

Supporting Information

Co(III)-catalyzed Z-selective oxidative C–H/C–H cross-coupling of alkenes with triisopropylsilylacetylene

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I. General remarks

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Substituted acrylamides **1**, **5** were prepared according to the reported literatures.¹ THF, DCE, DMF, 1,4-dioxane and toluene were dried using solvent purification system, while other solvents were dried according to known methods and distilled prior to use.²

NMR spectra were obtained on an Agilent 400-MR DD2 spectrometer. The ¹H NMR (400 MHz) chemical shifts were measured relative to CDCl₃ as the internal reference (CDCl₃: δ = 7.26 ppm). The ¹³C NMR (100 MHz) chemical shifts were given using CDCl₃ as the internal standard (CDCl₃: δ = 77.16 ppm). High resolution mass spectra (HR-MS) were obtained with a Shimadzu LCMS-IT-TOF (ESI). X-Ray single-crystal diffraction data were collected on an Oxford Xcalibur E single crystal diffractometer.

II. General procedure for the synthesis of acrylamides

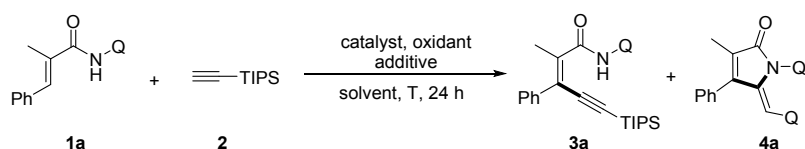
The synthesis of **1a** is representative: An oven-dried 100 mL round-bottom flask was charged with (*E*)-2-methyl-3-phenylacrylic acid (810.0 mg, 5 mmol) and DCM (20 mL) under N₂ atmosphere, the mixture was cooled to 0 °C, and then oxalyl chloride (0.6 mL, 7mmol) was added dropwise, then DMF (2 drops) was added. The mixture was stirred at room temperature for 3 h and then the solvent was evaporated to obtain the crude acid chloride, then without further purification the crude acid chloride dissolved in DCM (10 mL), then added dropwise to a solution of 8-aminoquinoline (748.8 mg, 5.2 mmol) and Et₃N (2 mL, 15 mmol) in DCM (20 mL) at 0 °C under N₂ atmosphere. The resulting mixture was stirred at room temperature overnight. Then water was added, and extracted with DCM three times, then dried over Na₂SO₄. After removal of the solvent under reduced pressure, the residue was purified by column

chromatography on silica gel (petroleum ether/ DCM = 3/1, v/v) to give the desired product as a white solid (1051.6 mg, 73% yield).

III. Optimization of the reaction conditions

An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with (*E*)-2-methyl-3-phenyl-*N*-(quinolin-8-yl)acrylamide **1a** (28.8 mg, 0.1 mmol, 1.0 equiv), catalyst, oxidant, additive. The Schlenk tube was evacuated and filled with a nitrogen gas three times, then ethynyltriisopropylsilane **2**, solvent (1.0 mL) were added under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 min, and then heated at the indicated temperature for 24 hours. The reaction mixture was cooled to ambient temperature, diluted with 5 mL of DCM, filtered through a celite pad, and washed with 20 mL of DCM. The combined filtrate was concentrated, and the resulting residue was purified by column chromatography on silica gel using petroleum ether/THF (v/v = 20/1) as eluent to provide the desired product **3a**.

Table S1. Optimization of the reaction conditions.^{a,b}



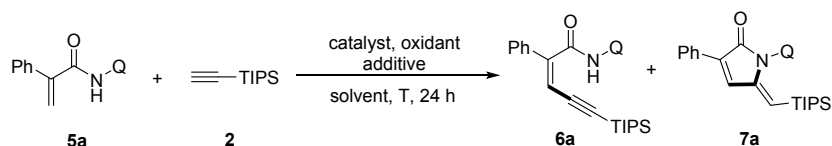
Entry	Catalyst	Oxidant	Additive	Solvent	Yield of 3a	Yield of 4a
1	Fe(OAc) ₂	Ag ₂ CO ₃	KOAc	THF	n.d	n.d
2	Co(OAc) ₂	Ag ₂ CO ₃	KOAc	THF	7%	n.d
3	Ni(OAc) ₂	Ag ₂ CO ₃	KOAc	THF	trace	n.d
4	Cu(OAc) ₂	Ag ₂ CO ₃	KOAc	THF	9%	n.d
5	Co(acac) ₂	Ag ₂ CO ₃	KOAc	THF	35%	5%
6	Co(acac) ₃	Ag ₂ CO ₃	KOAc	THF	39%	n.d
7	CoBr ₂	Ag ₂ CO ₃	KOAc	THF	17%	trace
8	CoCl ₂	Ag ₂ CO ₃	KOAc	THF	trace	n.d
9	Co ₂ (CO) ₈	Ag ₂ CO ₃	KOAc	THF	trace	n.d
10	Co ₂ O ₃	Ag ₂ CO ₃	KOAc	THF	n.d	n.d
11	Co(acac) ₃	Ag ₂ CO ₃	KOAc	DCE	27%	9%
12	Co(acac) ₃	Ag ₂ CO ₃	KOAc	DMF	n.d	n.d
13	Co(acac) ₃	Ag ₂ CO ₃	KOAc	toluene	23%	n.d

14	Co(acac) ₃	Ag ₂ CO ₃	KOAc	dioxane	9%	n.d
15	Co(acac) ₃	Ag ₂ CO ₃	KOAc	NMP	n.d	n.d
16	Co(acac) ₃	Ag ₂ CO ₃	KOAc	DMSO	n.d	n.d
17	Co(acac) ₃	Ag ₂ CO ₃	KOAc	<i>t</i> -BuOH	n.d	n.d
18	Co(acac) ₃	Ag ₂ CO ₃	HOAc	THF	trace	n.d
19	Co(acac) ₃	Ag ₂ CO ₃	Zn(OAc) ₂	THF	29%	n.d
20	Co(acac) ₃	Ag ₂ CO ₃	Mn(OAc) ₃	THF	56%	n.d
21	Co(acac)₃	Ag₂CO₃	Mn(OAc)₂	THF	73%	n.d
22	Co(acac) ₃	Ag ₂ CO ₃	MnCl ₂	THF	trace	n.d
23	Co(acac) ₃	Ag ₂ CO ₃	MnSO ₄	THF	43%	n.d
24	Co(acac) ₃	Ag ₂ CO ₃	--	THF	27%	n.d
25	--	Ag ₂ CO ₃	Mn(OAc) ₂	THF	n.d	n.d
26	Co(acac) ₃	--	Mn(OAc) ₂	THF	n.d	n.d
27 ^b	Co(acac) ₃	Ag ₂ CO ₃	Mn(OAc) ₂	THF	54%	n.d
28 ^c	Co(acac) ₃	Ag ₂ CO ₃	Mn(OAc) ₂	THF	67%	n.d
29 ^d	Co(acac) ₃	Ag ₂ CO ₃	Mn(OAc) ₂	THF	61%	n.d
30	Co(acac) ₃	Ag ₂ O	Mn(OAc) ₂	THF	29%	n.d
31	Co(acac) ₃	Ag ₂ SO ₄	Mn(OAc) ₂	THF	trace	n.d
32	Co(acac) ₃	AgOAc	Mn(OAc) ₂	THF	trace	n.d
33	Co(acac) ₃	AgOPiv	Mn(OAc) ₂	THF	24%	n.d
34	Co(acac) ₃	AgF	Mn(OAc) ₂	THF	n.d	n.d
35	Co(acac) ₃	AgBF ₄	Mn(OAc) ₂	THF	n.d	n.d
36	Co(acac) ₃	AgNO ₃	Mn(OAc) ₂	THF	n.d	n.d
37 ^e	Co(acac) ₃	Ag ₂ CO ₃	Mn(OAc) ₂	THF	59%	n.d
38 ^f	Co(acac) ₃	Ag ₂ CO ₃	Mn(OAc) ₂	THF	45%	n.d
39 ^g	Co(acac) ₃	Ag ₂ CO ₃	Mn(OAc) ₂	THF	46%	n.d
40 ^h	Co(acac) ₃	Ag ₂ CO ₃	Mn(OAc) ₂	THF	39%	n.d
41 ⁱ	Co(acac) ₃	Ag ₂ CO ₃ /O ₂	Mn(OAc) ₂	THF	38%	n.d
42	Co(acac) ₃	BQ	Mn(OAc) ₂	THF	n.d	n.d
43	Co(acac) ₃	DDQ	Mn(OAc) ₂	THF	n.d	n.d
44	Co(acac) ₃	PhI(OAc) ₂	Mn(OAc) ₂	THF	n.d	n.d
45	Co(acac) ₃	DTBP	Mn(OAc) ₂	THF	n.d	n.d
46	Co(acac) ₃	TBHP	Mn(OAc) ₂	THF	n.d	n.d
47	Co(acac) ₃	K ₂ S ₂ O ₈	Mn(OAc) ₂	THF	n.d	n.d
48	Co(acac) ₃	Mn(OAc) ₃ ·2H ₂ O	Mn(OAc) ₂	THF	n.d	n.d
49	Co(acac) ₃	NaClO ₃	Mn(OAc) ₂	THF	n.d	n.d
50	Co(acac) ₃	oxone	Mn(OAc) ₂	THF	n.d	n.d
51	Co(acac) ₃	Cu(OAc) ₂	Mn(OAc) ₂	THF	11%	n.d
52	Co(acac) ₃	CuOAc	Mn(OAc) ₂	THF	n.d	n.d
53	Co(acac) ₃	CuBr	Mn(OAc) ₂	THF	n.d	n.d
54	Co(acac) ₃	CuCl	Mn(OAc) ₂	THF	n.d	n.d
55	Co(acac) ₃	CuI	Mn(OAc) ₂	THF	n.d	n.d
56	Co(acac) ₃	Cu ₂ O	Mn(OAc) ₂	THF	n.d	n.d
57	Co(acac) ₃	O ₂	Mn(OAc) ₂	THF	n.d	n.d
58	Co(acac) ₃	Ag ₂ CO ₃	Mn(OAc) ₂	toluene	51%	n.d
59	Co(acac) ₃	Ag ₂ CO ₃	Mn(OAc) ₂	DME	n.d	n.d
60	Co(acac) ₃	Ag ₂ CO ₃	Mn(OAc) ₂	(<i>n</i> -Bu) ₂ O	46%	n.d
61	Co(acac) ₃	Ag ₂ CO ₃	Mn(OAc) ₂	dioxane	64%	n.d
62	Co(OAc) ₂	Ag ₂ CO ₃	Mn(OAc) ₂	THF	28%	n.d
63	Ni(OAc) ₂	Ag ₂ CO ₃	Mn(OAc) ₂	THF	17%	n.d

64	Cu(OAc) ₂	Ag ₂ CO ₃	Mn(OAc) ₂	THF	20%	n.d
65	Fe(OAc) ₂	Ag ₂ CO ₃	Mn(OAc) ₂	THF	n.d	n.d

^aReaction conditions: catalyst (0.01 mmol, 10 mol %), oxidant (0.2 mmol, 2.0 equiv), **1a** (28.8 mg, 0.1 mmol, 1.0 equiv), **2** (35 μ L, 0.15 mmol, 1.5 equiv), additive (0.1 mmol, 1.0 equiv), and solvent (1 mL) at 120 °C for 24 h under N₂ atmosphere. ^b100 °C. ^c140 °C. ^d**2** (0.12 mmol, 1.2 equiv). ^eAg₂CO₃ (1.5 equiv). ^fAg₂CO₃ (1.0 equiv). ^gAg₂CO₃ (1.5 equiv), 130 °C. ^hAg₂CO₃ (1.5 equiv), 140 °C. ⁱAg₂CO₃ (1.0 equiv), O₂. n.d = not detected.

