

Supporting Information

Photoinduced copper-catalyzed three-component alkylarylation of alkenes involving C-S bonds cleavage of sulfonium salts

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1. General Information

Unless otherwise stated, all commercial reagents were used as received. Carboxylic acid (BK, 99%), benzaldehyde (Innochem, >98%) were used without further treatment. All reagents and solvents were commercially available and used without any further purification unless specified. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (0.25mm, 300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 0.25mm 300-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). All reactions were carried out with magnetic stirring and in dried glassware. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^1H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded in CDCl_3 on a Bruker DRX-400 spectrometer operating at 400 MHz, 376 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. The solvent peak was used as a reference value, for ^1H NMR: TMS = 0.00 ppm, for ^{13}C NMR: CDCl_3 = 77.00 ppm. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet, and br = broad. High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

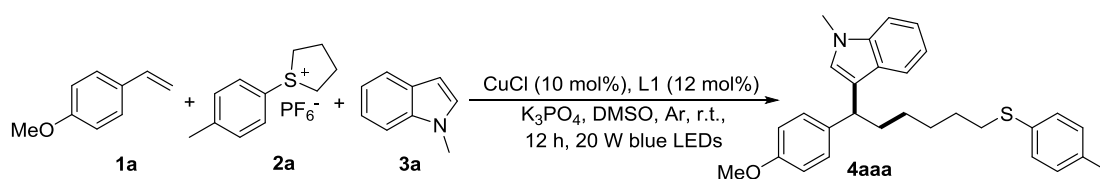
2. Experiment Section

2.1 General Procedure for the Synthesis of Substrates

General procedure for synthesis of **2a**.

Sulfonium salt **2a**^[1] were synthesized according to the known methods.

2.2 Typical Experimental Procedure



To a schlenk tube were added 1-methoxy-4-vinylbenzene **1a** (0.2 mmol, 26.8 mg),

sulfonium salt **2a** (2 equiv., 0.4 mmol, 129.6 mg), 1-methyl-1*H*-indole **3a** (0.6 mmol, 78.6 mg), K₃PO₄ (3 equiv., 0.6 mmol, 127.4 mg), CuCl (10 mol%, 2.0 mg), **L1** (12 mol%, 16.3 mg) and DMSO (2 mL). Then the tube was stirred at room temperature in Ar atmosphere for the indicated time until complete consumption of starting material as monitored by TLC analysis. The residue was purified by silica gel flash column chromatography (petroleum ether/ethyl acetate = 15 : 1) to afford the desired products.

2.3 Additional experimental details

The light source bought from SANYI (https://item.taobao.com/item.htm?_u=u10503hgcbel&id=597700668537&spm=a1z09.2.0.0.1f8a2e8dVdegb2&skuId=4812351826113), 35 W blue LED light bulb (E27). The wavelength was about 400-440 nm and the wavelength of peak intensity was about 465.0 nm. The picture of the visible-light source (Figure S1) was shown as follow:

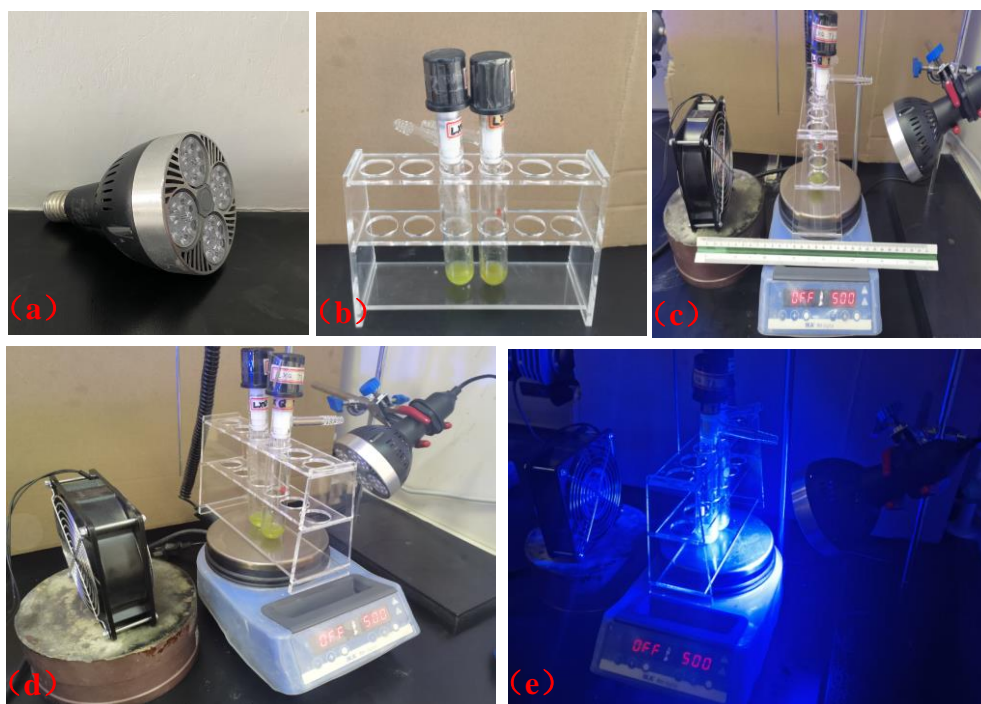
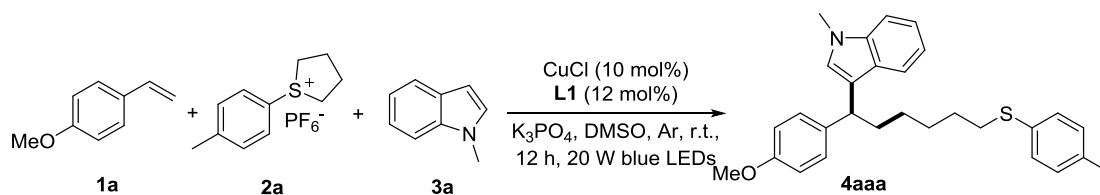


Figure S1. The light source and photographs of experimental setup: (a) 20 W blue LEDs. (b) Irradiation vial; (c) The distance from the Blue LED to the vial. (d) and (e) Reaction setup.

2.4 The Light On/Off Experiments



Time/h	0	4 (on)	8 (off)	12 (on)	16 (off)	20 (on)
Yield/%	0	25	25	58	58	73

The above depicted reaction was performed according to the general protocol established. The reaction was irradiated with 20W blue LEDs for 12 hour and then stirred in the dark for 8 hour. This procedure was repeated for 20 hours, and the yield of the product was determined by ¹H NMR with dibromomethane as an internal standard at each point the light was turned off or on. The results are shown in the graph above. This result shows that constant light irradiation is needed to progress the reaction.

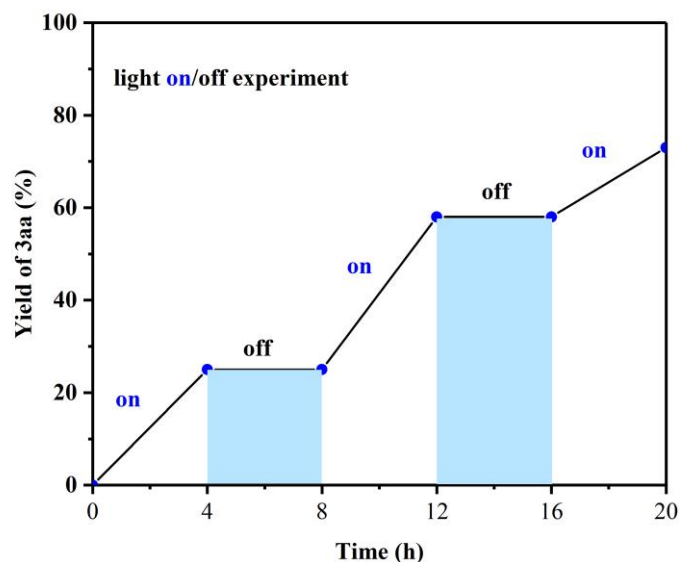


Figure S2 The light on/off Experiments

2.5 Stern-Volmer quenching experiments

Formulation solution: 1-methoxy-4-vinylbenzene **1a** (6.70 mg) was dissolved in DMSO in a 5 mL volumetric flask to set the concentration to be 0.01 M. Sulfonium salt **2a** (8.95 mg) was dissolved in DMSO in a 5 mL volumetric flask to set the

concentration to be 0.01 M. 1-methyl-1*H*-indole **3a** (6.55 mg) was dissolved in DMSO in a 5 mL volumetric flask to set the concentration to be 0.01 M. Catalyst CuCl (4.95 mg) and TolBINAP (33.9 mg) were dissolved in DMSO (5.0 mL) to set the concentration to be 0.01 M. The picture of the Stern-Volmer quenching experiments (Figure S3) was shown as follow:

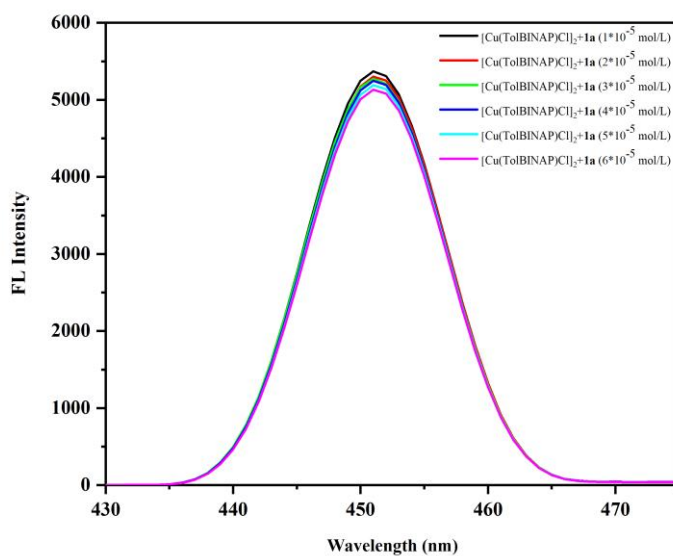


Figure S3 (a) $[\text{Cu}(\text{TolBINAP})\text{Cl}]_2$ quenched by **1a** in DMSO

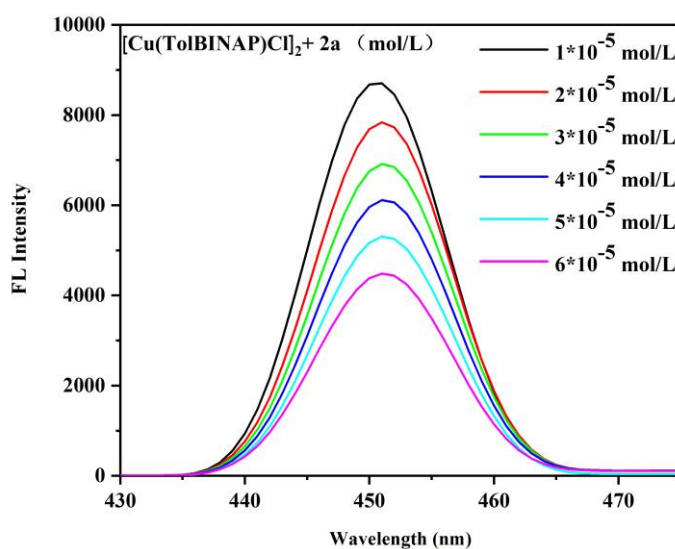


Figure S3 (b) $[\text{Cu}(\text{TolBINAP})\text{Cl}]_2$ quenched by **2a** in DMSO

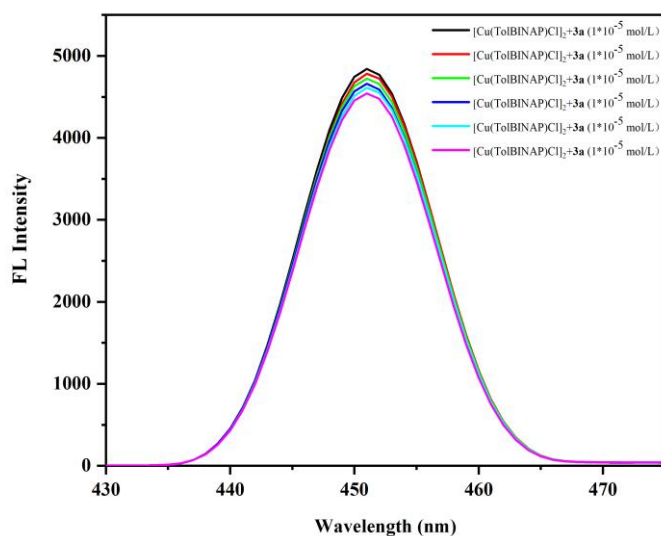


Figure S3 (c) $[\text{Cu}(\text{TolBINAP})\text{Cl}]_2$ quenched by 3a in DMSO

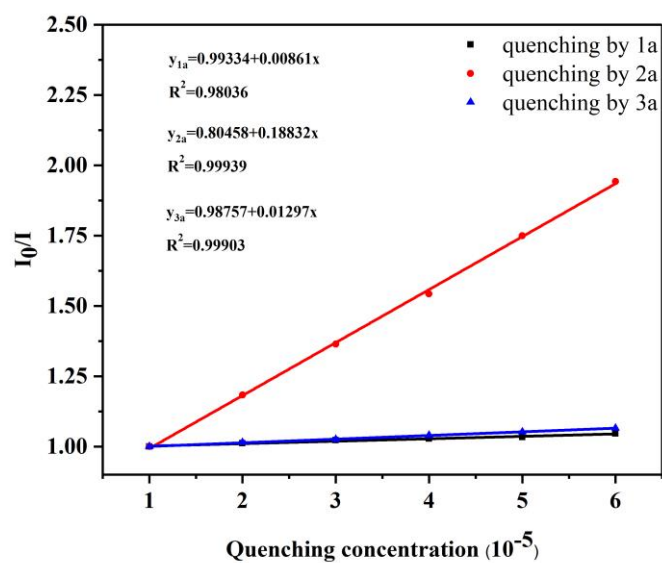


Figure S3 (d) Stern-Volmer plot of photocatalyst at different concentration

Additional experimental details: The samples were prepared by the copper-based photocatalyst $[\text{Cu}(\text{TolBINAP})\text{Cl}]_2$ (5×10^{-4} M) with different amount of quencher 1a in DMSO in a light path quartz fluorescence cuvette. The concentration of quencher 1a is 0.01 M in DMSO. For each S3 quenching experiment, 3 μL of quencher solution was separately titrated to the copperbased photocatalyst $[\text{Cu}(\text{TolBINAP})\text{Cl}]_2$ (3.0 mL).

The resulting mixture was sparged with nitrogen for 3 minutes and then irradiated at 450 nm. Fluorescence emission spectra were recorded (3 trials per sample). Into this solution, 3.0 μL of a 1-methoxy-4-vinylbenzene **1a** solution was successively added and uniformly stirred, and the resulting mixture was bubbled with nitrogen for 3 minutes and irradiated at 450 nm. Fluorescence emission spectra of 3.0 μL , 6.0 μL , 9.0 μL , 12.0 μL , 15.0 μL , 18.0 μL fluorescence intensity. Follow this method and make changes to the amount to obtain the Stern–Volmer relationship in turn.

Compared the figure S3 (a) of Stern-Volmer quenching experiments results, the emission intensity of the copperbased photocatalyst $[\text{Cu}(\text{TolBINAP})\text{Cl}]_2$ solution strongly affected by the gradual increase of the amount of **2a**, and the influence is not observed to **1a** and **3a**. These indicated that the single electron transfer (SET) process occurred in photocatalyst and sulfonium salt.

2.6 UV-Vis absorption experiments

UV-visible spectroscopy of reaction solution was recorded on a UV-2600 UV-Vis spectrophotometer. The sample was prepared by 1-methoxy-4-vinylbenzene **1a** (10^{-4} M), sulfonium salt **2a** (10^{-4} M), 1-methyl-1*H*-indole **3a** (10^{-4} M), CuCl (10^{-4} M), Tol-BINAP (10^{-4} M), $[\text{Cu}(\text{TolBINAP})\text{Cl}]_2$ (10^{-4} M) in DMSO. The absorption was collected and the result was listed in Figure S4.

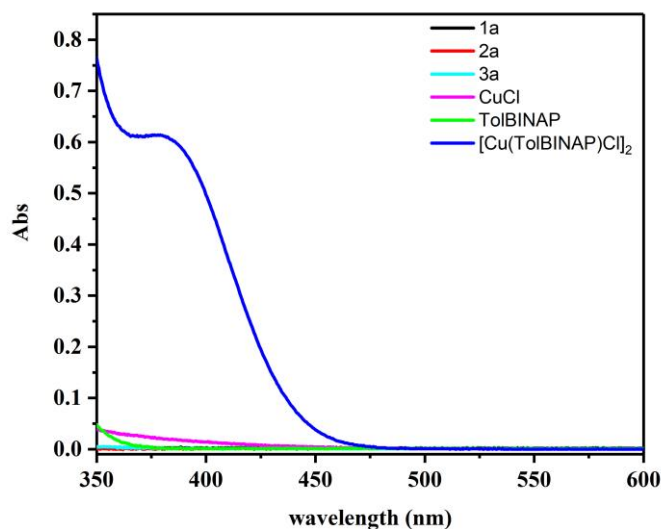


Figure S4 UV-Vis absorption experiments

2.7 Cyclic Voltammetry (CV) Experiments

Cyclic voltammetry was performed on a “computer-controlled CH Instrument Electrochemical Analyzer [CHI760E]” in a three-electrode cell connected to a schlenk line under argon at room temperature. The working electrode was a glassy carbon electrode (length: 80 mm, diameter: 3 mm), the counter electrode was a platinum wire (length: 37 mm, diameter: 0.5 mm, surface area: 0.59 cm²). The electrode was polished with figureeightS34motions on a cloth polishing pad in a water-alumina slurry. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution, and separated from the reaction by a salt bridge. 6 mL DMSO containing 0.1 M ⁿBu₄NBF₄ were poured into the electrochemical cell in all experiments. For the cyclic voltammetric measurement, IUPAC convention was followed. The scan rate was 0.1 V/s. All solutions used for the voltametric experiments were deoxygenated by purging with high purity argon gas up to 5 mins and measurements were performed in open air at room temperature (25 ± 2 °C).

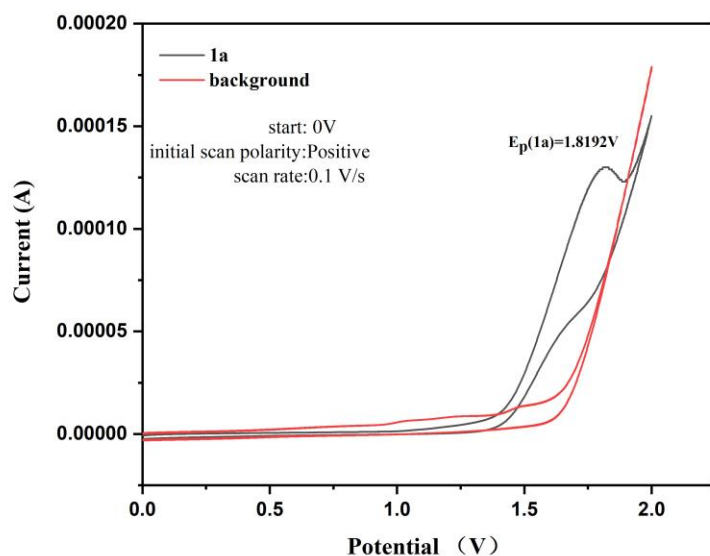


Figure S5 CV spectra of 1a (0.008 M) in 0.1 M tetrabutylammonium tetrafluoroborate in DMSO. Ep = 1.8129 V (vs. Ag/AgCl)

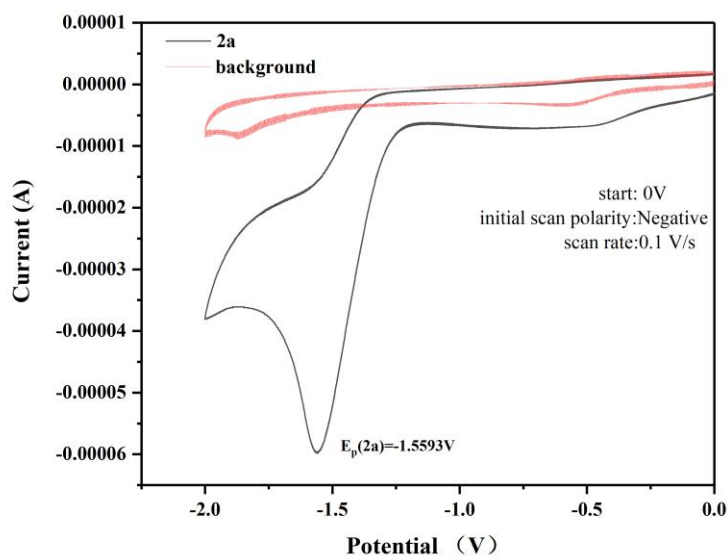


Figure S6 CV spectra of 2a (0.008 M) in 0.1 M tetrabutylammonium tetrafluoroborate in DMSO. $E_p = -1.5593\text{ V}$ (vs. Ag/AgCl)

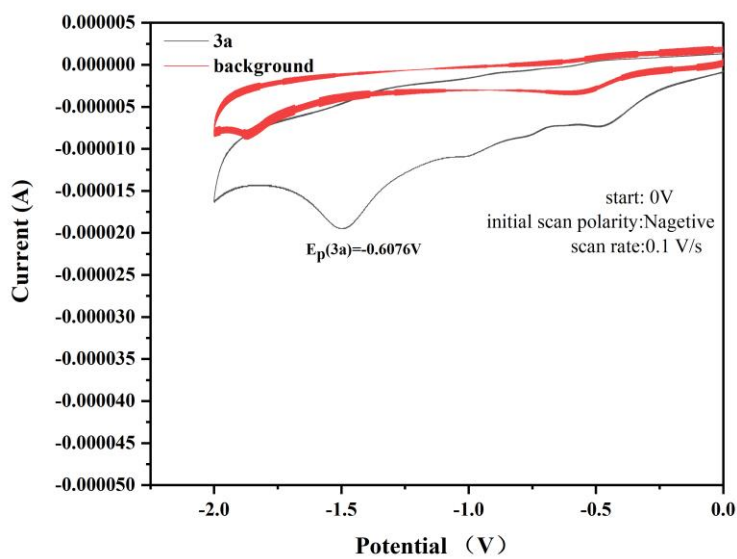


Figure S7 CV spectra of 3a (0.008 M) in 0.1 M tetrabutylammonium tetrafluoroborate in DMSO. $E_p = -0.6076\text{ V}$ (vs. Ag/AgCl)

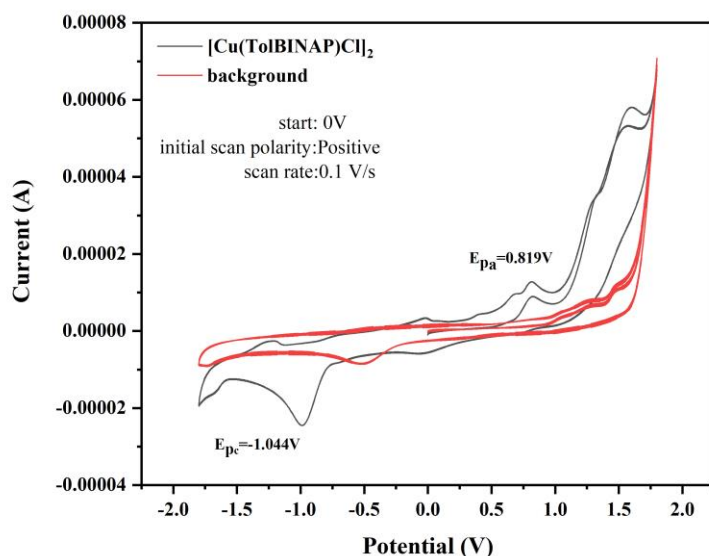


Figure S8 CV spectra of the copper-based photocatalyst [Cu(TolBINAP)Cl]₂ (1 mM) in 0.01 M tetrabutylammonium tetrafluoroborate in DMSO.

According to the emission spectra of the copper-based photocatalyst [Cu(TolBINAP)Cl]₂, the maximum emission wavelength is 549 nm.

$$E_{1/2}(\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}) = 0.113\text{V}$$

$$E_{0,0} = h\nu = \frac{hc}{\lambda} = 2.26\text{V}$$

$$E_{1/2}(\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}*}) = E_{1/2}(\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}) - E_{0,0} = 0.113 - 2.26 = -2.147\text{V}$$

Where h (J·s) is Planck's constant, c (m s^{-1}) is the speed of light and λ (m) is the maximum emission wavelength.

2.8 Quantum yield determination

Determination of the light intensity at 415 nm:

According to the procedure of Yoon² the photon flux of the blue LED ($\lambda_{\text{max}} = 415$ nm) was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H₂SO₄. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H₂SO₄. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 3.0 mL of the ferrioxalate solution was placed in a cuvette and

irradiated for 90.0 seconds at $\lambda = 415$ nm with an emission slit width at 10.0 nm. After irradiation, 0.53 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A nonirradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq 1.

$$\text{mol of Fe}^{2+} = \frac{V \cdot \Delta A_{510\text{nm}}}{l \cdot \epsilon} \quad (1)$$

$$\text{mol of Fe}^{2+} = \frac{(0.00353\text{L}) \cdot (2.094 - 0.197)}{(1.00\text{cm}) \cdot (11100 \frac{\text{L}}{\text{mol}} \text{cm}^{-1})} = 6.03 \times 10^{-7}$$

Where V is the total volume (0.00353 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.00 cm), and ϵ is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 L mol⁻¹ cm⁻¹).³ The photon flux can be calculated using eq 2.

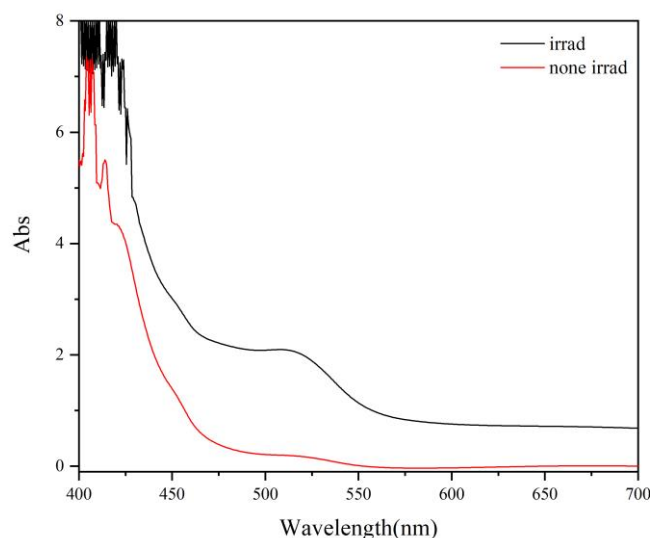
$$\text{Photo flux} = \frac{\text{mol of Fe}^{2+}}{\phi \cdot t \cdot f} \quad (2)$$

$$\text{Photo flux} = \frac{6.03 \times 10^{-7}}{(1.12) \cdot (90\text{s}) \cdot (0.999)} = 5.99 \times 10^{-9} \text{ einstein} / \text{s}$$

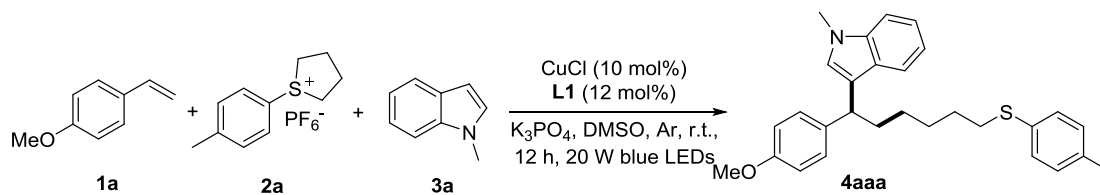
Where Φ is the quantum yield for the ferrioxalate actinometer (1.12 at $\lambda = 415$ nm), t is the time (90.0 s), and f is the fraction of light absorbed at 415 nm by the ferrioxalate actinometer. This value is calculated using eq 3 where $A_{415 \text{ nm}}$ is the absorbance of the ferrioxalate solution at 415 nm. An absorption spectrum gave an $A_{415 \text{ nm}}$ value of > 3 , indicating that the fraction of absorbed light (f) is > 0.999 .

$$f = 1 - 10^{-A_{415\text{nm}}} \quad (3)$$

The photon flux was thus calculated to be 5.99×10^{-9} einsteins s⁻¹



**Figure S9 Absorbance of the ferrioxalate actinometer solution
Determination of the reaction quantum yield.**



A cuvette was charged with 1-methoxy-4-vinylbenzene **1a** (0.2 mmol, 26.8 mg), sulfonium salt **2a** (2 equiv, 0.4 mmol, 129.6 mg), 1-methyl-1*H*-indole **3a** (0.6 mmol, 78.6 mg), K_3PO_4 (3 equiv, 0.4 mmol, 127.4 mg), CuCl (10 mol%, 2.0 mg), **L1** (12 mol%, 16.3 mg) and DMSO (2 mL). The reaction mixture was stirred at room temperature for 2 h (7200 s) under blue LED irradiation ($\lambda = 415$ nm). The solvent was removed in vacuo and the yield of formed product was determined by 1H NMR based on dibromomethane as internal standard. The quantum yield was determined using eq 4.

$$\phi = \frac{\text{mol of product}}{\text{flux} \cdot t \cdot f} \quad (4)$$

$$\phi = \frac{1.45 \times 10^{-5}}{(5.99 \times 10^{-9} \text{ einstein} / \text{s}) \cdot (7200 \text{ s}) \cdot (0.989)} = 0.34 < 1$$

The photon flux is 5.99×10^{-9} einsteins s^{-1} , t is the reaction time (7200 s). f is the fraction of incident light absorbed by the catalyst, determined using eq 3. An

absorption spectrum of the catalyst (0.001 M) gave an absorbance value of 0.658 at 415 nm (figure S6), indicating that the fraction of light absorbed by the photocatalyst (*f*) is 0.989.

Absorbance of catalyst:

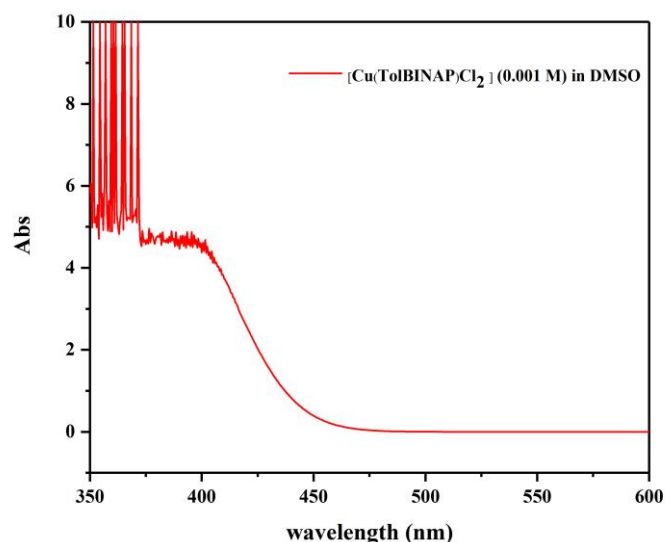
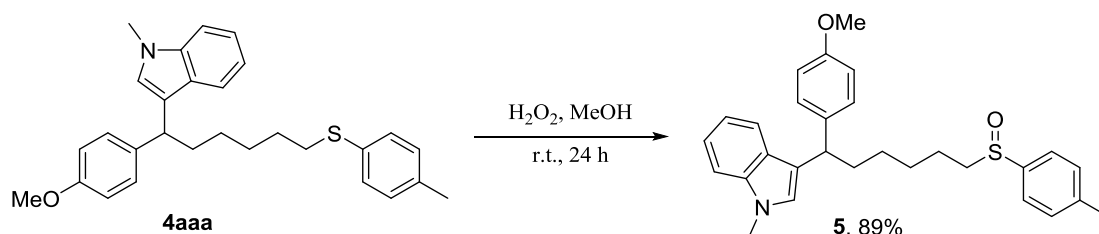


Figure S10 Absorption spectrum of [Cu(TolBINAP)Cl₂] [0.001 M] in DMSO

2.9 Product Derivatization^{[2][3]}



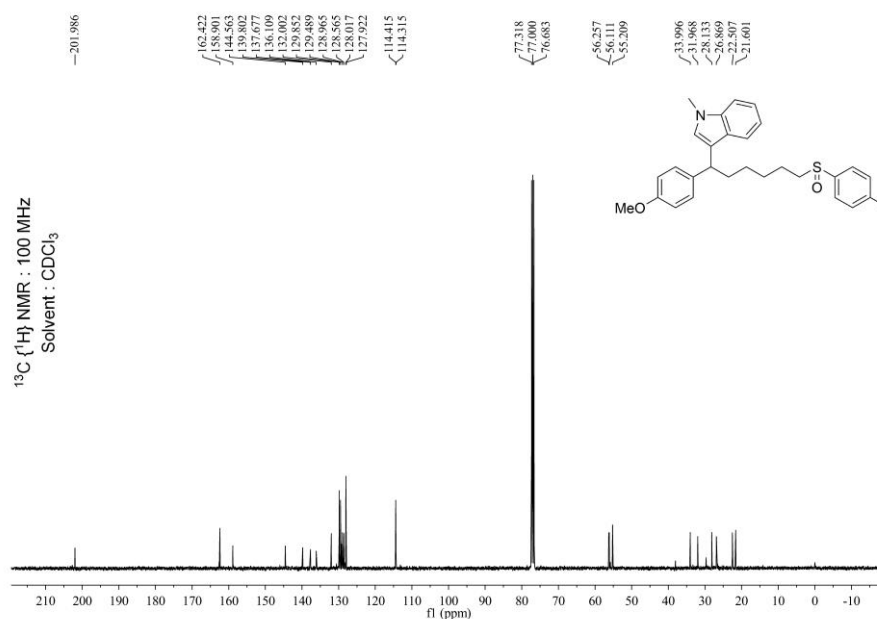
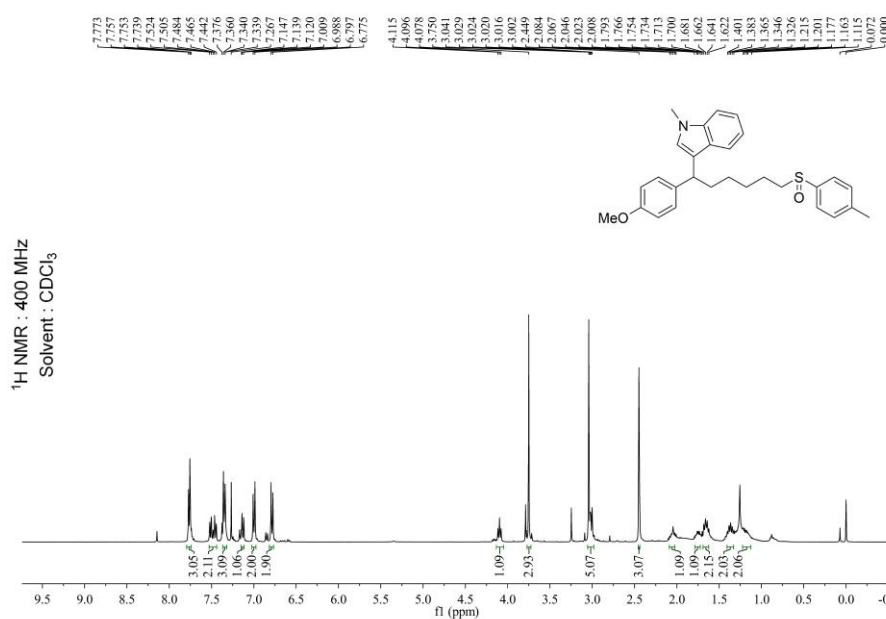
To a stirred solution of **4aaa** (88.6 mg, 0.2 mmol) in 1 mL methanol was added H₂O₂ (30% in water, 0.017 ml, 0.22 mmol, 1.1 equiv.) at room temperature. Then the reaction was kept stirring overnight at room temperature for 24 h. The crude product was further purified by silica gel flash chromatography to give **5** in yield of 89% as yellow oil.

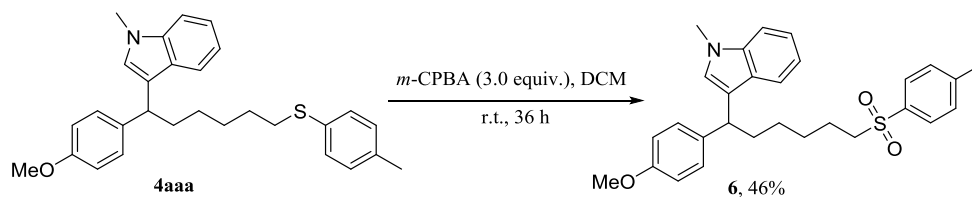
The date and NMR spectra of **5**.

3-(1-(4-Methoxyphenyl)-6-(*p*-tolylsulfonyl)hexyl)-1-methyl-1*H*-indole (5**)**. The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1 : 1) to afford a yellow oil in 89% yield (81.7 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.77-7.74

(m, 3H), 7.52-7.44 (m, 2H), 7.38-7.34 (m, 3H), 7.15-7.12 (m, 1H), 7.00 (d, $J = 8.4$ Hz, 2H), 6.79 (d, $J = 8.8$ Hz, 2H), 4.10 (t, $J = 7.6$ Hz, 1H), 3.75 (s, 3H), 3.04-3.00 (m, 5H), 2.45 (s, 3H), 2.08-2.00 (m, 1H), 1.79-1.70 (m, 1H), 1.68-1.62 (m, 2H), 1.40-1.33 (m, 2H), 1.22-1.12 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 202.0, 162.4, 158.9, 144.6, 139.8, 137.7, 136.1, 132.0, 129.9 (2C), 129.5 (2C), 129.0, 128.6, 128.0 (2C), 127.9, 114.4 (2C), 114.3, 56.3, 56.1, 55.2, 34.0, 32.0, 28.1, 26.9, 22.5, 21.6; HRMS (ESI-TOF) m/z : $\text{C}_{29}\text{H}_{34}\text{NO}_2\text{S}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 460.2305, found 460.2306.

3-(1-(4-Methoxyphenyl)-6-(*p*-tolylsulfinyl)hexyl)-1-methyl-1*H*-indole (5)



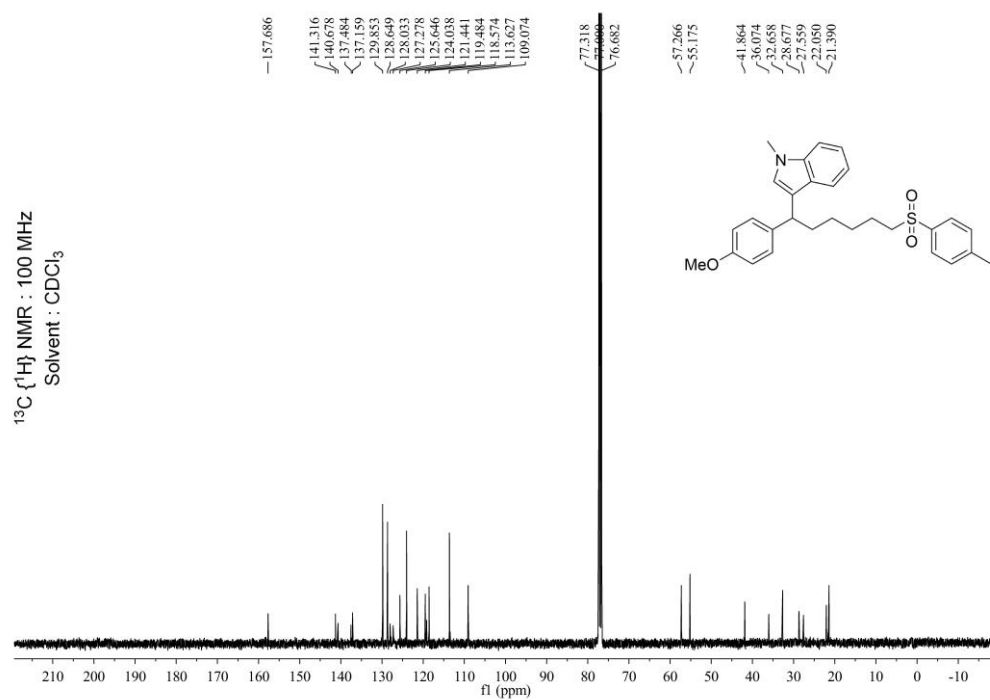
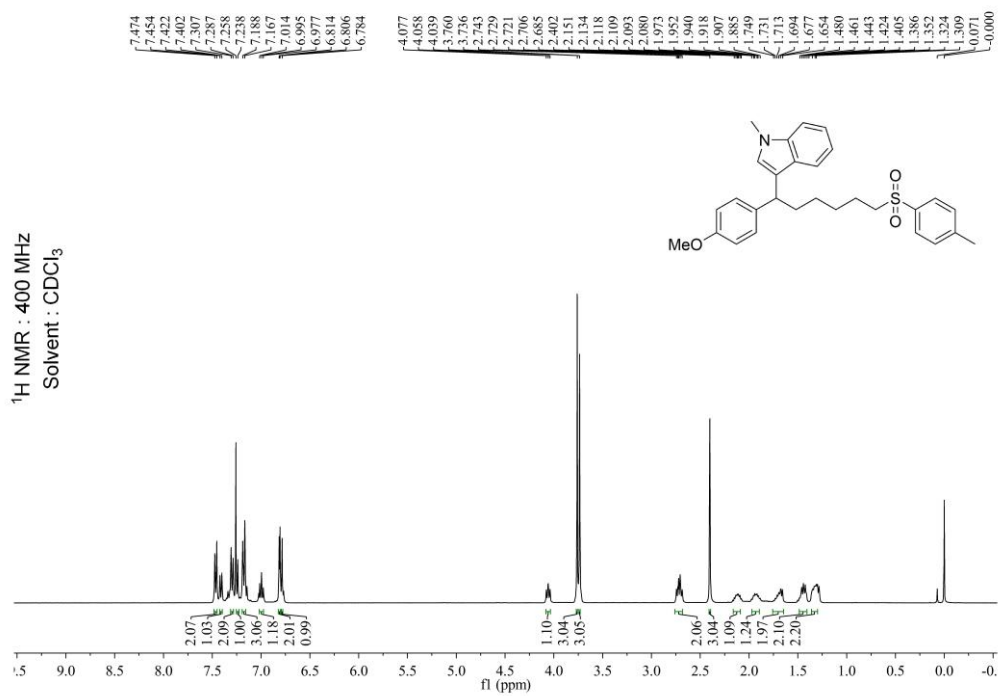


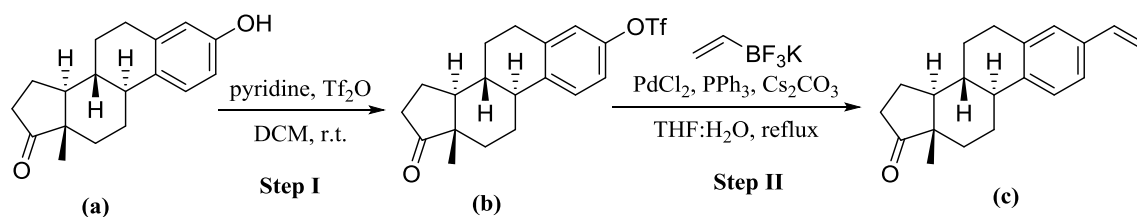
To a stirred solution of **4aaa** (88.6 mg, 0.2 mmol) in 1 mL CH₂Cl₂ was added *m*-CPBA (0.1032 g, 0.6 mmol, 3.0 equiv.) at room temperature. Then the reaction was kept stirring overnight at room temperature for 36 h. The reaction was then quenched with saturated 10 mL Na₂SO₃, extracted with 10 mL DCM, washed with saturated Na₂SO₃, dried over sodium sulfate, filtered and concentrated in vacuo in ice bath. The crude product was further purified by silica gel flash chromatography (DCM as the eluent) to give **6** (46% yield) as yellow oil.

The date and NMR spectra of 6.

3-(1-(4-Methoxyphenyl)-6-tosylhexyl)-1-methyl-1H-indole (6). The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (1 : 1) to afford a yellow oil in 46% yield (43.9 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.24 (s, 1H), 7.18 (d, *J* = 8.4 Hz, 3H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 3.2 Hz, 2H), 6.78 (s, 1H), 4.06 (t, *J* = 7.6 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 2.74-2.69 (m, 2H), 2.40 (s, 3H), 2.15-2.08 (m, 1H), 1.97-1.89 (m, 1H), 1.75-1.65 (m, 2H), 1.48-1.39 (m, 2H), 1.35-1.31 (m, 2H); ¹³C{¹H}NMR (100 MHz, CDCl₃) δ 157.7, 141.3, 140.7, 137.5, 137.2, 129.9, 128.6 (2C), 128.0 (2C), 127.3, 125.6, 124.0 (2C), 121.4, 119.5, 118.6, 113.6 (2C), 109.1, 57.3, 55.2, 41.9, 36.1, 32.7, 28.7, 27.6, 22.1, 21.4; HRMS (ESI-TOF) *m/z*: C₂₉H₃₄NO₃S⁺ (*M* + H)⁺ calcd for 476.2254, found 476.2258.

3-(1-(4-Methoxyphenyl)-6-tosylhexyl)-1-methyl-1H-indole (6)



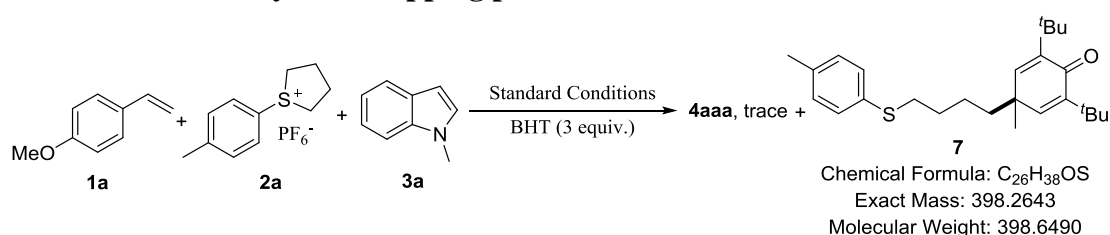


Step I: An oven dried 2-neck round bottom flask was charged with estrone ((a), 2.70 g, 10 mmol, 1 equiv.), pyridine (1.62 mL, 20 mmol, 2 equiv.), DCM (30 mL) and cooled to 0 °C. Triflic anhydride (2.02 mL, 12 mmol, 1.2 equiv.) was then added dropwise and the reaction was stirred at that temperature until completion (monitored by GC/MS). The reaction mixture was diluted with 30 mL H₂O and extracted 3 times with 25 mL DCM. Combined organic phases were dried over magnesium sulfate, filtered through short celite pad and concentrated under reduced pressure. Purification by silica gel column chromatography (hexane/ethyl acetate, 5/1) afforded corresponding triflate product as white solid (3.9 g, 97% yield).

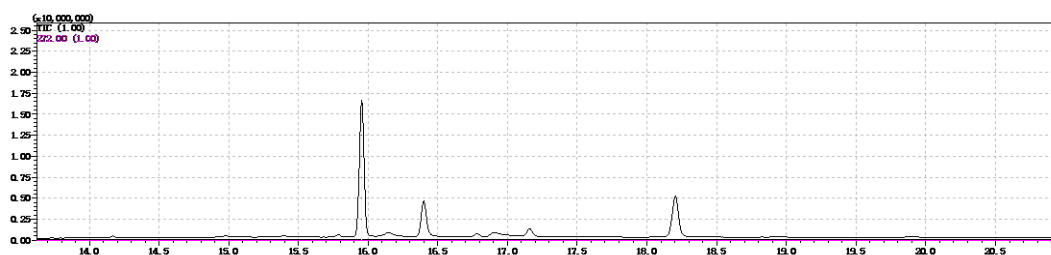
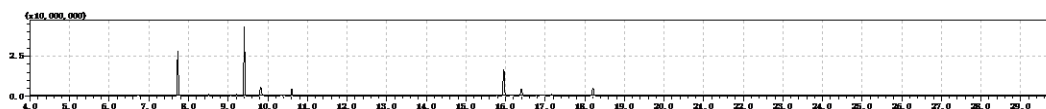
Step II: An oven dried 2-neck round bottom flask was charged with ((b), 2.01 g, 5 mmol, 1 equiv.), potassium vinyltrifluoroborate (1.01 g, 7.5 mmol, 1.5 equiv.), PdCl₂ (17.7 mg, 0.1 mmol, 0.02 equiv.), PPh₃ (78.7 mg, 0.3 mmol, 0.06 equiv.), Cs₂CO₃ (4.89 g, 15 mmol, 3 equiv.), THF (18 mL), H₂O (2 mL) and stirred under reflux until completion (monitored by TLC). Reaction mixture was then diluted with 50 mL H₂O and extracted 3 times with 25 mL DCM. Combined organic phases were dried over Na₂SO₄, filtered through short celite pad and concentrated under reduced pressure. Purification by silica gel column chromatography (hexane/ethyl acetate, 10/1) afforded corresponding alkenes (c) as a white solid (1.15 g, 82% yield). The spectroscopic data correspond to those were reported in the literature.

2.10 Control Experiments

2.10.1 GC-MS Analysis of trapping product 7^[4]



The GC spectra of raw reaction mixture



The MS spectra of the peak at 15.955 min



[MS Spectrum]

of Peaks 548

Raw Spectrum 15.955 (scan : 2392)

Background No Background Spectrum

Base Peak m/z 179.00 (Inten : 4,058,017)

Event# 1

m/z	Absolute Intensity	Relative Intensity
50.00	3079	0.08
51.00	13226	0.33
52.05	5349	0.13
53.00	54089	1.33
54.05	8499	0.21
55.05	402025	9.91
56.05	34630	0.85
57.05	1242640	30.62
58.05	57726	1.42
59.00	27158	0.67
60.00	3393	0.08
61.00	3713	0.09
62.05	2507	0.06
63.00	11066	0.27
64.05	4305	0.11
65.00	66601	1.64
66.00	9244	0.23
67.00	71666	1.77
68.05	6692	0.16
69.00	102537	2.53
70.00	9340	0.23
71.00	14052	0.35
72.00	1561	0.04
73.00	26212	0.65
74.00	3348	0.08
75.00	3580	0.09
76.05	3039	0.07
77.00	109713	2.70
78.05	30962	0.76
79.00	158682	3.91
80.05	16966	0.42
81.05	74023	1.82
82.05	9137	0.23
83.05	76039	1.87
84.05	6615	0.16
85.00	12665	0.31
86.05	3535	0.09
87.00	76306	1.88
88.05	6165	0.15
89.05	19690	0.49
90.05	9804	0.24
91.05	319934	7.88
92.05	42789	1.05
93.05	120991	2.98
94.05	14939	0.37
95.05	46961	1.16
96.05	12694	0.31
97.00	58319	1.44
98.05	5446	0.13
99.05	3953	0.10
100.05	722	0.02
101.00	3378	0.08
102.00	4422	0.11
103.00	29634	0.73
104.05	18990	0.47
105.05	181907	4.48
106.05	25037	0.62
107.05	94587	2.33
108.05	24506	0.60
109.05	55426	1.37

110.05	14205	0.35	153.95	4714	0.12	197.00	1343	0.03
111.05	11544	0.28	155.05	12759	0.31	198.05	870	0.02
112.15	1319	0.03	156.05	10800	0.27	199.05	86110.21	
113.10	1937	0.05	157.00	18364	0.45	200.00	3529	0.09
114.05	1416	0.03	158.05	10039	0.25	201.05	15235	0.38
115.00	56137	1.38	159.05	50870	1.25	202.05	7288	0.18
116.05	23838	0.59	160.05	19428	0.48	203.05	232952	5.74
117.05	55796	1.37	161.05	367500	9.06	204.05	53064	1.31
118.15	17405	0.43	162.05	73325	1.81	205.05	168096	4.14
119.05	157347	3.88	163.05	304717	7.51	206.05	28825	0.71
120.15	29624	0.73	164.05	77660	1.91	206.95	53324	1.31
121.05	183278	4.52	165.05	28446	0.70	207.95	11126	0.27
122.05	52134	1.28	166.05	9166	0.23	208.90	6970	0.17
123.00	309481	7.63	167.00	4921	0.12	209.90	1486	0.04
124.05	106916	2.63	167.60	1481	0.04	210.95	11410.03	
125.05	38952	0.96	168.65	2669	0.07	212.00	654	0.02
126.05	7775	0.19	169.65	4153	0.10	213.05	1488	0.04
127.10	15252	0.38	170.60	34975	0.86	214.05	815	0.02
128.10	50407	1.24	171.55	6931	0.17	215.05	35110.09	
129.05	65641	1.62	171.95	6908	0.17	216.05	2652	0.07
130.10	38905	0.96	173.05	24363	0.60	217.05	70566	1.74
131.05	68198	1.68	174.05	15071	0.37	218.10	50402	1.24
132.10	17100	0.42	175.05	117678	2.90	219.05	218541	5.39
133.10	136910	3.37	176.05	25145	0.62	220.05	141578	3.49
134.05	41778	1.03	177.05	182392	4.49	221.05	31536	0.78
135.05	147678	3.64	178.05	260918	6.43	222.10	111241	2.74
136.05	36512	0.90	179.00	4058017	100.00	223.10	20130	0.50
137.00	996754	24.56	180.00	530631	13.08	224.00	2471	0.06
138.05	102031	2.51	181.00	211145	5.20	224.95	798	0.02
139.05	53104	1.31	182.00	23772	0.59	225.95	646	0.02
140.05	5392	0.13	183.00	4010	0.10	226.95	11040.03	
141.05	27054	0.67	184.05	3390	0.08	227.95	794	0.02
142.05	21174	0.52	185.05	10472	0.26	229.00	1415	0.03
143.05	35678	0.88	186.05	5454	0.13	230.00	11140.03	
144.05	71311	1.76	187.05	16698	0.41	231.05	9881	0.24
145.05	82336	2.03	188.05	7199	0.18	232.05	3843	0.09
146.05	26102	0.64	189.05	53334	1.31	233.10	24386	0.60
147.05	113118	2.79	190.05	30076	0.74	234.05	7476	0.18
148.05	28364	0.70	191.00	47265	1.16	235.00	4482	0.11
149.05	116979	2.88	191.95	14089	0.35	236.00	1740	0.04
150.05	83782	2.06	193.00	14494	0.36	237.00	1314	0.03
151.00	52366	1.29	193.95	3887	0.10	238.05	463	0.01
152.05	15787	0.39	194.95	3197	0.08	238.95	582	0.01
153.00	14105	0.35	195.95	11780.03		239.90	380	0.01

240.95	1714	0.04	285.00	21030	0.52	329.05	5652	0.14
242.05	1073	0.03	286.00	12009	0.30	330.10	1454	0.04
243.05	2330	0.06	287.00	4230	0.10	331.00	404	0.01
244.00	934	0.02	288.00	11380	0.03	332.00	1202	0.03
245.00	4526	0.11	288.95	299	0.01	333.15	434	0.01
246.05	1804	0.04	289.90	762	0.02	334.10	5217	0.13
247.10	3132	0.08	291.05	493	0.01	335.05	1779	0.04
247.85	1430	0.04	292.05	18412	0.45	336.00	225	0.01
248.85	3272	0.08	293.00	4494	0.11	337.00	95	0.00
249.95	1259	0.03	294.00	698	0.02	337.80	130	0.00
251.00	2362	0.06	295.00	1908	0.05	338.75	727	0.02
251.95	912	0.02	295.85	559	0.01	340.05	11840	0.03
252.95	1570	0.04	296.80	742	0.02	341.05	25343	0.62
253.90	686	0.02	298.05	380	0.01	342.05	39793	0.98
254.90	530	0.01	299.05	4613	0.11	343.00	11071	0.27
256.05	481	0.01	300.10	1487	0.04	344.10	3641	0.09
257.05	2041	0.05	301.00	918	0.02	344.95	773	0.02
258.15	1063	0.03	302.15	960	0.02	345.90	289	0.01
259.10	16254	0.40	303.10	273	0.01	347.10	244	0.01
260.00	4801	0.12	304.10	138	0.00	348.15	8725	0.22
261.15	3273	0.08	305.10	95	0.00	349.10	39678	0.98
262.10	1596	0.04	305.80	222	0.01	350.10	10102	0.25
262.95	1086	0.03	306.80	335	0.01	351.05	1573	0.04
263.90	682	0.02	307.80	185	0.00	352.05	301	0.01
264.90	31190	0.08	308.95	645	0.02	352.90	554	0.01
265.95	622	0.02	309.90	234	0.01	354.00	177	0.00
266.90	4934	0.12	310.90	738	0.02	355.00	7914	0.20
267.90	1962	0.05	312.00	217	0.01	356.00	3108	0.08
268.95	1577	0.04	313.00	1988	0.05	356.95	1778	0.04
269.90	585	0.01	314.15	938	0.02	357.90	740	0.02
271.00	1417	0.03	315.15	1216	0.03	358.90	343	0.01
271.95	548	0.01	316.15	980	0.02	359.90	100	0.00
273.05	1080	0.03	317.05	360	0.01	360.90	81	0.00
274.15	3747	0.09	318.05	867	0.02	361.90	122	0.00
275.15	24971	0.62	319.05	439	0.01	362.90	281	0.01
276.10	7036	0.17	320.00	127	0.00	363.90	217	0.01
277.05	1629	0.04	321.00	98	0.00	365.05	1278	0.03
278.05	703	0.02	322.00	164	0.00	366.00	284	0.01
278.90	609	0.02	323.05	1003	0.02	367.10	746	0.02
279.90	207	0.01	324.05	575	0.01	368.00	247	0.01
280.95	15586	0.38	325.00	7847	0.19	369.05	1241	0.03
281.90	4674	0.12	326.05	2733	0.07	370.10	412	0.01
282.95	3367	0.08	327.05	47480	1.17	371.00	522	0.01
283.95	1388	0.03	328.00	11882	0.29	372.00	183	0.00

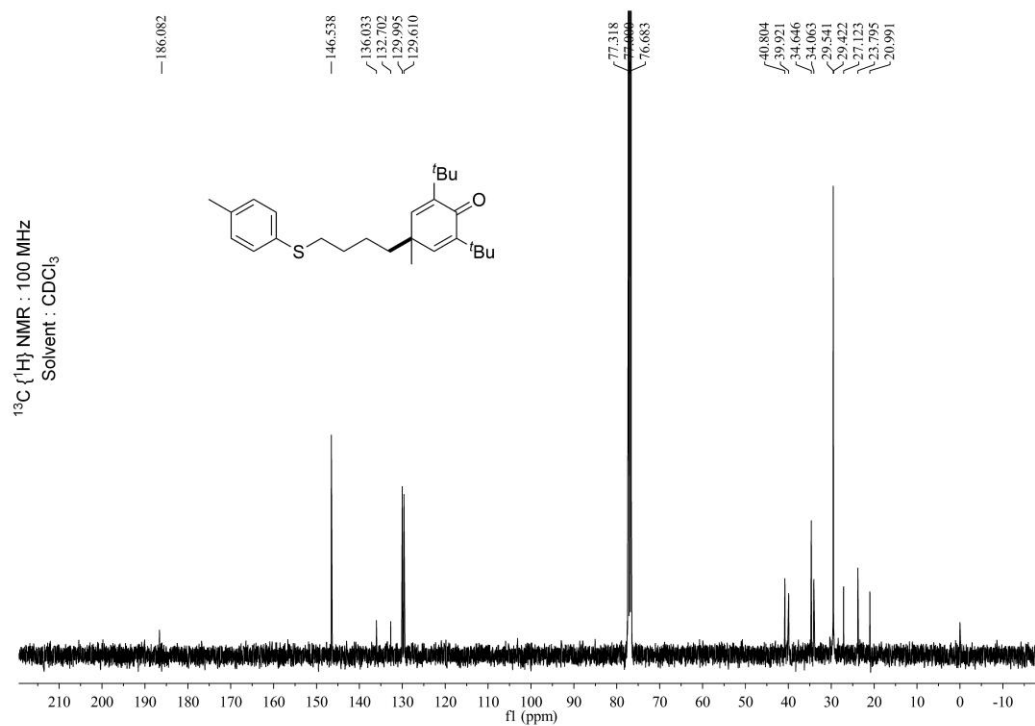
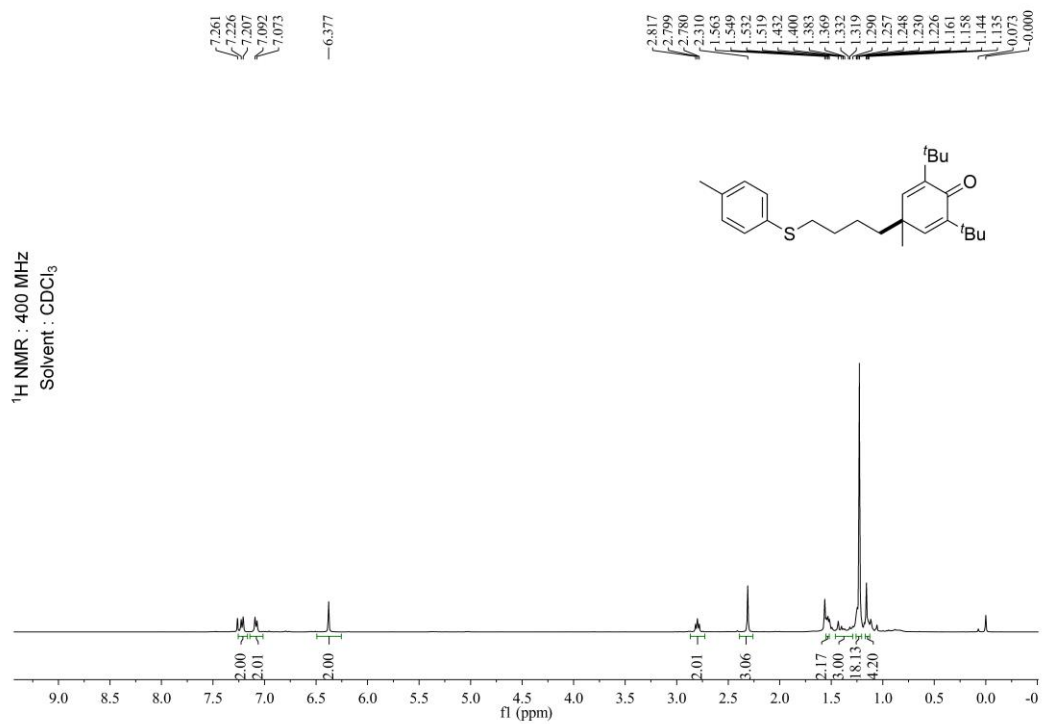
373.00	254	0.01	384.10	7838	0.19	394.80	84	0.00
374.00	111	0.00	385.05	2895	0.07	396.15	414	0.01
375.00	16	0.00	385.85	515	0.01	397.15	9671	0.24
376.00	57	0.00	386.80	873	0.02	398.10	489009	12.05
377.00	81	0.00	387.80	508	0.01	399.10	143673	3.54
378.00	34	0.00	388.80	316	0.01	400.10	44668	1.10
379.00	60	0.00	389.80	78	0.00	401.05	10772	0.27
380.00	66	0.00	390.80	36	0.00	402.00	2649	0.07
381.00	409	0.01	391.80	11	0.00	402.95	928	0.02
382.15	665	0.02	392.80	22	0.00	404.00	263	0.01
383.10	28079	0.69	393.80	81	0.00	405.00	193	0.00

The date and NMR spectra of 7.

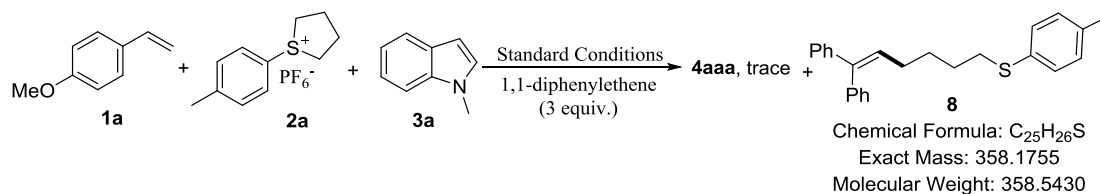
2,6-Di-*tert*-butyl-4-methyl-4-(4-(*p*-tolylthio)butyl)cyclohexa-2,5-dien-1-one (7).

The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40 : 1) to afford a yellow oil in 45% yield (36.0 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.22 (d, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 7.6 Hz, 2H), 6.38 (s, 2H), 2.80 (t, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.56-1.52 (m, 2H), 1.431.29 (m, 3H), 1.26-1.23 (m, 18H), 1.16-1.14 (m, 4H); ¹³C{¹H}NMR (100 MHz, CDCl₃): δ 186.1, 146.5 (4C), 136.0, 132.7, 130.0 (2C), 129.6 (2C), 40.8, 39.9, 34.6 (2C), 34.1, 29.5 (6C), 29.4, 27.1, 23.8, 21.0.

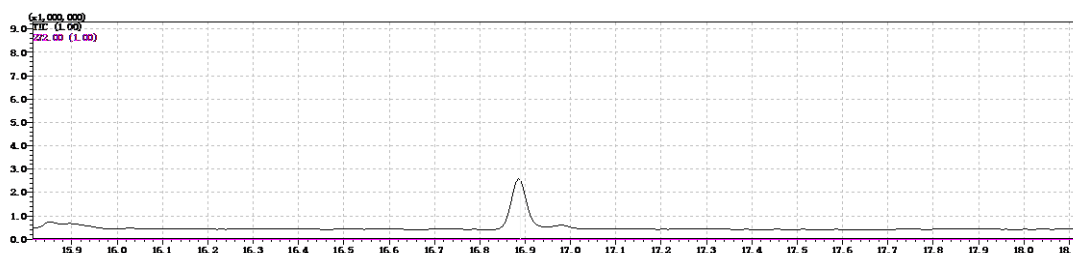
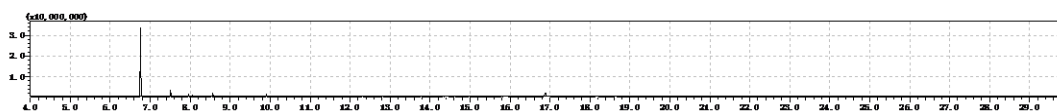
2,6-Di-*tert*-butyl-4-methyl-4-(4-(*p*-tolylthio)butyl)cyclohexa-2,5-dien-1-one (7)



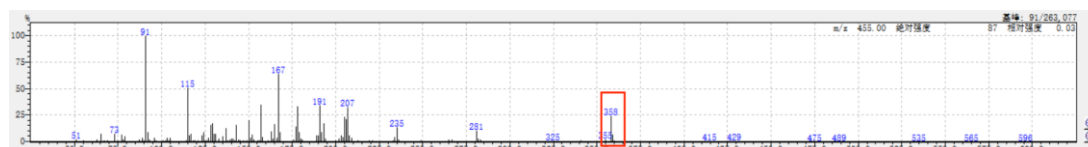
2.10.2 GC-MS Analysis of trapping product **8**^[4]



Spectra of GC-MS



MS Spectra of the peak at 16.85 min



[MS Spectrum]

of Peaks 550

Raw Spectrum 16.890 (scan : 2579)

Background No Background Spectrum

Base Peak m/z 91.05 (Inten : 263,077)

Event# 1

m/z Absolute Intensity Relative Intensity

50.05	1501	0.57	62.05	1089	0.41	74.00	2564	0.97
51.05	5229	1.99	63.05	5147	1.96	75.00	3414	1.30
52.05	11180.42		64.05	1242	0.47	76.05	2478	0.94
53.00	2857	1.09	65.05	19308	7.34	77.05	18900	7.18
54.05	380	0.14	66.05	1657	0.63	78.05	6345	2.41
55.05	4717	1.79	67.05	4751	1.81	79.05	13941	5.30
56.05	1259	0.48	68.05	621	0.24	80.05	1290	0.49
57.05	2351	0.89	69.00	3023	1.15	81.00	1844	0.70
58.00	828	0.31	70.05	1337	0.51	82.05	1899	0.72
59.00	2812	1.07	71.05	2447	0.93	83.00	2447	0.93
60.05	624	0.24	72.05	453	0.17	84.00	874	0.33
61.05	1570	0.60	73.00	19407	7.38	85.00	2068	0.79

86.00	11640.44		130.10	19468	7.40	174.00	209	0.08
87.00	6034	2.29	131.10	20135	7.65	175.00	1049	0.40
88.00	1950	0.74	132.05	2903	1.10	176.00	6188	2.35
89.05	10054	3.82	133.00	7215	2.74	177.00	37292	14.18
90.15	4993	1.90	134.00	2292	0.87	178.00	88801	33.75
91.05	263077	100.00	135.00	14519	5.52	179.00	23441	8.91
92.05	23231	8.83	136.05	2152	0.82	180.00	8247	3.13
93.10	5721	2.17	137.05	34477	13.11	181.00	5098	1.94
94.05	1230	0.47	138.05	3948	1.50	181.95	1551	0.59
95.05	1937	0.74	139.10	5297	2.01	183.10	439	0.17
96.00	9084	3.45	140.10	7250	2.76	184.10	220	0.08
96.95	4663	1.77	141.10	8527	3.24	185.10	151	0.06
98.05	756	0.29	142.10	3734	1.42	185.90	153	0.06
99.05	1767	0.67	143.10	41482	15.77	186.95	1030	0.39
99.95	667	0.25	144.10	5694	2.16	187.95	1548	0.59
101.05	4095	1.56	145.05	3896	1.48	189.00	15305	5.82
102.05	4645	1.77	146.05	598	0.23	190.00	15730	5.98
103.05	9127	3.47	147.00	4855	1.85	191.00	90111	34.25
104.05	4077	1.55	148.00	2038	0.77	192.00	24876	9.46
105.10	9266	3.52	149.00	4892	1.86	193.00	46895	17.83
106.05	11330.43		150.00	55018	20.91	193.95	7644	2.91
107.00	590	0.22	151.00	10801	4.11	195.05	1396	0.53
108.00	1753	0.67	152.00	17809	6.77	196.00	199	0.08
109.10	1556	0.59	153.00	5103	1.94	196.95	683	0.26
110.05	439	0.17	154.05	1352	0.51	198.05	535	0.20
111.10	11850.45		155.05	3500	1.33	199.05	431	0.16
112.10	561	0.21	156.15	4576	1.74	200.00	3406	1.29
113.15	1757	0.67	157.05	92189	35.04	201.00	15110.57	
114.15	3090	1.17	158.05	11541	4.39	202.00	7287	2.77
115.05	135207	51.39	159.05	840	0.32	203.00	15343	5.83
116.05	15402	5.85	160.05	563	0.21	204.05	11540	4.39
117.10	20484	7.79	161.00	3185	1.21	205.00	61604	23.42
118.10	3535	1.34	162.05	1337	0.51	206.00	57116	21.71
119.05	3385	1.29	163.00	26551	10.09	206.95	86703	32.96
120.00	378	0.14	164.05	7371	2.80	207.95	16831	6.40
121.00	3801	1.44	165.00	43257	16.44	208.95	10059	3.82
122.00	2234	0.85	166.05	9923	3.77	210.05	1860	0.71
123.05	16956	6.45	167.05	169718	64.51	210.95	910	0.35
124.05	24931	9.48	168.05	23145	8.80	212.05	400	0.15
125.05	4700	1.79	169.00	2217	0.84	213.00	4468	1.70
126.10	4142	1.57	170.10	1351	0.51	213.85	1007	0.38
127.10	9802	3.73	171.10	468	0.18	215.05	1679	0.64
128.10	42102	16.00	172.10	182	0.07	216.00	534	0.20
129.10	46230	17.57	173.10	110	0.04	217.05	919	0.35

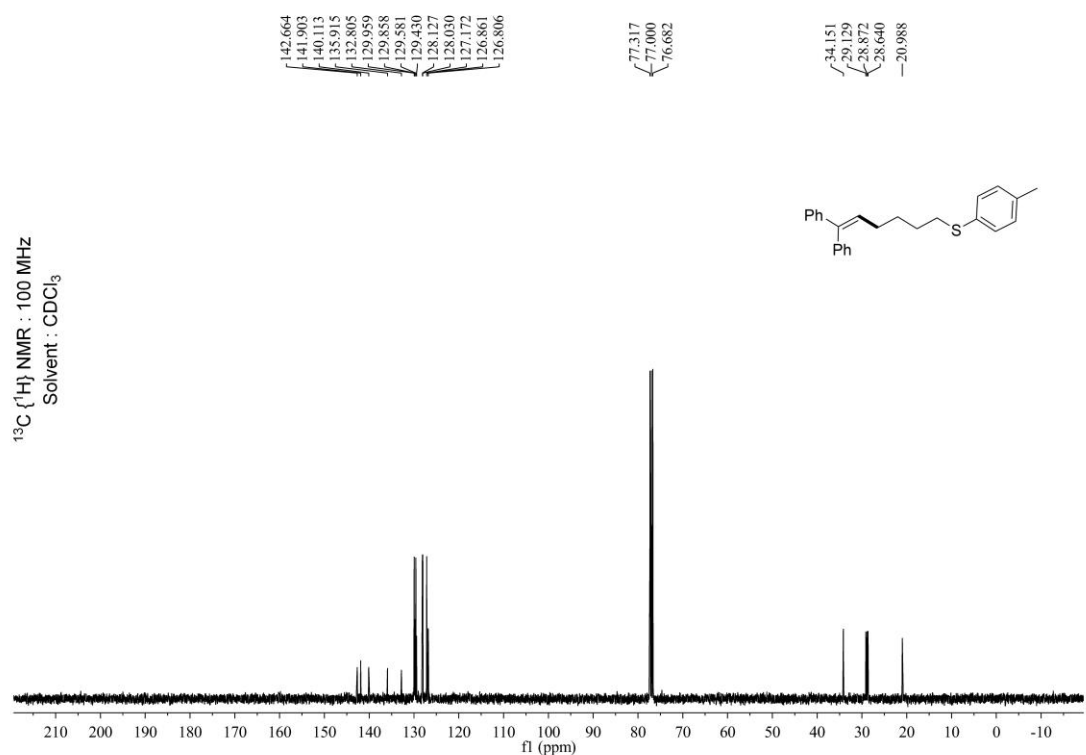
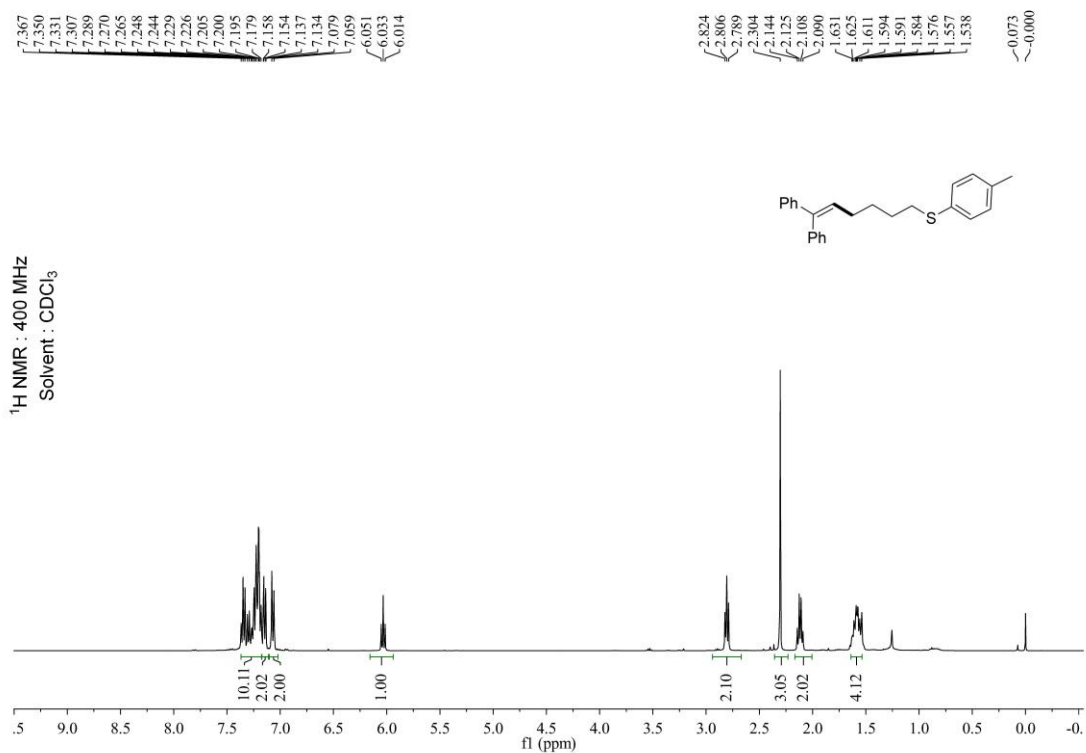
218.05	648	0.25	262.00	150	0.06	306.10	130	0.05
219.05	3852	1.46	263.00	132	0.05	307.00	433	0.16
220.05	1412	0.54	263.90	113	0.04	308.00	297	0.11
221.00	4103	1.56	264.90	5578	2.12	309.00	150	0.06
222.00	996	0.38	265.90	1926	0.73	310.00	134	0.05
223.05	11480.44		266.90	6070	2.31	311.00	183	0.07
224.00	375	0.14	267.85	1700	0.65	312.00	138	0.05
225.10	700	0.27	268.95	1982	0.75	313.00	287	0.11
226.10	258	0.10	270.00	582	0.22	314.00	119	0.05
227.10	177	0.07	271.00	676	0.26	315.00	127	0.05
228.10	260	0.10	272.00	223	0.08	316.00	108	0.04
229.10	212	0.08	273.00	161	0.06	317.00	140	0.05
230.10	250	0.10	274.00	105	0.04	318.00	55	0.02
231.10	281	0.11	275.00	151	0.06	319.00	92	0.03
232.05	413	0.16	276.00	137	0.05	320.00	97	0.04
233.05	3030	1.15	277.00	118	0.04	321.00	217	0.08
234.05	12945	4.92	278.00	214	0.08	322.00	62	0.02
235.05	35595	13.53	278.95	458	0.17	323.00	311	0.12
236.05	6145	2.34	280.05	570	0.22	323.90	142	0.05
237.00	11030.42		280.95	28442	10.81	324.90	1263	0.48
238.00	257	0.10	281.95	8765	3.33	325.95	393	0.15
239.05	477	0.18	283.00	5882	2.24	326.95	1527	0.58
240.00	172	0.07	283.90	1583	0.60	327.95	368	0.14
241.00	262	0.10	284.95	517	0.20	329.00	497	0.19
242.00	212	0.08	286.00	178	0.07	330.00	90	0.03
243.00	124	0.05	287.00	162	0.06	331.00	108	0.04
244.00	34	0.01	288.00	47	0.02	332.00	124	0.05
245.00	129	0.05	289.00	202	0.08	333.00	82	0.03
246.00	73	0.03	290.00	81	0.03	334.00	153	0.06
247.00	231	0.09	291.00	113	0.04	335.00	129	0.05
247.90	249	0.09	292.00	108	0.04	336.00	58	0.02
248.90	3852	1.46	293.05	434	0.16	337.00	159	0.06
249.95	1367	0.52	294.00	199	0.08	338.00	70	0.03
250.90	1801	0.68	295.00	951	0.36	338.90	409	0.16
251.85	897	0.34	296.05	381	0.14	339.90	137	0.05
252.95	1094	0.42	297.10	412	0.16	340.90	3759	1.43
253.95	478	0.18	298.10	222	0.08	341.95	11120.42	
254.90	591	0.22	299.10	338	0.13	342.90	1084	0.41
255.90	119	0.05	300.10	102	0.04	343.90	302	0.11
257.05	541	0.21	301.10	375	0.14	344.90	188	0.07
258.00	220	0.08	302.10	209	0.08	345.90	76	0.03
259.00	217	0.08	303.10	220	0.08	346.90	34	0.01
260.00	95	0.04	304.10	113	0.04	347.90	52	0.02
261.00	153	0.06	305.10	124	0.05	348.90	95	0.04

349.90	60	0.02	357.00	2182	0.83	364.10	33	0.01
350.90	137	0.05	358.05	64445	24.50	365.10	55	0.02
351.90	87	0.03	359.00	17498	6.65	366.10	27	0.01
352.90	193	0.07	360.00	5014	1.91	367.10	65	0.02
354.00	87	0.03	361.10	959	0.36	368.10	121	0.05
355.00	5385	2.05	362.10	167	0.06	369.00	558	0.21
355.95	2012	0.76	363.10	34	0.01	370.00	127	0.05

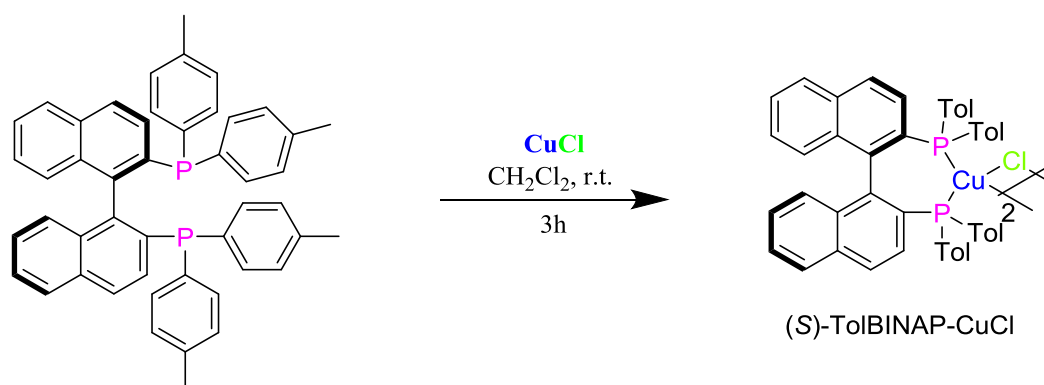
The date and NMR spectra of 8.

