Supporting Information

Light/copper catalysis 1,2-alkylarylation of allylic alcohols with sulfonium salts involving radical 1,2-aryl migrations

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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. ^{1}H 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 quated in Hz. The solvent peak was used as a reference value, for ^{1}H 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).

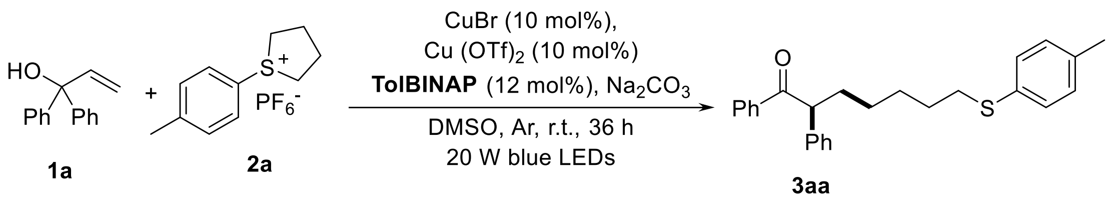
2. Experiment Section

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 1,1-diphenylprop-2-en-1-ol **1a** (0.2 mmol, 26.8 mg), sulfonium salt **2a** (2 equiv., 0.4 mmol, 129.6 mg), $Cu(OTf)_2$ (10 mol%, 7.2 mg), Na_2CO_3 (3 equiv., 0.6 mmol, 63.6 mg), CuBr (10 mol%, 2.9 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 = 150 : 1) to afford the desired products.

2.3 Additional experimental details

The light source bought from SANYI (https://item.taobao.com/item.htm?_u=u10503hgcbe1&id=597700668537&spm=a1z09.2.0.0.1f8a2e8dVdegb2&skuId=4812351826113), 20 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:

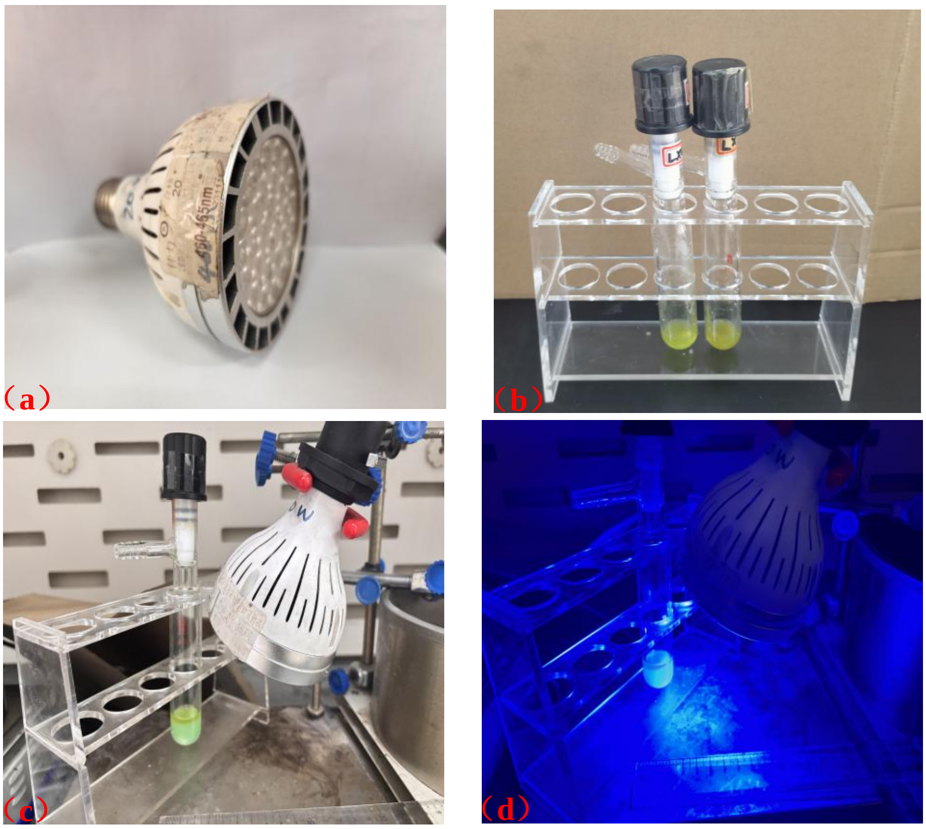
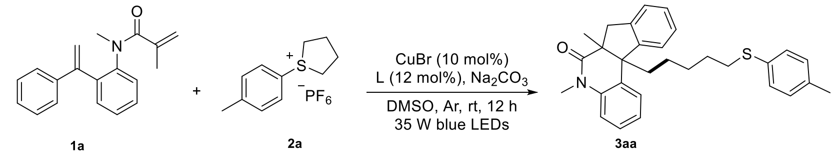
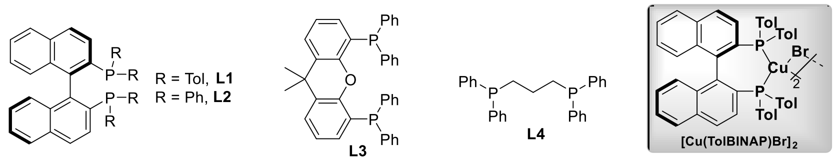


Figure S1. **The light source and photographs of experimental setup: (a) 20 W blue LEDs. (b) Irradiation vial.; (c) The distance from the Blue LED to the vial. (d) Reaction setup.**

2.4 Table S1. Screening of the Optimal Reaction Conditions[a]



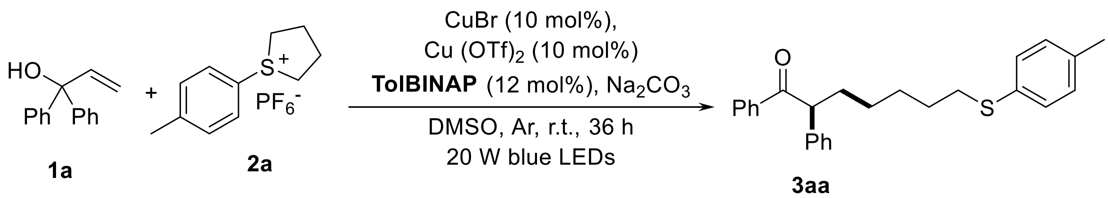


entry	variation from the standard conditions	yield (%)
1	none	65
2	$FeCl_3$ instead of $Cu(OTf)_2$	55
3	$CuBr_2$ instead of $Cu(OTf)_2$	62
4	$In(OTf)_3$ instead of $Cu(OTf)_2$	50
5	$Yb(OTf)_3$ instead of $Cu(OTf)_2$	57
6	without $Cu(OTf)_2$ and 20 mol% CuBr	35
7	CuCl or $Cu(CH_3CN)_4PF_6$ instead of CuBr	28-45
8	**L2** instead of **L1**	38
9	**L3 - L4** instead of **L1**	0
10	K_3PO_4 instead of Na_2CO_3	39
11	Na_2HPO_4 instead of Na_2CO_3	35
12	$^{i}Pr_2NEt$ instead of Na_2CO_3	39
13	$NaO^{t}Bu$ instead of Na_2CO_3	0
14	DMF instead of DMSO	40
15	NMP instead of DMSO	37
16	DCE instead of DMSO	0
17	at 40 ^{o}C	61
18	24 h instead of 36 h	54
19	48 h instead of 36 h	67
20	12 W instead of 20 W	32
21	35 W instead of 20 W	62
22	without CuBr or **L,** In dark (without light)	0
23[b]	none	61
24[c]	none	59

[a] Standard reaction conditions: 1a (0.2 mmol), 2a (0.4 mmol), CuBr (10 mol%), TolBINAP (12 mol%), $Cu(OTf)_2$ (10 mol%), Na_2CO_3 (3 equiv.), DMSO (2 mL; 0.1 M), argon, 20 W blue LEDs, room temperature and 36 h. [b] 1 mmol scale reaction. [c] 10 mol% $[Cu(TolBINAP)Br]_2$ instead of (CuBr/L).

Initially, we examined the reaction of *a*,*a*-diphenylprop-2-en-1-ol **1a** and sulfonium salt **2a** under the visible-light-induced copper catalysis conditions. As shown in Table 1, several lewis acids, including $FeCl_3$, $CuBr_2$, $In(OTf)_3$, and $Yb(OTf)_3$ were investigated in the presence of 10 mol% CuBr, 12 mol% TolBINAP and 3.0 equiv. of Na_2CO_3 in DMSO provided 1,2-diphenyl-7-(*p*-tolylthio)heptan-1-one **3aa** in 50-62% yields (entries 2-5). The control experiment shows that lewis acid $Cu(OTf)_2$ is crucially for the improvement of the reaction yield, the yield is only 35% when lewis acid is not added (entry 6). Other copper(I) salts including CuCl, and $Cu(CH_3CN)_4PF_6$ were then tested for this transformation, and the CuBr was found to be the optimal copper catalyst (entry 7). Subsequently, the ligands such as *rac*-BINAP **L2**, xantphos **L3**, and dppp **L4**, were employed instead of **L1** and all of them had a negative influence on the reaction efficiency (entries 8-9). We observed a strong absorbance peak at 350-450 nm in the UV-vis absorption spectra of CuBr/**L1** complexes and weak absorption peak of CuBr/**L2** complexes. There was absolutely no absorption in this wavelength range of the complexes formed from ligand **L3** or **L4** with CuBr. This was a possible reason for the high reaction conversion efficiency by employing the CuBr/**L1** complex as a photoredox. A screening study on different bases showed that Na_2CO_3 was superior to K_3PO_4, Na_2HPO_4, $^i Pr_2NEt$ and NaO^tBu (entries 10-13). Subsequently, the effect of reaction solvents including DMF, NMP and DCE were tested, and DMSO exhibited higher reaction efficiency (entries 14-16). And then, the effect of reaction temperatures (entry 17) and reaction times (entries 18-19) were also investigated. The results indicated that room temperature and 36 h were found to be the best choices. Next, we found that reducing or increasing light power could disadvantage the yield of the transformation, and 20 W was most efficient, delivering the desired product **3aa** in 65% isolated yield (entry 1 *vs* entries 20-21). In addition, no reaction can be performed without the copper salt, ligand or in dark (without light) (entry 22). A light on/off experiment results further explanation that continuous blue LEDs irradiation was necessary for this transformation (see the Supporting Information Figure S2 for details). To our satisfactory, the desired product 1,2-diphenyl-7-(*p*-tolylthio)heptan-1-one **3aa** could be isolated in 61% yield when the reaction was scaled up to 1 mmol scale (entry 23). Finally, we employing the copper(I)-based complexes $[Cu(TolBINAP)Br]_2$ was used as a photoredox catalyst instead of CuBr/**L**, could offer the desired product 6-keto-functionalized thioethers in 59% yield (entry 24).

2.5 The Light On/Off Experiments



Time/h	0	4 (on)	8 (off)	12 (on)	16 (off)	20 (on)
Yield/%	0	24	24	46	46	65

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.

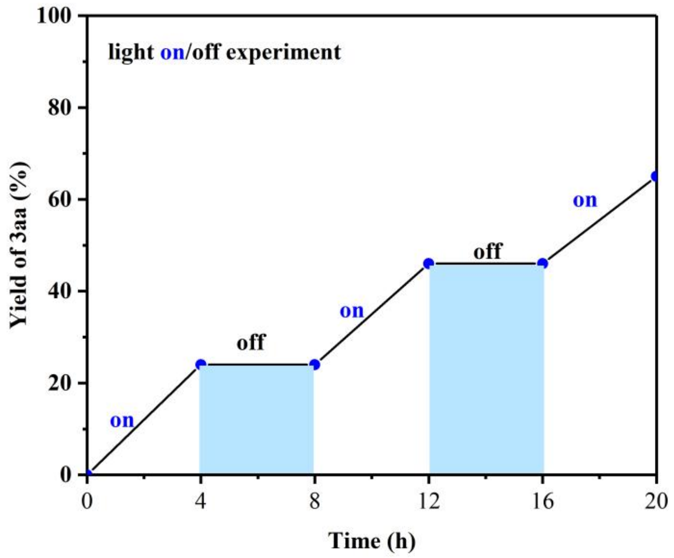


Figure S2 The light on/off Experiments

2.6 UV-Vis absorption experiments

(Copied from *Adv. Synth. Catal.* 2024, 366, 3868-3874)

UV-visible spectroscopy of reaction solution was recorded on a UV-2600 UV-Vis spectrophotometer. The sample was prepared by sulfonium salt **1a** (10^{-4} M), styrene **2a** (10^{-4} M), CuBr (10^{-4} M), TolBINAP (10^{-4} M), $[Cu(TolBINAP)Br]_2$ (10^{-4} M) in DMSO. The absorption was collected and the result was listed in Figure S3.

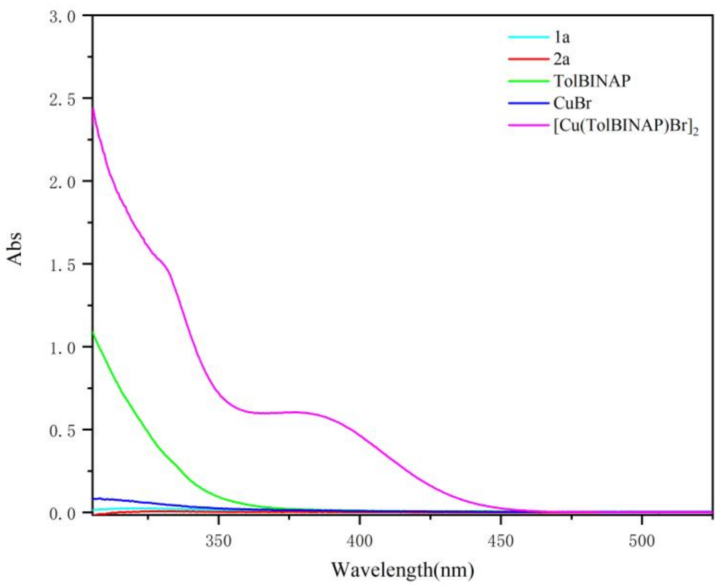


Figure S3 UV-Vis absorption experiments

The sample was prepared by sulfonium salt TolBINAP (10^{-3} M), $[Cu(TolBINAP)Br]_2$ (10^{-3} M), RacBINAP (10^{-3} M), $[Cu(RacBINAP)Br]_2$ (10^{-3} M), Xantphos (10^{-3} M), CuBr+Xantphos (10^{-3} M), DPPP (10^{-3} M), CuBr+DPPP (10^{-3} M)in DMSO. The absorption was collected and the result was listed in Figure S5.

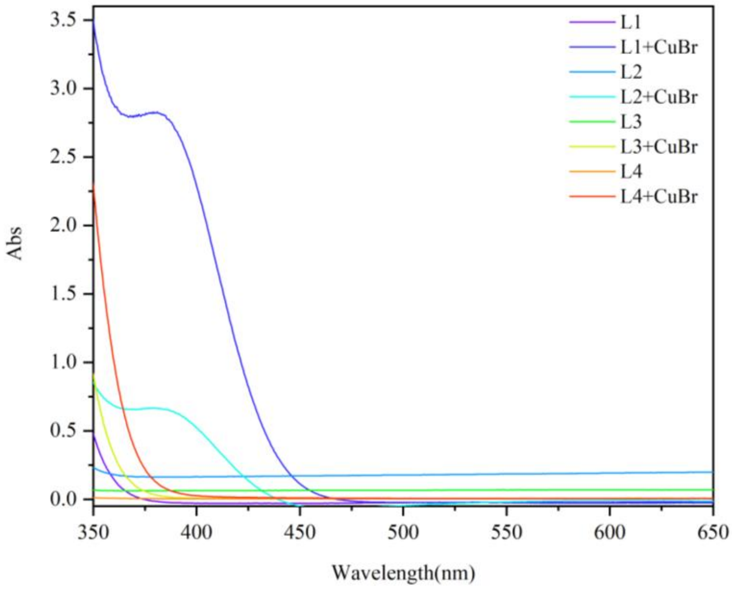


Figure S4 UV-Vis absorption experiments of Ligand and catalyst

2.7 Cyclic Voltammetry (CV) Experiments

(Copied from *Adv. Synth. Catal.* 2024, 366, 3868-3874)

Cyclic Voltammetry was performed on a CH Electrochemical Workstation model CHI760E. A solution of the sample in DMSO was tested with 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte, using a glassy carbon as the working electrode, a Pt as the counter electrode, and a Ag/AgCl as reference electrode. Scan rate = 100 mV/s. All measurements were carried out at room temperature.

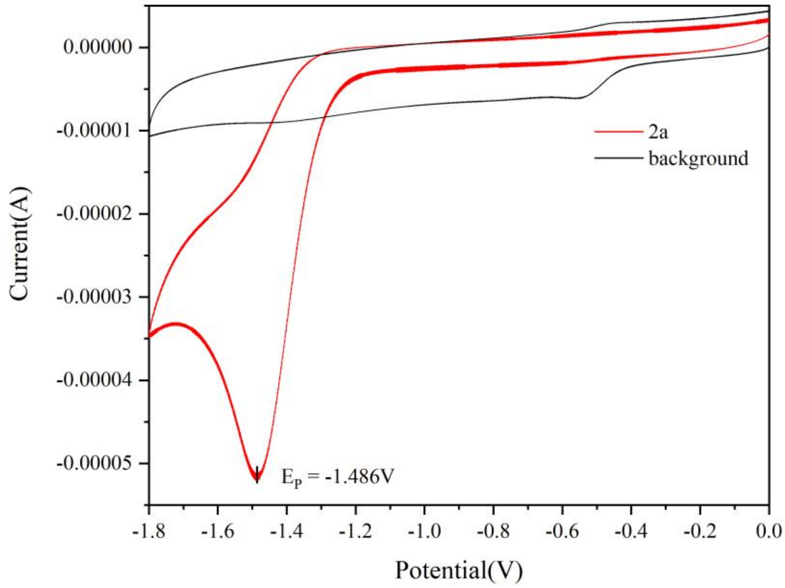


Figure S5 CV spectra of sulfonium salt 1a (0.01 M) in 0.1 M tetrabutylammonium tetrafluoroborate in DMSO.

Ep = −1.486 V (vs. Ag/AgCl)

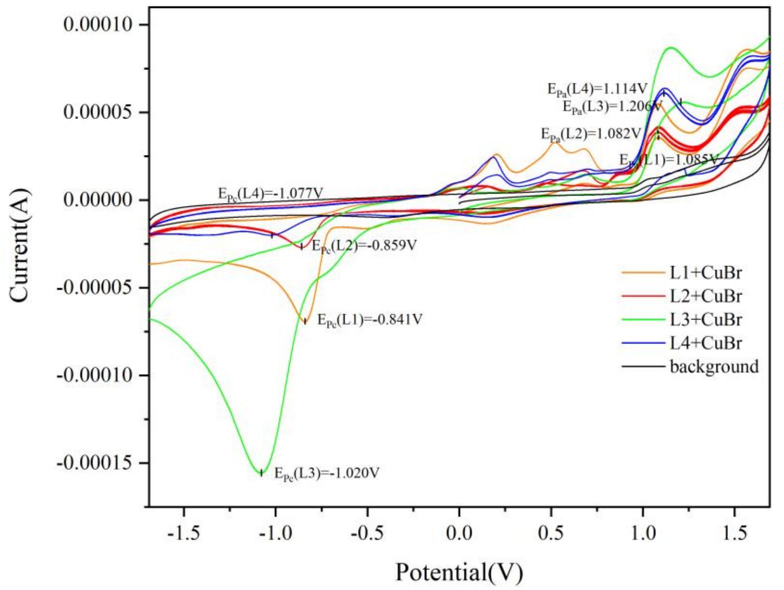


Figure S6. CV spectra of the copper-based photocatalyst catalyst (1 mM) in 0.1 M tetrabutylammonium tetrafluoroborate in DMSO.

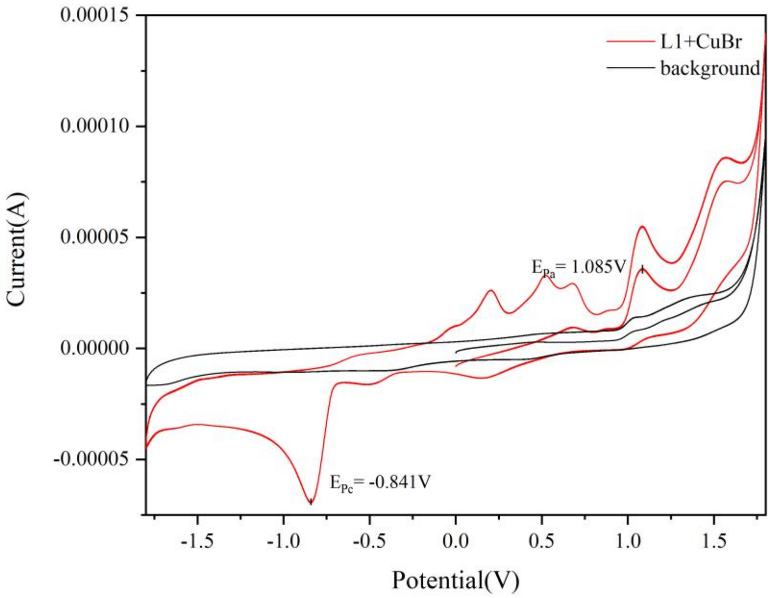


Figure S7. CV spectra of the copper-based photocatalyst [Cu(TolBINAP)Br]2 (1 mM) in 0.1 M tetrabutylammonium tetrafluoroborate in DMSO.

According to the emission spectra of the copper-based photocatalyst $[Cu(TolBINAP)Br]_2$, the maximum emission wavelength is 558 nm.

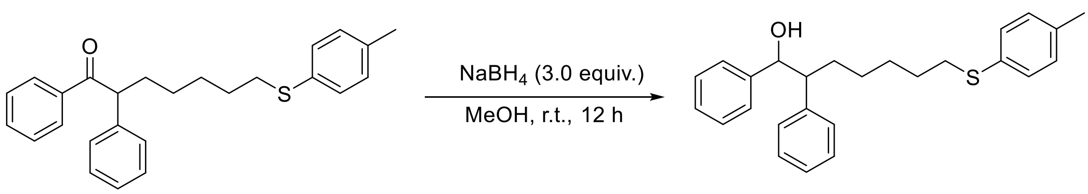
$$E_{1/2}(Cu^{II}/Cu^{I}) = 0.122V$$

$$E_{0\text{-}0} = hv = \frac{hc}{\lambda} = 2.22V$$

$$E_{1/2}(Cu^{II}/Cu^{I*}) = E_{1/2}(Cu^{II}/Cu^{I}) - E_{0\text{-}0} = 0.122 - 2.22 = -2.098V$$

Where h (J·s) is Planck's constant, c (m s^{-1}) is the speed of light and $\boldsymbol{\lambda}$ (m) is themaximum emission wavelength.

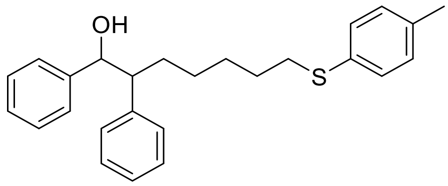
2.8 Product Derivatization[2][3]



3aa **4**, 84%

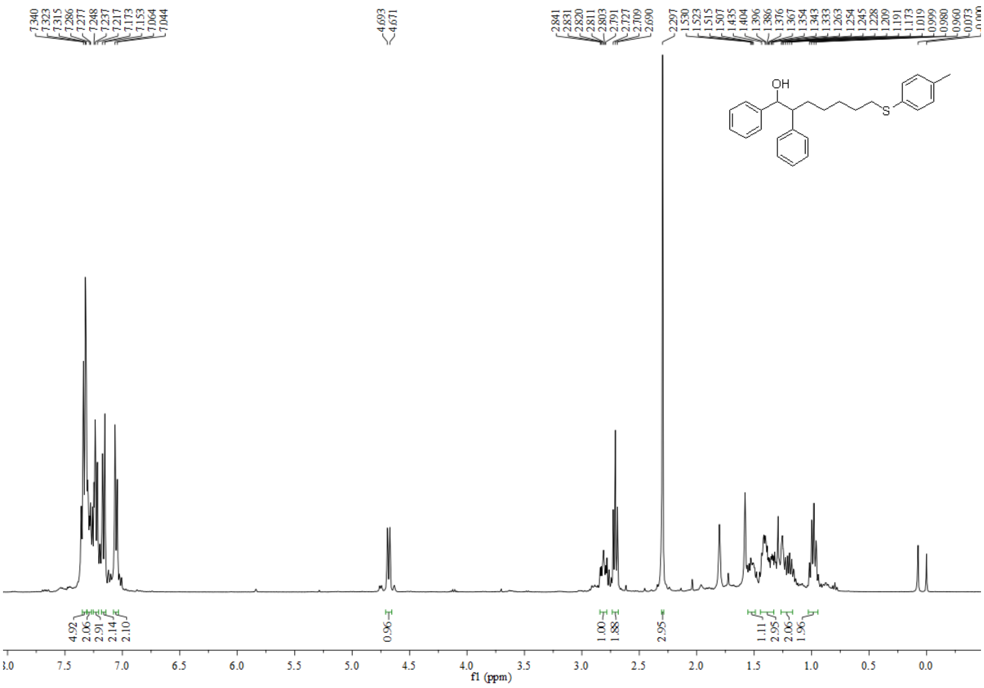
To a stirred solution of **3aa** (77.6 mg, 0.2 mmol) in 1 mL methanol was added $NaBH_4$ (21.6 mg, 0.6 mmol, 3.0 equiv.) at room temperature. Then the reaction was kept stirring at room temperature for 12 h. The crude product was further purified by silica gel flash chromatography to give **4** in yield of 84% as yellow oil.

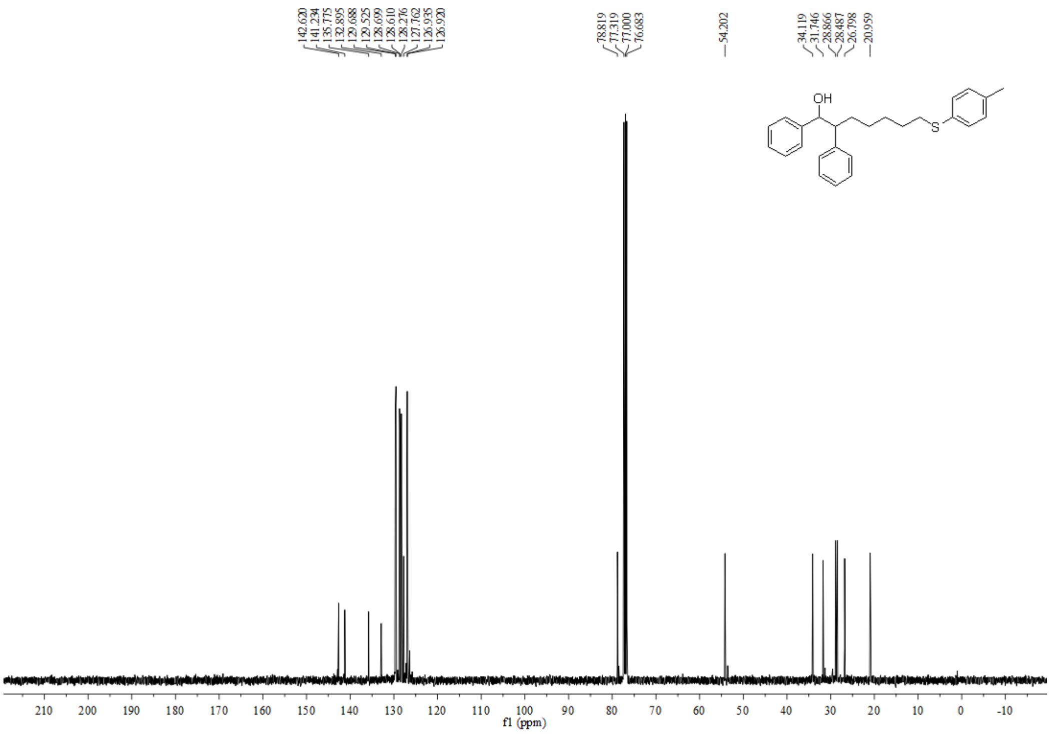
1,2-diphenyl-7-(*p*-tolylthio)heptan-1-ol: Yield: 65.5 mg, 84%; [1]H NMR (400 MHz,

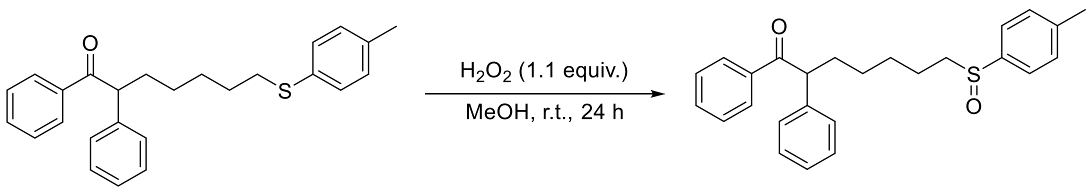


$CDCl_3$) δ 7.36 - 7.29 (m, 6H), 7.33 – 7.25 (m, 1H), 7.27 – 7.19 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 4.68 (d, *J* = 8.5 Hz, 1H), 2.82 (m, *J* = 8.2, 4.3 Hz, 1H), 2.71 (t, *J* = 7.3 Hz, 2H), 2.30 (s, 4H), 1.52 (m, *J* = 8.0, 5.1 Hz, 1H), 1.46 – 1.31 (m, 2H), 1.29 – 1.15 (m, 1H), 0.99 (m, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 141.2, 135.8, 132.9, 129.7, 129.5, 128.7, 128.6, 128.3, 127.8, 126.9, 126.9, 78.8, 54.2, 34.1, 31.7, 28.9, 28.5, 26.8, 21.0. HRMS (ESI-TOF) m/z: $C_{26}H_{31}OS^+$ (M + H)+ calcd for 391.5295, found 391.5260.

1,2-diphenyl-7-(*p*-tolylthio)heptan-1-ol (4)





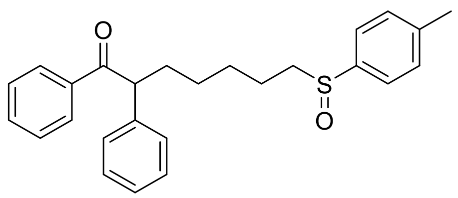


3aa **5**, 65%

To a stirred solution of **3aa** (77.6 mg, 0.2 mmol) in 1 mL methanol was added H_2O_2 (30% in water, 0.017 ml, 0.22 mmol, 1.1 equiv.) at room temperature. Then the reaction was kept stirring at room temperature for 24 h. The crude product was further purified by silica gel flash chromatography to give **5** in yield of 65% as yellow oil.

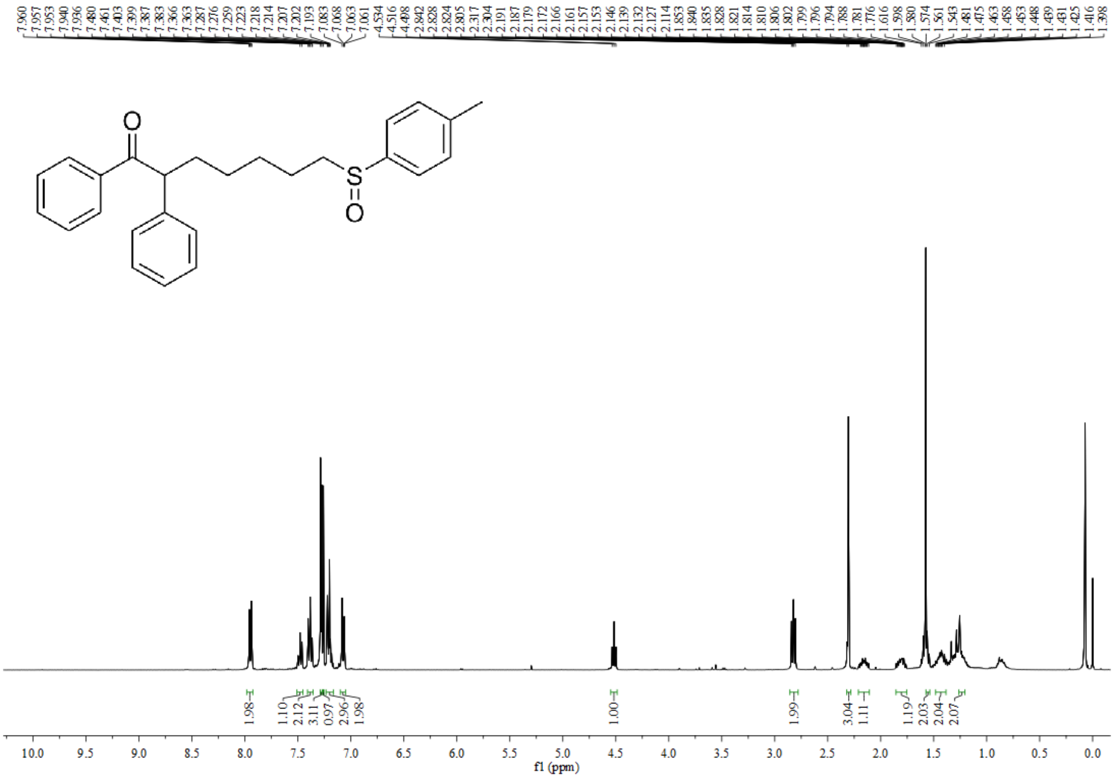
The date and NMR spectra of 5.

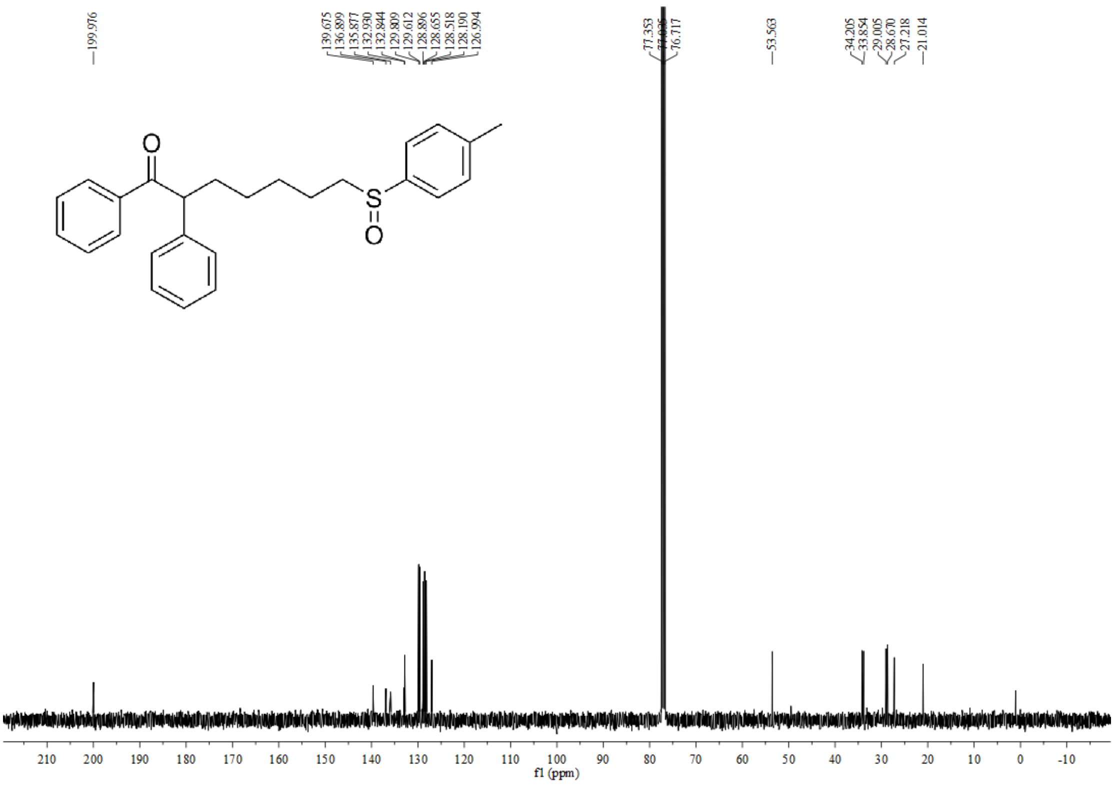
1,2-diphenyl-7-(*p*-tolylsulfinyl)heptan-1-one: Yield: 52.5 mg, 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.51 – 7.45 (m, 1H), 7.38 (m, *J* = 8.3, 6.8 Hz, 2H), 7.28 (d, *J* = 4.3 Hz, 3H), 7.23 – 7.17 (m, 3H), 7.07 (d, *J* = 7.8 Hz, 2H), 4.52 (t, *J* = 7.3 Hz, 1H), 2.82 (t, *J* = 7.6 Hz, 1H), 2.30 (s, 3H), 2.21 - 2.11 (m, 1H), 1.86 - 1.76 (m, 1H), 1.57-1.54 (m, 2H), 1.48 - 1.38 (m, 2H), 1.26 - 1.20 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 139.7, 136.9, 135.9, 132.9, 132.8, 129.8, 129.6, 128.9, 128.7, 128.5,

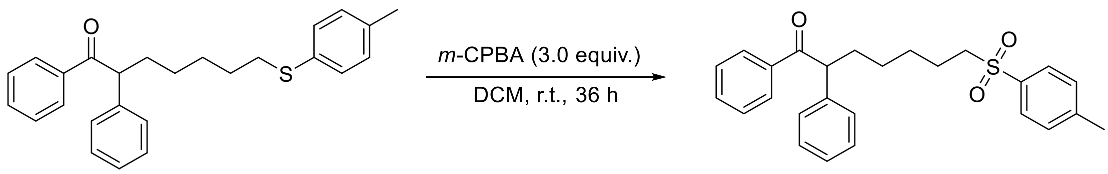


128.2, 127.0, 53.6, 34.2, 33.9, 29.0, 28.7, 27.2, 21.0. HRMS (ESI-TOF) m/z: $C_{26}H_{29}O_2S^+$ (M + H)+ calcd for 405.5755, found 405.5750.

1,2-diphenyl-7-(p-tolylsulfinyl)heptan-1-one (5)





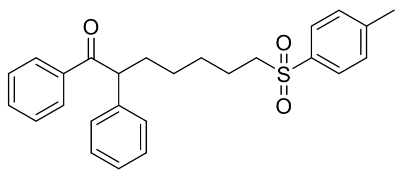


3aa **6**, 92%

To a stirred solution of **3aa** (77.6 mg, 0.2 mmol) in 1 mL CH_2Cl_2 was added *m*-CPBA (0.1032 g, 0.6 mmol, 3.0 equiv.) at room temperature. Then the reaction was kept stirring at room temperature for 36 h. The reaction was then quenched with saturated 10 mL Na_2SO_3, extracted with 10 mL DCM, washed with saturated Na_2SO_3, 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** (92% yield) as yellow oil.

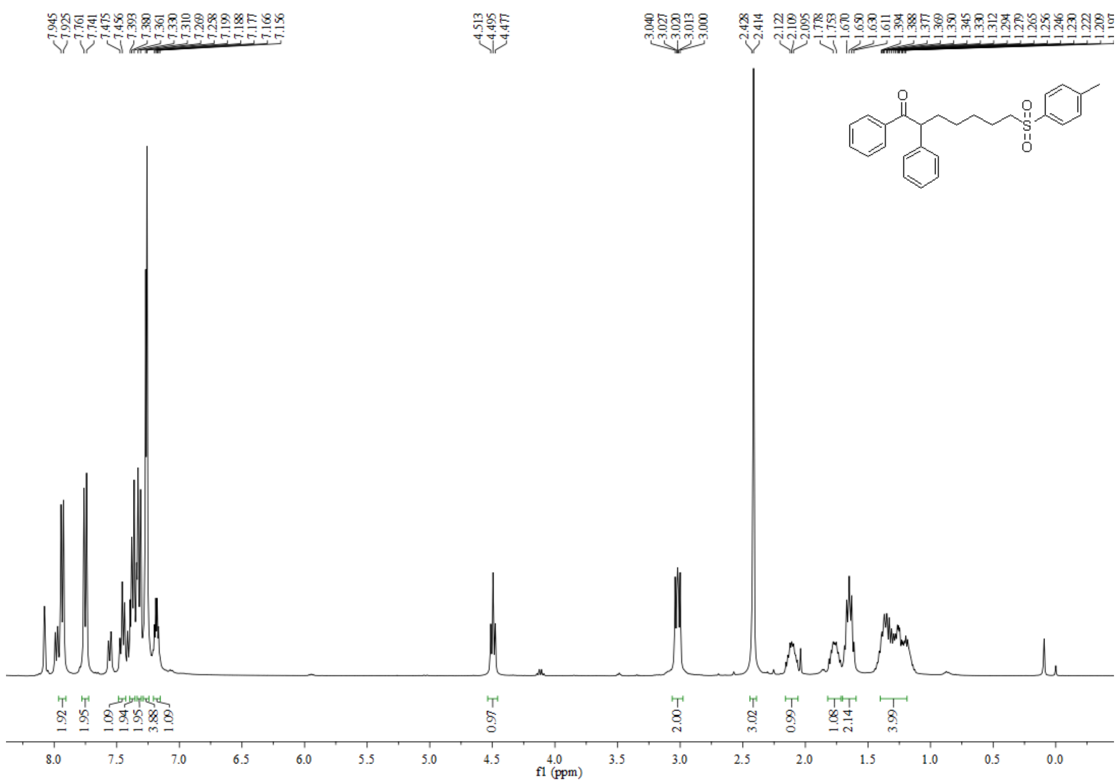
The date and NMR spectra of 6.

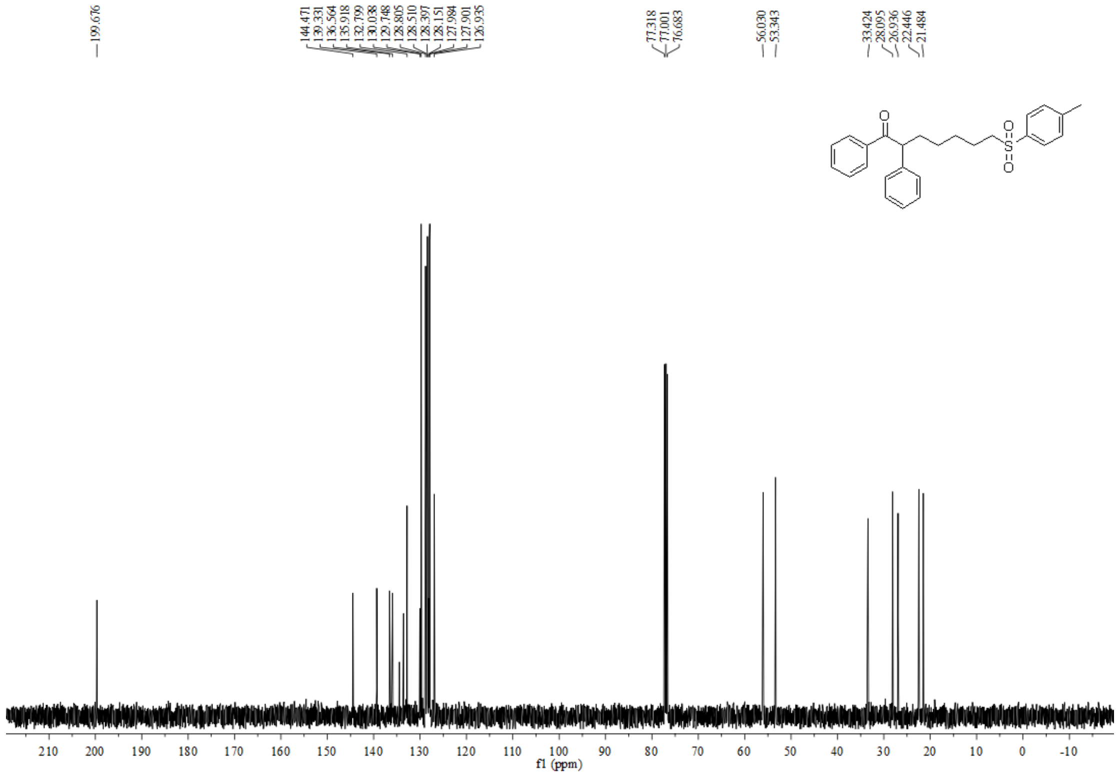
1,2-diphenyl-7-tosylheptan-1-one:Yield: 77.3 mg, 92%; ^{1}H NMR (400 MHz, $CDCl_3$)



δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 4.4 Hz, 4H), 7.18 (m, *J* = 8.7, 4.3 Hz, 1H), 4.49 (t, *J* = 7.2 Hz, 1H), 3.06 - 2.98 (m, 2H), 2.41 (s, 3H), 2.16 - 2.06 (m, 1H), 1.82 - 1.71 (m, 1H), 1.70 - 1.59 (m, 2H), 1.40 - 1.19 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 144.5, 139.3, 136.6, 135.9, 132.8, 130.0, 129.7, 128.8, 128.5, 128.4, 128.2, 128.0, 127.9, 126.9, 56.0, 53.3, 33.4, 28.1, 26.9, 22.4, 21.5. HRMS (ESI-TOF) m/z: $C_{26}H_{29}O_3S^+$ (M + H)+ calcd for 421.5745, found 421.5743.

