Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Zinc Complexes Supported by Pyridine-N-Oxide Ligands: Synthesis, Structure and Catalytic Michael Addition Reaction

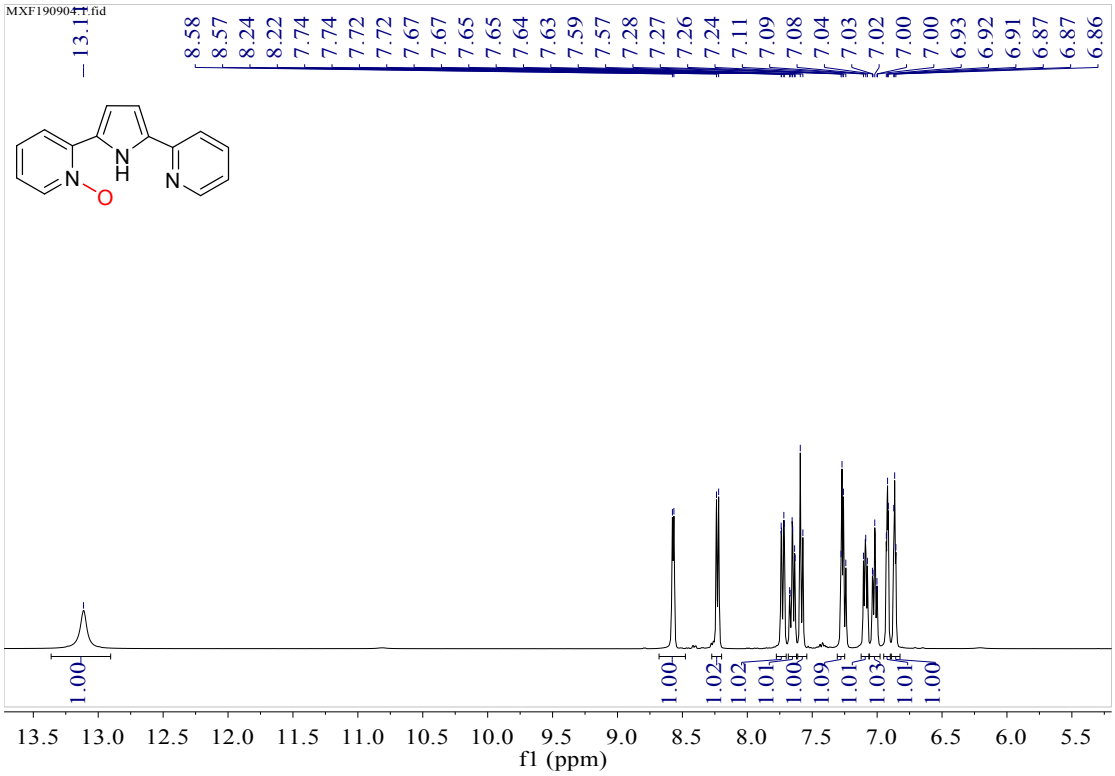
Xiu-Fang Mo,[a] Chang-Feng Xiong,[a] Ze-Wen Chen,[a] Chao Liu,[a] Piao He,[a] Hai-Xia Tong,[b] Xiao-Yi Yi*[a]

[a] Hunan Provincial Key Laboratory of Chemical Power Sources, College of Chemistry and Chemical Engineering, Central South University, Changsha, 410083, P.R. China.

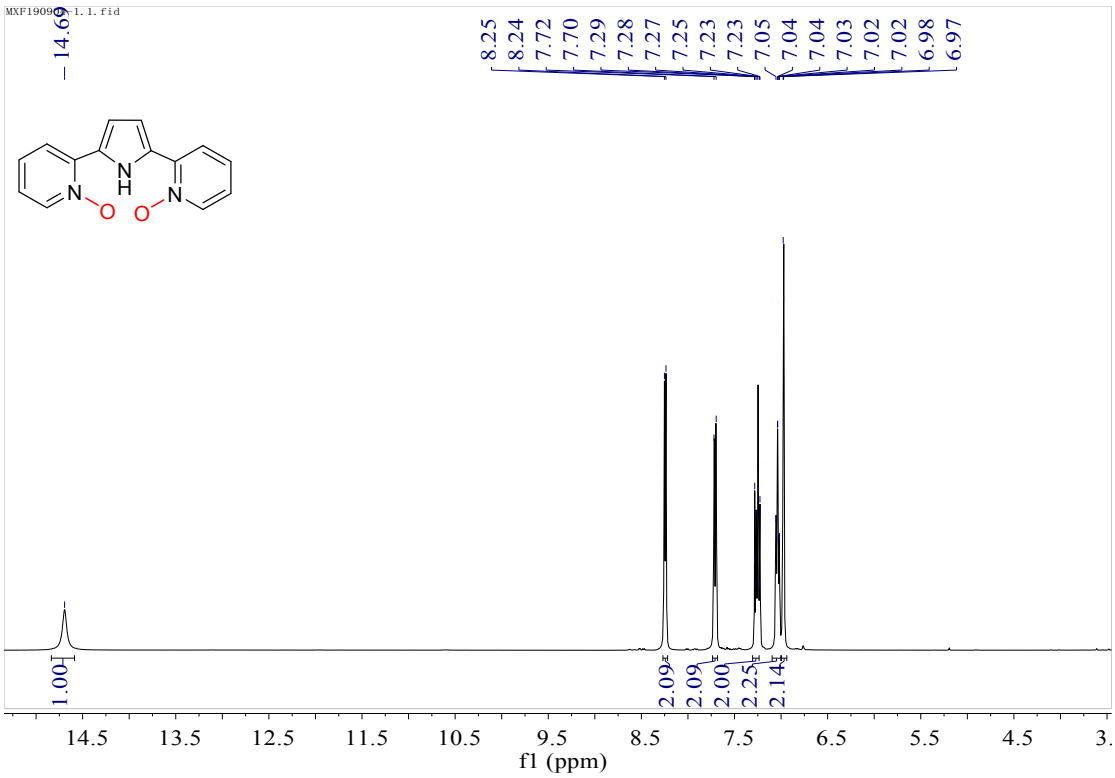
[b] School of Chemistry and Food Engineering, Changsha University of Science and Technology, China 410114, P.R. China.

Fax: 86 731 88879616; Tel: 86 731 88879616; E-mail: xyyi@csu.edu.cn

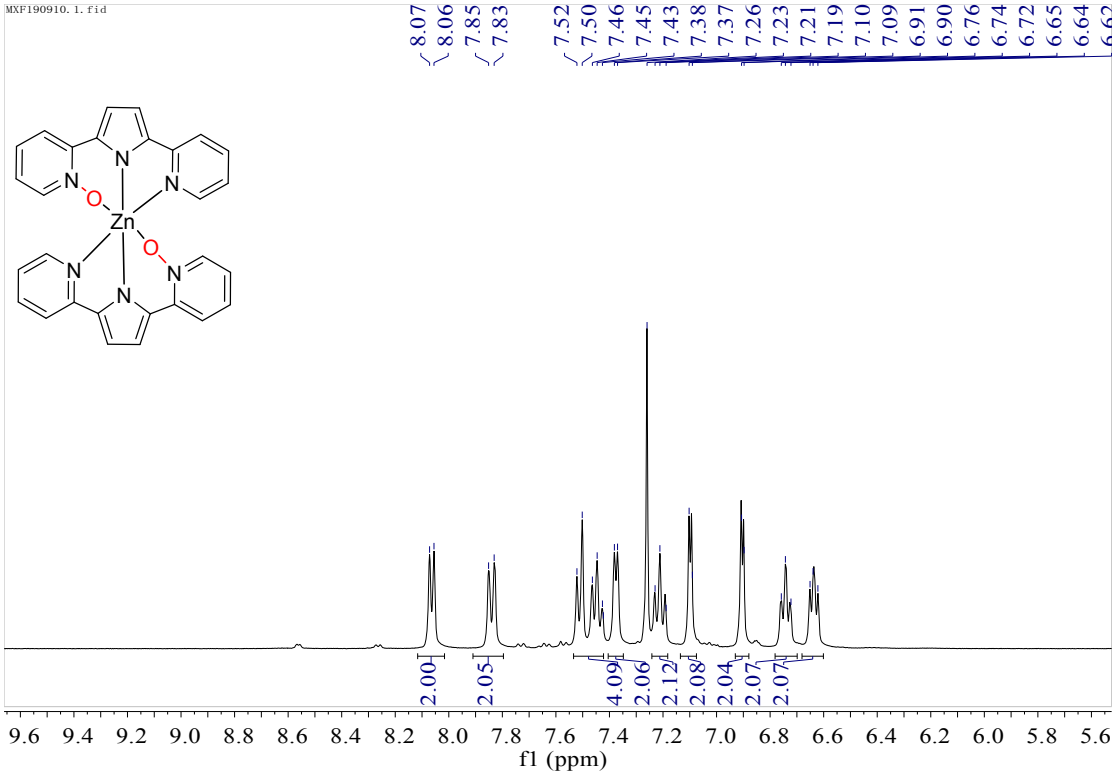
Figure S1. ^{1}H NMR spectra of ligands HL1, HL2 and complexes $[Zn(L1)_2]$, $[Zn(L2)_2]$



