Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

A copper(I)-catalyzed sulfonylation of (2-alkynylaryl)boronic acids with DABSO

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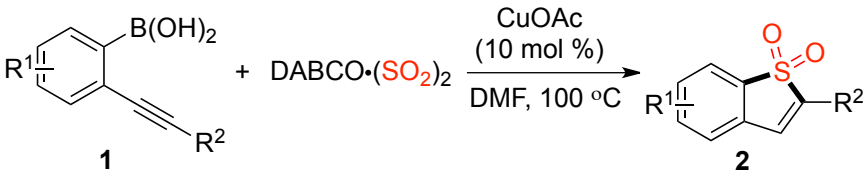
Supporting Information

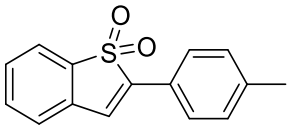
General experimental methods:

Unless otherwise stated, all commercial reagents were used as received. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63µm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr at 25–35°C. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-400 spectrometer operating at 400 MHz and 100 MHz, respectively. All chemical shift values are quoted in ppm and coupling constants quoted in Hz. High resolution mass spectrometry (HRMS) spectra were obtained on a micrOTOF II Instrument.

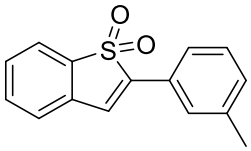
*General experimental procedure for the copper(I)-catalyzed reaction of (2-alkynylaryl)boronic acids **1** with DABCO•$(SO_2)_2$*



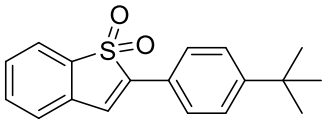
Copper(I) acetate (10 mol %) was added to a solution of (2-alkynylaryl)boronic acid **1** (0.2 mmol) and DABCO•$(SO_2)_2$ (0.4 mmol) in DMF (2.0 mL) under N_2. The mixture was stirred at 100 °C for 10-15 hours. After completion of reaction as indicated by TLC, the mixture was extracted with ethyl acetate. The combined organic solution was dried over Na_2SO_4, and the solvent was evaporated under reduced pressure. The residue was purified directly by flash column chromatograph (EtOAc/*n*-hexane) to give the desired product **2**.



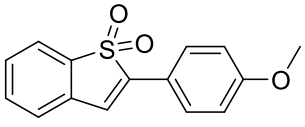
2-(*p*-Tolyl)benzo[*b*]thiophene 1,1-dioxide (**2a**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (t, *J* = 8.4Hz, 3H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.49 (t, *J* =7.0 Hz, 1H), 7.39 (d, *J* = 9.0 Hz, 1H), 7.29 (d, *J* = 9.0 Hz, 2H), 7.24 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 133.7, 131.3, 129.9, 129.6, 129.0, 128.5, 126.4, 124.8, 124.2, 122.6, 121.4, 21.5. HRMS (ESI) calcd for $C_{15}H_{12}NaO_2S^+$: 279.0450 ($M+Na^+$), found: 279.0449.



2-(*m*-Tolyl)benzo[*b*]thiophene 1,1-dioxide (**2b**)[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.4 Hz, 1H), 7.65 (d, *J* = 9.4 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.36-7.42 (m, 2H), 7.27-7.29 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0, 137.1, 133.7, 131.2, 129.8, 129.1, 128.1, 127.0, 125.0, 123.7, 123.5, 121.4, 21.4.

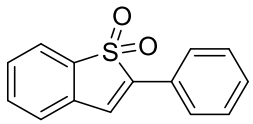


2-(4-(*tert*-Butyl)phenyl)benzo[*b*]thiophene 1,1-dioxide (**2c**)[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.81 (m, 3H), 7.57 (t, *J* = 6.8 Hz, 1H), 7.47-7.53 (m, 3H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.27 (s, 1H), 1.36 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 142.6, 137.0, 133.7, 131.4, 129.6, 126.3, 126.2, 124.9, 124.2, 122.6, 121.4, 34.9, 31.1.

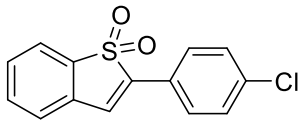


2-(4-Methoxyphenyl)benzo[*b*]thiophene 1,1-dioxide (**2d**)[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.4

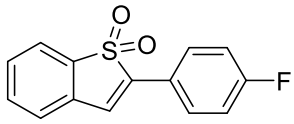
Hz, 1H), 7.36 (d, *J* = 7.4 Hz, 1H), 7.15 (s, 1H), 7.00 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 133.7, 131.5, 130.0, 129.3, 128.1, 124.7, 121.4, 121.3, 119.6, 114.7, 113.7, 55.4.



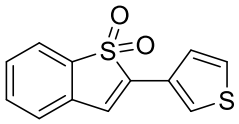
2-Phenylbenzo[*b*]thiophene 1,1-dioxide (**2e**)[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.7 Hz, 2H), 7.78 (d, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.48-7.53 (m, 4H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.30 (s, 1H), ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.0, 133.8, 131.1, 130.3, 129.9, 129.2, 127.1, 126.5, 125.0, 123.7, 121.5.



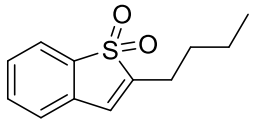
2-(4-Chlorophenyl)benzo[*b*]thiophene 1,1-dioxide (**2f**)[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 3H) 7.58 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 7.3 Hz, 1H), 7.29 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 133.9, 131.5, 130.9, 130.1, 129.5, 128.6, 127.8, 125.6, 125.2, 124.1, 121.5.



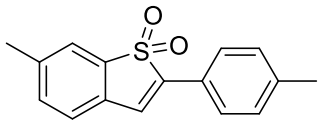
2-(4-Fluorophenyl)benzo[*b*]thiophene 1,1-dioxide (**2g**)[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.86 (m, 2H), 7.78 (d, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.4 Hz, 1H), 7.25 (s, 1H), 7.19 (t, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8 (d, ^1J_F = 251.0 Hz), 141.6, 136.8, 133.8, 131.0, 129.9, 128.7 (d, ^3J_F = 8.4 Hz), 125.0, 123.5, 121.5, 116.5 (d, ^2J_F = 22.0 Hz).



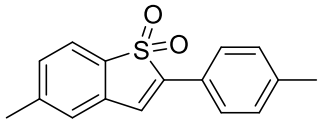
2-(Thiophen-3-yl)benzo[b]thiophene 1,1-dioxide (**2h**)[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.98 (m, 1H), 7.77 (d, *J* = 7.4 Hz, 1H), 7.55-7.59 (m, 1H), 7.38-7.51 (m, 4H), 1.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5, 136.4, 133.8, 131.6, ,129.6, 127.2, 125.4, 125.2, 125.0, 121.9, 121.5.



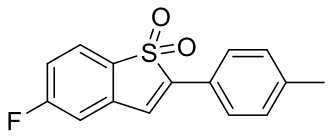
2-Butylbenzo[b]thiophene 1,1-dioxide (**2i**)[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54-7.62 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.7 Hz, 1H), 6.30 (s, 1H), 2.48 (t, *J* = 7.4 Hz, 2H), 1.63-1.70 (m, 2H), 1.37-1.47 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 133.4, 132.5, 127.4, 126.7, 126.4, 125.2, 103.4, 34.2, 28.2, 22.0, 13.8.



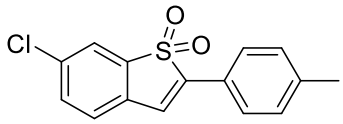
6-Methyl-2-(*p*-tolyl)benzo[b]thiophene 1,1-dioxide (**2j**)[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.58 (s, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.26-7.29 (m, 3H), 7.21 (s, 1H), 2.45 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 140.4, 137.1, 134.2, 129.9, 128.7, 128.5, 126.3, 124.6, 124.4, 122.7, 122.0, 29.7, 21.5.



5-Methyl-2-(*p*-tolyl)benzo[b]thiophene 1,1-dioxide (**2k**)[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.28-7.30 (m, 3H), 7.19 (s, 2H), 2.45 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.6, 140.6, 131.6, 130.1, 129.9, 129.2, 128.8, 126.4, 125.5, 124.4, 122.6, 121.3, 21.7, 21.5.



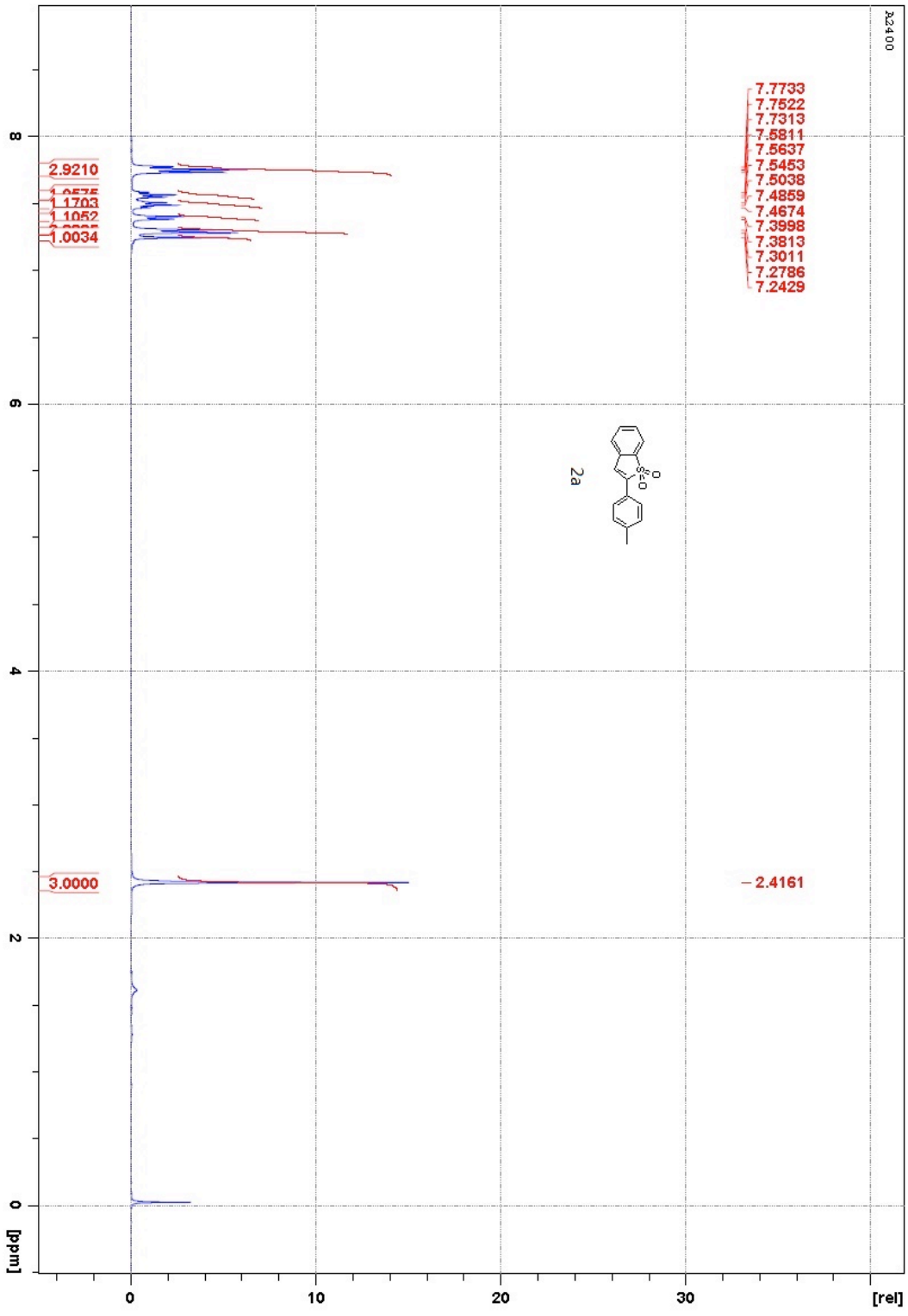
5-Fluoro-2-(*p*-tolyl)benzo[b]thiophene 1,1-dioxide (**2l**)[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.76 (m, 3H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.13-7.18 (m, 2H), 7.07 (d, *J* = 8.1 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8 (d, $^{1}J_F$ = 253.5 Hz), 144.5, 141.3, 134.4 (d, $^{3}J_F$ = 9.9 Hz), 130.0, 126.5, 123.9, 123.5 (d, $^{3}J_F$ = 9.8 Hz), 121.1, 116.2 (d, $^{2}J_F$ = 23.8 Hz), 112.4 (d, $^{2}J_F$ = 24.7 Hz), 21.5.



6-Chloro-2-(*p*-tolyl)benzo[b]thiophene 1,1-dioxide (**2m**)[1]: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 6.3 Hz, 3H), 7.53 (dd, J_1 = 1.9 Hz, J_2 = 8.0 Hz, 1H), 7.28-7.34 (m, 3H) 7.21 (s, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 138.3, 135.9, 133.6, 130.0, 129.7, 126.4, 125.6, 124.0, 122.1, 121.5, 21.5.

