A REMARKABLY USEFUL SULFUR BRIDGE AS SYNTHETIC LEVER IN AN APPROACH TO JAVANICIN B

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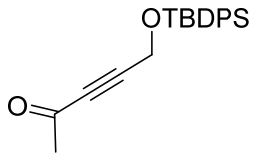
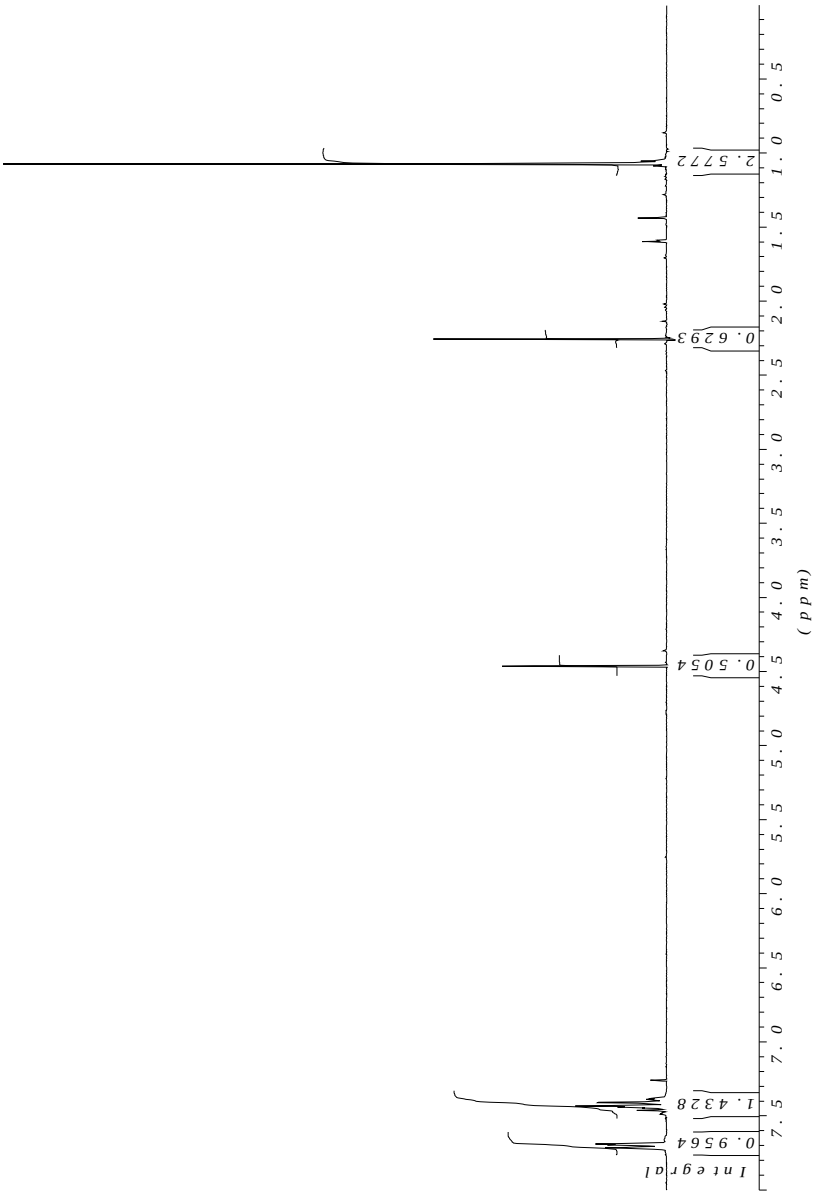
Supporting Information

Contents

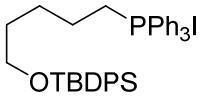
5-((*tert*-butyldiphenylsilyl)oxy)pent-3-yn-2-one (27)



^{1}H NMR



(5-((*tert*-butyldiphenylsilyl)oxy)pentyl)iodotriphenylphosphane (30)



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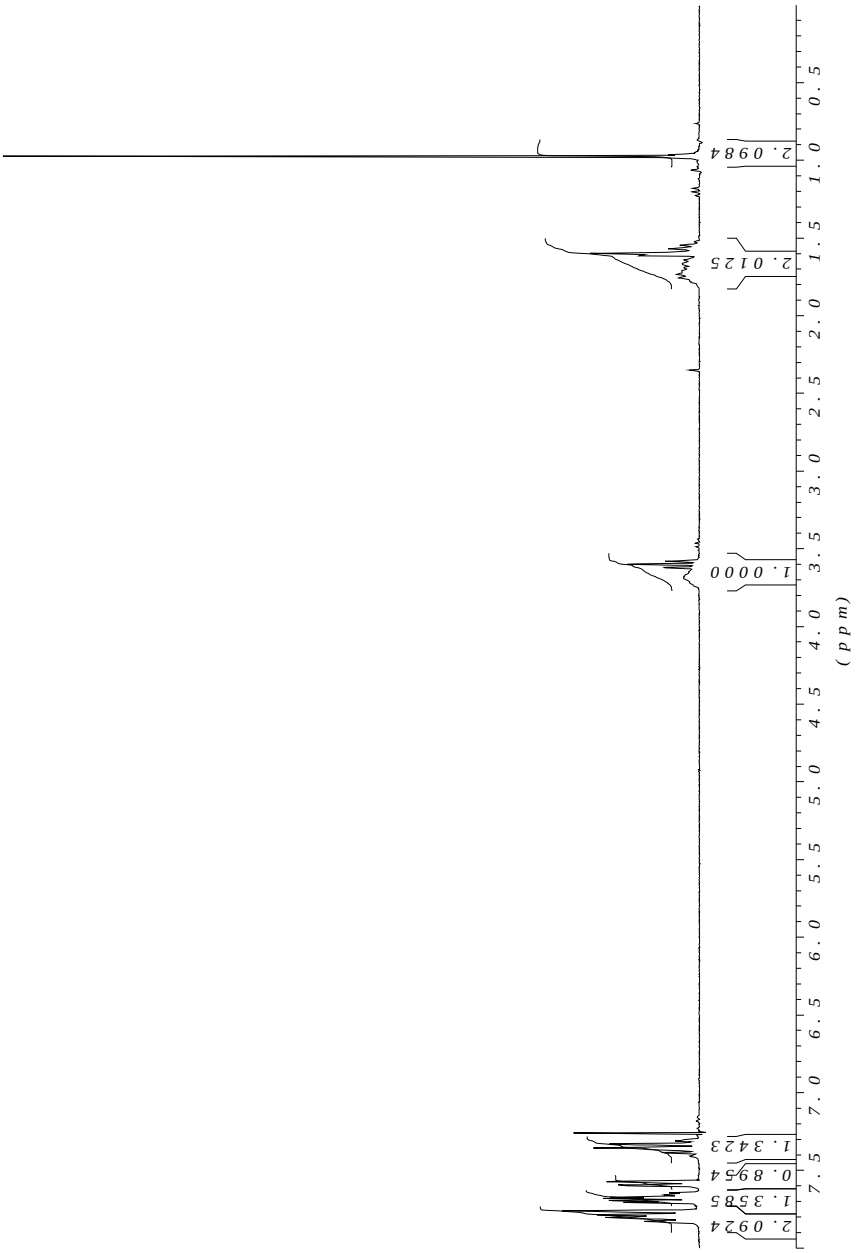
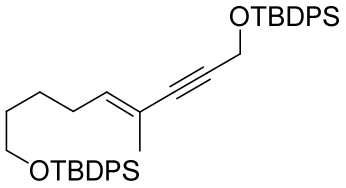


(*E*)-1,9-Bis(-(*tert*-butyldiphenylsilyl)oxy)-4-methylnon-4-en-2-yne (31)



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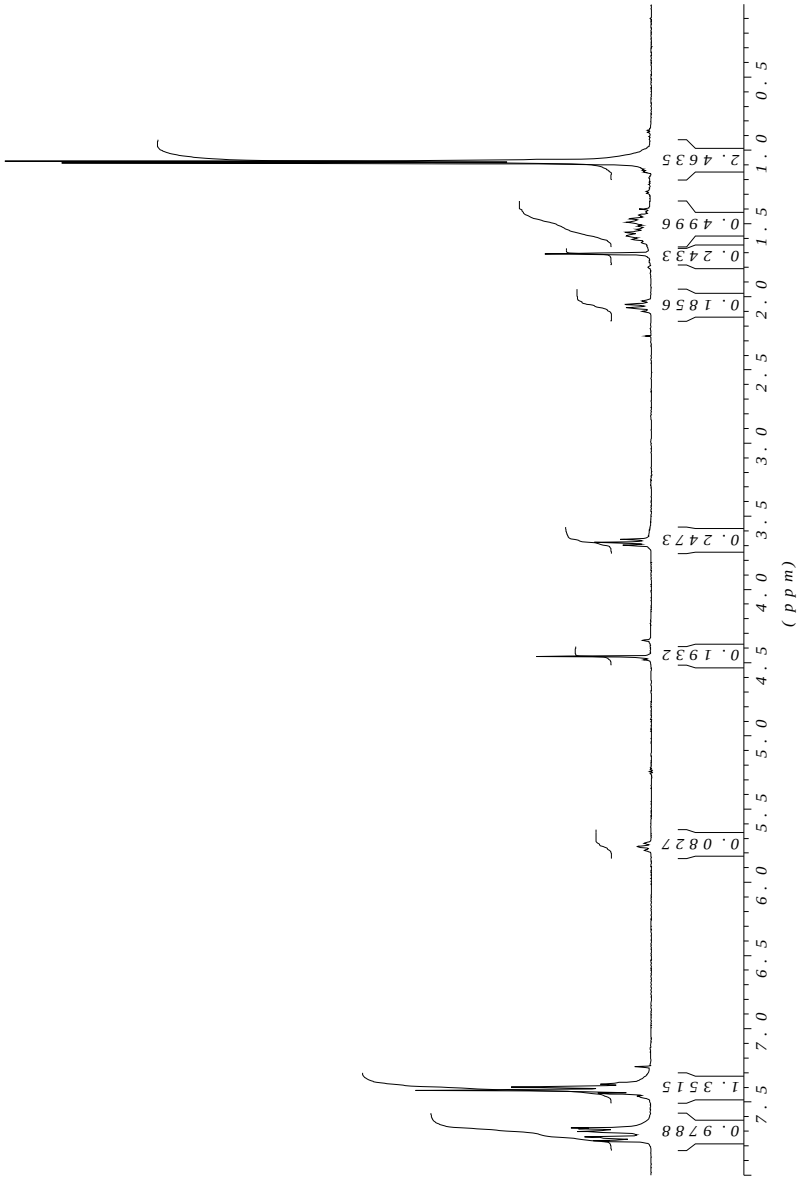
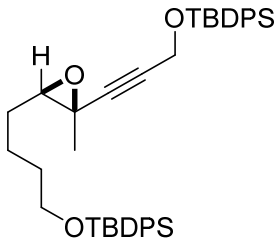


(+)-Epoxide 32



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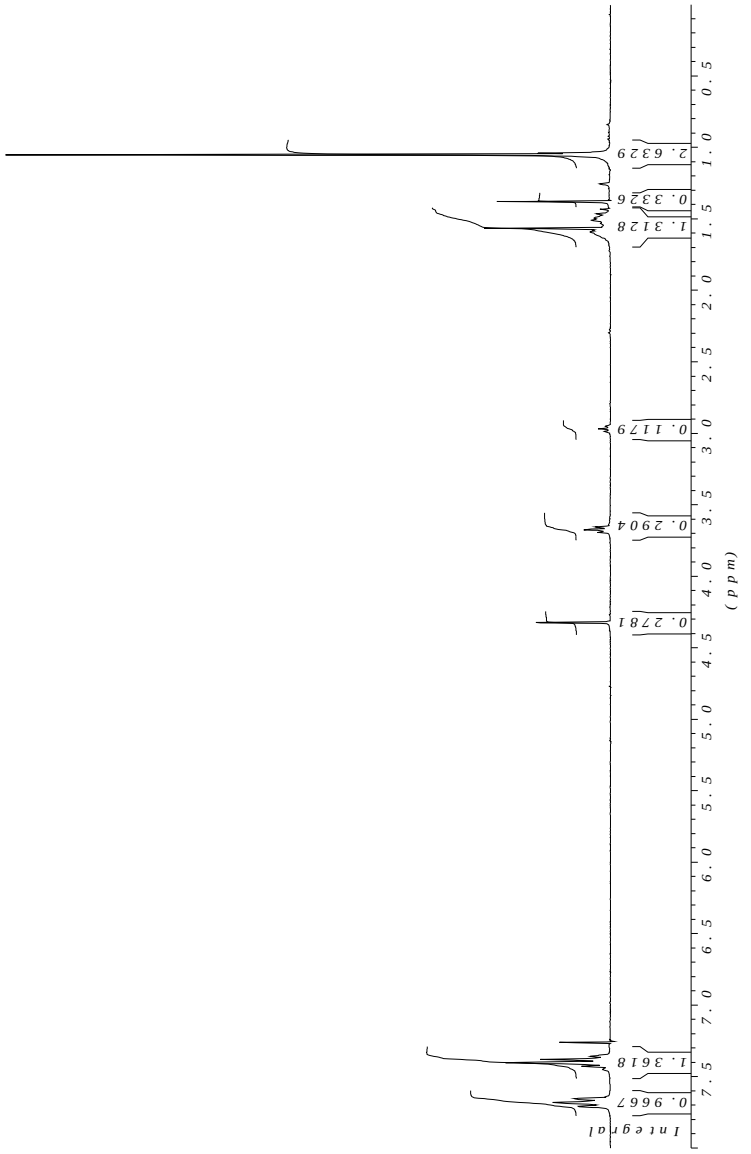

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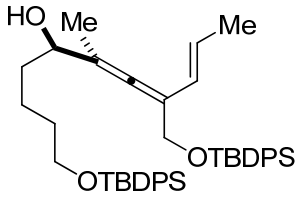

