Supplementary Information for:

Synthesis and Photophysical Characterization of Bacteriochlorins Equipped with Integral Swallowtail Substituents

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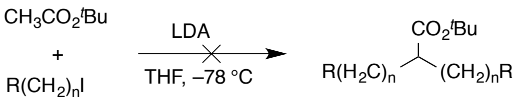
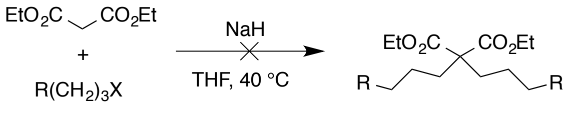
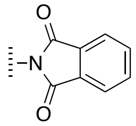
I. Attempted synthesis of swallowtail–bacteriochlorin precursors

Our initial designs focused on two- or three-carbon alkyl groups. The initial syntheses anticipated direct alkylation of *tert*-butyl acetate or diethyl malonate. In each case considerable difficulties were encountered (Table S1). The reactions were carried out in neat THF whereas subsequent study (see main text) found success upon reaction in the presence of a sizable quantity of HMPA in THF. The attempted alkylations displayed in Table S1 were not examined in the latter solvent mixture.

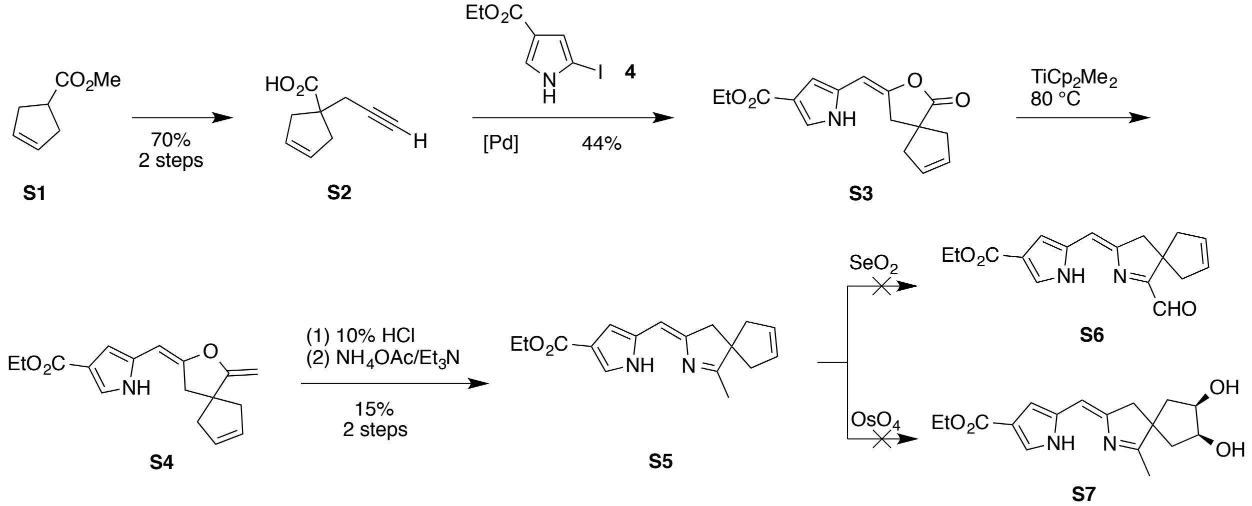
Table S1. Attempted alkylations





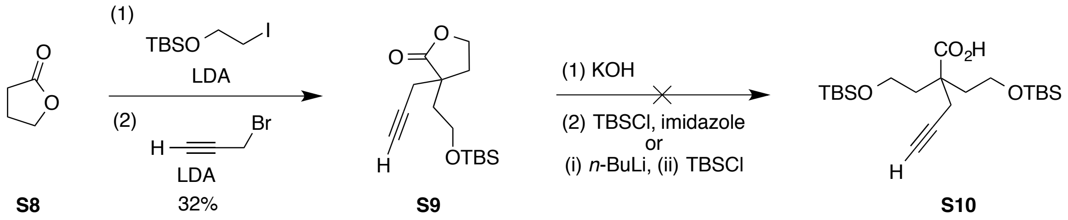
n = 2			
R = OTBS	No reaction	R = OTBS, X = I	Complicated mixture
R = OBn	No reaction	R = OBn, X = I	Complicated mixture
n = 3			
R = OTBS	Decomposition of $RO(CH_2)_nI$	R =  , X = Br	Decomposition of $R(CH_2)_3Br$
R = OBn	Decomposition of $RO(CH_2)_nI$		

An alternative design entailed a spiropentenyl motif as a swallowtail unit precursor, which was envisaged from starting material methyl cyclopent-3-enecarboxylate (**S1**). Alkylation with propargyl bromide gave **S2**, which upon Pd-coupling with iodopyrrole **4** gave lactone–pyrrole **S3** in modest yield of 44%. Subsequent Petasis reagent treatment gave **S4**, which upon Paal-Knorr type ring closure afforded dihydrodipyrrin **S5**, the dihydrodipyrrin bearing a spiropentenyl motif in position 2 (Scheme S1). Conversion to the swallowtail–bacteriochlorin requires oxidation of the 2-methyl group to form the carboxaldehyde followed by transformation to the dimethyl acetal (**S6**). However, treatment of dihydrodipyrrin **S5** directly with SeO_2 afforded a complicated mixture, no doubt due to the existence of multiple allylic positions. An alternative modification was to perform a dihydroxylation with OsO_4 to give **S7** followed by acetal protection if necessary, but this transformation also was not successful.



Scheme S1. Synthesis of a dihydrodipyrrin bearing an integral spiropentenyl motif.

An alternative approach toward the open-chain swallowtail design entailed successive alkylation of γ-butyrolactone **S8**, a substrate with diminished steric hindrance, to give the dialkyl–lactone **S9** (Scheme S2). Hydrolysis gave the desired carboxylic acid precursor (not shown). For the following step a symmetric precursor having both terminal –OH units in protected form was preferred, yet all attempts to protect the free hydroxyl group caused cyclization leading to **S9**, and no open-chain alkynoic acid **S10** was isolated.



Scheme S2. Attempted synthesis of a TBS-protected alkynoic acid.

Experimental section

1-(Prop-2-yn-1-yl)cyclopent-3-enecarboxylic acid (S2). A solution of methyl cyclopent-3-enecarboxylate (**S1**, 12.8 g, 101 mmol) in anhydrous THF (50 mL) was treated with LDA solution (66 mL, 2.0 M solution) at –78 °C under argon. After 1 h, a solution of propargyl bromide (14.1 mL, 160 mmol, 80% w/w solution in toluene) was added, and the mixture was kept at –78 °C for another 2 h. Afterwards, the reaction mixture was allowed to warm to 0 °C and then quenched by the addition of saturated NH_4Cl solution. The mixture was extracted with ethyl acetate (2 x 250 mL), dried ($NaSO_4$) and filtered. The filtrate was concentrated to dryness and treated with MeOH (20 mL), THF (20 mL) and water (80 mL) followed by KOH (12.0 g, excess). After stirring at room temperature for 16 h, the mixture was concentrated to dryness. Then, hydrochloric acid (6 M) was added to adjust the pH of the reaction mixture to 1. Diethyl ether (2 x 200 mL) and water (100 mL) were added to the mixture. The organic layer was separated, dried ($NaSO_4$) and concentrated to dryness. The resulting viscous clear oil was further purified using distillation to obtain a clear oil that solidified upon standing (10.7 g, 70%): mp 44–45 °C; ^{1}H NMR δ 1.98 (t, J = 2.7 Hz, 1H), 2.46–2.54 (m, 2H), 2.57 (d, J = 2.7 Hz, 2H), 2.88–2.98 (m, 2H), 5.63 (s, 2H); ^{13}C NMR δ 27.8, 42.5, 51.6, 70.2, 81.2, 128.4, 183.0; ESI-MS obsd 149.0608, calcd 149.0608 [(M – H)$^-$, M = $C_9H_{10}O_2$].

(*E*)-Ethyl 5-((1-oxo-2-oxaspiro[4.4]non-7-en-3-ylidene)methyl)-1*H*-pyrrole-3-carboxylate (S3). A solution of **S2** (3.27 g, 21.8 mmol), **4** (2.90 g, 10.9 mmol) and $BnNEt_3Cl$ (2.47 g, 10.9 mmol) in dry acetonitrile (50 mL) and Et_3N (11 mL) was added to a Schlenk flask. The mixture was deaerated by three freeze–pump–thaw cycles. A sample of $Pd(PPh_3)_4$ (629 mg, 0.545 mmol) was then added and the resulting mixture was further deaerated. The reaction mixture was heated to reflux for 24 h, and then CH_2Cl_2 and water were added. The organic layer was dried (Na_2SO_4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a light brown solid (1.38 g, 44%): ^{1}H NMR δ 1.35 (t, J = 7.2 Hz, 3H), 2.75 (ABq, $\Delta\delta_{AB}$ = 0.27, J = 15 Hz, 4H), 3.09 (d, J = 1.9 Hz, 2H), 4.29 (q, J = 7.2 Hz, 2H), 5.70 (s, 2H), 6.16 (t, J = 1.9 Hz, 1H), 6.40 (s, 1H), 7.42 (s, 1H), 8.76 (s, 1H); ^{13}C NMR δ 13.7, 14.7, 22.3, 25.3, 40.3, 41.3, 60.2, 108.7, 111.7, 117.4, 123.4, 129.8, 143.7, 165.2, 180.3; ESI-MS obsd 288.1221, calcd 288.1236 [(M + H)$^+$, M = $C_{16}H_{17}NO_4$].

(*Z*)-Ethyl 5-((1-methyl-2-azaspiro[4.4]nona-1,7-dien-3-ylidene)methyl)-1*H*-pyrrole-3-carboxylate (S5). This dihydrodipyrrin was synthesized directly from **S3** without column chromatographic purification after treatment with the Petasis reagent. A sample of **S3** (950 mg, 3.31 mmol) was treated with Petasis reagent generated from $TiCp_2Cl_2$ (3.91 g, 15.7 mmol) and LiMe (1.6 M in THF, 21.5 mL, 34 mmol) in anhydrous toluene (40 mL) following the general procedure described previously. After quenching the reaction following the standard procedure, the crude mixture was filtered through a pad of silica gel. The filtrate was concentrated to dryness and DMF (20 mL) was added, whereupon the resulting solution was treated with 1M aqueous HCl (1.0 mL). After 30 min, NH_4OAc (5.08 g, 66.0 mmol) and Et_3N (8.95 mL, 64.3 mmol) were added and the mixture was stirred at 55 °C for 4 h. Then, the reaction was quenched by the addition of saturated aqueous KH_2PO_4 solution. Ethyl acetate (100 mL) was added and the organic layer was washed (water), dried and concentrated. Column chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a white solid (140 mg, 15%): ^{1}H NMR δ 1.34 (t, J = 7.2 Hz, 3H), 2.14 (s, 3H), 2.50 (ABq, $\Delta\delta_{AB}$ = 0.27, J = 15 Hz, 4H), 2.78 (s, 2H), 4.26 (q, J = 7.2 Hz, 2H), 5.72 (s, 2H), 5.82 (s, 1H), 6.43 (s, 1H) 7.41–7.43 (m, 1H), 11.17 (s, 1H); ^{13}C NMR δ 14.8, 16.3, 44.6, 46.0, 57.5, 59.8, 105.7, 108.3, 116.5, 124.2, 129.5, 132.2, 150.9, 165.6, 185.9; ESI-MS obsd 285.1605, calcd 285.1603 [(M + H)$^+$, M = $C_{17}H_{20}N_2O_2$].

3-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)-3-(prop-2-yn-1-yl)dihydrofuran-2(3*H*)-one (S10). A stirred solution of γ-butyrolactone (**S8**, 430 mg, 5.00 mmol) in THF (10 mL) and HMPA (2.0 mL) was treated with LDA solution (2.0 M, 2.5 mL in THF/heptane/ethylbenzene, 5.0 mmol) at –78 °C under argon. After 30 min, *tert*-butyl(2-iodoethoxy)dimethylsilane (1.57 g, 5.50 mmol) was added dropwise, and the reaction mixture was allowed to warm to –40 °C. After 1 h, the mixture was cooled to –78 °C, and another portion of LDA (2.0 M, 2.5 mL in THF/heptane/ethylbenzene, 5.0 mmol) was added dropwise. After 30 min, propargyl bromide (0.750 g, 6.30 mmol) was added dropwise, and the reaction mixture was allowed to warm to room temperature. After 30 min, the reaction mixture was quenched by the addition of saturated aqueous NH_4Cl solution. Dichloromethane (100 mL) was added. The mixture was washed with water and brine. The organic layer was dried (Na_2SO_4), concentrated and chromatographed [silica, hexanes/ethyl acetate (10:1)] to afford a colorless liquid (451 mg, 32%): ^{1}H NMR δ 0.05 (s, 6H), 0.88 (s, 9H), 1.92 (q, J = 2.7 Hz, 2H), 2.04 (t, J = 2.7 Hz, 1H), 2.38–2.43 (m, 2H), 2.49–

2.51 (m, 2H), 3.72–3.77 (m, 2H), 4.26–4.35 (m, 2H); ^{13}C NMR δ –5.3, 3.7, 18.4, 26.1, 27.8, 31.6, 38.4, 45.4, 59.5, 65.8, 74.6.

II. Self-condensation condition screening

Because of the poor yield of self-condensation leading to 8,8,18,18-tetraphenylbacteriochlorin, we screened acids, solvents and different concentrations to improve the yield, but none gave better results (Table S1). Even though in neat TFA 5.7% yield of bacteriochlorin was observed by UV-Vis spectroscopy, isolation was not successful.

Table S1. Self-condensation of *Z*-dihydrodipyrrin–acetal (**8b-Z**) leads to a tetraphenylbacteriochlorin (**Ph-BC-Es^{2,12}**)[a]

Entry	**8b-Z** (mM)	Acid (mM)	Solvent	% Yield[b] of **Ph-BC-Es^{2,12}**
1	18	TMSOTf (70)/DTBP (280)	CH_2Cl_2	1.8
2	18	$BF_3{\cdot}O(Et)_2$ (140)	CH_3CN	-[c]
3	18	TFA (72)	CH_2Cl_2	1.4
4	18	-	neat TFA	5.2
5	18	-	neat TFA/ 50 °C	2.7
6	18	-	neat TFA/ 70 °C	-[c]
7	18	$TsOH{\cdot}H_2O$ (90)	CH_2Cl_2	-[c]
8	18	$MeSO_3H$ (90)	CH_2Cl_2	3.2
9	18	$SnCl_4$ (90)	CH_2Cl_2	-[c]
10	18	$TiCl_4$ (90)	CH_2Cl_2	-[c]
11	18	$Bi(OTf)_3$ (90)	CH_2Cl_2	-[c]
12	18	TMSOTf (90)/DTBP (360)	$ClCH_2CH_2Cl$	-[c]
13	18	TMSOTf (90)/DTBP (360)	$ClCH_2CH_2Cl$/ 80 °C	trace
14	5	TMSOTf (40)/DTBP (100)	CH_2Cl_2	1.0
15	18	TMSOTf (180)/DTBP (720)	CH_2Cl_2	2.3
16	18	TMSOTf (360)/DTBP (1440)	CH_2Cl_2	2.8
17	5	-	neat TFA	trace
18	10	-	neat TFA	1.9
19	15	-	neat TFA	1.9
20	20	-	neat TFA	5.7
21	40	-	neat TFA	3.5

[a] All reactions were carried out with 0.0036 mmol of dihydrodipyrrin–acetal, at room temperature for 18 h, unless noted otherwise.

[b] The yield was determined using UV-absorption spectroscopy (not isolated yield).

[c] Not detected.

III. X-ray crystallographic data

Table S2. Summary of data for 5a

CCDC registry	**1530919**
Formula	$C_{31}H_{35}NO_6$
Formula Weight (g/mol)	517.60
Crystal Dimensions (mm)	0.212 x 0.237 x 0.508
Crystal System	Monoclinic
Space Group	P 1 21/c 1
Temperature, K	100(2)
a, Å	14.307(10)
b, Å	7.170(5)
c, Å	26.494(19)
α, deg	90
β, deg	93.47(3)
γ, deg	90
V, Å^3	2713.(3)
Number of reflections to determine final unit cell	277
Min and Max 2θ for cell determination (deg)	3.562, 68.39
Z	4
F (000)	1104
ρ (g/cm)	1.267
λ, Å, (MoKα)	0.71073
μ, (mm^{-1})	0.087
Max 2θ for data collection (deg)	3.08, 66.36
Measured fraction of data	0.996
Number of reflections measured	66722
Unique reflections measured	10332
R_{merge}	3.56%
Number of parameters in least-squares	348
R_1	0.0421
wR_2	0.1057
R_1 (all data)	0.0607
wR_2 (all data)	0.1166

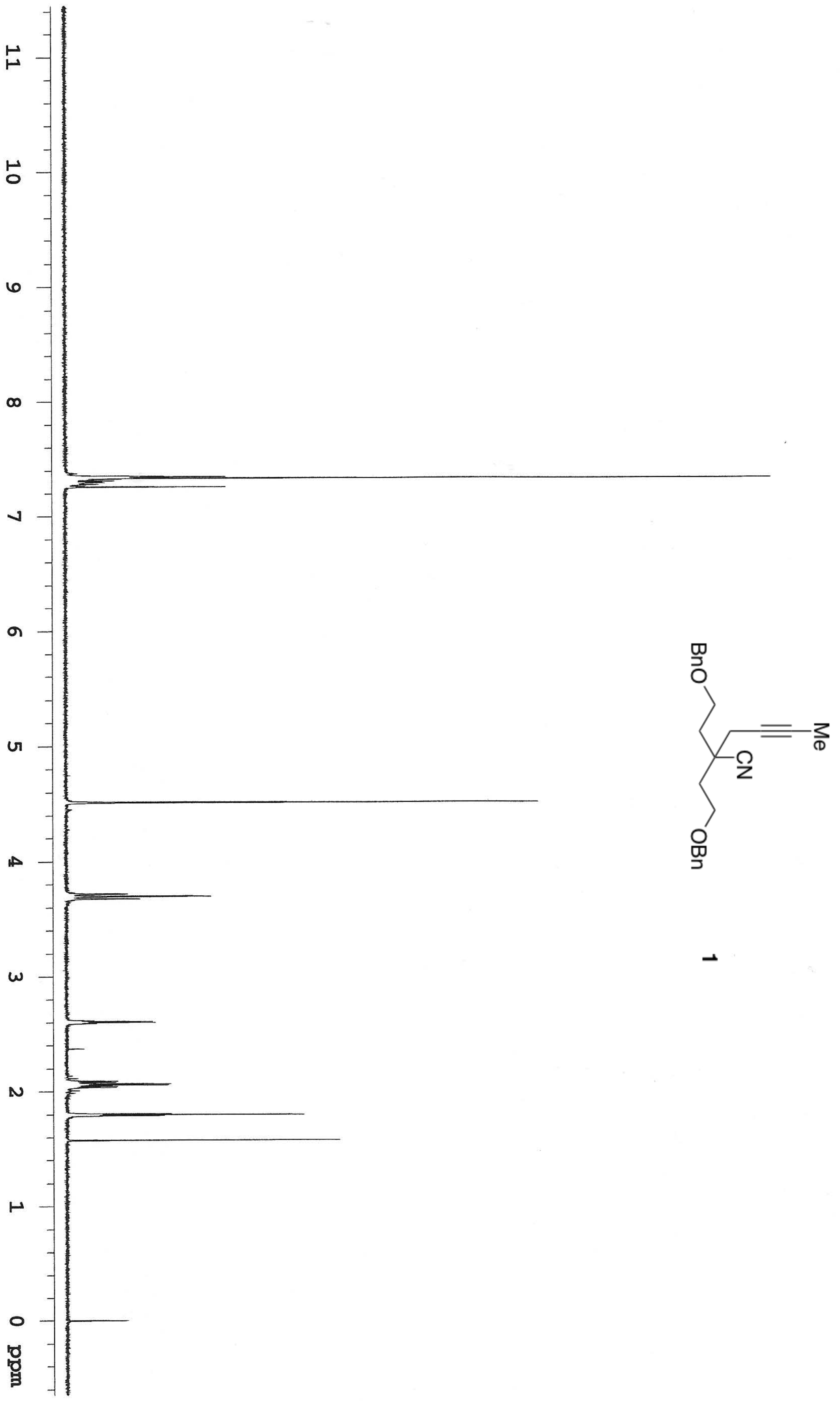
Table S3. Summary of data for 6b

CCDC registry	**1530918**
Formula	$C_{25}H_{23}NO_3$
Formula Weight (g/mol)	385.44
Crystal Dimensions (mm)	0.116 × 0.189 × 0.326
Crystal System	Orthorhombic
Space Group	P 21 21 21
Temperature, K	100(2)
a, Å	7.1439(2)
b, Å	7.4301(2)
c, Å	38.8575(9)
α, deg	90
β, deg	90
γ, deg	90
V, $Å^3$	2062.55(9)
Number of reflections to determine final unit cell	112
Min and Max 2θ for cell determination (deg)	15.1144, 57.6034
Z	4
F (000)	816
ρ (g/cm)	1.241
λ, Å, (MoKα)	0.71073
μ, (mm^{-1})	0.081
Max 2θ for data collection (deg)	4.20, 63.46
Measured fraction of data	0.998
Number of reflections measured	47990
Unique reflections measured	6992
R_{merge}	3.91%
Number of parameters in least-squares	266
R_1	0.0380
wR_2	0.0827
R_1 (all data)	0.0458
wR_2 (all data)	0.0853

