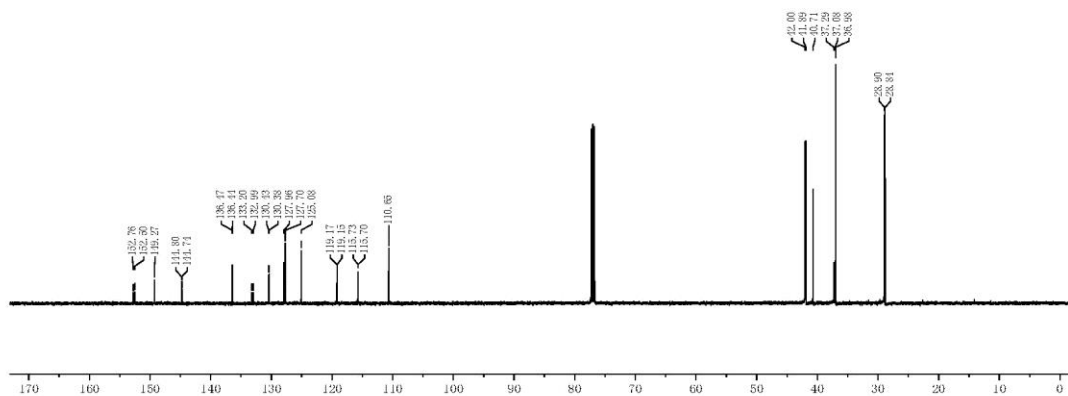
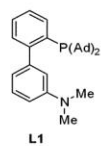


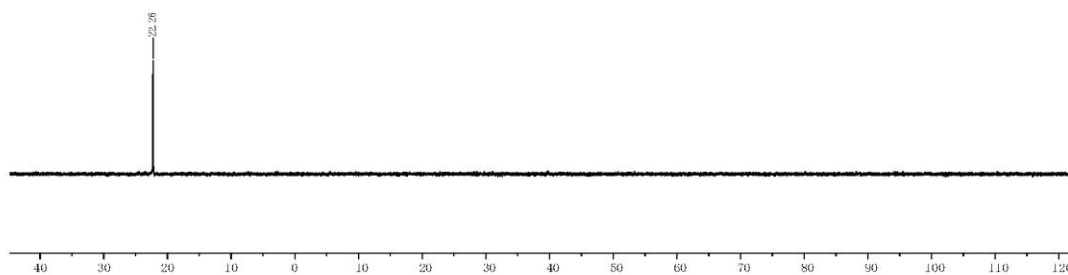
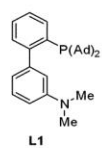
Supplementary Figure 1.  $^1\text{H}$  NMR spectrum of L1.

Parameter Value  
Title wyz7-296-7-C13  
Solvent CDCl3  
Spectrometer Frequency 125.70  
Nucleus 13C



Supplementary Figure 2. <sup>13</sup>C NMR spectrum of L1.

Parameter	Value
Title	wyz7-296-7-p31
Solvent	cdCl <sub>3</sub>
Spectrometer Frequency	161.90
Nucleus	<sup>31</sup> P



Supplementary Figure 3. <sup>31</sup>P NMR spectrum of L1.

## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

3843 formula(e) evaluated with 17 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 P: 0-2 Na: 0-1

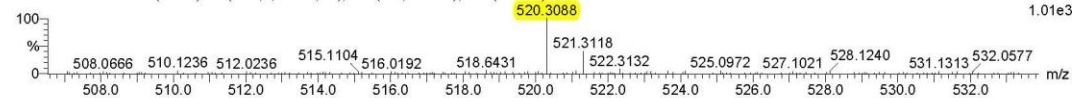
Wang/Zhang, wylL1, mw 497; ESI+

ZHA102213MA1 142 (2.700) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (83:151)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

1.01e3

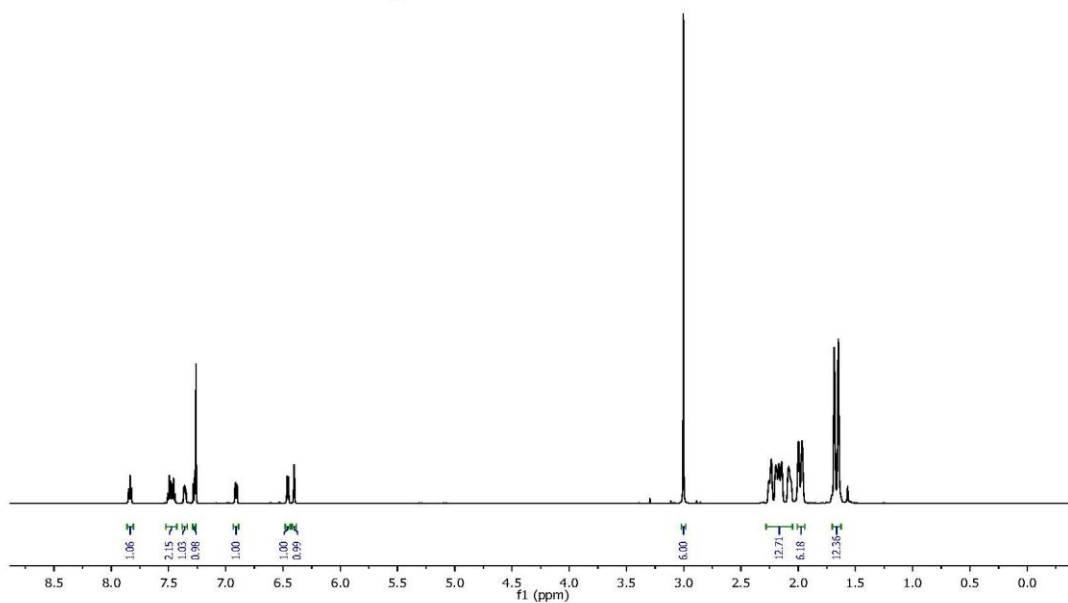
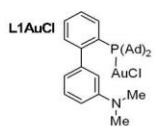


Minimum: -1.5  
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
520.3088	520.3085	0.3	0.6	4.5	13.8	C27 H49 N O3 P2 Na
	520.3093	-0.5	-1.0	12.5	3.1	C31 H43 N3 O2 P
	520.3083	0.5	1.0	8.5	15.8	C25 H44 N7 O P2
	520.3095	-0.7	-1.3	4.5	25.6	C21 H42 N7 O8
	520.3098	-1.0	-1.9	0.5	23.6	C23 H47 N O10 Na
	520.3076	1.2	2.3	17.5	0.6	C33 H38 N5 O
	520.3101	-1.3	-2.5	1.5	40.9	C18 H44 N9 O5 P Na
	520.3071	1.7	3.3	1.5	35.5	C19 H43 N7 O8 Na
	520.3069	1.9	3.7	9.5	7.1	C29 H44 N3 O2 P Na
	520.3069	1.9	3.7	3.5	20.8	C24 H48 N3 O5 P2
	520.3109	-2.1	-4.0	13.5	1.0	C34 H44 N P Na
	520.3109	-2.1	-4.0	7.5	8.0	C29 H48 N O3 P2
	520.3066	2.2	4.2	13.5	8.7	C27 H39 N9 P
	520.3111	-2.3	-4.4	-0.5	37.8	C19 H47 N5 O9 P
	520.3111	-2.3	-4.4	5.5	17.7	C24 H43 N5 O6 Na
	520.3063	2.5	4.8	12.5	1.8	C32 H42 N O5
	520.3059	2.9	5.6	5.5	23.9	C23 H45 N7 O P2 Na

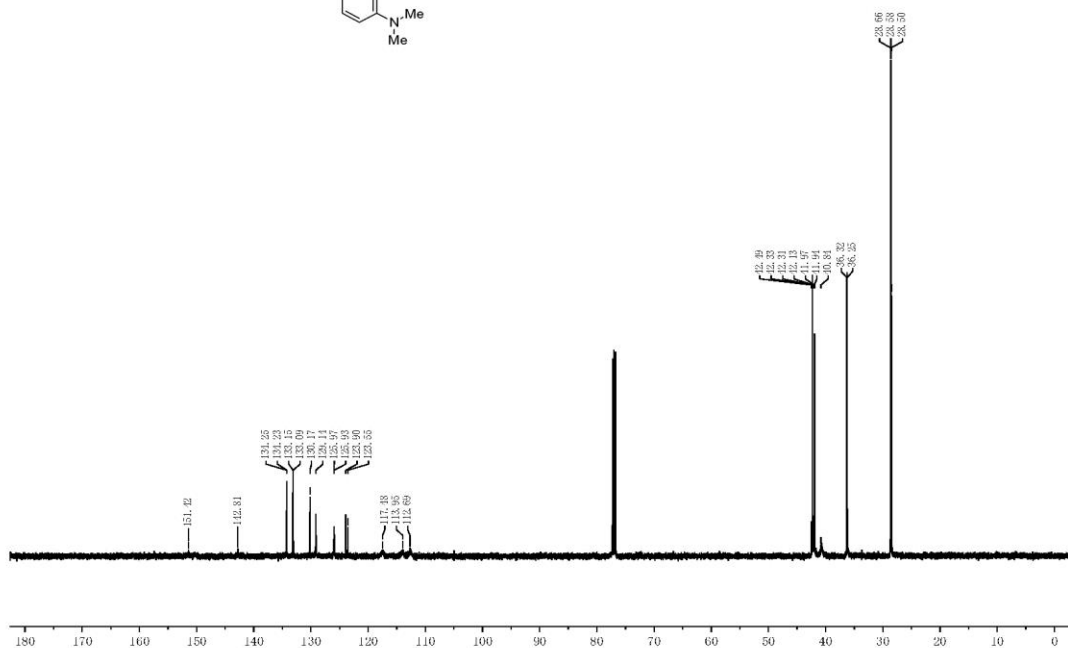
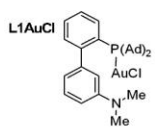
Supplementary Figure 4. HRMS of L1.

Parameter Value  
Title zhikun-3-L1AuCl-4  
Solvent cdcl3  
Spectrometer Frequency 599.64



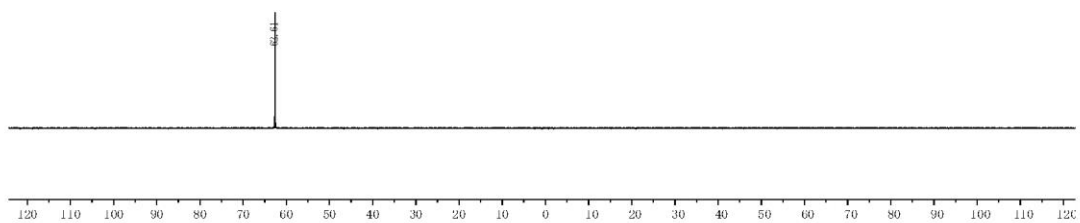
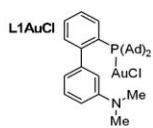
Supplementary Figure 5.  $^1\text{H}$  NMR spectrum of L1AuCl.

Parameter Value  
Title wy28-L1AuCl-C13  
Solvent CDCl3  
Spectrometer Frequency 125.70  
Nucleus 13C



Supplementary Figure 6.  $^{13}\text{C}$  NMR spectrum of L1AuCl.

Parameter	Value
Title	wyz8-L1AuCl-P31
Solvent	cdCl <sub>3</sub>
Spectrometer Frequency	161.90
Nucleus	<sup>31</sup> P



**Supplementary Figure 7. <sup>31</sup>P NMR spectrum of L1AuCl.**

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

3887 formula(e) evaluated with 10 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 Na: 0-1 P: 0-2 Cl: 0-2 Au: 0-4

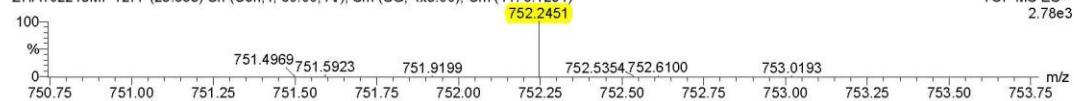
Wang/Zhang, wylL1AuCl, mw 729; ESI+

ZHA102213MI 1277 (23.685) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (1176:1294)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

2.78e3



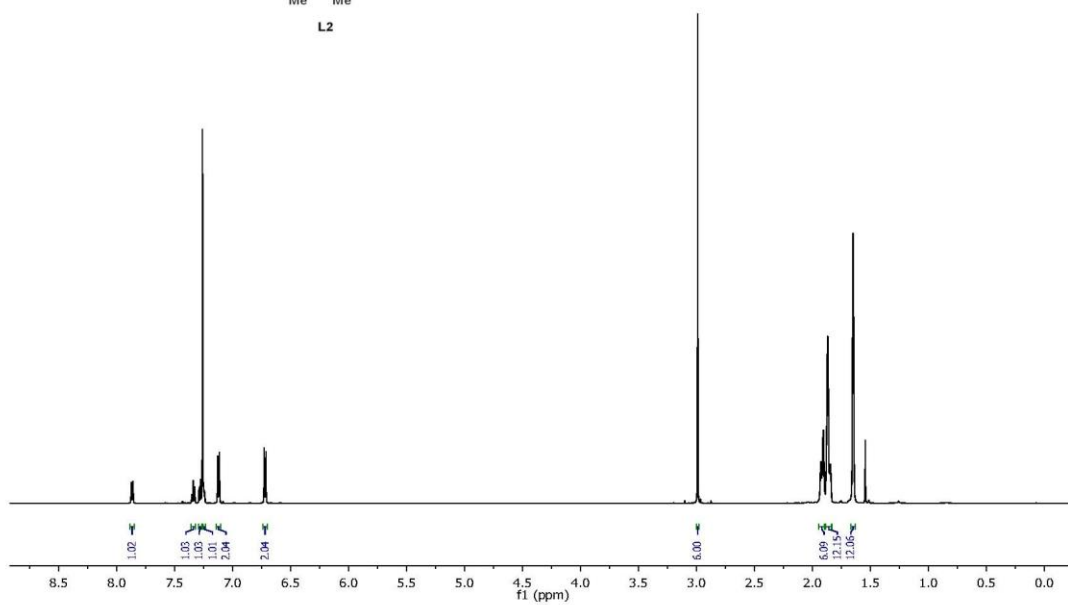
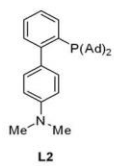
Minimum: -1.5  
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
752.2451	752.2453	-0.2	-0.3	24.5	5547413.0	C43 H42 N5 Na P Cl2
	752.2445	0.6	0.8	18.5	5547409.5	C35 H39 N3 Na P Au
	752.2458	-0.7	-0.9	32.5	5547412.0	C46 H36 N7 P Cl
	752.2440	1.1	1.5	37.5	5547411.5	C47 H31 N9 P
	752.2463	-1.2	-1.6	13.5	5547411.0	C34 H44 N Na P Cl Au
	752.2438	1.3	1.7	8.5	5547412.5	C26 H44 N7 P Cl2 Au
	752.2434	1.7	2.3	29.5	5547412.0	C44 H37 N7 Na P Cl
	752.2469	-1.8	-2.4	21.5	5547410.0	C37 H38 N3 P Au
	752.2431	2.0	2.7	2.5	5547401.0	C18 H41 N5 P Au2
	752.2477	-2.6	-3.5	27.5	5547413.0	C45 H41 N5 P Cl2

Supplementary Figure 8. HRMS of L1AuCl.

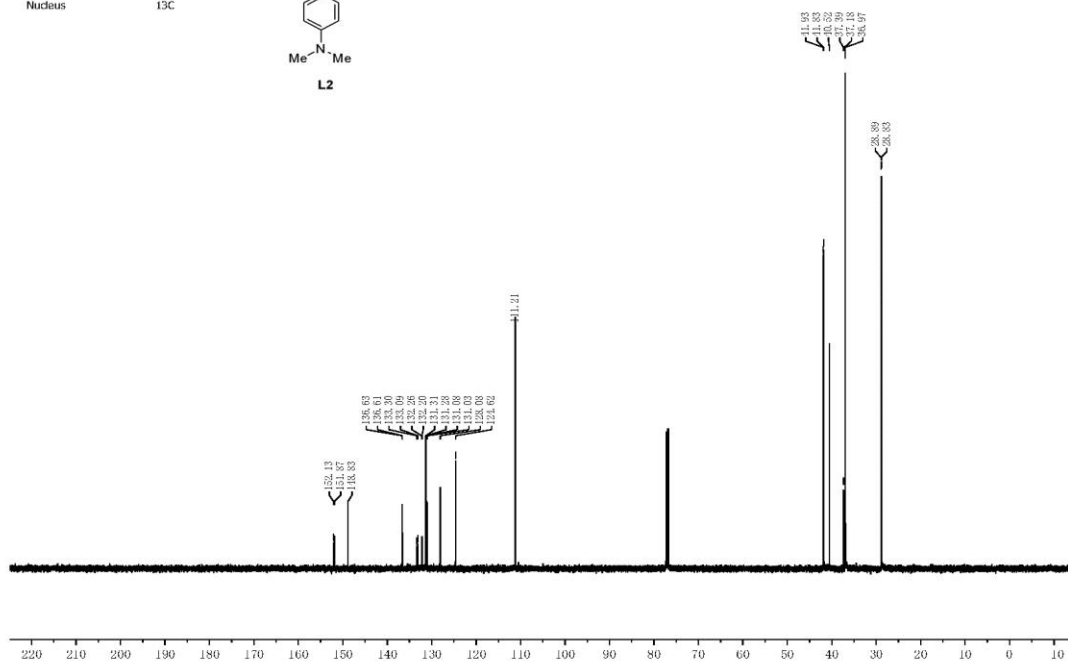
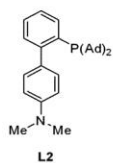


Parameter Value  
Title zhkun-3-L2  
Solvent cdcl3  
Spectrometer Frequency 599.64



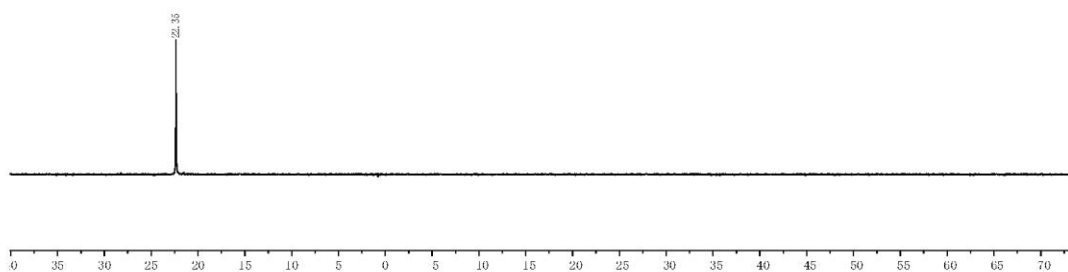
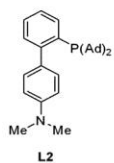
Supplementary Figure 9. <sup>1</sup>H NMR spectrum of L2.

Parameter Value  
Title wyz7-296-10-C13  
Solvent CDCl3  
Spectrometer Frequency 125.70  
Nucleus 13C



Supplementary Figure 10. <sup>13</sup>C NMR spectrum of L2.

Parameter Value  
Title wyz7-296-10-P31  
Solvent cdcCl3  
Spectrometer Frequency 161.90  
Nucleus 31P



Supplementary Figure 11.  $^{31}\text{P}$  NMR spectrum of L2.

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

3654 formula(e) evaluated with 14 results within limits (all results (up to 1000) for each mass)

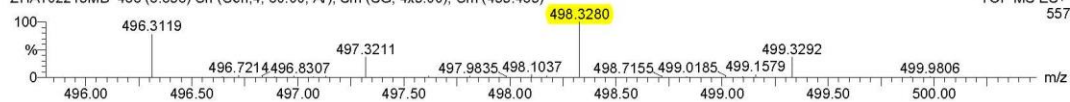
Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 P: 0-2

Wang/Zhang, wylzL2, mw 497; ESI+

ZHA102213MB 466 (8.838) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (435;483)

UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
557

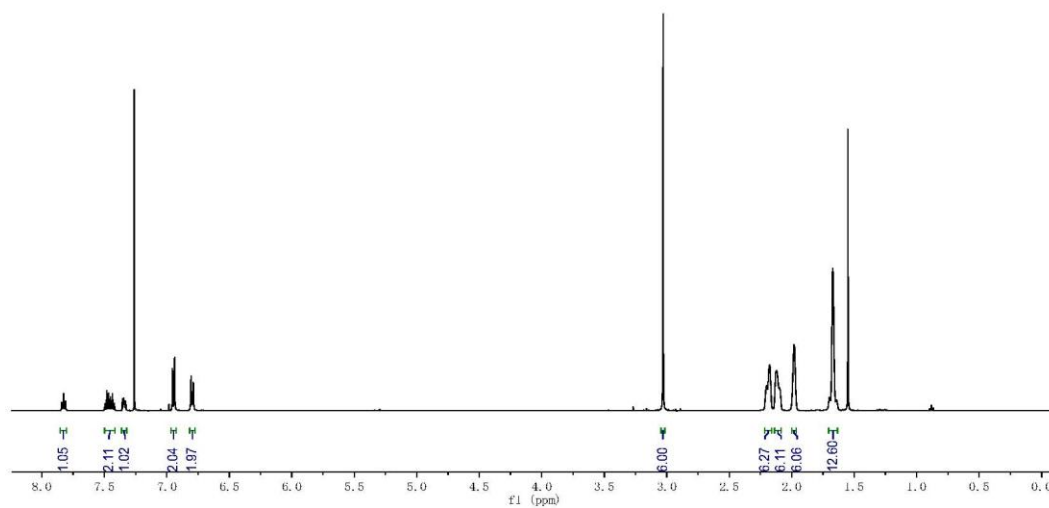
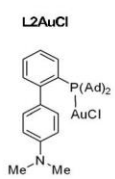


Minimum: -1.5  
Maximum: 3.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
498.3280	498.3281	-0.1	-0.2	7.5	2773187.3	C23 H41 N9 O2 Na
	498.3281	-0.1	-0.2	1.5	2773161.8	C18 H45 N9 O5 P
	498.3278	0.2	0.4	0.5	2773224.5	C23 H48 N O10
	498.3290	-1.0	-2.0	13.5	2773258.5	C34 H45 N P
	498.3292	-1.2	-2.4	5.5	2773215.8	C24 H44 N5 O6
	498.3268	1.2	2.4	2.5	2773197.0	C22 H45 N5 O6 Na
	498.3266	1.4	2.8	4.5	2773210.8	C27 H50 N O3 P2
	498.3266	1.4	2.8	10.5	2773240.5	C32 H46 N Na P
	498.3297	-1.7	-3.4	2.5	2773167.3	C21 H46 N7 O3 Na P
	498.3257	2.3	4.6	-1.5	2773142.8	C16 H46 N9 O5 Na P
	498.3305	-2.5	-5.0	10.5	2773209.0	C25 H40 N9 O2
	498.3308	-2.8	-5.6	0.5	2773199.3	C22 H49 N3 O7 P
	498.3308	-2.8	-5.6	6.5	2773224.0	C27 H45 N3 O4 Na
	498.3251	2.9	5.8	1.5	2773192.0	C19 H44 N7 O8

Supplementary Figure 12. HRMS of L2.

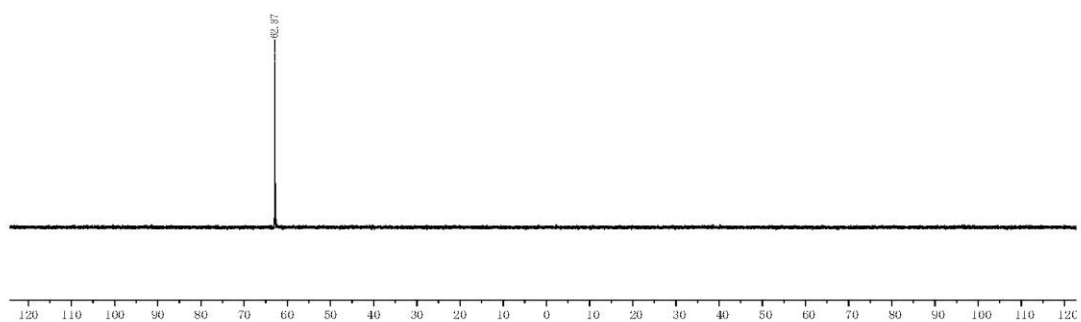
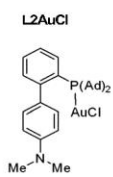
Parameter	Value
1 Title	zhixun-3-L2AuCl
2 Solvent	CDCl3
3 Spectrometer Frequency	499.86



Supplementary Figure 13.  $^1\text{H}$  NMR spectrum of L2AuCl.



Parameter	Value
Title	wyzS-L2AuCl-P31
Solvent	cdCl <sub>2</sub>
Spectrometer Frequency	161.90
Nucleus	<sup>31</sup> P



**Supplementary Figure 15. <sup>31</sup>P NMR spectrum of L2AuCl.**

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

3887 formula(e) evaluated with 11 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 Na: 0-1 P: 0-2 Cl: 0-2 Au: 0-4

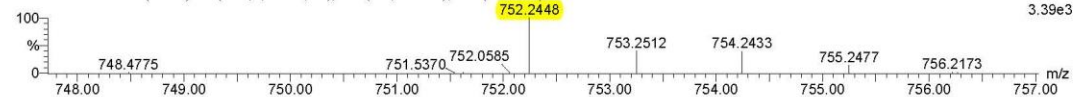
Wang/Zhang, wyl2AuCl, mw 729; ESI+

ZHA102213MJ 260 (4.937) Cn (Cen.4, 60.00, Ar); Sm (SG, 4x3.00); Cm (252.306)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

3.39e3



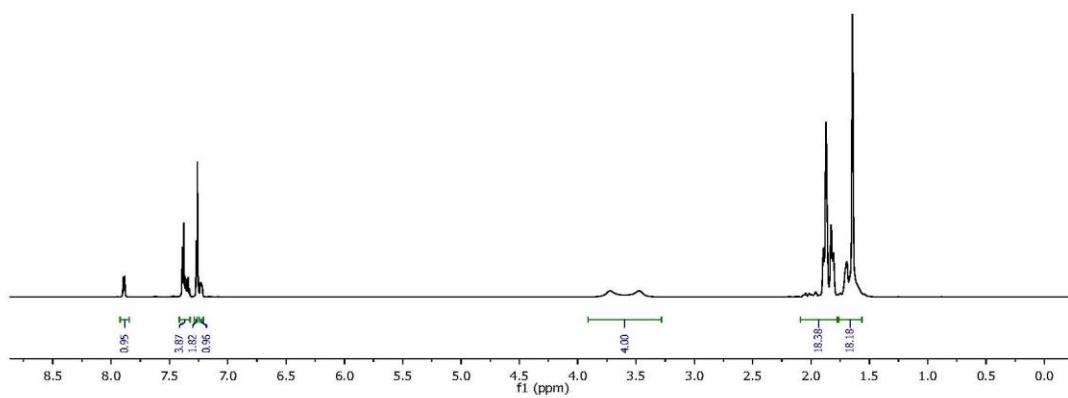
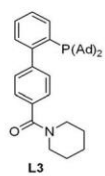
Minimum: -1.5  
Maximum: 3.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
752.2448	752.2445	0.3	0.4	18.5	423.1	C35 H39 N3 Na P Au
	752.2453	-0.5	-0.7	24.5	239.3	C43 H42 N5 Na P Cl2
	752.2440	0.8	1.1	37.5	346.4	C47 H31 N9 P
	752.2458	-1.0	-1.3	32.5	52.4	C46 H36 N7 P Cl
	752.2438	1.0	1.3	8.5	255.1	C26 H44 N7 P Cl2 Au
	752.2434	1.4	1.9	29.5	39.0	C14 H37 N7 Na P Cl
	752.2463	-1.5	-2.0	13.5	0.3	C34 H44 N Na P Cl Au
	752.2431	1.7	2.3	2.5	697.6	C18 H41 N5 P Au2
	752.2469	-2.1	-2.8	21.5	405.0	C37 H38 N3 P Au
	752.2420	2.8	3.7	13.5	11.9	C27 H39 N9 P Cl Au
	752.2477	-2.9	-3.9	27.5	247.0	C45 H41 N5 P Cl2

Supplementary Figure 16. HRMS of L2AuCl.

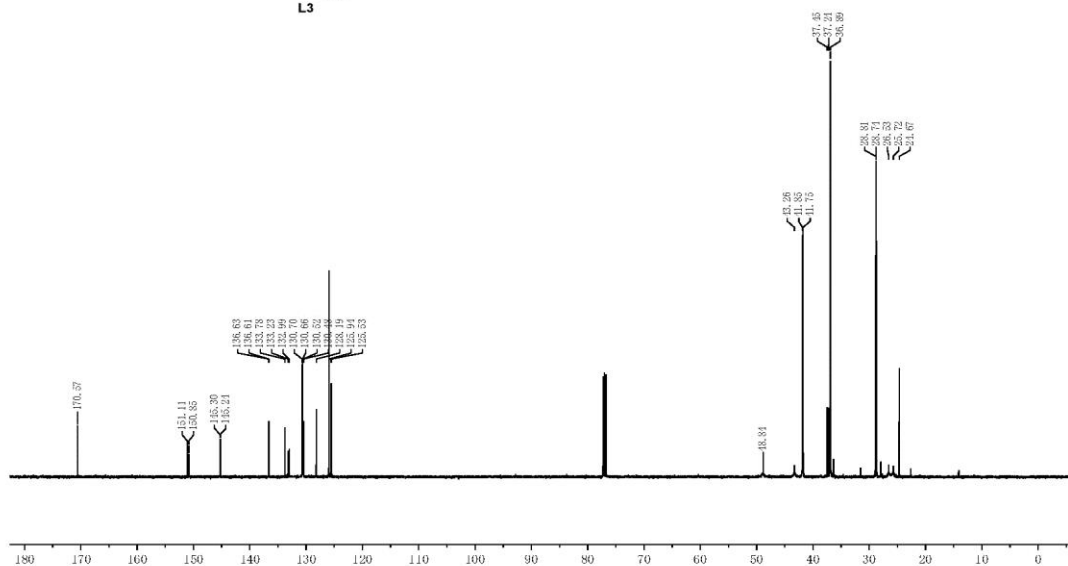
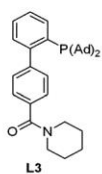


Parameter Value  
Title zhkun-3-13-1  
Solvent cdcl3  
Spectrometer Frequency 599.64



Supplementary Figure 17. <sup>1</sup>H NMR spectrum of L3.

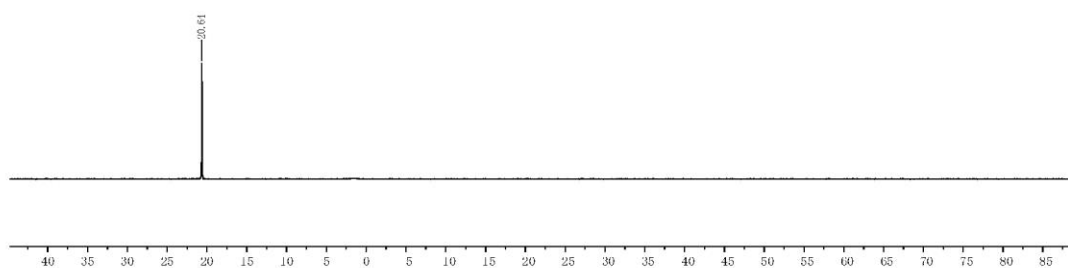
Parameter Value  
Title wyz7-296-9-C13  
Solvent CDCl3  
Spectrometer Frequency 125.70  
Nucleus 13C



Supplementary Figure 18.  $^{13}\text{C}$  NMR spectrum of L3.

Parameter	Value
Title	wyz7-296-9-P31-H3PO4
Solvent	cdcl3
Spectrometer Frequency	161.90
Nucleus	31P

C1CCN(C1)C(=O)c2ccc(cc2)C3=CC=C(C=C3)P(=O)(O)O  
L3



**Supplementary Figure 19. <sup>31</sup>P NMR spectrum of L3.**

## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

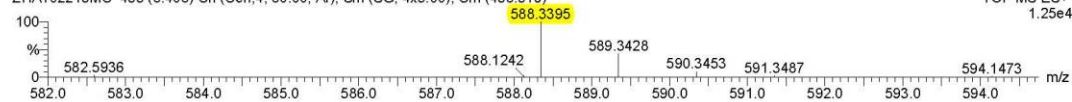
4441 formula(e) evaluated with 18 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 P: 0-2

Wang/Zhang, wylzL3, mw 565; ESI+

ZHA102213MC 453 (8.406) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (436-519)

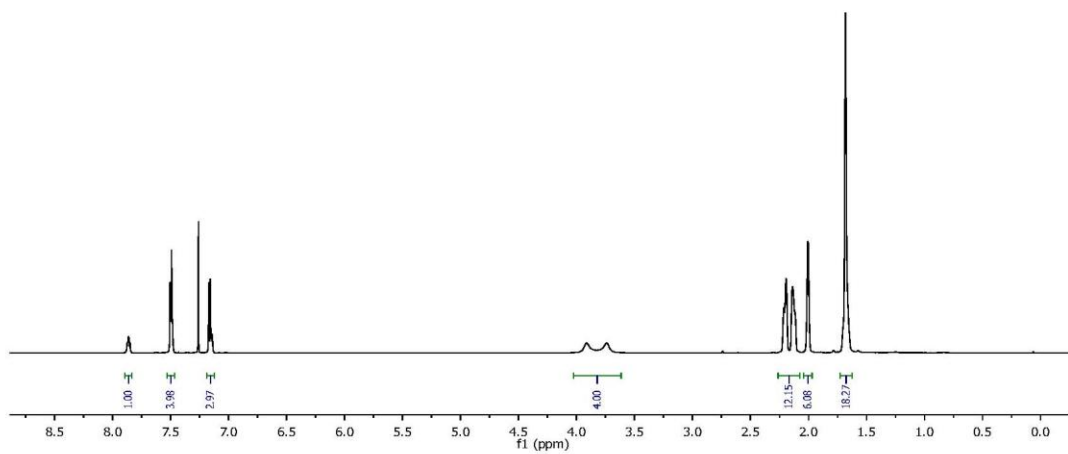
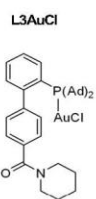
UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
1.25e4

Minimum: -1.5  
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
588.3395	588.3395	0.0	0.0	18.5	12.5	C40 H47 N O P
	588.3397	-0.2	-0.3	10.5	57.5	C30 H46 N5 O7
	588.3390	0.5	0.8	2.5	203.9	C26 H52 N3 O8 Na P
	588.3387	0.8	1.4	12.5	74.7	C29 H43 N9 O3 Na
	588.3403	-0.8	-1.4	1.5	352.4	C22 H52 N7 O7 P2
	588.3387	0.8	1.4	6.5	227.9	C24 H47 N9 O6 P
	588.3403	-0.8	-1.4	7.5	149.2	C27 H48 N7 O4 Na P
	588.3385	1.0	1.7	14.5	20.1	C34 H48 N5 P2
	588.3411	-1.6	-2.7	15.5	32.0	C31 H42 N9 O3
	588.3379	1.6	2.7	-1.5	478.0	C20 H53 N7 O7 Na P2
	588.3379	1.6	2.7	23.5	46.9	C42 H42 N3
	588.3413	-1.8	-3.1	11.5	22.7	C33 H47 N3 O5 Na
	588.3414	-1.9	-3.2	5.5	126.1	C28 H51 N3 O8 P
	588.3374	2.1	3.6	1.5	298.8	C23 H51 N5 O10 P
	588.3373	2.2	3.7	7.5	113.4	C28 H47 N5 O7 Na
	588.3372	2.3	3.9	9.5	36.7	C33 H52 N O4 P2
	588.3371	2.4	4.1	15.5	3.0	C38 H48 N O Na P
	588.3420	-2.5	-4.2	2.5	251.9	C25 H53 N5 O5 Na P2

Supplementary Figure 20. HRMS of L3.

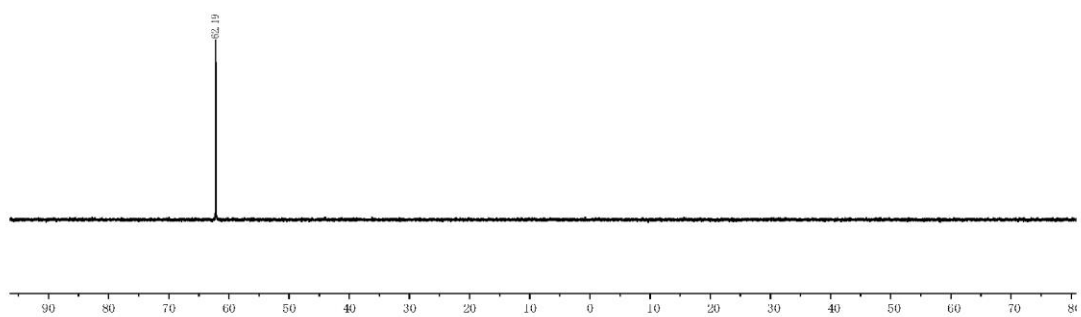
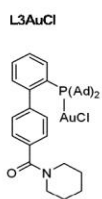
Parameter Value  
Title zhkum-3-L3AuCl  
Solvent cdcl3  
Spectrometer Frequency 599.64



Supplementary Figure 21. <sup>1</sup>H NMR spectrum of L3AuCl.



Parameter	Value
Title	wyz8-L3AuCl-P31
Solvent	cdCl <sub>3</sub>
Spectrometer Frequency	161.90
Nucleus	<sup>31</sup> P



**Supplementary Figure 23.** <sup>31</sup>P NMR spectrum of L3AuCl.

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

19911 formula(e) evaluated with 62 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 P: 0-1 Cl: 0-1 Au: 0-4

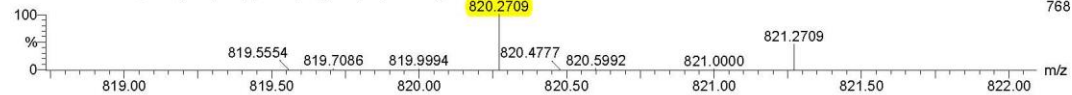
Wang/Zhang, wylL3AuCl, mw 797; ESI+

ZHA102213MK 89 (1.688) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (84:102)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

768



Minimum: -1.5  
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
820.2709	820.2709	0.0	0.0	12.5	2773436.0	C29 H42 N7 O7 Na Au
	820.2709	0.0	0.0	20.5	2773564.3	C40 H43 N3 Na Cl Au
	820.2709	0.0	0.0	14.5	2773564.3	C35 H47 N3 O3 P Cl Au
	820.2709	0.0	0.0	6.5	2773410.8	C24 H46 N7 O10 P Au
	820.2707	0.2	0.2	20.5	2773475.0	C39 H43 N3 O Na P Au
	820.2711	-0.2	-0.2	6.5	2773564.5	C25 H46 N7 O9 Cl Au
	820.2707	0.2	0.2	29.5	2773565.3	C49 H44 N3 O5 P Cl
	820.2707	0.2	0.2	35.5	2773565.5	C54 H40 N3 O2 Na Cl
	820.2707	0.2	0.2	27.5	2773515.8	C43 H39 N7 O9 Na
	820.2711	-0.2	-0.2	-0.5	2773563.8	C21 H50 N3 O P Cl Au2
	820.2705	0.4	0.5	35.5	2773531.0	C53 H40 N3 O3 Na P
	820.2713	-0.4	-0.5	43.5	2773538.5	C57 H34 N5 O2
	820.2704	0.5	0.6	39.5	2773565.3	C52 H35 N9 Cl
	820.2704	0.5	0.6	-1.5	2773564.5	C21 H52 N5 O10 Na P Cl Au
	820.2703	0.6	0.7	8.5	2773365.3	C28 H44 N O2 Au2
	820.2715	-0.6	-0.7	28.5	2773497.5	C43 H37 N5 Au
	820.2715	-0.6	-0.7	18.5	2773564.8	C36 H45 N9 O8 Na P Cl
	820.2702	0.7	0.9	39.5	2773529.3	C51 H35 N9 O P
	820.2717	-0.8	-1.0	3.5	2773564.3	C22 H48 N9 O6 Na P Cl Au
	820.2701	0.8	1.0	23.5	2773495.8	C42 H41 N O4 Au
	820.2699	1.0	1.2	38.5	2773537.5	C56 H38 N O6
	820.2721	-1.2	-1.5	34.5	2773565.3	C50 H40 N7 O P Cl
	820.2696	1.3	1.6	31.5	2773565.0	C48 H41 N7 O Na P Cl
	820.2695	1.4	1.7	4.5	2773563.8	C23 H45 N5 Cl Au2
	820.2723	-1.4	-1.7	30.5	2773565.3	C52 H45 N O3 Na P Cl
	820.2724	-1.5	-1.8	22.5	2773509.0	C41 H44 N5 O10 Na P
	820.2725	-1.6	-2.0	15.5	2773564.3	C38 H48 N O Na P Cl Au
	820.2725	-1.6	-2.0	22.5	2773565.0	C42 H44 N5 O9 Na Cl
	820.2693	1.6	2.0	19.5	2773564.3	C37 H42 N5 O2 Cl Au
	820.2693	1.6	2.0	11.5	2773427.5	C26 H41 N9 O9 Au
	820.2693	1.6	2.0	4.5	2773278.0	C22 H45 N5 O P Au2
	820.2726	-1.7	-2.1	7.5	2773418.8	C27 H47 N5 O8 Na P Au
	820.2727	-1.8	-2.2	7.5	2773564.3	C28 H47 N5 O7 Na Cl Au
	820.2691	1.8	2.2	34.5	2773565.5	C51 H39 N5 O4 Cl
	820.2691	1.8	2.2	19.5	2773466.5	C36 H42 N5 O3 P Au
	820.2691	1.8	2.2	25.5	2773487.5	C41 H38 N5 Na Au
	820.2728	-1.9	-2.3	1.5	2773564.5	C23 H51 N5 O10 P Cl Au
	820.2689	2.0	2.4	34.5	2773527.8	C50 H39 N5 O5 P
	820.2729	-2.0	-2.4	44.5	2773541.0	C60 H35 N3 Na
	820.2729	-2.0	-2.4	38.5	2773534.8	C55 H39 N3 O3 P
	820.2688	2.1	2.6	40.5	2773535.3	C55 H35 N5 O2 Na
	820.2731	-2.2	-2.7	30.5	2773521.5	C45 H38 N7 O9
	820.2731	-2.2	-2.7	23.5	2773486.8	C41 H42 N3 O P Au
	820.2687	2.2	2.7	3.5	2773564.5	C23 H47 N7 O9 Na Cl Au
	820.2731	-2.2	-2.7	38.5	2773565.8	C56 H39 N3 O2 Cl
	820.2685	2.4	2.9	3.5	2773391.5	C22 H47 N7 O10 Na P Au
	820.2733	-2.4	-2.9	23.5	2773564.5	C42 H42 N3 Cl Au
	820.2685	2.4	2.9	11.5	2773564.0	C33 H48 N3 O3 Na P Cl Au
	820.2733	-2.4	-2.9	15.5	2773452.0	C31 H41 N7 O7 Au
	820.2735	-2.6	-3.2	0.5	2773268.8	C17 H44 N7 O5 Au2
	820.2683	2.6	3.2	26.5	2773565.0	C47 H45 N3 O5 Na P Cl
	820.2736	-2.7	-3.3	11.5	2773461.0	C33 H46 N O9 Na Au
	820.2682	2.7	3.3	15.5	2773564.0	C31 H43 N9 O P Cl Au



Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

19911 formula(e) evaluated with 62 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 P: 0-1 Cl: 0-1 Au: 0-4

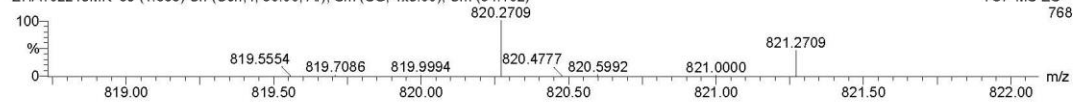
Wang/Zhang, wylL3AuCl, mw 797; ESI+

ZHA102213MK 89 (1.688) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (84:102)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

768

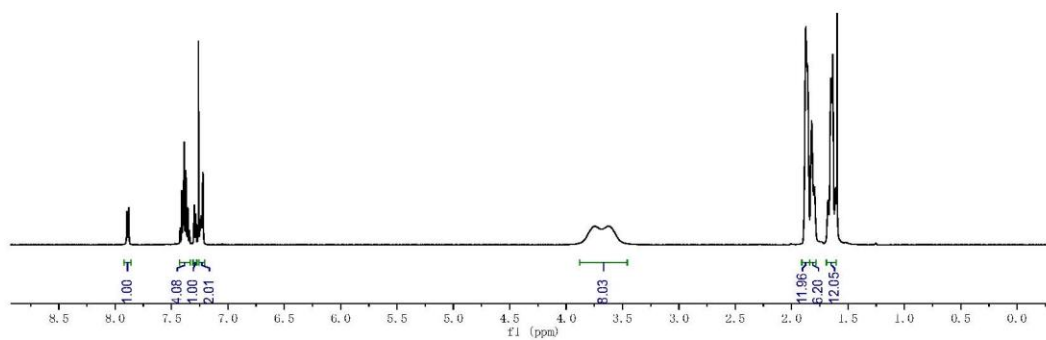
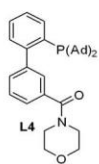


Minimum: -1.5  
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
820.2681	2.8	3.4	-0.5	2773564.0	C22 H49 N O4 Cl Au2	
820.2737	-2.8	-3.4	27.5	2773510.3	C42 H40 N9 O6 Na P	
820.2680	2.9	3.5	36.5	2773565.3	C50 H36 N9 Na Cl	
820.2680	2.9	3.5	-0.5	2773298.8	C21 H49 N O5 P Au2	
820.2680	2.9	3.5	30.5	2773565.0	C45 H40 N9 O3 P Cl	
820.2679	3.0	3.7	5.5	2773335.8	C26 H45 N O2 Na Au2	
820.2679	3.0	3.7	14.5	2773564.5	C36 H46 N O6 Cl Au	
820.2739	-3.0	-3.7	27.5	2773565.0	C43 H40 N9 O5 Na Cl	
820.2739	-3.0	-3.7	12.5	2773414.5	C28 H43 N9 O4 Na P Au	

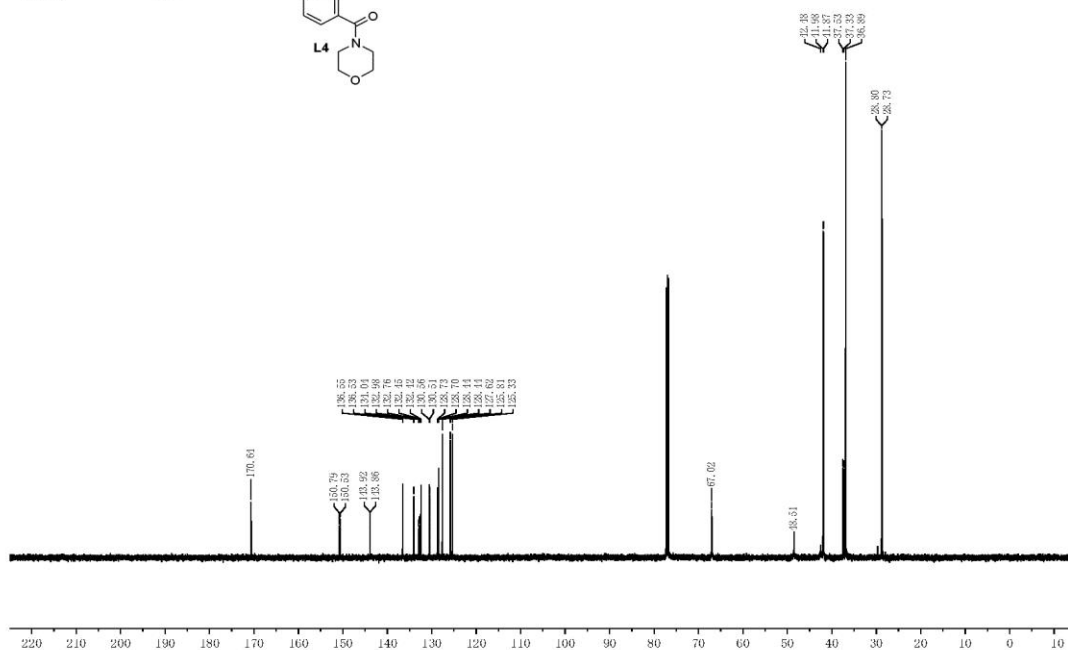
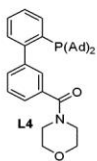
Supplementary Figure 24. HRMS of L3AuCl.

Parameter	Value
1 Title	zhixun-3-14
2 Solvent	CDCl3
3 Spectrometer Frequency	499.86



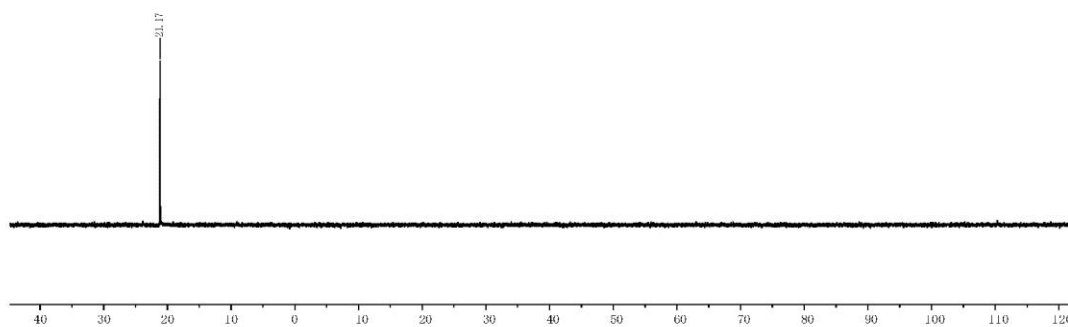
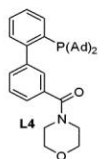
Supplementary Figure 25. <sup>1</sup>H NMR spectrum of L4.

Parameter Value  
Title wyz7-296-4-C13  
Solvent CDCl3  
Spectrometer Frequency 125.70  
Nucleus 13C



Supplementary Figure 26.  $^{13}\text{C}$  NMR spectrum of L4.

Parameter	Value
Title	wyz7-296-4-p31
Solvent	cdCl <sub>3</sub>
Spectrometer Frequency	161.90
Nucleus	<sup>31</sup> P



Supplementary Figure 27. <sup>31</sup>P NMR spectrum of L4.

