Supporting Information for

Phosphine-catalyzed [3+2] Cycloaddition of Morita–Baylis–Hillman Carbonates with Sulfamate-derived Cyclic Imines

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[b] Department of Chemistry, Case Western Reserve University, Cleveland, OH 44106-7078, United States

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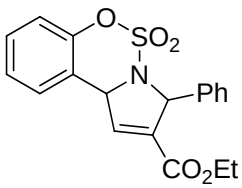
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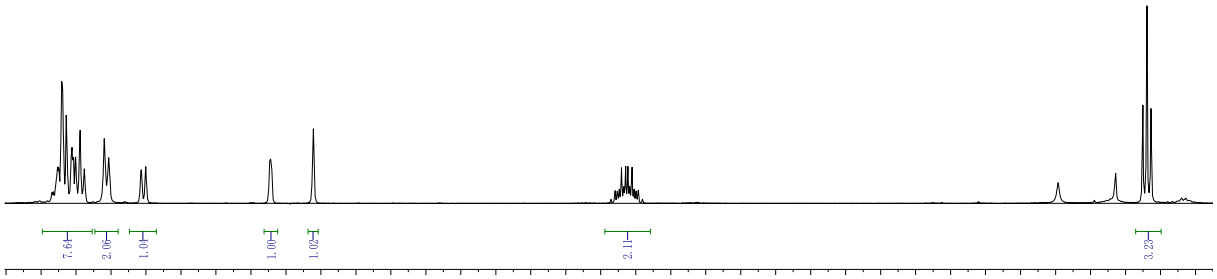
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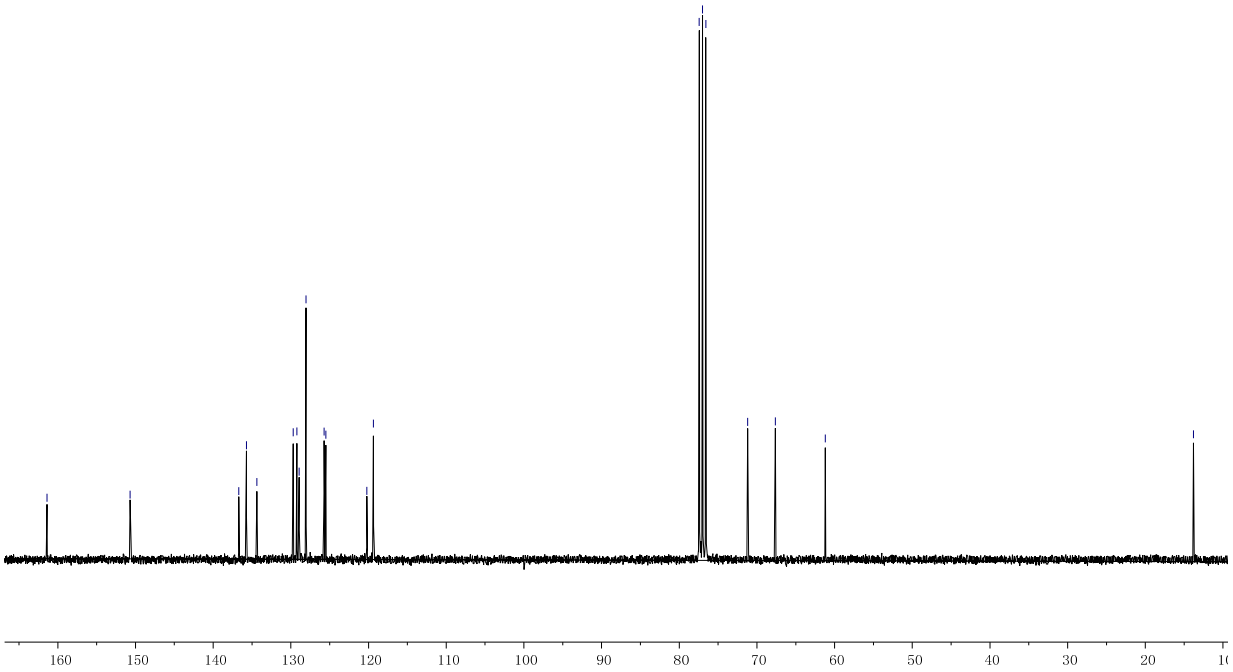
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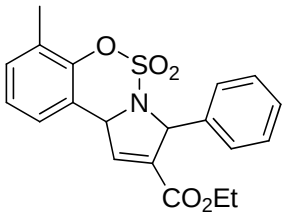

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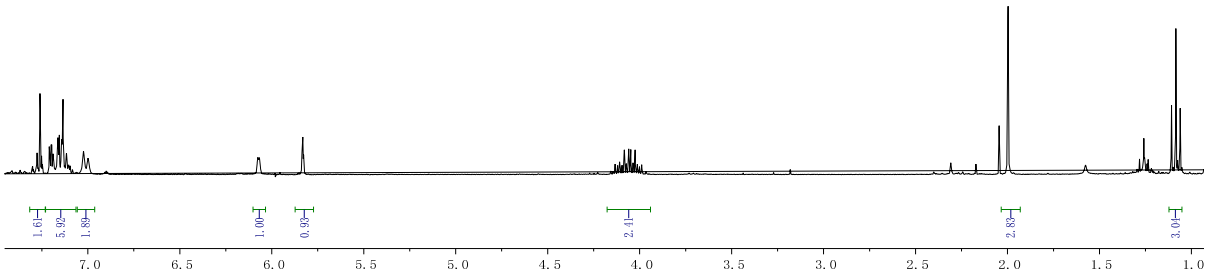

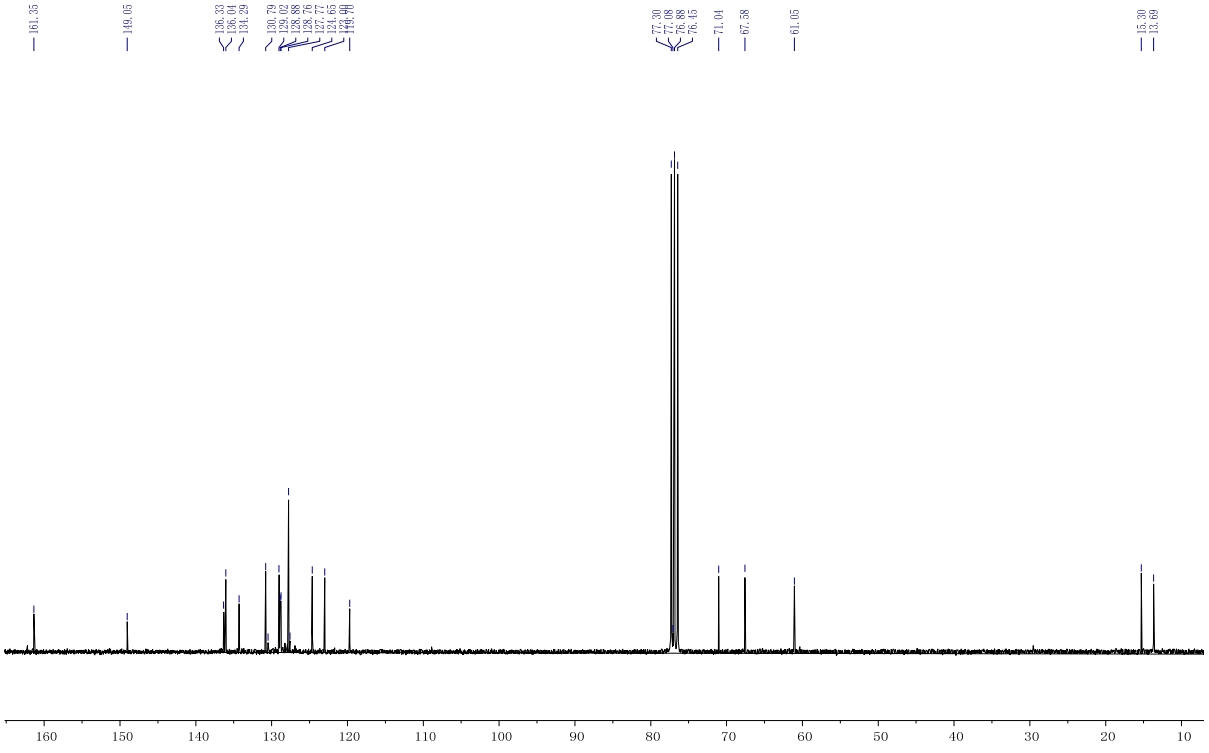

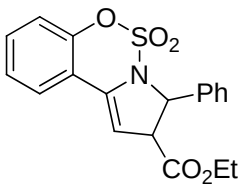
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N
Ph
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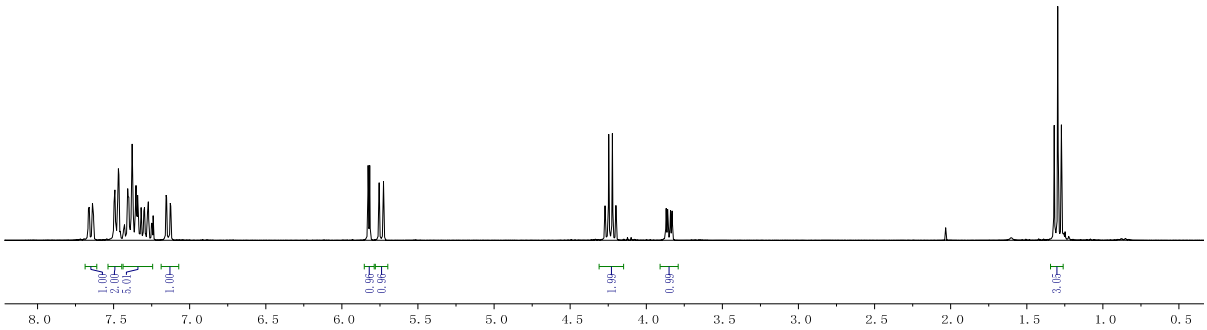
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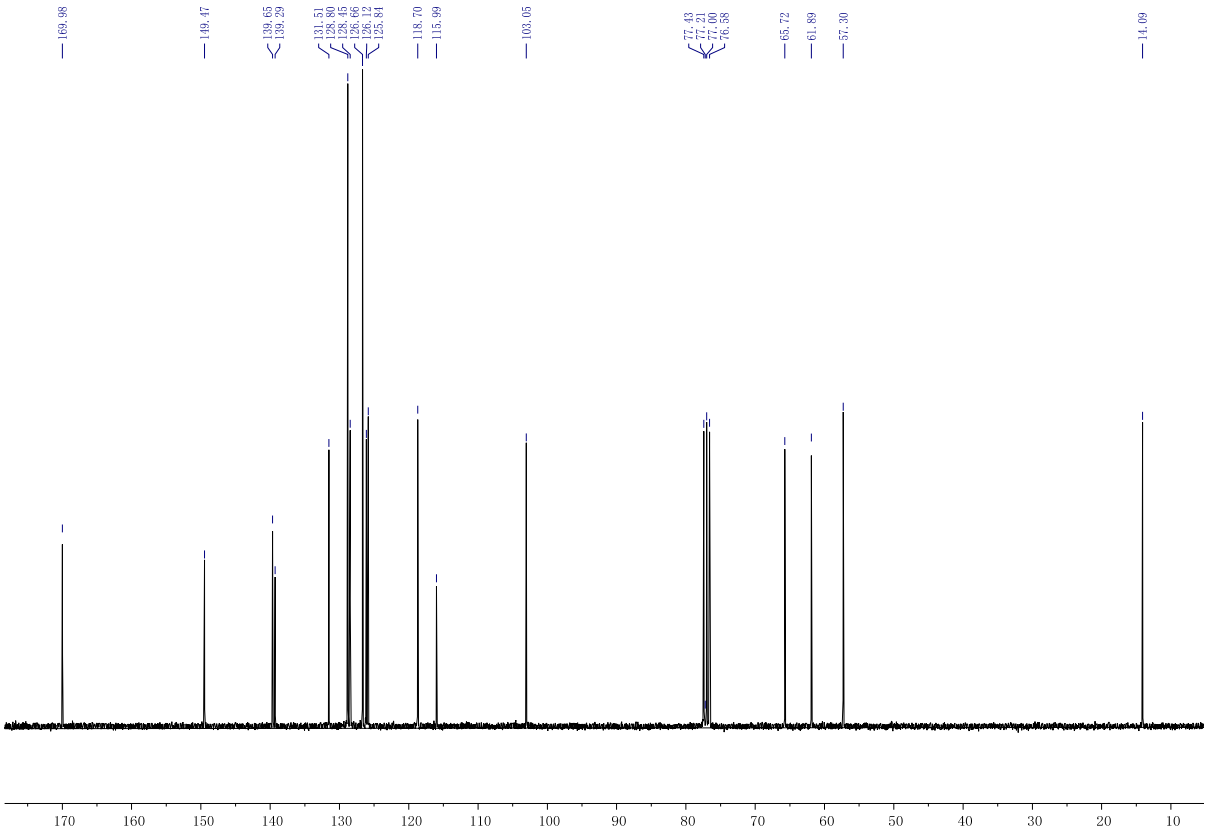
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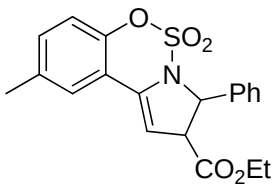

