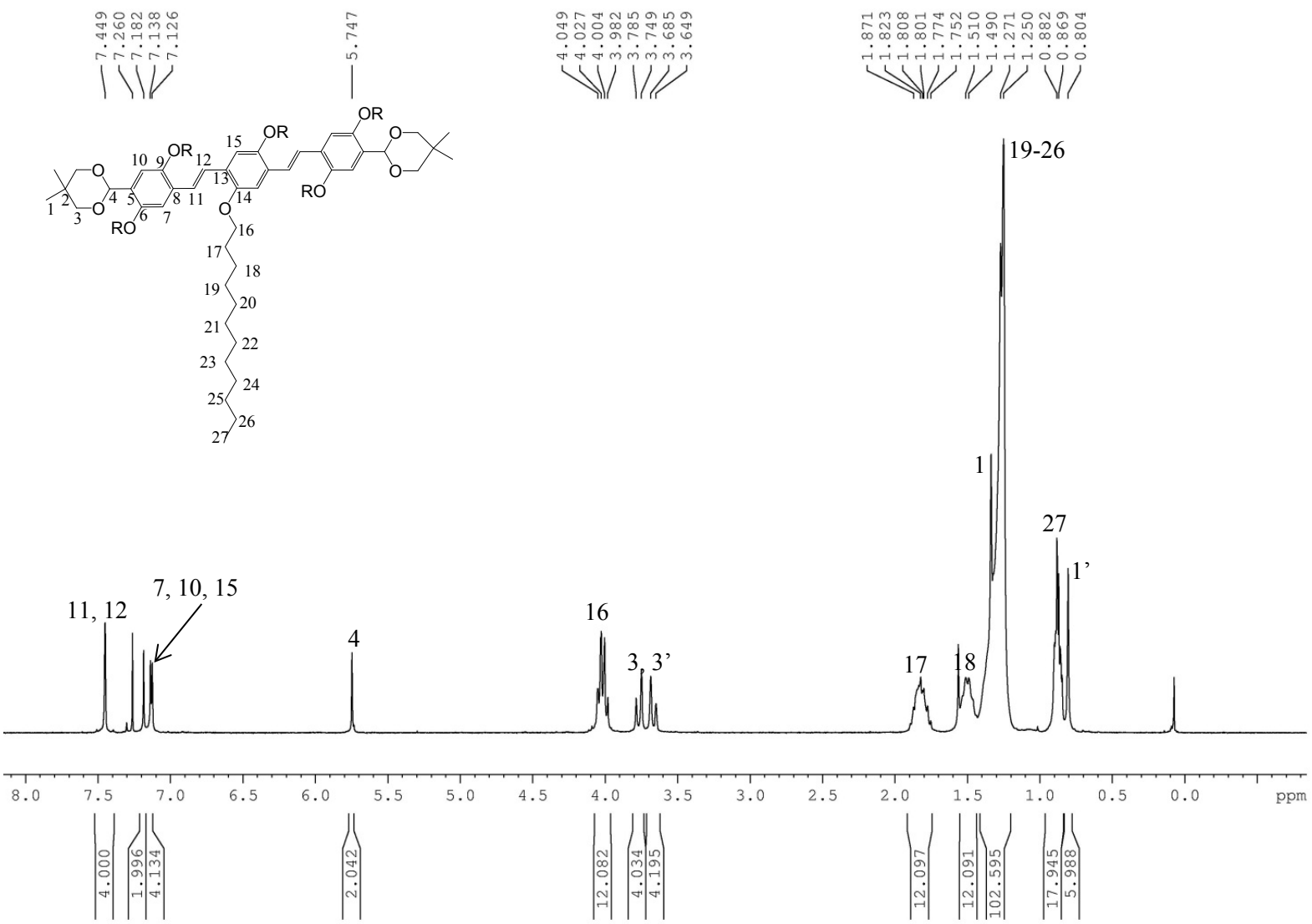


Figure S9a. ^{1}H-NMR spectrum in $CDCl_3$ of compound **13.**

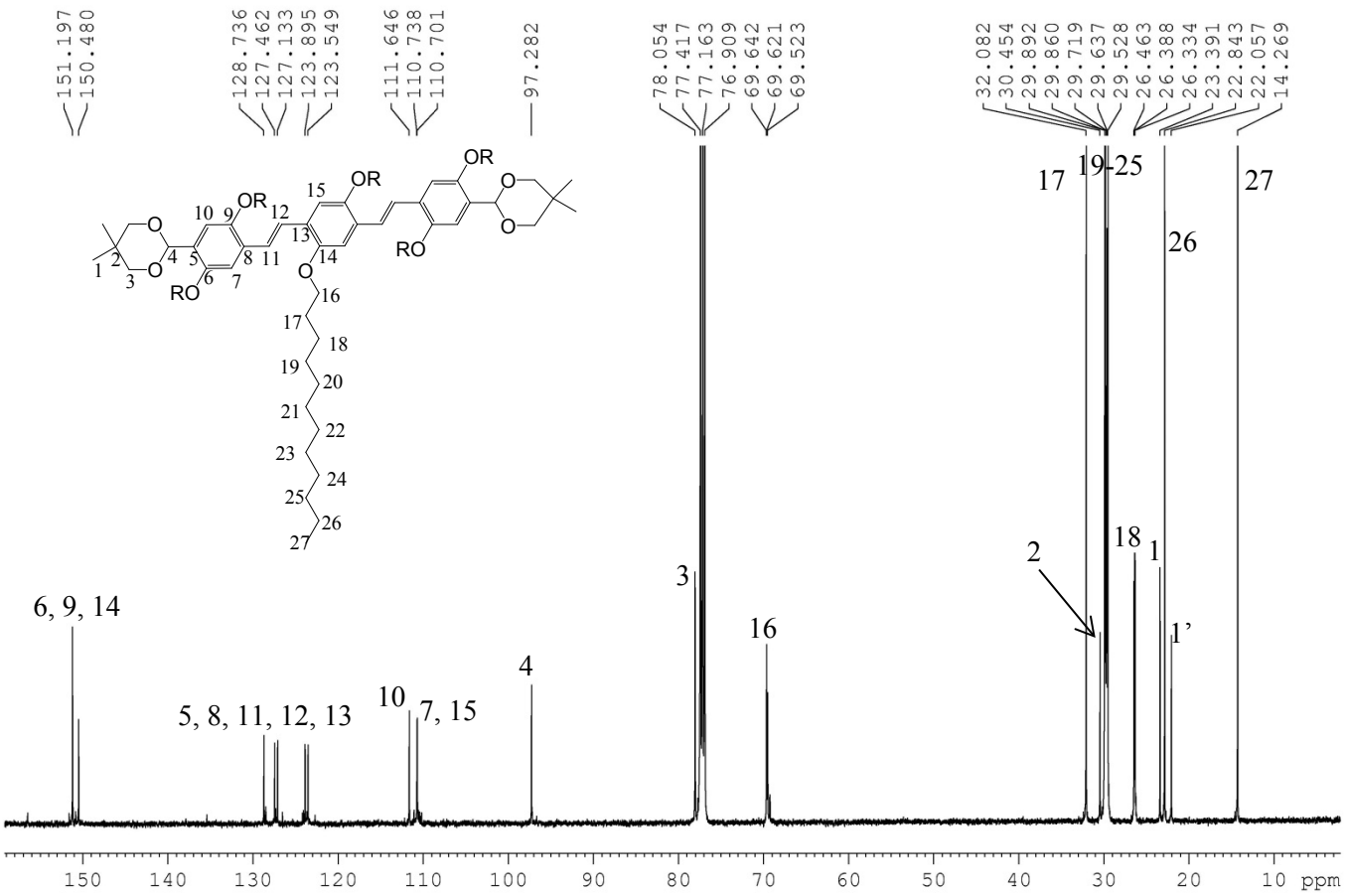


Figure S9b. ^{13}C-NMR spectrum in $CDCl_3$ of compound **13.**

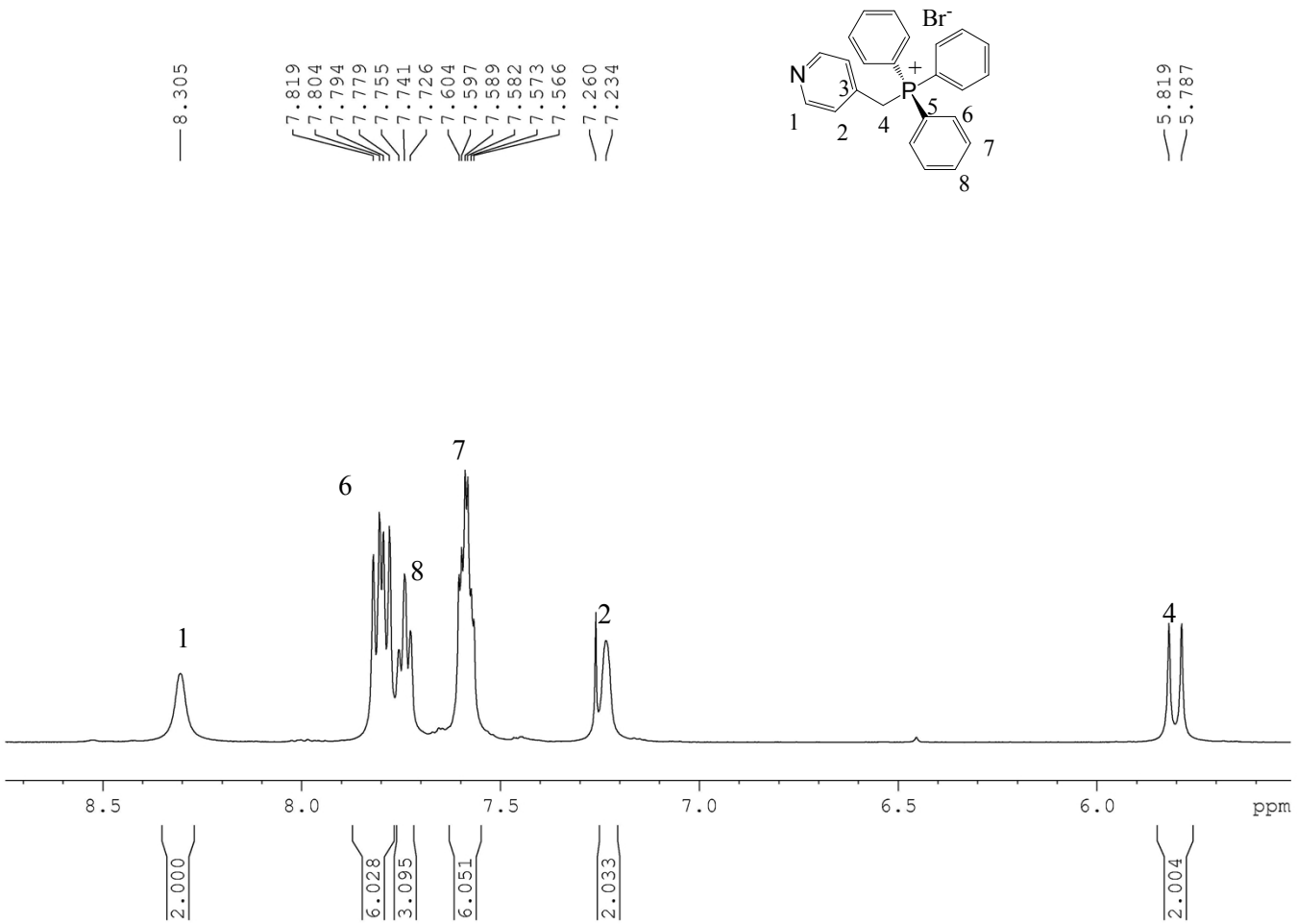


Figure S10a. ^{1}H-NMR spectrum in $CDCl_3$ of compound **2.**

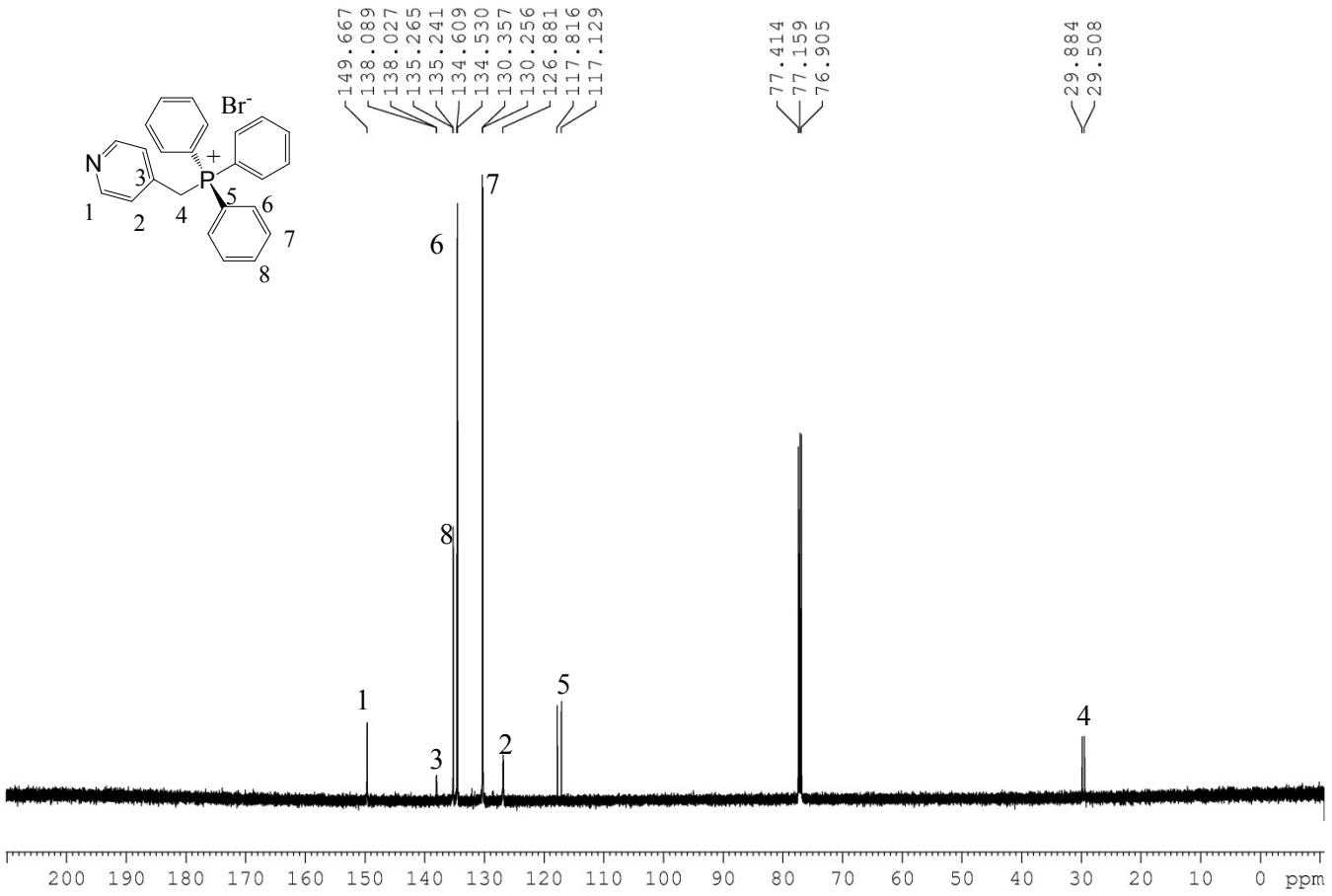