Table S4. Summary of data for 8b-E

CCDC registry	**1530920**
Formula	$C_{27}H_{28}N_2O_4$
Formula Weight (g/mol)	444.51
Crystal Dimensions (mm)	0.122 × 0.424 × 0.456
Crystal System	Monoclinic
Space Group	P 1 21/c 1
Temperature, K	100(2)
a, Å	14.9717(7)
b, Å	12.6634(6)
c, Å	12.1987(6)
α, deg	90
β, deg	95.207(2)
γ, deg	90
V, Å^3	2303.24(19)
Number of reflections to determine final unit cell	9858
Min and Max 2θ for cell determination (deg)	4.6464, 63.9916
Z	4
F (000)	944
ρ (g/cm)	1.282
λ, Å, (MoKα)	0.71073
μ, (mm^{-1})	0.086
Max 2θ for data collection (deg)	4.22, 64.12
Measured fraction of data	0.994
Number of reflections measured	48955
Unique reflections measured	7988
R_{merge}	3.33%
Number of parameters in least-squares	351
R_1	0.0473
wR_2	0.1141
R_1 (all data)	0.0660
wR_2 (all data)	0.1259

IV. Spectral data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OBn
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5
4
3
2
1
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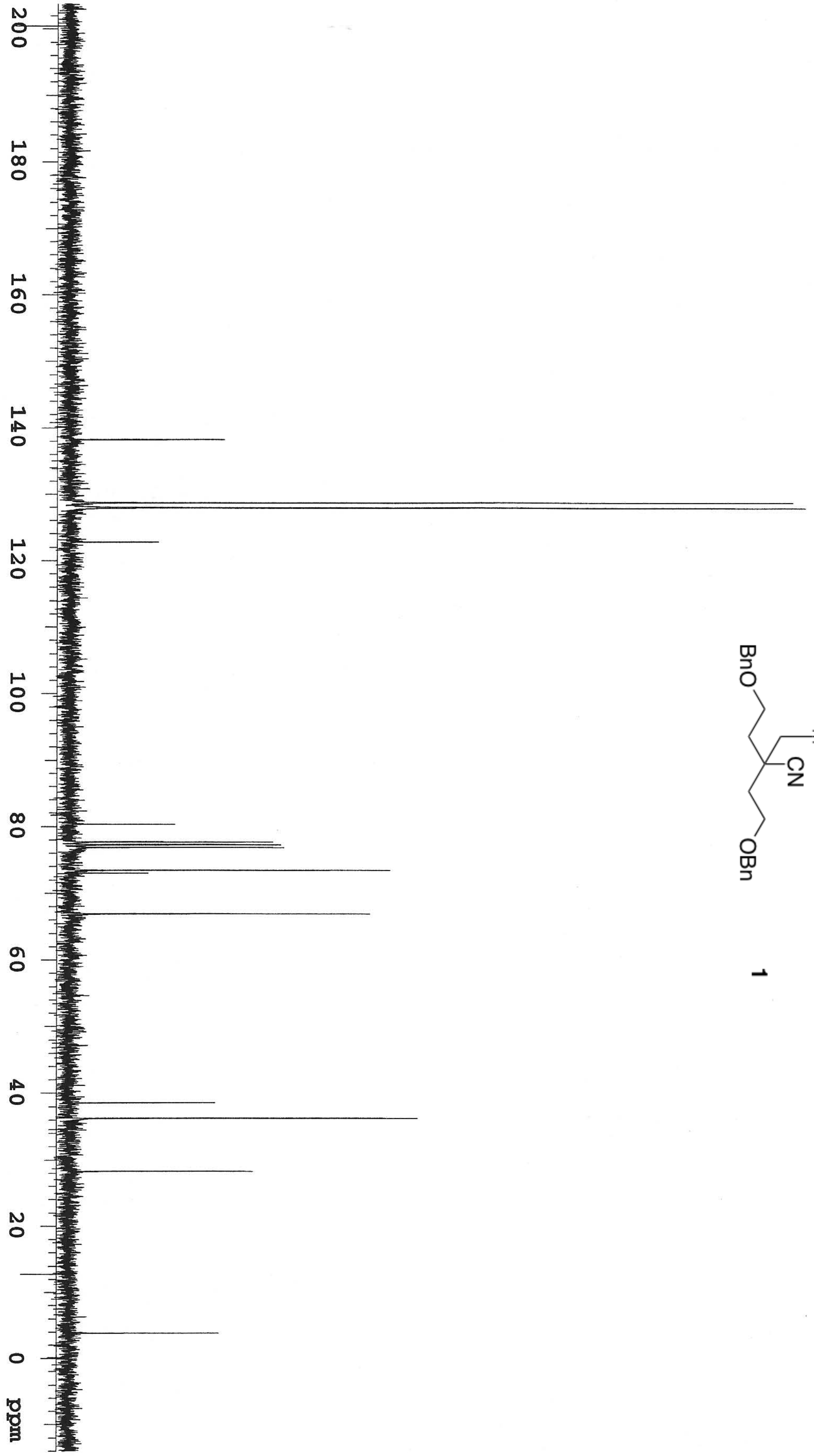

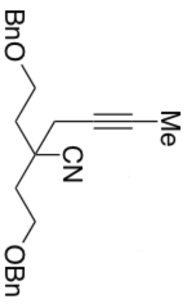

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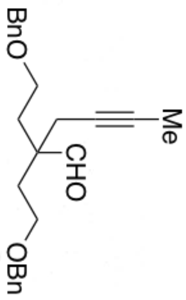

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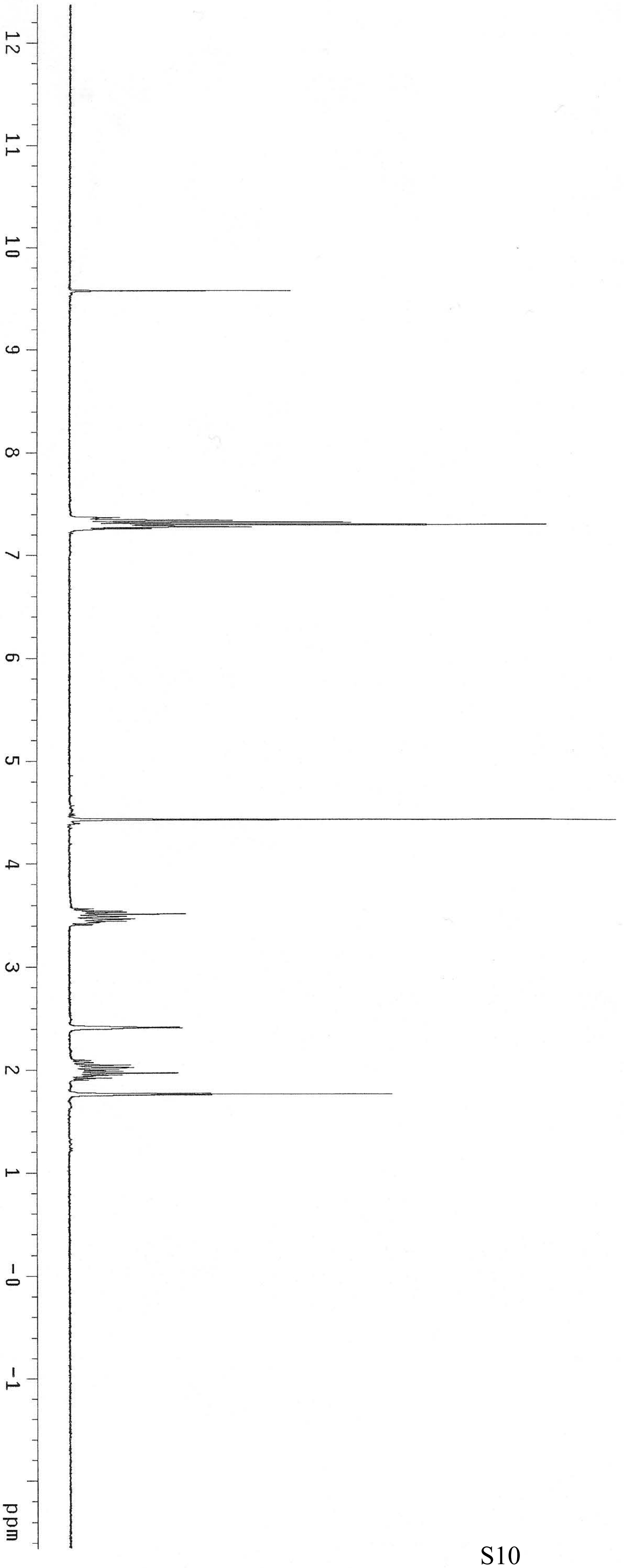

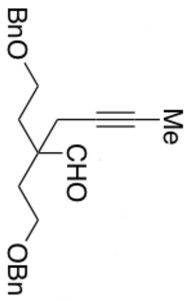

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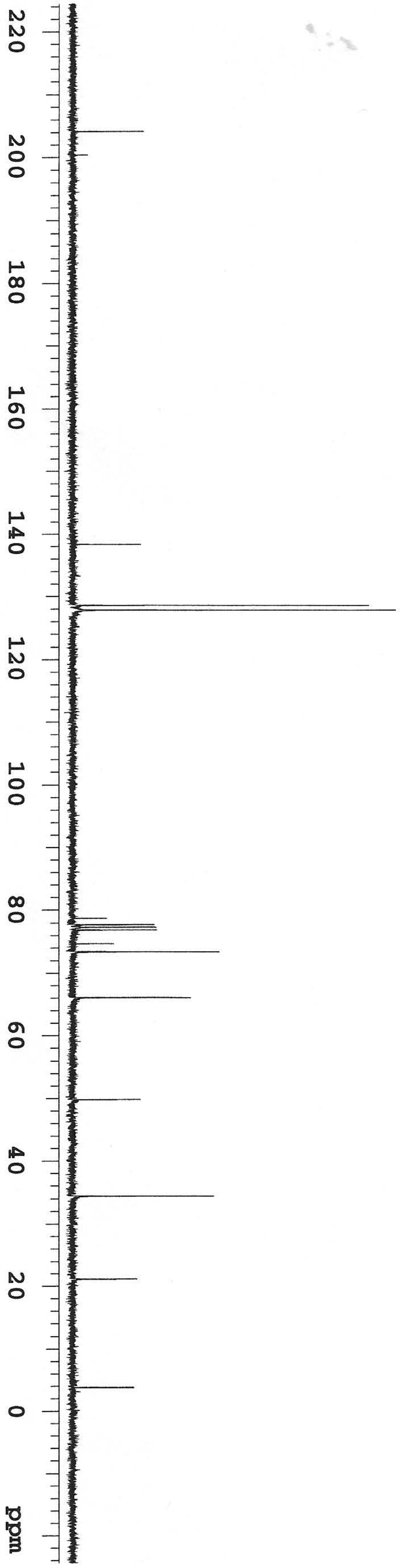

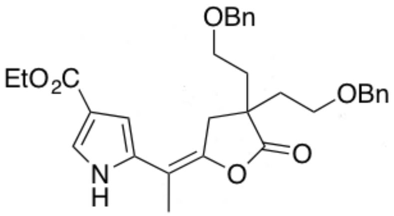

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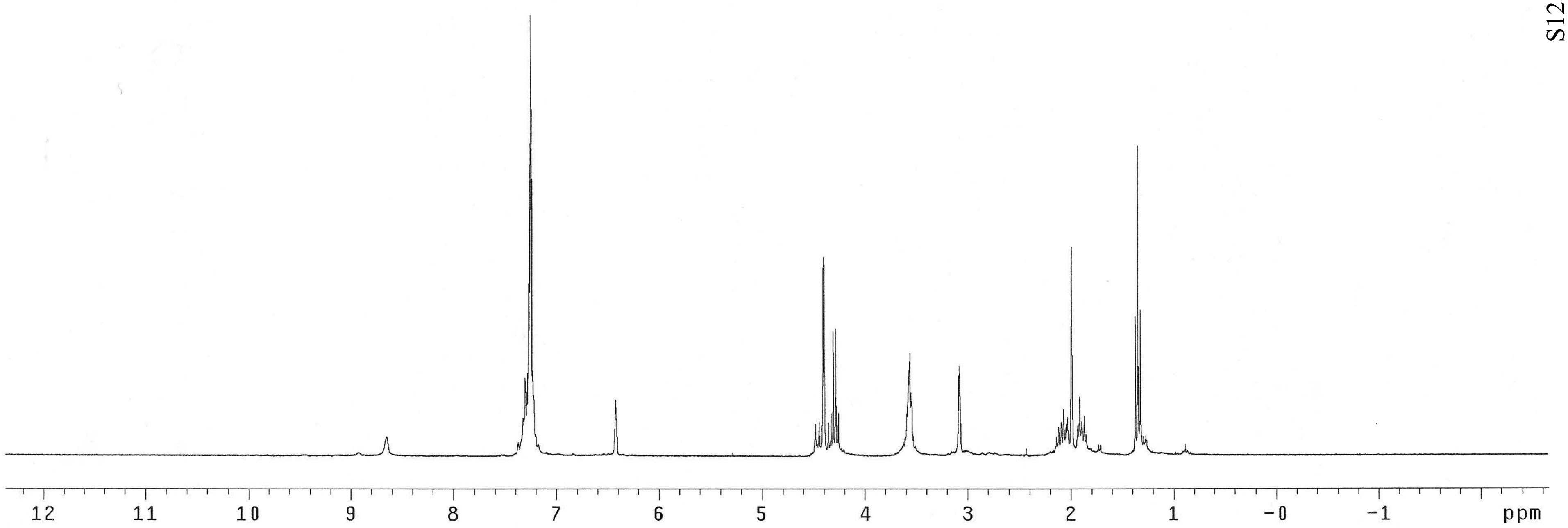

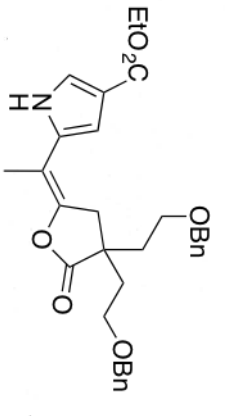

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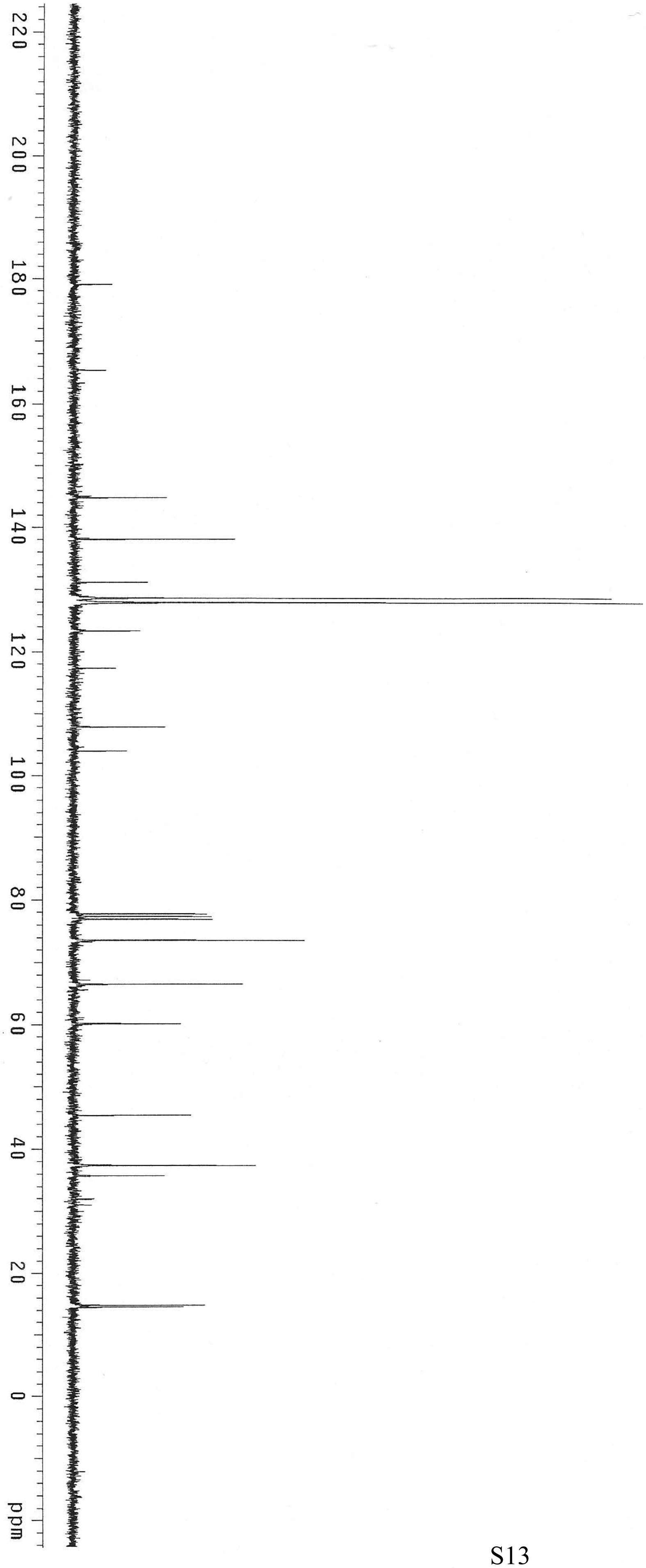

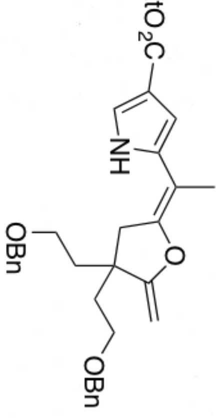

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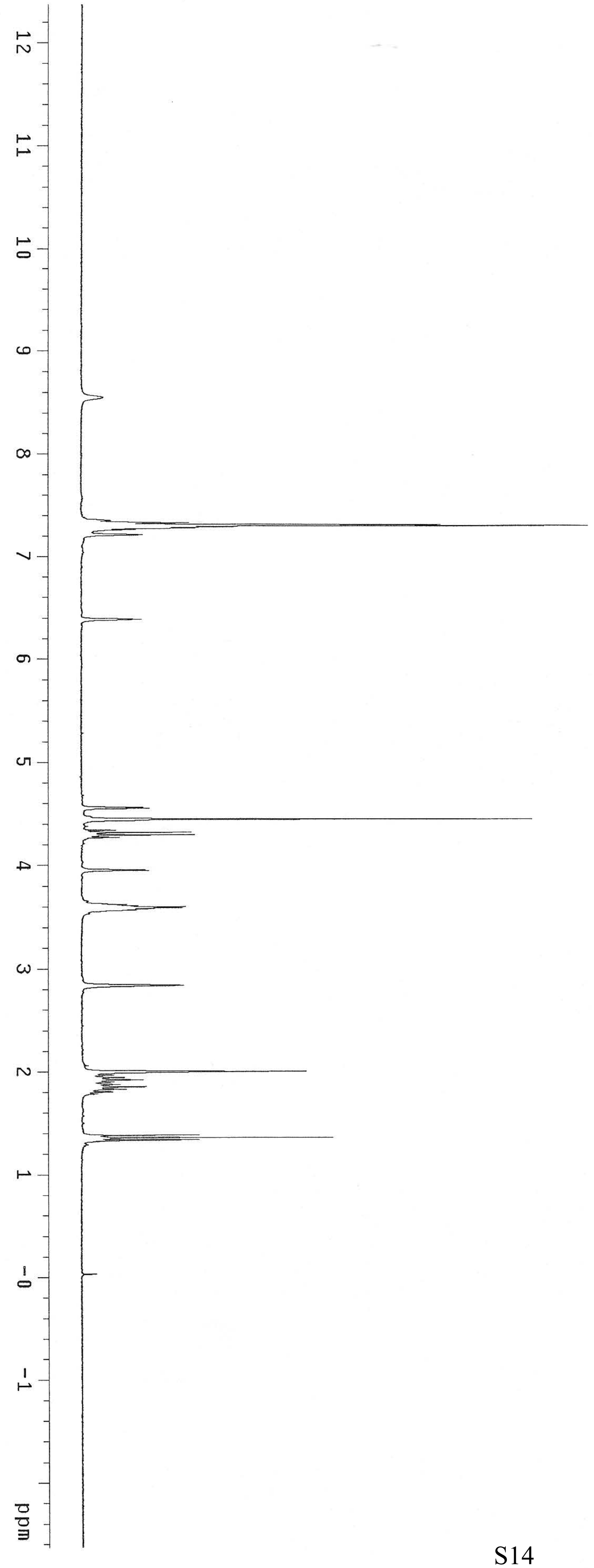