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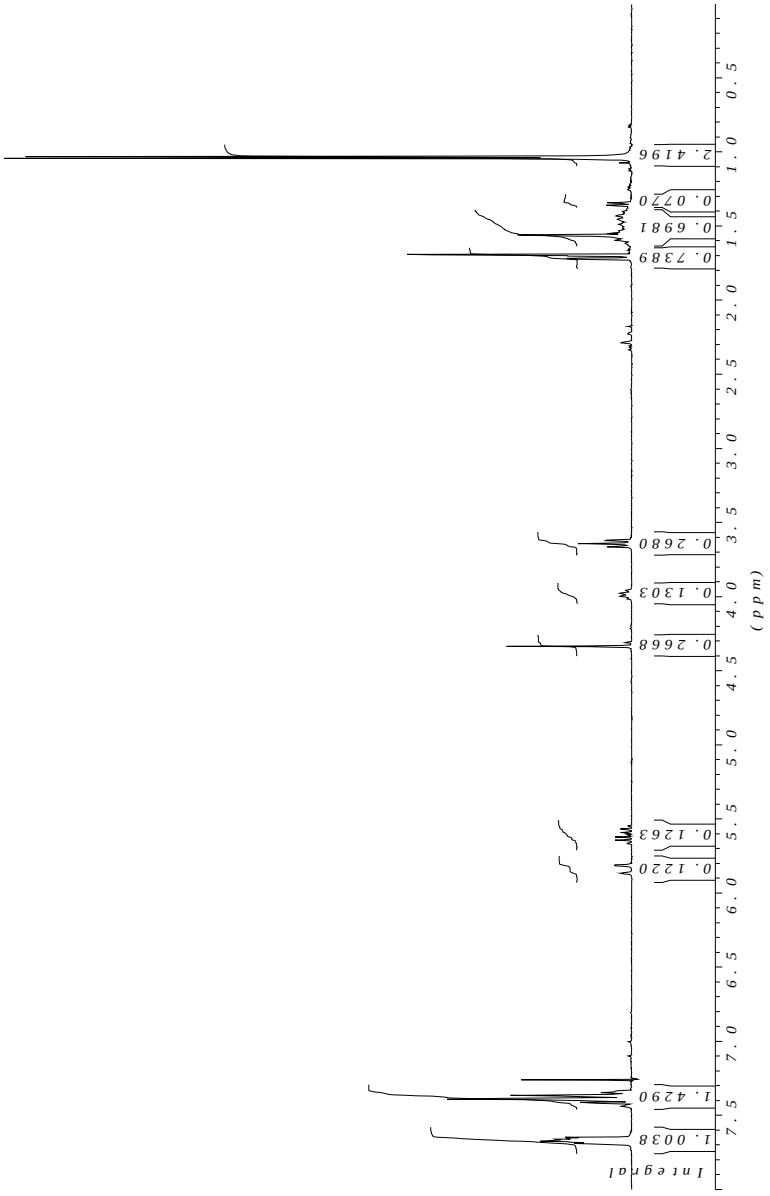

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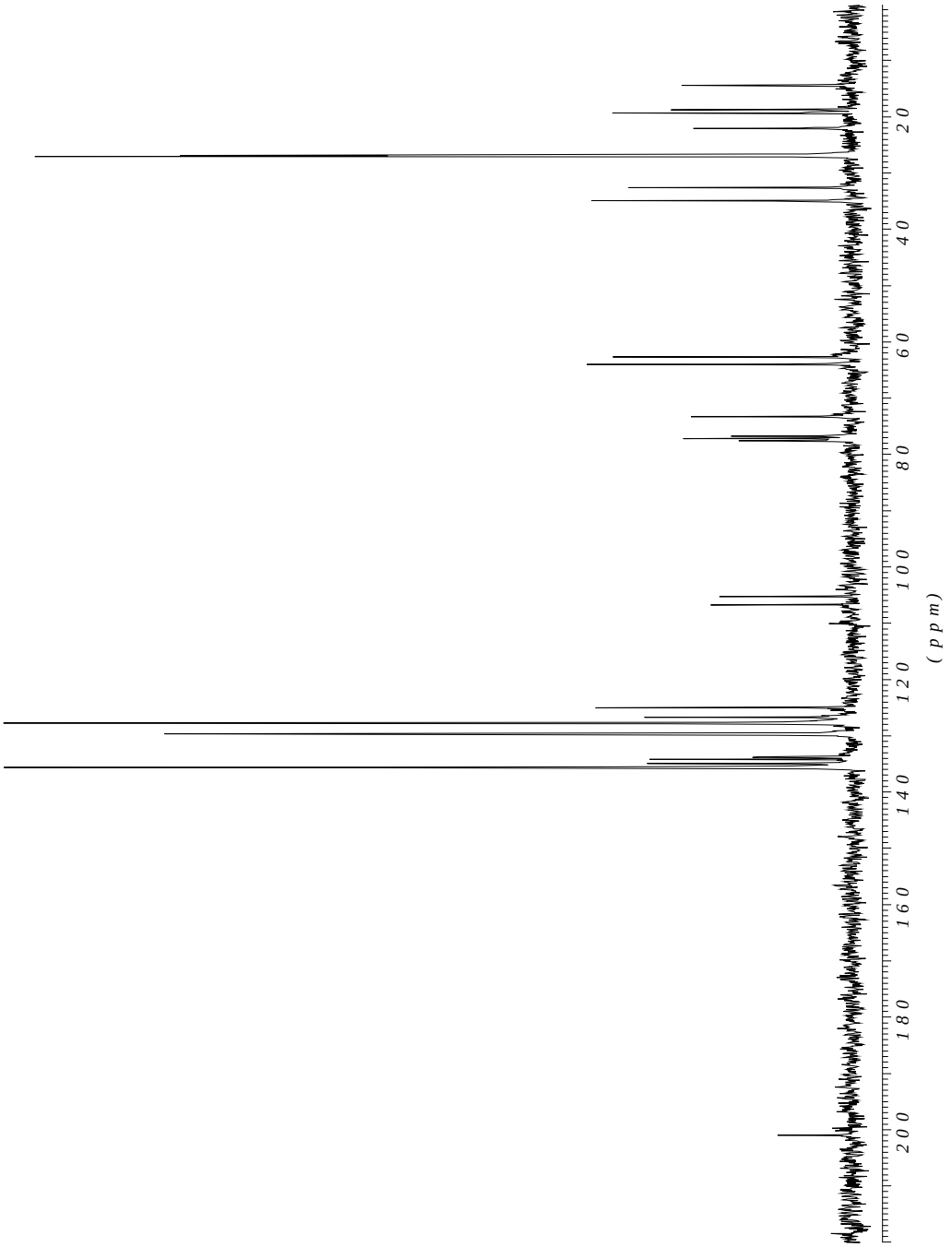
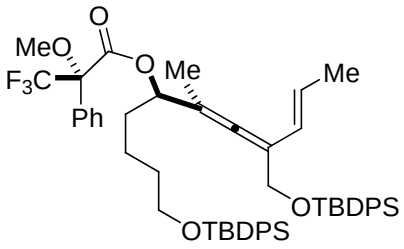


(+)-Mosher Ester 35



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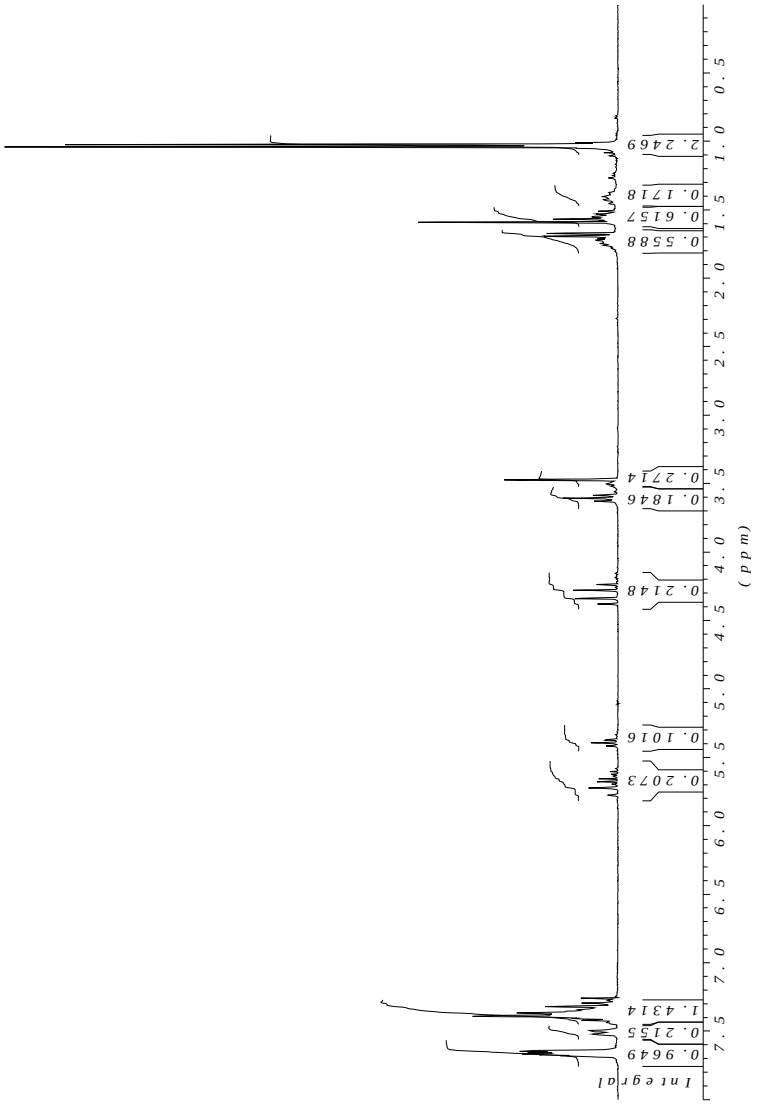

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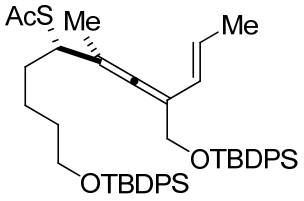

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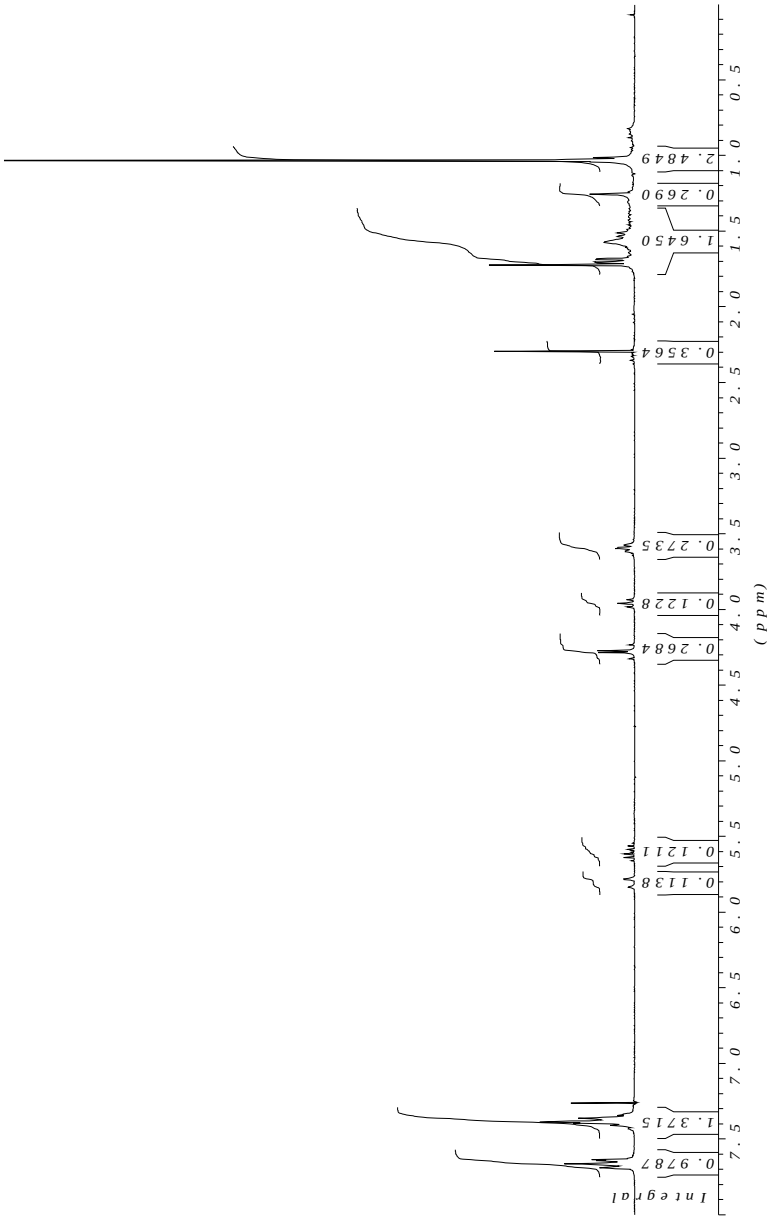

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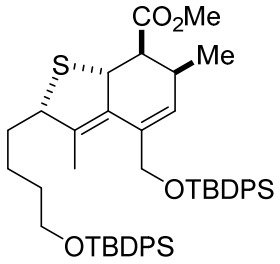

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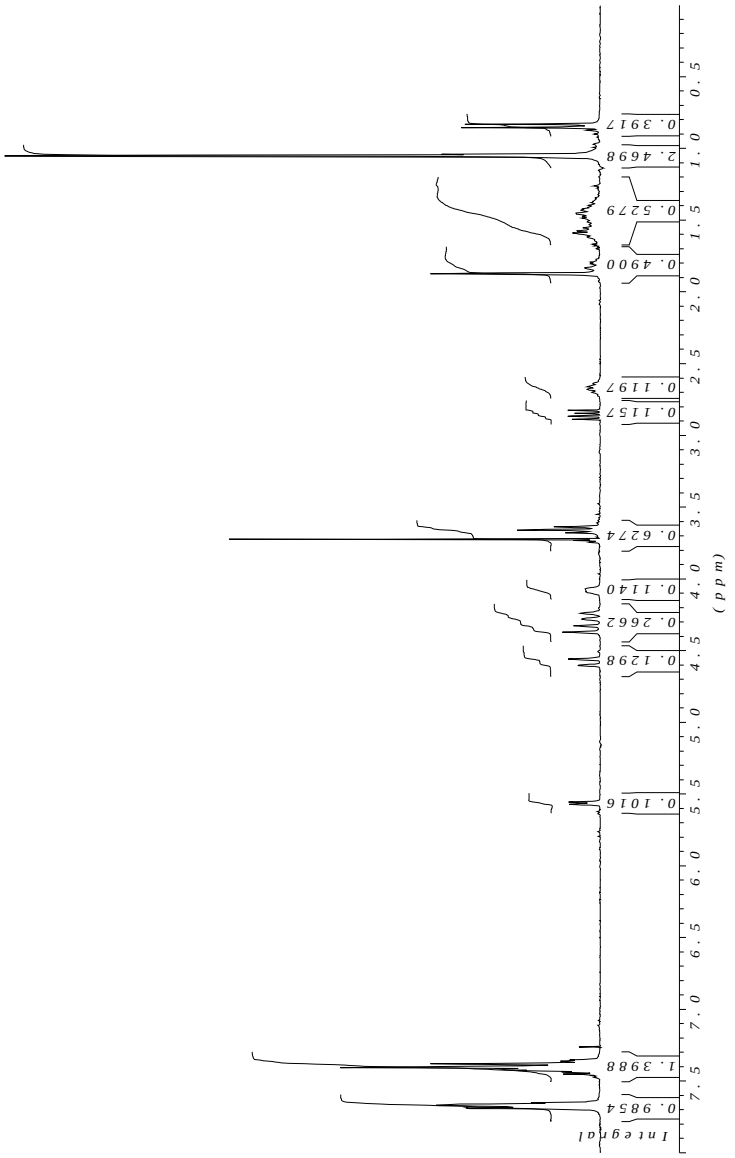

