

Electronic Supplementary Information

Phosphine-Promoted [4 + 3] Annulation of Allenolate with Aziridines for Synthesis of Tetrahydroazepines: Phosphine-Dependent [3 + 3] and [4 + 3] Pathways

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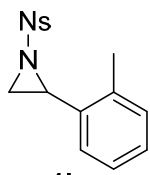
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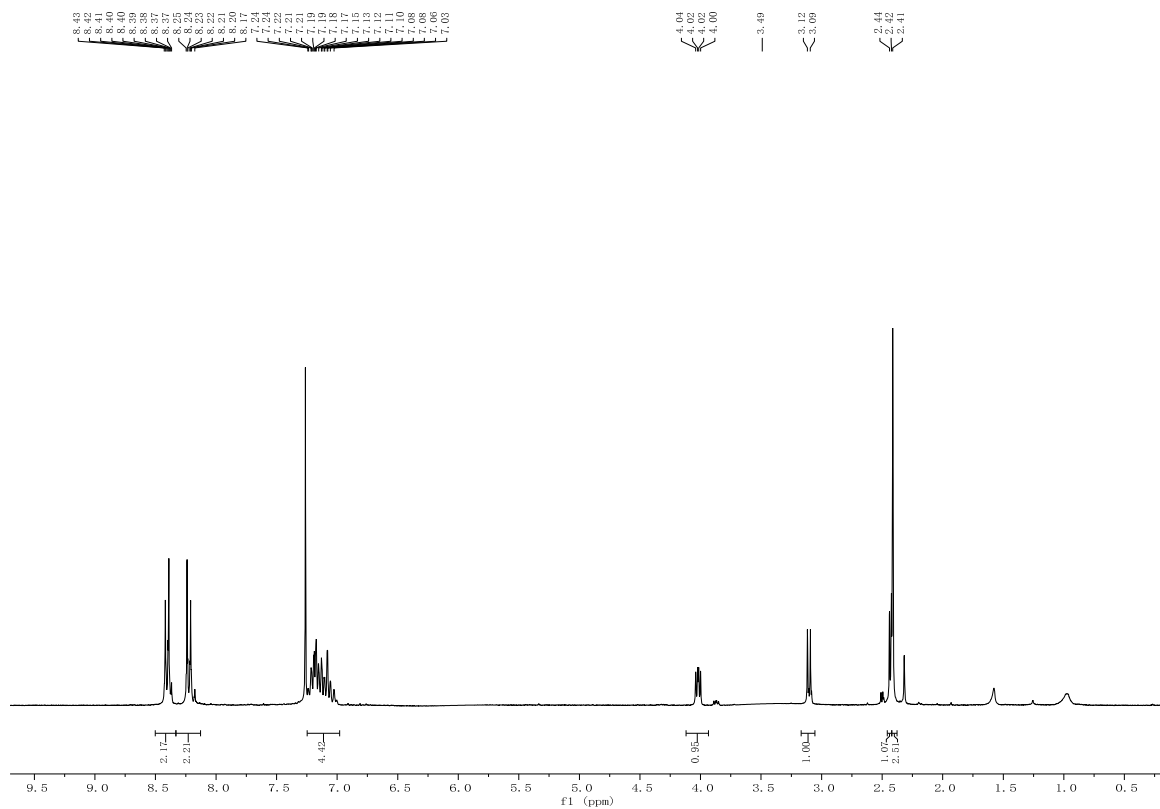
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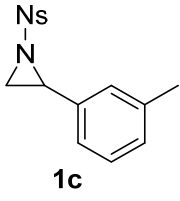
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¹H NMR Spectra of Substrates 1 and 2



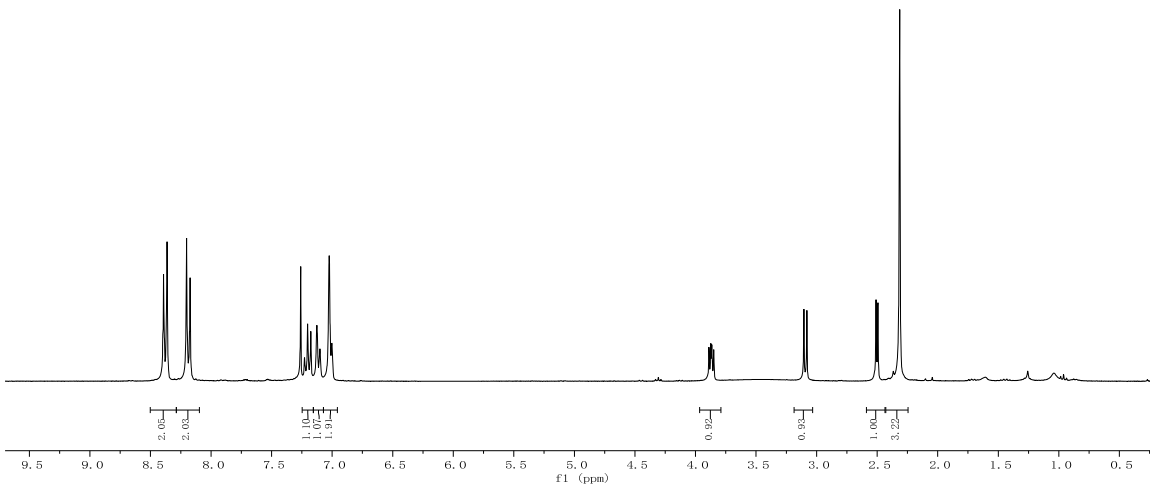
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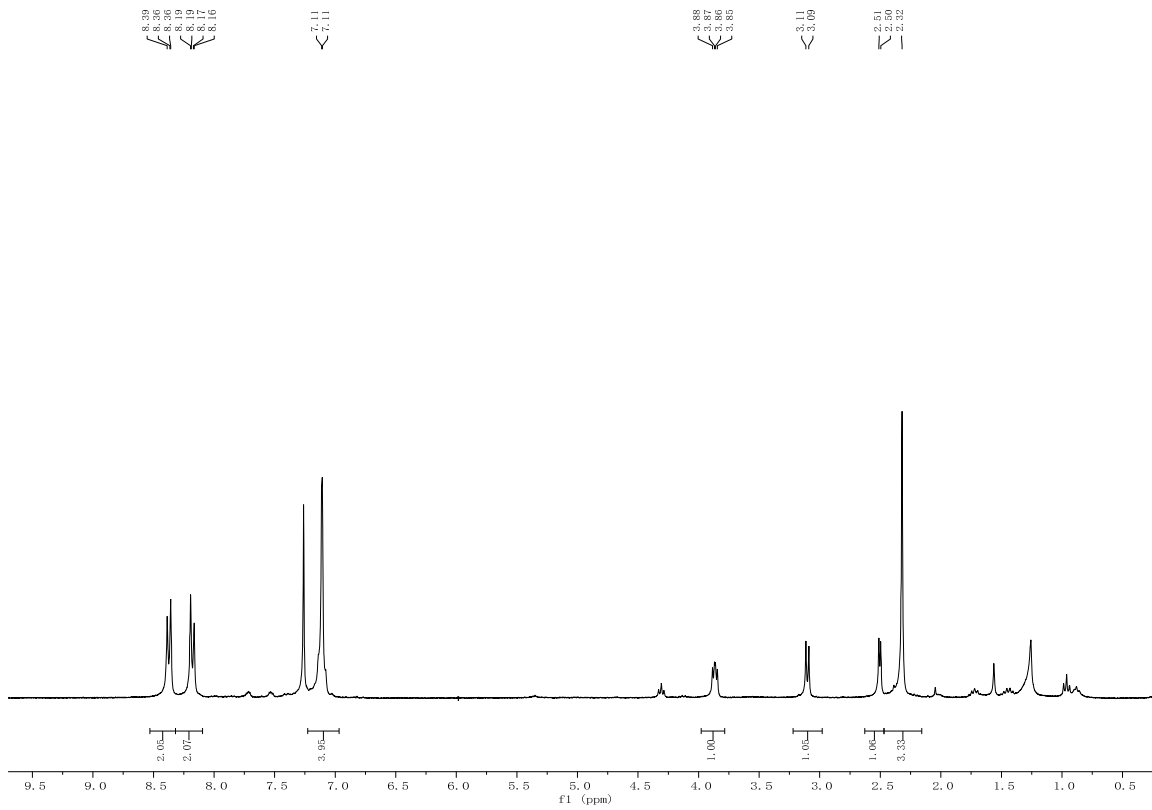
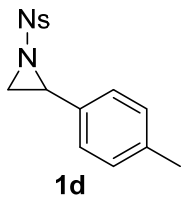


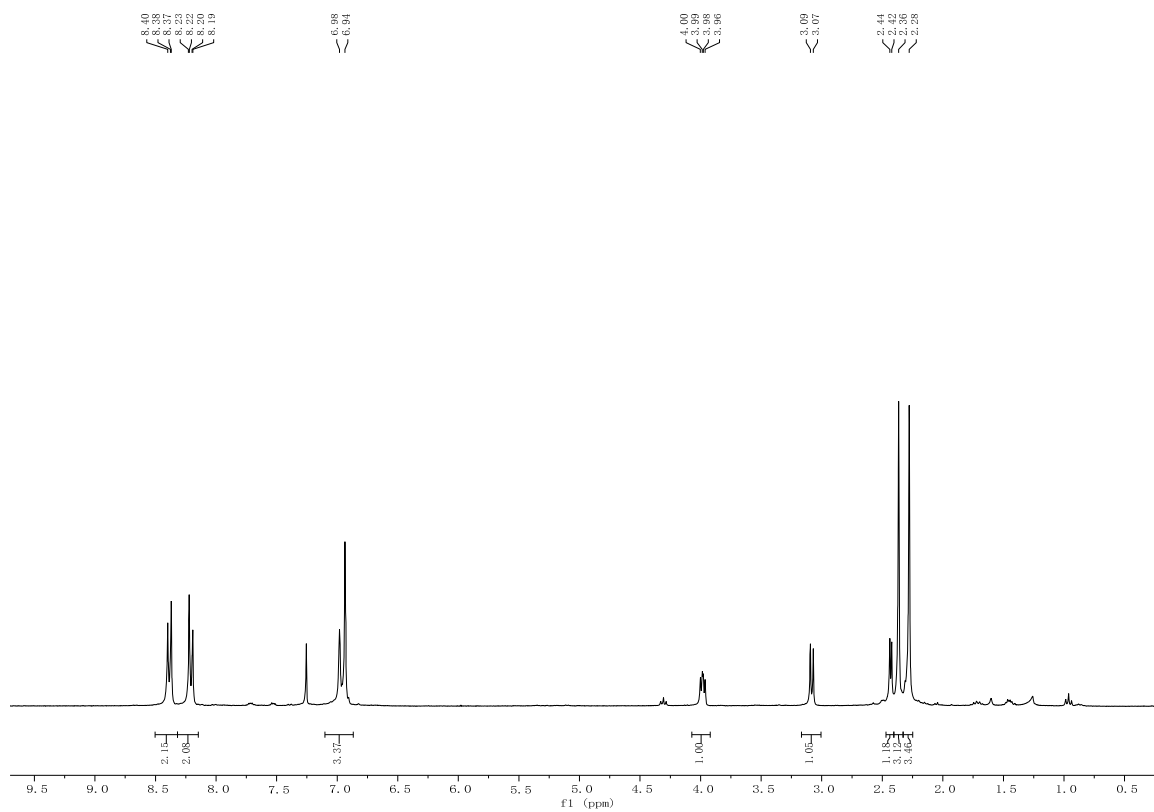
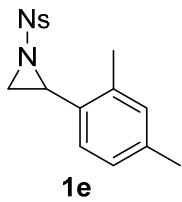


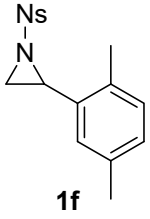
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2.31