References:

(1) Y. Luo, X. Pan, C. Chen, L. Yao and J. Wu, *Chem. Commun.,* 2015, **51**, 180.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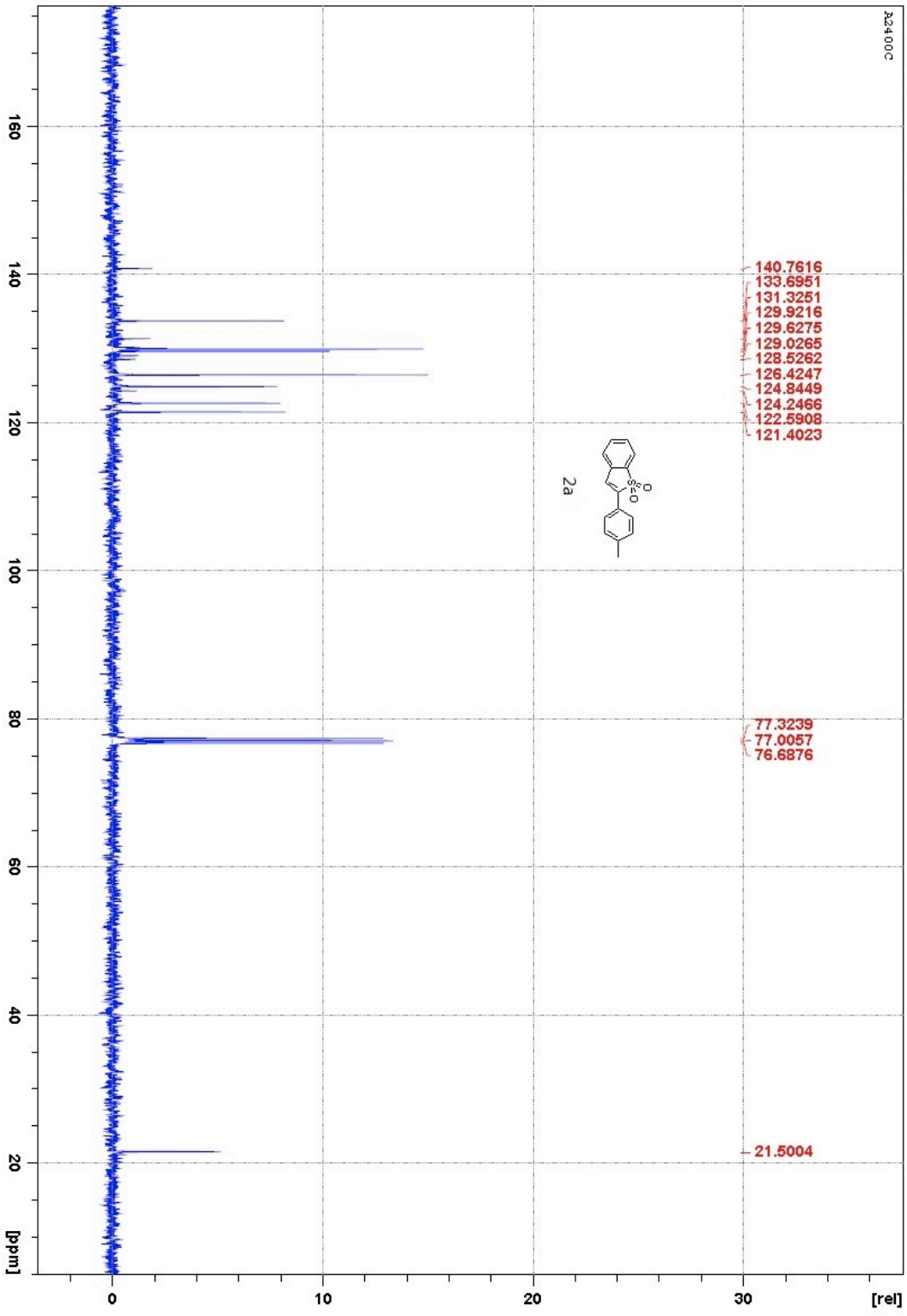
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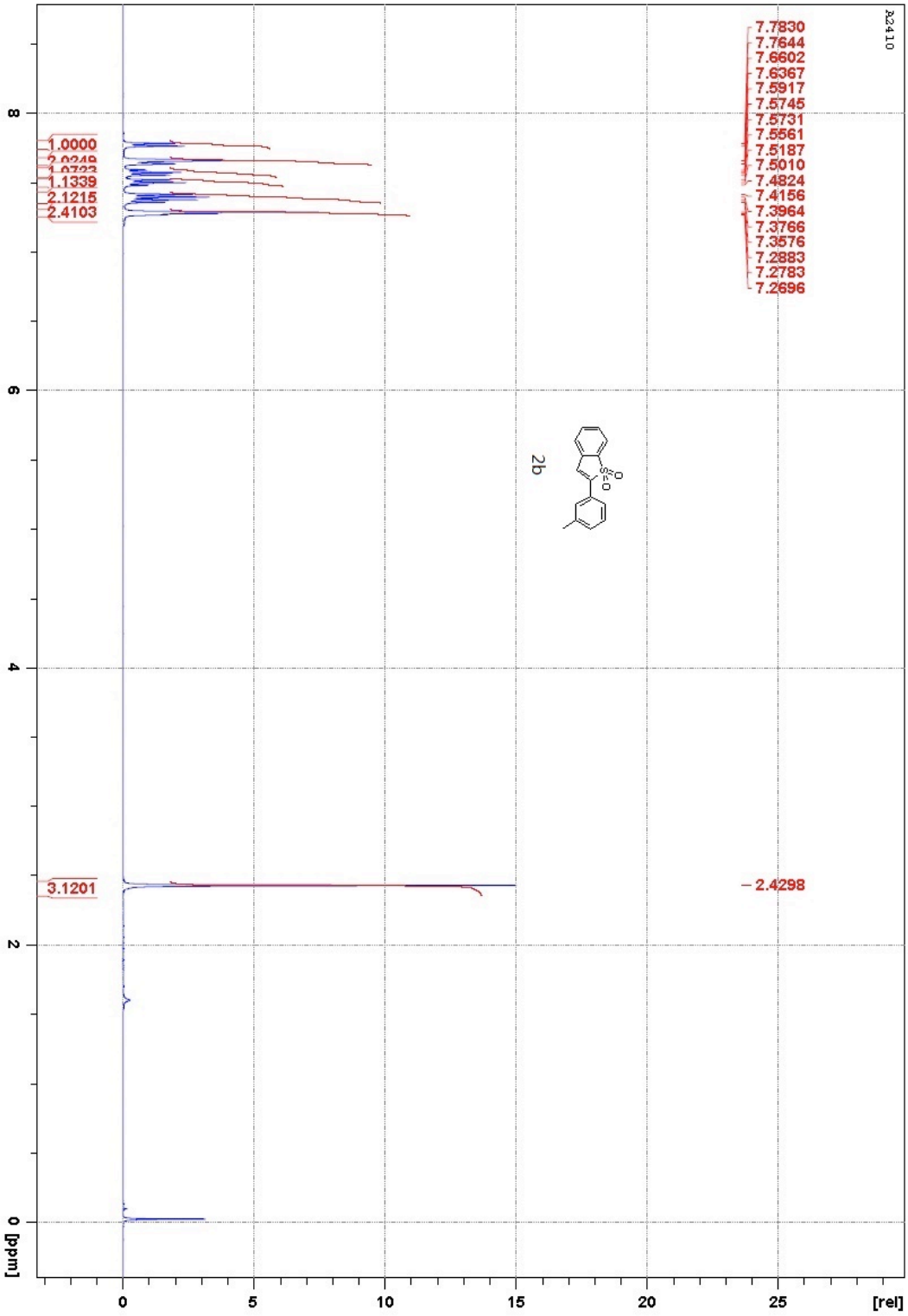
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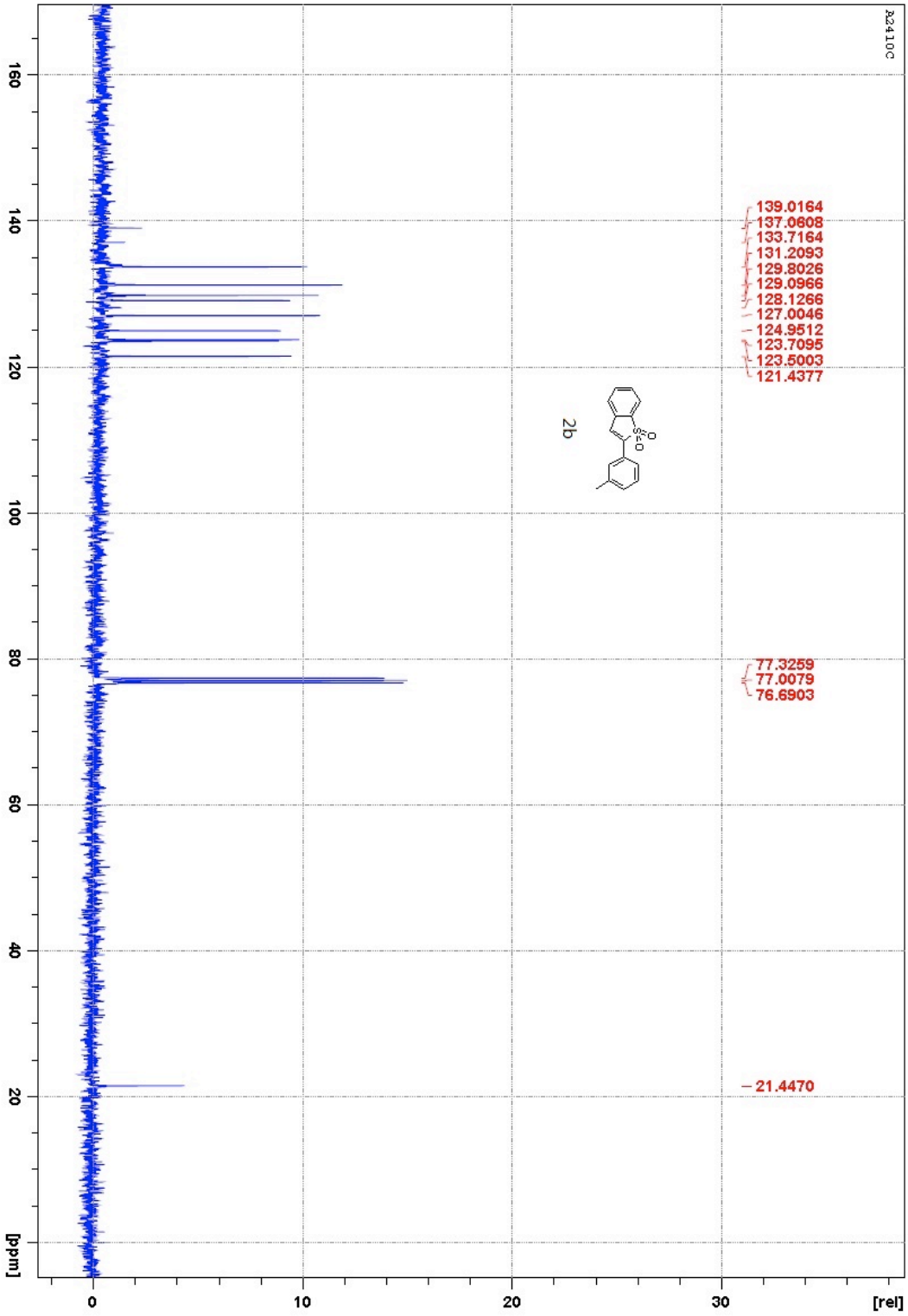
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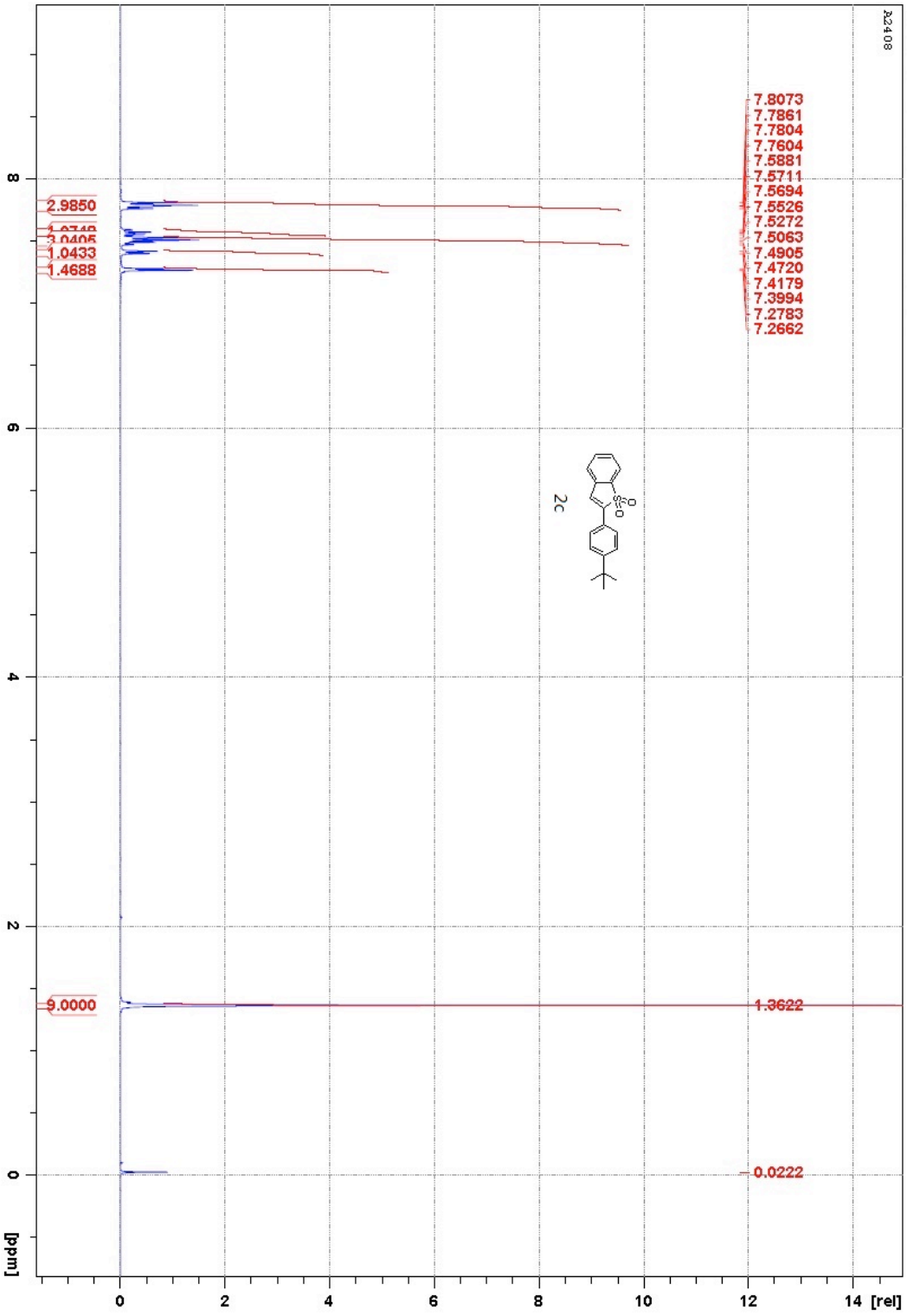
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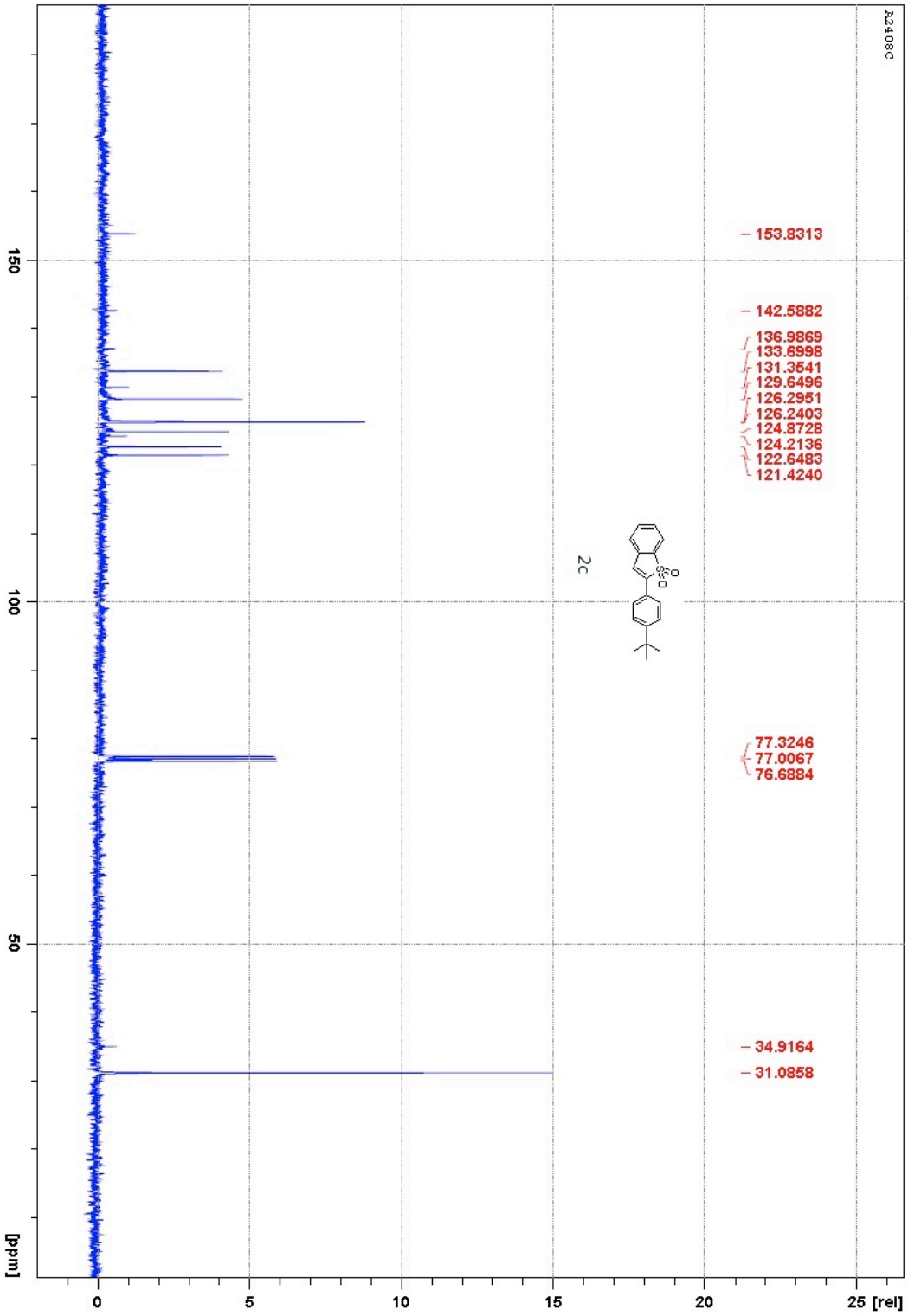
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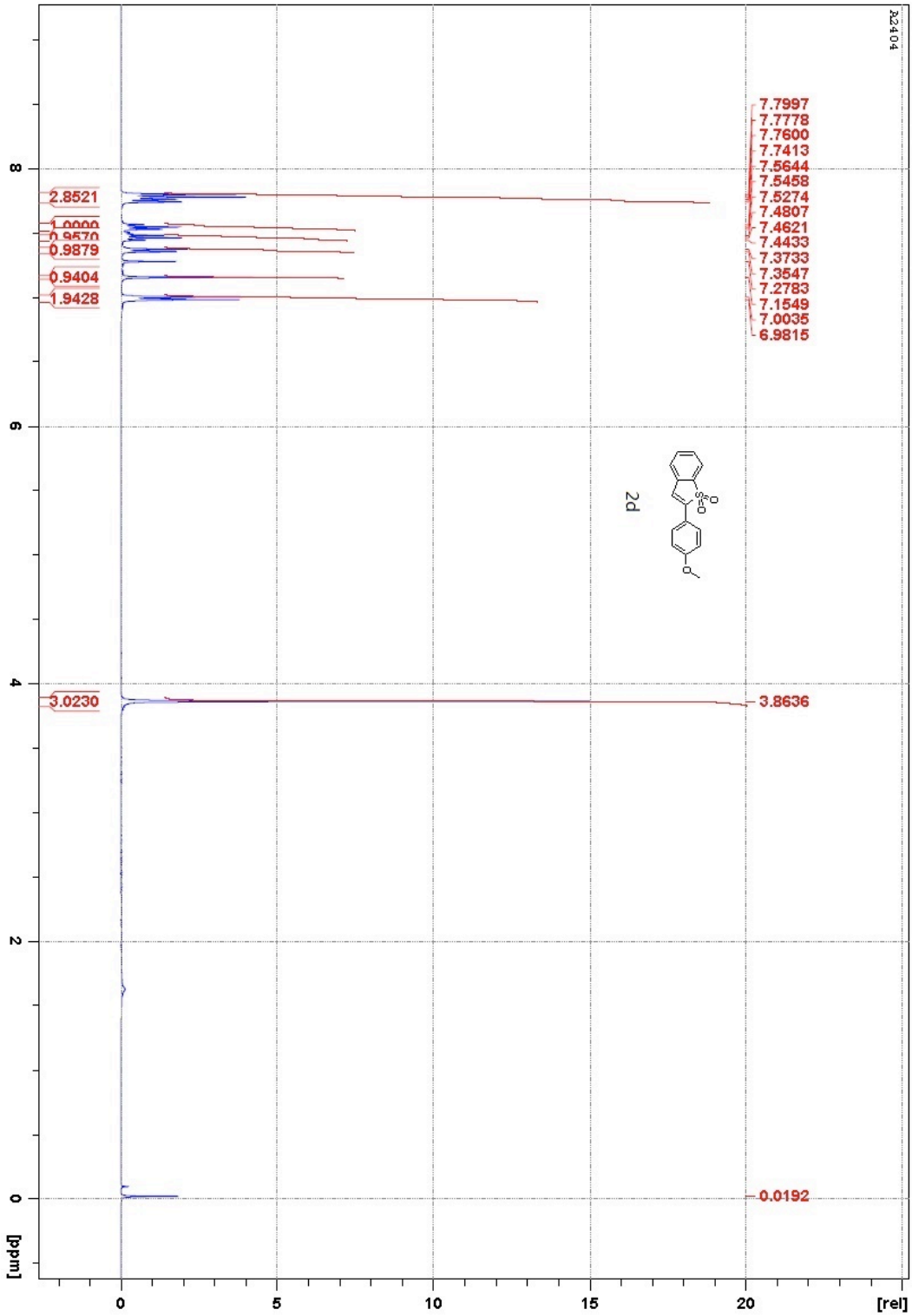
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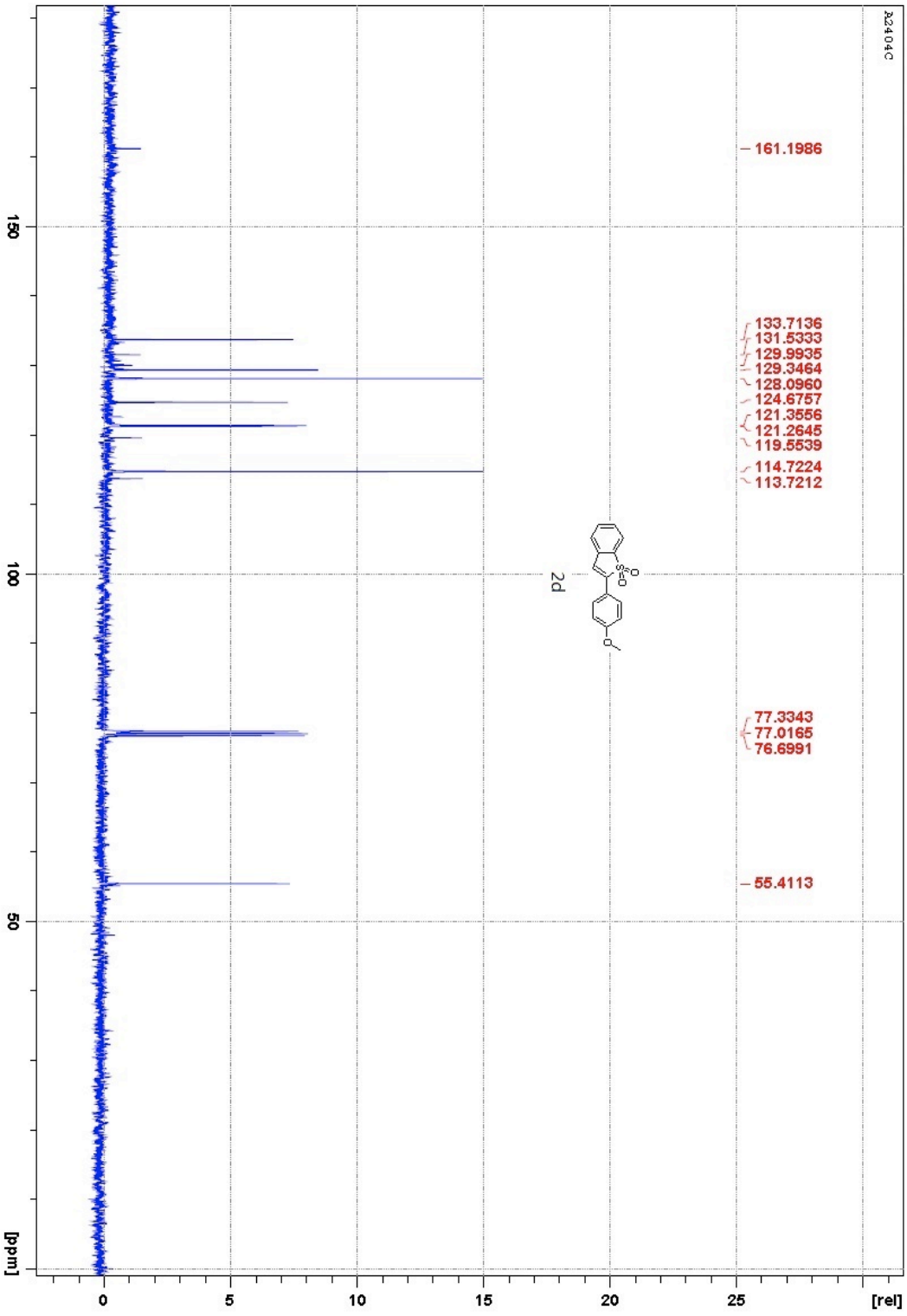
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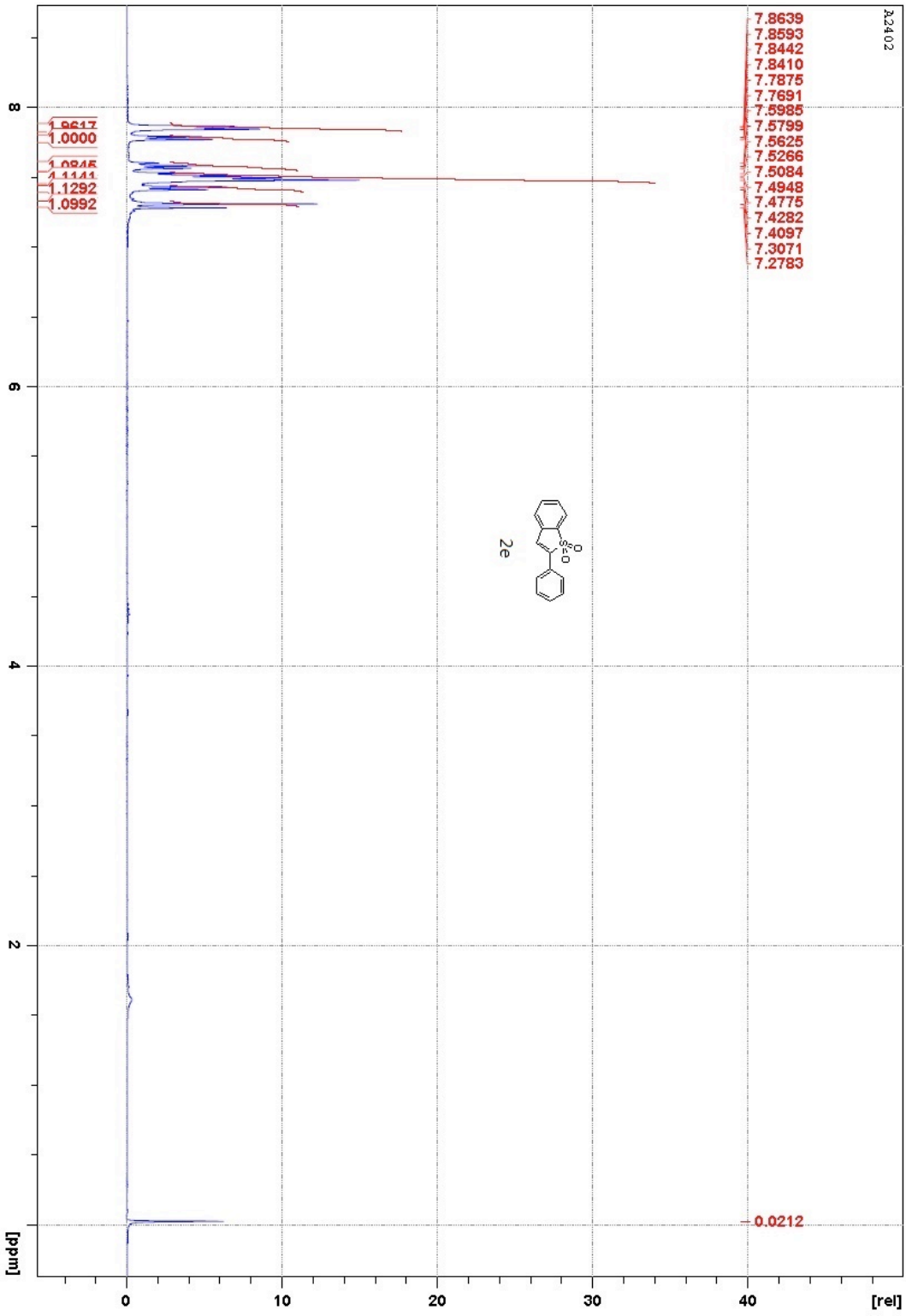
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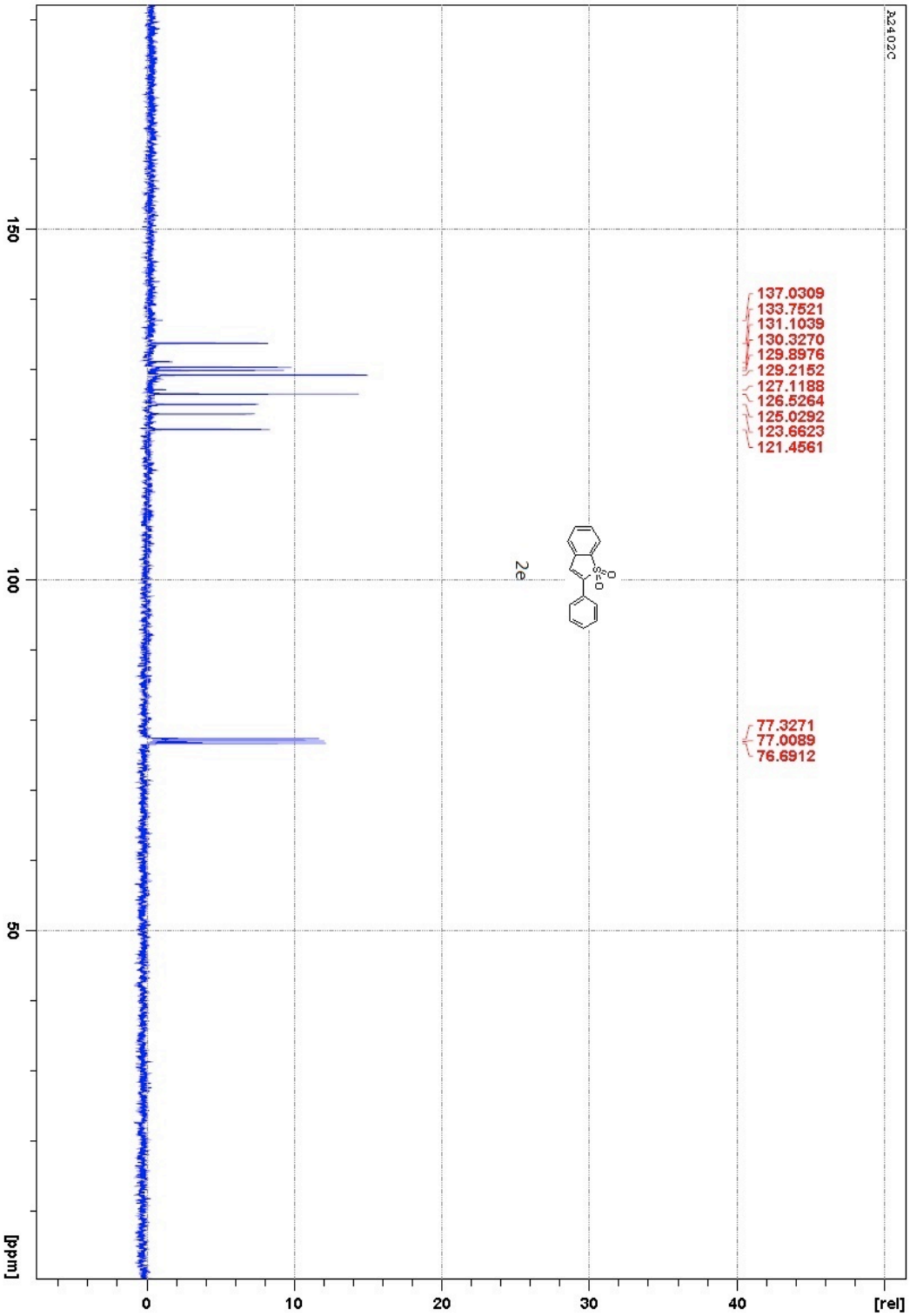
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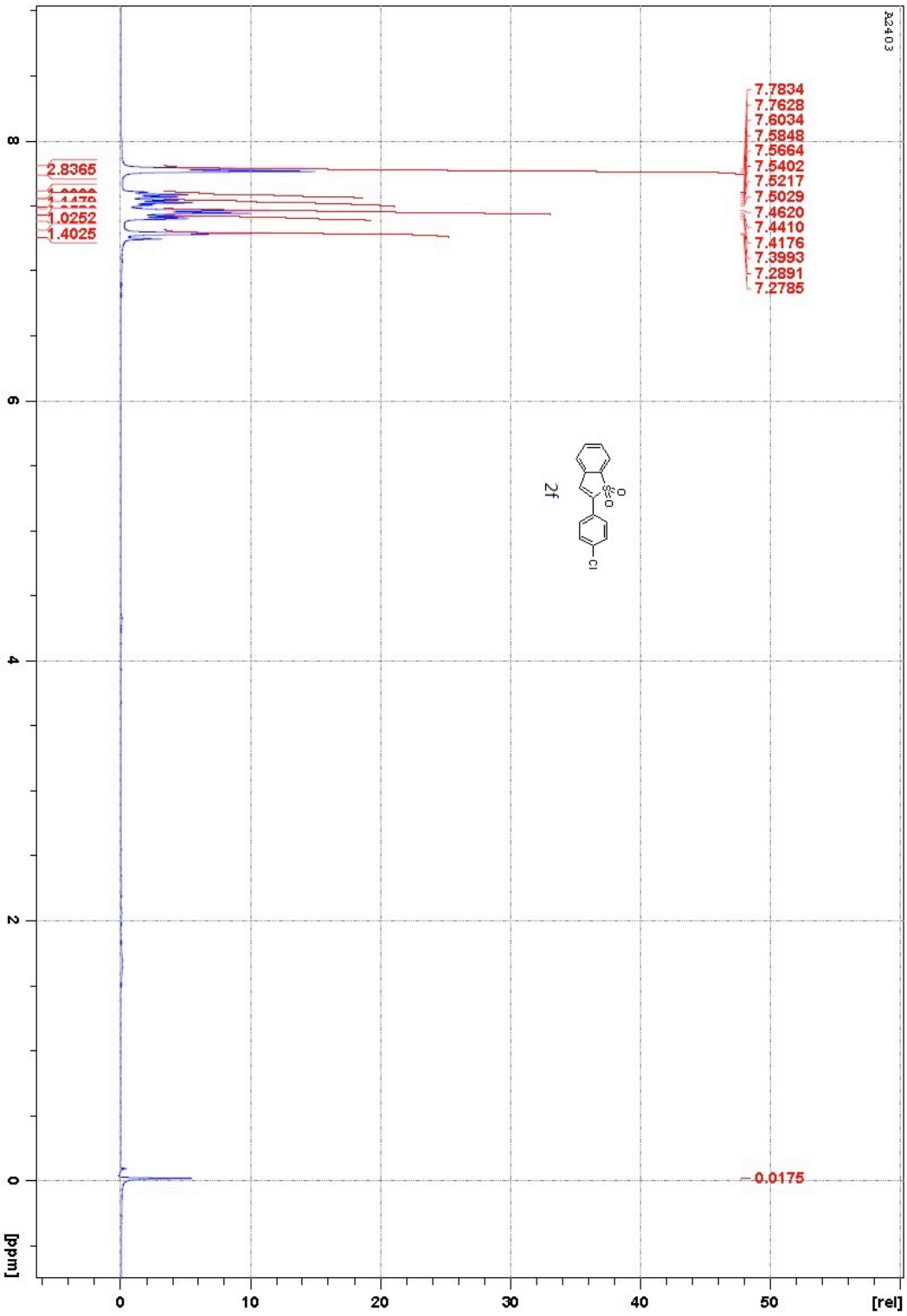
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7.5848