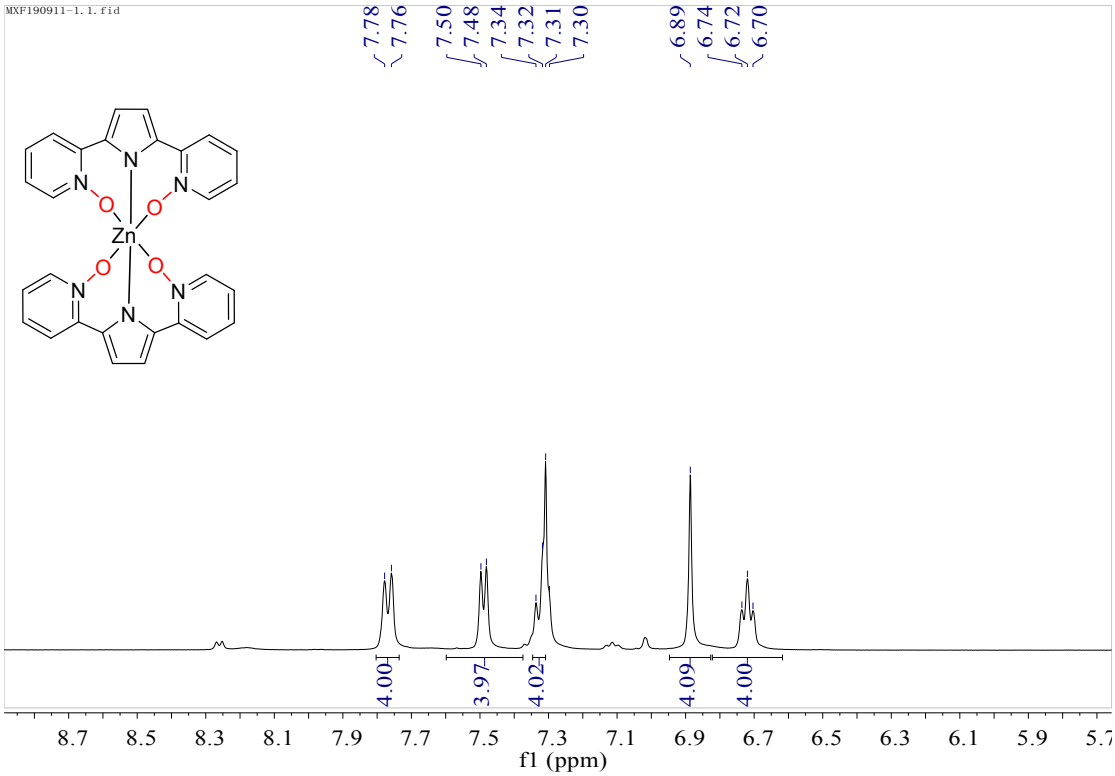
^{1}H NMR spectrum of ligand HL1



^{1}H NMR spectrum of ligand HL2

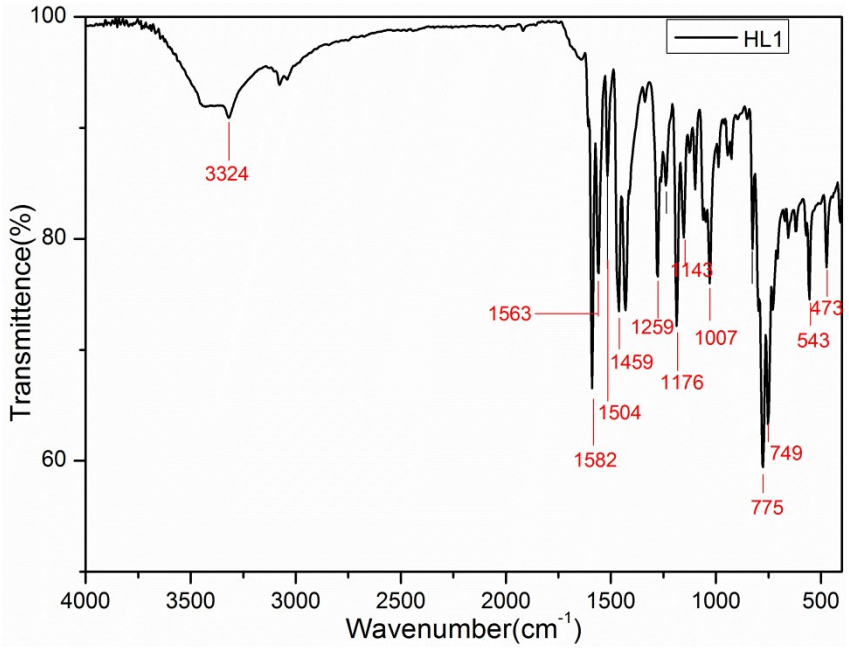


^{1}H NMR spectrum of Complex [Zn(L1)$_2$]

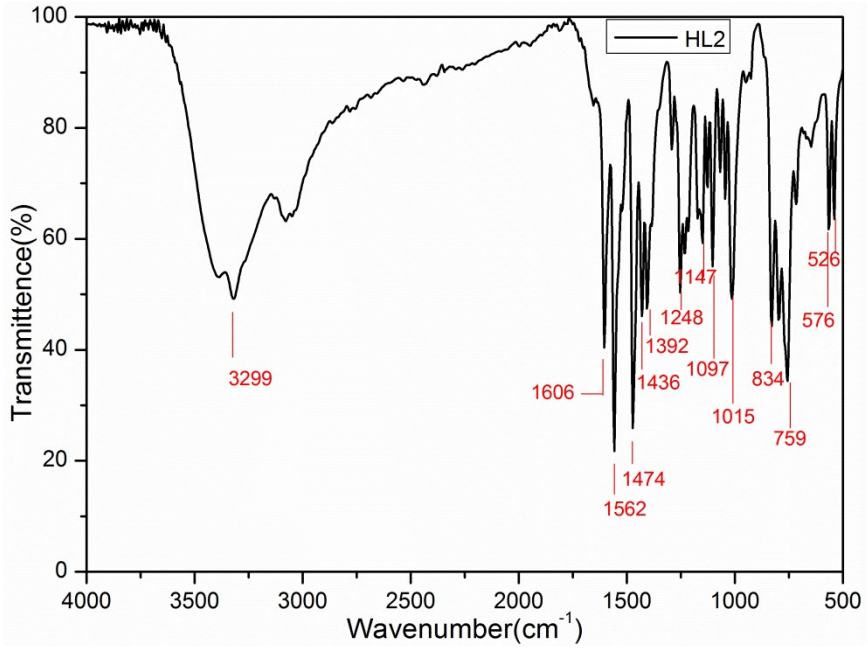


^{1}H NMR spectrum of Complex [Zn(L2)$_2$]

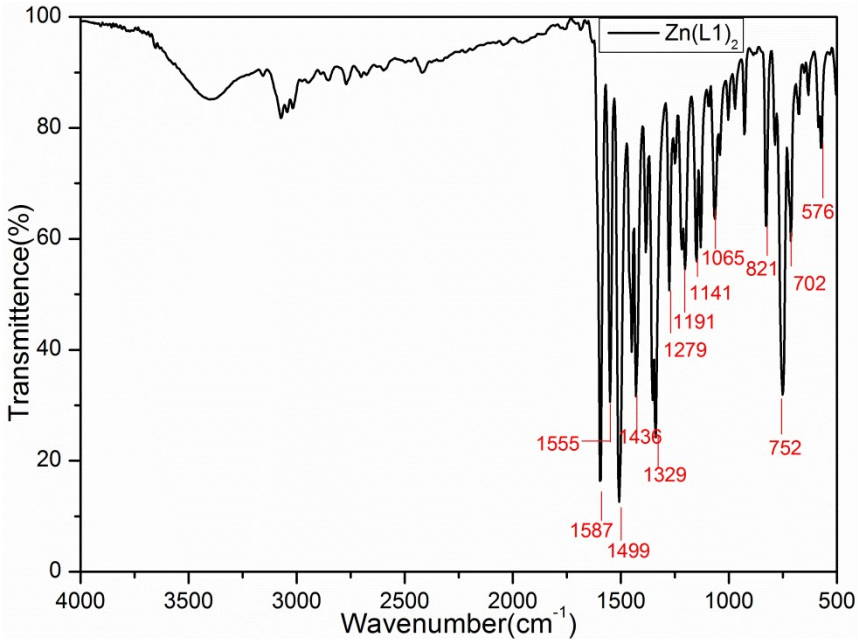
Figure S2. The IR spectra of ligands HL1, HL2 and complexes $[Zn(L1)_2]$, $[Zn(L2)_2]$.



