Supporting Information

Divergent Syntheses of Spiroindanones and 2-Substituted 1-Indanones by Ruthenium-Catalyzed Tandem Coupling and Cyclization of Aromatic Acids with α,β-Unsaturated Ketones

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1. The conversions of aromatic acids and the yields of byproducts

Table S1 The conversions of aromatic acids and the yields of byproducts in Table 2



 $R + C_2H_5$ 3-substituted phthalide 2-substituted 1-indanone
Conversion of Yield (%)^a

Enter	Product	Conversion of acid	Yield $(\%)^a$		Entry	Product	Conversion	Yield $(\%)^a$	
Enuy	Product		phthalide	1-indanone	Litti y	Floduct	of acid	phthalide	1-indanone
1	3a	100	4	18	19	3s	100	11	16
2	3b	100	3	16	20	3t	100	7	14
3	3c	100	5	19	21	3u	100	7	15
4	3d	100	trace	ND	22	3v	100	trace	12
5	3e	95	6	13	23	3w	100	trace	23
6	3f	96	5	11	24	3x	100	trace	23
7	3g	97	8	9	25	3y	100	trace	19
8	3h	98	7	14	26	3z	100	6	6
9	3i	96	12	14	27	3aa	97	8	6
10	3j	100	3	19	28	3ab	100	4	12
11	3k	100	trace	19	29	3ac	100	4	8
12	31	100	7	15	30	3ad	92	12	7
13	3m	100	4	16	31	3ae	93	7	12
14	3n	100	5	17	32	3af	100	3	ND
15	30	100	8	14	33	3ag	100	2	ND
16	3p	100	11	14	34	3ah	97	4	8
17	3q	100	7	17	35	3ai	83	2	4
18	3r	100	9	9					

^{*a*} Determined by ¹H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

Table S2 The conversions of aromatic acids and the yields of byproducts in Table 4

R	CO2H + ≫	R ['] [RuCl ₂ (<i>p</i> -cyme MnCO ₃ , CH ₃ Ct 20 h, Ar, 150	$\begin{array}{c} \begin{array}{c} ne)]_2 \\ \sqrt{H_2O} \\ 0 \\ 0 \\ \end{array} \\ \begin{array}{c} R \\ 1 \\ \end{array} \\ \begin{array}{c} r \\ 1 \\ \end{array} \\ \begin{array}{c} r \\ r \\ 4c-4a \end{array}$	Q R	+ R U	R.	
Entry	Product	Conversion of acid (%) ^{<i>a</i>}	Yield of phthalide (%) ^a	Entry	Product	Conversion of acid (%)	Yield of phthalide (%) ^a
1	4 a	100	6	23	4 w	100	6
2	4b	96	4	24	4x	100	ND
3	4c	96	4	25	4y	91	ND
4	4d	98	2	26	4z	85	ND
5	4 e	97	6	27	4 aa	96	6
6	4 f	93	5	28	4ab	94	6
7	4g	89	4	29	4ac	96	6
8	4h	88	5	30	4ad	94	5
9	4i	100	6	31	4ae	95	5
10	4j	100	4	32	4af	100	8
11	4k	100	2	33	4ag	100	3
12	41	99	5	34	4ah	100	2
13	4m	96	2	35	4ai	100	ND
14	4n	97	7	36	4aj	100	ND
15	40	97	3	37	4ak	100	ND
16	4p	100	10	38	4al	100	ND
17	4q	100	4	39	4am	100	ND
18	4r	100	6	40	4an	100	ND
19	4s	96	8	41	4ao	100	ND
20	4t	93	5	42	4ap	100	ND
21	4u	93	11	43	4aq	100	ND
22	4 v	97	7				

^{*a*} Determined by ¹H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

2. Mechanistic studies

Table S3. Experimental results using 5a as a reactant for the synthesis of 3a



Entry	Conditions	Yield (%) ^[b]
1	[RuCl ₂ (<i>p</i> -cymene)] ₂ (5 mol%), Mn(OAc) ₂ (0.75 equiv), CH ₃ CN (0.6 mL)	65%
2	Mn(OAc) ₂ (0.75 equiv), CH ₃ CN (0.6 mL)	61%
3	CH ₃ CN (0.6 mL)	ND

^{*a*} Reaction conditions: **5a** (0.1 mmol), **2a** (0.1 mmol), 150 °C for 20 h, under Ar in pressure tubes. ^{*b*} Determined by ¹H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. ^{*c*} ND = not detected.

