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Electronic Supplementary Information (ESI)

Palladium-catalysed stereoselective synthesis of 4-(diarylmethylidene)-3,4dihydroisoquinolin-1(2H)-ones: Expedient access to 4-substituted isoquinolin-1(2H)-ones and isoquinolines

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¹ H & ¹³ CNMR of 10ad	S84
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Figure S1: ORTEP¹ diagram of compound **7p** (drawn at 50% probability).



Figure S2: ORTEP¹ diagram of compound **9b** (drawn at 50% probability).

Note: ORTEP diagrams of 10ba and 14 have already been provided in the manuscript.

¹ O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschman; *OLEX2:A complete structure solution, refinement and analysis program. J. Appl. Cryst.* **2009**, *42*, 339.

	7p 9b	
Empirical	$C_{23}H_{21}N_3O_3$	C ₂₂ H ₁₇ NO
Formula		
Formula weight	387.43	311.36
Temperature (K)	273.15	296.15
Wavelength	0.71073	0.71073
Crystal System	Monoclinic	Triclinic
Space Group	I 1 2/a 1	P -1
	0	٥
	a=12.091(4) Å	a=6.6454(2) Å
Unit Cell	b=12.635(5) A	b=8.8659(4) Å
Dimension	c=25.986(10) Å	c=15.1694(5) Å
	α=90°	α=94.198(3)°
	β=92.324(14)°	β=102.080(2)°
	γ=90°	γ=102.439(2)°
0.2		
Volume Å ³	3967(3)	846.86(5)
Z	8	2
Density Calculated g/cm ³	1.298	1.221
Absorption	0.088	0.075
coefficient(Mu) mm ⁻¹		
F(000)	1632	328
Theta range for data	2.77 -23.59°	2.370-26.146°
collection		
	-15<=h<=15	-8<=h<=8
Index ranges	-14<=k<=15	-11<=k<=10
	-32<=l<=32	-18<=1<=18
Reflection Collected	24976	12644
Independent Reflections	4158	3416
	[R(int) = 0.0670]	[R(int) = 0.0361]
Completeness to the	99.2%	98.4%
theta=25.44	N 1.1	
Absorption Correction	Multi-scan	Multi-scan
Max. and min. Transmission	0.7455 and 0.6600	0.7454 and 0.6826
Refinement method	Full-matrix least-	Full-matrix least-
	squares on F^2	squares on F^2
Data/Restraints/parameter	4158/0/265	3416/0/217
$\frac{1}{10000000000000000000000000000000000$	1.038	0.996
Final R indices	R ₁ =0.0563	$R_1 = 0.0458$
$[I \ge 2 \operatorname{sigma}(I)]$	wR ₂ =0.1404	$wR_2 = 0.1258$
R indices (all data)	$R_1 = 0.1165$	$R_1 = 0.0743$
	wR ₂ =0.1729	$wR_2 = 0.1416$
Largest difference peak	0.191 and - 0.241	0.158 and -0.156
and hole		
[e. ⁶ - ³]		

Table S1 Important crystal data of products 7p, 9b

The crystal data of products **7p** and **9b** have been deposited at Cambridge Crystallographic Data Centre; the CCDC reference number s are 1571341 and 1571342, respectively.

	10ba	14
Empirical	C ₂₂ H ₁₇ NO C ₂₄ H ₁₇ NO ₃	
Formula		
Formula weight	311.36	367.38
Temperature (K)	296.15	273.15
Wavelength	0.71073	0.71073
Crystal System	monoclinic	monoclinic
Space Group	P 1 21/n 1	C 1 2/c 1
Unit Cell	a= 10.117(3) Å	a= 20.6490(17) Å
Dimension	b=13.923(4)Å	b=10.8202(8) Å
	c=12.307(4) Å	c= 20.1324(17) Å
	$\alpha = 90^{\circ}$	α=90°
	β=99.313(2)°	$\beta = 126.199(2)^{\circ}$
	γ=90°	γ=90°
Volume $Å^3$	1710.8(9)	3629.8(5)
Z	4	8
Density Calculated g/cm ³	1.209	1.345
Absorption	0.074	0.089
coefficient(Mu) mm ⁻¹		
F(000)	656	1536
Theta range for data	8.496 - 25.702 °	2.776 – 25.137 °
collection		
Index ranges	-12<=h<=12	-25<=h<=25
	-17<=k<=17	-13<=k<=13
	-15<=l<=12	-25<=l<=25
Reflection Collected	15040	40405
Independent Reflections	3644	3787
	[R(int) = 0.0473]	[R(int)=0.1134]
Completeness to the	95.8%	98.6%
theta=25.44°		
Absorption Correction	Multi-scan	Multi-scan
Max. and min.	0.7456 and 0.6789	0.7454 and 0.6395
Transmission		
Refinement method	Full-matrix least-	Full-matrix least-
	squares on F ²	squares on F ²
Data/Restraints/parameter	3644/0/218	3787/0/254
Goodness of fit on F ²	1.032	1.035
Final R indices	$R_1 = 0.0458$	$R_1 = 0.0405$
[I>=2sigma(I)]	$wR_2 = 0.1019$	$wR_2 = 0.1194$
R indices (all data)	$R_1 = 0.0670$	$R_1 = 0.0773$
	$wR_2 = 0.1131$	$wR_2=0.1620$
Largest difference peak	0.189 and -0.154	0.271 and -0.258
and hole		
[e. ^{°-3}]		

Table S2Important crystal data of compounds 10ba and 14

The crystal data of products **10ba** and **14** have been deposited at Cambridge Crystallographic Data Centre; the CCDC reference numbers are 1571343 and 1571344 respectively.