Figure S10b. ^{13}C-NMR spectrum in $CDCl_3$ of compound **2.**

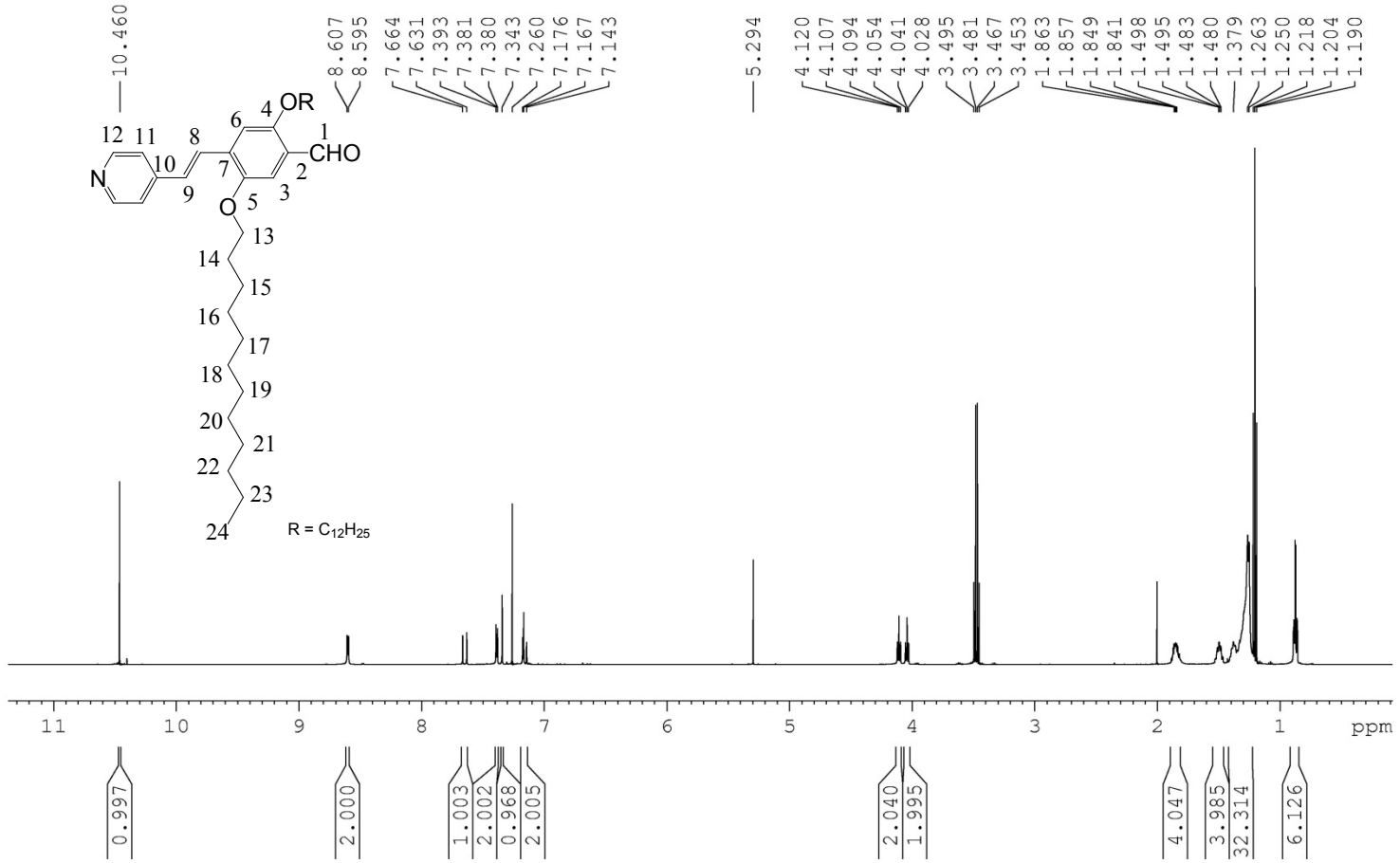


Figure S11a. ^{1}H-NMR spectrum in $CDCl_3$ of compound *E*-**6.**

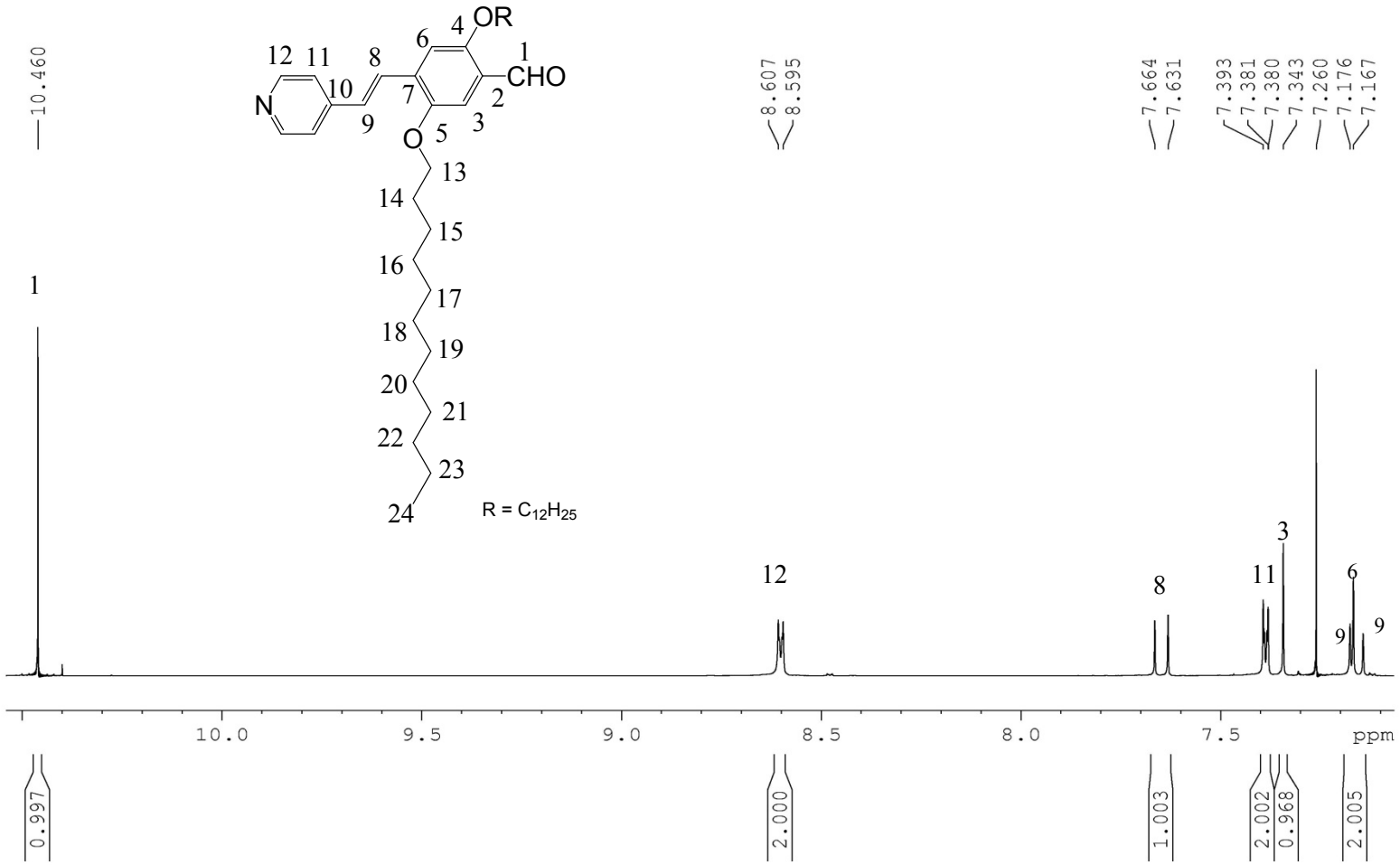


Figure S11b. ^{1}H-NMR spectrum in $CDCl_3$ of compound *E*-**6.**

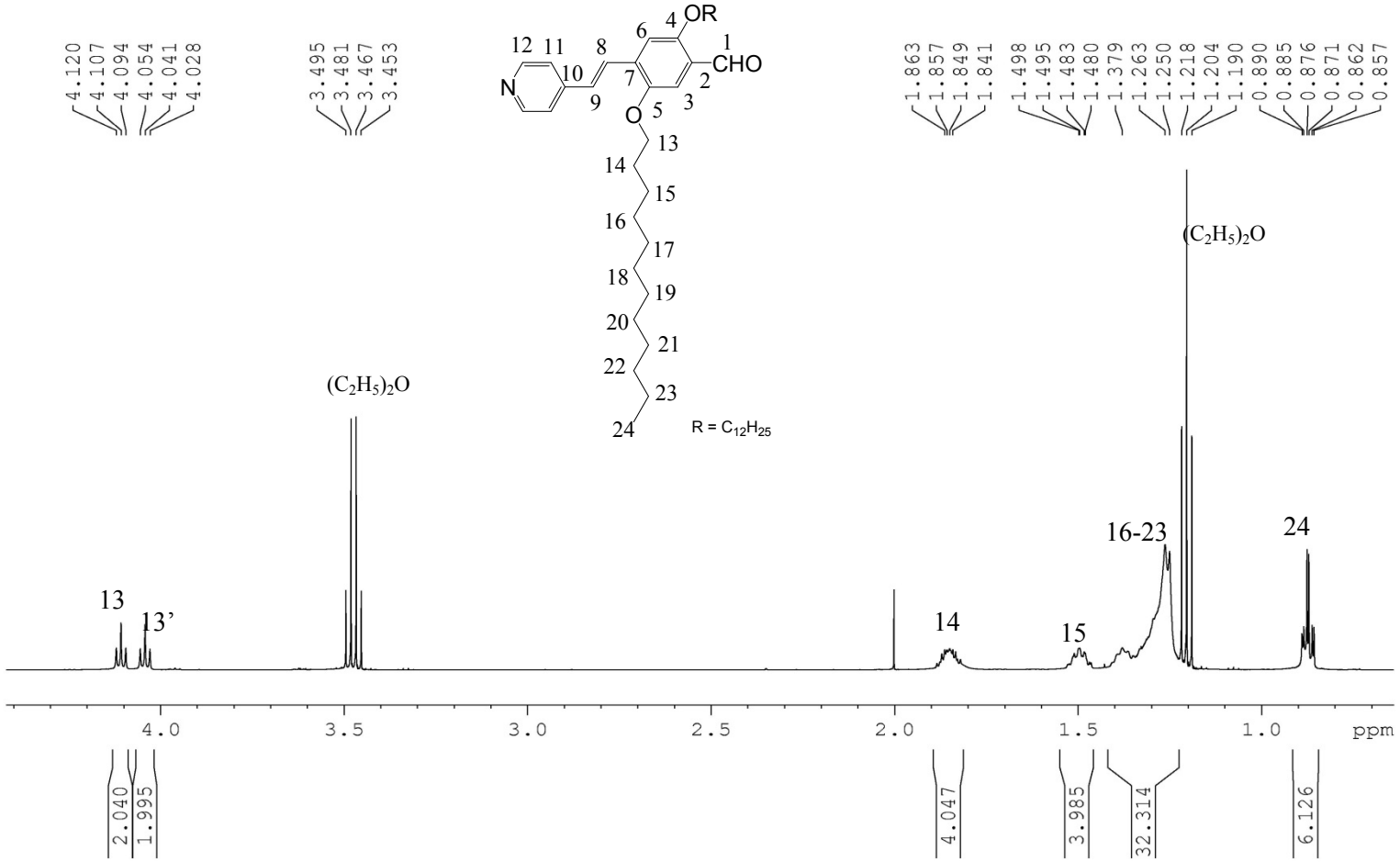


