# Supplementary Information

## Core-Shell Magnetic Nanoparticles Deliver Singlet Oxygen for Mild Oxidations: Rechargeable, Removable, Reusable

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**Table of Contents**

## General

All chemicals and reaction solvents purchased from Sigma Aldrich, Acros Organics and ABCR were used without purification. Column chromatography purifications were performed with glass columns using Merck Silica gel 60 (particle size: 0.040-0.063 mm, 230-400 mesh ASTM) and reactions were monitored by thin layer chromatography (TLC) using precoated silica gel plates (Merck Silica Gel PF-254). Chromatography solvents (DCM, n-hexane, EtOAc) were purchased as technical grade and were purified employing fractional distillation before use. Anhydrous THF and toluene was used freshly after refluxing over Na in the presence of benzophenone under Ar. DMF was used after keeping it over activated 4A molecular sieves for 24 hours.

NMR spectra were recorded on Bruker Spectrospin Avance DPX 400 spectrometer (operating at 400 MHz for $^{1}H$ NMR and 100 MHz for $^{13}C$ NMR) using deuterated solvents ($CDCl_3$, DMSO-$d_6$) with tetramethylsilane (TMS) as internal standard purchased from Merck. Spin multiplicities are reported as following: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), dd (doublet of doublets), dt (doublet of triplets), td(triplet of doublets), m (multiplet), bs (broad signal). High Resolution Mass Spectroscopy (HRMS) experiments were done on an Agilent Technologies-6530 Accurate-Mass Q-TOF-LC/MS. Absorption and Emission measurements were acquired using Varian Cary-100 Spectrophotometer and Varian Eclipse Spectrofluorometer. Malvern NanoZS DLS was used for the determination of nanoparticle size distribution. Transmission Electron Microscopy images were recorded with FEI Technai G2F30 High-Resolution TEM on carbon grid. X-Ray Powder Diffractometry measurements were carried on PANalytical X'Pert Powder Diffractometer. Gas Chromatography Mass Spectroscopy (GCMS) experiments were performed on Agilent Technologies 7890A GC System with Agilent Technologies 5975C inert MSD with Triple-Axis Detector.

## Synthesis of Photosensitizer

Synthesis of compound **2-6** was done according to the literature procedure[50].

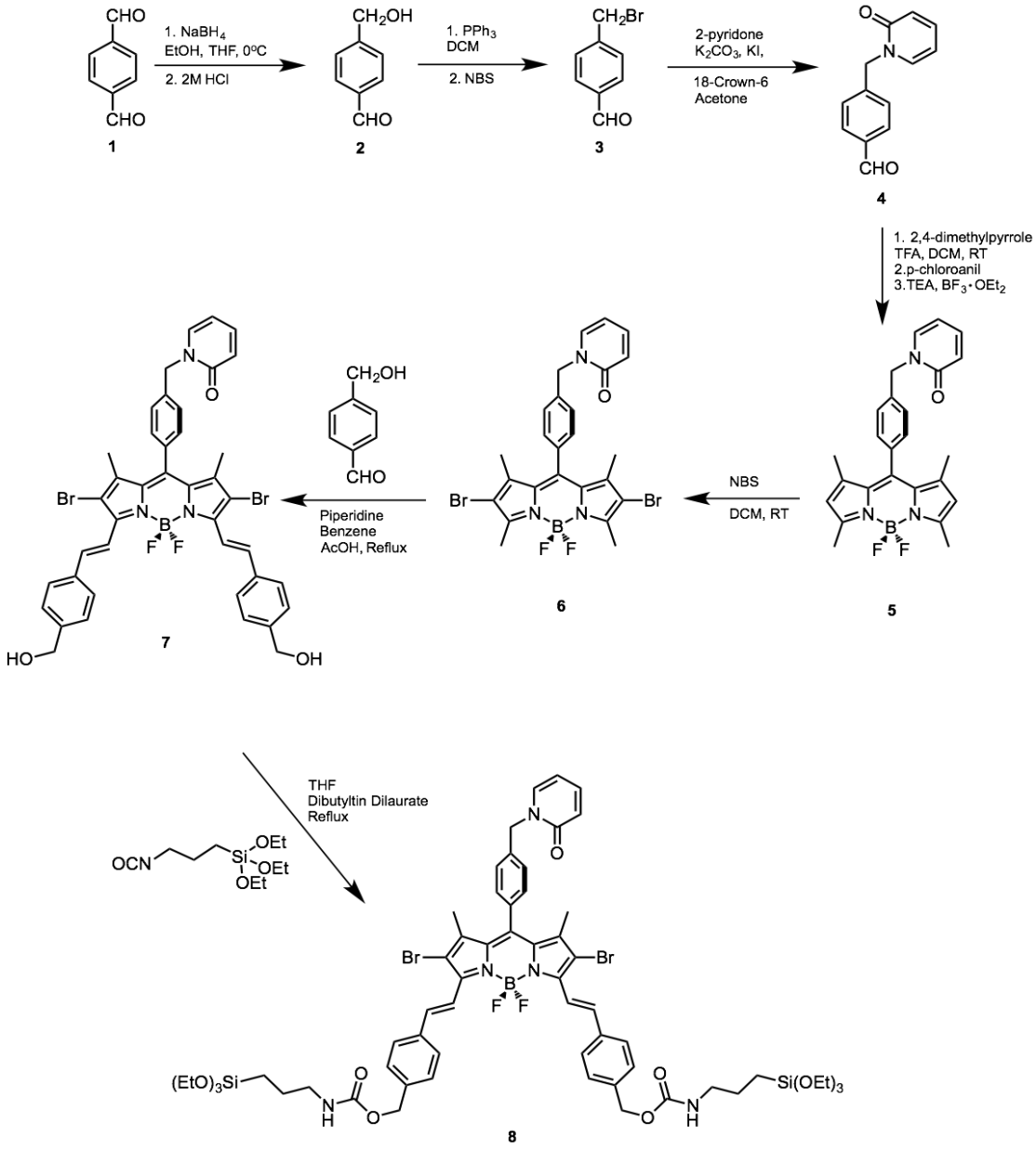



Figure S1: Synthesis scheme for the photosensitizer/storage module.

## Synthesis of 4-(hydroxymethyl) benzaldehyde (2)

Terephthalaldehyde (1.0 g, 7.46 mmol) is dissolved in 15 ml ethanol and 20 ml THF mixture. $NaBH_4$ (0.07 g, 1.85 mmol) is added in an ice bath slowly and reaction is kept in 0ºC for further 6 hours. Then, pH of the mixture is adjusted to 5 by addition of 2 M HCl solution. The reaction mixture is then extracted with EtOAc and water. Organic phases are combined and dried over anhydrous $Na_2SO_4$. Solvent is evaporated in vacuo and the product is purified by silica gel column chromatography using DCM/MeOH (98:2, v/v) as the eluent. Compound **2** was obtained as colorless oil (0.40 g, 40%).

$^1$H NMR (400 MHz, $CDCl_3$): δ 9.92 (s, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 4.74 (s, 2H), 3.25 (s, 1H).

$^{13}$C NMR (100 MHz, $CDCl_3$, δ ppm): 192.4, 148.2, 135.5, 130.0, 126.9, 64.3.

MS (TOF-ESI): m/z calculated for $C_8H_8O_2$ $[M-H]^-$: 135.04515, found for $[M-H]^-$: 135.04782, Δ= -19.75 ppm.

## Synthesis of 4-(bromomethyl) benzaldehyde (3)

Compound **2** (0.8 g, 5.87 mmol) and triphenyl phosphine (3.11 g, 11.89 mmol) are dissolved in 50 mL DCM at room temperature. N-bromosuccinimide (2.00 g, 11.43 mmol) is added portion wise. Reaction is kept at room temperature for overnight. Then, the reaction mixture is extracted with DCM and water. Organic phases are combined and dried over anhydrous $Na_2SO_4$. Solvent is evaporated in vacuo and the product is purified by silica gel column chromatography using EtOAc/Hexane (1:1, v/v) as the eluent. Compound **3** was obtained as white powder (0.60 g, 38%).

$^1$H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 7.86 (d, J = 8.1 Hz, 2H), 7.55 (d, J = 8.1 Hz, 2H), 4.51 (s, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$, δ ppm): 191.4, 144.2, 136.2, 130.1, 129.7, 31.9.

## Synthesis of Compound 4

Compound **3** (0.50 mg, 2.51 mmol), 2-pyridone (0.256 mg, 2.69 mmol) and potassium carbonate (1.25 g, 9.04 mmol) is dissolved in 50 ml acetone. 18-crown-6 and potassium iodide is added catalytic amount. Reaction is stirred at room temperature for overnight. The solids are filtered off and the eluent is evaporated in vacuo and the product is purified by silica gel column chromatography using DCM/Hexane (1:1, v/v) as the eluent. Compound **4** was obtained as white powder (1.2 g, 40%).

$^{1}$H NMR (400 MHz, $CDCl_3$): δ 10.01 (s, 1H), 7.87 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 7.41-7.34 (m, 1H), 7.30 (dd, J12=6.8Hz, J23=2.0 Hz, 1H), 6.66 (d, J=9.2Hz, 1H), 6.21 (dt, J12=6.8Hz, J23=1.4 Hz, 1H), 5.23 (s, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$, δ ppm): 191.7, 162.6, 143.1, 139.9, 137.4, 135.9, 130.2, 128.3, 121.4, 106.7, 52.0.

MS (TOF-ESI): m/z calculated for $C_{13}H_{11}NO_2$ $[M+H]^+$: 214.08626, found for $[M+H]^+$: 214.08808, Δ= -8.52 ppm.

## Synthesis of Compound 5

Compound **4** (0.50 g, 2.35 mmol) and 2,4-dimethylpyrrole (0.53 ml, 5.15 mmol) are dissolved in DCM, which is degassed by Ar purging for 30 mins. Two drops of trifluoroacetic acid was added dropwise. The red solution is stirred overnight in the dark at room temperature. p-Chloranil (0.58 g, 2.35 mmol) is added and reaction mixture is stirred further for one hour. Triethylamine (5.0 mL) and BF3•OEt2 (5.0 mL) are added dropwise to the reaction mixture consecutively and the resulting solution is stirred for one additional hour. Then, the reaction mixture is extracted with DCM and water. Organic phases are combined and dried over anhydrous $Na_2SO_4$. Solvent is evaporated in vacuo and the product is purified by silica gel column chromatography using EtOAc as the eluent. Compound **5** was obtained as red powder (0.90 g, 37%).

$^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 7.8 Hz, 2H), 7.36-7.40 (m, 1H), 7.27-7.31 (m, 3H), 6.68 (d, J = 9.2 Hz, 1H), 6.21 (t, J = 6.7 Hz, 1H), 5.99 (s, 2H), 5.26 (s, 2H), 2.56 (s, 6H), 1.37 (s, 6H).

$^{13}$C NMR (100 MHz, $CDCl_3$, δ ppm): 162.6, 155.6, 143.0, 141.0, 139.6, 137.6, 137.0, 134.8, 131.4, 128.62, 128.57, 121.4, 121.3, 106.6, 51.6, 14.6, 14.4.

MS (TOF-ESI): m/z calculated for $C_{25}H_{24}BF_2N_3O$ $[M-H]^-$: 429.19440, found for $[M-H]^-$: 429.19033, Δ= 9.49 ppm.

## Synthesis of Compound 6

Compound **5** (0.10 g, 0.23 mmol) is dissolved in 20 mL of DCM. N-bromosuccinimide (0.10 g, 0.56 mmol) is dissolved in minimum volume of DCM and added dropwise to reaction mixture at room temperature. The reaction is stirred for 10 mins and extracted with DCM and water. Organic phases are combined and dried over anhydrous $Na_2SO_4$. Solvent is evaporated in vacuo and the product is purified by silica gel column chromatography using EtOAc as the eluent. Compound **6** was obtained as red powder (0.100 g, 75%).

$^{1}$H NMR (400 MHz, $CDCl_3$): 7.46 (d, J=7.9 Hz, 2H), 7.37-7.42 (m, 1H), 7.32 (dd, J12=6.8 Hz, J23=2.1 Hz, 1H), 7.26 (d, J=7.9Hz ,2H), 6.70 (d, J=9.2Hz, 1H),6.24 (t, J=6.8Hz, 1H), 5.28 (s,2H), 2.61 (s, 6H), 1.36 (s, 6H).

$^{13}$C NMR (100 MHz, $CDCl_3$, δ ppm): 162.7, 154.1, 150.0, 141.4, 140.5, 139.9, 138.3, 137.0, 134.0, 128.8, 128.4, 121.4, 106.8, 51.7, 13.8, 13.7.

MS (TOF-ESI): m/z calculated for $C_{25}H_{22}BBr_2F_2N_3O$ $[M-H]^-$: 585.01543, found for $[M-H]^-$: 585.00912, Δ= 10.79 ppm.

## Synthesis of Compound 7

Compound **6** (0.09 g, 0.16 mmol) and 4-(hydroxymethyl)-benzaldehyde (**2**) (0.04 mg, 0.32 mmol) are dissolved in benzene (25 ml) in a round-bottomed flask. Glacial acetic

acid (0.20 ml) and piperidine (0.20 ml) are added to the reaction mixture. Dean-Stark apparatus is placed on the round-bottomed flask and reaction mixture is refluxed at 100ºC until all the starting material was consumed which is confirmed by TLC using DCM as the eluent. The reaction was diluted with DCM and extracted with water. Organic phases are combined and dried over anhydrous $Na_2SO_4$. Solvent is evaporated in vacuo and the product is purified by silica gel column chromatography with gradient elution from DCM to DCM/MeOH (98:2, v/v). Compound **7** was obtained as naive waxy (0.07 g, 52%).

$^1$H NMR (400 MHz, DMSO-$d_6$): δ 8.08 (d, J=16.0 Hz, 2H), 7.83 (d, J= 6.6 Hz, 2H) 7.70-7.86 (m, 5H), 7.40-7.50 (m, 9H), 6.49 (d, J= 9.3 Hz, 1H), 6.31 (t, J= 6.2 Hz, 1H), 5.32 (t, J= 5.1 Hz, 2H), 5.26 (s, 2H), 4.57 (s, 4H), 1.33 (s, 6H).

$^{13}$C NMR (100 MHz, DMSO-$d_6$) δ ppm): 162.0, 148.0, 145.3, 141.8, 140.9, 140.8, 139.7, 139.5, 139.4, 134.9, 133.2, 132.2, 128.9, 127.7, 127.6, 125.4, 120.4, 117.1, 110.4, 106.2, 63.0, 51.3, 13.9.

MS (TOF-ESI): m/z calculated for $C_{41}H_{34}BBr_2F_2N_3O_3$ $[M+Na]^+$: 845.09566, found for $[M+Na]^+$: 845.09677, Δ= -1.32 ppm.

## Synthesis of Compound 8

Compound **7** (0.10 g, 0.12 mmol) is dissolved in freshly distilled THF in an oven-dried round-bottomed flask. 3-(Triethoxysilyl)propyl isocyanate (64 µl, 0.26 mmol) and dibutyltin dilaurate (5 µl, 0.008 mmol) is added to the reaction mixture and the reaction mixture was refluxed at 70ºC overnight. Solvent is evaporated in vacuo and the product is purified by silica gel column chromatography with gradient elution from DCM to DCM/MeOH (98:2, v/v). Compound **8** was obtained as naive naive waxy (0.07 g, 52%).

$^1$H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, J=16.6 Hz, 2H), 7.74 (d, J=16.6 Hz, 2H), 7.66 (d, J= 8.0 Hz, 4H), 7.47 (d, J= 8.3, 2H), 7.43 (d, J=8.0, 4H), 7.37-7.41 (m, 1H), 7.33-7.34 (m, 1H), 7.31 (d, J= 8.3, 2H), 6.69 (dt, J12= 9.2 Hz, J23= 0.6 Hz, 1H), 6.24 (td, J12= 6.7 Hz, J23= 1.4 Hz, 1H), 5.29 (s, 2H), 5.14 (s, 4H), 3.84 (q, J= 7.0 Hz, 12H), 3.24 (q, J= 6.6 Hz, 4H), 1.67 (quintet, J= 7.4 Hz, 4H), 1.42 (s, 6H), 1.24 (t, J= 7.0 Hz, 18H) 0.66 (t, J= 8.1 Hz, 4H).

$^{13}C$ NMR (100 MHz, $CDCl_3$, δ ppm): 156.3, 148.6, 143.9, 141.3, 139.7, 139.1, 139.0, 138.4, 138.0, 137.0, 136.6, 134.4, 132.2, 128.8, 128.5, 127.8, 127.3, 121.6, 118.3, 110.6, 106.6, 66.2, 58.5, 51.6, 43.5, 23.3, 18.3, 13.9, 7.6.

MS (TOF-ESI): m/z calculated for $C_{61}H_{76}BBr_2F_2N_5O_{11}Si_2$ $[M+Na]^+$: 1339.34363, found for $[M+Na]^+$ : 1339.33954, Δ= 3.05 ppm.

## Preparation of SPIONs

### Synthesis of Iron Oxide Nanoparticles (9)


$FeCl_2 \cdot 4H_2O$ (2.15 g, 0.01 mol) and $FeCl_3 \cdot 6H_2O$ (5.84 g, 0.02 mol) are dissolved in argon bubbled deionized water (200 mL) at 90°C under mechanical stirring. Aqueous ammonia (25% $NH_3$ in water, 7.5 mL) solution is added to the reaction medium. Instant color change from orange to black indicated the formation of iron oxide nanoparticles. Reaction medium is kept at that temperature for 30 mins. Iron oxide nanoparticles are collected with neodymium magnet and washed three times with deionized water and ethanol. At the final stage iron oxide nanoparticles are dried under argon atmosphere for further functionalization.

### Synthesis of Silica coated Iron Oxide Nanoparticles (9s)


Freshly prepared iron oxide nanoparticles (2g) are dispersed in water (60mL), ethanol (240mL) and ammonia (25% $NH_3$ in water, 7.5 mL) containing mixture with ultra-

sonication for 30 mins at room temperature. To this dispersion is added tetraethyl orthosilicate (TEOS) (1.6 mL, 1.5g, 0.0072 mol). This mixture firstly ultra-sonicated for 30 mins then mechanically stirred for 12 hours at room temperature. The silica coated iron oxide nanoparticles are separated with neodymium magnet and washed 3 times with water and DMF. After this washing process, nanoparticles are immersed in HCl (4M) for 30 minutes to dissolve unreacted iron oxide nanoparticles. The coated nanoparticles are separated from HCl by washing with deionized water and separating with neodymium magnet until pH of the supernatant reaches 7. The coated iron oxide nanoparticles are dried under Ar atmosphere.

## Characterization of SPIONs

### X-Ray Diffraction Measurements of SPIONs (9 & 9s)

The XRD measurements are performed for the characterization of SPIONs (9) and silica coated Superparamagnetic Iron Oxides (SPIONs) (9s). d values, which are the specific parameters for the sets of separation between adjacent lattice planes are calculated according to Bragg's Law.

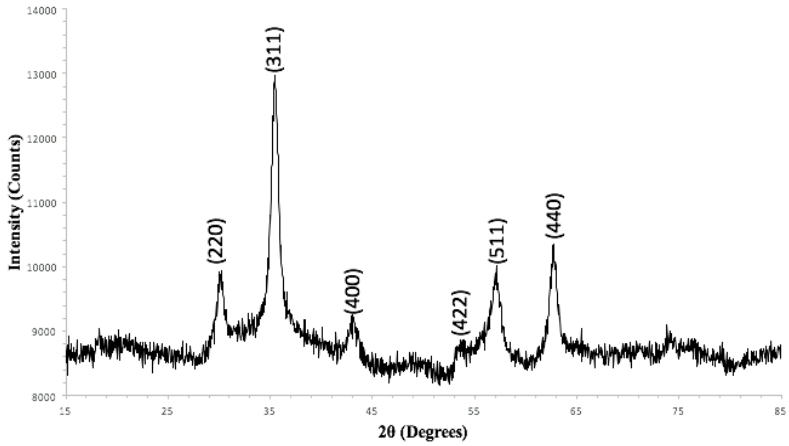



Figure S2: XRD spectrum of iron oxide nanoparticles (**9**) indicating the lattice structures.

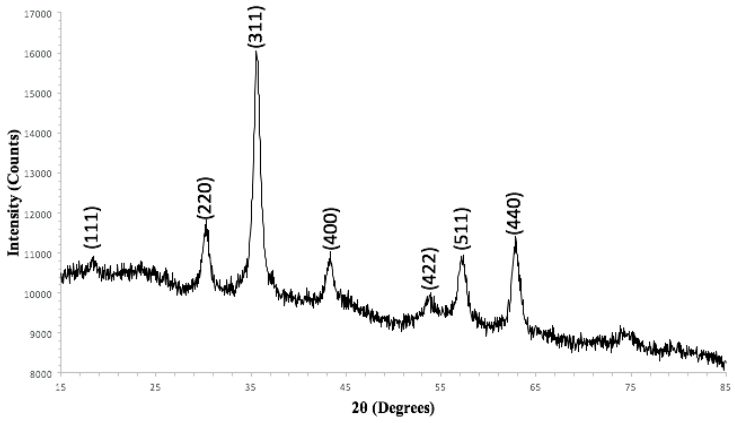



Figure S3: XRD spectrum of silica coated iron oxide nanoparticles (9s) indicating the lattice structures.

Table S1: d values obtained from XRD measurements and comparison with literature.

| SPIONs (9) | | Si-coated SPIONs (9s) | | Literature |
|---|---|---|---|---|
| **2θ(exp)** | **d (exp)** | **2θ(exp)** | **d (exp)** | **d ($Fe_2O_3$)** |
| - | - | 18.37 | *4.82* | *4.85* |
| 30.11 | *2.96* | 30.26 | *2.95* | *2.97* |
| 35.46 | *2.53* | 35.54 | *2.52* | *2.53* |
| 43.23 | *2.09* | 43.34 | *2.09* | *2.10* |
| 56.97 | *1.61* | 57.13 | *1.61* | *1.62* |
| 62.64 | *1.48* | 62.84 | *1.48* | *1.48* |

## Transmission Electron Microscopy Analysis of SPIONs (9, 9s)

The samples for TEM analysis were prepared by dropping dilute solutions of 9 and 9s in ethanol on the carbon coated copper grids. The samples were hold in room temperature for 5 minutes to allow drying before analysis.

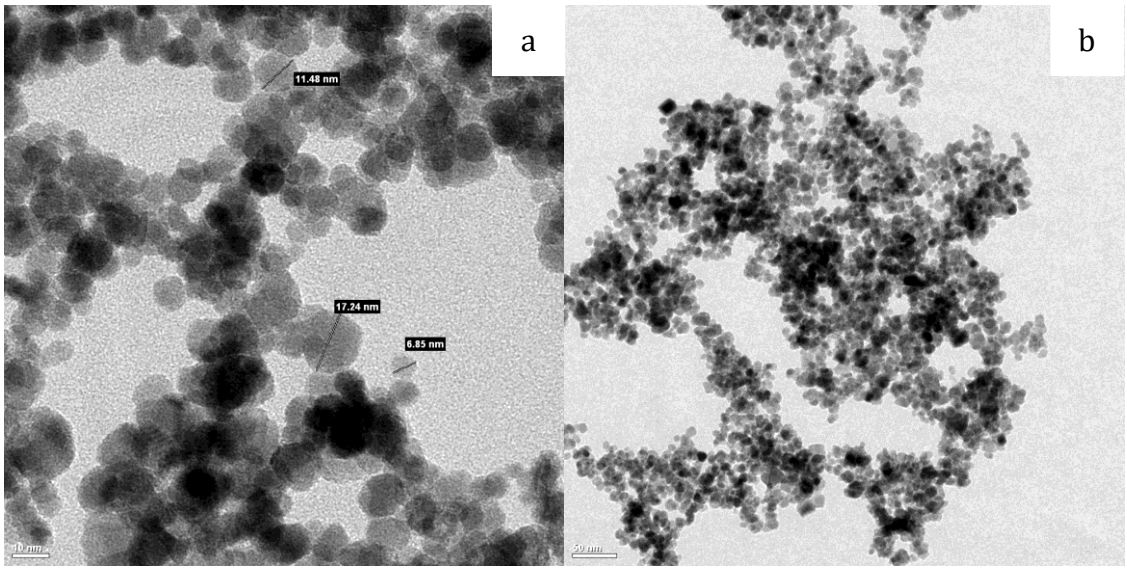



Figure S4: TEM images of SPIONs (9).