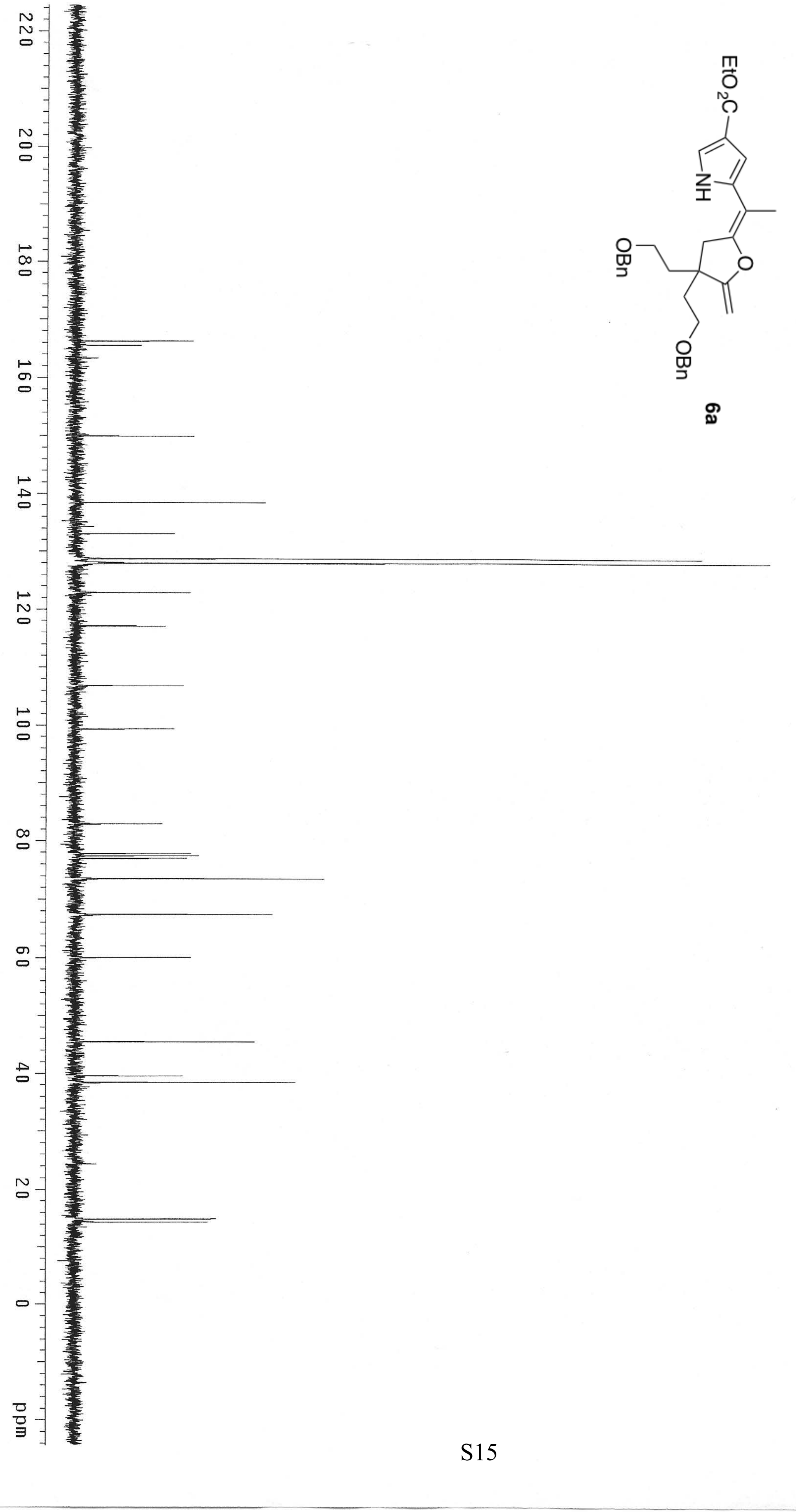

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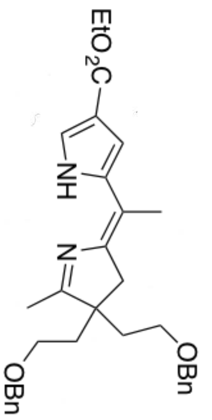
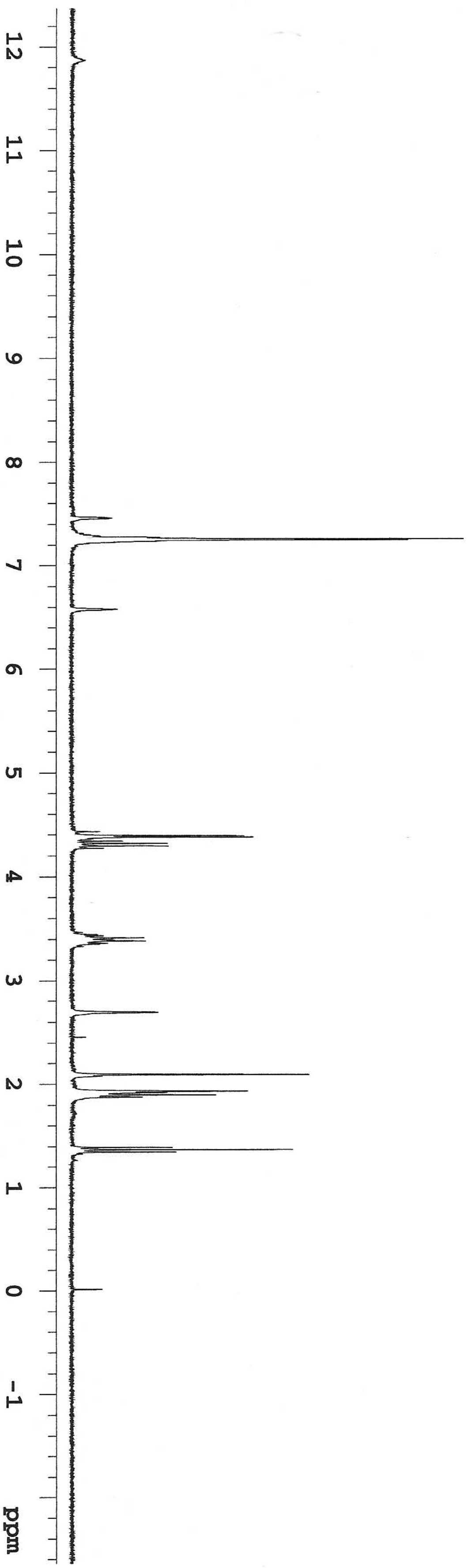
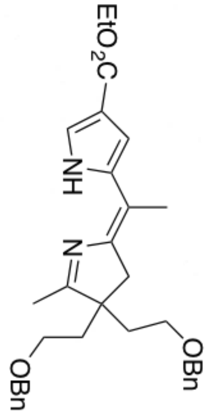


7a-Z





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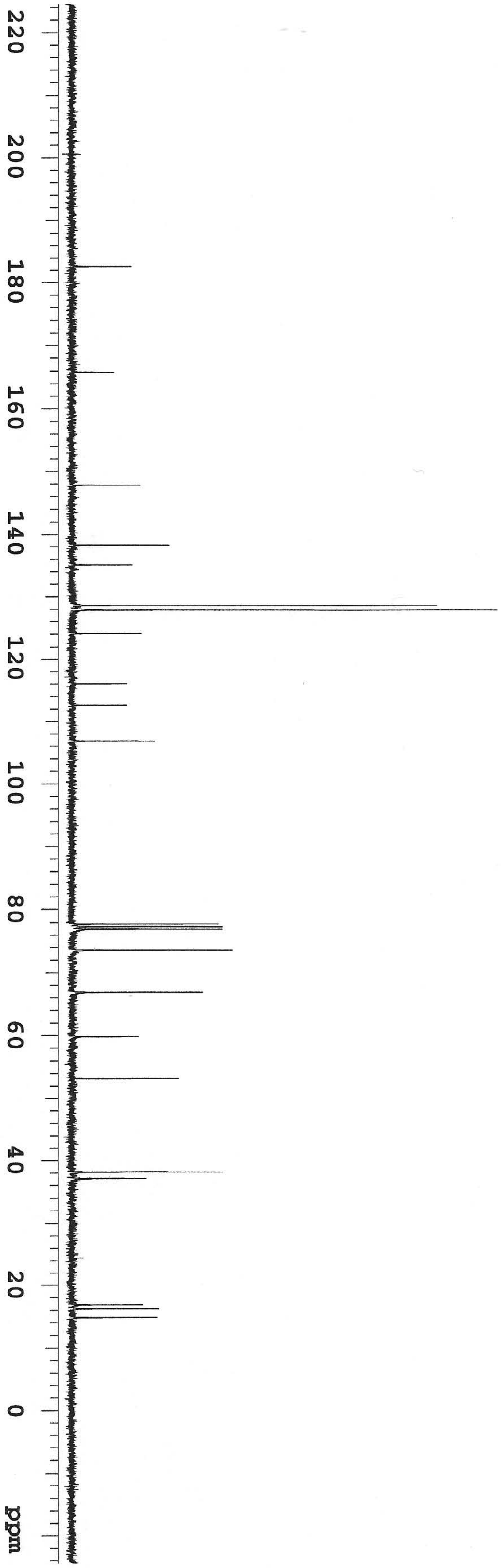

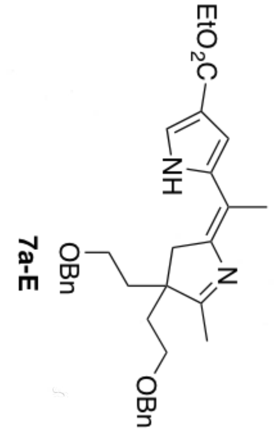

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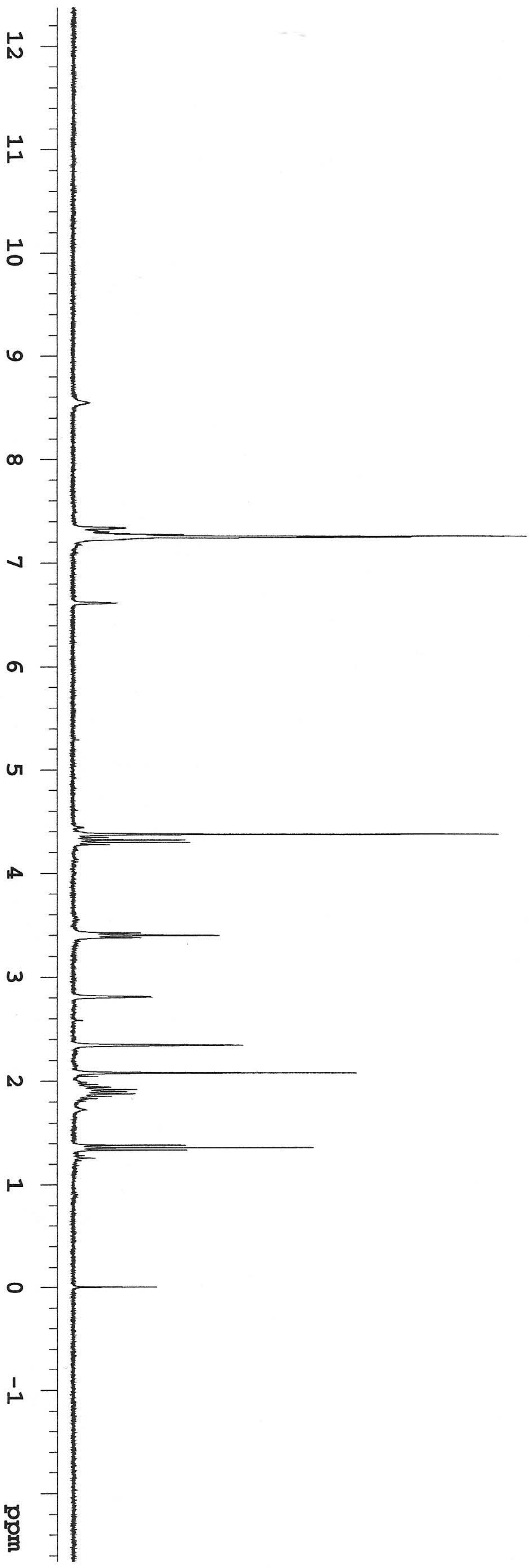

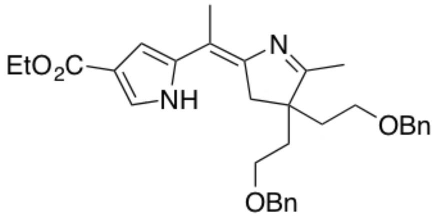

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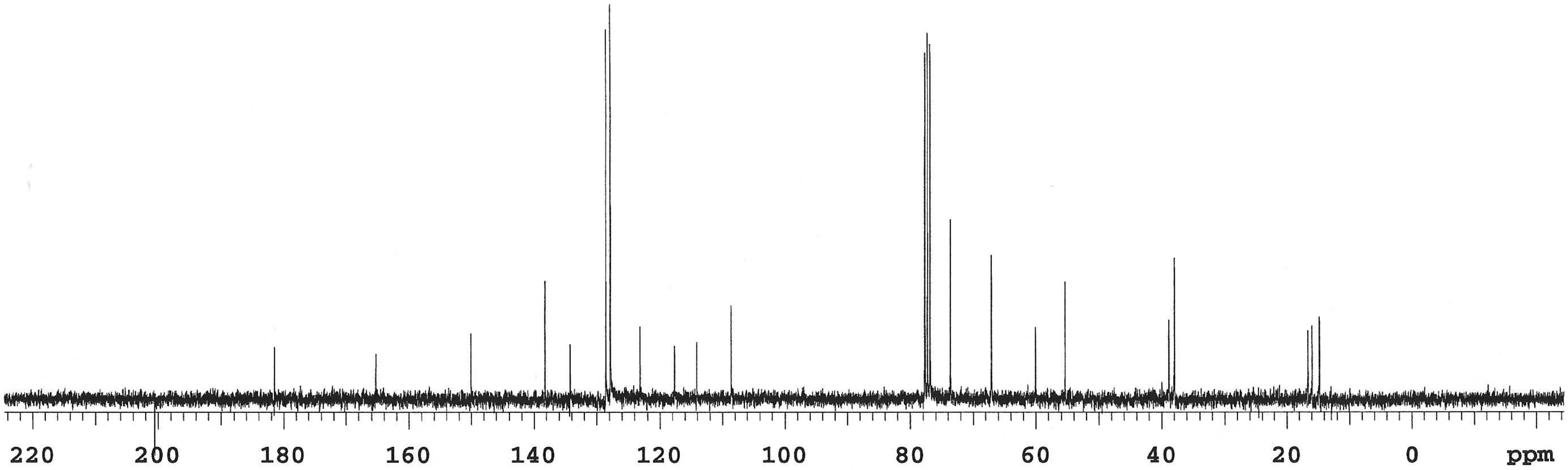

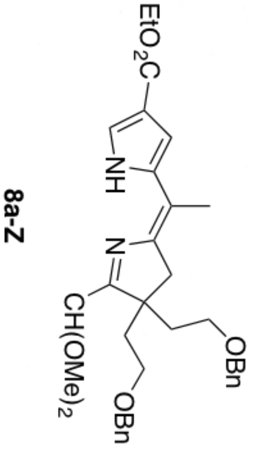

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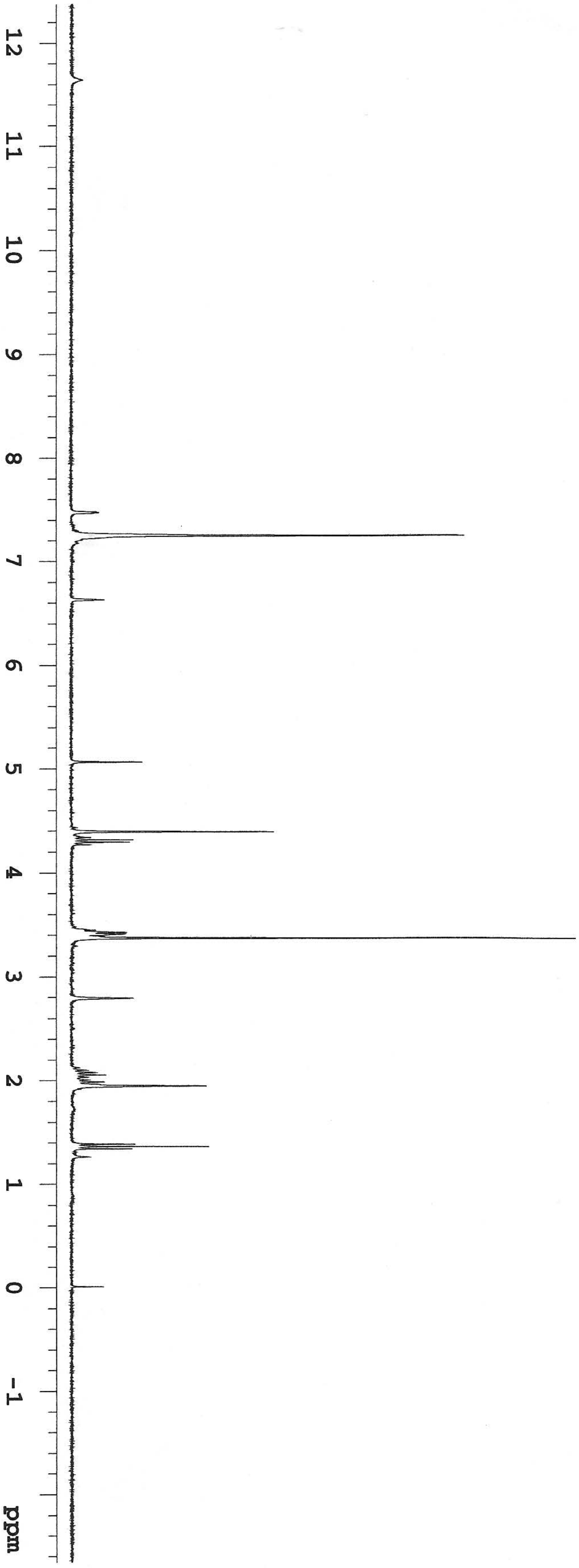
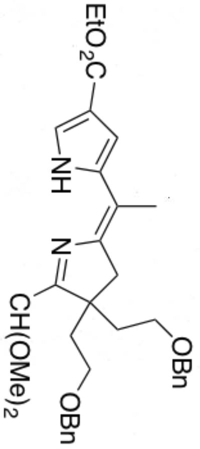
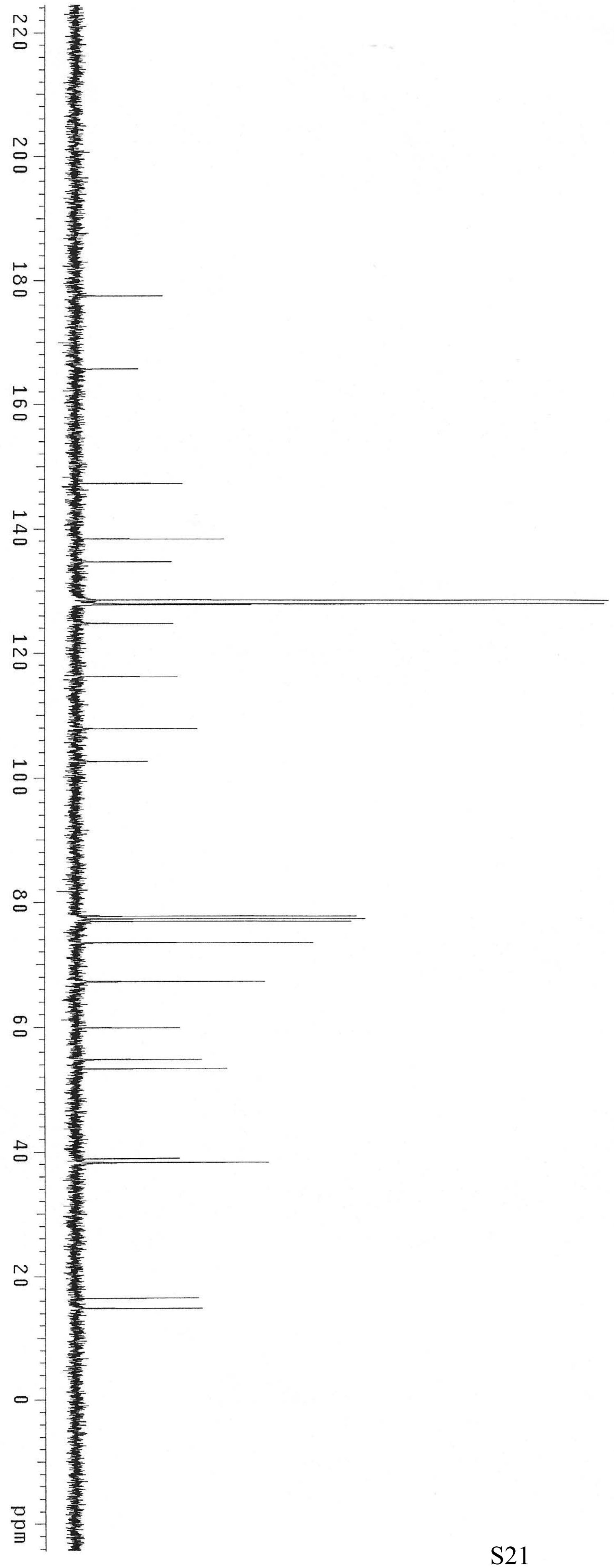