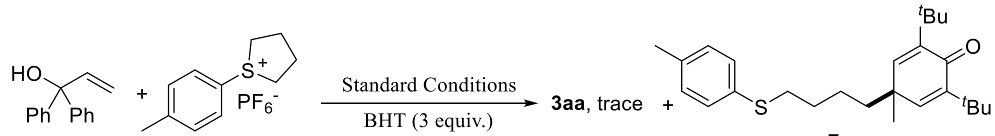
1,2-diphenyl-7-tosylheptan-1-one (6)





2.9 Control Experiments

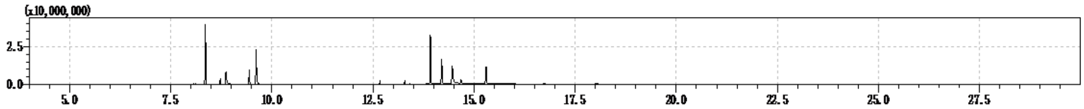
2.9.1 GC-MS Analysis of trapping product 7[4]

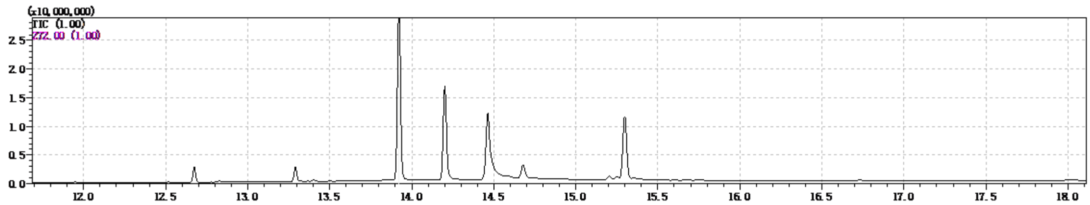


1a **2a** **7**

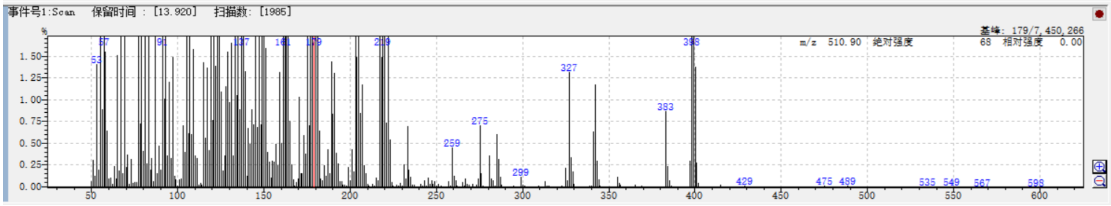
Chemical Formula: $C_{26}H_{38}OS$
Exact Mass: 398.2643
Molecular Weight: 398.6490

The GC spectra of raw reaction mixture





The MS spectra of the peak at 15.955 min



[MS Spectrum]
# of Peaks 543
Raw Spectrum 13.920 (scan : 1985)
Background No Background Spectrum
Base Peak m/z 179.00 (Inten : 7,450,266)
Event# 1

m/z	Absolute Intensity	Relative Intensity						
50.00	5127	0.07	58.05	115737	1.55	67.00	135236	1.82
51.00	23479	0.32	59.00	48215	0.65	68.05	12371	0.17
52.05	9562	0.13	59.95	7261	0.10	69.05	205298	2.76
53.05	105605	1.42	60.95	8161	0.11	70.00	17546	0.24
54.05	15363	0.21	61.95	3214	0.04	71.00	28306	0.38
55.05	823758	11.06	63.00	18161	0.24	72.05	3260	0.04
56.15	66667	0.89	64.05	7231	0.10	73.00	24439	0.33
57.05	2487554	33.39	65.00	113188	1.52	74.00	3838	0.05
			66.05	14498	0.19	75.00	4686	0.06

76.05	4733	0.06	120.10	57358	0.77	164.05	166177	2.23
77.00	200215	2.69	121.05	367697	4.94	165.00	56932	0.76
78.05	54757	0.73	122.05	103552	1.39	166.05	19635	0.26
79.05	291957	3.92	123.00	614695	8.25	167.00	6791	0.09
80.05	31178	0.42	124.00	211346	2.84	167.60	1521	0.02
81.05	151119	2.03	125.05	81874	1.10	168.65	4432	0.06
82.05	20221	0.27	126.05	14457	0.19	169.65	7264	0.10
83.05	161686	2.17	127.05	27150	0.36	170.55	77393	1.04
84.05	14891	0.20	128.05	86287	1.16	171.55	12484	0.17
85.00	25142	0.34	129.05	115682	1.55	171.95	11970	0.16
86.05	5244	0.07	130.05	72801	0.98	173.00	44876	0.60
87.00	150226	2.02	131.05	123554	1.66	174.05	28550	0.38
88.00	12486	0.17	132.05	27382	0.37	175.05	250130	3.36
89.00	35756	0.48	133.05	253996	3.41	176.05	53409	0.72
90.05	15257	0.20	134.05	78747	1.06	177.05	368493	4.95
91.05	567868	7.62	135.05	272075	3.65	178.05	472448	6.34
92.05	75727	1.02	136.05	66998	0.90	179.00	7450266	100.00
93.05	226217	3.04	137.00	2017598	27.08	180.00	1093468	14.68
94.05	27419	0.37	138.00	215052	2.89	181.00	432292	5.80
95.05	90144	1.21	139.00	99084	1.33	182.00	48754	0.65
96.05	25129	0.34	140.00	9655	0.13	183.00	7799	0.10
97.05	111430	1.50	141.00	50634	0.68	184.05	5964	0.08
98.05	9750	0.13	142.00	37218	0.50	185.00	18593	0.25
99.00	6702	0.09	143.05	66574	0.89	186.00	9516	0.13
100.00	1702	0.02	144.05	53423	0.72	187.00	32782	0.44
101.00	6498	0.09	145.05	147162	1.98	188.05	12152	0.16
102.05	7660	0.10	146.05	51221	0.69	189.00	107790	1.45
103.05	52914	0.71	147.05	206961	2.78	190.00	62778	0.84
104.05	30581	0.41	148.05	53474	0.72	191.05	97978	1.32
105.05	350938	4.71	149.05	248645	3.34	192.00	29370	0.39
106.05	46474	0.62	150.05	184701	2.48	192.95	20756	0.28
107.05	187465	2.52	151.00	118674	1.59	194.00	5271	0.07
108.05	45450	0.61	152.00	30444	0.41	194.95	5082	0.07
109.05	118565	1.59	153.00	22249	0.30	195.90	1974	0.03
110.05	27574	0.37	154.05	8184	0.11	197.00	2250	0.03
111.05	25335	0.34	155.00	22446	0.30	198.00	1478	0.02
112.10	2599	0.03	156.05	22193	0.30	199.05	17779	0.24
113.10	3817	0.05	157.00	37394	0.50	200.05	6163	0.08
114.05	2180	0.03	158.00	18978	0.25	201.00	32852	0.44
115.05	107041	1.44	159.00	98162	1.32	202.05	13418	0.18
116.05	42066	0.56	160.05	37643	0.51	203.05	497133	6.67
117.05	102294	1.37	161.00	769124	10.32	204.00	111244	1.49
118.10	31502	0.42	162.05	151776	2.04	205.05	372653	5.00
119.05	317982	4.27	163.00	633465	8.50	206.05	63476	0.85

206.95	87619	1.18	250.95	3036	0.04	295.00	1172	0.02
207.95	19310	0.26	251.90	1084	0.01	296.05	399	0.01
208.95	11935	0.16	252.95	1601	0.02	297.10	570	0.01
209.95	2793	0.04	253.95	484	0.01	298.05	502	0.01
211.00	1884	0.03	255.00	761	0.01	299.00	9180	0.12
212.00	902	0.01	256.05	730	0.01	300.00	2566	0.03
213.00	2903	0.04	257.05	5253	0.07	301.00	1818	0.02
213.95	1389	0.02	258.15	1491	0.02	302.05	951	0.01
215.05	8029	0.11	259.05	34173	0.46	303.00	367	0.00
216.05	5809	0.08	260.05	9876	0.13	304.00	158	0.00
217.05	156154	2.10	261.10	5980	0.08	305.00	170	0.00
218.05	111531	1.50	262.05	1417	0.02	306.00	76	0.00
219.05	534384	7.17	263.05	870	0.01	307.05	639	0.01
220.05	331508	4.45	263.95	358	0.00	308.00	143	0.00
221.05	55306	0.74	264.95	4559	0.06	309.05	1184	0.02
222.10	243238	3.26	266.00	1585	0.02	309.95	318	0.00
223.05	40891	0.55	266.95	7905	0.11	310.85	706	0.01
224.05	4291	0.06	268.00	2770	0.04	312.05	392	0.01
225.00	1446	0.02	269.00	2498	0.03	313.05	5293	0.07
226.05	1071	0.01	269.95	524	0.01	314.00	1434	0.02
227.00	1950	0.03	271.00	3223	0.04	315.00	1338	0.02
227.95	1351	0.02	272.10	798	0.01	316.00	399	0.01
229.00	3462	0.05	273.10	2146	0.03	317.00	218	0.00
230.00	1841	0.02	274.15	7260	0.10	318.00	209	0.00
231.05	19940	0.27	275.15	52900	0.71	319.00	98	0.00
232.05	7400	0.10	276.10	12335	0.17	320.00	68	0.00
233.10	52145	0.70	277.05	1743	0.02	321.00	140	0.00
234.05	15327	0.21	278.00	295	0.00	321.90	52	0.00
235.00	9234	0.12	279.00	737	0.01	322.95	1688	0.02
236.05	1933	0.03	279.95	319	0.00	324.15	1127	0.02
237.00	2209	0.03	280.95	27493	0.37	325.05	16898	0.23
237.95	780	0.01	281.95	7932	0.11	326.05	6080	0.08
238.90	879	0.01	282.95	6033	0.08	327.00	98802	1.33
240.00	406	0.01	284.00	1292	0.02	328.00	25430	0.34
241.00	3158	0.04	285.00	45530	0.61	329.00	14014	0.19
242.05	1701	0.02	286.00	24050	0.32	330.00	2746	0.04
243.00	5742	0.08	287.05	8921	0.12	331.00	711	0.01
244.05	1315	0.02	288.00	2319	0.03	332.00	119	0.00
245.05	8030	0.11	289.00	473	0.01	333.00	138	0.00
246.05	3002	0.04	290.00	159	0.00	334.00	71	0.00
247.10	6063	0.08	291.05	596	0.01	335.00	146	0.00
248.05	2717	0.04	292.10	239	0.00	336.00	70	0.00
248.95	5521	0.07	293.05	682	0.01	337.00	250	0.00
249.95	1881	0.03	294.00	422	0.01	337.90	121	0.00

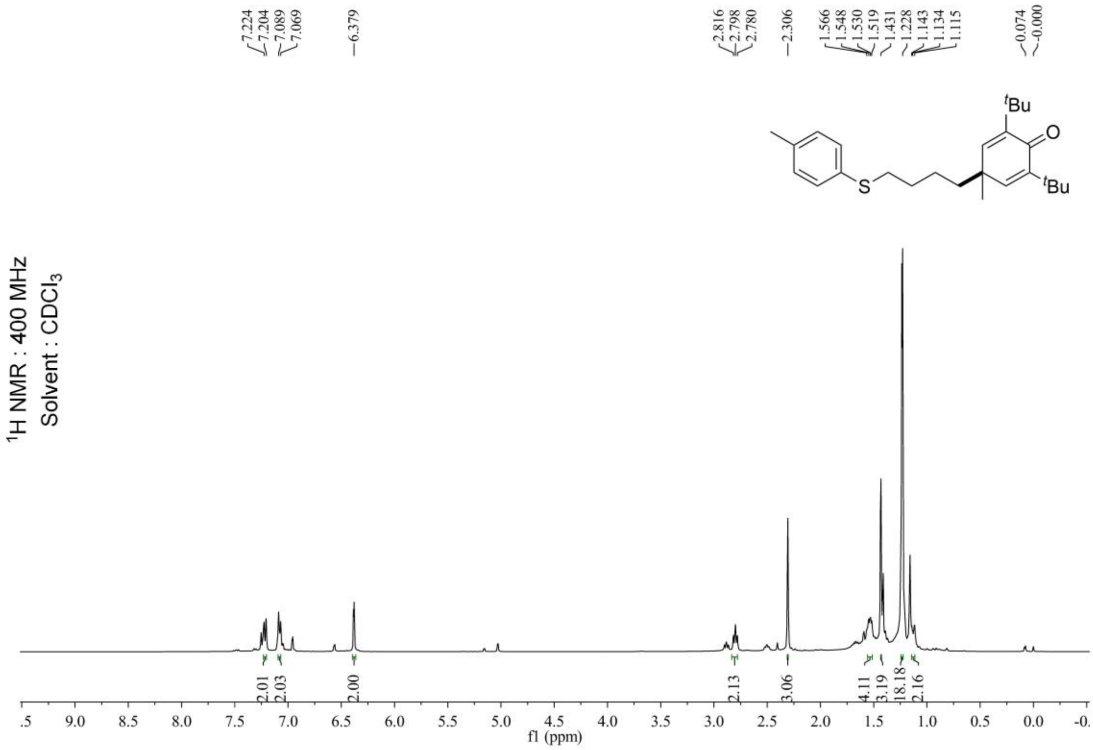
338.95	1155	0.02	360.90	393	0.01	382.05	1044	0.01
340.05	1226	0.02	361.90	194	0.00	383.05	65405	0.88
341.00	47841	0.64	362.90	183	0.00	384.05	18105	0.24
342.05	87684	1.18	364.10	74	0.00	385.05	6172	0.08
343.00	22593	0.30	365.05	2456	0.03	386.05	1222	0.02
344.05	6503	0.09	366.05	612	0.01	386.90	665	0.01
345.00	1447	0.02	367.00	1082	0.01	387.90	150	0.00
346.00	202	0.00	368.00	625	0.01	388.90	132	0.00
347.00	182	0.00	369.05	1803	0.02	389.90	57	0.00
349.00	82	0.00	370.05	588	0.01	390.90	42	0.00
350.00	46	0.00	371.10	169	0.00	391.90	46	0.00
351.00	148	0.00	372.10	153	0.00	392.90	60	0.00
352.00	228	0.00	373.10	191	0.00	393.90	46	0.00
353.00	391	0.01	374.10	218	0.00	394.90	86	0.00
353.90	202	0.00	375.10	86	0.00	396.05	1058	0.01
354.95	9340	0.13	376.10	74	0.00	**397.15**	**22861**	**0.31**
356.00	3558	0.05	377.10	97	0.00	**398.05**	**114780**	**15.41**
356.90	2215	0.03	378.10	82	0.00	**399.05**	**340531**	**4.57**
357.90	687	0.01	379.10	50	0.00	400.05	103359	1.39
358.85	399	0.01	380.00	217	0.00	401.05	21436	0.29
359.90	204	0.00	381.00	1082	0.01	402.00	3607	0.05

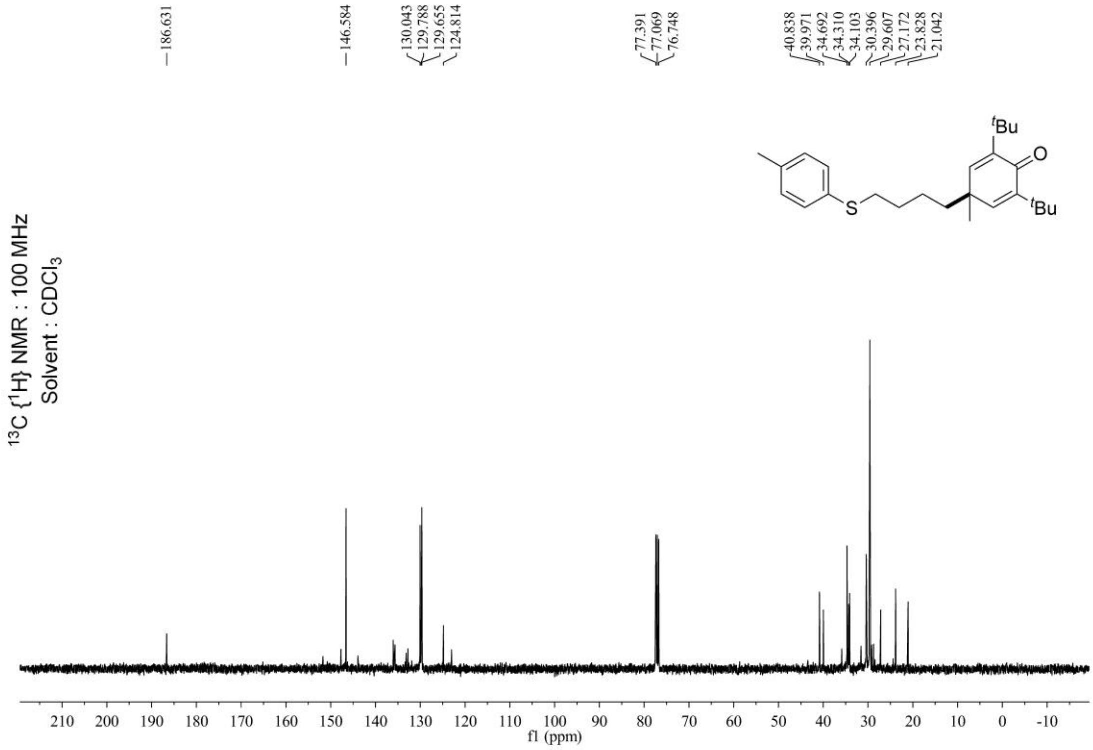
The date and NMR spectra of 7.

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

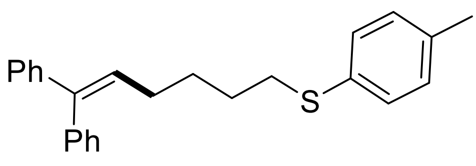
The title compound was prepared according to the general procedure and purified by column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (40 : 1) to afford a yellow oil in 45% yield (36.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.38 (s, 2H), 2.81 (d, J = 7.2 Hz, 2H), 2.31 (s, 3H), 1.57-1.52 (m, 4H), 1.43 (s, 3H), 1.23 (s, 18H), 1.14-1.12 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$): δ 186.6, 146.6(4C), 130.0(2C), 129.8, 129.7(2C), 124.8, 40.8, 40.0, 34.7, 34.3, 34.1, 30.4, 29.6(6C), 27.2, 23.8, 21.0.

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



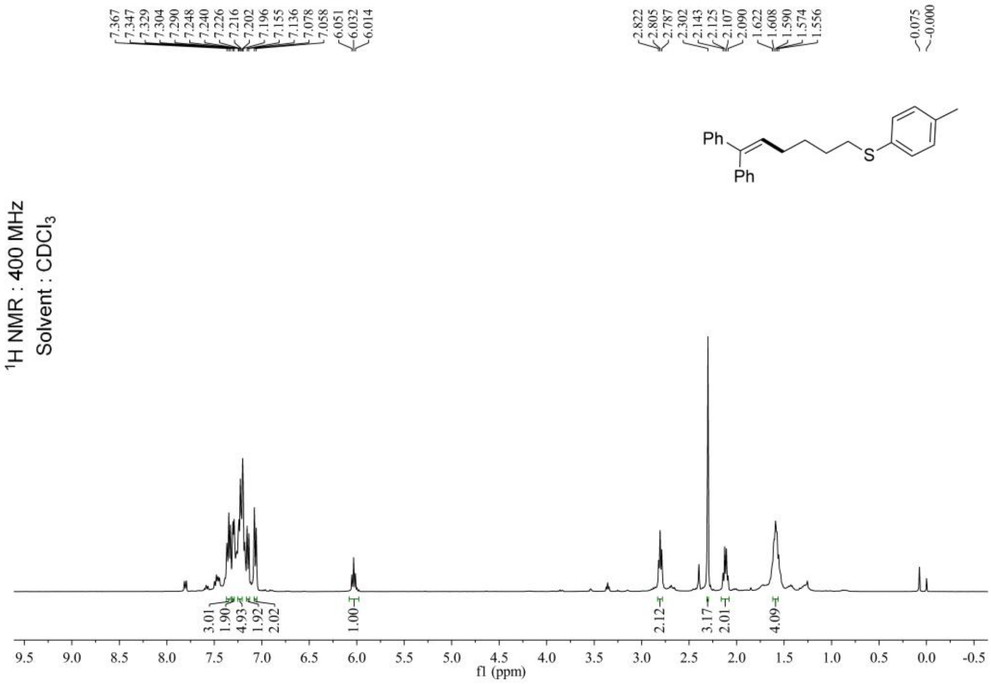


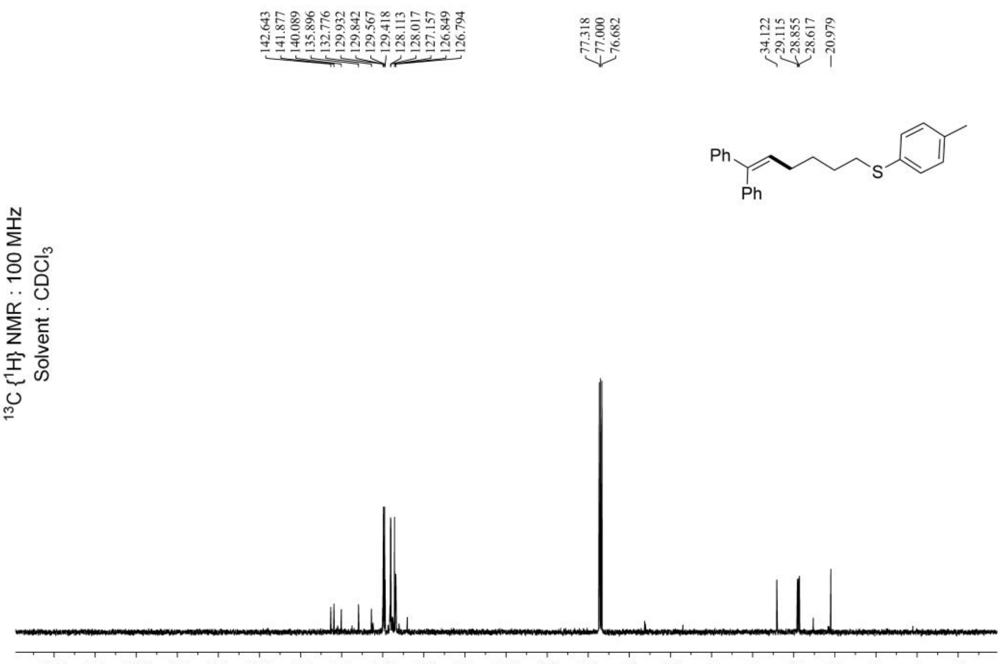
(6,6-diphenylhex-5-en-1-yl)(*p*-tolyl)sulfane (8) by silica gel column chromatography



(hexane/ethyl acetate = 150 : 1), Yield: 37.2 mg, 52%;[1]H NMR (400 MHz, $CDCl_3$) δ

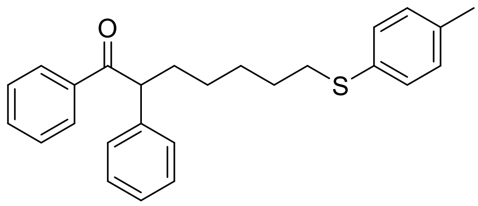
7.37-7.33 (m, 3H), 7.30 (d, J = 5.6 Hz, 2H), 7.25-7.20 (m, 5H), 7.15 (d, J = 7.6 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.03 (t, J = 7.6 Hz, 1H), 2.80 (t, J = 7.2 Hz, 2H), 2.30 (s, 3H), 2.14-2.09 (m, 2H), 1.62-1.56 (m, 4H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 142.6, 141.9, 140.1, 135.9, 132.8, 129.9(2C), 129.8(2C), 129.6(2C), 129.4, 128.1(2C), 128.0(2C), 127.2(2C), 126.8, 126.8, 34.1, 29.1, 28.9, 28.6, 21.0;



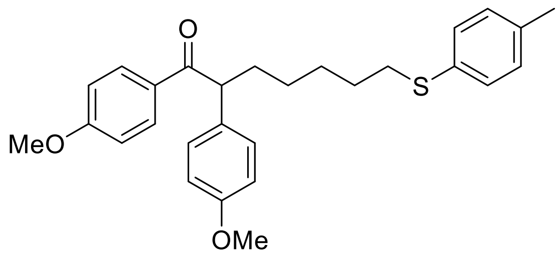


3. Characterization Data

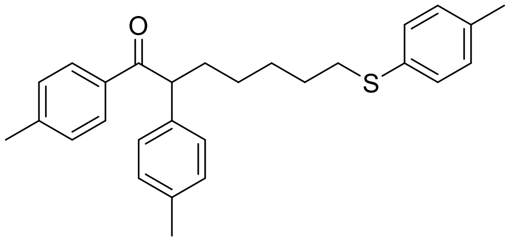
1,2-diphenyl-7-(*p*-tolylthio)heptan-1-one (3aa), by silica gel column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 50.5 mg, 65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.29-7.27 (m, 3H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 4.52 (t, *J* = 7.2 Hz, 1H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.30 (s, 3H), 2.19-2.11 (m, 1H), 1.85-1.76 (m, 1H), 1.62-1.56 (m, 3H), 1.48-1.38 (m, 2H), 1.32-1.21 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 199.9, 139.6, 136.9, 135.8, 132.9, 132.8, 129.8(2C), 129.6(2C), 128.9(2C), 128.6(2C), 128.5(2C), 128.1(2C), 127.0, 53.5, 34.2, 33.8, 29.0, 28.6, 27.2, 21.0; HRMS (ESI-TOF) m/z: $C_{26}H_{29}OS^+$ $(M + H)^+$ calcd for 389.1934, found 389.1932.



1,2-bis(4-methoxyphenyl)-7-(*p*-tolylthio)heptan-1-one (3ba), by silica gel column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 40.3 mg, 45%;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2H), 7.22-7.18 (m, 4H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 4.42 (t, *J* = 7.6 Hz, 1H), 3.81 (s, 3H), 3.74 (s, 3H), 2.82 (t, *J* = 7.2 Hz, 2H), 2.30 (s, 3H), 2.14-2.06 (m, 1H), 1.75-1.75 (m, 1H), 1.61-1.54 (m, 2H), 1.45-1.37 (m, 2H), 1.30-1.22 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 198.7, 163.1, 158.4, 135.8, 132.9, 132.0(2C), 130.9, 129.7, 129.7(2C), 129.5(2C), 129.0(2C), 114.1(2C), 113.6(2C), 55.4, 55.1, 52.1, 34.1, 33.8, 28.9, 28.6, 27.1, 21.0; HRMS (ESI-TOF) m/z: $C_{28}H_{33}O_3S^+$ $(M + H)^+$ calcd for 449.2145, found 449.2149.

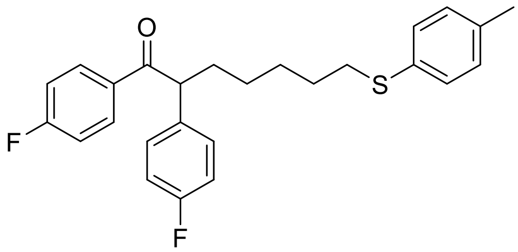


1,2-di-*p*-tolyl-7-(*p*-tolylthio)heptan-1-one (3ca), by silica gel column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 40.0 mg, 48%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2H), 7.22-7.15 (m, 6H), 7.07 (d, J = 7.6 Hz,



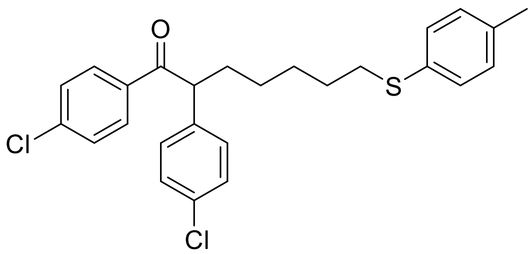
4H), 4.46 (t, J = 7.2 Hz, 1H), 2.82 (t, J = 7.2 Hz, 2H), 2.34 (s, 3H), 2.30 (s, 3H), 2.27 (s, 3H), 2.17-2.08 (m, 1H), 1.82-1.73 (m, 1H), 1.58-1.54 (m, 2H), 1.47-1.35 (m, 2H), 1.31-1.23 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 198.7, 163.1, 158.4, 135.8, 132.9, 132.0(2C), 130.9, 129.7, 129.7(2C), 129.5(2C), 129.0(2C), 114.1(2C), 113.6(2C), 55.4, 55.1, 52.1, 34.1, 33.8, 28.9, 28.6, 27.1, 21.0; HRMS (ESI-TOF) m/z: $C_{28}H_{33}OS^+$ $(M + H)^+$ calcd for 417.2247, found 417.2249.

1,2-bis(4-fluorophenyl)-7-(*p*-tolylthio)heptan-1-one (3da), by silica gel column



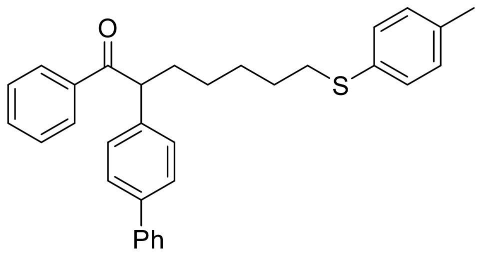
chromatography (hexane/ethyl acetate = 150 : 1), Yield: 35.6 mg, 42%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.94 (m, 2H), 7.25-7.20 (m, 4H), 7.08-7.03 (m, 4H), 6.97 (t, *J* = 8.8 Hz, 2H), 4.45 (t, *J* = 7.6 Hz, 1H), 2.83 (t, *J* = 7.2 Hz, 2H), 2.30 (s, 3H), 2.17-2.07 (m, 1H), 1.82-1.73 (m, 1H), 1.62-1.54 (m, 2H), 1.49-1.38 (m, 2H), 1.32-1.71 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: -105.1 (s, 1F), -115.3 (s, 1F); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 198.2, 165.5 (d, J_{C-F} = 253.4 Hz, 1C), 161.8 (d, J_{C-F} = 244.4 Hz, 1C), 135.8, 135.1 (d, J_{C-F} = 3.2 Hz, 1C), 132.9 (d, J_{C-F} = 2.9 Hz, 1C), 132.8, 131.2 (d, J_{C-F} = 9.3 Hz, 2C), 129.7(2C), 129.55(2C), 129.54 (d, J_{C-F} = 8.0 Hz, 2C), 115.8 (d, J_{C-F} = 21.3 Hz, 2C), 115.6 (d, J_{C-F} = 21.8 Hz, 2C), 52.5, 34.1, 33.8, 28.9, 28.5, 27.0, 20.9; HRMS (ESI-TOF) m/z: $C_{26}H_{27}F_2OS^+$ $(M + H)^+$ calcd for 425.1745, found 425.1742.

1,2-bis(4-chlorophenyl)-7-(*p*-tolylthio)heptan-1-one (3ea), by silica gel column



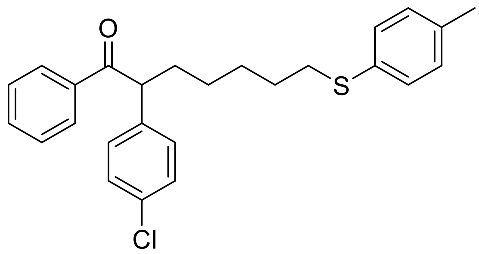
chromatography (hexane/ethyl acetate = 150 : 1), Yield: 52.9 mg, 58%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.27-7.17 (m, 6H), 7.08 (d, *J* = 7.6 Hz, 2H), 4.42 (t, *J* = 7.2 Hz, 1H), 2.83 (t, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 2.16-2.08 (m, 1H), 1.80-1.74 (m, 1H), 1.61-1.54 (m, 2H), 1.47-1.37 (m, 2H), 1.29-1.22 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 198.3, 139.5, 137.7, 135.9, 134.8, 133.0, 132.8, 130.0(2C), 129.7(2C), 129.6(2C), 129.4(2C), 129.1(2C), 128.9(2C), 52.8, 34.1, 33.6, 28.9, 28.5, 27.0, 21.0; HRMS (ESI-TOF) m/z: $C_{26}H_{27}Cl_2OS^+$ $(M + H)^+$ calcd for 457.1154, found 457.1149.

2-([1,1'-biphenyl]-4-yl)-1-phenyl-7-(*p*-tolylthio)heptan-1-one (3fa), by silica gel



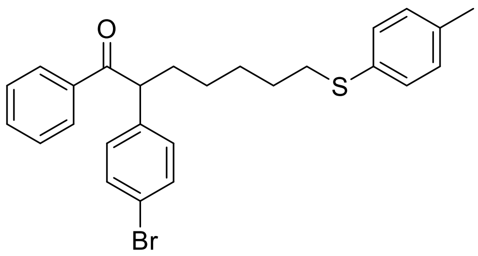
column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 65.0 mg, 70%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.54-7.48 (m, 5H), 7.42-7.30 (m, 7H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 4.57 (t, *J* = 7.2 Hz, 1H), 2.83 (t, *J* = 7.2 Hz, 2H), 2.30 (s, 3H), 2.24-2.17 (m, 1H), 1.88-1.81 (m, 1H), 1.63-1.56 (m, 2H), 1.52-1.40 (m, 2H), 1.37-1.26 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 199.9, 140.5, 139.8, 138.6, 136.8, 135.8, 132.9, 132.9, 129.7(2C), 129.6(2C), 128.7(2C), 128.6(2C), 128.5(2C), 128.5(2C), 127.6(2C), 127.2, 126.9(2C), 53.1, 34.1, 33.8, 28.9, 28.6, 27.2, 21.0; HRMS (ESI-TOF) m/z: $C_{32}H_{33}OS^+$ $(M + H)^+$ calcd for 465.2247, found 465.2248.

2-(4-chlorophenyl)-1-phenyl-7-(*p*-tolylthio)heptan-1-one (3ga), by silica gel



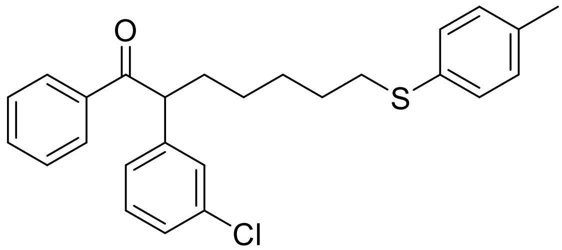
column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 49.0 mg, 58%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 2H), 7.26-7.20 (m, 6H), 7.08 (d, *J* = 8.0 Hz, 2H), 4.50 (t, *J* = 7.6 Hz, 1H), 2.82 (t, *J* = 6.8 Hz, 2H), 2.30 (s, 3H), 2.18-2.09 (m, 1H), 1.82-1.75 (m, 1H), 1.61-1.56 (m, 2H), 1.48-1.37 (m, 2H), 1.31-1.21 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 199.6, 138.0, 136.5, 135.9, 133.0, 132.8, 132.8, 129.8(2C), 129.6(2C), 129.5(2C), 129.0(2C), 128.6(2C), 128.5(2C), 52.7, 34.1, 33.7, 28.9, 28.5, 27.1, 21.0; HRMS (ESI-TOF) m/z: $C_{26}H_{28}ClOS^+$ $(M + H)^+$ calcd for 423.1544, found 423.1549.

2-(4-bromophenyl)-1-phenyl-7-(*p*-tolylthio)heptan-1-one (3ha), by silica gel column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 57.8 mg, 62%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.42-1.38 (m, 4H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.0



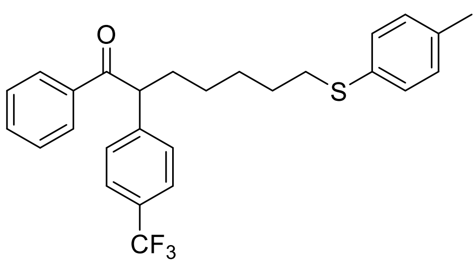
Hz, 2H), 4.49 (t, J = 7.2 Hz, 1H), 2.83 (t, J = 7.2 Hz, 2H), 2.31 (s, 3H), 2.17-2.08 (m, 1H), 1.82-1.73 (m, 1H), 1.59-1.54 (m, 2H), 1.48-1.37 (m, 2H), 1.29-1.22 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 199.5, 138.6, 136.5, 135.9, 133.1, 132.8, 132.0,(2C) 129.9(2C), 129.8(2C), 129.6(2C), 128.6(2C), 128.6(2C), 121.0, 52.8, 34.1, 33.7, 28.9, 28.5, 27.1, 21.0; HRMS (ESI-TOF) m/z: $C_{26}H_{28}BrOS^+$ $(M + H)^+$ calcd for 467.1039, found 467.1044.

1-(3-chlorophenyl)-2-phenyl-7-(*p*-tolylthio)heptan-1-one (3ia), by silica gel column



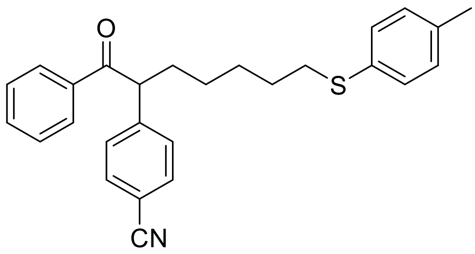
chromatography (hexane/ethyl acetate = 150 : 1), Yield: 40.5 mg, 48%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.6 Hz, 2H), 7.51 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.26-7.18 (m, 6H), 7.08 (d, J = 7.6 Hz, 2H), 4.50 (t, J = 7.2 Hz, 1H), 2.83 (t, J = 7.2 Hz, 2H), 2.30 (s, 3H), 2.19-2.10 (m, 1H), 1.83-1.74 (m, 1H), 1.60-1.54 (m, 2H), 1.49-1.38 (m, 2H), 1.33-1.21 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 199.3, 141.5, 136.5, 135.9, 134.6, 133.1, 132.8, 130.1, 129.8(2C), 129.6(2C), 128.6(2C), 128.6(2C), 128.2, 127.2, 126.4, 53.0, 34.1, 33.8, 28.9, 28.5, 27.1, 21.0; HRMS (ESI-TOF) m/z: $C_{26}H_{28}ClOS^+$ $(M + H)^+$ calcd for 423.1544, found 423.1550.

1-phenyl-7-(p-tolylthio)-2-(4-(trifluoromethyl)phenyl)heptan-1-one (3ja), by silica

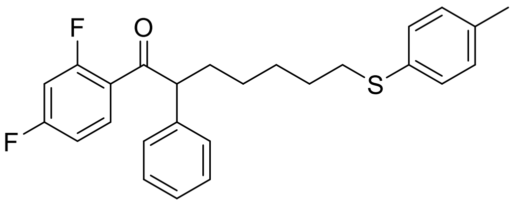


gel column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 57.4 mg, 63%; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.5 Hz, 2H), 7.56-7.49 (m, 3H), 7.47 - 7.38 (m, 4H), 7.22 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 4.61 (t, J = 7.2 Hz, 1H), 2.83 (t, J = 7.2 Hz, 2H), 2.31 (s, 3H), 2.21 - 2.14 (m, 1H), 1.86 - 1.77 (m, 1H), 1.59 - 1.53 (m, 2H), 1.47 - 1.39 (m, 2H), 1.28 - 1.22 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5; $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 199.3, 143.6, 136.5, 135.9, 133.2(2C), 132.8, 129.8(2C), 129.6(2C), 128.7(2C), 128.6(2C), 128.5(2C), 125.8(q, J = 3.7 Hz, 2C), 53.1, 34.2, 33.8, 28.9, 28.5, 27.1, 20.9; HRMS (ESI-TOF) m/z: $C_{27}H_{28}F_3OS^+$ $(M + H)^+$ calcd for 457.1807, found 457.1802.

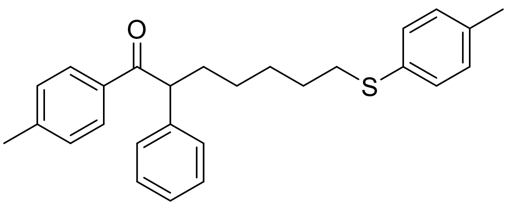
4-(1-oxo-1-phenyl-7-(p-tolylthio)heptan-2-yl)benzonitrile (3ka), by silica gel column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 45.4 mg, 55%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 2H), 7.58 (d, J = 6.7 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.47 - 7.39 (m, 4H), 7.21 (d, J = 7.2 Hz, 2H), 7.08 (d, J = 7.6 Hz, 2H), 4.60 (t, J = 7.3 Hz, 1H), 2.82 (t, J = 7.2 Hz, 2H), 2.31 (s, 3H), 2.22 – 2.13 (m, 1H), 1.84 – 1.76 (m, 1H), 1.60 - 1.54 (m, 2H), 1.48 - 1.38 (m, 2H), 1.31 - 1.17 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ 198.9, 144.9, 136.3, 135.9, 133.4, 132.8, 132.6, 129.8, 129.6, 129.0, 128.7, 128.5, 118.6, 111.0, 53.2, 34.1, 33.8, 28.8, 28.4, 27.1, 21.0; HRMS (ESI-TOF) m/z: $C_{27}H_{28}NOS$+ $(M + H)^+$ calcd for 414.1886, found 414.1889.



2-(2,4-difluorophenyl)-1-phenyl-7-(*p*-tolylthio)heptan-1-one (3la), by silica gel column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 42.4 mg, 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.94 (m, 2H), 7.25-7.20 (m, 4H), 7.09-7.04 (m, 4H), 6.98 (t, J = 8.8 Hz, 2H), 4.45 (t, J = 7.2 Hz, 1H), 2.83 (t, J = 7.2 Hz, 2H), 2.31 (s, 3H), 2.16-2.07 (m, 1H), 1.80-1.73 (m, 1H), 1.62-1.56 (m, 2H), 1.48-1.38 (m, 2H), 1.32-1.20 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: -105.1 (s, 1F), -115.4 (s, 1F); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 198.2, 165.5 (d, J_{C-F} = 253.4 Hz, 1C) , 161.8 (d, J_{C-F} = 244.2 Hz, 1C),135.9, 135.1 (d, J_{C-F} = 3.2 Hz, 1C), 133.0 (d, J_{C-F} = 2.9 Hz, 1C), 132.8, 131.3(2C), 131.2(2C), 129.7(2C), 129.6, 129.6(2C), 129.5, 115.8 (d, J_{C-F} = 21.2 Hz, 1C), 115.7 (d, J_{C-F} = 21.6 Hz, 1C), 52.6, 34.1, 33.8, 28.9, 28.5, 27.1, 21.0; HRMS (ESI-TOF) m/z: $C_{26}H_{27}F_2OS^+$ $(M + H)^+$ calcd for 403.2090, found 403.2091.