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

4463 formula(e) evaluated with 20 results within limits (all results (up to 1000) for each mass)

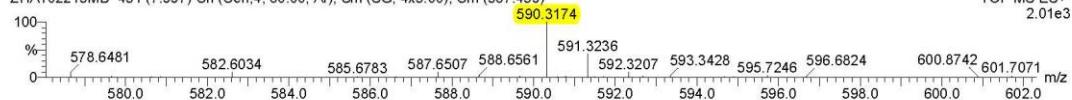
Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 P: 0-2

Wang/Zhang, wylL4, mw 567; ESI+

ZHA102213MD 431 (7.997) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (387;439)

UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
2.01e3

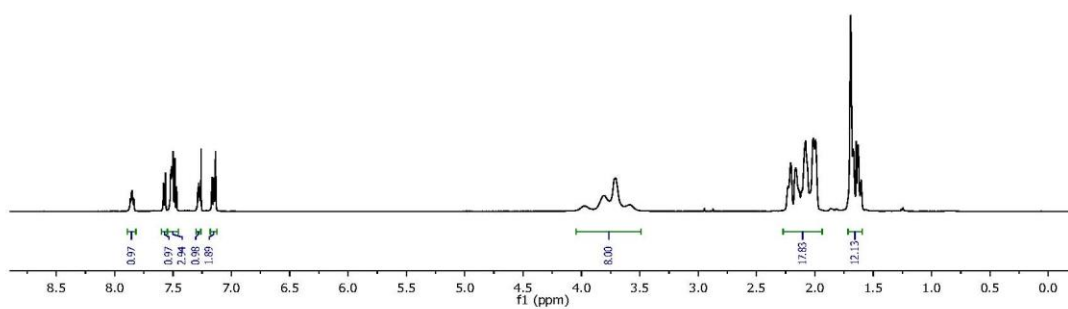
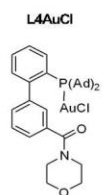


Minimum: -1.5  
Maximum: 3.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
590.3174	590.3172	0.2	0.3	-1.5	83.5	C19 H51 N7 O8 Na P2
	590.3171	0.3	0.5	23.5	6.1	C41 H40 N3 O
	590.3178	-0.4	-0.7	14.5	4.0	C33 H46 N5 O P2
	590.3179	-0.5	-0.8	12.5	14.2	C28 H41 N9 O4 Na
	590.3180	-0.6	-1.0	6.5	41.0	C23 H45 N9 O7 P
	590.3166	0.8	1.4	7.5	21.3	C27 H45 N5 O8 Na
	590.3182	-0.8	-1.4	2.5	37.1	C25 H50 N3 O9 Na P
	590.3164	1.0	1.7	9.5	7.4	C32 H50 N O5 P2
	590.3164	1.0	1.7	9.5	7.4	C32 H50 N O5 P2
	590.3164	1.0	1.7	9.5	7.4	C32 H50 N O5 P2
	590.3164	1.0	1.7	9.5	7.4	C32 H50 N O5 P2
	590.3161	1.3	2.2	19.5	0.8	C35 H41 N7 P
	590.3188	-1.4	-2.4	18.5	1.3	C39 H45 N O2 P
	590.3190	-1.6	-2.7	10.5	11.5	C29 H44 N5 O8
	590.3156	1.8	3.0	3.5	58.6	C21 H46 N9 O7 Na P
	590.3154	2.0	3.4	11.5	10.3	C31 H47 N5 O Na P2
	590.3196	-2.2	-3.7	7.5	27.3	C26 H46 N7 O5 Na P
	590.3196	-2.2	-3.7	1.5	62.3	C21 H50 N7 O8 P2
	590.3150	2.4	4.1	6.5	34.1	C24 H44 N7 O10
	590.3148	2.6	4.4	14.5	1.9	C34 H45 N3 O4 P
	590.3147	2.7	4.6	20.5	2.1	C39 H41 N3 O Na
	590.3203	-2.9	-4.9	15.5	6.6	C30 H40 N9 O4

Supplementary Figure 28. HRMS of L4.

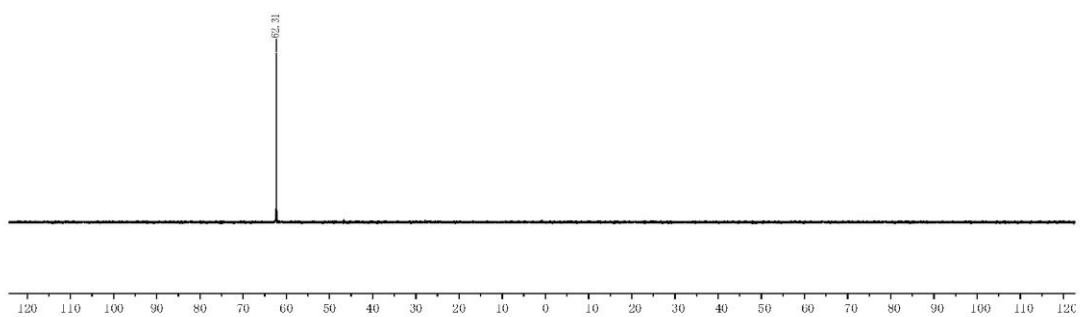
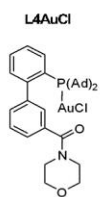
Parameter Value  
Title zhixun-3-L4AuCl  
Solvent CDCl3  
Spectrometer Frequency 499.86



Supplementary Figure 29.  $^1\text{H}$  NMR spectrum of L4AuCl.



Parameter	Value
Title	wyz8-LSAuCl-P31
Solvent	cdCl <sub>3</sub>
Spectrometer Frequency	161.90
Nucleus	<sup>31</sup> P



**Supplementary Figure 31. <sup>31</sup>P NMR spectrum of L4AuCl.**



Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

20027 formula(e) evaluated with 63 results within limits (all results (up to 1000) for each mass)

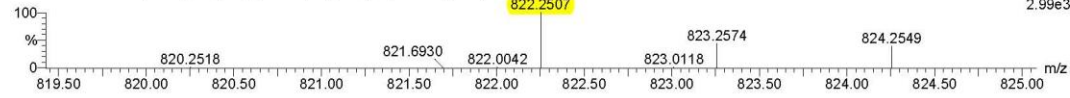
Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 P: 0-1 Cl: 0-1 Au: 0-4

Wang/Zhang, wylL4AuCl, mw 799; ESI+

ZHA102213ML 195 (3.698) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (181:229)

UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
2.99e3



Minimum: -1.5  
 Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
822.2507	822.2507	0.0	0.0	28.5	293.8	C42 H35 N5 O Au
	822.2508	-0.1	-0.1	18.5	4.1	C35 H43 N9 O9 Na P Cl
	822.2505	0.2	0.2	43.5	245.7	C56 H32 N5 O3
	822.2504	0.3	0.4	-0.5	113.1	C20 H48 N3 O2 P Cl Au2
	822.2504	0.3	0.4	6.5	50.2	C24 H44 N7 O10 Cl Au
	822.2510	-0.3	-0.4	3.5	73.4	C21 H46 N9 O7 Na P Cl Au
	822.2511	-0.4	-0.5	40.5	255.7	C53 H34 N7 Na P
	822.2502	0.5	0.6	12.5	392.9	C28 H40 N7 O8 Na Au
	822.2502	0.5	0.6	5.5	530.6	C24 H44 N3 Na P Au2
	822.2502	0.5	0.6	14.5	5.0	C34 H45 N3 O4 P Cl Au
	822.2513	-0.6	-0.7	34.5	45.1	C49 H38 N7 O2 P Cl
	822.2501	0.6	0.7	20.5	2.5	C39 H41 N3 O Na Cl Au
	822.2500	0.7	0.9	20.5	324.3	C38 H41 N3 O2 Na P Au
	822.2500	0.7	0.9	29.5	35.0	C48 H42 N3 O6 P Cl
	822.2500	0.7	0.9	27.5	252.0	C42 H37 N7 O10 Na
	822.2499	0.8	1.0	35.5	62.5	C53 H38 N3 O3 Na Cl
	822.2515	-0.8	-1.0	19.5	1.4	C35 H41 N7 P Cl Au
	822.2498	0.9	1.1	35.5	246.1	C52 H38 N3 O4 Na P
	822.2516	-0.9	-1.1	30.5	46.8	C51 H43 N O4 Na P Cl
	822.2497	1.0	1.2	39.5	60.6	C51 H33 N9 O Cl
	822.2497	1.0	1.2	24.5	334.9	C36 H36 N9 P Au
	822.2518	-1.1	-1.3	15.5	1.8	C37 H46 N O2 Na P Cl Au
	822.2518	-1.1	-1.3	22.5	11.6	C41 H42 N5 O10 Na Cl
	822.2496	1.1	1.3	8.5	469.5	C27 H42 N O3 Au2
	822.2518	-1.1	-1.3	7.5	426.6	C26 H45 N5 O9 Na P Au
	822.2495	1.2	1.5	39.5	252.8	C50 H33 N9 O2 P
	822.2494	1.3	1.6	23.5	291.5	C41 H39 N O5 Au
	822.2520	-1.3	-1.6	0.5	82.9	C23 H49 N Na P Cl Au2
	822.2520	-1.3	-1.6	7.5	32.0	C27 H45 N5 O8 Na Cl Au
	822.2521	-1.4	-1.7	44.5	251.8	C59 H33 N3 O Na
	822.2492	1.5	1.8	38.5	235.0	C55 H36 N O7
	822.2522	-1.5	-1.8	38.5	243.9	C54 H37 N3 O4 P
	822.2491	1.6	1.9	16.5	4.1	C33 H42 N7 Na P Cl Au
	822.2523	-1.6	-1.9	38.5	76.0	C55 H37 N3 O3 Cl
	822.2524	-1.7	-2.1	23.5	307.7	C40 H40 N3 O2 P Au
	822.2524	-1.7	-2.1	30.5	243.3	C44 H36 N7 O10
	822.2489	1.8	2.2	31.5	34.2	C47 H39 N7 O2 Na P Cl
	822.2526	-1.9	-2.3	8.5	494.0	C26 H43 N3 P Au2
	822.2526	-1.9	-2.3	23.5	5.7	C41 H40 N3 O Cl Au
	822.2526	-1.9	-2.3	15.5	365.8	C30 H39 N7 O8 Au
	822.2487	2.0	2.4	4.5	80.1	C22 H43 N5 O Cl Au2
	822.2486	2.1	2.6	4.5	564.3	C21 H43 N5 O2 P Au2
	822.2528	-2.1	-2.6	0.5	633.9	C16 H42 N7 O6 Au2
	822.2485	2.2	2.7	11.5	416.9	C25 H39 N9 O10 Au
	822.2529	-2.2	-2.7	11.5	354.1	C32 H44 N O10 Na Au
	822.2529	-2.2	-2.7	35.5	58.3	C52 H39 N5 Na P Cl
	822.2485	2.2	2.7	19.5	2.3	C36 H40 N5 O3 Cl Au
	822.2530	-2.3	-2.8	27.5	265.9	C41 H38 N9 O7 Na P
	822.2484	2.3	2.8	19.5	337.0	C35 H40 N5 O4 P Au
	822.2531	-2.4	-2.9	27.5	16.7	C42 H38 N9 O6 Na Cl
	822.2483	2.4	2.9	25.5	307.8	C40 H36 N5 O Na Au
	822.2483	2.4	2.9	34.5	49.3	C50 H37 N5 O5 Cl
	822.2532	-2.5	-3.0	21.5	5.6	C37 H42 N9 O9 P Cl

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

20027 formula(e) evaluated with 63 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 P: 0-1 Cl: 0-1 Au: 0-4

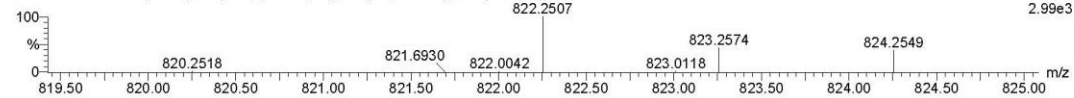
Wang/Zhang, wylL4AuCl, mw 799; ESI+

ZHA102213ML 195 (3.698) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (181:229)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

2.99e3

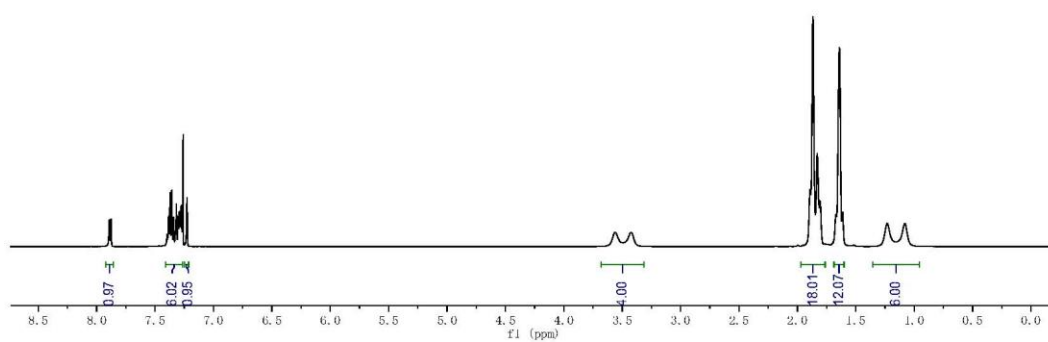
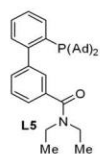


Minimum: -1.5  
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
822.2532	-2.5	-3.0	12.5	414.9	C27 H41 N9 O5 Na P Au	
822.2481	2.6	3.2	40.5	246.6	C54 H33 N5 O3 Na	
822.2481	2.6	3.2	34.5	244.3	C49 H37 N5 O6 P	
822.2533	-2.6	-3.2	12.5	18.8	C28 H41 N9 O4 Na Cl Au	
822.2480	2.7	3.3	3.5	69.7	C22 H45 N7 O10 Na Cl Au	
822.2534	-2.7	-3.3	6.5	53.4	C23 H45 N9 O7 P Cl Au	
822.2535	-2.8	-3.4	43.5	254.4	C55 H33 N7 P	
822.2478	2.9	3.5	11.5	10.6	C32 H46 N3 O4 Na P Cl Au	
822.2537	-3.0	-3.6	2.5	52.4	C25 H50 N3 O9 Na P Cl Au	
822.2477	3.0	3.6	0.5	147.0	C16 H44 N9 P Cl Au2	

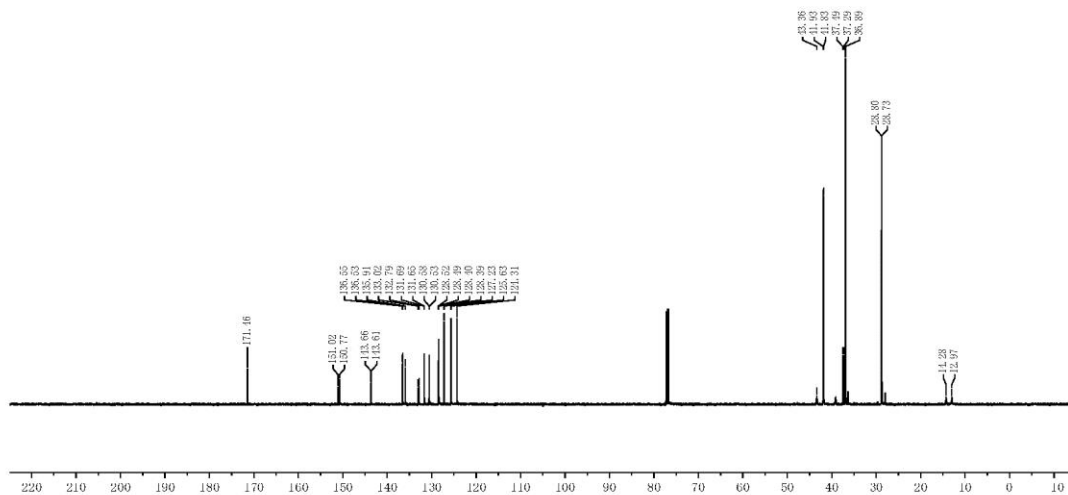
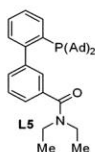
Supplementary Figure 32. HRMS of L4AuCl.

Parameter	Value
1 Title	zhixun-3-1.5
2 Solvent	CDCl <sub>3</sub>
3 Spectrometer Frequency	499.86



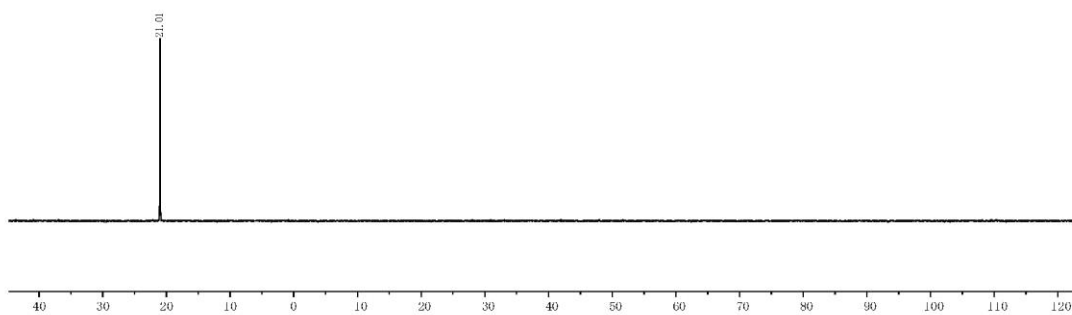
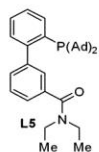
Supplementary Figure 33. <sup>1</sup>H NMR spectrum of L5.

Parameter Value  
Title wyz7-296-2-C13  
Solvent CDCl3  
Spectrometer Frequency 125.70  
Nucleus 13C



Supplementary Figure 34. <sup>13</sup>C NMR spectrum of L5.

Parameter	Value
Title	wyz7-296-2-p31
Solvent	cdcl3
Spectrometer Frequency	161.90
Nucleus	31P



Supplementary Figure 35. <sup>31</sup>P NMR spectrum of L5.

## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

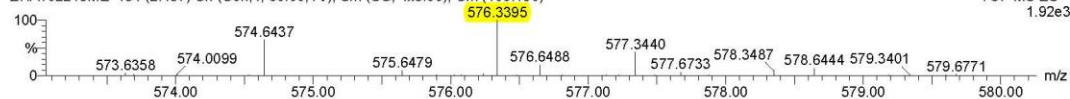
4336 formula(e) evaluated with 17 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 P: 0-2

Wang/Zhang, wylL5, mw 553; ESI+

ZHA102213ME 131 (2.437) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (108:190)

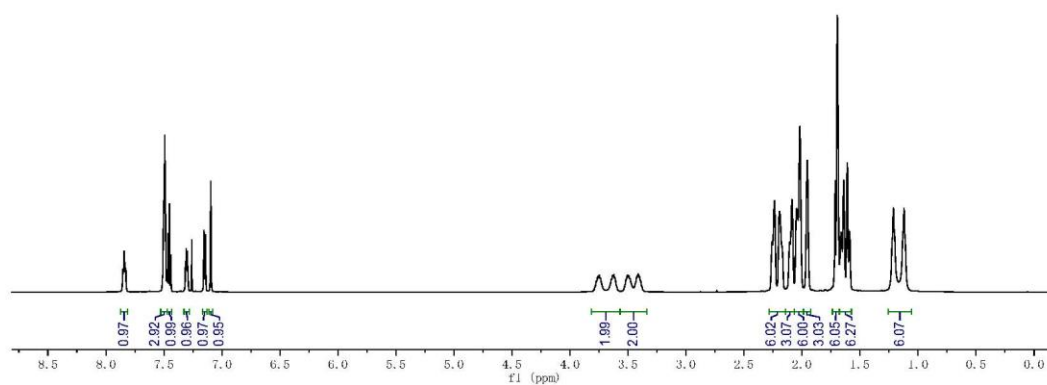
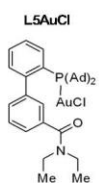
UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
1.92e3

Minimum: -1.5  
Maximum: 3.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
576.3395	576.3395	0.0	0.0	17.5	1.2	C39 H47 N O P
	576.3397	-0.2	-0.3	9.5	11.3	C29 H46 N5 O7
	576.3390	0.5	0.9	1.5	36.0	C25 H52 N3 O8 Na P
	576.3387	0.8	1.4	5.5	39.8	C23 H47 N9 O6 P
	576.3403	-0.8	-1.4	0.5	60.3	C21 H52 N7 O7 P2
	576.3387	0.8	1.4	11.5	13.6	C28 H43 N9 O3 Na
	576.3403	-0.8	-1.4	6.5	26.3	C26 H48 N7 O4 Na P
	576.3385	1.0	1.7	13.5	3.5	C33 H48 N5 P2
	576.3411	-1.6	-2.8	14.5	6.1	C30 H42 N9 O3
	576.3379	1.6	2.8	22.5	6.1	C41 H42 N3
	576.3413	-1.8	-3.1	10.5	4.8	C32 H47 N3 O5 Na
	576.3414	-1.9	-3.3	4.5	23.1	C27 H51 N3 O8 P
	576.3374	2.1	3.6	0.5	52.0	C22 H51 N5 O10 P
	576.3373	2.2	3.8	6.5	20.8	C27 H47 N5 O7 Na
	576.3372	2.3	4.0	8.5	7.2	C32 H52 N O4 P2
	576.3371	2.4	4.2	14.5	0.2	C37 H48 N O Na P
	576.3420	-2.5	-4.3	1.5	43.4	C24 H53 N5 O5 Na P2

Supplementary Figure 36. HRMS of L5.

Parameter	Value
1. Title	zhkum-3-L5AuCl
2. Solvent	cdcl3
3. Spectrometer Frequency	599.64

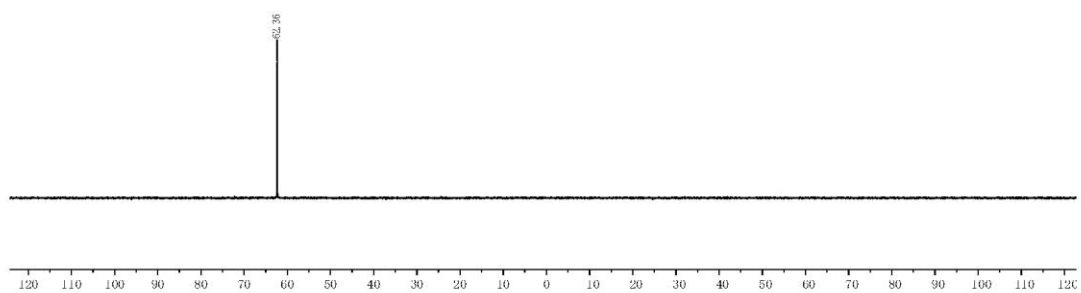
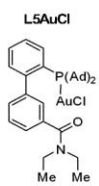


**Supplementary Figure 37. <sup>1</sup>H NMR spectrum of L5AuCl.**





Parameter	Value
Title	wyz8-L6AuCl-P31
Solvent	cdCl <sub>3</sub>
Spectrometer Frequency	161.90
Nucleus	<sup>31</sup> P



**Supplementary Figure 39. <sup>31</sup>P NMR spectrum of L5AuCl.**

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

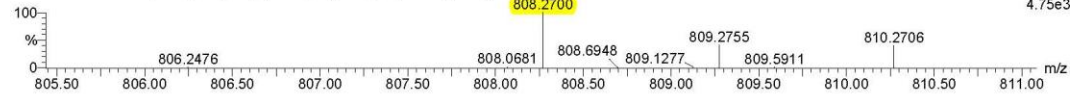
19398 formula(e) evaluated with 61 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 P: 0-1 Cl: 0-1 Au: 0-4

Wang/Zhang, wyl5AuCl, mw 785; ESI+  
ZHA102213MM 224 (4.248) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (194;257)

UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
4.75e3



Minimum: -1.5  
 Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
808.2700	808.2729	-2.9	-3.6	37.5	454.0	C54 H39 N3 O3 P
	808.2729	-2.9	-3.6	43.5	471.7	C59 H35 N3 Na
	808.2728	-2.8	-3.5	0.5	91.9	C22 H51 N5 O10 P Cl Au
	808.2727	-2.7	-3.3	6.5	31.9	C27 H47 N5 O7 Na Cl Au
	808.2726	-2.6	-3.2	6.5	696.0	C26 H47 N5 O8 Na P Au
	808.2725	-2.5	-3.1	14.5	0.7	C37 H48 N O Na P Cl Au
	808.2725	-2.5	-3.1	21.5	22.2	C41 H44 N5 O9 Na Cl
	808.2724	-2.4	-3.0	21.5	463.1	C40 H44 N5 O10 Na P
	808.2723	-2.3	-2.8	29.5	91.2	C51 H45 N O3 Na P Cl
	808.2721	-2.1	-2.6	33.5	89.0	C49 H40 N7 O P Cl
	808.2717	-1.7	-2.1	2.5	89.7	C21 H48 N9 O6 Na P Cl Au
	808.2715	-1.5	-1.9	17.5	3.0	C35 H45 N9 O8 Na P Cl
	808.2715	-1.5	-1.9	27.5	516.2	C42 H37 N5 Au
	808.2713	-1.3	-1.6	42.5	459.4	C56 H34 N5 O2
	808.2711	-1.1	-1.4	-1.5	149.5	C20 H50 N3 O P Cl Au2
	808.2711	-1.1	-1.4	5.5	55.9	C24 H46 N7 O9 Cl Au
	808.2709	-0.9	-1.1	5.5	735.2	C23 H46 N7 O10 P Au
	808.2709	-0.9	-1.1	13.5	0.9	C34 H47 N3 O3 P Cl Au
	808.2709	-0.9	-1.1	11.5	647.2	C28 H42 N7 O7 Na Au
	808.2709	-0.9	-1.1	19.5	6.1	C39 H43 N3 Na Cl Au
	808.2707	-0.7	-0.9	28.5	68.9	C48 H44 N3 O5 P Cl
	808.2707	-0.7	-0.9	19.5	556.1	C38 H43 N3 O Na P Au
	808.2707	-0.7	-0.9	26.5	450.9	C42 H39 N7 O9 Na
	808.2707	-0.7	-0.9	34.5	119.0	C53 H40 N3 O2 Na Cl
	808.2705	-0.5	-0.6	34.5	454.7	C52 H40 N3 O3 Na P
	808.2704	-0.4	-0.5	38.5	116.5	C51 H35 N9 Cl
	808.2703	-0.3	-0.4	7.5	762.8	C27 H44 N O2 Au2
	808.2702	-0.2	-0.2	38.5	465.0	C50 H35 N9 O P
	808.2701	-0.1	-0.1	22.5	508.3	C41 H41 N O4 Au
	808.2699	0.1	0.1	37.5	438.9	C55 H38 N O6
	808.2696	0.4	0.5	30.5	69.0	C47 H41 N7 O Na P Cl
	808.2695	0.5	0.6	3.5	100.9	C22 H45 N5 Cl Au2
	808.2693	0.7	0.9	3.5	904.0	C21 H45 N5 O P Au2
	808.2693	0.7	0.9	10.5	680.3	C25 H41 N9 O9 Au
	808.2693	0.7	0.9	18.5	1.0	C36 H42 N5 O2 Cl Au
	808.2691	0.9	1.1	18.5	571.3	C35 H42 N5 O3 P Au
	808.2691	0.9	1.1	33.5	94.5	C50 H39 N5 O4 Cl
	808.2691	0.9	1.1	24.5	534.4	C40 H38 N5 Na Au
	808.2689	1.1	1.4	33.5	448.1	C49 H39 N5 O5 P
	808.2688	1.2	1.5	39.5	458.1	C54 H35 N5 O2 Na
	808.2687	1.3	1.6	2.5	83.1	C22 H47 N7 O9 Na Cl Au
	808.2685	1.5	1.9	2.5	790.1	C21 H47 N7 O10 Na P Au
	808.2685	1.5	1.9	10.5	6.0	C32 H48 N3 O3 Na P Cl Au
	808.2683	1.7	2.1	25.5	51.3	C46 H45 N3 O5 Na P Cl
	808.2682	1.8	2.2	14.5	6.7	C30 H43 N9 O P Cl Au
	808.2681	1.9	2.4	-1.5	139.6	C21 H49 N O4 Cl Au2
	808.2680	2.0	2.5	29.5	49.4	C44 H40 N9 O3 P Cl
	808.2680	2.0	2.5	35.5	94.8	C49 H36 N9 Na Cl
	808.2680	2.0	2.5	-1.5	934.9	C20 H49 N O5 P Au2
	808.2679	2.1	2.6	13.5	1.2	C35 H46 N O6 Cl Au
	808.2679	2.1	2.6	4.5	815.2	C25 H45 N O2 Na Au2
	808.2678	2.2	2.7	35.5	469.4	C48 H36 N9 O Na P
	808.2678	2.2	2.7	13.5	573.1	C34 H46 N O7 P Au

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

19398 formula(e) evaluated with 61 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 P: 0-1 Cl: 0-1 Au: 0-4

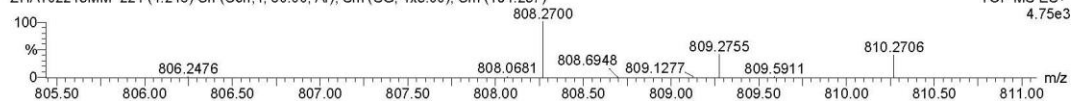
Wang/Zhang, wylL5AuCl, mw 785; ESI+

ZHA102213MM 224 (4.248) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (194:257)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

4.75e3

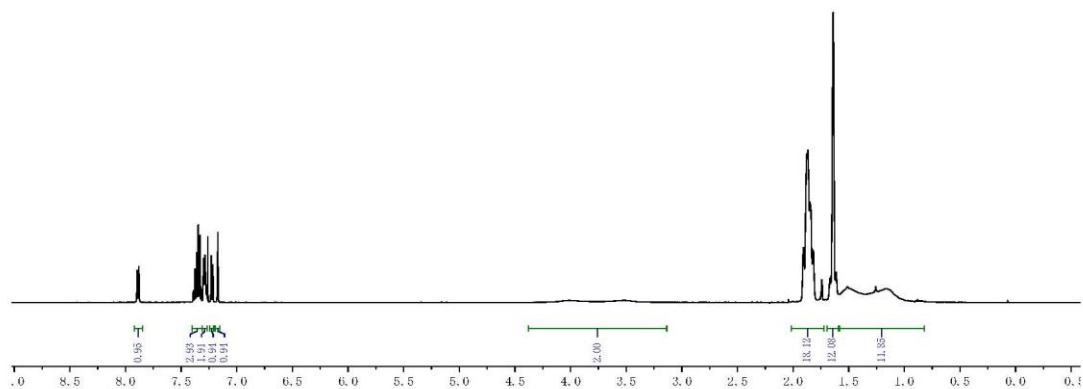
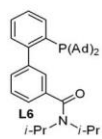


Minimum: -1.5  
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
808.2677	2.3	2.8	28.5	74.6	C49 H43 N O8 Cl	
808.2677	2.3	2.8	19.5	529.3	C39 H42 N O4 Na Au	
808.2676	2.4	3.0	8.5	837.7	C23 H40 N7 Au2	
808.2675	2.5	3.1	28.5	432.2	C48 H43 N O9 P	
808.2675	2.5	3.1	34.5	439.2	C53 H39 N O6 Na	
808.2674	2.6	3.2	23.5	545.3	C37 H37 N7 O2 Au	
808.2672	2.8	3.5	38.5	449.5	C51 H34 N7 O4	
808.2671	2.9	3.6	0.5	138.5	C20 H46 N5 Na Cl Au2	

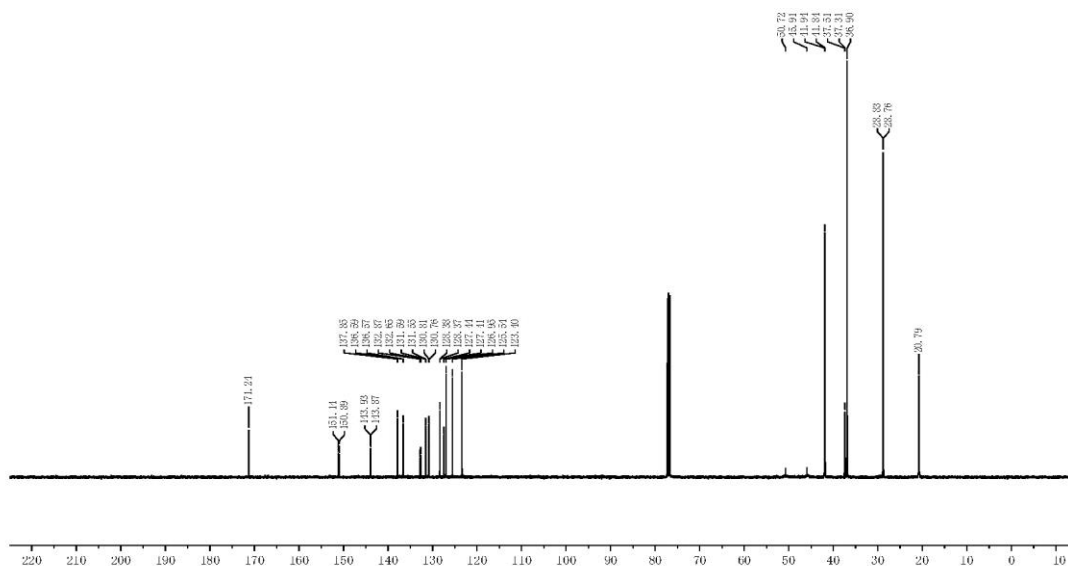
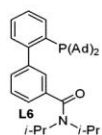
Supplementary Figure 40. HRMS of L5AuCl.

Parameter Value  
Title wy27-296-3-H1-again  
Solvent CDCl3  
Spectrometer Frequency 499.86  
Nucleus 1H



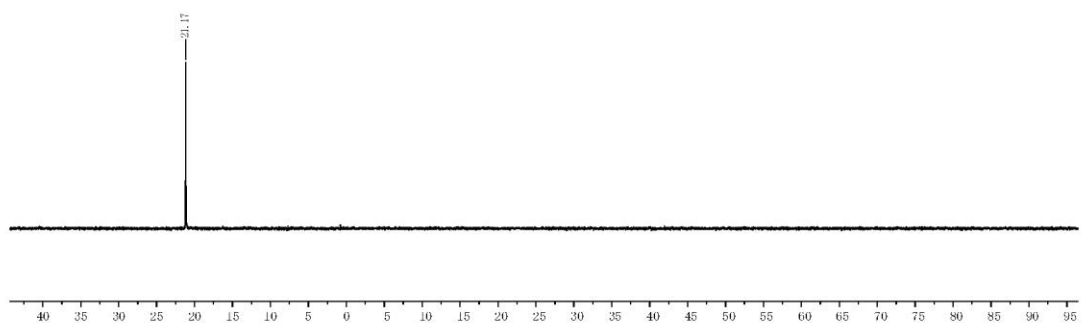
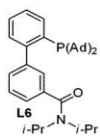
Supplementary Figure 41. <sup>1</sup>H NMR spectrum of L6.

Parameter Value  
Title wyz7-296-3-C13  
Solvent CDCl3  
Spectrometer Frequency 125.70  
Nucleus 13C



Supplementary Figure 42. <sup>13</sup>C NMR spectrum of L6.

Parameter	Value
Title	wyz7-296-3-p31
Solvent	cdcl3
Spectrometer Frequency	161.90
Nucleus	31P



Supplementary Figure 43. <sup>31</sup>P NMR spectrum of L6.

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

4578 formula(e) evaluated with 19 results within limits (all results (up to 1000) for each mass)

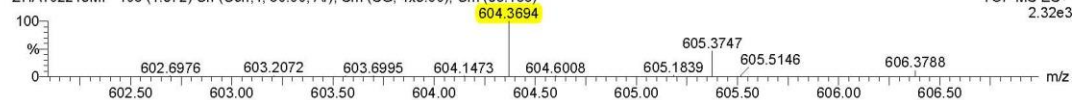
Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 P: 0-2

Wang/Zhang, wylL6, mw 581; ESI+

ZHA102213MF 106 (1.972) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (96:166)

UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
2.32e3

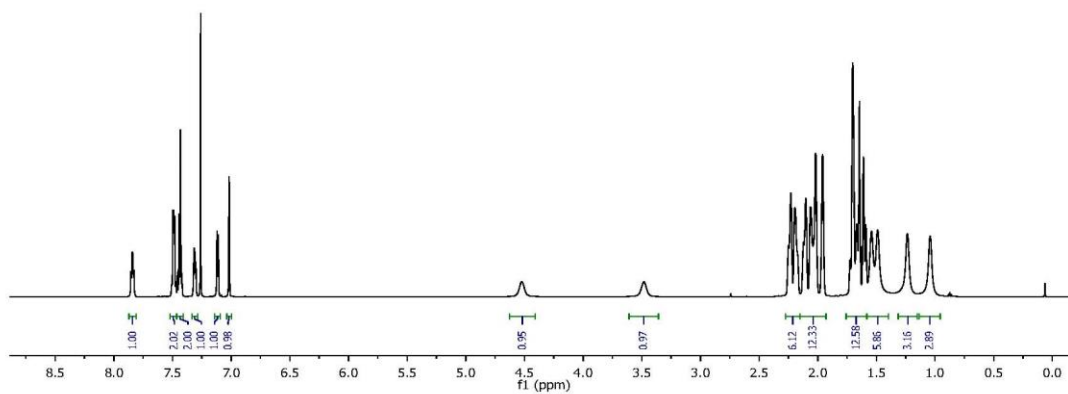
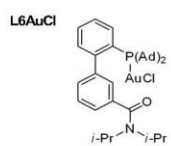


Minimum: -1.5  
Maximum: 3.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
604.3694	604.3692	0.2	0.3	22.5	3.3	C43 H46 N3
	604.3698	-0.4	-0.7	13.5	8.1	C35 H52 N5 P2
	604.3700	-0.6	-1.0	11.5	22.6	C30 H47 N9 O3 Na
	604.3700	-0.6	-1.0	5.5	56.6	C25 H51 N9 O6 P
	604.3687	0.7	1.2	0.5	71.5	C24 H55 N5 O10 P
	604.3686	0.8	1.3	6.5	31.8	C29 H51 N5 O7 Na
	604.3703	-0.9	-1.5	1.5	51.6	C27 H56 N3 O8 Na P
	604.3685	0.9	1.5	8.5	13.3	C34 H56 N O4 P2
	604.3684	1.0	1.7	14.5	1.0	C39 H52 N O Na P
	604.3708	-1.4	-2.3	17.5	0.2	C41 H51 N O P
	604.3710	-1.6	-2.6	9.5	18.9	C31 H50 N5 O7
	604.3676	1.8	3.0	2.5	78.1	C23 H52 N9 O6 Na P
	604.3674	2.0	3.3	10.5	17.2	C33 H53 N5 Na P2
	604.3716	-2.2	-3.6	0.5	82.5	C23 H56 N7 O7 P2
	604.3716	-2.2	-3.6	6.5	39.5	C28 H52 N7 O4 Na P
	604.3670	2.4	4.0	5.5	47.8	C26 H50 N7 O9
	604.3668	2.6	4.3	13.5	4.8	C36 H51 N3 O3 P
	604.3668	2.6	4.3	19.5	0.8	C41 H47 N3 Na
	604.3724	-3.0	-5.0	14.5	12.1	C32 H46 N9 O3

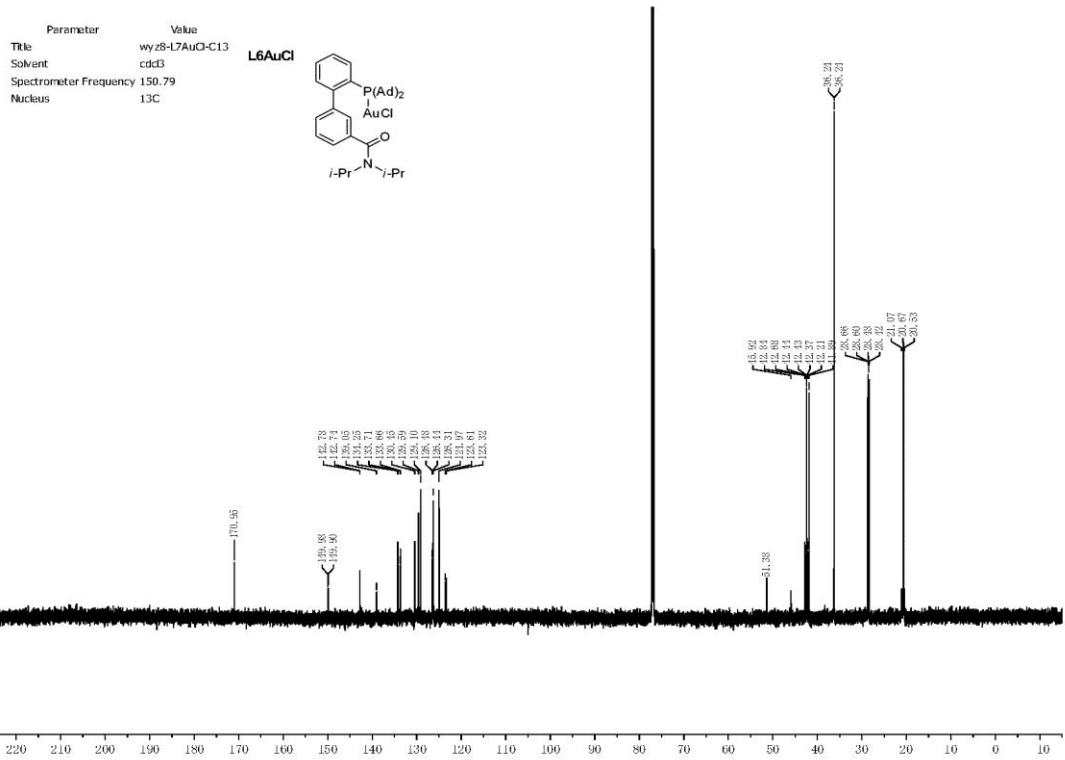
Supplementary Figure 44. HRMS of L6.

Parameter Value  
Title zhikun-3-L6AuCl  
Solvent cdcl3  
Spectrometer Frequency 599.64



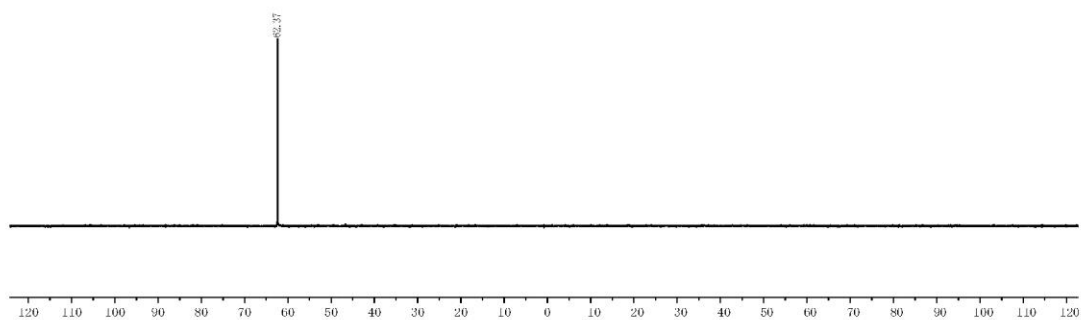
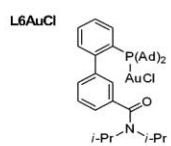
Supplementary Figure 45.  $^1\text{H}$  NMR spectrum of L6AuCl.





Supplementary Figure 46. <sup>13</sup>C NMR spectrum of L6AuCl.

Parameter Value  
Title wy28-L7AuCl-P31  
Solvent cdcCl3  
Spectrometer Frequency 161.90  
Nucleus 31P



**Supplementary Figure 47.  $^{31}\text{P}$  NMR spectrum of L6AuCl.**

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

20565 formula(e) evaluated with 60 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 P: 0-1 Cl: 0-1 Au: 0-4

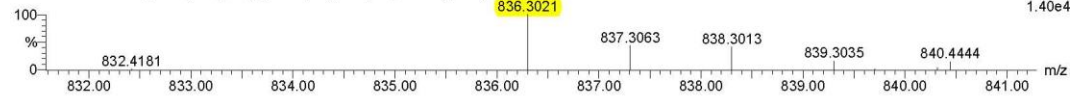
Wang/Zhang, wylL6AuCl, mw 813; ESI+

ZHA102213MN 188 (3.567) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (117.228)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

1.40e4



Minimum: -1.5  
 Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
836.3021	836.3050	-2.9	-3.5	26.5	1314.9	C43 H44 N9 O6 Na P
	836.3049	-2.8	-3.3	10.5	1690.3	C34 H50 N O9 Na Au
	836.3048	-2.7	-3.2	-0.5	2925.3	C18 H48 N7 O5 Au2
	836.3046	-2.5	-3.0	14.5	1743.8	C32 H45 N7 O7 Au
	836.3046	-2.5	-3.0	22.5	36.3	C43 H46 N3 Cl Au
	836.3044	-2.3	-2.8	22.5	1500.4	C42 H46 N3 O P Au
	836.3044	-2.3	-2.8	29.5	1214.8	C46 H42 N7 O9
	836.3044	-2.3	-2.8	37.5	388.2	C57 H43 N3 O2 Cl
	836.3042	-2.1	-2.5	37.5	1228.2	C56 H43 N3 O3 P
	836.3042	-2.1	-2.5	43.5	1267.9	C61 H39 N3 Na
	836.3041	-2.0	-2.4	0.5	265.4	C24 H55 N5 O10 P Cl Au
	836.3040	-1.9	-2.3	6.5	95.8	C29 H51 N5 O7 Na Cl Au
	836.3039	-1.8	-2.2	6.5	2006.7	C28 H51 N5 O8 Na P Au
	836.3038	-1.7	-2.0	14.5	1.3	C39 H52 N O Na P Cl Au
	836.3038	-1.7	-2.0	21.5	59.7	C43 H48 N5 O9 Na Cl
	836.3037	-1.6	-1.9	21.5	1294.2	C42 H48 N5 O10 Na P
	836.3036	-1.5	-1.8	29.5	246.2	C53 H49 N O3 Na P Cl
	836.3034	-1.3	-1.6	33.5	238.8	C51 H44 N7 O P Cl
	836.3030	-0.9	-1.1	2.5	259.2	C23 H52 N9 O6 Na P Cl Au
	836.3028	-0.7	-0.8	17.5	9.1	C37 H49 N9 O8 Na P Cl
	836.3028	-0.7	-0.8	27.5	1441.1	C44 H41 N5 Au
	836.3026	-0.5	-0.6	42.5	1238.0	C58 H38 N5 O2
	836.3024	-0.3	-0.4	-1.5	426.1	C22 H54 N3 O P Cl Au2
	836.3024	-0.3	-0.4	5.5	164.0	C26 H50 N7 O9 Cl Au
	836.3022	-0.1	-0.1	5.5	2125.3	C25 H50 N7 O10 P Au
	836.3022	-0.1	-0.1	13.5	4.4	C36 H51 N3 O3 P Cl Au
	836.3022	-0.1	-0.1	11.5	1860.0	C30 H46 N7 O7 Na Au
	836.3022	-0.1	-0.1	19.5	14.4	C41 H47 N3 Na Cl Au
	836.3020	0.1	0.1	28.5	185.6	C50 H48 N3 O5 P Cl
	836.3020	0.1	0.1	19.5	1571.3	C40 H47 N3 O Na P Au
	836.3020	0.1	0.1	26.5	1250.8	C44 H43 N7 O9 Na
	836.3020	0.1	0.1	34.5	322.2	C55 H44 N3 O2 Na Cl
	836.3018	0.3	0.4	34.5	1236.2	C54 H44 N3 O3 Na P
	836.3017	0.4	0.5	38.5	314.8	C53 H39 N9 Cl
	836.3016	0.5	0.6	7.5	2202.0	C29 H48 N O2 Au2
	836.3015	0.6	0.7	38.5	1266.2	C52 H39 N9 O P
	836.3014	0.7	0.8	22.5	1425.4	C43 H45 N O4 Au
	836.3012	0.9	1.1	37.5	1186.3	C57 H42 N O6
	836.3009	1.2	1.4	30.5	184.1	C49 H45 N7 O Na P Cl
	836.3008	1.3	1.6	3.5	290.4	C24 H49 N5 Cl Au2
	836.3006	1.5	1.8	3.5	2621.1	C23 H49 N5 O P Au2
	836.3006	1.5	1.8	10.5	1961.0	C27 H45 N9 O9 Au
	836.3006	1.5	1.8	18.5	2.5	C38 H46 N5 O2 Cl Au
	836.3004	1.7	2.0	18.5	1622.6	C37 H46 N5 O3 P Au
	836.3004	1.7	2.0	33.5	255.7	C52 H43 N5 O4 Cl
	836.3004	1.7	2.0	24.5	1500.0	C42 H42 N5 Na Au
	836.3002	1.9	2.3	33.5	1223.4	C51 H43 N5 O5 P
	836.3001	2.0	2.4	39.5	1239.6	C56 H39 N5 O2 Na
	836.3000	2.1	2.5	2.5	240.6	C24 H51 N7 O9 Na Cl Au
	836.2998	2.3	2.8	2.5	2287.5	C23 H51 N7 O10 Na P Au
	836.2998	2.3	2.8	10.5	20.0	C34 H52 N3 O3 Na P Cl Au
	836.2996	2.5	3.0	25.5	137.3	C48 H49 N3 O5 Na P Cl
	836.2995	2.6	3.1	14.5	21.7	C32 H47 N9 O P Cl Au

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

20565 formula(e) evaluated with 60 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 P: 0-1 Cl: 0-1 Au: 0-4

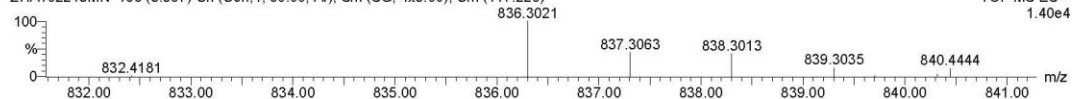
Wang/Zhang, wylL6AuCl, mw 813; ESI+

ZHA102213MN 188 (3.567) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (117:228)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

1.40e4

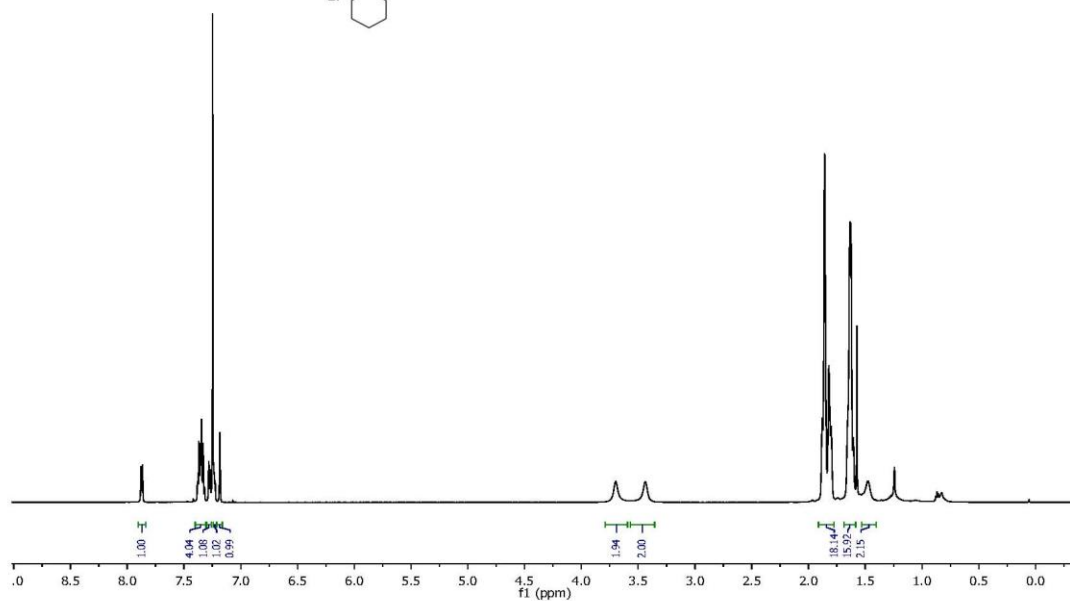
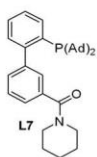


Minimum: -1.5  
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
836.2994	2.7	3.2	-1.5	398.8	C23 H53 N O4 Cl Au2	
836.2993	2.8	3.3	29.5	131.5	C46 H44 N9 O3 P Cl	
836.2993	2.8	3.3	35.5	254.9	C51 H40 N9 Na Cl	
836.2993	2.8	3.3	-1.5	2713.0	C22 H53 N O5 P Au2	
836.2992	2.9	3.5	13.5	5.4	C37 H50 N O6 Cl Au	
836.2992	2.9	3.5	4.5	2358.3	C27 H49 N O2 Na Au2	
836.2991	3.0	3.6	35.5	1284.5	C50 H40 N9 O Na P	

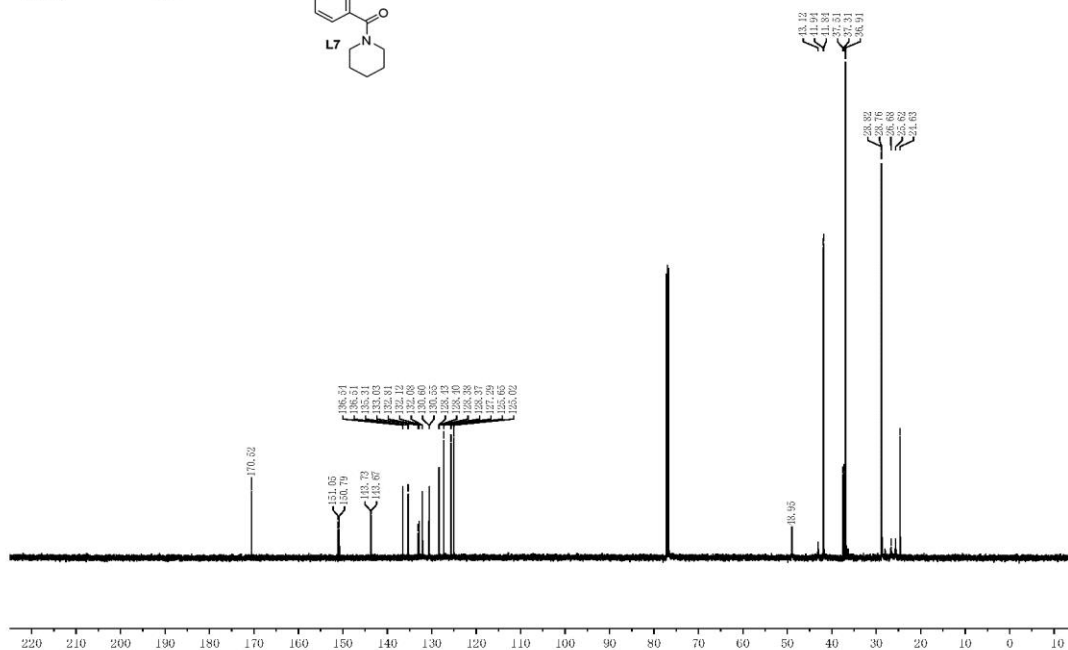
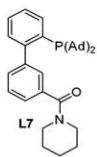
Supplementary Figure 48. HRMS of L6AuCl.