Table S2. Optimization of the reaction conditions for terminal acrylamides.^{a,b}

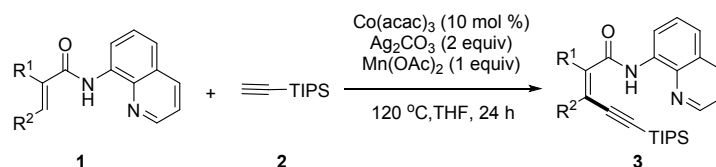


Entry	Co(acac) ₃	Additive	T (°C)	Yield of 6a	Yield of 7a	5a
1	10%	--	120 °C	20%	13%	0%
2	10%	KOAc (1 equiv)	120 °C	16%	24%	0%
3	10%	PivOH (1 equiv)	120 °C	25%	<10%	0%
4	10%	--	80 °C	20%	20%	55%
5	20%	--	80 °C	30%	37%	30%
6	30%	--	80 °C	40%	46%	0%
7	30%	PivOH (1 equiv)	80 °C	56%	32%	0%
8	30%	PivOH (2 equiv)	80 °C	70%	27%	0%
9	30%	PivOH (3 equiv)	80 °C	68%	24%	0%

^aReaction conditions: Co(acac)₃, Ag₂CO₃ (0.2 mmol, 2.0 equiv), Mn(OAc)₂ (0.1 mmol, 1.0 equiv), terminal acrylamides **5a** (0.1 mmol, 1.0 equiv), **2** (35 μ L, 0.15 mmol, 1.5 equiv), and THF (1 mL) for 24 h under a N₂ atmosphere. ^bIsolated yield.

IV. General procedure for the cross-coupling of acrylamides with triisopropylsilylacetylene

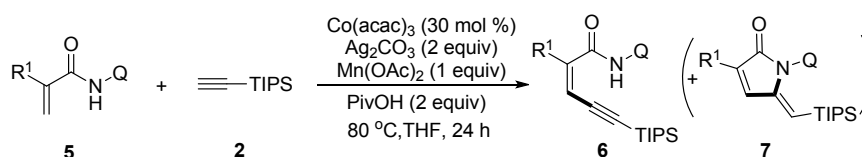
Internal acrylamides:



An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with Co(acac)₃ (3.6 mg, 0.01 mmol, 10 mol %), Ag₂CO₃ (55.2 mg, 0.2 mmol, 2.0 equiv), Mn(OAc)₂ (17.3 mg, 0.1 mmol, 1.0 equiv), internal acrylamides **1** (0.1 mmol, 1.0 equiv).

The Schlenk tube was evacuated and filled with a nitrogen gas three times. Then, ethynyltriisopropylsilane **2** (35 μ L, 0.15 mmol, 1.5 equiv), and THF (1 mL) were added under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 min, and then heated at 120 $^{\circ}$ C for 24 hours. Then the reaction mixture was cooled to ambient temperature, diluted with 5 mL of DCM, filtered through a celite pad, and washed with 20 mL of DCM. The combined filtrate was concentrated, and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

Terminal acrylamides:



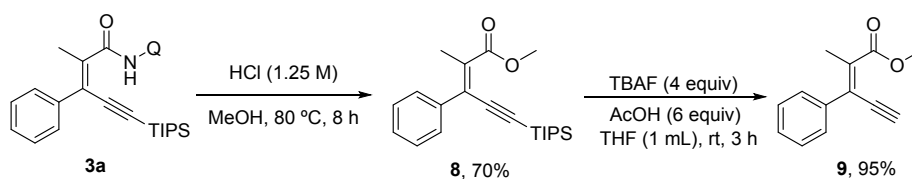
An oven-dried Schlenk tube equipped with a magnetic stir bar was charged with $\text{Co}(\text{acac})_3$ (10.8 mg, 0.03 mmol, 30 mol %), Ag_2CO_3 (55.2 mg, 0.2 mmol, 2.0 equiv), $\text{Mn}(\text{OAc})_2$ (17.3 mg, 0.1 mmol, 1.0 equiv), PivOH (20.4 mg, 0.2 mmol, 2.0 equiv) terminal acrylamides **5** (0.1 mmol, 1.0 equiv). The Schlenk tube was evacuated and filled with a nitrogen gas three times. Then, ethynyltriisopropylsilane **2** (35 μ L, 0.15 mmol, 1.5 equiv), and THF (1 mL) were added under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 min, and then heated at 80 $^{\circ}$ C for 24 hours. Then the reaction mixture was cooled to ambient temperature, diluted with 5 mL of DCM, filtered through a celite pad, and washed with 20 mL of DCM. The combined filtrate was concentrated, and the resulting residue was purified by column chromatography on silica gel to provide the desired product **6** and **7**.

V. Procedure for the recycle of silver carbonate³

After a standard reaction (0.1 mmol scale), the reaction mixture was cooled down to ambient temperature and diluted with 5 mL of DCM. A combination of 11 reaction mixtures was filtered through a celite pad. The residue was washed with DCM (50 mL) and H₂O (50 mL), and then dissolved in 30 mL of HNO₃ (20%, v/v in distilled water). After being stirred for 12 h, the mixture was filtered and the water phase was evaporated under vacuum to give a black solid. The solid was washed with ethanol and a small amount of acetone to remove the manganese salt. The crude AgNO₃ was redissolved in distilled water, and an 10% aqueous solution of Na₂CO₃ was added. The mixture was stirred for 2 hours to let Ag₂CO₃ precipitate out. After filtration, the solid was washed with distilled water (3 × 10 mL) to afford Ag₂CO₃ as a light brown solid (539.9 mg, 89% yield).

The cross-coupling reaction of **1a** with **2** under the optimal conditions by using the regenerated Ag₂CO₃ gave the desired enyne **3a** in 61% yield.

VI. Removal of the directing and protecting groups⁴

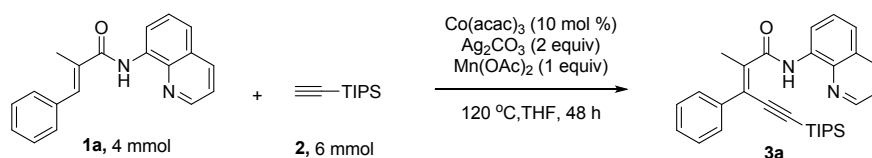


An oven-dried Schlenk tube with a magnetic stir bar was charged with **3a** (93.7 mg, 0.2 mmol) and 1.25 M HCl in MeOH (3 mL) were added, and then heated at 80 °C for 8 h. After being cooled to room temperature, Et₃N (1 mL) was added, then concentrated, and the resulting residue was purified via column chromatography on silica gel (petroleum ether/THF = 50/1, v/v) to provide the desired product **8** (49.9 mg,

70%).

Under a N₂ atmosphere, **8** (35.6 mg, 0.1 mmol, 1 equiv) dissolved in THF (1 mL) was added to a dry Schlenk tube, TBAF (52.3 mg, 0.2 mmol, 4 equiv) and acetic acid (18.0 mg, 0.3 mmol, 6 equiv) were added successively. The reaction mixture was stirred at room temperature for 3 h (checked by TLC). Then quenched with saturated NaHCO₃, extracted with DCM, the organic layer was removed by rotary evaporation, and the resulting residue was purified via column chromatography on silica gel (petroleum ether/THF = 50/1, v/v) to provide the desired product **9** (19.0 mg, 95%).

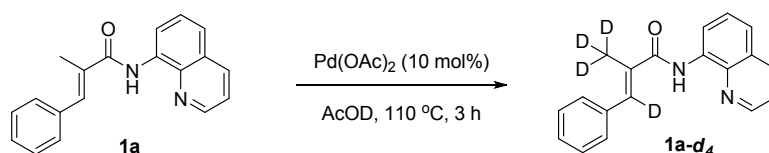
VII. Synthesis of **3a** on a 4 mmol scale



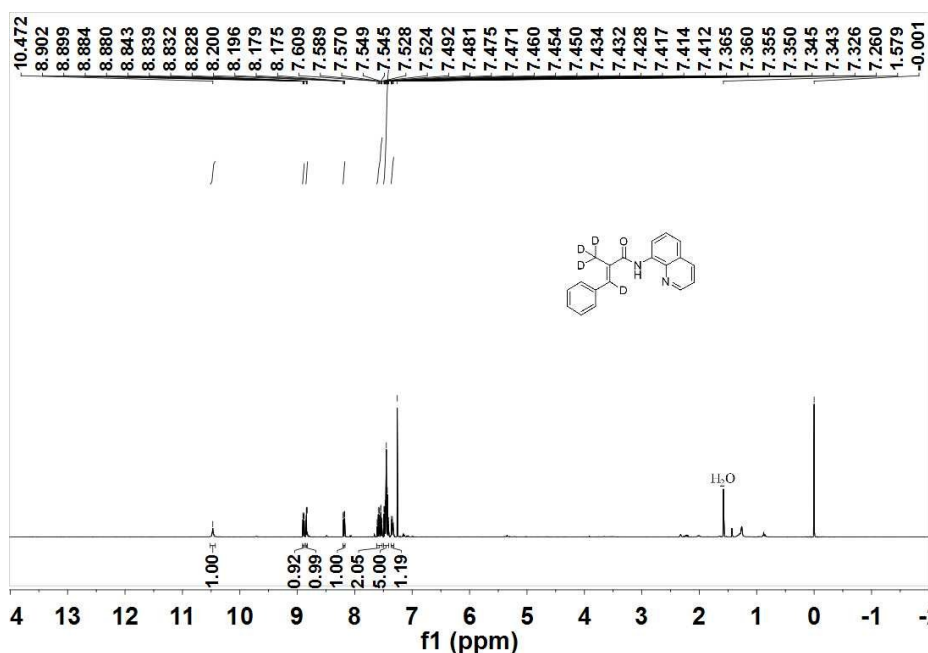
A 100 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with Co(acac)₃ (142.5 mg, 0.4 mmol, 10 mol %), Ag₂CO₃ (2206.0 mg, 8 mmol, 2.0 equiv), Mn(OAc)₂ (692.4 mg, 4 mmol, 1.0 equiv), acrylamides **1a** (1152.5 mg, 4 mmol, 1.0 equiv). The Schlenk tube was evacuated and filled with a nitrogen gas three times. Then, ethynyltriisopropylsilane **2** (1094.3 mg, 6 mmol, 1.5 equiv), and THF (5 mL) were added under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 min, and then heated at 120 °C for 48 hours. Then the reaction mixture was cooled to ambient temperature, diluted with 50 mL of DCM, filtered through a celite pad, and washed with 100 mL of DCM. The combined filtrate was concentrated, and the resulting residue was purified via column chromatography on silica gel (petroleum ether/THF = 20/1, v/v) providing the corresponding product **3a** (1273.6 mg, 68% yield).

