

Supporting Information

Palladium-catalysed alleneamination of γ,δ -unsaturated hydrazones with propargylic acetates: access to tetrahydropyridazines bearing allenes

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1. General Information:

Unless otherwise noted, all reactions were carried out under a air atmosphere; materials obtained from commercial suppliers were used directly without further purification. ^1H NMR spectra, ^{13}C NMR spectra, and ^{19}F NMR spectra were recorded on an Agilent 400 or on a Bruker 400 MHz or on a Bruker 500 MHz spectrometer in CDCl_3 . NMR experiments are reported in δ units, parts per million (ppm), and were referenced to CDCl_3 (δ 7.26 or 77.0 ppm) as the internal standard. The data is being reported as (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). All the solvents were used directly without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate. Copies of NMR were processed with MestReNova Software. All the γ,δ -unsaturated hydrazones were synthesized according to the literature ^[1-2], and the propargylic acetate were prepared according to the literature ^[3-5].

2. General procedure for synthesis of tetrahydropyridazines

Typical procedure A:

A sealed tube equipped with a magnetic stir bar was charged with Pd(cod)Cl₂ (8.5 mg, 0.03 mmol, 0.1 equiv), Xphos (17.6 mg, 0.036 mmol, 0.12 equiv), KO^tBu (50.5 mg, 0.45 mmol, 1.5 equiv), propargylic acetates (0.6 mmol, 2.0 equiv), γ,δ -unsaturated ketoximes (0.3 mmol, 1.0 equiv) and THF (2.0 mL). The tube was evacuated and refilled with argon for 3 times (3 $\times$ 1 min) at -78 °C. The reaction mixture was stirred at 50 °C for 48 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product.

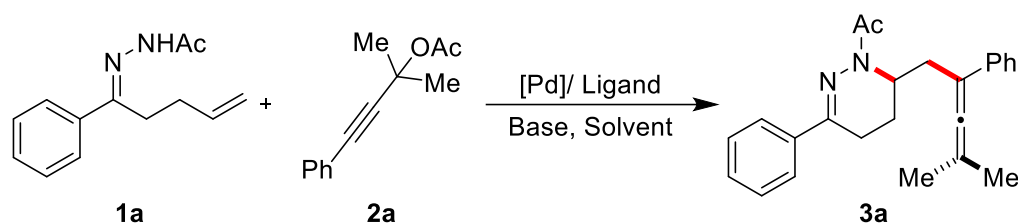
Typical procedure B:

A sealed tube equipped with a magnetic stir bar was charged with [Pd(allyl)Cl]₂ (5.5 mg, 0.015 mmol, 0.05 equiv), Xphos (17.6 mg, 0.036 mmol, 0.12 equiv), KO^tBu (50.5 mg, 0.45 mmol, 1.5 equiv), propargylic acetates (0.6 mmol, 2.0 equiv), γ,δ -unsaturated ketoximes (0.3 mmol, 1.0 equiv) and THF (2.0 mL). The tube was evacuated and refilled with argon for 3 times (3 $\times$ 1 min) at -78 °C. The reaction mixture was stirred at 70 °C for 48 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product.

Typical procedure C:

A sealed tube equipped with a magnetic stir bar was charged with [Pd(allyl)Cl]₂ (5.5 mg, 0.015 mmol, 0.05 equiv), Xphos (17.6 mg, 0.036 mmol, 0.12 equiv), KOH (25.2 mg, 0.45 mmol, 1.5 equiv), propargylic acetates (0.6 mmol, 2.0 equiv), γ,δ -unsaturated ketoximes (0.3 mmol, 1.0 equiv) and THF (2.0 mL). The tube was evacuated and refilled with argon for 3 times (3 $\times$ 1 min) at -78 °C. The reaction mixture was stirred at 70 °C for 48 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product.

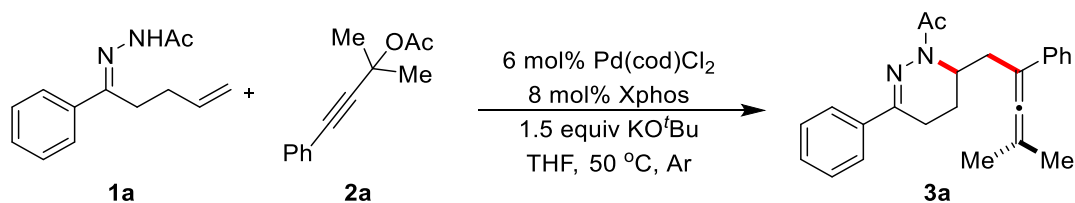
3. Table S1. Optimization of reaction conditions^a:



Entry	Pd catalyst	Ligand	Base	Solvent	Yield (%) ^b
1	Pd(cod)Cl ₂	PPh ₃	KO ^t Bu	THF	42
2	Pd(cod)Cl ₂	XPhos	KO ^t Bu	THF	73
3	Pd(cod)Cl ₂	Dpephos	KO ^t Bu	THF	22
4	Pd(cod)Cl ₂	RuPhos	KO ^t Bu	THF	72
5 ^c	Pd ₂ (dba) ₃	XPhos	KO ^t Bu	THF	57
6	Pd(OAc) ₂	XPhos	KO ^t Bu	THF	64
7	PdCl ₂	XPhos	KO ^t Bu	THF	trace
8 ^c	[Pd(allyl)Cl] ₂	XPhos	KO ^t Bu	THF	71
9	Pd(cod)Cl ₂	XPhos	K ₂ CO ₃	THF	0
10	Pd(cod)Cl ₂	XPhos	NaO ^t Bu	THF	36
11	Pd(cod)Cl ₂	XPhos	Cs ₂ CO ₃	THF	3
12	Pd(cod)Cl ₂	XPhos	KO ^t Bu	toluene	48
13	Pd(cod)Cl ₂	XPhos	KO ^t Bu	CH ₃ CN	trace
14	Pd(cod)Cl ₂	XPhos	KO ^t Bu	1,4-Dioxane	trace
15	Pd(cod)Cl ₂	XPhos	KO ^t Bu	DCE	7
16 ^d	Pd(cod)Cl ₂	XPhos	KO ^t Bu	THF	trace
17	Pd(cod)Cl ₂	--	KO ^t Bu	THF	0
18 ^e	Pd(cod)Cl ₂	XPhos	KO ^t Bu	THF	75

^aReaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol, 2 equiv), base (0.3 mmol, 1.5 equiv), Pd catalyst (10 mol%) and ligand (12 mol%) in solvent (2.0 mL) at 50 °C under Ar for 24 h. ^bIsolated yield. ^cPd catalyst (5 mol%) were used. ^dUnder air for 24 h. ^e**1a** (0.3 mmol), **2a** (0.6 mmol, 2 equiv), base (0.45 mmol, 1.5 equiv), Pd catalyst (10 mol%) and ligand (12 mol%) in solvent (2.0 mL) at 50 °C under Ar for 48 h.

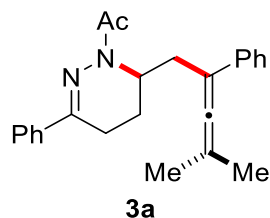
4. Gram-scale synthesis of **3a**:



An 100 mL Schlenk tube equipped with a magnetic stir bar was charged with Pd(cod)Cl₂ (85.7 mg, 0.3 mmol, 0.06 equiv), Xphos (190.7 mg, 0.4 mmol, 0.08 equiv), KO^tBu (841.6 mg, 7.5 mmol, 1.5 equiv), propargylic acetates (2.0225 g, 10 mmol, 2.0 equiv), γ,δ -unsaturated ketoximes (1.0814 g, 5 mmol, 1.0 equiv) and THF (34.0 mL). Degassed THF and backfilled with argon for 3 times (3×1 min) at -78 °C. The reaction mixture was stirred at 50 °C for 48 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product **3a** (66 % yield, 1.19 g).

5. Characterization data for the product

1-(6-(4-methyl-2-phenylpenta-2,3-dien-1-yl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (3a)

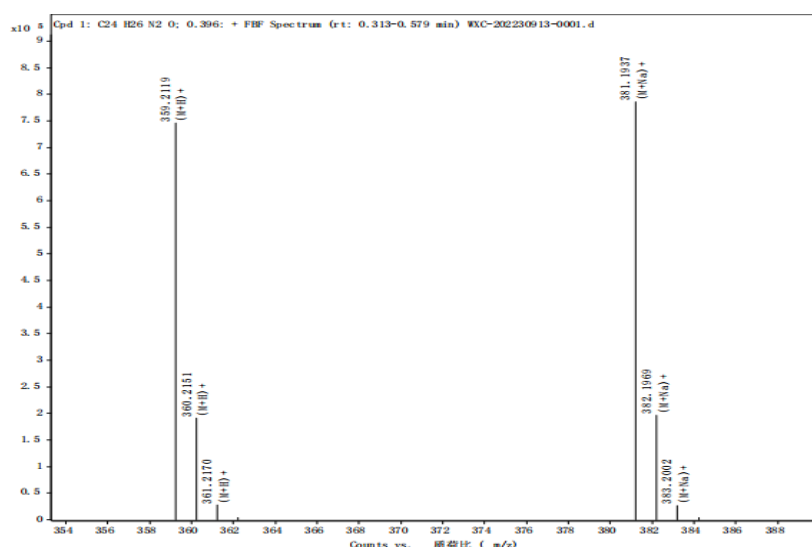


Prepared according to typical procedure A from propargylic acetates (121.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **3a** (80.7 mg, 75% yield) as a yellow solid. Mp: 114-117 °C.

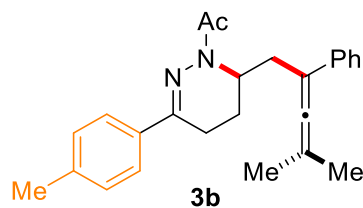
^1H NMR (CDCl_3 , 400 MHz) δ 7.82 (d, $J = 8.0$ Hz, 2H), 7.59 (d, $J = 8.0$ Hz, 2H), 7.45-7.35 (m, 5H), 7.22 (t, $J = 6.4$ Hz, 1H), 5.01-4.98 (m, 1H), 2.93 (dd, $J_1 = 14.0$ Hz, $J_2 = 4.0$ Hz, 1H), 2.70 (dd, $J_1 = 18.0$ Hz, $J_2 = 5.2$ Hz, 1H), 2.61-2.53 (m, 1H), 2.49 (s, 3H), 2.40 (dd, $J_1 = 13.6$ Hz, $J_2 = 11.6$ Hz, 1H), 2.29 (dd, $J_1 = 13.6$ Hz, $J_2 = 6.8$ Hz, 1H), 1.89 (s, 3H), 1.82 (s, 3H), 1.75-1.68 (m, 1H);

^{13}C NMR (CDCl_3 , 100 MHz) δ 203.0, 172.1, 145.9, 137.3, 136.4, 129.1, 128.4 (2C), 126.5, 126.2, 125.1, 99.0, 97.5, 45.3, 30.9, 21.6, 20.3, 20.2, 18.5, 18.2;

HRMS Calcd (ESI) m/z for $\text{C}_{24}\text{H}_{26}\text{N}_2\text{NaO}$ $[\text{M} + \text{Na}]^+$: 381.1937, found: 381.1937.



1-(6-(4-methyl-2-phenylpenta-2,3-dien-1-yl)-3-(p-tolyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (3b)

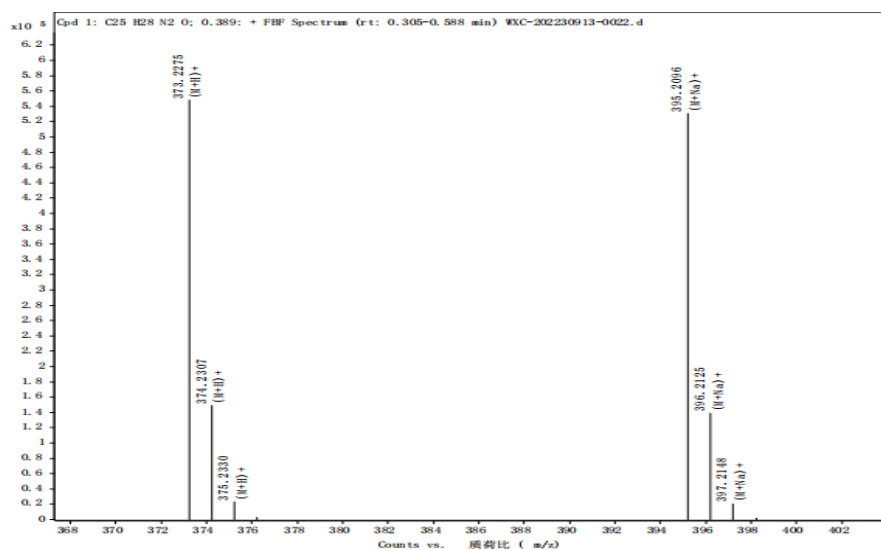


Prepared according to typical procedure **A** from propargylic acetates (121.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (69.1 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **3b** (80.5 mg, 72 % yield) as a yellow solid. Mp: 91-94 °C.

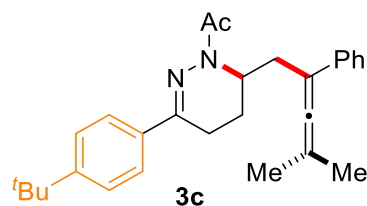
^1H NMR (CDCl_3 , 500 MHz) δ 7.70 (d, J = 8.0 Hz, 2H), 7.58-7.56 (m, 2H), 7.35 (t, J = 7.5 Hz, 2H), 7.23-7.19 (m, 3H), 4.99-4.96 (m, 1H), 2.91 (dd, J_1 = 14.0 Hz, J_2 = 4.0 Hz, 1H), 2.66 (dd, J_1 = 18.0 Hz, J_2 = 6.0 Hz, 1H), 2.56-2.50 (m, 1H), 2.46 (s, 3H), 2.39-2.35 (m, 4H), 2.26 (dd, J_1 = 14.0 Hz, J_2 = 7.0 Hz, 1H), 1.87 (s, 3H), 1.80 (s, 3H), 1.71-1.67 (m, 1H);

^{13}C NMR (CDCl_3 , 125 MHz) δ 203.0, 172.0, 146.1, 139.2, 136.5, 134.7, 129.1, 128.5, 126.5, 126.2, 125.1, 99.1, 97.5, 45.3, 30.9, 21.6, 21.3, 20.3, 20.2, 18.6, 18.2;

HRMS Calcd (ESI) m/z for $\text{C}_{25}\text{H}_{29}\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 373.2274, found: 373.2275.



1-(3-(4-(tert-butyl)phenyl)-6-(4-methyl-2-phenylpenta-2,3-dien-1-yl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (3c)

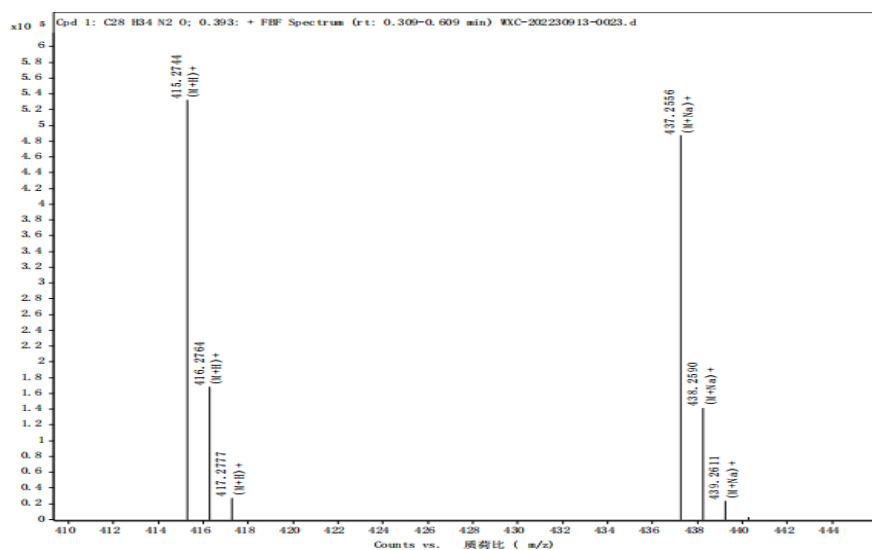


Prepared according to typical procedure A from propargylic acetates (121.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (81.7 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 18) give the product **3c** (97.9 mg, 79 % yield) as a yellow solid. Mp: 70-73 °C.

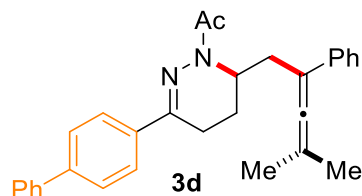
^1H NMR (CDCl_3 , 400 MHz) δ 7.78 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 6.8 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 6.8 Hz, 1H), 5.03-5.00 (m, 1H), 2.93 (dd, J_1 = 14.4 Hz, J_2 = 4.4 Hz, 1H), 2.71 (dd, J_1 = 18.0 Hz, J_2 = 5.2 Hz, 1H), 2.61-2.55 (m, 1H), 2.49 (s, 3H), 2.43-2.36 (m, 1H), 2.28 (dd, J_1 = 13.6 Hz, J_2 = 6.8 Hz, 1H), 1.90 (s, 3H), 1.82 (s, 3H), 1.75-1.69 (m, 1H), 1.38 (s, 9H);

^{13}C NMR (CDCl_3 , 125 MHz) δ 203.0, 172.0, 152.4, 146.1, 136.4, 134.6, 128.4, 126.5, 126.2, 125.3, 124.9, 99.1, 97.5, 45.2, 34.7, 31.2, 30.8, 21.6, 20.2 (2C), 18.6, 18.2;

HRMS Calcd (ESI) m/z for $\text{C}_{28}\text{H}_{35}\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 415.2744, found: 415.2744.