$\begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\$						
Sl. No	Reagents	equivalent	temperature	time (h)	product	yield ^d %
1 ^b	LiAlH ₄	20	reflux	2h	S15	50
2 ^b	LiAlH ₄	10	reflux	3h	S15	41
3	BH ₃ , Me ₂ S	2	rt	24h	11a	0
4	BH ₃ , Me ₂ S	100	rt	8h	11 a	62
5 ^c	BH ₃ , Me ₂ S	6	rt	17h	11a	40
6	BH ₃ , Me ₂ S	10	rt	24h	11a	89
7	BH ₃ , Me ₂ S	20	rt	8h	11a	83

Table S3 Optimisation of the reaction conditions for the synthesis of compound $11a^{a}$

^aReaction conditions: **7u** (1 equiv), LiAlH₄ or BH₃.Me₂S in dry THF under argon gas. ^bOnly detosylated product **S15** was produced. ^cStarting compound **7u** was recovered (45%).

Synthesis of 2-Iodo-*N*-methyl-*N*-(prop-2-ynyl)benzamide (5ah) and 4-Chloro-2-Iodo-*N*-methyl-*N*-(prop-2-ynyl)benzamide (S1)

2-Iodo-*N*-methyl-*N*-(prop-2-yn-1-yl)benzamide (**5ah**) was prepared according to the known procedure.² 4-Chloro-2-iodo-*N*-methyl-*N*-(prop-2-yn-1-yl)benzamide (**S1**) was prepared adopting the same procedure but using 4-Chloro-2-iodobenzoyl chloride in place of 2-iodobenzoyl chloride. The NMR spectra of these and other related amides showed multiplicity of peaks which merged at higher temperature, suggesting the influence of rotational isomerism as commonly observed with amides.

2-*Iodo-N-methyl-N-(prop-2-yn-1-yl)benzamide*² (*5ah*). Light yellow solid (96% yield); m.p.51-52 °C (reported^[2] m.p. 48-49 °C); ¹H NMR (CDCl₃, 300 MHz) δ (amide isomers) 7.85-7.82 (m, 1H), 7.44-7.38 (m, 1H), 7.30-7.21 (m, 1H), 7.13-7.06 (m, 1H), 4.43 (s, 1H), 3.89-3.87 (m, 1H), 3.21 and 2.91 (2×s, 3H, NCH₃), 2.30-2.29 (m, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 170.3, 141.9, 141.7, 139.3, 139.2, 130.5, 130.3, 128.4, 127.1, 127.0, 92.4, 92.2, 73.4, 72.6, 40.7, 35.9, 35.5, 32.1 ppm. HRMS (ESI⁺) *m/z* calculated for C₁₁H₁₁INO [M+H]⁺ 299.9885, found 299.9882.

4-*Chloro-2-iodo-N-methyl-N-(prop-2-yn-1-yl)benzamide* (*S1*). White solid (98% yield); mp 58-60 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.85-7.83 (m, 1H), 7.41-7.37 (m, 1H), 7.22-7.14 (m, 1H), 4.40 (d, *J* = 2.4 Hz, 1H), 3.86 (s, 1H), 3.19 and 2.90 (2xs, 3H, NCH₃), 2.31-2.28 (m, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 169.4, 140.2, 140.0, 138.6, 138.5, 135.3, 135.1, 128.7, 128.7, 127.8, 127.7, 92.6, 92.3, 73.6, 72.7, 40.6, 35.9, 35.4, 32.2 ppm. HRMS (EI⁺) *m/z* calculated for C₁₁H₉ClINO [M]⁺ 332.9417, found 332.9412.

General Procedure for the Synthesis of 2-Iodo-*N*-methyl-*N*-(3-arylprop-2-ynyl)benzamides (5aa-5ag) through *Sonogashira Reaction* between 2-Iodo-*N*-methyl-*N*-(3-prop-2-ynyl)benzamides (5ah) and Aryl Iodides

To a well-stirred and ice-cooled solution of $PdCl_2(PPh_3)_2$ (14.7 mg, 0.02 mmol) in dry DMF (3 mL) under argon atmosphere copper iodide (8.0 mg, 0.04 mmol), Et₃N (0.4 mL, 2.5 mmol) and

² P. Fretwell, R. Grigg, J. M. Sansano, V. Sridharan, S. Sukirthalingam, D. Wilson and J. Redpath *Tetrahedron*, 2000, **56**, 7525.

aryl iodide (1.05 mmol) were added and the reaction mixture was allowed to stir under argon atmosphere for 3-5 min. Thereafter, a solution of 2-iodo-*N*-methyl-*N*-(3-prop-2-ynyl)benzamide (299.0 mg, 1 mmol) dissolved in dry DMF (1.0 mL) was added to the reaction under ice-cold condition. The reaction mixture was then allowed to stir at rt for 1 h. After completion of the reaction (TLC), the solvent was evaporated *in vacuo*; the resulting residue was extracted with ethyl acetate (3 x 20 mL). The combined organic extracts were washed with water (10 mL), dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified through silica gel column chromatography using ethyl acetate-petroleum ether (v/v) as eluent to afford pure products (**5aa-5ag**).

