

SUPPORTING INFORMATION

**Facile Synthesis of Diverse Hetero Polyaromatic Hydrocarbons
(PAHs) via Styryl Diels-Alder Reaction of Conjugated Diynes**

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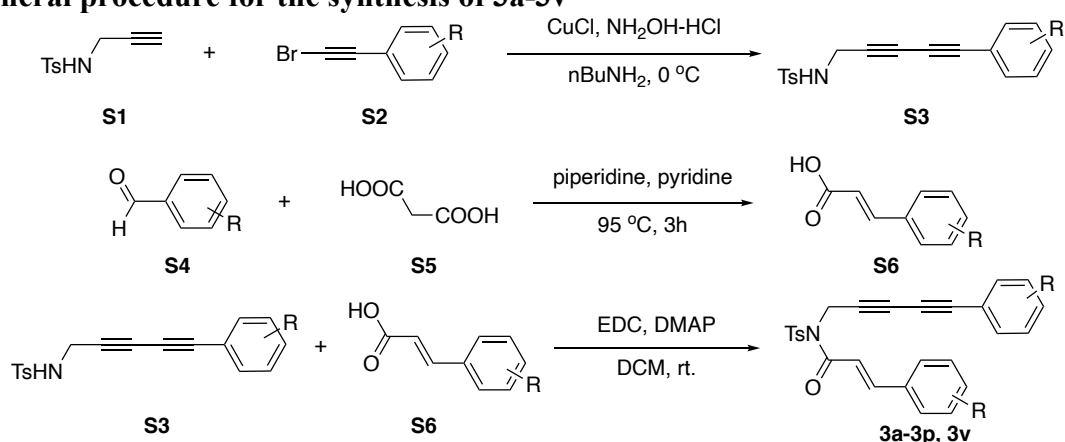
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I. General Methods and Materials

All of the reactions dealing with air and/or moisture-sensitive compounds were carried out under an atmosphere of argon using oven/flame-dried glassware and standard syringe/septa techniques. Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on Bruker Avance NEO-600 MHz and NEO-400 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) or CDCl_3 (δ 7.26 ppm) for ^1H and CDCl_3 (δ 77.00 ppm) for ^{13}C . Flash column chromatography was performed on 230-430 mesh silica gel. Analytical thin layer chromatography was performed with precoated glass baked plates (250 μ) and visualized by fluorescence and by charring after treatment with potassium permanganate stain. Chirality determination was measured in Agilent 1260 infinity HPLC system. HRMS were recorded on Agilent 6320 TOF MS/Agilent 1200 HPLC spectrometer and an Agilent 7890 GC-MS QTOF 7200 and 6540 LC/QTOF spectrometer in the mass-spec facility in the University of South Florida.

II. General Procedures

2.1 General procedure for the synthesis of 3a-3v



Method A: Synthesis of diynes S3

To a round bottom flask with CuCl (1.1 equiv.) add 30% (v/v) nBuNH₂ (0.25 M) aqueous solution at 0 °C. Fill flask with argon and add NH₂OH·HCl until the blue color disappeared. Refill flask with argon again. A solution of terminal alkyne S1 (1 equiv.) in DCM (1 M) (was then added, followed by the slow addition of a solution of bromoalkyne S2 (2 equiv.) in DCM (1 M) over 5 minutes. The reaction mixture was stirred until terminal alkyne disappear on TLC, quenched with saturated aqueous NH₄Cl and extracted with EtOAc for three times. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel to give the desired product.

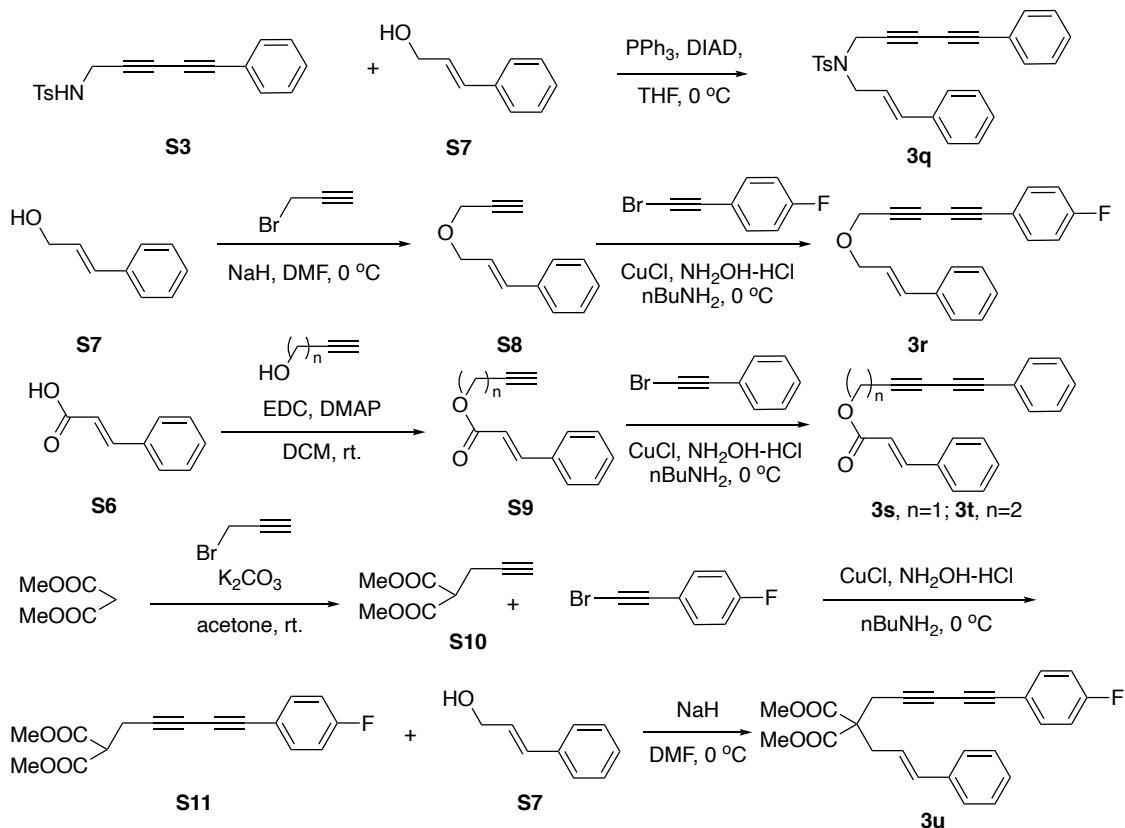
Method B: Synthesis of cinnamic acid S6

To a solution of aryl formaldehyde S4 (1.0 equiv) and malonic acid S5 (1.2 equiv) in dry pyridine (0.1 M) was added slowly of piperidine (0.05 equiv.) at room temperature. Then warm the mixture to 95°C for 3h. The solvent was then poured into a beaker with 1M cold hydrochloric

acid, and the crude products were collected by filtration. Products are further dried by lyophilizer.

Method C: Synthesis of 3a-3v

To a round bottom flask with diynes **S3** (1 equiv.), cinnamic acid **S6** (1.5 equiv.), 4-dimethylaminopyridine (0.1 equiv.) in anhydrous DCM at room temperature add EDC (2 equiv.) slowly. Track the reaction by TLC. The reaction was quenched with water and extracted with EtOAc for three times. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the desired products **3a-3v**.



Method C: Synthesis of 3q

To a solution of amide **S3** (1.0 equiv.), PPh_3 (2.0 equiv.), cinnamic alcohol **S7** (2.0 equiv.) in anhydrous THF (0.1 M) under argon at $0\text{ }^\circ\text{C}$ was added slowly of DIAD (2.2 equiv.). Then warm the mixture to room temperature for 3h. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the desired product **3q**.

Method D: Synthesis of 3r

To a round bottom flask with **S7** (1 equiv.), propargyl bromide (1.2 equiv.) in anhydrous DMF at $0\text{ }^\circ\text{C}$ add NaH (1.2 equiv, 60 % dispersion in mineral oil) slowly. After stirring for 30 min, the reaction solution was warmed up the room temperature for 4 h. The reaction was quenched with water and extracted with EtOAc for three times. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the desired product **S8**. Treat **S8** with **method A** to produce the desired product **3r**.

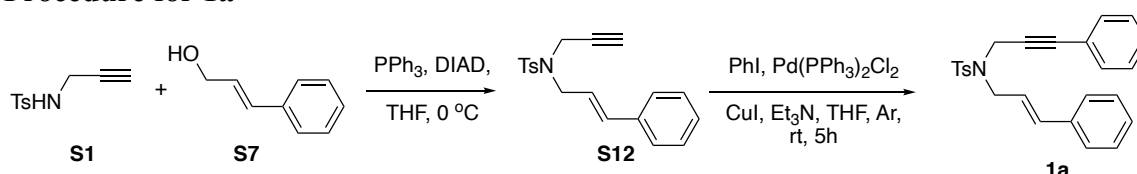
Method E: Synthesis of 3s and 3t

To a round bottom flask with alcohol (1 equiv.), cinnamic acid **S6** (1.5 equiv.), 4-dimethylaminopyridine (0.1 equiv.) in anhydrous DCM at room temperature add EDC (2 equiv.) slowly. Track the reaction by TLC. The reaction was quenched with water and extracted with EtOAc for three times. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the desired products **S9**. Treat **S9** with **method A** to produce the desired product **3s** and **3t**.

Method F: Synthesis of 3u

To a round bottom flask with dimethyl malonate (1 equiv.), propargyl bromide (1.2 equiv.) in anhydrous acetone at room temperature add K_2CO_3 (5 equiv.). After stirring for 12 h, the reaction was quenched with water and extracted with EtOAc for three times. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the desired product **S10**. Treat **S10** with **method A** to produce the desired product **S11**. Then treat **S11** with **method C** to produce the desired product **3u**.

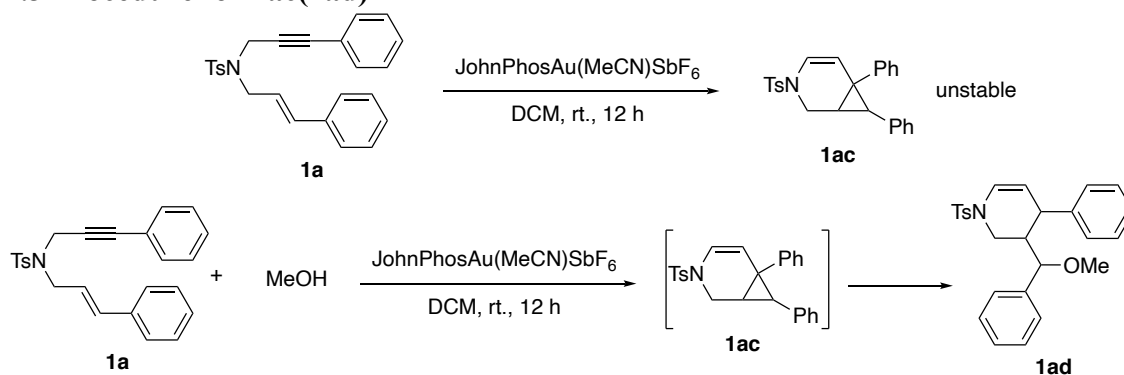
2.2 Procedure for 1a



To a solution of amide **S1** (1.0 equiv.), PPh_3 (2.0 equiv.), cinnamic alcohol **S7** (2.0 equiv.) in anhydrous THF (0.1 M) under argon at 0 °C was added slowly of DIAD (2.2 equiv.). Then warm the mixture to room temperature for 3h. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the desired product **S12**.

To a solution of amide **S12** (1.0 equiv.), $Pd(PPh_3)_2Cl_2$ (0.1 equiv.), CuI (0.05 equiv.) in anhydrous THF under argon at 0 °C was added Et_3N (5 equiv.), followed adding PhI (1.5 equiv.). Then stir the mixture at room temperature for 3h. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the desired product **1a**.

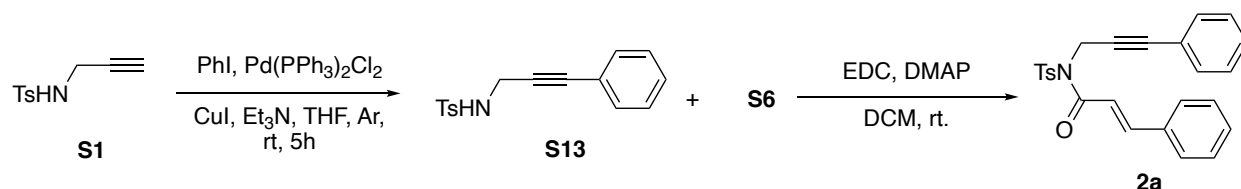
2.3 Procedure for 1ac(1ad)



To a solution of amide **1a** (1.0 equiv in anhydrous DCM (0.1 M) at room temperature was added $JohnPhosAu(MeCN)SbF_6$ (0.1 equiv.). After 12 h, the reaction is messy because of the

decomposition of **1ac**. The product **1ac** is not stable and easily decompose during separation. We use MeOH as nucleophile trapping **1ac** to produce product **1ad**. To a solution of amide **1a** (1.0 equiv.) and MeOH (10 equiv.) in anhydrous DCM (0.1 M) at room temperature was added JohnPhosAu(MeCN)SbF₆ (0.1 equiv.). The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the desired product **1ad**.

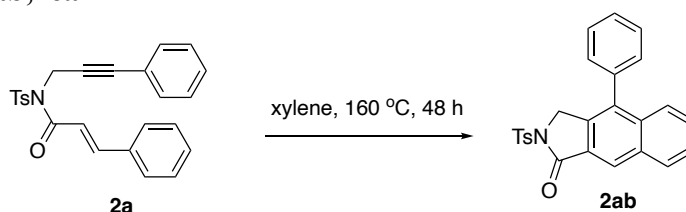
2.4 Procedure for 2a



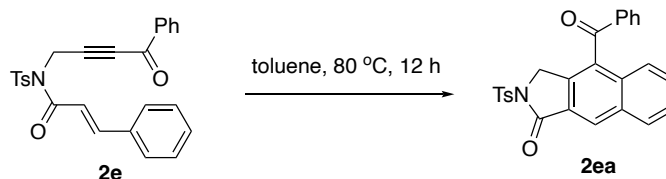
To a solution of amide **S1** (1.0 equiv.), Pd(PPh₃)₂Cl₂ (0.1 equiv.), CuI (0.05 equiv.) in anhydrous THF under argon at 0 °C was added Et₃N (5 equiv.), followed adding PhI (1.5 equiv.). Then stir the mixture at room temperature for 3h. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the desired product **S13**.

To a round bottom flask with amine **S13** (1 equiv.), cinnamic acid **S6** (1.5 equiv.), 4-dimethylaminopyridine (0.1 equiv.) in anhydrous DCM at room temperature add EDC (2 equiv.) slowly. Track the reaction by TLC. The reaction was quenched with water and extracted with EtOAc for three times. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the desired product **2a**.

2.5 Procedure for 2ab,2ea

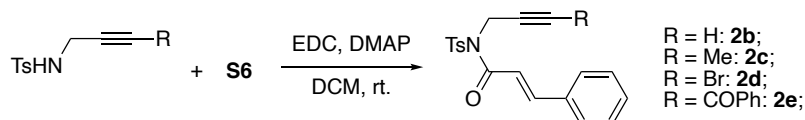


The resulting mixture of **2a** (0.2mmol) in xylene (10 mL) in a 20 mL vial was heated under 160 °C for 48 h in dark. Track the reaction by TLC. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the desired product **2ab**.



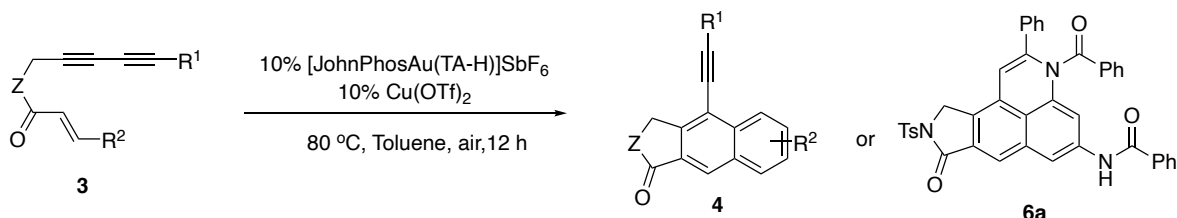
The resulting mixture of **2e** (0.2mmol) in toluene (10 mL) in a 20 mL vial was heated under 80 °C for 12 h dark. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the desired product **2ea** with 58% conversion and 53% yield.