EtO$_2$C
NH
N
CH(OMe)$_2$
OBn
OBn

8a-Z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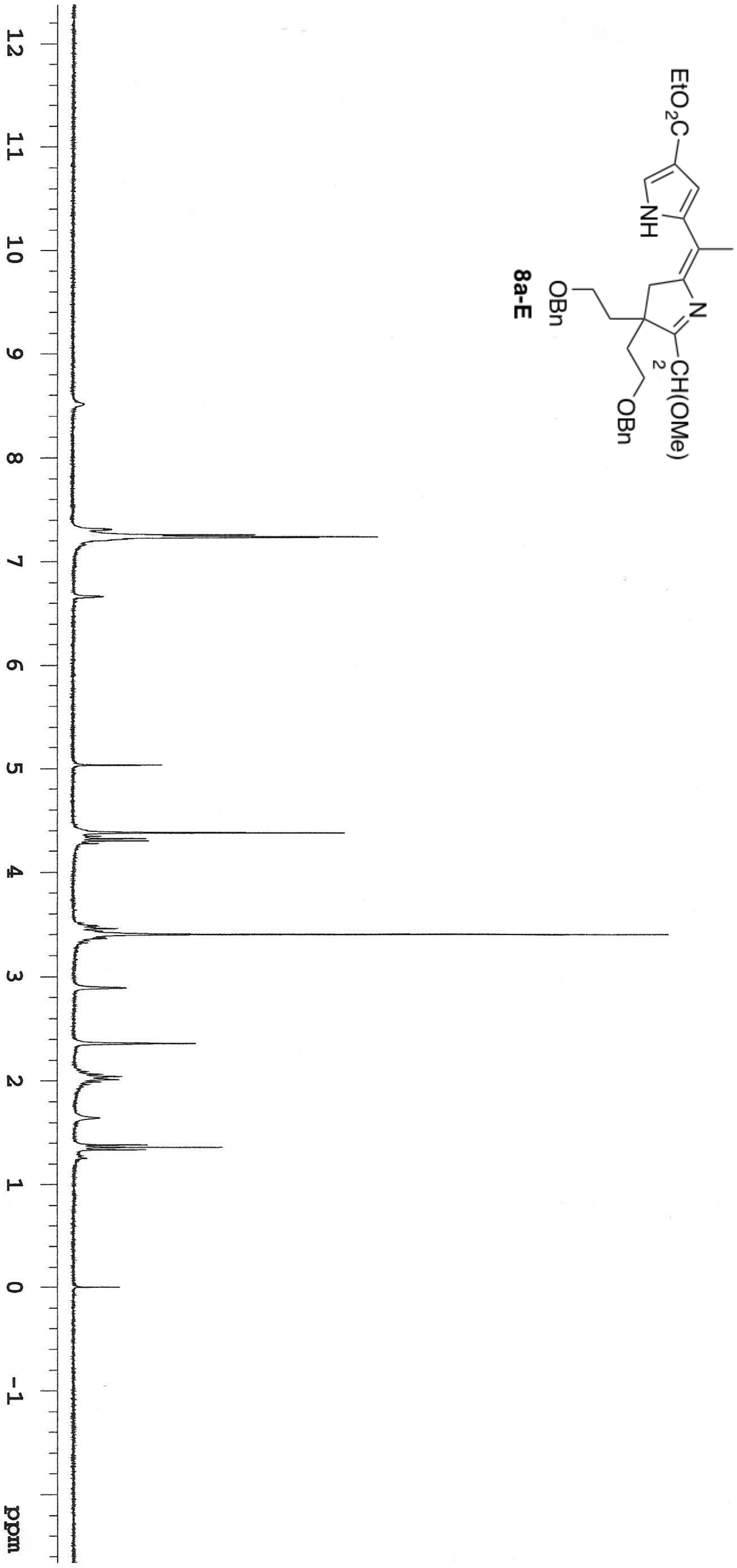
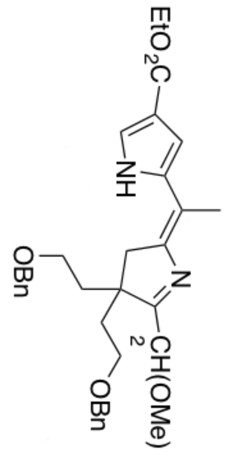


8a-E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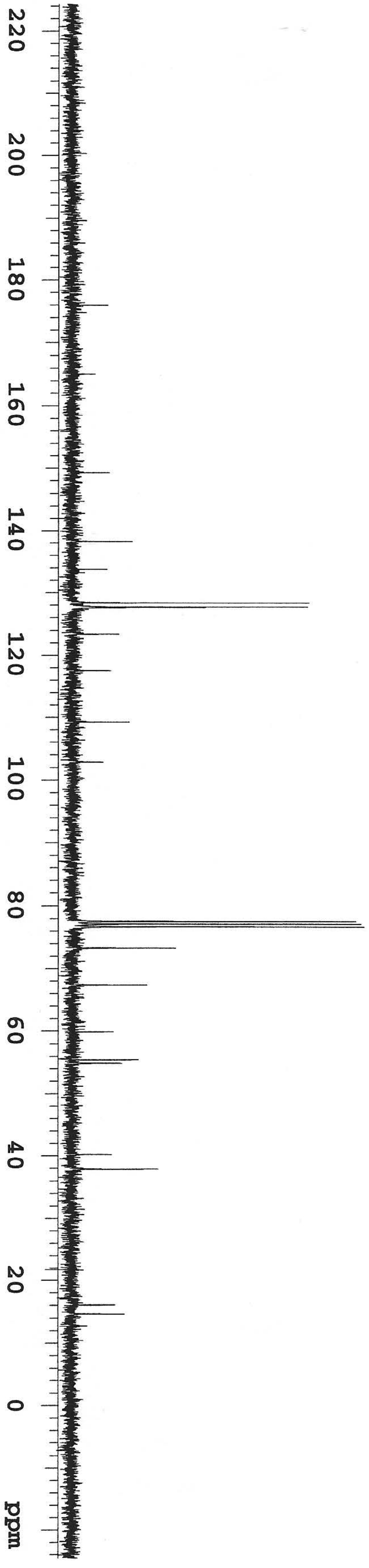
NH
N
CH(OMe)2
OBn
OBn

8a-E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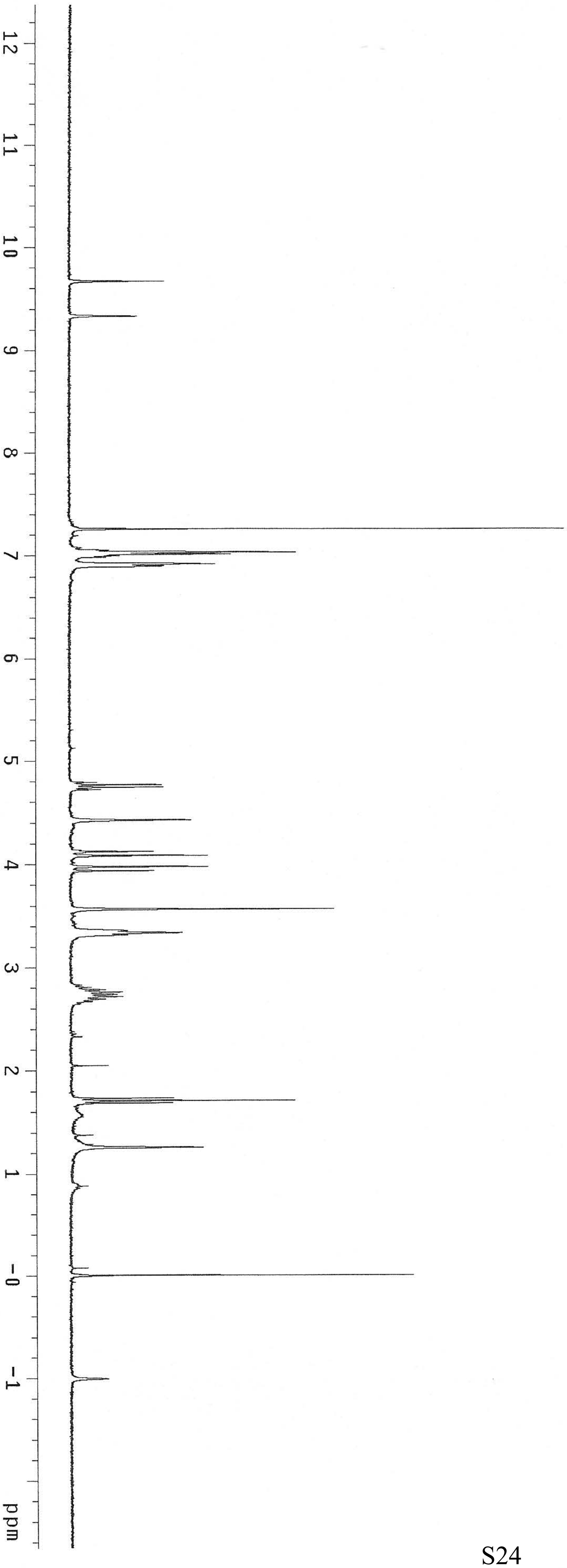
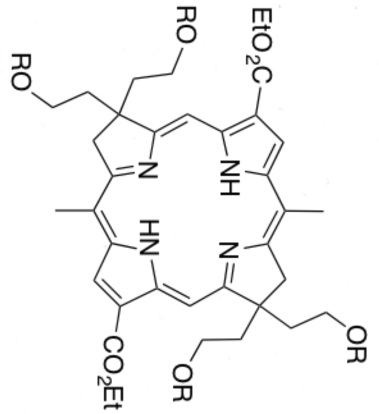
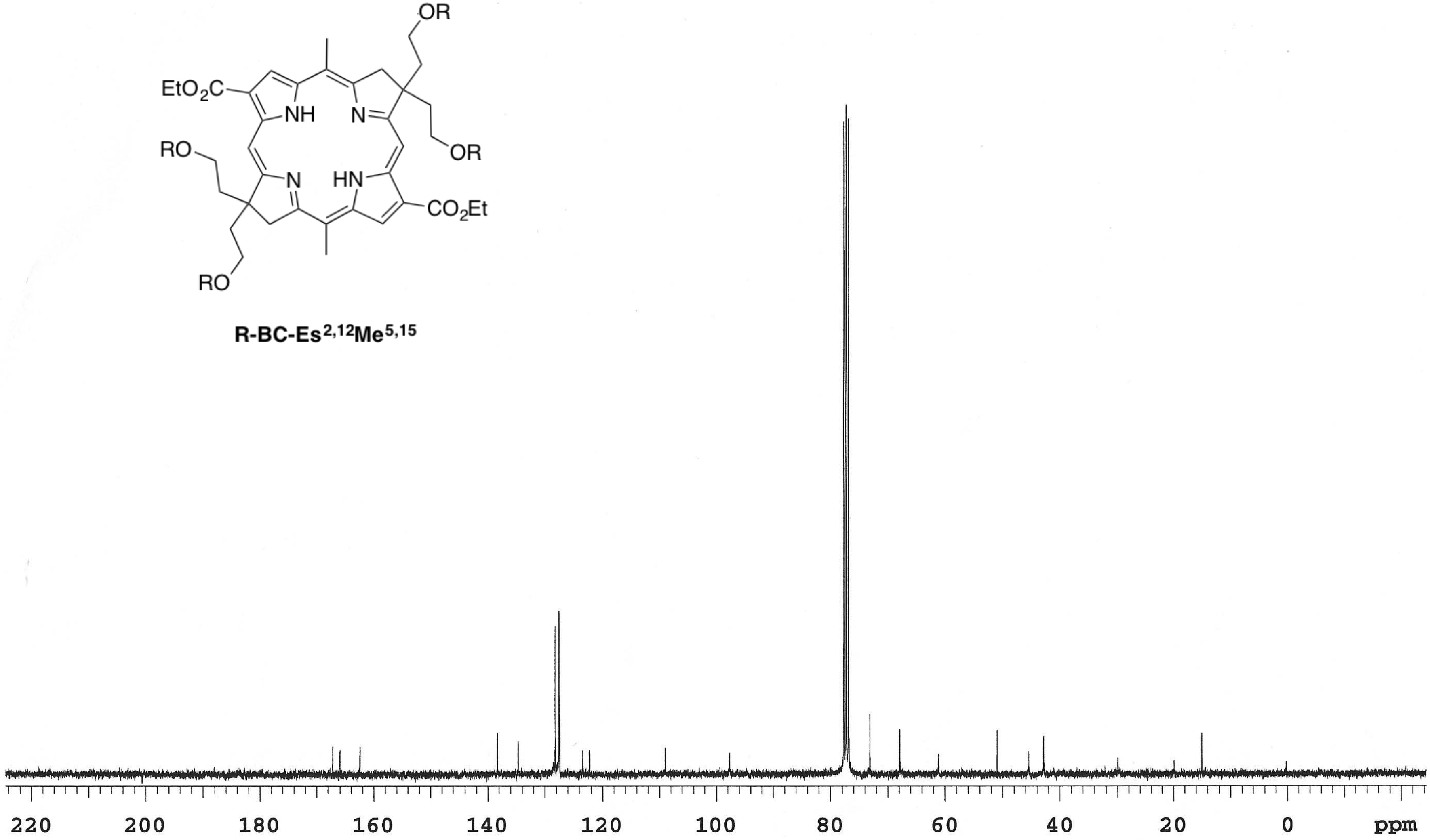




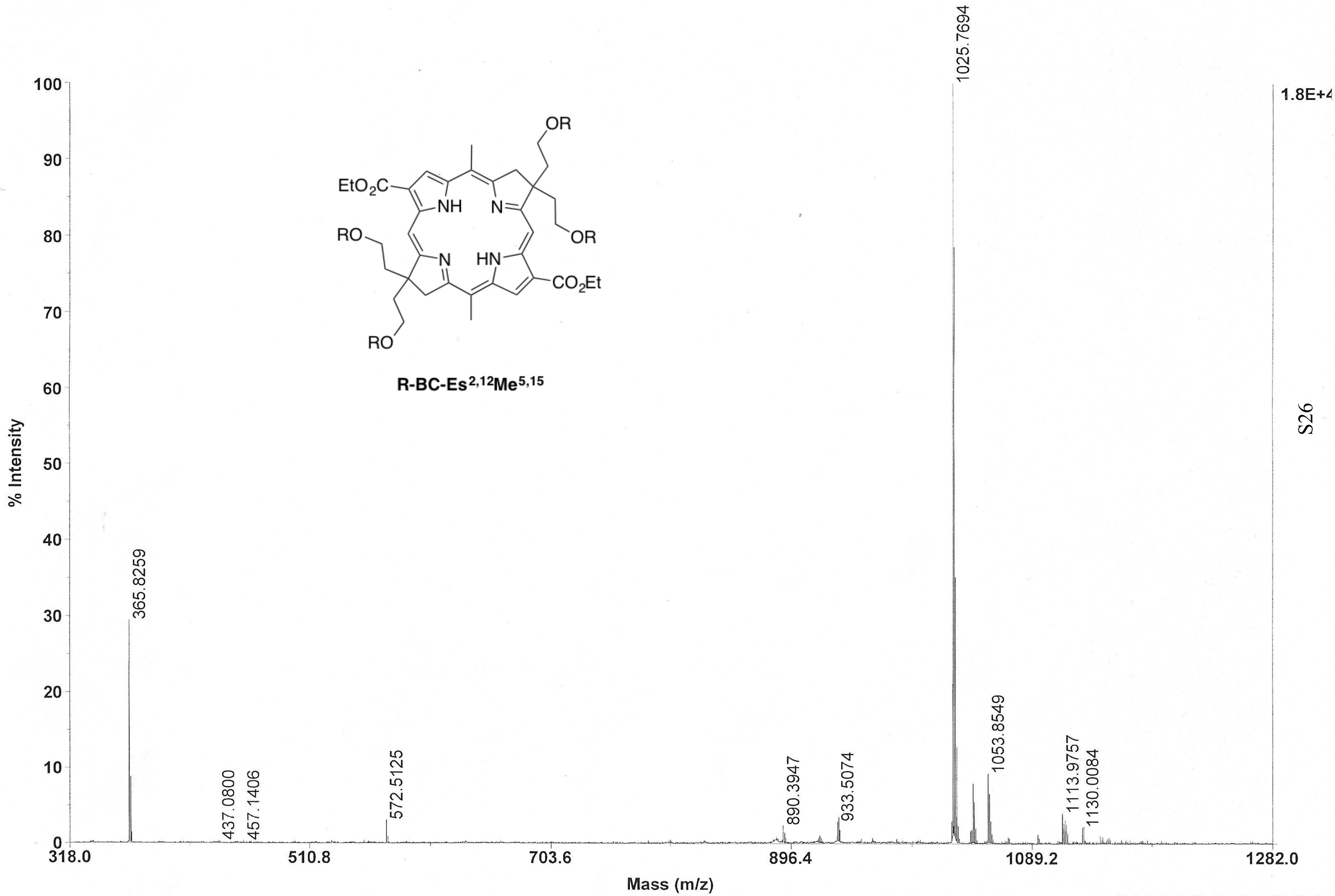
R-BC-Es^{2,12}Me^{5,15}



R-BC-Es^{2,12}Me^{5,15}

AB Sciex TOF/TOF™ Series Explorer™ 20981201

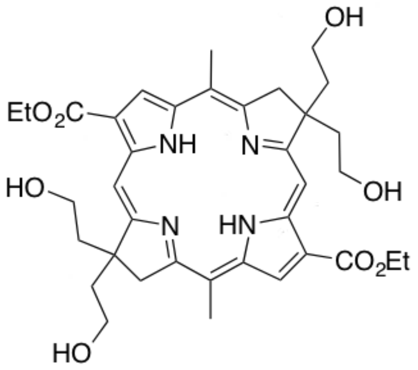
TOF/TOF™ Reflector Spec #1[BP = 1025.8, 17512]



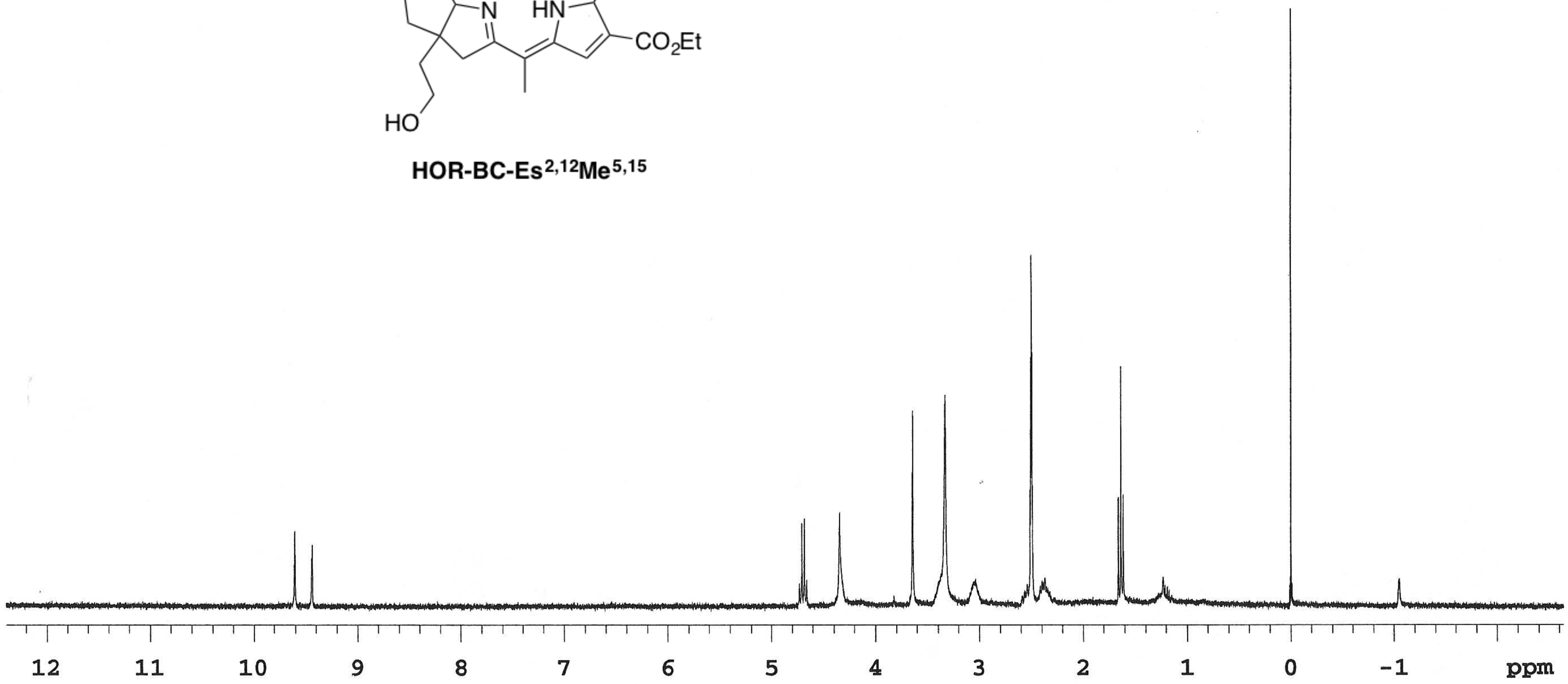
R-BC-Es^{2,12}Me^{5,15}

Printed: 11:39, October 27, 2016

F:\User Project 1\Lindsey\Nagarjuna\OH-SBC\OBn-HBC 27-10-16.T2D

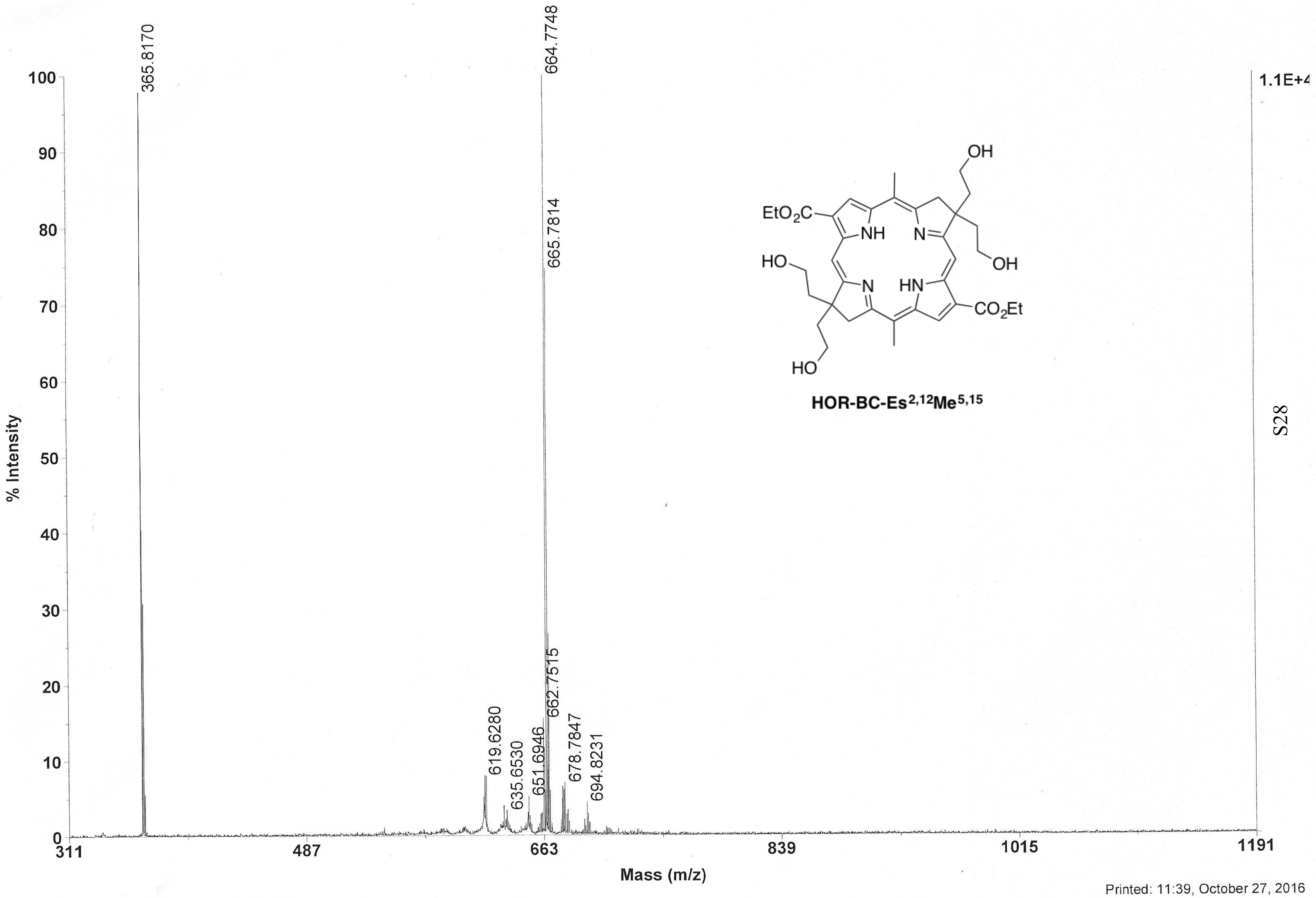


HOR-BC-Es^{2,12}Me^{5,15}



AB Sciex TOF/TOF™ Series Explorer™ 20981201

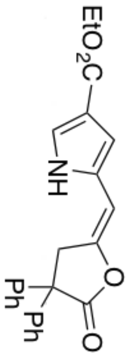
TOF/TOF™ Reflector Spec #1[BP = 664.8, 11436]