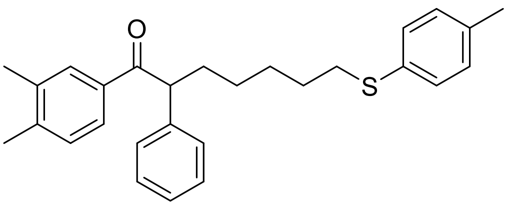


2-phenyl-1-(*p*-tolyl)-7-(*p*-tolylthio)heptan-1-one (3ma), by silica gel column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 50.7 mg, 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.6, 1H), 7.29-7.19 (m, 8H), 7.15 (t, J = 7.6 Hz, 2H), 7.08



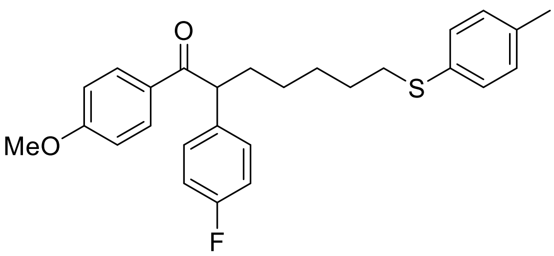
(d, J = 8.0 Hz, 2H), 4.33 (t, J = 7.2 Hz, 1H), 2.83 (t, J = 7.6 Hz, 2H), 2.30 (s, 3H), 2.29 (s, 3H), 2.23-2.14 (m, 1H), 1.85-1.76 (m, 1H), 1.63-1.55 (t, J = 7.3 Hz, 2H), 1.49-1.39 (m, 2H), 1.34-1.25 (m, 2H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 204.2, 138.8, 138.8, 137.8, 135.8, 132.8, 131.5, 130.7, 129.7(2C), 129.6(2C), 128.7(2C), 128.3(2C), 127.7, 127.0, 125.3, 56.7, 34.1, 33.1, 28.9, 28.6, 27.2, 21.0, 20.7; HRMS (ESI-TOF) m/z: $C_{27}H_{31}OS^+$ $(M + H)^+$ calcd for 403.2090, found 403.2091.

1-(3,4-dimethylphenyl)-2-phenyl-7-(*p*-tolylthio)heptan-1-one (3na), by silica gel



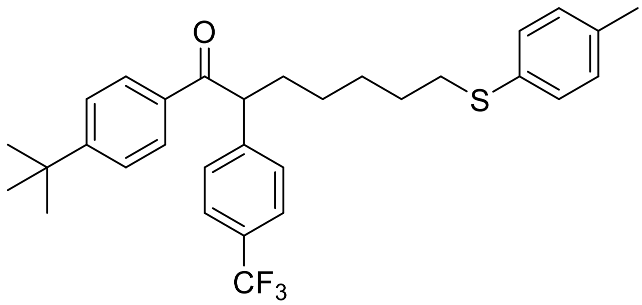
column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 45.8 mg, 55%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 7.18-7.15 (m, 4H), 7.07 (d, J = 8.0 Hz, 4H), 4.46 (t, J = 7.2 Hz, 1H), 2.82 (t, J = 7.2 Hz, 2H), 2.34 (s, 3H), 2.30 (s, 3H), 2.27 (s, 3H), 2.17-.08 (m, 1H), 1.80-1.73 (m, 1H), 1.61-1.54 (m, 2H), 1.46-1.37 (m, 2H), 1.29-1.20 (m, 2H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 199.6, 143.5, 136.8, 136.5, 135.8, 134.3, 132.9, 129.7(2C), 129.6(2C), 129.5(2C), 129.1(2C), 128.7(2C), 128.0(2C), 52.9, 34.1, 33.7, 29.0, 28.7, 27.2, 21.6, 21.0, 21.0.; HRMS (ESI-TOF) m/z: $C_{28}H_{33}OS^+$ $(M + H)^+$ calcd for 417.2247, found 417.2248.

2-(4-fluorophenyl)-1-(4-methoxyphenyl)-7-(*p*-tolylthio)heptan-1-one (3oa), by

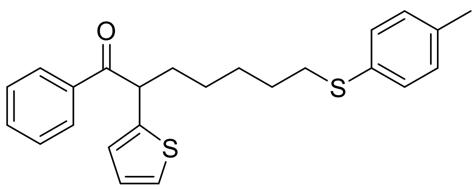


silica gel column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 50.6 mg, 58%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.8 Hz, 2H), 7.26-7.20 (m, 4H), 7.07 (d, J = 7.6 Hz, 2H), 6.96 (t, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 4.47 (t, J = 7.2 Hz, 1H), 3.83 (s, 3H), 2.82 (t, J = 7.2 Hz, 2H), 2.30 (s, 3H), 2.16-2.07 (m, 1H), 1.81-1.72 (m, 1H), 1.59-1.54 (m, 2H), 1.46-1.37 (m, 2H), 1.30-1.21 (m, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ: -115.9 (s, 1F), -115.4 (s, 1F); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 198.4, 163.4, 163.2 (d, J_{C-F} = 244.0 Hz, 1C), 135.9, 135.8 (d, J_{C-F} = 3.3 Hz, 1C), 132.9, 130.9(2C), 129.8(2C), 129.7, 129.6(2C), 129.6, 126.9, 126.6, 115.7 (d, J_{C-F} = 21.2 Hz, 1C), 113.8(2C), 55.5, 52.1, 34.2, 34.0, 29.0, 28.6, 27.2, 21.0; HRMS (ESI-TOF) m/z: $C_{27}H_{30}FO_2S^+$ $(M + H)^+$ calcd for 437.1945, found 437.1946.

1-(4-(tert-butyl)phenyl)-7-(p-tolylthio)-2-(4-(trifluoromethyl)phenyl)heptan-1-one (3pa), by silica gel column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 68.6 mg, 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.9 Hz, 2H), 7.54 (d, J = 7.9 Hz, 2H), 7.45 - 7.41 (m, 4H), 7.22 (d, J = 7.6 Hz, 2H), 7.08 (d, J = 7.5 Hz, 2H), 4.61 (t, J = 7.2 Hz, 1H), 2.83 (t, J = 7.2 Hz, 2H), 2.31 (s, 3H), 2.22 - 2.14 (m, 1H), 1.86 - 1.77 (m, 1H), 1.60 - 1.55 (m, 2H), 1.47 - 1.39 (m, 2H), 1.31 (s, 9H), 1.27 - 1.17 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4; ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: ^{13}C NMR (100 MHz, $CDCl_3$) δ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 157.1, 143.9, 135.9, 133.9, 132.9, 129.8(2C), 129.57, 129.61(2C), 128.6(2C), 128.5(2C), 125.8 (q, J_{C-F} = 3.5 Hz, 2C), 125.7(2C), 53.0, 35.1, 34.2, 34.0, 31.0, 29.0, 28.6, 27.2, 21.0; HRMS (ESI-TOF) m/z: $C_{31}H_{36}F_3OS^+$ $(M + H)^+$ calcd for 513.2433, found 513.2439.

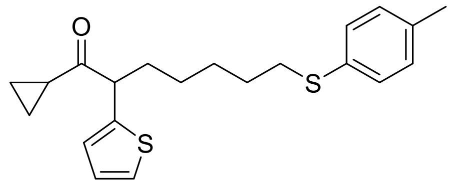


2-phenyl-1-(thiophen-2-yl)-7-(*p*-tolylthio)heptan-1-one (3qa), by silica gel column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 49.7 mg, 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.0 Hz, 2H), 7.53 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.2 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 4.8 Hz, 1H), 7.07 (d, J = 8.0 Hz, 2H), 6.90-6.89 (m, 2H), 4.85 (t, J = 7.2 Hz, 1H), 2.83 (t, J = 7.3 Hz, 2H), 2.30 (s, 3H), 2.20-2.11 (m, 1H), 1.93-1.84 (m, 1H), 1.62-1.55 (m, 2H), 1.50-1.39 (m, 2H), 1.34-1.27 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 198.9, 141.9, 136.3, 135.8, 133.1, 132.8, 129.8(2C), 129.6(2C), 128.6(2C), 128.6(2C), 126.8, 125.4, 124.7, 47.7, 34.7, 34.1,

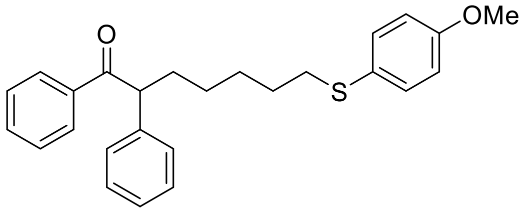


28.9, 28.5, 27.0, 21.0; HRMS (ESI-TOF) m/z: $C_{24}H_{27}OS_2^+$ $(M + H)^+$ calcd for 395.1498, found 395.1496.

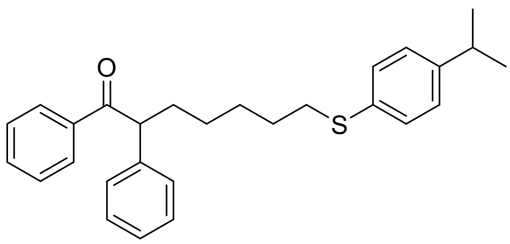
2-cyclopropyl-1-(thiophen-2-yl)-7-(*p*-tolylthio)heptan-1-one (3ra), by silica gel column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 38.7 mg, 54%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.21 (m, 3H), 7.08 (d, J = 7.6 Hz, 2H), 6.98-6.95 (m, 1H), 6.89 (d, J = 3.2 Hz, 1H), 4.02 (t, J = 7.6 Hz, 1H), 2.84 (t, J = 7.2 Hz, 2H), 2.31 (s, 3H), 2.11-2.03 (m, 1H), 2.00-1.95 (m, 1H), 1.79-1.74 (m, 1H), 1.61-1.56 (m, 2H), 1.47-1.39 (m, 2H), 1.31-1.25 (m, 2H), 1.03-0.98 (m, 2H), 0.87-0.78 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 209.2, 141.7, 135.9, 132.9, 129.8(2C), 129.6(2C), 126.9, 125.4, 124.6, 54.3, 34.2, 33.0, 28.9, 28.4, 26.9, 21.0, 19.5, 11.6, 11.5; HRMS (ESI-TOF) m/z: $C_{21}H_{27}OS_2^+$ $(M + H)^+$ calcd for 359.1498, found 359.1496.



7-((4-methoxyphenyl)thio)-1,2-diphenylheptan-1-one (3ab), by silica gel column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 34.0 mg, 52%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.6 Hz, 2H), 7.50-7.45 (m, 1H), 7.38 (t, J = 8.0 Hz, 2H), 7.31-7.28 (m, 5H), 7.21-7.17 (m, 1H), 6.86-6.81 (m, 3H), 4.52 (t, J = 7.2 Hz, 1H), 3.78 (s, 3H), 2.76 (t, J = 7.2 Hz, 2H), 2.21-2.11 (m, 1H), 1.85-1.76 (m, 1H), 1.56-1.50 (m, 2H), 1.46-1.36 (m, 2H), 1.30-1.19 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 199.9, 158.6, 139.6, 136.8, 132.9(2C), 132.8, 128.8(2C), 128.6(2C), 128.5(2C), 128.1(2C), 126.9, 114.5, 114.4(2C), 55.3, 53.5, 35.6, 33.8, 29.0, 28.5, 27.2; HRMS (ESI-TOF) m/z: $C_{26}H_{29}O_2S^+$ $(M + H)^+$ calcd for 405.1883, found 405.1889.

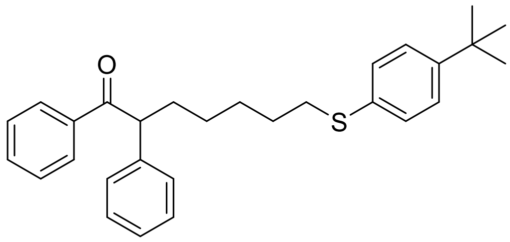


7-((4-isopropylphenyl)thio)-1,2-diphenylheptan-1-one (3ac), by silica gel column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 52.4 mg, 63%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 7.2 Hz, 2H), 7.47 (t, J = 7.6 Hz, 1H), 7.38 (t, J =



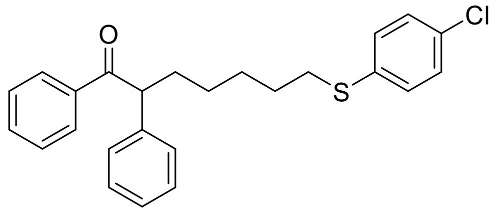
6.8 Hz, 2H), 7.30-7.27 (m, 4H), 7.25-7.23 (m, 2H), 7.13 (t, *J* = 6.8 Hz, 3H), 4.52 (t, *J* = 7.6 Hz, 1H), 2.88-2.82 (m, 3H), 2.21-7.12 (m, 1H), 1.85-1.78 (m, 1H), 1.6-1.57 (m, 2H), 1.47-1.41 (m, 2H), 1.34-1.27 (m, 2H), 1.23 (s, 3H), 1.21 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 199.9, 146.7, 139.6, 136.8, 133.3, 132.8, 129.9, 129.5(2C), 128.8(2C), 128.6(2C), 128.5(2C), 128.1(2C), 126.9(2C), 53.5, 34.0, 33.8, 33.6, 29.0, 28.7, 27.2, 23.9(2C); HRMS (ESI-TOF) m/z: $C_{28}H_{33}OS^+$ $(M + H)^+$ calcd for 417.2247, found 417.2249.

7-((4-(*tert*-butyl)phenyl)thio)-1,2-diphenylheptan-1-one (3ad), by silica gel column



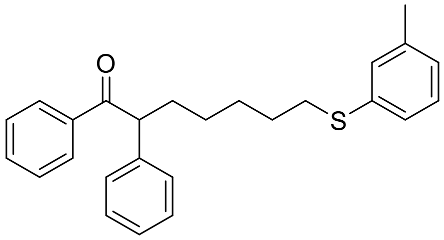
chromatography (hexane/ethyl acetate = 150 : 1), Yield: 65.4 mg, 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.8 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.29-7.27 (m, 7H), 7.25-7.24 (m, 2H), 4.52 (t, *J* = 7.2 Hz, 1H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.21-2.12 (m, 1H), 1.84-1.77 (m, 1H), 1.64-1.56 (m, 2H), 1.51-1.38 (m, 4H), 1.29 (s, 9H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 199.9, 148.9, 139.6, 136.8, 133.1, 132.8, 129.4, 129.0(2C), 128.8(2C), 128.6(2C), 128.5(2C), 128.1(2C), 126.9, 125.8, 53.5, 34.4, 33.8, 33.8, 31.2, 29.0, 28.7, 27.2(3C); HRMS (ESI-TOF) m/z: $C_{29}H_{35}OS^+$ $(M + H)^+$ calcd for 431.2403, found 431.2410.

7-((4-chlorophenyl)thio)-1,2-diphenylheptan-1-one (3ae), by silica gel column



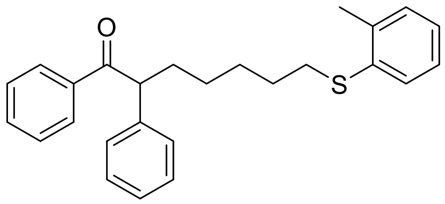
chromatography (hexane/ethyl acetate = 150 : 1), Yield: 40.0 mg, 49%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.29-7.28 (m, 4H), 7.24-7.18 (m, 5H), 4.52 (t, *J* = 7.2 Hz, 1H), 2.84 (t, *J* = 7.2 Hz, 2H), 2.21-2.12 (m, 1H), 1.85-1.76 (m, 1H), 1.63-1.58 (d, *J* = 7.5 Hz, 2H), 1.49-1.41 (m, 2H), 1.32-1.23 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 199.9, 139.6, 136.8, 135.3, 132.9(2C), 131.6, 130.2(2C), 128.9(2C), 128.6(2C), 128.5(2C), 128.1(2C), 127.0(2C), 53.5, 33.8, 33.6, 28.7, 28.6, 27.2; HRMS (ESI-TOF) m/z: $C_{25}H_{26}ClOS^+$ $(M + H)^+$ calcd for 409.1387, found 409.1386.

1,2-diphenyl-7-(*m*-tolylthio)heptan-1-one (3af), by silica gel column



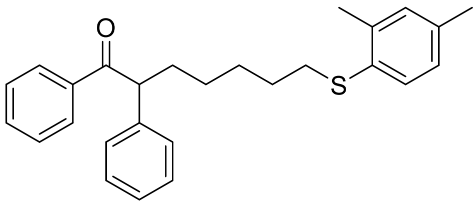
chromatography (hexane/ethyl acetate = 150 : 1), Yield: 42.7 mg, 55%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.29-7.28 (m, 3H), 7.21-7.08 (m, 5H), 6.96 (d, *J* = 7.2 Hz, 1H), 4.52 (t, *J* = 7.2 Hz, 1H), 2.86 (t, *J* = 7.2 Hz, 2H), 2.30 (s, 3H), 2.20-2.12 (m, 1H), 1.85-1.78 (m, 1H), 1.64-1.59 (m, 2H), 1.48-1.40 (m, 2H), 1.33-1.26 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 199.9, 139.6, 138.5, 136.8, 136.5, 132.8, 129.4, 128.9(2C), 128.6, 128.6(2C), 128.5(2C), 128.1(2C), 127.0, 126.5, 125.7, 53.5, 33.8, 33.3, 28.9, 28.7, 27.2, 21.3; HRMS (ESI-TOF) m/z: $C_{26}H_{29}OS^+$ $(M + H)^+$ calcd for 389.1934, found 389.1928.

1,2-diphenyl-7-(*o*-tolylthio)heptan-1-one (3ag), by silica gel column



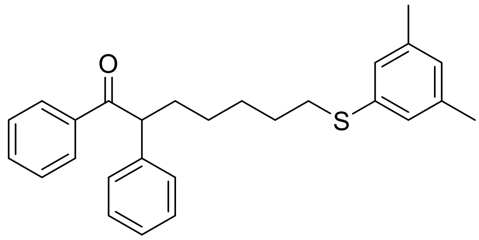
chromatography (hexane/ethyl acetate = 150 : 1), Yield: 41.1 mg, 53%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.29-7.28 (m, 4H), 7.22-7.17 (m, 2H), 7.14 (d, *J* = 7.2 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 4.53 (t, *J* = 7.2 Hz, 1H), 2.85 (t, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 2.24-2.13 (m, 1H), 1.87-1.78 (m, 1H), 1.67-1.60 (m, 2H), 1.54-1.42 (m, 2H), 1.35-1.23 (m, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ: 199.9, 139.6, 137.0, 136.8, 136.2, 132.8, 129.9, 128.9(2C), 128.6(2C), 128.5(2C), 128.1(2C), 127.1, 127.0, 126.3, 125.2, 53.5, 33.8, 32.5, 28.8, 28.7, 27.2, 20.3; HRMS (ESI-TOF) m/z: $C_{26}H_{29}OS^+$ $(M + H)^+$ calcd for 389.1934, found 389.1928.

7-((2,4-dimethylphenyl)thio)-1,2-diphenylheptan-1-one (3ah), by silica gel column



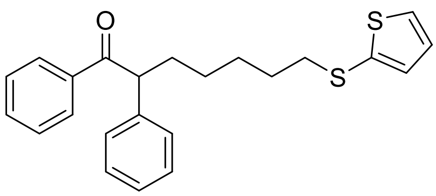
chromatography (hexane/ethyl acetate = 150 : 1), Yield: 53.9 mg, 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.2 Hz, 1H), 7.53-7.47 (m, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.29-7.14 (m, 9H), 7.08 (d, *J* = 7.6 Hz, 1H), 4.52 (t, *J* = 7.2 Hz, 0.5H), 4.33 (t, *J* = 7.6 Hz, 0.5H), 2.85-2.78 (m, 2H), 2.32-2.28 (m, 6H), 2.21-2.14 (m, 1H), 1.85-1.76 (m, 1H), 1.64-1.59 (m, 2H), 1.50-1.42 (m, 2H), 1.36-1.28 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 199.9, 139.6, 137.7, 136.8, 135.4, 132.8, 132.2, 130.9, 128.8(2C), 128.7, 128.6(2C), 128.5(2C), 128.1(2C), 127.0, 126.9, 53.5, 33.8, 33.3, 28.8(2C), 27.2, 20.8, 20.3; HRMS (ESI-TOF) m/z: $C_{27}H_{31}OS^+$ $(M + H)^+$ calcd for 403.2090, found 403.2091.

7-((3,5-dimethylphenyl)thio)-1,2-diphenylheptan-1-one (3ai), by silica gel column



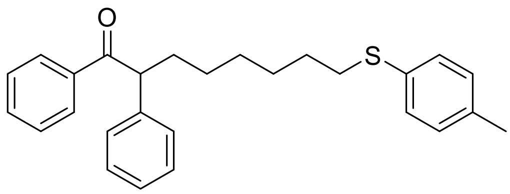
chromatography (hexane/ethyl acetate = 150 : 1), Yield: 55.5 mg, 69%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.29-7.28 (m, 4H), 7.23-7.17 (m, 1H), 6.91 (s, 2H), 6.78 (s, 1H), 4.53 (t, *J* = 7.2 Hz, 1H), 2.85 (t, *J* = 7.2 Hz, 2H), 2.26 (s, 6H), 2.22-2.13 (m, 1H), 1.85-1.81 (m, 1H), 1.64-1.59 (d, *J* = 7.4 Hz, 2H), 1.48-1.40 (m, 2H), 1.34-1.23 (m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 199.9, 139.6, 138.4(2C), 136.8, 136.3, 132.8, 128.9(2C), 128.6(2C), 128.5(2C), 128.1(2C), 127.5, 127.0, 126.4(2C), 53.5, 33.8, 33.3, 28.9, 28.7, 27.2, 21.2(2C); HRMS (ESI-TOF) m/z: $C_{27}H_{31}OS^+$ $(M + H)^+$ calcd for 403.2090, found 403.2091.

1,2-diphenyl-7-(thiophen-2-ylthio)heptan-1-one (3aj), by silica gel column



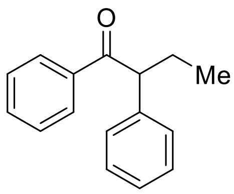
chromatography (hexane/ethyl acetate = 150 : 1), Yield: 43.3 mg, 57%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.32-7.28 (m, 5H), 7.22-7.18 (m, 1H), 7.07 (d, *J* = 3.6 Hz, 1H), 6.97-6.93 (m, 1H), 4.52 (t, *J* = 7.2 Hz, 1H), 2.74 (t, *J* = 7.2 Hz, 2H), 2.54-2.45 (m, 1H), 2.21-2.12 (m, 1H), 1.61-1.53 (m, 2H), 1.48-1.39 (m, 2H), 1.34-1.22(m, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$) δ: 199.9, 139.6, 136.9, 133.3, 132.8, 128.9(4C), 128.6(2C), 128.5(2C), 128.2(2C), 127.4, 127.0, 53.5, 38.8, 33.8, 29.1, 28.3, 27.2; HRMS (ESI-TOF) m/z: $C_{23}H_{25}OS_2^+$ $(M + H)^+$ calcd for 381.1341, found 381.1344.

1,2-diphenyl-8-(*p*-tolylthio)octan-1-one (3ak), by silica gel column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 38.6mg, 48%; ^{1}H NMR (400 MHz, $CDCl_3$) δ



7.95 (d, J = 7.6 Hz, 2H), 7.48 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 8.0 Hz, 2H), 7.29-7.28 (m, 4H), 7.22 (d, J = 8.0 Hz, 3H), 7.08 (d, J = 8.0 Hz, 2H), 4.52 (t, J = 7.2 Hz, 1H), 2.83 (t, J = 7.2 Hz, 2H), 2.31 (s, 3H), 2.20-2.12 (m, 1H), 1.85-1.76 (m, 1H), 1.59-1.53 (m, 2H), 1.39-1.32 (m, 6H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 200.0, 139.7, 136.8, 135.8, 132.9, 132.8, 129.7(2C), 129.6(2C), 128.8(2C), 128.6(2C), 128.5(2C), 128.1(2C), 126.9, 53.6, 34.2, 33.9, 29.1, 29.1, 28.5, 27.5, 21.0; HRMS (ESI-TOF) m/z: $C_{27}H_{31}OS^+$ $(M + H)^+$ calcd for 403.2090, found 403.2091.

1,2-diphenylbutan-1-one (3al), by silica gel column chromatography (hexane/ethyl acetate = 150 : 1), Yield: 25.1 mg, 56%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 7.2 Hz, 2H), 7.48 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.31-7.26 (m, 4H), 7.22-7.18 (m, 1H), 4.45 (t, J = 7.2 Hz, 1H), 2.26-2.19 (m, 1H), 1.91-1.81 (m, 1H), 0.90 (t, J = 7.6 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ: 199.0, 138.6, 135.9, 131.7, 127.8(2C), 127.6(2C), 127.4(2C), 127.2(2C), 125.9, 54.4, 26.1, 11.3; HRMS (ESI-TOF) m/z: $C_{16}H_{17}O^+$ $(M + H)^+$ calcd for 225.1274, found 225.1277.



4. Reference

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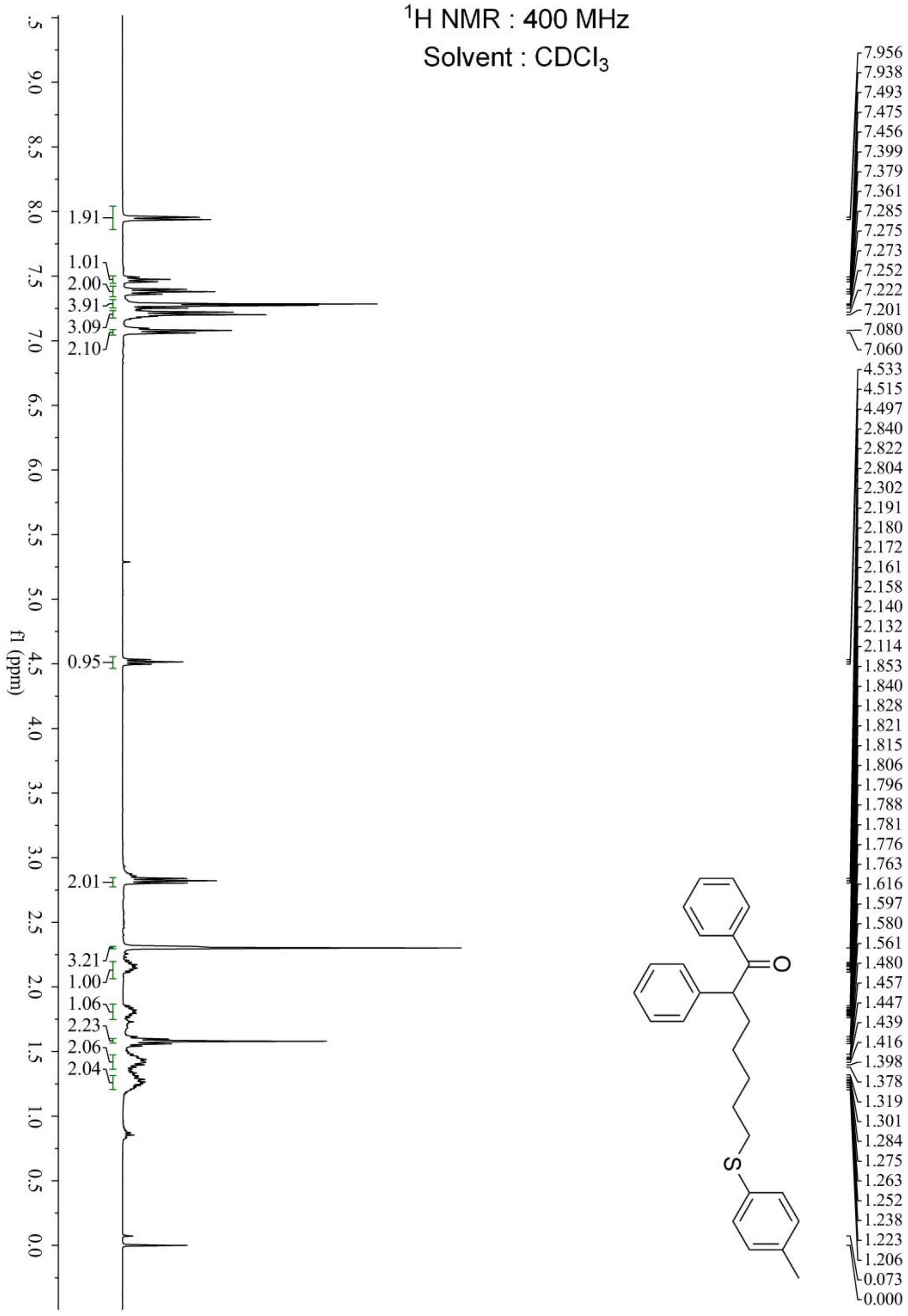
3. P.-F. Yuan, Z. Yang, S.-S. Zhang, C.-M. Zhu, X.-L. Yang, Q.-Y. Meng, Deconstructive Carboxylation of Activated Alkenes with Carbon Dioxide, *Angew. Chem. Int. Ed.* **2024**, *63, e202313030.*
4. L.-J. Zhong, H. Chen, X. Shang, J.-H. Fan, K.-W. Tang, Y. Liu, J.-H. Li, Photoredox Ring Opening 1,2-Alkylarylation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

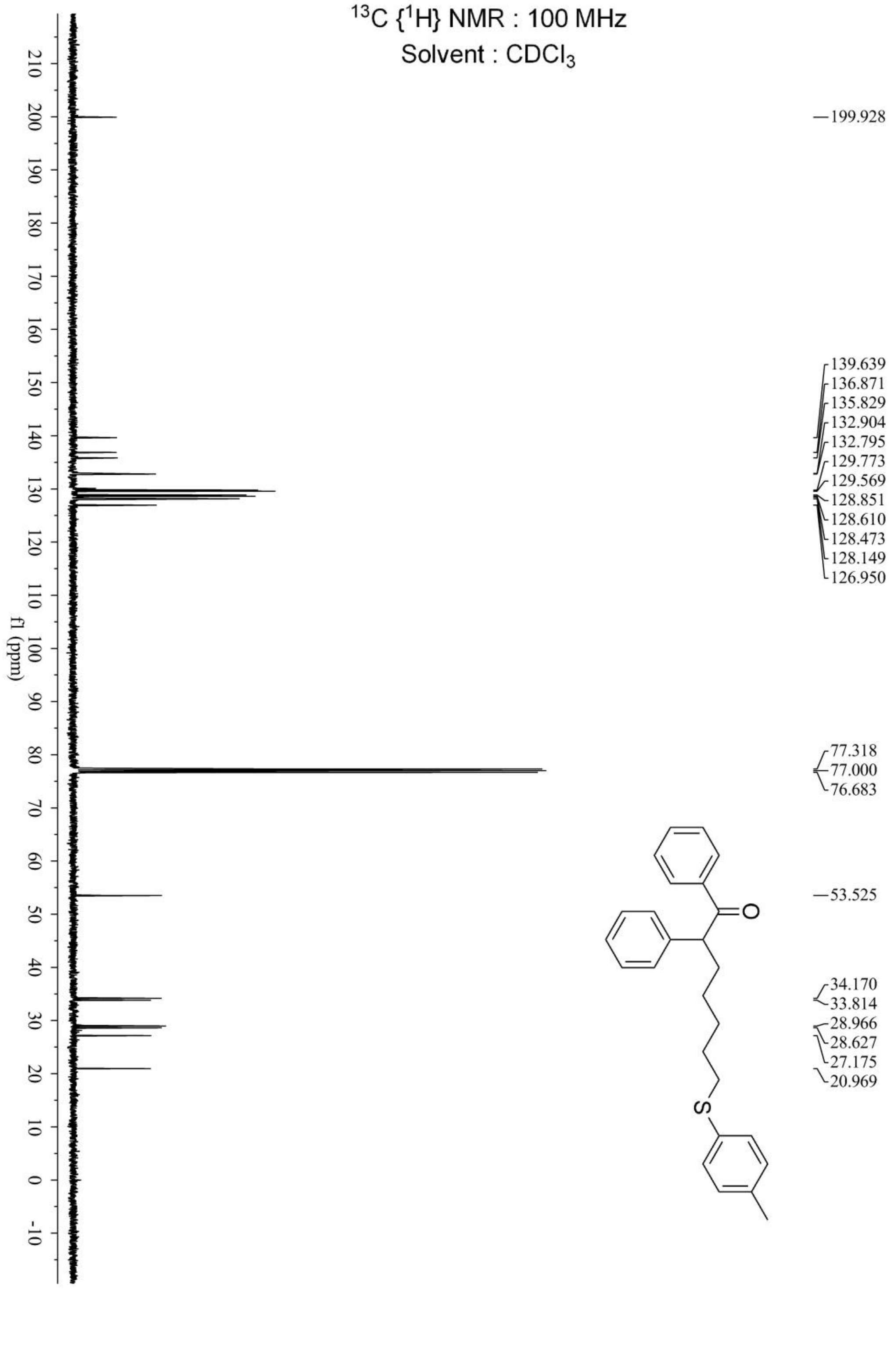
5.Spectra

1,2-diphenyl-7-(*p*-tolylthio)heptan-1-one (3aa)

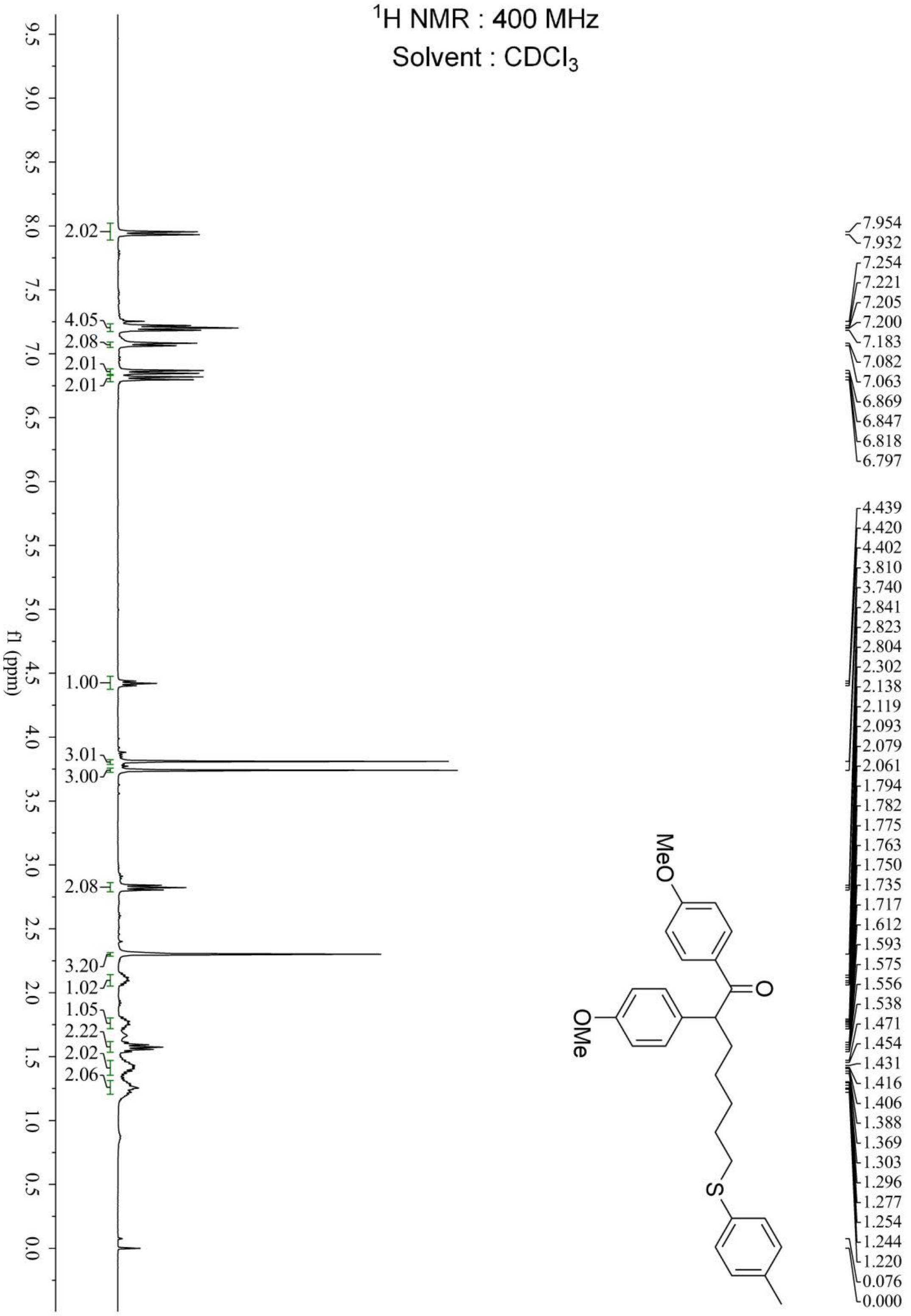


$^{13}C\ \{^1H\}$ NMR : 100 MHz

Solvent : $CDCl_3$

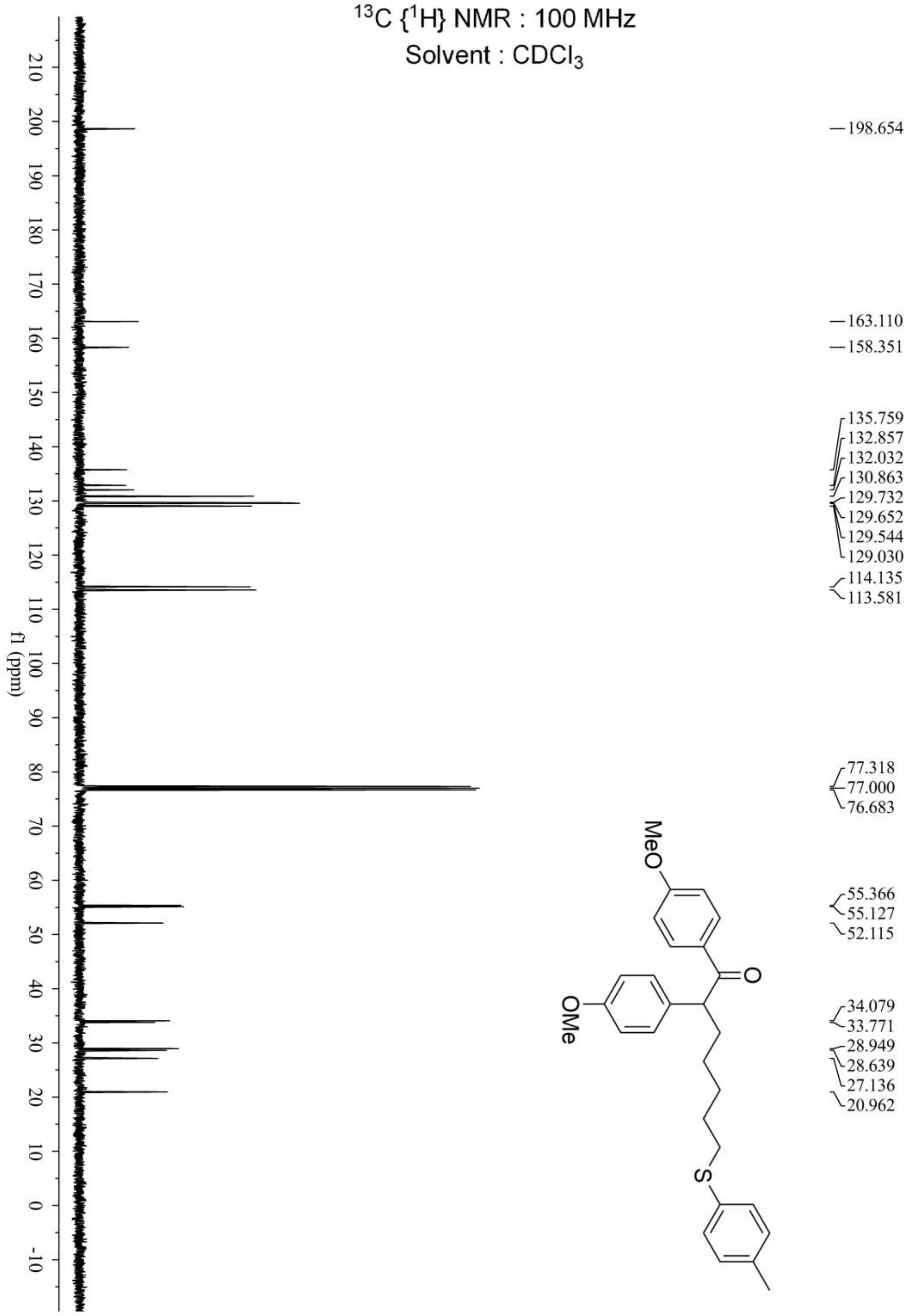


1,2-bis(4-methoxyphenyl)-7-(*p*-tolylthio)heptan-1-one (3ba)