Parameter Value  
Title zhkun-3-L7  
Solvent cdcl3  
Spectrometer Frequency 599.64



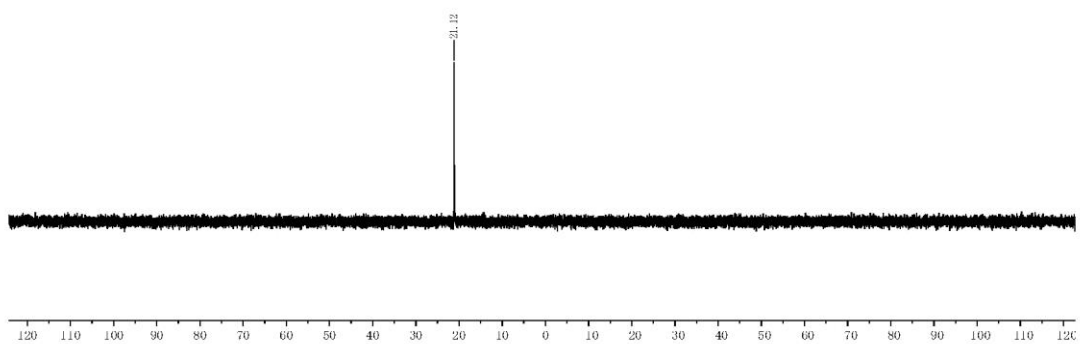
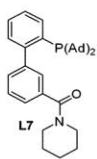
Supplementary Figure 49. <sup>1</sup>H NMR spectrum of L7.

Parameter Value  
Title wyz7-296-1-C13  
Solvent CDCl3  
Spectrometer Frequency 125.70  
Nucleus 13C



Supplementary Figure 50.  $^{13}\text{C}$  NMR spectrum of L7.

Parameter Value  
Title wvz7-296-1-p31  
Solvent cdcl3  
Spectrometer Frequency 161.90  
Nucleus 31P



Supplementary Figure 51.  $^{31}\text{P}$  NMR spectrum of L7.

## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

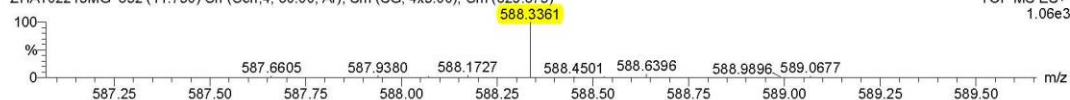
4441 formula(e) evaluated with 22 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 P: 0-2

Wang/Zhang, wylzL7, mw 565; ESI+

ZHA102213MG 632 (11.730) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (629:675)

UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
1.06e3

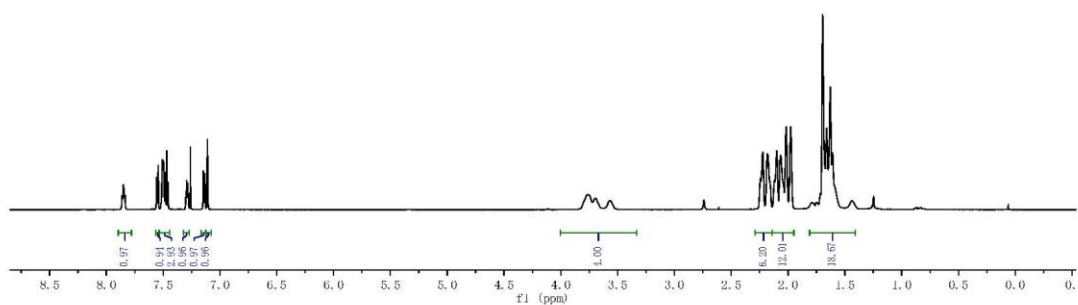
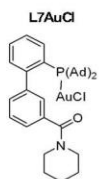
Minimum: -1.5  
Maximum: 3.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
588.3361	588.3361	0.0	0.0	11.5	5546549.0	C32 H49 N5 Na P2
	588.3363	-0.2	-0.3	3.5	5546545.5	C22 H48 N9 O6 Na P
	588.3357	0.4	0.7	6.5	5546547.0	C25 H46 N7 O9
	588.3355	0.6	1.0	14.5	5546549.5	C35 H47 N3 O3 P
	588.3355	0.6	1.0	20.5	5546550.5	C40 H43 N3 Na
	588.3371	-1.0	-1.7	15.5	5546550.0	C38 H48 N O Na P
	588.3350	1.1	1.9	-1.5	5546544.0	C21 H52 N5 O10 Na P
	588.3372	-1.1	-1.9	9.5	5546549.0	C33 H52 N O4 P2
	588.3373	-1.2	-2.0	7.5	5546548.0	C28 H47 N5 O7 Na
	588.3374	-1.3	-2.2	1.5	5546545.5	C23 H51 N5 O10 P
	588.3348	1.3	2.2	6.5	5546548.5	C31 H53 N O4 Na P2
	588.3345	1.6	2.7	10.5	5546548.5	C29 H48 N7 O2 P2
	588.3379	-1.8	-3.1	-1.5	5546544.0	C20 H53 N7 O7 Na P2
	588.3379	-1.8	-3.1	23.5	5546551.0	C42 H42 N3
	588.3339	2.2	3.7	19.5	5546550.0	C37 H42 N5 O2
	588.3385	-2.4	-4.1	14.5	5546549.5	C34 H48 N5 P2
	588.3387	-2.6	-4.4	6.5	5546546.5	C24 H47 N9 O6 P
	588.3387	-2.6	-4.4	12.5	5546548.5	C29 H43 N9 O3 Na
	588.3333	2.8	4.8	3.5	5546546.0	C23 H47 N7 O9 Na
	588.3390	-2.9	-4.9	2.5	5546546.5	C26 H52 N3 O8 Na P
	588.3331	3.0	5.1	5.5	5546547.5	C28 H52 N3 O6 P2
	588.3331	3.0	5.1	11.5	5546549.0	C33 H48 N3 O3 Na P

Supplementary Figure 52. HRMS of L7.



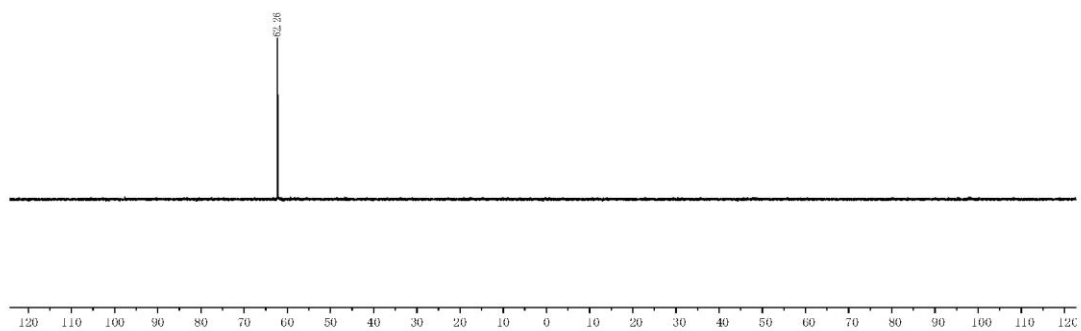
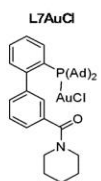
Parameter Value  
1 Data File Name C:/Users/zhang leptop/Desktop/NMR/ywang/wyz8-4.5AuCl.fid  
2 Title wyz8-4.5AuCl  
3 Solvent cdCl3  
4 Spectrometer Frequency 599.64



Supplementary Figure 53.  $^1\text{H}$  NMR spectrum of L7AuCl.



Parameter	Value
Title	wyz8-L5AuCl-P31
Solvent	cdCl <sub>3</sub>
Spectrometer Frequency	161.90
Nucleus	<sup>31</sup> P



**Supplementary Figure 55. <sup>31</sup>P NMR spectrum of L7AuCl.**

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

19910 formula(e) evaluated with 59 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 P: 0-1 Cl: 0-1 Au: 0-4

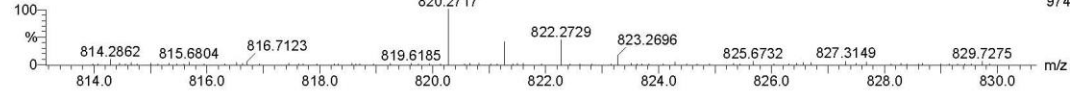
Wang/Zhang, wyl7AuCl, mw 797; ESI+

ZHA102213MO 146 (2.772) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (73:150)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

974

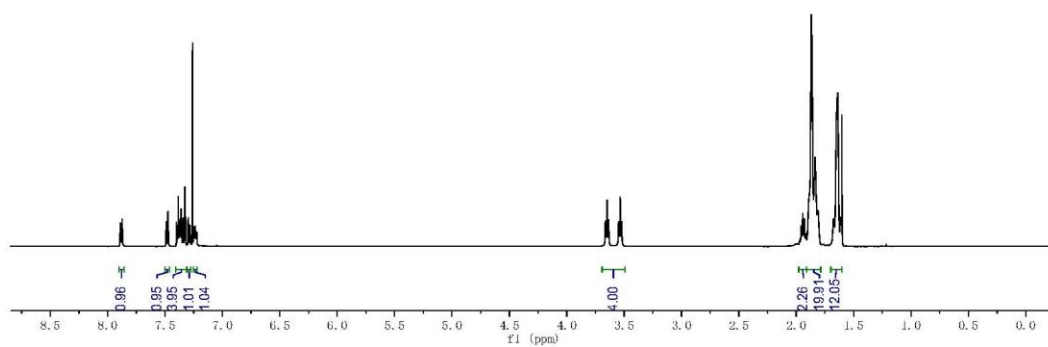
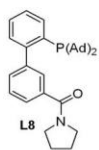


Minimum: -1.5  
 Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
820.2717	820.2717	0.0	0.0	3.5	19.1	C22 H48 N9 O6 Na P Cl Au
820.2715	820.2715	0.2	0.2	28.5	122.5	C43 H37 N5 Au
820.2713	820.2713	0.2	0.2	18.5	0.9	C36 H45 N9 O8 Na P Cl
820.2713	820.2713	0.4	0.5	43.5	108.3	C57 H34 N5 O2
820.2721	820.2721	-0.4	-0.5	34.5	18.4	C50 H40 N7 O P Cl
820.2711	820.2711	0.6	0.7	-0.5	32.0	C21 H50 N3 O P Cl Au2
820.2723	820.2723	-0.6	-0.7	30.5	18.6	C52 H45 N O3 Na P Cl
820.2711	820.2711	0.6	0.7	6.5	11.8	C25 H46 N7 O9 Cl Au
820.2724	820.2724	-0.7	-0.9	22.5	111.4	C41 H44 N5 O10 Na P
820.2709	820.2709	0.8	1.0	20.5	2.6	C40 H43 N3 Na Cl Au
820.2709	820.2709	0.8	1.0	12.5	150.1	C29 H42 N7 O7 Na Au
820.2725	820.2725	-0.8	-1.0	15.5	1.5	C38 H48 N O Na P Cl Au
820.2725	820.2725	-0.8	-1.0	22.5	4.4	C42 H44 N5 O9 Na Cl
820.2709	820.2709	0.8	1.0	6.5	168.0	C24 H46 N7 O10 P Au
820.2709	820.2709	0.8	1.0	14.5	1.4	C35 H47 N3 O3 P Cl Au
820.2726	820.2726	-0.9	-1.1	7.5	160.0	C27 H47 N5 O8 Na P Au
820.2707	820.2707	1.0	1.2	35.5	24.1	C54 H40 N3 O2 Na Cl
820.2707	820.2707	1.0	1.2	27.5	108.6	C43 H39 N7 O9 Na
820.2707	820.2707	1.0	1.2	20.5	131.1	C39 H43 N3 O Na P Au
820.2707	820.2707	1.0	1.2	29.5	14.0	C49 H44 N3 O5 P Cl
820.2727	820.2727	-1.0	-1.2	7.5	7.2	C28 H47 N5 O7 Na Cl Au
820.2728	820.2728	-1.1	-1.3	1.5	18.9	C23 H51 N5 O10 P Cl Au
820.2705	820.2705	1.2	1.5	35.5	108.3	C53 H40 N3 O3 Na P
820.2729	820.2729	-1.2	-1.5	38.5	107.7	C55 H39 N3 O3 P
820.2729	820.2729	-1.2	-1.5	44.5	110.5	C60 H35 N3 Na
820.2704	820.2704	1.3	1.6	39.5	23.8	C52 H35 N9 Cl
820.2704	820.2704	1.3	1.6	-1.5	26.0	C21 H52 N5 O10 Na P Cl Au
820.2731	820.2731	-1.4	-1.7	30.5	106.2	C45 H38 N7 O9
820.2703	820.2703	1.4	1.7	8.5	173.8	C28 H44 N O2 Au2
820.2731	820.2731	-1.4	-1.7	23.5	126.3	C41 H42 N3 O P Au
820.2731	820.2731	-1.4	-1.7	38.5	28.7	C56 H39 N3 O2 Cl
820.2702	820.2702	1.5	1.8	39.5	110.5	C51 H35 N9 O P
820.2701	820.2701	1.6	2.0	23.5	121.0	C42 H41 N O4 Au
820.2733	820.2733	-1.6	-2.0	23.5	4.2	C42 H42 N3 Cl Au
820.2733	820.2733	-1.6	-2.0	15.5	142.2	C31 H41 N7 O7 Au
820.2735	820.2735	-1.8	-2.2	0.5	223.4	C17 H44 N7 O5 Au2
820.2699	820.2699	1.8	2.2	38.5	104.4	C56 H38 N O6
820.2736	820.2736	-1.9	-2.3	11.5	138.4	C33 H46 N O9 Na Au
820.2737	820.2737	-2.0	-2.4	27.5	113.3	C42 H40 N9 O6 Na P
820.2696	820.2696	2.1	2.6	31.5	14.5	C48 H41 N7 O Na P Cl
820.2739	820.2739	-2.2	-2.7	21.5	2.0	C38 H44 N9 O8 P Cl
820.2739	820.2739	-2.2	-2.7	12.5	157.3	C28 H43 N9 O4 Na P Au
820.2739	820.2739	-2.2	-2.7	27.5	7.4	C43 H40 N9 O5 Na Cl
820.2695	820.2695	2.2	2.7	4.5	22.3	C23 H45 N5 Cl Au2
820.2693	820.2693	2.4	2.9	11.5	156.8	C26 H41 N9 O9 Au
820.2741	820.2741	-2.4	-2.9	6.5	13.4	C24 H47 N9 O6 P Cl Au
820.2693	820.2693	2.4	2.9	4.5	202.6	C22 H45 N5 O P Au2
820.2741	820.2741	-2.4	-2.9	12.5	4.6	C29 H43 N9 O3 Na Cl Au
820.2693	820.2693	2.4	2.9	19.5	1.4	C37 H42 N5 O2 Cl Au
820.2742	820.2742	-2.5	-3.0	17.5	2.1	C40 H49 N3 O10 Na P Cl
820.2691	820.2691	2.6	3.2	34.5	19.1	C51 H39 N5 O4 Cl
820.2691	820.2691	2.6	3.2	19.5	134.4	C36 H42 N5 O3 P Au
820.2691	820.2691	2.6	3.2	25.5	126.4	C41 H38 N5 Na Au

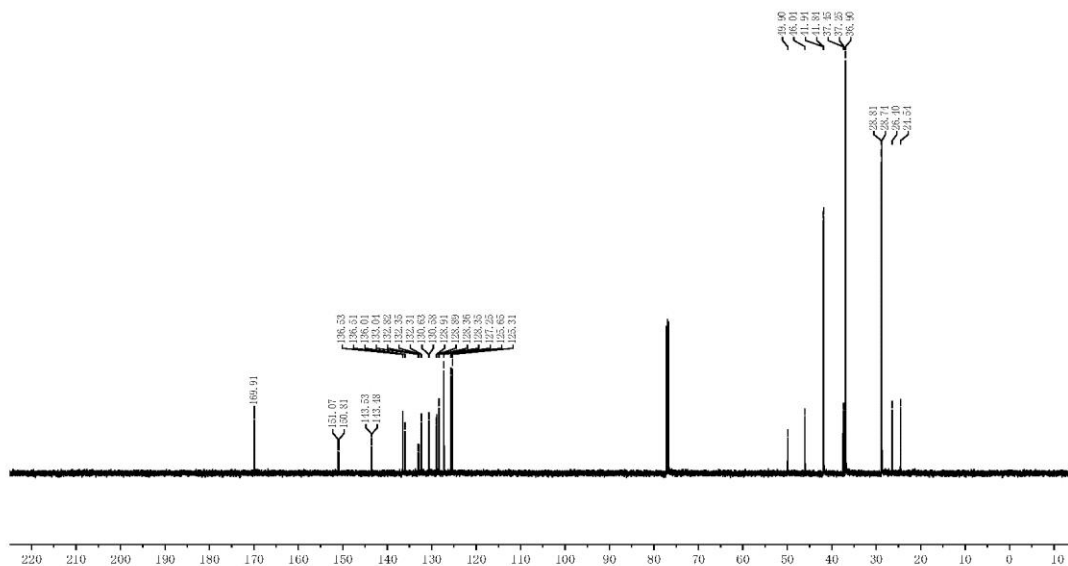
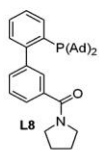


Parameter	Value
1 Title	zhixun-3-L8
2 Solvent	CDCl3
3 Spectrometer Frequency	499.86



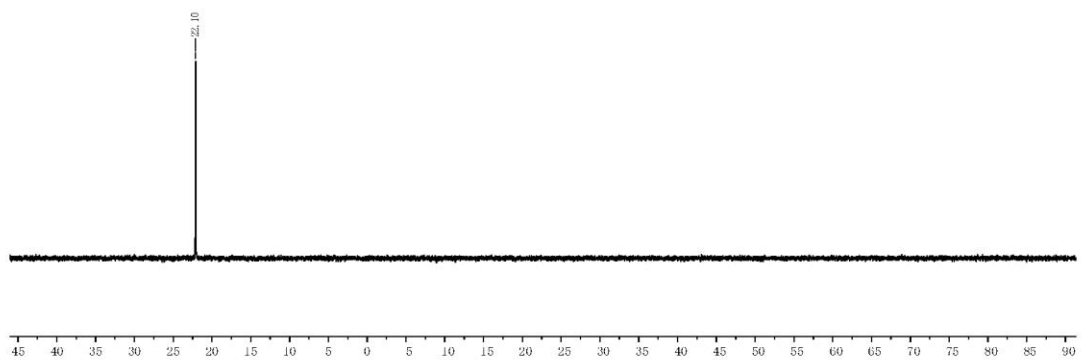
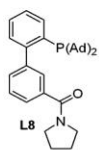
Supplementary Figure 57. <sup>1</sup>H NMR spectrum of L8.

Parameter Value  
Title wyz7-296-5-cl3  
Solvent CDCl3  
Spectrometer Frequency 125.70  
Nucleus 13C



Supplementary Figure 58.  $^{13}\text{C}$  NMR spectrum of L8.

Parameter Value  
Title wyz7-296-5-p31  
Solvent cdcl3  
Spectrometer Frequency 161.90  
Nucleus 31P



Supplementary Figure 59.  $^{31}\text{P}$  NMR spectrum of L8.



Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

4323 formula(e) evaluated with 20 results within limits (all results (up to 1000) for each mass)

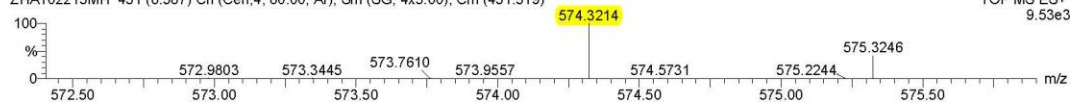
Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 P: 0-2

WangZhang, wylL8, mw 551; ESI+

ZHA102213MH 451 (8.367) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (451:519)

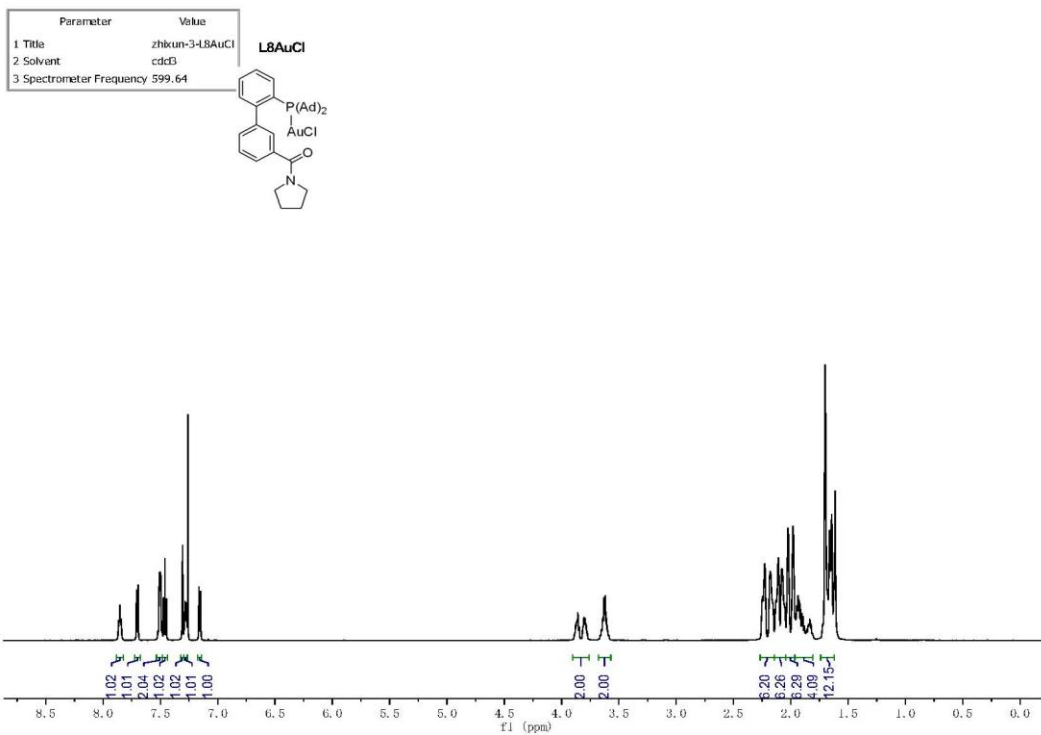
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TOF MS ES+  
9.53e3



Minimum: -1.5  
Maximum: 3.0 10.0 50.0

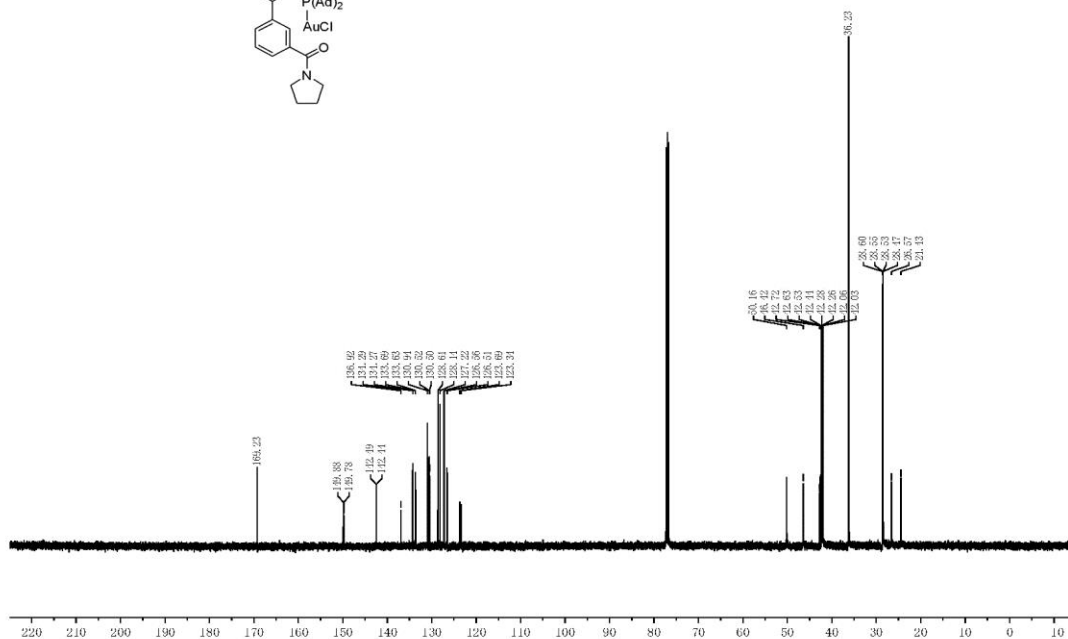
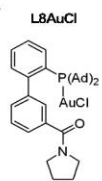
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
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	574.3215	-0.1	-0.2	15.5	2779617.8	C37 H46 N O Na P
	574.3217	-0.3	-0.5	1.5	2779490.3	C22 H49 N5 O10 P
	574.3217	-0.3	-0.5	7.5	2779543.8	C27 H45 N5 O7 Na
	574.3222	-0.8	-1.4	23.5	2779656.3	C41 H40 N3
	574.3206	0.8	1.4	3.5	2779408.0	C21 H46 N9 O6 Na P
	574.3223	-0.9	-1.6	-1.5	2779343.8	C19 H51 N7 O7 Na P2
	574.3204	1.0	1.7	11.5	2779534.0	C31 H47 N5 Na P2
	574.3201	1.3	2.3	6.5	2779527.5	C24 H44 N7 O9
	574.3228	-1.4	-2.4	14.5	2779572.5	C33 H46 N5 P2
	574.3199	1.5	2.6	14.5	2779603.0	C34 H45 N3 O3 P
	574.3198	1.6	2.8	20.5	2779639.8	C39 H41 N3 Na
	574.3230	-1.6	-2.8	12.5	2779536.5	C28 H41 N9 O3 Na
	574.3230	-1.6	-2.8	6.5	2779468.5	C23 H45 N9 O6 P
	574.3233	-1.9	-3.3	2.5	2779507.0	C25 H50 N3 O8 Na P
	574.3193	2.1	3.7	-1.5	2779443.0	C20 H50 N5 O10 Na P
	574.3191	2.3	4.0	6.5	2779539.0	C30 H51 N O4 Na P2
	574.3239	-2.5	-4.4	18.5	2779639.3	C39 H45 N O P
	574.3188	2.6	4.5	10.5	2779509.0	C28 H46 N7 O2 P2
	574.3241	-2.7	-4.7	10.5	2779577.3	C29 H44 N5 O7

Supplementary Figure 60. HRMS of L8.



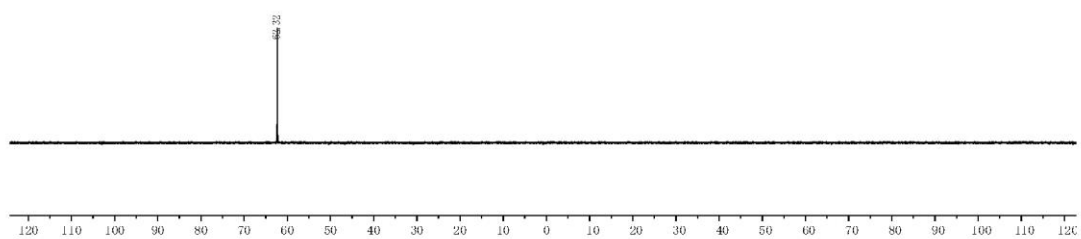
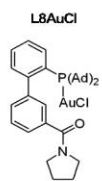
**Supplementary Figure 61.  $^1\text{H}$  NMR spectrum of L8AuCl.**

Parameter Value  
Title wy28-L9AuCl-C13  
Solvent CDCl3  
Spectrometer Frequency 125.70  
Nucleus 13C



Supplementary Figure 62.  $^{13}\text{C}$  NMR spectrum of L8AuCl.

Parameter	Value
Title	wyz8-L8AuCl-P31
Solvent	cdCl <sub>3</sub>
Spectrometer Frequency	161.90
Nucleus	<sup>31</sup> P



**Supplementary Figure 63. <sup>31</sup>P NMR spectrum of L8AuCl.**

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

19330 formula(e) evaluated with 62 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 P: 0-1 Cl: 0-1 Au: 0-4

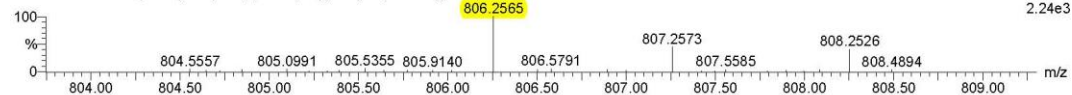
Wang/Zhang, wylL8AuCl, mw 783; ESI+

ZHA102213MP 12 (0.234) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (1:195)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

2.24e3



Minimum: -1.5  
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
806.2565	806.2564	0.1	0.1	34.5	25.1	C49 H38 N7 O P Cl
	806.2567	-0.2	-0.2	22.5	208.4	C40 H42 N5 O10 Na P
	806.2567	-0.2	-0.2	30.5	26.3	C51 H43 N O3 Na P Cl
	806.2569	-0.4	-0.5	15.5	1.8	C37 H46 N O Na P Cl Au
	806.2569	-0.4	-0.5	7.5	345.2	C26 H45 N5 O8 Na P Au
	806.2569	-0.4	-0.5	22.5	4.6	C41 H42 N5 O9 Na Cl
	806.2561	0.4	0.5	3.5	65.5	C21 H46 N9 O6 Na P Cl Au
	806.2571	-0.6	-0.7	1.5	66.9	C22 H49 N5 O10 P Cl Au
	806.2571	-0.6	-0.7	7.5	30.6	C27 H45 N5 O7 Na Cl Au
	806.2558	0.7	0.9	18.5	2.3	C35 H43 N9 O8 Na P Cl
	806.2572	-0.7	-0.9	44.5	186.5	C59 H33 N3 Na
	806.2558	0.7	0.9	28.5	231.3	C42 H35 N5 Au
	806.2573	-0.8	-1.0	38.5	183.7	C54 H37 N3 O3 P
	806.2556	0.9	1.1	43.5	183.1	C56 H32 N5 O2
	806.2574	-0.9	-1.1	38.5	46.0	C55 H37 N3 O2 Cl
	806.2555	1.0	1.2	6.5	45.7	C24 H44 N7 O9 Cl Au
	806.2575	-1.0	-1.2	23.5	244.2	C40 H40 N3 O P Au
	806.2575	-1.0	-1.2	30.5	189.9	C44 H36 N7 O9
	806.2555	1.0	1.2	-0.5	98.2	C20 H48 N3 O P Cl Au2
	806.2576	-1.1	-1.4	23.5	1.6	C41 H40 N3 Cl Au
	806.2553	1.2	1.5	6.5	367.9	C23 H44 N7 O10 P Au
	806.2553	1.2	1.5	14.5	5.7	C34 H45 N3 O3 P Cl Au
	806.2553	1.2	1.5	12.5	317.4	C28 H40 N7 O7 Na Au
	806.2577	-1.2	-1.5	15.5	295.5	C30 H39 N7 O7 Au
	806.2552	1.3	1.6	20.5	0.5	C39 H41 N3 Na Cl Au
	806.2551	1.4	1.7	20.5	258.4	C38 H41 N3 O Na P Au
	806.2551	1.4	1.7	29.5	18.5	C48 H42 N3 O5 P Cl
	806.2579	-1.4	-1.7	0.5	508.5	C16 H42 N7 O5 Au2
	806.2579	-1.4	-1.7	11.5	286.5	C32 H44 N O9 Na Au
	806.2550	1.5	1.9	27.5	198.1	C42 H37 N7 O9 Na
	806.2550	1.5	1.9	35.5	36.7	C53 H38 N3 O2 Na Cl
	806.2580	-1.5	-1.9	27.5	209.4	C41 H38 N9 O6 Na P
	806.2549	1.6	2.0	35.5	186.8	C52 H38 N3 O3 Na P
	806.2582	-1.7	-2.1	12.5	334.9	C27 H41 N9 O4 Na P Au
	806.2582	-1.7	-2.1	27.5	7.4	C42 H38 N9 O5 Na Cl
	806.2547	1.8	2.2	8.5	378.2	C27 H42 N O2 Au2
	806.2547	1.8	2.2	-1.5	86.4	C20 H50 N5 O10 Na P Cl Au
	806.2583	-1.8	-2.2	21.5	2.2	C37 H42 N9 O8 P Cl
	806.2547	1.8	2.2	39.5	35.4	C51 H33 N9 Cl
	806.2546	1.9	2.4	39.5	192.0	C50 H33 N9 O P
	806.2584	-1.9	-2.4	12.5	19.5	C28 H41 N9 O3 Na Cl Au
	806.2585	-2.0	-2.5	6.5	49.0	C23 H45 N9 O6 P Cl Au
	806.2545	2.0	2.5	23.5	231.2	C41 H39 N O4 Au
	806.2585	-2.0	-2.5	17.5	2.8	C39 H47 N3 O10 Na P Cl
	806.2587	-2.2	-2.7	2.5	48.0	C25 H50 N3 O8 Na P Cl Au
	806.2543	2.2	2.7	38.5	176.2	C55 H36 N O6
	806.2589	-2.4	-3.0	39.5	186.1	C57 H38 N O Na P
	806.2540	2.5	3.1	31.5	18.0	C47 H39 N7 O Na P Cl
	806.2590	-2.5	-3.1	39.5	57.0	C58 H38 N Na Cl
	806.2591	-2.6	-3.2	33.5	34.8	C53 H42 N O3 P Cl
	806.2591	-2.6	-3.2	25.5	198.4	C42 H41 N5 O10 P
	806.2591	-2.6	-3.2	31.5	187.8	C47 H37 N5 O7 Na
	806.2538	2.7	3.3	4.5	71.4	C22 H43 N5 Cl Au2

## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

19330 formula(e) evaluated with 62 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 P: 0-1 Cl: 0-1 Au: 0-4

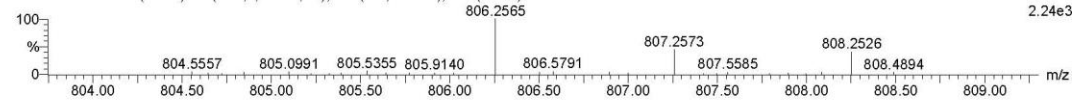
Wang/Zhang, wylL8AuCl, mw 783; ESI+

ZHA102213MP 12 (0.234) Cn (Cen, 4, 60.00, Ar); Sm (SG, 4x3.00); Cm (1;195)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

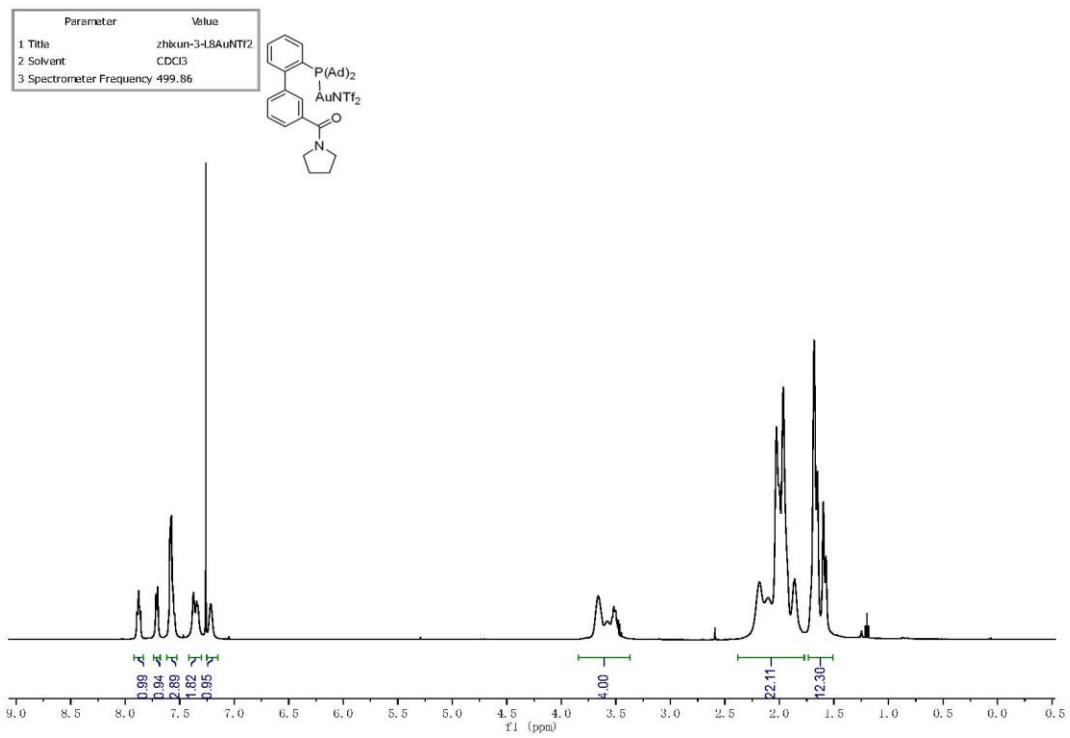
2.24e3



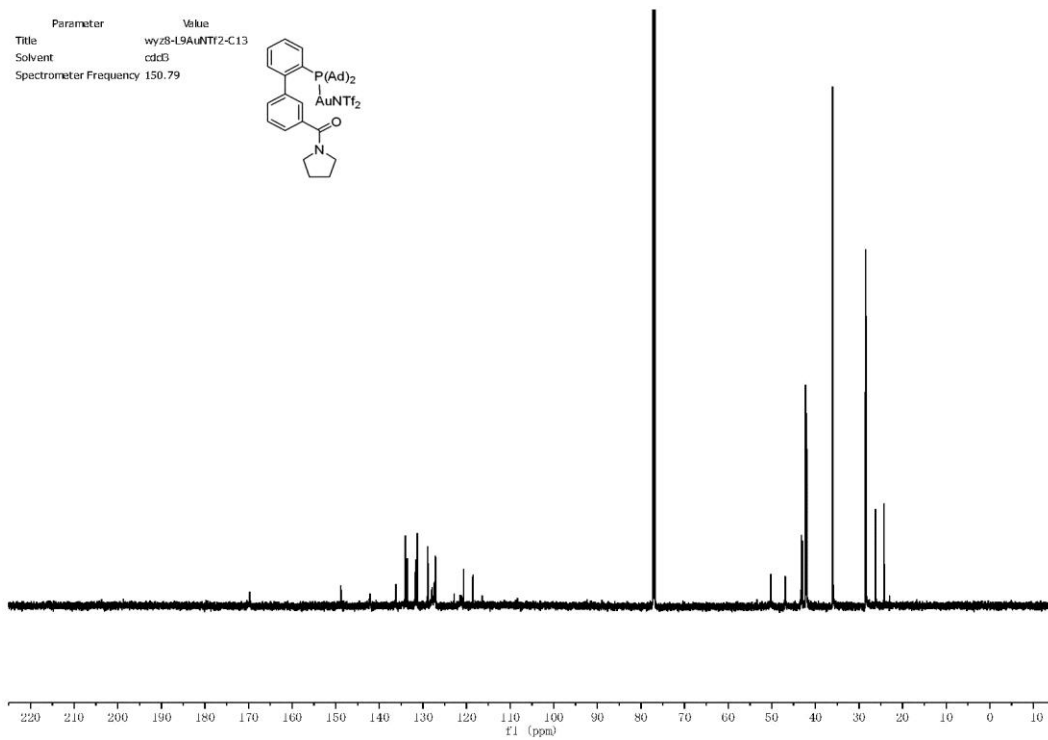
Minimum: -1.5  
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
806.2593	-2.8	-3.5	16.5	280.5	C33 H40 N5 O5 Na Au	
806.2593	-2.8	-3.5	18.5	0.9	C39 H45 N O P Cl Au	
806.2593	-2.8	-3.5	10.5	320.7	C28 H44 N5 O8 P Au	
806.2593	-2.8	-3.5	25.5	8.4	C43 H41 N5 O9 Cl	
806.2536	2.9	3.6	19.5	1.7	C36 H40 N5 O2 Cl Au	
806.2536	2.9	3.6	4.5	453.3	C21 H43 N5 O P Au2	
806.2536	2.9	3.6	11.5	337.2	C25 H39 N9 O9 Au	
806.2595	-3.0	-3.7	1.5	477.1	C19 H43 N5 O3 Na Au2	
806.2595	-3.0	-3.7	10.5	20.6	C29 H44 N5 O7 Cl Au	

## Supplementary Figure 64. HRMS of L8AuCl.



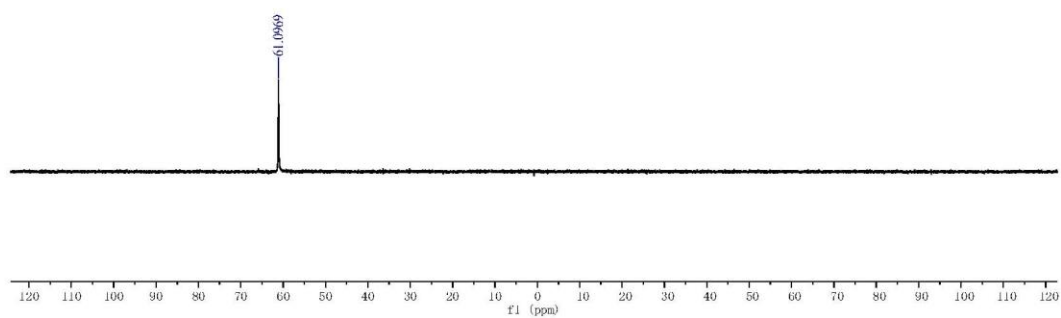
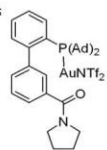
Supplementary Figure 65. <sup>1</sup>H NMR spectrum of L8AuNTf<sub>2</sub>.



Supplementary Figure 66.  $^{13}\text{C}$  NMR spectrum of L8AuNTf<sub>2</sub>.



Parameter Value  
Title wvz8-L8AuNTf2-P31-5  
Solvent cdcl3  
Spectrometer Frequency 161.90



Supplementary Figure 67.  $^{31}\text{P}$  NMR spectrum of L8AuNTf<sub>2</sub>.

(a)

### Elemental Composition Report

Page 1

#### Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

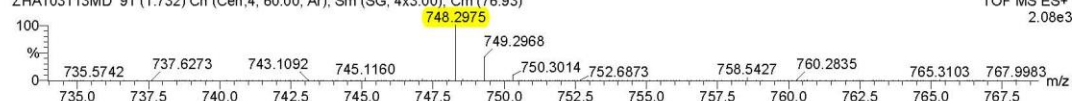
Monoisotopic Mass, Even Electron Ions

4563 formula(e) evaluated with 16 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 P: 0-1 Au: 0-4

Wang/Zhang, wxL8AuNTF2, mw 1028; ESI+  
ZHA103113MD 91 (1.732) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (76.93) UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
2.08e3



Minimum: -1.5  
Maximum: 3.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
748.2975	748.2974	0.1	0.1	4.5	58.6	C21 H46 N9 O6 P Au
	748.2972	0.3	0.4	19.5	3.2	C35 H43 N9 O8 P
	748.2981	-0.6	-0.8	31.5	70.6	C51 H43 N O3 P
	748.2983	-0.8	-1.1	23.5	20.8	C41 H42 N5 O9
	748.2983	-0.8	-1.1	16.5	0.2	C37 H46 N O P Au
	748.2966	0.9	1.2	21.5	2.4	C39 H41 N3 Au
	748.2985	-1.0	-1.3	8.5	20.7	C27 H45 N5 O7 Au
	748.2964	1.1	1.5	36.5	92.3	C53 H38 N3 O2
	748.2961	1.4	1.9	-0.5	73.6	C20 H50 N5 O10 P Au
	748.2954	2.1	2.8	32.5	49.3	C47 H39 N7 O P
	748.2996	-2.1	-2.8	28.5	27.0	C42 H38 N9 O5
	748.2998	-2.3	-3.1	13.5	13.6	C28 H41 N9 O3 Au
	748.2999	-2.4	-3.2	18.5	11.1	C39 H47 N3 O10 P
	748.3000	-2.5	-3.3	-1.5	166.1	C14 H44 N9 O Au2
	748.3001	-2.6	-3.5	3.5	37.0	C25 H50 N3 O8 P Au
	748.3004	-2.9	-3.9	40.5	132.5	C58 H38 N

(b)

### Elemental Composition Report

Page 1

#### Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

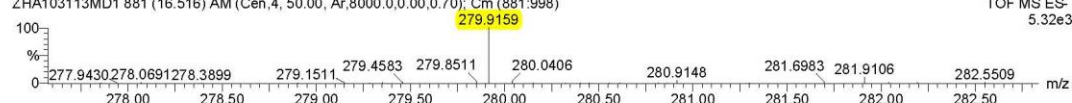
Monoisotopic Mass, Even Electron Ions

4960 formula(e) evaluated with 17 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 S: 0-4 F: 0-10

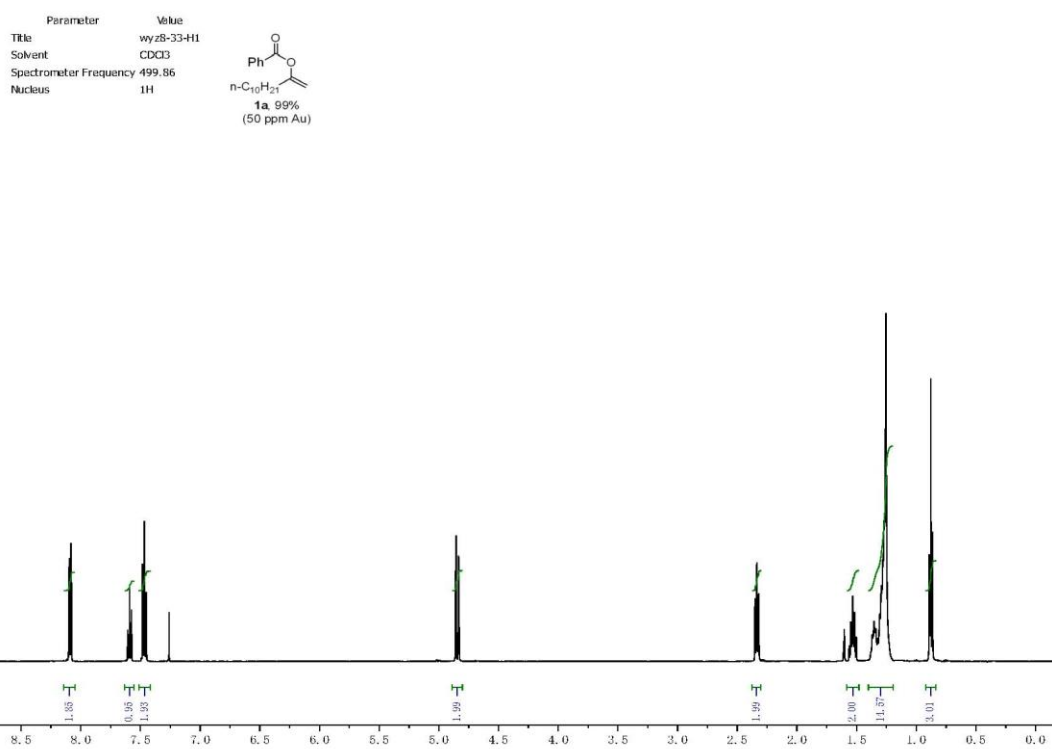
Wang/Zhang, wxL8AuNTF2, mw 1028; ESI-  
ZHA103113MD1 881 (16.516) AM (Cen,4, 50.00, Ar,8000.0,0.00,0.70); Cm (881.998) UCSB CHEM BIOCHEM QTOF2  
TOF MS ES-  
5.32e3



Minimum: -1.5  
Maximum: 3.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
279.9159	279.9159	0.0	0.0	0.5	29.7	C3 H N S3 F7
	279.9161	-0.2	-0.7	11.5	453.6	C11 N S3 F2
	279.9157	0.2	0.7	6.5	137.6	C5 H2 N3 O5 S3
	279.9154	0.5	1.8	2.5	149.0	C3 H4 N3 O2 S4 F2
	279.9166	-0.7	-2.5	-1.5	113.2	H5 N3 O3 S4 F3
	279.9168	-0.9	-3.2	2.5	42.9	C2 H3 N3 O6 S3 F
	279.9146	1.3	4.6	3.5	4.5	C2 N3 O7 S2 F2
	279.9172	-1.3	-4.6	7.5	253.6	C8 H N O S3 F3
	279.9173	-1.4	-5.0	0.5	2.8	C2 N O4 S2 F6
	279.9144	1.5	5.4	-0.5	29.6	H2 N3 O4 S3 F4
	279.9143	1.6	5.7	6.5	268.5	C6 H3 N3 O S4 F
	279.9182	-2.3	-8.2	2.5	1.9	C H2 N3 O10 S2
	279.9184	-2.5	-8.9	3.5	99.5	C5 H2 N O2 S3 F4
	279.9132	2.7	9.6	10.5	441.1	C9 H2 N3 S4
	279.9132	2.7	9.6	3.5	55.4	C3 H N3 O3 S3 F3
	279.9186	-2.7	-9.6	7.5	161.0	C7 N O5 S2 F2
	279.9130	2.9	10.4	-0.5	101.4	C H3 N3 S4 F5

Supplementary Figure 68. HRMS of (a) [L8Au], (b) [NTF<sub>2</sub>].