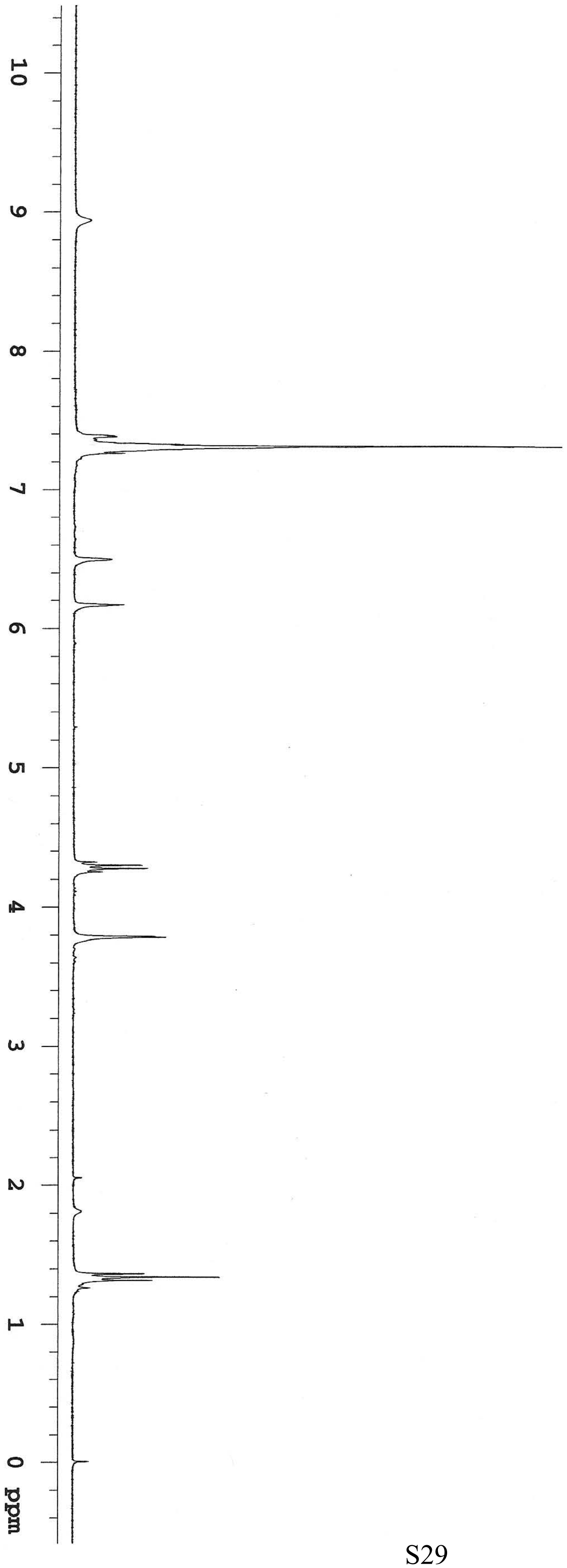
HOR-BC-Es^{2,12}Me^{5,15}

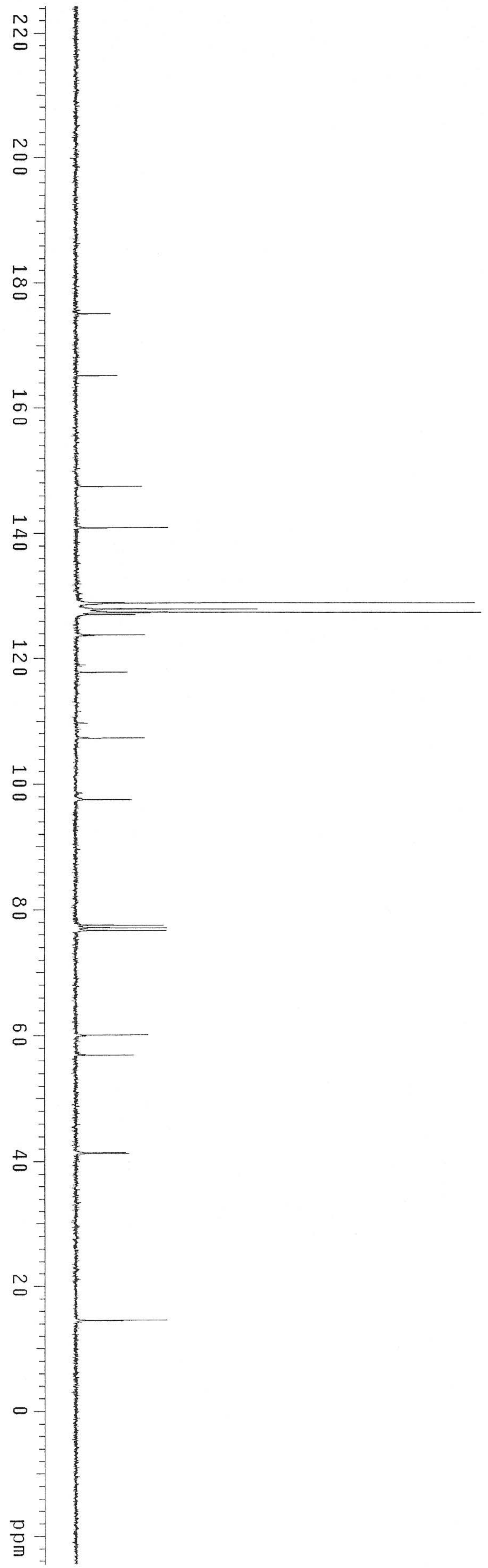
Printed: 11:39, October 27, 2016

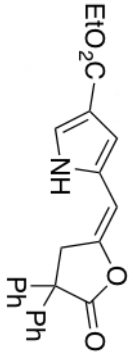
F:\User Project 1\Lindsey\Nagarjuna\OH-SBC\OH-HBC 27-10-16.T2D



5b







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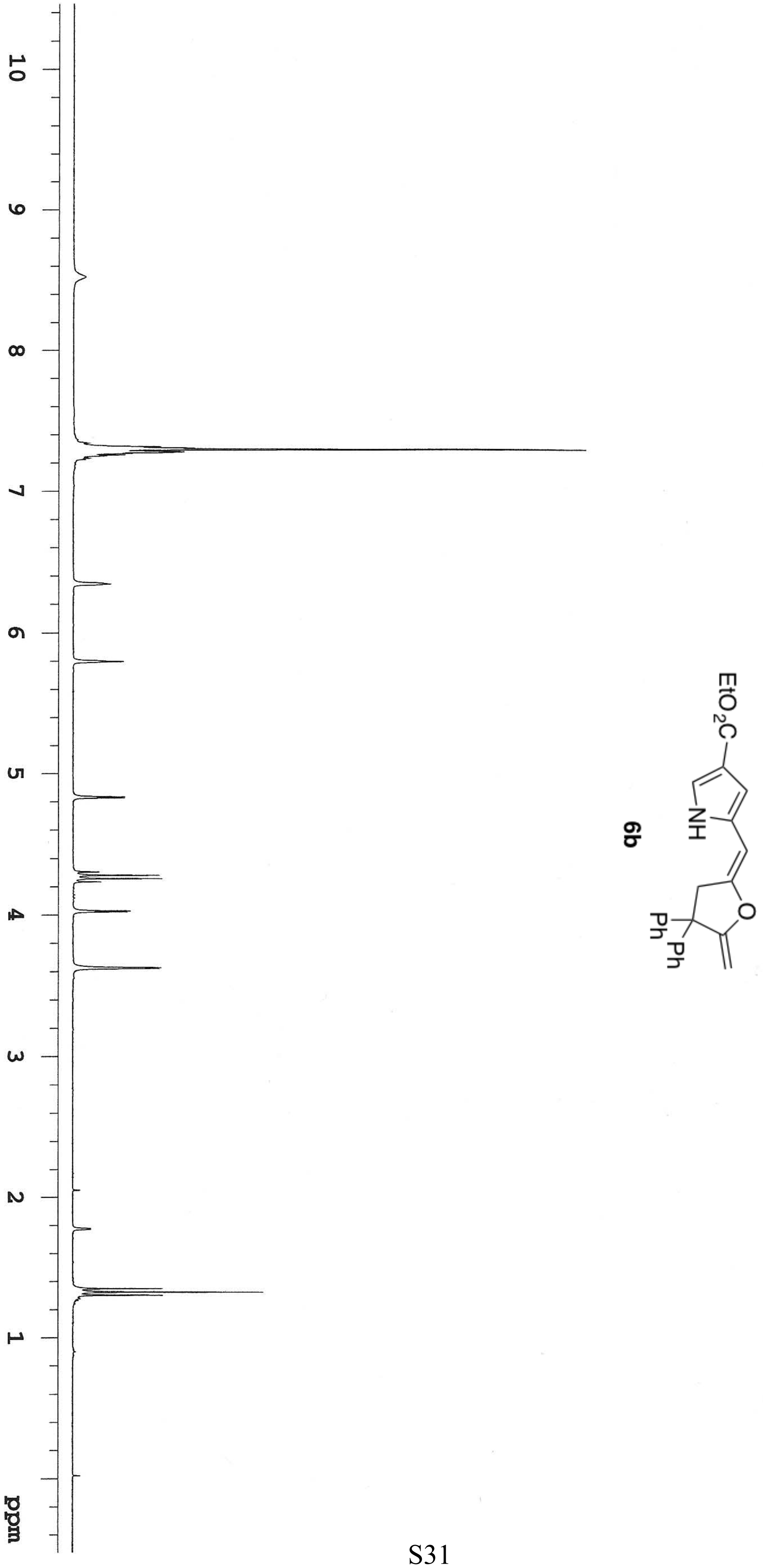
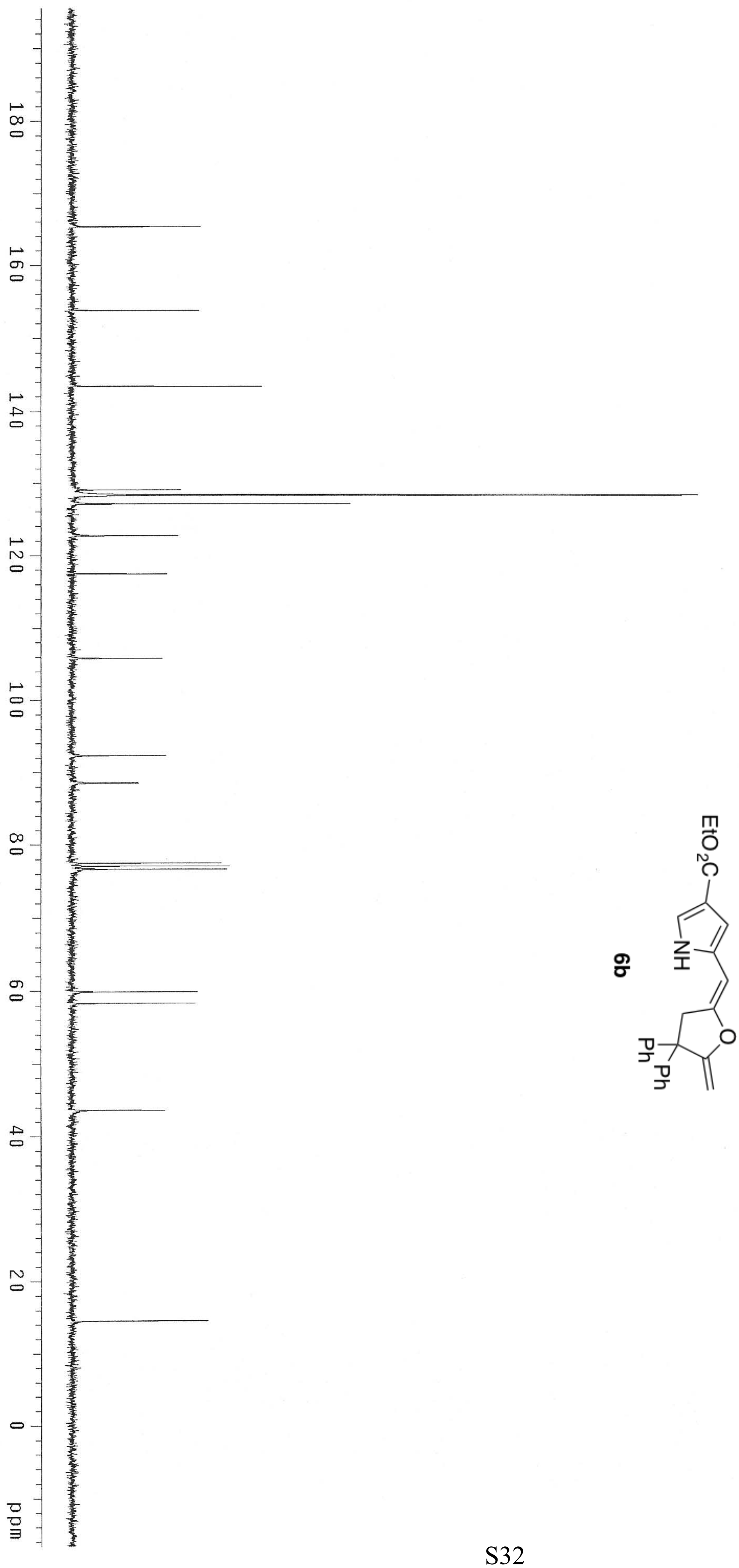


6b



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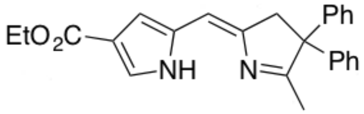
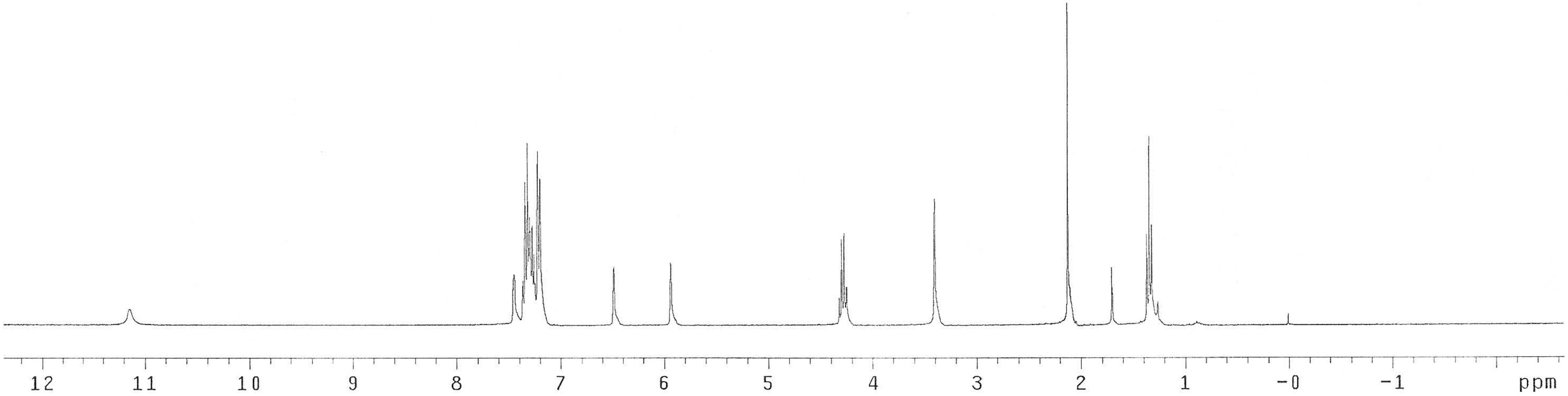
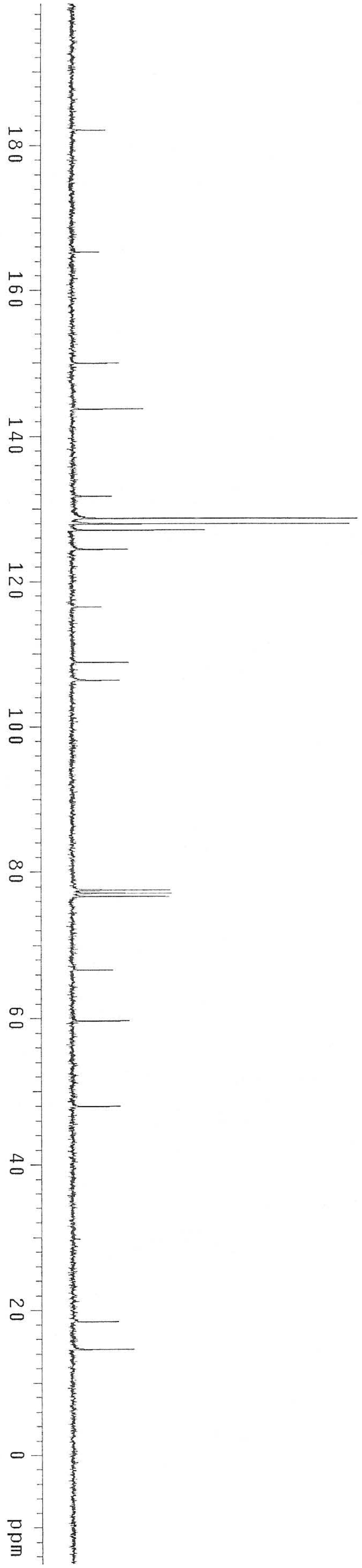
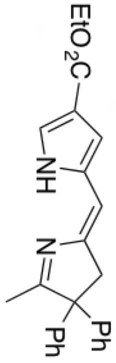