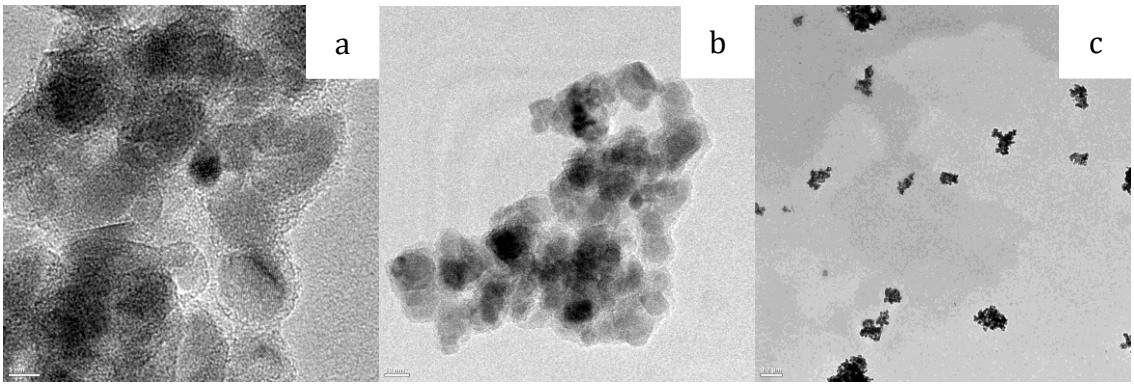



Figure S5: TEM images of silica coated SPIONs (9s).

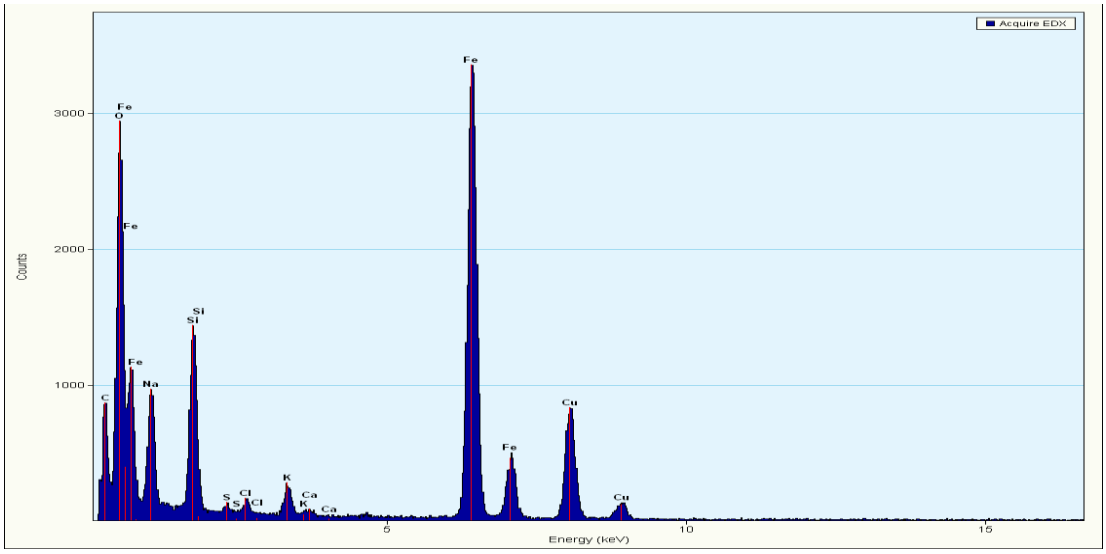



Figure S6: Energy Dispersive X-Ray analysis of silica coated SPIONs (**9s**)

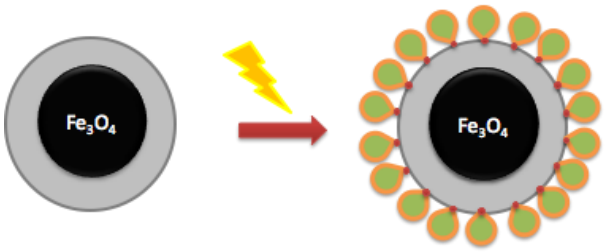
## Preparation of Photocatalyst

### Synthesis of BODIPY Functionalized Silica Coated Iron Oxide Nanoparticles (10)


The coated iron oxide nanoparticles are dried under Ar atmosphere. Silica coated iron oxide nanoparticles (85mg) are dispersed in dry toluene (45 mL) with ultra-sonication for 30 minutes under Ar atmosphere at room temperature. Compound **8** (6 mg, 0.005 mmol) is dissolved in the dispersion under mechanical stirring. Mixture is kept under mechanical stirring and reflux at 120°C for 48 hours. BODIPY functionalized nanoparticles are

collected with magnetization with neodymium magnet and centrifugation (7000rpm, 20mins). To get rid of any bound BODIPY in non-covalent manner, nanoparticles dispersed in ultra-sonication for 30 minutes and collected by magnetization with neodymium magnet centrifuged (7000 rpm, 20 mins). This procedure is applied in DCM and ethanol repeatedly until supernatant shows any sign of existence of BODIPY under UV light.

### Synthesis of Compound 11 (SPEPO)




BODIPY Functionalized Silica Coated Iron Oxide Nanoparticles (0.05 g) are dissolved in $CHCl_3$ (80 mL) with ultrasonication for 15 mins while bubbling solution with oxygen gas. The resulting solution is irradiated with 500W halogen lamp while oxygen gas is bubbling through it for an hour. The resulting nanoparticles are separated by neodymium magnet and nanoparticles are washed with $CHCl_3$ 3 times.

## Characterization of BODIPY-functionalized SPIONs

### Transmission Electron Microscopy Analysis of BODIPY-functionalized SPIONs (10)

The samples for TEM analysis were prepared by dropping dilute solutions of 10 in ethanol on the carbon coated copper grids. The samples were hold in room temperature for 5 minutes to allow drying before analysis.

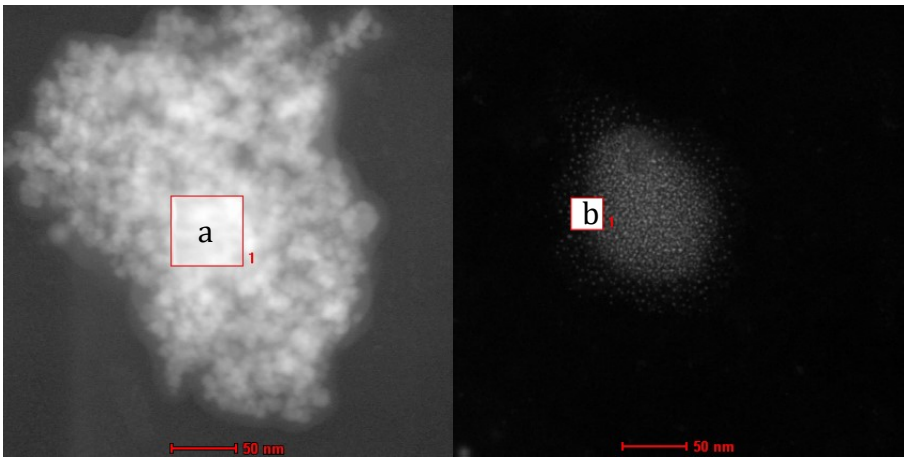



Figure S7: TEM images of BODIPY functionalized silica coated SPIONs (**10**).

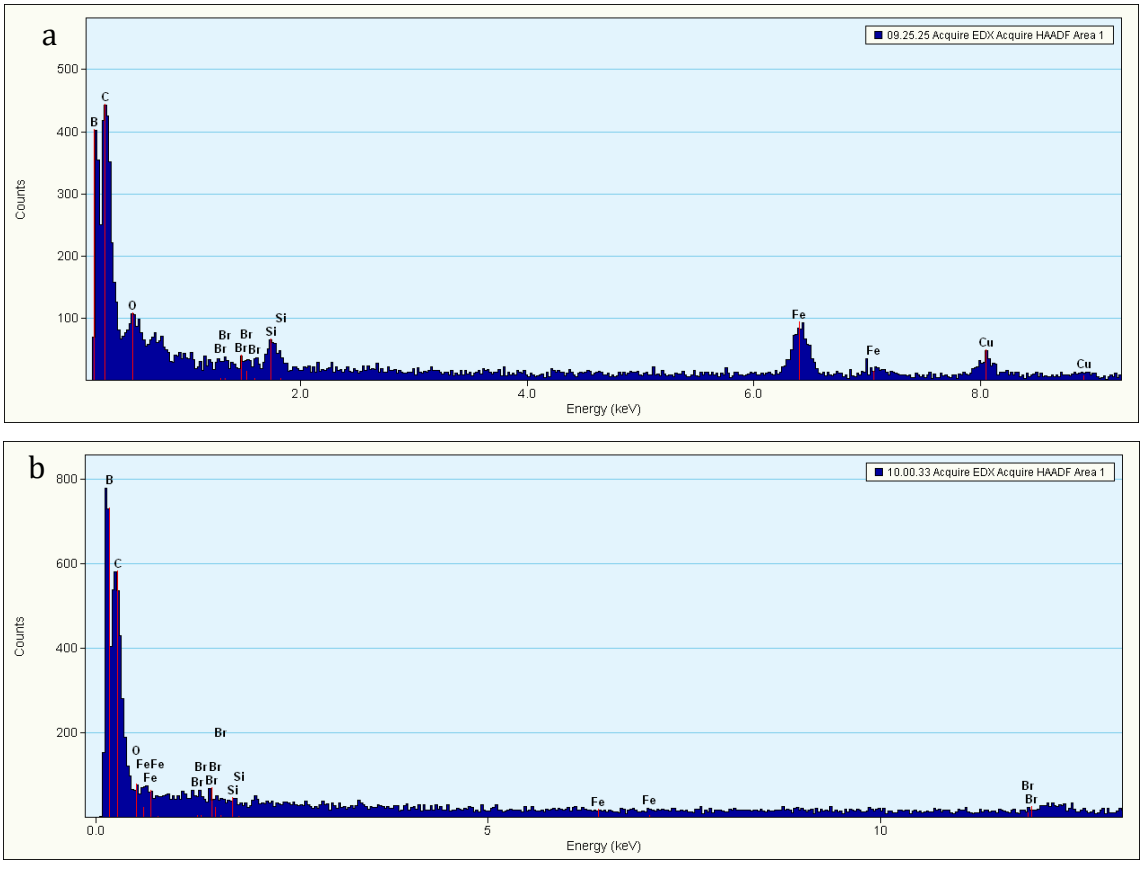



Figure S8: Energy Dispersive X-Ray analysis of BODIPY functionalized silica coated SPIONs (**10**) .

## Photophysical Measurements of 9s and 10

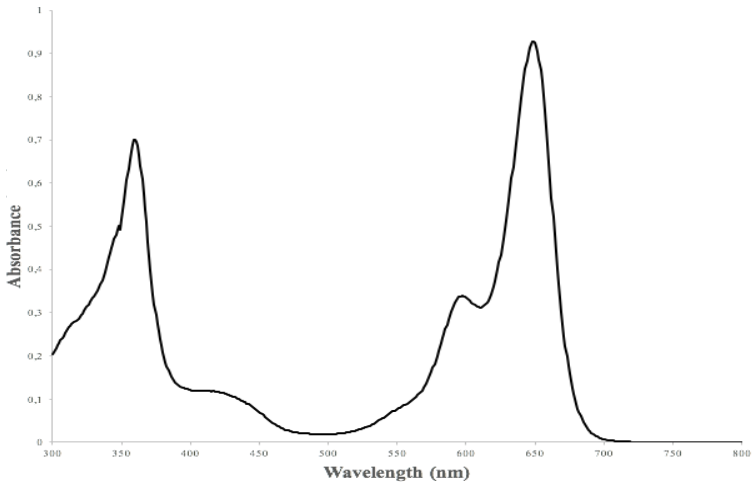



Figure S9: Absorption spectrum of compound **8** in $CHCl_3$.

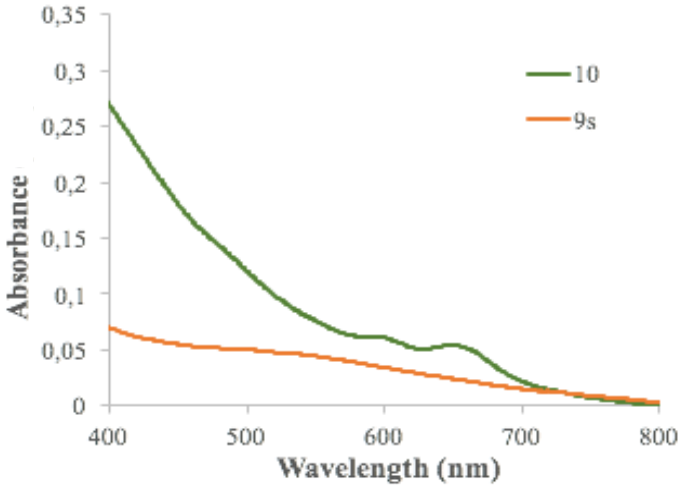



Figure S10: Absorption spectra of compound **9s** and **10** in chloroform as solvent.

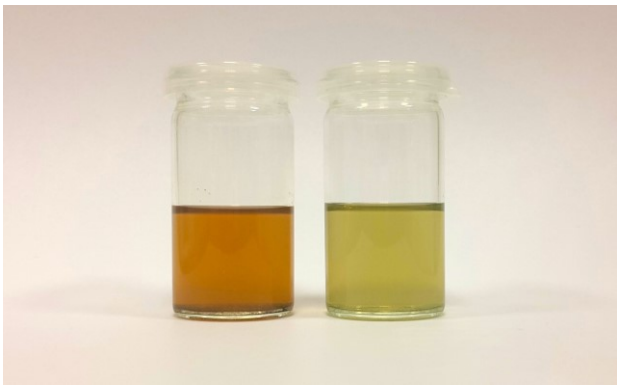


Figure S11: Solutions of **9s** (left) and **10** (right) in $CHCl_3$. The samples were ultrasonicated for 5 mins.

Figure S12: Magnetization of **9s** (left) (1min) and 10 (right) (3 min) in the presence of an external magnet.

## Singlet Oxygen Generation and Storage Experiments:

Generation and storage capabilities of BODIPY functionalized SPIONs (10) are investigated with the commercially available singlet oxygen trap, 1,3-diphenylisobenzofuran (DPBF) in oxygen deaerated chloroform. The cuvette is irradiated with 653 nm LED array (1.2 W/m2) from 10 cm distance with 1 minute time intervals and absorbance is recorded. In order to prevent the interference of the absorbance of iron oxide, the cuvette is hold on a neodymium magnet for 15 minutes to collect SPIONs at the bottom of cuvette before each measurement.

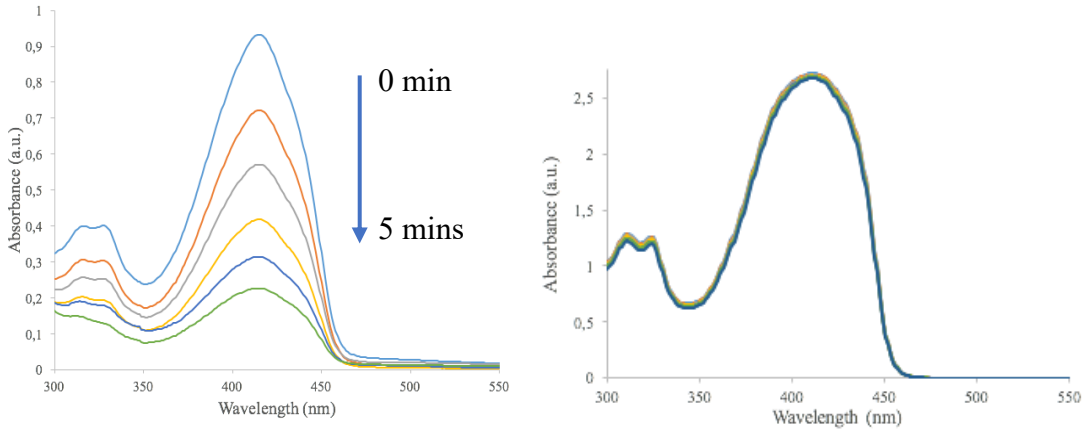



Figure S13: Left: Photobleaching of DPBF with the generation of singlet oxygen by 10. Right: Control experiment with trap.

10 is irradiated with light while cooling and oxygen gas is bubbling through it, forming 11. Then the solution of 11 is prepared in chloroform and DPBF is added as singlet oxygen trap. The cuvette is placed in heat bath at 50ºC with 30 minutes time intervals and absorbance is recorded for 2.5 hours. At the same time trap molecule is treated with same conditions as control experiment.

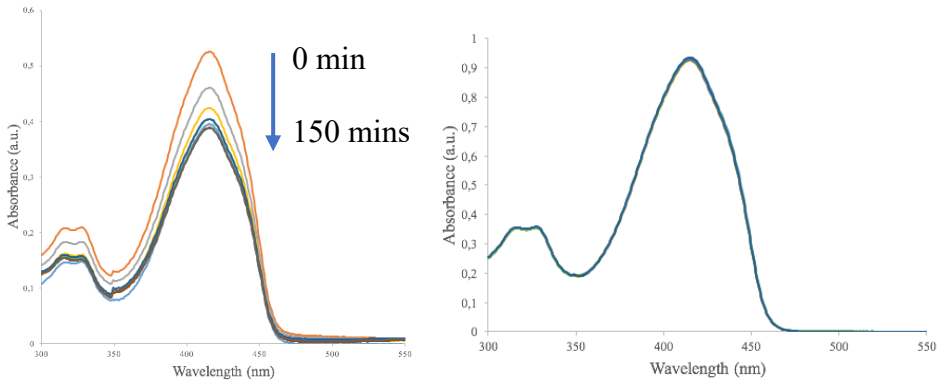



Figure S14: Left: Decrease in absorbance of DPBF with the release of singlet oxygen from pyridone moieties on 11 at 50ºC. Right: Control experiment with trap.

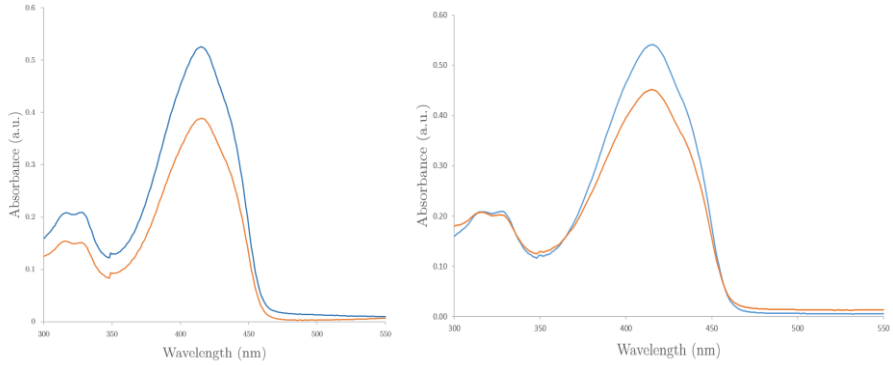
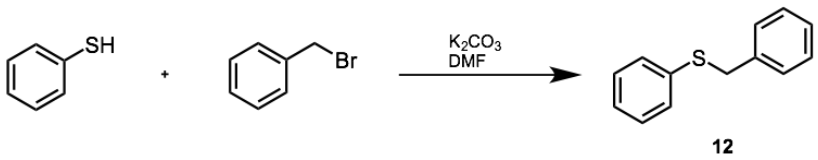



Figure S15: Absorbance spectra of the DPBF as a function of time, showing the recharging ability of the BODIPY functionalized silica coated SPIONs (**10**) in MeOH. **10** is converted into **11**, then reacted in dark with the singlet oxygen trap DBBF. Left: first cycle at 50 ºC for 2 hours. Right: second cycle at 50 ºC for 2 hours. Blue curve t=0. Red curve, t= 2 h.

## Preparation of Sulfides

### Synthesis of Benzyl Phenyl Sulfide (12)




**12**

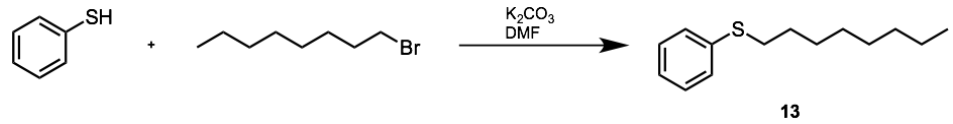
Thiophenol (0.26 mL, 2.5 mmol) and potassium carbonate (0.38 g, 2.75 mmol) are dissolved in 5 mL of DMF. Benzyl bromide (0.30 mL, 2.5 mmol) is added dropwise to reaction mixture at room temperature. The reaction is stirred for 4 hours and extracted with EtOAc and brine. Organic phases are combined and dried over anhydrous $Na_2SO_4$. Solvent is evaporated in vacuo and the product is purified by silica gel column chromatography using petroleum benzine as the eluent. Benzyl phenyl sulfide **(12)** was obtained as white solid (0.430 g, 86%).

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.31-7.37 (m, 7H), 7.31-7.29 (m, 1H), 7.26-7.28 (m, 1H), 4.16 (s, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$, δ ppm): 137.5, 136.4, 129.9, 128.8, 128.7, 128.5, 127.2, 126.4, 39.1.

MS (TOF-ESI): m/z calculated for $C_{13}H_{12}S$ $[M-H]^-$: 199.05869, found for $[M-H]^-$: 199.05911, Δ= -2.09 ppm.

## Synthesis of Octyl Phenyl Sulfide (13)




13

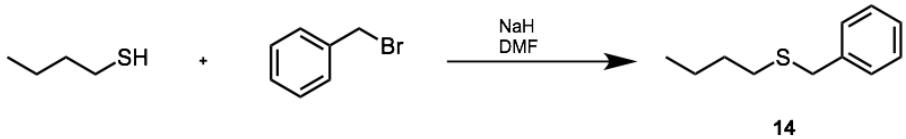
Thiophenol (1.86 mL, 18.2 mmol) and potassium carbonate (5.00 g, 36.4 mmol) are dissolved in 20 mL of DMF. n-octyl bromide (4.70 mL, 27.3 mmol) is added to the reaction mixture. The reaction is refluxed at 85ºC for overnight and extracted with $Et_2O$ and water. Organic phases are combined and dried over anhydrous $Na_2SO_4$. Solvent is evaporated in vacuo and the product is purified by silica gel column chromatography using petroleum benzine as the eluent. Octyl phenyl sulfide (**13**) was obtained as colorless liquid (2.6 g, 64%).

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.35- 7.38 (m, 1H), 7.29-7.34 (m, 2H), 7.16-7.22 (tt, J12= 7.2 Hz, J23= 1.4 Hz, 1H), 2.96 (t, J= 7.4 Hz, 2H), 1.69 (quint, J= 7.4 Hz, 2H), 1.47 (quint, J= 7.3 Hz, 2H), 1.30-1.33 (m, 8H), 0.93 (t, J= 6.9 Hz, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$, δ ppm): 137.1, 128.9, 128.8, 125.6, 33.6, 31.8, 29.2, 29.1, 28.9, 22.7, 14.1.

MS (TOF-APCI): m/z calculated for $C_{14}H_{22}S$ $[M+H]^+$: 223.1515, found for $[M+H]^+$: 223.15146, Δ= 0.17 ppm.

## Synthesis of Benzyl Butyl Sulfide (14)




14

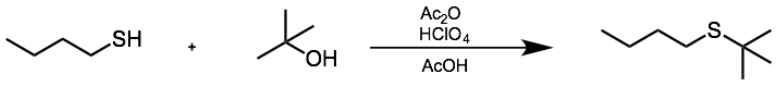
1-Butanethiol (1.00 mL, 9.3 mmol) and sodium hydride (60% dispersion in mineral oil, 0.37 g, 9.3 mmol) are dissolved in 10 mL of DMF under Argon atmosphere. When the starting compound is consumed by checking with TLC, benzyl bromide (1.05 mL, 8.9 mmol) is added dropwise to reaction mixture at room temperature. The reaction is stirred overnight and extracted with DCM and brine. Organic phases are combined and dried over anhydrous $Na_2SO_4$. Solvent is evaporated in vacuo and the product is purified by silica gel column chromatography using hexane to EtOAc/Hexane (2:98, v/v) as the eluent. Benzyl butyl sulfide (**14**) was obtained as white oil (1.4 g, 84%).

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.32-7.37 (m, 4H), 7.24-7.30 (m, 1H), 3.74 (s, 2H), 2.45 (t, J= 7.4 Hz, 2H), 1.58 (quint, J= 7.3 Hz, 2H), 1.41 (sextet, J=7.4 Hz, 2H), 0.92 (t, J= 7,3 Hz, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$, δ ppm): 138.7, 128.8, 128.4, 126.9, 36.3, 31.3, 31.1, 22.0, 13.7.