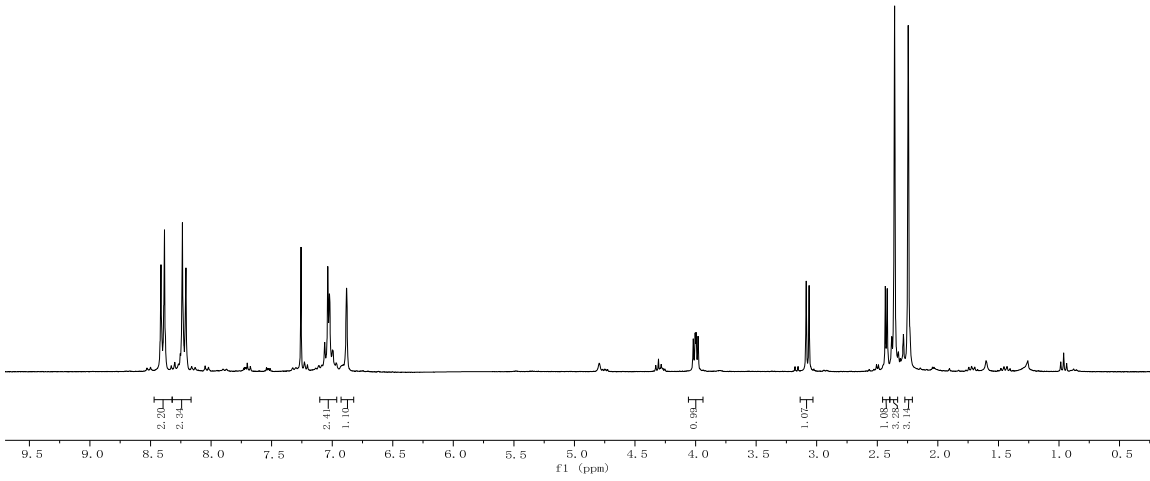
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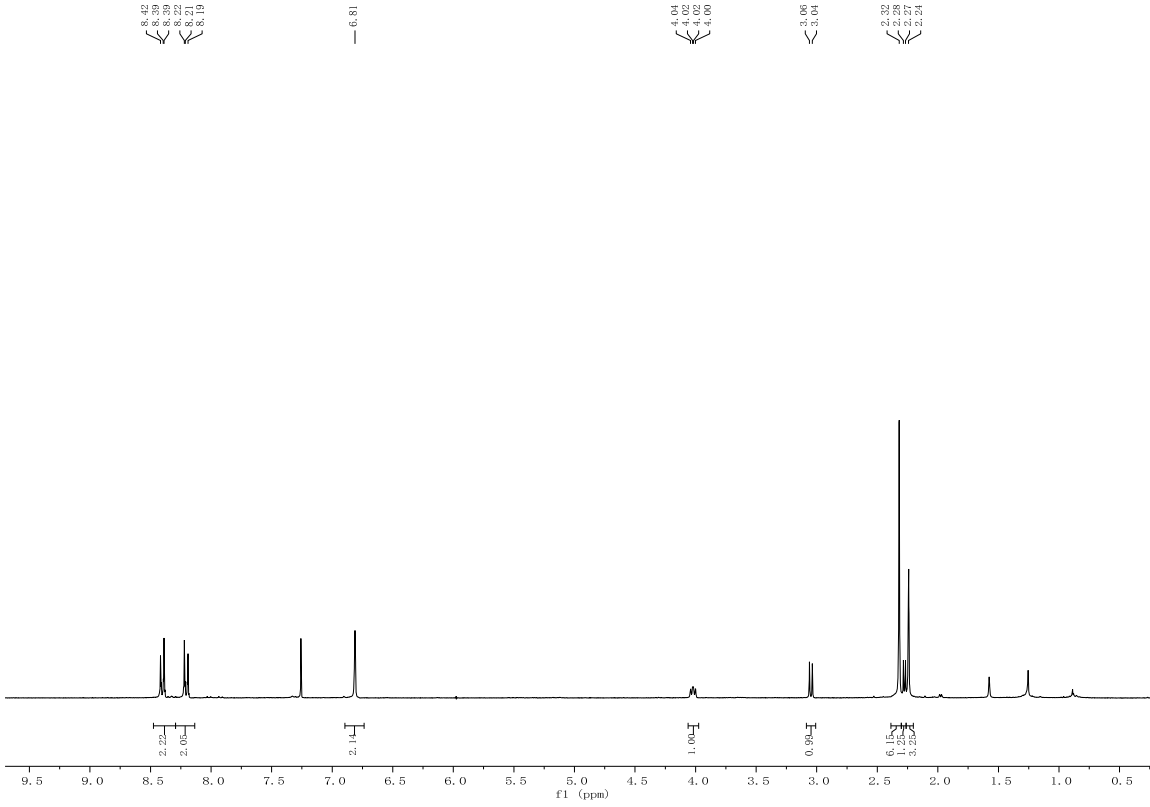
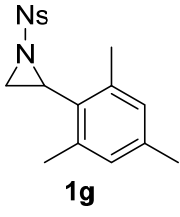
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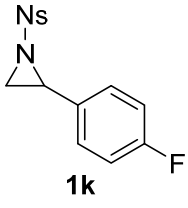
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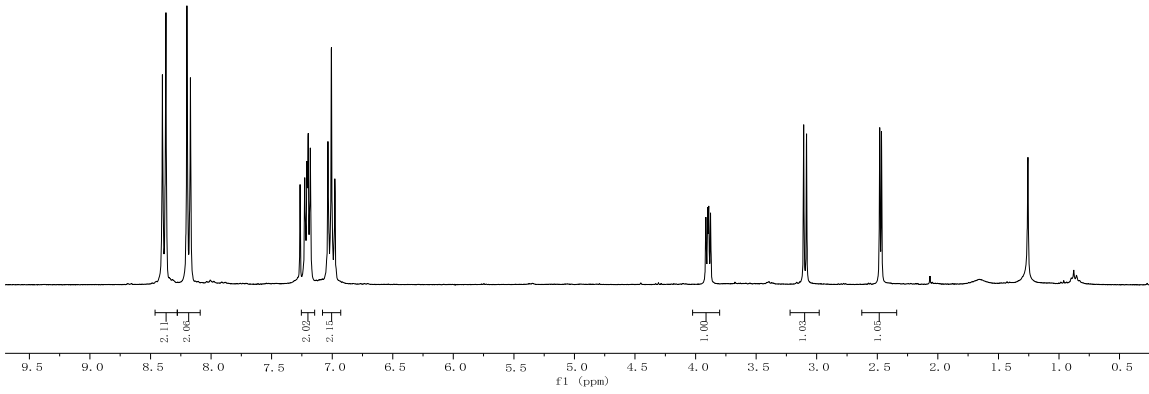


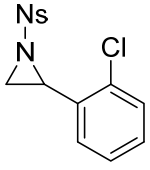
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 7.00
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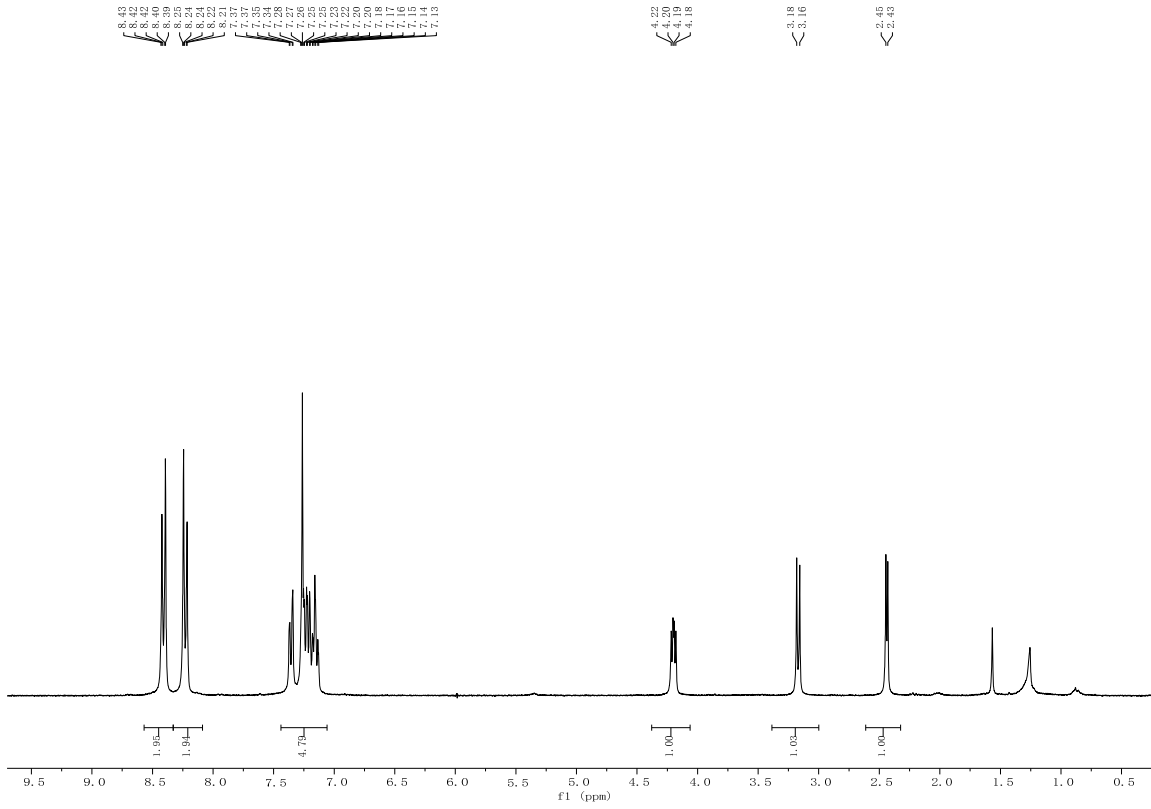
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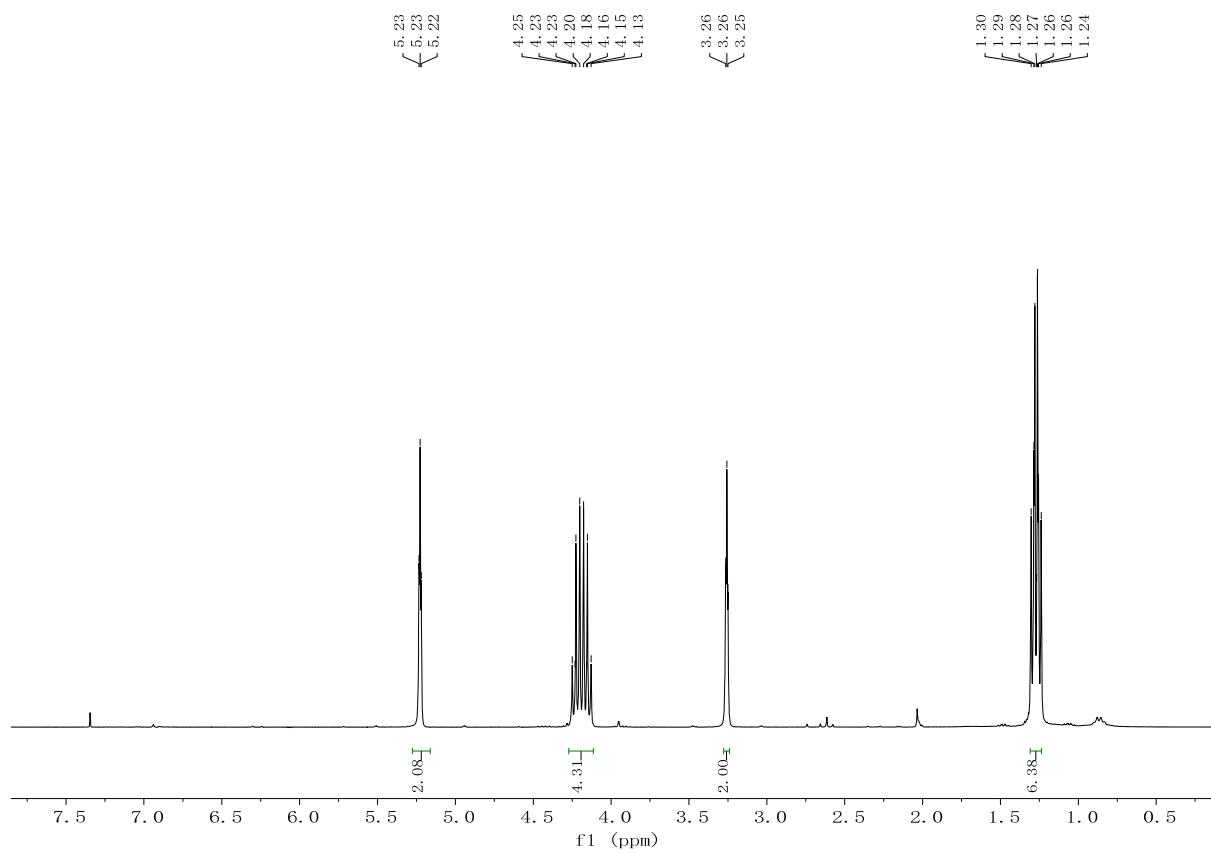
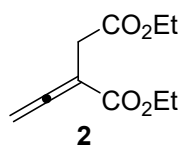
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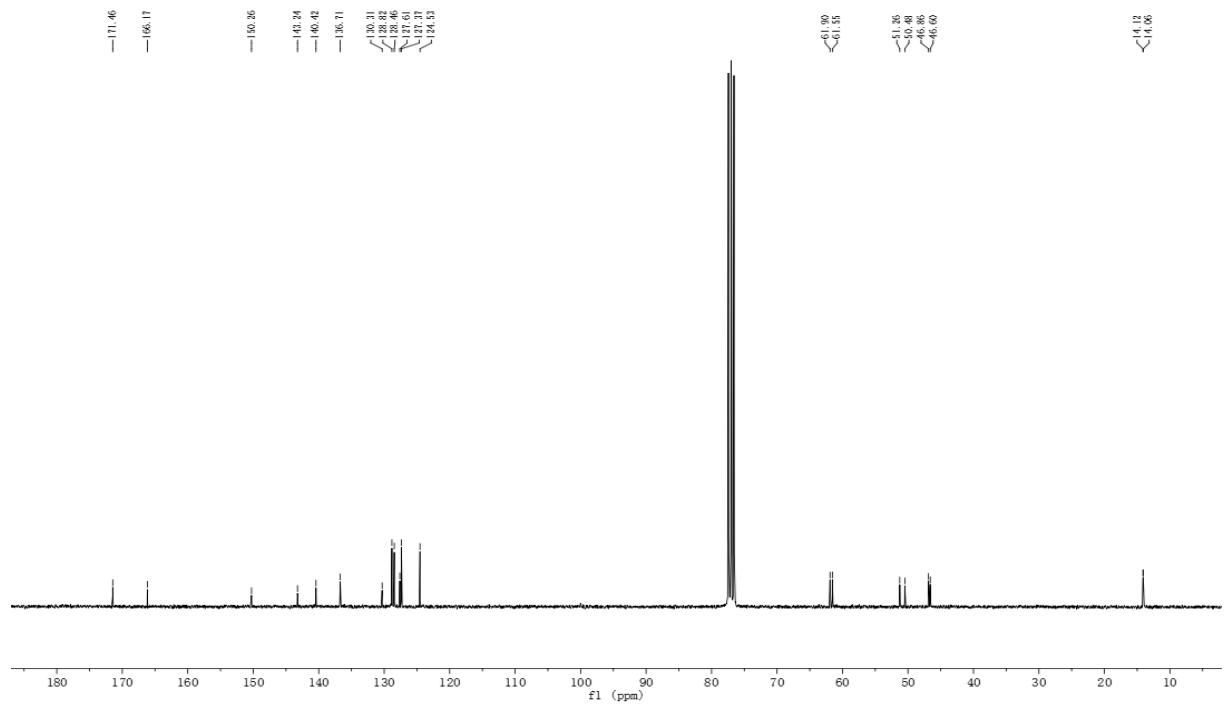
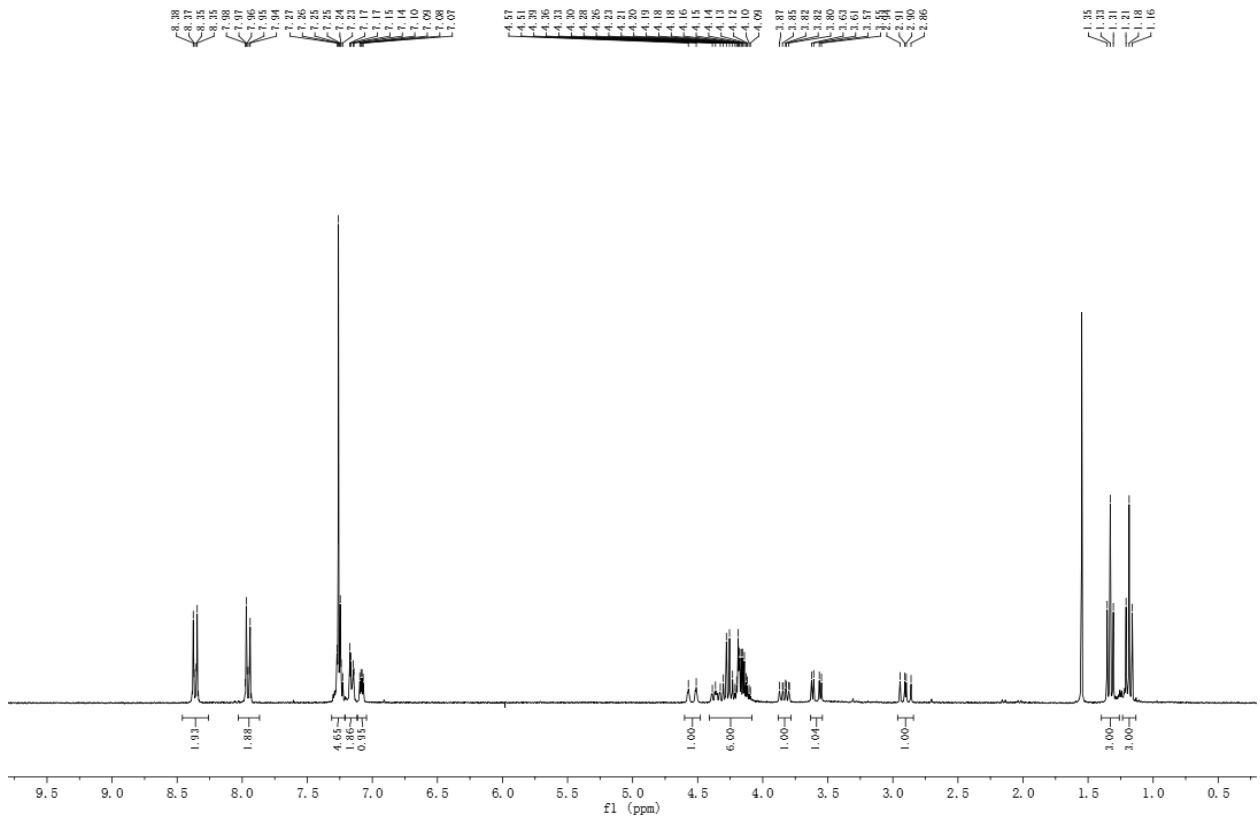
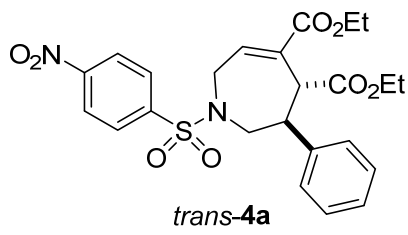