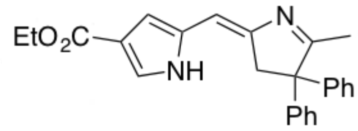
7b-Z



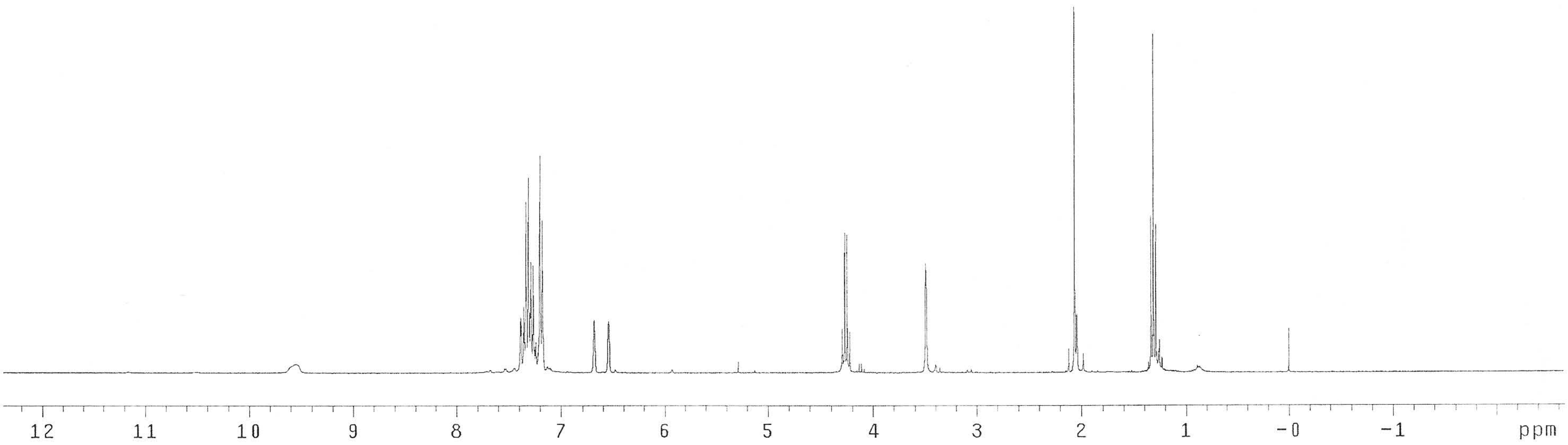


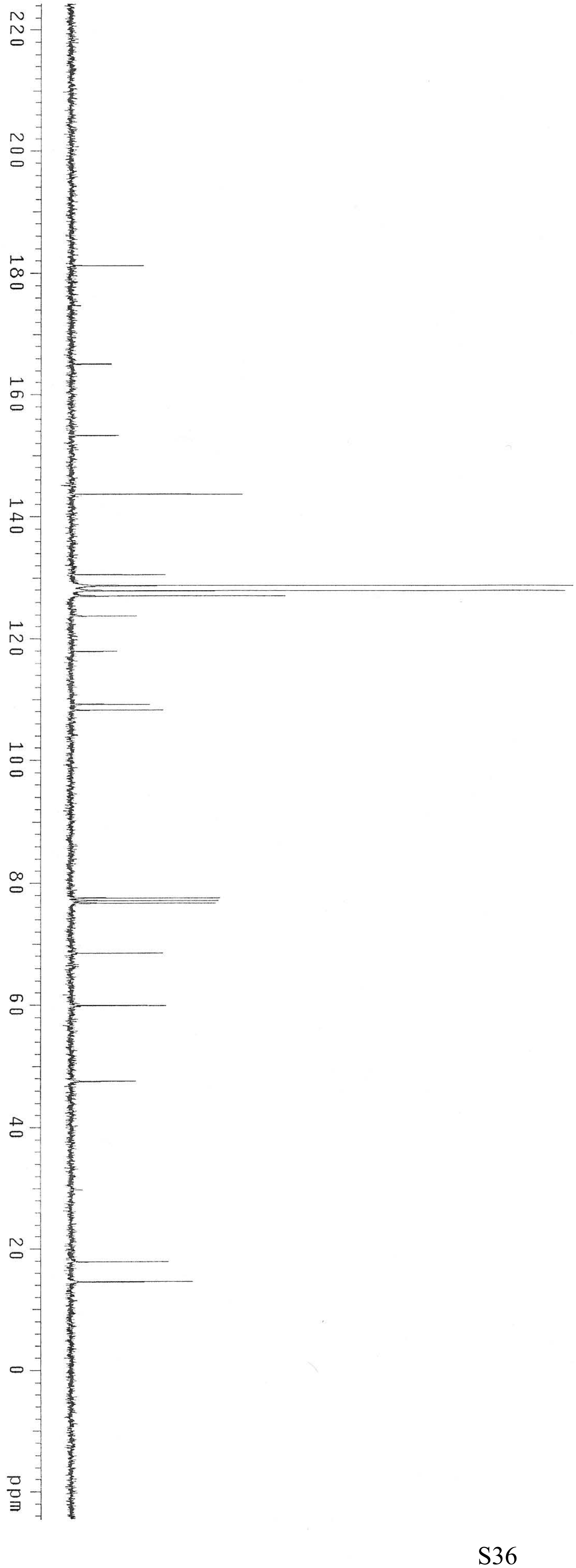


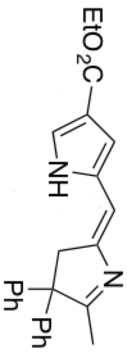
7b-Z



7b-E







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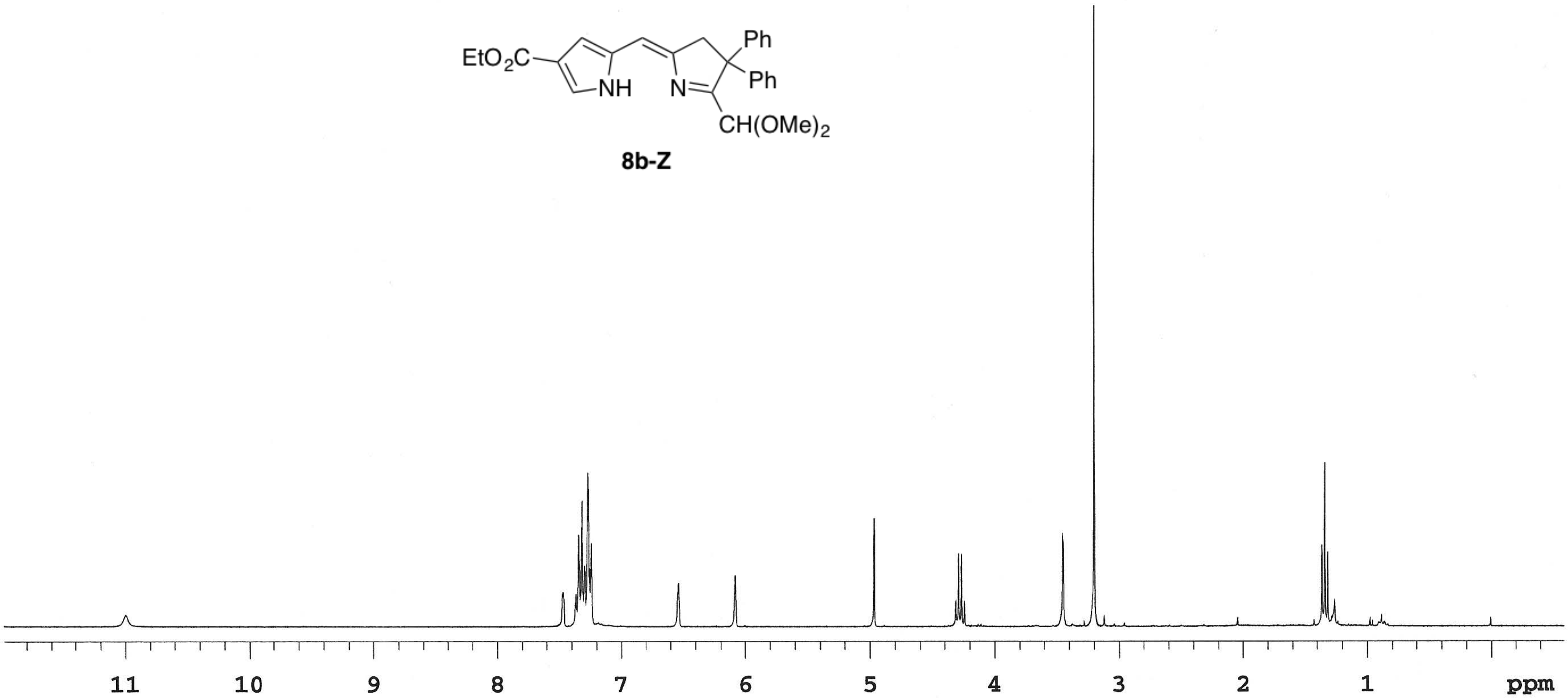
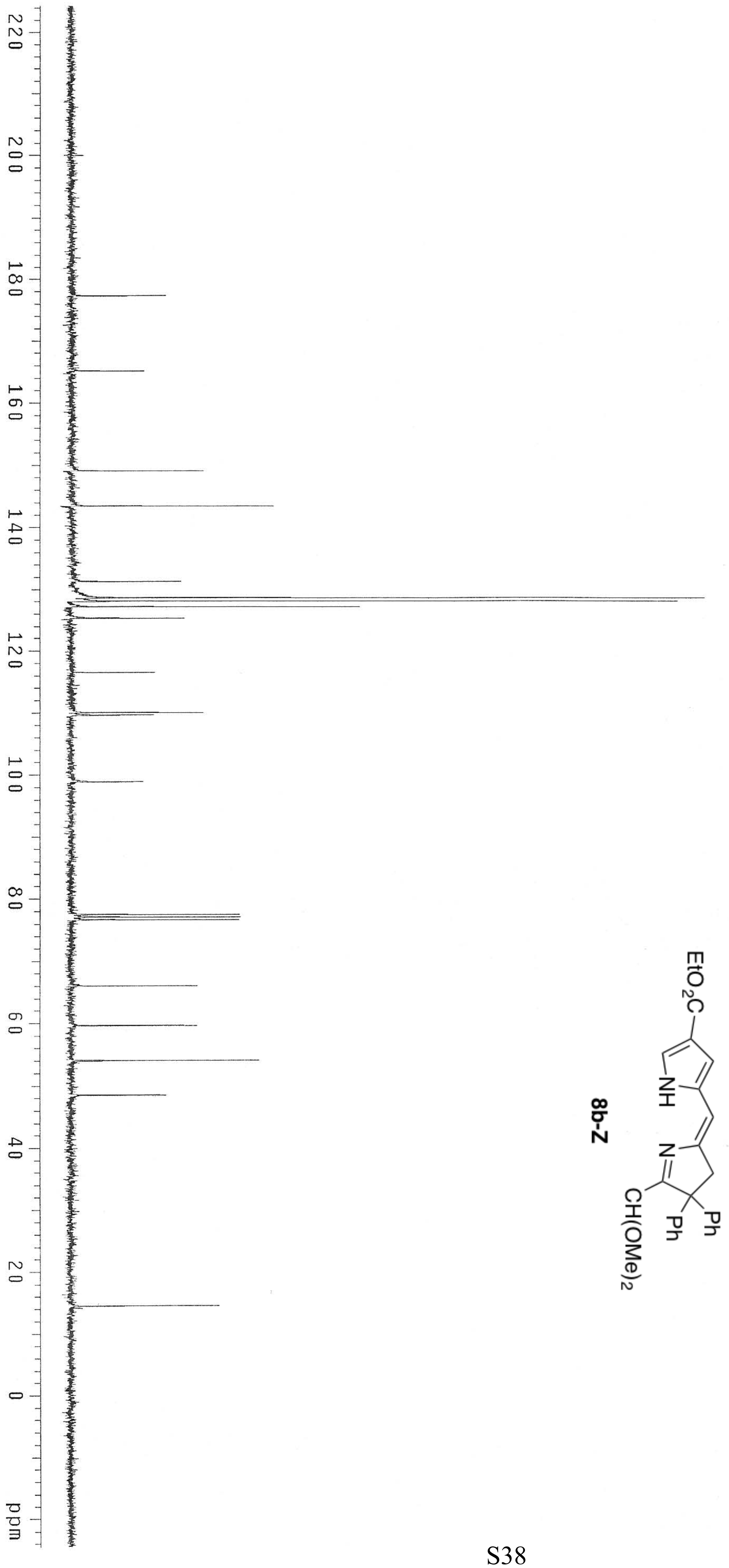
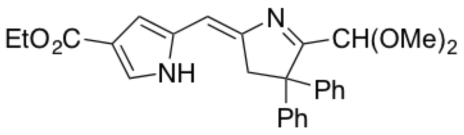


