Synthesis and Study of Au(III)-Indolizine Derivatives: Turn-on Luminescence by Photo-induced Control Release.

Supporting information

Table of Content:	
General Aspects:	s1
General Procedure for the Cycloisomerization Substrates Preparation:	s3
General and Representative Procedure for Cycloisomerization Reaction:	s6
a) General cycloisomerization procedure:	s6
b) General work up procedure	s6
c) Representative Procedure by using AuCl ₃	s6
d) Representative Procedure by using AuCl 2a	s7
e) Representative procedure by using CuCl 2d	s7
f) Table for preparation of complexes 3 and 4	s9
General Procedure for Photo-induced Reductive Elimination Reactions	s10
Characterization Data	s11
a) NMR of Product 3	s11
b) NMR of Product 4	s14
c) NMR of Product 5	s16
Selected Structural Information of Isolated Complexes for Comparison	s19
Absorption spectral changes of 3bb and 3cb	s20
UV Spectrum	s21
Fluorescence Spectrum	s23
Absorption and Emission Spectral Data of 3 and 5	s25
Singlet Oxygen Emission Study	s26
Cyctotoxicity evaluation of complex 3 on cancer cell lines	s27

General Aspects:

Unless otherwise indicated, all reactions were performed under a nitrogen atmosphere from which oxygen and moisture were rigidly excluded from reagents and glassware, and all the metal salts were stored in a glovebox and used without further purification: AuCl₃, AuBr₃ and AuCl were purchased from Alfa, CuCl and CuBr were purchased from J&K or Alfa. Starting materials for cycloisomerization substrate synthesis such as n-Butyllithium, iodomethane, the pyridine and the acetylene derivatives were stored in a refrigerator and used without further purification. THF was dried over NaH before use. Extra Dry DCM was used directly and purchased from J&K.

Analytical thin layer chromatography (TLC) was performed using EM Science silica gel 60 F254 plates. The developed chromatogram was analyzed by UV lamp (254 nm). Purification of product was performed by using Silica Gel (230–400 mesh, 0.040-0.063 mm) coarse fritted glass column.

¹H and ¹³C NMR spectra were recorded on Bruker spectrometers in deuteriated chloroform, acetone or DMSO (400 or 500 MHz for ¹H, and 100 or 125 MHz for ¹³C). Chemical shifts in ¹H NMR spectra are reported in ppm on the δ scale from an internal standard of TMS. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in hertz (Hz), and integration. Chemical shifts of ¹³C NMR spectra are reported in ppm from the central peak of D6-DMSO (δ 39.51 ppm), D6-Acetone, (δ 206.68, 29.92 ppm) or CDCl₃ (δ 77.13 ppm) on the δ scale.

Absorption spectra were recorded with a Cary 60 UV/Vis absorption spectrophotometer. Fluorescence spectra were recorded with an FS5 fluorescence spectrometer from Edinburgh InstrumentTM at room temperature. Emission of singlet oxygen were recorded with an FLS 980 fluorescence spectrometer from Edinburgh InstrumentTM equipped with an NIR-PMT detector and an 850 nm long pass filter in the emission arm. Quartz cuvettes (path length = 1 cm) were used for all spectrophotometric and fluorometric measurements.

High resolution mass spectra (HRMS) were obtained on a Finnigan MAT 95XL GC Mass Spectrometer of the Southern University of Science and Technology.

All crystal data was collected from Bruker D8-Venture X-Ray Spectrometer by Dr. Xiaoyong Chang of the Southern University of Science and Technology.

Cell Cultures: Human A549 (lung), HCT116 (colon) and HepG2 (liver) cancer cells were obtained from American Type Culture Collection (ATCC) and cultured in Dulbecco's modification of Eagle medium (DMEM) supplemented with 10% fetal bovine serum, 100 units/ml penicillin, and 100 mg/ml streptomycin. Cells were cultured at 37°C in an atmosphere of 5% CO₂ and 95% humidity.

Cell proliferation was assessed by MTT [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide] assay. Briefly, cells were plated in 96-well plates (2x103cells/well) and then treated with indolizine derivatives ligated Au(III) complexes for 72 h. Afterward, cells were treated with MTT reagent and the absorbance at 570 nm was measured using a microplate reader. The viability of control (untreated cells) was regarded as 100%.

Procedure for the Cycloisomerization Substrate Preparation:



1a-c are known compounds and was prepared according to literature procedure.^{1,2}

1a: *n*-Butyllithium (5.60 mL, 14.0 mmol, 2.5 M in hexanes) was added dropwise to trimethylsilyl acetylene (2.14 mL, 15.0 mmol) in Et₂O (10.0 mL) at 0 °C, and the resulting mixture was stirred for 30 min at this temperature. The lithium acetylide solution was added dropwise to a vigorously stirred mixture of 2-acetylpyridine (1.12 mL, 10.0 mmol) and lithium bromide (2.60 g, 30.0 mmol) in a 1:1 mixture of Et₂O and benzene (total volume = 60.0 mL). The reaction mixture was stirred at ambient temperature for 12 h at which point a saturated NH₄Cl_(aq) solution (30 mL) was added to quench the reaction. The aqueous layer was extracted with EA (3 x 40 mL). The organic layers were combined, washed with brine, dried over MgSO₄ and concentrated under reduced pressure to afford the trimethylsilyl alkyne **1a**, which was purified by silica gel column chromatography.



1a

1a: ¹H NMR (400 MHz, CDCl₃) δ 8.50 (s, 1H), 7.74 (s, 1H), 7.61 (d, J = 7.9 Hz, 1H), 7.26 (s, 1H), 5.49 (s, 1H), 1.75 (s, 3H), 0.16 (s, 9H)

¹ Hardin Narayan, Alison R., Sarpong, Richmond, Organic & Biomolecular Chemistry, **2012**,10, 70

² Cho, Hanyang, Kim, Ikyon, *Tetrahedron*, **2012**, 68, 5464

1b-c are known compound and were prepared as below:



To a stirred solution of terminal alkyne (1.2 equiv) in THF was added *n*-BuLi (1.1 equiv, 1.6 M solution in hexanes) at -78 °C. After 5 min, a solution of pyridinyl ketone (1.0 equiv) in THF was added to this mixture at -78 °C slowly. After 15 min at -78 °C, the reaction mixture was quenched with saturated NH₄Cl_(aq). The reaction mixture was diluted with EA and washed with NH₄Cl_(aq). The organic layer was dried over MgSO₄ and concentrated in vacuo to give a crude mixture, which was purified by silica gel column chromatography (hexane/EA/DCM) to afford the propargylic alcohol.

1b: ¹H NMR (500 MHz, CDCl₃) δ 8.54 (d, J = 4.5 Hz, 1H), 7.77 (td, J = 1.5, 8.0 Hz, 1H),
7.69 (d, J = 8.0 Hz, 1H), 7.49–7.44 (m, 2H), 7.31–7.24 (m, 4H), 5.62 (s, 1H), 1.87 (s, 3H)

1c: ¹H NMR (500 MHz, CDCl₃) δ 8.54 (d, *J* = 4.5 Hz, 1H), 7.77 (td, *J* = 1.0, 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.44 (dd, *J* = 1.0, 3.0 Hz, 1H), 7.27 (dd, *J* = 5.0, 7.0 Hz, 1H), 7.23 (dd, *J* = 3.0, 5.0 Hz, 1H), 7.10 (d, *J* = 5.0 Hz, 1H), 5.61 (s, 1H), 1.86 (s, 3H).

1d was prepared according to the above literature procedure for **1b-c** analogously:



1d: ¹H NMR (500 MHz, CDCl₃) δ 7.68 (t, J = 7.7 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.33 – 7.28 (m, 3H), 7.14 (d, J = 7.6 Hz, 1H), 6.09 (s, 1H), 2.60 (s, 3H), 1.87 (s, 3H).
¹³C NMR (126 MHz, CDCl₃) δ 160.91, 156.31, 137.80, 131.78, 128.31, 128.18, 122.75, 122.29, 117.08, 92.51, 83.39, 68.44, 32.34, 24.15.
HRMS-ESI (m/z): [M+H]⁺ calcd for C₁₆H₁₆ON: 238.12264; found 238.12209

1e-f were prepared by typical alcohol methylation procedure:



1e: A solution of propargylic alcohol **1a** (1.0 equiv) in THF was added NaH (60% in oil, 1.5 equiv) at 0 °C under nitrogen atmosphere. CH₃I (2.0 equiv) was added at 0 °C and stirred at 0 °C. After 40 mins, the mixture was quenched by $NH_4CI_{(aq)}$ and extracted by EA. Organic layer was subjected to silica gel column chromatography (hexane/EA = 5:1) to afford the product.

1e: ¹H NMR (500 MHz, CDCl₃) δ 8.68 (d, *J* = 5.4 Hz, 1H), 7.77 – 7.66 (m, 2H), 7.25 (ddd, *J* = 7.1, 4.8, 1.4 Hz, 1H), 3.35 (s, 3H), 1.82 (s, 3H), 0.26 (s, 9H).