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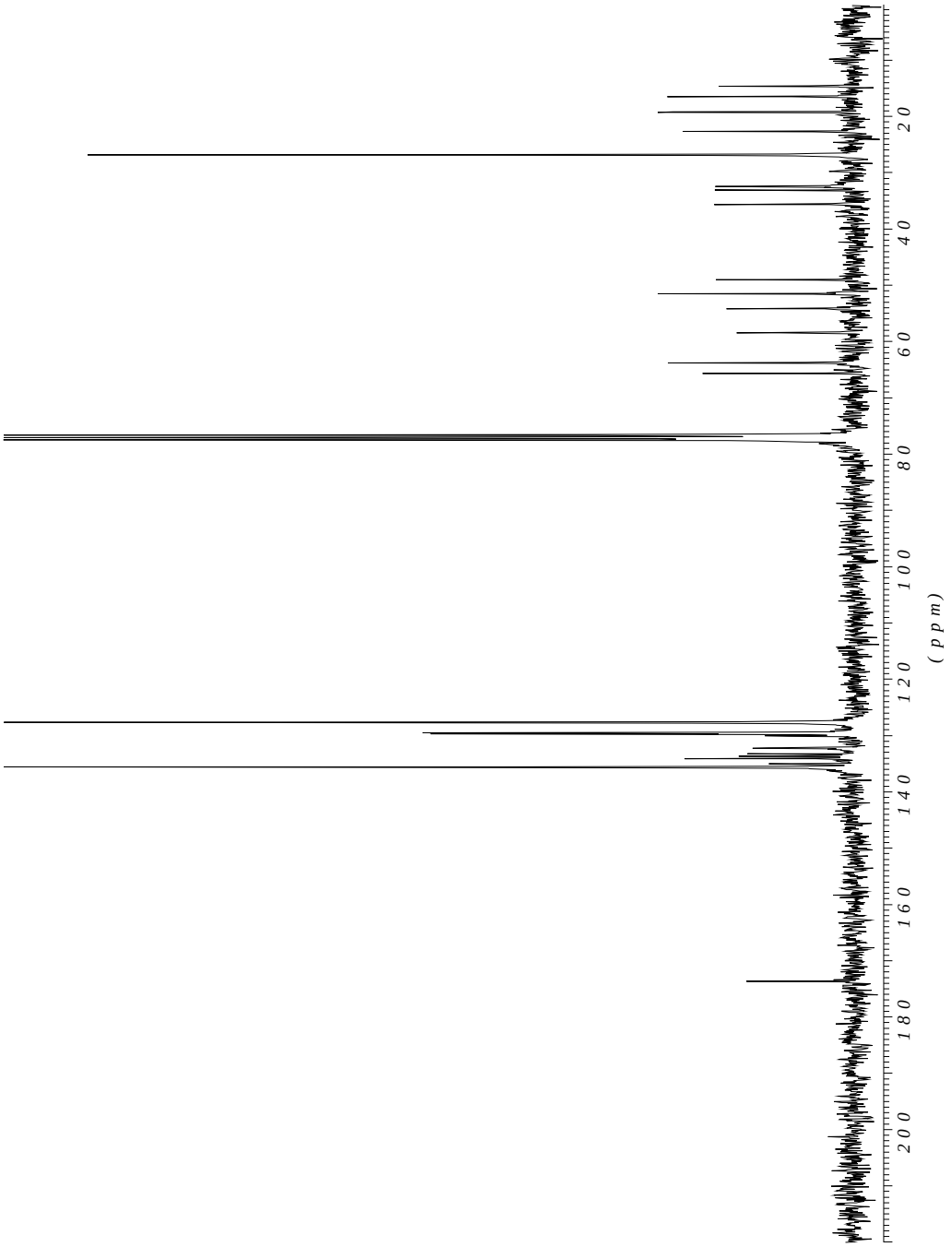
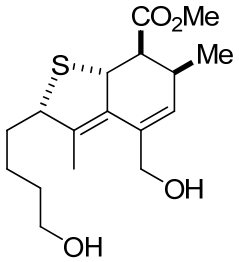


(+)-Diol 57



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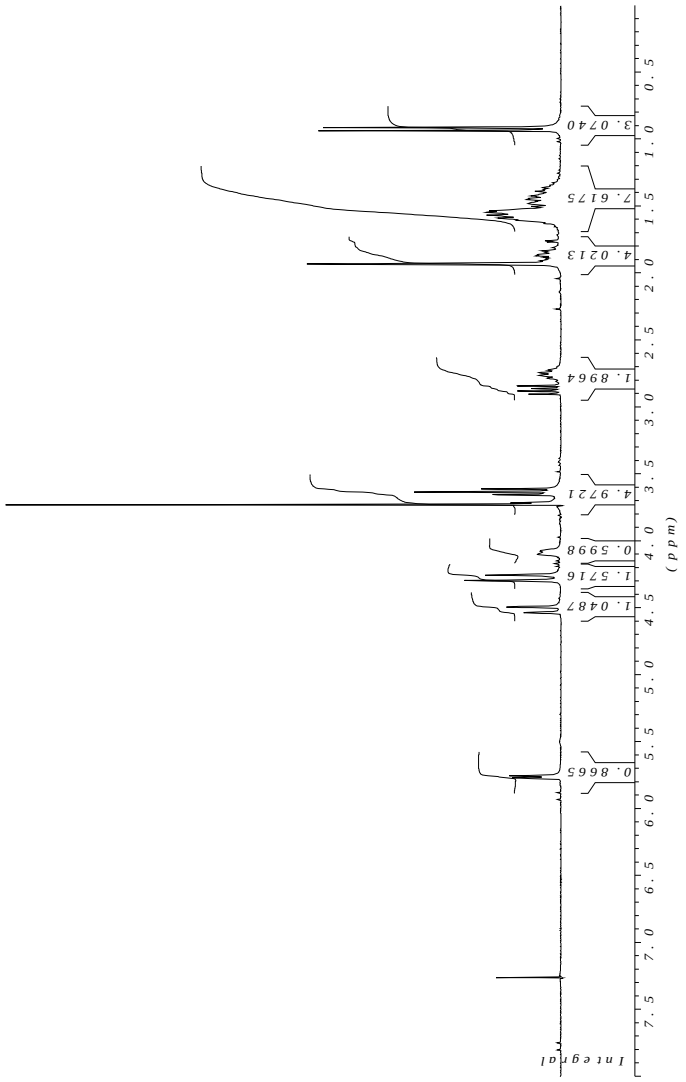

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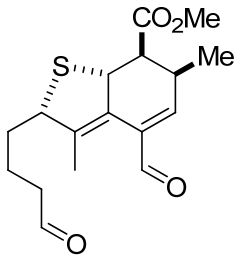

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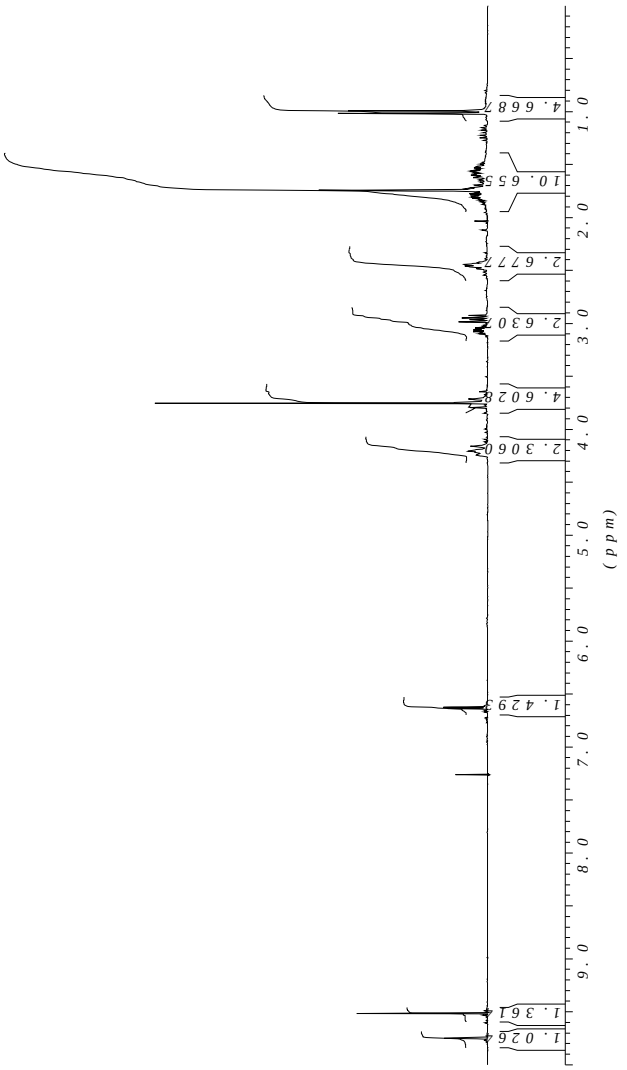

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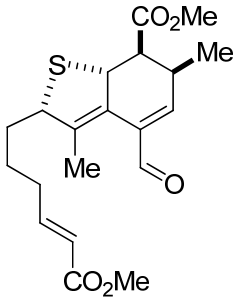

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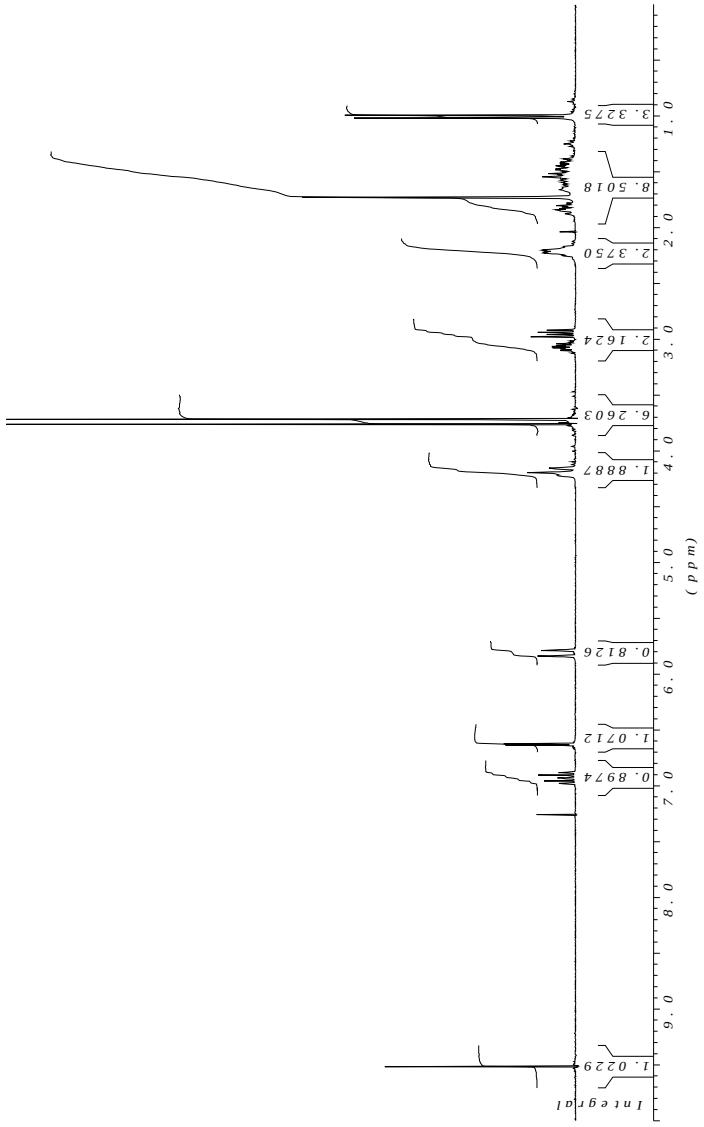
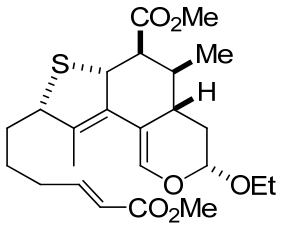


(-) Cycloadduct 40



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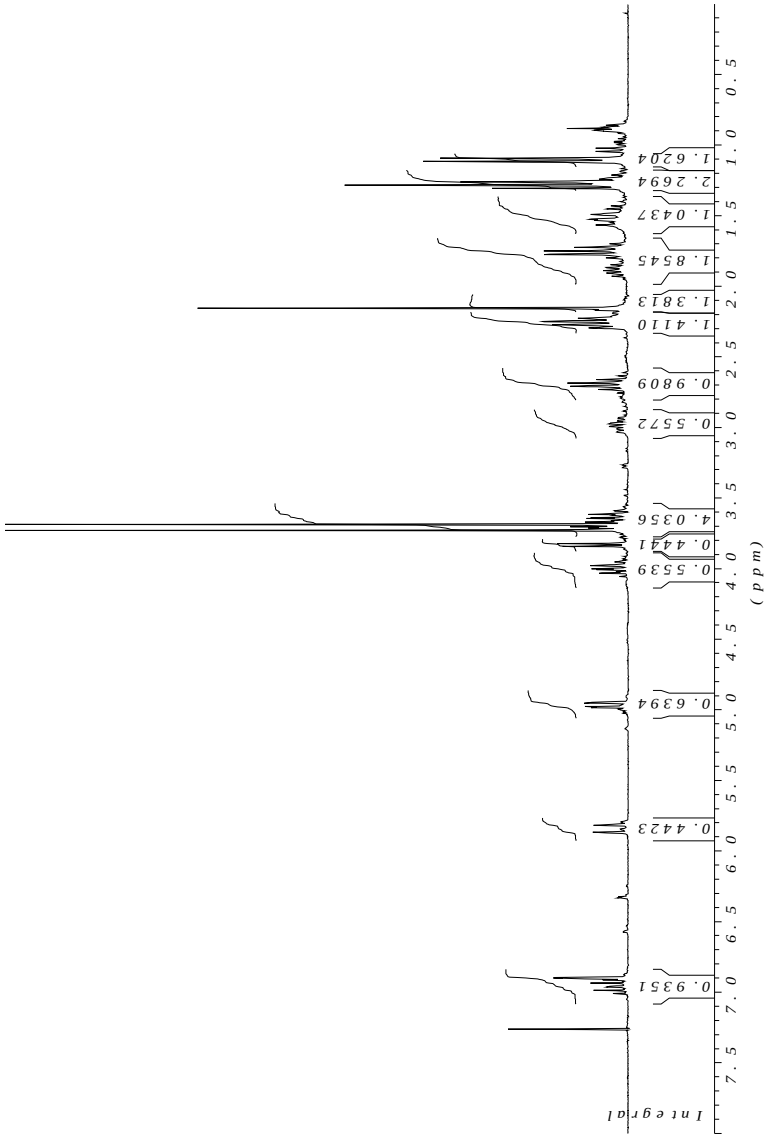