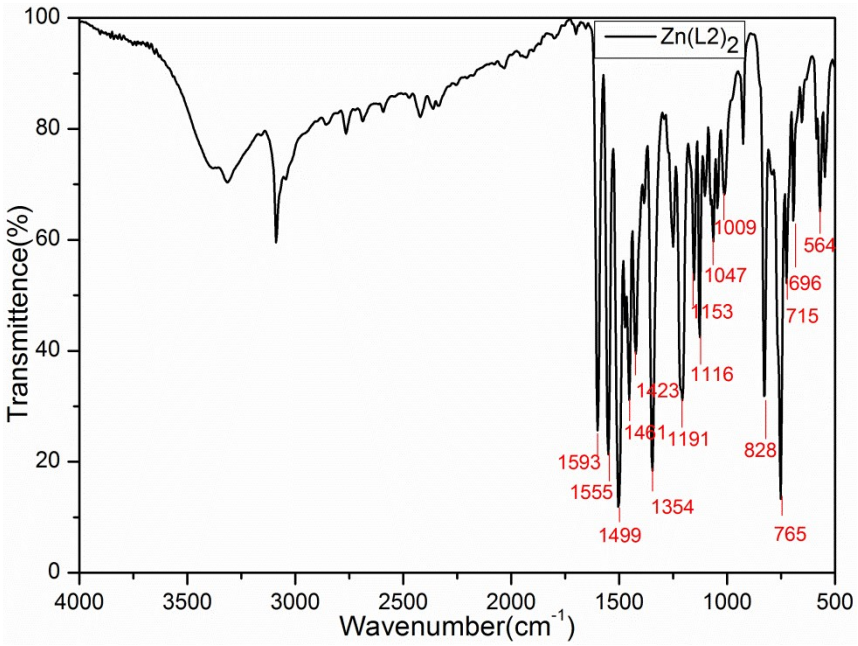
IR spectrum of ligand HL1



IR spectrum of ligand HL2

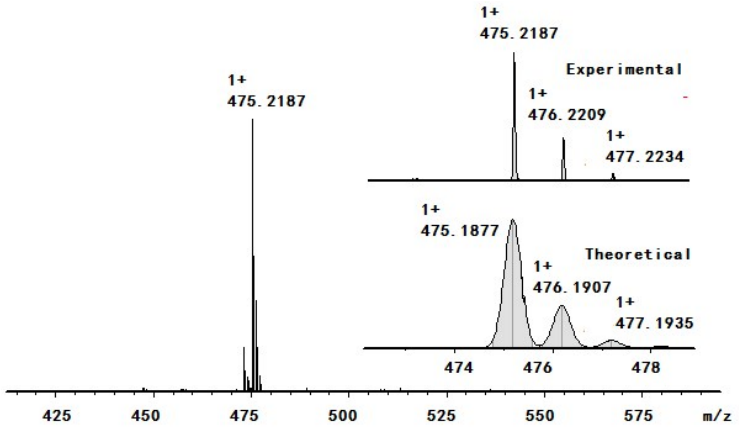


IR spectrum of complex $[Zn(L1)_2]$

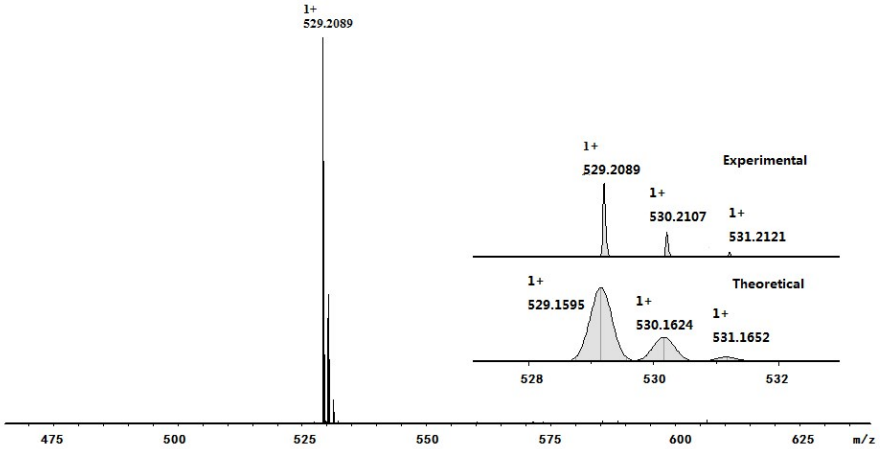


IR spectrum of complex $[Zn(L2)_2]$

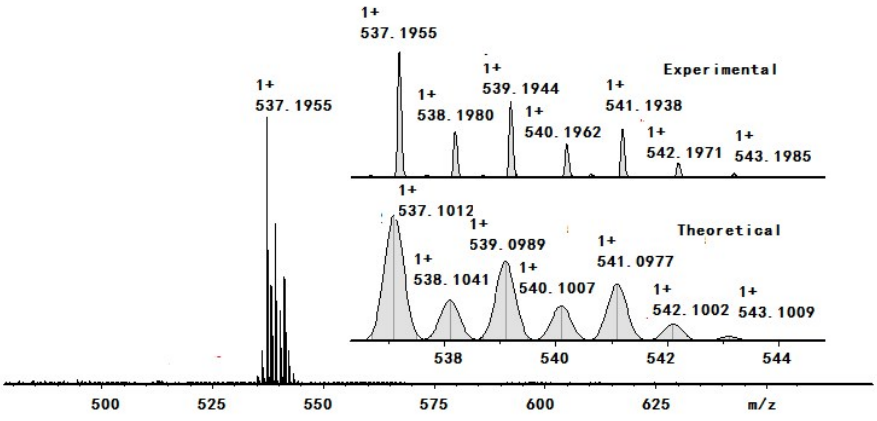
Figure S3. The ESI-MS spectra of ligands HL1, HL2 and complexes $[Zn(L1)_2]$, $[Zn(L2)_2]$.