MS (TOF-APCI): m/z calculated for $C_{11}H_{16}S$ $[M+H]^+$: 181.10455, found for $[M+H]^+$: 181.10439, Δ= 0.87 ppm.

## Synthesis of Butyl tert-butyl Sulfide (15)




**15**

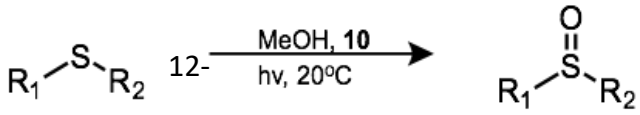
Perchloric acid (70% solution, 1.40 mL, 16.2 mmol) and acetic anhydride (2.40 mL, 25.4 mmol) are dissolved in 4 mL of acetic acid (glacial). The solution is stirred for 30 minutes at room temperature. 1-butanethiol (2.14 mL, 20.0 mmol) and tert-butanol (2.26 mL, 23.6 mmol) in 3 mL acetic acid is added dropwise to reaction mixture at room temperature. The reaction is stirred overnight at room temperature and extracted with $Et_2O$ and brine. Organic phases are combined and dried over anhydrous $Na_2SO_4$. Solvent is evaporated in vacuo to yield pure butyl tert-butyl sulfide (**15**) as slightly yellowish oil (2.9 g, 99%).

$^{1}$H NMR (400 MHz, $CDCl_3$): δ 2.50 (t, J=7.4 Hz, 2H), 1.53 (quint, J= 7.4 Hz, 2H), 1.40 (quint, J= 7.4 Hz, 2H), 1.29 (s, 9H), 0.89 (t, J= 7.3 Hz, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$, δ ppm): 41.6, 31.9, 30.9, 27.9, 22.3, 13.7.

## Preparation of Sulfoxides

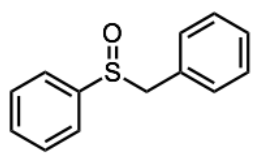
### General Procedure for Synthesis of Sulfoxides Under Light Irradiation




12-15 12a-15a

20 mg of BODIPY Functionalized Silica Coated Iron Oxide Nanoparticles (10) are dissolved by ultrasonication in 20 mL in MeOH for 5 mins. Corresponding sulfide (12-15, 0.05 mmol) is dissolved in 5 mL of MeOH and added to the reaction mixture. The resulting mixture is stirred with mechanical stirrer under light (500 W halogen lamp) while $O_2$ gas is bubbled and temperature is maintained at 20ºC. The reaction is monitored by TLC on silica with DCM as eluent, for given period of time as shown in Table 1. The BODIPY Functionalized Silica Coated Iron Oxide Nanoparticles are collected by neodymium magnet and the supernatant solution is filtered through a pad of silica and washed with DCM/MeOH (5:1, v/v). The filtrate is dried over anhydrous $Na_2SO_4$ and evaporated *in vacuo* to yield crude product (**12a-15a**). The sulfoxide is purified by silica gel column chromatography with gradient elution from DCM to DCM/MeOH (95:5, v/v).

**Benzyl Phenyl Sulfoxide (12a):**



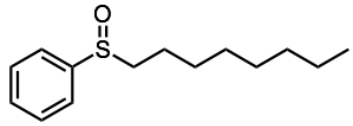

**12a**

$^{1}$H NMR (400 MHz, $CDCl_3$): δ 7.36-7.52 (m, 5H), 7.20-7.35 (m, 3H), 6.92-7.05 (m, 2H), 4.13 (d, J= 12.4 Hz, 1H), 4.02 (d, J= 12.4 Hz, 1H).

$^{13}$C NMR (100 MHz, $CDCl_3$, δ ppm): 142.7, 131.2, 130.4, 129.1, 128.9, 128.5, 128.3, 124.5, 63.6.

MS (TOF-APCI): m/z calculated for $C_{13}H_{12}OS$ $[M+H]^+$: 217.06816, found for $[M+H]^+$: 217.06749, Δ= 3.1 ppm.

**Octyl Phenyl Sulfoxide (13a):**



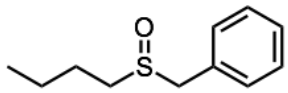
13a

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.61-7.67 (m, 2H), 7.48-7.58 (m, 3H), 2.80 (td, J12= 7.7 Hz, J23= 1.8 Hz, 2H) 1.75 (sextet, J= 6.7 Hz, 1H), 1.64 (sextet, J=6.7 Hz, 1H) 1.38-1.46 (m, 2H), 1.23-1.31 (bs, 8H), 0.88 (t, J=6.7 Hz, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$, δ ppm): 144.1, 130.9, 129.2, 124.0, 57.4, 31.7, 29.1, 29.0, 28.7, 22.6, 22.2, 14.0.

MS (TOF-APCI): m/z calculated for $C_{14}H_{22}OS$ $[M+H]^+$: 239.14641, found for $[M+H]^+$: 239.14633, Δ= 0.35 ppm.

**Benzyl Butyl Sulfoxide (14a)**



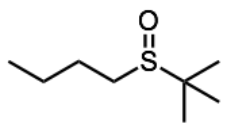
14a

$^1$H NMR (400 MHz, $CDCl_3$): δ 7.36-7.42 (m, 3H), 7.30-7.34 (m, 2H), 4.07 (d, J=12.9 Hz, 1H), 3.97 (d, J=12.9 Hz, 1H), 1.71-1.81 (m, 2H), 1.38-1.54 (m, 2H), 0.95 (t, J= 7.4 Hz, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$, δ ppm): 130.0, 129.0, 128.4, 128.2, 58.2, 50.6, 24.5, 22.0, 13.6.

MS (TOF-APCI): m/z calculated for $C_{11}H_{16}OS$ $[M+H]^+$: 197.09946, found for $[M+H]^+$: 197.09986, Δ= -2.02 ppm.

**Butyl tert-Butyl Sulfoxide (15a):**



15a

$^1$H NMR (400 MHz, $CDCl_3$): δ 2.36-2.43 (m, 2H), 1.63-1.84 (m, 2H), 1.34-1.52 (m, 2H) 1.18 (s, 9H), 0.90 (t, J= 7.3 Hz, 3H).

$^{13}$C NMR (100 MHz, $CDCl_3$, δ ppm): 52.6, 45.3, 25.7, 22.8, 22.1, 13.7.

MS (TOF-APCI): m/z calculated for $C_8H_{18}OS$ $[M+H]^+$: 163.11511, found for $[M+H]^+$: 163.11563, Δ= -3.17 ppm.

## Synthesis of Butyl tert-Butyl Sulfoxide by Compound 11

Nanoparticles **11** which is the endoperoxide form of **10** (25 mg) was dissolved in 4 mL of MeOH by ultrasonication in a 10 mL vial. Butyl tert-butyl sulfide (**15**) (2.5 mg, 0.017 mmol) and o-dichlorobenzene (internal standard for GSMS) (5µL, 0.044 mmol) are added to the vial and the vial is sealed. The vial is placed in 50ºC heat bath. After 4 hours, the nanoparticles are collected by neodymium magnet and the supernatant liquid is collected for GCMS experiment.

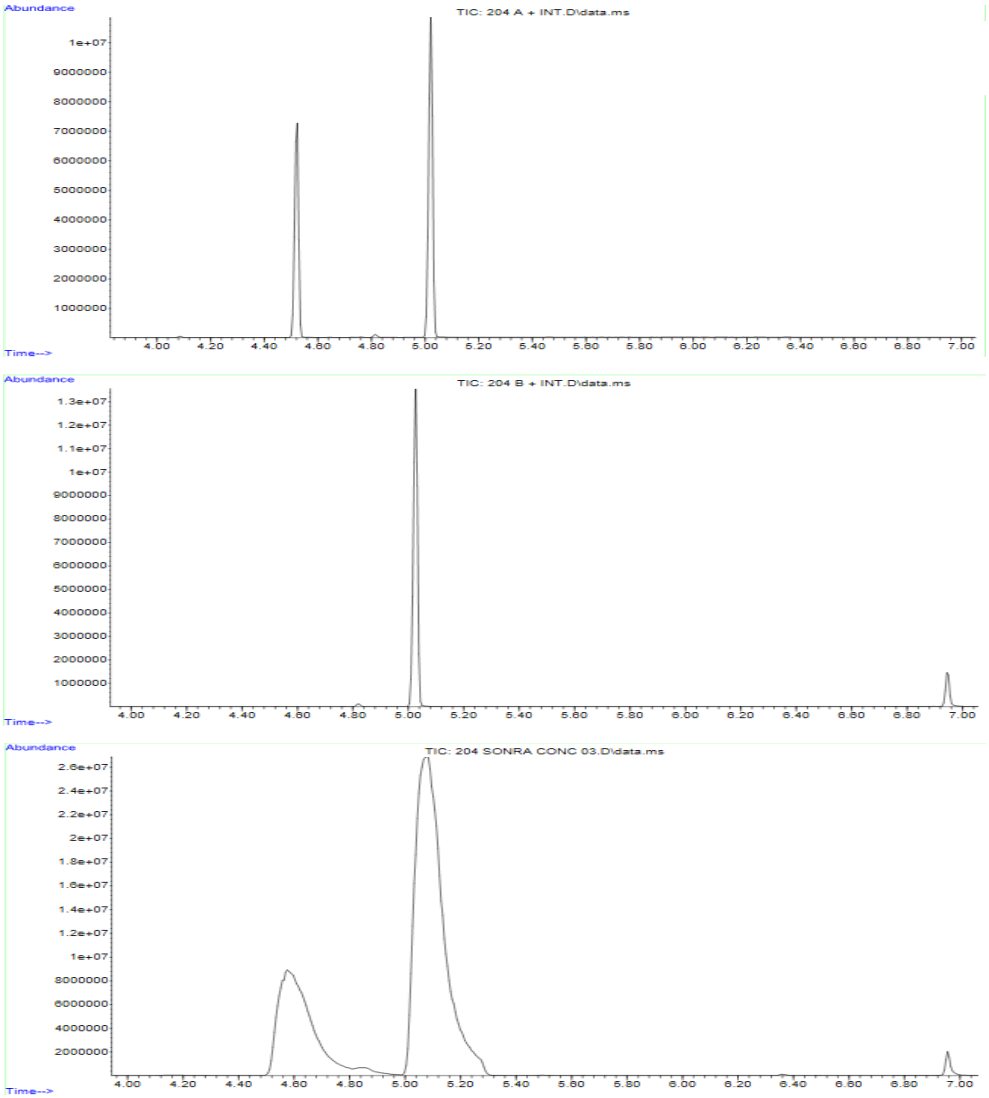



Figure S16: GCMS analysis with oxidation of sulfide **14** by release of singlet oxygen from 2-pyridone moiety of nanoparticles **11**. A contains starting sulfide and internal standard. B contains resulting sulfoxide and internal standard. C contains the reaction media after heating at 50ºC for 2 hours.

# NMR Spectra, HRMS Data &

# Zeta Size Analysis

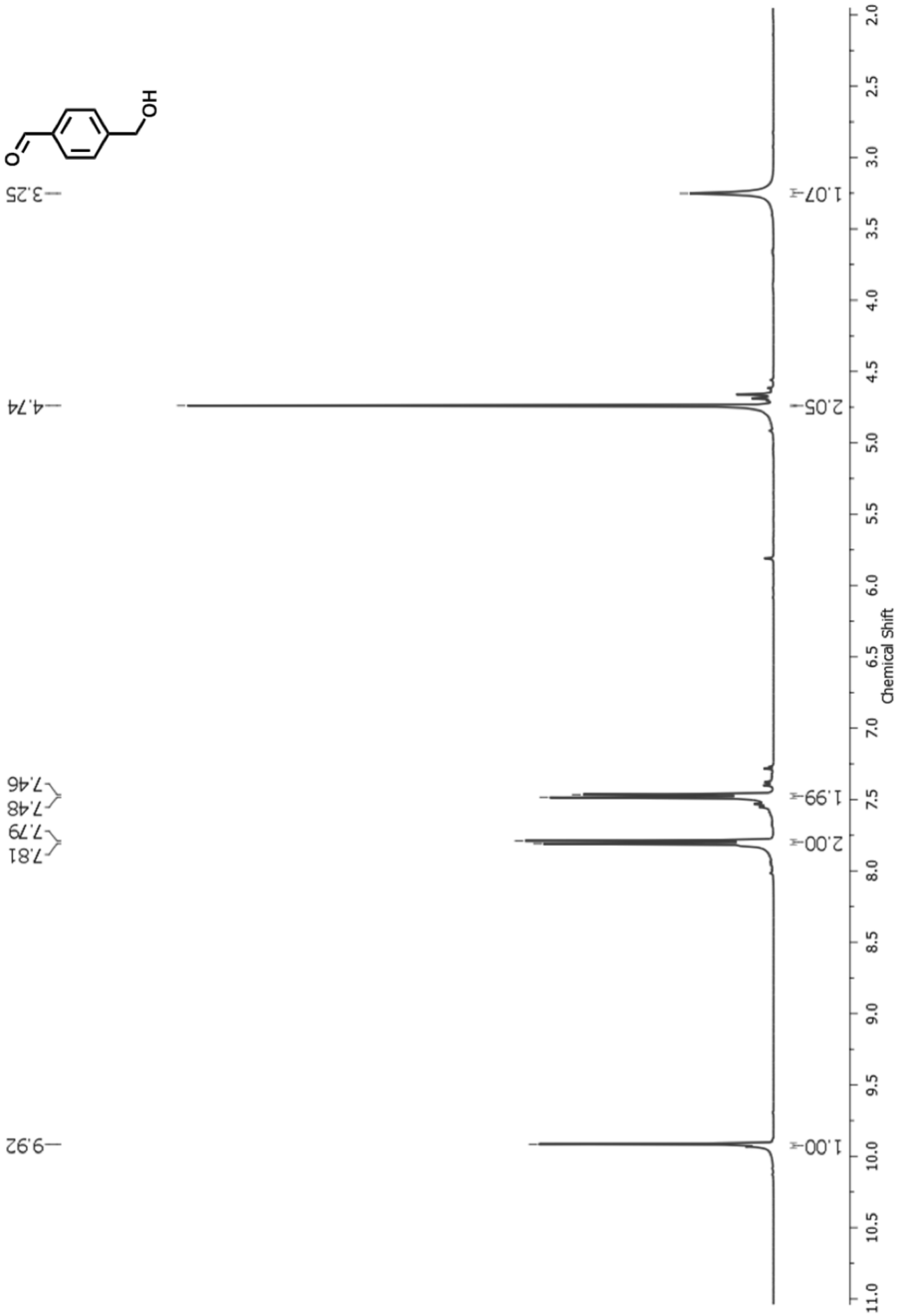



Figure S17: $^{1}H$ NMR of compound **2** in $CDCl_3$.

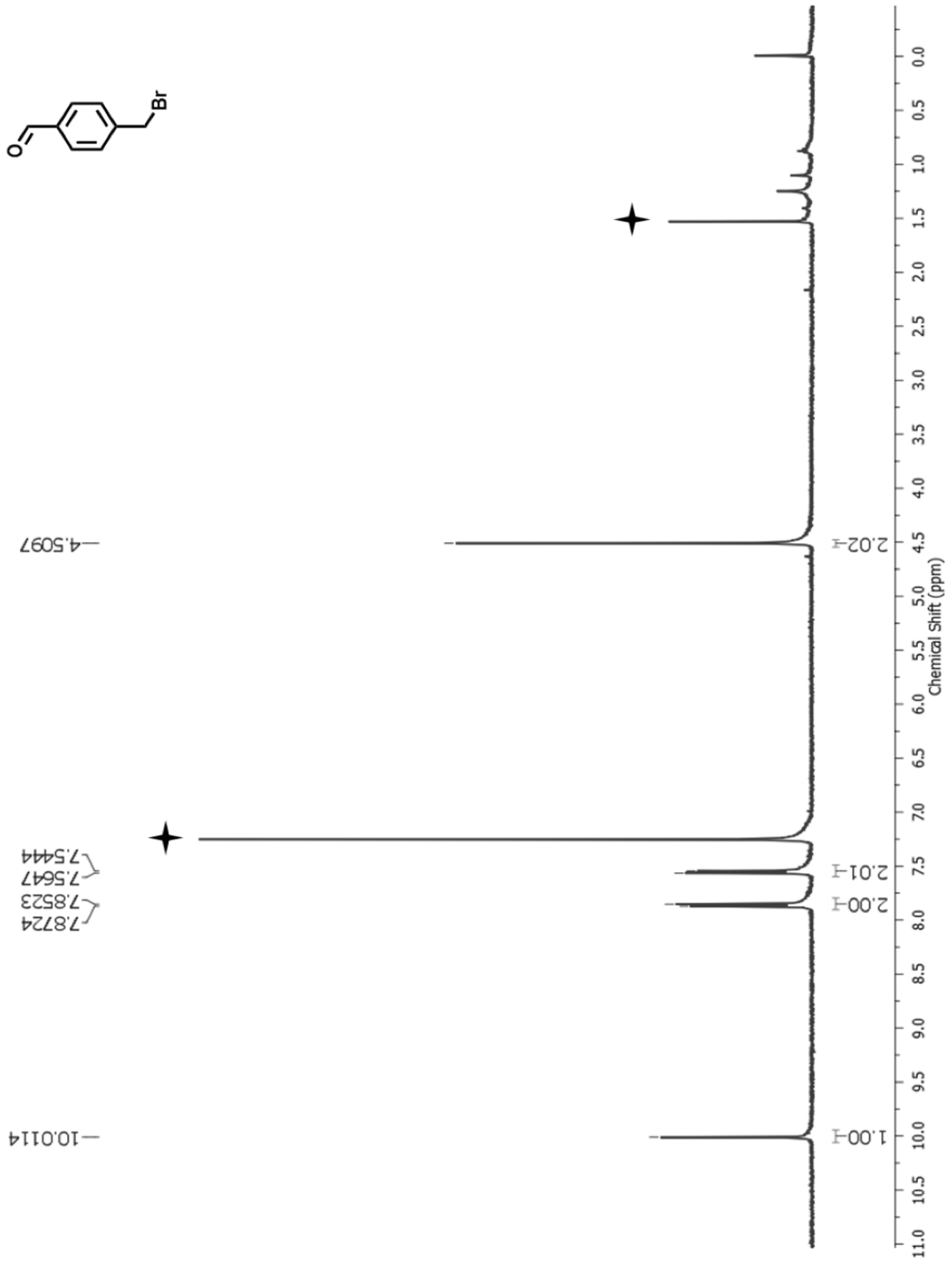



Figure S17: $^{1}H$ NMR of compound **3** in $CDCl_3$.

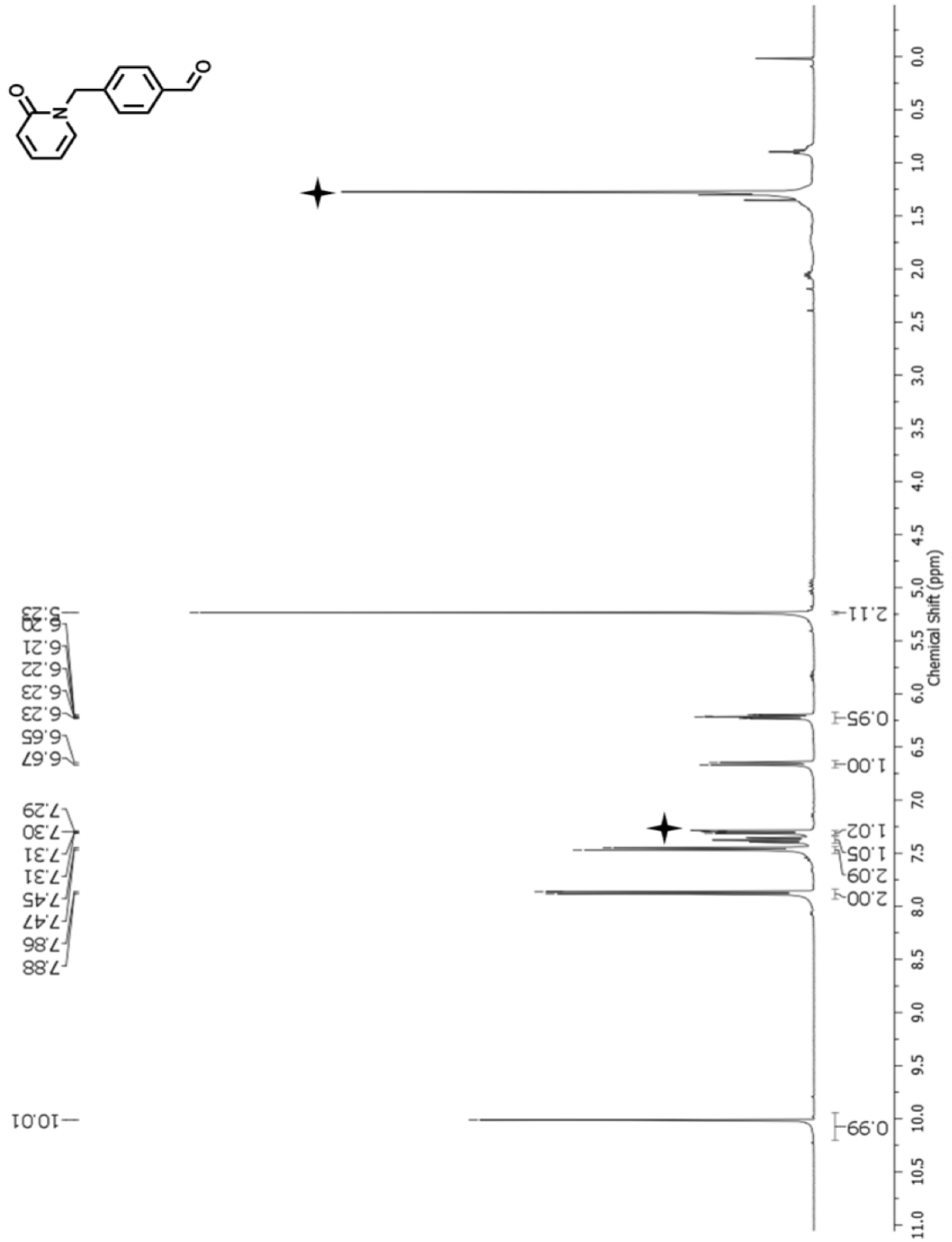



Figure S18: $^{1}H$ NMR of compound **4** in $CDCl_3$.

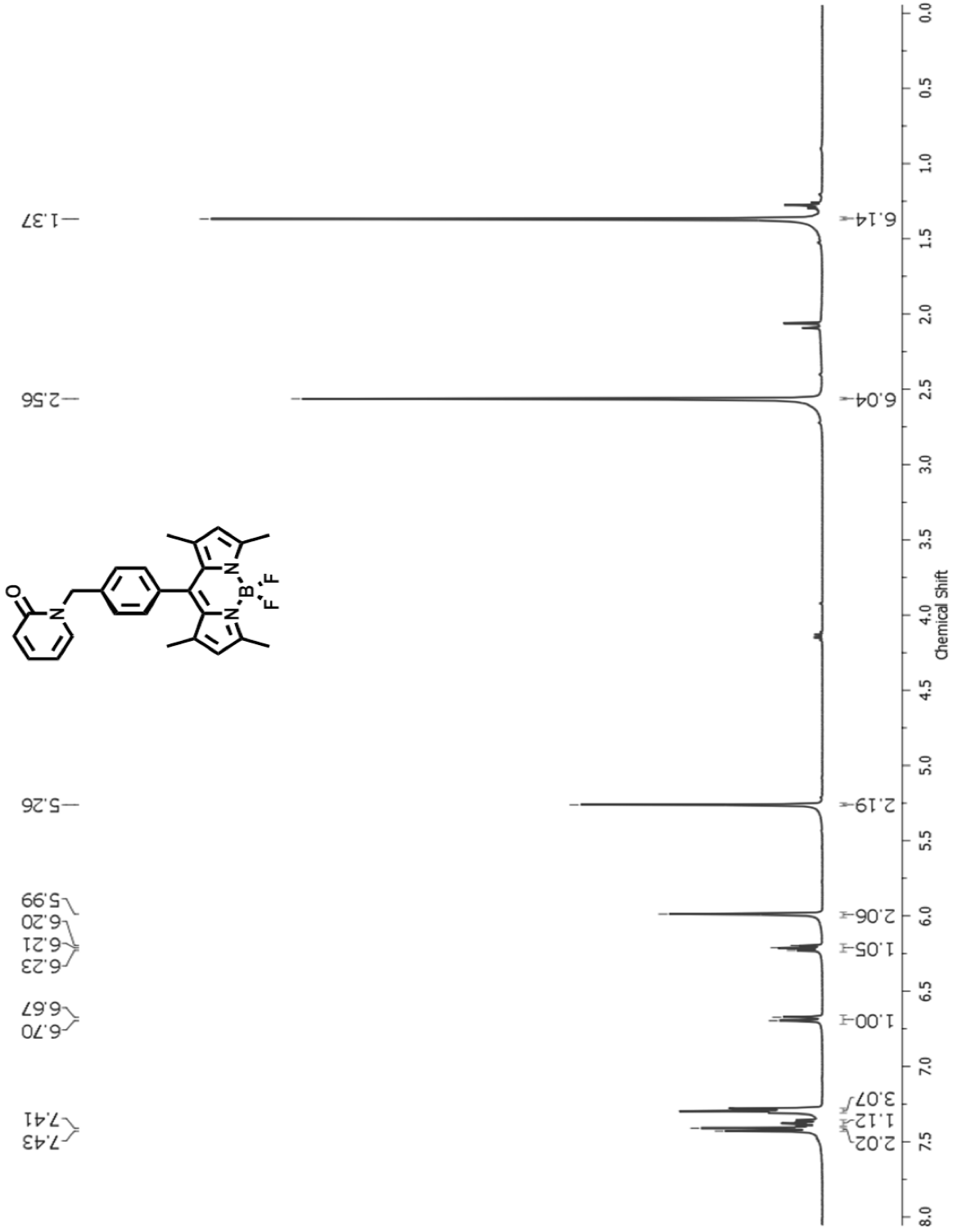



Figure S19: $^{1}H$ NMR of compound **5** in $CDCl_3$.

