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Electrochemical Rhodium Catalyzed Alkyne Annulation with Pyrazoles through Anodic Oxidation – a Metal Oxidant/Additive Free Methodology

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1. General considerations:

All the catalytic reactions were conducted under nitrogen atmosphere by using standard Schlenk technique. The solvents and chemicals were purchased from Aldrich and Chemtronica in Sweden. All glassware's dried overnight at 120°C and if needed flame dried further. Column chromatography was performed on silica gel (Carlo Erba, 60Å). Thin layer chromatography was performed on a silica gel precoated on aluminum foils with fluorescence indicator (254 nm). Preparative thin layer chromatography was performed on plates available at Aldrich (Analtech, UV_{254} 20×20 cm, 500 micron). Yields refer to isolated compounds and ¹H NMR determined their purity.

Nuclear magnetic resonance (NMR) spectroscopy was performed at 400 MHz (¹H NMR), 101 MHz (¹³C NMR), and 376 MHz (¹⁹F NMR) on Bruker Ascend 400 instrument. Chemical shifts (δ) are provided in ppm and spectra referred to non-deuterated solvent signal.

Mass spectra (HRMS) were obtained from Lund University Kemi Centrum Mass Spectrometry facility. Instrument: Waters XEVO-G2 QTOF. ESI+: Capillary voltage3 kV, Cone voltage 35V, Ext 4, Source Temp 120, Des Temp 300, Cone gas 50, Des gas 400. Continuum resolution mode, m/z 100-1200, manual lock mass correction by Leucine Enkephalin (m/z 556.2771).

Electrochemical reactions were carried out in undivided electrochemical cells (50 mL) using pre-dried glassware. RVC electrodes were obtained from SGL carbon, Wiesbaden, Germany and used with the following dimensions: (30 mm \times 5 mm). Platinum electrodes (99.9 %) were

obtained from ChemPur Karlsruhe, Germany and used with the following dimensions: (10 mm \times 6 mm). Ni foam electrodes were obtained from RECEMAT BV, The Netherlands and used with the following dimensions (30 mm \times 6 mm). Electrocatalysis was conducted using GAMRY instruments Reference 600 & 600 plus potentiostat in constant current mode.

Substituted pyrazoles 1 were prepared according to the reported methods.¹ Alkyne 2a, 4g-4k was commercially available and used as received. Alkynes 4a-f were synthesized according to the reported methods.²



2. Description of electrochemical setup

Figure S1: Glassware setup for electrochemical reactions



Figure S2: Arrangement of RVC and Ni electrodes



Figure S3: Final setup for reactions



Figure S4: Electrochemical station with GAMRY 600 Plus potentiostat



Figure S5: Electrochemical station with GAMRY 600 potentiostat

4. E-factor calculation

To evaluate the efficacy of this green methodology for the alkyne annulation with pyrazole, we undertook a study to calculate the E-factor associated with this reaction and found the total amount of 18.97, which is quite good, factor in comparison to the conventional methods.



Amount of waste: (11.663-0.584) g = 11.079 g E-factor = Amount of waste/Amount of product = 11.079/0.584 = 18.97

5. Cyclic voltammetry studies

Cyclic voltammetry were recorded with a Gamry potentiostat at room temperature. A Ni foam plate was used as counter electrode, a RVC electrode was used as the working electrode, and Ag wire electrode was used as the reference. The measurements were carried out at a scan rate of 100 mV/s.



Figure S7: Cyclic voltammetry at 100 mV/s: nBu_4NPF_6 (100 mM in MeCN), concentration of substrates (KOAc 100 mM), $[Cp*RhCl_2]_2$ catalyst - 5 mM, 2-phenyl pyrazole – 10 mM, diphenylacetylene – 10 mM.



Compound 3a, ¹H NMR, CDCl3, 400 MHz







HRMS spectra of **3a**





Compound 3b, ¹³C NMR, CDCl₃, 101 MHz

	+ 0.1% FA)					
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HRMS spectra of **3b**