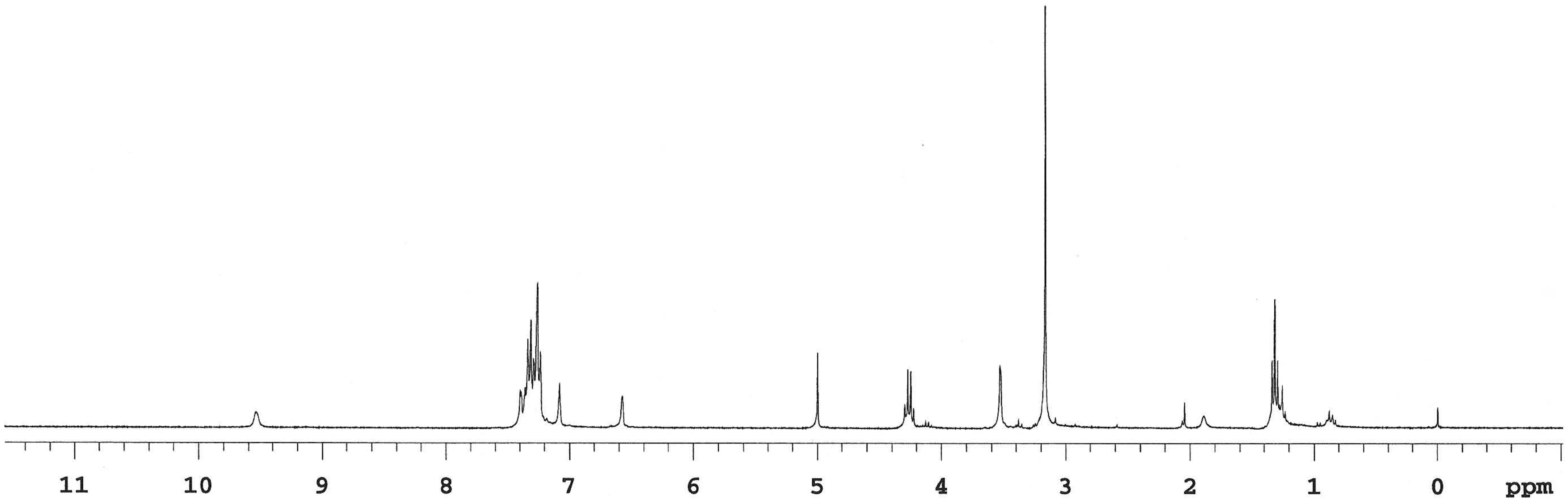
8b-Z

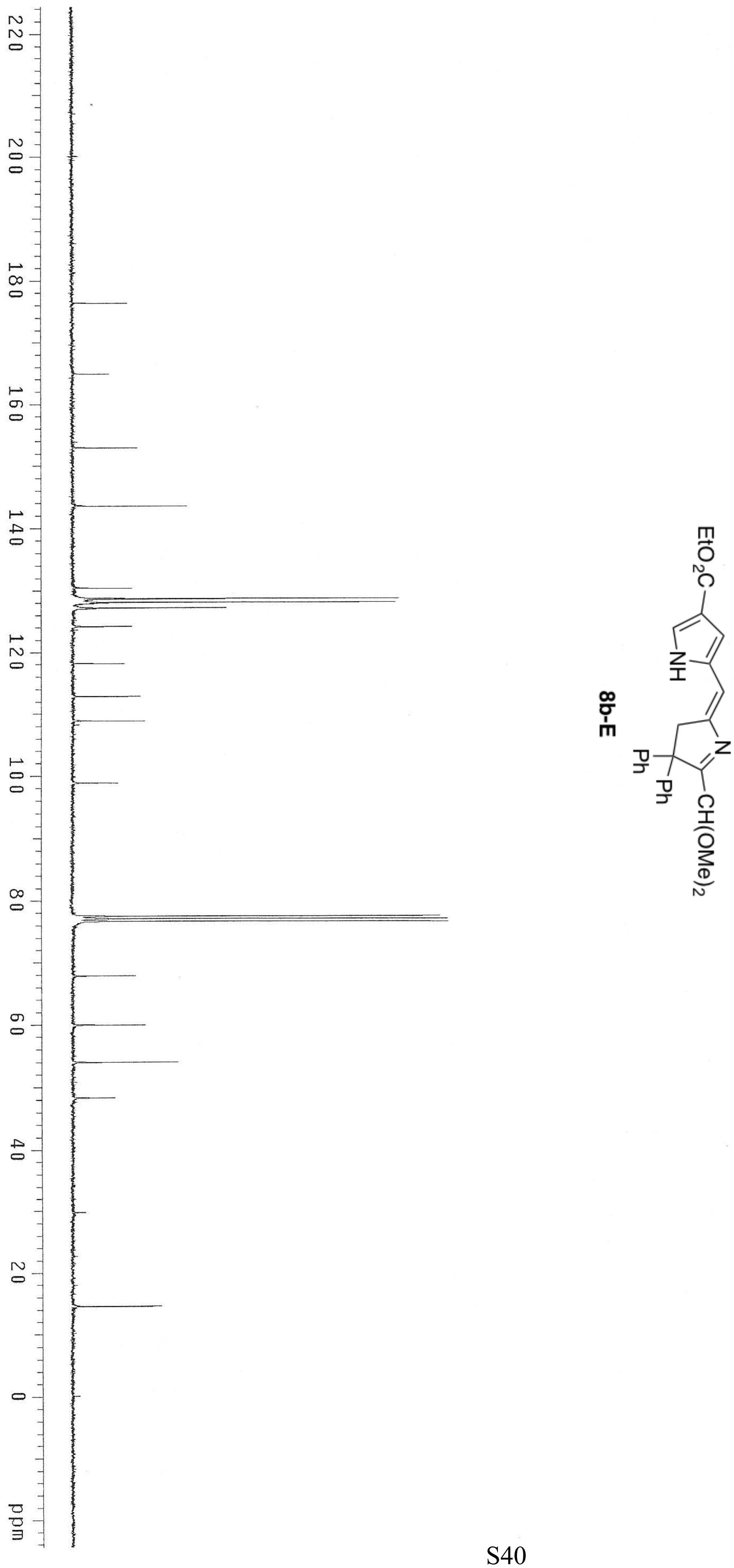

220
200
180
160
140
120
100
80
60
40
20
0
ppm
EtO$_2$C
NH
N
Ph
Ph
CH(OMe)$_2$

8b-Z

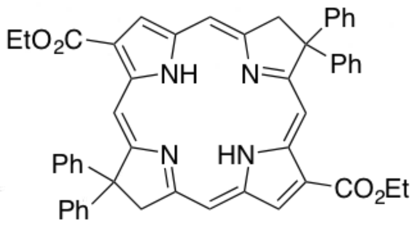


8b-E

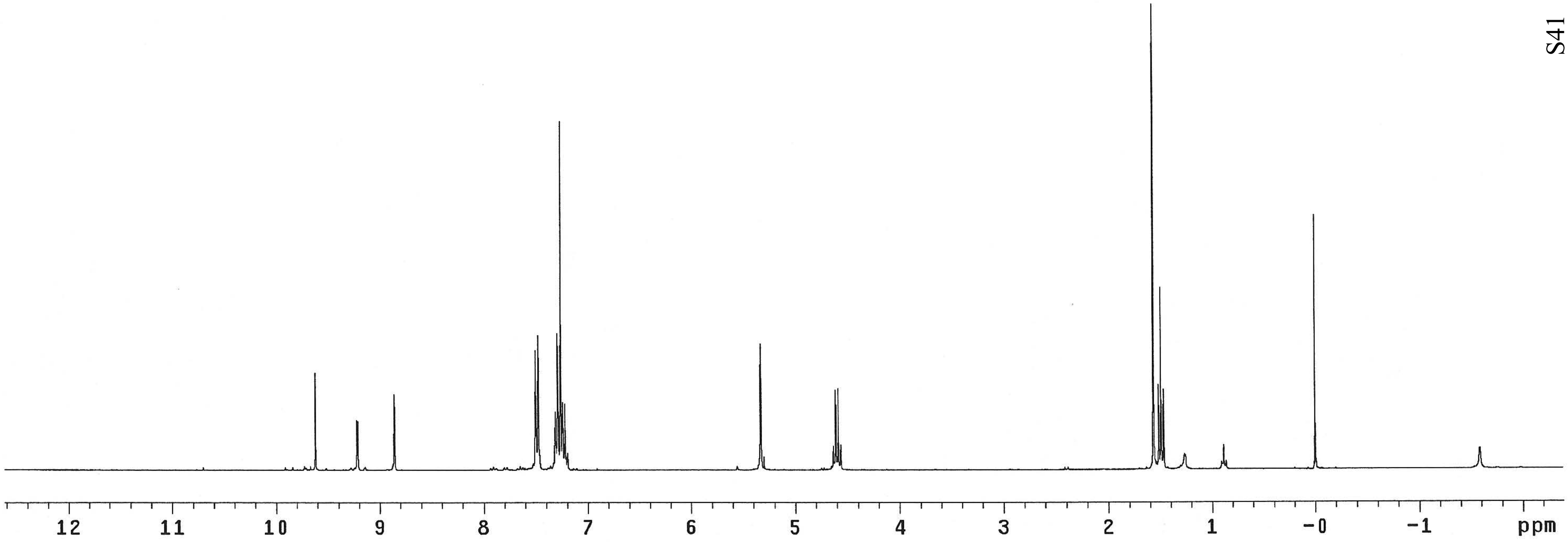



220
200
180
160
140
120
100
80
60
40
20
0
ppm
EtO$_2$C
NH
N
Ph
Ph
CH(OMe)$_2$

8b-E

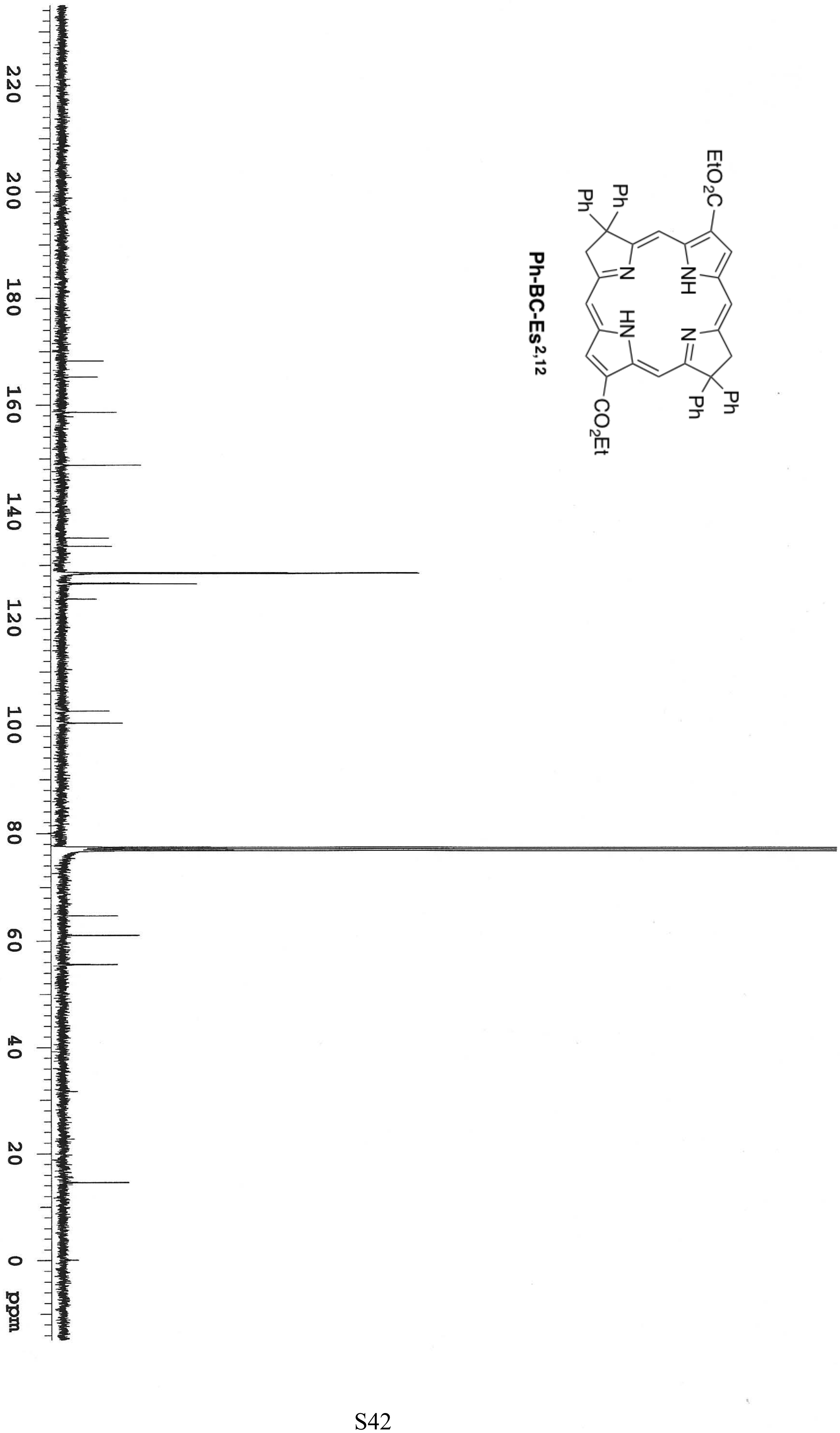


Ph-BC-Es^{2,12}



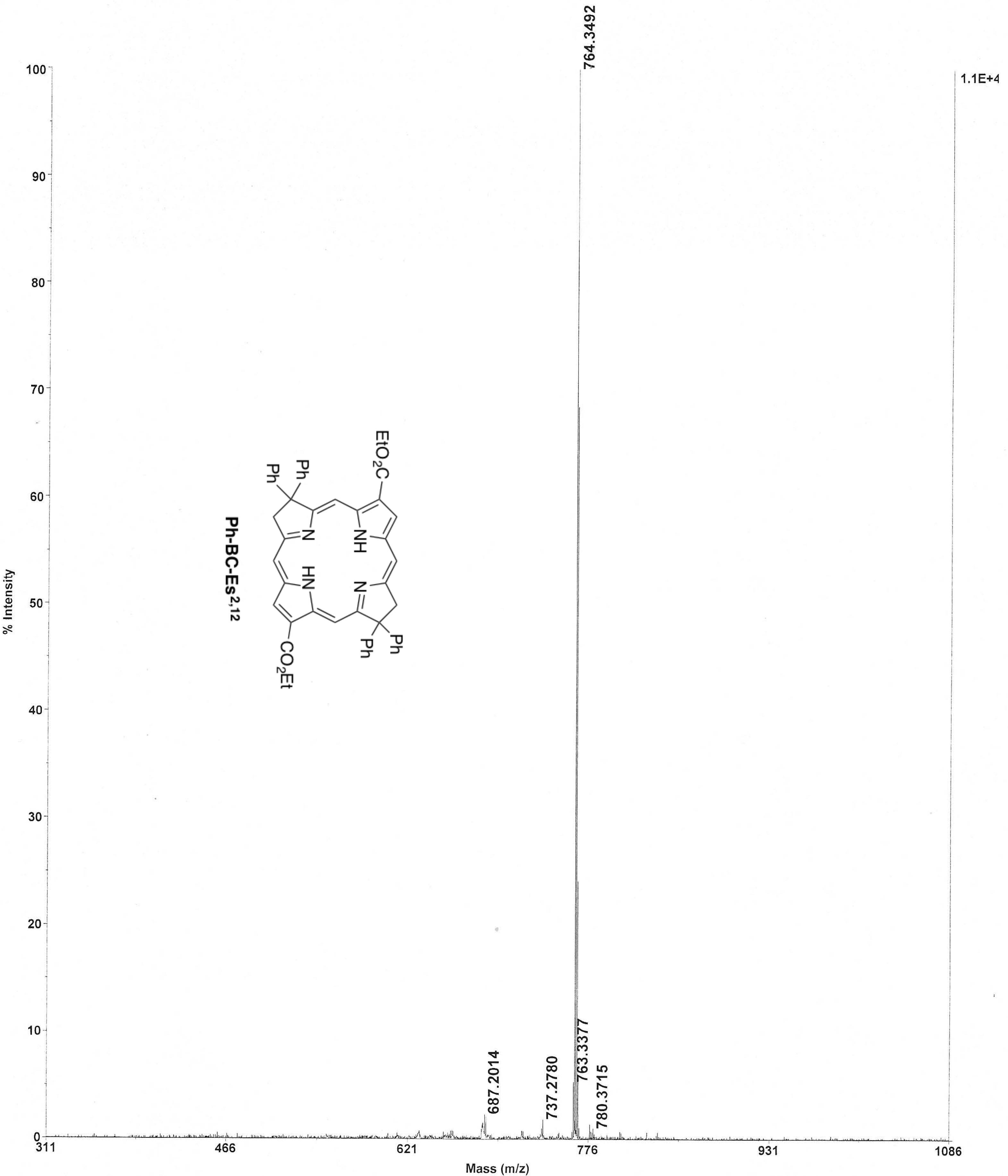
EtO$_2$C
Ph
Ph
NH
N
HN
N
Ph
Ph
CO$_2$Et

Ph-BC-Es^{2,12}


220
200
180
160
140
120
100
80
60
40
20
0
ppm

AB Sciex TOF/TOF™ Series Explorer™ 20981201

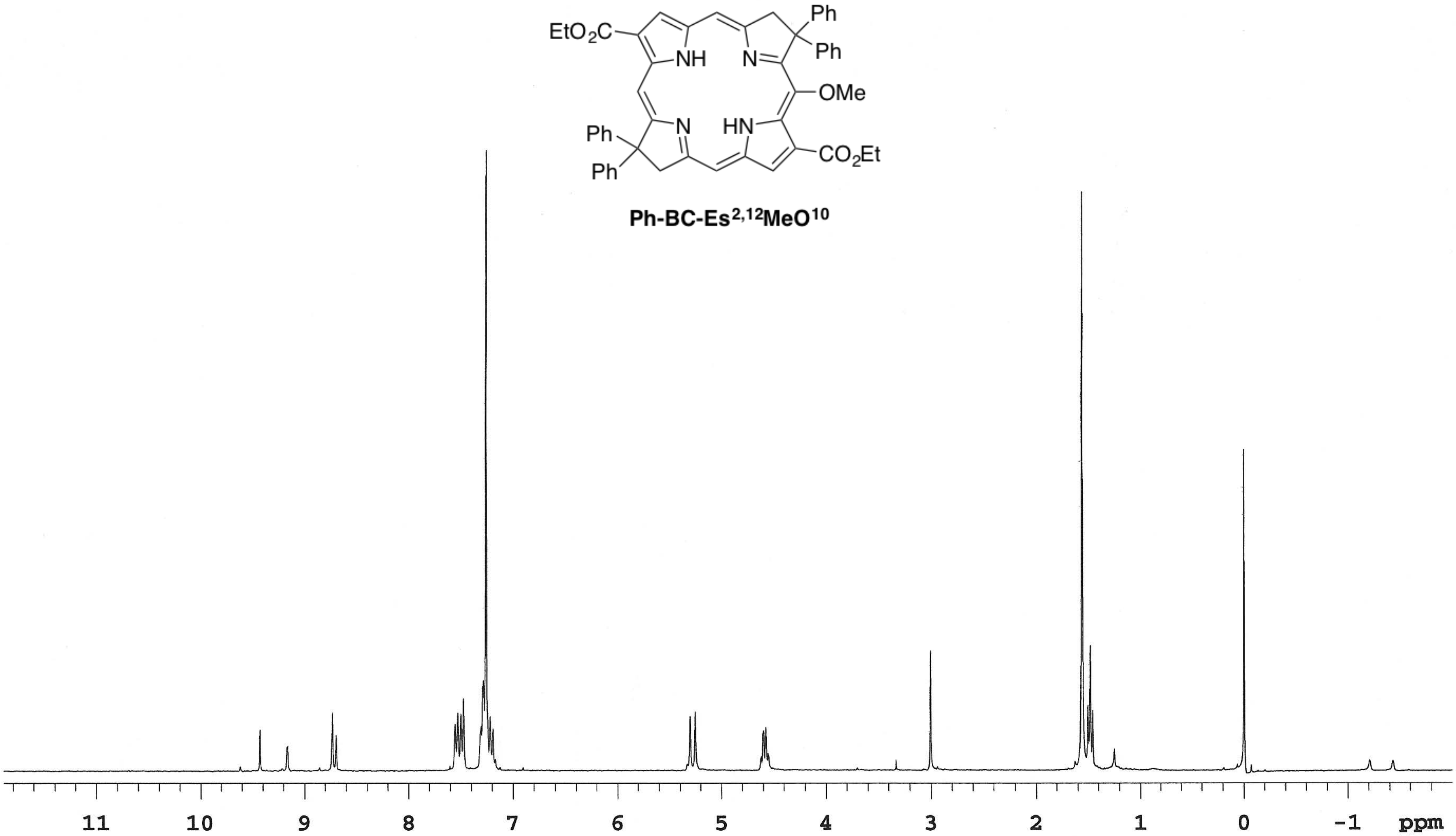
TOF/TOF™ Reflector Spec #1[BP = 764.4, 10825]



Ph-BC-Es^{2,12}

D:\User Project 1\Lindsey\Srinu\September 2016\Ph4BC_isolated pure.T2D

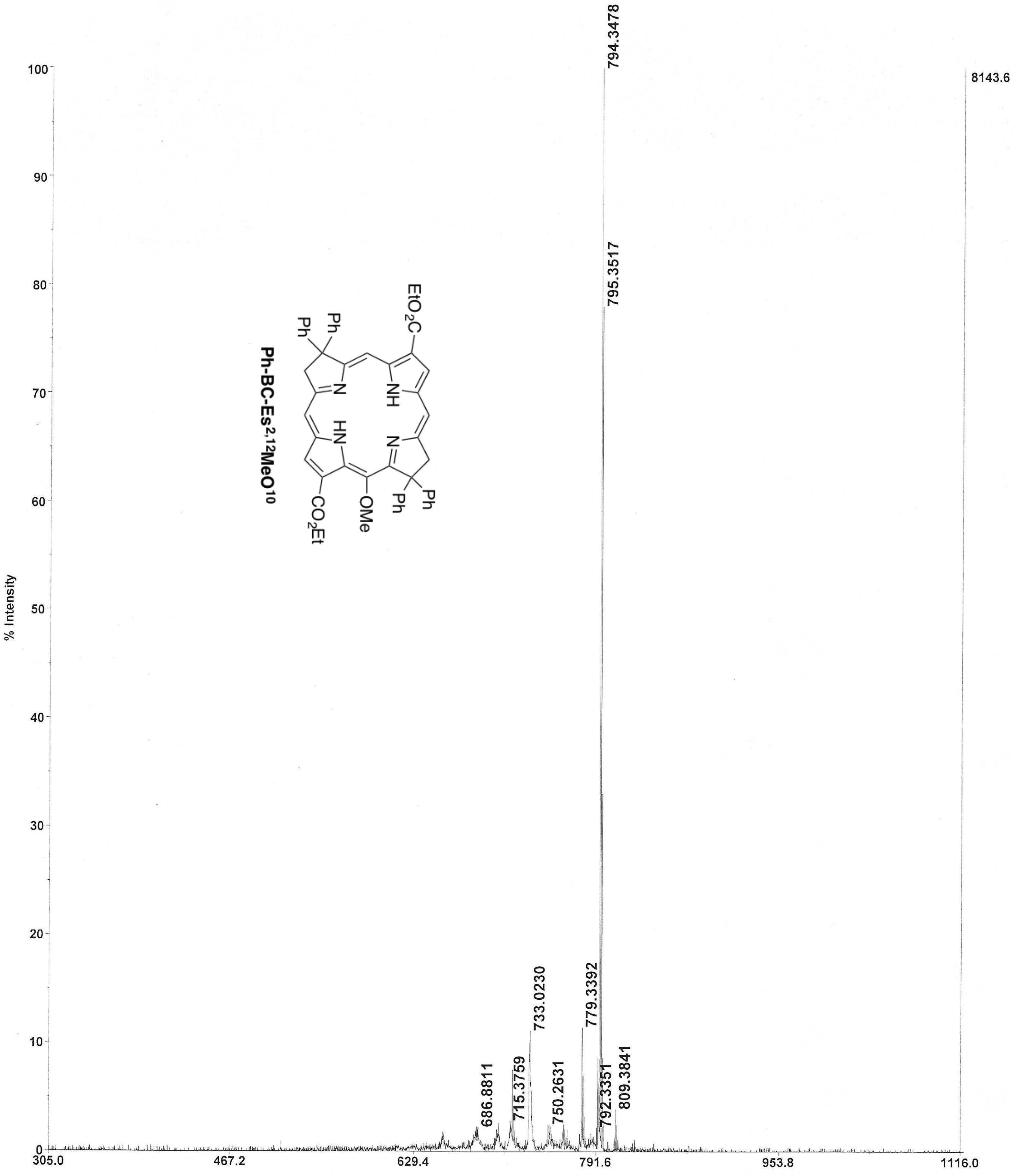
Printed: 14:37, September 14, 2016



Ph-BC-Es^{2,12}MeO^{10}

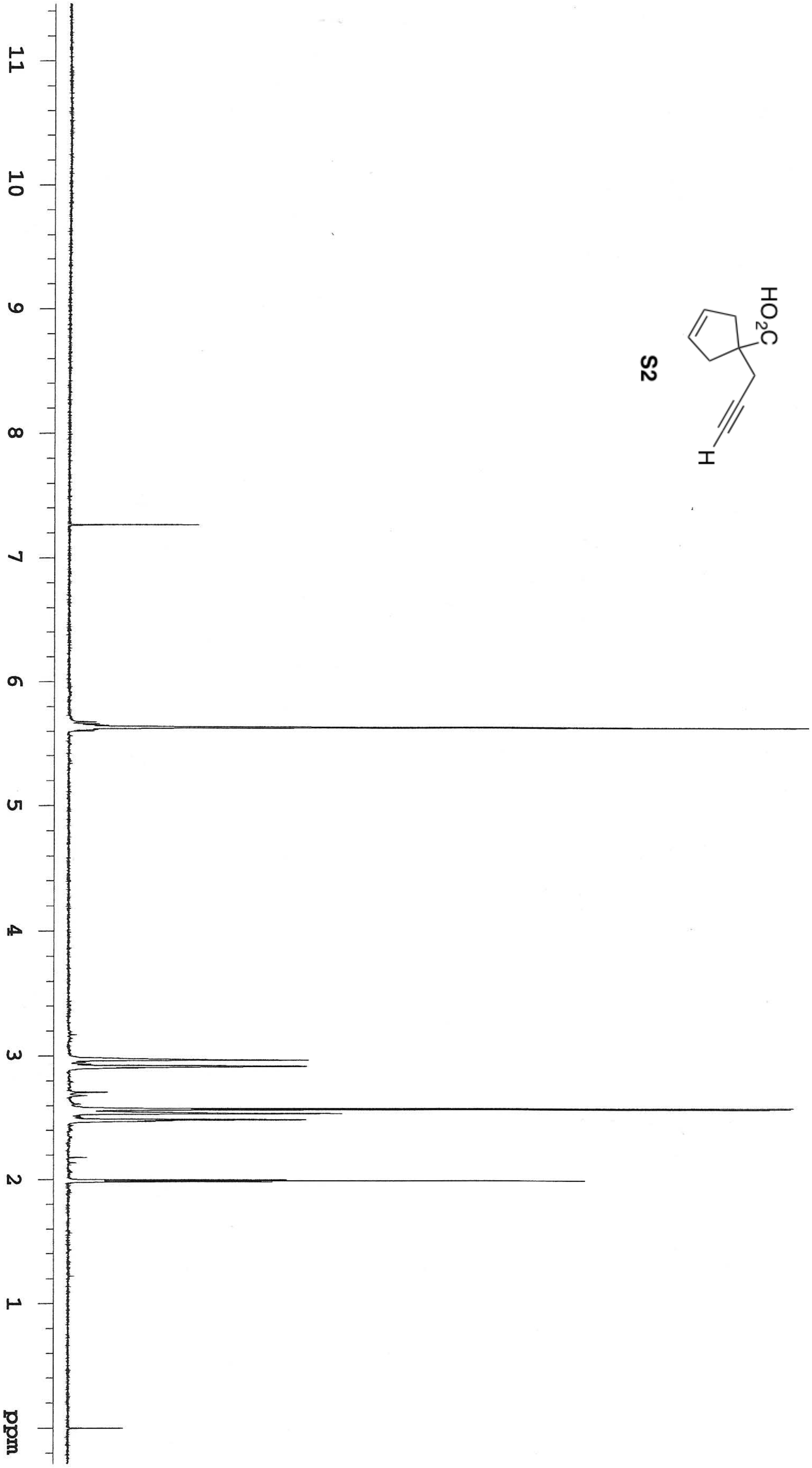
AB Sciex TOF/TOF™ Series Explorer™ 20981201

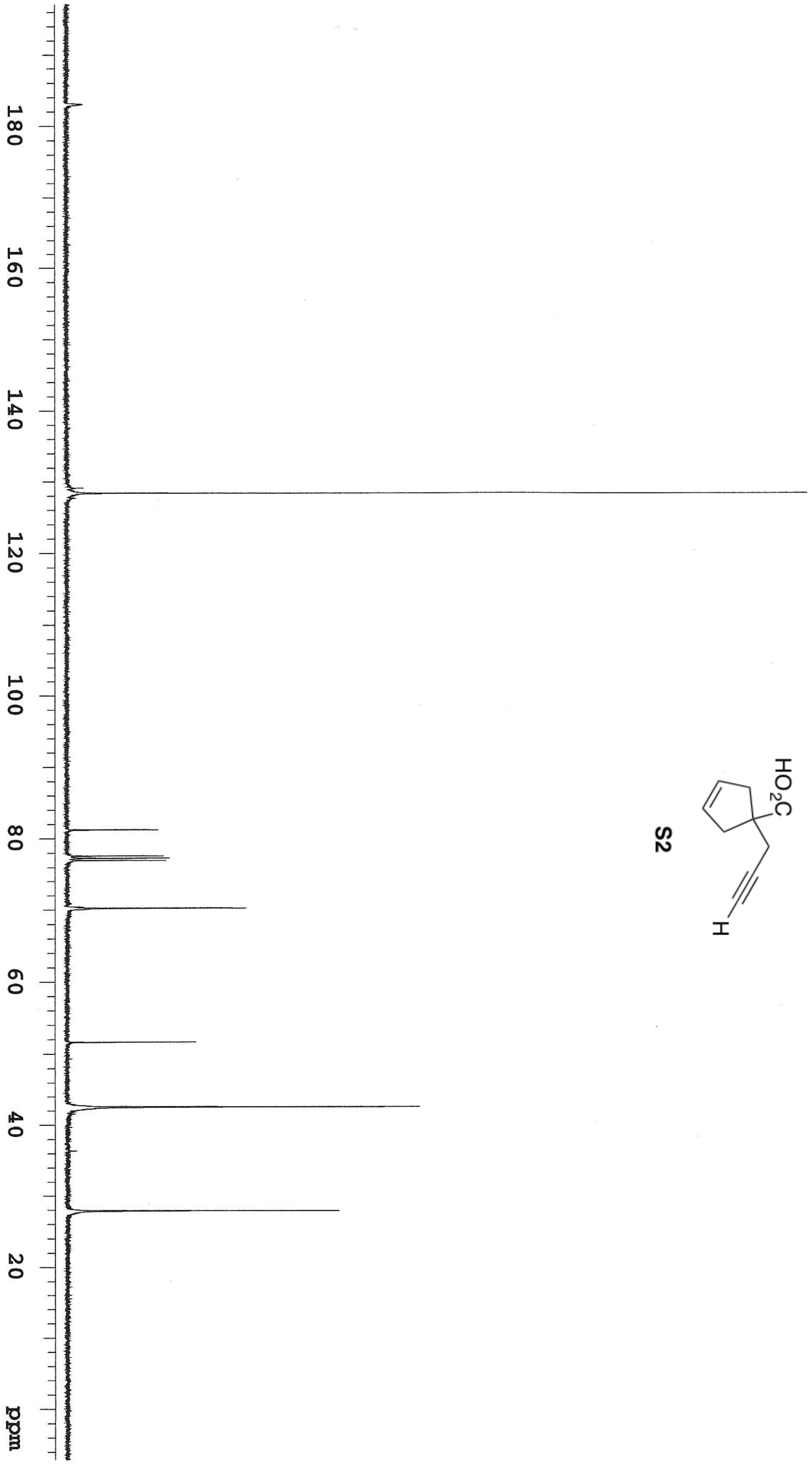
TOF/TOF™ Reflector Spec #1[BP = 794.3, 8144]