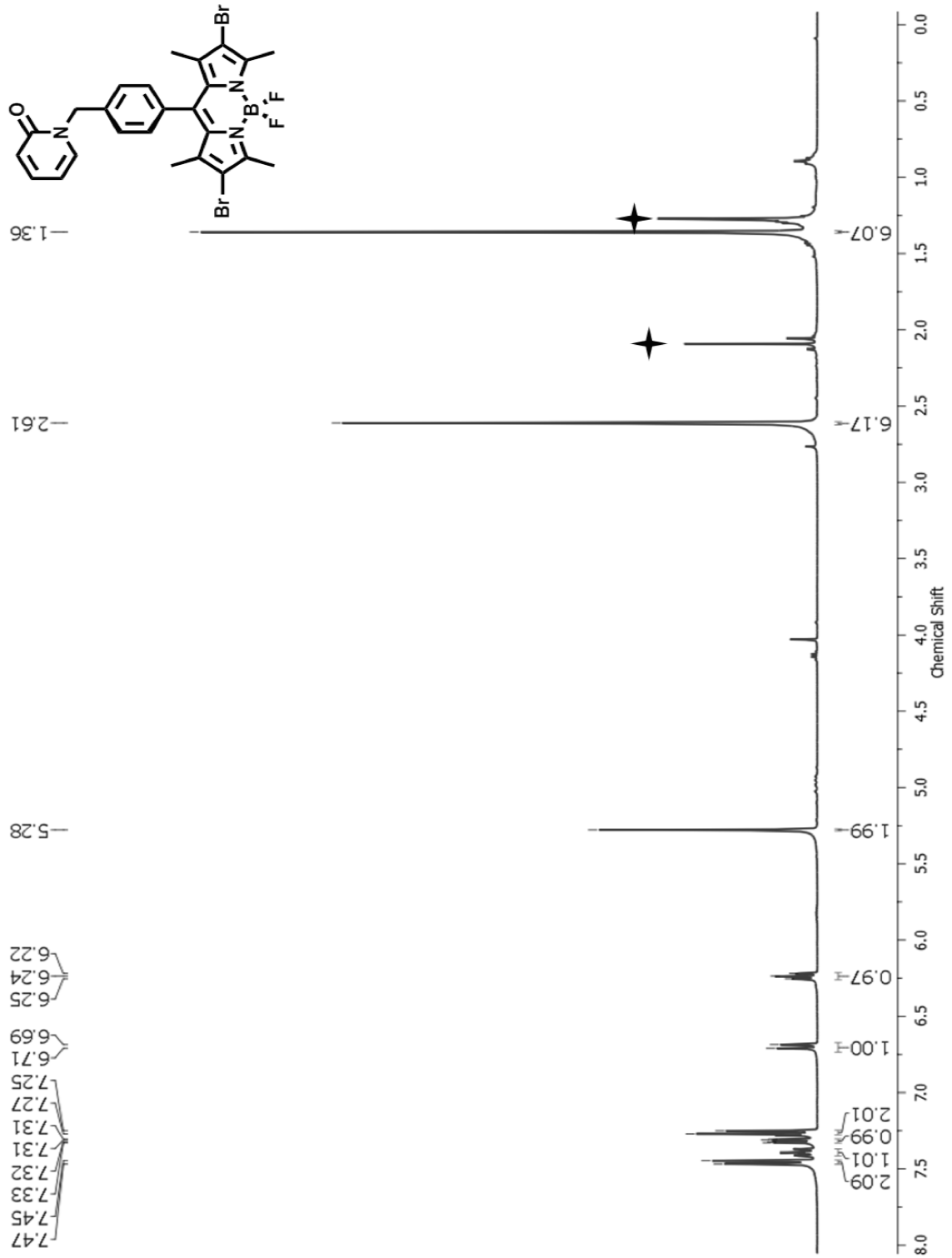



Figure S20: $^{1}H$ NMR of compound **6** in $CDCl_3$.

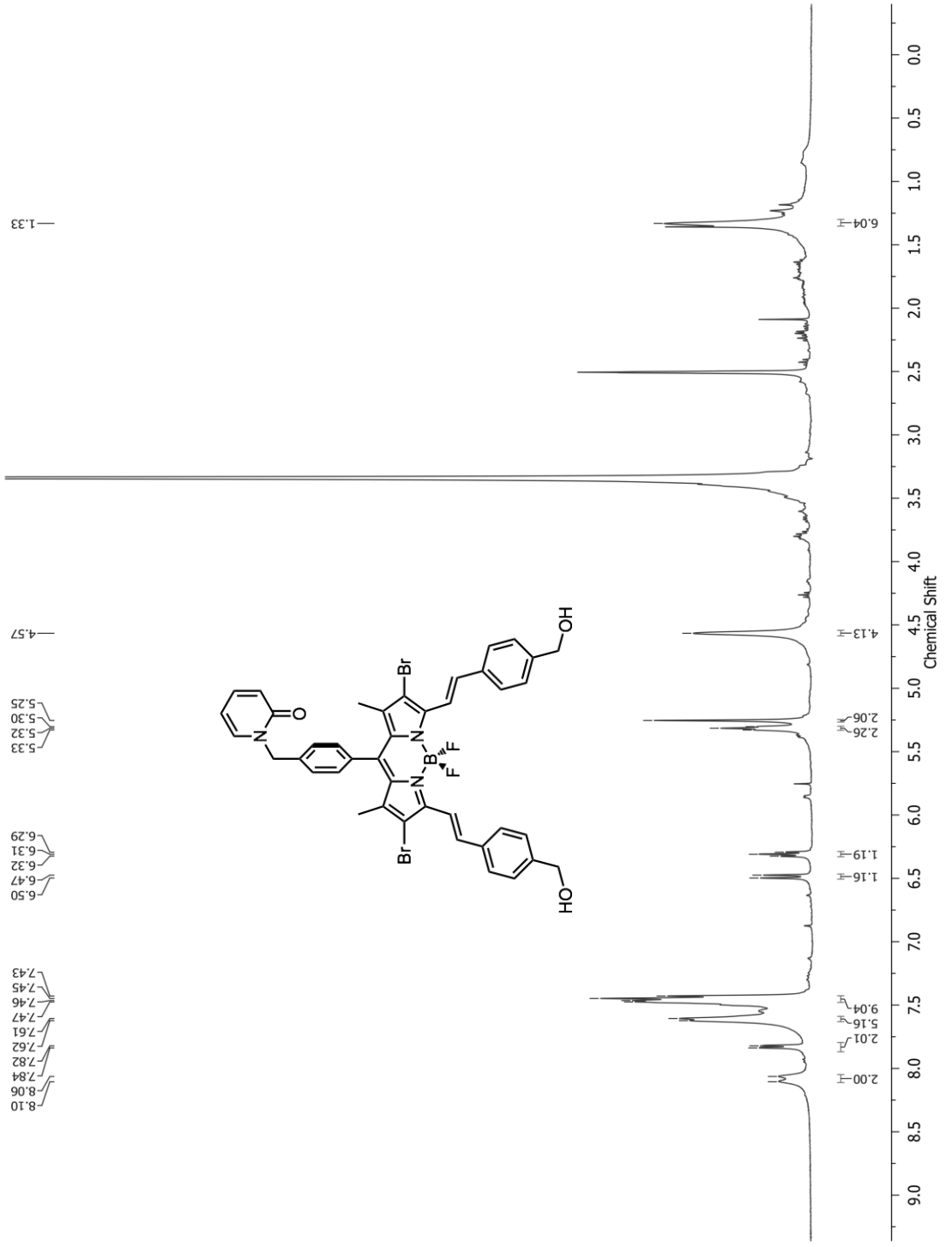



Figure S21: $^{1}H$ NMR of compound **7** in DMSO-$d_6$.

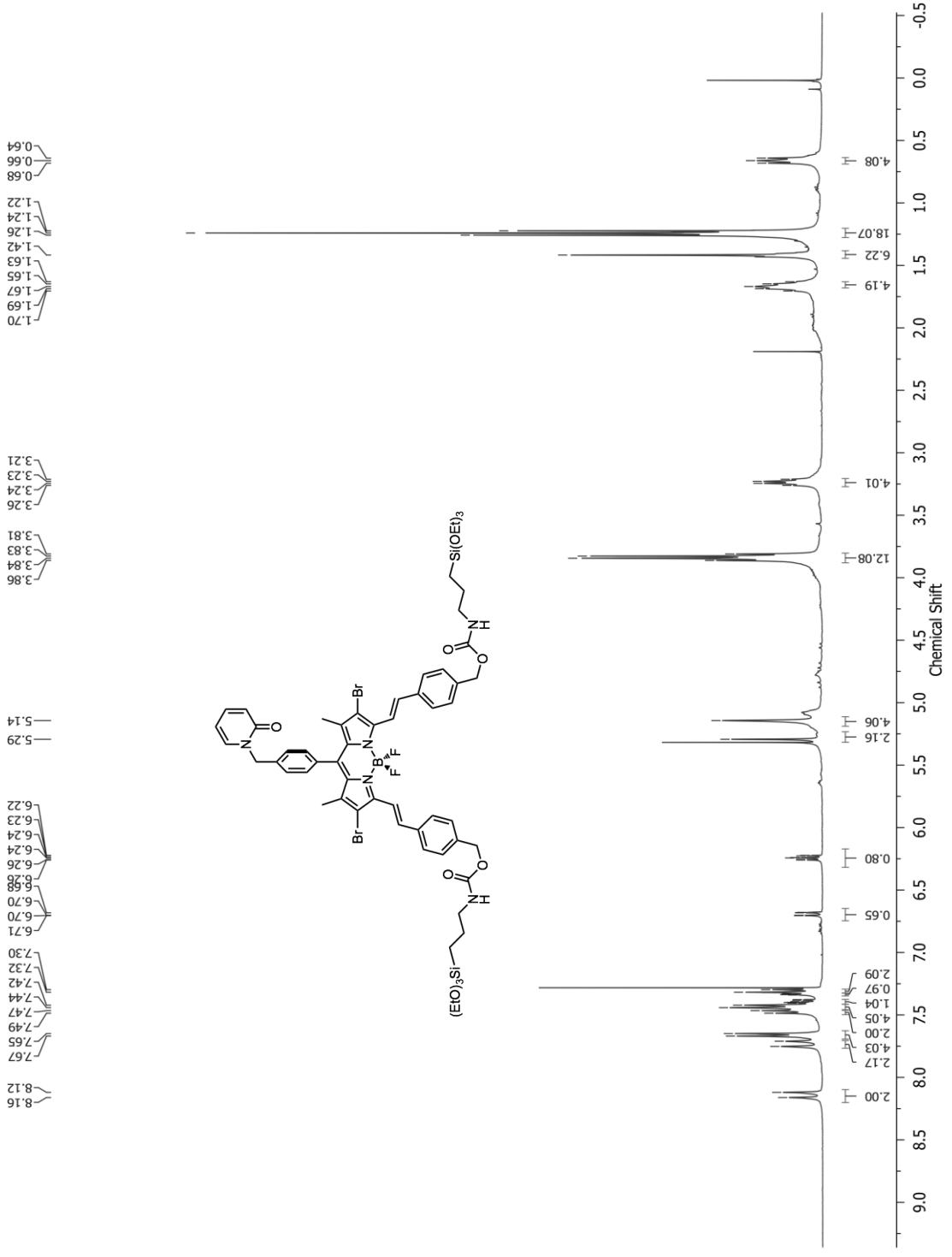



Figure S22: $^{1}H$ NMR of compound **8** in $CDCl_3$.

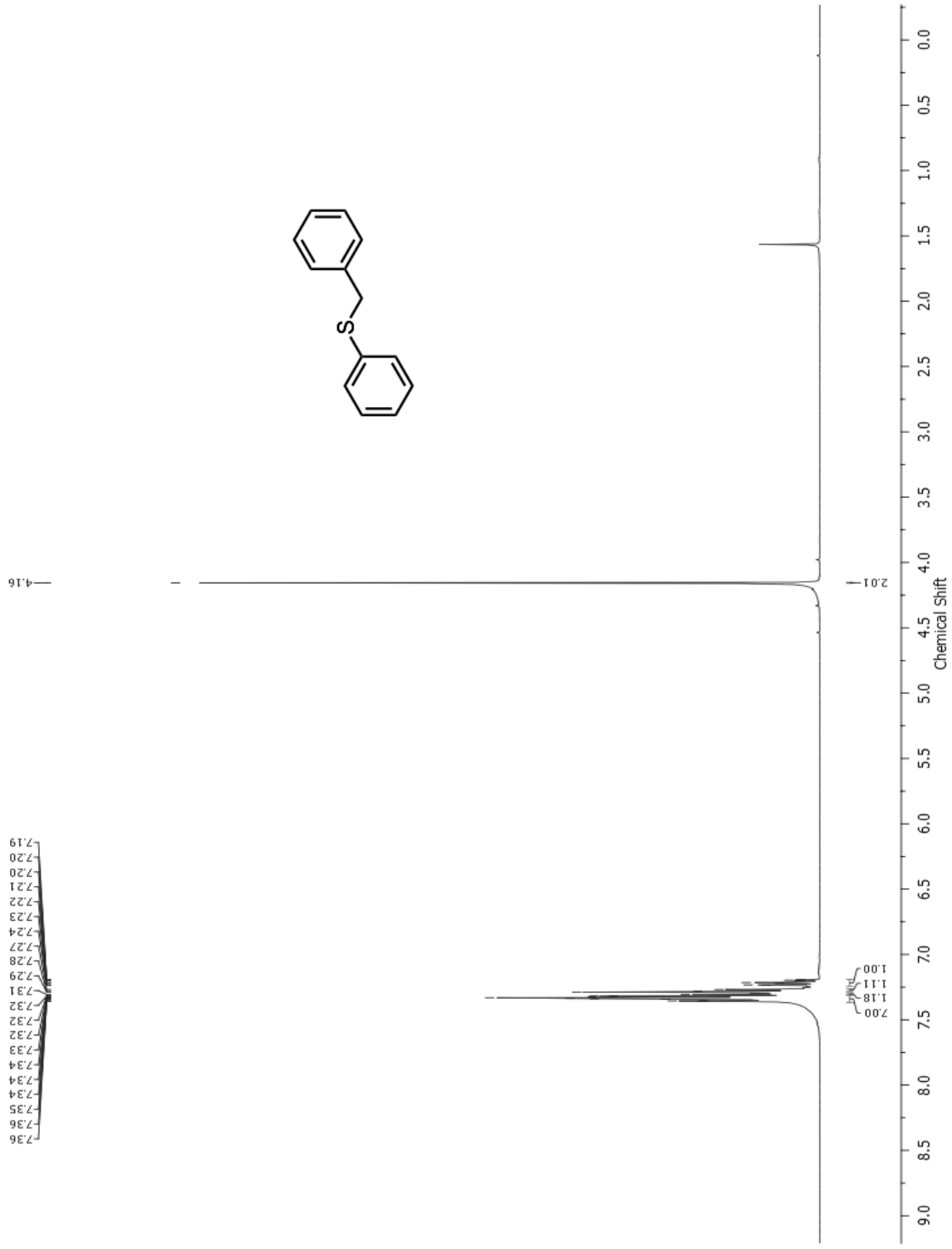



Figure S23: $^{1}H$ NMR of compound **12** in $CDCl_3$.

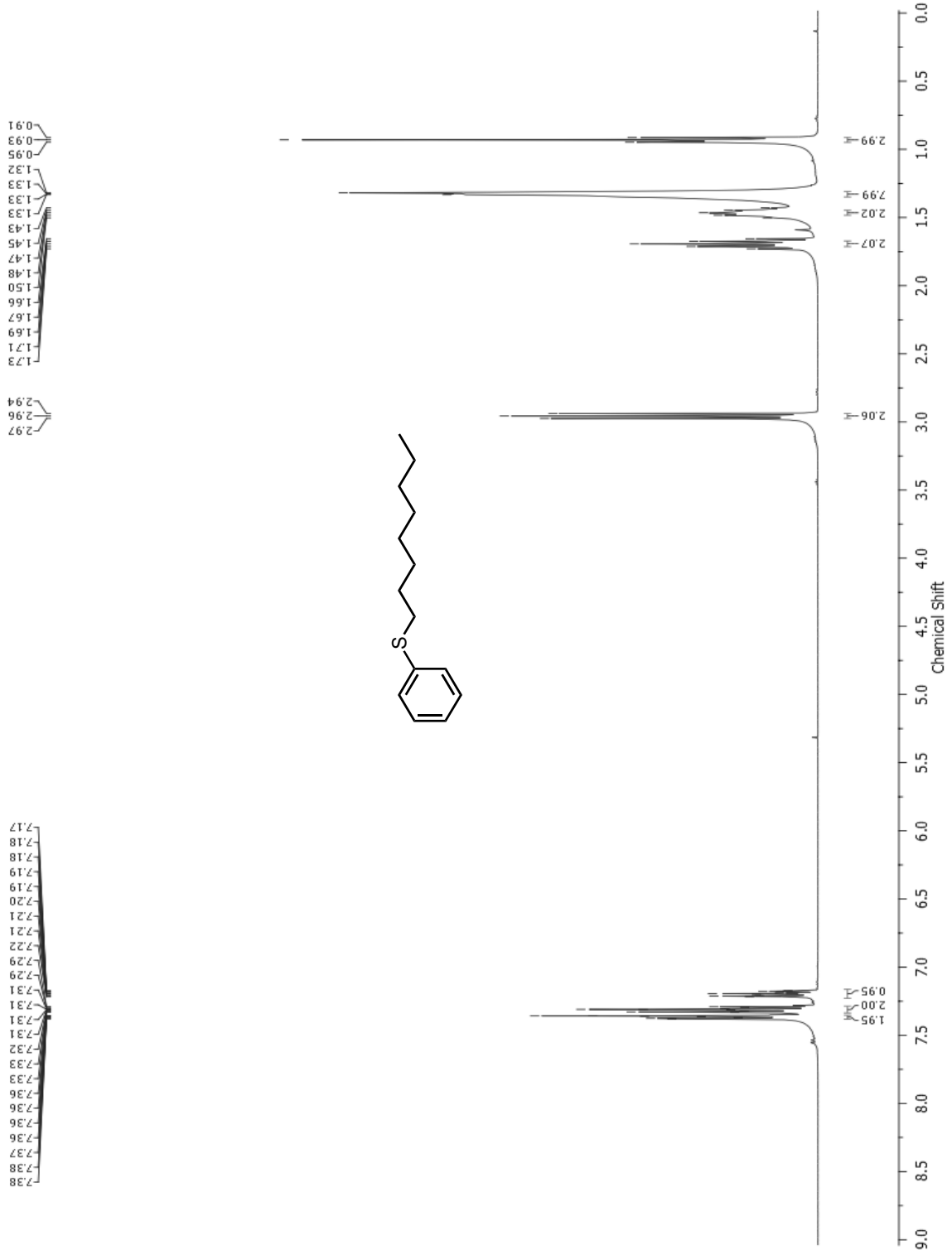



Figure S24: $^{1}H$ NMR of compound **13** in $CDCl_3$.

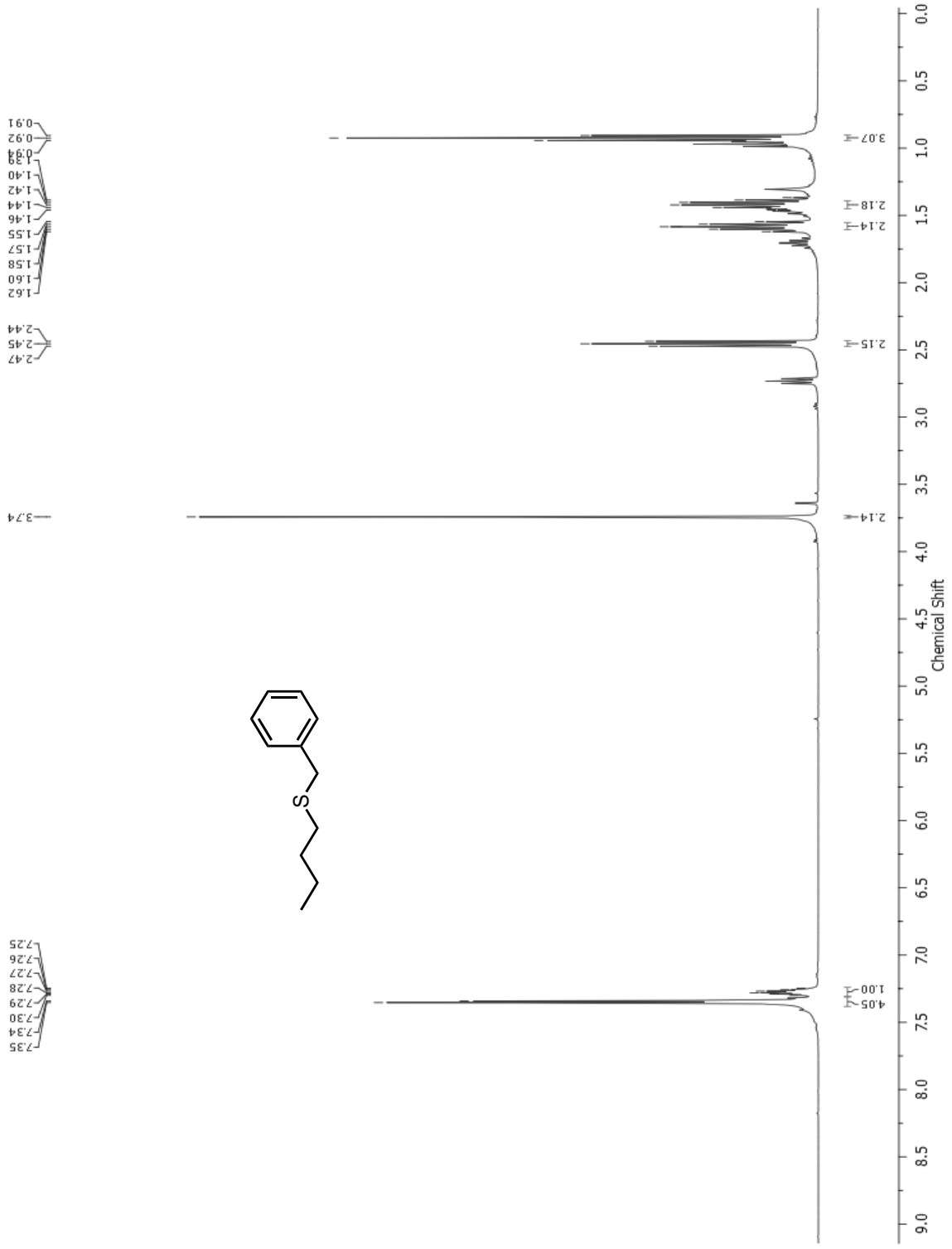



Figure S26: $^{1}H$ NMR of compound **14** in $CDCl_3$.