1-(3-([1,1'-biphenyl]-4-yl)-6-(4-methyl-2-phenylpenta-2,3-dien-1-yl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (3d)

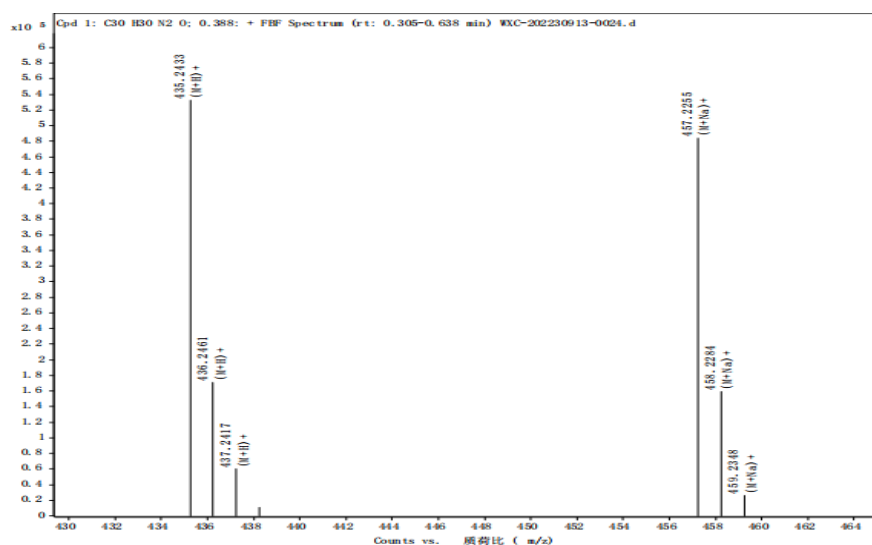


Prepared according to typical procedure **A** from propargylic acetates (121.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (87.7 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **3d** (86.3 mg, 66 % yield) as a white solid. Mp: 143-146 °C.

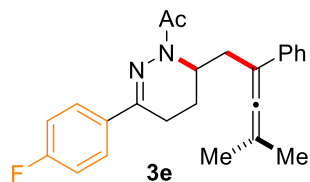
^1H NMR (CDCl_3 , 500 MHz) δ 7.89 (d, $J = 8.5$ Hz, 2H), 7.66 (t, $J = 8.5$ Hz, 4H), 7.60 (d, $J = 7.5$ Hz, 2H), 7.48 (t, $J = 7.5$ Hz, 2H), 7.41-7.36 (m, 3H), 7.22 (t, $J = 7.0$ Hz, 1H), 5.03-5.00 (m, 1H), 2.94 (dd, $J_1 = 14.5$ Hz, $J_2 = 4.0$ Hz, 1H), 2.73 (dd, $J_1 = 18.0$ Hz, $J_2 = 5.5$ Hz, 1H), 2.63-2.55 (m, 1H), 2.50 (s, 3H), 2.41 (dd, $J_1 = 14.0$ Hz, $J_2 = 11.5$ Hz, 1H), 2.30 (dd, $J_1 = 14.0$ Hz, $J_2 = 7.0$ Hz, 1H), 1.90 (s, 3H), 1.82 (s, 3H), 1.77-1.73 (m, 1H);

^{13}C NMR (CDCl_3 , 125 MHz) δ 203.0, 172.1, 145.6, 141.8, 140.4, 136.5, 136.3, 128.8, 128.5, 127.6, 127.0 (2C), 126.5, 126.2, 125.6, 99.1, 97.6, 45.4, 30.9, 21.6, 20.3, 20.2, 18.5, 18.2;

HRMS Calcd (ESI) m/z for $\text{C}_{30}\text{H}_{31}\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 435.2431, found: 435.2433.



1-(3-(4-fluorophenyl)-6-(4-methyl-2-phenylpenta-2,3-dien-1-yl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (3e)



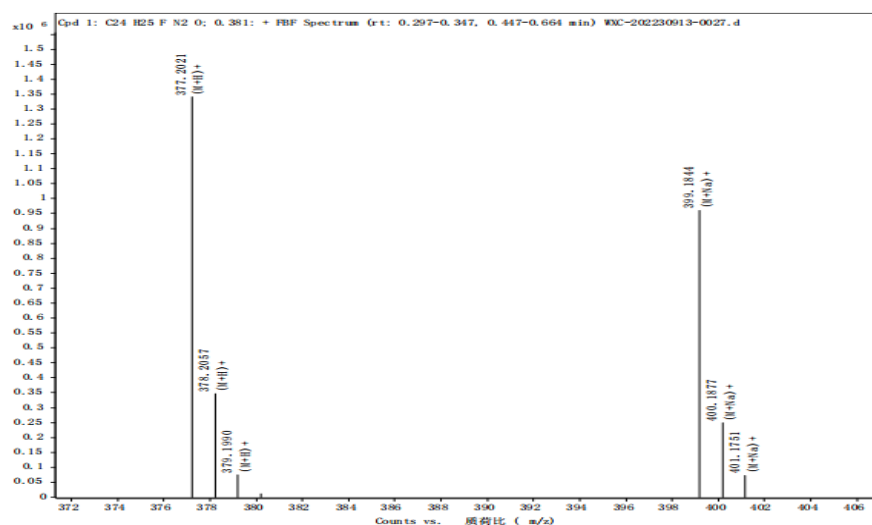
Prepared according to typical procedure **A** from propargylic acetates (121.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (70.3 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **3e** (83.7 mg, 74 % yield) as a white solid. Mp: 77-80 °C.

^1H NMR (CDCl_3 , 500 MHz) δ 7.80-7.77 (m, 2H), 7.56 (d, $J = 7.5$ Hz, 2H), 7.35 (t, $J = 7.5$ Hz, 2H), 7.20 (t, $J = 7.0$ Hz, 1H), 7.10 (t, $J = 8.5$ Hz, 2H), 4.98-4.96 (m, 1H), 2.91 (dd, $J_1 = 14.0$ Hz, $J_2 = 3.5$ Hz, 1H), 2.64 (dd, $J_1 = 18.0$ Hz, $J_2 = 5.5$ Hz, 1H), 2.56-2.48 (m, 1H), 2.45 (s, 3H), 2.37 (dd, $J_1 = 14.0$ Hz, $J_2 = 12.0$ Hz, 1H), 2.27 (dd, $J_1 = 14.0$ Hz, $J_2 = 7.0$ Hz, 1H), 1.87 (s, 3H), 1.80 (s, 3H), 1.71-1.63 (m, 1H);

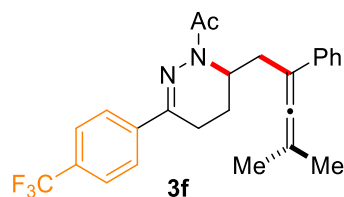
^{13}C NMR (CDCl_3 , 125 MHz) δ 203.0, 172.0, 163.4 (d, $J = 247.5$ Hz), 144.9, 136.4, 133.6 (d, $J = 3.3$ Hz), 128.5, 127.0 (d, $J = 8.1$ Hz), 126.5, 126.2, 115.3 (d, $J = 21.5$ Hz), 99.1, 97.6, 45.3, 30.9, 21.6, 20.3, 20.2, 18.5, 18.3;

^{19}F NMR (CDCl_3 , 376 MHz) δ -112.1;

HRMS Calcd (ESI) m/z for $\text{C}_{24}\text{H}_{25}\text{FN}_2\text{NaO}$ $[\text{M} + \text{Na}]^+$: 399.1843, found: 399.1844.



1-(6-(4-methyl-2-phenylpenta-2,3-dien-1-yl)-3-(4-(trifluoromethyl)phenyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (3f)



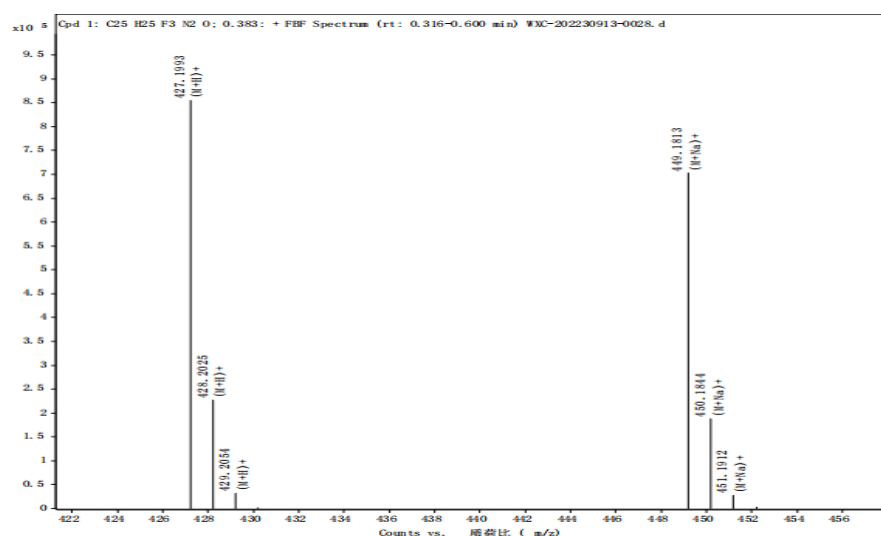
Prepared according to typical procedure **A** from propargylic acetates (121.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (85.3 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **3f** (87.5 mg, 68 % yield) as a yellow solid. Mp: 114-117 °C.

¹H NMR (CDCl₃, 400 MHz) δ 7.91 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 7.2 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 5.02-4.99 (m, 1H), 2.94 (dd, J_1 = 14.4 Hz, J_2 = 4.0 Hz, 1H), 2.69 (dd, J_1 = 18.0 Hz, J_2 = 5.6 Hz, 1H), 2.62-2.54 (m, 1H), 2.48 (s, 3H), 2.39 (dd, J_1 = 14.0 Hz, J_2 = 11.6 Hz, 1H), 2.32 (dd, J_1 = 13.6 Hz, J_2 = 6.8 Hz, 1H), 1.90 (s, 3H), 1.82 (s, 3H), 1.77-1.69 (m, 1H);

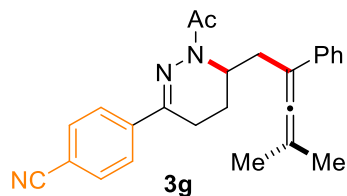
¹³C NMR (CDCl₃, 125 MHz) δ 203.0, 172.1, 144.3, 140.7, 136.4, 130.7 (q, J = 32.1 Hz), 128.5, 126.6, 126.2, 125.4, 125.3 (q, J = 3.8 Hz), 124.0 (q, J = 270.0 Hz), 99.0, 97.7, 45.5, 31.0, 21.6, 20.3, 20.2, 18.4, 18.3;

¹⁹F NMR (CDCl₃, 376 MHz) δ -62.7;

HRMS Calcd (ESI) m/z for C₂₅H₂₆F₃N₂O [M + H]⁺: 427.1992, found: 427.1993.



4-(1-acetyl-6-(4-methyl-2-phenylpenta-2,3-dien-1-yl)-1,4,5,6-tetrahydropyridazin-3-yl)benzonitrile (3g)

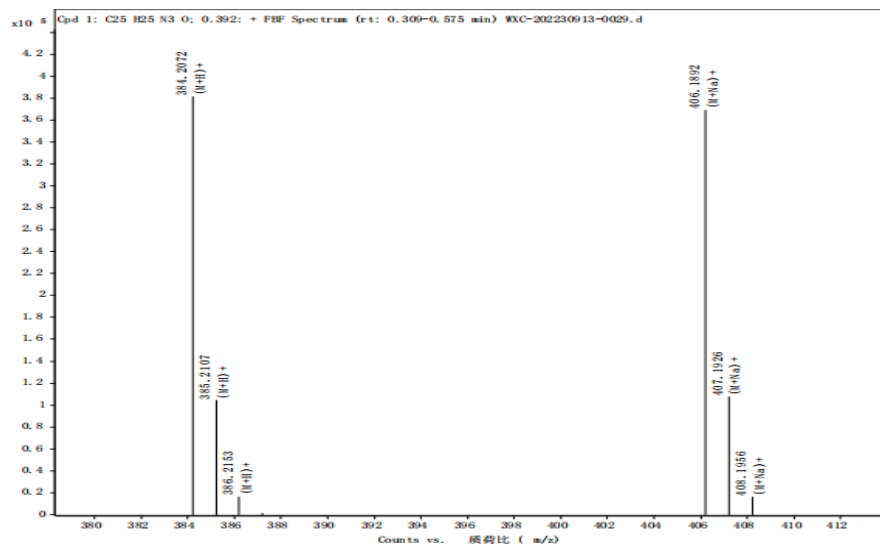


Prepared according to typical procedure **A** from propargylic acetates (121.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (72.4 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3g** (62.7 mg, 54 % yield) as a yellow solid. Mp: 128-131 °C.

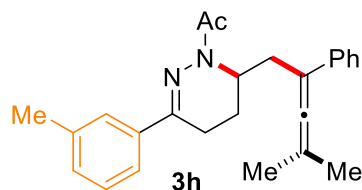
^1H NMR (CDCl_3 , 400 MHz) δ 7.88 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.8 Hz, 2H), 7.56-7.54 (m, 2H), 7.35 (t, J = 7.2 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 4.99-4.96 (m, 1H), 2.91 (dd, J_1 = 14.0 Hz, J_2 = 3.6 Hz, 1H), 2.65 (dd, J_1 = 18.0 Hz, J_2 = 5.6 Hz, 1H), 2.58-2.50 (m, 1H), 2.46 (s, 3H), 2.38-2.28 (m, 2H), 1.87 (s, 3H), 1.80 (s, 3H), 1.73-1.66 (m, 1H);

^{13}C NMR (CDCl_3 , 125 MHz) δ 203.0, 172.1, 143.7, 141.4, 136.3, 132.2, 128.5, 126.6, 126.1, 125.6, 118.7, 112.2, 98.9, 97.7, 45.6, 31.1, 21.6, 20.3, 20.2, 18.3, 18.1;

HRMS Calcd (ESI) m/z for $\text{C}_{25}\text{H}_{26}\text{N}_3\text{O}$ $[\text{M} + \text{H}]^+$: 384.2070, found: 384.2072.



1-(6-(4-methyl-2-phenylpenta-2,3-dien-1-yl)-3-(m-tolyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (3h)

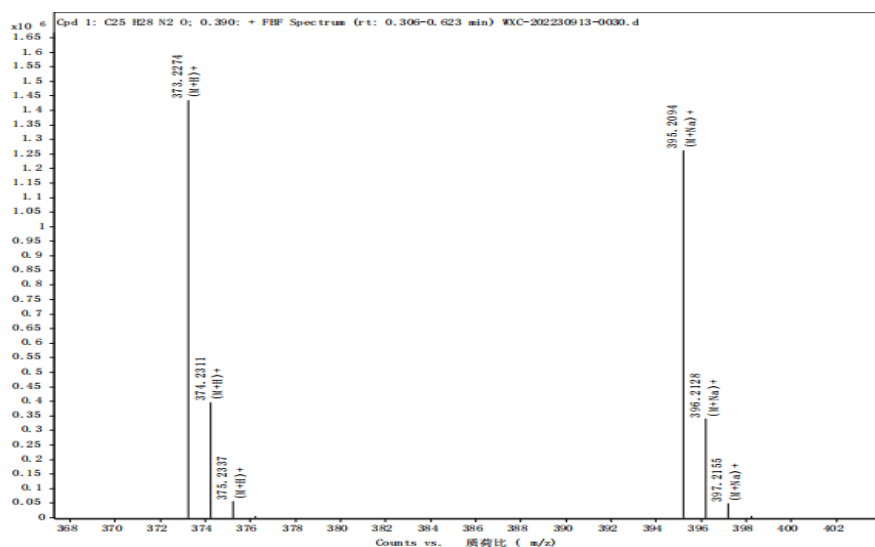


Prepared according to typical procedure **A** from propargylic acetates (121.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (69.1 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **3h** (51.2 mg, 46 % yield) as a yellow solid. Mp: 111-113 °C.

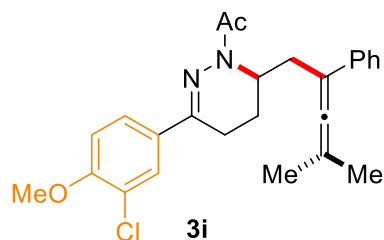
¹H NMR (CDCl₃, 500 MHz) δ 7.61 (d, J = 7.0 Hz, 2H), 7.59-7.57 (m, 2H), 7.36 (t, J = 8.0 Hz, 2H), 7.31 (t, J = 7.5 Hz, 1H), 7.21 (t, J = 7.0 Hz, 2H), 4.99-4.97 (m, 1H), 2.91 (dd, J_1 = 14.0 Hz, J_2 = 4.0 Hz, 1H), 2.68 (dd, J_1 = 18.0 Hz, J_2 = 5.5 Hz, 1H), 2.58-2.53 (m, 1H), 2.48 (s, 3H), 2.42 (s, 3H), 2.38 (dd, J_1 = 14.0 Hz, J_2 = 11.5 Hz, 1H), 2.27 (dd, J_1 = 14.0 Hz, J_2 = 7.0 Hz, 1H), 1.88 (s, 3H), 1.81 (s, 3H), 1.73-1.69 (m, 1H);

¹³C NMR (CDCl₃, 125 MHz) δ 203.0, 172.1, 146.2, 138.0, 137.4, 136.5, 129.9, 128.5, 128.3, 126.5, 126.2, 125.8, 122.4, 99.1, 97.5, 45.3, 30.9, 21.6, 21.6, 20.3, 20.2, 18.5, 18.3;

HRMS Calcd (ESI) m/z for C₂₅H₂₉N₂O [M + H]⁺: 373.2274, found: 373.2274.