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Single Mass Analysis Tolerance = 2.0 mDa / DBE: min = -1.5, max = 100.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3 Monoisotopic Mass, Even Electron Ions 413 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass) Elements Used: C: 0-50 H: 0-100 N: 0-5 O: 0-3 Na: 0-1 CI: 0-1 Mass Calc. Mass mDa PPM DBE Formula i Fit Conf % C H N O Na Cl 355.1001 355.1002 -0.1 -0.3 165 C23 H16 N2 Cl 6.0 100.00 23 16 2 1 DCM-> MeOH (2% H2O + 0.1% FA) 21.5 C24 H11 N4 7.1 0.00 24 11 4 100 355.1001 355.1001 2.84e+007 2.84e+007 2.84e+007 100 357.0982 321.1390 358.1008 427.1312,445.1291 533.1795 610.1862 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 HRMS spectra of 3c															
Single Mass Analysis Tolerance 2.0 mDa / DBE: min = -1.5, max = 100.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3 Monoisotopic Mass, Even Electron Ions 413 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass) Elements Used: C: 0-50 Calc. Mass mDa PPM DBE Formula i Fit Conf % C H N O Na Cl 355.1001 S55.1001 S55.1001 OL H O 100 N: 0-1 S55.1001 S55.1001 S55.1001 S55.1001 DCM-> MeOH (2% H2O + 0.1% FA) 2100 355.1001 S55.1001 S55.1001 1 TOF MS ES+ 2.84e+007 357.0982 357.0982 357.0982 357.0982 357.132.445.1291 357	Cinala		lucia	-	-										_
Total of the control of	Toleranc	e = 2.0 mD	a / D	BE: mi	n = -1 4	max =	100.0								
Number of isotope peaks used for i-FIT = 3 Monoisotopic Mass, Even Electron Ions 413 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass) Elements Used: C: 0-50 H: 0-100 No.05 O: 0-3 Mass Calc. Mass Masspectra of 3c Calc. Mass	Element	prediction:	Off			, man	100.0								
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Number	of isotope p	eaks us	sed for	i-FIT =	3									
413 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass) Elements Used: C: 0-50 H: 0-100 N: 0-5 O: 0-3 Na: 0-1 CI: 0-1 Mass Calc. Mass mDa PPM DBE Formula i Fit Conf % C H N O Na CI 355.1001 355.1002 -0.1 -0.3 16.5 C23 H16 N2 CI 6.0 100.00 23 16 2 1 355.1001 355.0984 1.7 4.8 21.5 C24 H11 N4 7.1 0.00 24 11 4 DCM-> MeOH (2% H2O + 0.1% FA) 210615_HRMS_IN_KS_4CIPy 1 (0.041) Cm (1:111) 1: TOF MS ES+ 2.84e+007 100 355.1001 355.1001 2.84e+007 96 321.1390 358.1008 427.1312,445.1291 533.1795 610.1862 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 HRMS	Monoisot	opic Mass, E	Even Ele	ctron Io	ns										
Elements Used: C: 0-50 H: 0-100 N: 0-5 O: 0-3 Na: 0-1 CI: 0-1 Mass Calc. Mass mDa PPM DBE Formula i Fit Conf % C H N O Na CI 355.1001 355.1002 -0.1 -0.3 16.5 C23 H16 N2 CI 6.0 100.00 23 16 2 1 355.0984 1.7 4.8 21.5 C24 H11 N4 7.1 0.00 24 11 4 DCM-> MeOH (2% H2O + 0.1% FA) 210615_HRMS_IN_KS_4CIPy 1 (0.041) Cm (1:111) 1: TOF MS ES+ 2.84e+007 355.1001 355.1001 2.84e+007 100 355.1001 355.1001 5.1001 2.84e+007 179.0373 247.1235 321.1390 358.1008 427.1312.445.1291 533.1795 610.1862 427.1312.445.1291 533.1795 610.1862 HRMS spectra of 3c	413 form	ula(e) evalua	ated with	1 2 resu	ilts withi	in limits (a	all results	(up to 10	000) for e	each mass)					
C: 0-50 H: 0-100 N: 0-5 O: 0-3 Na: 0-1 C: 0-1 Mass Calc. Mass mDa PPM DBE Formula i Fit Conf % C H N O Na Cl 355.1001 355.1002 -0.1 -0.3 16.5 C23 H16 N2 Cl 6.0 100.00 23 16 2 1 355.0984 1.7 4.8 21.5 C24 H11 N4 7.1 0.00 24 11 4 DCM-> MeOH (2% H2O + 0.1% FA) 210615_HRMS_IN_KS_4CIPy 1 (0.041) Cm (1:111) 1: TOF MS ES+ 2.84e+007 355.1001 2.84e+007 100 96- 179.0373 247.1235 321.1390 358.1008 179.0373 247.1235 400 425 450 475 500 525 550 575 600 HRMS spectra of 3c	Elements	Used:									-				
Mass Calc. Mass mDa PPM DBE Formula i Fit Conf % C H N O Na Cl 355.1001 355.1002 -0.1 -0.3 16.5 C23 H16 N2 Cl 6.0 100.00 23 16 2 1 355.1001 355.0984 1.7 4.8 21.5 C24 H11 N4 7.1 0.00 24 11 4 DCM-> MeOH (2% H2O + 0.1% FA) 210615_HRMS_IN_KS_4CIPy 1 (0.041) Cm (1:111) 1: TOF MS ES+ 2.84e+007 100 355.1001 355.1001 2.84e+007 100 355.1001 2.84e+007 100 355.1001 427.1312_445.1291 533.1795 610.1862 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600	C: 0-50	H:	0-100		N: 0-5		0:0-3		Na: 0-1	1	CI: 0-1	1			