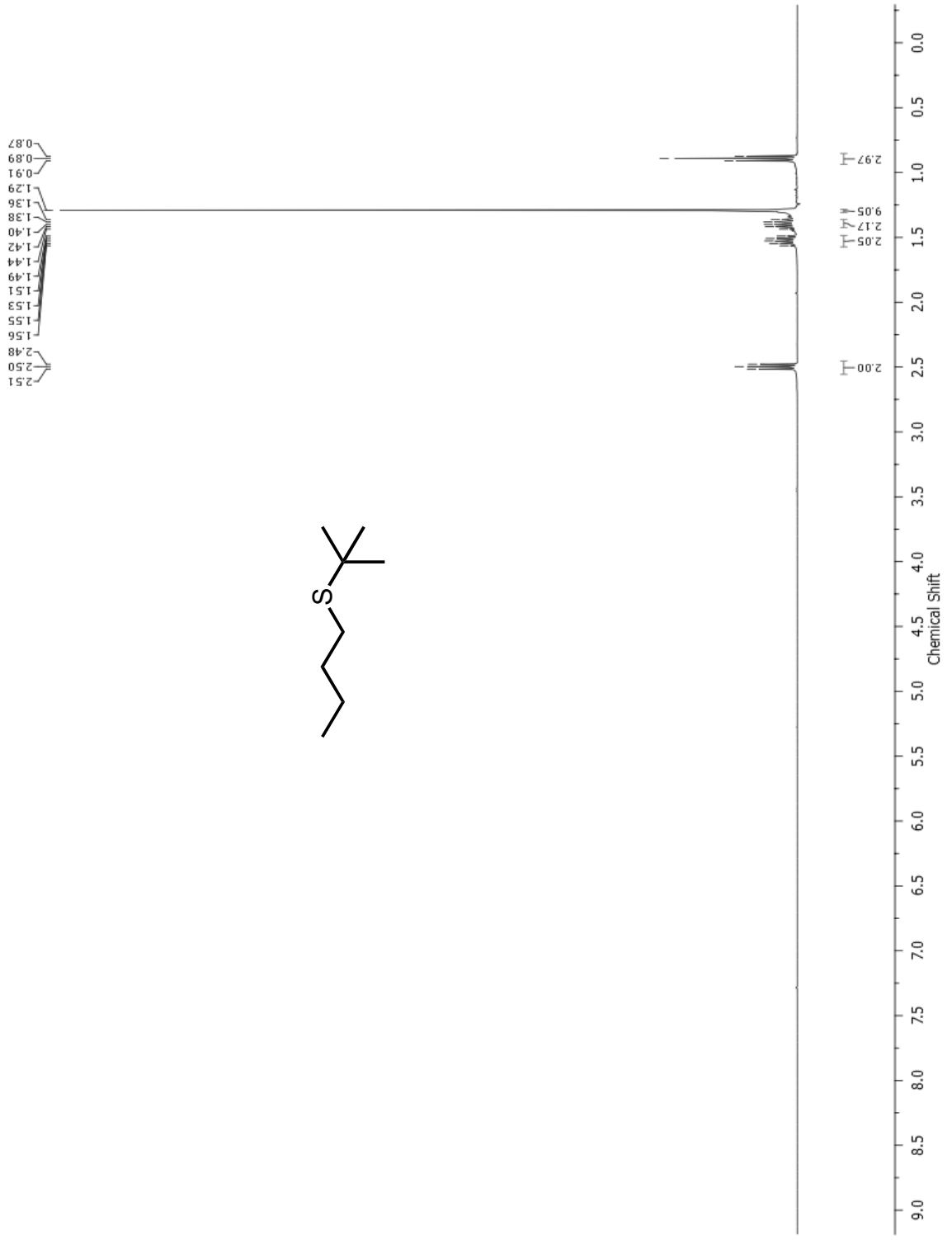



Figure S25: $^{1}H$ NMR of compound **15** in $CDCl_3$.

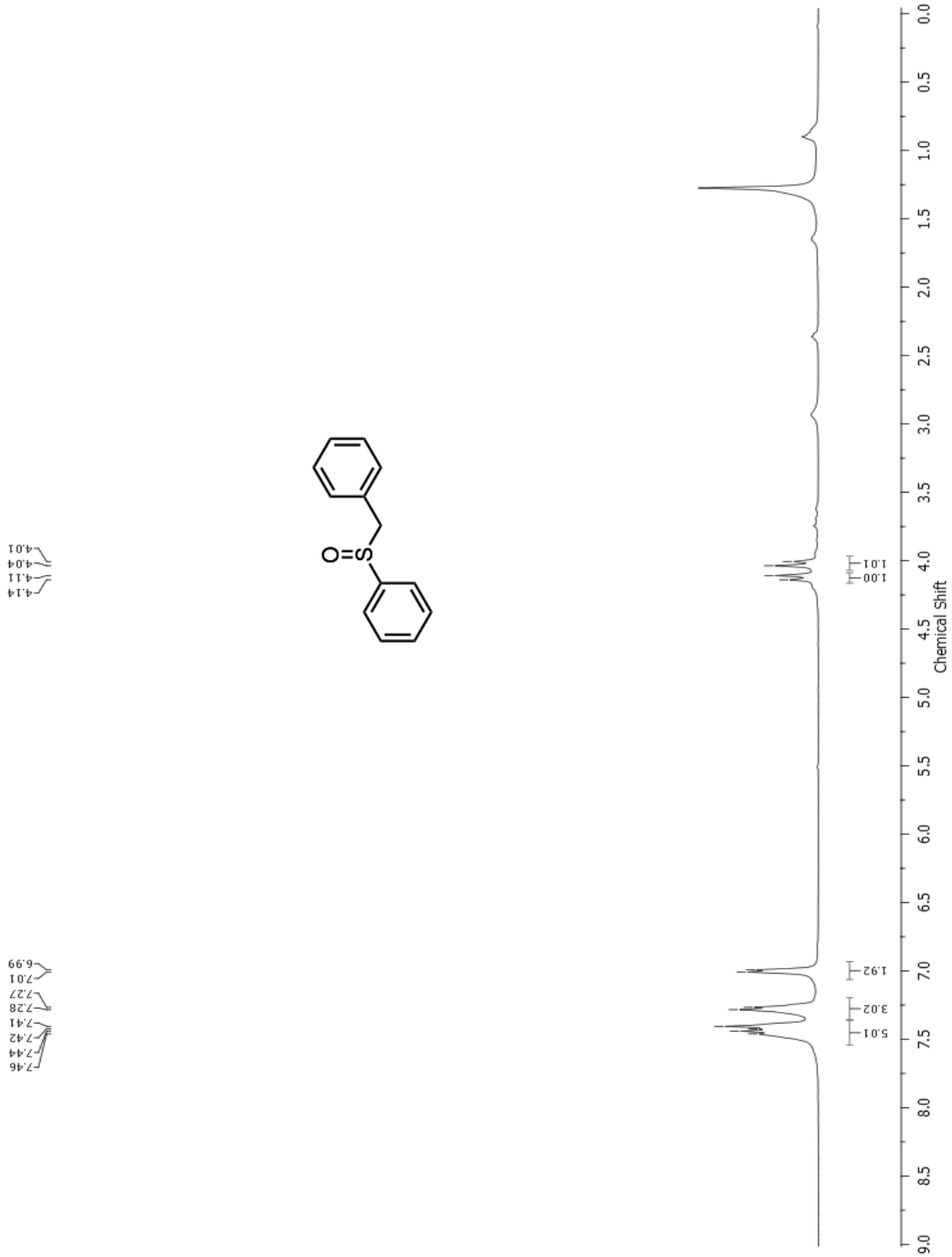



Figure S26: $^{1}H$ NMR of compound **12a** in $CDCl_3$.

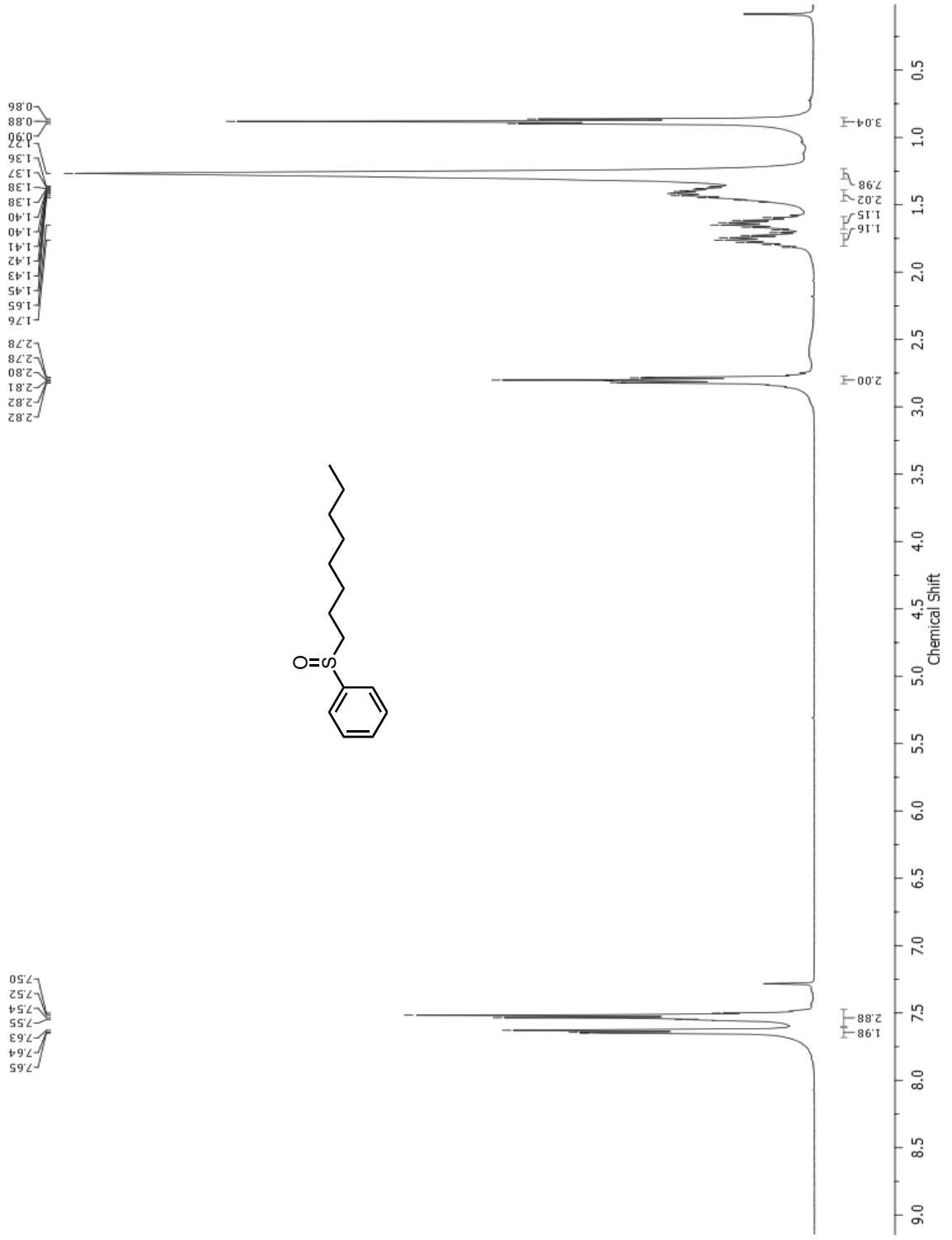



Figure S27: $^{1}H$ NMR of compound **13a** in $CDCl_3$.

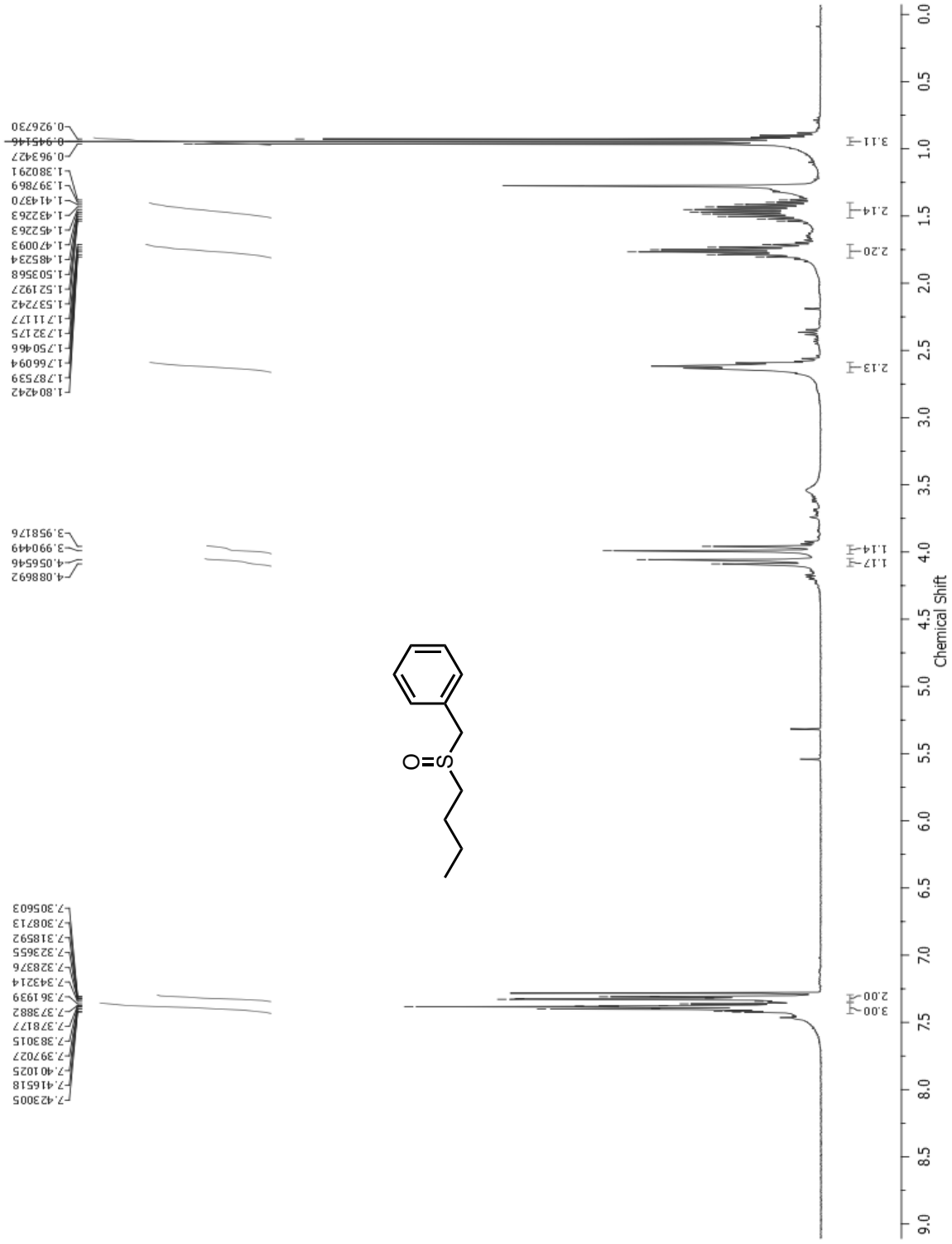



Figure S28: $^{1}H$ NMR of compound **14a** in $CDCl_3$.

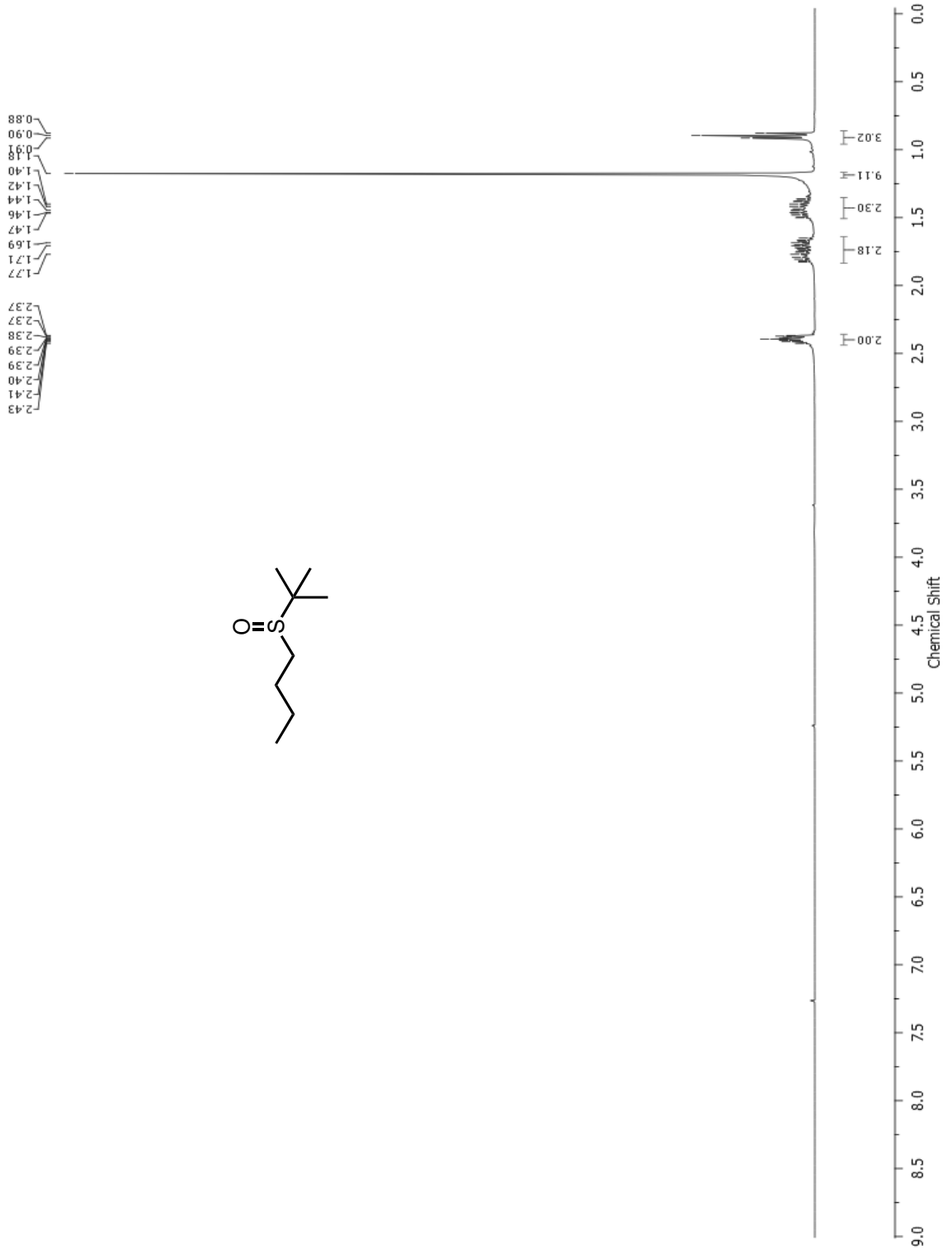



Figure S29: $^{1}H$ NMR of compound **15a** in $CDCl_3$.

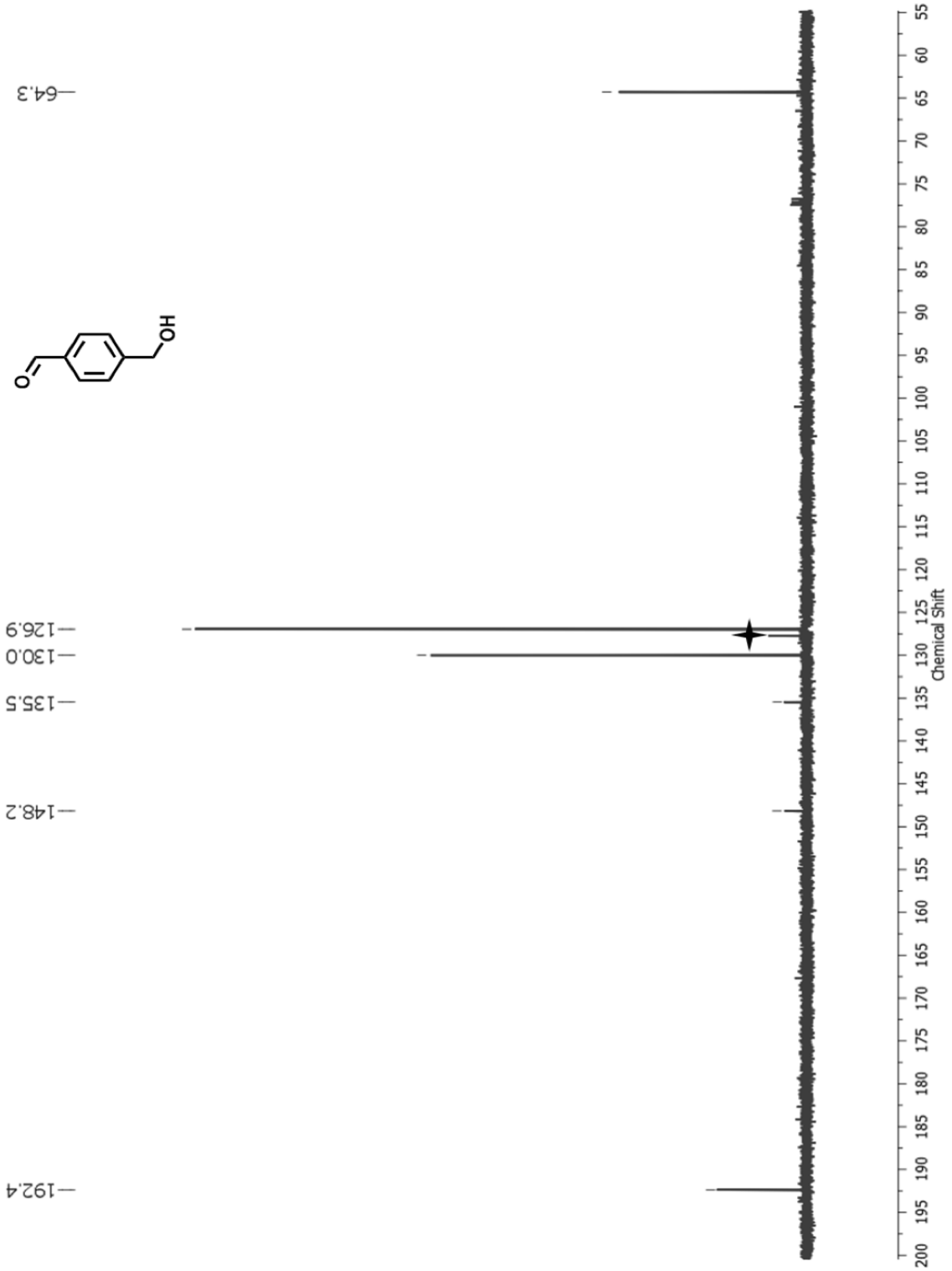



Figure S30: $^{13}C$ NMR of compound **2** in $CDCl_3$.

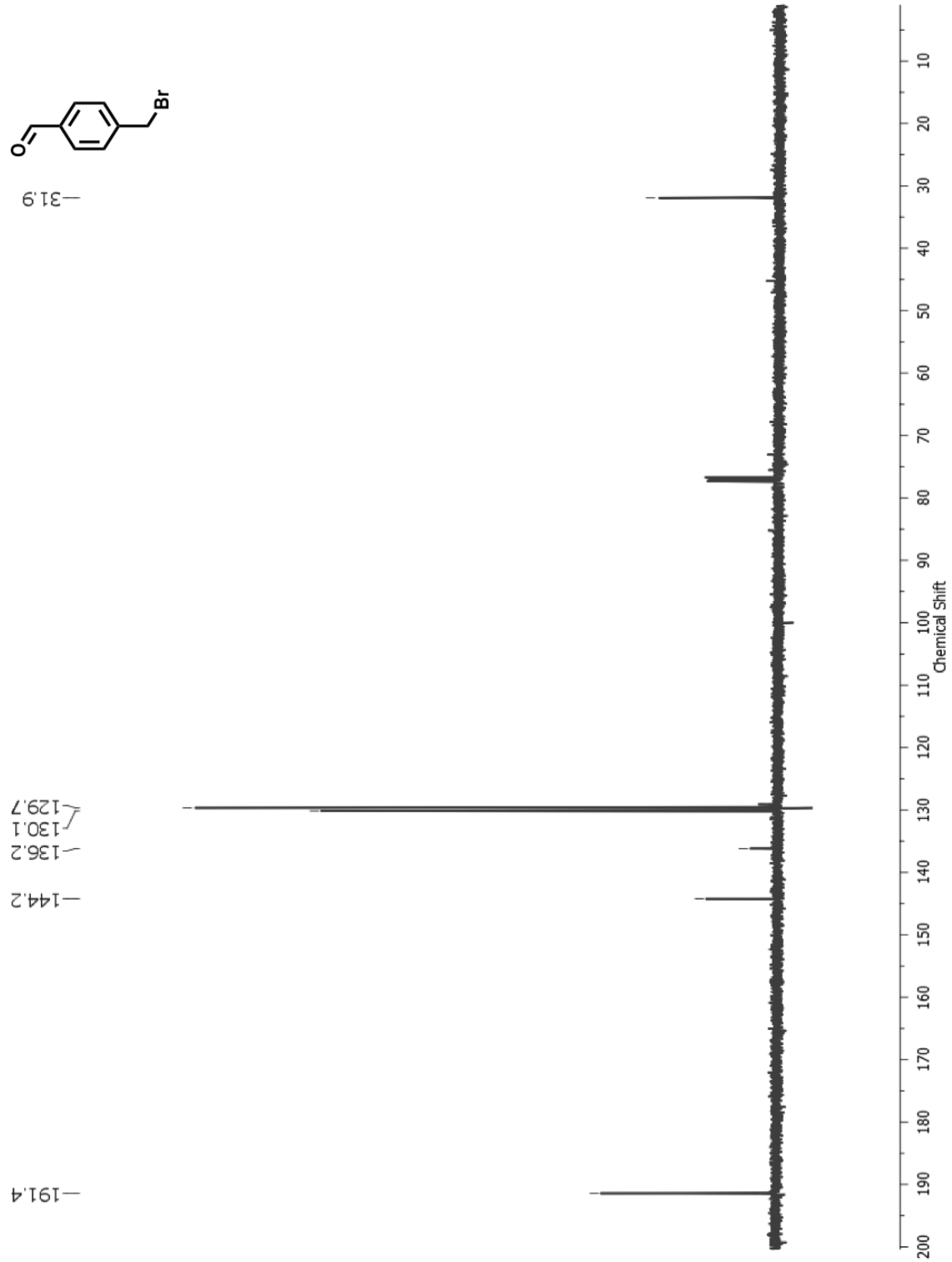



Figure S31: $^{13}C$ NMR of compound **3** in $CDCl_3$.