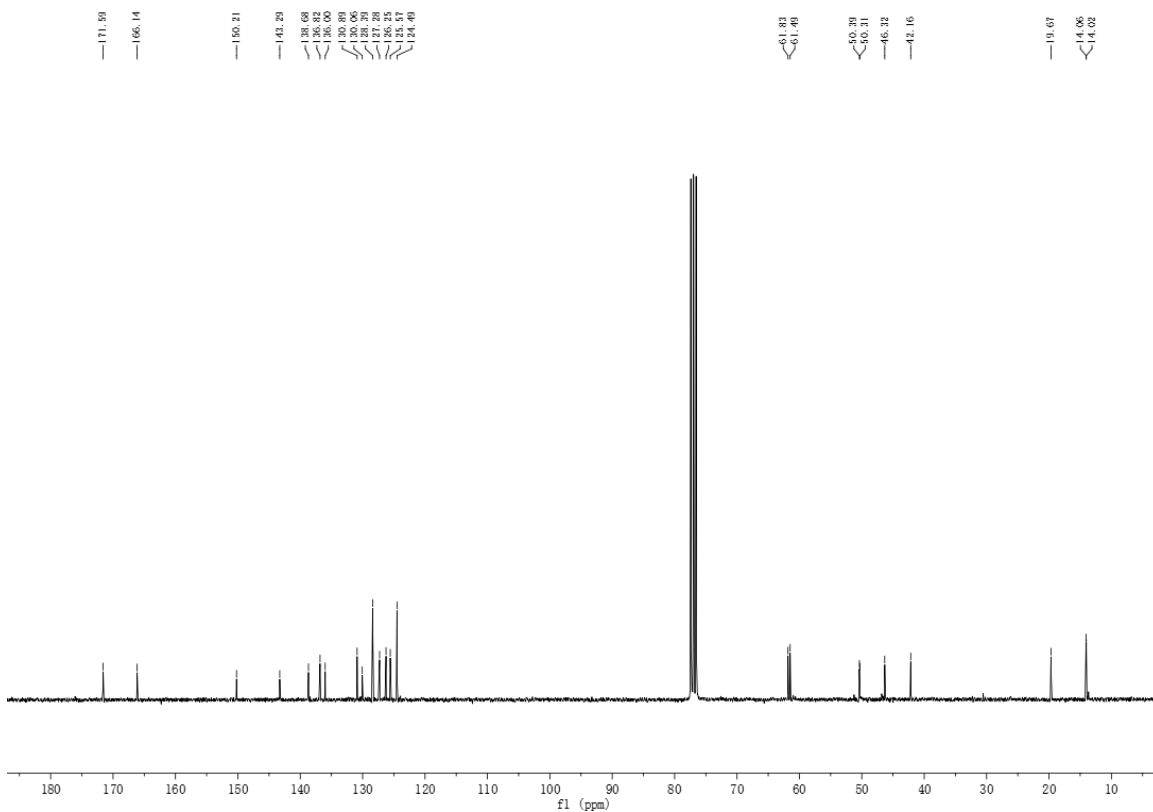
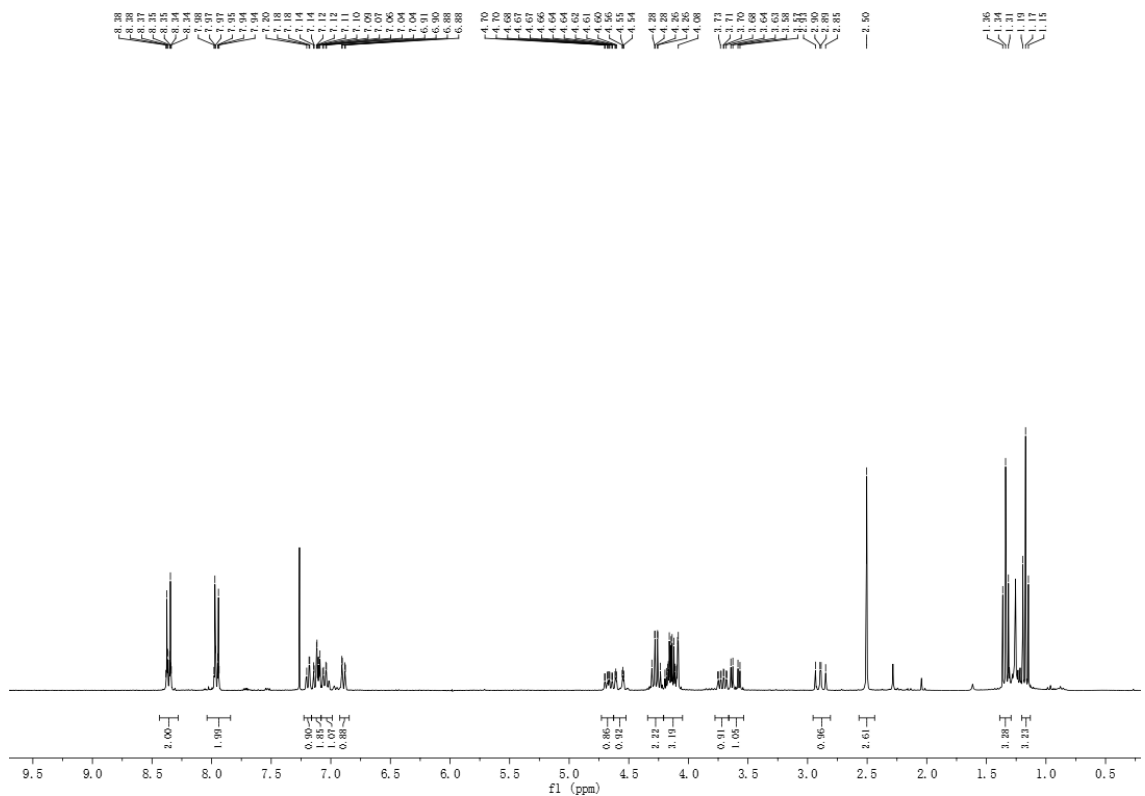
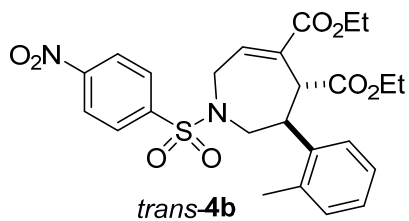
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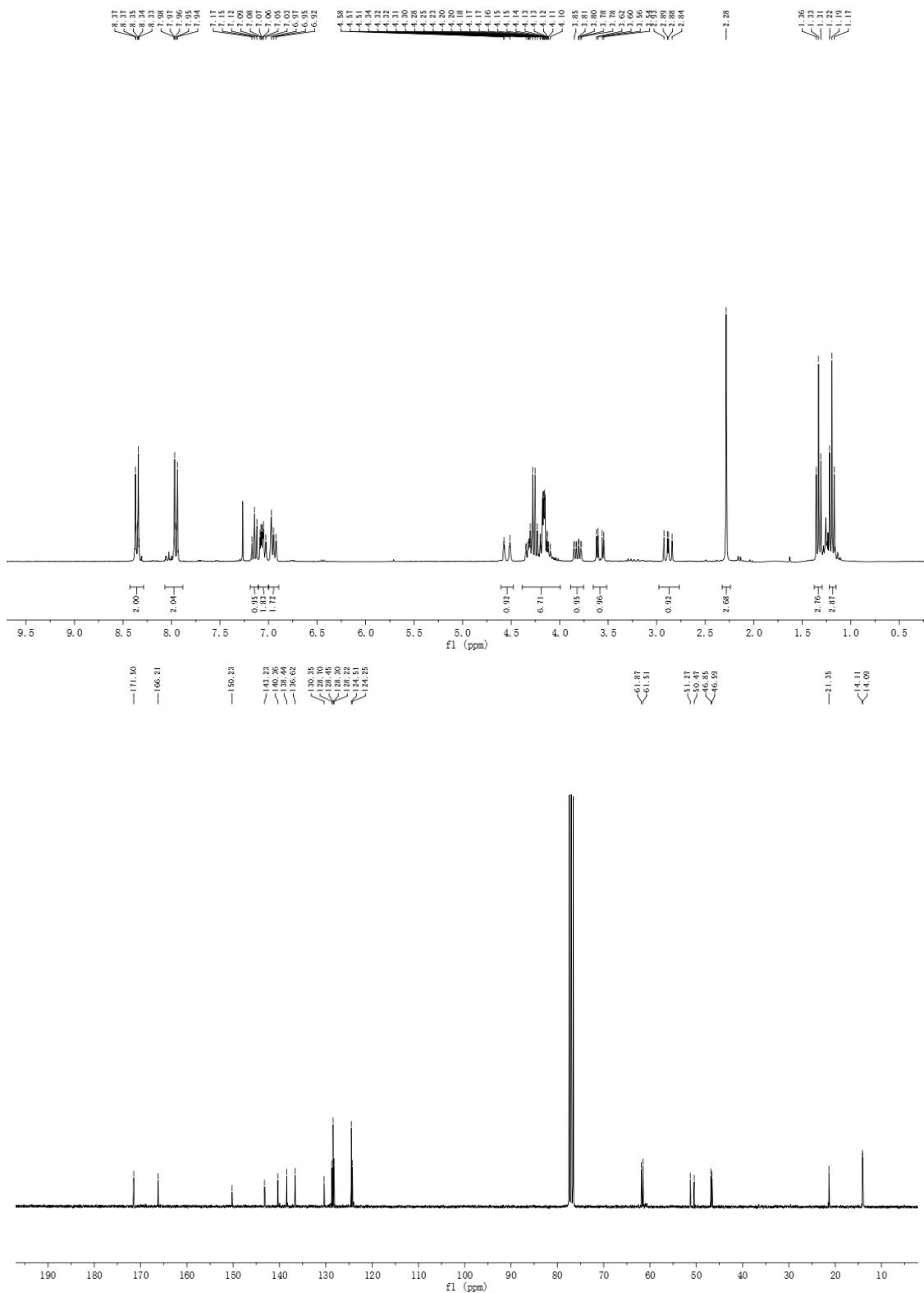
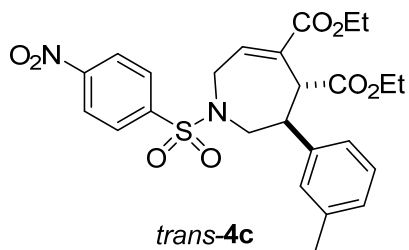


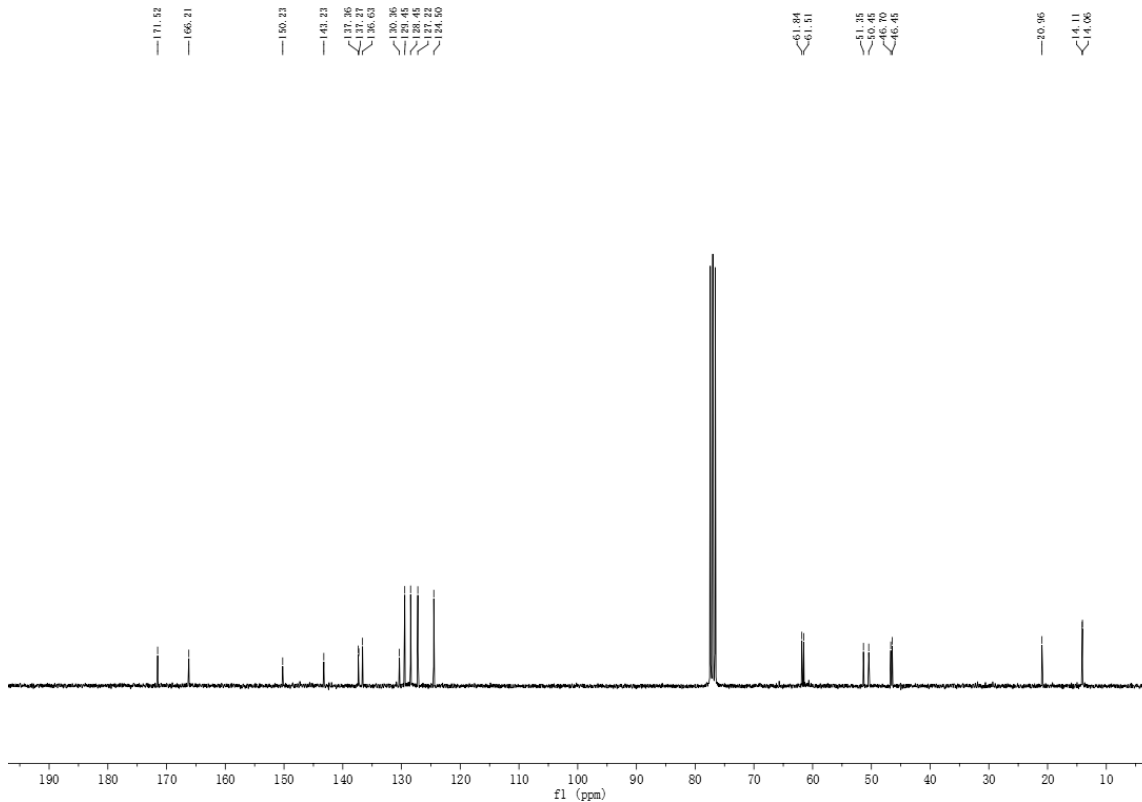
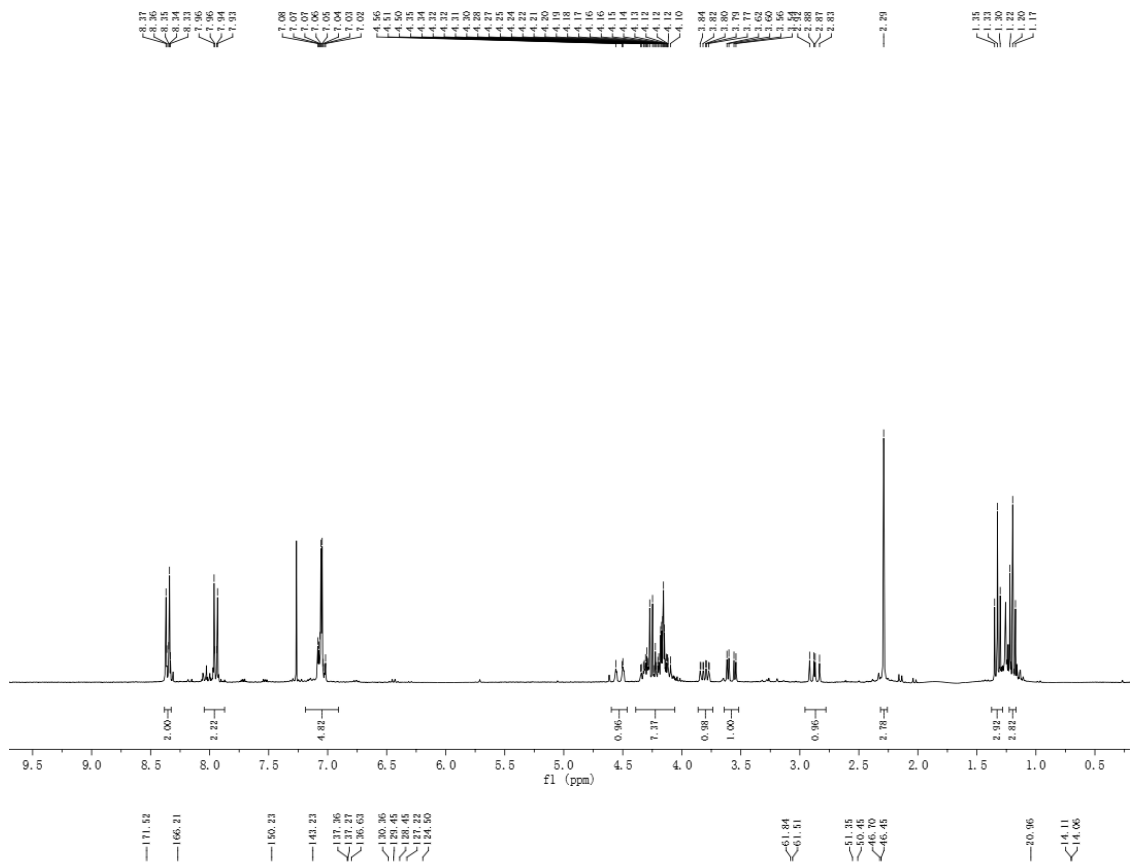
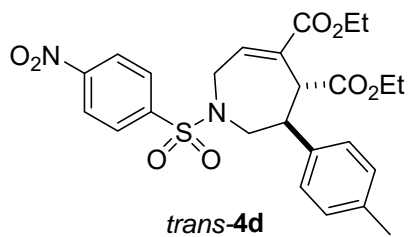


