A Novel and Efficient Zinc-catalyzed Thioetherification of aryl Halides

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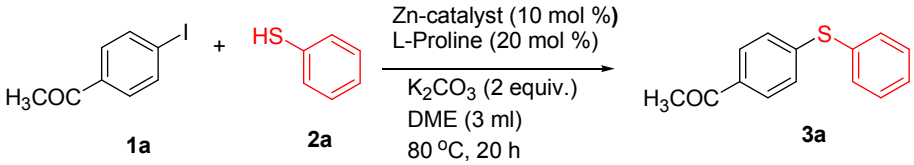
Table of Contents

1 General Remarks S1

The ligand L-proline was purchased from SRL Pvt. Ltd. India. Et_2Zn and NaO^{t}Bu were purchased from Sigma Aldrich chemical company, USA. Aryl halides and thiols were obtained from Alfa Aesar, United Kingdom. All these reagents were used as such. All solvents used for the reaction were purchased from NICE Chemicals Pvt. Ltd. India and distilled prior to use. The NMR spectra were recorded at 400 (^{1}H) and 100 (^{13}C) MHz respectively on a Bruker-400 MHz NMR spectrometer instrument. The chemical shift values are reported relative to Me_4Si (^{1}H) and $CDCl_3$ (^{13}C) as internal standards. The value of coupling constant (*J*) is stated in Hertz (Hz). FTIR were recorded on a PerkinElmer Spectrum 400 FT-IR spectrophotometer and are reported in frequency of absorption (cm^{-1}). The mass spectra were recorded under HRMS using XEVO G2 Q-TOF (Waters) mass spectrometer. Melting points were recorded on MPHT melting point apparatus and are uncorrected. Thin layer chromatography was carried out using Aluchrosep SilicaGel 60/UV_{254} purchased from S D Fine-Chem. Ltd, India and visualized using either by UV Fluorescence or by Iodine chamber. Column chromatography was performed using silica gel 100-200 mesh purchased from Merck Specialities Pvt. Ltd., India and mixtures of hexane-ethylacetate used for elution.

2 Optimization Reactions S1-S3

1. **Screening of Different Zinc-sources[a)]**



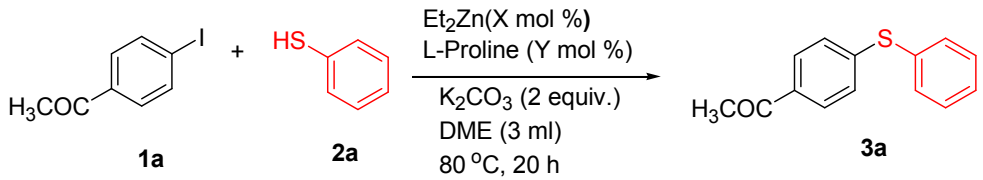
1a **2a** **3a**

Entry	Zn-source	Yield[b)]
1	Zn-granules	nd[c)]

2	Zn-powder	nd
3	$Zn(OAc)_2$	nd
4	Et_2Zn	54 %

[a] Reaction conditions: aryliodide (1mmol), thiophenol (1.1 mmol), K_2CO_3 (2 equiv.), Zn-source (10 mol %), L-proline (20 mol %), 80 °C, 20 h [b] isolated yield; [c] not detected

2. Effect of the amount of catalyst loading[a]

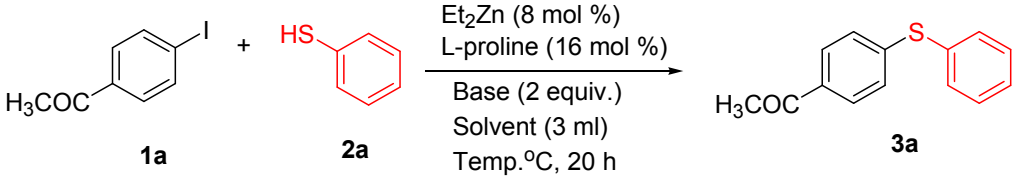


1a 2a 3a

Entry	Et_2Zn (mol %)	L-proline (mol %)	Yield[b]
1	10	20	54
2	**8**	**16**	**53**
3	6	12	35
4	4	8	19
5	2	4	10

[a] Reaction conditions: aryliodide (1mmol), thiophenol (1.1 mmol), K_2CO_3 (2 equiv.), DME (3 ml), 80 °C, 20 h [b] isolated yield

3. Optimization of Solvents, Bases and Temperature[a]



1a 2a 3a

Entry	Base (2 equiv.)	Solvent (3 ml)	Temperature (°C)	Time (h)	Yield[b] (%)
1	K_2CO_3	DME	80	20	54
2	K_2CO_3	THF	80	20	34
3	K_2CO_3	CH_3CN	80	20	81
4	K_2CO_3	DMF	80	20	nd[c]

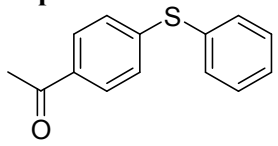
5	K_2CO_3	*t*-BuOH	80	20	34
6	K_2CO_3	DMSO	80	20	nd
7	K_2CO_3	toluene	80	20	nd
8	K_2CO_3	1,4-dioxane	80	20	nd
9	Cs_2CO_3	DME	80	20	75
10	NaO^{t}Bu	DME	80	20	64
11	NaH	DME	80	20	62
12	Et_3N	DME	80	20	nd
13	K_3PO_4	DME	80	20	14
14	KO^{t}Bu	CH_3CN	80	20	75
15	NaH	CH_3CN	80	20	20
16	Cs_2CO_3	CH_3CN	80	20	85
17	**NaO^{t}Bu**	**CH_3CN**	**80**	**20**	**95**
18	NaO^{t}Bu	CH_3CN	0	20	nd
19	NaO^{t}Bu	CH_3CN	rt	20	nd
20	NaO^{t}Bu	CH_3CN	125	20	54
21[d)]	NaO^{t}Bu	CH_3CN	80	20	43
22[e)]	NaO^{t}Bu	CH_3CN	80	20	traces
23	-	CH_3CN	80	20	nd
24[f)]	NaO^{t}Bu	CH_3CN	80	20	traces
25[g)]	NaO^{t}Bu	CH_3CN	80	20	traces

[a)] Reaction conditions: aryliodide (1mmol), thiophenol (1.1 mmol), NaO^{t}Bu (2 equiv.), Et_2Zn (8 mol %), L-proline (16 mol %), 80 ^{o}C, 20 h. [b)] isolated yield. [c)] not detected. [d)]1.5 equiv. of NaO^{t}Bu, [e)] Absence of Et_2Zn, [f)] Absence of L-proline, [g)] Absence of inert atmosphere

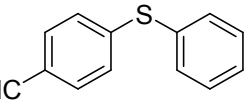
3 Typical Experimental Procedure S4

Synthesis of 1-(4-phenylsulfanyl-phenyl)-ethanone (3a): A dry sealed tube was charged with 1mmol (246 mg) of 4-iodoacetophenone, 16 mol% of L-proline (18 mg) and 2 equiv. of NaO^tBu (192 mg) under nitrogen. To the above mixture was added 8 mol % of Et_2Zn (1M in hexane, 0.08 ml) and 3 ml of acetonitrile followed by the addition of 1.1 mmol of thiophenol (0.11 ml) under nitrogen. The sealed tube was heated in an oil bath which was preheated to 80 ^oC and the reaction mixture was stirred under the same conditions for 20 hours. The reaction mixture was then cooled and extracted with ethyl acetate (3 x 15 ml) and the ethyl acetate layer was washed with saturated aqueous NaCl solution. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure in a rotary evaporator. The crude residue was purified by column chromatography using EtOAc-hexane as the eluent to get 217 mg (95 %) of the product as a colourless solid. All other products were synthesized by similar procedure.

4 Compound Characterization Data S4-S8

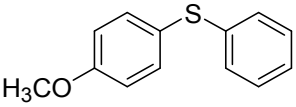
3a: 

1-(4-Phenylsulfanylphenyl)ethanone;[1] Chemical Formula: $C_{14}H_{12}OS$; Colourless solid; Yield: 217 mg (95 %); **M. P**: 67 ^oC (from Hexane); **^{1}H NMR** (400 MHz, $CDCl_3$)**:** δ 7.83(d, *J* = 8.4 Hz, 2H), 7.51-7.48 (m, 2H), 7.41-7.39 (m, 3H), 7.22 (d, *J* = 8.4 Hz, 2H), 2.55 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.10, 144.92, 134.55, 133.87, 132.16, 129.69, 128.91, 128.79, 127.52, 26.46; **IR** (neat): 3060, 1669, 1555, 1182, 819, 616 cm^{-1}; **HRMS** (QToF): $[M+H]^+$ calculated for $C_{14}H_{12}OS$ is 229.0687; found 229.0675

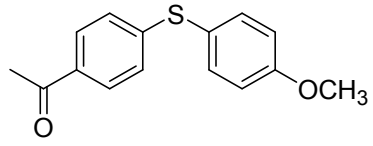
3d: 

4-Phenylsulfanylbenzonitrile;[2] Chemical Formula: $C_{13}H_9NS$; Yellow liquid; Yield:

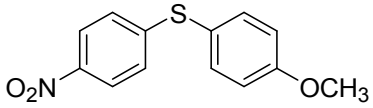
205 mg (97 %); **^{1}H NMR** (400 MHz, $CDCl_3$)**:** δ 7.52-7.50 (m, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.44-7.41 (m, 3H), 7.17 (d, *J* = 8.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 145.74, 135.07, 134.51, 132.37, 129.92, 129.42, 127.37, 118.81, 108.73; **IR** (neat): 3059, 2225, 821, 747, 616 cm^{-1}; **HRMS** (QToF): $[M+H]^+$ calculated for $C_{13}H_9NS$ is 212.0533; found 212.0526

3f: 

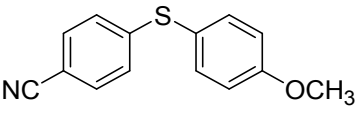
1-Methoxy-4-phenylsulfanylbenzene;[2] Chemical Formula: $C_{13}H_{12}OS$; Yellow liquid; Yield: 132 mg (61 %); **^{1}H NMR** (400 MHz, $CDCl_3$)**:** δ 7.42 (d, *J* = 8.8 Hz, 2H), 7.25-7.21 (m, 2H), 7.17-7.13 (m, 3H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.82 (s, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.83, 138.60, 135.36, 128.92, 128.21, 125.76, 124.22, 114.99, 55.36; **IR** (neat): 3068, 2967, 2887, 816, 658cm^{-1}; **HRMS** (QToF): $[M]^+$ calculated for $C_{13}H_{12}OS$ is 216.0609; found 216.0603