(6,6-Diphenylhex-5-en-1-yl)(*p*-tolyl)sulfane (8). The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40 : 1) to afford a yellow oil in 62% yield (44.4 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.37-7.18 (m, 10H), 7.16-7.13 (m, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.03 (t, *J* = 7.2 Hz, 1H), 2.81 (t, *J* = 7.2 Hz, 2H), 2.30 (s, 3H), 2.14-2.09 (m, 2H), 1.63-1.54 (m, 4H); ¹³C{¹H}NMR (100 MHz, CDCl₃): δ 142.7, 141.9, 140.1, 135.9, 132.8, 130.0 (2C), 129.9 (2C), 129.6 (2C), 129.4, 128.1 (2C), 128.0 (2C), 127.2 (2C), 126.9, 126.8, 34.2, 29.1, 28.9, 28.6, 21.0.

(6,6-Diphenylhex-5-en-1-yl)(*p*-tolyl)sulfane (8)



2.11 Synthesis of Copper-Based Photocatalyst^[2]

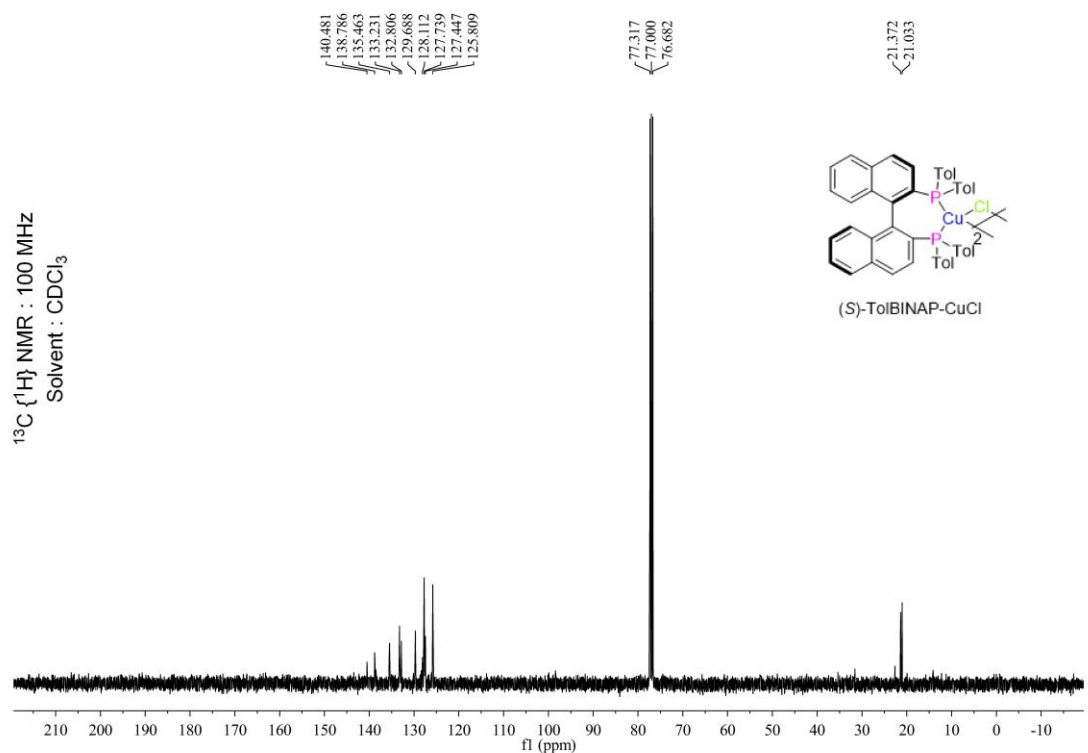
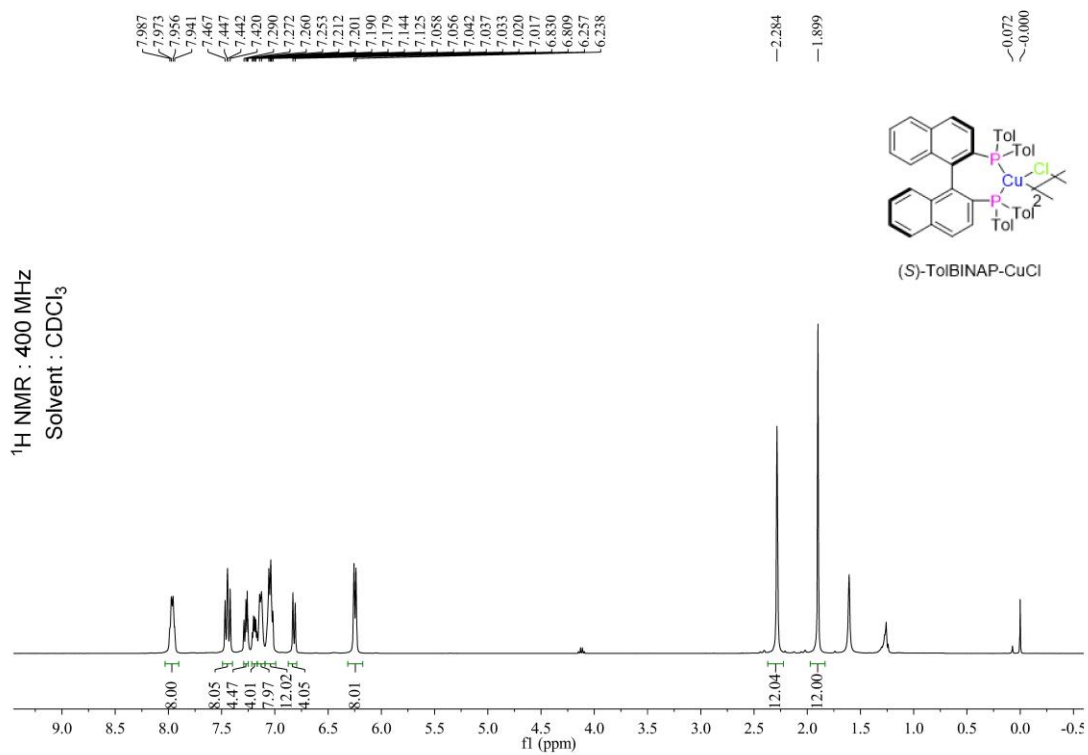


A solution of CuCl (0.099 g, 1 mmol) in 10 mL of DCM was added to a DCM solution of 35 mL with (S)-TolBINAP (0.679 g, 1 mmol). The solution was allowed to stir for 3 hours and the solvent was reduced in vacuo to 15 mL. Approximately 20 mL of hexanes was added to precipitate a yellow solid. The resulting solid was collected by vacuum filtration and dried under reduced pressure.

The date and NMR spectra of (S)-TolBINAP-CuCl.

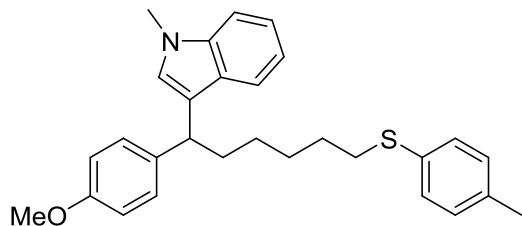
(S)-TolBINAP-CuCl. ^1H NMR (400 MHz, CDCl_3) δ 7.99-7.94 (m, 8H), 7.46-7.42 (m, 8H), 7.29-7.25 (m, 4H), 7.21-7.18 (m, 4H), 7.13 (d, $J = 7.6$ Hz, 8H), 7.06-7.02 (m, 12H), 6.82 (d, $J = 8.4$ Hz, 4H), 6.25 (d, $J = 7.6$ Hz, 8H), 2.28 (s, 12H), 1.90 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ : 140.5 (8C), 138.8 (8C), 135.5 (8C), 133.2 (4C), 132.8 (4C), 129.7 (8C), 128.1 (8C), 127.7 (16C), 127.4 (8C), 125.8 (16C), 21.4 (4C), 21.0 (4C).

(S)-TolBINAP-CuCl



3. Characterization Data

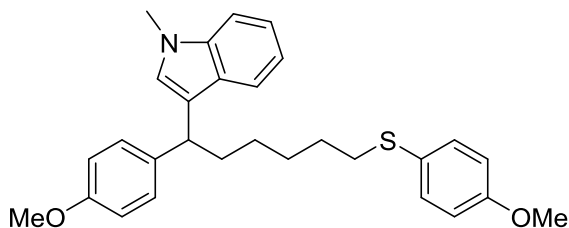
3-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (**4aaa**), by silica



gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 64.7 mg, 73%; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.42 (d, $J = 7.6$ Hz, 1H), 7.22-7.14 (m, 6H),

7.07 (d, $J = 8.0$ Hz, 2H), 6.99 (t, $J = 8.0$ Hz, 1H), 6.81 (d, $J = 2.4$ Hz, 2H), 6.78 (s, 1H), 4.07 (t, $J = 7.6$ Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 2.82 (t, $J = 7.2$ Hz, 2H), 2.30 (s, 3H), 2.17-2.10 (m, 1H), 1.98-1.89 (m, 1H), 1.62-1.54 (m, 2H), 1.49-1.40 (m, 2H), 1.36-1.25 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ : 157.6, 137.6, 137.1, 135.8, 133.0, 129.7 (2C), 129.6 (2C), 128.7 (2C), 127.3, 125.6, 121.4, 119.5, 119.3, 118.5, 113.6 (2C), 109.0, 55.1, 41.8, 36.2, 34.2, 32.6, 29.1, 28.8, 27.5, 21.0; HRMS (ESI-TOF) m/z : $\text{C}_{29}\text{H}_{34}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 444.2356, found 444.2357.

3-(1-(4-Methoxyphenyl)-6-((4-methoxyphenyl)thio)hexyl)-1-methyl-1*H*-indole

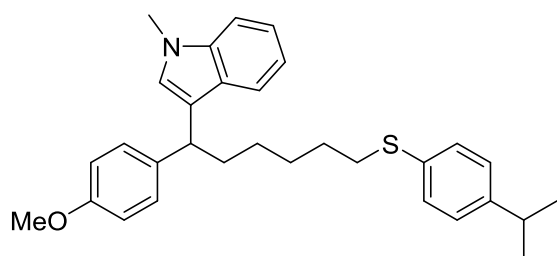


(**4aba**), by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 59.7 mg, 65%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ

7.42 (d, $J = 8.0$ Hz, 1H), 7.30 (d, $J = 6.8$ Hz, 2H), 7.24 (d, $J = 7.2$ Hz, 1H), 7.19-7.14 (m, 3H), 6.99 (t, $J = 7.6$ Hz, 1H), 6.82-6.78 (m, 5H), 4.07 (t, $J = 7.6$ Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.72 (s, 3H), 2.76 (t, $J = 6.8$ Hz, 2H), 2.16-2.08 (m, 1H), 1.97-1.88 (m, 1H), 1.54-1.47 (m, 2H), 1.45-1.35 (m, 2H), 1.33-1.27 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 158.7, 157.6, 137.7, 137.1, 132.9 (2C), 128.7 (2C), 127.3, 126.8, 125.6, 121.4, 119.5, 119.3, 118.5, 114.4 (2C), 113.6 (2C), 109.0, 55.3, 55.2, 41.9, 36.2, 35.7, 32.6, 29.2, 28.7, 27.6; HRMS (ESI-TOF) m/z : $\text{C}_{29}\text{H}_{34}\text{NO}_2\text{S}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 460.2305, found 460.2308.

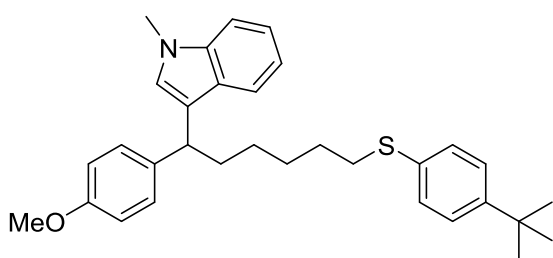
3-(6-((4-Isopropylphenyl)thio)-1-(4-methoxyphenyl)hexyl)-1-methyl-1*H*-indole

(**4aca**), by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 56.5 mg, 60 %; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.43 (d, $J = 8.0$ Hz, 1H), 7.25-7.23 (m, 3H), 7.18 (t, $J = 8.0$ Hz, 3H), 7.12 (d, $J = 8.4$ Hz, 2H), 7.00 (t, $J = 8.0$



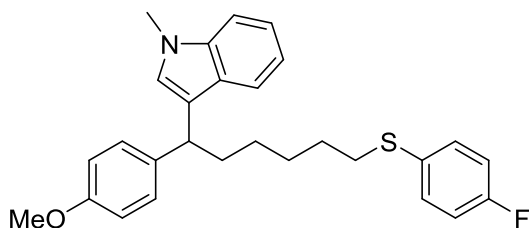
Hz, 1H), 6.81 (d, $J = 4.0$ Hz, 2H), 6.79 (s, 1H), 4.08 (t, $J = 7.2$ Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 2.88-2.82 (m, 3H), 2.18-2.09 (m, 1H), 1.99-1.90 (m, 1H), 1.64-1.58 (m, 2H), 1.49-1.41 (m, 2H), 1.37-1.29 (m, 2H), 1.22 (d, $J = 6.8$ Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.6, 146.7, 137.7, 137.2, 133.5, 130.2, 129.5 (2C), 128.7 (2C), 127.3, 126.9 (2C), 125.6, 121.4, 119.5, 119.3, 118.5, 113.6 (2C), 109.0, 55.2, 41.9, 36.2, 34.1, 33.6, 32.6, 29.1, 28.8, 27.6, 23.9; HRMS (ESI-TOF) m/z : $\text{C}_{31}\text{H}_{38}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 472.2669, found 472.2662.

3-(6-((4-(Tert-butyl)phenyl)thio)-1-(4-methoxyphenyl)hexyl)-1-methyl-1H-indole



(4ada), by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 65.0 mg, 67%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.43 (d, $J = 8.0$ Hz, 1H), 7.29-7.14 (m, 8H), 6.99 (t, $J = 8.0$ Hz, 1H), 6.81 (d, $J = 3.2$ Hz, 2H), 6.78 (s, 1H), 4.08 (t, $J = 8.0$ Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 2.84 (t, $J = 7.2$ Hz, 2H), 2.18-2.09 (m, 1H), 1.99-1.90 (m, 1H), 1.64-1.57 (m, 2H), 1.48-1.41 (m, 2H), 1.39-1.32 (m, 2H), 1.29 (s, 9H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.6, 148.9, 137.6, 137.1, 133.2, 129.0 (2C), 128.7 (2C), 127.3, 125.8 (2C), 125.6, 121.4, 119.5, 119.3, 118.5, 113.6 (2C), 109.0, 55.1, 41.9, 36.2, 34.4, 33.9, 32.6, 31.3 (3C), 29.1, 28.8, 27.6; HRMS (ESI-TOF) m/z : $\text{C}_{32}\text{H}_{40}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 486.2825, found 486.2829.

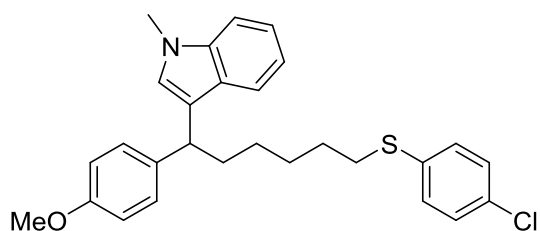
3-(6-((4-Fluorophenyl)thio)-1-(4-methoxyphenyl)hexyl)-1-methyl-1H-indole



(4aea), by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 65.3 mg, 73%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.43 (d, $J = 8.0$ Hz, 1H), 7.30-7.14 (m, 6H), 7.02-6.93 (m, 3H), 6.81-6.78 (m, 3H), 4.07 (t, $J = 8.4$ Hz, 1H), 3.74 (s, 3H), 3.71 (s, 3H), 2.80 (t, $J = 6.8$ Hz, 2H), 2.17-2.08 (m, 1H),

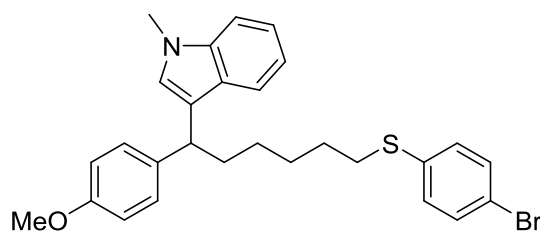
1.98-1.89 (m, 1H), 1.58-1.53 (m, 2H), 1.48-1.39 (m, 2H), 1.34-1.28 (m, 2H); ^{19}F NMR (282 MHz, CDCl_3) δ : -116.1 (s, 1F); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 160.5 (d, $J_{\text{C-F}} = 244.3$ Hz, 1C), 157.6, 137.6, 137.1 131.9 (d, $J_{\text{C-F}} = 7.9$ Hz, 2C), 131.6 (d, $J_{\text{C-F}} = 3.3$ Hz, 1C), 128.7 (2C), 127.3, 125.6, 121.4, 119.5, 119.3, 118.5, 115.8 (d, $J_{\text{C-F}} = 21.7$ Hz, 2C), 113.6 (2C), 109.0, 55.1, 41.8, 36.2, 34.8, 32.6, 29.0, 28.6, 27.5; HRMS (ESI-TOF) m/z : $\text{C}_{28}\text{H}_{31}\text{FNOS}^+$ (M + H) $^+$ calcd for 448.2105, found 448.2112.

3-((4-Chlorophenyl)thio)-1-(4-methoxyphenyl)hexyl)-1-methyl-1H-indole



(4afa), by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 72.2 mg, 78%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.43 (d, $J = 8.0$ Hz, 1H), 7.23-7.14 (m, 8H), 7.00 (t, $J = 7.2$ Hz, 1H), 6.81 (s, 2H), 6.78 (s, 1H), 4.08 (t, $J = 7.6$ Hz, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 2.83 (t, $J = 7.2$ Hz, 2H), 2.18-2.09 (m, 1H), 1.99-1.89 (m, 1H), 1.62-1.57 (m, 2H), 1.49-1.42 (m, 2H), 1.37-1.26 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.6, 137.6, 137.1, 135.4, 131.5, 130.1 (2C), 128.9 (2C), 128.7 (2C), 127.3, 125.6, 121.4, 119.5, 119.2, 118.5, 113.6 (2C), 109.1, 55.1, 41.8, 36.2, 33.7, 32.6, 28.8, 28.7, 27.5; HRMS (ESI-TOF) m/z : $\text{C}_{28}\text{H}_{31}\text{ClINOS}^+$ (M + H) $^+$ calcd for 464.1809, found 464.1815.

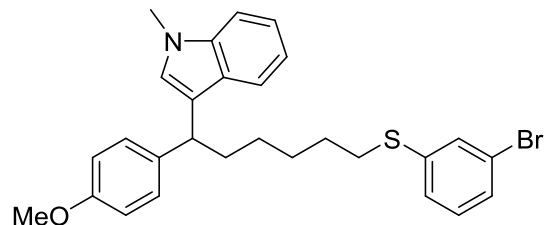
3-((4-Bromophenyl)thio)-1-(4-methoxyphenyl)hexyl)-1-methyl-1H-indole



(4aga), by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 62.9 mg, 62%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.43 (d, $J = 8.0$ Hz, 1H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 1H), 7.20-7.16 (m, 3H), 7.12 (d, $J = 8.4$ Hz, 2H), 7.00 (t, $J = 8.0$ Hz, 1H), 6.80 (s, 2H), 6.78 (s, 1H), 4.08 (t, $J = 8.0$ Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 2.82 (t, $J = 7.2$ Hz, 2H), 2.18-2.10 (m, 1H), 1.98-1.89 (m, 1H), 1.62-1.55 (m, 2H), 1.49-1.39 (m, 2H), 1.37-1.26 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.6, 137.6, 137.1, 136.2, 131.8 (2C), 130.3 (2C), 128.7 (2C), 127.3, 125.6, 121.4, 119.5, 119.3, 119.2, 118.5, 113.6 (2C), 109.1,

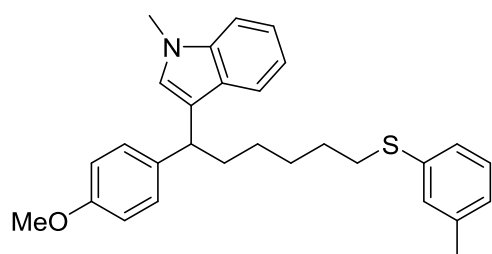
55.1, 41.8, 36.1, 33.5, 32.6, 28.8, 28.7, 27.5; HRMS (ESI-TOF) m/z : $C_{28}H_{31}BrNOS^+$ ($M + H$)⁺ calcd for 508.1304, found 508.1305.

3-(6-((3-Bromophenyl)thio)-1-(4-methoxyphenyl)hexyl)-1-methyl-1H-indole



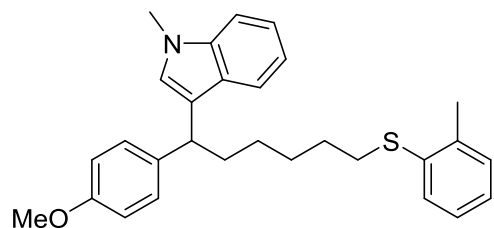
(**4aha**), by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 57.8 mg, 57%; yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.44-7.40 (m, 2H), 7.26-7.23 (m, 2H), 7.20-7.14 (m, 4H), 7.09 (t, J = 8.0 Hz, 1H), 7.00 (t, J = 7.2 Hz, 1H), 6.81 (d, J = 7.6 Hz, 2H), 6.79 (s, 1H), 4.06 (t, J = 8.0 Hz, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 2.85 (t, J = 7.6 Hz, 2H), 2.18-2.10 (m, 1H), 1.99-1.90 (m, 1H), 1.65-1.57 (m, 2H), 1.51-1.42 (m, 2H), 1.38-1.28 (m, 2H); ¹³C{¹H}NMR (100 MHz, CDCl₃): δ 157.6, 139.6, 137.6, 137.1, 130.7, 130.0, 128.7 (2C), 128.4, 127.3, 126.8, 125.6, 122.7, 121.4, 119.5, 119.2, 118.5, 113.6 (2C), 109.1, 55.1, 41.9, 36.2, 33.2, 32.6, 28.7, 28.7, 27.5; HRMS (ESI-TOF) m/z : $C_{28}H_{31}BrNOS^+$ ($M + H$)⁺ calcd for 508.1304, found 508.1299.

3-(1-(4-Methoxyphenyl)-6-(*m*-tolylthio)hexyl)-1-methyl-1H-indole (4aia), by silica



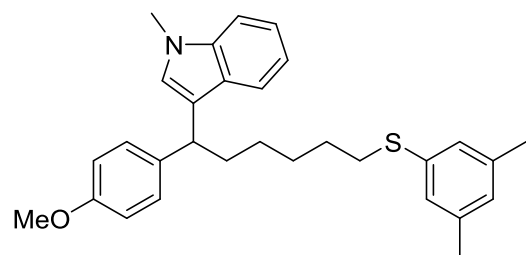
gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 59.4 mg, 67 %; yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.42 (d, J = 8.0 Hz, 1H), 7.24 (d, J = 8.8 Hz, 1H), 7.20-7.08 (m, 6H), 7.01-6.94 (m, 1H), 6.81 (d, J = 3.6 Hz, 2H), 6.78 (s, 1H), 4.08 (d, J = 7.6 Hz, 2H), 3.75 (s, 3H), 3.72 (s, 3H), 2.86 (t, J = 7.6 Hz, 2H), 2.30 (s, 3H), 2.18-2.09 (m, 1H), 1.99-1.90 (m, 1H), 1.65-1.57 (m, 2H), 1.51-1.40 (m, 2H), 1.36-1.26 (m, 2H); ¹³C{¹H}NMR (100 MHz, CDCl₃): δ 157.6, 138.5, 137.6, 137.1, 136.6, 129.4, 128.7 (2C), 128.6, 127.3, 126.5, 125.7, 125.6, 121.4, 119.5, 119.3, 118.5, 113.6 (2C), 109.0, 55.1, 41.9, 36.2, 33.4, 32.6, 29.0, 28.8, 27.6, 21.3; HRMS (ESI-TOF) m/z : $C_{29}H_{34}NOS^+$ ($M + H$)⁺ calcd for 444.2356, found 444.2357.

3-(1-(4-Methoxyphenyl)-6-(*o*-tolylthio)hexyl)-1-methyl-1H-indole (4aja), by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 55.8 mg, 63%;



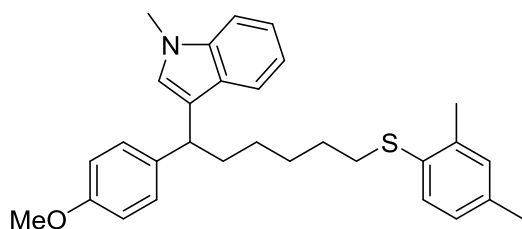
yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.43 (d, $J = 7.6$ Hz, 1H), 7.24-7.18 (m, 4H), 7.16-7.11 (m, 3H), 7.07 (d, $J = 8.0$ Hz, 1H), 7.00 (t, $J = 6.8$ Hz, 1H), 6.81 (d, $J = 4.4$ Hz, 2H), 6.79 (s, 1H), 4.09 (t, $J = 7.6$ Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 2.85 (t, $J = 7.2$ Hz, 2H), 2.34 (s, 3H), 2.19-2.10 (m, 1H), 2.00-1.91 (m, 1H), 1.68-1.60 (m, 2H), 1.51-1.44 (m, 2H), 1.39-1.29 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.7, 137.6, 137.2, 137.1, 136.3, 130.0, 128.7 (2C), 127.3, 127.2, 126.3, 125.6, 125.2, 121.4, 119.5, 119.3, 118.6, 113.6 (2C), 109.0, 55.2, 41.9, 36.2, 32.7, 32.6, 28.9, 28.8, 27.6, 20.3; HRMS (ESI-TOF) m/z : $\text{C}_{29}\text{H}_{34}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 444.2356, found 444.2357.

3-(6-((3,5-Dimethylphenyl)thio)-1-(4-methoxyphenyl)hexyl)-1-methyl-1H-indole



(4aka), by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 63.1 mg, 69%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.42 (d, $J = 8.0$ Hz, 1H), 7.23 (s, 1H), 7.19 (d, $J = 8.8$ Hz, 2H), 7.16-7.14 (m, 1H), 6.99 (t, $J = 7.2$ Hz, 1H), 6.91 (s, 2H), 6.81 (d, $J = 4.8$ Hz, 2H), 6.78 (s, 2H), 4.08 (t, $J = 8.0$ Hz, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 2.85 (t, $J = 7.6$ Hz, 2H), 2.26 (s, 6H), 2.17-2.10 (m, 1H), 1.99-1.90 (m, 1H), 1.65-1.57 (m, 2H), 1.51-1.42 (m, 2H), 1.36-1.28 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.6, 138.3, 137.6, 137.1, 136.4, 128.7 (2C), 127.5 (2C), 127.3, 126.4 (2C), 125.6, 121.4, 119.5, 119.3, 118.5, 113.6 (2C), 109.0, 55.1, 41.9, 36.2, 33.4, 32.6, 29.0, 28.8, 27.6, 21.2 (2C); HRMS (ESI-TOF) m/z : $\text{C}_{30}\text{H}_{36}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 458.2512, found 458.2519.

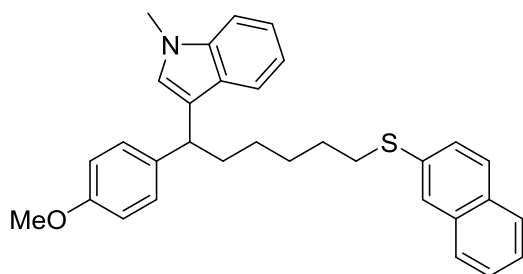
3-(6-((2,4-Dimethylphenyl)thio)-1-(4-methoxyphenyl)hexyl)-1-methyl-1H-indole



(4ala), by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 61.2 mg, 67%; yellow oil;

^1H NMR (400 MHz, CDCl_3): δ 7.42 (d, $J = 8.0$ Hz, 1H), 7.22-7.13 (m, 5H), 7.01-6.98 (m, 2H), 6.94 (d, $J = 8.0$ Hz, 1H), 6.81 (d, $J = 4.0$ Hz, 2H), 6.78 (s, 1H), 4.08 (t, $J = 7.6$ Hz, 1H), 3.75 (s, 3H), 3.72 (s, 3H), 2.79 (t, $J = 6.8$ Hz, 2H), 2.33 (s, 3H), 2.27 (s, 3H), 2.18-2.09 (m, 1H), 1.99-1.90 (m, 1H), 1.63-1.56 (m, 2H), 1.51-1.41 (m, 2H), 1.40-1.25 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.6, 137.7, 137.6, 137.1, 135.4, 132.3, 130.9, 128.8, 128.7 (2C), 127.3, 127.0, 125.6, 121.4, 119.5, 119.3, 118.5, 113.6 (2C), 109.0, 55.1, 41.9, 36.2, 33.4, 32.6, 29.0, 28.9, 27.6, 20.8, 20.3; HRMS (ESI-TOF) m/z : $\text{C}_{30}\text{H}_{36}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 458.2512, found 458.2519.

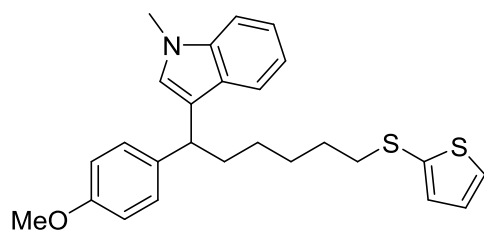
3-(1-(4-Methoxyphenyl)-6-(naphthalen-2-ylthio)hexyl)-1-methyl-1H-indole



(4ama), by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 63.2 mg, 66%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, $J = 7.8$ Hz, 1H), 7.72-1.69 (m, 3H), 7.46-7.37

(m, 4H), 7.24 (d, $J = 8.0$ Hz, 1H), 7.18 (d, $J = 8.6$ Hz, 2H), 7.15 (d, $J = 7.6$ Hz, 1H), 6.99 (t, $J = 8.0$ Hz, 1H), 6.80 (d, $J = 3.6$ Hz, 2H), 6.77 (s, 1H), 4.08 (d, $J = 8.0$ Hz, 1H), 3.74 (s, 3H), 3.70 (s, 3H), 2.97 (t, $J = 7.6$ Hz, 2H), 2.18-2.09 (m, 1H), 1.99-1.90 (m, 1H), 1.70-1.63 (m, 2H), 1.50-1.44 (m, 2H), 1.39-1.29 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.6, 137.6, 137.1, 134.5, 133.7, 131.5, 128.7 (2C), 128.2, 127.7, 127.3, 127.2, 126.9, 126.4, 126.2, 125.6, 125.4, 121.4, 119.5, 119.3, 118.5, 113.6 (2C), 109.0, 55.1, 41.8, 36.2, 33.3, 32.6, 28.9, 28.8, 27.5; HRMS (ESI-TOF) m/z : $\text{C}_{32}\text{H}_{34}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 480.2356, found 480.2349.

3-(1-(4-Methoxyphenyl)-6-(thiophen-2-ylthio)hexyl)-1-methyl-1H-indole (4ana),

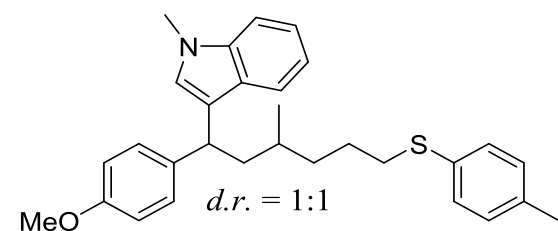


by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 51.3 mg, 59%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.43 (d, $J = 8.0$ Hz, 1H), 7.28 (d, $J = 5.6$ Hz, 1H), 7.24 (d, $J = 8.0$ Hz, 1H), 7.19 (d, $J = 8.8$ Hz, 2H), 7.15 (d, $J = 8.0$ Hz, 1H), 7.06

(d, $J = 3.6$ Hz, 1H), 6.99 (t, $J = 6.8$ Hz, 1H), 6.93 (t, $J = 4.8$ Hz, 1H), 6.80 (s, 2H), 6.78 (s, 1H), 4.07 (d, $J = 7.6$ Hz, 1H), 3.75 (s, 3H), 3.71 (s, 3H), 2.73 (t, $J = 7.6$ Hz,

2H), 2.17-2.08 (m, 1H), 1.98-1.88 (m, 1H), 1.59-1.53 (m, 2H), 1.47-1.38 (m, 2H), 1.34-1.26 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.6, 137.6, 137.1, 134.8, 133.2, 128.8, 128.7 (2C), 127.4, 127.3, 125.6, 121.4, 119.5, 119.3, 118.5, 113.6 (2C), 109.0, 55.1, 41.9, 38.8, 36.2, 32.6, 29.2, 28.4, 27.5; HRMS (ESI-TOF) m/z : $\text{C}_{26}\text{H}_{30}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 436.1763, found 436.1768.

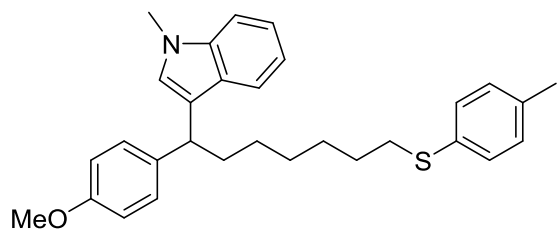
3-(1-(4-Methoxyphenyl)-3-methyl-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole



(4aoa) (*d.r.* = **1:1**), by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 52.8 mg, 55%; yellow oil;

^1H NMR (400 MHz, CDCl_3): δ 7.47-7.44 (m, 1H), 7.25-7.16 (m, 6H), 7.07 (d, J = 8.4 Hz, 2H), 7.03-6.98 (m, 1H), 6.82-6.76 (m, 3H), 4.26-4.21 (m, 1H), 3.75 (d, J = 4.8 Hz, 3H), 3.70 (d, J = 4.0 Hz, 3H), 2.81 (t, J = 6.4 Hz, 1H), 2.76 (t, J = 8.0 Hz, 1H), 2.30 (s, 3H), 2.15-2.10 (m, 0.5H), 2.02-1.96 (m, 0.5H), 1.92-1.86 (m, 0.5H), 1.79-1.72 (m, 0.5H), 1.62-1.59 (m, 1H), 1.46-1.40 (m, 2H), 1.35-1.26 (m, 2H), 0.96 (d, J = 6.0 Hz, 1.5H), 0.87 (d, J = 6.4 Hz, 1.5H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.7, 157.6, 138.1, 137.2, 137.1, 135.8, 133.0, 129.7, 129.6, 129.5, 129.5, 128.7, 128.7, 128.6, 125.7, 125.6, 121.4, 119.8, 119.5, 119.4, 118.8, 118.6, 118.5, 113.6, 113.6, 109.1, 55.1, 44.0, 43.5, 39.2, 36.5, 35.6, 34.5, 32.6, 30.0, 29.8, 26.4, 26.3, 21.0, 20.0, 19.5; HRMS (ESI-TOF) m/z : $\text{C}_{30}\text{H}_{36}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 458.2512, found 458.2513.

3-(1-(4-Methoxyphenyl)-7-(*p*-tolylthio)heptyl)-1-methyl-1*H*-indole (4apa), by

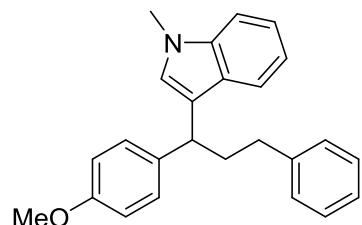


silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 53.0 mg, 58%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.43 (d, J = 8.0 Hz, 1H),

7.25-7.14 (m, 6H), 7.08 (d, J = 8.0 Hz, 2H), 7.00 (t, J = 8.0 Hz, 1H), 6.81 (d, J = 3.2 Hz, 2H), 6.79 (s, 1H), 4.07 (t, J = 8.0 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 2.83 (t, J = 7.6 Hz, 2H), 2.30 (s, 3H), 2.17-2.08 (m, 1H), 1.98-1.91 (m, 1H), 1.61-1.58 (m, 2H), 1.36-1.29 (m, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.6, 137.7, 137.1, 135.8, 133.0, 129.7 (2C), 129.6 (2C), 128.7 (2C), 127.3, 125.6, 121.4, 119.5, 119.4, 118.5,

113.6 (2C), 109.0, 55.2, 41.9, 36.3, 34.2, 32.6, 29.2 (2C), 28.7, 27.9, 21.0; HRMS (ESI-TOF) m/z : $C_{30}H_{36}NOS^+$ ($M + H$)⁺ calcd for 458.2512, found 458.2519.

3-(1-(4-Methoxyphenyl)-3-phenylpropyl)-1-methyl-1H-indole (4aqa), by silica gel



column chromatography (hexane/ethyl acetate = 15 : 1), yield: 34.1 mg, 48%; yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.41 (d, J = 8.0 Hz, 1H), 7.27-7.22 (m, 5H),

7.19-7.15 (m, 4H), 7.00 (t, J = 7.6 Hz, 1H), 6.84 (d, J =

4.4 Hz, 2H), 6.81 (s, 1H), 4.13 (d, J = 6.8 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 2.63 (t,

J = 8.0 Hz, 2H), 2.54-2.45 (m, 1H), 2.34-2.27 (m, 1H); ¹³C{¹H}NMR (100 MHz,

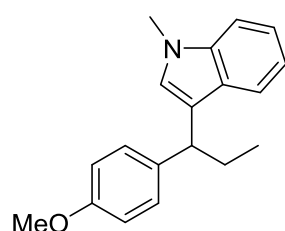
CDCl₃): δ 157.8, 142.4, 137.3, 137.2, 128.8 (2C), 128.5 (2C), 128.3 (2C), 127.3,

125.7, 125.7, 121.5, 119.5, 119.1, 118.6, 113.7 (2C), 109.1, 55.2, 41.4, 38.0, 34.2,

32.7; HRMS (ESI-TOF) m/z : $C_{25}H_{26}NO^+$ ($M + H$)⁺ calcd for 356.2009, found

356.2012.

3-(1-(4-Methoxyphenyl)propyl)-1-methyl-1H-indole (4ara), by silica gel column



chromatography (hexane/ethyl acetate = 15 : 1), yield: 34.6 mg, 62%; yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.43 (d,

J = 8.0 Hz, 1H), 7.24-7.14 (m, 4H), 7.00 (t, J = 8.0 Hz, 1H),

6.81 (t, J = 6.0 Hz, 3H), 3.99 (t, J = 6.8 Hz, 1H), 3.76 (s, 3H),

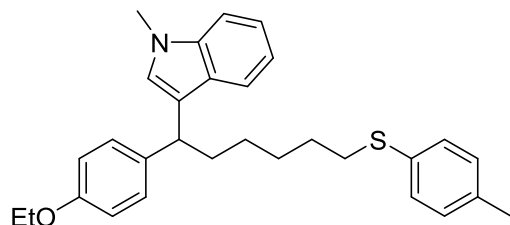
3.73 (s, 3H), 2.22-2.16 (m, 1H), 2.00-1.93 (m, 1H), 0.93 (t, J = 7.2 Hz, 3H);

¹³C{¹H}NMR (100 MHz, CDCl₃): δ 157.6, 137.6, 137.2, 128.8 (2C), 127.4, 125.7,

121.4, 119.6, 119.3, 118.5, 113.5 (2C), 109.0, 55.2, 43.9, 32.6, 29.2, 12.9; HRMS

(ESI-TOF) m/z : $C_{19}H_{22}NO^+$ ($M + H$)⁺ calcd for 280.1696, found 280.1699.

3-(1-(4-Ethoxyphenyl)-6-(p-tolylthio)hexyl)-1-methyl-1H-indole (4baa), by silica



gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 72.2 mg, 79%;

yellow oil; ¹H NMR (400 MHz, CDCl₃): δ

7.42 (d, J = 8.0 Hz, 1H), 7.23-7.12 (m, 6H),

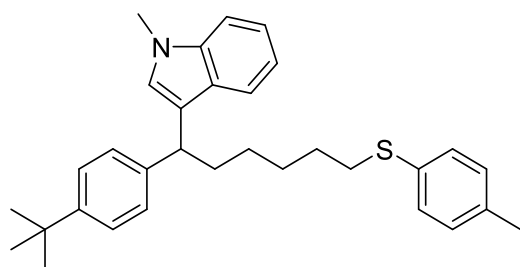
7.05 (d, J = 8.0 Hz, 2H), 6.98 (t, J = 7.6 Hz, 1H), 6.78 (s, 2H), 6.76 (s, 1H), 4.06 (t, J

= 7.2 Hz, 1H), 3.97-3.92 (m, 2H), 3.67 (s, 3H), 2.80 (t, J = 7.2 Hz, 2H), 2.28 (s, 3H),

2.16-2.07 (m, 1H), 1.97-1.89 (m, 1H), 1.61-1.54 (m, 2H), 1.48-1.40 (m, 2H),

1.37-1.26 (m, 5H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.0, 137.5, 137.1, 135.7, 133.0, 129.7 (2C), 129.5 (2C), 128.6 (2C), 127.3, 125.6, 121.3, 119.5, 119.3, 118.5, 114.1 (2C), 109.0, 63.2, 41.8, 36.2, 34.2, 32.5, 29.1, 28.7, 27.5, 20.9, 14.9; HRMS (ESI-TOF) m/z : $\text{C}_{30}\text{H}_{36}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 458.2512, found 458.2516.

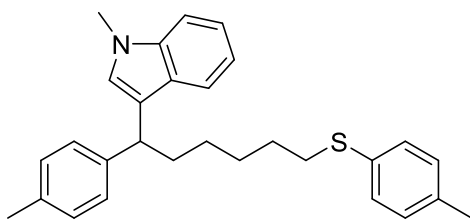
3-(1-(4-(*Tert*-butyl)phenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-*1H*-indole (4caa), by



silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 54.4 mg, 58%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.49 (d, $J = 8.0$ Hz, 1H), 7.24-7.15 (m, 8H), 7.07 (d, $J = 8.0$ Hz,

2H), 7.01 (t, $J = 7.6$ Hz, 1H), 6.84 (s, 1H), 4.10 (t, $J = 7.6$ Hz, 1H), 3.73 (s, 3H), 2.82 (t, $J = 7.2$ Hz, 2H), 2.30 (s, 3H), 2.16-2.09 (m, 1H), 2.03-1.94 (m, 1H), 1.62-1.56 (m, 2H), 1.47-1.43 (m, 2H), 1.30-1.26 (s, 11H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 148.4, 142.5, 137.1, 135.8, 133.0, 129.7 (2C), 129.6 (2C), 127.4 (2C), 127.3, 125.7 (2C), 125.1, 121.4, 119.6, 119.1, 118.5, 109.0, 42.2, 36.2, 34.3, 32.6, 31.4 (4C), 29.1, 28.8, 27.7, 21.0; HRMS (ESI-TOF) m/z : $\text{C}_{32}\text{H}_{40}\text{NS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 470.2876, found 470.2878.

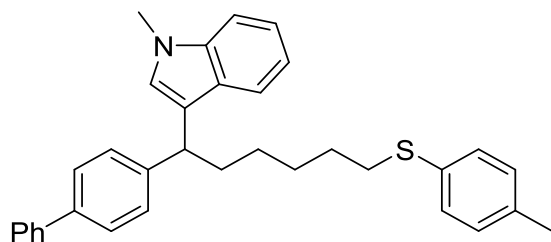
1-Methyl-3-(1-(*p*-tolyl)-6-(*p*-tolylthio)hexyl)-*1H*-indole (4daa), by silica gel column



chromatography (hexane/ethyl acetate = 15 : 1), yield: 40.1 mg, 47%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.44 (d, $J = 8.0$ Hz, 1H), 7.23-7.14 (m, 5H), 7.08-7.04 (m, 5H), 7.00 (t,

$J = 8.0$ Hz, 1H), 6.82 (s, 1H), 4.09 (t, $J = 7.6$ Hz, 1H), 3.72 (s, 3H), 2.82 (t, $J = 7.2$ Hz, 2H), 2.30 (s, 3H), 2.28 (s, 3H), 2.18-2.09 (m, 1H), 1.99-1.93 (m, 1H), 1.62-1.56 (m, 2H), 1.47-1.42 (m, 2H), 1.36-1.28 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 142.5, 137.1, 135.8, 135.2, 133.0, 129.7 (2C), 129.6 (2C), 128.9 (2C), 127.7 (2C), 127.4, 125.7, 121.4, 119.5, 119.2, 118.5, 109.0, 42.3, 36.2, 34.3, 32.6, 29.1, 28.8, 27.6, 21.0, 21.0; HRMS (ESI-TOF) m/z : $\text{C}_{29}\text{H}_{34}\text{NS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 428.2406, found 428.2409.

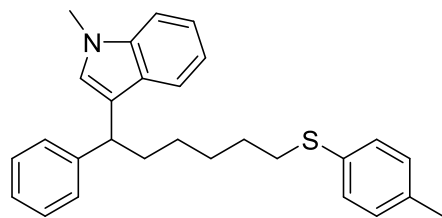
3-(1-([1,1'-Biphenyl]-4-yl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4eaa), by



silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 40.1 mg, 41%; yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.55 (d, *J* = 7.6 Hz, 2H),

7.48 (d, *J* = 8.0 Hz, 3H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.25-7.16 (m, 4H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 7.2 Hz, 1H), 6.88 (s, 1H), 4.17 (t, *J* = 7.6 Hz, 1H), 3.75 (s, 3H), 2.83 (t, *J* = 7.2 Hz, 2H), 2.29 (s, 3H), 2.23-2.14 (m, 1H), 2.03-1.98 (m, 1H), 1.62-1.57 (m, 2H), 1.50-1.43 (m, 2H), 1.39-1.31 (m, 2H); ¹³C{¹H}NMR (100 MHz, CDCl₃): δ 144.7, 141.1, 138.7, 137.2, 135.8, 133.0, 129.8 (2C), 129.6 (2C), 128.6 (2C), 128.2 (2C), 127.4, 127.0 (2C), 126.9 (3C), 125.8, 121.5, 119.5, 118.8, 118.6, 109.1, 42.4, 36.1, 34.3, 32.7, 29.1, 28.8, 27.6, 21.0; HRMS (ESI-TOF) *m/z*: C₃₄H₃₆NS⁺ (M + H)⁺ calcd for 490.2563, found 490.2566.

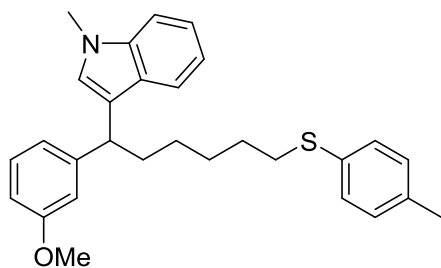
1-Methyl-3-(1-phenyl-6-(*p*-tolylthio)hexyl)-1*H*-indole (4faa), by silica gel column



chromatography (hexane/ethyl acetate = 15 : 1), yield: 34.7 mg, 42%; yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.43 (d, *J* = 8.0 Hz, 1H), 7.27.18 (m, 8H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 8.0

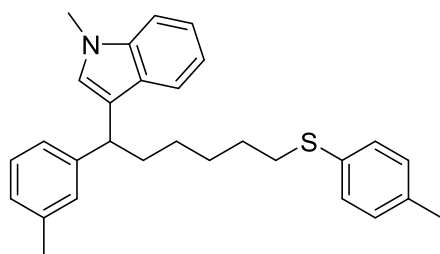
Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.84 (s, 1H), 4.13 (t, *J* = 7.2 Hz, 1H), 3.73 (s, 3H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.30 (s, 3H), 2.20-2.11 (m, 1H), 2.00-1.95 (m, 1H), 1.60-1.55 (m, 2H), 1.46-1.41 (m, 2H), 1.36-1.32 (m, 2H); ¹³C{¹H}NMR (100 MHz, CDCl₃): δ 145.5, 137.1, 135.8, 133.0, 129.8 (2C), 129.6 (2C), 128.3 (2C), 128.2 (2C), 127.8, 125.8, 125.7, 121.4, 119.5, 118.9, 118.6, 109.1, 42.8, 36.1, 34.3, 32.6, 29.1, 28.8, 27.6, 21.0; HRMS (ESI-TOF) *m/z*: C₂₈H₃₂NS⁺ (M + H)⁺ calcd for 414.2250, found 414.2259.

3-(1-(3-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4haa), by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 48.7 mg, 55%; yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.46 (d, *J* = 8.0 Hz, 1H), 7.23-7.15 (m, 5H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.02-6.98 (m, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.84 (s, 2H),



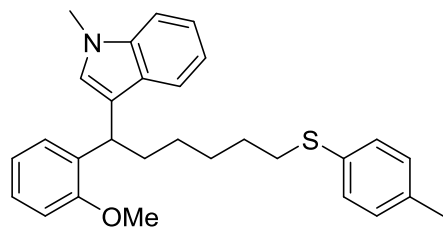
6.70 (d, $J = 8.0$ Hz, 1H), 4.10 (t, $J = 8.0$ Hz, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 2.82 (t, $J = 7.2$ Hz, 2H), 2.30 (s, 3H), 2.18-2.09 (m, 1H), 2.02-1.92 (m, 1H), 1.60-1.55 (m, 2H), 1.48-1.42 (m, 2H), 1.35-1.28 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 159.5, 147.3, 137.1, 135.8, 133.0, 129.8 (2C), 129.6 (2C), 129.1, 127.4, 125.7, 121.4, 120.4, 119.5, 118.8, 118.6, 114.0, 110.6, 109.0, 55.1, 42.8, 36.1, 34.3, 32.7, 29.1, 28.8, 27.6, 21.0; HRMS (ESI-TOF) m/z : $\text{C}_{29}\text{H}_{34}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 444.2356, found 444.2351.

1-Methyl-3-(1-(*m*-tolyl)-6-(*p*-tolylthio)hexyl)-1H-indole (4iaa), by silica gel column



chromatography (hexane/ethyl acetate = 15 : 1), yield: 50.4 mg, 59%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.46 (d, $J = 8.0$ Hz, 1H), 7.25-7.12 (m, 5H), 7.10-7.06 (m, 4H), 7.01 (t, $J = 7.6$ Hz, 1H), 6.96 (d, $J = 7.6$ Hz, 1H), 6.83 (s, 1H), 4.08 (t, $J = 7.6$ Hz, 1H), 3.73 (s, 3H), 2.82 (t, $J = 7.2$ Hz, 2H), 2.30 (s, 3H), 2.29 (s, 3H), 2.16-2.08 (m, 1H), 2.01-1.94 (m, 1H), 1.62-1.57 (m, 2H), 1.48-1.41 (m, 2H), 1.37-1.29 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 145.5, 137.7, 137.1, 135.8, 133.0, 129.7 (2C), 129.6 (2C), 128.6, 128.1, 127.4, 126.6, 125.7, 124.8, 121.4, 119.5, 119.1, 118.6, 109.0, 42.7, 36.2, 34.3, 32.7, 29.1, 28.8, 27.6, 21.5, 21.0; HRMS (ESI-TOF) m/z : $\text{C}_{29}\text{H}_{34}\text{NS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 428.2406, found 428.2409.

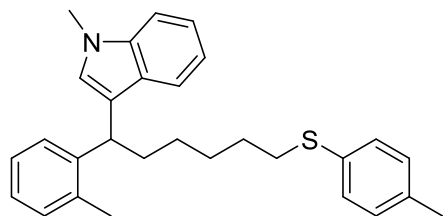
3-(1-(2-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1H-indole (4jaa), by silica



gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 47.0 mg, 53%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.49 (d, $J = 8.0$ Hz, 1H), 7.24-7.20 (m, 3H), 7.16 (d, $J = 7.2$ Hz, 2H), 7.11 (t, $J = 8.0$ Hz, 1H), 7.06 (d, $J = 8.0$ Hz, 2H), 6.99 (t, $J = 7.6$ Hz, 1H), 6.86-6.80 (m, 3H), 4.71 (t, $J = 7.6$ Hz, 1H), 3.84 (s, 3H), 3.71 (s, 3H), 2.82 (t, $J = 7.2$ Hz, 2H), 2.29 (s, 3H), 2.14-2.03 (m, 1H), 2.00-1.91 (m, 1H), 1.62-1.55 (m, 2H), 1.47-1.29 (m, 4H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 156.9, 137.0, 135.7, 134.1,

133.1, 129.7 (2C), 129.5 (2C), 128.0, 127.8, 126.6, 126.0, 121.3, 120.5, 119.6, 118.9, 118.4, 110.4, 108.9, 55.5, 35.5, 34.3, 33.9, 32.6, 29.1, 28.8, 27.5, 21.0; HRMS (ESI-TOF) m/z : $C_{29}H_{34}NOS^+$ ($M + H$) $^+$ calcd for 444.2356, found 444.2351.

1-Methyl-3-(1-(*o*-tolyl)-6-(*p*-tolylthio)hexyl)-1*H*-indole (4kaa), by silica gel column



chromatography (hexane/ethyl acetate = 15 : 1),

yield: 38.4 mg, 45%; yellow oil; 1H NMR (400

MHz, $CDCl_3$): δ 7.44 (d, $J = 8.0$ Hz, 1H),

7.26-7.06 (m, 10H), 7.02 (t, $J = 7.6$ Hz, 1H), 6.68

(s, 1H), 4.37 (t, $J = 7.6$ Hz, 1H), 3.70 (s, 3H), 2.82 (t, $J = 7.2$ Hz, 2H), 2.36 (s, 3H),

2.30 (s, 3H), 2.18-2.10 (m, 1H), 2.00-1.91 (m, 1H), 1.63-1.55 (m, 2H), 1.49-1.33 (m,

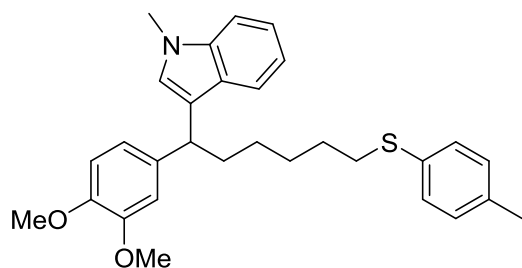
4H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 143.4, 137.0, 135.8 (2C), 133.0, 130.3,

129.7 (2C), 129.6 (2C), 127.6, 126.7, 126.3, 125.9, 125.6, 121.4, 119.2, 118.8, 118.6,

109.1, 37.9, 36.2, 34.3, 32.6, 29.2, 28.9, 27.7, 21.0, 19.8; HRMS (ESI-TOF) m/z :

$C_{29}H_{34}NS^+$ ($M + H$) $^+$ calcd for 428.2406, found 444.2409.

3-(1-(3,4-dimethoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4laa), by



silica gel column chromatography

(hexane/ethyl acetate = 15 : 1), yield: 75.7

mg, 80%; yellow oil; 1H NMR (400 MHz,

$CDCl_3$): δ 7.45 (d, $J = 8.0$ Hz, 1H),

7.25-7.15 (m, 4H), 7.07 (d, $J = 8.0$ Hz, 2H),

7.01 (t, $J = 8.0$ Hz, 1H), 6.85-6.76 (m, 4H), 4.07 (t, $J = 8.4$ Hz, 1H), 3.83 (s, 3H), 3.81

(s, 3H), 3.73 (s, 3H), 2.83 (t, $J = 7.2$ Hz, 1H), 2.30 (s, 3H), 2.19-2.10 (m, 1H),

2.001.92 (m, 1H), 1.61-1.56 (m, 2H), 1.51-1.41 (m, 2H), 1.37-1.27 (m, 2H);

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 148.7, 147.1, 138.1, 137.2, 135.8, 133.0, 129.7

(2C), 129.6 (2C), 127.3, 125.7, 121.4, 119.6, 119.5, 119.2, 118.6, 111.2, 110.9, 109.1,

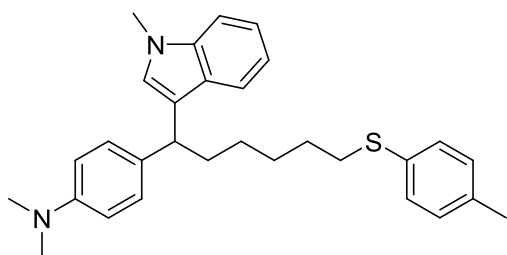
55.8, 42.4, 36.2, 34.2, 32.6, 29.1, 28.8, 27.6, 21.0; HRMS (ESI-TOF) m/z :

$C_{30}H_{36}NO_2S^+$ ($M + H$) $^+$ calcd for 474.2461, found 474.2466.

***N,N*-Dimethyl-4-(1-(1-methyl-1*H*-indol-3-yl)-6-(*p*-tolylthio)hexyl)aniline (4maa)**,

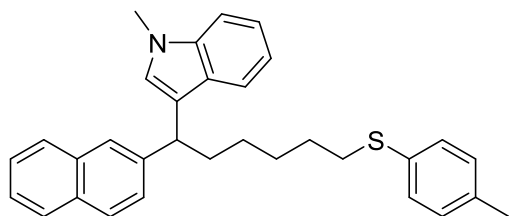
by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 62.0 mg,

68%; yellow oil; 1H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, $J = 8.0$ Hz, 1H), 7.23-7.20



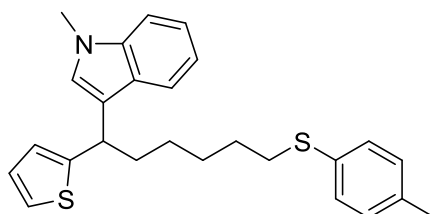
(m, 3H), 7.17-7.13 (m, 3H), 7.07 (d, $J = 8.0$ Hz, 2H), 6.99 (t, $J = 8.0$ Hz, 1H), 6.79 (s, 1H), 6.66 (d, $J = 8.8$ Hz, 2H), 4.04 (t, $J = 8.0$ Hz, 1H), 3.71 (s, 3H), 2.88 (s, 6H), 2.82 (t, $J = 7.2$ Hz, 2H), 2.30 (s, 3H), 2.16-2.07 (m, 1H), 1.99-1.91 (m, 1H), 1.62-1.55 (m, 2H), 1.47-1.42 (m, 2H), 1.35-1.29 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 148.9, 137.1, 135.7, 133.8, 133.1, 129.7 (2C), 129.6 (2C), 128.4 (2C), 127.4, 125.7, 121.3, 119.8, 119.6, 118.4, 112.8 (2C), 109.0, 41.7, 40.8 (2C), 36.3, 34.3, 32.6, 29.1, 28.8, 27.6, 21.0; HRMS (ESI-TOF) m/z : $\text{C}_{30}\text{H}_{37}\text{N}_2\text{S}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 457.2672, found 457.2673.

1-Methyl-3-(1-(naphthalen-2-yl)-6-(*p*-tolylthio)hexyl)-1*H*-indole (4naa), by silica



gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 49.1 mg, 53%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.78-7.70 (m, 4H), 7.46-7.38 (m, 4H), 7.25-7.13 (m, 4H), 7.04 (d, $J = 8.0$ Hz, 2H), 6.97 (t, $J = 7.2$ Hz, 1H), 6.86 (s, 1H), 4.29 (t, $J = 8.8$ Hz, 1H), 3.71 (s, 3H), 2.81 (t, $J = 6.8$ Hz, 2H), 2.28 (s, 3H), 2.24-2.17 (m, 1H), 2.13-2.06 (m, 1H), 1.59-1.54 (m, 2H), 1.49-1.39 (m, 2H), 1.33-1.28 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 142.9, 137.1, 135.8, 133.5, 133.0, 132.1, 129.7 (2C), 129.6 (2C), 127.9, 127.6, 127.5, 127.4, 126.6, 125.9, 125.8, 125.7, 125.1, 121.5, 119.5, 118.8, 118.6, 109.1, 42.8, 35.9, 34.2, 32.6, 29.1, 28.8, 27.6, 21.0; HRMS (ESI-TOF) m/z : $\text{C}_{32}\text{H}_{34}\text{NS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 464.2406, found 464.2402.

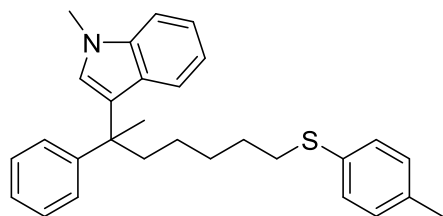
1-Methyl-3-(1-(thiophen-2-yl)-6-(*p*-tolylthio)hexyl)-1*H*-indole (4oaa), by silica gel



column chromatography (hexane/ethyl acetate = 15 : 1), yield: 51.1 mg, 61%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.51 (d, $J = 8.0$ Hz, 1H), 7.26-7.19 (m, 4H), 7.10-7.02 (m, 4H), 6.90-6.87 (m, 3H), 4.41 (t, $J = 7.6$ Hz, 1H), 3.74 (s, 3H), 2.82 (t, $J = 6.8$ Hz, 2H), 2.30 (s, 3H), 2.21-2.13 (m, 1H), 2.12-2.04 (m, 1H), 1.62-1.59 (m, 2H), 1.49-1.42 (m, 2H), 1.39-1.32 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 150.3, 137.1, 135.8, 133.0,

129.8 (2C), 129.6 (2C), 127.0, 126.3, 126.0, 123.6, 122.9, 121.5, 119.4, 118.7, 118.4, 109.2, 38.0, 37.3, 34.3, 32.7, 29.1, 28.6, 27.5, 21.0; HRMS (ESI-TOF) m/z : $C_{26}H_{30}NS_2^+$ ($M + H$) $^+$ calcd for 420.1814, found 420.1807.

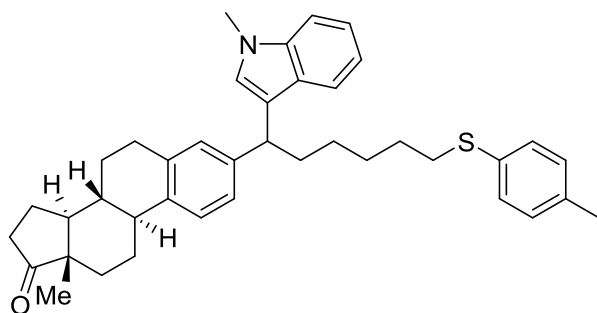
1-Methyl-3-(2-phenyl-7-(*p*-tolylthio)heptan-2-yl)-1*H*-indole (4qaa), by silica gel



column chromatography (hexane/ethyl acetate = 15 : 1), yield: 41.0 mg, 48%; yellow oil; 1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.18 (m, 7H), 7.12 (d, $J = 8.4$ Hz, 2H), 7.06 (d, $J = 8.0$ Hz, 2H), 6.97 (d,

$J = 8.0$ Hz, 1H), 6.91 (s, 1H), 6.83 (t, $J = 7.6$ Hz, 1H), 3.77 (s, 3H), 2.76 (t, $J = 7.2$ Hz, 2H), 2.30 (s, 3H), 2.24-2.19 (m, 1H), 2.11-2.04 (m, 1H), 1.56-1.50 (m, 4H), 1.39-1.32 (m, 3H), 1.15-1.06 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 149.0, 137.6, 135.8, 133.0, 129.7 (2C), 129.6 (2C), 127.8 (2C), 126.9 (2C), 126.4, 126.1, 125.4, 123.4, 121.3, 121.1, 118.2, 109.0, 42.2, 41.4, 34.2, 32.7, 29.7, 29.4, 29.1, 27.6, 24.1, 21.0; HRMS (ESI-TOF) m/z : $C_{29}H_{34}NS^+$ ($M + H$) $^+$ calcd for 428.2406, found 428.2409.

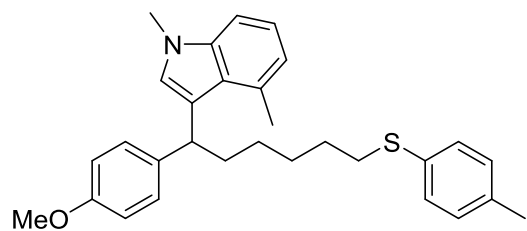
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(1-(1-methyl-1*H*-indol-3-yl)-6-(*p*-tolylthio)hexyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (4raa),



by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 61.3 mg, 52%; yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, $J = 8.0$ Hz, 1H), 7.25-7.15 (m, 5H), 7.08-6.99

(m, 5H), 6.84 (s, 1H), 4.06 (t, $J = 7.2$ Hz, 1H), 3.73 (s, 3H), 2.86-2.80 (m, 4H), 2.52-2.45 (m, 1H), 2.40-2.36 (m, 1H), 2.30 (s, 3H), 2.27-2.21 (m, 1H), 2.17-2.08 (m, 2H), 2.02-1.92 (m, 3H), 1.65-1.62 (m, 2H), 1.59-1.55 (m, 2H), 1.52-1.41 (m, 6H), 1.38-1.30 (m, 3H), 0.89 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ : 221.1, 143.1, 137.1, 136.1, 135.8, 133.0, 129.7 (2C), 129.6 (2C), 128.3, 128.3, 127.4, 125.7, 125.7, 125.1, 125.0, 121.4, 119.5, 118.5, 109.0, 50.5, 48.0, 44.3, 42.2, 38.1, 35.9, 34.3, 32.7, 31.6, 29.7, 29.5, 29.1, 28.8, 27.7, 26.6, 25.6, 21.6, 21.0, 13.9; HRMS (ESI-TOF) m/z : $C_{40}H_{48}NOS^+$ ($M + H$) $^+$ calcd for 590.3451, found 590.3455.

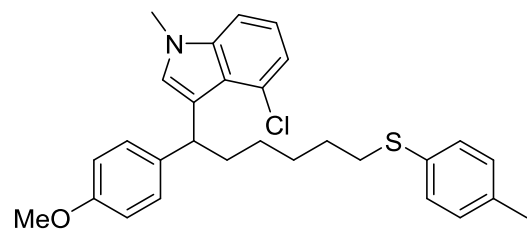
3-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1,4-dimethyl-1*H*-indole (4aab), by



silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 72.2 mg, 79%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.21 (d, *J* = 8.0 Hz, 2H),

7.10-7.02 (m, 6H), 6.84 (s, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 6.8 Hz, 1H), 4.40 (t, *J* = 7.6 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.53 (s, 3H), 2.29 (s, 3H), 2.07-1.98 (m, 1H), 1.92-1.82 (m, 1H), 1.63-1.56 (m, 2H), 1.47-1.40 (m, 4H); ¹³C{¹H}NMR (100 MHz, CDCl₃) δ: 157.5, 138.7, 137.4, 135.8, 133.0, 131.0, 129.7 (2C), 129.5 (2C), 128.9 (2C), 126.2, 126.1, 121.4, 120.6, 119.5, 113.5 (2C), 106.9, 55.1, 42.4, 38.4, 34.2, 32.8, 29.1, 28.8, 27.8, 20.9, 20.8; HRMS (ESI-TOF) *m/z*: C₃₀H₃₆NOS⁺ (M + H)⁺ calcd for 458.2512, found 458.2519.

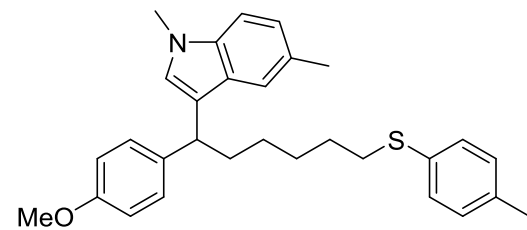
4-Chloro-3-(1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4aac),



by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 64.9 mg, 68%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.20 (d, *J* = 8.4 Hz, 4H), 7.11 (d,

J = 7.6 Hz, 1H), 7.06-6.99 (m, 4H), 6.81 (d, *J* = 6.8 Hz, 2H), 6.75 (s, 1H), 4.75 (t, *J* = 7.6 Hz, 1H), 3.75 (s, 3H), 3.66 (s, 3H), 2.81 (t, *J* = 6.4 Hz, 2H), 2.28 (s, 3H), 2.14-2.06 (m, 1H), 1.92-1.87 (m, 1H), 1.61-1.56 (m, 2H), 1.47-1.30 (m, 4H); ¹³C{¹H}NMR (100 MHz, CDCl₃) δ 157.6, 138.4, 137.7, 135.7, 133.0, 129.7 (2C), 129.5 (2C), 129.0 (2C), 127.3, 126.3, 123.8, 121.8, 120.2, 120.1, 113.5 (2C), 107.9, 55.1, 41.1, 37.9, 34.2, 32.9, 29.1, 28.8, 27.7, 20.9; HRMS (ESI-TOF) *m/z*: C₂₉H₃₃ClNOS⁺ (M + H)⁺ calcd for 478.1966, found 478.1959.

3-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1,5-dimethyl-1*H*-indole (4aad), by

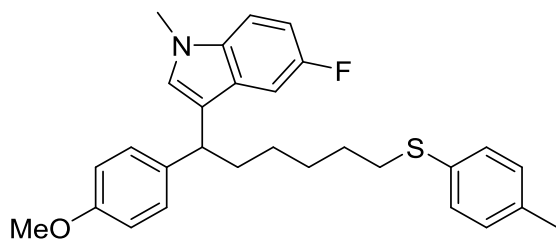


silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 63.1 mg, 69%; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.21 (d, *J* = 8.0 Hz, 4H), 7.18 (s,

1H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.79

(d, $J = 8.4$ Hz, 2H), 6.75 (s, 1H), 4.04 (t, $J = 7.6$ Hz, 1H), 3.75 (s, 3H), 3.67 (s, 3H), 2.82 (t, $J = 7.2$ Hz, 2H), 2.39 (s, 3H), 2.29 (s, 3H), 2.15-2.06 (m, 1H), 1.97-1.89 (m, 1H), 1.62-1.55 (m, 2H), 1.49-1.40 (m, 2H), 1.36-1.26 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.6, 137.8, 135.7, 135.6, 133.0, 129.7 (2C), 129.5 (2C), 128.6 (2C), 127.7, 127.5, 125.7, 123.0, 119.1, 118.7, 113.6 (2C), 108.8, 55.1, 41.8, 36.3, 34.2, 32.6, 29.1, 28.8, 27.6, 21.5, 21.0; HRMS (ESI-TOF) m/z : $\text{C}_{30}\text{H}_{36}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 458.2512, found 458.2519.

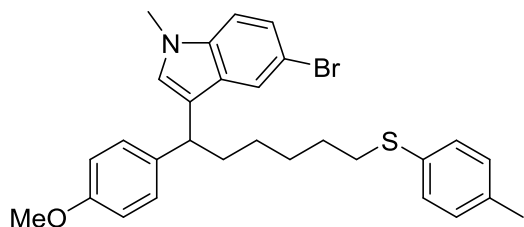
5-Fluoro-3-(1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4aae),



by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 61.8 mg, 67%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.21 (d, $J = 6.8$ Hz, 2H),

7.16 (d, $J = 7.6$ Hz, 2H), 7.12 (t, $J = 5.6$ Hz, 1H), 7.08-7.02 (m, 3H), 6.90 (d, $J = 8.8$ Hz, 1H), 6.86 (s, 1H), 6.80 (d, $J = 7.6$ Hz, 2H), 3.98 (t, $J = 7.6$ Hz, 1H), 3.75 (s, 3H), 3.69 (s, 3H), 2.82 (t, $J = 6.8$ Hz, 2H), 2.29 (s, 3H), 2.15-2.04 (m, 1H), 1.96-1.87 (m, 2H), 1.62-1.55 (m, 2H), 1.49-1.40 (m, 2H), 1.35-1.26 (m, 2H); ^{19}F NMR (282 MHz, CDCl_3) δ : -125.6 (s, 1F); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.7, 157.3 (d, $J_{\text{C-F}} = 232.2$ Hz, 1C), 137.2, 135.8, 133.8, 133.0, 129.7 (2C), 129.6 (2C), 128.6 (2C), 127.5 (d, $J_{\text{C-F}} = 9.6$ Hz, 1C), 127.2, 119.2 (d, $J_{\text{C-F}} = 4.9$ Hz, 1C), 113.7 (2C), 109.7 (d, $J_{\text{C-F}} = 16.0$ Hz, 1C), 109.6, 104.4 (d, $J_{\text{C-F}} = 23.2$ Hz, 1C), 55.1, 41.8, 36.0, 34.2, 32.9, 29.1, 28.7, 27.5, 20.9; HRMS (ESI-TOF) m/z : $\text{C}_{29}\text{H}_{33}\text{FNOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 462.2261, found 462.2269.

5-Bromo-3-(1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4aaf),

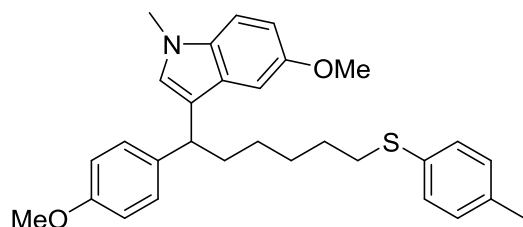


by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 68.8 mg, 66%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.53 (s, 1H), 7.23-7.20 (m, 3H),

7.15 (d, $J = 8.4$ Hz, 2H), 7.07 (t, $J = 8.0$ Hz, 3H), 6.81 (s, 2H), 6.79 (s, 1H), 3.99 (t, $J = 7.6$ Hz, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 2.82 (t, $J = 7.2$ Hz, 2H), 2.29 (s, 3H), 2.11-2.02 (m, 1H), 1.95-1.87 (m, 1H), 1.61-1.54 (m, 2H), 1.48-1.39 (m, 2H),

1.34-1.26 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.8, 137.1, 135.8, 133.0, 129.7 (2C), 129.6 (2C), 129.0, 128.5 (2C), 126.8, 124.2, 121.9, 119.0, 113.7 (2C), 112.0, 110.6, 55.2, 41.6, 36.2, 34.2, 32.8, 29.1, 28.7, 27.5, 21.0; HRMS (ESI-TOF) m/z : $\text{C}_{29}\text{H}_{33}\text{BrNOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 522.1461, found 522.1459.