 ^{13}C NMR (126 MHz, CDCl_3) δ 160.42, 149.49, 136.54, 122.70, 121.10, 105.05, 92.22, 52.51, 29.63, -0.02.

HRMS-ESI (m/z): [M+H]⁺ calcd for C₁₃H₂₀ONSi: 234.13087; found 234.13043

1f: A solution of propargylic alcohol **1b** (1.0 equiv) in THF was added NaH (60% in oil, 1.5 equiv) at 0 °C under nitrogen atmosphere. CH₃I (3.0 equiv) was added at 0 °C and was allowed to stir at r.t.. After 2 hrs, the mixture was quenched by $NH_4CI_{(aq)}$ and extracted by EA. Organic layer was subjected to silica gel column chromatography (hexane/EA = 5:1) to afford the product.

1f: ¹H NMR (400 MHz, CDCl₃) δ 8.68 (d, *J* = 4.0 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.72 (ddd, *J* = 7.7, 7.7, 1.8 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.36 – 7.30 (m, 3H), 7.23 (ddd, *J* = 7.4, 4.8, 1.1 Hz, 1H), 3.39 (s, 3H), 1.91 (s, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 160.83, 149.47, 136.64, 131.87, 128.52, 128.29, 122.75, 122.59, 121.00, 88.95, 87.40, 77.49, 52.68, 29.68.

HRMS-ESI (m/z): [M+H]⁺ calcd for C₁₆H₁₆ON: 238.12264; found 238.12204

General Procedure for the Cycloisomerization Reactions:

a) General cycloisomerization procedure:



The M salts **2** (1.0 equiv) and **1** (1.0 equiv) were added to a test tube inside the glove box. After sealed with rubber septum and parafilm, the tube was taken out of the glovebox and 1 ml dried DCM was added at bench top under N₂ protection. The reaction was then heated to 40 °C and was stirred for 12 hrs. The desired product **3** and **4** showed low solubility in DCM and would precipitate out gradually during the process. Using a hot plate with effective stirring is therefore recommended.

b) General work up procedure

The desired product (ppt) was collected by filtration after cooling the reaction mixture to r.t.. It was rinsed further by DCM 5 times (4 mL) before vacuum dried. Preparative TLC was employed for further purification when necessary.

c) Representative procedure by using AuCl₃



The cycloisomerization substrate **1b** and AuCl₃ **2b** (1.0 equiv, 0.2 mmol each) were added to a test tube inside the glove box. After sealed, 1 ml DCM was added at bench top under N₂ protection. The reaction was then heated to 40 °C and was stirred for 12 hrs. The desired product **3bb** was obtained by following the general work up procedure.

d) Representative procedure by using AuCl 2a



The cycloisomerization substrate **1b** and AuCl **2a** (1.0 equiv, 0.2 mmol each) were added to a test tube inside the glove box. After sealed, 1 ml DCM was added at bench top under N₂ protection. The reaction was then heated to 40 °C and was stirred for 12 hrs. The desired product **4ba** was obtained by following the general work up procedure. The crude product was purified by preparative TLC using 5% DCM in MeOH as eluent.

e) Representative procedure by using CuCl 2d



The cycloisomerization substrate **1a** and CuCl **2d** (1.0 equiv, 0.2 mmol each) were added to a test tube inside the glove box. After sealed, 1 ml DCM was added at bench top under N₂ protection. The reaction was then heated to 40 °C and was stirred for 12 hrs. The desired product **4ad** was obtained by following the general work up procedure, except the solvent was removed by trituration first followed by vacuum.

Table 1 Preparation of complex 3 and 4 by cycloisomerization of 1 and 2.^[a]

$= -F$ THF $-78^{\circ}C$ $R^{2} = F$ H H H H H H H	$R^{1} \qquad R^{3}$ $iBr \qquad R^{2}$ $R^{2} \qquad R^{2}$	1 0.2 m <u>Yield %</u> 81 N 72 83 62 89 95	Cycloisomerization M salts 2 DCM DCM amol 40°C M salts 2 DCM M salts 2 DCM AuCl 2b AuCl 2c AuBr 2d CuCl 2e CuBr	on $R^{3}O$ R^{2} Complex 3 M = 3 M =	^{/Ie} ⊖ —M ((3, 4 AuX ₃ AuCl CuX 0-80% yield 5-79% yield
entry	alkyne 1	M salt 2	complex 3 , 4	Yield ^[b]	
1		2a	4aa	71%	
2	1a	2b	3ab	72%	
3		20	3ac	68%	
4		2a	4ba	73%	
5	ıb	2b	3 <mark>bb</mark>	75%	
6		20	3 <mark>bc</mark>	70%	
7	10	2 a	4 <mark>ca</mark>	67%	
8 ^[c]		2b	3cb	80%	
9	ıd	2b	3db	63%	
10	1e	ah	3eb	75%	
11	ıf	20	3fb	73%	
12	12	2d	4ad	79%	
13	Id	28	4ae	65%	
	$ \begin{array}{c} \hline \\ n - BuLi, L \\ \hline \\ THF \\ -78 ^{\circ}C \\ \hline \\ -78 ^{\circ}C \\ \hline \\ R^2 = F \\ H \\ H \\ H \\ \hline \\ entry \\ 1 \\ 2 \\ \hline \\ 1 \\ 2 \\ \hline \\ 3 \\ 4 \\ \hline \\ 5 \\ 6 \\ \hline \\ 7 \\ 8^{[c]} \\ 9 \\ 10 \\ \hline \\ 11 \\ 12 \\ \hline \\ 13 \\ \end{array} $	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	R1 R3 Me Cycloisomerization R3 M n-BuLi,LiBr R1 M salts 2 DCM R2 R THF R2 1 0.2 mmol 40% C R2 R R2 R3 1 0% C R2 R M Salts 2 Complex H H 1a 81 NAH, 2a AuCl 3 M = H H 1c 83 Mel 0% C 2c AuR1 4 = 2c AuR1 4 = 2c AuR2 3 4 = 2c AuR1 3xx 60 2c AuR3 4 = 2d CuCl 3xx 60 2e CuBr 4xx 65 6 2c Aux 65 6 2c 3ab 72% 6 2c 3ab

[a] see s7-8 for details of the experimental procedure. [b] Isolated yield via chromatography or recrystallization; characterized by NMR spectroscopy and HRMS. [c] conducted at rt.

Highly substituted **3** with different functional groups (R¹, R², and R³), such as silyl, aryl, heteroaryl, methoxy, and alkyl, were obtained in good yield (entry 2, 5, and 8–11). The high generality of this approach is notable because it offers opportunities to both fine tune the photophysical properties of **3** and develop catalysts similar to NHC systems. Moreover, salts like **2a** and **c–e** were found to be compatible with the conditions (AuCl, AuBr₃, entry 1, 3, 4, 6, 7; CuCl, CuBr, entry 12 and 13), giving the corresponding Au(III) complexes **3**, Au(I) and Cu(I) complexes **4**. It allowed us to compare their properties as a function of M center, oxidation state, and counter ion later on.

General Procedure for Photo-induced Reductive Elimination Reactions:



A stirring solution of **3bb** (5 mg in 10 ml MeCN, see maintext for structure) was exposed to photo-excitation (280-330 nm) for 5-10 mins. The desired reductive elimination product **5bb** was obtained in quantitative yield and no corresponding indolizine-AuCl product was observed. The product structure was determined and characterization by ¹H, ¹³C NMR, HRMS. The characteristic vinyl halides C peaks were found in ¹³C NMR.

5	Yield		
5bc	quantitative		
5ab	92%		
5bb	quantitative		
5cb	quantitative		
5db	97%		
5fb	quantitative		
5ac	quantitative		

Characterization Data:

(a) <u>NMR of Product 3</u>



¹H NMR (400 MHz, D6-Acetone) δ 9.10 (d, *J* = 6.1 Hz, 1H), 8.58 (ddd, *J* = 7.8, 7.8, 1.1 Hz, 1H), 8.36 (d, *J* = 7.8 Hz, 1H), 8.15 (dd, *J* = 6.9, 6.9 Hz, 1H), 4.79 (s, 1H), 1.82 (s, 3H), 0.70 (s, 9H).

¹³C NMR (126 MHz, D6-Acetone) δ 162.34, 160.11, 143.29, 139.33, 137.01, 127.42, 122.76, 84.58, 25.44, -0.80.

HRMS-ESI (m/z): [M-CI]⁺ calcd for C₁₂H₁₇ONAuCl₂Si: 486.01220; found 486.01022



¹H NMR (400 MHz, D6-Acetone) δ 9.20 (d, *J* = 6.1 Hz, 1H), 8.66 (ddd, *J* = 7.8, 7.8,1.0 Hz, 1H), 8.36 (d, *J* = 7.8 Hz, 1H), 8.24 (dd, *J* = 6.9, 6.9 Hz, 1H), 3.09 (s, 3H), 1.81 (s, 3H), 0.75 – 0.72 (m, 9H).

¹³C NMR (101 MHz, D6-Acetone) δ 158.79, 158.32, 143.31, 142.37, 138.16, 128.16, 123.44, 90.77, 25.55, -0.60.