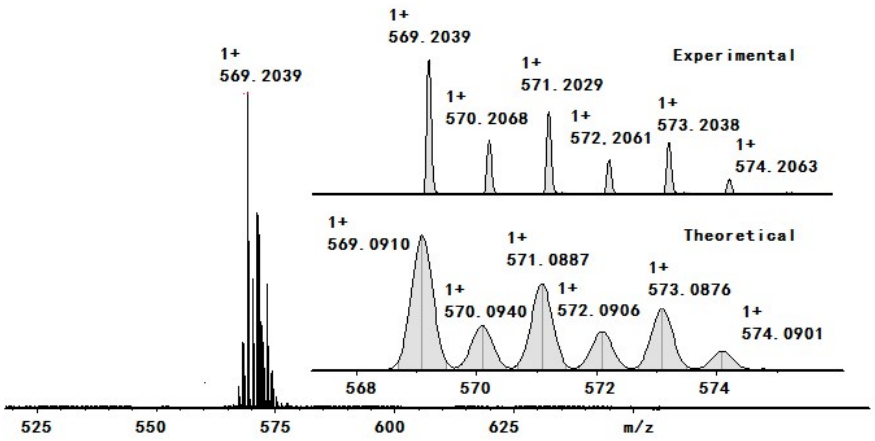
The ESI-MS spectrum of ligand HL1



The ESI-MS spectrum of ligand HL2

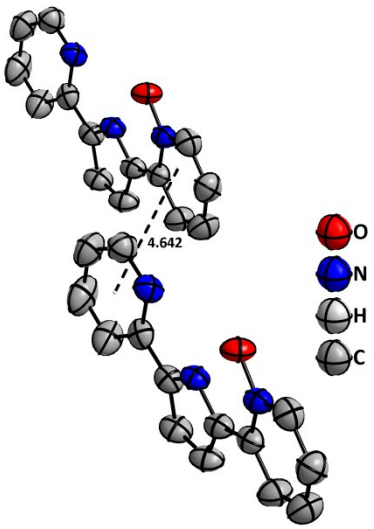


The ESI-MS spectrum of complex $[Zn(L1)_2]$

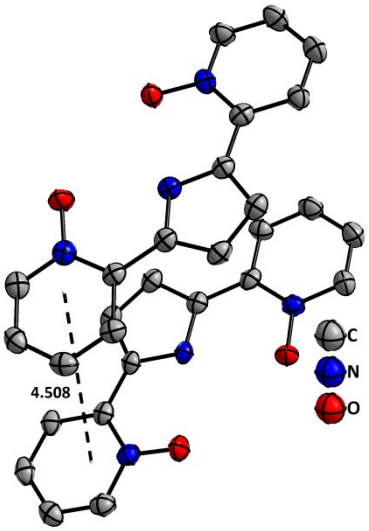


The ESI-MS spectrum of complex $[Zn(L2)_2]$

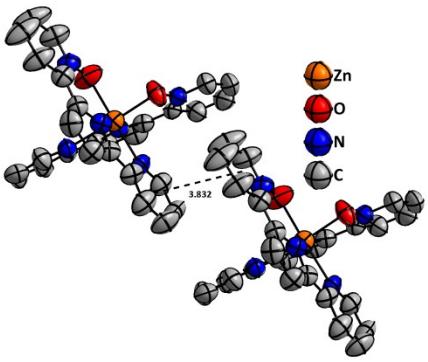
Figure S4. The intermolecular-stacking of ligands HL1, HL2 and complexes $[Zn(L1)_2]$, $[Zn(L2)_2]$.



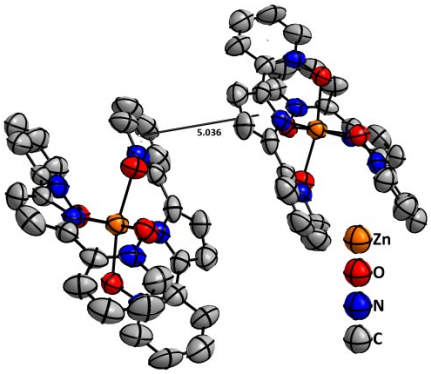
HL1



HL2



$[Zn(L1)_2]$



$[Zn(L1)_2]$

Table S1. X-ray crystallographic data for ligands HL1, HL2 and complexes $[Zn(L1)_2]$, $[Zn(L2)_2]$.

Complex	HL1	HL2	$Zn(L1)_2$	$Zn(L2)_2$
formula	$C_{14}H_{11}N_3O$	$C_{14}H_{17}N_3O_5$	$C_{56.5}H_{42}N_{12}O_4Zn_2$	$C_{32}H_{28}Cl_8N_6O_4Zn$
Formula weight	237.26	307.30	1119.21	909.57
Crystal system	orthorhombic	orthorhombic	monoclinic	orthorhombic
Space group	$P2_12_12_1$	Pbca	C2/c	Fddd
a, Å	10.3807(4)	16.0485(5)	31.091(3)	12.8301(9)
b, Å	10.4296(4)	8.2154(2)	17.2866(16)	16.4771(11)
c, Å	11.1541(4)	22.2672(6)	9.3852(9)	37.538(3)
α, °	90.00	90.00	90.00	90.00
β, °	90.00	90.00	92.426(6)	90.00
γ, °	90.00	90.00	90.00	90.00
V, $Å^3$	1207.62(8)	2935.82(14)	5039.8(8)	7935.6(10)
Z	4	8	4	8
ρ_{calc}, g cm^{-3}	1.305	1.391	1.475	1.523
T, K	296(2)	296(2)	293(2)	293(2)
μ, mm^{-1}	0.086	0.107	1.067	1.201
No. of reflections	16653	14549	18752	14968
No. of indep. refl	2365	2865	4426	1757
R_{int}	0.0165	0.0620	0.0922	0.1023
Goodness-of-fit[a]	1.043	1.064	0.893	1.147
R_1,[b] wR_2[c] $[I > 2\sigma(I)]$	0.0260, 0.0722	0.0793, 0.1896	0.0703, 0.1489	0.0783，0.1904
R_1, wR_2 [all data]	0.0289, 0.0740	0.1417, 0.2090	0.2148, 0.1806	0.1575，0.2155

[a]$GoF=[\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{param})]^{½}$.

[b]$R_1=\Sigma||F_o||F_c||/\Sigma|F_o|$.

[c]wR_2 $[(\Sigma w|F_o|-|F_c|)^2/\Sigma w^2|F_o|^2]^{½}$.

Table S2. Selected bond distances (Å) and bond angles (°) of ligand HL1 and HL2, complexes $[Zn(L1)_2]$, $[Zn(L2)_2]$.

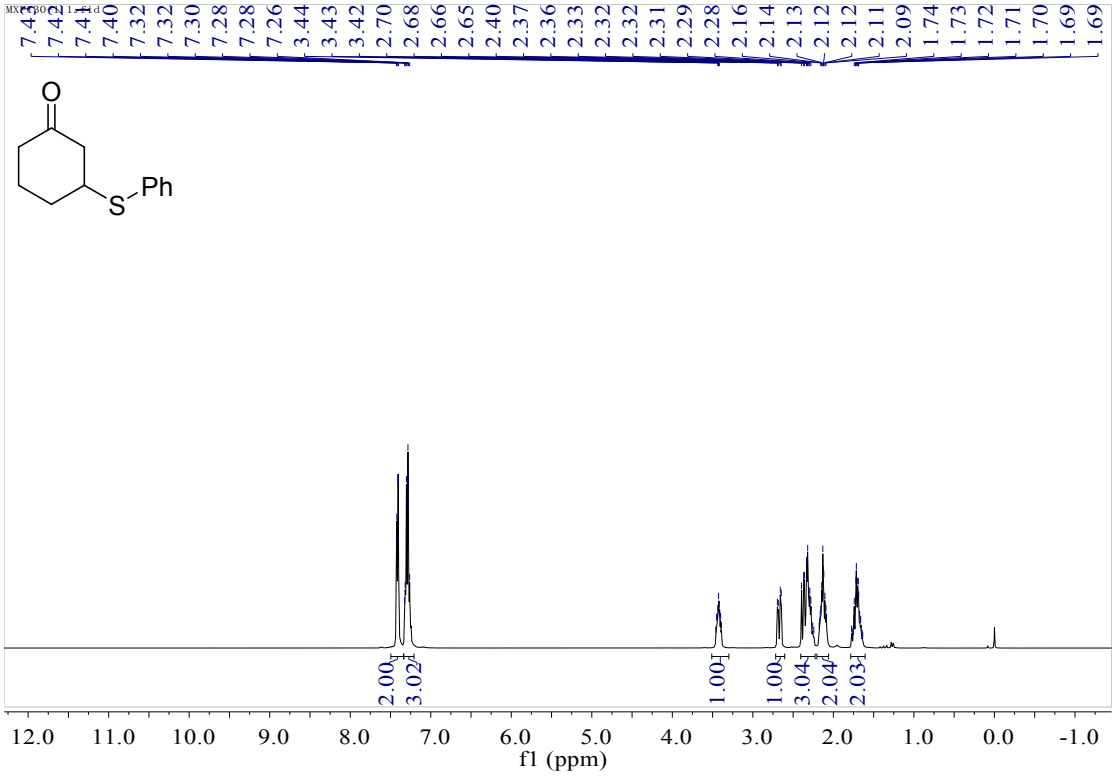
Ligand HL1			
N1-O1	1.3212(17)	C9-C10	1.450(2)
N1-C1	1.358(2)	O1-N1-C1	117.96(13)
N1-C5	1.370(2)	O1-N1-C5	121.29(13)
N2-C6	1.360(2)	N1-C5-C4	117.25(16)
N2-C9	1.357(2)	N1-C5-C6	120.46(15)
N3-C10	1.339(2)	N1-C1-C2	121.50(17)
N3-C14	1.331(2)	N2-C6-C5	124.72(14)
C1-C2	1.360(3)	N2-C6-C7	106.50(15)
C2-C3	1.380(3)	N2-C9-C8	106.57(16)
C3-C4	1.366(3)	N2-C9-C10	120.55(15)
C4-C5	1.391(2)	N3-C10-C9	116.31(15)
C5-C6	1.443(2)	N3-C10-C11	121.61(18)
C6-C7	1.389(2)	N3-C14-C13	124.1(2)
C7-C8	1.387(3)	C1-C2-C3	119.59(18)

