

ESI for:

**Organoselenium-Catalyzed Selectivity-Switchable Oxidation of β -
Ionone[†]**

Lei Yu,^{*ab} Zengbing Bai,^a Xu Zhang^{ab} Xiaohong Zhang,^a Yuanhua Ding^a and Qing Xu^{ab}

^a Jiangsu Co-innovation Center for Prevention and Control of Important Animal Infectious Diseases and Zoonoses, School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, Jiangsu 225002, China; Email: yulei@yzu.edu.cn.

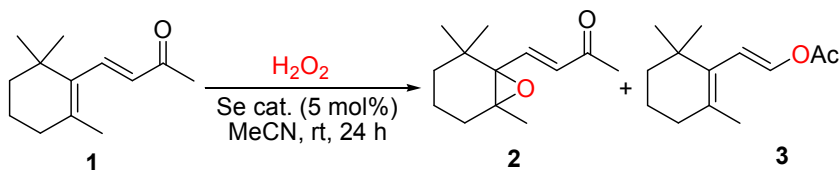
^b Zhejiang Key Laboratory of Carbon Materials, College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, Zhejiang 325035, China.

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Detailed Conditional Optimizations

Table S1. Screening of the Organoselenium Catalysts.^a

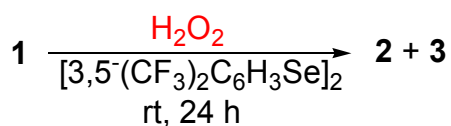


entry	Se cat.	2 / % ^b	3 / % ^b
1 ^c	-	8	0
2 ^c	SeO_2^d	21	24
3 ^c	PhSeEt^d	11	18
4 ^c	$\text{PhSe}(c\text{-C}_6\text{H}_{11})^d$	26	40
5 ^c	PhSePh^d	20	10
6 ^c	$(\text{PhSe})_2$	16	33
7 ^c	$(3\text{-MeC}_6\text{H}_4\text{Se})_2$	32	21
8 ^c	$(3\text{-MeOC}_6\text{H}_4\text{Se})_2$	31	20
9 ^c	$(4\text{-MeOC}_6\text{H}_4\text{Se})_2$	25	41
10 ^c	$(4\text{-ClC}_6\text{H}_4\text{Se})_2$	40	17
11 ^c	$(2\text{-FC}_6\text{H}_4\text{Se})_2$	35	24
12 ^c	$(3\text{-FC}_6\text{H}_4\text{Se})_2$	28	15
13 ^c	$(1\text{-C}_{10}\text{H}_7\text{Se})_2$	31	20
14	$(2\text{-CF}_3\text{C}_6\text{H}_4\text{Se})_2$	40	7
15	$(3\text{-CF}_3\text{C}_6\text{H}_4\text{Se})_2$	41	8
16	$(4\text{-CF}_3\text{C}_6\text{H}_4\text{Se})_2$	40	8
17	$[\text{3,5}-(\text{CF}_3)_2\text{C}_6\text{H}_3\text{Se}]_2$	70	0
18 ^c	$(c\text{-C}_6\text{H}_{11}\text{Se})_2$	36	45
19	$(n\text{-C}_4\text{H}_9\text{Se})_2$	15	67
20	$(\text{PhCH}_2\text{Se})_2$	10	77
21	$(2\text{-FC}_6\text{H}_4\text{CH}_2\text{Se})_2$	18	72
22	$(3\text{-FC}_6\text{H}_4\text{CH}_2\text{Se})_2$	16	69
23	$(4\text{-FC}_6\text{H}_4\text{CH}_2\text{Se})_2$	20	70
24	$(2\text{-ClC}_6\text{H}_4\text{CH}_2\text{Se})_2$	15	68
25	$(3\text{-ClC}_6\text{H}_4\text{CH}_2\text{Se})_2$	15	70
26	$(4\text{-ClC}_6\text{H}_4\text{CH}_2\text{Se})_2$	15	71
27	$(2,6\text{-Cl}_2\text{C}_6\text{H}_3\text{CH}_2\text{Se})_2$	15	75