1-(3-(3-chloro-4-methoxyphenyl)-6-(4-methyl-2-phenylpenta-2,3-dien-1-yl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (3i)

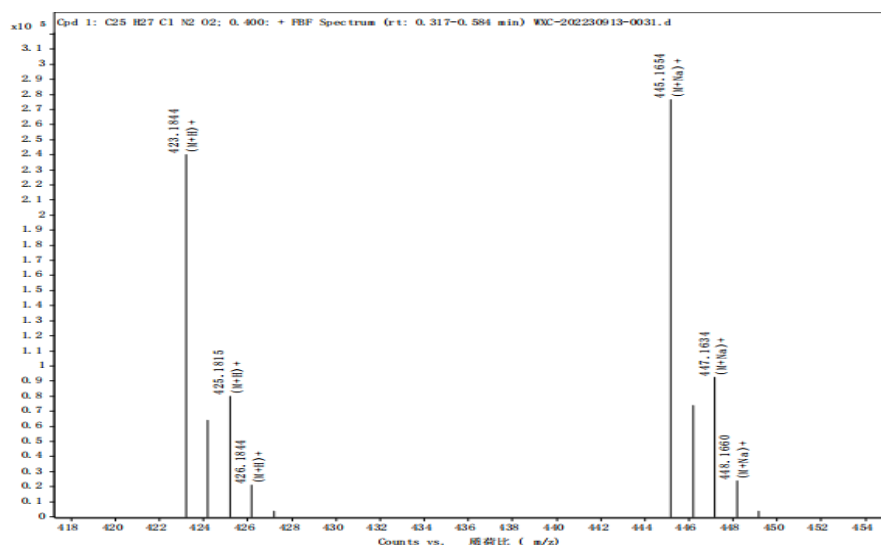


Prepared according to typical procedure **A** from propargylic acetates (121.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (84.2 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **3i** (58.2 mg, 46 % yield) as a yellow solid. Mp: 128-131 °C.

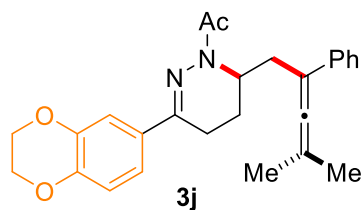
¹H NMR (CDCl₃, 400 MHz) δ 7.82 (s, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.57 (d, J = 7.6 Hz, 2H), 7.35 (t, J = 7.2 Hz, 2H), 7.20 (t, J = 6.8 Hz, 1H), 6.95 (d, J = 8.8 Hz, 1H), 4.98-4.96 (m, 1H), 3.94 (s, 3H), 2.92-2.88 (m, 1H), 2.62 (dd, J_1 = 17.2 Hz, J_2 = 4.4 Hz, 1H), 2.53-2.45 (m, 4H), 2.39-2.33 (m, 1H), 2.29-2.24 (m, 1H), 1.88 (s, 3H), 1.81 (s, 3H), 1.73-1.65 (m, 1H);

¹³C NMR (CDCl₃, 100 MHz) δ 202.9, 171.9, 155.6, 144.5, 136.4, 131.0, 128.4, 127.1, 126.5, 126.1, 124.7, 122.6, 111.5, 99.0, 97.6, 56.2, 45.3, 30.9, 21.6, 20.2, 20.2, 18.4, 18.1;

HRMS Calcd (ESI) m/z for C₂₅H₂₇ClN₂NaO₂ [M + Na]⁺: 445.1653, found: 445.1654.



1-(3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-6-(4-methyl-2-phenylpenta-2,3-dien-1-yl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (3j)

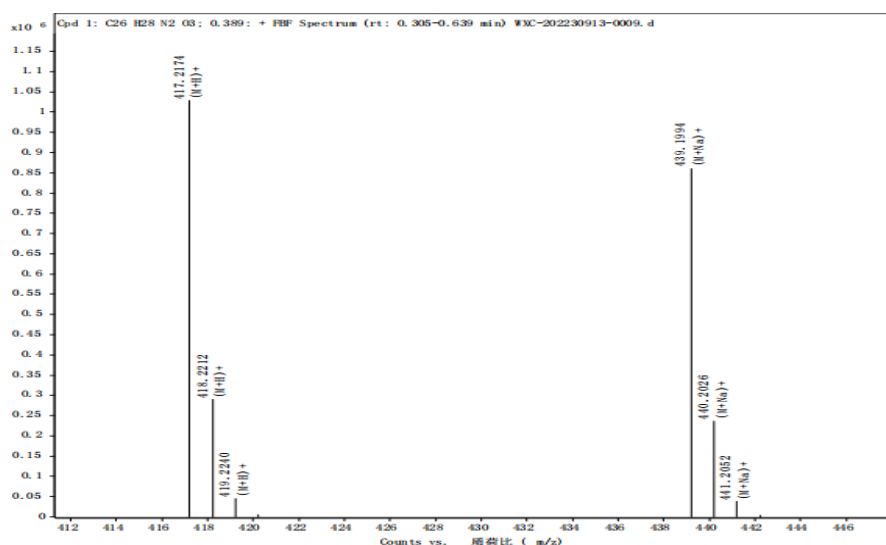


Prepared according to typical procedure **A** from propargylic acetates (121.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (82.3 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **3j** (83.6 mg, 67 % yield) as a yellow solid. Mp: 131-134 °C.

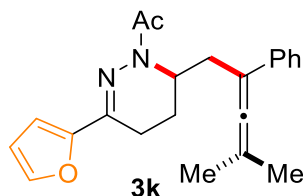
^1H NMR (CDCl_3 , 400 MHz) δ 7.56 (d, J = 8.4 Hz, 2H), 7.37-7.29 (m, 4H), 7.19 (t, J = 6.4 Hz, 1H), 6.89 (d, J = 8.8 Hz, 1H), 4.97-4.94 (m, 1H), 4.33-4.24 (m, 4H), 2.89 (dd, J_1 = 14.0 Hz, J_2 = 3.2 Hz, 1H), 2.61 (dd, J_1 = 18.0 Hz, J_2 = 5.2 Hz, 1H), 2.52-2.48 (m, 1H), 2.44 (s, 3H), 2.35 (dd, J_1 = 14.0 Hz, J_2 = 12.0 Hz, 1H), 2.23 (dd, J_1 = 13.6 Hz, J_2 = 6.4 Hz, 1H), 1.86 (s, 3H), 1.79 (s, 3H), 1.70-1.64 (m, 1H);

^{13}C NMR (CDCl_3 , 100 MHz) δ 203.0, 172.0, 145.5, 144.6, 143.3, 136.5, 131.2, 128.5, 126.5, 126.2, 118.6, 117.1, 114.2, 99.1, 97.5, 64.5, 64.3, 45.2, 30.8, 21.6, 20.3, 20.2, 18.6, 18.2;

HRMS Calcd (ESI) m/z for $\text{C}_{26}\text{H}_{29}\text{N}_2\text{O}_3$ $[\text{M} + \text{H}]^+$: 417.2173, found: 417.2173.



1-(3-(furan-2-yl)-6-(4-methyl-2-phenylpenta-2,3-dien-1-yl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (3k)

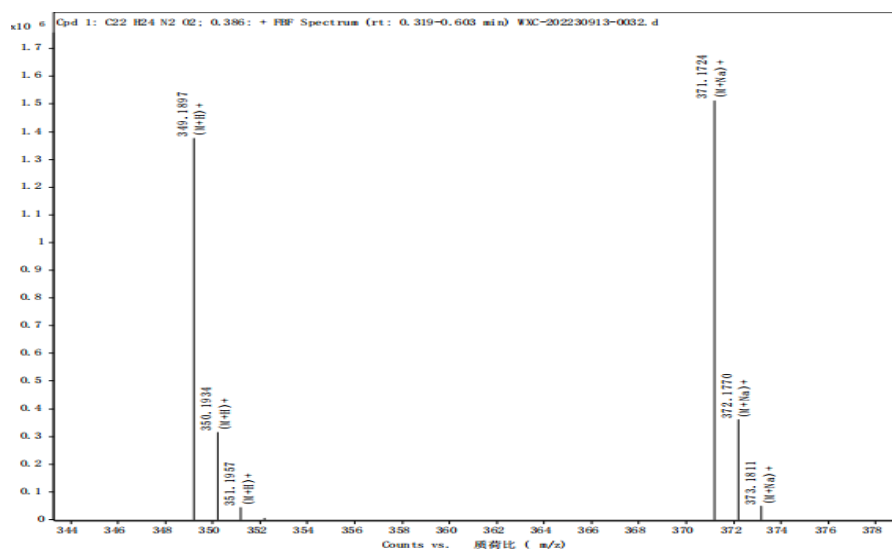


Prepared according to typical procedure **A** from propargylic acetates (121.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (61.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **3k** (47.6 mg, 46 % yield) as a white solid. Mp: 117-120 °C.

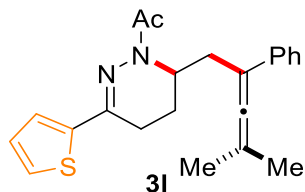
¹H NMR (CDCl₃, 400 MHz) δ 7.57 (d, J = 8.0 Hz, 2H), 7.49-7.48 (m, 1H), 7.35 (t, J = 8.0 Hz, 2H), 7.20 (t, J = 7.2 Hz, 1H), 6.71 (d, J = 3.6 Hz, 1H), 6.48-6.47 (m, 1H), 4.99-4.96 (m, 1H), 2.91 (dd, J_1 = 14.4 Hz, J_2 = 4.0 Hz, 1H), 2.63 (dd, J_1 = 18.0 Hz, J_2 = 5.6 Hz, 1H), 2.52-2.45 (m, 1H), 2.43-2.36 (m, 4H), 2.22 (dd, J_1 = 13.6 Hz, J_2 = 6.8 Hz, 1H), 1.86 (s, 3H), 1.80 (s, 3H), 1.71-1.63 (m, 1H);

¹³C NMR (CDCl₃, 100 MHz) δ 202.9, 171.9, 151.9, 143.1, 139.5, 136.4, 128.4, 126.5, 126.2, 111.5, 108.3, 99.0, 97.6, 45.6, 30.9, 21.3, 20.2 (2C), 18.0, 17.6;

HRMS Calcd (ESI) m/z for C₂₂H₂₄N₂NaO₂ [M + Na]⁺: 371.1730, found: 371.1724.



1-(6-(4-methyl-2-phenylpenta-2,3-dien-1-yl)-3-(thiophen-2-yl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (3l)

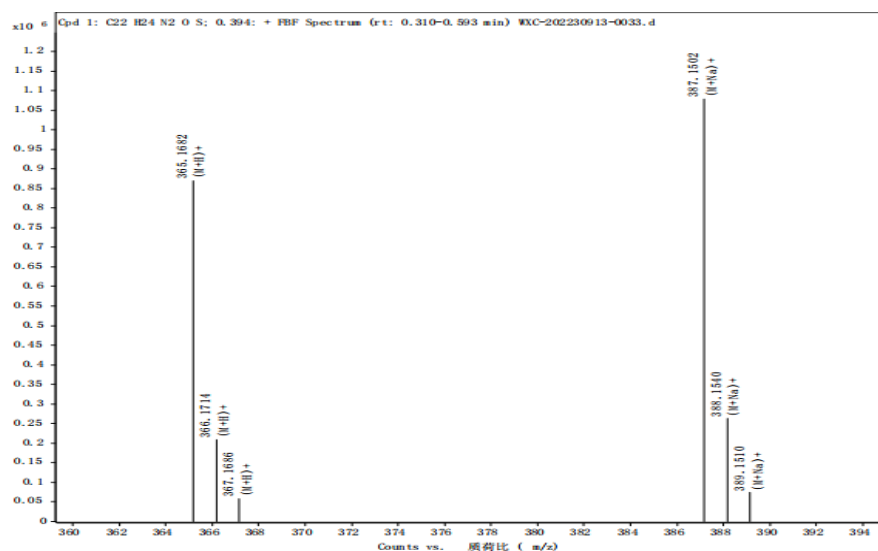


Prepared according to typical procedure **A** from propargylic acetates (121.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (66.7 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **3l** (64.6 mg, 59 % yield) as a yellow oil.

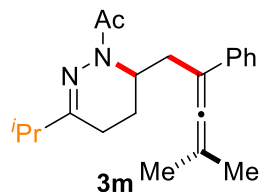
^1H NMR (CDCl_3 , 500 MHz) δ 7.55 (d, $J = 7.5$ Hz, 2H), 7.34 (t, $J = 7.5$ Hz, 2H), 7.31-7.30 (m, 1H), 7.25-7.24 (m, 1H), 7.19 (t, $J = 7.0$ Hz, 1H), 7.04-7.02 (m, 1H), 4.97-4.95 (m, 1H), 2.90 (dd, $J_1 = 14.0$ Hz, $J_2 = 3.5$ Hz, 1H), 2.67 (dd, $J_1 = 18.0$ Hz, $J_2 = 6.0$ Hz, 1H), 2.58-2.51 (m, 1H), 2.41-2.36 (m, 4H), 2.23 (dd, $J_1 = 13.5$ Hz, $J_2 = 6.5$ Hz, 1H), 1.85 (s, 3H), 1.79 (s, 3H), 1.73-1.67 (m, 1H);

^{13}C NMR (CDCl_3 , 125 MHz) δ 203.0, 171.8, 143.3, 142.8, 136.4, 128.5, 127.2, 127.0, 126.5, 126.2, 125.1, 99.1, 97.6, 45.5, 30.9, 21.4, 20.3, 20.2, 18.8, 18.4;

HRMS Calcd (ESI) m/z for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{NaOS}$ $[\text{M} + \text{Na}]^+$: 387.1502, found: 387.1502.



1-(3-isopropyl-6-(4-methyl-2-phenylpenta-2,3-dien-1-yl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (3m)

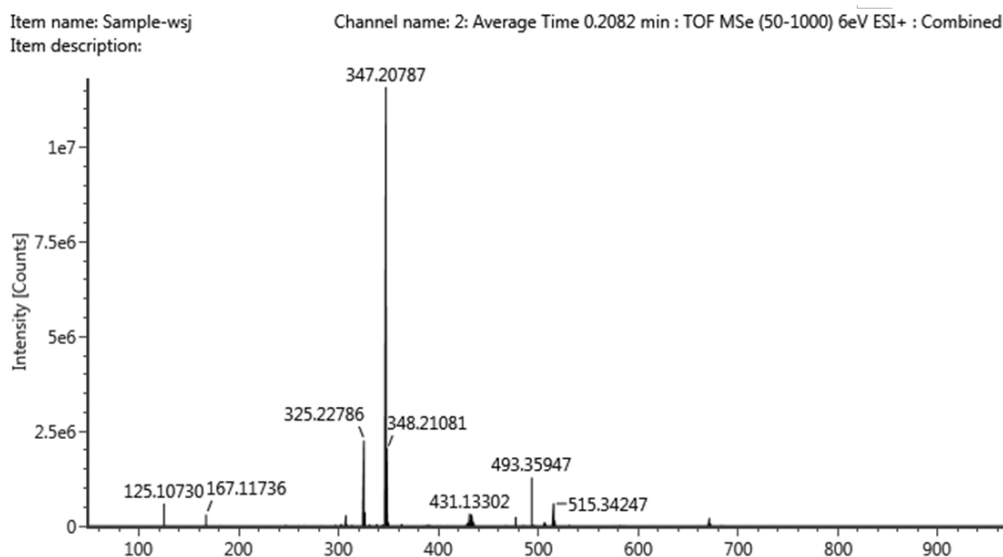


Prepared according to typical procedure **B** from propargylic acetates (121.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (54.7 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **3m** (30.8 mg, 32 % yield) as a yellow oil.

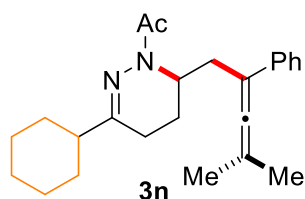
^1H NMR (CDCl_3 , 400 MHz) δ 7.56 (d, $J = 8.0$ Hz, 2H), 7.33 (t, $J = 7.6$ Hz, 2H), 7.18 (t, $J = 7.2$ Hz, 1H), 4.86-4.84 (m, 1H), 2.85 (dd, $J_1 = 14.0$ Hz, $J_2 = 4.0$ Hz, 1H), 2.49-2.42 (m, 1H), 2.30-2.24 (m, 4H), 2.21-2.13 (m, 1H), 2.11-2.03 (m, 2H), 1.83 (s, 3H), 1.79 (s, 3H), 1.57-1.47 (m, 1H), 1.15-1.13 (m, 6H);

^{13}C NMR (CDCl_3 , 100 MHz) δ 202.9, 171.8, 155.6, 136.5, 128.4, 126.4, 126.2, 99.2, 97.4, 45.1 (2C), 36.1, 30.7, 21.4, 20.3, 20.1, 19.6, 18.5 (2C);

HRMS Calcd (ESI) m/z for $\text{C}_{21}\text{H}_{28}\text{N}_2\text{NaO}$ $[\text{M} + \text{Na}]^+$: 347.20938, found: 347.20787.