2.6 Procedure for 2b-2e



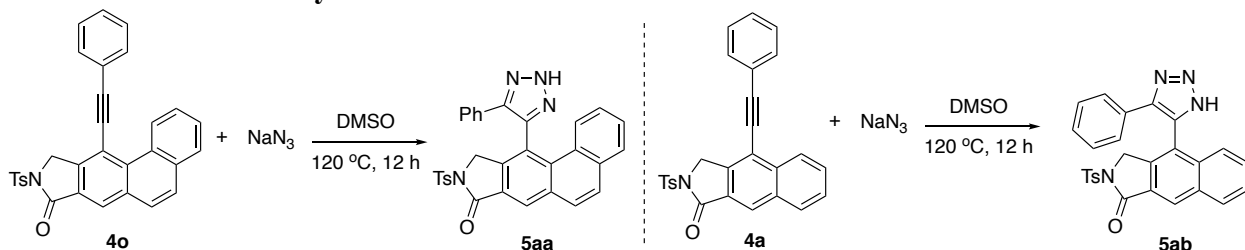
To a round bottom flask with amine (1 equiv.), cinnamic acid **S6** (1.5 equiv.), 4-dimethylaminopyridine (0.1 equiv.) in anhydrous DCM at room temperature add EDC (2 equiv.) slowly. Track the reaction by TLC. The reaction was quenched with water and extracted with EtOAc for three times. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the desired product **2b-2e**.

2.7 General procedure for the synthesis of 4a-4s and 6a



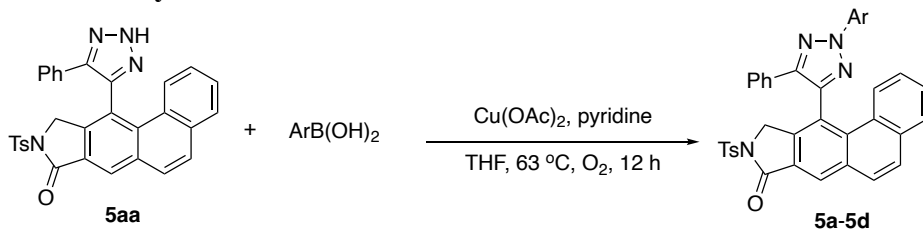
To a 20 mL vial with **3** (0.2mmol) in toluene (10 mL) was added 10% JohnPhosAu(TA-H)SbF₆ (17 mg), 10% Cu(OTf)₂ (7.2mg) subsequently. The resulting mixture was heated under 80 °C for 12 h in air under dark. Track the reaction by TLC. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the desired product **4a-4s** or **6a**.

2.8 Procedure for the synthesis of 5aa and 5ab



To a round bottom flask with **4o** or **4a** (1 equiv.) in DMSO (0.1 M) was added NaN₃ (2 equiv.) slowly at room temperature. Then warm the mixture to 120°C and stir for 12h. The reaction was quenched with water and extracted with EtOAc for three times. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the desired product **5aa** or **5ab**. Both **5aa** and **5ab** have poor solubility in CDCl₃, *d*₆-DMSO. We used CDCl₃:CD₃OD (10:1) as solvent for NMR.

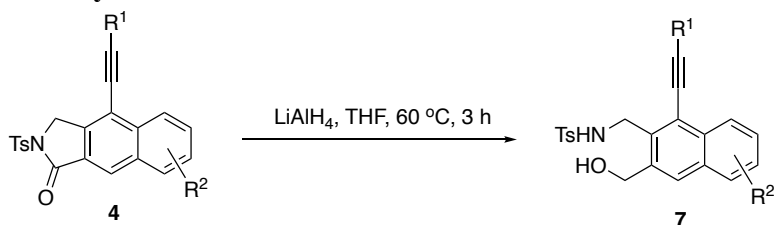
2.9 Procedure for the synthesis of 5a-5d



To a round bottom flask successively added triazole **5aa** (1 equiv.), arylboronic acid (2 equiv.), THF (0.1M), pyridine (2 equiv.) and Cu(OAc)₂ (0.1 equiv.) at room temperature. The bottle was

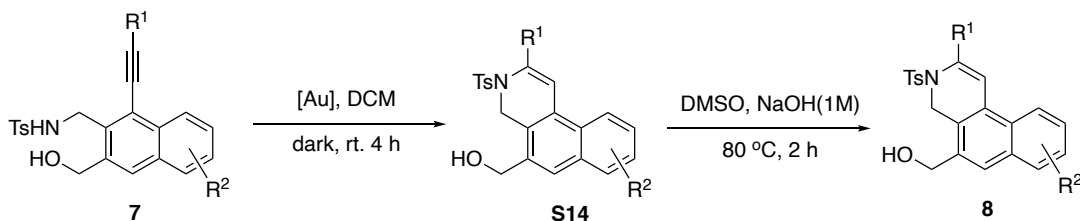
equipped with an oxygen balloon above. Then warm the mixture to 63°C and stir for 12h. Track the reaction by TLC. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the desired products **5a-5d**.

2.10 Procedure for the synthesis of **7a-7d**



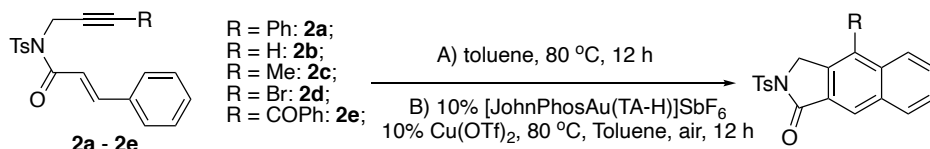
To a round bottom flask with **4** (1 equiv.) in dry THF (0.1 M) was added LiAlH₄ (2 equiv.) slowly at room temperature. Then warm the mixture to 60°C and stir for 3h. Track the reaction by TLC. The reaction was quenched with water and extracted with EtOAc for three times. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the desired products **7a-7d**.

2.11 Procedure for the synthesis of **8a-8d**



To a round bottom flask with **7a**, **7b**, **7d** (1 equiv.) in DCM (0.1 M) was added JohnPhosAu(MeCN)SbF₆ (0.1 equiv.) at room temperature in dark. (**7c** was added PPh₃AuNTf₂) at room temperature in dark). Then stir the mixture for 4 h. The solvent was then removed under reduced pressure to get products **S14**. Without purification, to the flask with **S14** was added DMSO and NaOH (1M aq., 3 equiv.) at room temperature. Then warm the mixture to 80°C and stir for 2 h. Track the reaction by TLC. The reaction was quenched with water and extracted with EtOAc for three times. The solvent was then removed under reduced pressure, and the crude product was purified by column chromatography on silica gel to afford the desired products **8a-8d**.

2.11 Procedure for the **2a-2e** ISDDA reaction



Condition A: The resulting mixture of **2a-2e** (0.2mmol) in toluene (10 mL) in a 20 mL vial was heated under 80 °C for 12 h dark. **2a-2d** have no conversion. **2e** afford the desired product **2ea** with 58% conversion and 53% yield.

Condition B: To a 20 mL vial with **2a-2e** (0.2mmol) in toluene (10 mL) was added 10% JohnPhosAu(TA-H)SbF₆ (17 mg), 10% Cu(OTf)₂ (7.2mg) subsequently. The resulting mixture

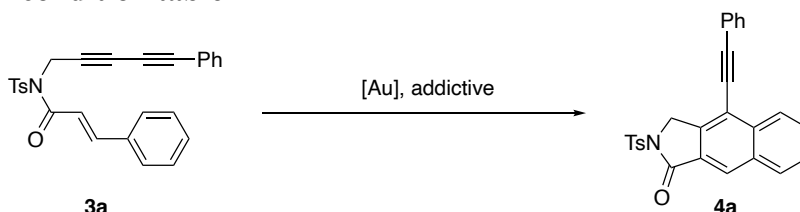
was heated under 80 °C for 12 h in air under dark. **2a** have no conversion. **2b** and **2c** starting materials decomposed and no clear products are identified. For **2d**, head-to-head coupling products are detected as literature reported.¹ **2e** afford the desired product **2ea** with 100% conversion and 40% yield.

Reference

1 M. Kreuzahler and G. Haberhauer, Cyclopropenylmethyl Cation: A Concealed Intermediate in Gold(I)-Catalyzed Reactions, *Angew. Chem. Int. Ed.*, 2020, **59**, 17739-17749.

III. Condition Optimization

3.1 Optimization condition table^{[a][b]}

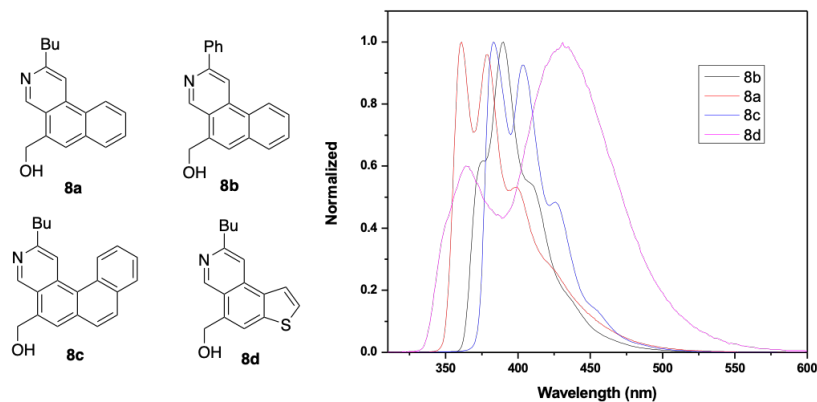


Entry	Au Catalyst (10%)	Additive (10%)	Temp. (°C)	Solvents	Yield (%) 2a
1	-	-	80	toluene	55
2	JohnPhos(TA-H)AuSbF ₆	-	80	toluene	84
3	JohnPhos(TA-H)AuSbF ₆	Cu(OTf) ₂	80	toluene	95
4	JohnPhos(TA-H)AuSbF ₆	Ga(OTf) ₃	80	toluene	14
6	JohnPhos(TA-H)AuSbF ₆	Zn(OTf) ₂	80	toluene	77
7	JohnPhos(TA-H)AuSbF ₆	Fe(OTf) ₃	80	toluene	5
8	JohnPhos(TA-H)AuSbF ₆	CuCl	80	toluene	77
9	JohnPhos(TA-H)AuSbF ₆	CuCl ₂	80	toluene	80
10	JohnPhos(TA-H)AuSbF ₆	Cu(OAc) ₂	80	toluene	72
11	JohnPhos(TA-H)AuSbF ₆	Cu(acac) ₂	80	toluene	65
12	JohnPhos(TA-H)AuSbF ₆	CuSO ₄	80	toluene	89
13	JohnPhos(TA-H)AuSbF ₆	CuOTf	80	toluene	84
14	JohnPhos(TA-H)AuSbF ₆	CuI	80	toluene	84
15	PPh ₃ AuNTf ₂	-	80	toluene	69
16	PPh ₃ AuCl	AgSbF ₆	80	toluene	34
17	PPh ₃ (TA-H)AuSbF ₆	-	80	toluene	75
18	IPrAuNTf ₂	-	80	toluene	51
19	JohnPhosAuCl	AgSbF ₆	80	toluene	60
20	XPhos(TA-H)AuSbF ₆	-	80	toluene	68
21	-	Ga(OTf) ₃	80	toluene	22
22	-	Cu(OTf) ₂	80	toluene	46
23	-	Zn(OTf) ₂	80	toluene	52
24	-	CuSO ₄	80	toluene	54
25	-	AgSbF ₆	80	toluene	48
26	JohnphosAuNTf ₂	-	80	toluene	76
27	XphosAuNTf ₂	-	80	toluene	65
28	JohnPhos(MeCN)AuSbF ₆	-	80	toluene	17
29	JohnPhos(2,4-NO ₂ -TA)AuSbF ₆	-	80	toluene	77
30	5% JohnPhos(TA-H)AuSbF ₆	5% Cu(OTf) ₂	80	toluene	75
31	JohnPhos(TA-H)AuSbF ₆	Cu(OTf) ₂	80	MeCN	50
32	JohnPhos(TA-H)AuSbF ₆	Cu(OTf) ₂	80	DCE	24
33	JohnPhos(TA-H)AuSbF ₆	Cu(OTf) ₂	80	DMSO	60
34	JohnPhos(TA-H)AuSbF ₆	Cu(OTf) ₂	80	DMF	67
35	JohnPhos(TA-H)AuSbF ₆	Cu(OTf) ₂	rt.	toluene	0
36	JohnPhos(TA-H)AuSbF ₆	Cu(OTf) ₂	60	toluene	26(conv.30%)
37	JohnPhos(TA-H)AuSbF ₆	Cu(OTf) ₂ (under light)	80	toluene	88
38	JohnPhos(TA-H)AuSbF ₆	Cu(OTf) ₂ (under argon)	80	toluene	27

^aStandard reaction conditions: to a solution of **3a** (0.2mmol) in toluene (10 mL), 10% JohnPhosAu(TA-H)SbF₆ (17 mg), 10% Cu(OTf)₂ (7.2mg) was added subsequently. The resulting mixture was heated under 80 °C for 12 h in air under dark. ^bisolated yields

IV. Optical Properties

Fluorescence detection Procedures: A series of stock solution of compound **8a-8d** (10^{-5} mol/L) was prepared by dissolving the corresponding amount of compound powder in DCE, which was stored in the dark. For fluorescence detection, 5mL stock solutions were used. The fluorescence spectra of mixed solutions were recorded with the corresponding excitation wavelength at room temperature (298 K).



Name	λ^{ex} (nm)	λ^{em} (nm)	$\Delta\lambda$ (nm)
8a	254	360&379	125
8c	286	384&406	120
8d	248	366&432	184
8b	287	370	83

V. ORTEP Drawing of the Crystal Structure

X-ray diffraction data were measured on Bruker D8 Venture PHOTON II CMOS diffractometer equipped with a Cu K α INCOATEC ImuS micro-focus source ($\lambda = 1.54178 \text{ \AA}$). Indexing was performed using APEX4 [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space group was determined using XPREP implemented in APEX3 [1]. Structure was solved using SHELXT [4] and refined using SHELXL-2018/3 [5] (full-matrix least-squares on F2) through OLEX2 interface program [6]. Ellipsoid plot was done with Platon [7]. **5ab**, **6a**: Hydrogen atoms of -NH groups were found from difference Fourier map and was freely refined. **6a**: Disordered chloroform molecule were refined with restraints. All remaining hydrogen atoms were refined using riding model. Data and refinement conditions are shown in **Tables S1 - S4**.

[1] Bruker (2022). APEX4. Bruker AXS LLC, Madison, Wisconsin, USA.

[2] Bruker SAINT. Bruker AXS LLC, Madison, Wisconsin, USA.

[3] Krause, L., Herbst-Irmer, R., Sheldrick, G. M., Stalke, D. (2015).

"Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination" *J. Appl. Cryst.* 48, 3-10.

[4] Sheldrick, G. M. (2015). "SHELXT - Integrated space-group and crystal-structure determination", *Acta Cryst.* A71, 3-8.

[5] Sheldrick, G. M. (2015) "Crystal structure refinement with SHELXL", *Acta Cryst.*, C71, 3-8

[6] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program (2009). *J. Appl. Cryst.*, 42, 339-341

[7] A.L.Spek, The Program PLATON is designed as a Multipurpose Crystallographic Tool.

1980-2021 A.L.Spek, Utrecht University, Utrecht, The Netherlands. *Acta Cryst.* 2020, E76, 1-11

Table S1 Crystal data and structure refinement for 4j.