Supplementary Figure 69. <sup>1</sup>H NMR spectrum of 1a.



Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

2040 formula(e) evaluated with 8 results within limits (all results (up to 1000) for each mass)

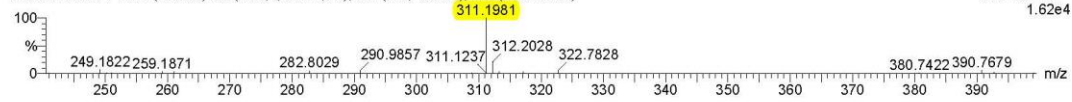
Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 Si: 0-2

Wang/Zhang, wyz1a, mw 288, ESI+

ZHA101413MA 1554 (28.809) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (1402:1564)

UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
1.62e4

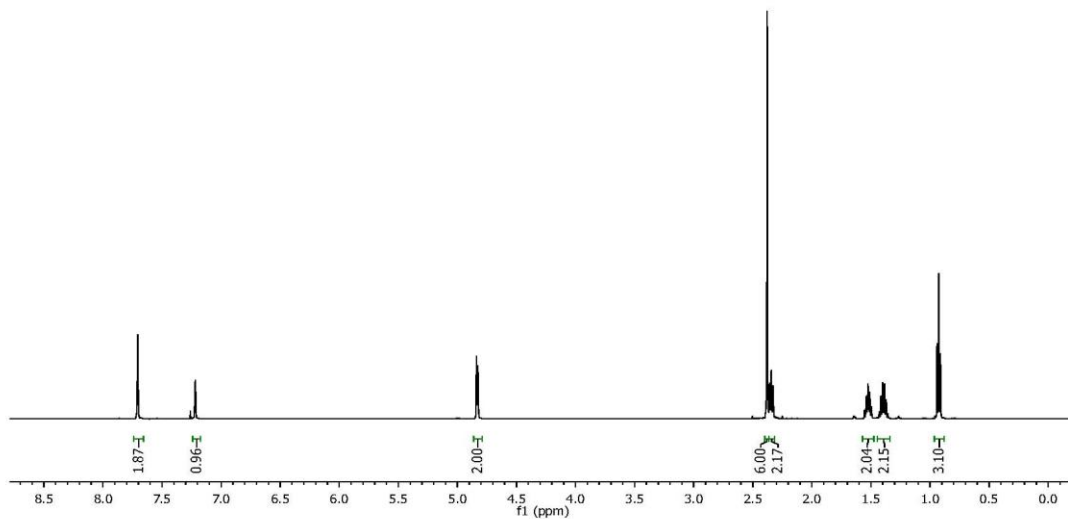
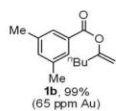


Minimum: -1.5  
Maximum: 3.0 10.0 50.0

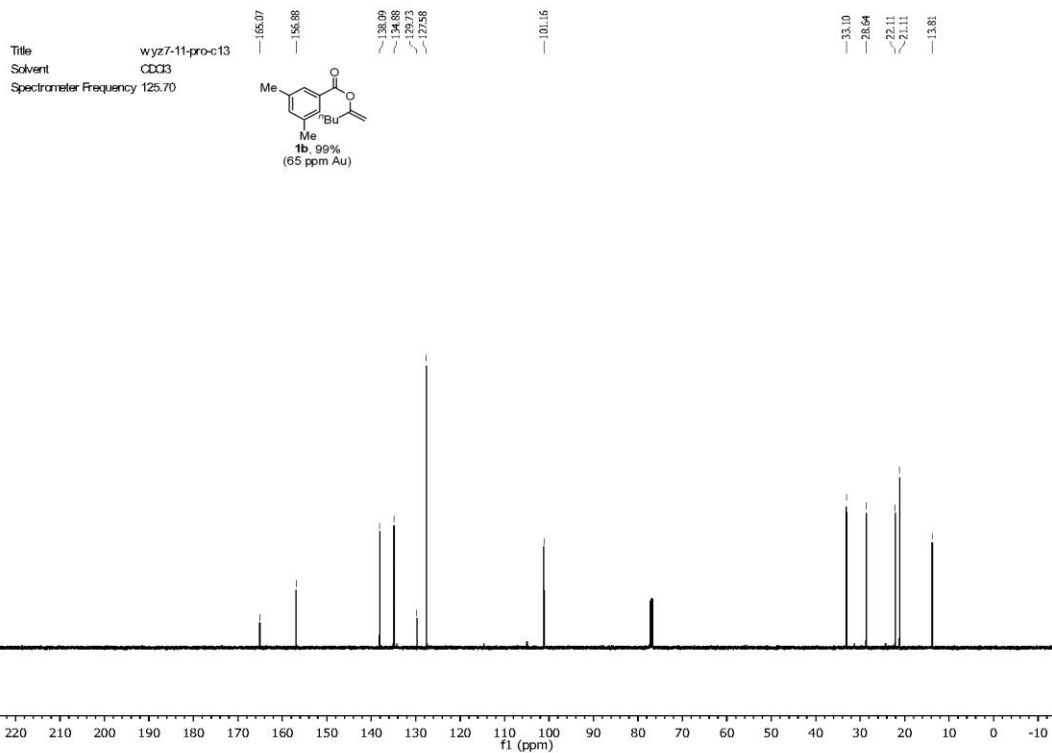
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
311.1981	311.1984	-0.3	-1.0	9.5	18.7	C17 H23 N6
	311.1975	0.6	1.9	0.5	192.5	C8 H27 N8 O3 Si
	311.1987	-0.6	-1.9	5.5	6.2	C19 H28 O2 Na
	311.1975	0.6	1.9	3.5	1138.4	C15 H31 N2 O Si2
	311.1971	1.0	3.2	4.5	15.5	C16 H27 N2 O4
	311.1992	-1.1	-3.5	1.5	150.4	C11 H28 N6 O Na Si
	311.2002	-2.1	-6.7	-0.5	256.5	C12 H31 N2 O5 Si
	311.1960	2.1	6.7	6.5	50.6	C15 H24 N6 Na

Supplementary Figure 71. HRMS of 1a.

Title wyz7-11-pro-h1  
Solvent CDCl3  
Spectrometer Frequency 499.86



Supplementary Figure 72. <sup>1</sup>H NMR spectrum of 1b.



Supplementary Figure 73. <sup>13</sup>C NMR spectrum of **1b**.

## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

558 formula(e) evaluated with 6 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1

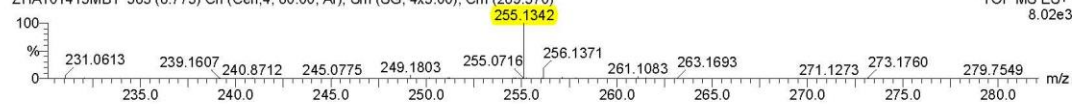
Wang/Zhang, wyz1b, mw 232, ESI+

ZHA101413MB1 365 (6.773) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (269.370)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

8.02e3



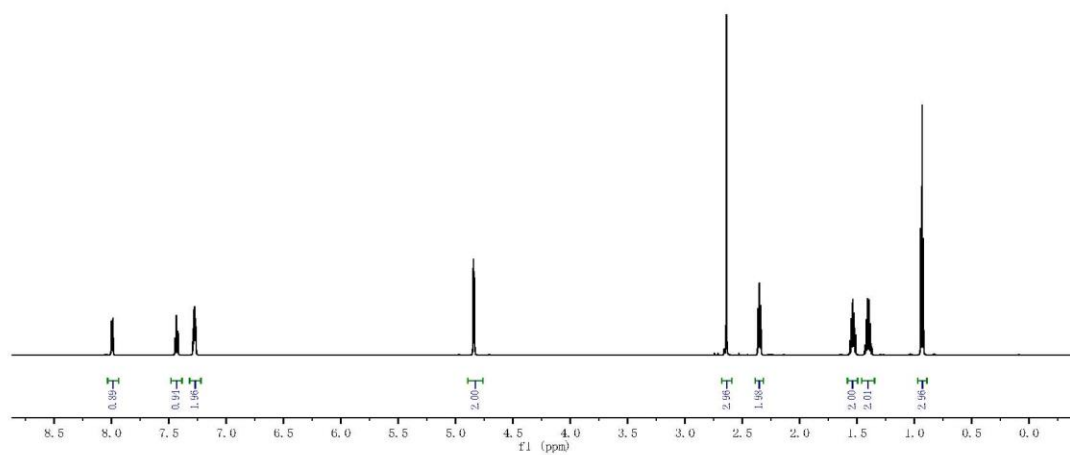
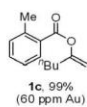
Minimum: -1.5  
 Maximum: 3.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
255.1342	255.1345	-0.3	-1.2	4.5	15.5	C12 H19 N2 O4
	255.1334	0.8	3.1	6.5	24.7	C11 H16 N6 Na
	255.1358	-1.6	-6.3	9.5	4.5	C13 H15 N6
	255.1361	-1.9	-7.4	5.5	2.0	C15 H20 O2 Na
	255.1321	2.1	8.2	1.5	54.1	C10 H20 N2 O4 Na
	255.1318	2.4	9.4	5.5	66.3	C8 H15 N8 O2

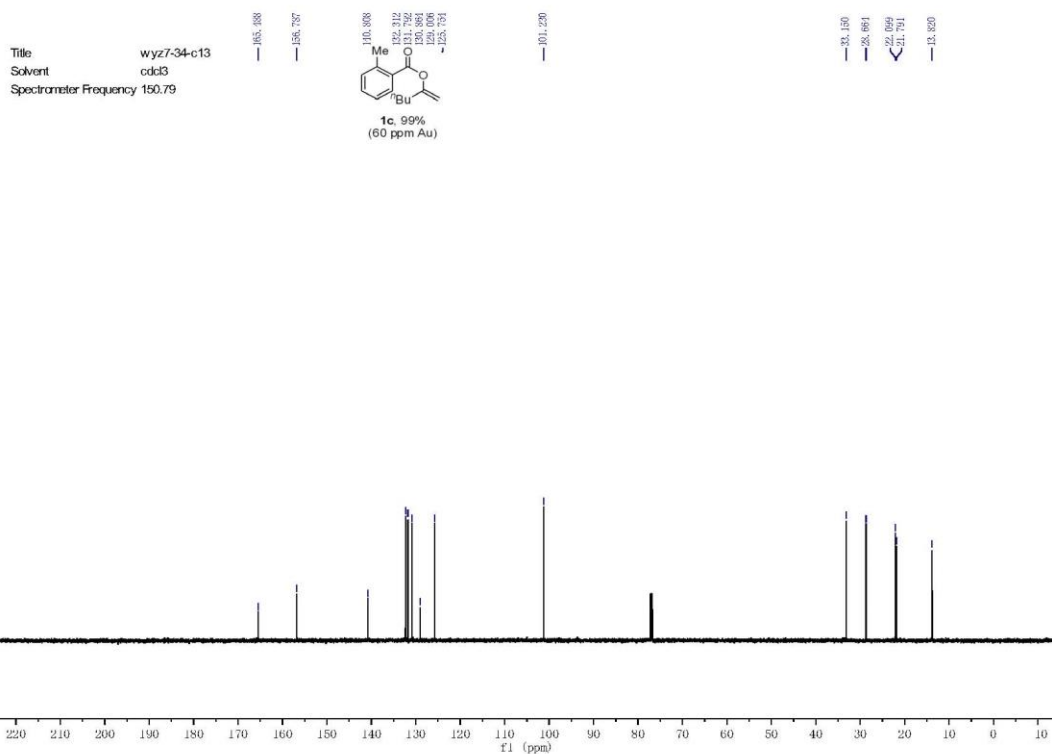
## Supplementary Figure 74. HRMS of 1b.



Title wyz7-34-h1  
Solvent cdcl3  
Spectrometer Frequency 599.64



Supplementary Figure 75. <sup>1</sup>H NMR spectrum of 1c.



Supplementary Figure 76.  $^{13}\text{C}$  NMR spectrum of 1c.

## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

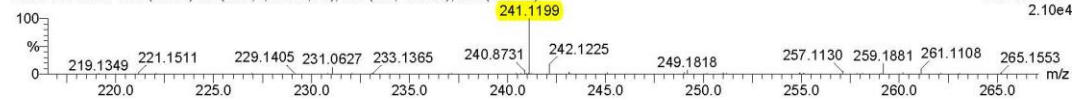
505 formula(e) evaluated with 5 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1

Wang/Zhang, wyz1c, mw 218, ESI+

ZHA101413MC 240 (4.456) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (41:243)

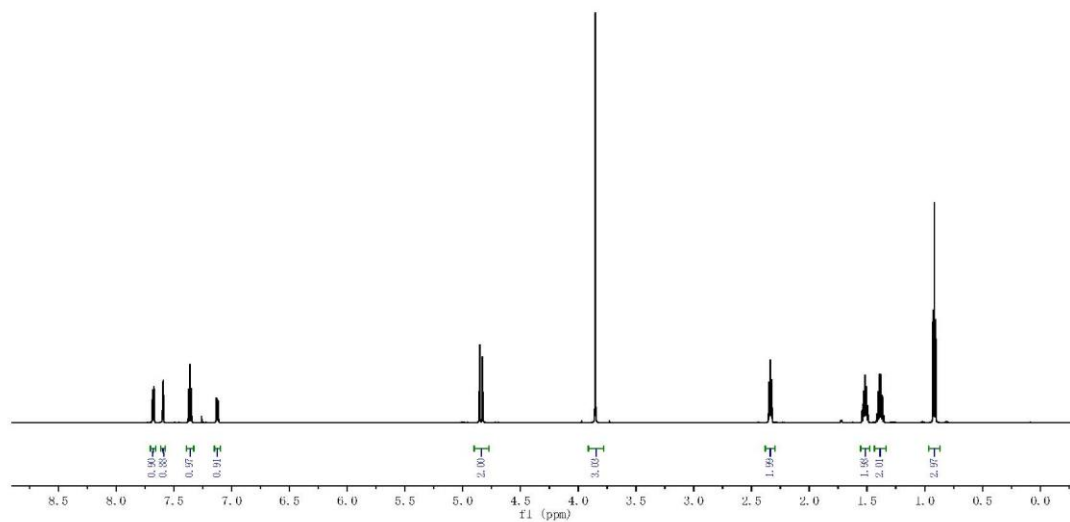
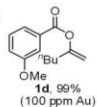
UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
2.10e4

Minimum: -1.5  
Maximum: 50.0

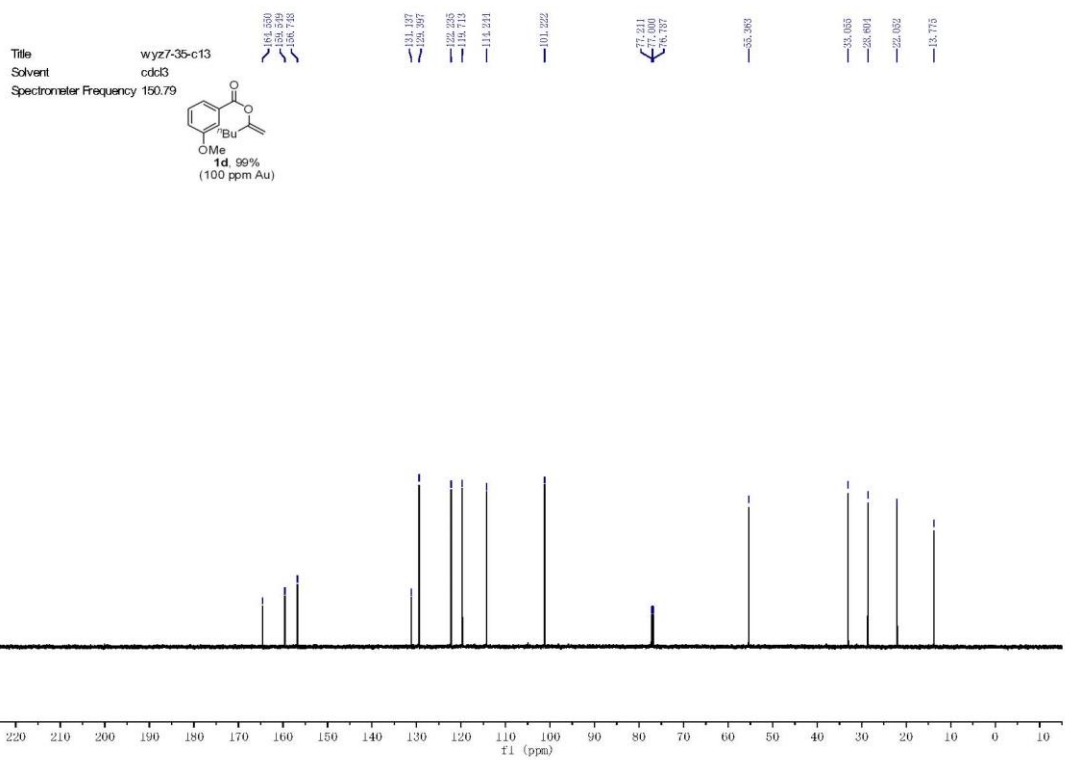
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
241.1199	241.1202	-0.3	-1.2	9.5	130.5	C12 H13 N6
	241.1204	-0.5	-2.1	5.5	82.3	C14 H18 O2 Na
	241.1188	1.1	4.6	4.5	111.0	C11 H17 N2 O4
	241.1178	2.1	8.7	6.5	209.7	C10 H14 N6 Na
	241.1229	-3.0	-12.4	8.5	91.7	C16 H17 O2

Supplementary Figure 77. HRMS of 1c.

Title wyz7-35-h1  
Solvent cdcl3  
Spectrometer Frequency 599.64



Supplementary Figure 78.  $^1\text{H}$  NMR spectrum of **1d**.



Supplementary Figure 79.  $^{13}\text{C}$  NMR spectrum of **1d**.

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

63 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass)

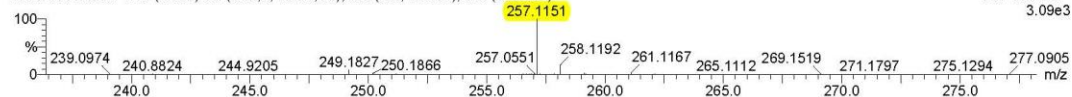
Elements Used:

C: 0-100 H: 0-100 O: 0-10 Na: 0-1

Wang/Zhang, wyz1d, mw 234, ESI+

ZHA101413MD2 210 (3.900) Cn (Cen, 4, 60.00, Ar); Sm (SG, 4x3.00); Cm (183.212)

UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
3.09e3

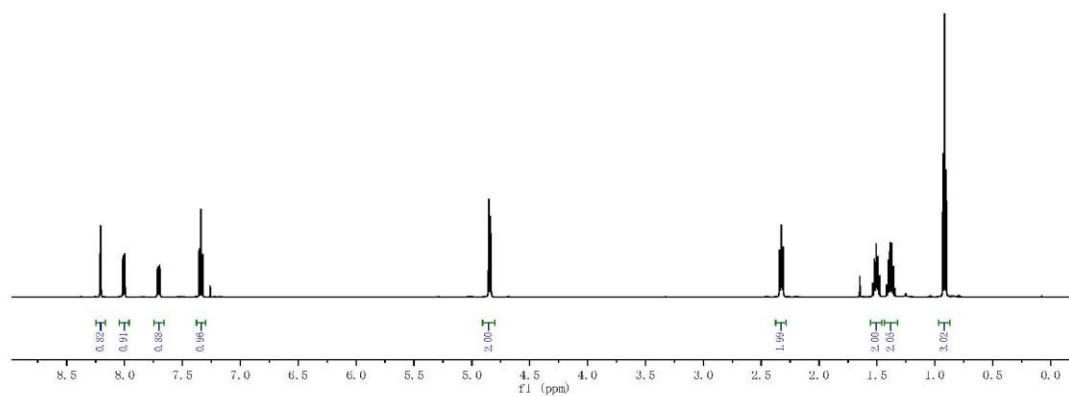
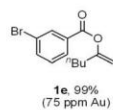


Minimum: -1.5  
Maximum: 3.0 10.0 50.0

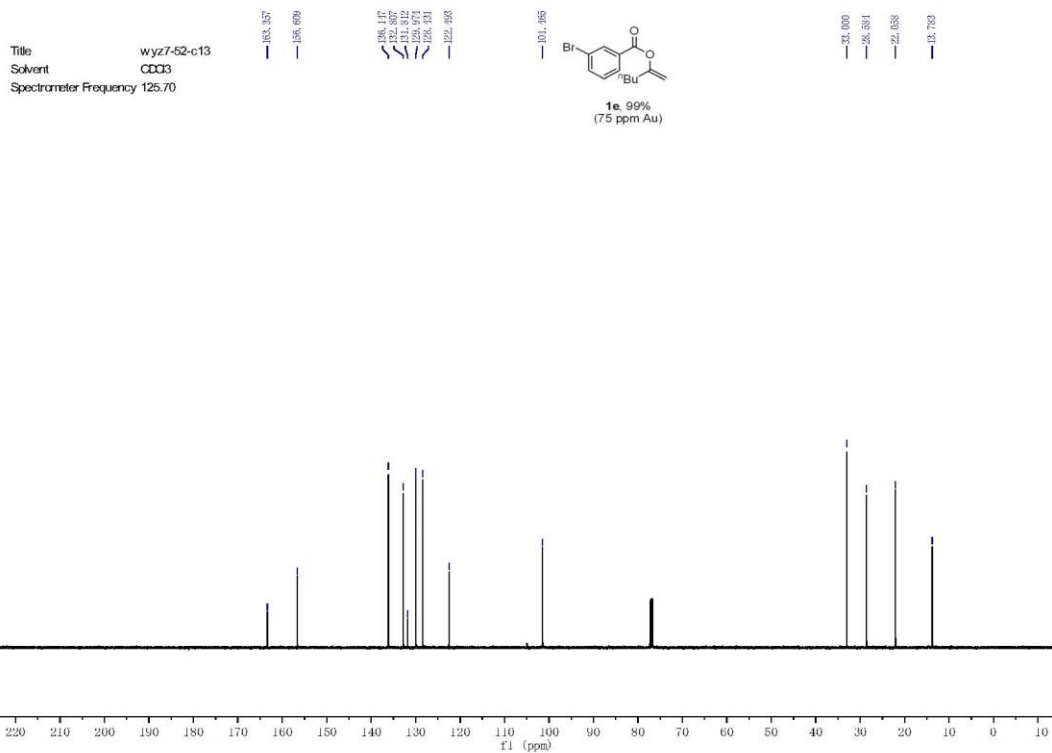
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
257.1151	257.1154	-0.3	-1.2	5.5	1.9	C14 H18 O3 Na
	257.1178	-2.7	-10.5	8.5	2.2	C16 H17 O3

Supplementary Figure 80. HRMS of 1d.

Title            wyz7-52-h1  
Solvent         CDCl3  
Spectrometer Frequency 499.86



Supplementary Figure 81. <sup>1</sup>H NMR spectrum of **1e**.



Supplementary Figure 82.  $^{13}\text{C}$  NMR spectrum of **1e**.



Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

1334 formula(e) evaluated with 12 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 Br: 0-2

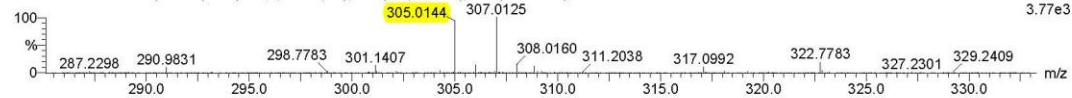
Wang/Zhang, wyz1e, mw 282, ESI+

ZHA101413ME 1038 (19.245) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (873;1051)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

3.77e3

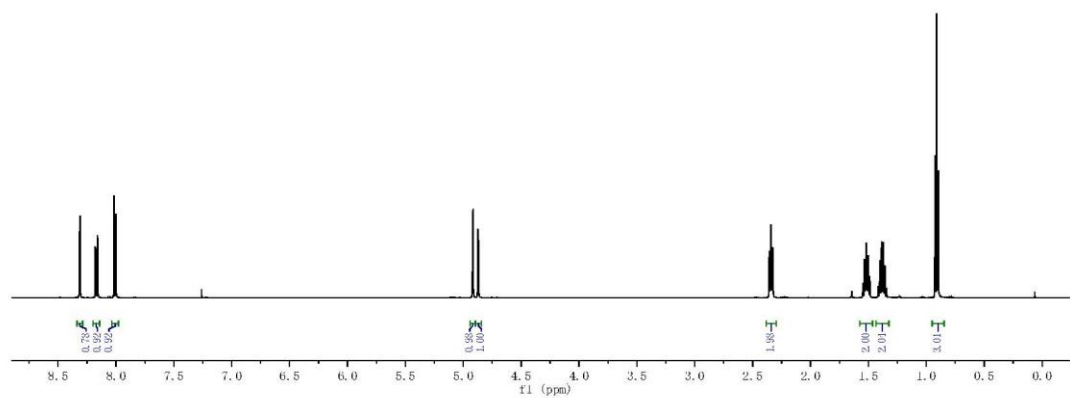
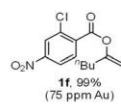


Minimum: -1.5  
Maximum: 50.0

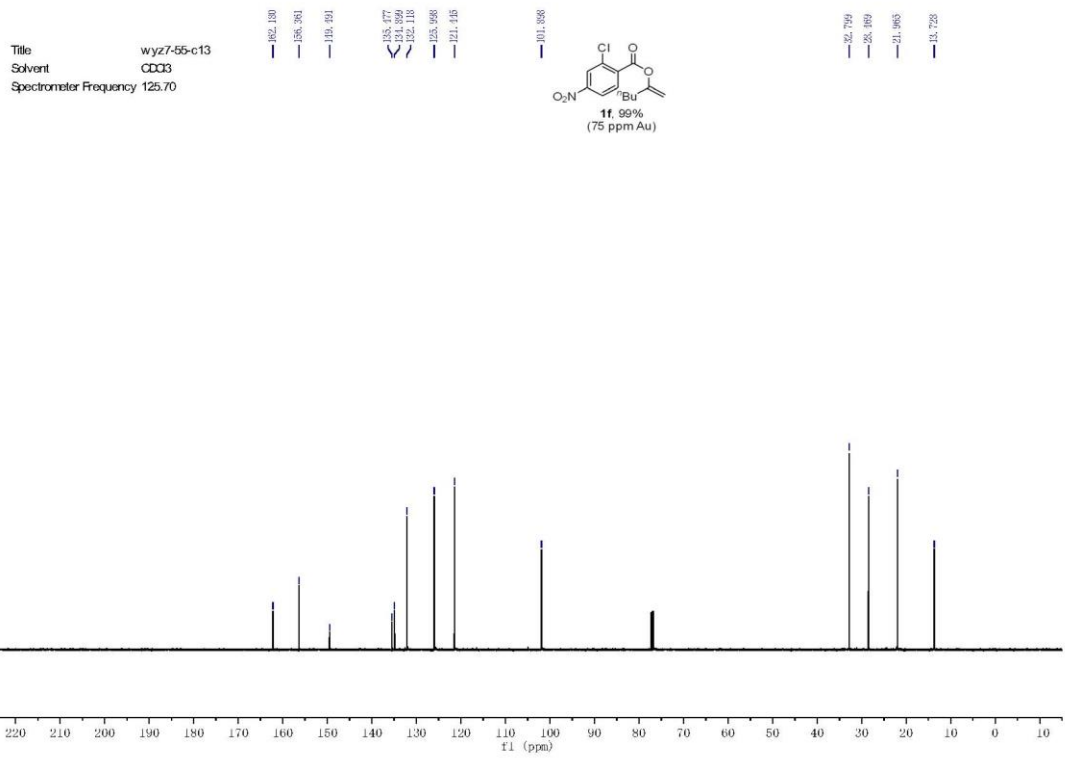
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
305.0144	305.0148	-0.4	-1.3	13.5	1834.2	C10 H2 N8 O3 Na
	305.0140	0.4	1.3	24.5	1877.2	C23 H N2
	305.0150	-0.6	-2.0	9.5	5.8	C11 H10 N6 Br
	305.0137	0.7	2.3	4.5	14.3	C10 H14 N2 O4 Br
	305.0153	-0.9	-3.0	5.5	5.2	C13 H15 O2 Na Br
	305.0134	1.0	3.3	8.5	1826.8	C9 H6 N4 O7 Na
	305.0131	1.3	4.3	12.5	1842.2	C7 H N10 O5
	305.0158	-1.4	-4.6	11.5	1809.7	C11 H5 N4 O7
	305.0126	1.8	5.9	6.5	14.8	C9 H11 N6 Na Br
	305.0118	2.6	8.5	7.5	1847.5	C6 H5 N6 O9
	305.0172	-2.8	-9.2	16.5	1827.8	C12 H N8 O3
	305.0116	2.8	9.2	21.5	1858.3	C21 H2 N2 Na

Supplementary Figure 83. HRMS of 1e.

Title            wyz7-55-h1  
Solvent         CDCl3  
Spectrometer Frequency 499.86



**Supplementary Figure 84. <sup>1</sup>H NMR spectrum of 1f.**



Supplementary Figure 85.  $^{13}\text{C}$  NMR spectrum of **1f**.

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

1803 formula(e) evaluated with 17 results within limits (all results (up to 1000) for each mass)

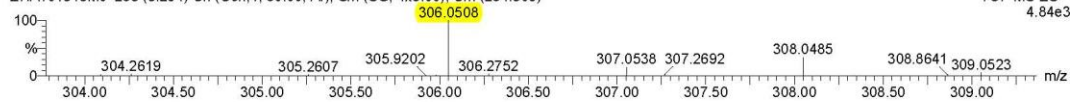
Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 Cl: 0-2

Wang/Zhang, wuz1F, mw 283; ESI+

ZHA101513MJ 285 (5.294) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (284:309)

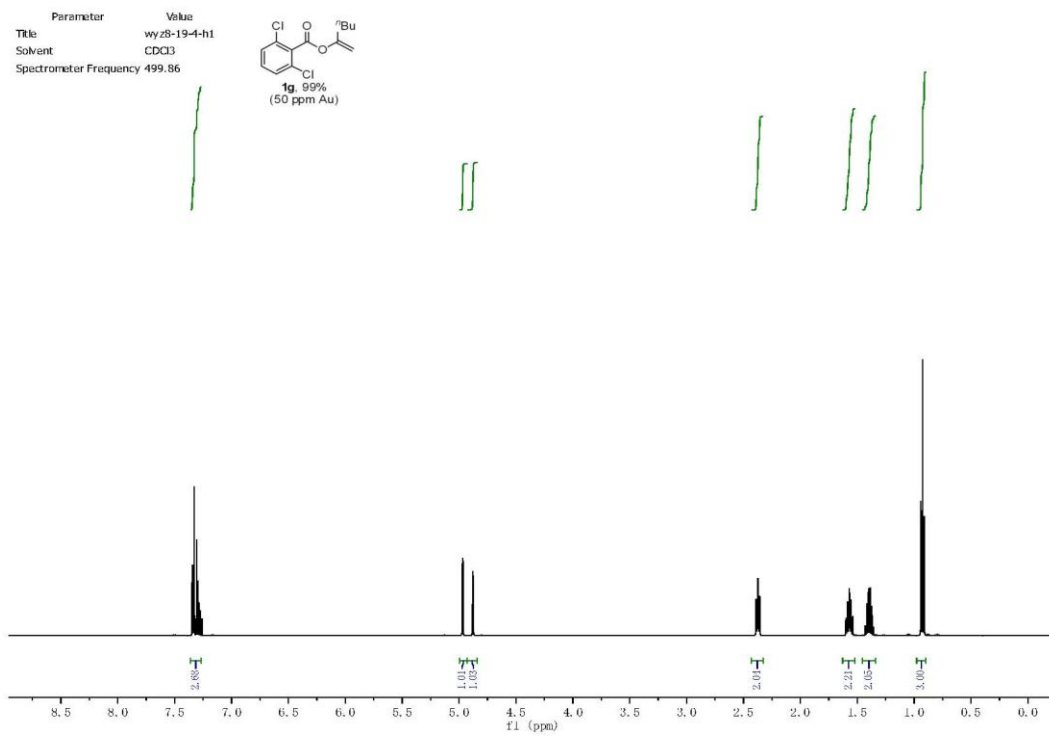
UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
4.84e3



Minimum: -1.5  
Maximum: 3.0 10.0 50.0

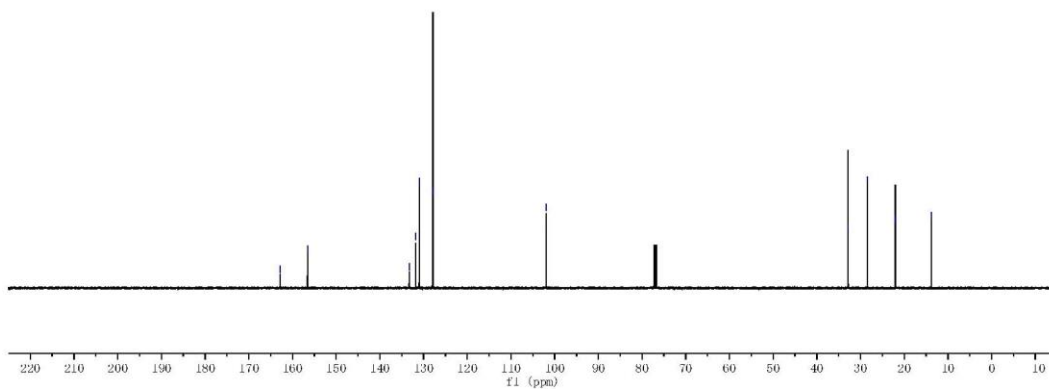
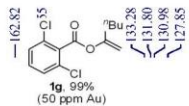
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
306.0508	306.0509	-0.1	-0.3	6.5	0.7	C13 H14 N O4 Na Cl
	306.0506	0.2	0.7	10.5	0.8	C11 H9 N7 O2 Cl
	306.0511	-0.3	-1.0	0.5	422.7	C9 H18 N O6 Cl2
	306.0504	0.4	1.3	16.5	744.9	C15 H5 N7 Na
	306.0501	0.7	2.3	2.5	407.3	C8 H15 N5 O2 Na Cl2
	306.0515	-0.7	-2.3	14.5	710.4	C16 H8 N3 O4
	306.0522	-1.4	-4.6	11.5	4.6	C14 H10 N5 Na Cl
	306.0493	1.5	4.9	5.5	15.0	C10 H13 N3 O6 Cl
	306.0523	-1.5	-4.9	3.5	844.0	C3 H9 N9 O7 Na
	306.0525	-1.7	-5.6	5.5	377.8	C10 H14 N5 O2 Cl2
	306.0491	1.7	5.6	11.5	711.4	C14 H9 N3 O4 Na
	306.0528	-2.0	-6.5	19.5	754.2	C17 H4 N7
	306.0488	2.0	6.5	15.5	729.7	C12 H4 N9 O2
	306.0531	-2.3	-7.5	15.5	739.7	C19 H9 N O2 Na
	306.0484	2.4	7.8	1.5	460.8	C5 H14 N7 O4 Cl2
	306.0533	-2.5	-8.2	9.5	4.8	C15 H13 N O4 Cl
	306.0482	2.6	8.5	7.5	14.0	C9 H10 N7 O2 Na Cl

Supplementary Figure 86. HRMS of 1f.



Supplementary Figure 87. <sup>1</sup>H NMR spectrum of **1g**.

Parameter Value  
Title wy28-19-4-C13  
Solvent CDCl3  
Spectrometer Frequency 125.70



Supplementary Figure 88.  $^{13}\text{C}$  NMR spectrum of **1g**.

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

1685 formula(e) evaluated with 18 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 Cl: 0-2

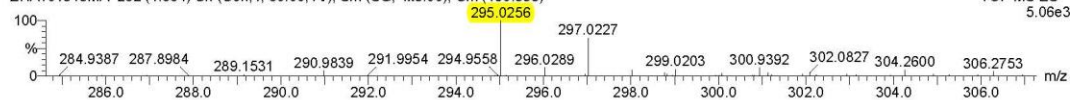
Wang/Zhang, wuz1G, mw 272; ESI+

ZHA101513MA 262 (4.864) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (190:335)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

5.06e3

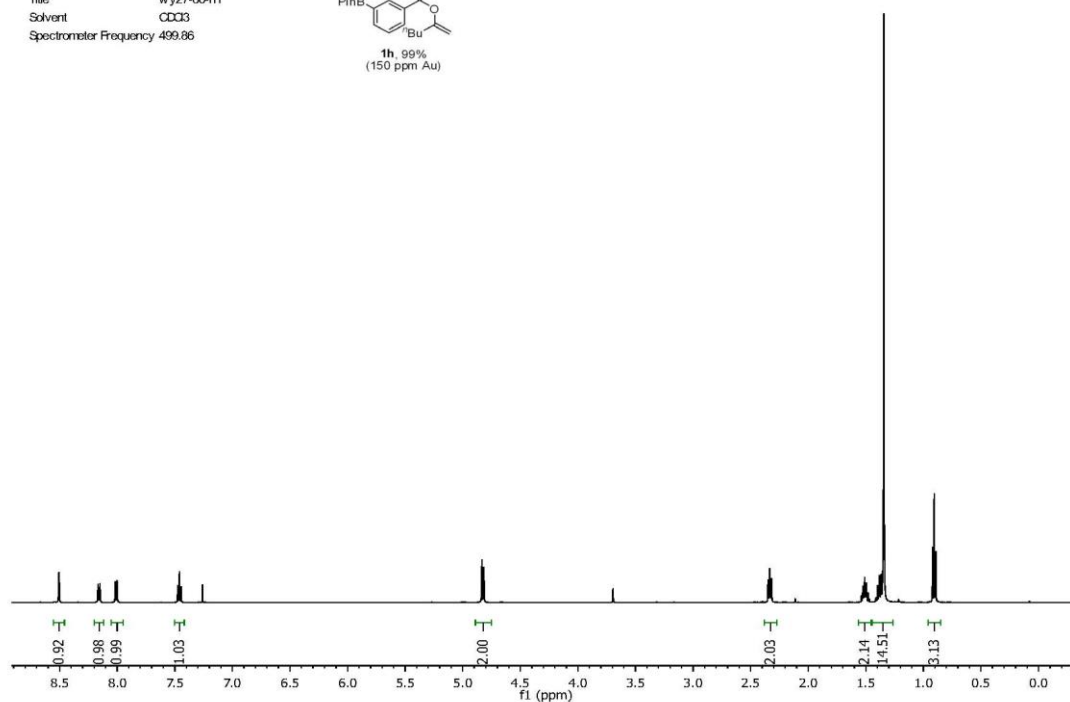
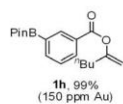


Minimum: -1.5  
Maximum: 3.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
295.0256	295.0256	0.0	0.0	18.5	1675.0	C17 H3 N4 O2
	295.0252	0.4	1.4	4.5	14.0	C10 H13 N2 O4 Cl2
	295.0250	0.6	2.0	10.5	413.0	C14 H9 N2 O2 Na Cl
	295.0250	0.6	2.0	2.5	1781.6	C3 H8 N6 O9 Na
	295.0264	-0.8	-2.7	7.5	1752.6	C4 H4 N10 O5 Na
	295.0247	0.9	3.1	14.5	422.1	C12 H4 N8 Cl
	295.0266	-1.0	-3.4	9.5	3.9	C11 H9 N6 Cl2
	295.0266	-1.0	-3.4	1.5	579.3	H8 N10 O7 Cl
	295.0243	1.3	4.4	13.5	1627.6	C16 H7 O6
	295.0269	-1.3	-4.4	5.5	3.3	C13 H14 O2 Na Cl2
	295.0242	1.4	4.7	6.5	14.3	C9 H10 N6 Na Cl2
	295.0272	-1.6	-5.4	19.5	1718.0	C20 H4 N2 Na
	295.0274	-1.8	-6.1	13.5	439.5	C16 H8 N2 O2 Cl
	295.0275	-1.9	-6.4	5.5	1719.1	C5 H7 N6 O9
	295.0234	2.2	7.5	9.5	393.6	C11 H8 N4 O4 Cl
	295.0232	2.4	8.1	15.5	1665.3	C15 H4 N4 O2 Na
	295.0282	-2.6	-8.8	2.5	499.0	C3 H9 N8 O5 Na Cl
	295.0228	2.8	9.5	1.5	44.2	C8 H14 N2 O4 Na Cl2

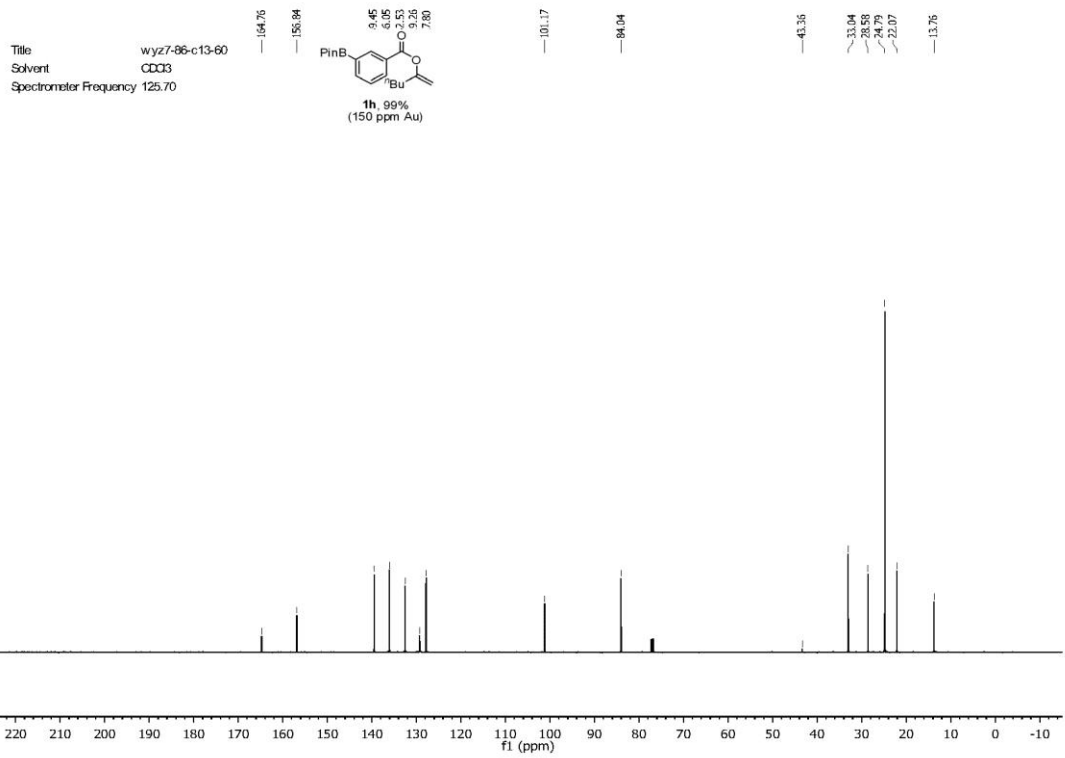
Supplementary Figure 89. HRMS of 1g.

Title wyz7-86-h1  
Solvent CDCl3  
Spectrometer Frequency 499.86



Supplementary Figure 90.  $^1\text{H}$  NMR spectrum of **1h**.





Supplementary Figure 91.  $^{13}\text{C}$  NMR spectrum of **1h**.

## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

1729 formula(e) evaluated with 11 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 10B: 0-1

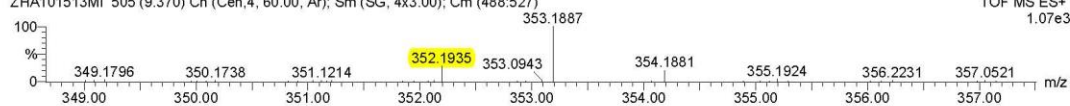
Wang/Zhang, wyz1H, mw 330; ESI+

ZHA101513MI 505 (9.370) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (488:527)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

1.07e3

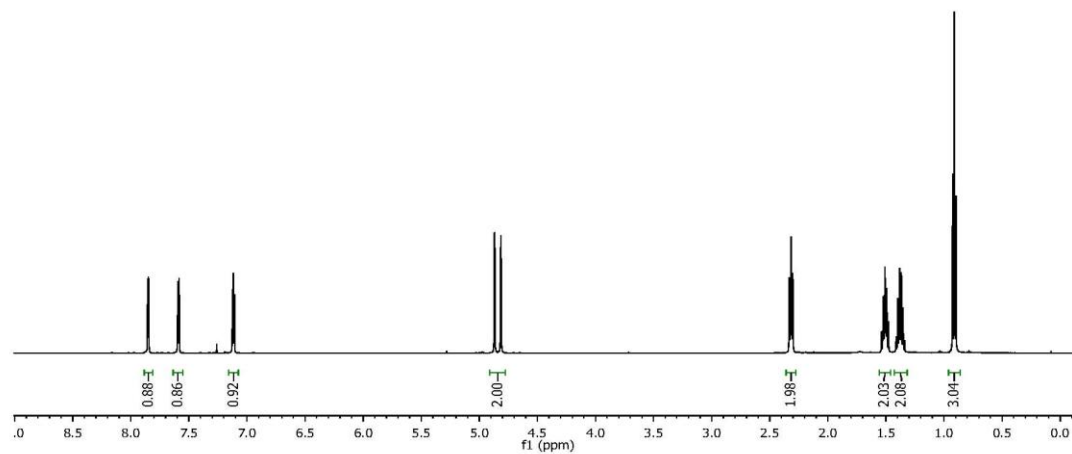
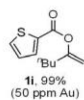


Minimum: -1.5  
Maximum: 3.0 10.0 50.0

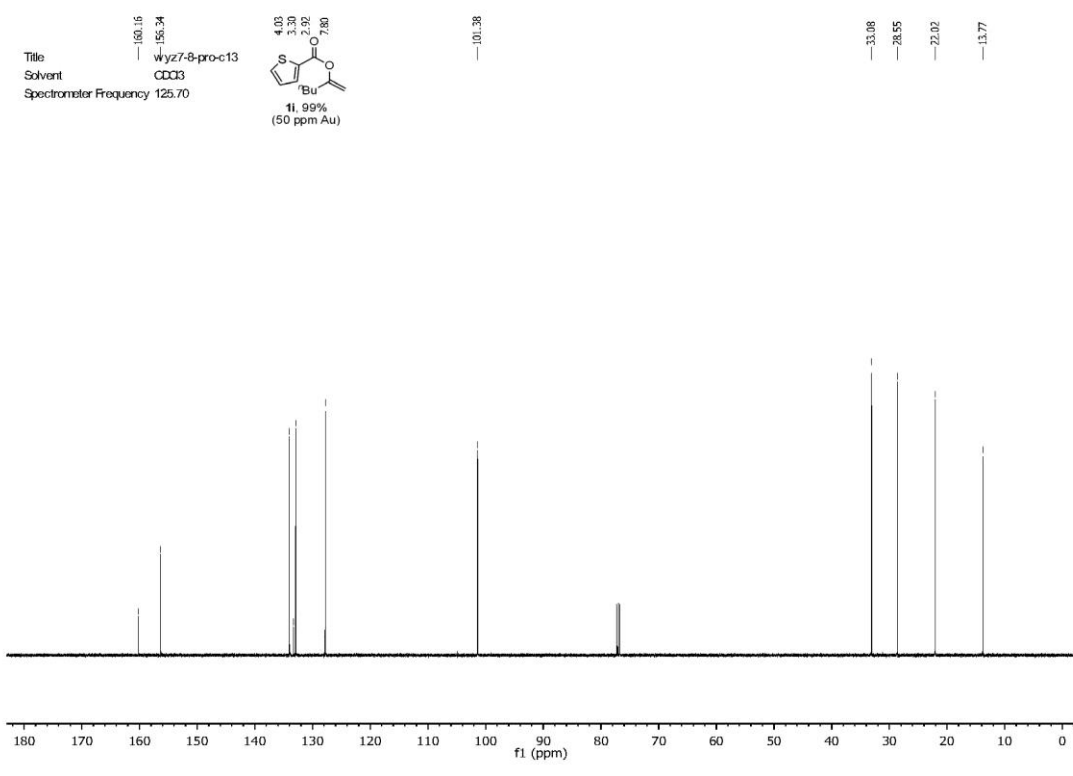
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
352.1935	352.1934	0.1	0.3	10.5	4.1	C17 H22 N6 O2 10B
	352.1936	-0.1	-0.3	6.5	4.4	C19 H27 O4 Na 10B
	352.1945	-1.0	-2.8	2.5	588.4	C11 H26 N7 O6
	352.1947	-1.2	-3.4	-1.5	587.1	C13 H31 N O8 Na
	352.1921	1.4	4.0	-0.5	595.8	C9 H27 N7 O6 Na
	352.1950	-1.5	-4.3	11.5	7.2	C20 H23 N4 Na 10B
	352.1920	1.5	4.3	5.5	3.7	C16 H26 N2 O6 10B
	352.1913	2.2	6.2	10.5	548.8	C22 H26 N O3
	352.1960	-2.5	-7.1	9.5	7.5	C21 H26 O4 10B
	352.1910	2.5	7.1	7.5	3.7	C15 H23 N6 O2 Na 10B
	352.1961	-2.6	-7.4	3.5	581.1	C14 H27 N5 O4 Na

## Supplementary Figure 92. HRMS of 1h.

Title           wyz7-8-pro-h1  
Solvent        CDCl3  
Spectrometer Frequency 499.86



Supplementary Figure 93. <sup>1</sup>H NMR spectrum of 1i.