1-(3-cyclohexyl-6-(4-methyl-2-phenylpenta-2,3-dien-1-yl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (3n)

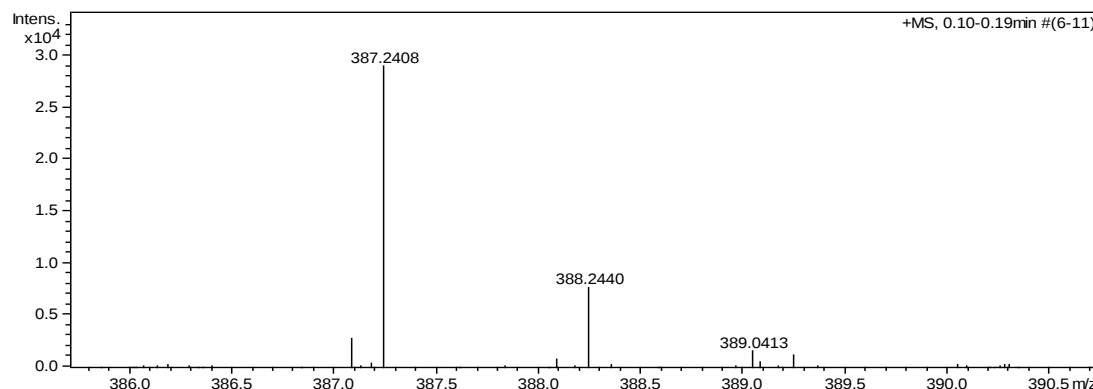


Prepared according to typical procedure **B** from propargylic acetates (121.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (66.7 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **3n** (52.5 mg, 48 % yield) as a yellow oil.

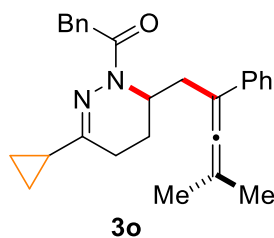
^1H NMR (CDCl_3 , 400 MHz) δ 7.54 (d, $J = 7.6$ Hz, 2H), 7.33 (t, $J = 7.2$ Hz, 2H), 7.18 (t, $J = 7.6$ Hz, 1H), 4.86-4.83 (m, 1H), 2.83 (dd, $J_1 = 14.0$ Hz, $J_2 = 2.8$ Hz, 1H), 2.29 (s, 3H), 2.26-2.21 (m, 1H), 2.18-2.02 (m, 4H), 1.86-1.75 (m, 9H), 1.70 (d, $J = 11.6$ Hz, 1H), 1.55-1.48 (m, 1H), 1.43-1.30 (m, 6H);

^{13}C NMR (CDCl_3 , 100 MHz) δ 203.0, 171.8, 155.2, 136.6, 128.4, 126.4, 126.2, 99.3, 97.4, 46.0, 45.2, 30.7, 30.5, 30.1, 29.7, 26.2, 26.1, 21.5, 20.3, 20.2, 19.0, 18.5;

HRMS Calcd (ESI) m/z for $\text{C}_{24}\text{H}_{32}\text{N}_2\text{NaO}$ $[\text{M} + \text{Na}]^+$: 387.2407, found: 387.2408.



1-(3-cyclopropyl-6-(4-methyl-2-phenylpenta-2,3-dien-1-yl)-5,6-dihydropyridazin-1(4H)-yl)-2-phenylethan-1-one (3o)

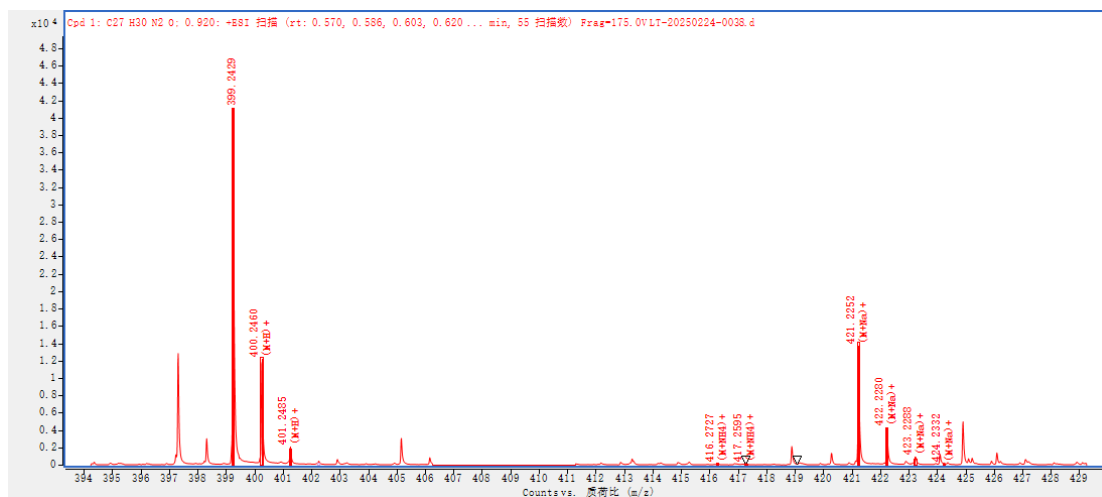


Prepared according to typical procedure C from propargylic acetates (121.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (76.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **3o** (38.9 mg, 33 % yield) as a yellow oil.

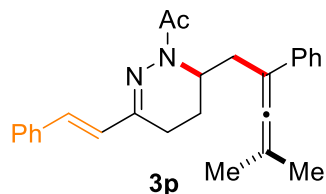
^1H NMR (CDCl_3 , 400 MHz) δ 7.53 (d, $J = 7.2$ Hz, 2H), 7.33-7.28 (m, 6H), 7.24-7.20 (m, 1H), 7.17 (t, $J = 7.2$ Hz, 1H), 4.89-4.86 (m, 1H), 4.06 (d, $J = 14.4$ Hz, 1H), 3.99 (d, $J = 14.4$ Hz, 1H), 2.85 (dd, $J_1 = 14.0$ Hz, $J_2 = 4.0$ Hz, 1H), 2.29-2.16 (m, 2H), 2.09-2.00 (m, 2H), 1.82 (s, 3H), 1.79 (s, 3H), 1.58-1.50 (m, 2H), 0.86-0.77 (m, 4H);

^{13}C NMR (CDCl_3 , 100 MHz) δ 202.9, 171.4, 152.9, 136.4, 129.3, 128.5, 128.3, 126.4, 126.3, 126.2, 99.1, 97.4, 45.4, 40.1, 30.5, 20.4, 20.3, 20.2, 18.4, 17.0, 7.2, 6.5;

HRMS Calcd (ESI) m/z for $\text{C}_{27}\text{H}_{31}\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 399.2431, found: 399.2429.



(E)-1-(6-(4-methyl-2-phenylpenta-2,3-dien-1-yl)-3-styryl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (3p)

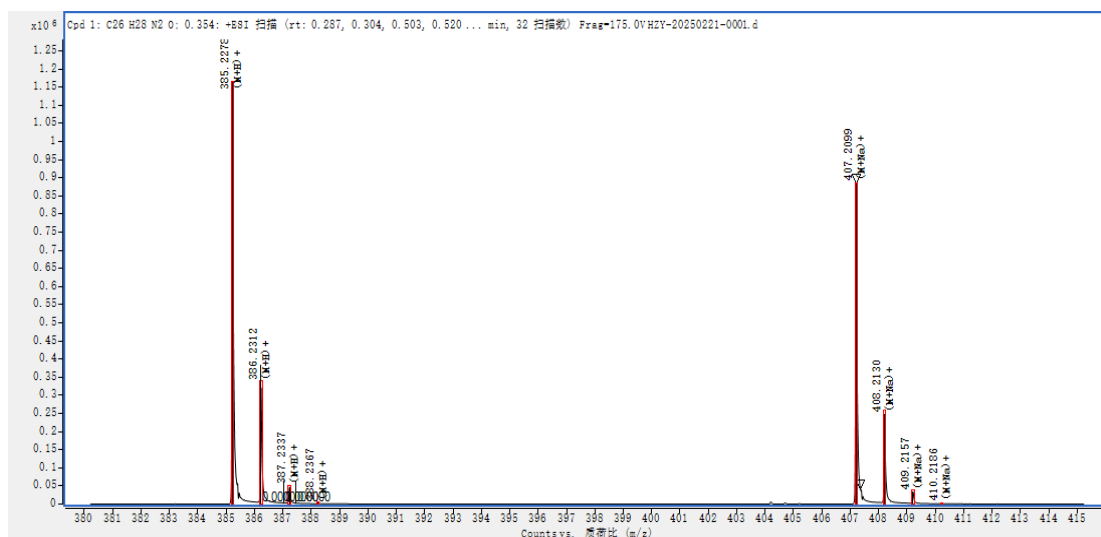


Prepared according to typical procedure **B** from propargylic acetates (121.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (72.7 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **3p** (53.7 mg, 47 % yield) as a yellow solid. Mp: 112-114 °C.

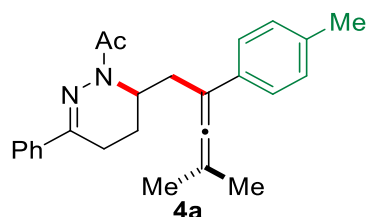
¹H NMR (CDCl₃, 400 MHz) δ 7.58 (d, J = 7.6 Hz, 2H), 7.51 (d, J = 7.2 Hz, 2H), 7.39-7.34 (m, 4H), 7.30 (t, J = 7.2 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 6.88 (s, 2H), 4.97-4.94 (m, 1H), 2.89 (dd, J_1 = 14.4 Hz, J_2 = 4.0 Hz, 1H), 2.55 (dd, J_1 = 18.0 Hz, J_2 = 5.6 Hz, 1H), 2.40-2.33 (m, 5H), 2.22 (dd, J_1 = 14.0 Hz, J_2 = 6.8 Hz, 1H), 1.88 (s, 3H), 1.82 (s, 3H), 1.68-1.61 (m, 1H);

¹³C NMR (CDCl₃, 100 MHz) δ 203.0, 171.9, 147.7, 136.4, 136.3, 131.8, 128.8, 128.7, 128.5, 128.3, 126.7, 126.5, 126.2, 99.1, 97.6, 45.8, 30.9, 21.5, 20.3, 20.2, 18.1, 16.9;

HRMS Calcd (ESI) m/z for C₂₆H₂₉N₂O [M + H]⁺: 385.2274, found: 385.2278.



1-(6-(4-methyl-2-(p-tolyl)penta-2,3-dien-1-yl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (4a)

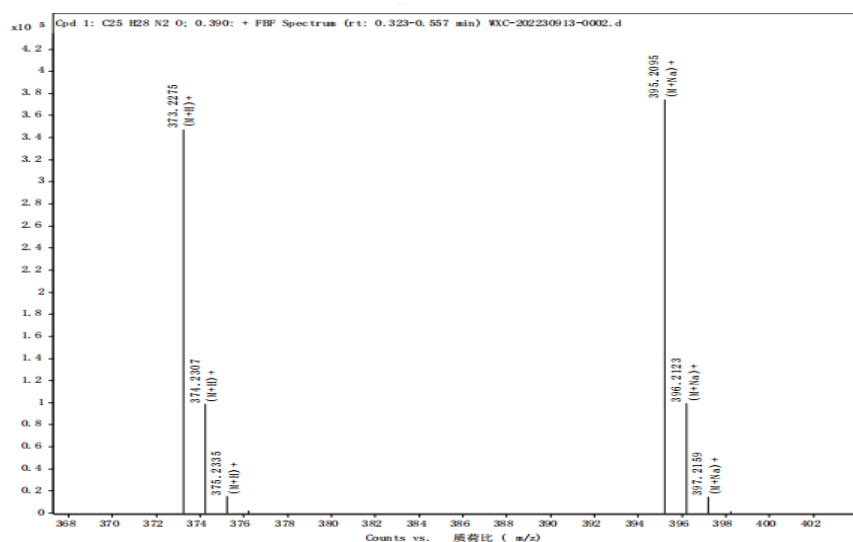


Prepared according to typical procedure **A** from propargylic acetates (129.8 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **4a** (87.1 mg, 78 % yield) as a yellow solid. Mp: 129-132 °C.

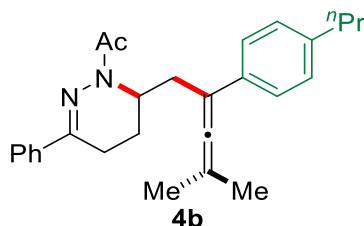
^1H NMR (CDCl_3 , 400 MHz) δ 7.83-7.80 (m, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 7.45-7.37 (m, 3H), 7.18 (d, $J = 8.0$ Hz, 2H), 5.00-4.97 (m, 1H), 2.92 (dd, $J_1 = 14.0$ Hz, $J_2 = 3.6$ Hz, 1H), 2.69 (dd, $J_1 = 18.0$ Hz, $J_2 = 5.6$ Hz, 1H), 2.60-2.53 (m, 1H), 2.48 (s, 3H), 2.40-2.34 (m, 4H), 2.30-2.25 (m, 1H), 1.88 (s, 3H), 1.80 (s, 3H), 1.73-1.66 (m, 1H);

^{13}C NMR (CDCl_3 , 100 MHz) δ 202.6, 172.0, 145.9, 137.4, 136.2, 133.4, 129.2, 129.1, 128.4, 126.1, 125.1, 98.9, 97.3, 45.3, 30.9, 21.6, 21.0, 20.3 (2C), 18.5, 18.2.

HRMS Calcd (ESI) m/z for $\text{C}_{25}\text{H}_{28}\text{N}_2\text{NaO}$ $[\text{M} + \text{Na}]^+$: 395.2094, found: 395.2095.



1-(6-(4-methyl-2-(4-propylphenyl)penta-2,3-dien-1-yl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (4b)

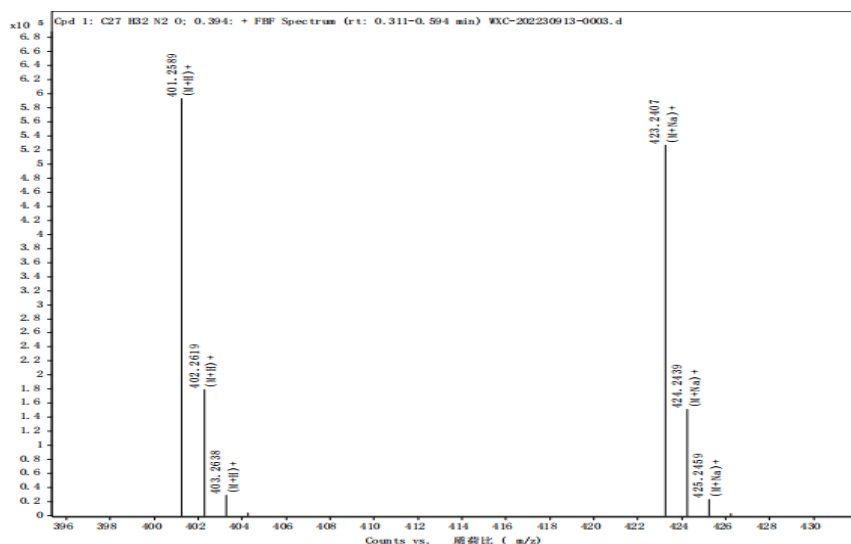


Prepared according to typical procedure **A** from propargylic acetates (146.6 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **4b** (85.3 mg, 71 % yield) as a yellow solid. Mp: 118-121 °C.

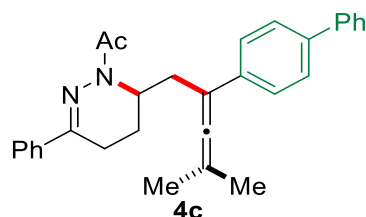
¹H NMR (CDCl₃, 400 MHz) δ 7.83-7.81 (m, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.45-7.39 (m, 3H), 7.18 (d, J = 8.0 Hz, 2H), 5.01-4.98 (m, 1H), 2.91 (dd, J_1 = 14.0 Hz, J_2 = 4.0 Hz, 1H), 2.69 (dd, J_1 = 18.4 Hz, J_2 = 6.0 Hz, 1H), 2.60-2.53 (m, 3H), 2.48 (s, 3H), 2.38 (dd, J_1 = 14.0 Hz, J_2 = 12.0 Hz, 1H), 2.29 (dd, J_1 = 14.0 Hz, J_2 = 7.2 Hz, 1H), 1.88 (s, 3H), 1.81 (s, 3H), 1.70-1.61 (m, 3H), 0.96 (t, J = 7.2 Hz, 3H);

¹³C NMR (CDCl₃, 100 MHz) δ 202.7, 172.0, 145.9, 141.0, 137.4, 133.7, 129.1, 128.6, 128.4, 126.0, 125.1, 98.9, 97.3, 45.3, 37.6, 30.9, 24.5, 21.6, 20.3, 20.2, 18.5, 18.2, 13.8;

HRMS Calcd (ESI) m/z for C₂₇H₃₂N₂NaO [M + Na]⁺: 423.2407, found: 423.2407.



1-(6-(2-([1,1'-biphenyl]-4-yl)-4-methylpenta-2,3-dien-1-yl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (4c)

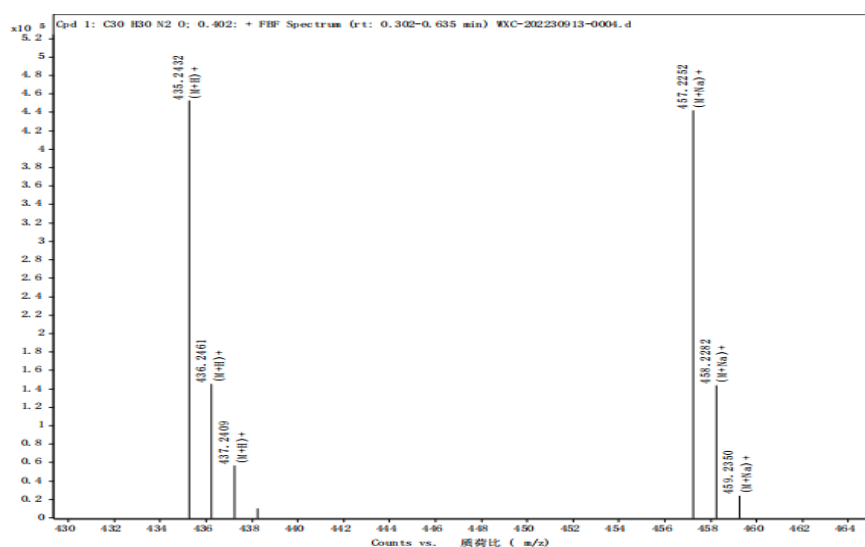


Prepared according to typical procedure **A** from propargylic acetates (167.0 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **4c** (79.7 mg, 61 % yield) as a yellow solid. Mp: 142-146 °C.