Table S4. Experimental	results using 6a	as a reactant for t	he synthesis of 3a
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	$\begin{array}{c} CH_3 & O & O \\ & & C_2H_5 \\ & & Ga \end{array} \xrightarrow{\begin{array}{c} CH_3 & O \\ & C_2H_5 \end{array}} \xrightarrow{\begin{array}{c} CC_2O \\ & O \end{array} \xrightarrow{\begin{array}{c} CC_2H_5 \\ & O \end{array}} \xrightarrow{\begin{array}{c} CC_2H_5 \\ & O \end{array} \xrightarrow{\begin{array}{c} CC_2H_5 \end{array}} \xrightarrow{\begin{array}{c} CC_2H_5 \\ & O \end{array} \xrightarrow{\begin{array}{c} CC_2H_5 \end{array} \xrightarrow{\begin{array}{c} CC_2H_5 \end{array} \xrightarrow{\begin{array}{c} CC_2H_5 \end{array} \xrightarrow{\begin{array}{c} CC_2H_5 \end{array} \xrightarrow{\begin{array}{c} CC}C_2H_5 \end{array} \xrightarrow{\begin{array}{c} CC_2H_5 \end{array} \xrightarrow{\begin{array}{c} CC_2H_5 \end{array} \xrightarrow{\begin{array}{c} CC_2H_5 \end{array} \xrightarrow{\begin{array}{c} CCC_2H_5 \end{array} \xrightarrow{\begin{array}{c} CCC_2H_5 \end{array} \xrightarrow{\begin{array}{c} CCC_2H_5 \end{array} \xrightarrow{\begin{array}{c} CCC_2H_5 \end{array} \xrightarrow{\begin{array}{c} CCC_2C_2H_5 \end{array} \xrightarrow{\begin{array}{c} CCC_2C_2H_5 \end{array} \xrightarrow{\begin{array}{c} CCC_2C_2H_5 \end{array} \xrightarrow{\begin{array}{c} CCC_2C_2H_5 \end{array} \xrightarrow{\begin{array}{c} CCC_2C_2C_2H_5 \end{array} \xrightarrow{\begin{array}{c} CCC_2C_2H_5 \end{array} \xrightarrow{\begin{array}{c} CCC_2C_2C_2H_5 \end{array} \xrightarrow{\begin{array}{c} CCC_2C_2C_2H_5 \end{array} \xrightarrow{\begin{array}{c} CC_2C_2C_2C_2H_5 \end{array} \xrightarrow{\begin{array}{c} CCC_2C_2C_2H_5 \end{array} \xrightarrow{\begin{array}{c} CCC_2C_2C_2C_2C_2H_5 \end{array} \xrightarrow{\begin{array}{c} CCC_2\mathsf$	
Entry	Conditions	Yield (%) ^[b]
1	[RuCl ₂ (<i>p</i> -cymene)] ₂ (5 mol%), Mn(OAc) ₂ (0.75 equiv), CH ₃ CN (0.6 mL)	56%
2	Mn(OAc) ₂ (0.75 equiv), CH ₃ CN (0.6 mL)	43%
3	CH ₃ CN (0.6 mL)	ND

^{*a*}Reaction conditions: **6a** (0.1 mmol), 150 °C for 20 h, under Ar in pressure tubes. ^{*b*} Determined by ¹H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. ^{*c*} ND = not detected.