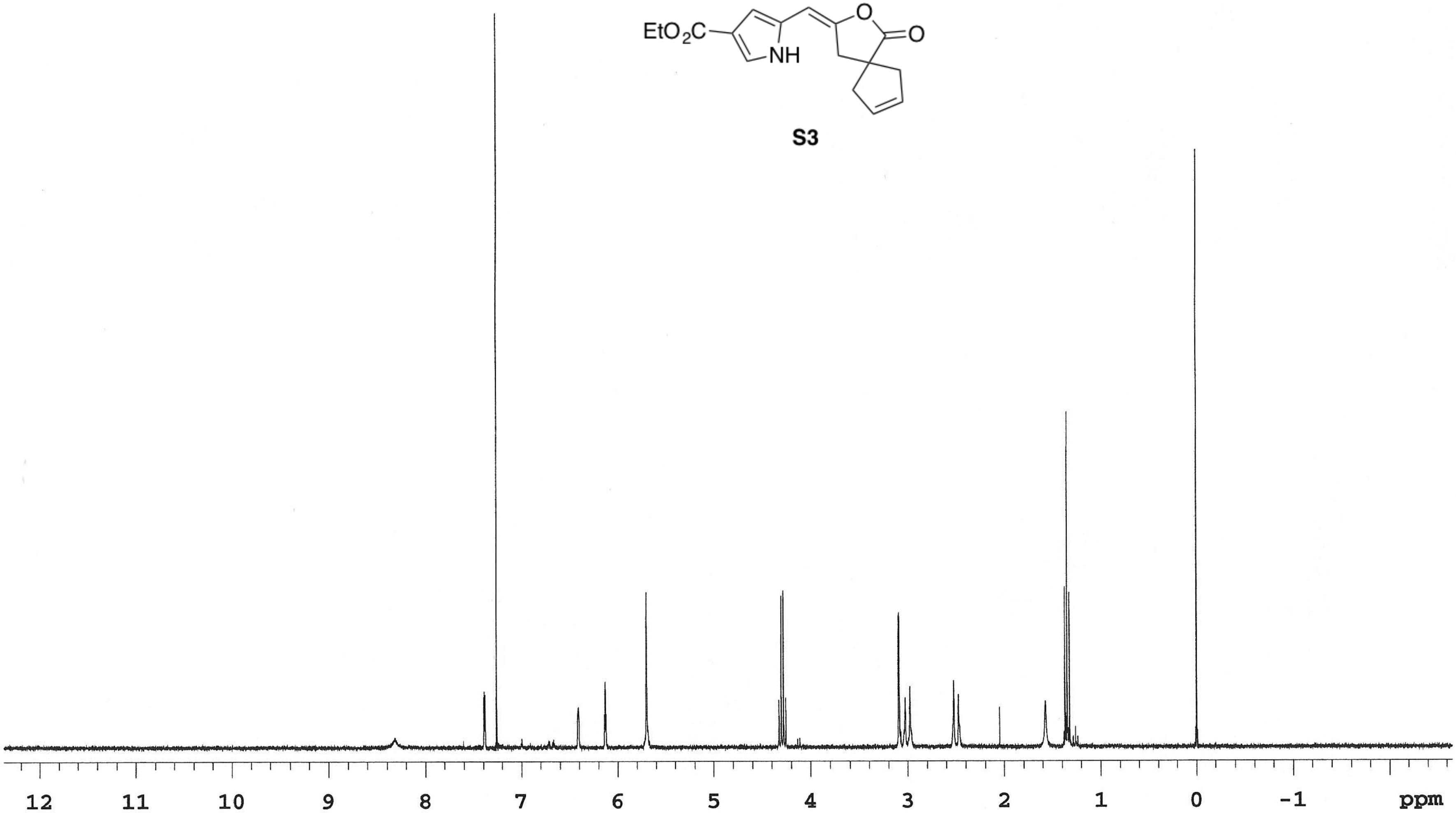
Printed: 14:38, September 14, 2016

D:\User Project 1\Lindsey\Srinu\September 2016\Ph4BC_2nd spot isolated pure.T2D

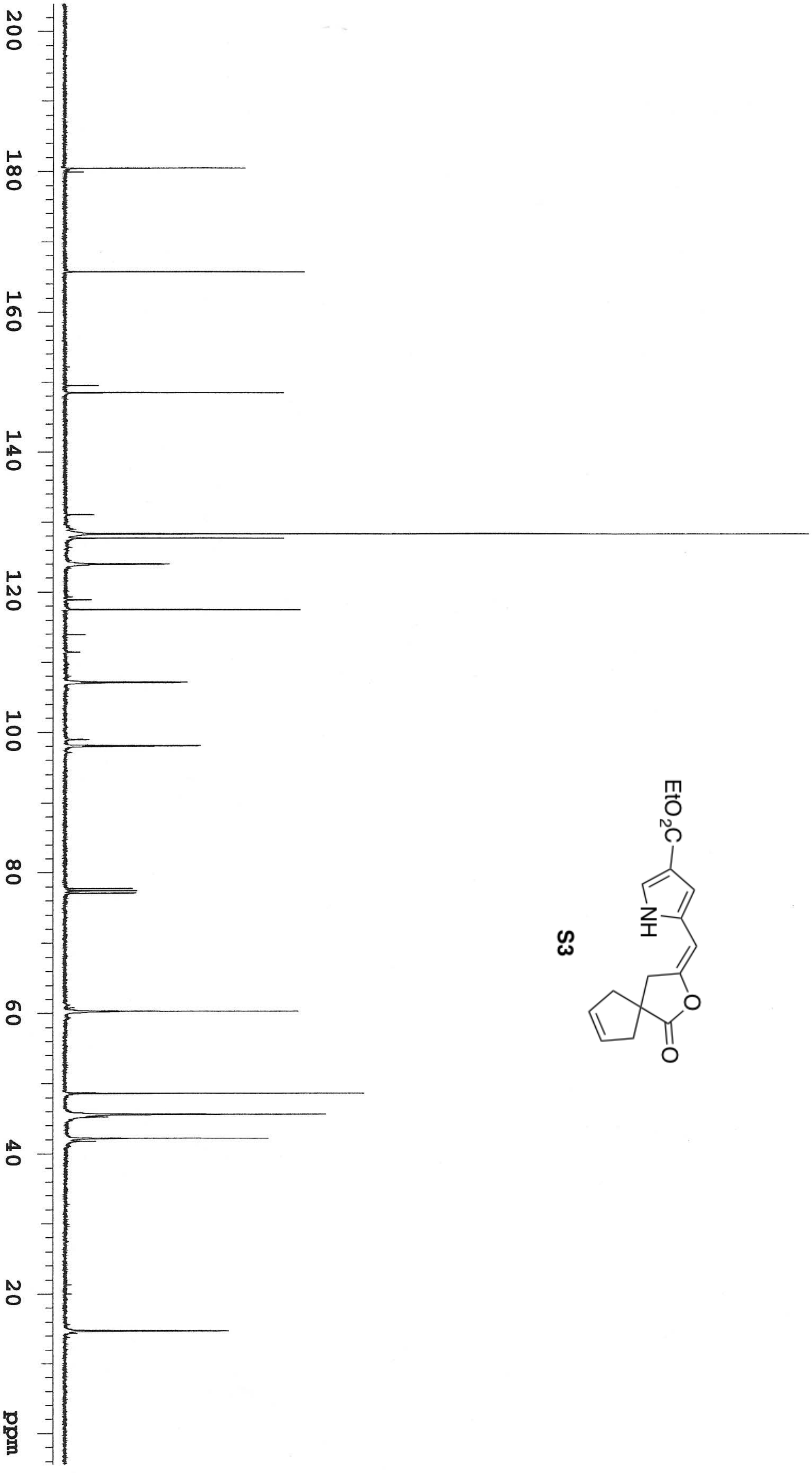

HO$_2$C
H
S2
11
10
9
8
7
6
5
4
3
2
1
ppm



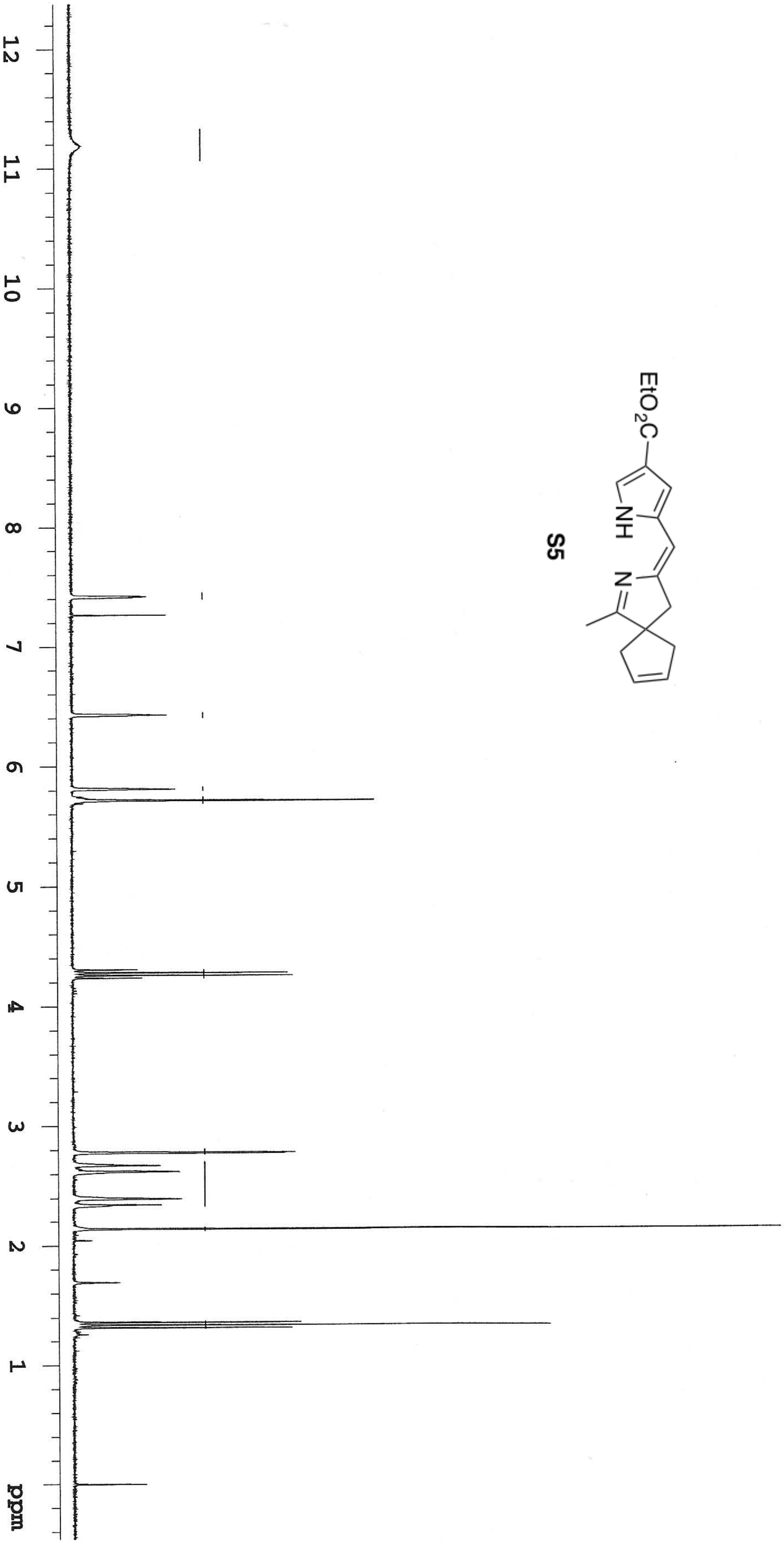
S2



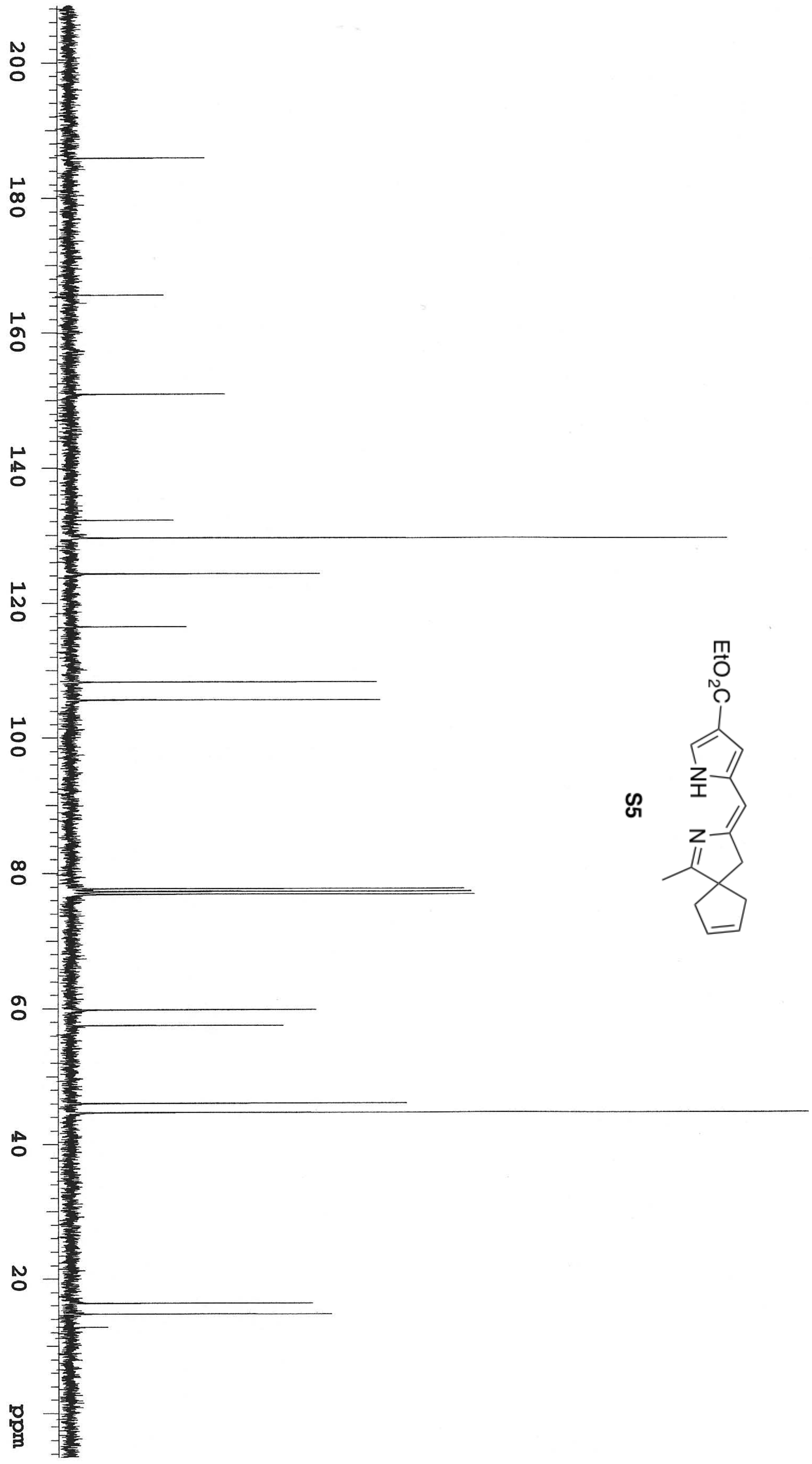
S3



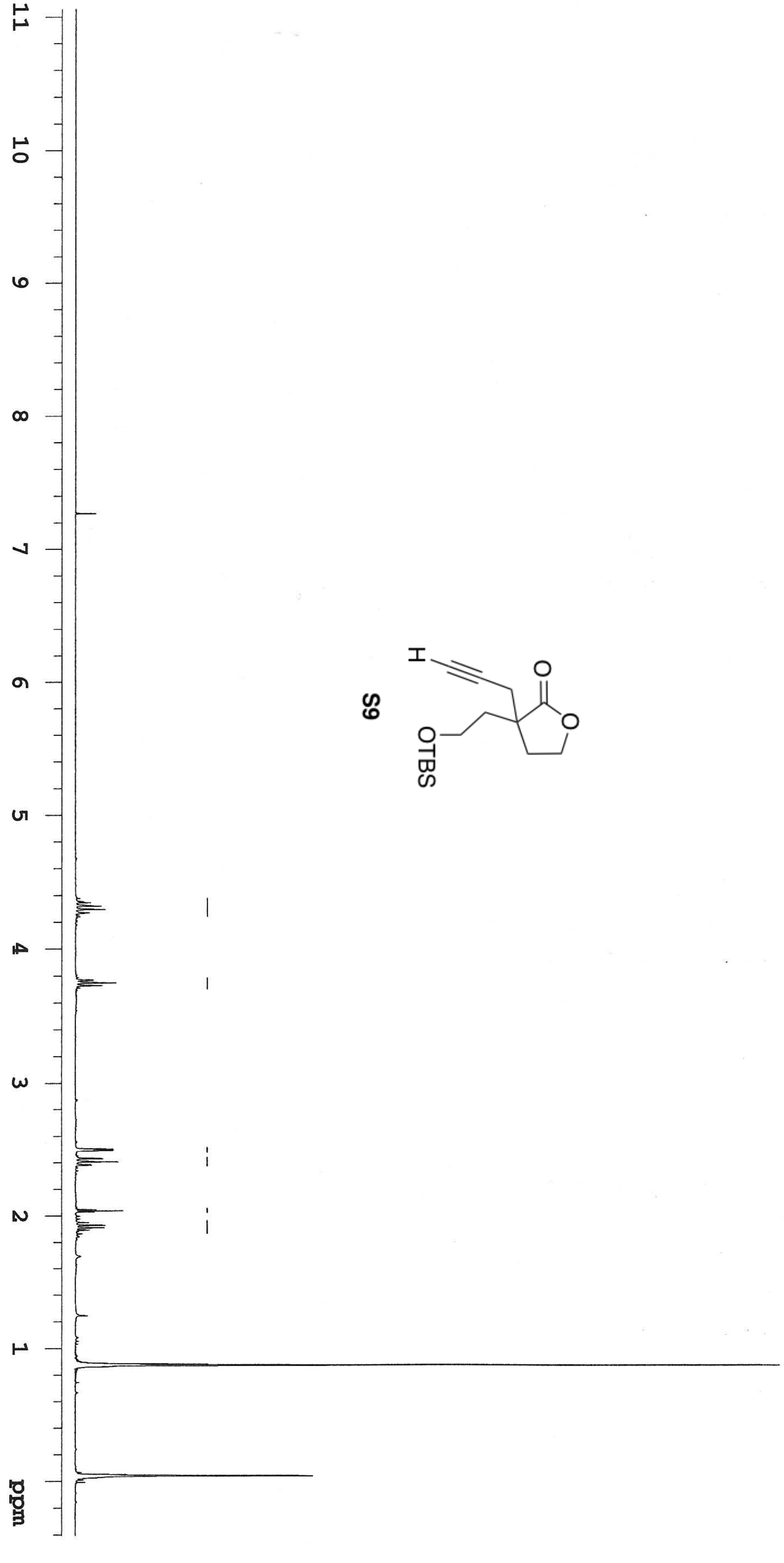
S3



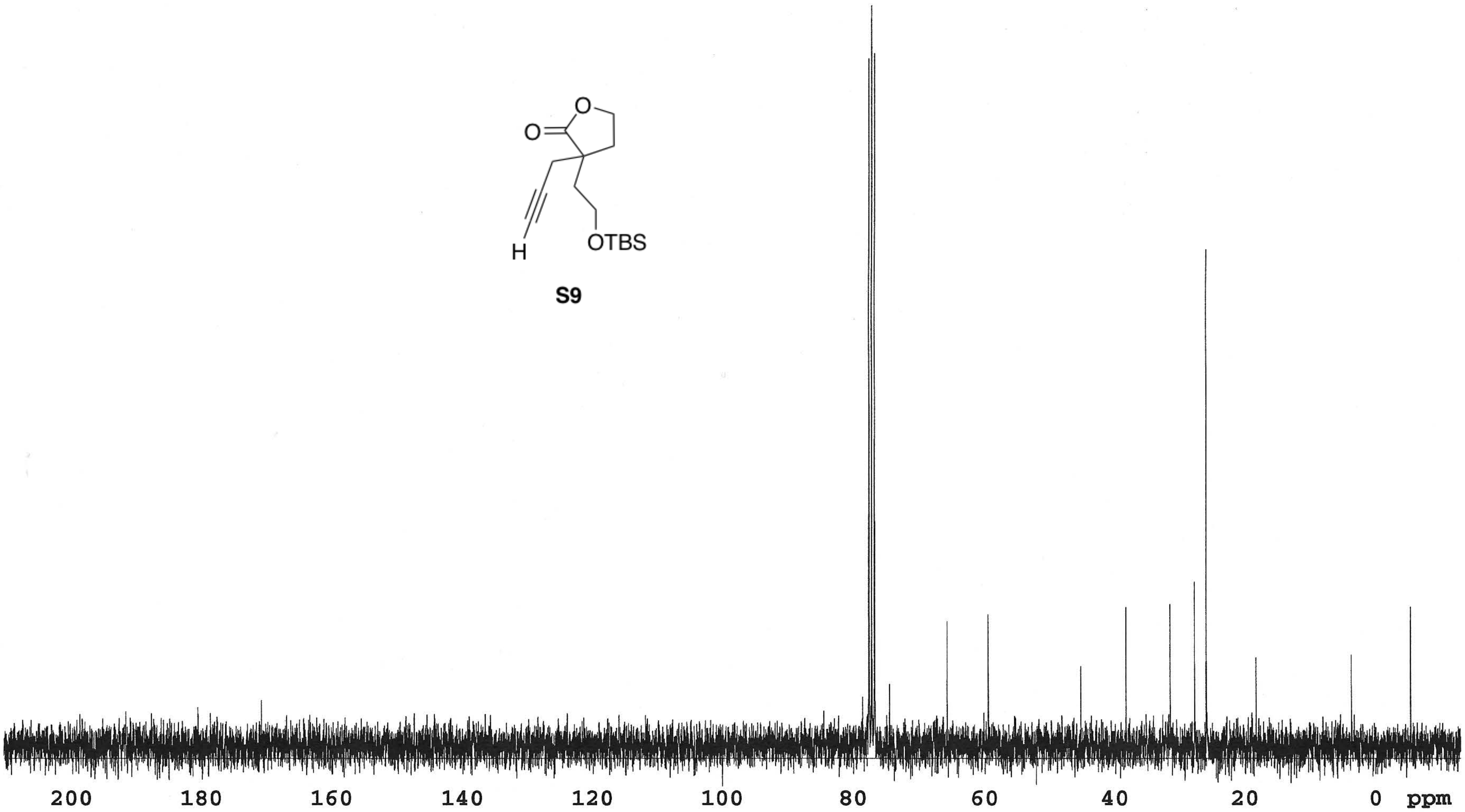
S5



S5



S9



S9