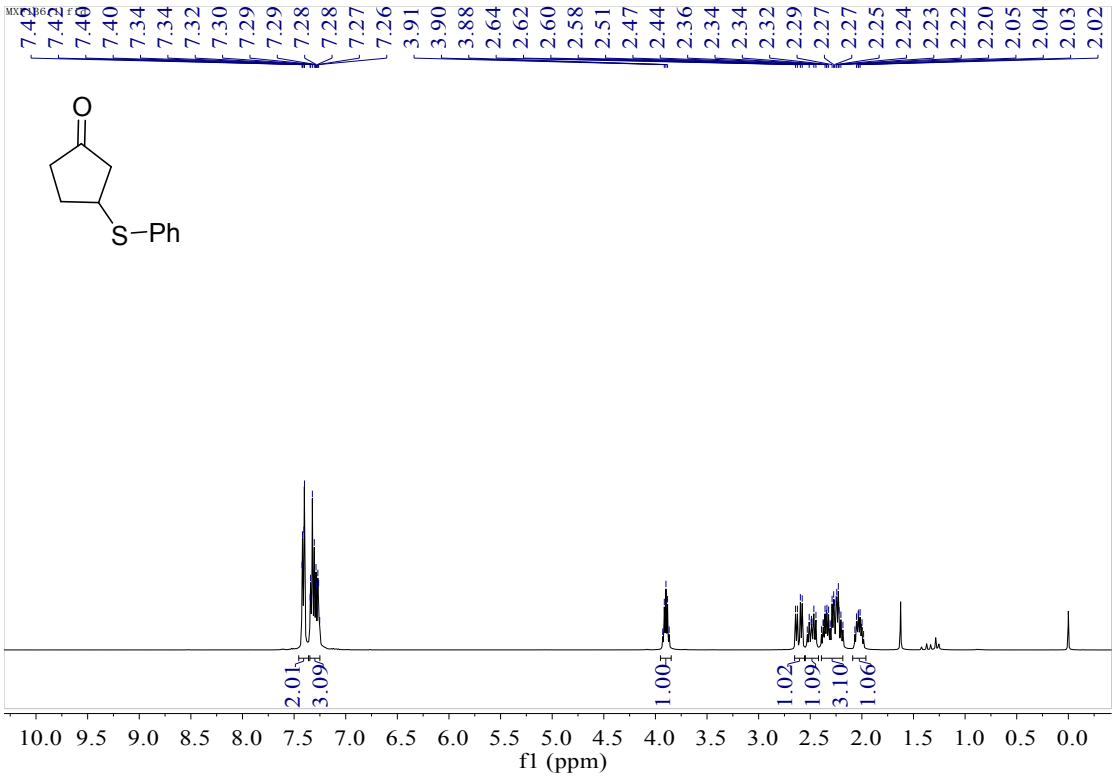
Ligand HL2			
N1-O1	1.325(3)	C7-C8	1.388(5)
N1-C1	1.354(4)	O1-N1-C1	117.8(3)
N1-C5	1.374(4)	O1-N1-C5	121.5(3)
N2-O2	1.336(3)	O2-N2-C10	120.9(3)
N2-C10	1.369(4)	O2-N2-C14	117.6(3)
N2-C14	1.358(4)	N1-C1-C2	121.7(3)
N3-C6	1.356(4)	N1-C5-C4	117.2(3)
N3-C9	1.359(4)	N2-C10-C9	121.3(3)
C1-C2	1.357(5)	N2-C10-C11	117.3(4)
C2-C3	1.383(5)	N3-C6-C5	124.2(4)
C3-C4	1.361(5)	N3-C9-C8	107.6(3)
C4-C5	1.386(4)	N3-C9-C10	127.7(3)
C5-C6	1.443(5)	C1-C2-C3	119.1(3)
C6-C7	1.391(5)	C6-N3-C9	110.0(3)

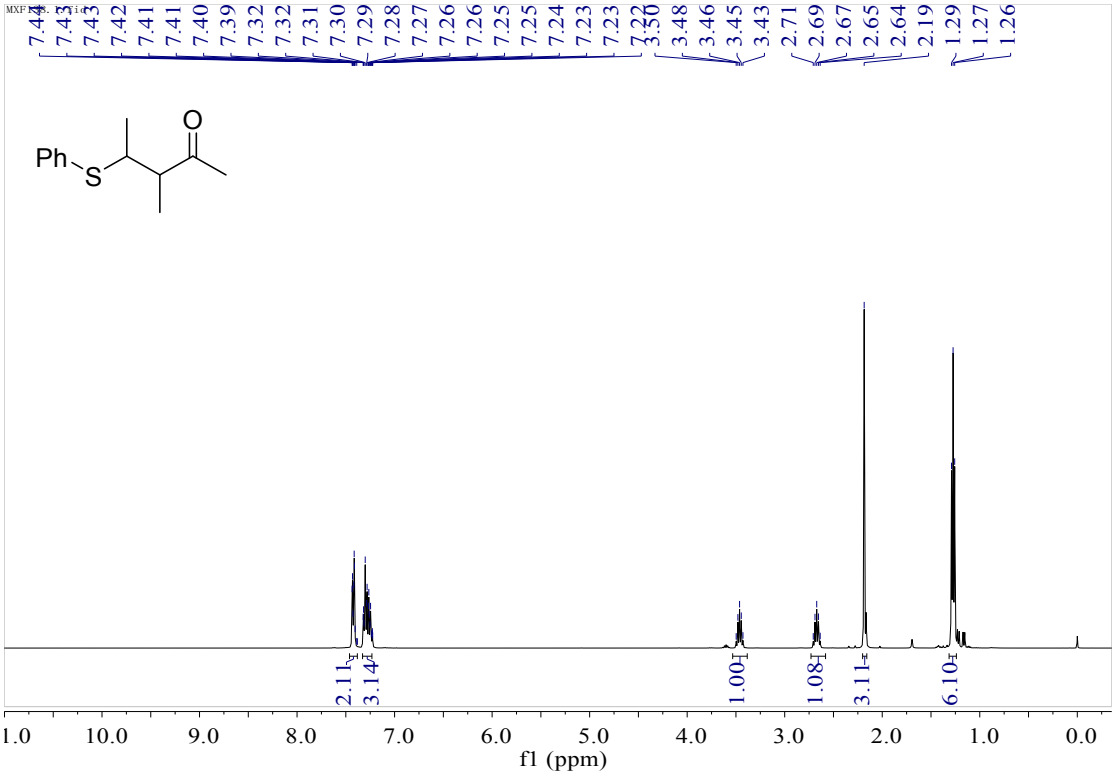
Complex $[Zn(L1)_2]$			
Zn1-O1	2.122(5)	O1-Zn1-O2	87.2(2)
Zn1-O2	2.116(5)	O1-Zn1-N1	83.1(2)
Zn1-N2	1.985(5)	O1-Zn1-N3	159.2(2)
Zn1-N3	2.248(5)	O1-Zn1-N4	90.6(2)
Zn1-N4	2.376(6)	O2-Zn1-N2	109.66(19)
Zn1-N5	1.955(5)	O2-Zn1-N3	93.7(2)
O1-N1	1.295(6)	O2-Zn1-N5	85.7(2)
O2-N6	1.303(6)	Zn1-O1-N1	132.7(4)
N1-C5	1.347(8)	Zn1-O2-N6	127.0(4)
N1-C29	1.369(8)	Zn1-N1-C1	130.4(5)
N2-C6	1.351(7)	O1-N1-C5	123.5(6)
N2-C9	1.352(7)	Zn1-N2-C6	131.3(5)
N3-C10	1.345(8)	Zn1-N2-C9	118.5(5)
N3-C14	1.335(8)	Zn1-N4-C15	131.6(5)
N4-C15	1.334(8)	Zn1-N4-C19	109.3(5)
N4-C19	1.350(7)	Zn1-N5-C23	130.4(5)
N5-C20	1.355(8)	N1-C29-C2	121.7(8)
N5-C23	1.357(7)	N2-C6-C5	124.6(7)
N6-C24	1.365(8)	N2-C6-C7	108.3(6)
N6-C28	1.357(7)	N2-C9-C10	117.4(7)
C5-C6	1.442(9)	N3-C10-C11	121.1(7)
C9-C10	1.461(9)	N5-C20-C19	118.1(7)
C19-C20	1.431(9)	N5-C23-C24	123.8(7)
C23-C24	1.431(9)	N6-C24-C25	115.8(7)
Complex $[Zn(L2)_2]$			
Zn1-O1	2.168(5)	O1-Zn1-O1A	90.3(3)
Zn1-O1A	2.168(5)	O1-Zn1-O2	165.38(18)
Zn1-O2	2.154(5)	O1-Zn1-O2A	91.4(2)
Zn1-O2A	2.154(5)	O1-Zn1-N2	82.9(2)
Zn1-N2	1.959(6)	O1-Zn1-N2A	97.3(2)
Zn1-N2A	1.959(6)	O2-Zn1-N2	82.5(2)
O1-N1	1,328(7)	O2-Zn1-N2A	97.3(2)
O2-N3	1.319(7)	O1A-Zn1-O2	91.4(2)
N1-C1	1.373(10)	O1A-Zn1-N2	97.3(2)
N1-C5	1.367(9)	O2A-Zn1-N2	97.3(2)
N2-C6	1.362(9)	O2A-Zn1-N2A	97.3(2)
N2-C9	1.357(9)	Zn1-O1-N1	117.3(4)
N3-C10	1.346(9)	Zn1-O2-N3	117.1(4)
N3-C14	1.357(10)	Zn1-N2-C6	127.4(5)

Symmetric code: [1]+X,7/4-Y,3/4-Z; [2]3/4-X,7/4-Y,+Z; [3]3/4-X,+Y,3/4-Z

Figure S5. ^{1}H NMR spectra of isolated addition products.