Figure S11c. ^{1}H-NMR spectrum in $CDCl_3$ of compound *E*-**6.**

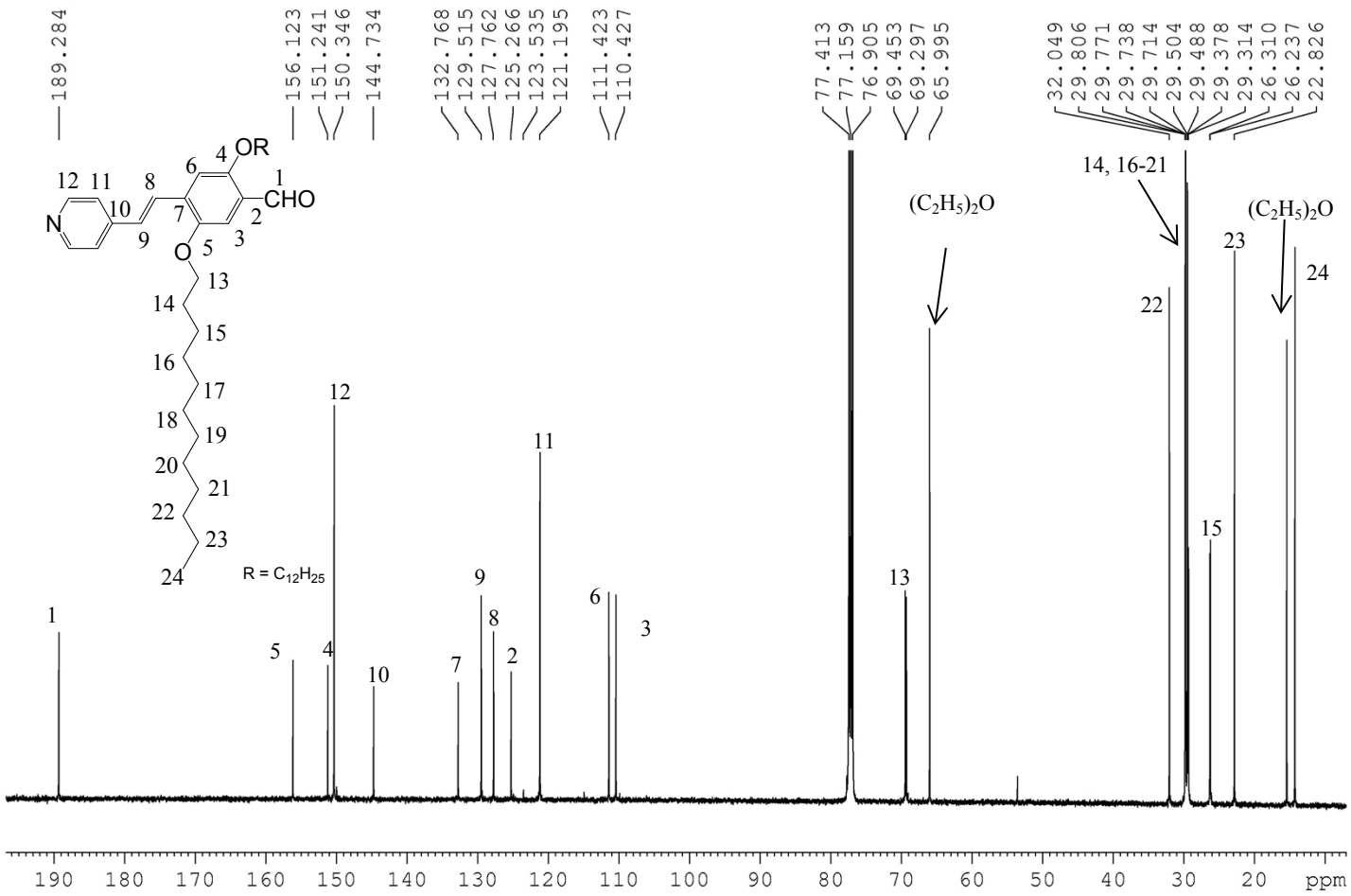


Figure S11d. ^{13}C-NMR spectrum in $CDCl_3$ of compound *E*-**6.**

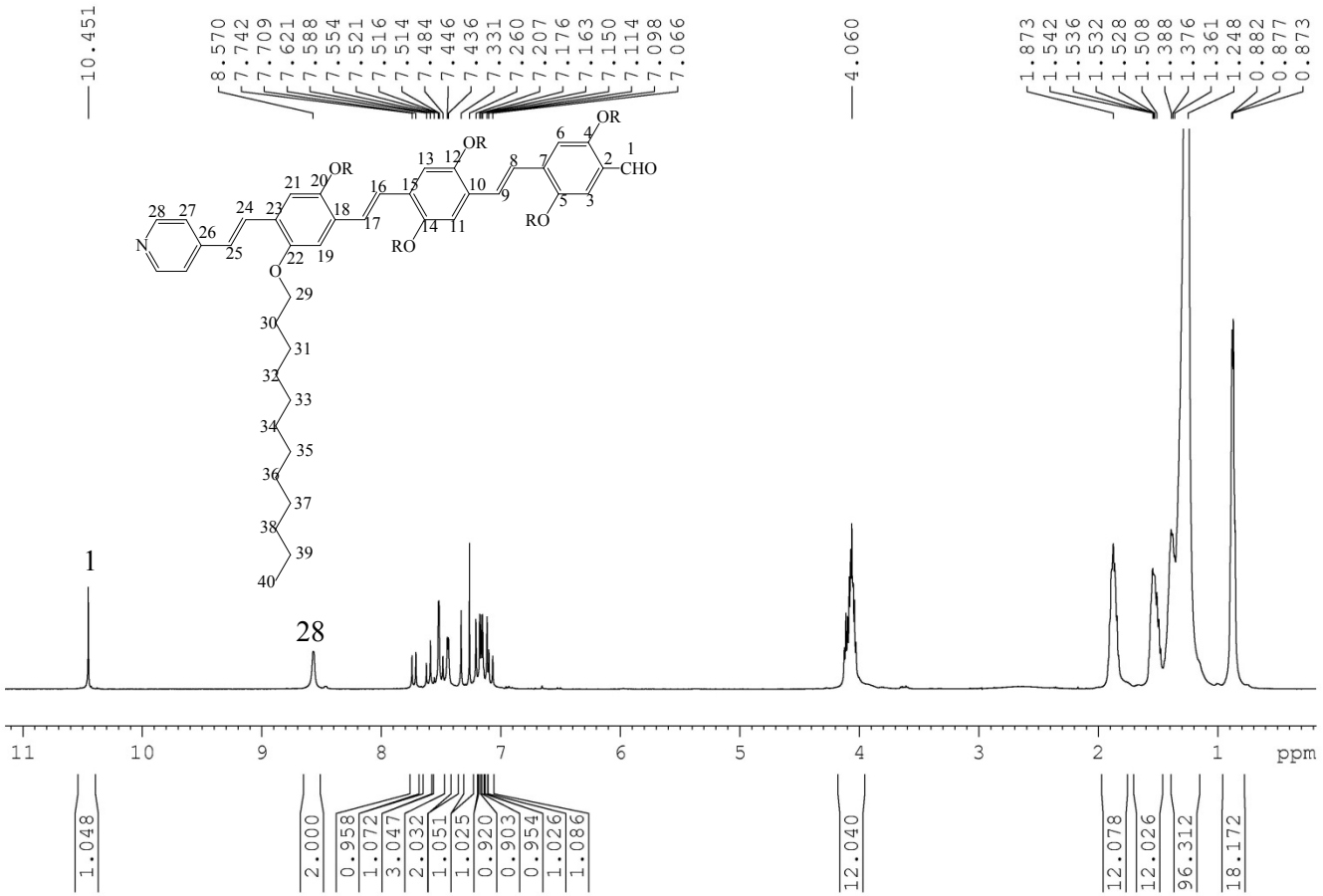


Figure S12a. ^{1}H-NMR spectrum in $CDCl_3$ of compound *E*-**5.**

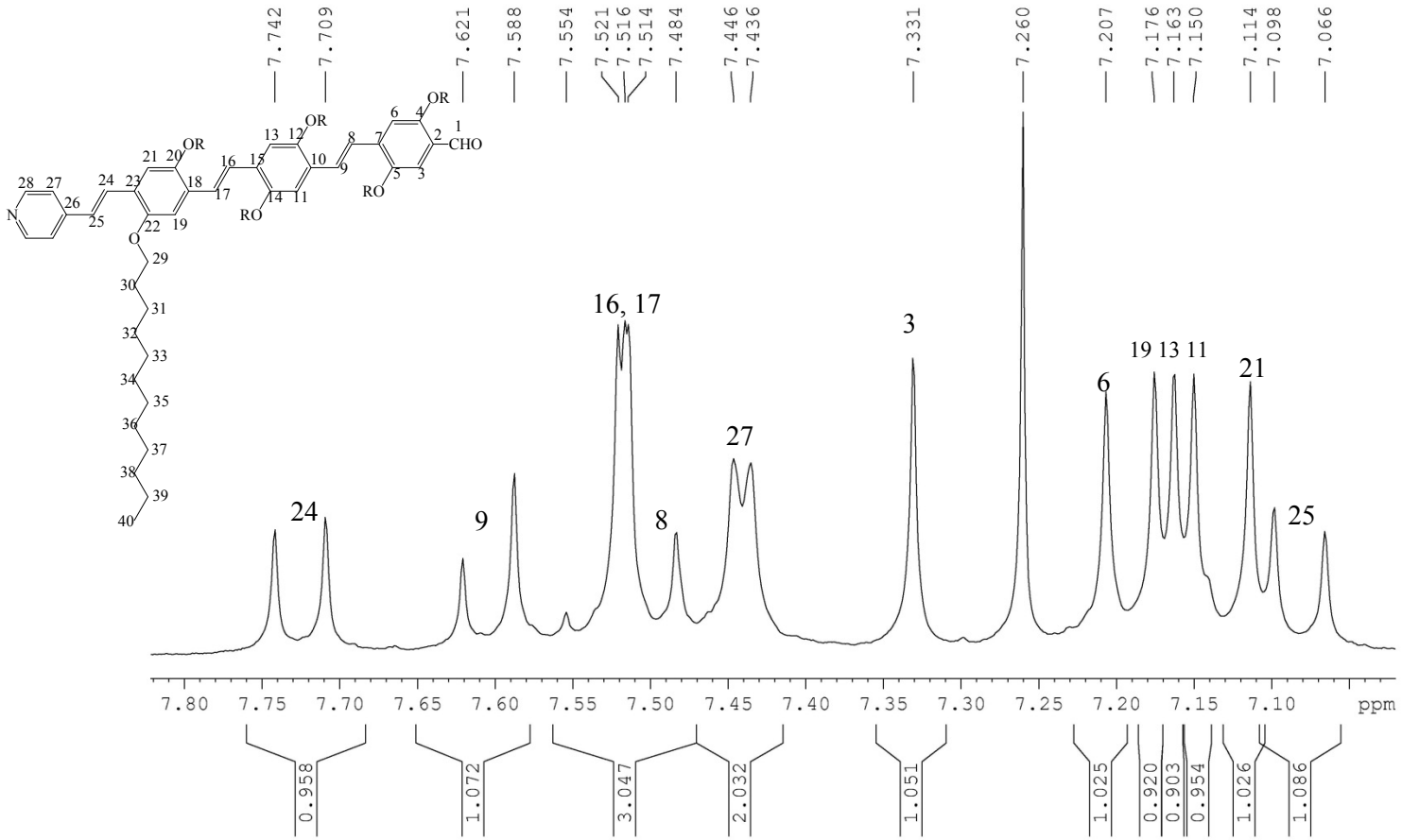


Figure S12b. ^{1}H-NMR spectrum in $CDCl_3$ of compound *E*-**5.**