Identification code	4j
Empirical formula	C ₂₇ H ₁₇ BrFNO ₃ S
Formula weight	534.39
Temperature/K	100.00
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	7.9493(2)
b/Å	24.1157(5)
c/Å	11.4002(2)
α/°	90
β/°	91.3000(10)
γ/°	90
Volume/Å ³	2184.89(8)
Z	4
ρ _{calc} /cm ³	1.625
μ/mm ⁻¹	3.806
F(000)	1080.0
Crystal size/mm ³	0.2 × 0.05 × 0.03
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	7.332 to 159.172
Index ranges	-9 ≤ h ≤ 10, -30 ≤ k ≤ 30, -14 ≤ l ≤ 13
Reflections collected	52092
Independent reflections	4705 [R _{int} = 0.0530, R _{sigma} = 0.0201]
Data/restraints/parameters	4705/0/308
Goodness-of-fit on F ²	1.057
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0290, wR ₂ = 0.0702
Final R indexes [all data]	R ₁ = 0.0339, wR ₂ = 0.0733
Largest diff. peak/hole / e Å ⁻³	0.33/-0.48

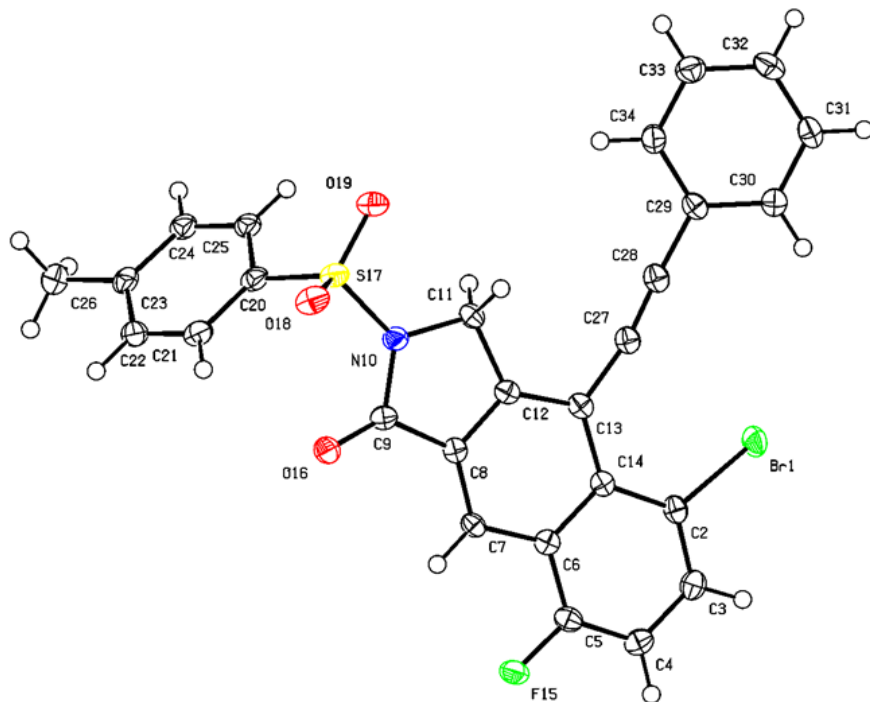


Figure S1. Ellipsoid plot of **4j**. Anisotropic displacement parameters were drawn at 50% probability level.
CCDC: 2161060

Table S2 Crystal data and structure refinement for 4s.

Identification code	4s
Empirical formula	C ₂₀ H ₁₂ O ₂
Formula weight	284.30
Temperature/K	100.00
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	16.0281(2)
b/Å	5.29640(10)
c/Å	16.7488(2)
α/°	90
β/°	99.9850(10)
γ/°	90
Volume/Å ³	1400.29(4)
Z	4
ρ _{calc} /cm ³	1.349
μ/mm ⁻¹	0.690
F(000)	592.0
Crystal size/mm ³	0.26 × 0.07 × 0.03
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	5.598 to 160.1
Index ranges	-20 ≤ h ≤ 20, -6 ≤ k ≤ 6, -21 ≤ l ≤ 21
Reflections collected	26828
Independent reflections	3037 [R _{int} = 0.0426, R _{sigma} = 0.0206]
Data/restraints/parameters	3037/0/199
Goodness-of-fit on F ²	1.056
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0359, wR ₂ = 0.0946
Final R indexes [all data]	R ₁ = 0.0402, wR ₂ = 0.0989
Largest diff. peak/hole / e Å ⁻³	0.20/-0.24

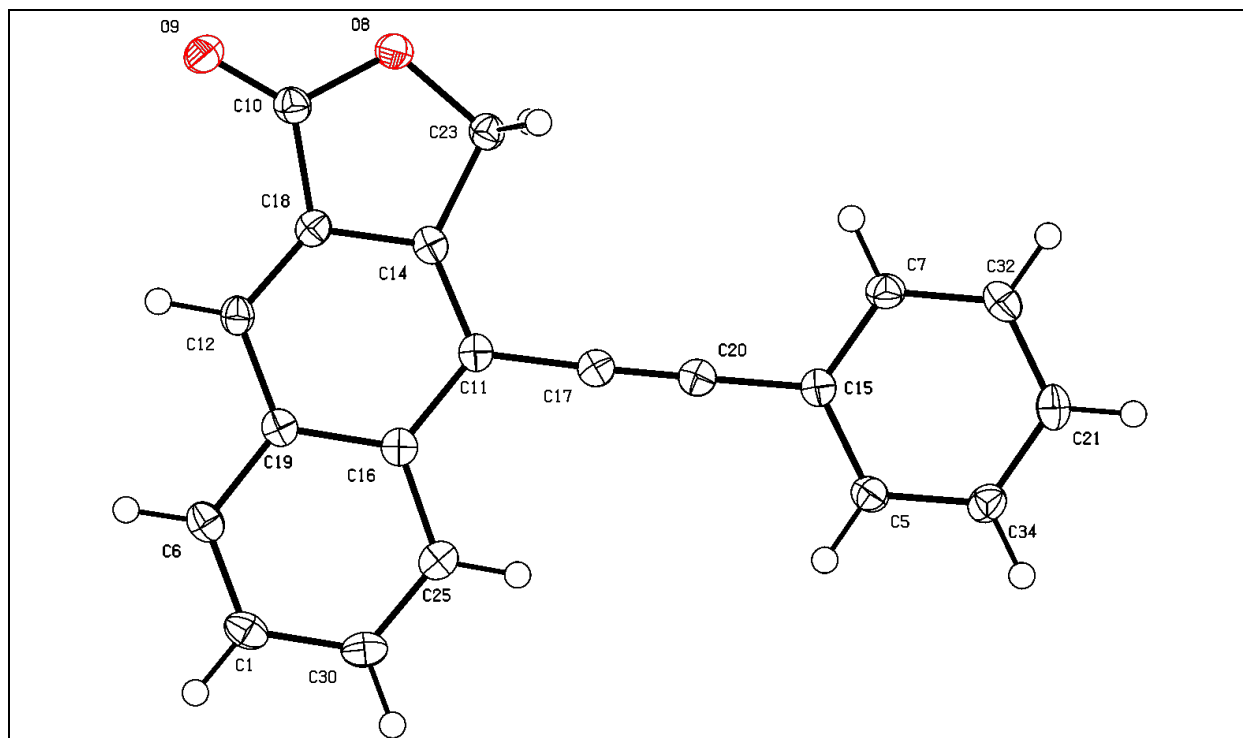


Figure S2. Ellipsoid plot of **4s**. Anisotropic displacement parameters were drawn at 50% probability level.
CCDC: 2161061

Table S3 Crystal data and structure refinement for 5ab.	
Identification code	5ab
Empirical formula	C ₂₇ H ₂₀ N ₄ O ₃ S
Formula weight	480.53
Temperature/K	296.00
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	9.2159(2)
b/Å	24.1709(5)
c/Å	21.1041(4)
α/°	90
β/°	101.4372(7)
γ/°	90
Volume/Å ³	4607.73(16)
Z	8
ρ _{calc} /cm ³	1.385
μ/mm ⁻¹	1.565
F(000)	2000.0
Crystal size/mm ³	0.19 × 0.16 × 0.04
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	5.624 to 160.73
Index ranges	-11 ≤ h ≤ 11, -29 ≤ k ≤ 30, -26 ≤ l ≤ 26
Reflections collected	99565
Independent reflections	10021 [R _{int} = 0.0503, R _{sigma} = 0.0250]
Data/restraints/parameters	10021/0/641
Goodness-of-fit on F ²	1.044
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0430, wR ₂ = 0.1153
Final R indexes [all data]	R ₁ = 0.0522, wR ₂ = 0.1242
Largest diff. peak/hole / e Å ⁻³	0.31/-0.48

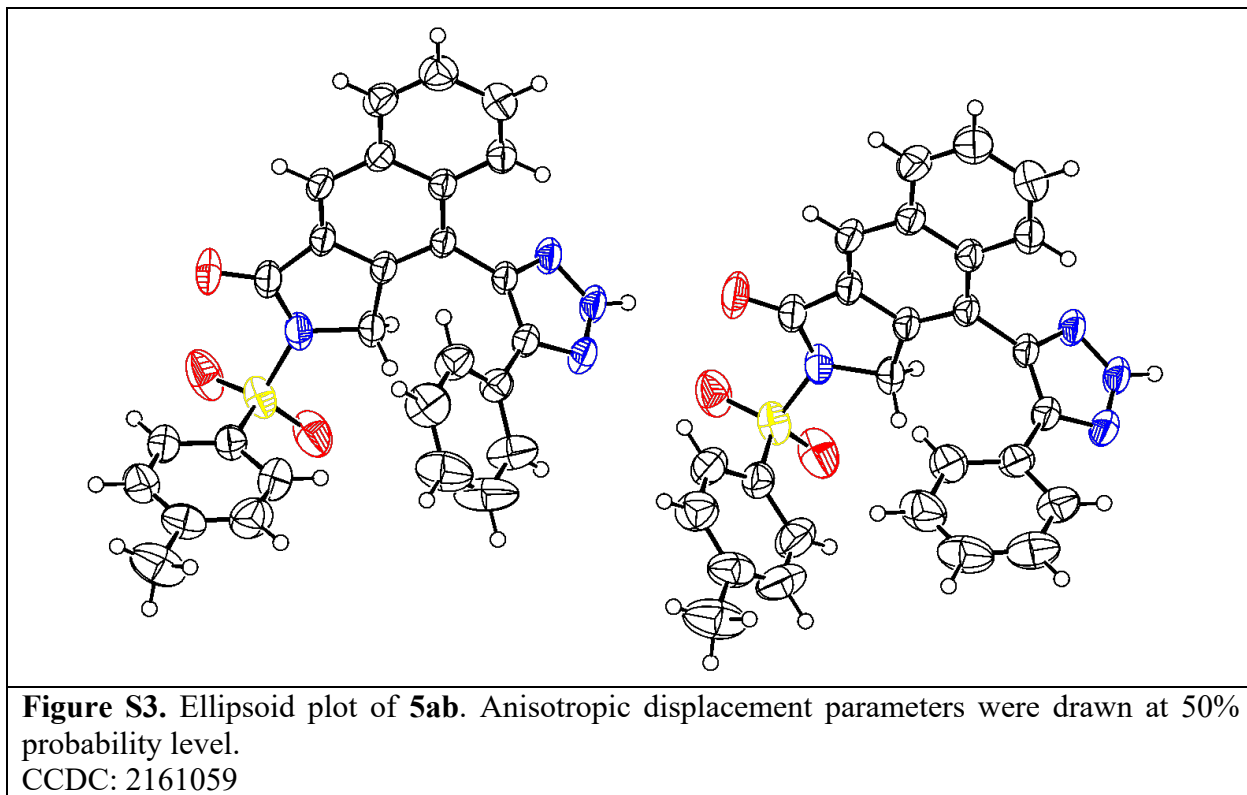


Table S4 Crystal data and structure refinement for 6a.

Identification code	6a
Empirical formula	C _{45.91} H _{38.84} Cl _{1.83} N ₃ O ₇ S
Moiety formula	C ₄₁ H ₂₉ N ₃ O ₅ S, C ₄ H ₈ O ₂ , 0.916(CH ₂ Cl ₂)
Formula weight	841.72
Temperature/K	100.00
Crystal system	triclinic
Space group	P-1
a/Å	10.6653(3)
b/Å	12.1532(3)
c/Å	16.9707(5)
α/°	70.450(1)
β/°	89.007(1)
γ/°	74.967(1)
Volume/Å ³	1996.1(1)
Z	2
ρ _{calc} /cm ³	1.400
μ/mm ⁻¹	2.327
F(000)	877.0
Crystal size/mm ³	0.2 × 0.13 × 0.03
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	5.542 to 158.934
Index ranges	-13 ≤ h ≤ 12, -15 ≤ k ≤ 15, -21 ≤ l ≤ 21
Reflections collected	40341
Independent reflections	8344 [R _{int} = 0.0364, R _{sigma} = 0.0240]
Data/restraints/parameters	8344/10/568
Goodness-of-fit on F ²	1.045
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0367, wR ₂ = 0.0946
Final R indexes [all data]	R ₁ = 0.0402, wR ₂ = 0.0977
Largest diff. peak/hole / e Å ⁻³	0.45/-0.48

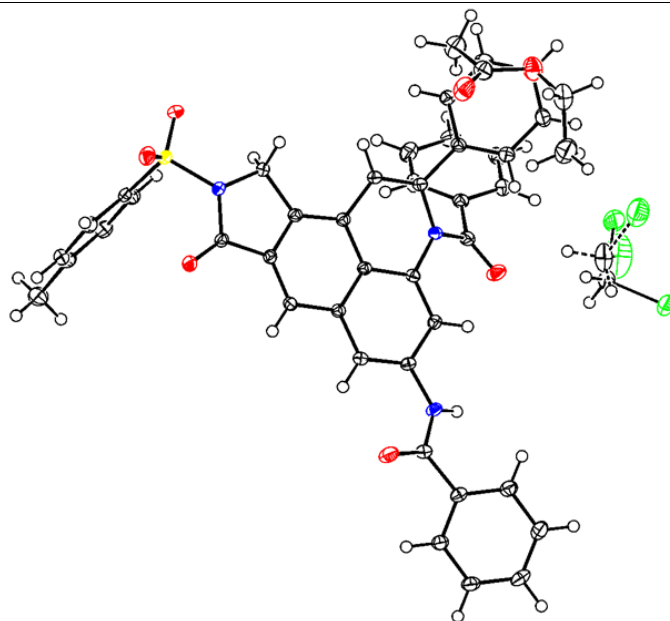
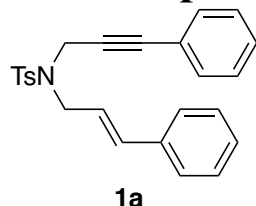


Figure S4. Ellipsoid plot of **6a**. Anisotropic displacement parameters were drawn at 50% probability level. Chloroform molecule is disordered.
CCDC: 2161058

VI. Compound Characterization



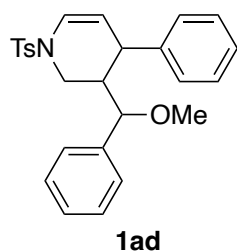
N-cinnamyl-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide

1a was prepared following the Procedure 2.2 and purified by column chromatography (Hexane: Ethyl acetate = 10:1) in 75% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.80 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.36-7.23 (m, 10H), 7.09-7.07 (m, 2H), 6.61 (d, *J* = 15.8 Hz, 1H), 6.16 (dt, *J* = 15.8, 6.8 Hz, 1H), 4.34 (s, 2H), 4.06-4.05 (m, 2H), 2.35 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 143.5, 136.17, 136.03, 134.9, 131.5, 129.6, 128.6, 128.4, 128.14, 128.06, 127.87, 126.6, 123.1, 122.2, 85.8, 81.8, 48.9, 36.9, 21.4

HRMS *m/z* (ESI) calcd. for C₂₅H₂₄NO₂S⁺ (M+H)⁺ 402.1523, found 402.1540



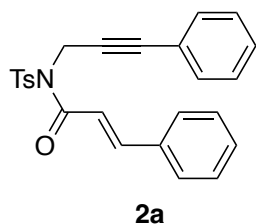
3-(methoxy(phenyl)methyl)-4-phenyl-1-tosyl-1,2,3,4-tetrahydropyridine

1ad was prepared following the Procedure 2.3 and purified by column chromatography (Hexane: Ethyl acetate = 10:1) in 85% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.03-6.98 (m, 8H), 6.83-6.81 (m, 2H), 5.68 (t, *J* = 3.3 Hz, 1H), 4.31 (d, *J* = 7.4 Hz, 1H), 4.02 (td, *J* = 11.4, 3.7 Hz, 2H), 3.52 (dt, *J* = 16.9, 2.6 Hz, 1H), 3.12 (s, 4H), 2.77 (dd, *J* = 11.2, 3.6 Hz, 1H), 2.44 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 143.6, 141.0, 139.0, 138.5, 133.2, 129.7, 127.78, 127.73, 127.4, 126.4, 126.2, 122.8, 83.2, 57.0, 45.6, 44.74, 44.58, 21.5

HRMS *m/z* (ESI) calcd. for C₂₆H₂₈NO₃S⁺ (M+H)⁺ 434.1785, found 434.1785



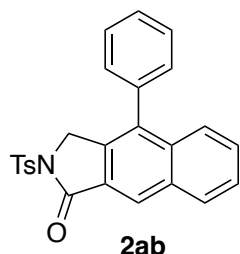
N-(3-phenylprop-2-yn-1-yl)-*N*-tosylcinnamamide

2a was prepared following the Procedure 2.4 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 83% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 15.4 Hz, 1H), 7.52-7.51 (m, 2H), 7.40-7.37 (m, 3H), 7.34 (dt, *J* = 6.1, 1.9 Hz, 2H), 7.32-7.27 (m, 4H), 4.98 (s, 2H), 2.37 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.3, 146.6, 145.0, 136.7, 134.4, 131.8, 130.7, 129.7, 129.0, 128.59, 128.40, 128.24, 128.0, 122.3, 117.6, 84.3, 83.8, 36.3, 21.6

HRMS *m/z* (ESI) calcd. for C₂₅H₂₂NO₃S⁺ (M+H)⁺ 416.1315, found 416.1311



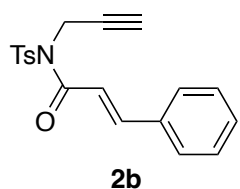
4-phenyl-2-tosyl-2,3-dihydro-1H-benzo[f]isoindol-1-one

2ab was prepared following the General Procedure 2.5 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 45% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 8.40 (s, 1H), 8.03 (d, *J* = 8.3 Hz, 3H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.58-7.52 (m, 5H), 7.34 (t, *J* = 8.5 Hz, 4H), 4.80 (s, 2H), 2.42 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 166.2, 145.2, 135.8, 135.41, 135.37, 134.9, 133.36, 133.30, 130.0, 129.8, 129.4, 129.1, 128.8, 128.5, 128.2, 127.4, 126.7, 126.0, 125.6, 49.6, 21.7

HRMS *m/z* (ESI) calcd. for C₂₅H₂₀NO₃S⁺ (M+H)⁺ 414.1159, found 414.1182



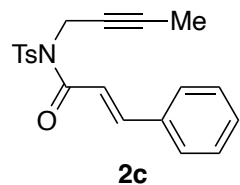
N-(prop-2-yn-1-yl)-N-tosylcinnamamide

2b was prepared following the General Procedure 2.6 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 92% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.93-7.92 (m, 2H), 7.69 (d, *J* = 15.4 Hz, 1H), 7.50-7.48 (m, 2H), 7.39 (td, *J* = 3.9, 2.5 Hz, 3H), 7.29 (q, *J* = 12.1 Hz, 3H), 4.75 (d, *J* = 2.4 Hz, 2H), 2.40 (s, 3H), 2.31 (t, *J* = 2.4 Hz, 1H).