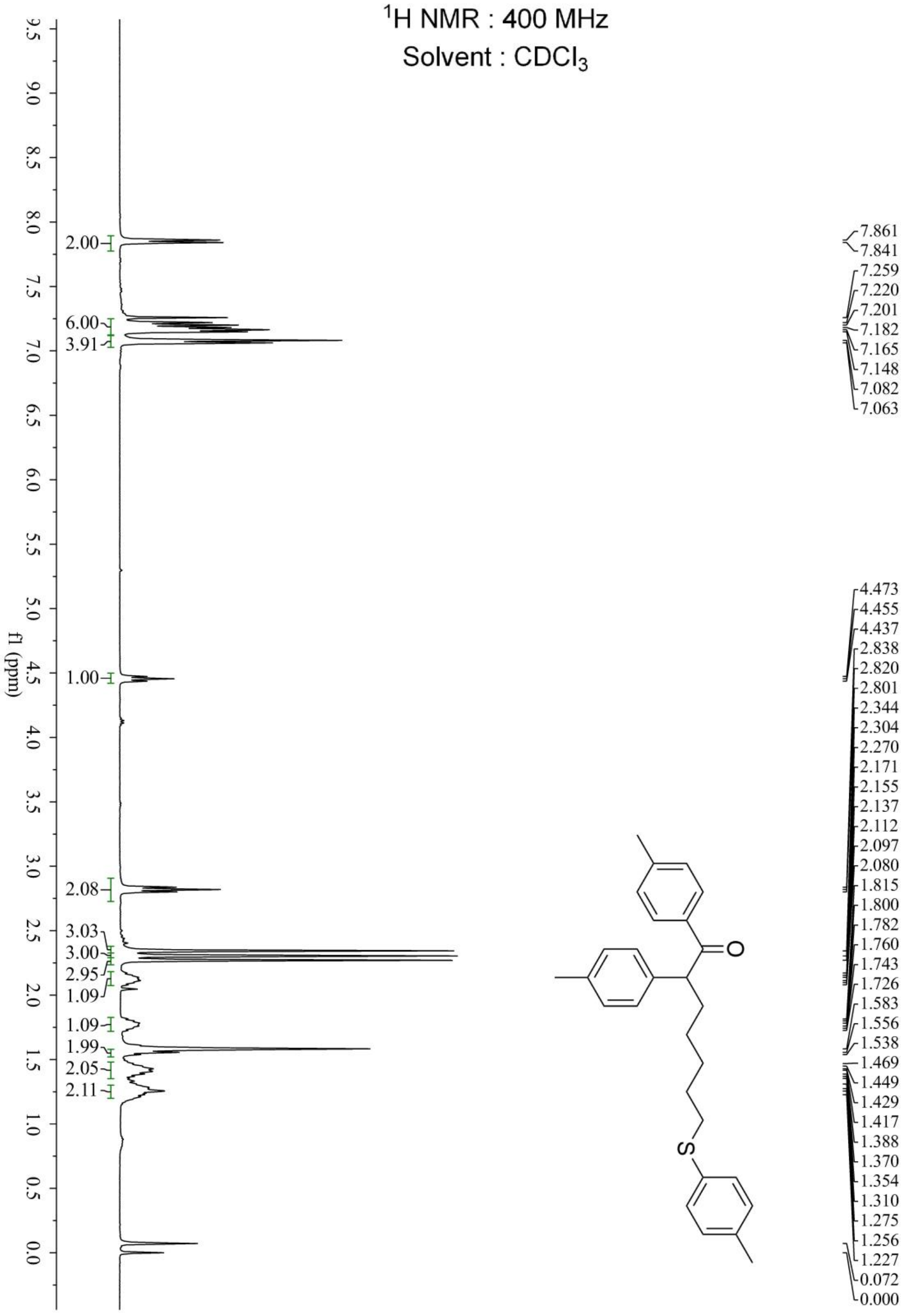


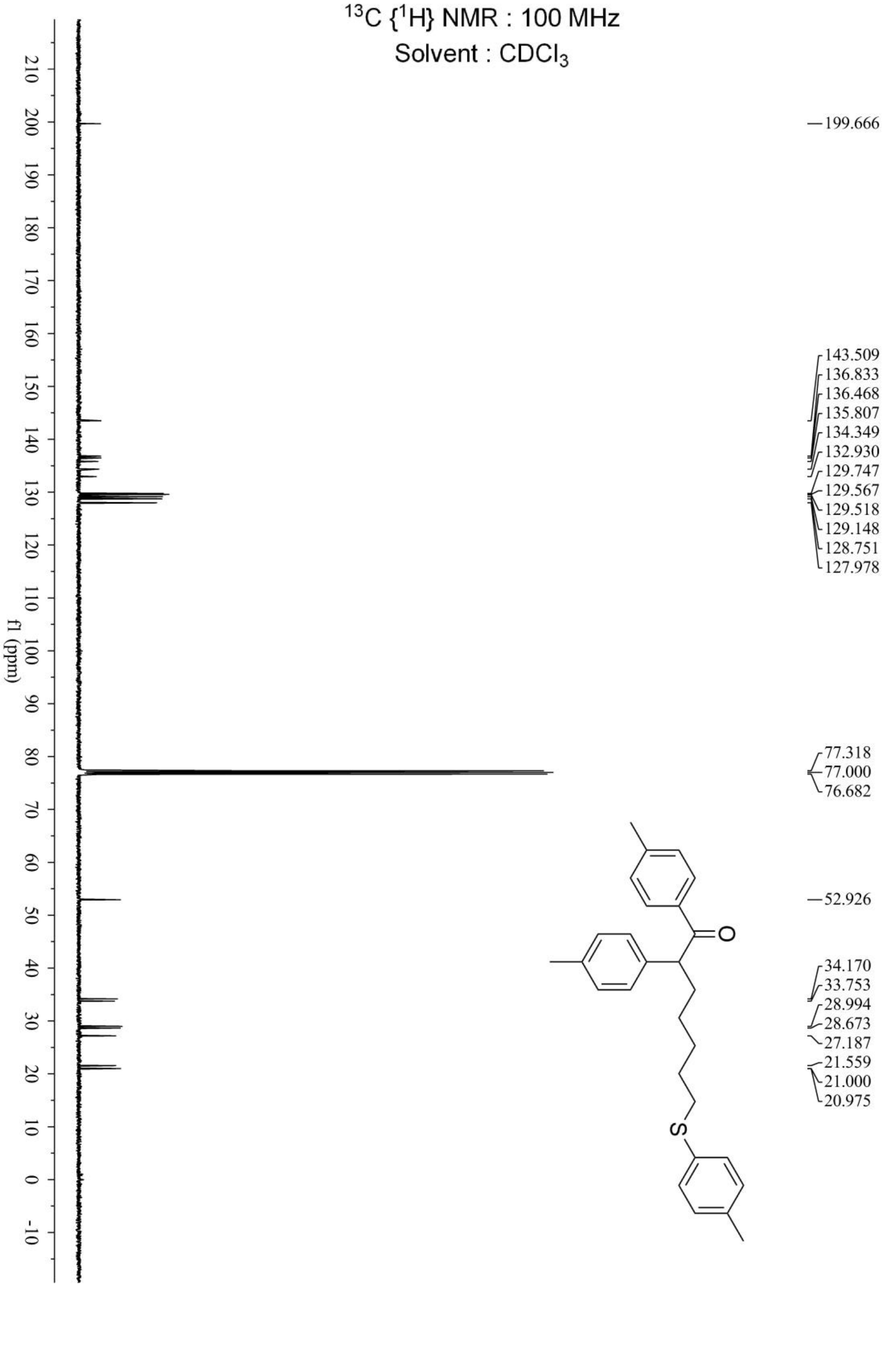
^{13}C {^{1}H} NMR : 100 MHz

Solvent : $CDCl_3$

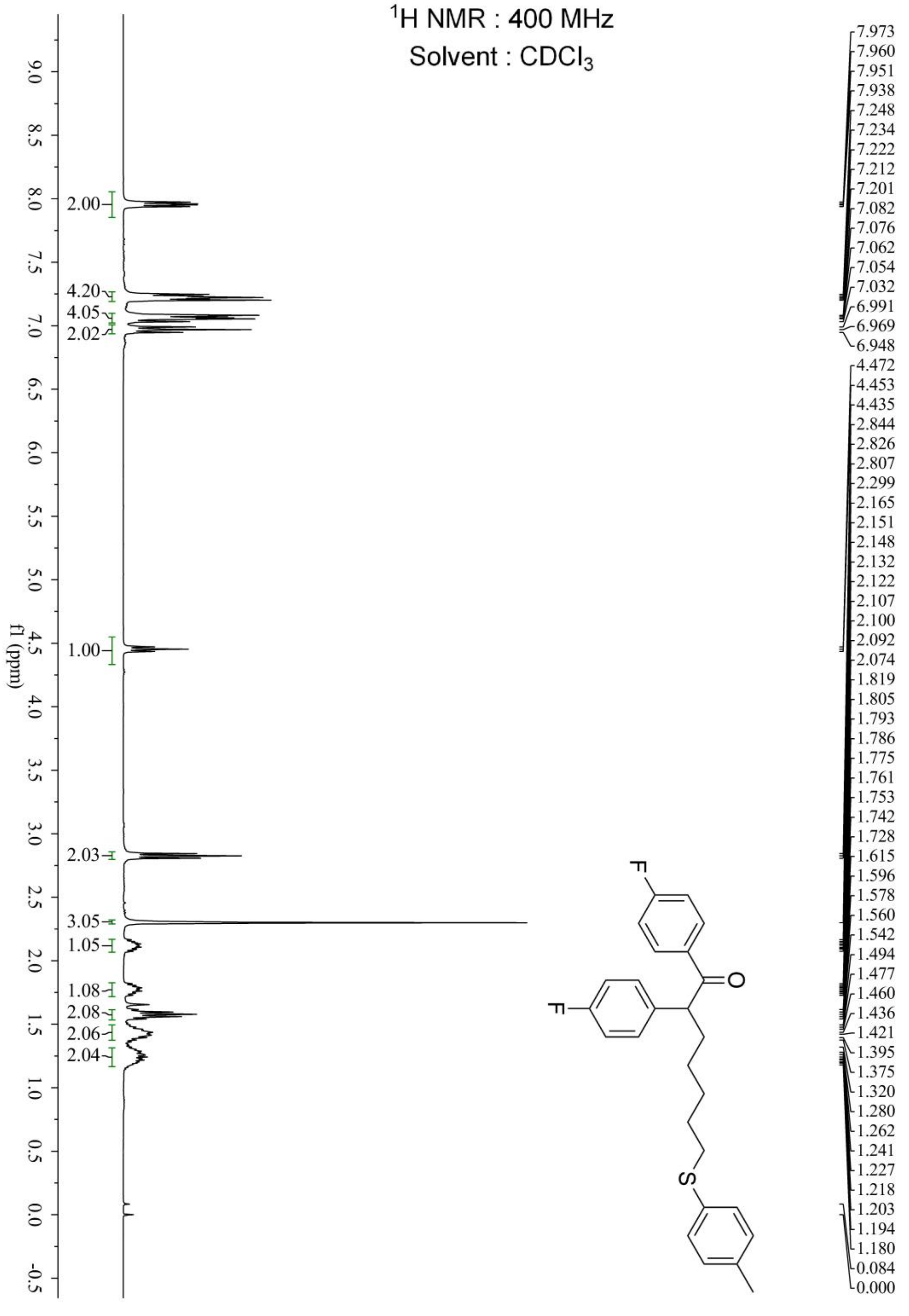


1,2-di-*p*-tolyl-7-(*p*-tolylthio)heptan-1-one (3ca)

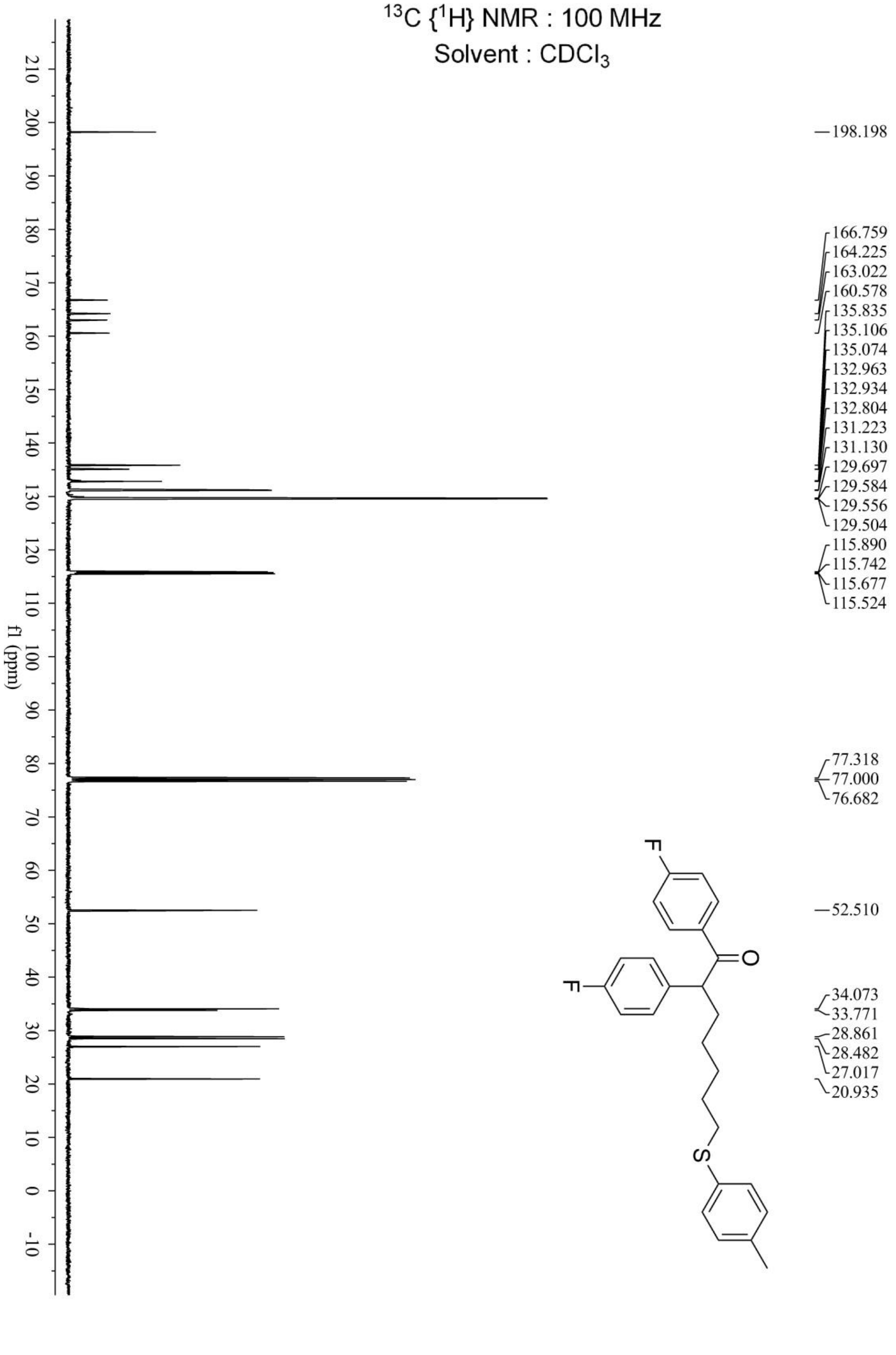



$^{13}C\ \{^1H\}$ NMR : 100 MHz
Solvent : $CDCl_3$
199.666
143.509
136.833
136.468
135.807
134.349
132.930
129.747
129.567
129.518
129.148
128.751
127.978
77.318
77.000
76.682
52.926
34.170
33.753
28.994
28.673
27.187
21.559
21.000
20.975
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
O
S

1,2-bis(4-fluorophenyl)-7-(*p*-tolylthio)heptan-1-one (3da)

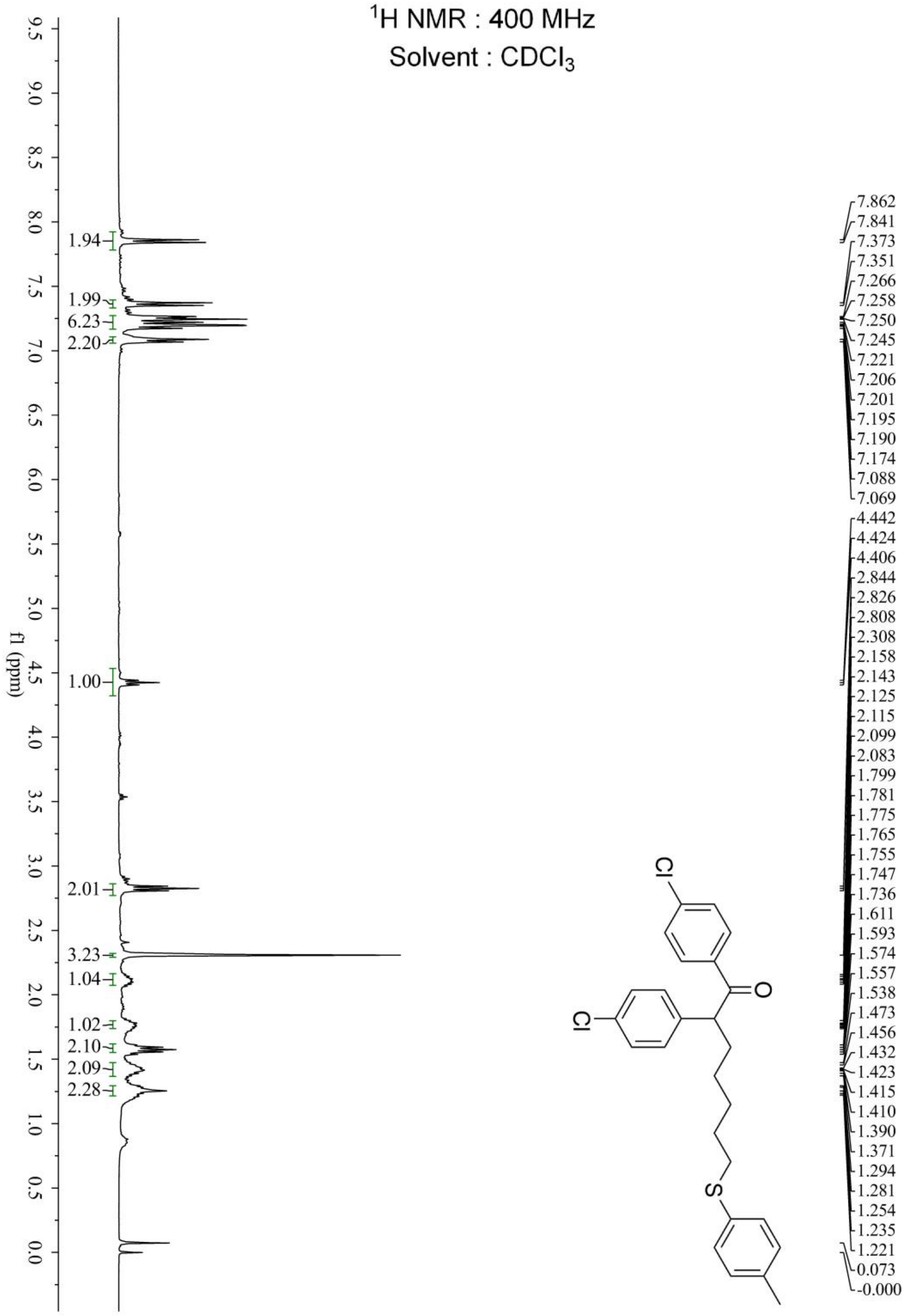


^{13}C {^{1}H} NMR : 100 MHz
Solvent : $CDCl_3$

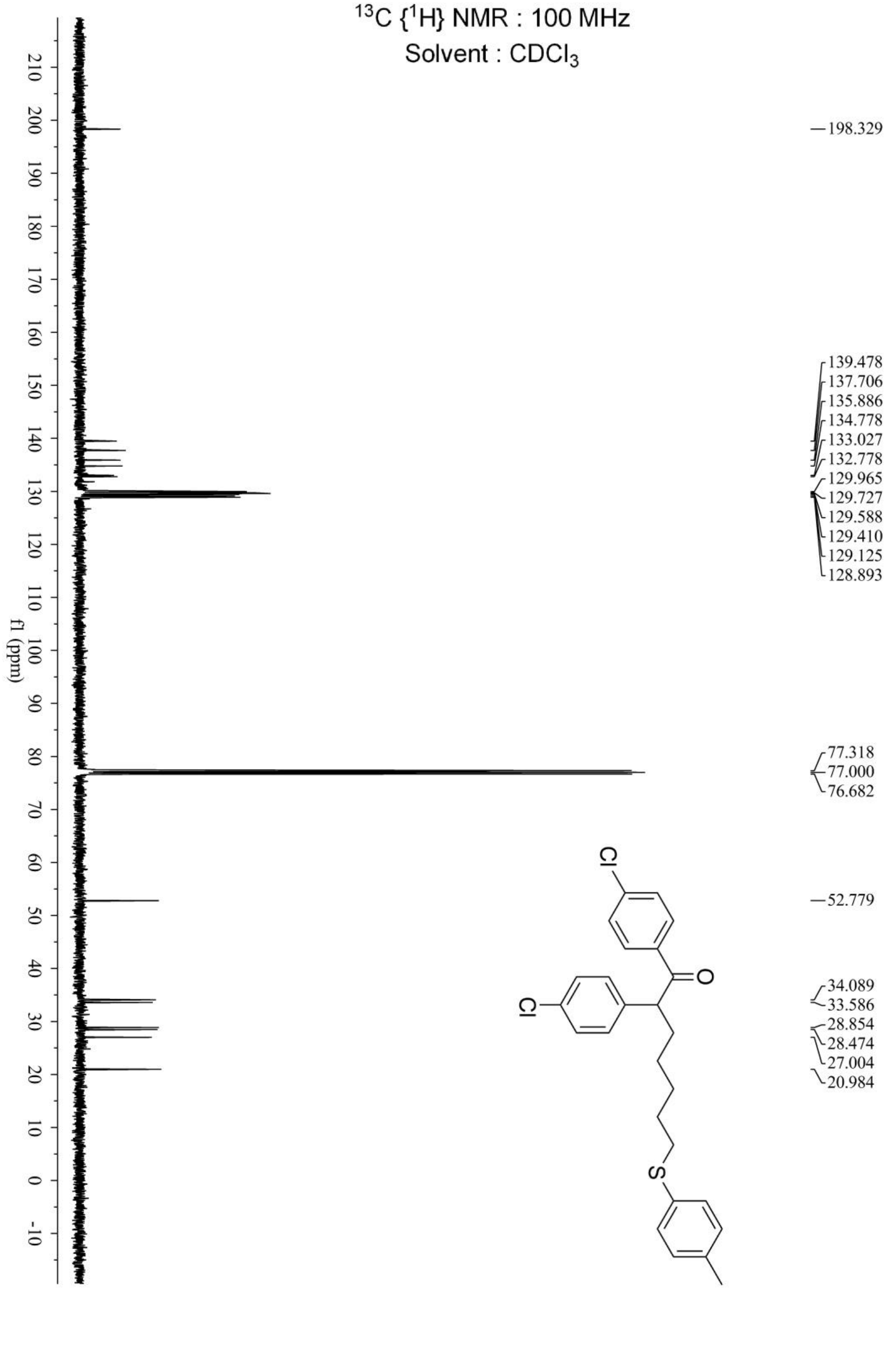


^{19}F NMR : 282 MHz
Solvent : $CDCl_3$

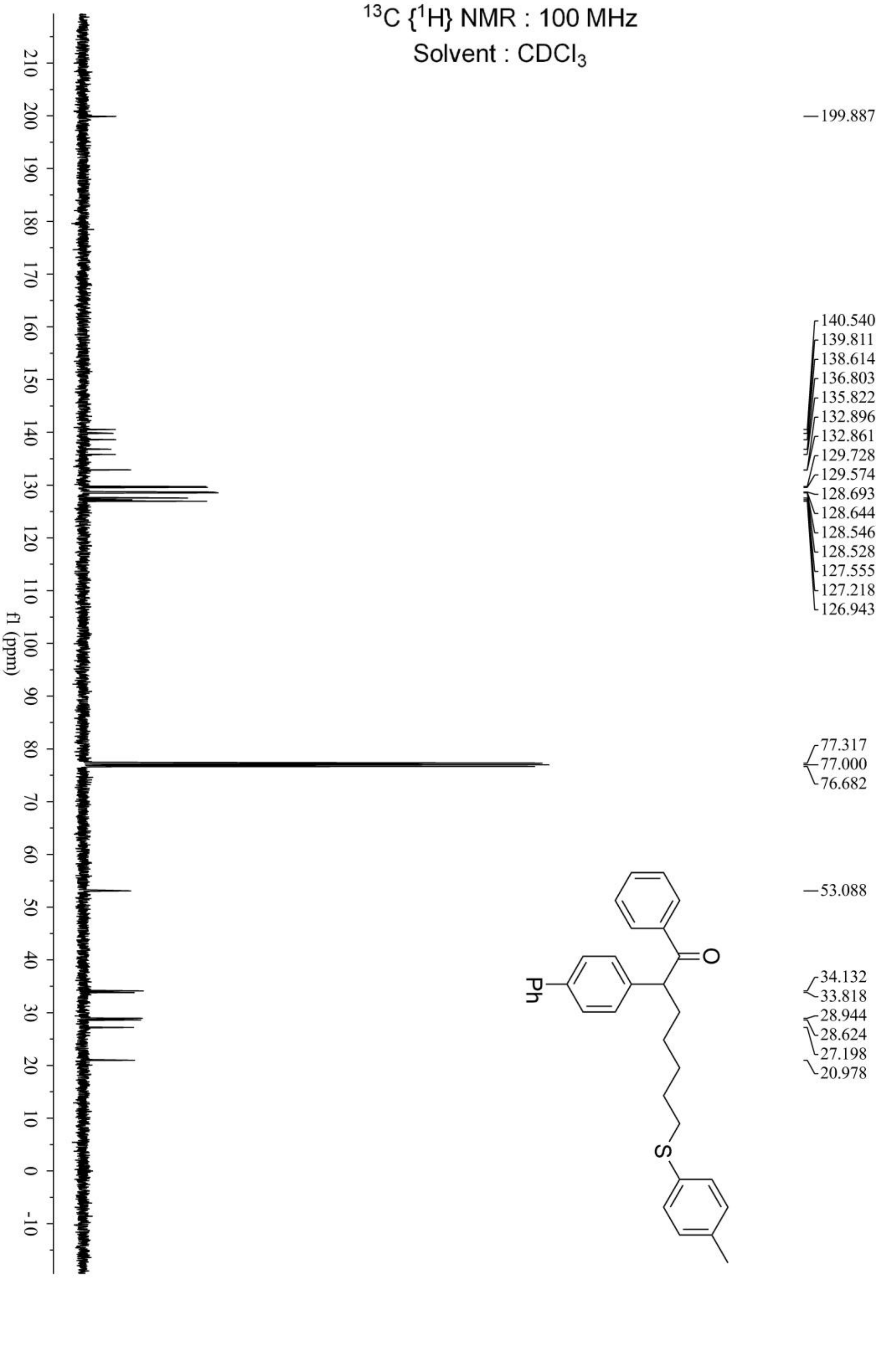
1,2-bis(4-chlorophenyl)-7-(*p*-tolylthio)heptan-1-one (3ea)

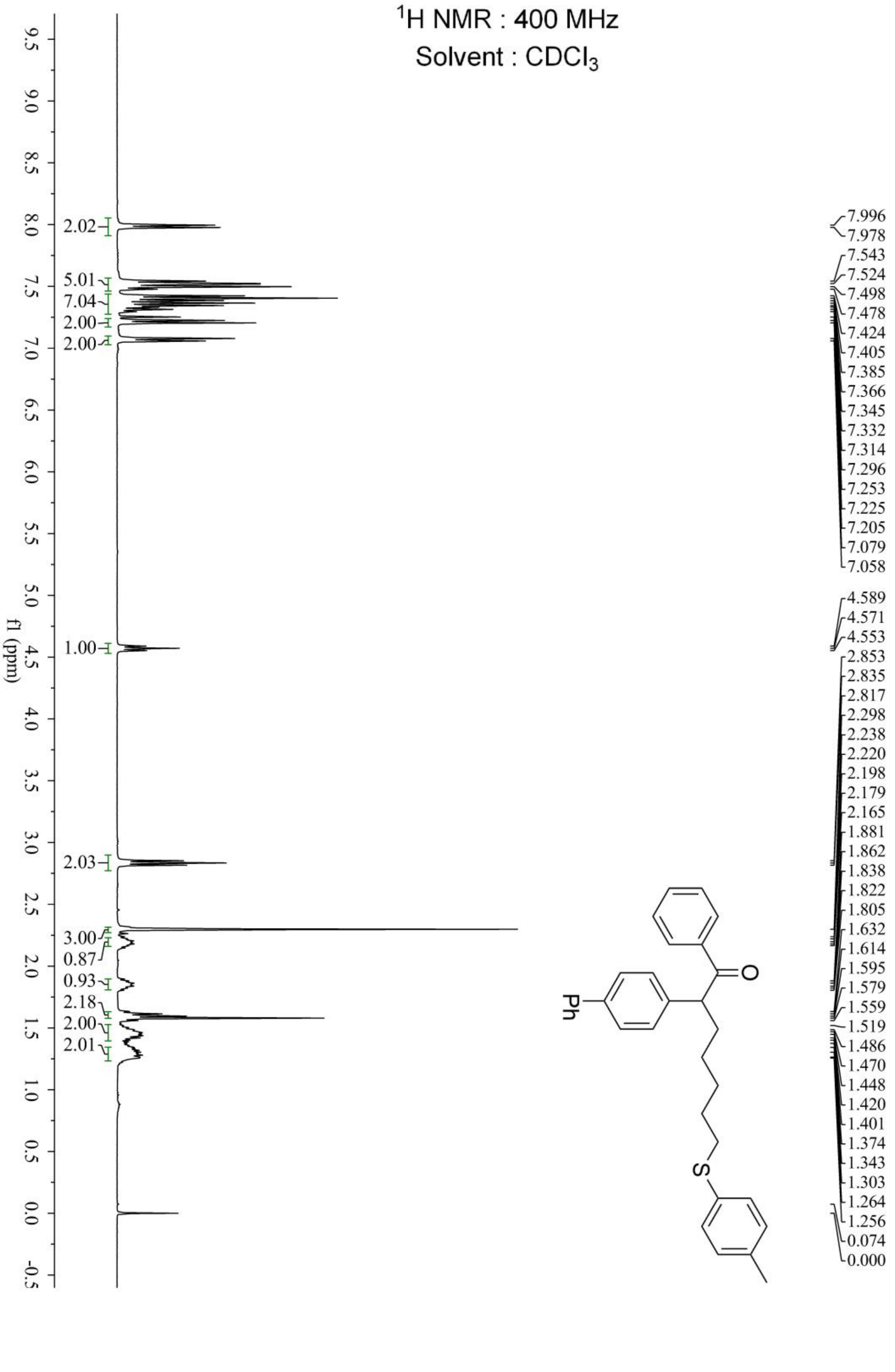


$^{13}C\ \{^1H\}$ NMR : 100 MHz
Solvent : $CDCl_3$

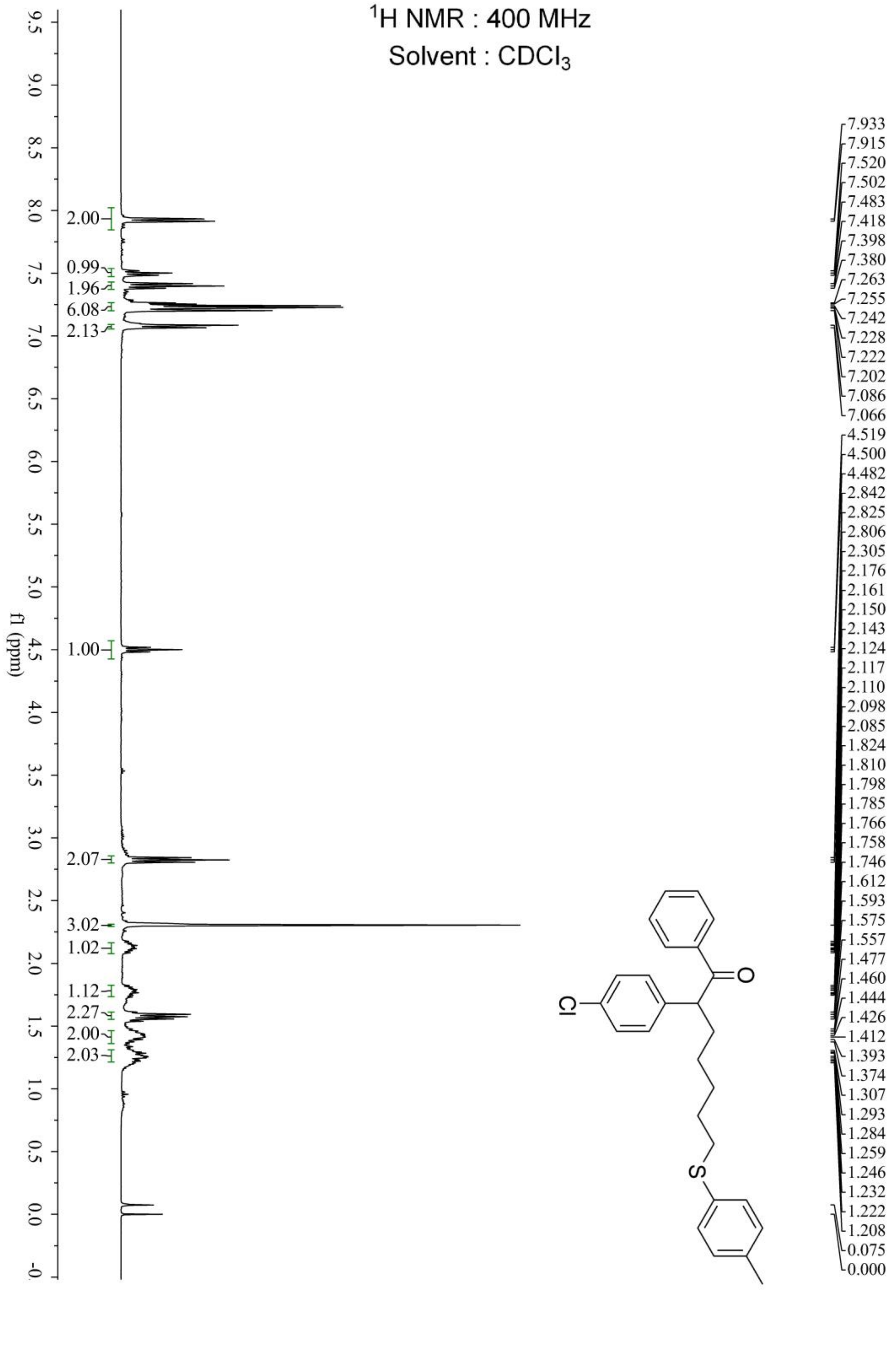


2- ([1,1'-biphenyl]-4-yl)-1-phenyl-7-(*p*-tolylthio)heptan-1-one (3fa)



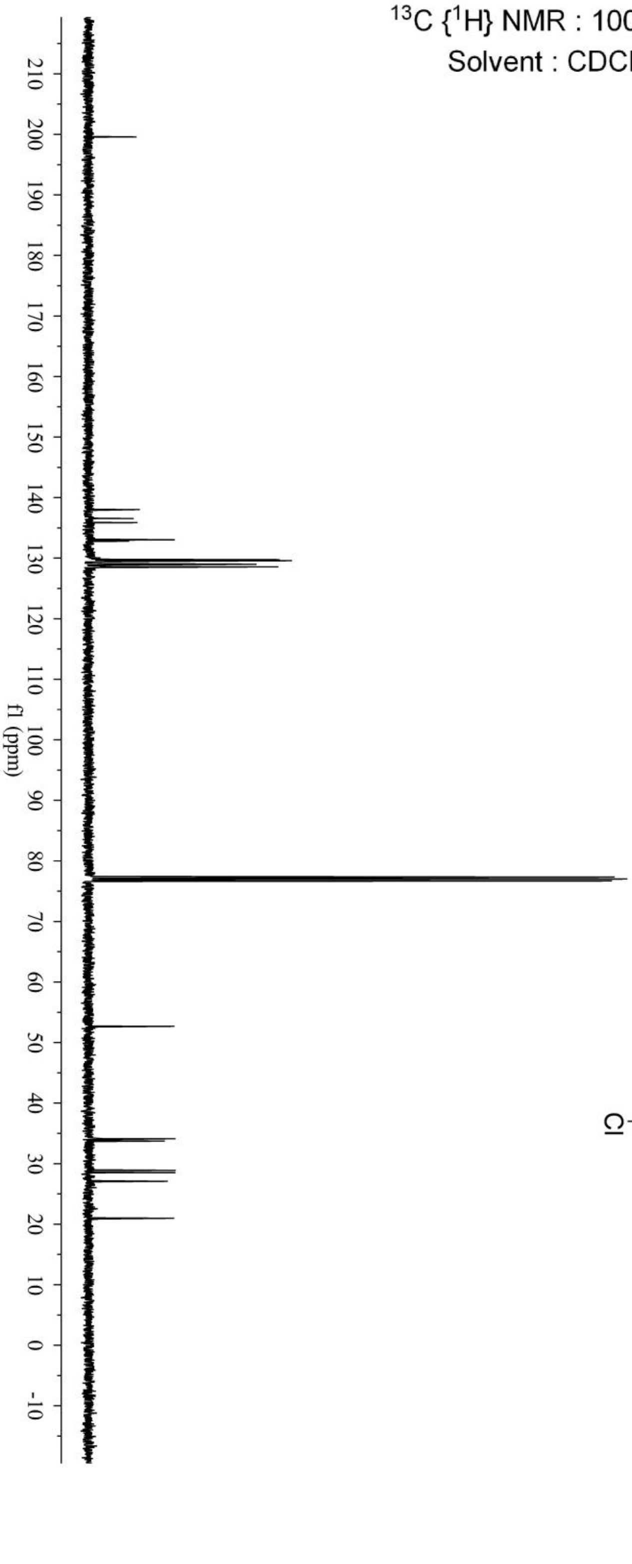

^{1}H NMR : 400 MHz
Solvent : $CDCl_3$
f1 (ppm)
2.02
5.01
7.04
2.00
2.00
1.00
2.03
3.00
0.87
0.93
2.18
2.00
2.01
7.996
7.978
7.543
7.524
7.498
7.478
7.424
7.405
7.385
7.366
7.345
7.332
7.314
7.296
7.253
7.225
7.205
7.079
7.058
4.589
4.571
4.553
2.853
2.835
2.817
2.298
2.238
2.220
2.198
2.179
2.165
1.881
1.862
1.838
1.822
1.805
1.632
1.614
1.595
1.579
1.559
1.519
1.486
1.470
1.448
1.420
1.401
1.374
1.343
1.303
1.264
1.256
0.074
0.000
Ph
O
S

3-(4-chlorophenyl)-1-phenyl-7-(*p*-tolylthio)heptan-1-one (3ga)



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

Solvent : $CDCl_3$



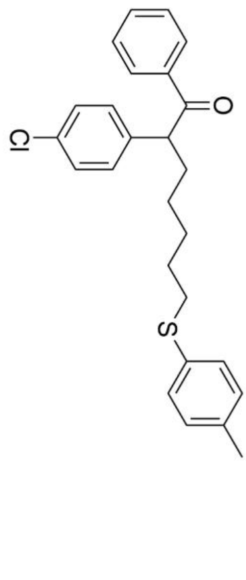
199.590

138.029
136.548
135.864
133.035
132.834
132.802
129.750
129.579
129.489
129.002
128.573
128.545

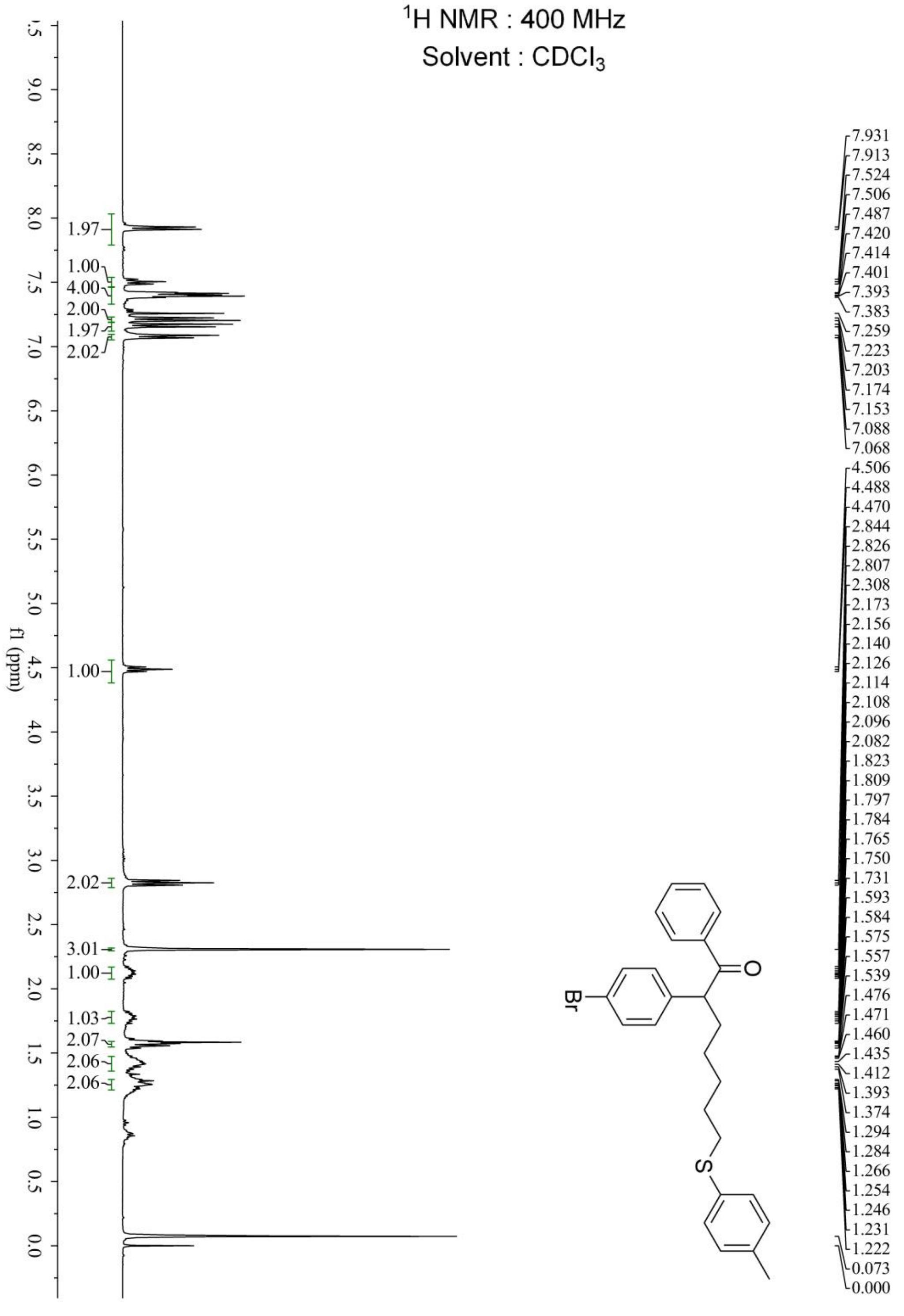
77.318
77.000
76.683

52.674

34.111
33.723
28.888
28.519
27.076
20.977

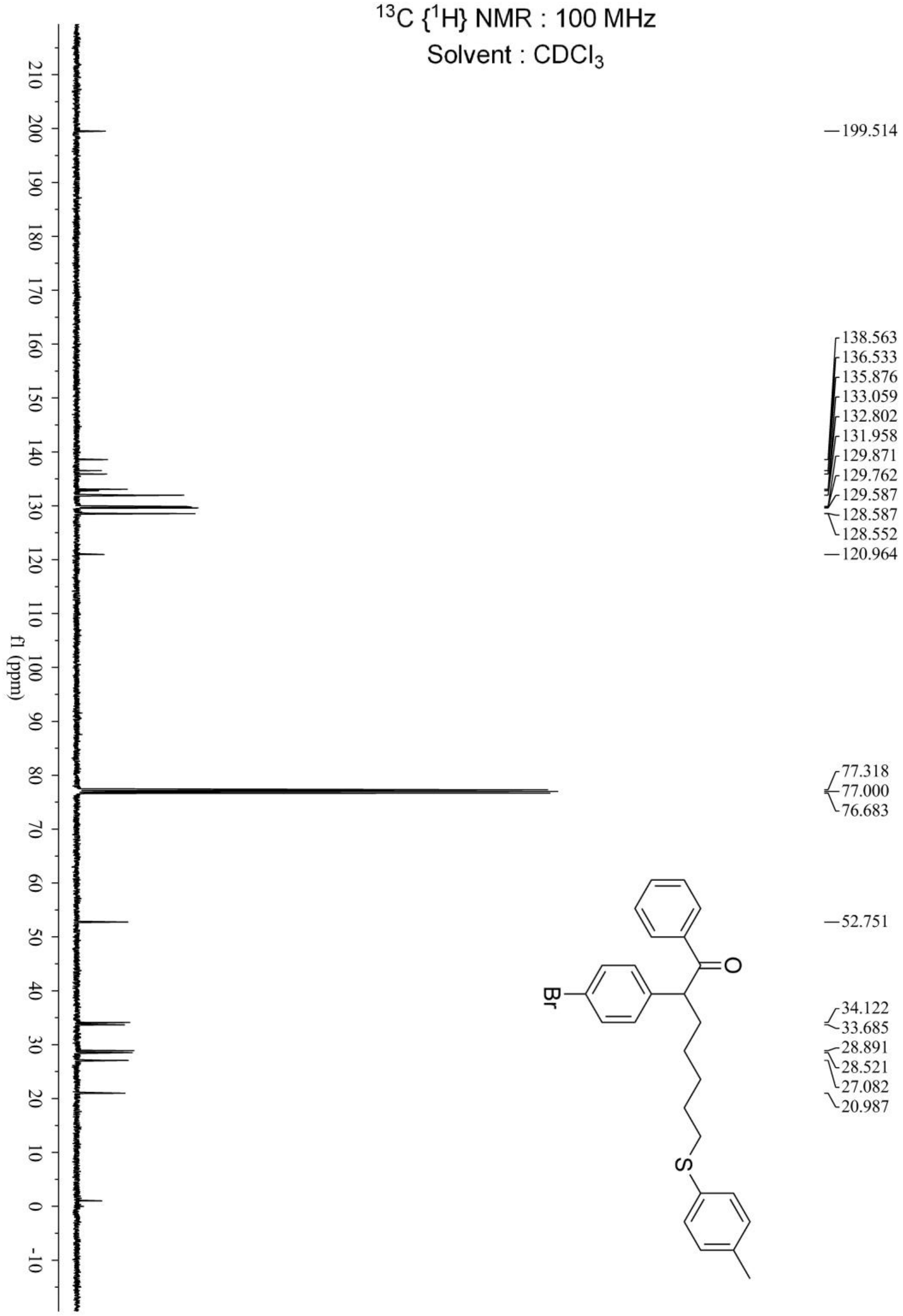


2-(4-bromophenyl)-1-phenyl-7-(*p*-tolylthio)heptan-1-one (3ha)