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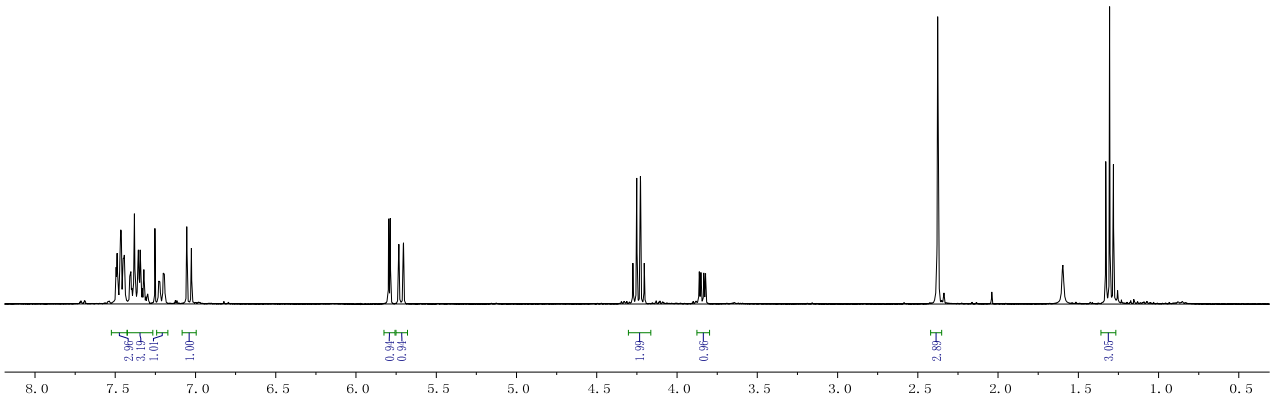

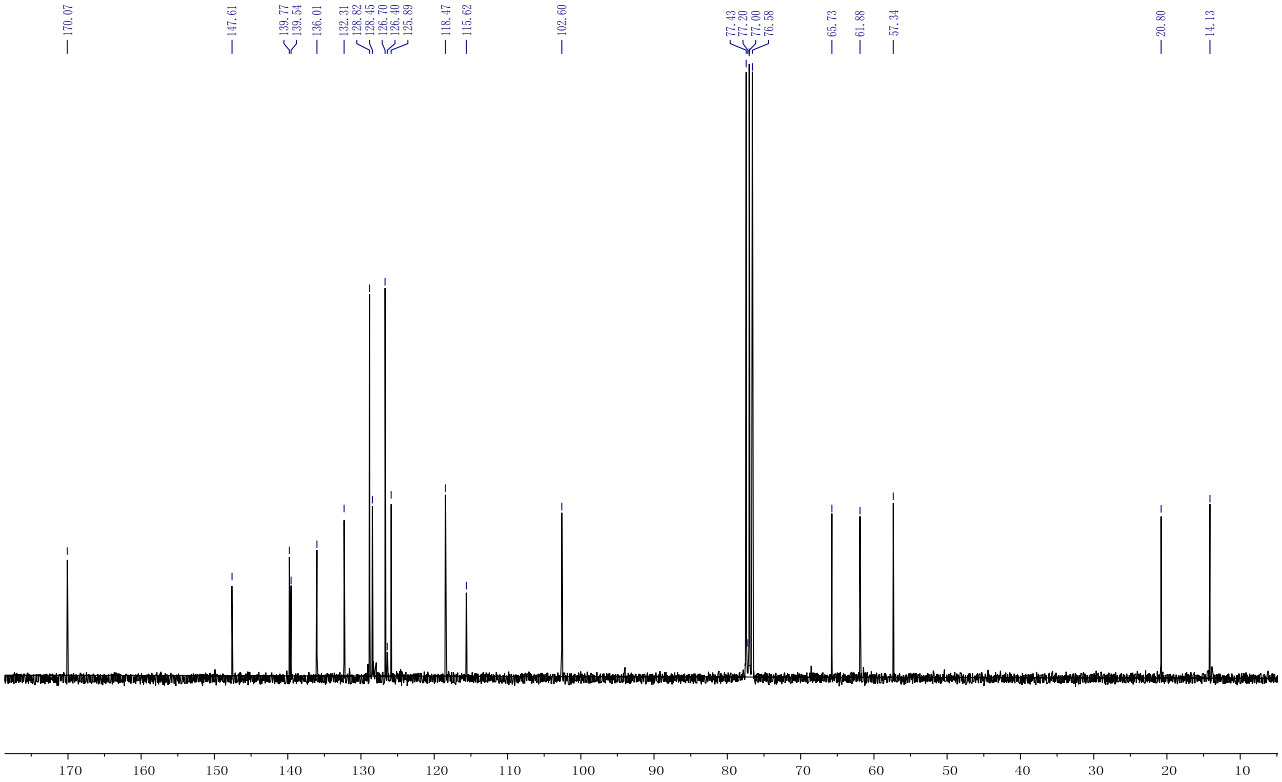

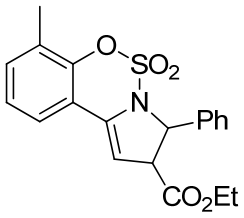

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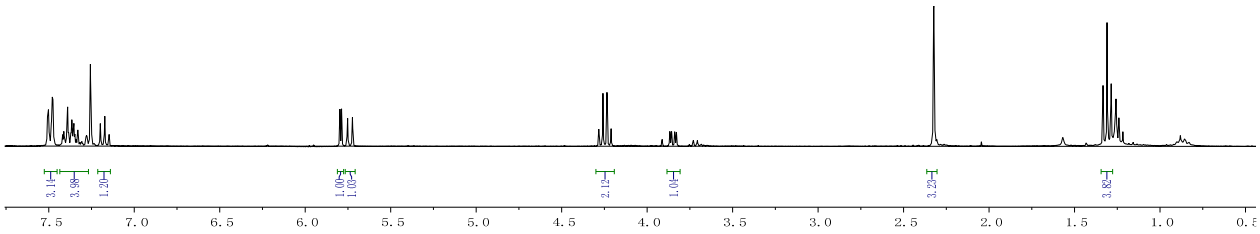

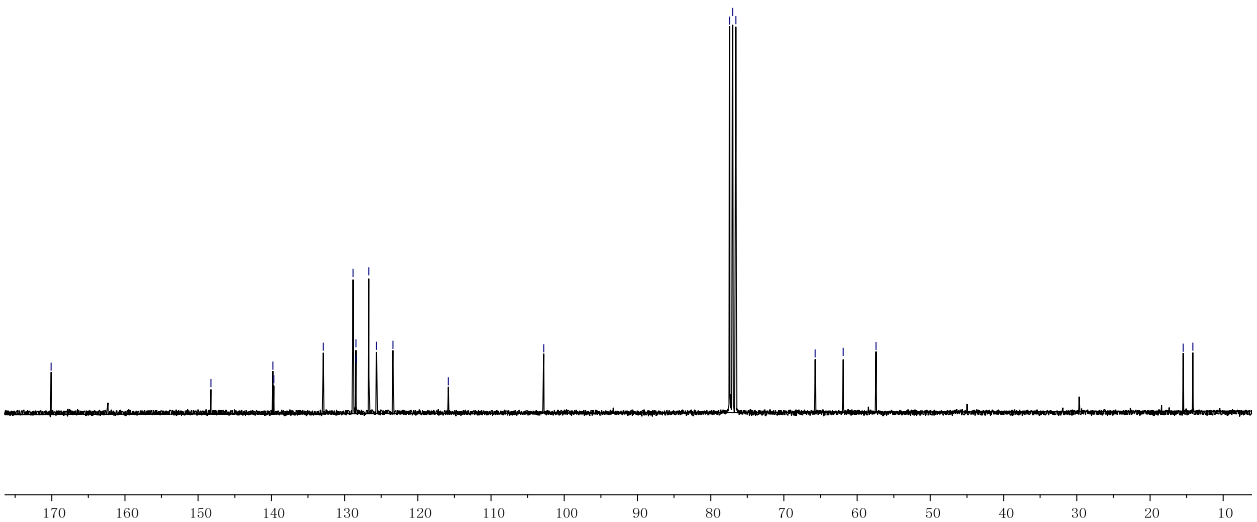

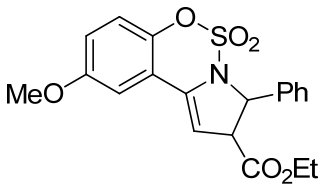
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Ph
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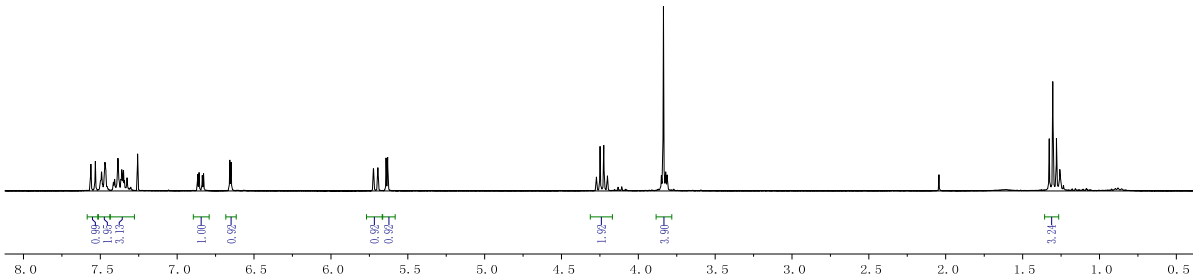
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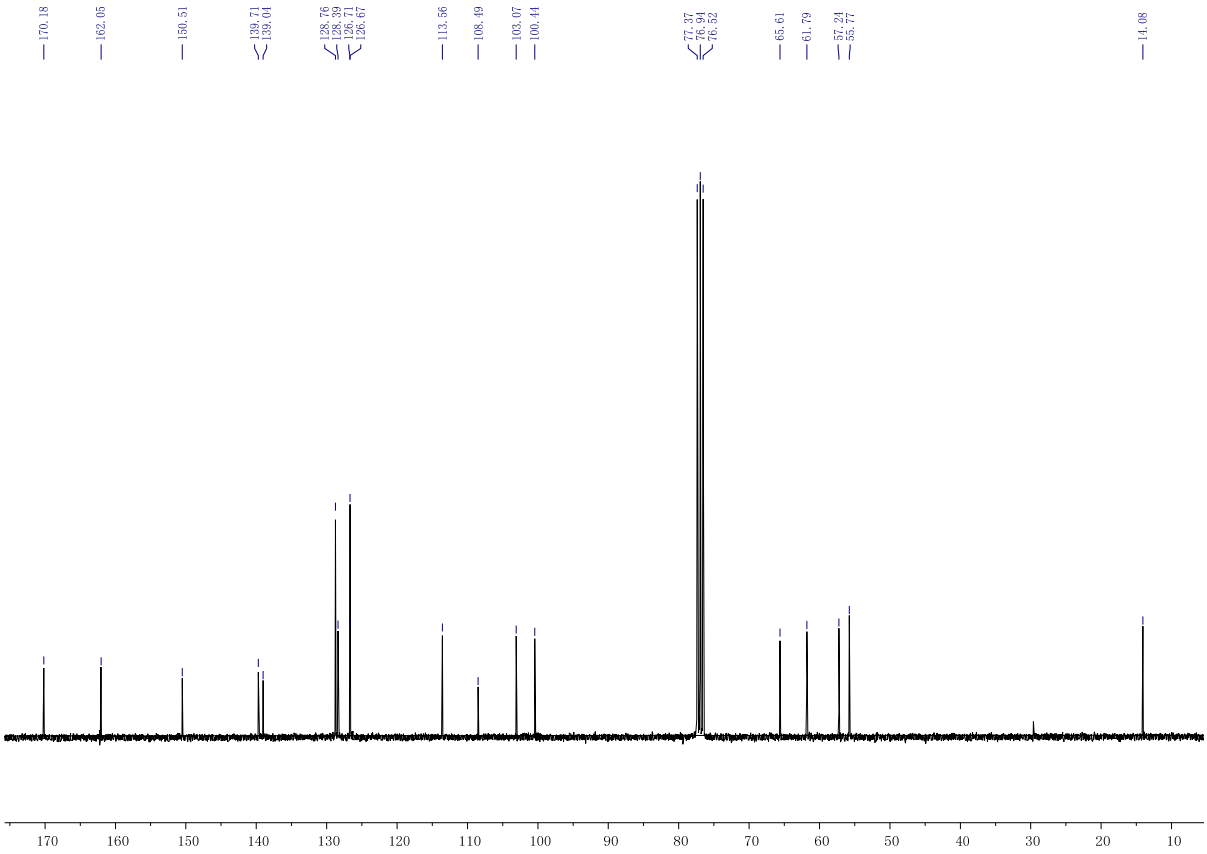
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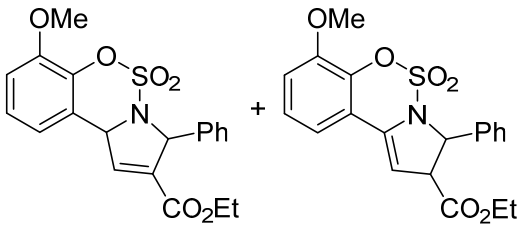

