ELECTRONIC SUPPORTING INFORMATION

A continuous flow approach for the C–H functionalization of 1,2,3-triazoles in γ -valerolactone as biomass-derived medium

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General Information

Unless otherwise stated, all solvents and reagents were used as obtained from commercial sources without further purification. GC analyses were performed using a Hewlett-Packard HP 5890A equipped with a capillary column DB-35MS (30 m, 0.53 mm) and a FID detector. GC-EIMS analyses were carried out using a Hewlett-Packard HP 6890N Network GC system/5975 MassSelective Detector equipped with an electron impact ionizer at 70 eV. NMR spectra were recorded on a Bruker DRX-ADVANCE 400 MHz (¹H at 400 MHz and ¹³C at 100.6 MHz). The deuterated solvent used was CDCl₃. Elemental Analyses were conducted on a Fisons EA1108CHN. Melting points were measured on a Büchi 510.

General larger scale procedures and E-factor calculations

General flow procedure using packed Pd/C reactor and organic TBAAc as base

(amounts and calculation for representative 100 mmol scale)

Main features:

- solvent recovery (90 %)
- catalyst safely packed into the reactor
- product isolation by re-crystallization

A premixed mixture of **1a** (100 mmol, 0.041 Kg), TBAAc (200 mmol, 0.060 Kg) and MesCO₂H (30 mol %, 30 mmol, 0.0050 Kg) in GVL (660 mL, 0.15M, 0.66 Kg) was charged into a glass column functioning as a reservoir. The equipment was connected, by using the appropriate valves, to a pump and installed into a box thermostated at 120 °C. The reaction mixture was continuously pumped (flow rate: 0.25 mL·min⁻¹; residence time: 80 min) through the catalyst column and the reaction was monitored by GC. Product was collected in fractions and palladium content of the GVL solution was periodically measured by MP-AES analysis. GVL was distilled from the reaction mixture and 0.594 Kg of GVL (90 % of the initial amount) was recovered as pure compound (confirmed by ¹H-NMR). Resulting oil was dissolved in acetone (40 mL, 0.031 Kg), and water (400 mL, 0.4 Kg) was added to precipitate pale brown crystals. Filtration and in vacuo drying gave pure compound (87 mmol, 0.024 Kg, 87 %).

 $\begin{array}{l} \mbox{E-factor (100 mmol scale)} = [(0.041 (\mbox{substrates}) + 0.060 (\mbox{TBAAc}) + 0.0050 (\mbox{MesCO}_2H) + 0.66 (\mbox{GVL}) + 0.4 (\mbox{water}) + 0.031 (\mbox{acetone})) - (0.594 (\mbox{recovered GVL}) + 0.0242 (\mbox{isolated product}))] / 0.0242 (\mbox{isolated product}) = \underline{23.9.} \end{array}$

Optimized larger scale batch procedure based on our literature protocol using Pd/C as catalyst and KTFA as base (100 mmol scale)

Main features:

- solvent recovery (90 %)
- product isolation by re-crystallization
- optimized amount of water used for washing the catalyst from inorganic salts

Pd/C (0.0054 Kg, 5.0 mol %, 5 mmol), MesCO₂H (0.005 Kg, 30 mol %, 30 mmol), KTFA (0.044 Kg, 300 mmol), substrate (0.0294 Kg, 100 mmol) in GVL (400 mL, 0.42 Kg) was charged into a round bottom flask equipped with magnetic stirring bar and reacted under N₂ for 16 h at 150 °C. After cooling to ambient temperature, the reaction mixture was filtered to separate the catalyst. The catalyst was washed with GVL (200 mL, 0.2 Kg) in order to extract residual product from the catalyst, followed by water (0.4 L, 0.4 Kg), and EtOH (0.2 L, 0.1596 Kg) to wash the catalyst from salts. To the remaining residue, EtOH (0.4 L, 0.318 Kg) was added and the mixture was treated with ultrasound in a sonication bath for 3 h. The solvent was removed after filtration and the residual Pd/C was dried in vacuum at 60 °C overnight. The recovered material was used for the subsequent run (99 % of the total mass of the catalyst was recovered, 0.0053 Kg). The GVL solution containing the products of reaction was distilled (90 % of the total mass of solvent was recovered as pure, 0.558 Kg). Resulting oil was dissolved in ethyl acetate (20 mL, 0.018 Kg), and hexane (0.4 L, 0.26 Kg) was added to precipitate pale brown crystals. Filtration and drying of the solid under vacuum afforded the pure product 3-*n*-Butyl-8*H*-[1,2,3]triazolo[5,1-a]isoindole (0.016 kg, 75 %).

 $\begin{array}{l} \mbox{E-factor (100 mmol scale)} = [(0.0294(\mbox{triazole}) + 0.0054(\mbox{Pd/C}) + 0.0050(\mbox{MesCO}_2\mbox{H}) + 0.0442(\mbox{KTFA}) + 0.62(\mbox{GVL}) + 0.4(\mbox{water}) + 0.4776(\mbox{EtOH}) + 0.018(\mbox{EtOAc}) + 0.26(\mbox{hexane})) - (0.0053(\mbox{recovered Pd/C}) + 0.558(\mbox{recovered GVL}) + 0.016(\mbox{isolated product})] / 0.016(\mbox{isolated product}) = \underline{80} \end{array}$