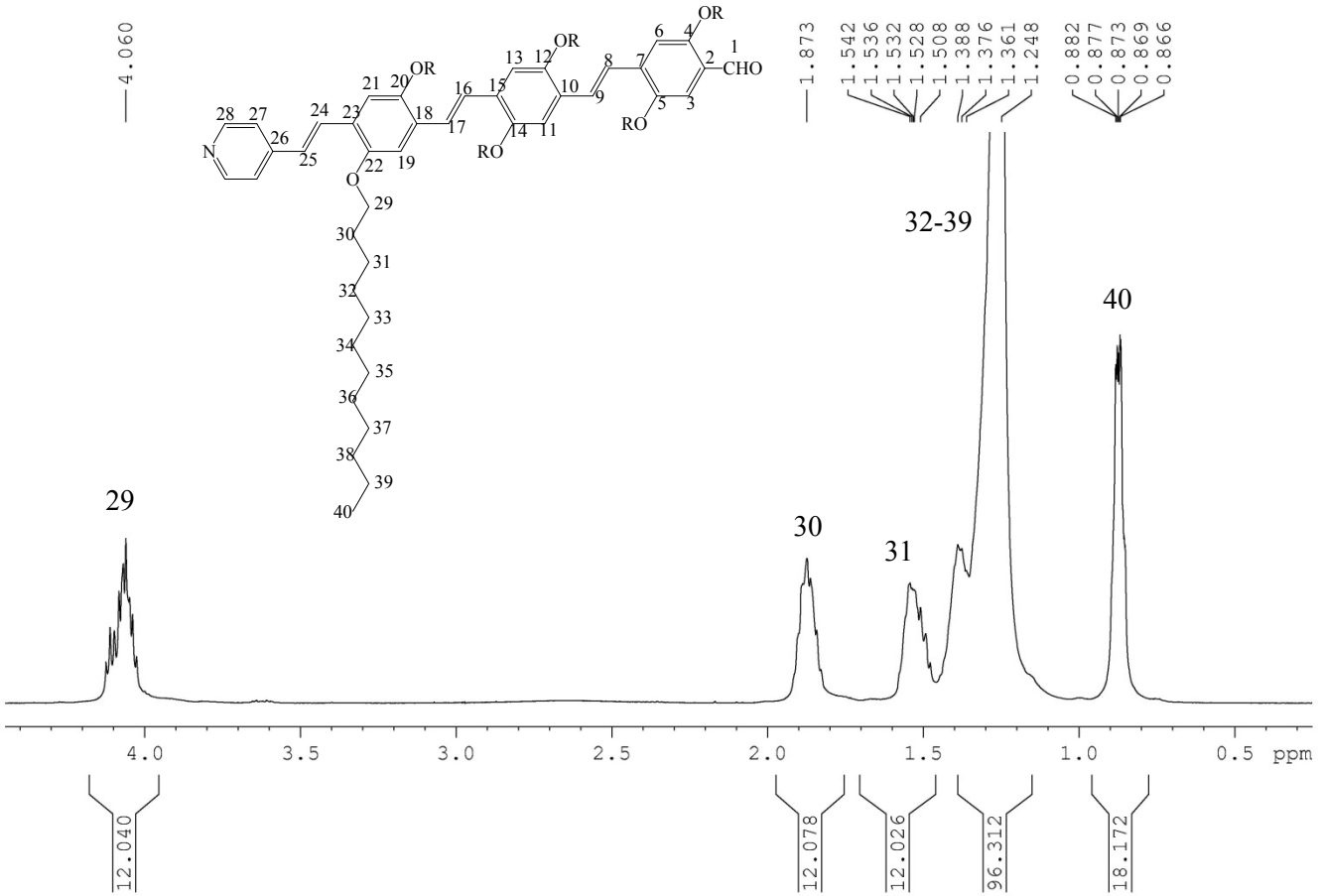


Figure S12c. ^{1}H-NMR spectrum in $CDCl_3$ of compound *E*-**5.**

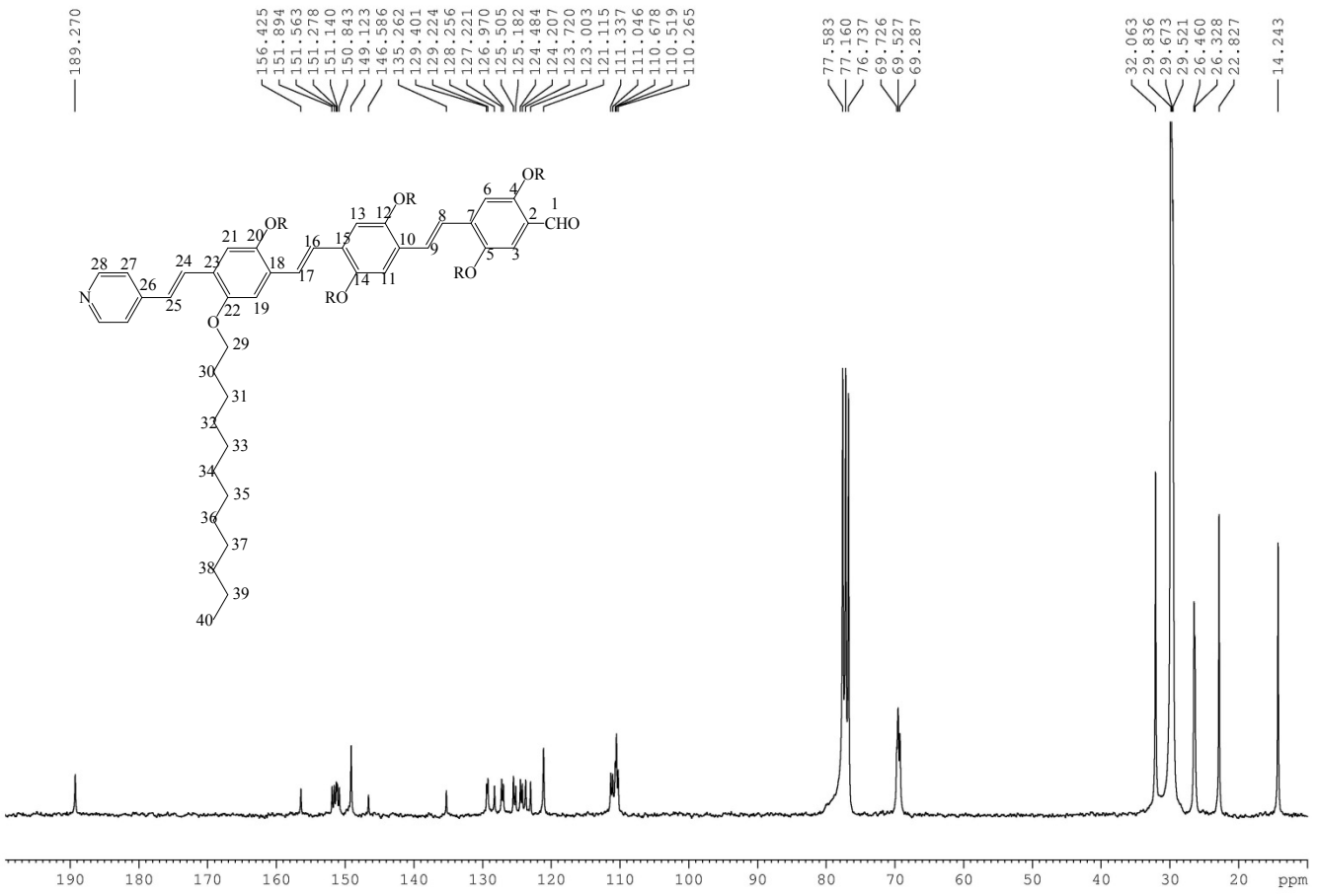


Figure S12d. ^{13}C-NMR spectrum in $CDCl_3$ of compound *E*-**5.**

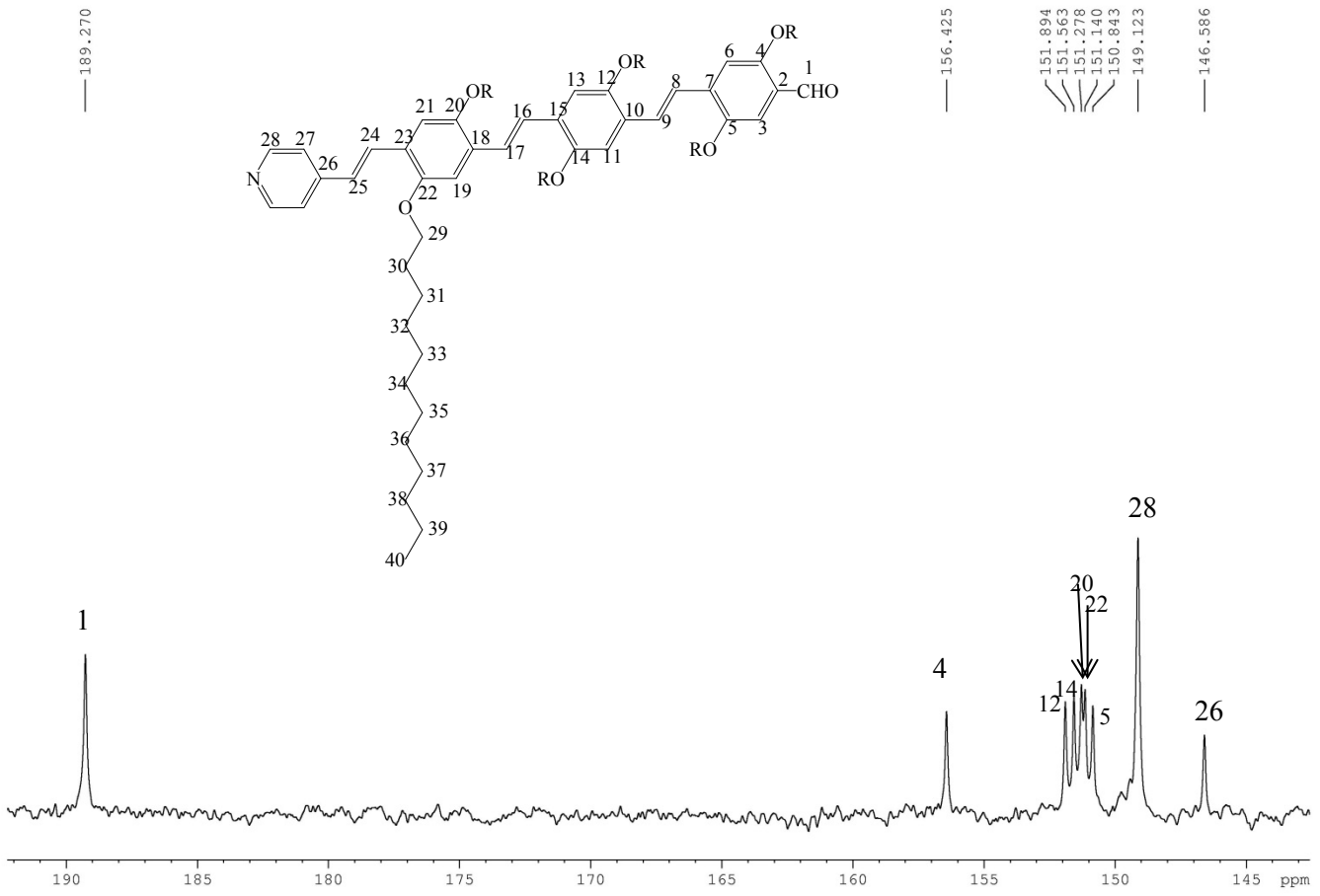


Figure S12e. ^{13}C-NMR spectrum in $CDCl_3$ of compound *E*-**5.**