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Ph
S
O
2.11
3.14
1.00
1.08
3.11
6.10
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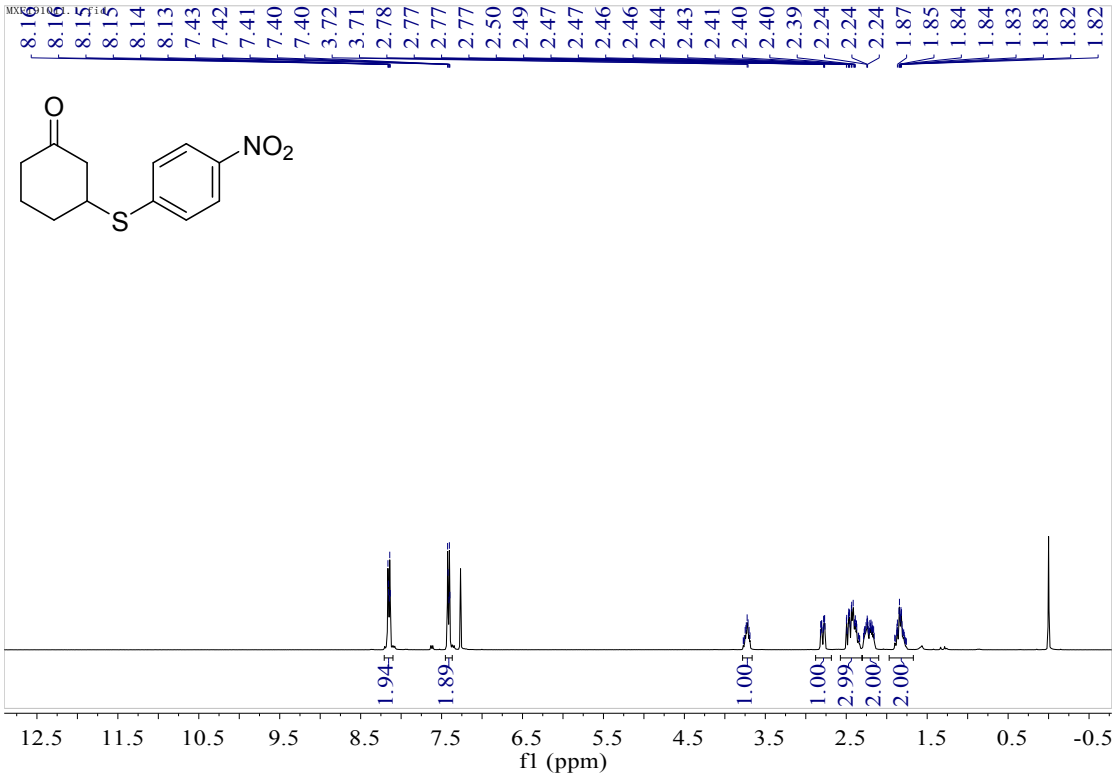
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O
NO2
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1.94
1.89
1.00
1.00
2.99
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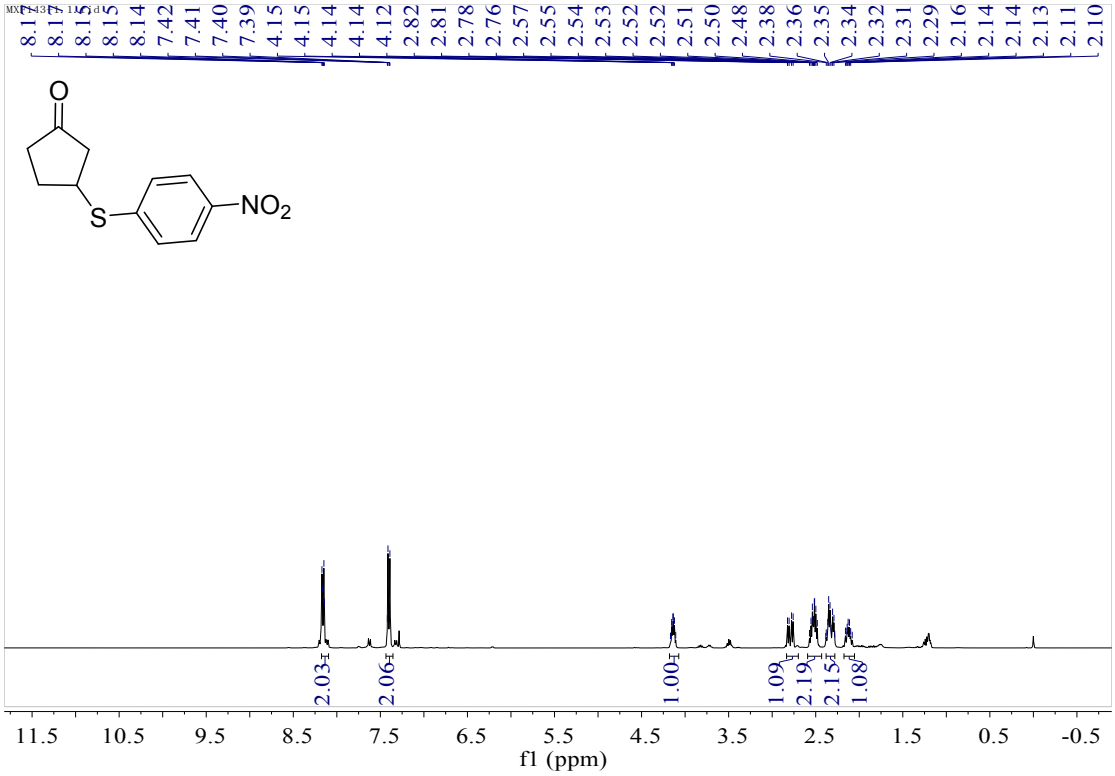
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O
S
NO2
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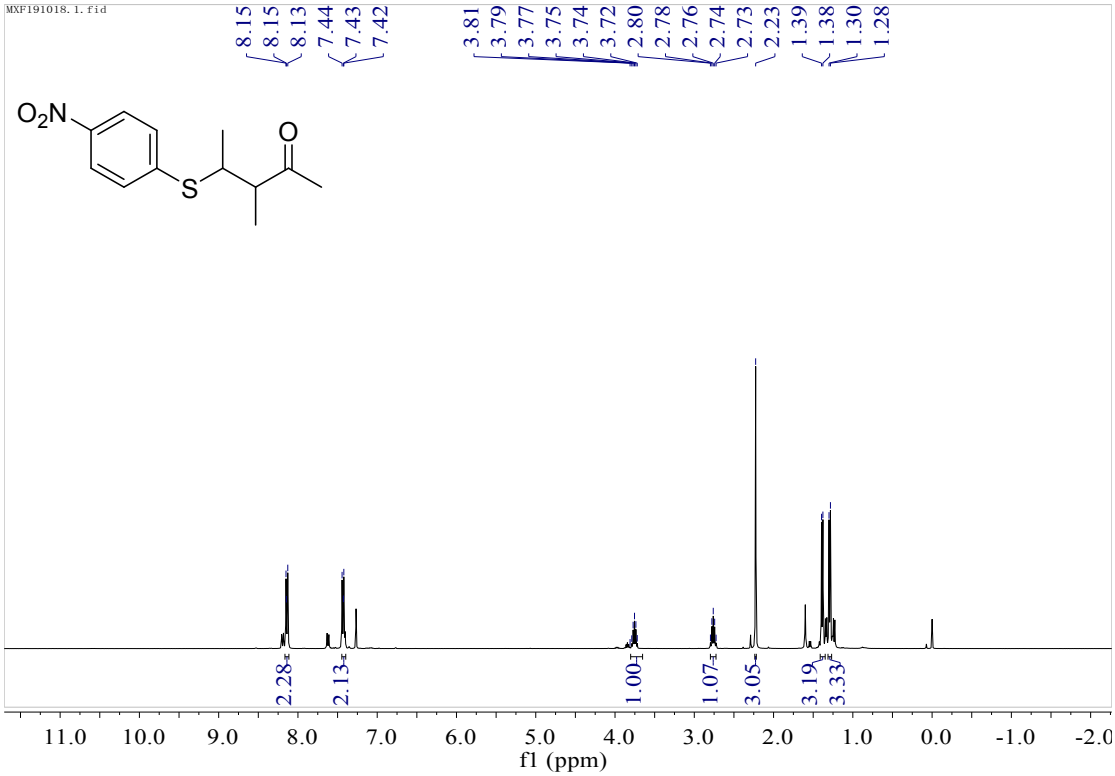
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O2N
O
S
2.28 2.13 1.00 1.07 3.05 3.19 3.33
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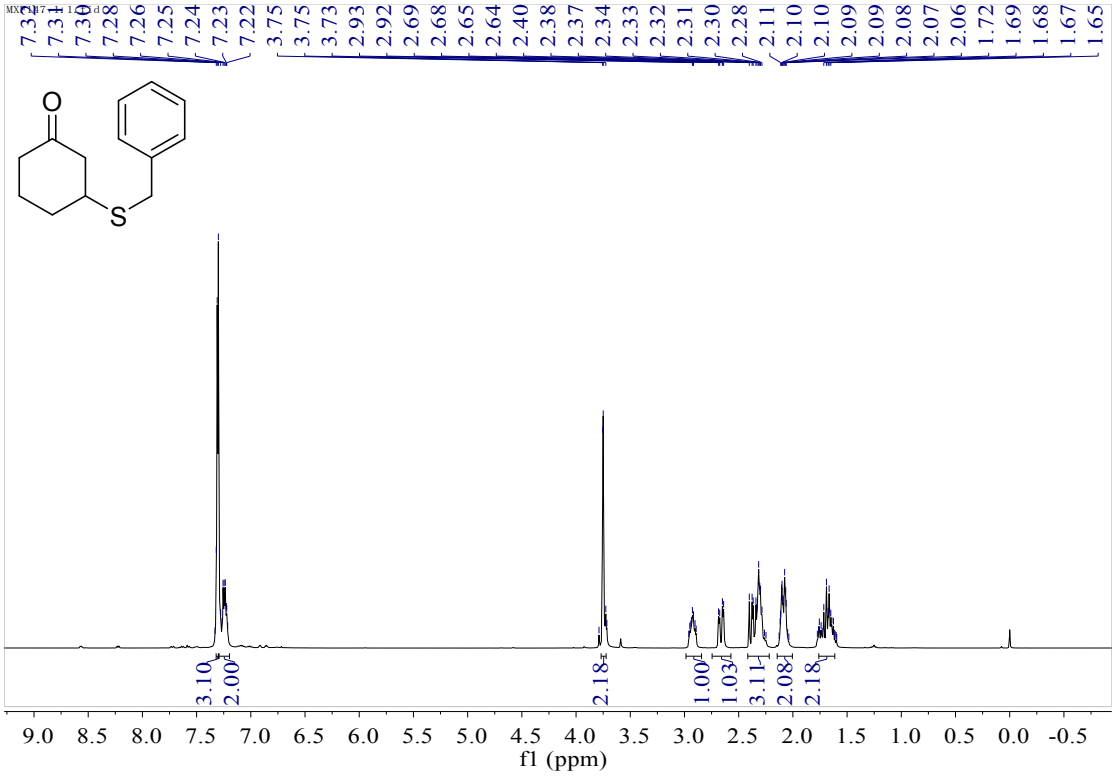
O
S
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3.10 2.00 2.18 1.00 1.03 3.11 2.08 2.18
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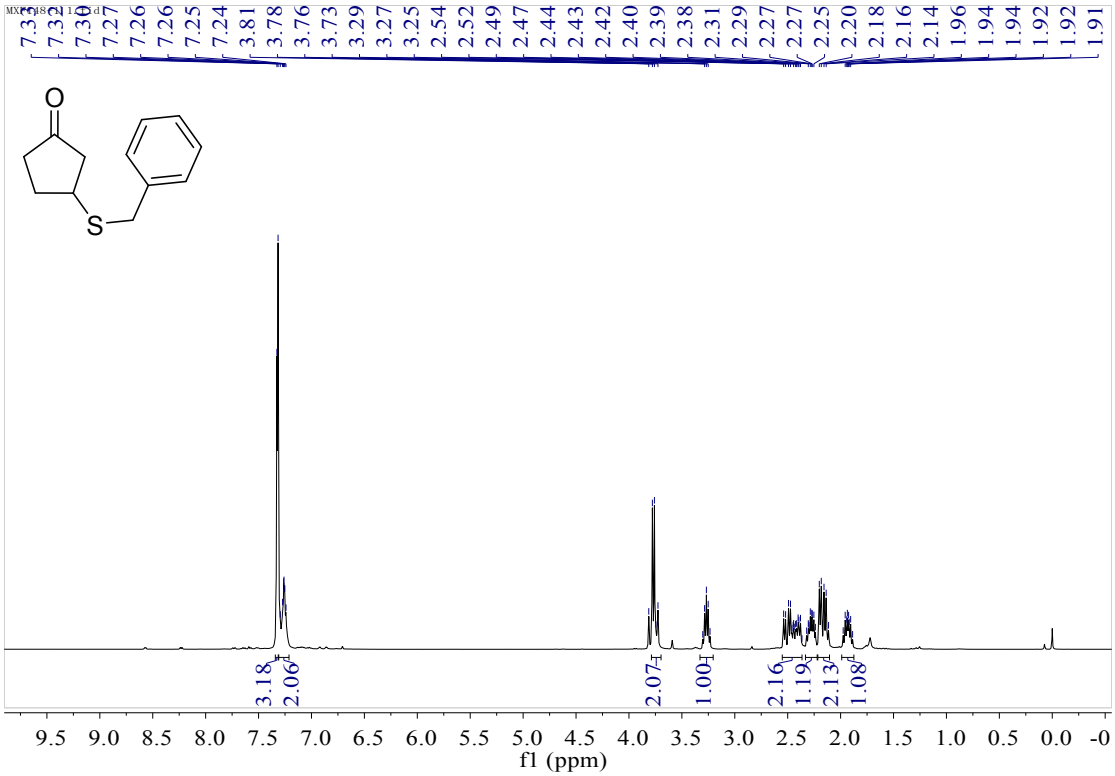
f1 (ppm)


