Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

SUPPORTING INFORMATION

Regioselective functionalisation of dibenzothiophenes through gold-catalysed intermolecular alkyne oxyarylation

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General Experimental

Commercially available chemicals/reagents were purchased from Sigma Aldrich, Acros, Strem, Alfa Aesar and used without further purification, unless reported. All catalysis reactions were carried out under argon in heat gun-dried glassware unless otherwise stated. Solvents were purified using a Pure Solv-MD solvent purification system except for $CHCl_3$ which was dried over activated 4 Å molecular sieves, and were transferred under argon. Asynt DrySyn heating blocks on stirrer hotplates were employed for reactions with temperature controlled *via* external probe. The following cooling baths were used: 0 ^oC (ice/water), -10 ^oC (NaCl/ice) and -78 ^oC (dry ice/acetone). Flash column chromatography: Fluorochem silica gel 60 (0.043-0.063 mm). Thin layer chromatography (TLC): Macherey Nagel silica gel 60 F_{254} analytical plates which were developed using standard visualizing agents: UV fluorescence (254 and 366 nm), phosphomolybdic acid /Δ, potassium permanganate /Δ and vanillin /Δ. IR: Perkin–Elmer Spectrum 100 FTIR spectrometer. Only selected absorbencies (υ_{max}) are reported in cm^{-1}. MS and HRMS (ES): Waters LCT, Time of Flight. HRMS was obtained using leucine enkephalin as lock-mass. NMR: Spectra were recorded on Bruker AVIII300 (^1H = 300 MHz, ^{13}C = 75.5 MHz) and Bruker AVIII400 (^1H = 400 MHz, ^{13}C = 101 MHz) with the spectrometers at 300 K in the solvents indicated; $CDCl_3$ purchased from Sigma Aldrich and DMSO-d_6 from Goss Scientific. ^{13}C NMR spectra were recorded using the UDEFT or PENDANT pulse sequences from the Bruker standard pulse program library. HSQC and HMBC spectra were recorded using the Bruker standard pulse program library. Chemical shifts (δ) are given in ppm relative to TMS. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_c = 77.16 ppm; residual $CHCl_3$ in $CDCl_3$: δ_c = 7.26 ppm). Coupling constants (J) are reported in Hz to one decimal place. Multiplicity is denoted in ^1H NMR by: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet), app. (apparent). Melting points were measured in open capillaries using Stuart Scientific melting point apparatus and are uncorrected.

m-CPBA was purified by washing with a pH 7 phosphate buffer unless otherwise stated: A buffer solution was prepared from 0.1 M NaOH (154 mL) and 0.2 M KH_2PO_4 (94 mL) and made up to 376 mL with distilled water. *m*-CPBA (77% w/w, 10 g) was dissolved in diethyl ether (100 mL) and washed four times with the buffer solution. The organic extract was dried over $MgSO_4$ and carefully evaporated under reduced pressure to yield pure *m*-CPBA (7.3 g).[1]

Crystal Data

The datasets were measured on an Agilent SuperNova diffractometer using an Atlas detector. The data collections were driven and processed and absorption corrections were applied using CrysAlisPro.[20] The structure was solved using ShelXS[21] and refined by a full-matrix least-squares procedure on F^2 in ShelXL.[21] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on the equivalent isotropic displacement parameter (U_{eq}) of the parent atom. Figures were produced using OLEX2.[22] The CIF for the crystal structure of **17a** has been deposited with the CCDC and have been given the deposition number 1405198.

Preparation of Starting Materials

Dibenzothiophene-S-oxide (1)

Prepared in 78% yield according to a literature procedure.[1] Data matches that reported in the literature.[2]

2,8-Dibromodibenzothiophene

Prepared in 43% yield according to the literature procedure.[3] Data matches that reported in the literature.[3]

tert-Butyl(hex-5-yn-1-yloxy)diphenylsilane

Prepared in 79% yield according to the literature procedure.[4] Data matches that reported in the literature.[4]

Dec-1-yn-3-ol

Prepared in 66% yield according to the literature procedure.[5] Data matches that reported in the literature.[6]

2-(2,2-Dibromovinyl)thiophene

Prepared in 94% yield according to the literature procedure.[7] Data matches that reported in the literature.[7]

1-Bromo-2-(2,2-dibromovinyl)benzene

Prepared in 56% yield according to the literature procedure.[7] Data matches that reported in the literature.[8]

1-(2,2-Dibromovinyl)-4-methoxybenzene

Prepared in 88% yield according to the literature procedure.[7] Data matches that reported in the literature.[7]

1-Ethynyl-4-methoxybenzene

Prepared in 79% yield according to the literature procedure.[7] Data matches that reported in the literature.[7]

1-Bromo-2-ethynylbenzene

Prepared in (68%) yield according to a literature procedure.[7] Data matches that reported in the literature.[9]

2-Ethynylthiophene

Prepared in 74% yield according to the literature procedure.[8] Data matches that reported in the literature.[8]

3-(Hex-1-yn-1-yl)oxazalidin-2-one (7)

Prepared in 59% yield according to the literature procedure.[10] Data matches that reported in the literature.[10]

4-Methyl-N-phenyl-N-(phenylethynyl)benzenesulfonamide (9)

Prepared in 68% yield according to the literature procedure.[10] Data matches that reported in the literature.[10]

3-(Prop-2-yn-1-yloxy)prop-1-ene (11a)

Prepared in 36% yield according to the literature procedure.[11] Data matches that reported in the literature.[11]

4-(Prop-2-yn-1-yloxy)but-1-ene (15)

Prepared in 17% yield according to the literature procedure.[12] Data matches that reported in the literature.[12]

E)-(3-(Prop-2-yn-1-yloxy)prop-1-en-1-yl)benzene (11b)

Prepared in 49% yield according to the literature procedure.[13] Data matches that reported in the literature.[13]

N-Allyl-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide (11c)

Prepared in 81% yield according to a literature procedure.[14] Data matches that reported in the literature.[14]

Diethyl 2,2-di(prop-2-yn-1-yl)malonate (19)

Prepared in 50% yield according to a literature procedure.[15] Data matches that reported in the literature.[15]

Dimethyl 2-allyl-2-(prop-2-yn-1-yl)malonate (11d)

Prepared in 92% yield according to the literature procedure.[16] Data matches that reported in the literature.[16]

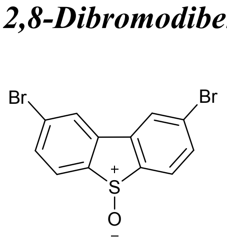
Chloro[tris(2,4-di-tert-butylphenyl)phosphite]gold

Prepared in 80% yield according to the literature procedure.[17] Data matches that reported in the literature.[17]

Acetonitrile[tris(2,4-di-tert-butylphenyl)phosphite]gold antimonate complex

Prepared in 80% yield according to the literature procedure.[18] Data matches that reported in the literature.[18]

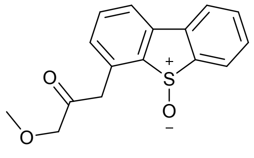
2,8-Dibromodibenzo[b,d]thiophene 5-oxide (5)



Prepared according to a modified literature procedure.[19] 2,8-Dibromodibenzothiophene (3.65 mmol, 1.25 g) was added to a 250 mL RBF under argon, followed by CH_2Cl_2 (75 mL). The reaction was cooled to 0 °C and *m*CPBA (630 mg, 3.65 mmol), in CH_2Cl_2 (75 mL) was added by syringe over 25 minutes. The reaction was allowed to warm to rt and was worked up after 7 hours. The reaction mixture was washed with $NaHCO_3$ (3 × 50 mL), extracted with CH_2Cl_2 (3 × 50 mL), dried Na_2SO_4, filtered, concentrated and purified by column chromatography (EtOAc:Hexanes 1:1) to afford the title compound as a white solid (170 mg, 13%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* 1.7, 2H), 7.86 (d, *J* 8.1, 2H), 7.67 (dd, *J* 8.1, 1.7, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 144.5, 138.0, 133.3, 129.1, 127.8, 125.7; IR (neat): *ν* = 3073, 3047, 3012, 1575, 1557, 1455, 1404, 1382, 1056, 1025, 811; Data matches that in the literature.[19]

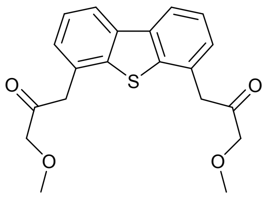
Additional Iterative Oxyarylation

1-Methoxy-3-(5-oxidodibenzo[b,d]thiophen-4-yl)propan-2-one (S1)



*m*CPBA (129 mg, 0.75 mmol, 1.1 equiv.) was added in 5 portions over 10 minutes to a solution of **3d** (184 mg, 0.68 mmol) in CH_2Cl_2 (15 mL) at 0 °C. The reaction was allowed to warm to rt over 2 hours, washed with $NaHCO_3$ (4 × 10 mL), extracted with CH_2Cl_2 (4 × 10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification by column chromatography (8:2 hexane:EtOAc to EtOAc) afforded firstly **3d** (37 mg, 20%) and then **S1** (120 mg, 61%) as a white solid; R_f 0.25 (EtOAc); mp: 110-112 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.95 (d, *J* 7.5, 1H), 7.79 (d, *J* 7.6, 1H), 7.73 (d, *J* 7.2, 1H), 7.59 (td, *J* 7.6 and 1.1, 1H), 7.56 (t, *J* 7.6, 1H), 7.49 (td, *J* 7.6 and 1.1, 1H), 7.29 (d, *J* 7.6, 1H), 4.34–4.15 (m, 4H), 3.46 (s, 3H); ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 204.4 (C), 144.6 (C), 143.9 (C), 137.7 (C), 137.2 (C), 134.9 (C), 133.1 (CH), 132.8 (CH), 131.6 (CH), 129.7 (CH), 127.5 (CH), 122.2 (CH), 121.1 (CH), 77.6 (CH_2), 59.6 (CH_3), 42.4 (CH_2); IR (neat): *ν* = 3047, 2925, 2827, 1725, 1448, 1049, 1012; HR-MS (ES-TOF): *m/z*: calcd for $C_{16}H_{14}O_3SNa$: 309.0561, found 309.0556 $[M + Na]^+$.

3,3'-(Dibenzo[b,d]thiophene-4,6-diyl)bis(1-methoxypropan-2-one) (S2)



Sulfoxide **S1** (85.9 mg, 0.3 mmol) and monomethyl propargyl ether (51 µl, 0.6 mmol) were dissolved in toluene (3 mL). Au-I (16.8 mg, 0.015 mmol) was added and the reaction was stirred at rt for 16 hours. The reaction mixture was filtered through a plug of silica and washed with CH_2Cl_2 (10 mL). The reaction mixture was concentrated under reduced pressure and purified by column chromatography (1:1 hexane:EtOAc) to afford **23** (60.5 mg, 58%) as a yellow crystalline solid; R_f 0.25 (1:1 hexane:EtOAc); mp: 70–72 °C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.10 (dd, *J* 7.9 and 0.9, 2H), 7.48 (app t, *J* 7.6, 2H), 7.35 (d, *J* 7.2, 2H), 4.13 (s, 4H), 4.05 (s, 4H), 3.42 (s, 6H); ^{13}C-NMR (101

MHz, $CDCl_3$): δ = 204.7 (2C), 139.5 (2C), 136.7 (2C), 128.3 (2CH), 128.2 (2C), 125.4 (2CH), 121.1 (2CH), 77.3 ($2CH_2$), 59.5 ($2CH_3$), 45.5 ($2CH_2$); IR (neat): v = 2927, 1721, 1572, 1049, 912, 778, 727; HR-MS (ES-TOF): *m/z*: calcd for $C_{20}H_{20}O_4NaS$: 379.0980, found 379.0999 $[M + Na]^+$.

References

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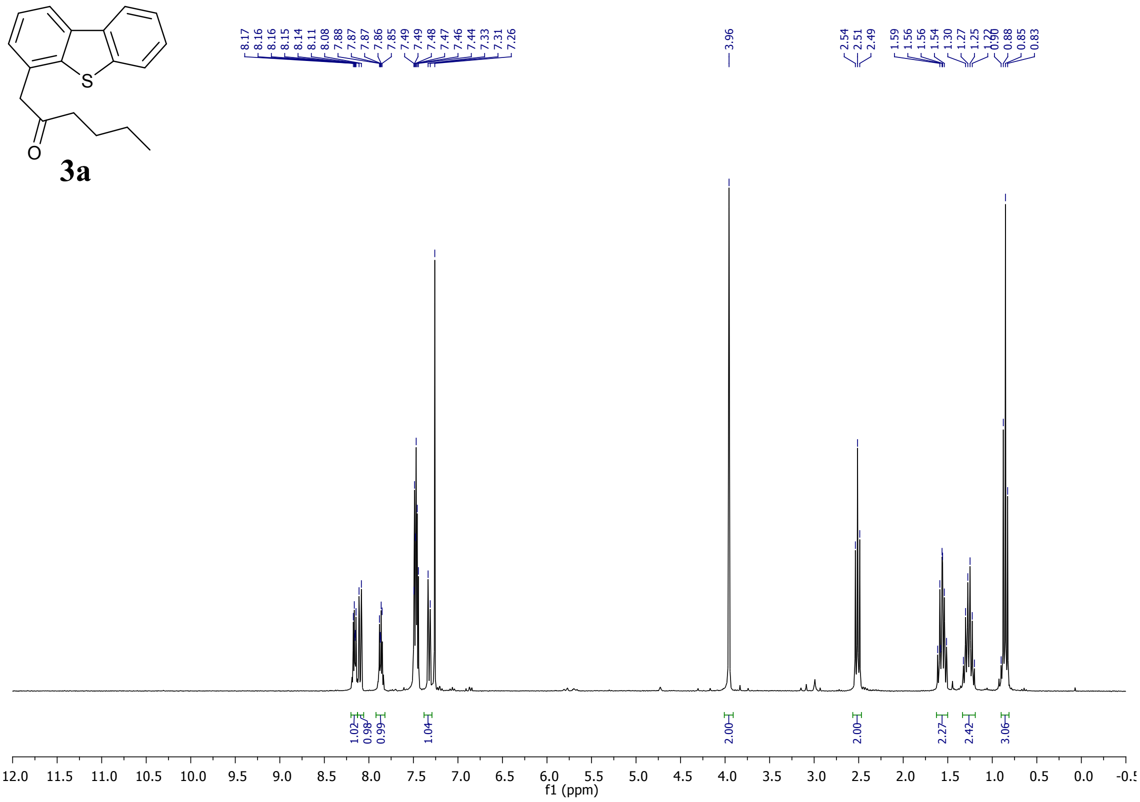
NMR Spectra



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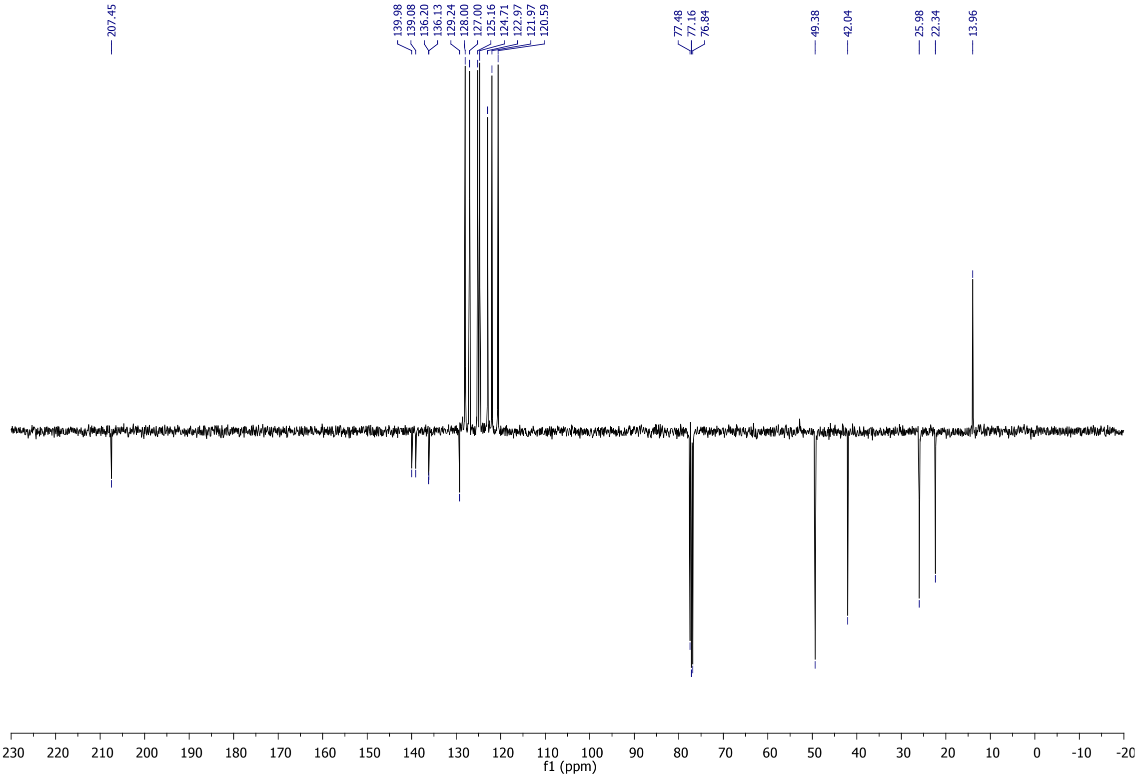