VIII. Mechanistic study

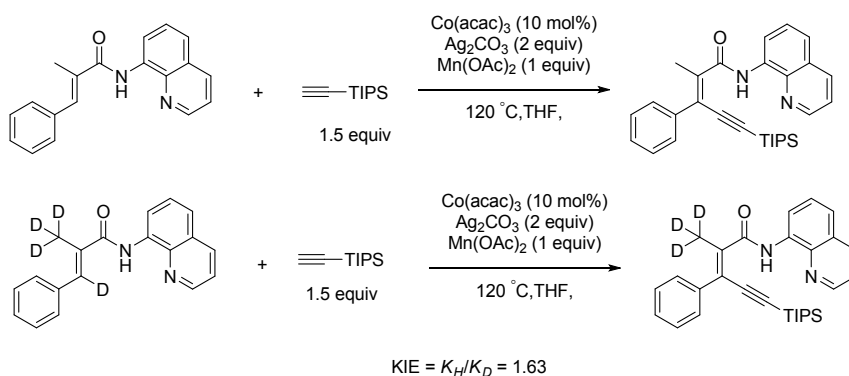
(i). Preparation of deuterated substrates¹



An oven-dried Schlenk tube with a magnetic stir bar was charged with (*E*)-2-methyl-3-phenyl-*N*-(quinolin-8-yl)acrylamide **1a** (288.1 mg, 1 mmol), Pd(OAc)₂ (22.4 mg, 0.1 mmol). The Schlenk tube was evacuated and filled with a nitrogen gas three times. Then, AcOD (1 mL) were added under a nitrogen atmosphere and the reaction mixture was allowed to stir at 110 °C for 3 h. After the mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The residue was purified by flash column chromatography on silica gel (petroleum ether/THF = 20/1, v/v). This sequence was repeated one more time to give the deuterium labeled product **1a-d₄** as a white solid (201.6 mg, 69%).



(ii). Kinetic Isotope Studies(parallel experiments)^{1b,4,5}



An oven-dried Schlenk tube with a magnetic stir bar was charged with $\text{Co}(\text{acac})_3$ (3.6 mg, 0.01 mmol, 10 mol %), Ag_2CO_3 (55.2 mg, 0.2 mmol, 2.0 equiv), $\text{Mn}(\text{OAc})_2$ (17.3 mg, 0.1 mmol, 1.0 equiv), **1a** or **1a-d₄** (0.1 mmol, 1.0 equiv). The Schlenk tube was evacuated and filled with a nitrogen gas three times. Then, ethynyltriisopropylsilane **2** (35 μL , 0.15 mmol, 1.5 equiv) and THF (1 mL) were added under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 min, and then heated at 120 °C for 0.5 h, 1 h, 1.5 h, 2 h. After the mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The crude residue was subjected to the ^1H NMR analysis, using CH_2Br_2 (7 μL , 0.1 mmol) as internal standard.

A KIE value of 1.63 was obtained.

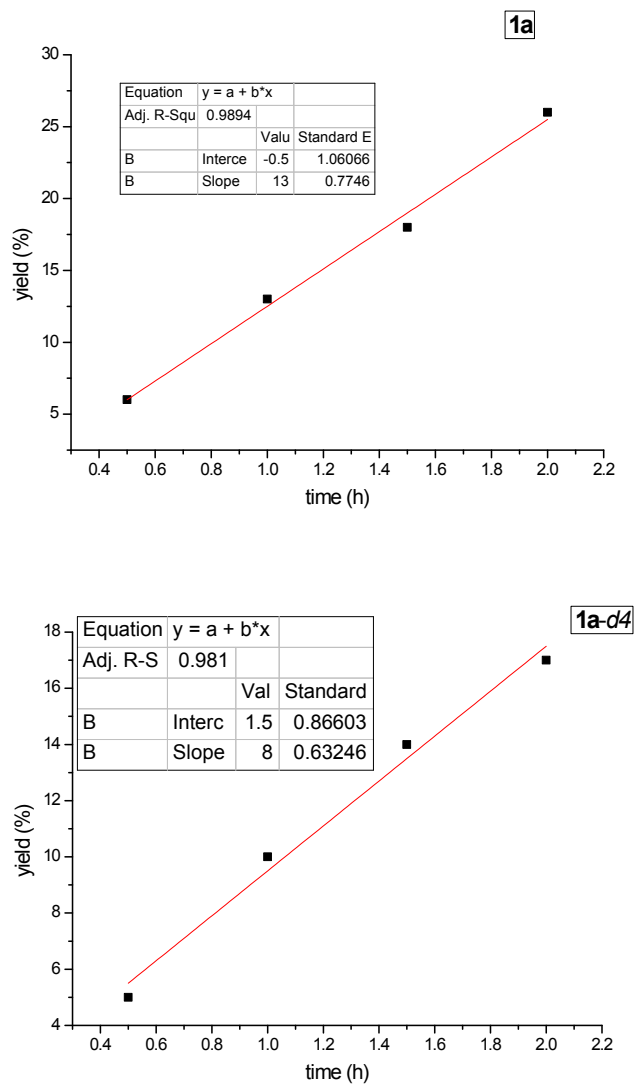
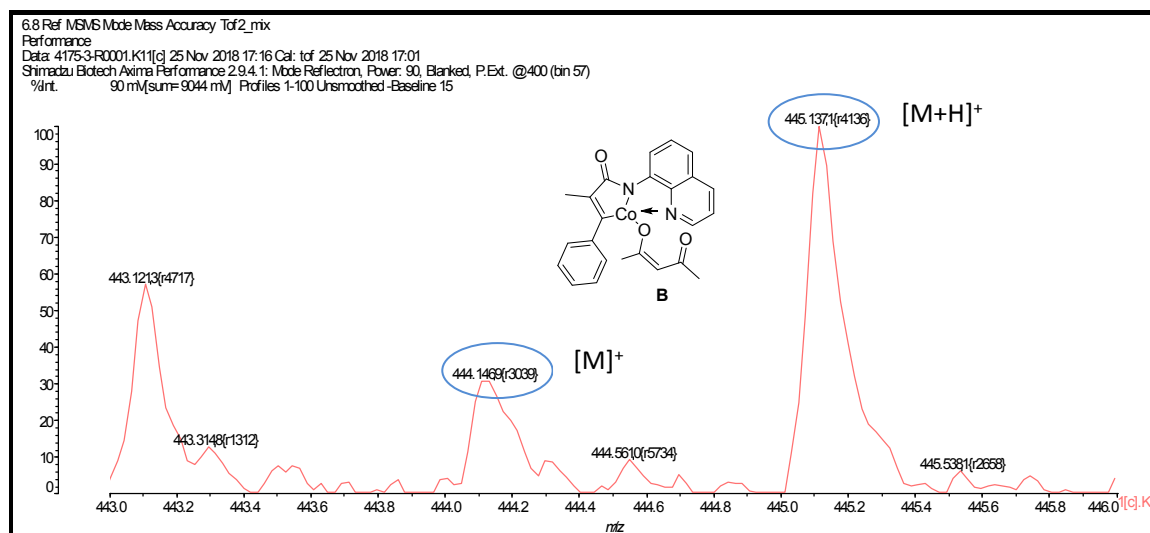
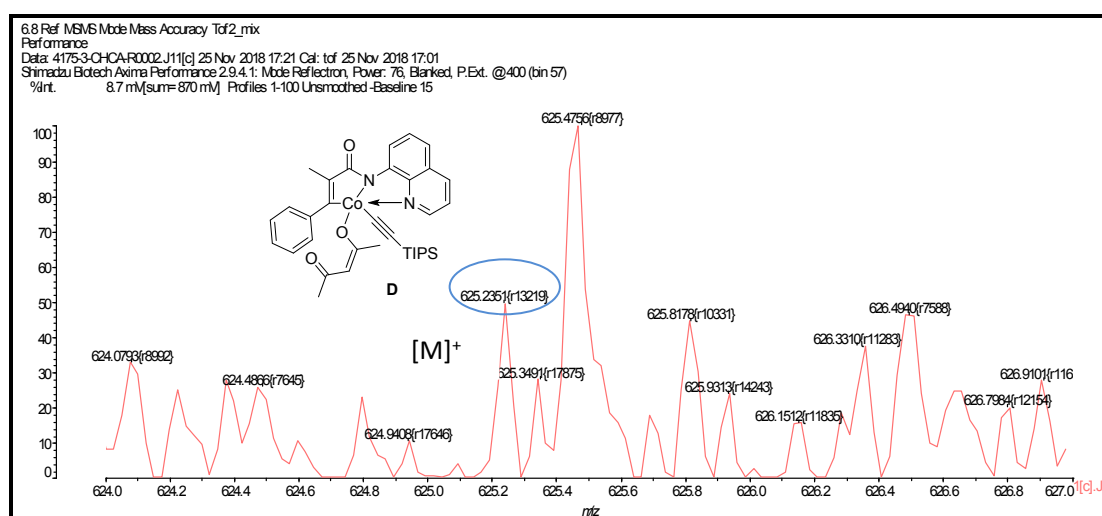


Figure S1 Kinetic experiments of **1a** and **1a-d₄**

(iii). MALDI-TOF-MS analysis



A MALDI-TOF analysis experiment was performed by the reaction **1a** with **2** under standard conditions for 3 h. A series of signals identified with acrylamide-Co intermediate **B**. MALDI-TOF-MS of **B** calcd for $C_{24}H_{21}CoN_2O_3$ $[M]^+$ 444.0884, found 444.1469, $C_{24}H_{22}CoN_2O_3$ $[M+H]^+$ 445.0962, found 445.1371.



MALDI-TOF-MS of **D** calcd for $C_{35}H_{42}CoN_2O_3Si$ $[M]^+$ 625.2297, found 625.2351.

(iv). Radical trapping experiments⁴

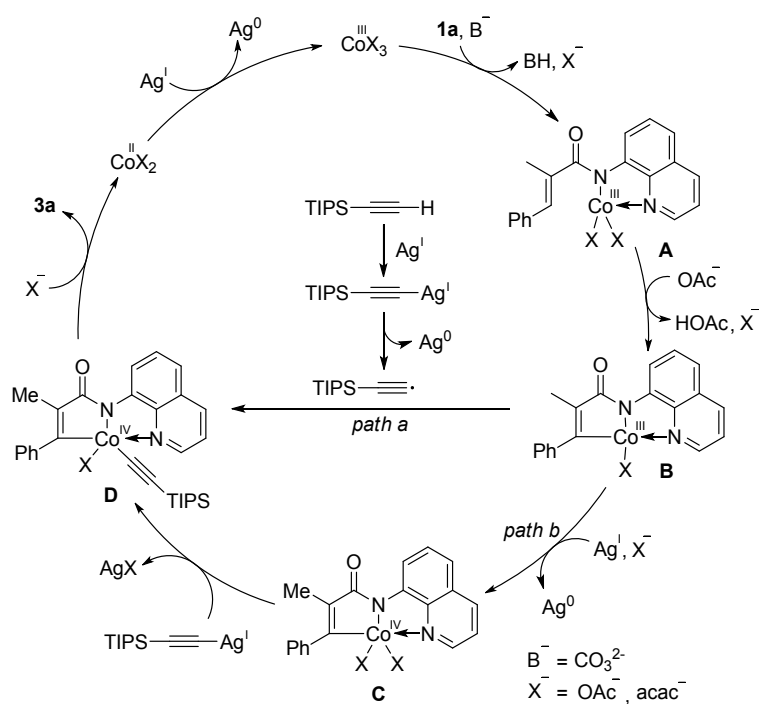
An oven-dried Schlenk tube with a magnetic stir bar was charged with $Co(acac)_3$ (3.6 mg, 0.01 mmol, 10 mol %), Ag_2CO_3 (55.2 mg, 0.2 mmol, 2.0 equiv), $Mn(OAc)_2$ (17.3 mg, 0.1 mmol, 1.0 equiv), and **1a** (28.8 mg, 0.1 mmol, 1.0 equiv), radical scavenger. The

Schlenk tube was evacuated and filled with a nitrogen gas three times. Then, ethynyltriisopropylsilane **2** (35 μ L, 0.15 mmol, 1.5 equiv) and THF (1 mL) were added under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 2 min, and then heated at 120 $^{\circ}$ C for 24h. After being cooled to room temperature, the reaction mixture was filtered through a silica-gel pad and washed with 10-20 mL of DCM. The filtrate was concentrated and was purified via column chromatography on silica gel gave **3a**.