Supplementary Figure 94.  $^{13}\text{C}$  NMR spectrum of **1i**.

## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

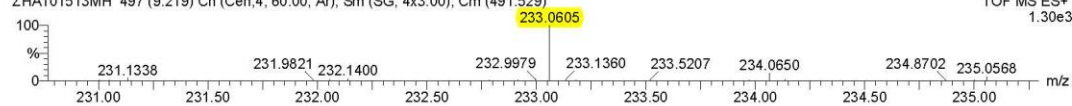
1078 formula(e) evaluated with 15 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 S: 0-2

Wang/Zhang, wyz11, mw 210; ESI+

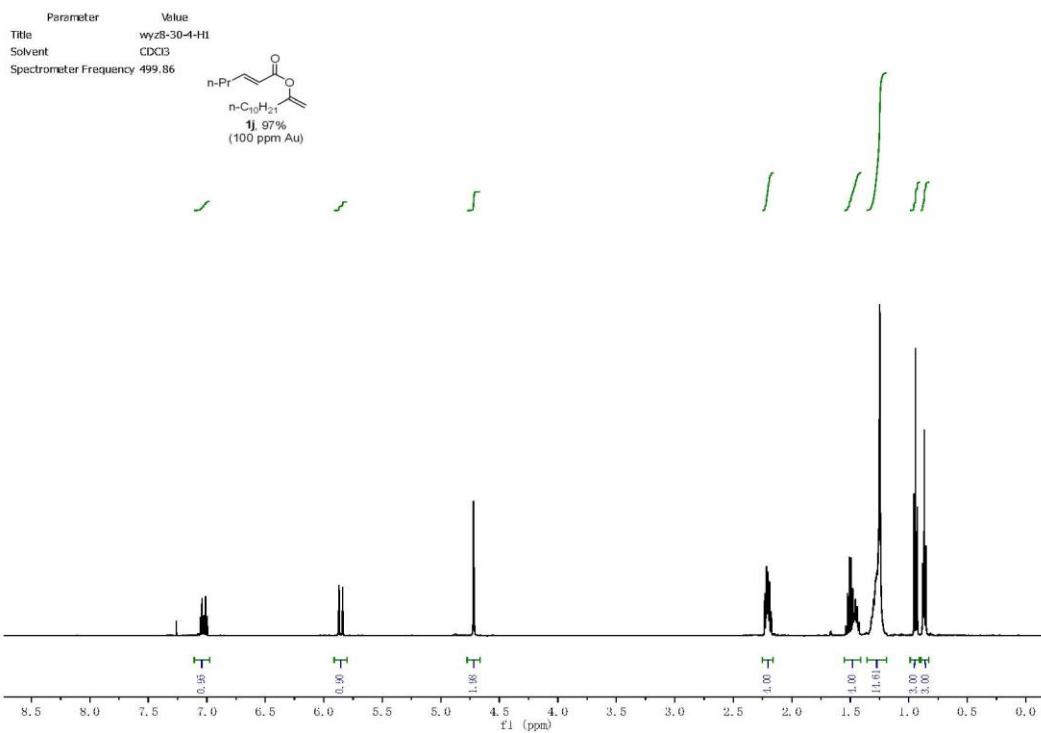
ZHA101513MH 497 (9.219) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (491.529)

UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
1.30e3

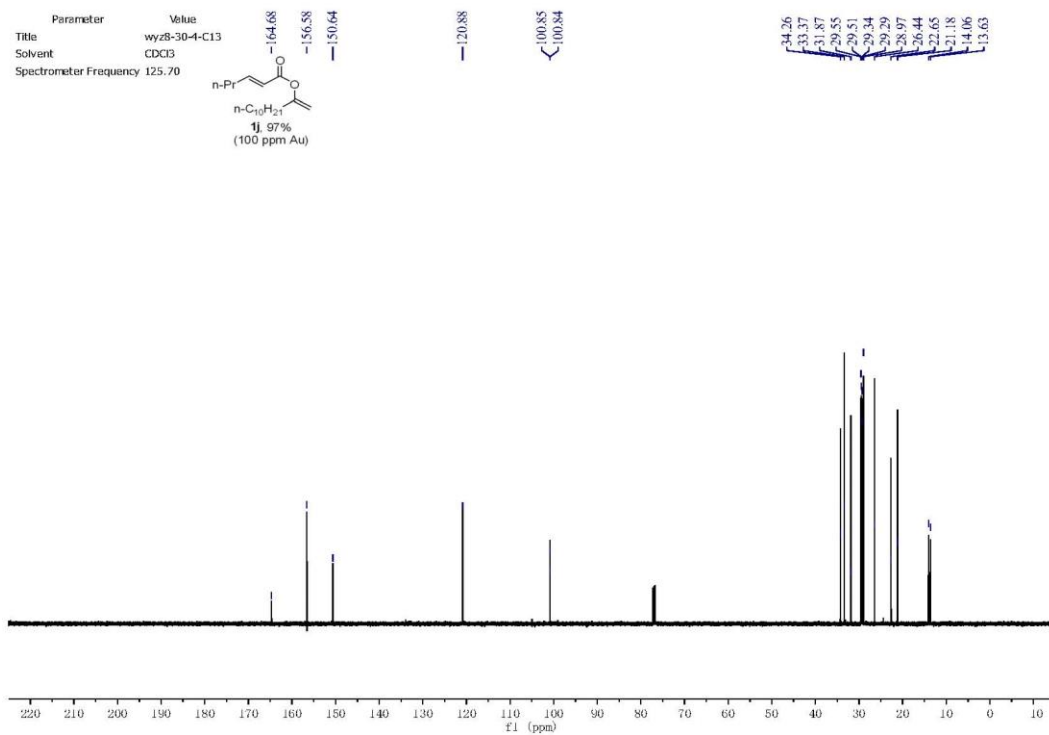
Minimum: -1.5  
Maximum: 3.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
233.0605	233.0603	0.2	0.9	12.5	33.6	C16 H9 O2
	233.0603	0.2	0.9	-0.5	34.8	C H13 N8 O2 S2
	233.0609	-0.4	-1.7	8.5	4.8	C9 H9 N6 S
	233.0610	-0.5	-2.1	1.5	66.0	C3 H10 N6 O5 Na
	233.0612	-0.7	-3.0	4.5	3.2	C11 H14 O2 Na S
	233.0596	0.9	3.9	3.5	7.3	C8 H13 N2 O4 S
	233.0594	1.1	4.7	0.5	85.8	H9 N8 O7
	233.0619	-1.4	-6.0	0.5	17.6	C4 H14 N6 Na S2
	233.0621	-1.6	-6.9	-0.5	59.0	C4 H13 N2 O9
	233.0624	-1.9	-8.2	6.5	58.4	C4 H6 N10 O Na
	233.0585	2.0	8.6	5.5	10.0	C7 H10 N6 Na S
	233.0630	-2.5	-10.7	-1.5	21.6	C5 H17 N2 O4 S2
	233.0578	2.7	11.6	9.5	32.8	C14 H10 O2 Na
	233.0576	2.9	12.4	13.5	37.1	C12 H5 N6
	233.0634	-2.9	-12.4	4.5	50.5	C5 H9 N6 O5

Supplementary Figure 95. HRMS of 1i.



Supplementary Figure 96. <sup>1</sup>H NMR spectrum of **1j**.



Supplementary Figure 97.  $^{13}\text{C}$  NMR spectrum of **1j**.

## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

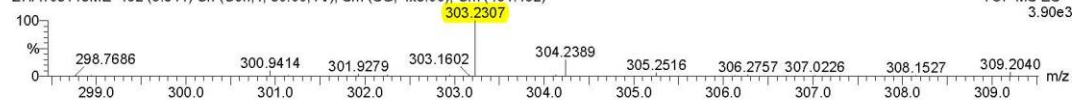
719 formula(e) evaluated with 6 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1

Wang/Zhang, wyz1J, mw 280; ESI+

ZHA103113ME 482 (8.941) Cn (Cen,4, 50.00, Ar); Sm (SG, 4x3.00); Cm (464:482)

UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
3.90e3

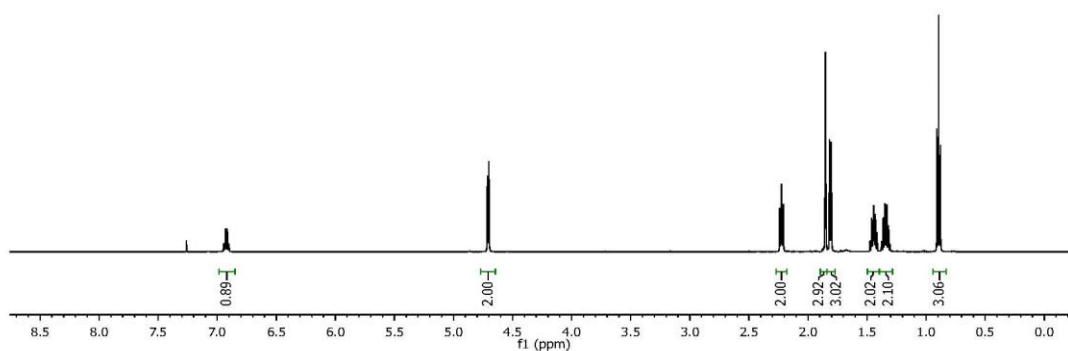
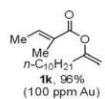
Minimum: -1.5  
Maximum: 3.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
303.2307	303.2311	-0.4	-1.3	6.0	73.3	C18 H29 N3 O
	303.2300	0.7	2.3	2.5	84.3	C18 H32 O2 Na
	303.2297	1.0	3.3	6.5	97.3	C16 H27 N6
	303.2324	-1.7	-5.6	5.5	53.1	C20 H31 O2
	303.2287	2.0	6.6	3.0	110.3	C16 H30 N3 O Na
	303.2284	2.3	7.6	1.5	119.9	C15 H31 N2 O4

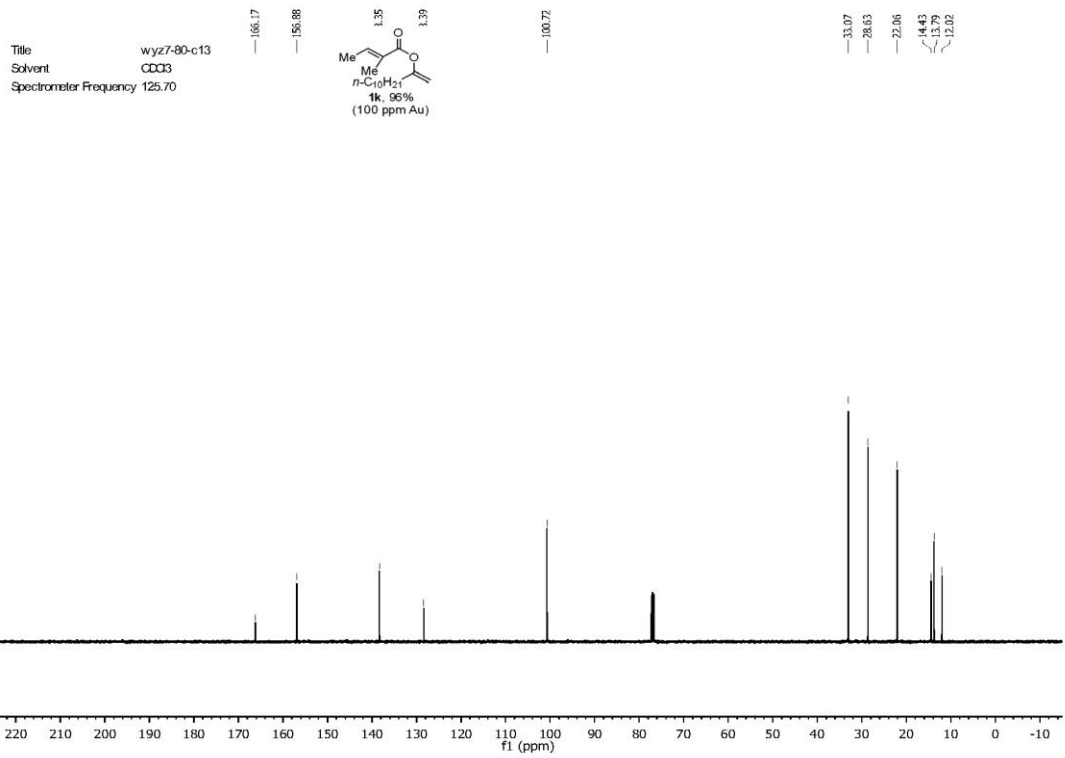
## Supplementary Figure 98. HRMS of 1j.



Title           wyz7-80-h1  
Solvent        CDCl3  
Spectrometer Frequency 499.86



**Supplementary Figure 99.** <sup>1</sup>H NMR spectrum of 1k.



Supplementary Figure 100. <sup>13</sup>C NMR spectrum of 1k.

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

669 formula(e) evaluated with 8 results within limits (all results (up to 1000) for each mass)

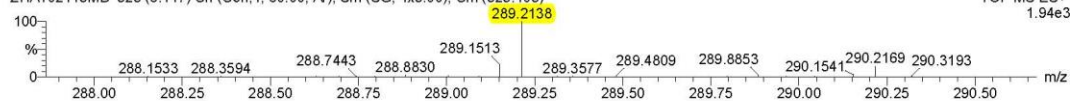
Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1

Wang/Zhang, wzy1K, mw 266; ESI+

ZHA102413MB 325 (6.147) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (325.405)

UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
1.94e3

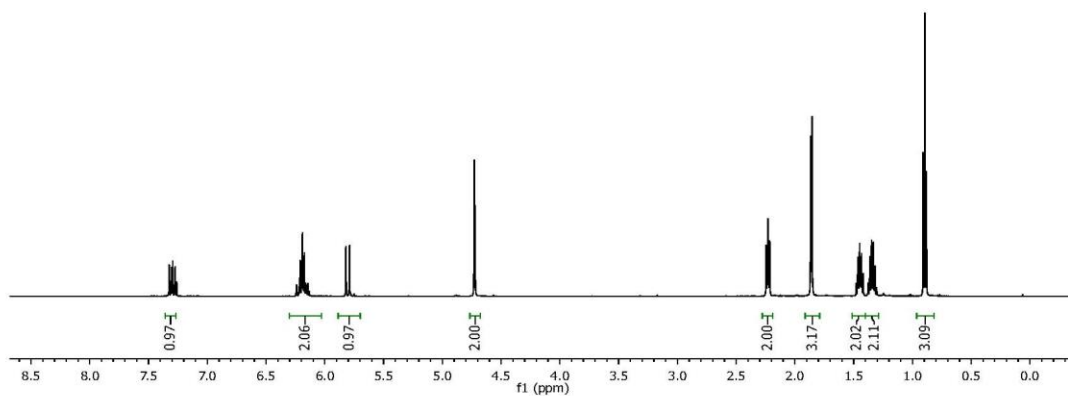
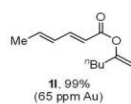


Minimum: -1.5  
Maximum: 3.0 10.0 50.0

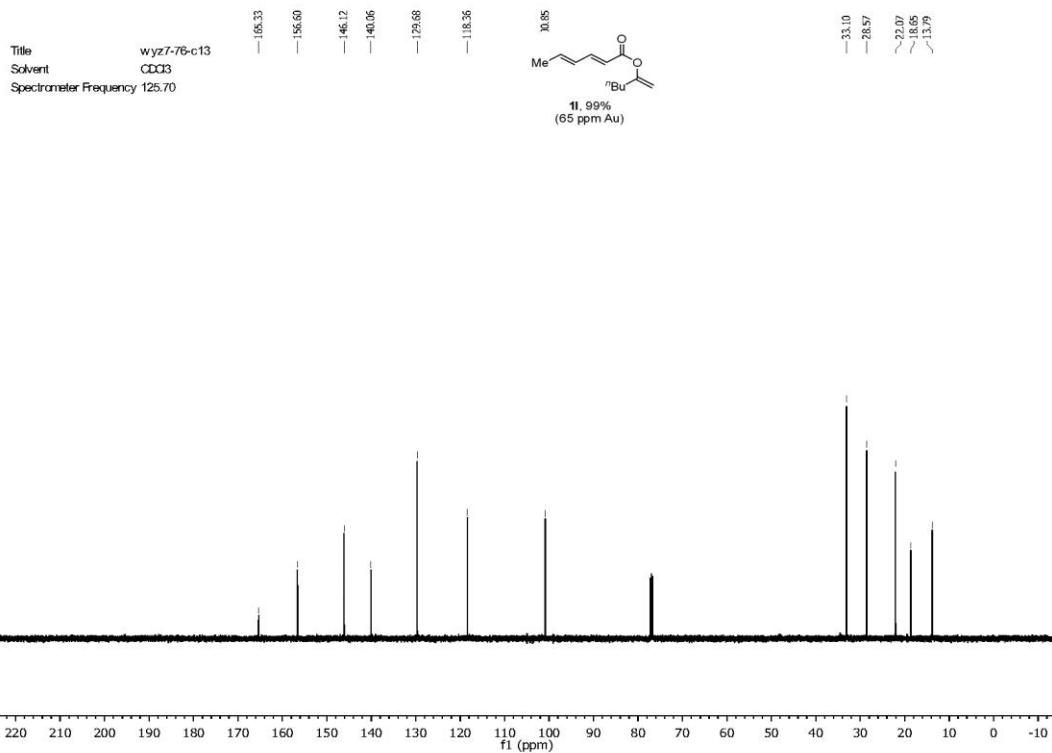
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
289.2138	289.2141	-0.3	-1.0	6.5	2773376.5	C15 H25 N6
	289.2144	-0.6	-2.1	2.5	2773492.5	C17 H30 O2 Na
	289.2130	0.8	2.8	3.0	2773384.0	C15 H28 N3 O Na
	289.2127	1.1	3.8	1.5	2773493.8	C14 H29 N2 O4
	289.2154	-1.6	-5.5	6.0	2773488.3	C17 H27 N3 O
	289.2117	2.1	7.3	3.5	2773271.3	C13 H26 N6 Na
	289.2114	2.4	8.3	2.0	2773394.3	C12 H27 N5 O3
	289.2168	-3.0	-10.4	5.5	2773589.0	C19 H29 O2

Supplementary Figure 101. HRMS of 1k.

Title            wyz7-76-h1  
Solvent         CDCl3  
Spectrometer Frequency 499.86



Supplementary Figure 102. <sup>1</sup>H NMR spectrum of 11.



Supplementary Figure 103. <sup>13</sup>C NMR spectrum of **11**.

## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

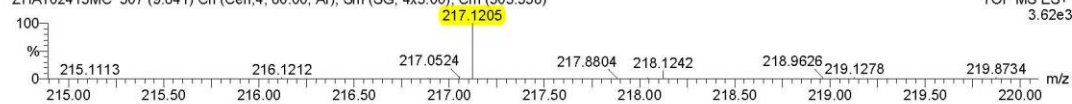
412 formula(e) evaluated with 7 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1

Wang/Zhang, wyz1L, mw 194; ESI+

ZHA102413MC 507 (9.641) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (505:556)

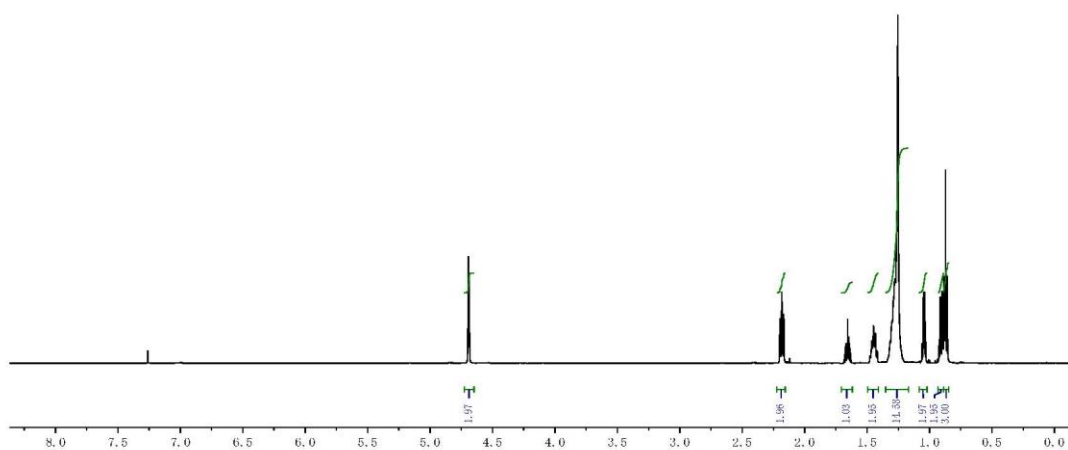
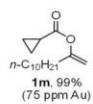
UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
3.62e3

Minimum: -1.5  
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
217.1205	217.1204	0.1	0.5	3.5	12.8	C12 H18 O2 Na
	217.1202	0.3	1.4	7.5	22.0	C10 H13 N6
	217.1215	-1.0	-4.6	7.0	15.3	C12 H15 N3 O
	217.1191	1.4	6.4	4.0	22.5	C10 H16 N3 O Na
	217.1188	1.7	7.8	2.5	19.7	C9 H17 N2 O4
	217.1229	-2.4	-11.1	6.5	14.3	C14 H17 O2
	217.1178	2.7	12.4	4.5	38.0	C8 H14 N6 Na

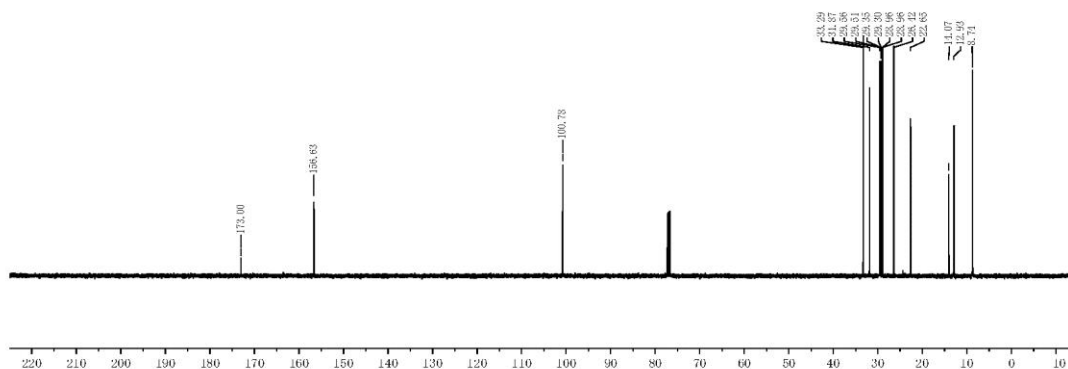
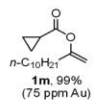
## Supplementary Figure 104. HRMS of 11.

Parameter Value  
Title wy28-32-3-h1  
Solvent CDCl3  
Spectrometer Frequency 499.86  
Nucleus 1H



Supplementary Figure 105. <sup>1</sup>H NMR spectrum of **1m**.

Parameter Value  
Title wy28-32-3-c13  
Solvent CDCl3  
Spectrometer Frequency 125.70  
Nucleus 13C



Supplementary Figure 106.  $^{13}\text{C}$  NMR spectrum of 1m.



## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

624 formula(e) evaluated with 9 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1

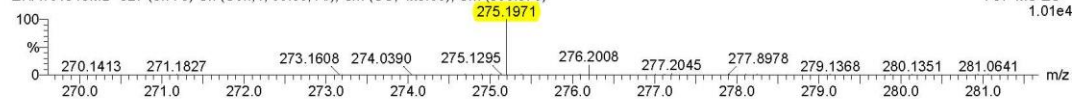
Wang/Zhang, wyz1M, mw 252; ESI+

ZHA101513MD 527 (9.775) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (508:578)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

1.01e4

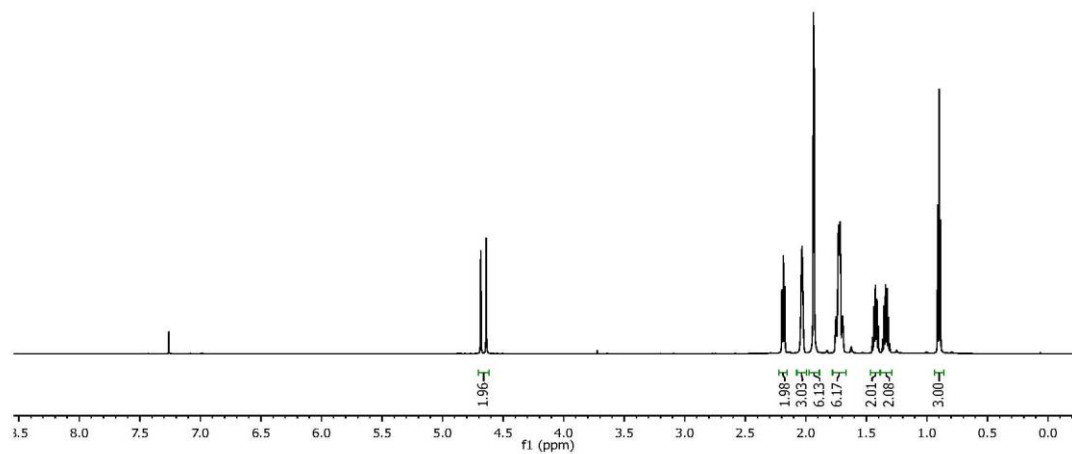
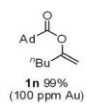


Minimum: -1.5  
 Maximum: 3.0 10.0 50.0

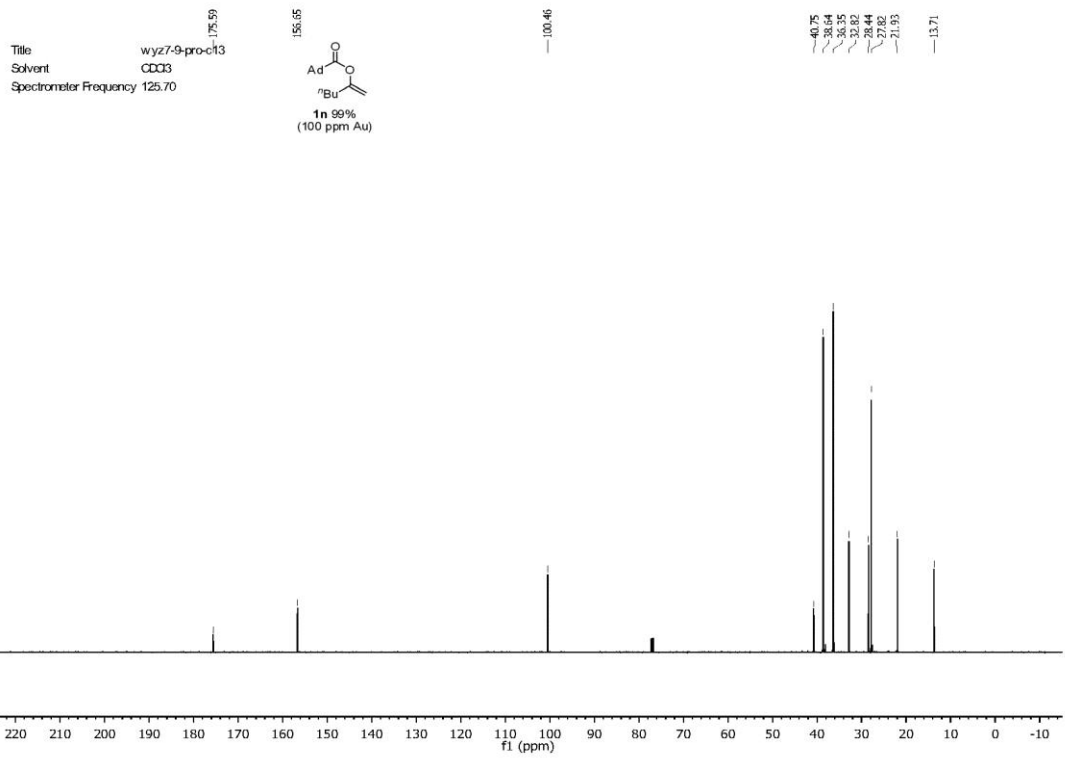
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
275.1971	275.1971	0.0	0.0	1.5	21.5	C13 H27 N2 O4
	275.1974	-0.3	-1.1	3.0	25.1	C14 H26 N3 O Na
	275.1960	1.1	4.0	3.5	53.1	C12 H24 N6 Na
	275.1984	-1.3	-4.7	6.5	25.4	C14 H23 N6
	275.1957	1.4	5.1	2.0	52.0	C11 H25 N5 O3
	275.1987	-1.6	-5.8	2.5	11.2	C16 H28 O2 Na
	275.1947	2.4	8.7	-1.5	71.8	C11 H28 N2 O4 Na
	275.1998	-2.7	-9.8	6.0	17.9	C16 H25 N3 O
	275.1944	2.7	9.8	2.5	96.6	C9 H23 N8 O2

## Supplementary Figure 107. HRMS of 1m.

Title           wyz7-9-pro-h1  
Solvent        cdcl3  
Spectrometer Frequency 599.63



Supplementary Figure 108. <sup>1</sup>H NMR spectrum of 1n.



Supplementary Figure 109.  $^{13}\text{C}$  NMR spectrum of 1n.

## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

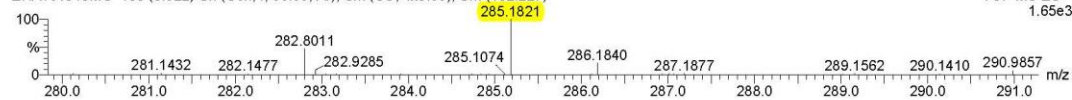
655 formula(e) evaluated with 7 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1

Wang/Zhang, wyz1N, mw 262; ESI+

ZHA101513MG 195 (3.622) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (192:227)

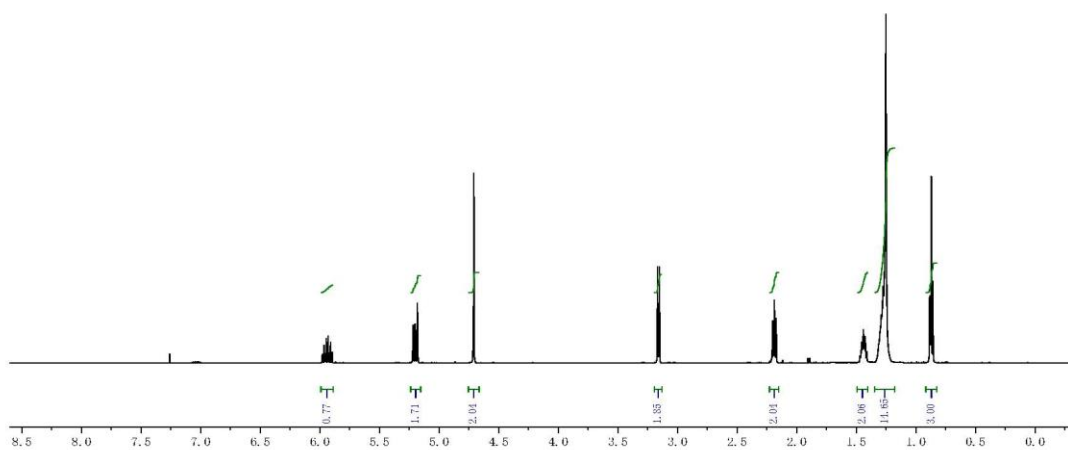
UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
1.65e3

Minimum: -1.5  
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
285.1821	285.1817	0.4	1.4	5.0	2.7	C15 H24 N3 O Na
	285.1814	0.7	2.5	3.5	5.0	C14 H25 N2 O4
	285.1828	-0.7	-2.5	8.5	1.4	C15 H21 N6
	285.1831	-1.0	-3.5	4.5	0.6	C17 H26 O2 Na
	285.1804	1.7	6.0	5.5	7.2	C13 H22 N6 Na
	285.1841	-2.0	-7.0	8.0	0.4	C17 H23 N3 O
	285.1801	2.0	7.0	4.0	9.6	C12 H23 N5 O3

## Supplementary Figure 110. HRMS of 1n.

Parameter Value  
Title wy28-14-4-h1  
Solvent CDCl3  
Spectrometer Frequency 499.86  
Nucleus 1H



Supplementary Figure 111. <sup>1</sup>H NMR spectrum of 10.



## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

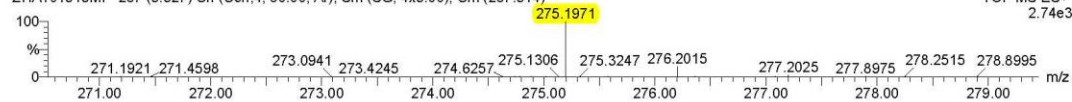
624 formula(e) evaluated with 9 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1

Wang/Zhang, wyz10, mw 252; ESI+

ZHA101513MF 287 (5.327) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (287:314)

UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
2.74e3

Minimum: -1.5  
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
275.1971	275.1971	0.0	0.0	1.5	9.9	C13 H27 N2 O4
	275.1974	-0.3	-1.1	3.0	11.4	C14 H26 N3 O Na
	275.1960	1.1	4.0	3.5	20.3	C12 H24 N6 Na
	275.1984	-1.3	-4.7	6.5	11.2	C14 H23 N6
	275.1957	1.4	5.1	2.0	19.6	C11 H25 N5 O3
	275.1987	-1.6	-5.8	2.5	6.2	C16 H28 O2 Na
	275.1947	2.4	8.7	-1.5	25.2	C11 H28 N2 O4 Na
	275.1998	-2.7	-9.8	6.0	7.7	C16 H25 N3 O
	275.1944	2.7	9.8	2.5	32.9	C9 H23 N8 O2

## Supplementary Figure 113. HRMS of 1o.



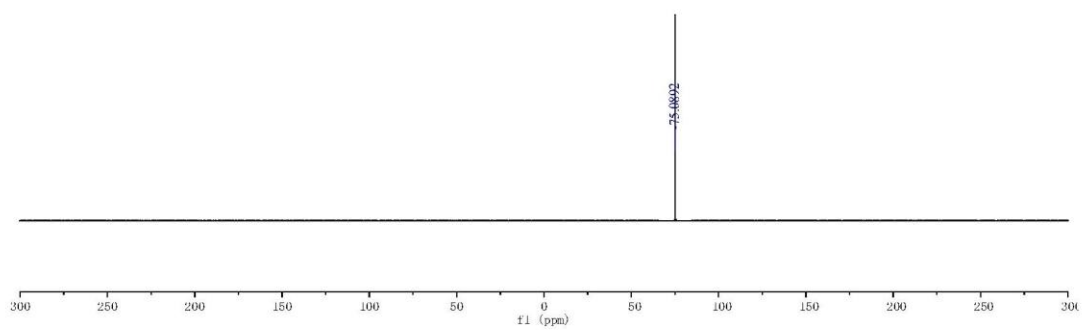




Parameter	Value
Title	wyz8-28-3-F19
Solvent	cdcl3
Spectrometer Frequency	376.33



**1p**, 99%  
(10 ppm Au)



**Supplementary Figure 116. <sup>19</sup>F NMR of 1p.**

## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 200.0

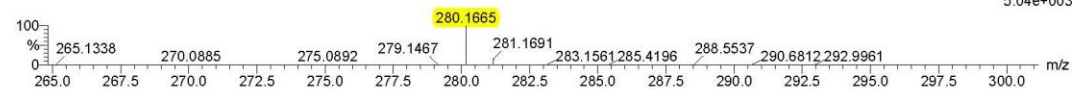
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions

1458 formula(e) evaluated with 17 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-200 N: 0-10 O: 0-10 F: 0-5

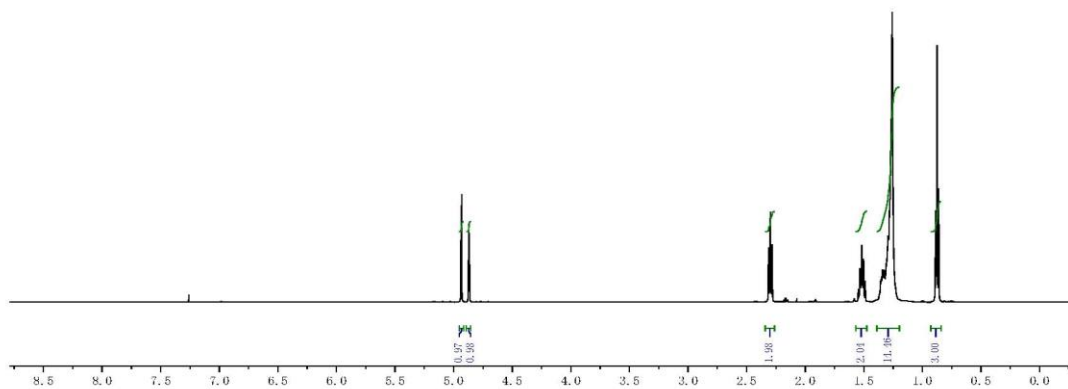
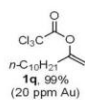
Wang/Zhang, wyz pr 5 1p CF3, mw 280, FI+  
ZHA060613PA 435 (7.250) Cn (Cen,3, 80.00, Ar); Sm (SG, 4x3.00); Cm (435:483)UCSB Chem\_Biochem GCT Premier  
TOF MS FI+  
5.04e+003

Minimum: -1.5  
Maximum: 200.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
280.1665	280.1661	0.4	1.4	5.5	406.1	C14 H22 N3 O3
	280.1659	0.6	2.1	2.0	197.7	C9 H21 N6 O3 F
	280.1657	0.8	2.9	-1.5	138.9	C4 H20 N9 O3 F2
	280.1673	-0.8	-2.9	1.5	307.0	C11 H23 N3 O4 F
	280.1675	-1.0	-3.6	5.0	557.9	C16 H24 O4
	280.1650	1.5	5.4	2.0	270.6	C14 H23 O2 F3
	280.1648	1.7	6.1	6.0	270.1	C12 H20 N6 O2
	280.1648	1.7	6.1	-1.5	114.6	C9 H22 N3 O2 F4
	280.1684	-1.9	-6.8	3.0	41.5	C7 H18 N10 F2
	280.1646	1.9	6.8	2.5	115.7	C7 H19 N9 O2 F
	280.1686	-2.1	-7.5	1.0	437.0	C13 H25 O5 F
	280.1686	-2.1	-7.5	-1.0	41.2	C9 H21 N4 F5
	280.1686	-2.1	-7.5	6.5	163.6	C12 H19 N7 F
	280.1688	-2.3	-8.2	10.0	441.5	C17 H20 N4
	280.1688	-2.3	-8.2	2.5	164.7	C14 H22 N F4
	280.1639	2.6	9.3	6.0	406.1	C17 H22 O F2
	280.1637	2.8	10.0	2.5	157.6	C12 H21 N3 O F3

Supplementary Figure 117. HRMS of 1p.

Parameter Value  
Title wyz8-28-1-h1  
Solvent CDCl3  
Spectrometer Frequency 499.86  
Nucleus 1H



Supplementary Figure 118. <sup>1</sup>H NMR spectrum of **1q**.



## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

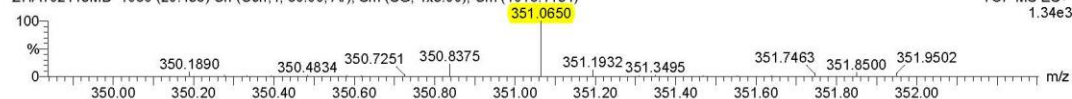
2711 formula(e) evaluated with 26 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 Cl: 0-3

Wang/Zhang, wuz1Q, mw 328; ESI+

ZHA102413MD 1080 (20.436) Cn (Cen.4, 60.00, Ar); Sm (SG, 4x3.00); Cm (1016:1154)

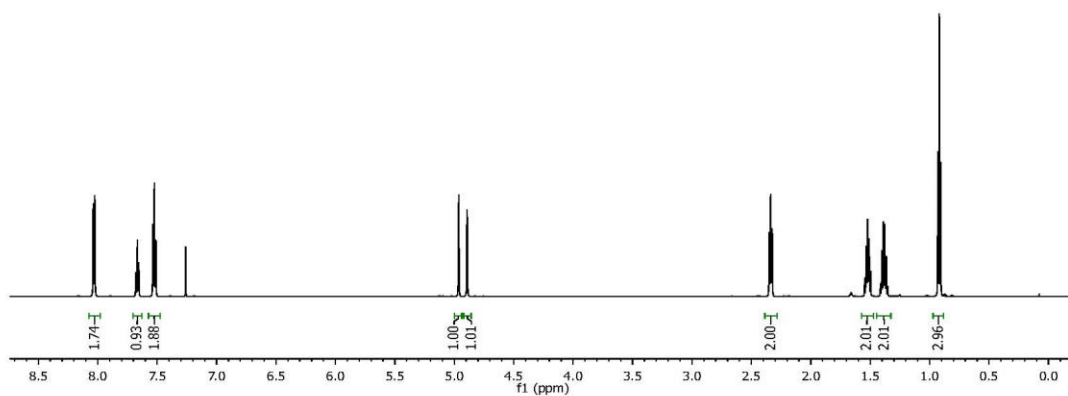
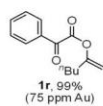
UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
1.34e3

Minimum: -1.5  
Maximum: 3.0 10.0 50.0

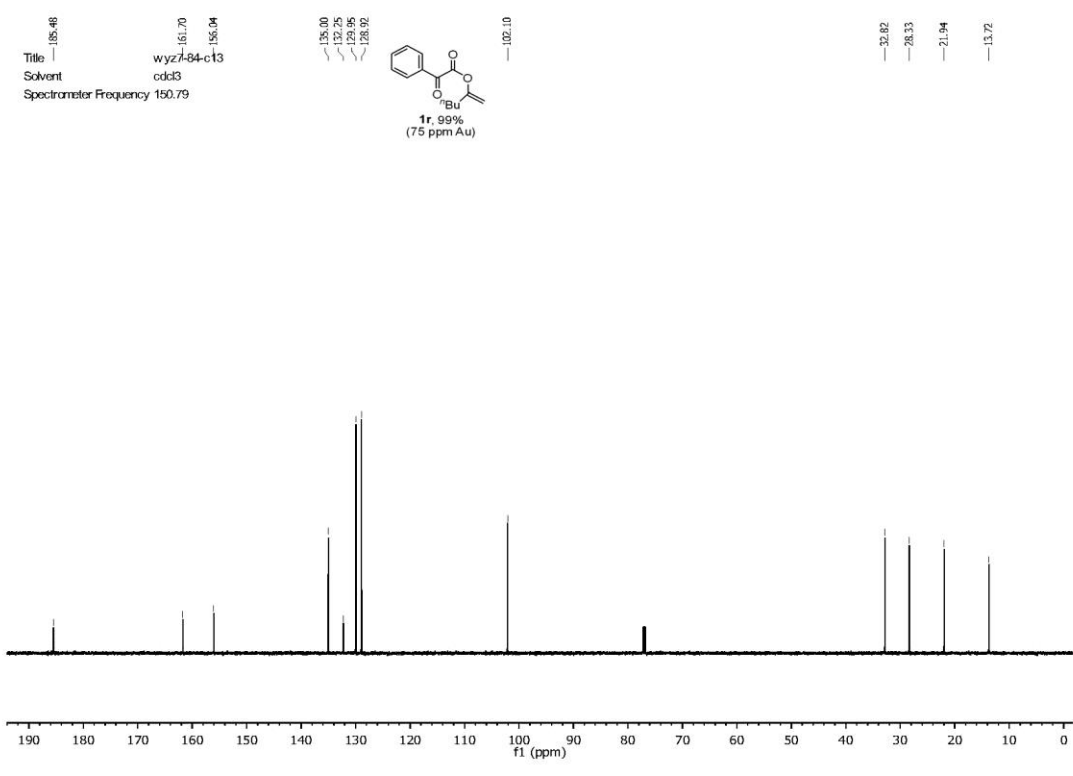
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
351.0650	351.0649	0.1	0.3	6.5	5546647.5	C7 H11 N8 O9
	351.0649	0.1	0.3	14.5	5546686.5	C18 H12 N4 O2 Cl
	351.0647	0.3	0.9	20.5	5546682.0	C22 H8 N4 Na
	351.0645	0.5	1.4	0.5	5546691.5	C11 H22 N2 O4 Cl3
	351.0657	-0.7	-2.0	3.5	5546685.5	C5 H13 N10 O5 Na Cl
	351.0643	0.7	2.0	6.5	5546690.5	C15 H18 N2 O2 Na Cl2
	351.0643	0.7	2.0	-1.5	5546686.0	C4 H17 N6 O9 Na Cl
	351.0657	-0.7	-2.0	18.5	5546682.0	C23 H11 O4
	351.0659	-0.9	-2.6	5.5	5546691.5	C12 H18 N6 Cl3
	351.0640	1.0	2.8	10.5	5546690.5	C13 H13 N8 Cl2
	351.0661	-1.1	-3.1	1.5	5546691.5	C14 H23 O2 Na Cl3
	351.0635	1.5	4.3	9.5	5546686.5	C17 H16 O6 Cl
	351.0665	-1.5	-4.3	15.5	5546687.0	C21 H13 N2 Na Cl
	351.0665	-1.5	-4.3	7.5	5546660.5	C10 H12 N6 O7 Na
	351.0634	1.6	4.6	2.5	5546691.5	C10 H19 N6 Na Cl3
	351.0667	-1.7	-4.8	9.5	5546690.5	C17 H17 N2 O2 Cl2
	351.0667	-1.7	-4.8	1.5	5546686.0	C6 H16 N6 O9 Cl
	351.0633	1.7	4.8	15.5	5546680.0	C21 H12 O4 Na
	351.0630	2.0	5.7	19.5	5546680.0	C19 H7 N6 O2
	351.0671	-2.1	-6.0	23.5	5546683.5	C24 H7 N4
	351.0627	2.3	6.6	5.5	5546690.5	C12 H17 N4 O4 Cl2
	351.0625	2.5	7.1	11.5	5546686.5	C16 H13 N4 O2 Na Cl
	351.0675	-2.5	-7.1	-1.5	5546690.5	C4 H18 N8 O5 Na Cl2
	351.0625	2.5	7.1	3.5	5546628.0	C5 H12 N8 O9 Na
	351.0622	2.8	8.0	15.5	5546686.5	C14 H8 N10 Cl
	351.0679	-2.9	-8.3	12.5	5546668.5	C11 H8 N10 O3 Na

Supplementary Figure 120. HRMS of 1q.

Title            wvz7-84-h1  
Solvent        cdcl3  
Spectrometer Frequency 599.63



Supplementary Figure 121. <sup>1</sup>H NMR spectrum of **1r**.



Supplementary Figure 122. <sup>13</sup>C NMR spectrum of **1r**.



## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

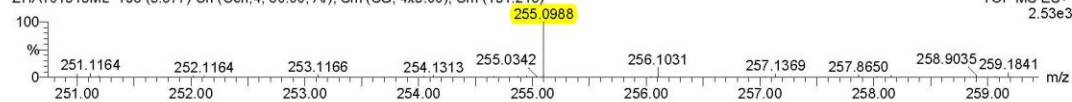
561 formula(e) evaluated with 9 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1

Wang/Zhang, wyz1R, mw 232; ESI+

ZHA101513ML 198 (3.677) Cn (Cen.4, 60.00, Ar); Sm (SG, 4x3.00); Cm (151:218)

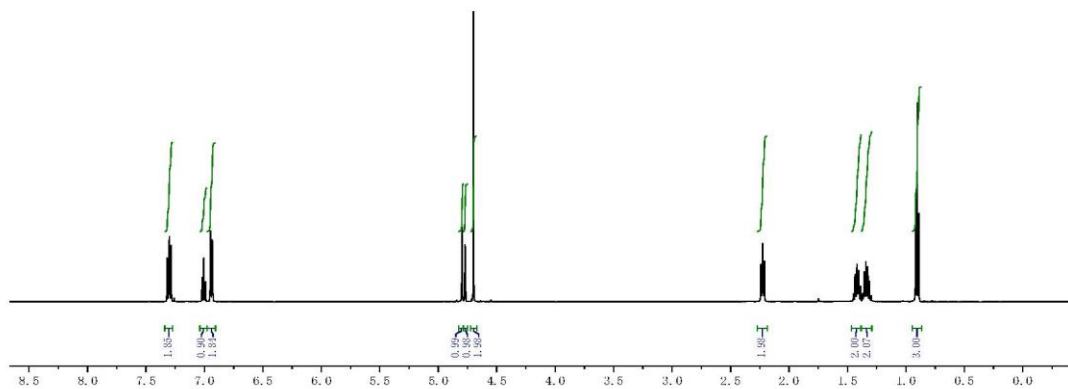
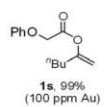
UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
2.53e3

Minimum: -1.5  
Maximum: 3.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
255.0988	255.0984	0.4	1.6	7.0	57.4	C12 H14 N3 O2 Na
	255.0994	-0.6	-2.4	10.5	55.1	C12 H11 N6 O
	255.0981	0.7	2.7	5.5	55.9	C11 H15 N2 O5
	255.0981	0.7	2.7	11.0	67.7	C10 H9 N9
	255.0997	-0.9	-3.5	6.5	46.1	C14 H16 O3 Na
	255.0970	1.8	7.1	7.5	71.6	C10 H12 N6 O Na
	255.1008	-2.0	-7.8	10.0	45.6	C14 H13 N3 O2
	255.0968	2.0	7.8	6.0	71.6	C9 H13 N5 O4
	255.1016	-2.8	-11.0	-1.0	174.7	C H14 N9 O5 Na

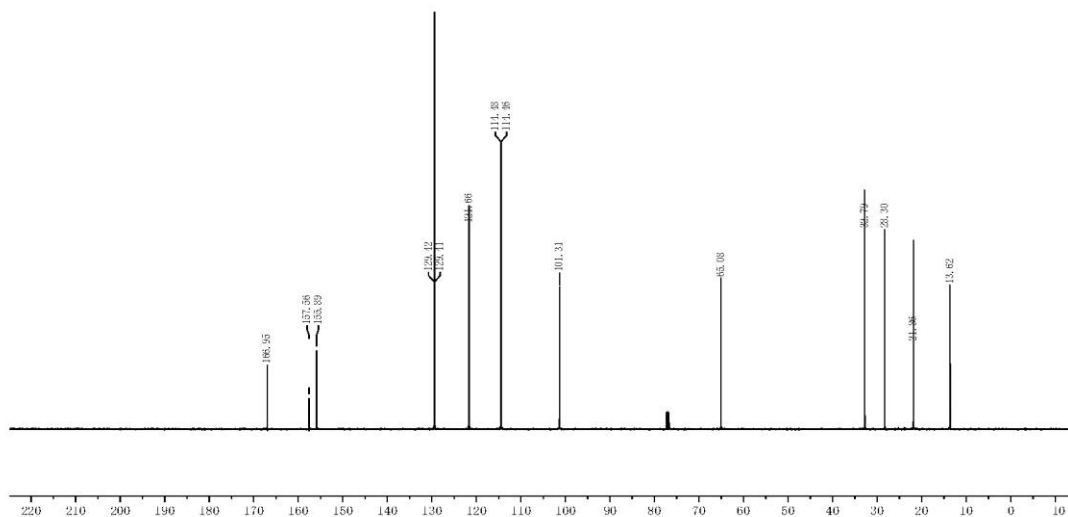
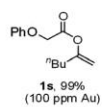
## Supplementary Figure 123. HRMS of 1r.