¹³C NMR ((151 MHz; CDCl₃): δ 165.2, 146.7, 145.2, 136.5, 134.3, 130.8, 129.8, 129.0, 128.4, 127.9, 117.4, 78.4, 72.6, 35.4, 21.7

HRMS *m/z* (ESI) calcd. for C₁₉H₁₈NO₃S⁺ (M+H)⁺ 340.1002, found 340.0989



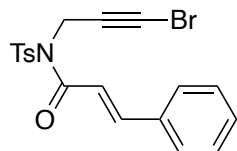
N-(but-2-yn-1-yl)-N-tosylcinnamamide

2c was prepared following the General Procedure 2.6 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 83% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 15.4 Hz, 1H), 7.50 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.39 (dt, *J* = 5.3, 2.8 Hz, 3H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.26 (s, 1H), 4.70 (q, *J* = 2.3 Hz, 2H), 2.41 (s, 3H), 1.79 (t, *J* = 2.3 Hz, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.4, 146.4, 144.9, 136.7, 134.4, 130.7, 129.6, 128.9, 128.4, 128.0, 117.6, 80.7, 73.8, 36.1, 21.6, 3.6

HRMS *m/z* (ESI) calcd. for C₂₀H₂₀NO₃S⁺ (M+H)⁺ 354.1159, found 354.1179



2d

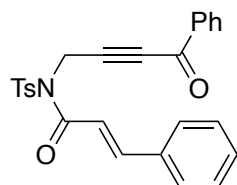
N-(3-bromoprop-2-yn-1-yl)-*N*-tosylcinnamamide

2d was prepared following the General Procedure 2.6 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 75% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 15.4 Hz, 1H), 7.52-7.50 (m, 2H), 7.40 (dq, *J* = 5.0, 2.5 Hz, 3H), 7.36 (d, *J* = 15.4 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 4.75 (s, 2H), 2.41 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.2, 146.8, 145.2, 136.4, 134.3, 130.8, 129.8, 129.0, 128.4, 127.8, 117.4, 74.7, 44.6, 36.5, 21.7

HRMS *m/z* (ESI) calcd. for C₁₉H₁₇BrNO₃S⁺ (M+H)⁺ 418.0108, found 418.0105



2e

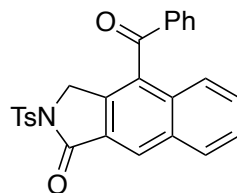
N-(4-oxo-4-phenylbut-2-yn-1-yl)-*N*-tosylcinnamamide

2e was prepared following the General Procedure 2.6 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 85% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 8.02-8.01 (m, 2H), 7.94-7.92 (m, 2H), 7.73 (d, *J* = 15.5 Hz, 1H), 7.61-7.58 (m, 1H), 7.54-7.53 (m, 2H), 7.46-7.41 (m, 6H), 7.28-7.26 (m, 2H), 5.01 (s, 2H), 2.33 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 177.1, 165.2, 147.1, 145.6, 136.29, 136.14, 134.28, 134.24, 130.9, 130.1, 129.6, 129.0, 128.59, 128.49, 127.8, 117.3, 88.6, 81.8, 35.7, 21.6

HRMS *m/z* (ESI) calcd. for C₂₆H₂₂NO₄S⁺ (M+H)⁺ 444.1265, found 444.1275



2ea

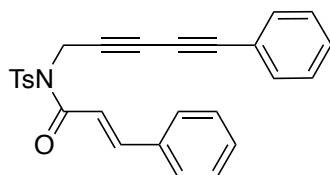
4-benzoyl-2-tosyl-2,3-dihydro-1*H*-benzo[*f*]isoindol-1-one

2ea was prepared following the General Procedure 2.5 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 53% yield (58% conversion) as white solid.

¹H NMR (600 MHz; CDCl₃): δ 8.50 (s, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.80-7.78 (m, 2H), 7.70-7.66 (m, 2H), 7.59-7.55 (m, 2H), 7.49 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 4.88 (s, 2H), 2.42 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 196.3, 165.3, 145.5, 136.6, 135.1, 134.7, 133.5, 133.26, 133.06, 132.5, 130.3, 129.94, 129.82, 129.64, 129.2, 128.2, 128.0, 127.6, 127.3, 125.8, 49.0, 21.7

HRMS *m/z* (ESI) calcd. for C₂₆H₂₀NO₄S⁺ (M+H)⁺ 442.1108, found 442.1120



3a

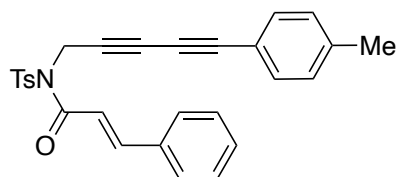
***N*-(5-phenylpenta-2,4-diyne-1-yl)-*N*-tosylcinnamamide**

3a was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 84% yield as yellow solid.

¹H NMR (600 MHz; CDCl₃): δ 7.93 (d, *J* = 6.9 Hz, 2H), 7.71 (dd, *J* = 15.4, 0.9 Hz, 1H), 7.52 (dd, *J* = 5.2, 2.0 Hz, 2H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.41-7.31 (m, 9H), 4.89 (d, *J* = 1.3 Hz, 2H), 2.39 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.2, 146.9, 145.4, 136.3, 134.3, 132.6, 130.9, 129.9, 129.5, 129.0, 128.5, 127.9, 121.3, 117.3, 77.9, 73.3, 69.1, 36.4, 21.7

HRMS *m/z* (ESI) calcd. for C₂₇H₂₂NO₃S⁺ (M+H)⁺ 440.1315, found 440.1313



3b

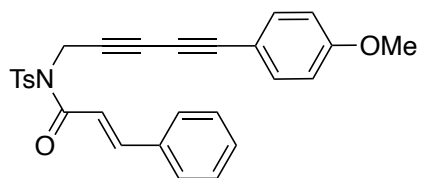
***N*-(5-(*p*-tolyl)penta-2,4-diyne-1-yl)-*N*-tosylcinnamamide**

3b was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 85% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 15.4 Hz, 1H), 7.52 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.40 (dd, *J* = 5.1, 1.7 Hz, 3H), 7.35 (q, *J* = 11.5 Hz, 5H), 7.13 (d, *J* = 8.1 Hz, 2H), 4.88 (s, 2H), 2.39 (s, 3H), 2.36 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.2, 146.8, 145.3, 139.8, 136.4, 134.3, 132.6, 130.8, 129.9, 129.2, 129.0, 128.5, 127.9, 118.2, 117.4, 78.2, 76.7, 72.7, 69.3, 36.4, 21.68, 21.64

HRMS *m/z* (ESI) calcd. for C₂₈H₂₄NO₃S⁺ (M+H)⁺ 454.1472, found 454.1500



3c

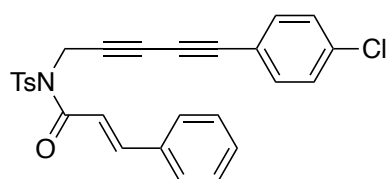
***N*-(5-(4-methoxyphenyl)penta-2,4-diyne-1-yl)-*N*-tosylcinnamamide**

3c was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 80% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.93-7.92 (m, 2H), 7.70 (d, *J* = 15.4 Hz, 1H), 7.52-7.51 (m, 2H), 7.43-7.40 (m, 5H), 7.35-7.32 (m, 3H), 6.85-6.83 (m, 2H), 4.88 (s, 2H), 3.82 (s, 3H), 2.39 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.2, 160.5, 146.8, 145.2, 136.4, 134.35, 134.28, 130.8, 129.9, 129.0, 128.5, 127.9, 117.4, 114.2, 113.2, 78.1, 76.4, 72.2, 69.4, 55.4, 36.4, 21.7

HRMS *m/z* (ESI) calcd. for C₂₈H₂₄NO₄S⁺ (M+H)⁺ 470.1421, found 470.1443



3d

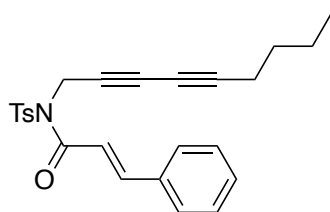
***N*-(5-(4-chlorophenyl)penta-2,4-diyne-1-yl)-*N*-tosylcinnamamide**

3d was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 82% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.92-7.90 (m, 2H), 7.71 (d, *J* = 15.4 Hz, 1H), 7.52 (dd, *J* = 7.2, 2.3 Hz, 2H), 7.42-7.39 (m, 5H), 7.37-7.29 (m, 5H), 4.88 (s, 2H), 2.40 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.2, 146.9, 145.3, 136.4, 135.6, 134.3, 133.8, 130.8, 129.9, 129.00, 128.88, 128.5, 127.8, 119.8, 117.3, 77.7, 76.6, 74.3, 68.8, 36.4, 21.7

HRMS *m/z* (ESI) calcd. for C₂₇H₂₁ClNO₃S⁺ (M+H)⁺ 474.0926, found 474.0949



3e

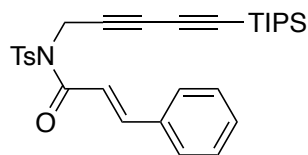
***N*-(nona-2,4-diyne-1-yl)-*N*-tosylcinnamamide**

3e was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 90% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 15.4 Hz, 1H), 7.50 (dd, *J* = 7.1, 2.3 Hz, 2H), 7.40 (m, 3H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 13.9 Hz, 1H), 4.79 (s, 2H), 2.41 (s, 3H), 2.26 (t, *J* = 7.0 Hz, 2H), 1.52-1.48 (m, 2H), 1.41 (ddd, *J* = 8.1, 7.0, 6.8 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.2, 146.7, 145.1, 136.4, 134.3, 130.8, 129.8, 129.0, 128.4, 127.9, 117.4, 81.1, 70.0, 69.6, 64.5, 36.2, 30.1, 21.9, 21.7, 18.9, 13.5

HRMS m/z (ESI) calcd. for C₂₅H₂₆NO₃S⁺ (M+H)⁺ 420.1628, found 420.1627



3f

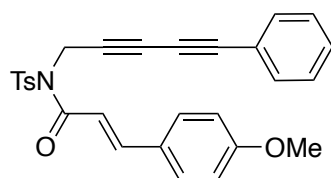
***N*-tosyl-*N*-(5-(triisopropylsilyl)penta-2,4-diyne-1-yl)cinnamamide**

3f was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 79% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 15.4 Hz, 1H), 7.52 (dd, *J* = 7.2, 2.3 Hz, 2H), 7.41-7.36 (m, 4H), 7.31 (d, *J* = 8.1 Hz, 2H), 4.82 (s, 2H), 2.40 (s, 3H), 1.08 (s, 21H).

¹³C NMR (151 MHz; CDCl₃): δ 165.2, 146.9, 145.2, 136.3, 134.3, 130.8, 129.8, 129.0, 128.5, 127.9, 117.4, 88.9, 84.2, 71.1, 69.7, 36.1, 21.6, 18.5, 11.2

HRMS m/z (ESI) calcd. for C₃₀H₃₈NO₃SSi⁺ (M+H)⁺ 520.2337, found 520.2331



3g

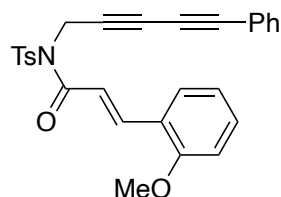
***(E)*-3-(4-methoxyphenyl)-*N*-(5-phenylpenta-2,4-diyne-1-yl)-*N*-tosylacrylamide**

3g was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 76% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 15.4 Hz, 1H), 7.48 (dd, *J* = 8.4, 1.4 Hz, 4H), 7.34-7.32 (m, 5H), 7.21 (d, *J* = 15.3 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.88 (s, 2H), 3.85 (s, 3H), 2.39 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.4, 161.9, 146.8, 145.2, 136.5, 132.6, 130.3, 129.8, 129.4, 128.4, 127.9, 127.1, 121.4, 114.7, 114.4, 77.8, 73.4, 72.5, 69.0, 55.4, 36.3, 21.7

HRMS m/z (ESI) calcd. for C₂₈H₂₄NO₄S⁺ (M+H)⁺ 470.1421, found 470.1392



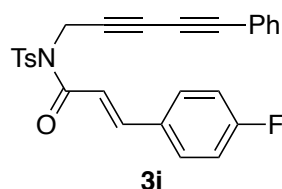
3h

***(E)*-3-(2-methoxyphenyl)-*N*-(5-phenylpenta-2,4-diyne-1-yl)-*N*-tosylacrylamide**

3h was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 75% yield as colorless oil.

¹H NMR (600 MHz; CDCl₃): δ 7.98-7.93 (m, 3H), 7.51 (d, *J* = 15.5 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 3H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.33-7.31 (m, 4H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 4.89 (s, 2H), 3.90 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (151 MHz; CDCl_3): δ 165.8, 158.9, 145.1, 142.8, 136.5, 132.6, 132.0, 130.2, 129.8, 129.4, 128.4, 128.0, 123.3, 121.4, 120.8, 118.0, 111.2, 77.8, 77.3, 73.4, 69.0, 55.5, 36.4, 21.7
HRMS m/z (ESI) calcd. for $\text{C}_{28}\text{H}_{24}\text{NO}_4\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 470.1421, found 470.1439



(E)-3-(4-fluorophenyl)-N-(5-phenylpenta-2,4-diyne-1-yl)-N-tosylacrylamide

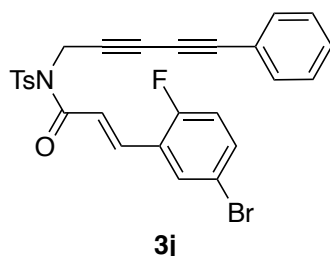
3i was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 92% yield as white solid.

^1H NMR (600 MHz; CDCl_3): δ 7.91 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 15.4 Hz, 1H), 7.52-7.50 (m, 2H), 7.48-7.47 (m, 2H), 7.39-7.27 (m, 6H), 7.11-7.08 (m, 2H), 4.87 (s, 2H), 2.40 (s, 3H).

^{13}C NMR (151 MHz; CDCl_3): δ 165.09, 164.31 (J = 252.5 Hz), 145.43 (J = 20.6 Hz), 136.3, 132.6, 130.61 (J = 3.6 Hz), 130.39 (J = 8.7 Hz), 129.9, 129.4, 128.5, 127.8, 121.3, 117.17 (J = 1.8 Hz), 116.28, 116.13, 77.9, 77.0, 73.3, 69.1, 36.4, 21.7

^{19}F NMR (564 MHz; CDCl_3): δ -108.48

HRMS m/z (ESI) calcd. for $\text{C}_{27}\text{H}_{21}\text{FNO}_3\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 458.1221, found 458.1221



(E)-3-(5-bromo-2-fluorophenyl)-N-(5-phenylpenta-2,4-diyne-1-yl)-N-tosylacrylamide

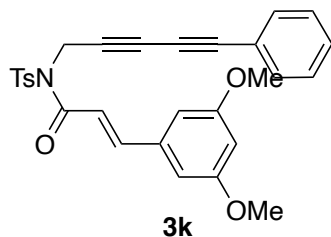
3j was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 78% yield as white solid.