28	(2,4-Cl ₂ C ₆ H ₃ CH ₂ Se) ₂	12	71
29	(4-MeOC ₆ H ₄ CH ₂ Se) ₂	20	65
30	(2-MeOC ₆ H ₄ CH ₂ Se) ₂	20	60
31	(3-MeC ₆ H ₄ CH ₂ Se) ₂	15	56
32	(4-MeC ₆ H ₄ CH ₂ Se) ₂	25	66

^a β -Ionone **1** (1 mmol), Se cat. (0.05 mmol, 5 mol%) and H₂O₂ (4 mmol, 400 %) in commercial MeCN (1 mL) was stirred at room temperature (ca. 25 °C) under air and monitored by TLC and/or GC. ^b Isolated yields based on **1**. ^c Reaction not completed. ^d 0.1 mmol (10 mol%) catalyst was employed.

Table S2. Conditional Optimizations for 2.^a

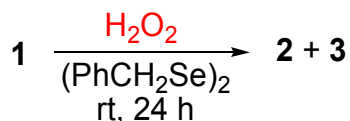


entry	Solvent (v / mL) ^b	cat. / % ^c	H ₂ O ₂ / % ^d	2 (3) / % ^e
1	MeCN (1)	5	400	70 (0)
2	CH ₂ Cl ₂ (1)	5	400	71 (0)
3 ^f	EtOH (1)	5	400	27 (50)
4 ^f	H ₂ O (1)	5	400	25 (23)
5 ^f	Acetone (1)	5	400	21 (41)
6 ^f	DMF (1)	5	400	20 (46)
7 ^f	THF (1)	5	400	36 (34)
8 ^f	MeCN (1)	0.5	400	40 (15)
9^f	MeCN (1)	1	400	72 (9)
10 ^{f,g}	MeCN (1)	1	400	72 (8)
11 ^f	MeCN (1)	2	400	71 (8)
12 ^f	MeCN (1)	3	400	70 (6)
13	MeCN (1)	10	400	63 (0)
14 ^f	MeCN (1)	1	100	40 (10)
15 ^f	MeCN (1)	1	120	43 (10)
16 ^f	MeCN (1)	1	150	47 (9)
17 ^f	MeCN (1)	1	200	53 (8)
18 ^f	MeCN (1)	1	300	61 (8)
19	MeCN (1)	1	500	70 (0)
20 ^f	MeCN (0.5)	1	400	65 (10)
21 ^f	MeCN (2)	1	400	60 (8)

22^f MeCN (4) 1 400 48 (8)
23^h MeCN (40) 1 400 70 (8)

^a β -Ionone **1** (1 mmol), [3,5-(CF₃)₂C₆H₃Se]₂ and H₂O₂ in commercial solvent was stirred at room temperature (ca. 25 °C) under air and monitored by TLC and/or GC. ^b Volume of solvent (mL). ^c Catalyst loading based on **1**. ^d H₂O₂ dosage based on **1**. ^e Isolated yields of **2** outside the parentheses; isolated yields of **3** inside the parentheses. ^f Reaction not completed. ^g Reaction time delayed to 48 h. ^h Reaction performed in 40 mmol scale