Table S3 Radical trapping experiments

entry	TEMPO	Yield
1	1 equiv	38%
2	2 equiv	20%
3	3 equiv	13%
4	6 equiv	15%

(v). Plausible mechanistic pathway

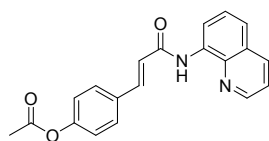


Scheme S1. Plausible Mechanism

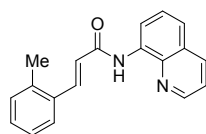
Based on the preliminary results and previous reports,⁶ a plausible mechanism is

proposed. The deprotonation of **1a** allows coordination of **1a** to [Co^{III}] to form the intermediate **A**. The vinylic C–H bond activation occurs to give the intermediate **B** with the assistance of acetate. **B** can be directly oxidized by the in situ generated alkynyl radical to form a [Co^{IV}] intermediate **D** (path a), or be oxidized to a [Co^{IV}] species **C** by Ag₂CO₃, followed by a transmetalation process with alkynyl-Ag^I species to generate **D** (path b). Finally, reductive elimination of **D** gave the cross-coupled product **3a** and a [Co^{II}] species. Oxidation of [Co^{II}] by silver will regenerate [Co^{III}] for the next catalytic cycle.

IX. Experimental data for the described substances

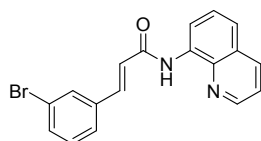


(E)-4-(3-oxo-3-(quinolin-8-ylamino)prop-1-en-1-yl)phenyl acetate (1d). A white solid. ¹H NMR (400 MHz, CDCl₃): δ = 2.33 (s, 3H), 6.77 (d, *J* = 15.2 Hz, 1H), 7.14-7.16 (m, 2H), 7.48 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.53-7.55 (m, 1H), 7.57-7.61 (m, 1H), 7.62-7.65 (m, 2H), 7.81 (d, *J* = 15.6 Hz, 1H), 8.19 (dd, *J* = 8.4, 2.0 Hz, 1H), 8.84 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.91 (dd, *J* = 7.6, 1.6 Hz, 1H), 10.01 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 20.3, 117.0, 121.80, 121.84, 121.9, 122.2, 127.7, 128.1, 129.3, 132.7, 134.7, 136.6, 138.6, 141.2, 148.3, 151.9, 164.1, 169.4 ppm. HRMS (ESI⁺): calcd for C₂₀H₁₆N₂NaO₃ [M+Na]⁺ 355.1059, found 355.1058.

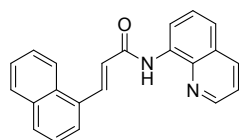


(E)-N-(quinolin-8-yl)-3-(o-tolyl)acrylamide (1e). A white solid. ¹H NMR (400 MHz, CDCl₃): δ = 2.51 (s, 3H), 6.73 (d, *J* = 15.2 Hz, 1H), 7.23-7.24 (m, 2H), 7.27-7.29 (m, 1H),

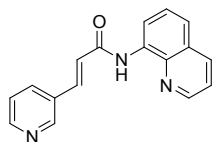
7.48 (dd, $J = 8.0, 4.0$ Hz, 1H), 7.53-7.55 (m, 1H), 7.57-7.61 (m, 1H), 7.66-7.68 (m, 1H), 8.13 (d, $J = 15.2$ Hz, 1H), 8.19 (dd, $J = 8.4, 1.6$ Hz, 1H), 8.84 (dd, $J = 4.0, 1.6$ Hz, 1H), 8.93 (dd, $J = 7.6, 1.6$ Hz, 1H), 10.02 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 20.1, 116.9, 121.80, 121.82, 122.7, 126.40, 126.42, 127.7, 128.1, 129.8, 130.9, 133.9, 134.8, 136.6, 137.9, 138.6, 140.1, 148.3, 164.4$ ppm. HRMS (ESI⁺): calcd for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 289.1341, found 289.1344.



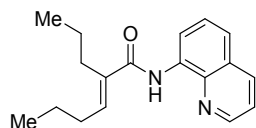
(E)-3-(3-bromophenyl)-N-(quinolin-8-yl)acrylamide (1j). A white solid. ^1H NMR (400 MHz, CDCl_3): $\delta = 6.81$ (d, $J = 15.6$ Hz, 1H), 7.29 (t, $J = 7.8$ Hz, 1H), 7.47-7.56 (m, 4H), 7.57-7.61 (m, 1H), 7.73-7.78 (m, 2H), 8.19 (dd, $J = 8.4, 2.0$ Hz, 1H), 8.84 (dd, $J = 4.0, 1.6$ Hz, 1H), 8.90 (dd, $J = 7.6, 1.6$ Hz, 1H), 10.04 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 117.1, 121.9, 122.0, 123.1, 123.2, 127.1, 127.6, 128.1, 130.5, 130.6, 132.8, 134.6, 136.6, 137.1, 138.6, 140.6, 148.4, 163.7$ ppm. HRMS (ESI⁺): calcd for $\text{C}_{18}\text{H}_{14}^{79}\text{BrN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 353.0290, found 353.0287; calcd for $\text{C}_{18}\text{H}_{14}^{81}\text{BrN}_2\text{O}$ $[\text{M}+\text{H}]^+$ 355.0269, found 355.0263.



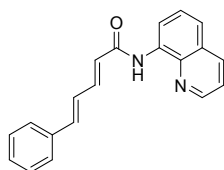
(E)-3-(naphthalen-1-yl)-N-(quinolin-8-yl)acrylamide (1l). A white solid. ^1H NMR (400 MHz, CDCl_3): $\delta = 6.90$ (d, $J = 15.6$ Hz, 1H), 7.49 (dd, $J = 8.4, 4.4$ Hz, 1H), 7.53-7.57 (m, 3H), 7.58-7.63 (m, 2H), 7.86-7.92 (m, 3H), 8.20 (dd, $J = 8.0, 1.6$ Hz, 1H), 8.31 (d, $J = 8.4$ Hz, 1H), 8.68 (d, $J = 15.6$ Hz, 1H), 8.85 (dd, $J = 4.0, 1.6$ Hz, 1H), 8.97 (dd, $J = 7.6, 1.6$ Hz, 1H), 10.09 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 117.0, 121.85, 121.88, 123.8, 124.4, 125.0, 125.6, 126.4, 126.9, 127.7, 128.1, 128.8, 130.3, 131.7, 132.4, 133.8, 134.8, 136.6, 138.6, 139.5, 148.3, 164.2$ ppm. HRMS (ESI⁺): calcd for $\text{C}_{22}\text{H}_{17}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 325.1341, found 325.1343.



(E)-3-(pyridin-3-yl)-N-(quinolin-8-yl)acrylamide (10). A white solid. ^1H NMR (400 MHz, CDCl_3): δ = 6.88 (d, J = 15.6 Hz, 1H), 7.34 (dd, J = 7.6, 4.8 Hz, 1H), 7.48 (dd, J = 8.4, 4.0 Hz, 1H), 7.53-7.60 (m, 2H), 7.80 (d, J = 15.6 Hz, 1H), 7.90 (dt, J = 8.0, 1.6 Hz, 1H), 8.18 (dd, J = 8.0, 1.6 Hz, 1H), 8.60 (dd, J = 4.8, 1.6 Hz, 1H), 8.83-8.84 (m, 2H), 8.90 (dd, J = 7.2, 1.6 Hz, 1H), 10.05 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 117.1, 121.9, 122.1, 123.7, 123.8, 127.6, 128.1, 130.7, 134.46, 134.50, 136.6, 138.5, 138.6, 148.4, 149.7, 150.8, 163.4 ppm. HRMS (ESI^+): calcd for $\text{C}_{17}\text{H}_{14}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 276.1137, found 276.1137.



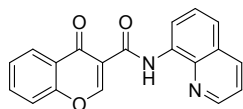
(E)-2-propyl-N-(quinolin-8-yl)hex-2-enamide (1r). A pale yellow liquid. ^1H NMR (400 MHz, CDCl_3): δ = 0.98-1.03 (m, 6H), 1.50-1.63 (m, 4H), 2.25 (dd, J = 14.8, 7.2 Hz, 2H), 2.48-2.52 (m, 2H), 6.59 (t, J = 7.4 Hz, 1H), 7.45 (dd, J = 8.4, 4.4 Hz, 1H), 7.48-7.50 (m, 1H), 7.53-7.57 (m, 1H), 8.16 (dd, J = 8.4, 2.0 Hz, 1H), 8.78-8.85 (m, 2H), 10.30 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 14.1, 14.3, 22.5, 22.6, 29.4, 30.7, 116.4, 121.3, 121.7, 127.6, 128.1, 135.0, 136.5, 137.1, 137.4, 138.9, 148.3, 167.9 ppm. HRMS (ESI^+): calcd for $\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 283.1810, found 283.1810.



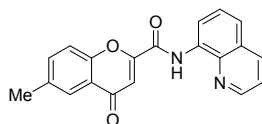
(2E, 4E)-5-phenyl-N-(quinolin-8-yl)penta-2,4-dienamide (1u). A pale yellow solid. ^1H NMR (400 MHz, CDCl_3): δ = 6.39 (d, J = 14.8 Hz, 1H), 6.93-7.02 (m, 2H), 7.29-7.33 (m, 1H), 7.36-7.39 (m, 2H), 7.46-7.49 (m, 2H), 7.51-7.53 (m, 2H), 7.55-7.63 (m, 2H), 8.18 (dd, J = 8.4, 1.6 Hz, 1H), 8.83 (dd, J = 4.4, 1.6 Hz, 1H), 8.90 (dd, J = 7.6, 1.6 Hz, 1H), 9.94 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 116.9, 121.7, 121.8, 125.0, 126.5, 127.2,

127.7, 128.1, 128.9, 129.0, 134.8, 136.4, 136.6, 138.6, 140.0, 142.2, 148.3, 164.5 ppm.

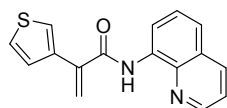
HRMS (ESI⁺): calcd for C₂₀H₁₇N₂O [M+H]⁺ 301.1341, found 301.1345.



4-oxo-*N*-(quinolin-8-yl)-4*H*-chromene-3-carboxamide (1v). A pale yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 7.34 (d, *J* = 4.4 Hz, 1H), 7.49-7.57 (m, 2H), 7.62-7.65 (m, 2H), 7.76-7.83 (m, 2H), 8.23-8.29 (m, 2H), 8.90-8.96 (m, 2H), 11.38 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 112.6, 117.7, 118.7, 122.2, 123.3, 124.5, 126.2, 127.5, 128.2, 133.29, 133.30, 134.8, 136.7, 138.9, 149.0, 155.2, 155.5, 157.2, 178.4 ppm. HRMS (ESI⁺): calcd for C₁₉H₁₃N₂O₃ [M+H]⁺ 317.0926, found 317.0927.

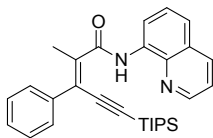


6-methyl-4-oxo-*N*-(quinolin-8-yl)-4*H*-chromene-2-carboxamide (1w). A pale yellow solid. ¹H NMR (400 MHz, CDCl₃): δ = 2.50 (s, 3H), 7.30 (s, 1H), 7.54 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.58-7.67 (m, 4H), 8.04 (s, 1H), 8.23 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.90 (dd, *J* = 6.8, 2.4 Hz, 1H), 8.94 (dd, *J* = 4.4, 1.6 Hz, 1H), 11.34 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 21.2, 112.4, 117.7, 118.4, 122.2, 123.3, 124.2, 125.5, 127.5, 128.2, 133.3, 136.0, 136.3, 136.6, 138.9, 149.0, 153.7, 155.1, 157.3, 178.5 ppm. HRMS (ESI⁺): calcd for C₂₀H₁₅N₂O₃ [M+H]⁺ 331.1083, found 331.1080.