Parameter Value  
Title wvz8-26-10-h1  
Solvent CDCl3  
Spectrometer Frequency 499.86  
Nucleus 1H



Supplementary Figure 124. <sup>1</sup>H NMR spectrum of **1s**.

Parameter Value  
Title wyz8-26-10-c13  
Solvent CDCl3  
Spectrometer Frequency 125.70  
Nucleus 13C



Supplementary Figure 125. <sup>13</sup>C NMR spectrum of **1s**.

## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

564 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1

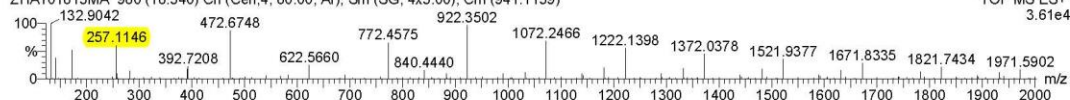
Wang/Zhang, wuz1s, 234, ESI+/TOF

ZHA101613MA 980 (18.540) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (941:1159)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

3.61e4

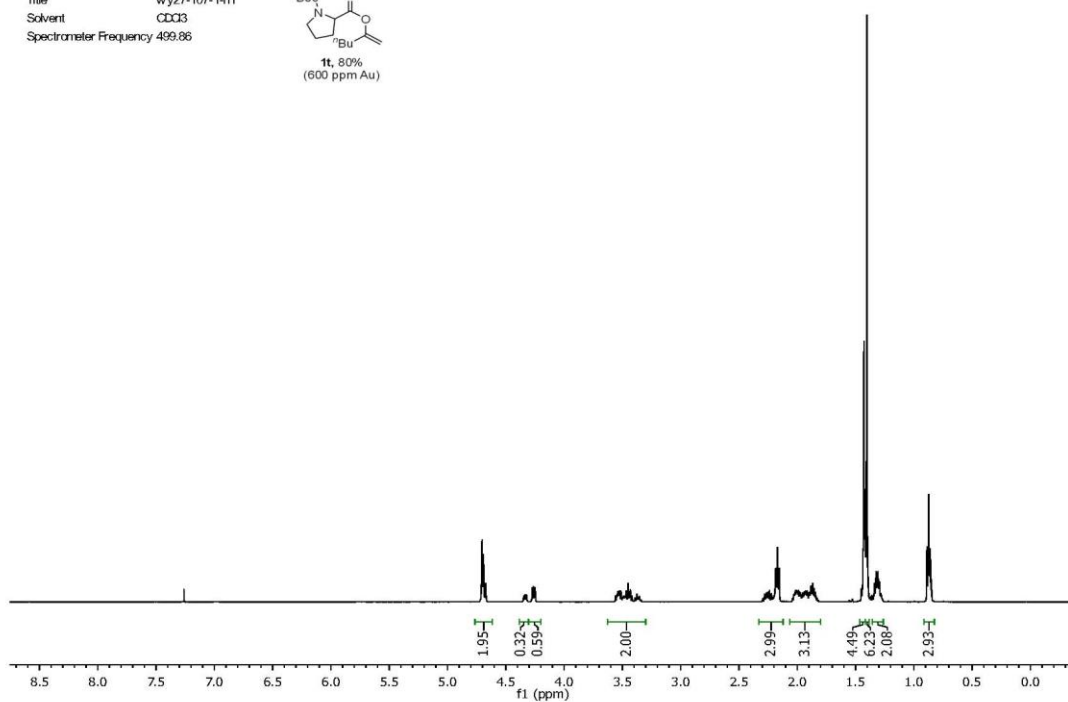
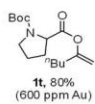


Minimum: -1.5  
 Maximum: 3.0 10.0 50.0

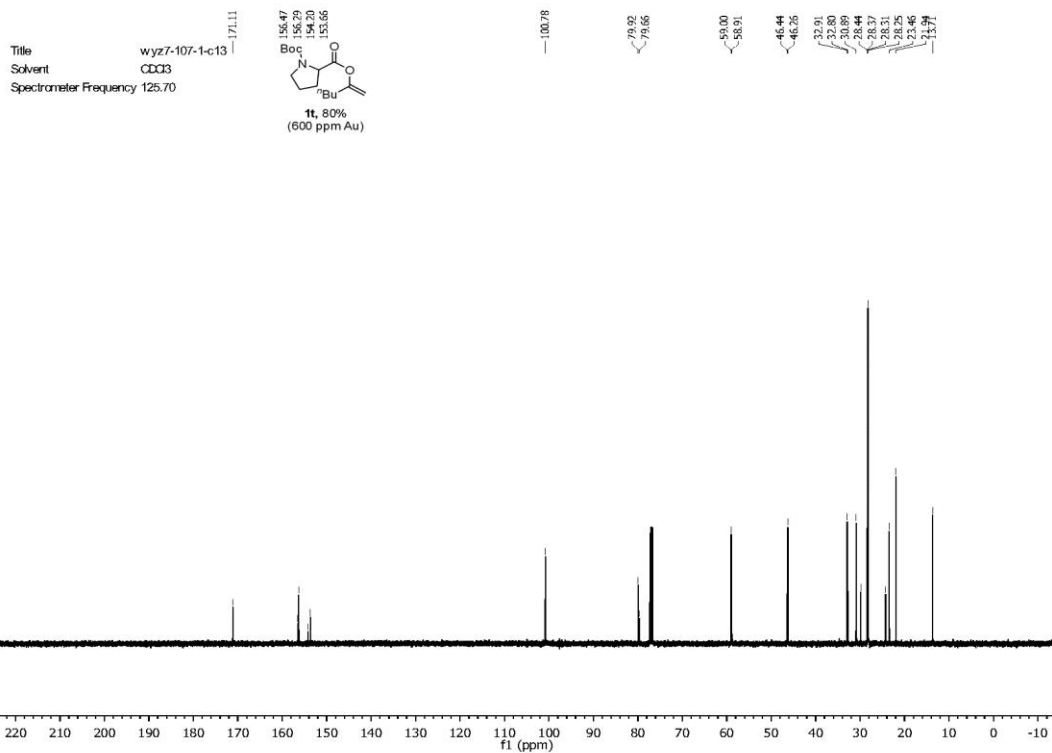
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
257.1146	257.1151	-0.5	-1.9	9.5	31.0	C12 H13 N6 O
	257.1154	-0.8	-3.1	5.5	7.1	C14 H18 O3 Na
	257.1137	0.9	3.5	4.5	43.5	C11 H17 N2 O5
	257.1127	1.9	7.4	6.5	96.8	C10 H14 N6 O Na

## Supplementary Figure 126. HRMS of 1s.

Title wyz7-107-1-h1  
Solvent CDCl3  
Spectrometer Frequency 499.86



Supplementary Figure 127. <sup>1</sup>H NMR spectrum of **1t**.



Supplementary Figure 128.  $^{13}\text{C}$  NMR spectrum of 1t.

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

774 formula(e) evaluated with 12 results within limits (all results (up to 1000) for each mass)

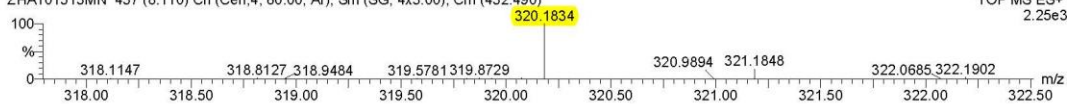
Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1

Wang/Zhang, wyz1T, mw 297; ESI+

ZHA101513MN 437 (8.110) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (432.490)

UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
2.25e3

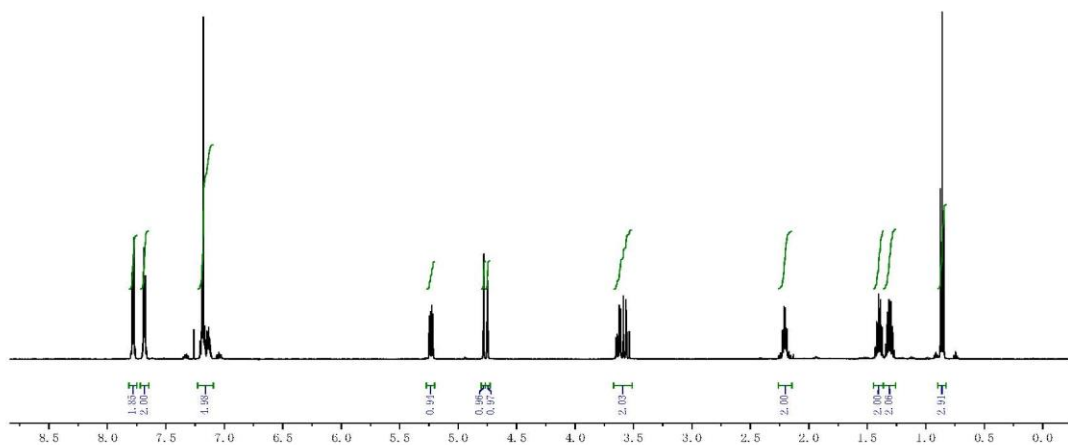
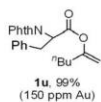


Minimum: -1.5  
Maximum: 3.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
320.1834	320.1835	-0.1	-0.3	2.0	2.1	C15 H28 O7
	320.1835	-0.1	-0.3	7.5	7.6	C14 H22 N7 O2
	320.1838	-0.4	-1.2	3.5	4.2	C16 H27 N O4 Na
	320.1824	1.0	3.1	4.0	7.5	C14 H25 N4 O3 Na
	320.1822	1.2	3.7	2.5	6.2	C13 H26 N3 O6
	320.1822	1.2	3.7	8.0	12.3	C12 H20 N10 O
	320.1848	-1.4	-4.4	7.0	5.6	C16 H24 N4 O3
	320.1851	-1.7	-5.3	8.5	11.6	C17 H23 N5 Na
	320.1811	2.3	7.2	4.5	13.5	C12 H23 N7 O2 Na
	320.1811	2.3	7.2	-1.0	8.9	C13 H29 O7 Na
	320.1808	2.6	8.1	3.0	13.0	C11 H24 N6 O5
	320.1862	-2.8	-8.7	6.5	6.3	C18 H26 N O4

Supplementary Figure 129. HRMS of 1t.

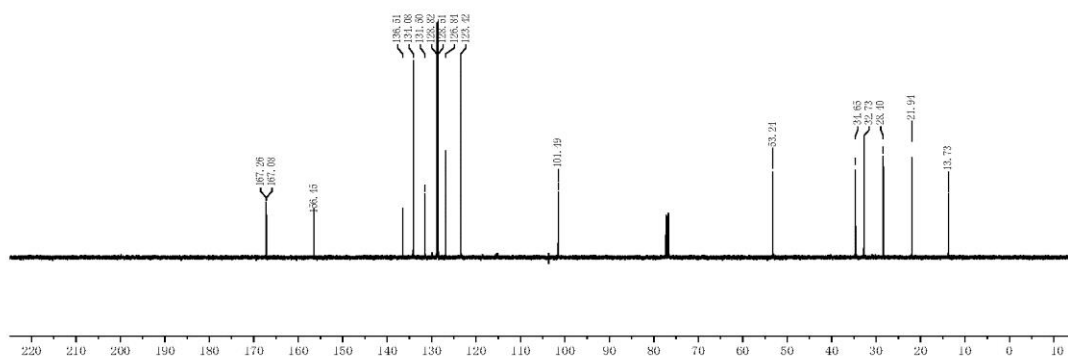
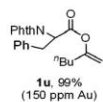
Parameter Value  
Title wvz8-31-1-h1  
Solvent CDCl3  
Spectrometer Frequency 499.86  
Nucleus 1H



Supplementary Figure 130. <sup>1</sup>H NMR spectrum of **1u**.



Parameter Value  
Title wyz8-31-1-c13  
Solvent CDCl3  
Spectrometer Frequency 125.70  
Nucleus 13C



Supplementary Figure 131. <sup>13</sup>C NMR spectrum of **1u**.

## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

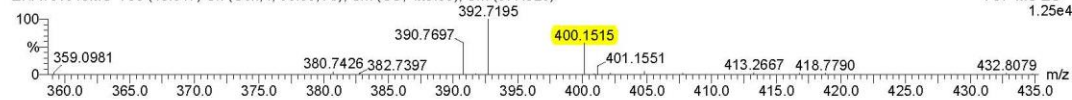
1010 formula(e) evaluated with 7 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1

Wang/Zhang, wyz1u, 377, ESI+/TOF

ZHA101613MC 793 (15.017) Cn (Cen, 4, 60.00, Ar); Sm (SG, 4x3.00); Cm (677:920)

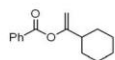
UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
1.25e4

Minimum: -1.5  
Maximum: 50.0

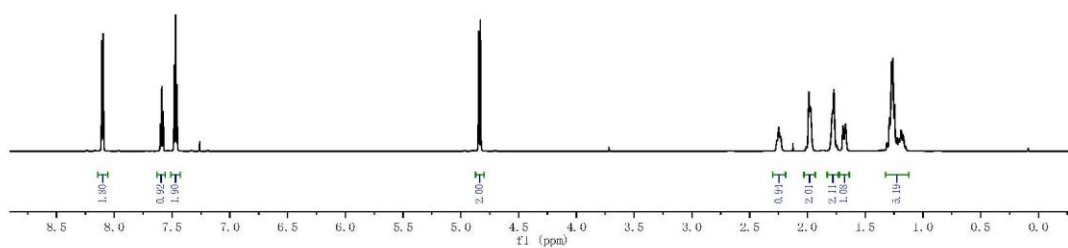
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
400.1515	400.1516	-0.1	-0.2	0.5	294.4	C7 H23 N9 O9 Na
	400.1509	0.6	1.5	11.5	9.7	C20 H22 N3 O6
	400.1522	-0.7	-1.7	16.5	9.4	C21 H18 N7 O2
	400.1525	-1.0	-2.5	12.5	4.0	C23 H23 N O4 Na
	400.1498	1.7	4.2	13.5	23.3	C19 H19 N7 O2 Na
	400.1538	-2.3	-5.7	17.5	15.6	C24 H19 N5 Na
	400.1540	-2.5	-6.2	3.5	208.6	C9 H22 N9 O9

Supplementary Figure 132. HRMS of 1u.

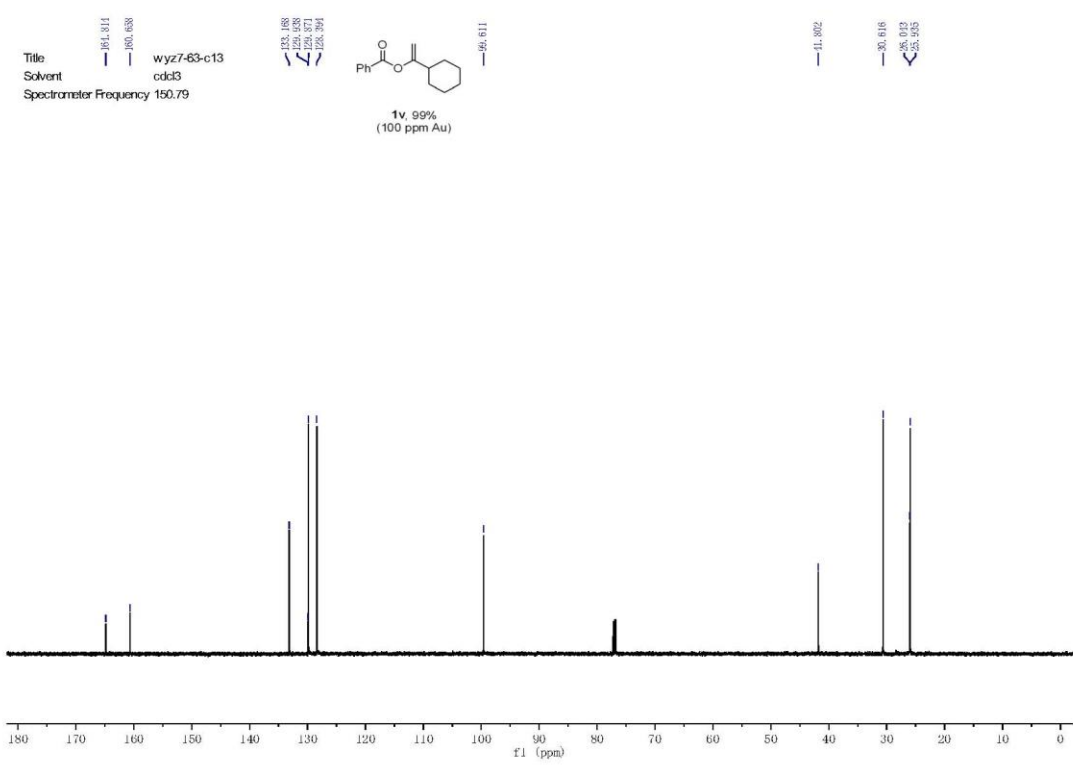
Title            wyz7-63-h1  
Solvent         cdcl3  
Spectrometer Frequency 599.64



1v, 99%  
(100 ppm Au)



Supplementary Figure 133. <sup>1</sup>H NMR spectrum of 1v.



Supplementary Figure 134. <sup>13</sup>C NMR spectrum of 1v.

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

549 formula(e) evaluated with 8 results within limits (all results (up to 1000) for each mass)

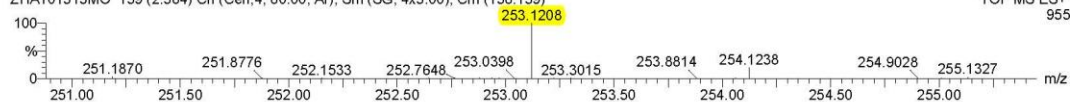
Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1

Wang/Zhang, wyz1V, mw 230; ESI+

ZHA101513MO 139 (2.584) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (136:159)

UCSB CHEM BIOCHEM QT02  
TOF MS ES+  
955

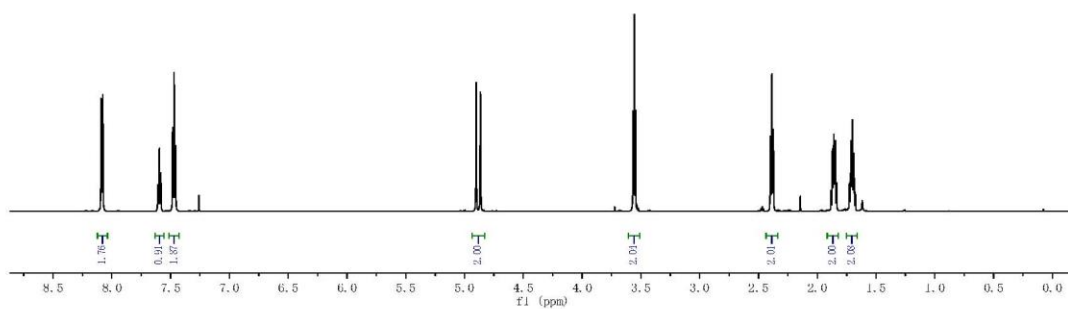
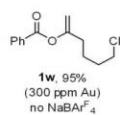


Minimum: -1.5  
Maximum: 3.0 10.0 50.0

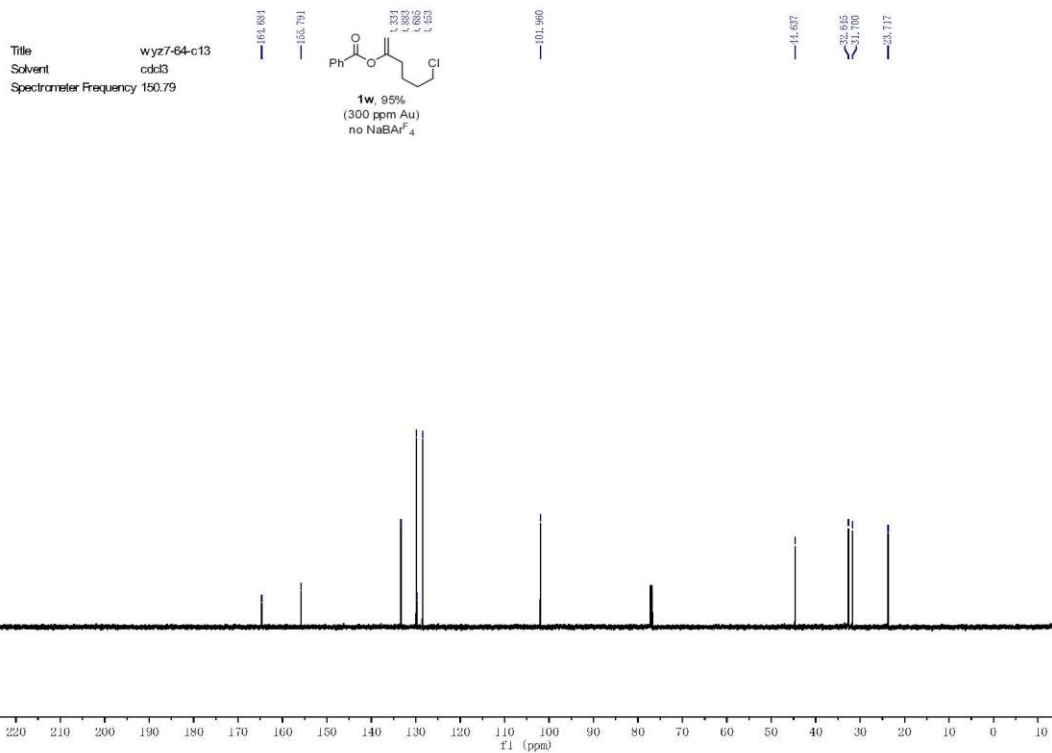
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
253.1208	253.1204	0.4	1.6	6.5	3.2	C15 H18 O2 Na
	253.1202	0.6	2.4	10.5	5.1	C13 H13 N6
	253.1215	-0.7	-2.8	10.0	2.3	C15 H15 N3 O
	253.1223	-1.5	-5.9	-1.0	52.0	C2 H16 N9 O4 Na
	253.1191	1.7	6.7	7.0	6.7	C13 H16 N3 O Na
	253.1188	2.0	7.9	5.5	8.2	C12 H17 N2 O4
	253.1229	-2.1	-8.3	9.5	0.8	C17 H17 O2
	253.1236	-2.8	-11.1	-1.5	42.8	C4 H18 N6 O5 Na

Supplementary Figure 135. HRMS of 1v.

Title            wyz7-64-h1  
Solvent        cdCl3  
Spectrometer Frequency 599.64



Supplementary Figure 136. <sup>1</sup>H NMR spectrum of **1w**.



Supplementary Figure 137. <sup>13</sup>C NMR spectrum of 1w.

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

1320 formula(e) evaluated with 16 results within limits (all results (up to 1000) for each mass)

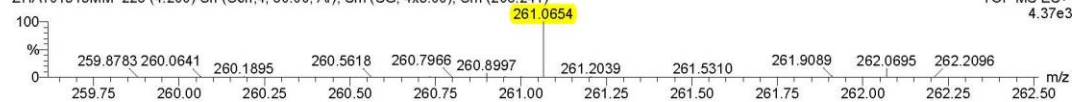
Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 Cl: 0-2

Wang/Zhang, wyz1W, mw 238; ESI+

ZHA101513MM 226 (4.200) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (206;241)

UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
4.37e3

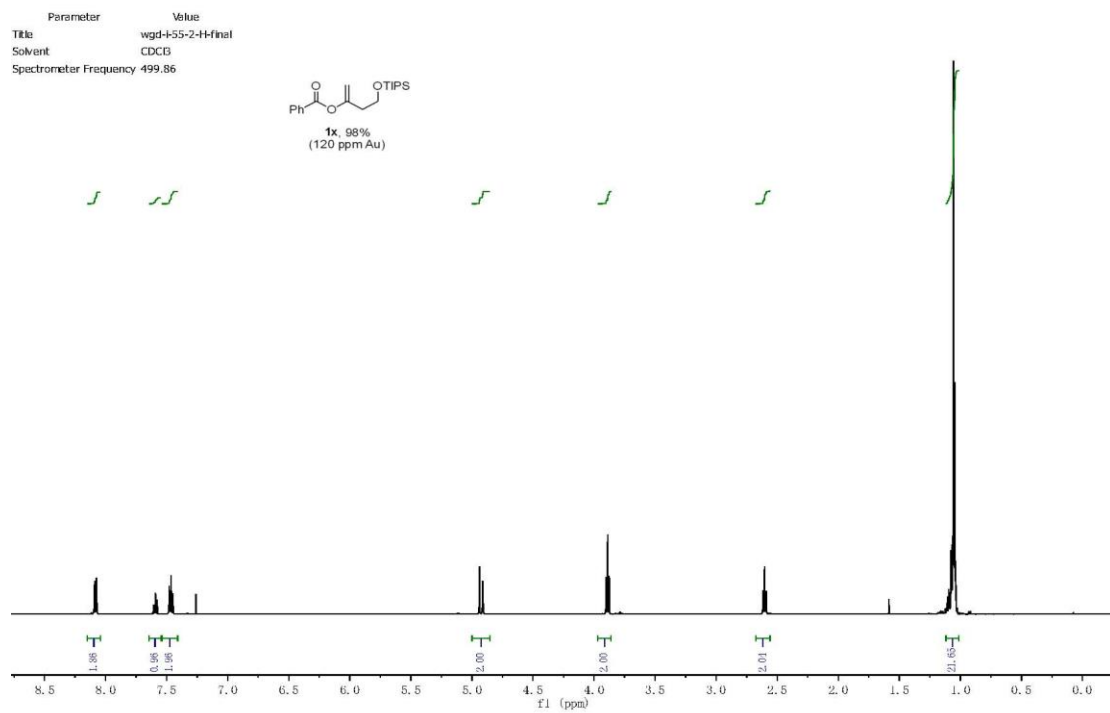


Minimum: -1.5  
Maximum: 3.0 10.0 50.0

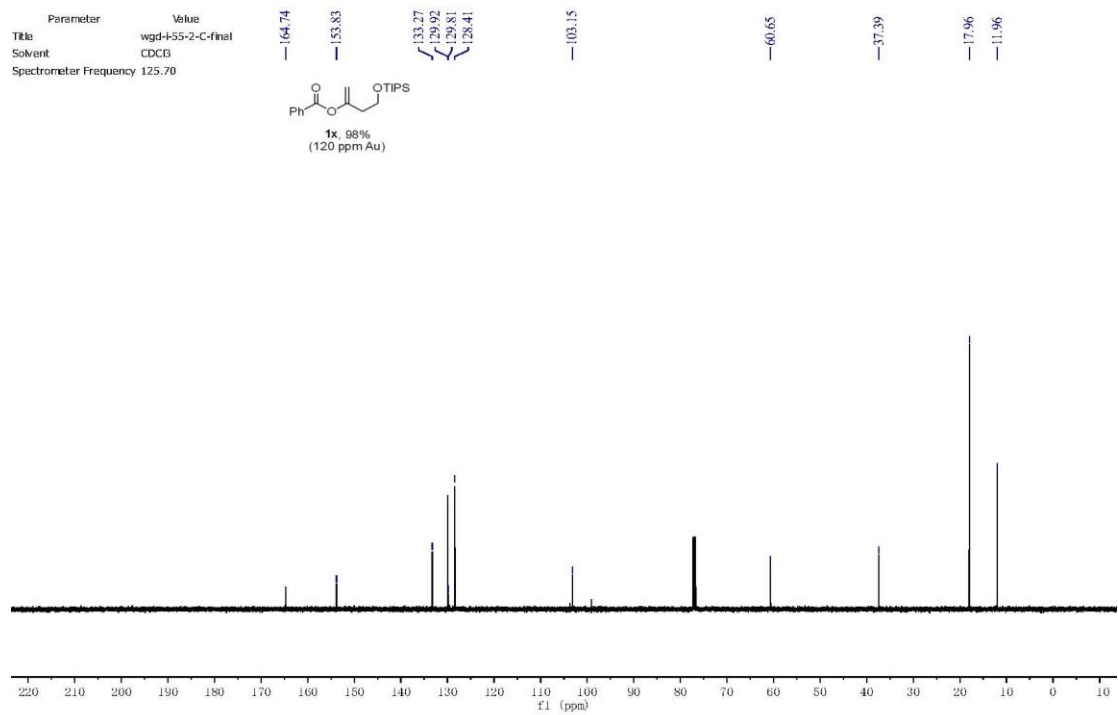
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
261.0654	261.0655	-0.1	-0.4	9.5	2775524.3	C11 H10 N6 Cl
	261.0656	-0.2	-0.8	1.5	2774297.5	H9 N10 O7
	261.0650	0.4	1.5	1.5	2775530.8	C8 H16 N4 Na Cl2
	261.0658	-0.4	-1.5	5.5	2775524.3	C13 H15 O2 Na Cl
	261.0660	-0.6	-2.3	-0.5	2775530.5	C9 H19 O4 Cl2
	261.0664	-1.0	-3.8	13.5	2774498.3	C16 H9 N2 O2
	261.0642	1.2	4.6	4.5	2775525.3	C10 H14 N2 O4 Cl
	261.0640	1.4	5.4	10.5	2774267.8	C14 H10 N2 O2 Na
	261.0637	1.7	6.5	14.5	2773916.0	C12 H5 N8
	261.0672	-1.8	-6.9	2.5	2774000.0	C3 H10 N8 O5 Na
	261.0674	-2.0	-7.7	4.5	2775531.3	C10 H15 N4 Cl2
	261.0634	2.0	7.7	0.5	2775531.8	C5 H15 N6 O2 Cl2
	261.0631	2.3	8.8	6.5	2775525.8	C9 H11 N6 Na Cl
	261.0680	-2.6	-10.0	14.5	2774530.0	C19 H10 Na
	261.0682	-2.8	-10.7	8.5	2775525.8	C15 H14 O2 Cl
	261.0683	-2.9	-11.1	0.5	2774600.8	C4 H13 N4 O9

Supplementary Figure 138. HRMS of 1w.





**Supplementary Figure 139.** <sup>1</sup>H NMR spectrum of **1x**.



**Supplementary Figure 140.** <sup>13</sup>C NMR spectrum of **1x**.

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

2628 formula(e) evaluated with 17 results within limits (all results (up to 1000) for each mass)

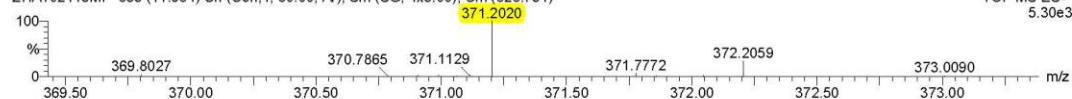
Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1 Si: 0-2

Wang/Zhang, wyz1X, mw 348; ESI+

ZHA102413MF 633 (11.984) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (626.731)

UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
5.30e3

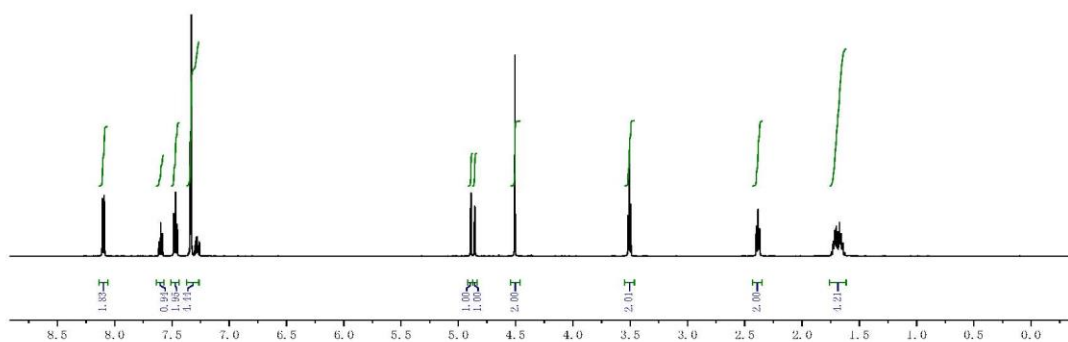
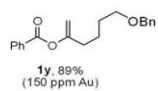


Minimum: -1.5  
Maximum: 3.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
371.2020	371.2019	0.1	0.3	2.5	2775492.0	C13 H28 N6 O5 Na
	371.2018	0.2	0.5	5.5	2776246.5	C20 H32 O3 Na Si
	371.2023	-0.3	-0.8	1.5	2776312.3	C12 H32 N6 O2 Na Si2
	371.2016	0.4	1.1	9.5	2776230.0	C18 H27 N6 O Si
	371.2011	0.9	2.4	13.5	2776014.0	C26 H27 O2
	371.2030	-1.0	-2.7	0.5	2775806.0	C14 H31 N2 O9
	371.2032	-1.2	-3.2	7.5	2775223.0	C14 H24 N10 O Na
	371.2007	1.3	3.5	0.5	2776312.5	C9 H31 N8 O4 Si2
	371.2034	-1.4	-3.8	-0.5	2776323.0	C13 H35 N2 O6 Si2
	371.2003	1.7	4.6	1.5	2775530.8	C10 H27 N8 O7
	371.2002	1.8	4.8	4.5	2776243.3	C17 H31 N2 O5 Si
	371.2042	-2.2	-5.9	8.5	2776263.3	C22 H31 O3 Si
	371.2043	-2.3	-6.2	5.5	2775651.8	C15 H27 N6 O5
	371.2046	-2.6	-7.0	1.5	2775799.5	C17 H32 O7 Na
	371.2047	-2.7	-7.3	4.5	2776318.8	C14 H31 N6 O2 Si2
	371.1992	2.8	7.5	6.5	2776209.8	C16 H28 N6 O Na Si
	371.2050	-3.0	-8.1	0.5	2776324.3	C16 H36 O4 Na Si2

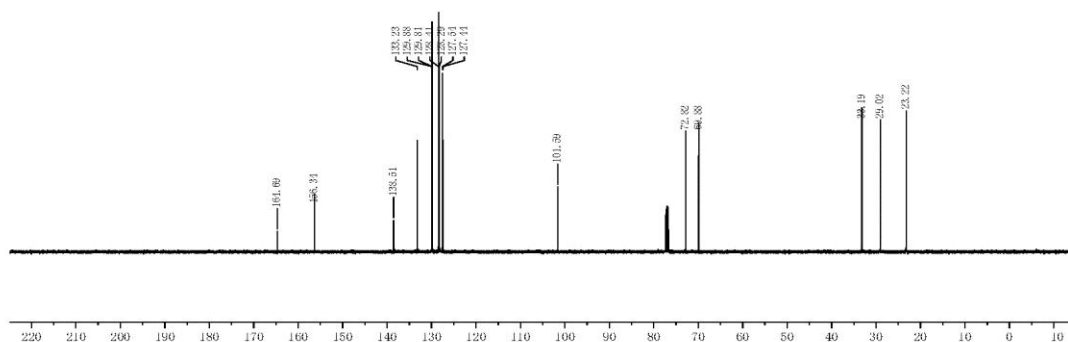
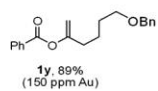
Supplementary Figure 141. HRMS of 1x.

Parameter Value  
Title wvz8-42-5-H1  
Solvent CDCl3  
Spectrometer Frequency 499.86  
Nucleus 1H



Supplementary Figure 142. <sup>1</sup>H NMR spectrum of 1y.

Parameter Value  
Title wyz8-42-5-C13  
Solvent CDCl3  
Spectrometer Frequency 125.70  
Nucleus 13C



Supplementary Figure 143.  $^{13}\text{C}$  NMR spectrum of **1y**.

Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

815 formula(e) evaluated with 7 results within limits (all results (up to 1000) for each mass)

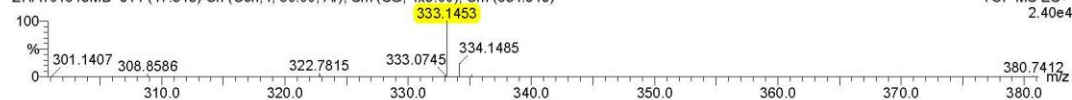
Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1

Wang/Zhang, wuz1y, 282, ESI+/TOF

ZHA101613MD 911 (17.313) Cn (Cen, 4, 60.00, Ar); Sm (SG, 4x3.00); Cm (654:919)

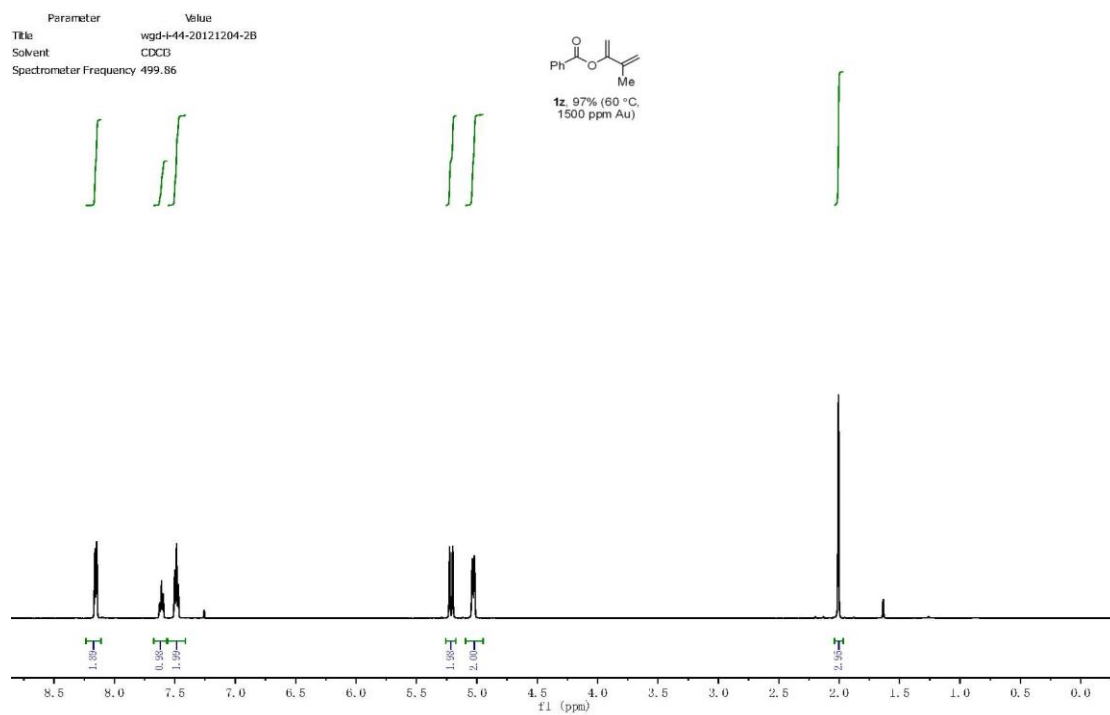
UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
2.40e4



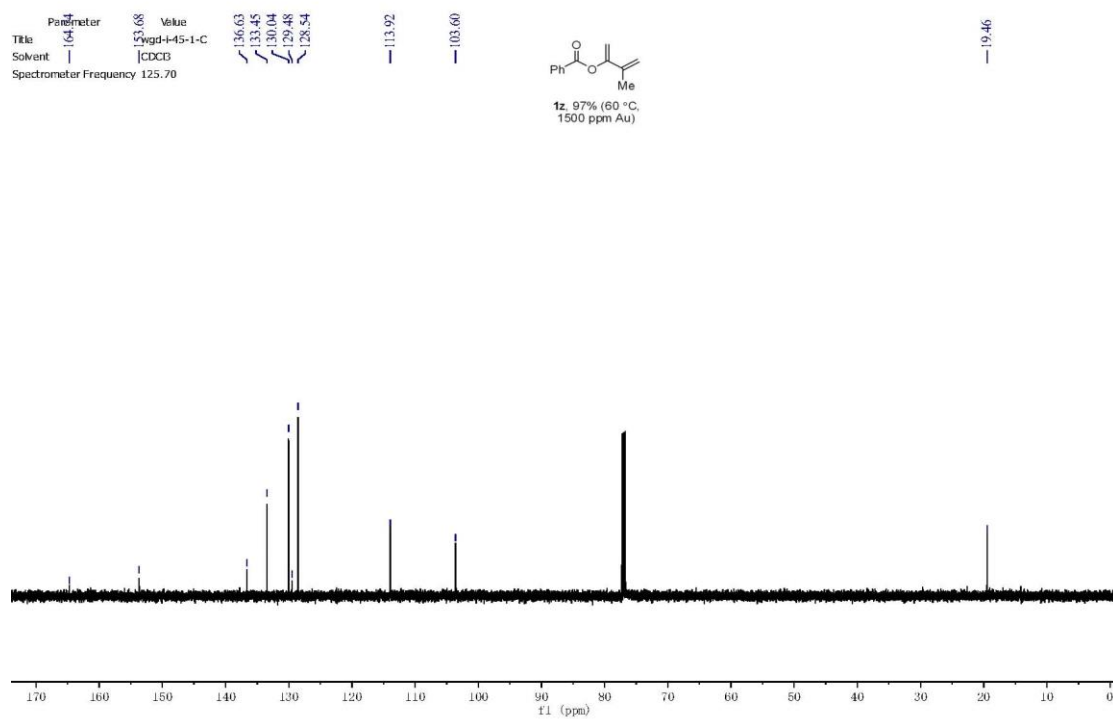
Minimum: -1.5  
Maximum: 3.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
333.1453	333.1450	0.3	0.9	8.5	63.4	C17 H21 N2 O5
	333.1464	-1.1	-3.3	13.5	53.4	C18 H17 N6 O
	333.1440	1.3	3.9	10.5	124.5	C16 H18 N6 O Na
	333.1467	-1.4	-4.2	9.5	25.3	C20 H22 O3 Na
	333.1426	2.7	8.1	5.5	176.1	C15 H22 N2 O5 Na
	333.1424	2.9	8.7	9.5	227.5	C13 H17 N8 O3
	333.1482	-2.9	-8.7	0.5	911.5	C6 H21 N8 O8

Supplementary Figure 144. HRMS of 1y.



**Supplementary Figure 145. <sup>1</sup>H NMR spectrum of 1z.**



**Supplementary Figure 146.** <sup>13</sup>C NMR spectrum of **1z**.



## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 200.0

Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions

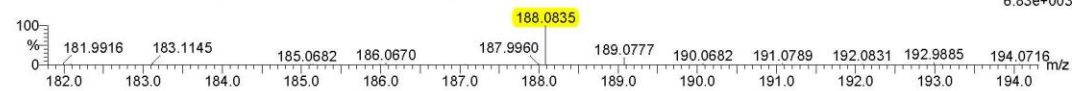
179 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-200 N: 0-10 O: 0-10

Wang/Zhang, wyz1z, mw 188, EI+

ZHA102913PA 274 (4.570) Cn (Cen,3, 80.00, Ar); Sm (SG, 4x3.00); Cm (274:389)

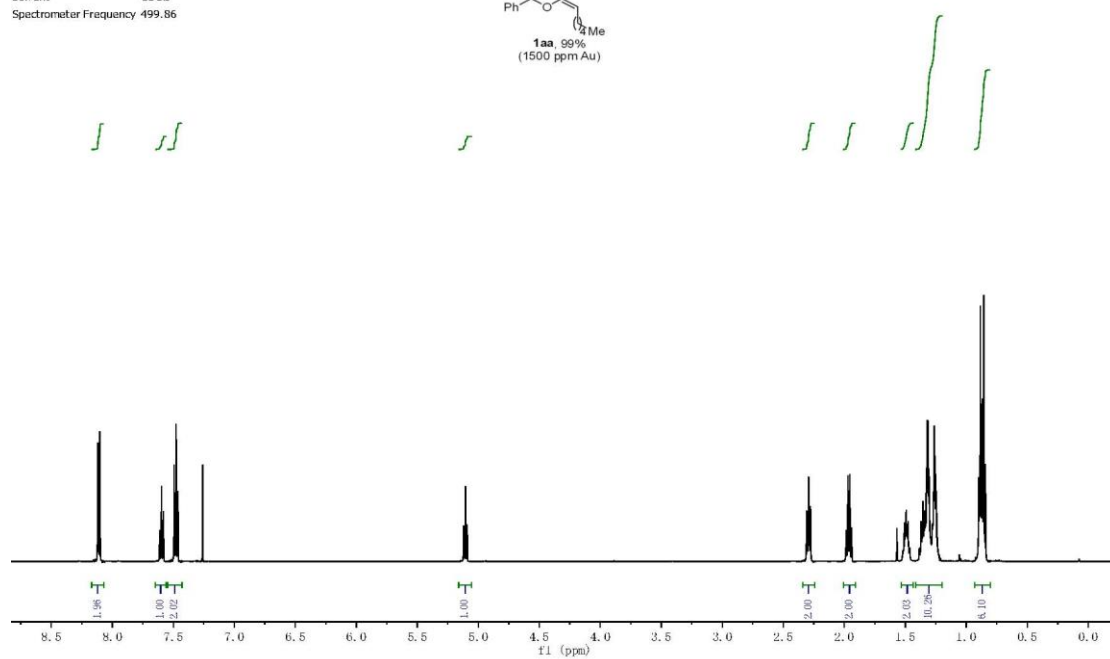
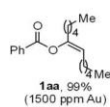
UCSB Chem\_Biochem GCT Premier  
TOF MS EI+  
6.83e+003

Minimum: -1.5  
Maximum: 200.0

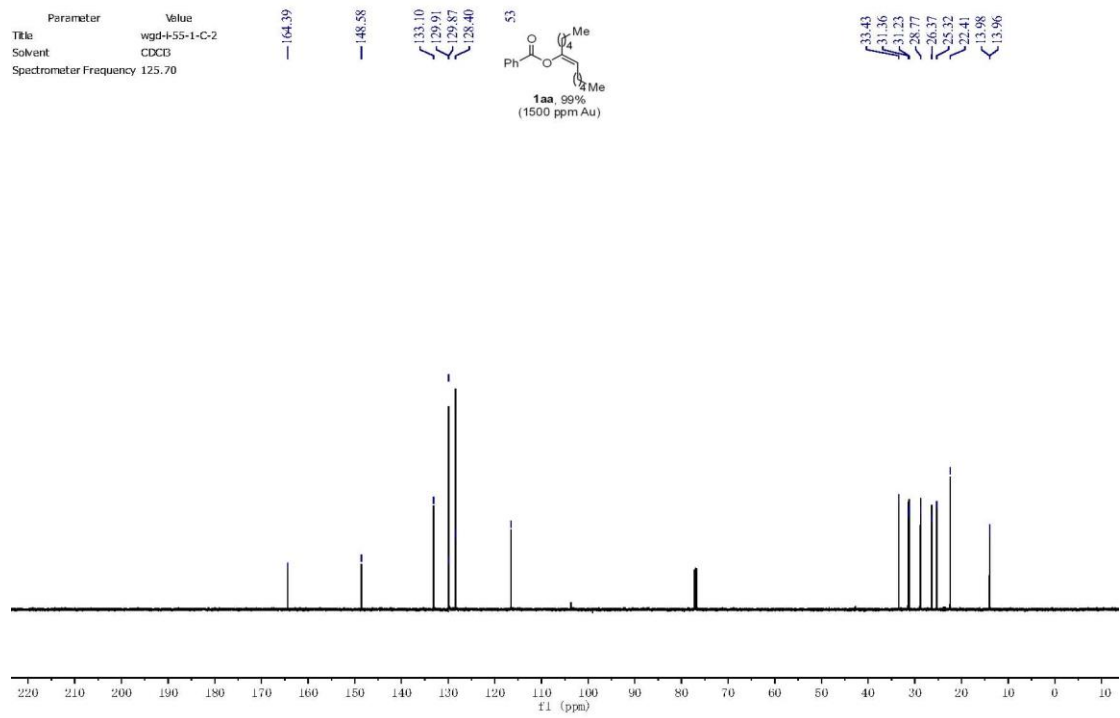
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
188.0835	188.0837	-0.2	-1.1	7.0	79.8	C12 H12 O2
	188.0824	1.1	5.8	7.5	111.7	C10 H10 N3 O
	188.0810	2.5	13.3	8.0	153.9	C8 H8 N6

Supplementary Figure 147. HRMS of 1z.