O
S
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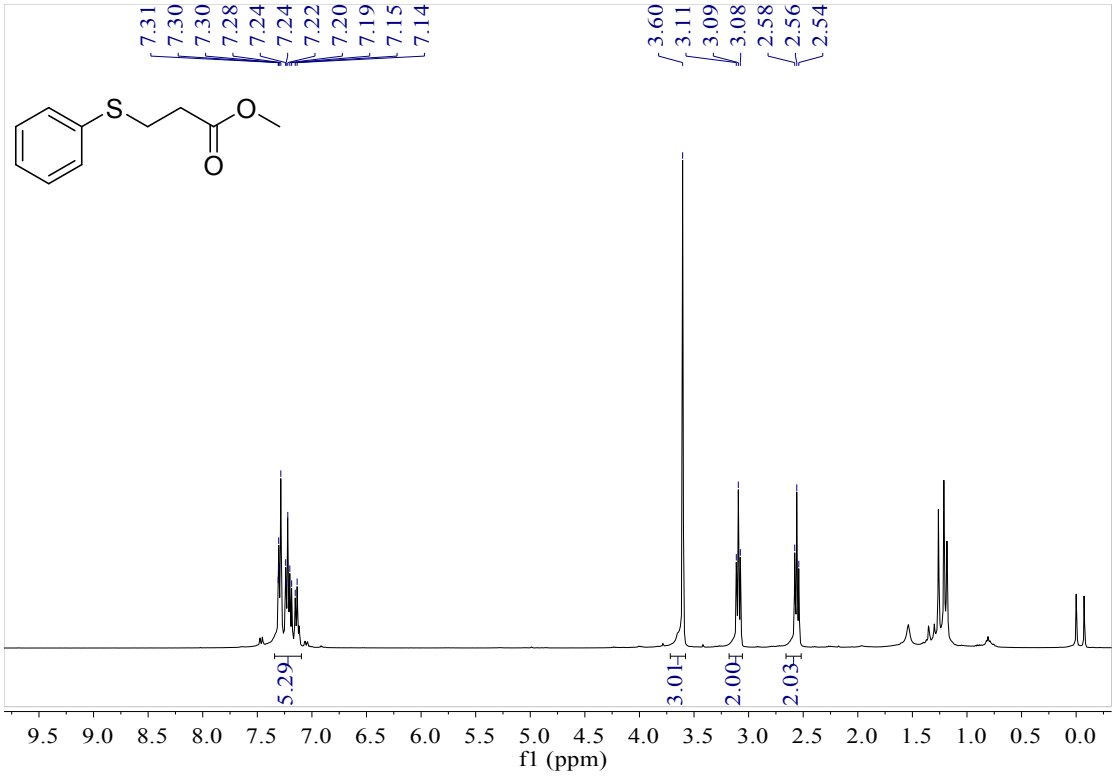
3.18 2.06 2.07 1.00 2.16 1.19 2.13 1.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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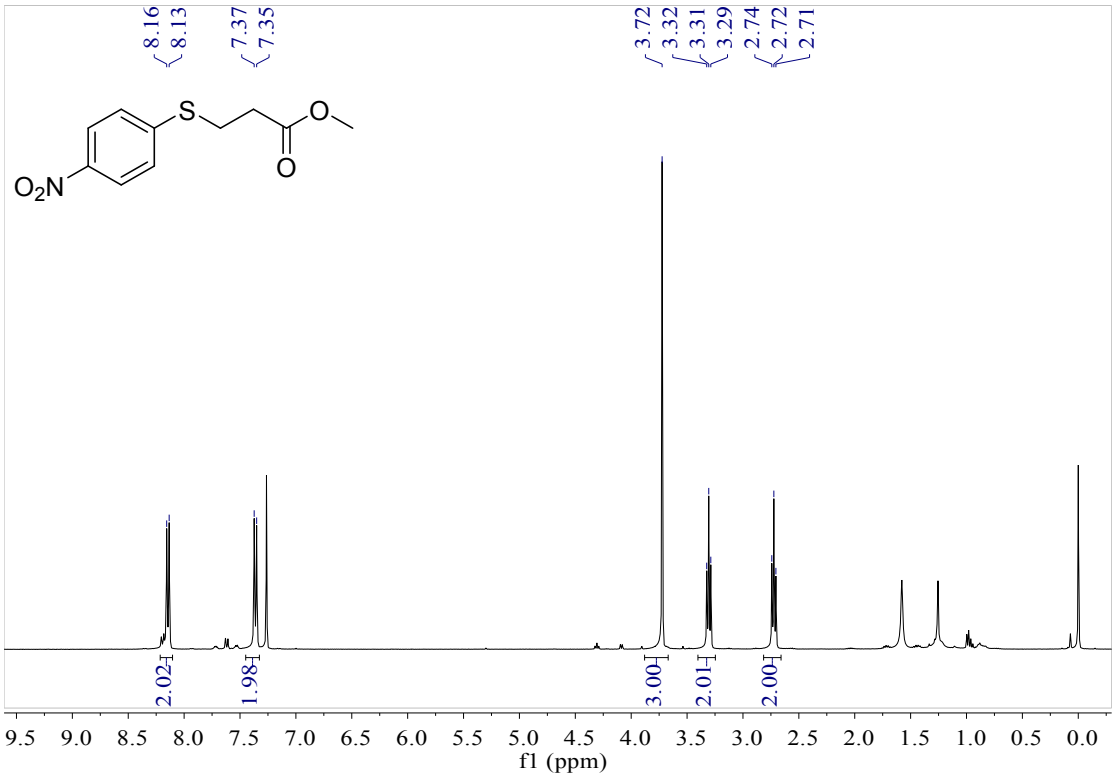
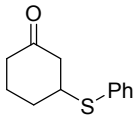
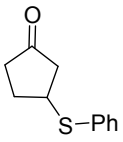
3.08
2.58
2.56
2.54
S
O
O
5.29
3.01
2.00
2.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