Table S3. Conditional Optimizations for 3.^a

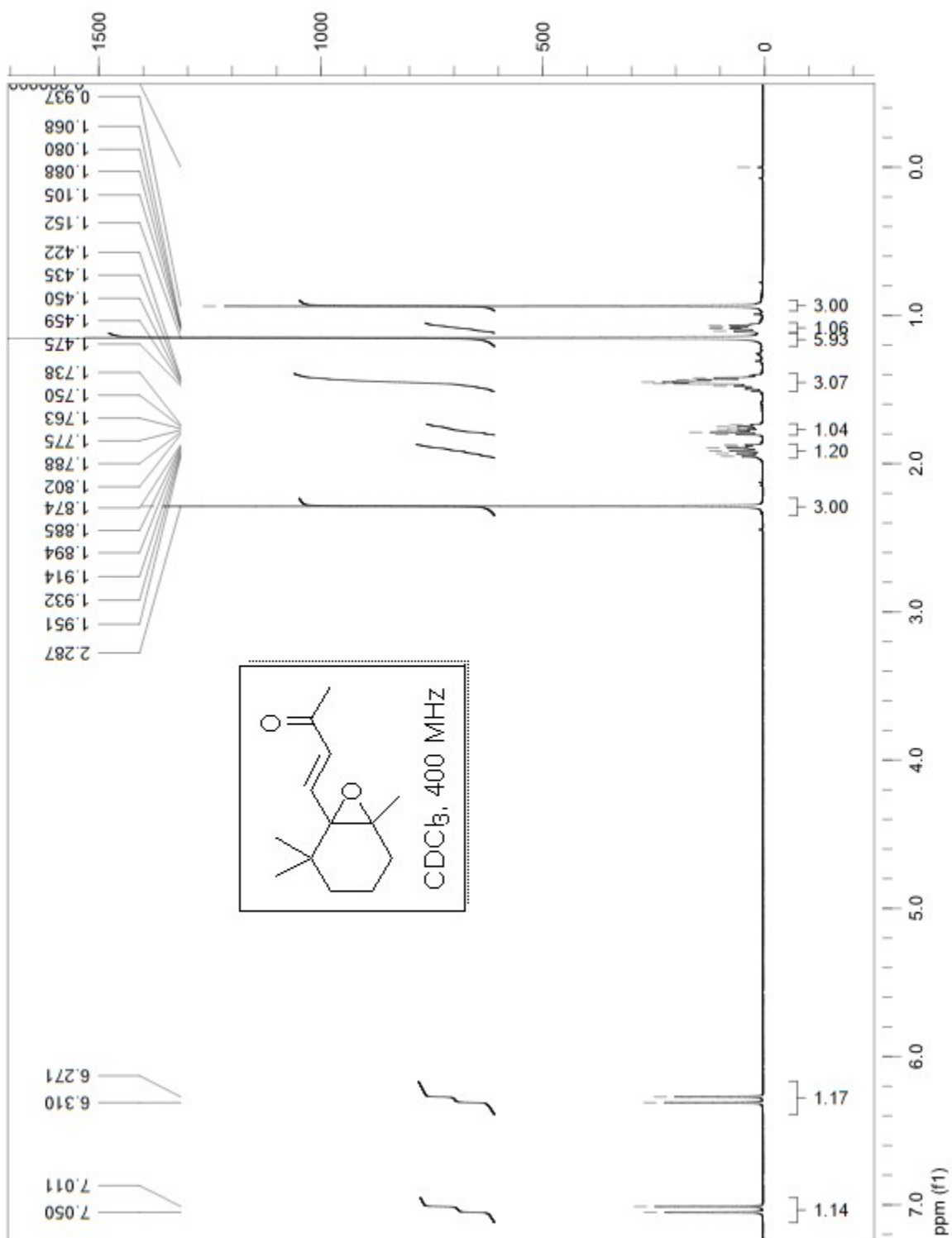


Entry	Solvent (v / mL) ^b	cat. / % ^c	H ₂ O ₂ / % ^d	3 (2) / % ^e
1	MeCN (1)	5	400	77 (10)
2	EtOH (1)	5	400	80 (12)
3	THF (1)	5	400	86 (8)
4 ^f	H ₂ O (1)	5	400	25 (20)
5 ^f	Acetone (1)	5	400	73 (15)
6 ^f	DMF (1)	5	400	70 (15)
7 ^f	CH ₂ Cl ₂	5	400	16 (9)
8 ^f	THF (1)	0.5	400	38 (5)
9 ^f	THF (1)	1	400	42 (9)
10 ^f	THF (1)	2	400	59 (8)
11 ^f	THF (1)	3	400	65 (8)
12	THF (1)	10	400	91 (5)
13	THF (1)	20	400	85 (6)
14 ^f	THF (1)	10	100	34 (5)
15 ^f	THF (1)	10	120	35 (6)
16 ^f	THF (1)	10	150	55 (5)
17 ^f	THF (1)	10	200	68 (8)
18 ^f	THF (1)	10	300	82 (8)
19	THF (1)	10	500	90 (5)
20	THF (0.5)	10	400	86 (10)
21 ^f	THF (2)	10	400	80 (5)
22 ^f	THF (4)	10	400	76 (0)
23^g	THF (40)	10	400	87 (6)