Table S5. Experimental results using 5a as a reactant for the synthesis of 4a



Entry	Conditions	Yield (%) ^[b]
1	[RuCl ₂ (<i>p</i> -cymene)] ₂ (5 mol%), MnCO ₃ (1.0 equiv), H ₂ O (38 µL), CH ₃ CN	61
	(0.6 mL)	
2	[RuCl ₂ (<i>p</i> -cymene)] ₂ (5 mol%), MnCO ₃ (1.0 equiv), H ₂ O (0.6 mL)	21
3	[RuCl ₂ (<i>p</i> -cymene)] ₂ (5 mol%), H ₂ O (0.6 mL)	ND
4	$[RuCl_2(p-cymene)]_2$ (5 mol%), H ₂ O (38 μ L), CH ₃ CN (0.6 mL)	ND
5	MnCO ₃ (1.0 equiv), H ₂ O (38 µL), CH ₃ CN (0.6 mL)	56
6	MnCO ₃ (1.0 equiv), H ₂ O (0.6 mL)	29
7	MnCO ₃ (1.0 equiv), CH ₃ CN (0.6 mL)	trace
8	H ₂ O (38 μL), CH ₃ CN (0.6 mL)	ND

^{*a*} Reaction conditions: **5a** (0.1 mmol), **2a** (0.1 mmol), 150 °C for 20 h, under Ar in pressure tubes. ^{*b*} Determined by ¹H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. ^{*c*} ND = not detected.

Table S6. Experimental results using 6a as a reactant for the synthesis of 4a



^{*a*} Reaction conditions: **6a** (0.1 mmol), 150 °C for 20 h, under Ar in pressure tubes. ^{*b*} Determined by ¹H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

3. Single crystal X-ray diffraction results

3.1 Single crystal X-ray diffraction result of 3q

The single crystal was obtained from n-hexane and ethyl acetate. Using Olex2,¹ the structure was solved with the XT structure solution program using Intrinsic Phasing and refined with the XL refinement package using Least Squares minimisation.²⁻³

Figure S1. Crystal structure of 3q



Compound Number	3q
Empirical formula	C ₁₉ H ₂₂ O ₂
Formula weight	282.36
Temperature/K	153.08
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	12.8547(16)
b/Å	16.926(2)
c/Å	7.0925(9)
α/°	90
β/°	102.502(3)
γ/°	90
Volume/Å ³	1506.6(3)
Ζ	4
pealeg/cm3	1.245
µ/mm ⁻¹	0.619
F(000)	608.0
Crystal size/mm ³	0.5 imes 0.4 imes 0.3
Radiation	$CuK\alpha$ ($\lambda = 1.54178$)
20 range for data collection/°	5.22 to 136.704
Index ranges	$-15 \le h \le 15, -20 \le k \le 20, -7 \le l \le 8$
Reflections collected	20710
Independent reflections	2719 [$R_{int} = 0.0534$, $R_{sigma} = 0.0324$]
Data/restraints/parameters	2719/0/195
Goodness-of-fit on F ²	1.087
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0989, wR_2 = 0.2813$
Final R indexes [all data]	$R_1 = 0.0998, wR_2 = 0.2819$
Largest diff. peak/hole / e Å ⁻³	0.79/-0.36

Table S7. Crystal data and structure refinement for 3q.

3.2 Single crystal X-ray diffraction result of 4a

The single crystal was obtained from n-hexane and ethyl acetate. Using Olex2,¹ the structure was solved with the XTstructure solution program using Intrinsic Phasing and refined with the XLrefinement package using Least Squares minimisation.²⁻³

Figure S2. Crystal structure of 4a



 Table S8. Crystal data and structure refinement for 4a.

Compound Number	4a
Empirical formula	C ₁₅ H ₁₈ O ₂
Formula weight	230.29
Temperature/K	297
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	12.6874(3)
b/Å	7.3742(2)
c/Å	27.9567(7)
α/°	90
β/°	98.825(2)
γ/°	90
Volume/Å ³	2584.65(11)
Z	8
$\rho_{calc}g/cm^3$	1.184
μ/mm ⁻¹	0.609
F(000)	992.0
Crystal size/mm ³	0.5 imes 0.4 imes 0.3
Radiation	$CuK\alpha (\lambda = 1.54184)$
20 range for data collection/°	11.014 to 144.306
Index ranges	$-15 \le h \le 15, -6 \le k \le 8, -34 \le l \le 34$
Reflections collected	29206
Independent reflections	4984 [R _{int} = 0.0306, R _{sigma} = 0.0155]
Data/restraints/parameters	4984/0/311
Goodness-of-fit on F ²	1.070
Final R indexes [I>= 2σ (I)]	$R_1 = 0.0625, wR_2 = 0.1687$
Final R indexes [all data]	$R_1 = 0.0737, wR_2 = 0.1789$
Largest diff. peak/hole / e Å ⁻³	0.15/-0.15