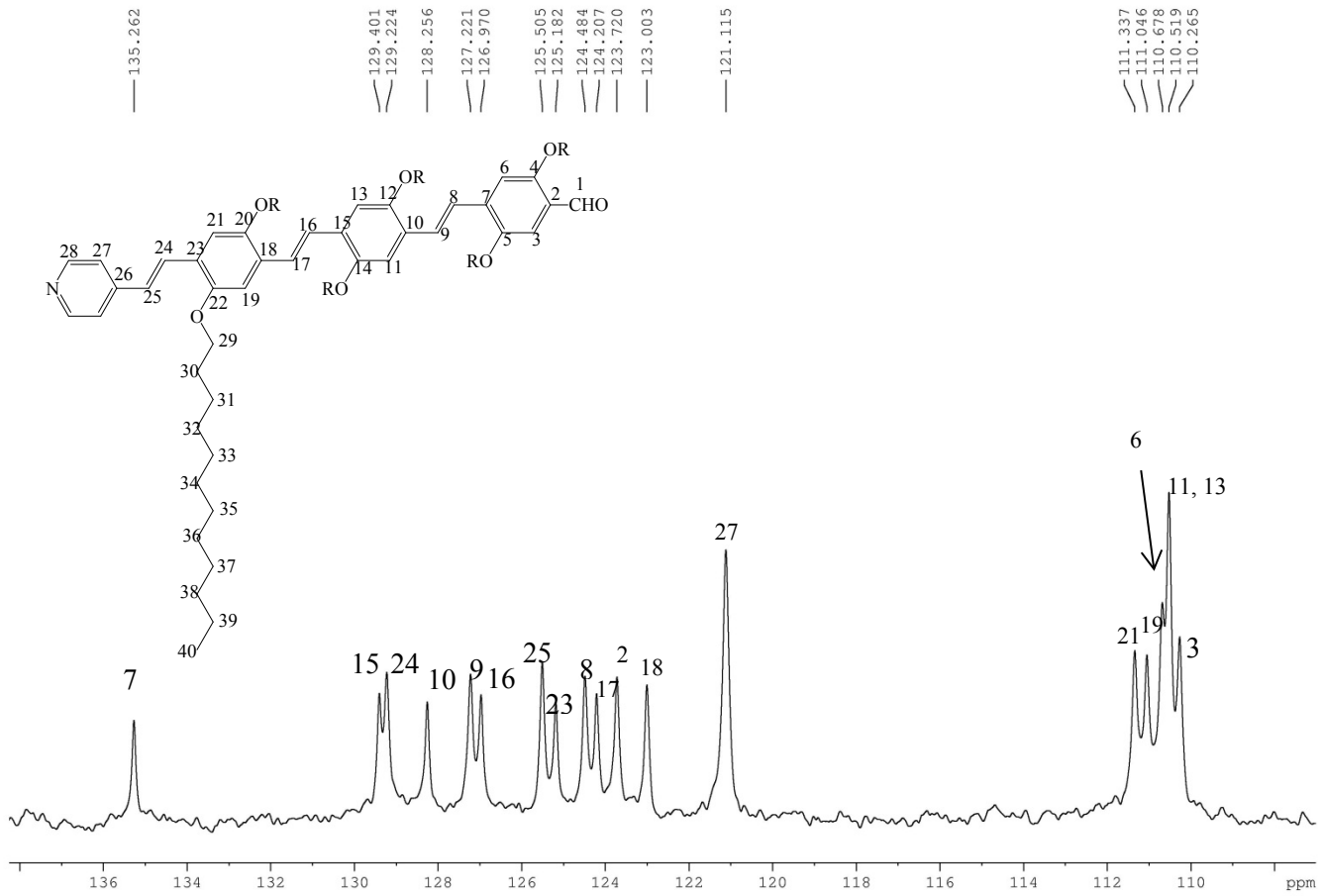


Figure S12f. ^{13}C-NMR spectrum in $CDCl_3$ of compound *E*-**5.**

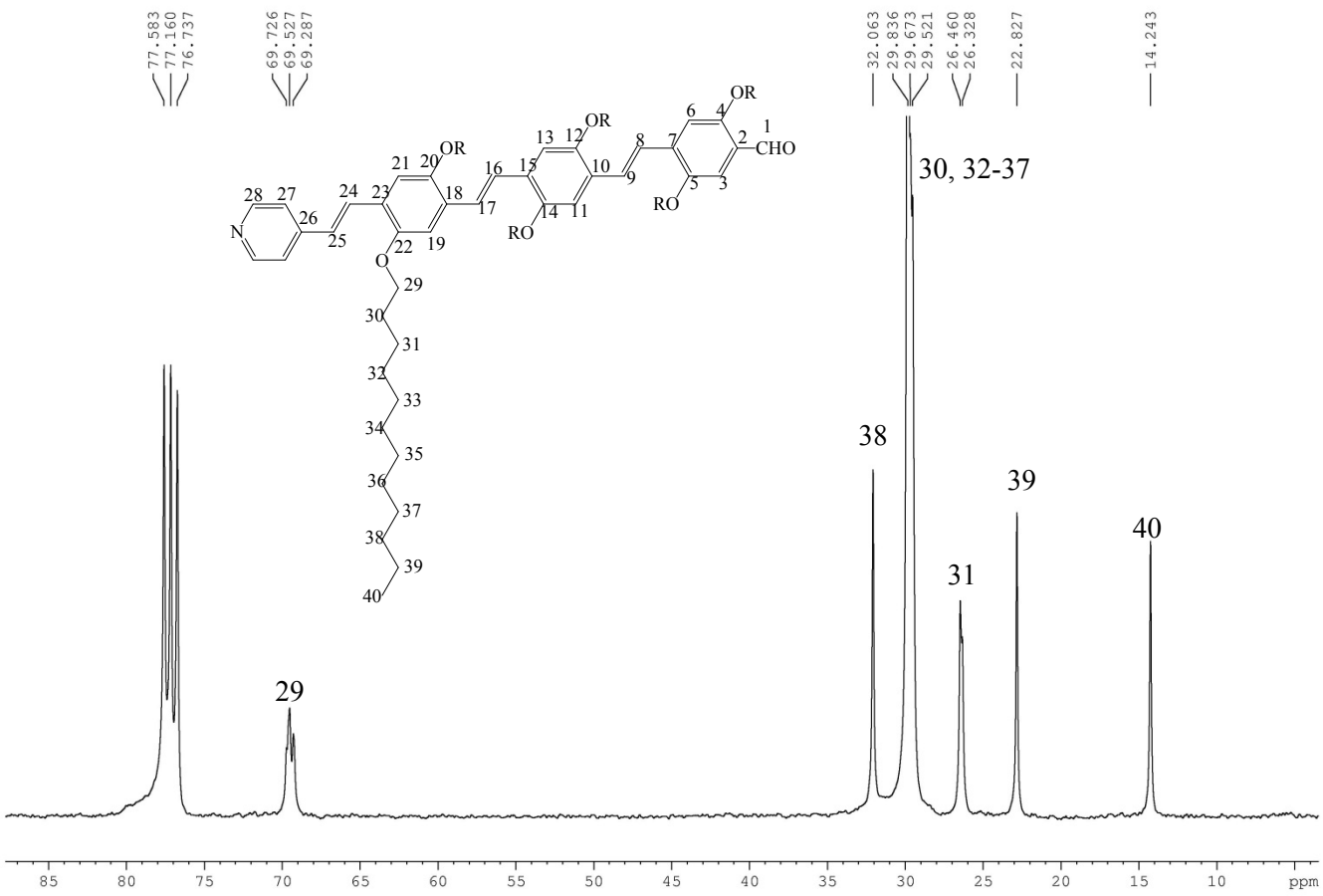


Figure S12g. ^{13}C-NMR spectrum in $CDCl_3$ of compound *E*-**5.**

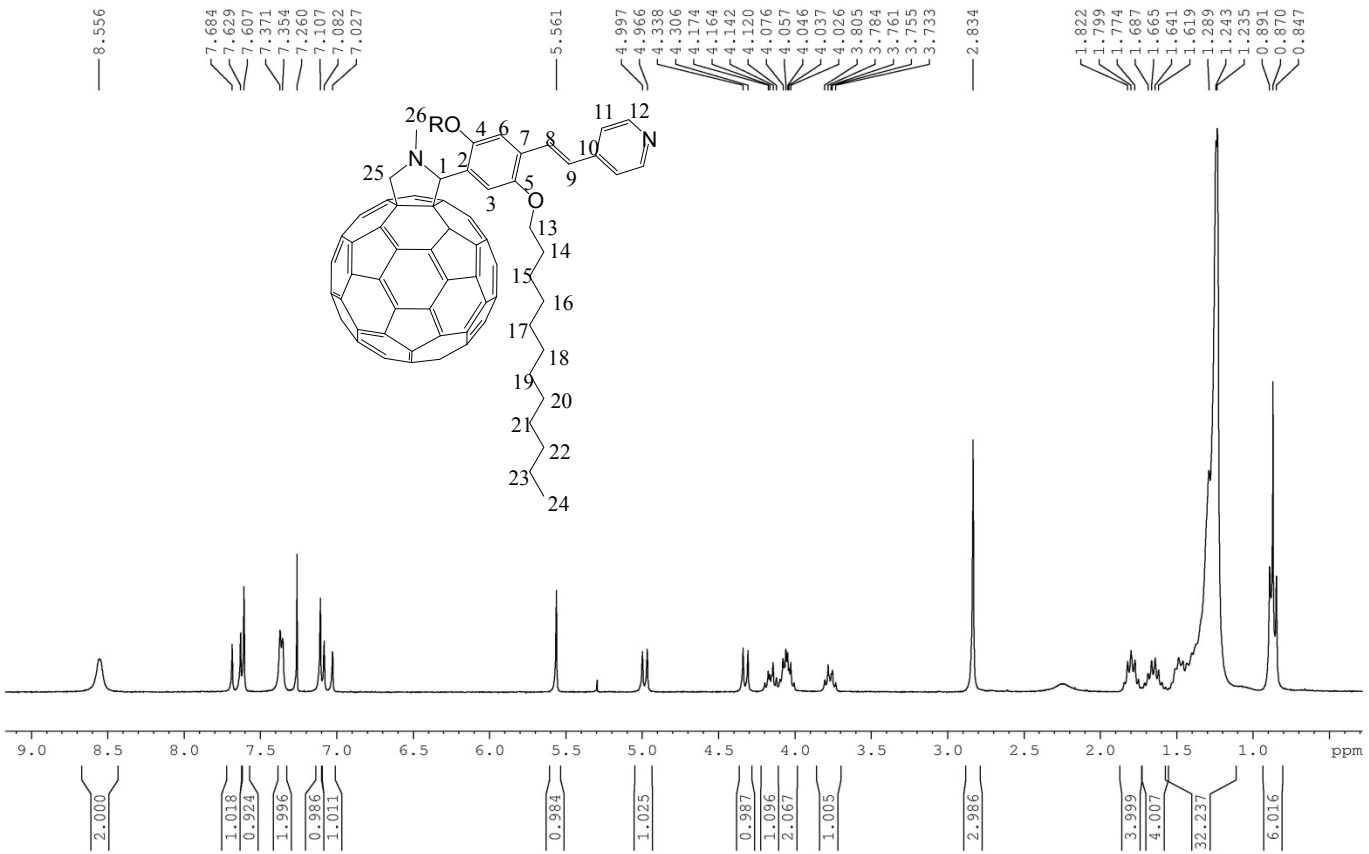


Figure S13a. ^{1}H-NMR spectrum in $CDCl_3$ of compound **C_{60}-PPV1-pyr.**