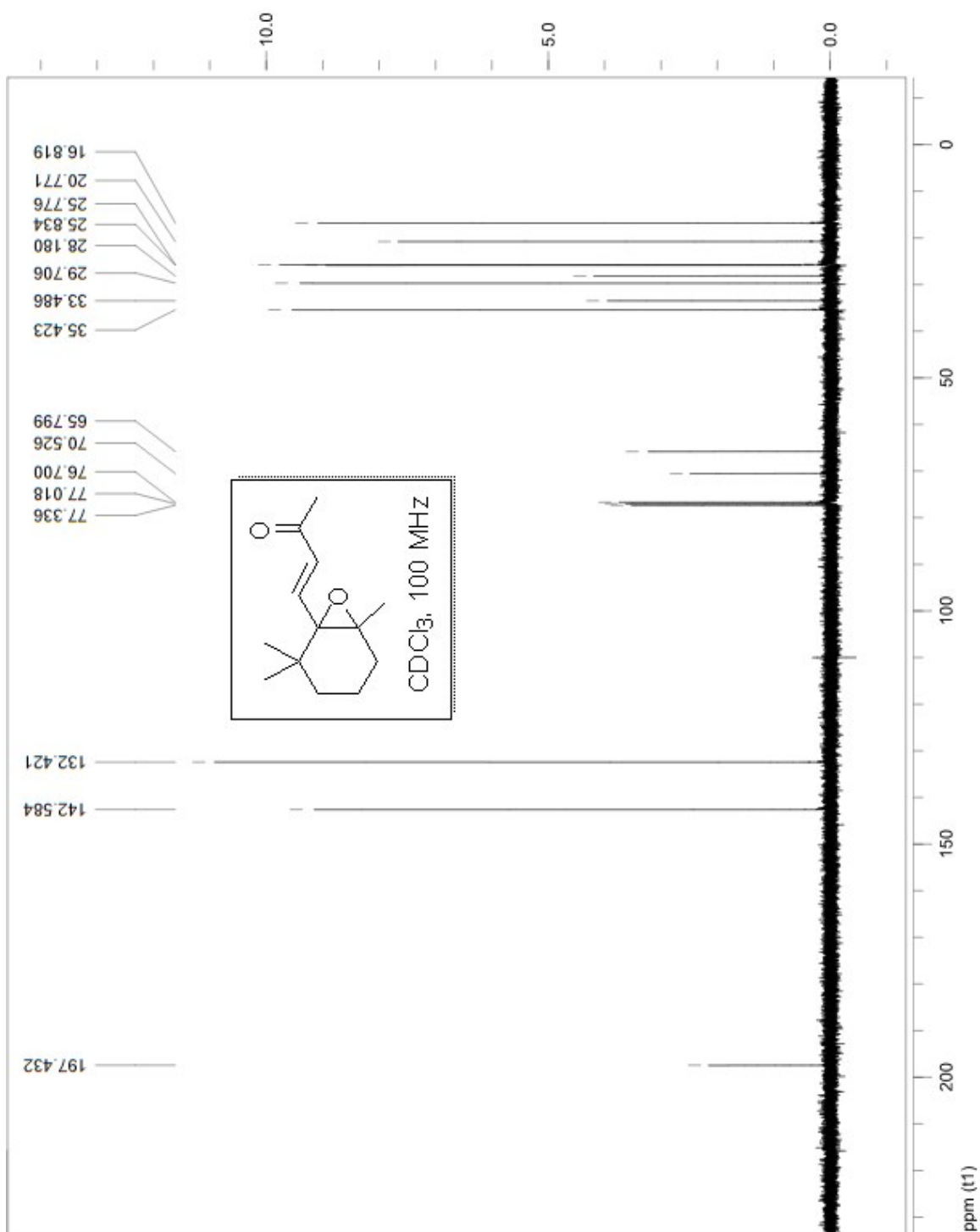
^a *β*-Ionone **1** (1 mmol), (PhCH₂Se)₂ and H₂O₂ in commercial solvent was stirred at room temperature (ca. 25 °C) under air and monitored by TLC and/or GC. ^b Volume of solvent (mL). ^c Catalyst loading based on **1**. ^d H₂O₂ dosage based on **1**. ^e Isolated yields of **3** outside the parentheses; isolated yields of **2** inside the parentheses. ^f Reaction not completed. ^g Reaction performed in 40 mmol scale.