^1H NMR (600 MHz; CDCl_3): δ 7.93-7.92 (m, 2H), 7.68 (d, J = 15.6 Hz, 1H), 7.58 (dd, J = 6.4, 2.4 Hz, 1H), 7.47 (ddt, J = 8.4, 6.6, 1.7 Hz, 3H), 7.42 (d, J = 15.6 Hz, 1H), 7.38 (t, J = 7.5 Hz, 3H), 7.32 (td, J = 7.4, 1.3 Hz, 2H), 7.01 (dd, J = 10.0, 8.9 Hz, 1H), 4.89 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (151 MHz; CDCl_3): δ 164.7, 160.42 (d, J = 255.2 Hz), 145.5, 137.7, 136.2, 134.67 (d, J = 8.8 Hz), 132.6, 132.17 (d, J = 3.1 Hz), 130.0, 129.4, 128.5, 127.9, 124.43 (d, J = 13.0 Hz), 121.42 (d, J = 7.6 Hz), 121.28, 118.09 (d, J = 23.3 Hz), 117.10 (d, J = 3.2 Hz), 77.9, 73.2, 69.2, 36.4, 21.7

^{19}F NMR (564 MHz; CDCl_3): δ -115.5

HRMS m/z (ESI) calcd. for $\text{C}_{27}\text{H}_{20}\text{BrFNO}_3\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 536.0326, found 536.0309



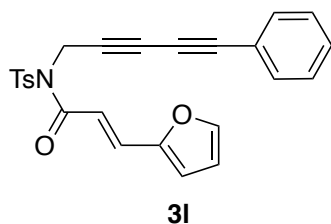
(E)-3-(3,5-dimethoxyphenyl)-N-(5-phenylpenta-2,4-diyne-1-yl)-N-tosylacrylamide

3k was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 83% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 15.4 Hz, 1H), 7.51-7.49 (m, 2H), 7.40-7.31 (m, 6H), 6.67 (d, *J* = 2.2 Hz, 2H), 6.54 (t, *J* = 2.2 Hz, 1H), 4.90 (s, 2H), 3.84 (s, 6H), 2.43 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.1, 161.0, 146.8, 145.3, 136.35, 136.21, 132.6, 129.9, 129.4, 128.4, 127.9, 121.3, 118.0, 106.43, 106.37, 102.9, 77.9, 73.3, 69.1, 55.51, 55.46, 36.4, 21.7

HRMS *m/z* (ESI) calcd. for C₂₉H₂₆NO₅S+ (M+H)⁺ 500.1527, found 500.1520



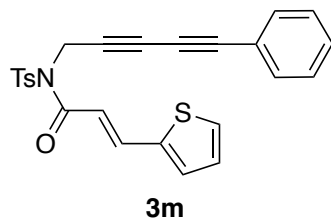
(E)-3-(furan-2-yl)-N-(5-phenylpenta-2,4-diyne-1-yl)-N-tosylacrylamide

3l was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 82% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 1.3 Hz, 1H), 7.49-7.45 (m, 3H), 7.38-7.31 (m, 5H), 7.19 (d, *J* = 15.1 Hz, 1H), 6.65 (d, *J* = 3.4 Hz, 1H), 6.49 (dd, *J* = 3.4, 1.8 Hz, 1H), 4.89 (s, 2H), 2.41 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.1, 151.0, 145.40, 145.20, 136.3, 132.9, 132.6, 129.8, 129.4, 128.49, 128.45, 128.1, 121.3, 116.5, 114.5, 112.6, 77.8, 77.1, 73.3, 69.0, 36.3, 21.7

HRMS *m/z* (ESI) calcd. for C₂₅H₂₀NO₄S+ (M+H)⁺ 430.1108, found 430.1102



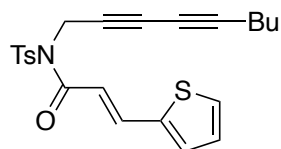
(E)-N-(5-phenylpenta-2,4-diyne-1-yl)-3-(thiophen-2-yl)-N-tosylacrylamide

3m was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 85% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.94-7.93 (m, 2H), 7.80 (d, *J* = 15.1 Hz, 1H), 7.49-7.47 (m, 2H), 7.42 (d, *J* = 5.1 Hz, 1H), 7.37-7.31 (m, 5H), 7.27 (s, 1H), 7.12 (d, *J* = 15.1 Hz, 1H), 7.06 (dd, *J* = 5.1, 3.7 Hz, 1H), 4.89 (s, 2H), 2.40 (s, 3H).

^{13}C NMR (151 MHz; CDCl_3): δ 164.9, 145.3, 139.7, 139.2, 136.4, 132.6, 132.1, 129.9, 129.40, 129.35, 128.44, 128.34, 127.9, 121.3, 116.0, 77.8, 77.1, 73.3, 69.0, 36.2, 21.7

HRMS m/z (ESI) calcd. for $\text{C}_{25}\text{H}_{20}\text{NO}_3\text{S}_2^+$ ($\text{M}+\text{H}$) $^+$ 446.0880, found 446.0878



3n

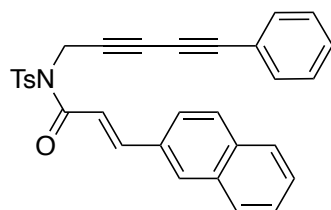
(E)-N-(nona-2,4-diyn-1-yl)-3-(thiophen-2-yl)-N-tosylacrylamide

3n was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 85% yield as white solid.

^1H NMR (600 MHz; CDCl_3): δ 7.93-7.91 (m, 2H), 7.77 (d, $J = 15.1$ Hz, 1H), 7.42 (d, $J = 5.1$ Hz, 1H), 7.33 (d, $J = 8.1$ Hz, 2H), 7.25 (d, $J = 3.6$ Hz, 1H), 7.08-7.05 (m, 2H), 4.79 (s, 2H), 2.41 (s, 3H), 2.27 (t, $J = 7.0$ Hz, 2H), 1.52-1.48 (m, 2H), 1.42 (td, $J = 8.2, 5.7$ Hz, 2H), 0.92 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (151 MHz; CDCl_3): δ 164.8, 145.1, 139.7, 139.0, 136.4, 132.0, 129.8, 129.3, 128.3, 128.0, 116.0, 81.0, 70.1, 69.5, 64.5, 36.1, 30.1, 21.9, 21.7, 18.9, 13.5

HRMS m/z (ESI) calcd. for $\text{C}_{23}\text{H}_{24}\text{NO}_3\text{S}_2^+$ ($\text{M}+\text{H}$) $^+$ 426.1193, found 426.1199



3o

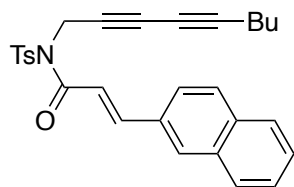
(E)-3-(naphthalen-2-yl)-N-(5-phenylpenta-2,4-diyn-1-yl)-N-tosylacrylamide

3o was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 10:1) in 73% yield as white solid.

^1H NMR (600 MHz; CDCl_3): δ 7.95 (d, $J = 8.4$ Hz, 2H), 7.91 (s, 1H), 7.86 (q, $J = 8.0$ Hz, 4H), 7.66 (dd, $J = 8.6, 1.3$ Hz, 1H), 7.55-7.51 (m, 2H), 7.49-7.46 (m, 3H), 7.38-7.31 (m, 5H), 4.91 (s, 2H), 2.38 (s, 3H).

^{13}C NMR (151 MHz; CDCl_3): δ 165.3, 147.0, 145.3, 136.4, 134.5, 133.2, 132.6, 131.8, 130.8, 129.9, 129.4, 128.85, 128.72, 128.4, 127.91, 127.81, 127.6, 126.9, 123.5, 121.3, 117.5, 77.9, 77.1, 73.3, 69.1, 36.4, 21.7.

HRMS m/z (ESI) calcd. for $\text{C}_{31}\text{H}_{24}\text{NO}_3\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 490.1471, found 490.1465



3p

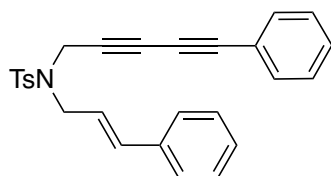
(E)-3-(naphthalen-2-yl)-N-(nona-2,4-diyn-1-yl)-N-tosylacrylamide

3p was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 10:1) in 83% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.90 (s, 1H), 7.85 (dt, *J* = 12.9, 8.1 Hz, 4H), 7.65 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.55-7.51 (m, 2H), 7.41 (d, *J* = 15.4 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 4.82 (s, 2H), 2.40 (s, 3H), 2.27 (t, *J* = 7.0 Hz, 2H), 1.53-1.48 (m, 2H), 1.44-1.38 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.2, 146.8, 145.2, 136.4, 134.4, 133.2, 131.8, 130.7, 129.8, 128.83, 128.71, 127.96, 127.81, 127.6, 126.9, 123.5, 117.4, 81.1, 70.0, 69.6, 64.5, 36.2, 30.1, 21.9, 21.7, 18.9, 13.5

HRMS *m/z* (ESI) calcd. for C₂₉H₂₈NO₃S⁺ (M+H)⁺ 470.1785, found 470.1807



3q

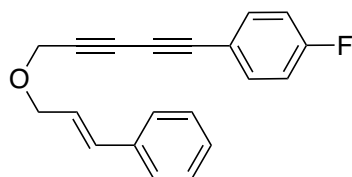
***N*-cinnamyl-4-methyl-*N*-(5-phenylpenta-2,4-diyne-1-yl)benzenesulfonamide**

3q was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 10:1) in 86% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.79-7.78 (m, 2H), 7.47-7.45 (m, 2H), 7.40-7.30 (m, 9H), 7.27 (t, *J* = 1.3 Hz, 1H), 6.60 (d, *J* = 15.8 Hz, 1H), 6.10 (dt, *J* = 15.8, 6.9 Hz, 1H), 4.26 (s, 2H), 4.00 (dd, *J* = 6.8, 0.7 Hz, 2H), 2.41 (s, 3H).

¹³C NMR (151 MHz, CDCl₃): δ 143.9, 136.1, 135.6, 135.2, 132.5, 129.7, 129.4, 128.64, 128.49, 128.1, 127.8, 126.6, 122.8, 121.3, 77.4, 75.6, 73.1, 70.4, 49.1, 36.9, 21.6.

HRMS *m/z* (ESI) calcd. for C₂₇H₂₄NO₂S⁺ (M+H)⁺ 426.1522, found 426.1525



3r

1-(5-(cinnamyloxy)penta-1,3-diyne-1-yl)-4-fluorobenzene

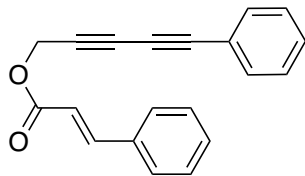
3r was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 72% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.50-7.47 (m, 2H), 7.40 (d, *J* = 7.4 Hz, 2H), 7.33-7.31 (m, 2H), 7.26-7.24 (m, 1H), 7.03-7.01 (m, 2H), 6.67 (d, *J* = 15.9 Hz, 1H), 6.28 (dt, *J* = 15.9, 6.2 Hz, 1H), 4.34 (s, 2H), 4.27 (dd, *J* = 6.2, 1.3 Hz, 2H).

¹³C NMR (151 MHz, CDCl₃): δ 163.06 (d, *J* = 251.6 Hz), 136.5, 134.67 (d, *J* = 8.3 Hz), 133.7, 128.6, 127.9, 126.6, 124.9, 117.6, 115.88 (d, *J* = 22.0 Hz), 78.8, 73.2, 70.9, 70.4, 70.2, 57.7

¹⁹F NMR (564 MHz, Chloroform-*d*) δ -108.4

HRMS *m/z* (ESI) calcd. for C₂₀H₁₆FO⁺ (M+H)⁺ 291.1180, found 291.1188



3s

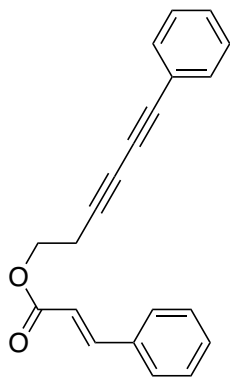
5-phenylpenta-2,4-diyne-1-yl cinnamate

3s was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 90% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.76 (d, *J* = 16.0 Hz, 1H), 7.54 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.50-7.49 (m, 2H), 7.41-7.39 (m, 3H), 7.38-7.36 (m, 1H), 7.33-7.31 (m, 2H), 6.47 (d, *J* = 16.0 Hz, 1H), 4.96 (s, 2H).

¹³C NMR (151 MHz; CDCl₃): δ 166.0, 146.1, 134.2, 132.7, 130.6, 129.5, 129.0, 128.5, 128.2, 121.2, 116.9, 78.8, 76.3, 73.1, 71.3, 52.7

HRMS *m/z* (ESI) calcd. for C₂₀H₁₅O₂⁺ (M+H)⁺ 287.1067, found 287.1075



3t

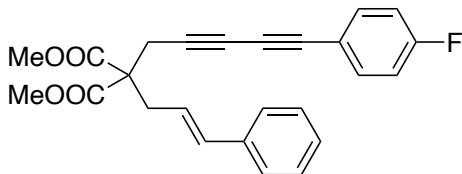
6-phenylhexa-3,5-diyne-1-yl cinnamate

3t was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 76% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.73 (d, *J* = 16.0 Hz, 1H), 7.55-7.53 (m, 2H), 7.48 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.39 (t, *J* = 3.2 Hz, 3H), 7.35-7.29 (m, 3H), 6.47 (d, *J* = 16.0 Hz, 1H), 4.35 (t, *J* = 6.7 Hz, 2H), 2.79 (t, *J* = 6.7 Hz, 2H).

¹³C NMR (151 MHz; CDCl₃): δ 145.5, 134.3, 132.6, 130.4, 129.06, 128.91, 128.4, 128.2, 121.7, 117.6, 79.9, 75.5, 74.0, 66.6, 61.9, 20.3

HRMS *m/z* (ESI) calcd. for C₂₁H₁₇O₂⁺ (M+H)⁺ 301.1224, found 301.1220



3u

dimethyl 2-cinnamyl-2-(5-(4-fluorophenyl)penta-2,4-diyne-1-yl)malonate

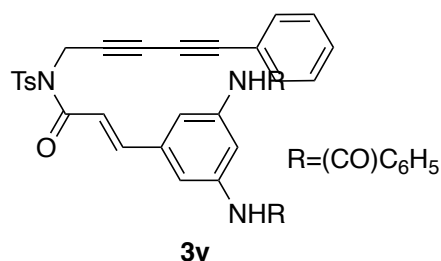
3u was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 78% yield as colorless oil.

¹H NMR (600 MHz; CDCl₃): δ 7.47 (ddd, *J* = 9.5, 5.1, 2.4 Hz, 2H), 7.35-7.34 (m, 2H), 7.31-7.28 (m, 2H), 7.24-7.21 (m, 1H), 7.01 (ddt, *J* = 8.7, 6.7, 2.2 Hz, 2H), 6.55 (d, *J* = 15.7 Hz, 1H), 6.02 (dt, *J* = 15.6, 7.7 Hz, 1H), 3.78 (s, 6H), 3.03 (s, 2H), 2.99 (dd, *J* = 7.7, 1.0 Hz, 2H).