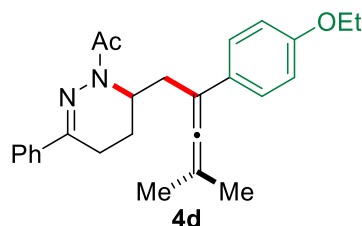
¹H NMR (CDCl₃, 400 MHz) δ 7.85 (d, J = 7.6 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.64-7.63 (m, 4H), 7.48-7.41 (m, 5H), 7.38-7.34 (m, 1H), 5.07-5.04 (m, 1H), 2.99 (dd, J_1 = 14.0 Hz, J_2 = 4.0 Hz, 1H), 2.73 (dd, J_1 = 18.0 Hz, J_2 = 5.2 Hz, 1H), 2.64-2.56 (m, 1H), 2.51 (s, 3H), 2.48-2.41 (m, 1H), 2.33 (dd, J_1 = 14.4 Hz, J_2 = 6.0 Hz, 1H), 1.93 (s, 3H), 1.86 (s, 3H), 1.78-1.72 (m, 1H).

¹³C NMR (CDCl₃, 125 MHz) δ 203.2, 172.1, 145.9, 140.8, 139.3, 137.4, 135.5, 129.2, 128.7, 128.4, 127.2, 127.1, 126.9, 126.6, 125.2, 98.9, 97.7, 45.3, 31.0, 21.6, 20.3 (2C), 18.5, 18.2.

HRMS Calcd (ESI) m/z for C₃₀H₃₁N₂O [M + H]⁺: 435.2431, found: 435.2432.

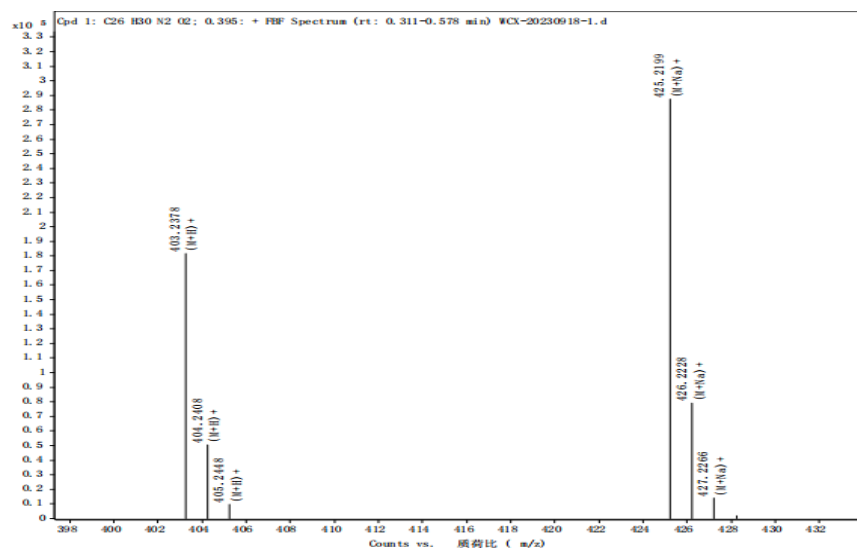


1-(6-(2-(4-ethoxyphenyl)-4-methylpenta-2,3-dien-1-yl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (4d)

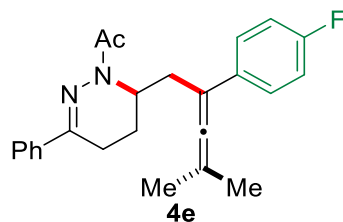


Prepared according to typical procedure **A** from propargylic acetates (147.8 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **4d** (85.9 mg, 71 % yield) as a yellow solid. Mp: 87-90 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.81 (d, $J = 7.2$ Hz, 2H), 7.50 (d, $J = 8.8$ Hz, 2H), 7.44-7.37 (m, 3H), 6.90 (d, $J = 8.4$ Hz, 2H), 4.99-4.96 (m, 1H), 4.04 (q, $J = 6.8$ Hz, 2H), 2.89 (dd, $J_1 = 14.0$ Hz, $J_2 = 4.4$ Hz, 1H), 2.68 (dd, $J_1 = 18.0$ Hz, $J_2 = 5.6$ Hz, 1H), 2.60-2.52 (m, 1H), 2.48 (s, 3H), 2.36 (dd, $J_1 = 13.6$ Hz, $J_2 = 11.6$ Hz, 1H), 2.28 (dd, $J_1 = 14.0$ Hz, $J_2 = 6.8$ Hz, 1H), 1.87 (s, 3H), 1.79 (s, 3H), 1.73-1.65 (m, 1H), 1.42 (t, $J = 7.2$ Hz, 3H); **^{13}C NMR** (CDCl_3 , 100 MHz) δ 202.3, 172.1, 157.7, 146.0, 137.4, 129.1, 128.5, 128.4, 127.3, 125.1, 114.5, 98.6, 97.2, 63.4, 45.3, 31.1, 21.6, 20.4 (2C), 18.4, 18.2, 14.8; **HRMS** Calcd (ESI) m/z for $\text{C}_{26}\text{H}_{30}\text{N}_2\text{NaO}_2$ $[\text{M} + \text{Na}]^+$: 425.2199, found: 425.2199.



1-(6-(2-(4-fluorophenyl)-4-methylpenta-2,3-dien-1-yl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (4e)



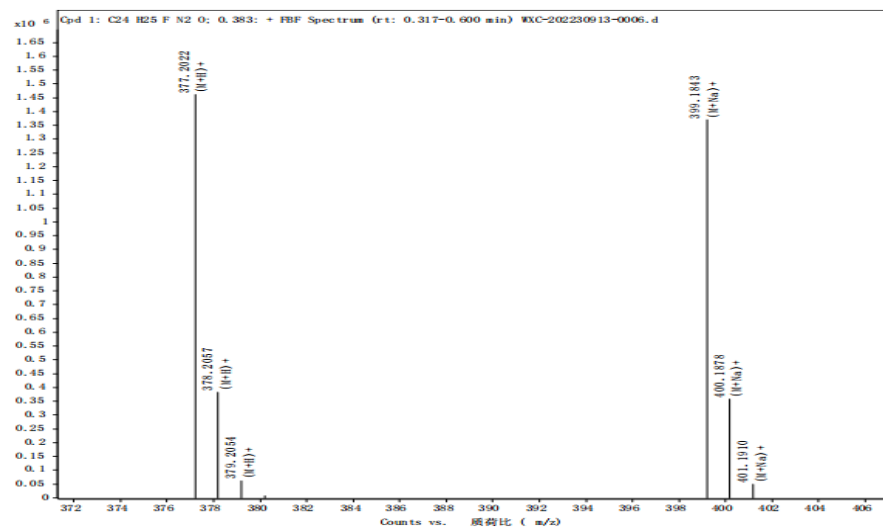
Prepared according to typical procedure **A** from propargylic acetates (132.1 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **4e** (85.6 mg, 76 % yield) as a white solid. Mp: 127-130 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.81-7.79 (m, 2H), 7.54-7.51 (m, 2H), 7.44-7.37 (m, 3H), 7.03 (t, J = 8.8 Hz, 2H), 4.94-4.91 (m, 1H), 2.86 (dd, J_1 = 14.0 Hz, J_2 = 4.0 Hz, 1H), 2.69 (dd, J_1 = 18.0 Hz, J_2 = 5.2 Hz, 1H), 2.58-2.50 (m, 1H), 2.46 (s, 3H), 2.36 (dd, J_1 = 14.0 Hz, J_2 = 12.0 Hz, 1H), 2.25 (dd, J_1 = 14.0 Hz, J_2 = 6.8 Hz, 1H), 1.87 (s, 3H), 1.79 (s, 3H), 1.74-1.68 (m, 1H);

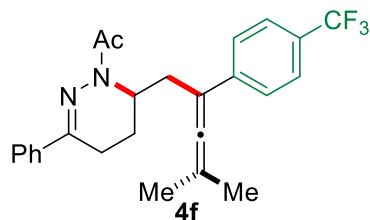
^{13}C NMR (CDCl_3 , 125 MHz) δ 202.8, 172.2, 161.7 (d, J = 244.0 Hz), 146.0, 137.3, 132.4 (d, J = 3.3 Hz), 129.2, 128.4, 127.7 (d, J = 7.8 Hz), 125.2, 115.3 (d, J = 21.1 Hz), 98.3, 97.7, 45.2, 31.2, 21.6, 20.3, 20.2, 18.5, 18.2;

^{19}F NMR (CDCl_3 , 376 MHz) δ -116.4;

HRMS Calcd (ESI) m/z for $\text{C}_{24}\text{H}_{25}\text{FN}_2\text{NaO}$ $[\text{M} + \text{Na}]^+$: 399.1843, found: 399.1843.



1-(6-(4-methyl-2-(4-(trifluoromethyl)phenyl)penta-2,3-dien-1-yl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (4f)



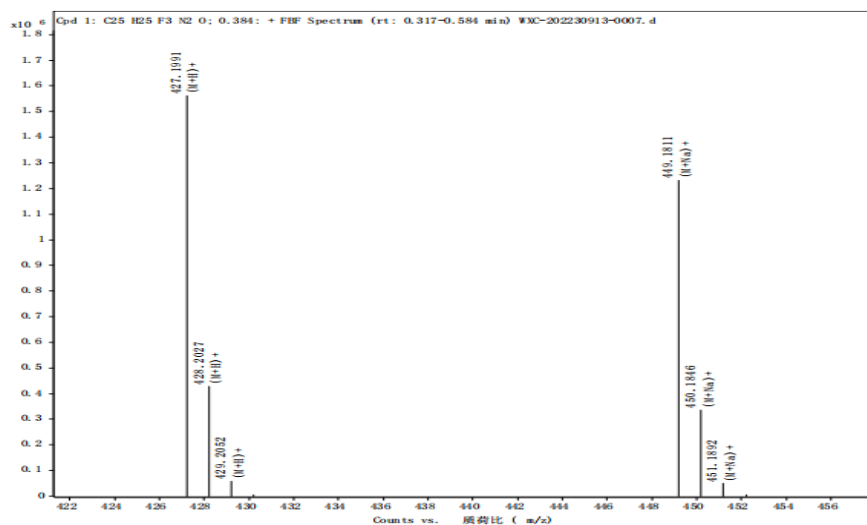
Prepared according to typical procedure **A** from propargylic acetates (162.2 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **4f** (100.8 mg, 79 % yield) as a yellow solid. Mp: 135-138 °C.

^1H NMR (CDCl_3 , 400 MHz) δ 7.83-7.81 (m, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.45-7.38 (m, 3H), 4.96-4.93 (m, 1H), 2.92 (dd, J_1 = 14.0 Hz, J_2 = 4.0 Hz, 1H), 2.72 (dd, J_1 = 18.4 Hz, J_2 = 5.6 Hz, 1H), 2.60-2.52 (m, 1H), 2.48 (s, 3H), 2.43 (dd, J_1 = 14.4 Hz, J_2 = 11.6 Hz, 1H), 2.25 (dd, J_1 = 14.0 Hz, J_2 = 7.2 Hz, 1H), 1.91 (s, 3H), 1.83 (s, 3H), 1.78-1.71 (m, 1H);

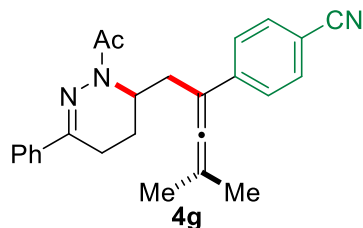
^{13}C NMR (CDCl_3 , 125 MHz) δ 203.9, 172.2, 145.9, 140.4, 137.3, 129.2, 128.4, 128.3 (q, J = 32.1 Hz), 126.4, 125.3 (q, J = 3.8 Hz), 125.2, 124.3 (q, J = 267.8 Hz), 98.5, 98.4, 45.2, 31.0, 21.6, 20.1, 20.0, 18.5, 18.1;

^{19}F NMR (CDCl_3 , 376 MHz) δ -62.4;

HRMS Calcd (ESI) m/z for $\text{C}_{25}\text{H}_{25}\text{F}_3\text{N}_2\text{NaO}$ $[\text{M} + \text{Na}]^+$: 449.1811, found: 449.1811.



4-(1-(2-acetyl-6-phenyl-2,3,4,5-tetrahydropyridazin-3-yl)-4-methylpenta-2,3-dien-2-yl)benzonitrile (4g)

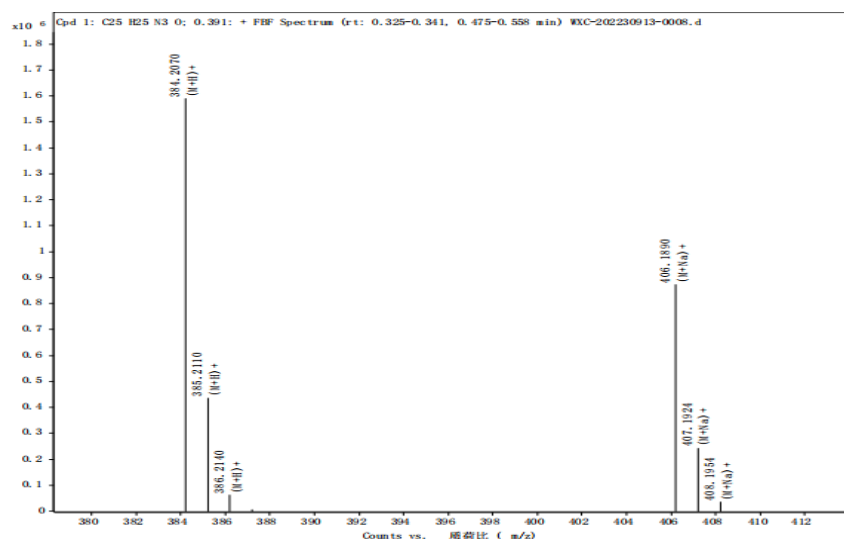


Prepared according to typical procedure **A** from propargylic acetates (136.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **4g** (57.8 mg, 50 % yield) as a yellow solid. Mp: 169-172 °C.

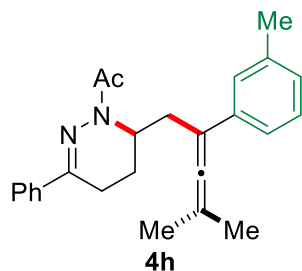
^1H NMR (CDCl_3 , 400 MHz) δ 7.81-7.79 (m, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.44-7.37 (m, 3H), 4.91-4.88 (m, 1H), 2.86 (dd, J_1 = 14.4 Hz, J_2 = 4.0 Hz, 1H), 2.72 (dd, J_1 = 18.0 Hz, J_2 = 5.6 Hz, 1H), 2.57-2.49 (m, 1H), 2.45 (s, 3H), 2.40 (dd, J_1 = 14.0 Hz, J_2 = 11.6 Hz, 1H), 2.21 (dd, J_1 = 13.6 Hz, J_2 = 6.8 Hz, 1H), 1.89 (s, 3H), 1.82 (s, 3H), 1.78-1.71 (m, 1H);

^{13}C NMR (CDCl_3 , 125 MHz) δ 204.4, 172.2, 146.0, 141.7, 137.2, 132.2, 129.3, 128.4, 126.7, 125.2, 119.2, 109.6, 98.8, 98.6, 45.1, 30.9, 21.6, 20.0 (2C), 18.5, 18.1;

HRMS Calcd (ESI) m/z for $\text{C}_{25}\text{H}_{25}\text{N}_3\text{NaO}$ $[\text{M} + \text{Na}]^+$: 406.1890, found: 406.1890.



1-(6-(4-methyl-2-(m-tolyl)penta-2,3-dien-1-yl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (4h)

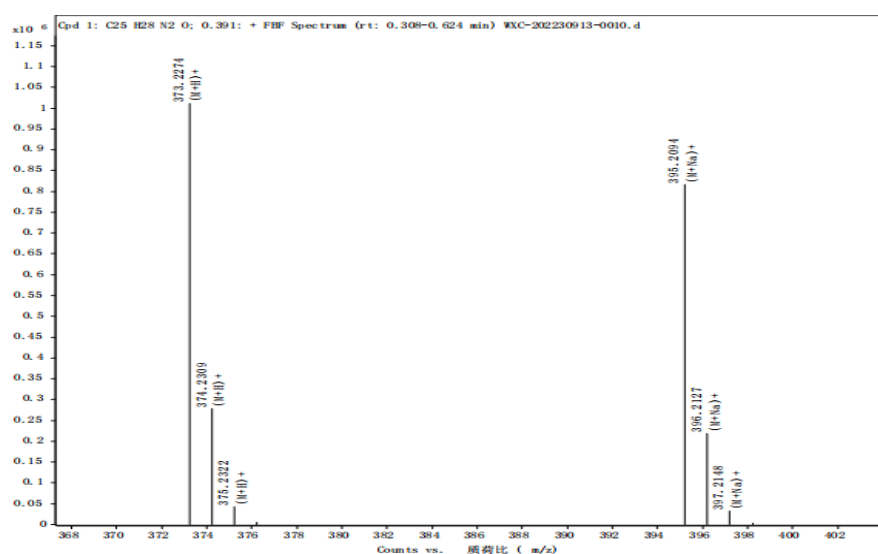


Prepared according to typical procedure **A** from propargylic acetates (129.8 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **4h** (85.8 mg, 77 % yield) as a yellow solid. Mp: 112-115 °C.