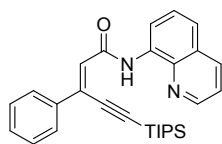
***N*-(quinolin-8-yl)-2-(thiophen-3-yl)acrylamide (5i).** A colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ = 5.88 (s, 1H), 6.19 (s, 1H), 7.33 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.38-7.44 (m, 2H), 7.51-7.54 (m, 1H), 7.55-7.59 (m, 1H), 7.62 (dd, *J* = 3.2, 1.6 Hz, 1H), 8.14 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.72 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.89 (dd, *J* = 7.6, 1.6 Hz, 1H), 10.36 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 116.8, 120.3, 121.7, 122.0, 124.5, 126.2,

127.1, 127.5, 128.0, 134.6, 136.4, 137.2, 138.8, 140.6, 148.4, 165.9 ppm. HRMS (ESI⁺): calcd for C₁₆H₁₃N₂OS [M+H]⁺ 281.0749, found 281.0745.

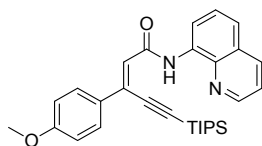


(Z)-2-methyl-3-phenyl-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide

(3a). A pale yellow solid (34.2 mg, 73% yield). ¹H NMR (400 MHz, CDCl₃): δ = 1.05 (m, 21H), 2.18 (s, 3H), 7.31-7.35 (m, 1H), 7.39-7.45 (m, 3H), 7.49-7.50 (m, 1H), 7.51-7.52 (m, 1H), 7.53-7.54 (m, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 8.16 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.81 (dd, *J* = 4.4, 1.6 Hz, 1H), 8.91 (dd, *J* = 7.2, 1.6 Hz, 1H), 10.40 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 11.1, 18.0, 18.4, 98.2, 105.1, 117.2, 121.6, 121.9, 124.2, 127.5, 128.0, 128.1, 128.3, 129.2, 134.7, 136.4, 137.8, 138.9, 141.5, 148.3, 168.8 ppm. HRMS (ESI⁺): calcd for C₃₀H₃₆N₂NaOSi [M+Na]⁺ 491.2495, found 491.2491.

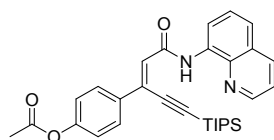


(Z)-3-phenyl-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide (3b). A pale yellow liquid (31.8 mg, 70% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.90-0.94 (m, 21H), 6.84 (s, 1H), 7.40-7.47 (m, 4H), 7.52-7.60 (m, 2H), 7.79-7.81 (m, 2H), 8.17 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.80 (dd, *J* = 4.4, 2.0 Hz, 1H), 8.85 (dd, *J* = 7.2, 1.2 Hz, 1H), 10.47 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 11.3, 18.6, 102.4, 104.7, 117.6, 121.6, 122.0, 127.1, 127.5, 128.0, 128.7, 129.3, 129.6, 130.6, 134.6, 136.4, 137.2, 139.0, 148.4, 164.2 ppm. HRMS (ESI⁺): calcd for C₂₉H₃₅N₂OSi [M+H]⁺ 455.2519, found 455.2523.



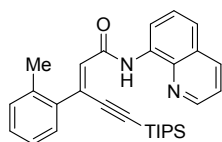
(Z)-3-(4-methoxyphenyl)-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide

(3c). A pale yellow solid (31.9 mg, 66% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.93-0.95 (m, 21H), 3.86 (s, 3H), 6.76 (s, 1H), 6.93-6.95 (m, 2H), 7.44 (dd, J = 8.4, 4.0 Hz, 1H), 7.51-7.59 (m, 2H), 7.73-7.76 (m, 2H), 8.16 (dd, J = 8.0, 1.6 Hz, 1H), 8.79 (dd, J = 4.0, 1.6 Hz, 1H), 8.84 (dd, J = 7.6, 1.6 Hz, 1H), 10.44 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.3, 18.6, 55.5, 102.6, 104.4, 114.0, 117.5, 121.6, 121.8, 127.3, 127.5, 128.0, 128.5, 129.6, 130.2, 134.7, 136.4, 139.0, 148.3, 160.8, 164.4 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{30}\text{H}_{36}\text{N}_2\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 485.2624, found 485.2626.



(Z)-4-(5-oxo-5-(quinolin-8-ylamino)-1-(triisopropylsilyl)pent-3-en-1-yn-3-yl)phenyl acetate (3d)

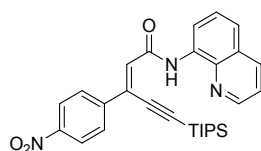
acetate (3d). A pale yellow liquid (28.2 mg, 55% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.93-0.95 (m, 21H), 2.33 (s, 3H), 6.81 (s, 1H), 7.15-7.17 (m, 2H), 7.45 (dd, J = 8.4, 4.4 Hz, 1H), 7.52-7.57 (m, 2H), 7.80-7.782 (m, 2H), 8.16 (dd, J = 8.4, 1.6 Hz, 1H), 8.79 (dd, J = 4.4, 2.0 Hz, 1H), 8.84 (dd, J = 7.2, 1.6 Hz, 1H), 10.44 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.3, 18.6, 21.3, 102.2, 105.0, 117.6, 121.6, 121.8, 122.0, 127.5, 128.1, 128.3, 129.3, 129.7, 134.6, 134.8, 136.4, 139.0, 148.4, 151.7, 164.0, 169.4 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{31}\text{H}_{37}\text{N}_2\text{O}_3\text{Si}$ $[\text{M}+\text{H}]^+$ 513.2573, found 513.2574.



(Z)-N-(quinolin-8-yl)-3-(o-tolyl)-5-(triisopropylsilyl)pent-2-en-4-ynamide (3e).

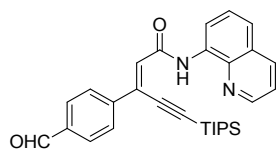
A pale yellow liquid (23.9 mg, 51% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.88-0.91 (m, 21H), 2.54 (s, 3H), 6.42 (s, 1H), 7.21-7.24 (m, 2H), 7.36-7.38 (m, 1H), 7.45 (dd, J = 8.0, 4.0 Hz, 1H), 7.52-7.60 (m, 2H), 8.17 (dd, J = 8.4, 2.0 Hz, 1H), 8.80 (dd, J = 4.0, 1.6 Hz, 1H), 8.86 (dd, J = 7.2, 1.6 Hz,

1H), 10.44 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.3, 18.5, 20.4, 102.9, 105.5, 117.6, 121.6, 122.0, 126.1, 127.5, 128.1, 128.6, 128.9, 130.7, 132.1, 133.5, 134.6, 135.7, 136.4, 139.0, 148.4, 163.7 ppm. HRMS (ESI⁺): calcd for $\text{C}_{30}\text{H}_{37}\text{N}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 469.2675, found 469.2676.



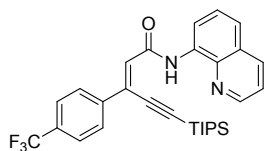
(Z)-3-(4-nitrophenyl)-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide (3f).

A yellow solid (25.9 mg, 52% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.92-0.96 (m, 21H), 6.93 (s, 1H), 7.47 (dd, J = 8.4, 4.4 Hz, 1H), 7.55-7.59 (m, 2H), 7.93-7.95 (m, 2H), 8.19 (dd, J = 8.0, 1.6 Hz, 1H), 8.27-8.30 (m, 2H), 8.80 (dd, J = 4.0, 1.6 Hz, 1H), 8.85 (dd, J = 6.8, 2.4 Hz, 1H), 10.46 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.2, 18.6, 101.3, 106.3, 117.6, 121.8, 122.4, 124.0, 127.5, 128.0, 128.1, 128.6, 132.0, 134.3, 136.5, 138.9, 143.5, 148.3, 148.4, 163.2 ppm. HRMS (ESI⁺): calcd for $\text{C}_{29}\text{H}_{33}\text{N}_3\text{NaO}_3\text{Si}$ $[\text{M}+\text{Na}]^+$ 522.2189, found 522.2190.

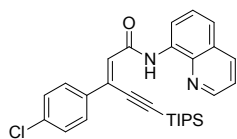


(Z)-3-(4-formylphenyl)-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide

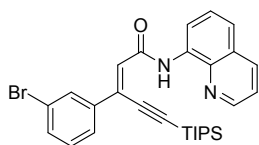
(3g). A yellow liquid (20.2 mg, 42% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.83-0.97 (m, 21H), 6.92 (s, 1H), 7.46 (dd, J = 8.4, 4.4 Hz, 1H), 7.56-7.61 (m, 2H), 7.68-7.73 (m, 1H), 7.95 (s, 3H), 8.18 (dd, J = 8.4, 1.6 Hz, 1H), 8.80 (dd, J = 4.0, 1.6 Hz, 1H), 8.86 (dd, J = 6.8, 2.0 Hz, 1H), 10.07 (s, 1H), 10.46 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.3, 18.6, 101.7, 105.8, 117.6, 121.7, 122.2, 127.6, 127.8, 128.1, 129.5, 130.1, 131.4, 134.4, 136.5, 136.8, 138.9, 143.1, 148.4, 163.5, 191.8 ppm. HRMS (ESI⁺): calcd for $\text{C}_{30}\text{H}_{35}\text{N}_2\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 483.2468, found 483.2470.



(Z)-N-(quinolin-8-yl)-3-(4-(trifluoromethyl)phenyl)-5-(triisopropylsilyl)pent-2-en-4-ynamide (3h). A yellow solid (38.1 mg, 73% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.92-0.95 (m, 21H), 6.88 (s, 1H), 7.46 (dd, J = 8.4, 4.4 Hz, 1H), 7.56-7.60 (m, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.90 (d, J = 8.4 Hz, 2H), 8.18 (dd, J = 8.0, 1.6 Hz, 1H), 8.80 (dd, J = 4.4, 1.6 Hz, 1H), 8.86 (dd, J = 7.2, 2.0 Hz, 1H), 10.45 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.3, 18.6, 101.8, 105.6, 117.6, 121.7, 122.2, 124.1 (q, $J_{\text{C-F}}$ = 271.0 Hz), 125.7 (q, $J_{\text{C-F}}$ = 3.0 Hz), 127.4, 127.5, 128.1, 129.3, 130.9, 131.3 (q, $J_{\text{C-F}}$ = 33.0 Hz), 134.4, 136.5, 138.9, 140.7 (q, $J_{\text{C-F}}$ = 2.0 Hz), 148.4, 163.6 ppm. HRMS (ESI⁺): calcd for $\text{C}_{30}\text{H}_{34}\text{F}_3\text{N}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 523.2392, found 523.2398.

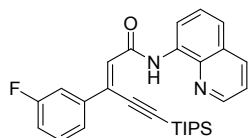


(Z)-3-(4-chlorophenyl)-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide (3i). A yellow solid (27.3 mg, 56% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.92-0.94 (m, 21H), 6.80 (d, J = 4.0 Hz, 1H), 7.38-7.41 (m, 2H), 7.43-7.47 (m, 1H), 7.52-7.57 (m, 2H), 7.70-7.73 (m, 2H), 8.15-8.18 (m, 1H), 8.78-8.80 (m, 1H), 8.83-8.84 (m, 1H), 10.43 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.3, 18.6, 102.1, 105.2, 117.6, 121.7, 122.1, 127.5, 128.1, 128.4, 128.9, 129.45, 129.52, 134.5, 135.6, 135.7, 136.4, 139.0, 148.4, 163.9 ppm. HRMS (ESI⁺): calcd for $\text{C}_{29}\text{H}_{34}^{35}\text{ClN}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 489.2129, found 489.2130; calcd for $\text{C}_{29}\text{H}_{34}^{37}\text{ClN}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 491.2099, found 491.2094.