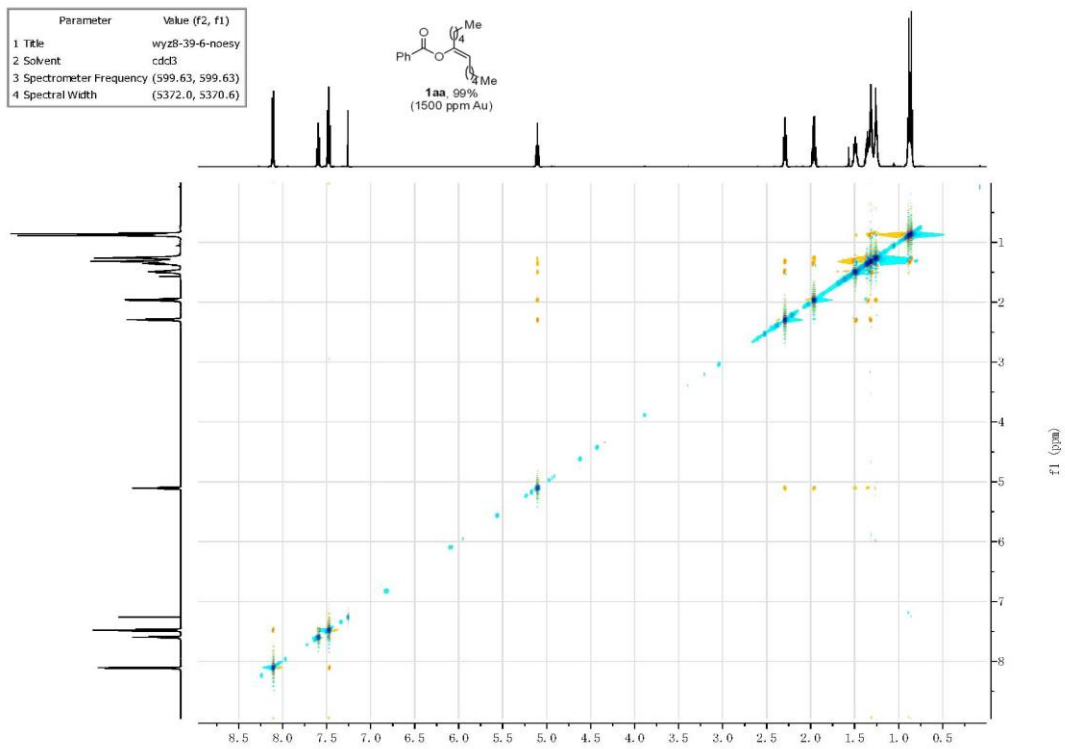
Parameter Value  
Title wgd-55-1-H-4  
Solvent CDCl3  
Spectrometer Frequency 499.86



Supplementary Figure 148. <sup>1</sup>H NMR spectrum of 1aa.



**Supplementary Figure 149.** <sup>13</sup>C NMR spectrum of 1aa.



**Supplementary Figure 150.  $^1\text{H}$ - $^1\text{H}$  NOESY spectrum of 1aa.**

## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

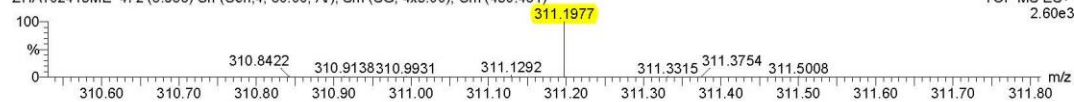
746 formula(e) evaluated with 7 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1

Wang/Zhang, wyz1aa, mw 288; ESI+

ZHA102413ME 472 (8.988) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (450:481)

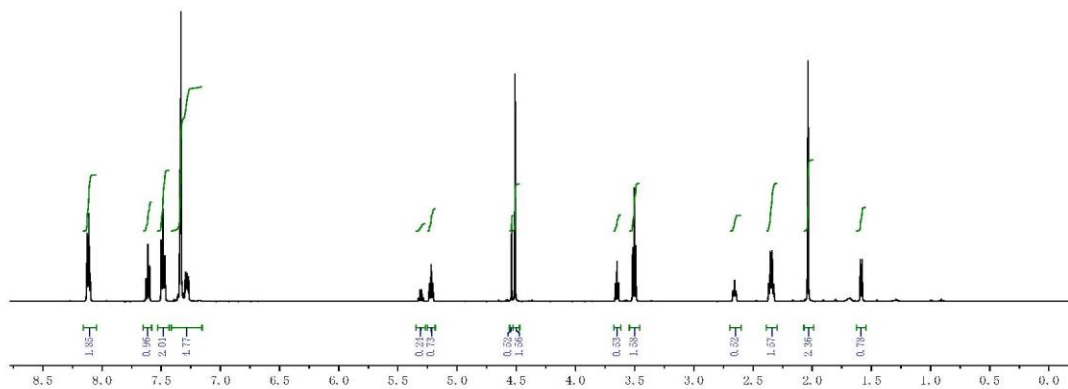
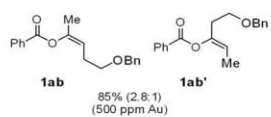
UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
2.60e3

Minimum: -1.5  
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
311.1977	311.1974	0.3	1.0	6.0	5547309.5	C17 H26 N3 O Na
	311.1971	0.6	1.9	4.5	5547307.5	C16 H27 N2 O4
	311.1984	-0.7	-2.2	9.5	5547310.5	C17 H23 N6
	311.1987	-1.0	-3.2	5.5	5547311.0	C19 H28 O2 Na
	311.1960	1.7	5.5	6.5	5547307.5	C15 H24 N6 Na
	311.1957	2.0	6.4	5.0	5547305.5	C14 H25 N5 O3
	311.1998	-2.1	-6.7	9.0	5547312.5	C19 H25 N3 O

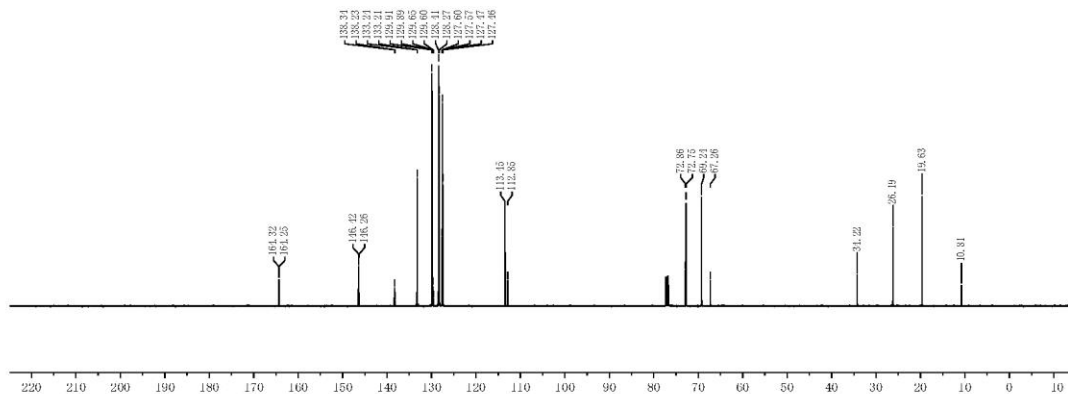
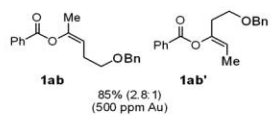
## Supplementary Figure 151. HRMS of 1aa.

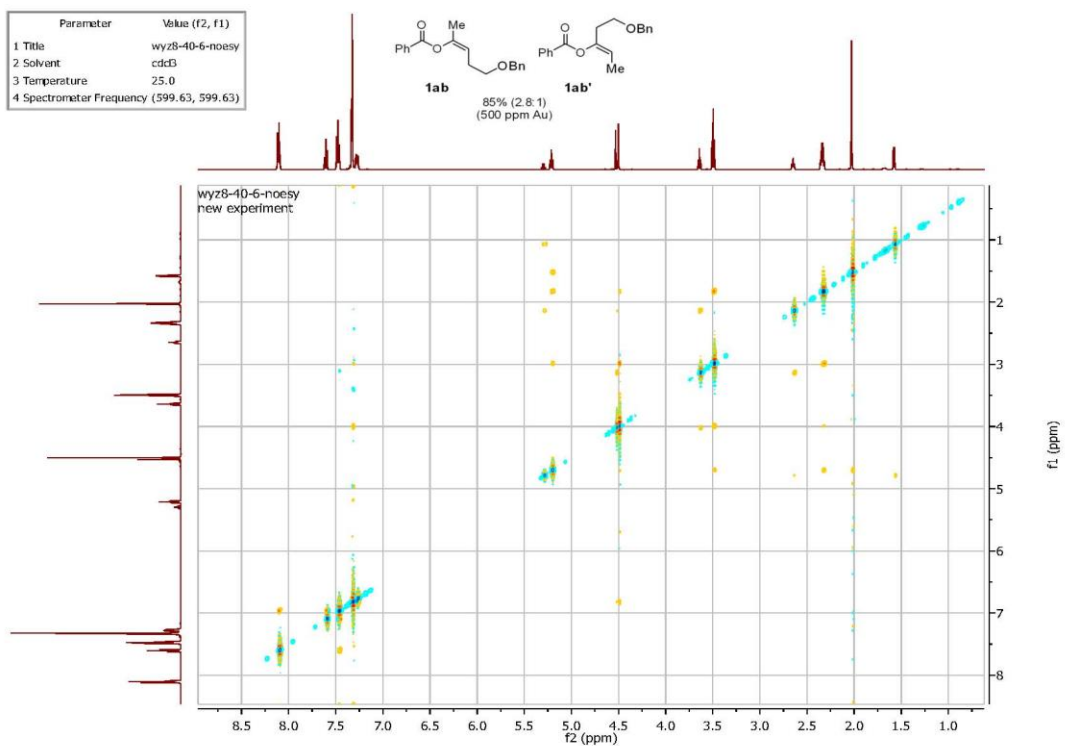
Parameter	Value
Title	wyz8-40-6-HI
Solvent	CDCl3
Spectrometer Frequency	499.86
Nucleus	<sup>1</sup> H



Supplementary Figure 152. <sup>1</sup>H NMR spectrum of mixture of 1ab and 1ab'.

Parameter	Value
Title	wyz8-40-6-C13
Solvent	CDCl3
Spectrometer Frequency	125.70
Nucleus	13C





Supplementary Figure 154.  $^1\text{H}$ - $^1\text{H}$  NOESY of mixture of **1ab** and **1ab'**.



## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

777 formula(e) evaluated with 13 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1

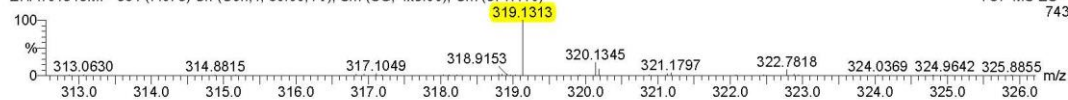
Wang/Zhang, wyz1AB, mw 296; ESI+

ZHA101513MP 381 (7.073) Cn (Cen,4, 60.00, Ar); Sm (SG, 4x3.00); Cm (371.410)

UCSB CHEM BIOCHEM QTOF2

TOF MS ES+

743

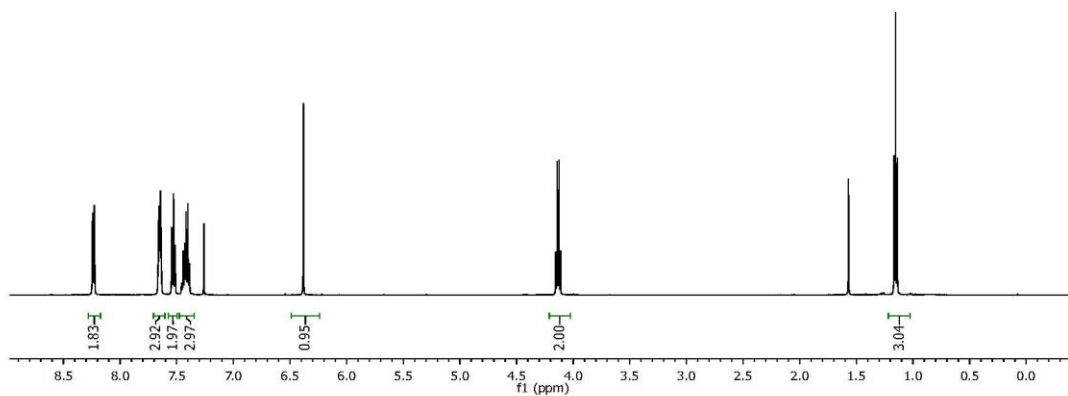
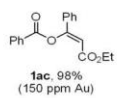


Minimum: -1.5  
Maximum: 3.0 10.0 50.0

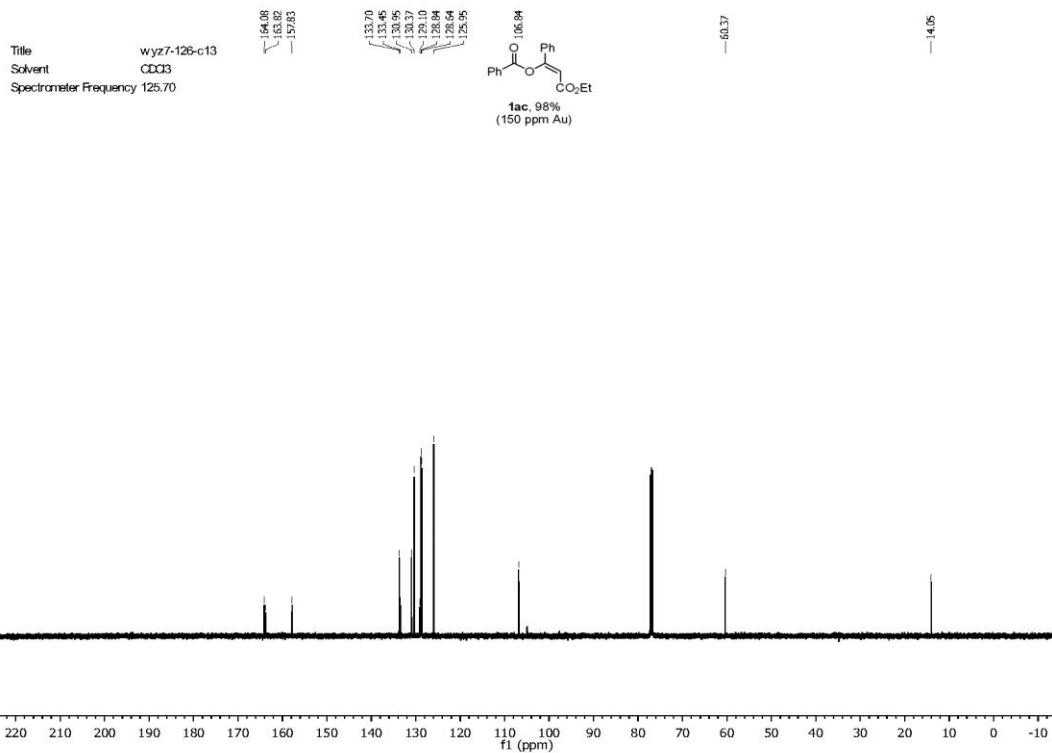
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
319.1313	319.1310	0.3	0.9	9.5	0.6	C19 H20 O3 Na
	319.1307	0.6	1.9	13.5	1.3	C17 H15 N6 O
	319.1321	-0.8	-2.5	13.0	0.3	C19 H17 N3 O2
	319.1326	-1.3	-4.1	0.5	32.5	C5 H19 N8 O8
	319.1329	-1.6	-5.0	2.0	28.2	C6 H18 N9 O5 Na
	319.1297	1.6	5.0	10.0	2.0	C17 H18 N3 O2 Na
	319.1294	1.9	6.0	14.0	3.2	C15 H13 N9
	319.1294	1.9	6.0	8.5	2.8	C16 H19 N2 O5
	319.1334	-2.1	-6.6	12.5	0.2	C21 H19 O3
	319.1337	-2.4	-7.5	14.0	0.7	C22 H18 N Na
	319.1339	-2.6	-8.1	0.0	26.6	C7 H21 N5 O9
	319.1342	-2.9	-9.1	1.5	22.5	C8 H20 N6 O6 Na
	319.1283	3.0	9.4	10.5	4.3	C15 H16 N6 O Na

Supplementary Figure 155. HRMS of mixture of 1ab and 1ab'.

Title wyz7-126-h1  
Solvent CDCl3  
Spectrometer Frequency 499.86



Supplementary Figure 156. <sup>1</sup>H NMR spectrum of 1ac.



Supplementary Figure 157.  $^{13}\text{C}$  NMR spectrum of 1ac.

## Single Mass Analysis

Tolerance = 3.0 mDa / DBE: min = -1.5, max = 50.0

Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions

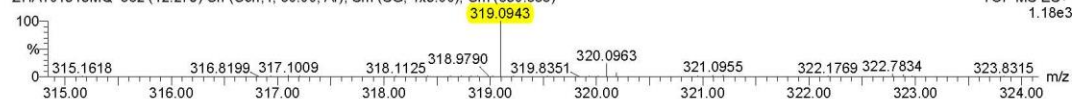
779 formula(e) evaluated with 13 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-100 H: 0-100 N: 0-10 O: 0-10 Na: 0-1

Wang/Zhang, wuz1AC, mw 296; ESI+

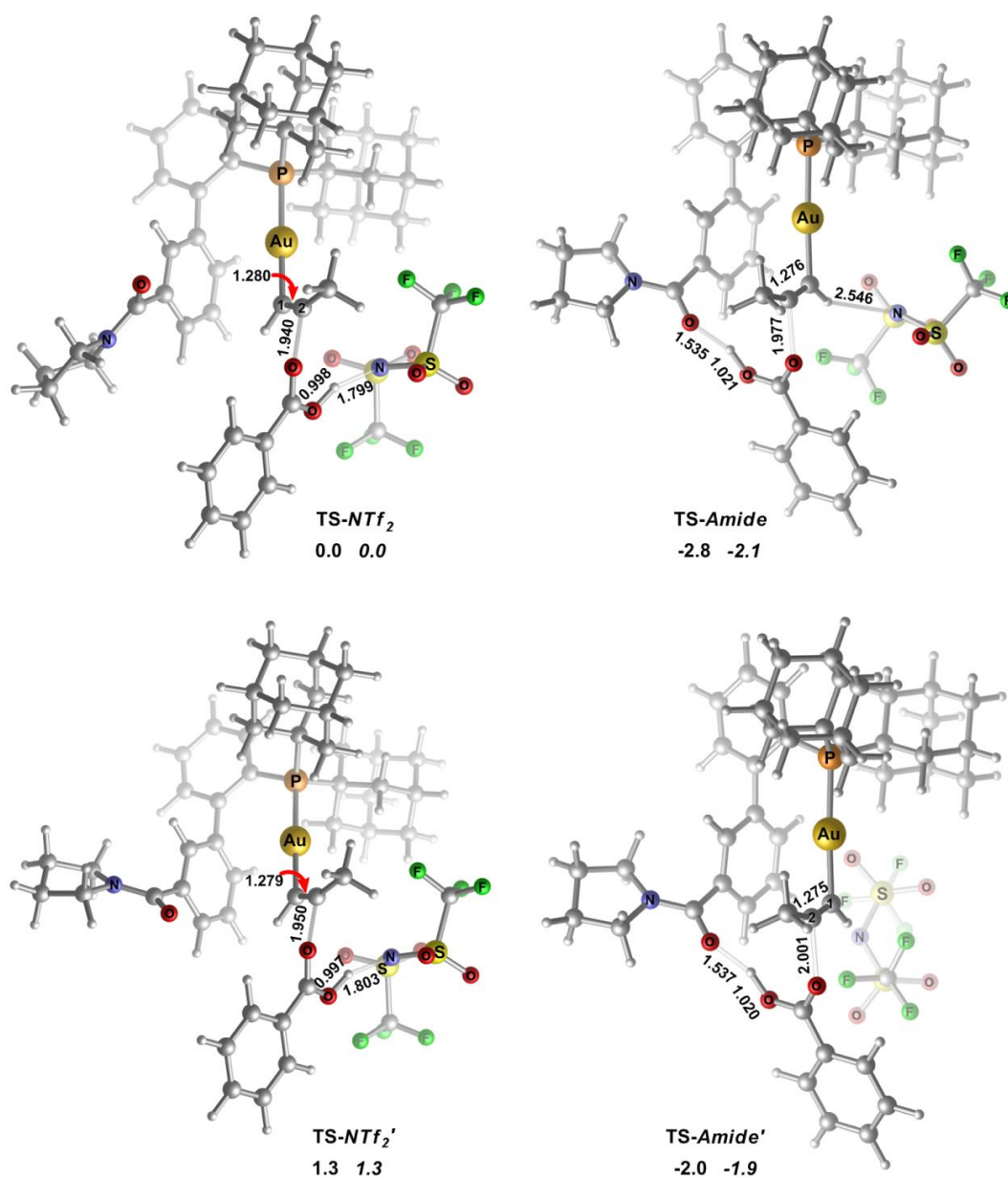
ZHA101513MQ 662 (12.279) Cn (Cen, 4, 60.00, Ar); Sm (SG, 4x3.00); Cm (650:668)

UCSB CHEM BIOCHEM QTOF2  
TOF MS ES+  
1.18e3

Minimum: -1.5  
Maximum: 3.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
319.0943	319.0943	0.0	0.0	14.5	2.0	C16 H11 N6 O2
	319.0946	-0.3	-0.9	10.5	1.5	C18 H16 O4 Na
	319.0938	0.5	1.6	-1.5	76.4	C2 H16 N8 O9 Na
	319.0933	1.0	3.1	11.0	3.4	C16 H14 N3 O3 Na
	319.0930	1.3	4.1	15.0	4.8	C14 H9 N9 O
	319.0930	1.3	4.1	9.5	5.9	C15 H15 N2 O6
	319.0957	-1.4	-4.4	14.0	0.7	C18 H13 N3 O3
	319.0960	-1.7	-5.3	15.5	0.4	C19 H12 N4 Na
	319.0962	-1.9	-6.0	1.5	57.2	C4 H15 N8 O9
	319.0965	-2.2	-6.9	3.0	48.9	C5 H14 N9 O6 Na
	319.0919	2.4	7.5	11.5	7.0	C14 H12 N6 O2 Na
	319.0917	2.6	8.1	10.0	9.6	C13 H13 N5 O5
	319.0970	-2.7	-8.5	13.5	0.9	C20 H15 O4

Supplementary Figure 158. HRMS of 1ac.



Supplementary Figure 159. The optimized NTf<sub>2</sub><sup>-</sup> activated transition states (TS-NTf<sub>2</sub> and TS-NTf<sub>2</sub>') and the amide group activated transition states (TS-Amide and TS-Amide'). The selected bond lengths are in angstroms, the relative energies  $\Delta E_{\text{sol}}$  and free energies  $\Delta G_{\text{sol}}$  (in italic, 298K) in dichloroethane are in kcal/mol.

**Supplementary Table 1. Crystal data and structure refinement for 12202013\_0m.**

Identification code	12202013_0m
Empirical formula	C <sub>37</sub> H <sub>46</sub> Au Cl N O P
Formula weight	784.13
Temperature	106(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/n
Unit cell dimensions	a = 10.0233(5) Å      a = 90° b = 18.3727(8) Å      b = 100.317(3)° c = 17.3365(9) Å      g = 90°
Volume	3141.0(3) Å <sup>3</sup>
Z	4
Density (calculated)	1.658 Mg/m <sup>3</sup>
Absorption coefficient	4.851 mm <sup>-1</sup>
F(000)	1576
Crystal size	0.15 x 0.15 x 0.10 mm <sup>3</sup>
Theta range for data collection	1.63 to 28.28°
Index ranges	-12 ≤ h ≤ 13, -23 ≤ k ≤ 24, -23 ≤ l ≤ 23
Reflections collected	21308
Independent reflections	7773 [R(int) = 0.0372]
Completeness to theta = 28.28°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7469 and 0.5890
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	7773 / 0 / 379
Goodness-of-fit on F <sup>2</sup>	1.018

Final R indices [ $I > 2\sigma(I)$ ]

R1 = 0.0248, wR2 = 0.0513

R indices (all data)

R1 = 0.0376, wR2 = 0.0549

Largest diff. peak and hole

0.884 and -0.597 e.Å<sup>-3</sup>

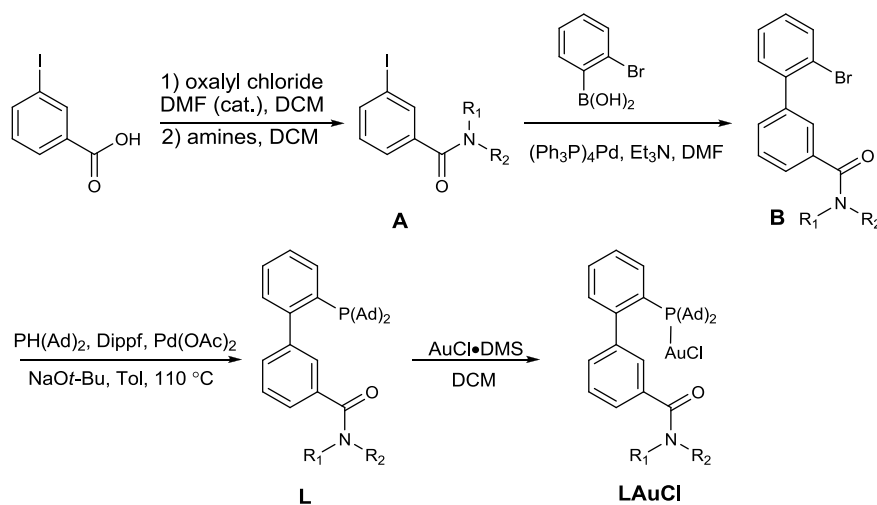
## Supplementary Methods

### General

Ethyl acetate (ACS grade), hexanes (ACS grade), diethyl ether (ACS grade), were purchased from Fisher Scientific and used without further purification. Anhydrous 1,2-dichloroethane were bought from Acros and used directly. Fluorobenzene was purchased from Synquest Labs, Inc and distilled over P<sub>2</sub>O<sub>5</sub> before use. Most commercially available carboxylic acids below 99.5% purify were recrystallized from distilled Fluorobenzene, and all commercially available alkynes were distilled over NaBH<sub>4</sub> before use. NaBAR<sup>F</sup><sub>4</sub> was purchased from Synquest Labs and dried by heating to 100 °C under high vacuum for overnight. Reactions were monitored by thin layer chromatography (TLC) using Silicycle precoated silica gel plates. Flash column chromatography was performed over Silicycle silica gel (230-400 mesh). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Varian 500/600 MHz Unity plus spectrometer and a Varian 400 MHz spectrometer using residue solvent peaks as internal standards (CDCl<sub>3</sub>, <sup>1</sup>H: 7.26 ppm; <sup>13</sup>C: 77.00 ppm). Infrared spectra were recorded with a Perkin Elmer FT-IR spectrum 2000 spectrometer and are reported in reciprocal centimeter (cm<sup>-1</sup>). Mass spectra were recorded Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer by electrospray method.



## General Procedure A: Synthesis of Ligands and Catalysts



### Step1:

To a dispersion of 10 mmol 3-iodobenzoic acid (1 equiv) in 50 mL dry  $\text{CH}_2\text{Cl}_2$  was added 25 mmol oxalyl chloride (2.5 equiv) and three drops of DMF, and the mixture was stirred for 2 - 4 h at room temperature. The reaction mixture was evaporated under reduced pressure and dried under vacuum to yield 3-iodobenzoyl chloride, which was dissolved in 50 mL dry  $\text{CH}_2\text{Cl}_2$  again and cooled in an ice bath. A 10 mL  $\text{CH}_2\text{Cl}_2$  solution containing 15 mmol amine (1.5 equiv) and 20 mmol  $\text{Et}_3\text{N}$  (2 equiv) was then added and the reaction mixture was stirred at room temperature under a nitrogen atmosphere. After 1 h, the solution was treated with 50 mL water and 100 mL DCM, and the organic phase was separated, dried, evaporated, and then purified by column chromatography to yield compound **A** in 90 - 95% yield.

### Step2:

A mixture of 8 mmol **A** (1 equiv), 8.8 mmol 2-bromophenylboronic acid (1.1 equiv) and 24 mmol  $\text{Et}_3\text{N}$  (3 equiv) in 40 mL DMF was stirred and bubbled with  $\text{N}_2$  gas for 15 minutes, and then 0.4 mmol  $\text{Pd}(\text{PPh}_3)_4$  (5 mol %) was added; the reaction mixture was heated at  $90^\circ\text{C}$  for 4 - 8 h under nitrogen atmosphere. Once TLC indicated **A** was completely consumed, the reaction was diluted with 500 mL  $\text{Et}_2\text{O}$  and washed with water to remove DMF. Then the organic layer was dried over  $\text{MgSO}_4$ , filtrated, evaporated, and then purified by column chromatography to yield product **B** in 85 - 92% yield.

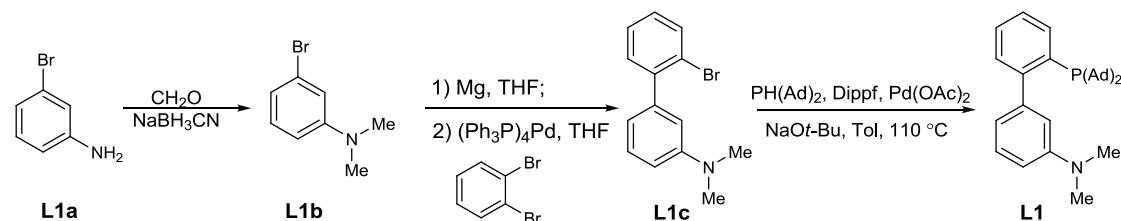
Step 3:

Under nitrogen atmosphere 2 mmol **B** (1 equiv), 0.1 mmol Pd(OAc)<sub>2</sub> (5 mol%), 0.12 mmol DiPPF (1,1'-bis(diisopropylphosphino)ferrocene, 6 mol%), 2.4 mmol NaOt-Bu (1.2 equiv) and 5 mL dry Toluene were added to a flamed dried Schlenk flask and the resulting suspension was stirred until apparently homogeneous (around 15 min). Added 2.2 mmol di(1-adamantyl)phosphine (1.1 equiv), the flask was heated at 110 °C in oil bath for 12 h, which then was cooled to room temperature, and purified by column chromatography without work-up to yield the final ligand **L** in 60 – 80% yield.

Step 4:

To a suspension of 1 mmol ligand **L** in 5 mL anhydrous DCM was added chloro(dimethylsulfide)gold(I) (294.5 mg, 1 mmol). The mixture was stirred for 30 min at room temperature and the solvent was evaporated off under reduced pressure to give the desired gold complex **LAuCl** in quantitative yield.

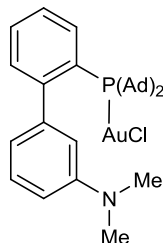
### 2'-(diadamantylphosphino)-N,N-dimethylbiphenyl-3-amine **L1**



3-Bromo-*N,N*-dimethylaniline **L1b** was prepared according to the literature procedure<sup>[47]</sup> and biaryl compound **L1c** was obtained by using same literature procedure<sup>[48]</sup>. Ligand **L1** was then synthesized in 67% yield through general procedure A, step 3. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.87 (d, *J* = 7.5 Hz, 1H), 7.40 – 7.27 (m, 3H), 7.24 – 7.18 (m, 1H), 6.74 – 6.67 (m, 1H), 6.62 – 6.55 (m, 2H), 2.95 (s, 6H), 1.90 (q, *J* = 12.2 Hz, 18H), 1.65 (s, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 152.63 (d, *J* = 32.5 Hz), 149.27, 144.77 (d, *J* = 7.5 Hz), 136.45 (*J* = 3.8 Hz), 133.10 (d, *J* = 26.3 Hz), 130.41 (d, *J* = 6.2 Hz), 127.96, 127.70, 125.08, 119.16 (d, *J* = 3.0 Hz), 115.72 (d, *J* = 3.6 Hz), 110.65, 42.00, 41.95 (d, *J* = 13.1 Hz), 37.18 (d, *J* = 26.0 Hz), 36.98, 28.87 (d, *J* = 8.5 Hz). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 22.26. IR (neat): 2901,

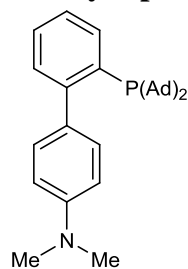
2847, 1602, 1584, 1498, 1449, 1343, 1301, 1047, 991, 955, 762, 743; HRMS ESI ( $m/z$ ): [MNa]<sup>+</sup> calcd. for C<sub>34</sub>H<sub>44</sub>NPNa, 520.3109; found, 520.3088.

### L1AuCl



Au complex **L1AuCl** was obtained in quantitative yield according to general procedure A, step 4. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.84 (t,  $J = 7.6$  Hz, 1H), 7.48 (dt,  $J = 21.5, 7.4$  Hz, 2H), 7.37 – 7.33 (m, 1H), 7.28 (bs, 1H), 6.93 (bs, 1H), 6.60 – 6.30 (m, 2H), 3.01 (s, 6H), 2.27 – 2.05 (m, 12H), 1.98 (d,  $J = 21.1$  Hz, 6H), 1.67 (d,  $J = 20.9$  Hz, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 151.42, 142.81, 134.24 (d,  $J = 2.3$  Hz), 133.12 (d,  $J = 7.3$  Hz), 130.17, 129.14, 125.95 (d,  $J = 6.2$  Hz), 123.90, 123.55, 117.48, 113.95, 112.69, 42.31 (d,  $J = 45.5, 45$  Hz), 42.14 (dd,  $J = 45.5, 2.7$  Hz), 40.84, 36.28 (d,  $J = 8.2$  Hz), 28.58 (dd,  $J_1 = J_2 = 9.9$  Hz). <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 62.61. IR (neat): 2904, 2849, 2803, 1600, 1585, 1500, 1450, 1431, 1355, 1344, 1301, 1260, 1178, 1163, 1124, 1045, 990, 972, 842, 770, 733; HRMS ESI ( $m/z$ ): [MNa]<sup>+</sup> calcd. for C<sub>34</sub>H<sub>44</sub>AuClNPNa, 754.2463; found, 754.2451.

### 2'-(diadamantylphosphino)-N,N-dimethylbiphenyl-4-amine L2

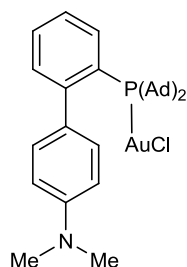


**L2**

Ligand **L2** was obtained in the same way to **L1**. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.88 (d,  $J = 7.6$  Hz, 1H), 7.35 (t,  $J = 7.3$  Hz, 1H), 7.31 – 7.23 (m, 2H), 7.13 (d,  $J = 8.4$  Hz, 2H), 6.75 – 6.70 (m, 2H), 3.00 (s, 6H), 1.90 (q,  $J = 12.2$  Hz, 18H), 1.66 (s, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 152.00 (d,  $J = 32.1$  Hz), 148.83, 136.62 (d,  $J = 2.9$  Hz), 133.19 (d,  $J = 26.3$  Hz), 132.23 (d,  $J = 7.1$  Hz), 131.29 (d,  $J = 3.9$  Hz), 131.06 (d,  $J =$

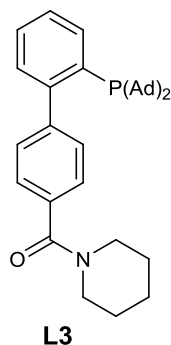
6.0 Hz), 128.08, 124.62, 111.21, 41.88 (d,  $J = 13.1$  Hz), 40.52, 37.28 (d,  $J = 25.9$  Hz), 36.97, 28.86 (d,  $J = 8.5$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  22.35 IR (neat): 3047, 2902, 2847, 1612, 1522, 1450, 1343, 1301, 1224, 1194, 1166, 1047, 970, 947, 814, 768, 743; HRMS ESI ( $m/z$ ):  $[\text{MH}]^+$  calcd. for  $\text{C}_{34}\text{H}_{45}\text{NP}$ , 498.3290; found, 498.3280.

### **L2AuCl**



Au complex **L2AuCl** was obtained in quantitative yield according to general procedure A, step 4.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) 7.83 (t,  $J = 7.5$  Hz, 1H), 7.46 (dt,  $J = 23.5, 7.6$  Hz, 2H), 7.36 – 7.29 (m, 1H), 6.97 (d,  $J = 8.1$  Hz, 2H), 6.87 (s, 2H), 3.05 (s, 6H), 2.24 – 2.05 (m, 12H), 1.98 (s, 6H), 1.67 (s, 12H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  151.06, 134.35, 133.85 (d,  $J = 7.7$  Hz), 130.27, 129.90, 129.66 (d,  $J = 7.8$  Hz), 125.94 (d,  $J = 6.5$  Hz), 124.12 (d,  $J = 45.1$  Hz), 113.37 (d,  $J = 61.3$  Hz), 42.45 (d,  $J = 23.5$  Hz), 42.09 (d,  $J = 2.5$  Hz), 36.25, 28.57 (d,  $J = 9.8$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  62.87. IR (neat): 2904, 2849, 2798, 1611, 1523, 1448, 1347, 1301, 1223, 1166, 1126, 1045, 972, 913, 815, 773, 744; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{34}\text{H}_{45}\text{AuClNPNa}$ , 752.2463; found, 752.2448.

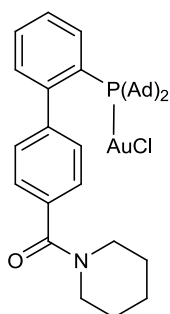
### **(2'-(diadamantylphosphino)biphenyl-4-yl)(piperidin-1-yl)methanone L3**



Ligand **L3** was obtained according to general procedure A.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J = 7.5$  Hz, 1H), 7.40 – 7.31 (m, 4H), 7.26 (t,  $J = 3.9$  Hz, 3H), 7.22

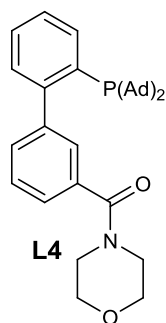
(ddd,  $J = 7.3, 4.0, 1.7$  Hz, 1H), 3.72 (bs, 2H), 3.47 (bs, 2H), 1.85 (q,  $J = 12.7$  Hz, 18H), 1.67 (m, 18 H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.57, 150.98 (d,  $J = 32.7$  Hz), 145.27 (d,  $J = 6.9$  Hz), 136.62 (d,  $J = 2.6$  Hz), 133.78, 133.11 (d,  $J = 29.0$  Hz), 130.68 (d,  $J = 4.1$  Hz), 130.50 (d,  $J = 6.2$  Hz), 128.19, 125.94, 125.53, 48.84, 43.26, 41.80 (d,  $J = 13.0$  Hz), 37.34 (d,  $J = 26.2$  Hz), 36.89, 28.78 (d,  $J = 8.6$  Hz), 26.53, 25.72, 24.67.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  20.64. IR (neat): 2911, 2861, 1627 (C=O), 1443, 1347, 1274, 1157, 1023, 751; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{38}\text{H}_{48}\text{NOPNa}$ , 588.3371; found, 588.3395.

### L3AuCl



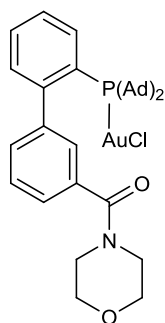
Au complex **L3AuCl** was obtained in quantitative yield according to general procedure A, step 4.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 – 7.84 (m, 1H), 7.50 (d,  $J = 7.7$  Hz, 4H), 7.16 (t,  $J = 7.5$  Hz, 3H), 4.05 – 3.60 (m, 4H), 2.26 – 2.09 (m, 12H), 2.01 (s, 6H), 1.69 (s, 18H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.85, 150.07 (d,  $J = 13.0$  Hz), 143.89 (d,  $J = 6.3$  Hz), 136.25, 134.36 (d,  $J = 2.3$  Hz), 133.94 (d,  $J = 7.5$  Hz), 130.48 (d,  $J = 2.3$  Hz), 129.68, 127.68, 126.44 (d,  $J = 6.4$  Hz), 123.03 (d,  $J = 43.5$  Hz), 49.77, 43.41, 42.66 (d,  $J = 23.9$  Hz), 42.13 (d,  $J = 2.5$  Hz), 36.23, 28.57 (d,  $J = 9.8$  Hz), 36.97, 25.78, 24.74.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  62.19. IR (neat): 2911, 2851, 1627 (C=O), 1443, 1347, 1274, 1157, 1023, 751; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $^{38}\text{H}_{48}\text{AuClINNaOP}$ , 820.2725; found, 820.2709.

### (2'-(diadamantylphosphino)biphenyl-3-yl)(morpholino)methanone **L4**



Ligand **L4** was obtained according to general procedure A.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (dd,  $J = 5.2, 3.7$  Hz, 1H), 7.45 – 7.33 (m, 4H), 7.31 – 7.27 (m, 1H), 7.25 – 7.19 (m, 2H), 3.86 – 3.39 (m, 8H), 1.84 (dd,  $J = 29.2, 9.6$  Hz, 18H), 1.64 (q,  $J = 12.6$  Hz, 12H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.64, 150.66 (d,  $J = 32.2$  Hz), 143.89 (d,  $J = 7.1$  Hz), 136.54 (d,  $J = 2.7$  Hz), 134.04, 132.87 (d,  $J = 27.6$  Hz), 132.44 (d,  $J = 4.1$  Hz), 130.54 (d,  $J = 6.1$  Hz), 128.71 (d,  $J = 3.8$  Hz), 128.44 (d,  $J = 1.1$  Hz), 127.62, 125.81, 125.33, 67.02, 48.51, 42.48, 41.92 (d,  $J = 12.8$  Hz), 37.43 (d,  $J = 25.2$  Hz), 36.89, 28.76 (d,  $J = 8.6$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  21.17. IR (neat): 2902, 2848, 1639 (C=O), 1450, 1301, 1273, 1166, 1115, 1018, 807, 743; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{37}\text{H}_{46}\text{NO}_2\text{PNa}$ , 590.3164; found, 590.3174.

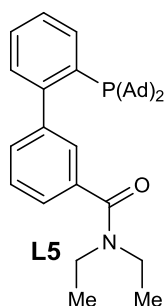
### **L4AuCl**



Au complex **L4AuCl** was obtained in quantitative yield according to general procedure A, step 4.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 – 7.84 (m, 1H), 7.57 (d,  $J = 7.8$  Hz, 1H), 7.54 – 7.46 (m, 3H), 7.30 – 7.26 (m, 1H), 7.18 – 7.10 (m, 2H), 4.03 – 3.48 (m, 8H), 2.27 – 2.13 (m, 6H), 2.04 (dd,  $J = 44.5, 13.8$  Hz, 12H), 1.75 – 1.59 (m, 12H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  170.11, 149.56 (d,  $J = 12.9$  Hz), 142.81 (d,  $J = 6.4$  Hz), 135.49, 134.32, 133.53 (d,  $J = 7.3$  Hz), 130.82, 130.57 (d,  $J = 2.1$  Hz),

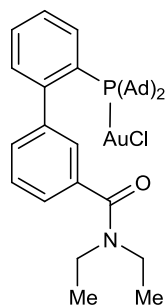
129.11, 127.69, 127.07, 126.66 (d,  $J = 6.6$  Hz), 123.48 (d,  $J = 43.8$  Hz), 67.55, 66.88, 48.80, 48.67, 42.65 (dd,  $J = 30.6, 23.7$  Hz), 42.19 (d,  $J = 45.5$  Hz), 36.23 (d,  $J = 8.0$  Hz), 28.52 (dd,  $J = 16.5, 9.8$  Hz).  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  62.31. IR (neat): 2908, 2851, 1738, 1634 (C=O), 1460, 1347, 1302, 1264, 1157, 1114, 1045, 799, 748; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{37}\text{H}_{46}\text{AuClINNaO}_2\text{P}$ , 822.2518; found, 822.2507.

### 2'-(diadamantylphosphino)-N,N-diethylbiphenyl-3-carboxamide **L5**



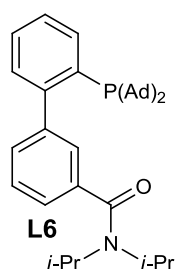
Ligand **L5** was obtained according to general procedure A.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (d,  $J = 7.5$  Hz, 1H), 7.41 – 7.33 (m, 3H), 7.33 – 7.25 (m, 3H), 7.22 (s, 1H), 3.49 (m, 4H), 1.96 – 1.78 (m, 18H), 1.70 – 1.52 (m, 12H), 1.36 – 0.98 (m, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.46, 150.89 (d,  $J = 32.1$  Hz), 143.63 (d,  $J = 7.0$  Hz), 136.54 (d,  $J = 2.6$  Hz), 135.91, 132.90 (d,  $J = 28.0$  Hz), 131.67 (d,  $J = 4.4$  Hz), 130.56 (d,  $J = 6.1$  Hz), 128.50 (d,  $J = 3.9$  Hz), 128.40 (d,  $J = 1.0$  Hz), 127.23, 125.63, 124.31, 43.36, 41.88 (d,  $J = 12.9$  Hz), 39.12, 37.39 (d,  $J = 25.7$  Hz), 36.89, 28.76 (d,  $J = 8.6$  Hz), 14.28, 12.97.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  21.01. IR (neat): 2902, 2847, 1635 (C=O), 1449, 1345, 1303, 1218, 1100, 970, 767, 731; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{37}\text{H}_{48}\text{NOPNa}$ , 576.3371; found, 576.3395.

### **L5AuCl**



Au complex **L5AuCl** was obtained in quantitative yield according to general procedure A, step 4.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 – 7.79 (m, 1H), 7.54 – 7.44 (m, 4H), 7.32 (dd,  $J = 9.1, 4.3$  Hz, 1H), 7.16 (d,  $J = 7.4$  Hz, 1H), 7.11 (s, 1H), 3.84 – 3.29 (m, 4H), 2.34 – 2.16 (m, 6H), 2.16 – 1.93 (m, 12H), 1.78 – 1.52 (m, 12H), 1.18 (dt,  $J = 45.6, 7.0$  Hz, 6H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.17, 149.86 (d,  $J = 12.6$  Hz), 142.68 (d,  $J = 6.3$  Hz), 137.60, 134.29 (d,  $J = 2.3$  Hz), 133.71 (d,  $J = 7.4$  Hz), 130.53 (d,  $J = 2.3$  Hz), 130.23, 129.01, 127.00, 126.51 (d,  $J = 6.6$  Hz), 126.00, 123.46 (d,  $J = 43.8$  Hz), 43.62, 42.61 (dd,  $J = 46.3, 23.6$  Hz), 42.18 (dd,  $J = 60.1, 2.6$  Hz) 39.13, 36.24, 28.54 (dd,  $J = 17.8, 9.8$  Hz) 14.54, 12.86.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  62.36. IR (neat): 2908, 2851, 1629 (C=O), 1451, 1346, 1302, 1159, 1071, 1046, 771, 747; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{37}\text{H}_{48}\text{AuClINNaOP}$ , 808.2725; found, 808.2700.

### 2'-(diadamantylphosphino)-N,N-diisopropylbiphenyl-3-carboxamide **L6**

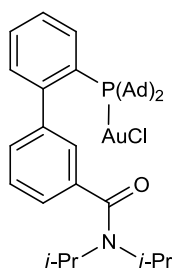


Ligand **L6** was obtained according to general procedure A.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J = 7.5$  Hz, 1H), 7.41 – 7.31 (m, 3H), 7.31 – 7.26 (m, 2H), 7.22 (dt,  $J = 7.4, 1.4$  Hz, 1H), 7.17 (t,  $J = 1.5$  Hz, 1H), 4.2 – 3.2 (m, 2H), 1.94 – 1.78 (m, 18H), 1.70 – 1.59 (m, 12H), 1.59 – 0.9 (m, 12H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  171.24, 151.01 (d,  $J = 32.1$  Hz), 143.90 (d,  $J = 6.9$  Hz), 137.85, 136.58 (d,  $J = 2.7$  Hz), 132.76 (d,  $J = 27.9$  Hz), 131.57 (d,  $J = 5.3$  Hz), 130.78 (d,  $J = 6.2$  Hz), 128.38 (d,  $J =$



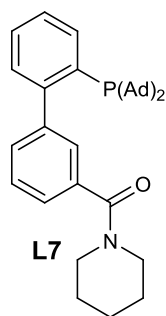
1.1 Hz), 127.43 (d,  $J = 2.6$  Hz), 126.95, 125.54, 123.40, 50.72, 45.91, 41.89 (d,  $J = 12.9$  Hz), 37.41 (d,  $J = 25.6$  Hz), 36.90, 28.80 (d,  $J = 8.6$  Hz), 20.79.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  21.17. IR (neat): 2905, 2849, 1738, 1634 (C=O), 1445, 1373, 1340, 1212, 1158, 1041, 768; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{39}\text{H}_{52}\text{NOPNa}$ , 604.3684; found, 604.3694.

### **L6AuCl**



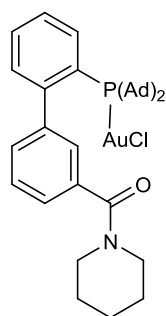
Au complex **L6AuCl** was obtained in quantitative yield according to general procedure A, step 4.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (t,  $J = 7.9$  Hz, 1H), 7.50 (q,  $J = 6.0, 4.2$  Hz, 2H), 7.47 – 7.41 (m, 2H), 7.31 (t,  $J = 5.1$  Hz, 1H), 7.12 (d,  $J = 7.0$  Hz, 1H), 7.02 (s, 1H), 4.53 (bs, 1H), 3.49 (bs, 1H), 2.29 – 2.18 (m, 6H), 2.14 – 2.00 (m, 12H), 1.96 (s, 3H), 1.77 – 1.45 (m, 15H), 1.30 – 1.19 (m, 3H), 1.08 – 0.96 (m, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  170.95, 149.94 (d,  $J = 13.1$  Hz), 142.76 (d,  $J = 6.5$  Hz), 139.05, 134.25, 133.68 (d,  $J = 7.3$  Hz), 130.45, 129.59, 129.10, 126.46 (d,  $J = 6.5$  Hz), 126.31, 124.97, 123.46 (d,  $J = 43.9$  Hz), 51.38, 45.92, 42.53 (d,  $J = 93.5$  Hz, 23.6 Hz), 42.17 (d,  $J = 82.5$  Hz), 36.24, 28.54 (dd,  $J = 27.1, 9.8$  Hz), 21.07, 20.67, 20.53.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  62.37. IR (neat): 2917, 2850, 1736, 1628 (C=O), 1577, 1540, 1448, 1373, 1343, 1301, 1211, 1105, 1019, 973, 772, 747, 710; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{39}\text{H}_{52}\text{AuClINNaOP}$ , 836.3038; found, 836.3021.