HRMS-ESI (m/z): [M-Cl]⁺ calcd for C₁₃H₁₉ONAuCl₂Si: 500.02730; found 500.02662



¹H NMR (400 MHz, D6-Acetone) δ 9.08 (d, *J* = 6.1 Hz, 1H), 8.55 (ddd, *J* = 7.8, 7.8, 1.0 Hz, 1H), 8.36 (d, *J* = 7.8 Hz, 1H), 8.15 (dd, *J* = 6.9, 6.9 Hz, 1H), 4.67 (s, 1H), 1.84 (s, 3H), 0.68 (d, *J* = 3.3 Hz, 9H).

¹³C NMR (126 MHz, D6-Acetone) δ 159.80, 143.07, 139.53, 136.81, 127.29, 122.73, 84.34, 26.74, -0.74.

HRMS-ESI (m/z): [M-Br]⁺ calcd for C₁₂H₁₇ONAuBr₂Si: 573.91117; found 573.90918



¹H NMR (500 MHz, D6-DMSO) δ 8.54 (d, *J* = 6.1 Hz, 1H), 8.50 (ddd, *J* = 7.8, 7.8, 1.2 Hz, 1H), 8.36 (d, *J* = 7.8 Hz, 1H), 7.93 (ddd, *J* = 7.6, 6.2, 1.4 Hz, 1H), 7.78 (d, *J* = 7.3 Hz, 2H), 7.71 – 7.61 (m, 3H), 6.40 (s, 1H), 1.79 (s, 3H).

¹³C NMR (126 MHz, D6-DMSO) δ 161.51, 145.71, 144.31, 136.02, 135.21, 131.04, 130.87, 129.82, 127.56, 127.46, 122.96, 82.74, 26.16.

HRMS-ESI (m/z): [M+NH₄]⁺ calcd for C₁₅H₁₇ON₂AuCl₃: 543.00665; found 543.00671



¹H NMR (400 MHz, D6-DMSO) δ 8.48 (m, 2H), 8.37 (d, *J* = 7.7 Hz, 1H), 7.92 (ddd, *J* = 7.6, 6.1, 1.4 Hz, 1H), 7.81 – 7.76 (m, 2H), 7.69 – 7.62 (m, 3H), 6.33 (s, 1H), 1.82 (s, 3H).

¹³C NMR (126 MHz, D6-DMSO) δ 161.69, 145.52, 144.11, 135.82, 134.99, 130.96, 130.94, 129.73, 127.77, 127.38, 122.99, 82.59, 27.31.

HRMS-ESI (m/z): [M+Br]⁻ calcd for C₁₅H₁₃ONAuBr₄: 735.74061; found 735.74072



¹H NMR (400 MHz, D6-DMSO) δ 8.63 (d, J = 6.1 Hz, 1H), 8.57 (ddd, J = 7.8, 7.8, 1.2 Hz, 1H), 8.42 (d, J = 8.0 Hz, 1H), 8.00 (ddd, J = 7.6, 6.1, 1.3 Hz, 1H), 7.85 - 7.81 (m, 2H), 7.70 - 7.65 (m, 3H), 5.76 (s, 1H), 3.14 (s, 3H), 1.84 (s, 3H).
¹³C NMR (126 MHz, D6-DMSO) δ 157.38, 144.53, 141.94, 139.45, 136.88, 131.24, 131.08, 129.77, 128.14, 127.43, 123.46, 88.87, 54.66, 25.63.

HRMS-ESI (m/z): [M+H]⁺ calcd for C₁₆H₁₆ONAuCl₃: 539.9968; found539.9971



¹H NMR (500 MHz, D6-DMSO) δ 8.33 (dd, *J* = 7.8, 7.8 Hz, 1H), 8.16 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.68 (d, *J* = 7.0 Hz, 1H), 7.65 – 7.54 (m, 4H), 6.36 (s, 1H), 2.06 (s, 3H), 1.77 (s, 3H).

¹³C NMR (126 MHz, D6-DMSO) δ 163.24, 150.22, 147.12, 143.47, 137.39, 132.24, 131.95, 131.76, 130.74, 130.51, 129.15, 129.00, 120.78, 81.70, 26.80, 21.94. HRMS-ESI (m/z): $[M-H]^{-}$ calcd for C₁₆H₁₄ONAuCl₃: 537.98120; found 537.98181



¹H NMR (400 MHz, D6-DMSO) δ 8.70 (d, *J* = 6.1 Hz, 1H), 8.51 (ddd, *J* = 7.7, 7.7, 1.1 Hz, 1H), 8.35 (d, *J* = 7.7 Hz, 1H), 8.16 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.97 (ddd, *J* = 7.6, 6.1, 1.3 Hz, 1H), 7.92 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.58 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.41 (s, 1H), 1.77 (s, 3H).

¹³C NMR (101 MHz, D6-DMSO) δ 161.38, 145.82, 144.37, 135.39, 132.00, 130.33, 128.81, 128.76, 127.50, 127.46, 122.91, 82.54, 26.15.

HRMS-ESI (m/z): [M-H]⁻ calcd for C₁₃H₁₀ONAuCl₃S: 529.9209; found 529.9205.

(b) NMR of Product 4



¹H NMR (500 MHz, D6-Acetone) δ 8.91 (d, *J* = 6.1 Hz, 1H), 8.42 (ddd, *J* = 7.7, 7.7, 1.2 Hz, 1H), 8.19 (d, *J* = 7.7 Hz, 1H), 8.01 (dd, *J* = 6.9, 6.9 Hz, 1H), 4.96 (s, 1H), 1.61 (s, 3H), 0.58 (s, 9H).

¹³C NMR (126 MHz, D6-Acetone) δ 184.64, 163.43, 142.16, 140.83, 135.52 – 134.96, 126.79, 122.27, 87.80, 26.37, 0.02.

HRMS-ESI (m/z): [M-CI]⁺ calcd for C₁₂H₁₇ONAuSi: 416.07394; found 416.07223



¹H NMR (400 MHz, D6-DMSO) δ 8.53 (d, *J* = 6.1 Hz, 1H), 8.39 (dd, *J* = 7.7, 7.7 Hz, 1H), 8.24 (d, *J* = 7.7 Hz, 1H), 7.85 (dd, *J* = 6.9, 6.9 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.60 – 7.52 (m, 3H), 6.08 (s, 1H), 1.59 (s, 3H).

¹³C NMR (101 MHz, D6-DMSO) δ 168.63, 163.39, 142.11, 140.16, 133.52, 131.15, 130.41, 129.62, 129.35, 127.10, 122.53, 85.21, 26.58.

HRMS-ESI (m/z): [M-H]⁻ calcd for C₁₅H₁₂ONAuCl: 454.02784; found 454.02795



¹H NMR (400 MHz, D6-DMSO) δ 8.68 (d, *J* = 6.1 Hz, 1H), 8.39 (dd, *J* = 7.7, 7.7 Hz, 1H), 8.22 (d, *J* = 7.7 Hz, 1H), 8.00 (d, *J* = 1.8 Hz, 1H), 7.89 (dd, *J* = 6.5, 6.5 Hz, 1H), 7.77 (dd, *J* = 4.9, 2.9 Hz, 1H), 7.56 – 7.52 (m, 1H), 6.04 (s, 1H), 1.58 (s, 3H).

¹³C NMR (126 MHz, D6-DMSO) δ 168.71, 163.20, 142.17, 135.79, 133.70, 131.28, 129.29, 127.41, 127.15, 122.43, 85.00, 26.56.

HRMS-ESI (m/z): [M-H]⁻ calcd for C₁₃H₁₁ONAuClS: 459.9843 found 459.9842



¹H NMR (500 MHz, D6- Acetone) δ 8.55 (d, *J* = 4.8 Hz, 1H), 8.18 (ddd, *J* = 7.8, 7.8, 1.7 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.67 (ddd, *J* = 7.6, 5.2, 1.2 Hz, 1H), 6.12 (s, 1H), 1.90 (s, 3H), 0.37 (s, 9H).

¹³C NMR (126 MHz, D6- Acetone) δ 167.29, 147.62, 140.19, 125.07, 121.82, 111.68, 96.04, 77.19, 31.44, -0.91.

HRMS-ESI (m/z): [M-Br]⁺ calcd for C₁₂H₁₇ONCuSi: 282.03699; found 282.03650

¹H NMR (500 MHz, D6-Acetone) δ 8.50 (d, *J* = 4.8 Hz, 1H), 8.15 (ddd, *J* = 7.8, 7.8, 1.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.63 (ddd, *J* = 7.5, 5.2, 1.2 Hz, 1H), 6.10 (s, 1H), 1.87 (s, 3H), 0.33 (s, 9H).

¹³C NMR (126 MHz, D6-Acetone) δ 168.97, 149.17, 142.01, 126.83, 123.50, 112.90,

97.55, 78.85, 33.28, 0.90.