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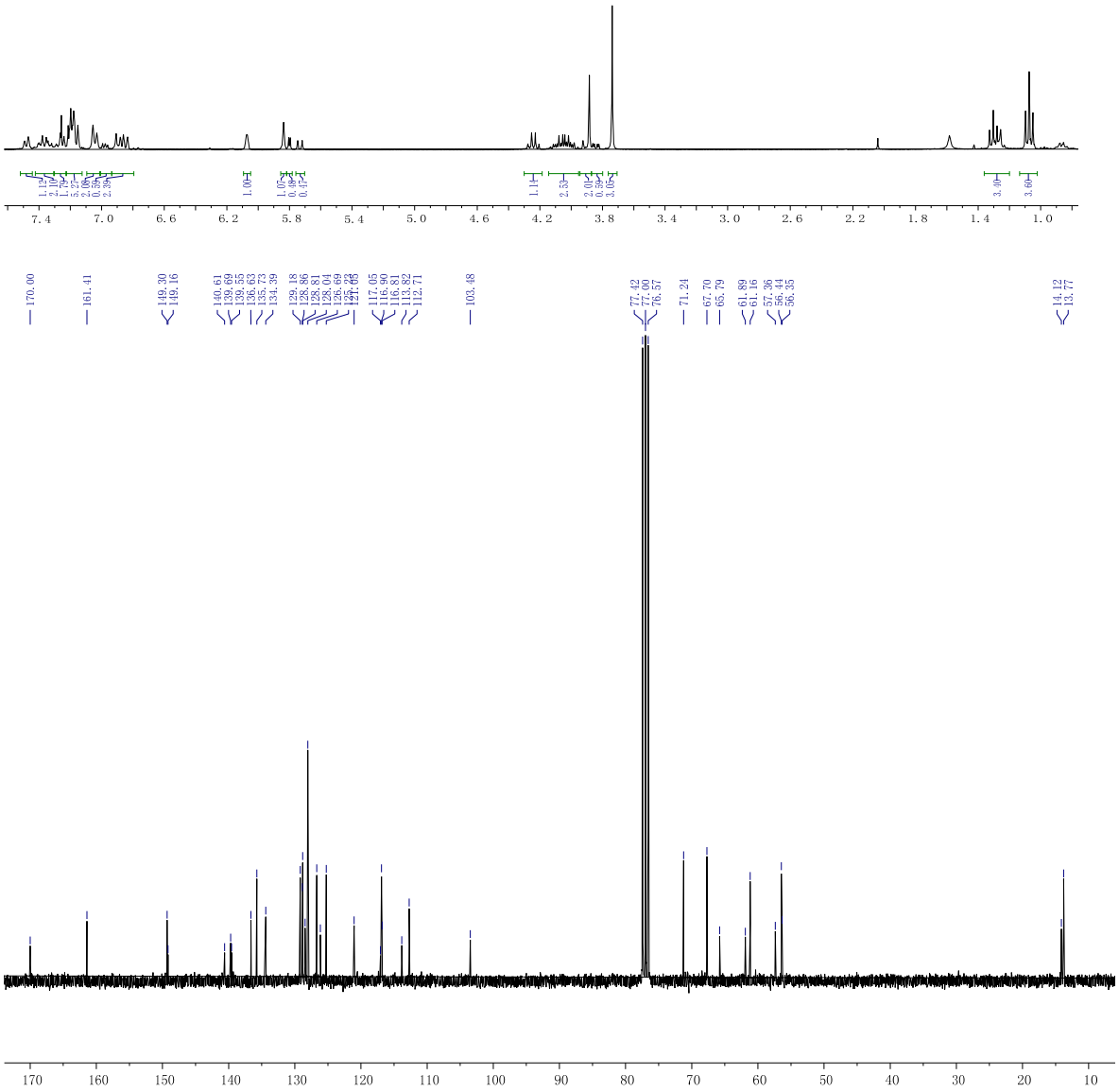

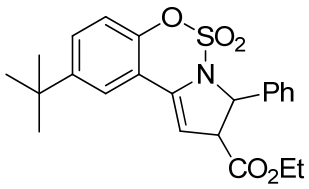

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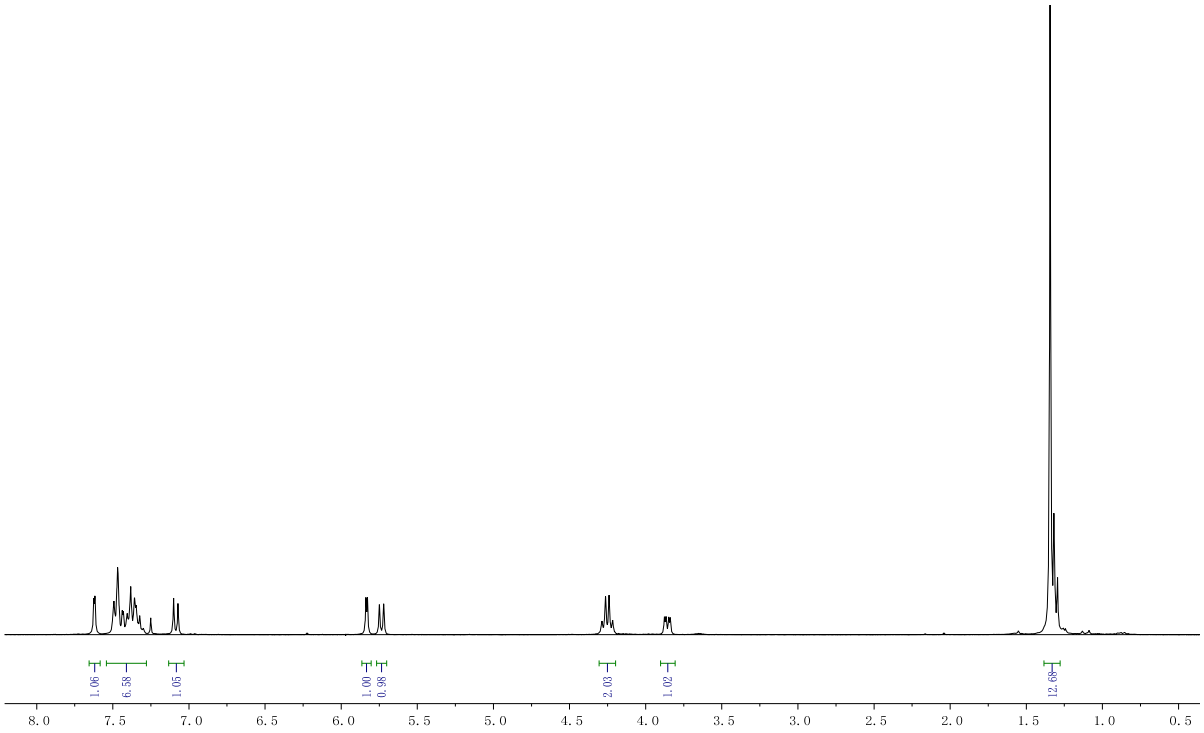

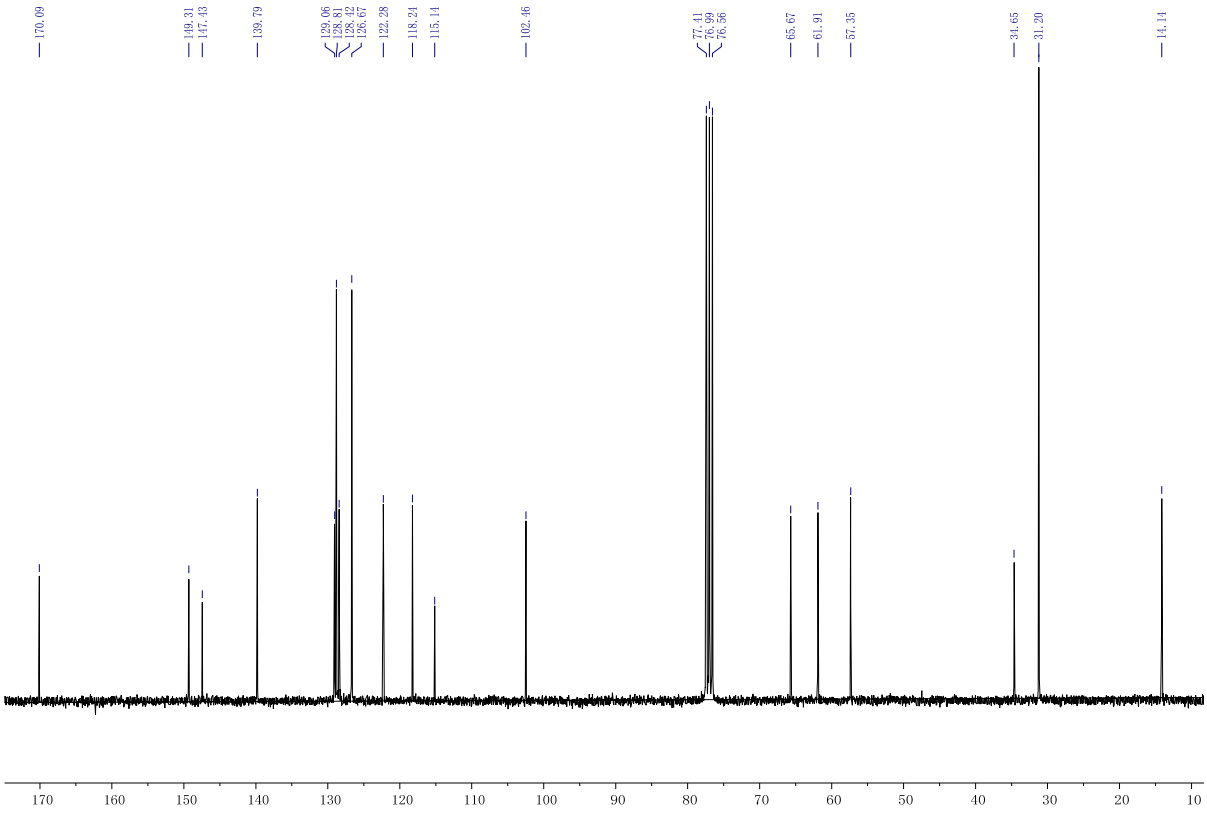

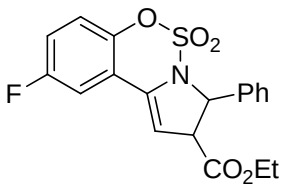

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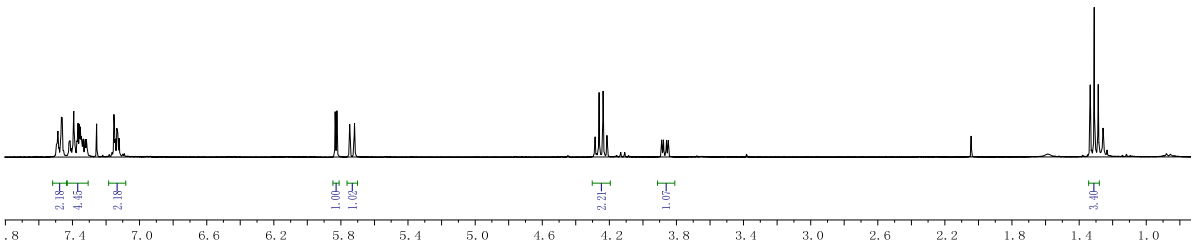

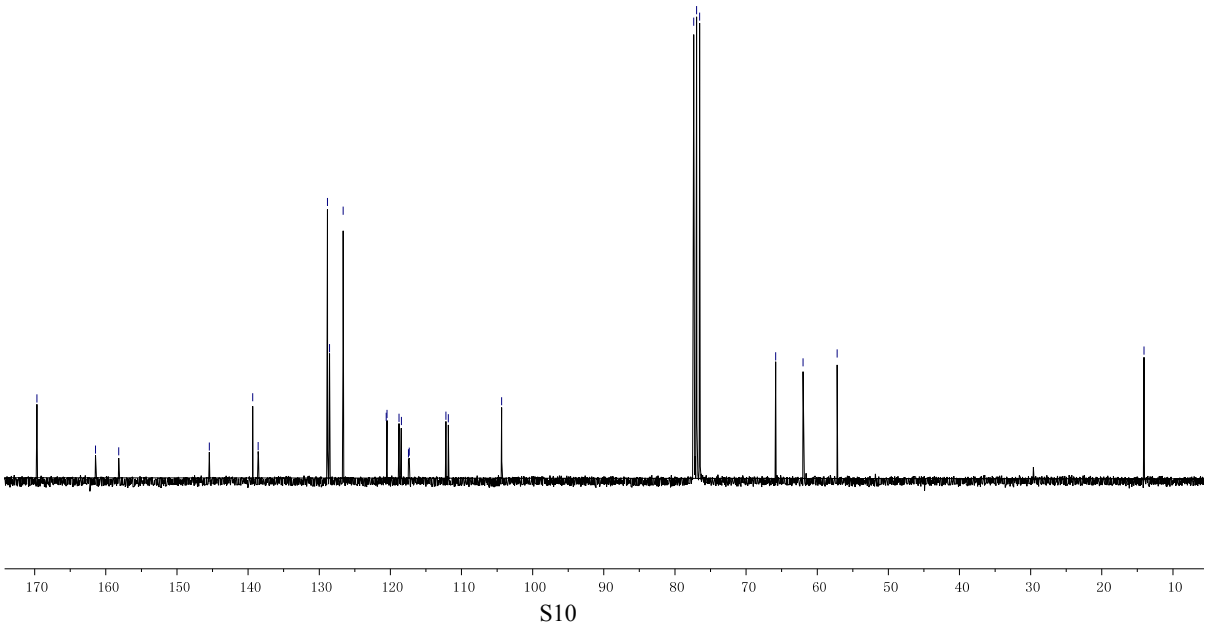

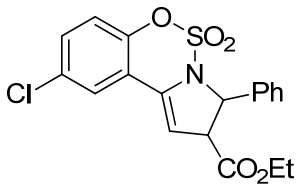

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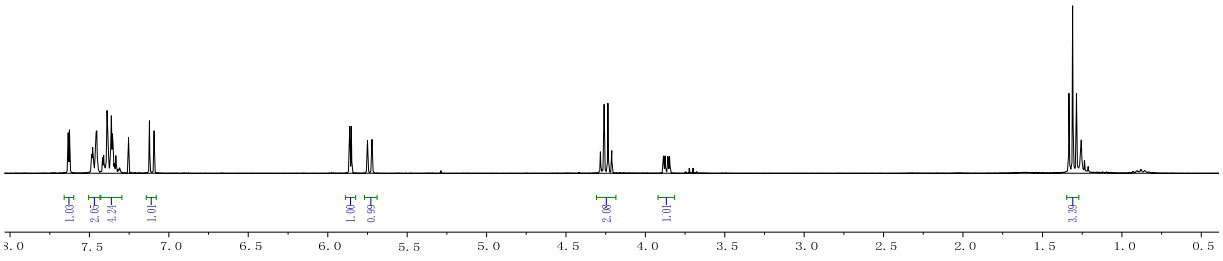

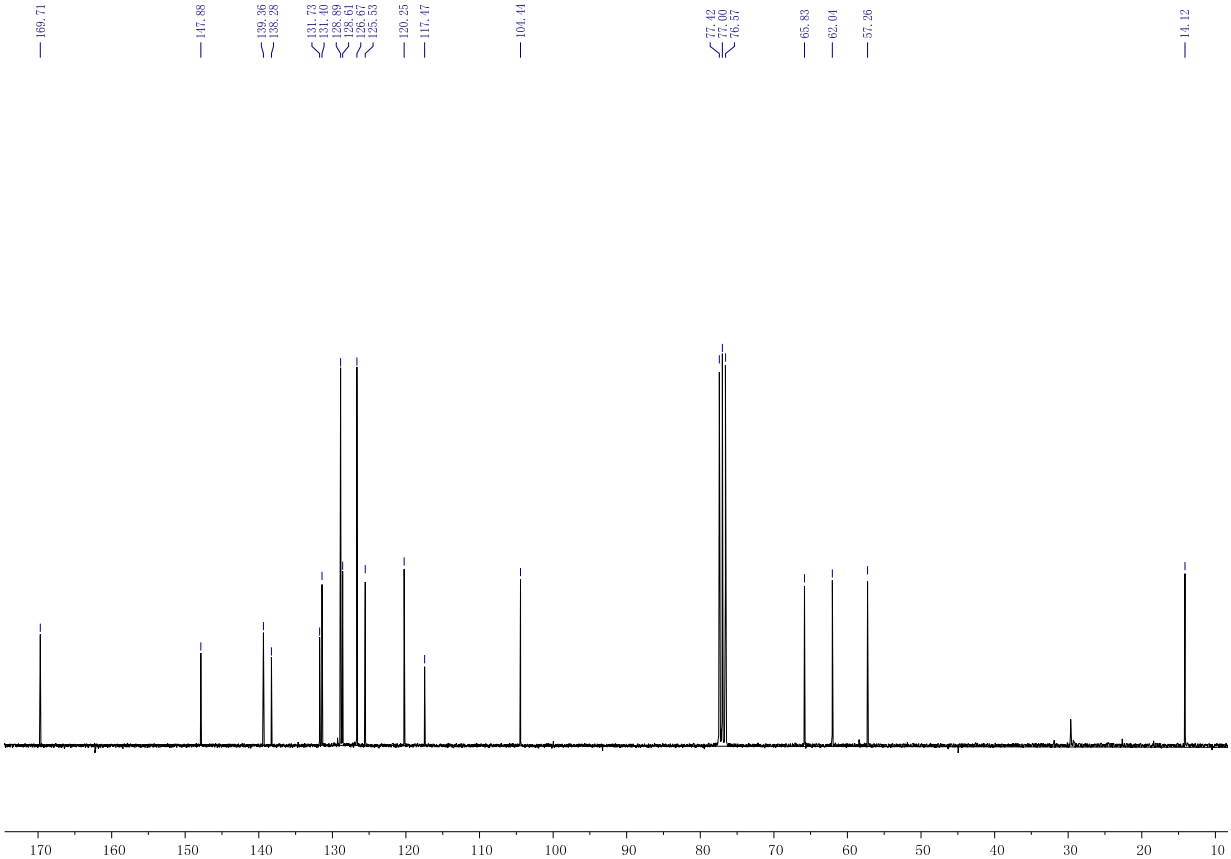

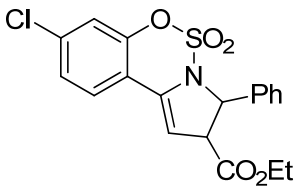

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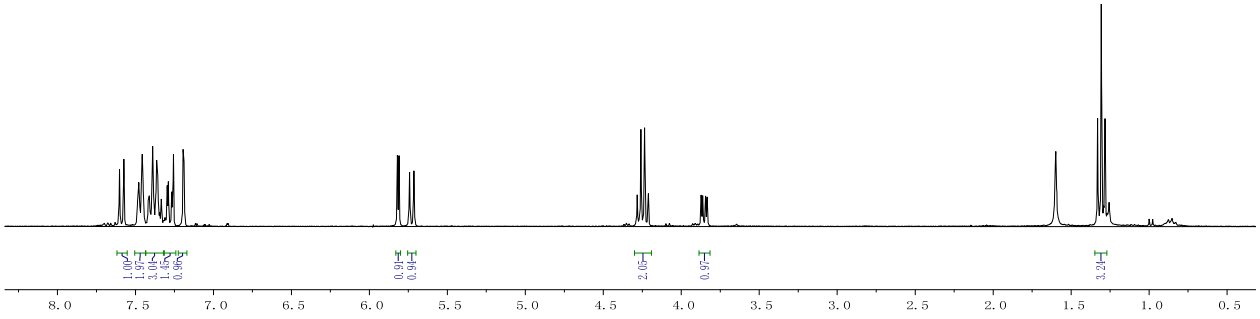

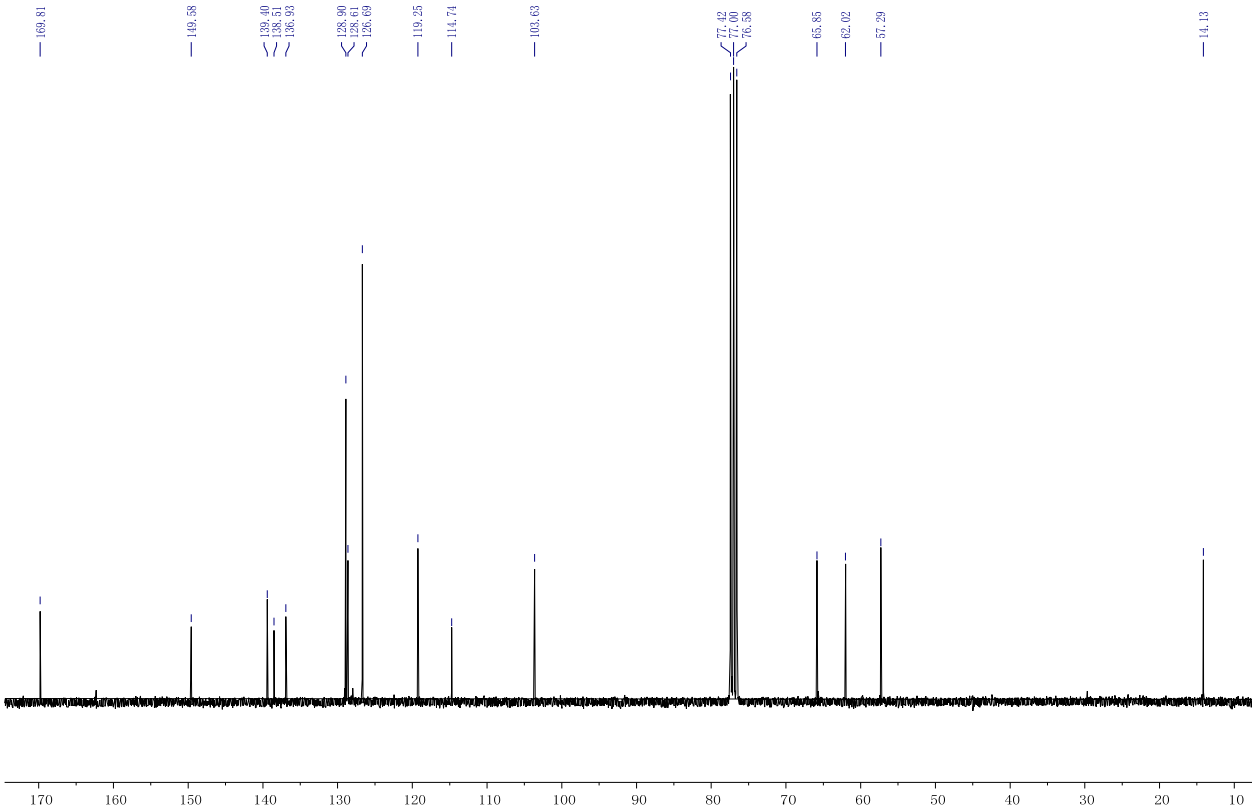

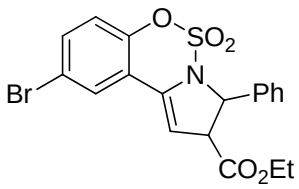
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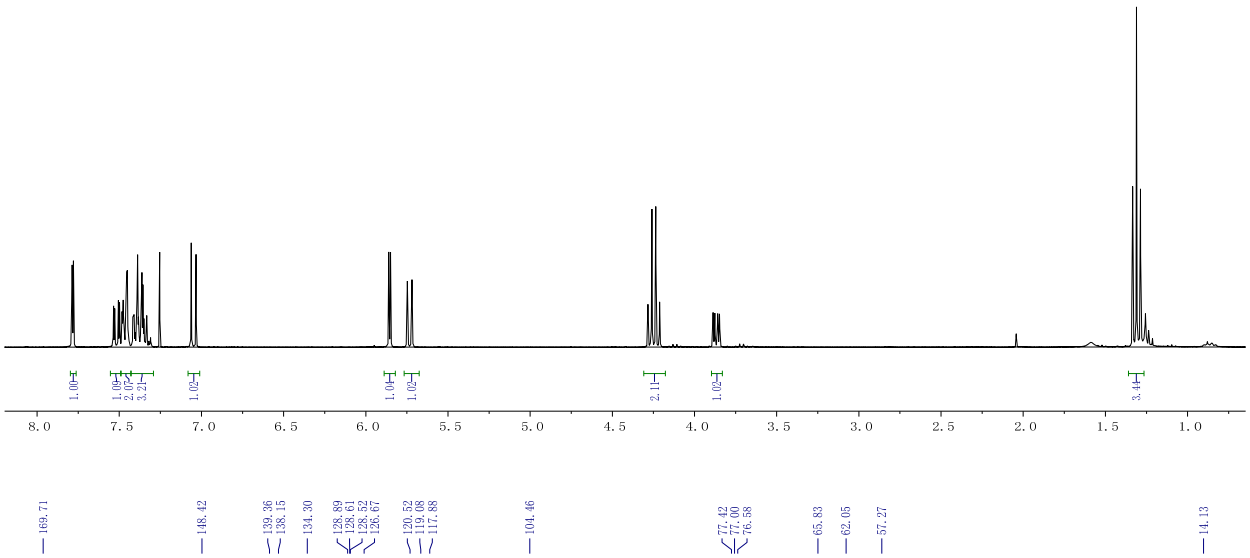
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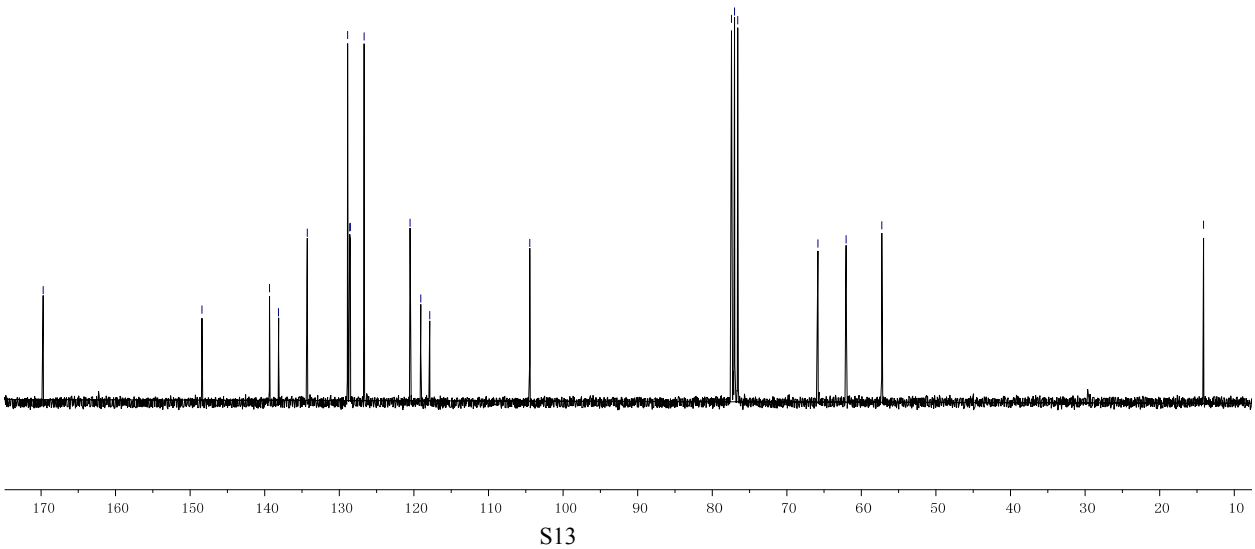
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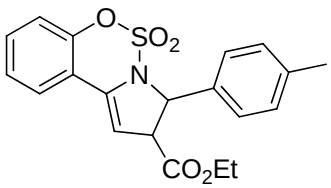

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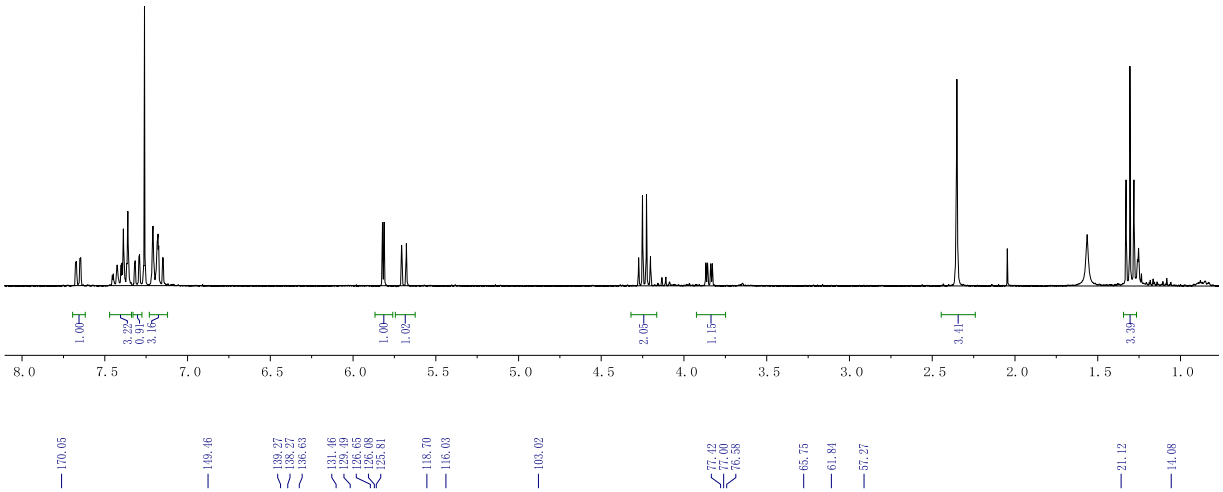

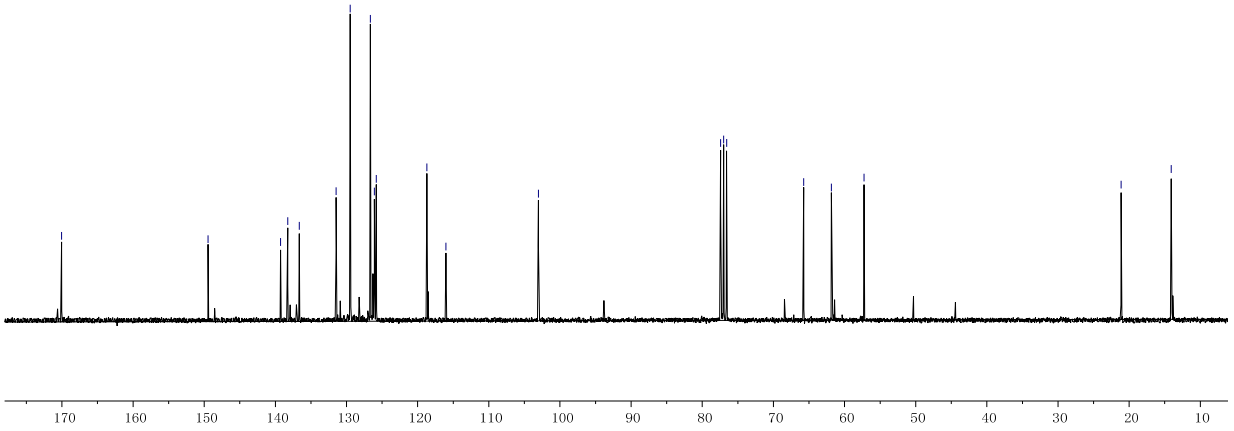

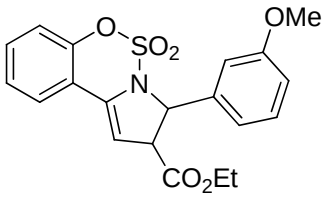

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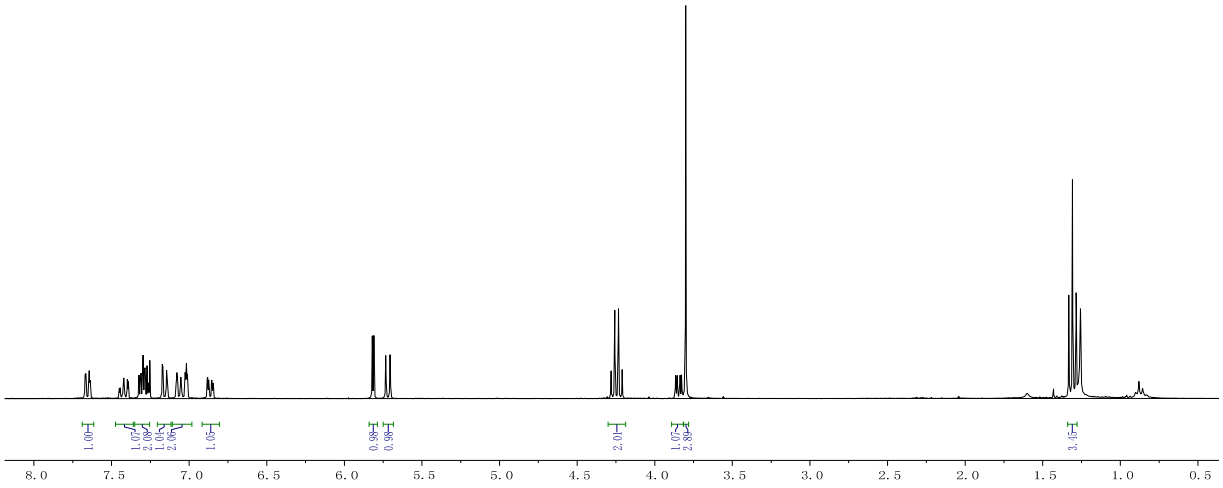

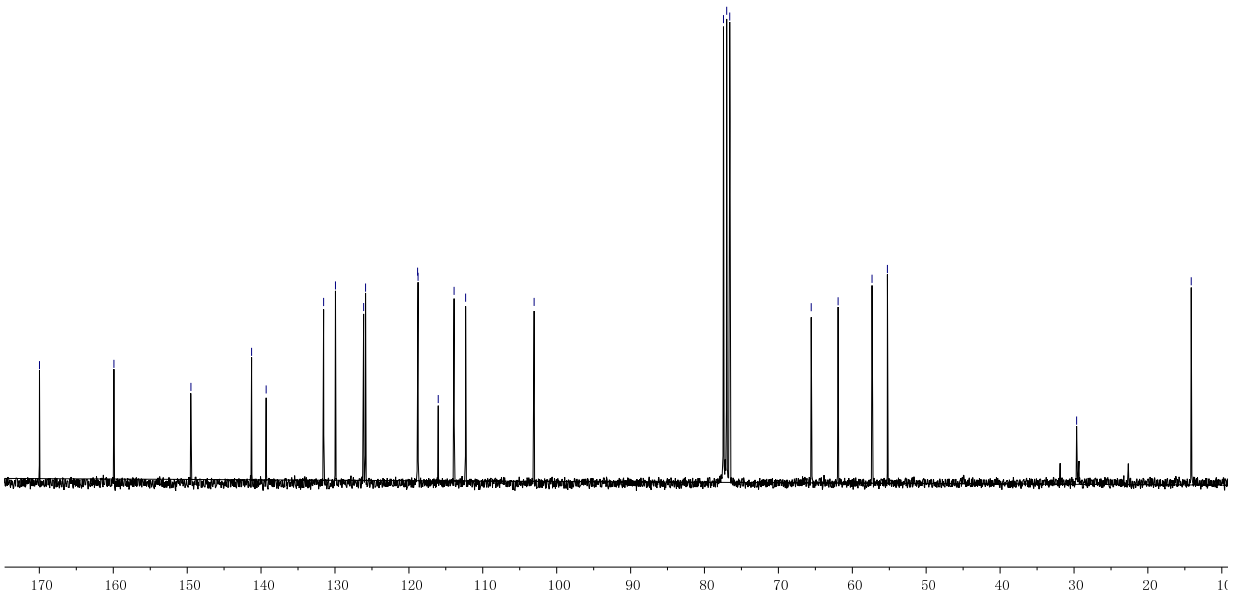

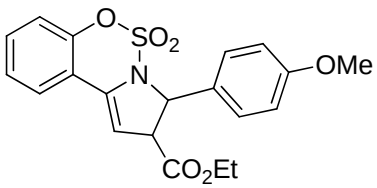
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N
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CO2Et

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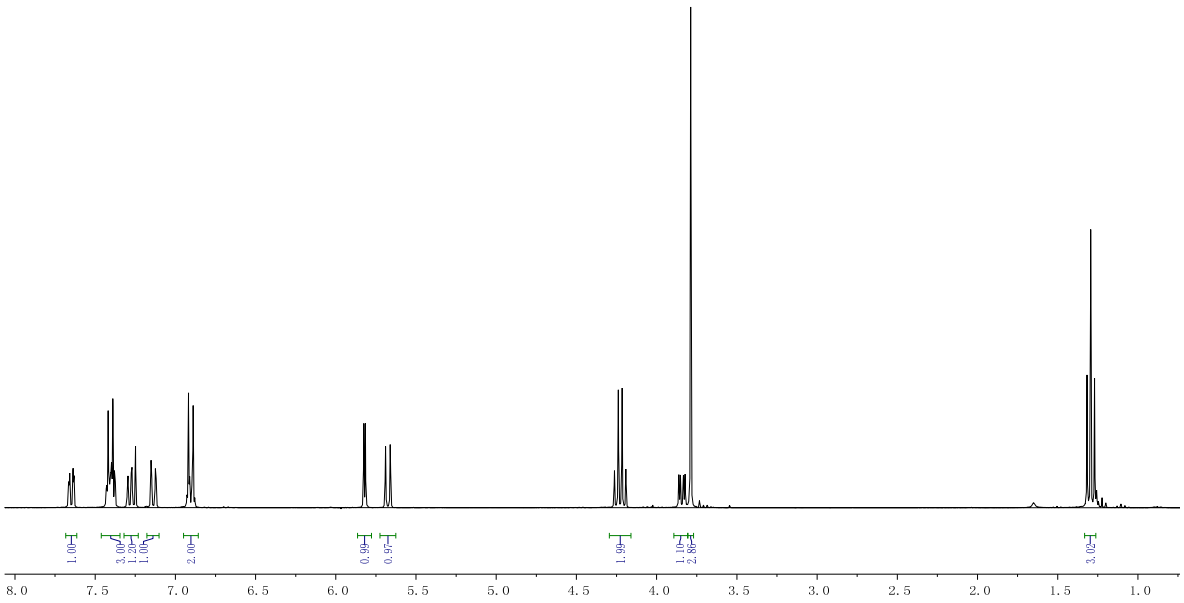
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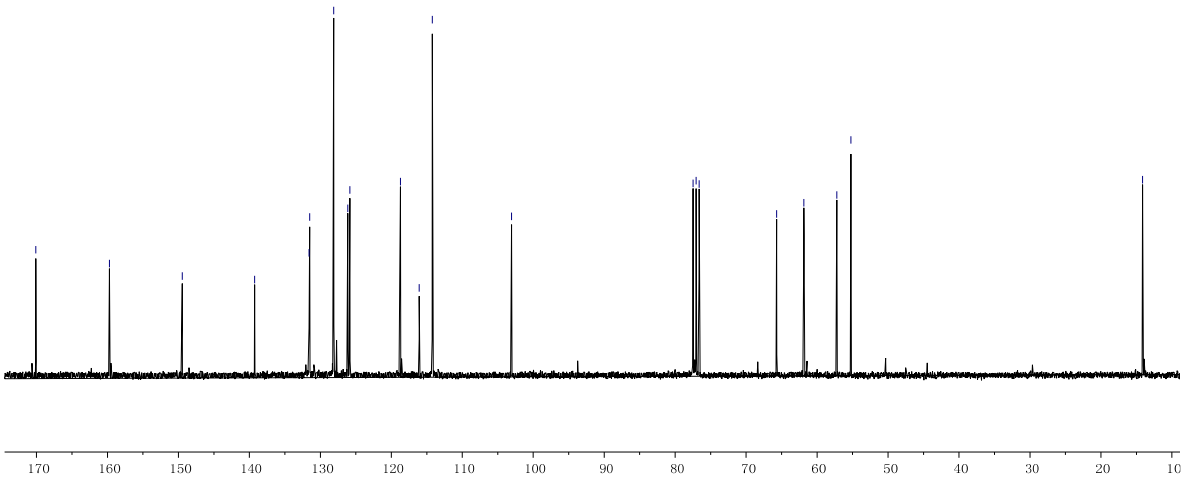
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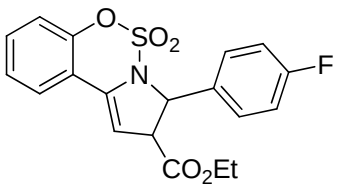

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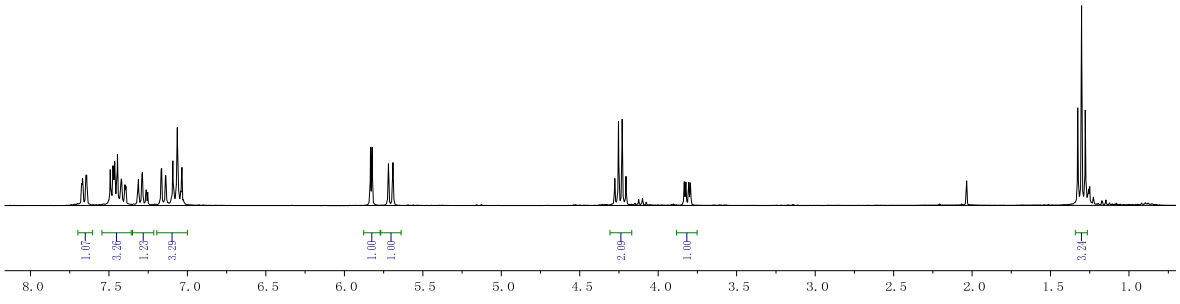

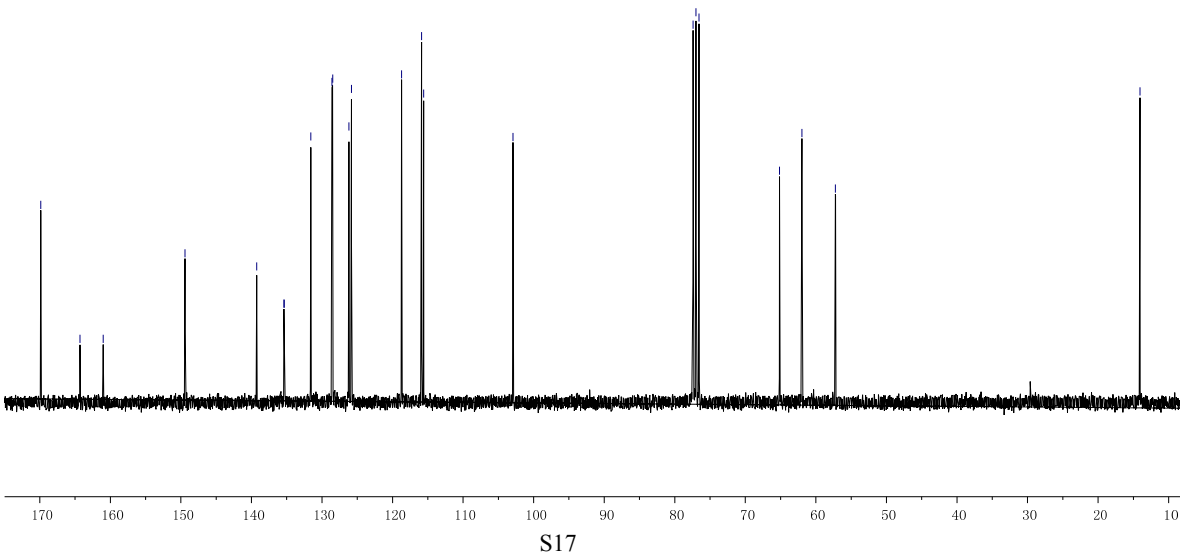

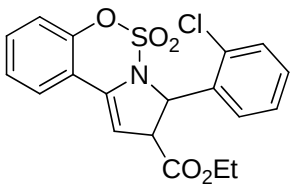

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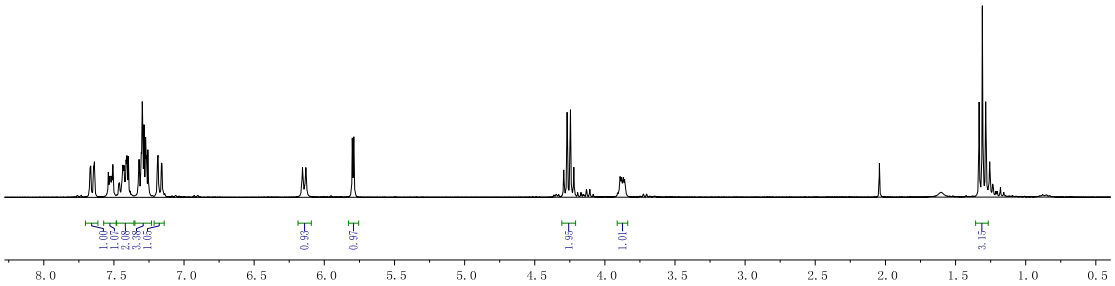
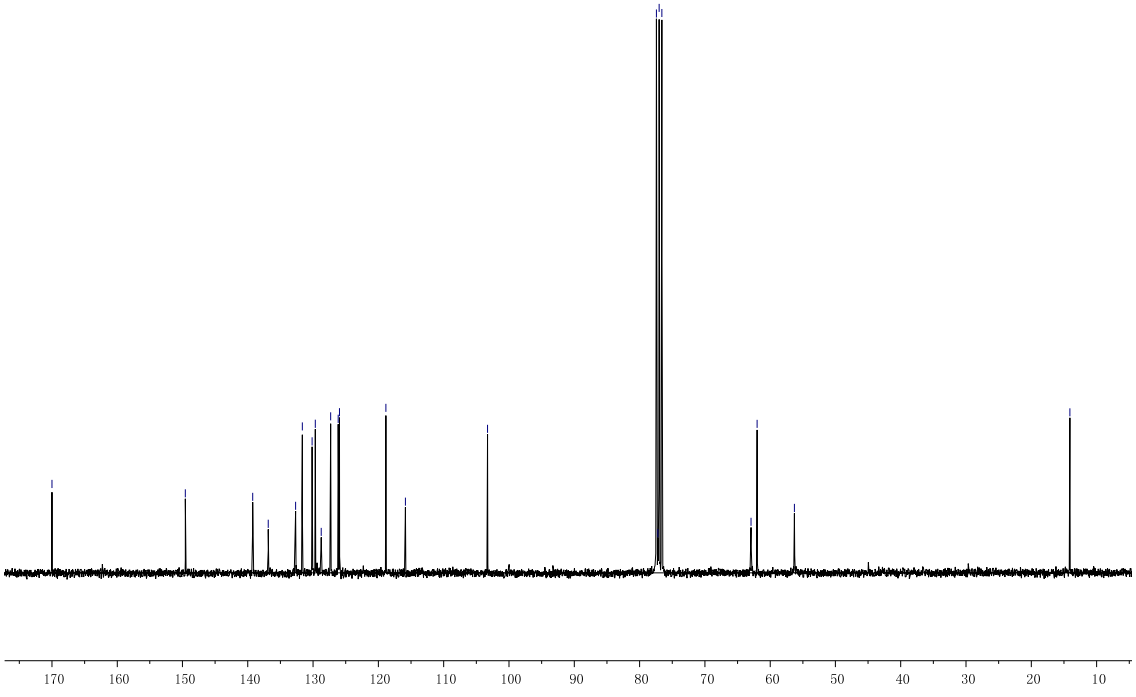
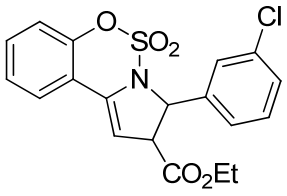
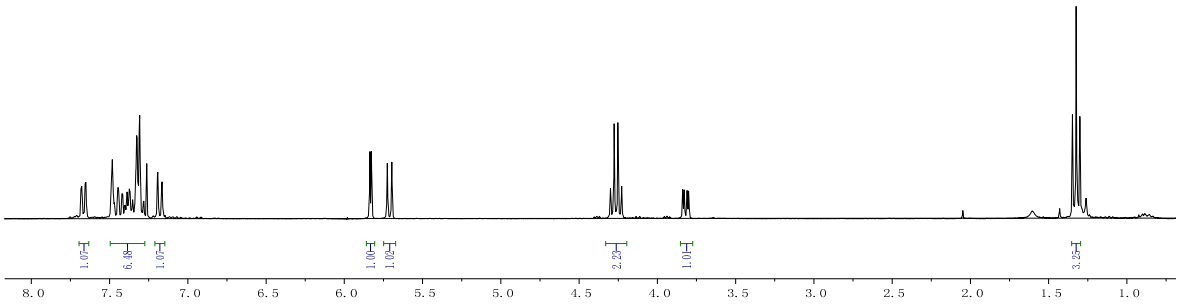
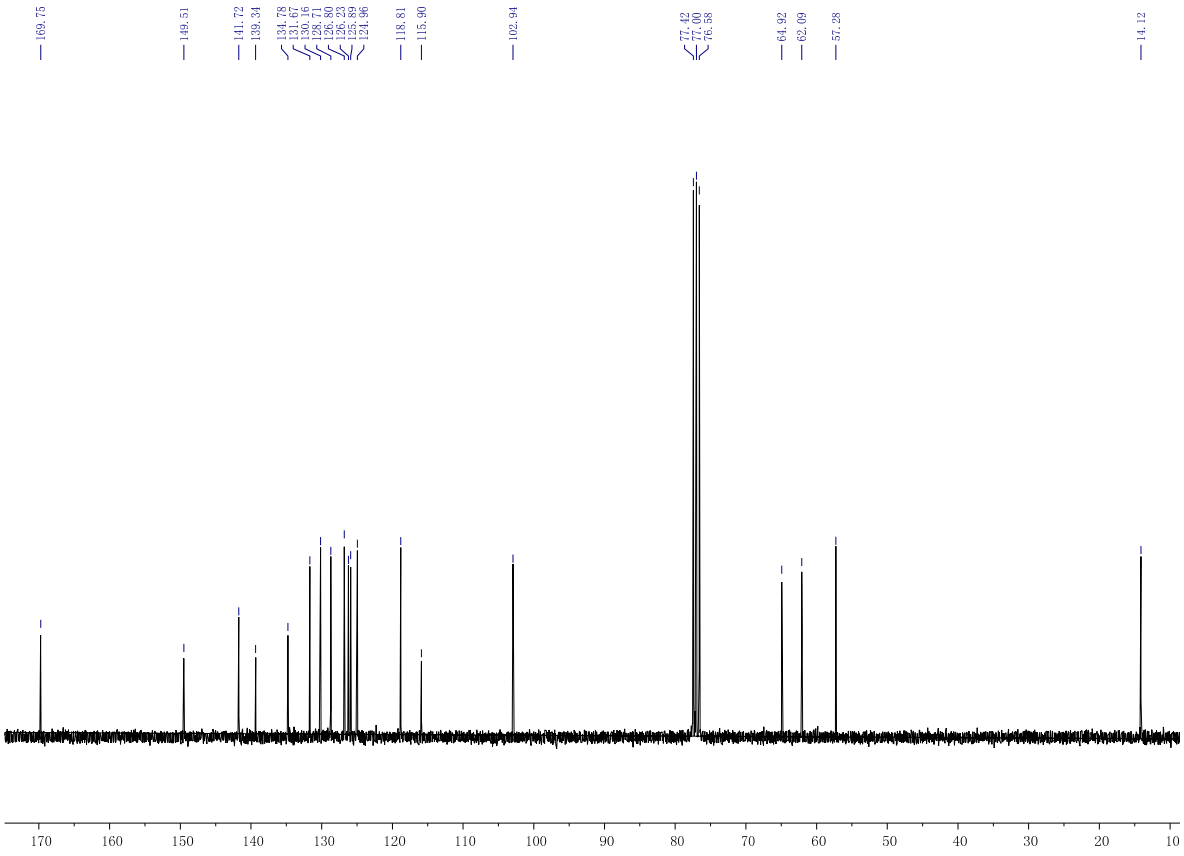