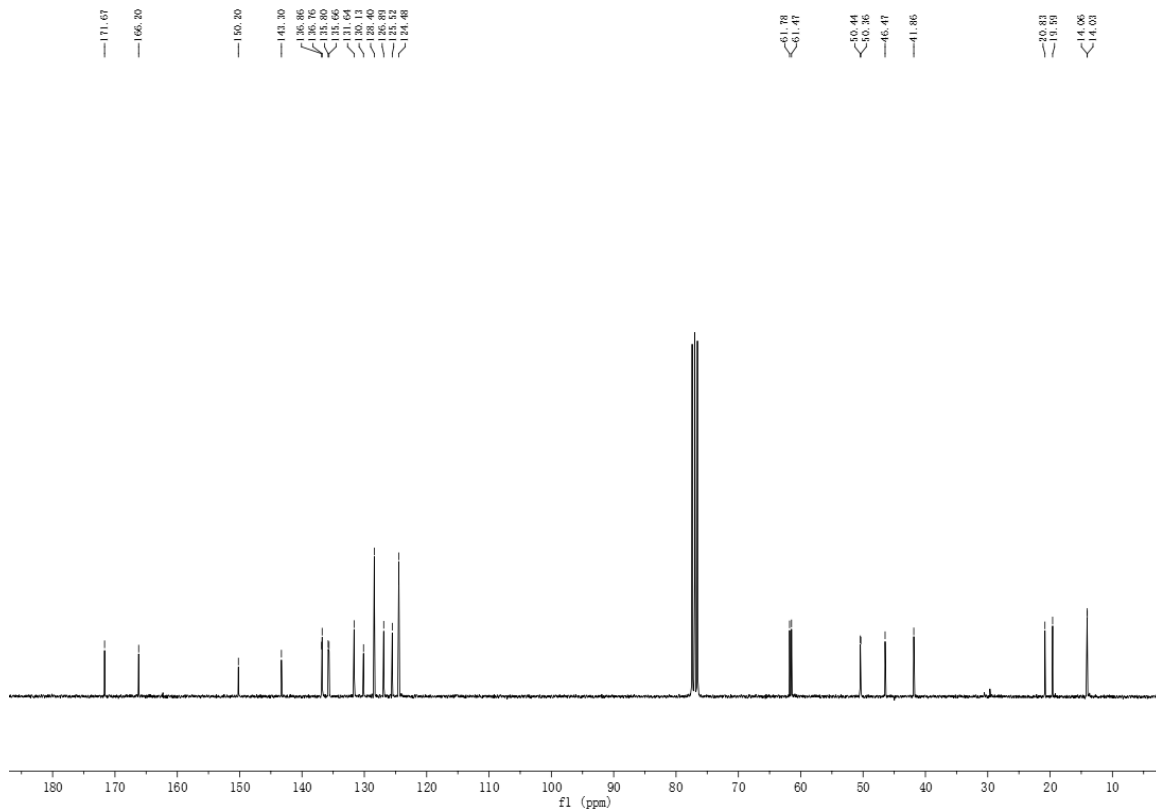
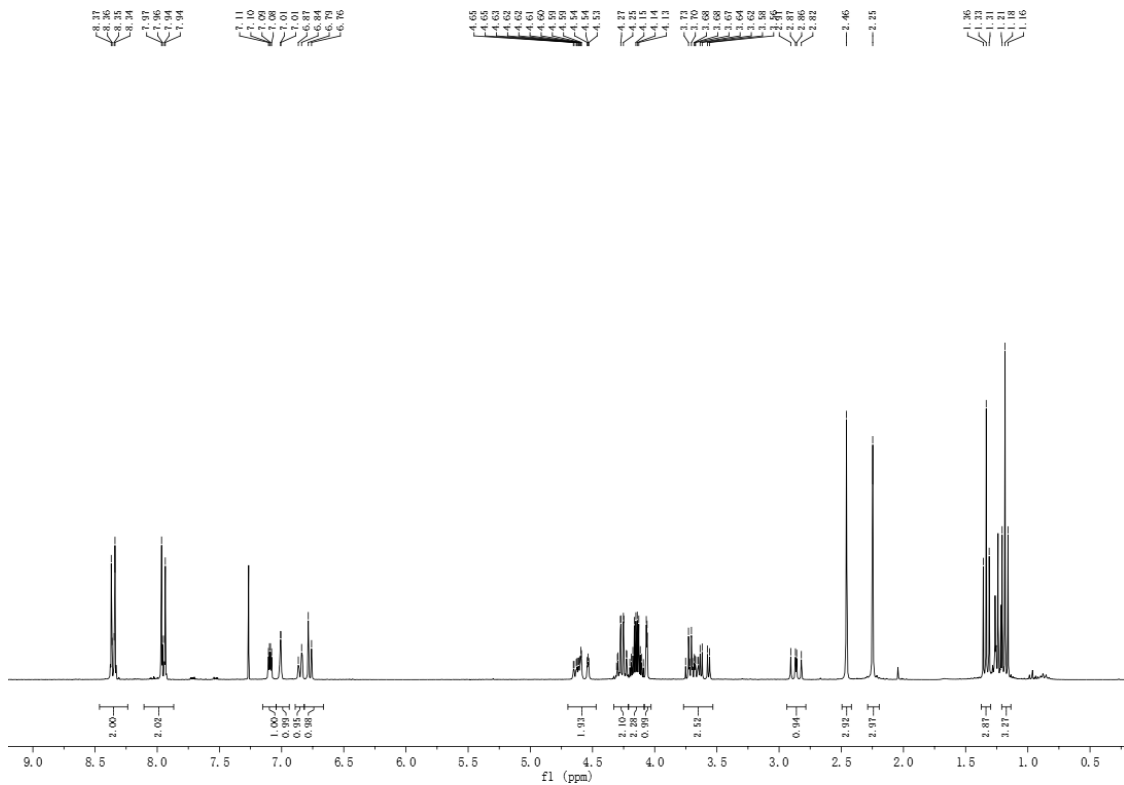
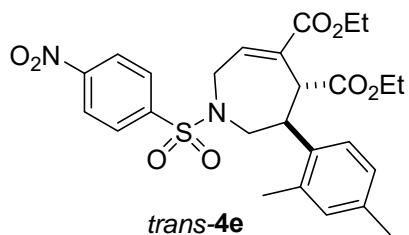
¹H and ¹³C NMR Spectra of All Products 4

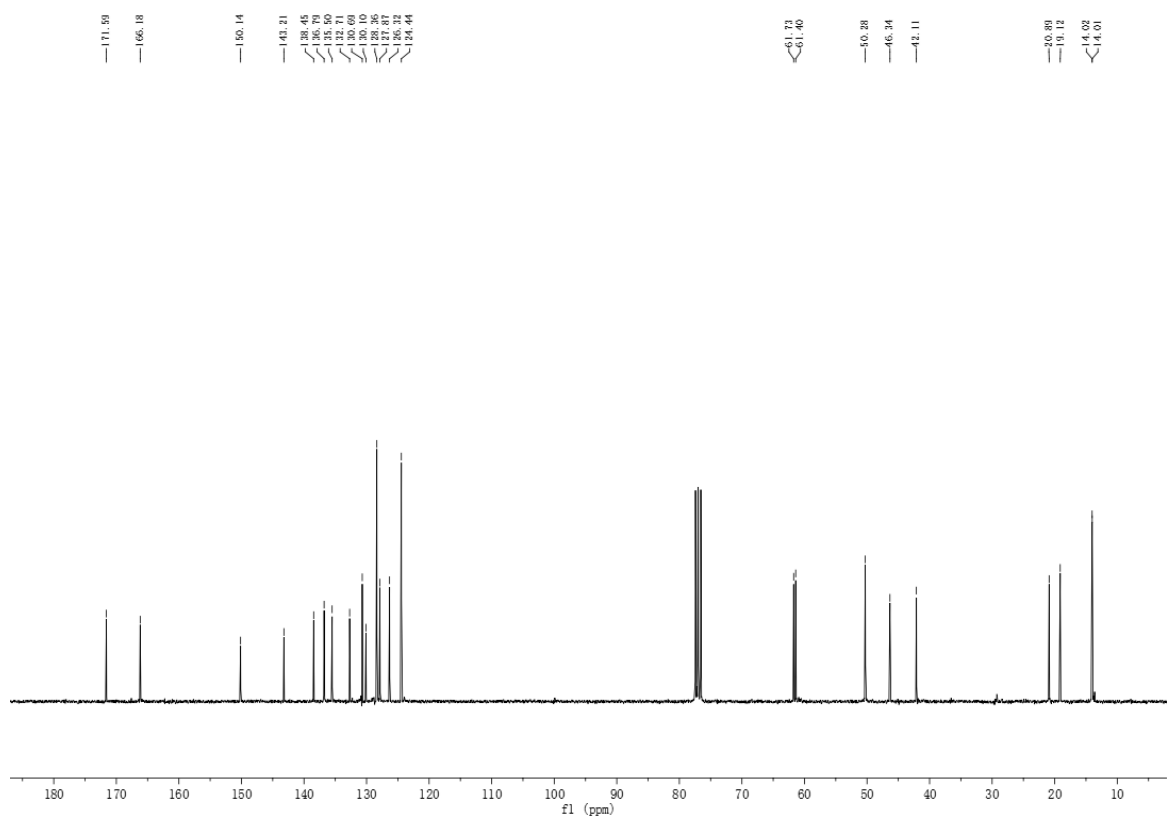
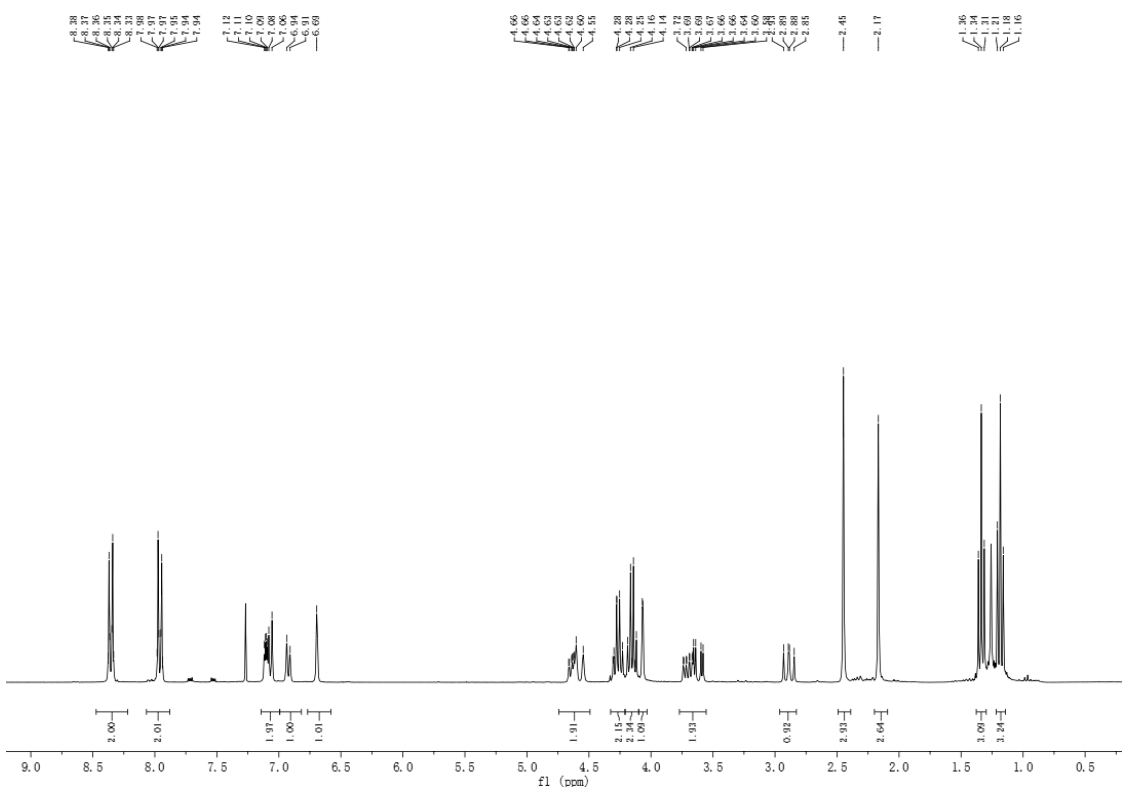
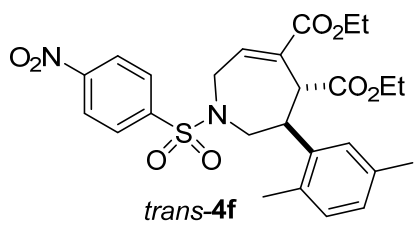


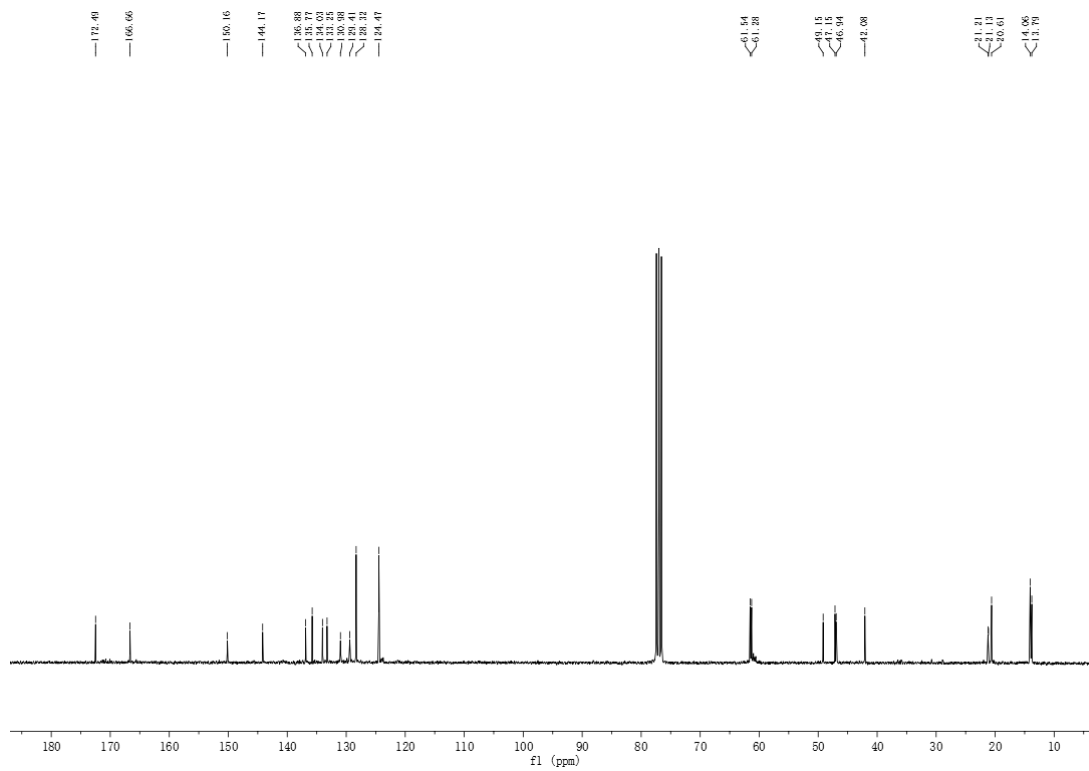
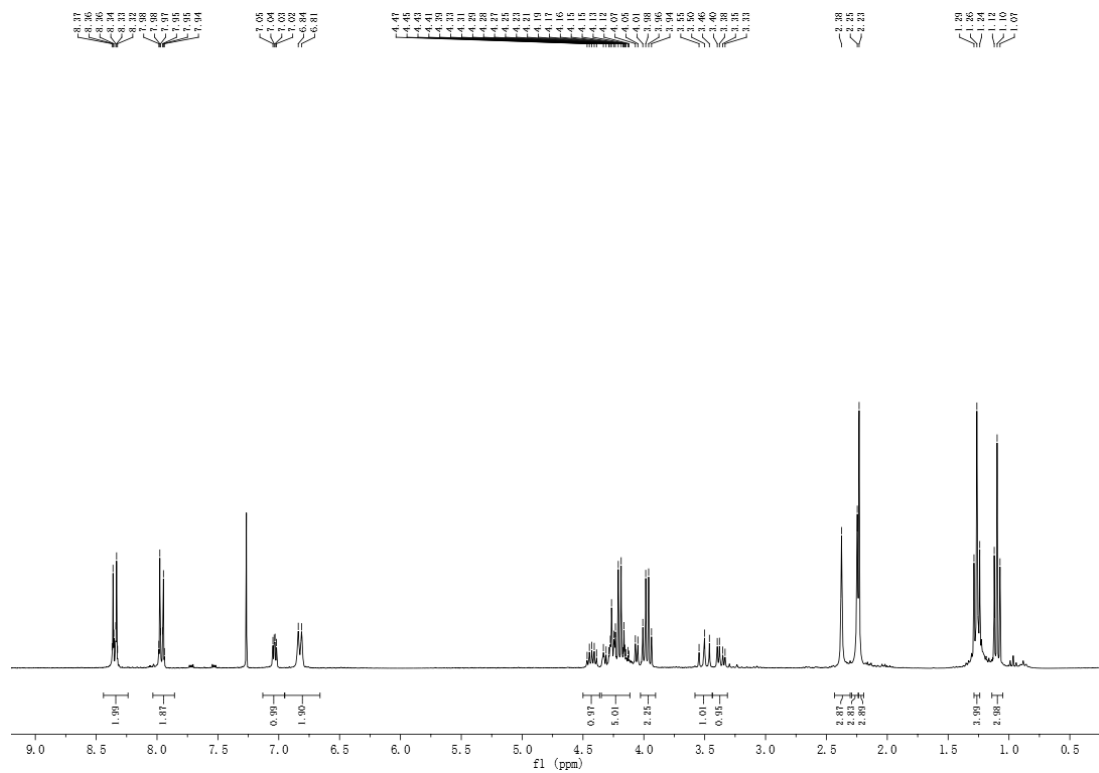
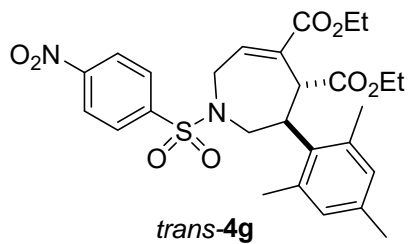


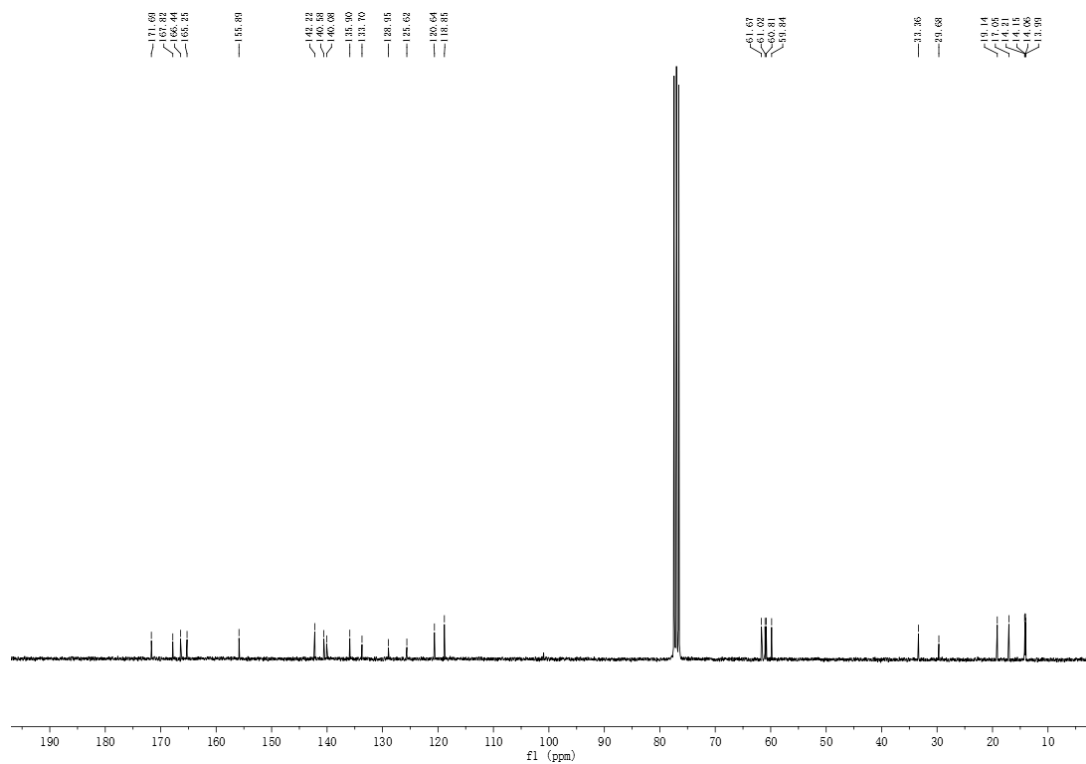
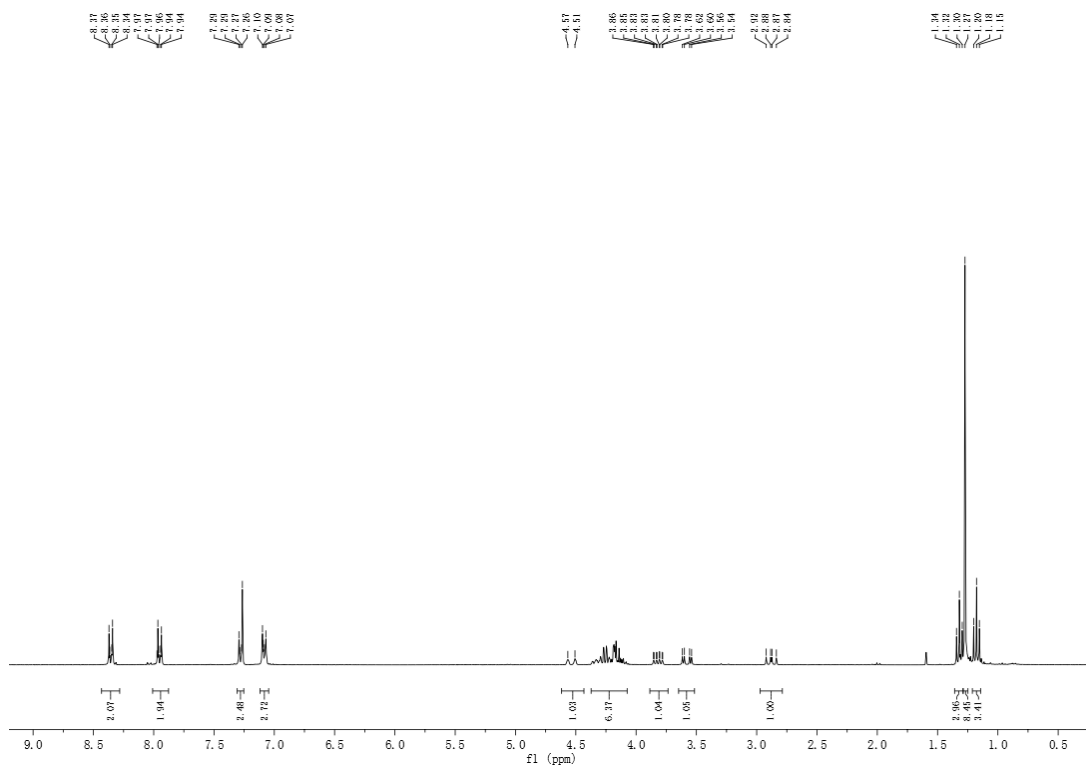
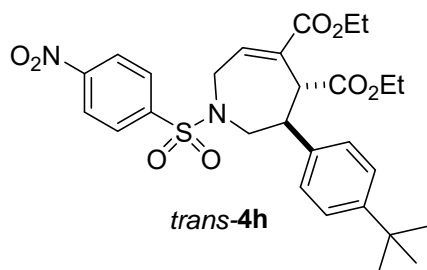


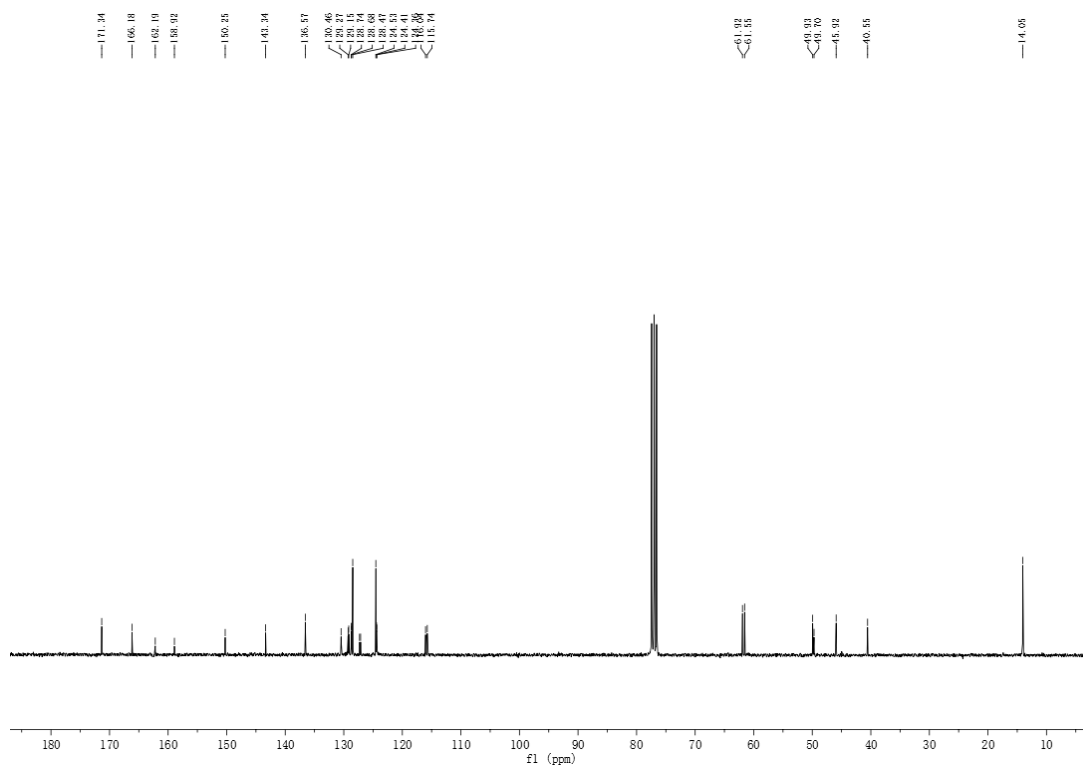
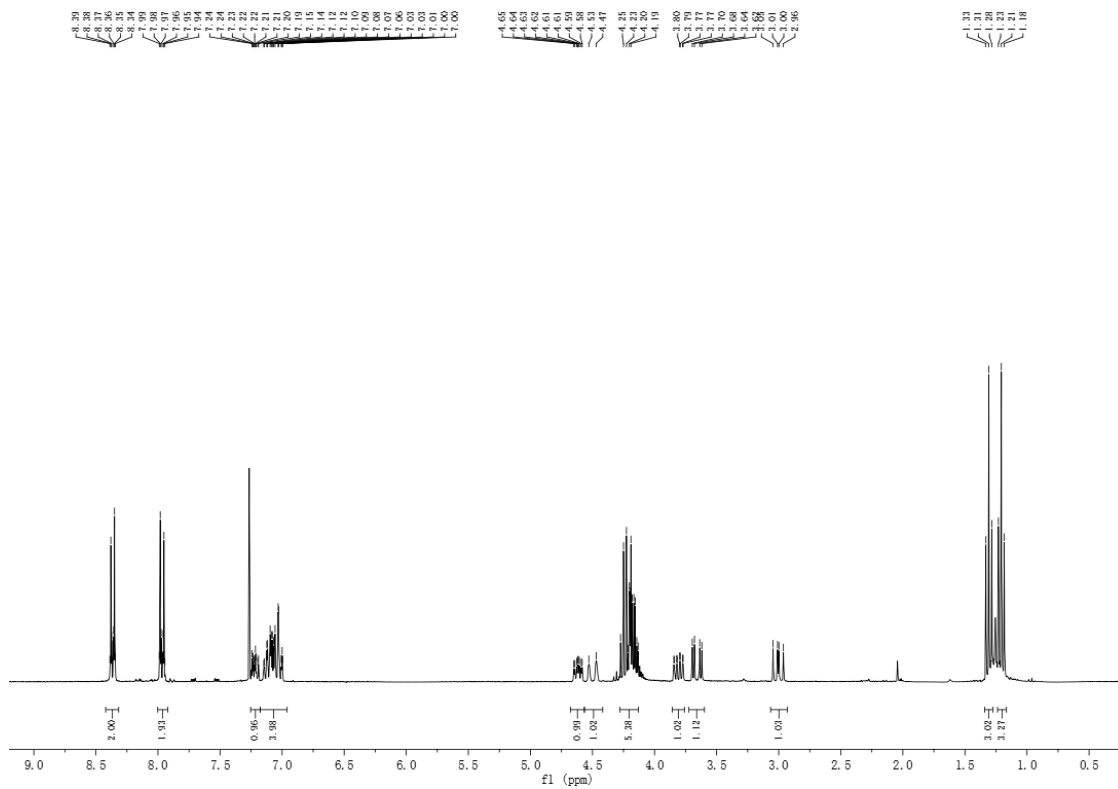
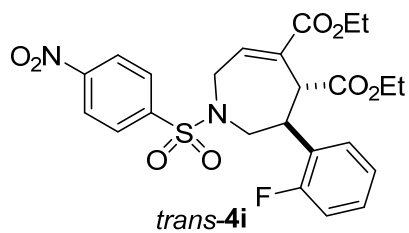


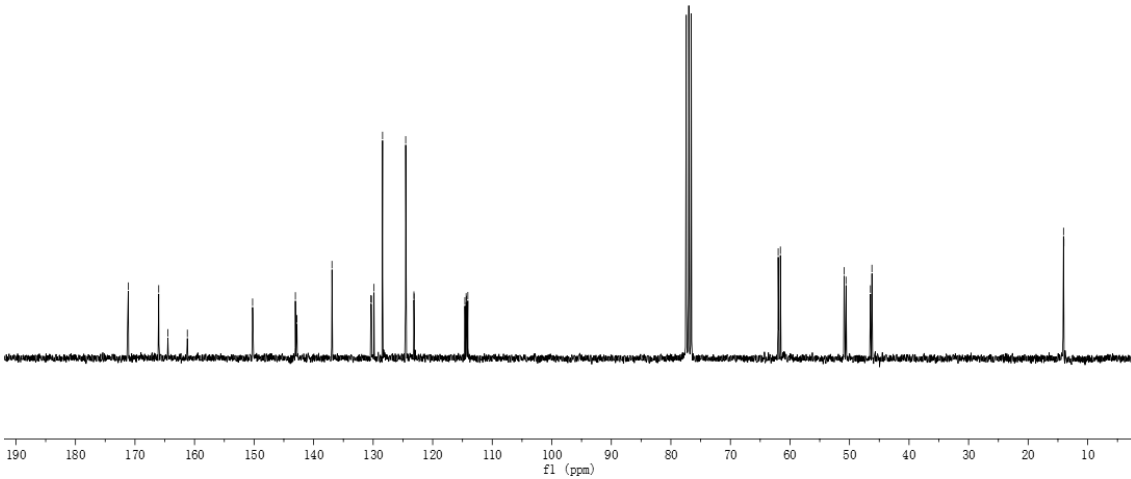
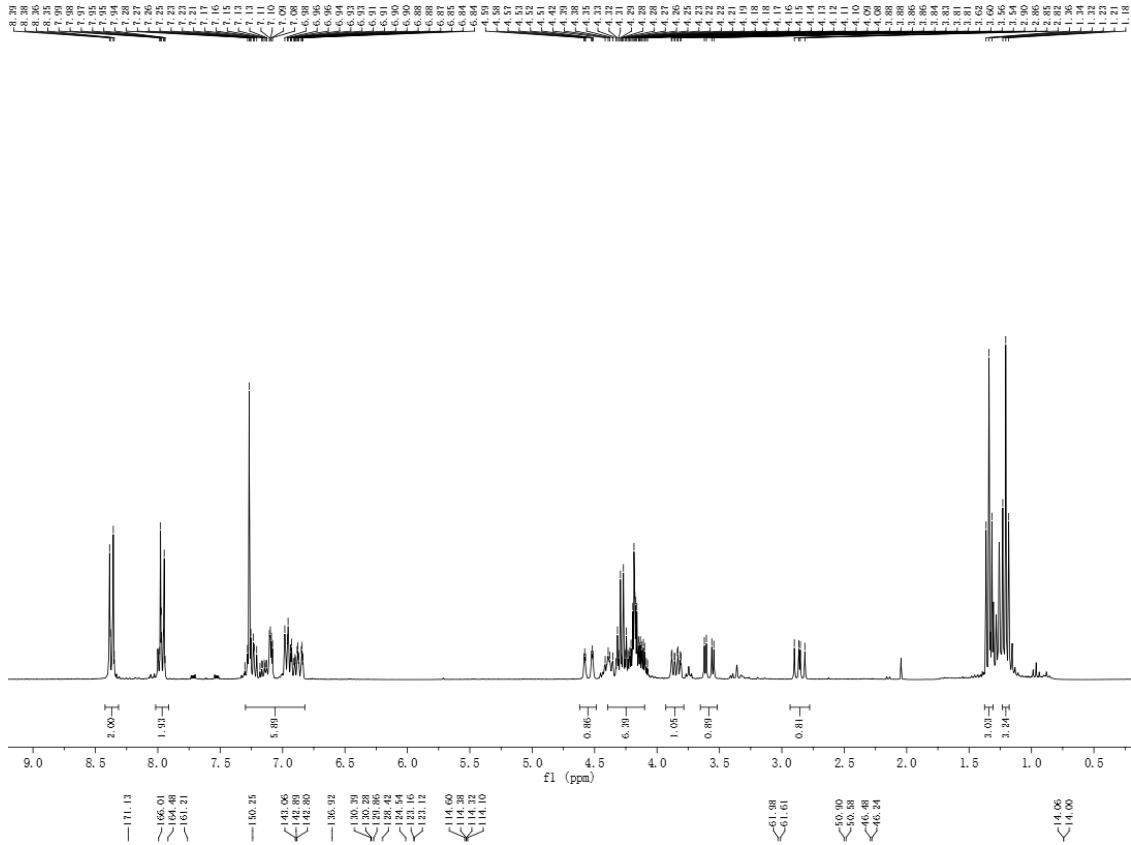
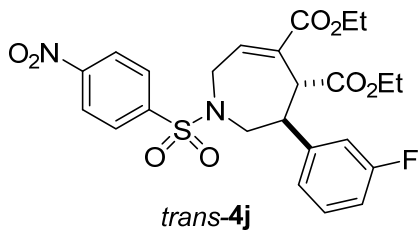


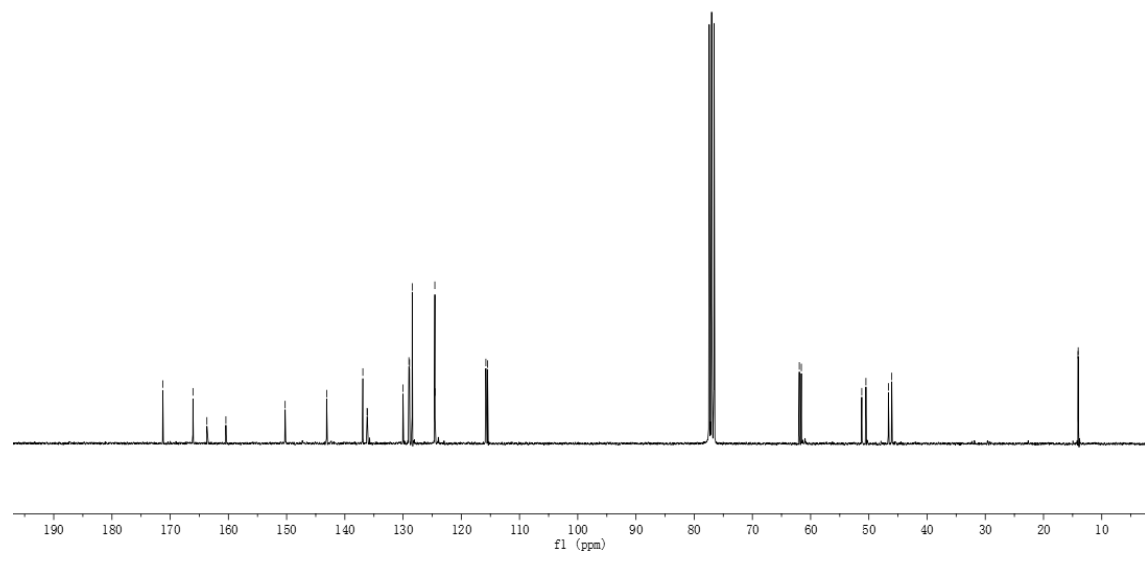
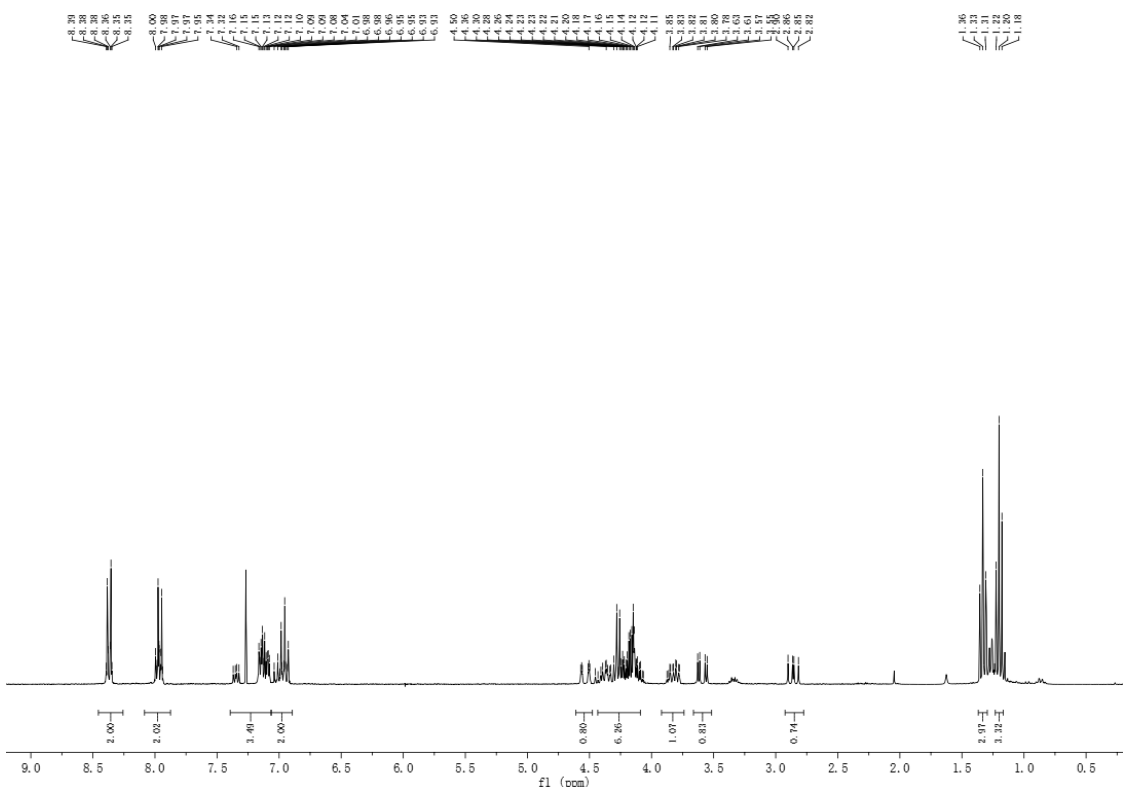
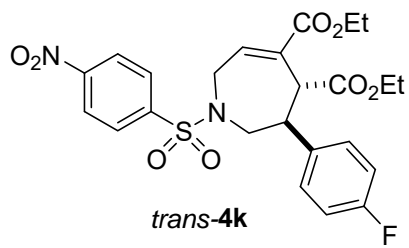