3.3 References

- (1) Dolomanov, O.V.; Bourhis, L.J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339–341.
- (2) Sheldrick, G. M. SHELXT Integrated space-group and crystal structure determination. *Acta Crystallogr. A* 2015, *71*, 3–8.
- (3) Sheldrick, G. M. A short history of SHELX. Acta Crystallogr. A 2008, 64, 112-122.

4. Copies of NMR spectra

¹H NMR spectra of compound 3a



¹H NMR spectra of compound 3a'



¹H NMR spectra of compound 3b









¹³C NMR spectra of compound 3b





¹H NMR spectra of compound 3c







¹³C NMR spectra of compound 3c







¹H NMR spectra of compound 3d

7,4383 7,72812 7,72812 7,72812 7,72812 7,72817 7,7281 7,7281 7,7281 7,7281 7,7281 7,7281 7,7281 7,7281 7,7281 7,7283 7,2383 7,23333 7,233333 7,233333 7,23333 7,23333 7,23333 7,23333 7,23333 7,23333 7





¹³C NMR spectra of compound 3d

-204.997 -197.220 -197.220 -197.2393 -16.1.273 -153.933 -133.362 -133.286 -133.286 -123.2303 -123.2303 -123.236 -123.		∫37.640 37.0970 -34.031 -34.031 28.454 26.694	11.6613
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¹H NMR spectra of compound 3e

7.5937.57507.57507.45527.44187.44187.44187.44187.44187.42617.42617.42307.741567.742307.741567.742307.72367.73287.73287.73287.725867.725867.725867.72586







¹³C NMR spectra of compound 3e

038	712	592	865 865 865 865 865 867 8679 852 852 405 405	81 29	29	46 69 35	27
03.2	97.0	61.4	25.22.1.1.22.22.22.22.22.22.22.22.22.22.22	7.31	9.52	7.74 1.26 8.40 6.60	1.58
1	ī	ī		4	-5	2227	57





¹H NMR spectra of compound 3f



3.7958
 3.7674
 2.9861
 2.9879
 2.9579
 2.9529
 2.8500
 2.8516
 2.3518
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¹³C NMR spectra of compound 3f

200.8493 196.3040	161.7068 156.5811 155.4304	136.2049 129.7903 128.9915 124.5150 124.4710 120.3687 119.9654 114.8928	77.3172 76.9996 76.6820	59.9367	37,8653 31,4622 28,4908 26,7192	11.6685
1.1	151	141×1	4	1	1551	52



¹H NMR spectra of compound 3g





¹³C NMR spectra of compound 3g





¹H NMR spectra of compound 3h



_	1.		6.4	1-01-1-00-0				
9	00	4	2	0 00 00 00 00 00	00 4 0	6	5000	
3	4	5	9	0 - 00 - 0	- 0 %	C	4000	500
6	P	8	2	-40000	- 0 %	0	0000	~ - m
-	10		10	in all all all all all all	700	0	4040	0 00
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					C. C. C.	Ŷ	Ci Ci Ci Ci Ci	1. 1





¹H NMR spectra of compound 3i









## ¹³C NMR spectra of compound 3i







¹H NMR spectra of compound 3j









# ¹³C NMR spectra of compound 3j







¹H NMR spectra of compound 3k









## ¹³C NMR spectra of compound 3k

204.7555	196.7601	161.4880 156.6474	136.0972 132.8924 129.7055 129.3658 129.3658 128.9511 128.8923 128.1537 126.5420 123.6641 123.6641	77.3177 77.0002 76.6826	59,9816	38.3894 31.5245 28.4937 26.7434	11.6966
1	1	1 1			1		52



## ¹H NMR spectra of compound 31



## ¹³C NMR spectra of compound 31





#### ¹H NMR spectra of compound 3m



110 100 fl (ppm) 