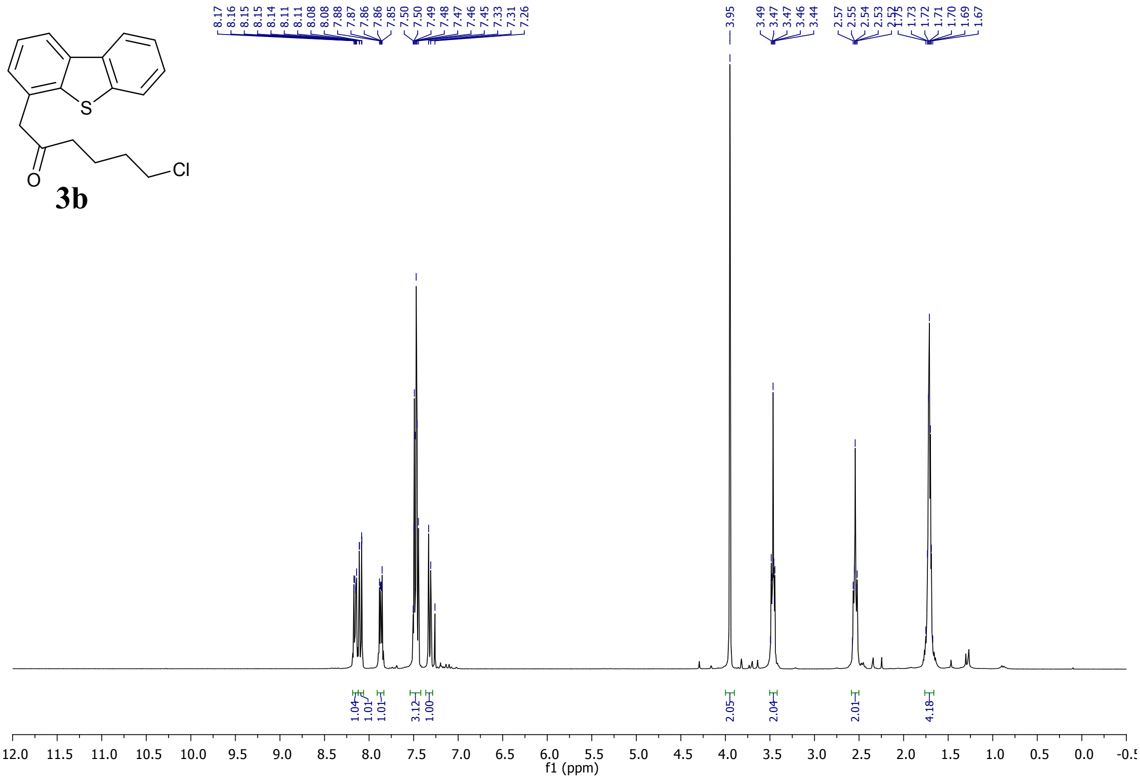
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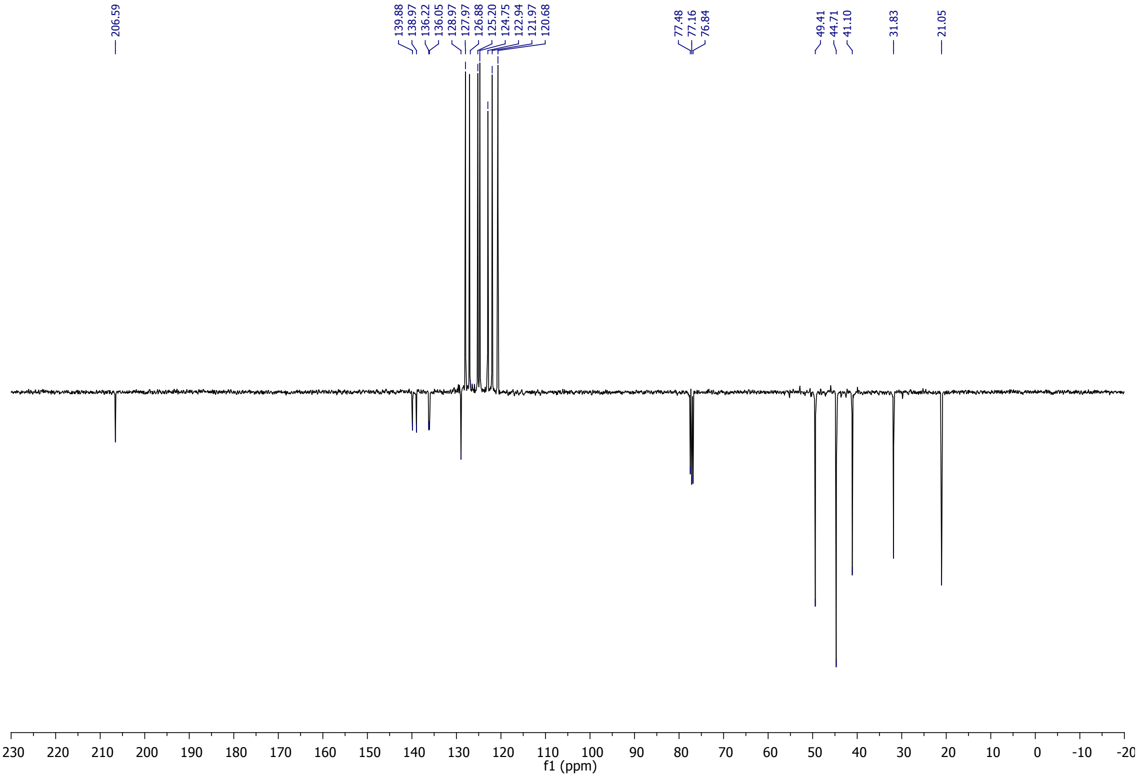
3b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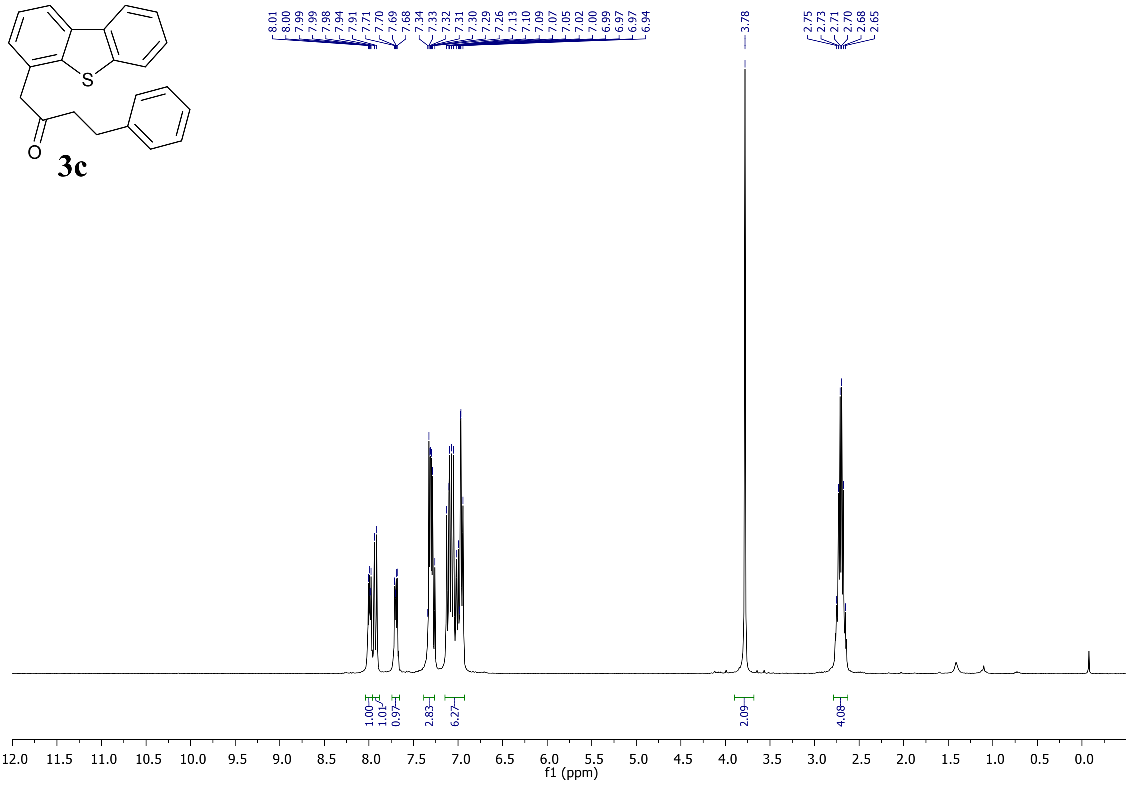
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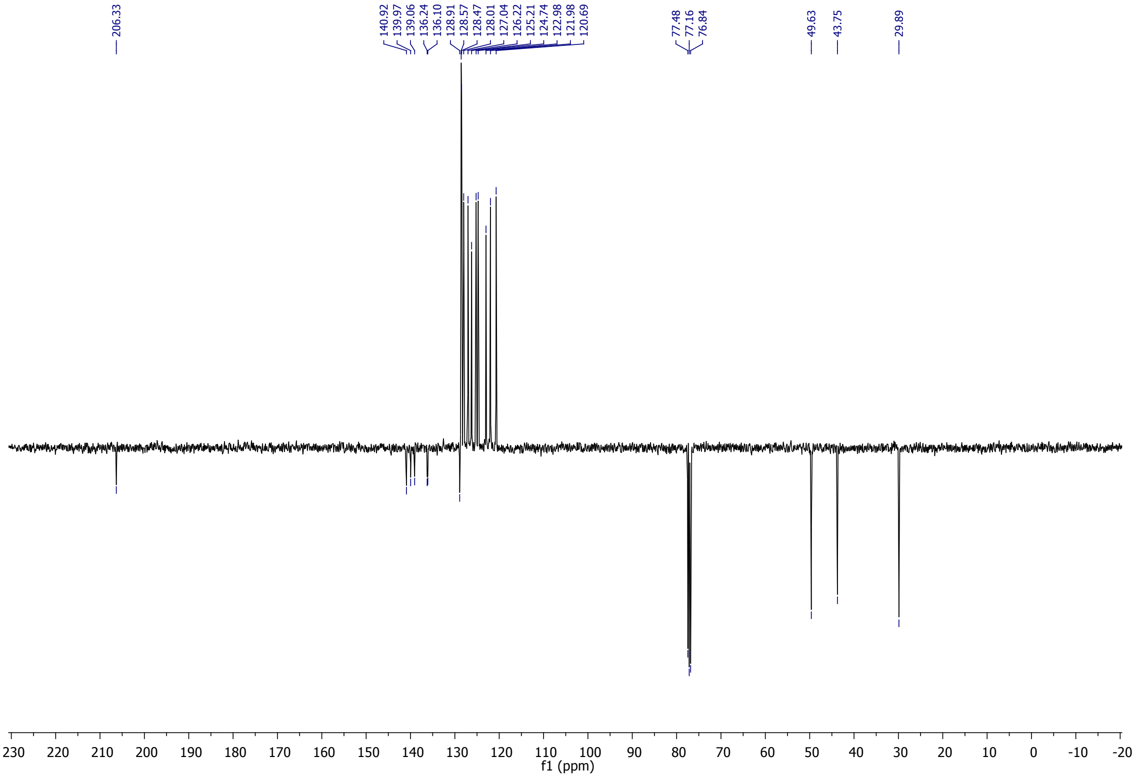
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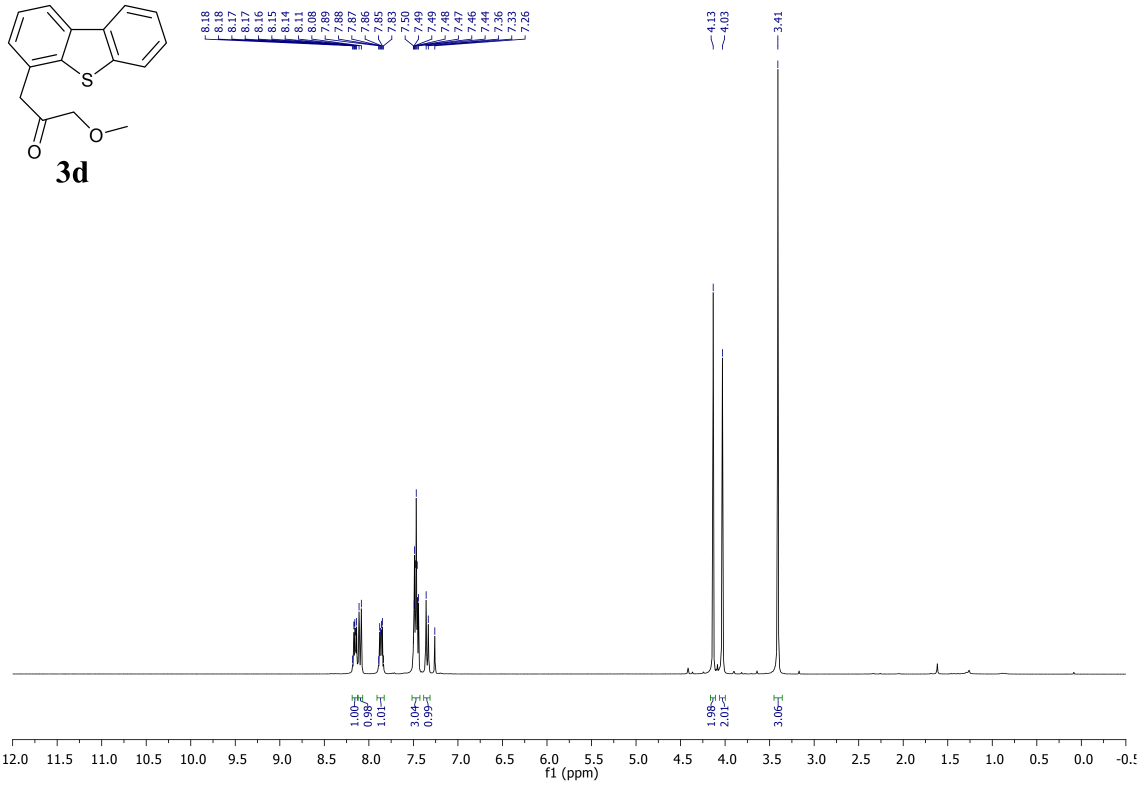
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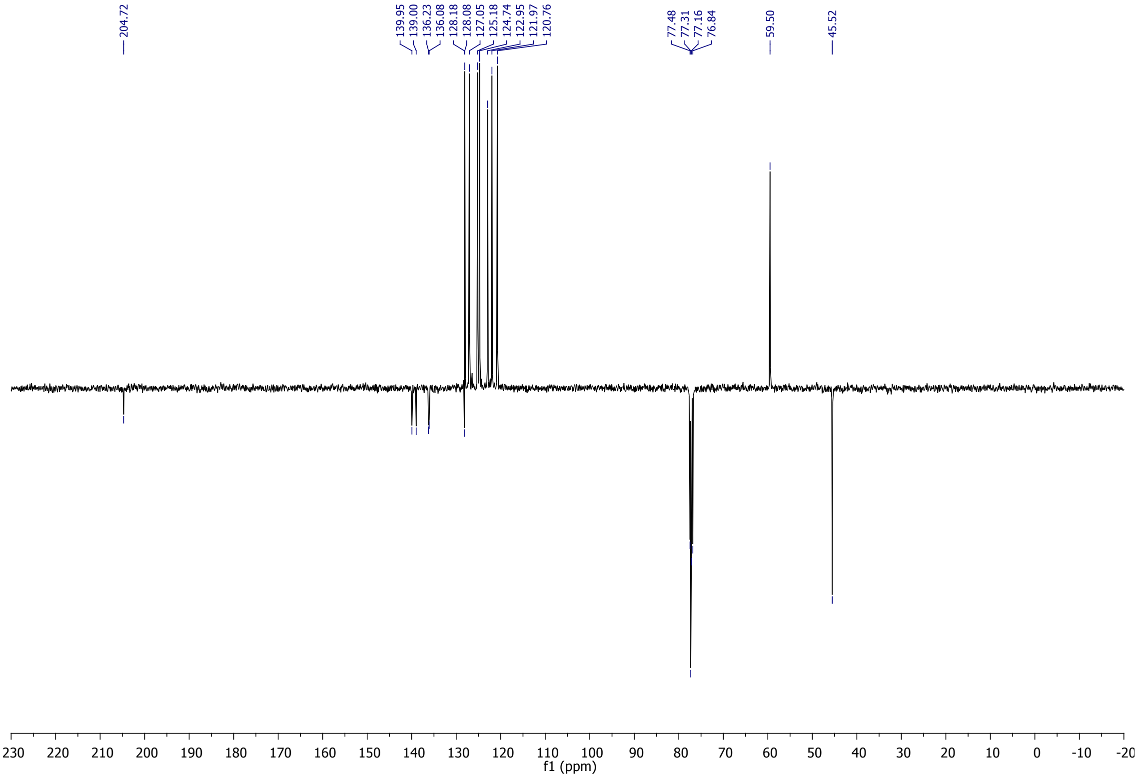
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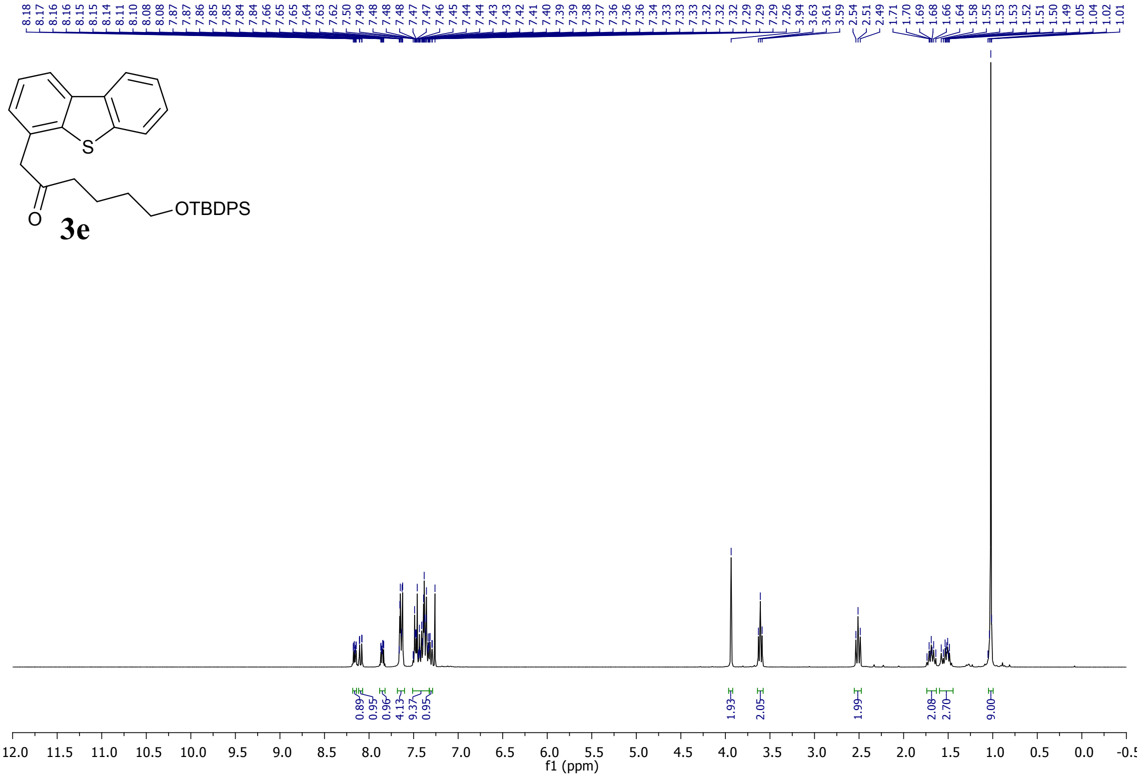
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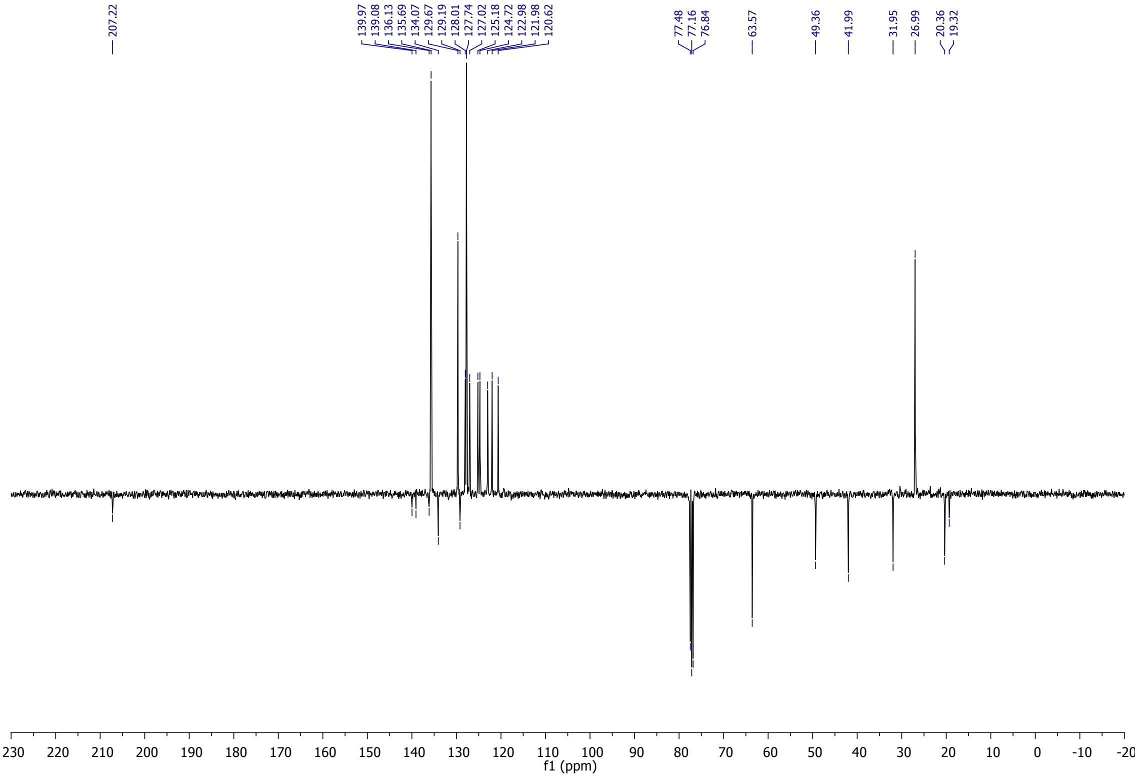
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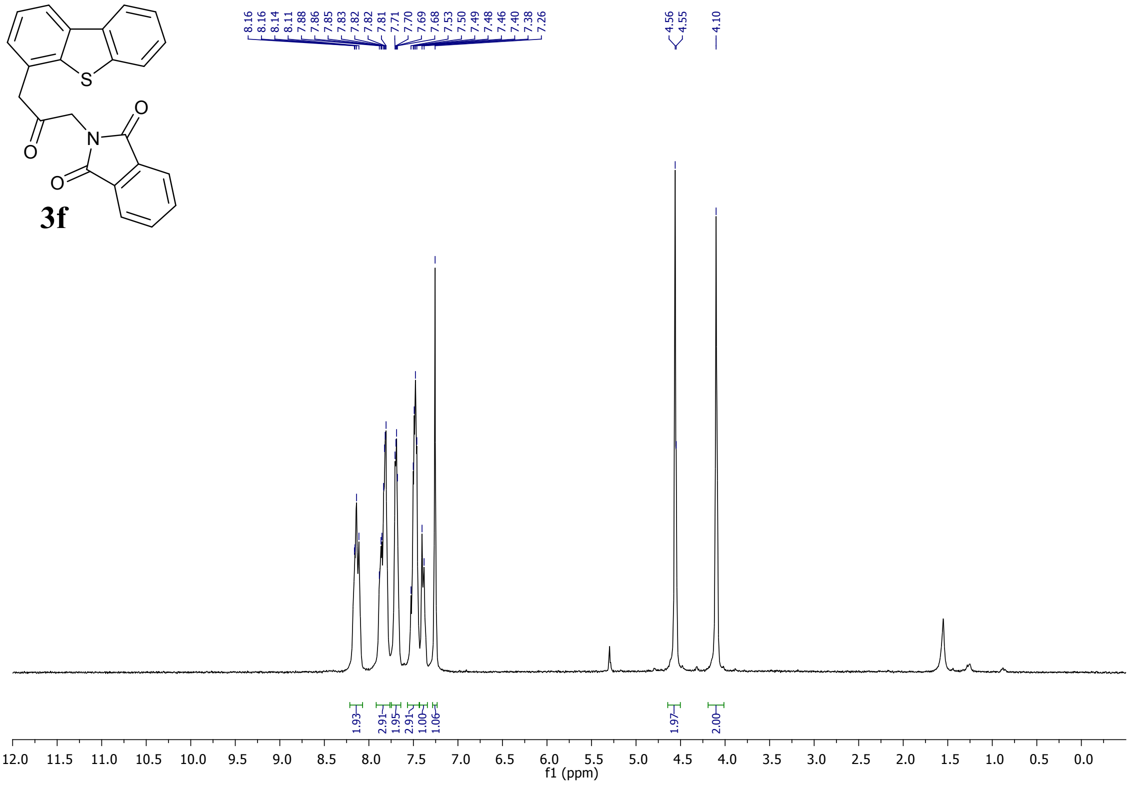

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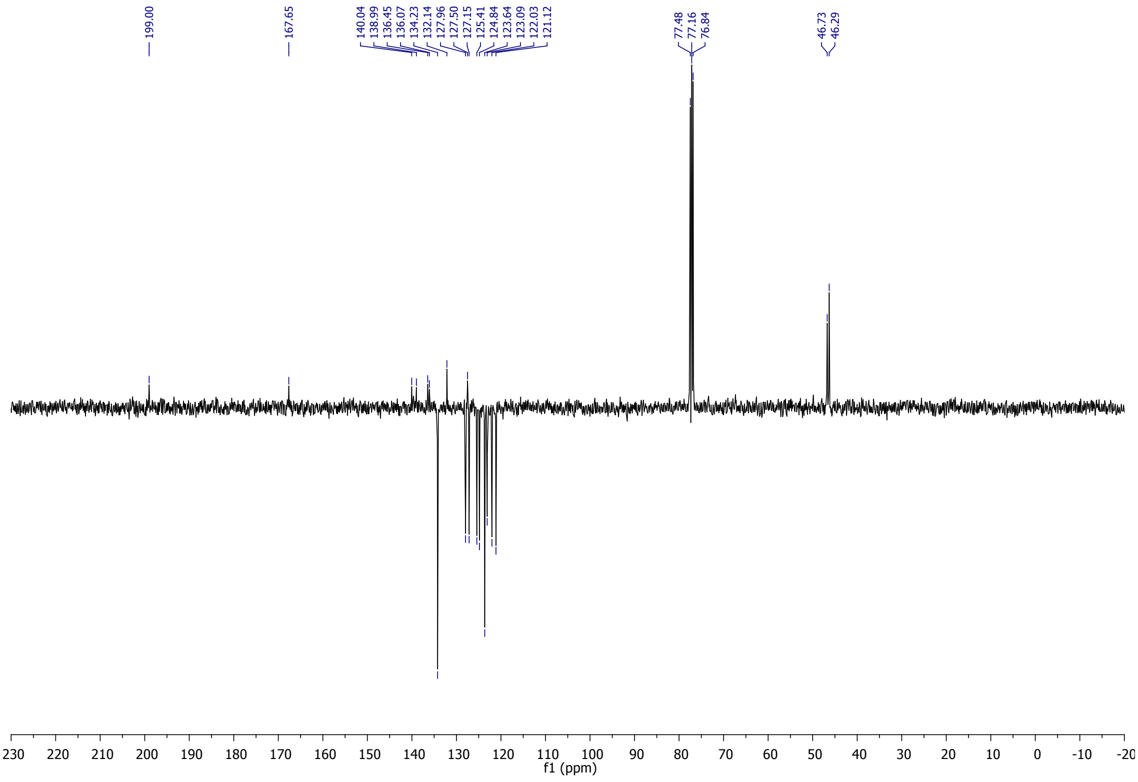
O
O