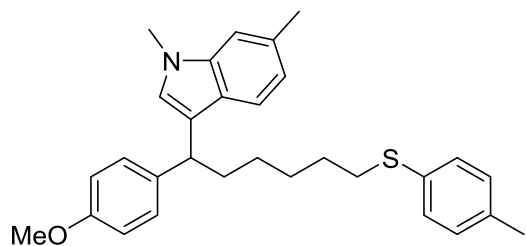
5-Methoxy-3-(1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole



(4aag), by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 58.7 mg, 62%; yellow oil;

^1H NMR (400 MHz, CDCl_3): δ 7.26 (s, 1H), 7.22-7.18 (m, 4H), 7.13 (d, $J = 8.4$ Hz, 1H), 7.07 (d, $J = 7.6$ Hz, 2H), 6.85-6.83 (m, 1H), 6.81-7.89 (m, 3H), 4.01 (t, $J = 7.6$ Hz, 1H), 3.76 (s, 6H), 3.70 (s, 3H), 2.83 (t, $J = 6.8$ Hz, 2H), 2.30 (s, 3H), 2.15-2.07 (m, 1H), 1.97-1.88 (m, 1H), 1.64-1.59 (m, 2H), 1.49-1.40 (m, 2H), 1.35-1.28 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.6, 153.3, 137.6, 135.8, 133.0, 132.6, 129.7 (2C), 129.6 (2C), 128.7 (2C), 127.6, 126.3, 118.7, 113.6 (2C), 111.3, 109.7, 101.8, 55.9, 55.2, 41.9, 36.1, 34.3, 32.8, 29.1, 28.8, 27.6, 21.0; HRMS (ESI-TOF) m/z : $\text{C}_{30}\text{H}_{36}\text{NO}_2\text{S}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 474.2461, found 474.2462.

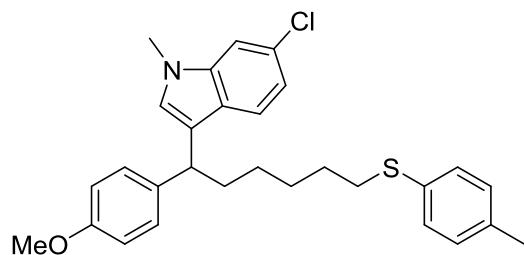
3-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1,6-dimethyl-1*H*-indole (4aah), by



silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 62.2

mg, 68%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.25 (d, $J = 6.8$ Hz, 1H), 7.22-7.16 (m, 4H), 7.06 (d, $J = 7.2$ Hz, 2H), 6.87-6.84 (m, 2H), 6.78 (d, $J = 6.8$ Hz, 2H), 6.69 (s, 1H), 4.03 (t, $J = 7.6$ Hz, 1H), 3.96 (s, 3H), 3.73 (s, 3H), 2.82 (t, $J = 6.8$ Hz, 2H), 2.70 (s, 3H), 2.29 (s, 3H), 2.14-2.05 (m, 1H), 1.95-1.87 (m, 1H), 1.61-1.54 (m, 2H), 1.48-1.39 (m, 2H), 1.36-1.26 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.6, 137.6, 135.8, 135.7, 133.0, 129.7 (2C), 129.5 (2C), 128.6 (2C), 128.4, 127.3, 124.1, 121.0, 118.9, 118.8, 117.5, 113.5 (2C), 55.1, 41.7, 36.6, 36.2, 34.2, 29.1, 28.8, 27.5, 20.9, 19.7; HRMS (ESI-TOF) m/z : $\text{C}_{30}\text{H}_{36}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 458.2512, found 458.2519.

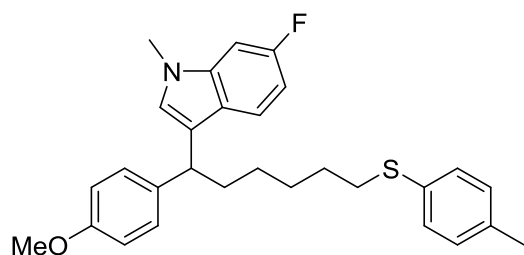
6-Chloro-3-(1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4aai),



by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 67.7 mg, 71%; yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.28 (d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 3H), 7.15 (d, *J* = 8.0 Hz, 2H),

7.07 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.80 (s, 2H), 6.78 (s, 1H), 4.02 (t, *J* = 7.6 Hz, 1H), 3.75 (s, 3H), 3.67 (s, 3H), 2.82 (t, *J* = 6.8 Hz, 2H), 2.30 (s, 3H), 2.13-2.04 (m, 1H), 1.96-1.87 (m, 1H), 1.62-1.56 (m, 2H), 1.47-1.41 (m, 2H), 1.34-1.27 (m, 2H); ¹³C{¹H}NMR (100 MHz, CDCl₃): δ 157.7, 137.6, 137.3, 135.8, 133.0, 129.7 (2C), 129.6 (2C), 128.6 (2C), 127.5, 126.3, 125.9, 120.4, 119.6, 119.2, 113.6 (2C), 109.1, 55.1, 41.7, 36.1, 34.2, 32.7, 29.1, 28.7, 27.5, 21.0; HRMS (ESI-TOF) *m/z*: C₂₉H₃₃ClNOS⁺ (M + H)⁺ calcd for 478.1966, found 478.1967.

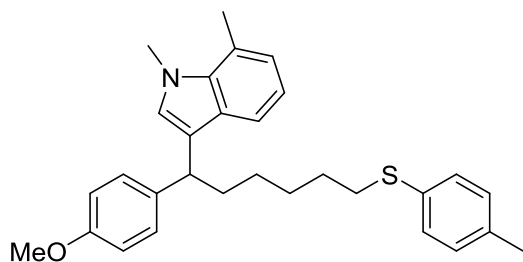
6-Fluoro-3-(1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4aaj),



by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 67.3 mg, 73%; yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.29-7.26 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 7.06

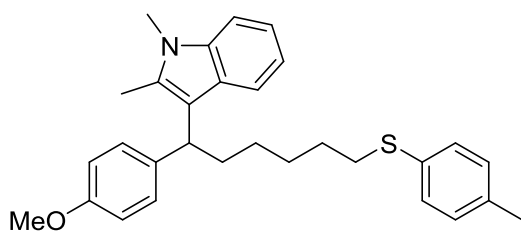
(d, *J* = 8.0 Hz, 2H), 6.90-6.87 (m, 1H), 6.80-6.78 (m, 2H), 6.76-6.71 (m, 1H), 4.02 (t, *J* = 6.8 Hz, 1H), 3.74 (s, 3H), 3.64 (s, 3H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.29 (s, 3H), 2.13-2.05 (m, 1H), 1.96-1.87 (m, 1H), 1.62-1.54 (m, 2H), 1.49-1.40 (m, 2H), 1.35-1.26 (m, 2H); ¹⁹F NMR (282 MHz, CDCl₃) δ: -121.3 (s, 1F); ¹³C{¹H}NMR (100 MHz, CDCl₃): δ 159.8 (d, *J*_{C-F} = 235.4 Hz, 1C), 157.7, 137.4, 137.1 (d, *J*_{C-F} = 12.0 Hz, 1C), 135.8, 133.0, 129.7 (2C), 129.6 (2C), 128.6 (2C), 125.8 (d, *J*_{C-F} = 3.8 Hz, 1C), 123.9, 120.3 (d, *J*_{C-F} = 10.1 Hz, 1C), 119.6, 113.6 (2C), 107.2 (d, *J*_{C-F} = 24.5 Hz, 1C), 95.4 (d, *J*_{C-F} = 25.9 Hz, 1C), 55.1, 41.8, 36.1, 34.2, 32.7, 29.1, 28.7, 27.5, 20.9; HRMS (ESI-TOF) *m/z*: C₂₉H₃₃FNOS⁺ (M + H)⁺ calcd for 462.2261, found 462.2268.

3-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1,7-dimethyl-1*H*-indole (4aak), by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 61.2 mg,



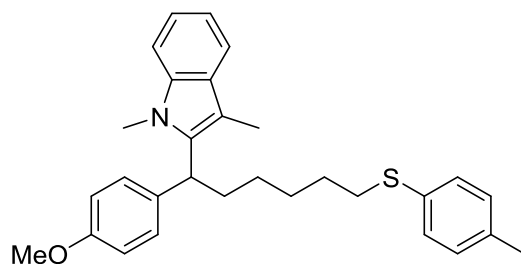
67%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.25 (d, $J = 6.8$ Hz, 1H), 7.21 (d, $J = 6.8$ Hz, 2H), 7.17 (d, $J = 7.2$ Hz, 2H), 7.06 (d, $J = 7.2$ Hz, 2H), 6.87-6.84 (m, 2H), 6.78 (d, $J = 6.8$ Hz, 2H), 6.69 (s, 1H), 4.03 (t, $J = 7.6$ Hz, 1H), 3.96 (s, 3H), 3.73 (s, 3H), 2.82 (t, $J = 6.8$ Hz, 2H), 2.70 (s, 3H), 2.29 (s, 3H), 2.14-2.05 (m, 1H), 1.96-1.87 (m, 1H), 1.61-1.54 (m, 2H), 1.48-1.39 (m, 2H), 1.36-1.26 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.6, 137.6, 135.8, 135.7, 133.0, 129.7 (2C), 129.5 (2C), 128.6 (2C), 128.4, 127.3, 124.1, 121.0, 118.9, 118.8, 117.5, 113.5 (2C), 55.1, 41.7, 36.6, 36.2, 34.2, 29.1, 28.8, 27.5, 20.9, 19.7; HRMS (ESI-TOF) m/z : $\text{C}_{30}\text{H}_{36}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 458.2512, found 458.2519.

3-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1,2-dimethyl-1H-indole (4aa), by



silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 59.4 mg, 65%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.51 (d, $J = 8.0$ Hz, 1H), 7.23-7.17 (m, 5H), 7.10 (t, $J = 7.2$ Hz, 1H), 7.05 (d, $J = 8.0$ Hz, 2H), 6.97 (t, $J = 8.0$ Hz, 1H), 6.76 (d, $J = 8.8$ Hz, 2H), 4.11 (t, $J = 6.4$ Hz, 1H), 3.72 (s, 3H), 3.60 (s, 3H), 2.78 (t, $J = 7.2$ Hz, 2H), 2.33 (s, 3H), 2.29 (s, 3H), 2.23-2.16 (m, 2H), 1.59-1.53 (m, 2H), 1.47-1.40 (m, 2H), 1.27-1.23 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.3, 138.1, 136.7, 135.7, 133.0, 133.0, 129.7 (2C), 129.5 (2C), 128.4 (2C), 126.8, 120.1, 119.4, 118.5, 113.7, 113.4 (2C), 108.5, 55.1, 41.4, 34.6, 34.2, 29.5, 29.1, 28.7, 27.9, 20.9, 10.6; HRMS (ESI-TOF) m/z : $\text{C}_{30}\text{H}_{36}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 458.2512, found 458.2519.

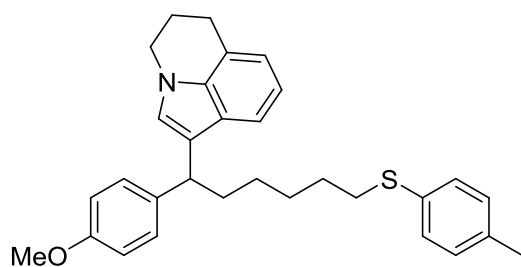
2-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1,3-dimethyl-1H-indole (4aam), by



silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 48.4 mg, 53%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.54 (d, $J = 7.6$ Hz, 1H),

7.21-7.14 (m, 4H), 7.11-7.05 (m, 5H), 6.79 (d, $J = 8.4$ Hz, 2H), 4.35-4.31 (m, 1H), 3.76 (s, 3H), 3.41 (s, 3H), 2.82 (t, $J = 7.2$ Hz, 2H), 2.33 (s, 3H), 2.30 (s, 3H), 2.24-2.18 (m, 1H), 2.16-2.08 (m, 1H), 1.62-1.54 (m, 2H), 1.51-1.41 (m, 2H), 1.36-1.27 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 150.8, 130.6, 129.8, 128.9, 127.9, 125.8, 122.8 (2C), 122.6 (2C), 121.5, 121.4 (2C), 113.8, 111.5, 111.1, 106.7 (2C), 101.5, 100.8, 48.2, 33.5, 27.3, 26.1, 23.4, 22.0, 21.8, 20.6, 14.0, 2.4; HRMS (ESI-TOF) m/z : $\text{C}_{30}\text{H}_{36}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 458.2512, found 458.2519.

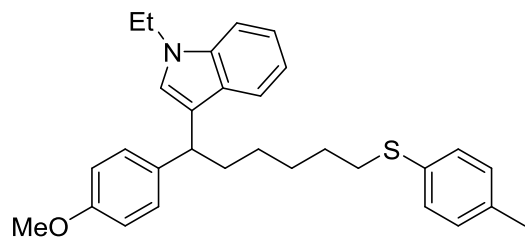
1-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]qui



noline (4aan), by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 74.1 mg, 79%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.24-7.19 (m, 5H), 7.06 (d, $J = 8.0$ Hz, 2H), 6.90 (t,

$J = 7.6$ Hz, 1H), 6.84 (d, $J = 7.2$ Hz, 1H), 6.80 (d, $J = 2.4$ Hz, 2H), 6.78 (s, 1H), 4.08-4.04 (m, 3H), 3.74 (s, 3H), 2.93 (t, $J = 6.0$ Hz, 2H), 2.81 (t, $J = 7.6$ Hz, 2H), 2.29 (s, 3H), 2.21-2.12 (m, 3H), 1.99-1.90 (m, 1H), 1.61-1.54 (m, 2H), 1.48-1.41 (m, 2H), 1.36-1.26 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.6, 137.8, 135.7, 134.6, 133.0, 129.7 (2C), 129.5 (2C), 128.7 (2C), 124.7, 123.0, 121.5, 119.4, 118.9, 118.3, 117.1, 113.5 (2C), 55.1, 43.8, 42.3, 36.2, 34.2, 29.1, 28.8, 27.6, 24.6, 22.8, 20.9; HRMS (ESI-TOF) m/z : $\text{C}_{31}\text{H}_{36}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 470.2512, found 470.2509.

1-Ethyl-3-(1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1*H*-indole (4aao), by silica

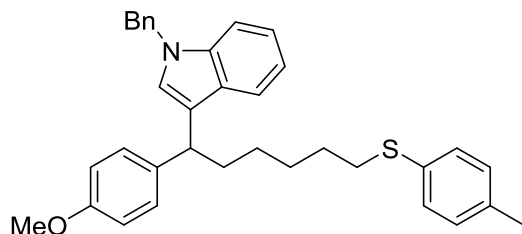


gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 64.0 mg, 70%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.41 (d, $J = 8.0$ Hz, 1H), 7.26 (d, $J = 8.4$

Hz, 1H), 7.22-7.11 (m, 5H), 7.06 (d, $J = 7.2$ Hz, 2H), 6.97 (t, $J = 7.6$ Hz, 1H), 6.87 (s, 1H), 6.79 (d, $J = 7.2$ Hz, 2H), 4.11-4.05 (m, 3H), 3.74 (s, 3H), 2.81 (t, $J = 7.2$ Hz, 2H), 2.29 (s, 3H), 2.16-2.09 (m, 1H), 1.98-1.91 (m, 1H), 1.62-1.55 (m, 2H), 1.49-1.39 (m, 5H), 1.32-1.28 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.6, 137.6, 136.2, 135.7, 133.0, 129.7 (2C), 129.5 (2C), 128.7 (2C), 127.5, 123.8, 121.2, 119.6, 119.3,

118.5, 113.5 (2C), 109.1, 55.1, 41.9, 40.7, 36.2, 34.2, 29.1, 28.7, 27.5, 20.9, 15.5; HRMS (ESI-TOF) m/z : $C_{30}H_{36}NOS^+$ ($M + H$)⁺ calcd for 458.2512, found 458.2519.

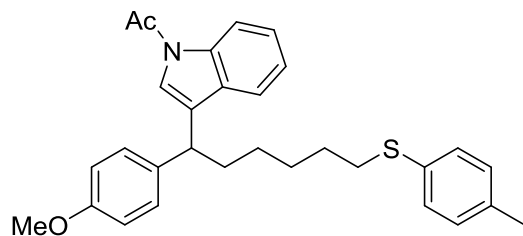
1-Benzyl-3-(1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1*H*-indole (4aap), by silica



gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 61.2 mg, 59%;

yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.42 (d, $J = 7.6$ Hz, 1H), 7.28-7.17 (m, 8H), 7.10-7.08 (m, 4H), 6.99 (t, $J = 7.2$ Hz, 1H), 6.93 (s, 1H), 6.79 (d, $J = 8.8$ Hz, 2H), 6.72-6.66 (m, 1H), 5.28 (s, 2H), 4.09 (t, $J = 7.2$ Hz, 1H), 3.76 (s, 3H), 2.83-2.76 (m, 2H), 2.30 (s, 3H), 2.16-2.08 (m, 1H), 1.98-1.89 (m, 1H), 1.61-1.58 (m, 2H), 1.47-1.27 (m, 4H); ¹³C{¹H}NMR (100 MHz, CDCl₃): δ 157.7, 137.8, 137.6, 136.9, 135.8, 133.0, 129.7 (2C), 129.6 (2C), 128.7 (2C), 128.7 (2C), 127.6, 127.4, 126.5 (2C), 125.1, 121.6, 119.9, 119.7, 118.8, 113.6 (2C), 109.5, 55.2, 49.9, 41.9, 36.2, 34.2, 29.1, 28.7, 27.5, 21.0; HRMS (ESI-TOF) m/z : $C_{35}H_{38}NOS^+$ ($M + H$)⁺ calcd for 520.2669, found 520.2668.

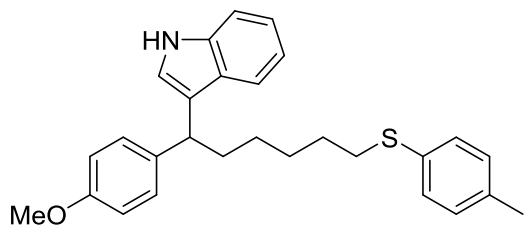
1-(3-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1*H*-indol-1-yl)ethan-1-one (4aaq),



by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 48.0

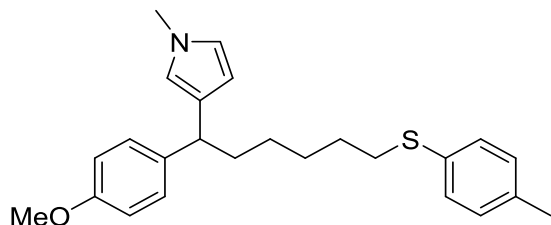
mg, 51%; yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.34-7.27 (m, 2H), 7.23-7.16 (m, 6H), 7.08 (d, $J = 8.0$ Hz, 2H), 6.82 (d, $J = 8.8$ Hz, 2H), 4.00 (t, $J = 6.0$ Hz, 2H), 3.77 (s, 3H), 2.84 (t, $J = 6.8$ Hz, 2H), 2.62 (s, 3H), 2.31 (s, 3H), 2.15-2.08 (m, 1H), 1.99-1.89 (m, 1H), 1.64-1.58 (m, 2H), 1.50-1.43 (m, 2H), 1.39-1.30 (m, 2H); ¹³C{¹H}NMR (100 MHz, CDCl₃): δ 168.4, 158.1, 136.1, 135.9, 135.5, 132.9, 129.8 (2C), 129.6 (2C), 128.7 (2C), 127.0, 125.1, 123.3, 121.3, 119.7, 116.6, 116.5, 113.9 (2C), 55.2, 41.7, 35.4, 34.2, 29.0, 28.6, 27.3, 24.1, 21.0; HRMS (ESI-TOF) m/z : $C_{30}H_{34}NO_2S^+$ ($M + H$)⁺ calcd for 472.2305, found 472.2309.

3-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1*H*-indole (4aas), by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 57.5 mg, 67%; yellow oil; ¹H NMR (400 MHz, CDCl₃): δ 7.89 (s, 1H), 7.41 (d, $J = 8.0$ Hz, 1H), 7.28 (d, $J =$



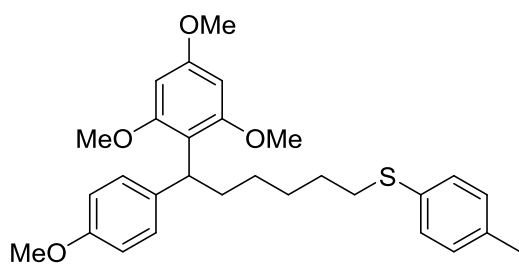
8.4 Hz, 1H), 7.21 (d, $J = 8.0$ Hz, 2H), 7.17 (d, $J = 8.8$ Hz, 2H), 7.12 (t, $J = 7.6$ Hz, 1H), 7.06 (d, $J = 8.0$ Hz, 2H), 6.99 (t, $J = 7.6$ Hz, 1H), 6.94 (s, 1H), 6.79 (d, $J = 8.8$ Hz, 2H), 4.07 (t, $J = 7.6$ Hz, 1H), 3.74 (s, 3H), 2.81 (t, $J = 7.2$ Hz, 2H), 2.29 (s, 3H), 2.17-2.09 (m, 1H), 1.98-1.89 (m, 1H), 1.61-1.54 (m, 2H), 1.49-1.39 (m, 2H), 1.36-1.28 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.6, 137.5, 136.4, 135.8, 133.0, 129.7 (2C), 129.6 (2C), 128.7 (2C), 126.9, 121.8, 120.8, 120.7, 119.5, 119.1, 113.6 (2C), 111.0, 55.1, 41.9, 36.0, 34.2, 29.1, 28.7, 27.5, 21.0; HRMS (ESI-TOF) m/z : $\text{C}_{28}\text{H}_{32}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 430.2199, found 430.2198.

3-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1H-pyrrole (4aat), by



silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 37.7 mg, 48%; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : ^1H NMR (400 MHz, CDCl_3): δ 7.22 (d, $J = 8.0$ Hz, 2H), 7.08 (d, $J = 8.0$ Hz, 2H), 6.98 (d, $J = 8.0$ Hz, 2H), 6.78 (d, $J = 8.0$ Hz, 2H), 6.49 (s, 1H), 6.08 (s, 2H), 3.80 (s, 0.2H), 3.76 (s, 3H), 3.72 (d, $J = 7.5$ Hz, 0.8H), 3.26 (s, 3H), 2.83 (t, $J = 7.2$ Hz, 2H), 2.31 (s, 3H), 2.05-1.97 (m, 1H), 1.83-1.76 (m, 1H), 1.62-1.56 (m, 2H), 1.46-1.33 (m, 3H), 1.29-1.22 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.8, 136.2, 135.8, 133.0, 129.8, 129.6 (2C), 129.5 (2C), 128.7 (2C), 121.5, 113.7 (2C), 106.1, 105.3, 55.2, 42.5, 36.4, 34.2, 33.8, 29.0, 28.7, 27.3, 21.0; HRMS (ESI-TOF) m/z : $\text{C}_{25}\text{H}_{32}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 394.2199, found 394.2196.

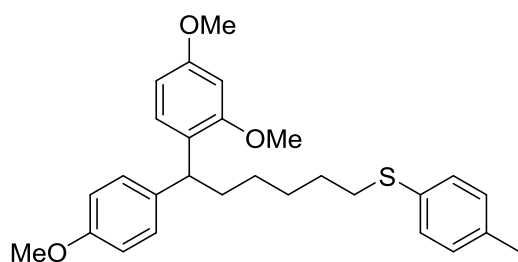
(6-(4-Methoxyphenyl)-6-(2,4,6-trimethoxyphenyl)hexyl)(*p*-tolyl)sulfane (4aau),



by silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 53.8 mg, 56%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.23-7.20 (m, 4H), 7.07 (d, $J = 8.0$ Hz, 2H), 6.75 (d, $J = 8.4$ Hz, 2H), 6.10 (s, 2H), 4.49 (t, $J = 6.8$ Hz, 2H), 3.77 (s, 3H), 3.74 (s, 3H), 3.71 (s, 6H), 2.81 (t, $J =$

7.2 Hz, 2H), 2.30 (s, 3H), 2.22-2.14 (m, 1H), 2.08-2.00 (m, 1H), 1.60-1.54 (m, 2H), 1.47-1.37 (m, 2H), 1.26-1.16(m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 159.2, 159.1, 157.1, 138.1, 135.7, 133.2, 129.7 (2C), 129.5 (2C), 128.8 (2C), 114.2, 113.6, 112.9 (2C), 91.2 (2C), 55.7 (2C), 55.2, 55.1, 38.5, 34.3, 32.1, 29.1, 28.9, 27.9, 21.0; HRMS (ESI-TOF) m/z : $\text{C}_{29}\text{H}_{37}\text{O}_4\text{S}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 481.2407, found 481.2415.

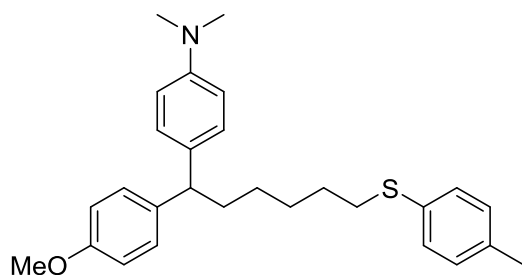
(6-(2,4-Dimethoxyphenyl)-6-(4-methoxyphenyl)hexyl)(*p*-tolyl)sulfane (4aav), by



silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 31.5 mg, 35%; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.21 (d, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 8.8$ Hz, 2H), 7.08-7.05 (m, 4H), 6.78

(d, $J = 8.4$ Hz, 2H), 6.41 (t, $J = 3.2$ Hz, 1H), 4.20 (t, $J = 7.6$ Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.74 (s, 3H), 2.82 (d, $J = 7.2$ Hz, 2H), 2.31 (s, 3H), 1.94-1.88 (m, 2H), 1.63-1.56 (m, 2H), 1.46-1.38 (m, 2H), 1.28-1.22 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 158.8, 157.8, 157.5, 137.6, 135.8, 133.0, 129.8 (2C), 129.6 (2C), 128.8 (2C), 127.7, 126.5, 113.4 (2C), 104.0, 98.6, 55.4, 55.2, 55.1, 41.7, 35.1, 34.3, 29.1, 28.7, 27.5, 21.0; HRMS (ESI-TOF) m/z : $\text{C}_{28}\text{H}_{35}\text{O}_3\text{S}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 451.2301, found 451.2302.

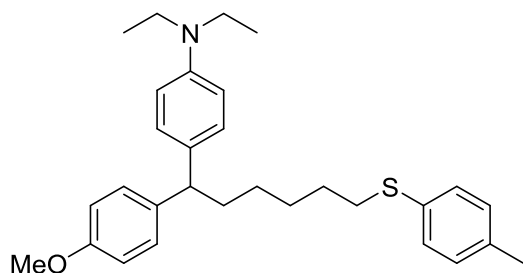
4-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-*N,N*-dimethylaniline (4aaw), by



silica gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 54.6 mg, 63%; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ : 7.21 (d, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 7.08-7.04 (m, 4H), 6.79

(d, $J = 8.4$ Hz, 2H), 6.65 (d, $J = 8.4$ Hz, 2H), 3.75 (s, 3H), 3.71 (d, $J = 8.0$ Hz, 1H), 2.88 (s, 6H), 2.81 (t, $J = 7.6$ Hz, 2H), 2.30 (s, 3H), 1.96-1.91 (m, 2H), 1.61-1.53 (m, 2H), 1.46-1.38 (m, 2H), 1.28-1.21 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ : 157.6, 148.9, 138.2, 135.8, 133.7, 133.0, 129.8 (2C), 129.5 (2C), 128.6 (2C), 128.2 (2C), 113.6 (2C), 112.7 (2C), 55.2, 49.3, 40.7 (2C), 35.9, 34.3, 29.1, 28.7, 27.6, 21.0; HRMS (ESI-TOF) m/z : $\text{C}_{28}\text{H}_{36}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 434.2512, found 434.2516.

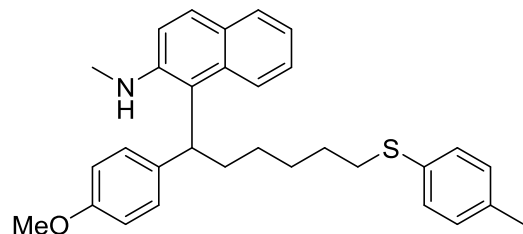
***N,N*-Diethyl-4-(1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexyl)aniline (4aax)**, by silica



gel column chromatography (hexane/ethyl acetate = 15 : 1), yield: 62.8 mg, 67%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.68 (t, $J = 8.8$ Hz, 2H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.35 (t, $J = 8.0$ Hz, 1H), 7.28 (d,

$J = 9.2$ Hz, 1H), 7.21-7.15 (m, 5H), 7.05 (d, $J = 8.0$ Hz, 2H), 6.93 (s, 1H), 6.82 (d, $J = 8.8$ Hz, 2H), 5.03 (t, $J = 6.4$ Hz, 1H), 3.78 (s, 3H), 2.82 (t, $J = 7.2$ Hz, 2H), 2.70 (s, 3H), 2.29 (s, 3H), 2.03-1.96 (m, 2H), 1.63-1.58 (m, 2H), 1.50-1.45 (m, 2H), 1.41-1.33 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 158.5, 148.7, 135.9, 135.1, 133.2, 132.9, 129.8 (2C), 129.6 (2C), 128.8, 128.3 (2C), 127.4, 126.9, 126.2, 126.1, 122.0, 116.9, 113.6 (2C), 106.9, 61.1, 55.2, 34.2, 31.6, 31.5, 29.1, 28.7, 26.5, 21.0; HRMS (ESI-TOF) m/z : $\text{C}_{31}\text{H}_{36}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 470.2512, found 470.2513.

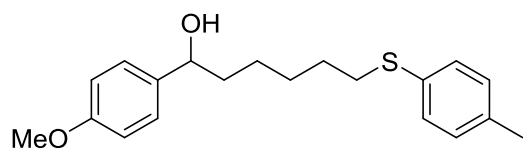
1-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-*N*-methylnaphthalen-2-amine (4aay), by silica gel column



chromatography (hexane/ethyl acetate = 15 : 1), yield: 50.7 mg, 55%; yellow oil;

^1H NMR (400 MHz, CDCl_3): δ 7.21 (d, $J = 7.6$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H), 7.07 (d, $J = 8.0$ Hz, 2H), 7.02 (d, $J = 8.4$ Hz, 2H), 6.79 (d, $J = 8.4$ Hz, 2H), 6.58 (d, $J = 8.8$ Hz, 2H), 3.75 (s, 3H), 3.70 (t, $J = 8.0$ Hz, 1H), 3.13-3.26 (m, 4H), 2.82 (t, $J = 7.6$ Hz, 2H), 2.30 (s, 3H), 1.96-1.90 (m, 2H), 1.61-1.54 (m, 2H), 1.46-1.38 (m, 2H), 1.28-1.24 (m, 2H), 1.11 (t, $J = 7.2$ Hz, 6H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 157.5, 146.1, 138.3, 135.8, 133.0, 132.4, 129.8 (2C), 129.5 (2C), 128.6 (2C), 128.4 (2C), 113.6 (2C), 111.8 (2C), 55.2, 49.3, 44.3 (2C), 36.0, 34.3, 29.1, 28.7, 27.6, 21.0, 12.6 (2C); HRMS (ESI-TOF) m/z : $\text{C}_{30}\text{H}_{40}\text{NOS}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 462.2825, found 462.2822.

1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexan-1-ol, by silica gel column chromatography (hexane/ethyl acetate = 5 :



1), yield: 34.2 mg, 52%; yellow oil; ^1H NMR (400 MHz, CDCl_3): δ 7.24-7.21 (m, 4H), 7.07 (d, $J = 8.0$ Hz, 2H), 6.86 (d, $J = 8.4$ Hz, 2H), 4.57 (t, $J = 6.8$ Hz, 1H), 3.79 (s, 3H), 2.83 (t, $J = 7.2$ Hz, 2H), 2.30 (s, 3H), 1.84-1.82 (m, 1H), 1.77-1.74 (m, 1H), 1.67-1.55 (m, 3H), 1.43-1.39 (m, 2H), 1.27-1.23 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 158.9, 136.9, 135.8, 132.9, 129.7 (2C), 129.5 (2C), 127.1 (2C), 113.7 (2C), 74.0, 55.2, 38.7, 34.2, 29.1, 28.5, 25.3, 20.9; HRMS (ESI-TOF) m/z : $\text{C}_{20}\text{H}_{27}\text{O}_2\text{S}^+$ ($\text{M} + \text{H}$) $^+$ calcd for 331.1726, found 331.1722.

4. Reference

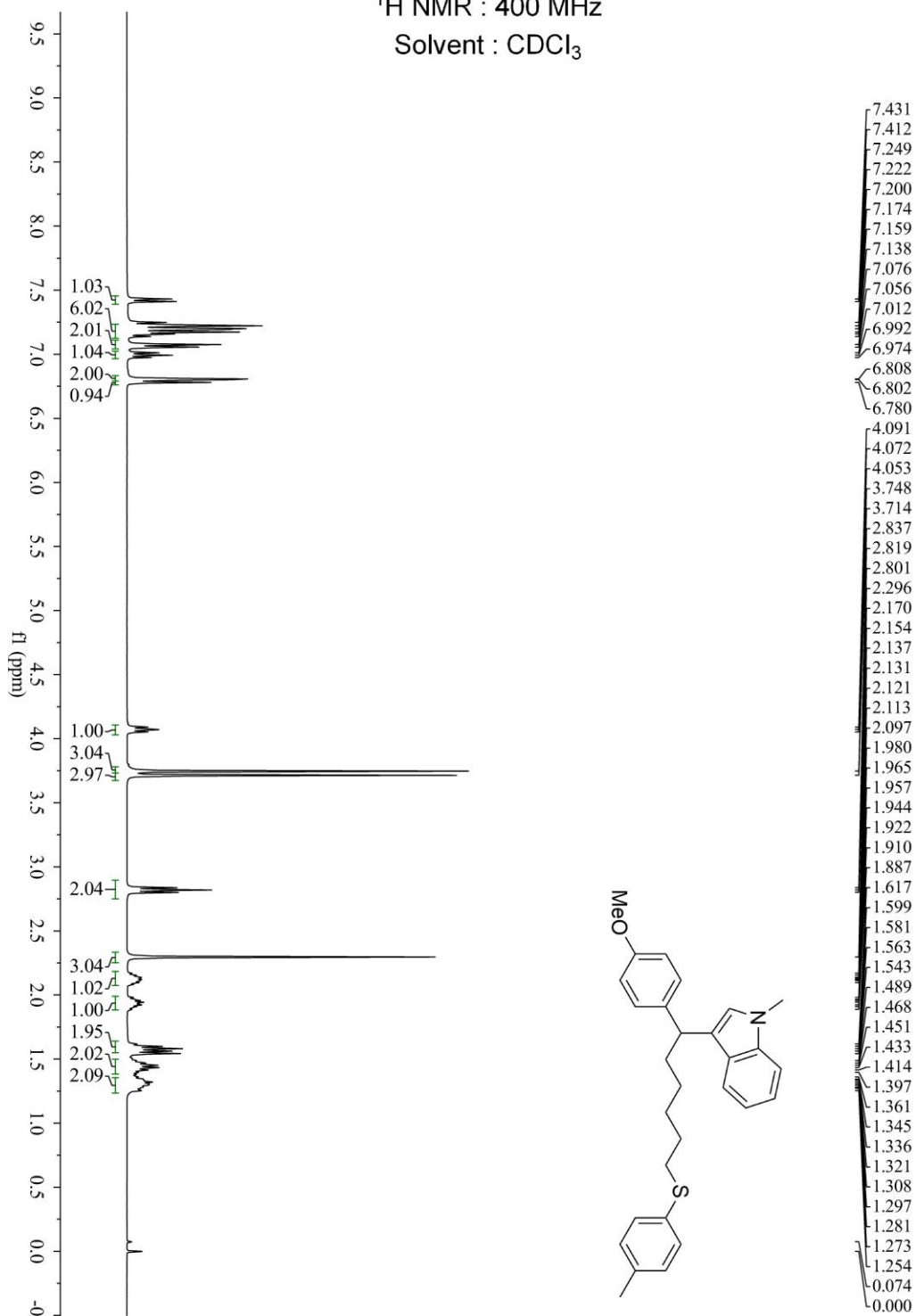
1. W.-W. Cui, X.-F. Li, G.-J. Guo, X.-Y. Song, J. Lv, D.-S. Yang, Radial Type Ring Opening of Sulfonium Salts with Dichalcogenides by Visible Light and Copper Catalysis, *Org. Lett.* **2022**, 24, 5391-5396.
2. X.-Q. Liu, X.-F. Li, L.-Y. Wang, Y.-J. Shi, J. Lv, D.-S. Yang, Visible Light/Copper Catalysis Enabled Heck-Like Coupling between Alkenes and Cyclic Sulfonium Salts via Selective C-S Bond Cleavage, *Org. Chem. Front.* **2024**, 11, 2195-2200.
3. P.-F. Yuan, Z. Yang, S.-S. Zhang, C.-M. Zhu, X.-L. Yang, Q.-Y. Meng, Deconstructive Carboxylation of Activated Alkenes with Carbon Dioxide, *Angew. Chem. Int. Ed.* **2024**, 63, e202313030.
4. L.-J. Zhong, H. Chen, X. Shang, J.-H. Fan, K.-W. Tang, Y. Liu, J.-H. Li, Photoredox Ring Opening 1,2-Alkylarylation of Alkenes with Sulfonium Salts Toward Thioether-Substituted Oxindoles, *J. Org. Chem.* **2024**, 89, 12, 8721-8733.

4.Spectra

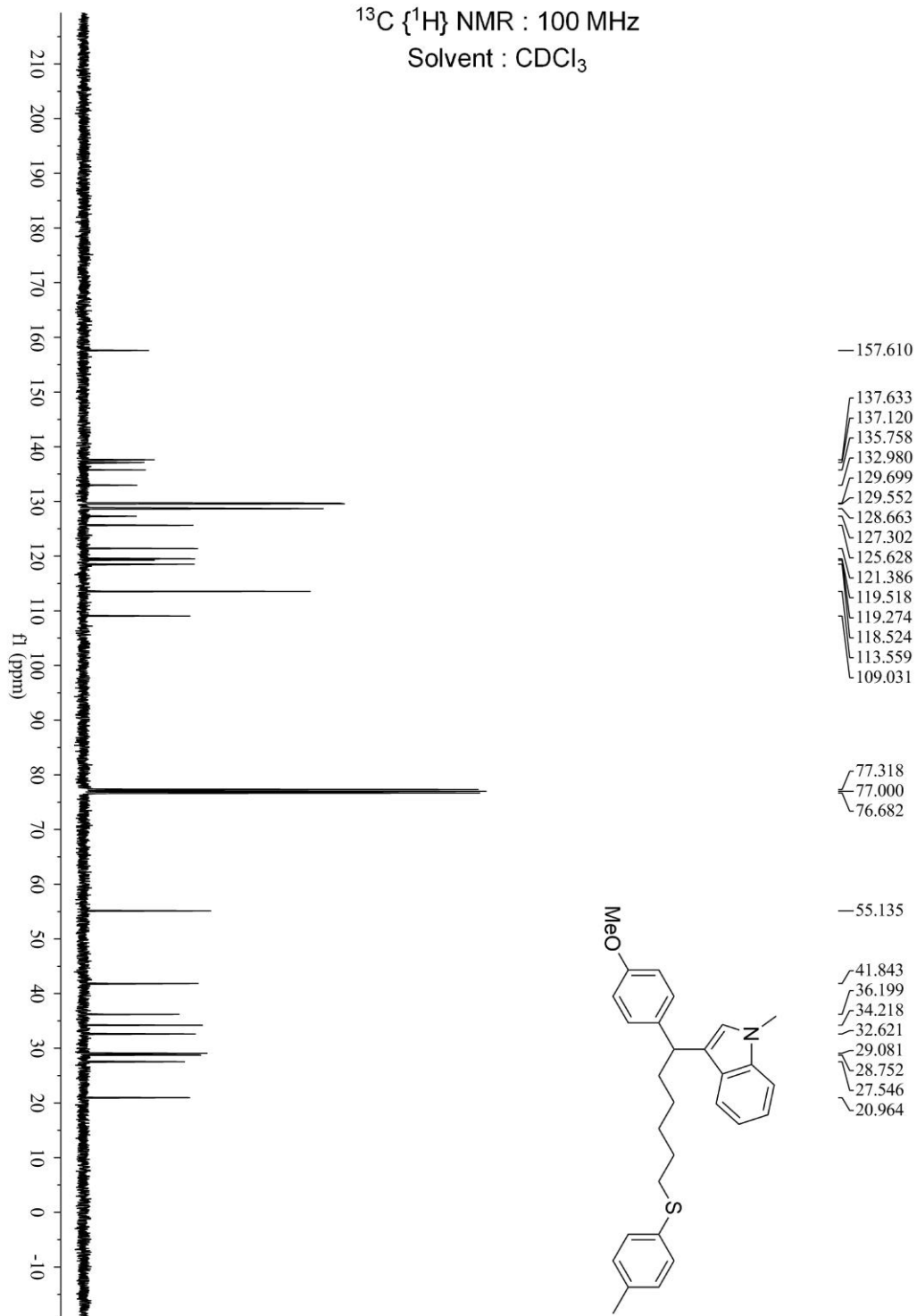
1,3-Dimethyl-3-(5-(*p*-tolylthio)pentyl)indolin-2-one (4aaa)

^1H NMR : 400 MHz

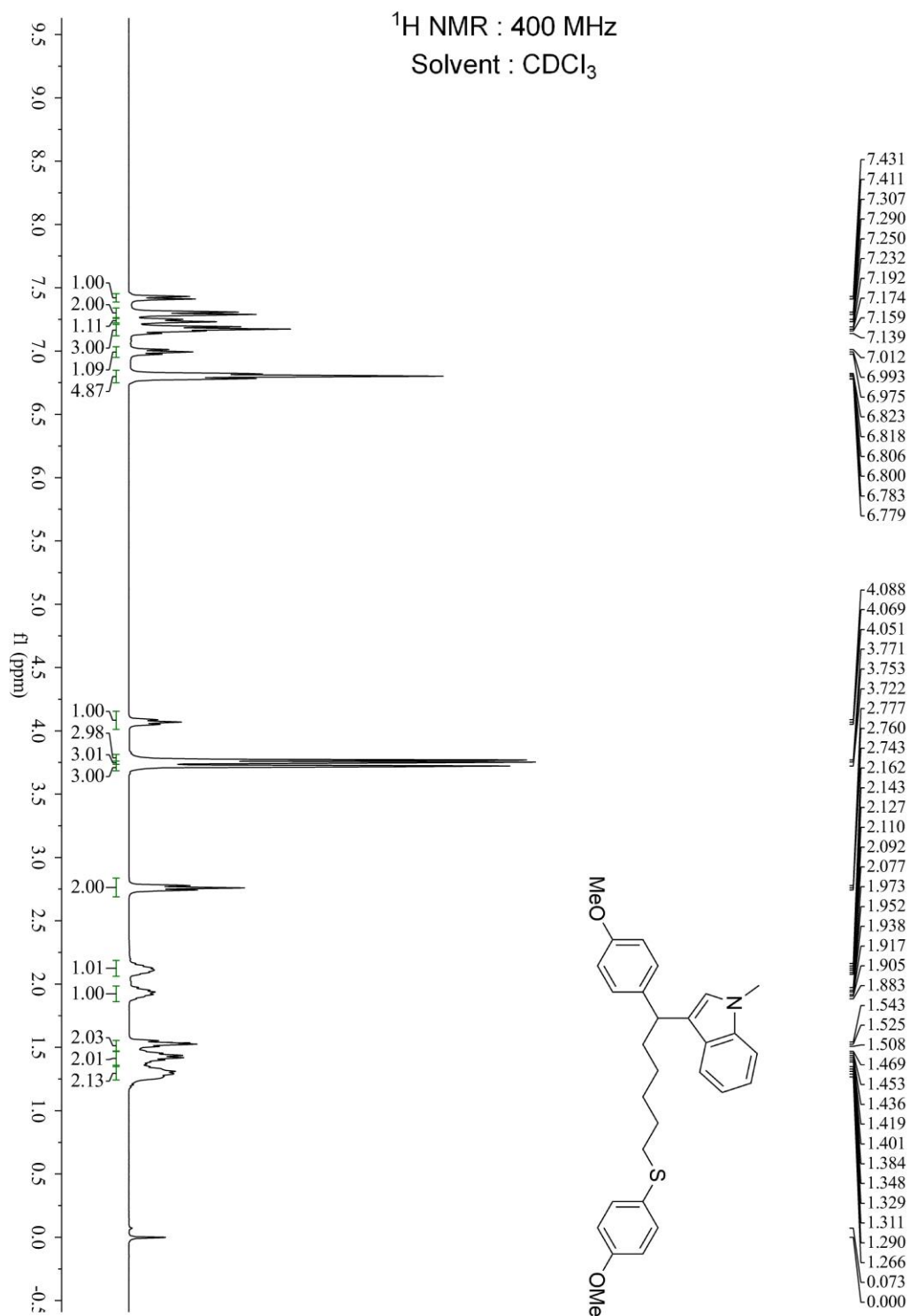
Solvent : CDCl_3



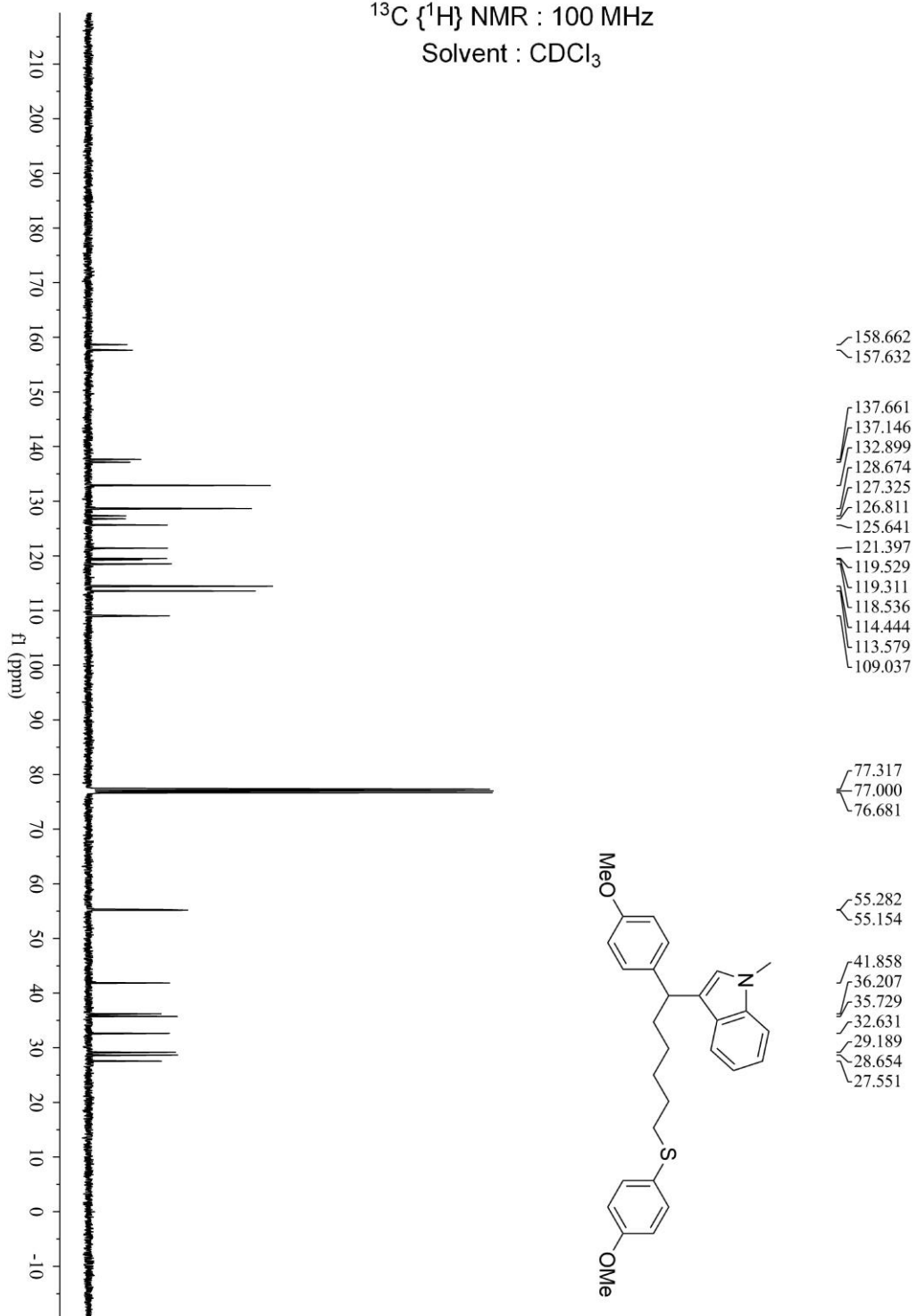
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



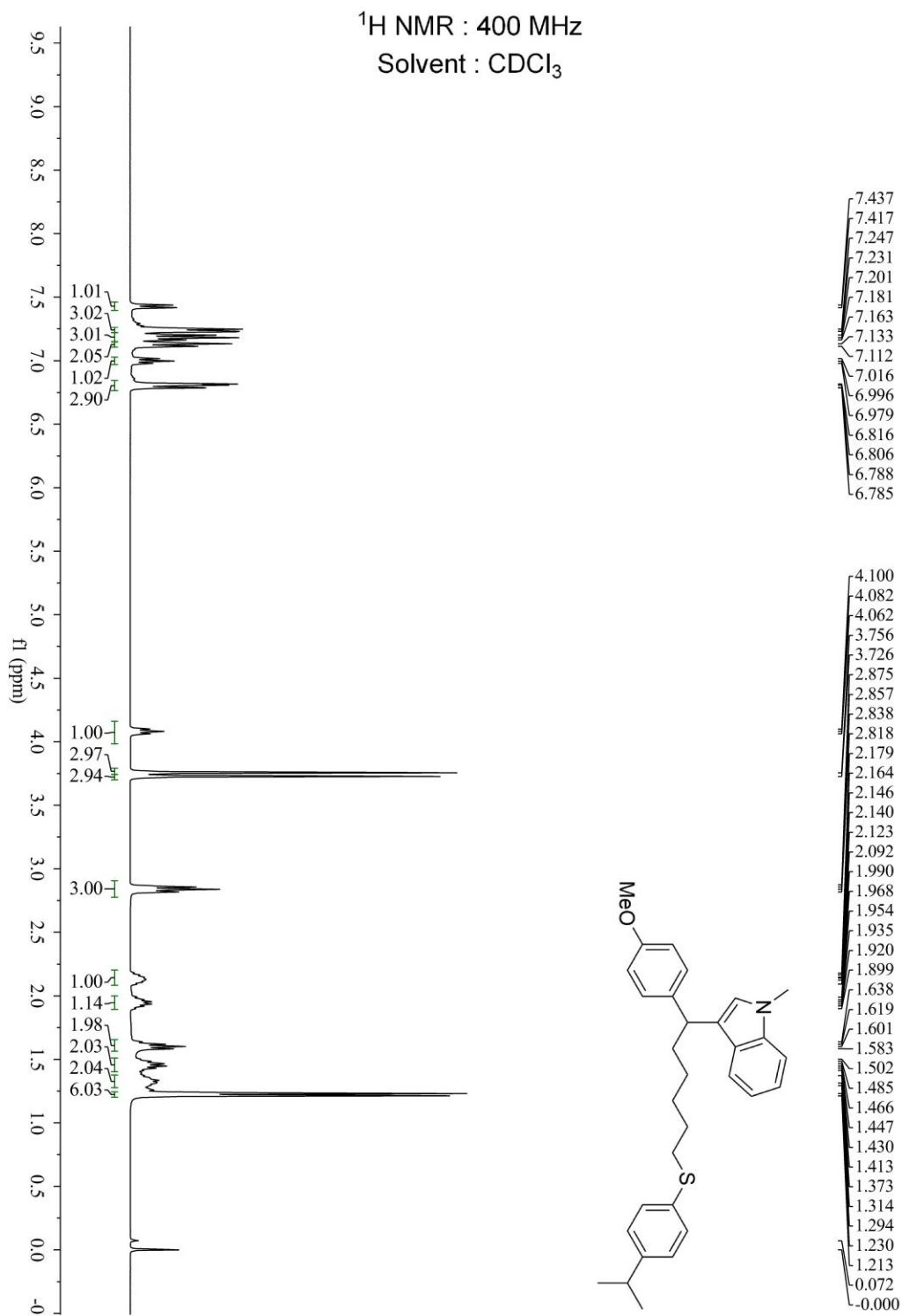
**3-(1-(4-Methoxyphenyl)-6-((4-methoxyphenyl)thio)hexyl)-1-methyl-1H-indole
(4aba)**



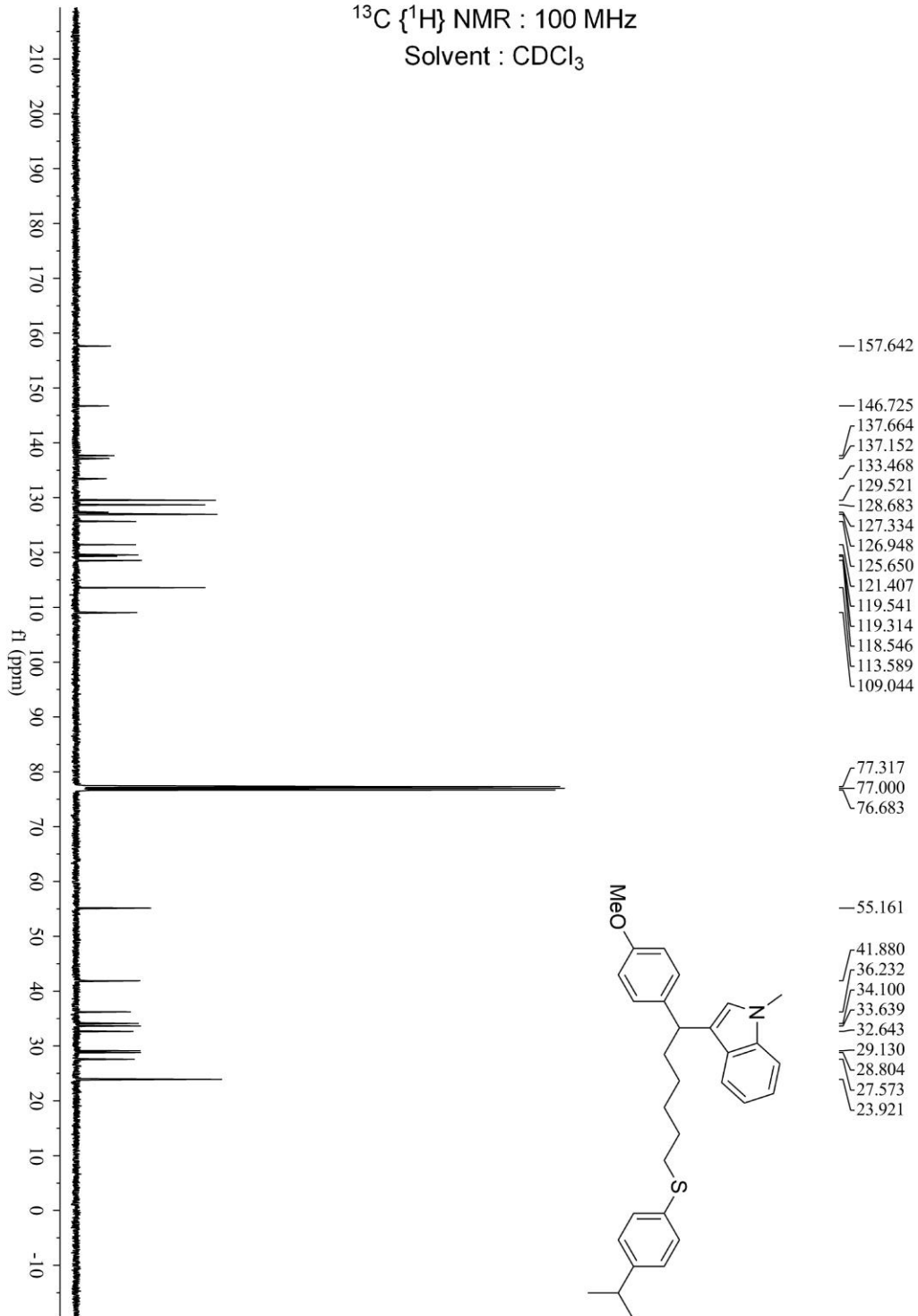
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



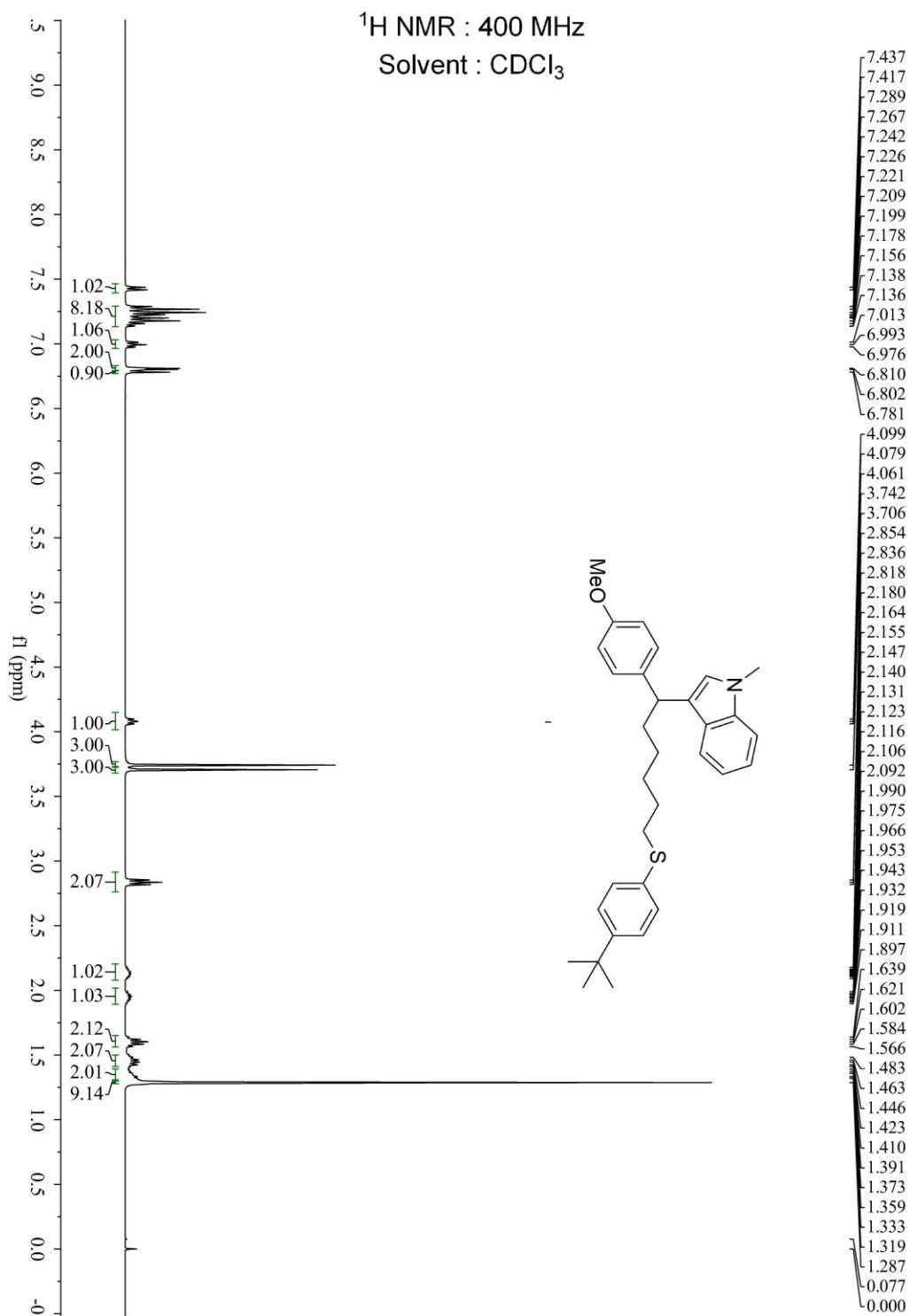
**3-(6-((4-Isopropylphenyl)thio)-1-(4-methoxyphenyl)hexyl)-1-methyl-1H-indole
(4aca)**



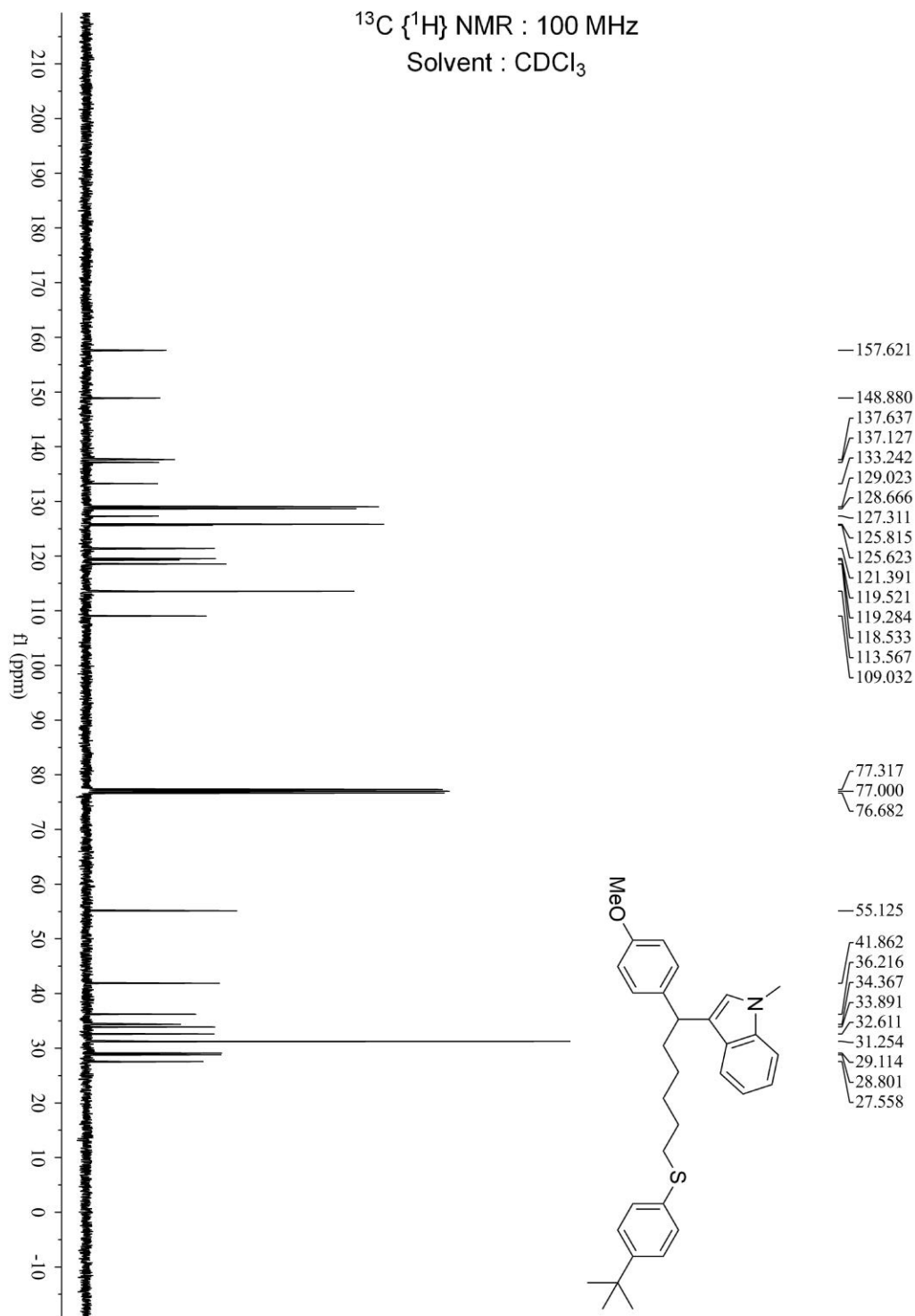
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



**3-(6-((4-(*Tert*-butyl)phenyl)thio)-1-(4-methoxyphenyl)hexyl)-1-methyl-1*H*-indole
(4ada)**



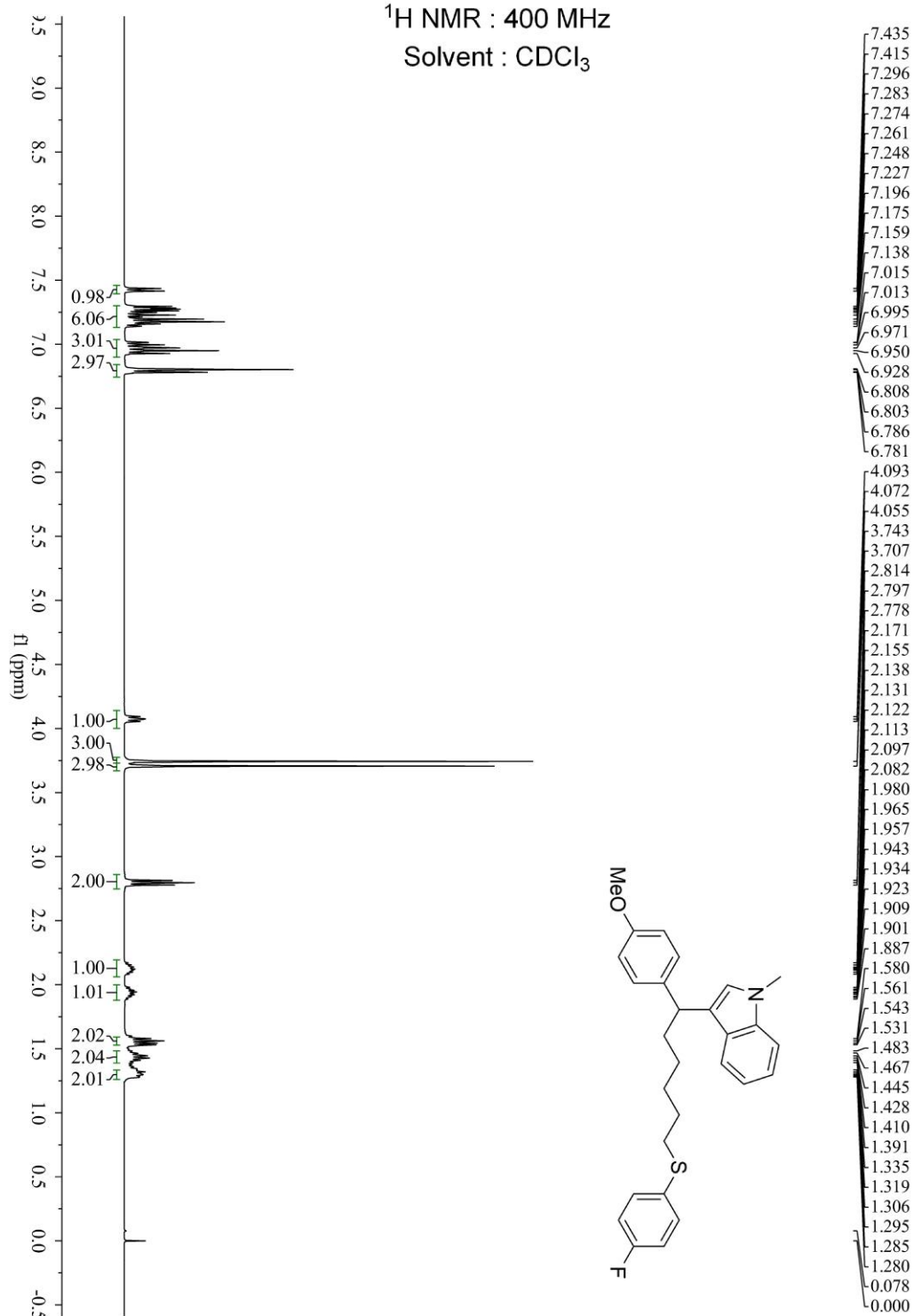
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



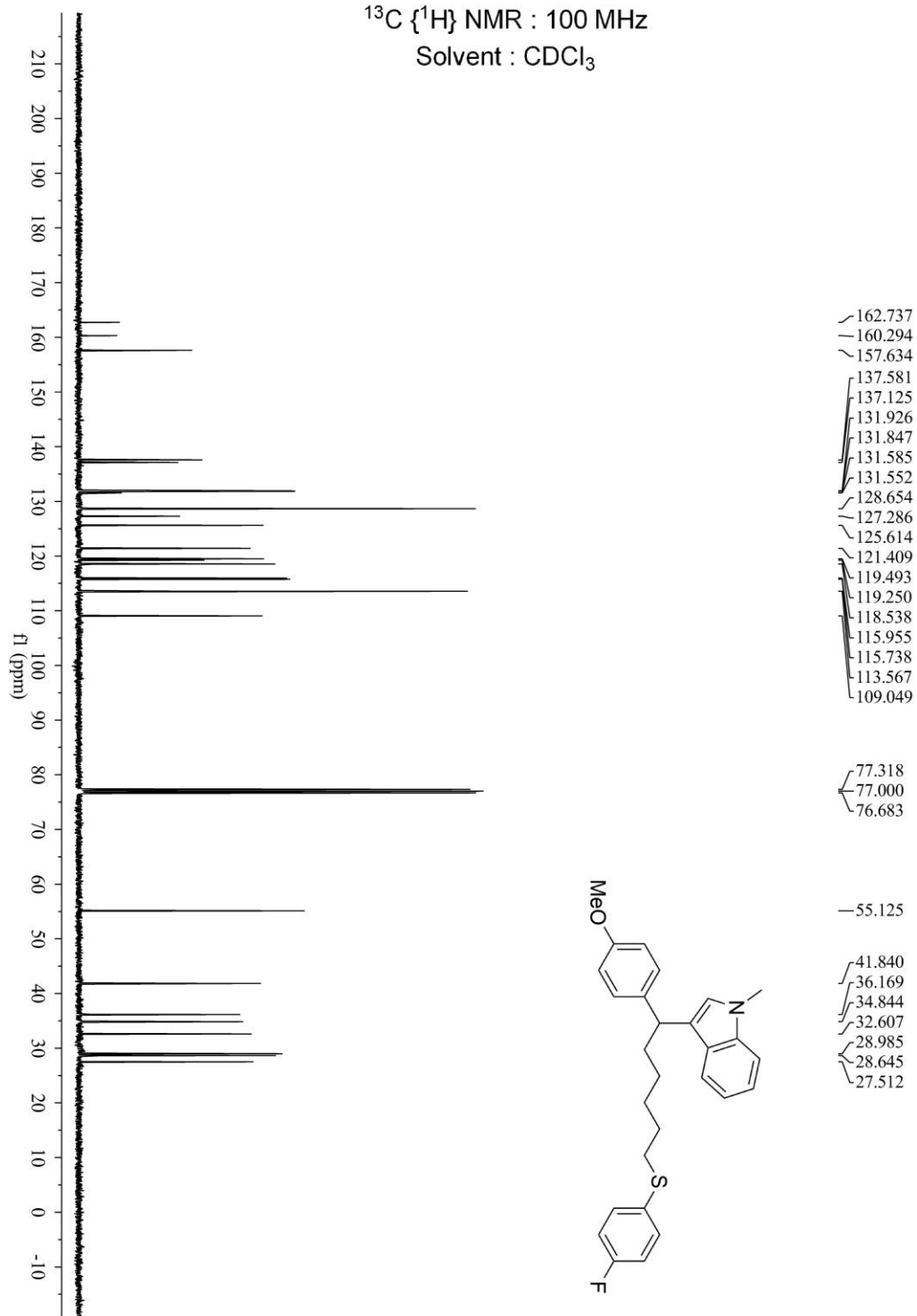
**3-(6-((4-Fluorophenyl)thio)-1-(4-methoxyphenyl)hexyl)-1-methyl-1H-indole
(4aea)**

¹H NMR : 400 MHz

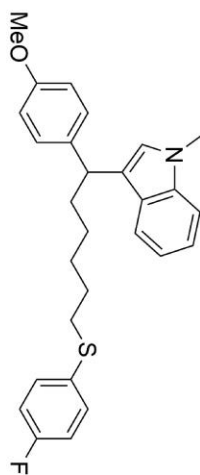
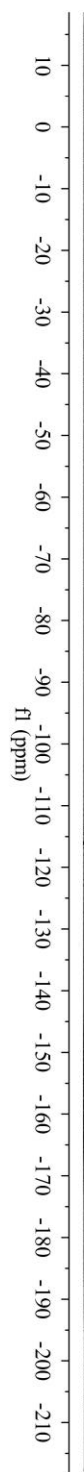
Solvent : CDCl₃



$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3

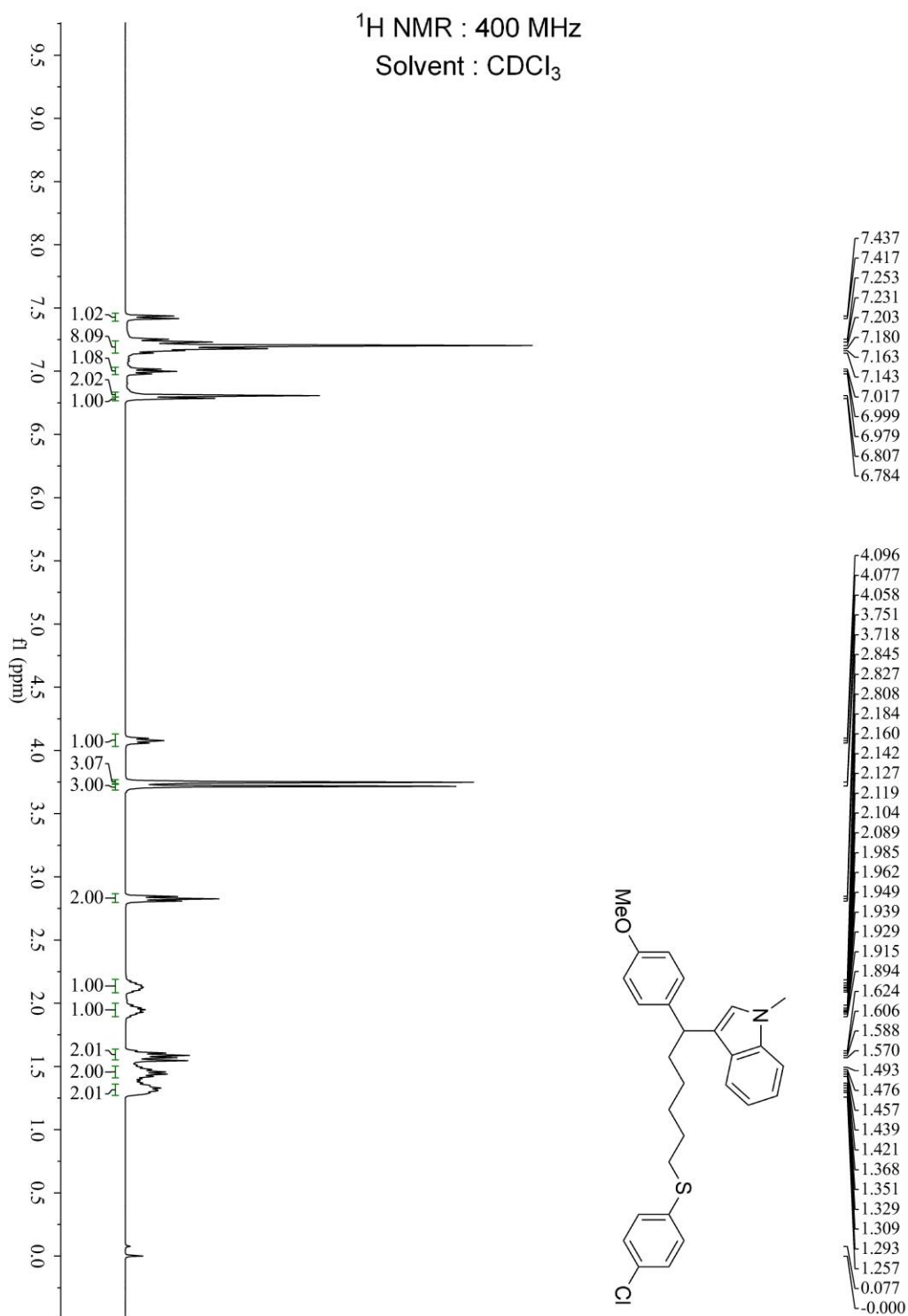


^{19}F NMR : 282 MHz
Solvent : CDCl_3

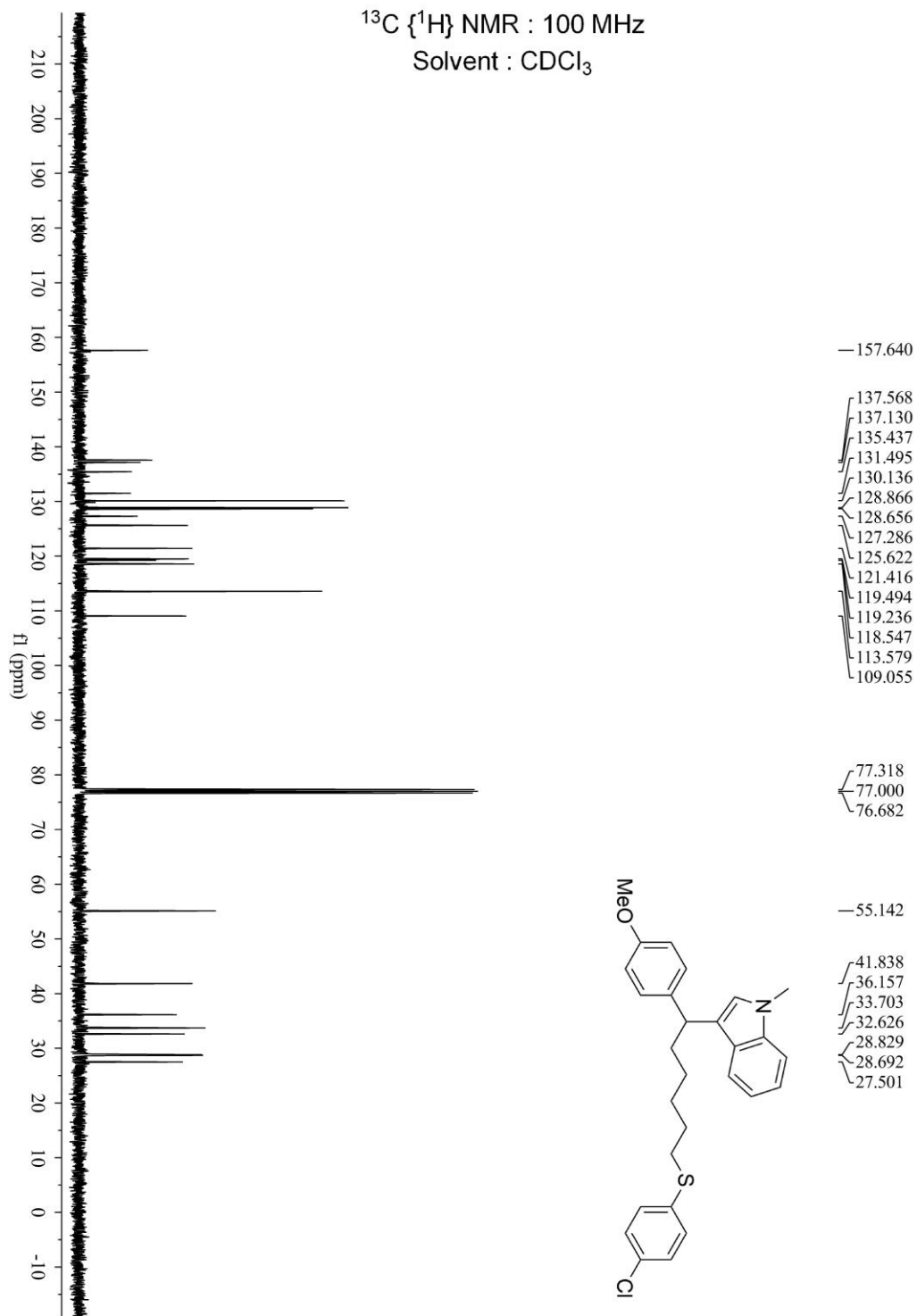


—-116.075

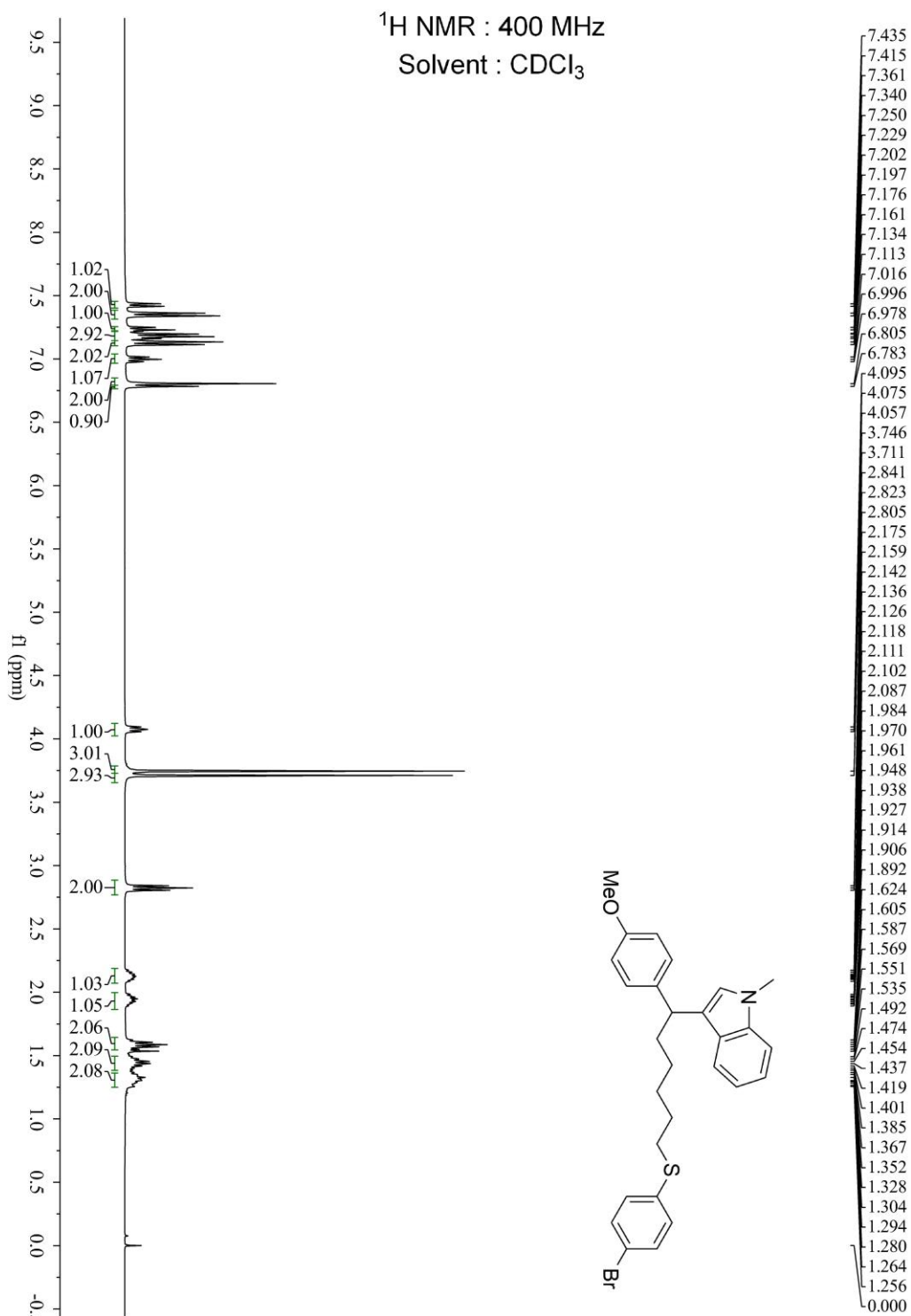
**3-(6-((4-Chlorophenyl)thio)-1-(4-methoxyphenyl)hexyl)-1-methyl-1H-indole
(4afa)**