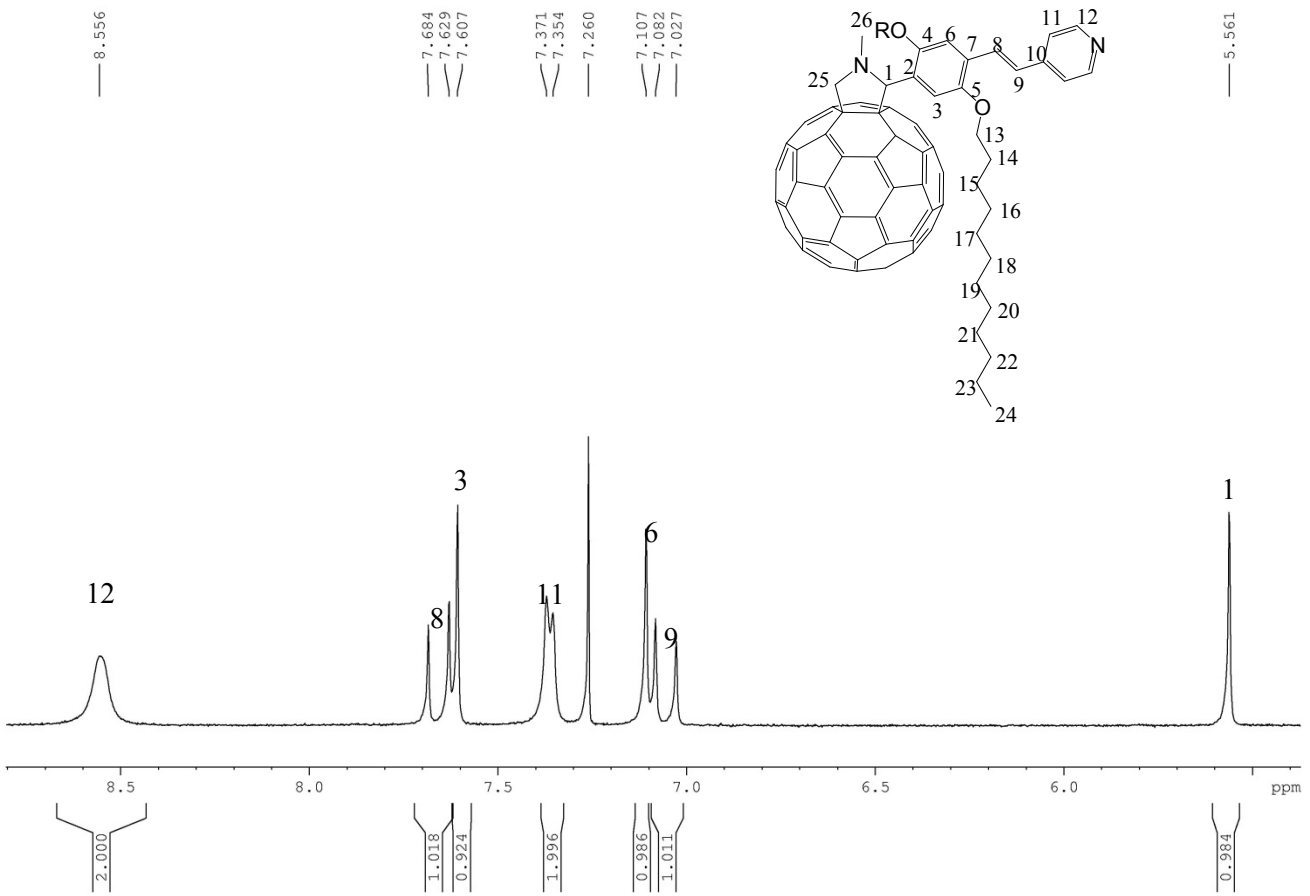


Figure S13b. ^{1}H-NMR spectrum in $CDCl_3$ of compound **C_{60}-PPV1-pyr.**

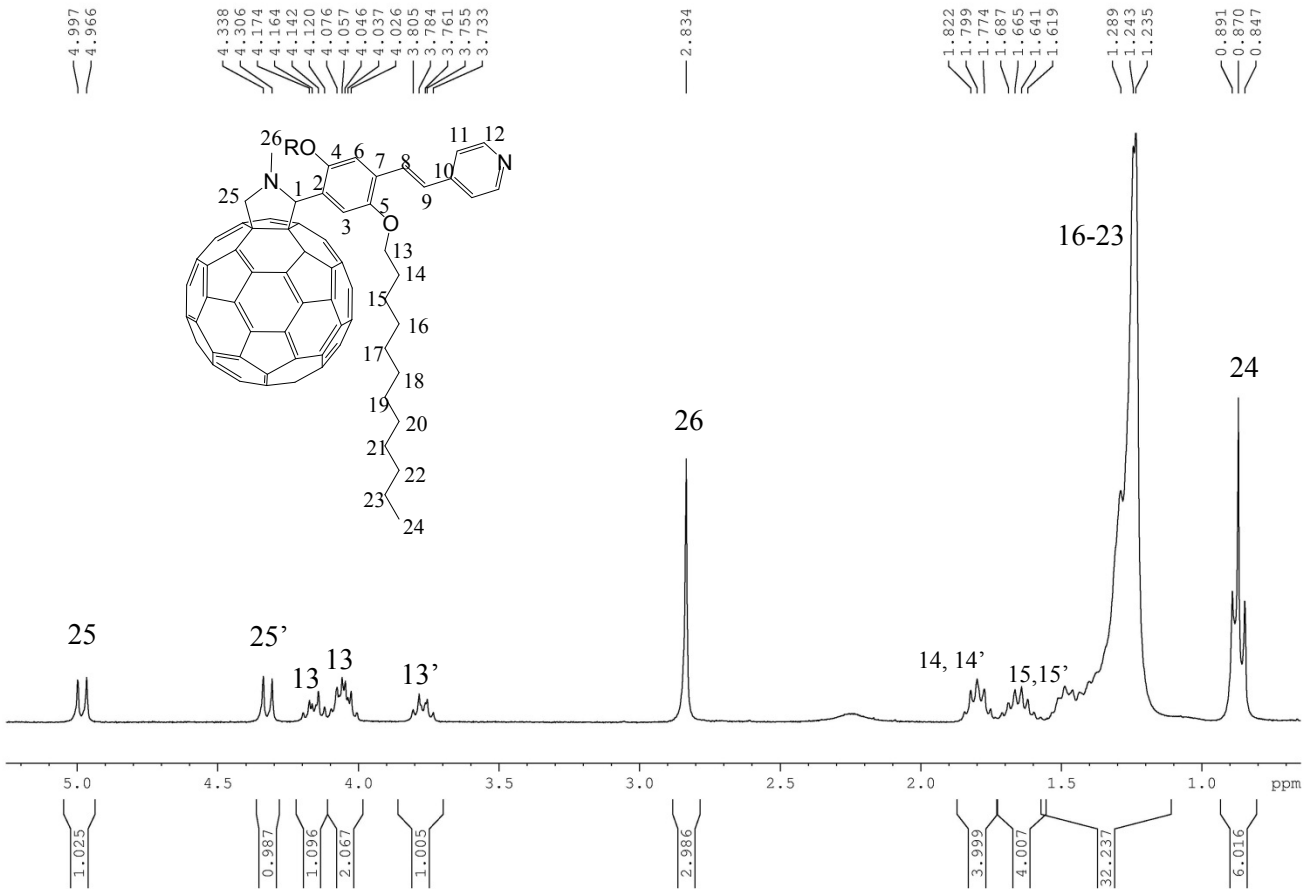


Figure S13c. ^{1}H-NMR spectrum in $CDCl_3$ of compound **C_{60}-PPV1-pyr.**

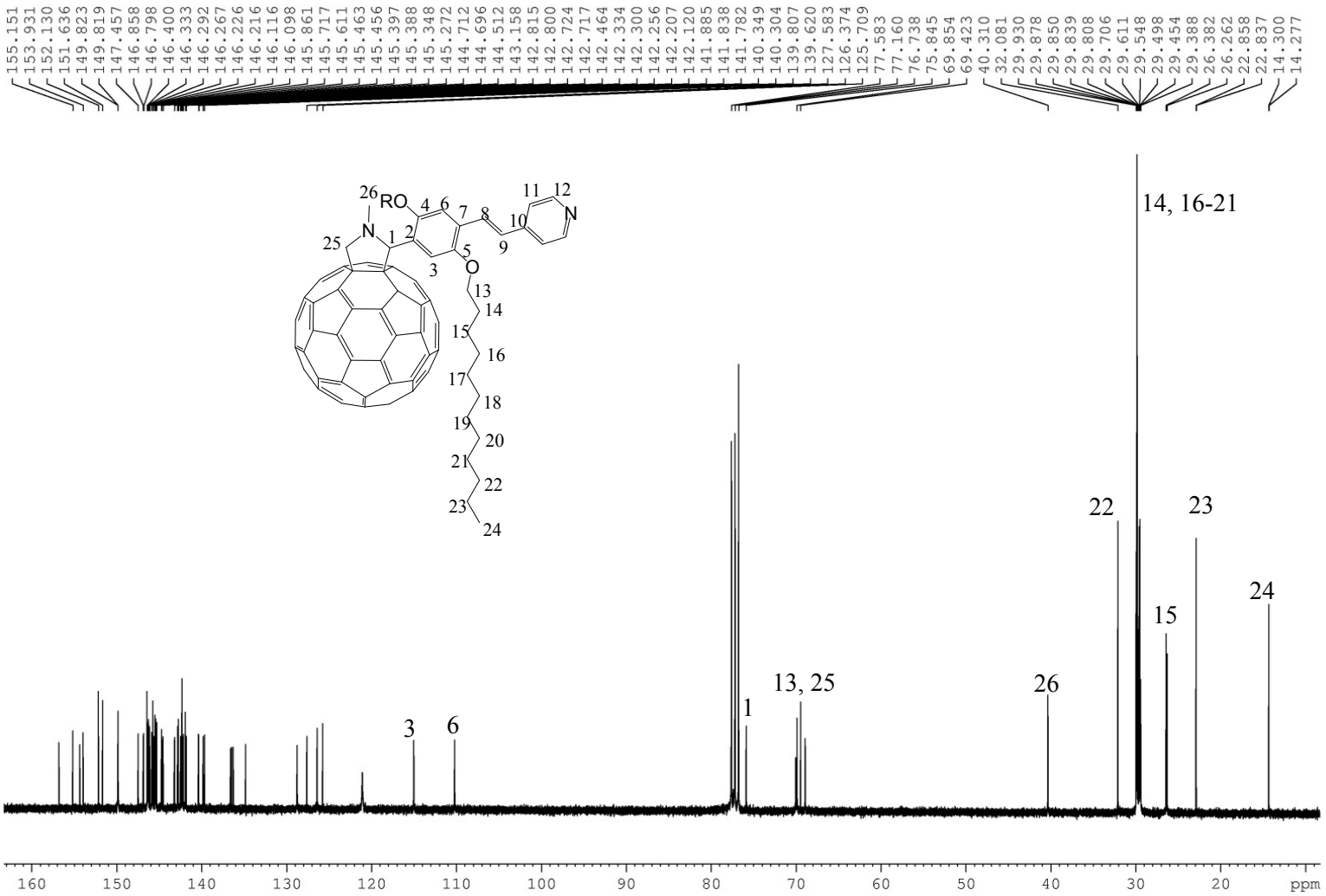


Figure S13d. ^{13}C-NMR spectrum in $CDCl_3$ of compound **C_{60}-PPV1-pyr.**