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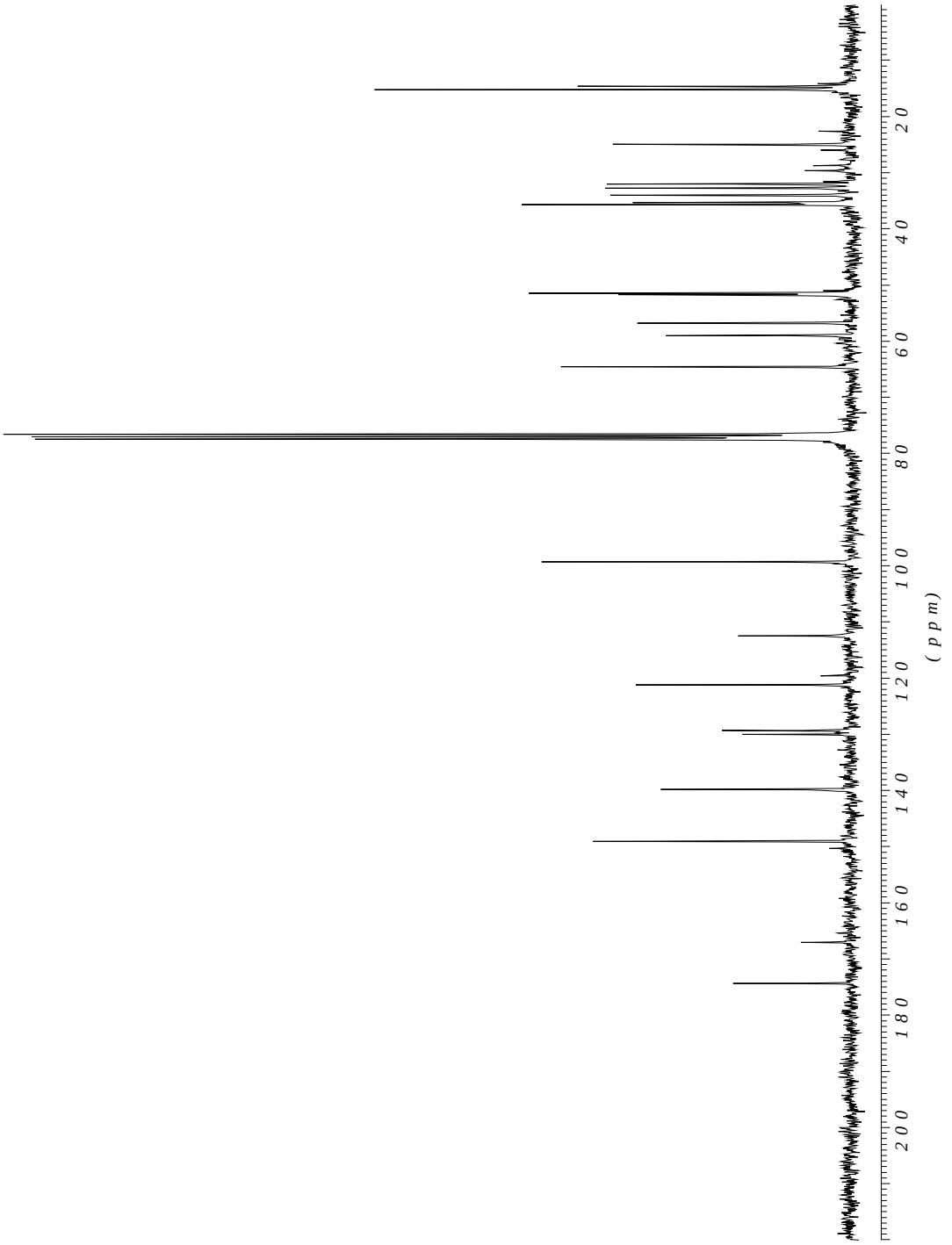
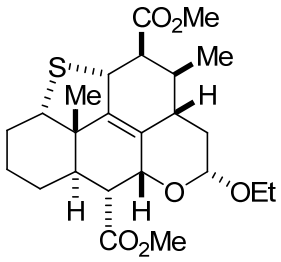


(+) Cycloadduct 41



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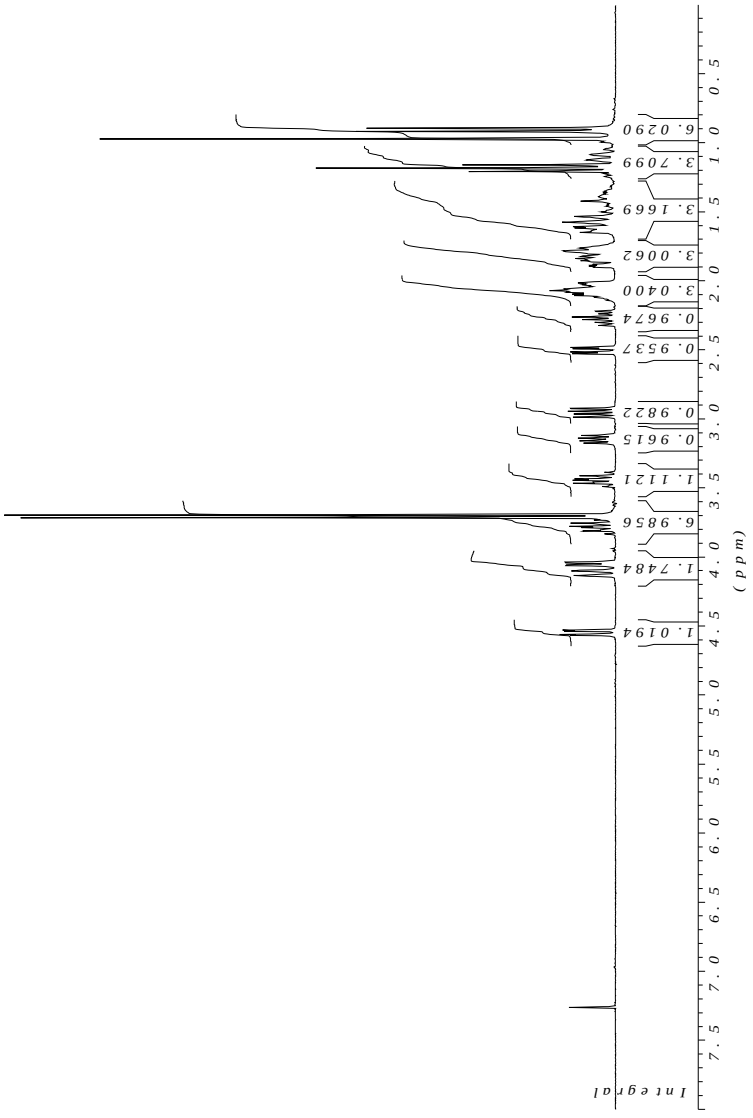

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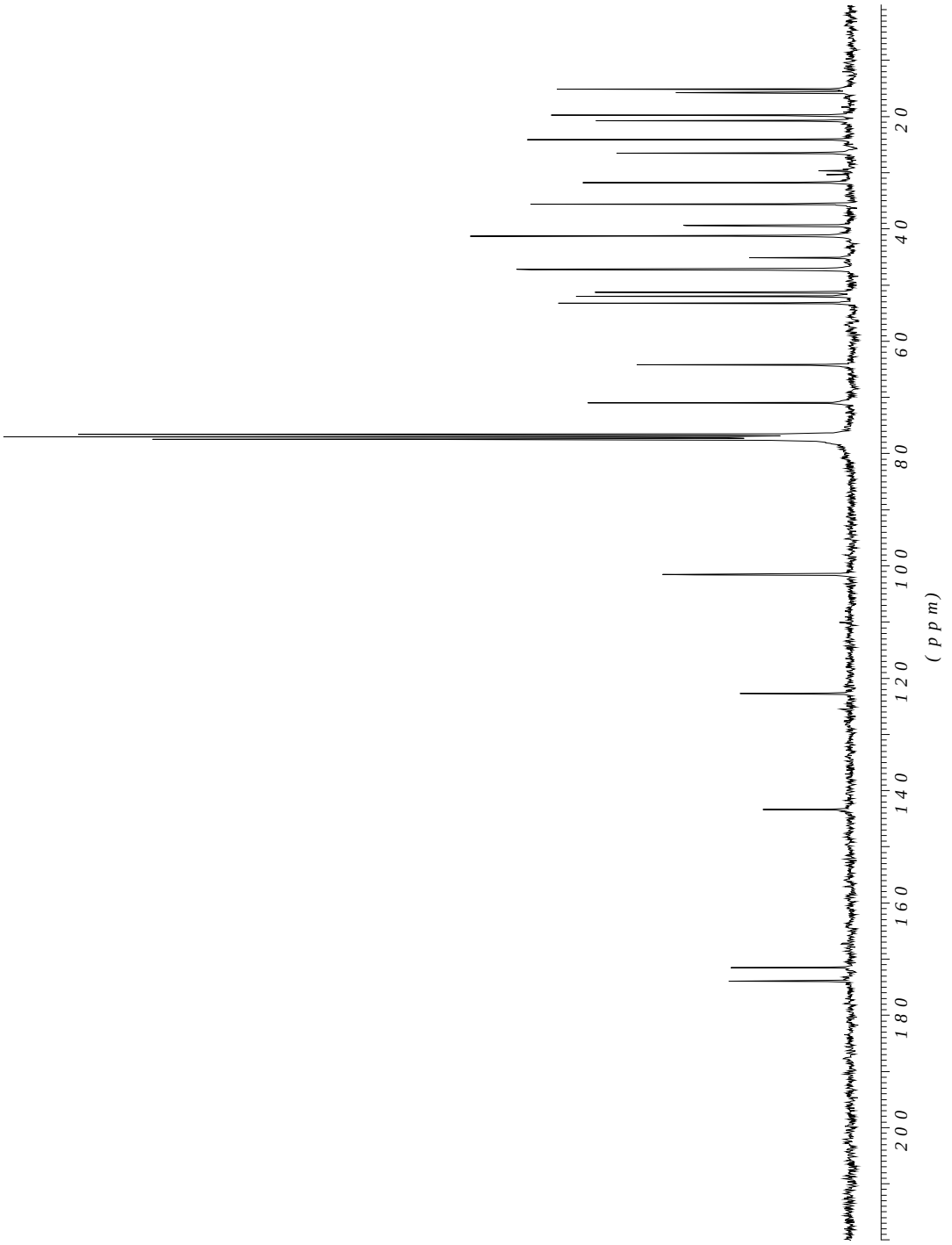
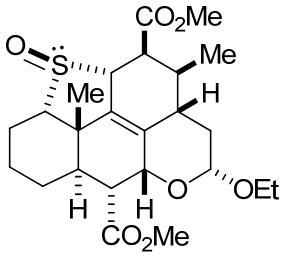


Sulfoxide 43



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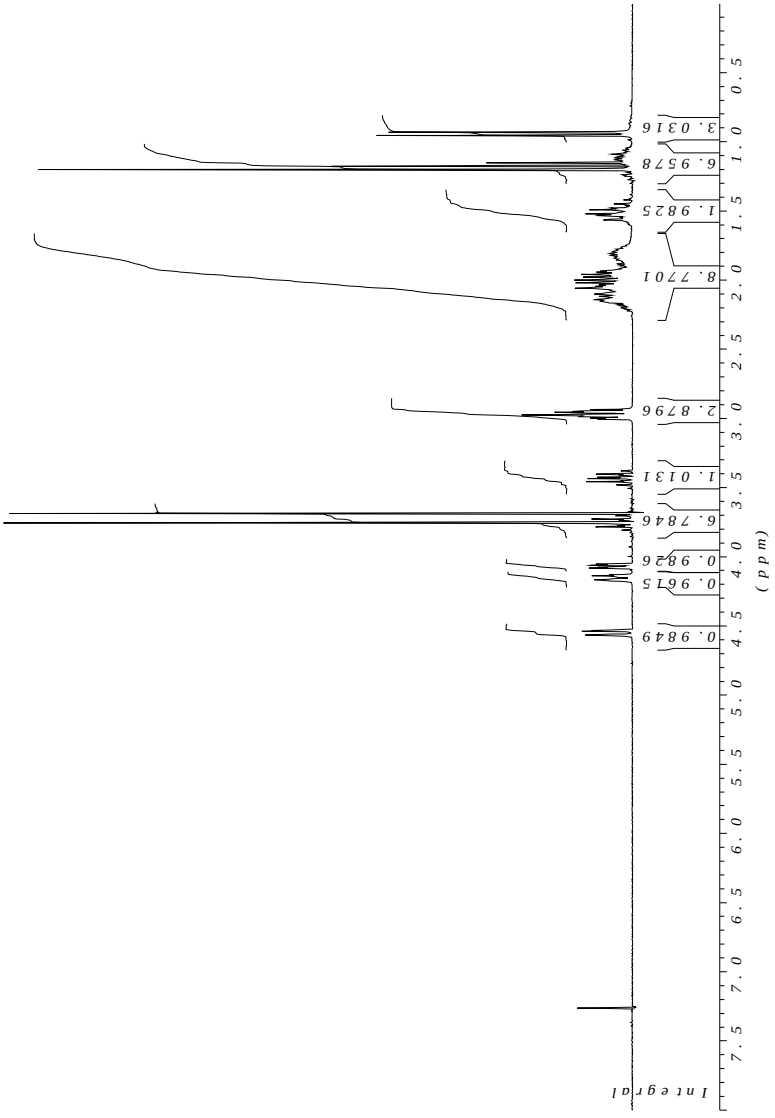
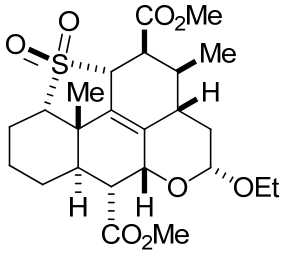


Sulfone 44



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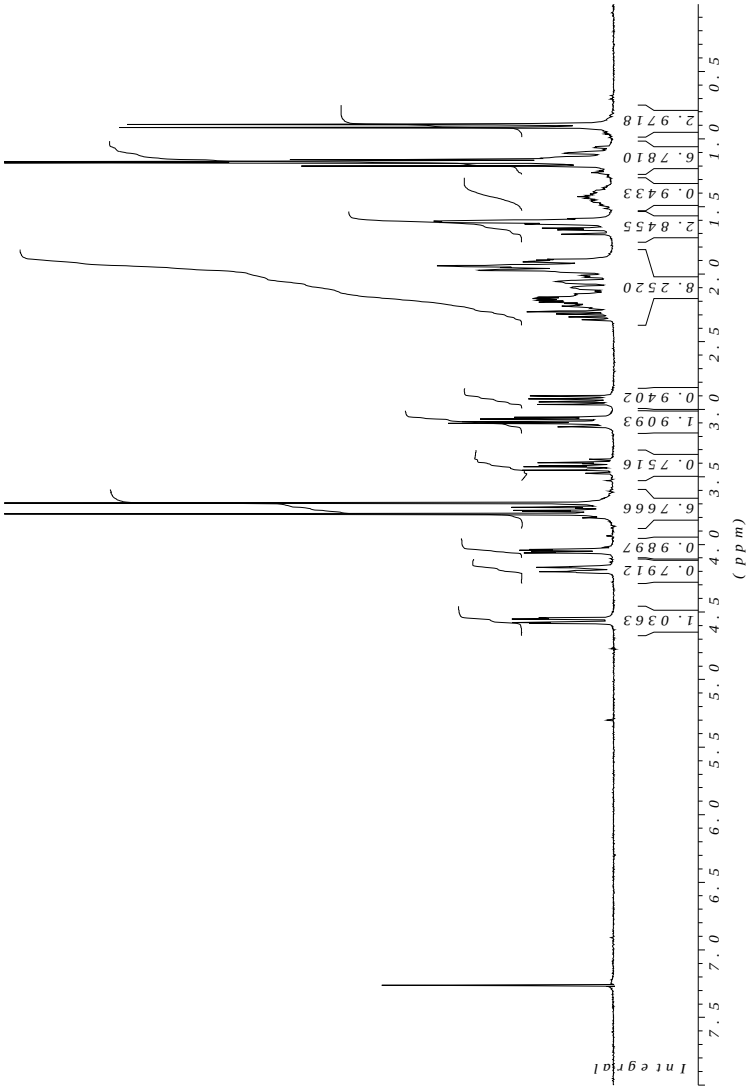
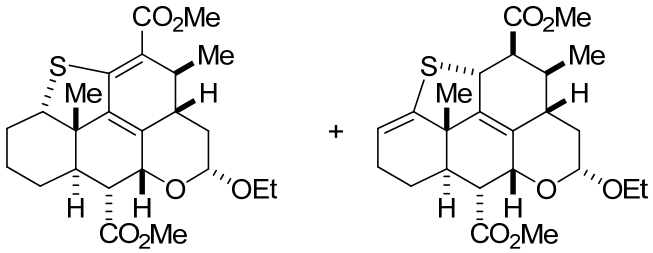