Mass Calc. Mass mDa PPM DBE Formula i Fit Conf % C H N O Na Cl 355.1001 355.1002 -0.1 -0.3 16.5 C23 H16 N2 Cl 6.0 100.00 23 16 2 1 355.1001 355.0984 1.7 4.8 21.5 C24 H11 N4 7.1 0.00 24 11 4 DCM-> MeOH (2% H2O + 0.1% FA) 210615_HRMS_IN_KS_4CIPy 1 (0.041) Cm (1:111) 1: TOF MS ES+ 2.84e+007 100 355.1001 355.1001 2.84e+007 2.84e+007 % 357.0982 357.0982 358.1008 357.0982 150 175 200 225 250 275 300 325 350 375 427.1312_445.1291 533.1795 610.1862 150 175 200 225 250 275 300 325 350 375 400 425 450															
355.1001 355.1002 -0.1 -0.3 16.5 C23 H16 N2 Cl 6.0 100.00 23 16 2 1 355.1001 355.1002 -0.1 -0.3 16.5 C23 H16 N2 Cl 6.0 100.00 23 16 2 1 DCM-> MeOH (2% H2O + 0.1% FA) 210615_HRMS_IN_KS_4CIPy 1 (0.041) Cm (1:111) 1: TOF MS ES+ 100 355.1001 355.1001 2.84e+007 % 357.0982 321.1390 358.1008 0 179.0373 247.1235 427.1312.445.1291 533.1795 610.1862 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 HRMS spectra of 3c 5c 5c 5c 5c 5c 5c 5c 5c 600	Mass	Calc Mass	mDa	DDM	DRE	Formula			i-	Fit Conf %		н	NC	Na	CL
355.0984 1.7 4.8 21.5 C24 H11 N4 7.1 0.00 24 11 4 DCM-> MeOH (2% H2O + 0.1% FA) 210615_HRMS_IN_KS_4CIPy 1 (0.041) Cm (1:111) 1: TOF MS ES+ 2.84e+007 355.1001 357.0982 357.0982 358.1008 427.1312,445.1291 353.1795 610.1862 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 HRMS spectra of 3 c	355.1001	355.1002	-0.1	-0.3	16.5	C23 H16	N2 CI		6.0	100.00	23	16	2	/ 140	1
DCM-> MeOH (2% H2O + 0.1% FA) 210615_HRMS_IN_KS_4CIPy 1 (0.041) Cm (1:111) 1: TOF MS ES+ 2.84e+007 355.1001 355.1001 357.0982 358.1008 179.0373 247.1235 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 HRMS spectra of 3 c		355.0984	1.7	4.8	21.5	C24 H11	N4		7.1	0.00	24	11	4		-
DCM-> MeOH (2% H2O + 0.1% FA) 210615_HRMS_IN_KS_4CIPy 1 (0.041) Cm (1:111) 100 355.1001 2.84e+007 357.0982 358.1008 179.0373 247.1235 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 HRMS spectra of 3c															
DCM-> MeOH (2% H2O + 0.1% FA) 210615_HRMS_IN_KS_4CIPy 1 (0.041) Cm (1:111) 100 9% 100 179.0373 247.1235 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 HRMS spectra of 3c															
210615_HRMS_IN_KS_4CIPy 1 (0.041) Cm (1:111) 1: TOF MS ES+ 2.84e+007 2.84e+007 355.1001 358.1008 358.1008 179.0373 247.1235 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 HRMS spectra of 3c	DCM-> Me	OH (2% H2	0 + 0.19	6 FA)											
100 % 100 % 100 100 100 100 100	210615_H	RMS_IN_K	S_4CIPy	1 (0.04	1) Cm ((1:111)							1:	TOF M	SES+
% 357.0982 358.1008 179.0373 247.1235 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 HRMS spectra of 3c	100					3	355.1001							2.84	e+007
% 357.0982 358.1008 179.0373 247.1235 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 HRMS spectra of 3c															
% 357.0982 321.1390 358.1008 179.0373 247.1235 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 HRMS spectra of 3c															
% 357.0982 358.1008 179.0373 247.1235 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 HRMS spectra of 3c															
321.1390 321.1390 358.1008 427.1312_445.1291 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 HRMS spectra of 3c	%-						257	0000							
321.1390 358.1008 427.1312,445.1291 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 HRMS spectra of 3c							357.	0902							
0 179.0373 247.1235 427.1312.445.1291 533.1795 610.1862 150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 HRMS spectra of 3c						321 1200	358	1008							
150 175 200 225 250 275 300 325 350 375 400 425 450 475 500 525 550 575 600 HRMS spectra of 3c		179.0373	2	47.1238	5	521.1590		4	27.1312	445.1291	53	3.179	5	610	0.1862
HRMS spectra of 3c	1	50 175 20	0 225	250	275 3	00 325	350 37	5 400	425 4	50 475 5	00 52	25 5	50 5	75 60	++ m/z 0
	HRMS s	pectra of	3c												-