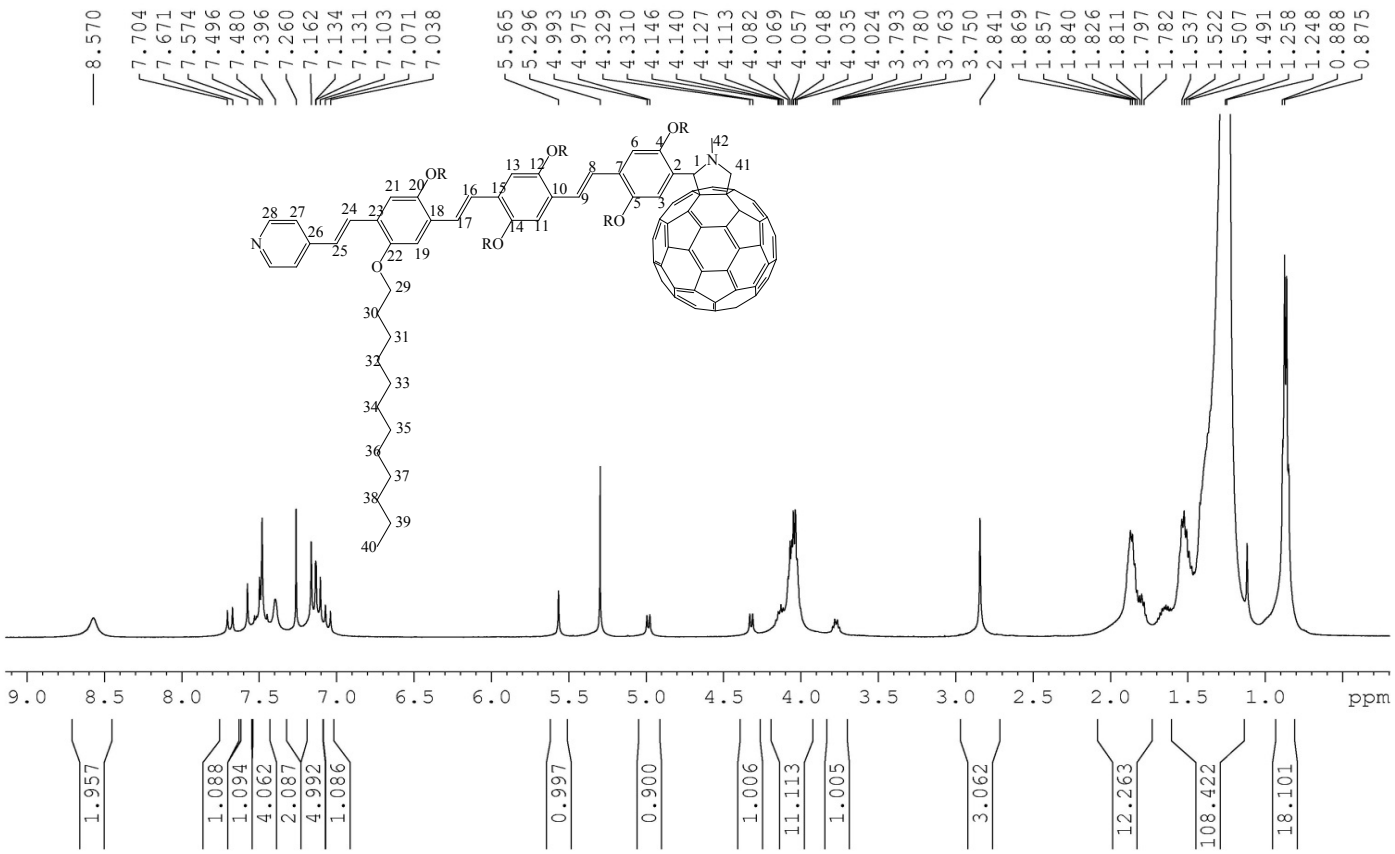


Figure S14a. ^{1}H-NMR spectrum in $CDCl_3$ of compound **C_{60}-PPV3-pyr.**

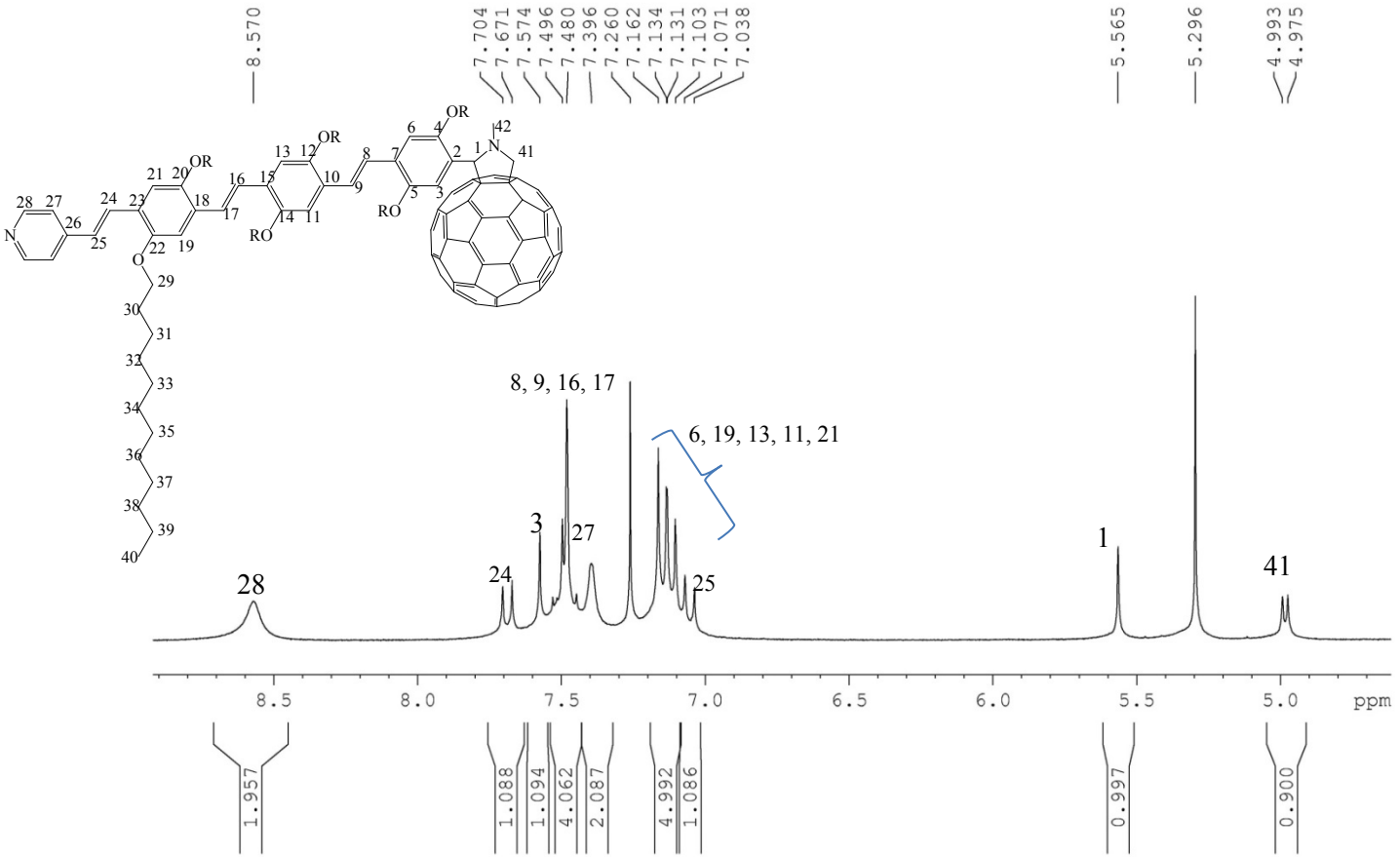


Figure S14b. ^{1}H-NMR spectrum in $CDCl_3$ of compound **C_{60}-PPV3-pyr.**

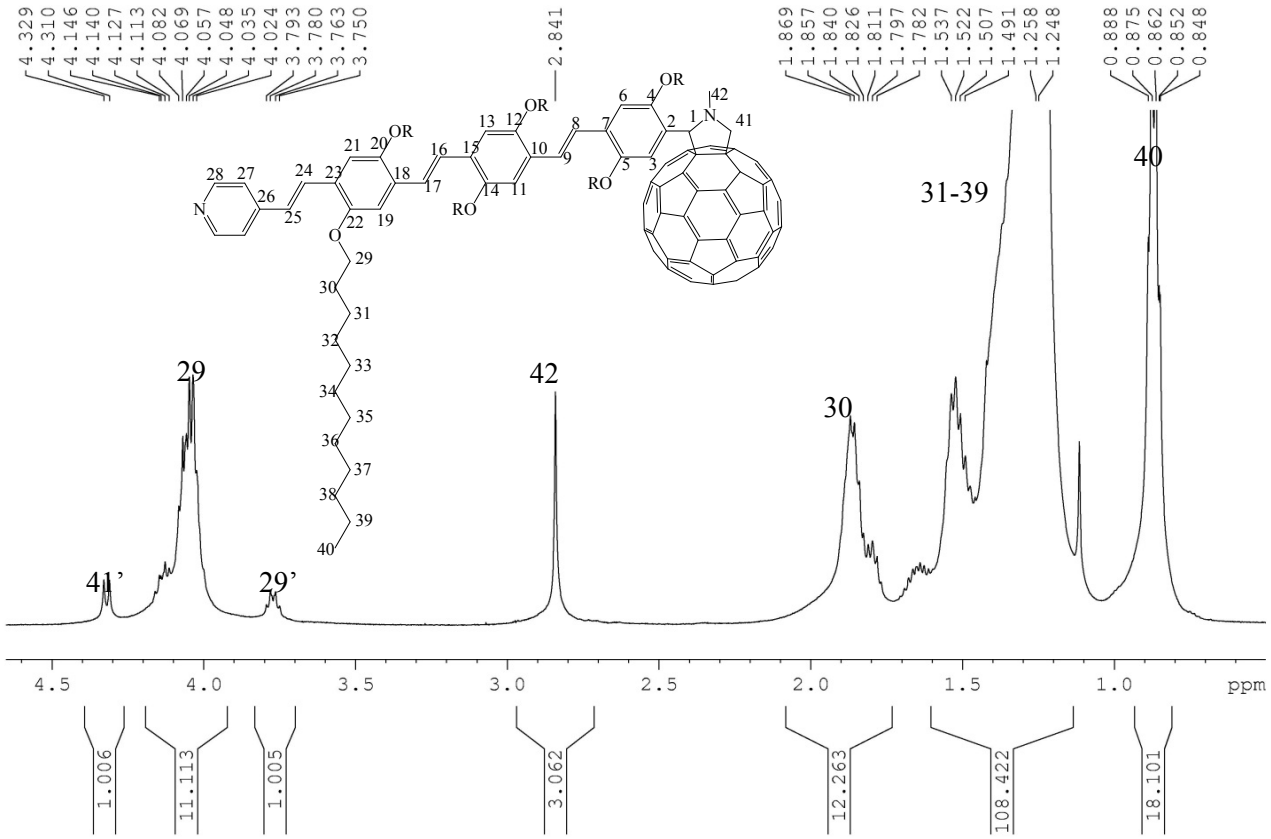


Figure S14c. ^{1}H-NMR spectrum in $CDCl_3$ of compound **C_{60}-PPV3-pyr.**