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7.5402
7.5217
7.5029
7.4620
7.4410
7.4176
7.3993
7.2891
7.2785
2.8365
1.0252
1.4025
0.0175
2f
O
S
O
Cl
8
6
4
2
0
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0
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20
30
40
50
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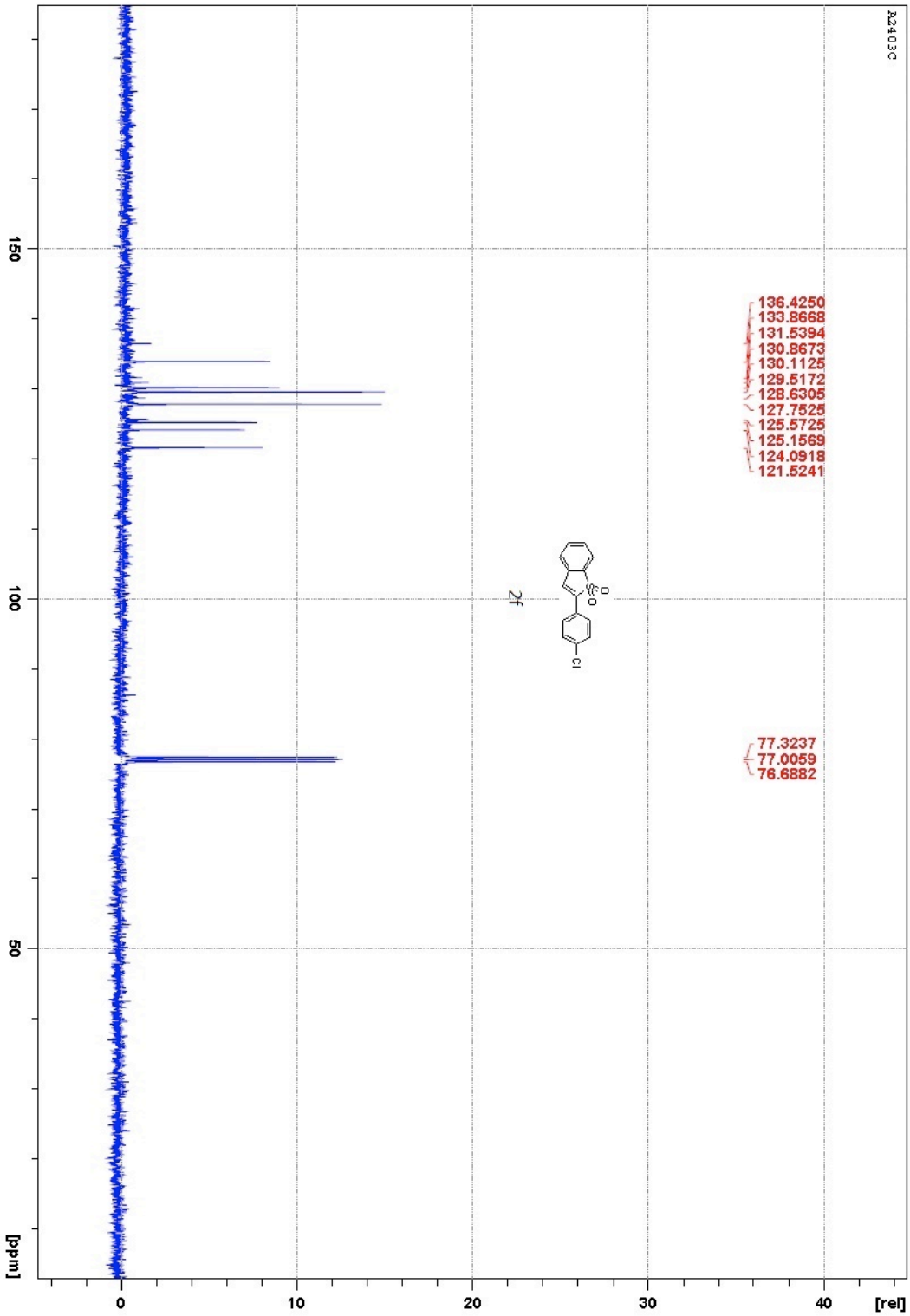
A2403C
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133.8668
131.5394
130.8673
130.1125
129.5172
128.6305
127.7525
125.5725
125.1569
124.0918
121.5241
77.3237
77.0059
76.6882
2f
O
S
O
Cl
150
100
50
[ppm]
0
10
20
30
40
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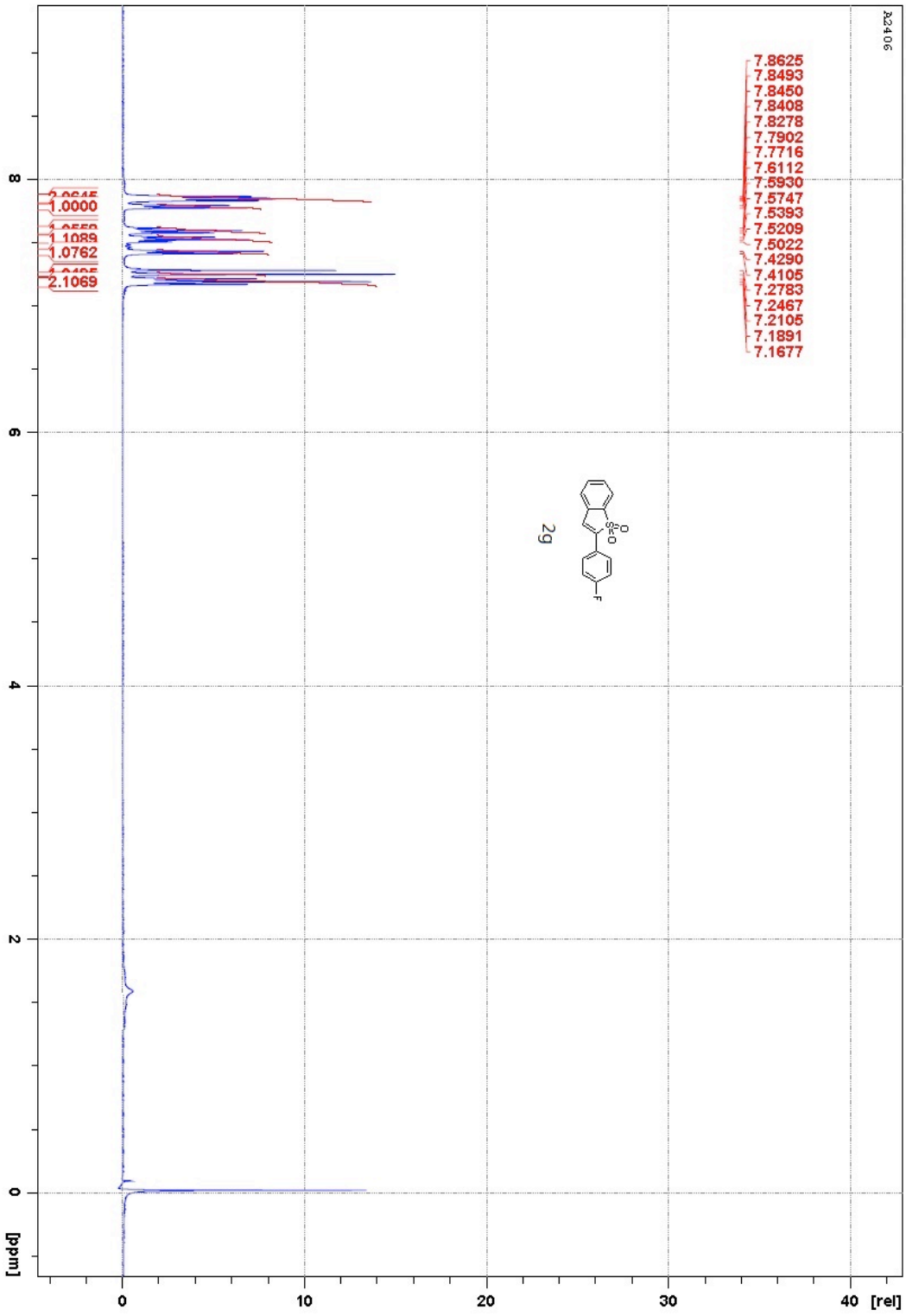
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7.7716
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7.5930
7.5747
7.5393
7.5209
7.5022
7.4290
7.4105
7.2783
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1.0000
1.1089
1.0762
2.1069
2g
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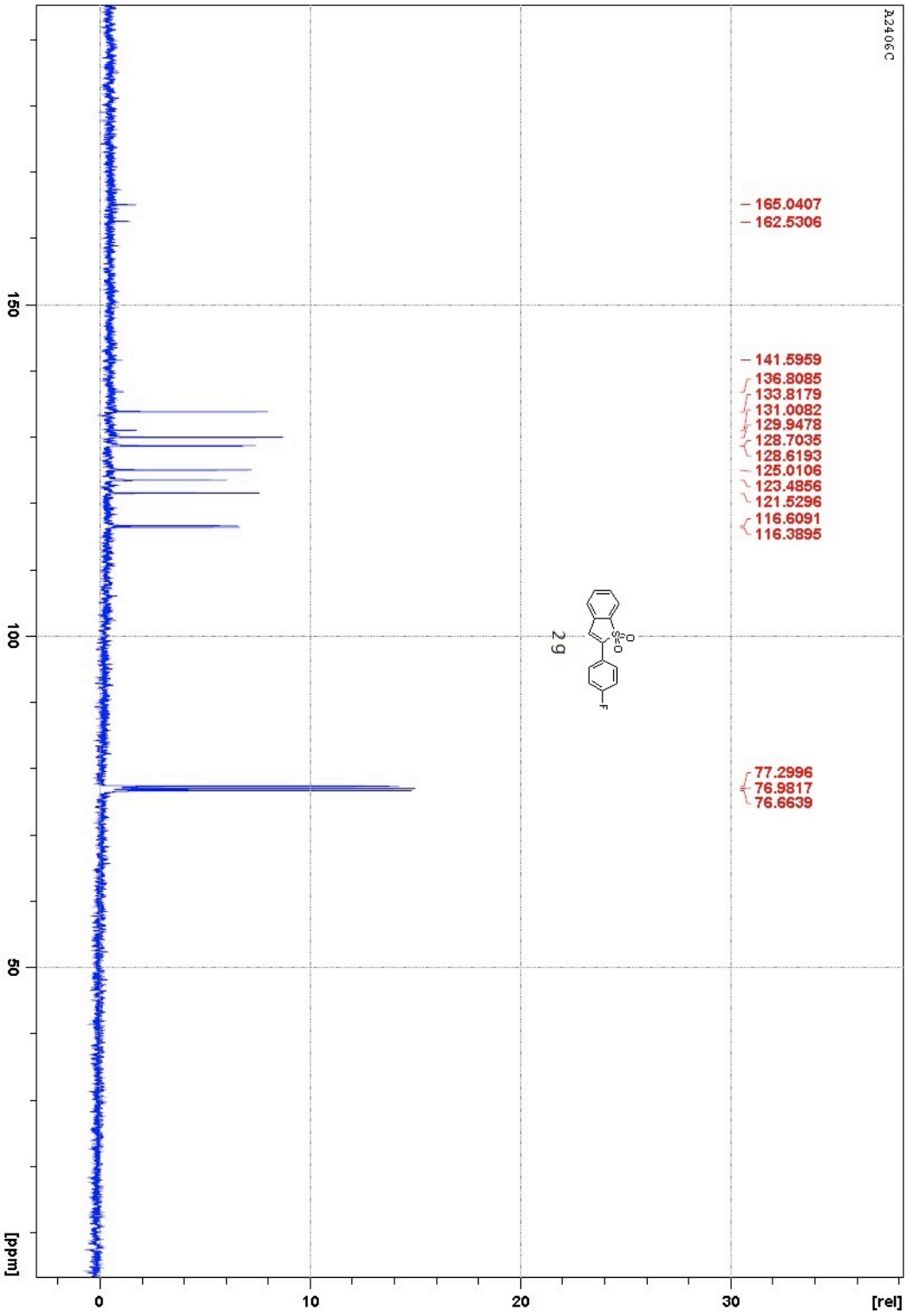
[rel]