2-Iodo-*N***-methyl-***N***-(3-phenylprop-2-ynyl)benzamide**³ (**5aa**). Pale yellow gum (281.2 mg, 75%); ¹H NMR (CDCl₃, 300 MHz) δ 7.88-7.83 (m, 1H), 7.47-7.39 (m, 3H), 7.35-7.32 (m, 3H), 7.26-7.24 (m, 1H), 7.14-7.07 (m, 1H), 4.66 and 4.11 (2×s, 2H, NCH₂), 3.27and 2.97 (2×s, 3H, NCH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 170.3, 170.2, 141.9, 141.7, 139.2, 139.0, 131.7, 131.5, 130.3, 130.2, 129.2, 128.5, 128.3, 128.2, 128.2, 127.1, 126.9, 122.6, 122.1, 92.4, 92.1, 85.0, 84.2, 83.1, 82.8, 41.4, 36.6, 35.5, 32.2 ppm. HRMS (EI⁺) *m/z* calculated for C₁₇H₁₄INO [M]⁺ 375.0120, found 375.0123.

Methyl 4-[3-(2-iodo-N-methylbenzamido)prop-1-ynyl]benzoate (5ab). Brown gum (337.7 mg, 78%); ¹H NMR (CDCl₃, 300 MHz) δ 7.98 (d, J = 8.4 Hz, 2H), 7.85 (t, J = 7.2 Hz, 1H), 7.52-7.39 (m, 3H), 7.33-7.24 (m, 1H), 7.14-7.07 (m, 1H), 4.66 and 4.12 (2×s, 2H, NCH₂) (s, 1H), 3.92 (s, 3H), 3.26 and 2.97 (2×s, 3H, NCH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 170.3, 166.3, 141.7, 141.6, 139.2, 139.1, 131.6, 131.5, 130.4, 130.3, 129.8, 129.6, 129.4, 129.3, 128.4, 128.3, 127.2, 127.1, 126.9, 126.7, 92.4, 92.0, 86.3, 85.8, 84.2, 83.4, 52.1, 41.4, 36.6, 35.6, 32.3 ppm. HRMS (EI⁺) *m/z* calculated for C₁₉H₁₆INO₃ [M]⁺ 433.0175, found 433.0166.

N-[3-(4-Fluorophenyl)prop-2-ynyl]-2-iodo-*N*-methylbenzamide (5ac). Yellow gum (220.1 mg, 56%); ¹H NMR (CDCl₃, 300 MHz) δ 7.84 (t, *J* = 7.0 Hz, 1H), 7.46-7.36 (m, 3H), 7.33-7.24 (m, 1H), 7.14-7.07 (m, 1H), 7.01 (t, *J*= 8.7 Hz, 2H), 4.63 and 4.09 (2×s, 2H, NCH₂), 3.25 and 2.96 (2×s, 3H, NCH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 170.4, 170.3, 162.5 (d, *J* = 248.2 Hz), 141.9, 141.8, 139.3, 139.2, 133.7 (d, *J* = 8.3 Hz), 133.6 (d, *J*= 8.2 Hz), 130.5, 130.3, 128.5, 128.4,

³ D. Brown, R. Grigg, V. Sridharan, V. Tamhyrajah and M. Thornton- Pett, *Tetrahedron*, 1998, 54, 2595.

127.2, 127.1, 118.7 (d, J = 3.4 Hz), 118.3 (d, J = 3.4 Hz), 115.7 (d, J = 22.0 Hz), 115.6 (d, J = 22 Hz), 41.5, 36.7, 35.7, 32.3 ppm. MS (ESI⁺) m/z calculated for C₁₇H₁₃FINONa [M+Na]⁺ 415.9923, found 415.9925.

2-Iodo-*N***-methyl**-*N*-(**3**-*p***-tolylprop-2-ynyl)benzamide (5ad).** Brown gum (210.1 mg, 54%); ¹H NMR (CDCl₃, 300 MHz) δ 7.84 (t, *J* = 7.0 Hz, 1H), 7.44-7.38 (m, 1H), 7.36-7.31 (m, 2H), 7.28-7.24 (m, 1H), 7.13-7.06 (m, 3H), 4.64 and 4.09 (2×s, 2H, NCH₂), 3.26 and 2.96 (2×s, 3H, NCH₃), 2.35 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 170.5, 170.3, 142.0, 141.9, 139.3, 139.2, 138.8, 138.6, 131.7, 131.5, 130.4, 130.3, 129.1, 129.1, 128.4, 128.4, 127.2, 127.1, 119.6, 119.1, 92.5, 92.2, 85.2, 84.4, 82.5, 82.1, 41.6, 36.8, 35.6, 32.3, 21.5 ppm. MS (EI⁺) *m/z* calculated for C₁₈H₁₆INO [M]⁺ 389.0277, found 389.0280.