HRMS-ESI (m/z): [M-Cl]⁺ calcd for C₁₂H₁₇ONCuSi: 282.03699; found 282.03641

(c) NMR of Product 5

Structural assignment of **5** was done by NMR, HRMS and comparison of the relevant species reported in the literature: This included the spectroscopic comparison with the corresponding organometallic Au(I) species isolated as shown in the above, as well as non-organometallic species like the 2-halobenzimidazole³, 2-haloindene⁴ and conjugated indolizine⁵ derivatives.



¹H NMR (500 MHz, D6-DMSO) δ 8.88 (d, *J* = 6.1 Hz, 1H), 8.70 (dd, *J* = 7.8, 7.8 Hz, 1H), 8.49 (d, *J* = 7.8 Hz, 1H), 8.26 (dd, *J* = 3.0, 1.5 Hz, 1H), 8.10 (dd, *J* = 7.0, 7.0 Hz, 1H), 7.98 (d, *J* = 3.3 Hz, 1H), 7.48 (d, *J* = 5.0 Hz, 1H), 7.07 (s, 1H), 1.75 (s, 3H). 13C NMR (126 MHz, D6-DMSO) δ 157.94, 146.31, 138.37, 137.24, 133.23, 132.39, 129.41, 128.29, 128.12, 123.34, 122.80, 79.33, 22.42.

HRMS-ESI (m/z): [M-AuCl₂]⁺ calcd for C₁₃H₁₁ONClS: 264.0244; found 264.0243



¹H NMR (500 MHz, D6-DMSO) δ 8.75 (d, *J* = 6.1 Hz, 1H), 8.71 (dd, *J* = 7.8, 7.8 Hz, 1H), 8.51 (d, *J* = 7.9 Hz, 1H), 8.06 (t, *J* = 6.9 Hz, 1H), 7.71-7.64 (m, 5H), 7.03 (s, 1H), 1.77 (s, 3H).

¹³C NMR (126 MHz, D6-DMSO) δ 158.10, 146.38, 138.65, 137.14, 137.07, 132.24, 130.91, 130.18, 128.18, 123.46, 123.36, 79.53, 22.33.

HRMS-ESI (m/z): [M-AuCl₂]⁺ calcd for C₁₅H₁₃ONCl: 258.0680; found 258.0675.

³ Galy, J.-P.; Hanoun, J.-P.; Pique, V.; Jagerovic, N.; Eguero, J. J. Heterocyclic Chem. **1997**, 34, 1781.

⁴ a) Anke, L.; Weyerstahl, P. *Chemische Berichte* **1985**, *118*, 613; b) Schlegel, G.; Schaefer, H. J. *Chemische Berichte* **1983**, *116*, 960.

⁵ For 1-haloindolizine: a) Yang, Y.; Kuang, C.; Jin, H.; Yang, Q. *Synthesis* **2011**, 3447; For simple indolizine: b) Chernyak, D.; Gadamsetty, S. B.; Gevorgyan, V. *Org. Letts.* **2008**, *10*, 2307.



¹H NMR (500 MHz, D6-Acetone) δ 9.27 (d, *J* = 6.1 Hz, 1H), 8.77 (dd, *J* = 7.8, 7.8 Hz, 1H), 8.52 (d, *J* = 7.8 Hz, 1H), 8.27 (dd, *J* = 7.1, 7.1 Hz, 1H), 6.01 (s, 1H), 1.78 (s, 3H), 0.68 (s, 10H).

¹³C NMR (126 MHz, D6-Acetone) δ 159.56, 145.38, 145.14, 142.57, 139.06, 128.12, 123.51, 23.04, -1.19.

HRMS-ESI (m/z): [M-AuBr₂]⁺ calcd for C₁₂H₁₇ONBrSi: 298.02573; found 298.02542



¹H NMR (500 MHz, D6-Acetone) δ 9.25 (d, *J* = 6.2 Hz, 1H), 8.77 (ddd, *J* = 7.9, 7.9, 1.2 Hz, 1H), 8.51 (d, *J* = 7.9 Hz, 1H), 8.28 (ddd, *J* = 7.7, 6.1, 1.4 Hz, 1H), 1.82 (d, *J* = 1.7 Hz, 3H), 0.66 (s, 9H).

¹³C NMR (126 MHz, D6-Acetone) δ 158.93, 153.27, 145.28, 140.40, 139.29, 128.21,

123.39, 80.97, 22.14, -1.62.

HRMS-ESI (m/z): [M-AuCl₂]⁺ calcd for C₁₂H₁₇ONClSi: 254.07624; found 254.07584



¹H NMR (500 MHz, D6-DMSO) δ 8.72 – 8.67 (m, 2H), 8.51 (d, *J* = 7.8 Hz, 1H), 8.04 (dd, *J* = 7.7, 6.0 Hz, 1H), 7.71-7.64 (m, 5H), 1.74 (s, 3H).

 ^{13}C NMR (126 MHz, D6-DMSO) δ 158.92, 146.06, 139.04, 136.88, 132.10, 131.52,

130.90, 130.11, 128.11, 124.35, 123.53, 80.51, 23.12.

HRMS-ESI (m/z): [M-AuBr₂] + calcd for C₁₅H₁₃ONBr: 202.01750; found 202.01758.



¹H NMR (500 MHz, D6-DMSO) δ 8.86 (d, *J* = 6.1 Hz, 1H), 8.76 (dd, *J* = 7.8, 7.8 Hz, 1H), 8.55 (d, *J* = 7.8 Hz, 1H), 8.14 (dd, *J* = 7.0, 7.0 Hz, 1H), 7.83 – 7.78 (m, 2H), 7.77 – 7.71 (m, 3H), 3.08 (s, 3H), 1.80 (s, 3H).

¹³C NMR (126 MHz, D6-DMSO) δ 154.26, 146.45, 139.98, 138.72, 134.76, 132.37, 131.13, 130.01, 128.72, 123.91, 123.12, 85.48, 53.80, 22.11.

HRMS-ESI (m/z): [M-AuCl₂] + calcd for C₁₆H₁₅ONCl: 272.08367; found 272.08267



¹H NMR (500 MHz, D6-DMSO) δ 8.54 (dd, J = 7.9, 7.9 Hz, 1H), 8.32 (d, J = 7.8 Hz, 1H),
7.91 (d, J = 7.9 Hz, 1H), 7.72 – 7.59 (m, 5H), 7.04 (s, 1H), 2.15 (s, 3H), 1.75 (s, 3H).
¹³C NMR (126 MHz, DMSO) δ 159.84, 151.96, 145.24, 140.84, 139.02, 131.80, 131.18,
131.07, 131.04, 129.85, 129.72, 127.97, 121.25, 78.27, 23.05, 22.14.
HRMS-ESI (m/z): [M-AuCl₂] ⁺ calcd for C₁₆H₁₅ONCI: 272.08367; found 272.08279

Selected Structural Information of Isolated Complexes

Selected bond lengths (A) and angles (deg) of **3ab**, **3bb**, **3cb**, **3fb** and **3bc**, and the ¹³C NMR of the Au-C (ppm).

entry	1	2	3	4	5
Complex 3	3ab	3 <mark>bb</mark>	3cb	3 <mark>fb</mark>	3 <mark>bc</mark>
Dihedral angle of R ¹ and core	n.a.	54.53	40.48	52.76	53.63
Au-C	2.0053	1.9949	1.9935	2.0017	2.030
Au-X _{trans}	2.3631	2.3565	2.3561	2.3372	2.4753
Δ11_Χ	2.2871	2.2802	2.2961	2.2932	2.4084
	2.2911	2.2841	2.2862	2.2842	2.4224
2 ∠2 X ∠3	1 = 85.40	87.27	86.77	88.82	86.99
C-Au—X //∠1 ↓ ∠4	2 = 91.35	90.34	90.47	90.22	91.09
X	3 = 92.78	91.60	91.50	89.38	91.26
∠ 1, 2,3, 4	4 = 90.67	90.86	91.12	91.61	90.85
Length of C=C	1.337	1.329	1.329	1.329	1.270
¹³ C NMR	160.11		1 45 82	144.50	145 50
at Au-C	100.11	145.70	145.02	144.53	145.52

Absorption spectral changes of 3bb and 3cb

The absorption spectral changes of **3bb** (top, $R^1 = Ph$) and **3cb** (bottom, $R^1 = thiophen$) upon the irradiation of UV light (280 nm).

Inserts show the absorbance change of selected wavelength upon different irradiation duration.



UV spectrum:



Figure 1: UV abs Comparisons of product 3 and product 5



Figure 2: UV abs of other product 3

Fluorescence spectrum:



Figure 3: Emission scan of product 3 before and after irradiation comparisons (photo induced R.E. reaction)



Figure 2: Emission scan of other product 3

Absorption and Emission Wavelength Data of 3, 4 and 5





entry	M =	3,4	λ_{Abs} (nm)	$\lambda_{Em} (nm)^{[b]}$
1	AuCl	4 <mark>aa</mark>	334·3 ^[c]	473.6
2	AuCl ₃	3ab	289.3	413.2
3	AuBr ₃	3ac	282.1	398.0
4	AuCl	4 <mark>ba</mark>	340.3 ^[c]	510.0
5	AuCl ₃	3 <mark>bb</mark>	281.0	474.3
6	AuBr ₃	3 <mark>bc</mark>	283.5	468.0
7	AuCl	4 <mark>ca</mark>	350.2 ^[c]	515.6
8	AuCl ₃	3 <mark>cb</mark>	280.5	538.1
9		3db	292.0	468.0
10	AuCl ₃	3eb	292.1	383.0
11		3 <mark>fb</mark>	283.9	481.0
12	CuCl	4 <mark>ad</mark>	261.3 ^[c]	406.7
13	CuBr	4ae	263.0 ^[c]	448.5

All the studies were conducted in degassed CH₃CN at r.t.. [a] $\lambda_{\text{Excitation}}$ = 330 and 350 nm [b] $\lambda_{\text{Excitation}}$ = 284 nm, λ_{em} before and after the photo-excitation are essentially the same (~ 5 nm differences).