Compound 3d, ¹³C NMR, CDCl₃, 101 MHz

DCM-> I	MeOH (2% H2O	+ 0.1% FA)						
210615_	HRMS_IN_KS_4B	rPy 73 (1.324)	Cm (9:111)				1: TOF MS ES+
100		401.0477						1.74e7
•	321.1	1389					N	
1							•	
					Br	Ĩ		
%-							\checkmark	
1						\sim		
		-402.0	507					
152	2.0709	403.05	59					
0- <mark></mark> 100	200 300	400	500	600 70	0 80	0 900	1000	m/z 1100
Element Number Monoiso 439 form Element C: 0-50	t prediction: Off of isotope peaks i htopic Mass, Even E hula(e) evaluated wi is Used: H: 0-100	used for i-FIT = lectron lons ith 2 results witi N: 0-5	: 3 hin limits (a	all results (up 1 O: 0-3	to 1000) fo Na:	or each mas 0-1	s) Br: 0-1	
Mass	Calc. Mass mDa	PPM DBE	Formula		i-FI	Fit Conf %	CHN	O Na Br
399.0493	399.0494 -0.1 399.0497 -0.4	-0.3 20.5 -1.0 16.5	C22 H8 I C23 H16	N4 O3 Na N2 Br	51 30.000	0.00 100.00	22 8 4 23 16 2	3 1 1
DCM-> M	eOH (2% H2O + 0.1	1% FA)						
210615_1	HRMS_IN_KS_4BrF	Py 73 (1.324) Ci	m (9:111)	401.0477				1: TOF MS ES+ 1.74e+007
100								
-								
%-								
-				402.0	507			
36	0.0389.363.0404 3	377.0486 3	89.1536	403.	0559411.	1366 4	27.1312	
• • • • •	360.0 370.0	380.0	390.0	400.0	410.0	420.0	430.0	440.0 m/z

HRMS spectra of **3d**





{name, 0}



DCM-> MeOH (2% H2O +	0.1% FA)	
210615_HRMS_IN_KS_4FP	/ 33 (0.611) Cm (11:111)	1: TOF MS ES+
^{339.}	1294	6.41e7
	340.1325 341.1396 400 500 600 700 80	m/z 900 1000 1100
100 200 000	100 000 000 100 000	
Cingle Mass Analysis		
Tolerance = 2.0 mDa / Di Element prediction: Off Number of isotope peaks us Monoisotopic Mass, Even Ele 404 formula(e) evaluated with Elements Used: C: 0-50 H: 0-100	3E: min = -1.5, max = 100.0 red for i-FIT = 3 ctron lons 1 results within limits (all results (up to 1000) fo N: 0-5 O: 0-3 F: 0-	r each mass) 1 Na: 0-1
Mass Calc Mass mDa	PPM DBE Formula	Fit Conf % C H N O F Na
339.1294 339.1298 -0.4	-1.2 16.5 C23 H16 N2 F 4n/a	n/a 23 16 2 1
210615_HRMS_IN_KS_4FPy	33 (0.611) Cm (11:111)	1: TOF MS ES+
100 -	339.1294	6.41e+007
%-	340.1325	
300 4407 3	15.1309 221 1280 335.1553 341.1396	361 1117 371 1546
0-1	310 315 320 325 330 335 340 345 350	355 360 365 370 375 380 385

HRMS spectra of **3e**

25

HRMS spectra of 3f

HRMS spectra of **3g**

Compound 3h, ¹³C NMR, CDCl₃, 101 MHz

DCM-> N	AeOH (2%	H2O -	+ 0.1%	FA)										
210615 H	RMS IN K	S 24-0	liMePy	12 (0.	234) Cm	(11:111)						-	1: TOF N	AS ES+
100-		349	9.1700											1.22e7
%-								Me	Me					
1			350	1733										
2			371	1523										
1	73 1075		17	. 1525										
0-4	11111111111111111111111111111111111111		-hh					1					100	m m /z
100	200	300	40	0	500	600	700	800	900	10	00	1	100	
			-							_	_	_		_
Tolerance Element Number Monoiso 216 form	e = 2.0 mDa prediction: of isotope p topic Mass, E ula(e) evalua	a / D Off eaks u Even Ele ated wit	BE: mi sed for ectron lo h 2 resu	in = -1 i-FIT = ons ults wit	.5, max = = 3 hin limits	= 100.0 (all result	s (up to 1	000) for	each mass)					
C: 0-50	H:	0-100		N: 0-5	;	0:0-3		Na: 0	-1					
		-		DOD										
Mass 240.1700	Calc. Mass	mDa	1 /	DBE	Cos Los	N/2		I-FL	10 50	25	1 21	2	O. Na	
549.1700	349.1703	1.9	5.4	13.5	C23 H21	N2 Na		50.206	81.42	23	22	2	1	
DCM-> Me 210615 H	OH (2% H20 RMS IN KS	0 + 0.19 3 24-di	% FA) MePv 1:	2 (0 23	(11) 4) Cm	(-111)							1. TOF	MS ES+
400	interio_int_ite		mer y n	2 (0.20	,4) Olli (1	349	1700						1.2	2e+007
1007														
%-														
							350.17	33						
1							351.1	739	371.1523					
0-4-1-1-	305 310	315	320 33	5 220	1 335 2	10 345	350 355	360	365 370 27	5 20	20 2	85	300 20	m/z
300	505 510	515 5	520 52	5 330	5 333 34	40 345	550 555	500 .	505 510 31	5 30	JU 3	00	350 39	-