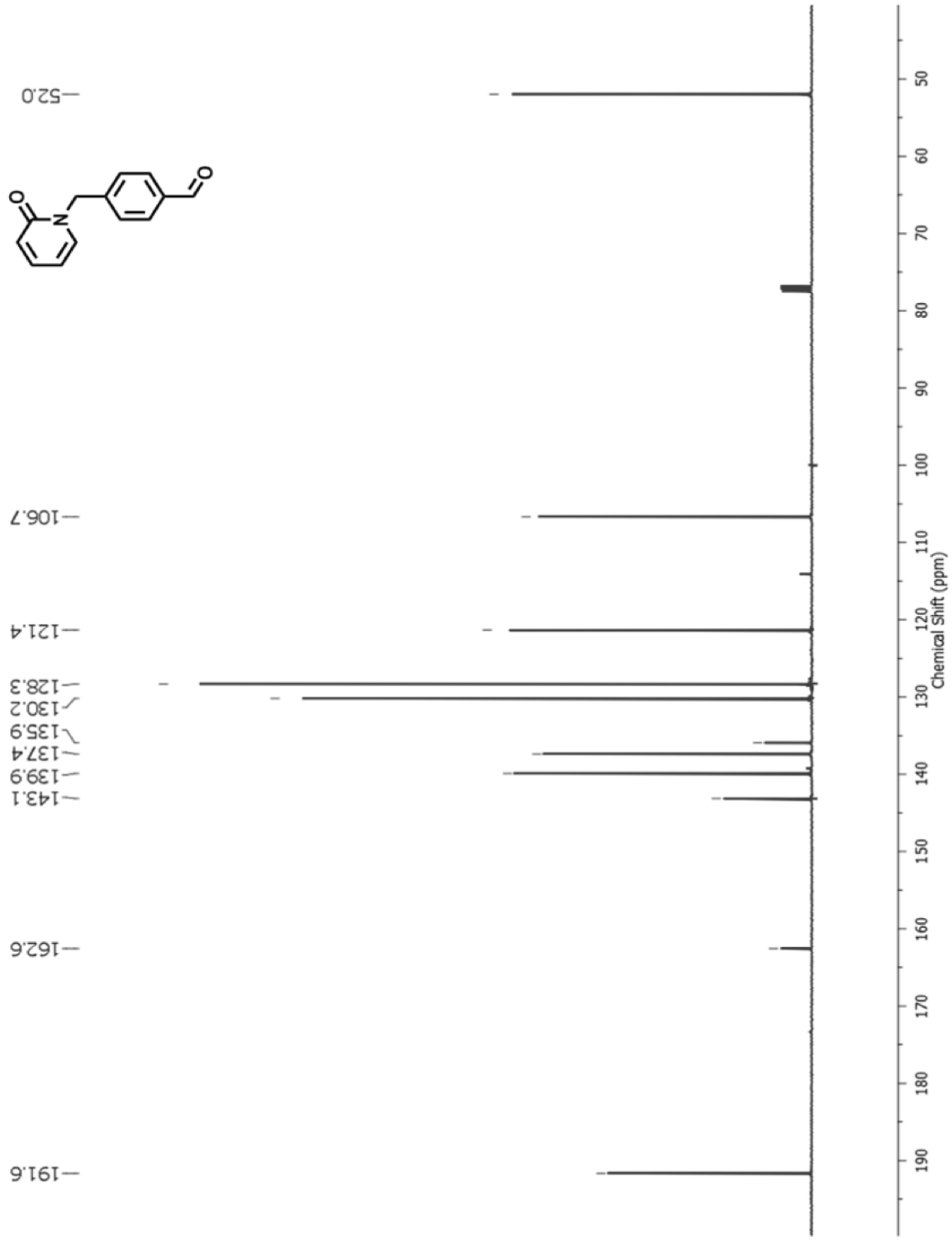



Figure S32: $^{13}C$ NMR of compound **4** in $CDCl_3$.

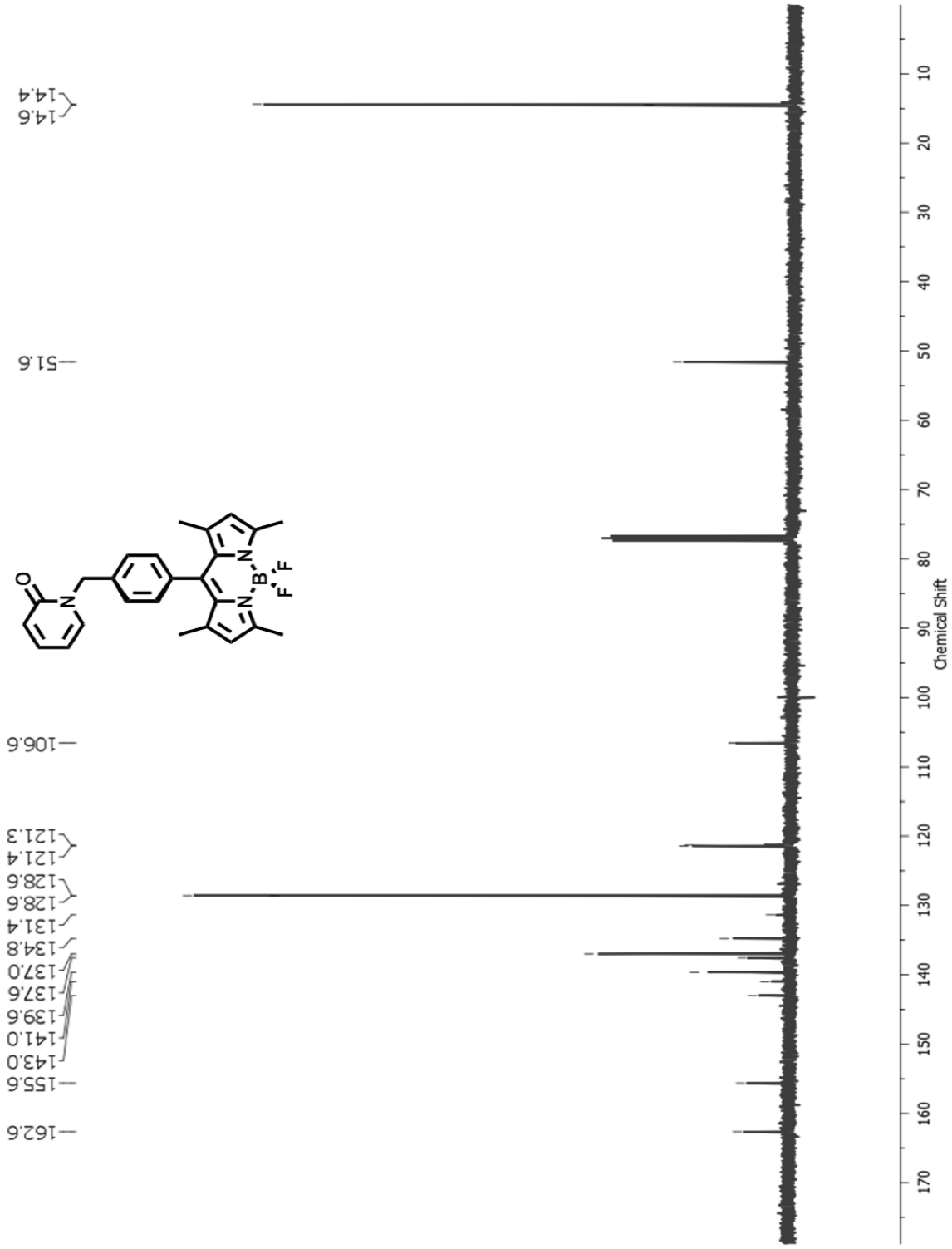



Figure S33: $^{13}C$ NMR of compound **5** in $CDCl_3$.

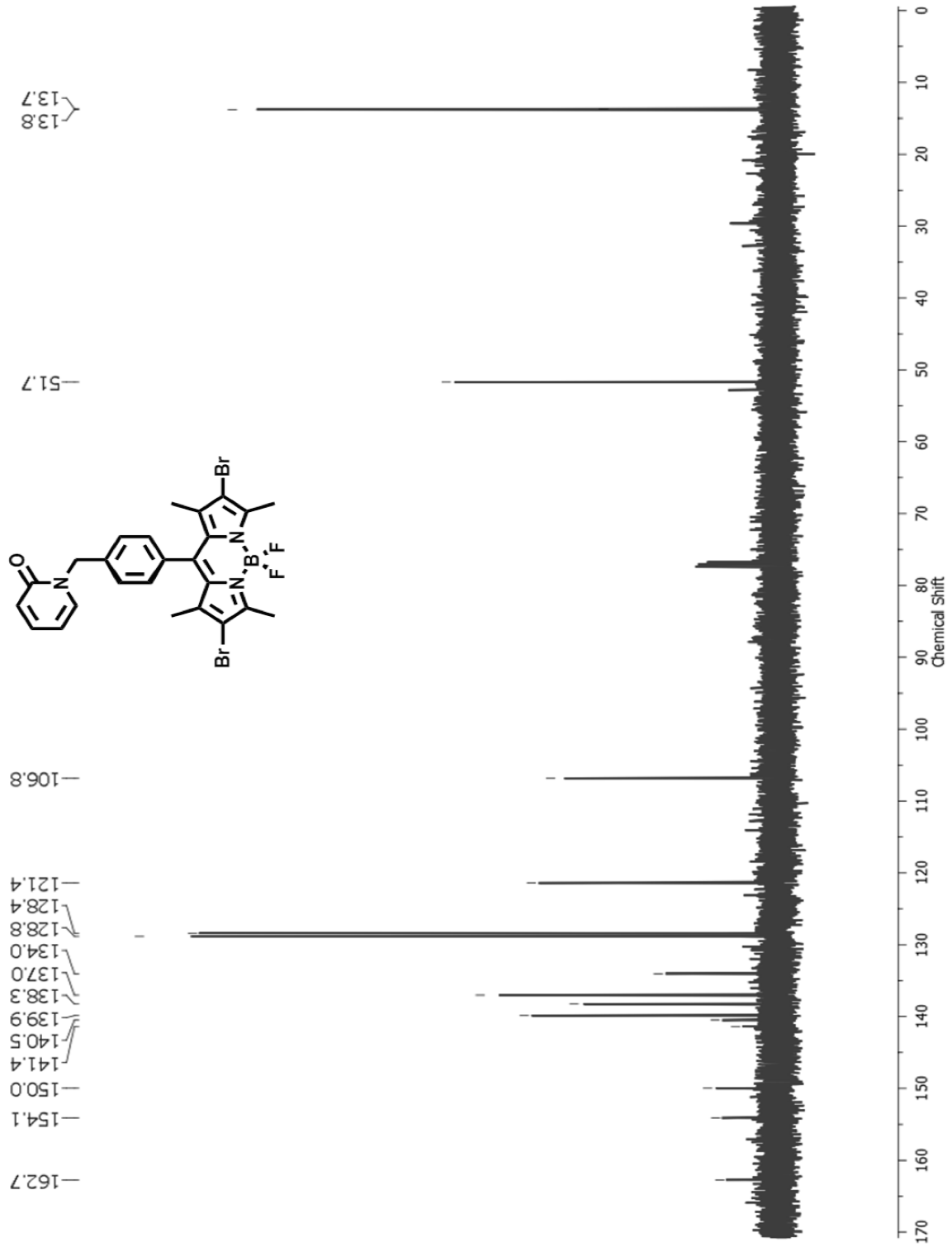



Figure S34: $^{13}C$ NMR of compound **6** in $CDCl_3$.

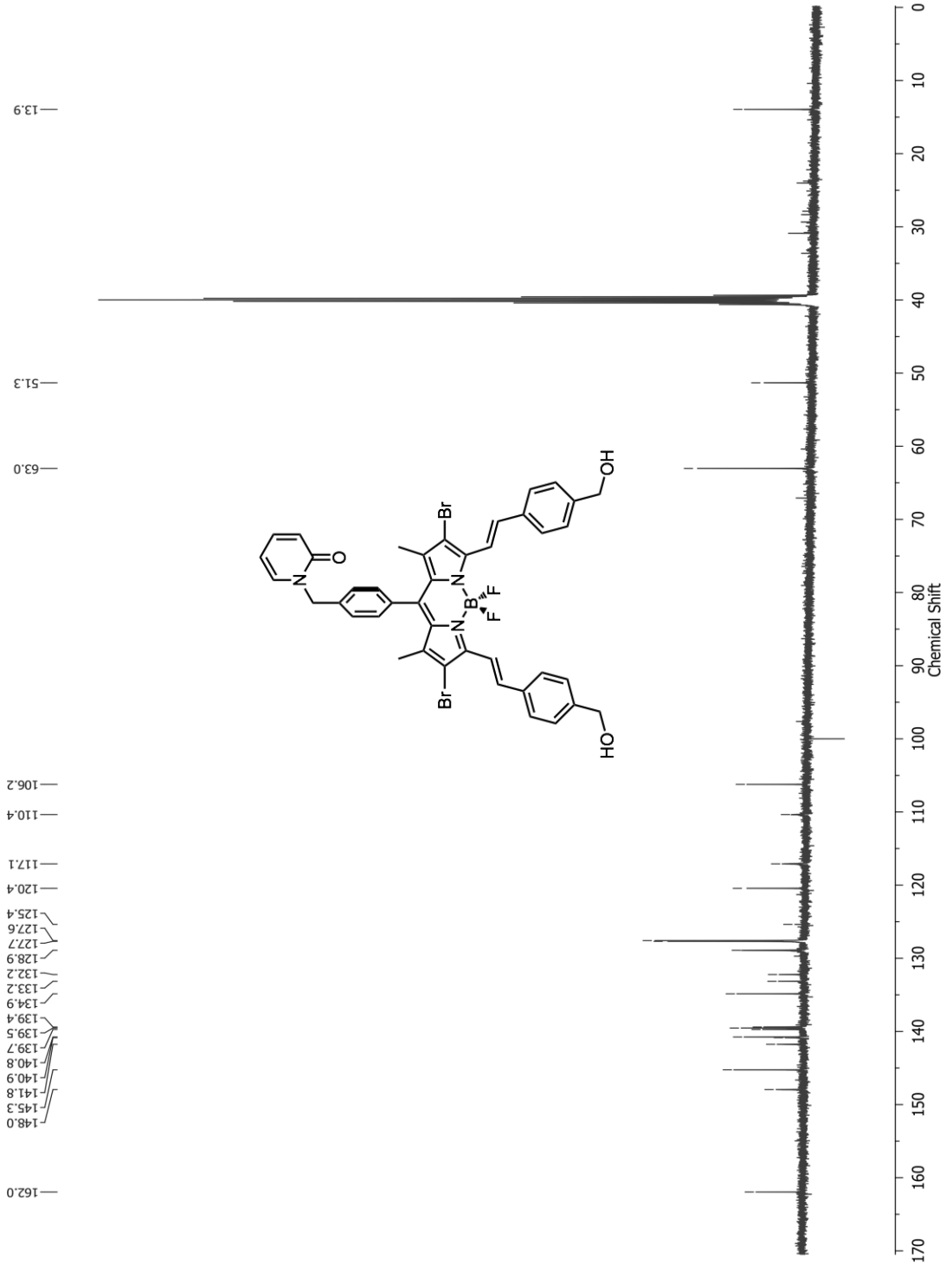



Figure S35: $^{13}C$ NMR of compound **7** in DMSO-$d_6$.

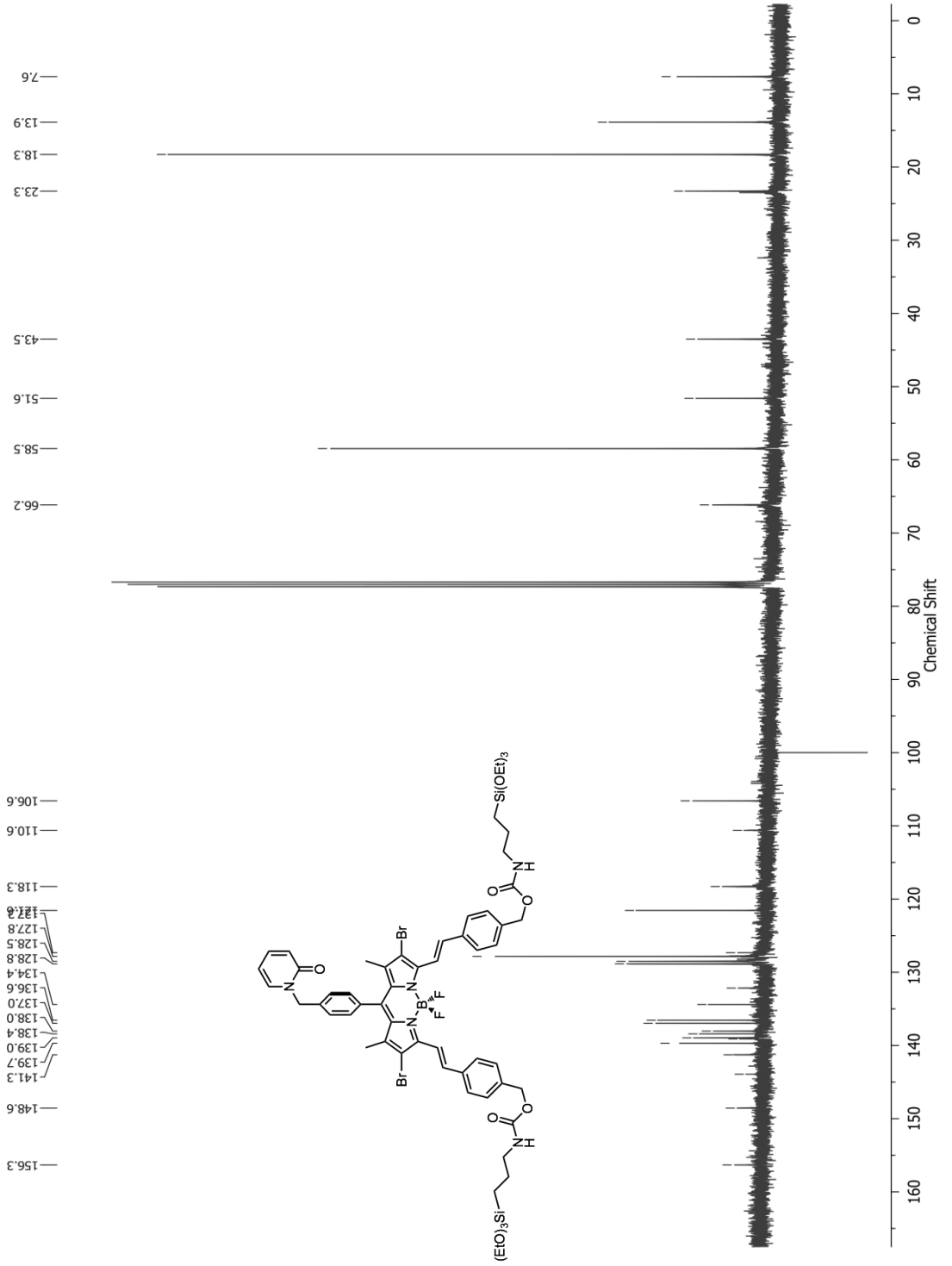



Figure S36 $^{13}C$ NMR of compound **8** in $CDCl_3$.

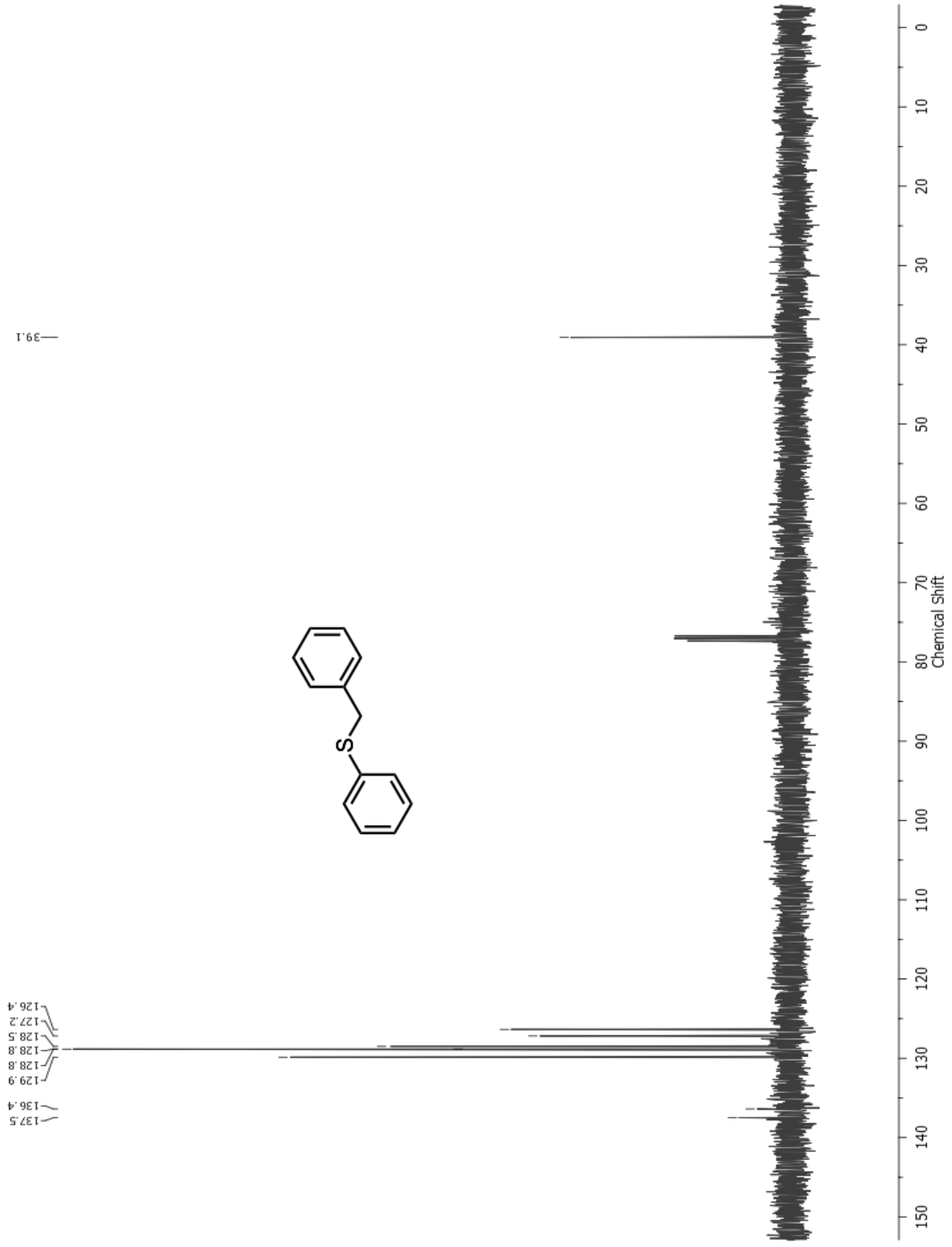



Figure S37: $^{13}C$ NMR of compound **12** in $CDCl_3$.