[c] No obvious change in $\lambda_{\mbox{\tiny abs}}$ (~ 5 nm differences) and intensity after photo-excitation.

Singlet Oxygen Emission Signal Study:

As mentioned in the maintext, we suspected that there was an intersystem crossing (ISC) of Au (III) and the indolizine derivatives at their excited states, which turned the emissive singlet to the dark triplet excited state. So, we conducted experiment to detect the singlet oxygen generation and the results were summarized as follow:

compound	Single oxygen quantum yield
3cb	26%
3bb	25%
3ac	14%

Table S1: singlet oxygen generation quantum yield

Emission of singlet oxygen was recorded with an FLS 980 fluorescence spectrometer from Edinburgh InstrumentTM equiped with an NIR-PMT detector and an 850 nm long pass filter in the emission arm. Quartz cuvettes (path length = 1 cm).



Figure 3: The NIR emission of ¹O₂

Singlet oxygen quantum yields of the compounds were determined by measuring the peak areas of the NIR emission of ${}^{1}O_{2}$ centered at 1270 nm generated by these compounds and compared to that generated from the reference standard Rose Bengal (Qy = 76%) upon photo-excitation at 328 nm.

Cyctotoxicity evaluation of complex 3 on cancer cell lines

Cell Cultures

Human A549 (lung), HCT116 (colon) and HepG2 (liver) cancer cells were obtained from American Type Culture Collection (ATCC) and cultured in Dulbecco's modification of Eagle medium (DMEM) supplemented with 10% fetal bovine serum, 100 units/ml penicillin, and 100 mg/ml streptomycin. Cells were cultured at 37°C in an atmosphere of 5% CO₂ and 95% humidity.

Cell proliferation assay

Cell proliferation was assessed by MTT [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide] assay. Briefly, cells were plated in 96-well plates (2x10³cells/well) and then treated with indolizine derivatives ligated Au(III) complexes for 72 h. Afterward, cells were treated with MTT reagent and the absorbance at 570 nm was measured using a microplate reader. The viability of control (untreated cells) was regarded as 100%.

Cytotoxic effects of indolizine derivatives ligated Au(III) complexes.

A549 (lung), HCT116 (colon) and HepG2 (liver) cancer cells were untreated or treated with different concentrations of indolizine derivatives ligated Au(III) complexes for 72 h. Cell viability was assessed by the MTT assay. IC50 represents the drug concentration required for 50% inhibition of cell proliferation. The data are presented as the mean ± SD of three replicates. Results are representative of 2 independent experiments.

<u>Results</u>

To determine the potential anticancer activity of indolizine derivatives ligated Au(III) complexes, three human cancer cell lines (A549, HCT116 and HepG2) were treated with different concentrations of Au(III) complexes and then assayed for cell viability. Conducted at 0.1% v/v DMSO in cell culture medium.



This preliminary study showed that the substituent effect is very critical, in which complex **3ac** exerted a good cytotoxic effects to those cell lines with IC50 values of 27.2 to 55.7μ M, compared with other Au(III) complexes.

Raw data for the graphs above:

<u>A549</u>

	<u>% Survival</u>						
	3cb	3fb	3bc	3ac	3db	3ac	
<u>uM</u>							
160	87.48	29.66	75.73	79.61	86.37	3.55	
80	89.62	39.37	90.11	84.88	87.55	3.25	
40	92.95	85.59	89.97	90.58	87.71	80.59	
20	93.84	96.19	96.30	92.02	93.42	99.66	
10	98.94	98.12	94.64	102.04	96.63	98.74	
0	100.00	100.00	100.00	100.00	100.00	100.00	

<u>St. Dev.</u>							
	3cb	3fb	3bc	3ac	3db	3ac	
<u>uM</u>							
160	7.38	0.25	3.07	5.14	4.16	0.10	
80	7.09	0.74	5.74	7.42	0.60	0.16	
40	7.72	2.92	6.47	9.65	4.16	6.11	
20	4.55	6.13	2.15	8.12	5.11	7.76	
10	9.18	4.16	1.65	6.23	2.90	6.22	
0	6.11	8.01	5.77	0.90	3.31	2.02	

<u>H116</u>

	<u>% Survival</u>						
	3cb	3fb	3bc	3ac	3db	3ac	
<u>uM</u>							
160	45.82	12.13	55.72	57.45	65.97	5.36	
80	72.49	45.12	81.85	73.35	82.41	4.76	
40	87.49	81.21	94.30	90.05	85.02	7.97	
20	88.18	95.50	93.12	90.84	90.58	73.70	
10	98.43	94.14	94.07	97.79	95.29	92.63	
0	100.00	100.00	100.00	100.00	100.00	100.00	

<u>St. Dev.</u>							
	3cb	3fb	3bc	3ac	3db	3ac	
<u>uM</u>							
160	2.56	0.91	3.89	0.62	9.04	0.19	
80	1.00	0.99	0.80	0.67	1.42	0.16	
40	3.76	1.61	7.12	4.11	1.98	0.90	
20	1.77	4.18	1.46	2.71	6.65	2.98	
10	4.10	6.01	1.99	4.52	2.88	3.28	
0	1.04	5.35	1.28	1.06	1.09	1.22	

HepG2

	<u>% Survival</u>						
	3cb	3fb	3bc	3ac	3db	3ac	
<u>uM</u>							
160	41.71	26.07	50.56	49.05	62.14	4.56	
80	62.96	57.66	76.10	68.06	84.60	4.15	
40	77.98	73.93	84.57	82.69	85.94	13.69	
20	87.16	89.15	95.60	85.85	93.45	72.13	
10	95.39	92.41	96.03	89.68	93.21	94.27	
0	100.00	100.00	100.00	100.00	100.00	100.00	

	<u>St. Dev.</u>						
	3cb	3fb	3bc	3ac	3db	3ac	
<u>uM</u>							
160	4.21	1.44	2.32	3.89	1.99	0.12	
80	4.91	1.64	0.72	1.94	4.75	0.12	
40	6.93	0.81	4.84	1.54	7.12	1.56	
20	4.79	3.04	1.64	3.37	5.58	2.46	
10	2.96	3.09	2.34	3.90	3.30	1.43	
0	4.17	0.71	5.81	2.40	5.87	1.53	



—160.42	—149.49	—136.54	∕_122.70 ∕_121.10				52.51		0.02	
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17 Acquisition Date 2018-08-16T14:15:54 18 Modification Date 2018-08-16T15:57:08 19 Spectrometer Frequency 125:76 20 Spectral Width 29761.9 21 Lowest Frequency -2305.8 22 Nucleus 13C 23 Acquired Size 32768 24 Spectral Size 65536	16 Acquisition Time	1.1010				ŀ.			
18 Modification Date 2018-08-16T15:57:08 19 Spectrometer Frequency 125.76 20 Spectral Width 29761.9 21 Lowest Frequency -2305.8 22 Nucleus 13C 23 Acquired Size 32768 24 Spectral Size 65536	17 Acquisition Date	2018-08-16T14:15:54							
19 Spectrometer Frequency 125.7620 Spectral Width29761.921 Lowest Frequency-2305.822 Nucleus13C23 Acquired Size3276824 Spectral Size65536	18 Modification Date	2018-08-16T15:57:08							
20 Spectral Width 29/61.9 21 Lowest Frequency -2305.8 22 Nucleus 13C 23 Acquired Size 32768 24 Spectral Size 65536	19 Spectrometer Frequent	cy 125.76							
21 Lowest Frequency -2303.8 22 Nucleus 13C 23 Acquired Size 32768 24 Spectral Size 65536	20 Spectral width	29761.9							
23 Acquired Size 32768 24 Spectral Size 65536	22 Nuclous	-2303. 8							
24 Spectral Size 65536	23 Acquired Size	32768							
	24 Spectral Size	65536							

165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 f1 (ppm)

Parameter	Value
Title	YJ-01-131-P
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	spect
7 Author	
8 Solvent	CDC13
9 Temperature	295.7
11 Experiment	2g30 1D
12 Number of Scans	8
13 Receiver Gain	22
14 Relaxation Delay	1.0000
15 Pulse Width	10.0000
16 Acquisition Time	1.9999
17 Acquisition Date	2018-08-16T21:55:33
19 Spectrometer Frequen	2018-08-27119.37.40 cv 400_13
20 Spectral Width	8012.8
21 Lowest Frequency	-1535.4
22 Nucleus	1H
23 Acquired Size	16025
24 Spectral Size	32768
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00.1	1.11 1.13 3.18 1.10
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9.0 8.5 8.	0 7.5 7.0