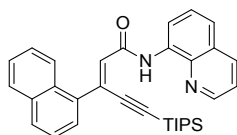
(Z)-3-(3-bromophenyl)-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide

(3j). A yellow solid (30.3 mg, 57% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.95-0.96 (m, 21H), 6.82 (s, 1H), 7.27-7.31 (m, 1H), 7.45 (dd, J = 8.4, 4.4 Hz, 1H), 7.51-7.57 (m, 3H), 7.70 (dq, J = 7.6, 1.2 Hz, 1H), 7.98 (t, J = 1.8 Hz, 1H), 8.17 (dd, J = 8.0, 1.6 Hz, 1H), 8.80 (dd, J = 4.4, 1.6 Hz, 1H), 8.85 (dd, J = 7.2, 2.0 Hz, 1H), 10.44 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.3, 18.6, 101.9, 105.6, 117.6, 121.7, 122.1, 122.9, 125.4, 127.5, 128.0, 129.3, 129.9, 130.2, 130.5, 132.4, 134.5, 136.4, 138.9, 139.2, 148.4, 163.7 ppm. HRMS (ESI^+): calcd for $\text{C}_{29}\text{H}_{34}^{79}\text{BrN}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 533.1624, found 533.1626; calcd for $\text{C}_{29}\text{H}_{34}^{81}\text{BrN}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 535.1603, found 535.1598.



(Z)-3-(3-fluorophenyl)-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide

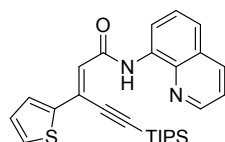
(3k). A yellow solid (33.0 mg, 70% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.94-0.95 (m, 21H), 7.10 (tdd, J = 8.3, 2.4, 0.8 Hz, 1H), 7.36-7.41 (m, 1H), 7.45 (dd, J = 8.0, 4.0 Hz, 1H), 7.49-7.53 (m, 1H), 7.54-7.59 (m, 3H), 8.17 (dd, J = 8.4, 1.6 Hz, 1H), 8.80 (dd, J = 4.0, 1.6 Hz, 1H), 8.85 (dd, J = 7.2, 1.6 Hz, 1H), 10.45 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.3, 18.5, 101.9, 105.2, 114.3 (d, $J_{\text{C-F}}$ = 24.0 Hz), 116.4 (d, $J_{\text{C-F}}$ = 21.0 Hz), 117.6, 121.7, 122.1, 122.6 (d, $J_{\text{C-F}}$ = 3.0 Hz), 127.5, 128.0, 129.4 (d, $J_{\text{C-F}}$ = 3.0 Hz), 130.0, 130.2 (d, $J_{\text{C-F}}$ = 8.0 Hz), 134.5, 136.4, 138.9, 139.4 (d, $J_{\text{C-F}}$ = 7.0 Hz), 148.4, 163.0 (d, $J_{\text{C-F}}$ = 245.0 Hz), 163.8 ppm. HRMS (ESI^+): calcd for $\text{C}_{29}\text{H}_{34}\text{FN}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 473.2424, found 473.2425.



(Z)-3-(naphthalen-1-yl)-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide

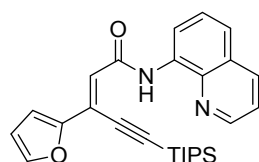
(3l). A pale yellow liquid (20.2 mg, 40% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.84-0.92 (m, 21H), 6.66 (s, 2H), 7.44-7.62 (m, 7H), 7.87-7.90 (m, 2H), 8.18 (dd, J = 8.4, 1.6 Hz, 1H), 8.45-8.48

(m, 1H), 8.82 (dd, $J = 4.4, 2.0$ Hz, 1H), 8.91 (dd, $J = 7.6, 1.6$ Hz, 1H), 10.54 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 11.3, 18.5, 103.8, 106.1, 117.6, 121.7, 122.0, 125.4, 126.0, 126.2, 126.37, 126.44, 127.6, 128.1, 128.4, 129.3, 130.6, 131.1, 133.8, 134.2, 134.6, 136.4, 137.3, 139.0, 148.4, 163.6$ ppm. HRMS (ESI⁺): calcd for $\text{C}_{33}\text{H}_{37}\text{N}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 505.2675, found 505.2681.



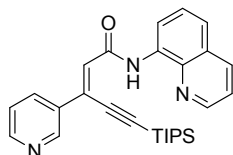
(E)-N-(quinolin-8-yl)-3-(thiophen-2-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide

(3m). A yellow solid (18.5 mg, 40% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 0.97\text{--}0.98$ (m, 21H), 6.77 (s, 1H), 7.07 (dd, $J = 5.2, 3.6$ Hz, 1H), 7.37 (dd, $J = 5.2, 1.2$ Hz, 1H), 7.45 (dd, $J = 8.0, 4.0$ Hz, 1H), 7.53–7.57 (m, 4H), 8.16 (dd, $J = 8.4, 1.6$ Hz, 1H), 8.80 (dd, $J = 4.4, 1.6$ Hz, 1H), 8.83 (dd, $J = 7.6, 1.6$ Hz, 1H), 10.37 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 10.3, 17.6, 100.4, 102.9, 109.2, 116.5, 120.6, 120.9, 123.7, 125.1, 126.5, 126.7, 126.9, 127.1, 133.7, 135.4, 138.0, 141.3, 147.3, 162.6$ ppm. HRMS (ESI⁺): calcd for $\text{C}_{27}\text{H}_{32}\text{N}_2\text{NaOSSi}$ $[\text{M}+\text{Na}]^+$ 483.1902, found 483.1905.



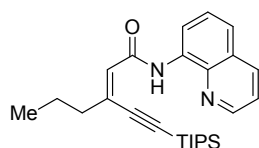
(E)-3-(furan-2-yl)-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide (3n).

A pale yellow liquid (20.0 mg, 45% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 1.00\text{--}1.01$ (m, 21H), 6.50 (dd, $J = 3.6, 1.6$ Hz, 1H), 6.81–6.82 (m, 1H), 6.90 (s, 1H), 7.44 (dd, $J = 8.0, 4.0$ Hz, 1H), 7.47 (m, 1H), 7.50–7.58 (m, 2H), 8.15 (dd, $J = 8.4, 1.6$ Hz, 1H), 8.79 (dd, $J = 4.4, 1.6$ Hz, 1H), 8.85 (dd, $J = 7.2, 1.6$ Hz, 1H), 10.31 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 10.3, 17.6, 99.2, 101.4, 111.4, 111.9, 116.4, 119.5, 120.6, 120.8, 123.5, 126.6, 127.0, 133.7, 135.4, 137.9, 143.1, 147.3, 151.0, 162.6$ ppm. HRMS (ESI⁺): calcd for $\text{C}_{27}\text{H}_{32}\text{N}_2\text{NaO}_2\text{Si}$ $[\text{M}+\text{Na}]^+$ 467.2131, found 467.2126.



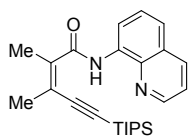
(Z)-3-(pyridin-3-yl)-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide (3o). A

pale yellow liquid (27.3 mg, 60% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.91-0.98 (m, 21H), 6.86 (s, 1H), 7.36 (ddd, J = 5.6, 4.8, 0.8 Hz, 1H), 7.46 (dd, J = 8.0, 4.0 Hz, 1H), 7.54-7.60 (m, 2H), 8.05 (dq, J = 8.4, 2.0 Hz, 1H), 8.18 (dd, J = 8.4, 1.6 Hz, 1H), 8.64 (dd, J = 4.8, 1.6 Hz, 1H), 8.80 (dd, J = 4.0, 1.6 Hz, 1H), 8.85 (dd, J = 7.2, 2.0 Hz, 1H), 9.04 (dd, J = 2.4, 0.4 Hz, 1H), 10.45 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.3, 18.6, 101.4, 105.9, 117.6, 121.7, 122.2, 123.5, 127.5, 127.8, 128.1, 130.5, 133.0, 134.2, 134.4, 136.5, 138.9, 148.4, 148.5, 150.4, 163.5 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{28}\text{H}_{34}\text{N}_3\text{OSi}$ $[\text{M}+\text{H}]^+$ 456.2471, found 456.2475.



(Z)-N-(quinolin-8-yl)-3-((triisopropylsilyl)ethynyl)hex-2-enamide (3p). A pale yellow

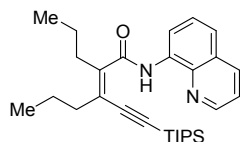
liquid (29.8 mg, 71% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.94-0.97 (m, 21H), 1.09 (t, J = 14.8 Hz, 3H), 2.25-2.32 (m, 2H), 3.44 (s, 2H), 6.30 (t, J = 15.2 Hz, 1H), 7.43 (dd, J = 8.0, 4.0 Hz, 1H), 7.48-7.54 (m, 2H), 8.13 (dd, J = 8.0, 1.6 Hz, 1H), 8.77 (d, J = 1.6 Hz, 1H), 8.78 (dd, J = 3.2, 2.0 Hz, 1H), 10.15 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.3, 13.6, 18.7, 22.4, 41.2, 88.9, 108.3, 116.1, 116.6, 121.6, 121.7, 127.4, 128.0, 134.7, 136.2, 138.8, 144.8, 148.3, 168.3 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{26}\text{H}_{37}\text{N}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 421.2675, found 421.2679.



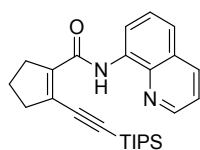
(Z)-2,3-dimethyl-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide (3q). A

yellow solid (30.0 mg, 74% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.65-0.74 (m, 21H), 2.03 (d, J

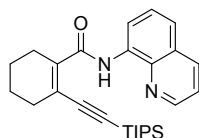
= 0.8 Hz, 3H), 2.07 (d, J = 0.8 Hz, 3H), 7.42 (dd, J = 8.4, 4.4 Hz, 1H), 7.48-7.55 (m, 2H), 8.14 (dd, J = 8.0, 1.6 Hz, 1H), 8.78 (dd, J = 4.4, 1.6 Hz, 1H), 8.82 (dd, J = 7.2, 1.6 Hz, 1H), 10.26 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.1, 16.3, 18.4, 20.5, 41.2, 96.6, 106.2, 117.1, 119.4, 121.5, 121.7, 127.5, 128.0, 134.7, 136.3, 138.9, 140.0, 148.3, 168.7 ppm. HRMS (ESI^+): calcd for $\text{C}_{25}\text{H}_{34}\text{N}_2\text{NaOSi}$ $[\text{M}+\text{Na}]^+$ 429.2338, found 429.2335.



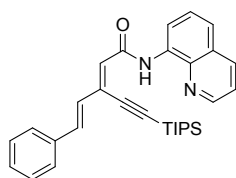
(Z)-2-propyl-N-(quinolin-8-yl)-3-((triisopropylsilyl)ethynyl)hex-2-ena-mide (3r). A pale yellow liquid (37.9 mg, 82% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.62-0.73 (m, 21H), 0.96-1.03 (m, 6H), 1.53-1.59 (m, 2H), 1.69-1.71 (m, 2H), 2.29-2.33 (m, 2H), 2.46-2.50 (m, 2H), 7.41 (dd, J = 8.0, 4.0 Hz, 1H), 7.47-7.54 (m, 2H), 8.13 (dd, J = 8.0, 1.6 Hz, 1H), 8.78 (dd, J = 4.4, 2.0 Hz, 1H), 8.86 (dd, J = 7.6, 2.0 Hz, 1H), 10.21 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 10.8, 11.1, 14.0, 14.3, 18.4, 21.7, 22.2, 32.2, 34.7, 96.8, 105.2, 116.8, 121.5, 121.6, 123.6, 127.5, 128.0, 134.9, 136.2, 138.9, 145.0, 148.3, 168.9 pm. HRMS (ESI^+): calcd for $\text{C}_{29}\text{H}_{43}\text{N}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 463.3145, found 463.3146.