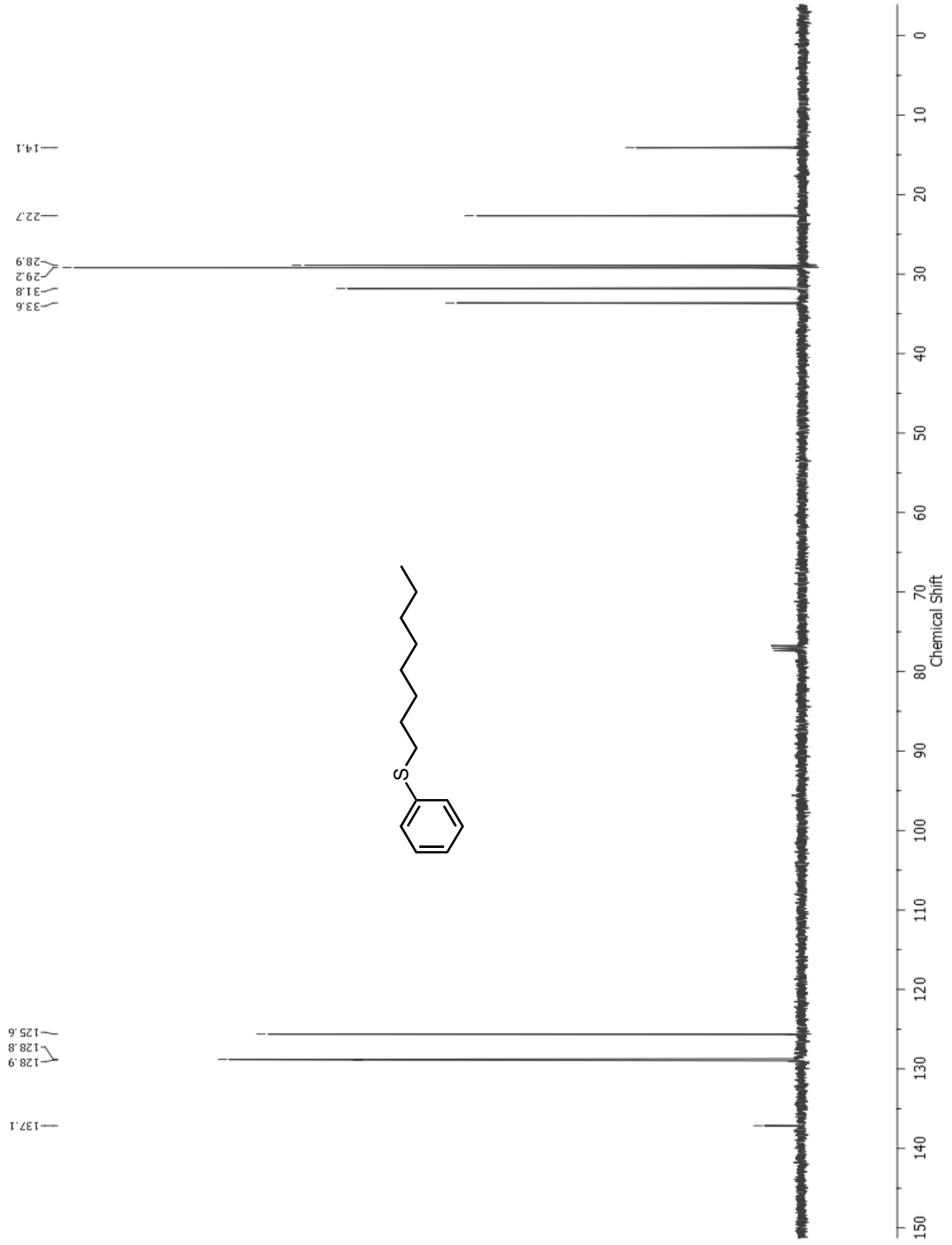



Figure S38: $^{13}C$ NMR of compound **13** in $CDCl_3$.

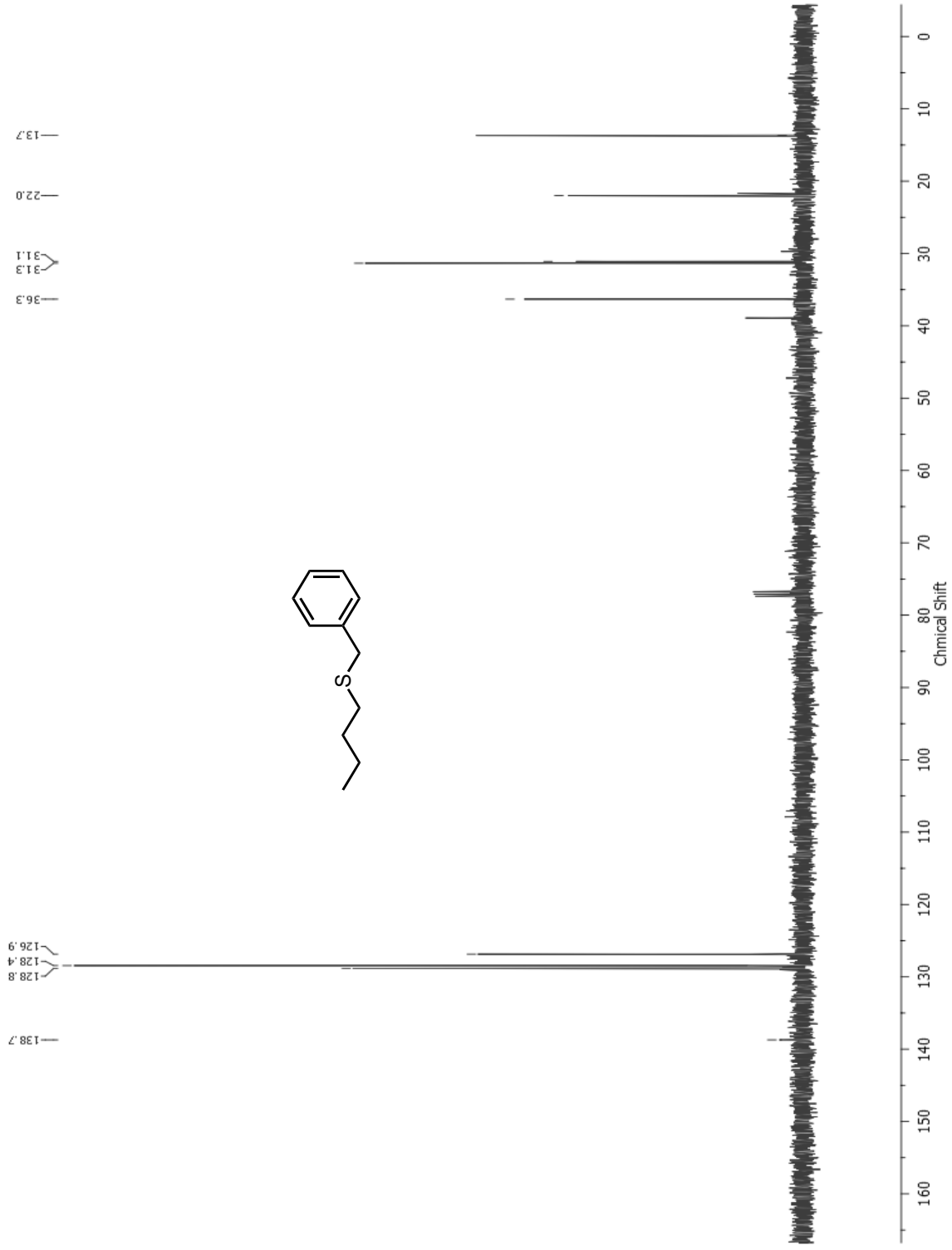



Figure S39: $^{13}C$ NMR of compound **14** in $CDCl_3$.

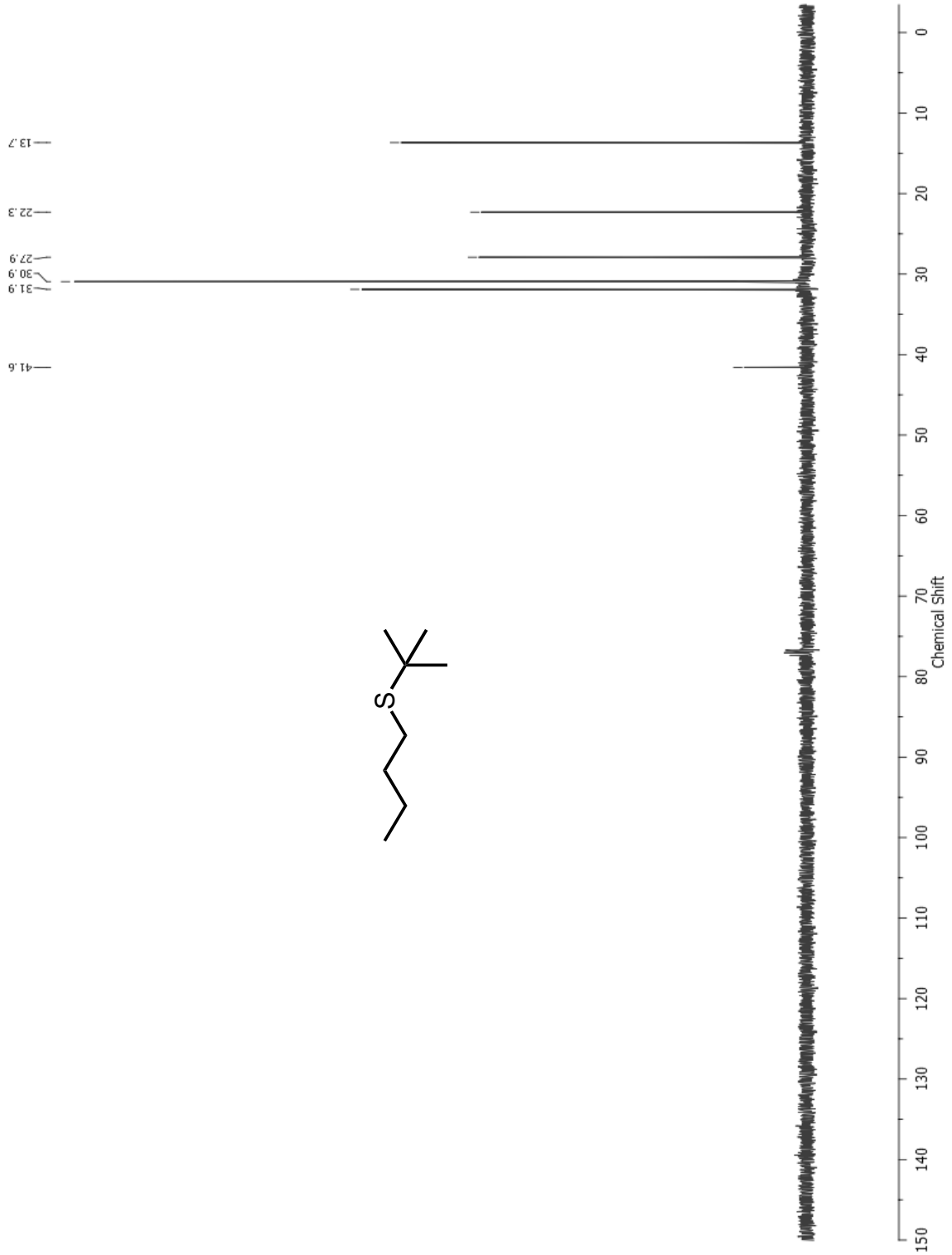



Figure S40: $^{13}C$ NMR of compound **15** in $CDCl_3$.

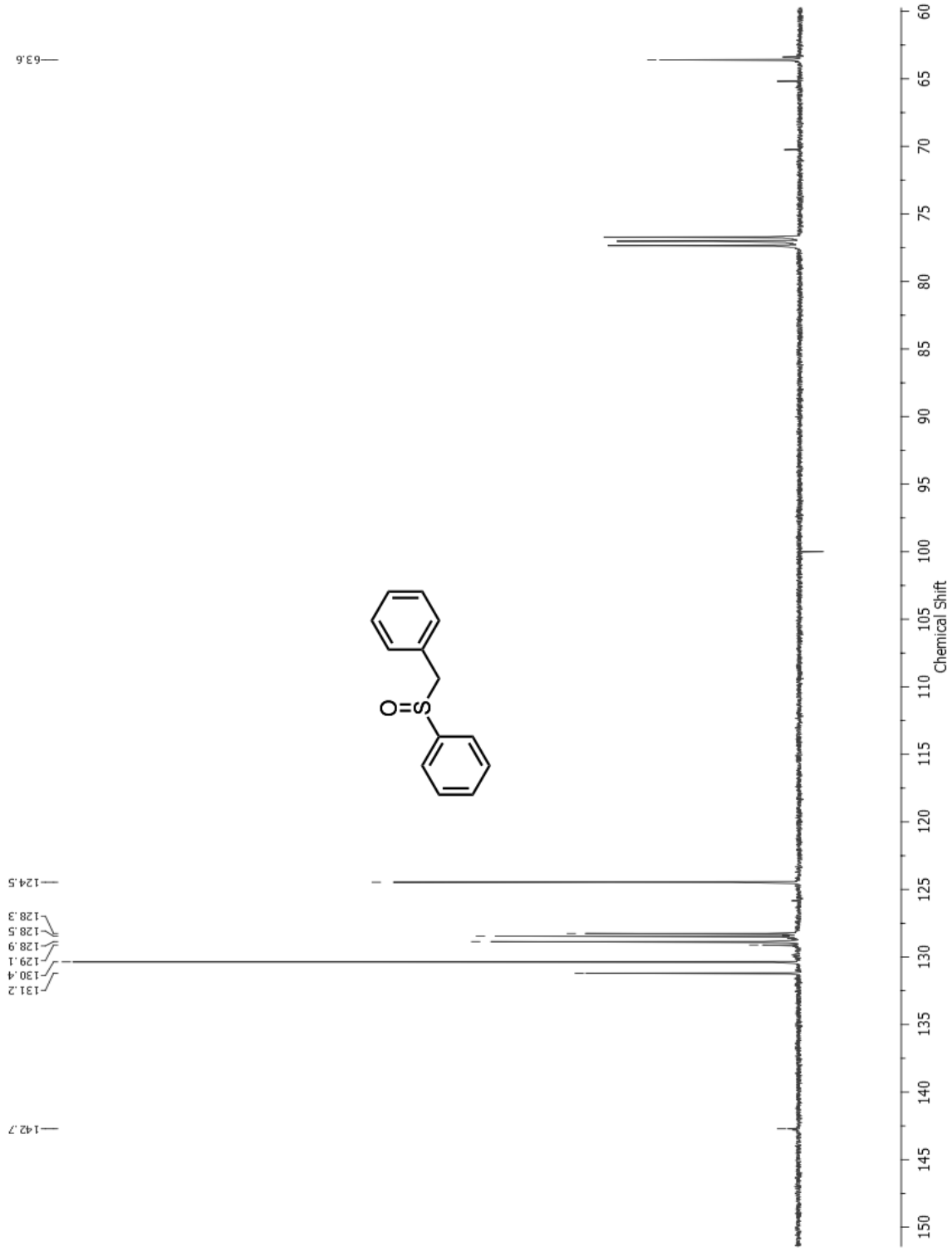



Figure S41: $^{13}C$ NMR of compound **12a** in $CDCl_3$.

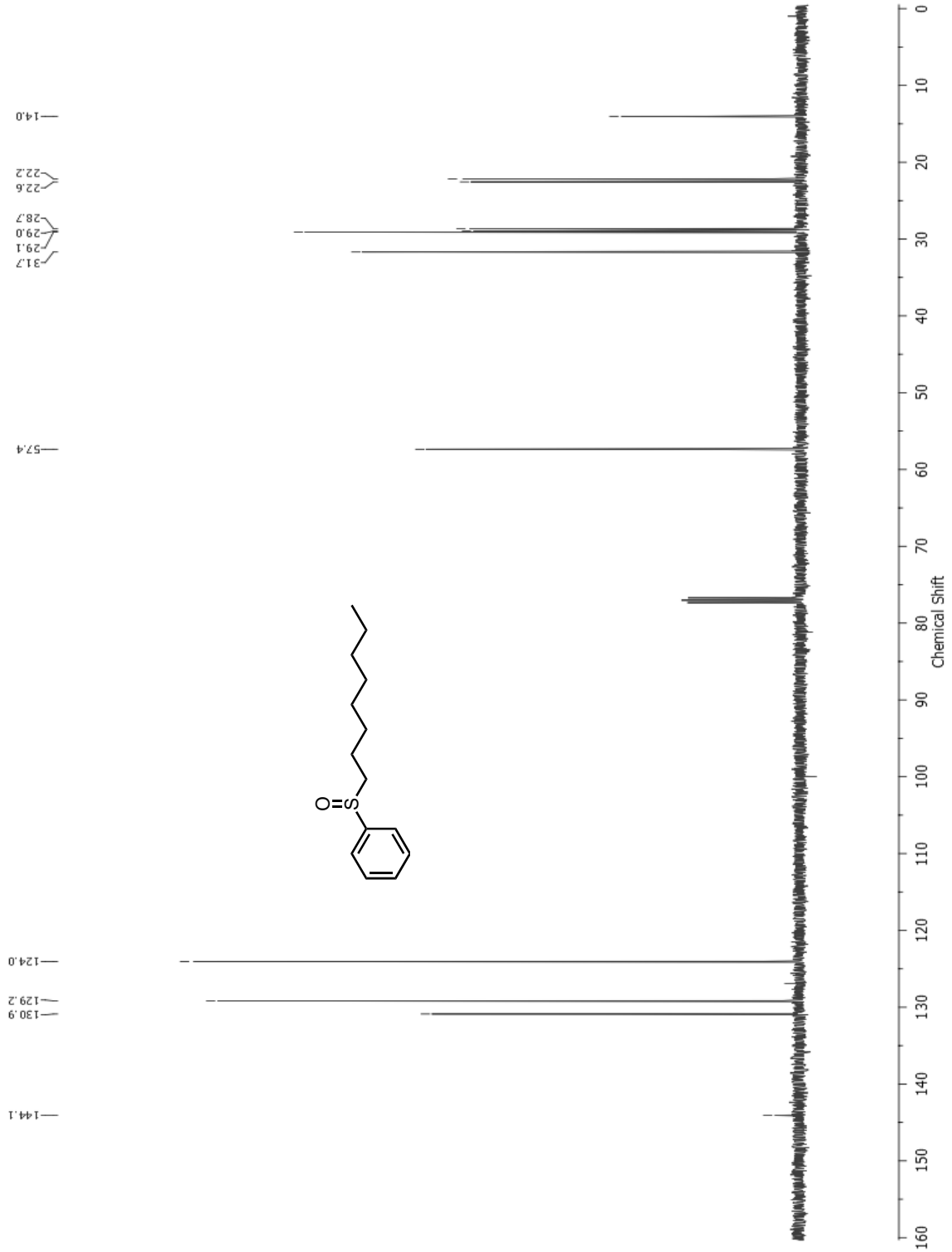



Figure S42: $^{13}C$ NMR of compound **13a** in $CDCl_3$.

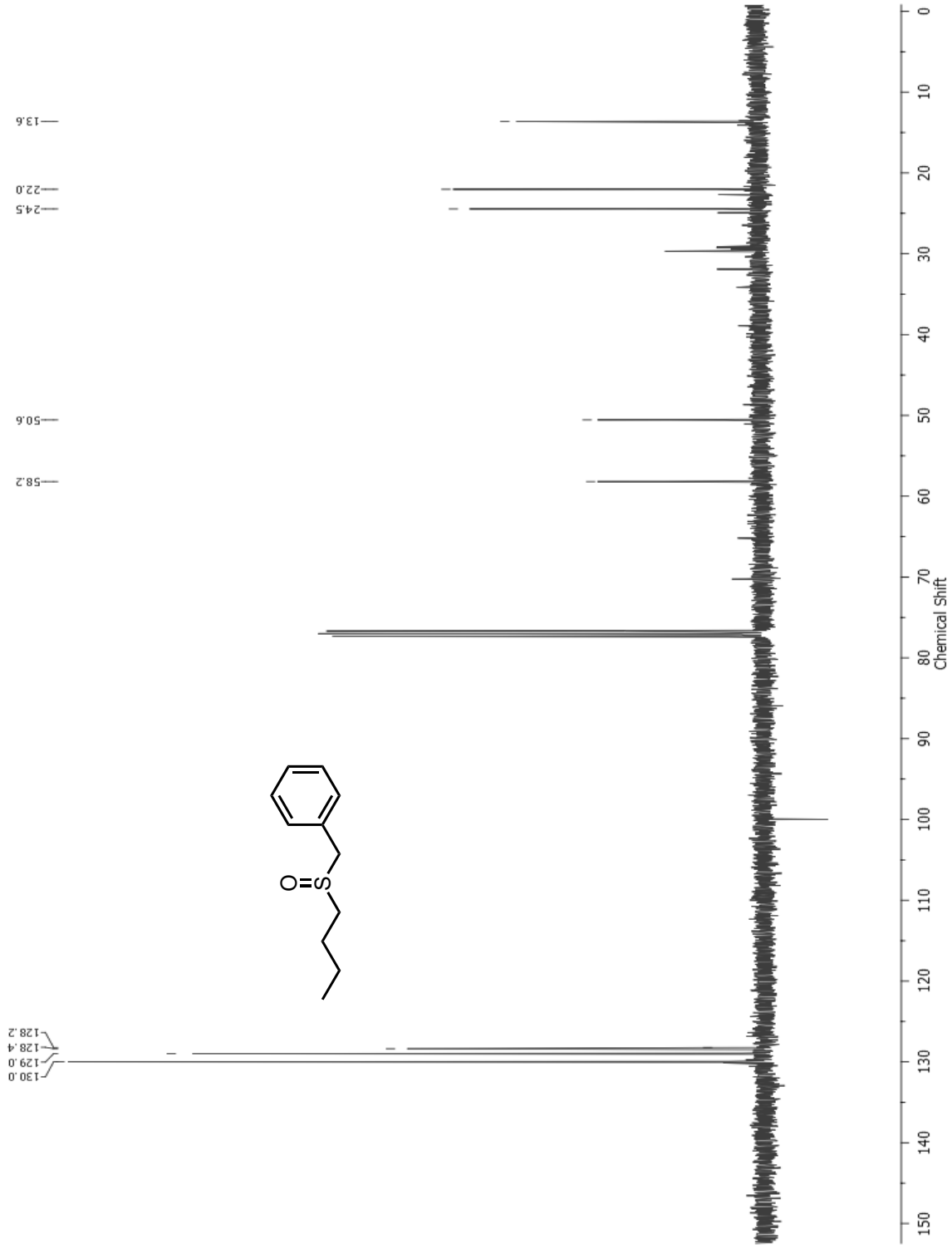



Figure S43: $^{13}C$ NMR of compound **14a** in $CDCl_3$.