60.83	49.47	36.64 31.87 28.52 28.29	22.75 22.59 21.00
Ī	T I		

Paramet	ver Value
1 Title	YJ-01-131-P
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	spect
7 Author	
8 Solvent	CDC13
9 Temperature	295.8
10 Pulse Sequenc	e zgpg30
11 Experiment	1D
12 Number of Sca	ns 29
13 Receiver Gain	196
14 Relaxation De	lay 2.0000
15 Pulse Width	10.0000
16 Acquisition T	ime 1.3631
17 Acquisition D	ate 2018-08-16T21:59:19
18 Modification	Date 2018-08-27T19:37:40
19 Spectrometer	Frequency 100.61
20 Spectral Widt	h 24038.5
21 Lowest Freque	ncy -1958.0
22 Nucleus	13C
23 Acquired Size	32768
24 Spectral Size	65536

~88.95 ~87.40

-77.49



-29.68

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65	160	155	150	145	140	135	130	125	120	115	110	105	100	95	90	85	80	75	70	65	60	55	50	45	40	35	30	2!
	f1 (ppm)																											

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Parameter	Value
1 Title	zxh-s-1-57-20160812
2 Comment	zxh-s-1-57-20160812
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
o Site	
6 Spectrometer	spect
Author	
3 Solvent	Acetone
9 Temperature	298.1
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	10
13 Receiver Gain	174
14 Relaxation Delay	1.0000
15 Pulse Width	9.6000
16 Acquisition Time	1.9999
17 Acquisition Date	2016-08-12T09:53:12
18 Modification Date	2016-08-12T10:16:27
19 Spectrometer Frequence	y 400.13
20 Spectral Width	8012.8
21 Lowest Frequency	-1535.4
22 Nucleus	1H
23 Acquired Size	16025
24 Spectral Size	32768
F4 F4 F4	ЬЧ
	0
0.0	7.0
9.0 9.0 8.9	0.0 1.0 1.0

~162.34 ~160.11	143.29 137.01 127.42 122.76	
Parameter 1 Title	Value zxh-s-1-57 13C	
2 Comment		
3 Origin	Bruker BioSpin GmbH	
4 Owner	nmr	
6 Spectrometer	spect	1
7 Author		
8 Solvent	Acetone	
9 Temperature	296.2	
10 Pulse Sequence	zgpg30	
11 Experiment	1D	
12 Number of Scans	3000	
13 Receiver Gain	193	
14 Relaxation Delay	2.0000	
15 Pulse Width	10.0000	
16 Acquisition Time	1.1010	
17 Acquisition Date	2016-01-17T08:08:42	
18 Modification Date	2016-01-18T09:44:09	
19 Spectrometer Frequen	су 125.77	
20 Spectral Width	29761.9	
21 Lowest Frequency	-2305.8	
22 Nucleus	13C	
23 Acquired Size	32768	
24 Spectral Size	65536	
		,

-10 f1 (ppm)

Parameter	Value								
1 Title	zxh-s-1-76-f1								
2 Comment	zxh-s-1-76-f1								I
3 Origin	Bruker BioSpin GmbH								
4 Owner	nmr								
5 Site									
6 Spectrometer	spect								
7 Author									
8 Solvent	Acetone								
9 Temperature	294.5								
10 Pulse Sequence	zg30								
11 Experiment	1D								
12 Number of Scans	8								
13 Receiver Gain	62								
14 Relaxation Delay	1.0000								
15 Pulse Width	9.6000		04	lo.					
16 Acquisition Time	1.9999			ic 1e					
17 Acquisition Date	2016-03-15T12:26:12								
18 Modification Date	2016-03-15T13:01:41								
19 Spectrometer Frequer	ncv 400. 13		~⊕ <u>`</u>	~					
20 Spectral Width	8012.8		IM	S					
21 Lowest Frequency	-1535.4								
22 Nucleus	1H								
23 Acquired Size	16025								
24 Spectral Size	32768								
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10.5 10.0 9.5	90 85 80 7	7.0 6 5	5 60	55 50	4.5 4.0	35	3.0 9	25 20 15	10 05
10.0 10.0 0.0	0.0 0.0 0.0 1		, 0.0	f1 (ppm)	1.0 1.0	0.0	0.0 2	2.0 2.0 1.0	1.0 0.0

58.79 58.32	43.31 42.37 38.16	28.16	23.44
~ ~	~ ~ ~	<u> </u>	~
\mathbf{Y}	$\langle 2 \rangle$		

	Parameter	Value
1	Title	zxh-s-1-76-f1-13C
2	Comment	zxh-s-1-76-f1-13C
3	Origin	Bruker BioSpin GmbH
4	Owner	nmr
5	Site	
6	Spectrometer	spect
7	Author	
8	Solvent	Acetone
9	Temperature	294.5
10	Pulse Sequence	zgpg30
11	Experiment	1D
12	Number of Scans	473
13	Receiver Gain	196
14	Relaxation Delay	2.0000
15	Pulse Width	10.0000
16	Acquisition Time	1.3631
17	Acquisition Date	2016-03-15T12:29:27
18	Modification Date	2016-03-15T13:01:43
19	Spectrometer Frequency	100.61
20	Spectral Width	24038.5
21	Lowest Frequency	-1958.0
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536

f1 (ppm)

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le	zxh-s-1-76-f1-13C
nent	zxh-s-1-76-f1-13C
gin	Bruker BioSpin GmbH
er	nmr
þ	
ctrometer	spect
lor	
vent	Acetone
perature	294.5
se Sequence	zgpg30
eriment	1D
per of Scans	473
eiver Gain	196
axation Delay	2.0000
se Width	10.0000
isition Time	1.3631
isition Date	2016-03-15T12:29:27
ification Date	2016-03-15T13:01:43
ctrometer Frequend	cy 100.61
etral Width	24038.5
est Frequency	-1958.0
ired Size	13U 22769
atral Sizo	02100 65536
strar Size	00000
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www.	annal laga ann ha airma an airmheannan

Parameter	Value								
Title Comment Origin Owner Site	zxh-s-1-117-2-F1 zxh-s-1-117-2-F1 Bruker BioSpin GmbH nmr								
Spectrometer Author	spect								
Solvent Temperature 0 Pulse Sequence 1 Experiment 2 Number of Scans 3 Receiver Gain 4 Relaxation Delay 5 Pulse Width 6 Acquisition Time 7 Acquisition Date 8 Modification Date 9 Spectrometer Frequency 20 Spectral Width 1 Lowest Frequency 22 Nucleus 23 Acquired Size 24 Spectral Size	Acetone 299.6 zg30 1D 11 155 1.0000 9.6000 1.9999 2016-05-09T22:13:49 2016-05-10T09:09:39 ncy 400.13 8012.8 -1535.4 1H 16025 32768	Ĉ. €	OH AuCI TMS						
1.00 ≖	1.03 ⊥ 1.05 ⊥ 1.00 ⊥		0.85			3.25	9.33 ⊥		
0 9.5 9.0 8.	.5 8.0 7.5 7.0	6.5 6.0 5.5	5.0 4.5 f1 (ppm)	4.0 3.5	3.0 2.5	2.0 1.5	1.0 0.5	0.0	-0.5 -

	142.15 140.82 135.21	—126.78 —122.27			-26.37	-0.02
Parameter	Value					
1 Title 2 Comment	zxh-s-1-117-13C					
3 Origin 4 Owner 5 Site	Bruker BioSpin GmbH nmr					
<pre>6 Spectrometer 7 Author</pre>	spect	OH I Mo				
8 Solvent 9 Temperature 10 Pulse Sequence 11 Experiment 12 Number of Scans 13 Receiver Gain 14 Relaxation Delay 15 Pulse Width 16 Acquisition Time 17 Acquisition Date 18 Modification Date 19 Spectrometer Frequence 20 Spectral Width	Acetone 296.1 zgpg30 1D 2800 196 2.0000 10.0000 1.3631 2016-08-11T01:41:42 2016-08-11T09:49:23 zy 100.62 24038.5	TMS				
21 Lowest Frequency 22 Nucleus 23 Acquired Size	-1958.0 13C 32768					
24 Spectral Size	65536					
				างกับและการระบบเป็นเป็นเป็นเป็นเป็นเป็นเป็นเป็นเป็นเป็น		mantheaterman
190 180 170	160 150 140	130 120 110 100 f	90 80 70 1 (ppm)	60 50 40	30 20 10	0