NMR Spectra of the Products

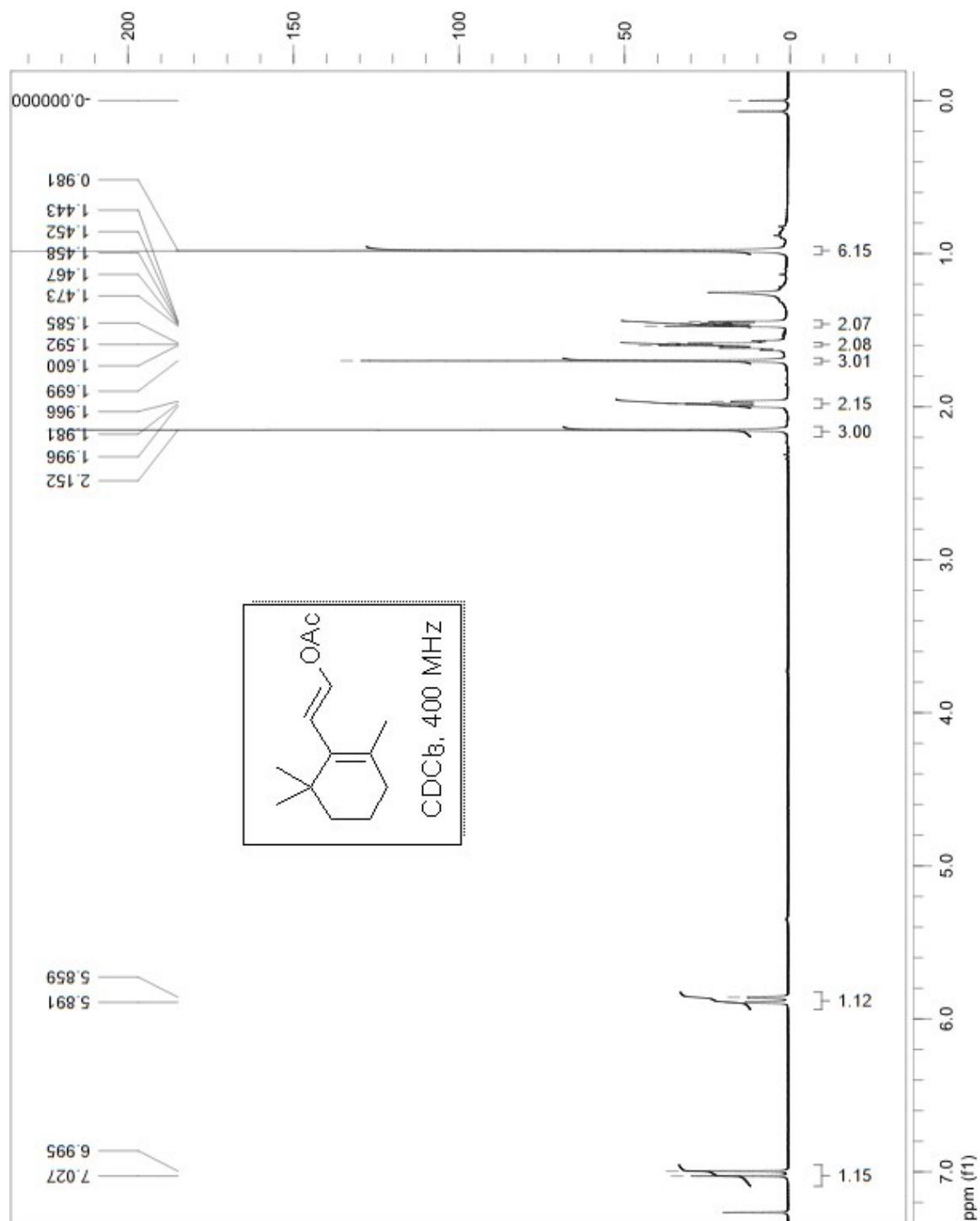
^1H NMR of 2



¹³C NMR of 2



¹H NMR of 3



¹³C NMR of 3