HRMS spectra of **3h**

Compound 3i, ¹³C NMR, CDCl₃, 101 MHZ
DCM-> MeOH (2% H2O + 0.1% FA)	0.000		
210615_HRMS_IN_KS_20MePy 51 (0.930)	Cm (17:111)		1: TOF MS ES+
100 J 351.1493	С.		9.17e6
	Ĭ	N N	
		N [°]	
		\checkmark	
8-			
1.0			
-352.1525			
175.0960 373.1317			
	705.2913		m/z
100 200 300 400 5	00 600 700	800 900	1000 1100
Single Mass Analysis			
Tolerance = 2.0 mDa / DBE: min = -1.5.	max = 100.0		
Element prediction: Off			
Number of isotope peaks used for i-FIT = 3			
Monoisotopic Mass, Even Electron Ions	lineite (ell es sulte (un te 40)	00) (
Elements Lload:	minus (all results (up to To	ou) for each mass)	
C: 0-50 H: 0-100 N: 0-5	0:0-3	Na: 0-1	
0.000 1.000 1.00	0.00	110.01	
Mass Calc. Mass mDa PPM DBE Fo	rmula	i Fit Conf	% C H N O Na
351.1493 351.1497 -0.4 -1.1 16.5 C2	24 H19 N2 O	30 45.56	24 19 2 1
351.1473 2.0 5.7 13.5 C2	22 H20 N2 O Na	30 54.44	22 20 2 1 1
DOM > MoOH (2% H20 + 0.1% EA)			
210615_HRMS_IN_KS_20MePy 51 (0.930) Cr	m (17:111)		1: TOF MS ES+
100	351.1493		9.17e+006
100-			
%-			
1.00	000 1000		
1 1			
	352.1525		
320 1288 335 1526	352.1525	373.1317	389 1525 397.1525
320.1288 335.1536	352.1525	373.1317	389.1525 397.1525 795 200 205 400 405

HRMS spectra of **3i**





Compound 3J, ¹³C NMR, CDCl₃, 101 MHz

DCM-> N	MeOH (2%	H2O -	+ 0.1%	6 FA)								
210615_H	HRMS_IN_K	S_1Na	pPy 33	8 (0.61	1) Cm (11	1:111)	$\mathbf{\wedge}$	_			1: TOF	MS ES+
100-		3	371.154	15				N N				4.29e7
								N				
								\checkmark				
									ļ			
							ſ	~				
%-												
			27	0 1576								
			51.	2.1070								
			3	93.13	64							
0			mp. I. fr									m/z
100	200	300	40	00	500	600	700 800	900	10	00	1100	
Single	Mass Ana	lysis	-	-					_	_		
Toleranc	e = 2.0 mD	a / D	BE: m	in = -1	.5. max :	= 100.0						
Element	prediction:	Off										
Number	of isotope p	eaks u	sed for	i-FIT :	= 3							
Monoiso	topic Mass, E	Even El	ectron l	ons								
227 form	ula(e) evalua	ated wit	h 1 resi	ults wit	thin limits	(all results	(up to 1000) for	r each mass)			
Element	s Used:				28.1							
C: 0-50	H:	0-100		N: 0-5	0	0:0-3	Na: 0)-1				
Mass	Calc Mass	mDa	DDM	DRE	Formula		i-FIT Norm	Fit Conf %	CH		O Na	
371.1545	371.1548	-0.3	-0.8	19.5	C27 H19	N2	3h/a	n/a	27 1	9 2	0. 140	
DCM-> Me	eOH (2% H2	0 + 0.1	% FA)									
210615_H	HRMS_IN_K	S_1Nap	oPy 33 (0.611)	Cm (11:1	11)					1: TO	F MS ES+
100-						371.154	5				4	4.29e+007
1												
%-												
						37	2 1576					
						1						
						li						
1	321.1392	220.4	420	254	1407	3	73.1614 393	1364399.04	96	10	7 4240	
0-4,	321.1392	332.1	439	35	1.1497	3	73.1614 393.	1364399.04	96 	42	27.1312	ייייד m/z