A2406C
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162.5306
141.5959
136.8085
133.8179
131.0082
129.9478
128.7035
128.6193
125.0106
123.4856
121.5296
116.6091
116.3895
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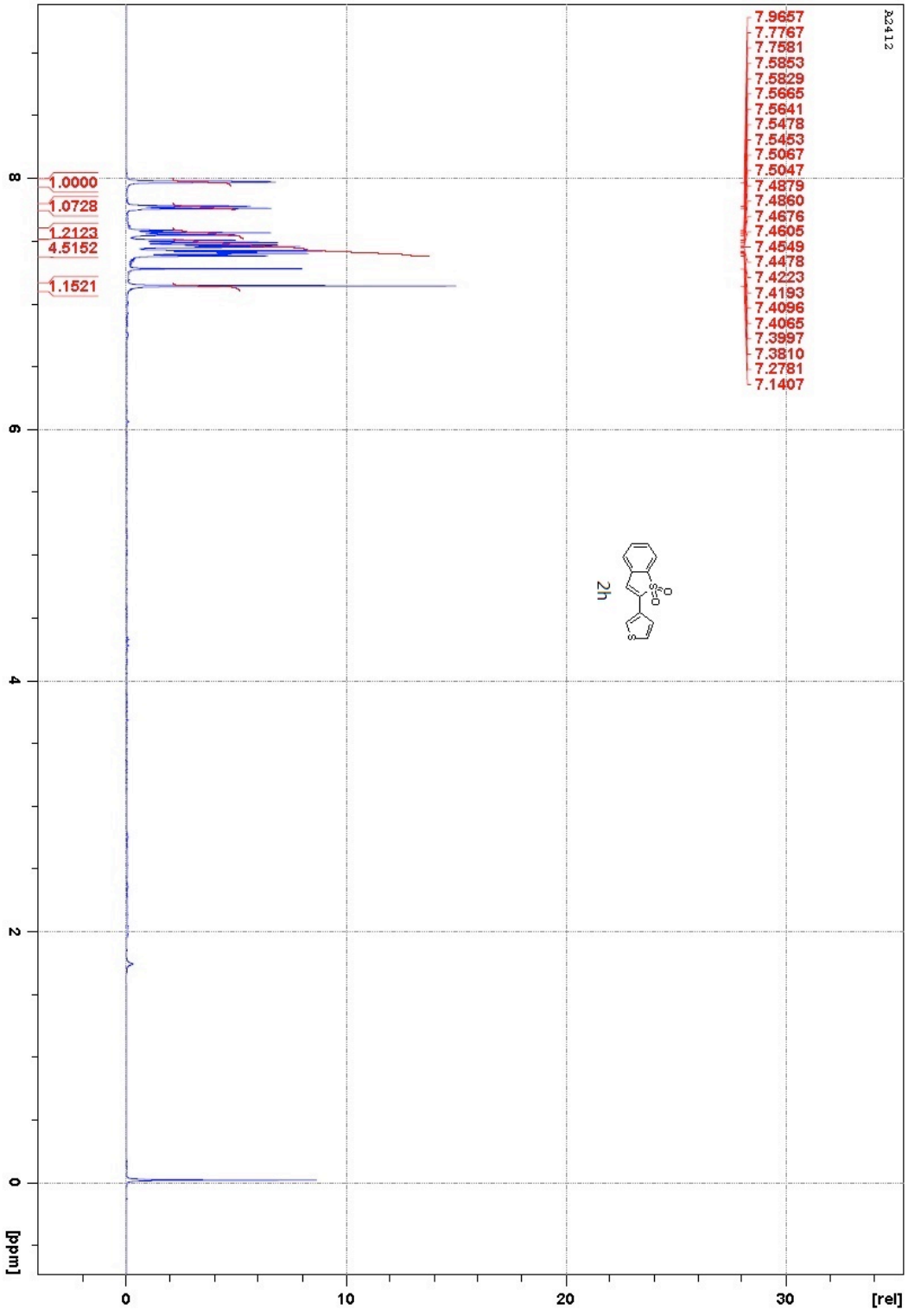
76.9817
76.6639
2g
150
100
50
[ppm]
0
10
20
30
[rel]