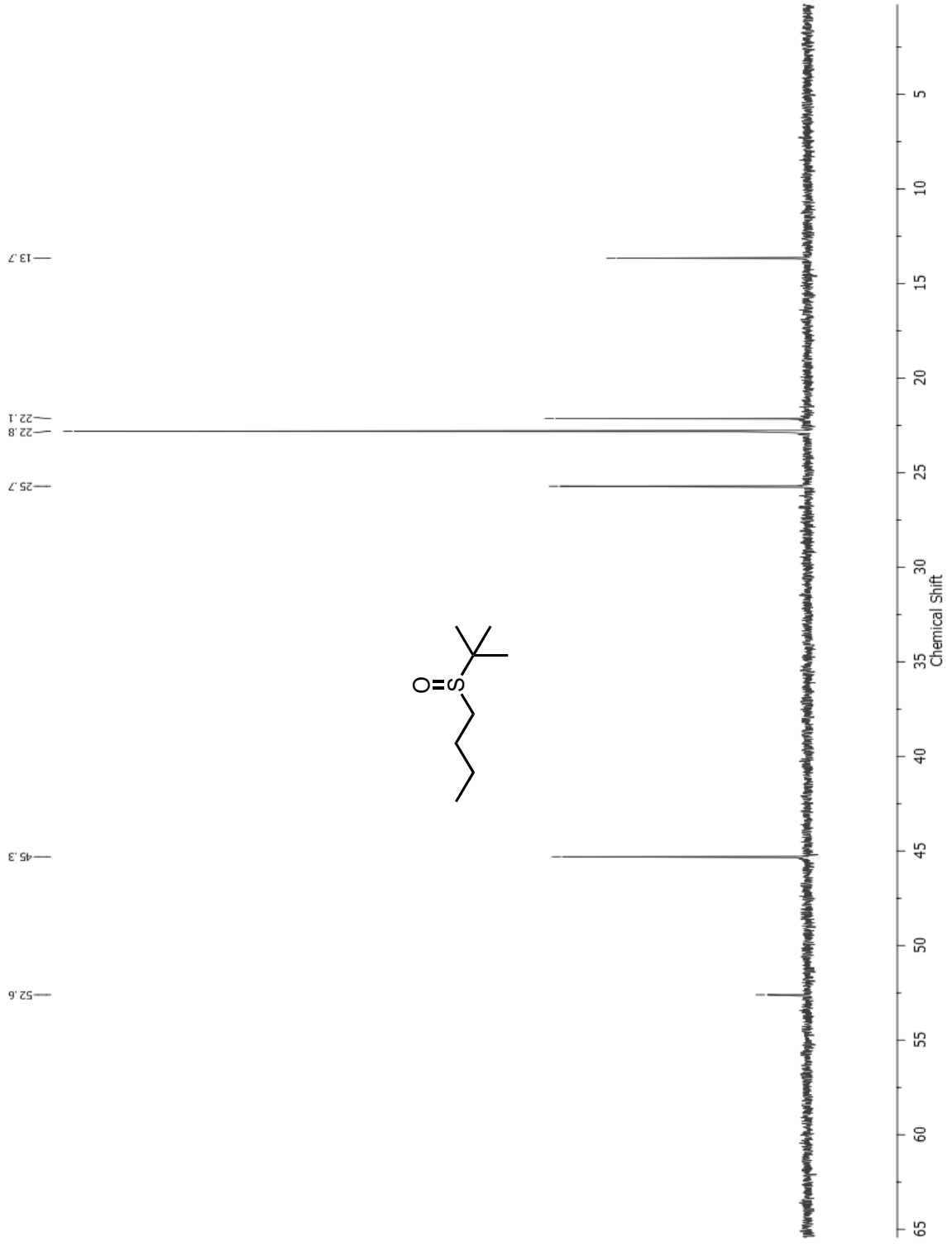



Figure S44: $^{13}C$ NMR of compound **15a** in $CDCl_3$.

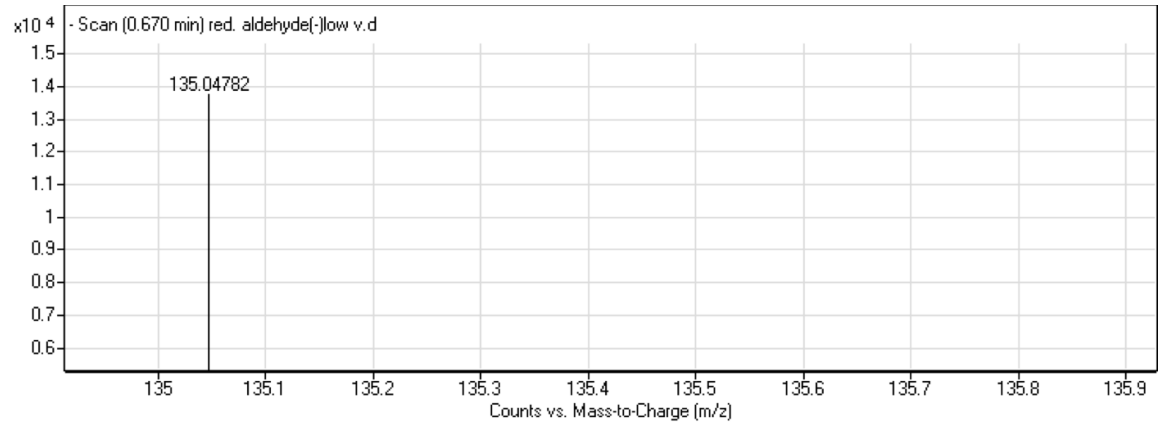



Figure S45: ESI - HRMS of compound **2**.

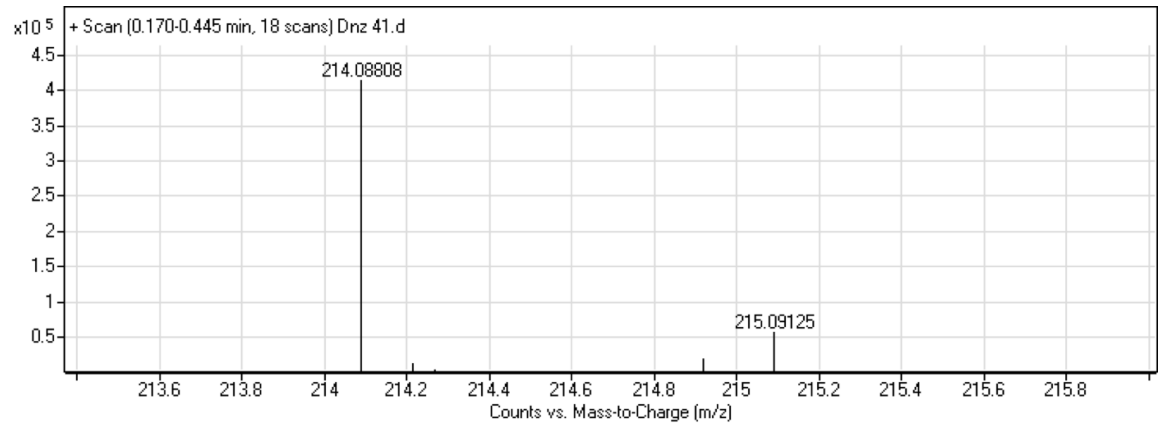



Figure S46: ESI - HRMS of compound **4**.

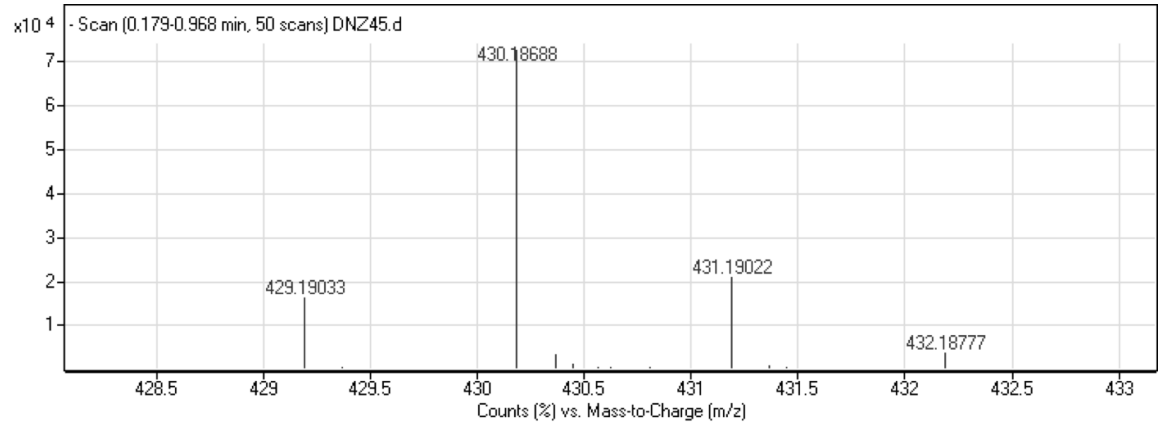



Figure S49: ESI - HRMS of compound **5**.

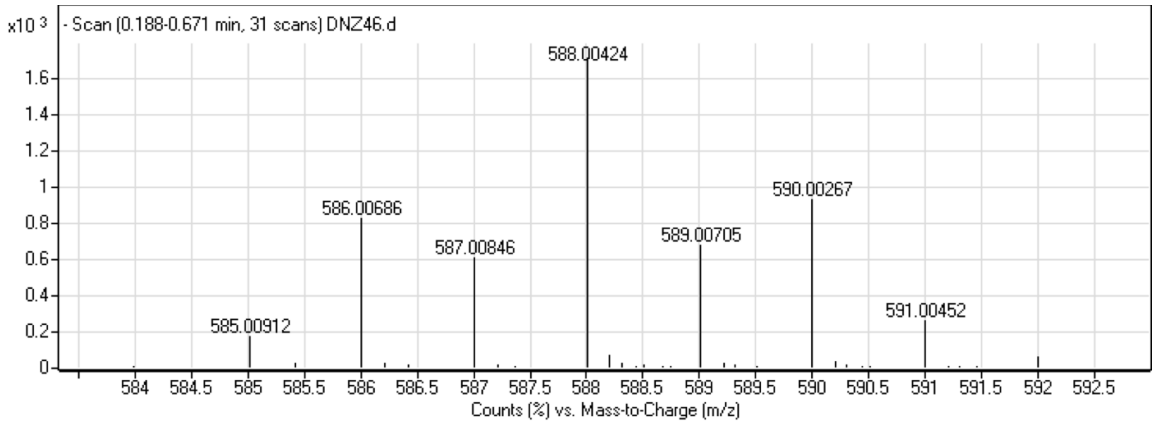



Figure S47: ESI - HRMS of compound **6**.

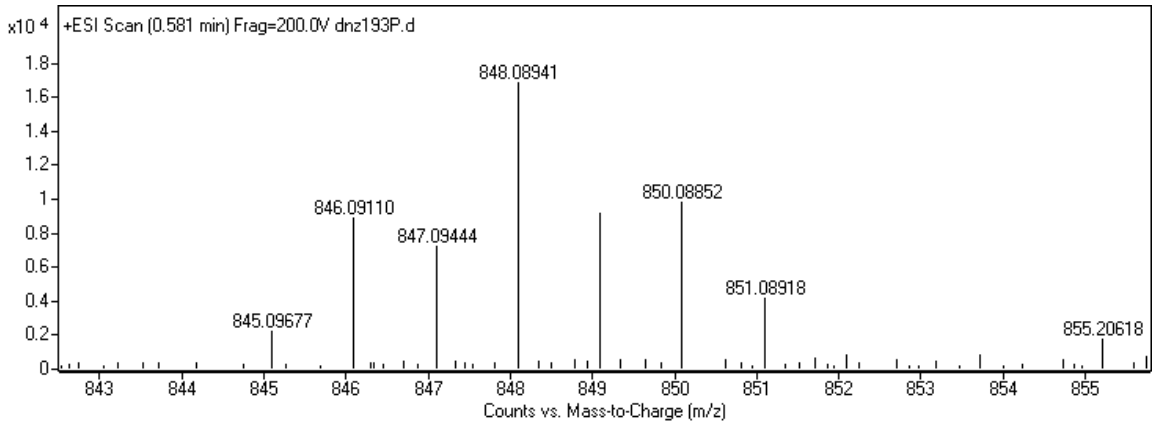



Figure S48: ESI - HRMS of compound **7**.

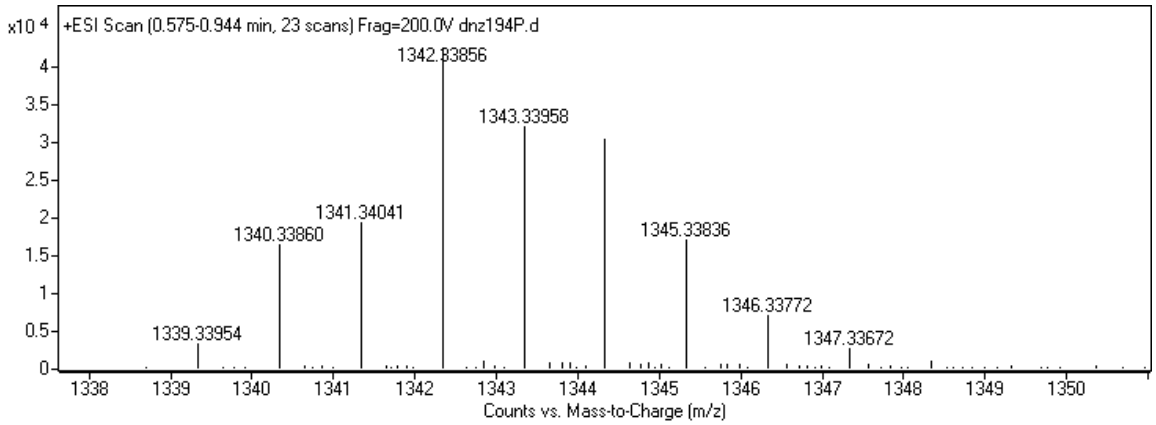



Figure S49: ESI - HRMS of compound **8**.

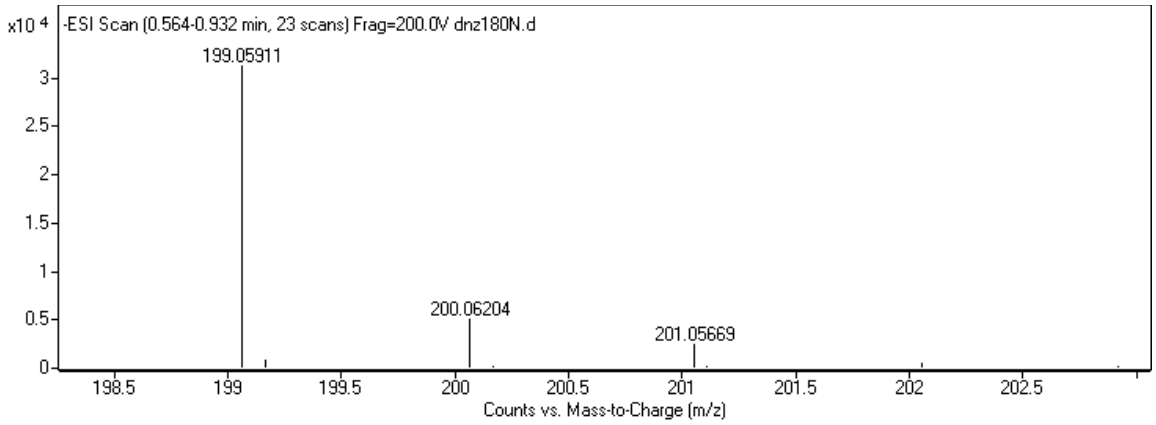



Figure S50: ESI - HRMS of compound **12**.

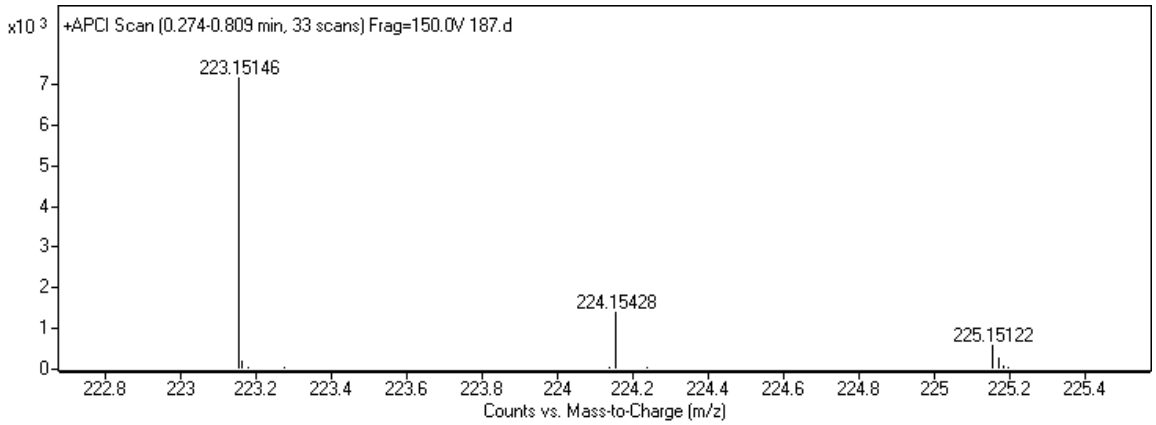



Figure S51: APCI - HRMS of compound **13**.

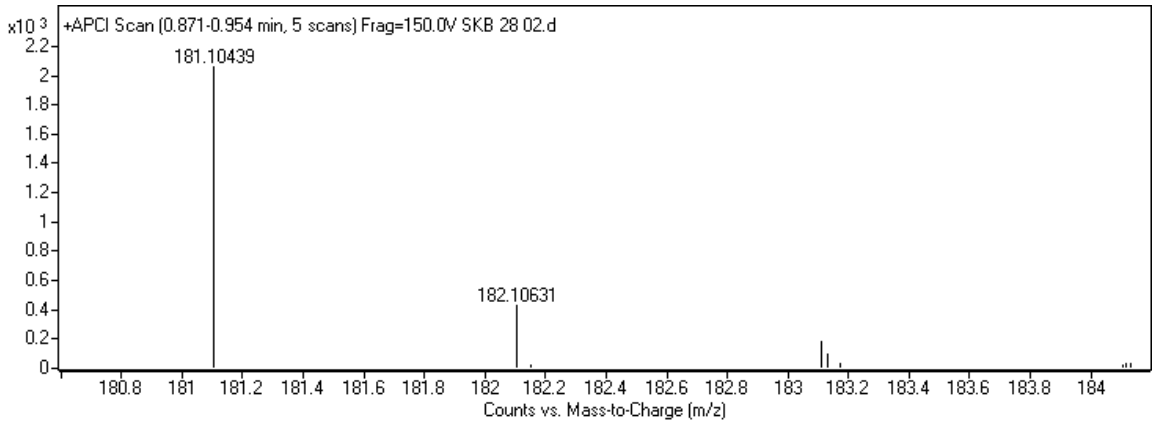



Figure S52: APCI - HRMS of compound **14**.

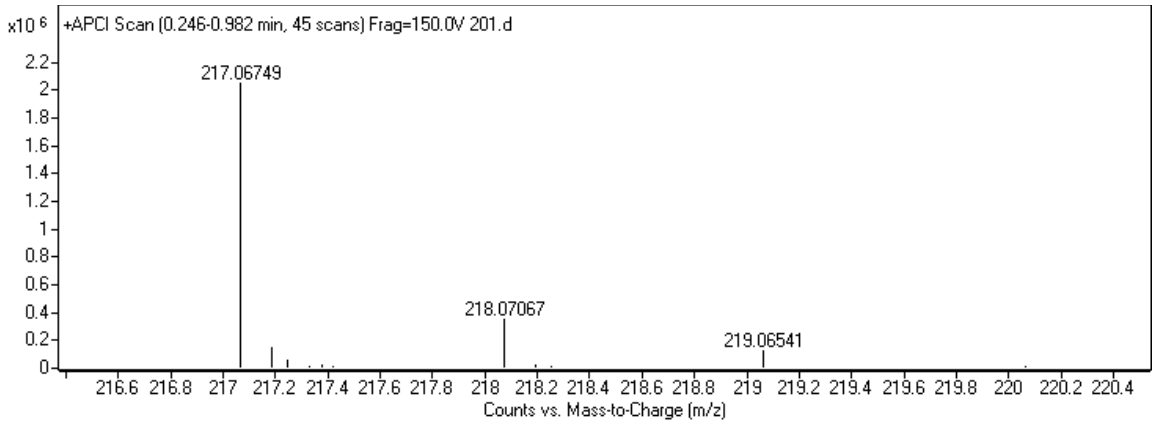



Figure S53: APCI - HRMS of compound **15**.

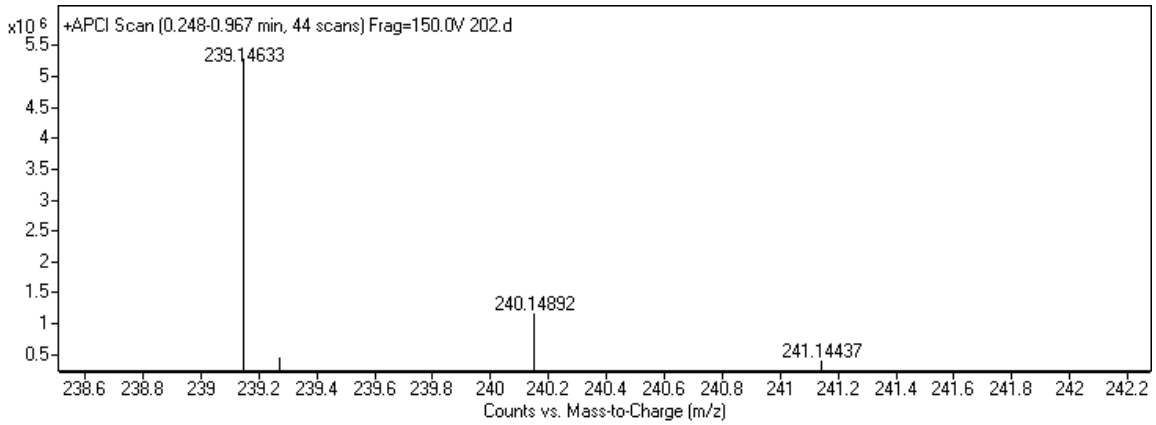



Figure S54: APCI - HRMS of compound **12a**.

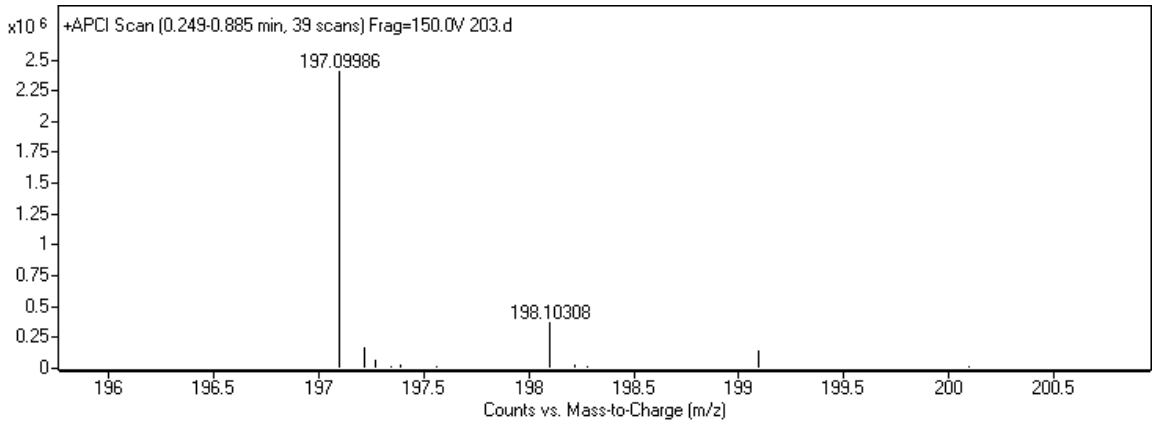



Figure S55: APCI - HRMS of compound **13a**.


Figure S56: APCI - HRMS of compound **14a**.

| | | | |
|---|---|---|---|
| **Sample Name:** | NP in etoh 3 | | |
| **SOP Name:** | mansettings.nano | | |
| **File Name:** | NP 13042017.dts | **Dispersant Name:** | ethanol |
| **Record Number:** | 3 | **Dispersant RI:** | 1,361 |
| **Material RI:** | 2,42 | **Viscosity (cP):** | 1,2000 |
| **Material Absorbtion:** | 0,00 | **Measurement Date and Time:** | 13 Nisan 2017 Perşembe 11:41:40 |
| **Temperature (°C):** | 25,0 | **Duration Used (s):** | 80 |
| **Count Rate (kcps):** | 161,1 | **Measurement Position (mm):** | 4,65 |
| **Cell Description:** | Glass cuvette with square aperture | **Attenuator:** | 7 |

| | | **Diam. (nm)** | **% Number** | **Width (nm)** |
|---|---|---|---|---|
| **Z-Average (r.nm):** | 94,41 | **Peak 1:** | 62,24 | 100,0 | 15,70 |
| **PdI:** | 0,171 | **Peak 2:** | 0,000 | 0,0 | 0,000 |
| **Intercept:** | 0,924 | **Peak 3:** | 0,000 | 0,0 | 0,000 |

**Result quality :** Good

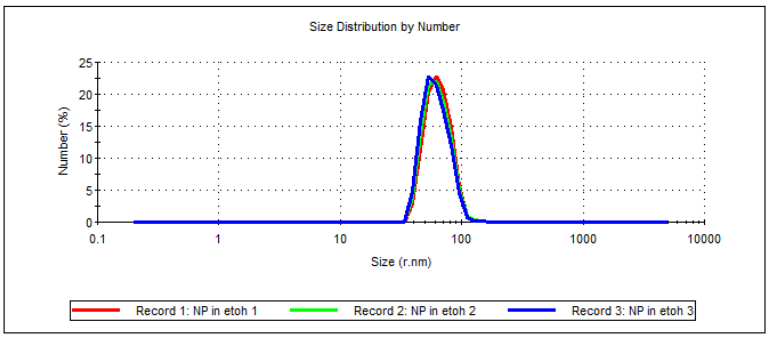



Figure S57: Size Distribution of BODIPY functionalized silica coated SPIONs (**10**) in EtOH.