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Parameter	Value								
1 Title	YJ-01-130-ACETONE								
2 Comment									
3 Origin	Bruker BioSpin GmbH								
4 Owner	nmr								
5 Site									
6 Spectrometer	spect								
7 Author		ОН				1			
8 Solvent	Acetone	ALME							
9 Temperature	295.6	íĩ≻–a	uBr ₃						
10 Pulse Sequence	zg30	<u>∿</u> _{ ©							
11 Experiment	1D	Ϋ́ TMS							1
12 Number of Scans	32								
13 Receiver Gain	174								
14 Relaxation Delay	1.0000								
15 Pulse Width	8.7300								
16 Acquisition Time	1.9999								
17 Acquisition Date	2018-07-02T17:36:07								
18 Modification Date	2018-07-03T14:42:49								
19 Spectrometer Frequenc	ey 400. 13								
20 Spectral Width	8012.8								
21 Lowest Frequency	-1535.4								
22 Nucleus	1H								
23 Acquired Size	16025								
24 Spectral Size	32768								
u 1.,		1							
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<u> </u>		.60				.91	ļ	4	
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	√143.07√139.53√136.81	—127.30 —122.73			-26.74	
Parameter 1 Title	Value zxh-1-59_13C					
2 Comment 3 Origin 4 Owner 5 Site	Bruker BioSpin GmbH nmr					
6 Spectrometer 7 Author	spect					
Solvent Temperature O Pulse Sequence 1 Experiment 2 Number of Scans 3 Receiver Gain 4 Relaxation Delay 5 Pulse Width 6 Acquisition Time 7 Acquisition Date 8 Modification Date 9 Spectrometer Frequenc 20 Spectral Width 21 Lowest Frequency 22 Nucleus	Acetone 296.2 zgpg30 1D 500 193 2.0000 1.0486 2016-01-19T05:49:37 2016-01-19T10:53:47 y 125.77 31250.0 -3049.8 13C		H H AuBr ₃ TMS			
23 Acquired Size 24 Spectral Size	32768 65536					
Wyrdarydd ^a Myflunysyllangaassanwawaanynadagadaayahyfrigy	ประวัติสูงสาวที่สามารถสาวที่มายใหญ่ได้ เหตุสาวที่มายารสาวที่ เป็นประชุญาตาวที่สามารถสาวที่มายใหญ่ได้ เหตุสาวที่มายารสาวที่	รงปลุกราชไปไปการการเป็นปลุกสุดที่เหลือเป็นปล	เ มหายาศตรรุกรับสุขิทรงที่มีการสารประกับสายครับสายสารสารสารสารสารสารสารสารสารสารสารสารสารส	na skjel klane man andre sta v stor folk folk folk for all bei for all and stare on the final star of the star s		gungal ata/vanivuminumatanananataja
180 170 160	150 140 1	30 120	110 100 90 80 70 60) 50 40 30	0 20 10	0 -10

Parameter	Value										
1 Title	YI-01-101-F1-DMS0										
2 Comment	Y I-01-101-F1-DMS0										
3 Origin	Bruker BioSpin GmbH										
4 Owner	nmr										
5 Site											
6 Spectrometer	spect										
7 Author											
8 Solvent	DMSO										
) Temperature	293. 1			он							
10 Pulse Sequence	zg30		\sim	Me							
1 Experiment	1D		L .N.	/≻АµСI							
2 Number of Scans	32			Ϋ́							
3 Receiver Gain	142			Ph							
4 Relaxation Delay	1.0000										
5 Pulse Width	8.7300										
6 Acquisition Time	1.9999										
7 Acquisition Date	2018-02-24T12:46:40										
8 Modification Date	2018-02-26T09:37:06										
9 Spectrometer Frequenc	cy 400. 13										
20 Spectral Width	8012.8						I				
1 Lowest Frequency	-1535.4										
22 Nucleus	1H										
23 Acquired Size	16025										
24 Spectral Size	32768										
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.0 8.5 8.0	7.5 7.0 6.5	6.0	5.5 5.	0	4.0	3.5 3.0	2.5	2.0 1.5	1.0	0.5	0.0



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180 170

18 Modification Date

20 Spectral Width

23 Acquired Size

24 Spectral Size

22 Nucleus

90

21 Lowest Frequency

19 Spectrometer Frequency 100.61

160 150

140

2018-01-30T11:17:31

24038.5

-1956.8

13C

32768

65536

130 120

100 9 f1 (n

110

90 f1 (ppm)

80

70 60

50

40 30

20

0

10





Parameter 1 Title	Value YJ-01-89-H													
2 Comment														
3 Origin	Bruker BioSpin GmbH													
4 Owner 5 Site	nmr													
6 Spectrometer	spect													
7 Author														
8 Solvent	DMSO													
9 Temperature	296.1			ОН										
10 Pulse Sequence	zg30			~ IM	е									
12 Number of Scans	18			$[] \rightarrow$	AuBr ₃									
13 Receiver Gain	95				Θ									
14 Relaxation Delay	1.0000			Ŭ Ph										
15 Pulse Width	11.2900													
16 Acquisition Time	3. 2768													
17 Acquisition Date	2017-11-08T13:27:37													
18 Modification Date	2017-11-08T14:24:49													
19 Spectrometer Frequency	500.13													
20 Spectral Width	10000.0													
21 Lowest Frequency	-1911.5													
22 Nucleus	1H													
23 Acquired Size	32768 GEE26													
24 Spectral Size	00000													
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K k	1 k						N							
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00.	1.01 30.02 3.05	.07								3.15				
····					· · · ·						<u> </u>	· .	· · · ·	
9.5 9.0 8.5	8.0 7.5 7.0	6.5	5.0 5	5.5 5.0 f1	4.5 (ppm)	4.0	3.5	3.0	2.5	2.0 1.	5 1.0	0.5	0.0	-0.











25.63





f1 (ppm)

		DC	CM			
Parameter1Title2Comment3Origin4Owner5Site6Spectrometer7Author8Solvent9Temperature10Pulse Sequence11Experiment12Number of Scans13Receiver Gain14Relaxation Delay15Pulse Width16Acquisition Time17Acquisition Date18Modification Date19Spectrometer Frequent20Spectral Width21Lowest Frequency22Nucleus23Acquired Size24Spectral Size	Value YJ-01-25-DMSO YJ-01-25-DMSO Bruker BioSpin GmbH nmr spect DMSO 296.7 zg30 1D 32 98 1.0000 9.6000 1.9999 2016-07-24T18:36:38 2017-07-25T20:00:00 ncy 400.13 8012.8 -1535.4 1H 16025 32768		$\begin{array}{c} \leftarrow \\ \\ \leftarrow \\$			
0.87 0.087 0.94 0.87 0.94 0.94 0.94	86. 0 7.5 7.0	02.0 6.5 6.0	5.5 5.0 4.5 f1 (ppm)	4.0 3.5	3.0 2.5	2.0 1.5



	1.00 [▲] 1.05 [▲] 0.94 [▲] 0.94 [▲]	 0.89 -		 	3.00 ⊥	
	./					
4 Spectral Size	32768					
3 Acquired Size	16025				1	
2 Nucleus	1H					
1 Lowest Frequency	-1535.4					
)Spectral Width	8012.8					
Spectrometer Fre	auency 400 13					
Acquisition Date	$2010 \ 0.0 \ 0.1110.00.11$					
7 Acquisition Data	$\begin{array}{c} 1.3333\\ 2018-05-07T18\cdot 30\cdot 11 \end{array}$			1		
Sloquisition Time						
4 Keraxation Delay 5 Pulso Width	8 7300		3			
A Releveting Del	1 (4		لا ک			
2 Number of Scans	84					
l Experiment	1D		~⊕~ ~			
0 Pulse Sequence	zg30					
Temperature	299.1		A the			
Solvent	DMSO		OH			
Author						
Spectrometer	spect					
Site						
Owner	nmr					
Origin	Bruker BioSpin GmbH					
Comment	YJ-01-127-2					
Title	YJ-01-127-2					
i di dille t ti	value					



fl (ppm)

Parameter	Value
1 Title	zxh-s-1-137-H
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	spect
7 Author	
8 Solvent	Acetone
9 Temperature	296.1
10 Pulse Sequence	zg30
11 Experiment	1D
12 Number of Scans	16
13 Keceiver Gain	125
14 Kelaxation Delay	1.0000
16 Acquisition Time	3 2768
17 Acquisition Date	2016-06-13T17:40:15
18 Modification Date	2016-06-13T19:05:59
19 Spectrometer Frequenc	y 500.13
20 Spectral Width	10000.0
21 Lowest Frequency	-1911.5
22 Nucleus	1H
23 Acquired Size	32768
24 Spectral Size	65536
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1.02 1.02 1.02	<u>-</u>