¹³C NMR (151 MHz; CDCl₃): δ 169.9, 162.82 (*J* = 251.0 Hz), 136.9, 134.9, 134.63, 134.58, 128.5, 127.6, 126.4, 122.9, 115.82 (*J* = 21.8 Hz), 78.5, 74.6, 73.8, 68.0, 57.4, 53.0, 36.3, 24.2

¹⁹F NMR (564 MHz; CDCl₃): δ -108.82

HRMS *m/z* (ESI) calcd. for C₂₅H₂₂FO₄⁺ (M+H)⁺ 405.1497, found 405.1518



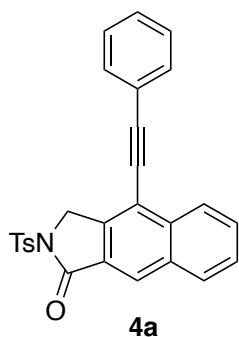
(*E*)-*N,N'*-(5-(3-((4-methyl-*N*-(5-phenylpenta-2,4-diyne-1-yl)phenyl)sulfonamido)-3-oxoprop-1-en-1-yl)-1,3-phenylene)dibenzamide

3v was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 65% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 8.18 (s, 3H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.88-7.87 (m, 4H), 7.62 (d, *J* = 1.8 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 3H), 7.48-7.46 (m, 6H), 7.38-7.36 (m, 3H), 7.33-7.31 (m, 3H), 4.87 (s, 2H), 2.39 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 166.09, 166.07, 164.9, 145.8, 145.4, 139.2, 136.1, 135.7, 134.4, 132.6, 132.1, 130.1, 129.4, 128.8, 128.4, 128.0, 127.18, 127.14, 121.3, 118.5, 116.02, 115.99, 114.4, 77.9, 77.1, 73.3, 69.1, 36.3, 31.6, 21.7

HRMS *m/z* (ESI) calcd. for C₄₁H₃₂N₃O₅S⁺ (M+H)⁺ 678.2058, found 678.2047



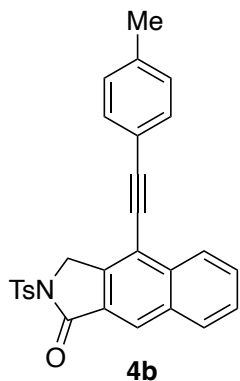
4-(phenylethynyl)-2-tosyl-2,3-dihydro-1*H*-benzo[*f*]isoindol-1-one

4a was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 90% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 8.45 (d, *J* = 8.4 Hz, 1H), 8.30 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.72 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.69-7.68 (m, 2H), 7.62-7.59 (m, 1H), 7.45 (dd, *J* = 6.4, 2.7 Hz, 3H), 7.36 (d, *J* = 8.2 Hz, 2H), 5.15 (s, 2H), 2.42 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.8, 145.4, 138.1, 135.7, 135.4, 132.8, 131.9, 130.3, 129.8, 129.6, 129.3, 128.7, 128.2, 127.6, 127.4, 126.04, 126.03, 122.3, 116.5, 100.9, 82.6, 49.9, 21.7

HRMS *m/z* (ESI) calcd. for C₂₇H₂₀NO₃S⁺ (M+H)⁺ 438.1159, found 438.1141



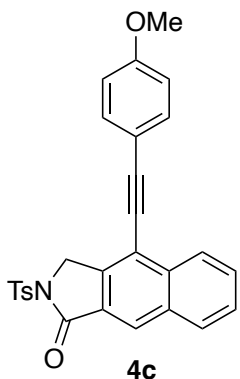
4-(*p*-tolylethynyl)-2-tosyl-2,3-dihydro-1*H*-benzo[*f*]isoindol-1-one

4b was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 92% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 8.45 (d, *J* = 8.4 Hz, 1H), 8.29 (s, 1H), 8.09 (d, *J* = 8.3 Hz, 2H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.59 (dd, *J* = 17.8, 7.8 Hz, 3H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 6.3 Hz, 2H), 5.15 (s, 2H), 2.43 (d, *J* = 9.2 Hz, 6H).

¹³C NMR (151 MHz; CDCl₃): δ 165.8, 145.3, 139.7, 137.9, 135.6, 135.4, 132.8, 131.8, 130.2, 129.8, 129.48, 129.40, 128.2, 127.6, 127.3, 126.1, 125.8, 119.2, 116.7, 101.2, 82.1, 49.9, 21.70, 21.66

HRMS *m/z* (ESI) calcd. for C₂₈H₂₂NO₃S⁺ (M+H)⁺ 452.1315, found 452.1301



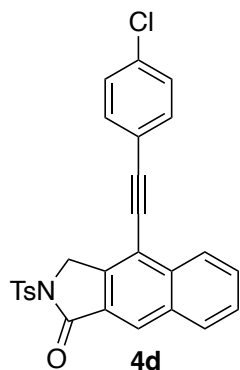
4-((4-methoxyphenyl)ethynyl)-2-tosyl-2,3-dihydro-1*H*-benzo[*f*]isoindol-1-one

4c was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 89% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 8.44 (d, *J* = 8.4 Hz, 1H), 8.27 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.70 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.62-7.58 (m, 3H), 7.35 (d, *J* = 8.3 Hz, 2H), 6.97-6.96 (m, 2H), 5.14 (s, 2H), 3.89 (s, 3H), 2.42 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.9, 160.4, 145.3, 137.7, 135.59, 135.41, 133.4, 132.8, 130.2, 129.8, 129.4, 128.2, 127.5, 127.3, 126.1, 125.6, 116.9, 114.3, 101.2, 81.5, 55.4, 50.0, 21.7

HRMS *m/z* (ESI) calcd. for C₂₈H₂₂NO₄S⁺ (M+H)⁺ 468.1265, found 468.1255



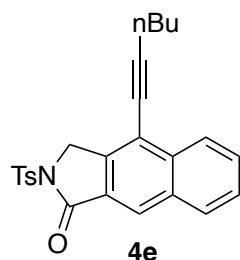
4-((4-chlorophenyl)ethynyl)-2-tosyl-2,3-dihydro-1H-benzo[f]isoindol-1-one

4d was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 83% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 8.42 (d, *J* = 8.5 Hz, 1H), 8.32 (s, 1H), 8.09 (d, *J* = 8.3 Hz, 2H), 8.00 (dd, *J* = 8.0, 4.2 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 6.6 Hz, 3H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 5.15 (s, 2H), 2.42 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.7, 145.4, 138.2, 135.61, 135.47, 135.33, 133.1, 132.8, 130.4, 129.83, 129.68, 129.0, 128.2, 127.61, 127.43, 126.3, 125.9, 120.7, 116.1, 99.6, 83.6, 49.9, 21.7

HRMS *m/z* (ESI) calcd. for C₂₇H₁₉ClNO₃S⁺ (M+H)⁺ 472.0769, found 472.0797



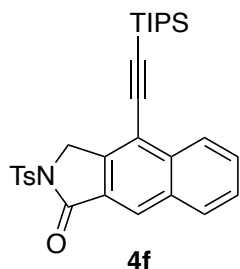
4-(hex-1-yn-1-yl)-2-tosyl-2,3-dihydro-1H-benzo[f]isoindol-1-one

4e was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 78% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 8.35 (d, *J* = 8.3 Hz, 1H), 8.25 (s, 1H), 8.07 (d, *J* = 7.8 Hz, 2H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 2H), 5.06 (s, 2H), 2.65 (t, *J* = 6.9 Hz, 2H), 2.42 (s, 3H), 1.74 (q, *J* = 7.1 Hz, 2H), 1.60 (t, *J* = 7.6 Hz, 2H), 1.03 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.9, 145.3, 137.8, 136.0, 135.4, 132.8, 130.2, 129.8, 129.3, 128.2, 127.4, 127.1, 126.1, 125.2, 117.4, 102.8, 74.2, 50.0, 30.9, 22.2, 21.7, 19.6, 13.7

HRMS *m/z* (ESI) calcd. for C₂₅H₂₄NO₃S⁺ (M+H)⁺ 418.1472, found 418.1437



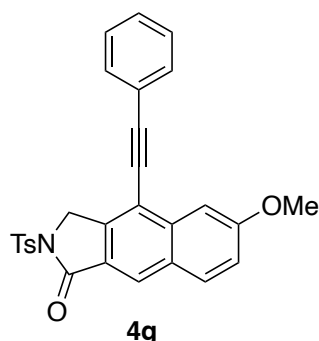
2-tosyl-4-((triisopropylsilyl)ethynyl)-2,3-dihydro-1H-benzo[f]isoindol-1-one

4f was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 76% yield as white solid.

$^1\text{H NMR}$ (600 MHz; CDCl_3): δ 8.41 (d, $J = 8.4$ Hz, 1H), 8.32 (s, 1H), 8.07 (d, $J = 8.3$ Hz, 2H), 7.99 (d, $J = 8.2$ Hz, 1H), 7.72 (dd, $J = 8.2, 7.1$ Hz, 1H), 7.60 (t, $J = 7.5$ Hz, 1H), 7.36 (d, $J = 8.3$ Hz, 2H), 5.08 (s, 2H), 2.42 (s, 3H), 1.23 (d, $J = 5.4$ Hz, 21H).

$^{13}\text{C NMR}$ (151 MHz; CDCl_3): δ 165.7, 145.3, 138.8, 135.9, 135.4, 132.8, 130.3, 129.79, 129.67, 128.3, 127.5, 127.3, 126.13, 126.00, 116.7, 103.9, 99.8, 50.0, 21.7, 18.8, 11.3

HRMS m/z (ESI) calcd. for $\text{C}_{30}\text{H}_{36}\text{NO}_3\text{SSi}^+$ ($\text{M}+\text{H}$) $^+$ 518.2180, found 518.2173



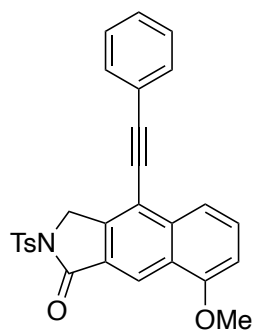
6-methoxy-4-(phenylethynyl)-2-tosyl-2,3-dihydro-1H-benzo[f]isoindol-1-one

4g was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 82% yield as white solid.

$^1\text{H NMR}$ (600 MHz; CDCl_3): δ 8.22 (s, 1H), 8.08 (d, $J = 8.2$ Hz, 2H), 7.87 (d, $J = 9.0$ Hz, 1H), 7.71 (s, 1H), 7.66 (d, $J = 3.5$ Hz, 2H), 7.45 (t, $J = 2.5$ Hz, 3H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.25-7.24 (m, 1H), 5.13 (s, 2H), 4.01 (s, 3H), 2.42 (s, 3H).

$^{13}\text{C NMR}$ (151 MHz; CDCl_3): δ 165.9, 160.8, 145.2, 139.1, 137.8, 135.5, 131.85, 131.78, 129.8, 129.2, 128.7, 128.33, 128.20, 125.8, 125.4, 122.4, 120.4, 114.6, 104.2, 100.6, 82.8, 55.5, 49.9, 21.7

HRMS m/z (ESI) calcd. for $\text{C}_{28}\text{H}_{22}\text{NO}_4\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 468.1264, found 468.1264

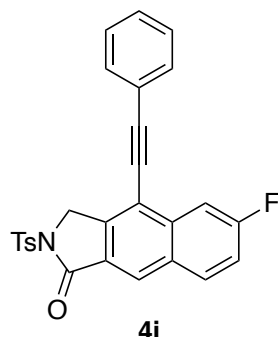


8-methoxy-4-(phenylethynyl)-2-tosyl-2,3-dihydro-1H-benzo[f]isoindol-1-one

4h was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 75% yield as white solid.

$^1\text{H NMR}$ (600 MHz; CDCl_3): δ 8.70 (s, 1H), 8.08 (d, $J = 8.3$ Hz, 2H), 7.93 (d, $J = 8.5$ Hz, 1H), 7.66 (dd, $J = 6.5, 2.9$ Hz, 2H), 7.58 (t, $J = 8.1$ Hz, 1H), 7.43 (t, $J = 3.2$ Hz, 3H), 7.35 (d, $J = 8.3$ Hz, 2H), 6.87 (d, $J = 7.7$ Hz, 1H), 5.09 (s, 2H), 4.00 (s, 3H), 2.41 (s, 3H).

^{13}C NMR (151 MHz; CDCl_3): δ 165.9, 157.2, 145.3, 138.7, 136.7, 135.5, 131.8, 130.1, 129.8, 129.2, 128.6, 128.2, 126.4, 125.4, 122.4, 121.0, 117.8, 115.6, 105.0, 100.5, 82.9, 55.8, 49.9, 21.7
HRMS m/z (ESI) calcd. for $\text{C}_{28}\text{H}_{22}\text{NO}_4\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 468.1264, found 468.1260



6-fluoro-4-(phenylethynyl)-2-tosyl-2,3-dihydro-1H-benzo[f]isoindol-1-one

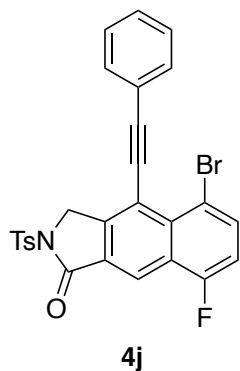
4i was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 69% yield as white solid.

^1H NMR (600 MHz; CDCl_3): 8.32 (s, 1H), 8.09-8.06 (m, 3H), 8.02 (dd, $J = 9.0, 5.6$ Hz, 1H), 7.68 (dt, $J = 3.9, 2.7$ Hz, 2H), 7.46 (t, $J = 3.2$ Hz, 3H), 7.40 (td, $J = 8.5, 2.1$ Hz, 1H), 7.36 (d, $J = 8.2$ Hz, 2H), 7.26 (s, 1H), 5.17 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (151 MHz; CDCl_3): δ 165.5, 163.00 ($J = 252.8$ Hz), 145.4, 139.1, 137.20 ($J = 9.8$ Hz), 135.3, 132.94 ($J = 9.5$ Hz), 131.9, 129.90, 129.84, 129.5, 128.7, 128.2, 127.29 ($J = 2.9$ Hz), 125.9, 122.0, 118.10 ($J = 26.0$ Hz), 116.06, 116.02, 110.01 ($J = 22.8$ Hz), 101.3, 82.0, 60.4, 49.9, 21.7

^{19}F NMR (564 MHz; CDCl_3): δ -107.19

HRMS m/z (ESI) calcd. for $\text{C}_{27}\text{H}_{19}\text{FNO}_3\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 456.1065, found 456.1058



5-bromo-8-fluoro-4-(phenylethynyl)-2-tosyl-2,3-dihydro-1H-benzo[f]isoindol-1-one

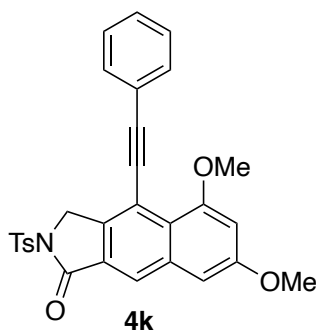
4j was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 86% yield as white solid.

^1H NMR (600 MHz; CDCl_3): δ 8.60 (s, 1H), 8.09 (d, $J = 7.9$ Hz, 2H), 7.92 (t, $J = 6.7$ Hz, 1H), 7.65 (s, 2H), 7.46 (s, 3H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.11 (t, $J = 8.7$ Hz, 1H), 5.14 (s, 2H), 2.43 (s, 3H).

^{13}C NMR (151 MHz; CDCl_3): δ 164.9, 145.6, 143.0, 135.88, 135.82, 135.1, 131.2, 129.9, 129.5, 128.7, 128.35, 128.30, 122.6, 119.33, 119.28, 115.02, 114.99, 111.50, 111.36, 106.6, 84.1, 50.7, 21.7

^{19}F NMR (564 MHz; CDCl_3): δ -117.2

HRMS m/z (ESI) calcd. for $\text{C}_{27}\text{H}_{18}\text{BrFNO}_3\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 534.0169, found 534.0169



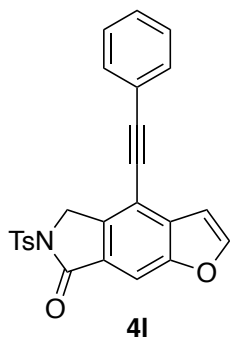
5,7-dimethoxy-4-(phenylethynyl)-2-tosyl-2,3-dihydro-1H-benzo[f]isoindol-1-one

4k was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 74% yield as white solid.

$^1\text{H NMR}$ (600 MHz; CDCl_3): δ 8.08 (t, $J = 4.2$ Hz, 3H), 7.63 (dd, $J = 7.7, 1.6$ Hz, 2H), 7.45-7.42 (m, 3H), 7.36 (d, $J = 8.2$ Hz, 2H), 6.81 (d, $J = 2.2$ Hz, 1H), 6.66 (d, $J = 2.2$ Hz, 1H), 5.08 (s, 2H), 4.02 (s, 3H), 3.92 (s, 3H), 2.42 (s, 3H).