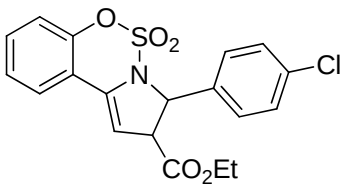




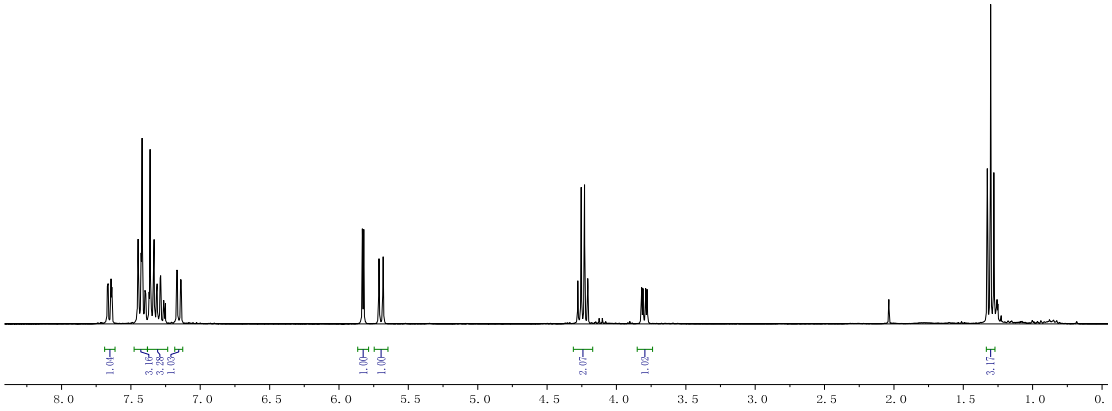
4ag

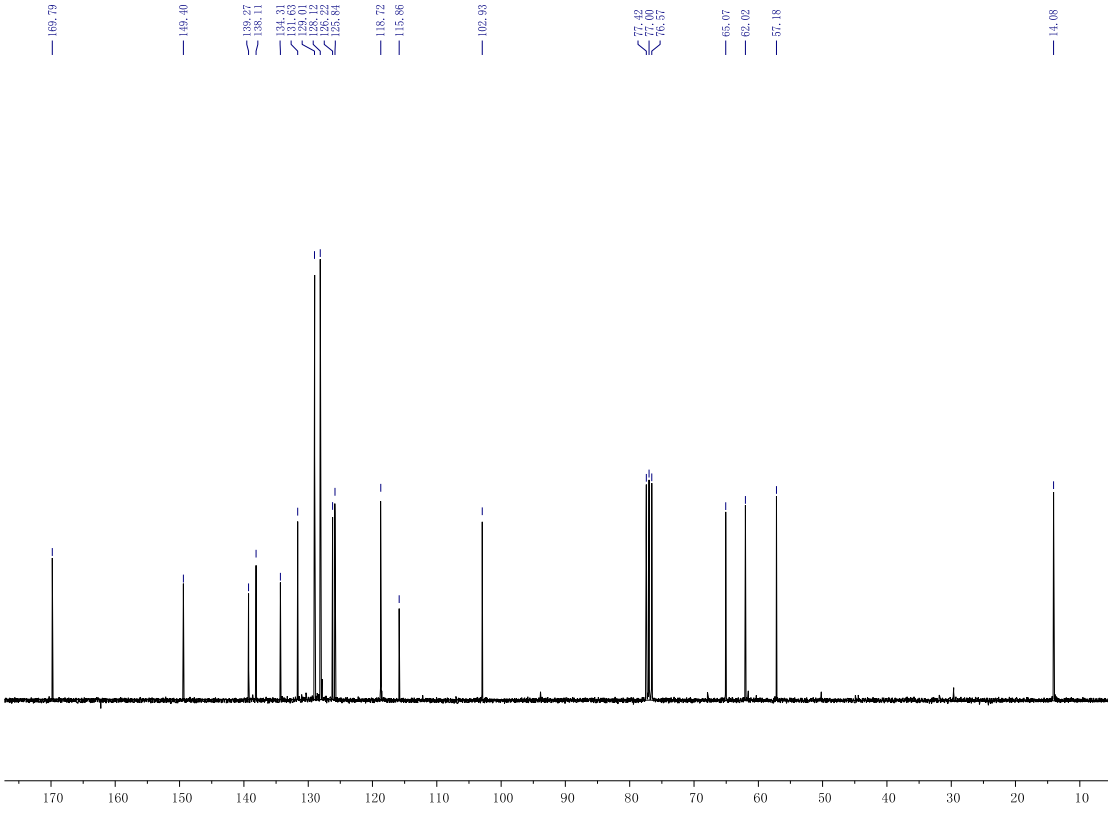


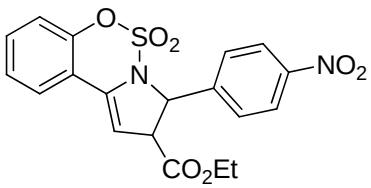




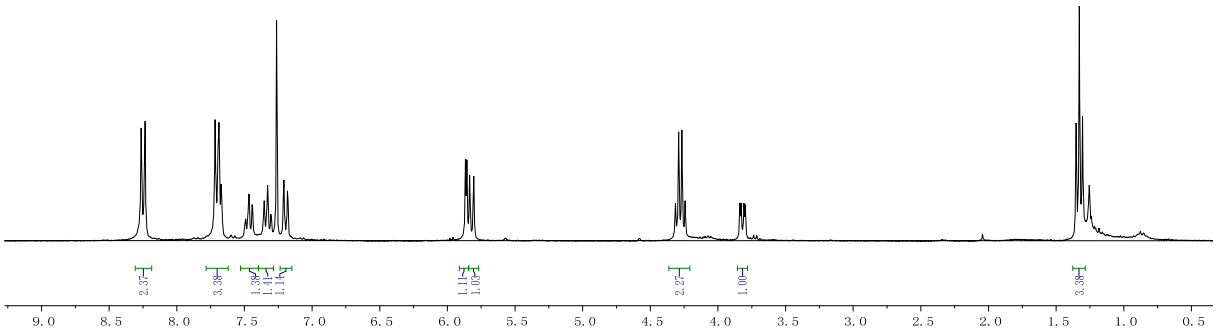
4ah

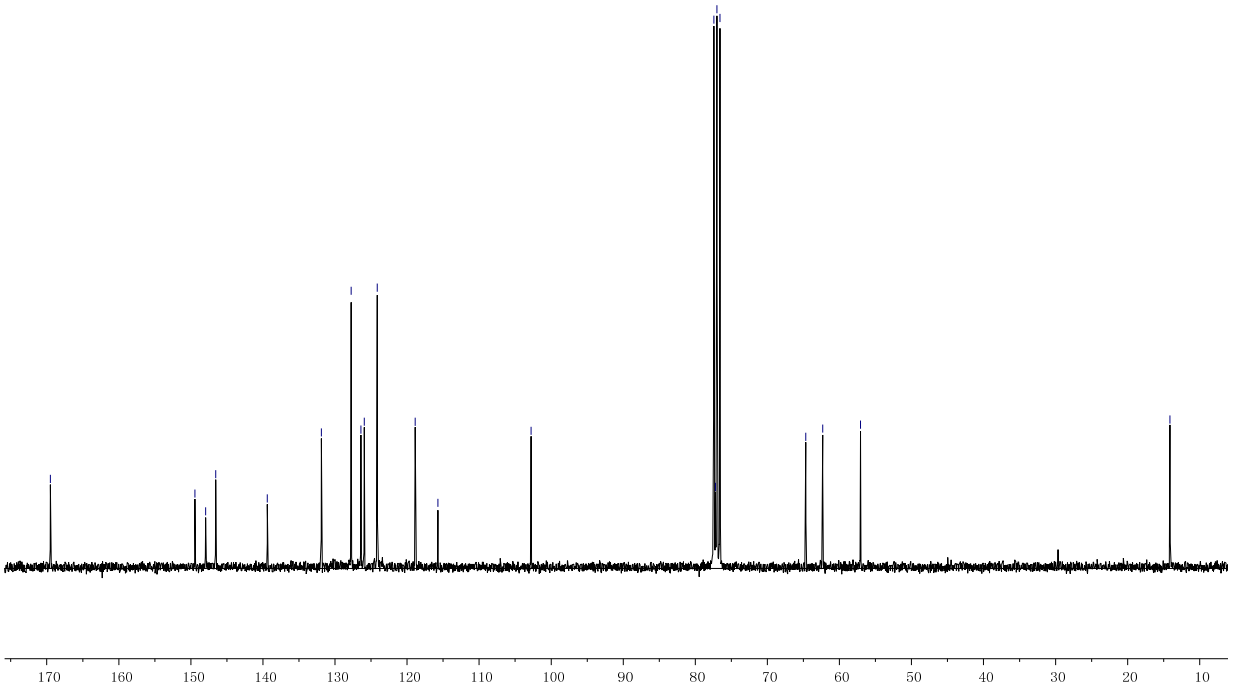






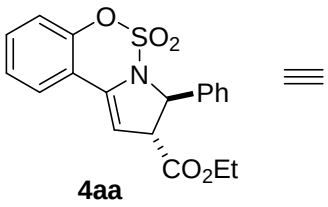
4ai





X-Ray Crystallographic Data

Crystallographic data for **4aa** have been deposited with the Cambridge Crystallographic Data Centre as deposition number CCDC 938727. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.



4aa

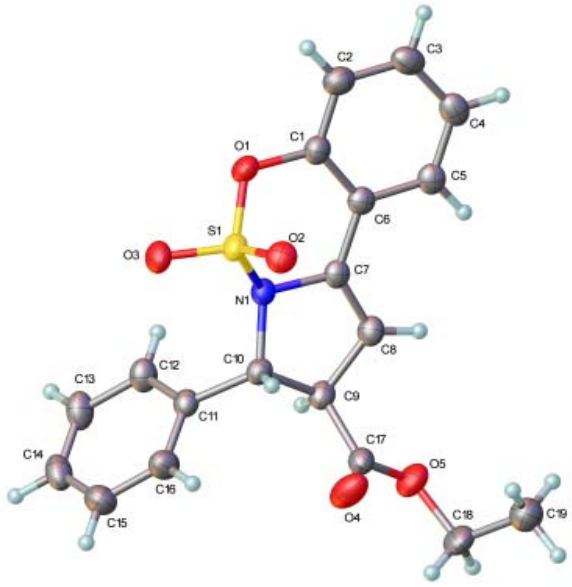


Table 1. Crystal data and structure refinement for **4aa**.

Identification code	**4aa**
Empirical formula	$C_{19}H_{17}NO_5S$
Formula weight	371.40
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 10.341(2) Å α= 90°.
	b = 10.832(2) Å β = 100.20(3) °.
	c = 15.797(3) Å γ = 90 °.
Volume	1741.4(6) $Å^3$
Z, Calculated density	4, 1.417 Mg/m^3
Absorption coefficient	0.217 mm^{-1}
F(000)	776

Crystal size	0.31 x 0.29 x 0.27 mm^3
Theta range for data collection	2.00 to 27.50 °.
Limiting indices	-13<=h<=13, -13<=k<=13, -20<=l<=20
Reflections collected / unique	14885 / 3977 [R(int) = 0.0396]
Completeness to theta = 27.50	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.6676
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3977 / 0 / 236
Goodness-of-fit on F^2	1.226
Final R indices [I>2sigma(I)]	R1 = 0.0531, wR2 = 0.1510
R indices (all data)	R1 = 0.0568, wR2 = 0.1585
Largest diff. peak and hole	0.323 and -0.335 e. $Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **4aa**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	6627(1)	2085(1)	455(1)	29(1)
O(1)	6492(1)	652(1)	616(1)	34(1)
O(2)	7054(2)	2265(2)	-343(1)	35(1)
O(3)	5429(1)	2624(2)	587(1)	39(1)
O(4)	10136(2)	5398(2)	1005(1)	55(1)
O(5)	11703(2)	4541(2)	2000(1)	43(1)
N(1)	7787(2)	2407(2)	1282(1)	27(1)
C(1)	7647(2)	-71(2)	638(1)	30(1)
C(2)	7488(2)	-1249(2)	307(1)	36(1)
C(3)	8595(2)	-1981(2)	346(2)	37(1)
C(4)	9832(2)	-1523(2)	697(1)	35(1)

C(5)	9964(2)	-329(2)	1012(1)	30(1)
C(6)	8858(2)	427(2)	998(1)	27(1)
C(7)	8979(2)	1696(2)	1305(1)	26(1)
C(8)	10030(2)	2366(2)	1630(1)	29(1)
C(9)	9629(2)	3647(2)	1836(1)	29(1)
C(10)	8183(2)	3742(2)	1380(1)	27(1)
C(11)	7342(2)	4514(2)	1870(1)	27(1)
C(12)	6837(2)	4046(2)	2563(1)	35(1)
C(13)	6183(2)	4826(2)	3045(2)	40(1)
C(14)	6026(2)	6055(2)	2842(2)	43(1)
C(15)	6516(3)	6524(2)	2153(2)	46(1)
C(16)	7169(2)	5746(2)	1666(2)	40(1)
C(17)	10488(2)	4646(2)	1550(1)	32(1)
C(18)	12693(2)	5380(2)	1768(2)	46(1)
C(19)	13370(3)	4798(3)	1113(2)	50(1)

Table 3. Bond lengths [Å] and angles [°] for **4aa**.