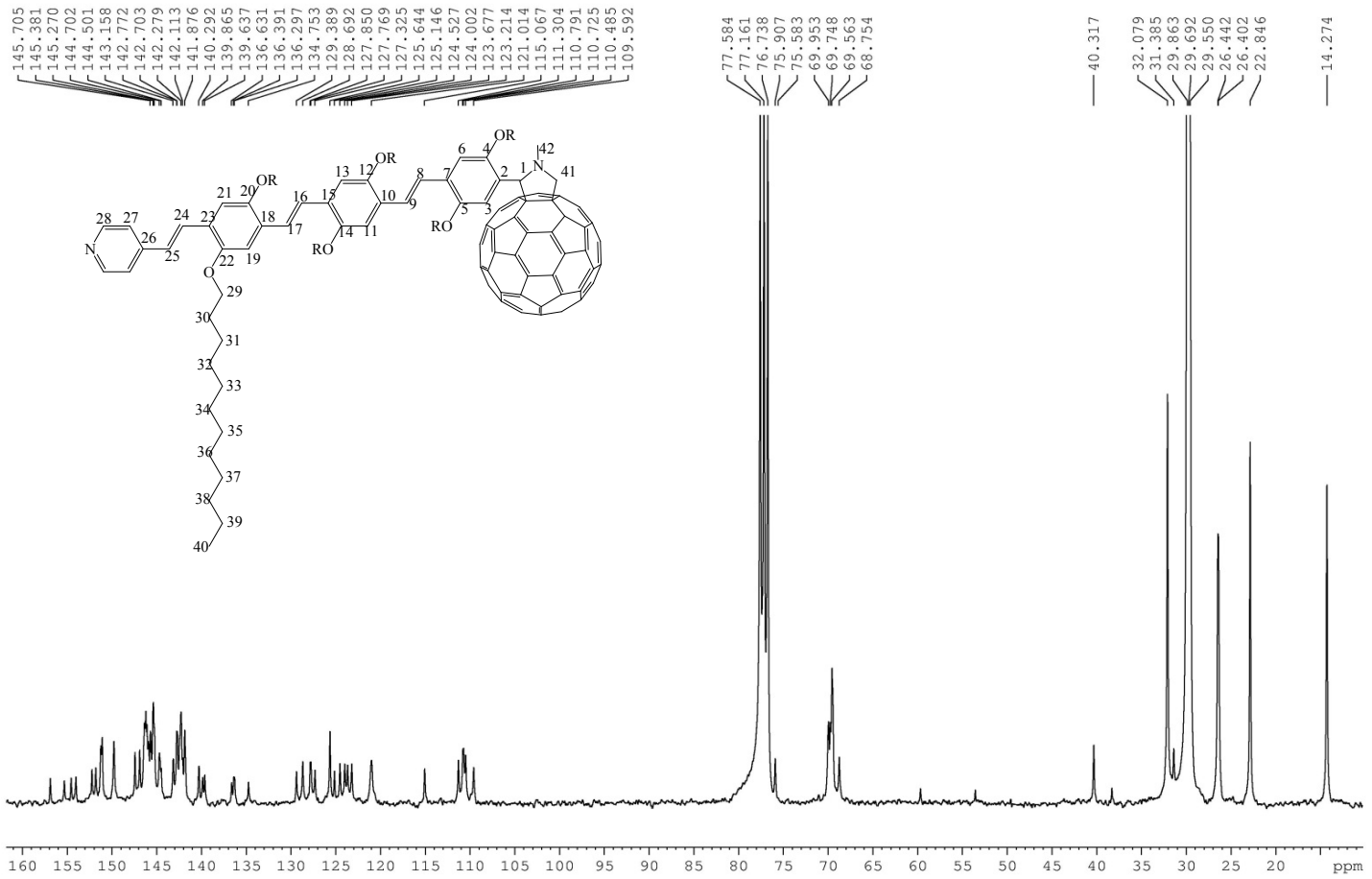


Figure S14d. ^{13}C-NMR spectrum in $CDCl_3$ of compound **C_{60}-PPV3-pyr.**

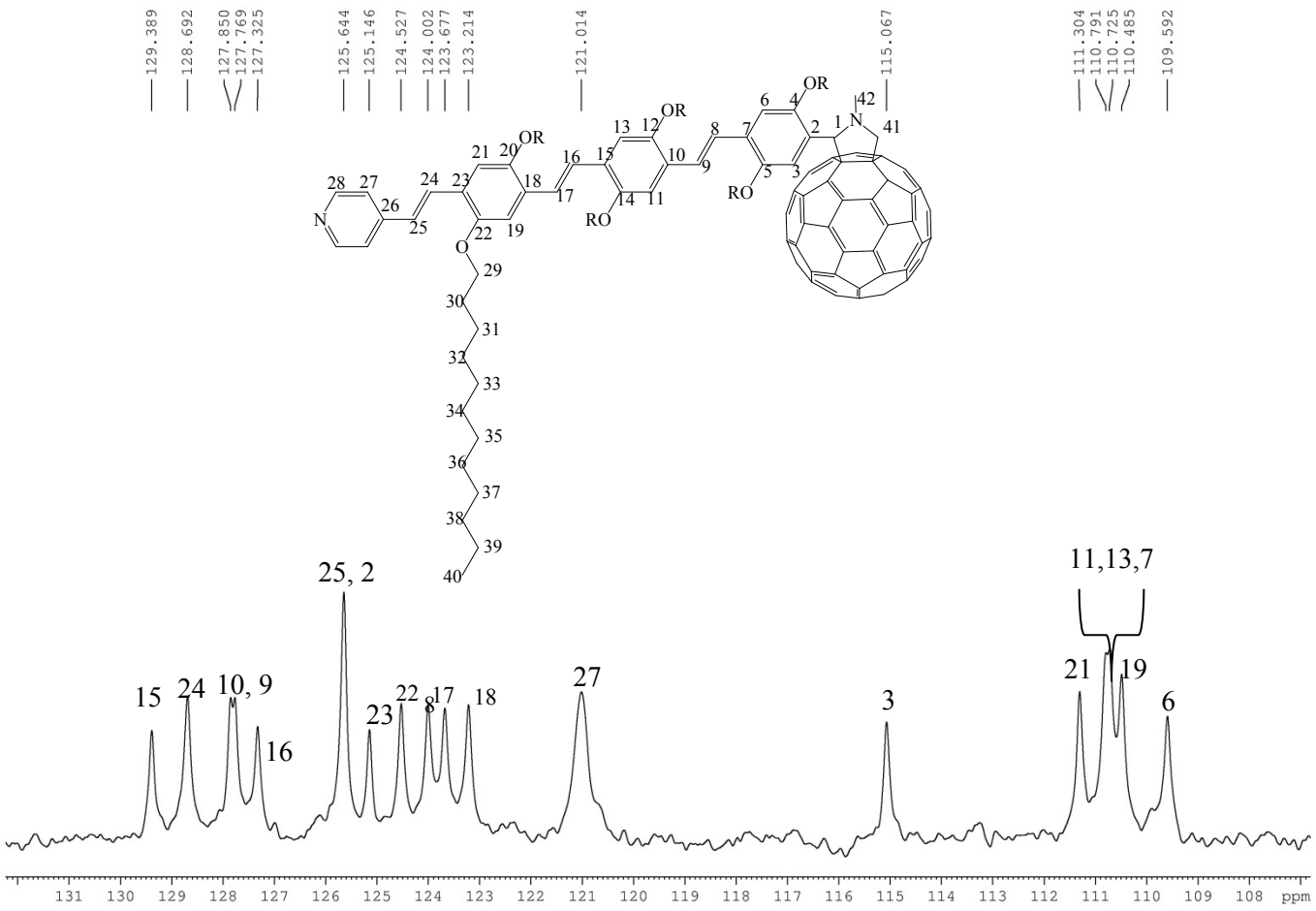


Figure S14e. ^{13}C-NMR spectrum in $CDCl_3$ of compound **C_{60}-PPV3-pyr.**

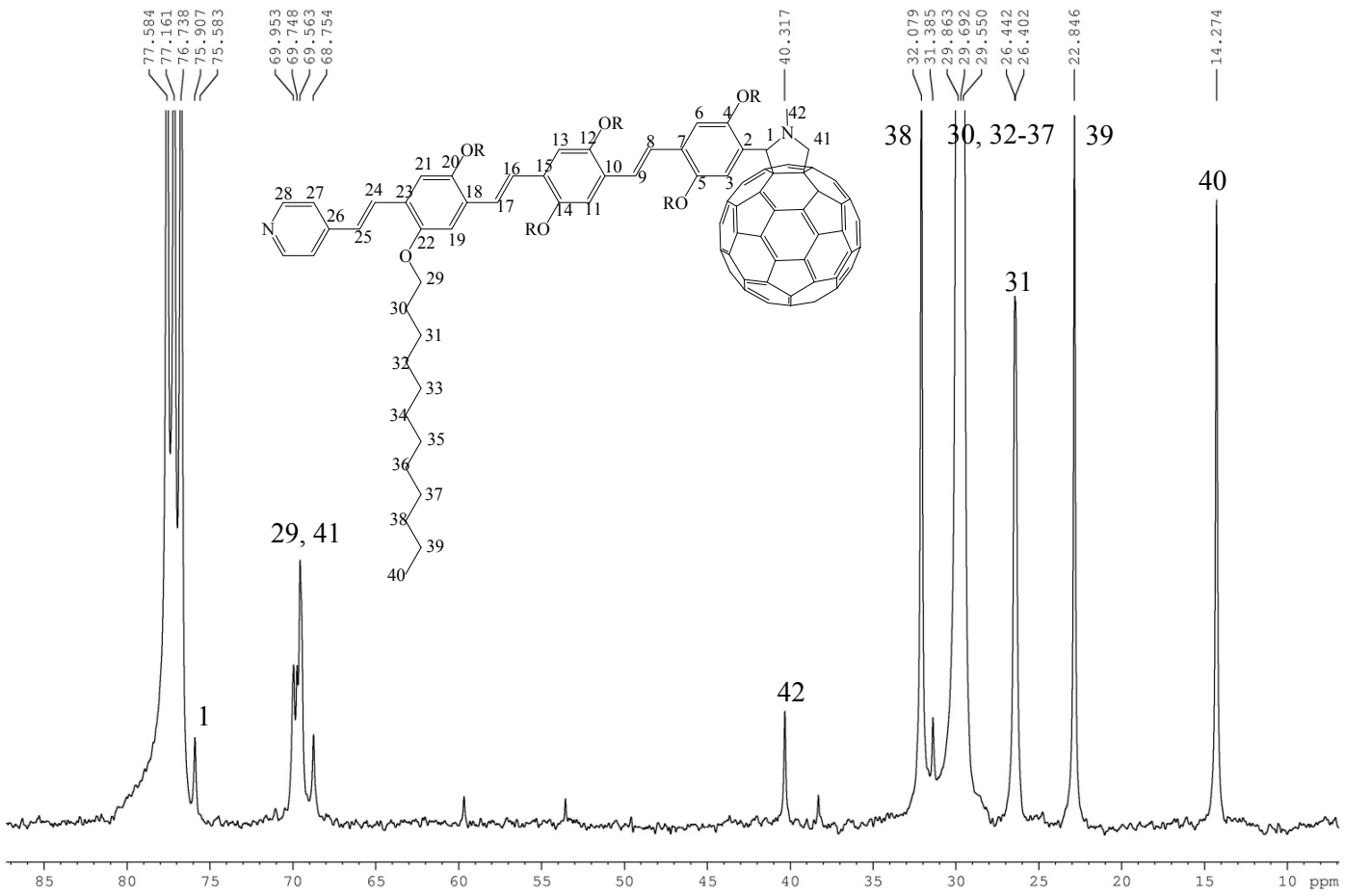


Figure S14f. ^{13}C-NMR spectrum in $CDCl_3$ of compound **C_{60}-PPV3-pyr.**