Dienes 45 and 46



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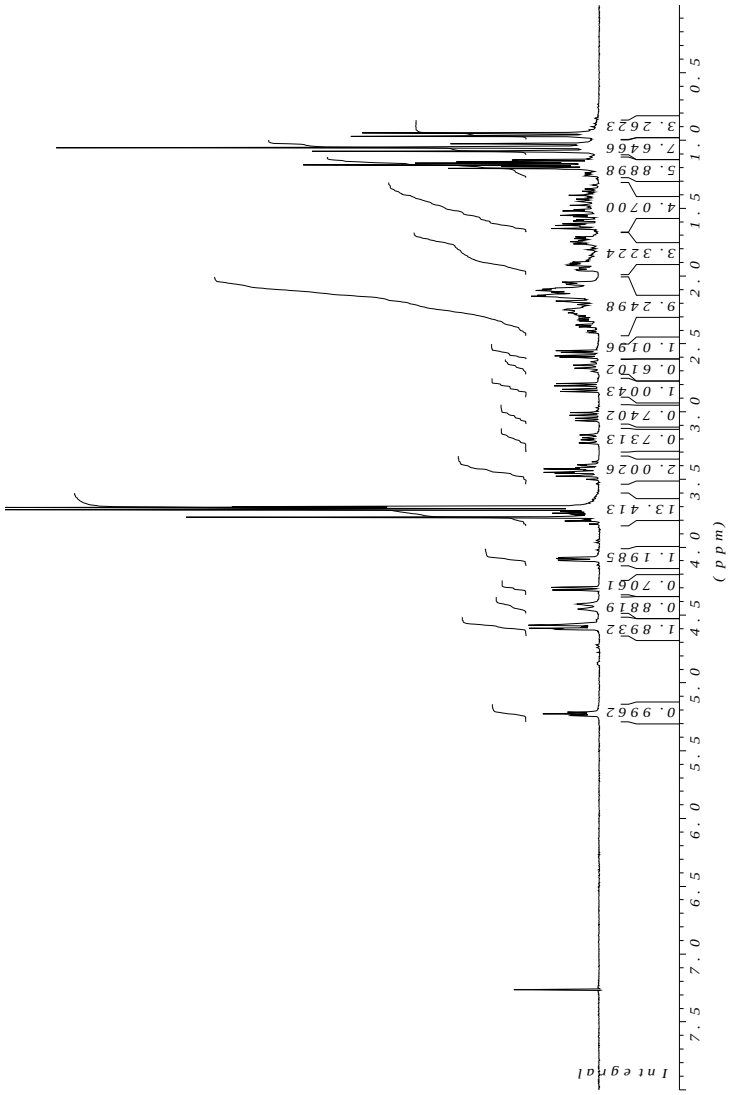
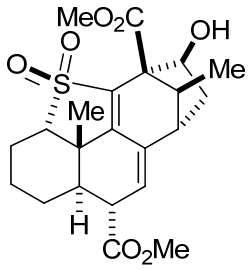


Tetracyclic aldol adduct 47



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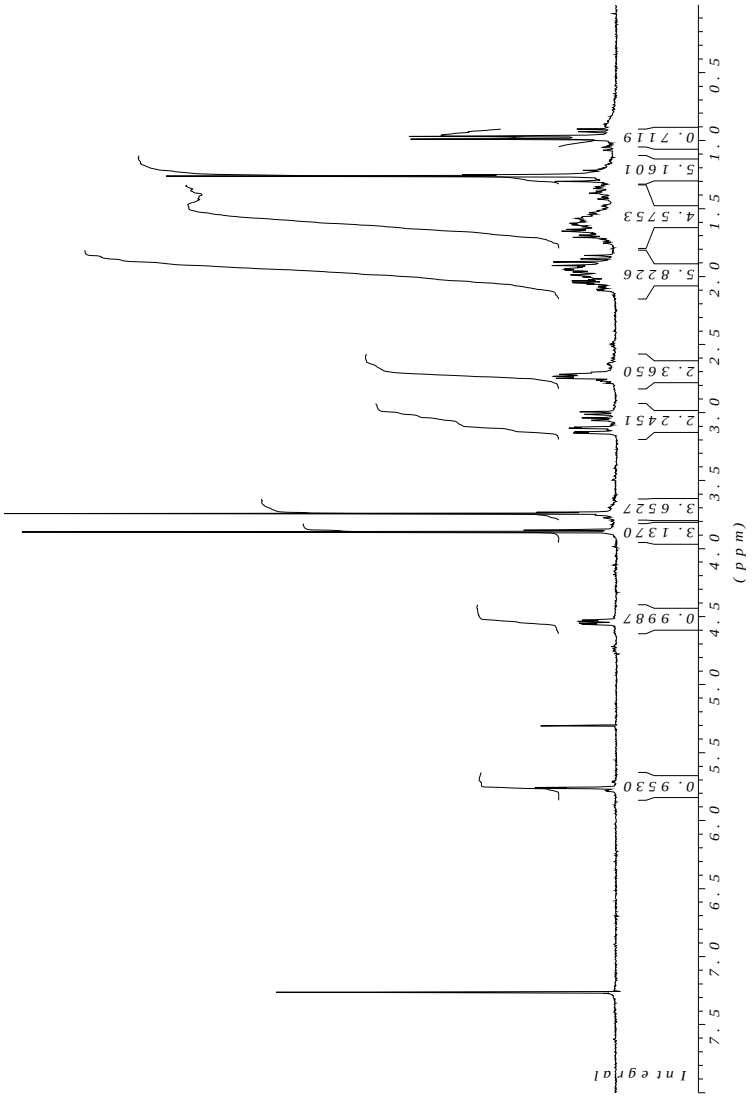
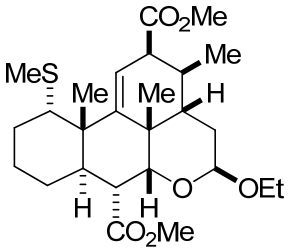


Cuprate adduct 53



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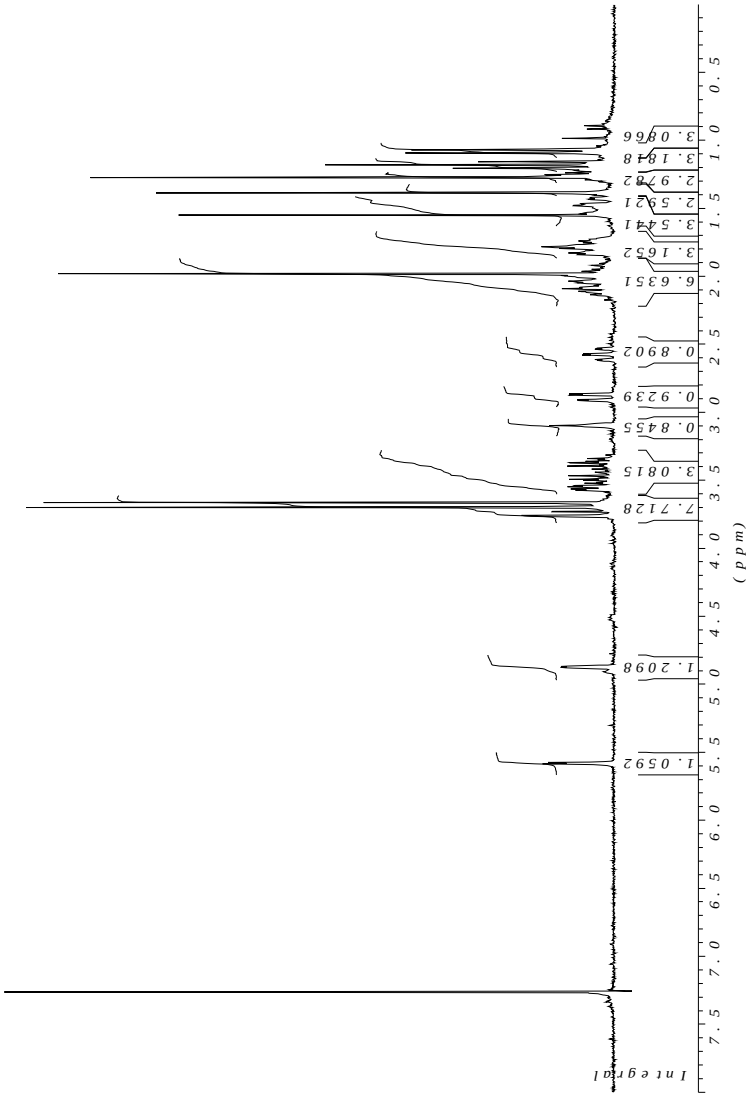

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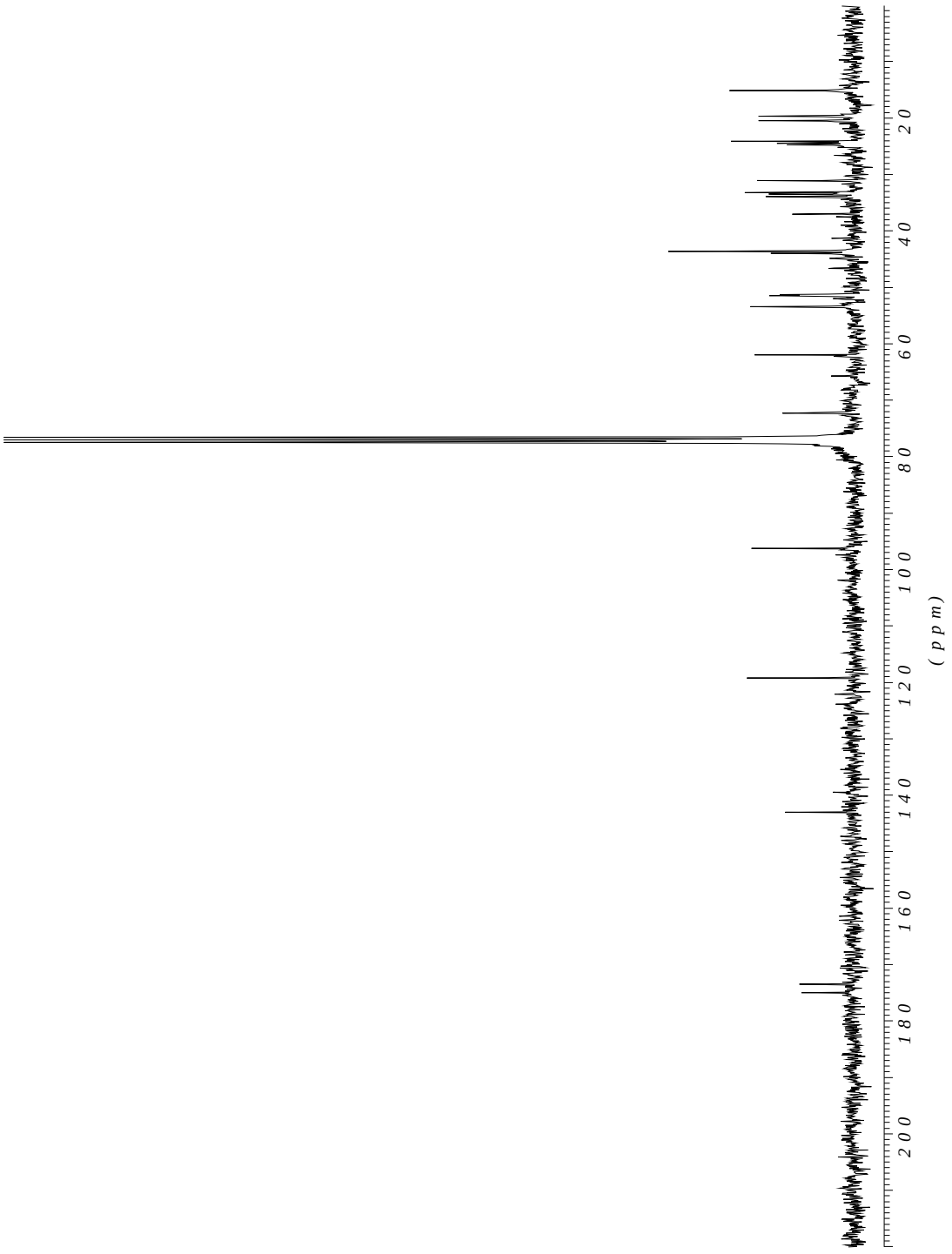
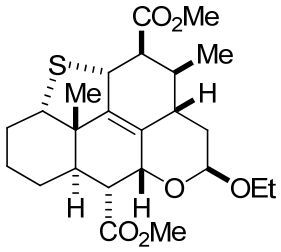


Demethylation product 54



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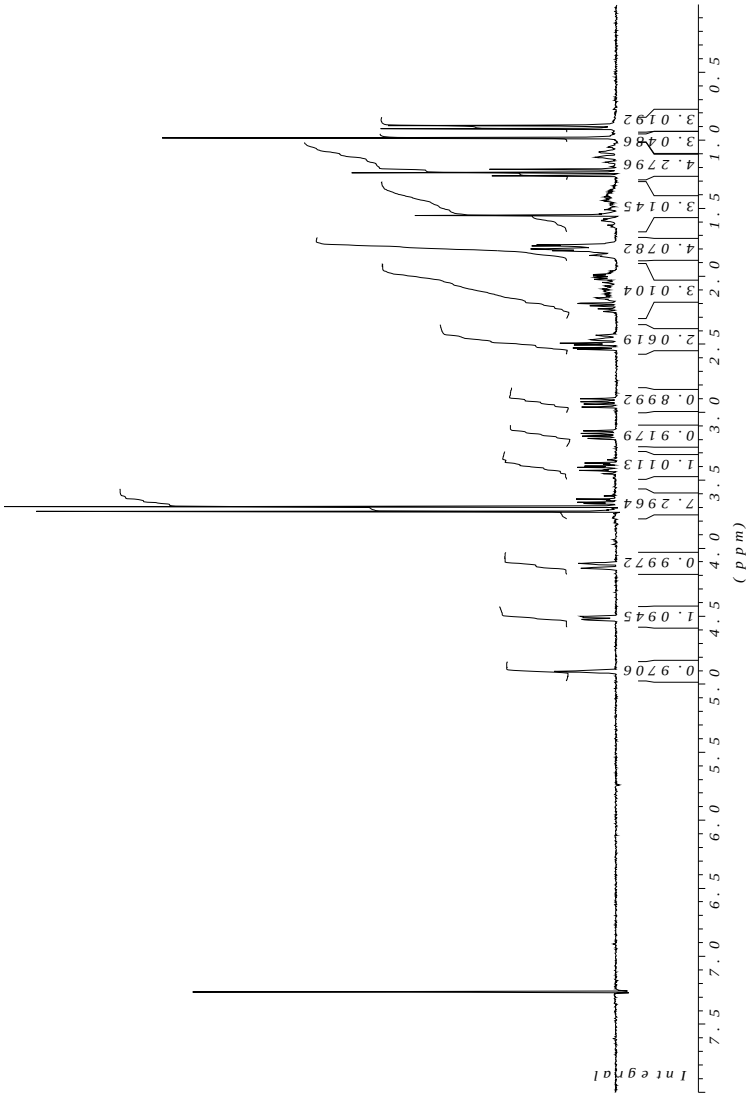
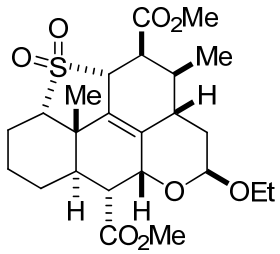