Experiment replicating flow conditions in batch

In order to analyze the differences between flow and batch conditions, we performed a batch reaction using the same catalyst/reactants ratio present at any time in the flow reactor. Therefore, substrate **1a** (1.2 mmol, 0.48 g), TBAAc (2.4 mmol, 0.72 g), GVL (0.15M, 7.7 mL, 7.73 g) and MesCO₂H (30 mol %, 0.36 mmol, 0.06 g), were consecutively added in vial followed by Pd/C (1.88 mmol, 2g). The reaction mixture was stirred at 120 °C and periodically analyzed by GC analysis. After 80 min conversion to product was complete. The reaction mixture was cooled to ambient temperature, and filtered to separate the catalyst. The catalyst was washed first with GVL (12 mL, 12.06 g), in order to extract residual product and TBAAc, followed by EtOH (15 mL, 11.83 g), to wash the catalyst from GVL. Residual Pd/C was dried in vacuum at 60 °C overnight. The recovered material was used for the subsequent reaction run (97 % of the total mass of the catalyst was recovered, 1.94 g). The GVL solution containing the products of reaction was distilled (90 % of the total mass of solvent was recovered as pure, 54.27 g). Resulting oil was dissolved in 0.5 mL of acetone (0.4 g) and 5 mL of cold water (5 g) was added to precipitate the product. Filtration and drying gave the pure product as pale brown crystals (0.285 g, 85 % yield).

 $\begin{array}{l} \mbox{E-factor:} = \left[\left(0.48 (\mbox{substrates}) + 0.72 (\mbox{TBAAc}) + 0.06 (\mbox{MesCO}_2 \mbox{H}) + 7.73 (\mbox{GVL}) + 12.06 (\mbox{GVL wash}) + 11.83 (\mbox{EtOH}) \\ \mbox{wash} + 0.4 (\mbox{acetone}) + 5 (\mbox{water}) \right) - \left(17.81 (\mbox{recovered GVL}) + 1.94 (\mbox{recovered catalyst}) + 0.285 (\mbox{isolated product}) \right) \right] / \\ \mbox{0.285(isolated product)} = 64 \end{array}$

Concentration of Pd measured by MP-AES analysis in the GVL solution: 2.74 ppm

Calculation of E-factors for Representative Literature Procedures

The procedures and *E*-factor calculations described below are representative. In the evaluation of the results obtained, it should be considered that these procedures have not been specifically optimized for larger scale and/or waste minimization protocols.

Reference	General Procedure	E-factor calculation
<i>Org. Lett.</i> , 2010, 12 , 2056–2059 Lutz Ackermann, Rajkumar Jeyachandran, Harish K. Potukuchi, Petr Novák and Lea Büttner	Pd(OAc) ₂ (11.2 mg, 0.05 mmol, 5.0 mol %), Cu(OAc) ₂ ·H ₂ O (200 mg, 1.00 mmol), PivOH (500 mg, 4.90 mmol) and triazole 1a (287 mg, 1.00 mmol) in dry toluene (3 mL) were stirred in a sealed tube at 140 °C for 20 h. H ₂ O (50 mL) was added at ambient temperature, and the resulting mixture was extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with sat. aq. NH ₄ Cl (50 mL), H ₂ O (50 mL) and brine (50 mL), dried over Na ₂ SO ₄ , filtered and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (n-hexane/EtOAc = 10/1 \rightarrow 5/1) to yield 2a (274 mg, 96%) as a yellow oil.	Calculation of <i>E</i> -factor (1 mmol scale) (0.96 mmol, yield 96%)=[(0.287 (triazole)) + 0.011(Pd(OAc) ₂) + 0.200(Cu(OAc) ₂) + 0.500(PivOH) + 2.61 (toluene, density = 0.87 g/mL) + 53 (NH ₄ Cl density = 1.06 g/mL) + 135 (EtOAc density = 0.902 g/mL) + 150 (water)] - [(0.274 (isolated product))] / 0.274 (isolated product) = 1245 (column chromatography was not considered in <i>E</i> -factor calculation)
RSC Adv., 2013, 3 , 2710–2719 Chung-Yu Chen, Cheng-Hao Yang, Wan-Ping Hu, Jaya Kishore Vandavasi, Mei-Ing Chunga and Jeh-Jeng Wang	The starting material (4-((2-iodophenoxy)methyl)-1- phenyl1H-1,2,3-triazole derivates) (1.0 mmol, 377 mg) was dissolved in the dry N,N -dimethylformamide (10 mL, 9.4 g), followed by treating with tetrabutylammonium iodide (TBAI, 3.0 mmol 967 mg), after which Pd(OAc) ₂ 5 mol% (5 mg) was added to the reaction and stirred for 6– 12 h at 100 C. Progress was monitored by TLC to confirm the starting materials had been consumed and then the reaction mixture was poured out on ice cooled water and extracted with ethyl acetate (2 x 200 mL 360 g) and the combined organic layers were washed with water (2 x 200 mL 400 g), brine (1 x 200 mL 238 g), dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure. Crude product was purified by column chromatography (silica gel 0.040–0.633 mm, Ethyl acetate: Hexane = 1:3) to obtain a white solid 209.3 mg (84%)	Calculation of <i>E</i> -factor (1 mmol scale) (0.84 mmol, yield 84%)=[(0.377(triazole) + 0.005(Pd(OAc)_2) + 0.967(TBAI) + 9.4 (DMF, density = 0.944 g/mL) + 360 (EtOAc density = 0.944 g/mL) + 400 (water) + 238 (brine density = 1.19 g/mL)] - [(0.209 (isolated product))] / 0.209 (isolated product) = 4825 (column chromatography was not considered in <i>E</i> -factor calculation)
Eur. J. Org. Chem. 2012, 2013–2022. M. Nagarjuna Reddy and K. C. Kumara Swamy	An oven-dried Schlenk tube with a magnetic stirrer bar was charged with Cul (10 mol % 0.05 mmol 9 mg), TMEDA (20 mol % 0.1 mmol 1 mg), and DMF (1 mL, 944 mg) under a nitrogen atmosphere. O-Alkynyliodophenol (0.5 mmol 66 mg) and azide (0.5 mmol 74 mg) were added by syringe. The mixture was stirred for 1 h at room temperature, and the formation of triazole was monitored by TLC. After the complete formation of triazole, lithium tert-butoxide (3.0 equiv. 1.5 mmol, 120 mg) was added, and the mixturewas heated at 140 °C for 4 h. The mixture was then cooled to ambient temperature, diluted with ethyl acetate (2 mL, 1.8 g), passed through a plug of celite, and washed with ethyl acetate (10 mL, 9.02 g).The filtrate was washed with water (10 mL 10 g) and brine (10 mL 12 g). The organic layer was evaporated and the residue purified by columnchromatography on silica gel by using hexane/ethyl acetate (75:25)as eluent to afford the desired product. (Yield 70 % 0.35 mmol, 0.0977 mg)	Calculation of <i>E</i> -factor (0.5 mmol scale) (0.35 mmol, yield 70 %)=[($0.009(Cul)$ + 0.001(TMEDA) + 0.944 (DMF, density = 0.944 g/mL) + $0.066(O-Alkynyliodophenol)$ + 0.074 (azide) + 0.120 (Lithium tert butoxide) + 10.82 (EtOAc density = 0.944 g/mL) + 10 (water) + 12 (brine density = 1.19 g/mL)) - (0.097 (isolated product))] / 0.097 (isolated product) = 349 (column chromatography was not considered in <i>E</i> -factor calculation)