### **(2'-(diadamantylphosphino)biphenyl-3-yl)(piperidin-1-yl)methanone L7**



Ligand **L7** was obtained according to general procedure A.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 – 7.84 (m, 1H), 7.41 – 7.31 (m, 4H), 7.29 (ddd,  $J = 7.3, 2.6, 1.6$  Hz, 1H), 7.26 – 7.23 (m, 1H), 7.20 (d,  $J = 1.6$  Hz, 1H), 3.71 (s, 2H), 3.47 (s, 2H), 1.85 (q,  $J = 11.9$  Hz, 18H), 1.69 – 1.39 (m, 18H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.52, 150.92 (d,  $J = 32.3$  Hz), 143.70 (d,  $J = 7.1$  Hz), 136.53 (d,  $J = 2.6$  Hz), 135.31, 132.92 (d,  $J = 27.9$  Hz), 132.10 (d,  $J = 4.7$  Hz), 130.58 (d,  $J = 6.1$  Hz), 128.41 (d,  $J = 3.1$  Hz), 128.37 (d,  $J = 1.1$  Hz), 127.29, 125.65, 125.02, 48.95, 43.12, 41.89 (d,  $J = 12.9$  Hz), 37.41 (d,  $J = 25.5$  Hz), 36.91, 28.79 (d,  $J = 8.6$  Hz), 26.68, 25.62, 24.63.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  21.12. IR (neat): 2901, 2847, 1630 (C=O), 1443, 1343, 1300, 1265, 1228, 1110, 1026, 1002, 970, 907, 826, 809, 765, 731; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{38}\text{H}_{48}\text{NOPNa}$ , 588.3371; found, 588.3361.

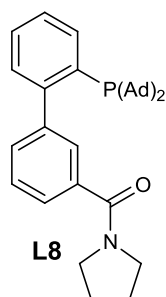
### **L7AuCl**



Au complex **L7AuCl** was obtained in quantitative yield according to general procedure A, step 4.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 – 7.82 (m, 1H), 7.55 (d,  $J = 7.8$  Hz, 1H), 7.52 – 7.45 (m, 3H), 7.31 – 7.27 (m, 1H), 7.14 (d,  $J = 7.6$  Hz, 1H), 7.11 (s, 1H), 3.86 – 3.53 (m, 4H), 2.28 – 1.91 (m, 18H), 1.84 – 1.42 (m, 18H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  170.05, 149.81 (d,  $J = 12.9$  Hz), 142.54 (d,  $J = 6.6$  Hz), 136.66, 134.29, 134.27, 133.57 (d,  $J = 7.3$  Hz), 130.50 (d,  $J = 2.2$  Hz), 130.35, 129.05, 127.38,

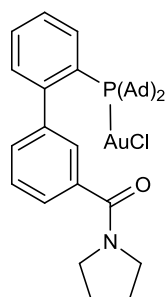
126.70, 126.53 (d,  $J = 6.6$  Hz), 123.49 (d,  $J = 43.9$  Hz), 49.33, 43.16, 42.61 ( $J = 37.5$  Hz, 23.8 Hz), 42.16 (dd,  $J = 55.0, 2.6$  Hz) 36.25, 36.23, 36.22, 28.54 (dd,  $J = 15.1, 9.8$  Hz), 26.78, 25.75, 24.66.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  62.26. IR (neat): 2906, 2851, 2231, 1625 (C=O), 1444, 1344, 1301, 1253, 1228, 1109, 1042, 1002, 972, 915, 852, 804, 772, 729; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd.  $\text{C}_{38}\text{H}_{48}\text{AuCINNaOP}$ , 820.2725; found, 820.2717.

## (2'-(diadamantylphosphino)biphenyl-3-yl)(pyrrolidin-1-yl)methanone **L8**



Ligand **L8** was obtained according to general procedure A.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 – 7.85 (m, 1H), 7.48 (dt,  $J = 7.6, 1.4$  Hz, 1H), 7.42 – 7.31 (m, 4H), 7.29 (d,  $J = 7.6$  Hz, 1H), 7.25 – 7.21 (m, 1H), 3.65 (t,  $J = 7.0$  Hz, 2H), 3.53 (t,  $J = 6.6$  Hz, 2H), 2.00 – 1.78 (m, 22H), 1.72 – 1.55 (m, 12H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.91, 150.94 (d,  $J = 32.3$  Hz), 143.51 (d,  $J = 7.0$  Hz), 136.52 (d,  $J = 2.7$  Hz), 136.01, 132.93 (d,  $J = 27.7$  Hz), 132.33 (d,  $J = 4.3$  Hz), 130.60 (d,  $J = 6.1$  Hz), 128.90 (d,  $J = 3.6$  Hz), 128.35 (d,  $J = 1.1$  Hz), 127.25, 125.65, 125.31, 49.90, 46.04, 41.89 (d,  $J = 12.9$  Hz), 37.35 (d,  $J = 25.5$  Hz), 36.90, 28.78 (d,  $J = 8.6$  Hz), 26.40, 24.54.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  22.10. IR (neat): 2901, 2847, 1628 (C=O), 1424, 1342, 1301, 1253, 1162, 1047, 971, 921, 808, 767, 730; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{37}\text{H}_{46}\text{NOPNa}$ , 574.3215; found, 574.3214.

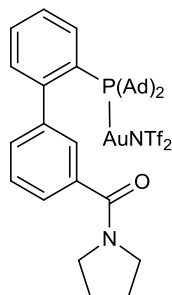
## **L8AuCl**



Au complex **L8AuCl** was obtained in quantitative yield according to general procedure A, step 4.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (t,  $J = 8.1$  Hz, 1H), 7.69 (d,  $J = 7.8$  Hz, 1H), 7.54 – 7.42 (m, 3H), 7.29 (d,  $J = 18.1$  Hz, 2H), 7.16 (d,  $J = 7.6$  Hz, 1H), 3.93 – 3.53 (m, 4H), 2.30 – 1.79 (m, 22H), 1.73 – 1.59 (m, 12H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  169.23, 149.83 (d,  $J = 13.0$  Hz), 142.46 (d,  $J = 6.4$  Hz), 136.92, 134.28 (d,  $J = 2.4$  Hz), 133.66 (d,  $J = 7.4$  Hz), 130.94, 130.51 (d,  $J = 2.4$  Hz), 128.61, 128.14,

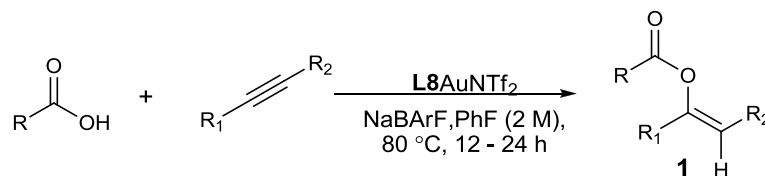
127.22, 126.54 (d,  $J = 6.5$  Hz), 123.52 (d,  $J = 43.7$  Hz), 50.16, 46.42, 42.58 (dd,  $J = 23.7, 11.7$  Hz), 42.16 (dd,  $J = 28.6, 2.6$  Hz), 36.23, 28.54 (dd,  $J = 9.9, 7.1$  Hz), 26.57, 24.43.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  62.32. IR (neat): 2906, 2851, 2232, 1620 (C=O), 1598, 1575, 1442, 1344, 1301, 1259, 1198, 1104, 1045, 972, 914, 806, 772, 730; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{37}\text{H}_{46}\text{AuClINaOP}$ , 806.2569; found, 806.2565.

### **L8AuNTf<sub>2</sub>**



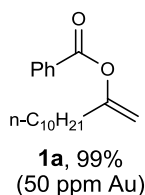
To a suspension of 0.95 mmol Au complex **L8AuCl** in vial with 5 mL anhydrous DCM was added  $\text{AgNTf}_2$  (0.95 mmol). The mixture was stirred for 30 min at room temperature and the vial was left in a centrifuge for 5 min after which  $\text{AgCl}$  all stayed in the bottom. After passing through a Teflon syringe filter (0.2  $\mu\text{m}$ ), the solvent was evaporated off under reduced pressure to give the desired gold complex **L8AuNTf<sub>2</sub>** in 95% yield.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 – 7.85 (m, 1H), 7.68 (d,  $J = 7.7$  Hz, 1H), 7.62 – 7.53 (m, 3H), 7.35 (bs, 1H), 7.30 (d,  $J = 7.3$  Hz, 1H), 7.24 (bs, 1H), 3.72 – 3.40 (m, 4H), 2.24 – 1.82 (m, 22H), 1.76 – 1.53 (m, 12H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  169.75, 148.81 (d,  $J = 10.6$  Hz), 142.12, 136.21, 134.06, 133.59 (d,  $J = 7.4$  Hz), 131.69, 131.29, 128.88, 127.66 (d,  $J = 87.8$  Hz), 127.11 (d,  $J = 7.4$  Hz), 121.30 (d,  $J = 44.7$  Hz), 119.62 (dd,  $J = 324$  Hz), 50.24, 46.92, 43.08 (d,  $J = 24.6$  Hz), 42.14 (d,  $J = 38.5$  Hz), 36.03, 28.48 (dd,  $J = 12.3, 10.2$  Hz), 26.20, 24.24.  $^{31}\text{P}$  NMR (162 MHz,  $\text{CDCl}_3$ )  $\delta$  61.10. IR (neat): 2908, 2853, 1622 (C=O), 1596, 1575, 1451, 1354, 1229, 1196, 1138, 1061; HRMS ESI<sup>+</sup> ( $m/z$ ):  $[\text{M-NTf}_2]^+$  calcd. for  $\text{C}_{37}\text{H}_{46}\text{NOAuP}$ , 748.2983; found, 748.2975; ESI<sup>-</sup> ( $m/z$ ):  $[\text{M-L8Au}]^-$  calcd. For  $\text{C}_2\text{NO}_4\text{S}_2\text{F}_6$ , 279.9173; found, 279.9159.

## General procedure B: Preparation of Enol Esters **1** (50 ppm)



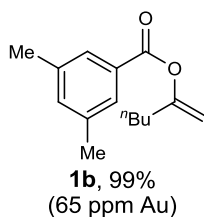
In a sealed 1 dr reaction vial equipped with a magnetic stirring bar, 3 mmol carboxylic acids (1 equiv), 4.4 mmol 1-hexyne (1.45 equiv) or 3.6 mmol other alkynes (1.2 equiv) and 3.1 mg NaBArF<sub>4</sub> (1200 ppm) were added to 0.6 mL fluorobenzene. L8AuNTf<sub>2</sub> (50 μL of a 3.09 mg/mL solution in PhF, 0.150 μmol, 50 ppm) was added to the above vial and then the reaction mixture was heated at 80 °C for 12 - 24 h. Once the reaction finished by TLC, it was concentrated and left on the high vacuum pump for overnight to give the NMR pure product. If crude NMR was not pure, the residue was further purified through silica gel flash chromatography to give the desired product **1**.

### dodec-1-en-2-yl benzoate **1a**



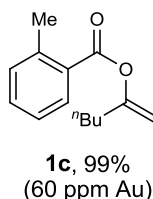
857 mg Compound **1a** was obtained in 99% yield according to general procedure B after chromatography (eluent: ethyl acetate: hexanes = 1: 30). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.14 – 8.05 (m, 2H), 7.63 – 7.55 (m, 1H), 7.51 – 7.42 (m, 2H), 4.84 (dt, *J* = 12.5, 2.0 Hz, 2H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.58 – 1.48 (m, 2H), 1.40 – 1.19 (m, 14H), 0.88 (t, *J* = 7.0 Hz, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 164.74, 156.83, 133.23, 129.92, 129.90, 128.42, 101.27, 33.43, 31.88, 29.56, 29.52, 29.35, 29.30, 28.99, 26.54, 22.66, 14.09. IR (neat): 3118, 2954, 2925, 2854, 1733 (C=O), 1666, 1602, 1454, 1378, 1314, 1270, 1222, 1172, 1068, 863, 705; HRMS ESI (*m/z*): [MNa]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>29</sub>O<sub>2</sub>Na, 311.1987; found, 311.1981.

### hex-1-en-2-yl 3,5-dimethylbenzoate **1b**



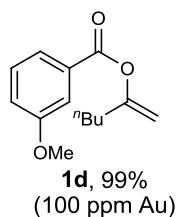
693 mg Compound **1b** was obtained in 99% yield according to general procedure B without chromatography.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (s, 2H), 7.23 (s, 1H), 4.83 (d,  $J = 0.5$  Hz, 2H), 2.38 (d,  $J = 0.5$  Hz, 6H), 2.35 (t,  $J = 7.5$  Hz, 2H), 1.59 – 1.48 (m, 2H), 1.45 – 1.34 (m, 2H), 0.92 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  165.07, 156.88, 138.09, 134.88, 129.73, 127.58, 101.16, 33.10, 28.64, 22.11, 21.11, 13.81. IR (neat): 3116, 2958, 2931, 2873, 2864, 1732 (C=O), 1667, 1610, 1466, 1382, 1204, 867, 761; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{15}\text{H}_{20}\text{O}_2\text{Na}$ , 255.1361; found, 255.1342.

### hex-1-en-2-yl 2-methylbenzoate **1c**



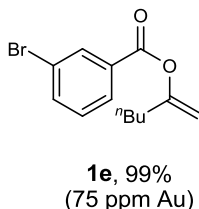
652 mg Compound **1c** was obtained in 99% yield according to general procedure B without chromatography.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 – 7.92 (m, 1H), 7.43 (td,  $J = 7.5, 1.3$  Hz, 1H), 7.34 – 7.16 (m, 2H), 4.84 (dd,  $J = 6.1, 1.2$  Hz, 2H), 2.64 (s, 3H), 2.35 (t,  $J = 7.5$  Hz, 2H), 1.63 – 1.47 (m, 2H), 1.46 – 1.34 (m, 2H), 0.93 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  165.49, 156.79, 140.81, 132.31, 131.79, 130.86, 129.01, 125.75, 101.23, 33.15, 28.66, 22.10, 21.79, 13.82. IR (neat): 3072, 2957, 2932, 2873, 2864, 1735 (C=O), 1666, 1603, 1458, 1383, 1294, 865, 737; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{14}\text{H}_{18}\text{O}_2\text{Na}$ , 241.1204; found, 241.1199.

### hex-1-en-2-yl 3-methoxybenzoate **1d**



698 mg Compound **1d** was obtained in 99% yield according to general procedure B without chromatography.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 – 7.64 (m, 1H), 7.59 (dd,  $J = 2.5, 1.5$  Hz, 1H), 7.36 (dd,  $J = 10.3, 5.6$  Hz, 1H), 7.12 (ddd,  $J = 8.2, 2.7, 0.8$  Hz, 1H), 4.84 (dd,  $J = 15.3, 1.4$  Hz, 2H), 3.85 (s, 3H), 2.34 (t,  $J = 7.8$  Hz, 2H), 1.57 – 1.46 (m, 2H), 1.45 – 1.31 (m, 2H), 0.92 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  164.55, 159.55, 156.75, 131.14, 129.40, 122.24, 119.71, 114.25, 101.22, 55.36, 33.06, 28.61, 22.05, 13.78. IR (neat): 3078, 2957, 2932, 2873, 2864, 1735 (C=O), 1666, 1586, 1488, 1466, 1432, 1278, 1213, 869, 750; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{14}\text{H}_{18}\text{O}_3\text{Na}$ , 257.1154; found, 257.1151.

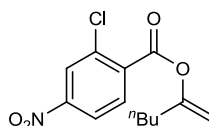
### hex-1-en-2-yl 3-bromobenzoate **1e**



845 mg Compound **1e** was obtained in 99% yield according to general procedure B without chromatography.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.21 (t,  $J = 1.8$  Hz, 1H), 8.05 – 7.94 (m, 1H), 7.70 (ddd,  $J = 8.0, 2.0, 1.1$  Hz, 1H), 7.34 (dd,  $J = 9.9, 5.9$  Hz, 1H), 4.84 (dt,  $J = 3.7, 1.5$  Hz, 2H), 2.33 (t,  $J = 7.5$ , 2H), 1.51 (tdd,  $J = 8.4, 7.3, 5.1$  Hz, 2H), 1.38 (dq,  $J = 14.4, 7.3$  Hz, 2H), 0.92 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  163.36, 156.61, 136.15, 132.82, 131.81, 129.98, 128.43, 122.49, 101.47, 33.00, 28.59, 22.06, 13.78. IR (neat): 3070, 2959, 2932, 2873, 2864, 1737 (C=O), 1668, 1571, 1468, 1423, 1291, 1251, 1233, 1173, 1116, 1067, 869, 806, 742; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{13}\text{H}_{15}\text{BrO}_2\text{Na}$ , 305.0153; found, 305.0144.



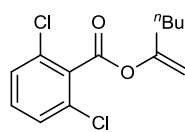
### hex-1-en-2-yl 2-chloro-4-nitrobenzoate **1f**



**1f**, 99%  
(75 ppm Au)

847 mg Compound **1f** was obtained in 99% yield according to general procedure B without chromatography.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.31 (d,  $J = 2.2$  Hz, 1H), 8.17 (dd,  $J = 8.6, 2.2$  Hz, 1H), 8.08 – 7.93 (m, 1H), 5.16 – 4.67 (m, 2H), 2.34 (t,  $J = 7.6$  Hz, 2H), 1.57 – 1.47 (m, 2H), 1.38 (dq,  $J = 14.4, 7.3$  Hz, 3H), 0.91 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  162.18, 156.36, 149.49, 135.48, 134.90, 132.12, 126.00, 121.45, 101.90, 32.80, 32.80, 28.47, 28.47, 21.97, 21.97, 13.73, 13.73. IR (neat): 3041, 2959, 2931, 2873, 2864, 1745 (C=O), 1668, 1590, 1528, 1467, 1388, 1348, 1280, 1220, 1127, 1042, 860, 764, 732; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{13}\text{H}_{14}\text{ClNO}_4\text{Na}$ , 306.0509; found, 306.0508.

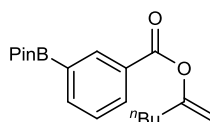
### hex-1-en-2-yl 2,6-dichlorobenzoate **1g**



**1g**, 99%  
(50 ppm Au)

816 mg Compound **1g** was obtained in 99% yield according to general procedure B without chromatography.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 – 7.25 (m, 3H), 4.97 (d,  $J = 1.9$  Hz, 1H), 4.88 (q,  $J = 1.3$  Hz, 1H), 2.41 – 2.34 (m, 2H), 1.62 – 1.52 (m, 2H), 1.45 – 1.35 (m, 2H), 0.93 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) 162.82, 156.55, 133.28, 131.80, 130.98, 127.85, 101.94, 32.86, 28.42, 22.02, 13.79. IR (neat): 3087, 2959, 2933, 2874, 1756 (C=O), 1670, 1586, 1565, 1434, 1381, 1272, 1225, 1196, 1166, 1139, 1082, 1053, 931, 881, 802, 780, 746; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{13}\text{H}_{14}\text{Cl}_2\text{O}_2\text{Na}$ , 295.0269; found, 295.0256.

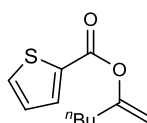
### hex-1-en-2-yl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate **1h**



**1h**, 99%  
(150 ppm Au)

987 mg Compound **1h** was obtained in 99% yield according to general procedure B without chromatography.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.52 (d,  $J = 18.9$  Hz, 1H), 8.16 (dt,  $J = 7.8, 1.5$  Hz, 1H), 8.01 (d,  $J = 7.4$  Hz, 1H), 7.46 (dd,  $J = 9.3, 5.9$  Hz, 1H), 4.93 – 4.71 (m, 2H), 2.35 (dd,  $J = 23.6, 16.1$  Hz, 2H), 1.57 – 1.44 (m, 2H), 1.43 – 1.26 (m, 16H), 0.91 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  164.76, 156.84, 139.45, 136.05, 132.53, 129.26, 127.80, 101.17, 84.04, 43.36, 33.04, 28.58, 24.79, 22.07, 13.77. IR (neat): 3065, 2979, 2960, 2933, 2874, 1735 (C=O), 1667, 1606, 1422, 1362, 1327, 1248, 1222, 1144, 965, 857, 753; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{18}\text{H}_{27}\text{BO}_4\text{Na}$ , 353.1900; found, 353.1887.

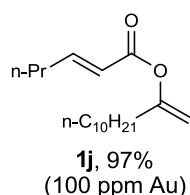
### hex-1-en-2-yl thiophene-2-carboxylate **1i**



**1i**, 99%  
(50 ppm Au)

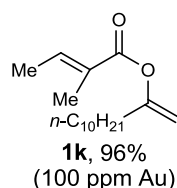
627 mg Compound **1i** was obtained in 99% yield according to general procedure B without chromatography.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 – 7.80 (m, 1H), 7.68 – 7.51 (m, 1H), 7.19 – 7.05 (m, 1H), 4.87 (d,  $J = 1.3$  Hz, 1H), 4.81 (s, 1H), 2.32 (t,  $J = 7.5$  Hz, 2H), 1.70 – 1.48 (m, 2H), 1.45 – 1.25 (m, 2H), 0.91 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  160.16, 156.34, 134.03, 133.30, 132.92, 127.80, 101.38, 33.08, 28.55, 22.02, 13.77. IR (neat): 3116, 2956, 2932, 2873, 2864, 1725 (C=O), 1667, 1524, 1417, 1254, 1071, 864, 744; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{11}\text{H}_{14}\text{O}_4\text{SNa}$ , 233.0612; found, 233.0605.

**(E)-hex-1-en-2-yl hex-2-enoate 1j**



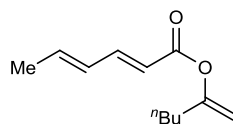
814 mg Compound **1j** was obtained in 97% yield according to general procedure B after chromatography (eluent: ethyl acetate: hexanes = 1: 30).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.03 (dt,  $J = 15.6, 6.9$  Hz, 1H), 5.85 (dt,  $J = 15.4, 1.5$  Hz, 1H), 4.72 (d,  $J = 2.5$  Hz, 2H), 2.25 – 2.15 (m, 4H), 1.55 – 1.42 (m, 4H), 1.33 – 1.21 (m, 14H), 0.94 (t,  $J = 7.3$  Hz, 3H), 0.87 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  164.68, 156.58, 150.64, 120.88, 100.85, 100.84, 34.26, 33.37, 31.87, 29.55, 29.51, 29.34, 29.29, 28.97, 26.44, 22.65, 21.18, 14.06, 13.63. IR (neat): 3056, 2956, 2928, 2856, 1737 (C=O), 1654, 1466, 1379, 1319, 1218, 1158, 1120, 983, 866; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{18}\text{H}_{32}\text{O}_2\text{Na}$ , 303.2300; found, 303.2307.

**(E)-hex-1-en-2-yl 2-methylbut-2-enoate 1k**



766 mg Compound **1j** was obtained in 96% yield according to general procedure B after chromatography (eluent: ethyl acetate: hexanes = 1: 30).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.92 (dddd,  $J = 8.4, 7.1, 5.8, 1.4$  Hz, 1H), 4.78 – 4.58 (m, 2H), 2.23 (t,  $J = 7.5$  Hz, 2H), 1.87 – 1.84 (m, 3H), 1.81 (dd,  $J = 7.1, 1.0$  Hz, 3H), 1.49 – 1.41 (m, 2H), 1.34 (dq,  $J = 14.3, 7.1$  Hz, 2H), 0.89 (t,  $J = 7.3$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.17, 156.88, 138.35, 128.39, 100.72, 33.07, 28.63, 22.06, 14.43, 13.79, 12.02. IR (neat): 3118, 2957, 2927, 2856, 1720 (C=O), 1666, 1654, 1467, 1380, 1342, 1264, 1225, 1145, 1124, 1068, 868, 729; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{17}\text{H}_{30}\text{NaO}_2$ , 289.2144; found, 289.2138.

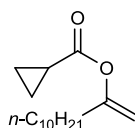
### (2E, 4E)-hex-1-en-2-yl hexa-2,4-dienoate **1l**



**1l**, 99%  
(65 ppm Au)

580 mg Compound **1l** was obtained in 99% yield according to general procedure B without chromatography.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.20 (m, 1H), 6.30 – 6.06 (m, 2H), 5.79 (dd,  $J = 19.5, 15.7$  Hz, 1H), 4.78 – 4.67 (m, 2H), 2.23 (t,  $J = 7.5, 2\text{H}$ ), 1.86 (d,  $J = 5.8$  Hz, 3H), 1.50 – 1.40 (m, 2H), 1.34 (dq,  $J = 14.3, 7.1$  Hz, 2H), 0.89 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  165.33, 156.60, 146.12, 140.06, 129.68, 118.37, 100.85, 33.10, 28.57, 22.07, 18.65, 13.79. IR (neat): 3029, 2960, 2930, 2874, 2864, 1728 (C=O), 1646, 1617, 1329, 1228, 1177, 1128, 1000, 867; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{12}\text{H}_{18}\text{NaO}_2$ , 217.1204; found, 217.1205.

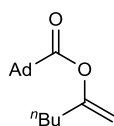
### dodec-1-en-2-yl cyclopropanecarboxylate **1m**



**1m**, 99%  
(75 ppm Au)

748 mg Compound **1m** was obtained in 99% yield according to general procedure B after chromatography (eluent: ethyl acetate: hexanes = 1: 30).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.69 (d,  $J = 2.8$  Hz, 2H), 2.18 (t,  $J = 7.6$  Hz, 2H), 1.65 (qd,  $J = 6.8, 5.6, 2.7$  Hz, 1H), 1.45 (p,  $J = 7.4$  Hz, 2H), 1.27 (d,  $J = 12.5$  Hz, 15H), 1.08 – 1.02 (m, 2H), 0.93 – 0.89 (m, 2H), 0.87 (t,  $J = 6.8$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  173.00, 156.63, 100.78, 33.29, 31.87, 29.56, 29.51, 29.35, 29.30, 28.96, 28.96, 26.42, 22.65, 14.07, 12.93, 8.74. HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{11}\text{H}_{14}\text{O}_4\text{SNa}$ , 275.1987; found, 275.1971.

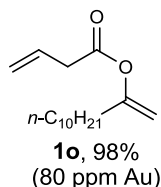
### hex-1-en-2-yl adamantylcarboxylate **1n**



**1n** 99%  
(100 ppm Au)

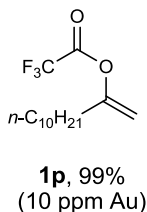
778 mg Compound **1n** was obtained in 99% yield according to general procedure B after chromatography (eluent: ethyl acetate: hexanes = 1: 30). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 4.68 (d, *J* = 1.0 Hz, 1H), 4.64 (s, 1H), 2.19 (t, *J* = 7.2 Hz, 2H), 2.03 (s, 3H), 1.93 (d, *J* = 2.9 Hz, 6H), 1.78 – 1.67 (m, 6H), 1.48 – 1.38 (m, 2H), 1.34 (dq, *J* = 14.3, 7.1 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 175.59, 156.65, 100.46, 40.76, 38.64, 36.35, 32.82, 28.44, 27.82, 21.94, 13.71. IR (neat): 3115, 2957, 2933, 2908, 2864, 1743 (C=O), 1666, 1454, 1212, 1181, 1065, 865, 736; HRMS ESI (*m/z*): [MNa]<sup>+</sup> calcd. for C<sub>17</sub>H<sub>26</sub>O<sub>2</sub>Na, 285.1830; found, 285.1821.

#### dodec-1-en-2-yl but-3-enoate **1o**



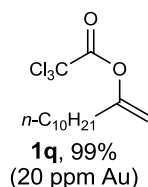
742 mg Compound **1o** was obtained in 98% yield according to general procedure B after chromatography (eluent: ethyl acetate: hexanes = 1: 30). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 5.94 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.25 – 5.08 (m, 2H), 4.71 (s, 3H), 3.16 (d, *J* = 7.0 Hz, 2H), 2.21 – 2.15 (m, 2H), 1.44 (p, *J* = 7.4 Hz, 2H), 1.35 – 1.20 (d, *J* = 11.8 Hz, 14H), 0.87 (t, *J* = 6.9 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 169.54, 156.52, 129.83, 118.81, 101.02, 39.12, 33.21, 33.21, 31.86, 29.54, 29.49, 29.33, 29.28, 28.92, 26.36, 22.64, 14.05. IR (neat): 3118, 3085, 2957, 2927, 2856, 1757 (C=O), 1667, 1645, 1330, 1292, 1223, 1447, 1147, 992, 976, 921, 869; HRMS ESI (*m/z*): [MNa]<sup>+</sup> calcd. for C<sub>16</sub>H<sub>28</sub>O<sub>2</sub>Na, 275.1987; found, 275.1971.

#### dodec-1-en-2-yl 2,2,2-trifluoroacetate **1p**



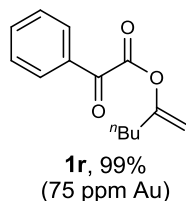
832 mg Compound **1p** was obtained in 99% yield according to general procedure B after chromatography (eluent: hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.95 (d,  $J = 2.7$  Hz, 1H), 4.91 – 4.85 (m, 1H), 2.27 (t,  $J = 7.6$  Hz, 2H), 1.49 (p,  $J = 7.5$  Hz, 2H), 1.38 – 1.20 (m, 14H), 0.88 (t,  $J = 6.9$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  155.71, 155.40 (q,  $J = 42.5$  Hz), 114.50 (q,  $J = 283.75$  Hz), 102.43, 32.63, 31.91, 29.56, 29.48, 29.32, 29.27, 29.27, 28.79, 26.11, 22.69, 14.05.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -75.09. IR (neat): 2929, 2886, 2858, 1798 (C=O), 1675, 1468, 1360, 1228, 1172, 1142, 879, 771. HRMS FI ( $m/z$ ):  $[\text{M}]^+$  calcd. for  $\text{C}_{14}\text{H}_{23}\text{F}_3\text{O}_2$ , 280.1650; found, 280.1665.

#### dodec-1-en-2-yl 2,2,2-trichloroacetate **1q**



978 mg Compound **1q** was obtained in 99% yield according to general procedure B after chromatography (eluent: hexanes).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.93 (d,  $J = 0.8$  Hz, 1H), 4.87 (d,  $J = 3.2$  Hz, 1H), 2.30 (t,  $J = 7.6$  Hz, 2H), 1.52 (p,  $J = 7.5$  Hz, 2H), 1.36 – 1.20 (m, 14H), 0.87 (t,  $J = 6.9$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.84, 156.69, 102.00, 89.78, 32.50, 32.50, 31.88, 29.54, 29.46, 29.30, 29.26, 28.79, 28.78, 26.16, 22.66, 14.08. IR (neat): 3121, 2957, 2928, 2856, 1779 (C=O), 1673, 1467, 1379, 1201, 1107, 961, 878, 823; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{14}\text{H}_{23}\text{Cl}_3\text{O}_2\text{Na}$ , 351.0661; found, 351.0650.

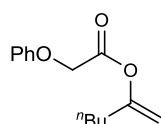
#### hex-1-en-2-yl 2-oxo-2-phenylacetate **1r**



693 mg Compound **1r** was obtained in 99% yield according to general procedure B without chromatography.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.10 – 7.95 (m, 2H), 7.67 (t,  $J = 7.4$  Hz, 1H), 7.52 (t,  $J = 7.8$  Hz, 2H), 5.00 – 4.84 (m, 2H), 2.34 (t,  $J = 7.6$  Hz, 2H), 1.52 (dt,  $J = 15.3, 7.5$  Hz, 2H), 1.45 – 1.31 (m, 2H), 0.92 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C}$

NMR (150 MHz, CDCl<sub>3</sub>)  $\delta$  185.48, 161.70, 156.04, 135.00, 132.25, 129.95, 128.92, 102.10, 32.82, 28.33, 21.94, 13.72. IR (neat): 3066, 2960, 2934, 2874, 2864, 1752 (C=O), 1691 (C=O), 1598, 1452, 1322, 1193, 1168, 987, 878, 746; HRMS ESI ( $m/z$ ): [MNa]<sup>+</sup> calcd. for C<sub>14</sub>H<sub>16</sub>O<sub>3</sub>Na, 255.0997; found, 255.0988.

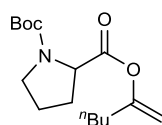
### hex-1-en-2-yl 2-phenoxyacetate **1s**



**1s**, 99%  
(100 ppm Au)

698 mg Compound **1s** was obtained in 99% yield according to general procedure B without chromatography. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.33 – 7.28 (m, 2H), 7.01 (t,  $J$  = 7.4 Hz, 1H), 6.96 – 6.92 (m, 2H), 4.80 (d,  $J$  = 1.8 Hz, 1H), 4.77 (d,  $J$  = 1.6 Hz, 1H), 4.70 (s, 2H), 2.23 (t,  $J$  = 7.5 Hz, 2H), 1.42 (tt,  $J$  = 8.3, 6.9 Hz, 2H), 1.38 – 1.28 (m, 2H), 0.90 (t,  $J$  = 7.2 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  166.95, 157.56, 155.89, 129.42, 129.41, 121.66, 114.48, 114.46, 101.31, 65.08, 32.79, 28.30, 21.86, 13.62. IR (neat): 3067, 2959, 2933, 2873, 2864, 1777 (C=O), 1652, 1668, 1601, 1590, 1497, 1459, 1458, 1438, 1379, 1162, 1108, 963, 876, 753; HRMS ESI ( $m/z$ ): [MNa]<sup>+</sup> calcd. for C<sub>14</sub>H<sub>18</sub>O<sub>3</sub>Na, 257.1154; found, 257.1144.

### 1-tert-butyl 2-hex-1-en-2-yl pyrrolidine-1,2-dicarboxylate **1t**

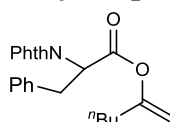


**1t**, 80%  
(600 ppm Au)

712 mg Compound **1t** was obtained in 80% yield according to general procedure B (600 ppm L8AuNTf<sub>2</sub>, 2500 ppm NaBAr<sup>F</sup><sub>4</sub>) after chromatography (eluent: ethyl acetate: hexanes = 1: 2). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  4.79 – 4.59 (m, 2H), 4.33 (dd,  $J$  = 8.6, 3.6 Hz, 1H), 4.26 (dd,  $J$  = 8.7, 4.0 Hz, 1H), 3.59 – 3.31 (m, 2H), 2.34 – 2.13 (m, 3H), 2.07 – 1.78 (m, 3H), 1.46 – 1.42 (m, 4H), 1.40 (d,  $J$  = 6.5 Hz, 6H), 1.36 – 1.26 (m, 2H), 0.92 – 0.81 (m, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  171.11, 156.47, 156.29, 154.20, 153.66, 100.78, 79.92, 79.66, 59.00, 58.91, 46.44, 46.26, 32.91,

32.80 , 30.89 , 29.87 , 28.44 , 28.37 , 28.31 , 28.25 , 24.28 , 23.46 , 21.94 , 13.71. IR (neat): 3116, 2976, 2961, 2934, 2876, 1763 (C=O), 1705 (C=O), 1396, 1152, 1088, 957, 871, 773; HRMS ESI ( $m/z$ ):  $[MNa]^+$  calcd. for  $C_{16}H_{27}NO_4Na$ , 320.1838; found, 320.1834.

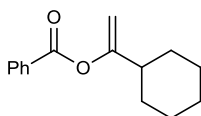
### hex-1-en-2-yl 2-(1,3-dioxoisindolin-2-yl)-3-phenylpropanoate **1u**



**1u**, 99%  
(150 ppm Au)

1128 mg Compound **1u** was obtained in 99% yield according to general procedure B without chromatography.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.78 (dd,  $J = 5.4, 3.1$  Hz, 2H), 7.68 (dd,  $J = 5.5, 3.0$  Hz, 2H), 7.22 – 7.10 (m, 5H), 5.23 (dd,  $J = 11.3, 5.2$  Hz, 1H), 4.78 (d,  $J = 1.8$  Hz, 1H), 4.75 (d,  $J = 1.7$  Hz, 1H), 3.68 – 3.51 (m, 2H), 2.21 (td,  $J = 7.5, 4.5$  Hz, 2H), 1.40 (qd,  $J = 8.1, 7.5, 5.6$  Hz, 2H), 1.35 – 1.24 (m, 2H), 0.86 (t,  $J = 7.3$  Hz, 3H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  167.26, 167.08, 156.45, 136.51, 134.08, 131.50, 128.82, 128.51, 126.84, 123.42, 101.49, 53.24, 34.65, 32.73, 28.40, 21.94, 13.73. IR (neat): 3065, 2958, 2933, 2873, 2865, 1778 (C=O), 1759 (C=O), 1718 (C=O), 1669, 1607, 1498, 1468, 1288, 1222, 1170, 1105, 1000, 961, 915, 876, 720; HRMS ESI ( $m/z$ ):  $[MNa]^+$  calcd. for  $C_{23}H_{23}NO_4Na$ , 400.1525; found, 400.1515.

### 1-cyclohexylvinyl benzoate **1v**



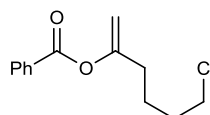
**1v**, 99%  
(100 ppm Au)

686 mg Compound **1v** was obtained in 99% yield according to general procedure B without chromatography.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  8.16 – 8.03 (m, 2H), 7.59 (t,  $J = 7.4$  Hz, 1H), 7.47 (t,  $J = 7.8$  Hz, 2H), 4.91 – 4.76 (m, 2H), 2.25 (td,  $J = 10.7, 3.0$  Hz, 1H), 1.99 (t,  $J = 10.5$  Hz, 2H), 1.87 – 1.73 (m, 2H), 1.72 – 1.64 (m, 2H), 1.34 – 1.13 (m, 6H).  $^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  164.82, 160.66, 133.17, 129.94, 129.87, 128.40, 99.61, 41.80, 30.62, 26.05, 25.94. IR (neat): 3064, 2930, 2855, 1733 (C=O),



1661, 1601, 1451, 1314, 1271, 1240, 1194, 1169, 1133, 1092, 1068, 1026, 872, 705;  
HRMS ESI ( $m/z$ ): [MNa]<sup>+</sup> calcd. for C<sub>15</sub>H<sub>18</sub>NO<sub>2</sub>Na, 253.1208; found, 253.1204.

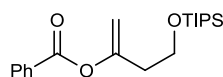
#### 6-chlorohex-1-en-2-yl benzoate **1w**



**1w**, 95%  
(300 ppm Au)  
no NaBAR<sup>F</sup><sub>4</sub>

678 mg Compound **1w** was obtained in 95% yield when 1,2-dichloroethane was used as a solvent instead of PhF. (0.5 M, 300 ppm **L8**AuNTf, no NaBAR<sup>F</sup><sub>4</sub>) after chromatography (eluent: ethyl acetate: hexanes = 1: 30). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.09 (t,  $J$  = 8.4 Hz, 2H), 7.67 – 7.53 (m, 1H), 7.47 (t,  $J$  = 7.7 Hz, 2H), 4.88 (d,  $J$  = 21.0 Hz, 2H), 3.63 – 3.48 (m, 2H), 2.39 (t,  $J$  = 7.5 Hz, 2H), 1.88 (qd,  $J$  = 14.9, 6.9 Hz, 2H), 1.76 – 1.63 (m, 2H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 164.68, 155.79, 133.33, 129.88, 129.69, 128.45, 101.96, 44.64, 32.64, 31.70, 23.72. IR (neat): 3064, 2955, 2870, 2847, 1730 (C=O), 1667, 1602, 1492, 1452, 1272, 1026, 875, 801, 746; HRMS ESI ( $m/z$ ): [MNa]<sup>+</sup> calcd. for C<sub>13</sub>H<sub>15</sub>ClO<sub>2</sub>Na, 261.0658; found, 261.0654.

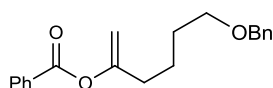
#### 4-(triisopropylsilyloxy)but-1-en-2-yl benzoate **1x**



**1x**, 98%  
(120 ppm Au)

1023 mg Compound **1x** was obtained in 98% yield according to general procedure B (2500 ppm NaBAR<sup>F</sup><sub>4</sub>) after chromatography (eluent: ethyl acetate: hexanes = 1: 50). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.13 – 8.01 (m, 2H), 7.69 – 7.52 (m, 1H), 7.50 – 7.37 (m, 2H), 5.00 – 4.84 (m, 2H), 3.89 (td,  $J$  = 6.6, 0.8 Hz, 2H), 2.69 – 2.51 (m, 2H), 1.17 – 0.97 (m, 21H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 164.74, 153.83, 133.27, 129.92, 128.41, 103.97 – 103.59 (m), 103.15, 99.07, 60.64, 37.38, 17.96, 11.95. IR (neat): 3064, 2944, 2893, 2867, 1736 (C=O), 1670, 1602, 1464, 1384, 1268, 1233, 1175, 1092, 1069, 1026, 882, 706; HRMS ESI ( $m/z$ ): [MNa]<sup>+</sup> calcd. for C<sub>20</sub>H<sub>32</sub>NaO<sub>3</sub>Si, 371.2018; found, 371.2020.

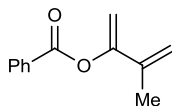
#### 4-(benzyloxy)but-1-en-2-yl benzoate **1y**



**1y**, 89%  
(150 ppm Au)

828 mg Compound **1y** was obtained in 89% yield according to general procedure B (2500 ppm NaBAr<sup>F</sup><sub>4</sub>) after chromatography (eluent: ethyl acetate: hexanes = 1: 20). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.15 – 7.97 (m, 2H), 7.63 – 7.54 (m, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.38 – 7.17 (m, 5H), 4.89 (d, *J* = 1.6 Hz, 1H), 4.87 – 4.85 (m, 1H), 4.51 (s, 2H), 3.51 (t, *J* = 6.1 Hz, 2H), 2.38 (t, *J* = 7.2 Hz, 2H), 1.77 – 1.51 (m, 4H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 164.69, 156.34, 138.51, 133.23, 129.88, 129.81, 128.41, 128.29, 127.54, 127.44, 101.59, 72.82, 69.88, 33.19, 29.02, 23.22. IR (neat): 3185, 2962, 2935, 2873, 2876, 1761 (C=O), 1674, 1250, 1217, 847, 833; HRMS ESI (*m/z*): [MNa]<sup>+</sup> calcd. for C<sub>20</sub>H<sub>22</sub>O<sub>3</sub>Na, 333.1467; found, 333.1453.

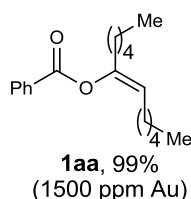
#### 3-methylbuta-1,3-dien-2-yl benzoate **1z**



**1z**, 97% (60 °C,  
1500 ppm Au)

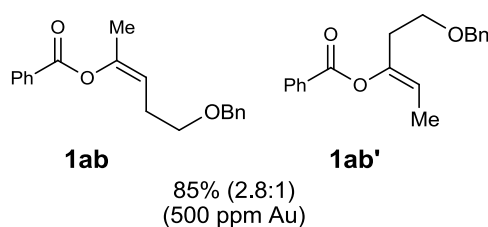
547 mg Compound **1z** was obtained in 97% yield according to general procedure B (2 equiv 2-methylbut-1-en-3-yne, 5000 ppm NaBAr<sup>F</sup><sub>4</sub>, 60 °C) after chromatography (eluent: ethyl acetate: hexanes = 1: 20). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.16 (dtd, *J* = 8.1, 2.1, 1.3 Hz, 1H), 7.67 – 7.57 (m, 1H), 7.55 – 7.42 (m, 1H), 5.32 – 5.14 (m, 2H), 5.04 (ddd, *J* = 7.9, 2.9, 1.5 Hz, 2H), 2.01 (d, *J* = 0.7 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 165.13 – 164.49 (m), 154.09 – 153.24 (m), 136.63, 133.45, 130.04, 129.68 – 129.31 (m), 128.54, 113.92, 103.60, 19.46. IR (neat): 3063, 2976, 2954, 2928, 2902, 2855, 1738 (C=O), 1603, 1452, 1263, 1152, 1090, 1068, 1026, 887, 707; HRMS EI (*m/z*): [M]<sup>+</sup> calcd. for C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>, 188.0837; found, 188.0835.

**(Z)-hex-3-en-3-yl benzoate 1aa**



855 mg Compound **1aa** was obtained in 99% yield according to general procedure B (5000 ppm NaBAr<sup>F</sup><sub>4</sub>) after chromatography (eluent: ethyl acetate: hexanes = 1: 30). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.12 (dt, *J* = 8.4, 1.6 Hz, 2H), 7.83 – 7.54 (m, 1H), 7.54 – 7.40 (m, 2H), 5.11 (t, *J* = 7.3 Hz, 1H), 2.41 – 2.19 (m, 2H), 1.97 (q, *J* = 7.3 Hz, 2H), 1.57 – 1.45 (m, 2H), 1.43 – 1.16 (m, 10H), 0.98 – 0.74 (m, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 164.39, 148.58, 133.10, 129.91, 129.87, 128.40, 116.53, 33.43, 31.36, 31.23, 28.77, 26.37, 25.31, 22.41, 22.40, 13.98, 13.96. IR (neat): 3064, 2957, 2930, 2872, 2859, 1733 (C=O), 1452, 1259, 1089, 1068, 1026, 708; HRMS ESI (*m/z*): [MNa]<sup>+</sup> calcd. for C<sub>19</sub>H<sub>28</sub>O<sub>2</sub>Na, 311.1987; found, 311.1977.

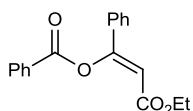
**(Z)-5-(benzyloxy)pent-2-en-2-yl benzoate 1ab + (Z)-5-(benzyloxy)pent-2-en-3-yl benzoate 1ab'**



755 mg Compounds **1ab and 1ab'** were obtained in 85% yield (2.8:1) according to general procedure B (2500 ppm NaBAr<sup>F</sup><sub>4</sub>) after chromatography (eluent: ethyl acetate: hexanes = 1: 15). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.15 – 8.07 (m, 2H), 7.64 – 7.58 (m, 1H), 7.52 – 7.46 (m, 2H), 7.38 – 7.26 (m, 5H), 5.31 (qd, *J* = 6.8, 0.9 Hz, 0.25H), 5.25 – 5.19 (m, 0.73H), 4.54 (s, 0.52H), 4.51 (s, 1.55H), 3.65 (td, *J* = 6.6, 1.1 Hz, 0.53H), 3.50 (td, *J* = 6.8, 1.1 Hz, 1.56H), 2.70 – 2.61 (m, 0.52H), 2.41 – 2.30 (m, 1.57H), 2.07 – 1.99 (m, 2.35H), 1.59 (dd, *J* = 6.8, 1.2 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 164.32, 164.25, 146.42, 146.26, 138.34, 138.23, 133.24, 133.21, 129.91, 129.89, 129.65, 129.60, 128.41, 128.27, 127.60, 127.57, 127.47, 127.46, 113.45,

112.85, 72.86, 72.75, 69.24, 67.26, 34.22, 26.19, 19.63, 10.81. HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{19}\text{H}_{20}\text{O}_3\text{Na}$ , 319.1310; found, 319.1313.

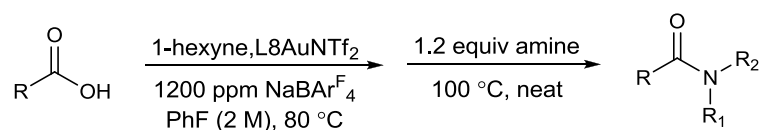
### (Z)-3-ethoxy-3-oxo-1-phenylprop-1-enyl benzoate **1ac**



**1ac**, 98%  
(150 ppm Au)

870 mg Compound **1ac** was obtained in 98% yield according to general procedure B after chromatography (eluents: ethyl acetate: hexanes = 1: 4). This compound is known and the spectrum are consistent with literature data.<sup>[49]</sup>  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 (dd,  $J = 8.3, 1.2$  Hz, 2H), 7.72 – 7.59 (m, 3H), 7.53 (dd,  $J = 10.8, 4.8$  Hz, 2H), 7.47 – 7.34 (m, 3H), 6.38 (s, 1H), 4.13 (q,  $J = 7.1$  Hz, 2H), 1.15 (t,  $J = 7.1$  Hz, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  164.08, 163.82, 157.83, 133.70, 133.45, 130.95, 130.37, 129.11, 128.84, 128.64, 125.95, 106.84, 60.38, 14.05. IR (neat): 2918, 2951, 1742 (C=O), 1714, 1636, 1449, 1279, 1234, 1157, 1080, 1064, 1023, 765; HRMS ESI ( $m/z$ ):  $[\text{MNa}]^+$  calcd. for  $\text{C}_{18}\text{H}_{16}\text{O}_4\text{Na}$ , 319.0946; found, 319.0943.

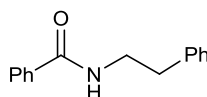
### General procedure C: Preparation of Amides by a One-pot Sequence



In a sealed 1 dr reaction vial equipped with a magnetic stirring bar, 3 mmol carboxylic acids (1 equiv), 4.4 mmol 1-hexyne (1.45 equiv) and 3.1 mg  $\text{NaBARF}_4$  (1200 ppm) were added to 0.6 mL fluorobenzene. **L8AuNTf<sub>2</sub>** (50  $\mu\text{L}$  of a 3.09 mg/mL solution in PhF, 0.150  $\mu\text{mol}$ , 50 ppm or 100  $\mu\text{L}$ , 100 ppm) was added to the above vial and then the reaction mixture was heated at 80 °C for 12 - 18 h. Once the reaction finished by TLC, it was concentrated and left on the high vacuum pump for overnight to give the crude product, followed by adding 3.6 mmol amine (1.2 equiv) and stirring at 100 °C for 6 - 24 h. Once the reaction completed by TLC, the mixture was purified through

silica gel flash chromatography (eluents: ethyl acetate: hexanes = 1: 3) to give the desired product.

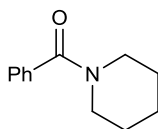
### ***N*-phenethylbenzamide**



*N*-phenethylbenzamide was obtained in 96% overall yield according to general procedure C. This compound is known and the spectrum are consistent with literature data.

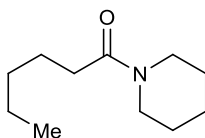
[50]

### **phenyl(piperidin-1-yl)methanone**



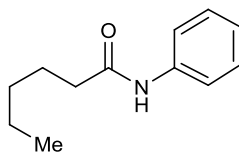
Phenyl(piperidin-1-yl)methanone was obtained in 93% overall yield according to general procedure C. This compound is known and the spectrum are consistent with literature data.<sup>[51]</sup>

### **1-(piperidin-1-yl)hexan-1-one**



1-(Piperidin-1-yl)hexan-1-one was obtained in 94% overall yield according to general procedure C. This compound is known and the spectrum are consistent with literature data.<sup>[52]</sup>

### ***N*-phenylhexanamide**



*N*-Phenylhexanamide was obtained in 90% overall yield according to general procedure C. This compound is known and the spectrum are consistent with literature data.<sup>[53]</sup>

## **DFT calculation results**

### **The four optimized transition states**

Two transition structures were obtained for  $\text{NTf}_2^-$  activation mode (**TS-NTf<sub>2</sub>** and **TS-NTf<sub>2</sub>'**) and the amide group activation mode (**TS-Amide** and **TS-Amide'**), respectively (shown in Supplementary Figure 159). For the Calculated total energies and geometrical coordinates, please see Supplementary Data 1.

## Supplementary References

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