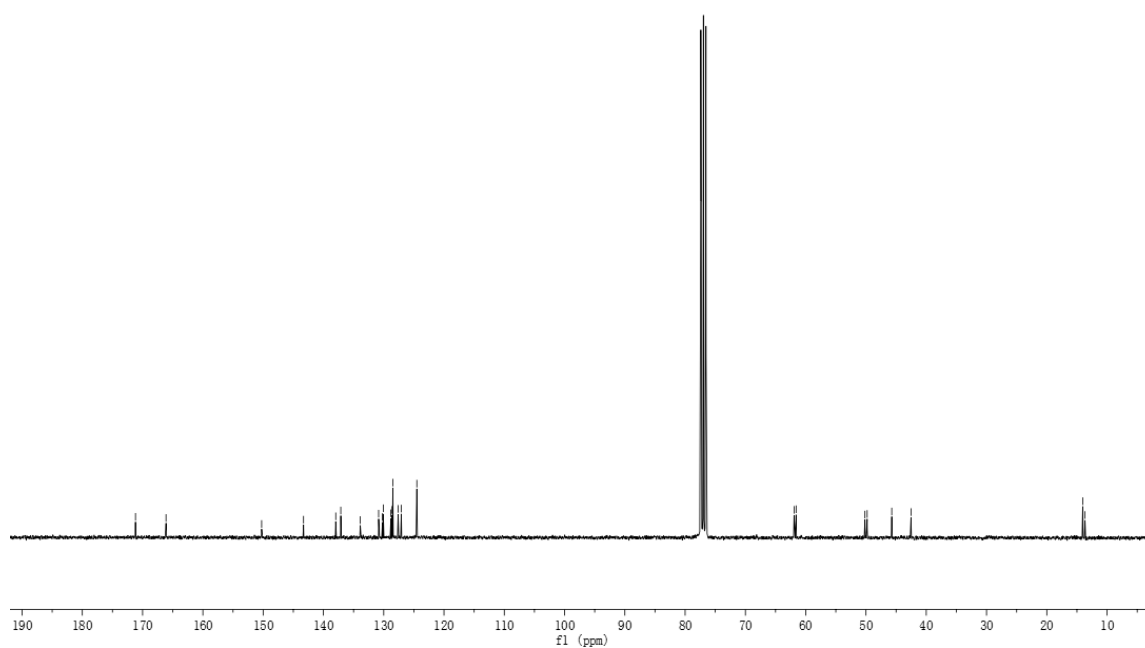
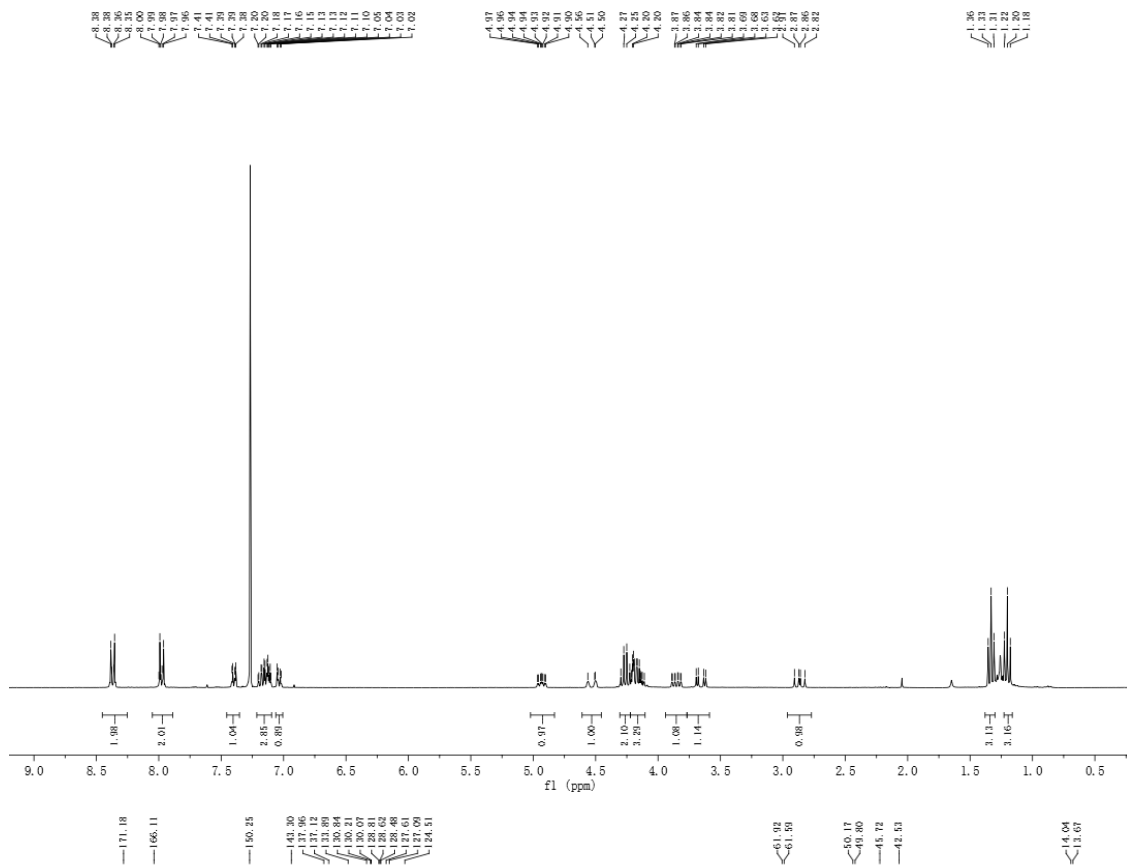
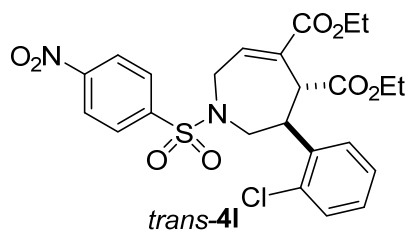


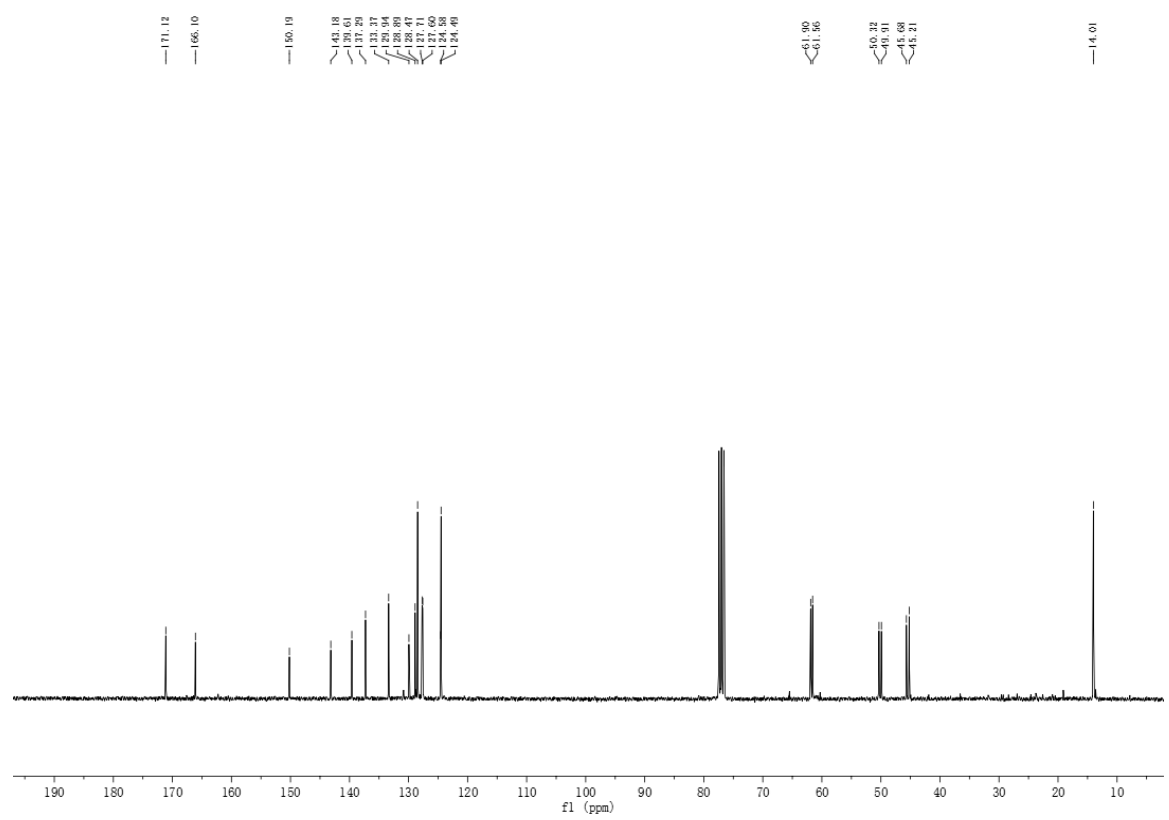
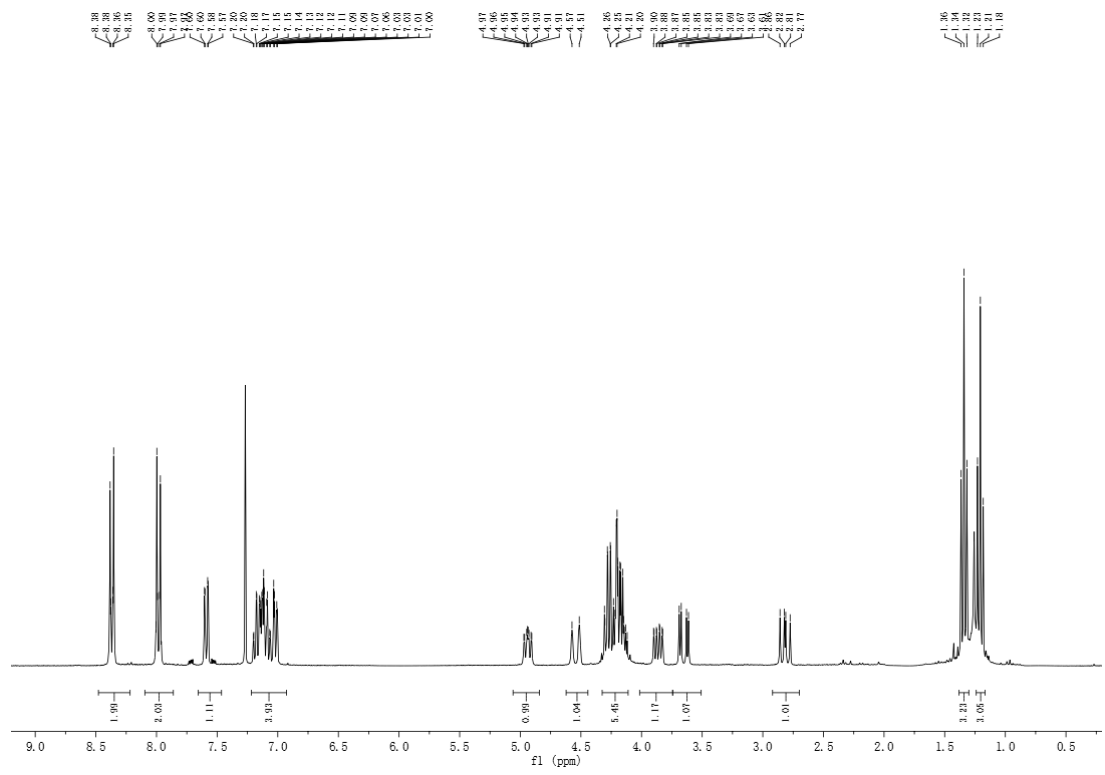
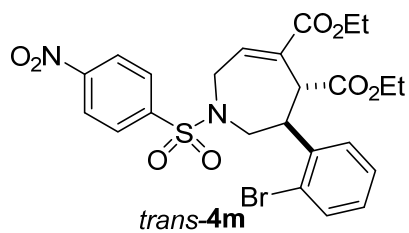


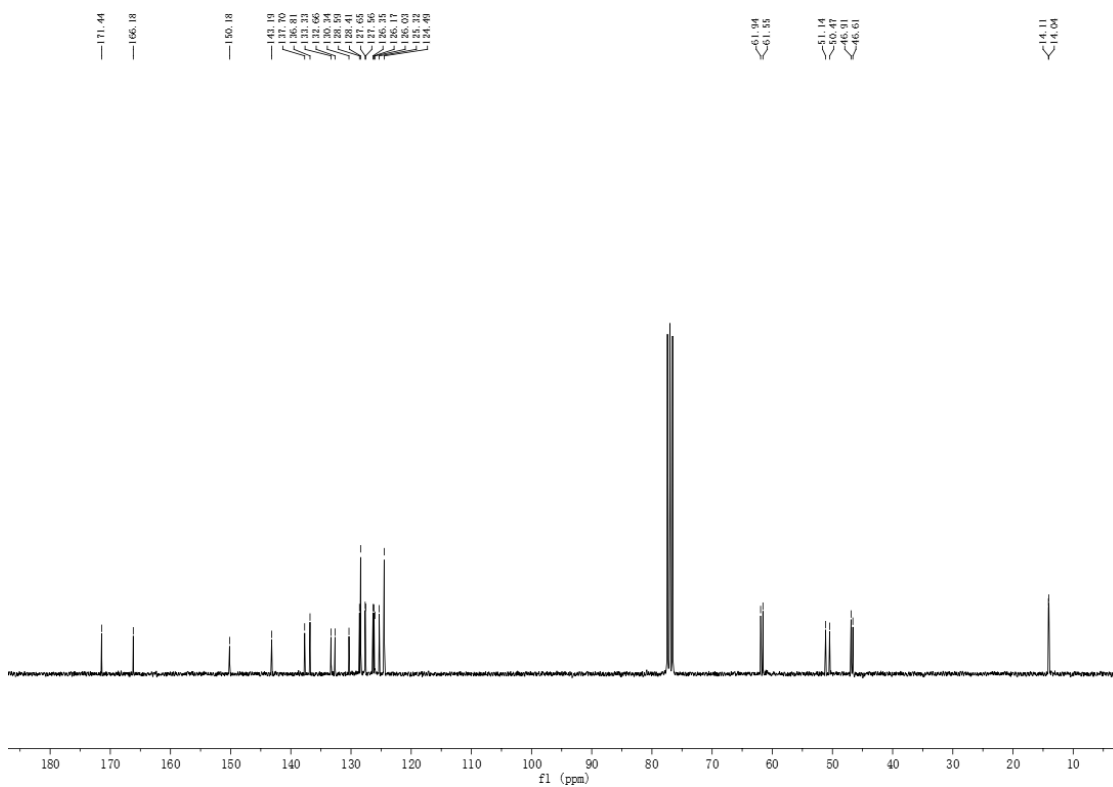
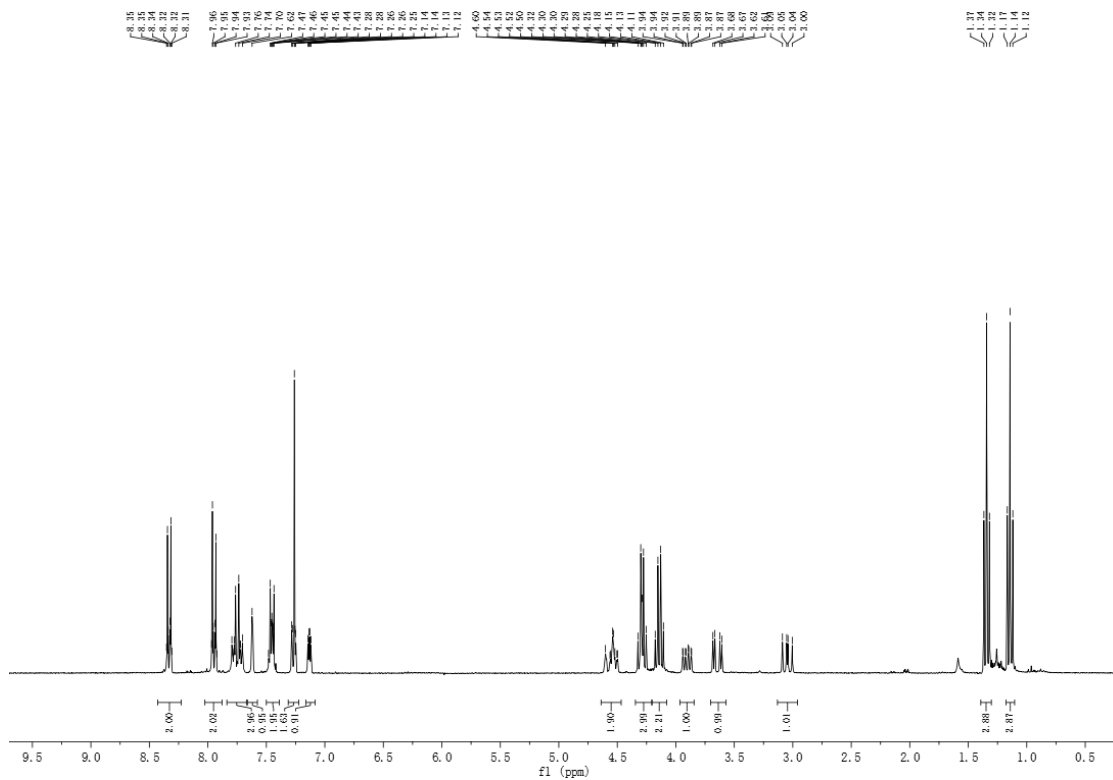
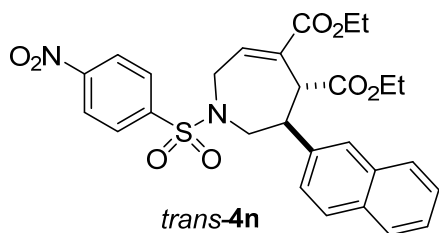












X-Ray Crystallographic Information

Crystallographic data for *trans*-**4a** has been deposited with the Cambridge Crystallographic Data Centre as. 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.