2-Iodo-*N***-[3-(4-methoxyphenyl)prop-2-ynyl]***-N***-methylbenzamide (5ae).** Brown gum (210.6 mg, 52%); ¹H NMR (CDCl₃, 300 MHz) δ 7.85 (t, *J* = 7.0 Hz, 1H), 7.45-7.25 (m, 4H), 7.14-7.07 (m, 1H), 6.85 (d, *J* = 9 Hz, 2H), 4.64 and 4.09 (2×s, 2H, NCH₂), 3.82 (s, 3H), 3.26 and 2.97 (2×s, 3H, NCH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 170.4, 170.3, 159.8, 159.6, 142.0, 141.9, 139.2, 139.1, 133.2, 133.1, 130.4, 130.2, 128.4, 128.3, 127.2, 127.0, 114.7, 114.3, 114.0, 113.9, 92.5, 92.2, 84.9, 84.2, 81.7, 81.4, 55.3, 41.6, 36.7, 35.5, 32.2 ppm. MS (ESI⁺) *m*/*z* calculated for C₁₈H₁₆INO₂Na [M+Na]⁺ 428.0123, found 428.0121.

N-[3-(2,4-Dimethoxypyrimidin-5-yl)prop-2-ynyl]-2-iodo-*N*-methylbenzamide (5af). Yellow gum (297.2 mg, 68%); ¹H NMR (CDCl₃, 300 MHz) δ 8.33-8.29 (m, 1H), 7.87-7.82 (m, 1H), 7.44-7.39 (m, 1H), 7.35-7.24 (m, 1H), 7.11-7.07 (m, 1H), 4.68 and 4.13 (2×s, 2H, NCH₂), 4.04,4.01 (2×s, 2×3H, 2×OCH₃), 3.26 and 2.96 (2×s, 3H, NCH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 170.6, 170.4, 170.3, 161.5, 161.5, 141.8, 141.7, 139.2, 139.1, 130.4, 130.3, 128.4, 128.3, 127.2, 127.0, 92.4, 92.1, 89.6, 89.2, 75.8, 55.1, 55.1, 54.5, 54.5, 41.6, 36.8, 35.6, 32.3 ppm. HRMS (EI⁺) *m/z* calculated for C₁₇H₁₆IN₃O₃ [M]⁺ 437.0236, found 437.0228.

2-Iodo-*N***-methyl**-*N*-**[3-(thiophen-2-yl)prop-2-ynyl]benzamide (5ag).** Brown gum (259.1 mg, 68%); ¹H NMR (CDCl₃, 300 MHz) δ 7.85 (t, *J* = 7.3 Hz, 1H), 7.46-7.39 (m, 1H), 7.34-7.31 (m, 1H), 7.28-7.20 (m, 2H), 7.14-7.06 (m, 1H), 6.99-6.96 (m, 1H), 4.66 and 4.12 (2×s, 2H, NCH₂),

3.25 and 2.95 (2×s, 3H, NCH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 170.4, 170.3, 141.9, 141.8, 139.3, 139.2, 132.4, 132.3, 130.5, 130.3, 128.4, 127.5, 127.2, 127.0, 127.0, 126.9, 122.6, 92.5, 92.2, 87.4, 86.9, 41.7, 36.9, 35.7, 32.4 ppm. HRMS (ESI⁺) *m/z* calculated for C₁₅H₁₂INOSNa [M+Na]⁺ 403.9582, found 403.9586.

Substrate **5ba** was prepared using 4-chloro-2-iodo-*N*-methyl-*N*-(prop-2-yn-1-yl)benzamide (**S1**) (333.0 mg, 1 mmol) and phenyl iodide (214.2 mg, 1.05 mmol) as reactants and adopting the above procedure.

4-Chloro-2-iodo-N-methyl-*N***-(3-phenylprop-2-yn-1-yl)benzamide (5ba).** Brown gum (184.0 mg, 45%); ¹H NMR (CDCl₃, 300 MHz) δ 7.89-7.86 (m, 1H), 7.48-7.40 (m, 3H), 7.35-7.33 (m, 2H), 7.29-7.26 (m, 1H), 7.22-7.19 (m, 1H), 4.65 and 4.10 (2xs, 2H, NCH₂), 3.27 and 2.98 (2xs, 3H, NCH₃); ¹³C NMR (CDCl₃, 75 MHz) δ 169.6, 169.5, 140.4, 140.3, 138.7, 138.6, 135.4, 135.2, 131.8, 131.6, 128.8, 128.7, 128.7, 128.5, 128.4, 128.3, 127.9, 127.8, 122.5, 122.1, 92.7, 92.4, 85.3, 84.4, 83.0, 82.6, 41.6, 36.8, 35.6, 32.4 ppm. HRMS (EI⁺) *m*/*z* calculated for C₁₇H₁₃ClINO [M]⁺ 408.9730, found 408.9730.

General Procedure for the Synthesis of 2-Iodo-*N*-(3-arylprop-2-ynyl)-*N*-tosylbenzamides (5ca, 5cc, 5ce, 5ci, 5cj): Syntheses of substrates 5ca, 5cc, 5ce, 5ci, 5cj were achieved through condensation between benzoyl chloride and 4-methyl-*N*-(3-arylprop-2-ynyl)benzenesulfonamide (S3-7) which in turn could easily be accessed via *Sonogashira reaction* between commercially available aryl iodide and known 4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide.⁴

General Procedure for the Synthesis of 4-Methyl-N-(3-arylprop-2-ynyl)benzenesulfonamides (S3-7)