#### ¹H NMR spectra of compound 3n









# ¹³C NMR spectra of compound 3n







# ¹H NMR spectra of compound 30







## ¹³C NMR spectra of compound 30







#### ¹H NMR spectra of compound 3p





#### ¹³C NMR spectra of compound 3p

-204.209; -196.4822 -161.547; -152.9890 -152.9891; -123.1016; -123.1016; -123.1016; -123.1016; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124.8657; -124	$\underbrace{77.3176}{77.0000}\\76.6824$	60.0983	-36.9603 -31.3093 -28.4539 -26.6296	-17.0918 -11.6517 -10.7506
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#### ¹H NMR spectra of compound 3q



## ¹³C NMR spectra of compound 3q

-204.526 -197.081 -197.081 -154.304 -145.364 -145.364 -139.288 -139.288 -139.288 -124.051 -124.051 -124.051 -124.051 -124.051 -124.051 -124.051		-37.4956 31.4897 28.4228 -26.7081 -21.8058 -18.2351 -18.2351 -18.2351 -10.7481
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## ¹H NMR spectra of compound 3r





# ¹H NMR spectra of compound 3s







## ¹³C NMR spectra of compound 3t









#### ¹H NMR spectra of compound 3v



# ¹³C NMR spectra of compound 3v





¹H NMR spectra of compound 3w



## ¹³C NMR spectra of compound 3w







# ¹H NMR spectra of compound 3x



## ¹³C NMR spectra of compound 3x





# ¹H NMR spectra of compound 3y



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#### ¹H NMR spectra of compound 3z



#### ¹H NMR spectra of compound 3aa







#### ¹³C NMR spectra of compound 3aa




#### ¹H NMR spectra of compound 3ab

# 



### ¹³C NMR spectra of compound 3ab





#### ¹H NMR spectra of compound 3ac

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### ¹³C NMR spectra of compound 3ac





#### ¹H NMR spectra of compound 3ad

# 



### ¹³C NMR spectra of compound 3ad





#### ¹H NMR spectra of compound 3ae

#### 7,2602 66515 66515 66515 66515 66515 65515 7,2558 7,35882 7,35882 7,35882 7,35882 7,35882 7,35184 7,35184 7,35184 7,35184 7,35184 7,35184 7,35184 7,35184 7,25185 7,25184 7,25185 7,25184 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25195 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25185 7,25



### ¹³C NMR spectra of compound 3ae





#### ¹H NMR spectra of compound 3af

# 



### ¹³C NMR spectra of compound 3af







#### ¹H NMR spectra of compound 3ag

#### 7, 2597 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6, 6146 6,





### ¹³C NMR spectra of compound 3ag





# ¹H NMR spectra of compound 3ah



# ¹H NMR spectra of compound 3ai





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℃H₃

└ CH₃ ¹H NMR spectra of compound 4a







# ¹³C NMR spectra of compound 4a







# ¹H NMR spectra of compound 4b





# ¹³C NMR spectra of compound 4b





### ¹H NMR spectra of compound 4c





110 100 fl (ppm) 

#### ¹H NMR spectra of compound 4d







### ¹³C NMR spectra of compound 4d







#### ¹H NMR spectra of compound 4e





### ¹³C NMR spectra of compound 4e







#### ¹H NMR spectra of compound 4f





### ¹³C NMR spectra of compound 4f







#### ¹H NMR spectra of compound 4g







# ¹³C NMR spectra of compound 4g





### ¹H NMR spectra of compound 4h





### ¹³C NMR spectra of compound 4h







### ¹H NMR spectra of compound 4i





# ¹³C NMR spectra of compound 4i





# ¹H NMR spectra of compound 4j





# ¹³C NMR spectra of compound 4j







110 100 fl (ppm) 

### ¹H NMR spectra of compound 4k







# ¹³C NMR spectra of compound 4k





### ¹H NMR spectra of compound 41



#### ¹H NMR spectra of compound 4m







### ¹³C NMR spectra of compound 4m







# ¹H NMR spectra of compound 4n



# ¹³C NMR spectra of compound 4n





# ¹H NMR spectra of compound 40





### ¹³C NMR spectra of compound 40







#### ¹H NMR spectra of compound 4p

#### 7,75854 7,77520 7,77520 7,77520 7,77520 7,77520 7,77520 1,77520 1,77520 1,77520 1,77520 1,77520 1,25670 1,25670 1,25670 1,25670 1,25670 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,26709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27709 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,27009 2,2700