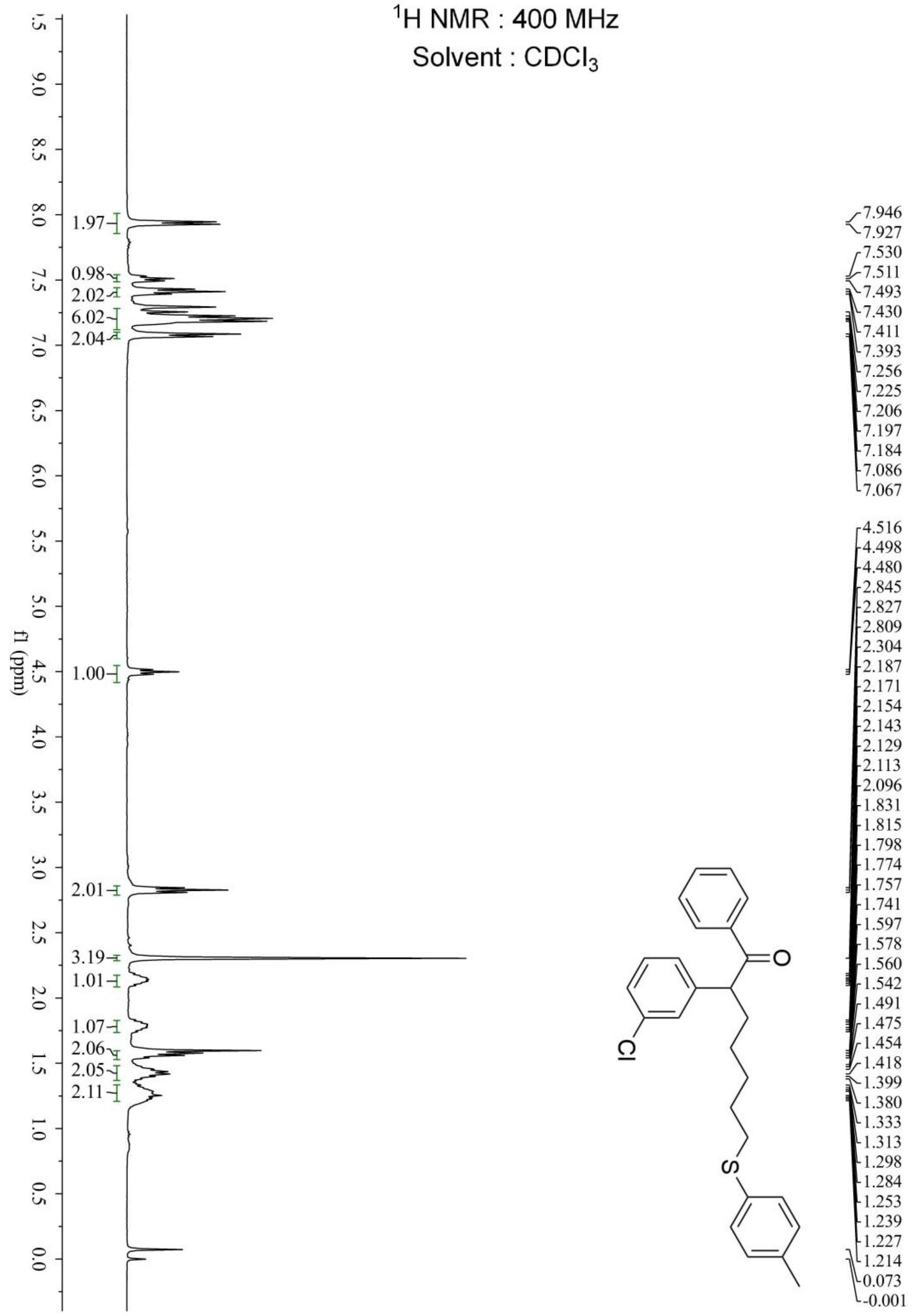


$^{13}C\ \{^{1}H\}$ NMR : 100 MHz

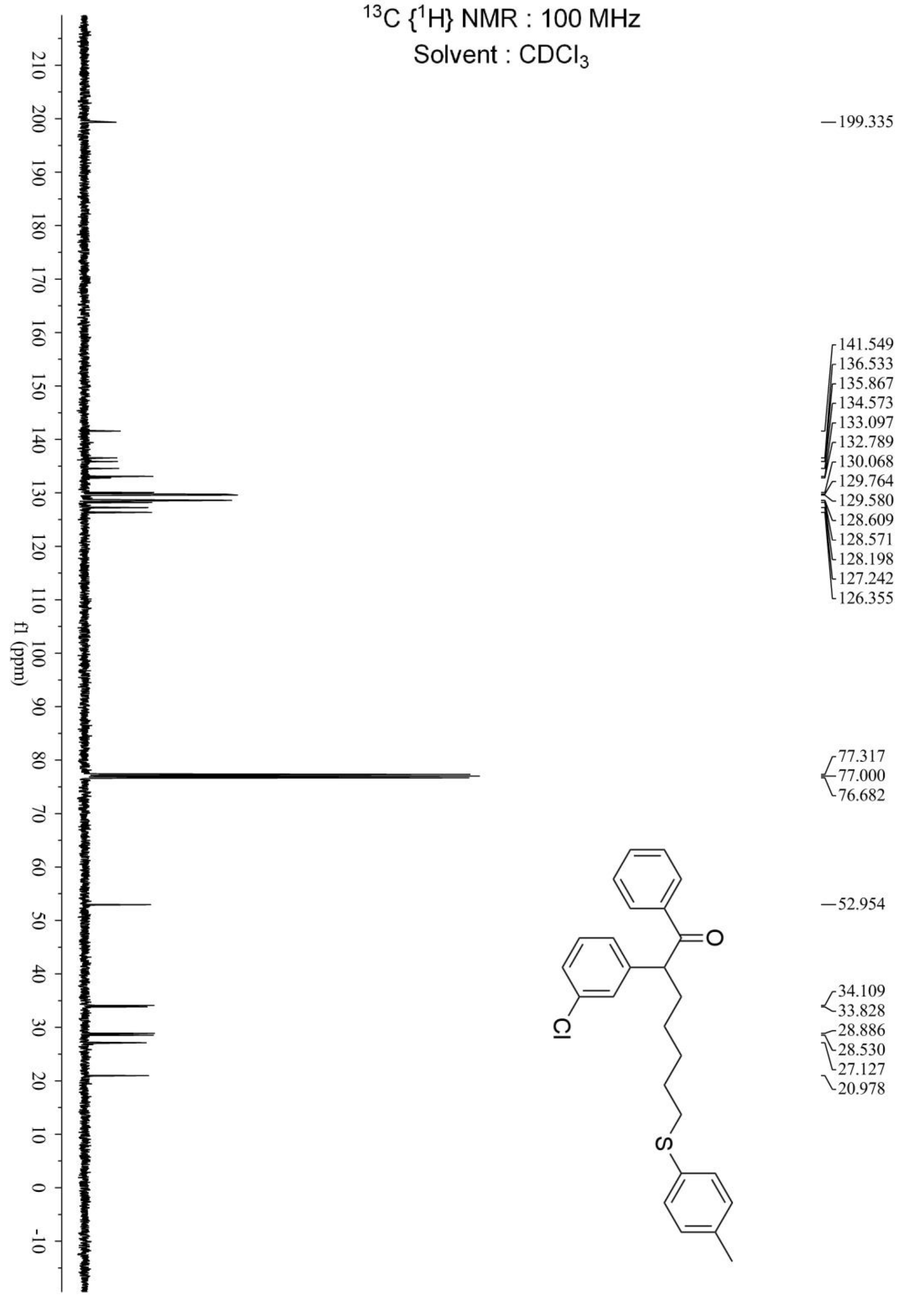
Solvent : $CDCl_3$



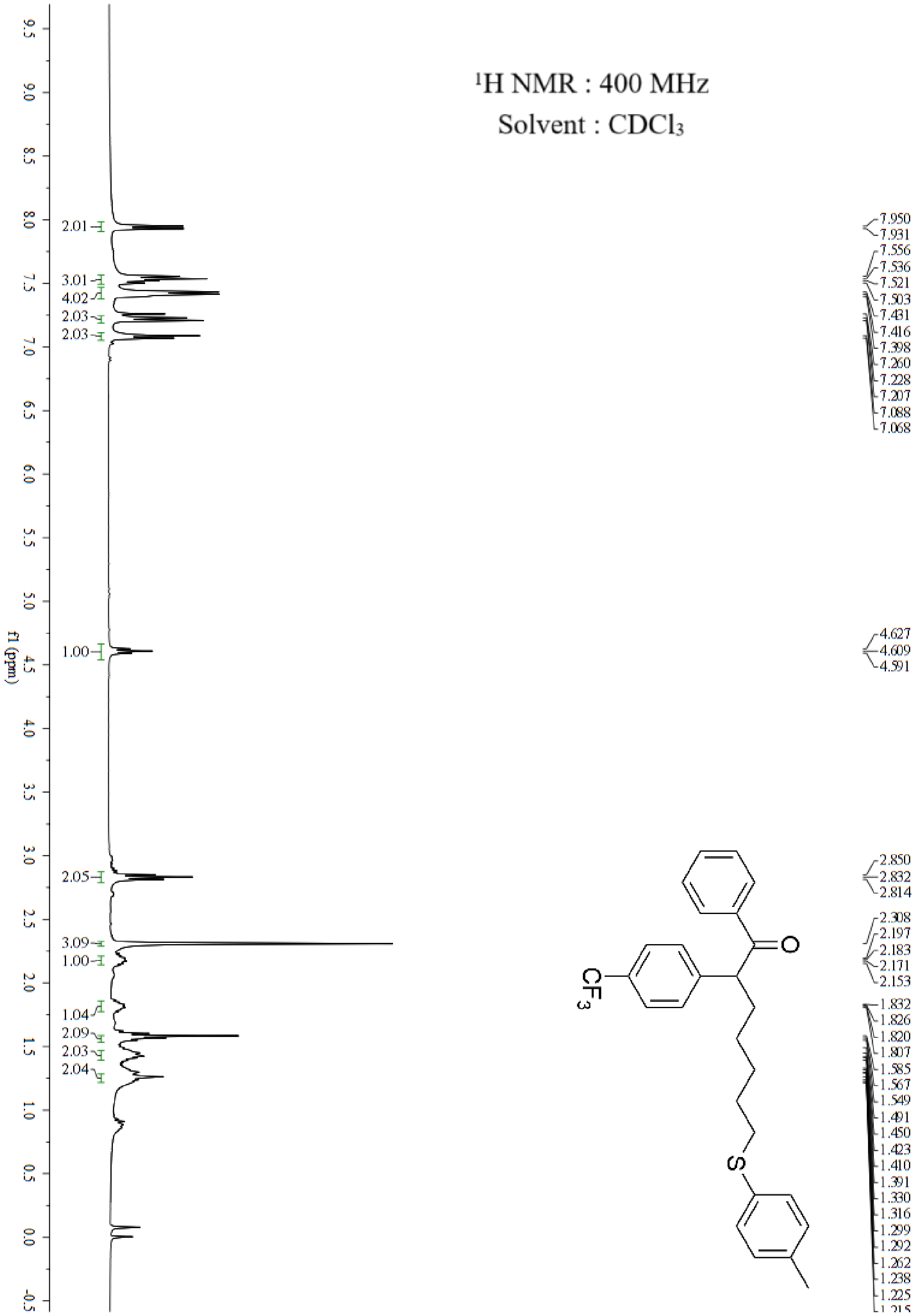
1-(3-chlorophenyl)-2-phenyl-7-(*p*-tolylthio)heptan-1-one (3ia)

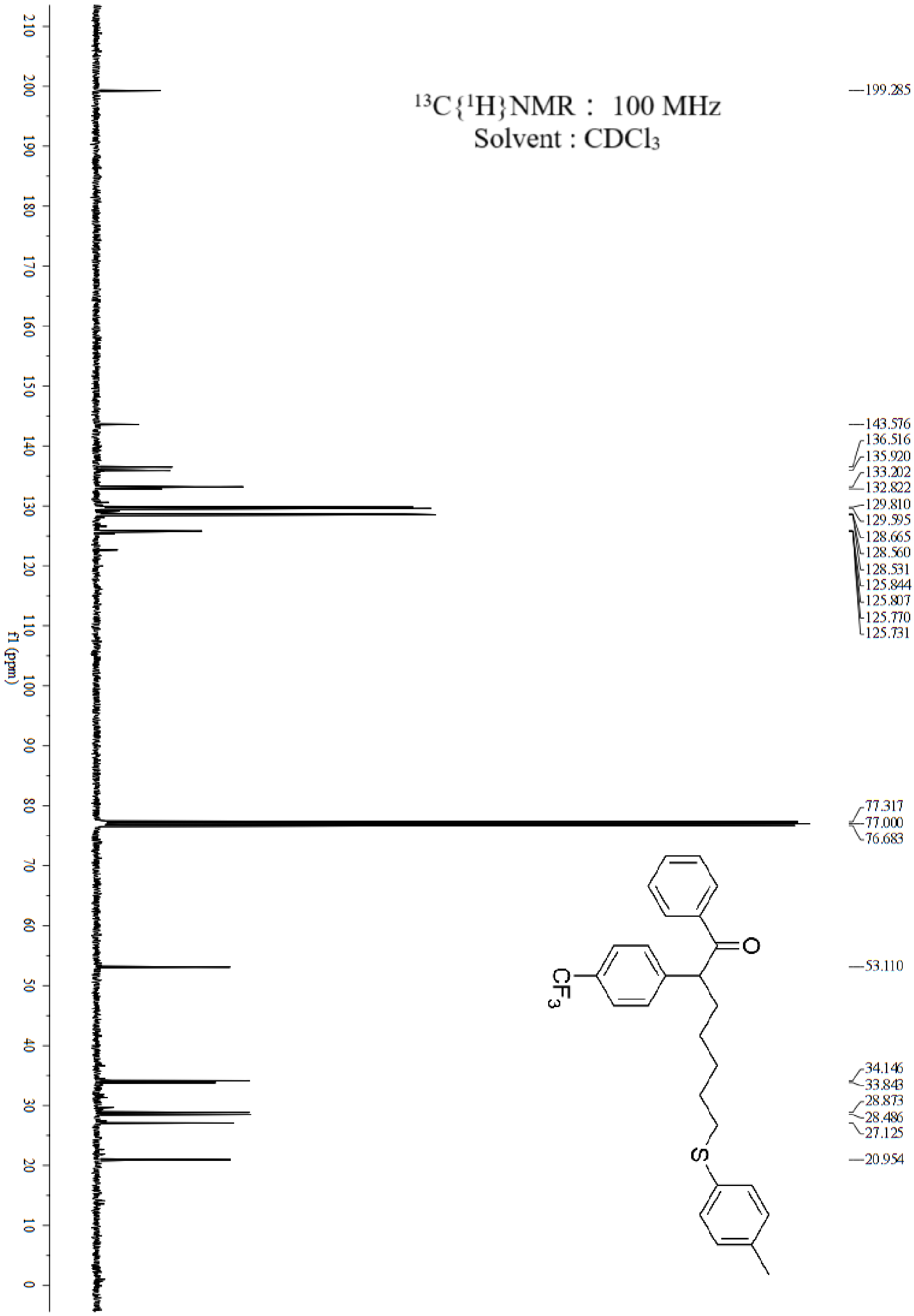


$^{13}C\ \{^{1}H\}$ NMR : 100 MHz
Solvent : $CDCl_3$

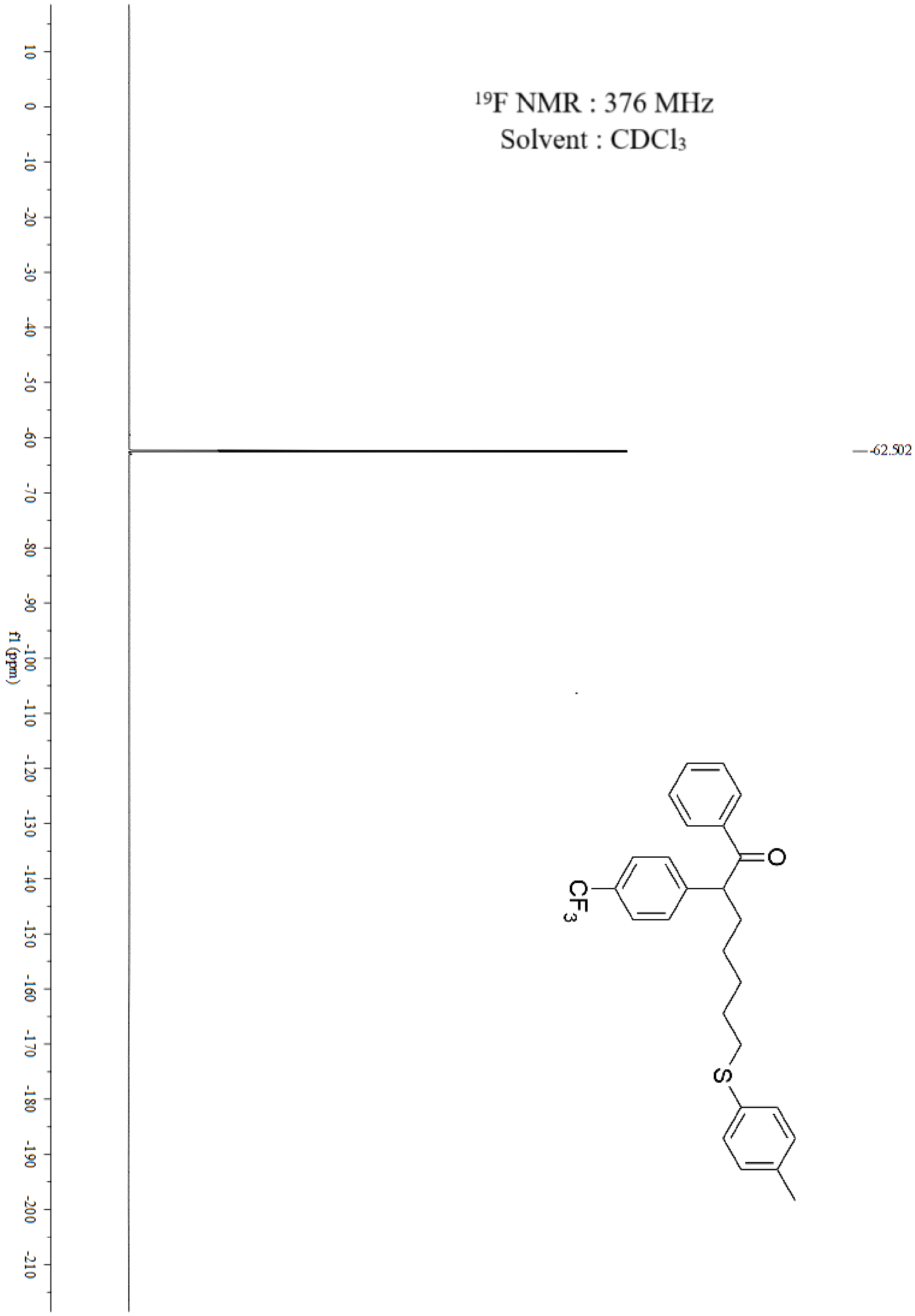


phenyl-7-(p-tolylthio)-2-(4-(trifluoromethyl)phenyl)heptan-1-one (3ja)

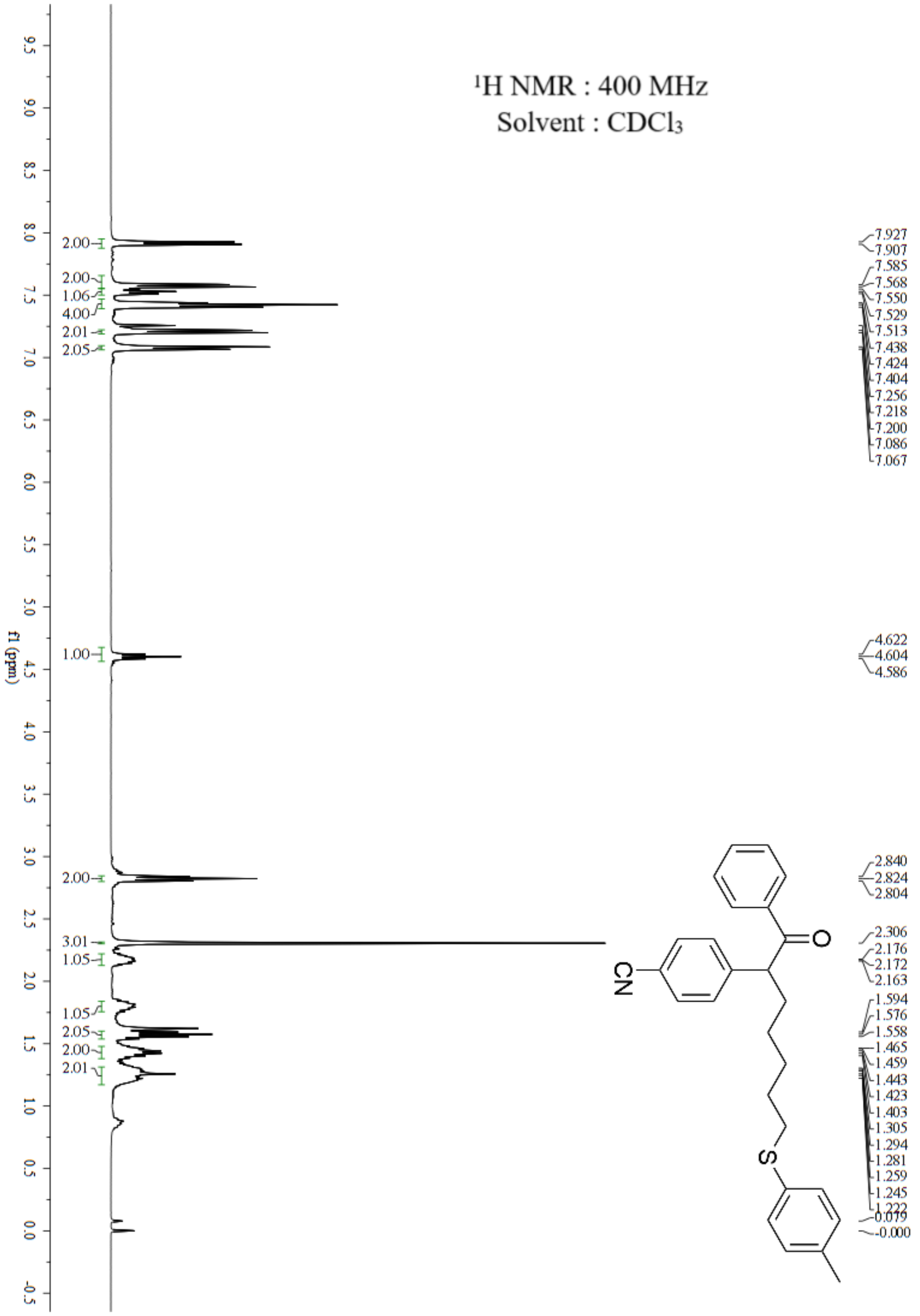


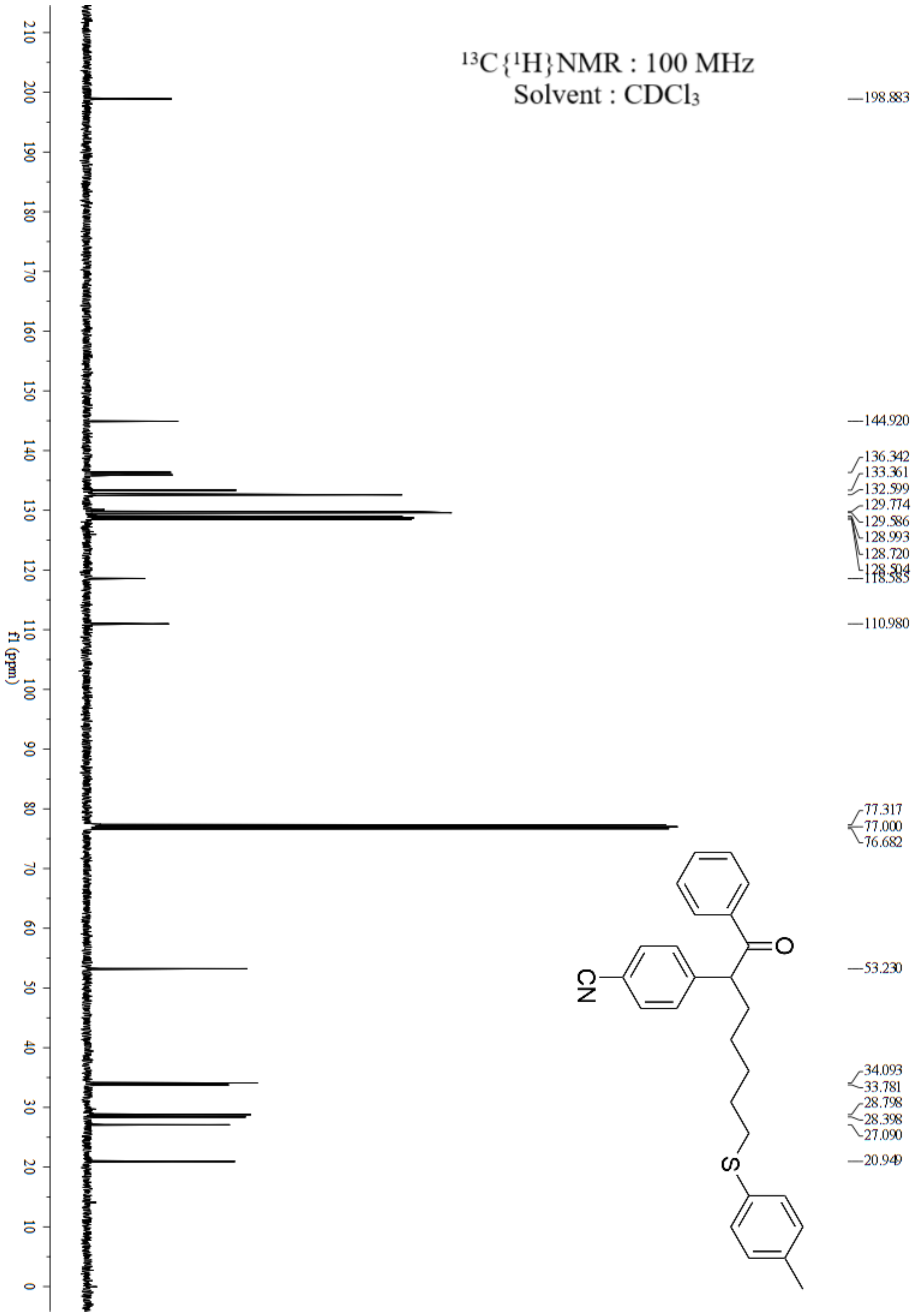

$^{13}C\{^{1}H\}$NMR : 100 MHz
Solvent : $CDCl_3$
199.285
143.576
136.516
135.920
133.202
132.822
129.810
129.595
128.665
128.560
128.531
125.844
125.807
125.770
125.731
77.317
77.000
76.683
53.110
34.146
33.843
28.873
28.486
27.125
20.954
f1 (ppm)
O
CF_3
S

^{19}F NMR : 376 MHz
Solvent : $CDCl_3$



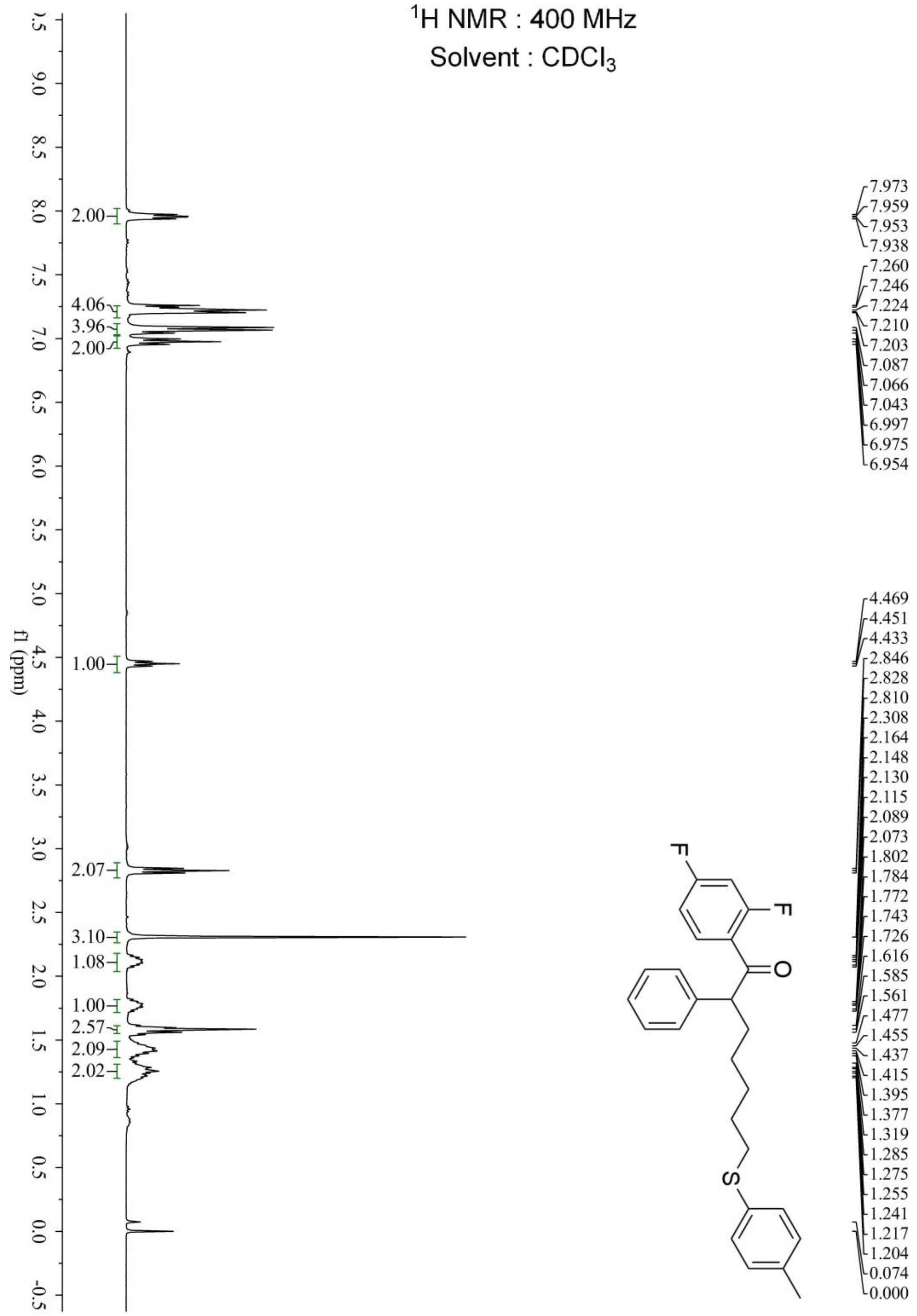
4-(1-oxo-1-phenyl-7-(p-tolylthio)heptan-2-yl)benzonitrile (3ka)

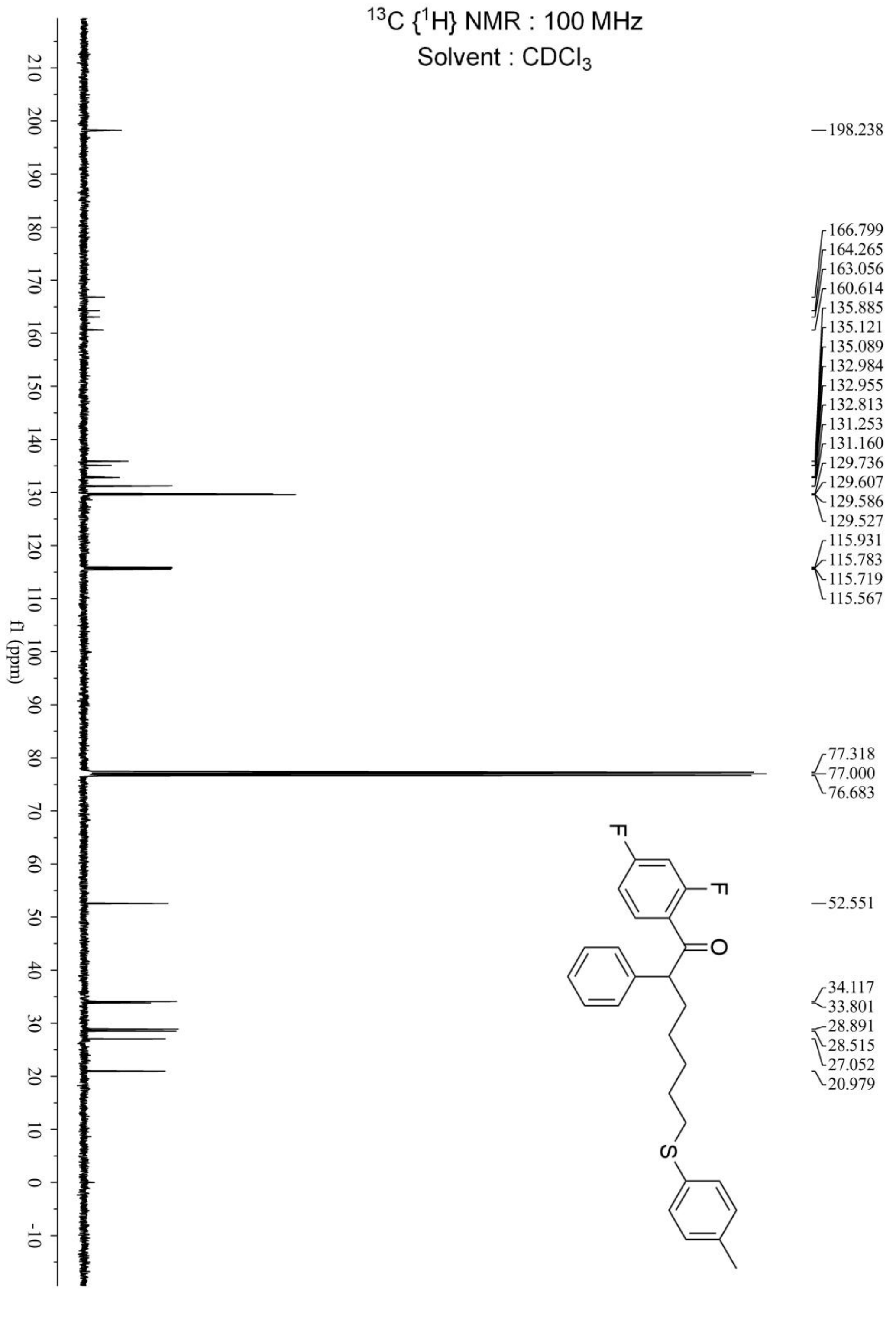


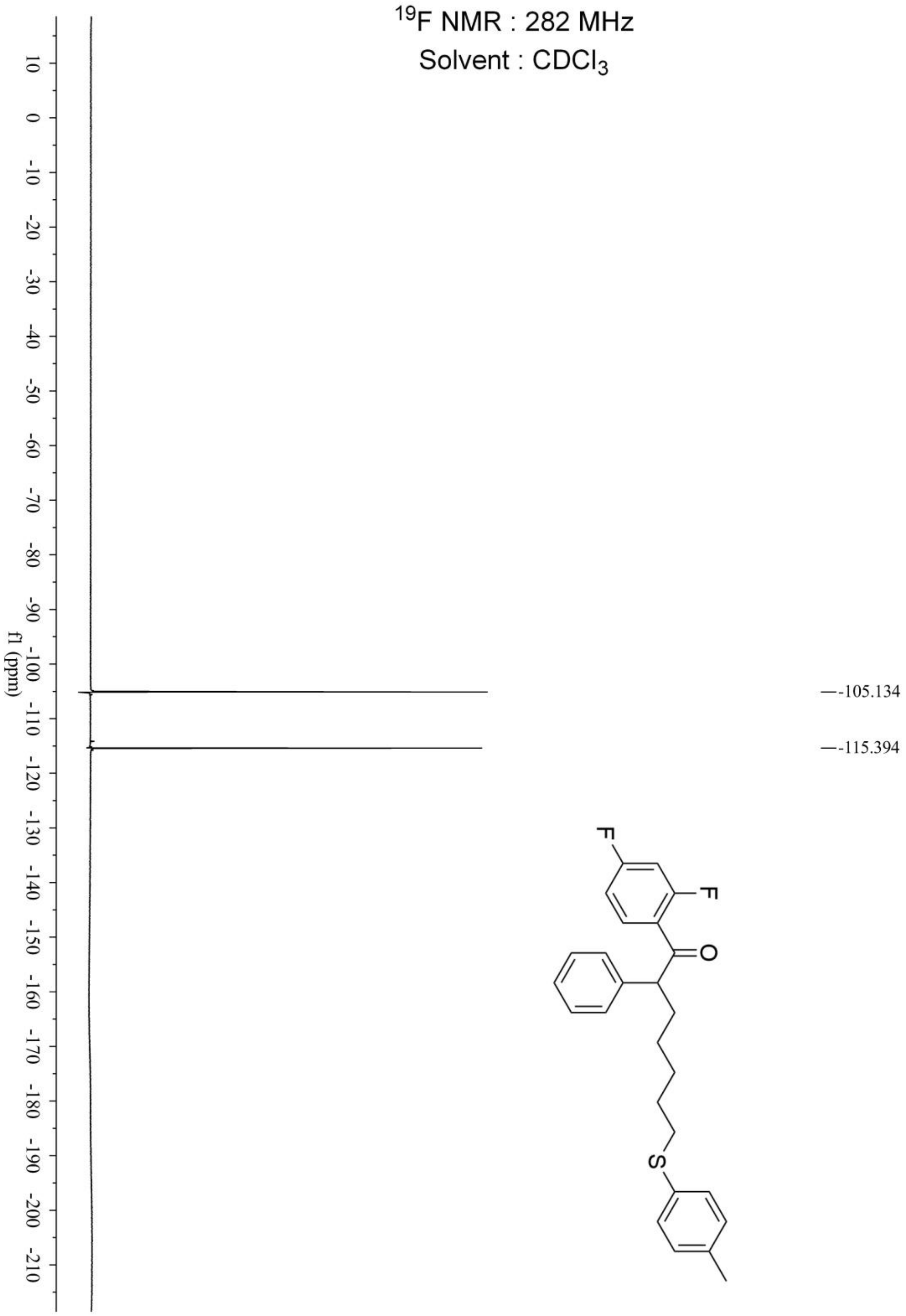


$^{13}C\{^1H\}$NMR : 100 MHz
Solvent : $CDCl_3$
198.883
144.920
136.342
133.361
132.599
129.774
129.586
128.993
128.720
128.504
118.585
110.980
77.317
77.000
76.682
53.230
34.093
33.781
28.798
28.398
27.090
20.949
f1 (ppm)

1-(2,4-difluorophenyl)-1-phenyl-7-(*p*-tolylthio)heptan-1-one (3la)

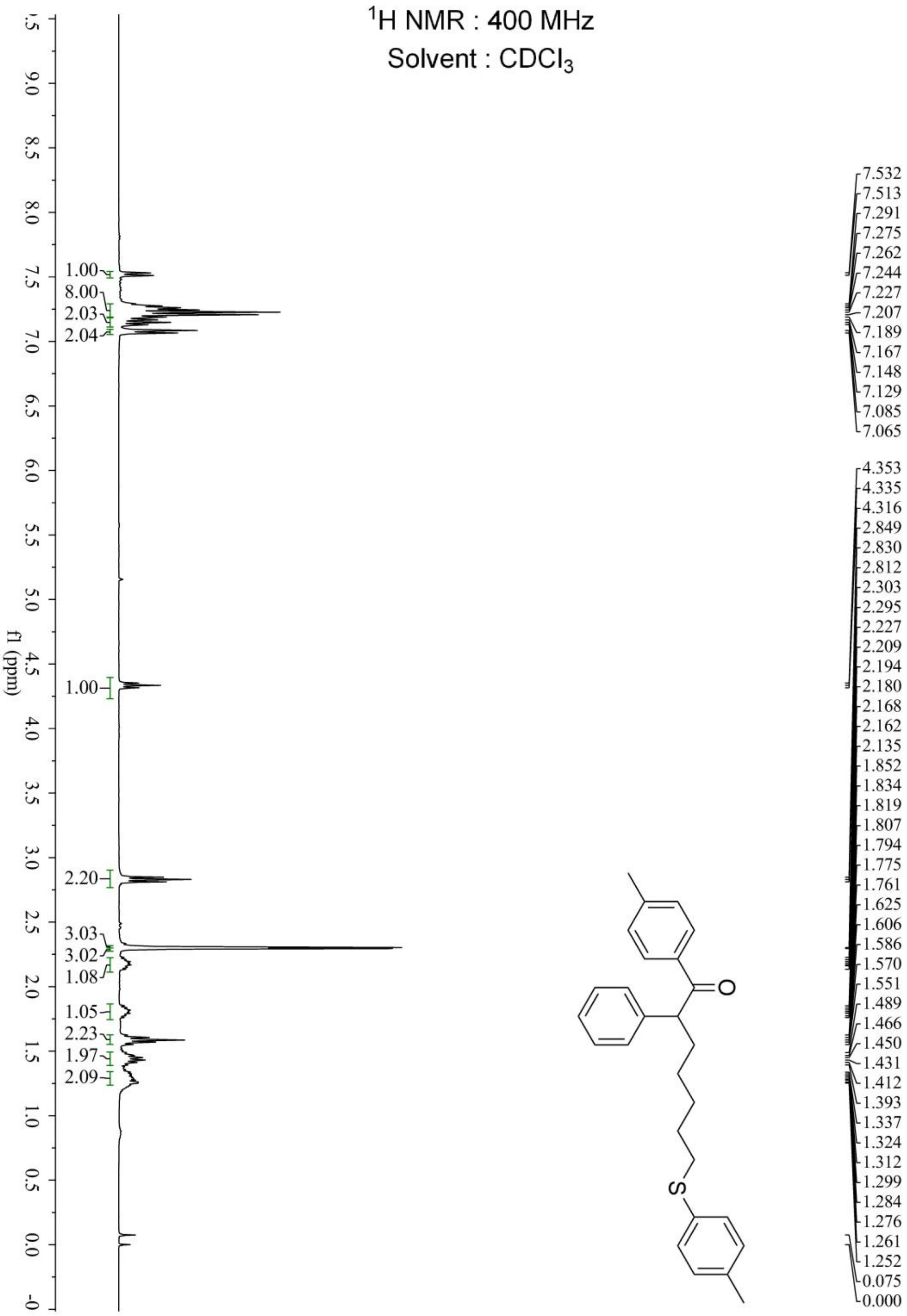



$^{13}C\ \{^1H\}$ NMR : 100 MHz
Solvent : $CDCl_3$
198.238
166.799
164.265
163.056
160.614
135.885
135.121
135.089
132.984
132.955
132.813
131.253
131.160
129.736
129.607
129.586
129.527
115.931
115.783
115.719
115.567
77.318
77.000
76.683
52.551
34.117
33.801
28.891
28.515
27.052
20.979
f1 (ppm)
F
F
O
S



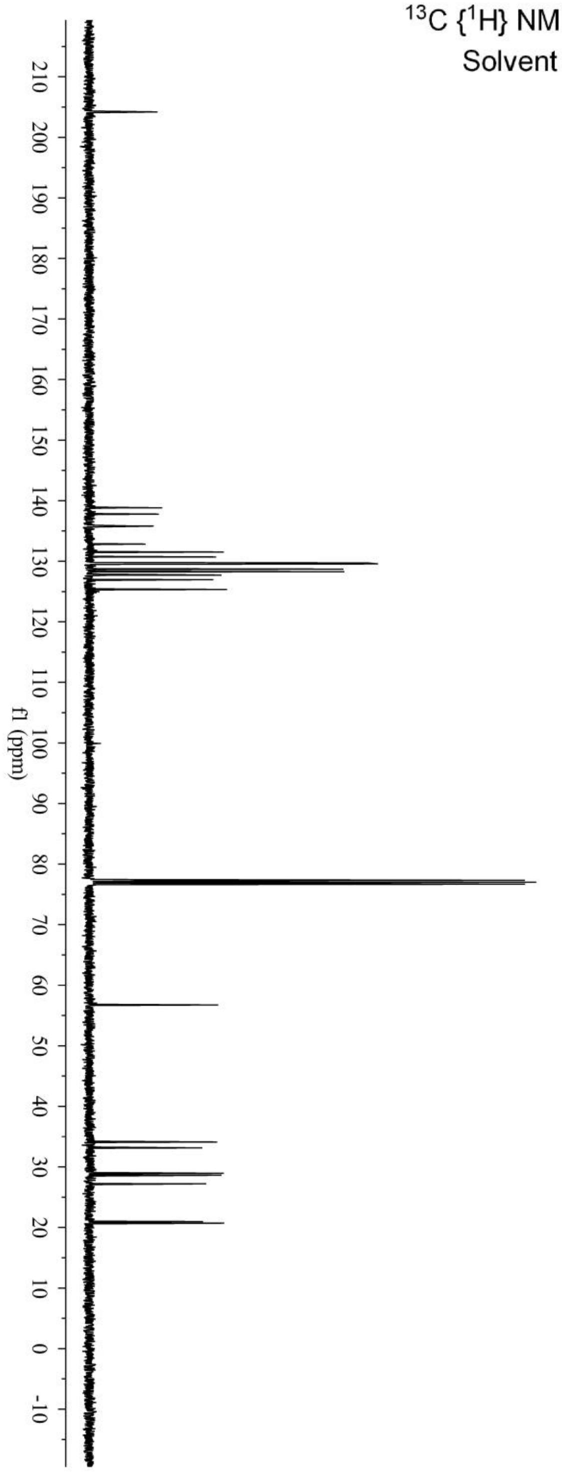
19F NMR : 282 MHz
Solvent : CDCl3
-105.134
-115.394
f1 (ppm)
F
F
O
S

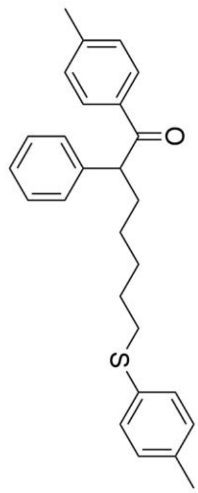
1-phenyl-1-(*p*-tolyl)-7-(*p*-tolylthio)heptan-1-one (3ma)



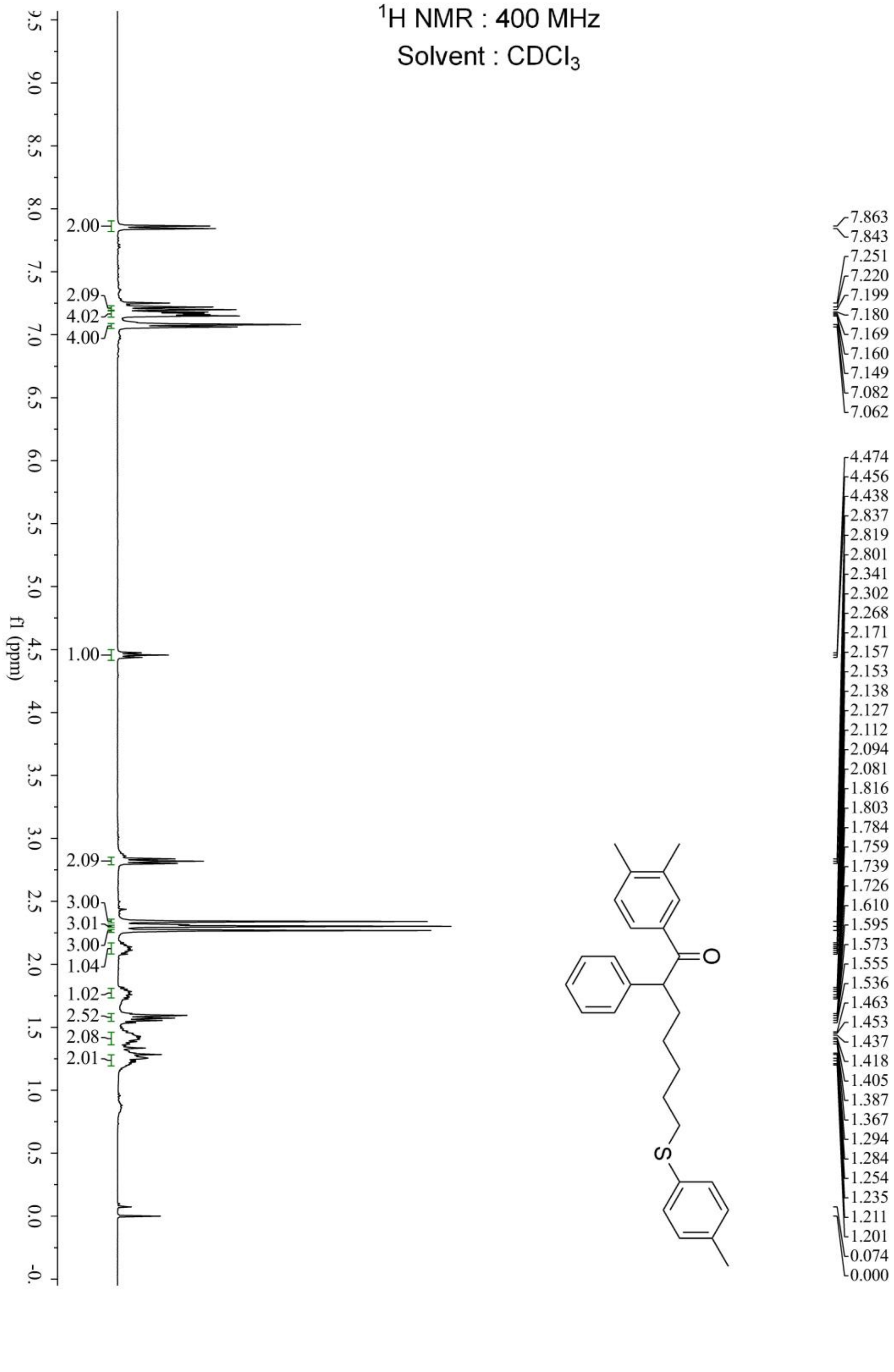
$^{13}C\ \{^1H\}$ NMR : 100 MHz

Solvent : $CDCl_3$



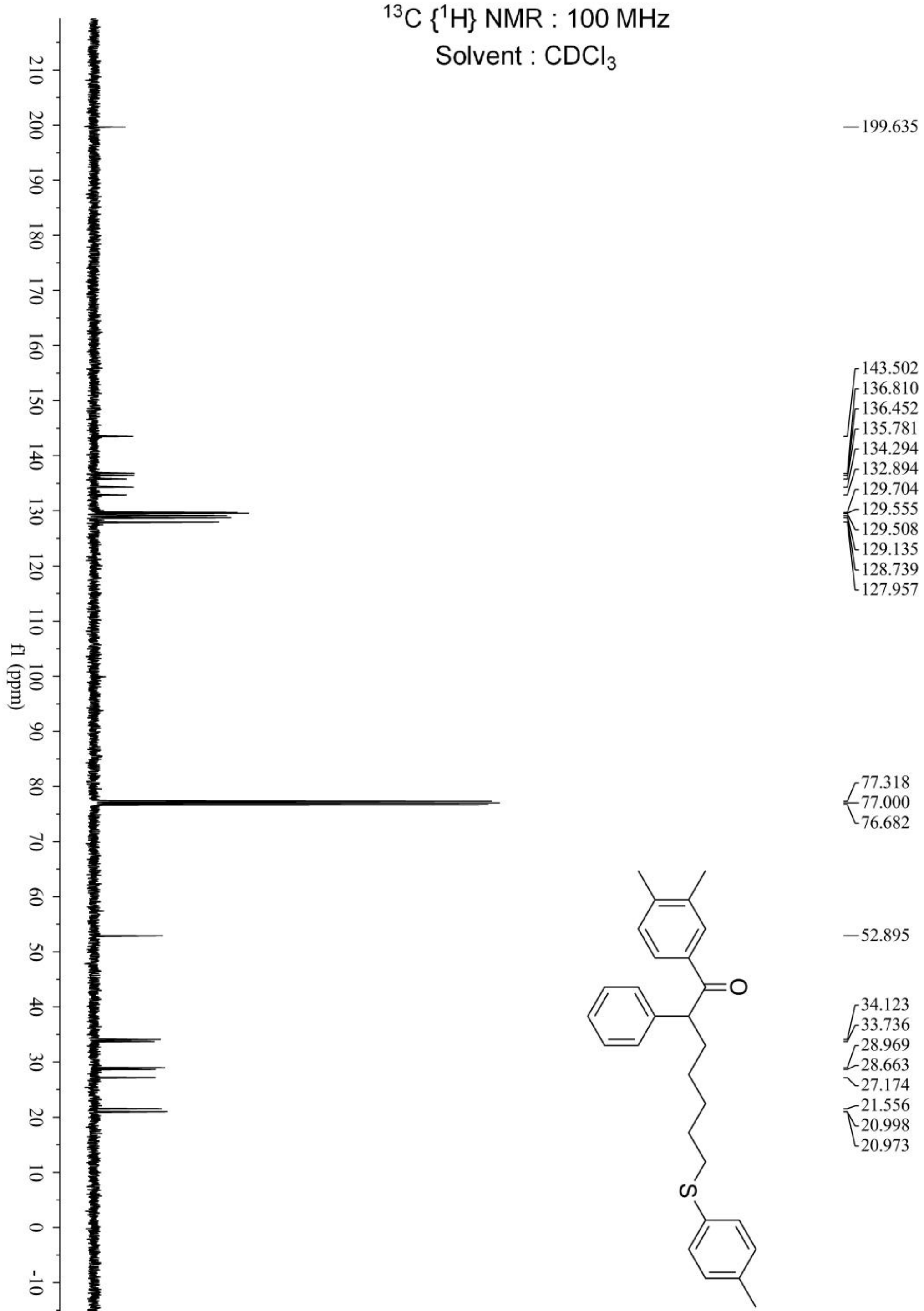


1-(3,4-dimethylphenyl)-2-phenyl-7-(*p*-tolylthio)heptan-1-one (3na)

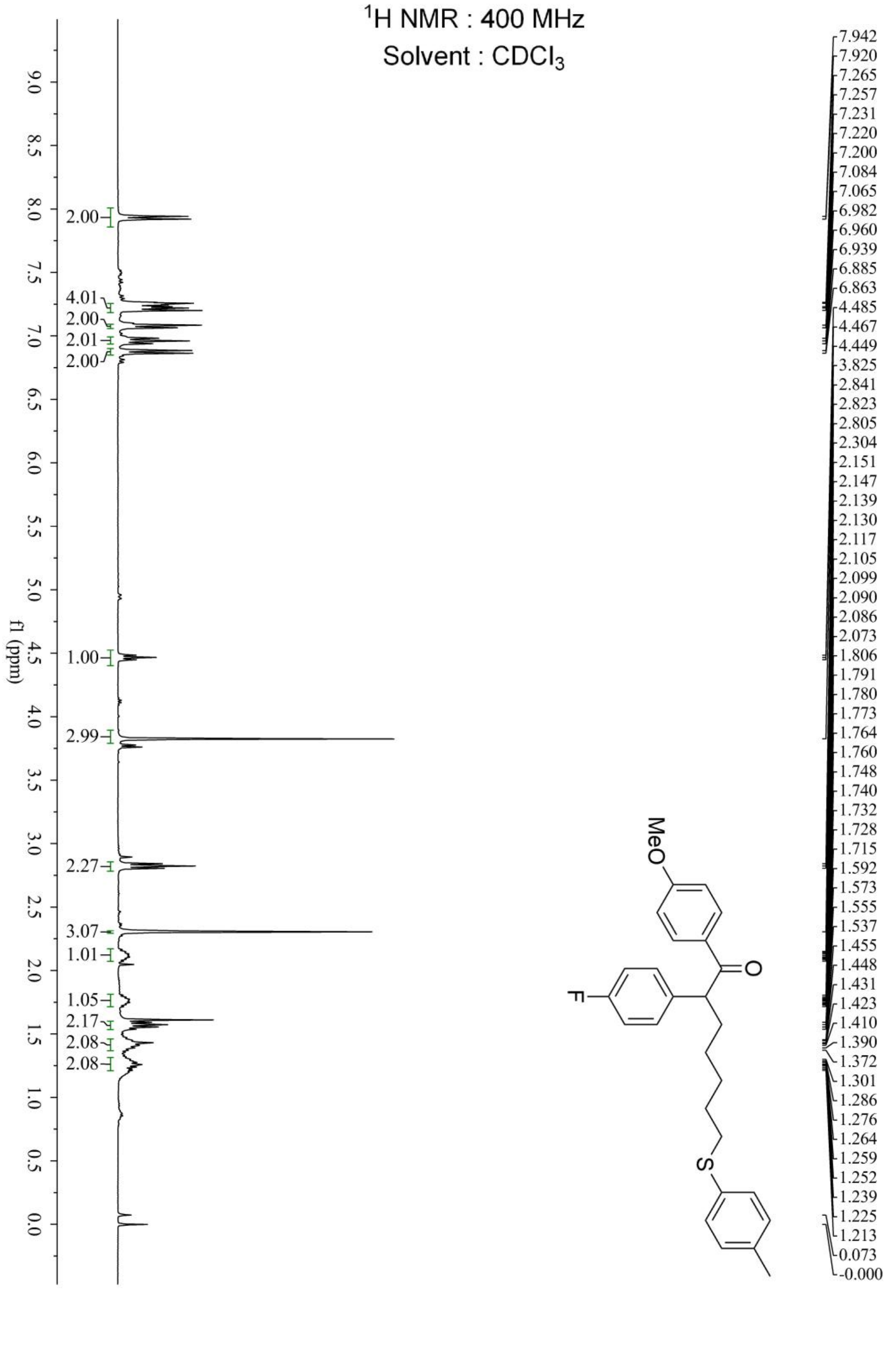


$^{13}C\ \{^1H\}$ NMR : 100 MHz

Solvent : $CDCl_3$

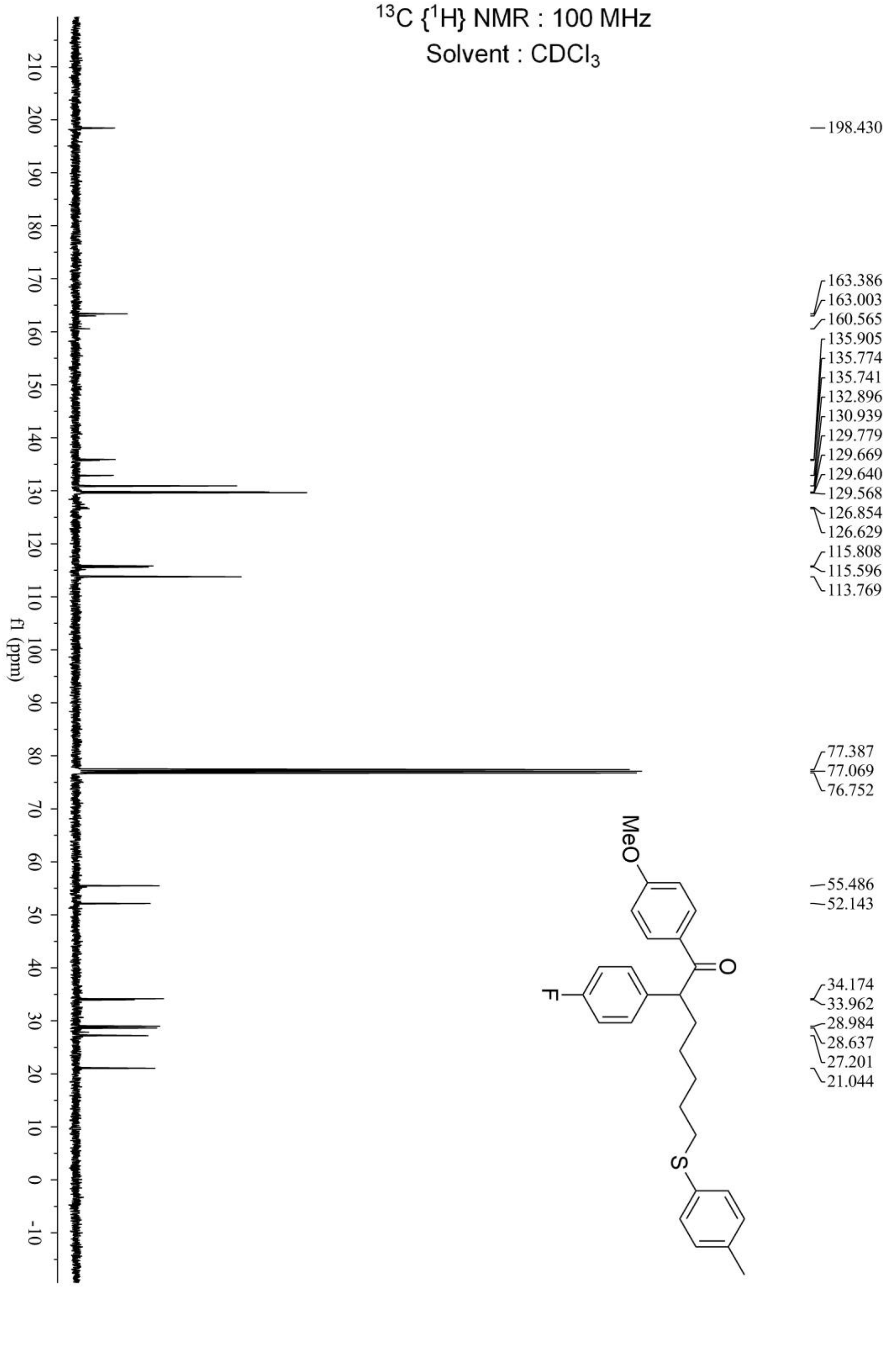


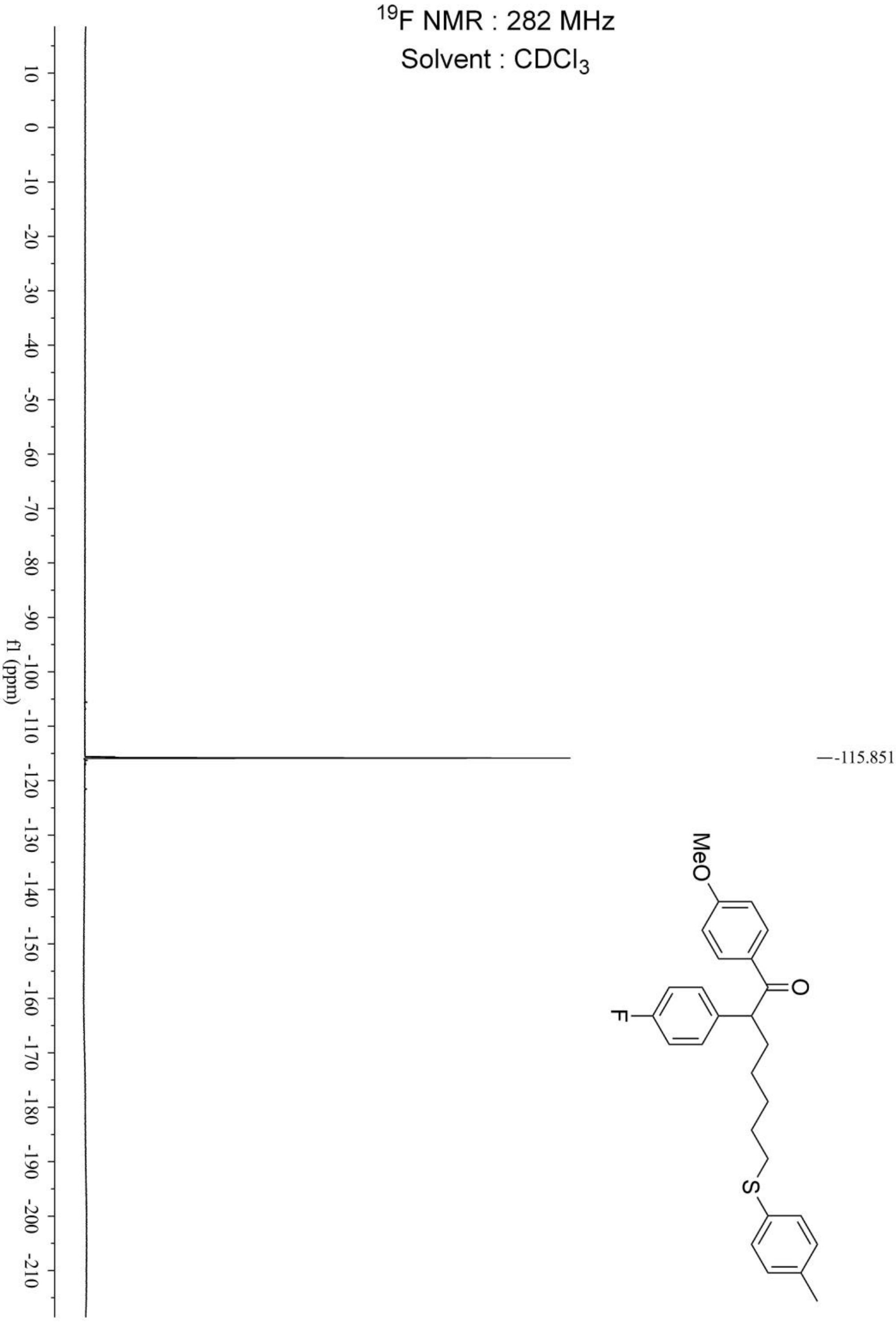
3-(4-fluorophenyl)-1-(4-methoxyphenyl)-7-(*p*-tolylthio)heptan-1-one (3oa)



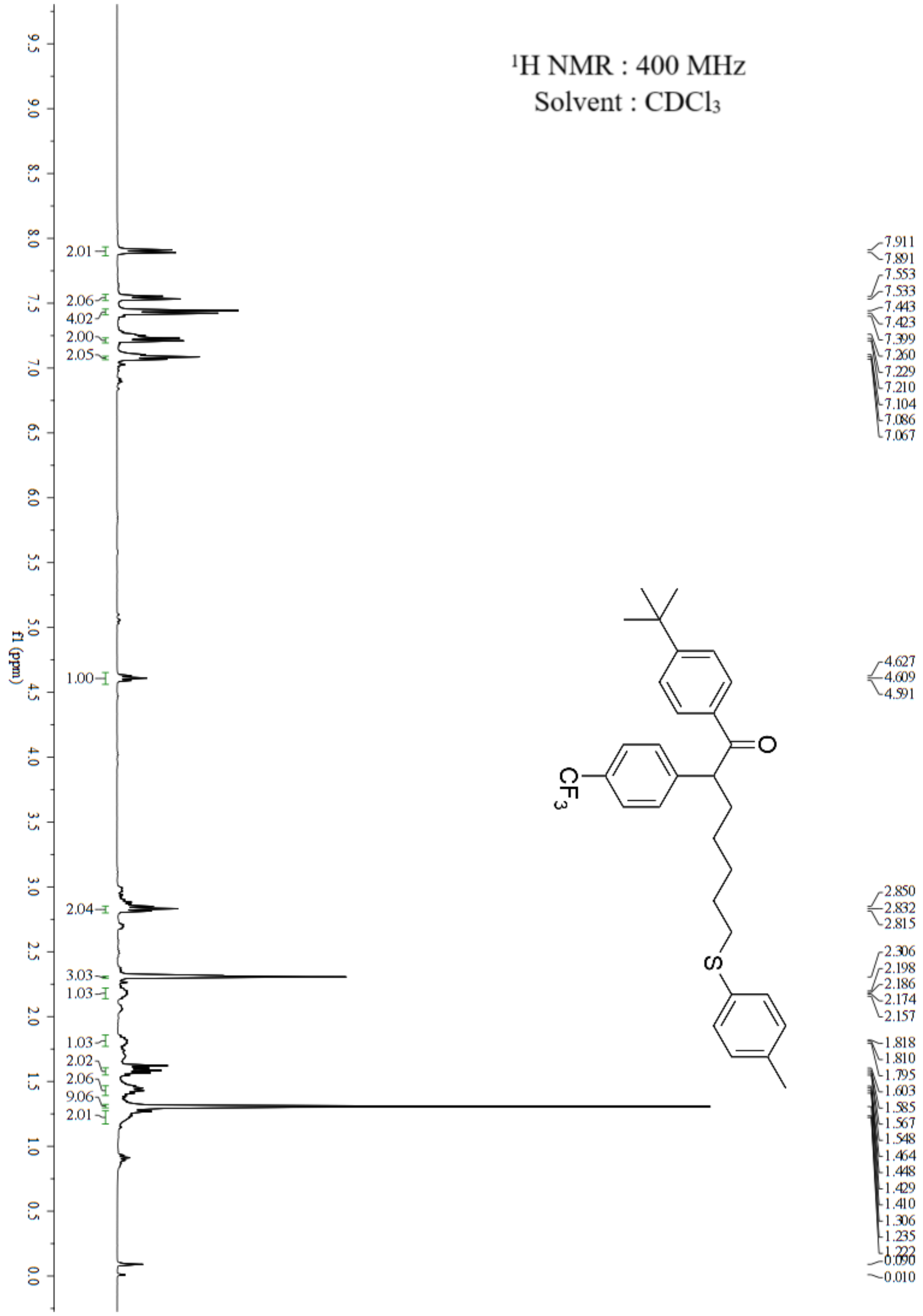
$^{13}C\ \{^1H\}$ NMR : 100 MHz

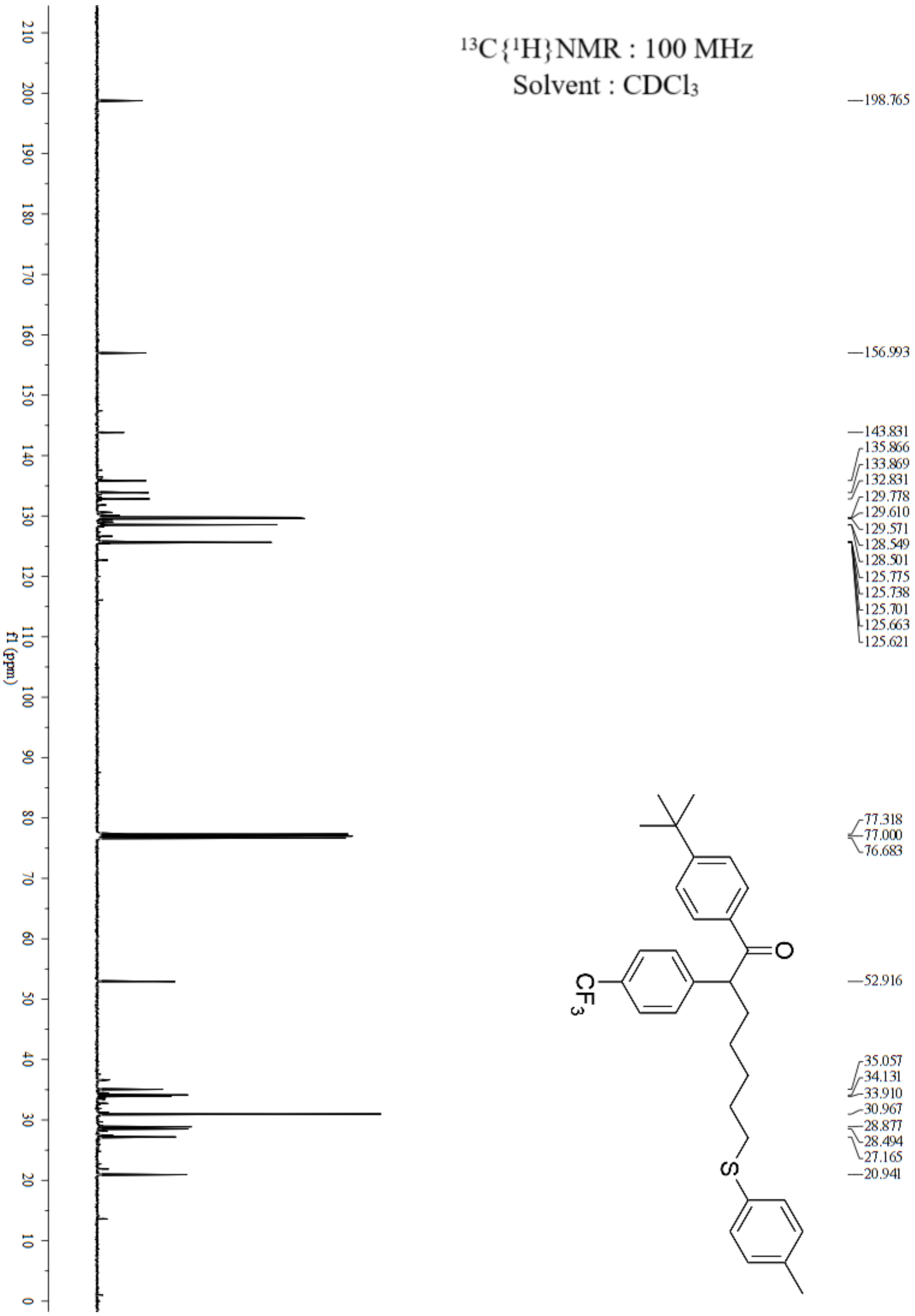
Solvent : $CDCl_3$

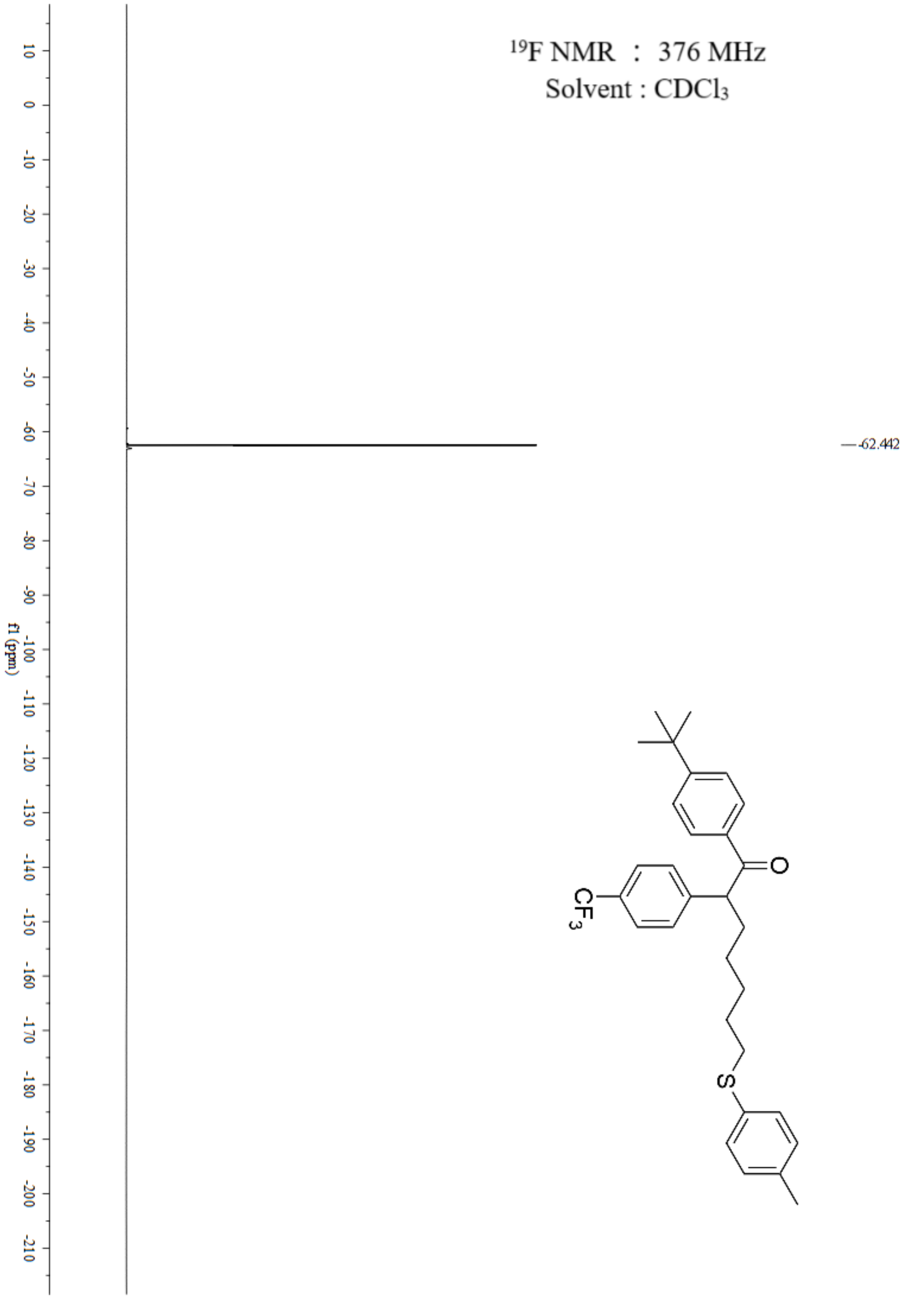



^{19}F NMR : 282 MHz
Solvent : $CDCl_3$
-115.851
fl (ppm)
MeO
O
F
S

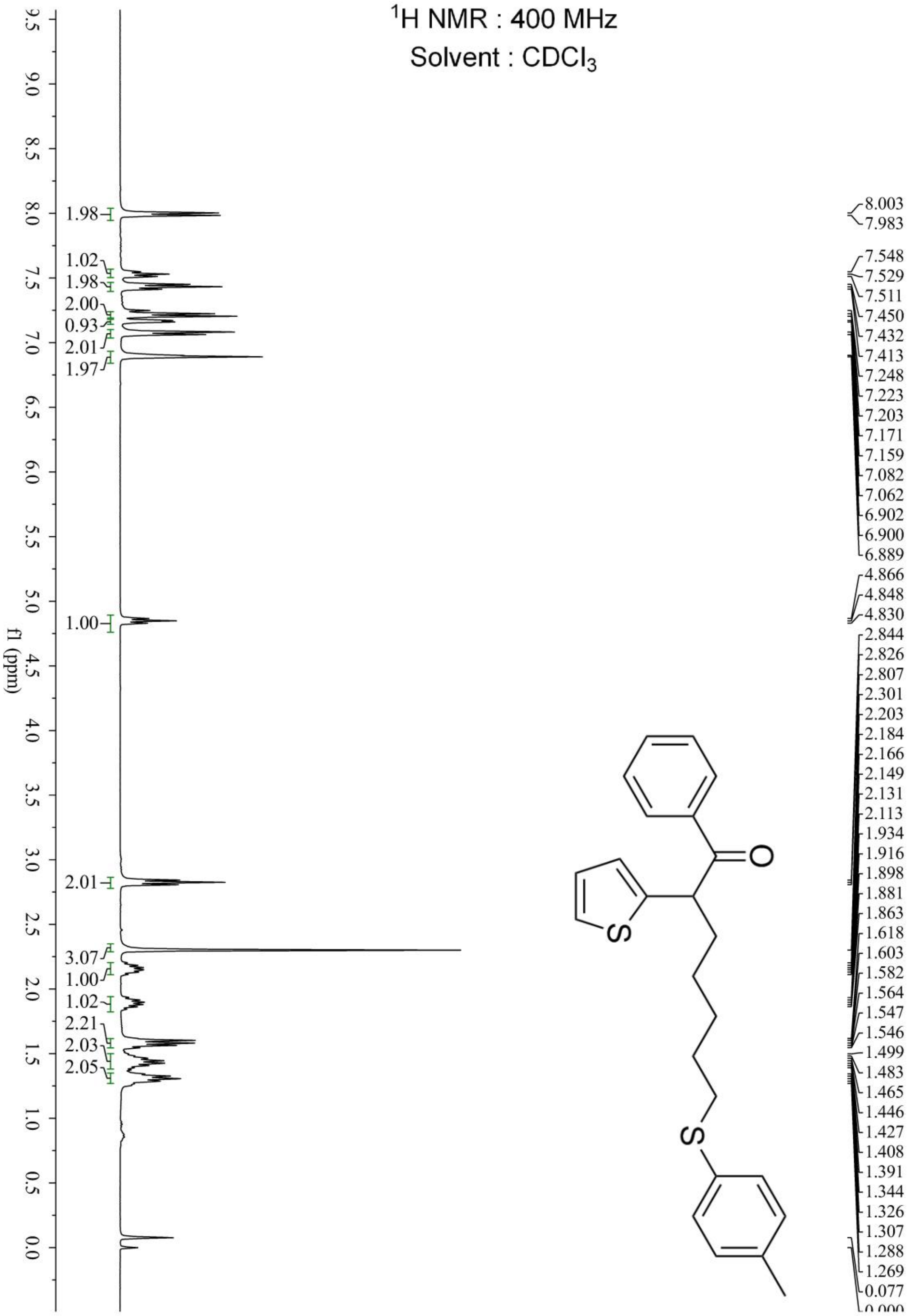
1-(4-(tert-butyl)phenyl)-7-(p-tolylthio)-2-(4-(trifluoromethyl)phenyl)heptan-1-one (3pa)



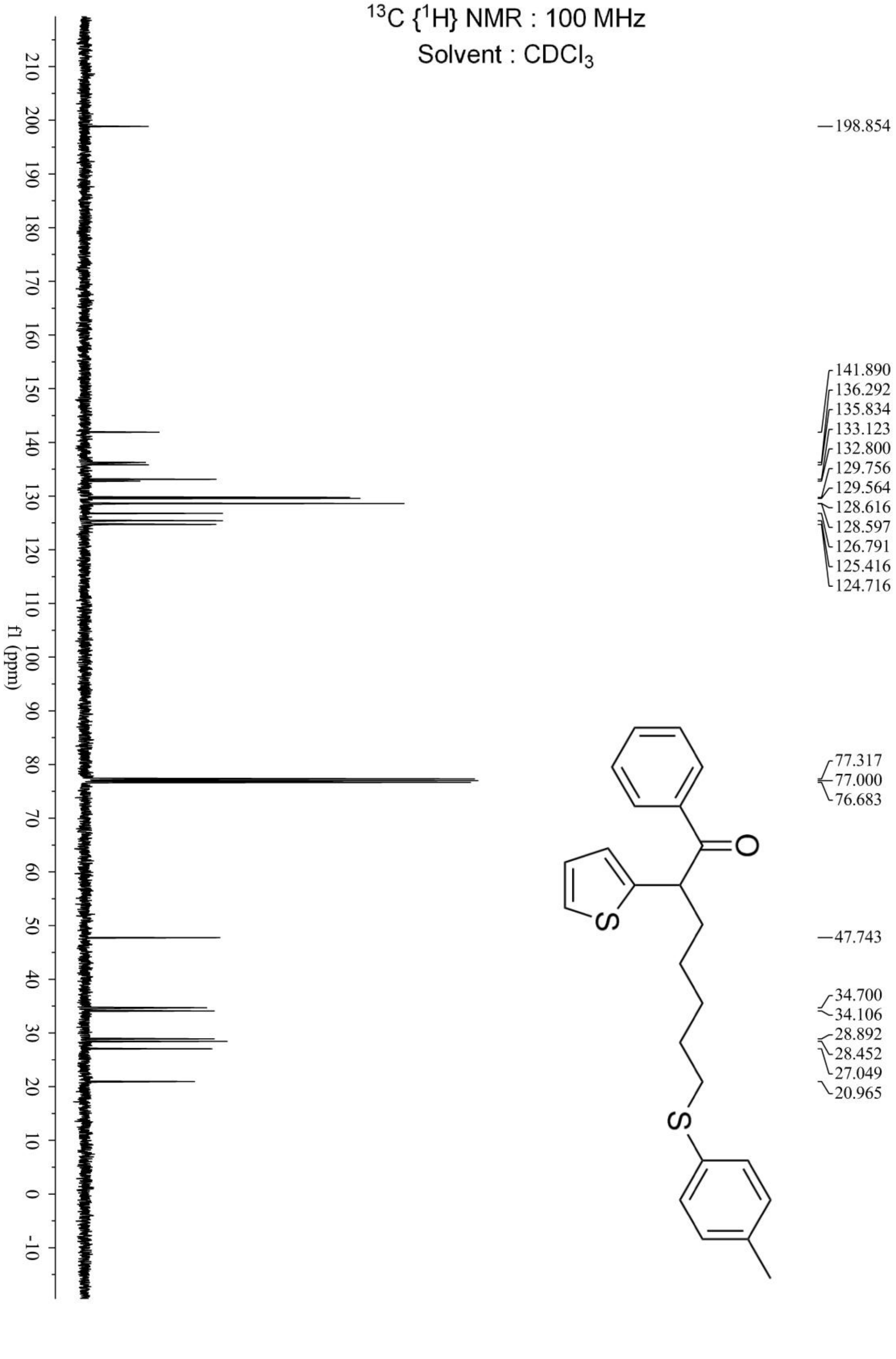

$^{13}C\{^1H\}$NMR : 100 MHz
Solvent : $CDCl_3$
198.765
156.993
143.831
135.866
133.869
132.831
129.778
129.610
129.571
128.549
128.501
125.775
125.738
125.701
125.663
125.621
77.318
77.000
76.683
52.916
35.057
34.131
33.910
30.967
28.877
28.494
27.165
20.941
CF3
O
S
f1 (ppm)


^{19}F NMR ： 376 MHz
Solvent : $CDCl_3$
-62.442
f1 (ppm)
CF3
O
S

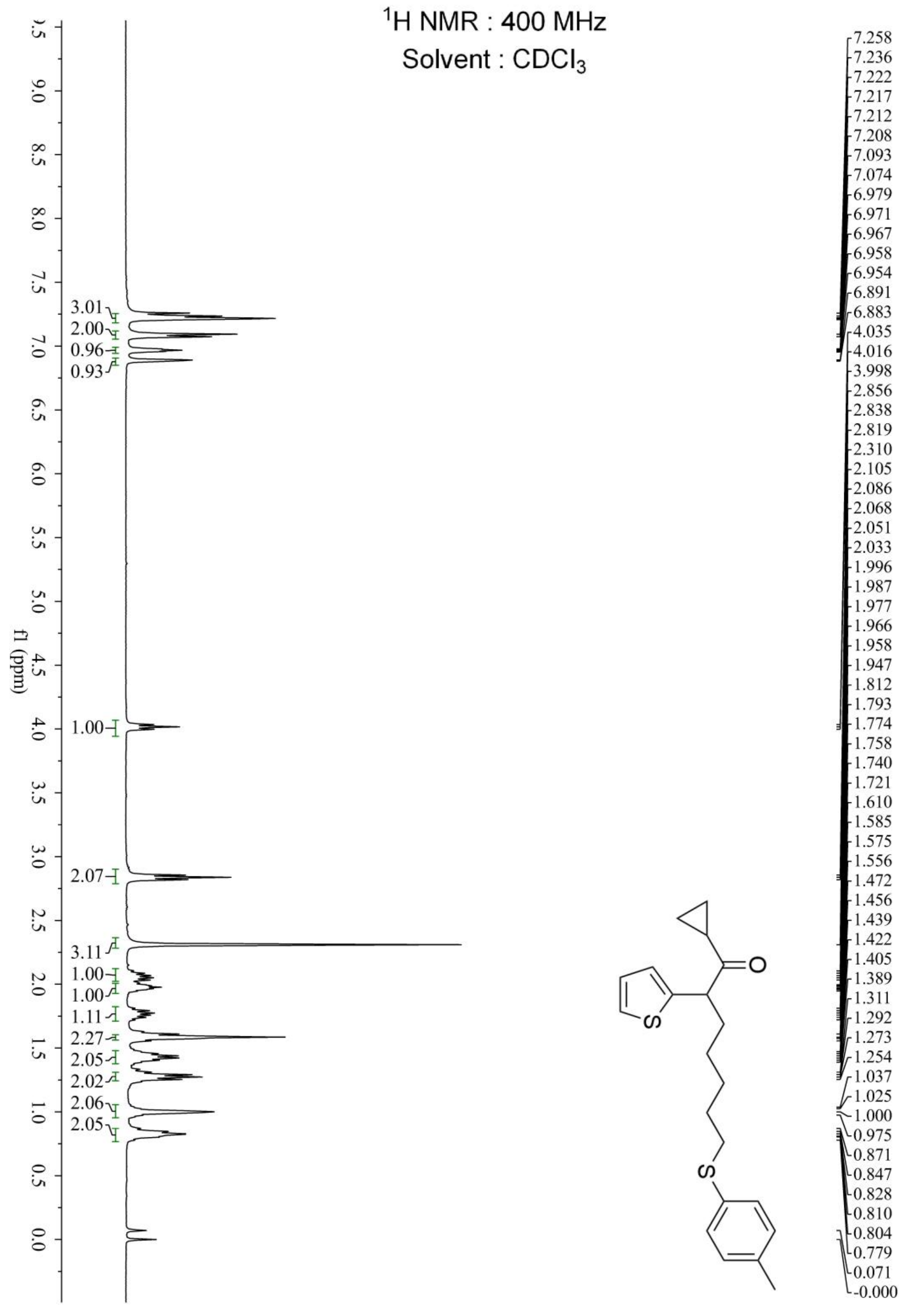
2-phenyl-1-(thiophen-2-yl)-7-(*p*-tolylthio)heptan-1-one (3qa)

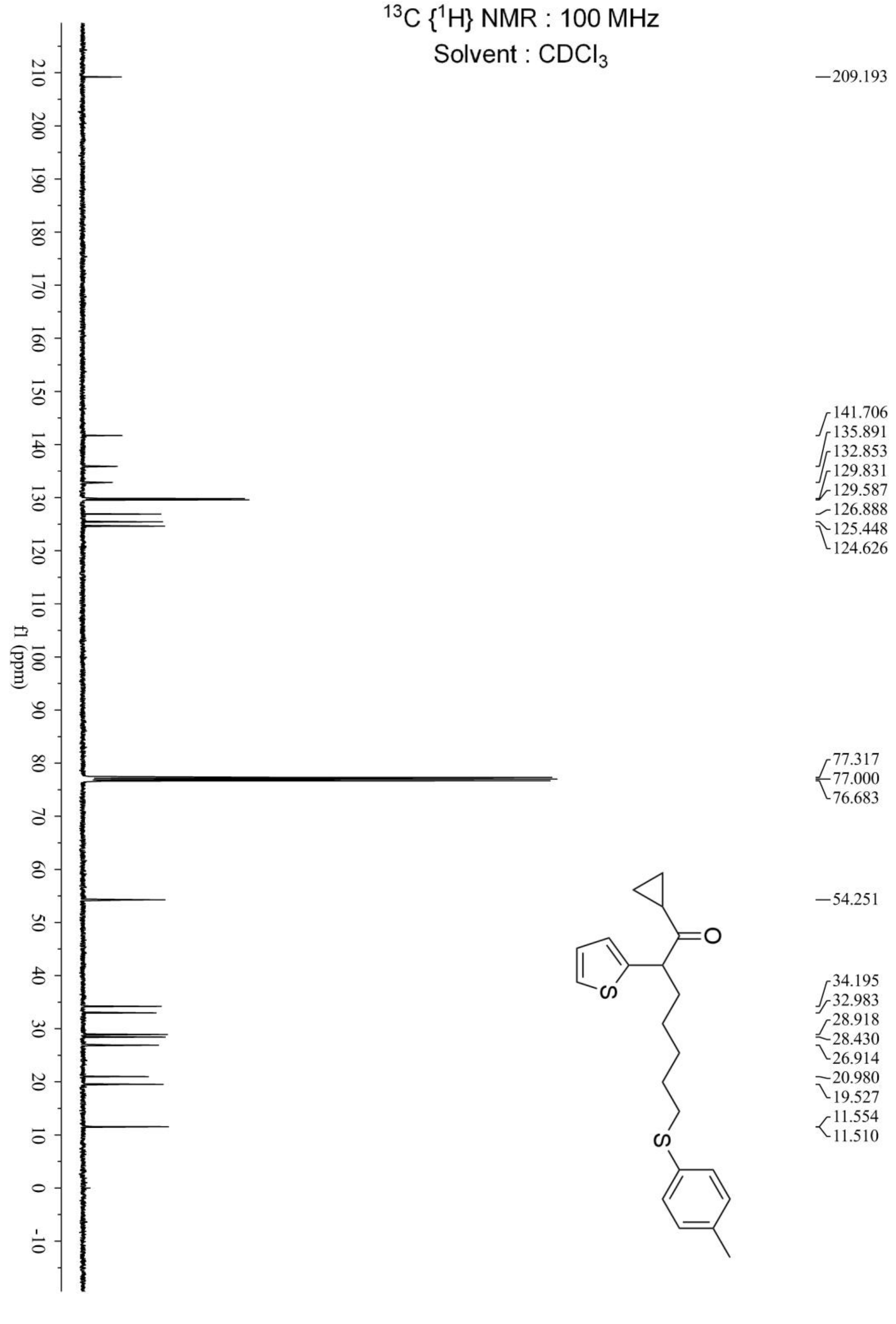


$^{13}C\ \{^1H\}$ NMR : 100 MHz
Solvent : $CDCl_3$



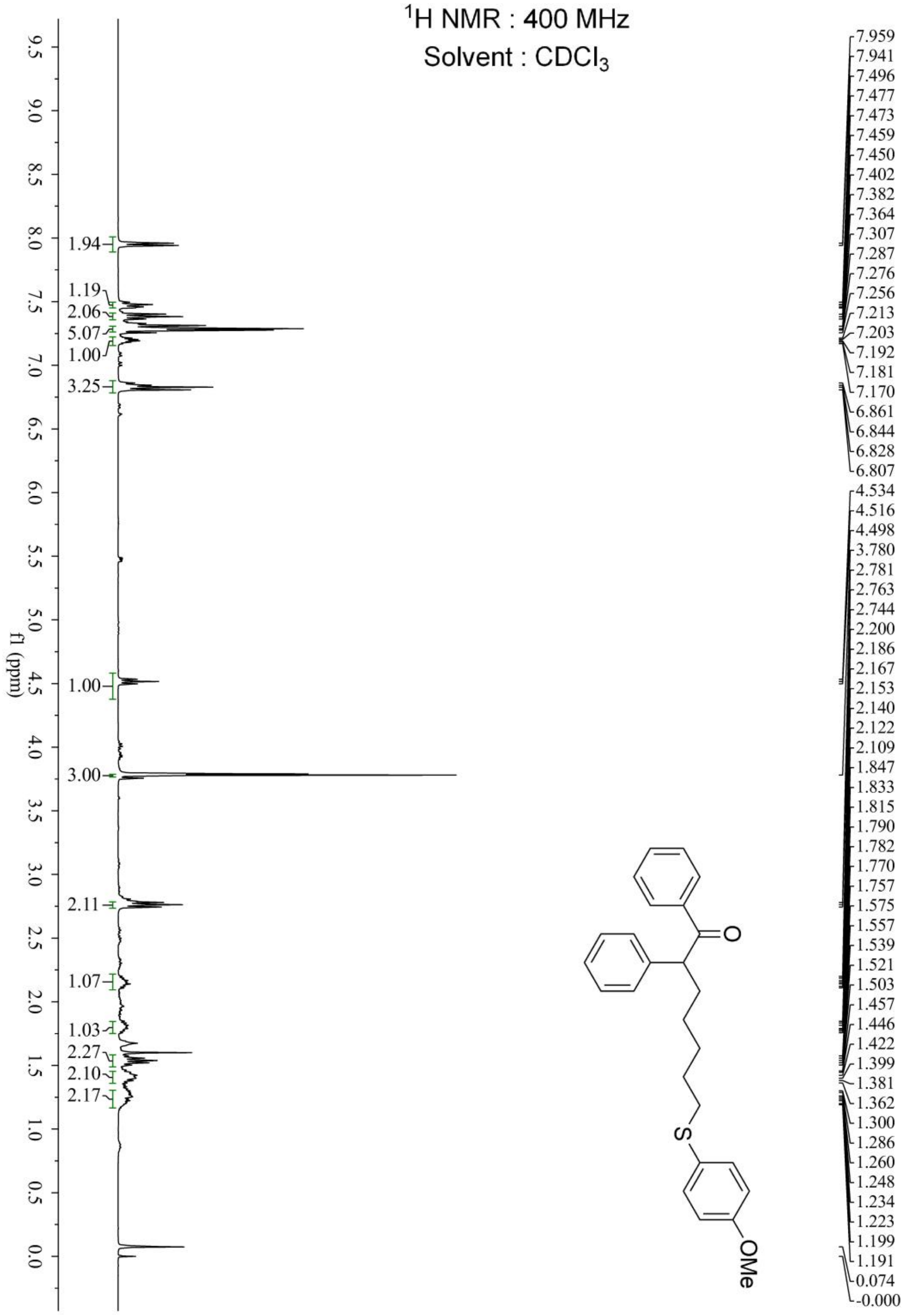
1-cyclopropyl-1-(thiophen-2-yl)-7-(*p*-tolylthio)heptan-1-one (3ra)

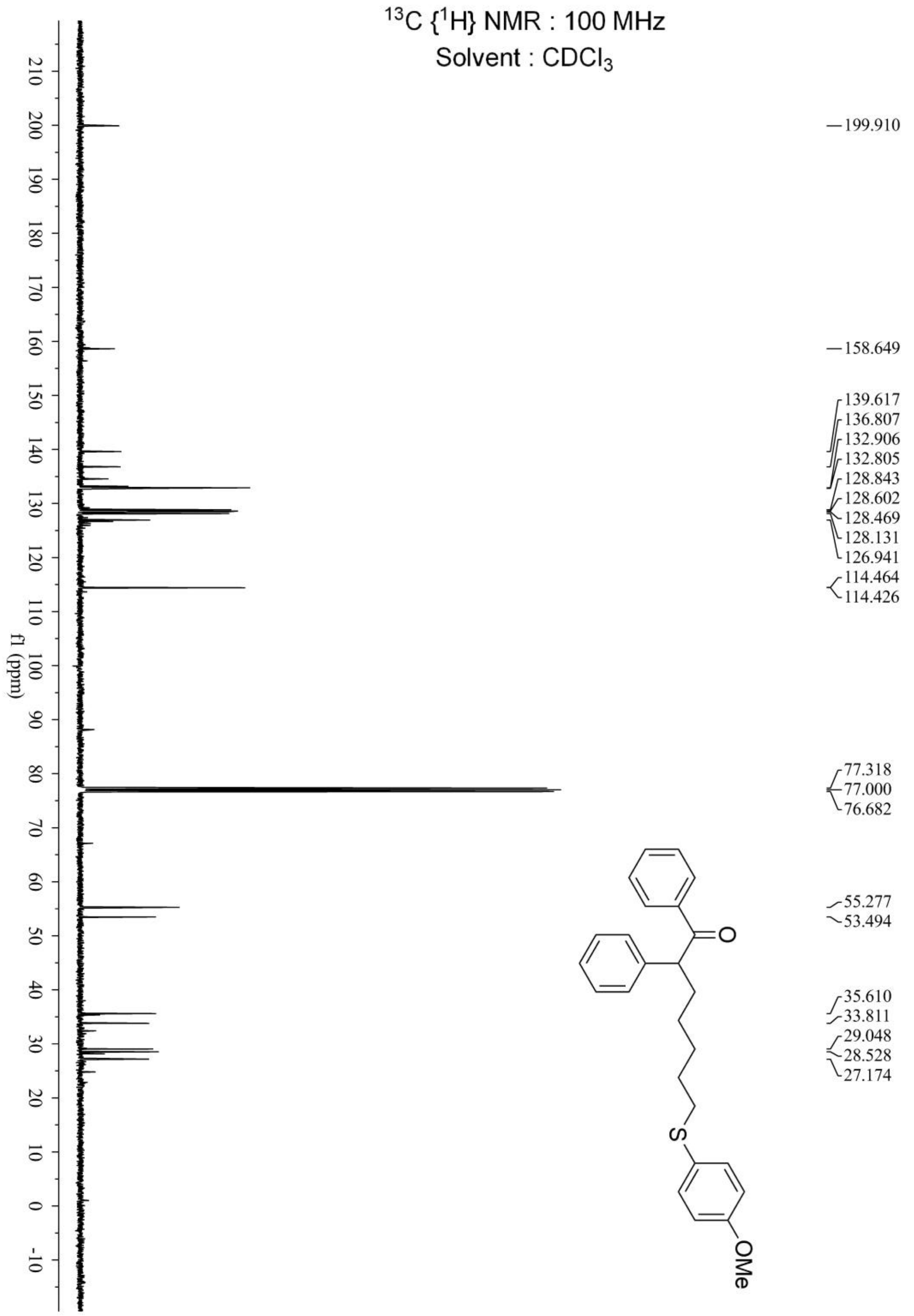




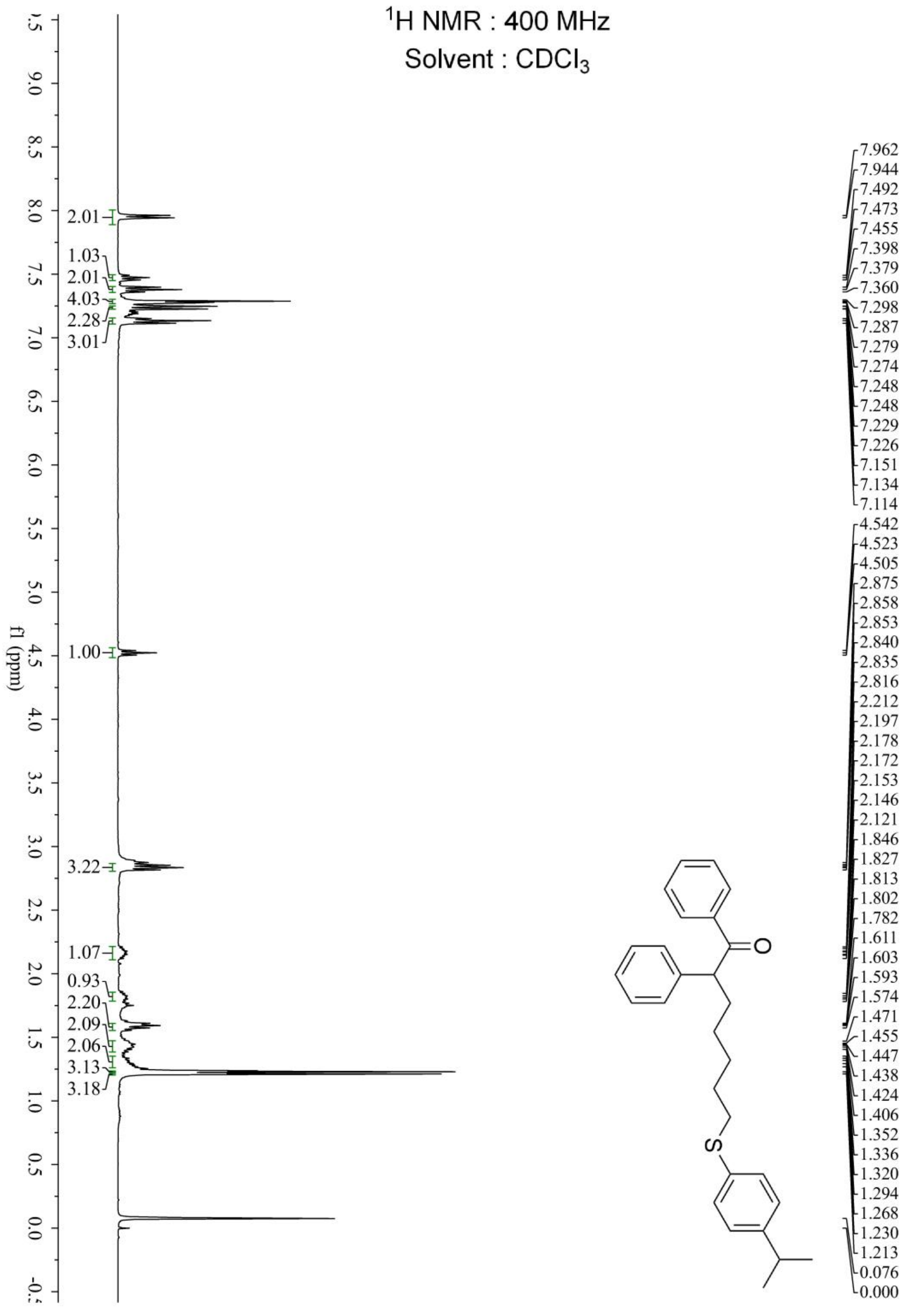
$^{13}C\ \{^{1}H\}$ NMR : 100 MHz
Solvent : $CDCl_3$
209.193
141.706
135.891
132.853
129.831
129.587
126.888
125.448
124.626
77.317
77.000
76.683
54.251
34.195
32.983
28.918
28.430
26.914
20.980
19.527
11.554
11.510
f1 (ppm)

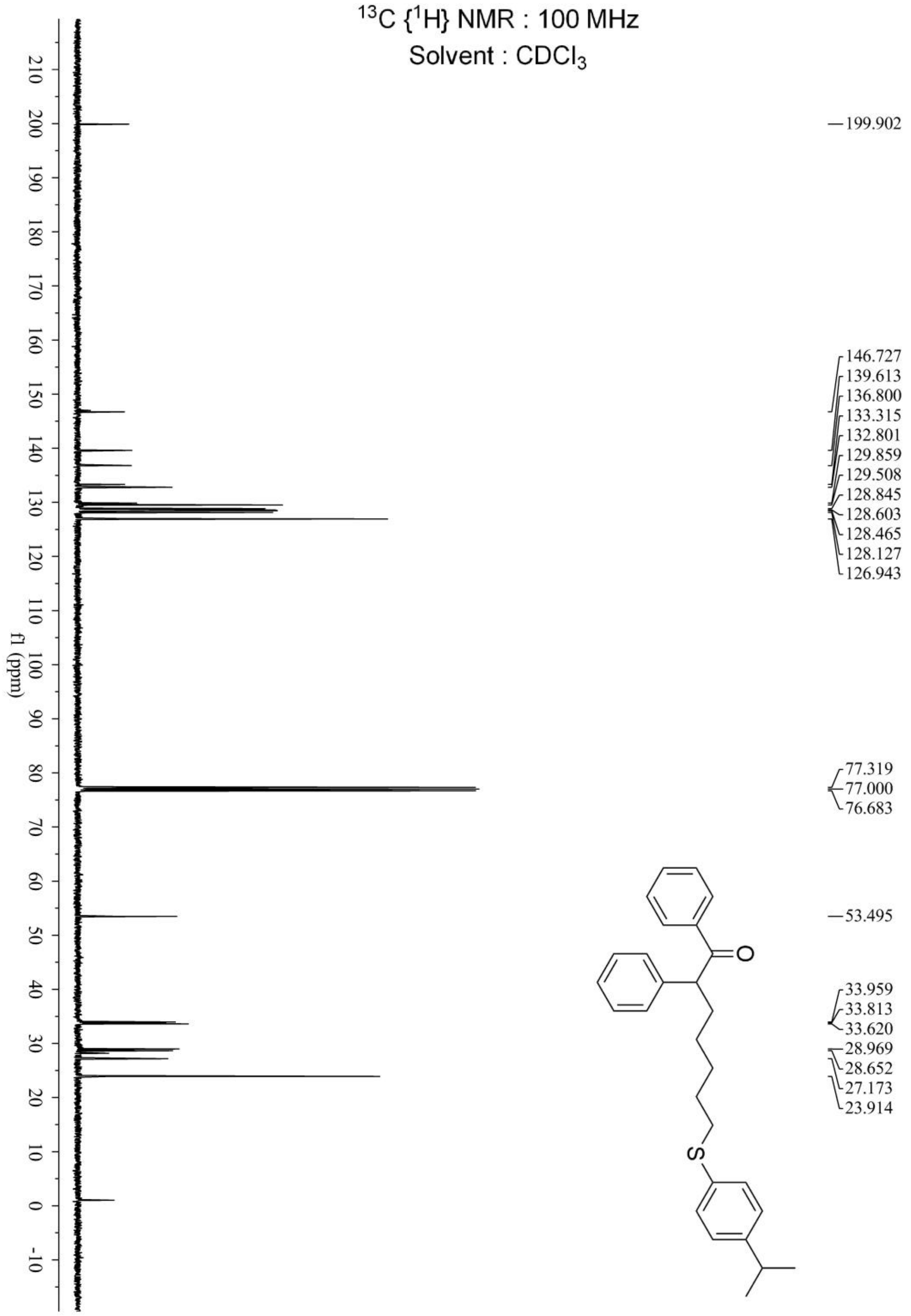
7-((4-methoxyphenyl)thio)-1,2-diphenylheptan-1-one (3ab)



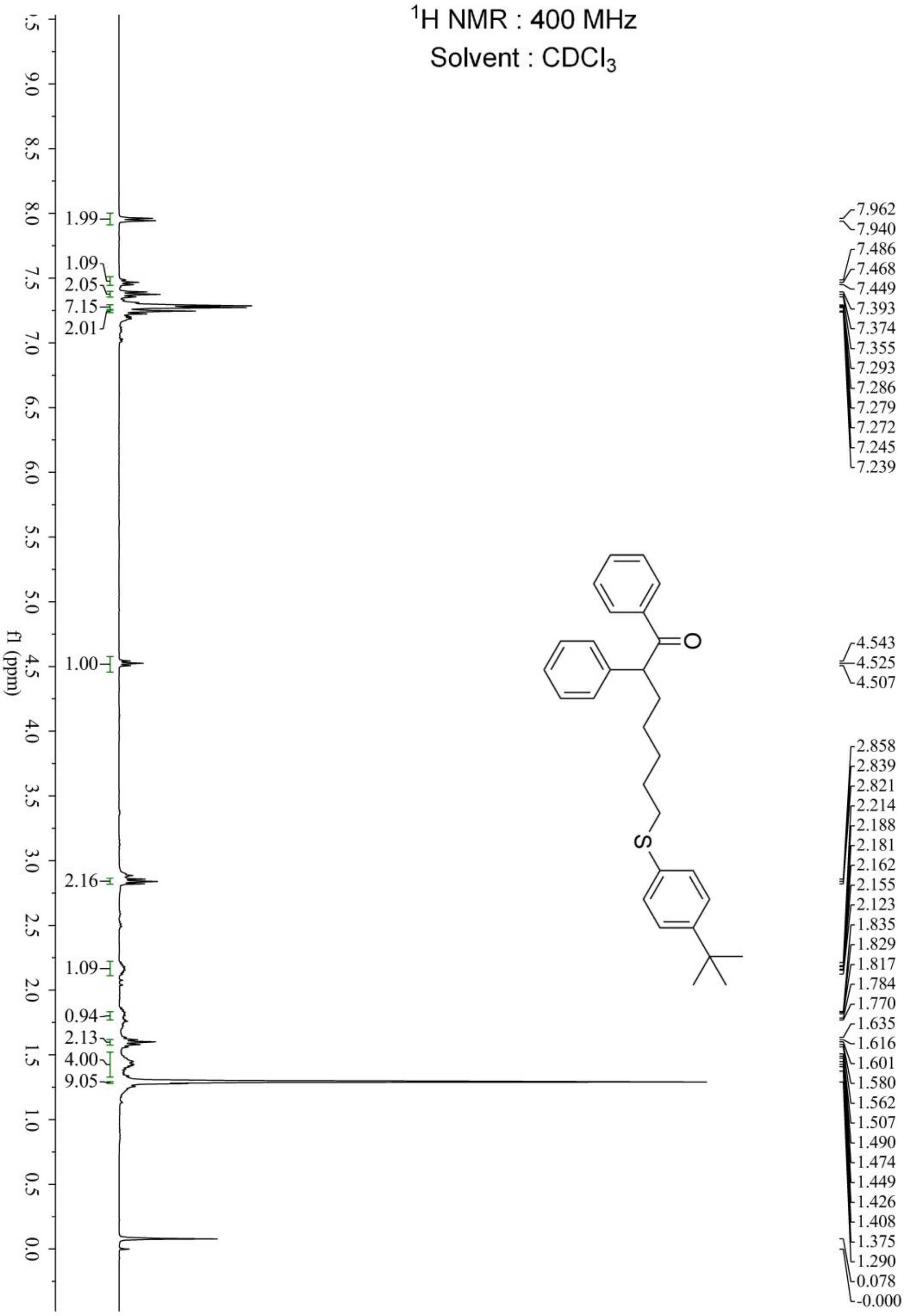

13C {1H} NMR : 100 MHz
Solvent : CDCl3
199.910
158.649
139.617
136.807
132.906
132.805
128.843
128.602
128.469
128.131
126.941
114.464
114.426
77.318
77.000
76.682
55.277
53.494
35.610
33.811
29.048
28.528
27.174
f1 (ppm)
O
S
OMe

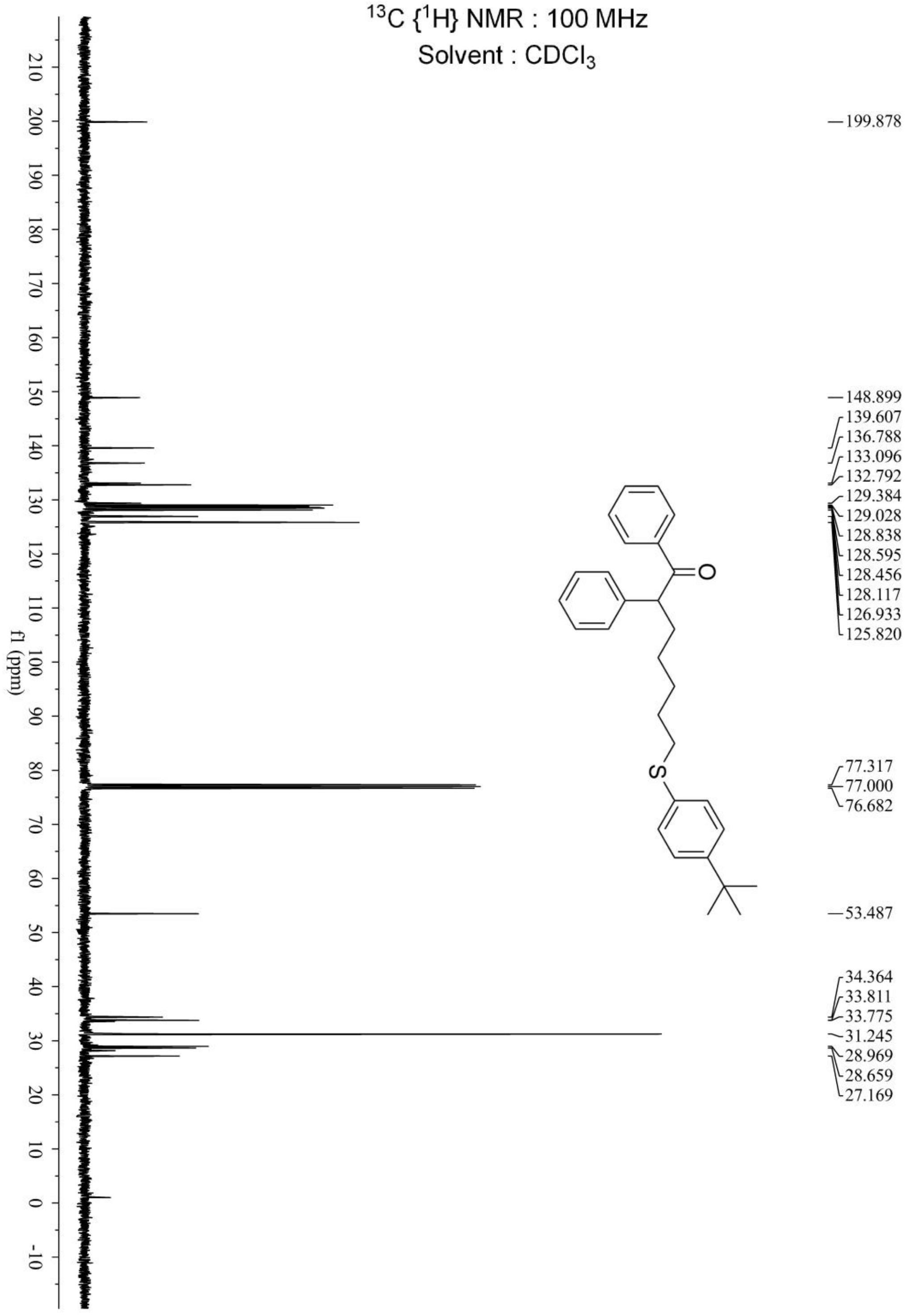
8-((4-isopropylphenyl)thio)-1,2-diphenylheptan-1-one (3ac)



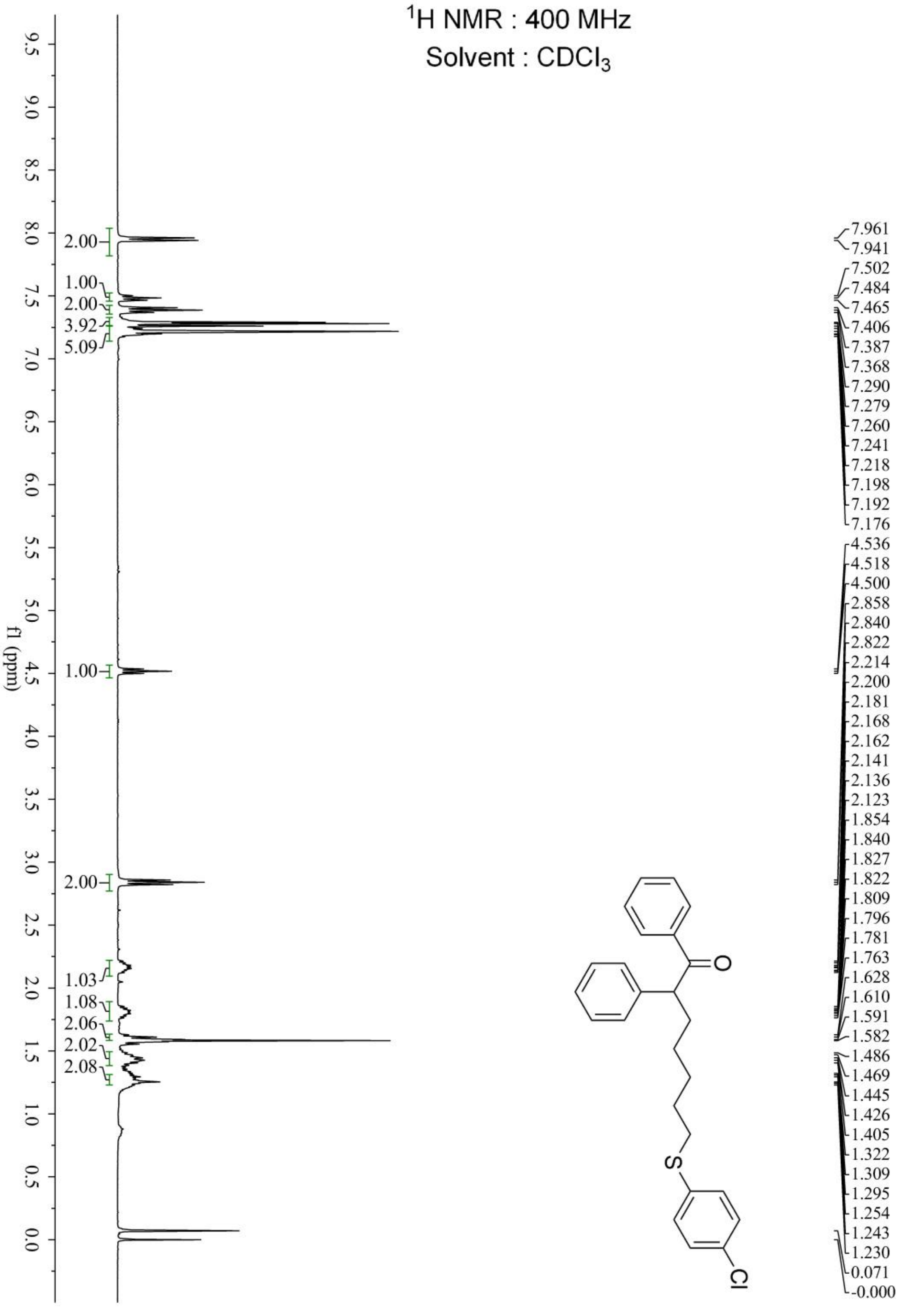

13C {1H} NMR : 100 MHz
Solvent : CDCl3
199.902
146.727
139.613
136.800
133.315
132.801
129.859
129.508
128.845
128.603
128.465
128.127
126.943
77.319
77.000
76.683
53.495
33.959
33.813
33.620
28.969
28.652
27.173
23.914
O
S
fl (ppm)

7-((4-(*tert*-butyl)phenyl)thio)-1,2-diphenylheptan-1-one (3ad)

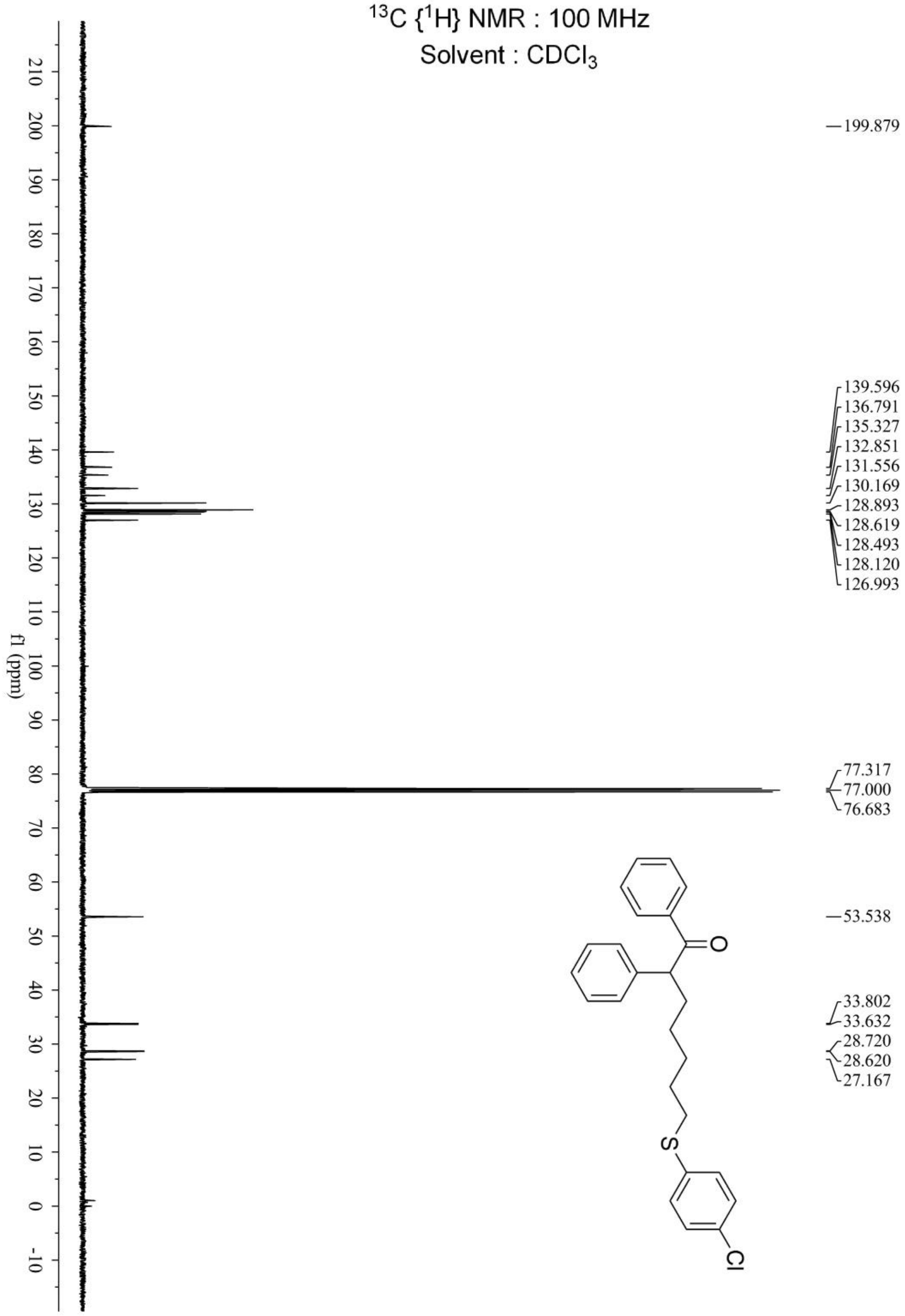



$^{13}C\ \{^1H\}$ NMR : 100 MHz
Solvent : $CDCl_3$
199.878
148.899
139.607
136.788
133.096
132.792
129.384
129.028
128.838
128.595
128.456
128.117
126.933
125.820
77.317
77.000
76.682
53.487
34.364
33.811
33.775
31.245
28.969
28.659
27.169
O
S
f1 (ppm)

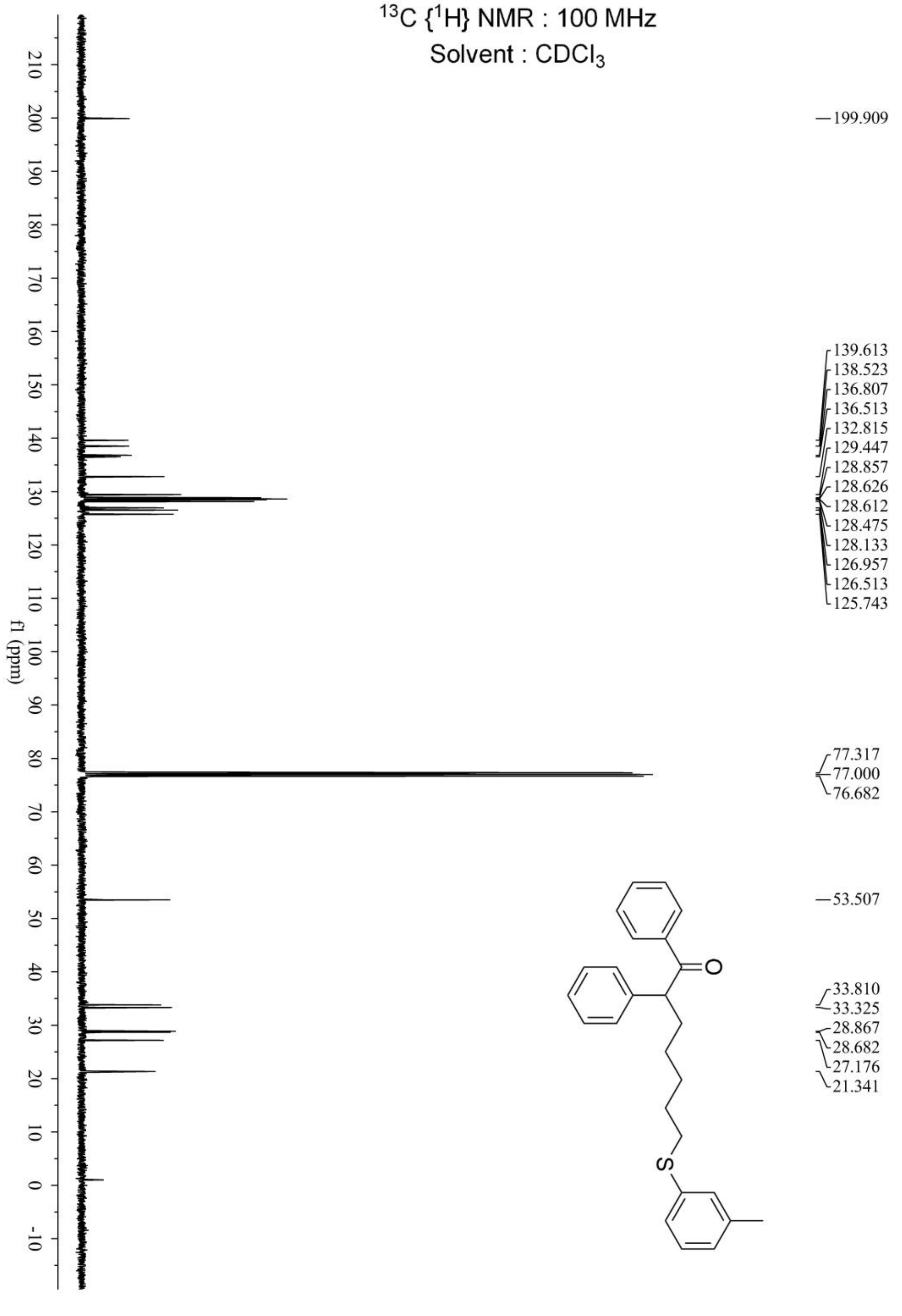
8-((4-chlorophenyl)thio)-1,2-diphenylheptan-1-one (3ae)

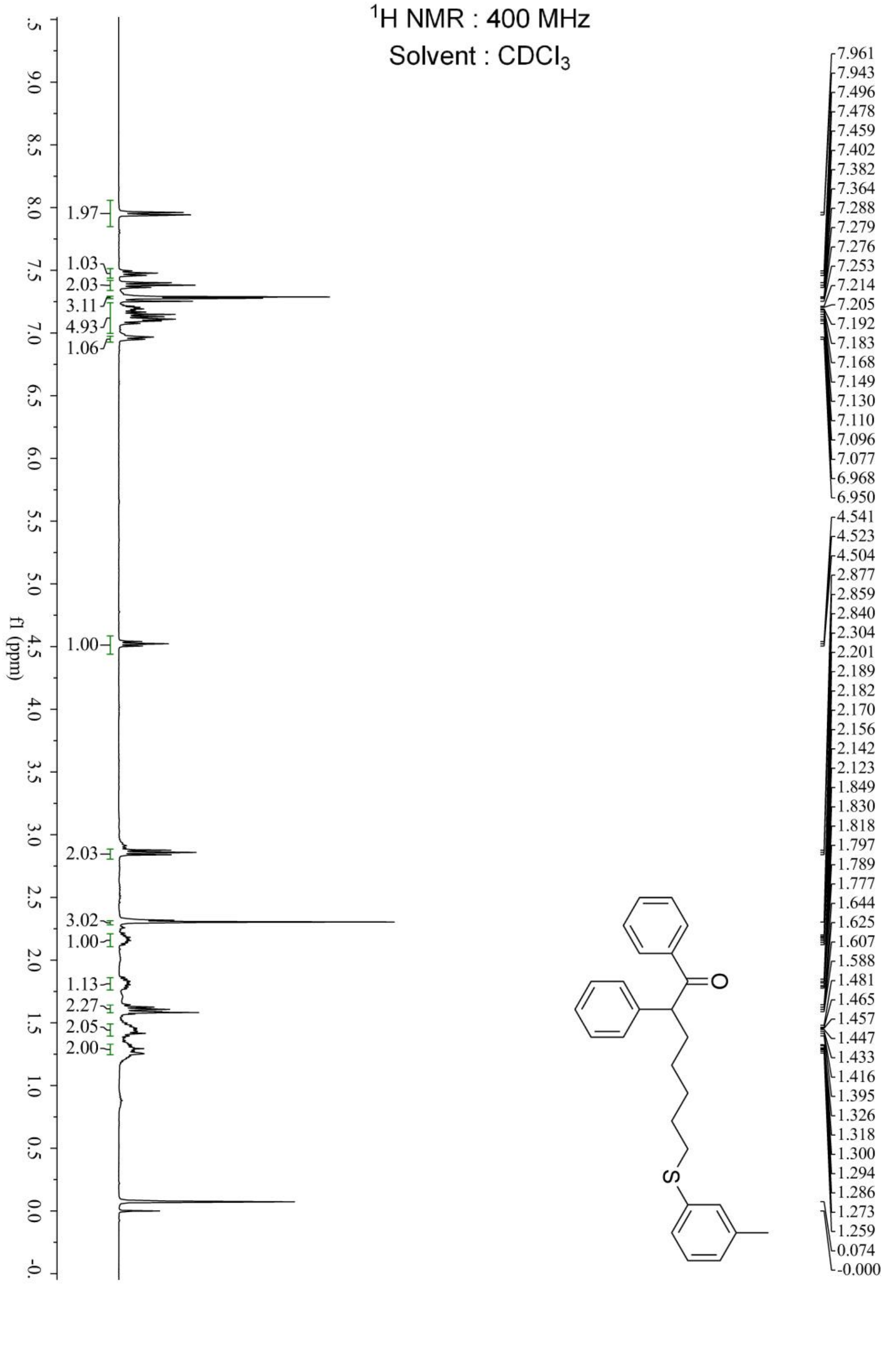


$^{13}C\ \{^{1}H\}$ NMR : 100 MHz
Solvent : $CDCl_3$

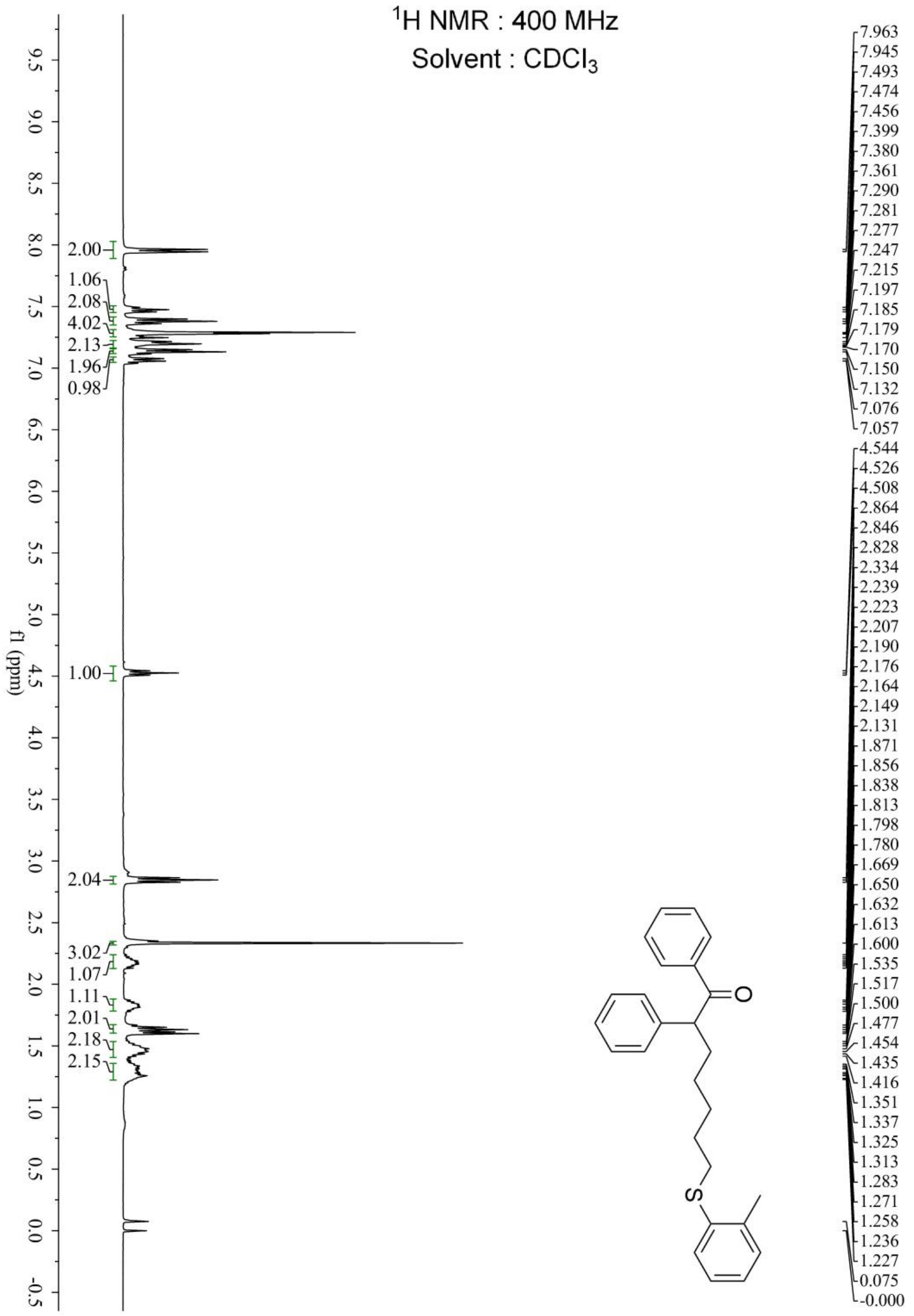


1,2-diphenyl-7-(*m*-tolylthio)heptan-1-one (3af)

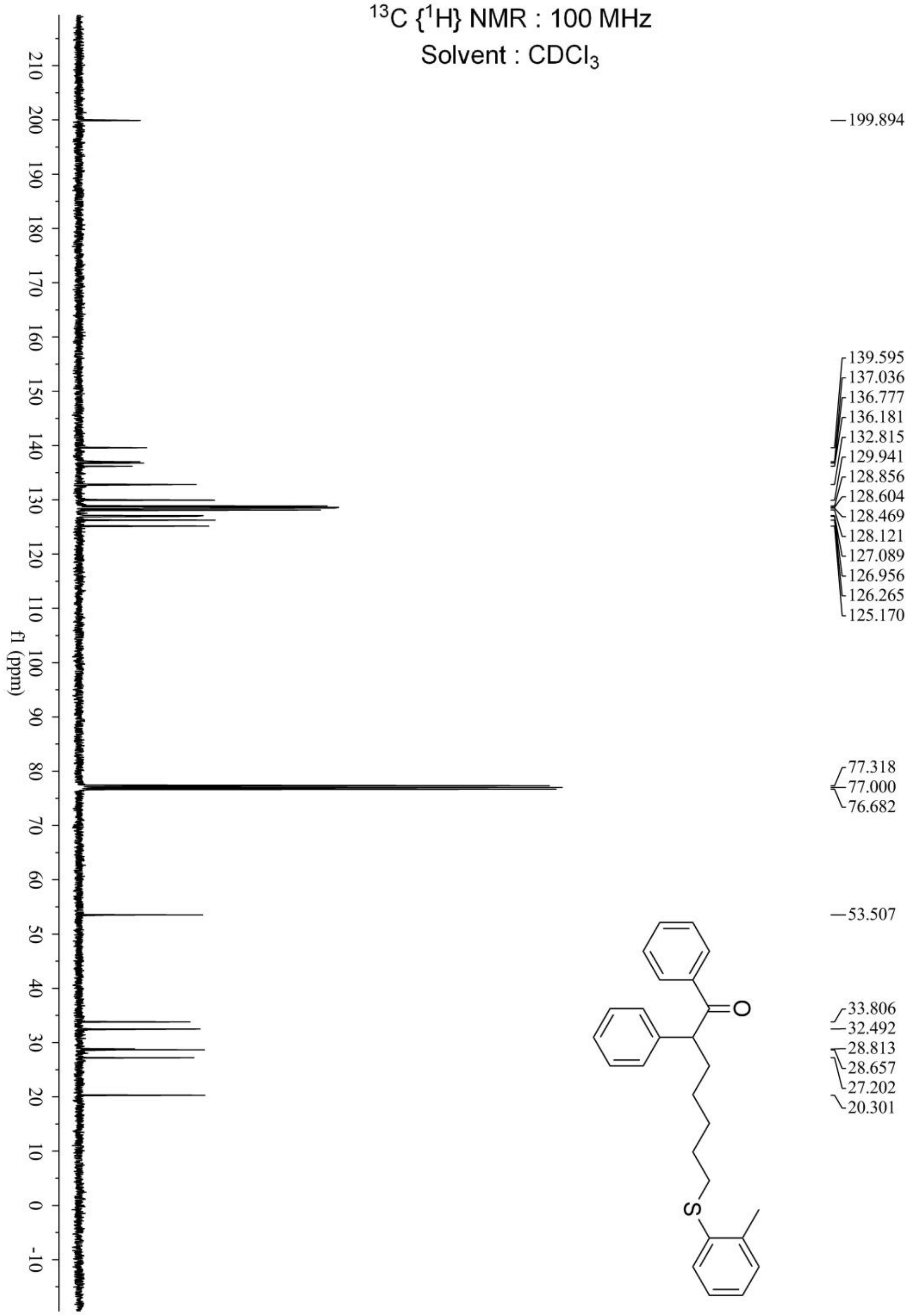



^{1}H NMR : 400 MHz
Solvent : $CDCl_3$
7.961
7.943
7.496
7.478
7.459
7.402
7.382
7.364
7.288
7.279
7.276
7.253
7.214
7.205
7.192
7.183
7.168
7.149
7.130
7.110
7.096
7.077
6.968
6.950
4.541
4.523
4.504
2.877
2.859
2.840
2.304
2.201
2.189
2.182
2.170
2.156
2.142
2.123
1.849
1.830
1.818
1.797
1.789
1.777
1.644
1.625
1.607
1.588
1.481
1.465
1.457
1.447
1.433
1.416
1.395
1.326
1.318
1.300
1.294
1.286
1.273
1.259
0.074
-0.000
1.97
1.03
2.03
3.11
4.93
1.06
1.00
2.03
3.02
1.00
1.13
2.27
2.05
2.00
fl (ppm)
O
S

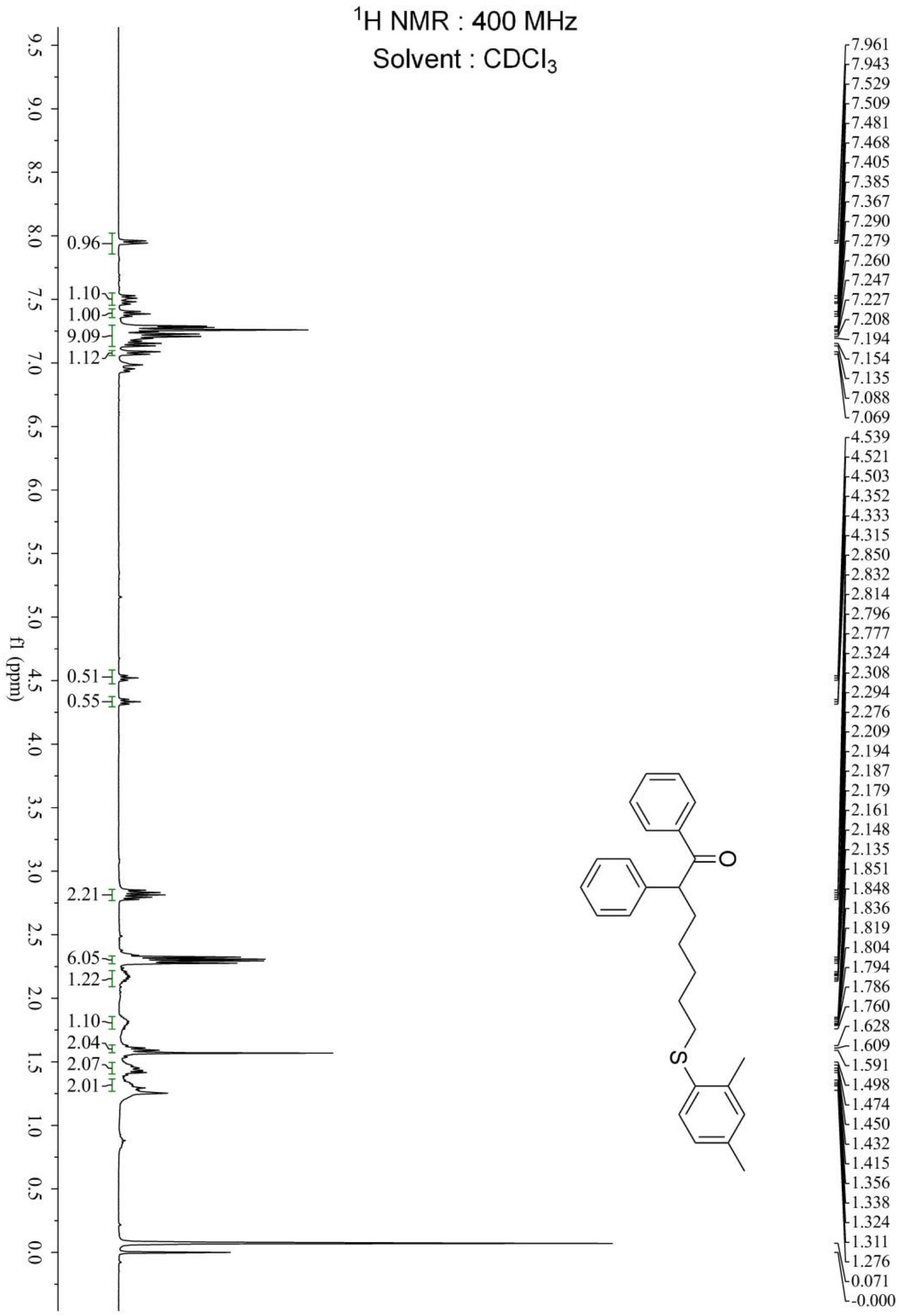
1,2-diphenyl-7-(*o*-tolylthio)heptan-1-one (3ag)

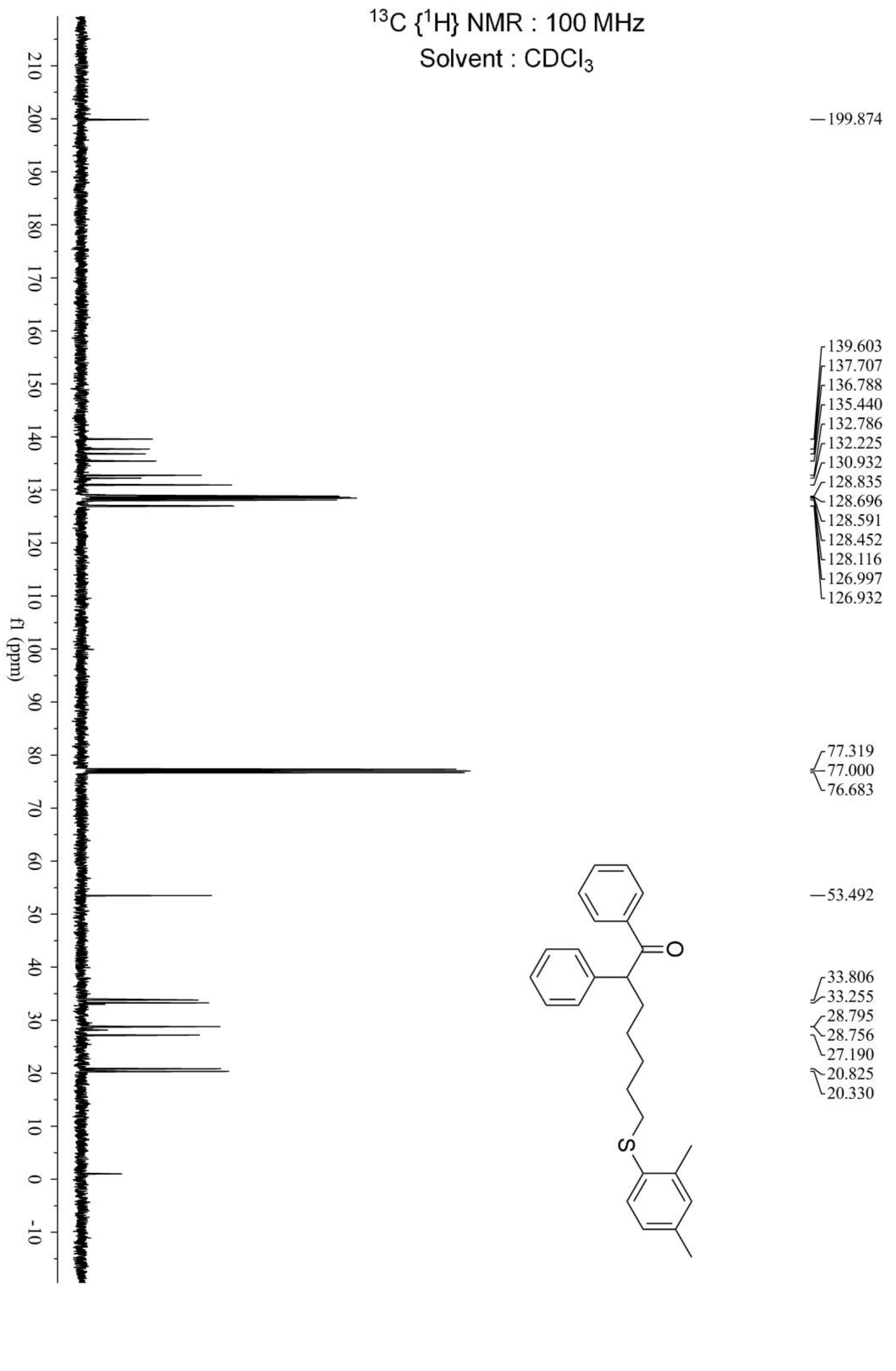


$^{13}C\ \{^{1}H\}$ NMR : 100 MHz
Solvent : $CDCl_3$

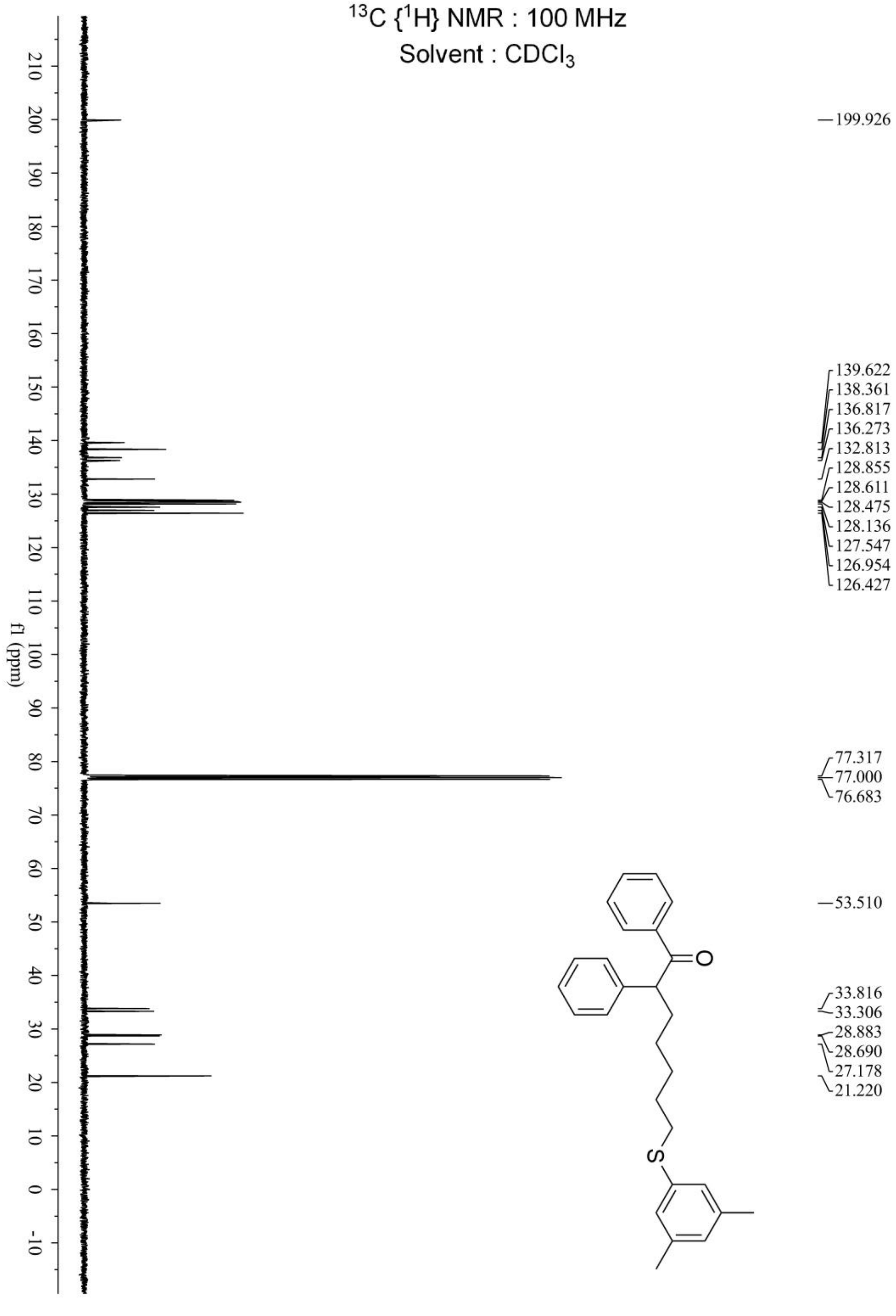


7-((2,4-dimethylphenyl)thio)-1,2-diphenylheptan-1-one (3ah)



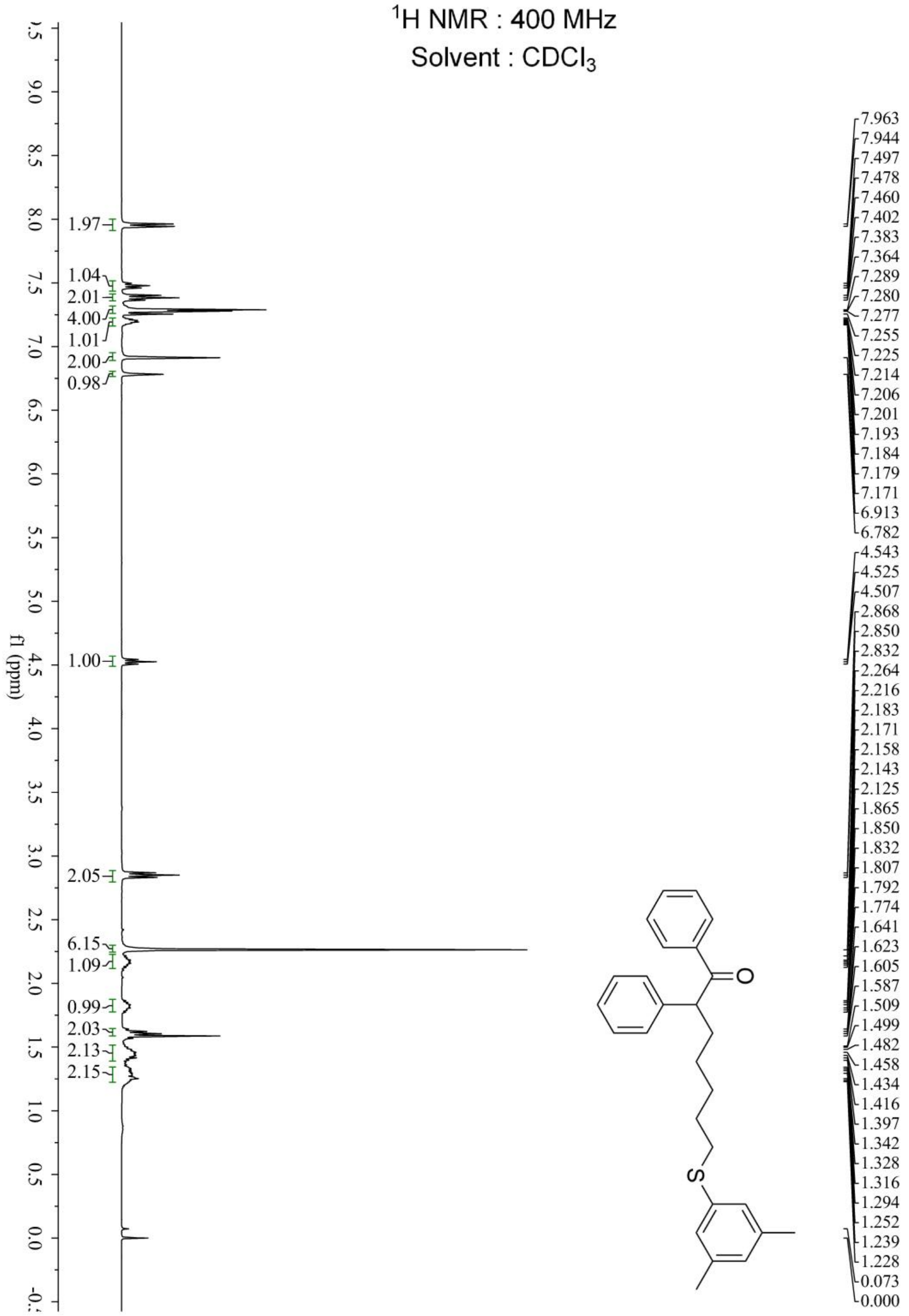

$^{13}C\ \{^{1}H\}$ NMR : 100 MHz
Solvent : $CDCl_3$
199.874
139.603
137.707
136.788
135.440
132.786
132.225
130.932
128.835
128.696
128.591
128.452
128.116
126.997
126.932
77.319
77.000
76.683
53.492
33.806
33.255
28.795
28.756
27.190
20.825
20.330
O
S
fl (ppm)

8-((3,5-dimethylphenyl)thio)-1,2-diphenylheptan-1-one (3ia)

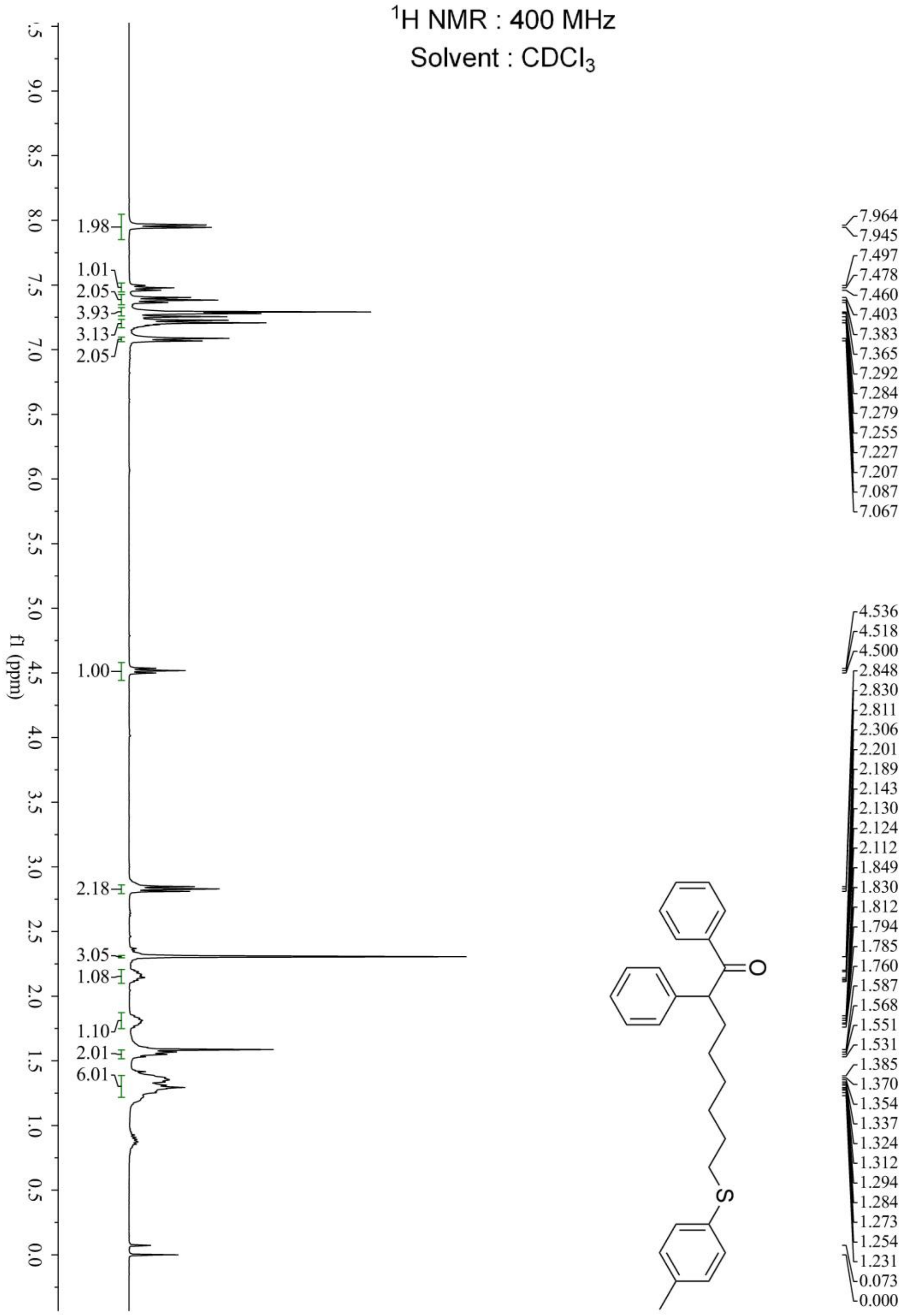


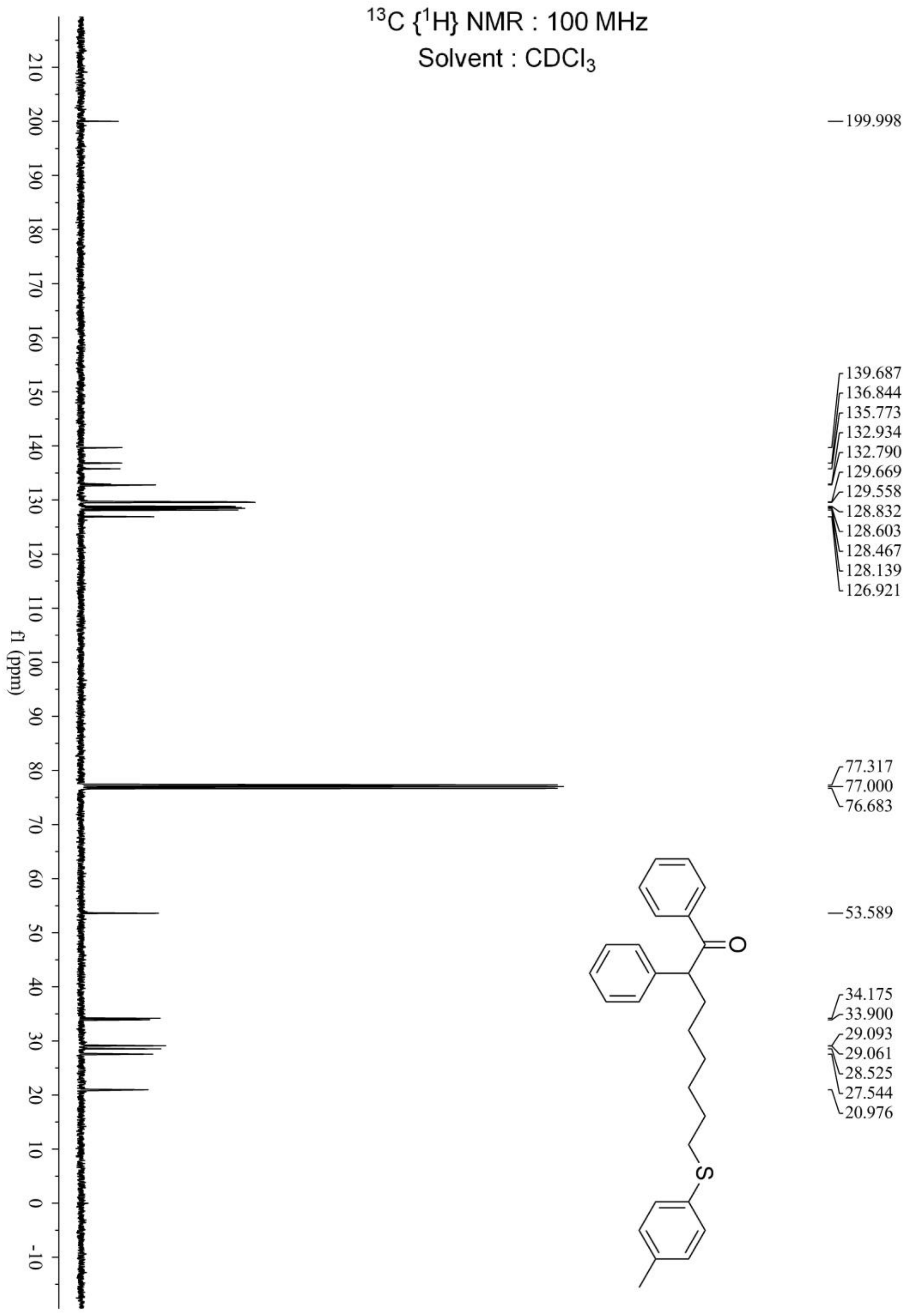
^{1}H NMR : 400 MHz

Solvent : $CDCl_3$

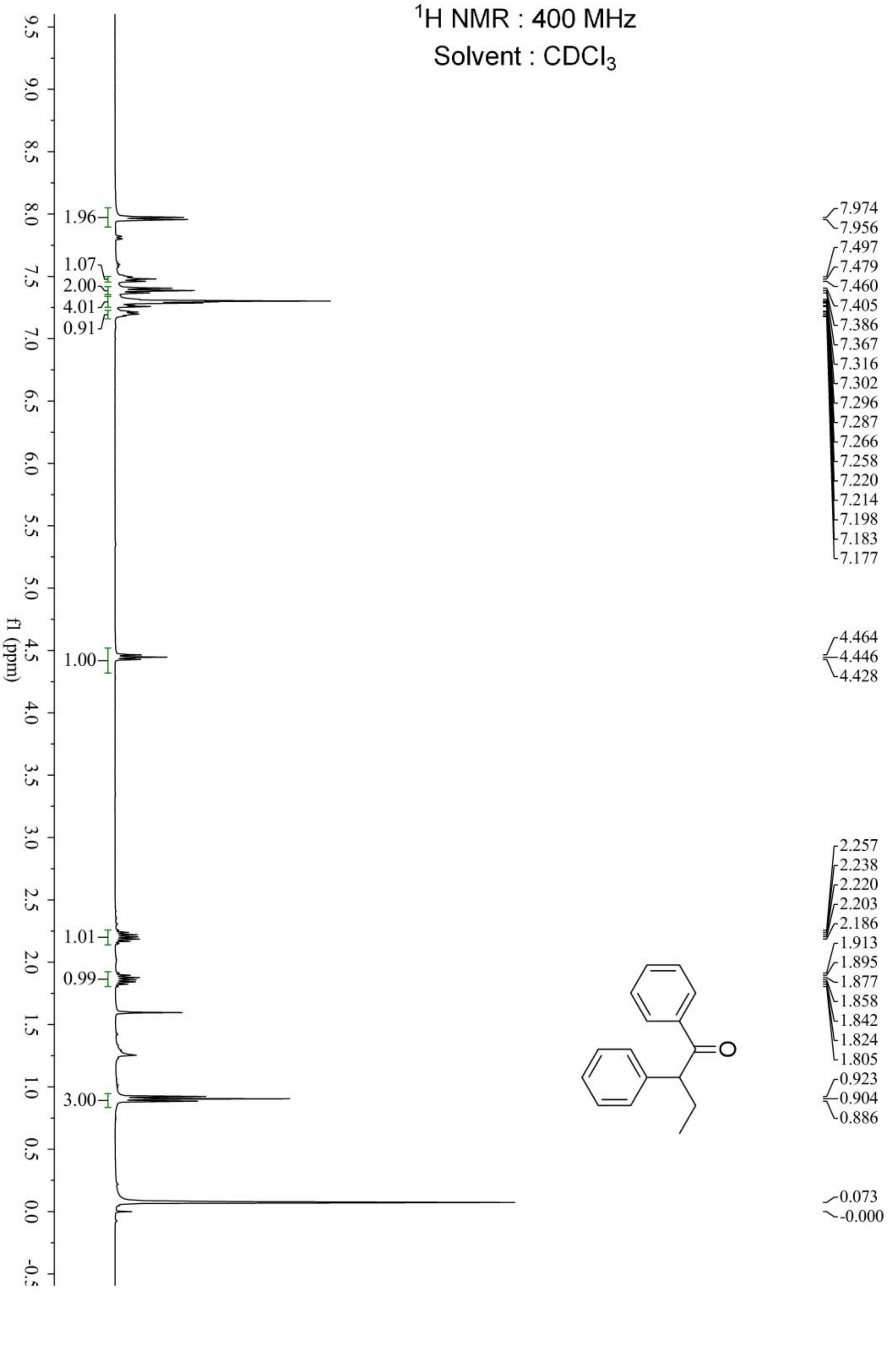


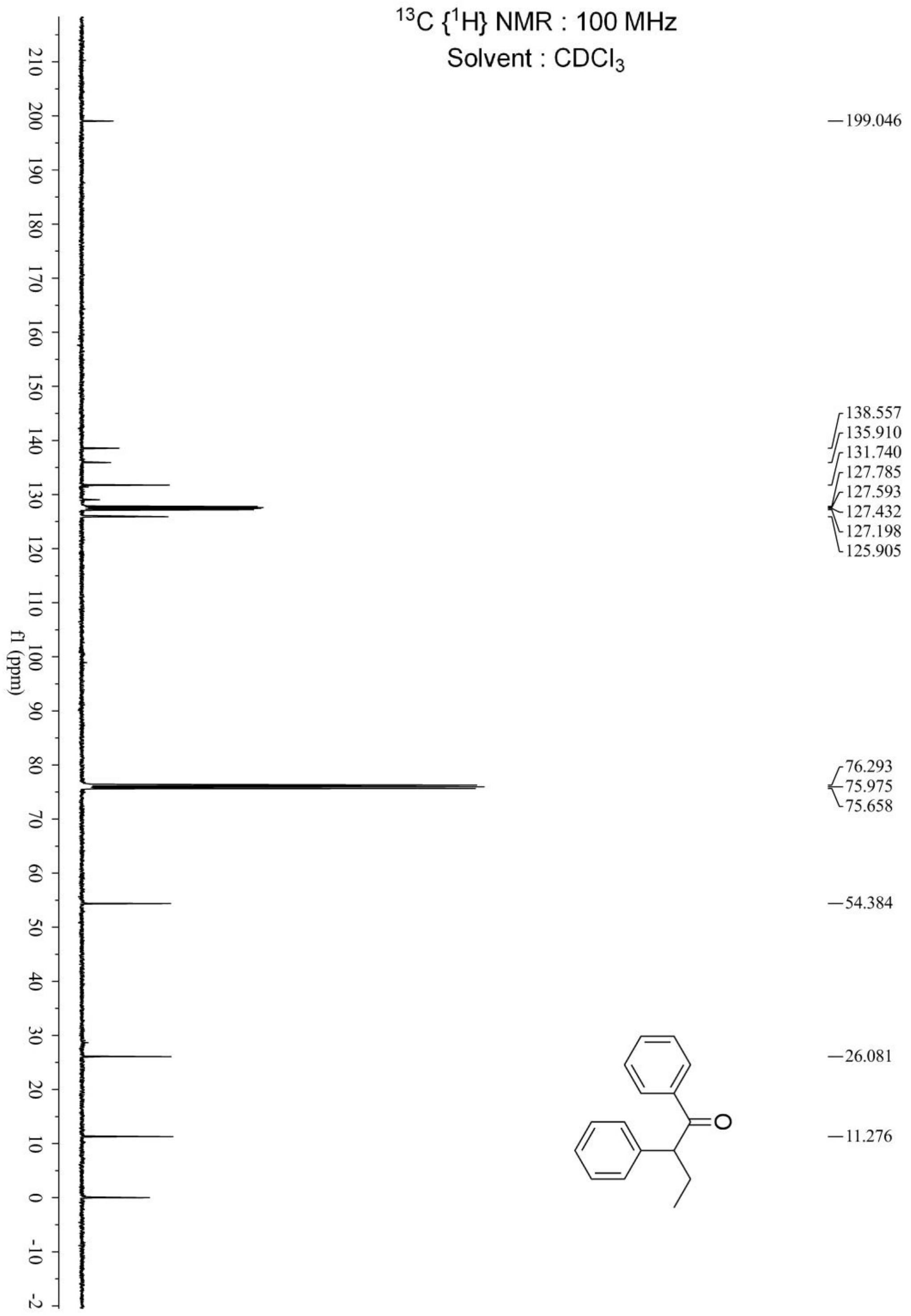
1,2-diphenyl-8-(*p*-tolylthio)octan-1-one (3ja)




$^{13}C\ \{^1H\}$ NMR : 100 MHz
Solvent : $CDCl_3$
199.998
139.687
136.844
135.773
132.934
132.790
129.669
129.558
128.832
128.603
128.467
128.139
126.921
77.317
77.000
76.683
53.589
34.175
33.900
29.093
29.061
28.525
27.544
20.976
fl (ppm)
S
O

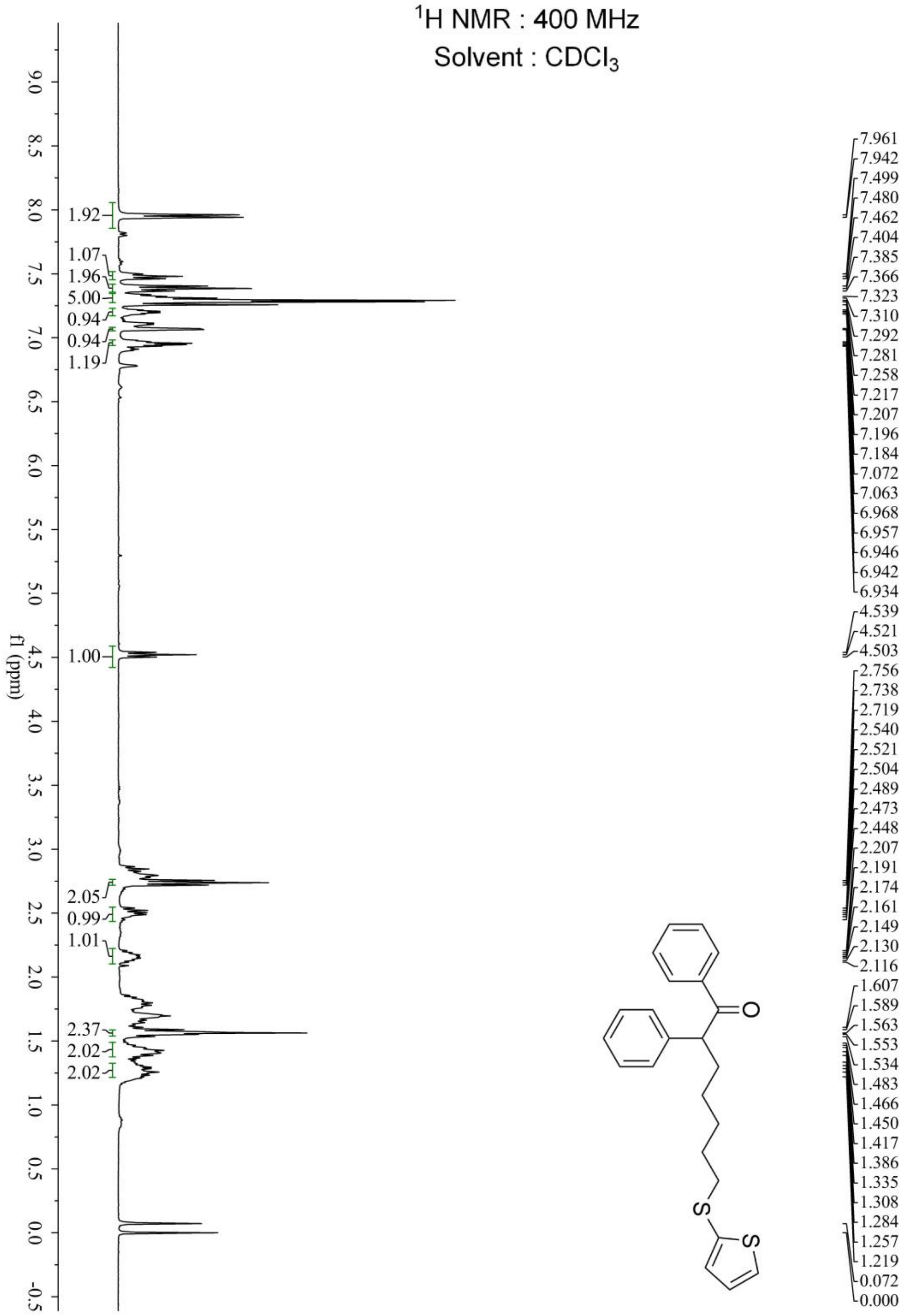
1,2-diphenylbutan-1-one (3ka)





$^{13}C\ \{^{1}H\}$ NMR : 100 MHz
Solvent : $CDCl_3$
199.046
138.557
135.910
131.740
127.785
127.593
127.432
127.198
125.905
76.293
75.975
75.658
54.384
26.081
11.276
f1 (ppm)

1,2-diphenyl-7-(thiophen-2-ylthio)heptan-1-one (3la)



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

Solvent : $CDCl_3$