A mixture of aryl iodide (1.05 mmol), $Pd(PPh_3)_2Cl_2$ (14.7 mg, 0.021 mmol), CuI (8.0 mg, 0.042 mmol) and Et₃N (0.4 mL, 2.5 mmol) in dry DMF (3.0 mL) was stirred under argon atmosphere for few minutes. Next, a solution of 4-methyl-*N*-(prop-2-ynyl)benzenesulfonamide (209 mg, 1 mmol) in dry DMF (1.0 mL) was added slowly and the reaction mixture was allowed

⁴ Y. Hu, R. Yi, X. Yu, X. Xin, C. Wang and B. Wan, *Chem. Commun.*, 2015, **51**, 15398.

to stir at rt. After completion of reaction (TLC), the solvent was evaporated under reduced pressure and the residue was extracted with ethyl acetate (3x 20 mL). The combined organic extracts were washed with water (10 mL), dried over Na₂SO₄ and concentrated *in vacuo*. The crude residue was then purified through silica gel column chromatography using ethyl acetate-petroleum ether (v/v) as eluent to afford 4-methyl-*N*-(3-arylprop-2-ynyl)benzenesulfonamides (**S3-7**).

4-Methyl-*N***-(3-phenylprop-2-ynyl)benzenesulfonamide (S3).** Brown solid (219.4 mg, 77% yield); mp 112-113 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.27-7.20 (m, 5H), 7.13-7.10 (m, 2H), 5.02-5.01 (m, 1H), 4.06 (d, *J* = 6.0 Hz, 2H), 2.33 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 143.7, 136.8, 131.5, 129.7, 128.5, 128.1, 127.5, 122.0, 84.6, 83.2, 33.7, 21.4 ppm; HRMS (EI⁺) *m*/*z* calculated for C₁₆H₁₅NO₂S [M]⁺ 285.0823, found 285.0829.

N-[3-(4-Fluorophenyl)prop-2-ynyl]-4-methylbenzenesulfonamide (S4). Yellow solid (245.4 mg, 81% yield); mp 150-152 °C; ¹H NMR (CDCl₃, 600 MHz) δ 7.82 (d, J = 8.4 Hz, 2H), 7.27-7.26 (m, 2H), 7.12-7.09 (m, 2H), 6.94-6.91 (m, 2H), 4.99 (brs, 1H), 4.05 (d, J = 6.0 Hz, 2H), 2.35 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 162.5 (d, J = 249.0 Hz), 143.7, 136.9, 133.5 (d, J = 7.5Hz), 129.7, 127.5, 118.2 (d, J = 4.5 Hz), 115.5 (d, J = 22.5 Hz), 83.7, 83.0, 33.7, 21.5 ppm; HRMS (EI⁺) *m*/*z* calculated for C₁₆H₁₄FNO₂S [M]⁺ 303.0729, found 303.0717.

N-[3-(4-Methoxyphenyl)prop-2-ynyl]-4-methylbenzenesulfonamide (S5). Pale yellow crystalline solid (214.2 mg, 68% yield); mp 116-117 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.81 (d, J = 8.1 Hz, 2H), 7.30-7.27 (m, 2H), 7.09 (d, J = 9 Hz, 2H), 6.77 (d, J = 9 Hz, 2H), 4.64 (t, J = 5.8 Hz, 1H), 4.06 (d, J = 6 Hz, 2H), 3.80 (s, 3H), 2.38 (s, 3H) ; ¹³C NMR (CDCl₃, 75 MHz) δ 159.7, 143.7, 136.8, 133.0, 129.7, 127.5, 114.1, 113.8, 84.6, 81.8, 55.3, 33.8, 21.5 ppm; HRMS (EI⁺) m/z calculated for C₁₇H₁₇NO₃S [M]⁺ 315.0929, found 315.0922.

4-Methyl-*N*-**{3-[4-(trifluoromethyl)phenyl]prop-2-ynyl}benzenesulfonamide** (S6). Brown solid (293.0 mg, 83% yield); mp 122-123 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.30-7.23 (m, 4H), 4.64 (t, *J* = 5.7 Hz, 1H), 4.11 (d, *J* = 6.3 Hz, 2H), 2.36 (s, 3H) ; ¹³C NMR (CDCl₃, 75 MHz) δ 143.8, 136.8, 131.8, 130.2 (q, *J* = 32.5 Hz), 129.7, 127.5, 125.9, 125.1 (q, *J* = 3.9 Hz), 85.8, 83.3, 33.6, 21.4 ppm; HRMS (EI⁺) *m/z*

calculated for $C_{17}H_{14}F_3NO_2S$ [M]⁺ 353.0697, found 353.0693.

4-Methyl-*N***-[3-(pyridin-3-yl)prop-2-ynyl]benzenesulfonamide (S7).** Light-yellow solid (263.1 mg, 92% yield); mp 82-83 °C; ¹H NMR (CDCl₃, 300 MHz) δ 8.52-8.36 (m, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.29-7.19 (m, 3H), 6.03 (t, *J* = 5.8 Hz, 1 H), 4.08 (d, *J* = 6 Hz, 2 H), 2.33 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 152.0, 148.7, 143.9, 138.7, 136.9, 129.8, 129.7, 127.5, 127.3, 87.1, 81.2, 33.6, 21.5 ppm; HRMS (EI⁺) *m/z* calculated for C₁₅H₁₄N₂O₂S [M]⁺ 286.0776, found 286.0775.