199.00
167.65
140.04
138.99
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134.23
132.14
127.96
127.50
127.15
125.41
124.84
123.64
123.09
122.03
121.12
77.48
77.16
76.84
46.73
46.29
230
220
210
200
190
180
170
160
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100
90
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60
50
40
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20
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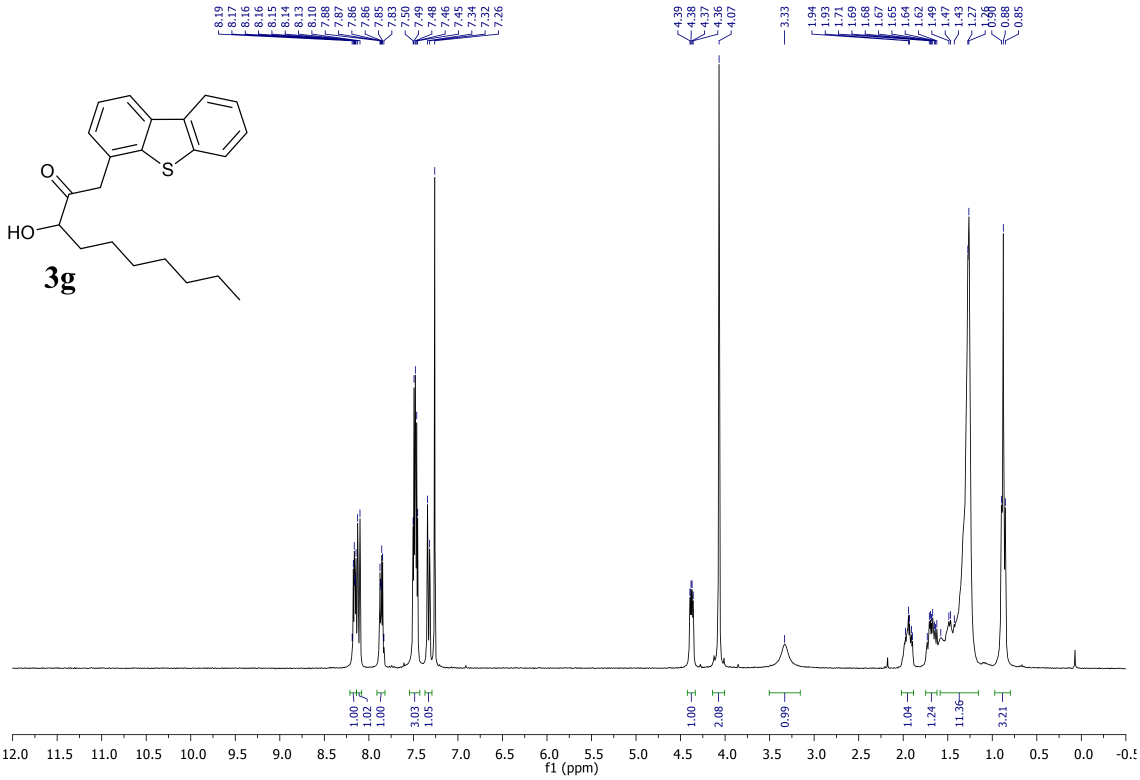
-10
-20
f1 (ppm)



8.19
8.17
8.16
8.16
8.15
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8.13
8.10
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7.87
7.86
7.85
7.83
7.50
7.49
7.48
7.46
7.45
7.34
7.32
7.26
4.39
4.38
4.37
4.36
4.07
3.33
1.94
1.93
1.71
1.69
1.68
1.67
1.65
1.64
1.62
1.49
1.47
1.43
1.27
1.26
0.90
0.88
0.85
O
HO
S
1.00
1.02
1.00
3.03
1.05
1.00
2.08
0.99
1.04
1.24
11.36
3.21
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
2.0
1.5
1.0
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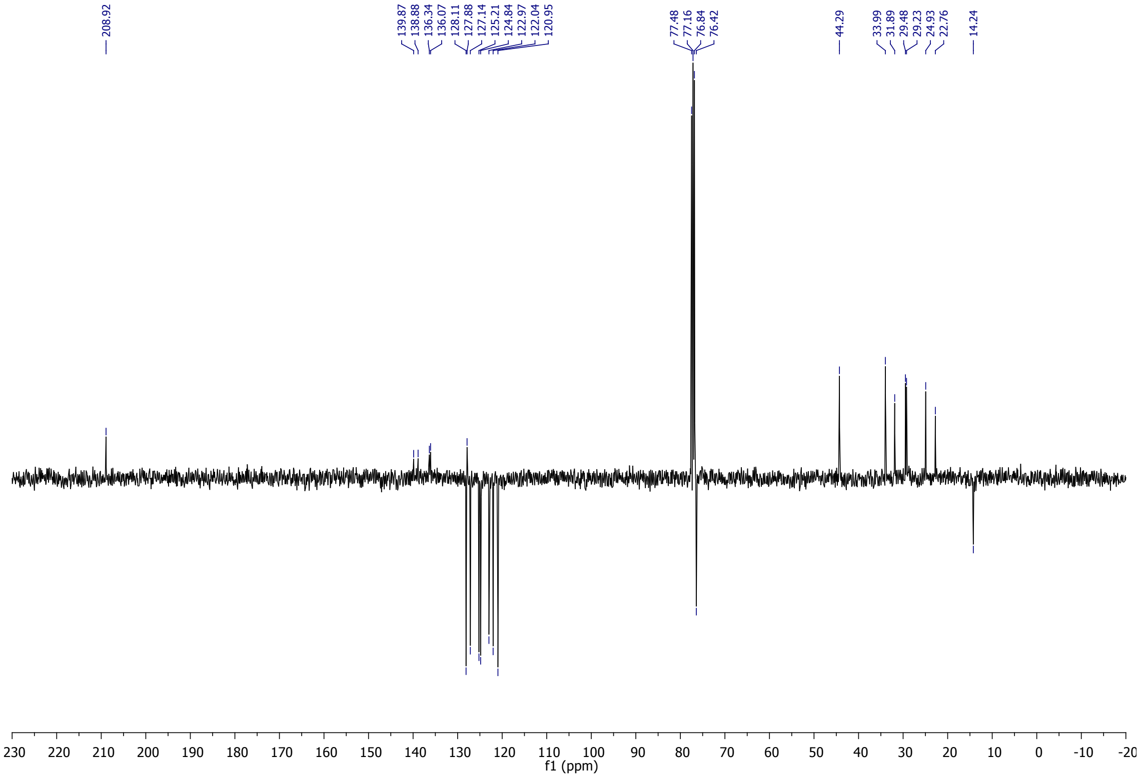
0.0
f1 (ppm)

3g



208.92
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127.88
127.14
125.21
124.84
122.97
122.04
120.95
77.48
77.16
76.84
76.42
44.29
33.99
31.89
29.48
29.23
24.93
22.76
14.24
230
220
210
200
190
180
170
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100
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80
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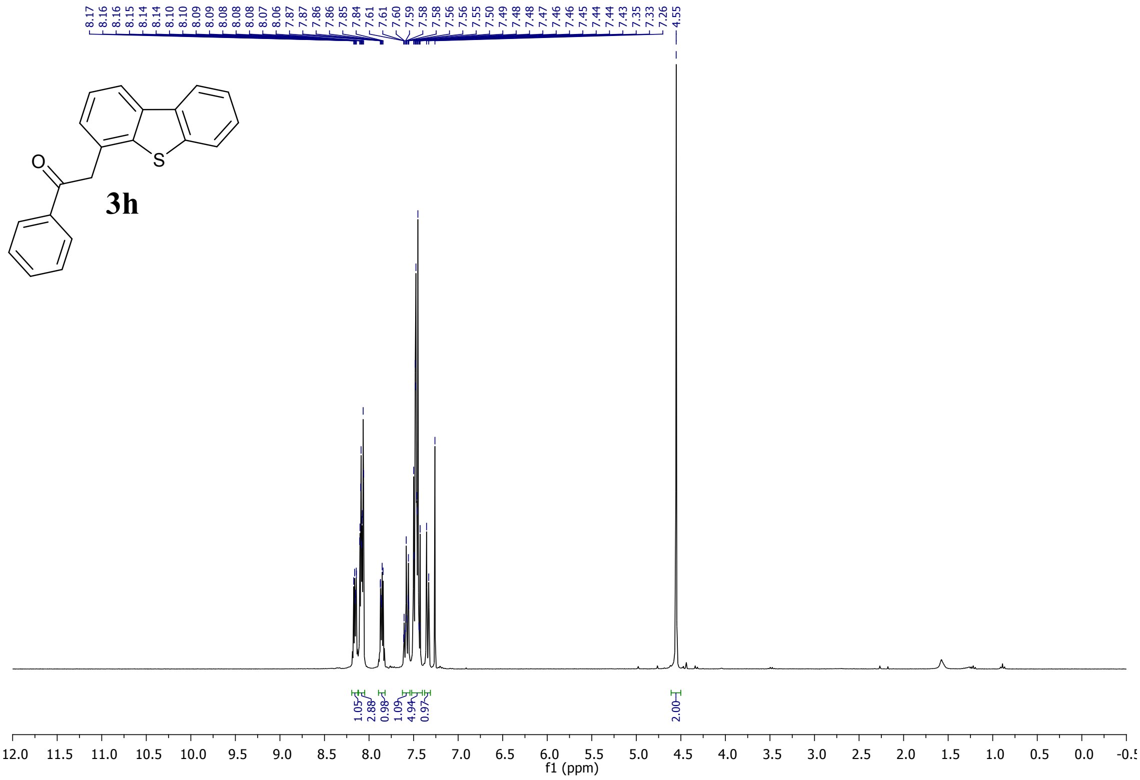
-10
f1 (ppm)


3h

8.17
8.16
8.16
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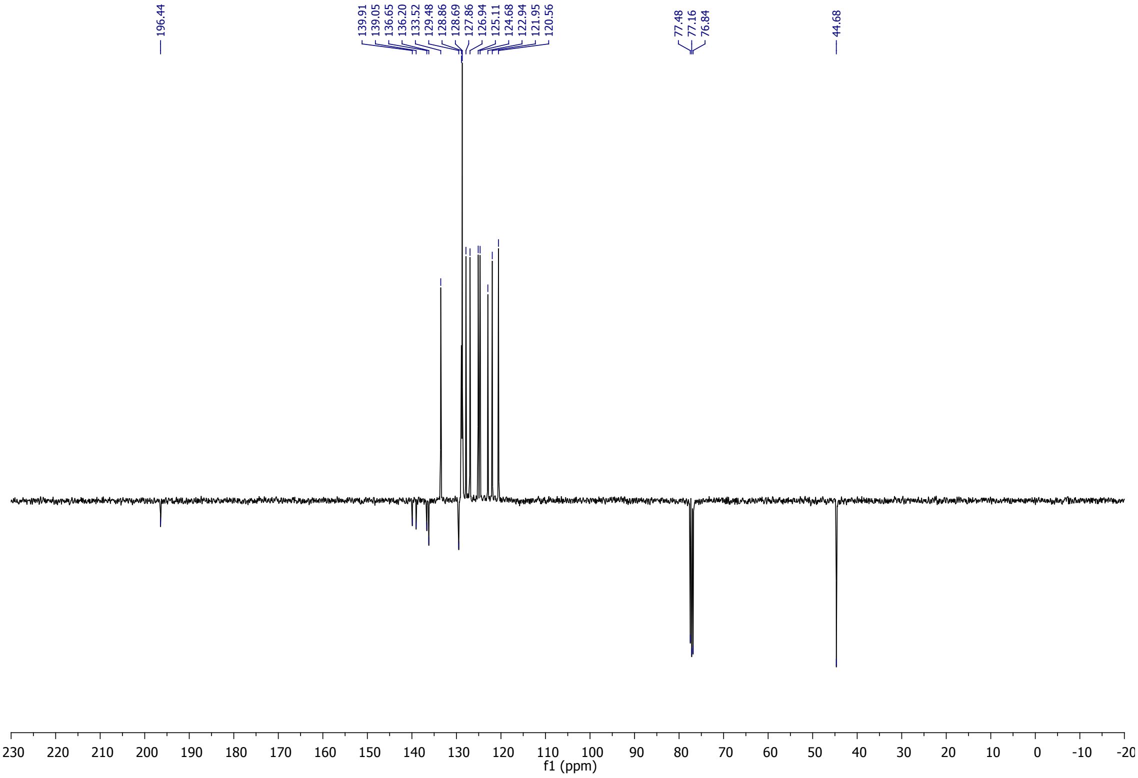
8.10
8.10
8.09
8.09
8.08
8.08
8.08
8.07
8.06
7.87
7.87
7.86
7.86
7.85
7.84
7.61
7.61
7.60
7.59
7.58
7.58
7.56
7.56
7.55
7.50
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.44
7.44
7.43
7.35
7.33
7.26
4.55
O
S
1.05
2.88
0.98
1.09
4.94
0.97
2.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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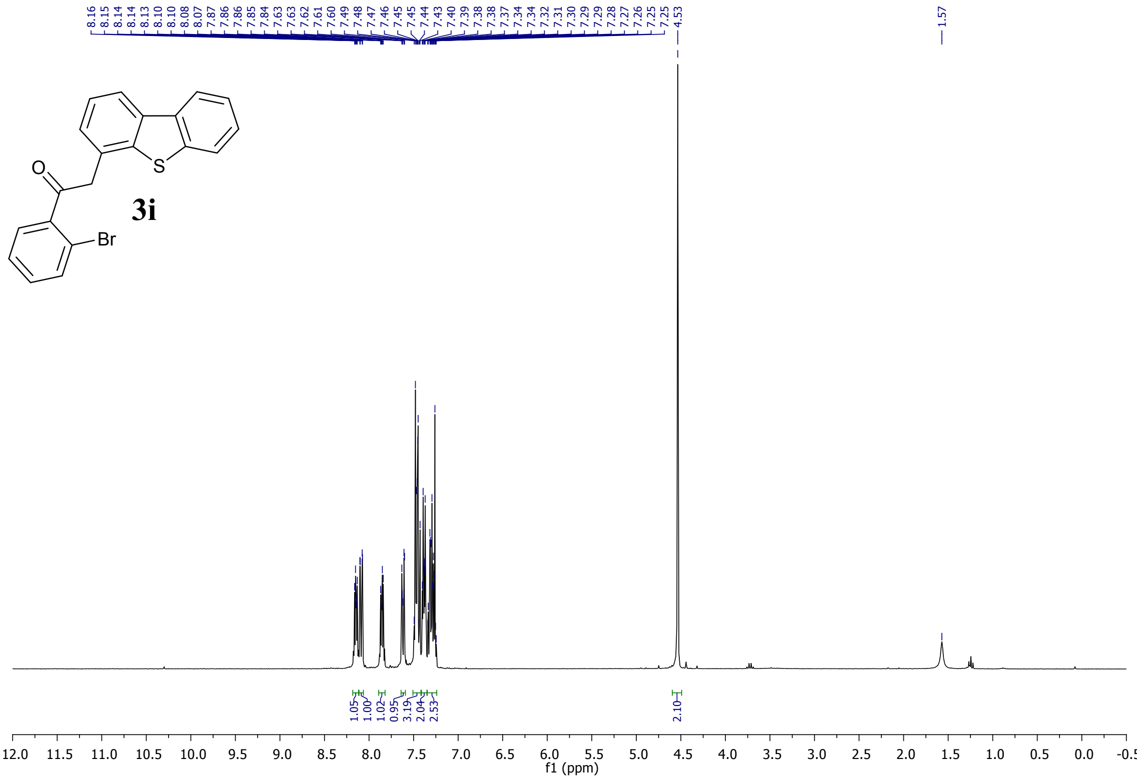
128.69
127.86
126.94
125.11
124.68
122.94
121.95
120.56
77.48
77.16
76.84
44.68
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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8.10
8.10
8.08
8.07
7.87
7.86
7.85
7.84
7.63
7.63
7.62
7.61
7.60
7.49
7.48
7.47
7.46
7.45
7.45
7.44
7.43
7.40
7.39
7.38
7.38
7.37
7.34
7.34
7.32
7.31
7.30
7.29
7.29
7.28
7.27
7.26
7.25
7.25
4.53
1.57
O
S
Br
1.05
1.00
1.02
0.95
3.19
2.04
2.53
2.10
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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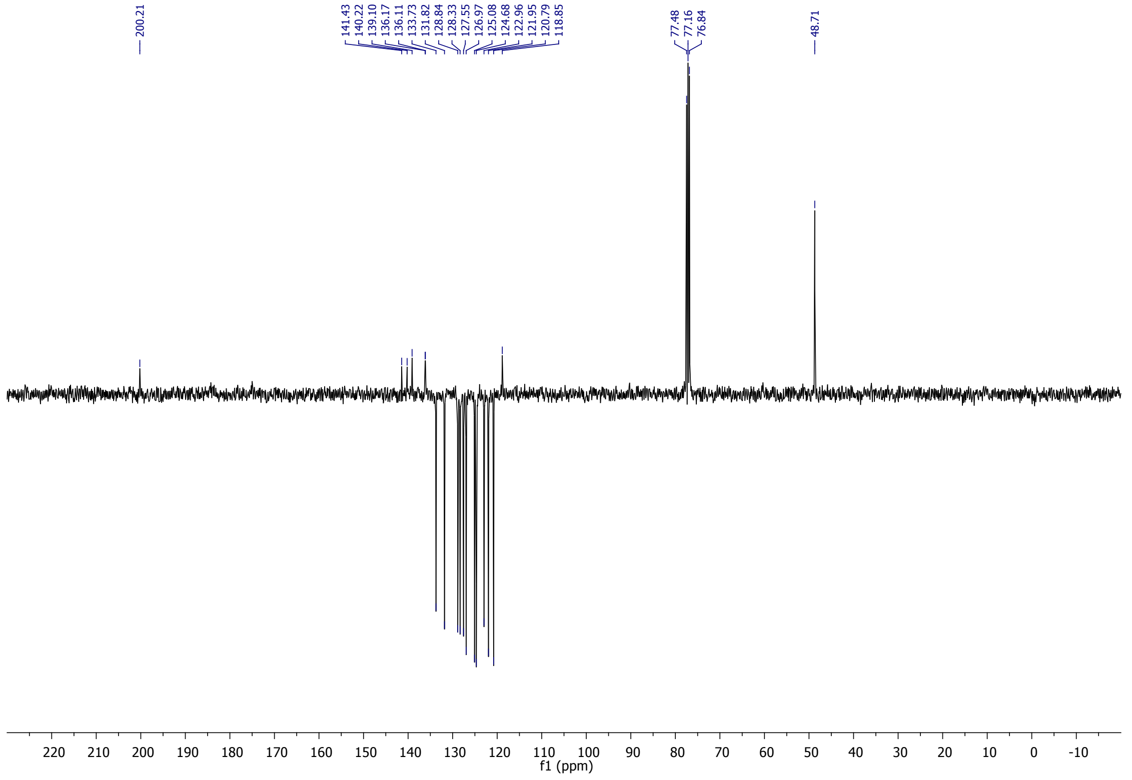
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