7.9657
7.7767
7.7581
7.5853
7.5829
7.5665
7.5641
7.5478
7.5453
7.5067
7.5047
7.4879
7.4860
7.4676
7.4605
7.4549
7.4478
7.4223
7.4193
7.4096
7.4065
7.3997
7.3810
7.2781
7.1407
1.0000
1.0728
1.2123
4.5152
1.1521
2h
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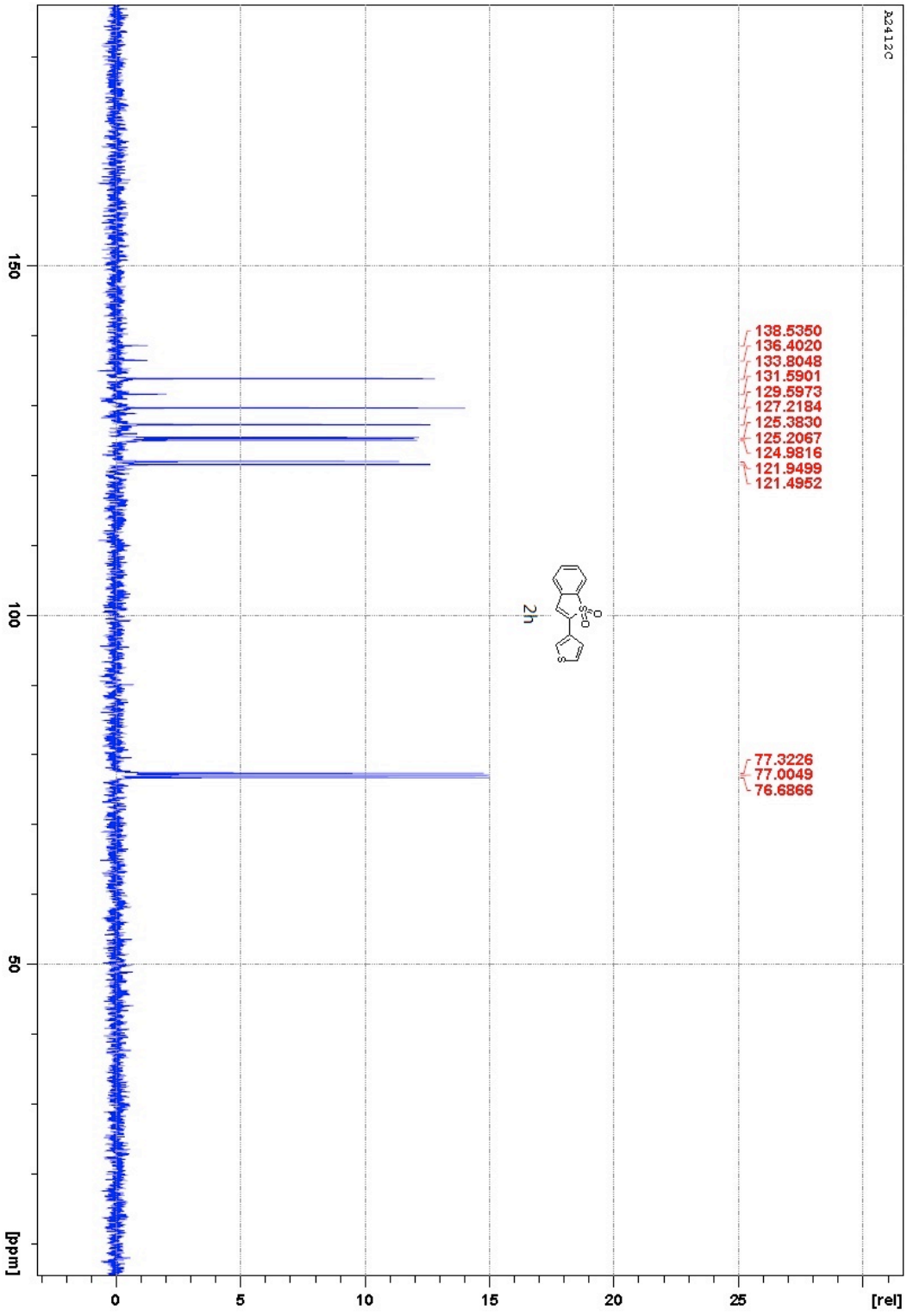
[rel]


A2412C
138.5350
136.4020
133.8048
131.5901
129.5973
127.2184
125.3830
125.2067
124.9816
121.9499
121.4952
77.3226
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76.6866
2h
150
100
50
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10
15
20
25
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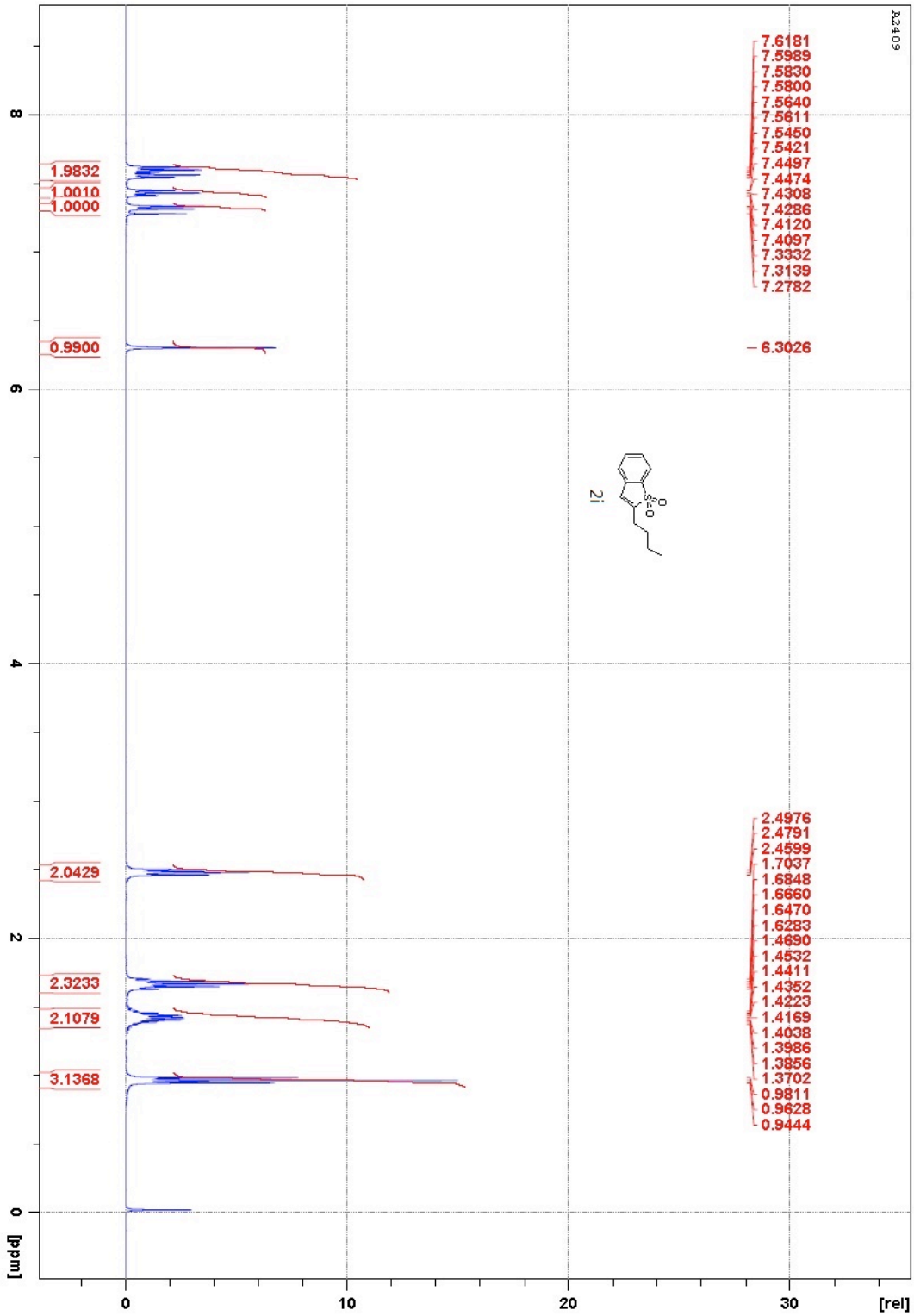
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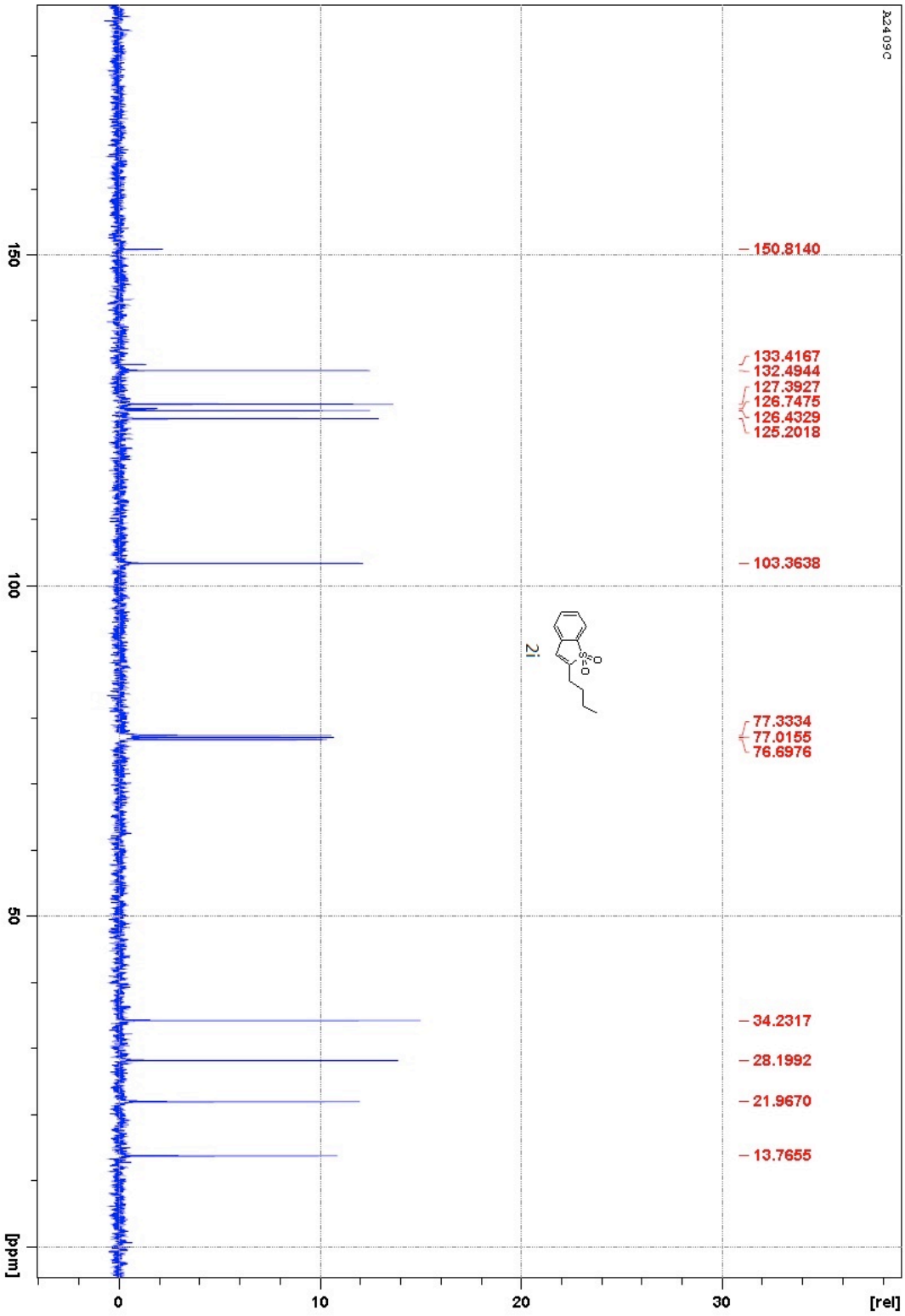
7.5989
7.5830
7.5800
7.5640
7.5611
7.5450
7.5421
7.4497
7.4474
7.4308
7.4286
7.4120
7.4097
7.3332
7.3139
7.2782
6.3026
1.9832
1.0010
1.0000
0.9900
2.0429
2.3233
2.1079
3.1368
2.4976
2.4791
2.4599
1.7037
1.6848
1.6660
1.6470
1.6283
1.4690
1.4532
1.4411
1.4352
1.4223
1.4169
1.4038
1.3986
1.3856
1.3702
0.9811
0.9628
0.9444
2i
[ppm]
[rel]


A24090
150.8140
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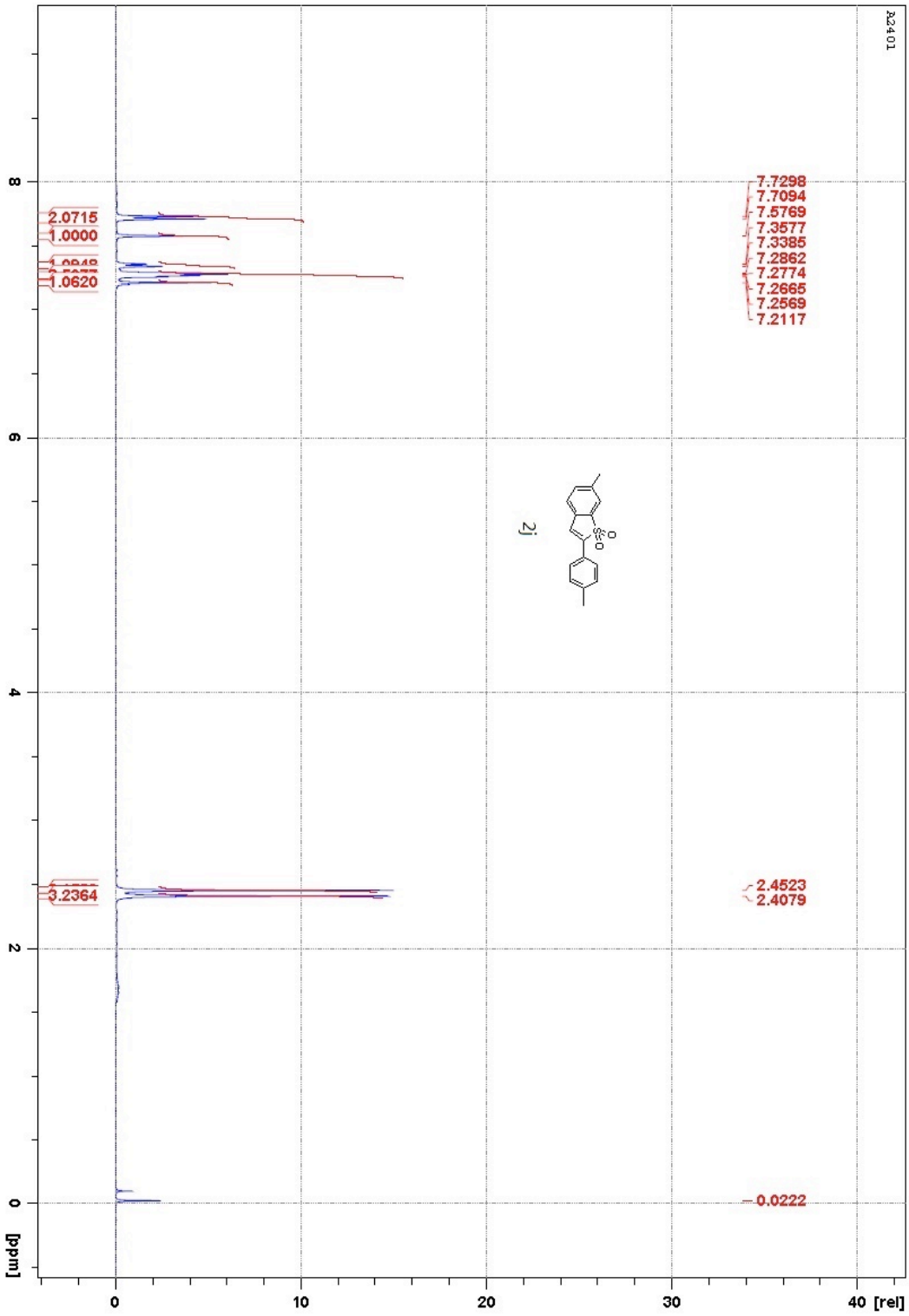
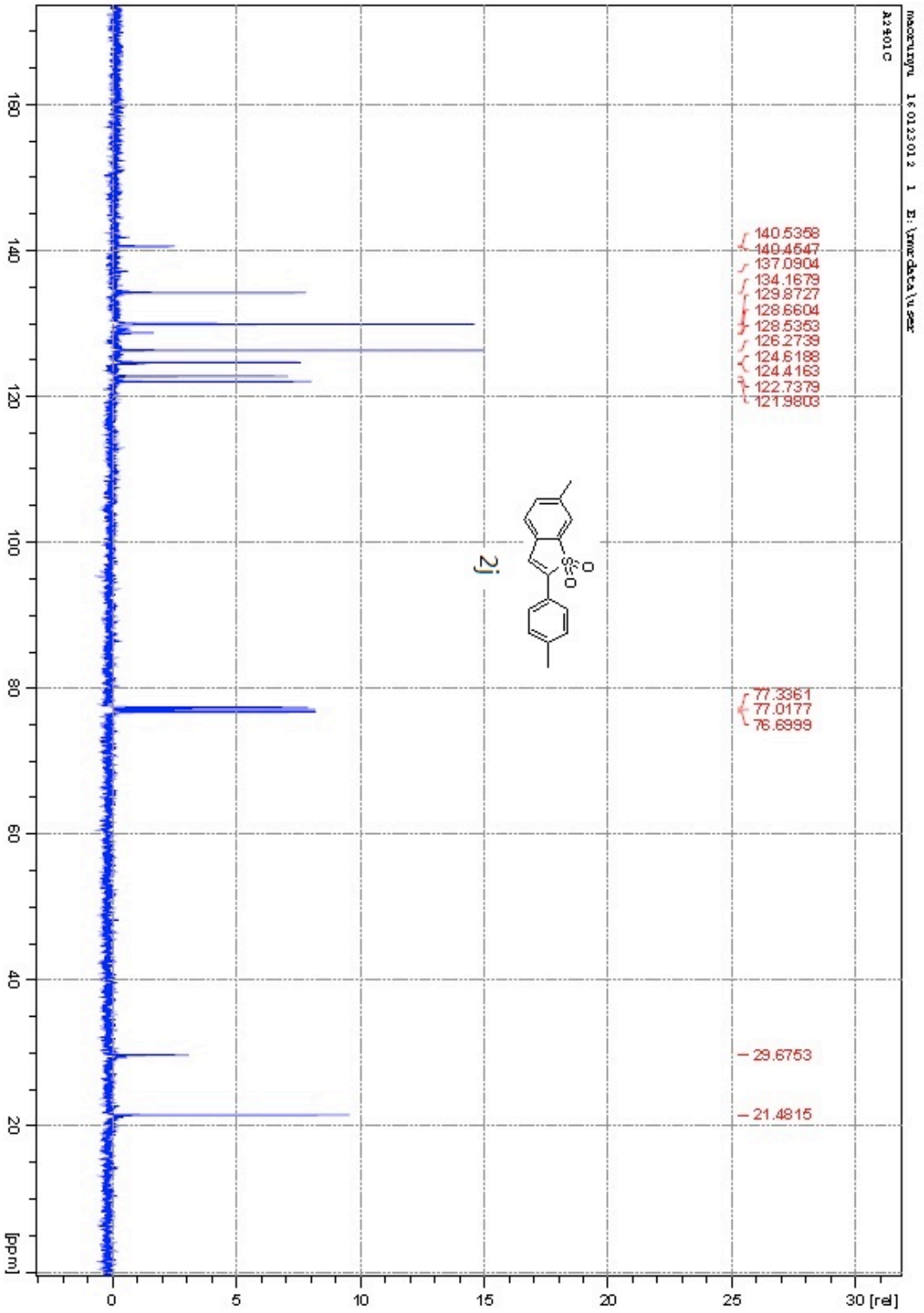
132.4944
127.3927
126.7475
126.4329
125.2018
103.3638
77.3334
77.0155
76.6976
34.2317
28.1992
21.9670
13.7655
2i
150
100
50
[ppm]
0
10
20
30
[rel]


A2401
7.7298
7.7094
7.5769
7.3577
7.3385
7.2862
7.2774
7.2665
7.2569
7.2117
2.0715
1.0000
1.0620
3.2364
2.4523
2.4079
0.0222
2j
O
O
S
8
6
4
2
0
[ppm]
0
10
20
30
40 [rel]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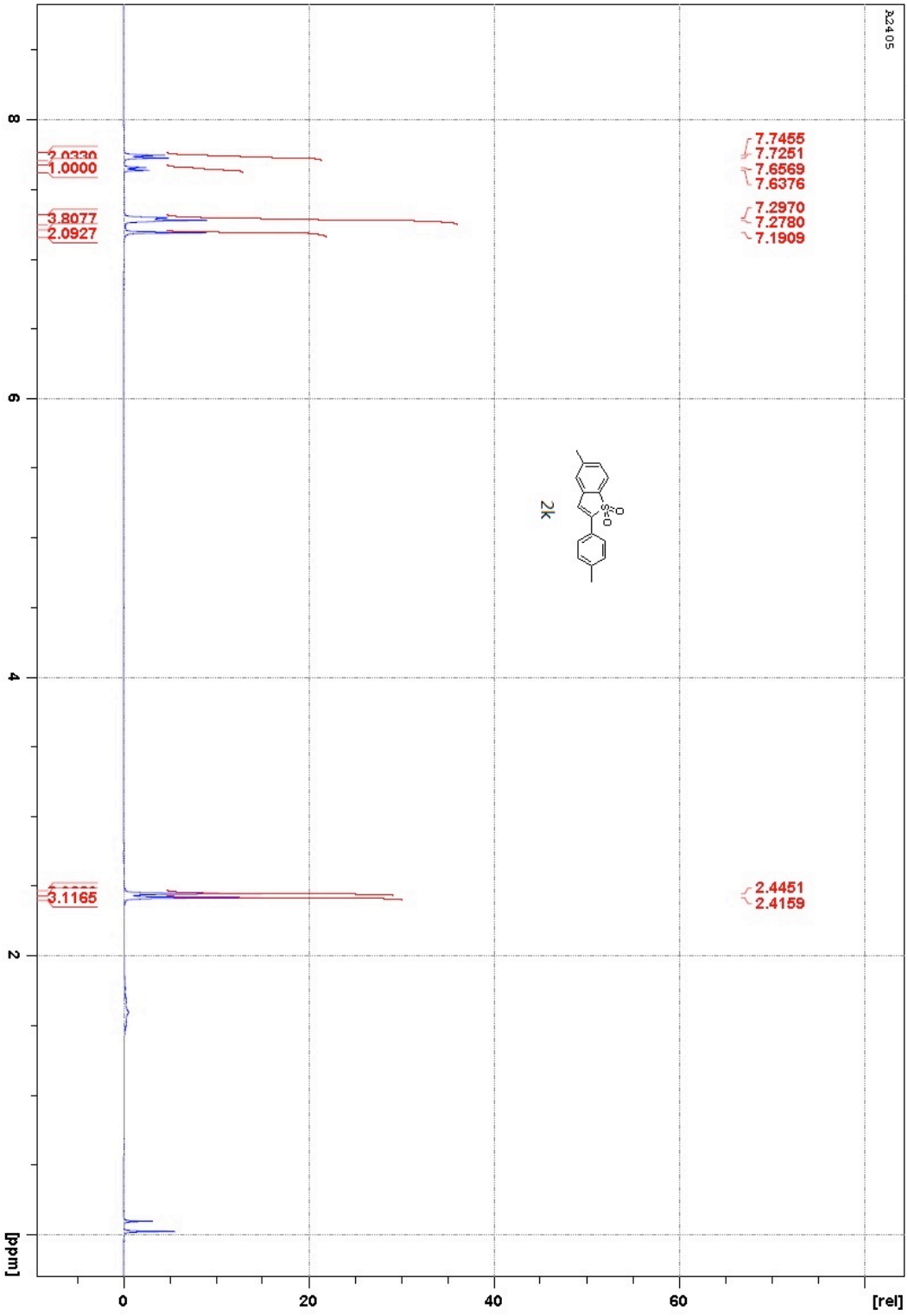
140.4647
137.0904
134.1679
129.8727
128.6604
128.5363
126.2739
124.6188
124.4163
122.7379
121.9803
77.3361
77.0177
76.6999
29.6753
21.4815
2j
[ppm]
0
5
10
15
20
25
30 [rel]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4
2
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20
40
60
[rel]
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1.0000
3.8077
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3.1165
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7.6569
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7.2970
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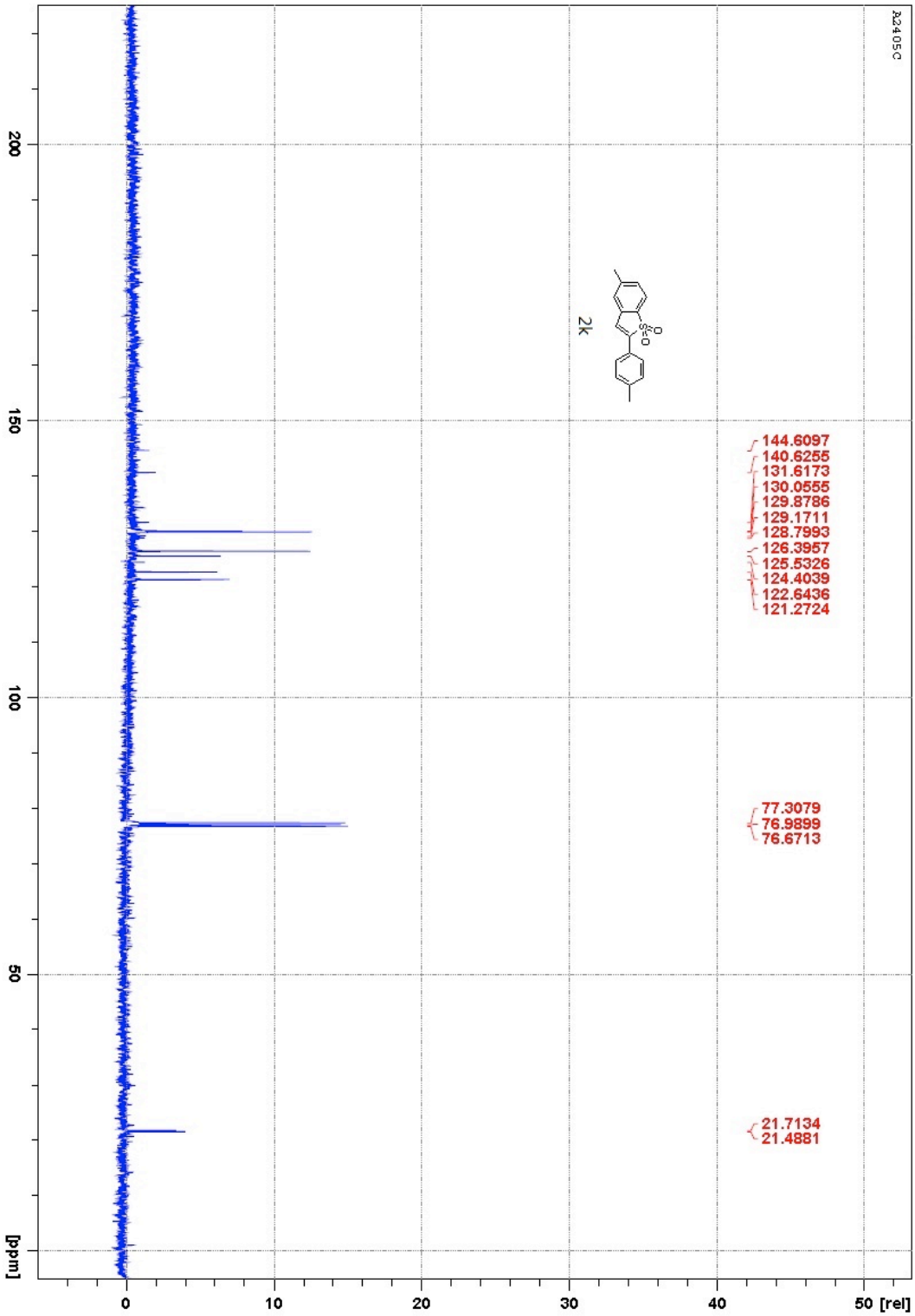
7.1909
2.4451
2.4159
2k


A2405C
2k
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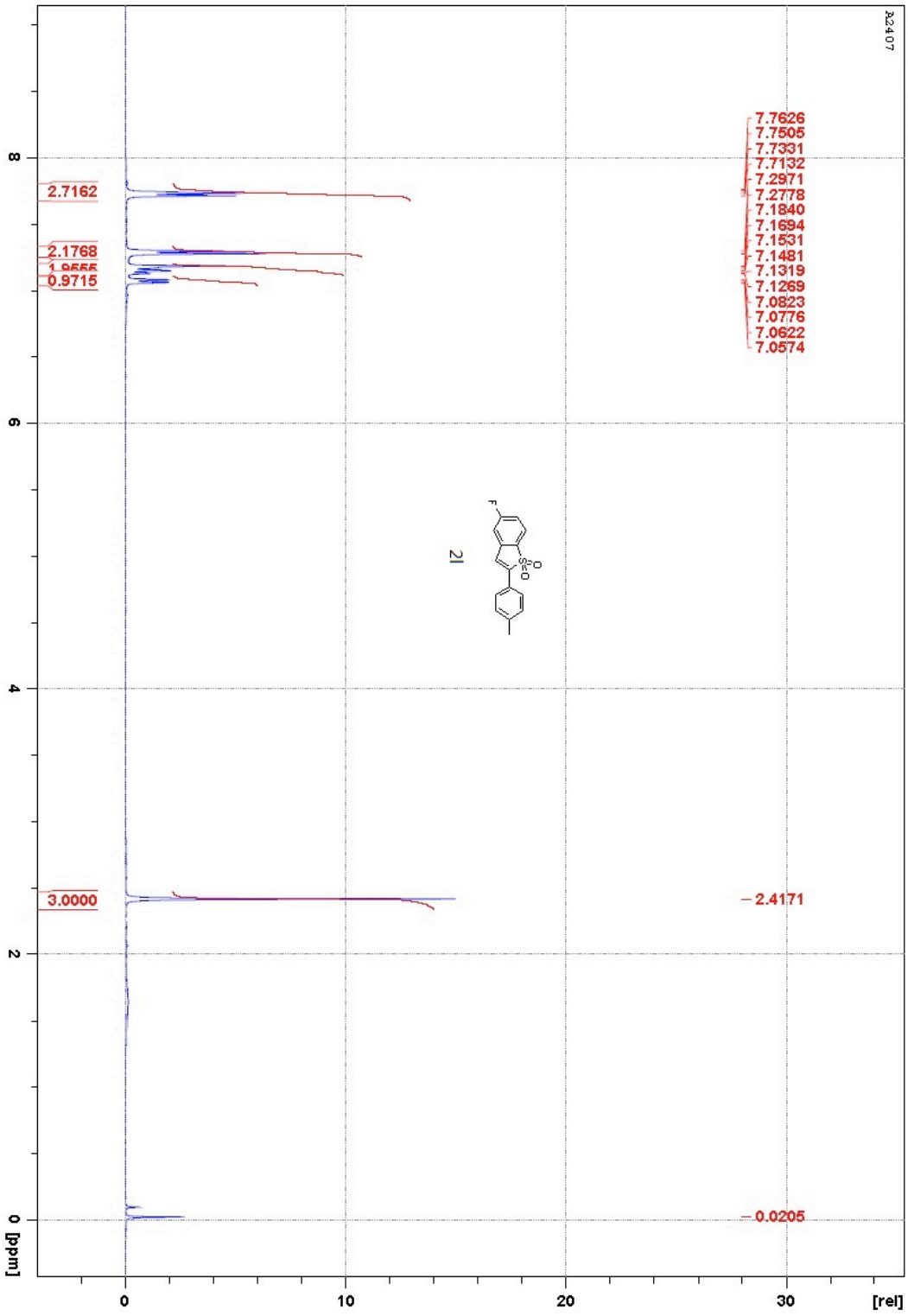
130.0555
129.8786
129.1711
128.7993
126.3957
125.5326
124.4039
122.6436
121.2724
77.3079
76.9899
76.6713
21.7134
21.4881
200
150
100
50
[ppm]
0
10
20
30
40
50 [rel]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7.7331
7.7132
7.2971
7.2778
7.1840
7.1694
7.1531
7.1481
7.1319
7.1269
7.0823
7.0776
7.0622
7.0574
2.4171
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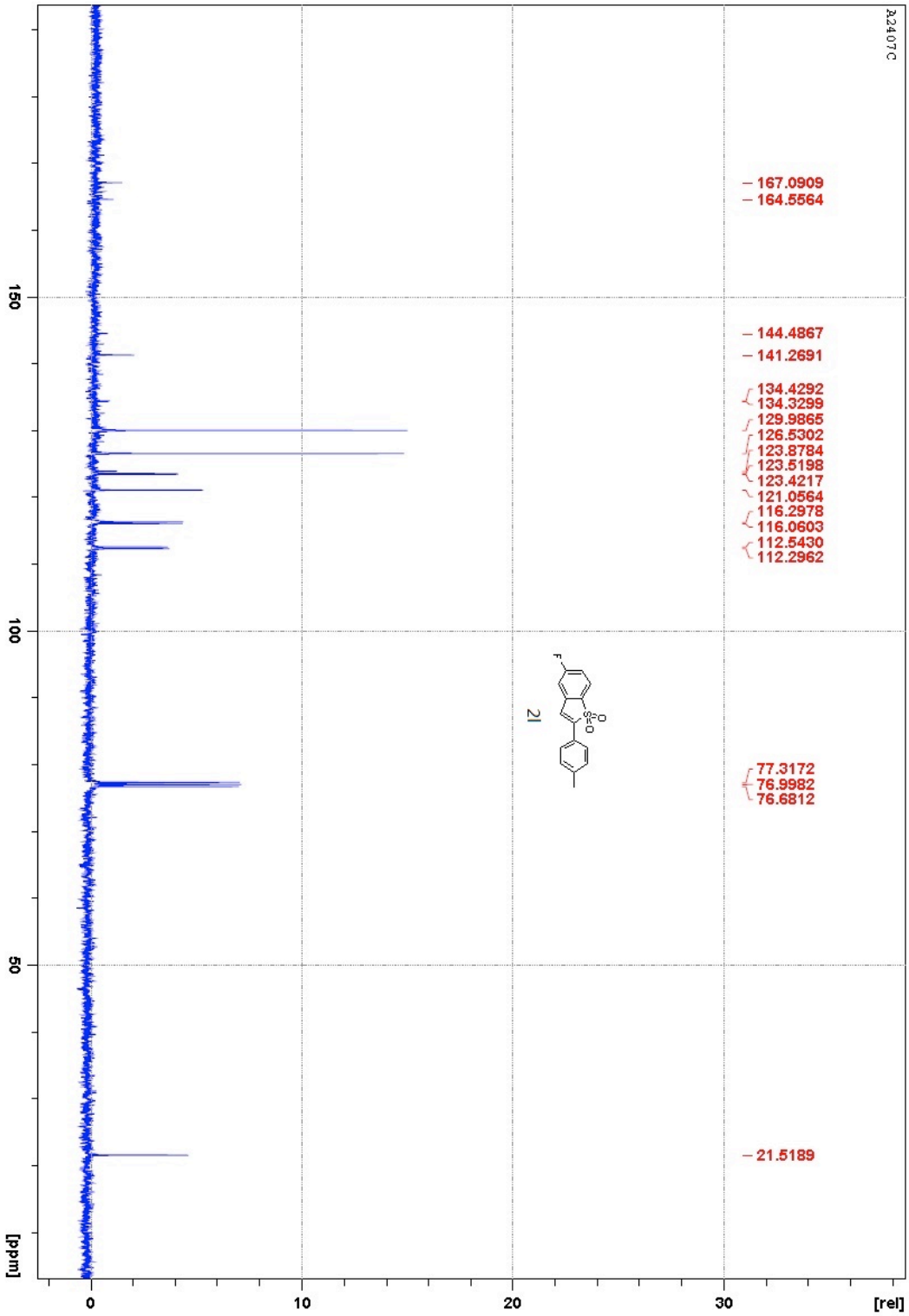
21
[ppm]
[rel]


2.2407C
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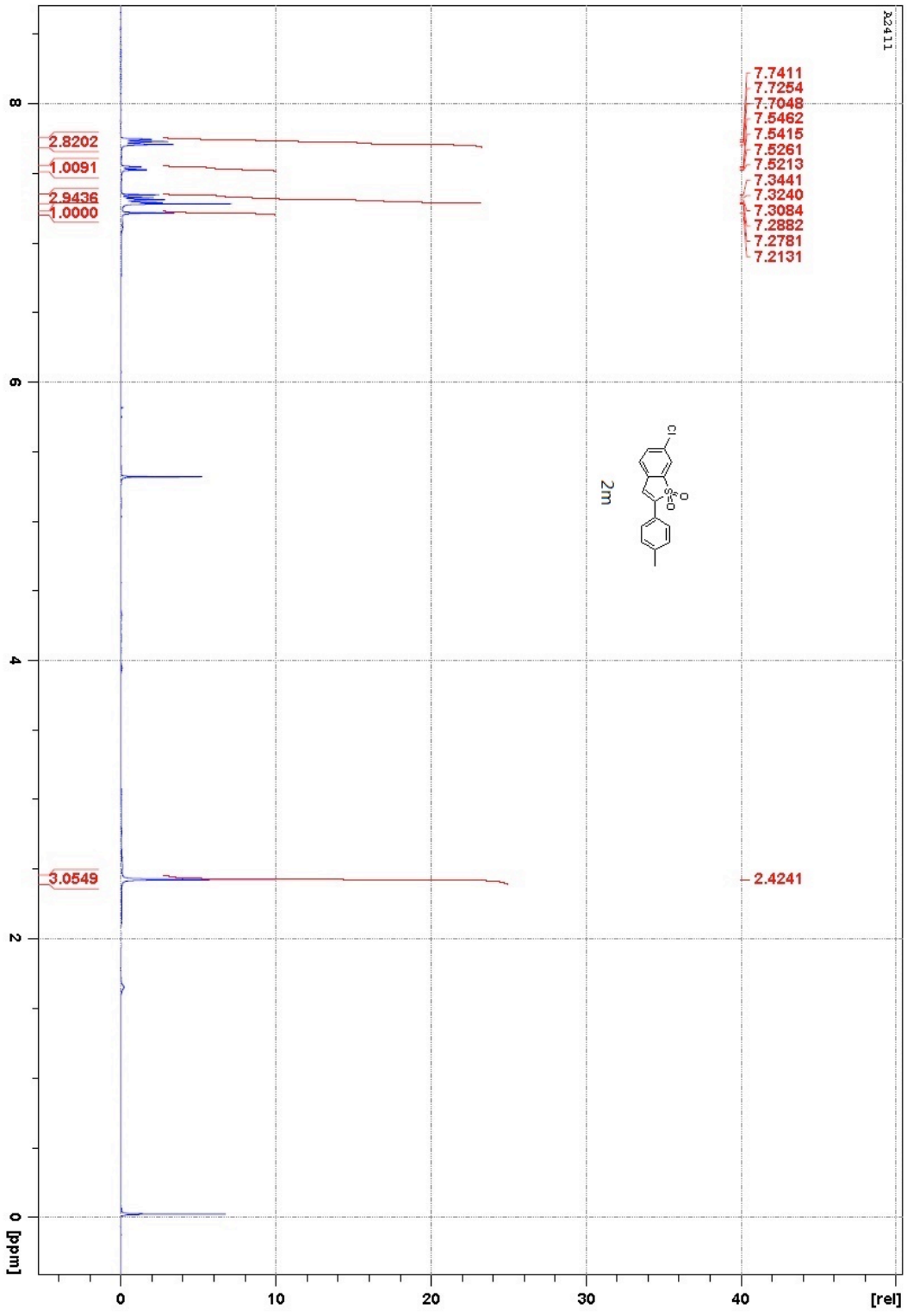
164.5564
144.4867
141.2691
134.4292
134.3299
129.9865
126.5302
123.8784
123.5198
123.4217
121.0564
116.2978
116.0603
112.5430
112.2962
77.3172
76.9982
76.6812
21.5189
2l
F
O
S
O
150
100
50
[ppm]
0
10
20
30
[rel]


2411
7.7411
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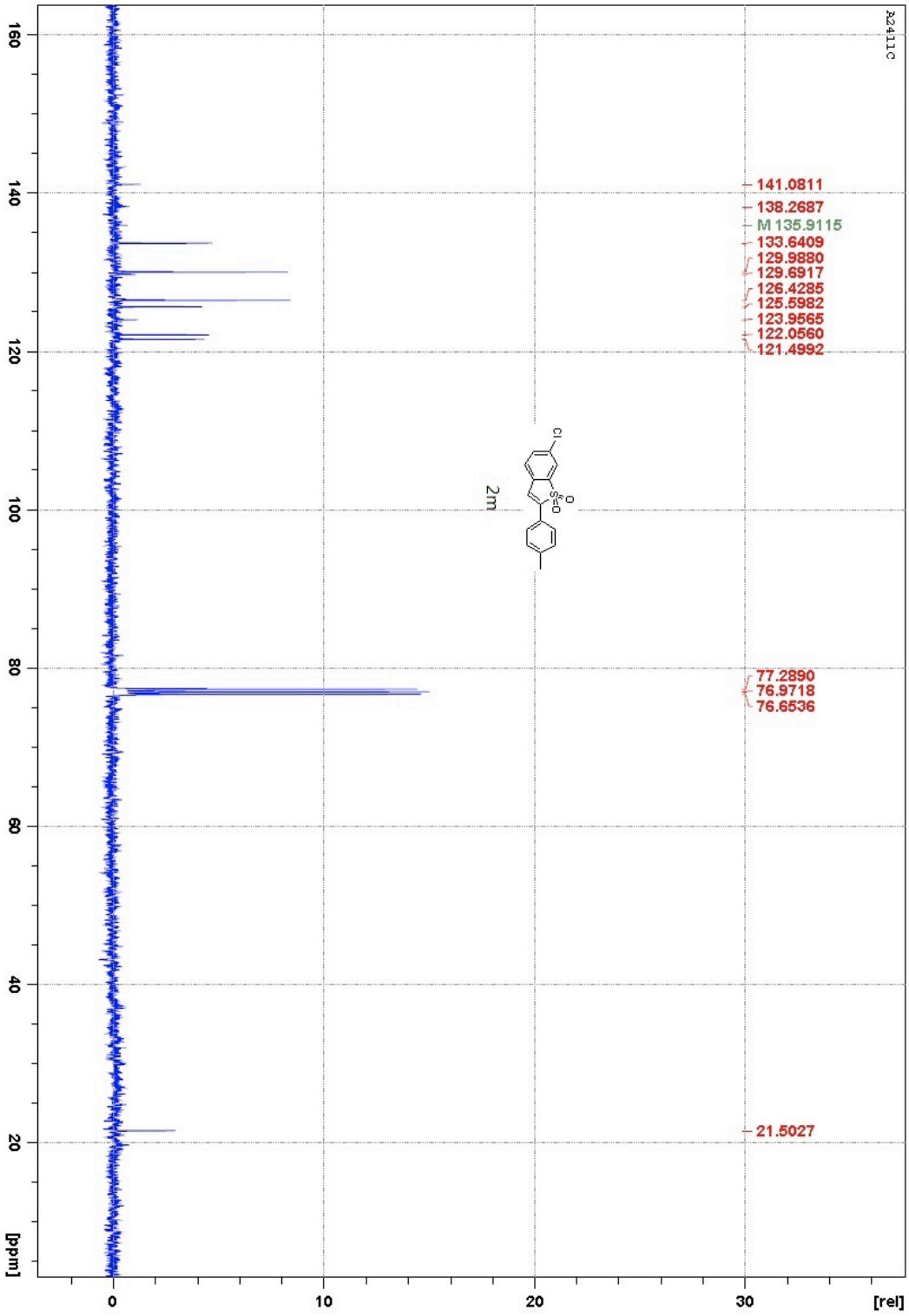
7.7048
7.5462
7.5415
7.5261
7.5213
7.3441
7.3240
7.3084
7.2882
7.2781
7.2131
2.8202
1.0091
2.9436
1.0000
3.0549
2.4241
2m
Cl
O
S
O
8
6
4
2
0 [ppm]
0
10
20
30
40
[rel]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138.2687
M 135.9115
133.6409
129.9880
129.6917
126.4285
125.5982
123.9565
122.0560
121.4992
77.2890
76.9718
76.6536
21.5027
2m
Cl
S
O
O
160
140
120
100
80
60
40
20
[ppm]
0
10
20
30
[rel]