3h: 

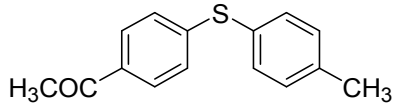
1-[4-(4-Methoxyphenylsulfanyl)phenyl]ethanone;[1] Chemical Formula: $C_{15}H_{14}O_2S$; Appearance: colourless crystals; **MP**: 40 °C (from Hexane); Yield: 222 mg (86 %); **^{1}H NMR** (400 MHz, $CDCl_3$)**:** δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.53 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.14, 160.68, 146.89, 136.82, 133.90, 128.80, 125.83, 121.43, 115.38, 55.43, 26.42; **IR** (neat): 3060, 2879, 1672, 1557, 1183, 820, 617 cm^{-1}; **HRMS** (QToF): $[M+H]^+$ calculated for $C_{15}H_{14}O_2S$ is 259.0787; found 259.0783

3i: 

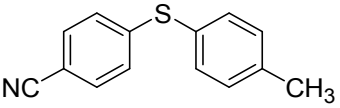
4-Nitrophenyl-4-Methoxysulfide;[5] Chemical Formula: $C_{13}H_{11}NO_3S$; Appearance: light yellow crystals; MP: 65-67 °C (from Hexane); Yield: 183 mg (70 %); **^{1}H NMR** (400 MHz, $CDCl_3$)**:** δ 8.02 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.10, 150.07, 137.13, 132.62, 125.54, 123.92, 115.66, 114.61, 55.45; **IR** (neat): 3001, 2834, 1573, 1334, 821, 622 cm^{-1}; **HRMS** (QToF): $[M+H]^+$calculated for $C_{13}H_{11}NO_3S$ is 262.0532; found 262.0539

3j: 

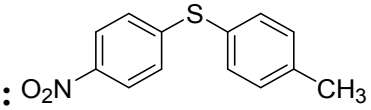
4-(4-Methoxyphenylsulfanyl)benzonitrile;[6] Chemical Formula: $C_{14}H_{11}NOS$; Appearance: colourless solid; MP: 96-98 ^oC (from ethylacetate); Yield: 207 mg (86 %); **^{1}H NMR** (400 MHz, $CDCl_3$)**:** δ 7.48-7.43 (m, 4H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.98, 147.37, 137.10, 132.25, 126.07, 120.41, 118.95, 115.58, 108.04, 55.45; **IR** (neat): 3084, 2835, 2224, 1079, 812, 649 cm^{-1}; **HRMS** (QToF) $[M+H]^+$ calculated for $C_{14}H_{11}NOS$ is 242.0639; found 242.0627

3k: 

1-(4-Tolylsulfanylphenyl)ethanone;[3] Chemical Formula: $C_{15}H_{14}OS$; Appearance: colourless solid; **MP**: 89-91 ^oC (from Hexane); Yield: 129 mg (53 %); **^{1}H NMR** (400 MHz, $CDCl_3$)**:** δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.23(d, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 2.54 (s, 3H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.16, 145.96, 139.36, 134.51, 134.14, 130.54, 128.83, 127.91, 126.66, 26.45, 21.28; **IR** (neat): 3060, 2879, 1669, 1555, 819, 616 cm^{-1}; **HRMS** (QToF): $[M+H]^+$ calculated for $C_{15}H_{14}OS$ is 243.0840; found 243.0844

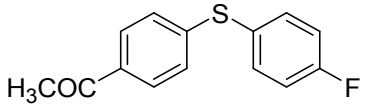
3l: 

4-Tolylsulfanylbenzonitrile;[4] Chemical Formula: $C_{14}H_{11}NS$ Appearance: colourless solid; **MP**: 100-102 ^oC (from Hexane); Yield: 146 mg (65 %); **^{1}H NMR** (400 MHz, $CDCl_3$)**:** δ 7.46-7.40 (m, 4H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 139.96, 134.95, 134.83, 132.28, 130.75, 126.81, 126.70, 118.90, 108.30, 21.31; **IR** (neat): 3024, 2923, 2223, 1589, 812, 624 $cm^{-1;}$ **HRMS** (QToF): $[M+H]^+$ calculated for $C_{14}H_{11}NS$ is 226.0684; found 226.0683

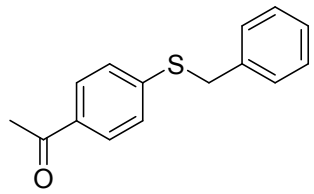
3n: 

4-Nitrophenyl-4-tolyl sulfide;[3] Chemical Formula: $C_{13}H_{11}NO_2S$; Appearance: light yellow solid; MP: 79-81 ^oC (from Hexane); Yield: 201mg (82 %); **^{1}H NMR** (400

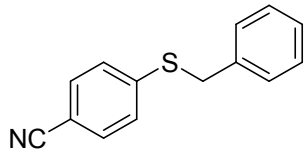
MHz, $CDCl_3$)**:** δ 8.06 (d, *J* = 8.8 Hz, 2H), 7.45(d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.35, 145.16, 140.25, 135.09, 130.87, 126.51, 126.15, 123.99, 21.34; **IR** (neat): 2924, 1506, 1334, 839, 640 cm^{-1}; **HRMS** (QToF): $[M+H]^+$ calculated for $C_{13}H_{11}NO_2S$ is 246.0589; found 246.0588

3o: 

1-[4-(Fluorophenylsulfanyl)phenyl]ethanone;[7] Chemical Formula: $C_{14}H_{11}FOS$; Appearance: yellow liquid; Yield: 208 mg (85 %); **^{1}H NMR** (400 MHz, $CDCl_3$)**:** δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.52-7.48 (m, 2H), 7.15-7.09 (m, 4H), 2.54 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.07, 162.03, 145.17, 138.04, 136.56, 136.48, 128.94, 126.83, 117.08, 26.45; **IR** (neat): 3065, 2963, 1678, 1487, 815, 617, 468 cm^{-1}**; HRMS** (QToF) $[M+H]^+$ calculated for $C_{14}H_{11}FOS$ is 247.0587; found 247.0589

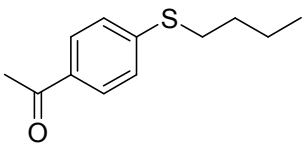
3p: 

1-(4-Benzylsulfanylphenyl)ethanone;[7] Chemical Formula: $C_{15}H_{14}OS$; Appearance: colourless solid; **MP**: 110-112 °C (from Hexane); Yield: 218 mg (90 %); **^{1}H NMR** (400 MHz, $CDCl_3$)**:** δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 6.8 Hz, 2H), 7.32-7.27 (m, 4H), 7.25-7.24 (m, 1H), 4.21 (s, 2H) 2.55 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.19, 144.21, 136.26, 134.20, 128.74, 128.70, 127.53, 126.94, 126.81, 37.20, 26.43; **IR** (neat): 3022, 2919, 1675, 1358, 816, 624 cm^{-1}; **HRMS** (QToF): $[M+H]^+$ calculated for $C_{15}H_{14}OS$ is 243.0844; found 243.0839

3q: 

4-Benzylsulfanylbenzonitrile;[7] Chemical Formula: $C_{14}H_{11}NS$; Appearance: yellow liquid; Yield: 158 mg (70 %); **^{1}H NMR** (400 MHz, $CDCl_3$)**:** δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.36-7.26 (m, 7H), 4.20 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 144.48, 135.73, 132.22, 128.79, 128.70, 127.71, 127.37, 118.81, 108.60, 37.11; **IR** (neat): 3032, 2876, 2219, 1486, 818, 640 cm^{-1}; **HRMS** (QToF) $[M+H]^+$ calculated for $C_{14}H_{11}NS$ is 226.0684; found 226.0680

3r



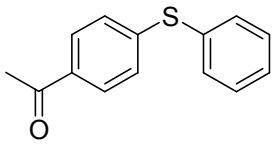
1-(4-Butylsulfanyl-phenyl)ethanone;[8] Chemical Formula: $C_{12}H_{16}OS$; Appearance: colourless liquid; Yield: 108 mg (52 %); **^{1}H NMR** (400 MHz, $CDCl_3$)**:** δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.56 (s, 3H), 1.70-1.67 (m, 2H), 1.51-1.45 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 197.08, 145.01, 133.82, 128.74, 126.35, 31.73, 30.85, 26.37, 22.03, 13.61; **IR** (neat): 3032, 2978, 2876, 1678, 1486, 818, 640 cm^{-1}; **HRMS** (QToF) $[M+H]^+$ calculated for $C_{12}H_{16}OS$ is 209.0994; found 209.0992