3i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140.22
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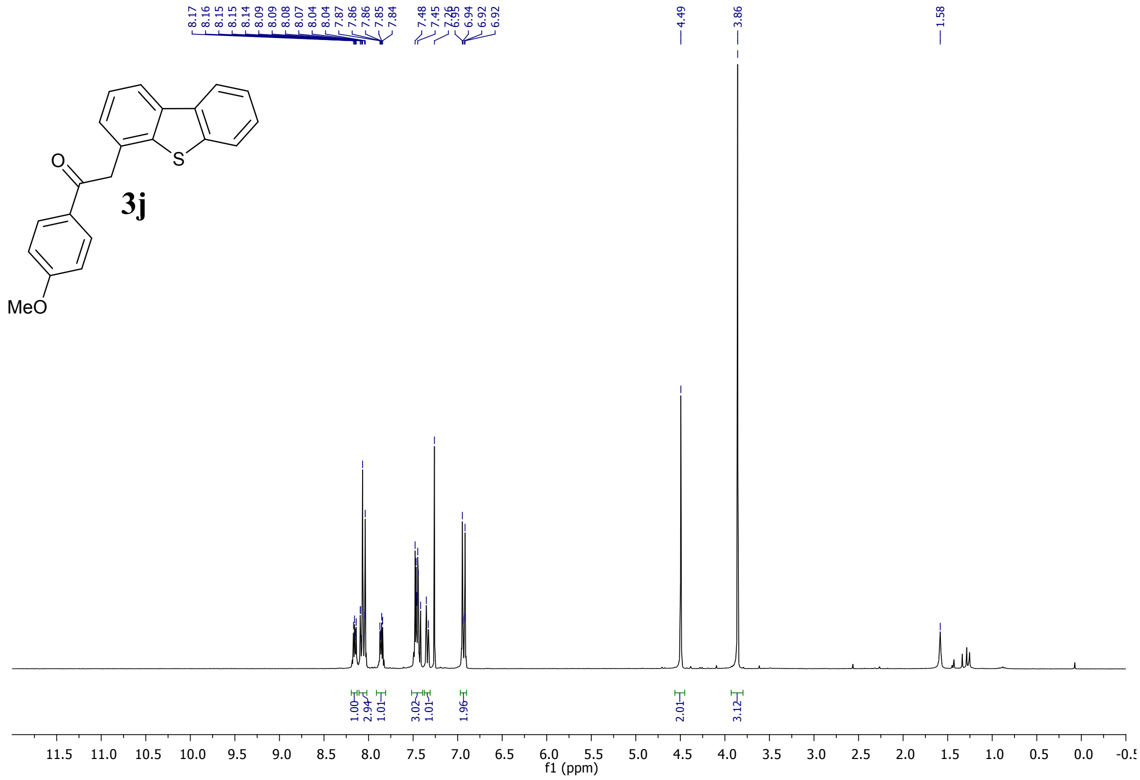
136.11
133.73
131.82
128.84
128.33
127.55
126.97
125.08
124.68
122.96
121.95
120.79
118.85
77.48
77.16
76.84
48.71
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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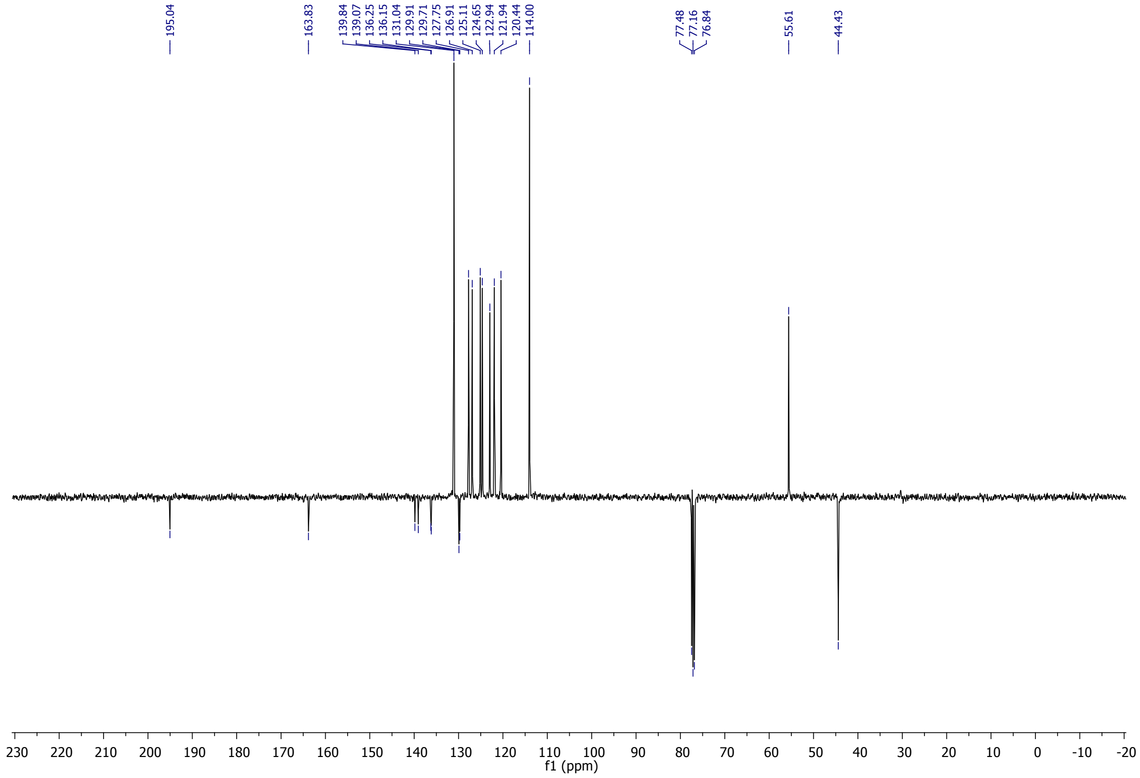
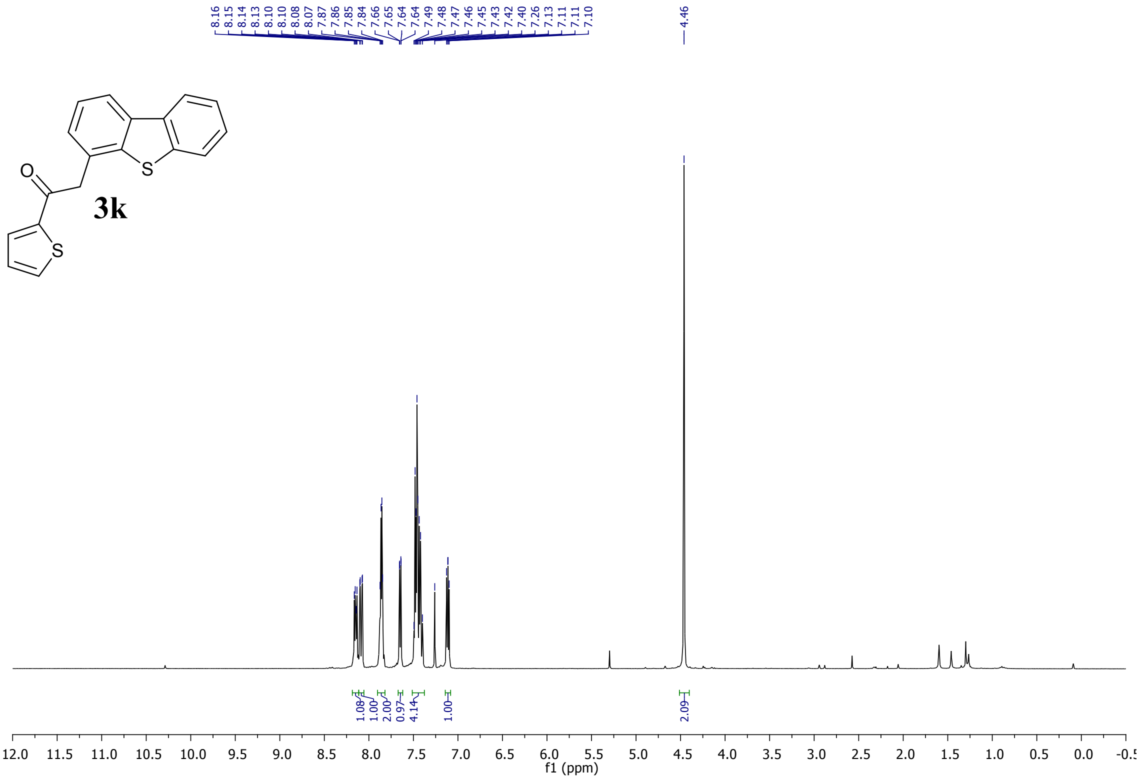
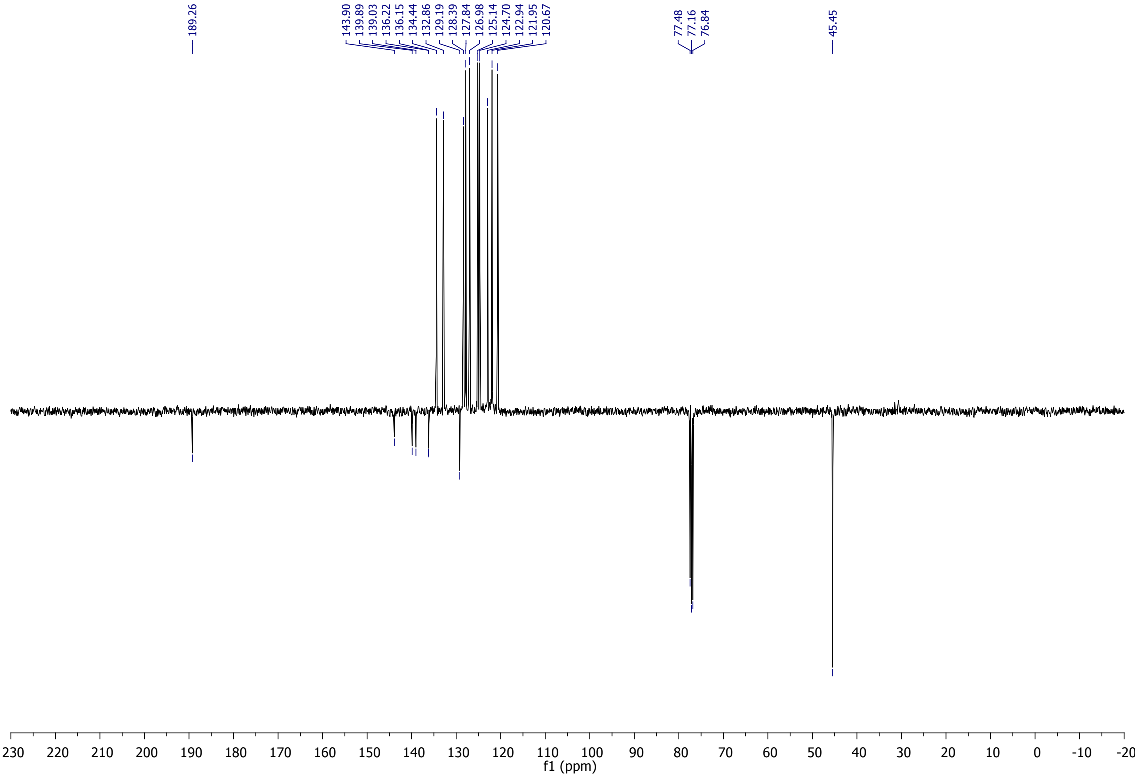
8.16
8.15
8.15
8.14
8.09
8.09
8.08
8.07
8.04
8.04
7.87
7.86
7.86
7.85
7.84
7.48
7.45
7.26
6.95
6.94
6.92
6.92
4.49
3.86
1.58
O
S
3j
MeO
1.00
2.94
1.01
3.02
1.01
1.96
2.01
3.12
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


195.04
163.83
139.84
139.07
136.25
136.15
131.04
129.91
129.71
127.75
126.91
125.11
124.65
122.94
121.94
120.44
114.00
77.48
77.16
76.84
55.61
44.43
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)



3k

8.16
8.15
8.14
8.13
8.10
8.10
8.08
8.07
7.87
7.86
7.85
7.84
7.66
7.65
7.64
7.64
7.49
7.48
7.47
7.46
7.45
7.43
7.42
7.40
7.26
7.13
7.11
7.11
7.10
4.46
1.08
1.00
2.00
0.97
4.14
1.00
2.09
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


189.26
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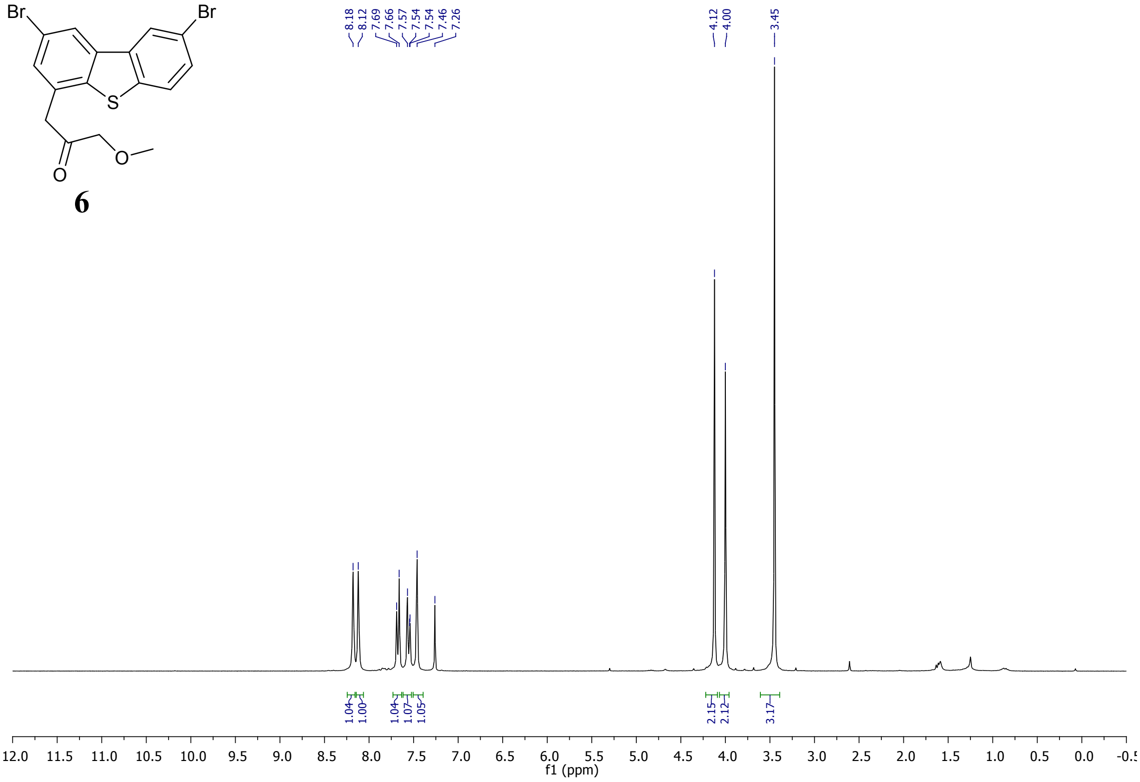
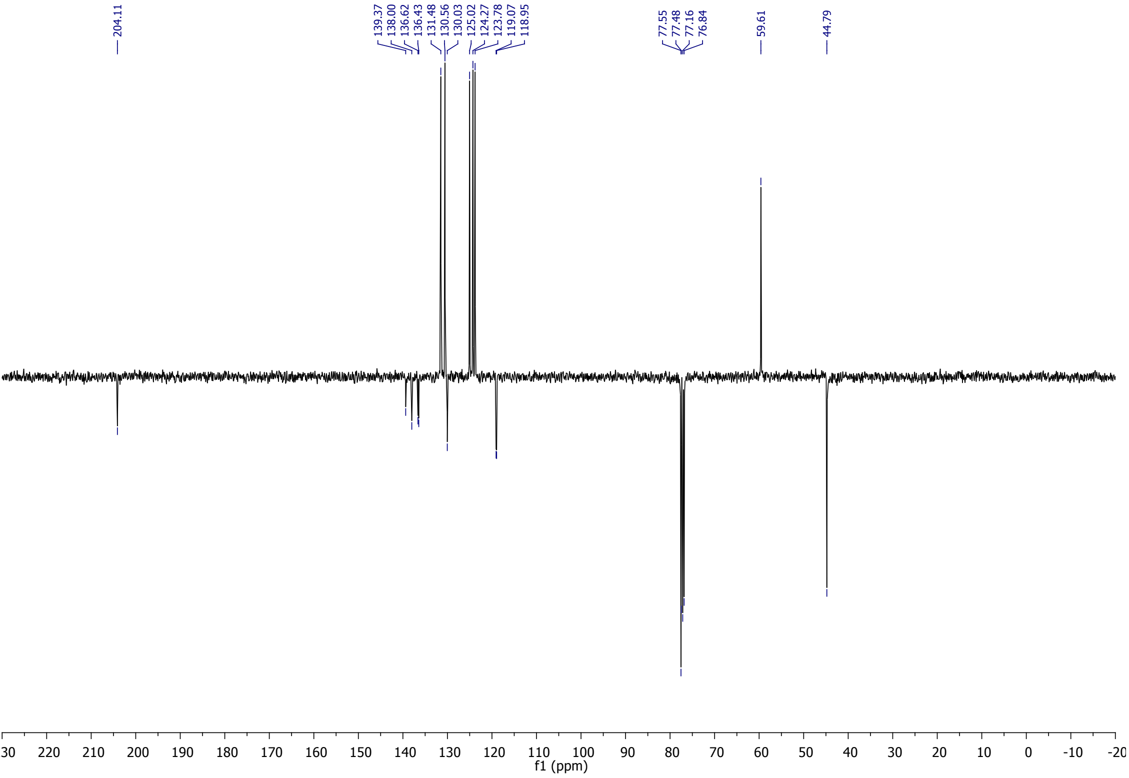
139.89
139.03
136.22
136.15
134.44
132.86
129.19
128.39
127.84
126.98
125.14
124.70
122.94
121.95
120.67
77.48
77.16
76.84
45.45
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

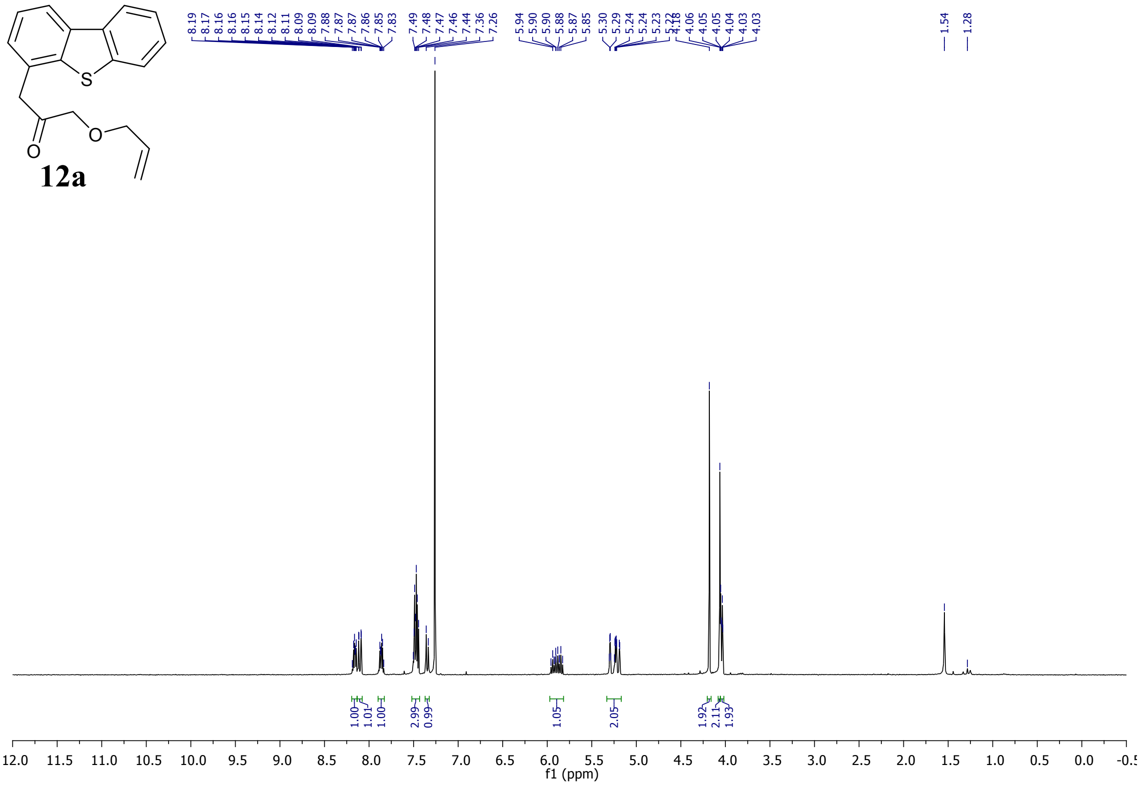


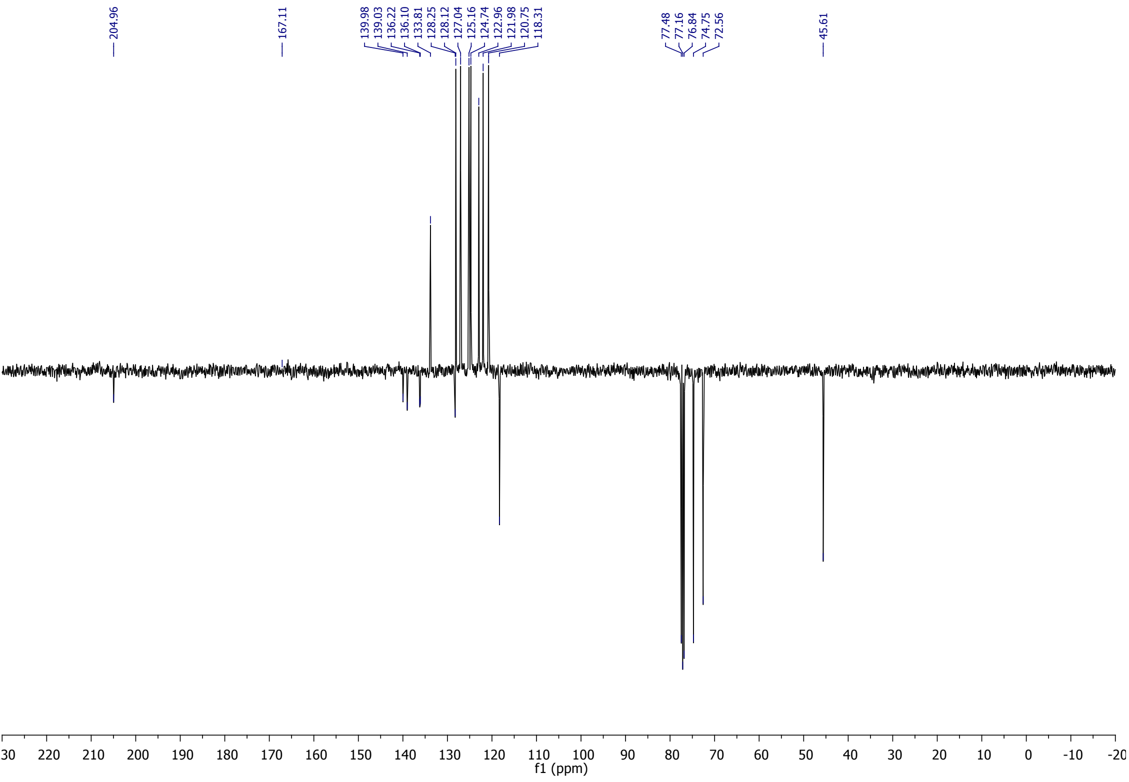
6

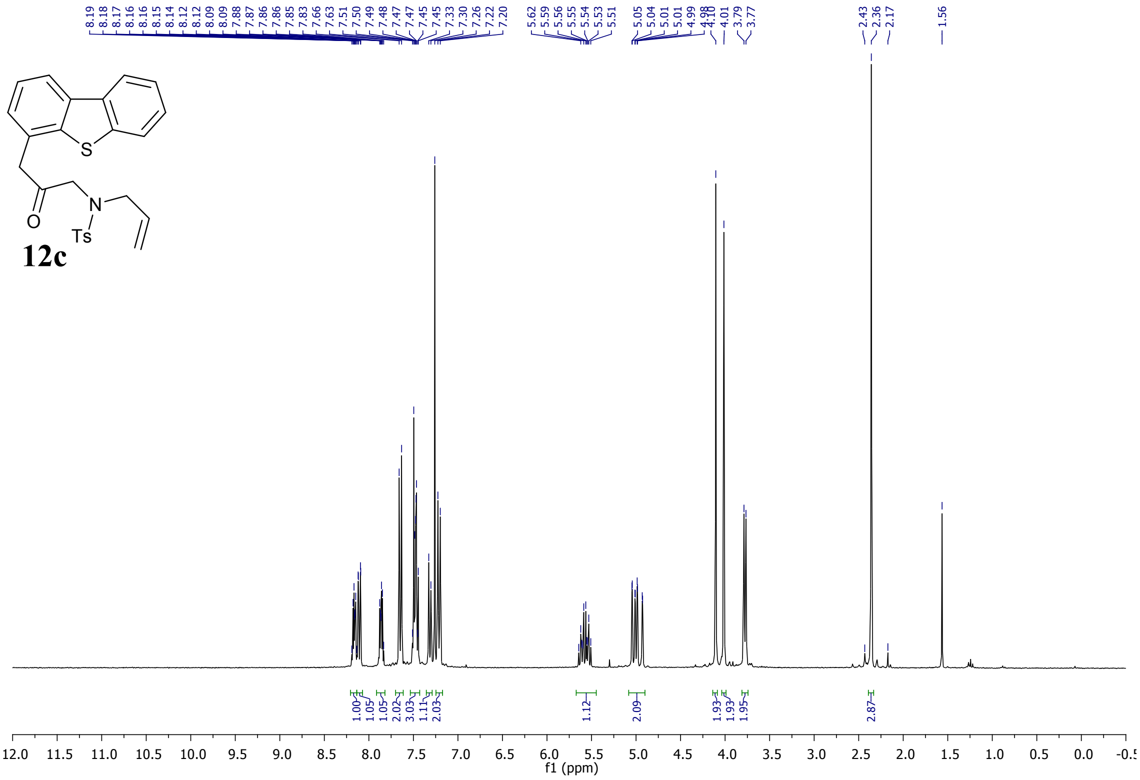
Br
Br
S
O
O
8.18
8.12
7.69
7.66
7.57
7.54
7.54
7.46
7.26
4.12
4.00
3.45
1.04
1.00
1.04
1.07
1.05
2.15
2.12
3.17
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



204.11
139.37
138.00
136.62
136.43
131.48
130.56
130.03
125.02
124.27
123.78
119.07
118.95
77.55
77.48
77.16
76.84
59.61
44.79
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