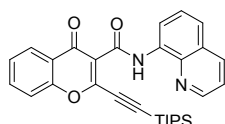
N-(quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)cyclopent-1-enecarboxa-mide (3s). A white solid (33.4 mg, 80% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.86-0.96 (m, 21H), 1.94-2.02 (m, 2H), 2.77 (tt, J = 7.8, 2.4 Hz, 2H), 2.90 (tt, J = 7.6, 2.8 Hz, 2H), 7.42 (dd, J = 8.4, 4.4 Hz, 1H), 7.49-7.56 (m, 2H), 8.13 (dd, J = 8.4, 1.6 Hz, 1H), 8.75 (dd, J = 7.2, 1.6 Hz, 1H), 8.78 (dd, J = 4.4, 1.6 Hz, 1H), 10.51 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.2, 18.5, 22.2, 34.2, 39.8, 101.8, 102.8, 117.8, 121.5, 121.9, 127.4, 127.8, 128.1, 134.6, 136.3, 139.3, 144.3, 148.4, 163.8 pm. HRMS (ESI^+): calcd for $\text{C}_{26}\text{H}_{35}\text{N}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 419.2519, found 419.2522.



***N*-(quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)cyclohex-1-enecarbox-amide (3t).** A white solid (35.0 mg, 81% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.70-0.76 (m, 21H), 1.71-1.72 (m, 4H), 2.37 (d, J = 2.0 Hz, 2H), 2.37 (d, J = 2.4 Hz, 2H), 7.40-7.44 (m, 1H), 7.47-7.55 (m, 2H), 8.12-8.15 (m, 1H), 8.77-8.84 (m, 2H), 10.29 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.1, 18.4, 21.7, 22.0, 26.6, 31.4, 97.2, 105.4, 117.2, 121.5, 121.7, 121.8, 127.5, 128.0, 134.7, 136.3, 139.0, 141.5, 148.3, 168.1 ppm. HRMS (ESI^+): calcd for $\text{C}_{27}\text{H}_{37}\text{N}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 433.2675, found 433.2680.

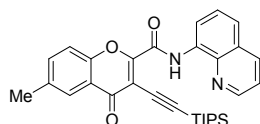


(2Z,4E)-5-phenyl-*N*-(quinolin-8-yl)-3-((triisopropylsilyl)ethynyl)penta-2,4-dienamide (3u). A yellow solid (22.6 mg, 47% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.99-1.00 (m, 21H), 6.45 (s, 1H), 6.88 (d, J = 15.2 Hz, 1H), 7.32-7.33 (m, 1H), 7.36-7.40 (m, 3H), 7.43-7.45 (m, 1H), 7.47-7.51 (m, 3H), 7.53-7.58 (m, 2H), 8.16 (dd, J = 8.4, 1.6 Hz, 1H), 8.80 (dd, J = 4.0, 1.6 Hz, 1H), 8.82 (dd, J = 7.2, 1.6 Hz, 1H), 10.41 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.3, 18.7, 110.2, 117.6, 121.6, 121.9, 127.3, 127.5, 128.1, 128.2, 128.9, 129.0, 129.7, 131.0, 134.7, 136.3, 136.4, 137.1, 139.0, 148.3, 164.0 ppm. HRMS (ESI^+): calcd for $\text{C}_{31}\text{H}_{36}\text{N}_2\text{NaOSi}$ $[\text{M}+\text{Na}]^+$ 503.2495, found 503.2498.

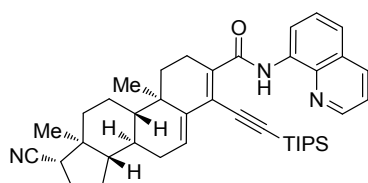


4-oxo-*N*-(quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)-4H-chromene-3-carboxamide (3v). A yellow solid (23.3 mg, 47% yield). ^1H NMR (400 MHz, CDCl_3): δ = 1.01 (s, 21H), 7.45-

7.51 (m, 2H), 7.61-7.66 (m, 3H), 7.74-7.79 (m, 1H), 8.21 (dd, $J = 8.4, 2.0$ Hz, 1H), 8.27 (dd, $J = 8.0, 1.6$ Hz, 1H), 8.85 (dd, $J = 8.4, 1.6$ Hz, 1H), 8.89-8.93 (m, 1H), 11.06 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 11.3, 18.6, 95.4, 106.4, 110.2, 117.8, 118.7, 122.0, 122.8, 123.1, 126.3, 126.3, 127.5, 128.1, 133.6, 134.8, 136.5, 138.9, 148.8, 154.9, 157.7, 158.3, 176.4$ pm. HRMS (ESI⁺): calcd for $\text{C}_{30}\text{H}_{33}\text{N}_2\text{O}_3\text{Si}$ $[\text{M}+\text{H}]^+$ 497.2260, found 497.2258.

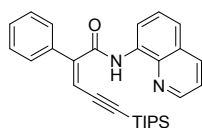


6-methyl-4-oxo-*N*-(quinolin-8-yl)-3-((triisopropylsilyl)ethynyl)-4*H*-chromene-2-carboxamide (3w). A pale yellow liquid (23.0 mg, 45% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 1.01$ (s, 21H), 2.48 (s, 3H), 7.49 (dd, $J = 8.0, 4.0$ Hz, 1H), 7.52-7.56 (m, 2H), 7.61 (s, 1H), 7.62 (s, 1H), 8.04 (s, 1H), 8.21 (dd, $J = 8.0, 1.2$ Hz, 1H), 8.85 (dd, $J = 4.0, 1.2$ Hz, 1H), 8.89-8.93 (m, 1H), 11.04 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 11.3, 18.6, 21.2, 95.6, 106.2, 117.8, 118.4, 122.0, 122.4, 123.1, 125.6, 127.5, 128.1, 133.6, 136.1, 136.4, 136.5, 138.9, 148.8, 153.2, 157.8, 158.1, 176.5$ pm. HRMS (ESI⁺): calcd for $\text{C}_{31}\text{H}_{35}\text{N}_2\text{O}_3\text{Si}$ $[\text{M}+\text{H}]^+$ 511.2417, found 511.2414.

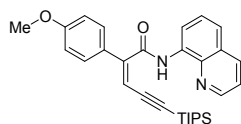


(8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-cyano-10,13-dimethyl-*N*-(quinolin-8-yl)-4-((triisopropylsilyl)ethynyl)-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1*H*-cyclopenta[*a*]phenanthrene-3-carboxamide (3x). A white solid (49.3 mg, 78% yield). ^1H NMR (400 MHz, CDCl_3): $\delta = 0.63$ -0.77 (m, 21H), 0.97 (s, 3H), 1.04-1.05 (m, 2H), 6.46-6.47 (m, 1H), 7.42 (dd, $J = 8.4, 4.4$ Hz, 1H), 7.50-7.51 (m, 1H), 7.54 (d, $J = 8.4$ Hz, 1H), 8.14 (dd, $J = 8.4, 2.0$ Hz, 1H), 8.77 (dd, $J = 4.4, 1.6$ Hz, 1H), 8.84 (dd, $J = 7.2, 2.0$ Hz, 1H), 10.28 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): $\delta = 11.2, 14.4, 18.4, 19.2, 20.9, 24.3, 24.7, 26.7, 30.4, 31.8, 32.3, 32.8, 35.0, 40.2, 44.4, 48.4, 54.8, 98.8, 102.1, 117.1, 120.8, 121.3, 121.5, 121.7, 125.6, 127.4, 127.8,$

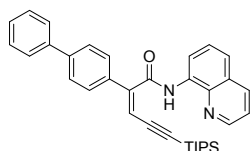
128.0, 134.7, 136.3, 138.9, 139.2, 148.3, 168.3 pm. HRMS (ESI⁺): calcd for C₄₁H₅₄N₃OSi [M+H]⁺ 632.4036, found 632.4034.



(Z)-2-phenyl-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide (6a). A pale yellow liquid (32.3 mg, 70% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.76-0.78 (m, 21H), 6.34 (s, 1H), 7.34-7.39 (m, 3H), 7.44 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.53-7.60 (m, 4H), 8.16 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.76 (dd, *J* = 4.0, 1.6 Hz, 1H), 8.96 (dd, *J* = 6.8, 2.0 Hz, 1H), 10.33 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 1.2, 18.4, 102.8, 109.4, 110.2, 117.1, 121.6, 122.1, 126.6, 127.5, 128.0, 128.9, 129.3, 134.7, 135.5, 136.3, 138.7, 148.4, 149.2, 166.2 ppm. HRMS (ESI⁺): calcd for C₂₉H₃₅N₂OSi [M+H]⁺ 455.2519, found 455.2521.

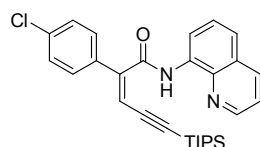


(Z)-2-(4-methoxyphenyl)-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide (6b). A white solid (25.1 mg, 52% yield). ¹H NMR (400 MHz, CDCl₃): δ = 0.72-0.77 (m, 21H), 3.82 (s, 3H), 6.24 (s, 1H), 6.88-6.90 (m, 2H), 7.43 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.51-7.59 (m, 4H), 8.16 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.76 (dd, *J* = 4.4, 2.0 Hz, 1H), 8.95 (dd, *J* = 6.8, 2.0 Hz, 1H), 10.31 (s, 1H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 11.2, 18.4, 55.5, 99.9, 103.1, 107.2, 114.3, 117.1, 121.6, 122.0, 127.5, 127.98, 128.01, 134.7, 136.3, 138.7, 148.4, 148.8, 160.6, 166.8 ppm. HRMS (ESI⁺): calcd for C₃₀H₃₆N₂NaO₂Si [M+Na]⁺ 507.2444, found 507.2445.



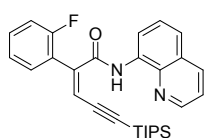
(Z)-2-([1,1'-biphenyl]-4-yl)-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-

ynamide (6c). A white solid (26.5 mg, 50% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.77-0.79 (m, 21H), 6.40 (s, 1H), 7.33-7.38 (m, 1H), 7.42-7.46 (m, 3H), 7.54-7.57 (m, 2H), 7.59-7.60 (m, 2H), 7.61-7.62 (m, 2H), 7.66-7.67 (m, 1H), 7.68-7.69 (m, 1H), 8.17 (dd, J = 8.4, 2.0 Hz, 1H), 8.77 (dd, J = 4.0, 1.6 Hz, 1H), 8.98 (dd, J = 7.2, 2.0 Hz, 1H), 10.38 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.2, 18.4, 101.1, 102.9, 109.1, 117.1, 121.7, 122.1, 127.1, 127.2, 127.5, 127.6, 127.8, 128.0, 129.0, 134.4, 134.7, 136.3, 138.7, 140.4, 142.0, 148.4, 148.8, 166.2 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{35}\text{H}_{39}\text{N}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 531.2832, found 531.2830.