$^{13}\text{C NMR}$ (151 MHz; CDCl_3): δ 166.0, 158.7, 157.5, 145.3, 137.8, 136.1, 135.4, 131.7, 129.84, 129.80, 128.83, 128.64, 128.59, 128.24, 128.18, 124.1, 123.5, 123.3, 114.0, 101.7, 100.1, 99.6, 86.2, 55.9, 55.5, 50.3, 29.7, 21.7

HRMS m/z (ESI) calcd. for $\text{C}_{29}\text{H}_{24}\text{NO}_5\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 498.1370, found 498.1370



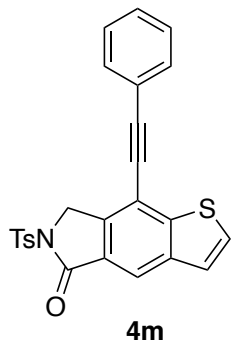
4-(phenylethynyl)-6-tosyl-5,6-dihydro-7H-furo[2,3-f]isoindol-7-one

4l was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 55% yield as white solid.

$^1\text{H NMR}$ (600 MHz; CDCl_3): δ 8.07 (d, $J = 8.0$ Hz, 2H), 7.86 (d, $J = 20.4$ Hz, 2H), 7.62 (d, $J = 3.5$ Hz, 2H), 7.44 (s, 3H), 7.35 (d, $J = 7.9$ Hz, 2H), 7.06 (s, 1H), 5.06 (s, 2H), 2.42 (s, 3H).

$^{13}\text{C NMR}$ (151 MHz; CDCl_3): δ 166.0, 154.5, 149.4, 145.3, 137.4, 135.4, 134.9, 131.9, 129.8, 129.4, 128.6, 128.2, 127.0, 122.0, 111.4, 108.1, 106.6, 98.6, 82.1, 49.4, 21.7

HRMS m/z (ESI) calcd. for $\text{C}_{25}\text{H}_{18}\text{NO}_4\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 428.0952, found 428.0934



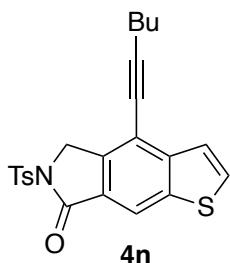
8-(phenylethynyl)-6-tosyl-6,7-dihydro-5H-thieno[2,3-f]isoindol-5-one

4m was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 72% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 8.25 (s, 1H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.76 (d, *J* = 5.3 Hz, 1H), 7.70 (d, *J* = 5.2 Hz, 1H), 7.64 (d, *J* = 2.6 Hz, 2H), 7.44 (s, 3H), 7.35 (d, *J* = 7.8 Hz, 2H), 5.09 (s, 2H), 2.42 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.7, 145.3, 144.5, 140.2, 138.4, 135.4, 132.4, 131.9, 129.8, 129.4, 128.6, 128.2, 126.7, 123.2, 122.1, 119.5, 113.7, 99.1, 82.7, 49.5, 21.7

HRMS *m/z* (ESI) calcd. for C₂₅H₁₈NO₃S₂⁺ (M+H)⁺ 444.0723, found 444.0708



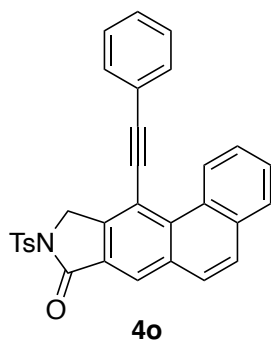
4-(hex-1-yn-1-yl)-6-tosyl-5,6-dihydro-7H-thieno[2,3-f]isoindol-7-one

4n was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 81% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 8.19 (s, 1H), 8.05 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 5.5 Hz, 1H), 7.58 (d, *J* = 5.5 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 4.98 (s, 2H), 2.59 (t, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.70 (quintet, *J* = 7.3 Hz, 2H), 1.57 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.02 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.8, 145.2, 144.8, 140.0, 138.3, 135.5, 131.8, 129.8, 128.2, 126.5, 123.2, 118.7, 114.6, 101.0, 74.4, 49.6, 30.8, 22.1, 21.7, 19.5, 13.6

HRMS *m/z* (ESI) calcd. for C₂₃H₂₂NO₃S₂⁺ (M+H)⁺ 424.1036, found 424.1036



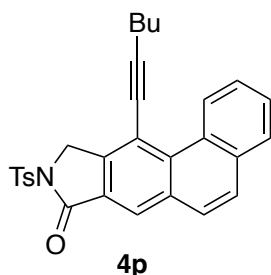
11-(phenylethynyl)-9-tosyl-9,10-dihydro-8H-naphtho[1,2-f]isoindol-8-one

4o was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 75% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 10.36 (d, *J* = 4.9 Hz, 1H), 8.26 (s, 1H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.93-7.93 (m, 1H), 7.80-7.71 (m, 5H), 7.50 (s, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 5.13 (s, 2H), 2.42 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.8, 145.3, 142.5, 135.5, 133.9, 133.3, 133.1, 131.6, 130.2, 129.8, 129.5, 128.93, 128.82, 128.73, 128.5, 128.2, 127.8, 127.4, 126.62, 126.56, 125.7, 122.5, 115.0, 102.3, 86.6, 50.7, 21.7

HRMS *m/z* (ESI) calcd. for C₃₁H₂₂NO₃S⁺ (M+H)⁺ 488.1315, found 488.1313

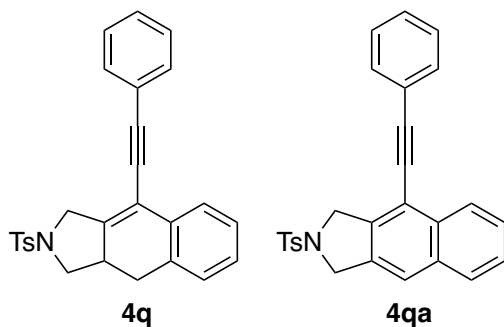
**11-(hex-1-yn-1-yl)-9-tosyl-9,10-dihydro-8H-naphtho[1,2-f]isoindol-8-one**

4p was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 77% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 10.33 (d, *J* = 8.4 Hz, 1H), 8.15 (s, 1H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 7.0 Hz, 1H), 7.73-7.63 (m, 4H), 7.36 (d, *J* = 8.3 Hz, 2H), 4.98 (s, 2H), 2.73 (t, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.81 (quintet, *J* = 7.4 Hz, 2H), 1.65 (q, *J* = 7.5 Hz, 2H), 1.07 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.9, 145.3, 142.5, 135.5, 133.6, 133.22, 133.06, 130.3, 129.8, 128.65, 128.57, 128.28, 128.20, 127.8, 127.2, 126.5, 126.2, 124.9, 115.8, 104.7, 78.2, 50.8, 30.6, 22.3, 21.7, 20.0, 13.7

HRMS *m/z* (ESI) calcd. for C₂₉H₂₆NO₃S⁺ (M+H)⁺ 468.1628, found 468.1629

**4q: 9-(phenylethynyl)-2-tosyl-2,3,3a,4-tetrahydro-1H-benzo[f]isoindole****4qa: 4-(phenylethynyl)-2-tosyl-2,3-dihydro-1H-benzo[f]isoindole**

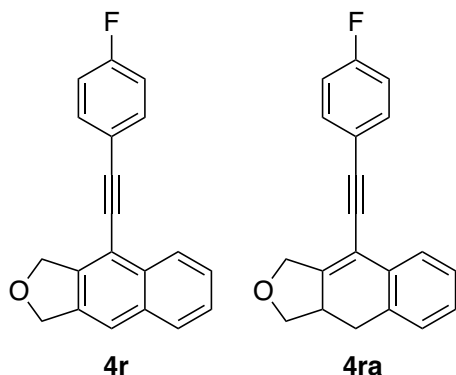
4q:4qa=1:1.2 was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 10:1) in 40% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 8.34 (d, *J* = 8.3 Hz, 1H), 7.84-7.82 (m, 2H), 7.79-7.77 (m, 2H), 7.65-7.63 (m, 2H), 7.60-7.48 (m, 5H), 7.45-7.41 (m, 3H), 7.39-7.32 (m, 5H), 7.25 (t, *J* = 5.5 Hz, 1H), 7.17 (td, *J* = 7.4, 1.1 Hz, 0.7H), 7.10 (d, *J* = 7.4 Hz, 0.7H), 4.90 (s, 2H), 4.79 (d, *J* = 0.7 Hz,

2H), 4.47 (dd, $J = 16.9, 2.4$ Hz, 0.7H), 4.12 (dd, $J = 16.9, 3.3$ Hz, 0.7H), 4.03 (dd, $J = 9.2, 8.0$ Hz, 0.7H), 3.12-3.08 (m, 0.7H), 2.87 (ddd, $J = 10.9, 9.0, 8.2$ Hz, 1.4H), 2.54 (t, $J = 15.2$ Hz, 0.7H), 2.43 (s, 2H), 2.39 (s, 3H).

$^{13}\text{C NMR}$ (151 MHz; CDCl_3): δ 146.5, 143.8, 138.4, 134.2, 133.5, 133.00, 132.92, 132.89, 132.73, 132.65, 131.76, 131.64, 129.91, 129.89, 128.9, 128.67, 128.54, 128.46, 128.2, 127.79, 127.76, 127.74, 127.67, 127.2, 126.9, 126.6, 125.8, 125.0, 122.80, 122.75, 121.6, 115.2, 114.2, 99.2, 96.3, 84.2, 83.7, 54.8, 53.76, 53.74, 51.6, 39.1, 31.7, 21.58, 21.52

HRMS m/z (ESI) calcd. for **4q**: $\text{C}_{27}\text{H}_{24}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 426.1523, found 426.1512; **4qa**: $\text{C}_{27}\text{H}_{22}\text{NO}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 424.1366, found 424.1371



4r: 4-((4-fluorophenyl)ethynyl)-1,3-dihydroindolo[2,3-c]naphthalene

4ra: 9-((4-fluorophenyl)ethynyl)-1,3,3a,4-tetrahydroindolo[2,3-c]naphthalene

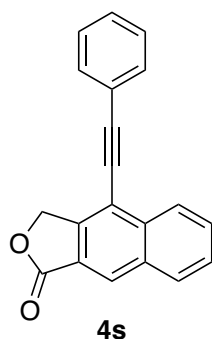
4r:**4ra**=7:1 was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 10:1) in 32% yield as white solid.

$^1\text{H NMR}$ (600 MHz; CDCl_3): δ 8.36 (d, $J = 8.3$ Hz, 1H), 7.84 (d, $J = 8.1$ Hz, 1H), 7.66 (s, 1H), 7.62-7.59 (m, 2H), 7.57 (ddd, $J = 8.2, 6.9, 1.3$ Hz, 1H), 7.51 (td, $J = 7.5, 1.2$ Hz, 1H), 7.11-7.09 (m, 2H), 5.37 (s, 2H), 5.28 (d, $J = 1.0$ Hz, 2H), 4.82 (dd, $J = 16.1, 2.1$ Hz,), 4.72 (d, $J = 3.2$ Hz,).

$^{13}\text{C NMR}$ (151 MHz; CDCl_3): δ 162.82 ($J = 250.6$ Hz), 141.9, 137.6, 133.62, 133.56, 133.2, 132.8, 128.4, 126.6, 126.3, 125.7, 119.9, 119.16 ($J = 3.3$ Hz), 115.90, 115.76, 113.1, 97.2, 84.4, 73.53, 73.47

$^{19}\text{F NMR}$ (564 MHz; CDCl_3): δ -110.2, -110.7

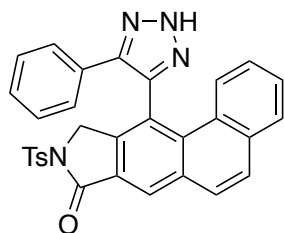
HRMS m/z (ESI) calcd. for **4r**: $\text{C}_{20}\text{H}_{14}\text{FO}^+$ ($\text{M}+\text{H}$) $^+$ 289.1024, found 289.1017; **4ra**: $\text{C}_{20}\text{H}_{16}\text{FO}^+$ ($\text{M}+\text{H}$) $^+$ 291.1180, found 291.1183



4-(phenylethynyl)naphtho[2,3-c]furan-1(3H)-one

4s was prepared following the General Procedure 2.7 and purified by column chromatography (Hexane: Ethyl acetate = 5:1) in 75% yield as white solid.

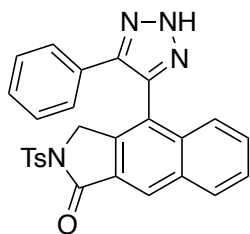
¹H NMR (600 MHz; CDCl₃): δ 8.51 (d, *J* = 8.5 Hz, 1H), 8.48 (s, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.78 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.68-7.65 (m, 3H), 7.44 (dt, *J* = 4.5, 1.7 Hz, 3H), 5.60 (s, 2H).
¹³C NMR (151 MHz; CDCl₃): δ 170.7, 143.2, 135.8, 133.2, 131.8, 130.5, 129.8, 129.3, 128.6, 127.4, 127.1, 126.1, 123.3, 122.3, 115.3, 100.6, 82.6, 69.8
HRMS *m/z* (ESI) calcd. for C₂₀H₁₃O₂⁺ (M+H)⁺ 285.0911, found 285.0903



5aa

11-(5-phenyl-2H-1,2,3-triazol-4-yl)-9-tosyl-9,10-dihydro-8H-naphtho[1,2-f]isoindol-8-one
5aa was prepared following the General Procedure 2.8 and purified by column chromatography (DCM: MeOH = 20:1) in 92% yield as white solid.

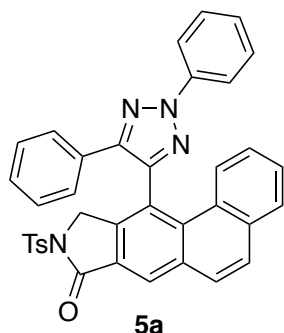
¹H NMR (500 MHz; CDCl₃:CD₃OD (10:1)): δ 8.43 (s, 1H), 7.90-7.73 (m, 6H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.34-7.11 (m, 8H), 4.68 (d, *J* = 16.2 Hz, 1H), 4.37 (d, *J* = 16.4 Hz, 1H), 2.39 (s, 3H).
¹³C NMR δ (126 MHz; CDCl₃:CD₃OD (10:1)): δ 165.9, 145.4, 139.2, 134.9, 134.3, 133.95, 133.88, 129.7, 129.05, 128.93, 128.87, 128.80, 128.78, 128.69, 128.62, 128.0, 127.64, 127.50, 127.1, 126.70, 126.65, 126.3, 40.4, 21.6
HRMS *m/z* (ESI) calcd. for C₃₁H₂₃N₄O₃S⁺ (M+H)⁺ 531.1486, found 531.1508



5ab

4-(5-phenyl-2H-1,2,3-triazol-4-yl)-2-tosyl-2,3-dihydro-1H-benzo[f]isoindol-1-one
5ab was prepared following the General Procedure 2.8 and purified by column chromatography (DCM: MeOH = 20:1) in 90% yield as white solid. **5ab** have poor solubility in CDCl₃ and *d*₆-DMSO.