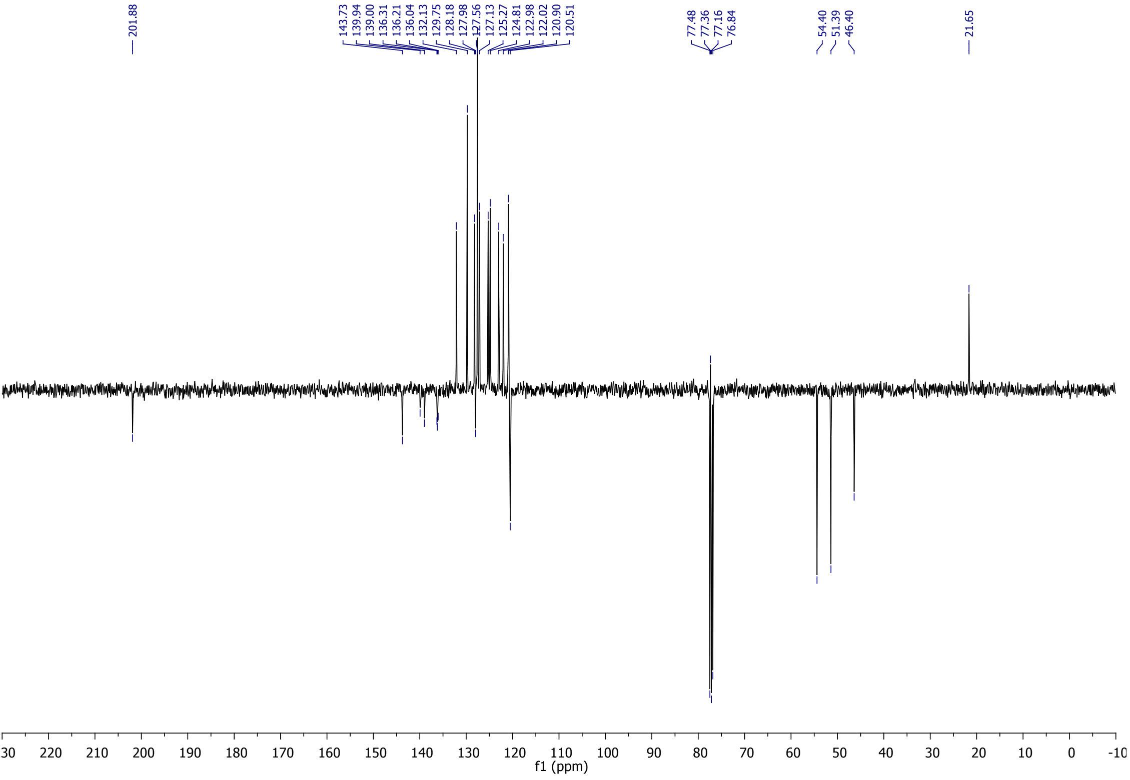

12a
S
O
O
8.19 8.17 8.16 8.15 8.14 8.12 8.11 8.09 8.09 7.88 7.87 7.87 7.86 7.85 7.83
7.49 7.48 7.47 7.46 7.44 7.36 7.26
5.94 5.90 5.90 5.88 5.87 5.85
5.30 5.29 5.24 5.24 5.23 5.22 4.18 4.06 4.05 4.05 4.04 4.03 4.03
1.54
1.28
1.00 1.01 1.00 2.99 0.99 1.05 2.05 1.92 2.11 1.93
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


204.96
167.11
139.98 139.03 136.22 136.10 133.81 128.25 128.12 127.04 125.16 124.74 122.96 121.98 120.75 118.31
77.48 77.16 76.84 74.75 72.56
45.61
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

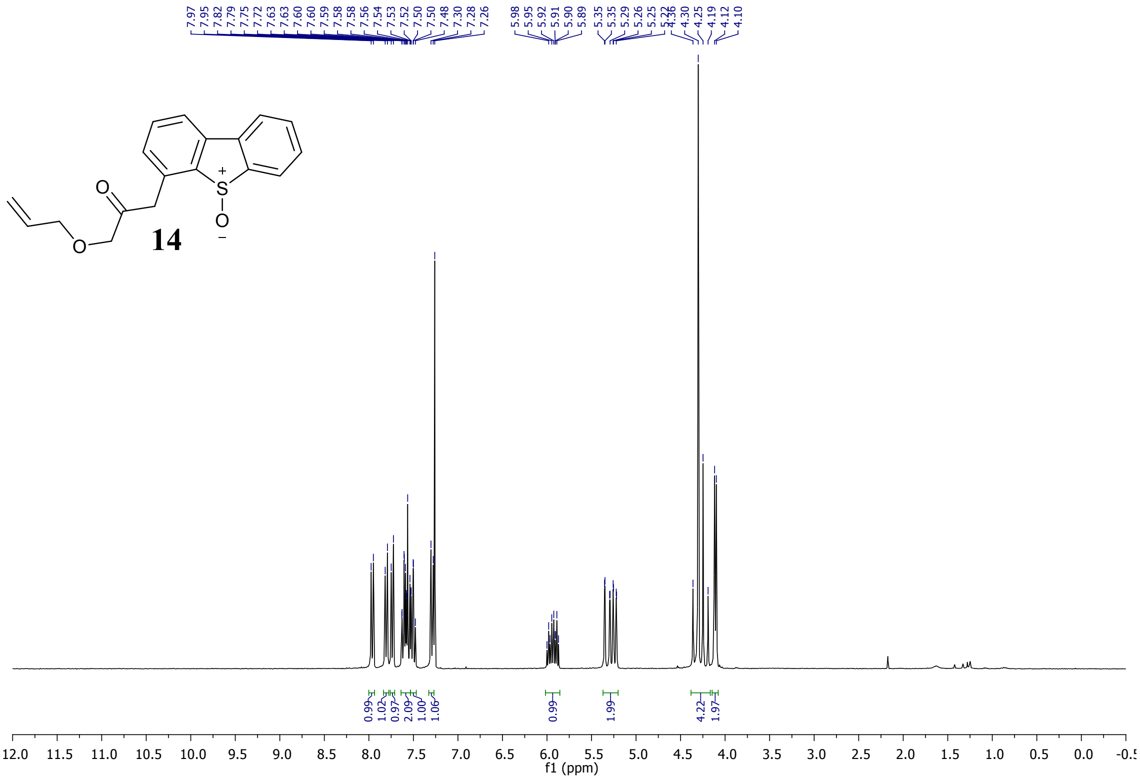


S
O
N
Ts
8.19
8.18
8.17
8.16
8.16
8.15
8.14
8.12
8.12
8.09
8.09
7.88
7.87
7.86
7.86
7.85
7.83
7.66
7.63
7.51
7.50
7.49
7.48
7.47
7.47
7.45
7.45
7.33
7.30
7.26
7.22
7.20
5.62
5.59
5.56
5.55
5.54
5.53
5.51
5.05
5.04
5.01
5.01
4.99
4.98
4.10
4.01
3.79
3.77
2.43
2.36
2.17
1.56
1.00
1.05
1.05
2.02
3.03
1.11
2.03
1.12
2.09
1.93
1.93
1.95
2.87
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

12c

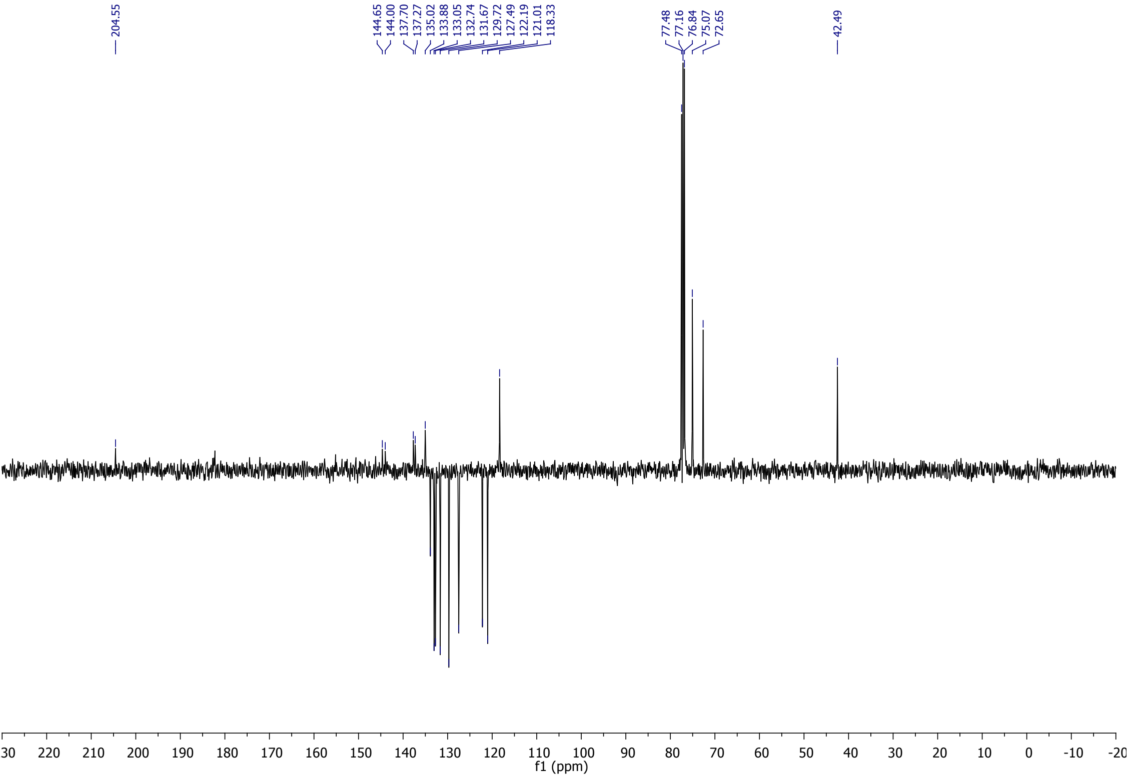


201.88
143.73
139.94
139.00
136.31
136.21
136.04
132.13
129.75
128.18
127.98
127.56
127.13
125.27
124.81
122.98
122.02
120.90
120.51
77.48
77.36
77.16
76.84
54.40
51.39
46.40
21.65
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

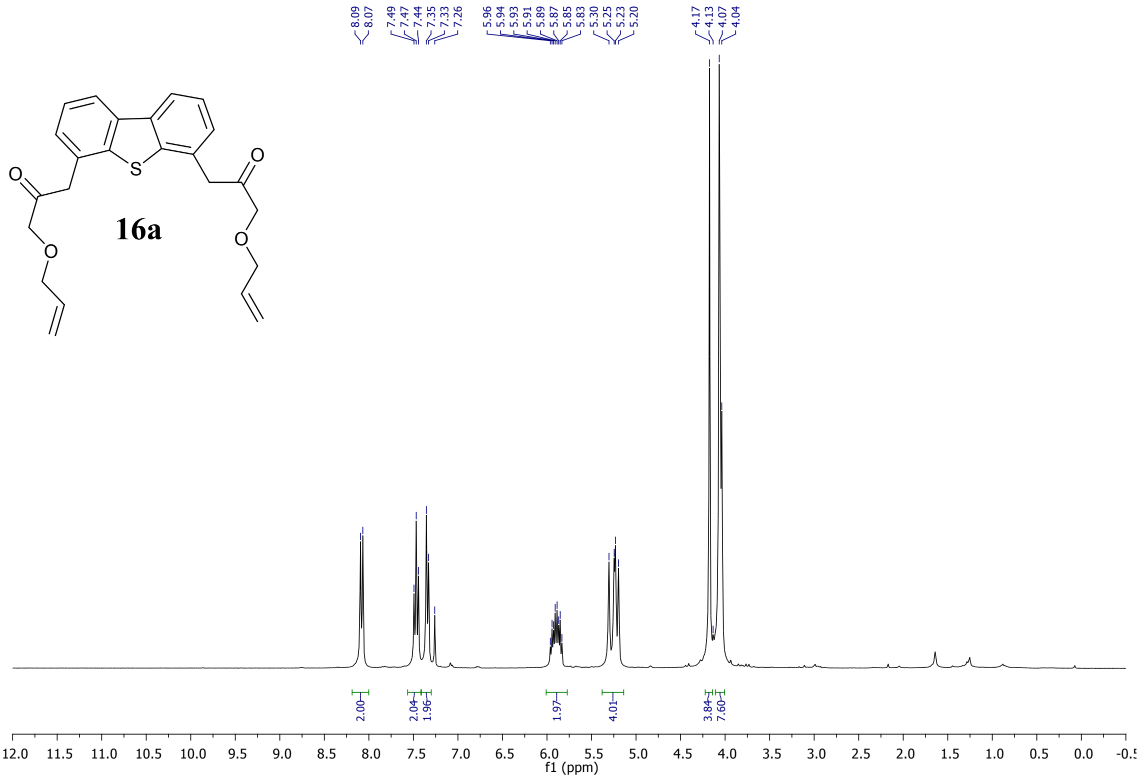


14

7.97
7.95
7.82
7.79
7.75
7.72
7.63
7.63
7.60
7.60
7.59
7.58
7.58
7.56
7.54
7.53
7.52
7.50
7.50
7.48
7.30
7.28
7.26
5.98
5.95
5.92
5.91
5.90
5.89
5.35
5.35
5.29
5.26
5.25
5.22
4.36
4.30
4.25
4.19
4.12
4.10
0.99
1.02
0.97
2.09
1.00
1.06
0.99
1.99
4.22
1.97
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
O
S
+
O
−



204.55
144.65
144.00
137.70
137.27
135.02
133.88
133.05
132.74
131.67
129.72
127.49
122.19
121.01
118.33
77.48
77.16
76.84
75.07
72.65
42.49
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


16a

8.09
8.07
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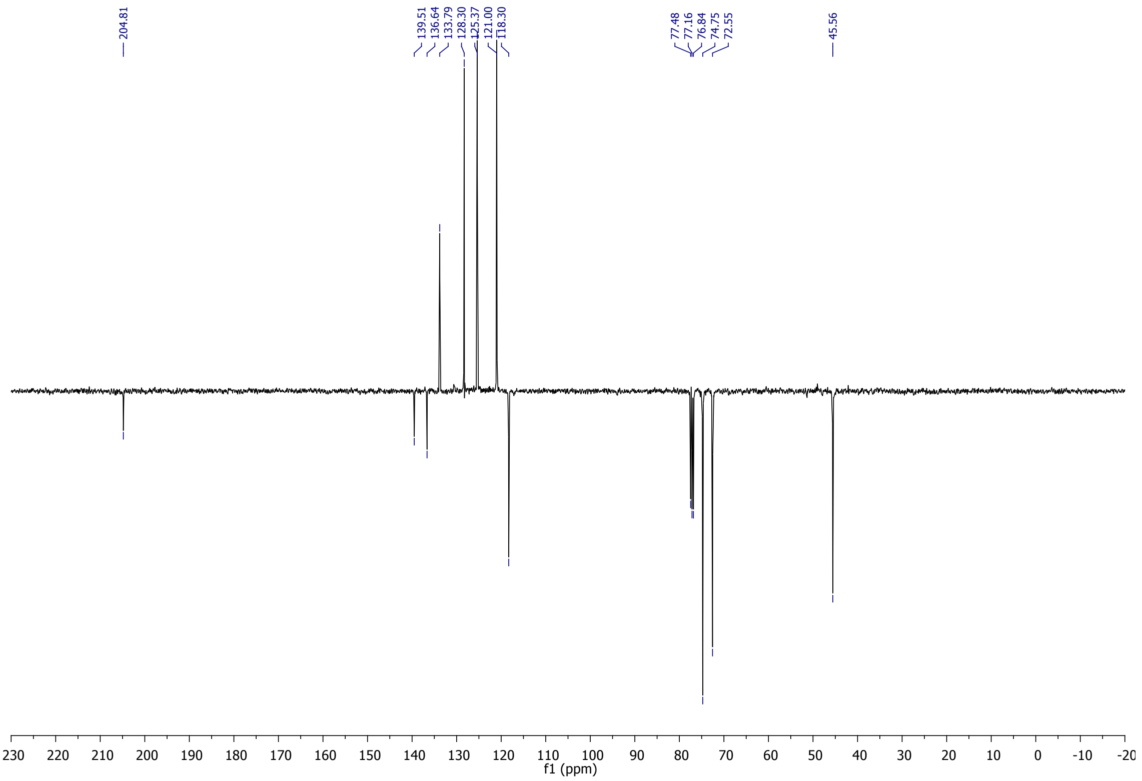
7.33
7.26
5.96
5.94
5.93
5.91
5.89
5.87
5.85
5.83
5.30
5.25
5.23
5.20
4.17
4.13
4.07
4.04
2.00
2.04
1.96
1.97
4.01
3.84
7.60
O
S
O
O
O
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


204.81
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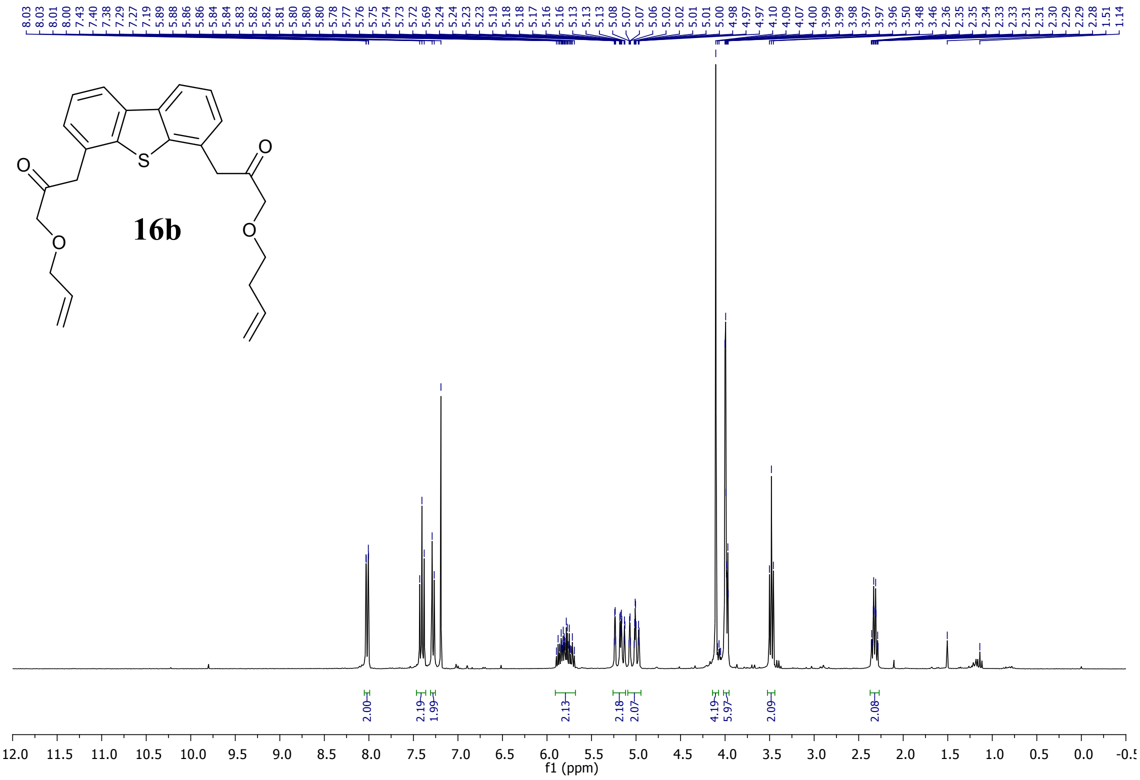
128.30
125.37
121.00
118.30
77.48
77.16
76.84
74.75
72.55
45.56
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



16b

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8.03
8.01
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7.29
7.27
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5.88
5.86
5.86
5.84
5.84
5.83
5.82
5.82
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5.80
5.78
5.77
5.76
5.75
5.74
5.73
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5.23
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5.19
5.18
5.18
5.17
5.16
5.16
5.13
5.13
5.13
5.08
5.07
5.07
5.06
5.02
5.02
5.01
5.01
5.00
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4.10
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4.07
4.00
3.99
3.99
3.98
3.97
3.97
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2.34
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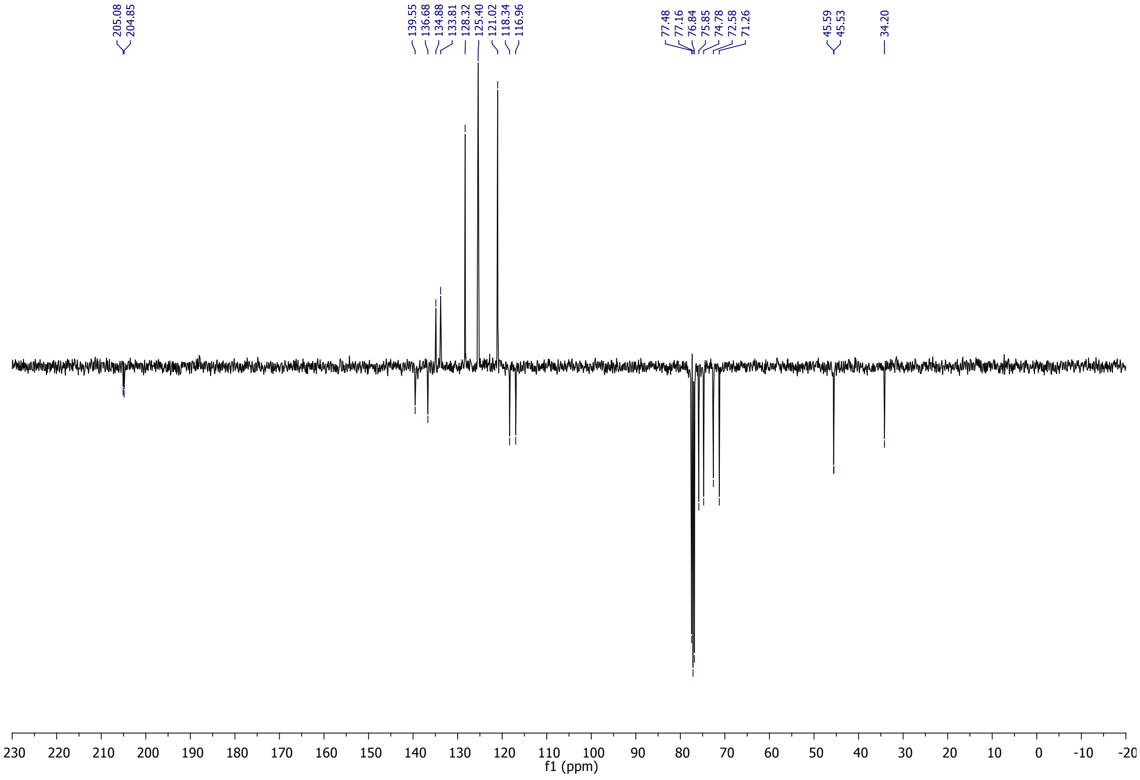
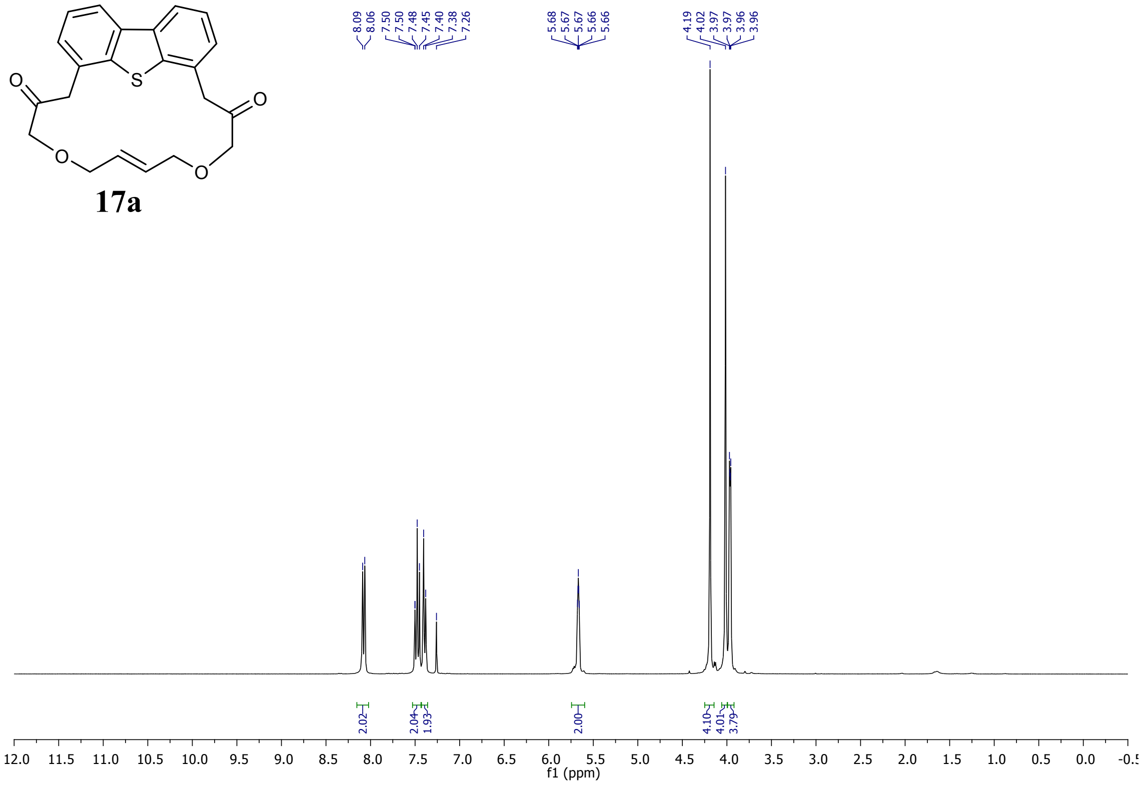
2.33
2.31
2.30
2.29
2.29
2.28
1.51
1.14
O
S
O
O
O
2.00
2.19
1.99
2.13
2.18
2.07
4.19
5.97
2.09
2.08
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)