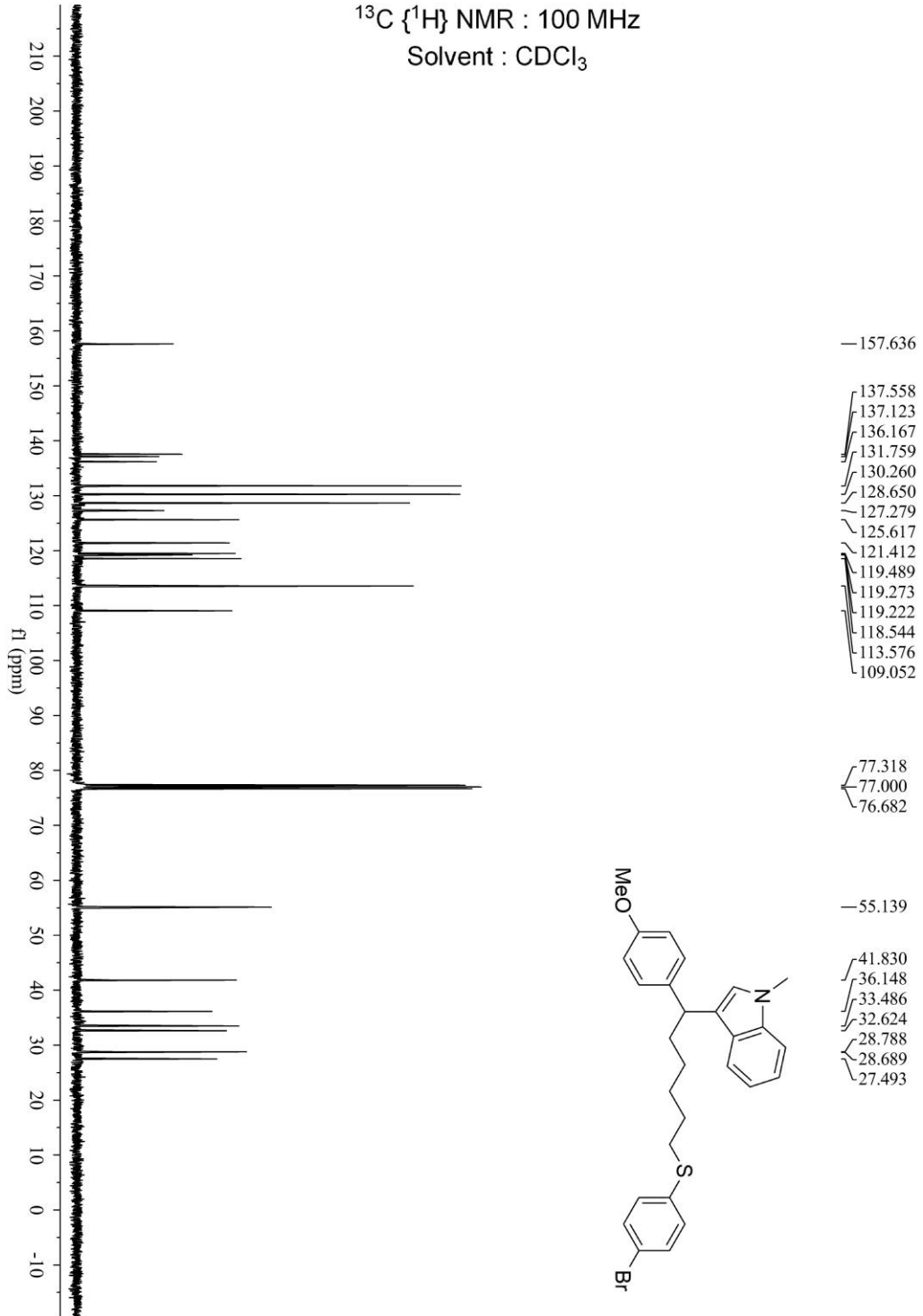
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



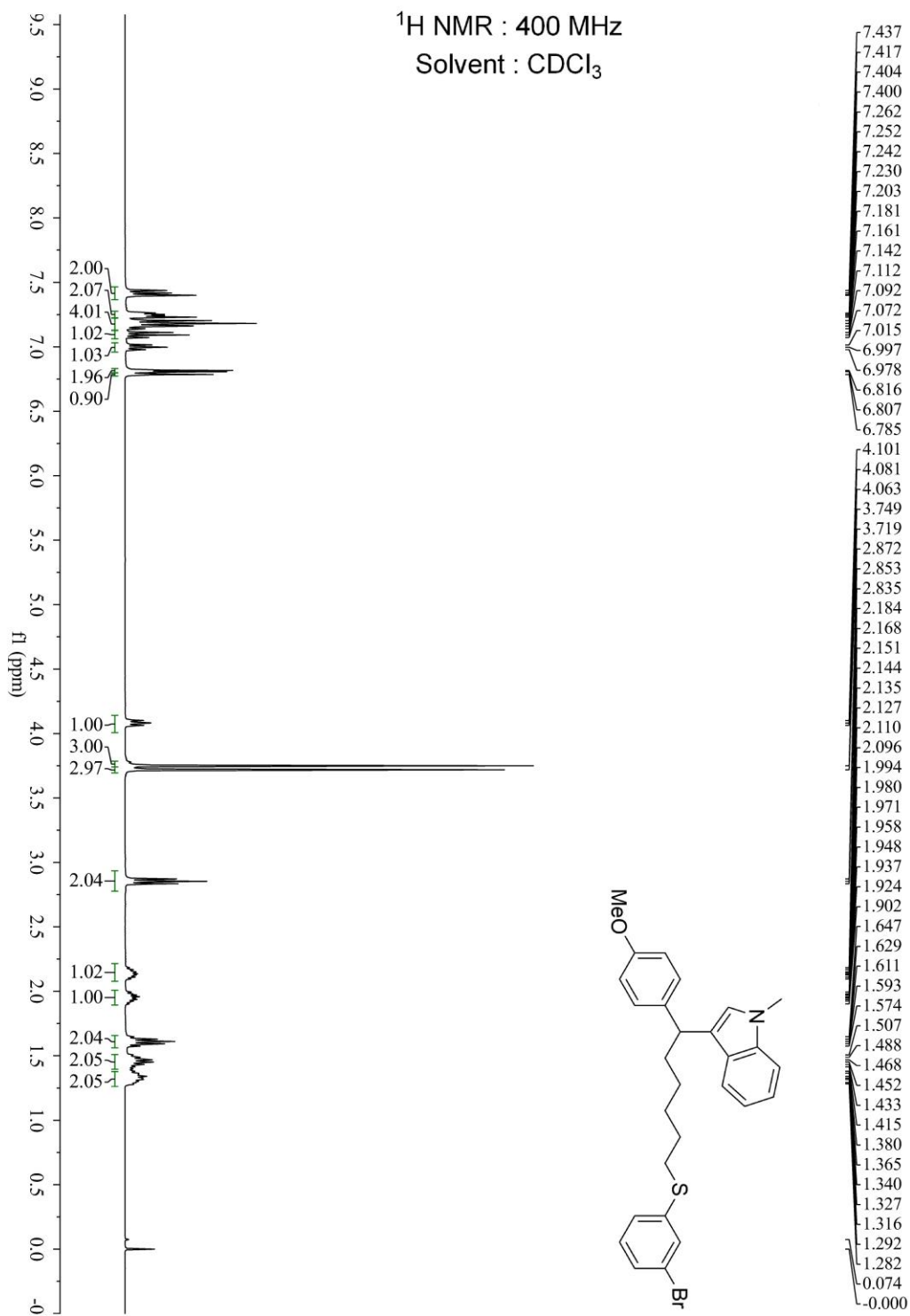
**3-(6-((4-Bromophenyl)thio)-1-(4-methoxyphenyl)hexyl)-1-methyl-1H-indole
(4aga)**



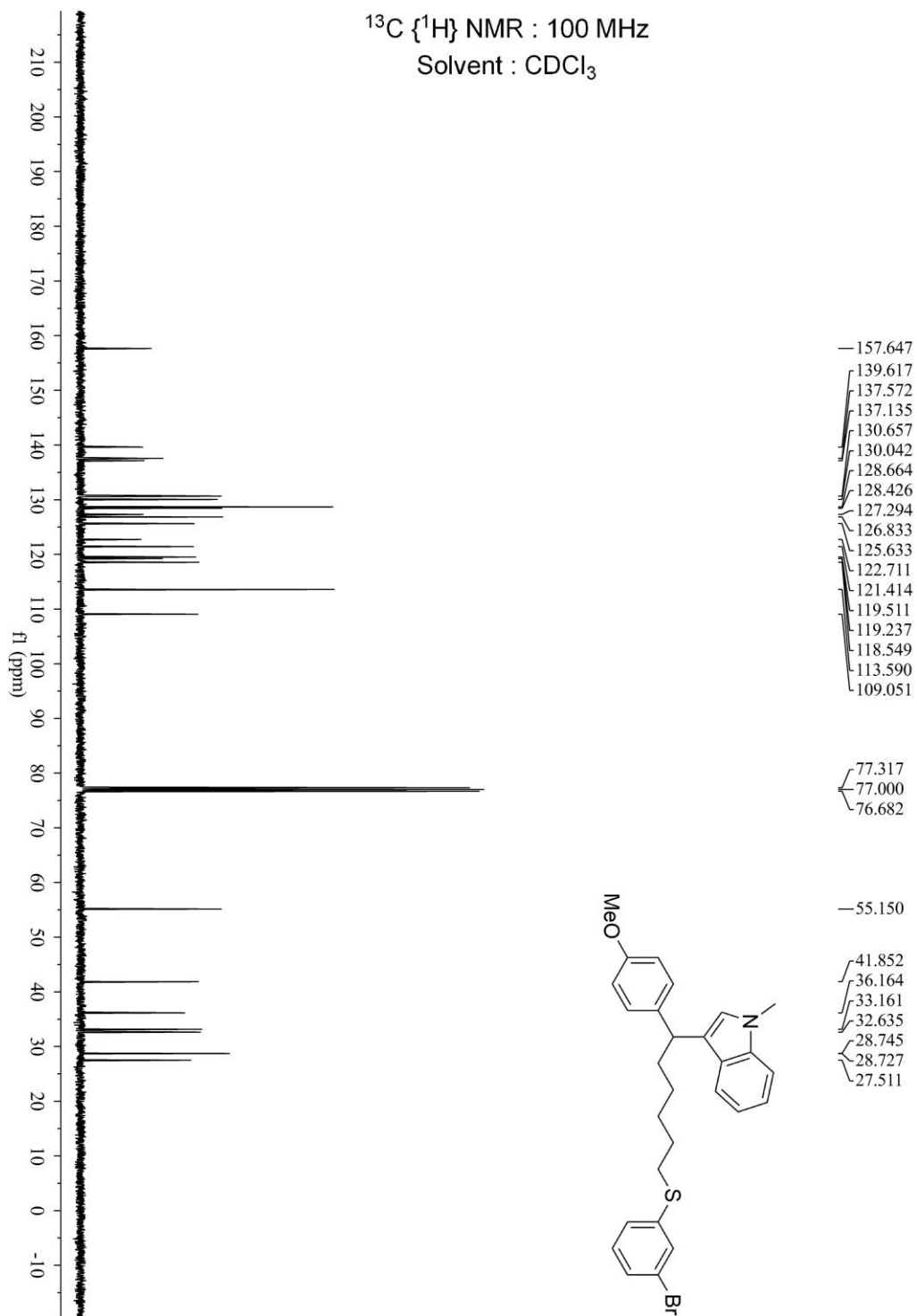
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



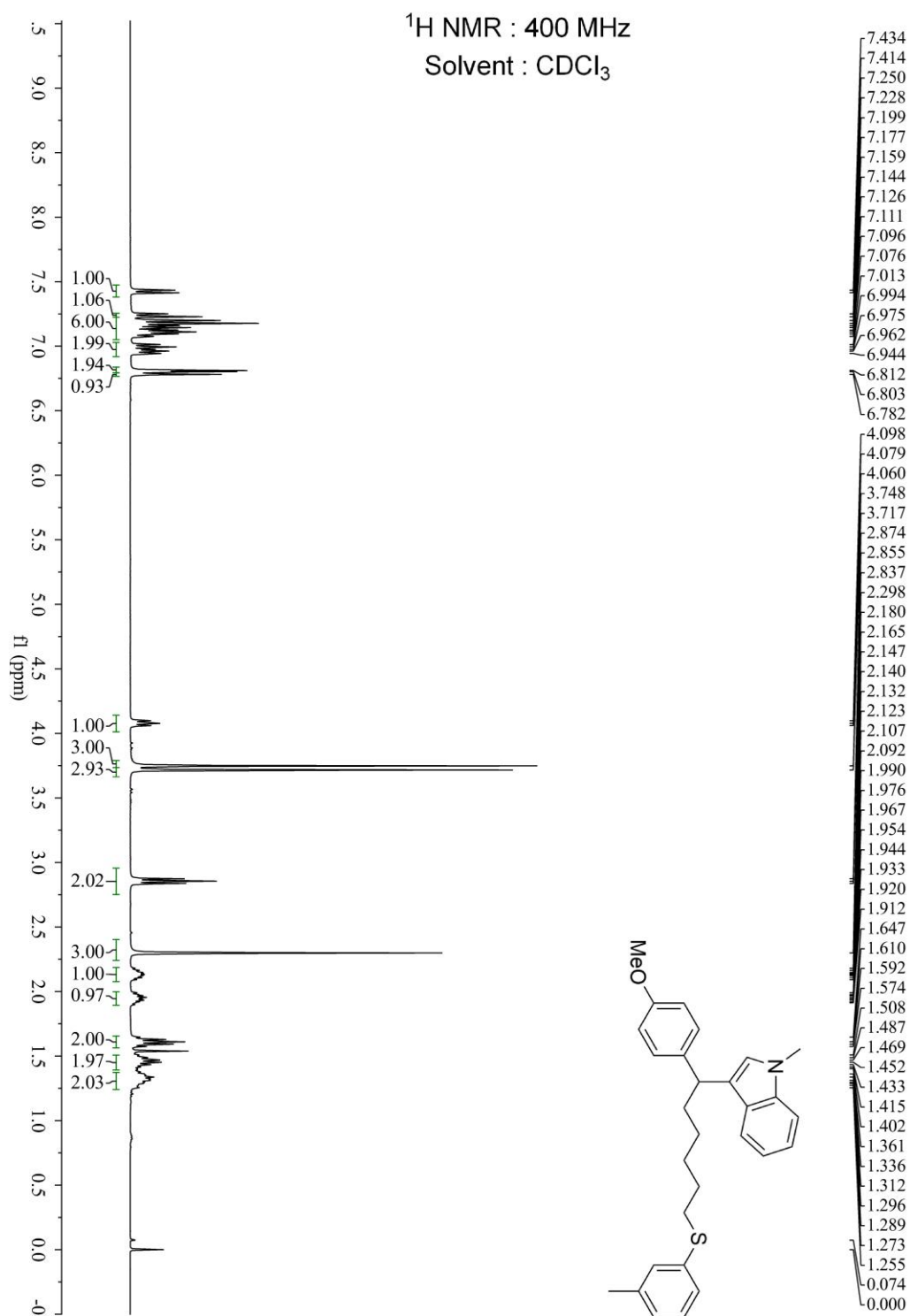
**3-(6-((3-Bromophenyl)thio)-1-(4-methoxyphenyl)hexyl)-1-methyl-1H-indole
(4aha)**



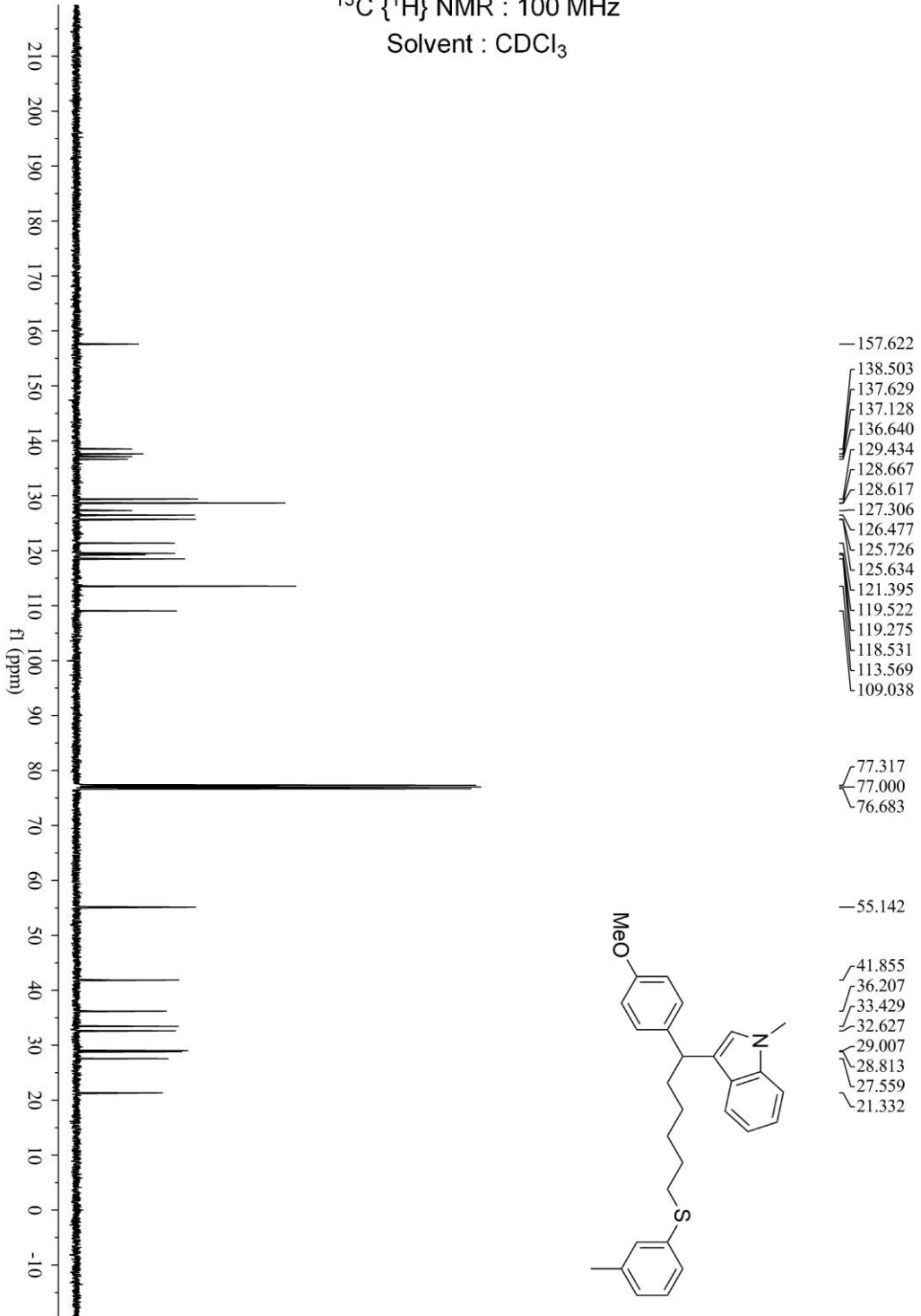
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



3-(1-(4-Methoxyphenyl)-6-(*m*-tolylthio)hexyl)-1-methyl-1*H*-indole (4aia)



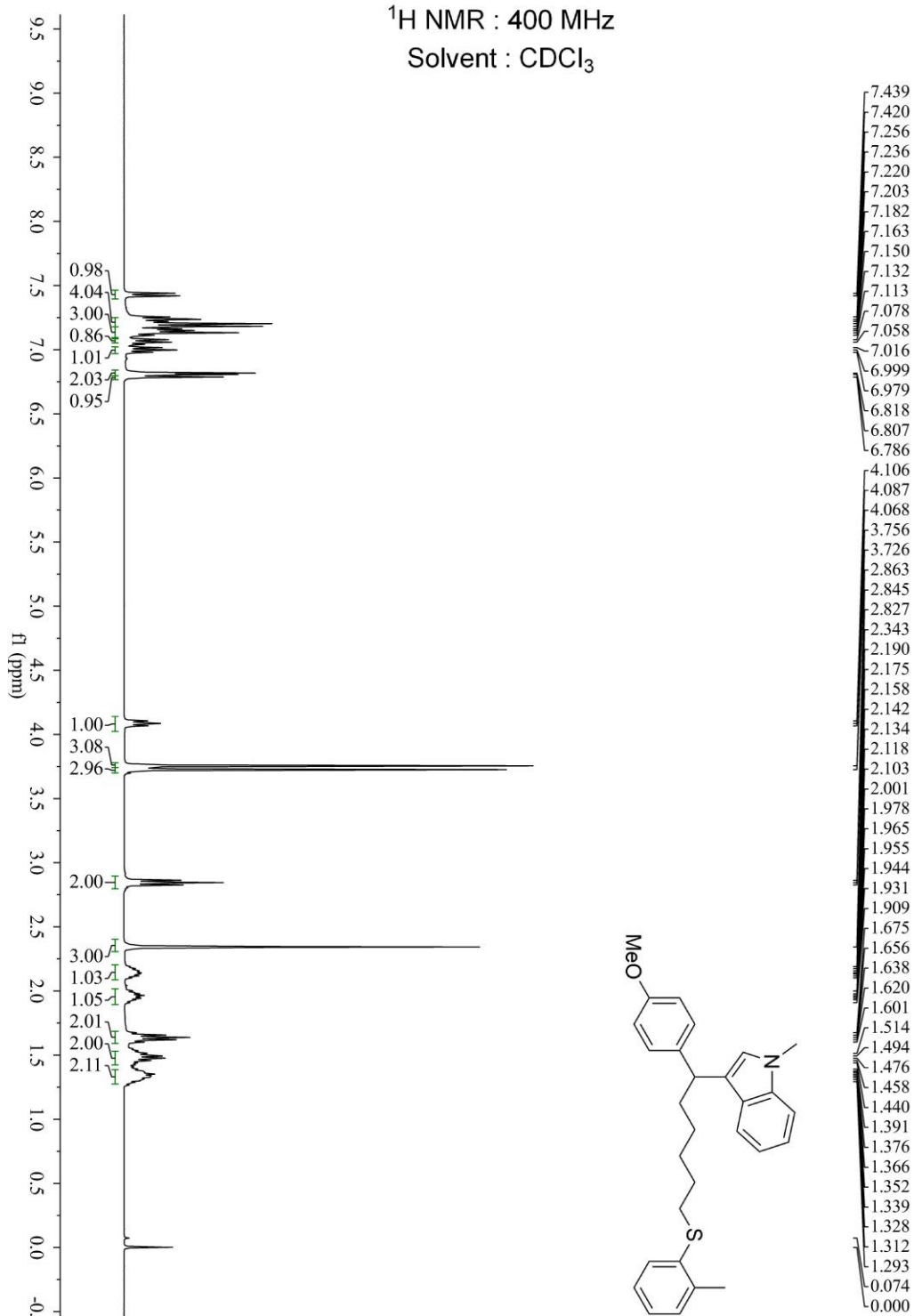
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



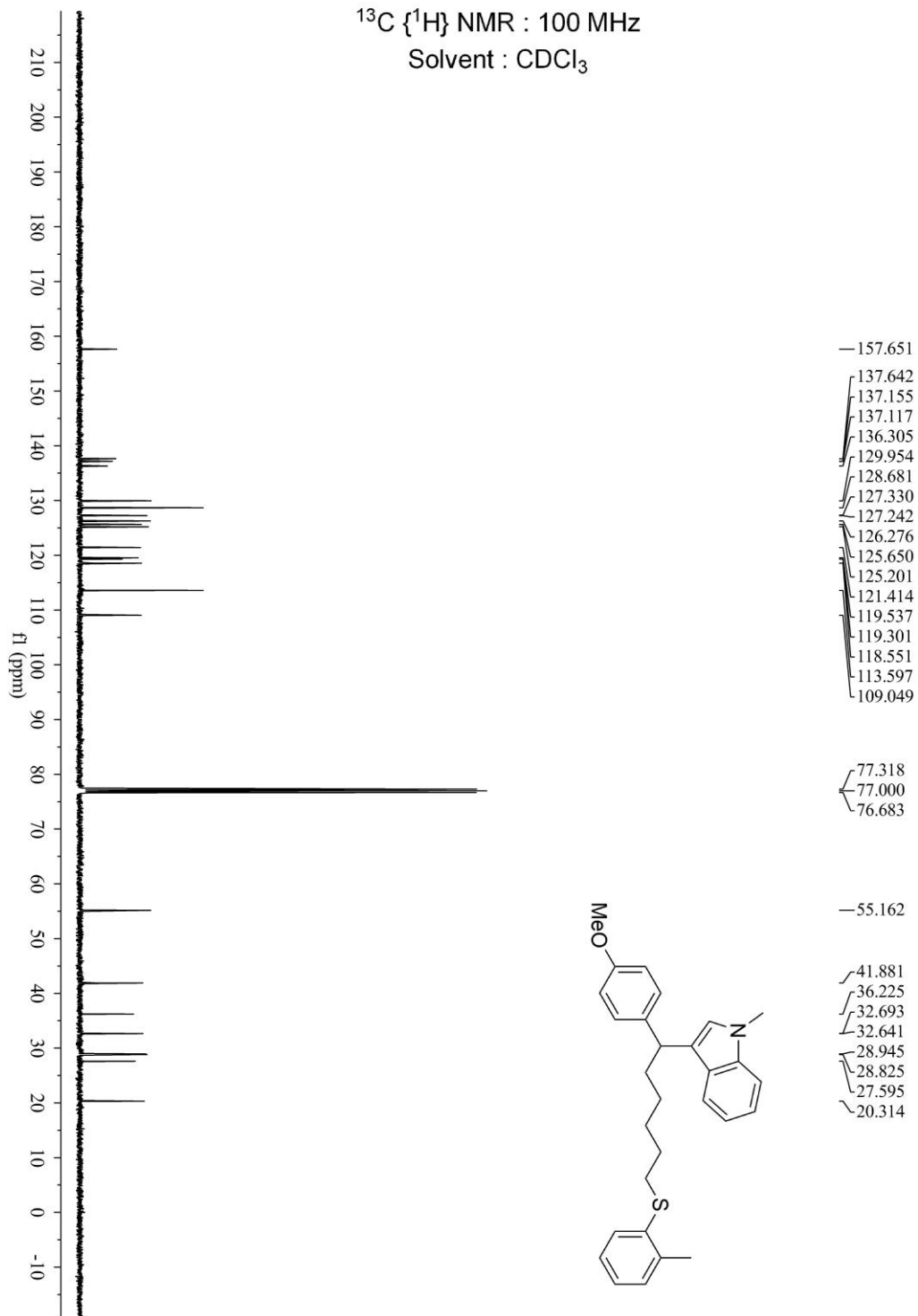
3-(1-(4-Methoxyphenyl)-6-(*o*-tolylthio)hexyl)-1-methyl-1*H*-indole(4aja)

¹H NMR : 400 MHz

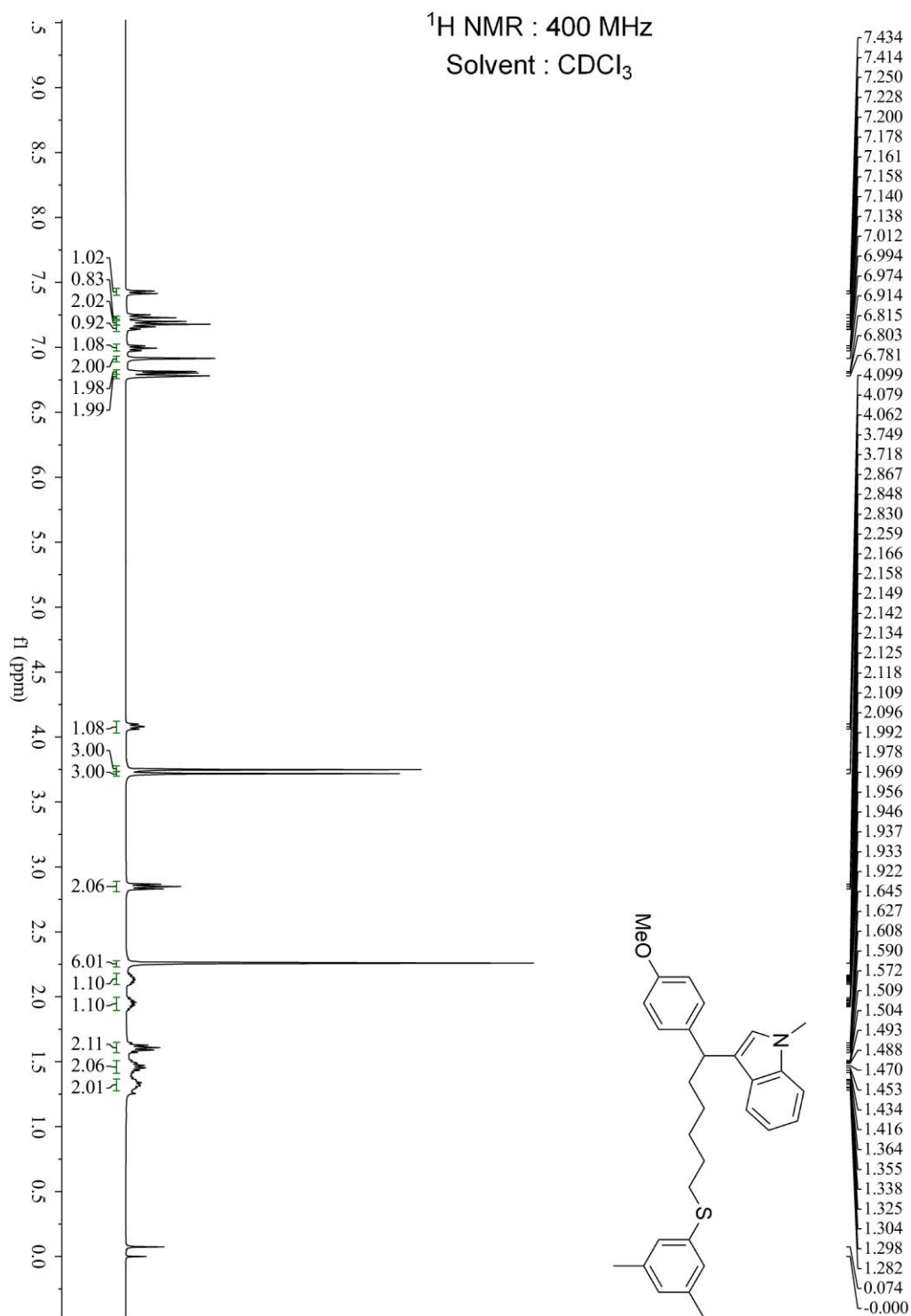
Solvent : CDCl₃



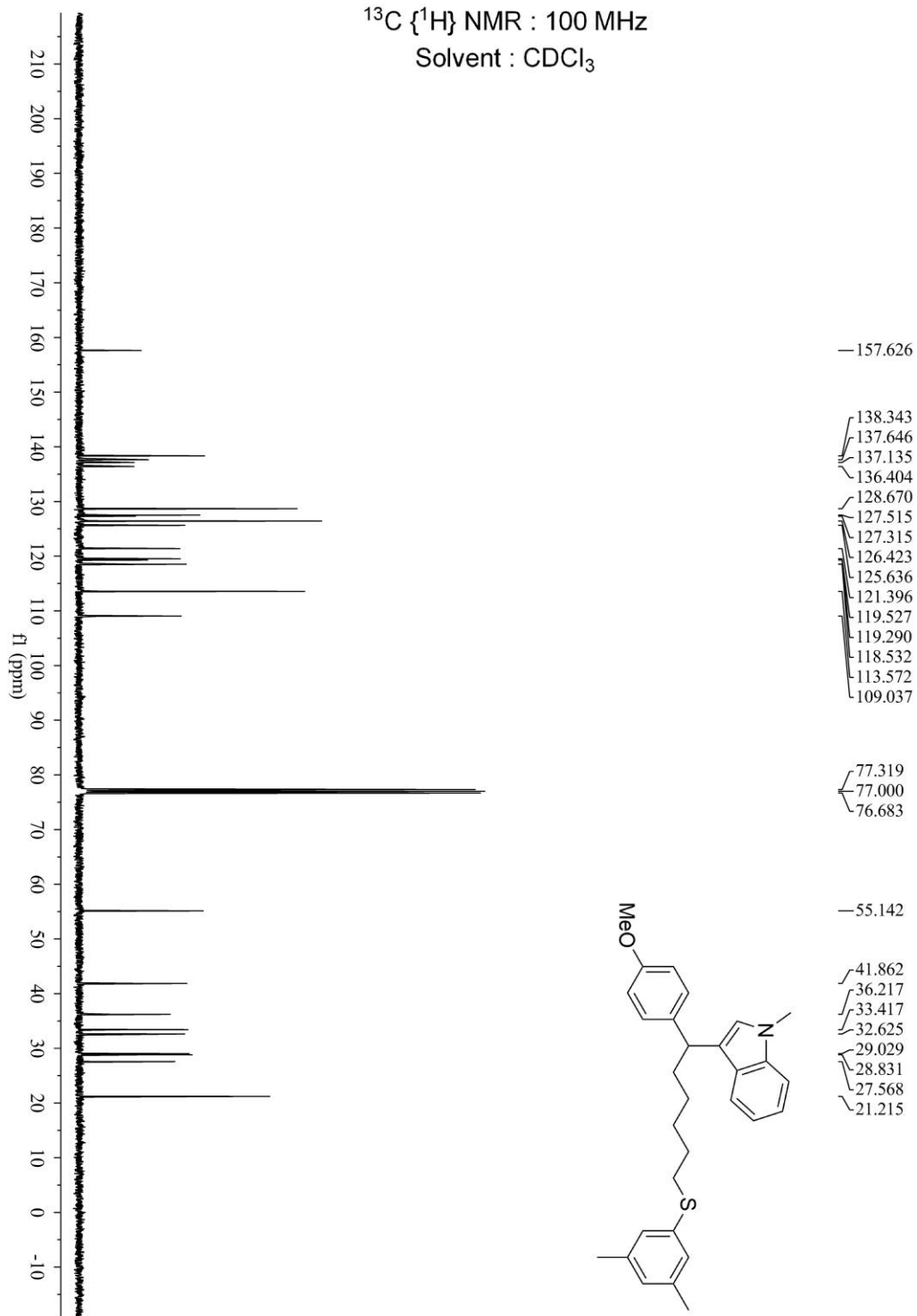
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



**3-(6-((3,5-Dimethylphenyl)thio)-1-(4-methoxyphenyl)hexyl)-1-methyl-1H-indole
(4aka)**



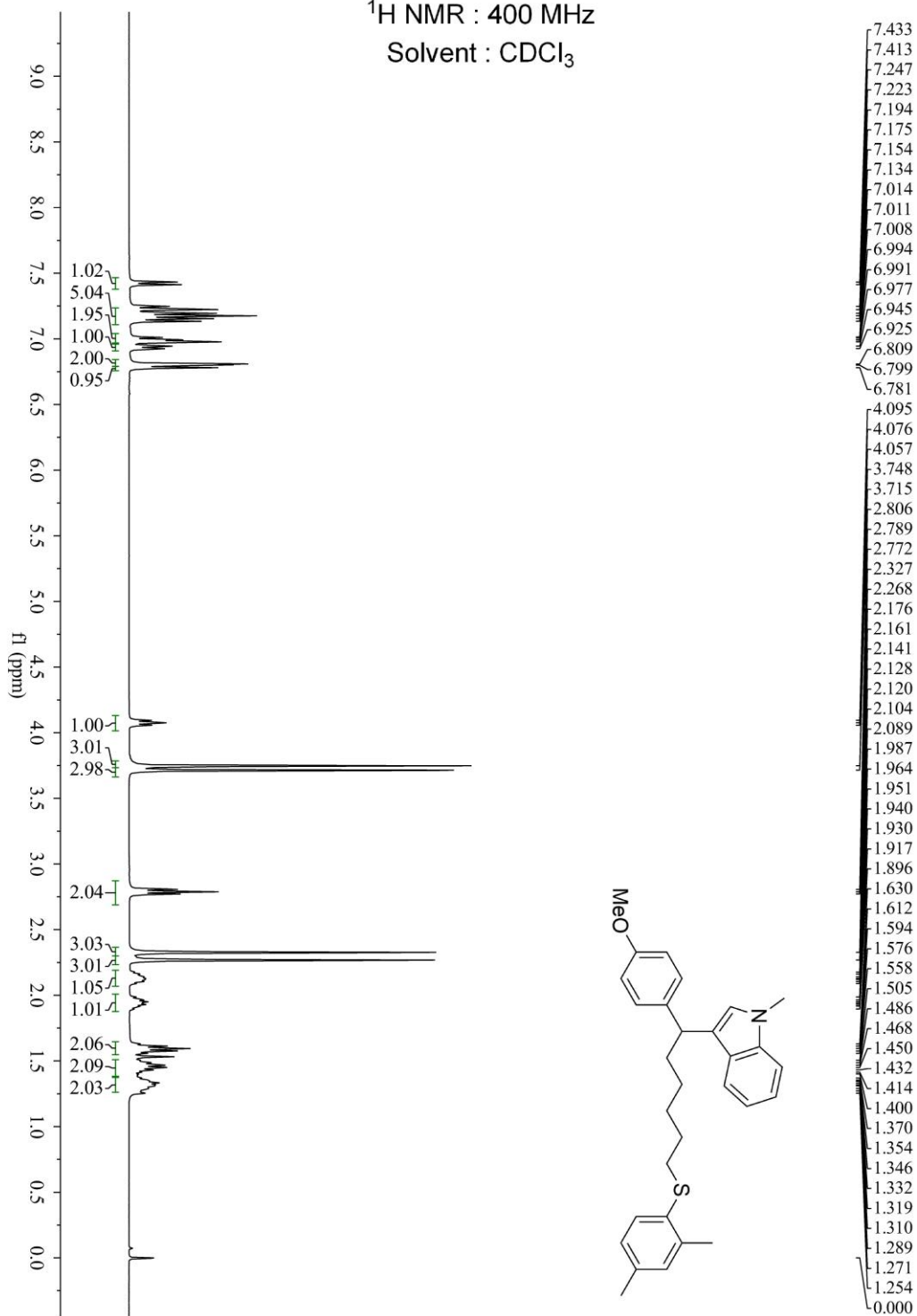
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



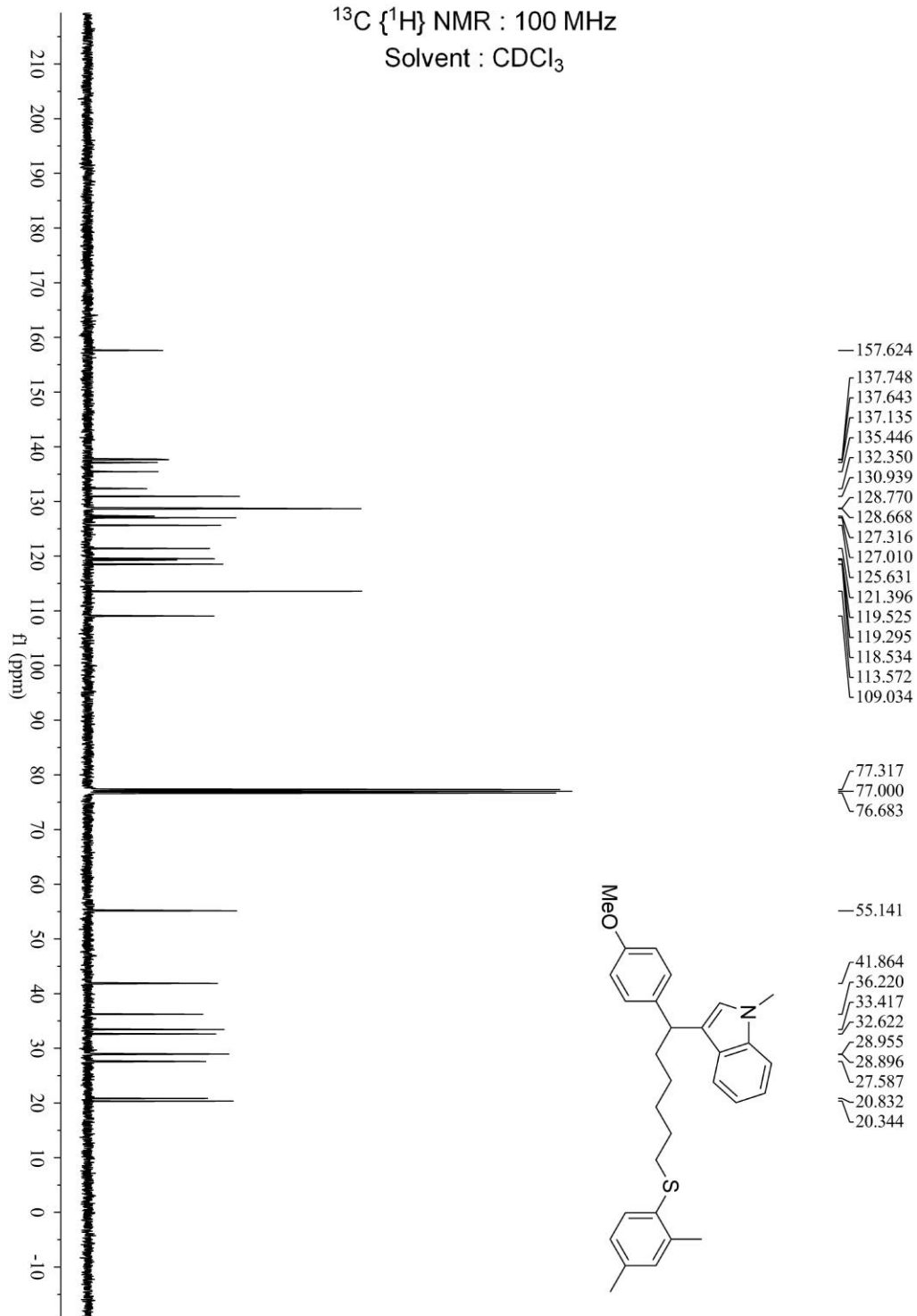
**3-(6-((2,4-Dimethylphenyl)thio)-1-(4-methoxyphenyl)hexyl)-1-methyl-1H-indole
(4ala)**

¹H NMR : 400 MHz

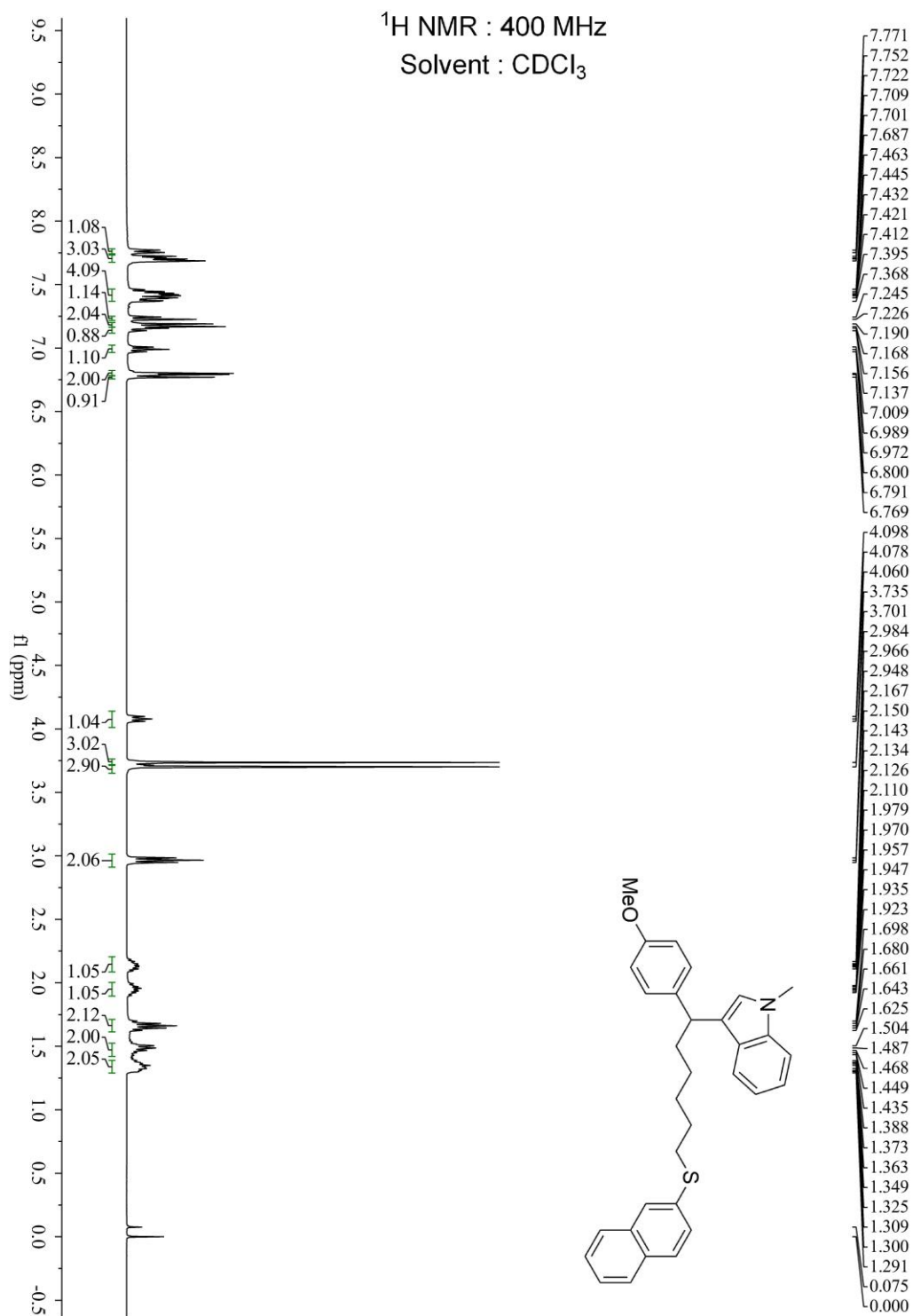
Solvent : CDCl₃



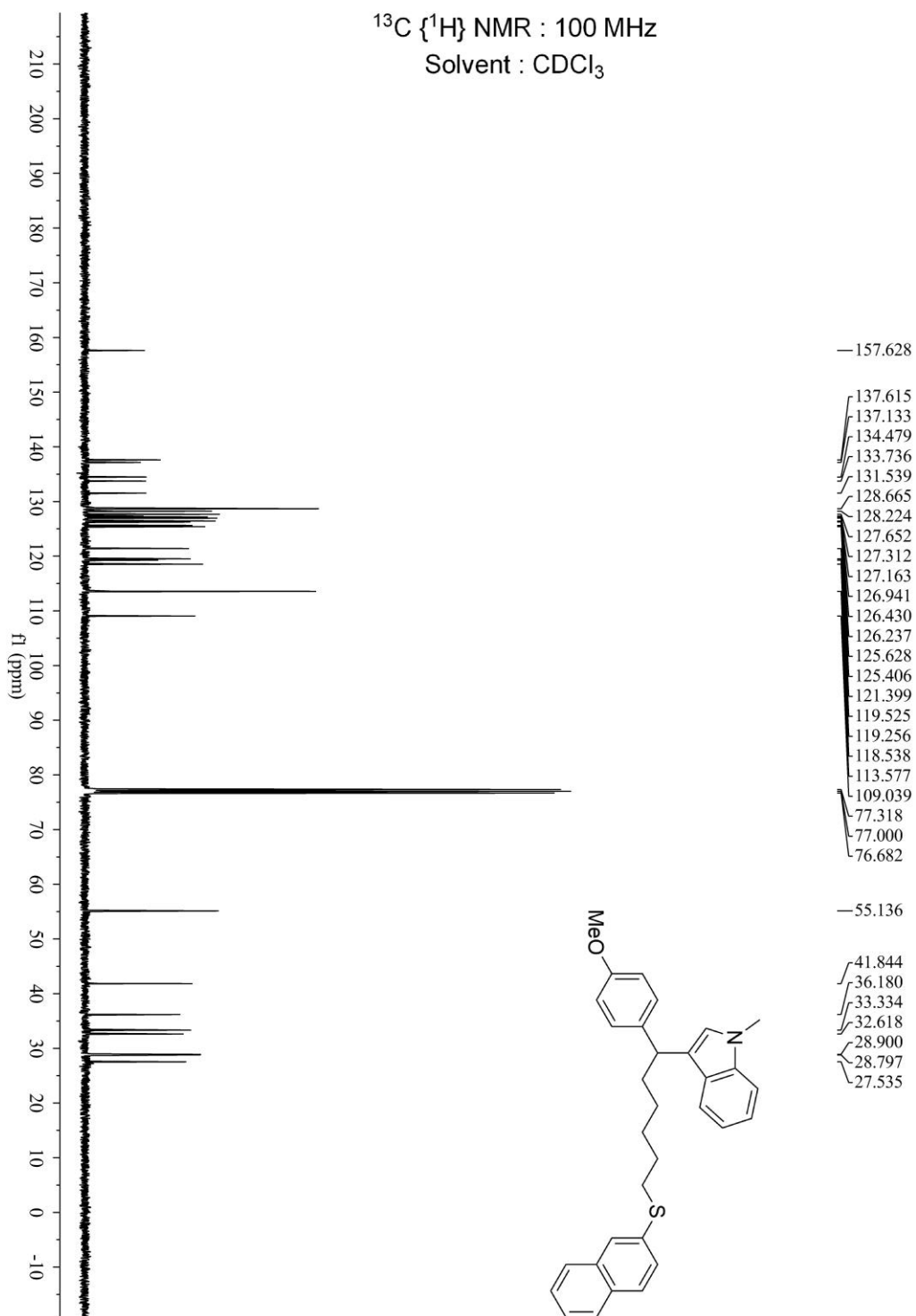
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



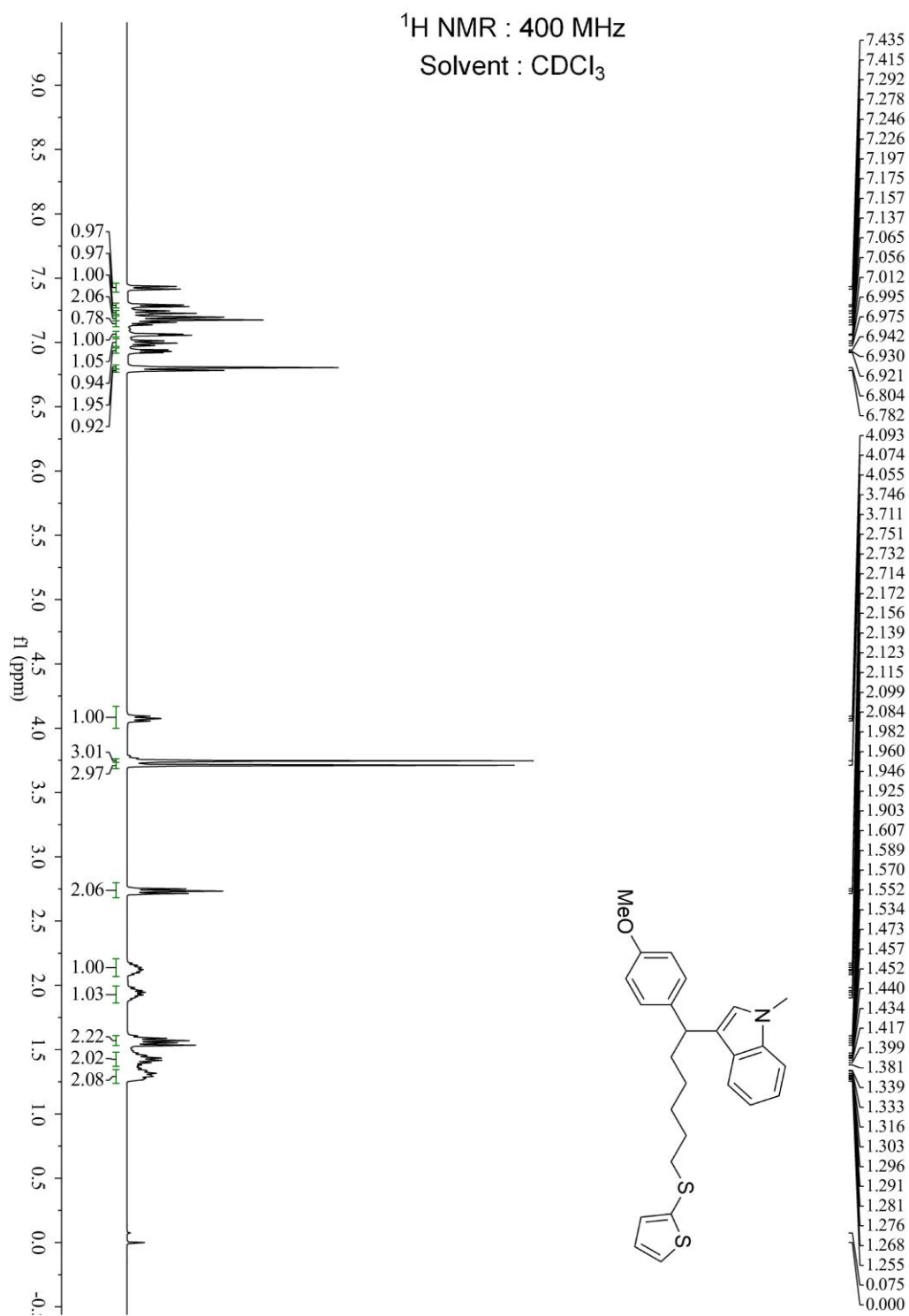
**3-(1-(4-Methoxyphenyl)-6-(naphthalen-2-ylthio)hexyl)-1-methyl-1H-indole
(4ama)**



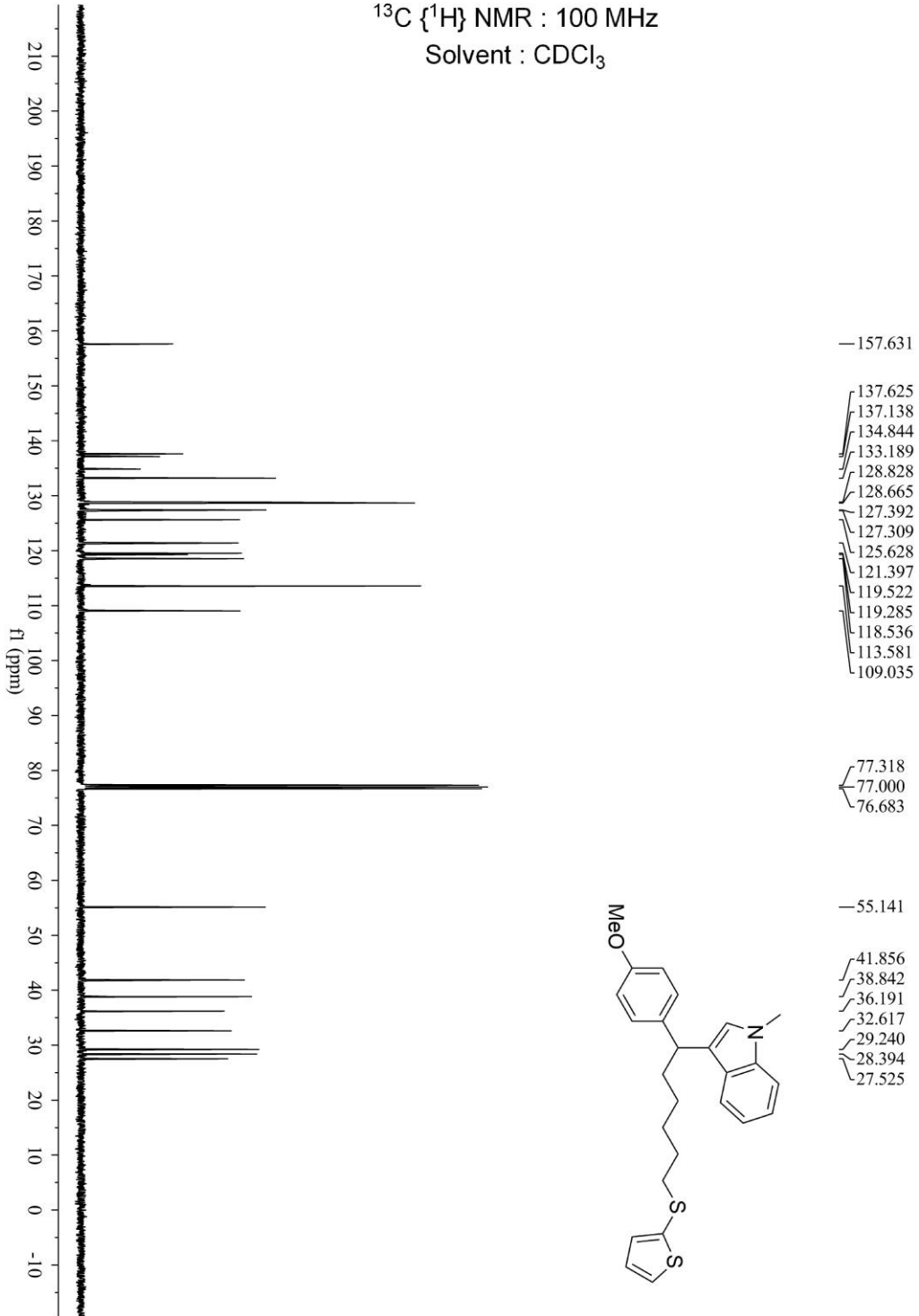
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



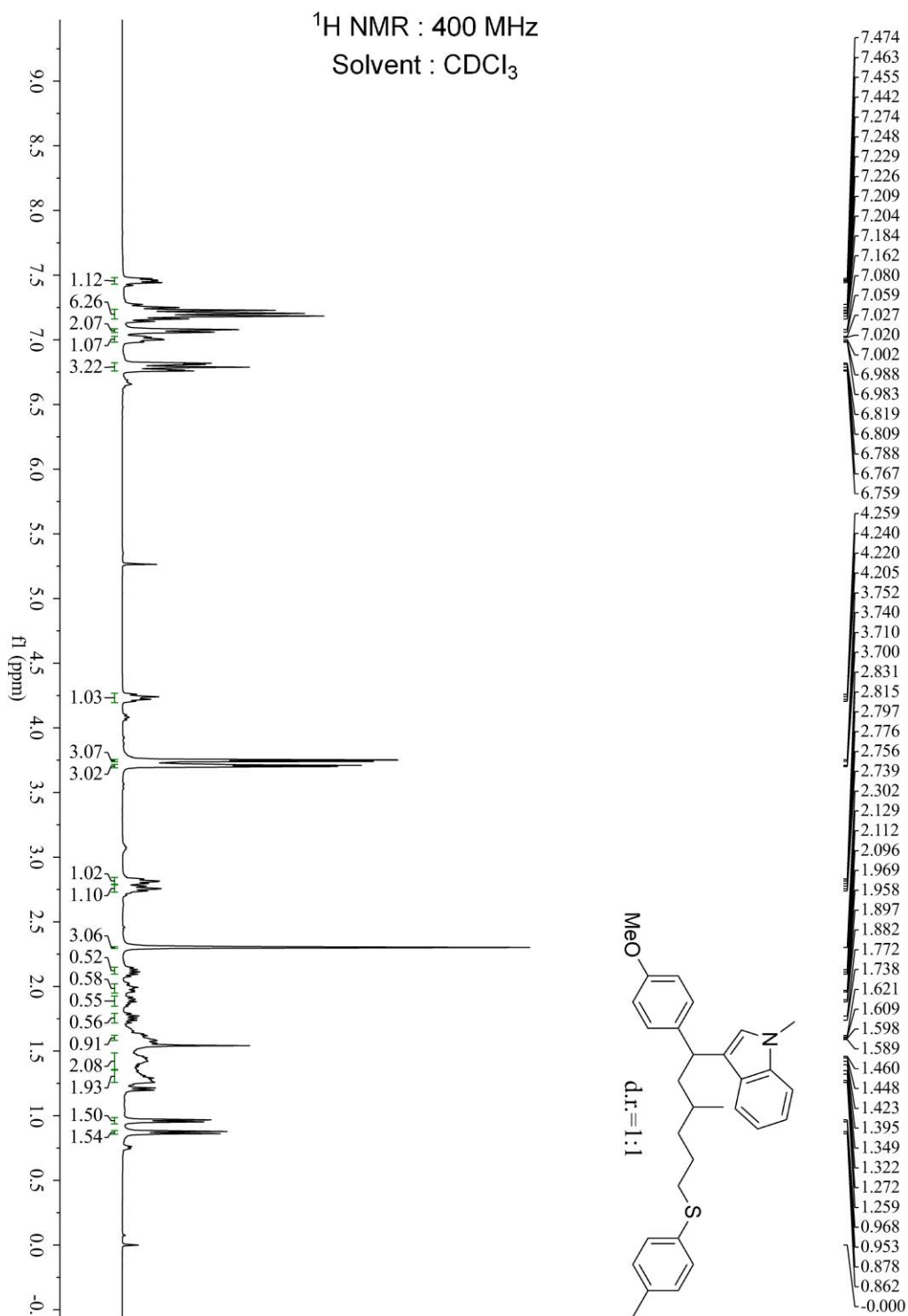
3-(1-(4-Methoxyphenyl)-6-(thiophen-2-ylthio)hexyl)-1-methyl-1H-indole (4ana)



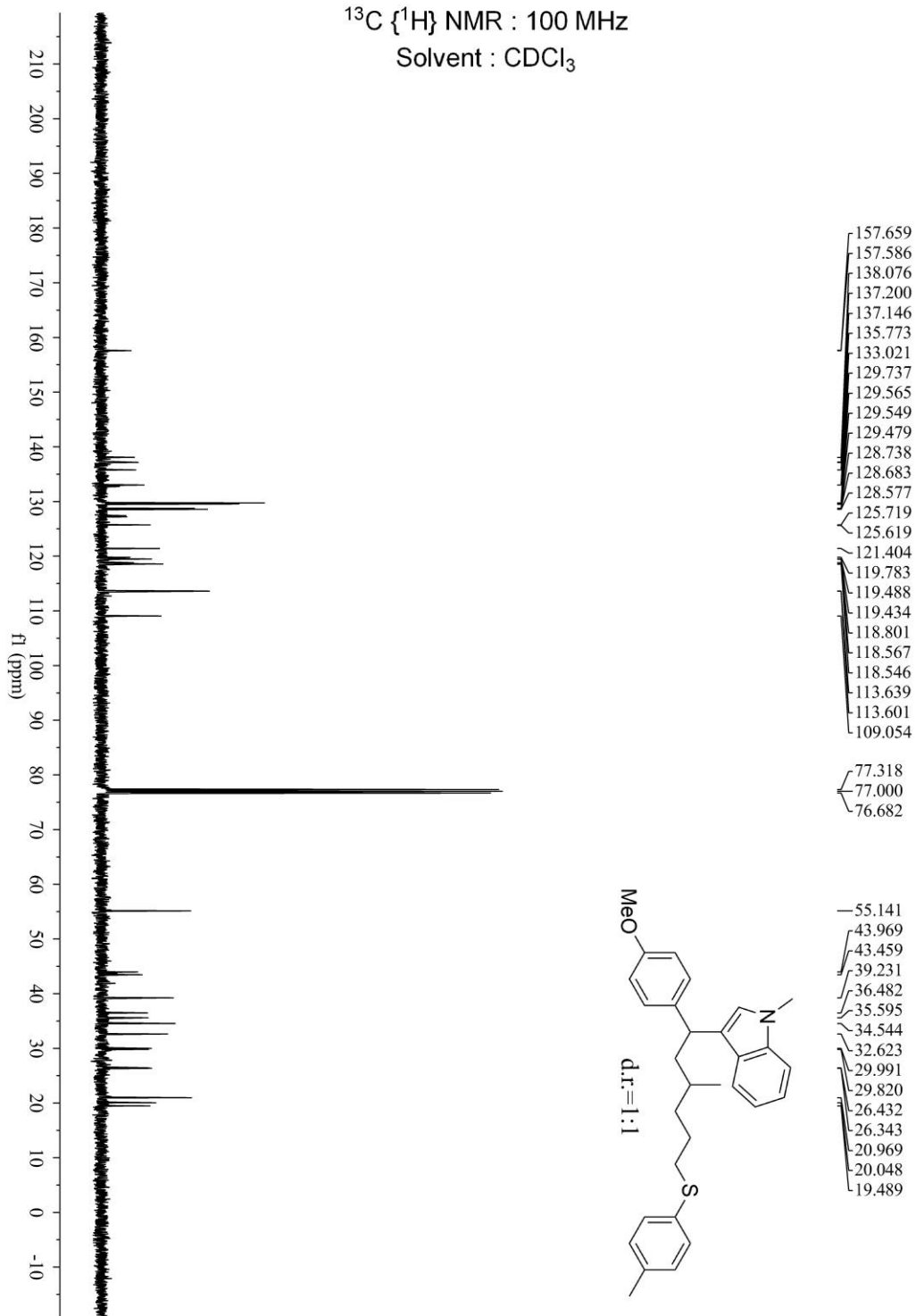
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



**3-(1-(4-Methoxyphenyl)-3-methyl-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole
(4a0a)**



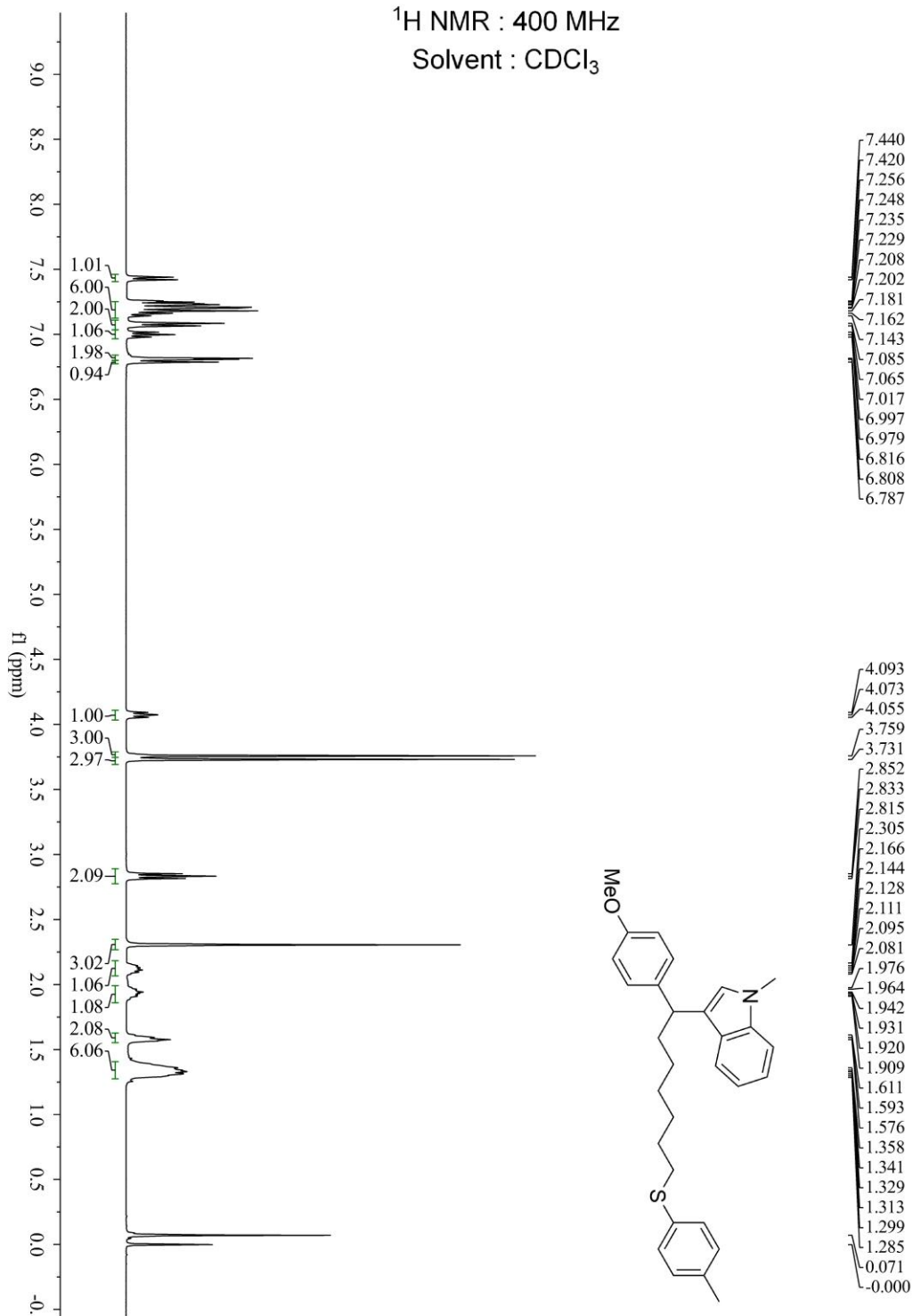
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



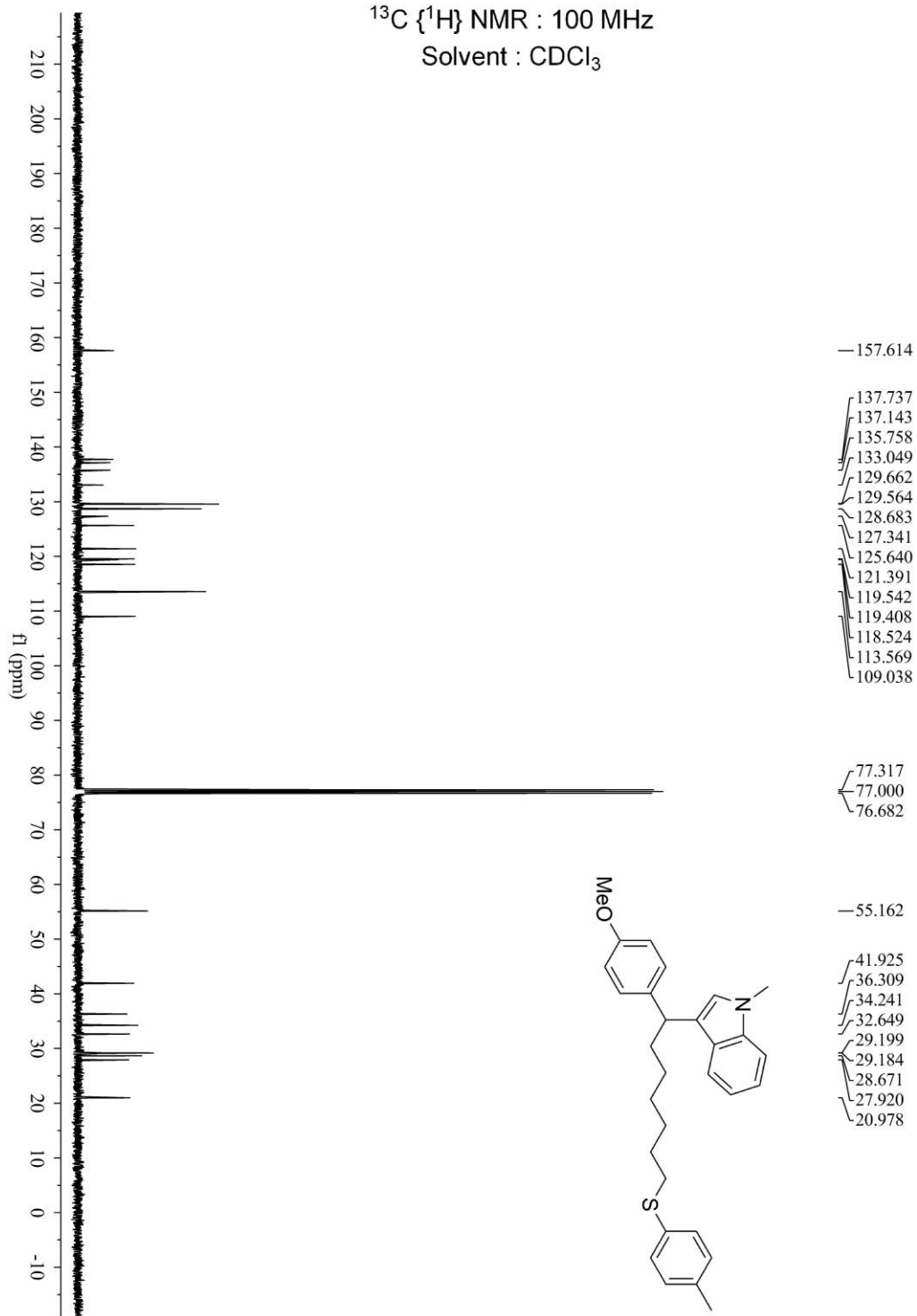
3-(1-(4-Methoxyphenyl)-7-(*p*-tolylthio)heptyl)-1-methyl-1*H*-indole (4apa)