HRMS spectra of **3**j



Compound 3K+3K', ¹H NMR, CDCl₃, 400 MHZ





HRMS spectra of **3K + 3K'**





DCM-> N	MeOH (2%	H2O -	+ 0.1%	FA)										
210615	HRMS IN K	S 4Me	65 (1	181) C	m (17·11	1)		-	7				1. TOP	MS ES+
100		349	9.1701	101/0		.,			Ň					2.53e7
100							Í	Ĭ.						
-								\sim	\searrow					
									, V	Me				
									J	Wie				
1								Ŷ						
								Me						
8-														
1														
-														
			350	.1733										
2			371	1523										
-	00	1 0046	Ĭ											
0-	28 	1.2016	· .											m/z
100	200	300	40	0	500	600	700	800) 9	000	1000)	1100	
			_	-			_			-	_	_		
Single	Mass Ana	lysis	-		-	100.0								
lolerand	:e = 2.0 mD	a / L	BE: m	in = -1.	.5, max =	= 100.0								
Element	prediction:	Off			-									
Number	of isotope p	eaks u	sed for	1-FII =	: 3									
Monoiso	topic Mass, E	Even Ele	ectron I	ons		(-II Ik- (00016						
2101011	iuia(e) evalua	ated wit	n Trest	uits with	in imits	(all results (up to h	000) 101	each m	iass)				
Element	s Used:													
C: 0-50	H:	0-100		N: 0-5		0:0-3		Na: 0)-1					
							1	1 1						
Mass	Calc. Mass	mDa	PPM	DBE	Formula	9	i-FIT	i f	Fit Conf	% C	H	N	D. Na	
349.1701	349.1705	-0.4	-1.1	16.5	C25 H2	1 N2	41.5	n r	n/a	25	21	2		
DCM-> M	eOH (2% H20	0 + 0.19	% FA)											
210615_H	HRMS_IN_KS	S_4Me	65 (1.18	31) Cm	(17:111)								1: TO	F MS ES+
100-					349.1	701								2.53e+007
100														
-														
-														
1														
%-														
1						350 1722								
]						330.1735								
- 3	10.1597	1740	225 4	540		351.1784		371.152	23	20	0.000	0		
0-4-	315 320	325 2	30 32	5 340	345 2	50 355 26	0 365	370	375 20	30 325	3002	305	400	405 m/z
510	315 320	320 3	50 55	5 340	340 3	50 355 30	0 305	570	315 36	0 300	390	290	400	400