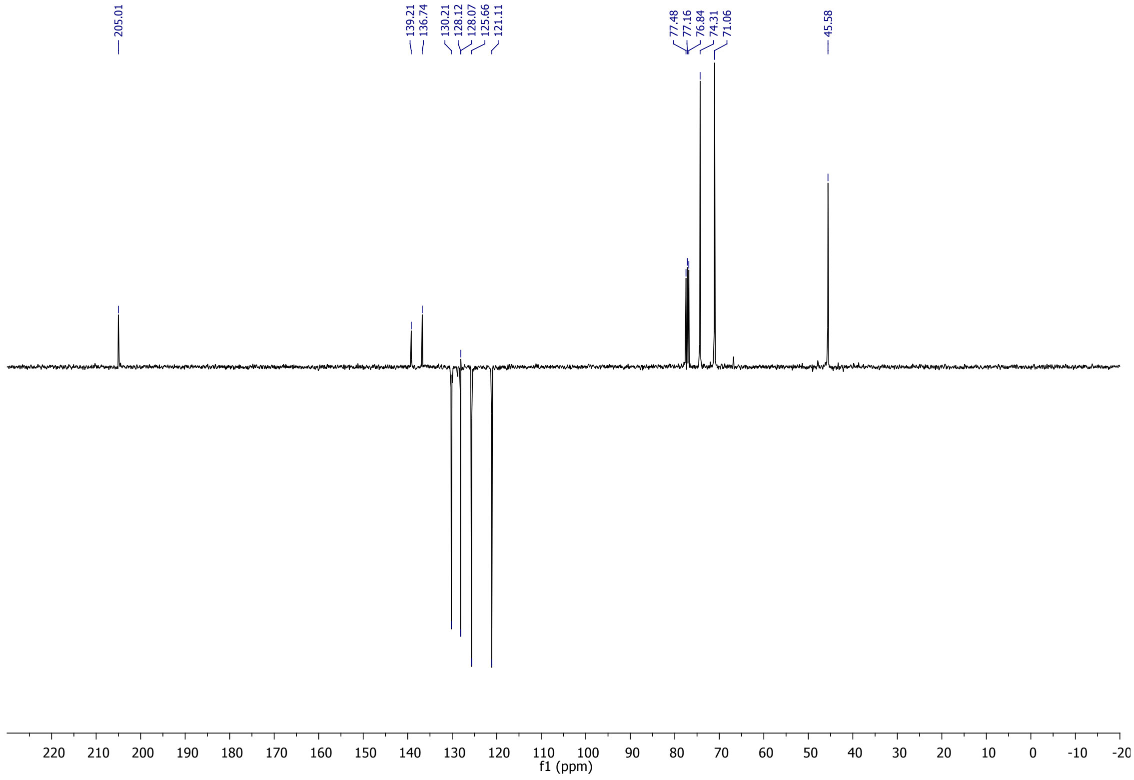


205.08
204.85
139.55
136.68
134.88
133.81
128.32
125.40
121.02
118.34
116.96
77.48
77.16
76.84
75.85
74.78
72.58
71.26
45.59
45.53
34.20
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

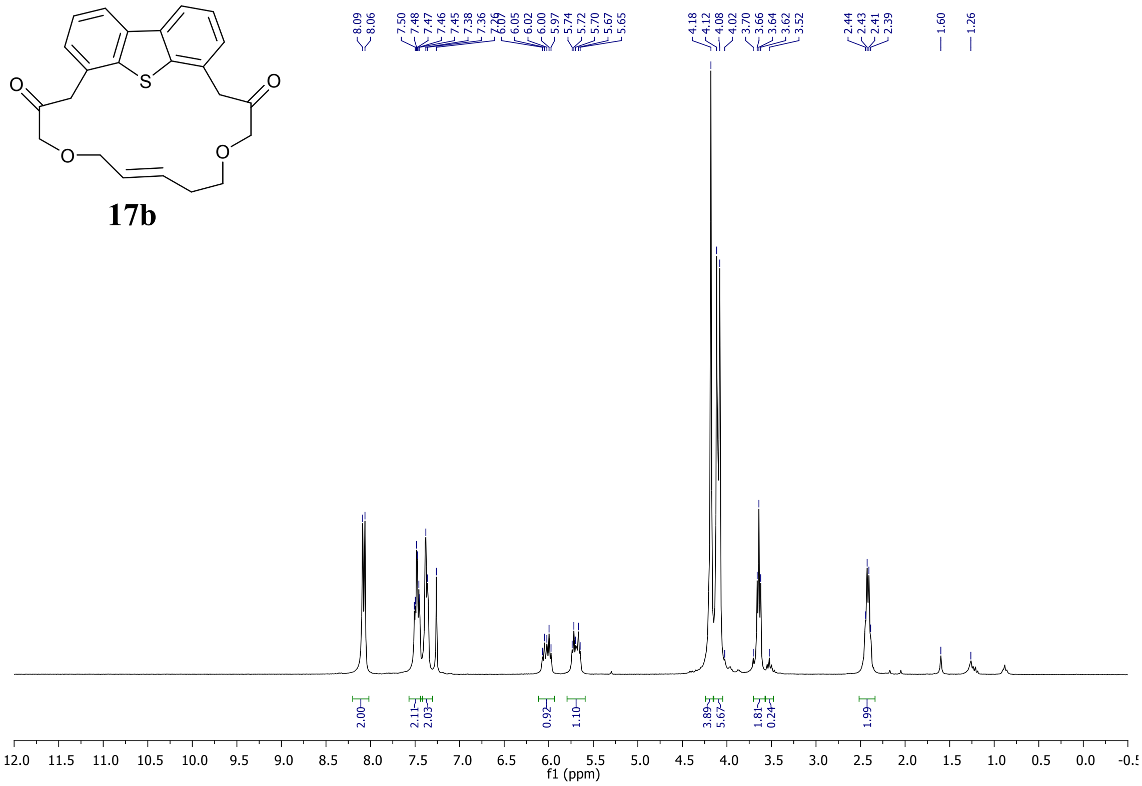


17a

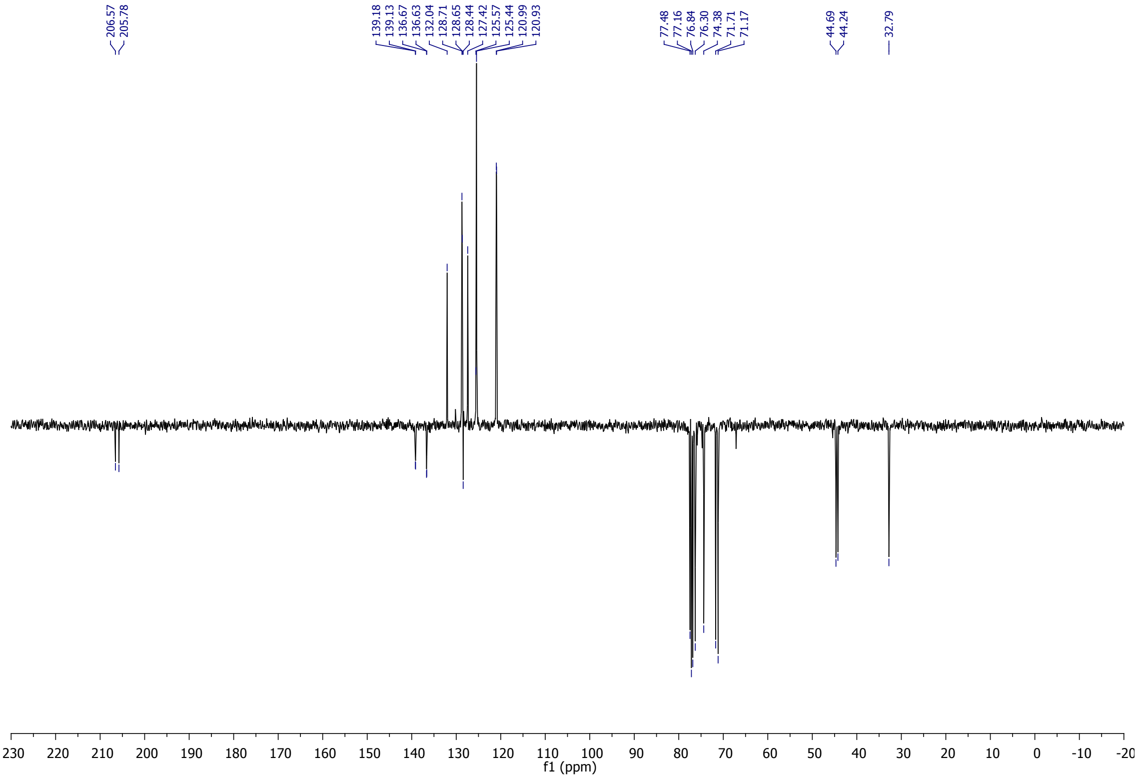
8.09
8.06
7.50
7.50
7.48
7.45
7.40
7.38
7.26
5.68
5.67
5.67
5.66
5.66
4.19
4.02
3.97
3.97
3.96
3.96
2.02
2.04
1.93
2.00
4.10
4.01
3.79
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
O
S
O
O
O

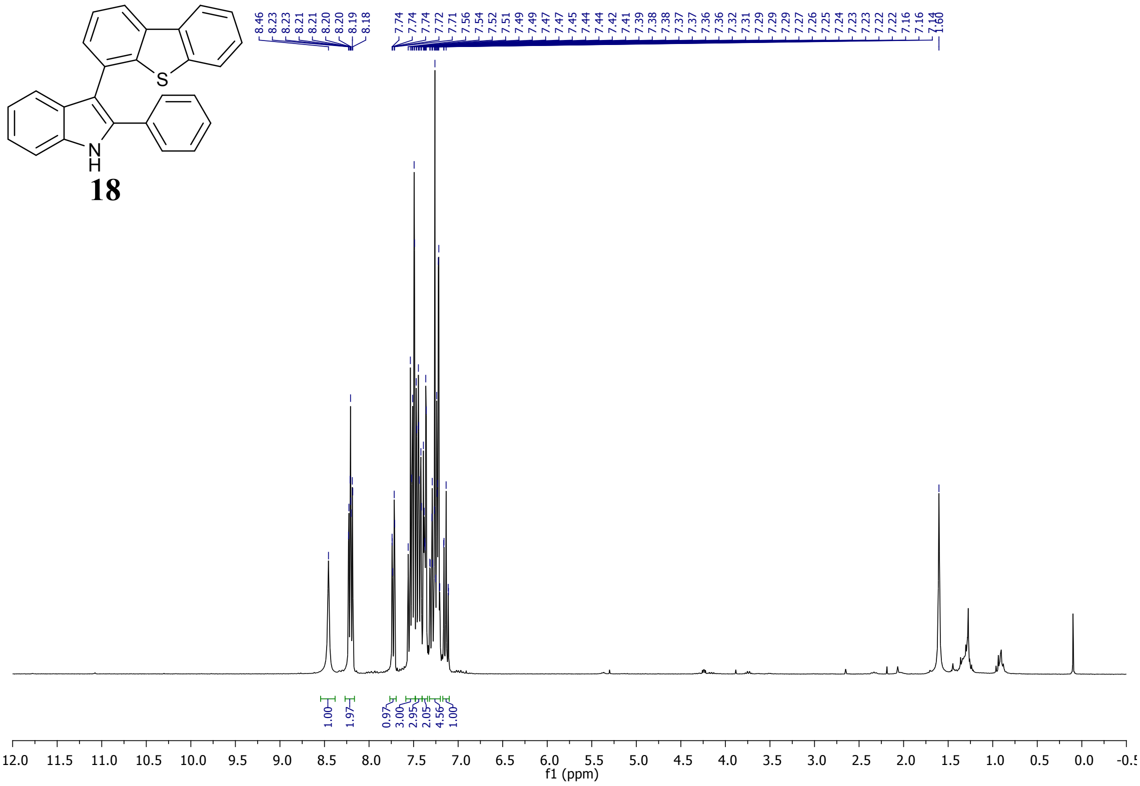


205.01
139.21
136.74
130.21
128.12
128.07
125.66
121.11
77.48
77.16
76.84
74.31
71.06
45.58
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


O
S
O
O
O
8.09
8.06
7.50
7.48
7.47
7.46
7.45
7.38
7.36
7.26
6.07
6.05
6.02
6.00
5.97
5.74
5.72
5.70
5.67
5.65
4.18
4.12
4.08
4.02
3.70
3.66
3.64
3.62
3.52
2.44
2.43
2.41
2.39
1.60
1.26
2.00
2.11
2.03
0.92
1.10
3.89
5.67
1.81
0.24
1.99
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

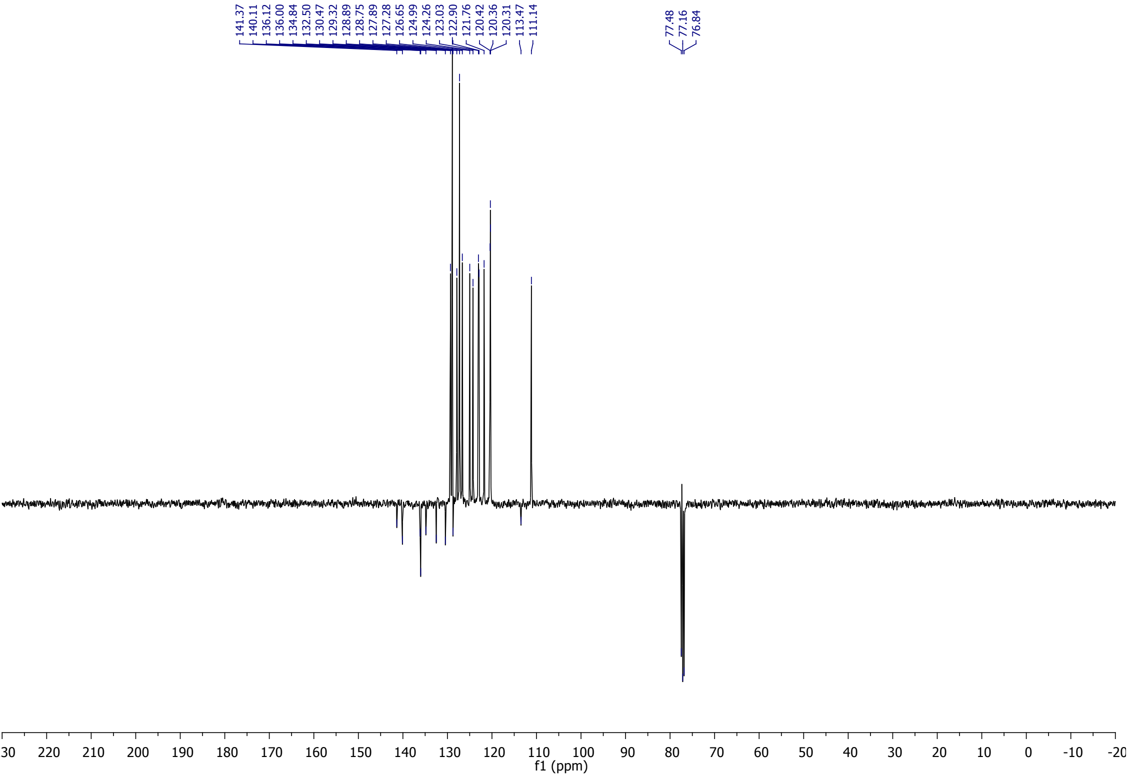
17b


206.57
205.78
139.18
139.13
136.67
136.63
132.04
128.71
128.65
128.44
127.42
125.57
125.44
120.99
120.93
77.48
77.16
76.84
76.30
74.38
71.71
71.17
44.69
44.24
32.79
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

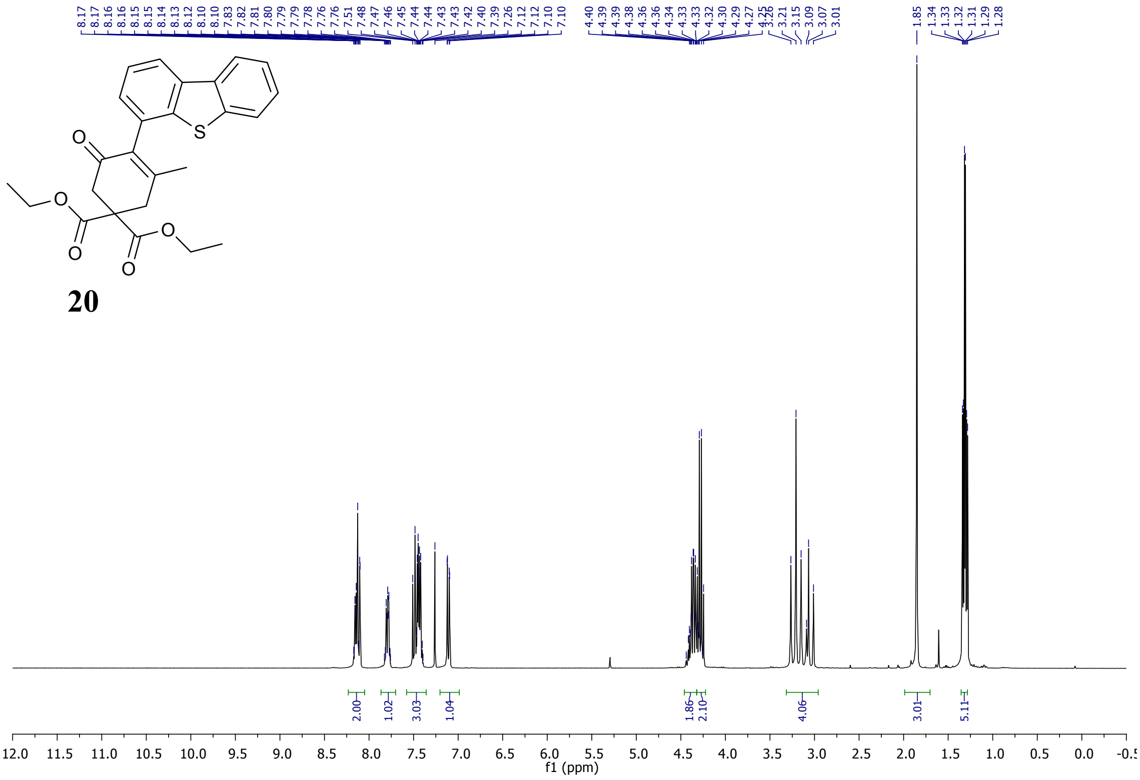


18

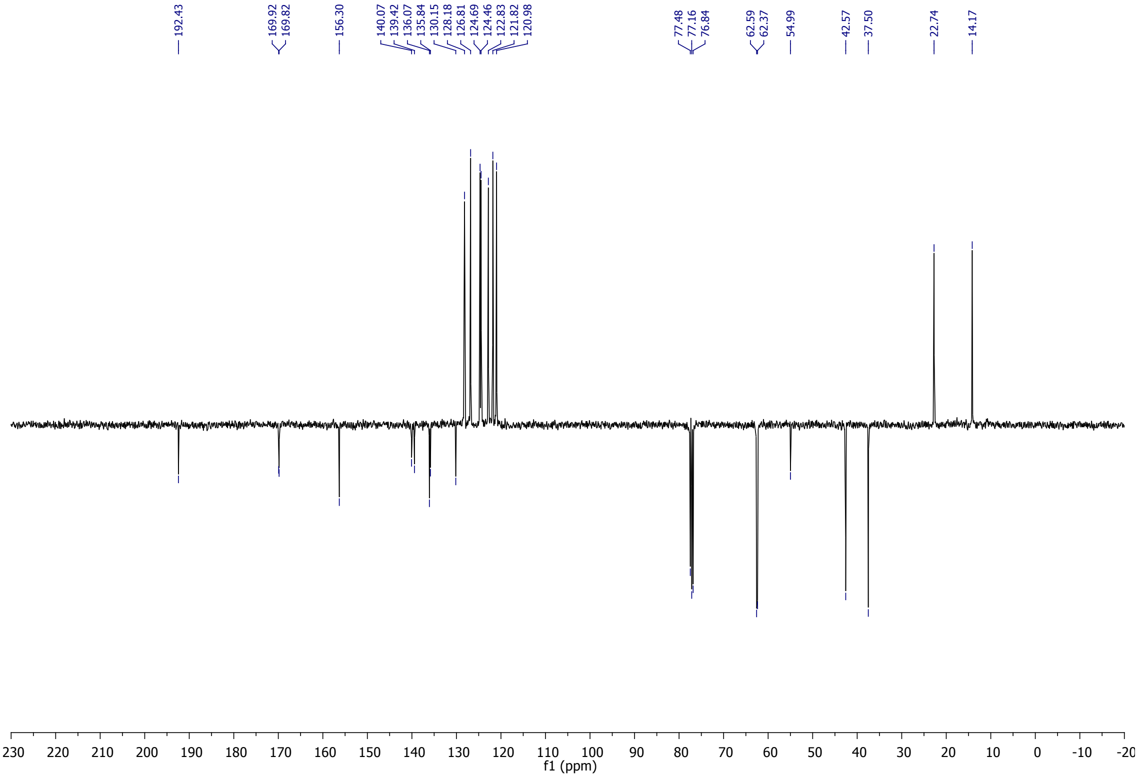
S
N
H
8.46
8.23
8.23
8.21
8.21
8.20
8.20
8.19
8.18
7.74
7.74
7.74
7.72
7.71
7.56
7.54
7.52
7.51
7.49
7.47
7.45
7.44
7.44
7.42
7.41
7.39
7.38
7.38
7.37
7.37
7.36
7.36
7.32
7.31
7.29
7.29
7.27
7.26
7.25
7.24
7.23
7.23
7.22
7.22
7.16
7.14
1.60
1.00
1.97
0.97
3.00
2.95
2.05
4.56
1.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