Pentacyclic sulfone 55



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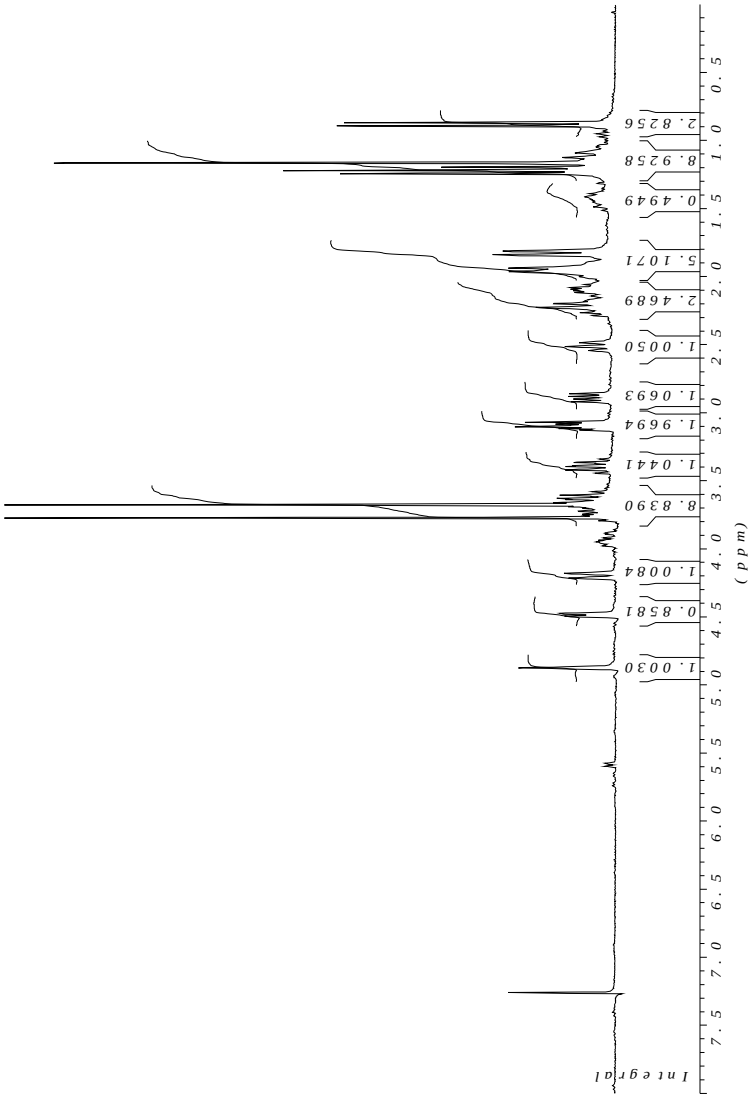
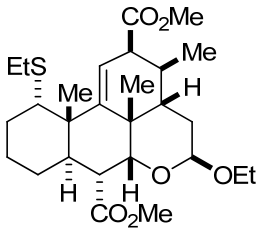


Cuprate adducts (+)-58



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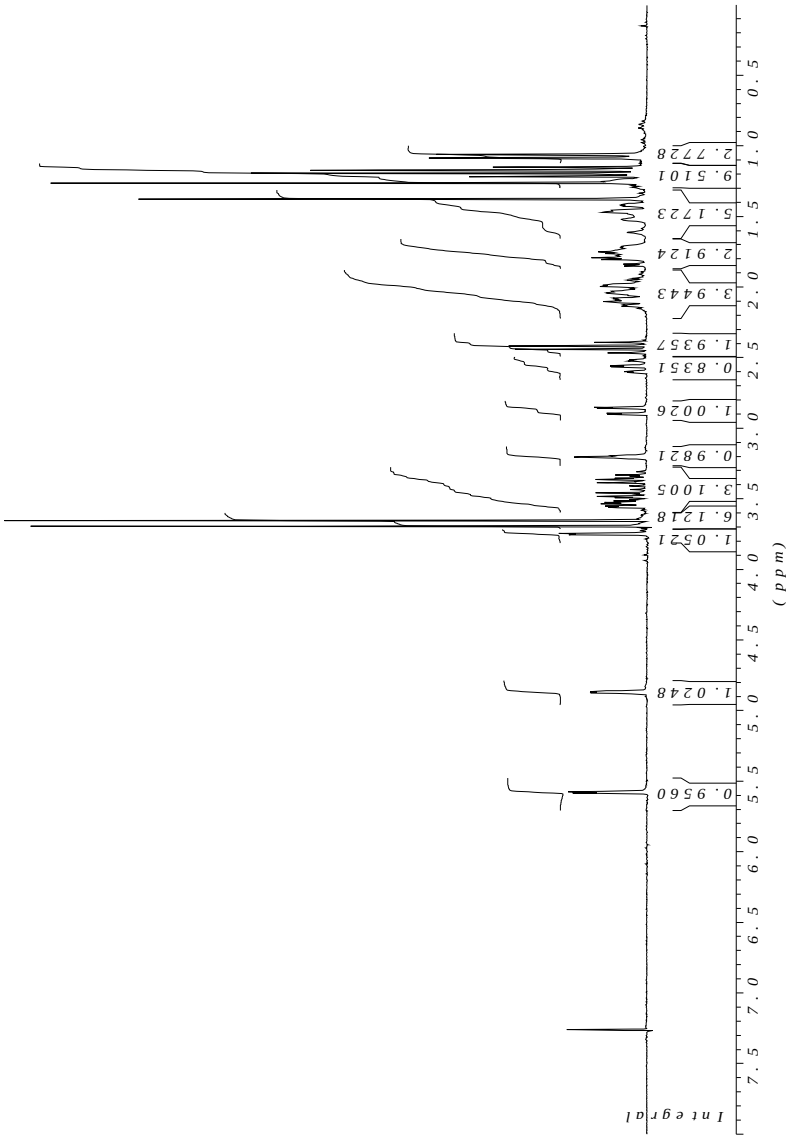

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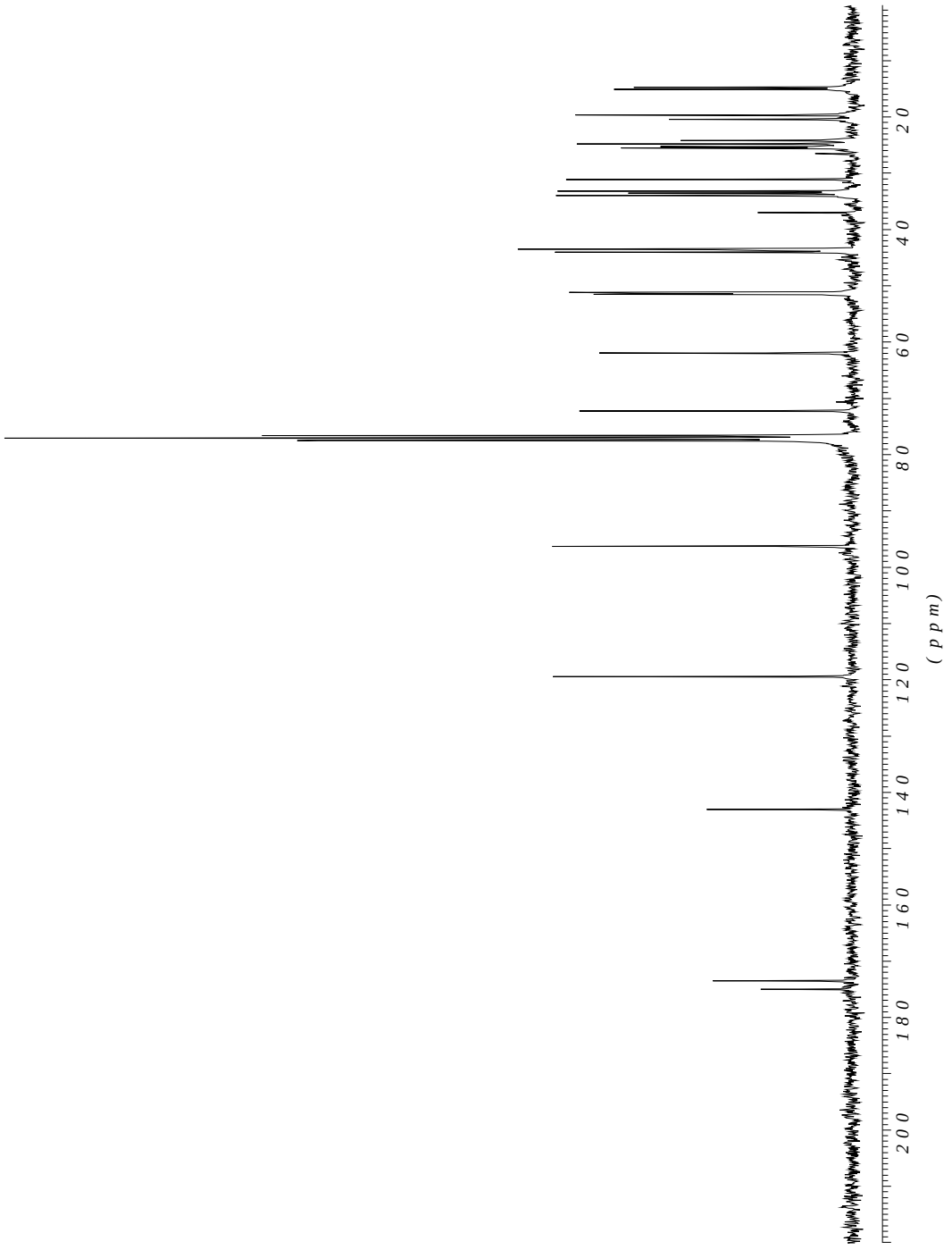
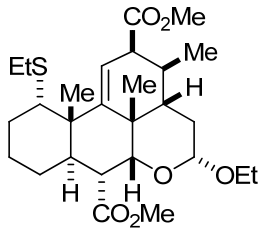


Cuprate adducts (+)-59



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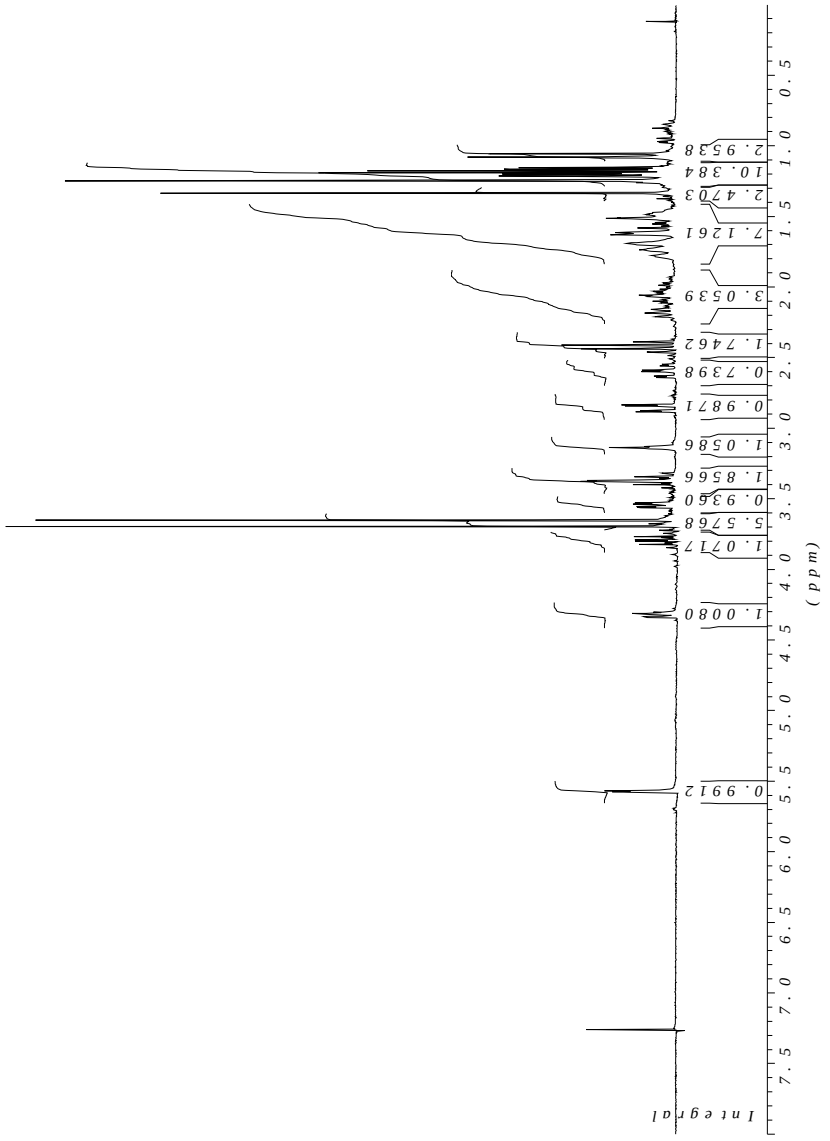
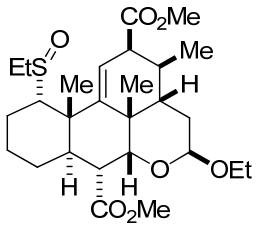


(+)-Sulfoxide 63



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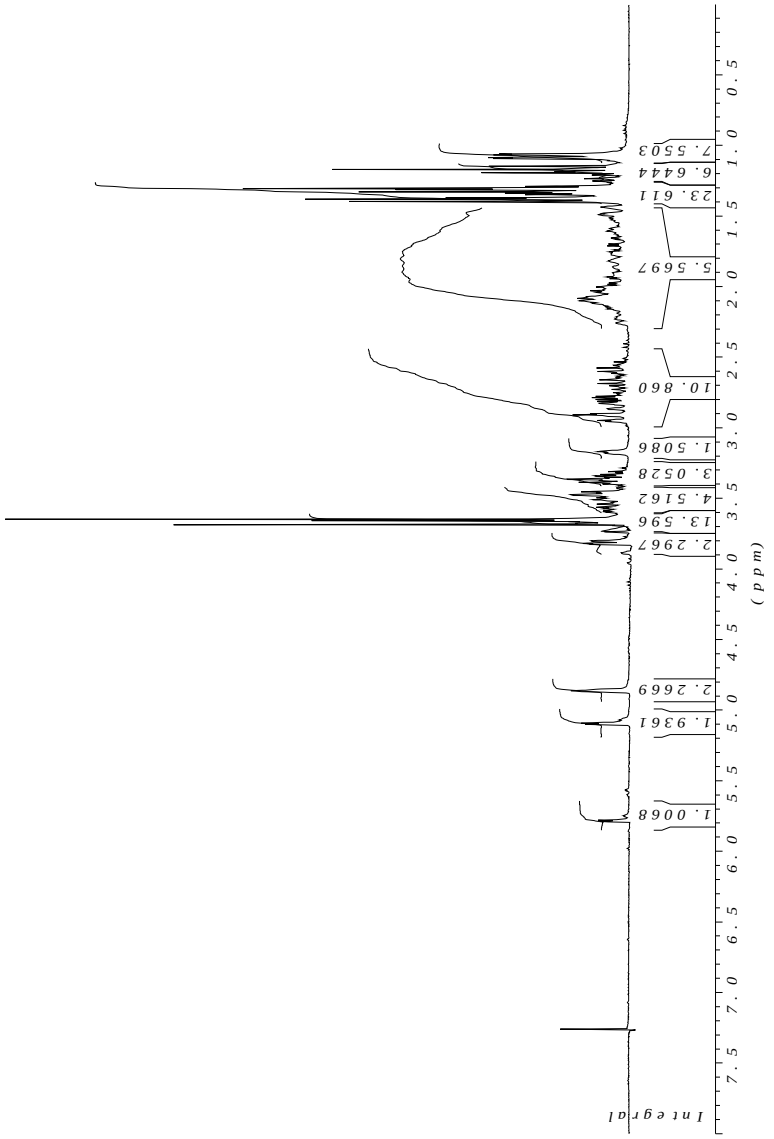
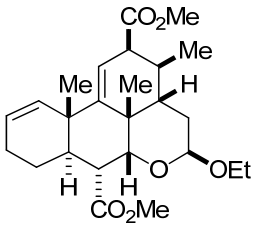