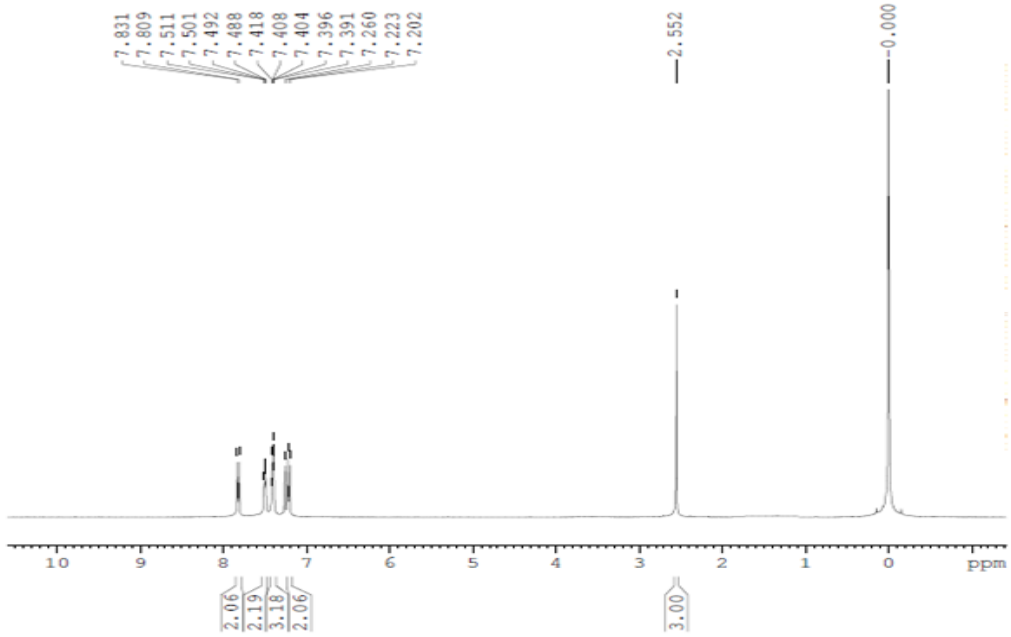
5 References S8

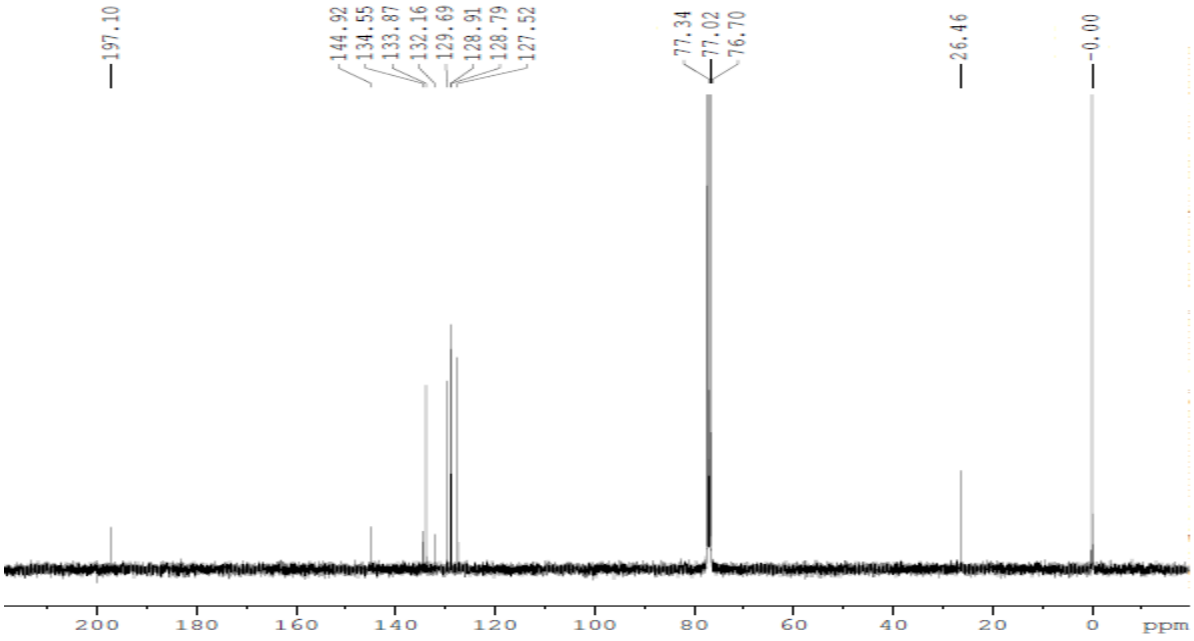
1. J. R. C. Antonino, T. García, P. R. Marques, J. A. V. Moya, A. L. Perez,S. S. Al-Deyab, S. I. Al-Resayes, U. Díaz, A. Corma, *ACS Catal.,* 2011, **1**, 147
2. C. C. Eichmann, J. P. Stambulli, *J. Org. Chem*., 2009, **74**, 4005
3. D. J. C. Prasad, G. Sekhar, *Org. Lett.,* 2011, **13**, 1008
4. Law, H. Gao, *J. Am. Chem. Soc.*, 1930, **52**, 3623
5. Ariswa, Mieko, *J. Am. Chem. Soc*., 2008, **4**, 640
6. S. Kov´acs and Z. Nov´ak, *Org. Biomol. Chem.*, 2011, **9**, 711
7. P. Guan, C. Cao, Y. Liu, Y. Li, P. He, Q. Chen, G. Liu, Y. Shi, *Tetra. Lett*., 2012, **53**, 5987
8. H. Zhang, W. Cao, D. Ma, *Synth. Commun.,* 2007, **37**, 25

6 ^{1}H and ^{13}C Spectra of Compounds S9-S21

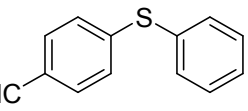
3a:

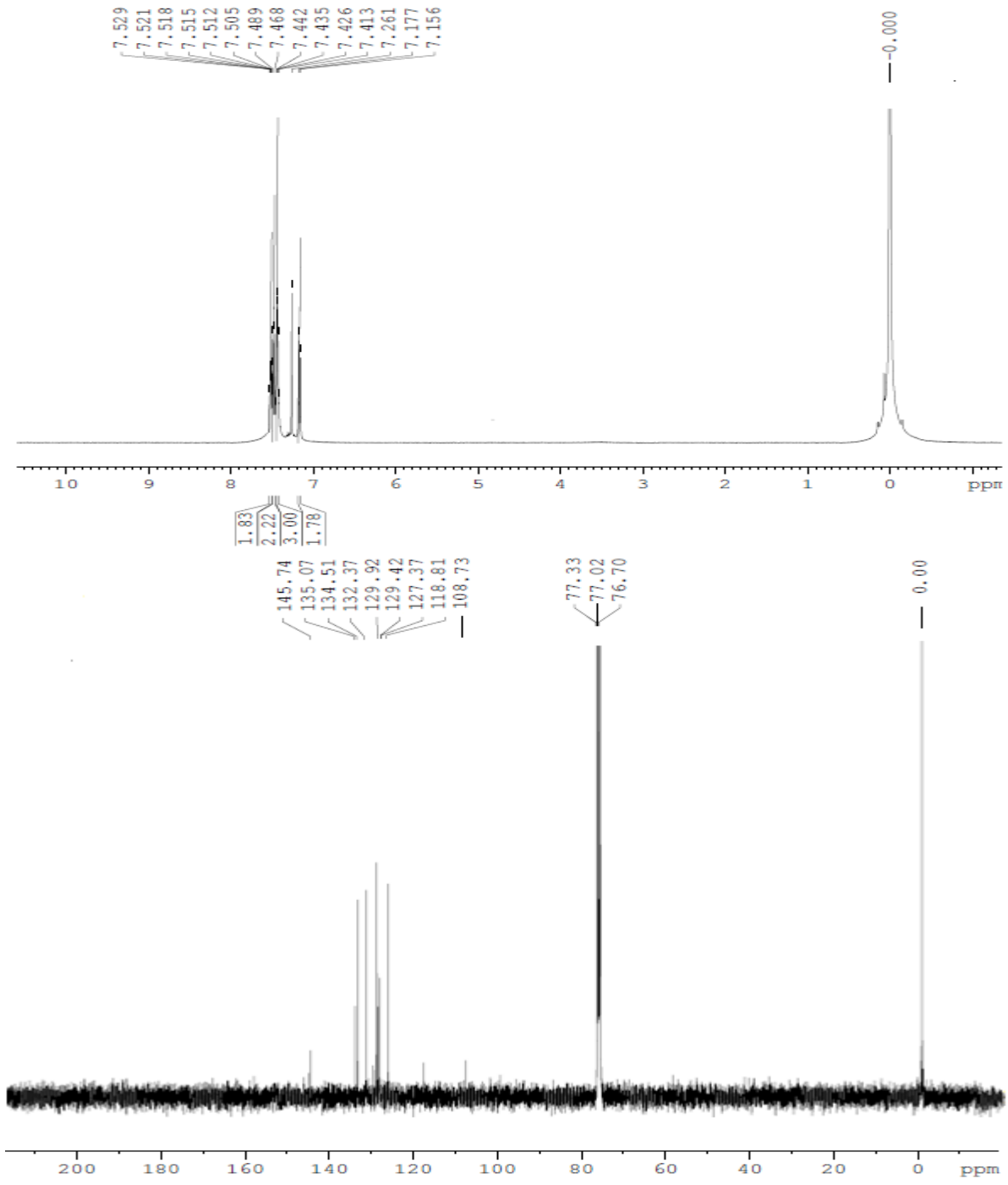


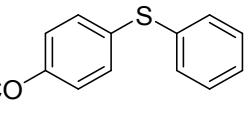


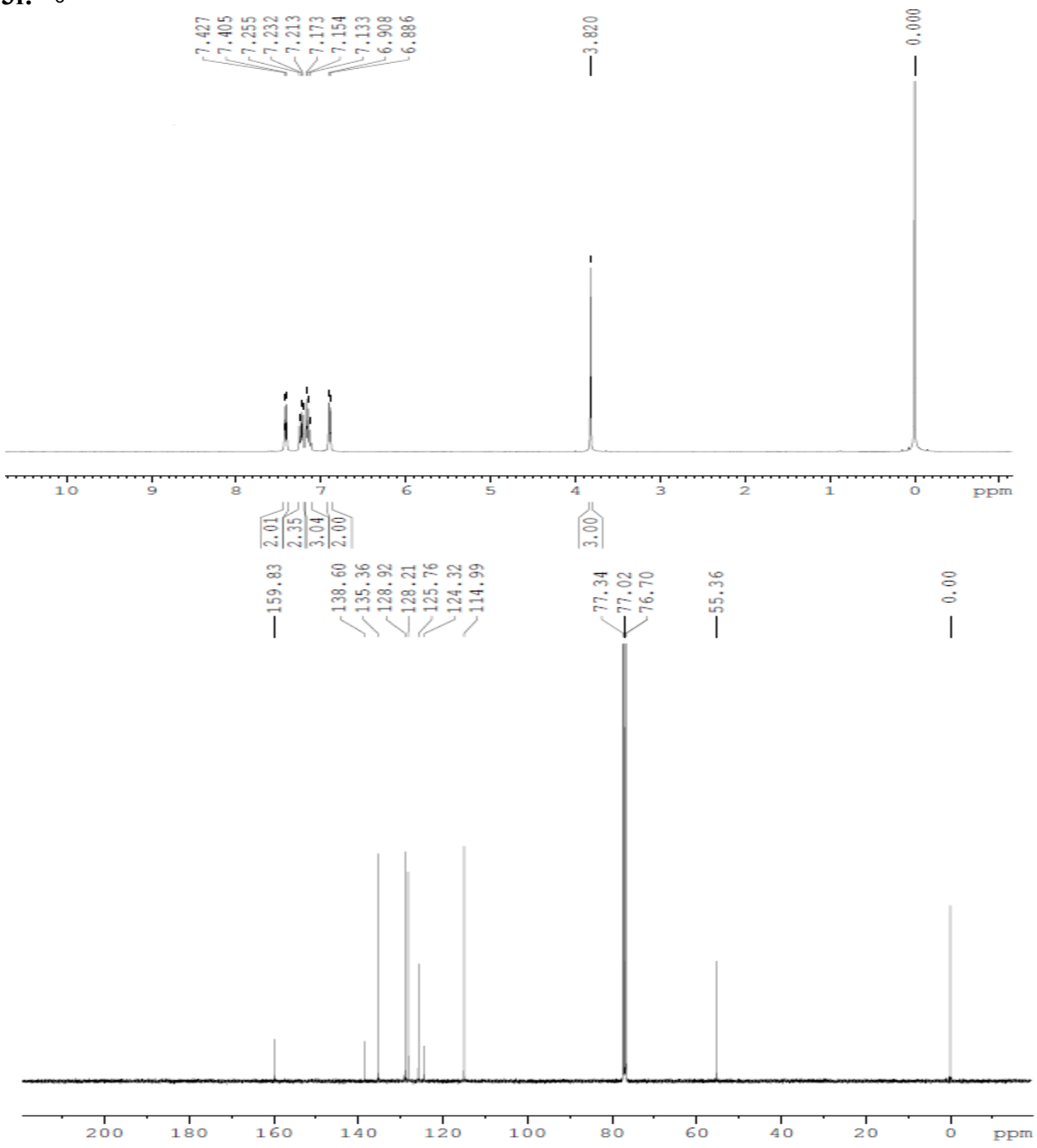


3d:

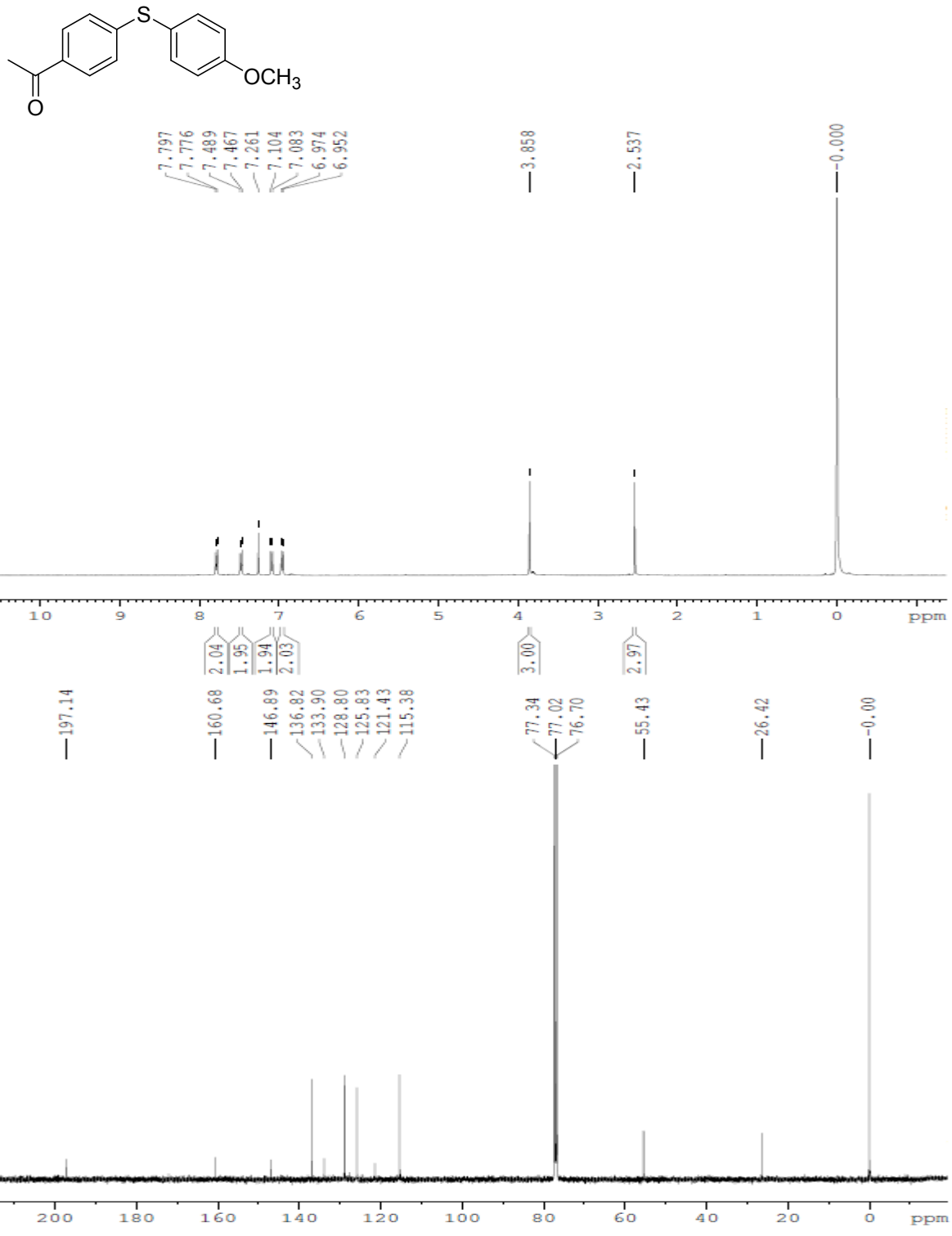

S
NC

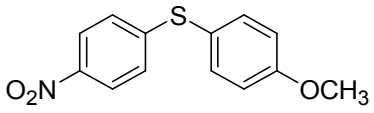

7.529
7.521
7.518
7.515
7.512
7.505
7.489
7.468
7.442
7.435
7.426
7.413
7.261
7.177
7.156
0.000
10
9
8
7
6
5
4
3
2
1
0
ppm
1.83
2.22
3.00
1.78
145.74
135.07
134.51
132.37
129.92
129.42
127.37
118.81
108.73
77.33
77.02
76.70
0.00
200
180
160
140
120
100
80
60
40
20
0
ppm

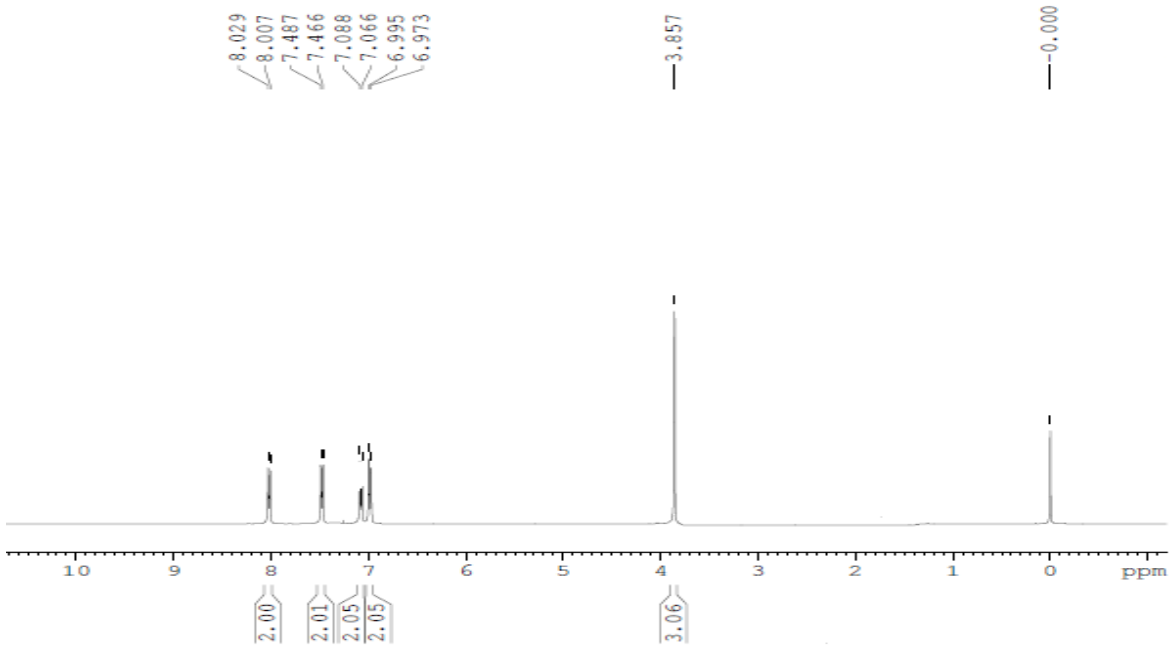
3f: 
S
H3CO

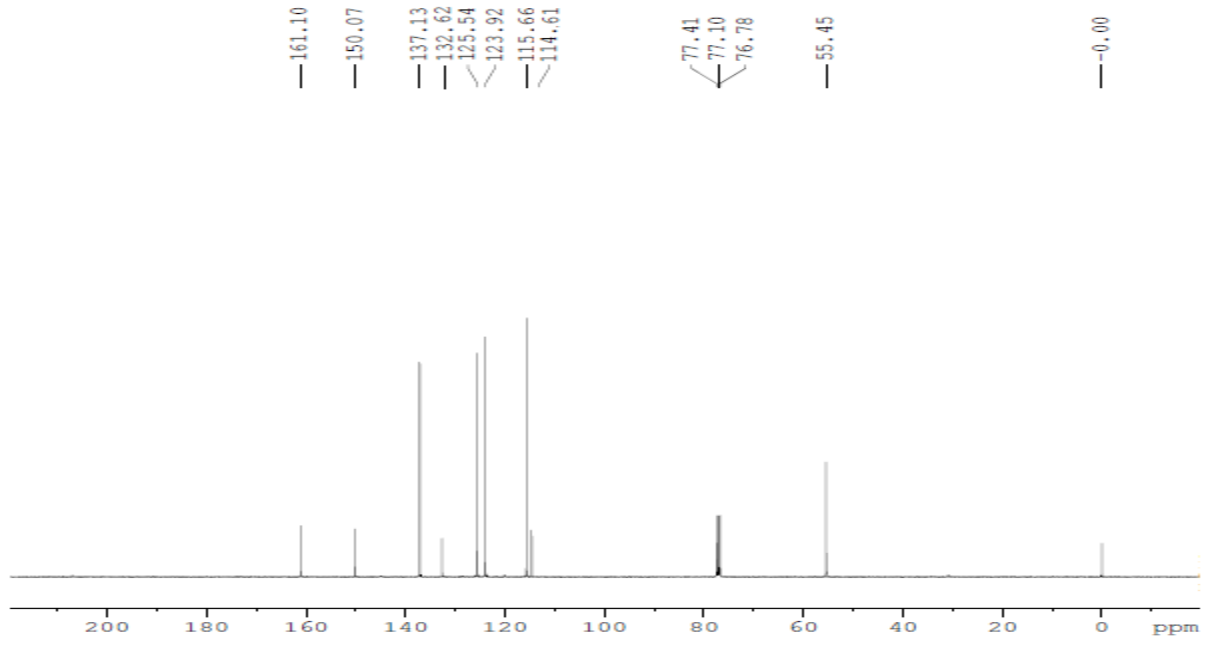

7.427
7.405
7.255
7.232
7.213
7.173
7.154
7.133
6.908
6.886
3.820
0.000
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
2.35
3.04
2.00
3.00
159.83
138.60
135.36
128.92
128.21
125.76
124.32
114.99
77.34
77.02
76.70
55.36
0.00
200
180
160
140
120
100
80
60
40
20
0
ppm