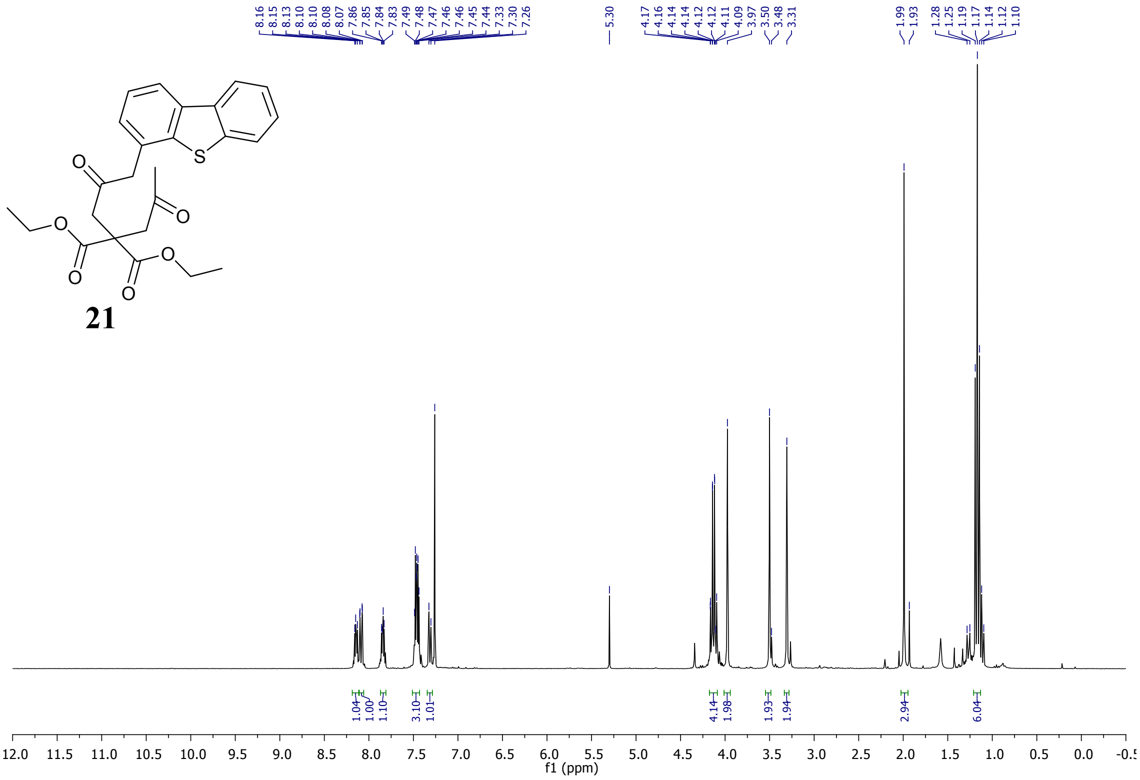


141.37
140.11
136.12
136.00
134.84
132.50
130.47
129.32
128.89
128.75
127.89
127.28
126.65
124.99
124.26
123.03
122.90
121.76
120.42
120.36
120.31
113.47
111.14
77.48
77.16
76.84
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


8.17
8.17
8.16
8.15
8.15
8.14
8.13
8.12
8.10
8.10
7.83
7.82
7.81
7.80
7.79
7.79
7.78
7.76
7.51
7.48
7.47
7.46
7.45
7.44
7.44
7.43
7.43
7.42
7.40
7.39
7.26
7.12
7.10
7.10
4.40
4.39
4.39
4.38
4.36
4.36
4.34
4.33
4.33
4.32
4.30
4.29
4.27
4.25
3.26
3.21
3.15
3.09
3.07
3.01
1.85
1.34
1.33
1.32
1.31
1.29
1.28
O
S
O
O
O
O
2.00
1.02
3.03
1.04
1.86
2.10
4.06
3.01
5.11
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

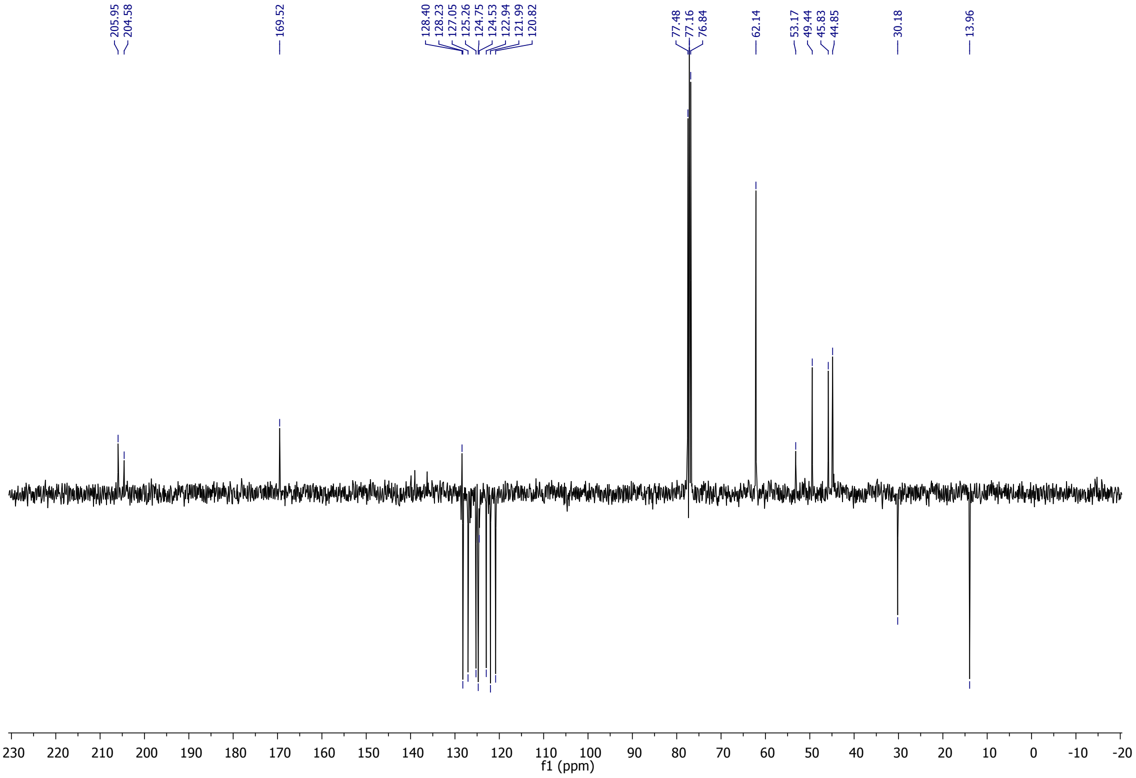
20


192.43
169.92
169.82
156.30
140.07
139.42
136.07
135.84
130.15
128.18
126.81
124.69
124.46
122.83
121.82
120.98
77.48
77.16
76.84
62.59
62.37
54.99
42.57
37.50
22.74
14.17
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

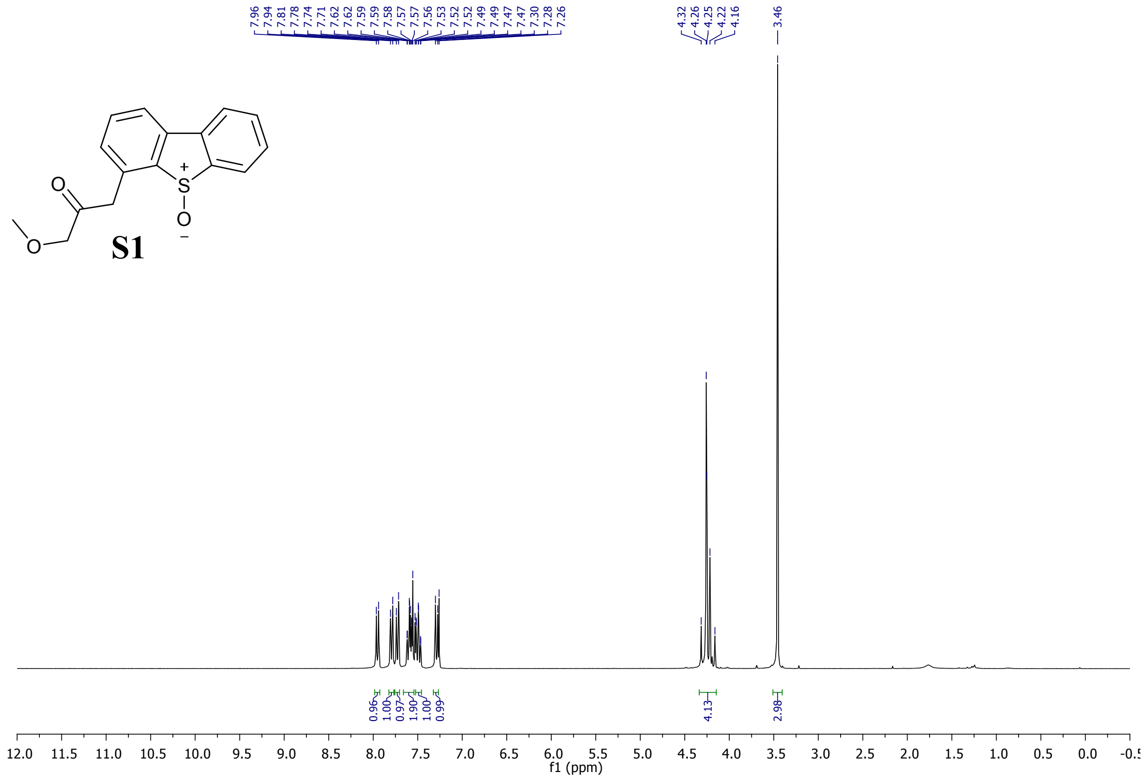


21

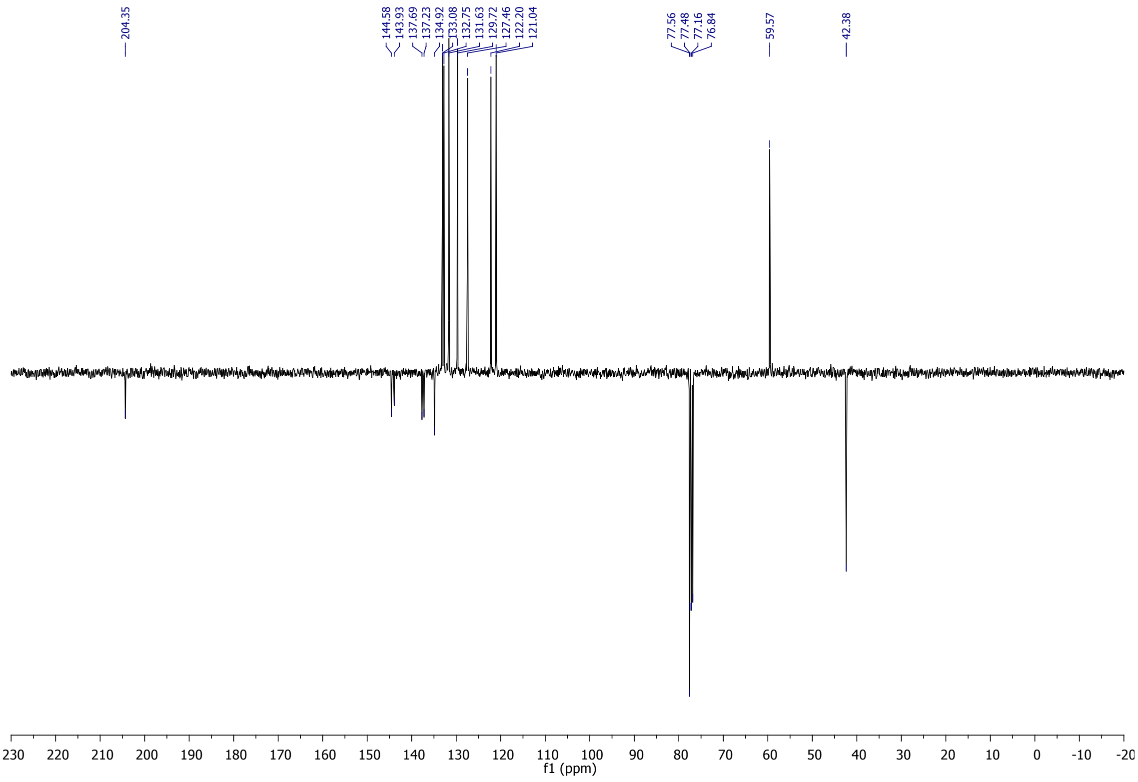
8.16
8.15
8.13
8.10
8.10
8.08
8.07
7.86
7.85
7.84
7.83
7.49
7.48
7.47
7.46
7.46
7.45
7.44
7.33
7.30
7.26
5.30
4.17
4.16
4.14
4.14
4.12
4.12
4.11
4.09
3.97
3.50
3.48
3.31
1.99
1.93
1.28
1.25
1.19
1.17
1.14
1.12
1.10
1.04
1.00
1.10
3.10
1.01
4.14
1.98
1.93
1.94
2.94
6.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
O
S
O
O
O
O
O

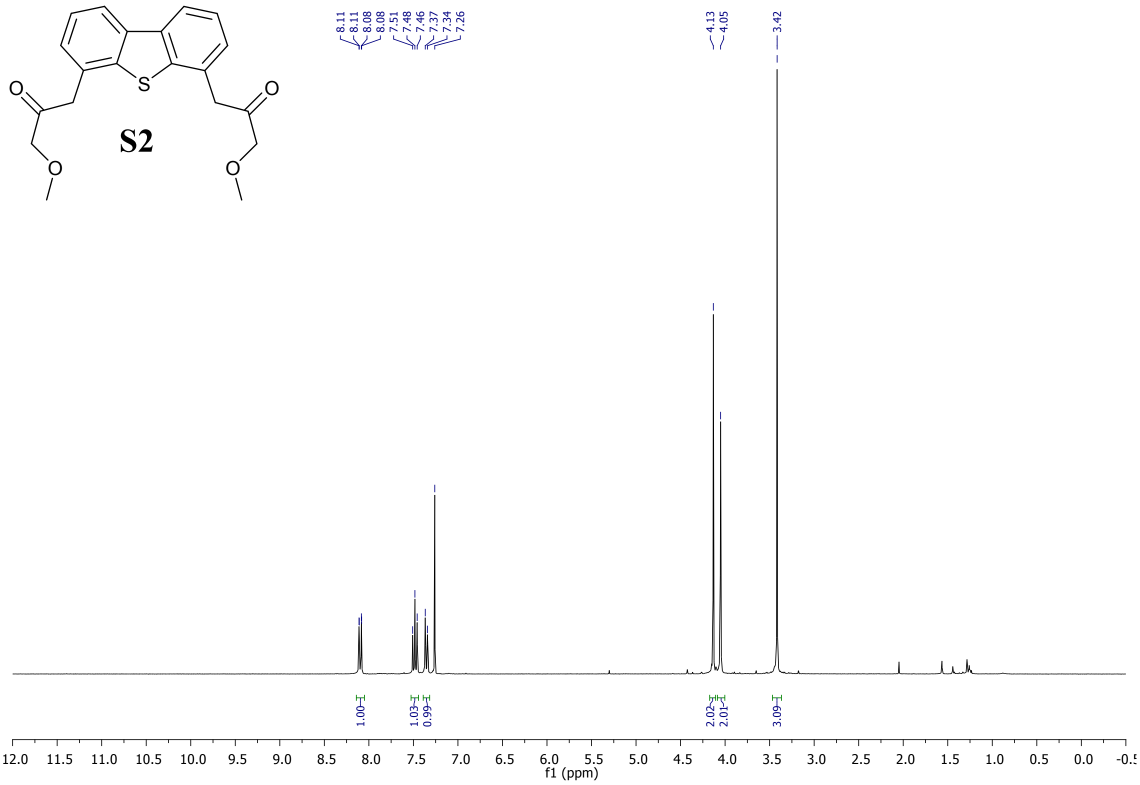


205.95
204.58
169.52
128.40
128.23
127.05
125.26
124.75
124.53
122.94
121.99
120.82
77.48
77.16
76.84
62.14
53.17
49.44
45.83
44.85
30.18
13.96
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

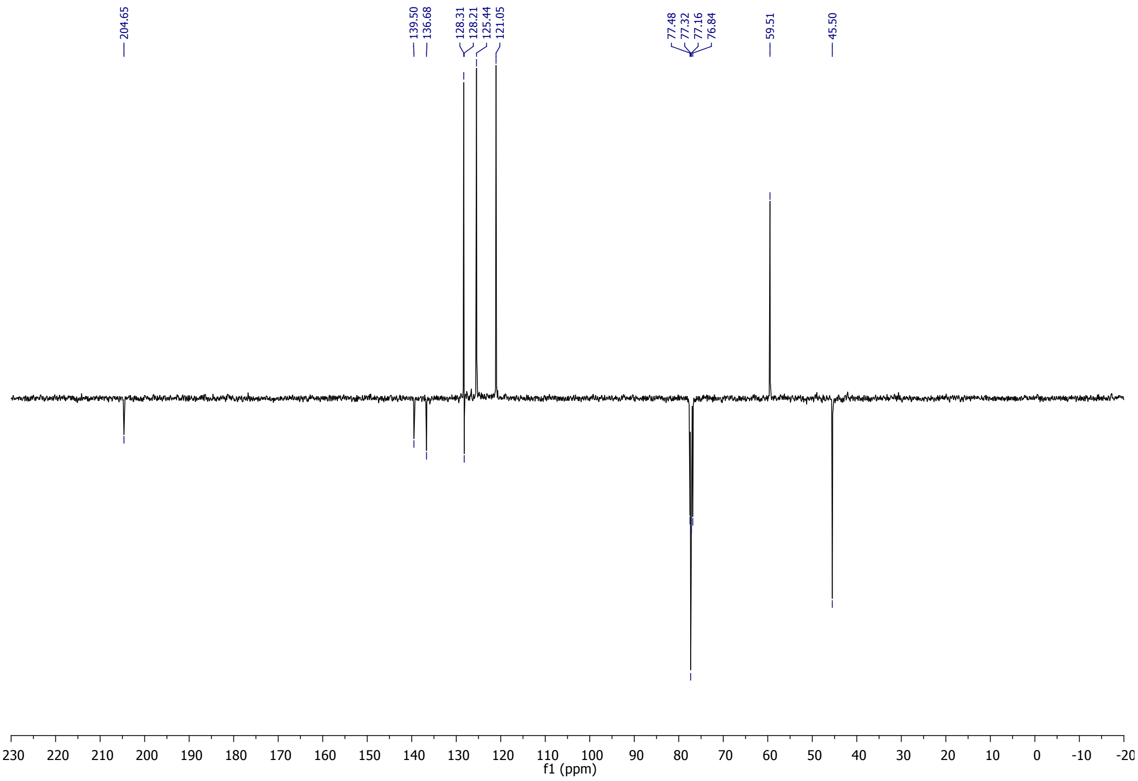

O
S
+
O
−
7.96
7.94
7.81
7.78
7.74
7.71
7.62
7.62
7.59
7.59
7.58
7.57
7.57
7.56
7.53
7.52
7.52
7.49
7.49
7.47
7.47
7.30
7.28
7.26
4.32
4.26
4.25
4.22
4.16
3.46
0.96
1.00
0.97
1.90
1.00
0.99
4.13
2.98
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

S1


204.35
144.58
143.93
137.69
137.23
134.92
133.08
132.75
131.63
129.72
127.46
122.20
121.04
77.56
77.48
77.16
76.84
59.57
42.38
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