### ¹³C NMR spectra of compound 4p





# ¹H NMR spectra of compound 4q





# ¹³C NMR spectra of compound 4q







#### ¹H NMR spectra of compound 4r







# ¹H NMR spectra of compound 4s





# ¹H NMR spectra of compound 4t



### ¹H NMR spectra of compound 4u





### ¹³C NMR spectra of compound 4u







# ¹H NMR spectra of compound 4v



110 100 fl (ppm) 

# ¹H NMR spectra of compound 4w



# ¹³C NMR spectra of compound 4w







# ¹H NMR spectra of compound 4x





# ¹H NMR spectra of compound 4y

#### (7, 7, 3384) (7, 7, 5382) (7, 7, 5382) (7, 7, 5382) (7, 7, 5382) (7, 7, 5382) (7, 7, 5382) (7, 7, 5382) (7, 7, 5382) (7, 7, 5382) (7, 5385) (7, 5386) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2, 65819) (2,



# ¹³C NMR spectra of compound 4y





### ¹H NMR spectra of compound 4z

# 



# ¹³C NMR spectra of compound 4z





### ¹H NMR spectra of compound 4aa







#### ¹H NMR spectra of compound 4ab





### ¹³C NMR spectra of compound 4ab


#### ¹H NMR spectra of compound 4ac

# 7,7259 7,7259 7,7259 7,7259 7,7259 7,7259 7,7259 7,7259 7,7259 7,7259 7,3257 7,3257 7,3257 7,3257 7,3258 7,3188 7,3258 7,3188 7,3256 7,3256 7,3257 7,3257 7,3257 7,3257 7,3257 7,3257 7,3257 7,3257 7,3257 7,3257 7,3257 7,3257 7,3257 7,3377 7,357 7,357 7,357 7,357 7,357 7,357 7,357 7,357 7,357 7,357 7,357 7,375 7,375 7,375





# ¹³C NMR spectra of compound 4ac



# ¹H NMR spectra of compound 4ad

# 





# ¹³C NMR spectra of compound 4ad



#### ¹H NMR spectra of compound 4ae

#### 7,4223 7,725964 7,722964 7,722964 7,722964 7,722964 7,32489 7,32489 7,32489 7,32489 7,32489 7,32489 7,32489 7,32489 7,25915 7,26939 7,26939 7,26939 7,26939 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,26039 7,





# ¹³C NMR spectra of compound 4ae





# ¹H NMR spectra of compound 4af







# ¹³C NMR spectra of compound 4af







#### ¹H NMR spectra of compound 4ag







# ¹³C NMR spectra of compound 4ag





#### ¹H NMR spectra of compound 4ah

# 





# ¹³C NMR spectra of compound 4ah





# ¹H NMR spectra of compound 4ai





# ¹³C NMR spectra of compound 4ai









¹H NMR spectra of compound 4aj



# ¹³C NMR spectra of compound 4aj





¹H NMR spectra of compound 4ak



# ¹³C NMR spectra of compound 4ak





¹H NMR spectra of compound 4al



# ¹³C NMR spectra of compound 4al







#### ¹H NMR spectra of compound 4am



# ¹³C NMR spectra of compound 4am





¹H NMR spectra of compound 4an



# ¹³C NMR spectra of compound 4an





# ¹H NMR spectra of compound 4ao



# ¹³C NMR spectra of compound 4ao





¹H NMR spectra of compound 4ap





# ¹³C NMR spectra of compound 4ap





# ¹H NMR spectra of compound 4aq







#### ¹³C NMR spectra of compound 4aq









110 100 fl (ppm) 

¹H NMR spectra of compound 6a



# ¹³C NMR spectra of compound 6a

~ 209.9077 206.9866 ~ 204.1865		-139.5531 -134.6818 ~132.8186 ~129.5931 -123.6689	77,2120 76,9999 -66,9536	237.3472 35.8015 35.8015 34.8401 31.4844 28.6259 18.2447 18.2447	×7.6088
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