—167.29	—147.62 —140.19	—125.07 —121.82	—111.68	—96.04	-77.19		-31.44	
Parameter	Value							
1 Title 2 Comment	zxh-s-1-137-13C							
3 Origin	Bruker BioSpin G	nbH						
4 Owner	nmr							
5 Site				01				
6 Spectrometer	spect			∽ L-Me				
7 Author					uBr			
8 Solvent	Acetone			~ <u>~</u>	9			
9 Temperature	296.1			TMS				
10 Pulse Sequence	zgpg30							
11 Experiment	1D							
12 Number of Scans	715							
13 Receiver Gain	193							
14 Relaxation Delay	2.0000							
15 Pulse Width	10.0000							
16 Acquisition Time	1.1010	4.0						
17 Acquisition Date	2016-06-13T17:57	:48						
18 Modification Date	2016-06-13119:06	:00						
19 Spectrometer Frequer	20761 0							
20 Spectral with	-2305 8							
22 Nucleus	130							1
23 Acquired Size	32768							
24 Spectral Size	65536							
1								
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							1 11	
, manuaran arasalan kanan k	(พรุ)าย41/พร ^ม ทางในสุขรับกรุงสมารณ์เหตุส์ได้รูปขึ้นสมมาณ _{์ส} องไปสมสุขร้านหรือไฟสมด์	anen eusen jar aller ander ander ander	๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛	๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛	มมมระสงกระสุทธรรมสาวารสุด มมมระสงกระสุทธรรมสาวารสาวารสาวารสาวารสาวารสาวารสาว	ſijġĸţĊĸĸŧġĬĸŊĸĬĠĸġĬĊĊijĸĊġĊĊĊĬĸġĸţĸĸĊĸſŶſſĬĬĸŶŊġŖĬĊij		สราวการการการการการการการการการการการการการก
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Parameter	Value							
1 Title 2 Comment	YJ-01-67-IR-DMS0		НО					
3 Origin 4 Owner 5 Site	Bruker BioSpin GmbH nmr							
6 Spectrometer 7 Author	spect							
8 Solvent	DMSO		2-					
9 Temperature	296.1							
10 Pulse Sequence	zg30							
11 Experiment	1D							
12 Number of Scans	32							
13 Receiver Gain	71							
14 Relaxation Delay	1.0000							
15 Pulse Width	10.7100							
16 Acquisition Time	3.2768							
17 Acquisition Date	2018-03-07116:12:40							
18 Modification Date	2018-03-08119:40:13							
19 Spectrometer Frequend	cy 500. 13							
20 Spectral Width	1011 5							
21 Lowest Frequency	-1911.5							
22 Nucleus	20769							
23 Acquired Size	65536							
							1	
1.02 d → 1.08 d → 1.	1.02					3.26 L		
9.0 8.5 8.0	7.5 7.0 6.5	6.0	5.5 5.0 4.5 f1 (p	4.0 3.5 pm)	3.0 2	2.5 2.0	1.5 1.0	0.5 0.0

157.94	146.31	138.37 137.24	133.23 132.39	129.41 128.29	128.12 123.34 122.80
1	Ĩ.	5	5	SF	

	Parameter	Value
1	Title	YJ-01-67-IR-DMSO
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmr
5	Site	
6	Spectrometer	spect
7	Author	
8	Solvent	DMSO
9	Temperature	296.2
10	Pulse Sequence	zgpg30
11	Experiment	1D
12	Number of Scans	436
13	Receiver Gain	193
14	Relaxation Delay	2.0000
15	Pulse Width	9.6000
16	Acquisition Time	1.1010
17	Acquisition Date	2018-03-07T17:38:00
18	Modification Date	2018-03-08T19:40:13
19	Spectrometer Frequency	125.77
20	Spectral Width	29761.9
21	Lowest Frequency	-2305.8
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536



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Parameter	Value									
Title	YJ-01-93-IR-DMSO									
Comment										
Origin	Bruker BioSpin GmbH									
Owner	nmr									
Site										
Spectrometer	spect									
Author										
Solvent	DMSO									
Temperature	296.1		A Me							
Pulse Sequence	zg30	ſ								
Experiment	1D	l								
Number of Scans	16									
BReceiver Gain	78									
Relaxation Delay	1.0000									
Pulse Width	10.7100									
Acquisition Time	3. 2768									
Acquisition Date	2018-01-27T18:44:00									
3 Modification Date	2018-01-29T14:09:16									
)Spectrometer Frequen	су 500.13									
)Spectral Width	10000.0									
Lowest Frequency	-1914.6									
2 Nucleus	1H									
Acquired Size	32708						1			
topectial Size	00000									
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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	1



	Parameter	Value
1	Title	YJ-01-93-IR-DMSO
2	Comment	
3	Origin	Bruker BioSpin GmbH
4	Owner	nmr
5	Site	
6	Spectrometer	spect
7	Author	
8	Solvent	DMSO
9	Temperature	296.1
10	Pulse Sequence	zgpg30
11	Experiment	1D
12	Number of Scans	821
13	Receiver Gain	193
14	Relaxation Delay	2.0000
15	Pulse Width	9.6000
16	Acquisition Time	1.1010
17	Acquisition Date	2018-01-27T18:50:00
18	Modification Date	2018-01-29T14:09:17
19	Spectrometer Frequency	125.76
20	Spectral Width	29761.9
21	Lowest Frequency	-2302.7
22	Nucleus	13C
23	Acquired Size	32768
24	Spectral Size	65536





-22.33

170	160	150	140	130	120	110	100	90 91	80 (ppm)	70	60	50	40	30	20	10	0



Parameter	Value											
1 Title	YJ-01-89-DMSO-CONVERTED											
2 Comment												
3 Origin	Bruker BioSpin GmbH											
4 Owner	nmr											
5 Site												
6 Spectrometer	spect											
7 Author												
8 Solvent	DMSO											
9 Temperature	296.1											
10 Pulse Sequence	zg30			HQ Ma								
11 Experiment	1D											
12 Number of Scans	16				3r							
13 Receiver Gain	88			₩ () () () () () () () () () ()	∃r⊖							
14 Relaxation Delay	1.0000			T Ph A	NuBr							
15 Pulse Width	10.7100											
16 Acquisition lime	3. 2708 2018-07-20T06.22.07											
18 Modification Date	2018-07-20100.33.07 2018-07-23T17.51.42											
19 Spectrometer Freque	2010 01 20111.01.42											
20 Spectral Width	10000.0											
21 Lowest Frequency	-1911.5											
22 Nucleus	1H											
23 Acquired Size	32768											
24 Spectral Size	65536											
							1					
M	Mana											
—————————————————————————————————————	H											
2 2	т Г							<u> </u>				
2.0 1.0	5.2							3.0				
90 85 80	75 70 65		55	50 45	4 0	3.5	3.0 2.5	2.0	1 5	1 0	0.5	
0.0 0.0	1.0 1.0 0.0	0.0	0.0	f1 (ppm	у.г.)	0.0	0.0 2.0	2.0	1.0	1.0	0.0	0.0



fl (ppm)



Parameter	Value
1 Title	YJ-01-114-CONVERTED
2 Comment	
3 Origin	Bruker BioSpin GmbH
4 Owner	nmr
5 Site	
6 Spectrometer	spect
7 Author	speci
8 Solvent	Acetone
9 Temperature	296.1
10 Pulse Sequence	zg30
11 Experiment	1U 20
12 Number of Scans	3Z
13 Receiver Gain	108
14 Kelaxation Delay	1.0000
15 Pulse width	10.7100
16 Acquisition lime	3.2708 2010 07 0FT02.FF.FF
17 Acquisition Date	2018-07-05103:55:55
18 Modification Date	2018-07-05114:53:58
19 Spectrometer Frequence	cy 500. 13
20 Spectral Width	10000.0
21 Lowest Frequency	-1917.5
22 Nucleus	1H 22769
23 Acquired Size	32708
24 Spectral Size	00030
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7 2 2	
	:
9.5 9.0 8.5	8.0 7.5 7.




8.5 8.0 7.5 7.0 6.5 5.0 4.5 3.5 2.0 1.5 9.0 6.0 5.5 4.0 3.0 2.5 1.0 0.5 0.0 -0.

9.5

f2 (ppm)









fl (ppm)



Parameter	Value											
1 Title 2 Comment	YJ-01-129-IR											
3 Origin 4 Owner 5 Site	Bruker BioSpin GmbH nmr											
6 Spectrometer 7 Author	spect											
8 Solvent 9 Temperature 10 Pulse Sequence 11 Experiment 12 Number of Scans 13 Receiver Gain 14 Relaxation Delay 15 Pulse Width 16 Acquisition Time 17 Acquisition Date 18 Modification Date 19 Spectrometer Freque 20 Spectral Width 21 Lowest Frequency 22 Nucleus 23 Acquired Size	DMS0 296.1 zg30 1D 8 78 1.0000 10.7100 3.2768 2018-08-25T19:27:40 2018-08-25T19:57:53 ncy 500.13 10000.0 -1911.5 1H 32768			HO Me C D D D D D D D	I CI⊖ AuCI							
24 Spectral Size												
1.00 ⊥ 1.05 ⊥ 1.01 ⊥	5.24 ∃ 0.84 ∃										3.03⊣	3.14⊣
8.5 8.0	7.5 7.0	6.5	6.0	5.5 5 f1 (pr	. 0 om)	4.5	4.0	3.5	3. 0	2.5	2.0	1.5





hanashanan kalada shana kala sakiri kasa na ningina kanala ya siya ka siya ka ka siya ka ka siya siya siya ka y

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เขาไขสมเหล่งใหม่มีสูงในประกังการการการการการการการการการการการการการก	44(4)4.)101934247411414349114444444444444444444444444	Num
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160 155 $150 \quad 145 \quad 140 \quad 135$ 130 125 120 115 110 105 f1 (ppm)