Chem. Name	1-(4-methoxyphenyl)-1,4-dihydrochromeno[3,4- <i>d</i>][1,2,3]triazole (2a)
Lit. Ref.	Eur. J. Org. Chem. 2012 , 2013–2022
М	$eO \xrightarrow{N=N}_{I} \xrightarrow{O}_{I} \xrightarrow{flow reactor} MeO \xrightarrow{N=N}_{I} \xrightarrow{N=N}_{I}$

Substrate **1a** (1.2 mmol, 488 mg), TBAAc (2.4 mmol, 723 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 4:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was dissolved in 0.5 mL of acetone and 5 mL of cold water was added to precipitate the product. Filtration and drying gave the pure product as pale brown crystals (292 mg, 87% yield).

Mol Formula	C ₁₆ H ₁₃ N ₃ O ₂	m.p.	151-153 °C

Elemental Analysis: Calc.: C, 68.81; H, 4.69; N, 15.05. Found: C, 68.84; H, 4.63; N, 15.01

	δ value	No. H	Mult.	i value/Hz
¹ H NMR 400 MHz	7.48-7.43	2	m	
CDCI ₃	7.23-7.19	1	т	
	7.11-7.05	2	т	
	7.02	1	d	8.0
	6.90	1	dd	1.6, 7.6
	6.82–6.78	1	т	
	5.53	2	S	
	3.92	3	S	

¹³C NMR (100.6 MHz, CDCl₃) δ: 160.9, 153.8, 139.2, 130.7, 129.6, 128.4, 127.1, 122.4, 121.8, 117.9, 114.8, 114.0, 64.5, 55.7

GC-EIMS (m/z, %): 279 (18), 251 (35), 250 (38), 237 (17), 236 (100), 220 (16), 208 (31), 207 (33), 89 (15), 63 (17).

Chem. Name	1-(4-methoxyphenyl)-1,4-dihydrochromeno[3,4- <i>d</i>][1,2,3]triazole (2a)			
Lit. Ref.	Eur. J. Org. Chem. 2012 , 2013–2022			
	$MeO \xrightarrow{N=N}_{Br} \xrightarrow{O}_{flow reactor} MeO \xrightarrow{N=N}_{IaBr} MeO \xrightarrow{V=N}_{2a}$			

Substrate **1aBr** (1.2 mmol, 432 mg), TBAAc (2.4 mmol, 723 mg), TBAI (1.44 mmol, 532 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 4:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was dissolved in 0.5 mL of acetone and 5 mL of cold water was added to precipitate the product. Filtration and drying gave the pure product as pale brown crystals (274 mg, 82% yield).

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Elemental Analysis: Calc.: C, 68.81; H, 4.69; N, 15.05. Found: C, 68.79; H, 4.64; N, 15.02

	δ value	No. H	Mult.	j value/Hz	
400 MHz	7.48-7.43	2	т		
	7.23-7.19	1	т		
	7.11-7.05	2	т		
	7.02	1	d	8.0	
	6.90	1	dd	1.6, 7.6	
	6.82–6.78	1	т		
	5.53	2	S		
	3.92	3	S		

¹³C NMR (100.6 MHz, CDCI₃) δ: 160.9, 153.8, 139.2, 130.7, 129.6, 128.4, 127.1, 122.4, 121.8, 117.9, 114.8, 114.0, 64.5, 55.7

GC-EIMS (m/z, %): 279 (18), 251 (35), 250 (38), 237 (17), 236 (100), 220 (16), 208 (31), 207 (33), 89 (15), 63 (17).