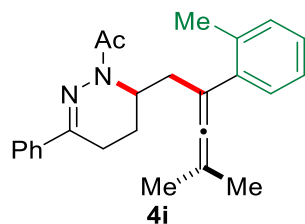
^1H NMR (CDCl_3 , 400 MHz) δ 7.71 (d, J = 7.6 Hz, 2H), 7.34-7.27 (m, 5H), 7.15 (t, J = 7.2 Hz, 1H), 6.93 (d, J = 7.6 Hz, 1H), 4.91-4.88 (m, 1H), 2.81 (dd, J_1 = 14.0 Hz, J_2 = 4.0 Hz, 1H), 2.58 (dd, J_1 = 18.4 Hz, J_2 = 6.0 Hz, 1H), 2.50-2.42 (m, 1H), 2.37 (s, 3H), 2.30-2.24 (m, 4H), 2.17 (dd, J_1 = 13.6 Hz, J_2 = 6.4 Hz, 1H), 1.78 (s, 3H), 1.71 (s, 3H), 1.64-1.57 (m, 1H);

^{13}C NMR (CDCl_3 , 100 MHz) δ 202.9, 172.1, 145.9, 138.0, 137.4, 136.4, 129.1, 128.4, 127.3, 126.9 (2C), 125.1, 123.3, 99.1, 97.4, 45.3, 31.0, 21.6, 21.6, 20.3, 20.2, 18.5, 18.2;

HRMS Calcd (ESI) m/z for $\text{C}_{25}\text{H}_{28}\text{N}_2\text{NaO}$ $[\text{M} + \text{H}]^+$: 395.2094, found: 395.2094.



1-(6-(4-methyl-2-(o-tolyl)penta-2,3-dien-1-yl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (4i)

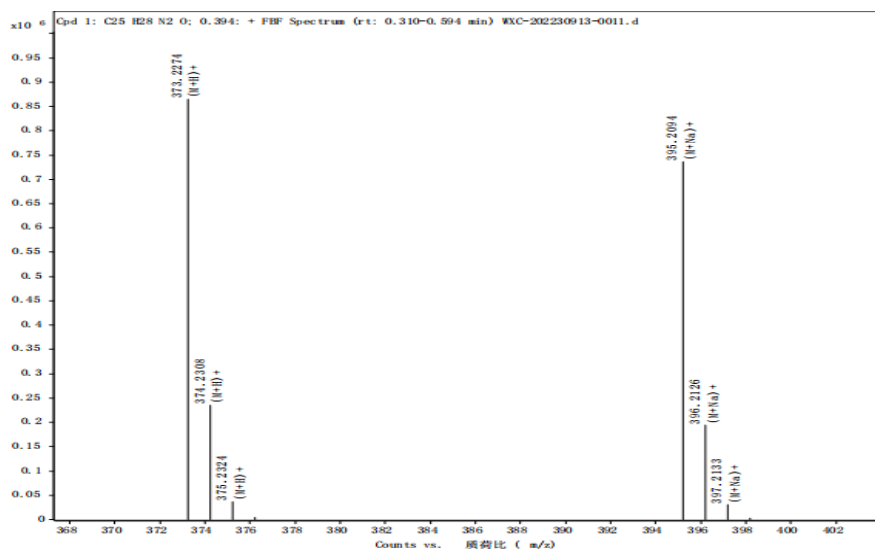


Prepared according to typical procedure **A** from propargylic acetates (129.8 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **4i** (45.9 mg, 41 % yield) as a yellow solid. Mp: 108-111 °C.

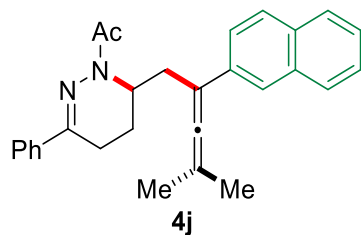
^1H NMR (CDCl_3 , 400 MHz) δ 7.79 (d, J = 7.6 Hz, 2H), 7.43-7.36 (m, 4H), 7.24-7.12 (m, 3H), 4.84-4.82 (m, 1H), 2.87-2.84 (m, 1H), 2.70 (dd, J_1 = 17.6 Hz, J_2 = 5.2 Hz, 1H), 2.57-2.50 (m, 1H), 2.42 (s, 3H), 2.39 (s, 3H), 2.30-2.22 (m, 2H), 1.81 (s, 3H), 1.76-1.66 (m, 4H);

^{13}C NMR (CDCl_3 , 125 MHz) δ 202.7, 171.8, 145.7, 137.4, 136.9, 135.8, 130.7, 129.1, 128.4, 127.9, 126.7, 126.0, 125.1, 97.9, 95.1, 45.4, 33.9, 21.6, 21.0, 20.4 (2C), 19.0, 18.5;

HRMS Calcd (ESI) m/z for $\text{C}_{25}\text{H}_{28}\text{N}_2\text{NaO}$ $[\text{M} + \text{H}]^+$: 395.2094, found: 395.2094.



1-(6-(4-methyl-2-(naphthalen-2-yl)penta-2,3-dien-1-yl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (4j)

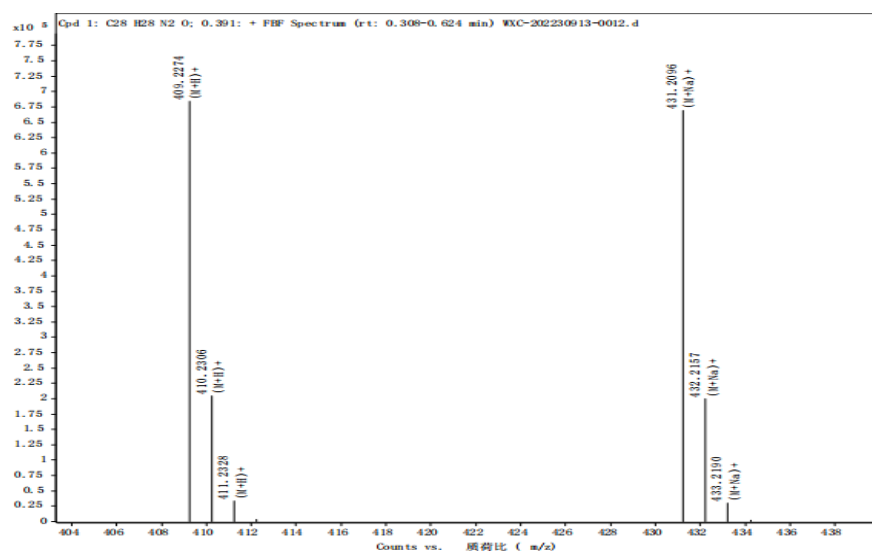


Prepared according to typical procedure **A** from propargylic acetates (151.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **4j** (53.2 mg, 43 % yield) as a white solid. Mp: 120-123 °C.

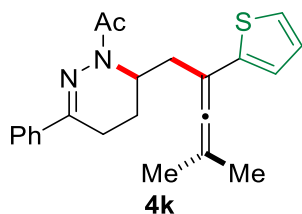
¹H NMR (CDCl₃, 400 MHz) δ 8.15 (s, 1H), 7.97 (d, J = 7.6 Hz, 1H), 7.86-7.84 (m, 2H), 7.82-7.78 (m, 2H), 7.67-7.65 (m, 1H), 7.51-7.41 (m, 5H), 5.15-5.12 (m, 1H), 3.09 (dd, J_1 = 14.0 Hz, J_2 = 3.6 Hz, 1H), 2.71 (dd, J_1 = 18.0 Hz, J_2 = 6.0 Hz, 1H), 2.65-2.57 (m, 1H), 2.55-2.48 (m, 4H), 2.32 (dd, J_1 = 14.0 Hz, J_2 = 6.8 Hz, 1H), 1.96 (s, 3H), 1.88 (s, 3H), 1.77-1.70 (m, 1H).

¹³C NMR (CDCl₃, 100 MHz) δ 203.6, 172.2, 145.9, 137.4, 133.8, 133.7, 132.3, 129.2, 128.4, 128.4, 127.7, 127.3, 126.0, 125.6, 125.3, 125.2, 124.1, 99.4, 97.9, 45.4, 31.1, 21.6, 20.4, 20.3, 18.6, 18.2;

HRMS Calcd (ESI) m/z for C₂₈H₂₉N₂O [M + H]⁺: 409.2274, found: 409.2274.



1-(6-(4-methyl-2-(thiophen-2-yl)penta-2,3-dien-1-yl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (4k)

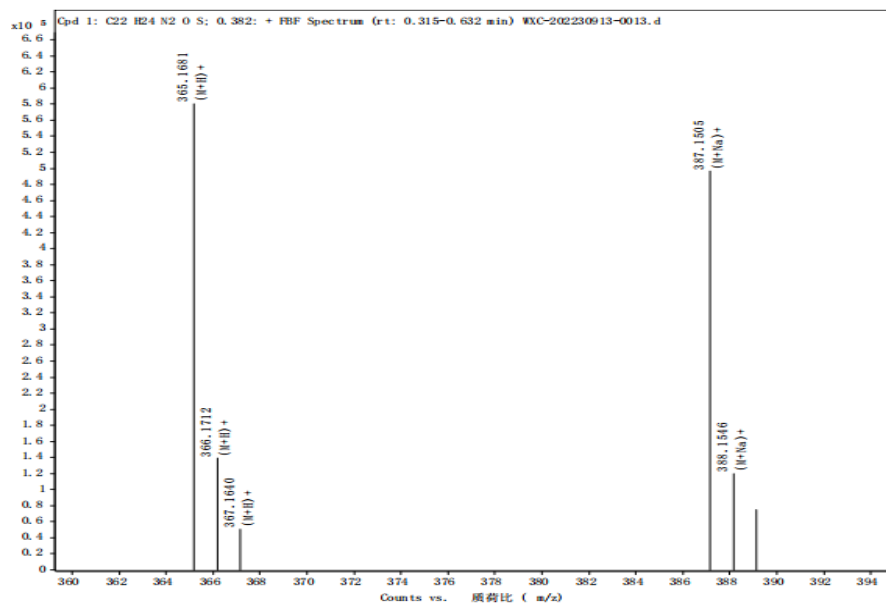


Prepared according to typical procedure **A** from propargylic acetates (125.0 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **4k** (45.8 mg, 42 % yield) as a yellow oil.

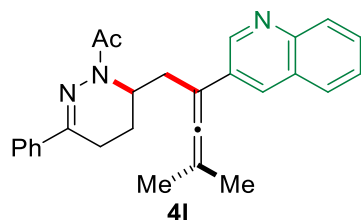
^1H NMR (CDCl_3 , 400 MHz) δ 7.83-7.80 (m, 2H), 7.45-7.38 (m, 3H), 7.31-7.30 (m, 1H), 7.15-7.13 (m, 1H), 7.01-6.99 (m, 1H), 5.07-5.04 (m, 1H), 2.83 (dd, $J_1 = 13.6$ Hz, $J_2 = 3.6$ Hz, 1H), 2.70 (dd, $J_1 = 18.4$ Hz, $J_2 = 6.0$ Hz, 1H), 2.59-2.52 (m, 1H), 2.48 (s, 3H), 2.38 (dd, $J_1 = 14.0$ Hz, $J_2 = 12.0$ Hz, 1H), 2.31 (dd, $J_1 = 14.0$ Hz, $J_2 = 7.2$ Hz, 1H), 1.87 (s, 3H), 1.81 (s, 3H), 1.78-1.71 (m, 1H);

^{13}C NMR (CDCl_3 , 100 MHz) δ 201.8, 172.0, 145.9, 142.4, 137.3, 129.1, 128.4, 127.8, 125.1, 124.1, 123.4, 98.6, 95.3, 45.3, 32.2, 21.6 (2C), 20.3, 18.5, 18.2;

HRMS Calcd (ESI) m/z for $\text{C}_{22}\text{H}_{25}\text{N}_2\text{OS}$ $[\text{M} + \text{H}]^+$: 365.1682, found: 365.1681.



1-(6-(4-methyl-2-(quinolin-3-yl)penta-2,3-dien-1-yl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (4I)

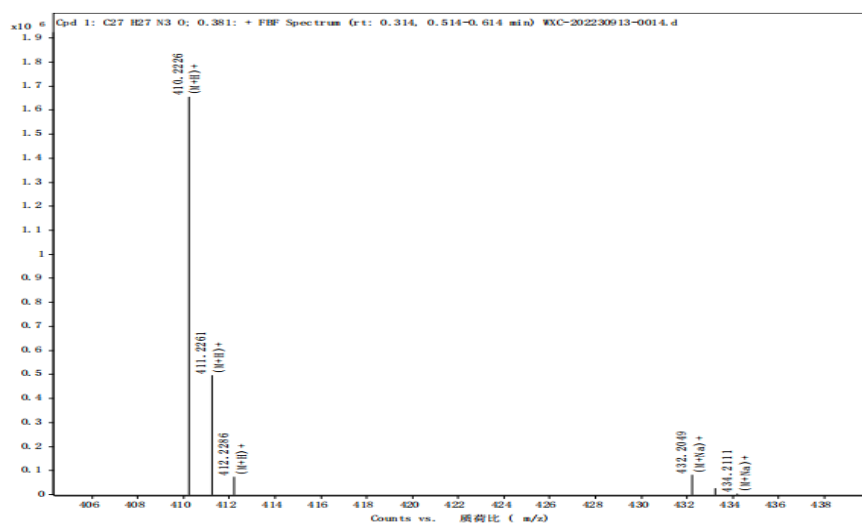


Prepared according to typical procedure **A** from propargylic acetates (152.0 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 3) give the product **4I** (59.8 mg, 49 % yield) as a white solid. Mp: 75-78 °C.

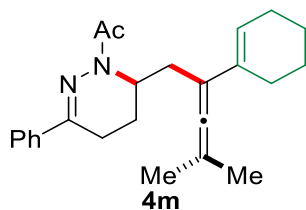
^1H NMR (CDCl_3 , 400 MHz) δ 9.01 (s, 1H), 8.44 (s, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 7.92 (d, $J = 8.0$ Hz, 1H), 7.81 (d, $J = 8.0$ Hz, 2H), 7.64 (t, $J = 7.2$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.44-7.37 (m, 3H), 5.05-5.01 (m, 1H), 2.99 (dd, $J_1 = 14.0$ Hz, $J_2 = 4.0$ Hz, 1H), 2.72 (dd, $J_1 = 17.2$ Hz, $J_2 = 6.0$ Hz, 1H), 2.62-2.54 (m, 1H), 2.50 (s, 3H), 2.42 (d, $J = 21.6$ Hz, 1H), 2.28 (dd, $J_1 = 14.0$ Hz, $J_2 = 7.2$ Hz, 1H), 1.92 (s, 3H), 1.86 (s, 3H), 1.78-1.71 (m, 1H).

^{13}C NMR (CDCl_3 , 100 MHz) δ 203.6, 172.2, 150.7, 146.4, 146.0, 137.2, 130.9, 129.2, 128.8 (2C), 128.4, 128.2, 128.1, 126.7, 126.1, 125.1, 99.0, 96.9, 45.0, 31.0, 21.6, 20.2 (2C), 18.5, 18.1;

HRMS Calcd (ESI) m/z for $\text{C}_{27}\text{H}_{28}\text{N}_3\text{O}$ $[\text{M} + \text{H}]^+$: 410.2227, found: 410.2226.



1-(6-(2-(cyclohex-1-en-1-yl)-4-methylpenta-2,3-dien-1-yl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (4m)

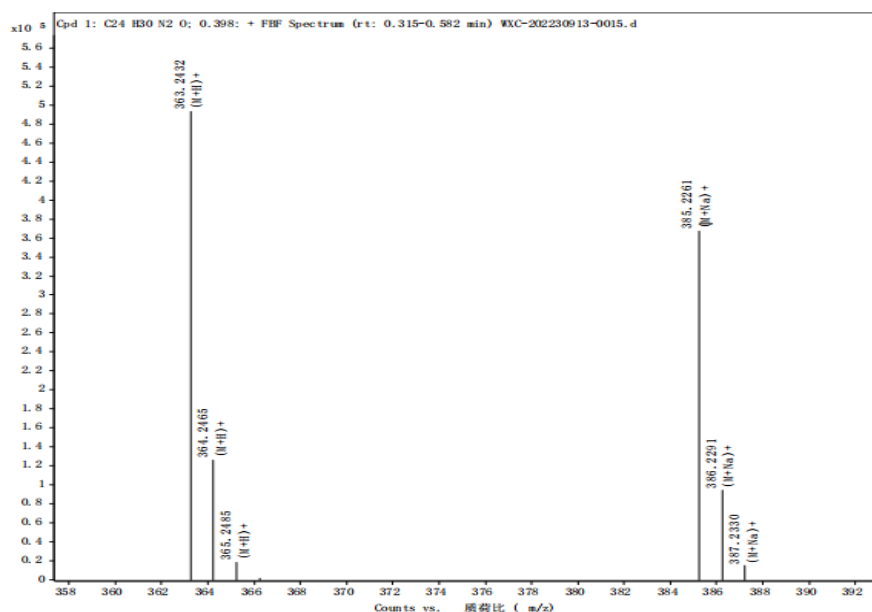


Prepared according to typical procedure **A** from propargylic acetates (123.8 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 20) give the product **4m** (76.3 mg, 70 % yield) as a yellow oil.