3h:

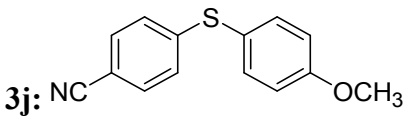

7.797
7.776
7.489
7.467
7.261
7.104
7.083
6.974
6.952
3.858
2.537
0.000
ppm
2.04
1.95
1.94
2.03
3.00
2.97
197.14
160.68
146.89
136.82
133.90
128.80
125.83
121.43
115.38
77.34
77.02
76.70
55.43
26.42
0.00
ppm

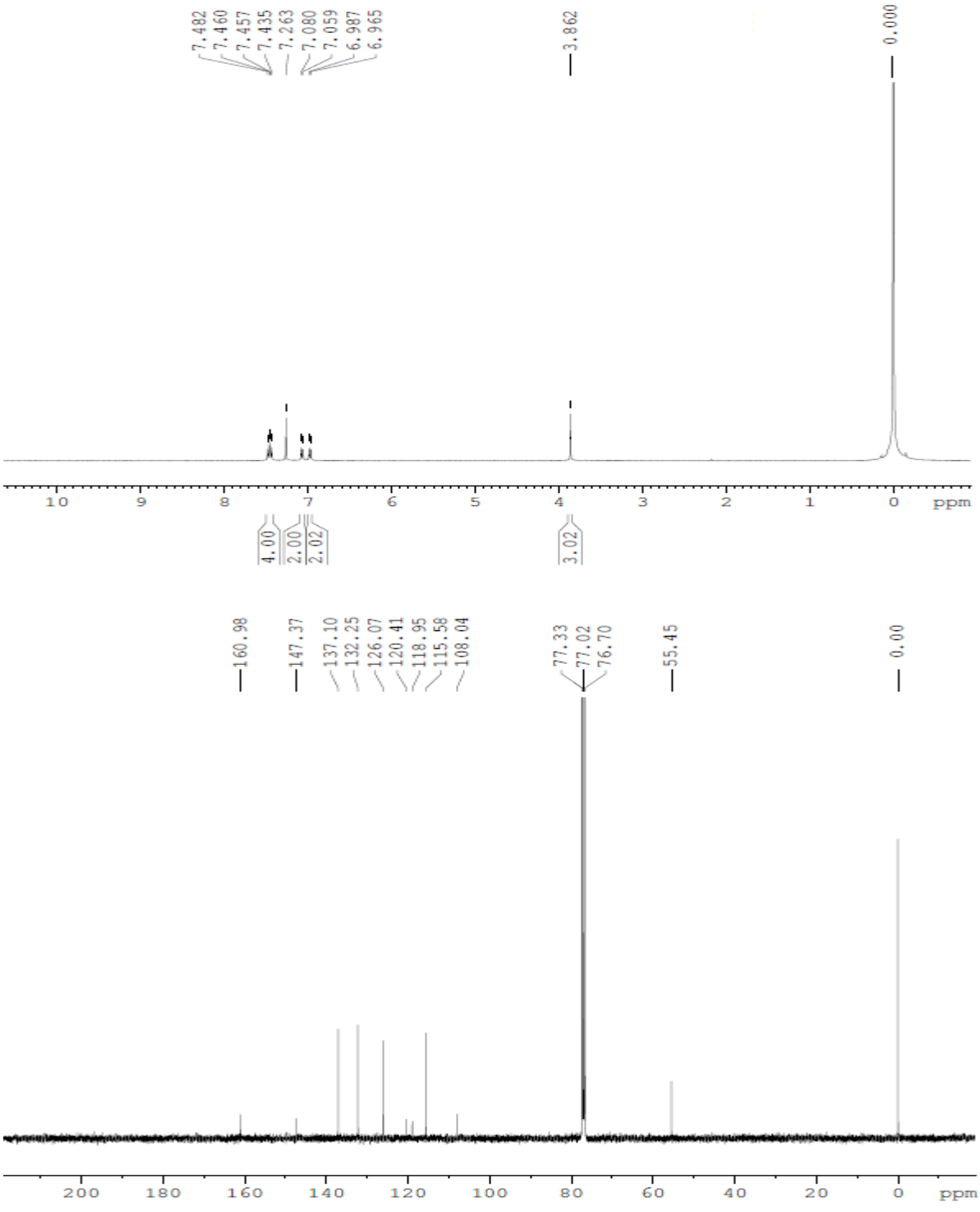
3i: 
S
O2N
OCH3

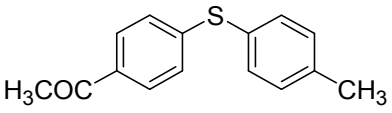

8.029
8.007
7.487
7.466
7.088
7.066
6.995
6.973
3.857
0.000
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.01
2.05
2.05
3.06

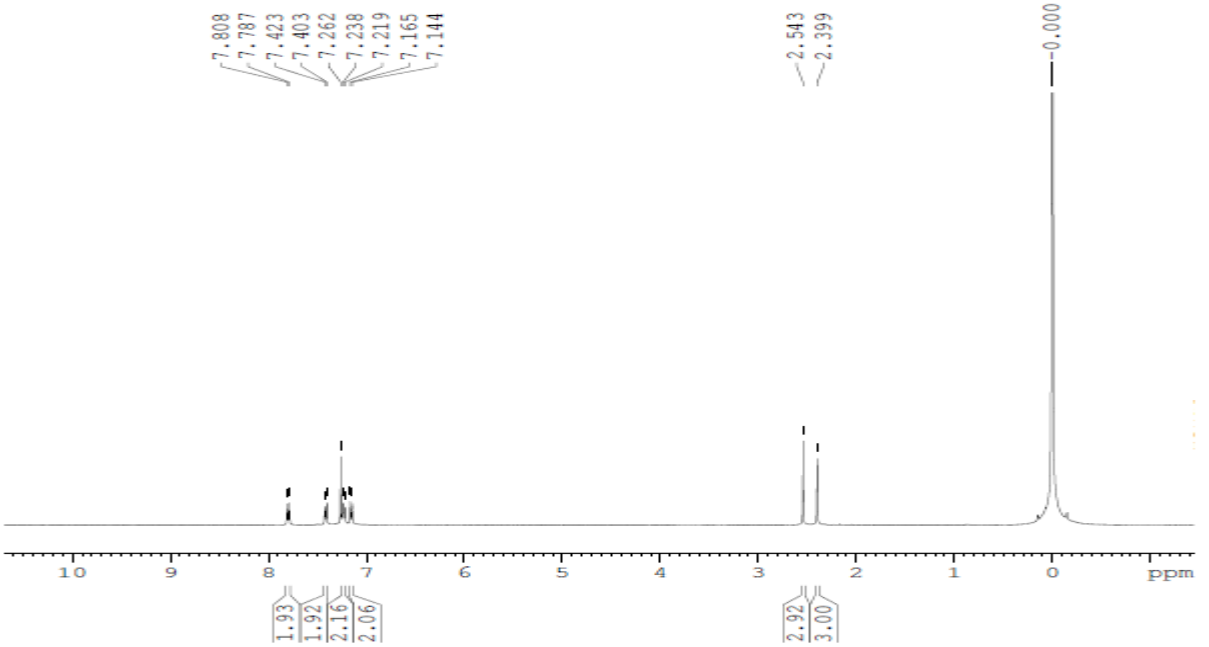

161.10
150.07
137.13
132.62
125.54
123.92
115.66
114.61
77.41
77.10
76.78
55.45
0.00
200
180
160
140
120
100
80
60
40
20
0
ppm

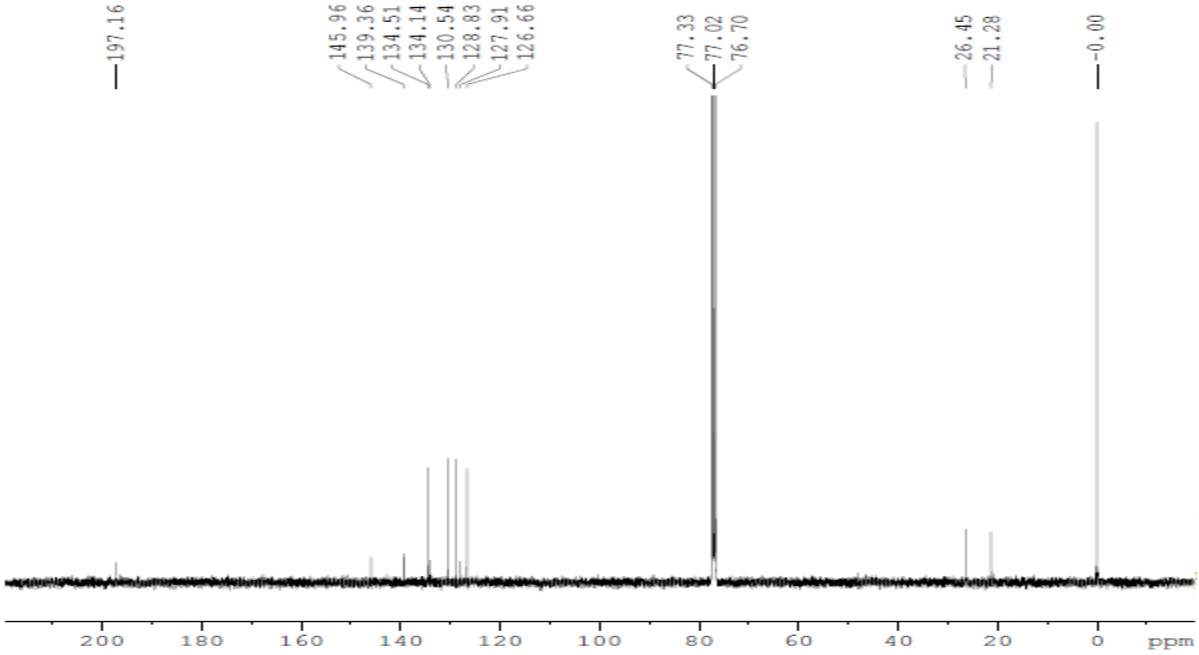
3j:


S
NC
OCH3

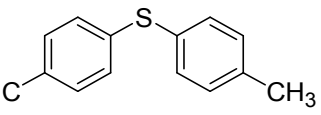

7.482
7.460
7.457
7.435
7.263
7.080
7.059
6.987
6.965
3.862
0.000
10
9
8
7
6
5
4
3
2
1
0
ppm
4.00
2.00
2.02
3.02
160.98
147.37
137.10
132.25
126.07
120.41
118.95
115.58
108.04
77.33
77.02
76.70
55.45
0.00
200
180
160
140
120
100
80
60
40
20
0
ppm

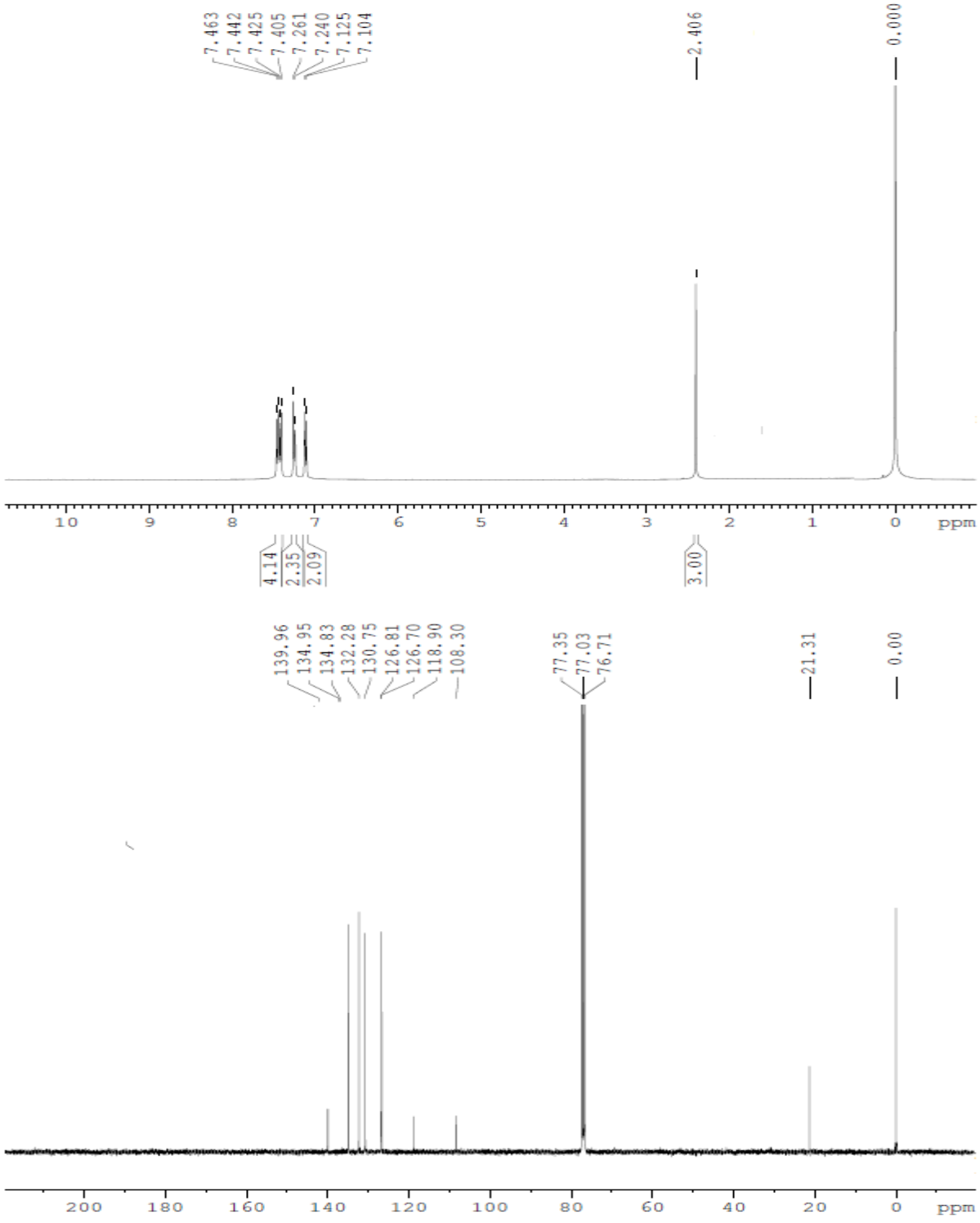
3k: 
S
H3COC
CH3

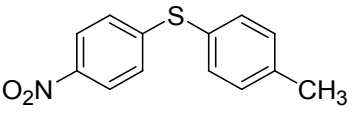

7.808
7.787
7.423
7.403
7.262
7.238
7.219
7.165
7.144
2.543
2.399
0.000
10
9
8
7
6
5
4
3
2
1
0
ppm
1.93
1.92
2.16
2.06
2.92
3.00

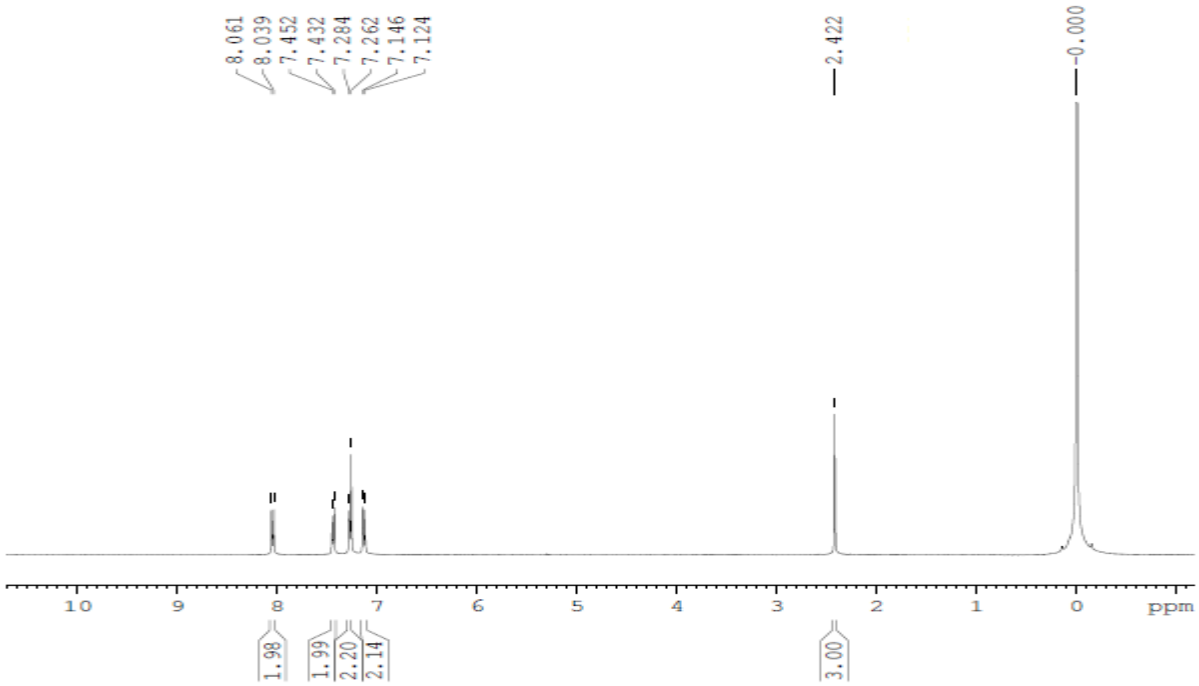

197.16
145.96
139.36
134.51
134.14
130.54
128.83
127.91
126.66
77.33
77.02
76.70
26.45
21.28
0.00
200
180
160
140
120
100
80
60
40
20
0
ppm

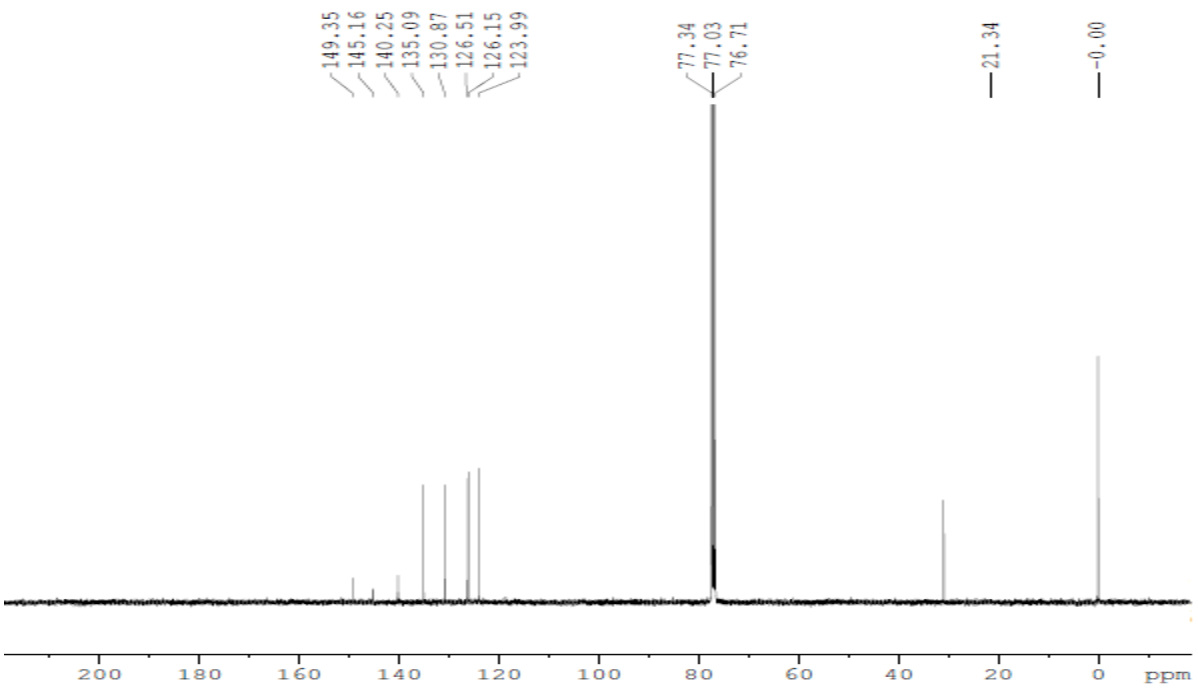
3l:

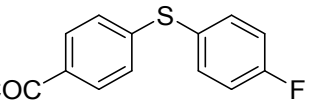

S
NC
CH3

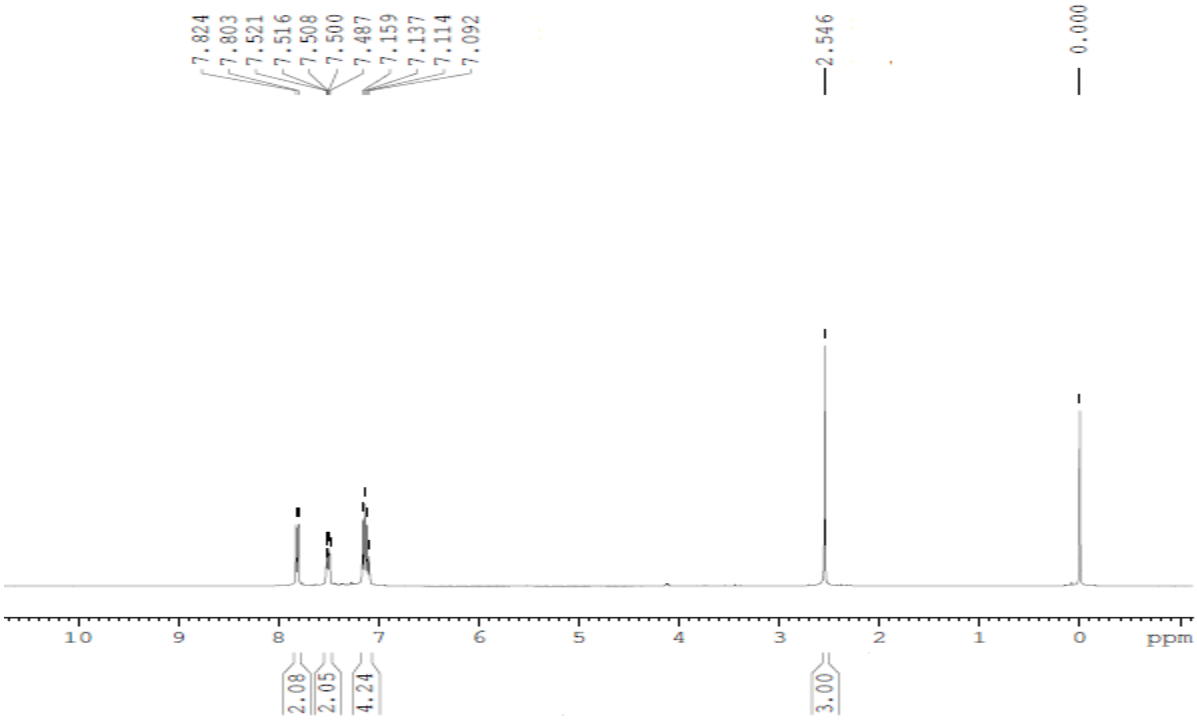

7.463
7.442
7.425
7.405
7.261
7.240
7.125
7.104
2.406
0.000
10
9
8
7
6
5
4
3
2
1
0
ppm
4.14
2.35
2.09
3.00
139.96
134.95
134.83
132.28
130.75
126.81
126.70
118.90
108.30
77.35
77.03
76.71
21.31
0.00
200
180
160
140
120
100
80
60
40
20
0
ppm

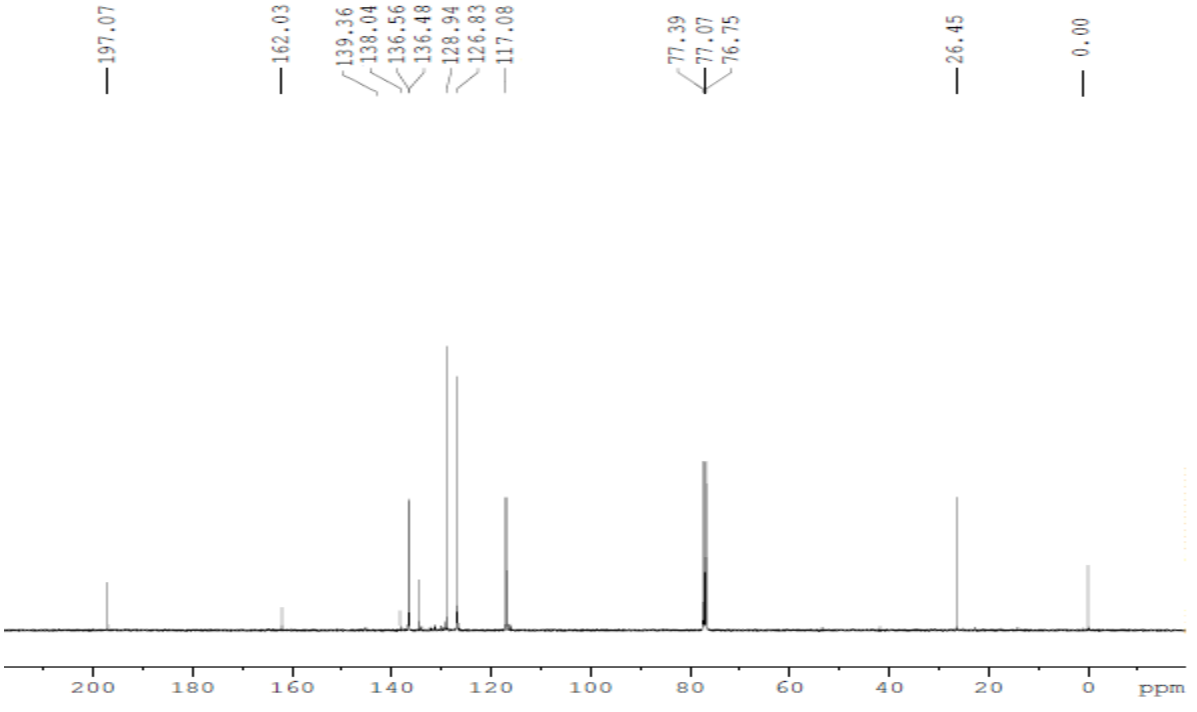
3n: 
S
O2N
CH3


8.061
8.039
7.452
7.432
7.284
7.262
7.146
7.124
2.422
0.000
10
9
8
7
6
5
4
3
2
1
0
ppm
1.98
1.99
2.20
2.14
3.00

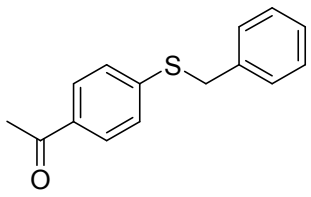

149.35
145.16
140.25
135.09
130.87
126.51
126.15
123.99
77.34
77.03
76.71
21.34
0.00
200
180
160
140
120
100
80
60
40
20
0
ppm

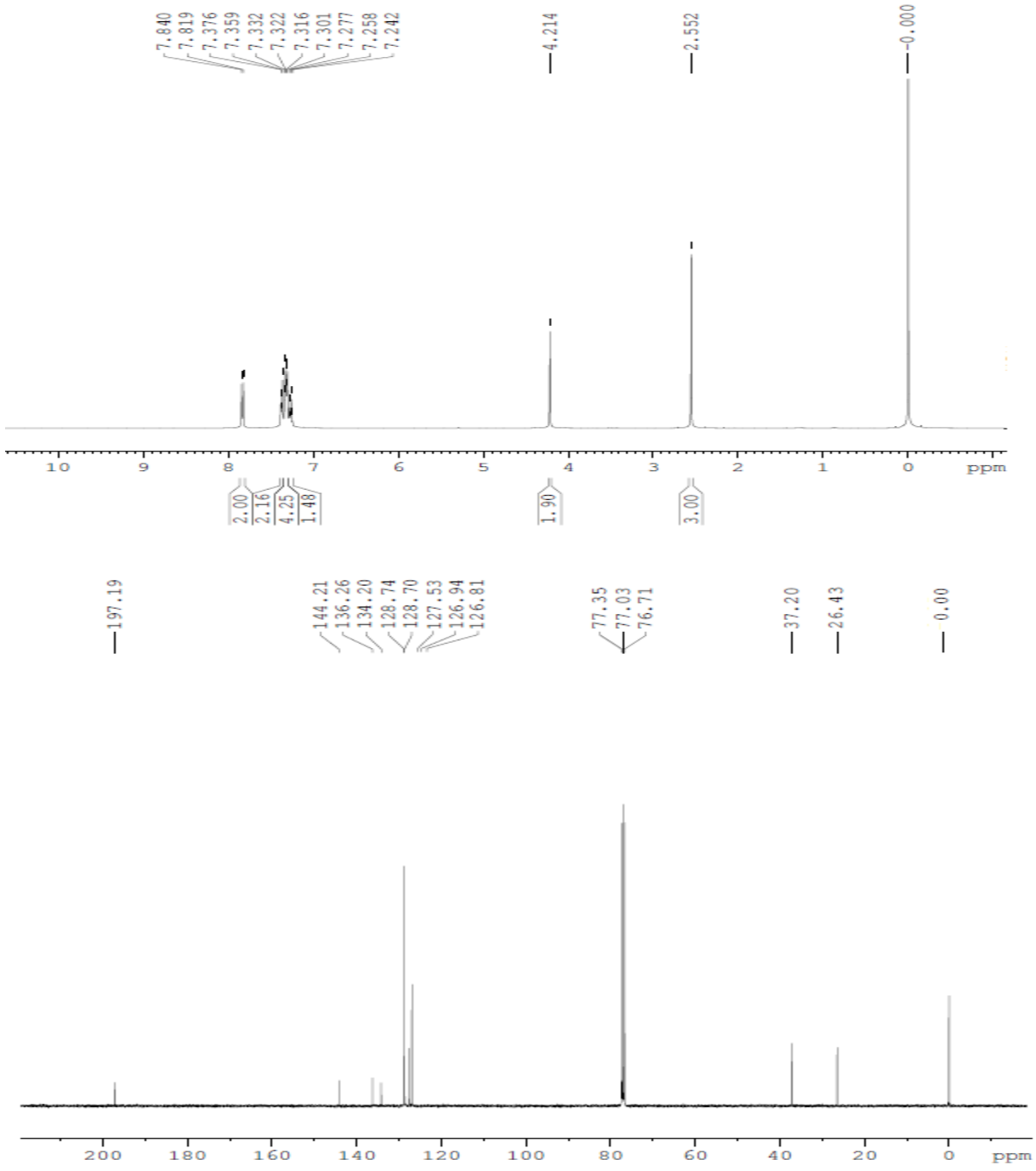
3o: 
S
H3COC
F


7.824
7.803
7.521
7.516
7.508
7.500
7.487
7.159
7.137
7.114
7.092
2.546
0.000
10
9
8
7
6
5
4
3
2
1
0
ppm
2.08
2.05
4.24
3.00

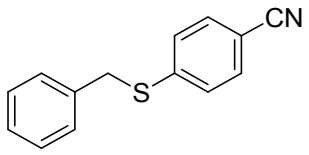

197.07
162.03
139.36
138.04
136.56
136.48
128.94
126.83
117.08
77.39
77.07
76.75
26.45
0.00
200
180
160
140
120
100
80
60
40
20
0
ppm