¹H NMR (500 MHz; CDCl₃:CD₃OD (10:1)): δ 8.47 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.54 (dd, *J* = 19.6, 7.5 Hz, 2H), 7.31-7.19 (m, 7H), 4.69 (s, 2H), 2.41 (s, 3H).
¹³C NMR (126 MHz; CDCl₃:CD₃OD): δ 166.0, 145.3, 135.5, 135.02, 134.92, 133.3, 130.2, 129.7, 129.5, 128.91, 128.72, 128.69, 128.0, 127.48, 127.30, 127.12, 126.5, 125.5, 21.6
HRMS *m/z* (ESI) calcd. for C₂₇H₂₁N₄O₃S⁺ (M+H)⁺ 481.1329, found 481.1331



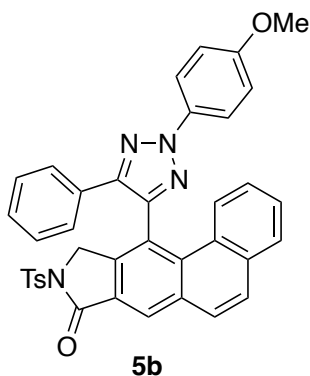
4-(2,5-diphenyl-2H-1,2,3-triazol-4-yl)-2-tosyl-2,3-dihydro-1H-benzo[f]isoindol-1-one

5a was prepared following the General Procedure 2.9 and purified by column chromatography (Hexane: Ethyl acetate = 3:1) in 92% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 8.48 (s, 1H), 8.24-8.23 (m, 2H), 7.94 (dd, *J* = 16.0, 8.6 Hz, 3H), 7.89-7.82 (m, 3H), 7.58-7.51 (m, 3H), 7.46-7.42 (m, 3H), 7.29-7.25 (m, 3H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 2H), 4.79 (d, *J* = 16.3 Hz, 1H), 4.49 (d, *J* = 16.4 Hz, 1H), 2.39 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.6, 146.0, 145.3, 143.7, 139.6, 139.3, 135.2, 134.3, 134.1, 133.8, 129.81, 129.75, 129.5, 129.27, 129.19, 129.04, 128.89, 128.18, 128.10, 128.08, 127.82, 127.76, 127.3, 126.8, 126.6, 126.3, 124.2, 119.0, 49.9, 21.7

HRMS *m/z* (ESI) calcd. for C₃₇H₂₇N₄O₃S⁺ (M+H)⁺ 607.1799, found 607.1817



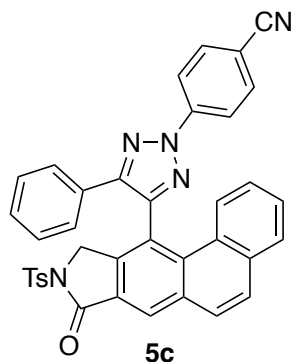
11-(2-(4-methoxyphenyl)-5-phenyl-2H-1,2,3-triazol-4-yl)-9-tosyl-9,10-dihydro-8H-naphtho[1,2-f]isoindol-8-one

5b was prepared following the General Procedure 2.9 and purified by column chromatography (Hexane: Ethyl acetate = 3:1) in 83% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 8.48 (s, 1H), 8.14 (d, *J* = 9.0 Hz, 2H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.89-7.82 (m, 3H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.29-7.24 (m, 3H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 2H), 7.06 (d, *J* = 9.0 Hz, 2H), 4.78 (d, *J* = 16.3 Hz, 1H), 4.48 (d, *J* = 16.4 Hz, 1H), 3.90 (s, 3H), 2.39 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.7, 159.5, 145.5, 145.3, 143.1, 139.3, 135.2, 134.4, 134.1, 133.9, 133.4, 129.85, 129.74, 129.4, 129.16, 129.02, 128.88, 128.17, 128.07, 127.79, 127.77, 127.2, 126.80, 126.63, 126.3, 124.4, 120.4, 114.5, 55.7, 50.0, 21.7

HRMS *m/z* (ESI) calcd. for C₃₈H₂₉N₄O₄S⁺ (M+H)⁺ 637.1905, found 637.1917



4-(4-(8-oxo-9-tosyl-9,10-dihydro-8H-naphtho[1,2-f]isoindol-11-yl)-5-phenyl-2H-1,2,3-triazol-2-yl)benzonitrile

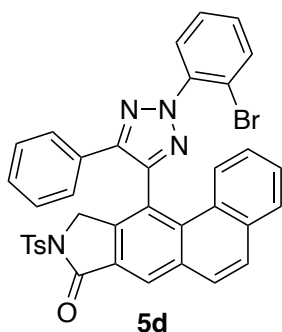
5c was prepared following the General Procedure 2.9 and purified by column chromatography (Hexane: Ethyl acetate = 3:1) in 77% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 8.51 (s, 1H), 8.36 (d, *J* = 8.8 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.90-7.84 (m, 6H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.41-7.39 (m, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.27-7.23 (m, 2H), 7.14 (t, *J* = 7.8 Hz, 2H), 4.80 (d, *J* = 16.3 Hz, 1H), 4.47 (d, *J* = 16.3 Hz, 1H), 2.40 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.4, 147.4, 145.42, 145.30, 142.1, 139.1, 135.1, 134.4, 134.1, 133.71, 133.66, 129.77, 129.59, 129.56, 129.29, 129.18, 128.99, 128.6, 128.2, 127.91, 127.76, 127.58, 126.8, 126.44, 126.36, 123.5, 119.2, 118.2, 111.4, 49.8, 21.7

¹⁹F NMR (564 MHz; CDCl₃): δ -117.2

HRMS *m/z* (ESI) calcd. for C₃₈H₂₆N₅O₃S⁺ (M+H)⁺ 632.1751, found 632.1752



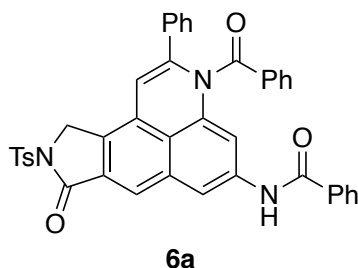
11-(2-(2-bromophenyl)-5-phenyl-2H-1,2,3-triazol-4-yl)-9-tosyl-9,10-dihydro-8H-naphtho[1,2-f]isoindol-8-one

5d was prepared following the General Procedure 2.9 and purified by column chromatography (Hexane: Ethyl acetate = 3:1) in 45% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 8.47 (s, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.87-7.80 (m, 5H), 7.55 (dt, *J* = 17.2, 8.2 Hz, 2H), 7.44-7.39 (m, 3H), 7.30 (t, *J* = 10.3 Hz, 3H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 2H), 4.88 (d, *J* = 16.3 Hz, 1H), 4.55 (d, *J* = 16.3 Hz, 1H), 2.39 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 165.6, 146.2, 145.3, 143.8, 139.5, 139.3, 135.2, 134.36, 134.27, 134.03, 133.93, 131.1, 129.78, 129.73, 129.17, 129.08, 129.01, 128.90, 128.37, 128.20, 128.15, 128.12, 127.78, 127.71, 127.3, 126.90, 126.76, 126.4, 123.9, 119.0, 50.1, 21.7

HRMS *m/z* (ESI) calcd. for C₃₇H₂₆BrN₄O₃S⁺ (M+H)⁺ 685.0904, found 685.0899



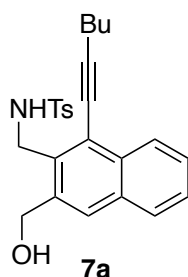
***N*-(3-benzoyl-8-oxo-2-phenyl-9-tosyl-3,8,9,10-tetrahydroisoindolo[4,5,6-*de*]quinolin-5-yl)benzamide**

6a was prepared following the General Procedure 2.1 and purified by column chromatography (Hexane: Ethyl acetate = 3:1) in 83% yield as red solid.

¹H NMR (600 MHz; CDCl₃): δ 8.30 (d, *J* = 1.6 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 1.7 Hz, 1H), 8.00 (s, 1H), 7.90 (d, *J* = 7.4 Hz, 2H), 7.85 (s, 1H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 7.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.17-7.14 (m, 7H), 6.03 (s, 1H), 4.92 (s, 2H), 2.43 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 172.4, 166.04, 165.89, 145.3, 144.4, 138.7, 138.0, 137.4, 136.3, 135.37, 135.29, 134.6, 132.4, 132.1, 129.80, 129.77, 128.92, 128.86, 128.81, 128.75, 128.34, 128.23, 127.10, 126.98, 126.1, 125.6, 124.2, 121.0, 112.3, 107.3, 105.6, 48.5, 21.7

HRMS *m/z* (ESI) calcd. for C₄₁H₃₂N₃O₅S⁺ (M+H)⁺ 678.2058, found 678.2083



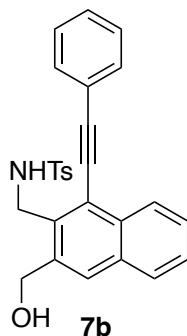
***N*-((1-(hex-1-yn-1-yl)-3-(hydroxymethyl)naphthalen-2-yl)methyl)-4-methylbenzenesulfonamide**

7a was prepared following the General Procedure 2.10 and purified by column chromatography (Hexane: Ethyl acetate = 3:1) in 82% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 8.21 (d, *J* = 8.2 Hz, 1H), 7.74 (dt, *J* = 17.3, 8.6 Hz, 4H), 7.54-7.47 (m, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 5.42 (t, *J* = 6.5 Hz, 1H), 4.84 (s, 2H), 4.57 (d, *J* = 6.6 Hz, 2H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.64-1.59 (m, 3H), 1.49 (q, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 143.3, 136.7, 136.3, 134.6, 133.2, 132.5, 129.7, 129.4, 128.3, 128.0, 127.13, 127.01, 126.84, 126.45, 126.42, 122.9, 101.3, 76.2, 63.9, 43.5, 30.8, 22.2, 21.4, 19.5, 13.6

HRMS *m/z* (ESI) calcd. for C₂₅H₂₆NO₂S⁺ (M-OH)⁺ 404.1679, found 404.1675



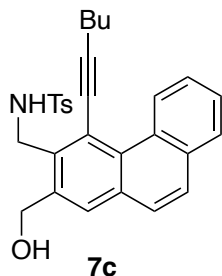
***N*-((3-(hydroxymethyl)-1-(phenylethynyl)naphthalen-2-yl)methyl)-4-methylbenzenesulfonamide**

7b was prepared following the General Procedure 2.10 and purified by column chromatography (Hexane: Ethyl acetate = 3:1) in 92% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 8.33 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 5.2 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.57 (dt, *J* = 31.8, 7.4 Hz, 2H), 7.42 (ddd, *J* = 26.8, 14.0, 6.3 Hz, 5H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.34 (s, 2H), 5.02 (t, *J* = 6.2 Hz, 1H), 4.66 (d, *J* = 6.4 Hz, 2H), 2.30 (s, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 170.6, 143.4, 136.5, 134.9, 133.1, 132.5, 132.3, 131.7, 130.5, 129.6, 129.0, 128.5, 128.3, 127.7, 127.27, 127.11, 126.3, 122.5, 122.2, 99.7, 84.7, 64.4, 43.5, 21.5, 21.1

HRMS *m/z* (ESI) calcd. for C₂₇H₂₂NO₂S⁺ (M-OH)⁺ 424.1366, found 424.1371



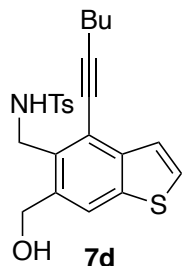
***N*-((4-(hex-1-yn-1-yl)-2-(hydroxymethyl)phenanthren-3-yl)methyl)-4-methylbenzenesulfonamide**

7c was prepared following the General Procedure 2.10 and purified by column chromatography (Hexane: Ethyl acetate = 3:1) in 83% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 10.18 (d, *J* = 8.4 Hz, 1H), 7.85 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.73 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 3H), 7.62-7.56 (m, 3H), 7.11 (d, *J* = 7.9 Hz, 2H), 5.49 (t, *J* = 6.7 Hz, 1H), 4.87 (s, 2H), 4.63 (d, *J* = 6.7 Hz, 2H), 2.59 (d, *J* = 1.4 Hz, 1H), 2.48 (t, *J* = 7.2 Hz, 2H), 2.19 (s, 3H), 1.66-1.63 (m, 2H), 1.54-1.50 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 143.3, 137.04, 137.00, 136.83, 133.2, 132.6, 130.3, 129.8, 129.4, 129.2, 128.4, 126.95, 126.90, 126.2, 125.6, 120.8, 102.6, 80.7, 63.5, 53.4, 43.4, 30.3, 22.3, 21.3, 19.8, 13.7

HRMS *m/z* (ESI) calcd. for C₂₉H₂₈NO₂S⁺ (M-OH)⁺ 454.1836, found 454.1830



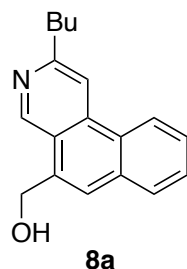
***N*-((4-(hex-1-yn-1-yl)-6-(hydroxymethyl)benzo[*b*]thiophen-5-yl)methyl)-4-methylbenzenesulfonamide**

7d was prepared following the General Procedure 2.10 and purified by column chromatography (Hexane: Ethyl acetate = 3:1) in 85% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 7.74 (s, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 5.4 Hz, 1H), 7.42-7.41 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 4.78 (s, 2H), 4.49 (s, 2H), 2.43 (t, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.61-1.56 (m, 2H), 1.51-1.46 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 143.2, 141.0, 139.1, 136.7, 135.4, 132.5, 129.7, 129.4, 127.6, 127.1, 126.4, 123.8, 122.6, 119.9, 99.4, 76.6, 63.8, 43.0, 30.8, 22.2, 21.4, 19.4, 13.6

HRMS *m/z* (ESI) calcd. for C₂₃H₂₄NO₂S₂⁺ (M-OH)⁺ 410.1243, found 410.1245



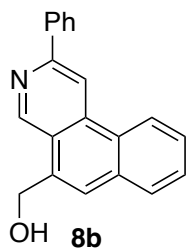
(2-butylbenzo[*f*]isoquinolin-5-yl)methanol

8a was prepared following the General Procedure 2.11 and purified by column chromatography (Hexane: Ethyl acetate = 2:1) in 63% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 9.46 (s, 1H), 8.66-8.64 (m, 1H), 8.28 (s, 1H), 7.91-7.89 (m, 1H), 7.80 (s, 1H), 7.71-7.68 (m, 2H), 5.26 (d, *J* = 0.6 Hz, 2H), 3.04 (t, *J* = 7.8 Hz, 2H), 2.61 (s, 3H), 1.87-1.84 (m, 2H), 1.46 (dt, *J* = 14.9, 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 158.1, 147.6, 136.1, 134.0, 133.2, 128.80, 128.76, 128.5, 127.0, 125.9, 123.17, 123.05, 114.6, 63.0, 41.0, 38.3, 32.4, 22.6, 14.0

HRMS *m/z* (ESI) calcd. for C₁₈H₂₀NO⁺ (M+H)⁺ 266.1540, found 266.1545



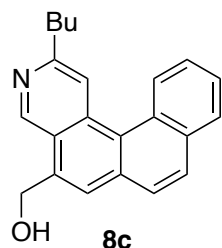
(2-phenylbenzo[*f*]isoquinolin-5-yl)methanol

8b was prepared following the General Procedure 2.11 and purified by column chromatography (Hexane: Ethyl acetate = 2:1) in 72% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 9.58 (s, 1H), 8.79 (s, 1H), 8.70 (dd, *J* = 5.8, 3.4 Hz, 1H), 8.17 (d, *J* = 7.7 Hz, 2H), 7.89 (dd, *J* = 5.9, 3.2 Hz, 1H), 7.79 (s, 1H), 7.71 (dq, *J* = 6.1, 3.1 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.48-7.45 (m, 1H), 5.27 (s, 2H).

¹³C NMR (151 MHz; CDCl₃): δ 153.2, 148.1, 139.7, 136.2, 133.9, 133.3, 128.93, 128.91, 128.88, 128.81, 128.75, 127.24, 127.17, 126.6, 124.0, 123.0, 112.7, 63.0

HRMS *m/z* (ESI) calcd. for C₂₀H₁₆NO⁺ (M+H)⁺ 286.1227, found 286.1286



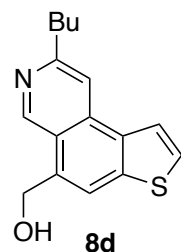
(2-butyl-naphtho[1,2-f]isoquinolin-5-yl)methanol

8c was prepared following the General Procedure 2.11 and purified by column chromatography (Hexane: Ethyl acetate = 2:1) in 25% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 9.55 (s, 1H), 8.91 (d, *J* = 8.4 Hz, 1H), 8.64 (s, 1H), 8.00 (d, *J* = 7.8 Hz, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.83 (s, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.69-7.67 (m, 1H), 7.63 (t, *J* = 7.3 Hz, 1H), 5.27 (s, 2H), 3.01 (t, *J* = 7.7 Hz, 2H), 1.82 (dt, *J* = 15.2, 7.6 Hz, 2H), 1.44 (dt, *J* = 14.9, 7.4 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 156.9, 147.9, 135.33, 135.25, 133.4, 132.9, 130.1, 129.6, 128.9, 127.0, 126.82, 126.67, 126.18, 125.2, 124.1, 119.0, 62.3, 38.1, 32.3, 22.5, 14.0

HRMS *m/z* (ESI) calcd. for C₂₂H₂₂NO⁺ (M+H)⁺ 316.1696, found 316.1749



(8-butylthieno[3,2-f]isoquinolin-5-yl)methanol

8d was prepared following the General Procedure 2.11 and purified by column chromatography (Hexane: Ethyl acetate = 2:1) in 55% yield as white solid.

¹H NMR (600 MHz; CDCl₃): δ 9.49 (s, 1H), 7.96 (s, 1H), 7.93 (d, *J* = 5.3 Hz, 1H), 7.89 (s, 1H), 7.61 (d, *J* = 5.3 Hz, 1H), 5.25 (s, 2H), 2.99 (t, *J* = 7.8 Hz, 2H), 1.82 (q, *J* = 7.7 Hz, 2H), 1.44 (q, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

¹³C NMR (151 MHz; CDCl₃): δ 157.1, 148.3, 140.7, 134.0, 133.60, 133.54, 126.6, 122.2, 121.9, 120.0, 115.2, 62.7, 38.0, 32.3, 22.6, 14.0

HRMS *m/z* (ESI) calcd. for C₁₆H₁₈NOS⁺ (M+H)⁺ 272.1104, found 272.1186

VII. NMR Spectra Data