¹H NMR : 400 MHz

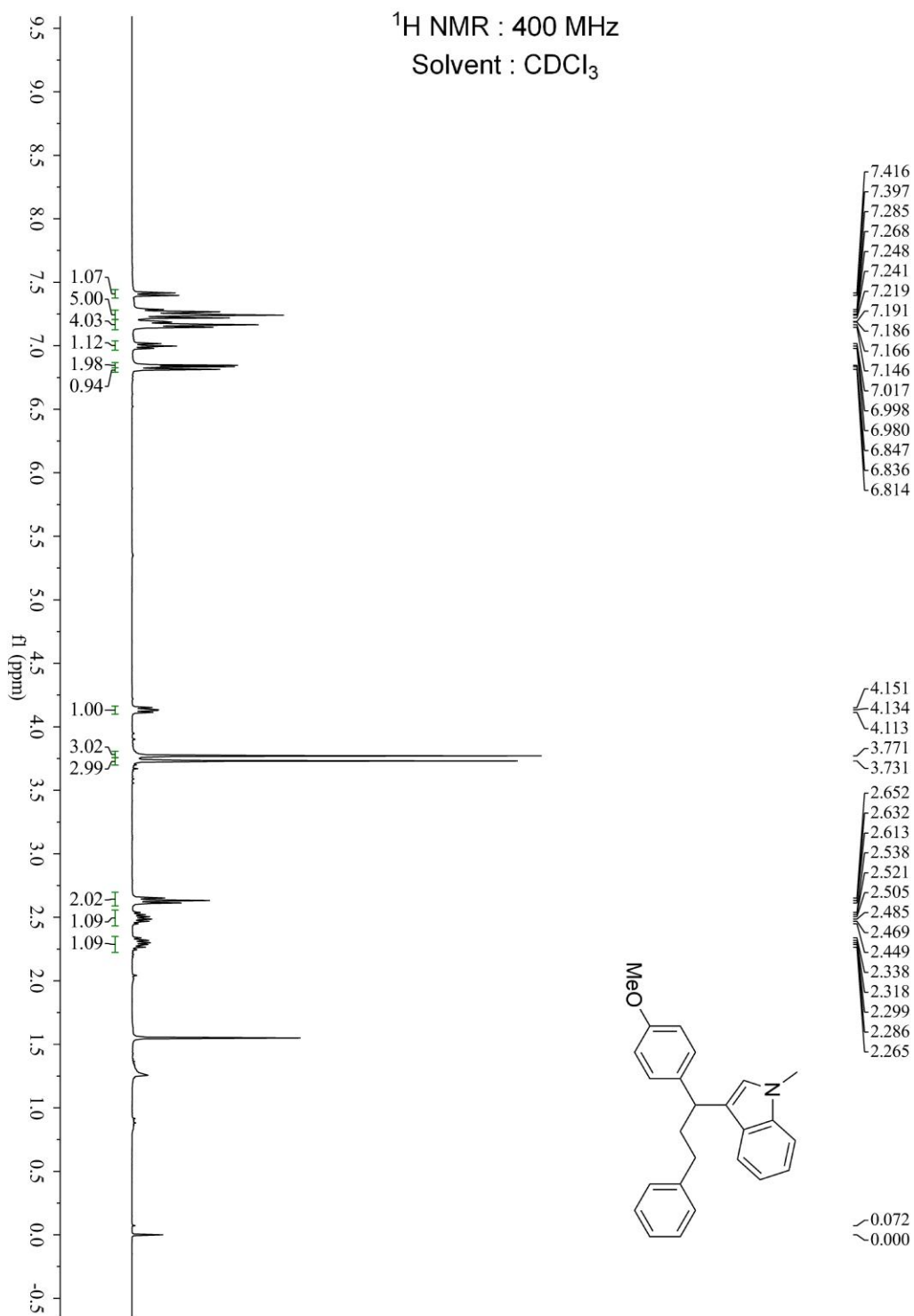
Solvent : CDCl₃



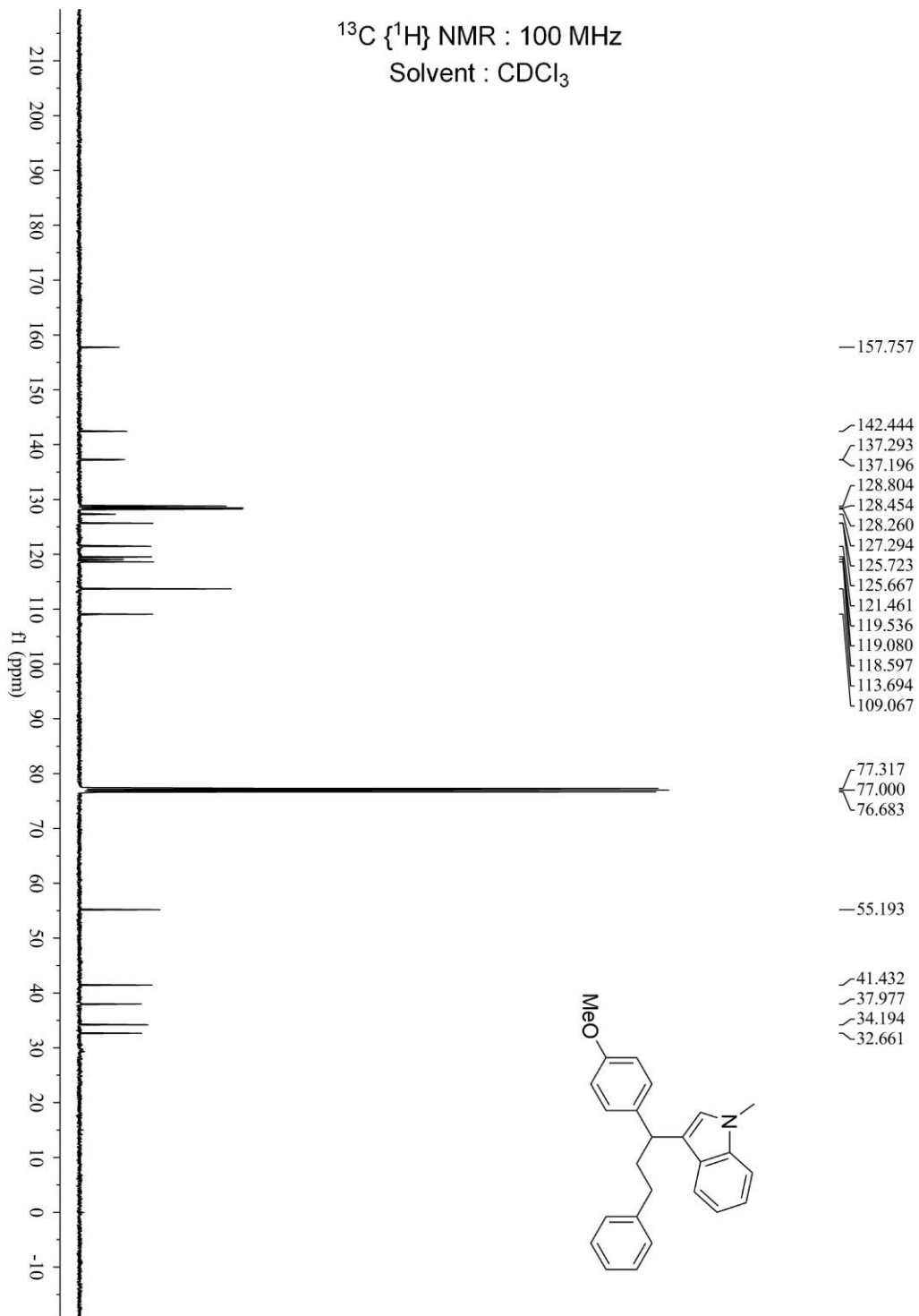
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



3-(1-(4-Methoxyphenyl)-3-phenylpropyl)-1-methyl-1H-indole (4aqa)



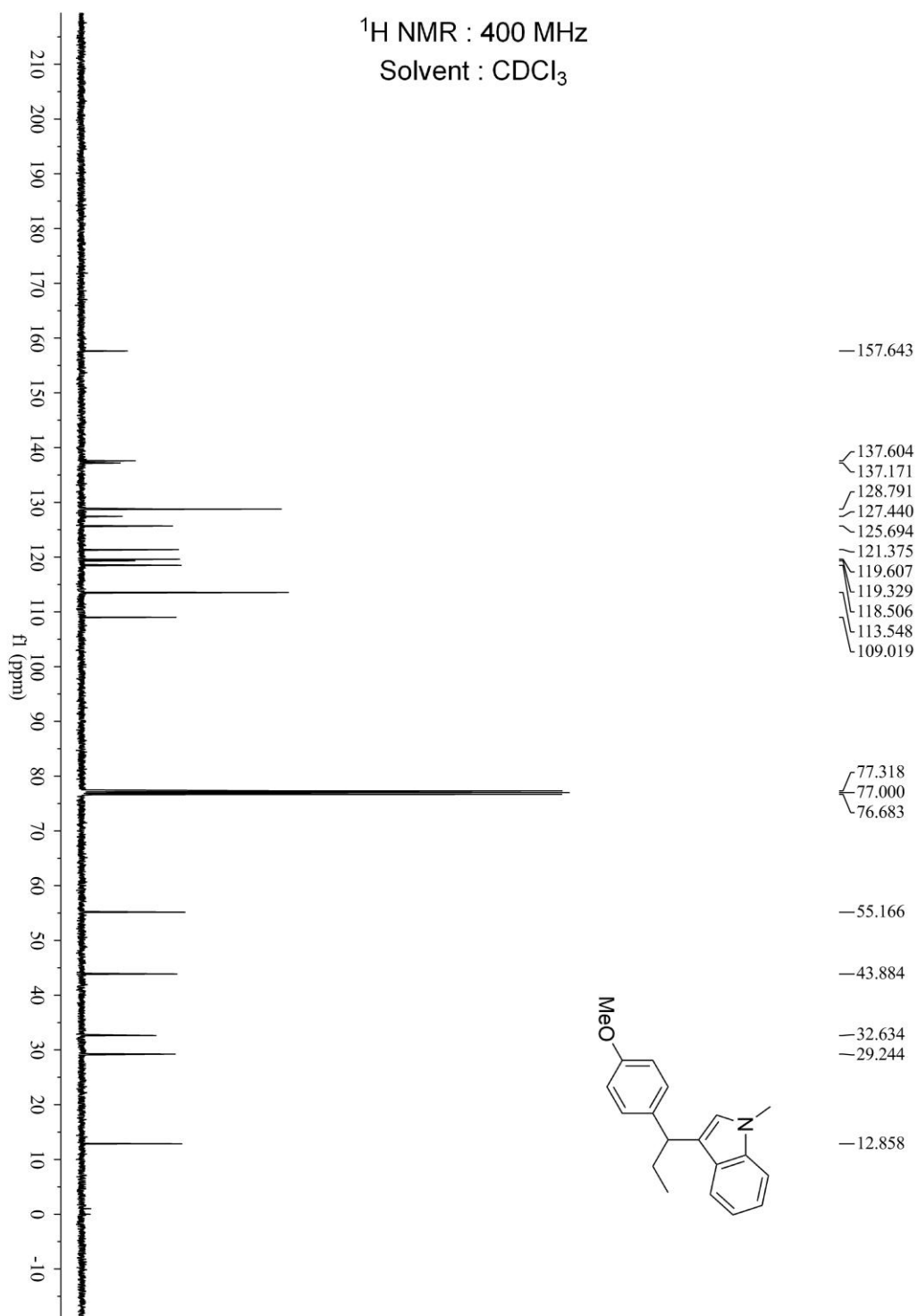
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



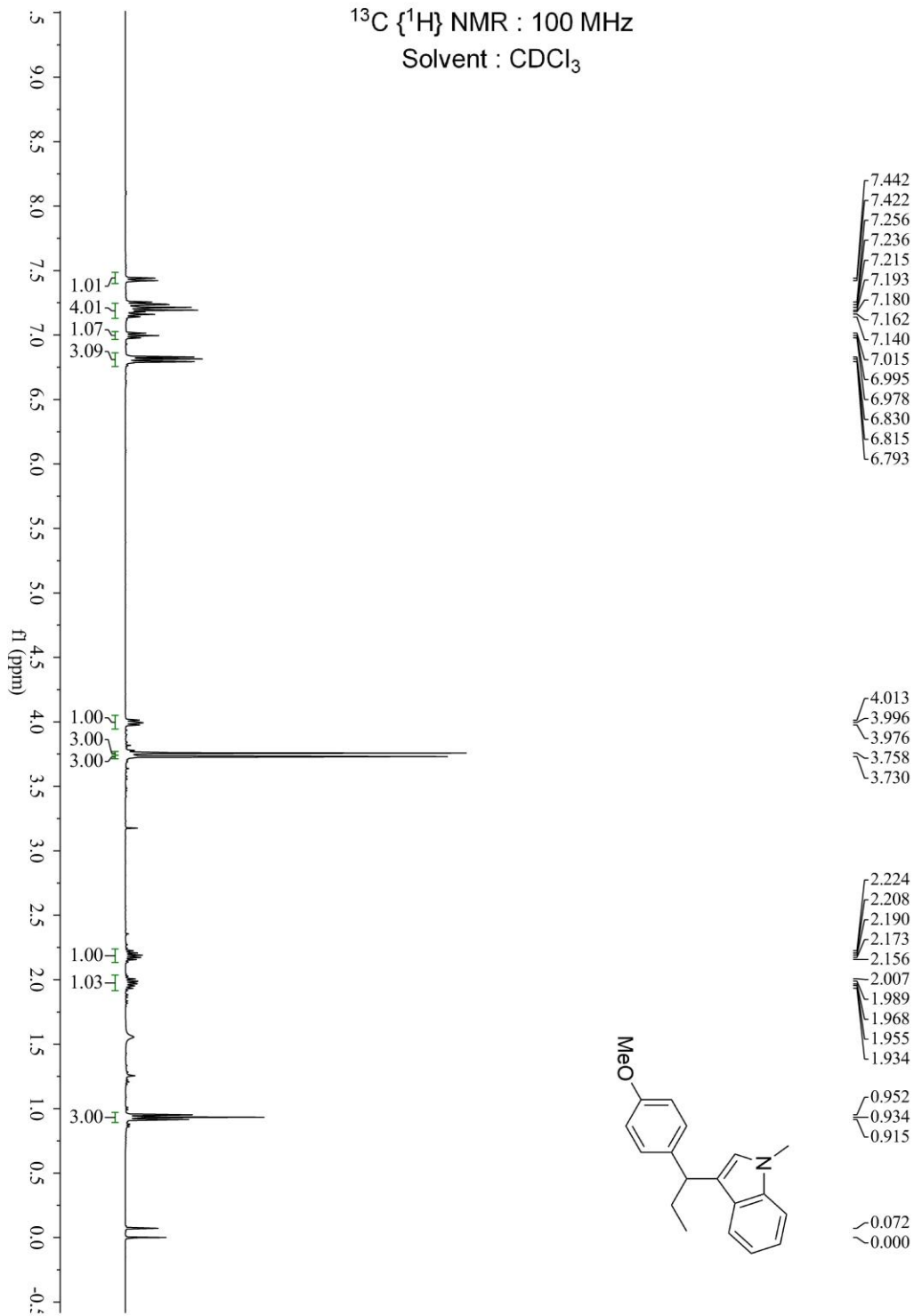
3-(1-(4-Methoxyphenyl)propyl)-1-methyl-1H-indole (4ara)

^1H NMR : 400 MHz

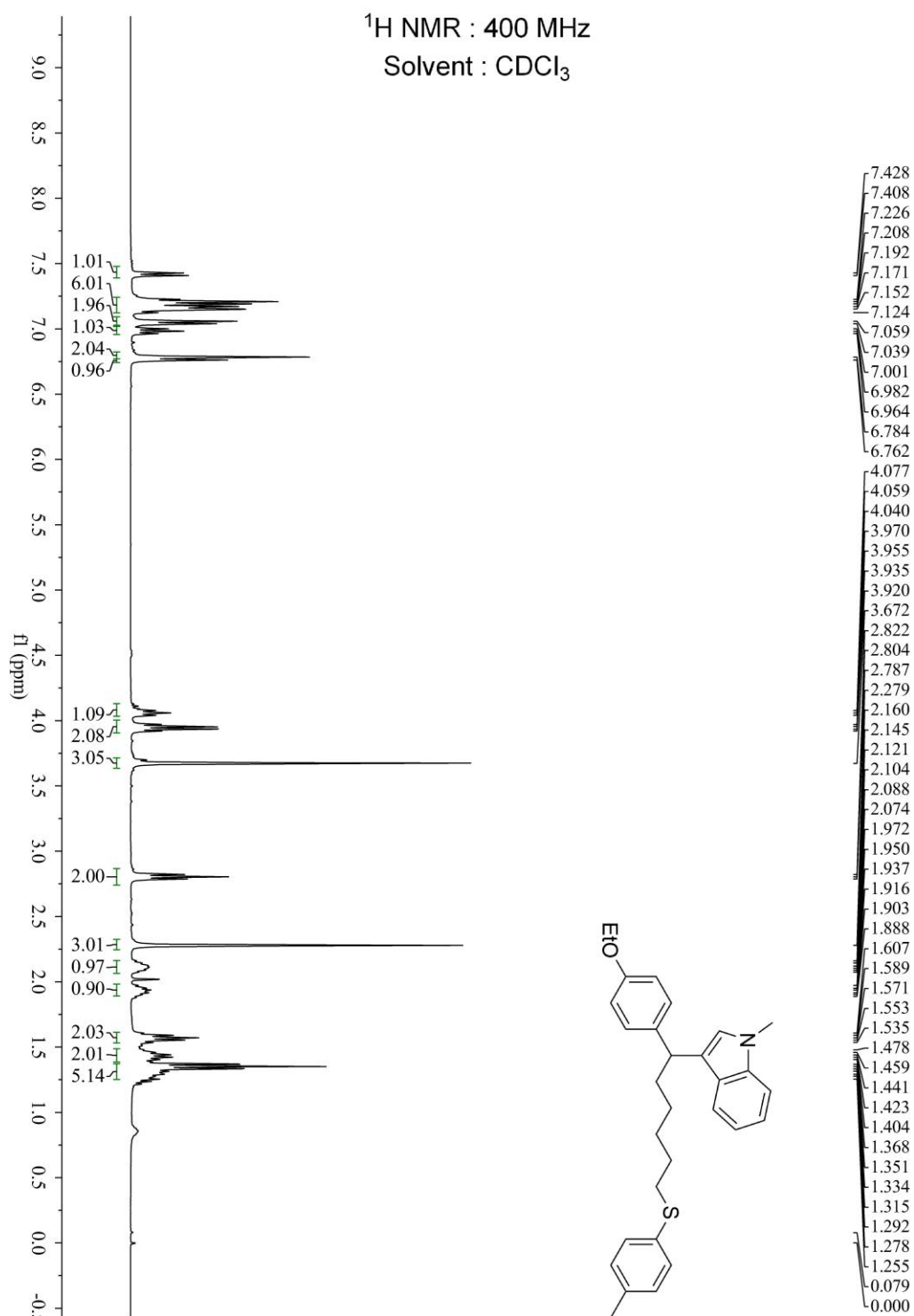
Solvent : CDCl_3



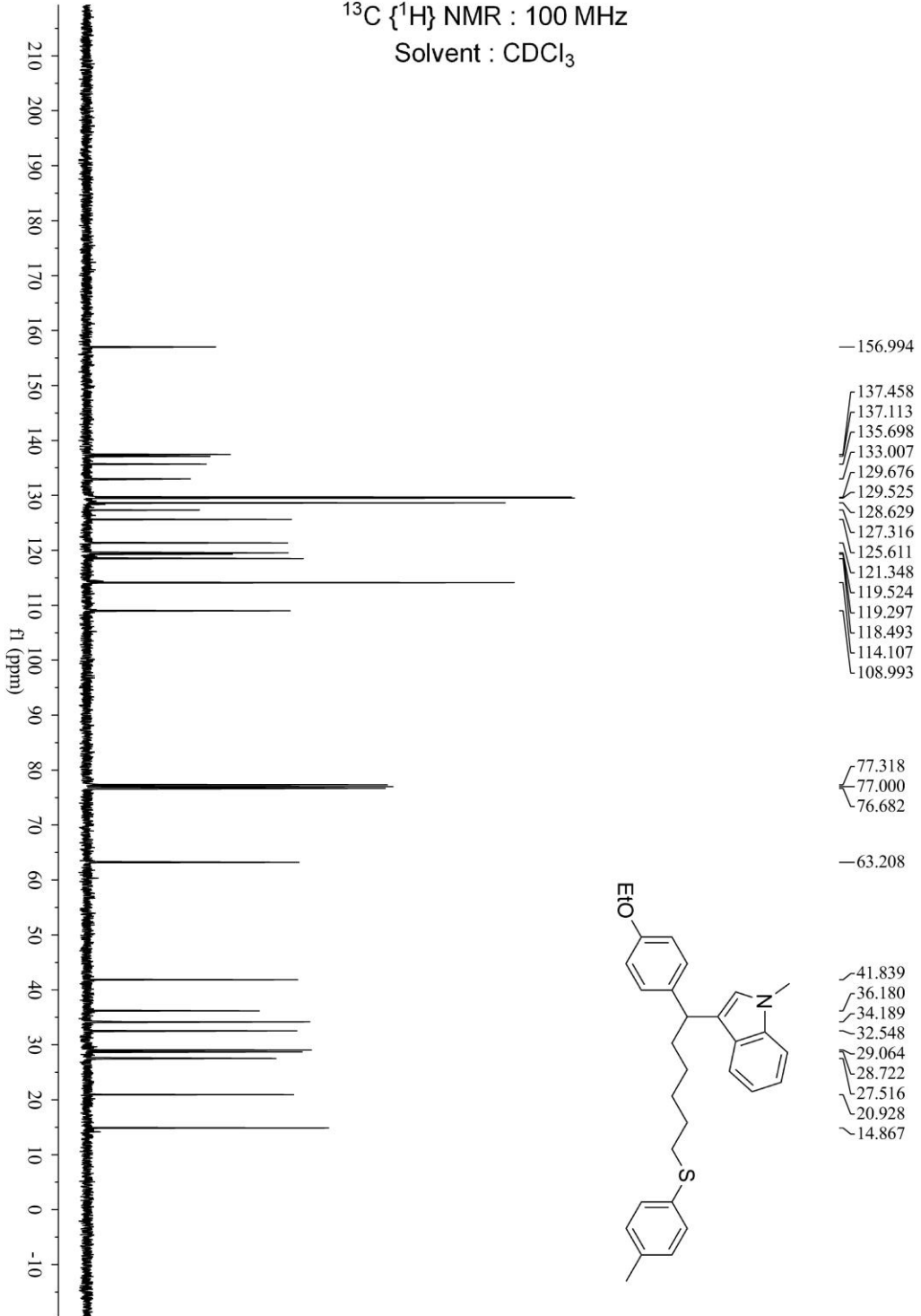
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



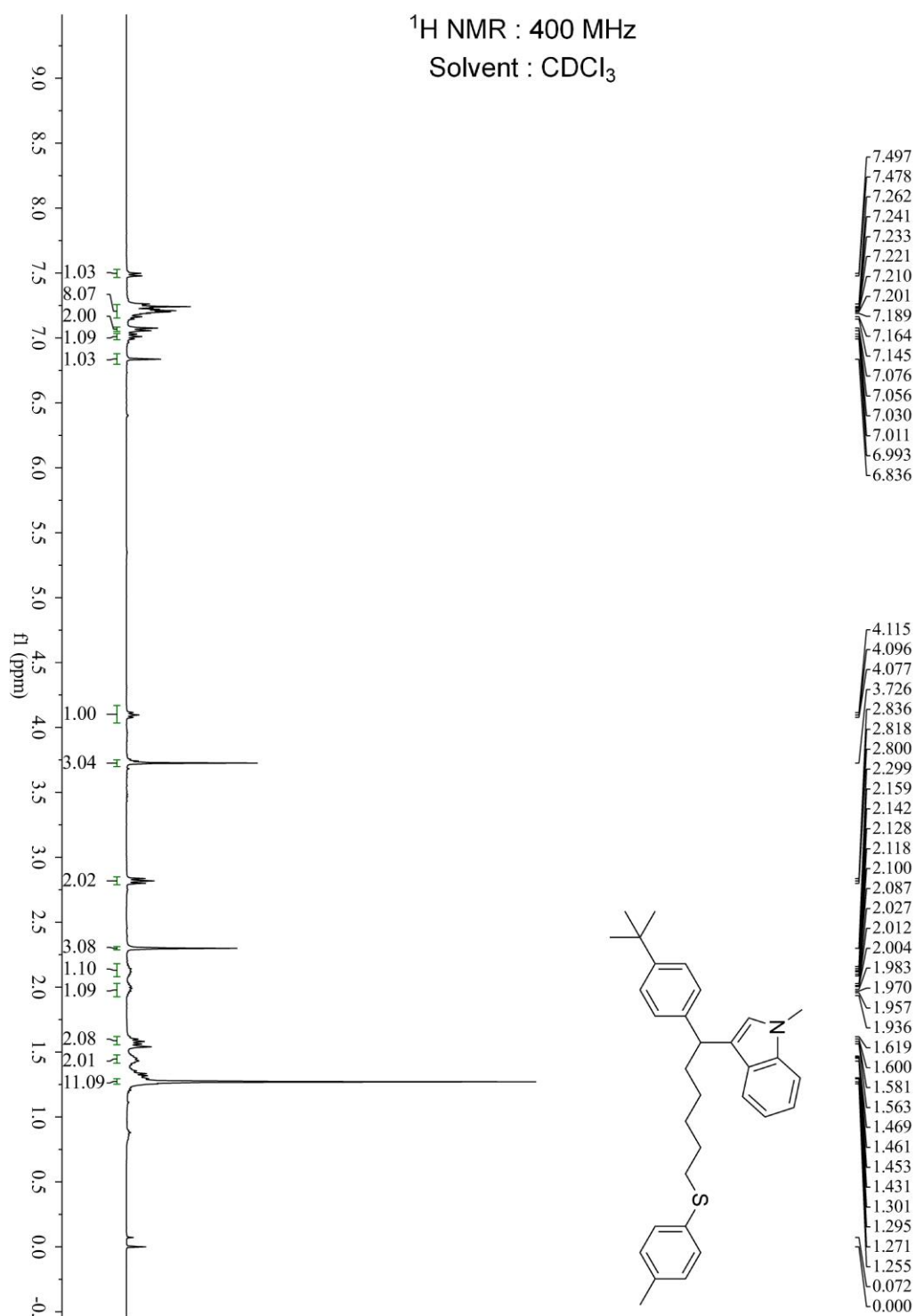
3-(1-(4-Ethoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4baa)



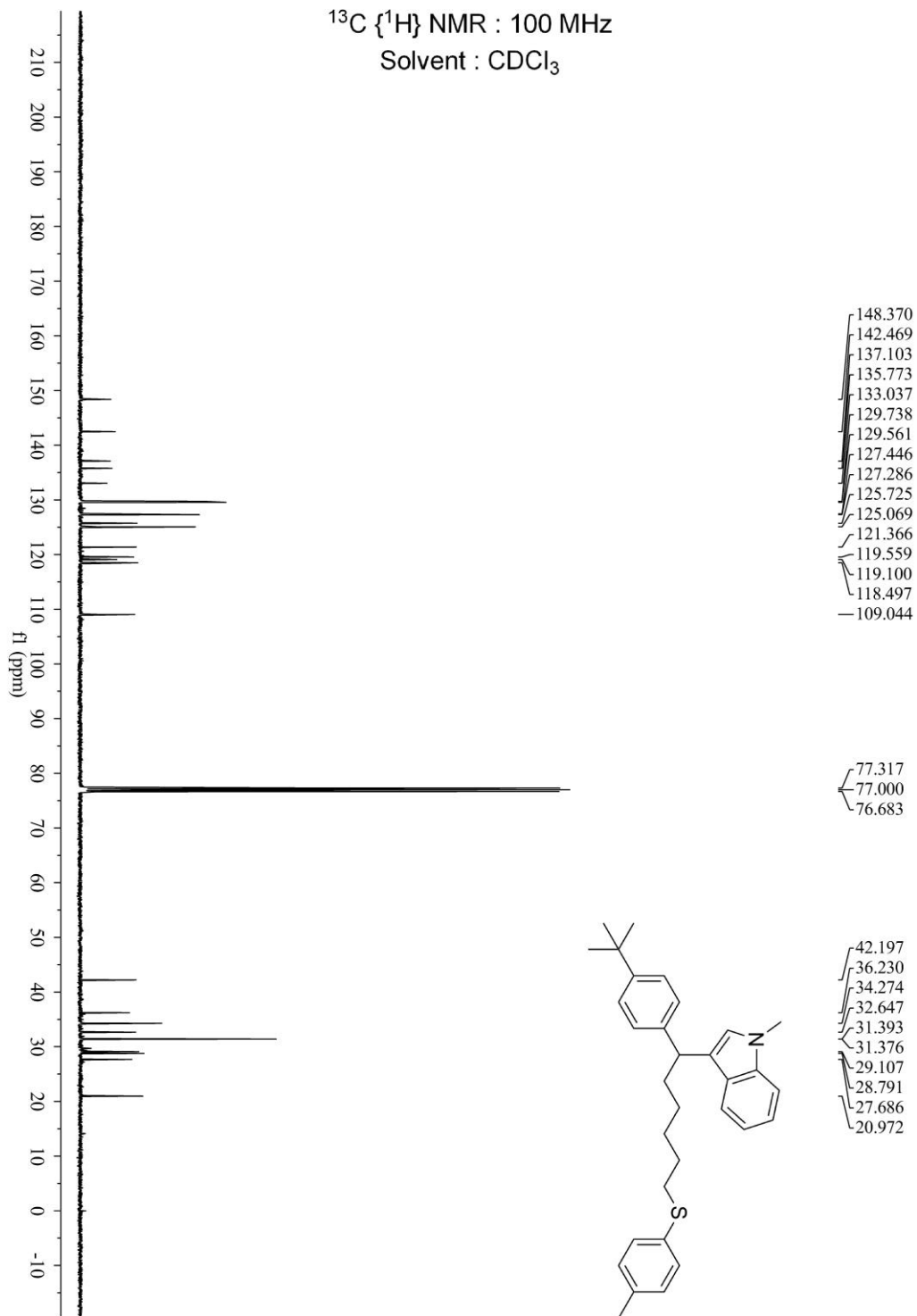
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



3-(1-(4-(Tert-butyl)phenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4caa)



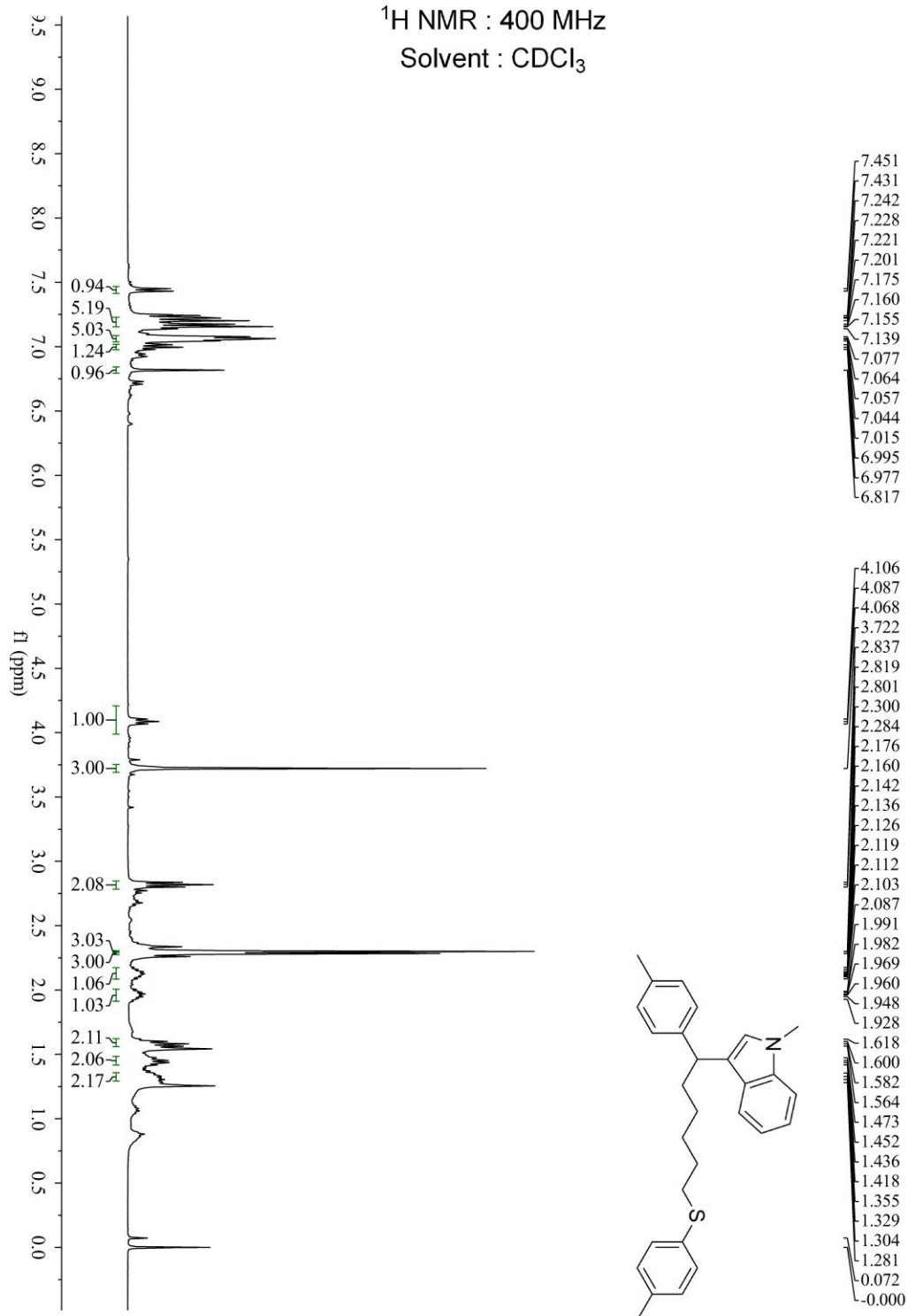
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



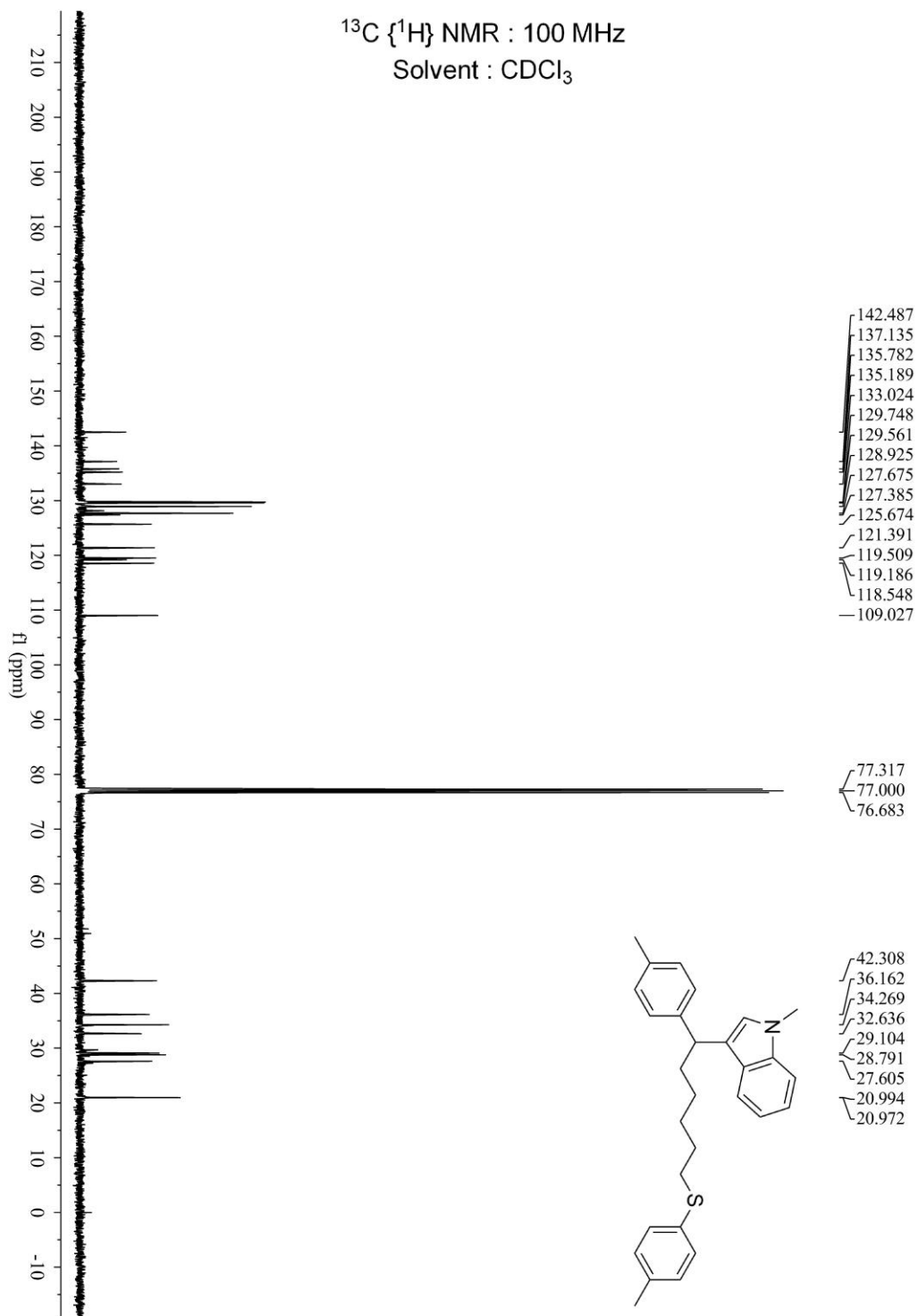
1-Methyl-3-(1-(*p*-tolyl)-6-(*p*-tolylthio)hexyl)-1*H*-indole (4daa)

¹H NMR : 400 MHz

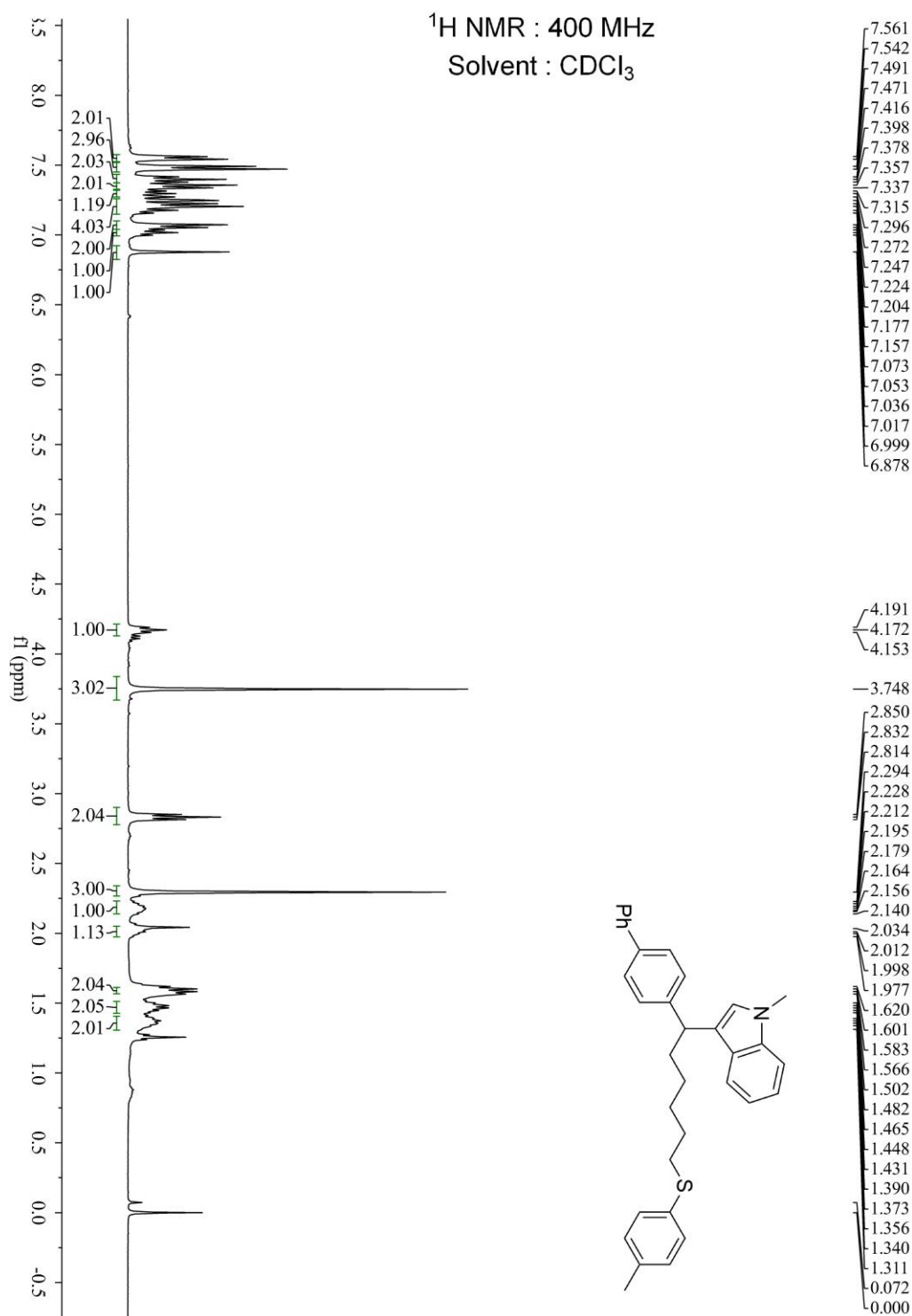
Solvent : CDCl₃



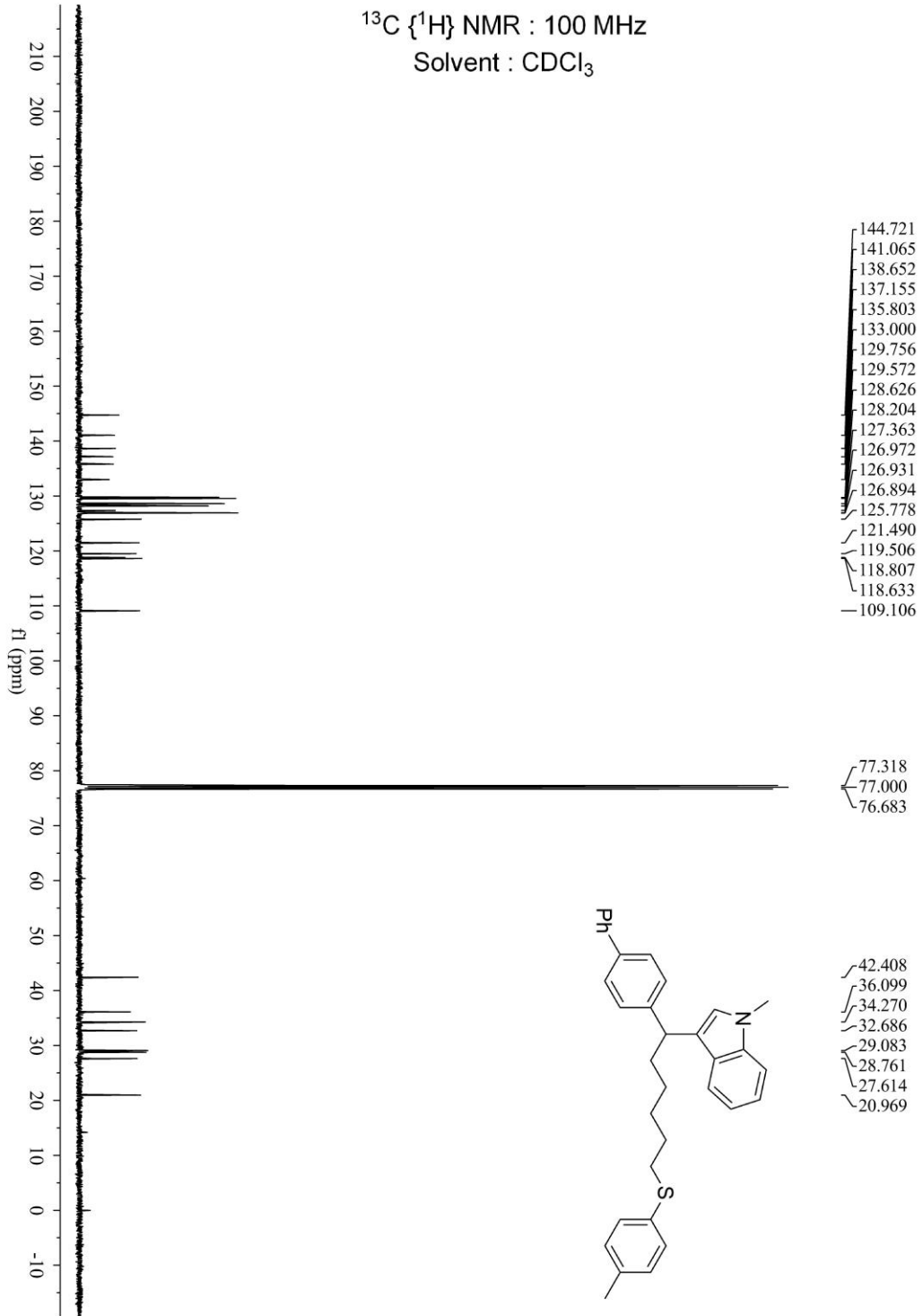
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



3-(1-([1,1'-Biphenyl]-4-yl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4ea)



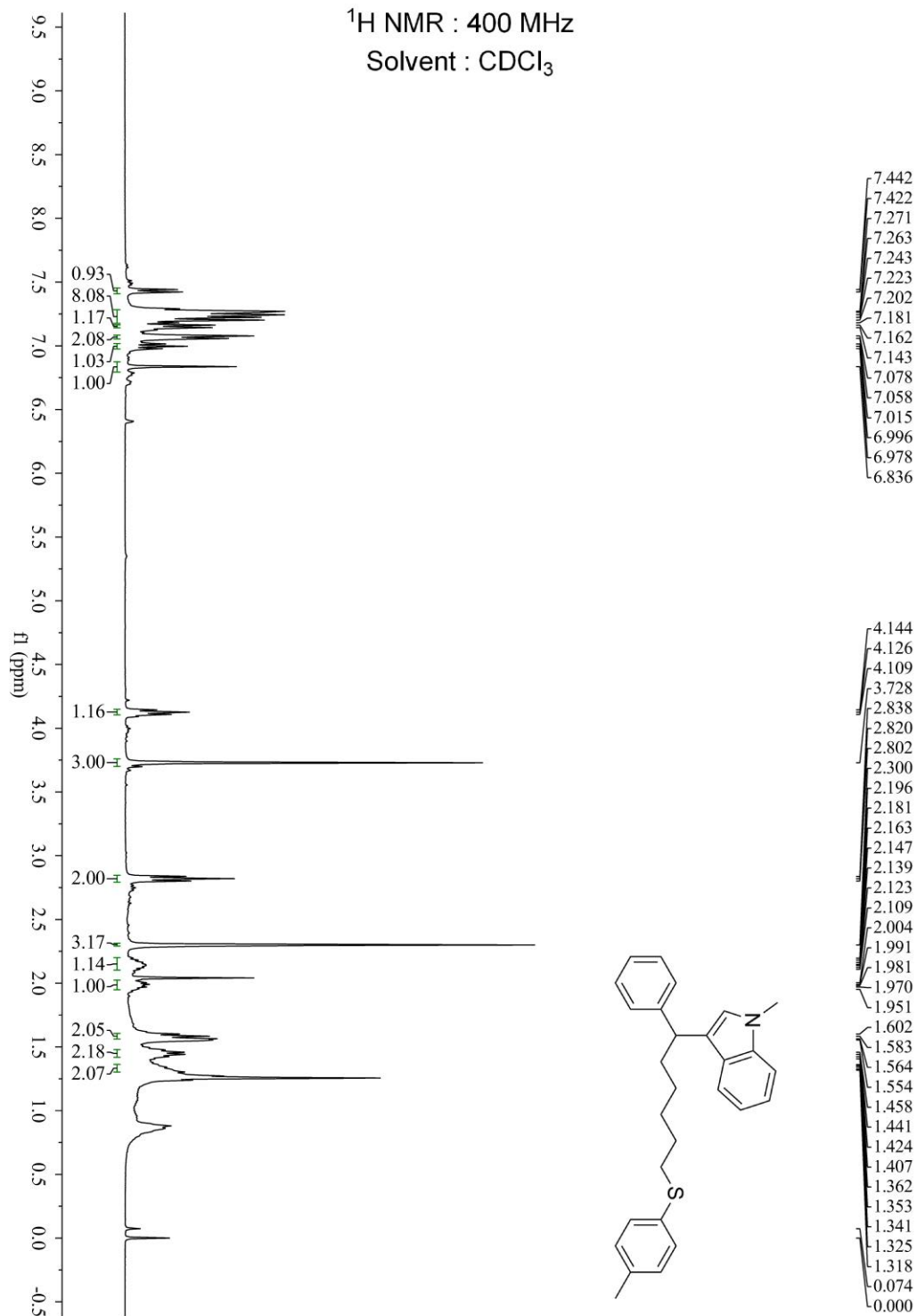
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



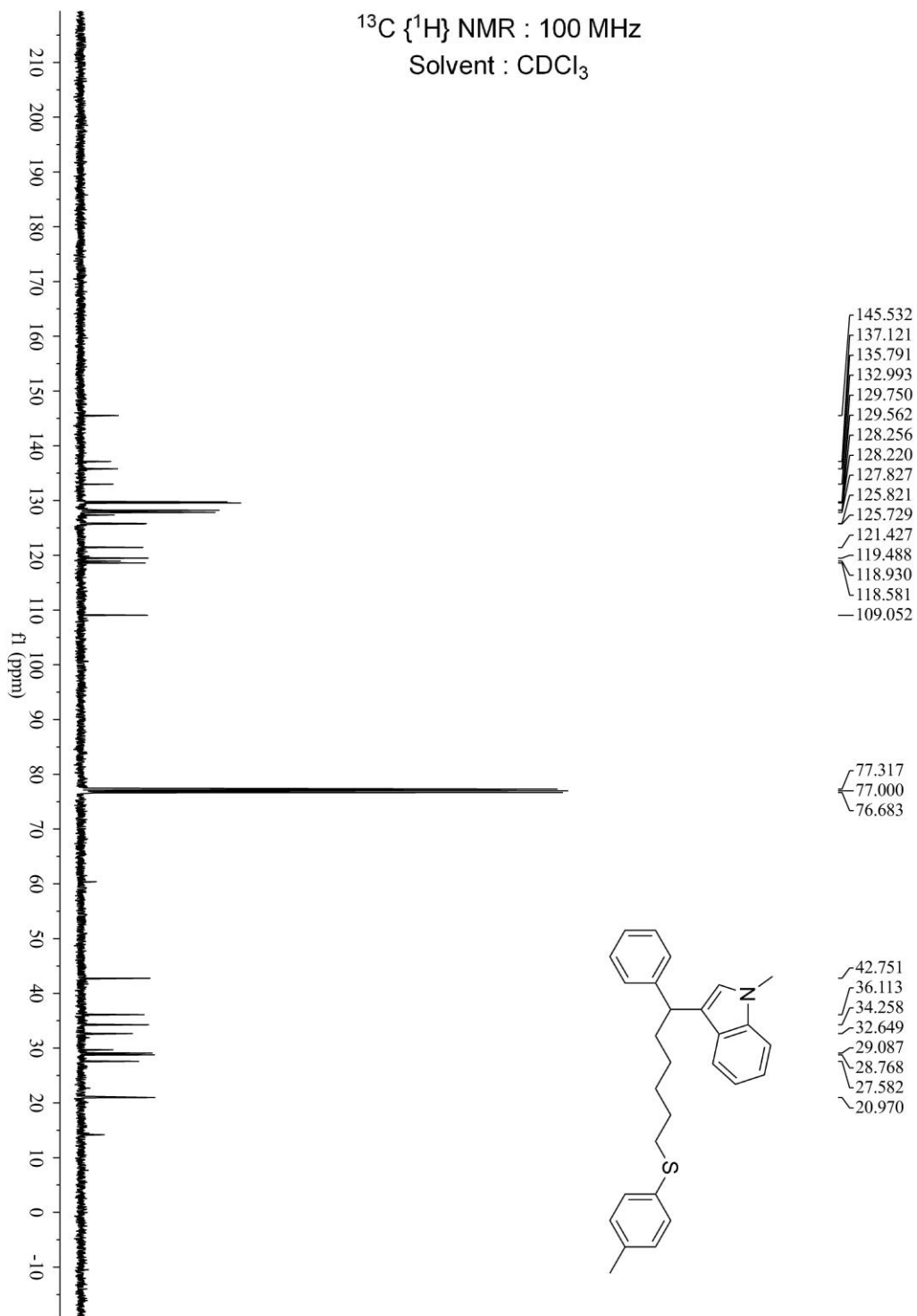
1-Methyl-3-(1-phenyl-6-(*p*-tolylthio)hexyl)-1*H*-indole (4faa)

¹H NMR : 400 MHz

Solvent : CDCl₃



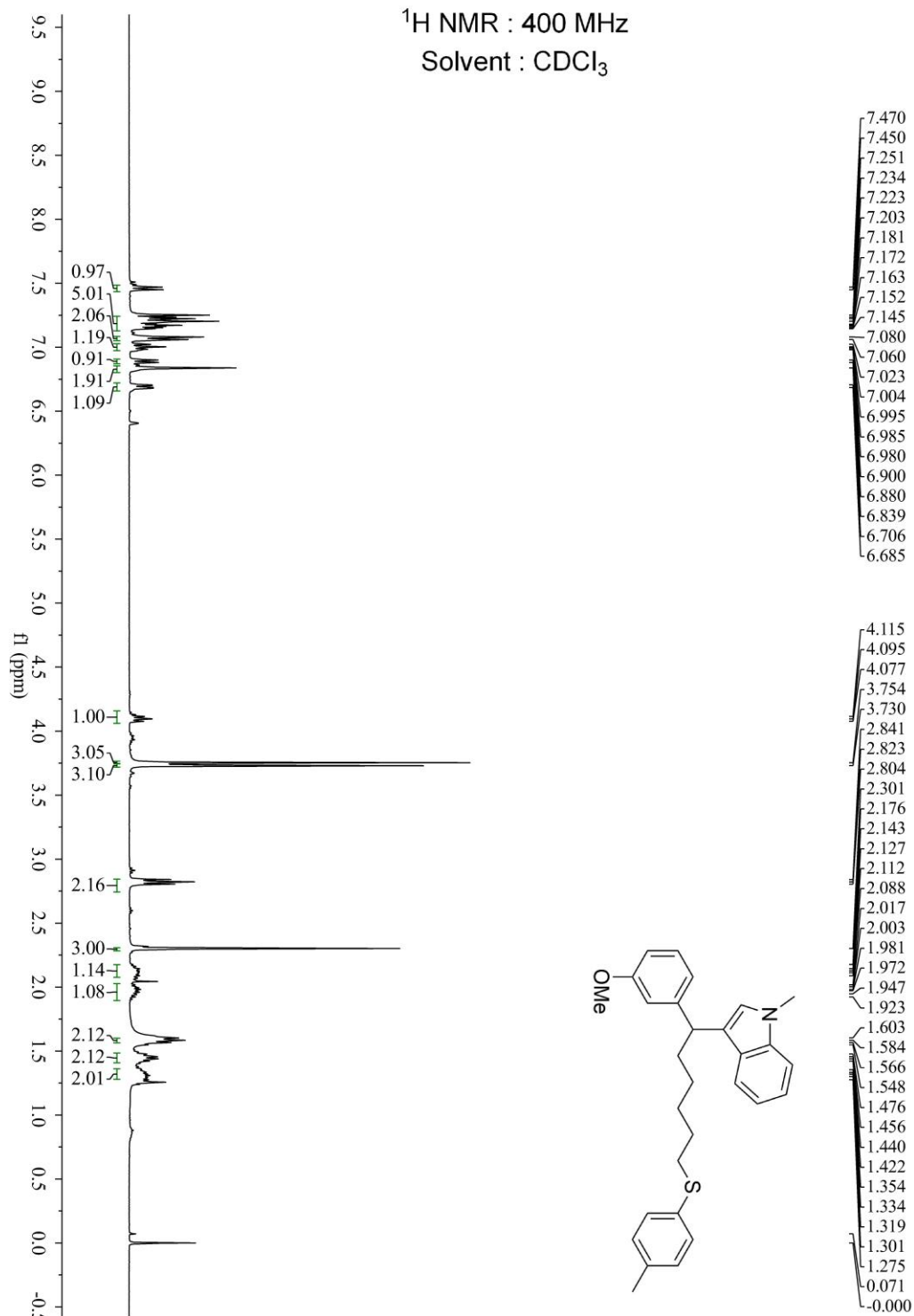
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



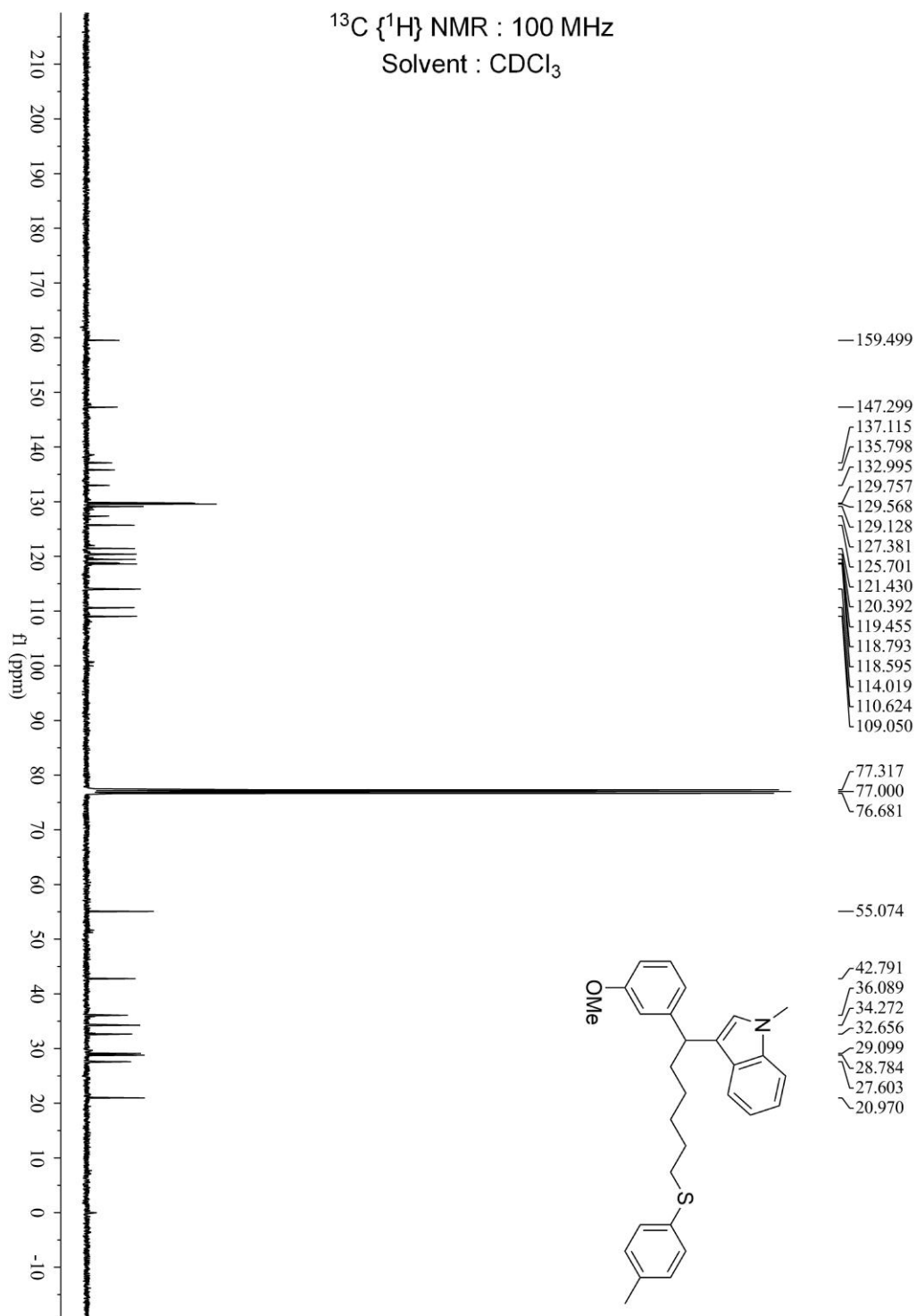
3-(1-(3-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4haa)

¹H NMR : 400 MHz

Solvent : CDCl₃



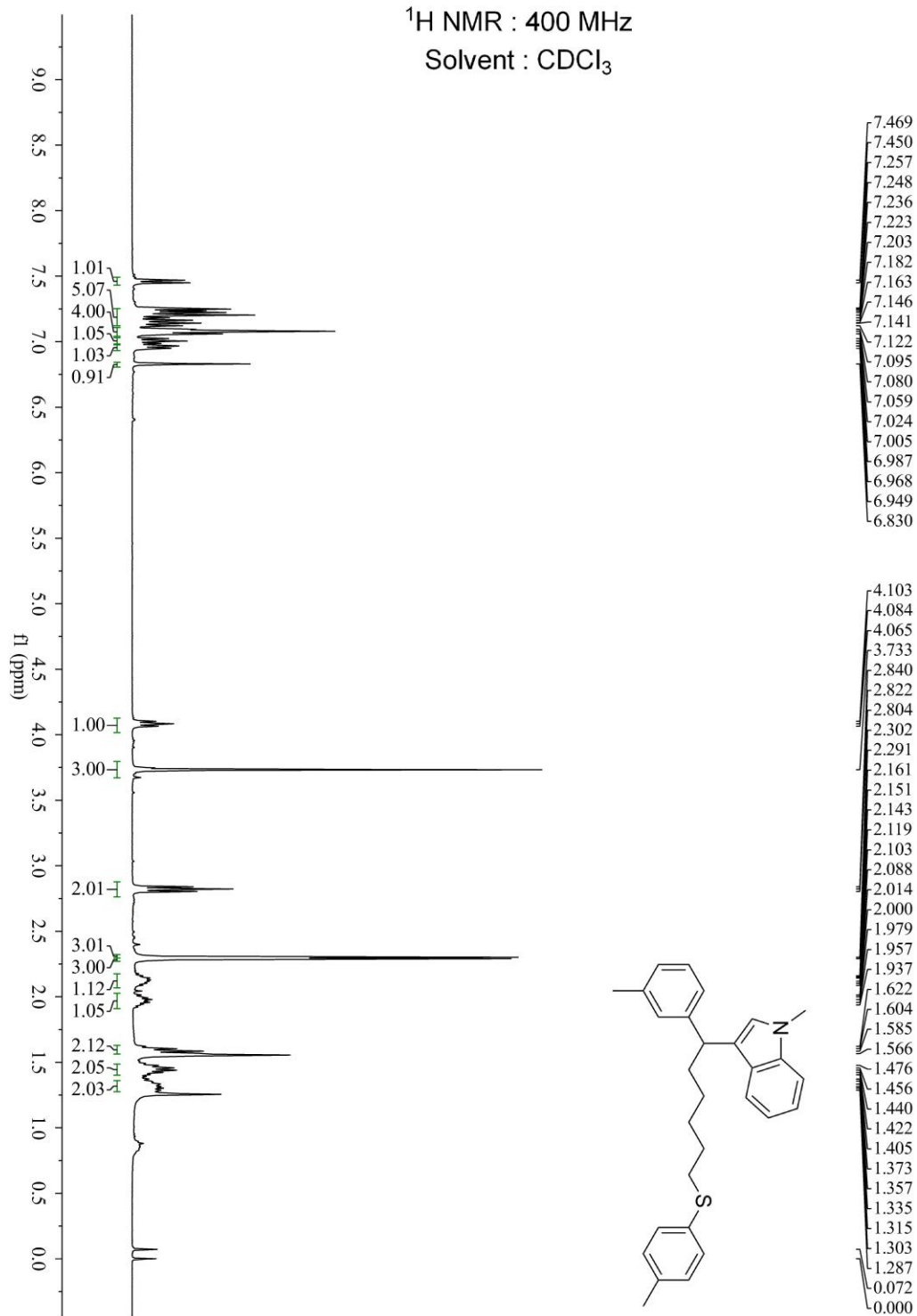
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



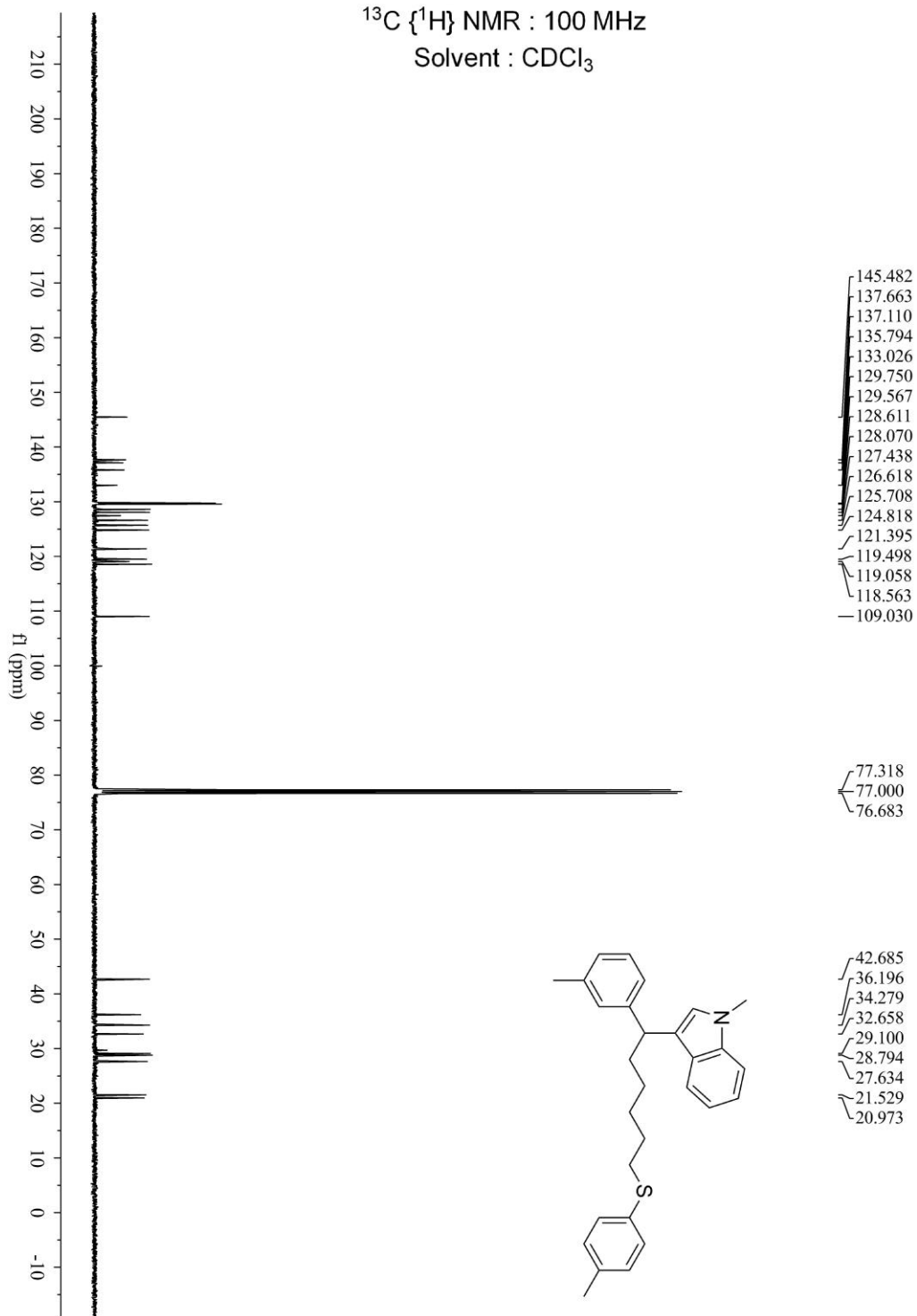
1-Methyl-3-(1-(*m*-tolyl)-6-(*p*-tolylthio)hexyl)-1*H*-indole (4iaa)

^1H NMR : 400 MHz

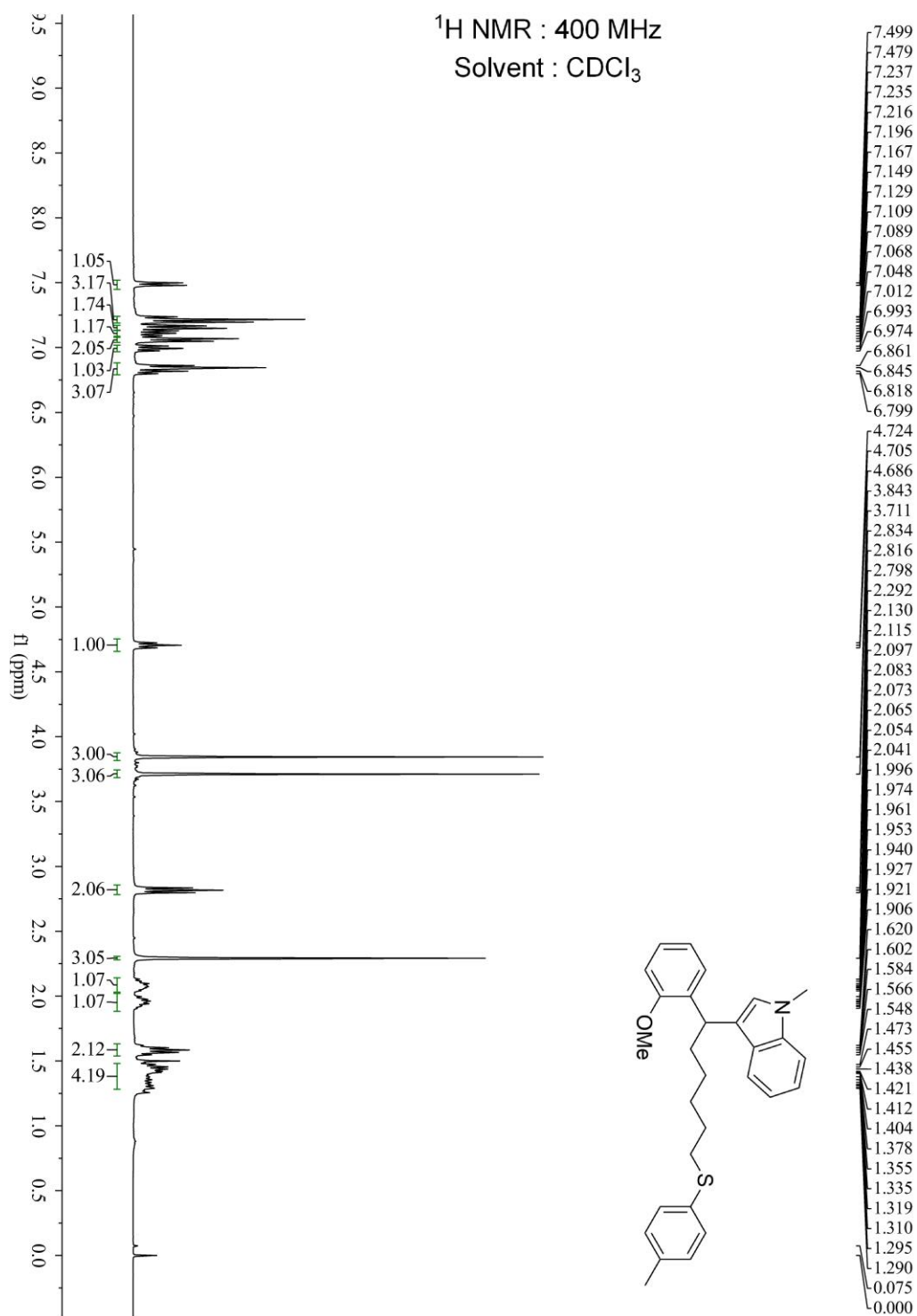
Solvent : CDCl_3



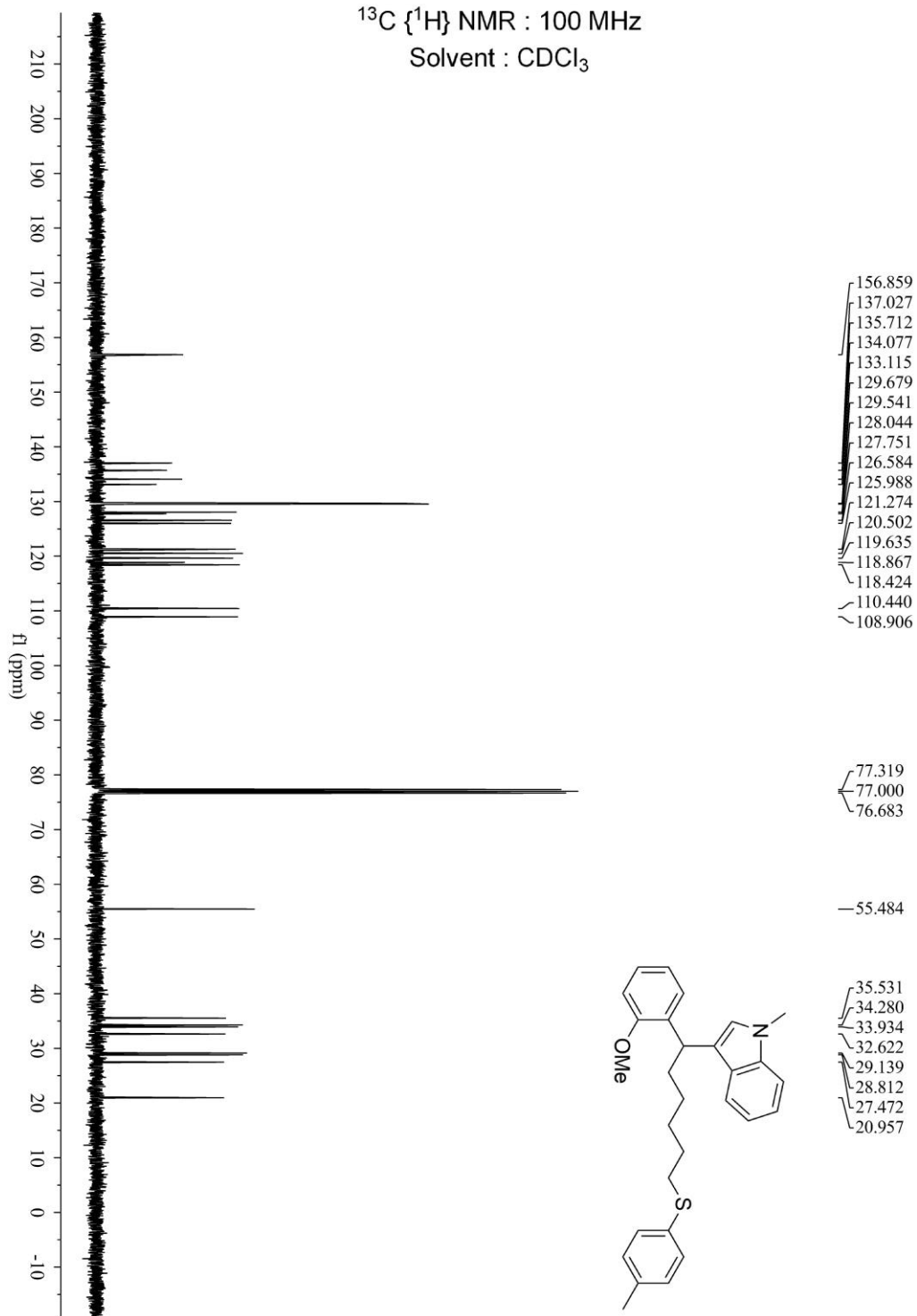
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



3-(1-(2-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4jaa)



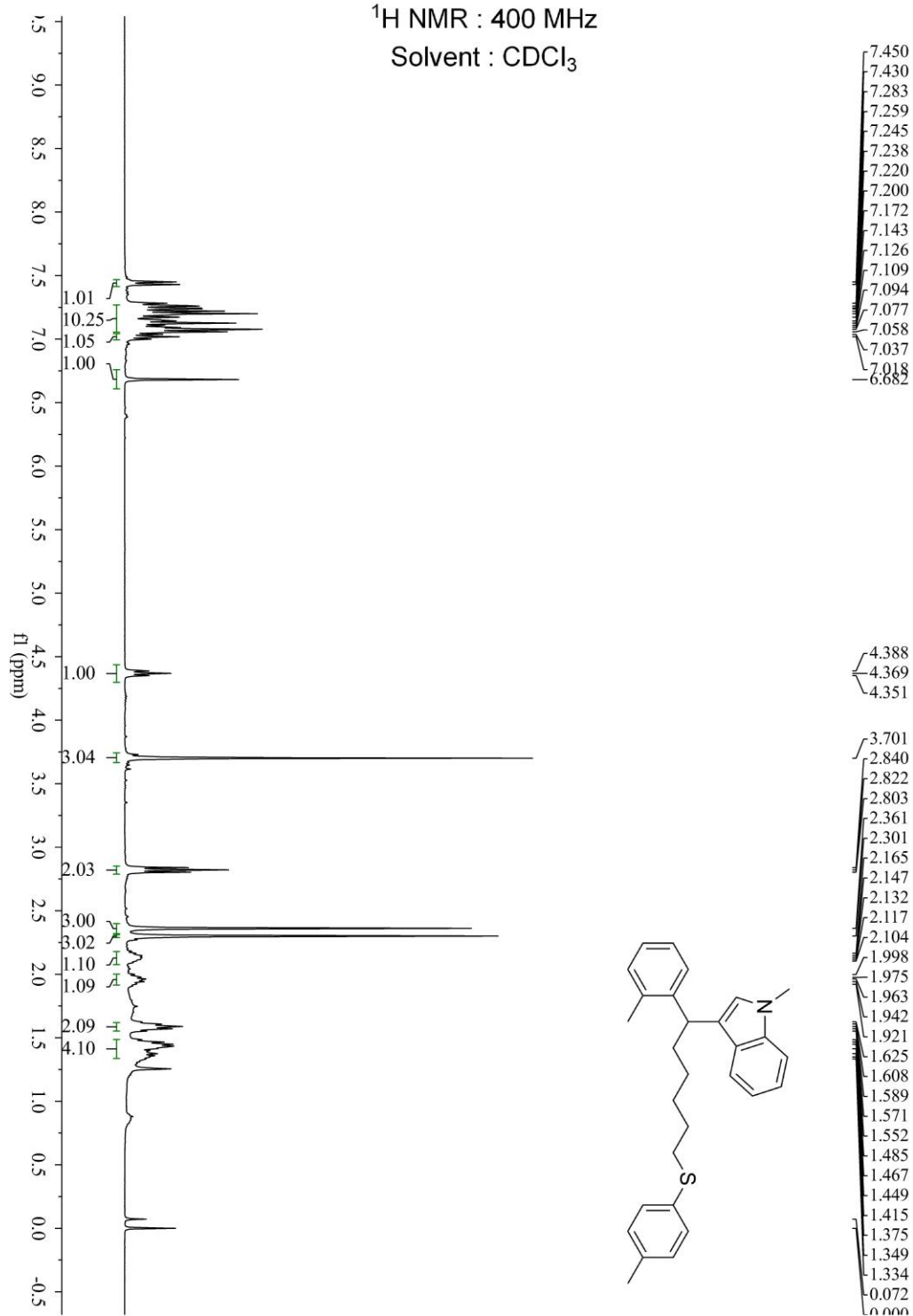
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