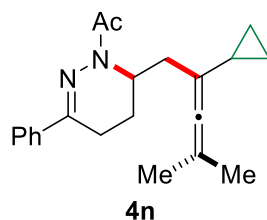
^1H NMR (CDCl_3 , 400 MHz) δ 7.80-7.77 (m, 2H), 7.42-7.34 (m, 3H), 6.06-6.04 (m, 1H), 4.94-4.91 (m, 1H), 2.64 (dd, $J_1 = 18.4$ Hz, $J_2 = 6.0$ Hz, 1H), 2.59 (dd, $J_1 = 14.0$ Hz, $J_2 = 3.6$ Hz, 1H), 2.54-2.47 (m, 1H), 2.43 (s, 3H), 2.23-2.10 (m, 4H), 2.08-1.98 (m, 2H), 1.75 (s, 3H), 1.73-1.73 (m, 1H), 1.70 (s, 3H), 1.67-1.62 (m, 2H), 1.59-1.54 (m, 2H);

^{13}C NMR (CDCl_3 , 125 MHz) δ 202.4, 172.0, 146.0, 137.5, 132.4, 129.1, 128.4, 125.1, 123.0, 101.2, 96.4, 45.5, 30.3, 27.2, 26.0, 23.0, 22.4, 21.6, 20.6 (2C), 18.7, 18.3;

HRMS Calcd (ESI) m/z for $\text{C}_{24}\text{H}_{31}\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 363.2431, found: 363.2432.



1-(6-(2-cyclopropyl-4-methylpenta-2,3-dien-1-yl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (4n)

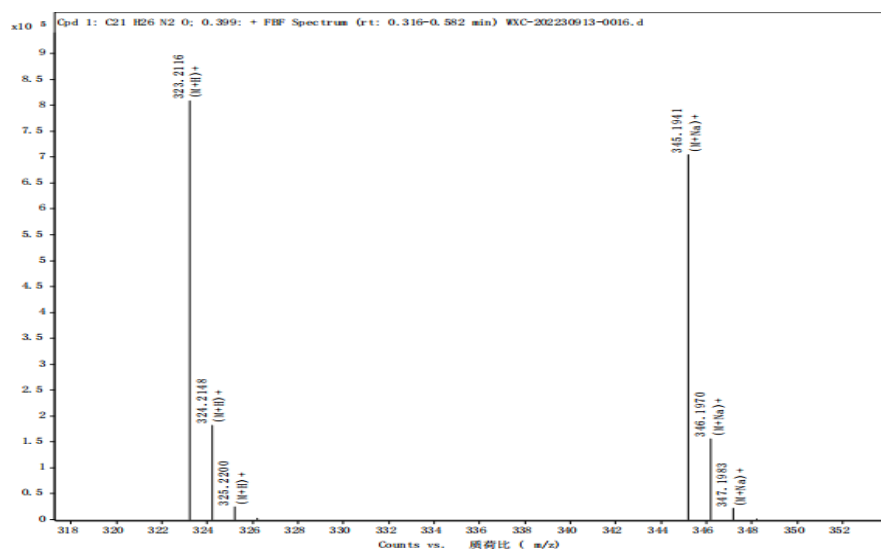


Prepared according to typical procedure **A** from propargylic acetates (99.7 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **4n** (53.5 mg, 55 % yield) as a colourless oil.

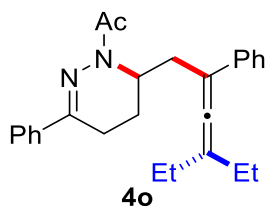
^1H NMR (CDCl_3 , 400 MHz) δ 7.80-7.77 (m, 2H), 7.42-7.34 (m, 3H), 4.99-4.96 (m, 1H), 2.66 (dd, $J_1 = 18.0$ Hz, $J_2 = 5.6$ Hz, 1H), 2.54-2.46 (m, 1H), 2.43 (s, 3H), 2.34 (dd, $J_1 = 14.0$ Hz, $J_2 = 4.4$ Hz, 1H), 2.28-2.23 (m, 1H), 2.10 (dd, $J_1 = 13.6$ Hz, $J_2 = 11.2$ Hz, 1H), 1.78-1.72 (m, 1H), 1.68 (s, 3H), 1.64 (s, 3H), 1.20-1.13 (m, 1H), 0.72-0.61 (m, 2H), 0.38-0.27 (m, 2H);

^{13}C NMR (CDCl_3 , 100 MHz) δ 198.1, 171.8, 146.0, 137.4, 129.0, 128.3, 125.1, 101.2, 97.0, 45.3, 34.0, 21.6, 20.9, 20.7, 18.8, 18.4, 12.2, 7.6, 6.6;

HRMS Calcd (ESI) m/z for $\text{C}_{21}\text{H}_{27}\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 323.2118, found: 323.2116.



1-(6-(4-ethyl-2-phenylhexa-2,3-dien-1-yl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (4o)

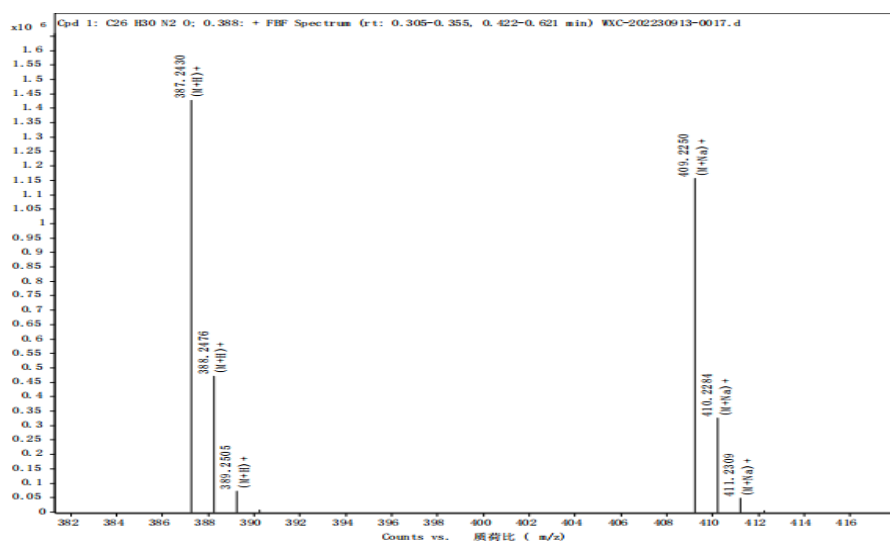


Prepared according to typical procedure **A** from propargylic acetates (138.2 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **4o** (82.3 mg, 71 % yield) as a yellow solid. Mp: 84-87 °C.

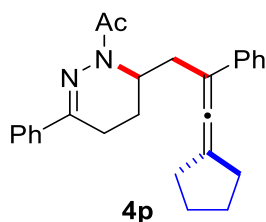
^1H NMR (CDCl_3 , 400 MHz) δ 7.84-7.82 (m, 2H), 7.63 (d, $J = 7.6$ Hz, 2H), 7.46-7.30 (m, 5H), 7.22 (t, $J = 7.6$ Hz, 1H), 5.05-5.02 (m, 1H), 2.99 (dd, $J_1 = 14.0$ Hz, $J_2 = 3.6$ Hz, 1H), 2.69 (dd, $J_1 = 18.0$ Hz, $J_2 = 5.6$ Hz, 1H), 2.62-2.533 (m, 1H), 2.49 (s, 3H), 2.44 (dd, $J_1 = 14.0$ Hz, $J_2 = 11.6$ Hz, 1H), 2.32 (dd, $J_1 = 14.0$ Hz, $J_2 = 6.8$ Hz, 1H), 2.21 (q, $J = 7.2$ Hz, 2H), 2.15-2.09 (m, 2H), 1.75-1.67 (m, 1H), 1.19 (t, $J = 7.6$ Hz, 3H), 1.02 (t, $J = 7.6$ Hz, 3H);

^{13}C NMR (CDCl_3 , 125 MHz) δ 201.6, 172.1, 145.8, 137.4, 136.8, 129.1, 128.4 (2C), 126.4, 125.9, 125.1, 110.7, 103.0, 45.3, 31.3, 26.2, 25.9, 21.6, 18.5, 18.3, 12.7, 12.4;

HRMS Calcd (ESI) m/z for $\text{C}_{26}\text{H}_{31}\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 387.2431, found: 387.2430.



1-(6-(3-cyclopentylidene-2-phenylallyl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (4p)

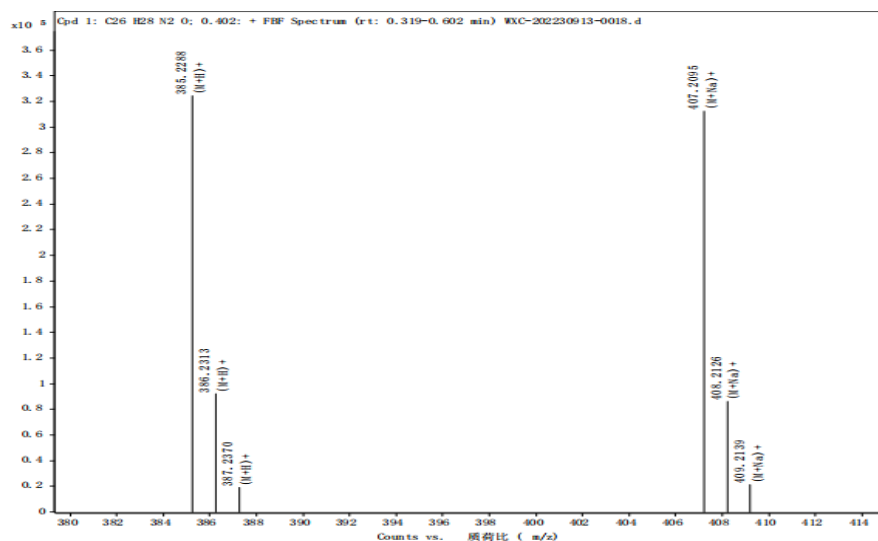


Prepared according to typical procedure **A** from propargylic acetates (137.0 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **4p** (77.5 mg, 67 % yield) as a colorless oil.

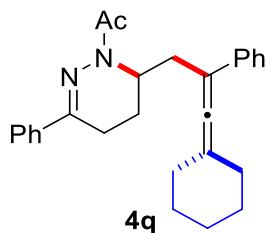
^1H NMR (CDCl_3 , 400 MHz) δ 7.83-7.80 (m, 2H), 7.60-7.57 (m, 2H), 7.45-7.34 (m, 5H), 7.20 (t, $J = 7.2$ Hz, 1H), 5.01-4.98 (m, 1H), 2.93 (dd, $J_1 = 14.0$ Hz, $J_2 = 3.6$ Hz, 1H), 2.69 (dd, $J_1 = 18.4$ Hz, $J_2 = 5.6$ Hz, 1H), 2.60-2.54 (m, 2H), 2.53-2.38 (m, 7H), 2.30 (dd, $J_1 = 13.6$ Hz, $J_2 = 6.8$ Hz, 1H), 1.84-1.74 (m, 4H), 1.72-1.66 (m, 1H);

^{13}C NMR (CDCl_3 , 125 MHz) δ 198.7, 172.2, 146.0, 137.4, 136.6, 129.2, 128.5, 128.4, 126.4, 126.2, 125.2, 106.1, 101.4, 45.4, 31.1, 31.0, 30.9, 27.2, 27.1, 21.6, 18.5, 18.2;

HRMS Calcd (ESI) m/z for $\text{C}_{26}\text{H}_{28}\text{N}_2\text{NaO}$ $[\text{M} + \text{Na}]^+$: 407.2094, found: 407.2095.



1-(6-(3-cyclohexylidene-2-phenylallyl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (4q)

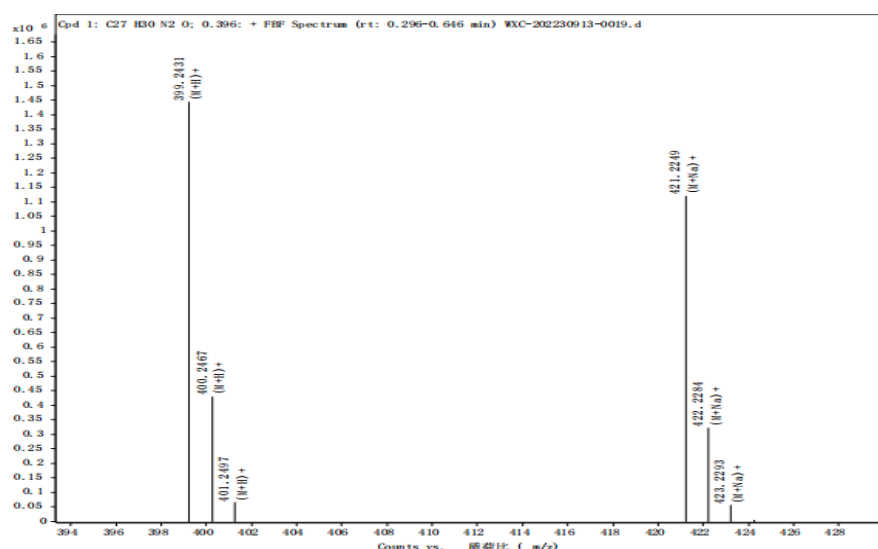


Prepared according to typical procedure **A** from propargylic acetates (145.4 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 15) give the product **4q** (87.3 mg, 73 % yield) as a colorless oil.

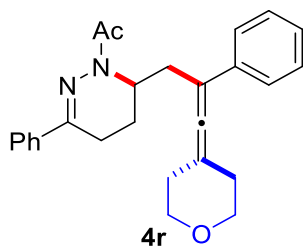
^1H NMR (CDCl_3 , 400 MHz) δ 7.83-7.81 (m, 2H), 7.61 (d, $J = 7.6$ Hz, 2H), 7.45-7.35 (m, 5H), 7.21 (t, $J = 7.6$ Hz, 1H), 5.02-4.99 (m, 1H), 2.94 (dd, $J_1 = 14.0$ Hz, $J_2 = 4.0$ Hz, 1H), 2.68 (dd, $J_1 = 18.0$ Hz, $J_2 = 5.6$ Hz, 1H), 2.62-2.54 (m, 1H), 2.48 (s, 3H), 2.40 (dd, $J_1 = 14.0$ Hz, $J_2 = 11.6$ Hz, 1H), 2.35-2.17 (m, 5H), 1.80-1.58 (m, 7H);

^{13}C NMR (CDCl_3 , 125 MHz) δ 199.4, 172.1, 145.9, 137.4, 136.5, 129.1, 128.5, 128.4, 126.4, 126.0, 125.1, 104.9, 98.8, 45.3, 31.4, 31.3, 31.1, 27.8, 27.7, 26.1, 21.6, 18.5, 18.3;

HRMS Calcd (ESI) m/z for $\text{C}_{27}\text{H}_{31}\text{N}_2\text{O}$ $[\text{M} + \text{H}]^+$: 399.2431, found: 399.2431.



1-(3-phenyl-6-(2-phenyl-3-(tetrahydro-4H-pyran-4-ylidene)allyl)-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (4r)

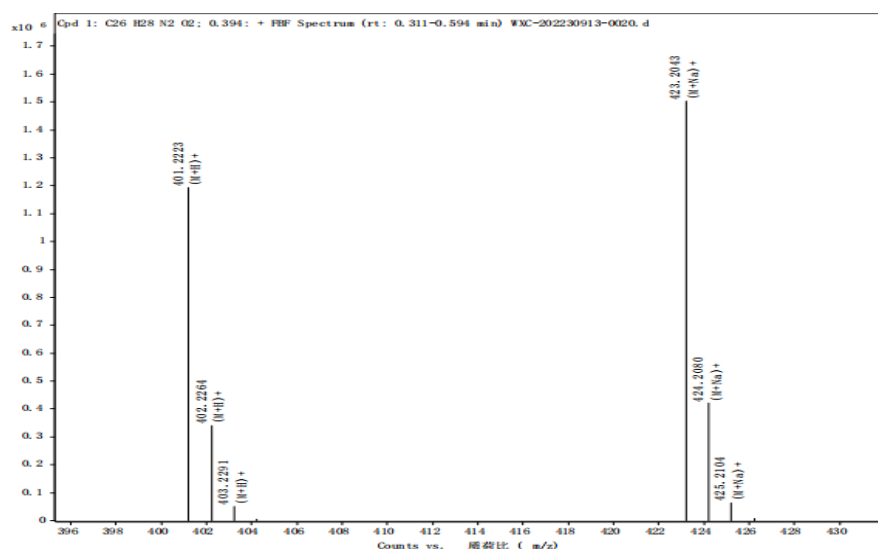


Prepared according to typical procedure **A** from propargylic acetates (146.6 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **4r** (59.8 mg, 50 % yield) as a yellow solid. Mp: 121-124 °C.

