

Supporting Information

Dearomatisation approaches to Spirocyclic Dienones via the Electrophilic Activation of Alkynes

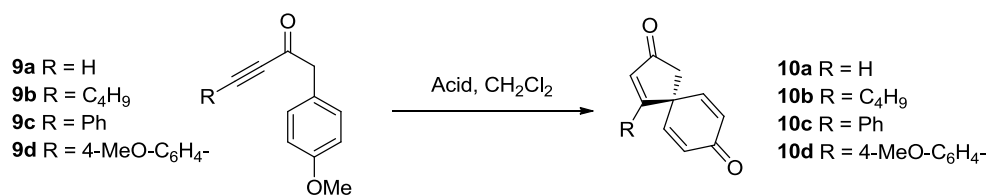
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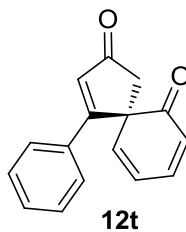
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Table S1. Full optimisation of acid-catalysed ynone spirocyclisation



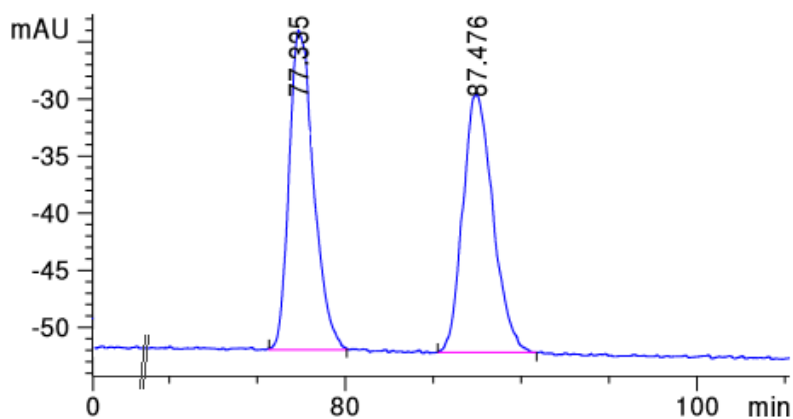
Entry	Ynone	Catalyst	Equiv/ Time [h]/ Temp [°C]	Conversion ^{[a],[b]} (isolated yield in brackets)
1	9a	SnCl ₂ .2H ₂ O	5/20/RT	No Reaction
2	9a	SnCl ₂ .2H ₂ O	5/20/45	No Reaction
3	9b	SnCl ₂ .2H ₂ O	5/20/RT	No Reaction
4	9b	SnCl ₂ .2H ₂ O	5/20/45	No Reaction
5	9c	SnCl ₂ .2H ₂ O	5/20/RT	No Reaction
6	9c	SnCl ₂ .2H ₂ O	5/20/45	10%
7	9d	SnCl ₂ .2H ₂ O	5/20/RT	75% (57%)
8	9d	SnCl ₂ .2H ₂ O H ₂ O (50 eq.)	5/20/RT	No Reaction
9	9d	Dry SnCl ₂	5/20/RT	10%
10	9d	SnCl ₂ .2H ₂ O	1/20/RT	65%
11	9d	SnCl ₂ .2H ₂ O	0.1/72/RT	30%
12	9d	Yb(OTf) ₂	1/20/RT	No Reaction
13	9d	Au(PPh ₃)Cl	1/20/RT	No Reaction
14	9d	Formic acid	1/20/RT	No Reaction
15	9d	Zn(OTf) ₂	1/20/RT	No Reaction
16	9d	ZnCl ₂	1/20/RT	No Reaction
17	9d	PdCl ₂ (PPh ₃) ₂	1/20/RT	No Reaction
18	9d	Sc(OTf) ₃	1/20/RT	25%
9	9d	SnCl ₄	1/20/RT	1:1 9d:10d mixture (with impurities)
20	9d	TFA	1/20/RT	3:1 9d:10d mixture (with impurities)
21	9d	BF ₃ .OEt ₂	1/20/RT	1:9 9d:10d mixture (with impurities)
22	9d	c. HCl aq.	1/4/RT	Complex mixture
23	9d	TfOH	1/1/RT	Complex mixture
24	9d	p-TSA.H ₂ O	1/20/RT	Complex mixture
25	9d	Au(PPh ₃)Cl and AgOTf	1/1/RT	Complex mixture
26	9d	AgOTf	1/20/RT	10%
27	9d	AuCl ₃ .H ₂ O	1/0.25/RT	Complex mixture
28	9d	Cu(OTf) ₂	1/1/RT	>95% (80%)

[a] All reactions performed on 0.09–0.2 mmol of ynone in CH₂Cl₂ (0.1M); [b] Conversion measured from crude ¹H NMR spectra.



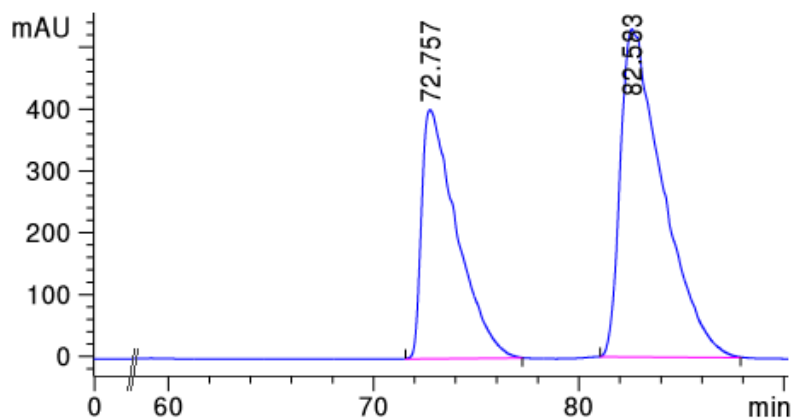
CSP-HPLC of **12t** using Chiralpak ID column, eluting with 20% IPA in hexanes.

1. Racemic **12t** recorded at 280 nm



Peak No.	Retention Time / min	Peak Area	Peak Area / %
1	77.3	2726	50.2
2	87.5	2696	49.7

2. (+)**12t** recorded at 280 nm



Peak No.	Retention Time / min	Peak Area	Peak Area / %
1	72.8	47799	38.4
2	82.6	76541	61.6