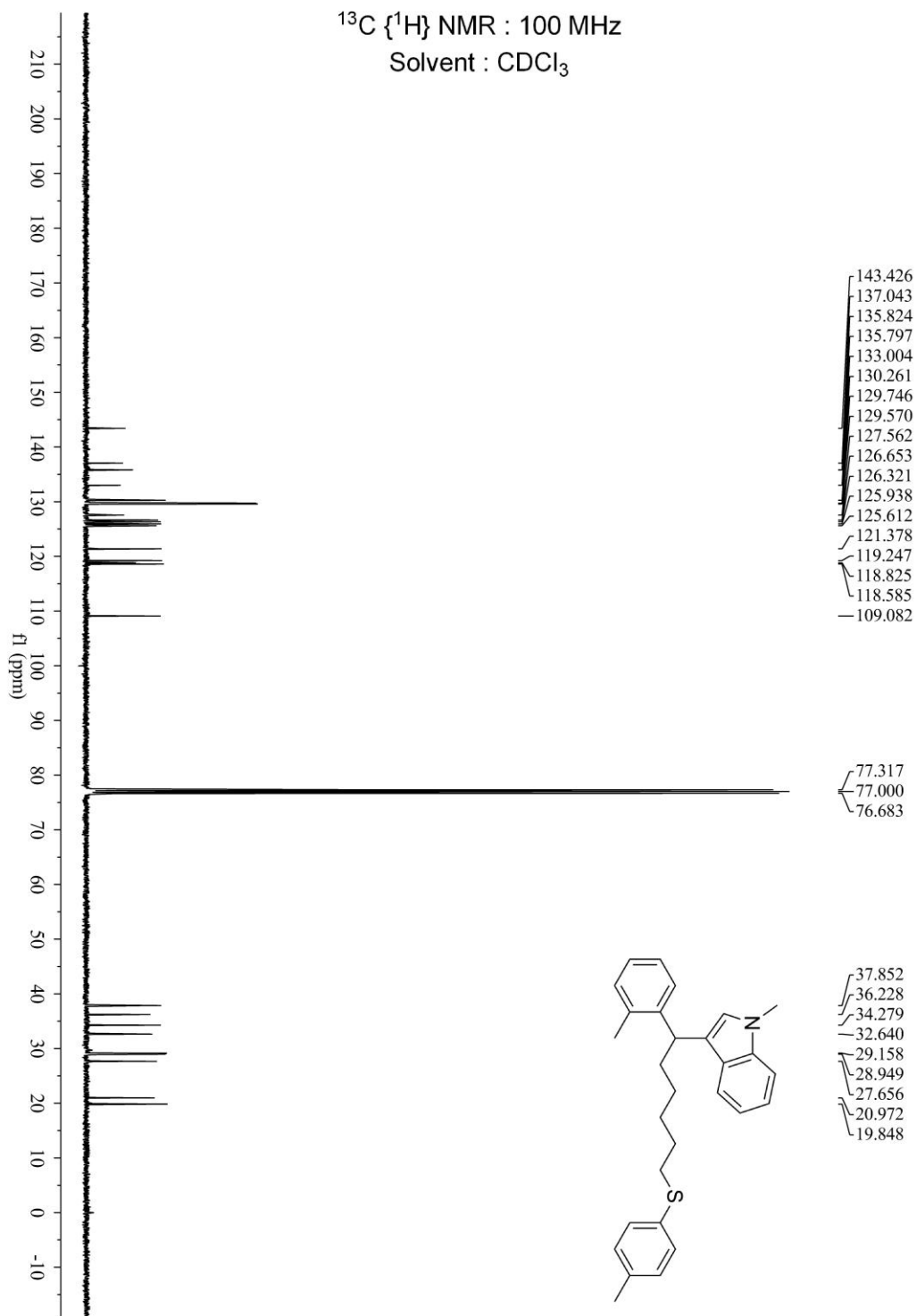
1-Methyl-3-(1-(*o*-tolyl)-6-(*p*-tolylthio)hexyl)-1*H*-indole (4kaa)

¹H NMR : 400 MHz

Solvent : CDCl₃



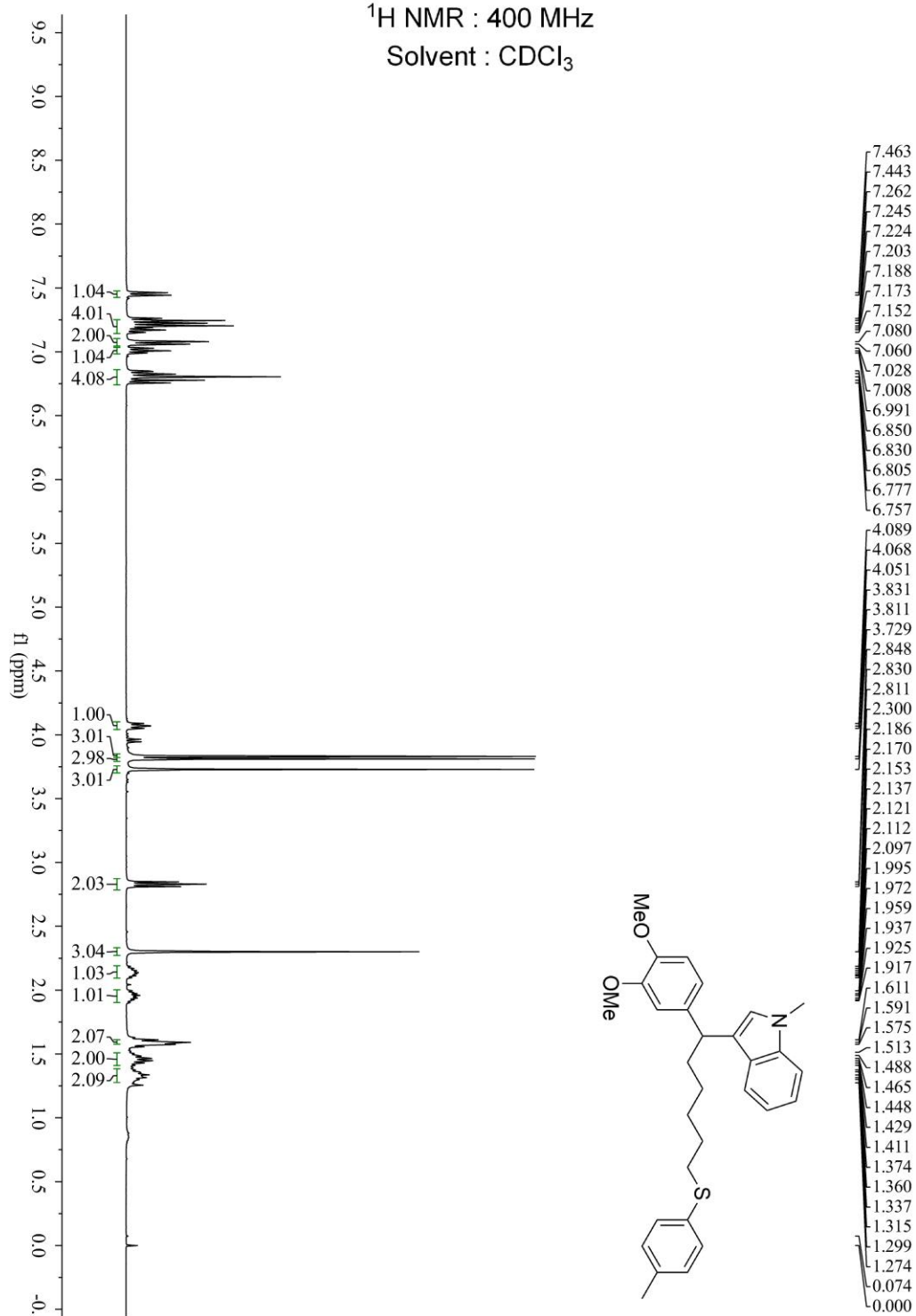
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



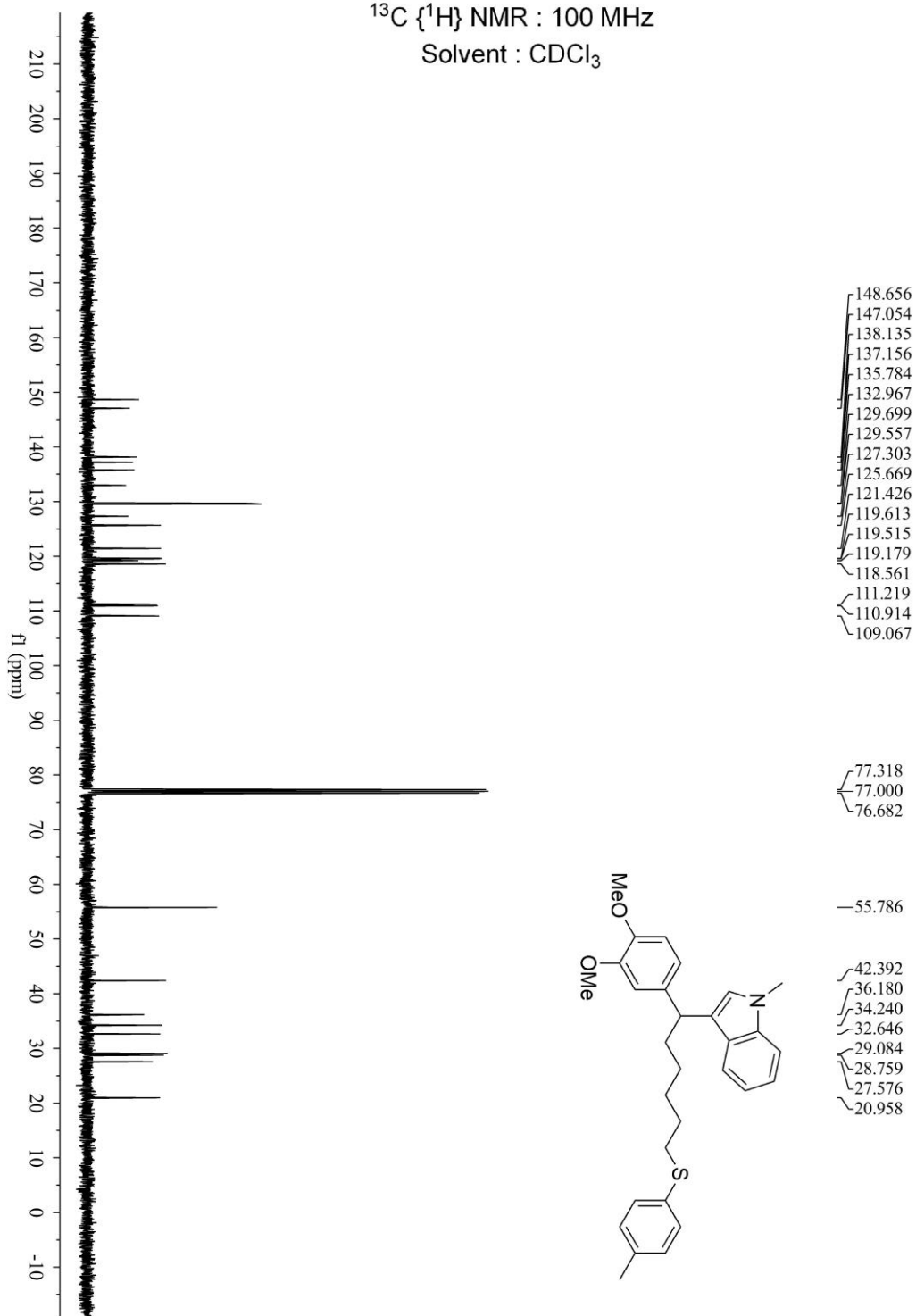
3-(1-(3,4-Dimethoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4laa)

¹H NMR : 400 MHz

Solvent : CDCl₃



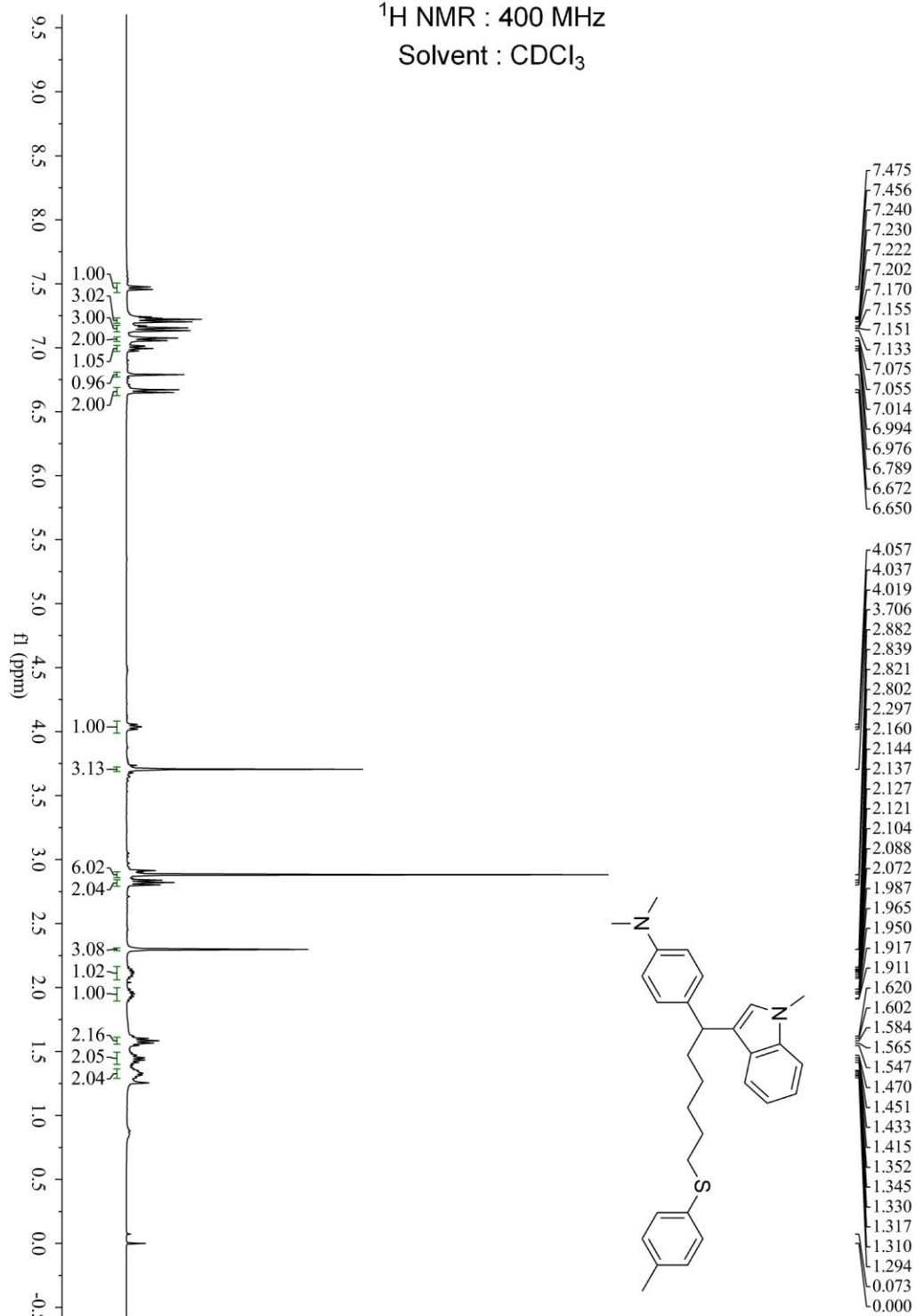
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



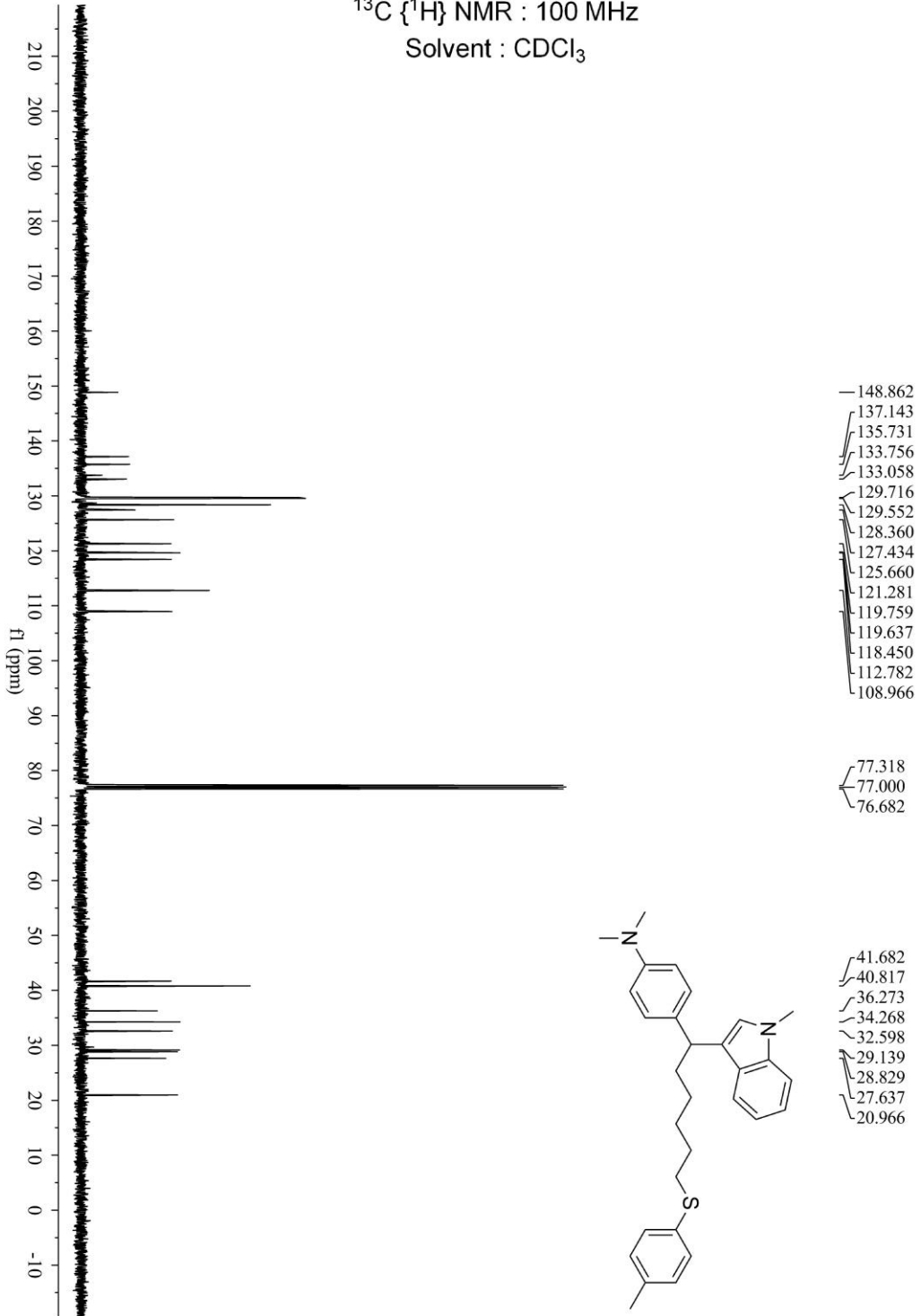
***N,N*-Dimethyl-4-(1-(1-methyl-1*H*-indol-3-yl)-6-(*p*-tolylthio)hexyl)aniline (4maa)**

¹H NMR : 400 MHz

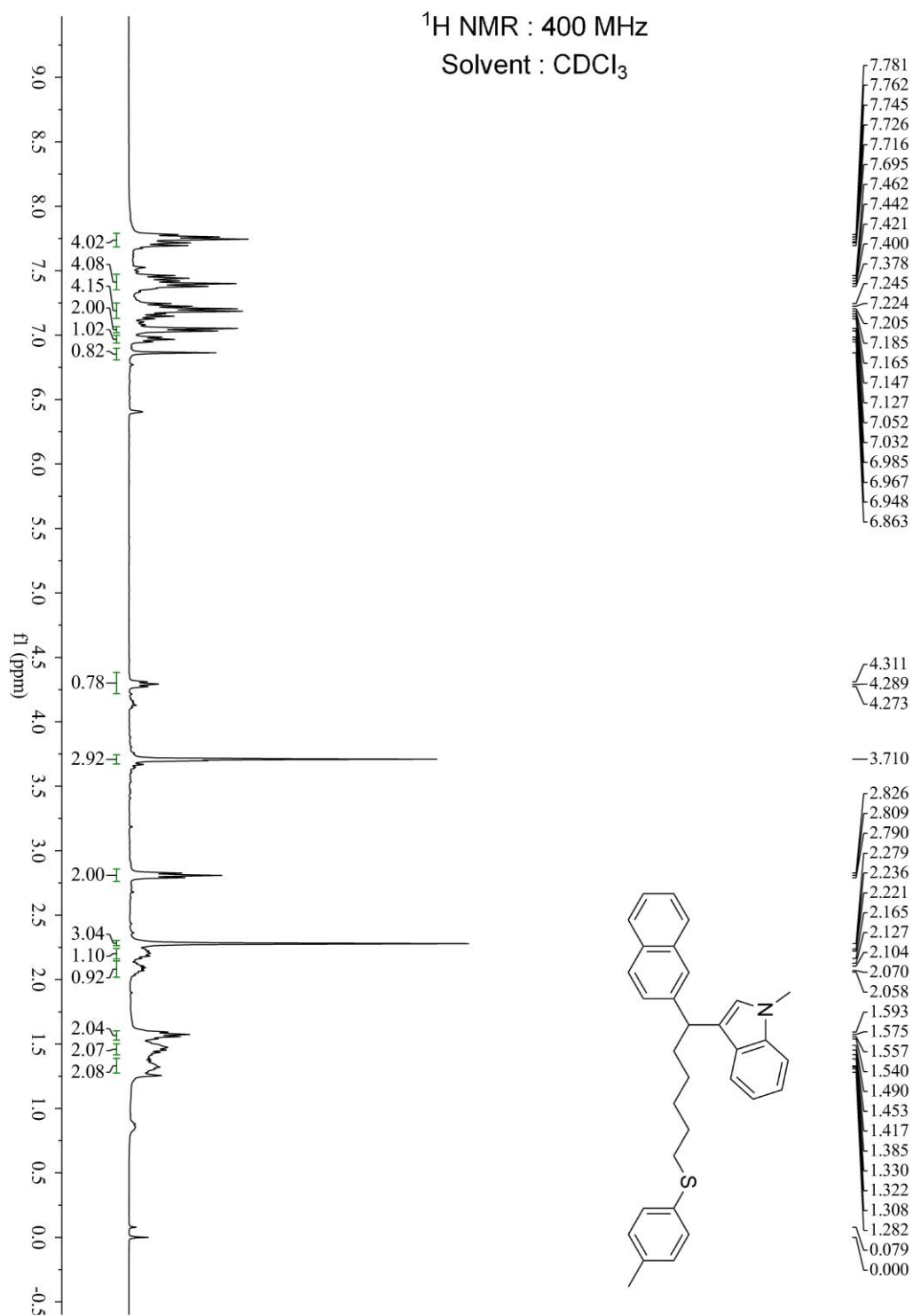
Solvent : CDCl₃



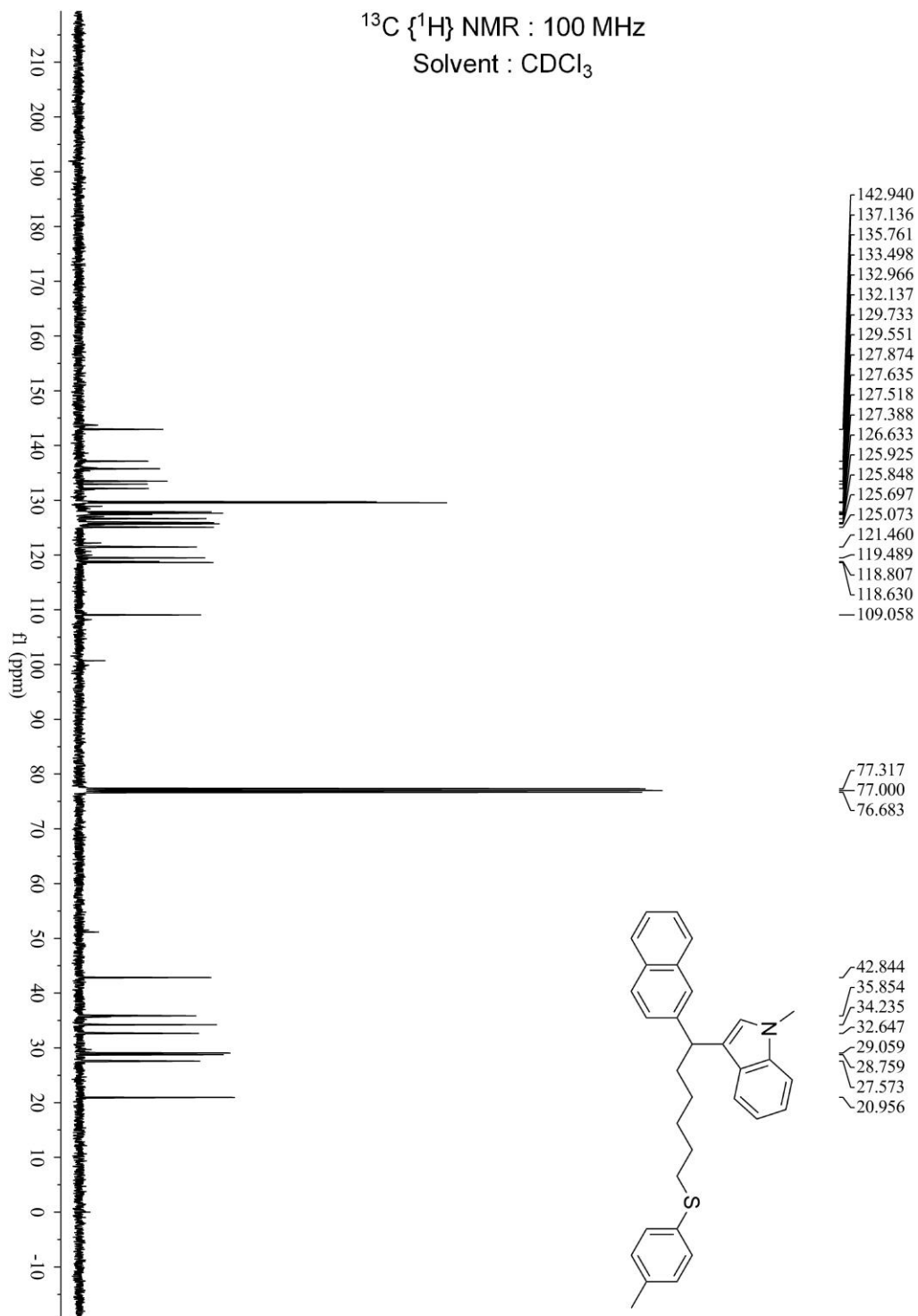
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



1-Methyl-3-(1-(naphthalen-2-yl)-6-(p-tolylthio)hexyl)-1H-indole (4naa)



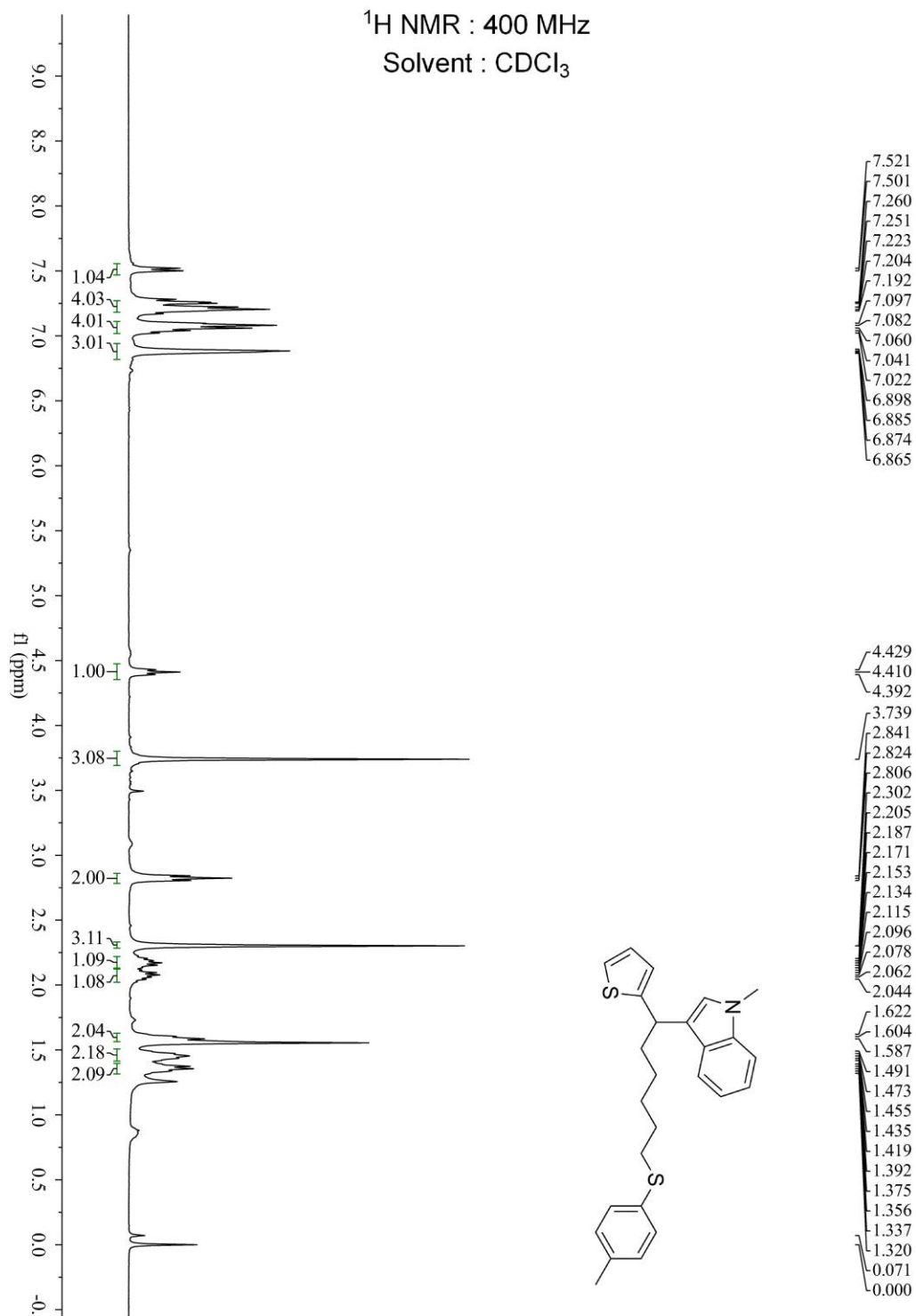
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



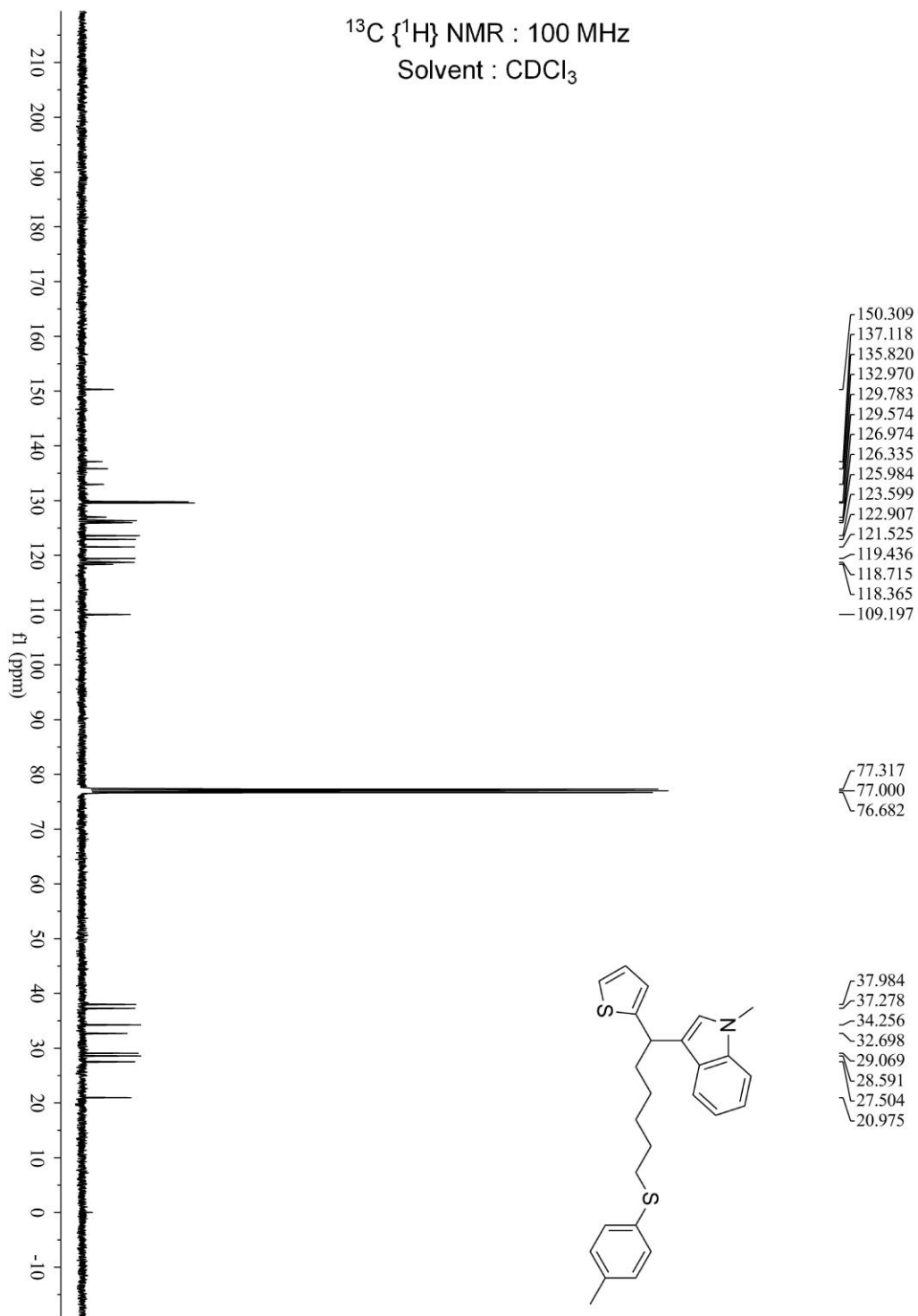
1-Methyl-3-(1-(thiophen-2-yl)-6-(*p*-tolylthio)hexyl)-1*H*-indole (40aa)

¹H NMR : 400 MHz

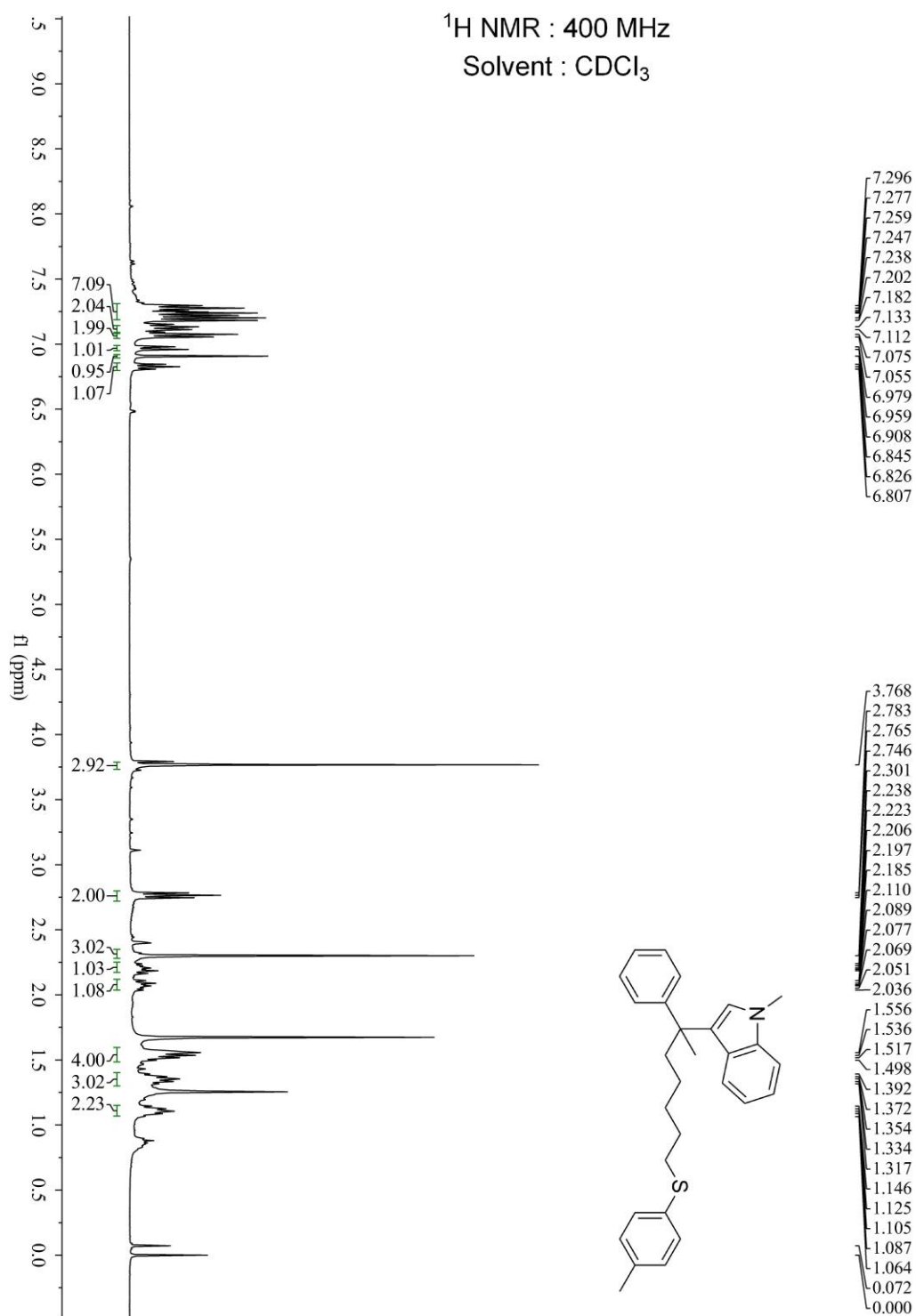
Solvent : CDCl₃



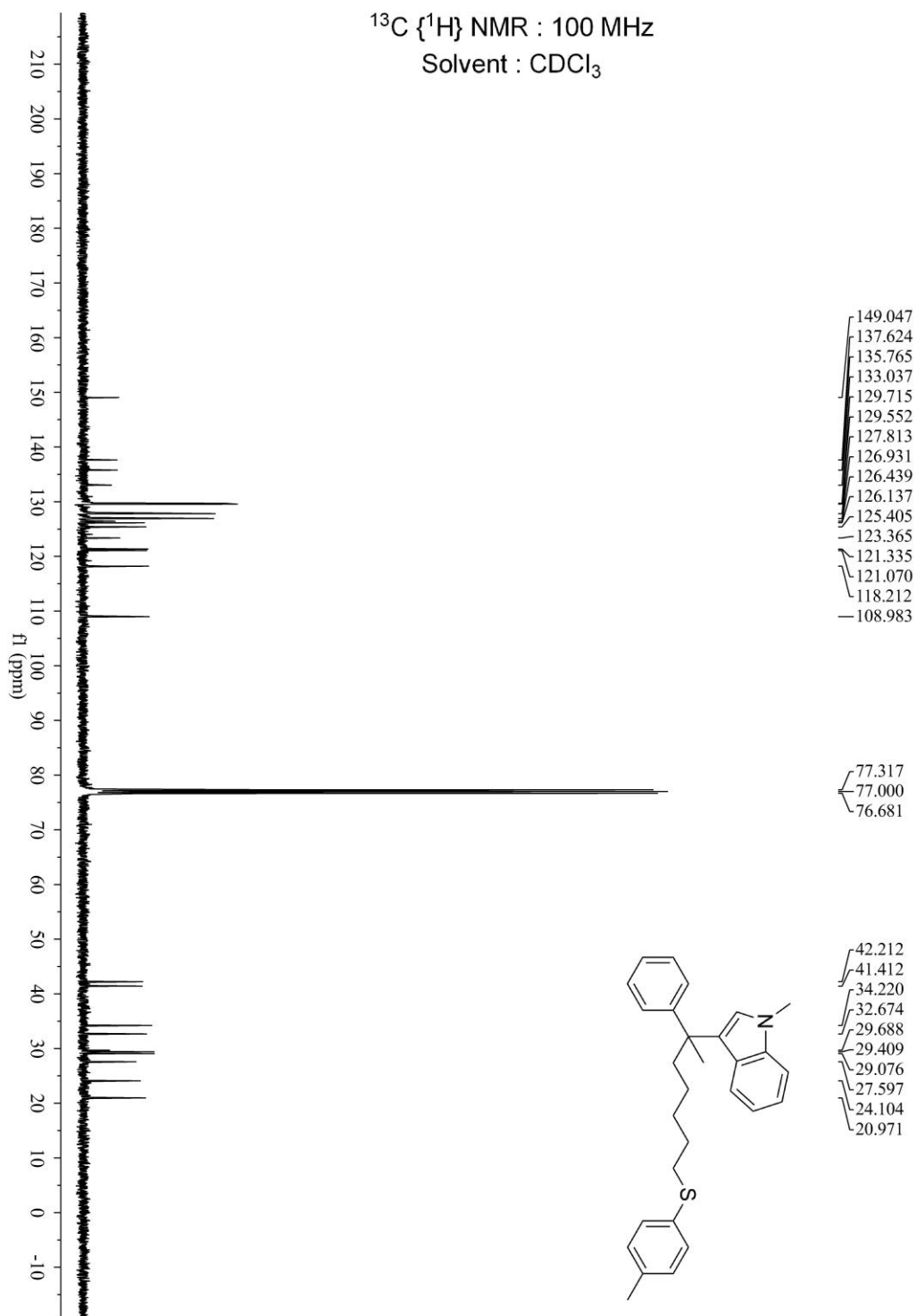
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



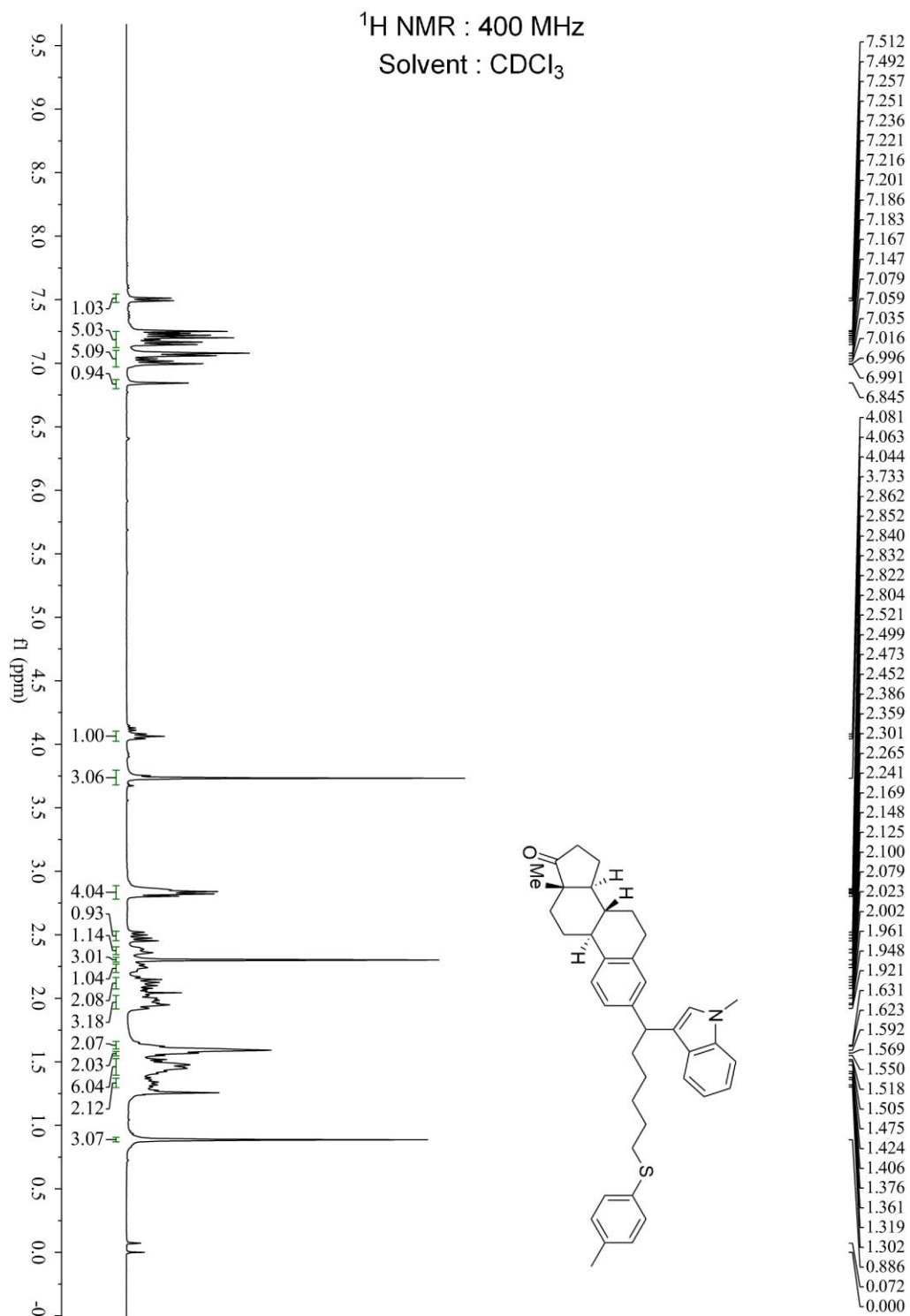
1-Methyl-3-(2-phenyl-7-(*p*-tolylthio)heptan-2-yl)-1*H*-indole (4paa)



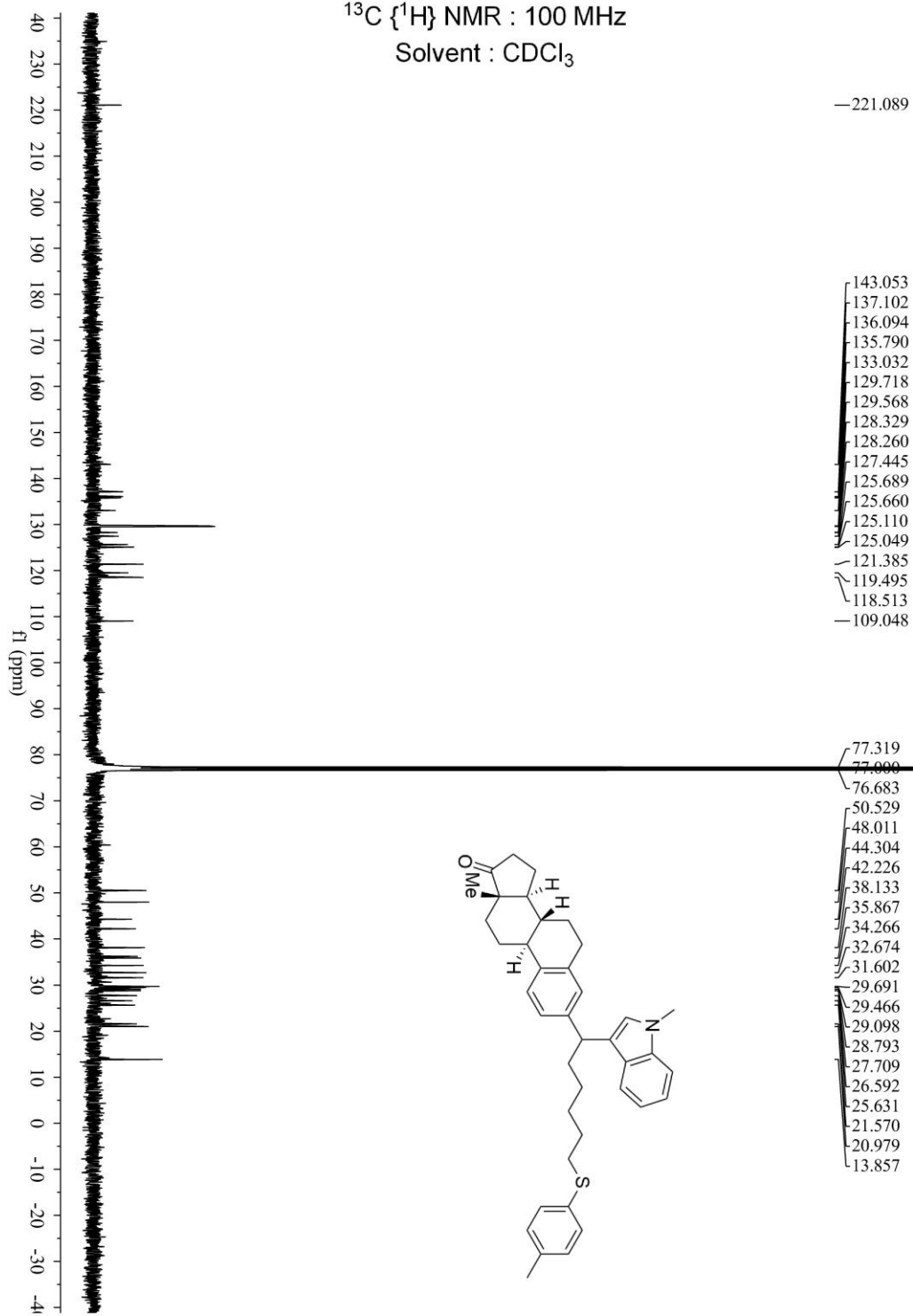
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(1-(1-methyl-1*H*-indol-3-yl)-6-(*p*-tolylthio)hexyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (4raa)



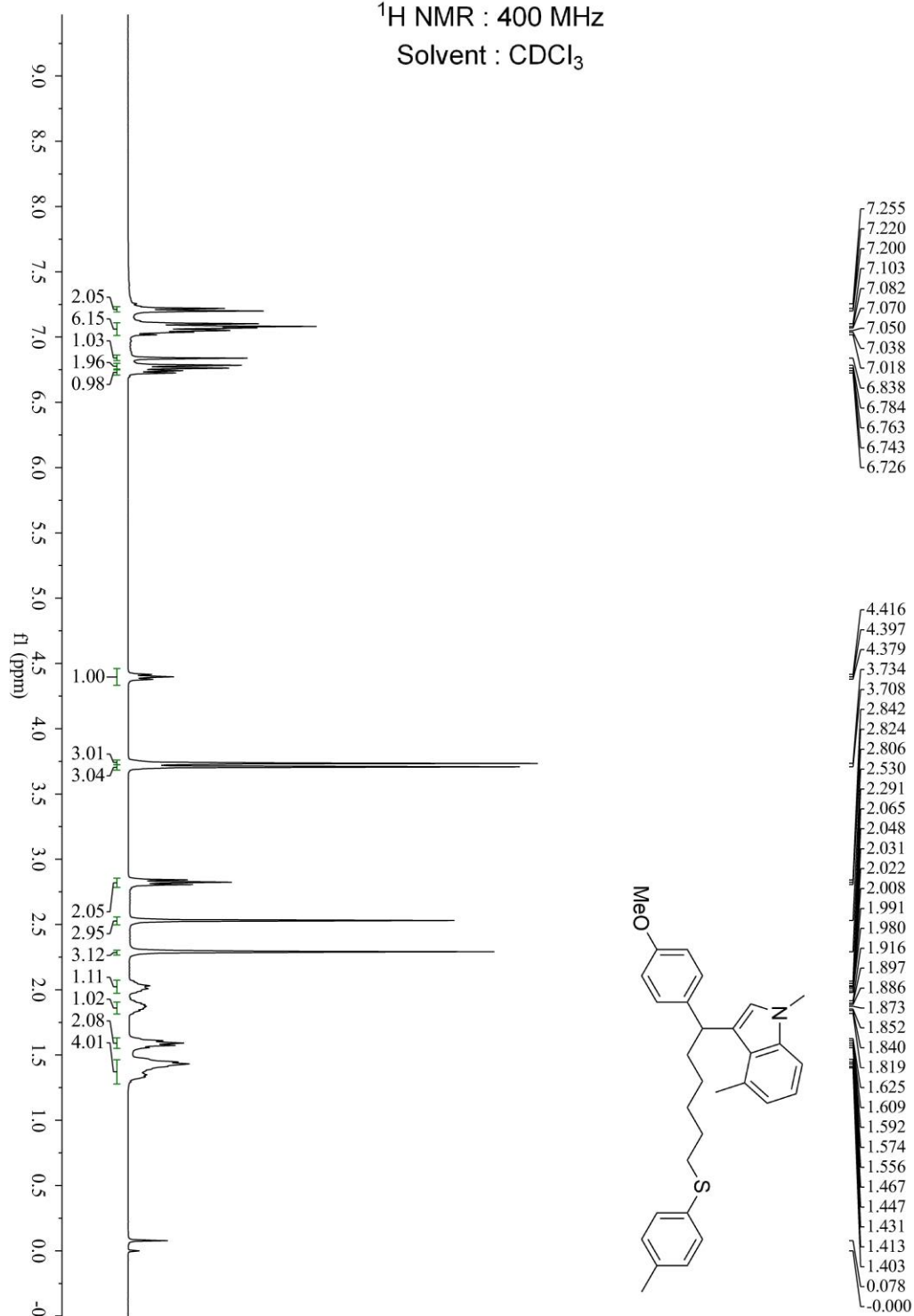
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



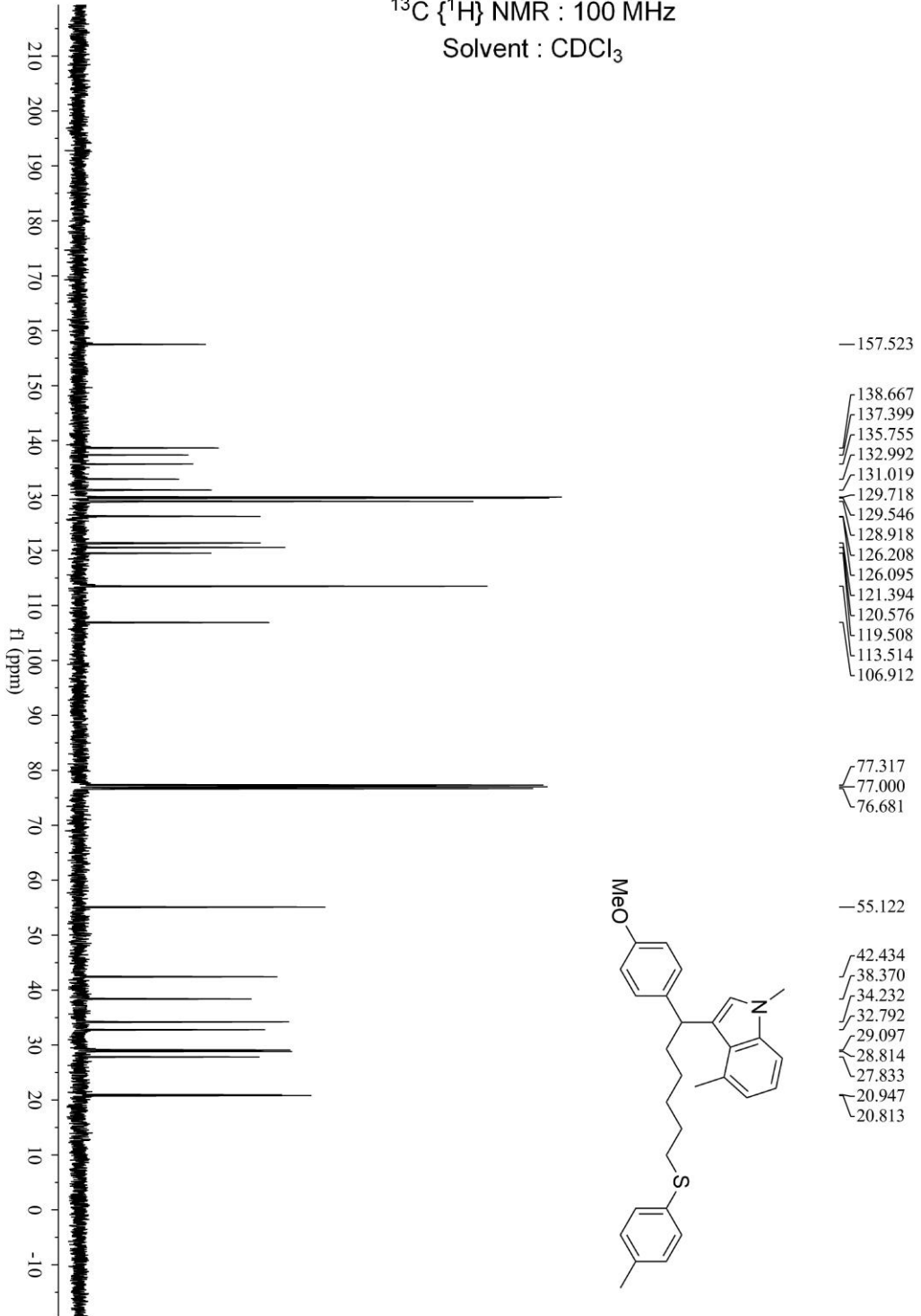
3-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1,4-dimethyl-1*H*-indole (4aab)

¹H NMR : 400 MHz

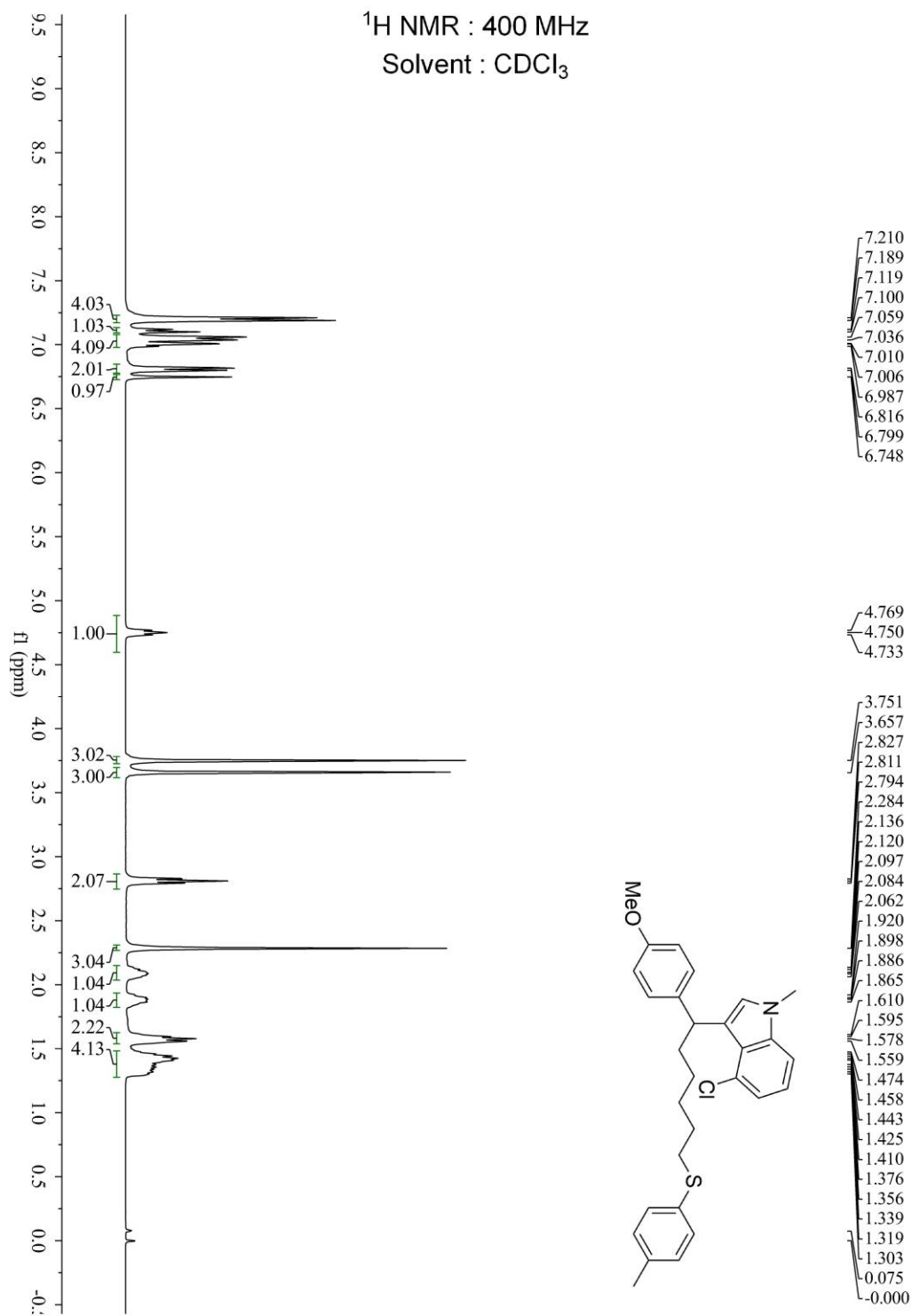
Solvent : CDCl₃



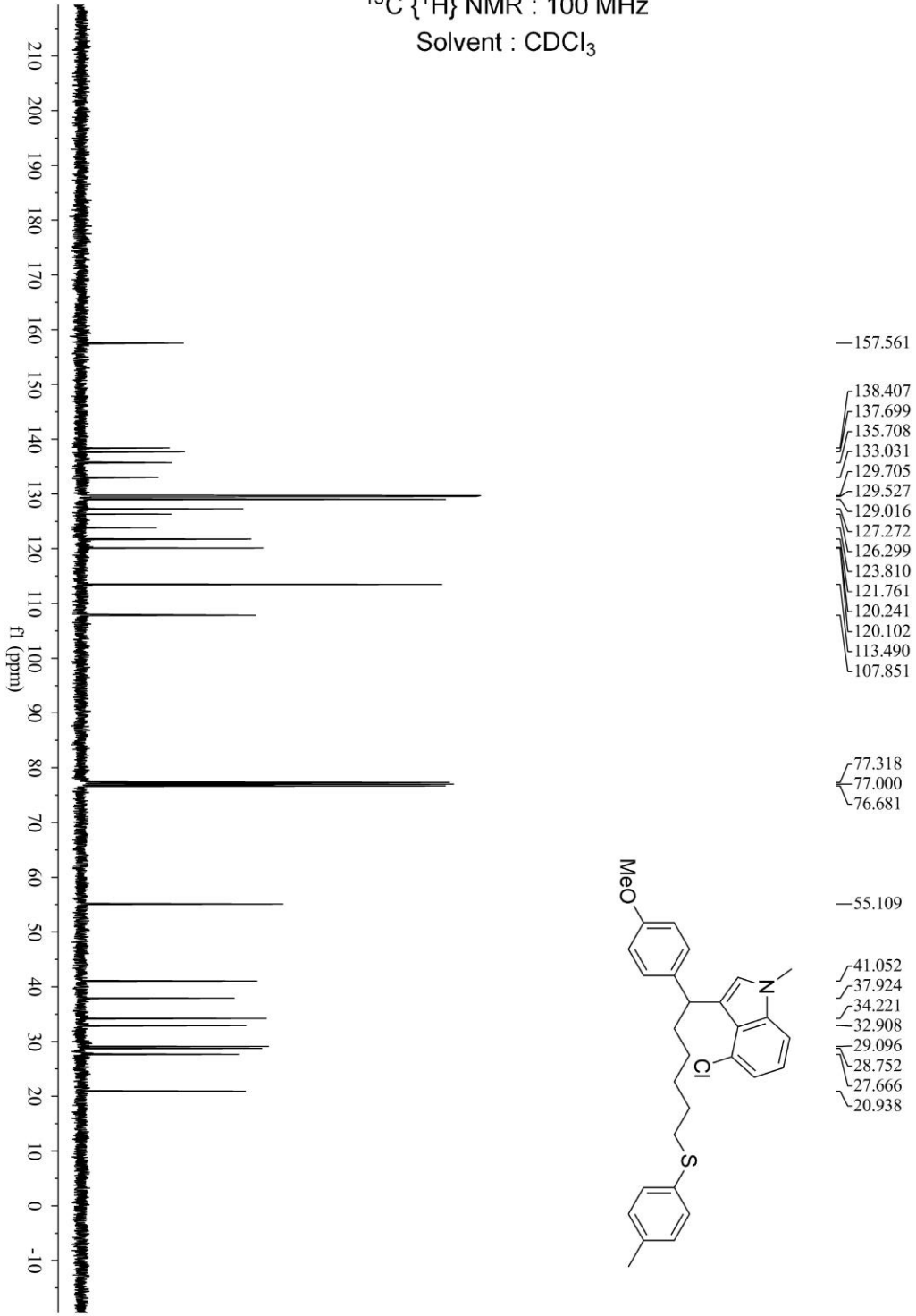
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



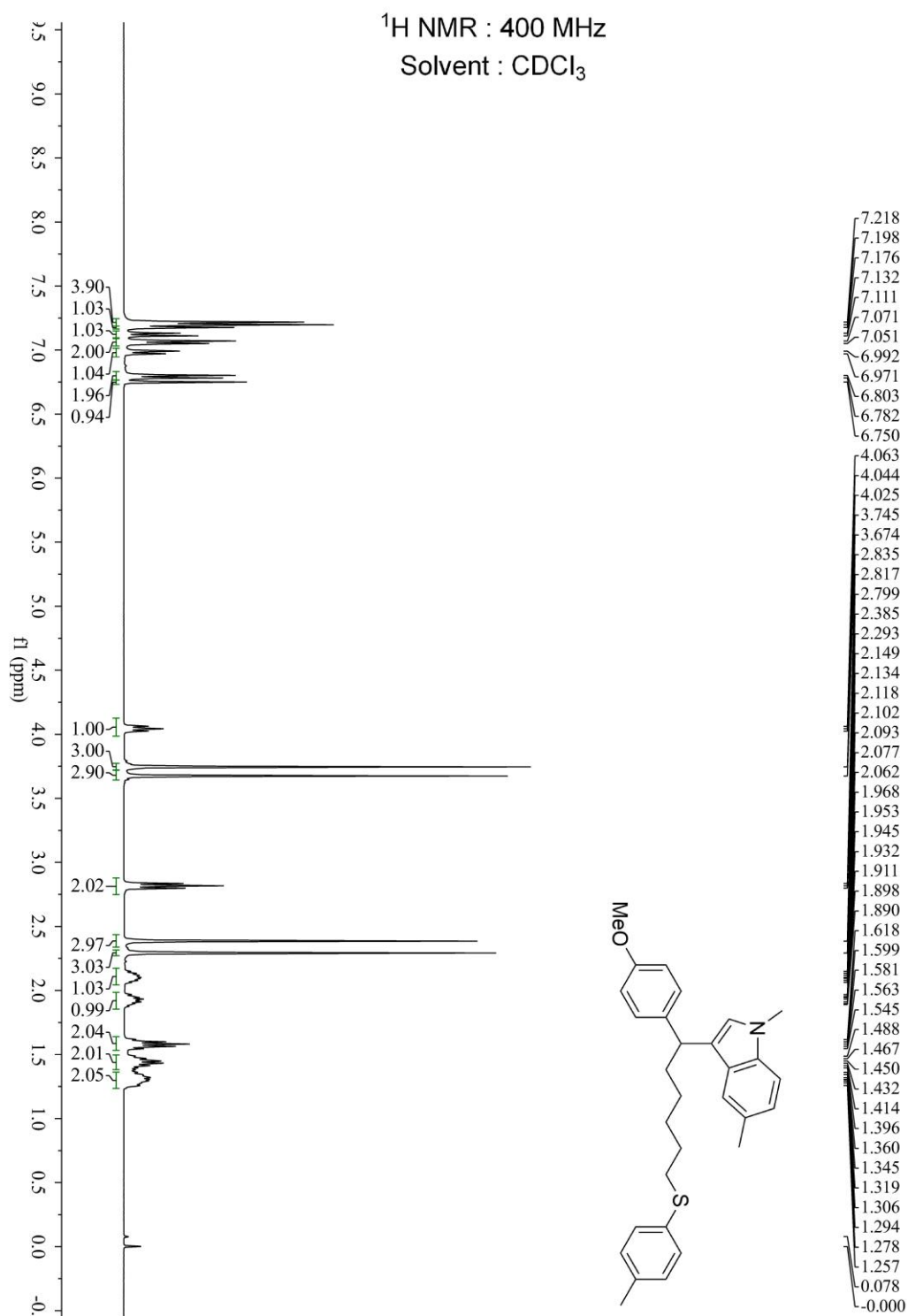
4-Chloro-3-(1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4aac)



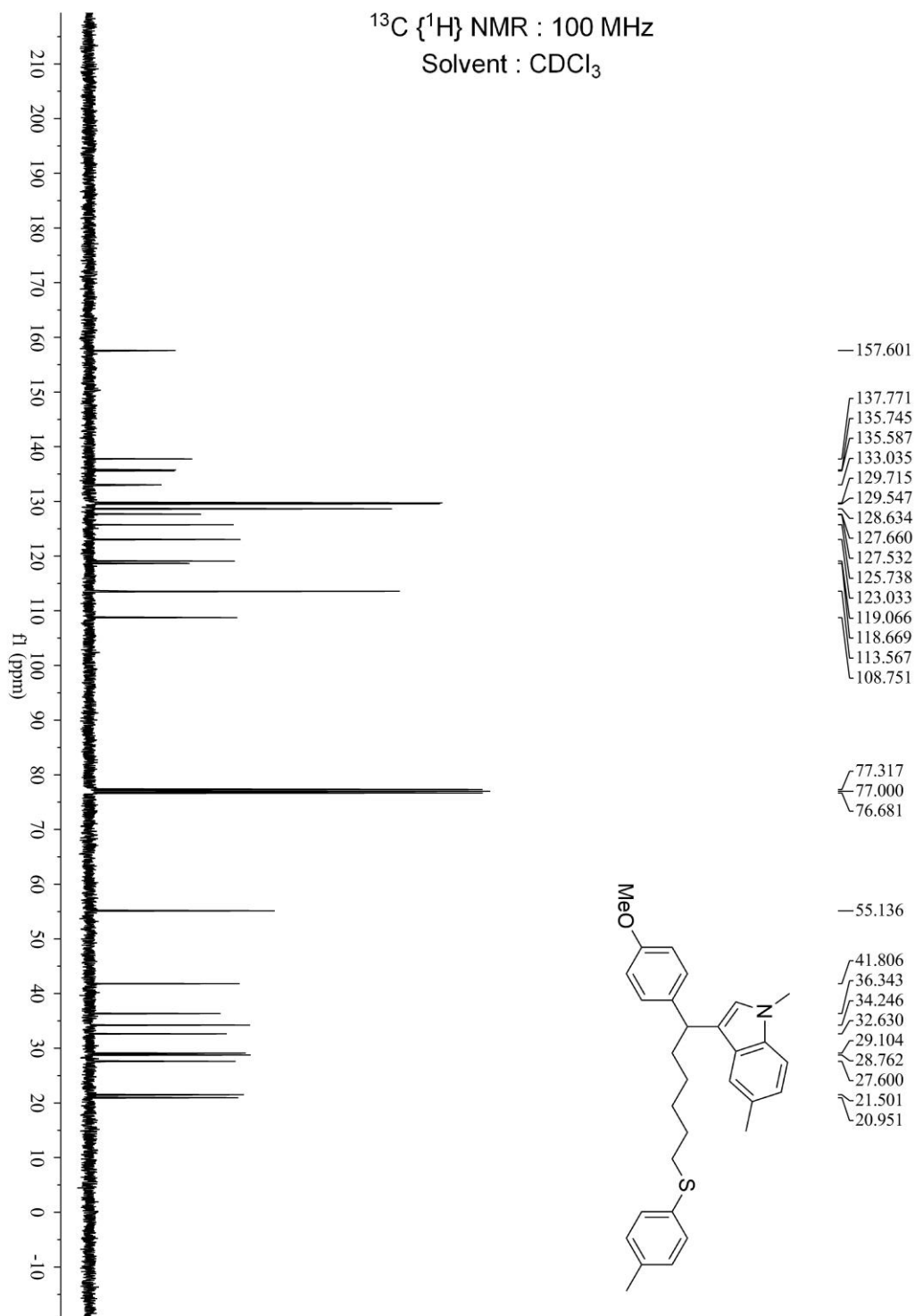
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



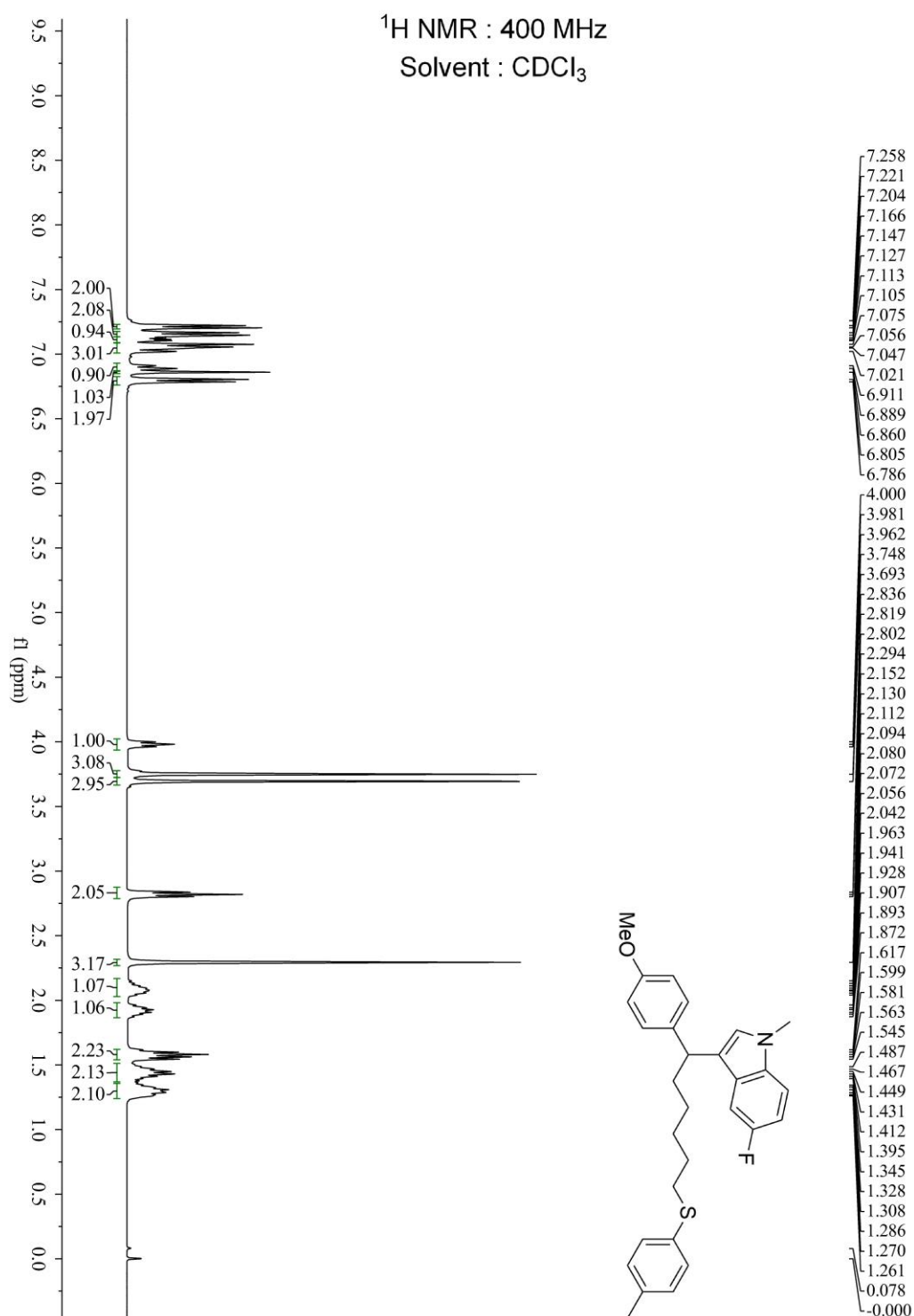
3-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1,5-dimethyl-1*H*-indole (4aad)



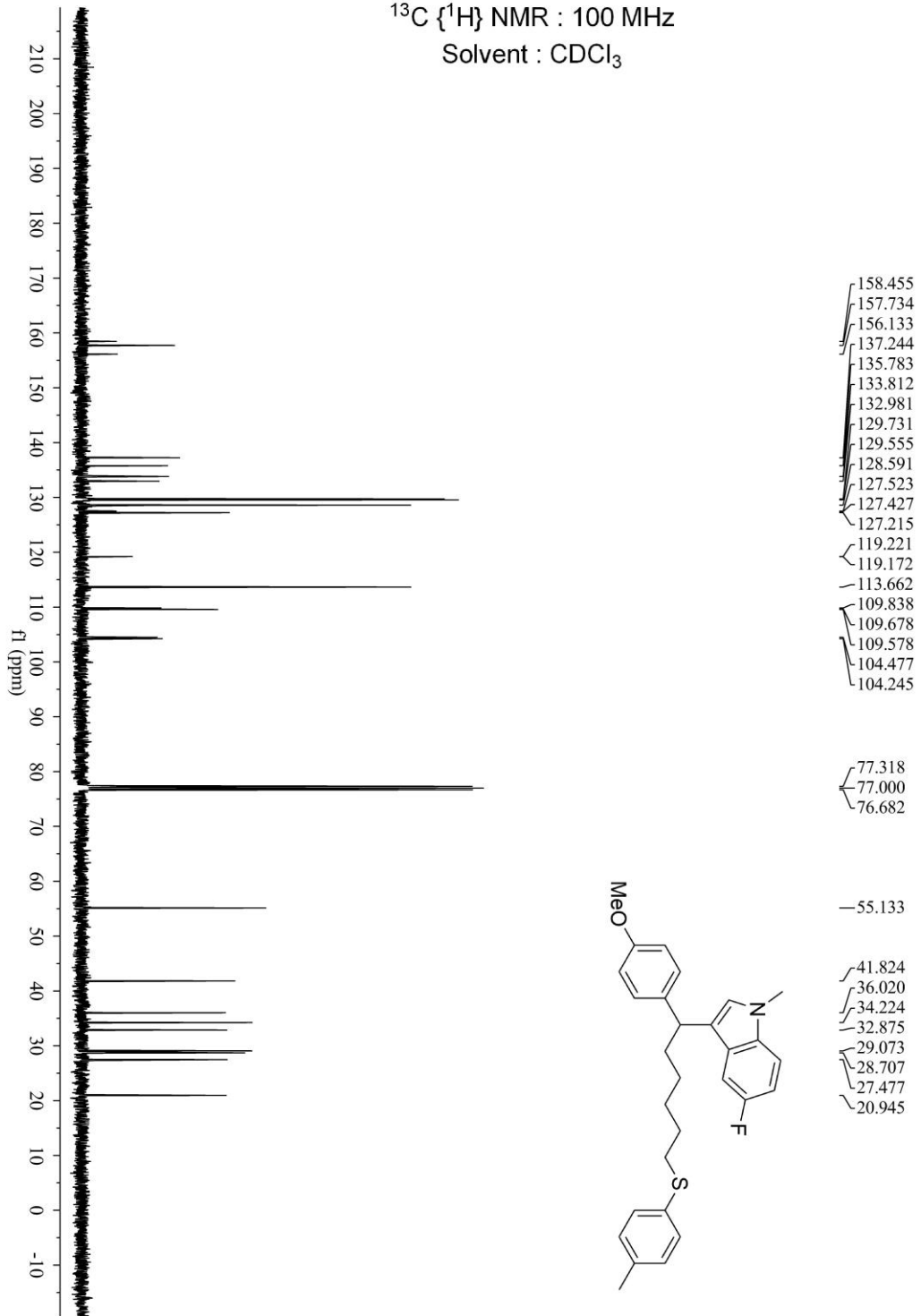
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



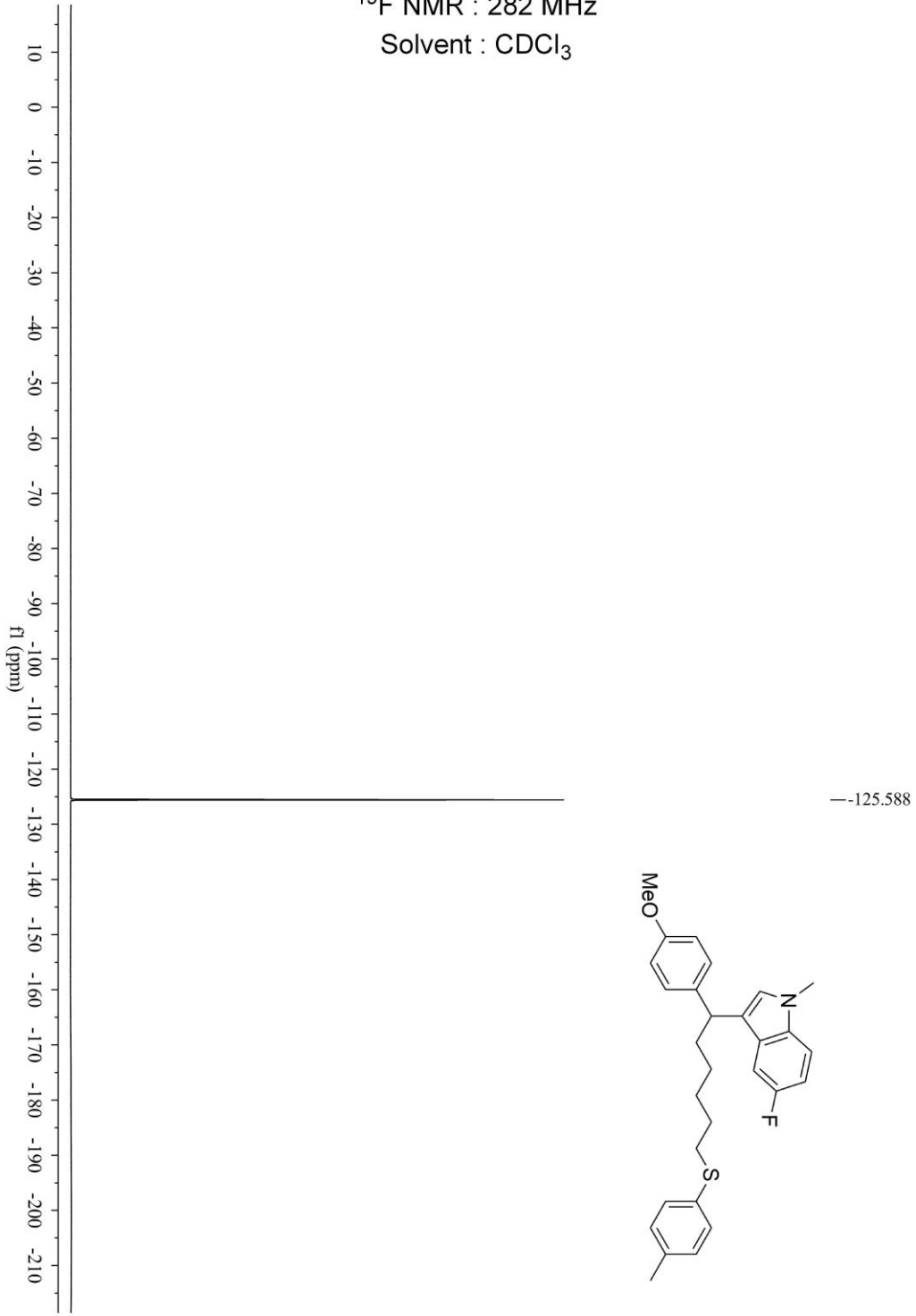
5-Fluoro-3-(1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4aae)



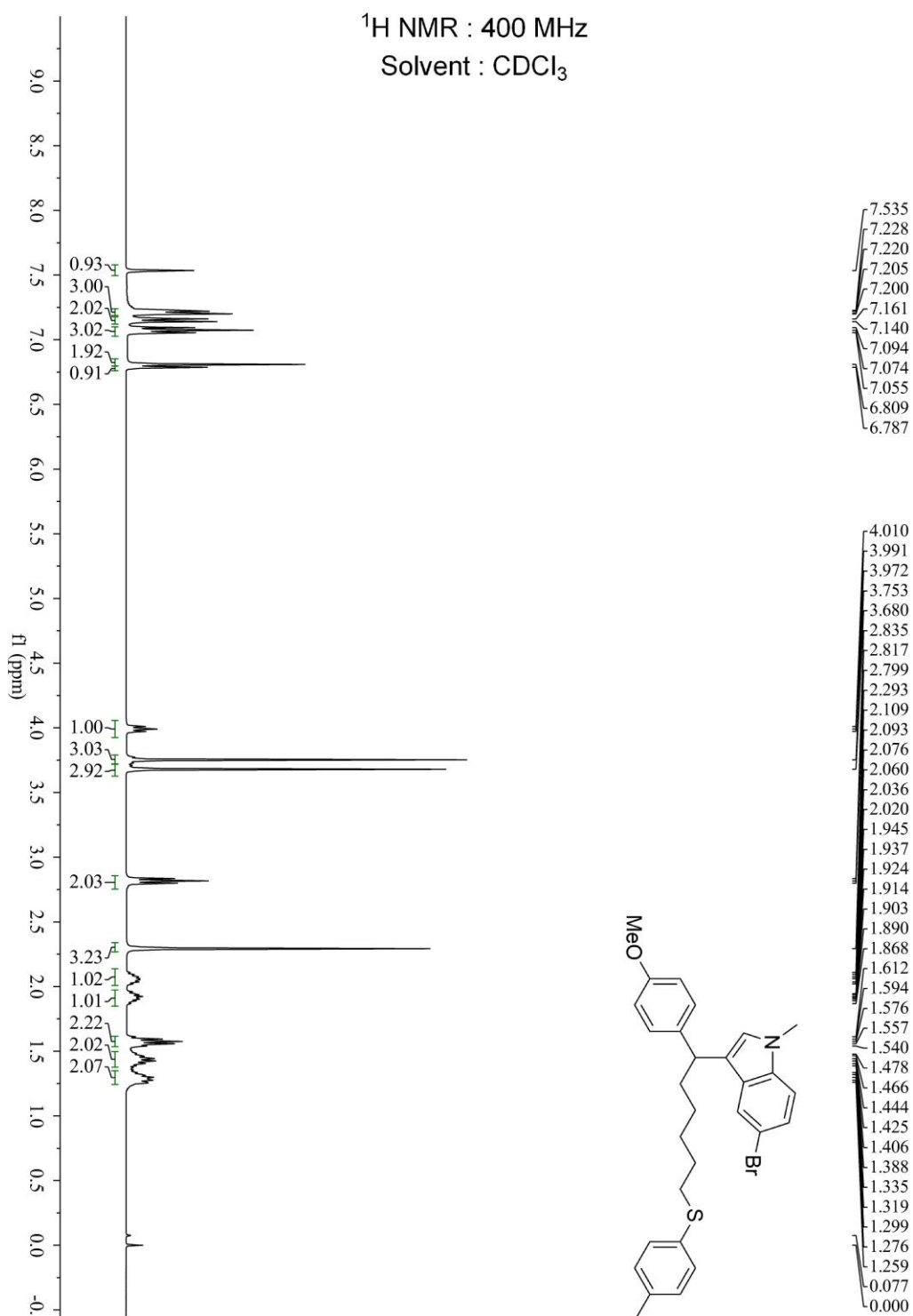
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



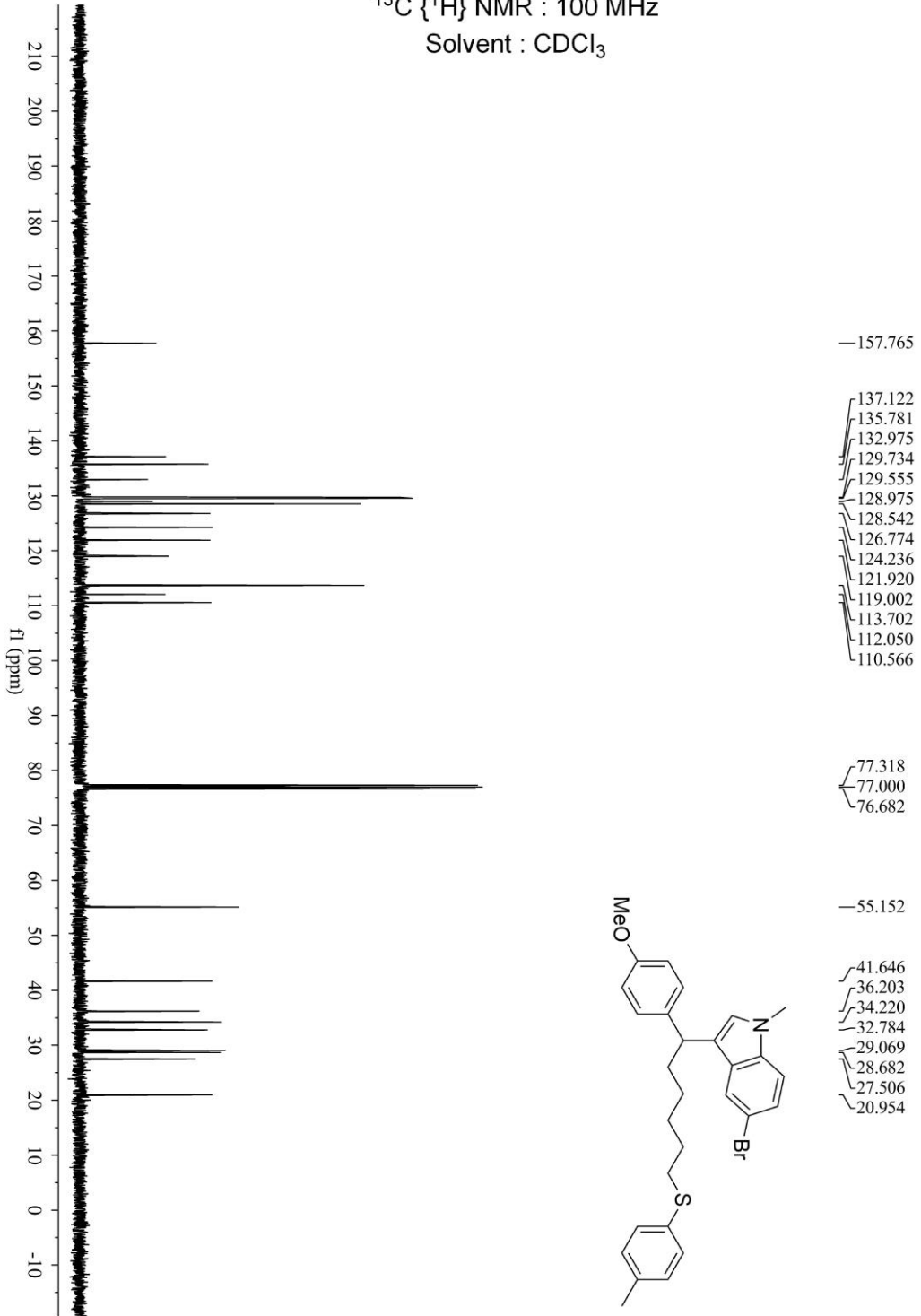
^{19}F NMR : 282 MHz
Solvent : CDCl_3



5-Bromo-3-(1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4aaf)



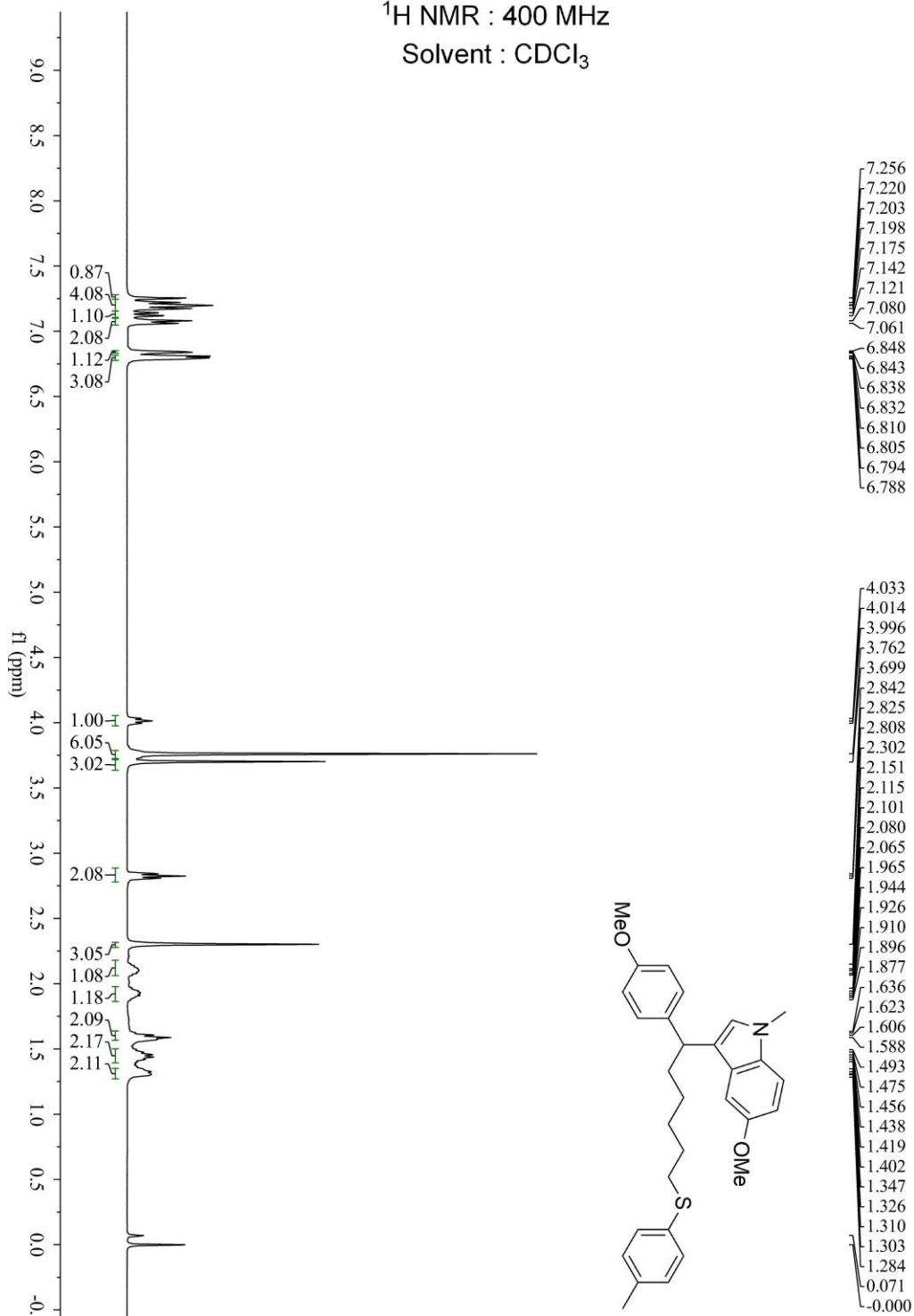
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



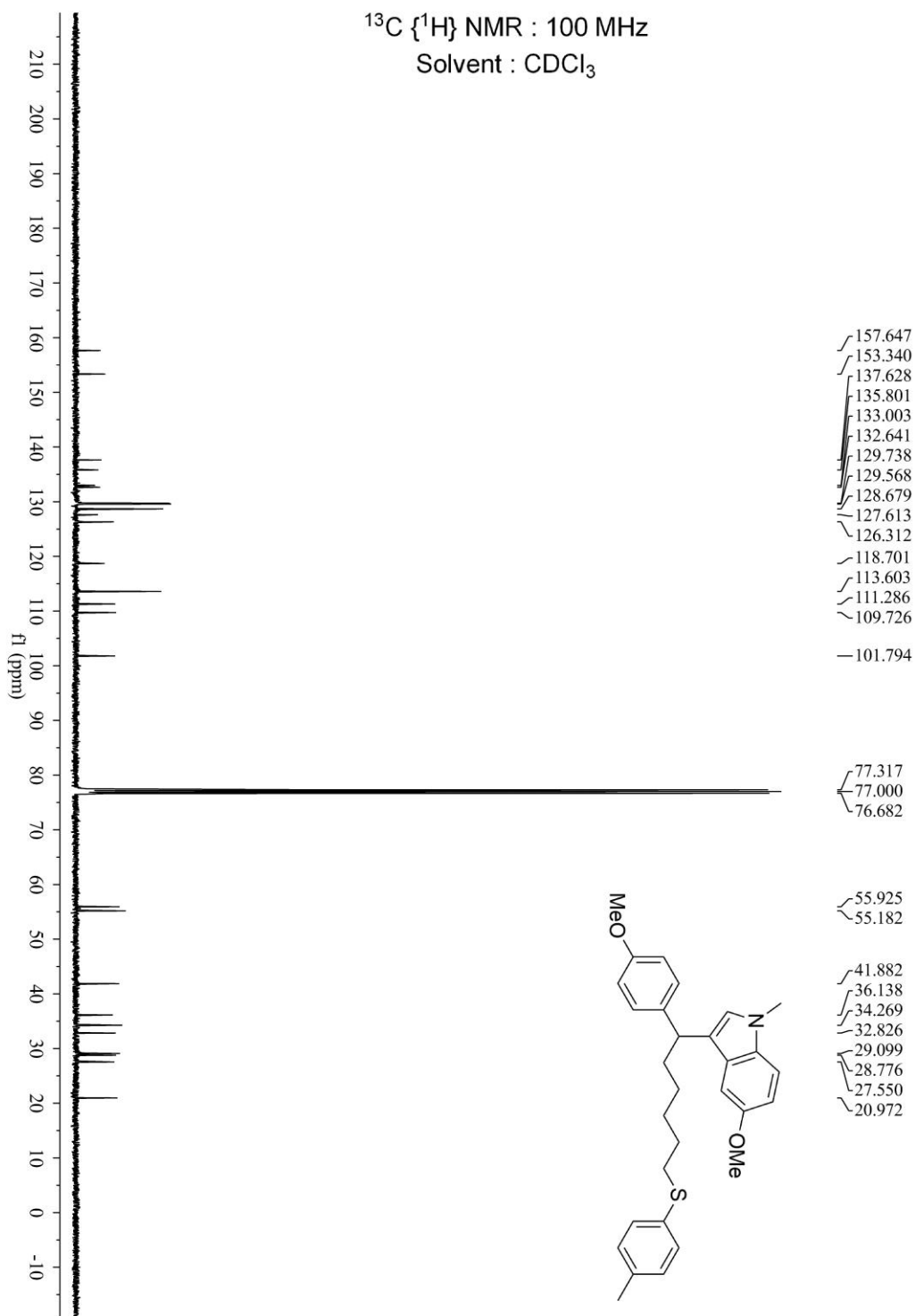
**5-Methoxy-3-(1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole
(4aag)**

^1H NMR : 400 MHz

Solvent : CDCl_3



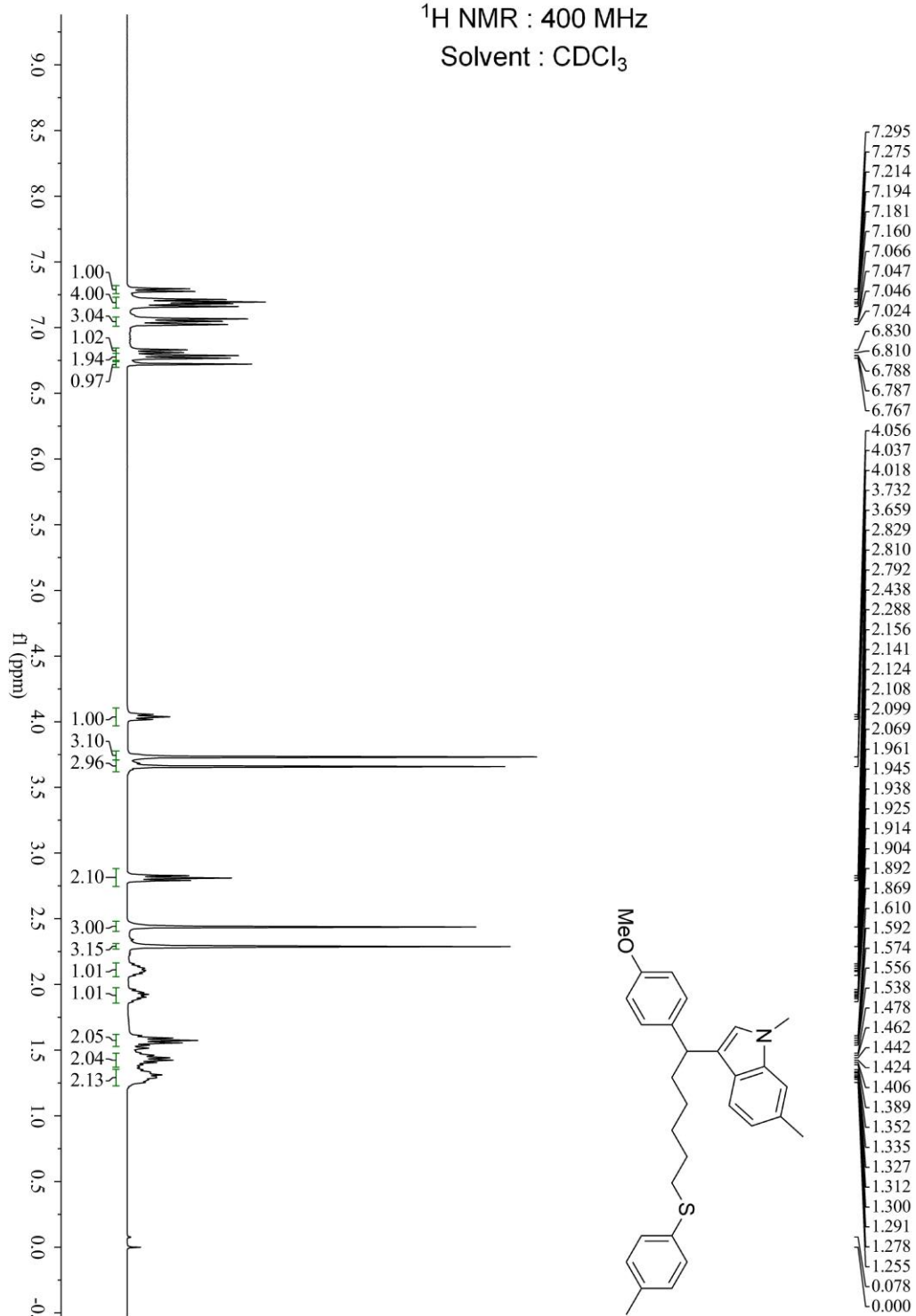
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



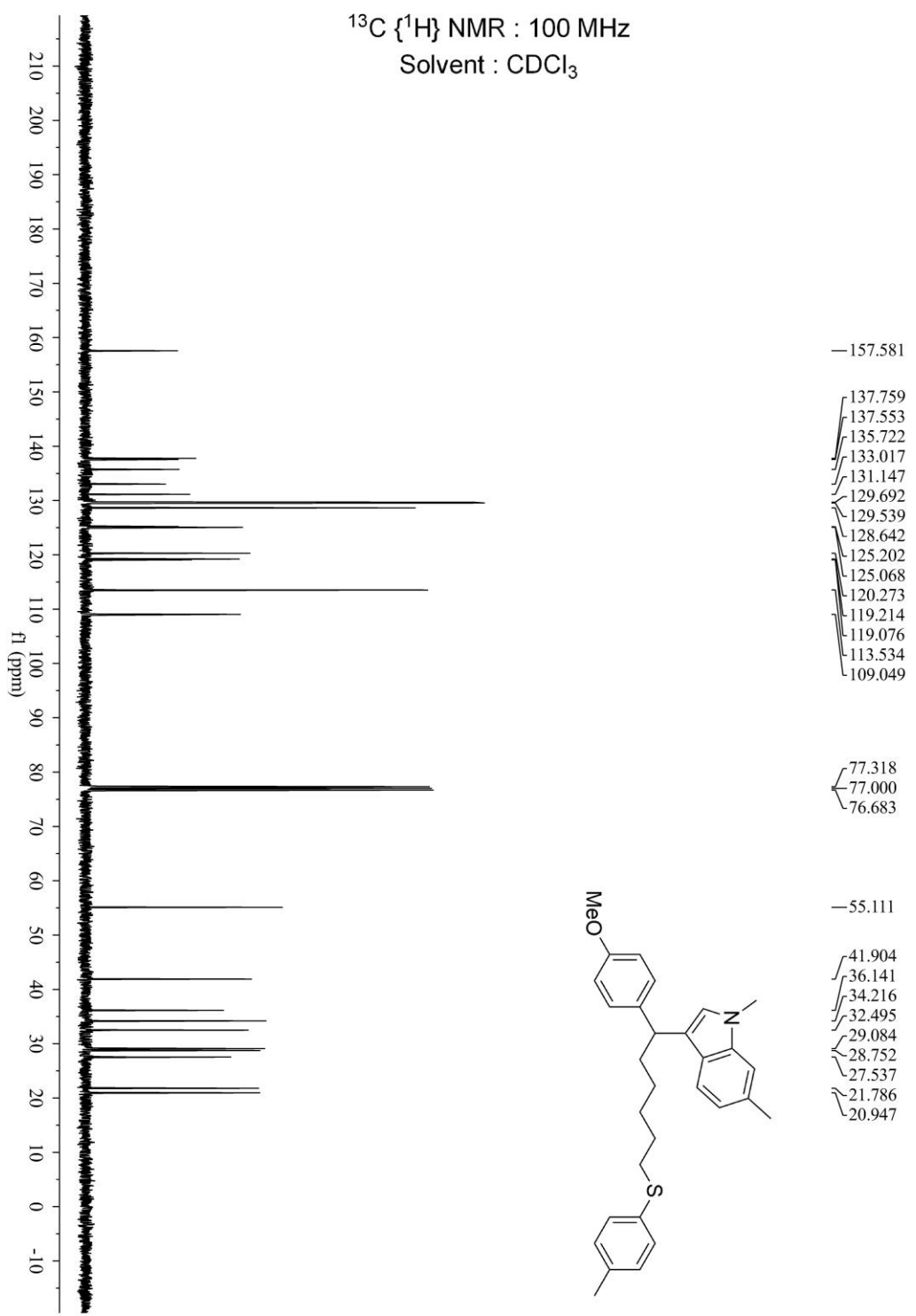
3-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1,6-dimethyl-1*H*-indole (4aah)

^1H NMR : 400 MHz

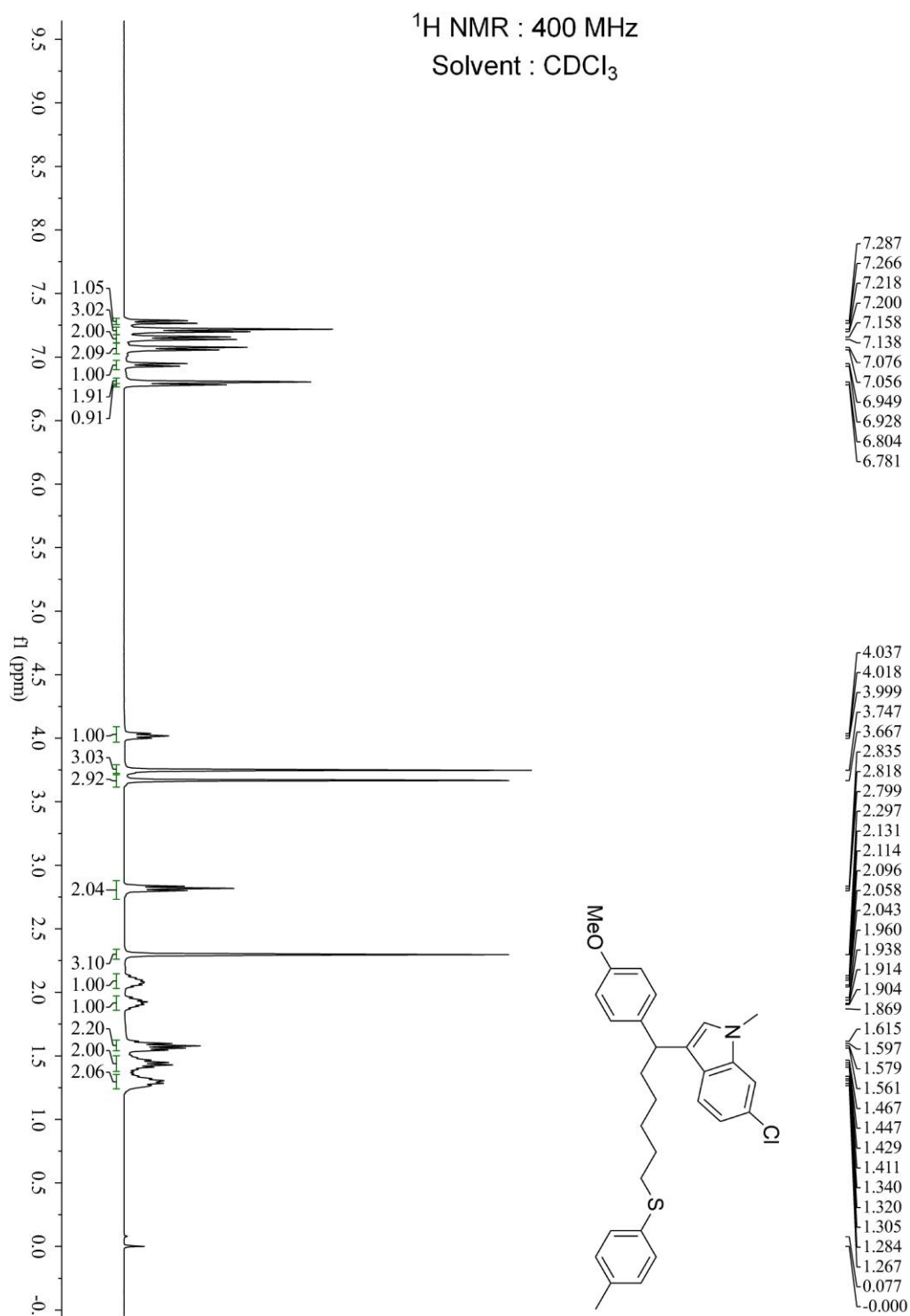
Solvent : CDCl_3



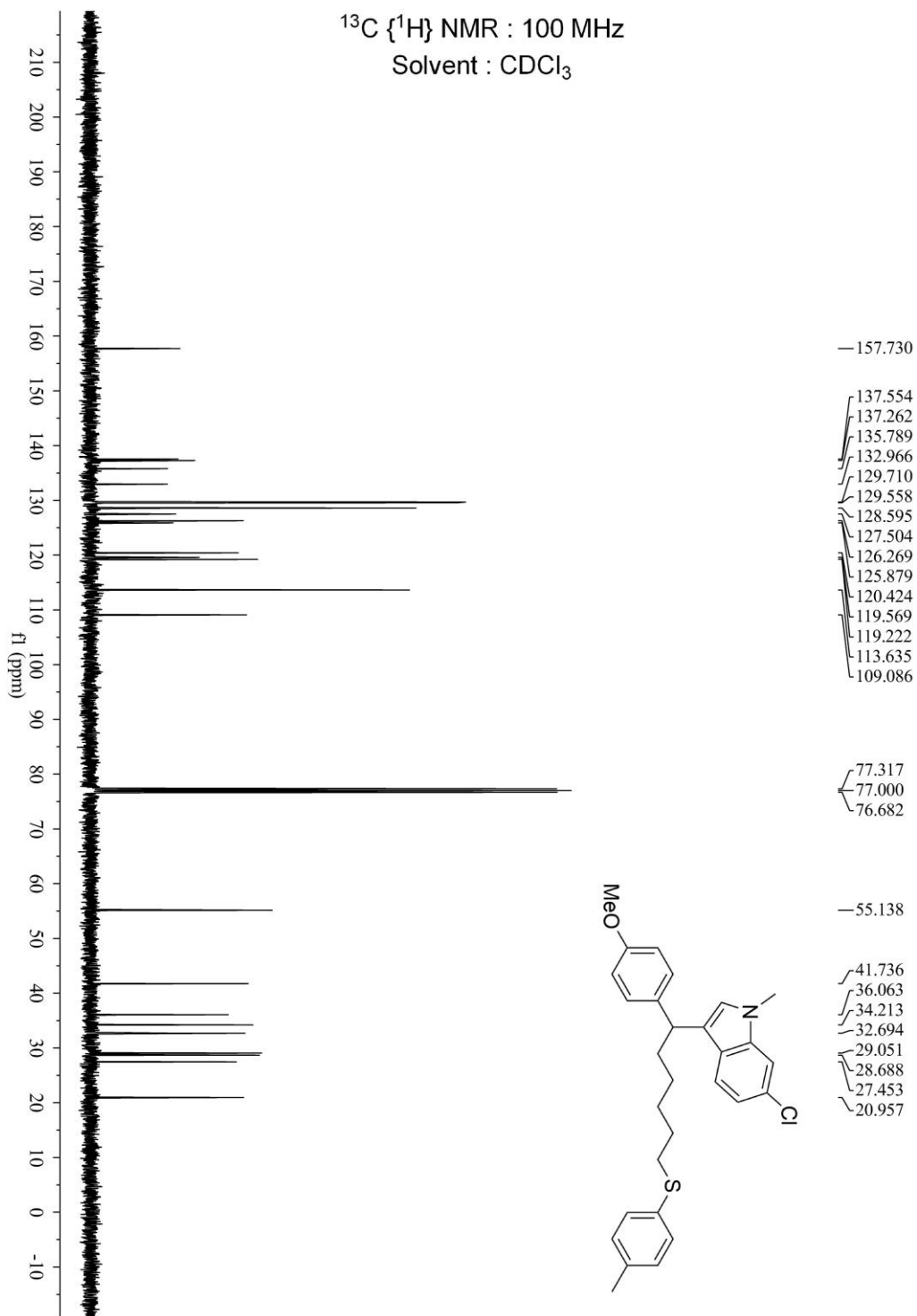
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



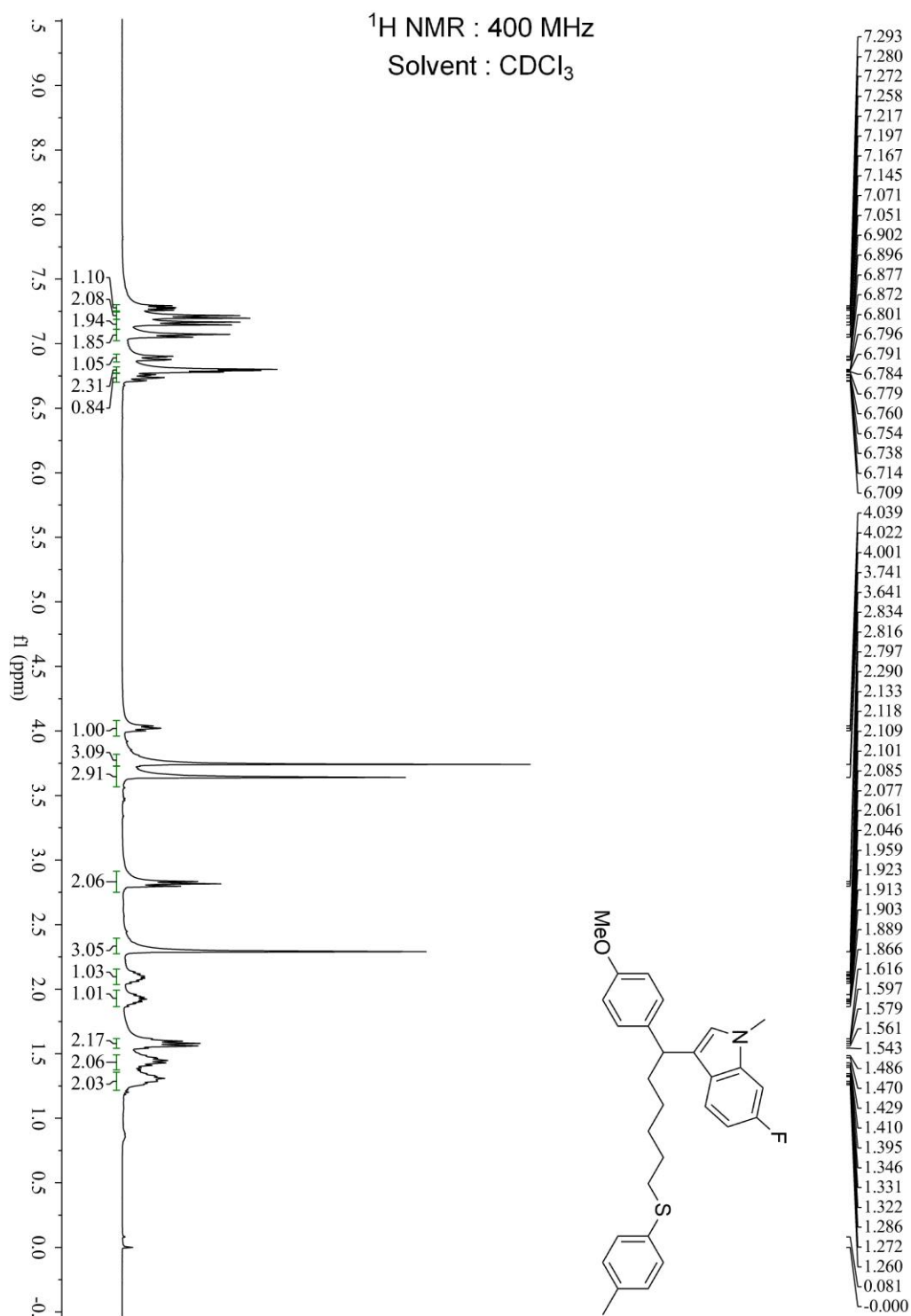
6-Chloro-3-(1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4aai)



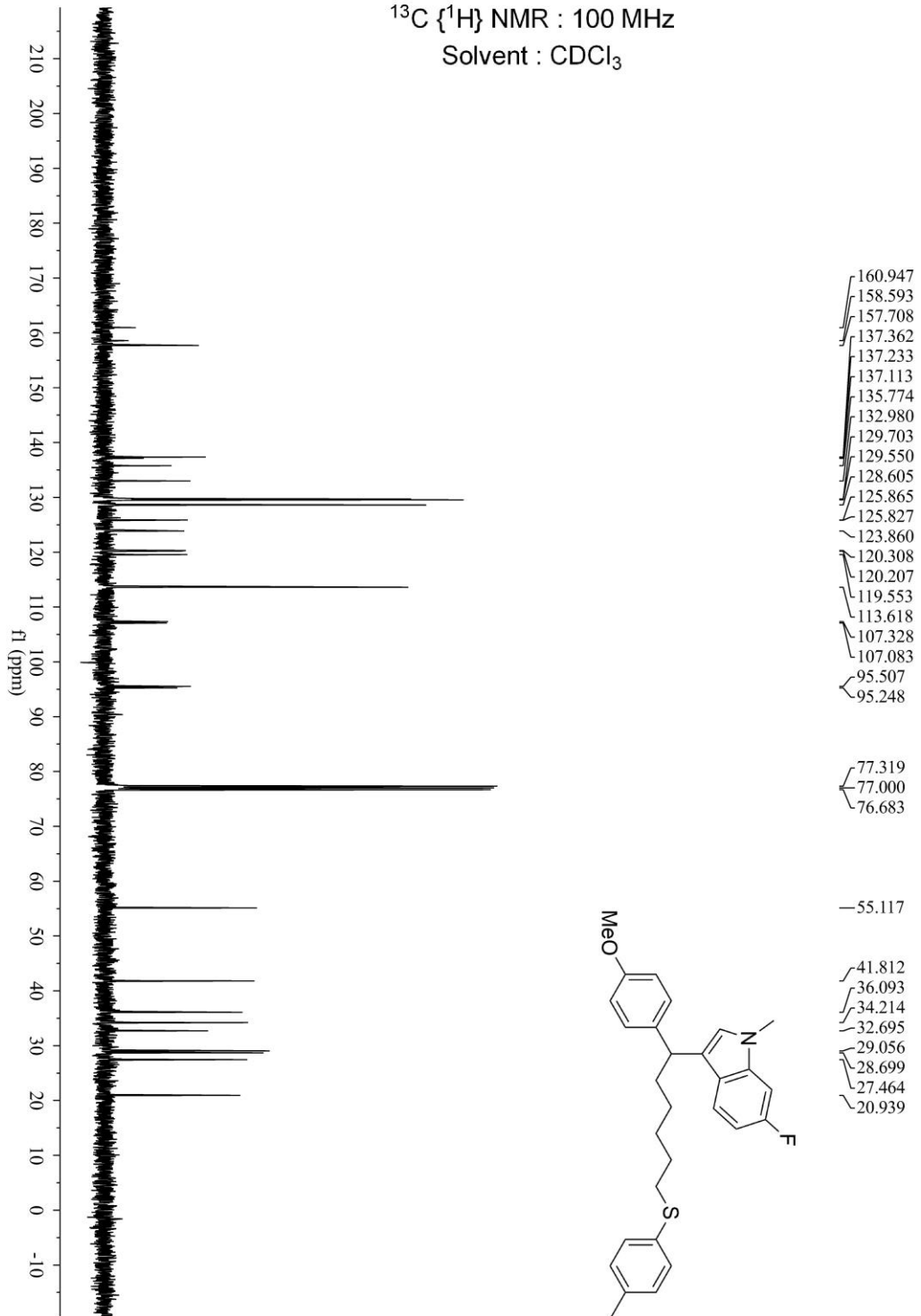
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



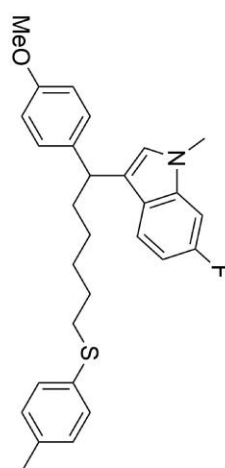
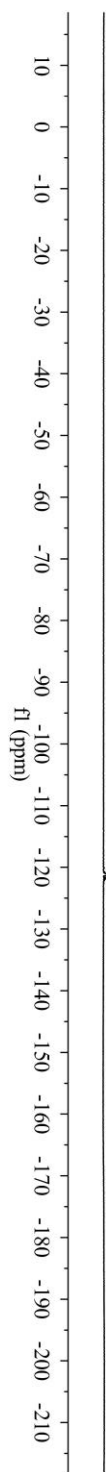
6-Fluoro-3-(1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-indole (4aaj)



^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3

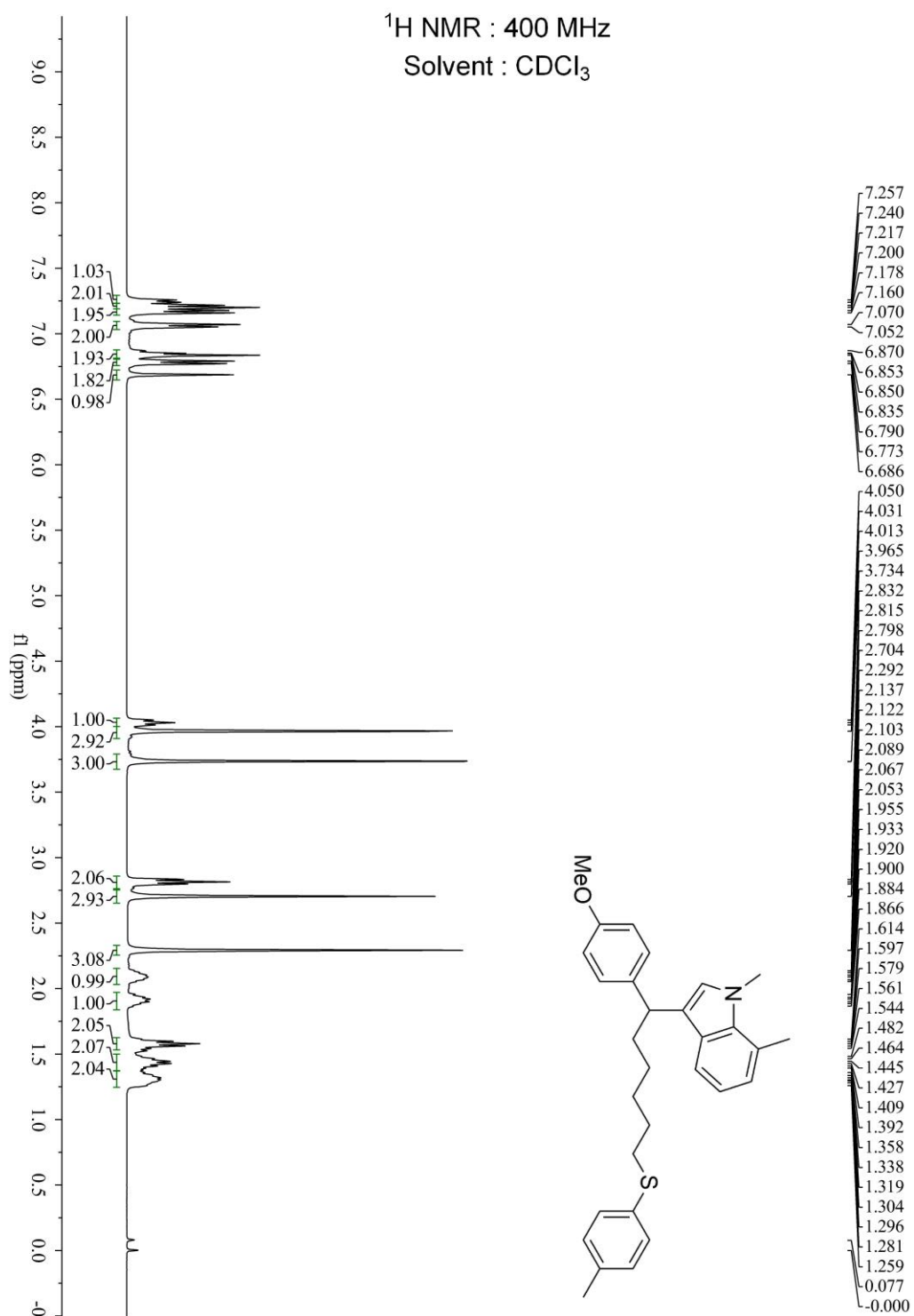


^{19}F NMR : 282 MHz
Solvent : CDCl_3

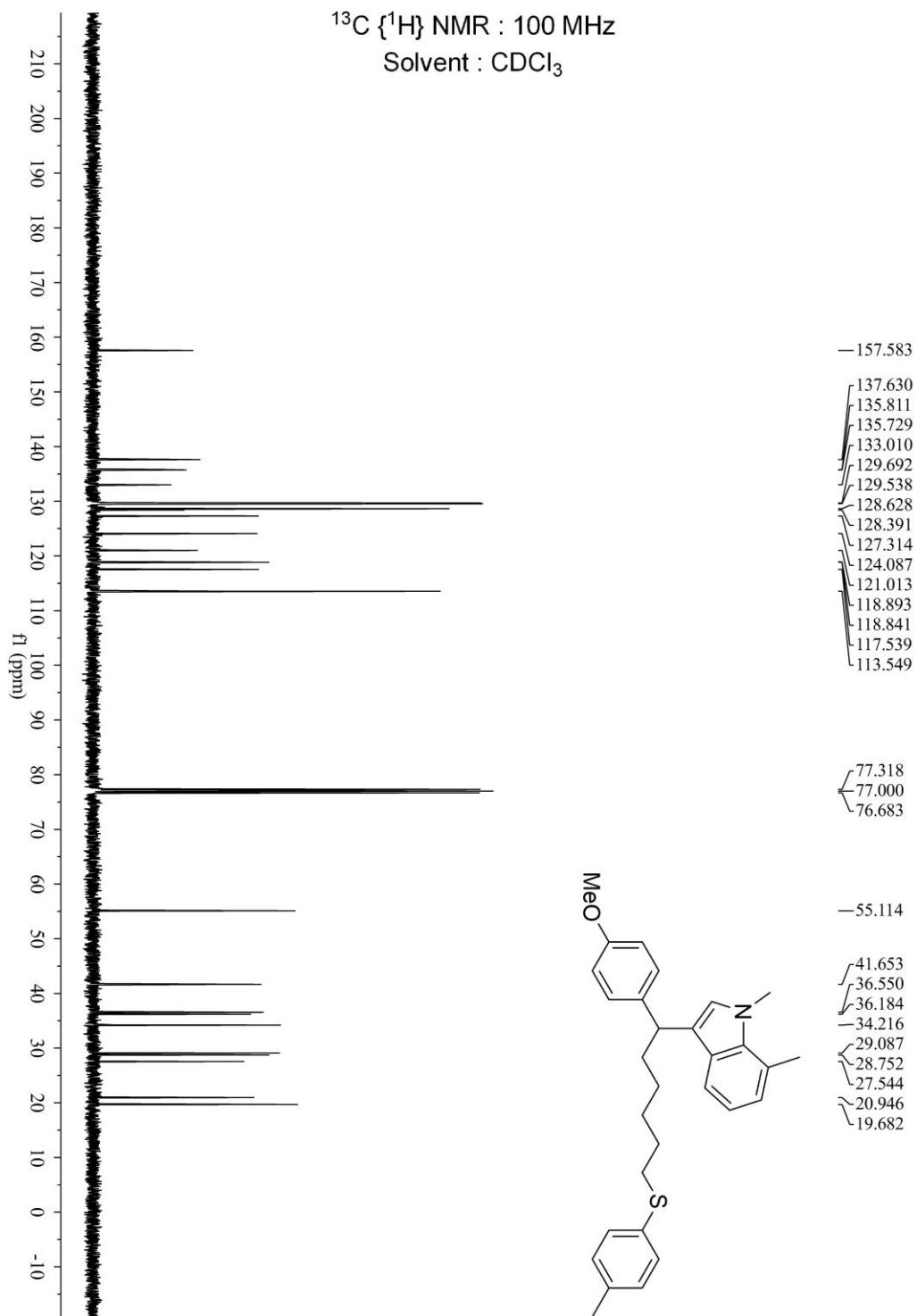


—121.285

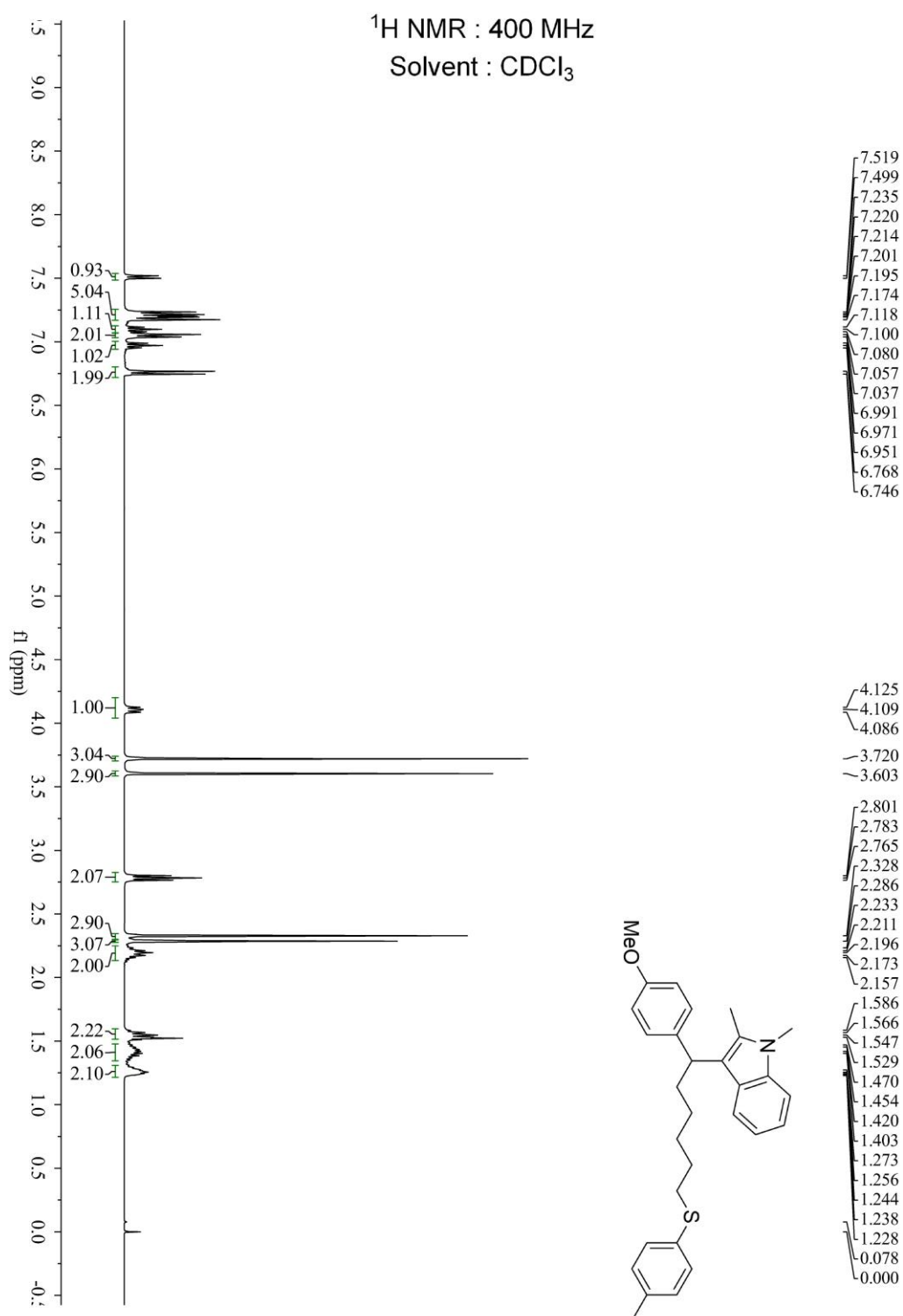
3-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1,7-dimethyl-1*H*-indole (4aak)



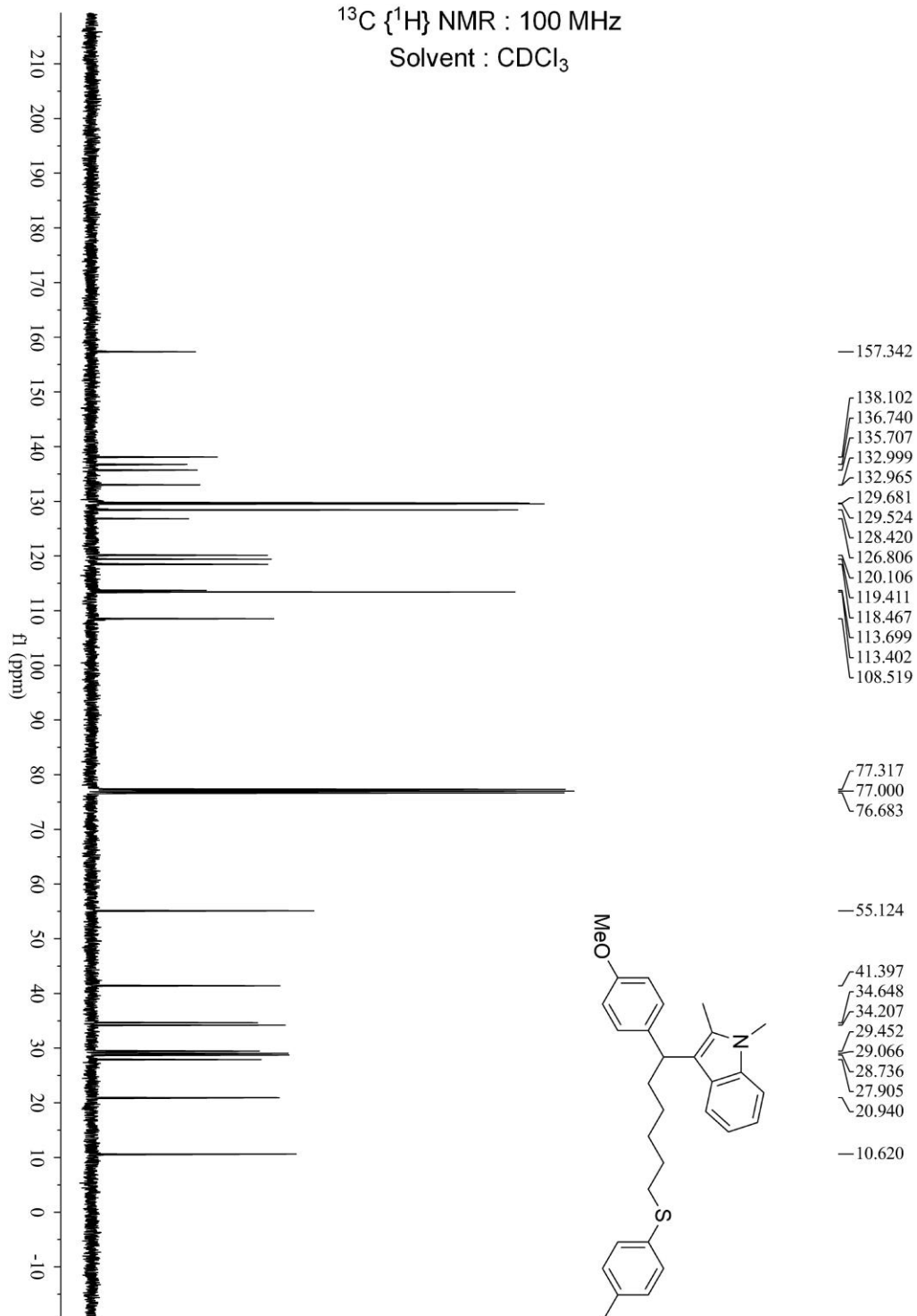
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



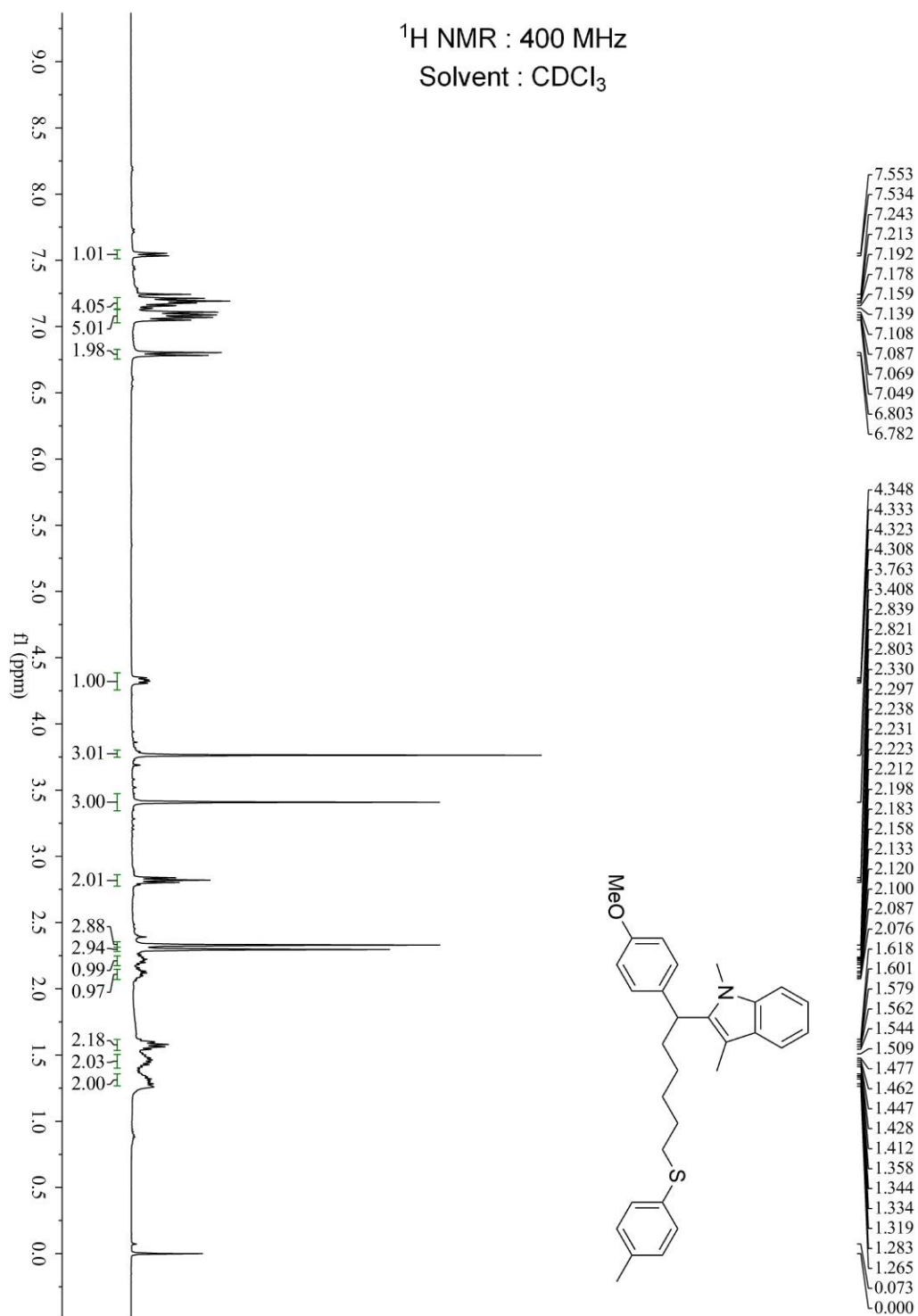
3-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1,2-dimethyl-1*H*-indole (4a*a*)



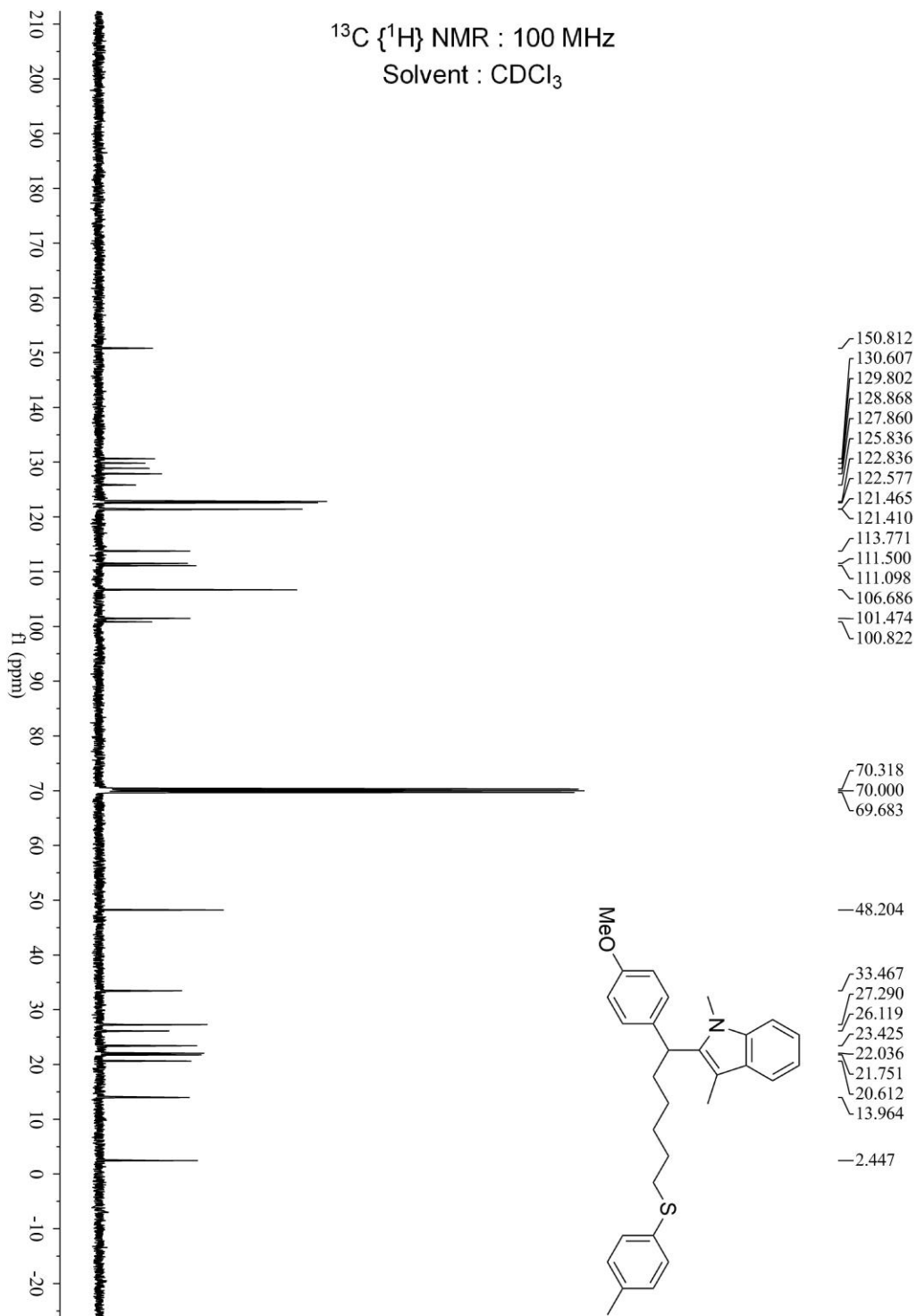
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



2-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1,3-dimethyl-1*H*-indole (4aam)



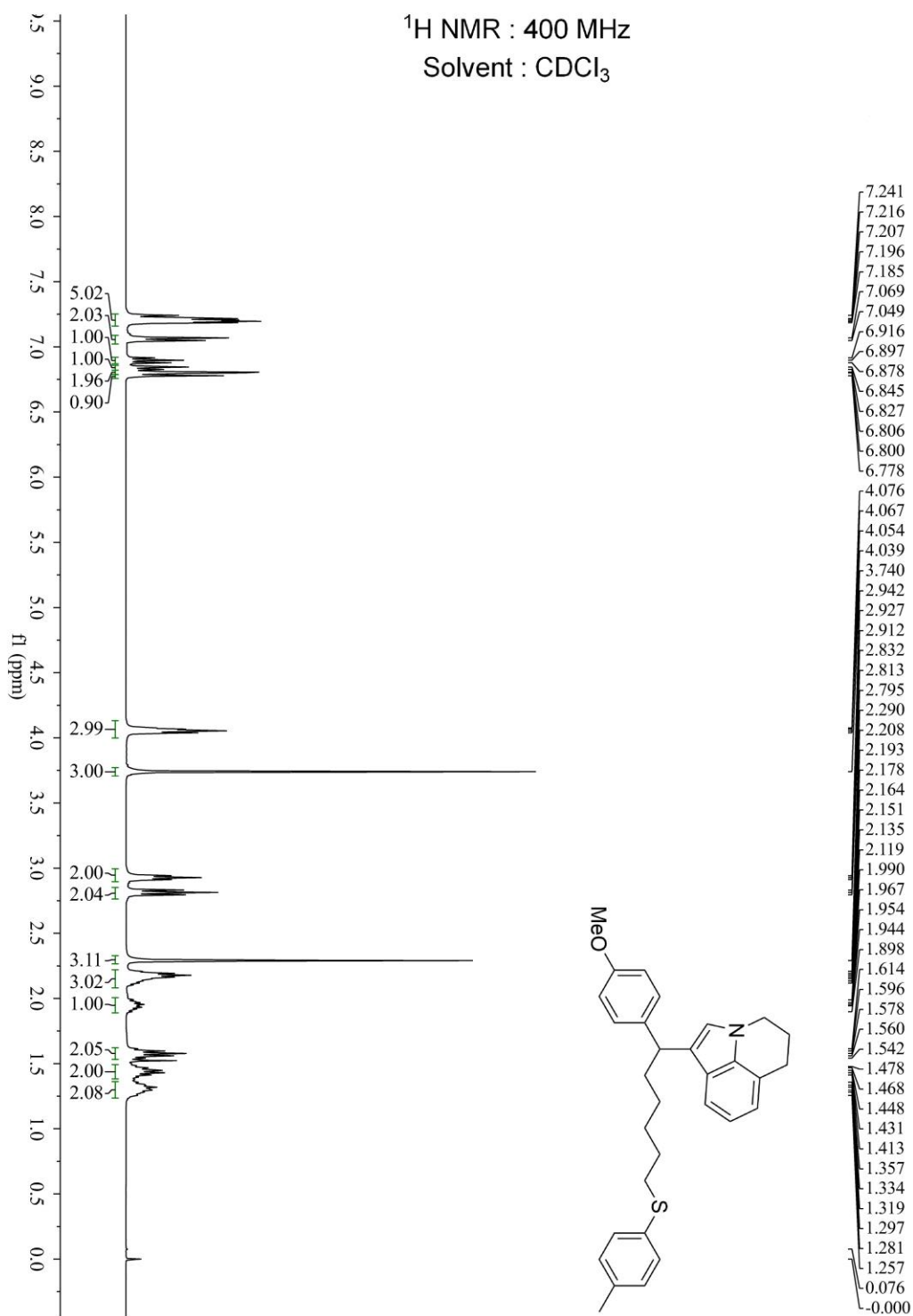
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



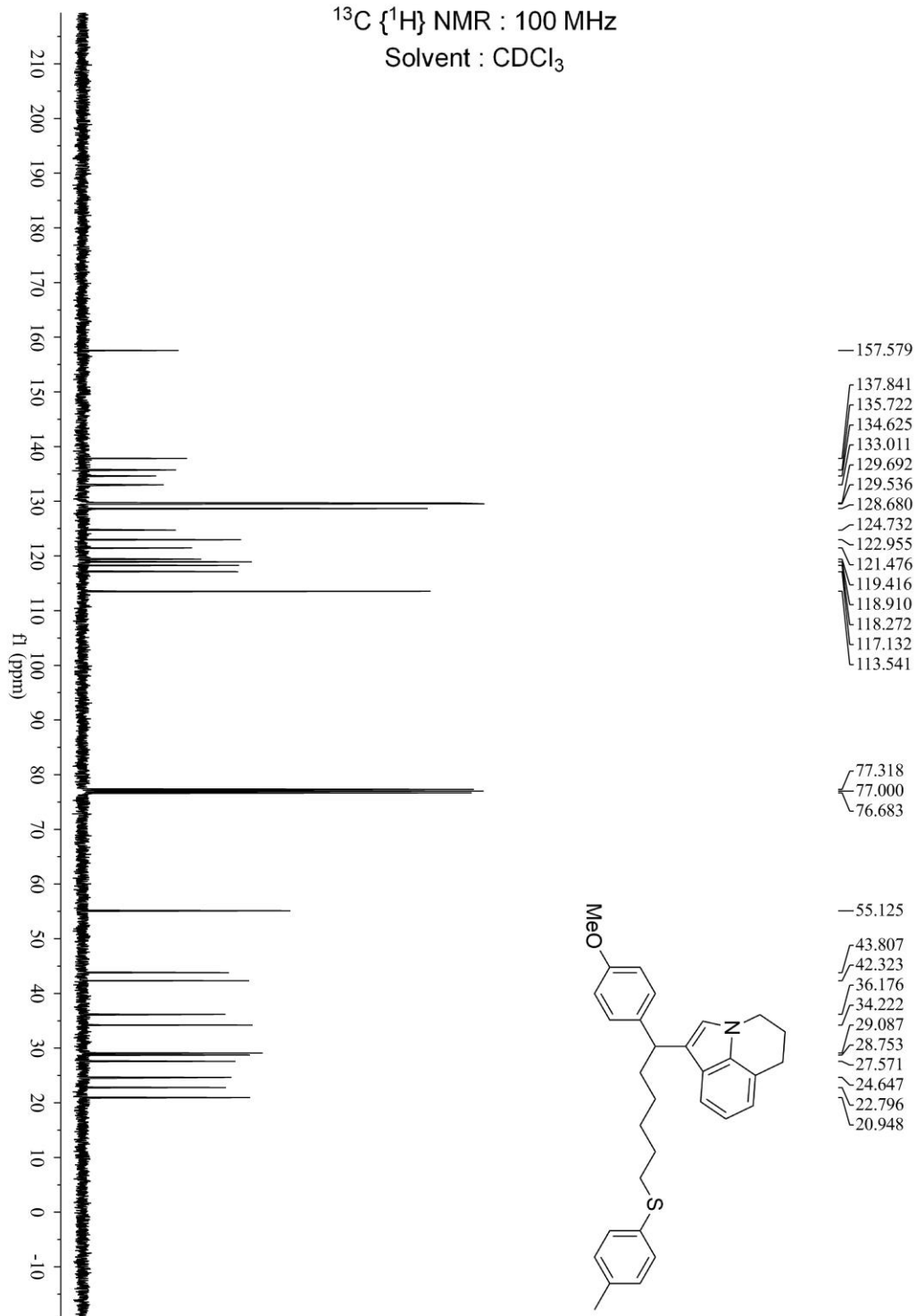
1-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (4aan)

¹H NMR : 400 MHz

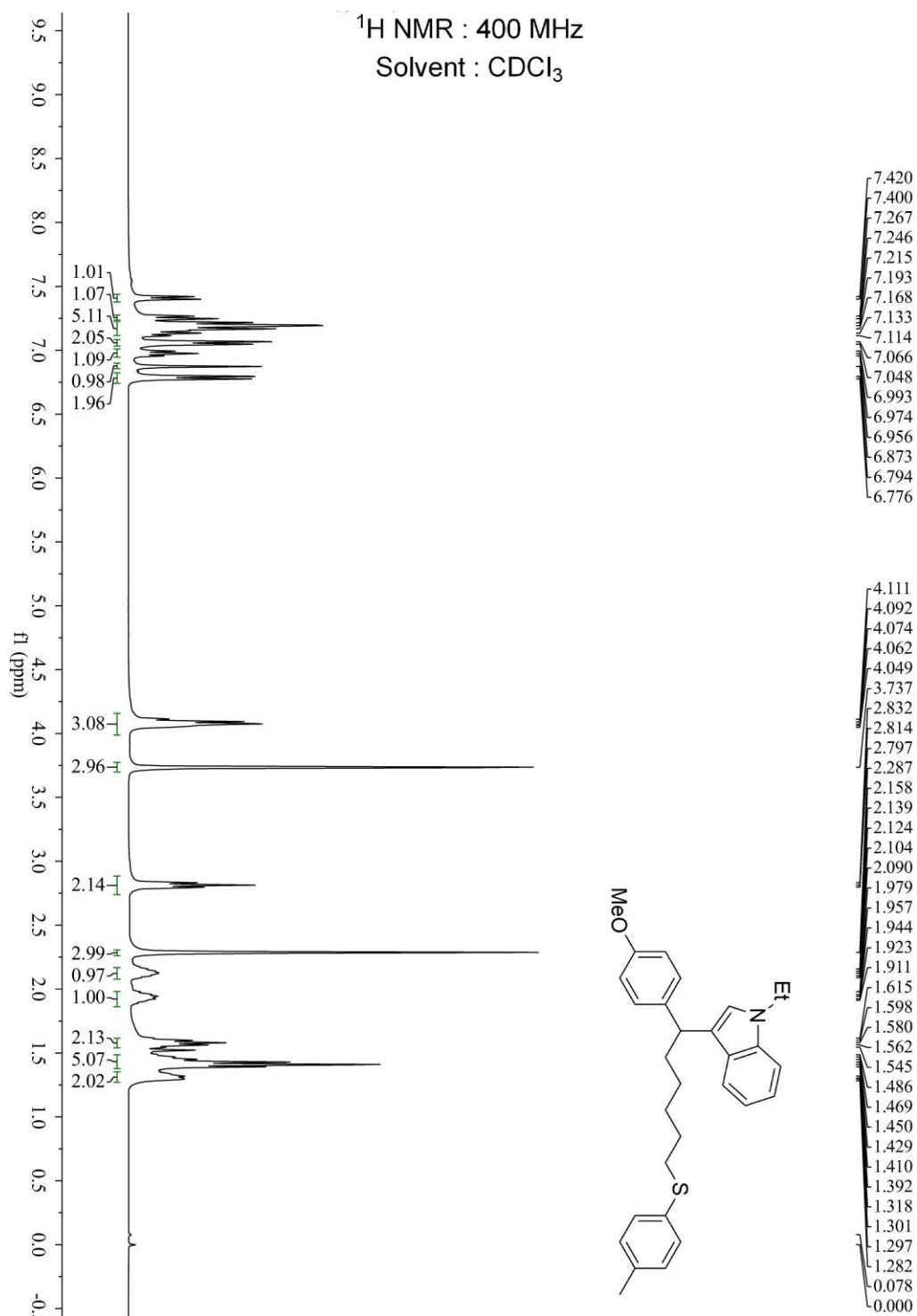
Solvent : CDCl₃



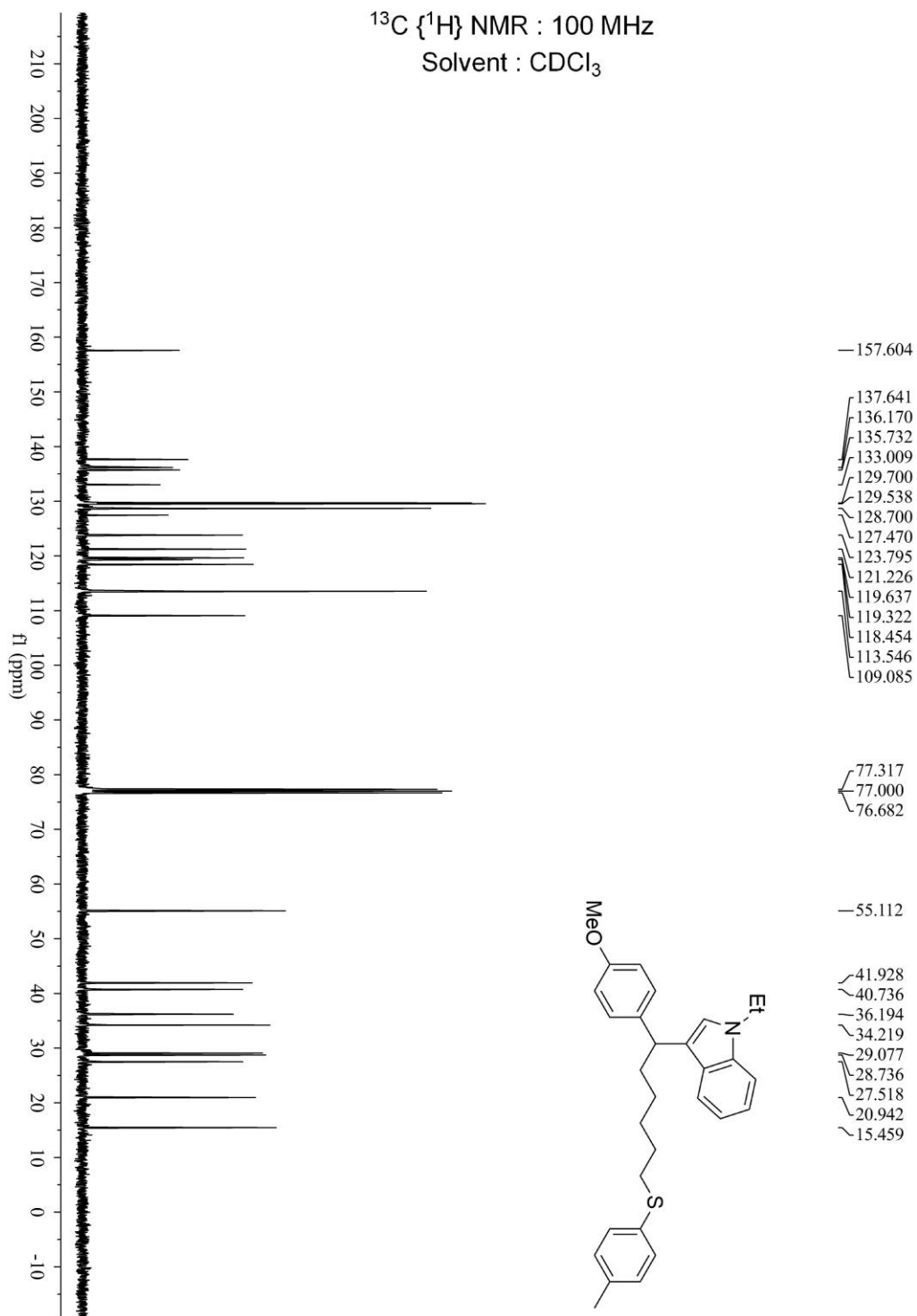
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



1-Ethyl-3-(1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1*H*-indole (4aa0)



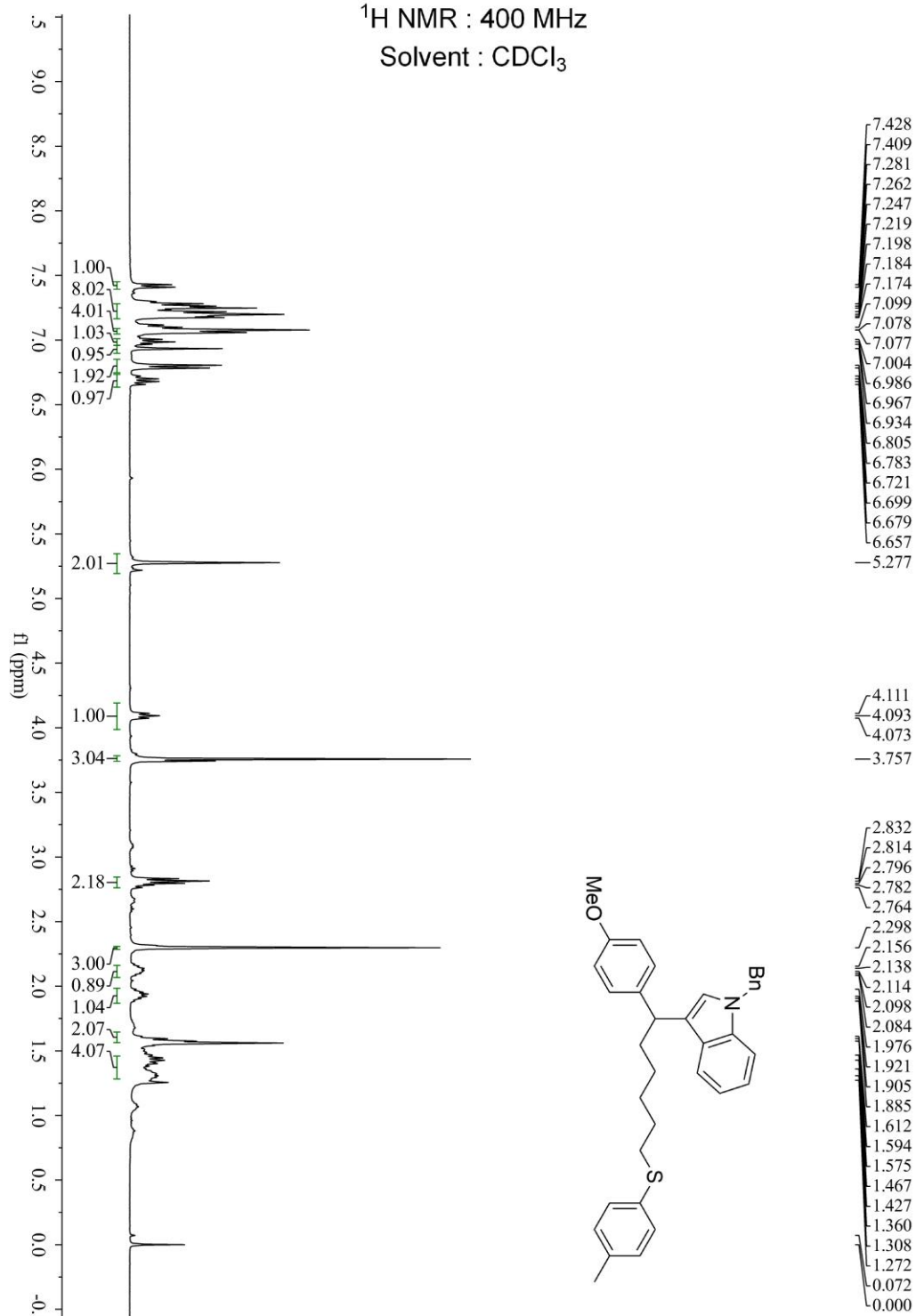
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



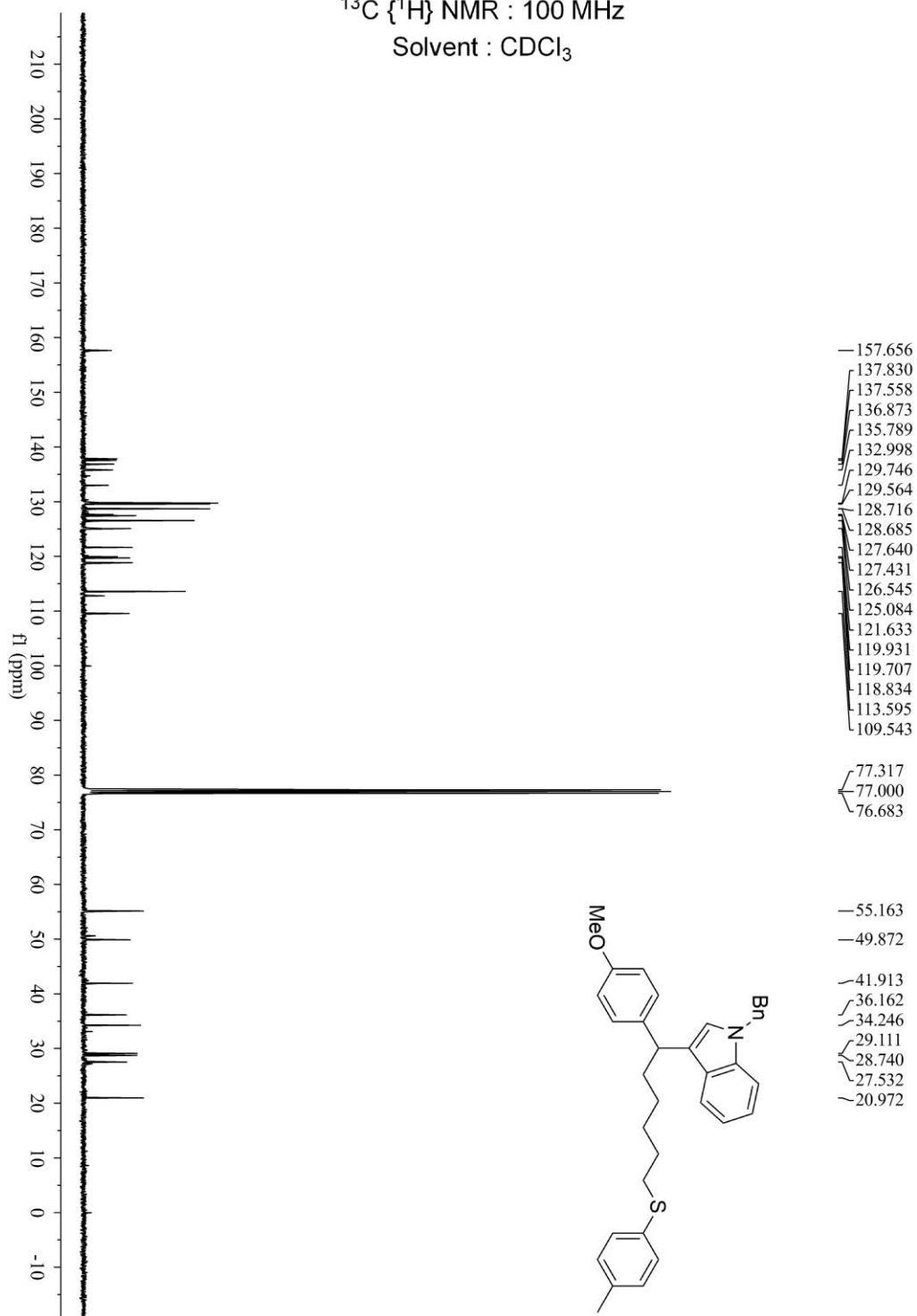
1-Benzyl-3-(1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1*H*-indole (4aap)

¹H NMR : 400 MHz

Solvent : CDCl₃

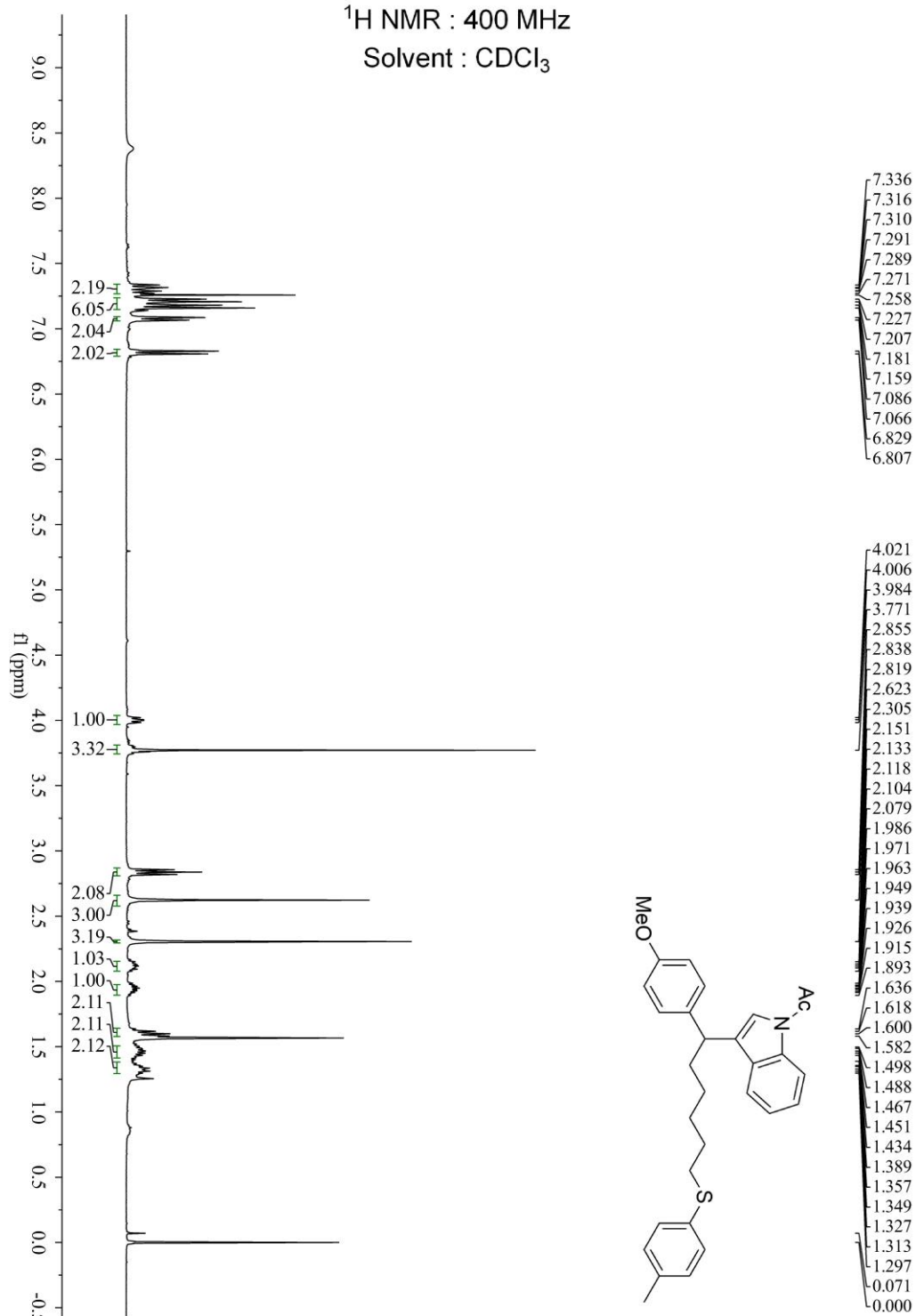


^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3

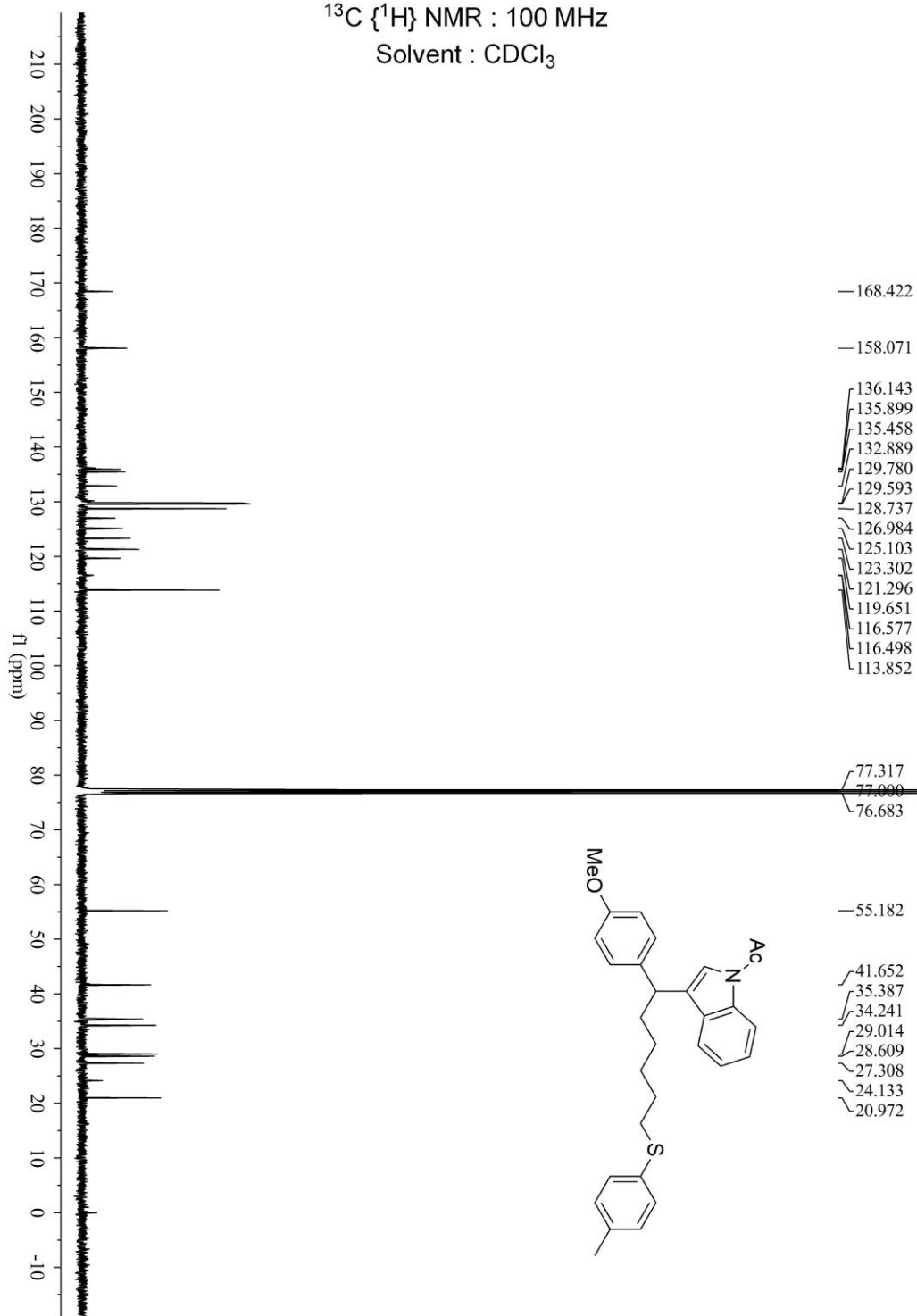


1-(3-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1*H*-indol-1-yl)ethan-1-one (4aaq)

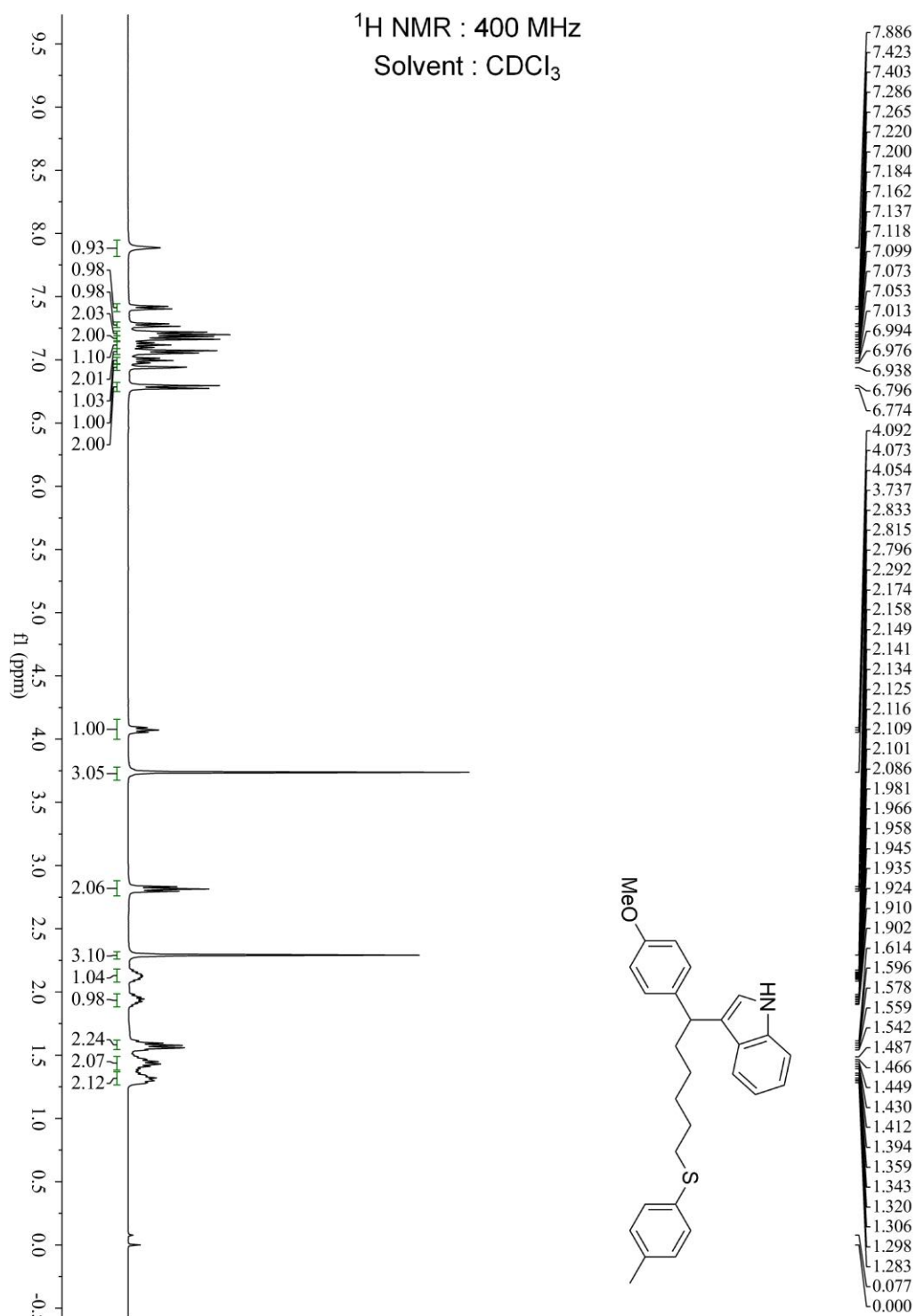
¹H NMR : 400 MHz
Solvent : CDCl₃



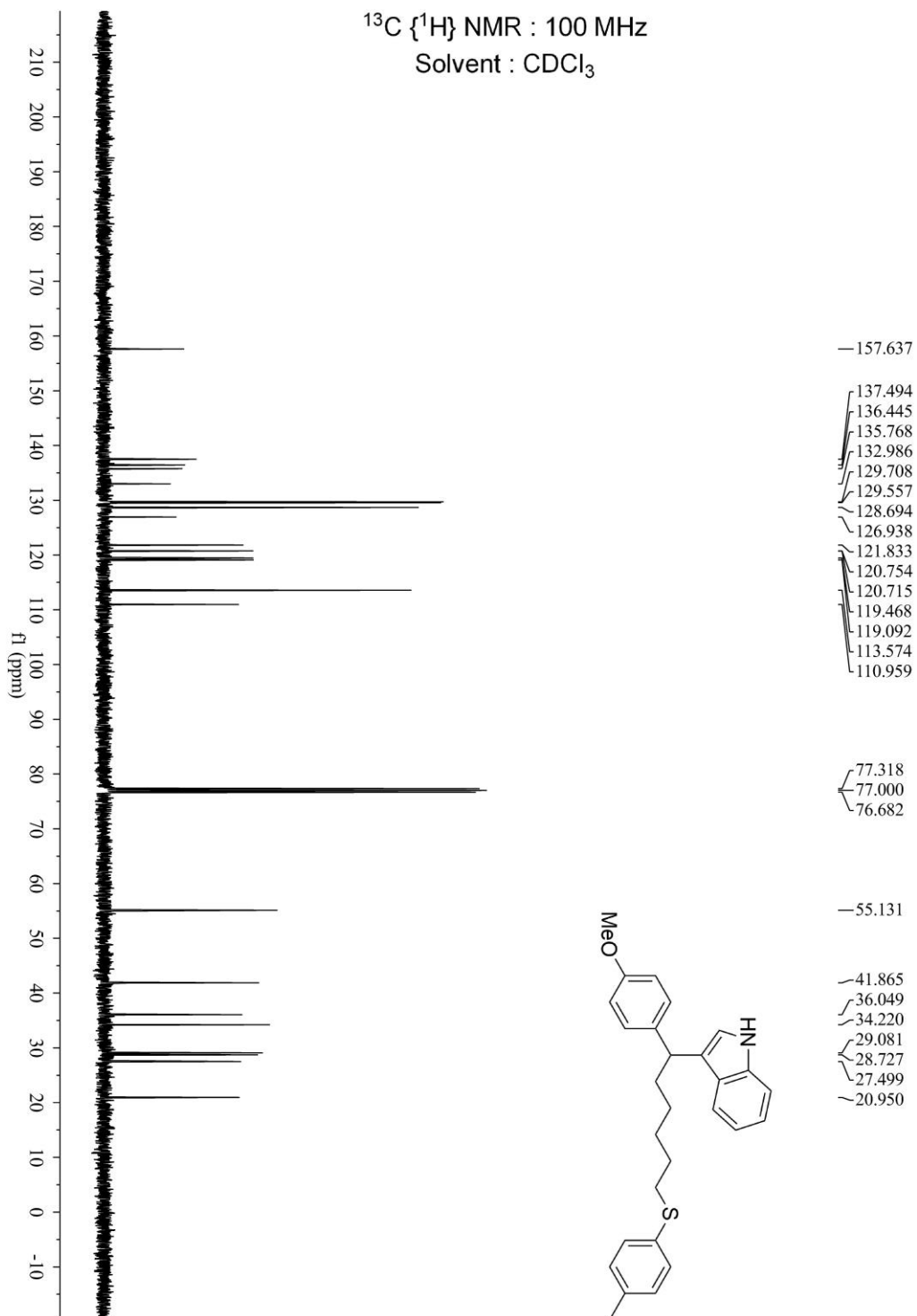
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



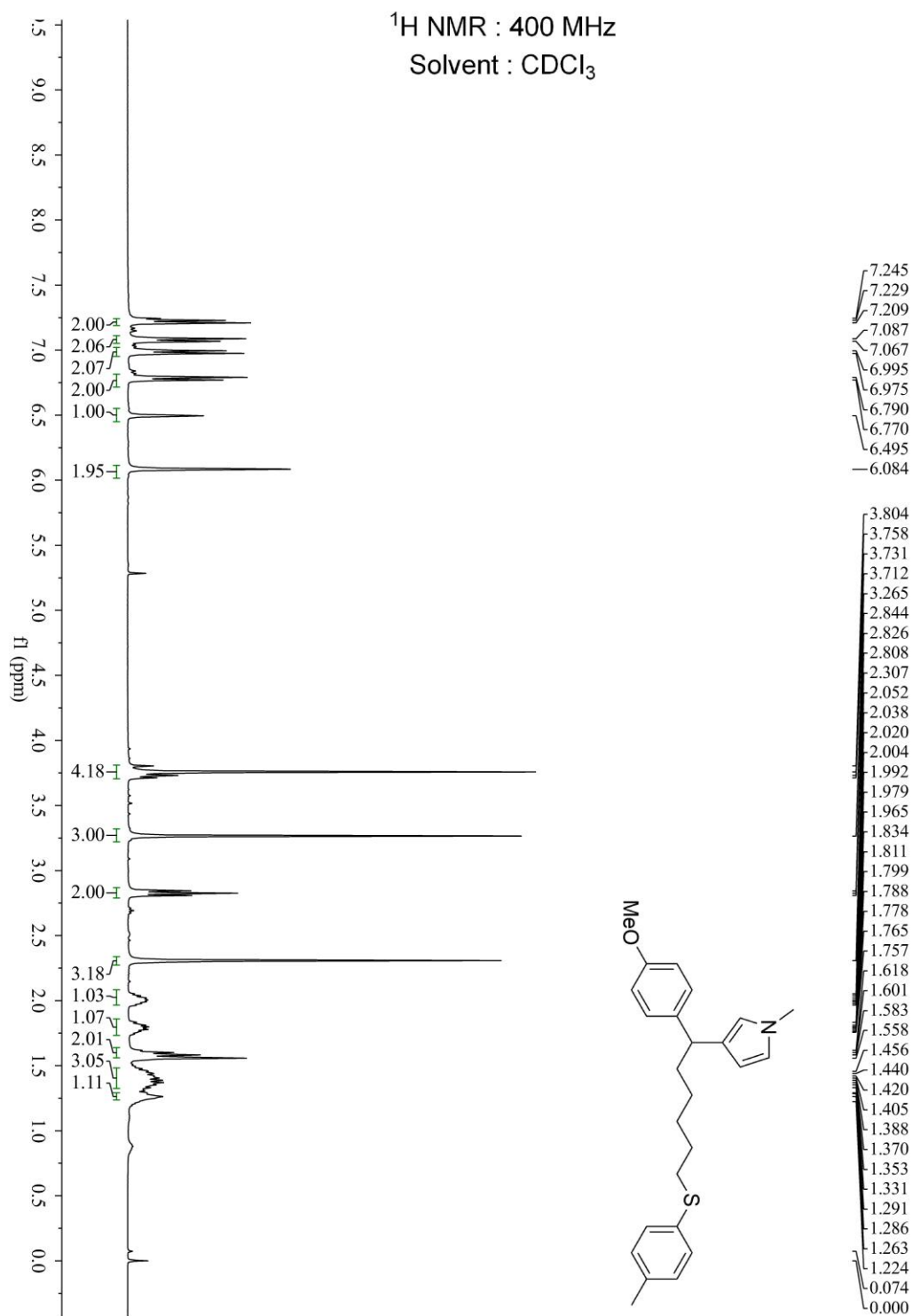
3-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1*H*-indole (4aas)



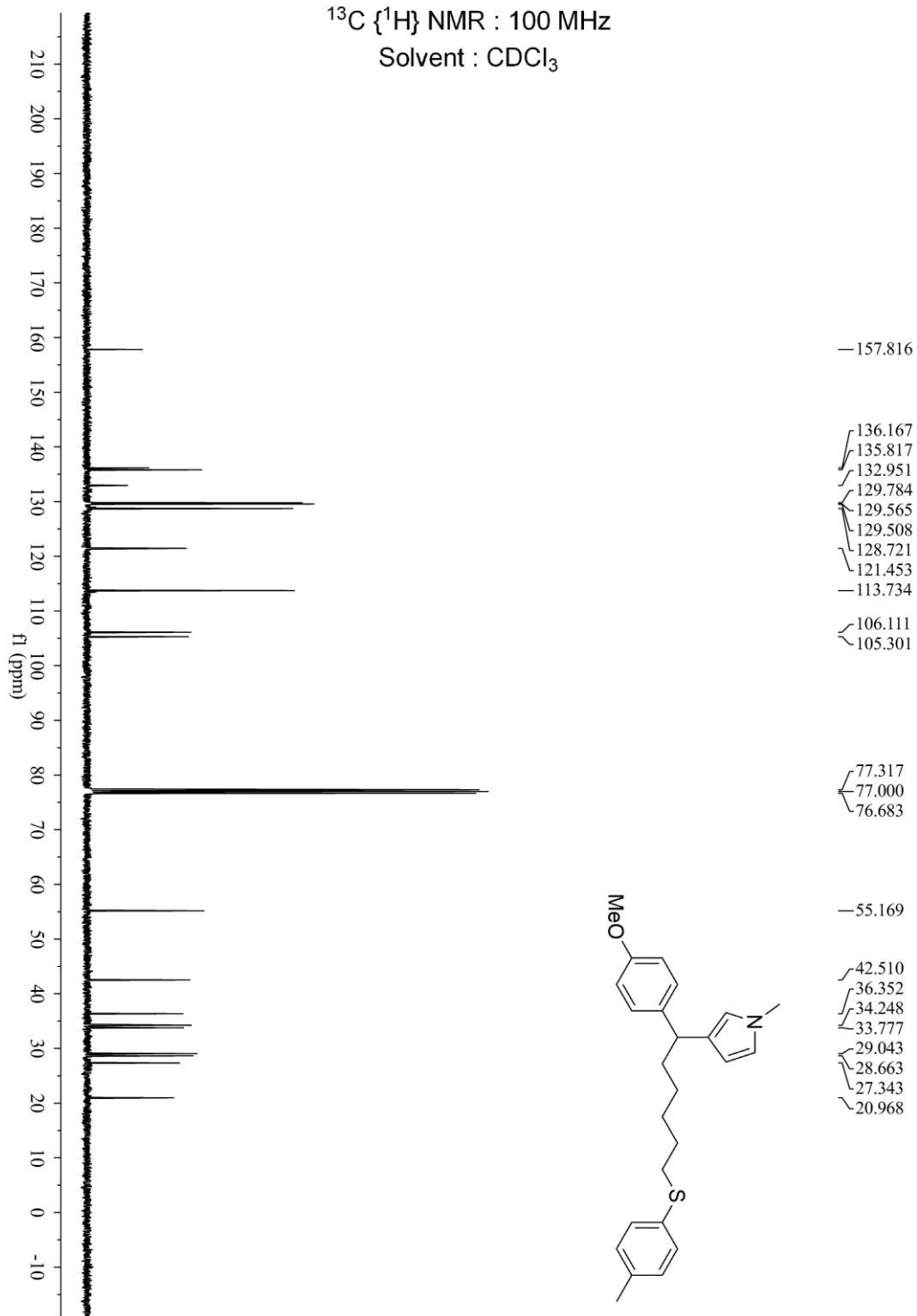
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



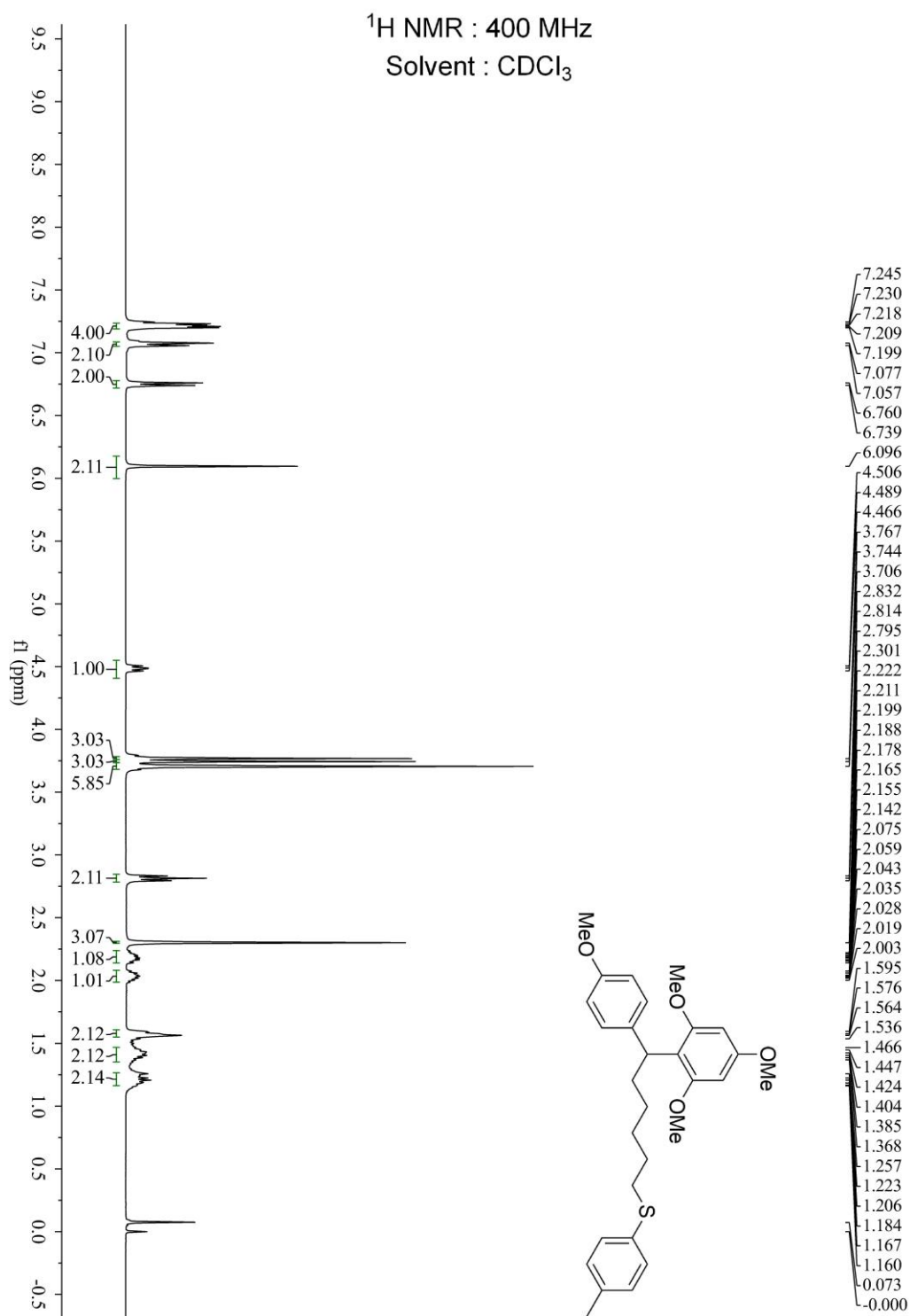
3-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-1-methyl-1*H*-pyrrole (4aat)



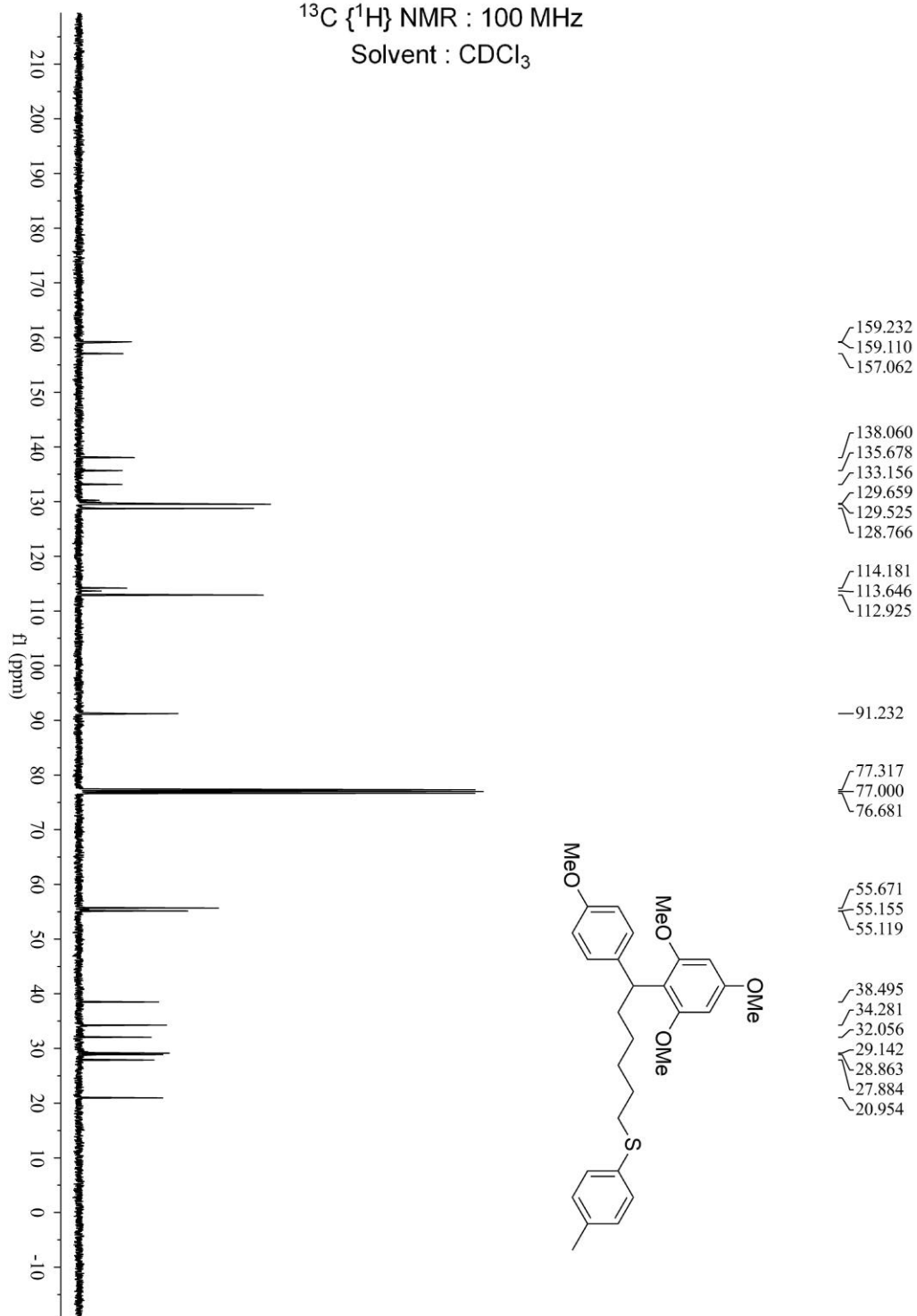
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



(6-(4-Methoxyphenyl)-6-(2,4,6-trimethoxyphenyl)hexyl)(*p*-tolyl)sulfane (4aau)



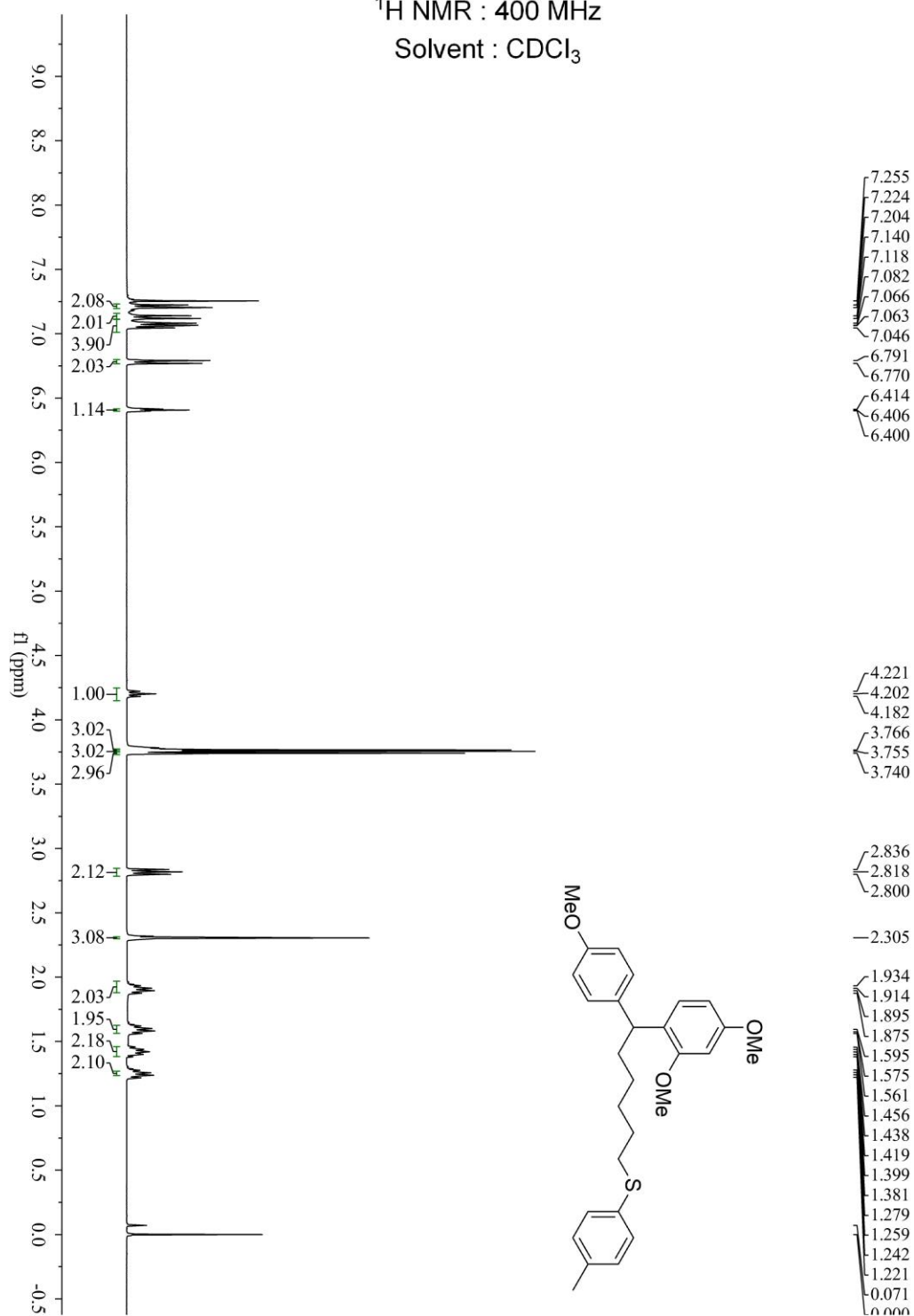
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



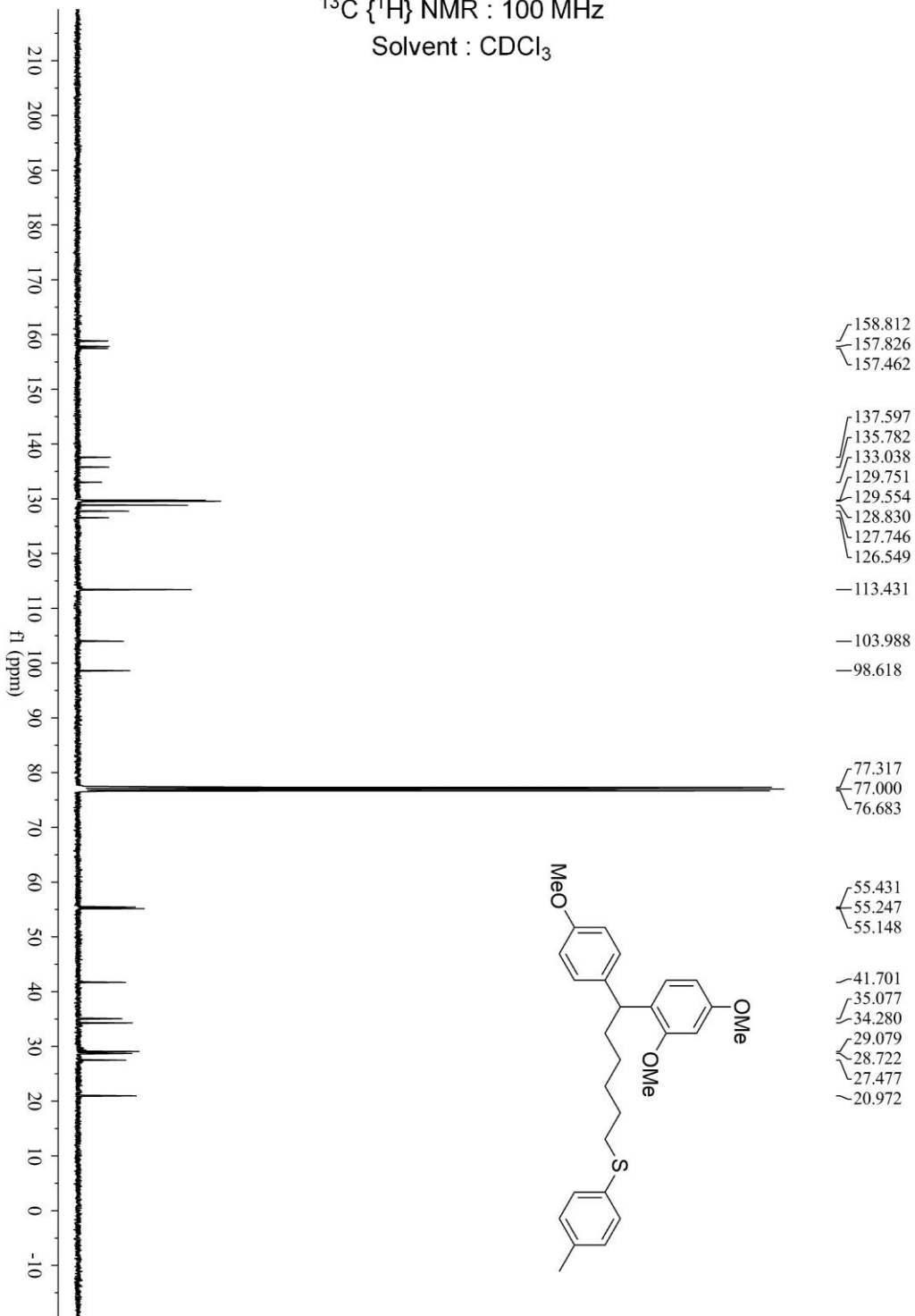
(6-(2,4-Dimethoxyphenyl)-6-(4-methoxyphenyl)hexyl)(p-tolyl)sulfane (4aav)

¹H NMR : 400 MHz

Solvent : CDCl₃



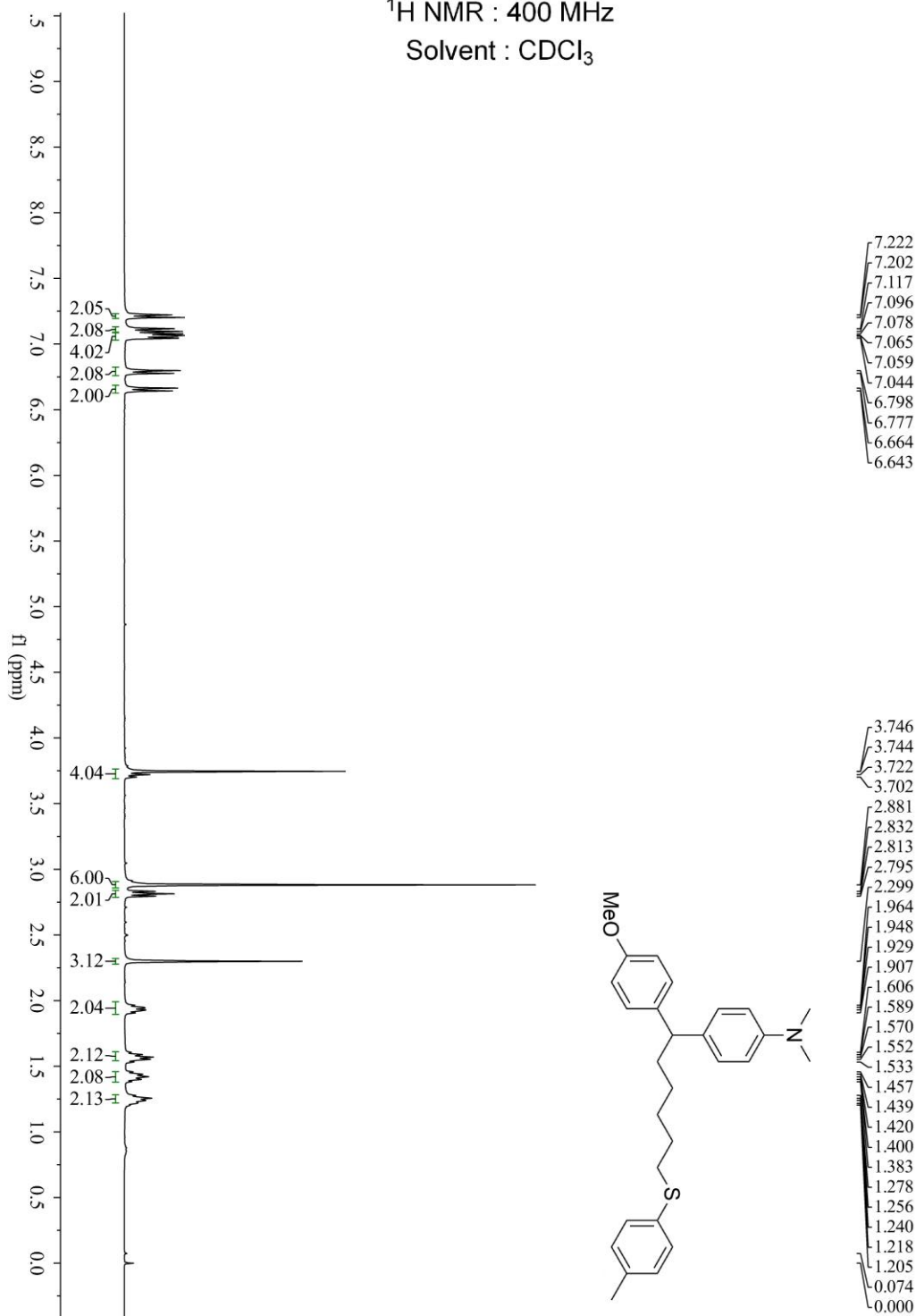
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



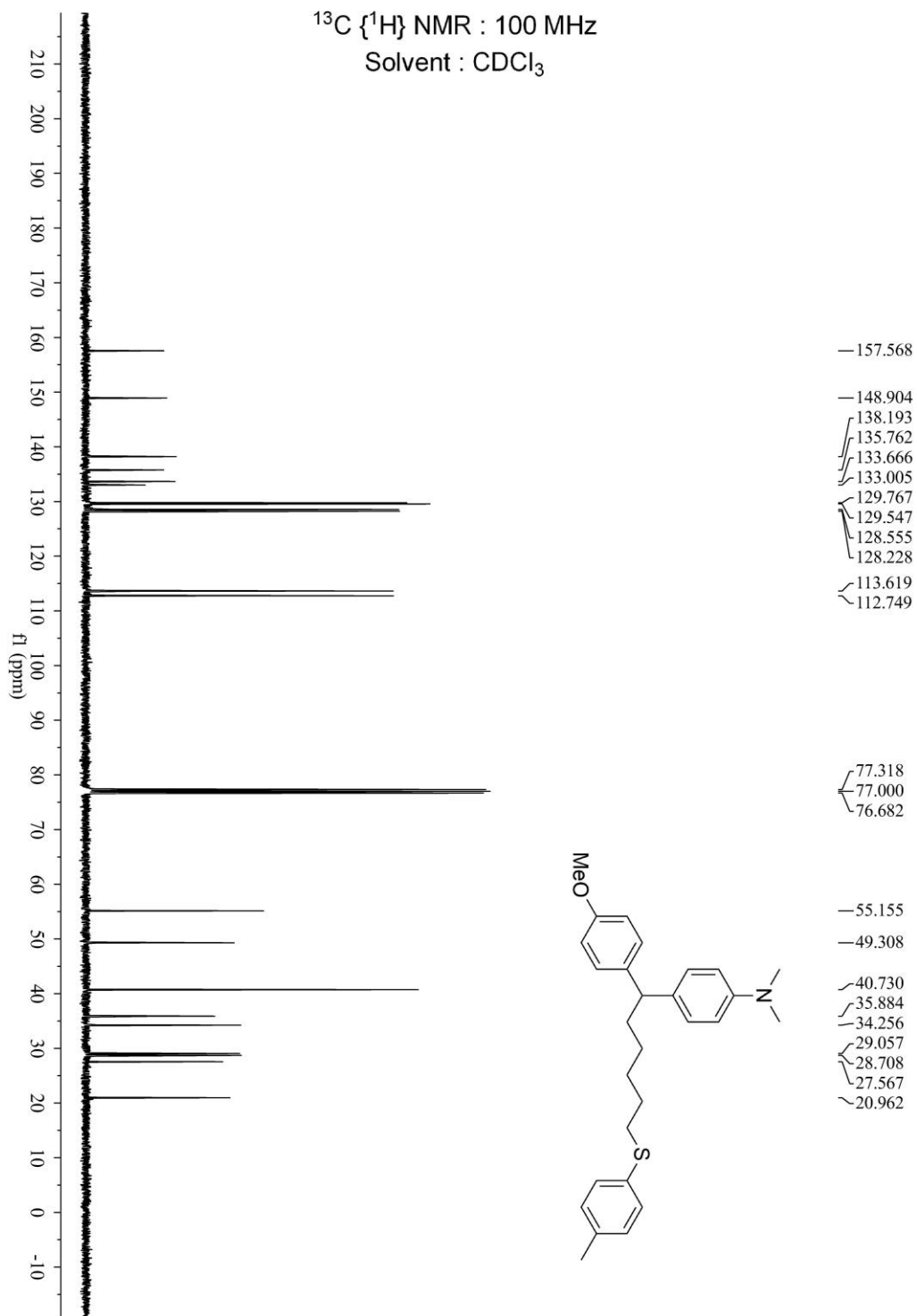
4-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-*N,N*-dimethylaniline (4aaw)

¹H NMR : 400 MHz

Solvent : CDCl₃



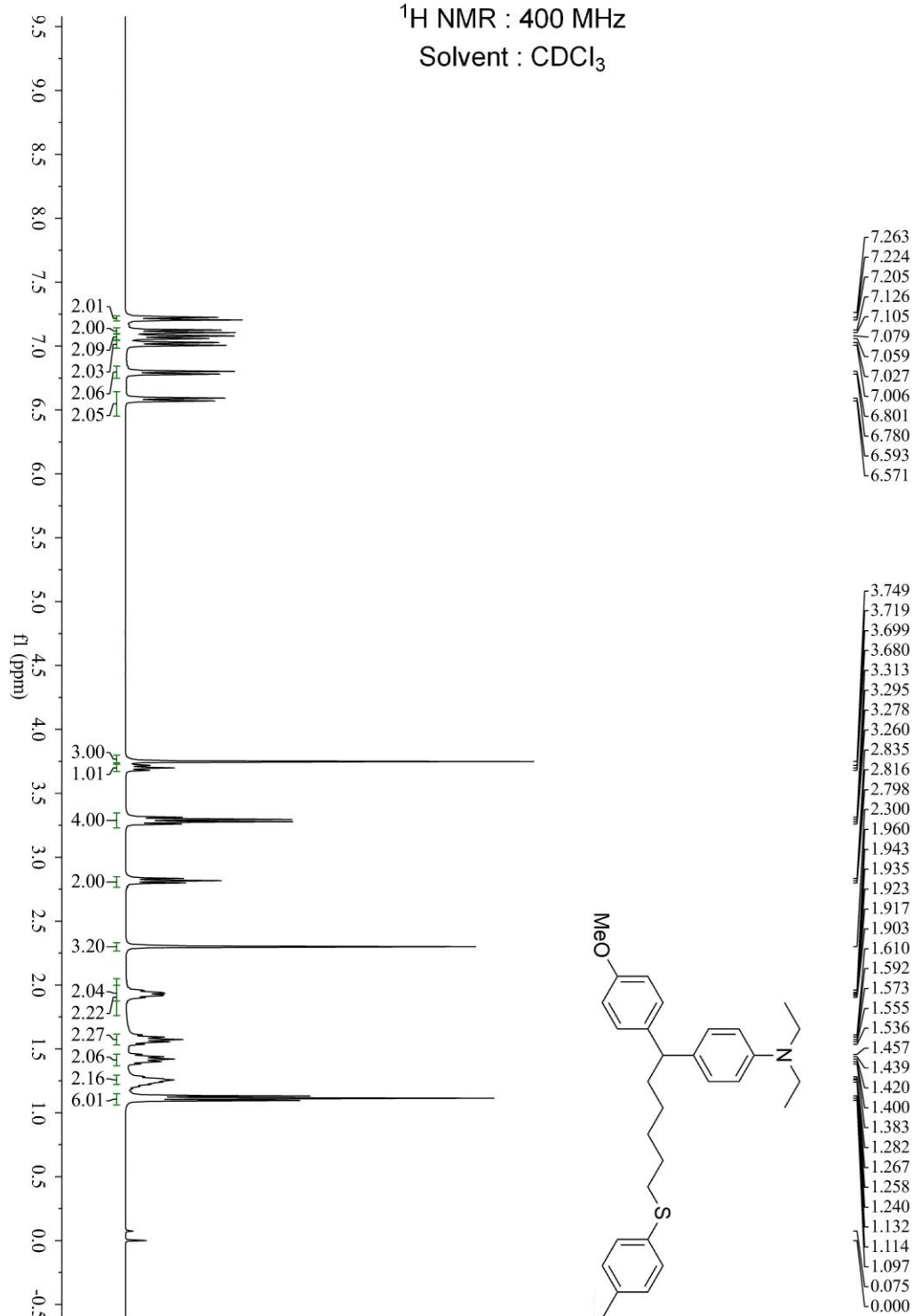
^{13}C $\{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



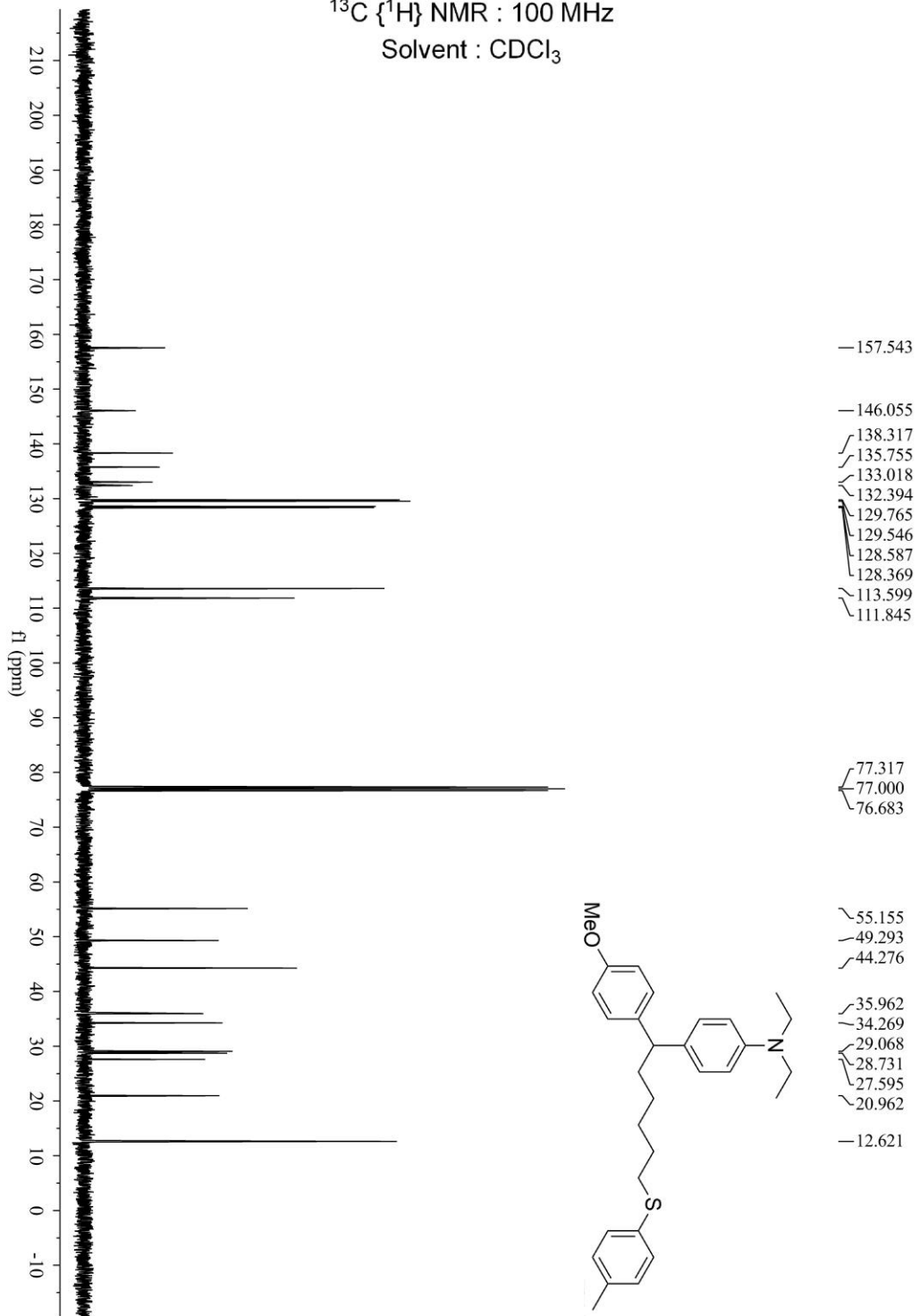
***N,N*-Diethyl-4-(1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexyl)aniline (4aax)**

¹H NMR : 400 MHz

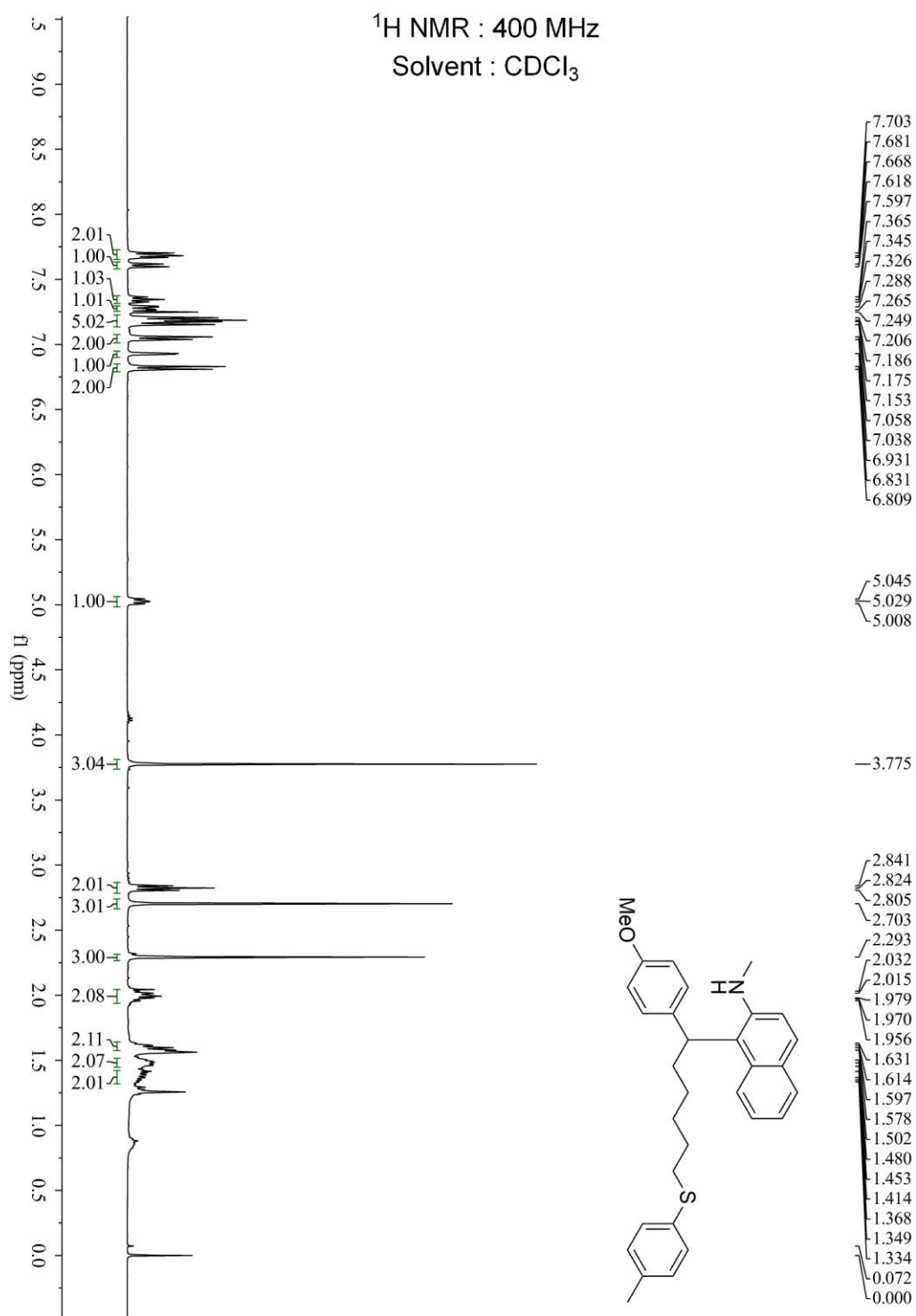
Solvent : CDCl₃



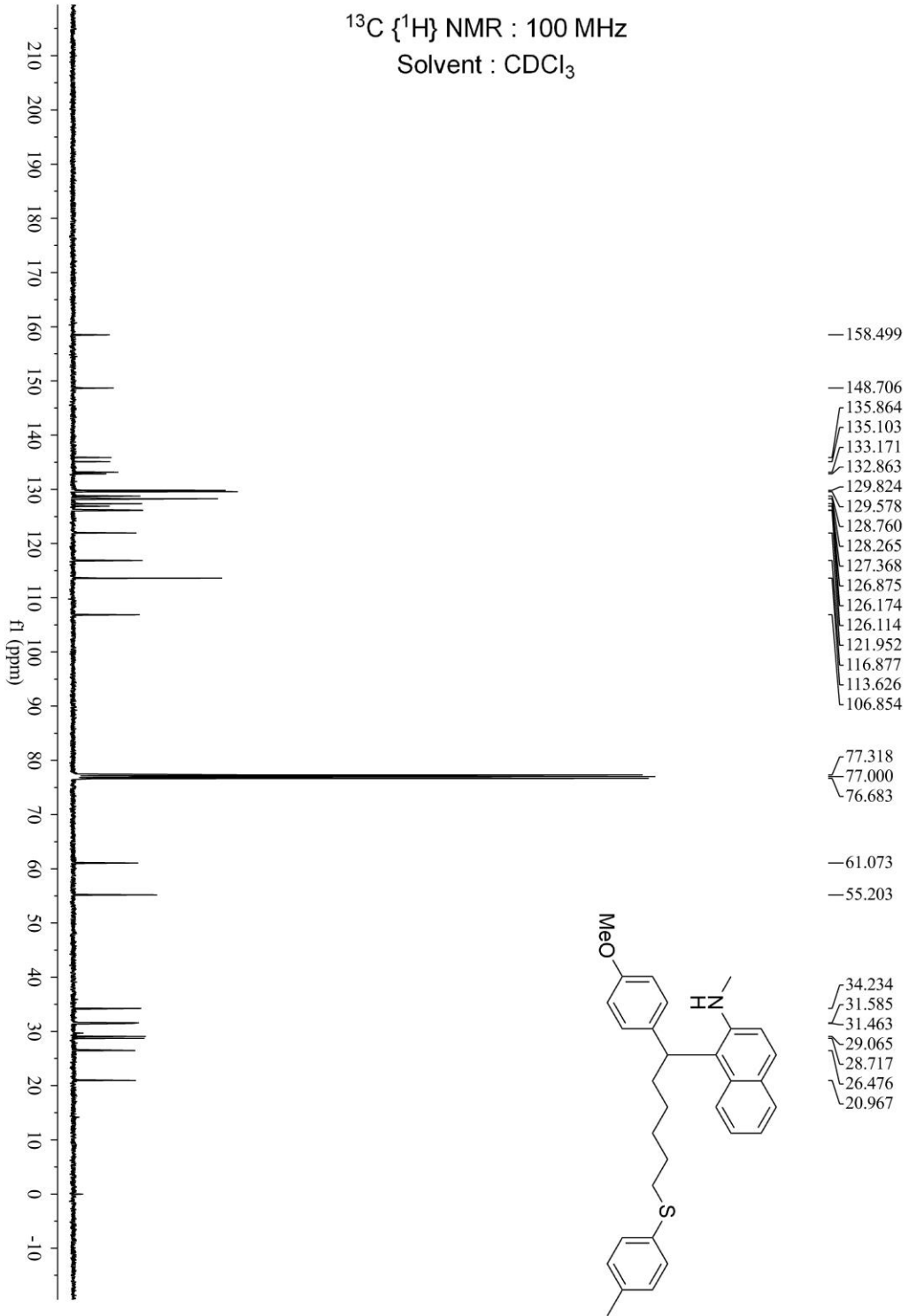
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



**1-(1-(4-Methoxyphenyl)-6-(*p*-tolylthio)hexyl)-*N*-methylnaphthalen-2-amine
(4aay)**



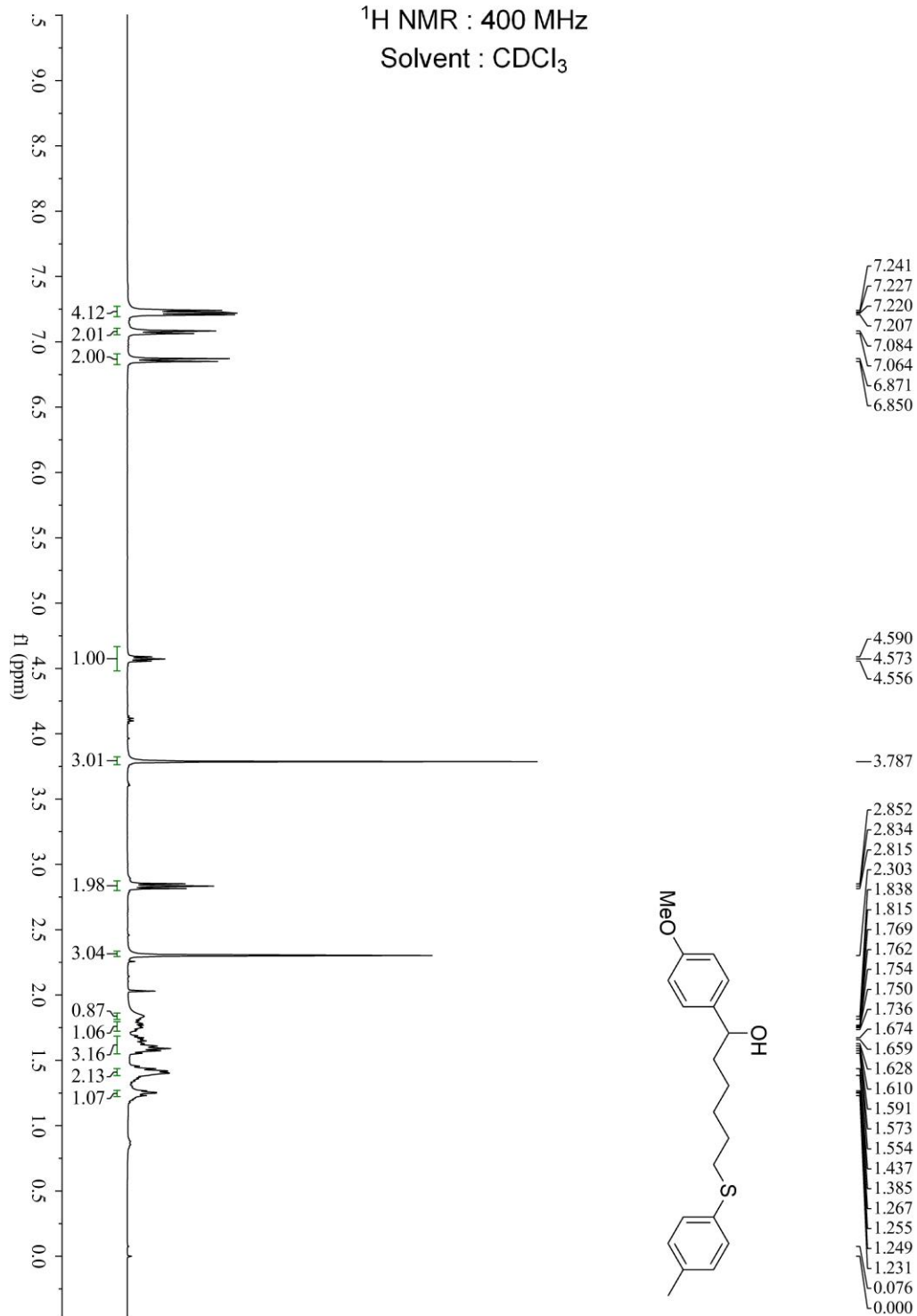
$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3



1-(4-methoxyphenyl)-6-(*p*-tolylthio)hexan-1-ol

$^1\text{H NMR}$: 400 MHz

Solvent : CDCl_3



$^{13}\text{C} \{^1\text{H}\}$ NMR : 100 MHz
Solvent : CDCl_3