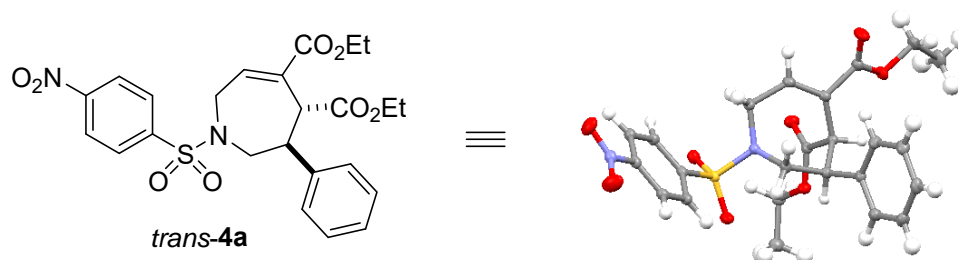


Table 1. Crystal data and structure refinement for *trans*-**4a**.

Identification code	<i>trans</i> - 4a	
Empirical formula	C ₃₆ H ₂₈ N ₂ O ₈ S ₂	
Formula weight	528.58	
Space group	P ⁻¹	
Unit cell dimensions	a = 10.136(3) Å	alpha= 104.454 (3)°.
	b = 10.925(3) Å	beta= 109.130(3)°.
	c = 11.309 (2) Å	gamma = 91.112(3)°.
Volume	1138.67(4) Å ³	
Z	2	
Z'	0	

Table 2. Bond lengths [Å] and angles [°] for *trans*-**4a**.

S1-O3	1.430(1)
S1-O4	1.429(1)
S1-N2	1.631(1) 1
S1-C6	1.772(2) 1
O1-N1	1.213(2) 1
O2-N1	1.222(2) 1
O5-C19	1.205(1) 2

O6-C19	1.338(2) 1
O6-C20	1.455(2) 1
O7-C22	1.211(2) 2
O8-C22	1.342(2) 1
O8-C23	1.454(2) 1
N1-C3	1.479(2) 1
N2-C7	1.470(2) 1
N2-C12	1.469(2) 1
C1-H1	0.99(2) 1
C1-C2	1.391(3)
C1-C6	1.388(2) 1
C2-H2	0.93(2) 1
C2-C3	1.384(2)
C3-C4	1.380(2)
C4-H4	0.98(2) 1
C4-C5	1.391(2)
C5-H5	0.92(2) 1
C5-C6	1.391(2) 1
C7-H7A	0.96(2) 1
C7-H7B	1.494(2) 1
C8-H8	0.98(2) 1
C8-C9	1.332(2)
C9-C10	1.520(2) 1
C9-C22	1.489(2)
C10-H10	0.98(2) 1
C10-C11	1.553(2) 1

C10-C19	1.532(2) 1
C11-H11	0.98(2) 1
C11-C12	1.543(2) 1
C11-C13	1.513(2) 1
C12-H12A	0.99(2) 1
C12-H12B	0.99(2) 1
C13-C14	1.390(2)
C13-C18	1.396(2)
C14-H14	0.96(2) 1
C14-C15	1.389(2)
C15-H15	0.95(2) 1
C15-C16	1.384(2)
C16-H16	0.91(2) 1
C16-C17	1.384(2)
C17-H17	0.96(2) 1
C17-C18	1.389(2)
C18-H18	0.95(1) 1
C20-H20A	0.96(2) 1
C20-H20B	1.00(2) 1
C20-C21	1.499(2) 1
C21-H21A	0.99(2) 1
C21-H21B	0.98(2) 1
C21-H21C	0.97(2) 1
C23-H23A	0.97(2) 1
C23-H23B	0.93(2) 1
C23-C24	1.502(3) 1

C24-H24A	0.99(2) 1
C24-H24B	0.97(2) 1
C24-H24C	0.97(2) 1
O3-S1-O4	120.51(6)
O3-S1-N2	106.93(6)
O3-S1-C6	108.28(7)
O4-S1-N2	106.93(6)
O4-S1-C6	107.76(7)
N2-S1-C6	105.48(7)
C19-O6-C20	115.2(1)
C22-O8-C23	115.8(1)
O1-N1-O2	124.2(1)
O1-N1-C3	118.1(1)
O2-N1-C3	117.7(1)
S1-N2-C7	117.6(1)
S1-N2-C12	118.5(1)
C7 N2 C12	114.3(1)
H1-C1-C2	121(1)
H1-C1-C6	120(1)
C2-C1-C6	119.5(1)
C1-C2-H2	120(1)
C1-C2-C3	117.7(1)
H2-C2-C3	122(1)
N1-C3-C2	117.8(1)
N1-C3-C4	118.5(1)
C2-C3-C4	123.6(1)

C3-C4-H4	121(1)
C3-C4-C5	118.3(1)
H4-C4-C5	120(1)
C4-C5-H5	120(1)
C4-C5-C6	119.0(1)
H5-C5-C6	121(1)
S1-C6-C1	118.9(1)
S1-C6-C5	119.3(1)
C1-C6-C5	121.8(1)
N2-C7-H7A	111(1)
N2-C7-H7B	110(1)
N2-C7-C8	112.4(1)
H7A-C7-H7B	107(2)
H7A-C7-C8	107(1)
H7B-C7-C8	108(1)
C7-C8-H8	115(1)
C7-C8-C9	128.3(1)
H8-C8-C9	116(1)
C8-C9-C10	125.2(1)
C8-C9-C22	115.4(1)
C10-C9-C22	119.1(1)
C9-C10-H10	107(1)
C9-C10-C11	114.3(1)
C9-C10-C19	109.0(1)
H10-C10-C11	107(1)
H10-C10-C19	108(1)

C11-C10-C19	112.4(1)
C10-C11-H11	107(1)
C10-C11-C12	111.1(1)
C10-C11-C13	115.9(1)
H11-C11-C12	106(1)
H11-C11-C13	108(1)
C12-C11-C13	108.4(1)
N2-C12-C11	110.8(1)
N2-C12-H12A	107(1)
N2-C12-H12B	111(1)
C11-C12-H12A	112(1)
C11-C12-H12B	109(1)
H12A-C12-H12B	106(2)
C11-C13-C14	119.4(1)
C11-C13-C18	122.5(1)
C14-C13-C18	117.8(1)
C13-C14-H14	119(1)
C13-C14-C15	121.3(1)
H14 -C14-C15	120(1)
C14-C15-H15	120(1)
C14-C15-C16	120.3(2)
H15-C15-C16	120(1)
C15-C16-H16	118(1)
C15-C16-C17	119.2(1)
H16-C16-C17	122(1)
C16-C17-H17	120(1)

C16-C17-C18	120.4(1)
H17-C17-C18	120(1)
C13-C18-C17	121.1(1)
C13-C18-H18	120(1)
C17-C18-H18	119(1)
O5-C19-O6	123.9(1)
O5-C19-C10	124.3(1)
O6-C19-C10	111.8(1)
O6-C20-H20A	108(1)
O6-C20-H20B	107(1)
O6-C20-C21	107.1(1)
H20A-C20-H20B	111(2)
H20A-C20-C21	112(1)
H20B-C20-C21	111(1)
C20-C21-H21A	111(1)
C20-C21-H21B	110(1)
C20-C21-H21C	111(1)
H21A-C21-H21B	108(2)
H21A-C21-H21C	111(2)
H21B-C21-H21C	106(2)
O7-C22-O8	123.3(1)
O7-C22-C9	125.1(1)
O8-C22-C9	111.5(1)
O8-C23-H23A	107(1)
O8-C23-H23B	106(1)
O8-C23-C24	107.7(1)

H23A-C23-H23B	113(2)
H23A C23 C24	111(1)
H23B C23 C24	112(1)
C23-C24 -H24A	110(1)
C23-C24-H24B	111(1)
C23-C24-H24C	107(1)
H24A-C24-H24B	109(2)
H24A-C24-H24C	109(2)
H24B-C24-H24C	111(2)

Table 3. Torsion angles [°] for *trans*-**4a**.

O3-S1-N2-C7	178.6(1)
O3-S1-N2-C12	-37.0(1)
O4-S1-N2-C7	48.3(1)
O4-S1-N2-C12	-167.3(1)
C6-S1-N2-C7	-66.3(1)
C6-S1-N2-C12	78.1(1)
O3-S1-C6-C1	25.8(1)
O3-S1-C6-C5	-156.6(1)
O4-S1-C6-C1	157.6(1)
O4-S1-C6-C5	-24.8(1)
N2-S1-C6-C1	-88.4(1)
N2-S1-C6-C5	89.2(1)
C2-O6-C19-O5	-5.3(2)
C20-O6-C19-C10	177.2(1)
C19-O6-C20-C21	-174.9(1)
C23-O8-C22-O7	-0.7(2)

C23-O8-C22-C9	177.5(1)
C22-O8-C23-C24	177.8(1)
O1-N1-C3-C2	-6.2(2)
O1-N1-C3-C4	172.9(1)
O2-N1-C3-C2	173.4(1)
O2-N1-C3-C4	-7.4(2)
S1-N2-C7-C8	-161.3(1)
C12-N2-C7-C8	52.9(2)
S1-N2-C12-C11	116.2(1)
C7-N2-C12-C11	-98.2(1)
H1-C1-C2-H2	-0(2)
H1-C1-C2-C3	180(1)
C6-C1-C2-H2	179(1)
C6-C1-C2-C3	-0.4(2)
H1-C1-C6-S1	-3(1)
H1-C1-C6-C5	179(1)
C2-C1-C6-S1	176.9(1)
C2-C1-C6-C5	-0.7(2)
C1-C2-C3-N1	-179.5(1)
C1-C2-C3-C4	1.4(2)
H2-C2-C3-N1	1(1)
H2-C2-C3-C4	-178(1)
N1-C3-C4-H4	-4(1)
N1-C3-C4-C5	179.7(1)
C2-C3-C4-H4	175(1)
C2-C3-C4-C5	-1.2(2)

C3-C4-C5-H5	179(1)
C3-C4-C5-C6	0.1(2)
H4-C4-C5-H5	3(2)
H4-C4-C5-C6	-176(1)
C4-C5-C6-S1	-176.7(1)
C4-C5-C6-C1	0.9(2)
H5-C5-C6-S1	4(1)
H5-C5-C6-C1	-178(1)
N2-C7-C8-H8	-170(1)
N2-C7-C8-C9	13.9(2)
H7A-C7-C8-H8	67(2)
H7A-C7-C8-C9	-109(1)
H7B-C7-C8-H8	-49(2)
H7B-C7-C8-C9	136(1)
C7-C8-C9-C10	-0.7(2)
C7-C8-C9-C22	173.8(1)
H8-C8-C9-C10	-176(1)
H8-C8-C9-C22	-2(1)
C8-C9-C10-H10	-179(1)
C8-C9-C10-C11	-62.0(2)
C8-C9-C10-C19	64.7(2)
C22-C9-C10-H10	6(1)
C22-C9-C10-C11	123.7(1)
C22-C9-C10-C19	-109.6(1)
C8-C9-C22-O7	32.0(2)
C8-C9-C22-O8	-146.1(1)

C10-C9-C22-O7	-153.1(1)
C10-C9-C22-O8	28.7(2)
C9-C10-C11-H11	163(1)
C9-C10-C11-C12	48.1(2)
C9-C10-C11-C13	-76.2(2)
H10-C10-C11-H11	-80(1)
H10-C10-C11-C12	165(1)
H10-C10-C11-C13	41(1)
C19-C10-C11-H11	38(1)
C19-C10-C11-C12	-76.8(1)
C19-C10-C11-C13	159.0(1)
C9-C10-C19-O5	18.1(2)
C9-C10-C19-O6	-164.4(1)
H10-C10-C19-O5	-97(1)
H10-C10-C19-O6	80(1)
C11-C10-C19-O5	145.8(1)
C11-C10-C19-O6	-36.7(2)
C10-C11-C12-N2	32.0(2)
H11-C11-C12-N2	-84(1)
C13-C11-C12-N2	160.4(1)
C10-C11-C13-C14	-134.6(1)
C10-C11-C13-C18	52.0(2)
H11-C11-C13-C14	-14(1)
H11-C11-C13-C18	172(1)
C12-C11-C13-C14	99.8(2)
C12-C11-C13-C18	-73.6(2)

C11-C13-C14-H14	7(1)
C11-C13-C14-C15	-172.4(1)
C18-C13-C14-H14	-179(1)
C18-C13-C14-C15	1.3(2)
C11-C13-C18-C17	173.0(1)
C11-C13-C18-H18	-5(1)
C14-C13-C18-C17	-0.5(2)
C14-C13-C18-H18	-179(1)
C13-C14-C15-H15	179(1)
C13-C14-C15-C16	-0.6(2)
H14-C14-C15-H15	-0(2)
H14-C14-C15-C16	-180(1)
C14-C15-C16-H16	180(1)
C14-C15-C16-C17	-0.8(2)
H15-C15-C16-H16	0(2)
H15-C15-C16-C17	179(1)
C15-C16-C17-H17	-178(1)
C15-C16-C17-C18	1.6(2)
H16-C16-C17-H17	1(2)
H16-C16-C17-C18	-179(2)
C16-C17-C18-C13	-0.9(2)
C16-C17-C18-H18	178(1)
H17-C17-C18-C13	179(1)
H17-C17-C18-H18	-3(2)