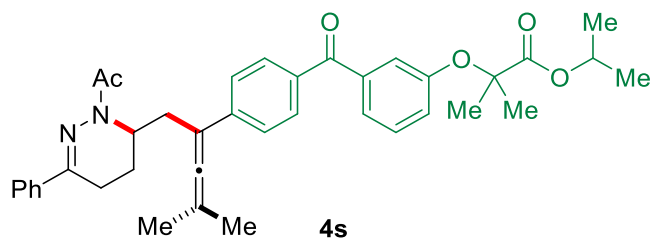
¹H NMR (CDCl₃, 400 MHz) δ 7.81 (d, J = 7.2 Hz, 2H), 7.61 (d, J = 7.6 Hz, 2H), 7.43-7.36 (m, 5H), 7.23 (t, J = 7.6 Hz, 1H), 5.02-4.99 (m, 1H), 3.89-3.81 (m, 4H), 2.95 (dd, J_1 = 14.0 Hz, J_2 = 3.2 Hz, 1H), 2.69 (dd, J_1 = 17.6 Hz, J_2 = 4.8 Hz, 1H), 2.60-2.53 (m, 1H), 2.47 (s, 3H), 2.43-2.41 (m, 3H), 2.36-2.35 (m, 2H), 2.24 (dd, J_1 = 13.6 Hz, J_2 = 6.4 Hz, 1H), 1.76-1.69 (m, 1H);

¹³C NMR (CDCl₃, 125 MHz) δ 199.6, 172.1, 145.8, 137.3, 135.9, 129.2, 128.6, 128.5, 126.9, 126.1, 125.1, 100.6, 100.5, 68.9 (2C), 45.3, 31.5, 31.4, 31.1, 21.6, 18.6, 18.2;

HRMS Calcd (ESI) m/z for C₂₆H₂₈N₂NaO₂ [M + Na]⁺: 423.2043, found: 423.2043.



isopropyl 2-(3-(4-(1-(2-acetyl-6-phenyl-2,3,4,5-tetrahydropyridazin-3-yl)-4-methylpenta-2,3-dien-2-yl)benzoyl)phenoxy)-2-methylpropanoate (4s)

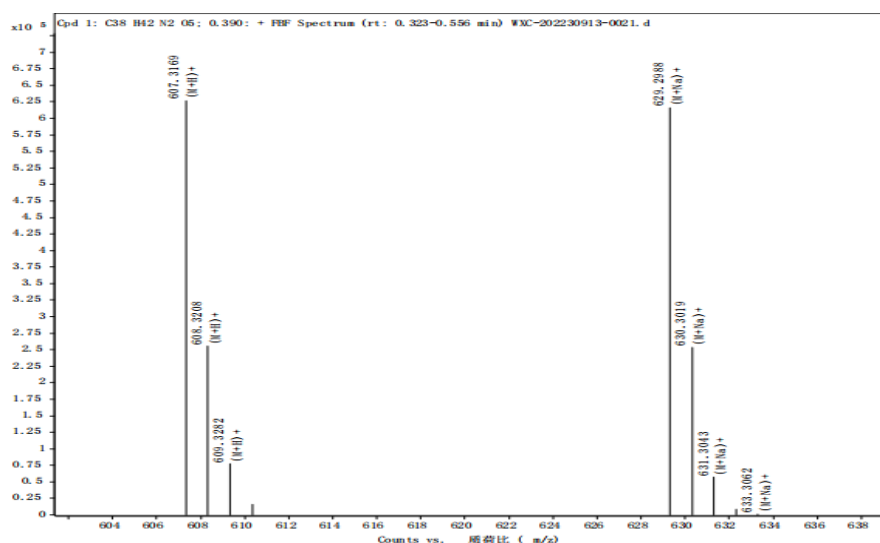


Prepared according to typical procedure **A** from propargylic acetates (270.3 mg, 0.6 mmol, 2.0 equiv) and γ,δ -unsaturated ketoximes (64.9 mg, 0.3 mmol, 1.0 equiv), flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **4s** (100.9 mg, 55 % yield) as a colorless oil.

^1H NMR (CDCl_3 , 400 MHz) δ 7.81-7.75 (m, 6H), 7.66 (d, $J = 8.4$ Hz, 2H), 7.42-7.35 (m, 3H), 6.86 (d, $J = 8.8$ Hz, 2H), 5.11-5.05 (m, 1H), 4.99-4.96 (m, 1H), 2.92 (dd, $J_1 = 14.4$ Hz, $J_2 = 4.0$ Hz, 1H), 2.70 (dd, $J_1 = 18.4$ Hz, $J_2 = 5.6$ Hz, 1H), 2.59-2.51 (m, 1H), 2.45-2.38 (m, 4H), 2.26 (dd, $J_1 = 14.0$ Hz, $J_2 = 6.8$ Hz, 1H), 1.89 (s, 3H), 1.82 (s, 3H), 1.76-1.72 (dd, $J_1 = 10.6$ Hz, $J_2 = 5.0$ Hz, 1H), 1.65 (s, 6H), 1.21 (s, 3H), 1.19 (s, 3H);

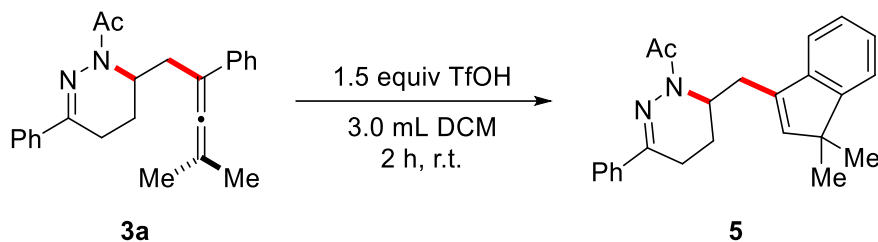
^{13}C NMR (CDCl_3 , 125 MHz) δ 204.1, 195.0, 173.2, 172.2, 159.3, 146.0, 140.7, 137.3, 135.9, 131.9, 130.8, 130.2, 129.2, 128.4, 125.9, 125.2, 117.2 (2C), 98.9, 98.2, 79.3, 69.3, 45.3, 31.0, 25.4, 25.3, 21.6 (2C), 21.5 (2C), 20.1 (2C), 18.6, 18.2;

HRMS Calcd (ESI) m/z for $\text{C}_{38}\text{H}_{43}\text{N}_2\text{O}_5$ $[\text{M} + \text{H}]^+$: 607.3166, found: 607.3169.



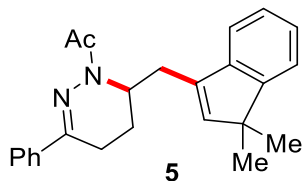
6. Synthetic transformations

6.1 Experimental procedure for synthesis of 5



A sealed tube (10 mL) equipped with a magnetic stir bar was charged with the compound **3a** (107.5 mg, 0.3 mmol, 1.0 equiv) in DCM (3.0 mL) was added TfOH (67.5 mg, 0.45 mmol, 1.5 equiv) at room temperature. The resulting mixture was stirred at room temperature for 2 h. Then, the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with ethyl acetate: petroleum ether (1:5) as eluent to give the desired product **5**.

1-(6-((1,1-dimethyl-1H-inden-3-yl)methyl)-3-phenyl-5,6-dihydropyridazin-1(4H)-yl)ethan-1-one (**5**)

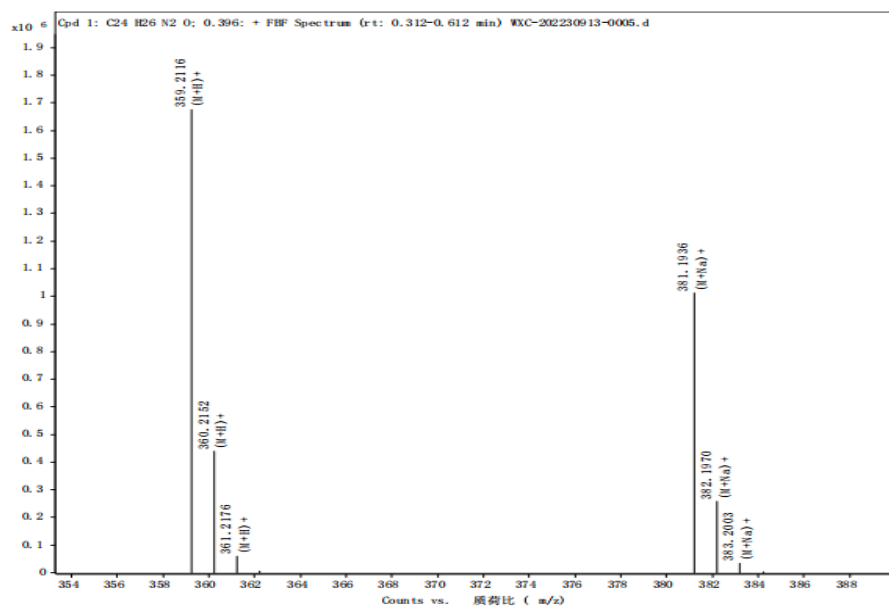


Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **5** (67.4 mg, 63 % yield) as a yellow oil.

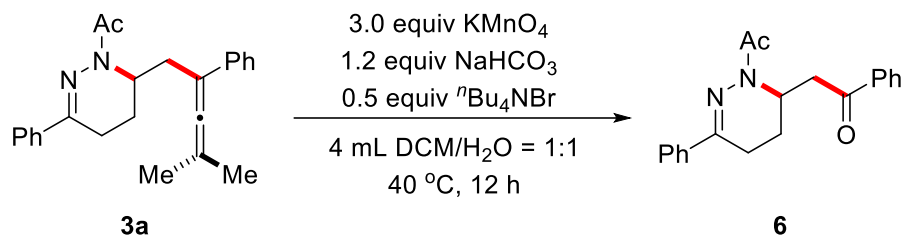
¹H NMR (CDCl₃, 500 MHz) δ 7.84-7.82 (m, 2H), 7.69-7.68 (m, 1H), 7.45-7.40 (m, 3H), 7.33-7.30 (m, 2H), 7.25-7.22 (m, 1H), 6.13 (s, 1H), 5.15-5.12 (m, 1H), 2.89 (dd, $J_1 = 13.5$ Hz, $J_2 = 4.0$ Hz, 1H), 2.71 (dd, $J_1 = 18.0$ Hz, $J_2 = 6.0$ Hz, 1H), 2.66-2.61 (m, 1H), 2.57 (dd, $J_1 = 13.5$ Hz, $J_2 = 11.0$ Hz, 1H), 2.49 (s, 3H), 2.09 (dd, $J_1 = 14.0$ Hz, $J_2 = 7.0$ Hz, 1H), 1.73-1.67 (m, 1H), 1.34 (s, 3H), 1.31 (s, 3H);

¹³C NMR (CDCl₃, 125 MHz) δ 172.1, 153.8, 145.8, 144.1, 142.5, 137.4, 136.0, 129.2, 128.4, 126.7, 125.3, 125.2, 121.0, 120.1, 48.4, 45.1, 28.4, 24.8, 24.5, 21.7, 18.5, 18.3;

HRMS Calcd (ESI) m/z for C₂₄H₂₇N₂O [M + H]⁺: 359.2118, found: 359.2116.

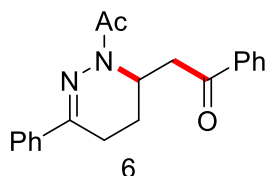


6.2 Experimental procedure for synthesis of 6



A round bottle flask with a magnetic stir bar was charged with the compound **3a** (107.5 mg, 0.3 mmol, 1.0 equiv), KMnO_4 (142.2 mg, 0.9 mmol, 3.0 equiv), $n\text{Bu}_4\text{NBr}$ (116.1 mg, 0.36 mmol, 1.2 equiv), DCM (2.0 mL) and H_2O (2.0 mL). The reaction mixture was stirred at 40 °C for 12 h. Then, the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product **6**.

2-(2-acetyl-6-phenyl-2,3,4,5-tetrahydropyridazin-3-yl)-1-phenylethan-1-one (**6**)



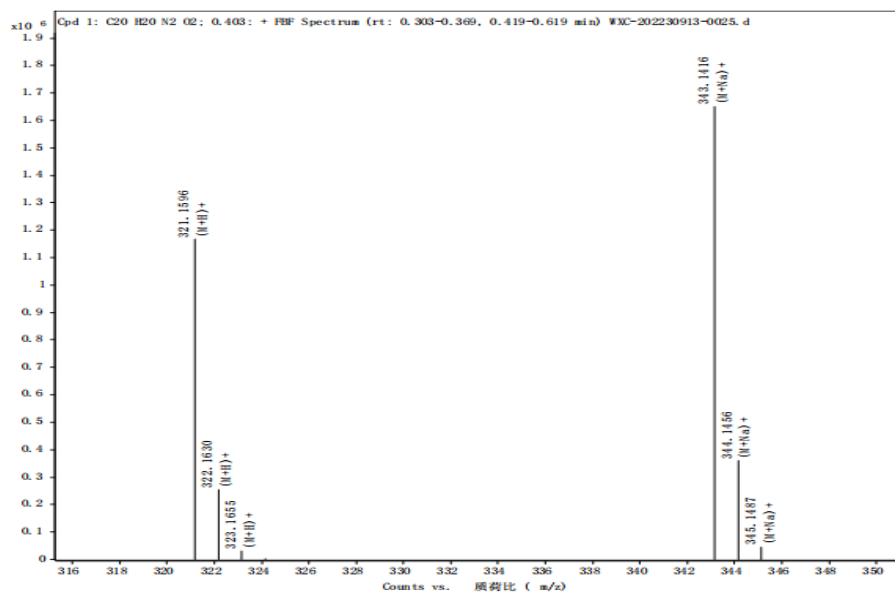
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 30) give the product **6** (74.0 mg, 77 % yield) as a colorless oil.

^1H NMR (CDCl_3 , 400 MHz) δ 8.08 (d, J = 8.0 Hz, 2H), 7.81-7.79 (m, 2H), 7.60-7.56 (m, 1H), 7.48 (t, J = 6.8 Hz, 2H), 7.43-7.36 (m, 3H), 5.28-5.25 (m, 1H), 3.45 (dd, J_1 =

14.8 Hz, $J_2 = 3.6$ Hz, 1H), 2.92 (dd, $J_1 = 14.8$ Hz, $J_2 = 11.2$ Hz, 1H), 2.72 (dd, $J_1 = 18.0$ Hz, $J_2 = 6.0$ Hz, 1H), 2.67-2.59 (m, 1H), 2.45 (s, 3H), 2.23-2.17 (m, 1H), 1.91-1.82 (m, 1H);

^{13}C NMR (CDCl_3 , 100 MHz) δ 197.7, 172.1, 146.1, 137.0, 136.3, 133.4, 129.3, 128.7, 128.4, 125.1, 44.2, 39.3, 21.5, 19.7, 18.4;

HRMS Calcd (ESI) m/z for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{NaO}_2$ $[\text{M} + \text{Na}]^+$: 343.1417, found: 343.1416.



7. Single Crystal X-Ray Diffraction

Crystals of **3a** were obtained by slow diffusion from a solution of the compounds in CHCl_3 layered with petroleum ether at room temperature for several days (Figure S1). Crystal data and details of the structure determination are presented in Table S2.

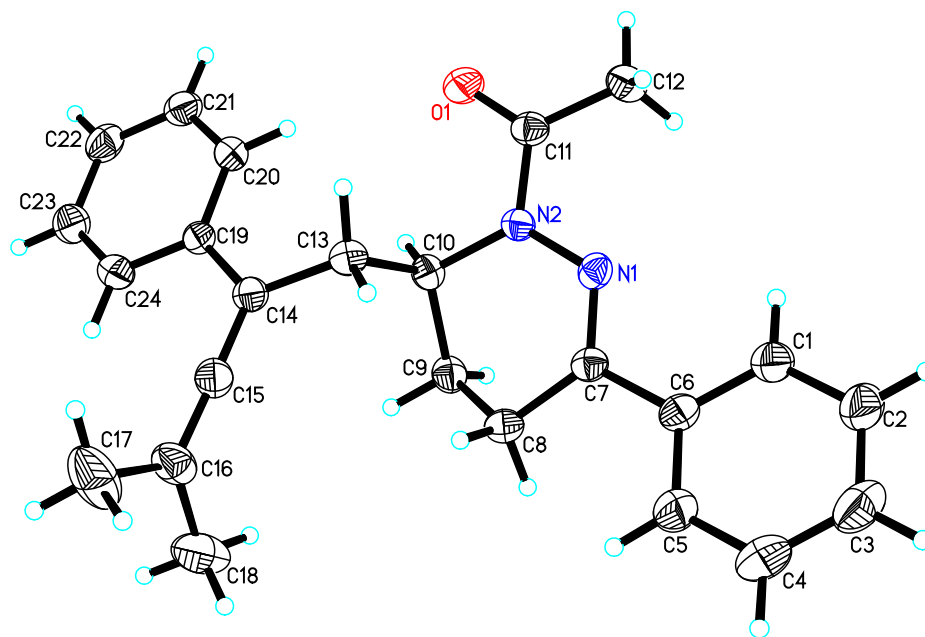


Figure S1. ORTEP drawing (30%) of the Crystal structure of **3a**

Table S2 The single crystal data of compounds **3a**

Phase	3a
Identification code	XSJ20230411
Empirical formula	C ₂₄ H ₂₆ N ₂ O
Formula weight	358.47
Temperature/K	296(2)
Wavelength/ Å	0.71073
Crystal system	Orthorhombic
Space group	P2(1)2(1)2(1)
<i>a</i> / Å	7.1976(4)
<i>b</i> / Å	23.2687(13)
<i>c</i> / Å	24.5001(12)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å ³)	4103.2(4)
<i>Z</i>	8
Calculated density (mg·m ⁻³)	1.161
Absorption coefficient (mm ⁻¹)	0.071
<i>F</i> (000)	1536
Crystal size (mm)	0.240 x 0.220 x 0.180
θ range for data collection (deg)	2.414 to 25.998
Limiting indices	-8 $\leq$ h $\leq$ 8, -28 $\leq$ k $\leq$ 28, -30 $\leq$ l $\leq$ 30
Reflections collected/unique	39193 / 8048 [R(int) = 0.0886]
Completeness to theta	99.9 %
Max. and min. transmission	0.7456 and 0.6939
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	8048 / 0 / 493
Goodness-of-fit on F ²	1.028
Final <i>R</i> indices[I>2sigma(I)]	R1 = 0.0585, wR2 = 0.0885
<i>R</i> indices (all data)	R1 = 0.1460, wR2 = 0.1091
Largest diff. peak and hole / (e · Å ⁻³)	0.150 and -0.179

8. References:

- [1] Y. Guo, J. Zhao, Q. Zhang, *Adv. Synth. Catal.* 2020, **362**, 1208-1212.
- [2] M.-N. Yang, D.-M. Yan, Q.-Q. Zhao, J.-R. Chen, W.-J. Xiao, *Org. Lett.* 2017 **19**, 5208-5211.
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9. Copies of NMR spectra