Chem. Name	1-benzyl-1,4-dihydrochromeno[3,4- <i>d</i>][1,2,3]triazole (2b)
Lit. Ref.	Eur. J. Org. Chem. 2012 , 2013–2022
	N=N N=N flow reactor

Substrate **1b** (1.2 mmol, 469 mg), TBAAc (2.4 mmol, 723 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 4:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was dissolved in 0.5 mL of acetone and 5 mL of cold water was added to precipitate the product. Filtration and drying gave the pure product as pale brown crystals (265 mg, 82% yield).

2b

Elemental Analysis: Calc.: C, 72.99; H, 4.98; N, 15.96. Found: C, 73.02; H, 4.97; N, 15.99

1b

	δ value	No. H	Mult.	j value/Hz
400 MHz	7.39–7.30	3	т	
CDCI ₃	7.24-7.18	4	т	
	7.01	1	d	8.0
	6.91	1	t	8.0
	5.83	2	S	
	5.50	2	S	

¹³C NMR (100.6 MHz, CDCI₃) δ: 153.8, 139.9, 134.8, 130.7, 129.3, 128.5, 127.9, 126.6, 122.7, 122.2, 118.1, 114.0, 64.6, 53.2

GC-EIMS (m/z, %): 263 (100), 234 (67), 116 (15), 91 (74), 89 (16), 65 (16)

Chem. Name	1-benzyl-1,4-dihydrochromeno[3,4- <i>d</i>][1,2,3]triazole (2b)		
Lit. Ref.	Eur. J. Org. Chem. 2012 , 2013–2022		
	$ \begin{array}{c} N = N \\ N = N \\ Br \end{array} $ $ \begin{array}{c} N = N \\ \hline H = N \\ $		
	1bBr 2b		

Substrate **1bBr** (1.2 mmol, 413 mg), TBAAc (2.4 mmol, 723 mg), TBAI (1.44 mmol, 532 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 4:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was dissolved in 0.5 mL of acetone and 5 mL of cold water was added to precipitate the product. Filtration and drying gave the pure product as pale brown crystals (253 mg, 80% yield).

Mol Formula	C16H13N3O	m.p.	141-143 °C

Elemental Analysis: Calc.: C, 72.99; H, 4.98; N, 15.96. Found: C, 72.97; H, 4.96; N, 15.93

4	δ value	No. H	Mult.	j value/Hz
'H NMR 400 MHz	7.39–7.30	3	т	
CDCI ₃	7.24-7.18	4	т	
	7.01	1	d	8.0
	6.91	1	t	8.0
	5.83	2	S	
	5.50	2	S	

¹³C NMR (100.6 MHz, CDCI₃) δ: 153.8, 139.9, 134.8, 130.7, 129.3, 128.5, 127.9, 126.6, 122.7, 122.2, 118.1, 114.0, 64.6, 53.2

GC-EIMS (m/z, %): 263 (100), 234 (67), 116 (15), 91 (74), 89 (16), 65 (16)

Chem. Name	1-(<i>p</i> -tolyl)-1,4-dihydrochromeno[3,4- <i>d</i>][1,2,3]triazole (2c)
Lit. Ref.	Eur. J. Org. Chem. 2012 , 2013–2022

1c





METHOD:

Substrate **1c** (1.2 mmol, 469 mg), TBAAc (2.4 mmol, 723 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 4:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was dissolved in 0.5 mL of acetone and 5 mL of cold water was added to precipitate the product. Filtration and drying gave the pure product as pale brown crystals (268 mg, 85% yield).

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Elemental Analysis: Calc.: C, 72.99; H, 4.98; N, 15.96. Found: C, 72.96; H, 5.00; N, 15.99

	δ value	No. H	Mult.	j value/Hz
400 MHz	7.46-7.36	4	т	
CDCI ₃	7.22	1	t	7.2
	7.04	1	d	8.0
	6.92	1	d	7.2
	6.81	1	t	7.6
	5.54	2	S	
	2.51	3	S	

¹³C NMR (100.6 MHz, CDCl₃) δ: 153.9, 140.6, 139.5, 134.4, 130.8, 130.4, 128.3, 125.6, 122.6, 121.9, 118.0, 114.1, 64.6, 21.5

GC-EIMS (m/z, %): 263 (100), 234 (72), 233 (28), 130 (54), 118 (40), 116 (32), 89 (20), 77 (15)

Chem. Name	1-(<i>p</i> -tolyl)-1,4-dihydrochromeno[3,4- <i>d</i>][1,2,3]triazole (2c)
Lit. Ref.	Eur. J. Org. Chem. 2012 , 2013–2022
	$ \begin{array}{c} N=N\\ N=N\\ Hr \end{array} $ Flow reactor $ \begin{array}{c} N=N\\ Hr \end{array} $

2c

1cBr

METHOD:

Substrate **1cBr** (1.2 mmol, 413 mg), TBAAc (2.4 mmol, 723 mg), TBAI (1.44 mmol, 532 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 4:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was dissolved in 0.5 mL of acetone and 5 mL of cold water was added to precipitate the product. Filtration and drying gave the pure product as pale brown crystals (249 mg, 79% yield).

Mol Formula C₁₆H₁₃N₃O m.p. 74-77 °C

Elemental Analysis: Calc.: C, 72.99; H, 4.98; N, 15.96. Found: C, 72.95; H, 4.94; N, 15.94

4	δ value	No. H	Mult.	j value/Hz	
400 MHz	7.46-7.36	4	т		
	7.22	1	t	7.2	
	7.04	1	d	8.0	
	6.92	1	d	7.2	
	6.81	1	t	7.6	
	5.54	2	S		
	2.51	3	S		

¹³C NMR (100.6 MHz, CDCl₃) δ: 153.9, 140.6, 139.5, 134.4, 130.8, 130.4, 128.3, 125.6, 122.6, 121.9, 118.0, 114.1, 64.6, 21.5

GC-EIMS (m/z, %): 263 (100), 234 (72), 233 (28), 130 (54), 118 (40), 116 (32), 89 (20), 77 (15)

Chem. Name	1-pentyl-1,4-dihydrochromeno[3,4- <i>d</i>][1,2,3]triazole (2d)
Lit. Ref.	Org. Lett. 2010, 12, 2056–2059
	N=N N=N flow reactor
	1d 2d

Substrate **1d** (1.2 mmol, 445 mg), TBAAc (2.4 mmol, 723 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 4:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was dissolved in 0.5 mL of acetone and 5 mL of cold water was added to precipitate the product. Filtration and drying gave the pure product as pale yellow crystals (265 mg, 91% yield).

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Elemental Analysis: Calc.: C, 69.11 H, 7.04; N, 17.27. Found: C, 69.14; H, 7.07; N, 17.23

	Σνοίμο		Mult	i voluo/Hz
	0 value	NO. П	iviuit.	j value/Hz
400 MHz	7.44	1	d	1.6
CDCI₃	7.42-7.29	1	т	
	7.10-7.02	2	т	
	5.46	2	S	
	4.60	2	t	7.2
	1.97	2	т	
	1.46-1.32	4	т	
	0.92	3	t	6.4

¹³C NMR (100.6 MHz, CDCl₃) δ: 153.7, 132.1, 130.5, 125.1, 122.2, 122.1, 118.2, 114.2, 64.5, 50.0, 29.6, 28.6, 22.2, 13.9

GC-EIMS (m/z, %): 243 (100), 214 (37), 200 (16), 187 (26), 186 (46), 173 (29), 172 (74), 160 (15), 159 (37), 158 (100), 145 (86), 130 (30), 118 (46), 89 (33), 77 (31), 63 (17)

Chem. Name	1-pentyl-1,4-dihydrochrome	eno[3,4- <i>d</i>][1,2,3]triazole (2d)
Lit. Ref.	Org. Lett. 2010 ,	12, 2056–2059
	N=N N O Br flow reactor	
	1dBr	2d

Substrate **1dBr** (1.2 mmol, 389 mg), TBAAc (2.4 mmol, 723 mg), TBAI (1.44 mmol, 532 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 4:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was dissolved in 0.5 mL of acetone and 5 mL of cold water was added to precipitate the product. Filtration and drying gave the pure product as pale yellow crystals (254 mg, 87% yield).

	J (1	
Mol Formula	C14H17N3O	m.p.	24-26 °C

Elemental Analysis: Calc.: C, 69.11 H, 7.04; N, 17.27. Found: C, 69.15; H, 7.05; N, 17.24

	δ value	No. H	Mult.	i value/Hz
¹ H NMR 400 MHz	7.44	1	d	1.6
CDCI ₃	7.42-7.29	1	т	
	7.10-7.02	2	т	
	5.46	2	S	
	4.60	2	t	7.2
	1.97	2	т	
	1.46-1.32	4	т	
	0.92	3	t	6.4

¹³C NMR (100.6 MHz, CDCl₃) δ : 153.7, 132.1, 130.5, 125.1, 122.2, 122.1, 118.2, 114.2, 64.5, 50.0, 29.6, 28.6, 22.2, 13.9

GC-EIMS (m/z, %): 243 (100), 214 (37), 200 (16), 187 (26), 186 (46), 173 (29), 172 (74), 160 (15), 159 (37), 158 (100), 145 (86), 130 (30), 118 (46), 89 (33), 77 (31), 63 (17)

Chem. Name	3-butyl-8 <i>H</i> -[1,2,3]triazolo[5,1- <i>a</i>]isoindole (4a)
Lit. Ref.	Chem. Commun. 2016 , <i>5</i> 2, 9777–9780
	$ \begin{array}{c} N=N\\ N=N\\ flow reactor \end{array} $

Substrate **3a** (1.2 mmol, 409 mg), TBAAc (2.4 mmol, 723 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 4:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was dissolved in 0.5 mL of ethyl acetate and 5 mL of cold hexane was added to precipitate the product. Filtration and drying gave the pure product as pale brown crystals (238 mg, 93% yield).

Mol Formula	C ₁₃ H ₁₅ N ₃	m.p.	74-75 °C

Elemental Analysis: Calc.: C, 73.21; H, 7.09; N, 19.70. Found: C, 73.18; H, 7.12; N, 19.73

	δ value	No. H	Mult.	j value/Hz
400 MHz	7.62	1	d	7.6
CDCI₃	7.54-7.41	2	т	
	7.38	1	t	7.6
	5.31	2	S	
	2.96	2	t	7.2
	1.87-1.78	2	т	
	1.50-1.41	2	т	
	0.98	3	t	7.2

¹³C NMR (100.6 MHz, CDCI₃) δ: 140.8, 139.5, 139.5, 128.9, 128.7, 127.8, 124.3, 121.0, 51.1, 31.8, 25.8, 22.5, 14.0

GC-EIMS (m/z, %): 213 (26), 184 (52), 170 (100), 168 (25), 157 (16), 156 (72), 154 (27), 142 (43), 129 (41), 115 (56), 89 (33), 63 (17)



Substrate **3aBr** (1.2 mmol, 353 mg), TBAAc (2.4 mmol, 723 mg), TBAI (1.44 mmol, 532 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 4:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was dissolved in 0.5 mL of ethyl acetate and 5 mL of cold hexane was added to precipitate the product. Filtration and drying gave the pure product as pale brown crystals (223 mg, 87% yield).

 Mol Formula
 C13H15N3
 m.p.
 74-75 °C

Elemental Analysis: Calc.: C, 73.21; H, 7.09; N, 19.70. Found: C, 73.19; H, 7.06; N, 19.66

	δ value	No. H	Mult.	j value/Hz
400 MHz	7.62	1	d	7.6
CDCI ₃	7.54-7.41	2	т	
	7.38	1	t	7.6
	5.31	2	S	
	2.96	2	t	7.2
	1.87-1.78	2	т	
	1.50-1.41	2	т	
	0.98	3	t	7.2

¹³C NMR (100.6 MHz, CDCI₃) δ: 140.8, 139.5, 139.5, 128.9, 128.7, 127.8, 124.3, 121.0, 51.1, 31.8, 25.8, 22.5, 14.0

GC-EIMS (m/z, %): 213 (26), 184 (52), 170 (100), 168 (25), 157 (16), 156 (72), 154 (27), 142 (43), 129 (41), 115 (56), 89 (33), 63 (17)



Substrate **3b** (1.2 mmol, 433 mg), TBAAc (2.4 mmol, 723 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 4:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was dissolved in 0.5 mL of acetone and 5 mL of cold water was added to precipitate the product. Filtration and drying gave the pure product as pale brown crystals (252 mg, 90% yield).

Mol Formula	C15H11N3	m.p.	155-158 °C
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Elemental Analysis: Calc.: C, 77.23; H, 4.75; N, 18.01. Found: C, 77.27; H, 4.72; N, 18.05

	δ value	No. H	Mult.	j value/Hz
400 MHz	7.94	2	d	7.2
CDCI ₃	7.88	1	d	7.6
	7.54-7.50	3	т	
	7.48-7.37	3	т	
	5.35	2	S	

¹³C NMR (100.6 MHz, CDCl₃) δ: 141.2, 139.3, 139.0, 131.3, 129.0, 128.8, 128.4, 128.2, 128.1, 127.0, 124.2, 121.3, 51.0

GC-EIMS (m/z, %): 233 (8), 205 (71), 204 (100), 176 (25), 102 (52), 89 (54), 63 (18)



Substrate **3c** (1.2 mmol, 443 mg), TBAAc (2.4 mmol, 723 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 4:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was dissolved in 0.5 mL of ethyl acetate and 5 mL of cold hexane was added to precipitate the product. Filtration and drying gave the pure product as pale brown crystals (260 mg, 90% yield).

Elemental Analysis: Calc.: C, 74.65; H, 7.94; N, 17.41. Found: C, 74.69; H, 7.97; N, 17.39

	δ value	No. H	Mult.	j value/Hz
400 MHz	7.59	1	d	7.6
CDCI ₃	7.51-7.40	2	т	
	7.36	1	t	7.2
	5.28	2	S	
	2.93	2	t	7.6
	1.84-1.76	2	т	
	1.48-1.25	6	т	
	0.87	3	t	6.8

¹³C NMR (100.6 MHz, CDCI₃) δ: 140.8, 139.4, 128.8, 128.6, 128.4, 127.8, 124.2, 120.9, 51.0, 31.7, 29.6, 29.1, 26.0, 22.7, 14.2

GC-EIMS (m/z, %): 241 (10), 212 (23), 184 (24), 171 (21), 170 (100), 157 (15), 156 (55), 143 (25), 129 (23), 115 (36), 89 (18)

Chem. Name	3-(cyclopentylmethyl)-8 <i>H</i> -[1,2,3]triazolo[5,1- <i>a</i>]isoindole (4d)
Lit. Ref.	Tetrahedron 2010 , 66, 8846–8853
	$ \begin{array}{c} N = N \\ N = N \\ \hline A \\ $

Substrate **3d** (1.2 mmol, 440 mg), TBAAc (2.4 mmol, 723 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 4:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was dissolved in 0.5 mL of acetone and 5 mL of cold water was added to precipitate the product. Filtration and drying gave the pure product as pale brown crystals (264 mg, 92% yield).

Mol Formula	C15H17N3	m.p.	107-110 °C

Elemental Analysis: Calc.: C, 75.28; H, 7.16; N, 17.56. Found: C, 75.22; H, 7.17; N, 17.59

	δ value	No. H	Mult.	j value/Hz
400 MHz	7.62	1	d	7.6
CDCI ₃	7.52-7.43	2	т	
	7.37	1	td	7.6, 1.2
	5.29	2	S	
	2.95	2	d	7.2
	2.41-2.30	1	т	
	1.85-1.74	2	т	
	1.70-1.62	2	т	
	1.58-1.53	2	т	
	1.34-1.25	2	т	

¹³C NMR (100.6 MHz, CDCl₃) δ: 140.8, 139.6, 138.9, 128.8, 128.7, 127.8, 124.3, 120.9, 51.0, 40.7, 32.5, 31.8, 25.1

GC-EIMS (m/z, %): 239 (15), 210 (63), 183 (33), 182 (100), 168 (28), 167 (17), 143 (36), 115 (18), 89 (21)



Substrate **3e** (1.2 mmol, 440 mg), TBAAc (2.4 mmol, 723 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 4:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was dissolved in 0.5 mL of acetone and 5 mL of cold water was added to precipitate the product. Filtration and drying gave the pure product as pale brown crystals (238 mg, 83% yield).

Mol Formula C ₁₅ H ₁₇ N ₃ m.p. 128-130 °C
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Elemental Analysis: Calc.: C, 75.28; H, 7.16; N, 17.56. Found: C, 75.26; H, 7.20; N, 17.55

	δ value	No. H	Mult.	j value/Hz
'H NMR 400 MHz	7.68	1	d	7.6
CDCI ₃	7.51-7.43	2	т	
	7.37	1	t	7.6
	5.29	2	S	
	3.08-2.96	1	т	
	2.11-2.00	2	т	
	1.94-1.85	2	т	
	1.82-1.65	3	т	
	1.54-1.31	3	т	

¹³C NMR (100.6 MHz, CDCI₃) δ: 144.8, 140.8, 138.7, 128.8, 128.7, 127.8, 124.2, 121.6, 60.0, 36.4, 32.8, 26.6, 26.2

GC-EIMS (m/z, %): 239 (7), 211 (19), 210 (61), 183 (43), 182 (100), 168 (37), 167 (26), 154 (26), 130 (16), 127 (16), 115 (16), 89 (16)



Substrate **3f** (1.2 mmol, 450 mg), TBAAc (2.4 mmol, 723 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 4:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was dissolved in 0.5 mL of acetone and 5 mL of cold water was added to precipitate the product. Filtration and drying gave the pure product as pale brown crystals (273 mg, 92% yield).

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Elemental Analysis: Calc.: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.67; H, 5.32; N, 16.96

	δ value	No. H	Mult.	j value/Hz
400 MHz	7.89	1	d	7.2
CDCI ₃	7.86-7.82	2	т	
	7.53	1	d	7.6
	7.49-7.40	2	т	
	7.35-7.31	2	т	
	5.36	2	S	
	2.44	3	S	

¹³C NMR (100.6 MHz, CDCl₃) δ: 141.2, 139.5, 138.9, 138.2, 129.7, 128.9, 128.5, 128.4, 128.4, 127.0, 124.3, 121.3, 51.0, 21.5

GC-EIMS (m/z, %): 247 (8), 219 (61), 218 (100), 204 (72), 189 (21), 166 (15), 109 (37), 89 (21), 63 (24)

Chem. Name	3-((2-iodophenoxy)methyl)-8 <i>H</i> -[1,2,3]triazolo[5,1- <i>a</i>]isoindole (4g)
Lit. Ref.	
	$ \begin{array}{c} $

Substrate **3g** (1.2 mmol, 620 mg), TBAAc (2.4 mmol, 723 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 4:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was dissolved in 0.5 mL of acetone and 5 mL of cold water was added to precipitate the product. Filtration and drying gave the pure product as pale brown crystals (383 mg, 82% yield).

Mol Formula	C ₁₆ H ₁₂ IN ₃ O	m.p.	294-296 °C (decomp.)
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Elemental Analysis: Calc.: C, 49.38; H, 3.11; N, 10.80. Found: C, 49.34; H, 3.08; N, 10.83

	δ value	No. H	Mult.	j value/Hz
400 MHz	7.98	1	d	8.0
CDCI ₃	7.75	1	dd	1.2, 8.0
	7.48	2	t	6.8
	7.42-7.38	1	т	
	7.28-7.24	1	т	
	7.07	1	d	7.6
	6.70	1	td	8.0, 1.2
	5.53	2	S	
	5.32	2	S	

¹³C NMR (100.6 MHz, CDCl₃) δ: 156.8, 142.0, 140.9, 139.8, 134.7, 129.7, 129.0, 128.7, 127.6, 124.0, 123.6, 123.2, 113.1, 86.5, 63.8, 51.5

GC-EIMS (m/z, %): 389 (2), 319 (23), 290 (100), 235 (21), 234 (64), 221 (17), 220 (54), 204 (32), 179 (40), 130 (35), 65 (16)

Chem. Name	Ethyl 4-(4-butyl-1-phenyl-1 <i>H</i> -1,2,3-triazol-5-yl)benzoate (7a)			
Lit. Ref.	Chem. Commun. 2016 , 52, 9777–9780			
	N = N $N = N$ $N = N$ $N = N$ H R			
	5a 6b EtO ₂ C 7a			

Triazole **5a** (1.2 mmol, 241 mg), **6b** (3.6 mmol, 825 mg, 588 μl) TBAAc (2.4 mmol, 723 mg), TBAI (1.44 mmol, 532 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 15:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was purified by column chromatography on silica gel (petroleum ether/EtOAc, 15:1) to give the pure product as a colorless oil (327 mg, 78% yield).

Mol Formula	C21H23N3O2	m.p.	

Elemental Analysis: Calc.: C, 72.18; H, 6.63; N, 12.03. Found: C, 72.15; H, 6.69; N, 11.99

	δ value	No. H	Mult.	j value/Hz
400 MHz	7.98-7.92	2	т	
CDCI ₃	7.33-7.29	3	т	
	7.21-7.10	4	т	
	4.30	2	q	6.8
	2.67	2	t	7.6
	1.67-1.58	2	т	
	1.34-1.22	5	т	
	0.80	3	t	7.2

¹³C NMR (100.6 MHz, CDCI₃) δ: 165.89, 146.7, 136.6, 132.9, 132.2, 130.8, 129.9, 129.5, 129.3, 129.0, 124.9, 61.3, 31.7, 24.9, 22.5, 14.3, 13.8

GC-EIMS (m/z, %): 349 (7), 321 (25), 279 (21), 278 (100), 175 (35), 147 (18), 104 (16), 77 (39)

Chem. Name	Ethyl 4-(4-	-butyl-1-phenyl-1 <i>H</i> -1,2,3-	triazol-5-yl)benzoate (7a)
Lit. Ref.		Chem. Commun. 2016, S	52, 9777–9780
	N≈N N_N nBu	+ CO ₂ Et	N ^N N nBu
	5a	6a	EtO ₂ C [/] 7a

Triazole **5a** (1.2 mmol, 241 mg), **6a** (3.6 mmol, 994 mg, 605 µl) TBAAc (2.4 mmol, 723 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 15:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was purified by column chromatography on silica gel (petroleum ether/EtOAc, 15:1) to give the pure product as a colorless oil (343 mg, 82% yield).

	Mol Formula	C ₂₁ H ₂₃ N ₃ O ₂	m.p.	
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Elemental Analysis: Calc.: C, 72.18; H, 6.63; N, 12.03. Found: C, 72.14; H, 6.67; N, 12.06

	δ value	No. H	Mult.	j value/Hz
400 MHz CDCI ₃	7.98-7.92	2	т	
	7.33-7.29	3	т	
	7.21-7.10	4	т	
	4.30	2	q	6.8
	2.67	2	t	7.6
	1.67-1.58	2	т	
	1.34-1.22	5	т	
	0.80	3	t	7.2

¹³C NMR (100.6 MHz, CDCI₃) δ: 165.89, 146.7, 136.6, 132.9, 132.2, 130.8, 129.9, 129.5, 129.3, 129.0, 124.9, 61.3, 31.7, 24.9, 22.5, 14.3, 13.8

GC-EIMS (m/z, %): 349 (7), 321 (25), 279 (21), 278 (100), 175 (35), 147 (18), 104 (16), 77 (39)



Triazole **5b** (1.2 mmol, 258 mg), **6b** (3.6 mmol, 825 mg, 588 µl) TBAAc (2.4 mmol, 723 mg), TBAI (1.44 mmol, 532 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 15:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was purified by column chromatography on silica gel (petroleum ether/EtOAc, 15:1) to give the pure product as a colorless oil (371 mg, 85% yield).

Mol Formula	C22H25N3O2	m.p.	

Elemental Analysis: Calc.: C, 72.70; H, 6.93; N, 11.56. Found: C, 72.66; H, 6.94; N, 11.52

	δ value	No. H	Mult.	j value/Hz
400 MHz CDCI ₃	8.05-7.98	2	т	
	7.25-7.20	2	т	
	7.13	4	S	
	4.36	2	q	7.2
	2.73	2	t	7.6
	2.33	3	S	
	1.75-1.65	2	т	
	1.39-1.30	5	т	
	0.86	3	t	7.2

¹³C NMR (100.6 MHz, CDCl₃) δ: 165.89, 146.48, 139.1, 134.1, 132.9, 132.3, 130.7, 129.9, 129.8, 129.5, 124.7, 61.3, 31.7, 24.9, 22.4, 21.1, 14.3, 13.8

GC-EIMS (m/z, %): 363 (2), 334 (15), 335 (48), 293 (21), 292 (100), 175 (25), 147 (16), 104 (15), 77 (41), 51 (15)



Triazole **5b** (1.2 mmol, 258 mg), **6a** (3.6 mmol, 994 mg, 605 µl) TBAAc (2.4 mmol, 723 mg), GVL (0.15M, 7.7 mL) and MesCO₂H (30 mol %, 0.36 mmol, 60 mg), were consecutively added to a reservoir tube and the resulting mixture was pumped at 0.25 mL/min through a coil reactor filled with Pd/C and thermostated at 120 °C. Reaction progress was monitored with TLC (petroleum ether/EtOAc, 15:1). Reaction mixture was collected in a glass tube and GVL was distilled off using a Kugelrhor apparatus (0.3 mbar at 150 °C). The resulting oil was purified by column chromatography on silica gel (petroleum ether/EtOAc, 15:1) to give the pure product as a colorless oil (379 mg, 87% yield).

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Mol	Formula	C22H25N3O2	m.p.	

Elemental Analysis: Calc.: C, 72.70; H, 6.93; N, 11.56. Found: C, 72.67; H, 6.89; N, 11.53

	δ value	No. H	Mult.	j value/Hz
400 MHz CDCI ₃	8.05-7.98	2	т	
	7.25-7.20	2	т	
	7.13	4	S	
	4.36	2	q	7.2
	2.73	2	t	7.6
	2.33	3	S	
	1.75-1.65	2	т	
	1.39-1.30	5	m	
	0.86	3	t	7.2

¹³C NMR (100.6 MHz, CDCl₃) δ: 165.89, 146.48, 139.1, 134.1, 132.9, 132.3, 130.7, 129.9, 129.8, 129.5, 124.7, 61.3, 31.7, 24.9, 22.4, 21.1, 14.3, 13.8

GC-EIMS (m/z, %): 363 (2), 334 (15), 335 (48), 293 (21), 292 (100), 175 (25), 147 (16), 104 (15), 77 (41), 51 (15)