Supporting Information

Reversible Triplet Excitation Transfer in a Trimethylene – Linked Thioxanthone and Benzothiophene-2-carboxanilide that Photochemically Expels Leaving Group Anions.

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Absorption Spectra.

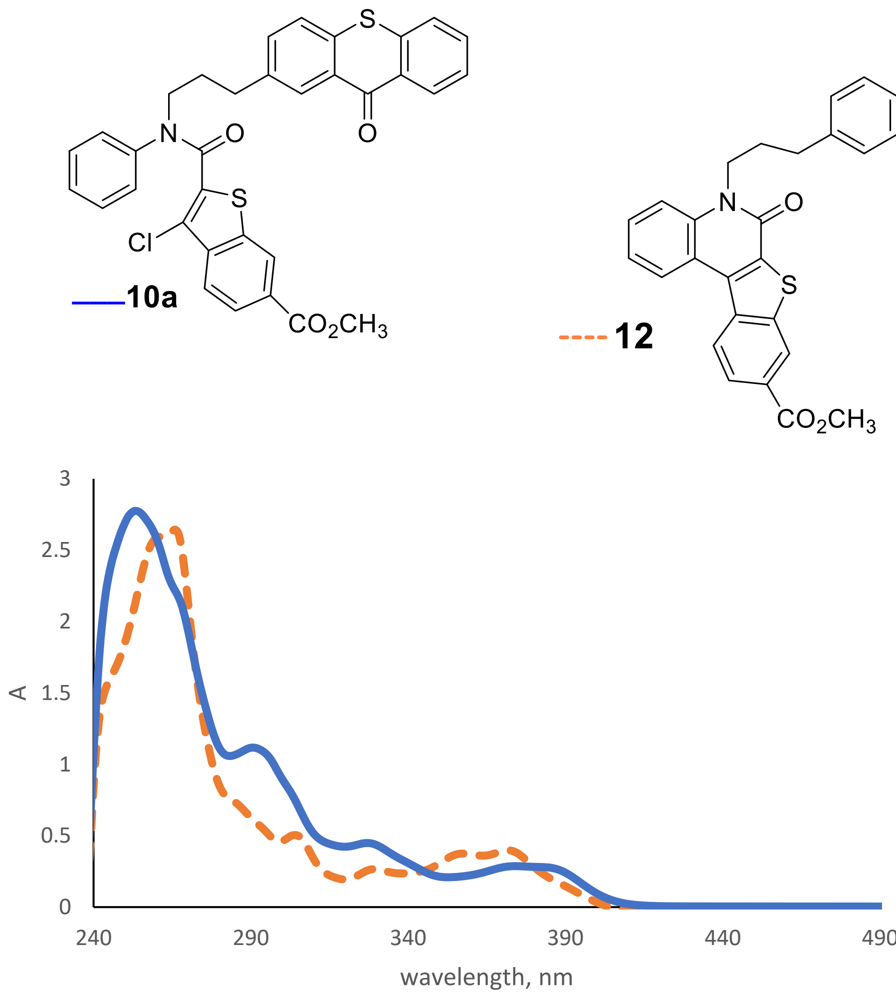


Figure S1. Absorption spectra of reactant **10a** (—) and photoproduct **12** (- - - -). Concentrations were 3.21 x 10^{-5} M and 3.85 x 10^{-5} M, respectively in 20% water and 80% dioxane containing 10 mM phosphate buffer.

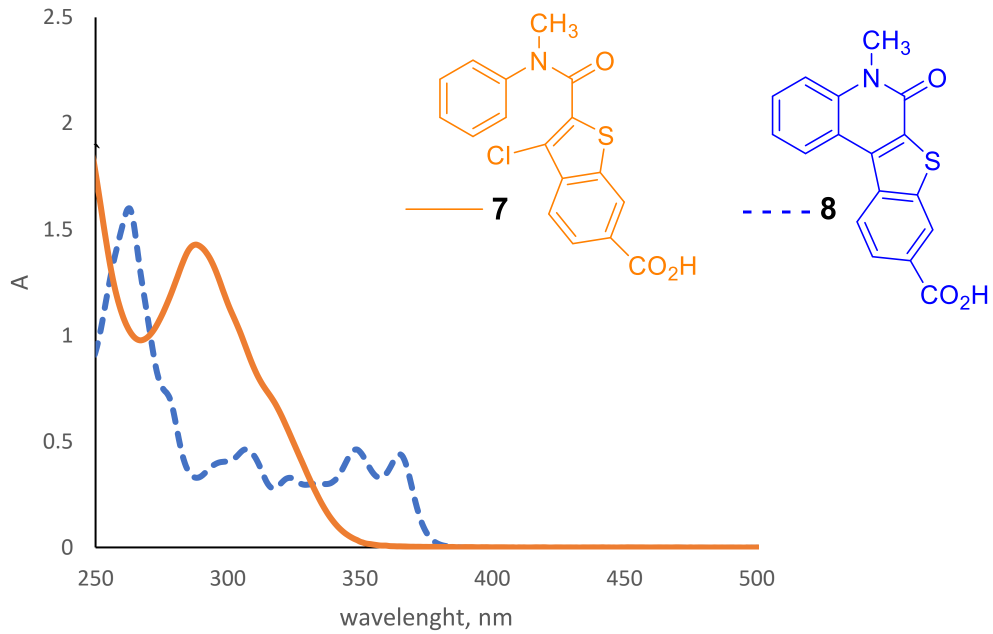


Figure S2. Absorption spectrum of 7.14 x 10^{-5} M anilide **7** (——) and 4.01 x 10^{-5} M photoproduct **8** (-----) in 80% dioxane and 20% aqueous 100 mM potassium phosphate buffer at pH 7.2

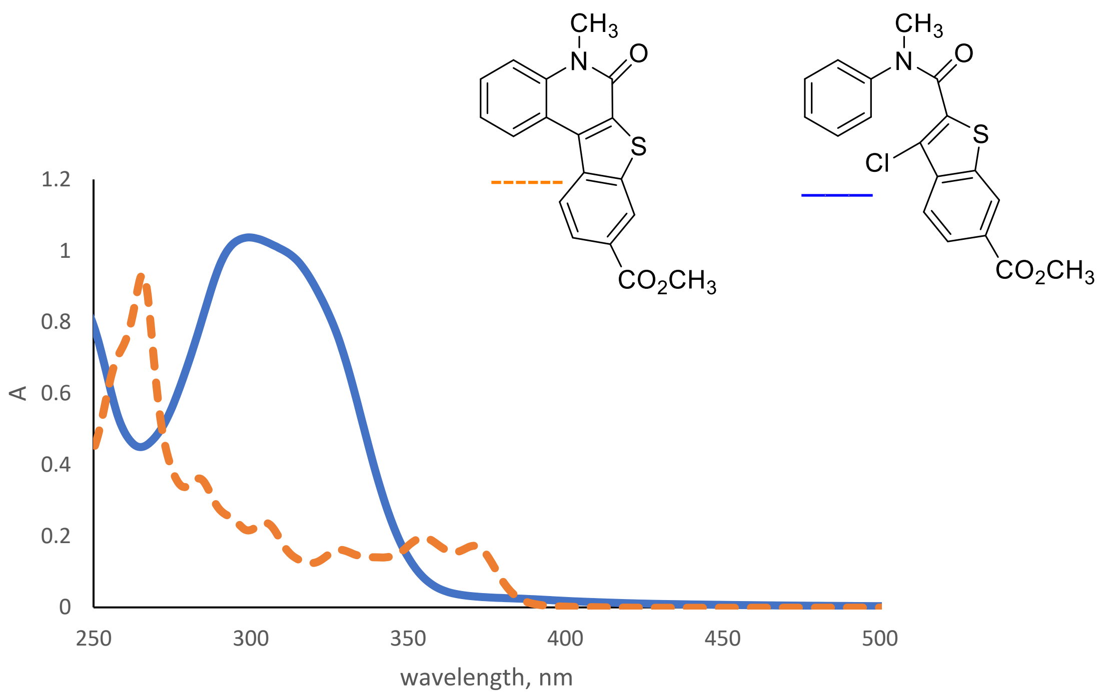


Figure S3. Absorption spectrum of 2.22 x 10^{-5} M of ester of anilide **7** (——) and 2.24 x 10^{-5} M of ester of photoproduct **8** (-----) in 80% dioxane and 20% aqueous 100 mM potassium phosphate buffer at pH 7.

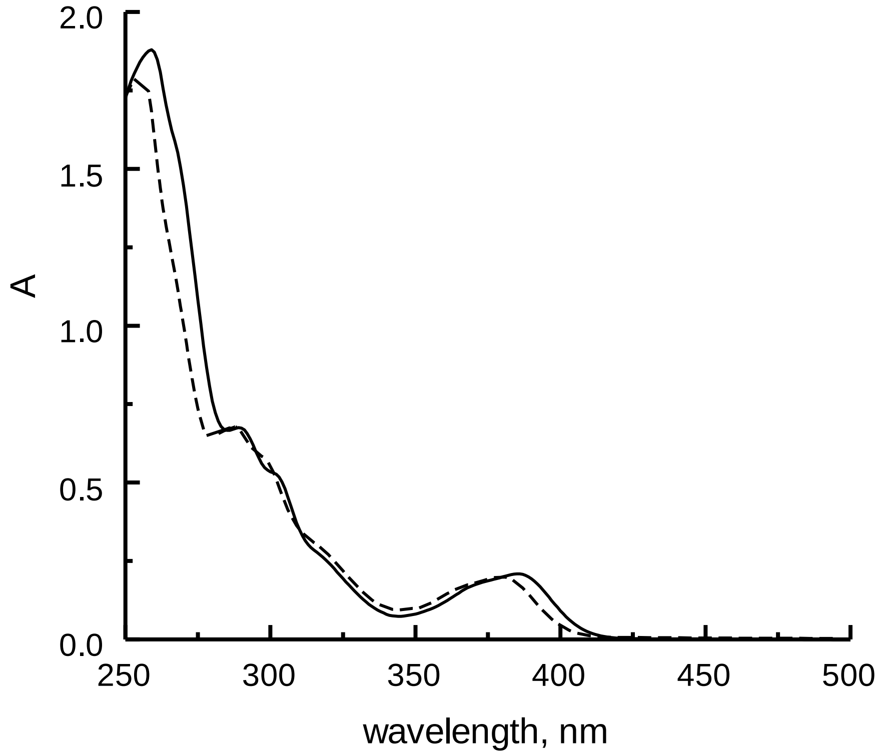


Figure S4. Absorption spectrum of 3.21 x 10^{-5} M **9a** (——) and 2.86 x 10^{-5} M of each of thioxanthone and anilide **7** (– – –) in 80% dioxane and 20% aqueous 100 mM potassium phosphate buffer at pH 7.2.

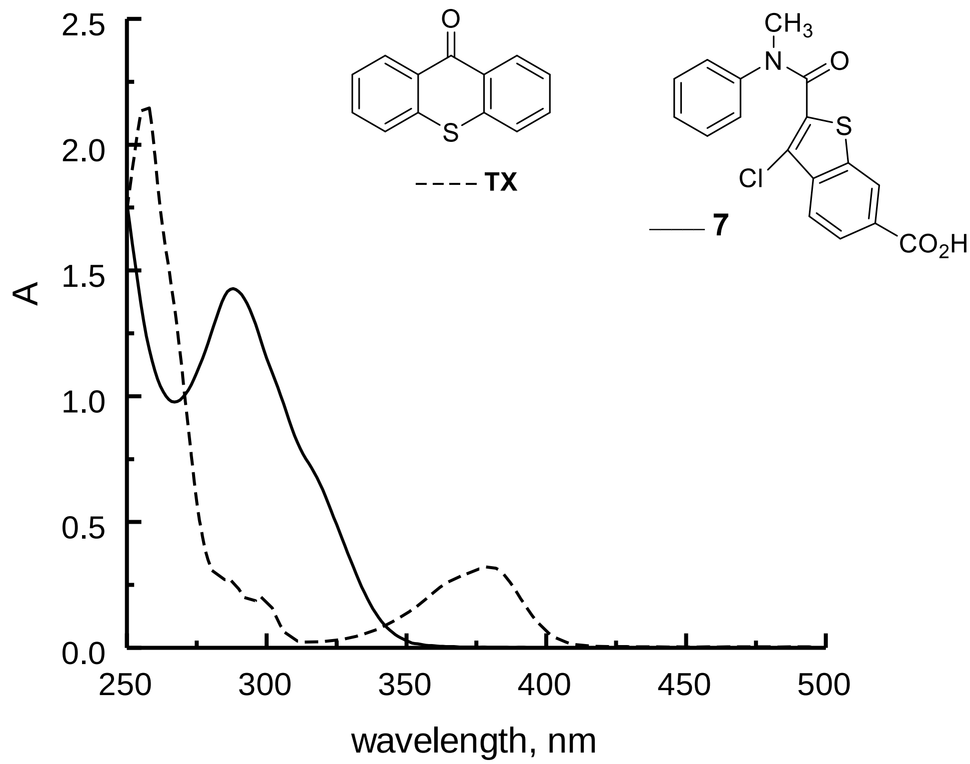


Figure S5. Absorption spectrum of 2.84 x 10^{-5} M thioxanthone (**-----**) and 7.12 x 10^{-5} M anilide **7** (——) in 80% dioxane and 20% aqueous 100 mM potassium phosphate buffer at pH 7.2.

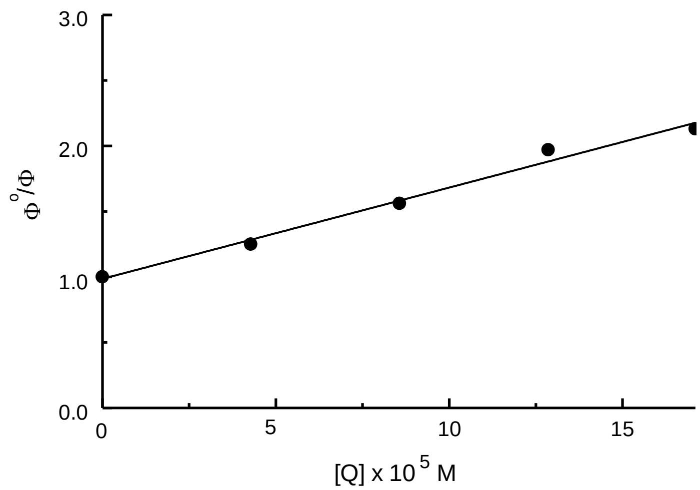


Figure S6. Stern-Volmer Plot for quenching of 3.00 x 10^{-3} M Anilide **7** by Varying Concentrations of Cyclohexadiene.

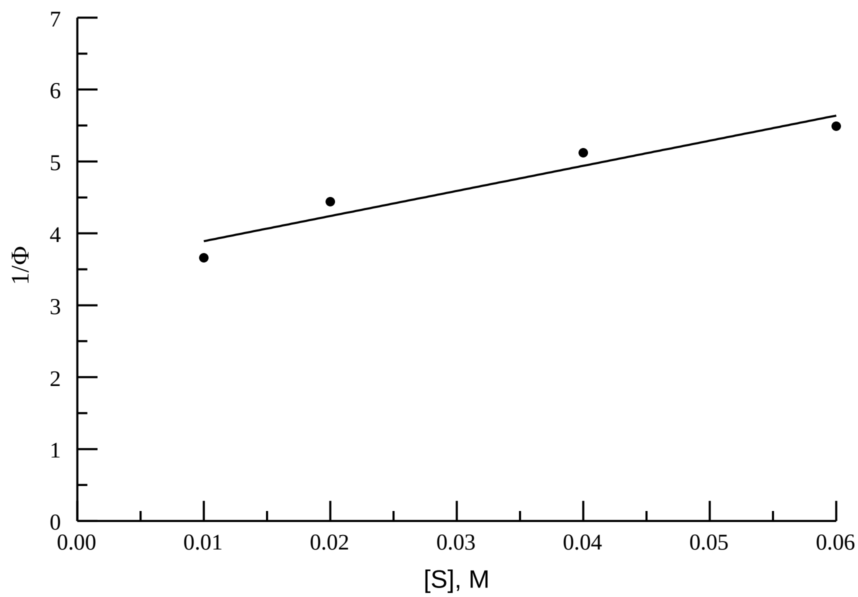


Figure S7. Φ^{-1} vs. [**S**] with Constant Concentration of 2.00 x 10^{-2} M Anilide **7**.

Crystallography data for Compound 7, 10a, 12, and 20

The dataset was collected with an Oxford SuperNova diffractometer using Mo(Kα) radiation at 100K. A suitable crystal was selected and, on a SuperNova, Dual, Cu at home/near, Atlas diffractometer. In all cases, the crystal was kept at 100.15 K during data collection. Using Olex2[1], the structures were solved with the olex2.solve[2] structure solution program using Charge Flipping and refined with the ShelXL[3] refinement package using Least Squares minimisation.

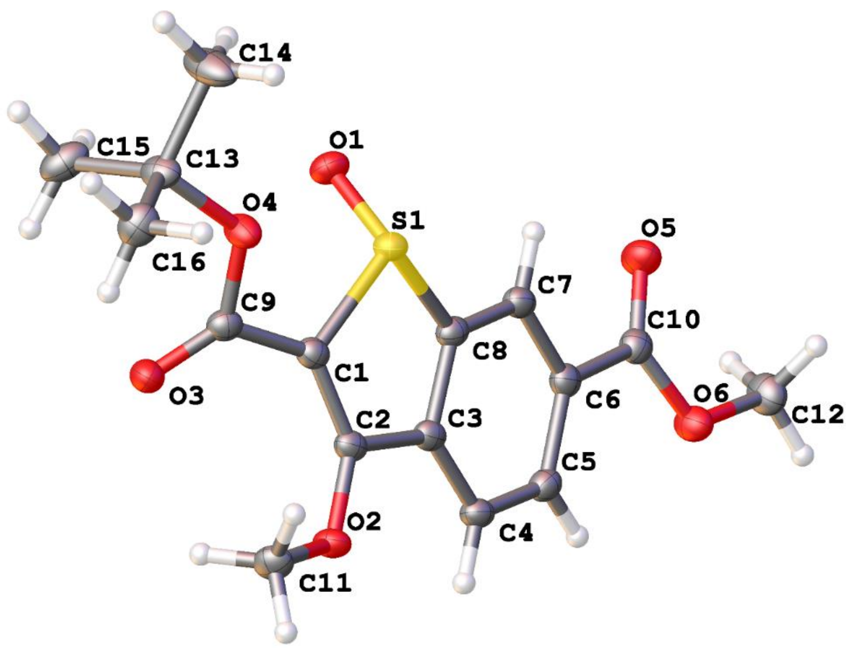


Figure S8. Crystal structure of compound **20.** Ellipsoid contour % probability levels for the X-ray structure were 50%. The carbomethoxy and methoxy substituents are pi-conjugated with the central benzo-thiophene moiety (dihedral angles 12.8 and 10.5°, respectively). The carbo-t-butyloxy group deviates from the conjugation by 27.0°. It is noteworthy that the cyclic sulfur(IV) monoxide is chiral, but the crystal is formed by the racemate.

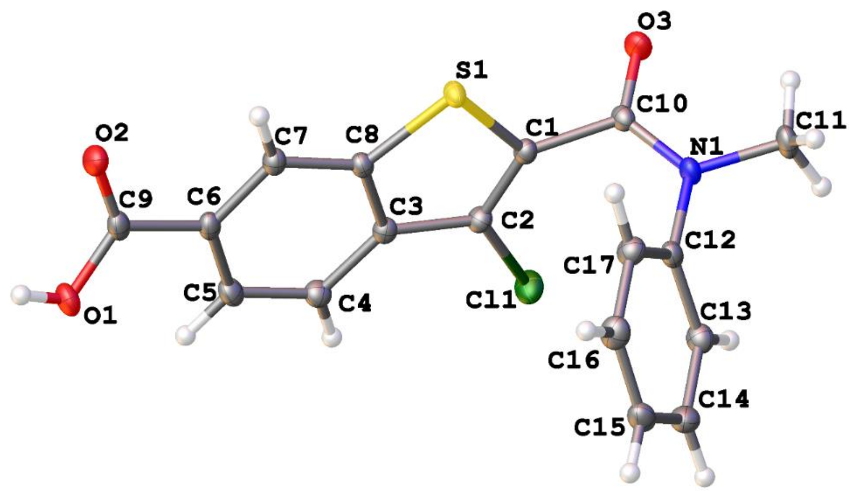


Figure S9. Crystal structure of compound **7**. Ellipsoid contour % probability levels for the X-ray structure were 50%. The molecule has a folded conformation – the benzothiophene and phenyl moieties are cis-positioned. Both groups are nearly perpendicular to the central amide plane (no conjugation).

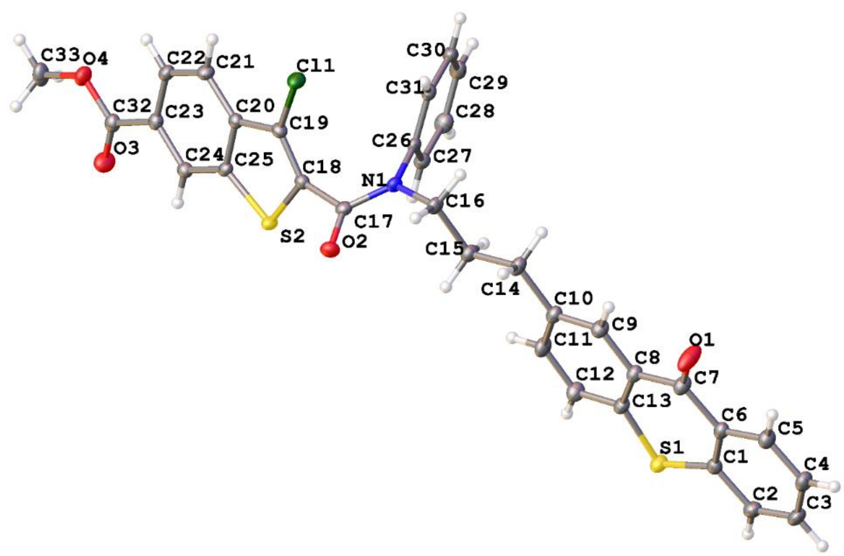


Figure S10. Crystal structure of compound **10a.** Ellipsoid contour % probability levels for the X-ray structure were 50%. The molecule has an extended conformation (with both S atoms oriented in the same direction relative to the plane of the amide group). The trimethylene-thioxanthone and the benzothiophene moieties are trans-positioned. The all-transoid trimethylene bridge is also essentially orthogonal to the amide group and lies in the plane of the thioxanthone moiety.

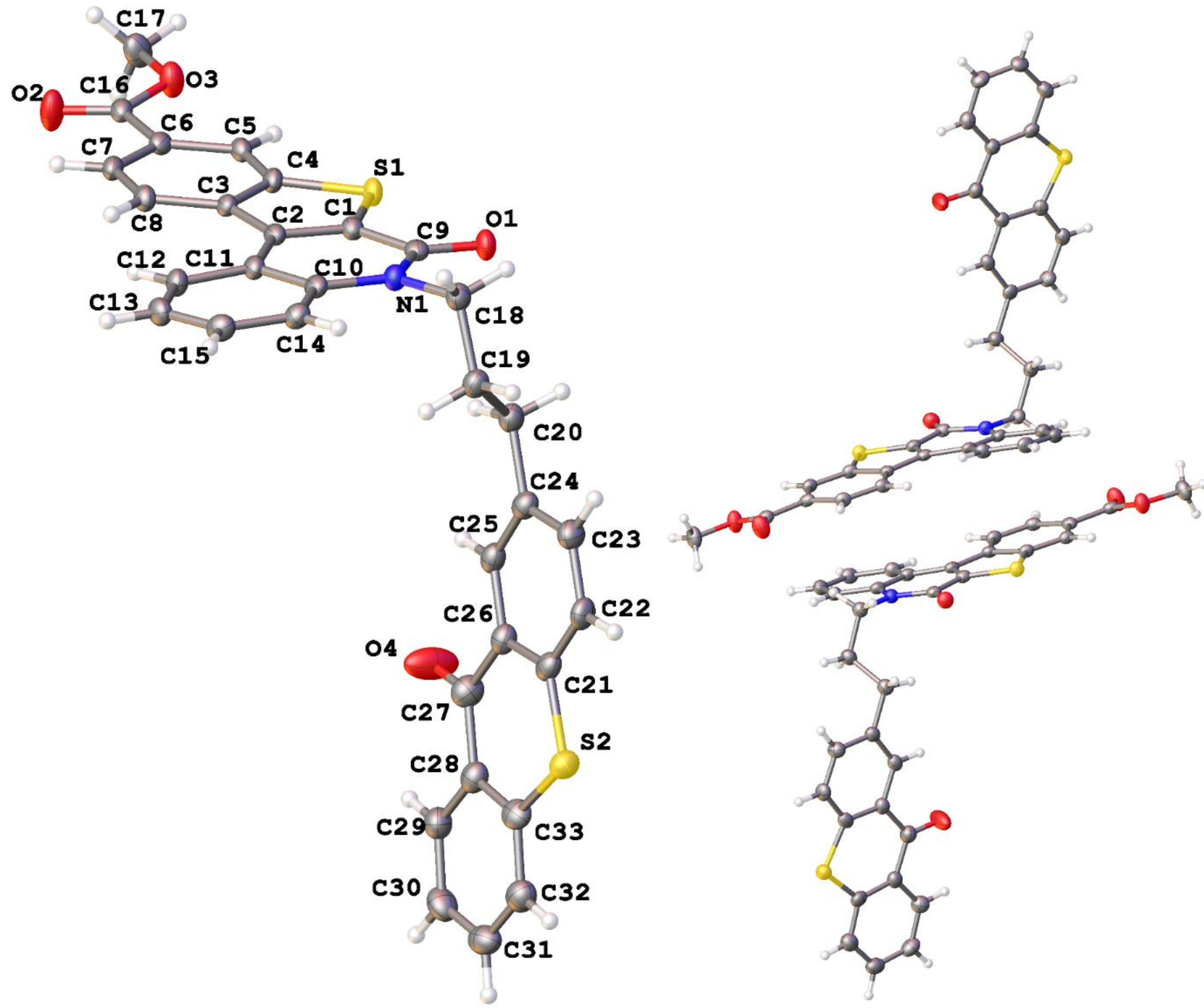


Figure S11. Crystal structure of compound **12**. Ellipsoid contour % probability levels for the X-ray structure were 50%. There are 2 symmetrically independent molecules having a very similar L-shaped conformation with mutually orthogonal aromatic moieties (because of trans,gauche-conformation of the trimethylene bridge

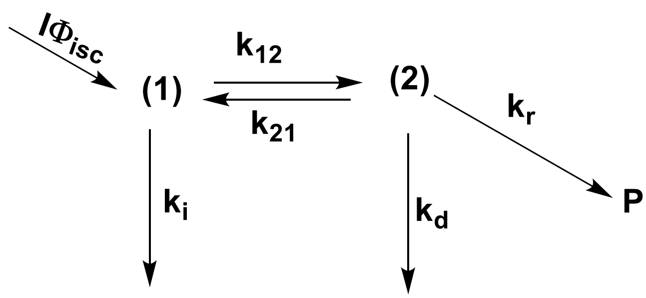
Table S1. Crystal data and structure refinement for compounds **20** and **7**

Identification code	Compound **20**	Compound **7**
Empirical formula	$C_{16}H_{18}O_6S$	$C_{17}H_{12}ClNO_3S$
Formula weight	338.36	345.79
Temperature/K	100.15	100.15
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/c$	Pbca
a/Å	16.5505(3)	11.8228(2)
b/Å	10.3454(2)	12.38285(19)
c/Å	9.53748(17)	20.3843(4)
α/°	90	90.00
β/°	101.3266(17)	90.00
γ/°	90	90.00
Volume/Å^3	1601.22(5)	2984.27(9)
Z	4	8
ρ_{calc}g/cm^3	1.404	1.539
μ/mm^{-1}	2.059	0.410
F(000)	712.0	1424.0
Crystal size/mm^3	0.383 × 0.227 × 0.03	0.48 × 0.44 × 0.38
Radiation	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)
2Θ range for data collection/°	10.14 to 140.972	6.88 to 59.28
Index ranges	$-20 \leq h \leq 20$, $-12 \leq k \leq 12$, $-11 \leq l \leq 11$	$-11 \leq h \leq 16$, $-16 \leq k \leq 16$, $-23 \leq l \leq 27$
Reflections collected	15126	21307
Independent reflections	3033 [R_{int} = 0.0374, R_{sigma} = 0.0246]	3906 [R_{int} = 0.0231, R_{sigma} = 0.0184]
Data/restraints/parameters	3033/0/213	3906/0/213
Goodness-of-fit on F^2	1.043	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0341, Wr_2 = 0.0852	R_1 = 0.0302, Wr_2 = 0.0754
Final R indexes [all data]	R_1 = 0.0414, Wr_2 = 0.0903	R_1 = 0.0347, Wr_2 = 0.0784
Largest diff. peak/hole / e Å^{-3}	0.28/-0.32	0.34/-0.34
CCDC deposition number	1842115	1842113

Table S2. Crystal data and structure refinement for compounds **10a** and **12**

Identification code	Compound **10a**	Compound **12**
Empirical formula	$C_{33}H_{24}NO_4S_2Cl$	$C_{33}H_{23}NO_4S_2$
Formula weight	598.10	561.64
Temperature/K	100.15	100.15
Crystal system	triclinic	orthorhombic
Space group	P-1	$Pna2_1$
a/Å	8.4756(2)	15.1873(2)
b/Å	9.5981(2)	8.41771(12)
c/Å	17.4464(4)	39.3945(7)
α/°	78.921(2)	90.00
β/°	83.629(2)	90.00
γ/°	81.536(2)	90.00
Volume/$Å^3$	1372.62(6)	5036.27(14)
Z	2	8
$\rho_{calc}g/cm^3$	1.447	1.481
μ/mm^{-1}	0.333	2.273
F(000)	620.0	2336.0
Crystal size/mm^3	0.426 × 0.289 × 0.191	0.393 × 0.134 × 0.023
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.96 to 59.32	8.98 to 141.18
Index ranges	$-11 \le h \le 11, -12 \le k \le 13, -24 \le l \le 23$	$-18 \le h \le 18, -10 \le k \le 10, -44 \le l \le 47$
Reflections collected	31139	24616
Independent reflections	7034 [R_{int} = 0.0280, R_{sigma} = 0.0268]	8269 [R_{int} = 0.0320, R_{sigma} = 0.0331]
Data/restraints/parameters	7034/0/371	8269/1/724
Goodness-of-fit on F^2	1.042	1.151
Final R indexes [I>=2σ (I)]	R_1 = 0.0343, Wr_2 = 0.0810	R_1 = 0.0417, Wr_2 = 0.1058
Final R indexes [all data]	R_1 = 0.0431, Wr_2 = 0.0868	R_1 = 0.0443, Wr_2 = 0.1073
Largest diff. peak/hole / e $Å^{-3}$	0.36/-0.30	0.43/-0.34
Flack parameter		0.00(18)
CCDC deposition number	1842112	1842114

A. Reversible Intramolecular Sensitized Photolysis Where Only One State (Second Excited State) react in rapid equilibrium Φº.