HRMS spectra of **5a**







HRMS spectra of 5b





Compound 5c, $^{\rm 13}{\rm C}$ NMR, CDCl_3, 101 MHz



Compound 5c, ¹³C NMR, CDCl₃, 101 MHz

	· 0.1% FA)				
210615_HRMS_IN_KS_4F_I	3 9 (0.184) Cm (1:110)			1: TOF MS ES+
100 35	7.1200		ſ		1.50e8
				N	
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1					
				ך ערייקער אין	
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1			F		
	358.1231				
145.0759285.1387	-359,1283 573	1953			
0-4	hhilippinghinipping	· · · · · · · · · · · · · · · · · · ·			m/z
100 200 300	400 500	600 700	800 90	1000	1100
Single Mass Analysis					
Tolerance = 2.0 mDa / D	BE: min = -1.5. max :	= 100.0			
Element prediction: Off					
Number of isotope peaks us	sed for i-FIT = 3				
Monoisotopic Mass, Even Ele	ctron lons				
615 formula(e) evaluated with	n 2 results within limits	(all results (up to	1000) for each ma	ass)	
Elements Used:					
C: 0-50 H: 0-100	N: 0-5	O: 0-3	F: 0-2	Na: 0-1	
Mass Calc. Mass mDa	PPM DBE Formula	CALL	i-FI Fit Conf	% C H N (D F Na
357.1200 357.1203 -0.3	-0.8 16.5 C23 H15	N2 F2	4.Q 43.00	23 15 2	and an and a second sec
357.1215 -1.5	-4.2 12.5 C20 H18	110 00 11		LJ 1J L	2
	112 1215 620 1120	NZ O3 Na	4.0 57.00	20 18 2	2 3 1
		NZ O3 Na	4.0 57.00	20 18 2 3	2 3 1
		NZ O3 Na	4.0 57.00	20 18 2 3	3 1
DCM-> MeOH (2% H2O + 0.19	6 FA)	3 N2 O3 Na	4.Ω 57.00	20 18 2 3	3 1
DCM-> MeOH (2% H2O + 0.19 210615_HRMS_IN_KS_4F_B	6 FA) 9 (0.184) Cm (1:110)	3 NZ O3 Na	4.Ω 57.00	20 18 2 3	2 3 1 1: TOF MS ES+
DCM-> MeOH (2% H2O + 0.19 210615_HRMS_IN_KS_4F_B	6 FA) 9 (0.184) Cm (1:110)	3 NZ O3 Na 357.1200	4.Q 57.00	20 18 2 3	2 3 1 1: TOF MS ES+ 1.50e+008
DCM-> MeOH (2% H2O + 0.19 210615_HRMS_IN_KS_4F_B	6 FA) 9 (0.184) Cm (1:110)	3 NZ O3 Na 357.1200	4.Ω 57.00	20 18 2 3	2 3 1 1: TOF MS ES+ 1.50e+008
DCM-> MeOH (2% H2O + 0.19 210615_HRMS_IN_KS_4F_B 100	6 FA) 9 (0.184) Cm (1:110)	3 NZ O3 Na 357.1200	4.Ω 57.00	20 18 2 3	2 3 1 1: TOF MS ES+ 1.50e+008
DCM-> MeOH (2% H2O + 0.19 210615_HRMS_IN_KS_4F_B 100- -	6 FA) 9 (0.184) Cm (1:110)	3 NZ O3 Na 357.1200	4.Ω 57.00	20 18 2 3	2 3 1 1: TOF MS ES+ 1.50e+008
DCM-> MeOH (2% H2O + 0.19 210615_HRMS_IN_KS_4F_B 100- 	6 FA) 9 (0.184) Cm (1:110)	3 NZ O3 Na 357.1200	4.Ω 57.00	20 18 2 3	2 3 1 1: TOF MS ES+ 1.50e+008
DCM-> MeOH (2% H2O + 0.19 210615_HRMS_IN_KS_4F_B 100 %	6 FA) 9 (0.184) Cm (1:110)	3 NZ O3 Na 357.1200	4.Ω 57.00	20 18 2 3	2 3 1 1: TOF MS ES+ 1.50e+008
DCM-> MeOH (2% H2O + 0.19 210615_HRMS_IN_KS_4F_B 100	6 FA) 9 (0.184) Cm (1:110)	3 NZ O3 Na 357.1200 358.1231	4.Ω 57.00	20 18 2 3	2 3 1 1: TOF MS ES+ 1.50e+008
DCM-> MeOH (2% H2O + 0.19 210615_HRMS_IN_KS_4F_B 100	6 FA) 9 (0.184) Cm (1:110)	3 NZ O3 Na 357.1200 358.1231	4.Ω 57.00	20 18 2 3	2 3 1 1: TOF MS ES+ 1.50e+008
DCM-> MeOH (2% H2O + 0.19 210615_HRMS_IN_KS_4F_B 100 %- 	6 FA) 9 (0.184) Cm (1:110) 333.1212 339.1298	3 NZ O3 Na 357.1200 358.1231 359.1283	4.0 57.00 379.1019 409	1132	2 3 1 1: TOF MS ES+ 1.50e+008 457.0459
DCM-> MeOH (2% H2O + 0.19 210615_HRMS_IN_KS_4F_B 100 % % 285.1387 0285.1387	6 FA) 9 (0.184) Cm (1:110) 333.1212.339.1298	357.1200 358.1231 359.1283	4.0 57.00 379.1019 409	.1132	2 3 1 1: TOF MS ES+ 1.50e+008 457.0459

HRMS spectra of **5c**







HRMS spectra of **5d**



Compound 5e, ¹H NMR, CDCl₃, 400 MHz





HRMS spectra of 5e



Compound 5f, ¹H NMR, CDCl₃, 400 MHz



Compound 5f, ¹³C NMR, CDCl₃, 101 MHz

DCM-> MeOH (2% H2O + 0.1% FA) 210615_HRMS_IN_KS_3CI 1 (0.041) Cm (1:111)