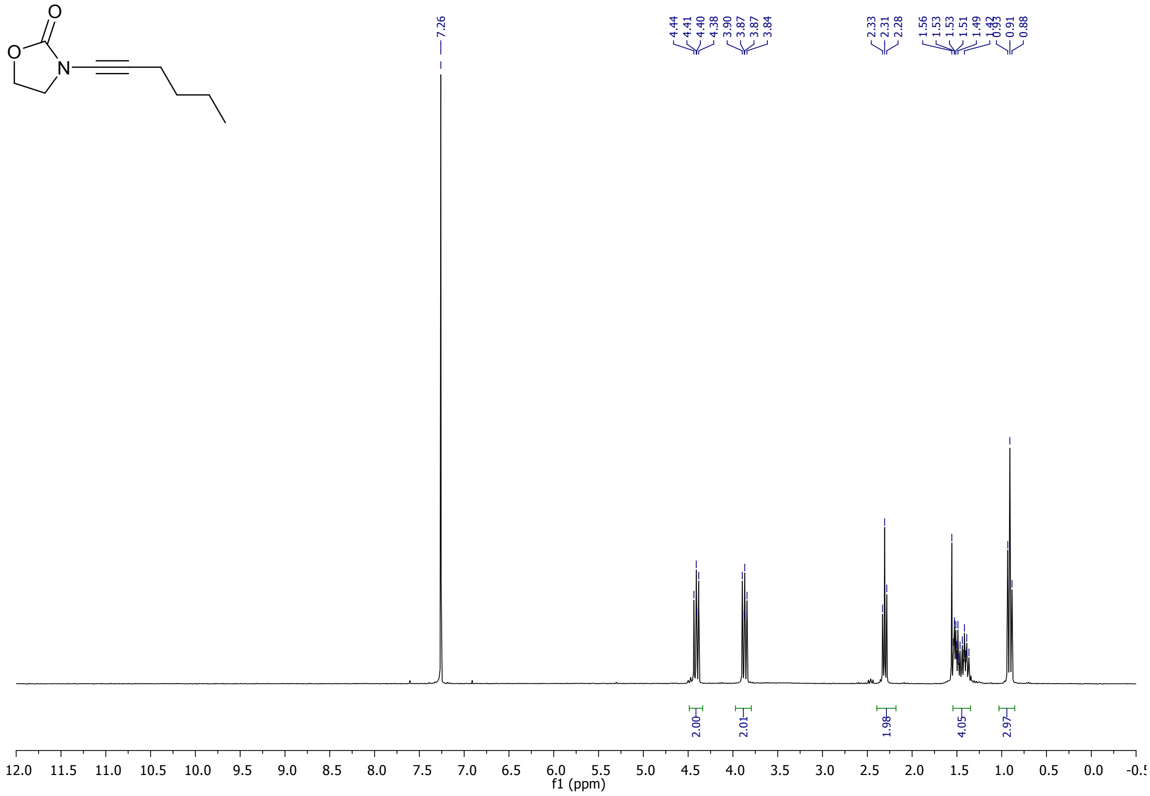

O
S
O
O
O
8.11
8.11
8.08
8.08
7.51
7.48
7.46
7.37
7.34
7.26
4.13
4.05
3.42
1.00
1.03
0.99
2.02
2.01
3.09
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

S2

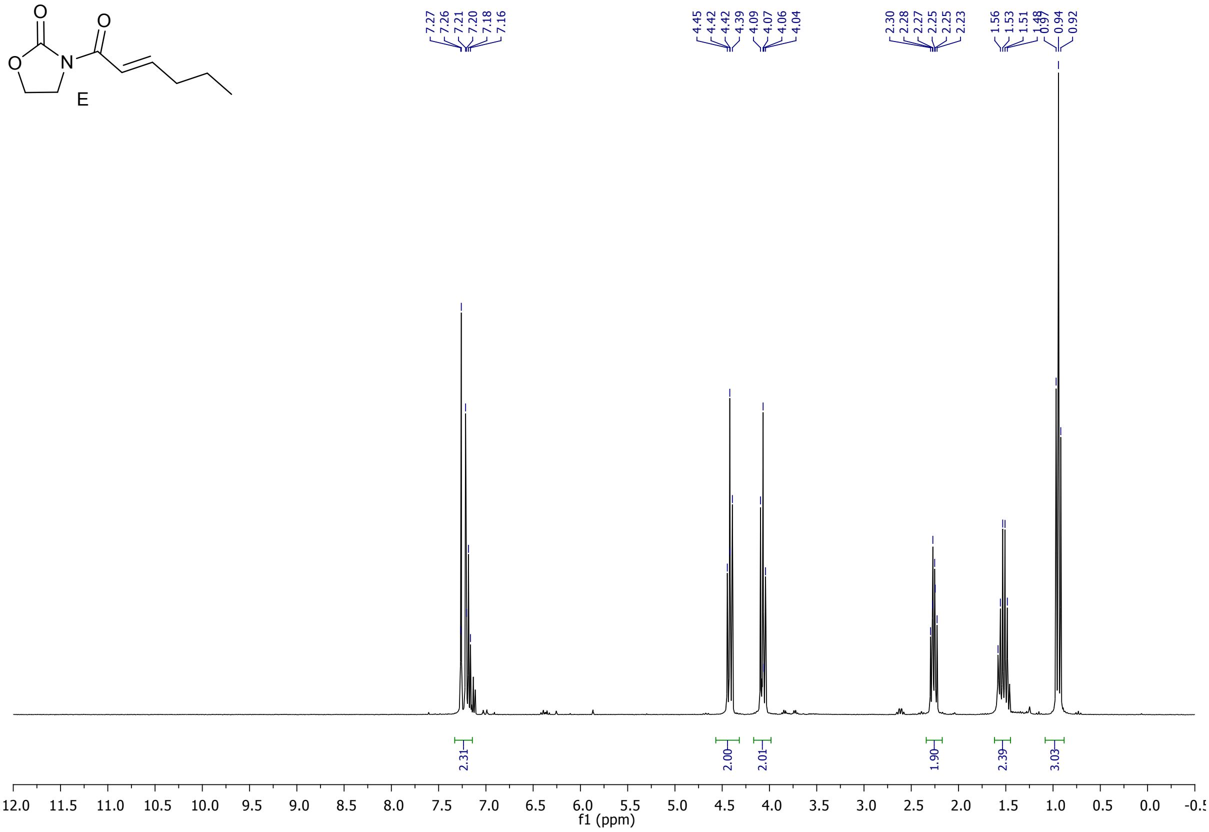

204.65
139.50
136.68
128.31
128.21
125.44
121.05
77.48
77.32
77.16
76.84
59.51
45.50
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

Benchmarking dibenzothiophene-*S*-oxide as an oxygen transfer agent (Scheme 4)

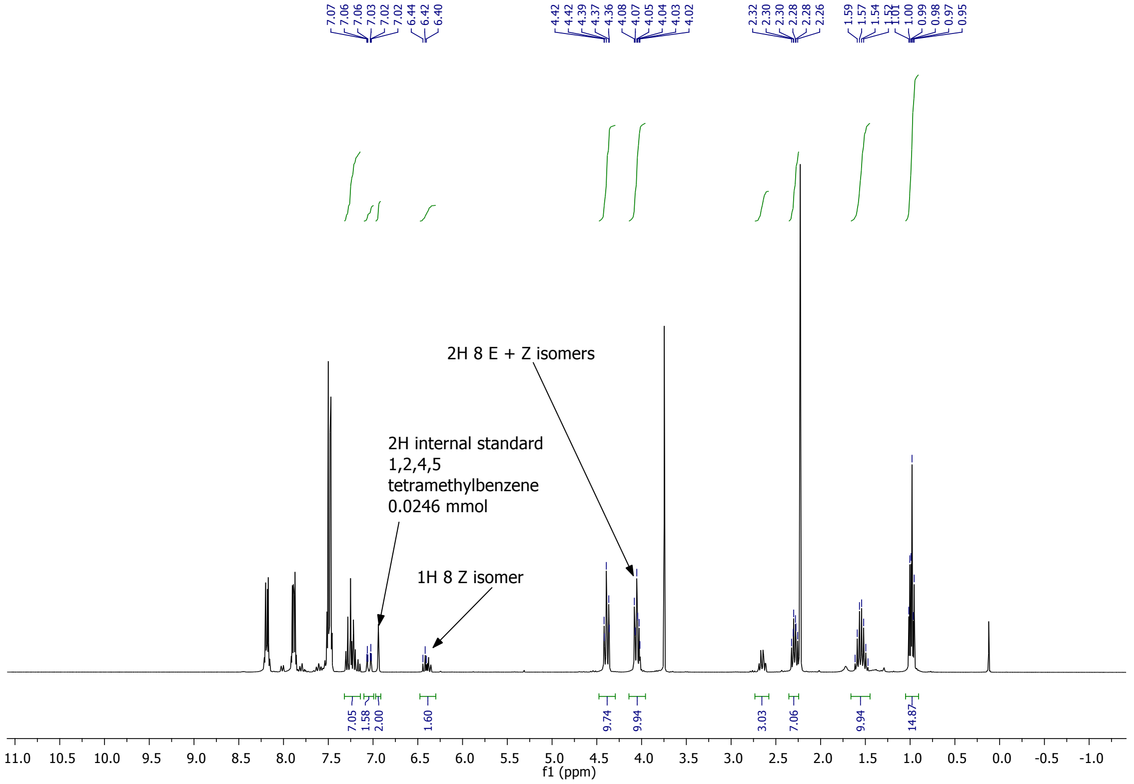
Ynamide **7**



8



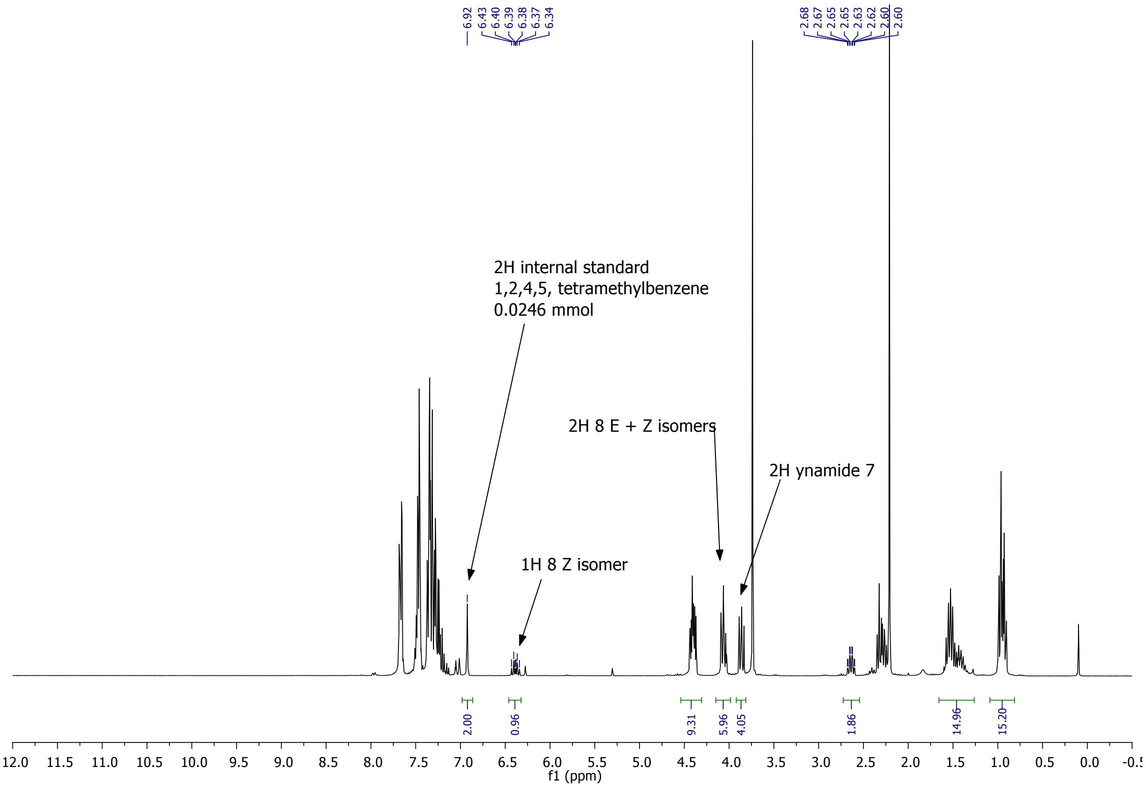
Reaction of dibenzothiophene-*S*-oxide with ynamide **7** (0.15 mmol scale)


2H 8 E + Z isomers

2H internal standard
1,2,4,5
tetramethylbenzene
0.0246 mmol

1H 8 Z isomer

Reaction of diphenyl sulfoxide with ynamide **7** (0.15 mmol scale)

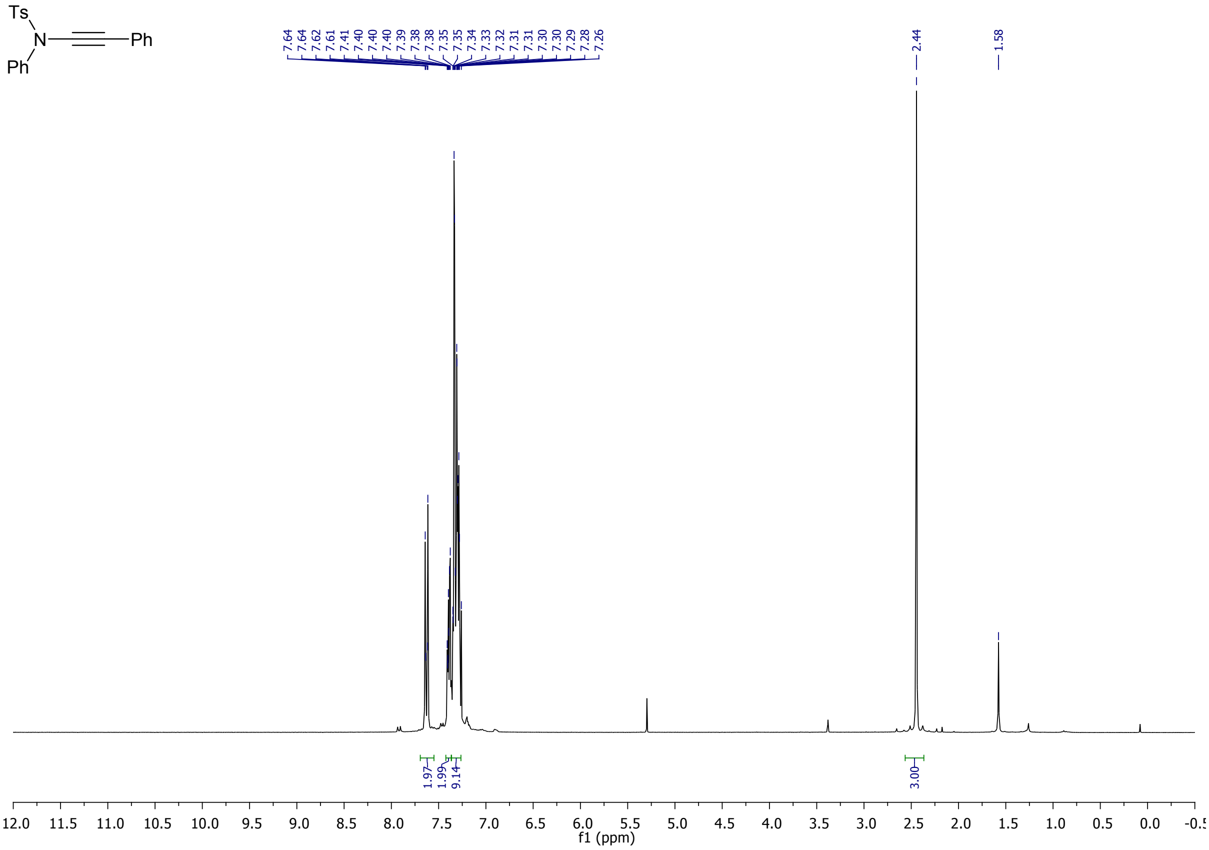

2H internal standard
1,2,4,5, tetramethylbenzene
0.0246 mmol

2H 8 E + Z isomers

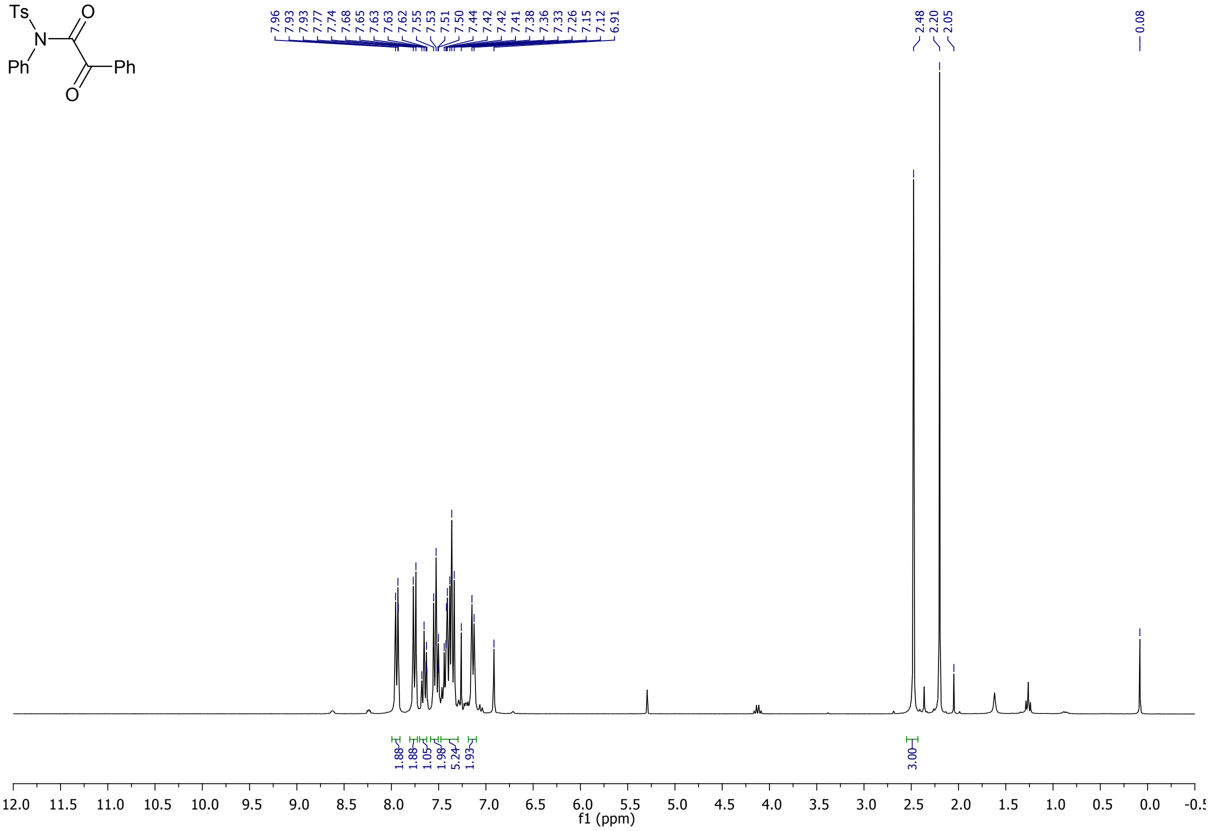
2H ynamide 7

1H 8 Z isomer

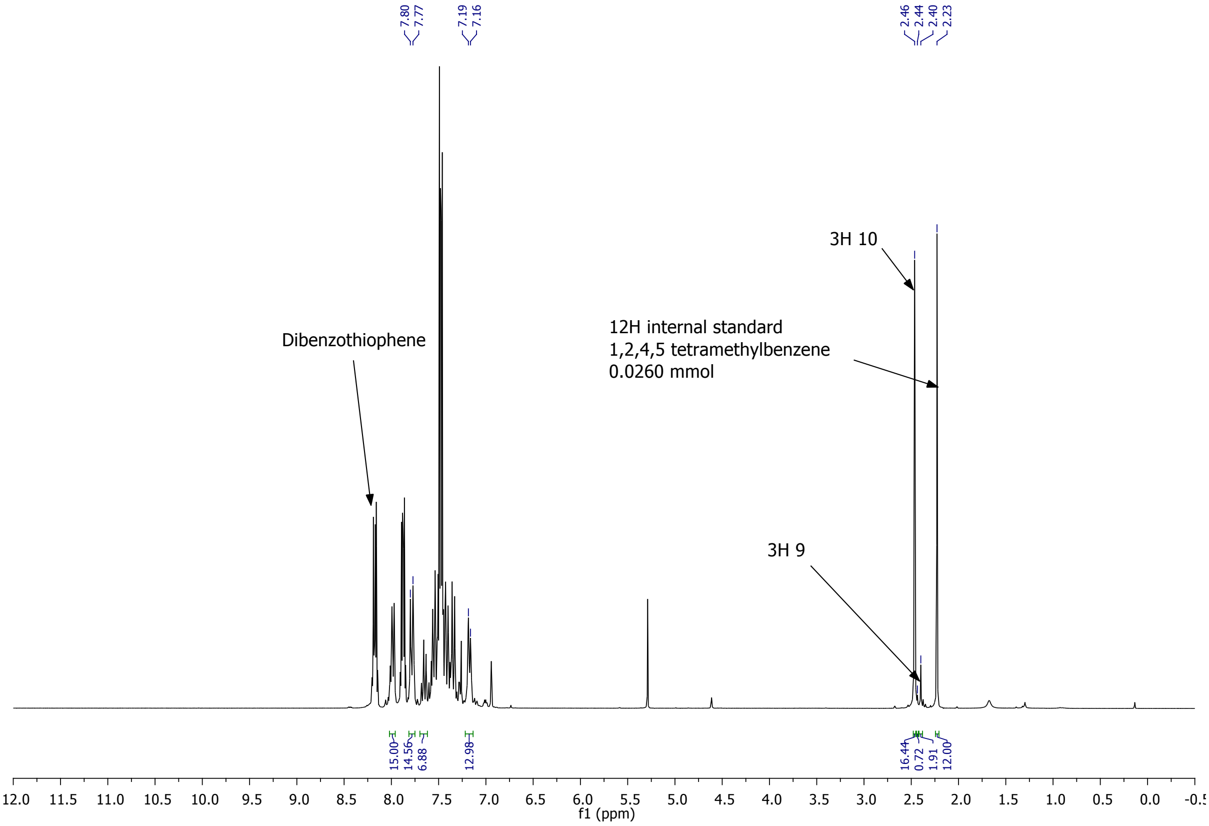
Ynamide **9**



10 (+ 1,2,4,5-tetramethylbenzene)



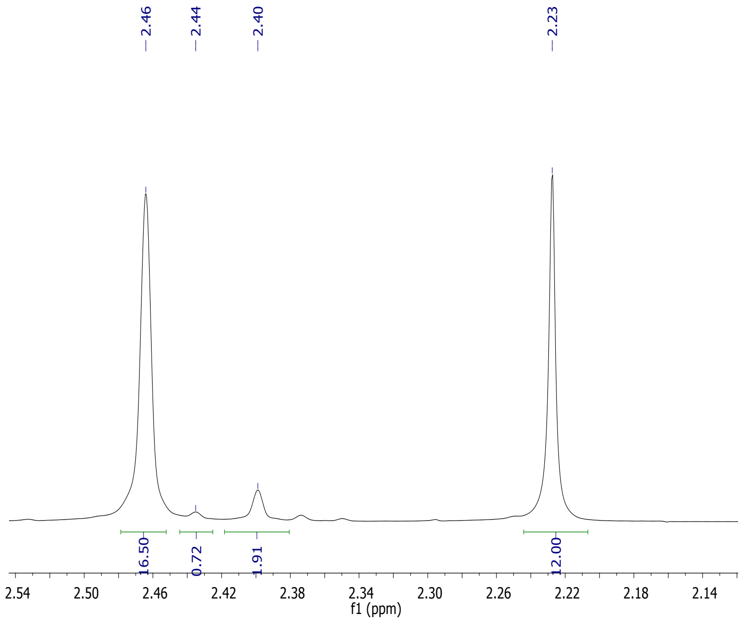
Reaction of dibenzothiophene-*S*-oxide with ynamide **9** (0.20 mmol scale)


Dibenzothiophene

12H internal standard
1,2,4,5 tetramethylbenzene
0.0260 mmol

3H 10

3H 9



Reaction of diphenyl sulfoxide with ynamide **9** (0.20 mmol scale)