8.16
8.13
7.37
7.35
3.72
3.32
3.31
3.29
2.74
2.72
2.71
S
O
O
O2N
2.02
1.98
3.00
2.01
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

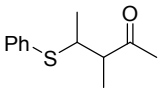
The corresponding NMR data of isolated addition products.



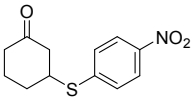
3-(Phenylsulfanyl)cyclohexanone ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.40 (m, 2H), 7.32-7.26 (m, 3H), 3.46-3.39 (m, 1H), 2.67 (dd, J = 12.0 Hz, 4.0 Hz, 1H), 2.40-2.24 (m, 3H), 2.18-2.09 (m, 2H), 1.77-1.64 (m, 2H).



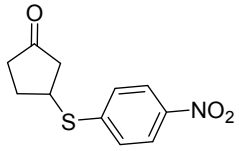
4-(Phenylsulfanyl)cyclopentanone ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.40 (m, 2H), 7.34-7.25 (m, 3H), 3.93-3.87 (m, 1H), 2.61 (dd, J = 16.0 Hz, 8.0 Hz, 1H), 2.53-2.44 (m, 1H), 2.38-2.18 (m, 3H), 2.07-1.98 (m, 1H).



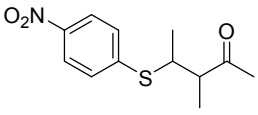
3-methyl-4-(phenylthio)-2-pentanone ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.38 (m, 2H), 7.32-7.22 (m, 3H), 3.50-3.43 (m, 1H), 2.71-2.64 (m, 1H), 2.19 (s, 3H), 1.27 (t, J = 8.0 Hz, 6H).



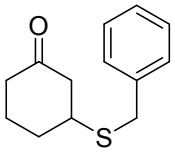
3-[(4-nitrophenyl)thio] -cyclohexanone ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.13 (m, 2H), 7.43-7.40 (m, 2H), 3.77-3.69 (m, 1H), 2.82-2.76 (m, 1H), 2.50-2.33 (m, 3H), 2.29-2.15 (m, 2H), 1.90-1.76 (m, 2H).



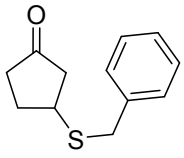
3-[(4-nitrophenyl)thio]-cyclopentanone ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17-8.14 (m, 2H), 7.42-7.39 (m, 2H), 4.17-4.11 (m, 1H), 2.80 (dd, J = 12.0 Hz, 4.0 Hz, 1H), 2.57-2.48 (m, 2H), 2.38-2.28 (m, 2H), 2.16-2.08 (m, 1H).



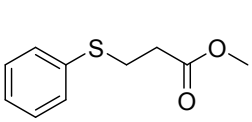
3-methyl-4-nitrophenyl)thio-2-Pentanone ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15-8.13 (m, 2H), 7.44-7.42 (m, 3H), 3.81-3.72 (m, 1H), 2.80-2.73 (m, 1H), 2.23 (s, 3H), 1.38 (d, J = 4.0 Hz, 3H), 1.29 (d, J = 8.0Hz, 3H).



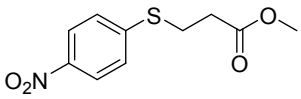
3-[(phenylmethyl)thio]-cyclohexanone ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.30 (m, 3H), 7.28-7.21 (m, 2H), 3.79-3.72 (m, 2H), 2.96-2.89 (m, 1H), 2.69-2.64 (m, 1H), 2.67 (dd, J = 12.0 Hz, 4.0 Hz, 1H), 2.40-2.25 (m, 3H), 2.13-2.04 (m, 2H), 1.77-1.60 (m, 2H).



3-[(phenylmethyl)thio]-Cyclopentanone ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.30 (m, 3H), 7.27-7.24 (m, 2H), 3.81-3.73 (m, 2H), 3.30-3.23 (m, 1H), 2.54-2.37 (m, 2H), 2.32-2.24 (m, 1H), 2.20-2.11 (m, 2H), 1.98-1.89 (m, 1H).



Methyl-3-(phenylthiol) propanoate ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.14 (m, 5H), 3.6 (s, 3H), 3.09 (t, J = 4.0 Hz, 2H), 2.56 (t, J = 8.0 Hz, 2H)



Propanoic-3-(*p*-nitrophenyl thio) methyl ester ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 12.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 3.72 (s, 3H), 3.31 (t, J = 4.0 Hz, 2H), 2.72 (t, J = 4.0 Hz, 2H).