S(1)-O(3)	1.4179(15)
S(1)-O(2)	1.4205(16)
S(1)-O(1)	1.5832(16)
S(1)-N(1)	1.6475(18)
O(1)-C(1)	1.424(3)
O(4)-C(17)	1.195(3)
O(5)-C(17)	1.335(3)
O(5)-C(18)	1.463(3)
N(1)-C(7)	1.448(2)
N(1)-C(10)	1.503(3)
C(1)-C(2)	1.378(3)

C(1)-C(6)	1.390(3)
C(2)-C(3)	1.385(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.391(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.384(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.404(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.456(3)
C(7)-C(8)	1.332(3)
C(8)-C(9)	1.500(3)
C(8)-H(8)	0.9500
C(9)-C(17)	1.519(3)
C(9)-C(10)	1.544(3)
C(9)-H(9)	1.0000
C(10)-C(11)	1.514(3)
C(10)-H(10)	1.0000
C(11)-C(16)	1.376(3)
C(11)-C(12)	1.390(3)
C(12)-C(13)	1.391(3)
C(12)-H(12)	0.9500
C(13)-C(14)	1.372(4)
C(13)-H(13)	0.9500
C(14)-C(15)	1.377(4)
C(14)-H(14)	0.9500
C(15)-C(16)	1.393(3)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(18)-C(19)	1.488(4)

C(18)-H(18B)	0.9900
C(18)-H(18A)	0.9900
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
O(3)-S(1)-O(2)	119.45(10)
O(3)-S(1)-O(1)	106.01(9)
O(2)-S(1)-O(1)	109.13(9)
O(3)-S(1)-N(1)	109.15(9)
O(2)-S(1)-N(1)	112.17(9)
O(1)-S(1)-N(1)	98.75(9)
C(1)-O(1)-S(1)	116.48(13)
C(17)-O(5)-C(18)	116.7(2)
C(7)-N(1)-C(10)	107.10(15)
C(7)-N(1)-S(1)	113.82(13)
C(10)-N(1)-S(1)	115.60(13)
C(2)-C(1)-C(6)	123.5(2)
C(2)-C(1)-O(1)	117.24(19)
C(6)-C(1)-O(1)	119.21(18)
C(1)-C(2)-C(3)	118.1(2)
C(1)-C(2)-H(2)	120.9
C(3)-C(2)-H(2)	120.9
C(2)-C(3)-C(4)	120.5(2)
C(2)-C(3)-H(3)	119.7
C(4)-C(3)-H(3)	119.7
C(5)-C(4)-C(3)	120.1(2)
C(5)-C(4)-H(4)	119.9
C(3)-C(4)-H(4)	119.9
C(4)-C(5)-C(6)	120.8(2)
C(4)-C(5)-H(5)	119.6

C(6)-C(5)-H(5)	119.6
C(1)-C(6)-C(5)	116.92(19)
C(1)-C(6)-C(7)	121.35(18)
C(5)-C(6)-C(7)	121.66(19)
C(8)-C(7)-N(1)	110.65(18)
C(8)-C(7)-C(6)	131.18(19)
N(1)-C(7)-C(6)	118.16(17)
C(7)-C(8)-C(9)	110.44(18)
C(7)-C(8)-H(8)	124.8
C(9)-C(8)-H(8)	124.8
C(8)-C(9)-C(17)	113.33(17)
C(8)-C(9)-C(10)	104.06(16)
C(17)-C(9)-C(10)	112.50(17)
C(8)-C(9)-H(9)	108.9
C(17)-C(9)-H(9)	108.9
C(10)-C(9)-H(9)	108.9
N(1)-C(10)-C(11)	114.43(16)
N(1)-C(10)-C(9)	101.95(15)
C(11)-C(10)-C(9)	113.26(16)
N(1)-C(10)-H(10)	109.0
C(11)-C(10)-H(10)	109.0
C(9)-C(10)-H(10)	109.0
C(16)-C(11)-C(12)	119.12(19)
C(16)-C(11)-C(10)	118.59(19)
C(12)-C(11)-C(10)	122.05(19)
C(11)-C(12)-C(13)	119.8(2)
C(11)-C(12)-H(12)	120.1
C(13)-C(12)-H(12)	120.1
C(14)-C(13)-C(12)	120.7(2)
C(14)-C(13)-H(13)	119.7

C(12)-C(13)-H(13)	119.7
C(13)-C(14)-C(15)	119.9(2)
C(13)-C(14)-H(14)	120.1
C(15)-C(14)-H(14)	120.1
C(14)-C(15)-C(16)	119.7(2)
C(14)-C(15)-H(15)	120.2
C(16)-C(15)-H(15)	120.2
C(11)-C(16)-C(15)	120.9(2)
C(11)-C(16)-H(16)	119.6
C(15)-C(16)-H(16)	119.6
O(4)-C(17)-O(5)	125.4(2)
O(4)-C(17)-C(9)	125.5(2)
O(5)-C(17)-C(9)	109.07(19)
O(5)-C(18)-C(19)	110.3(2)
O(5)-C(18)-H(18B)	109.6
C(19)-C(18)-H(18B)	109.6
O(5)-C(18)-H(18A)	109.6
C(19)-C(18)-H(18A)	109.6
H(18B)-C(18)-H(18A)	108.1
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **4aa**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2 a^{*2} U^{11}$ + ... + 2 h k a* b* U^{12}]

	U11	U22	U33	U23	U13	U12
S(1)	21(1)	33(1)	31(1)	-4(1)	4(1)	-1(1)
O(1)	24(1)	33(1)	45(1)	-3(1)	8(1)	-6(1)
O(2)	33(1)	42(1)	28(1)	-2(1)	3(1)	-1(1)
O(3)	23(1)	43(1)	52(1)	-8(1)	5(1)	2(1)
O(4)	36(1)	48(1)	79(1)	20(1)	4(1)	-7(1)
O(5)	27(1)	51(1)	50(1)	-2(1)	4(1)	-8(1)
N(1)	23(1)	30(1)	27(1)	-4(1)	5(1)	0(1)
C(1)	28(1)	34(1)	29(1)	1(1)	9(1)	0(1)
C(2)	38(1)	35(1)	36(1)	-1(1)	9(1)	-6(1)
C(3)	51(1)	29(1)	34(1)	2(1)	16(1)	-1(1)
C(4)	42(1)	34(1)	30(1)	9(1)	14(1)	8(1)
C(5)	32(1)	34(1)	24(1)	6(1)	8(1)	3(1)
C(6)	29(1)	30(1)	22(1)	3(1)	7(1)	0(1)
C(7)	26(1)	31(1)	21(1)	3(1)	7(1)	1(1)
C(8)	26(1)	35(1)	26(1)	1(1)	3(1)	2(1)
C(9)	25(1)	36(1)	25(1)	-5(1)	5(1)	-2(1)
C(10)	25(1)	31(1)	25(1)	-2(1)	6(1)	-2(1)
C(11)	23(1)	33(1)	26(1)	-4(1)	4(1)	0(1)
C(12)	33(1)	42(1)	30(1)	4(1)	10(1)	5(1)
C(13)	34(1)	56(2)	32(1)	-2(1)	10(1)	8(1)
C(14)	32(1)	53(2)	43(1)	-18(1)	7(1)	6(1)
C(15)	45(1)	33(1)	62(2)	-6(1)	16(1)	1(1)
C(16)	44(1)	34(1)	46(1)	-1(1)	20(1)	-3(1)
C(17)	25(1)	32(1)	39(1)	-9(1)	7(1)	-2(1)
C(18)	29(1)	43(1)	66(2)	-13(1)	9(1)	-10(1)
C(19)	45(1)	46(2)	61(2)	-3(1)	17(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **4aa**.

	x	y	z	U(eq)
H(2)	6643	-1551	59	43
H(3)	8510	-2802	132	44
H(4)	10586	-2031	720	41
H(5)	10813	-18	1240	35
H(8)	10910	2073	1720	35
H(9)	9665	3716	2471	34
H(10)	8154	4110	797	32
H(12)	6939	3195	2707	41
H(13)	5840	4504	3520	48
H(14)	5580	6581	3177	51
H(15)	6410	7375	2010	55
H(16)	7499	6069	1188	48
H(18B)	13345	5584	2288	55
H(18A)	12267	6157	1536	55
H(19A)	12731	4636	589	75
H(19B)	13773	4019	1340	75
H(19C)	14053	5356	980	75

Table 6. Torsion angles [°] for **4aa**.

O(3)-S(1)-O(1)-C(1)	-171.55(14)
O(2)-S(1)-O(1)-C(1)	58.59(16)
N(1)-S(1)-O(1)-C(1)	-58.64(15)
O(3)-S(1)-N(1)-C(7)	167.76(14)
O(2)-S(1)-N(1)-C(7)	-57.54(16)
O(1)-S(1)-N(1)-C(7)	57.35(15)
O(3)-S(1)-N(1)-C(10)	-67.63(16)

O(2)-S(1)-N(1)-C(10)	67.07(15)
O(1)-S(1)-N(1)-C(10)	-178.04(13)
S(1)-O(1)-C(1)-C(2)	-144.83(17)
S(1)-O(1)-C(1)-C(6)	36.1(2)
C(6)-C(1)-C(2)-C(3)	1.0(3)
O(1)-C(1)-C(2)-C(3)	-178.06(18)
C(1)-C(2)-C(3)-C(4)	-1.2(3)
C(2)-C(3)-C(4)-C(5)	0.1(3)
C(3)-C(4)-C(5)-C(6)	1.2(3)
C(2)-C(1)-C(6)-C(5)	0.3(3)
O(1)-C(1)-C(6)-C(5)	179.32(17)
C(2)-C(1)-C(6)-C(7)	177.29(19)
O(1)-C(1)-C(6)-C(7)	-3.7(3)
C(4)-C(5)-C(6)-C(1)	-1.4(3)
C(4)-C(5)-C(6)-C(7)	-178.35(18)
C(10)-N(1)-C(7)-C(8)	16.9(2)
S(1)-N(1)-C(7)-C(8)	145.94(15)
C(10)-N(1)-C(7)-C(6)	-163.88(16)
S(1)-N(1)-C(7)-C(6)	-34.8(2)
C(1)-C(6)-C(7)-C(8)	-176.7(2)
C(5)-C(6)-C(7)-C(8)	0.1(3)
C(1)-C(6)-C(7)-N(1)	4.3(3)
C(5)-C(6)-C(7)-N(1)	-178.92(17)
N(1)-C(7)-C(8)-C(9)	-2.0(2)
C(6)-C(7)-C(8)-C(9)	178.93(19)
C(7)-C(8)-C(9)-C(17)	-135.64(19)
C(7)-C(8)-C(9)-C(10)	-13.1(2)
C(7)-N(1)-C(10)-C(11)	-146.14(16)
S(1)-N(1)-C(10)-C(11)	85.84(18)
C(7)-N(1)-C(10)-C(9)	-23.50(18)

S(1)-N(1)-C(10)-C(9)	-151.52(13)
C(8)-C(9)-C(10)-N(1)	21.72(18)
C(17)-C(9)-C(10)-N(1)	144.79(16)
C(8)-C(9)-C(10)-C(11)	145.17(17)
C(17)-C(9)-C(10)-C(11)	-91.8(2)
N(1)-C(10)-C(11)-C(16)	-149.4(2)
C(9)-C(10)-C(11)-C(16)	94.3(2)
N(1)-C(10)-C(11)-C(12)	36.2(3)
C(9)-C(10)-C(11)-C(12)	-80.1(2)
C(16)-C(11)-C(12)-C(13)	-0.8(3)
C(10)-C(11)-C(12)-C(13)	173.6(2)
C(11)-C(12)-C(13)-C(14)	0.2(4)
C(12)-C(13)-C(14)-C(15)	0.2(4)
C(13)-C(14)-C(15)-C(16)	0.0(4)
C(12)-C(11)-C(16)-C(15)	1.0(4)
C(10)-C(11)-C(16)-C(15)	-173.5(2)
C(14)-C(15)-C(16)-C(11)	-0.6(4)
C(18)-O(5)-C(17)-O(4)	-3.3(3)
C(18)-O(5)-C(17)-C(9)	175.98(18)
C(8)-C(9)-C(17)-O(4)	114.0(3)
C(10)-C(9)-C(17)-O(4)	-3.7(3)
C(8)-C(9)-C(17)-O(5)	-65.2(2)
C(10)-C(9)-C(17)-O(5)	177.05(17)
C(17)-O(5)-C(18)-C(19)	-91.8(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **4aa** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)