(+)-Diene 60



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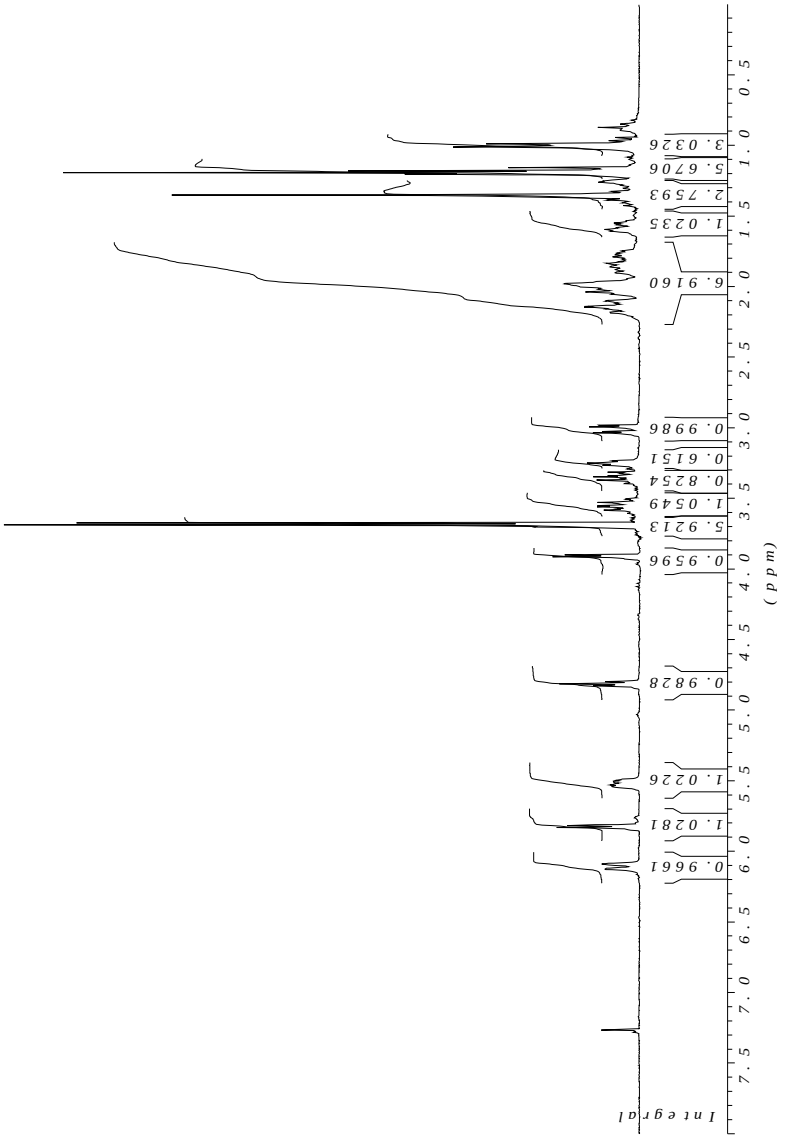
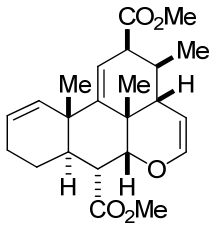


(+)-Triene 64



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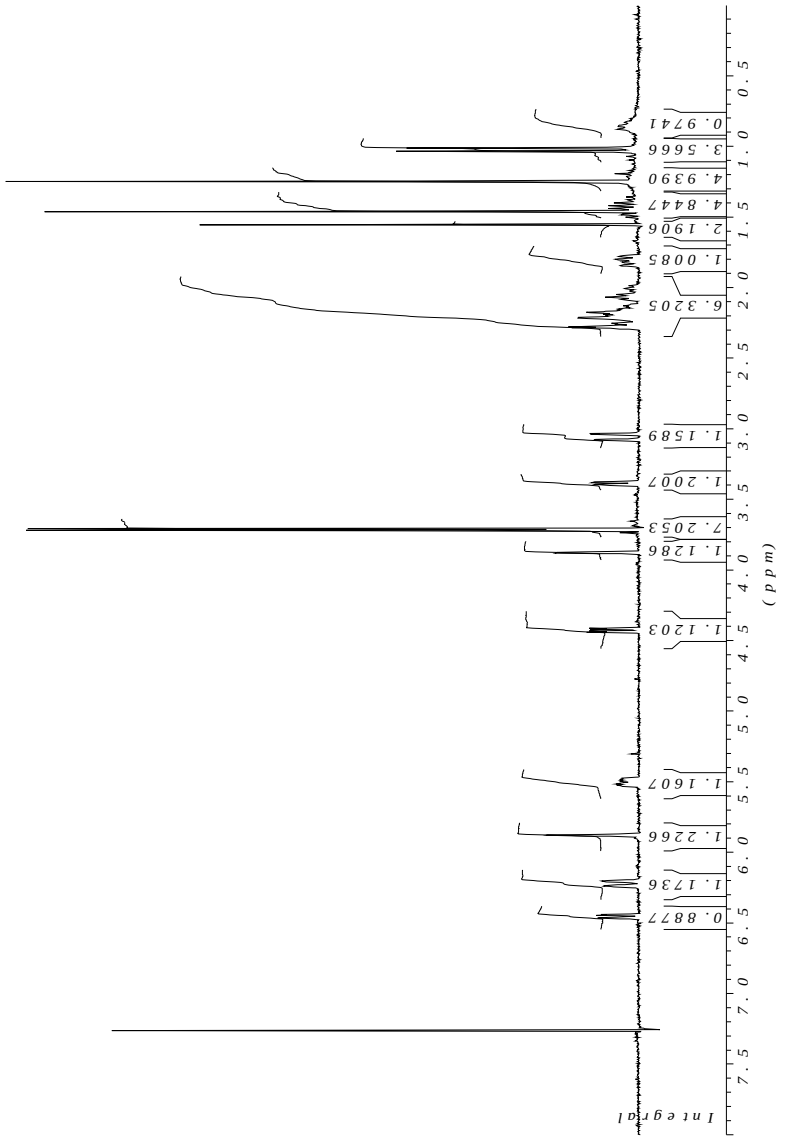
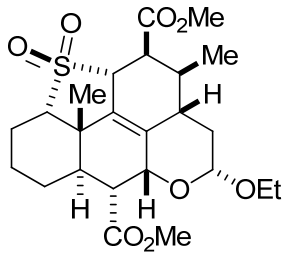


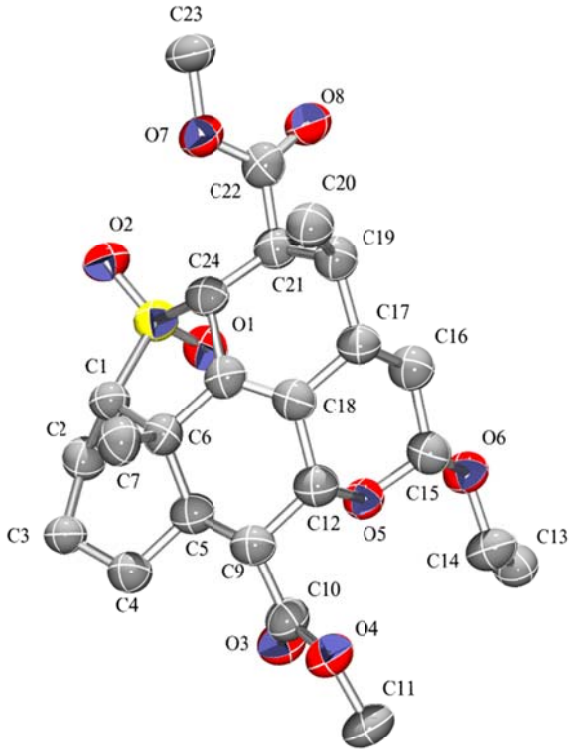
X-Ray crystallographic analyses data and ORTEP

Sulfone 44



The crystals were grown by slow evaporation of an ethyl acetate solution at room temperature**.** One single crystal of 0.4 X 0.3 X 0.3 mm was mounted in Paratone oil using a glass fiber on the goniometer at 183(2) K. Data were collected on an Enraf-Nonius CAD-4 automatic diffractometer at the Université de Sherbrooke using ω scans. The DIFRAC[(1)] program was used for centering, indexing, and data collection. Two standard reflections were measured every 100 reflections, no intensity decay was observed during data collection. The data were corrected for absorption by numerical methods and reduced with the NRCVAX[(2)] programs. They were solved using SHELXS-97[(3)] and refined by full-matrix least squares on F^2 with SHELXL-97[(4)]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at idealized calculated geometric position and refined isotropically using a riding model. The crystal was twinned with a BASF parameter of 0.47(6). For this reason, the final absolute structure[(5)] could not be determined by anomalous dispersion effects.

1) H.D. Flack, E. Blanc and D. Schwarzenbach (1992), *J. Appl. Cryst.*, **25**, 455-459.
2) E.J. Gabe, Y. Le Page, J.-P. Charland, F.L. Lee, and P.S. White, (1989) *J. Appl. Cryst*., **22**, 384-387.
3) G. M. Sheldrick, SHELXS-97, G.M. Sheldrick, University of Göttingen, Germany, 1997, Release 97-2.
4) G. M. Sheldrick, SHELXL-97, G.M. Sheldrick, University of Göttingen, Germany, 1997, Release 97-2.
(5) Flack H D (1983), *Acta Cryst.* A39, 876-881.

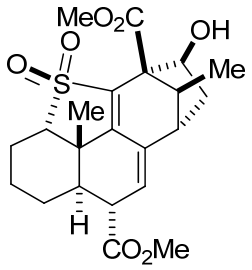


Ellipsoid probability set at 50%

Table 1. Crystal data and structure refinement for ad451a.

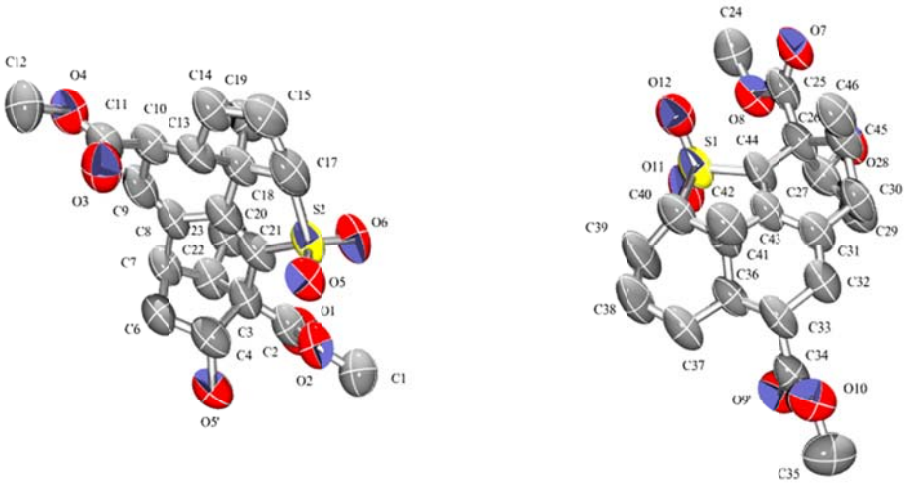
Identification code	ad451a	
Empirical formula	$C_{24}H_{34}O_8S$	
Formula weight	482.59	
Temperature	183(2) K	
Wavelength	1.54176 Å	
Crystal system	Orthorhombic	
Space group	P212121	
Unit cell dimensions	a = 7.848(6) Å	α= 90°.
	b = 15.969(5) Å	β= 90°.
	c = 18.794(6) Å	γ = 90°.
Volume	2355(2) $Å^3$	
Z	4	
Density (calculated)	1.361 Mg/m^3	
Absorption coefficient	1.627 mm^{-1}	
F(000)	1032	
Crystal size	0.4 x 0.3 x 0.3 mm^3	
Theta range for data collection	3.63 to 69.89°.	
Index ranges	0<=h<=9, 0<=k<=19, 0<=l<=22	
Reflections collected	2457	
Independent reflections	2457 [R(int) = 0.0000]	
Completeness to theta = 69.89°	96.1 %	
Absorption correction	Numerical	
Max. and min. transmission	0.5209 and 0.4819	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2457 / 0 / 305	
Goodness-of-fit on F^2	1.071	
Final R indices [I>2sigma(I)]	R1 = 0.0747, wR2 = 0.1997	
R indices (all data)	R1 = 0.0926, wR2 = 0.2210	
Absolute structure parameter	0.47(6)	
Extinction coefficient	0.053(5)	
Largest diff. peak and hole	0.392 and -0.523 e.$Å^{-3}$	

Tetracyclic aldol adduct 47



The crystals were grown by slow evaporation of a CH_2Cl_2 solution at room temperature**.** One single crystal of 0.45 X 0.40 X 0.25 mm^3 was mounted using a glass fiber on the goniometer at 293(2) K. Data were collected on an Enraf-Nonius CAD-4 automatic diffractometer at the Université de Sherbrooke using ω scans. The DIFRAC[(1)] program was used for centering, indexing, and data collection. Two standard reflections were measured every 100 reflections, 5% intensity decay was observed during data collection. The data were corrected for absorption by empirical methods based on psi scans and reduced with the NRCVAX[(2)] programs. They were solved using SHELXS-97[(3)] and refined by full-matrix least squares on F^2 with SHELXL-97[(4)]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at idealized calculated geometric position and refined isotropically using a riding model.

1) H.D. Flack, E. Blanc and D. Schwarzenbach (1992), J. Appl. Cryst., **25**, 455-459.
2) E.J. Gabe, Y. Le Page, J.-P. Charland, F.L. Lee, and P.S. White, (1989) *J. Appl. Cryst*., **22**, 384-387.
3) G. M. Sheldrick, SHELXS-97, G.M. Sheldrick, University of Göttingen, Germany, 1997, Release 97-2.
4) G. M. Sheldrick, SHELXL-97, G.M. Sheldrick, University of Göttingen, Germany, 1997, Release

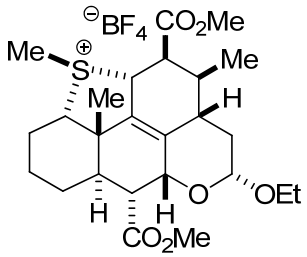


Ellipsoid probability set at 50%.97-2.