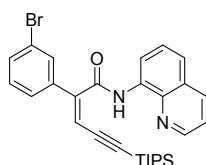
(Z)-2-(4-chlorophenyl)-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide

(6d). A white solid (30.7 mg, 63% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.75-0.77 (m, 21H), 6.33 (s, 1H), 7.32-7.36 (m, 2H), 7.44 (dd, J = 8.4, 4.0 Hz, 1H), 7.51-7.52 (m, 1H), 7.53-7.54 (m, 1H), 7.56-7.60 (m, 2H), 8.17 (dd, J = 8.4, 1.6 Hz, 1H), 8.77 (dd, J = 4.0, 2.0 Hz, 1H), 8.93 (dd, J = 6.4, 2.4 Hz, 1H), 10.35 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.1, 18.4, 101.8, 102.4, 110.1, 117.2, 121.7, 122.2, 127.5, 127.98, 127.99, 129.1, 134.1, 134.5, 135.2, 136.4, 138.7, 147.8, 148.4, 165.8 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{29}\text{H}_{34}^{35}\text{ClN}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 489.2129, found 489.2130; calcd for $\text{C}_{29}\text{H}_{34}^{37}\text{ClN}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 491.2099, found 491.2091.



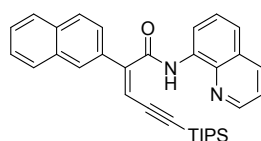
(Z)-2-(2-fluorophenyl)-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide

(6e). A colorless liquid (23.2 mg, 49% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.76-0.80 (m, 21H), 6.43 (s, 1H), 7.06-7.11 (m, 1H), 7.16 (td, J = 8.8, 1.2 Hz, 1H), 7.30-7.36 (m, 1H), 7.44 (dd, J = 8.4, 2.2 Hz, 1H), 7.49-7.53 (m, 1H), 7.54-7.58 (m, 2H), 8.16 (dd, J = 8.4, 2.0 Hz, 1H), 8.79 (dd, J = 2.2, 1.6 Hz, 1H), 8.90 (dd, J = 6.8, 2.4 Hz, 1H), 10.48 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.1, 18.4, 102.2, 102.5, 113.8 (d, $J_{\text{C-F}}$ = 6.0 Hz), 116.3 (d, $J_{\text{C-F}}$ = 22.0 Hz), 117.1, 121.6, 122.0, 124.5 (d, $J_{\text{C-F}}$ = 8.0 Hz), 124.6 (d, $J_{\text{C-F}}$ = 4.0 Hz), 127.5, 128.0, 130.3 (d, $J_{\text{C-F}}$ = 3.0 Hz), 130.8 (d, $J_{\text{C-F}}$ = 9.0 Hz), 134.6, 136.3, 138.8, 144.1, 148.4, 160.3 (d, $J_{\text{C-F}}$ = 250.0 Hz), 165.4 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{29}\text{H}_{34}\text{FN}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 473.2424, found 473.2427.



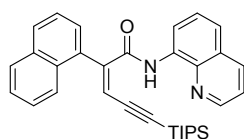
(Z)-2-(3-bromophenyl)-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide

(6f). A pale yellow liquid (27.1 mg, 51% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.75-0.77 (m, 21H), 6.34 (s, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.43-7.45 (m, 1H), 7.46-7.49 (m, 1H), 7.50-7.57 (m, 3H), 7.58-7.60 (m, 1H), 7.73-7.75 (m, 1H), 8.17 (dd, J = 8.4, 1.6 Hz, 1H), 8.77 (dd, J = 4.4, 1.6 Hz, 1H), 8.93 (dd, J = 6.4, 2.4 Hz, 1H), 10.36 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.1, 18.4, 102.24, 102.27, 111.0, 117.2, 121.7, 122.3, 123.0, 125.4, 127.5, 128.0, 129.6, 130.3, 132.1, 134.4, 136.4, 137.7, 138.7, 147.5, 148.4, 165.5 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{29}\text{H}_{34}^{79}\text{BrN}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 533.1624, found 533.1627; calcd for $\text{C}_{29}\text{H}_{34}^{81}\text{BrN}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 535.1603, found 535.1598.



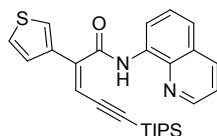
(Z)-2-(naphthalen-2-yl)-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide

(6g). A pale yellow liquid (36.3 mg, 72% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.77-0.79 (m, 21H), 6.49 (s, 1H), 7.42-7.48 (m, 3H), 7.55-7.62 (m, 2H), 7.69 (dd, J = 8.4, 1.6 Hz, 1H), 7.80-7.85 (m, 3H), 8.05 (d, J = 1.6 Hz, 1H), 8.17 (dd, J = 8.4, 1.6 Hz, 1H), 8.76 (dd, J = 4.4, 1.6 Hz, 1H), 8.93 (dd, J = 7.6, 1.6 Hz, 1H), 10.40 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.2, 18.4, 101.3, 102.9, 109.6, 117.2, 121.7, 122.1, 123.5, 126.6, 126.7, 126.9, 127.5, 127.7, 128.0, 128.6, 128.8, 132.6, 133.4, 133.6, 134.7, 136.3, 138.7, 148.4, 149.1, 166.3 ppm. HRMS (ESI^+): calcd for $\text{C}_{33}\text{H}_{37}\text{N}_2\text{OSi}$ [$\text{M}+\text{H}$] $^+$ 505.2675, found 505.2681.



(Z)-2-(naphthalen-1-yl)-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide

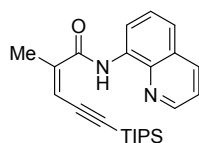
(6h). A pale yellow liquid (21.2 mg, 42% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.90-0.91 (m, 21H), 6.31 (s, 1H), 7.40-7.54 (m, 7H), 7.62-7.64 (m, 1H), 7.85-7.90 (m, 2H), 8.12-8.15 (m, 2H), 8.72 (dd, J = 4.4, 2.0 Hz, 1H), 8.85 (dd, J = 6.4, 2.8 Hz, 1H), 10.56 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.3, 18.5, 102.3, 102.4, 116.1, 117.1, 121.6, 122.0, 125.5, 126.2, 126.9, 127.5, 127.7, 128.0, 128.6, 129.5, 131.8, 133.9, 134.6, 135.4, 136.3, 138.9, 148.2, 148.4, 165.3 ppm. HRMS (ESI^+): calcd for $\text{C}_{33}\text{H}_{37}\text{N}_2\text{OSi}$ [$\text{M}+\text{H}$] $^+$ 505.2675, found 505.2673.



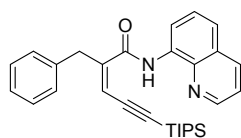
(Z)-N-(quinolin-8-yl)-2-(thiophen-3-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide (6i).

A pale yellow liquid (15.2 mg, 33% yield). ^1H NMR (400 MHz, CDCl_3): δ = 0.74-0.76 (m, 21H), 6.30 (s, 1H), 7.31-7.33 (m, 2H), 7.44 (dd, J = 8.0, 4.0 Hz, 1H), 7.53-7.59 (m, 3H), 8.16 (dd, J = 8.4, 1.6 Hz, 1H), 8.77 (dd, J = 4.0, 1.6 Hz, 1H), 8.93 (dd, J = 7.2, 2.0 Hz, 1H), 10.32 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.0, 18.2, 101.1, 102.4, 108.1, 117.0, 121.5, 121.9, 124.3, 124.9, 126.4, 127.3, 127.8, 134.4, 136.2, 136.7, 138.6, 143.9, 148.2, 165.6 ppm. HRMS (ESI^+):

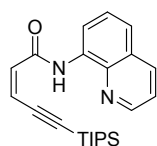
calcd for $C_{27}H_{33}N_2O$ Si $[M+H]^+$ 461.2083, found 461.2081.



(Z)-2-methyl-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide (6j). A white solid (18.0 mg, 46% yield). 1H NMR (400 MHz, $CDCl_3$): δ = 0.75-0.78 (m, 21H), 2.15 (d, J = 1.6 Hz, 3H), 5.95 (q, J = 1.6 Hz, 1H), 7.43 (dd, J = 8.4, 4.4 Hz, 1H), 7.50-7.57 (m, 2H), 8.15 (dd, J = 8.4, 1.6 Hz, 1H), 8.78-8.81 (m, 2H), 10.41 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.1, 18.4, 20.5, 99.0, 102.2, 111.4, 117.4, 121.6, 122.0, 127.4, 128.0, 134.4, 136.3, 139.0, 145.8, 148.4, 166.6 ppm. HRMS (ESI $^+$): calcd for $C_{24}H_{33}N_2O$ Si $[M+H]^+$ 393.2362, found 393.2366.

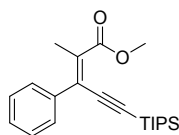


(Z)-2-benzyl-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide (6k). A colorless liquid (21.5 mg, 46% yield). 1H NMR (400 MHz, $CDCl_3$): δ = 0.68-0.77 (m, 21H), 3.84 (d, J = 1.6 Hz, 2H), 5.73 (t, J = 1.8 Hz, 1H), 7.21-7.25 (m, 1H), 7.28-7.34 (m, 4H), 7.42 (dd, J = 8.4, 4.4 Hz, 1H), 7.50-7.56 (m, 2H), 8.14 (dd, J = 8.0, 1.6 Hz, 1H), 8.76 (dd, J = 4.0, 1.6 Hz, 1H), 8.81 (dd, J = 6.8, 2.0 Hz, 1H), 10.40 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 11.1, 18.4, 39.8, 100.4, 102.0, 112.0, 117.3, 121.6, 122.0, 126.9, 127.4, 128.0, 128.8, 129.6, 134.4, 136.3, 137.7, 139.0, 148.4, 149.5, 166.1 ppm. HRMS (ESI $^+$): calcd for $C_{30}H_{37}N_2O$ Si $[M+H]^+$ 469.2675, found 469.2676.

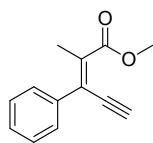


(Z)-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide (6l). A pale yellow liquid (17.8 mg, 47% yield). 1H NMR (400 MHz, $CDCl_3$): δ = 0.91-0.93 (m, 21H), 6.17 (d, J = 12.0 Hz, 1H), 6.38 (d, J = 12.0 Hz, 1H), 7.44 (dd, J = 8.4, 4.0 Hz, 1H), 7.51-7.57 (m, 2H), 8.15 (dd, J = 8.0,

1.6 Hz, 1H), 8.78-8.81 (m, 2H), 10.36 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.2, 18.5, 101.9, 104.1, 117.2, 117.6, 121.6, 122.1, 127.5, 128.0, 134.4, 135.0, 136.4, 139.0, 148.4, 163.5 ppm. HRMS (ESI^+): calcd for $\text{C}_{23}\text{H}_{31}\text{N}_2\text{OSi}$ $[\text{M}+\text{H}]^+$ 379.2206, found 379.2210.



(Z)-methyl 2-methyl-3-phenyl-5-(triisopropylsilyl)pent-2-en-4-ynoate (8). A colourless liquid (49.9 mg, 70%). ^1H NMR (400 MHz, CDCl_3): δ = 1.04-1.11 (m, 21H), 1.98 (s, 3H), 3.83 (s, 3H), 7.28-7.41 (m, 5H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 11.4, 17.6, 18.8, 52.2, 99.4, 106.0, 128.1, 128.2, 128.4, 128.9, 135.5, 138.4, 169.5 ppm. HRMS (ESI^+): calcd for $\text{C}_{22}\text{H}_{33}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 357.2250, found 357.2251.



(E)-methyl 2-methyl-3-phenylpent-2-en-4-ynoate (9). A colourless liquid (19.0 mg, 95% yield). ^1H NMR (400 MHz, CDCl_3): δ = 1.97 (s, 3H), 3.45 (d, J = 4.0 Hz, 1H), 3.85 (s, 3H), 7.31-7.35 (m, 3H), 7.37-7.41 (m, 2H) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ = 17.3, 52.2, 83.2, 85.4, 128.4, 128.45, 128.51, 128.7, 136.7, 138.1, 168.7 ppm. HRMS (ESI^+): calcd for $\text{C}_{13}\text{H}_{12}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$ 223.0735, found 223.0727.

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XI. Copies of ^1H , ^{13}C NMR spectra