Scheme S1. Energy state diagram for reversible triplet-triplet energy transfer between two states in the absence of a quencher

Using steady state approximation

$$\frac{d[1]}{dt} = I\Phi_{isc} + k_{21}[2] - k_{12}[2] - k_i[1] = 0$$

$$[1] = \frac{IQ_{isc} + k_{21}[2]}{k_{12} + k_i}$$

$$\frac{d[2]}{dt} = k_{12}[1] - k_{21}[2] - k_d[2] - k_r[2]$$

$$[2] = \frac{k_{12}[1]}{k_{21} + k_d + k_r}$$

$$(2) = \frac{k_{12}(\frac{I\Phi_{isc} + k_{21}[2]}{k_{12} - k_i})}{k_{21} + k_d + k_r}$$

$$[2] = \frac{I\Phi_{isc}k_{12}(k_{12} + k_i) + k_{12}k_{21}[2]}{(k_{21} + k_d + k_r)(k_{12} + k_i)}$$

$$[2]\left\{1 - \frac{k_{12}k_{21}}{(k_{21} + k_d + k_r)(k_{12} + k_i)}\right) = \frac{I\Phi_{isc}k_{12}(k_{12} + k_i)}{(k_{21} + k_d + k_r)(k_{12} + k_i)}$$

$$[2] = \frac{I\Phi_{isc}k_{12}(k_{12} + k_i)}{\left\{1 - \frac{k_{12}\,k_{21}}{(k_{21} + k_d + k_r)(k_{12} + k_i)}\right)(k_{21} + k_d + k_r)(k_{12} + k_i)}$$

$$[2] = \frac{I\Phi_{isc}k_{12}(k_{12} + k_i)}{(k_{21} + k_d + k_r)(k_{12} + k_i) - k_{12}k_{21}}$$

$$\frac{dp}{dt} = \Phi^o I\Phi_{isc} = k_r[2]$$

$$\Phi^0 = \frac{k_r k_{12}(k_{12} + k_i)}{k_{21}k_{12} + k_{21}k_i + k_d k_{12} + k_d k_i + k_r k_{12} + k_r k_i - k_{12}k_{21}}$$

$$\Phi^0 = \frac{k_r k_{12}(k_{12} + k_i)}{k_{21}k_i + k_d k_{12} + k_d k_i + k_r k_{12} + k_r k_i}$$

$$= \frac{k_r k_{12}(k_{12} + k_i)}{k_i\,(k_{21} + k_d + k_r) + k_{12}(k_d + k_r)}$$

$if\ we\ assume\ k_{12} > k_i\ \ and\ k_{21} > k_d + k_r$

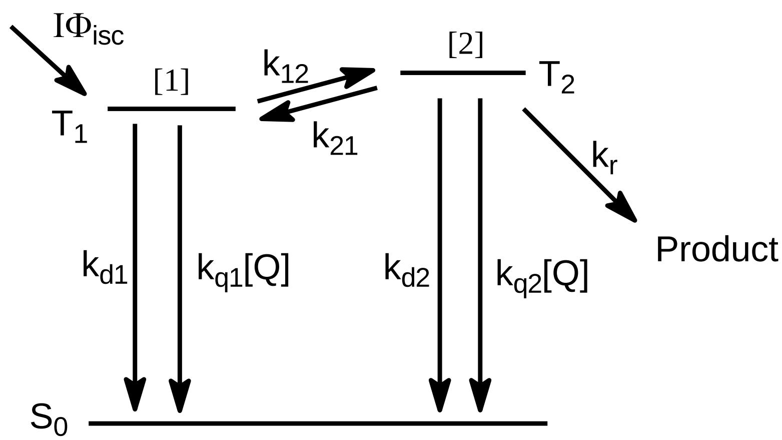
$$= \frac{k_r k_{12}(k_{12})}{k_i\,(k_{21}) + k_{12}(k_d + k_r)}$$

$$X_1 = \frac{k_{21}}{k_{21} + k_{12}} \qquad X_2 = \frac{k_{12}}{k_{21} + k_{12}}$$

$$= \frac{k_r k_{12}\left(\frac{k_{12}}{k_{12} + k_{21}}\right)}{k_i\left(\frac{k_{21}}{k_{12} + k_{21}}\right) + \frac{k_{12}}{k_{12} + k_{21}}(k_d + k_r)}$$

$$\Phi^0 = \frac{k_r X_2 k_{12}}{k_i X_1 + (k_d + k_r)X_2}$$

B. Reversible Intramolecular Triplet Energy Transfer with Quenching of Both Triplet Excited States by Quencher [Q].



Scheme S2. State Energy Diagram for Reversible Triplet-Triplet Energy Transfer between Two States with Quenching by [Q]

Using steady state approximation

$$\frac{d[1]}{dt} = 0 = I\Phi_{isc} - k_i[1] - k_{q1}[Q][1] + k_{21}[2] - k_{12}[1]$$

$$[1] = \frac{I + k_{21}[2]}{k_i + k_{12} + k_{q1}[Q]}$$

$$\frac{d[2]}{dt} = 0 = k_{12}[1] - k_{21}[2] - k_d[2] - k_r[2] - k_{q2}[Q][2]$$

$$[2] = \frac{k_{12}[1]}{k_{21} + k_d + k_r + k_{q2}[Q]}$$

$$[1]\ in\ [2] \ \rightarrow [2] \ = \frac{k_{12}I\Phi_{isc}(k_i+k_{12}+k_{q1}[Q])+k_{12}k_{21}[2]}{(k_{21}+k_d+k_r+k_{q2}[Q])(k_i+k_{12}+k_{q1}[Q]}$$

$$[2] \ - \frac{k_{12}k_{21}[2]}{(k_{21}+k_d+k_r+k_{q2}[Q])(k_i+k_{12}+k_{q1}[Q])} = \frac{k_{12}I\Phi_{isc}(k_i+k_{12}+k_{q1[Q]})}{(k_{21}+k_d+k_r+k_{q2}[Q])(k_i+k_{12}+k_{q1}[Q]}$$

$$[2] \ \left\{1 - \frac{k_{12}k_{21}}{(k_{21} + k_d + k_r + k_{q2}[Q])(k_i + k_{12} + k_{q1}[Q]}\right\} = \frac{(k_{12}I\Phi_{isc}(k_i + k_{12} + k_{q1}[Q])}{(\ ,,\ )(\ „\ )}$$

$$[2] = \frac{k_{12}I\Phi_{isc}(\mathrm{k_i} + k_{12} + k_{q1}[Q])}{(k_{21} + k_d + k_{q2}[Q])(k_i + k_{12} + k_{q1}[Q]) - k_{12}k_{21}}$$

$$[2] = \frac{(k_{12} I\Phi_{isc}(k_i + k_{12} + k_{q1}[Q])}{k_{21}k_i + k_{21}k_{12} + k_{21}k_{q1}[Q] + k_d k_i + k_d k_{12} + k_d k_{q1}[Q] + k_r k_i + k_r k_{12} + k_r k_{q1}[Q] + k_i k_{q2}[Q] + k_{12}k_{q2}[Q] + k_{q1}[Q]k_{q2}[Q] - k_{12}k_{21}}$$

$$\frac{dP}{dt} = \Phi I\Phi_{isc} = k_r[2]$$

$$\Phi = \frac{(k_r k_{12}(k_i + k_{12} + k_{q1}[Q])}{k_i(k_{21} + k_d) + k_d k_{12} + k_r(k_i + k_{12}) + [Q](k_{21}k_{q1} + k_d k_{q1} + k_r k_{q1} + k_i k_{q2} + k_{12}k_{q2}) + k_{q1}k_{q2}[Q]^2}$$

$$k_{21} > k_d + k_r \text{ and } k_{12} > k_i$$

$$\frac{1}{\Phi} = \frac{(k_i k_{21} + k_d k_{12} + k_r k_{12} + (k_{21} + k_d + k_r)k_{q1}[Q] + (k_i + k_{12})k_{q2}[Q] + k_{q1}k_{q2}[Q]^2)}{(k_r k_{12}(k_i + k_{12} + k_{q1}[Q])}$$

Multiply top and bottom by $1/k_{12}+k_{21}$

$$\frac{1}{\Phi} = \frac{k_i X_1 + k_d X_2 + X_1 k_{q1}[Q] + X_2 k_{q2}[Q] + k_{q1}k_{q2}[Q]^2(k_{12} + k_{21})^{-1}}{k_r X_2(k_i + k_{12} + k_{q1}[Q])}$$

$$X_1 = \frac{k_{21}}{K_{21} + K_{12}} \quad \text{and} \quad X_2 = \frac{k_{12}}{k_{21} + k_{12}}$$

$$\Phi^O = \frac{X_2 k_{12} k_r}{X_1 k_i + X_2(k_d + k_r)} \qquad \mathrm{T}_e = \frac{1}{X_1 k_i (k_r + k_d) X_2}$$

$$\frac{\Phi^O}{\Phi} = \frac{k_{12} k_r X_2 \{k_i X_1 + X_2(k_d + k_r) + X_1 k_{q1}[Q] + X_2 k_{q2}[Q] + k_{q1}k_{q2}[Q]^2(k_{12} + k_{21})^{-1}\}}{X_1 k_i + X_2(k_d + k_r)\{k_r X_2(k_i + k_{12} + k_{q1}[Q])\}}$$

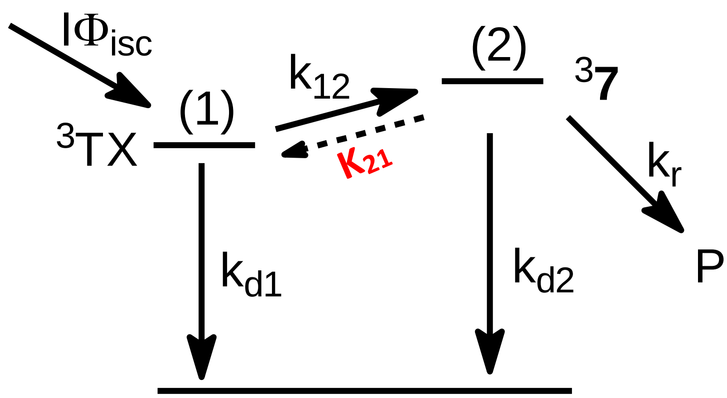
$$\frac{\Phi^0}{\Phi} = \frac{k_{12}\{1 + X_1 k_{q1}\tau_e[Q] + X_2 k_{q2}\tau_e[Q] + k_{q1}k_{q2}\tau_e[Q]^2(k_{12} + k_{21})^{-1}\}}{(k_i + k_{12} + k_{q1}[Q])}$$

$k_{12} >> k_i$

$$\frac{\Phi^0}{\Phi} = \frac{k_{12}\{1 + X_1 k_{q1}\tau_e[Q] + X_2 k_{q2}\tau_e[Q] + k_{q1}k_{q2}\tau_e[Q]^2(k_{12} + k_{21})^{-1}\}}{(k_{12} + k_{q1}[Q])}$$

$$= \frac{\{1 + X_1 k_{q1}\tau_e[Q] + X_2 k_{q2}\tau_e[Q] + k_{q1}k_{q2}\tau_e[Q]^2(k_{12} + k_{21})^{-1}\}}{1 + {k_{q1}[Q]}/{k_{12}}}$$

C. Intermolecular Sensitized Photolysis with Both States in Equilibrium



Scheme S3. Kinetic Scheme for Sensitized Photolysis of Benzothiophene-2-Carboxanilide **7** by Thioxanthone TX

Let $[^3S]$ = [1] and $[^3A]$ = 2 where S is the thioxanthone sensitizer and A is the anilide

$$\frac{d[2]}{dt} = k_{12}[A][1] - k_{21}[S][2] - k_r[2] - k_{d2}[2] = 0$$

$$\frac{k_{12}[A][1]}{k_{21}[S] + k_r + k_{d2}} = [2]$$

$$\frac{d[1]}{dt} = k_{21}[S][2] + I\Phi_{isc} - k_{d1}[1] - k_{12}[A][1] = 0$$

$$[1]\,(k_{d1} - k_{12}[A]) = k_{21}\,[S][2] + I\Phi_{isc}$$

$$[1](k_{d1} - k_{12}[A]) = k_{21}[S]^3(\frac{k_{12}[A][1]}{k_{21}[S] + k_r + k_{d2}}) + I\Phi_{isc}$$

$$[1](k_{d1} - k_{12}[A]) - k_{21}[S]^3\left(\frac{k_{21}[s]k_{12}[A][1]}{k_{21}[S] + k_r + k_{d2}}\right) = I\Phi_{isc}$$

$$[1](k_{21}[S] + k_r + k_{d2})(k_{d1} - k_{12}[A]) - k_{21}[S]k_{12}[A][1] = I\Phi_{isc}(k_{21}[S] + k_r + k_{d2})$$

$$[1] = \frac{I\Phi_{isc}(k_{21}[S] + k_r + k_{d2})}{(k_{21}[S] + k_r + k_{d2})(k_{d1} - k_{12}[A]) - k_{21}[S]k_{12}[A]}$$

$$[1] = \frac{I\Phi_{isc}(k_{21}[S] + k_r + k_{d2})}{k_{d1}k_{21}[S] + k_{d1}k_r + k_{d1}k_{d2} + k_{12}[A]k_{21}[S] + k_{12}[A]k_r + k_{12}[A]k_{d2} - k_{21}[S]k_{12}[A]}$$

$$\frac{dp}{dt} = \Phi I\Phi_{isc} = k_r[2]$$

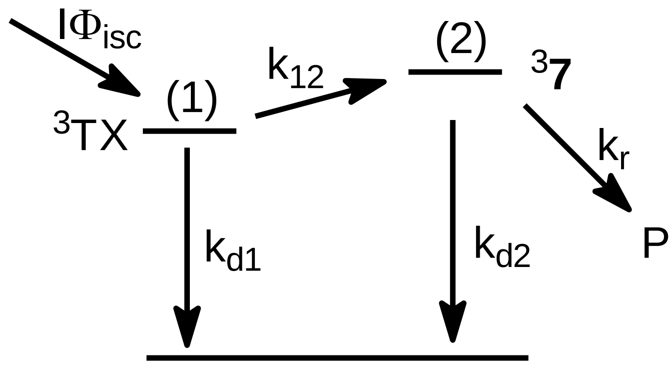
$$\Phi = \frac{k_r k_{12}[\mathrm{A}]\Phi_{isc}(k_{21}[S] + k_r + k_{d2})}{(k_{21}[S] + k_r + k_{d2})(k_{d1}k_{21}[S] + k_{d1}k_r + k_{d1}k_{d2} + k_{12}[A]k_r + k_{12}[A]k_{d2})}$$

$$\frac{1}{\Phi} = \frac{k_{d1}k_{21}[S] + k_{d1}k_r + k_{d1}k_{d2} + k_{12}[A]k_r + k_{12}[A]k_{d2}}{k_r k_{12}[\mathrm{A}]\Phi_{isc}}$$

$$\frac{1}{\Phi} = \frac{k_{d1}k_{21}[S] + k_{d1}k_r + k_{d1}k_{d2}}{k_r k_{12}[\mathrm{A}]\Phi_{isc}} + \frac{k_r + k_{d2}}{k_r\Phi_{isc}}$$

D. Intermolecular sensitization: Non-Reversible Triplet Energy Transfer.

For non-reversible intermolecular energy transfer, $k_{21} = 0$ as shown in the following energy diagram.

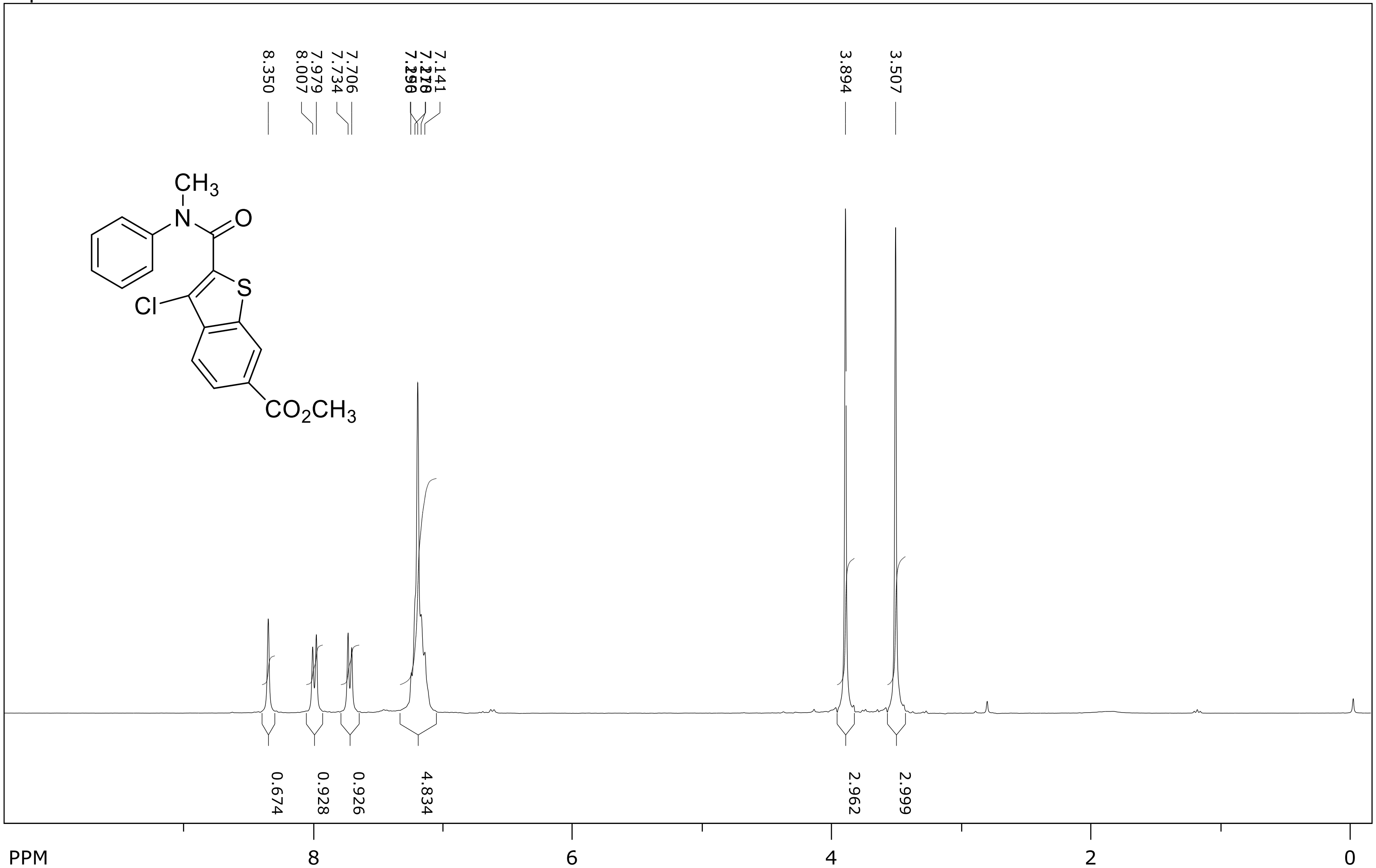


Scheme S4. Energy state diagram for non-reversible intermolecular triplet-triplet energy transfer between two states

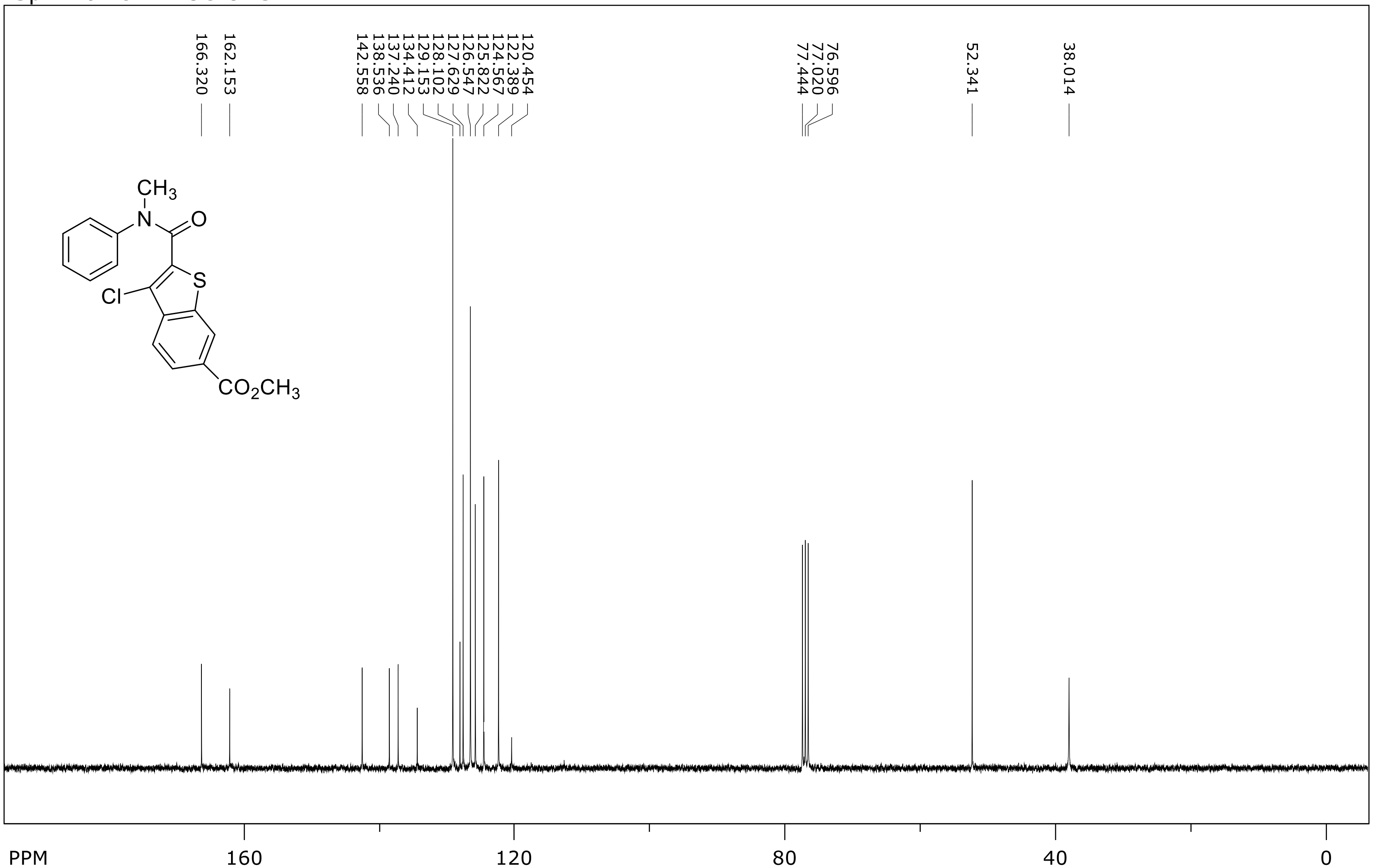
For $k_{21} = 0$, the equation describing this diagram is

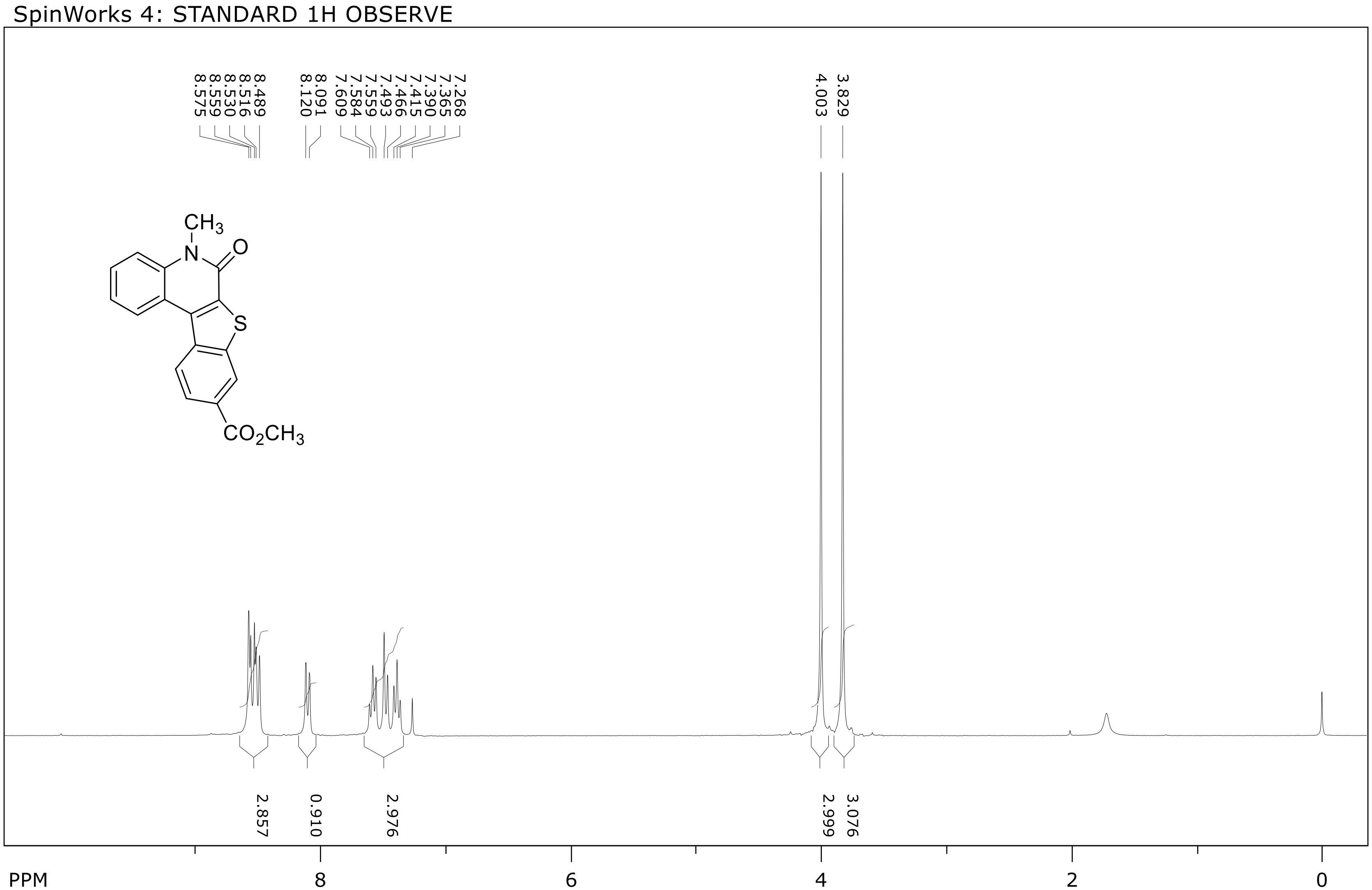
$$\frac{1}{\Phi} = \frac{k_{d1}k_r + k_{d1}\,k_{d2}}{k_r k_{12}[\mathrm{A}]\Phi_{isc}} + \frac{k_r + k_{d2}}{k_r \Phi_{isc}}$$

SpinWorks 4: STANDARD 1H OBSERVE

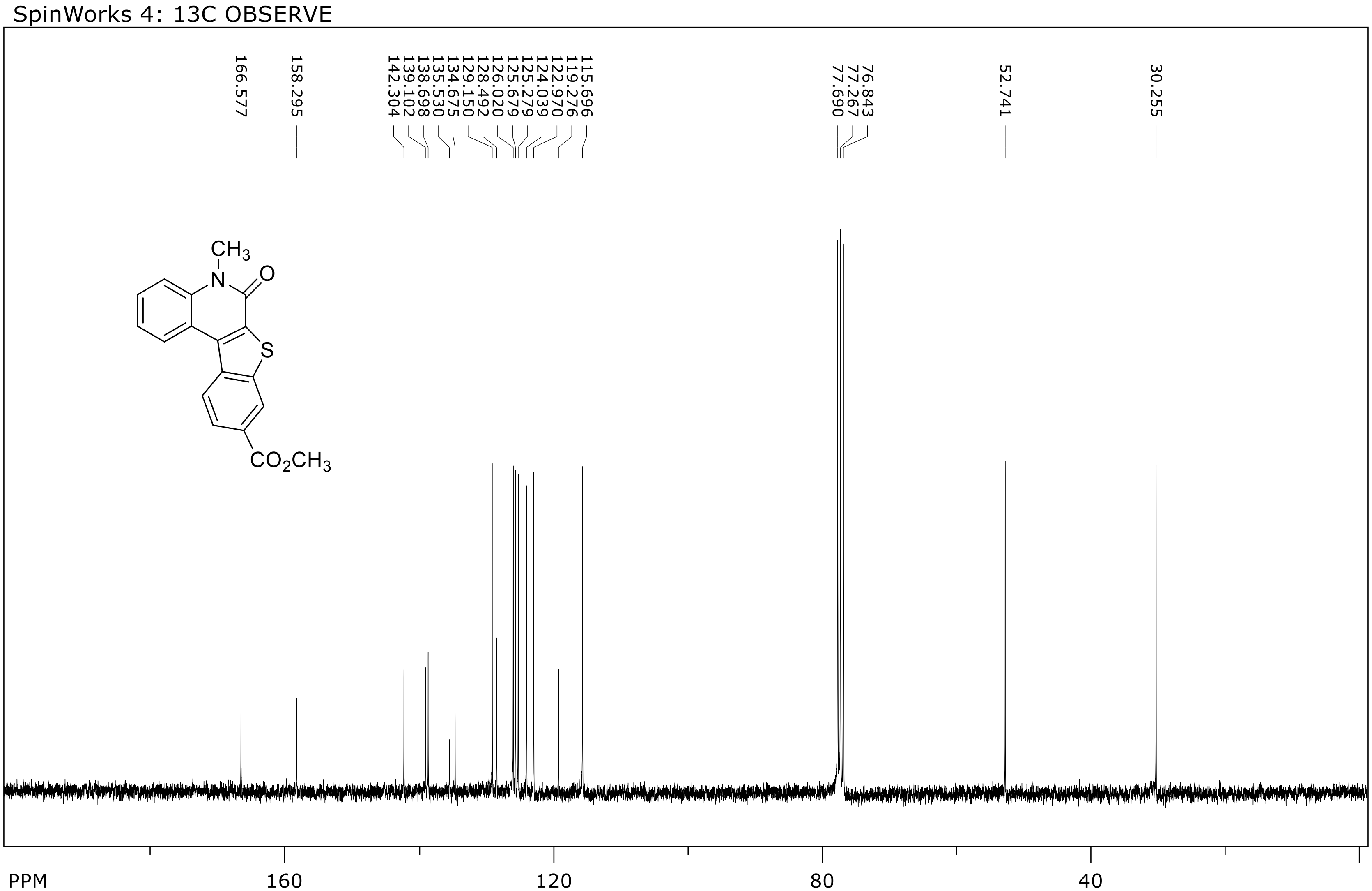


SpinWorks 4: 13C OBSERVE

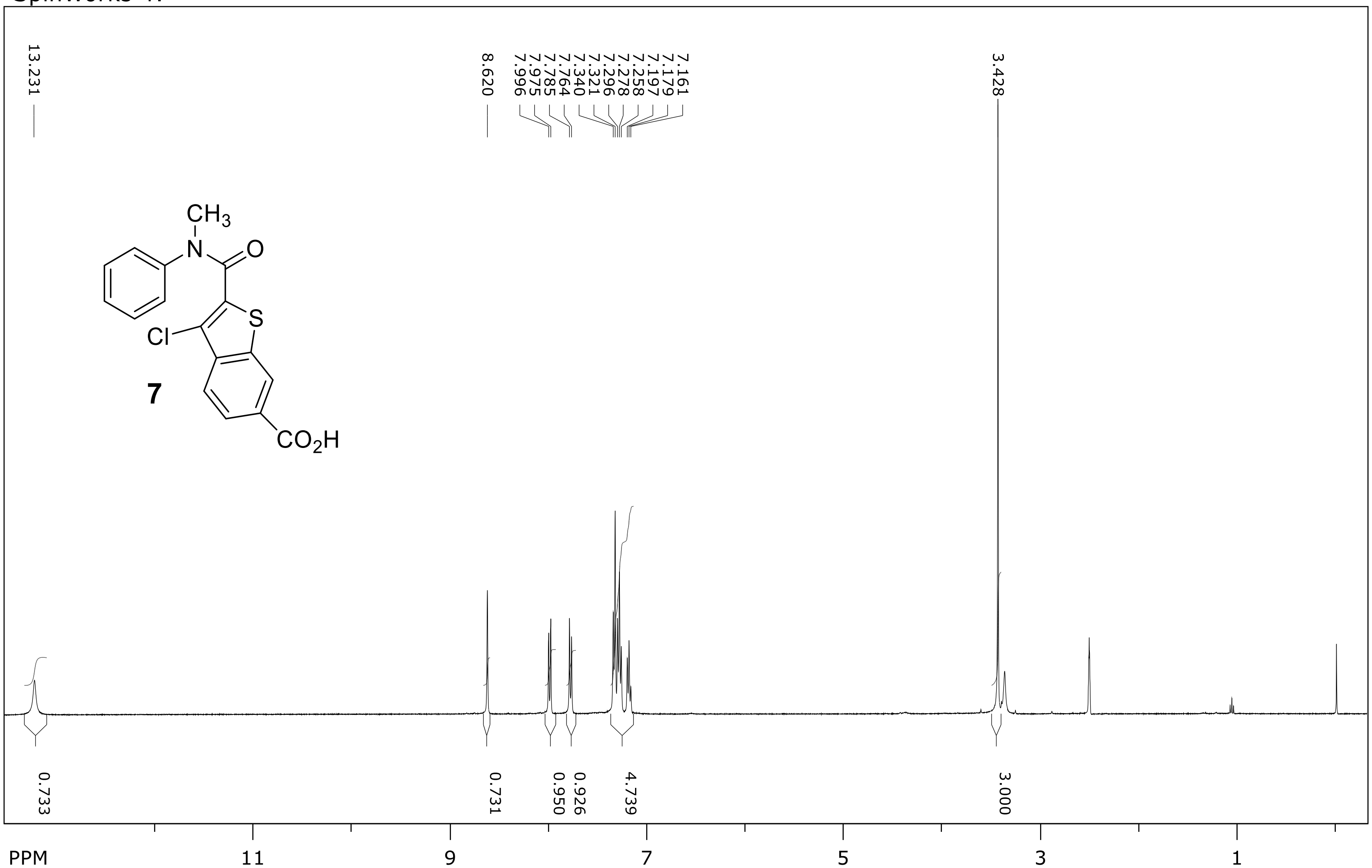




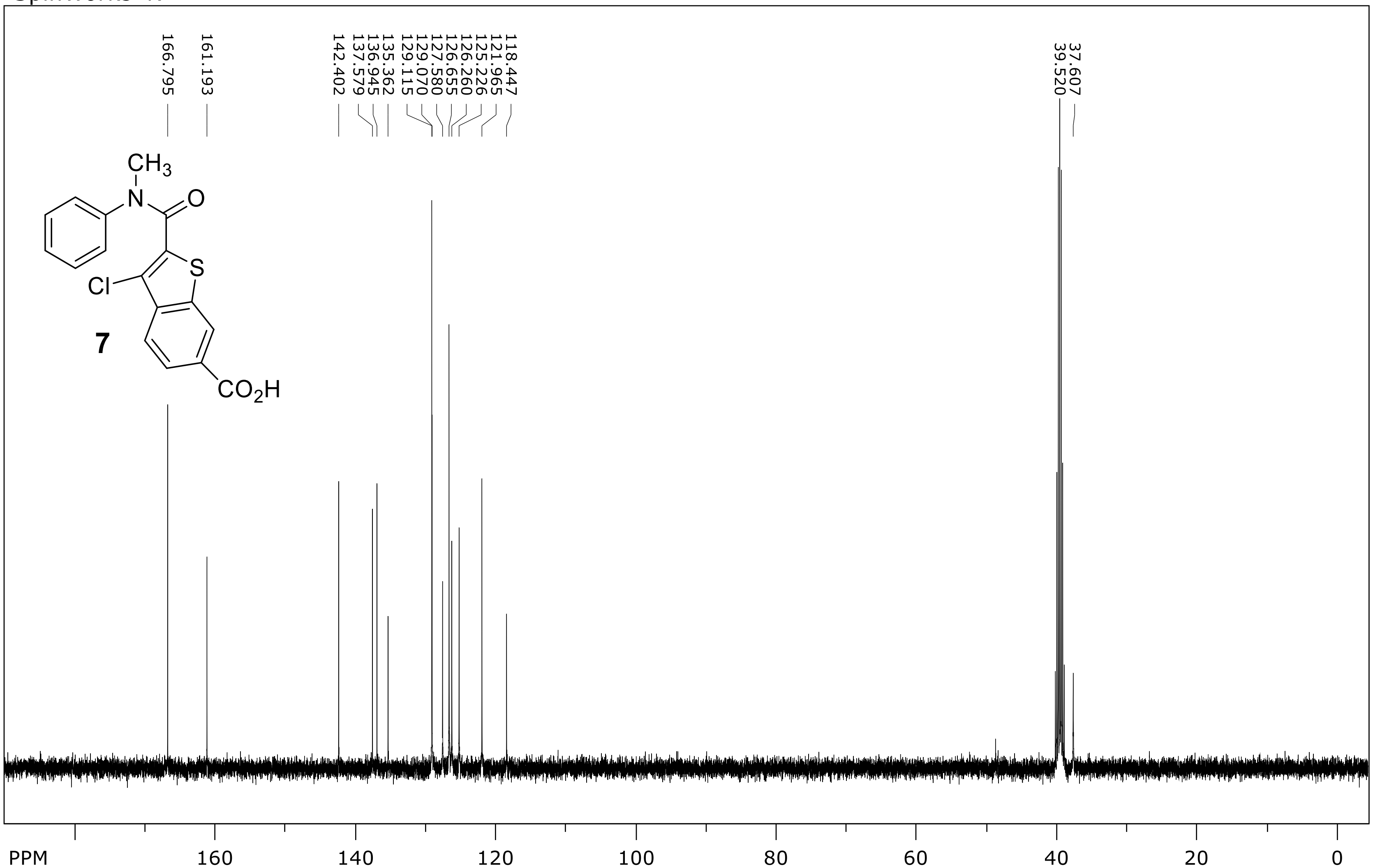
SpinWorks 4: STANDARD 1H OBSERVE
8.575
8.559
8.530
8.516
8.489
8.120
8.091
7.609
7.584
7.559
7.493
7.466
7.415
7.390
7.365
7.268
4.003
3.829
CH3
N
O
S
CO2CH3
2.857
0.910
2.976
2.999
3.076
PPM
8
6
4
2
0


SpinWorks 4: 13C OBSERVE
166.577
158.295
142.304
139.102
138.698
135.530
134.675
129.150
128.492
126.020
125.679
125.279
124.039
122.970
119.276
115.696
77.690
77.267
76.843
52.741
30.255
CH3
N
O
S
CO2CH3
PPM
160
120
80
40

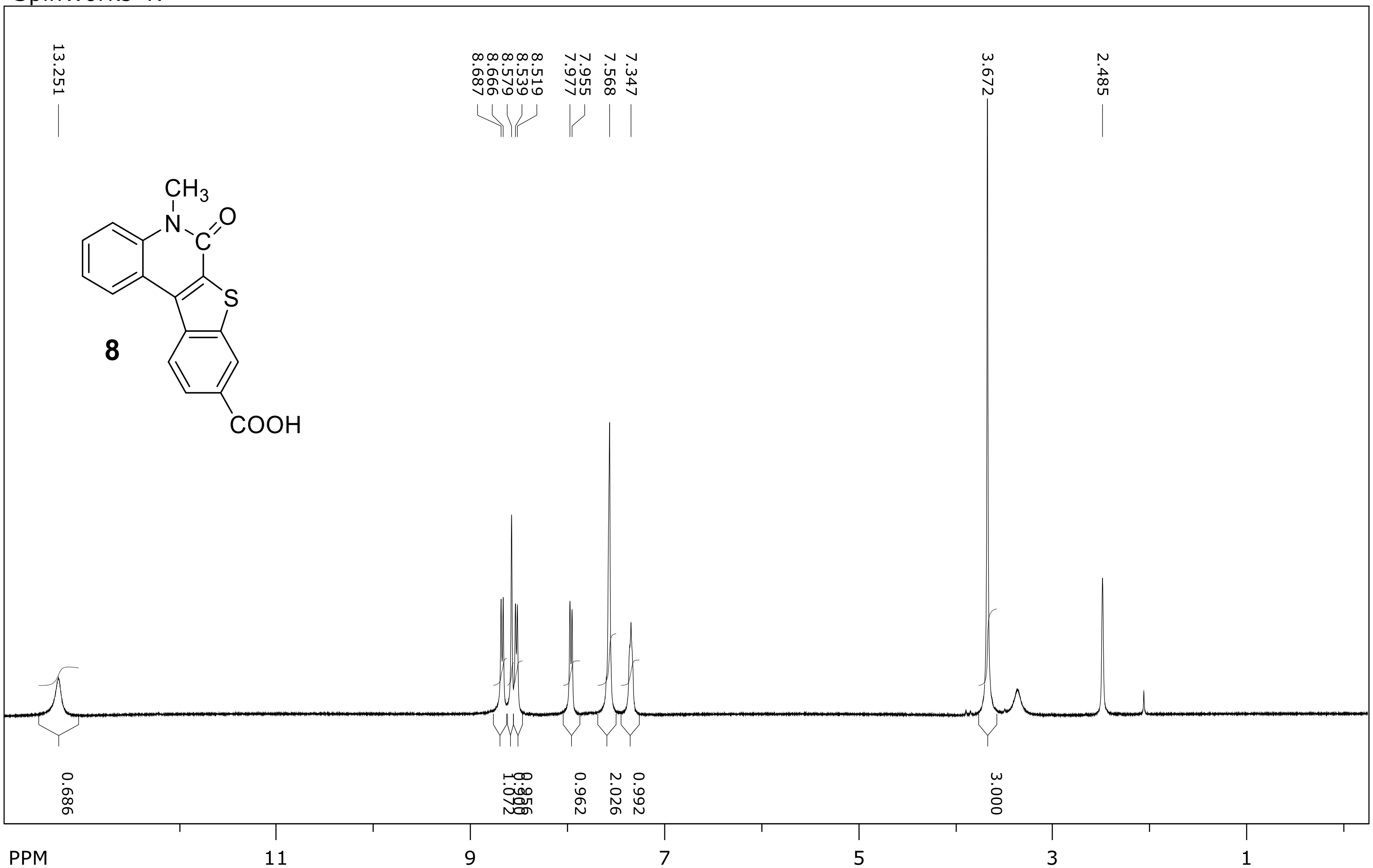
SpinWorks 4:

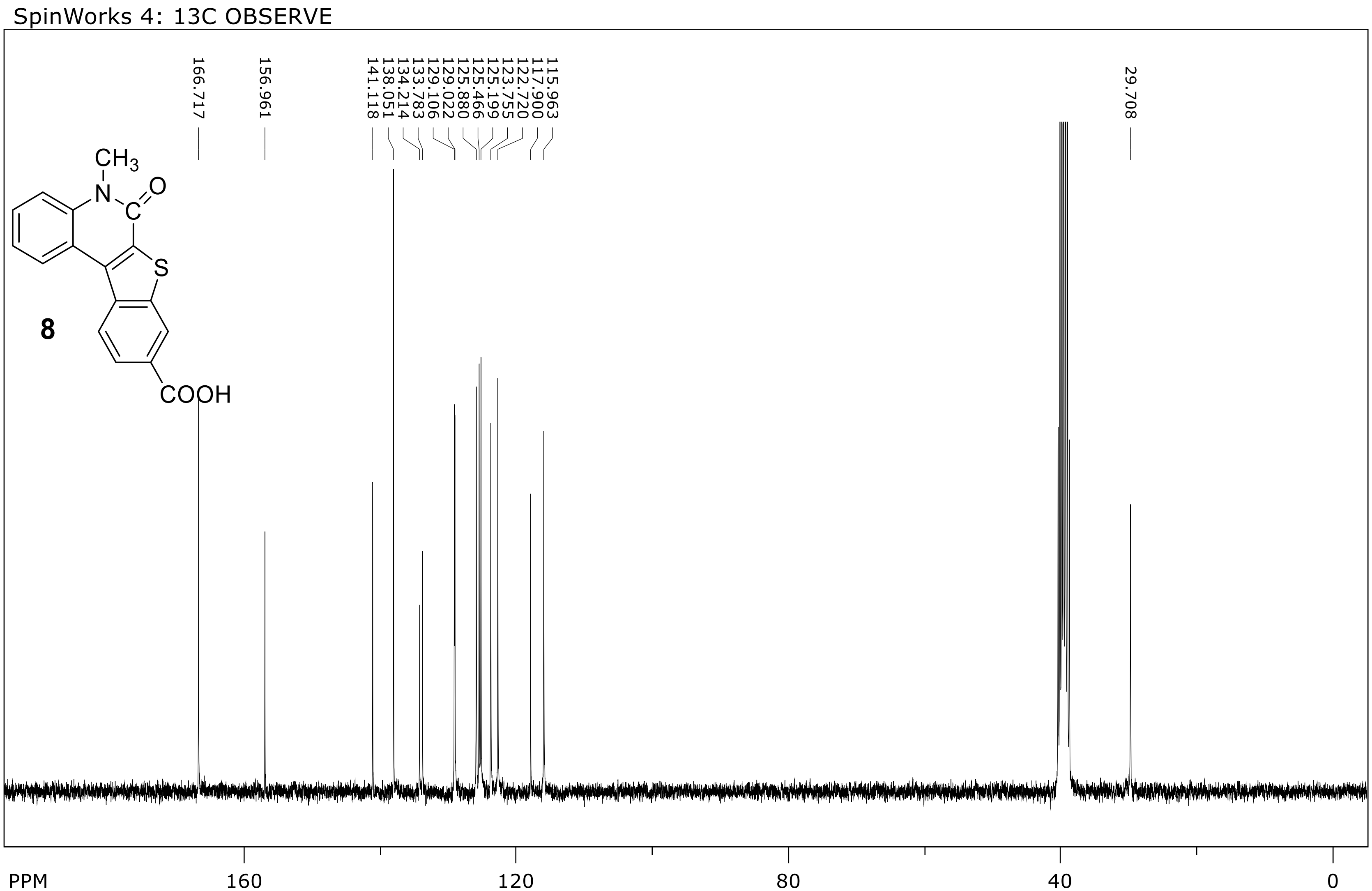

13.231
8.620
7.996
7.975
7.785
7.764
7.340
7.321
7.296
7.278
7.258
7.197
7.179
7.161
3.428
CH3
N
O
S
Cl
7
CO2H
0.733
0.731
0.950
0.926
4.739
3.000
PPM
11
9
7
5
3
1

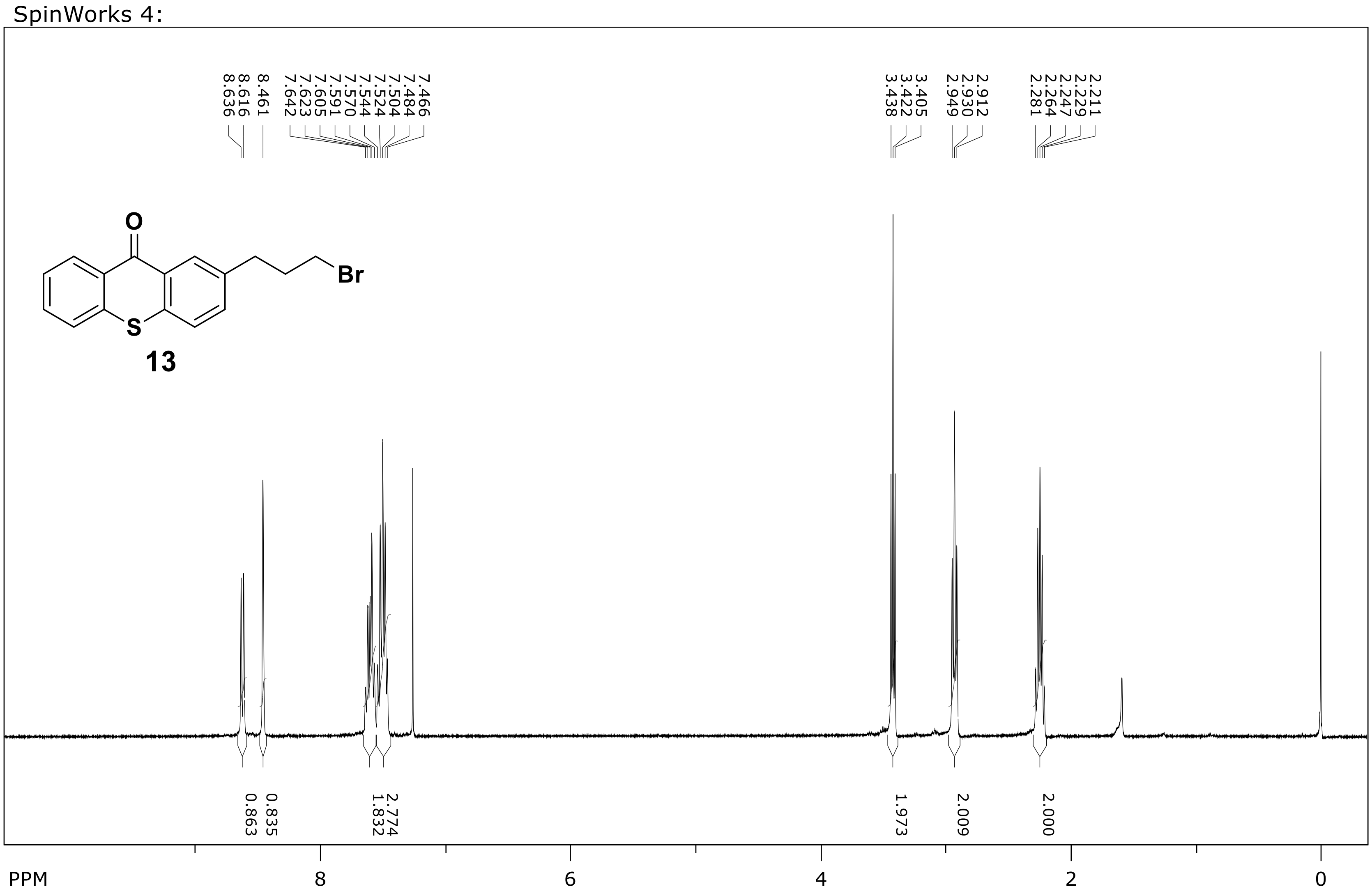
SpinWorks 4:

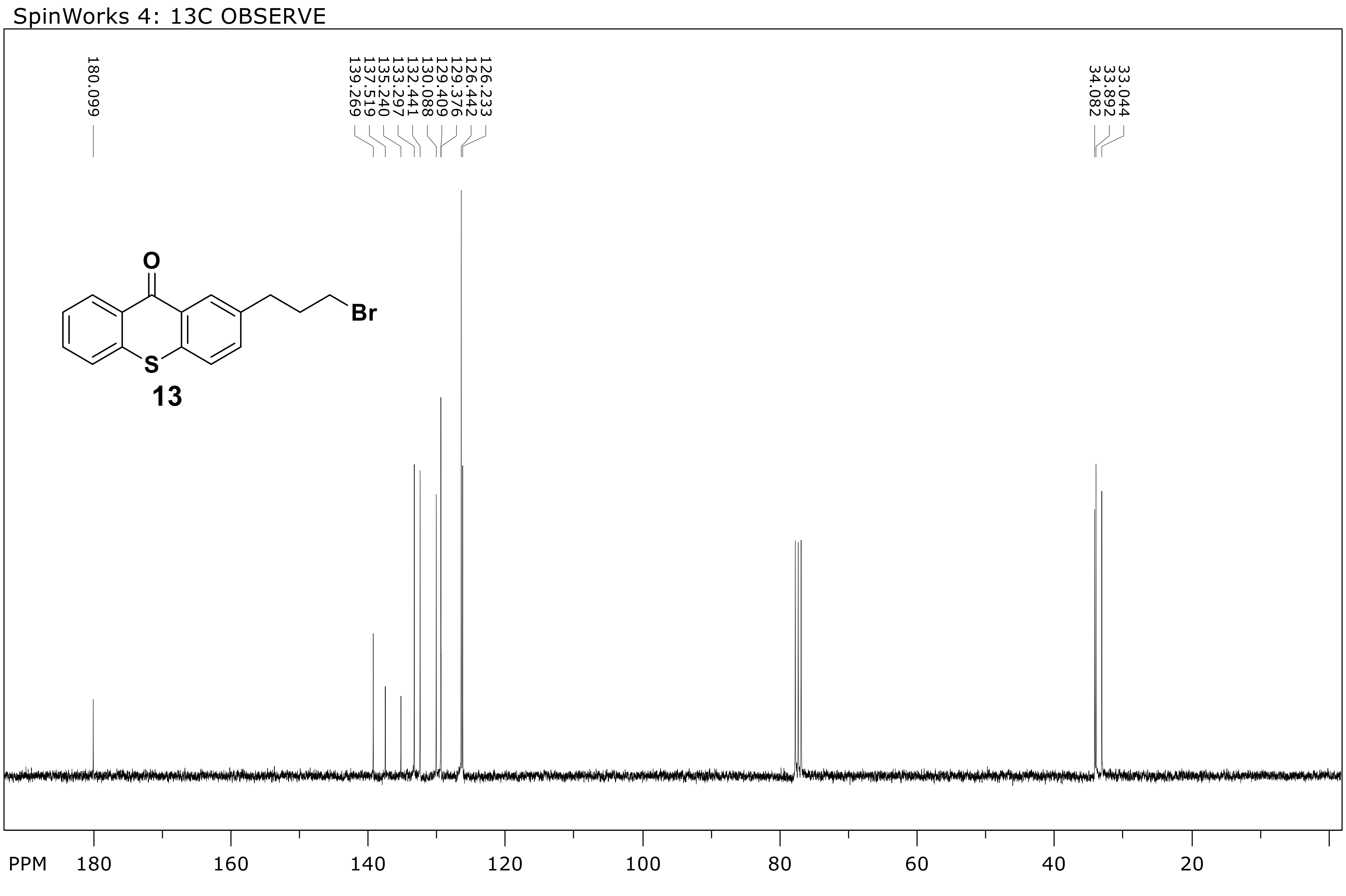

166.795
161.193
142.402
137.579
136.945
135.362
129.115
129.070
127.580
126.655
126.260
125.226
121.965
118.447
39.520
37.607
CH3
N
O
S
Cl
7
CO2H
PPM
160
140
120
100
80
60
40
20
0

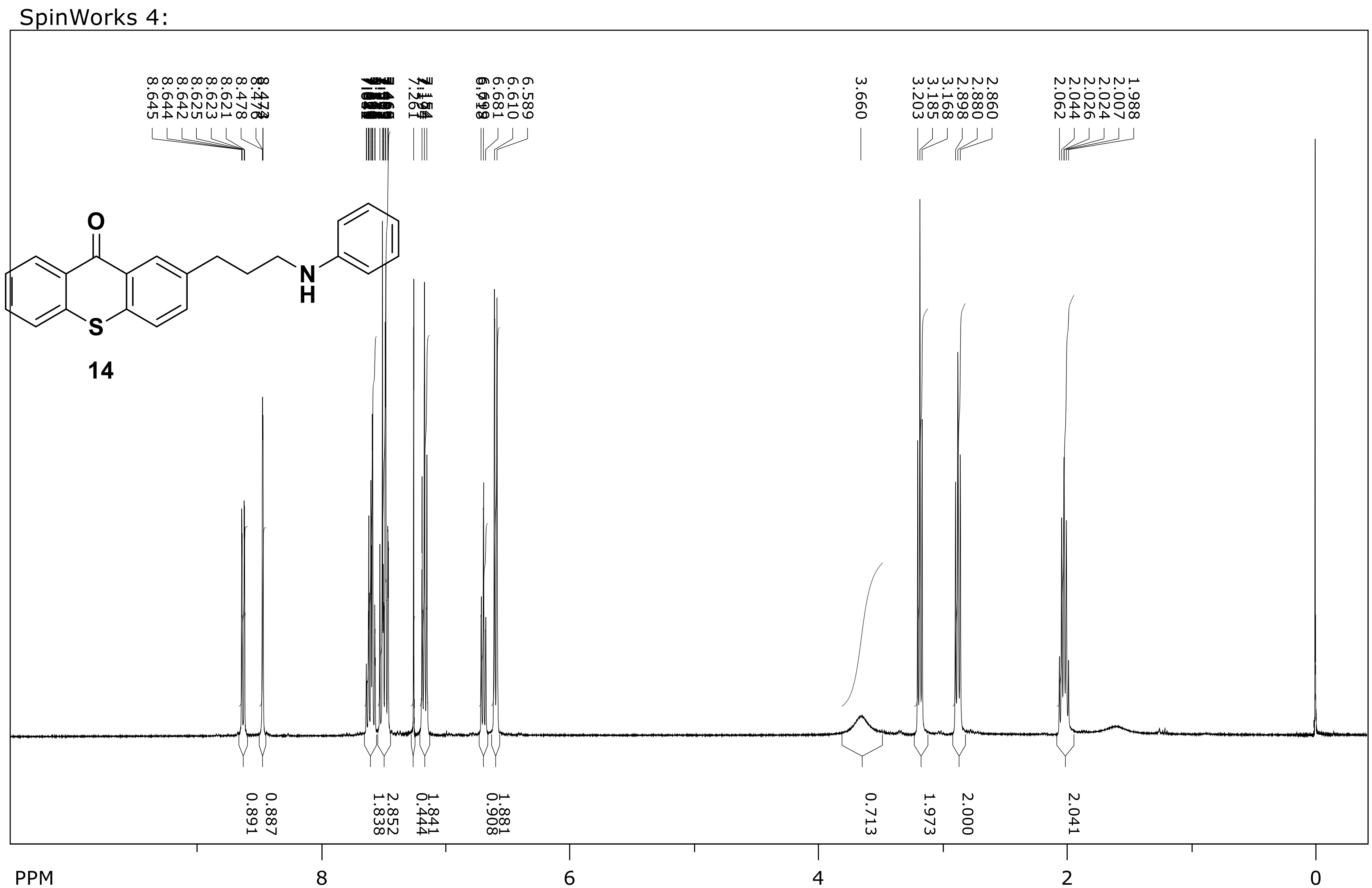
SpinWorks 4:


13.251
8.687
8.666
8.579
8.539
8.519
7.977
7.955
7.568
7.347
3.672
2.485
CH3
N
C
O
S
8
COOH
0.686
0.962
2.026
0.992
3.000
PPM
11
9
7
5
3
1

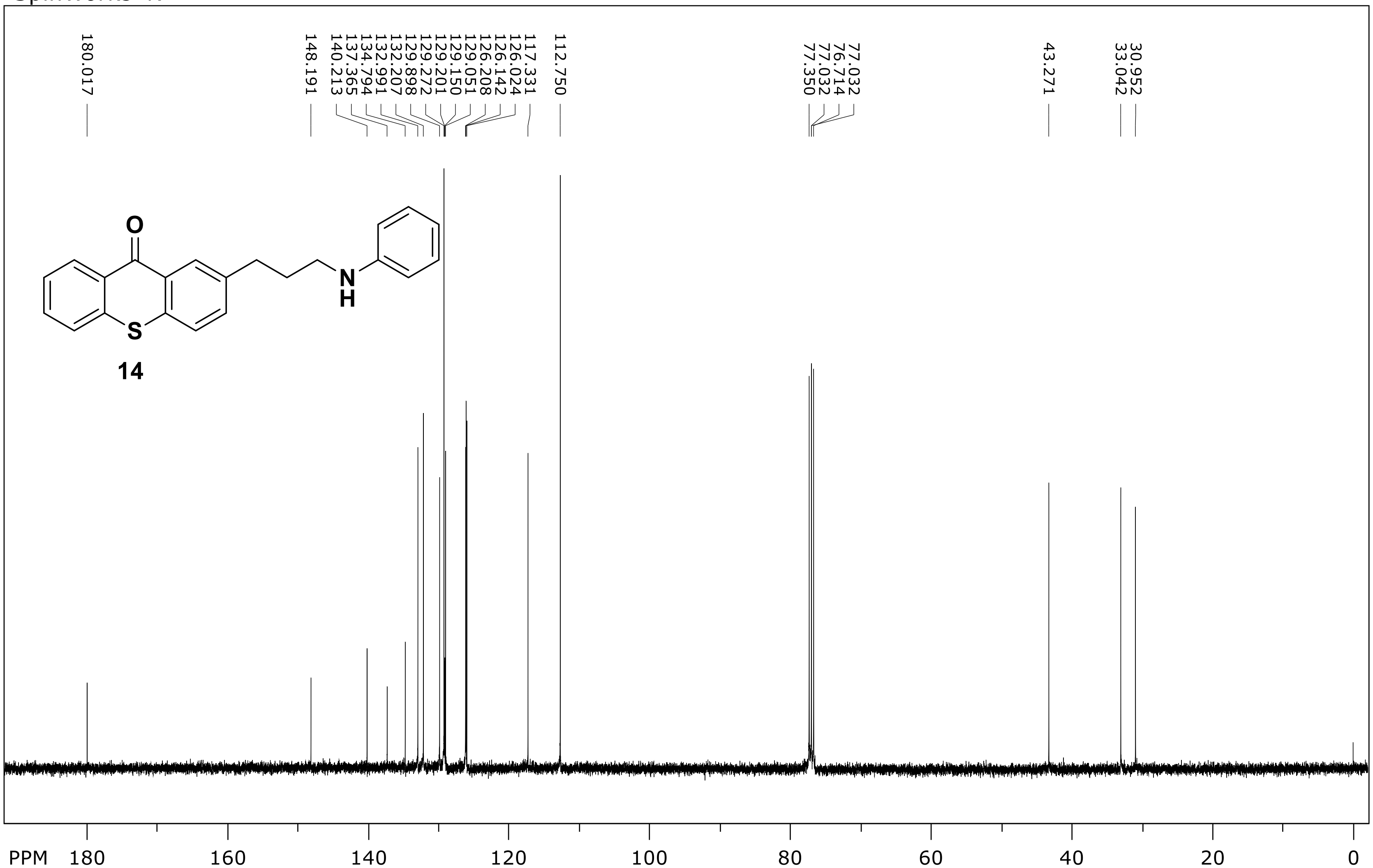

SpinWorks 4: 13C OBSERVE
166.717
156.961
141.118
138.051
134.214
133.783
129.106
129.022
125.880
125.466
125.199
123.755
122.720
117.900
115.963
29.708
CH3
N
C
O
S
COOH
8
PPM
160
120
80
40
0

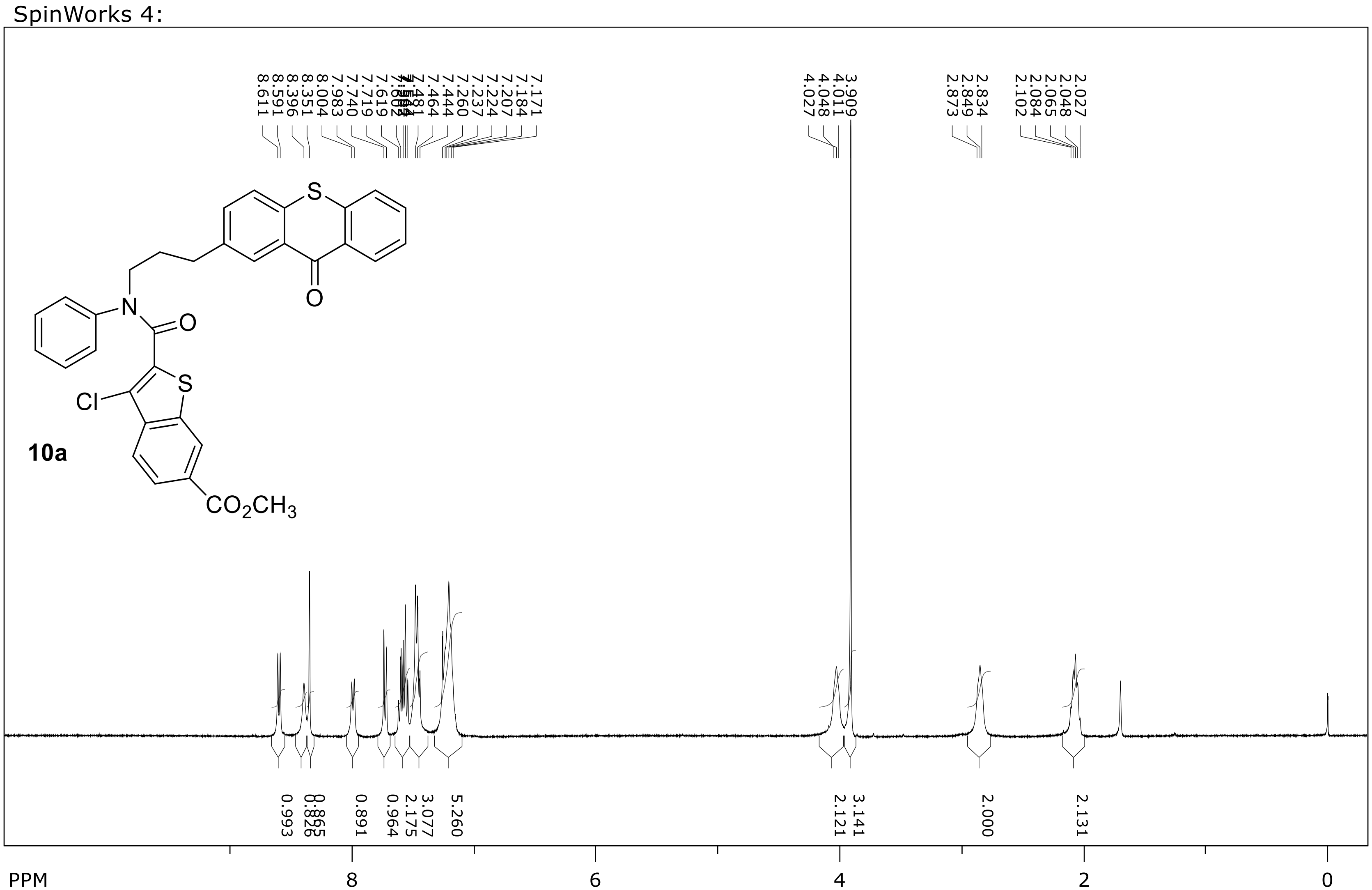

SpinWorks 4:
8.636
8.616
8.461
7.642
7.623
7.605
7.591
7.570
7.544
7.524
7.504
7.484
7.466
3.438
3.422
3.405
2.949
2.930
2.912
2.281
2.264
2.247
2.229
2.211
O
Br
S
13
0.863
0.835
1.832
2.774
1.973
2.009
2.000
PPM
8
6
4
2
0


SpinWorks 4: 13C OBSERVE
180.099
139.269
137.519
135.240
133.297
132.441
130.088
129.409
129.376
126.442
126.233
34.082
33.892
33.044
O
S
Br
13
PPM
180
160
140
120
100
80
60
40
20

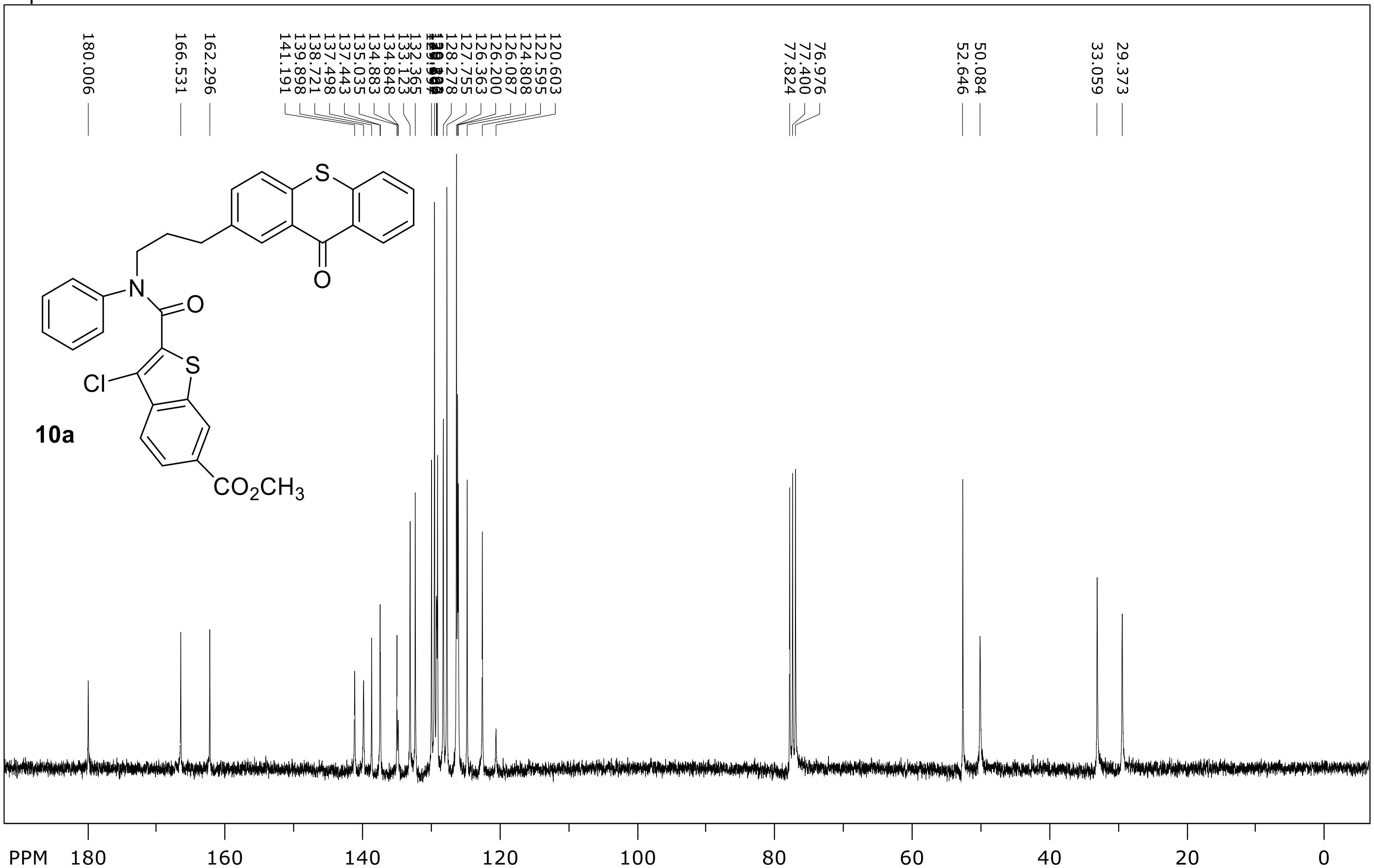

SpinWorks 4:
O
S
N
H
14
PPM
8
6
4
2
0

SpinWorks 4:

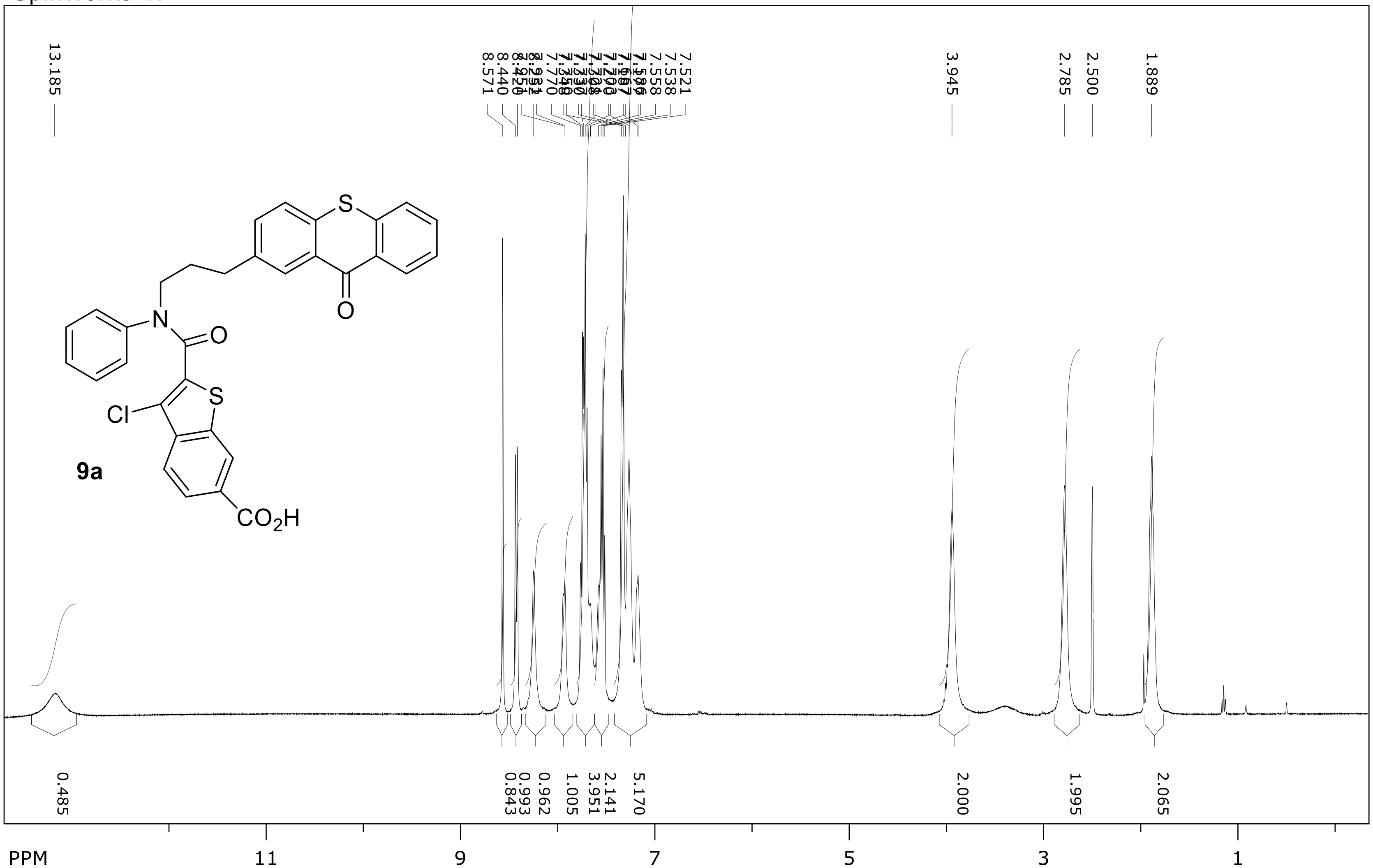

180.017
148.191
140.213
137.365
134.794
132.991
132.207
129.898
129.272
129.201
129.150
129.051
126.208
126.142
126.024
117.331
112.750
77.350
77.032
76.714
77.032
43.271
33.042
30.952
O
S
N
H
14
PPM 180 160 140 120 100 80 60 40 20 0

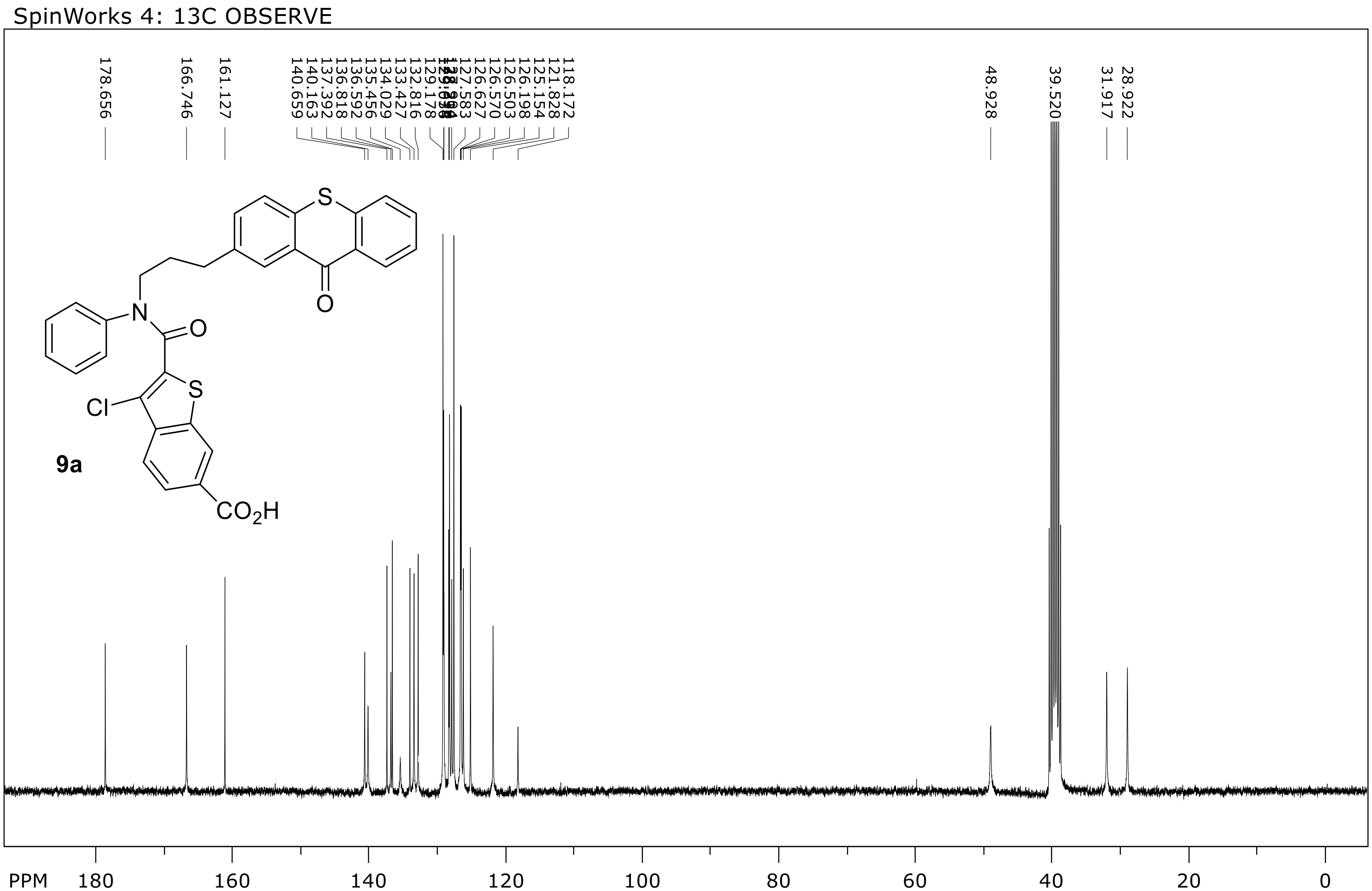

SpinWorks 4:
8.611
8.591
8.396
8.351
8.004
7.983
7.740
7.719
7.619
7.602
7.481
7.464
7.444
7.260
7.237
7.224
7.207
7.184
7.171
4.027
4.048
4.011
3.909
2.873
2.849
2.834
2.102
2.084
2.065
2.048
2.027
10a
Cl
S
N
O
CO2CH3
0.993
0.826
0.865
0.891
0.964
2.175
3.077
5.260
2.121
3.141
2.000
2.131
PPM
8
6
4
2
0

SpinWorks 4: 13C OBSERVE

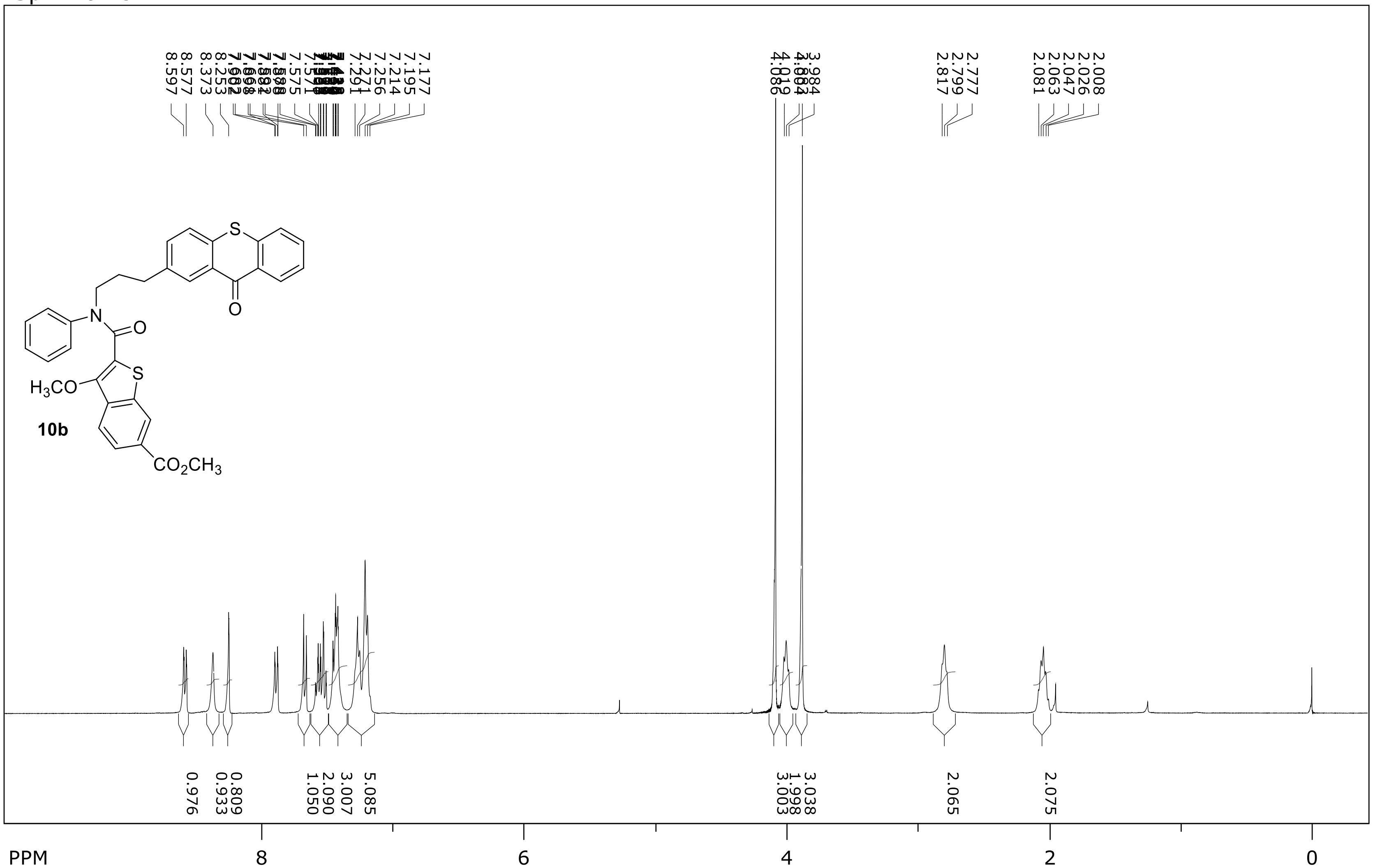


SpinWorks 4:

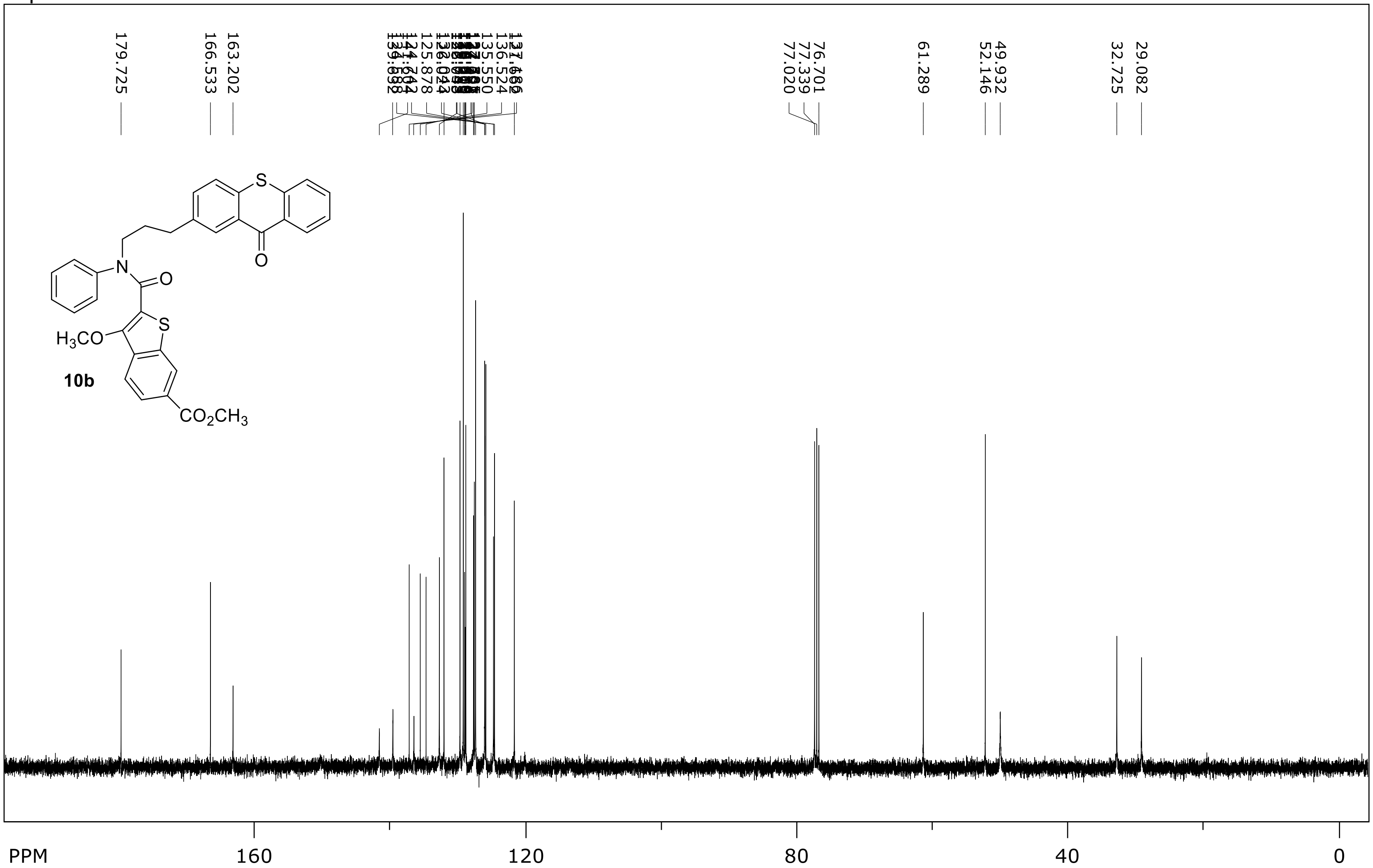

13.185
8.571
8.440
7.770
7.558
7.538
7.521
3.945
2.785
2.500
1.889
S
O
N
Cl
CO2H
9a
0.485
0.843
0.993
0.962
1.005
3.951
2.141
5.170
2.000
1.995
2.065
PPM
11
9
7
5
3
1


SpinWorks 4: 13C OBSERVE
178.656
166.746
161.127
140.659
140.163
137.392
136.818
136.592
135.456
134.029
133.427
132.816
129.178
127.583
126.627
126.570
126.503
126.198
125.154
121.828
118.172
48.928
39.520
31.917
28.922
S
O
N
O
S
Cl
9a
CO2H
PPM 180 160 140 120 100 80 60 40 20 0

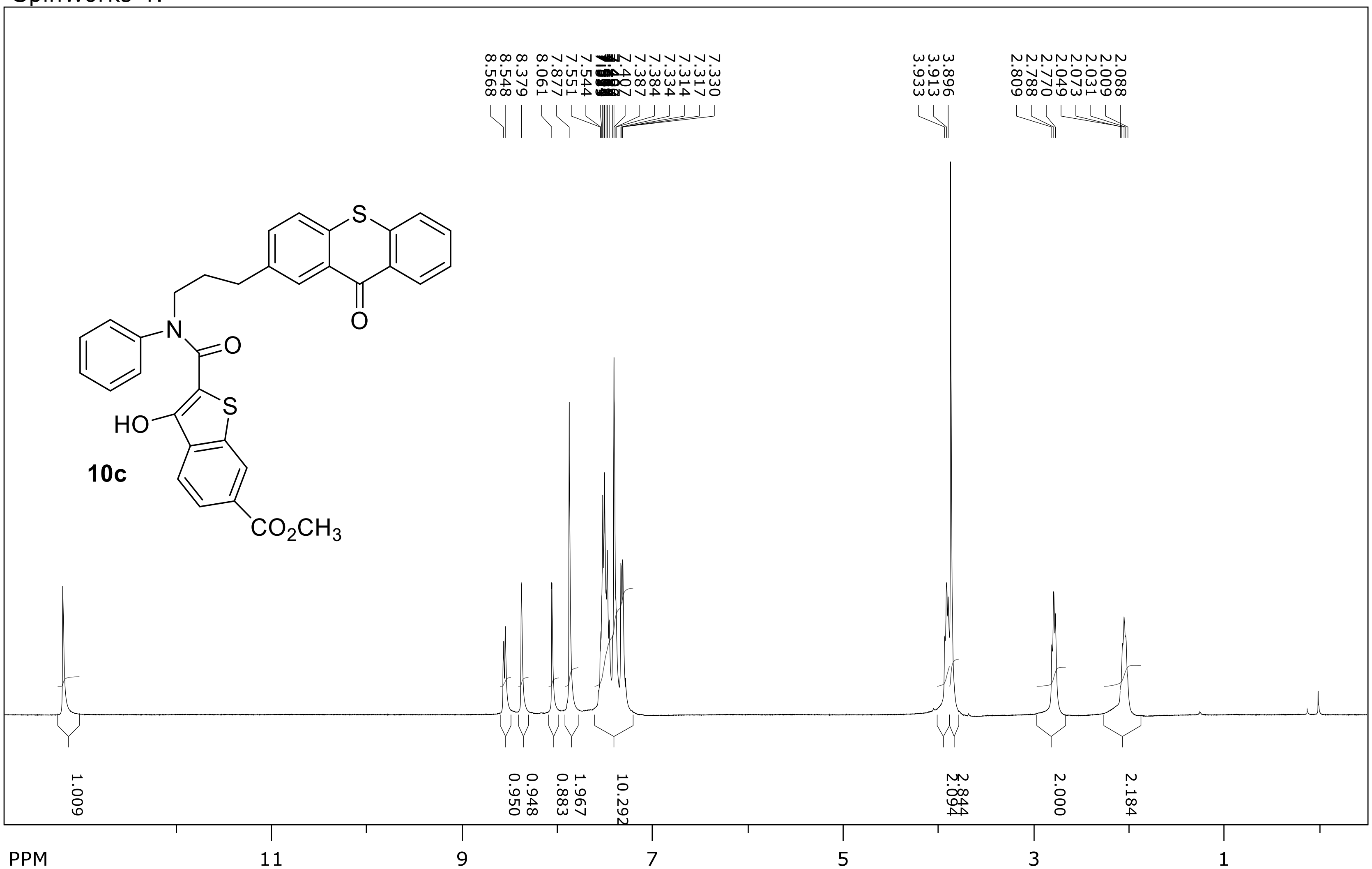
SpinWorks 4:



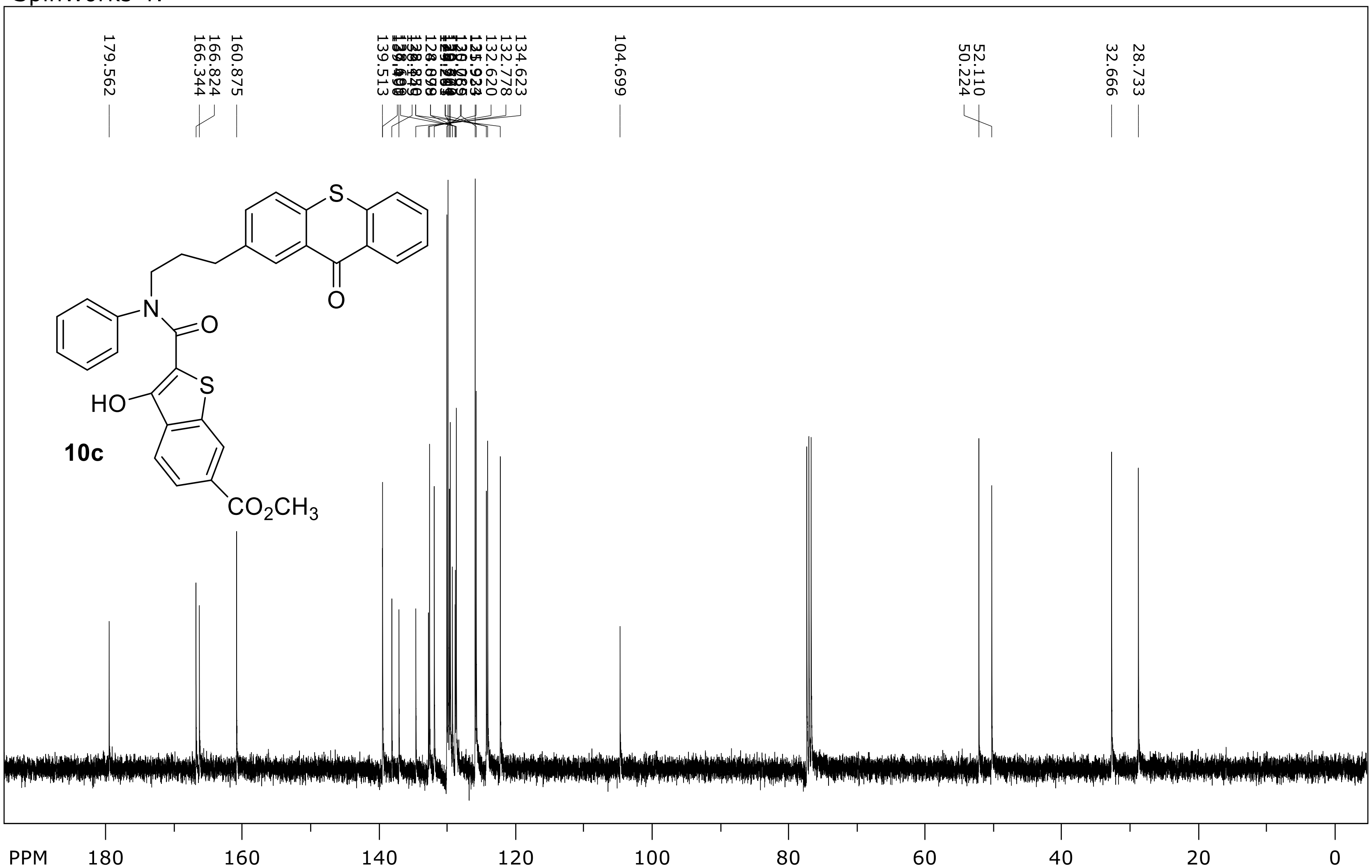
SpinWorks 4:

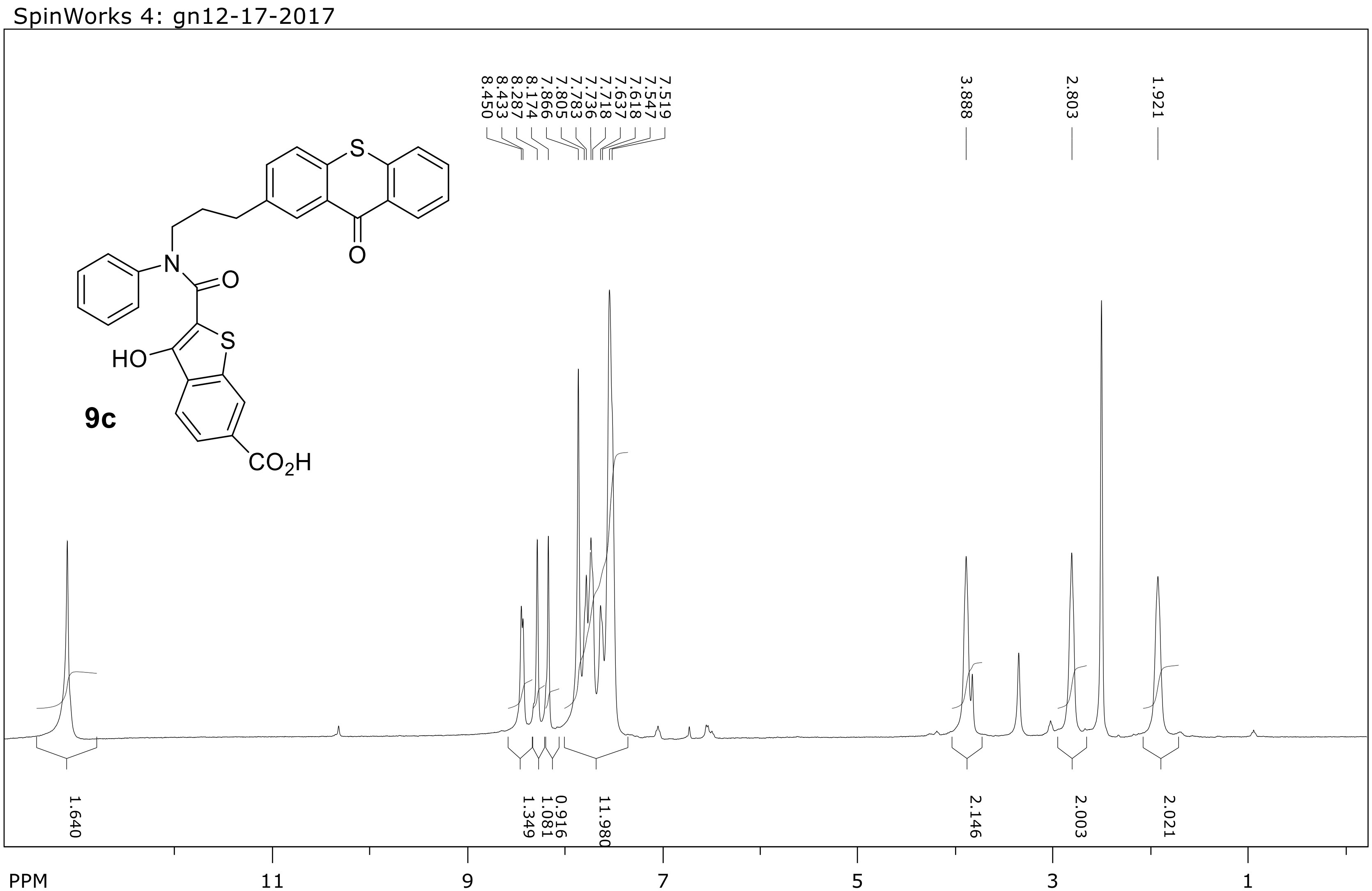

179.725
166.533
163.202
61.289
52.146
49.932
32.725
29.082
77.020
77.339
76.701
S
N
O
H3CO
10b
CO2CH3
PPM
160
120
80
40
0

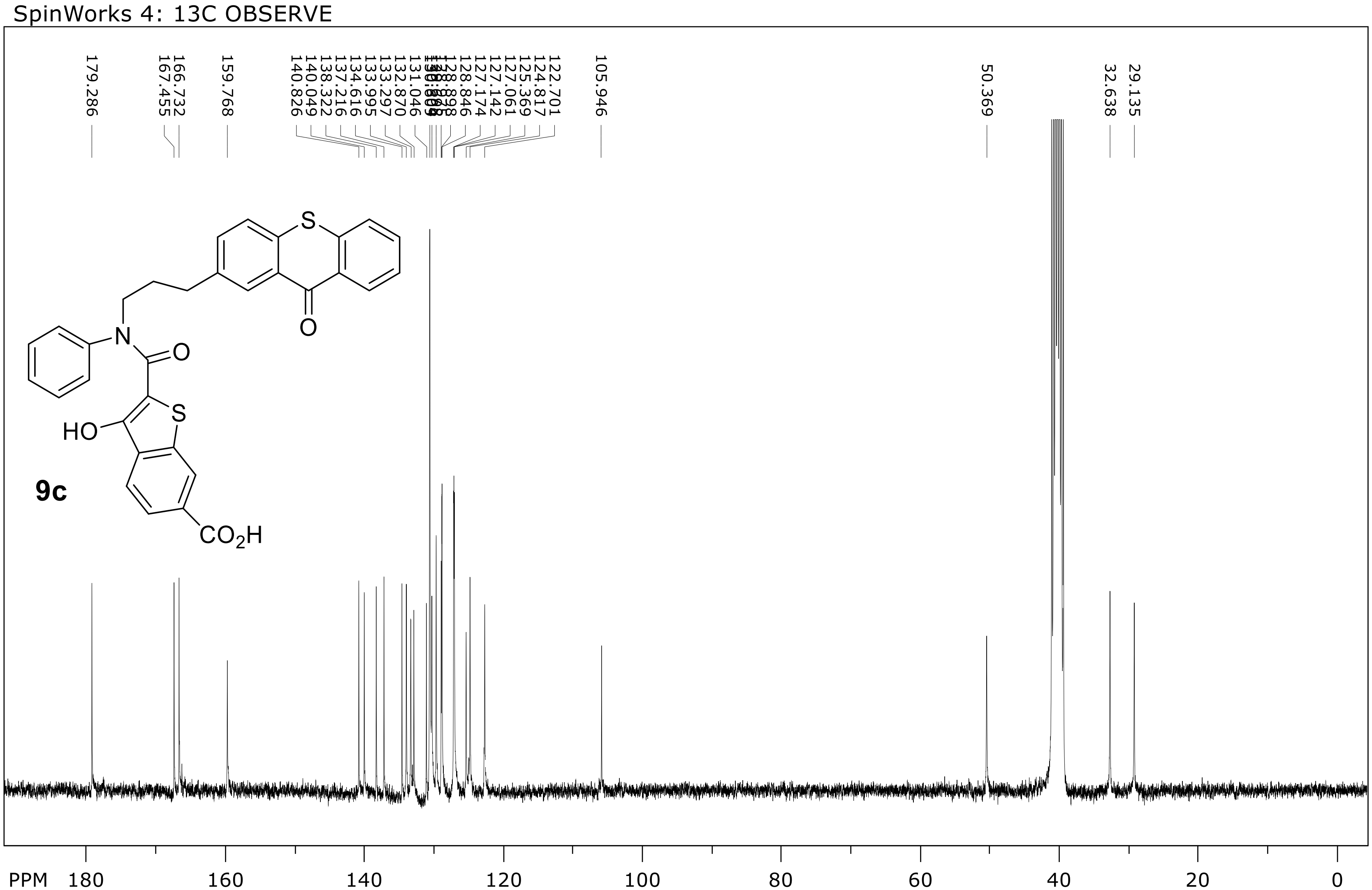
SpinWorks 4:

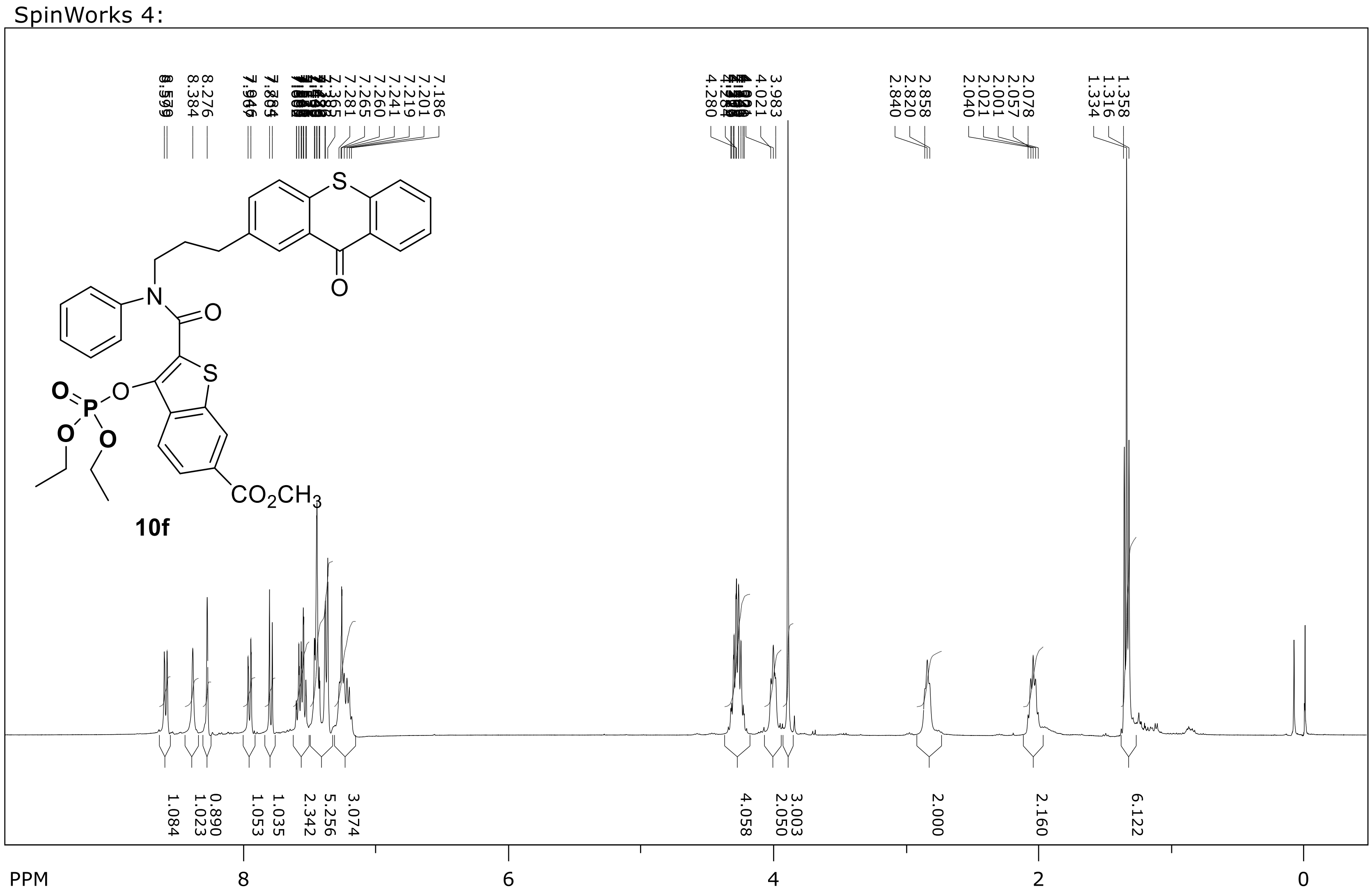

8.568
8.548
8.379
8.061
7.877
7.551
7.544
7.407
7.387
7.384
7.334
7.314
7.317
7.330
3.933
3.913
3.896
2.809
2.788
2.770
2.049
2.073
2.031
2.009
2.088
S
O
N
O
S
HO
10c
CO_2CH_3
1.009
0.950
0.948
0.883
1.967
10.292
2.094
2.844
2.000
2.184
PPM
11
9
7
5
3
1

SpinWorks 4:

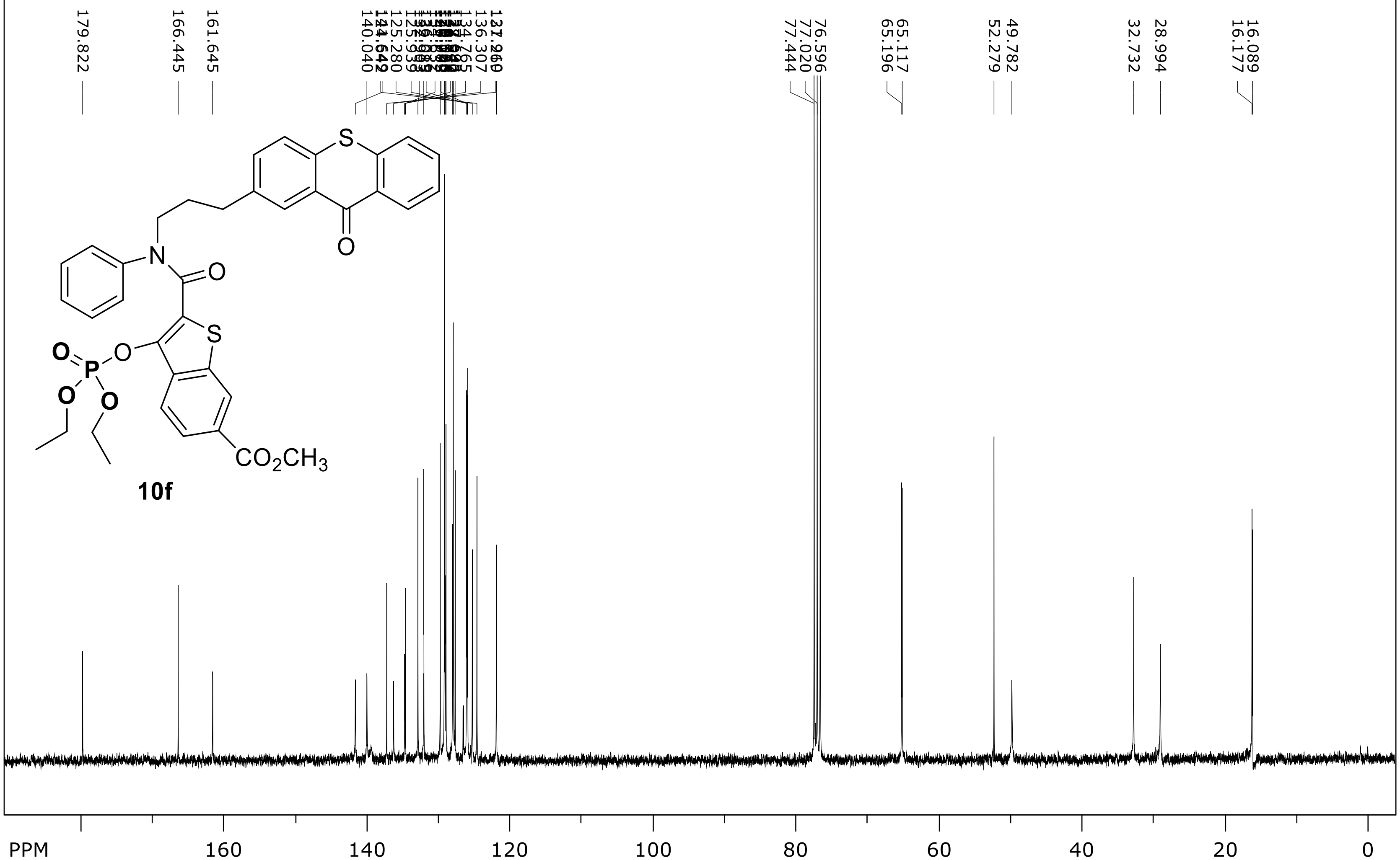

179.562
166.824
166.344
160.875
139.513
134.623
132.778
132.620
104.699
52.110
50.224
32.666
28.733
S
O
N
O
S
HO
10c
CO_2CH_3
PPM
180
160
140
120
100
80
60
40
20
0


SpinWorks 4: gn12-17-2017
8.450
8.433
8.287
8.174
7.866
7.805
7.783
7.783
7.736
7.718
7.637
7.637
7.618
7.547
7.519
3.888
2.803
1.921
9c
HO
S
N
O
S
O
CO2H
1.640
1.349
1.081
0.916
11.980
2.146
2.003
2.021
PPM
11
9
7
5
3
1

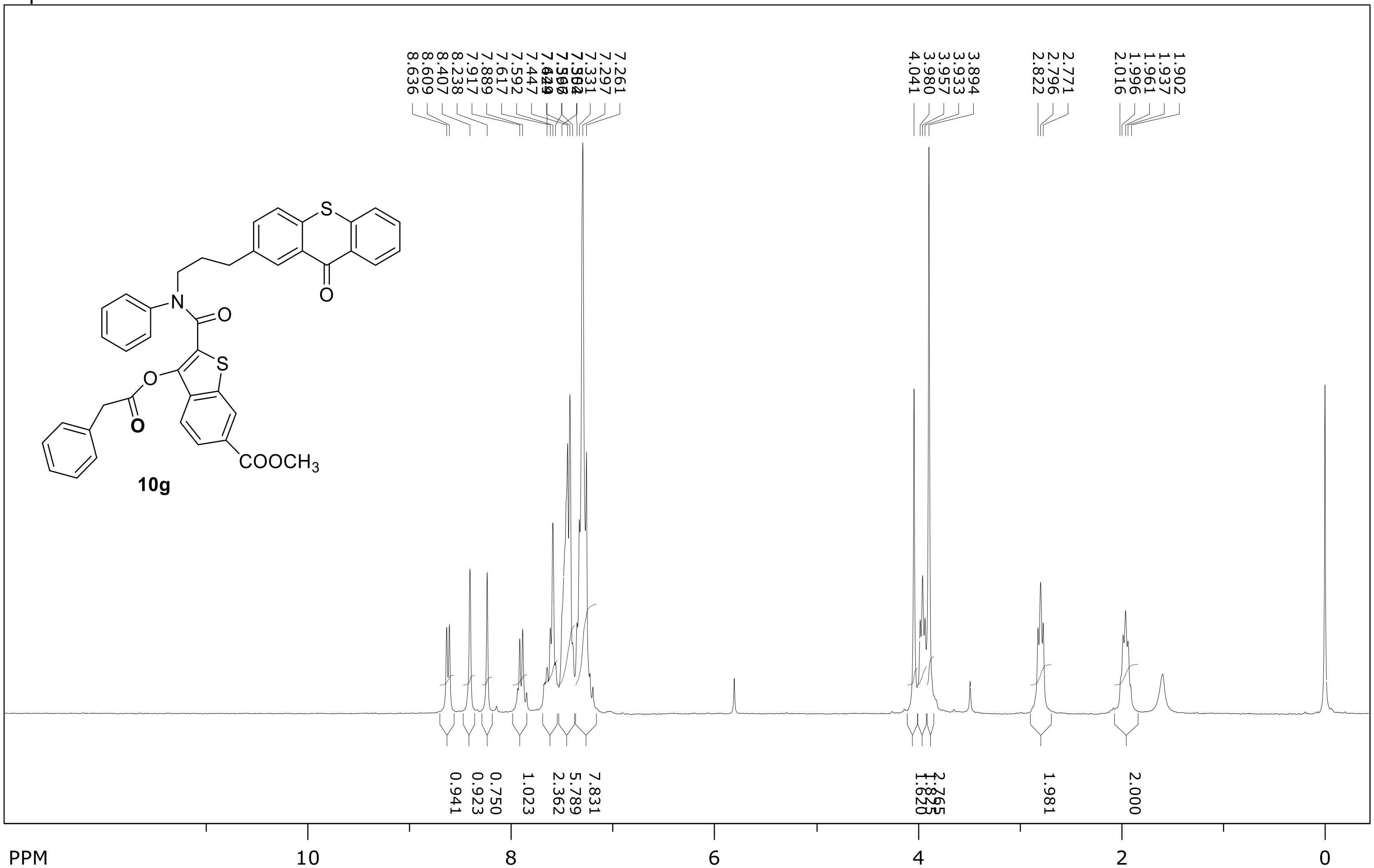

SpinWorks 4: 13C OBSERVE
179.286
166.732
167.455
159.768
140.826
140.049
138.322
137.216
134.616
133.995
133.297
132.870
131.046
128.898
128.846
127.174
127.142
127.061
125.369
124.817
122.701
105.946
50.369
32.638
29.135
HO
S
N
O
CO2H
9c
PPM 180 160 140 120 100 80 60 40 20 0


SpinWorks 4:
8.276
8.384
7.260
7.241
7.219
7.201
7.186
4.021
3.983
4.280
2.858
2.820
2.840
2.078
2.057
2.040
2.021
2.001
1.358
1.316
1.334
S
N
O
S
O
P
O
O
O
CO_2CH_3
10f
1.084
1.023
0.890
1.053
1.035
2.342
5.256
3.074
4.058
2.050
3.003
2.000
2.160
6.122
PPM
8
6
4
2
0

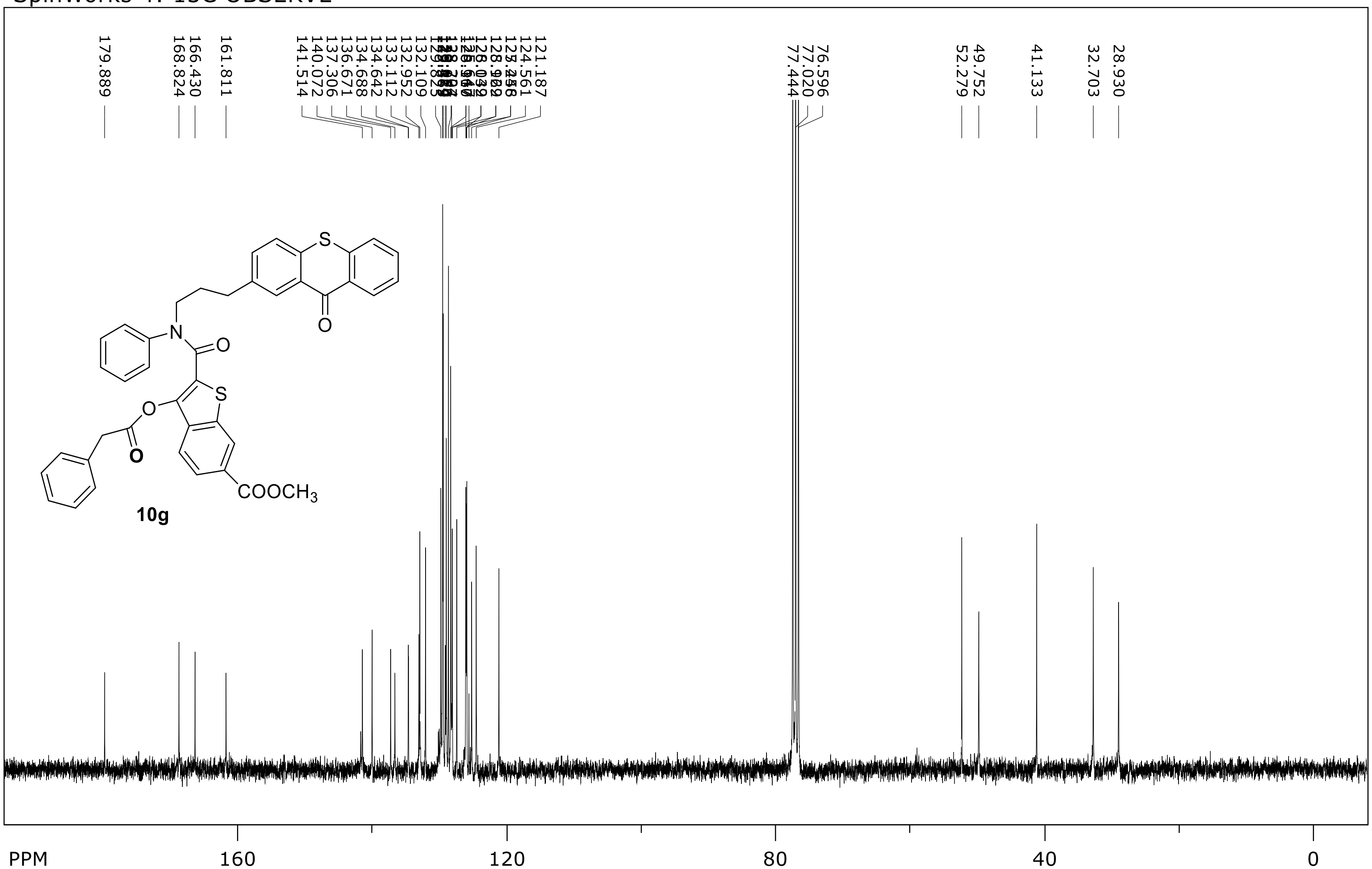
SpinWorks 4: 13C OBSERVE



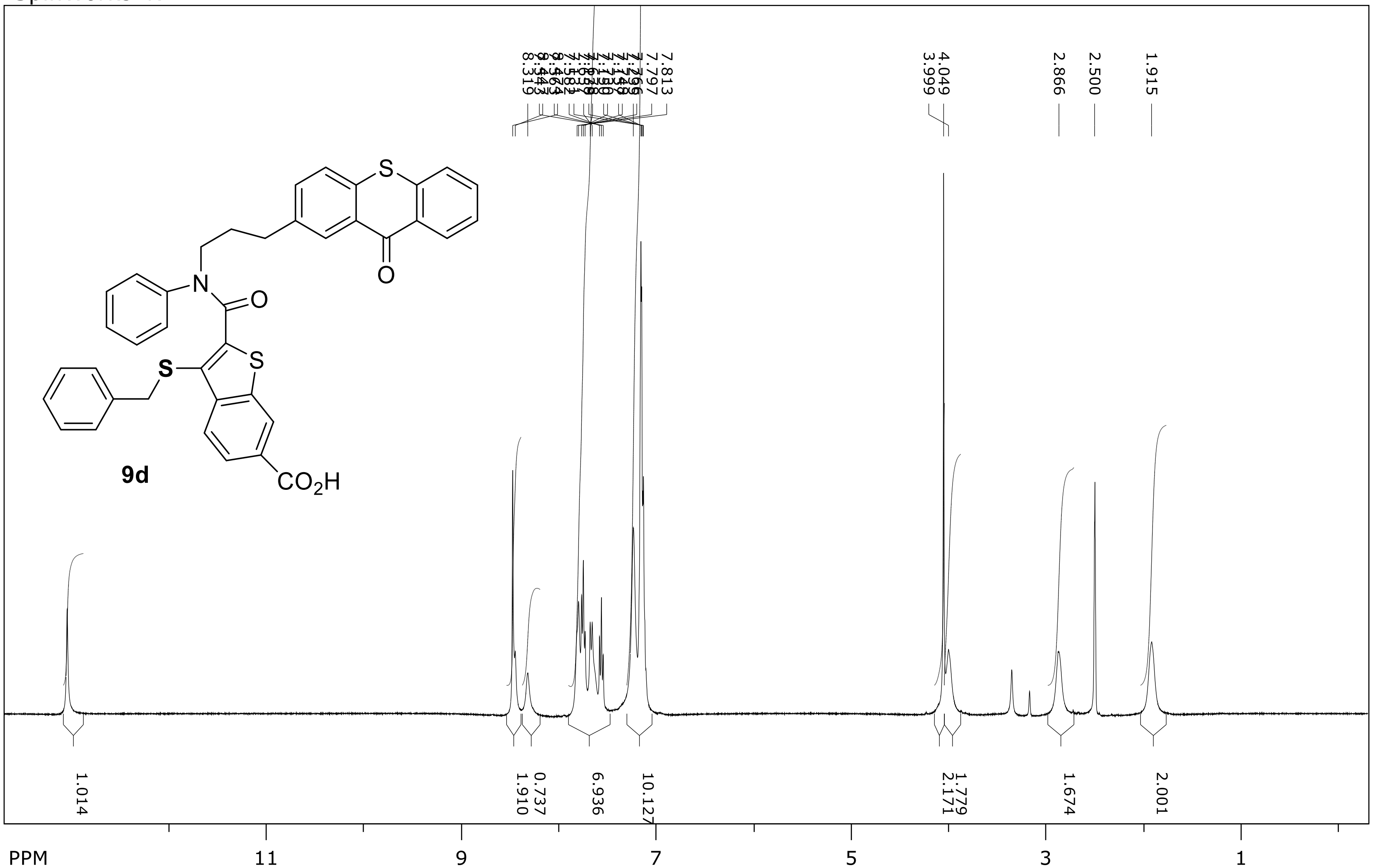
SpinWorks 4: STANDARD 1H OBSERVE



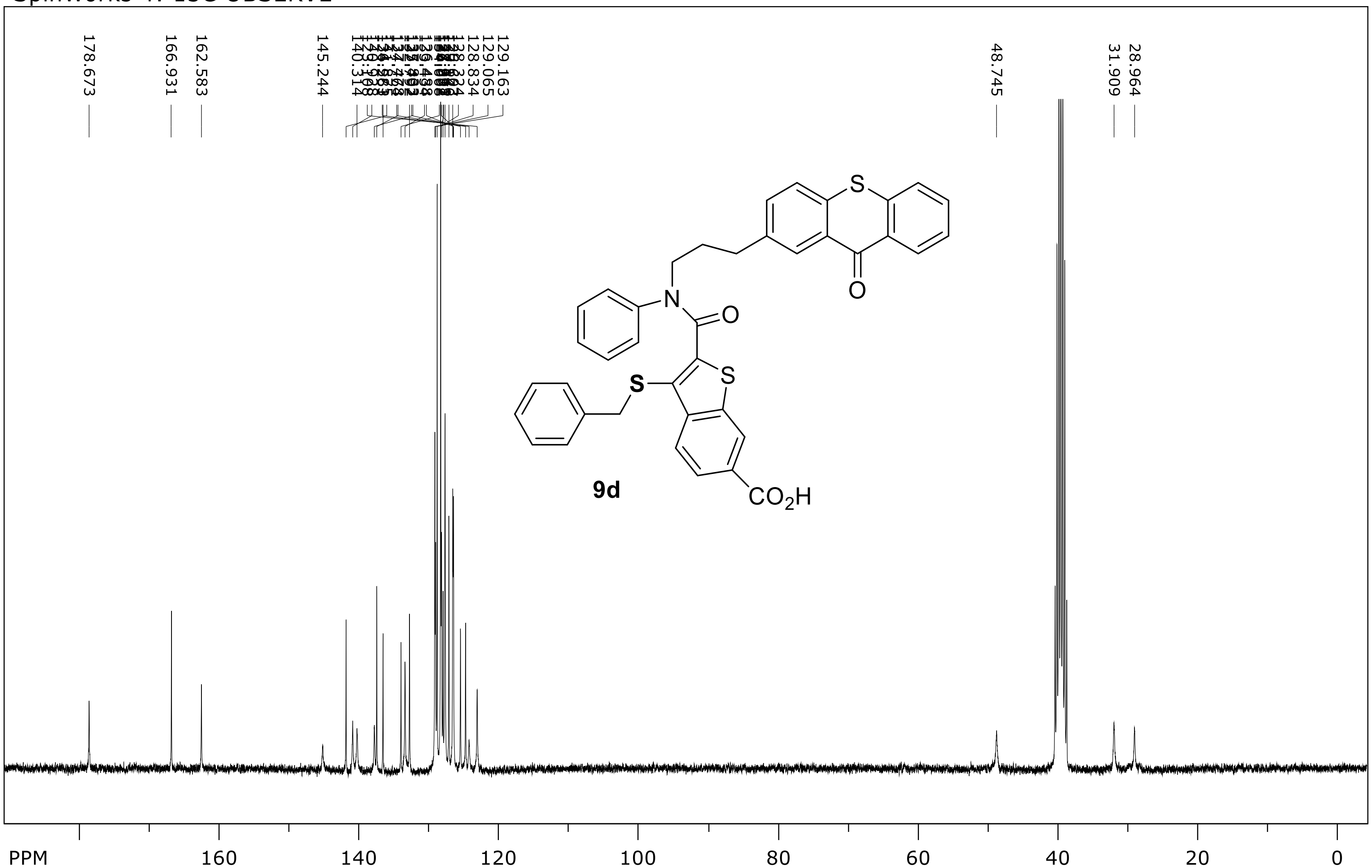
SpinWorks 4: 13C OBSERVE

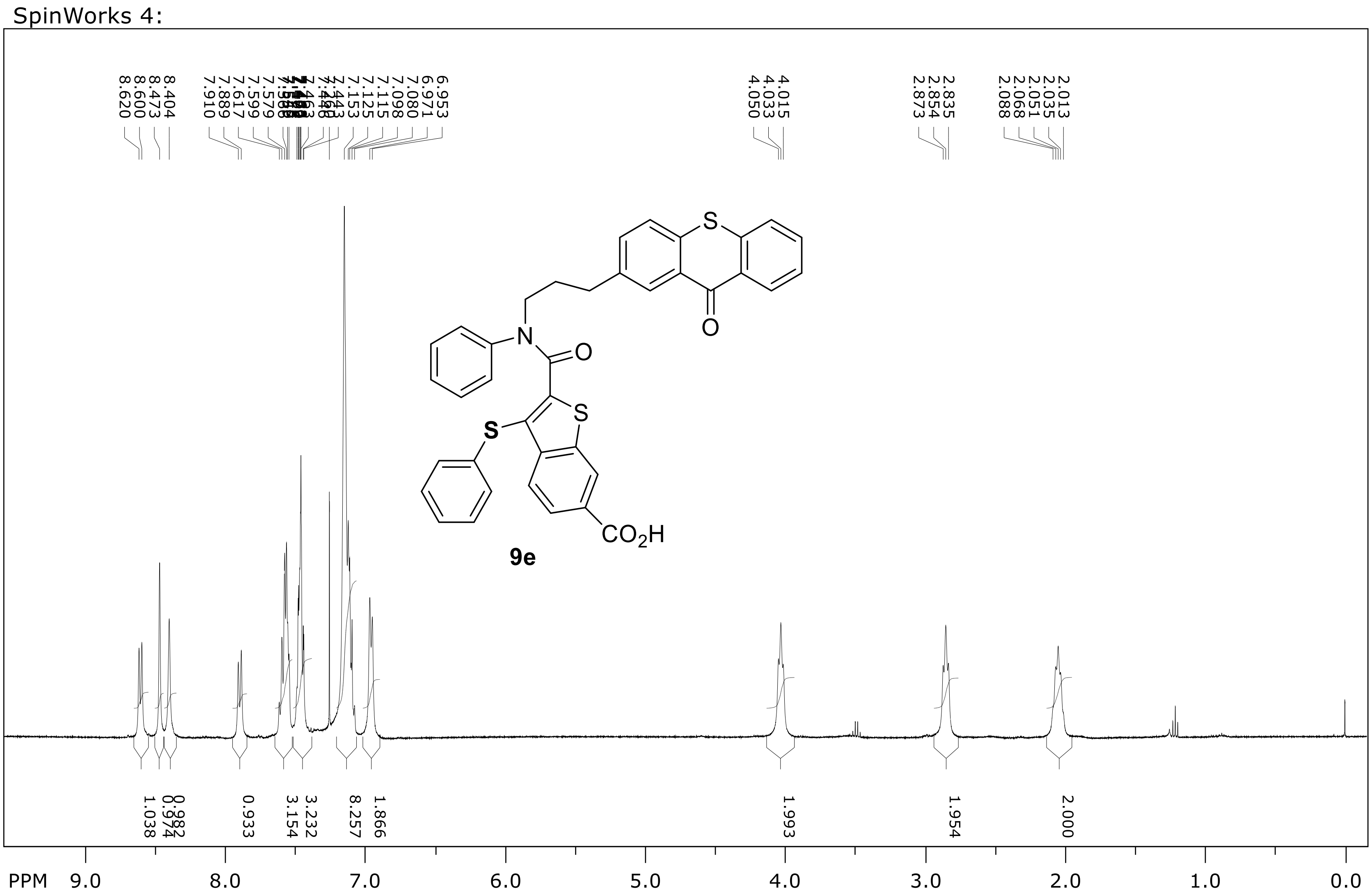


SpinWorks 4:


9d
CO2H
PPM
11
9
7
5
3
1
4.049
3.999
2.866
2.500
1.915
1.014
1.910
0.737
6.936
10.127
2.171
1.779
1.674
2.001

SpinWorks 4: 13C OBSERVE




SpinWorks 4:
8.620
8.600
8.473
8.404
7.910
7.889
7.617
7.599
7.579
7.463
7.153
7.125
7.115
7.098
7.080
6.971
6.953
4.050
4.033
4.015
2.873
2.854
2.835
2.088
2.068
2.051
2.035
2.013
S
N
O
S
S
CO2H
9e
1.038
0.974
0.982
0.933
3.154
3.232
8.257
1.866
1.993
1.954
2.000
PPM
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8.0
7.0
6.0
5.0
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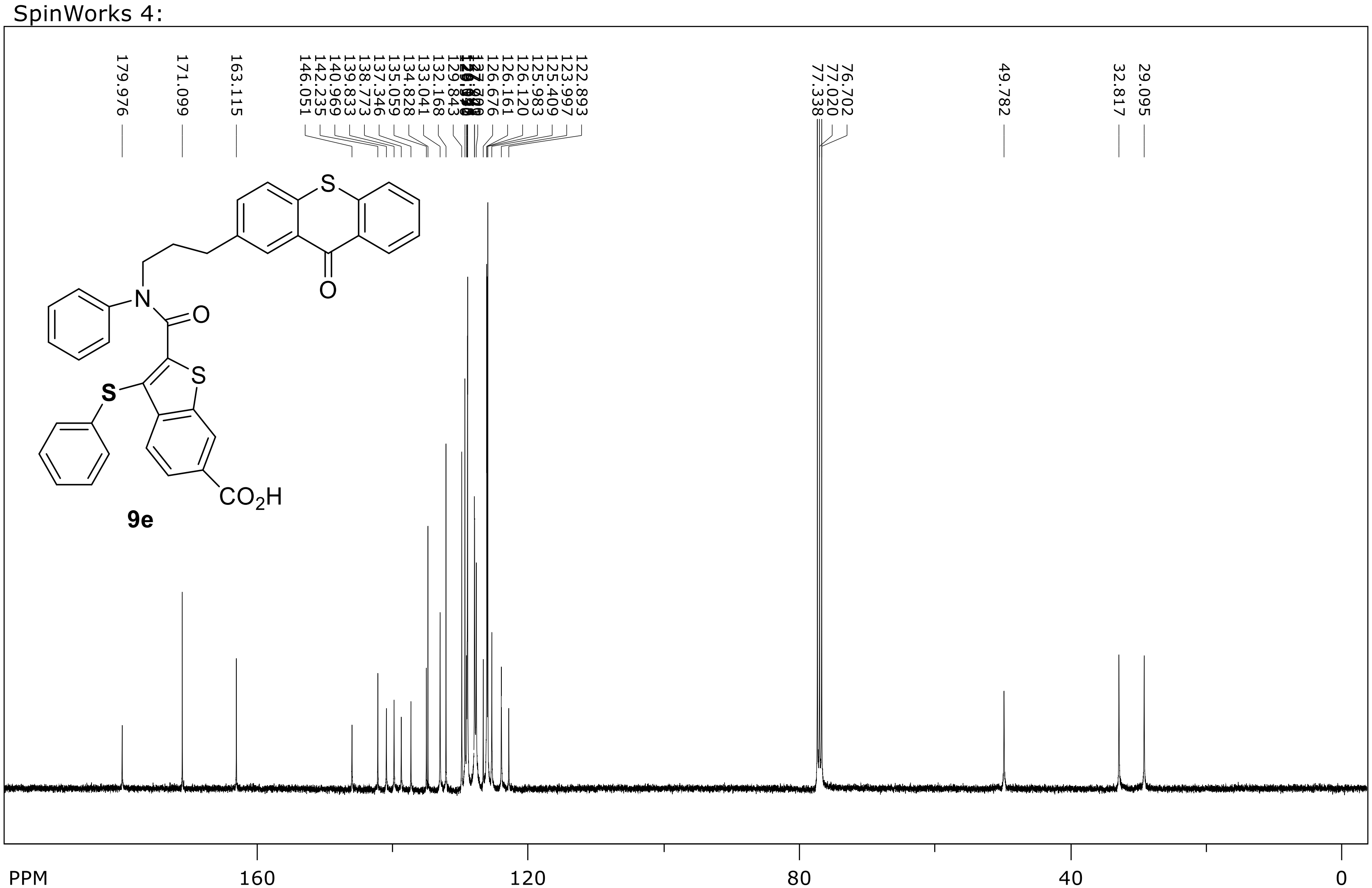
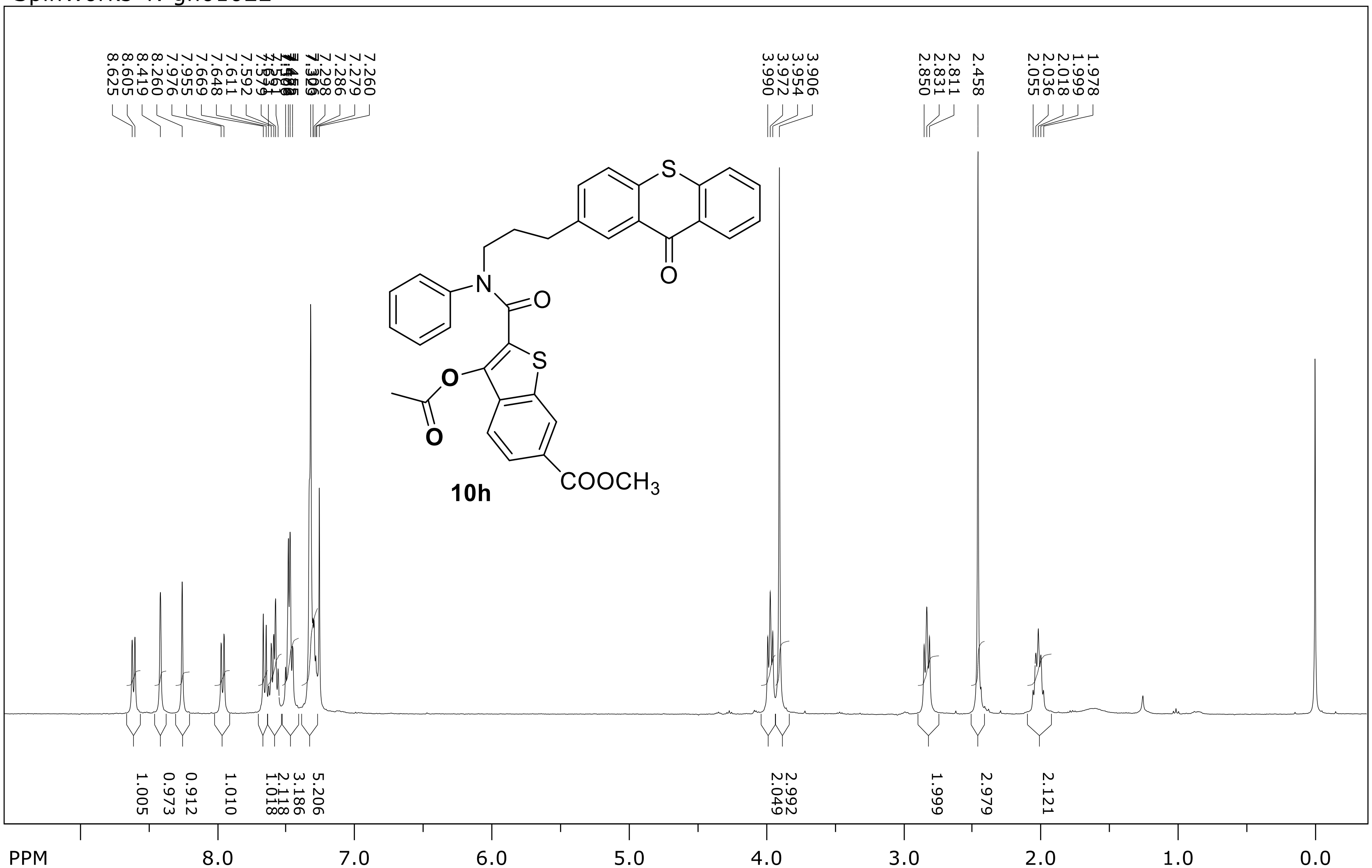
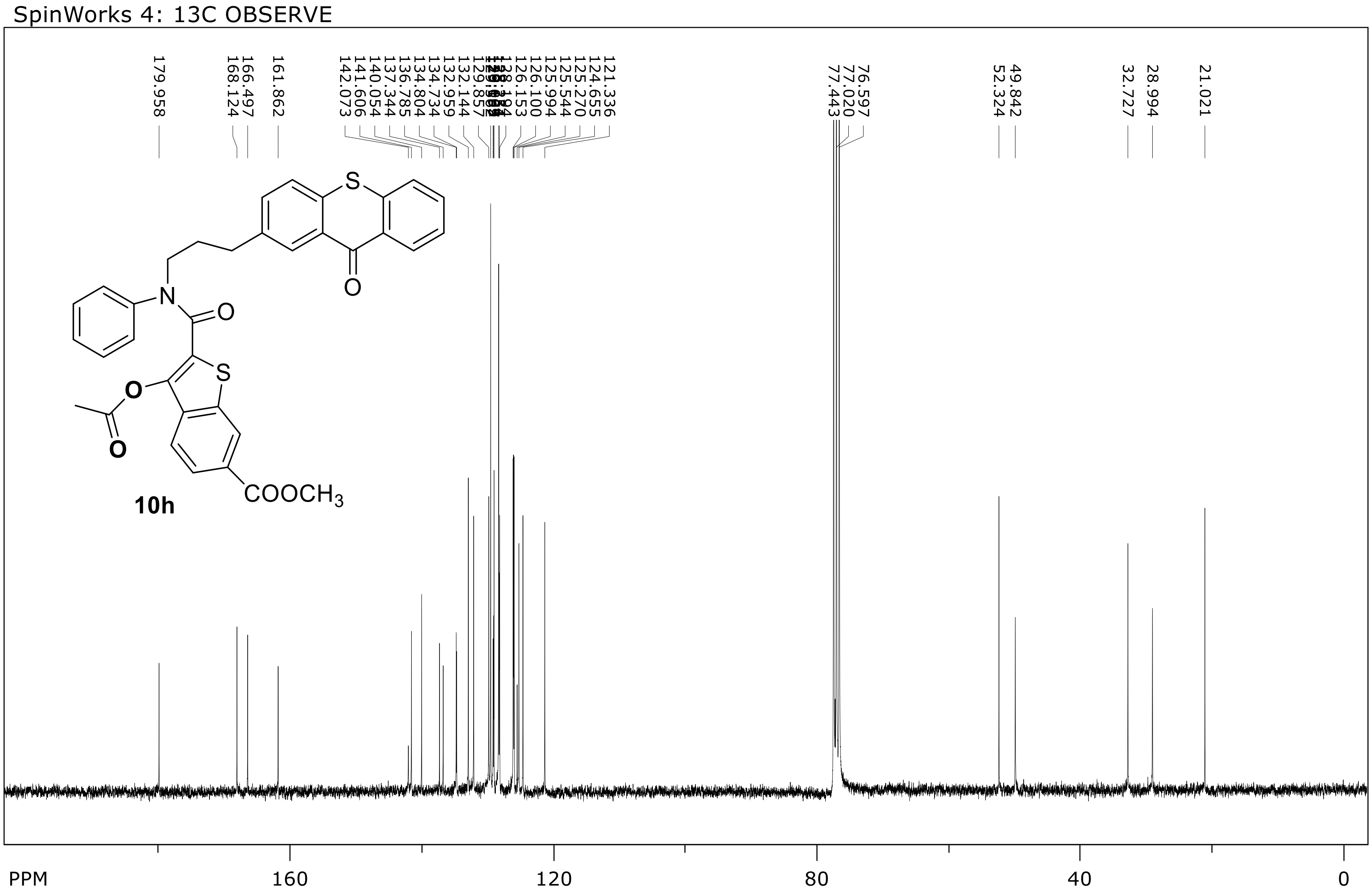
2.0
1.0
0.0

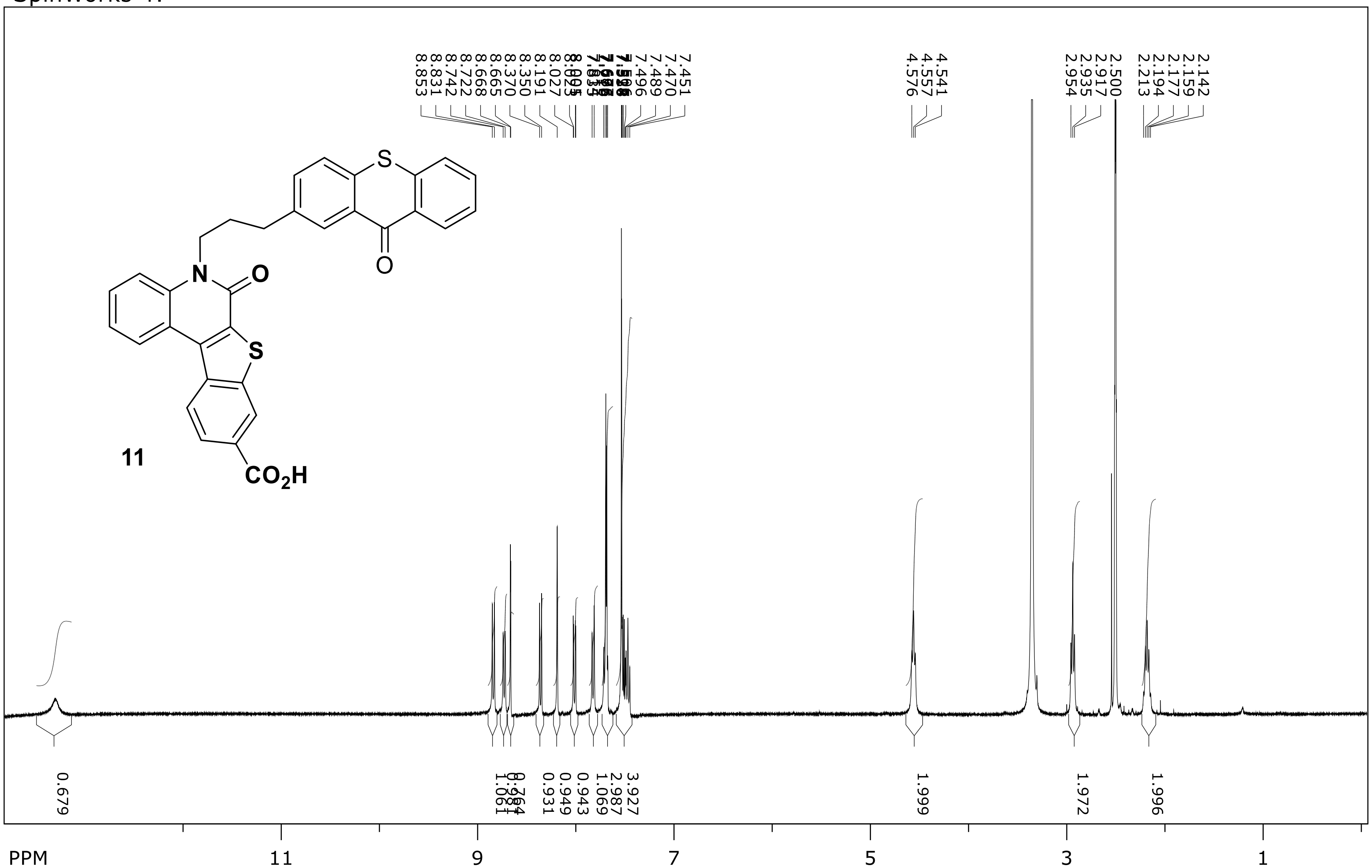

SpinWorks 4:
179.976
171.099
163.115
146.051
142.235
140.969
139.833
138.773
137.346
135.059
134.828
133.041
132.168
129.843
126.676
126.161
126.120
125.983
125.409
123.997
122.893
77.338
77.020
76.702
49.782
32.817
29.095
S
O
N
O
S
S
CO2H
9e
PPM
160
120
80
40
0

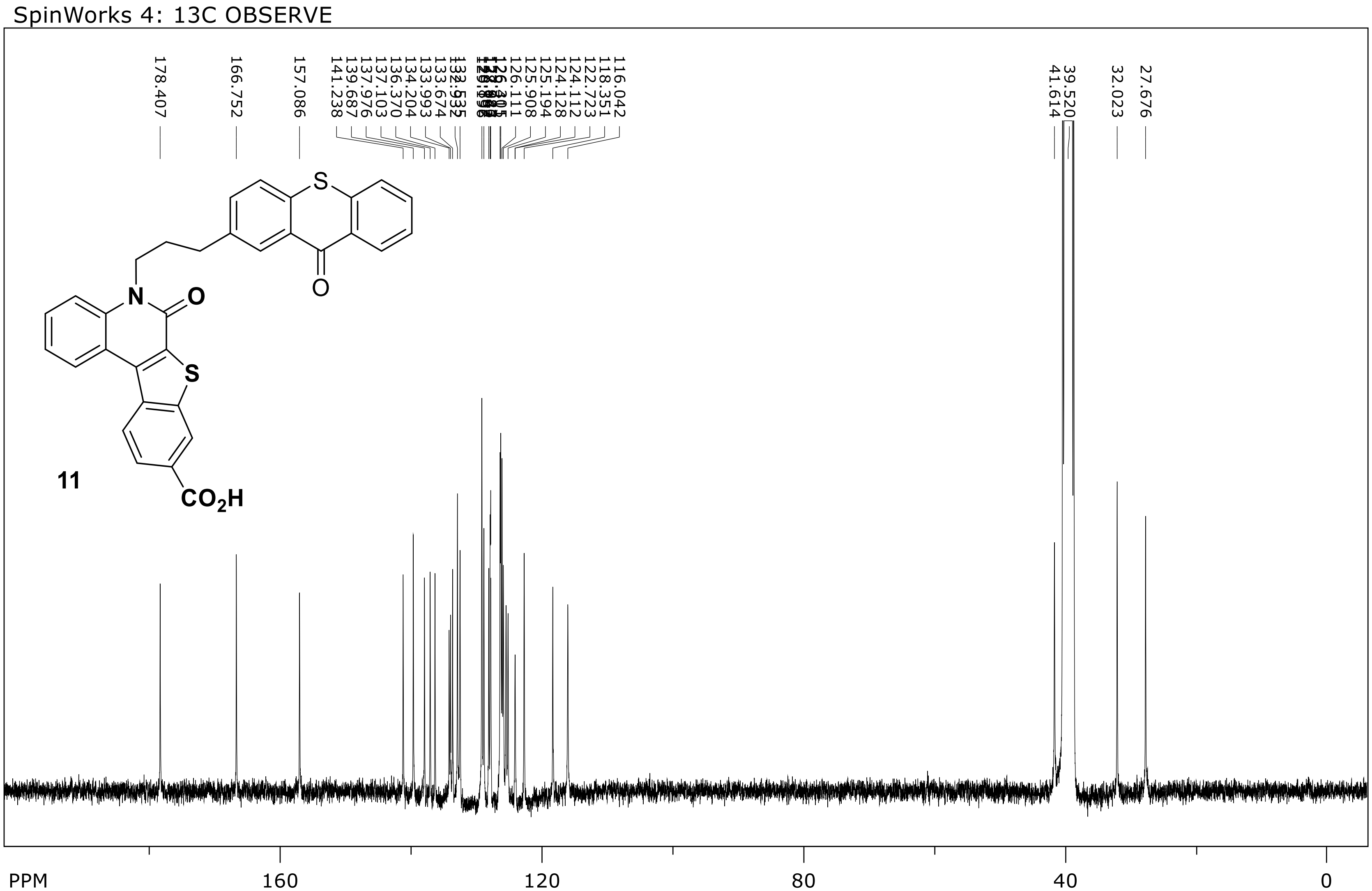
SpinWorks 4: gn01022



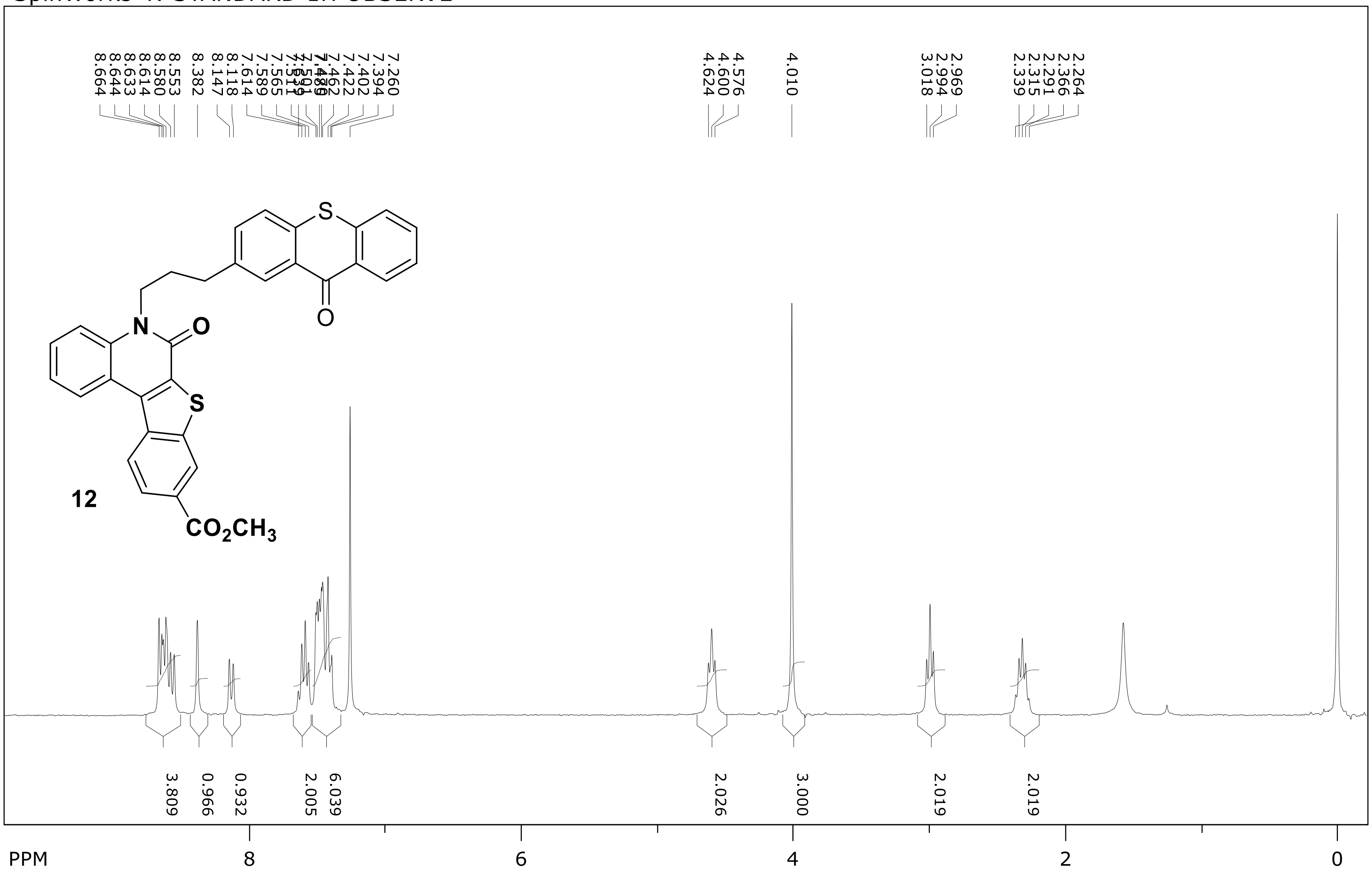

SpinWorks 4: 13C OBSERVE
179.958
168.124
166.497
161.862
142.073
141.606
140.054
137.344
136.785
134.804
134.734
132.959
132.144
129.857
126.153
126.100
125.994
125.544
125.270
124.655
121.336
77.443
77.020
76.597
52.324
49.842
32.727
28.994
21.021
S
O
N
O
S
O
O
COOCH3
10h
PPM
160
120
80
40
0

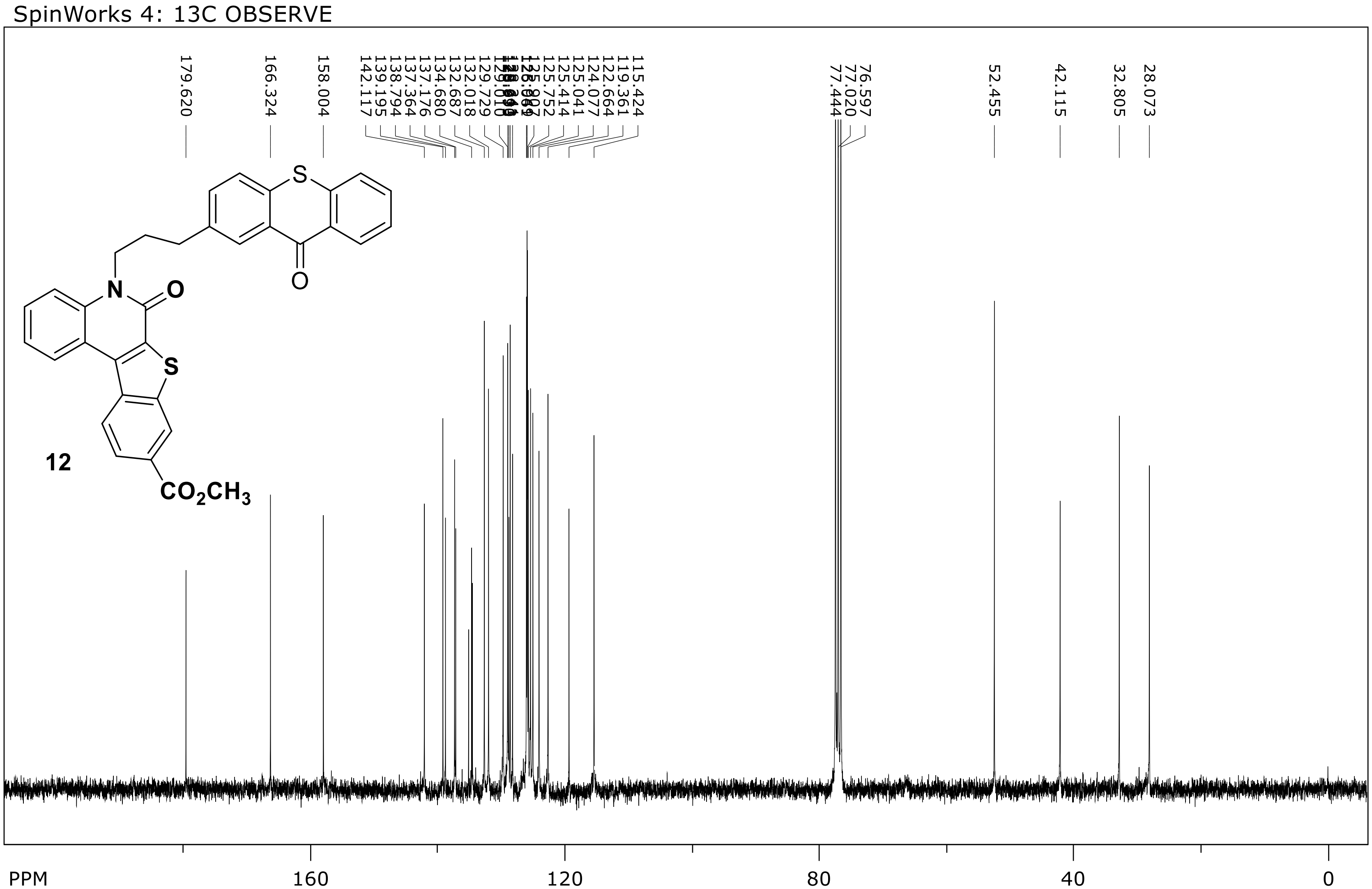
SpinWorks 4:


8.853
8.831
8.742
8.722
8.668
8.665
8.370
8.350
8.191
8.027
7.496
7.489
7.470
7.451
4.576
4.557
4.541
2.954
2.935
2.917
2.500
2.213
2.194
2.177
2.159
2.142
S
O
N
O
S
11
CO2H
0.679
1.061
0.931
0.949
0.943
1.069
2.987
3.927
1.999
1.972
1.996
PPM
11
9
7
5
3
1

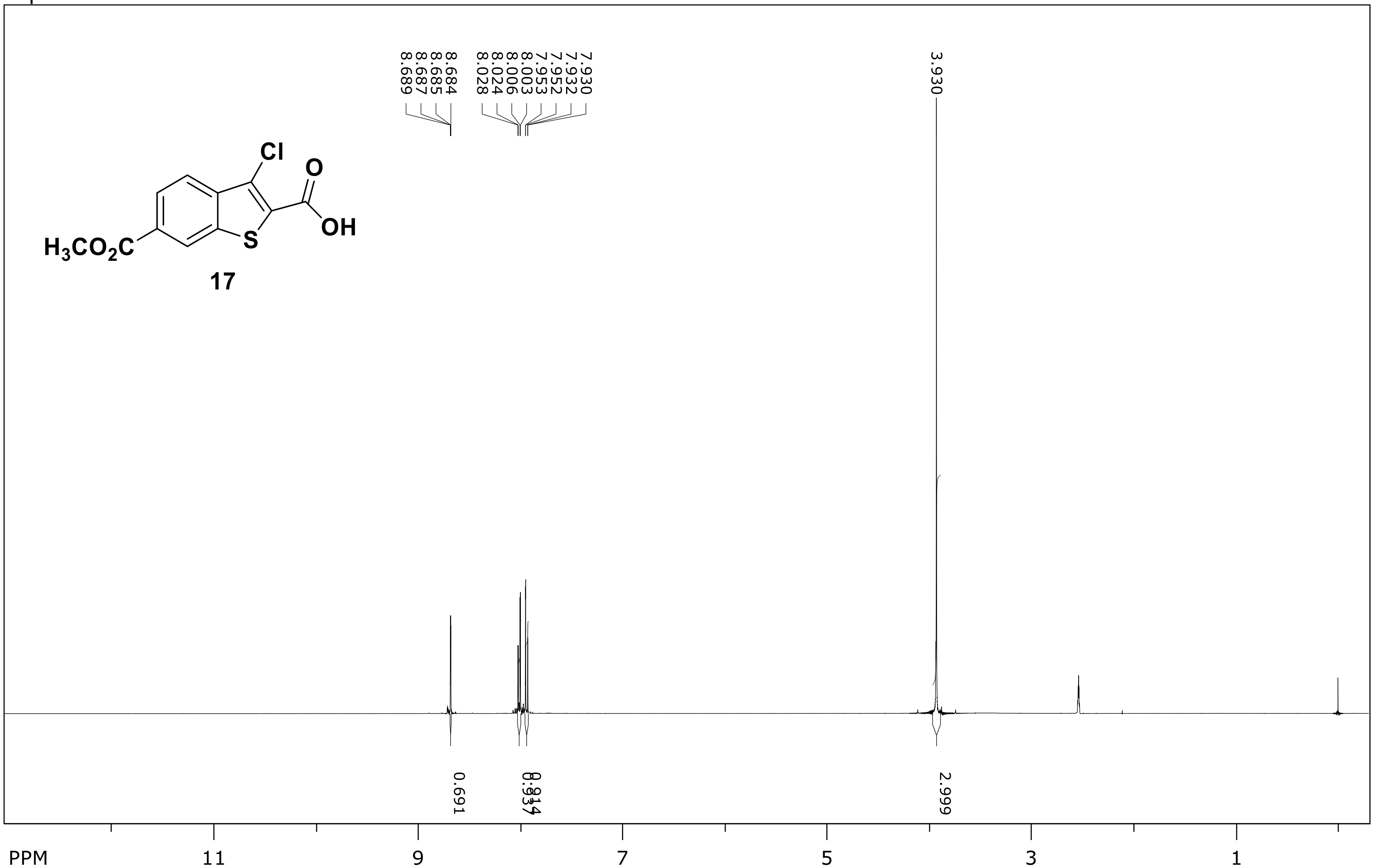

SpinWorks 4: 13C OBSERVE
178.407
166.752
157.086
141.238
139.687
137.976
137.103
136.370
134.204
133.993
133.674
116.042
118.351
122.723
124.112
124.128
125.194
125.908
126.111
41.614
39.520
32.023
27.676
S
O
N
O
S
11
CO2H
PPM
160
120
80
40
0

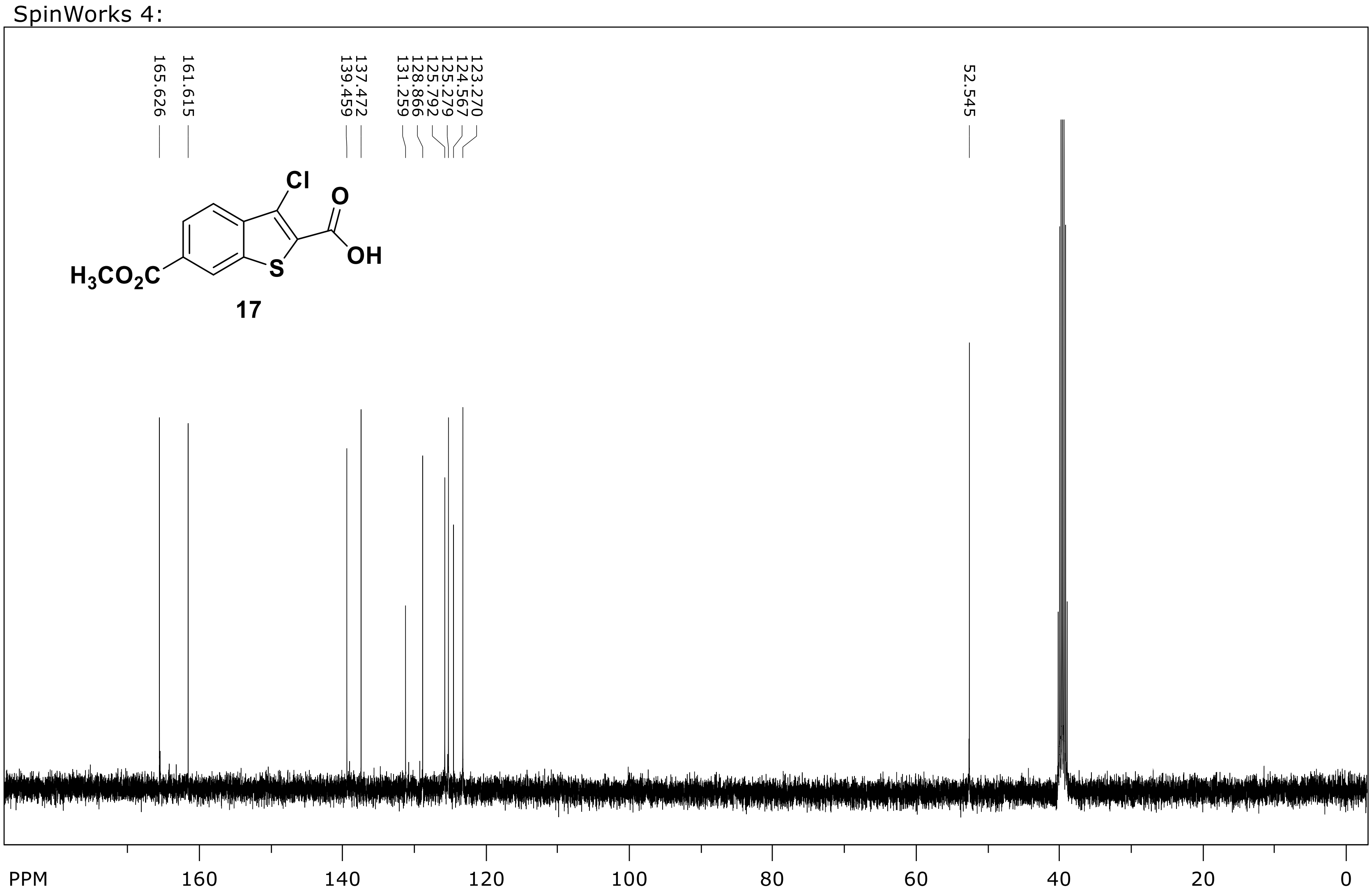
SpinWorks 4: STANDARD 1H OBSERVE

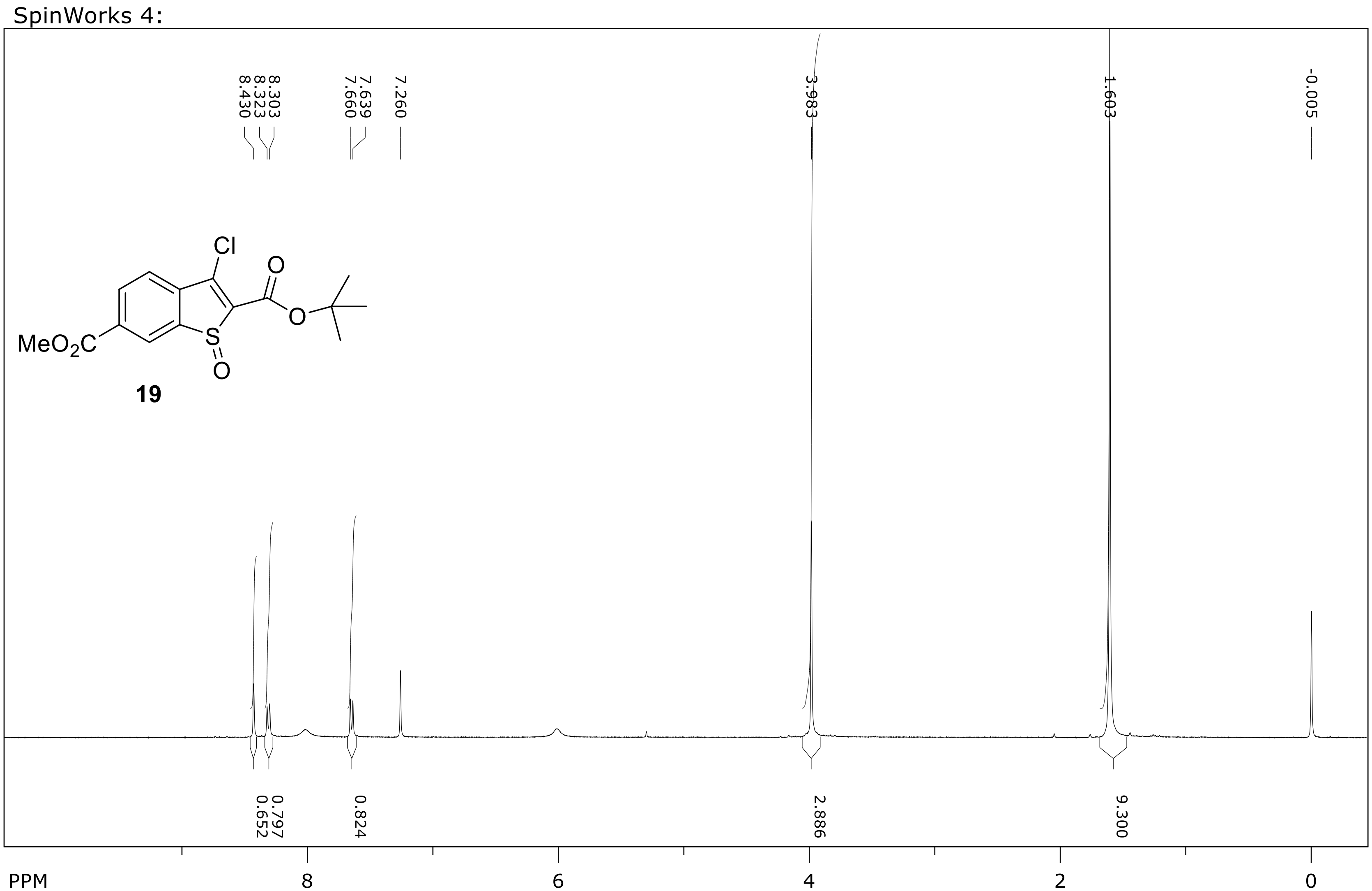


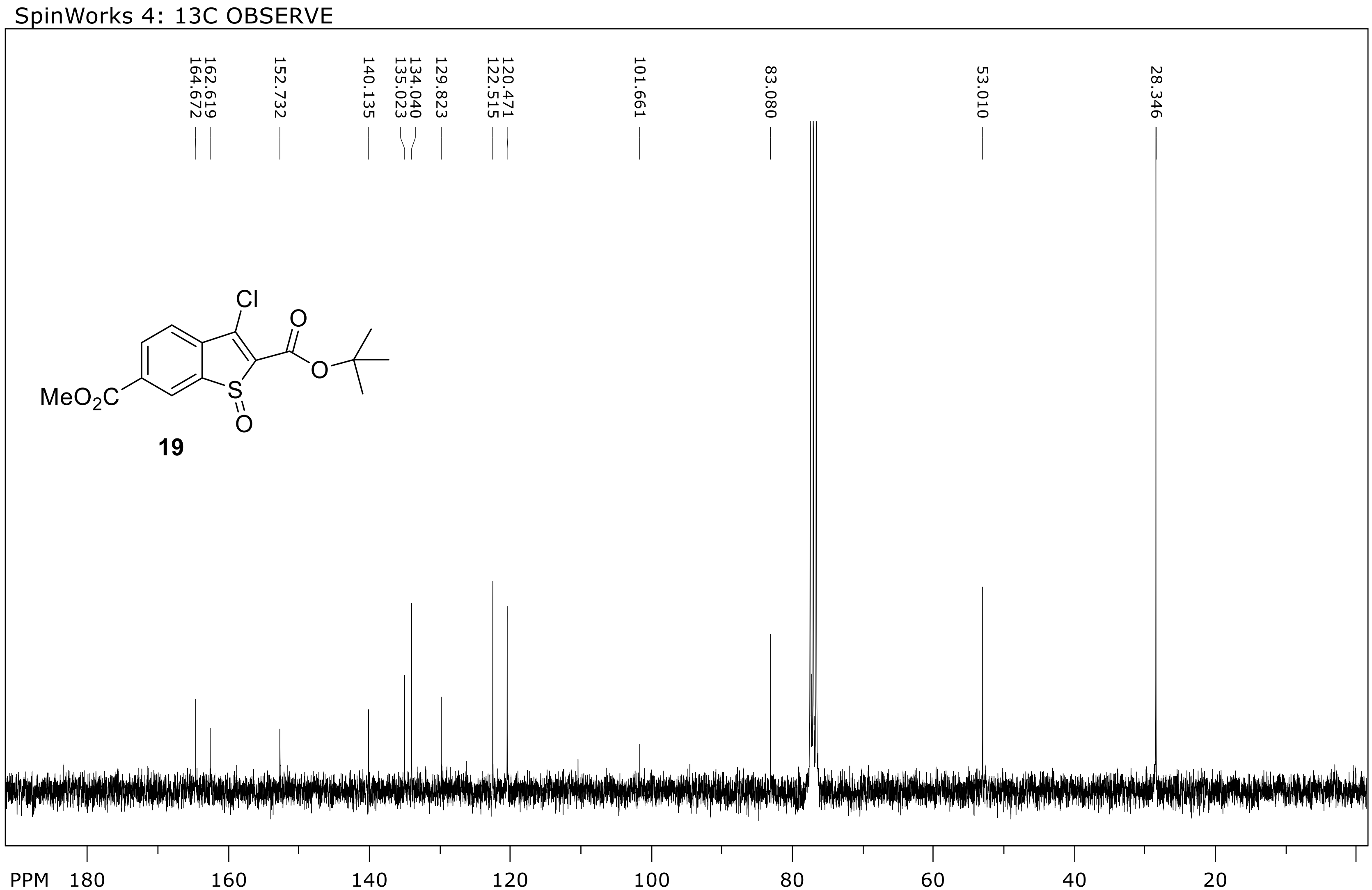

SpinWorks 4: 13C OBSERVE
179.620
166.324
158.004
142.117
139.195
138.794
137.364
137.176
134.680
132.687
132.018
129.729
125.752
125.414
125.041
124.077
122.664
119.361
115.424
77.444
77.020
76.597
52.455
42.115
32.805
28.073
12
N
O
S
S
O
CO_2CH_3
PPM
160
120
80
40
0

SpinWorks 4:

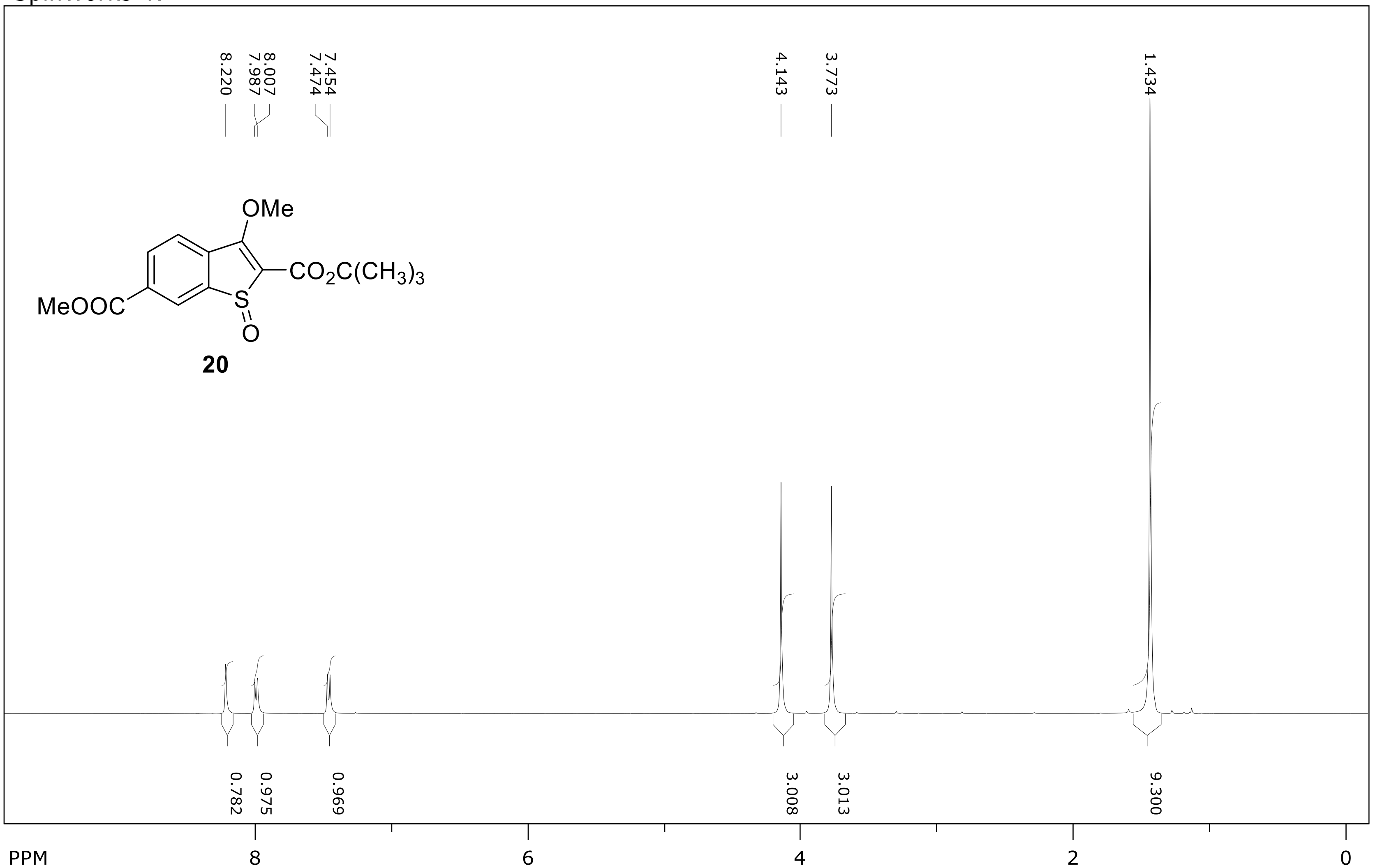

8.689
8.687
8.685
8.684
8.028
8.024
8.006
8.003
7.953
7.952
7.932
7.930
3.930
Cl
O
OH
S
H3CO2C
17
0.691
0.914
0.937
2.999
PPM
11
9
7
5
3
1


SpinWorks 4:
165.626
161.615
139.459
137.472
131.259
128.866
125.792
125.279
124.567
123.270
52.545
Cl
O
OH
S
H_3CO_2C
17
PPM
160
140
120
100
80
60
40
20
0

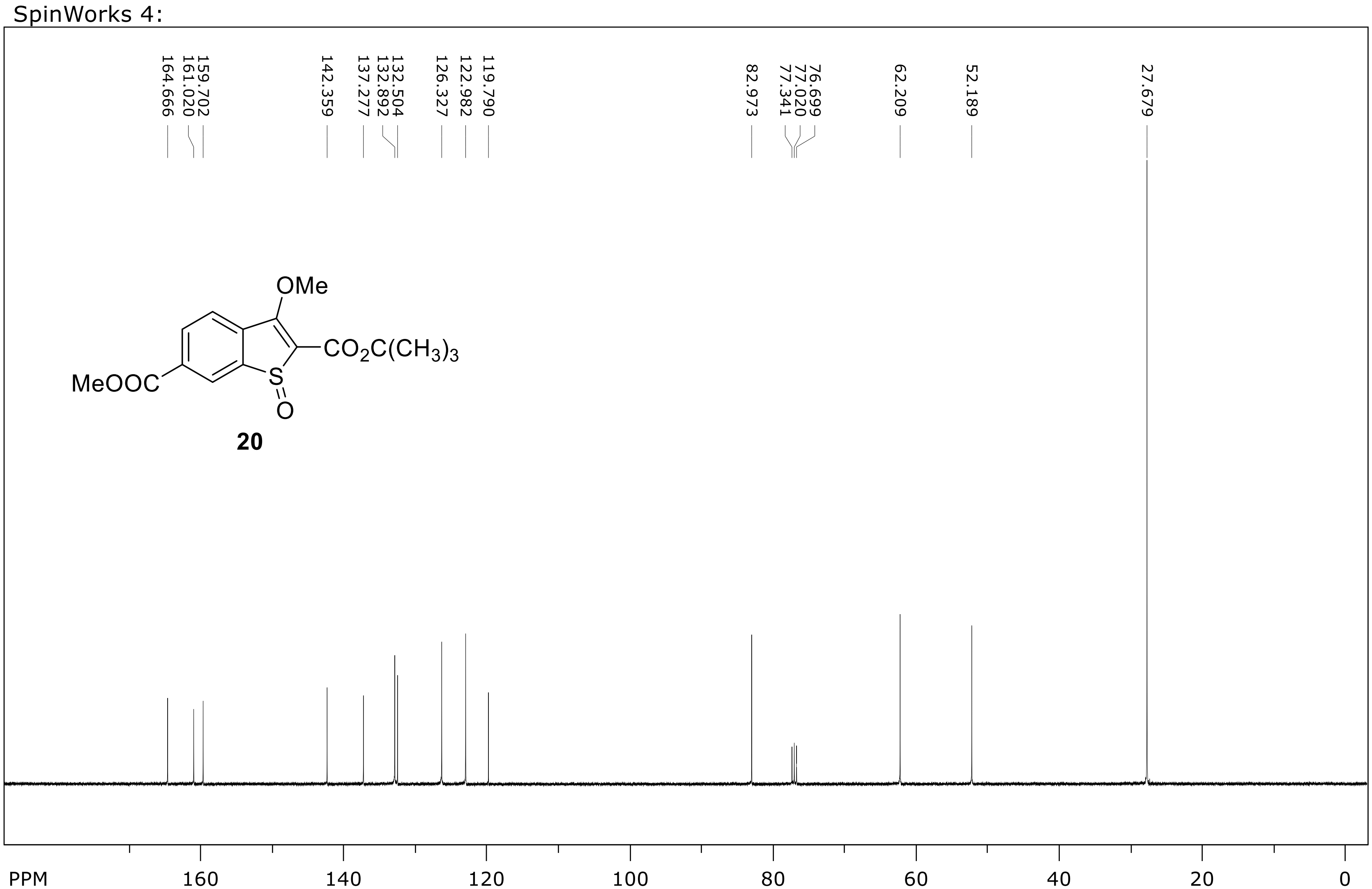

SpinWorks 4:
8.430
8.323
8.303
7.660
7.639
7.260
3.983
1.603
-0.005
Cl
O
O
MeO2C
S
O
19
0.652
0.797
0.824
2.886
9.300
PPM
8
6
4
2
0

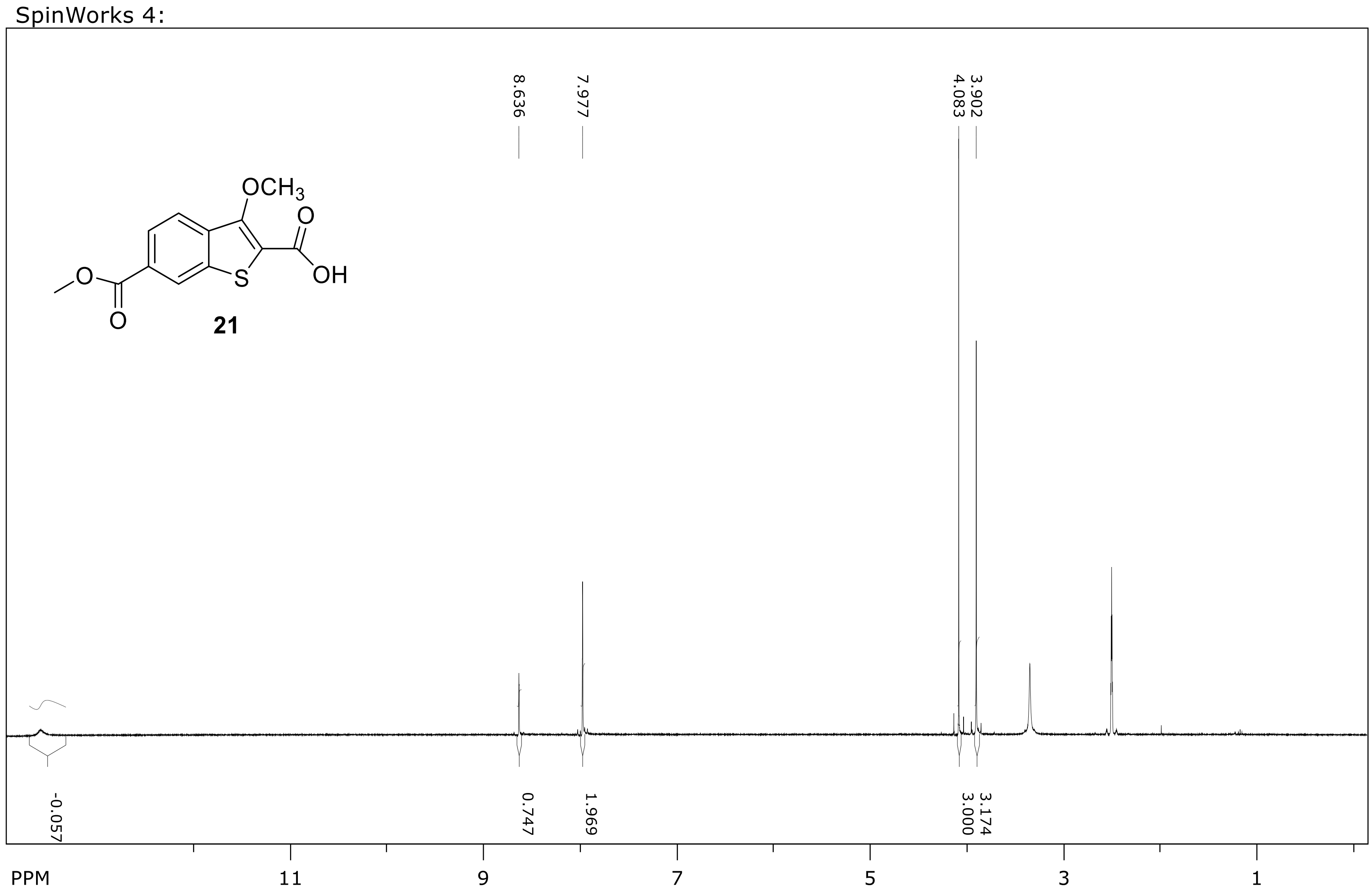

SpinWorks 4: 13C OBSERVE
164.672
162.619
152.732
140.135
135.023
134.040
129.823
122.515
120.471
101.661
83.080
53.010
28.346
Cl
O
O
MeO2C
S
O
19
PPM 180 160 140 120 100 80 60 40 20

SpinWorks 4:

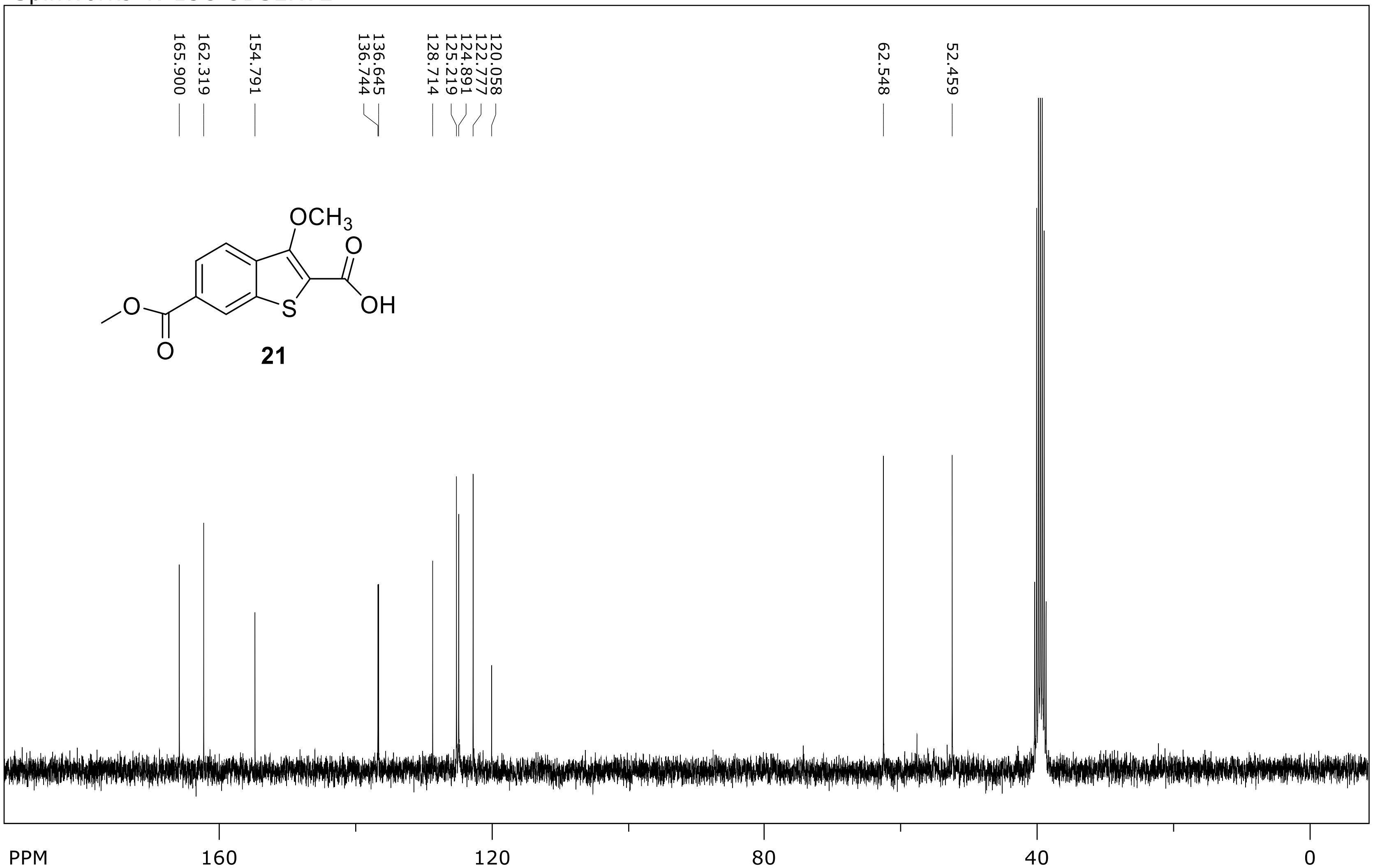


8.220
7.987
8.007
7.454
7.474
4.143
3.773
1.434
OMe
$CO_2C(CH_3)_3$
MeOOC
S
O
20
0.782
0.975
0.969
3.008
3.013
9.300
PPM
8
6
4
2
0


SpinWorks 4:
164.666
161.020
159.702
142.359
137.277
132.892
132.504
126.327
122.982
119.790
82.973
77.341
77.020
76.699
62.209
52.189
27.679
OMe
$CO_2C(CH_3)_3$
MeOOC
S
O
20
PPM
160
140
120
100
80
60
40
20
0


SpinWorks 4:
8.636
7.977
4.083
3.902
OCH3
O
OH
S
O
O
21
-0.057
0.747
1.969
3.000
3.174
PPM
11
9
7
5
3
1

SpinWorks 4: 13C OBSERVE



References

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H., *J. Appl. Cryst*. **2009**, *42*, 339-341.
2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. *Acta Cryst*. **2015**, *A71*, 59-75.
3. Sheldrick, G.M. *Acta Cryst.* **2015** *C71*, 3-8.