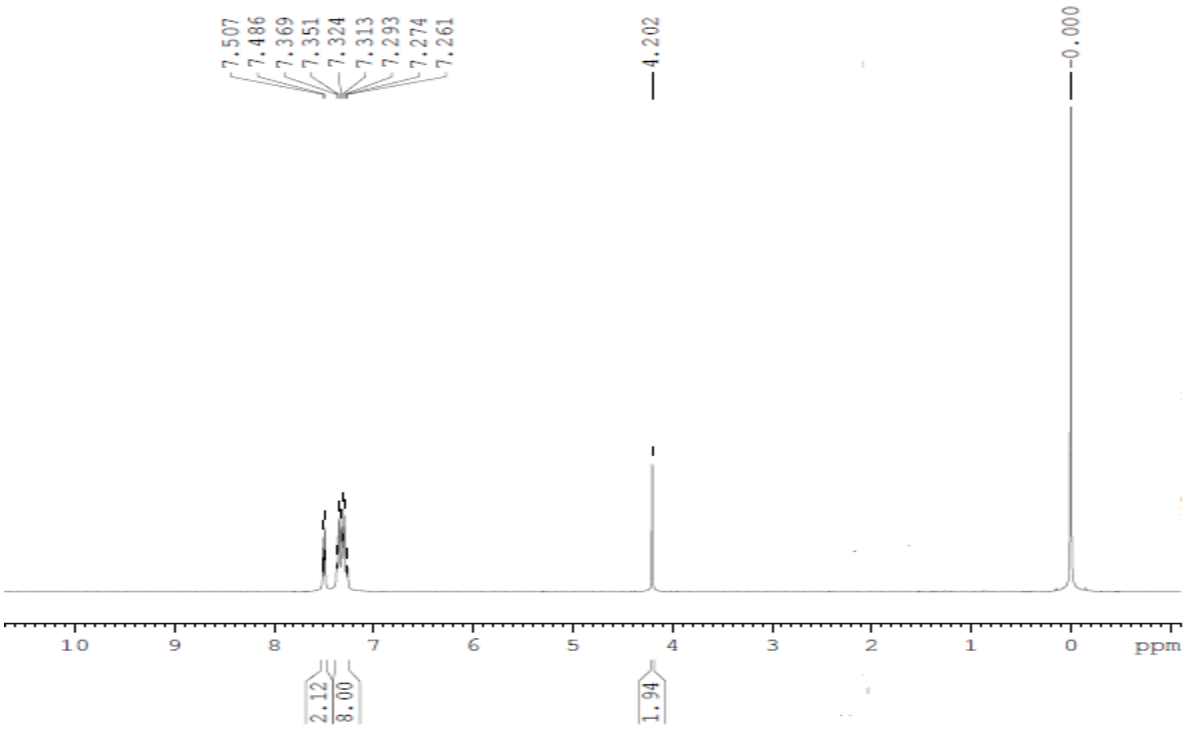
3p:

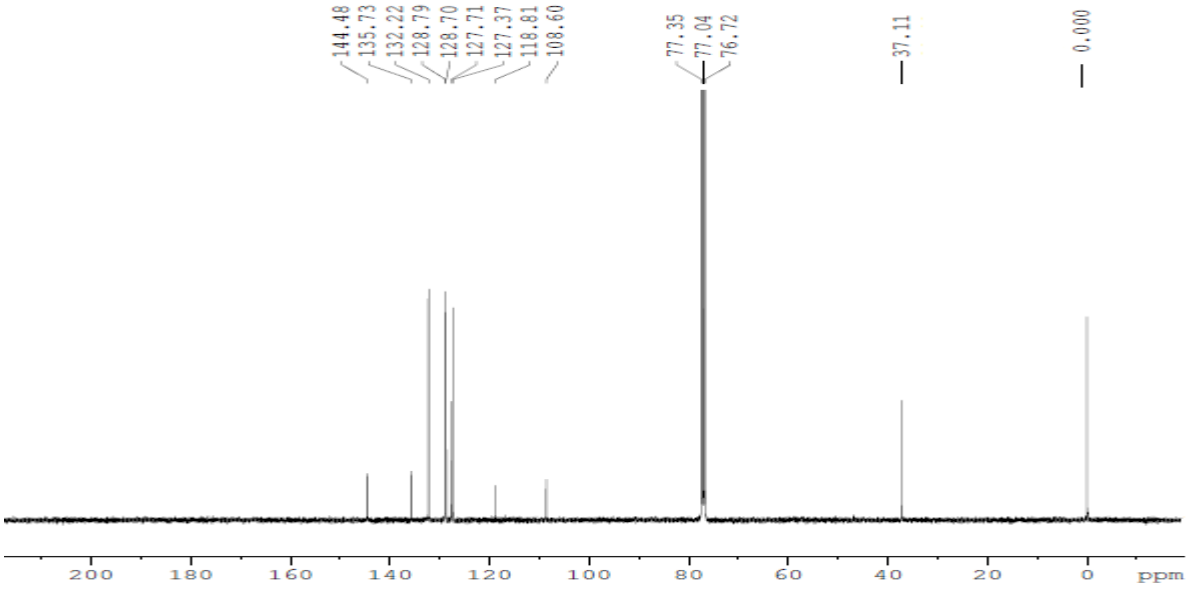

S
O


7.840
7.819
7.376
7.359
7.332
7.322
7.316
7.301
7.277
7.258
7.242
4.214
2.552
0.000
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.16
4.25
1.48
1.90
3.00
197.19
144.21
136.26
134.20
128.74
128.70
127.53
126.94
126.81
77.35
77.03
76.71
37.20
26.43
0.00
200
180
160
140
120
100
80
60
40
20
0
ppm

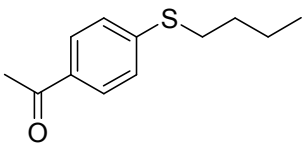
3q:

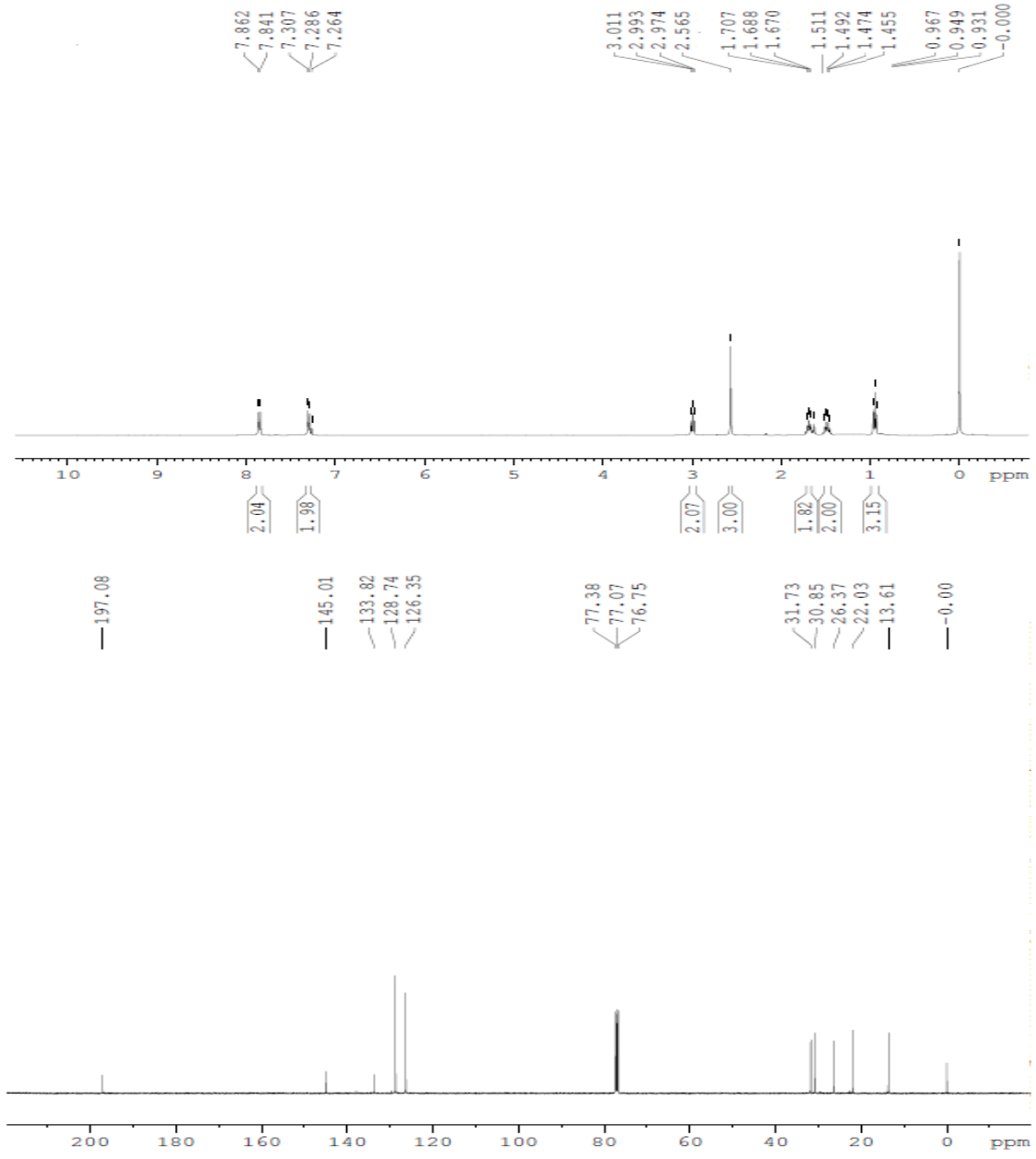

CN
S


7.507
7.486
7.369
7.351
7.324
7.313
7.293
7.274
7.261
4.202
0.000
10
9
8
7
6
5
4
3
2
1
0
ppm
2.12
8.00
1.94


144.48
135.73
132.22
128.79
128.70
127.71
127.37
118.81
108.60
77.35
77.04
76.72
37.11
0.000
200
180
160
140
120
100
80
60
40
20
0
ppm

3r


S
O


7.862
7.841
7.307
7.286
7.264
3.011
2.993
2.974
2.565
1.707
1.688
1.670
1.511
1.492
1.474
1.455
0.967
0.949
0.931
-0.000
10
9
8
7
6
5
4
3
2
1
0
ppm
2.04
1.98
2.07
3.00
1.82
2.00
3.15
197.08
145.01
133.82
128.74
126.35
77.38
77.07
76.75
31.73
30.85
26.37
22.03
13.61
-0.00
200
180
160
140
120
100
80
60
40
20
0
ppm