General procedure for the synthesis of 2-Iodo-N-(3-arylprop-2-ynyl)-N-tosylbenzamides (5ca, 5cc, 5ce, 5ci, 5cj)

To a well-stirred solution of 2-iodobenzoyl chloride (266.0 mg, 1 mmol) in THF (3.0 mL), a solution of 4-methyl-*N*-(3-arylprop-2-ynyl)benzenesulfonamide (0.4 mmol) in THF (1.0 mL) was added dropwise over a period of 3 min. The resulting solution was cooled to 0 °C and NaH (60% oil suspension; 80 mg, 2 mmol) was added to it slowly. The reaction mixture was then allowed to reach room temperature gradually and stirred at rt until completion (TLC). After quenching with water (2.0 mL), the mixture was extracted with ethyl acetate (3x20 mL). The combined organic extracts were washed consecutively with saturated NaHCO₃ solution (20 mL) and water (10 mL) and dried over anhydrous sodium sulfate. After evaporation of solvent, the residue was purified by silica gel column chromatography using 5-10% ethyl acetate-petroleum ether (v/v) as eluent to afford the product **5ca/5cc/5ce/5ci/5cj**.

2-Iodo-*N***-(3-phenylprop-2-ynyl)**-*N***-tosylbenzamide (5ca).** White solid (156.6 mg, 76% yield); mp 127-129 °C; ¹H NMR (CDCl₃, 600 MHz) δ 7.96 (d, *J* = 9 Hz, 2H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.39-7.35 (m, 4H), 7.35-7.32 (m, 2H), 7.28-7.26 (m, 3H), 7.14 (td, *J*₁= 7.6 Hz, *J*₂= 1.6 Hz, 1H), 4.78 (brs, 2H), 2.42 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 169.0, 145.3, 140.1, 139.3, 135.4, 131.7, 131.3, 129.3, 129.3, 128.8, 128.4, 128.0, 127.8, 122.1, 92.1, 84.8, 83.5, 38.0, 21.8 ppm; HRMS (EI⁺) *m*/*z* calculated for C₂₃H₁₈INO₃S [M]⁺ 515.0052, found 515.0036.

N-(3-(4-Fluorophenyl)prop-2-ynyl)-2-iodo-*N*-tosylbenzamide (5cc). White solid (145.0 mg, 68% yield); mp 138-140 °C; ¹H NMR (CDCl₃, 600 MHz) δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.35-7.32 (m, 2H), 7.27-7.26 (m, 3H), 7.15-7.12 (m, 1H), 7.02 (t, *J* = 8.7 Hz, 2H), 4.76 (brs, 2H), 2.42 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 169.0, 162.7 (d, *J* = 248.7 Hz), 145.3, 140.1, 139.3, 135.4, 133.7 (d, *J* = 8.7 Hz), 131.4, 129.3, 129.2, 128.0, 127.8, 118.2 (d, *J* = 3.3 Hz), 115.7 (d, *J* = 21.7 Hz), 92.2, 83.7, 83.3, 37.9, 21.8 ppm; HRMS (EI⁺) *m*/*z* calculated for C₂₃H₁₇FINO₃S [M]⁺ 532.9958, found 532.9961.

2-Iodo-*N***-**[**3**-(**4-methoxyphenyl**)**prop-2-ynyl**]-*N***-tosylbenzamide** (**5ce**). Light-yellow solid (130.8 mg, 60% yield); mp 152-154 °C; ¹H NMR (CDCl₃, 600 MHz) δ 8.05 (d, *J* = 7.8 Hz, 1H), 8.00-7.96 (m, 3H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.30-7.26 (m, 1H), 7.20 (t, *J* = 7.2 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 2H), 4.74 (brs, 2H), 3.83 (s, 3H), 2.42 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 169.1, 159.9, 145.2, 141.9, 140.1, 139.3, 135.4, 133.2, 131.9, 131.3, 129.3, 128.0, 127.7, 114.0, 92.1, 84.8, 82.2, 55.3, 38.1, 21.7 ppm; HRMS (ESI⁺) *m/z* calculated for C₂₄H₂₁INO₄S [M+H]⁺ 546.0236, found 546.0238.

2-Iodo-*N***-tosyl-***N***-{3-[4-(trifluoromethyl)phenyl]prop-2-ynyl}***-N***-tosylbenzamide (5ci).** White solid (116.6 mg, 50% yield); mp 160-162 °C; ¹H NMR (CDCl₃, 600 MHz) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.80-7.78 (m, 1H), 7.58 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.39 (td, *J*₁ = 7.5 Hz, *J*₂ = 0.6 Hz, 1H), 7.28-7.26 (m, 3H), 7.14 (td, *J*₁ = 7.6 Hz, *J*₂ = 1.6 Hz, 1H), 4.81 (brs, 2H), 2.43(s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 168.9, 145.5, 140.0, 139.4, 135.3, 132.0, 131.4, 130.5 (q, *J* = 32.5 Hz), 129.4, 129.2, 128.0, 127.8, 125.9, 125.3 (q, *J* = 3.5 Hz), 123.8 (q, *J* = 271 Hz), 92.2, 86.0, 83.3, 37.7, 21.8 ppm; HRMS (ESI⁺) *m*/*z* calculated for C₂₄H₁₇F₃INO₃SNa [M+Na]⁺ 605.9824, found 605.9822.