HRMS spectra of 5f









HRMS spectra of **5h**





Compound 5i, ¹³C NMR, CDCl₃, 101 MHz



Compound 5i, DEPT135, CDCl₃



HRMS spectra of 5i



Compound 5j, ¹H NMR, CDCl₃, 400 MHz



Compound 5j, ¹³C NMR, CDCl₃, 101 MHz



HRMS spectra of 5j


Compound 5k, ¹³C NMR, CDCl₃, 101 MHz





HRMS spectra of **5k**







HRMS spectra of **5**





DOM-~ IV	MeOH (2%	H2O ·	+ 0.1%	FA)											
210615_H	HRMS_IN_K	S_PhF	Pentyne	_B1	(0.041)	Cm (1:111)							1: TO	F MS ES+	
100	28	87.1542												2.52e7	
%								ĺ							
8		288	1575												
10		30	9 1362												
5			310.139	7											
0-4	ښتينېنېن 200	300	10		500		700	 81	00 90	0	100	0	1100	m/z	
100	200	500	40	0	500	000	100	0	50 50		100				
Single	Mass Ana	lysis	-	-	_		_	-		-	-	-			
Toleranc Element Number Monoisot 179 form Elements	I olerance = 2.0 mDa / DBE: min = -1.5, max = 100.0 Element prediction: Off Number of isotope peaks used for i-FIT = 3 Monoisotopic Mass, Even Electron Ions 179 formula(e) evaluated with 2 results within limits (all results (up to 1000) for each mass) Elements Used:														
C: 0-50	H:	0-100		N: 0-5	5	0: 0-3		Na	0-1						
Mass	Calc. Mass	mDa	PPM	DBE	Formu	la		i	Fit Conf %	C					
287.1542	287.1548	-0.6	-2.1	12.5	C20 11			the second se				N	O. Na		
					C20 H	19 N2		3.0	42.44	20	19	N 2	O. Na	2	
	287.1524	1.8	6.3	9.5	C18 H	19 N2 20 N2 Na		3.0 3.0	42.44 57.56	20 18	19 20	2 2	0. Na 1		
DCM-> Me	287.1524 eOH (2% H2	1.8 0 + 0.1	6.3 % FA)	9.5	C18 H	19 N2 20 N2 Na		3.0 3.0	42.44 57.56	20 18	19 20	N 2 2	0. Na 1		
DCM-> Me 210615_F	287.1524 eOH (2% H2 HRMS_IN_K	1.8 0 + 0.1 S_PhPe	6.3 % FA) entyne_l	9.5 B 1 (0.	C18 H	19 N2 20 N2 Na n (1:111)	1540	3.0 3.0	42.44 57.56	20 18	19 20	N 2 2	0. Na 1 1: T(DF MS ES+ 2 52e+007	
DCM-> Me 210615_F 100_]	287.1524 eOH (2% H2 HRMS_IN_K	1.8 0 + 0.1 3_PhPe	6.3 % FA) entyne_l	9.5 B 1 (0.	C18 H	19 N2 20 N2 Na n (1:111) 287	.1542	3.0 3.0	42.44 57.56	20 18	19 20	N 2 2	0. Na 1 1: T(DF MS ES+ 2.52e+007	
DCM-> Me 210615_F 100-	287.1524 eOH (2% H2 HRMS_IN_K	1.8 0 + 0.1 S_PhPe	6.3 % FA) entyne_l	9,5 B 1 (0.	C18 H	19 N2 20 N2 Na n (1:111) 287	.1542	3.0 3.0	42.44 57.56	20 18	19 20	N 2 2	0. Na 1 1: T(DF MS ES+ 2.52e+007	
DCM-> Me 210615_F 100	287.1524 eOH (2% H2 HRMS_IN_K	1.8 O + 0.1' S_PhPe	6.3 % FA) entyne_l	9.5 B 1 (0.	041) Cr	19 N2 20 N2 Na n (1:111) 287	.1542	3.0 3.0	42.44 57.56	20 18	H 19 20	2 2	0. Na 1 1: T(DF MS ES+ 2.52e+007	
DCM-> Me 210615_H 100 -	287.1524 eOH (2% H2 HRMS_IN_K	1.8 0 + 0.1' S_PhPe	6.3 % FA) entyne_1	9.5 B 1 (0.	041) Cr	19 N2 20 N2 Na n (1:111) 287	.1542	3.0	42.44 57.56	20 18	H 19 20	N 2 2 2	0. Na 1 1: T(DF MS ES+ 2.52e+007	
DCM-> Me 210615_F	287.1524 eOH (2% H2 HRMS_IN_K	1.8 O + 0.1' S_PhPe	6.3 % FA) entyne_l	9.5 B 1 (0.	041) Cr	19 N2 20 N2 Na n (1:111) 287	288.15	3.0	42.44 57.56	20 18	19 20	N 2 2 2	0. Na 1 1: T(DF MS ES+ 2.52e+007	
DCM-> Me 210615_F 100	287.1524 eOH (2% H2 HRMS_IN_K	1.8 0 + 0.1 ¹ S_PhPe	6.3 % FA) entyne_1	9.5 B 1 (0.	041) Cr	19 N2 20 N2 Na n (1:111) 287 285.1392	288.15	3.0 3.0 775 615	42.44 57.56 309	20 18	19 20	N 2 2 2	0. Na 1 1: T(DF MS ES+ 2.52e+007	
DCM-> Me 210615_F	287.1524 eOH (2% H2 HRMS_IN_K 45.1075.248	1.8 0 + 0.1 ¹ S_PhPe	6.3 % FA) entyne_1	9.5 B 1 (0.	041) Cr	19 N2 20 N2 Na n (1:111) 285.1392	288.15	3.0 3.0 615	42.44 57.56 309	20 18 1362	19 20	N 2 2 2 3221.	0. Na 1 1: T(1501_32	DF MS ES+ 2.52e+007	

HRMS spectra of 5l'





Compound 5m, ¹³C NMR, CDCl₃, 101 MHz



HRMS spectra of 5m







HRMS spectra of **5n**

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