Table 1. Crystal data and structure refinement for ad4761a

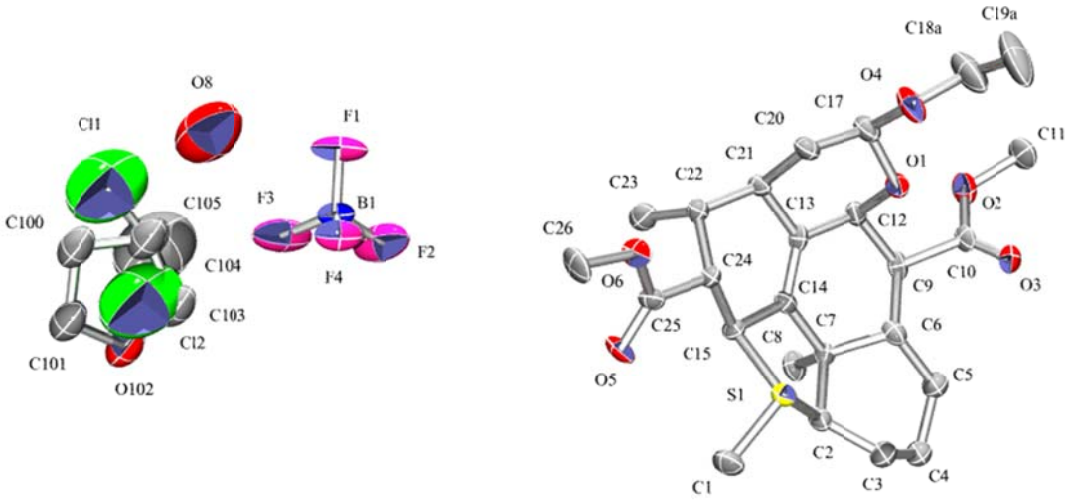
Identification code	ad4761a	
Empirical formula	$C_{22}H_{28}O_7S$	
Formula weight	436.50	
Temperature	293(2) K	
Wavelength	1.54176 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.240(3) Å	α= 83.27(4)°.
	b = 11.921(6) Å	β= 82.09(2)°.
	c = 22.119(5) Å	γ = 81.40(4)°.
Volume	2117.6(14) $Å^3$	
Z	4	
Density (calculated)	1.369 Mg/m^3	
Absorption coefficient	1.718 mm^{-1}	
F(000)	928	
Crystal size	0.45 x 0.40 x 0.25 mm^3	
Theta range for data collection	2.03 to 69.97°.	
Index ranges	-9<=h<=10, 0<=k<=14, -26<=l<=26	
Reflections collected	7468	
Independent reflections	7468 [R(int) = 0.0000]	
Completeness to theta = 69.97°	93.1 %	
Absorption correction	Empirical	
Max. and min. transmission	0.7944 and 0.7172	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7468 / 0 / 552	
Goodness-of-fit on F^2	0.955	
Final R indices [I>2sigma(I)]	R1 = 0.0890, wR2 = 0.2376	
R indices (all data)	R1 = 0.1701, wR2 = 0.2854	
Extinction coefficient	0.0131(12)	
Largest diff. peak and hole	0.256 and -0.356 $e.Å^{-3}$	

Methylsulfonium tetrafluoroborate 50



The crystals were grown by slow evaporation of a CH_2Cl_2/THF solution mixture at room temperature**.** One single crystal of 0.30 X 0.40 X 0.45 mm^3 was mounted using a glass fiber on the goniometer at 198(2) K. Data were collected on an Enraf-Nonius CAD-4 automatic diffractometer at the Université de Sherbrooke using ω scans. The DIFRAC[(1)] program was used for centering, indexing, and data collection. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection. The data were reduced with the NRCVAX[(2)] programs, solved using SHELXS-97[(3)] and refined by full-matrix least squares on F^2 with SHELXL-97[(4)]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at idealized calculated geometric position and refined isotropically using a riding model. Three disordered solvent molecules were found in a packing crystal cavity. One H_2O and a mixture of THF and CH_2Cl_2 very close on a same crystallographic site. The two last were refined with partial occupations factors and found to be 51% THF and 49% CH_2Cl_2. These disordered solvent molecules mostly contributed to reduce the data quality.

1) H.D. Flack, E. Blanc and D. Schwarzenbach (1992), J. Appl. Cryst., **25**, 455-459.
2) E.J. Gabe, Y. Le Page, J.-P. Charland, F.L. Lee, and P.S. White, (1989) *J. Appl. Cryst*., **22**, 384-387.
3) G. M. Sheldrick, SHELXS-97, G.M. Sheldrick, University of Göttingen, Germany, 1997, Release 97-2.
4) G. M. Sheldrick, SHELXL-97, G.M. Sheldrick, University of Göttingen, Germany, 1997, Release 97-2.

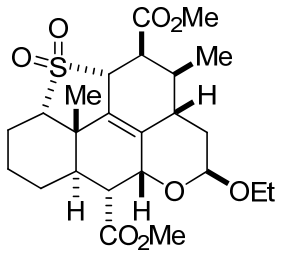


Ellipsoid probability set at 50%.

Table 1. Crystal data and structure refinement for ad71511.

Identification code	ad71511	
Empirical formula	$C_{27.50}H_{44}BClF_4O_{7.50}S$	
Formula weight	648.95	
Temperature	198(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 14.686(9) Å	α= 90°.
	b = 15.801(9) Å	β= 115.69(4)°.
	c = 14.910(8) Å	γ = 90°.
Volume	3118(3) $Å^3$	
Z	4	
Density (calculated)	1.382 Mg/m^3	
Absorption coefficient	0.258 mm^{-1}	
F(000)	1372	
Crystal size	0.45 x 0.40 x 0.30 mm^3	
Theta range for data collection	2.07 to 25.52°.	
Index ranges	-17<=h<=16, 0<=k<=19, 0<=l<=18	
Reflections collected	5634	
Independent reflections	5634 [R(int) = 0.0000]	
Completeness to theta = 25.52°	97.0 %	
Absorption correction	Psi-Scan	
Max. and min. transmission	0.9266 and 0.8928	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5634 / 9 / 382	
Goodness-of-fit on F^2	0.951	
Final R indices [I>2sigma(I)]	R1 = 0.0992, wR2 = 0.1991	
R indices (all data)	R1 = 0.2313, wR2 = 0.2380	
Extinction coefficient	0.0043(11)	
Largest diff. peak and hole	0.544 and -0.466 $e.Å^{-3}$	

Pentacyclic sulfone 55



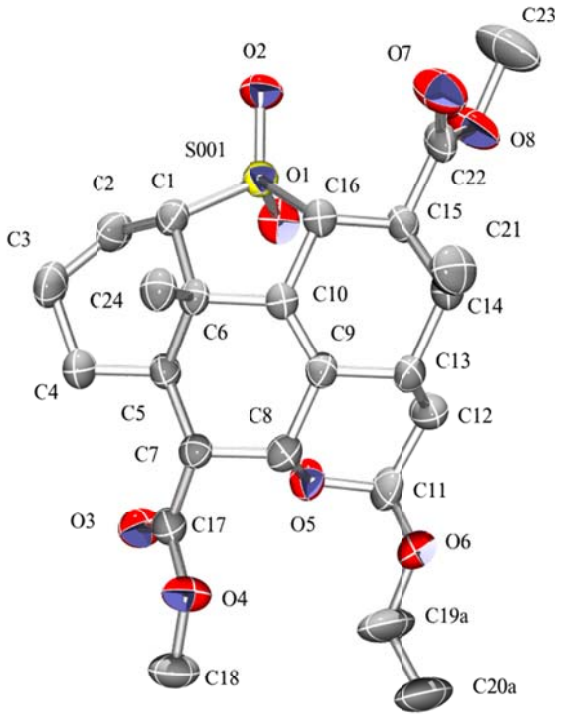
The crystals were grown by vapor diffusion of THF on a CH_2Cl_2 solution at room temperature**.** One single crystal of 0.20 X 0.40 X 0.40 mm^3 was mounted using a glass fiber on the goniometer at 273(2) K. Data were collected on an Enraf-Nonius CAD-4 automatic diffractometer at the Université de Sherbrooke using ω scans. The DIFRAC[(1)] program was used for centering, indexing, and data collection. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection. The data were reduced with the NRCVAX[(2)] programs, solved using SHELXS-97[(3)] and refined by full-matrix least squares on F^2 with SHELXL-97[(4)]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at idealized calculated geometric position and refined isotropically using a riding model. C_{19} and C_{20} were disordered, and they were refined with partial occupation factors. Only the major site with 67% occupation is shown for clarity.

1) H.D. Flack, E. Blanc and D. Schwarzenbach (1992), J. Appl. Cryst., **25**, 455-459.

2) E.J. Gabe, Y. Le Page, J.-P. Charland, F.L. Lee, and P.S. White, (1989) *J. Appl. Cryst*., **22**, 384-387.

3) G. M. Sheldrick, SHELXS-97, G.M. Sheldrick, University of Göttingen, Germany, 1997, Release 97-2.

4) G. M. Sheldrick, SHELXL-97, G.M. Sheldrick, University of Göttingen, Germany, 1997, Release 97-2.

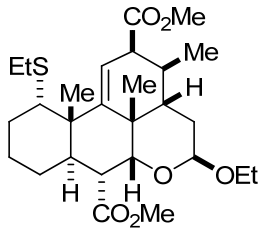


Ellipsoid probability set at 50%.

Table 1. Crystal data and structure refinement for ad8391b.

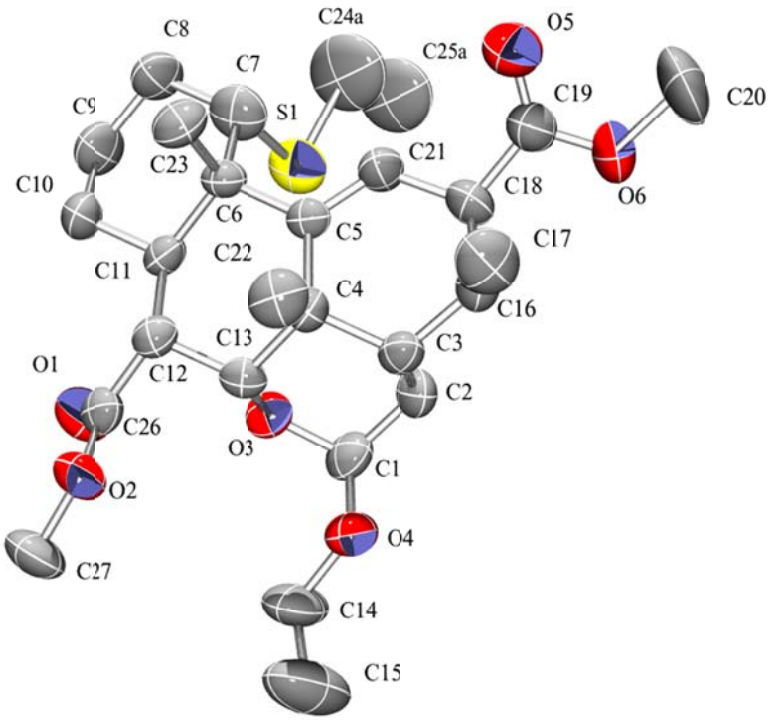
Identification code	ad8391b	
Empirical formula	C_{24} H_{34} O_8 S	
Formula weight	482.57	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.111(3) Å	α= 68.38(3)°.
	b = 10.252(4) Å	β= 86.83(3)°.
	c = 12.207(5) Å	γ = 89.26(3)°.
Volume	1174.5(7) $Å^3$	
Z	2	
Density (calculated)	1.365 Mg/m^3	
Absorption coefficient	0.185 mm^{-1}	
F(000)	516	
Crystal size	0.40 x 0.40 x 0.20 mm^3	
Theta range for data collection	1.80 to 25.54°.	
Index ranges	-12<=h<=12, 0<=k<=12, -13<=l<=14	
Reflections collected	4357	
Independent reflections	4357 [R(int) = 0.0000]	
Completeness to theta = 25.50°	98.9 %	
Absorption correction	Psi-Scan	
Max. and min. transmission	0.9638 and 0.9295	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4357 / 1 / 305	
Goodness-of-fit on F^2	0.918	
Final R indices [I>2sigma(I)]	R1 = 0.0616, wR2 = 0.1169	
R indices (all data)	R1 = 0.1597, wR2 = 0.1411	
Largest diff. peak and hole	0.266 and -0.260 $e.Å^{-3}$	

Cuprate adducts (+)-58



The crystals were grown by slow evaporation of Hexane/Ethyl Acetate solution mixture at room temperature**.** One single crystal of 0.40 X 0.40 X 0.60 mm^3 was mounted using a glass fiber on the goniometer at 273(2) K. Data were collected on an Enraf-Nonius CAD-4 automatic diffractometer at the Université de Sherbrooke using ω scans. The DIFRAC[(1)] program was used for centering, indexing, and data collection. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection. The data were reduced with the NRCVAX[(2)] programs, solved using SHELXS-97[(3)] and refined by full-matrix least squares on F^2 with SHELXL-97[(4)]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at idealized calculated geometric position and refined isotropically using a riding model. C_{24} and C_{25} were disordered, and they were refined with partial occupation factors. Only the major site with 70% occupation is shown for clarity.

1) H.D. Flack, E. Blanc and D. Schwarzenbach (1992), J. Appl. Cryst., **25**, 455-459.
2) E.J. Gabe, Y. Le Page, J.-P. Charland, F.L. Lee, and P.S. White, (1989) *J. Appl. Cryst*., **22**, 384-387.
3) G. M. Sheldrick, SHELXS-97, G.M. Sheldrick, University of Göttingen, Germany, 1997, Release 97-2.
4) G. M. Sheldrick, SHELXL-97, G.M. Sheldrick, University of Göttingen, Germany, 1997, Release 97-2.



Ellipsoid probability set at 50%.

Table 1. Crystal data and structure refinement for ad8401b.

Identification code	ad8401b	
Empirical formula	C27 H42 O6 S	
Formula weight	494.67	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P21/n	
Unit cell dimensions	a = 13.729(3) Å	α= 90°.
	b = 11.422(3) Å	β= 94.20(2)°.
	c = 17.143(5) Å	γ = 90°.
Volume	2681.0(12) $Å^3$	
Z	4	
Density (calculated)	1.226 Mg/m^3	
Absorption coefficient	0.159 mm^{-1}	
F(000)	1072	
Crystal size	0.60 x 0.40 x 0.40 mm^3	
Theta range for data collection	1.84 to 25.51°.	
Index ranges	-16<=h<=16, 0<=k<=13, 0<=l<=20	
Reflections collected	4930	
Independent reflections	4930 [R(int) = 0.0000]	
Completeness to theta = 25.50°	98.9 %	
Absorption correction	Psi-Scan	
Max. and min. transmission	0.9392 and 0.9108	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4930 / 3 / 310	
Goodness-of-fit on F^2	0.901	
Final R indices [I>2sigma(I)]	R1 = 0.0819, wR2 = 0.1809	
R indices (all data)	R1 = 0.2201, wR2 = 0.2211	
Largest diff. peak and hole	0.493 and -0.245 $e.Å^{-3}$	