2-Iodo-*N***-[3-(pyridin-3-yl)prop-2-ynyl]***-N***-tosylbenzamide (5cj).** White solid (156.9 mg, 76% yield); mp 100-102 °C; ¹H NMR (CDCl₃, 600 MHz) δ 8.57-8.56 (m, 2H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.28-7.24 (m, 4H), 7.12 (td, *J*₁= 7.5 Hz, *J*₂ = 1.2 Hz, 1H), 4.80 (brs, 2H), 2.40 (s, 3H); ¹³C NMR (CDCl₃, 150 MHz) δ 168.9, 152.0, 148.8, 145.6, 139.9, 139.4, 139.0, 135.2, 131.5, 129.4, 129.2, 128.0, 127.8,

123.3, 92.3, 87.2, 81.2, 37.7, 21.7 ppm; HRMS (EI⁺) m/z calculated for C₂₂H₁₇IN₂O₃S [M]⁺ 516.0005, found 516.0017.

Reduction of 4-[bis(phenyl)methylidene]-N-tosyl-3,4-dihydroisoquinolin-1(2H)-one (7r)using LiAlH₄ (see Table S3).

To a well-stirred and ice-cooled solution of **7r** (46.5 mg, 0.1 mmol) in dry THF (4 mL) under argon atmosphere lithium aluminium hydride (76 mg, 2 mmol) was added and the reaction mixture was allowed to stir at rt followed by heating under reflux. After completion of the reaction (TLC) (2 h), the solvent was evaporated *in vacuo* and LiAlH₄ was quenched using standard procedure. After usual workup, combined organic extracts (diethyl ether) were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The crude product was purified through silica gel column chromatography using ethyl acetate-petroleum ether (v/v) as eluent to afford pure product **S15** which was unanticipated.

However, the synthesis of desired product **11a** was achieved by the reduction of 7r using BH₃.Me₂S that has been described in the manuscript under experimental section.

4-(Diphenylmethylene)-3,4-dihydroisoquinolin-1(*2H*)**-one (S15).** White gum (15.6 mg, 50% yield); ¹H NMR (CDCl₃, 300 MHz) δ 8.06 (d, *J* = 7.5 Hz, 1H), 7.39-7.37 (m, 4H), 7.24-7.07 (m, 8H), 6.86-6.84 (m, 1H), 6.19 (brs, 1H), 4.25 (d, *J* = 2.4 Hz, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 165.7, 142.5, 141.5, 141.4, 137.8, 131.0, 130.9, 130.0, 129.2, 129.1, 128.3, 128.0, 127.7, 127.6, 126.5, 45.5 ppm; HRMS (EI⁺) *m*/*z* calculated for C₂₂H₁₇NO [M]⁺ 311.1310, found 311.1281.

¹H NMR (CDCl₃, 300 MHz) spectrum of **5ah**:



 ^{13}C NMR (CDCl₃, 75 MHz) spectrum of compound **5ah**:



S19



¹H NMR (CDCl₃, 300 MHz) spectrum of **S1**:

¹H NMR (CDCl₃, 300 MHz) spectrum of **5aa**:

¹³C NMR (CDCl₃, 75 MHz) spectrum of **5aa**:

¹H NMR (CDCl₃, 300 MHz) spectrum of **5ab**:

S23

¹H NMR (CDCl₃, 300 MHz) spectrum of **5ad**:

¹³C NMR (CDCl₃, 75 MHz) spectrum of compound 2-iodo-N-methyl-N-(3-p-tolylprop-2ynyl)benzamide (5ad):

¹H NMR (CDCl₃, 300 MHz) spectrum of **5ae**:

¹H NMR (CDCl₃, 300 MHz) spectrum of **5af**:

-7.412 -7.279 -7.265 -7.247 -7.236 -7.236 -7.236 -7.238 -4.663-4.118 7.850 -6.976 -6.964 -2.955 -1.582-7.874 --7.850 --7.825 7.436 7.431 7.431 7.530 7.531 7.5351 7.55517 7.55517 7.55517 7.55517 7.55517 7.555517 7.55517 Me 5ag 0.98 1.00 1.34 0.74 3.56 1.19 0.97 1.38 1.39 2.06 7.5 7 Ц Ц Ц Ц Ц 8.0 3.0 0 0.5 6.5 7.0 2.5 4.5 4.0 Chemical Shift (ppm) 6.0 5.5 3.5 2.0 1.5 1.0 5.0

¹H NMR (CDCl₃, 300 MHz) spectrum of **5ag**:

¹³C NMR (CDCl₃, 75 MHz) spectrum of compound **5ag**:

¹H NMR (CDCl₃, 300 MHz) spectrum of **5ba**:

¹³C NMR (CDCl₃, 75 MHz) spectrum of compound **5ba**:

1 H NMR (CDCl₃, 300 MHz) spectrum of **S3**:

^{13}C NMR (CDCl₃, 75 MHz) spectrum of compound **S3**:

 1 H NMR (CDCl₃, 600 MHz) spectrum of S4:

 ^{13}C NMR (CDCl₃, 150 MHz) spectrum of compound S4:

 1 H NMR (CDCl₃, 300 MHz) spectrum of **S5**:

 ^{13}C NMR (CDCl_3, 75 MHz) spectrum of compound S5:

1 H NMR (CDCl₃, 300 MHz) spectrum of **S6**:

¹H NMR (CDCl₃, 600 MHz) spectrum of **5ca**:

¹³C NMR (CDCl₃, 150 MHz) spectrum of compound **5ca**:

¹H NMR (CDCl₃, 600 MHz) spectrum of **5cc**:

¹³C NMR (CDCl₃, 150 MHz) spectrum of compound **5cc**:

¹H NMR (CDCl₃, 600 MHz) spectrum of **5ce**:

¹H NMR (CDCl₃, 600 MHz) spectrum of **5ci**:





¹³C NMR (CDCl₃, 150 MHz) spectrum of compound **5cj**:





¹H NMR (CDCl₃, 300 MHz) spectrum of **7b**:





¹H NMR (CDCl₃, 300 MHz) spectrum of **7d**:



¹³C NMR (CDCl₃, 75 MHz) spectrum of compound **7d**:



¹H NMR (CDCl₃, 300 MHz) spectrum of **7e**:







HRMS (ESI⁺) spectrum of compound **7f**:

¹H NMR (CDCl₃, 300 MHz) spectrum of **7g**:





¹H NMR (CDCl₃, 300 MHz) spectrum of **7i**:



¹³C NMR (CDCl₃, 75 MHz) spectrum of compound **7i**:



¹H NMR (CDCl₃, 600 MHz) spectrum of **7j**:





HRMS (ESI⁺) spectrum of compound 7j:

¹H NMR (CDCl₃, 600 MHz) spectrum of **7k**:



S51



HRMS (ESI⁺) spectrum of compound **7k**:

¹H NMR (CDCl₃, 300 MHz) spectrum of **71**:





¹H NMR (CDCl₃, 300 MHz) spectrum of **7m**:

¹H NMR (CDCl₃, 600 MHz) spectrum of **7n**:



¹H NMR (CDCl₃, 300 MHz) spectrum of **70**:





¹³C NMR (CDCl₃, 75 MHz) spectrum of compound **7p**:



¹H NMR (CDCl₃, 300 MHz) spectrum of **7q**:



¹H NMR (CDCl₃, 300 MHz) spectrum of **7r**:



¹H NMR (CDCl₃, 300 MHz) spectrum of **7s**:



S60

¹H NMR (CDCl₃, 600 MHz) spectrum of **7t**:



¹H NMR (CDCl₃, 300 MHz) spectrum of **7u**:



 ^{13}C NMR (CDCl₃, 75 MHz) spectrum of compound **7u**:



¹H NMR (CDCl₃, 600 MHz) spectrum of **7v**:



¹H NMR (CDCl₃, 600 MHz) spectrum of **7w**:







¹H NMR (CDCl₃, 600 MHz) spectrum of **7**y:



¹H NMR (CDCl₃, 600 MHz) spectrum of **7z**:





¹H NMR (CDCl₃, 300 MHz) spectrum of **7z''**:





¹H NMR (CDCl₃, 600 MHz) spectrum of **8a**:





¹H NMR (CDCl₃, 300 MHz) spectrum of **8b**:



¹³C NMR (CDCl₃, 75 MHz) spectrum 8b:



¹H NMR (CDCl₃, 300 MHz) spectrum of **8c**:



¹³C NMR (CDCl₃, 75 MHz) spectrum of **8c**:


1 H NMR (CDCl₃, 600 MHz) spectrum of **8d**:







¹H NMR (CDCl₃, 300 MHz) spectrum of 8g:





¹H NMR (CDCl₃, 600 MHz) spectrum of **9a**:



¹H NMR (CDCl₃, 600 MHz) spectrum of **9b**:



¹³C NMR (CDCl₃, 150 MHz) spectrum of **9b**:





¹H NMR (CDCl₃, 600 MHz) spectrum of **10aa**:



¹H NMR (CDCl₃, 600 MHz) spectrum of **10ab**:



 ^{13}C NMR (CDCl₃, 150 MHz) spectrum of **10ab**:





 1 H NMR (CDCl₃, 600 MHz) spectrum of **10ad**:



¹³C NMR (CDCl₃, 150 MHz) spectrum of **10ad**:



 1 H NMR (CDCl₃, 600 MHz) spectrum of **10ae**:



¹H NMR (CDCl₃, 600 MHz) spectrum of **10ba**:



¹³C NMR (CDCl₃, 150 MHz) spectrum of **10ba**:





1 H NMR (CDCl₃, 600 MHz) spectrum of **10bb**:

¹³C NMR (CDCl₃, 150 MHz) spectrum of **10bb**:



¹H NMR (CDCl₃, 600 MHz) spectrum of **10bc**:



S88

Chemical Shift (ppm)

Т

Т

¹H NMR (CDCl₃, 600 MHz) spectrum of **10bd**:



¹H NMR (CDCl₃, 600 MHz) spectrum of **10be**:



¹H NMR (CDCl₃, 600 MHz) spectrum of **11a**:



¹H NMR (CDCl₃, 600 MHz) spectrum of **11b**:



¹H NMR (CDCl₃, 600 MHz) spectrum of **11c**:



¹H NMR (CDCl₃, 600 MHz) spectrum of **11d**:



¹H NMR (CDCl₃, 600 MHz) spectrum of **11e**:



¹H NMR (CDCl₃, 600 MHz) spectrum of **12**:



ppm ¹H NMR (CDCl₃, 300 MHz) spectrum of **13**:



¹³C NMR (CDCl₃, 75 MHz) spectrum of **13**:





¹H NMR (CDCl₃, 300 MHz) spectrum of **S15**:

