Supplementary Information

Dirhodium(II)-Catalyzed Cycloisomerization of Azaenyne: Rapid Assembly of Centrally and Axially Chiral Isoindazoles Frameworks

Shaotong Qiu, Xiang Gao, and Shifa Zhu*†‡
†Key Lab of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P. R. China
zhusf@scut.edu.cn
‡ Guangdong Youmei Institute of Intelligent Bio-manufacturing Co., Ltd.

Table of content

1. HPLC analysis of product 2m’ and 2m”.................................................................2
2. Proposed mechanism for central-to-axial chirality transfer of 4 to 5........................2
3. Experimental procedures and spectroscopic data..................................................3
   3.1 General information .........................................................................................3
   3.2 General procedure for the preparation of azaenyenes ......................................3
   3.3 Procedures for initial investigation of cycloisomerization of azaenyne (imine, triazene and diazene) .................................................................15
   3.4 General procedures for cycloisomerization of azaenyne 1.................................17
   3.5 General procedures for cycloisomerization of azaenyne 3.................................26
   3.6 Procedures for central-to-axial chirality transfer reaction of 2m .......................29
   3.7 General procedures for central-to-axial chirality transfer reactions of 4 ...............30
   3.8 Procedures for late-modification of chiral isoindazoles ....................................33
   3.9. Reference ........................................................................................................38
4. X-Ray diffraction analysis....................................................................................39
   4.1 Crystal data and structure refinement for 2h ..................................................39
   4.2 Crystal data and structure refinement for 4g ..................................................40
   4.3 Crystal data and structure refinement for 5g ..................................................41
5. Copies of NMR spectrum ....................................................................................42
6. Data of HPLC .......................................................................................................149
1. HPLC analysis of product 2m’ and 2m”

Two peaks featuring a continuing vague boundary was found via analysis of products 2m’ and 2m” by HPLC using a chiral stationary phase at room temperature, which indicated that 2m’ and 2m” were in a fast equilibrium with each other.

2. Proposed mechanism for central-to-axial chirality transfer of 4 to 5

It’s well known that DDQ is a common oxidant for oxidative aromatization process, wherein DDQ first induced a hydride transfer assisted by long pair of heteroatom to form a stable carbocation, then followed by a β-proton elimination to afford the aromatization product[1]. Based on the reported literatures, we proposed the following possible mechanism for our oxidative central-to-axial chirality transfer process. As shown in Scheme 1S, centrally chiral starting material 4 first underwent hydride transfer to afford intermediate Int-A under DDQ oxidation condition. Then a fast equilibrium between Int-A and Int-A’ might be established through the rotation of isoindozale group, and the intermediate Int-A’ would be more stable due to less steric hindrance. In the consequent β-proton elimination process, path a might proceed easier than path b due to the potential π-π stacking interaction between DDQH+ and the capping 4-bromophenyl group of TS-B’, and therefore resulted in the formation of 5 as the major enantioisomer. As for path b, the steric repulsion between the isoindozale wall and DDQH+ in TS-B will slow down the corresponding transformation.
3. Experimental procedures and spectroscopic data

3.1 General information

All reactions were carried out under an inert atmosphere of dry N₂ in Schlenk tube, solvents were purified by standard method. ¹H, ¹³C, ¹⁹F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ¹H; 101 MHz for ¹³C; 376 MHz for ¹⁹F) or Bruker AVANCE 500 (500 MHz for ¹H; 126 MHz for ¹³C; 471 MHz for ¹⁹F). ¹H NMR and ¹³C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and ¹⁹F NMR chemical shifts were determined relative to CFCl₃ as external standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra (MS) were obtained using ESI mass spectrometer. Melting points were determined using a hot stage apparatus. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

3.2 General procedure for the preparation of azaenyenes

**General procedure for preparation of azaenyenes 1 and 3**

![Chemical diagram]

**Typical procedure for preparation of S2[2]**

Aniline S1 (14.9 mmol, 1.00 equiv) was dissolved in 45 ml of DCM. To this solution Oxone (17.9 g, 29.8 mmol, 2.00 equiv) dissolved in 180 ml of water was added. The solution was stirred under nitrogen at room temperature until TLC monitoring indicated complete consumption of the starting material. After separation of the layers, the aqueous layer was extracted with DCM twice. The combined organic layers were washed with 1N HCl, saturated sodium bicarbonate solution, water,
brine and dried (magnesium sulfate). Removal of the solvent in vacuo yielded S2.

**Typical procedure for preparation of S4**[43]

Substituted nitrosobenzene S2 (1.0 equiv) was added to the substituted iodinated aniline S3 (1.0 equiv) dissolved in AcOH (0.1 M). The solution was heated to 85 °C for 40 h. The resulting mixture was cooled to room temperature, diluted with DCM, and washed with brine and H2O. The organic layer was dried through anhydrous Na2SO4, filtered over Celite, and concentrated in vacuo. Column chromatography on silica gel gave the corresponding 2-idoazobenzenes S4.

**Typical procedure for preparation of S7**

An oven-dried round bottom flask was charged with 2-iodophenols S5 (1.0 equiv), K2CO3 (2.0 equiv), acetone (0.5 M) and alkyl bromide (1-1.5 equiv). The reaction mixture was stirred at 60 °C in an oil bath for 10 h. After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the product S6.

Under nitrogen atmosphere, a mixture of S6 (1.0 eq.), CuI (5 mol%), Pd(PPh3)2Cl2 (3 mol%) were added to a schlenk tube, Et3N (2.5M) and THF (0.5 M) as co-solvent was added to the reaction mixture, then alkyne (1.2 eq) was added slowly. The reaction was stirred at room temperature until the starting material was disappeared. After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator The residue was dissolved in THF (0.5 M), and TBAF tetrabutylammonium fluoride (1 eq) was added and stirred for 5-30 minutes. The mixture was diluted with H2O, and extracted with CH2Cl2. The extract was dried over MgSO4 and evaporated under reduced pressure. The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford S7.

**Typical procedure for preparation of 1.**[41]

2-idoazobenzene S4 (1.0 equiv), Pd(PPh3)2Cl2(0.04 equiv), CuI (0.08 equiv) and nBuNH2 (6.0 mmol, 6.0 equiv) were dissolved in anhydrous THF (0.1 M) under N2 atmosphere. To the resulting solution terminal alkyne S7 (1.2 equiv) was added dropwise. The mixture was stirred at room temperature. After the reaction was completed (detected by TLC) (2-7 h), saturated NH4Cl aqueous solution was added. The organic layer was separated, and the aqueous layer was extracted twice with ethyl acetate. The combined organic layers were dried over Na2SO4 and concentrated in vacuo (without heated). The crude residue was purified by column chromatography on silica gel to afford 1.

**(E)-1-(2-((2-benzyl oxy)phenyl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (1a)**

![Image](https://via.placeholder.com/150)

Yield 52% red solid, m. p. 96-97 °C, Rf = 0.4 (EtOAc/petroleum ether = 1/20);

1H NMR (400 MHz, CDCl3) δ 7.84 (d, J = 8.5 Hz, 2H), 7.77 – 7.67 (m, 2H), 7.56 (d, J = 6.6 Hz, 1H), 7.50 – 7.37 (m, 6H), 7.31 – 7.27 (m, 2H), 7.26 – 7.20 (m, 2H), 7.00 – 6.91 (m, 2H), 5.22 (s, 2H); 13C NMR (101 MHz, CDCl3) δ 159.4, 152.7, 151.6, 137.0, 133.60, 133.57, 132.3, 130.9, 130.0, 128.8, 128.5, 127.7, 126.7, 125.6, 124.8, 124.6, 121.0, 116.0, 113.5, 113.2, 92.5, 91.0, 70.5; IR (KBr, cm−1) 3741, 3194, 3062, 2926, 2359, 1570, 1489, 1283, 1232, 1011, 831, 747; HRMS (ESI) Calcd for C29H19BrN3NaO (M+Na)+ 489.0573, Found 489.0565.

**(E)-1-(4-bromophenyl)-2-(2-((2-(4-methylbenzyl oxy)phenyl)ethynyl)phenyl)diazene (1b)**

![Image](https://via.placeholder.com/150)

Yield 40%, red solid, m. p. 113-114 °C, Rf = 0.5 (EtOAc/petroleum ether = 1/40); 1H NMR (400 MHz, CDCl3) δ 7.79 – 7.69 (m, 2H), 7.62 (dd, J = 11.9, 7.7, 1.6 Hz, 2H), 7.45 (dd, J = 7.6, 1.8 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.34 –
7.25 (m, 2H), 7.23 (d, J = 7.7 Hz, 2H), 7.19 – 7.10 (m, 1H), 6.97 (d, J = 7.7 Hz, 2H), 6.90 – 6.78 (m, 2H), 5.07 (s, 2H), 2.19 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 159.5, 152.7, 151.6, 137.4, 134.0, 133.64, 133.60, 132.2, 130.9, 130.0, 129.2, 128.7, 126.7, 125.6, 124.8, 124.7, 121.0, 115.9, 113.5, 113.3, 92.7, 91.0, 70.5, 21.2; IR (KBr, cm⁻¹) 2954, 2918, 2850, 2215, 1589, 1498, 1444, 1227, 1045, 748; HRMS (ESI) Calcd for C28H24BrN2O (M+H)+ 481.0910, Found 481.0907.

(E)-1-(4-bromophenyl)-2-(2-((4-methoxybenzyl)oxy)phenyl)ethynylphenyl)diazene (1c)

Yield 38%, red solid, m.p. 60-61 °C, Rf = 0.4 (DCM/petroleum ether = 1/5); 1H NMR (400 MHz, CDCl3) δ 7.83 (d, J = 8.6 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.70 – 7.64 (m, 1H), 7.54 (dd, J = 7.5, 1.4 Hz, 1H), 7.49 (d, J = 8.6 Hz, 2H), 7.46 – 7.37 (m, 2H), 7.34 (d, J = 8.6 Hz, 2H), 7.29 – 7.23 (m, 1H), 6.98 – 6.89 (m, 2H), 6.79 (d, J = 8.7 Hz, 2H), 5.13 (s, 2H), 3.74 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 159.5, 159.2, 152.6, 151.6, 133.62, 133.6, 132.3, 129.0, 130.0, 128.7, 128.3, 125.6, 124.8, 124.7, 121.0, 115.9, 113.9, 113.6, 113.5, 92.6, 91.0, 70.5, 55.3; IR (KBr, cm⁻¹) 3068, 2926, 2900, 2842, 2215, 1587, 1572, 1513, 1463, 1493, 1444, 1227, 1241, 1033, 831; HRMS (ESI) Calcd for C29H23BrN2O2 (M+H)+ 497.0859, Found 497.0855.

(E)-1-(4-bromophenyl)-2-(2-((4-fluorobenzyl)oxy)phenyl)ethynylphenyl)diazene (1d)

Yield 45%, red solid, m. p. 100-101 °C, Rf = 0.5 (DCM/petroleum ether = 1/10); 1H NMR (400 MHz, CDCl3) δ 7.74 (d, J = 8.3 Hz, 2H), 7.65 (d, J = 7.8 Hz, 1H), 7.59 (d, J = 7.5 Hz, 1H), 7.47 (d, J = 7.5 Hz, 1H), 7.43 (d, J = 8.3 Hz, 2H), 7.37 – 7.30 (m, 4H), 7.19 (q, J = 7.3, 6.8 Hz, 1H), 6.92 – 6.83 (m, 4H), 5.06 (s, 2H); 13C NMR (101 MHz, CDCl3) δ 163.1 (d, J = 246.0 Hz), 159.3, 152.7, 151.6, 133.5 (d, J = 7.2 Hz), 132.7 (d, J = 3.2 Hz), 132.2, 130.9, 130.0, 128.8, 128.6, 128.5, 125.6, 124.8, 124.5, 121.3, 116.0, 115.3 (d, J = 21.4 Hz), 113.7, 113.4, 92.4, 91.1, 70.1; 19F NMR (376 MHz, CDCl3) δ -114.6; IR (KBr, cm⁻¹) 3060, 2955, 2853, 2215, 1604, 1573, 1510, 1494, 1447, 1278, 1225, 832, 749; HRMS (ESI) Calcd for C27H19BrFN3O (M+H)+ 485.0659, Found 485.0663.

(E)-1-(4-bromophenyl)-2-(2-((4-chlorobenzyl)oxy)phenyl)ethynylphenyl)diazene (1e)

Yield 50%, red solid, m. p. 113-114 °C, Rf = 0.5 (DCM/petroleum ether = 1/5); 1H NMR (500 MHz, CDCl3) δ 7.81 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 7.5 Hz, 1H), 7.56 (dd, J = 7.6, 1.7 Hz, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.48 – 7.39 (m, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.31 – 7.25 (m, 1H), 7.20 (d, J = 8.1 Hz, 2H), 6.98 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H), 5.14 (s, 2H); 13C NMR (126 MHz, CDCl3) δ 159.2, 152.7, 151.5, 135.4, 133.6, 133.5, 133.4, 132.2, 130.9, 130.0, 128.8, 128.6, 128.0, 125.6, 124.7, 124.5, 121.3, 116.0, 113.7, 113.2, 92.3, 91.1, 69.9; IR (KBr, cm⁻¹) 3006, 2924, 2851, 2210, 1572, 1495, 1411, 1275, 1260, 834, 763, 749; HRMS (ESI) Calcd for C27H17BrClIN2O (M+Na)+ 523.0183, Found 523.0185.

(E)-1-(2-((4-bromobenzyl)oxy)phenyl)ethynylphenyl)-2-(4-bromophenyl)diazene (1f)

Yield 50%, red solid, m. p. 122-123 °C, Rf = 0.5 (DCM/petroleum ether = 1/5); 1H NMR (500 MHz, CDCl3) δ 7.81 (d, J = 8.3 Hz, 2H), 7.73 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 8.3 Hz, 2H), 7.46 – 7.39 (m, 2H), 7.35 (d, J = 8.1 Hz, 2H), 7.30 (s, 1H), 7.29 – 7.20
(m, 2H), 6.98 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 5.12 (s, 2H); 13C NMR (126 MHz, CDCl3) δ 159.1, 152.7, 151.5, 136.0, 133.6, 133.5, 132.2, 131.5, 130.9, 130.0, 128.8, 128.3, 125.6, 124.7, 124.5, 121.6, 121.3, 116.0, 113.6, 113.2, 92.3, 91.1, 69.9; IR (KBr, cm⁻¹) 3006, 2918, 2851, 2220, 1572, 1408, 1275, 1260, 833, 763, 750; HRMS (ESI) Calcd for C27H16Br2N2O (M+Na)+ 566.9678, Found 544.9855.

(E)-1-(4-bromophenyl)-2-(2-((4-(trifluoromethyl)benzyl)oxy)phenyl)ethylphenyldiazenie (1g)

Yield 41%, red solid, m. p. 147-148 °C, Rf = 0.5 (DCM/petroleum ether = 1/1); 1H NMR (400 MHz, CDCl3) δ 7.80 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.0 Hz, 1H), 7.69 (dd, J = 7.4, 1.9 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.51 – 7.34 (m, 6H), 7.30 (t, J = 8.0 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 7.6 Hz, 1H), 5.23 (s, 1H); 13C NMR (101 MHz, CDCl3) δ 159.0, 152.7, 151.5, 141.0, 133.6, 133.5, 132.2, 130.9, 130.0, 128.9, 127.3, 126.7, 125.6, 125.4 (q, J = 4.0 Hz), 124.7, 124.4, 121.4, 116.0, 113.6, 113.0, 92.2, 91.2, 69.7; 19F NMR (376 MHz, CDCl3) δ -62.5; IR (KBr, cm⁻¹) 2926, 2217, 1573, 1469, 1445, 1421, 1325, 1280, 1164, 1115, 1066, 822, 762; HRMS (ESI) Calcd for C28H19Br2N2O (M+H)+ 535.0627, Found 535.0625.

(E)-4-((2-((4-bromophenyl)diazenyl)phenyl)ethynyl)phenoxy)methyl)benzonitrile (1h)

Yield 39%, red solid, m. p. 235-236 °C, Rf = 0.8 (DCM/petroleum ether = 1/2); 1H NMR (400 MHz, CDCl3) δ 7.25 – 7.3 (m, 3H), 7.70 (dd, J = 7.3, 1.8 Hz, 1H), 7.58 (dd, J = 7.6, 1.8 Hz, 1H), 7.53 (d, J = 8.2 Hz, 2H), 7.51 – 7.39 (m, 6H), 7.31 (d, J = 7.9, 1.8 Hz, 1H), 7.02 (td, J = 7.5, 1.0 Hz, 1H), 6.92 (d, J = 8.3 Hz, 1H), 5.21 (s, 2H); 13C NMR (101 MHz, CDCl3) δ 158.8, 152.7, 151.4, 142.3, 133.7, 133.4, 132.2, 131.0, 130.1, 129.0, 125.7, 124.7, 124.4, 121.6, 118.7, 116.1, 113.7, 113.0, 111.5, 92.1, 91.3, 69.5; IR (KBr, cm⁻¹) 3060, 2900, 2867, 2225, 2214, 1589, 1572, 1495, 1278, 1238, 1108, 833, 815, 748; HRMS (ESI) Calcd for C23H13BrN2O (M+H)+ 492.0706, Found 492.0702.

(E)-1-(2-((3-bromobenzyl)oxy)phenyl)ethylphenyldiazenie (1i)

Yield 38%, red solid, m. p. 105-106 °C, Rf = 0.5 (DCM/petroleum ether = 1/10); 1H NMR (500 MHz, CDCl3) δ 7.72 (d, J = 8.4 Hz, 2H), 7.67 – 7.60 (m, 2H), 7.56 (s, 1H), 7.46 (dd, J = 7.6, 1.7 Hz, 1H), 7.40 (d, J = 8.3 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.29 (t, J = 7.7 Hz, 1H), 7.23 (t, J = 8.4 Hz, 2H), 7.17 (td, J = 7.9, 1.7 Hz, 1H), 7.01 (t, J = 7.8 Hz, 1H), 6.88 (t, J = 7.5 Hz, 1H), 6.80 (d, J = 8.3 Hz, 1H), 5.02 (s, 2H); 13C NMR (126 MHz, CDCl3) δ 159.1, 152.7, 151.6, 139.3, 133.7, 133.6, 132.2, 131.0, 130.8, 130.03, 130.00, 129.6, 128.9, 125.6, 125.1, 124.8, 124.5, 122.7, 121.4, 116.0, 113.6, 113.1, 92.3, 91.3, 69.7; IR (KBr, cm⁻¹) 3061, 2954, 2924, 2853, 2215, 1590, 1572, 1495, 1478, 1279, 1239, 1065, 1006, 832, 740; HRMS (ESI) Calcd for C27H16Br2N2O (M+H)+ 544.9859, Found 544.9852.

(E)-1-(2-((2-bromobenzyl)oxy)phenyl)ethylphenyldiazenie (1j)

Yield 45%, red solid, m. p. 115-116 °C, Rf = 0.4 (EtOAc/petroleum ether = 1/40); 1H NMR (400 MHz, CDCl3) δ 7.80 (d, J = 8.4 Hz, 2H), 7.76 – 7.70 (m, 2H), 7.70 – 7.65 (m, 1H), 7.57 (dd, J = 7.6, 1.8 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.48
\( (E) - 1 - (4\text{-bromophenyl})-2 - (2 - ((2\text{-methoxybenzyl})\text{-oxy})\text{phenyl})\text{ethynyl}\text{phenyl})\text{diazene} \) (I)

\[
\begin{align*}
\text{Yield 55\%, red solid, m. p.} & \text{ 90-91 °C, R}_2 \text{ = 0.6 (EtOAc/petroleum ether = 1/20); } \\
\text{H NMR (500 MHz, CDCl}_3 \text{) } & \delta \text{ 7.88 – 7.79 (m, 2H), 7.73 (dd, } J = 7.6, 4.5, 1.4 \text{ Hz, 2H), 7.57 (ddd, } J = 9.8, 7.6, 1.7 \text{ Hz, 2H), 7.48 – 7.36 (m, 4H), 7.27 (td, } J = 7.9, 1.7 \text{ Hz, 1H), 7.20 (td, } J = 7.9, 1.7 \text{ Hz, 1H), 6.95 (t, } J = 7.5 \text{ Hz, 2H), 6.88 – 6.79 (m, 2H), 5.25 (s, 2H), 3.85 (s, 3H); } \\
\text{C NMR (126 MHz, CDCl}_3 \text{) } & \delta \text{ 159.6, 156.2, 152.7, 151.6, 133.5, 133.4, 132.2, 130.9, 130.0, 128.7, 128.4, 127.4, 125.5, 125.4, 124.8, 124.0, 120.7, 115.9, 113.3, 112.9, 109.9, 92.7, 90.9, 65.6, 55.4; } \\
\text{IR (KBr, cm}^{-1} \text{) } & \text{3059, 2959, 2928, 2857, 2216, 1734, 1590, 1573, 1495, 1278, 1244, 1048, 1031, 834, 740; } \\
\text{HRMS (ESI) Caled for C}_{27}\text{H}_{12}\text{Br}_{2}\text{N}_2\text{O (M+H)}^+ \text{544.9859, Found 544.9855}
\end{align*}
\]

\( (E) - 1 - (4\text{-bromophenyl})-2 - (2 - ((2\text{-naphthalen-1-ylmethoxy})\text{phenyl})\text{ethynyl}\text{phenyl})\text{diazene} \) (II)

\[
\begin{align*}
\text{Yield 41\%, red solid, m. p.} & \text{ 120-121 °C, R}_2 \text{ = 0.6 (DCM/petroleum ether = 1/10); } \\
\text{H NMR (500 MHz, CDCl}_3 \text{) } & \delta \text{ 8.12 – 8.07 (m, 1H), 7.85 – 7.80 (m, 1H), 7.80 – 7.76 (m, 2H), 7.74 (d, } J = 8.3 \text{ Hz, 1H), 7.72 – 7.67 (m, 1H), 7.65 (d, } J = 7.0 \text{ Hz, 1H), 7.56 (dd, } J = 7.7, 1.7 \text{ Hz, 1H), 7.52 – 7.46 (m, 1H), 7.46 – 7.38 (m, 4H), 7.38 – 7.30 (m, 3H), 7.27 (td, } J = 7.8, 1.7 \text{ Hz, 1H), 7.02 (d, } J = 8.3 \text{ Hz, 1H), 6.97 (t, } J = 7.4 \text{ Hz, 1H), 5.63 (s, 2H); } \\
\text{C NMR (126 MHz, CDCl}_3 \text{) } & \delta \text{ 159.5, 152.6, 151.5, 133.7, 133.61, 133.56, 132.2, 131.0, 130.8, 130.0, 128.71, 128.6, 126.4, 125.8, 125.6, 125.59, 125.3, 124.7, 124.6, 123.5, 121.3, 115.9, 113.8, 113.6, 92.6, 91.2, 69.4; } \\
\text{IR (KBr, cm}^{-1} \text{) } & \text{3059, 2924, 2215, 1590, 1573, 1494, 1478, 1446, 1278, 1265, 1234, 1065, 1006, 748; } \\
\text{HRMS (ESI) Caled for C}_{28}\text{H}_{12}\text{Br}_{2}\text{N}_2\text{O} (M+Na)}^+ \text{519.0679, Found 519.0682}
\end{align*}
\]

\( (E) - 1 - (4\text{-bromophenyl})-2 - (2 - ((2\text{-naphthalen-2-ylmethoxy})\text{phenyl})\text{ethynyl}\text{phenyl})\text{diazene} \) (IIm)

\[
\begin{align*}
\text{Yield 39\%, red solid, m. p.} & \text{ 119-120 °C, R}_2 \text{ = 0.4 (DCM/petroleum ether = 1/5); } \\
\text{H NMR (500 MHz, CDCl}_3 \text{) } & \delta \text{ 7.90 (s, 1H), 7.79 – 7.75 (m, 3H), 7.76 – 7.70 (m, 3H), 7.70 – 7.65 (m, 1H), 7.57 (dd, } J = 8.0, 1.7 \text{ Hz, 1H), 7.52 (dd, } J = 8.4, 1.7 \text{ Hz, 1H), 7.44 – 7.37 (m, 6H), 7.26 (td, } J = 7.9, 1.8 \text{ Hz, 1H), 7.02 – 6.93 (m, 2H), 5.34 (s, 2H); } \\
\text{C NMR (126 MHz, CDCl}_3 \text{) } & \delta \text{ 159.5, 152.7, 151.5, 134.5, 133.64, 133.55, 133.3, 133.0, 132.1, 130.9, 130.0, 128.8, 128.3, 127.9, 127.7, 126.2, 125.9, 125.5, 124.7, 124.6, 121.1, 116.0, 113.7, 113.3, 92.6, 91.2, 70.8; } \\
\text{IR (KBr, cm}^{-1} \text{) } & \text{3057, 2924, 2853, 2215, 1590, 1573, 1494, 1479, 1446, 1278, 1239, 1148, 1007, 833, 814, 749; } \\
\text{HRMS (ESI) Caled for C}_{28}\text{H}_{12}\text{Br}_{2}\text{N}_2\text{O} (M+H)}^+ \text{517.0910, Found 517.0901}
\end{align*}
\]
(E)-1-(2-((2-allyloxy)phenyl)ethynyl)phenyl-2-(4-bromophenyl)diazene (1n)

Yield 40%, red solid, m. p. 70–71 °C, Rf = 0.4 (EtOAc/petroleum ether = 1:20); 1H NMR (500 MHz, CDCl3) δ 7.94 – 7.86 (m, 2H), 7.72 (dd, J = 7.8, 1.5 Hz, 2H), 7.62 (d, J = 8.7 Hz, 2H), 7.54 (dd, J = 7.6, 1.8 Hz, 1H), 7.44 (td, J = 7.4, 1.5 Hz, 1H), 7.38 (td, J = 7.6, 1.6 Hz, 1H), 7.28 (td, J = 7.9, 1.8 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 6.02 (ddt, J = 17.4, 10.1, 4.8 Hz, 1H), 5.46 (dd, J = 17.2, 1.8 Hz, 1H), 5.22 (dd, J = 10.7, 1.7 Hz, 1H), 4.65 (dt, J = 4.8, 1.8 Hz, 2H); 13C NMR (126 MHz, CDCl3) δ 159.2, 152.7, 151.7, 133.7, 133.6, 133.0, 132.3, 130.9, 129.9, 128.7, 125.6, 124.9, 124.6, 120.8, 117.2, 116.0, 113.3, 112.8, 92.5, 90.8, 69.4; IR (KBr, cm⁻¹) 2959, 2924, 2216, 1591, 1573, 1494, 1445, 1278, 1225, 1006, 928, 832,748; HRMS (ESI) Calcd for C23H13BrN2O (M+H)+ 417.0597, Found 417.0602.

(ESI)-1-(4-bromophenyl)-2-(2-((2-but-2-yn-1-yloxy)phenyl)ethynyl)phenyl)diazene (1o)

Yield 43%, red solid m. p. 60–61 °C; Rf = 0.4 (EtOAc/petroleum ether = 1:20); 1H NMR (500 MHz, CDCl3) δ 7.99 – 7.90 (m, 2H), 7.73 (ddd, J = 7.7, 4.0, 1.4 Hz, 2H), 7.71 – 7.65 (m, 2H), 7.55 (dd, J = 7.5, 1.7 Hz, 1H), 7.43 (td, J = 7.4, 1.4 Hz, 1H), 7.38 (td, J = 7.7, 1.6 Hz, 1H), 7.35 – 7.29 (m, 1H), 7.10 (d, J = 8.3 Hz, 1H), 6.98 (t, J = 7.5 Hz, 1H), 4.76 (d, J = 2.4 Hz, 2H), 1.83 (s, t, J = 2.4 Hz, 3H); 13C NMR (126 MHz, CDCl3) δ 158.6, 152.6, 151.7, 133.7, 133.5, 132.4, 130.9, 129.9, 128.8, 125.6, 125.0, 124.7, 121.2, 115.8, 113.3, 113.0, 92.4, 90.9, 84.3, 74.2, 57.2, 3.8; IR (KBr, cm⁻¹) 3064, 2920, 2863, 2223, 1585, 1486, 1288, 1223, 1002, 831, 752; HRMS (ESI) Calcd for C22H13BrN2O (M+Na)+ 451.0416, Found 451.0408.

(ESI)-1-(4-bromophenyl)-2-(2-((3-(trimethylsilyl)prop-2-yn-1-yloxy)phenyl)ethynyl)phenyl)diazene (1p)

Yield 39%, red oil, Rf = 0.4 (EtOAc/petroleum ether = 1:20); 1H NMR (500 MHz, CDCl3) δ 7.79 – 7.90 (m, 2H), 7.81 – 7.51 (m, 4H), 7.39 (dd, J = 7.5, 1.8 Hz, 1H), 7.27 (td, J = 7.4, 1.4 Hz, 1H), 7.22 (td, J = 7.6, 1.6 Hz, 1H), 7.16 (td, J = 7.9, 1.7 Hz, 1H), 6.96 (d, J = 8.3 Hz, 1H), 6.84 (t, J = 7.5 Hz, 1H), 4.63 (s, 2H), 0.00 (s, 9H); 13C NMR (126 MHz, CDCl3) δ 158.8, 152.9, 152.0, 133.9, 133.7, 132.7, 131.2, 130.1, 129.1, 126.0, 125.3, 124.9, 121.7, 116.1, 113.8, 113.7, 100.4, 93.7, 92.5, 91.3, 57.9, 0.0; IR (KBr, cm⁻¹) 3065,2956, 2218, 2178, 1581, 1484, 1406, 1252, 1218, 1154, 1052, 927, 846, 756; HRMS (ESI) Calcd for C26H23BrN2O4Si (M+H)+ 847.0836, Found 847.0831.

(ESI)-1-(4-bromophenyl)-2-(2-((3-phenylpropoxy)phenyl)ethynyl)phenyl)diazene (1q)

Yield 58%, red solid, m. p. 110–111 °C, Rf = 0.6 (EtOAc/petroleum ether = 1:40); 1H NMR (500 MHz, CDCl3) δ 7.86 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 7.7 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 7.5 Hz, 1H), 7.44 – 7.33 (m, 2H), 7.26 (t, J = 7.8 Hz, 1H), 7.20 (d, J = 8.0 Hz, 2H), 7.13 (t, J = 8.1 Hz, 3H), 6.93 (t, J = 7.5 Hz, 1H), 6.85 (d, J = 8.3 Hz, 1H), 4.02 (t, J = 6.2 Hz, 2H), 2.79 (t, J = 7.6 Hz, 2H), 2.11 – 2.02 (m, 2H); 13C NMR (126 MHz, CDCl3) δ 159.7, 152.7, 151.7, 141.5, 133.6, 133.5, 132.3, 130.9, 130.0, 128.7, 128.6, 128.4, 125.9, 125.7, 124.9, 124.7, 120.6, 116.1, 113.2, 112.4, 92.7, 90.8, 67.6, 32.0, 30.9; IR (KBr, cm⁻¹) 3061, 3026, 2954, 2923, 2853,
(E)-1-(4-bromophenyl)-2-(2-(2-isopentylxoxy)phenyl)ethynyl)phenyl)diazene (1r)

Yield 72%, red solid, m. p. 70-71 °C, Rf = 0.6 (petroleum ether); 1H NMR (400 MHz, CDCl3) δ 7.94 – 7.82 (m, 2H), 7.75 – 7.67 (m, 2H), 7.67 – 7.60 (m, 2H), 7.52 (dd, J = 7.6, 1.8 Hz, 1H), 7.47 – 7.33 (m, 2H), 7.29 (td, J = 7.9, 1.8 Hz, 1H), 6.97 – 6.87 (m, 2H), 4.07 (t, J = 6.7 Hz, 2H), 1.91 – 1.78 (m, 1H), 1.67 (dd, J = 6.7, 6.3 Hz, 2H), 0.91 (d, J = 6.6 Hz, 6H); 13C NMR (101 MHz, CDCl3) δ 159.9, 152.6, 151.7, 133.5, 132.3, 130.8, 130.0, 128.6, 125.6, 124.9, 124.7, 120.4, 116.0, 113.1, 112.2, 92.8, 90.6, 67.4, 37.9, 25.2, 22.7; IR (KBr, cm\(^{-1}\)) 2956, 2928, 2871, 2222, 1591, 1573, 1495, 1444, 1279, 1244, 1066, 743; HRMS (ESI) Calcd for C\(_{29}\)H\(_{22}\)BrN\(_2\)O (M+H\(^+\)) 495.1067, Found 495.1065.

(2,6-Br\(_2\), 92, 132.3)-Calcd for C\(_{29}\)H\(_{22}\)BrN\(_2\)O (M+H\(^+\)) 495.1067, Found 495.1065.

(E)-1-(4-bromophenyl)-2-(2-isobutoxyphenyl)ethynyl)phenyl)diazene (1s)

Yield 50%, red solid, m. p. 65-66 °C, Rf = 0.5 (EtOAc/petroleum ether = 1/50); 1H NMR (500 MHz, CDCl3) δ 7.89 (d, J = 8.4 Hz, 2H), 7.74 – 7.68 (m, 2H), 7.64 (d, J = 8.3 Hz, 2H), 7.51 (dd, J = 7.6, 1.7 Hz, 1H), 7.45 (td, J = 7.5, 1.3 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.33 – 7.27 (m, 1H), 6.97 – 6.87 (m, 2H), 3.81 (d, J = 6.6 Hz, 2H), 2.15 – 2.05 (m, 1H), 1.02 (d, J = 6.7 Hz, 6H); 13C NMR (126 MHz, CDCl3) δ 159.9, 152.7, 151.7, 133.6, 133.4, 132.3, 130.8, 130.0, 128.6, 125.6, 124.8, 124.7, 120.4, 116.0, 113.1, 112.2, 92.6, 90.5, 75.1, 28.4, 19.2; IR (KBr, cm\(^{-1}\)) 2970, 2936, 2873, 2220, 1573, 1496, 1275, 1260, 764, 749; HRMS (ESI) Calcd for C\(_{29}\)H\(_{22}\)BrN\(_2\)O (M+H\(^+\)) 433.0910, Found 433.0911.

(E)-1-(4-bromophenyl)-2-(2-(2-cyclopropylmethoxy)phenyl)ethynyl)phenyl)diazene (1t)

Yield 52%, red solid, m. p. 69-70 °C, Rf = 0.4 (EtOAc/petroleum ether = 1/50); 1H NMR (400 MHz, CDCl3) δ 7.93 – 7.84 (m, 2H), 7.76 – 7.68 (m, 2H), 7.65 – 7.60 (m, 2H), 7.52 (dd, J = 7.6, 1.8 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.40 – 7.34 (m, 1H), 7.27 (t, J = 7.8 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 3.93 (d, J = 6.5 Hz, 2H), 1.27 – 1.19 (m, 1H), 0.56 – 0.49 (m, 2H), 0.38 – 0.31 (m, 2H); 13C NMR (126 MHz, CDCl3) δ 159.8, 152.7, 151.7, 133.6, 133.5, 132.3, 130.9, 130.0, 128.7, 125.6, 124.9, 124.7, 120.8, 116.0, 113.6, 113.4, 92.8, 90.7, 73.5, 10.4, 3.2; IR (KBr, cm\(^{-1}\)) 3079, 3006, 2923, 2871, 2215, 1590, 1573, 1494, 1440, 1446, 1279, 1241, 1108, 1022, 1007, 834, 750; HRMS (ESI) Calcd for C\(_{32}\)H\(_{28}\)BrN\(_2\)O (M+H\(^+\)) 431.0754, Found 431.0746.

(E)-1-(4-bromophenyl)-2-(2-(2-(3-methoxypropoxy)phenyl)ethynyl)phenyl)diazene (1u)

Yield 51%, red solid, m. p. 60-61 °C, Rf = 0.6 (EtOAc/petroleum ether = 1/20); 1H NMR (500 MHz, CDCl3) δ 7.88 (d, J = 8.6 Hz, 2H), 7.70 (ddd, J = 7.6, 3.3, 1.4 Hz, 2H), 7.66 – 7.61 (m, 2H), 7.52 (dd, J = 7.5, 1.7 Hz, 1H), 7.42 (td, J = 7.5, 1.3 Hz, 1H), 7.37 (ddd, J = 8.7, 7.3, 1.5 Hz, 1H), 7.32 – 7.25 (m, 1H), 6.97 – 6.89 (m, 2H), 4.14 (t, J = 6.3 Hz, 2H), 3.53 (t, J = 6.2 Hz, 2H), 3.26 (s, 3H), 2.02 (p, J = 6.3 Hz, 2H); 13C NMR (126 MHz, CDCl3) δ 159.6, 152.6, 151.7, 133.6, 133.5, 132.4, 130.9, 130.1, 128.7, 125.7, 124.8, 124.7, 120.6, 116.0, 113.1, 112.4, 92.7, 90.7, 69.1, 65.7, 58.7, 29.6; IR (KBr, cm\(^{-1}\)) 3062, 2927, 2877, 2215, 1645, 1596, 1494, 1453, 1279, 1246, 1115, 833, 750; HRMS (ESI) Calcd for C\(_{32}\)H\(_{32}\)BrN\(_2\)O\(_2\) (M+H\(^+\)) 449.0859, Found 449.0862.
(E)-1-(2-((2-benzyloxy)phenyl)ethyl)phenyl)-2-phenyldiazone (1v)

Yield 42%, red solid, m. p. 110-111 °C, Rf = 0.6 (EtOAc/petroleum ether = 1/40); 1H NMR (500 MHz, CDCl3) δ 8.05 – 7.98 (m, 2H), 7.74 (dd, J = 6.9, 2.3 Hz, 1H), 7.69 (dd, J = 6.6, 2.5 Hz, 1H), 7.57 (dd, J = 7.6, 1.8 Hz, 1H), 7.49 – 7.44 (m, 2H), 7.44 – 7.35 (m, 5H), 7.31 – 7.22 (m, 4H), 6.95 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 8.3 Hz, 1H), 5.21 (s, 2H); 13C NMR (126 MHz, CDCl3) δ 159.4, 153.0, 152.9, 137.1, 133.6, 133.55, 131.2, 130.5, 129.9, 129.0, 128.8, 128.5, 127.7, 126.8, 124.3, 123.4, 121.0, 116.1, 113.7, 113.3, 92.3, 91.2, 70.5; IR (KBr, cm⁻¹) 3061, 2962, 2213, 1586, 1488, 1451, 1279, 1230, 1155, 1107, 1015, 753, 692; HRMS (ESI) Calcd for C27H21N2O (M+H)⁺ 389.1649, Found 389.1643.

(4E)-1-(2-((2-benzyloxy)phenyl)ethyl)phenyl)-2-(4-methoxyphenyl)diazene (1w)

Yield 49%, red oil, Rf = 0.4 (DCM/petroleum ether = 1/5); 1H NMR (400 MHz, CDCl3) δ 8.11 – 8.01 (m, 2H), 7.82 – 7.76 (m, 1H), 7.76 – 7.72 (m, 1H), 7.64 (dd, J = 7.6, 1.6 Hz, 1H), 7.53 (d, J = 7.2 Hz, 2H), 7.48 – 7.40 (m, 2H), 7.39 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 7.01 (td, J = 7.5, 0.8 Hz, 1H), 6.97 – 6.89 (m, 3H), 5.29 (s, 2H), 3.84 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 162.3, 159.4, 153.1, 147.4, 137.2, 133.6, 133.5, 129.9, 128.8, 128.5, 127.7, 126.7, 125.3, 123.8, 121.0, 116.0, 114.2, 113.8, 113.3, 92.1, 91.4, 70.5, 55.6; IR (KBr, cm⁻¹) 3062, 2933, 2213, 1593, 1498, 1451, 1258, 1145, 1103, 1025, 837, 752, 697; HRMS (ESI) Calcd for C28H23N2O (M+H)⁺ 419.1754, Found 419.1749.

(4E)-1-(2-((2-benzyloxy)phenyl)ethyl)-4-fluorophenyl)-2-(4-bromophenyl)diazene (1x)

Yield 41%, red solid, m. p. 110-111 °C, Rf = 0.6 (DCM/petroleum ether = 1/5); 1H NMR (500 MHz, CDCl3) δ 7.82 (d, J = 8.3 Hz, 2H), 7.78 (dd, J = 9.1, 5.6 Hz, 1H), 7.55 (d, J = 7.6 Hz, 1H), 7.51 – 7.42 (m, 4H), 7.36 (dd, J = 9.0, 2.7 Hz, 1H), 7.33 – 7.25 (m, 4H), 7.09 (td, J = 8.4, 2.8 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 5.22 (s, 2H); 13C NMR (126 MHz, CDCl3) δ 163.9 (d, J = 252.9 Hz), 159.5, 151.4, 149.2 (d, J = 3.1 Hz), 136.9, 133.6, 132.3, 130.4, 128.5, 127.8, 126.9 (d, J = 10.6 Hz), 126.6, 125.6, 124.8, 121.0, 119.6 (d, J = 23.9 Hz), 117.9 (d, J = 9.6 Hz), 116.4 (d, J = 23.3 Hz), 113.0, 93.7, 89.9 (d, J = 2.9 Hz), 70.5; 19F NMR (471 MHz, CDCl3) δ -109.4; IR (KBr, cm⁻¹) 3744, 3153, 2199, 1574, 1510, 1279, 1174, 1132, 803, 689; HRMS (ESI) Calcd for C28H19BrF2N2O (M+H)⁺ 485.0659, Found 485.0654.

(4E)-1-(2-((2-benzyloxy)phenyl)ethyl)-4-methoxyphenyl)-2-(4-bromophenyl)diazene (1y)

Yield 45%, red solid, m. p. 80-81 °C, Rf = 0.4 (DCM/petroleum ether = 1/5); 1H NMR (500 MHz, CDCl3) δ 7.81 (t, J = 8.3 Hz, 3H), 7.62 – 7.54 (m, 1H), 7.47 (d, J = 8.0 Hz, 4H), 7.29 (t, J = 7.3 Hz, 3H), 7.25 – 7.21 (m, 1H), 7.16 (d, J = 2.9 Hz, 1H), 7.02 – 6.91 (m, 3H), 5.23 (s, 2H), 3.86 (s, 3H); 13C NMR (126 MHz, CDCl3) δ 161.8, 159.5, 151.7, 147.1, 137.0, 133.6, 132.2, 130.1, 128.5, 127.7, 126.9, 126.7, 124.8, 124.5, 121.0, 117.4, 116.4, 113.4, 113.1, 92.5, 91.1, 70.5, 55.7; IR (KBr, cm⁻¹) 3749, 3736, 2362, 1684, 1671, 1635, 1540, 1521, 1508, 1492, 1270, 751; HRMS (ESI) Calcd for C28H26Br2N2O2 (M+H)⁺ 497.0859, Found 497.0863.
(E)-1-(2-(2-benzylthio)phenyl)ethynyl)-2-(4-bromophenyl)diazene (1ac)

Yield 30%, red solid, m. p. 88-89 °C, Rf = 0.35 (EtOAc/petroleum ether = 1/20);

1H NMR (500 MHz, CDCl3) δ 8.17 (d, J = 8.5 Hz, 2H), 8.08 (d, J = 8.6 Hz, 2H), 7.90 (d, J = 8.3 Hz, 2H), 7.79 – 7.71 (m, 2H), 7.66 – 7.59 (m, 4H), 7.49 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 7.4 Hz, 2H), 7.17 (t, J = 7.4 Hz, 1H), 4.19 (s, 2H); 13C NMR (126 MHz, CDCl3) δ 152.7, 151.4, 142.6, 139.9, 136.7, 133.8, 133.0, 132.2, 132.1, 132.0, 130.9, 129.1, 128.9, 128.6, 127.4, 127.3, 125.5, 125.0, 123.9, 116.0, 93.5, 92.9, 37.4; IR (KBr, cm⁻¹) 3545, 3059, 2932, 1593, 1485, 1450, 1383, 1068, 751, 703; HRMS (ESI) Calcd for C27H27BrN3 (M+H)+ 483.0525, Found 483.0516.

(E)-1-(2-(2-benzylthio)naphthalen-1-yl)ethynylphenyl)-2-(4-bromophenyl)diazene (3a)

Yield 72%, red solid, m. p. 125-126 °C, Rf = 0.6 (DCM/petroleum ether = 1/2); 1H NMR (500 MHz, CDCl3) δ 8.48 – 8.42 (m, 1H), 7.94 – 7.88 (m, 2H), 7.80 – 7.73 (m, 4H), 7.58 – 7.51 (m, 4H), 7.47 (td, J = 7.4, 1.4 Hz, 1H), 7.43 – 7.37 (m, 3H), 7.34 (dd, J = 8.3, 6.6 Hz, 2H), 7.31 – 7.26 (m, 1H), 7.24 (d, J = 6.1 Hz, 1H), 5.37
(s, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 158.5, 152.8, 151.7, 137.2, 134.8, 133.5, 132.3, 131.0, 130.4, 128.9, 128.7, 128.6, 128.1, 127.9, 127.4, 127.0, 125.9, 125.7, 125.01, 124.99, 124.6, 116.0, 115.2, 107.9, 96.7, 91.0, 71.6; IR (KBr, cm$^{-1}$) 3053, 2193, 1592, 1451, 1269, 1147, 1071, 801, 749, 694; HRMS (ESI) Calcd for C$_{35}$H$_{27}$Br$_{2}$N$_{2}$O (M+H)$^+$ 517.0910, Found 517.0901.

**Methyl (E)-4-(((1-((2-((4-bromophenyl)diazenyl)phenyl)ethynyl)naphthalen-2-yl)oxy)methyl)benzoate (3b)**

Yield 48%, red solid, m. p. 144-145 °C, $R_t$ = 0.6 (DCM/petroleum ether = 1/1); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.49 – 8.40 (m, 1H), 8.03 – 7.96 (m, 2H), 7.92 – 7.84 (m, 2H), 7.81 – 7.73 (m, 4H), 7.60 (d, $J = 8.1$ Hz, 2H), 7.57 – 7.51 (m, 2H), 7.48 (td, $J = 7.5$, 1.4 Hz, 1H), 7.46 – 7.36 (m, 3H), 7.21 (d, $J = 9.1$ Hz, 1H), 5.37 (s, 2H), 3.90 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.8, 158.0, 152.8, 142.3, 134.8, 133.3, 132.3, 131.1, 130.4, 129.8, 129.6, 129.0, 128.8, 128.1, 127.5, 126.6, 125.9, 125.7, 125.0, 124.8, 124.7, 116.1, 114.9, 108.1, 96.8, 90.7, 70.9, 52.1; IR (KBr, cm$^{-1}$) 3055, 2944, 2197, 1814, 1718, 1579, 1441, 1271, 1184, 1106, 1013, 806, 754; HRMS (ESI) Calcd for C$_{35}$H$_{27}$Br$_{2}$N$_{2}$O (M+Na)$^+$ 597.0784, Found 597.0781.

**(E)-1-((4-bromophenyl)-2-((2-(naphthalen-2-ylmethoxy)naphthalen-1-yl)ethynyl)phenyl)diazene (3c)**

Yield 52%, red solid, m. p. 134-135 °C, $R_t$ = 0.3 (DCM/petroleum ether = 1/1); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.49 – 8.42 (m, 1H), 7.99 (s, 1H), 7.91 – 7.85 (m, 2H), 7.84 – 7.73 (m, 7H), 7.63 (dd, $J = 8.5$, 1.8 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.48 – 7.38 (m, 6H), 7.30 (d, $J = 9.0$ Hz, 1H), 5.51 (s, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 158.5, 152.8, 151.6, 134.8, 134.7, 133.5, 133.3, 133.1, 132.2, 131.0, 130.4, 129.0, 128.8, 128.4, 128.1, 128.0, 127.8, 127.4, 126.2, 126.0, 125.9, 125.8, 124.94, 124.86, 124.6, 116.1, 115.3, 108.1, 96.8, 91.0, 71.8; IR (KBr, cm$^{-1}$) 3053, 2937, 2199,1572, 1507, 1468, 1330, 1272, 1068, 812, 742; HRMS (ESI) Calcd for C$_{35}$H$_{27}$Br$_{2}$N$_{2}$O (M+H)$^+$ 567.1067, Found 567.1074.

**(E)-1-((4-chlorophenyl)-2-((2-((3,5-dibromobenzyl)oxy)naphthalen-1-yl)ethynyl)phenyl)diazene (3d)**

Yield 50%, red solid, m. p. 161-162 °C, $R_t$ = 0.6 (DCM/petroleum ether = 1/1); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.49 – 8.44 (m, 1H), 8.01 – 7.96 (m, 2H), 7.90 – 7.79 (m, 4H), 7.69 (s, 2H), 7.59 (s, 1H), 7.55 – 7.49 (m, 1H), 7.49 – 7.40 (m, 5H), 7.27 (s, 1H), 5.29 (s, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 157.7, 152.8, 151.3, 141.1, 137.2, 134.7, 133.6, 133.5, 131.1, 130.5, 129.3, 129.1, 128.9, 128.5, 128.1, 127.5, 125.9, 124.9, 124.7, 124.6, 123.1, 116.0, 114.9, 108.3, 97.0, 90.3, 70.0; IR (KBr, cm$^{-1}$) 2999, 2193, 1721, 1583, 1423, 1267, 1144, 1093, 835, 800, 752, 660; HRMS (ESI) Calcd for C$_{35}$H$_{27}$Br$_{2}$Cl$_{2}$N$_{2}$O (M+H)$^+$ 628.9626, Found 628.9619.
(E)-1-(4-bromophenyl)-2-((2-(3,5-difluorobenzyl)oxy)naphthalen-1-yl)ethynyl)phenyl)diazene

(3e)

Yield 55%, red solid, m. p. 146-147 °C, Rf = 0.3 (DCM/petroleum ether = 1/1);

1H NMR (500 MHz, CDCl3) δ 8.46 (d, J = 7.5 Hz, 1H), 7.91 (d, J = 8.3 Hz, 2H), 7.88 – 7.74 (m, 5H), 7.59 (d, J = 8.3 Hz, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.13 (d, J = 7.0 Hz, 2H), 6.73 (t, J = 8.8 Hz, 1H), 5.33 (s, 2H); 13C NMR (126 MHz, CDCl3) δ 163.2 (dd, J = 249.0, 12.7 Hz), 157.7, 152.8, 151.6, 141.2 (t, J = 9.1 Hz), 134.8, 133.3, 132.5, 131.3, 130.5, 129.1, 128.9, 128.1, 127.5, 125.7, 125.0, 124.9, 124.7, 116.1, 114.8, 109.5 (dd, J = 19.7, 6.1 Hz), 108.2, 103.1 (t, J = 25.3 Hz), 96.9, 90.5, 70.2; 19F NMR (471 MHz, CDCl3) δ -109.3; IR (KBr, cm⁻¹) 3780, 3545, 1595, 1439, 1268, 1113, 755, 540; HRMS (ESI) Calcd for C31H20BrF2N2O (M+H)⁺ 606.9953, Found 606.9953.

dimethyl (E)-5-((1-(2-(4-bromophenyl)diazene)phenyl)ethynyl)naphthalen-2-yl)oxy)methyl)-isophthalate (3g)

Yield 68%, red solid, m. p. 140-141 °C, Rf = 0.6 (DCM/EtOAc /petroleum ether = 40/1/40); 1H NMR (500 MHz, CDCl3) δ 8.55 (s, 1H), 8.48 – 8.43 (m, 1H), 8.39 (s, 2H), 7.87 – 7.75 (m, 6H), 7.52 (t, J = 8.4 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.45 – 7.40 (m, 3H), 7.29 (d, J = 9.0 Hz, 1H), 5.38 (s, 2H), 3.83 (s, 6H); 13C NMR (126 MHz, CDCl3) δ 166.0, 158.0, 152.8, 151.5, 138.1, 134.7, 133.6, 132.20, 132.16, 131.0, 130.9, 130.5, 130.3, 129.1, 128.8, 128.2, 127.5, 125.9, 125.6, 124.9, 115.9, 115.1, 108.4, 97.0, 90.5, 70.9, 52.3; IR (KBr, cm⁻¹) 2995, 1719, 1562, 1436, 1271, 1107, 806, 754, 548; HRMS (ESI) Calcd for C33H25BrN2O5 (M+Na)⁺ 633.1028, Found 633.1028.

(3h)

Yield 45% red solid, m. p. 70-71 °C, Rf = 0.6 (DCM/petroleum ether = 1/1);

1H NMR (500 MHz, CDCl3) δ 8.48 – 8.42 (m, 1H), 7.93 – 7.88 (m, 2H), 7.83 (dd, J = 7.6, 1.5 Hz, 1H), 7.78 (d, J = 8.5 Hz, 3H), 7.59 – 7.53 (m, 2H), 7.47 (dd, J = 7.4, 1.4 Hz, 1H), 7.44 – 7.38 (m, 3H), 7.26 (d, J = 9.1 Hz, 1H), 6.71 (d, J = 2.4 Hz, 2H), 6.36 (t, J = 2.4 Hz, 1H), 5.32 (s, 2H), 3.72 (s, 6H); 13C
NMR (101 MHz, CDCl₃) δ 161.0, 158.4, 152.8, 151.6, 139.6, 134.8, 133.6, 132.3, 131.0, 130.4, 128.9, 128.8, 128.1, 127.4, 125.8, 125.0, 124.9, 124.6, 116.0, 115.1, 107.9, 104.7, 99.8, 96.6, 90.9, 71.4, 55.4; IR (KBr, cm⁻¹) 3057, 2999, 2942, 2839, 2201, 1599, 1467, 1381, 1276, 1206, 1152, 1012, 824, 755; HRMS (ESI) Calcd for C₃₃H₂₅BrN₂O₃ (M+Na)⁺ 599.0941, Found 599.0943.

**Procedure for preparation of azaenyene (imine)**

![Diagram](image)

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, S₈ (1.0 eq.), S₇ (1.1 eq), CuI (5 mol%), Pd(PPh₃)₂Cl₂ (3 mol%) were added, and Et₃N (2.5M) and THF (0.5 M) as co-solvent were added to the reaction mixture, The mixture was stirred at room temperature until the substrate S₈ was completely consumed. After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the product S₉.

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, 4 Å MS (100 mg) was activated by heat gun. After cooling the tube to room temperature, S₉ (1 eq), tBuNH₂ (2 eq), dry DCM (0.25 M) were added. The mixtures were stirred at room temperature until the starting material was consumed. After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was used as substrate directly.

**1-(2-(2-(benzylxy)phenyl)ethyl)(phenyl)-N-(tert-butyl)methanimine**

Yield 80%, light yellow oil, Rₜ = 0.7 (EtOAc/petroleum ether = 1/20); ¹H NMR (500 MHz, CDCl₃) δ 8.97 (s, 1H), 8.12 – 8.05 (m, 1H), 7.54 (dd, J = 6.0, 3.0 Hz, 1H), 7.51 (dd, J = 7.6, 1.5 Hz, 1H), 7.47 (d, J = 7.4 Hz, 2H), 7.38 – 7.32 (m, 4H), 7.28 (dd, J = 9.6, 7.1 Hz, 2H), 6.98 – 6.91 (m, 2H), 5.23 (s, 2H), 1.26 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 159.2, 154.6, 137.0, 133.4, 132.4, 129.9, 129.7, 128.6, 128.5, 127.8, 126.9, 126.8, 125.9, 124.5, 121.0, 113.2, 113.0, 91.4, 90.9, 70.4, 57.7, 29.7; IR (KBr, cm⁻¹) 3064, 3033, 2964, 2925, 2865, 2745, 2212, 1695, 1636, 1590, 1488, 1451, 1379, 754; HRMS (ESI) Calcd for C₂₆H₂₆NO (M+H)⁺ 368.2009, Found 368.2011.

**Procedure for preparation of azaenyene (triazene)**

![Diagram](image)

The o-iodoaniline S₃ (23 mmol, 1.0 eq.) was dissolved in a 2:1 mixture of acetonitrile–water (30 mL) and cooled to 0 °C. Concentrated aqueous HCl (7.6 mL, 91 mmol, 4.0 eq.) was added dropwise. The
reaction mixture was further cooled to −5 °C and aqueous solution of NaNO₂ (2.4 g, 34 mmol in 30 mL water, 1.5 eq.) was introduced slowly, while maintaining the reaction temperature below 0 °C. After the addition was complete, the reaction mixture was stirred at between −5 °C and 0 °C for 30 minutes and was added slowly to a stirred solution of piperidine S10 (5.6 mL, 57 mmol, 2.5 eq.) and potassium carbonate (16 g, 119 mmol, 5.2 eq) in a 2:1 mixture of acetonitrile and water (120 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and was stirred at that temperature for 1 hour. The resulting solution was extracted three times using ethyl acetate (20 mL × 3). The combined organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated under reduced pressure. The residue was purified by flash silica gel column chromatography (petroleum ether–ethyl acetate = 30:1) to give the corresponding ortho-iodo triazene substrate S11.

Ortho-iodo triazene substrate S11 (1.0 eq), Pd(PPh₃)₄Cl₂ (0.04 equiv), CuI (0.08 equiv) and nBuNH₂ (6.0 mmol, 6.0 equiv) were dissolved in anhydrous THF (0.1 M) under N₂ atmosphere. To the resulting solution terminal alkyne S7 (1.2 equiv) was added dropwise. The mixture was stirred at room temperature. After the reaction was completed (detected by TLC), saturated NH₄Cl aqueous solution was added. The organic layer was separated, and the aqueous layer was extracted twice with ethyl acetate. The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel to afford the desired triazene product.

(E)-1-((2-((2-benzyloxy)phenyl)ethynyl)phenyl)diazzenyl)piperidine

Yield 44%, white solid, m. p. 96-97 °C, Rf = 0.35 (EtOAc/petroleum ether = 1/20); ¹H NMR (500 MHz, CDCl₃) δ 7.59 – 7.42 (m, 5H), 7.32 (t, J = 7.4 Hz, 2H), 7.26 (t, J = 7.9 Hz, 2H), 7.22 – 7.17 (m, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.95 – 6.86 (m, 2H), 5.20 (s, 2H), 3.79 (s, 4H), 1.61 (s, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 159.1, 151.7, 137.3, 133.5, 133.1, 129.3, 128.8, 128.5, 127.6, 126.8, 125.2, 121.0, 118.8, 117.0, 114.4, 113.3, 92.4, 90.1, 70.5, 52.2, 44.7, 25.4, 24.4; IR (KBr, cm⁻¹) 3061, 2936, 2855, 2211, 1586, 1489, 1419, 1363, 1287, 1226, 1178, 1101, 853, 751; HRMS (ESI) Calcd for C₂₆H₂₆N₃O (M+H)+ 396.2075, Found 396.2075.

3.3 Procedures for initial investigation of cycloisomerization of azaenyne (imine, triazene and diazene)

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, imine (0.2 mmol, 73 mg), DCE (0.1 M, 2 ml) were added with or without Rh₂(OAc)₄ (2 mol%, 2.64 mg). The mixtures were stirred at 100 °C for 48 h. After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the product.
3-(2-(benzyloxy)phenyl)isoquinoline

![Reaction Scheme]

Yield 39%, white solid, m. p. 80-81 °C, Rf = 0.5 (EtOAc/petroleum ether = 1/10); 1H NMR (500 MHz, CDCl₃) δ 9.37 (s, 1H), 8.35 (s, 1H), 8.05 – 7.95 (m, 2H), 7.75 (d, J = 8.2 Hz, 1H), 7.67 (t, J = 7.3 Hz, 1H), 7.59 (t, J = 7.3 Hz, 1H), 7.41 (d, J = 7.3 Hz, 2H), 7.39 – 7.27 (m, 4H), 7.16 (t, J = 7.4 Hz, 1H), 7.11 (d, J = 8.2 Hz, 1H), 5.19 (s, 2H); 13C NMR (101 MHz, CDCl₃) δ 156.3, 151.8, 148.7, 137.1, 136.2, 131.5, 130.4, 129.6, 129.3, 128.5, 127.8, 127.5, 127.4, 127.2, 127.1, 127.0, 121.59, 121.57, 113.4, 70.8; IR (KBr, cm⁻¹) 3445, 3059, 3032, 2919, 2852, 1649, 1574, 1492, 1453, 1279, 1233, 1118, 1021, 754, 697; HRMS (ESI) Calcd for C₂₂H₂₈NO (M+H)⁺ 312.1383, Found 312.1380.

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, triazene (0.2 mmol, 79 mg), DCE (0.1 M, 2 ml) were added with or without Rh₂(OAc)₄ (2 mol%, 2.64 mg). The mixtures were stirred at 100 °C for 48 h. After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the product.

3-(2-phenyl-2,3-dihydrobenzofuran-3-yl)-2-(piperidin-1-yl)-2H-indazole

Yield 30%, white solid, m. p. 142-143 °C, Rf = 0.5 (EtOAc/petroleum ether = 1/20); 1H NMR (400 MHz, CDCl₃) δ 7.48 (d, J = 8.7 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.15 – 7.00 (m, 8H), 6.95 (t, J = 7.3 Hz, 1H), 6.78 – 6.71 (m, 1H), 6.39 (d, J = 7.4 Hz, 1H), 6.01 (d, J = 8.1 Hz, 1H), 5.58 (d, J = 8.5 Hz, 1H), 3.19 (s, 1H), 3.06 (s, 2H), 1.94 – 1.68 (m, 5H), 1.60 (s, 1H), 1.30 (s, 1H); 13C NMR (101 MHz, CDCl₃) δ 160.5, 145.2, 136.4, 130.1, 129.6, 128.3, 127.94, 127.86, 126.9, 126.2, 125.8, 121.7, 121.2, 120.4, 119.3, 117.0, 110.2, 88.6, 57.6, 55.1, 44.8, 26.2, 26.0, 23.4; IR (KBr, cm⁻¹) 3055, 2937, 2852, 1599, 1470, 1383, 1267, 1157, 974, 746, 694; HRMS (ESI) Calcd for C₂₆H₂₆N₃O (M+H)⁺ 396.2071, Found 396.2070.

1-(benzyloxy)-2-(phenylethynyl)benzene

Yield 41%, light yellow oil, Rf = 0.8 (EtOAc/petroleum ether = 1/20); 1H NMR (500 MHz, CDCl₃) δ 7.56 – 7.48 (m, 5H), 7.38 (t, J = 7.6 Hz, 2H), 7.36 – 7.26 (m, 5H), 6.96 (t, J = 7.3 Hz, 2H), 5.21 (s, 2H); 13C NMR (126 MHz, CDCl₃) δ 159.3, 137.1, 133.3, 131.6, 129.6, 128.5, 128.3, 128.1, 127.8, 126.9, 123.7, 121.0, 113.5, 112.9, 93.8, 85.9, 70.5.
In a Schlenk tube with a magnetic bar under nitrogen atmosphere, diazenes (0.2 mmol), DCE (0.1 M, 2 ml) were added with or without Rh\(_2\)(OAc)_4 (2 mol%, 2.64 mg). The mixtures were stirred at room temperature for 48 h. After rapid filtration of silica gel, the solvent was evaporated (without heated) by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the products.

### 3.4 General procedures for cycloisomerization of azaenyne 1

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, 1a (0.2 mmol, 93.4 mg), DCE (0.1 M, 2 ml), Rh\(_2\)(S-TFPTTL)$_4$ (2 mol%, 7.1 mg) were added. The mixtures were stirred at room temperature until the starting material was consumed (TLC detected). After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the product 2a (0.196 mmol, 91.5 mg).

The procedures of other substrates 1, were similar with that mentioned above.

### 2-(4-bromophenyl)-3-[(2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl]-2H-indazole (2a)

Yield 98%, > 99:1 dr, pale solid, m. p. 145-146 °C; Rf = 0.4 (EtOAc/petroleum ether = 1/10); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.54 (d, \(J = 8.2\) Hz, 2H), 7.44 (d, \(J = 8.8\) Hz, 1H), 7.29 (t, \(J = 7.8\) Hz, 1H), 7.12 – 7.06 (m, 2H), 7.01 (t, \(J = 7.6\) Hz, 2H), 6.94 – 6.89 (m, 5H), 6.76 (d, \(J = 7.6\) Hz, 2H), 6.70 (t, \(J = 7.6\) Hz, 1H), 6.41 (d, \(J = 8.7\) Hz, 1H), 5.70 (d, \(J = 8.6\) Hz, 1H), 5.21 (d, \(J = 8.5\) Hz, 1H); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 160.2, 148.7, 138.5, 135.9, 133.1, 132.3, 129.9, 128.5, 128.4, 127.9, 127.2, 126.8, 126.5, 126.1, 123.3, 122.0, 121.92, 121.88, 120.6, 117.5, 110.3, 88.1, 45.6; IR (KBr, cm\(^{-1}\)) 3061, 2962, 2926, 1726, 1597, 1514, 1495, 1478, 1379, 1264, 1233, 1070, 1013, 833, 747; HRMS (ESI) Calcd for C\(_{27}\)H\(_{19}\)BrN\(_2\)O (M+Na\(^{+}\)) 489.0573, Found 489.0579; HPLC: INAg column, 90:10 hexanes:isopropanol, 1.00 mL/min, \(t_R\) = major: 21.4 min, minor: 19.6 min, 98:2 er; \([\alpha]_D^{24}\) 65.4° (c 0.29, CH\(_2\)Cl\(_2\)).
2-(4-bromophenyl)-3-((2R,3R)-2-(p-tolyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2b)

Yield 87%, > 99:1 dr, pale solid, m. p. 160-161 °C, Rf = 0.4
(EtOAc/petroleum ether = 1/10); 1H NMR (400 MHz, CDCl3) δ 7.53 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.7 Hz, 1H), 7.28 (t, J = 7.8 Hz, 1H), 7.11 – 7.07 (m, 2H), 7.01 (d, J = 8.1 Hz, 1H), 6.95 – 6.82 (m, 3H), 6.79 – 6.69 (m, 3H), 6.65 (d, J = 7.8 Hz, 2H), 6.42 (d, J = 8.7 Hz, 1H), 5.66 (d, J = 8.5 Hz, 1H), 5.13 (d, J = 8.5 Hz, 1H), 2.11 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 160.2, 148.6, 138.4, 138.3, 133.4, 132.8, 132.3, 129.9, 128.7, 128.6, 127.4, 126.9, 126.5, 126.2, 123.3, 122.0, 121.91, 121.87, 120.7, 117.4, 110.3, 88.2, 45.5, 21.1; IR (KBr, cm⁻¹) 3053, 2922, 1610, 1596, 1515, 1495, 1477, 1461, 1380, 1264, 1233, 1070, 1013, 833, 750; HRMS (ESI) Calcd for C27H18BrN3O (M+H)+ 481.0910, Found 481.0906; HPLC: WHELK column, 90:10 hexanes/isopropanol, 0.80 mL/min, tR = major: 20.1 min, minor: 18.1 min, 98.2 er; [α]D²⁴ 65.8° (c 0.29, CH₂Cl₂).

2-(4-bromophenyl)-3-((2R,3R)-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2c)

Yield 97%, > 99:1 dr, pale solid, m. p. 152-153 °C, Rf = 0.4
(EtOAc/petroleum ether = 1/8); 1H NMR (400 MHz, CDCl3) δ 7.61 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.9 Hz, 1H), 7.36 (t, J = 7.8 Hz, 1H), 7.18 (d, J = 7.1 Hz, 2H), 7.08 (d, J = 8.1 Hz, 1H), 7.02 – 6.89 (m, 3H), 6.82 – 6.75 (m, 3H), 6.54 (d, J = 8.7 Hz, 2H), 6.47 (d, J = 8.6 Hz, 1H), 5.73 (d, J = 8.4 Hz, 1H), 5.19 (d, J = 8.4 Hz, 1H), 3.67 (s, 3H); 13C NMR (101 MHz, CDCl3) δ 160.1, 159.7, 148.7, 138.4, 133.5, 132.3, 129.9, 128.6, 128.3, 127.8, 126.5, 126.2, 123.3, 122.1, 122.0, 121.9, 120.6, 117.6, 113.4, 110.3, 88.1, 55.2, 55.2, 45.5; IR (KBr, cm⁻¹) 3054, 2960, 2932, 2837, 1727, 1611, 1596, 1515, 1495, 1477, 1461, 1380, 1302, 1252, 1175, 1013, 831, 750; HRMS (ESI) Calcd for C30H22BrN3O (M+H)+ 497.0859, Found 497.0849; HPLC: INN column, 90:10 hexanes/isopropanol, 1.00 mL/min, tR = major: 23.3 min, minor: 25.1 min, 97:3 er; [α]D²⁴ 34.8° (c 0.17, CH₂Cl₂).

2-(4-bromophenyl)-3-((2R,3R)-2-(4-fluorophenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2d)

Yield 88%, > 99:1 dr, pale solid, m. p. 174-175 °C, Rf = 0.4
(EtOAc/petroleum ether = 1/10); 1H NMR (400 MHz, CDCl3) δ 7.57 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.8 Hz, 1H), 7.30 (t, J = 7.8 Hz, 1H), 7.13 – 7.07 (m, 2H), 7.02 (d, J = 8.0 Hz, 1H), 6.98 – 6.87 (m, 3H), 6.75 – 6.70 (m, 3H), 6.62 (t, J = 8.5 Hz, 2H), 6.38 (d, J = 8.7 Hz, 1H), 5.68 (d, J = 8.6 Hz, 1H), 5.22 (d, J = 8.6 Hz, 1H); 13C NMR (101 MHz, CDCl3) δ 162.5 (d, J = 247.8 Hz), 160.0, 148.7, 138.4, 132.8, 132.5, 131.8 (d, J = 3.1 Hz), 130.0, 128.5 (d, J = 8.4 Hz), 128.4, 126.9, 126.6, 126.2, 123.4, 122.11, 122.08, 122.0, 120.4, 117.6, 114.9 (d, J = 21.6 Hz), 110.3, 87.4, 45.5; 19F NMR (376 MHz, CDCl3) δ -112.9; IR (KBr, cm⁻¹) 3056, 2926, 1624, 1607, 1513, 1495, 1380, 1265, 1226, 1158, 1114, 1070, 832, 746; HRMS (ESI) Calcd for C32H18BrF3N2O (M+Na)+ 507.0479, Found 507.0476; HPLC: WHELK column, 90:10 hexanes/isopropanol, 0.80 mL/min, tR = major: 18.4 min, minor: 17.4 min, 99:1 er; [α]D²⁴ 60.8° (c 0.26, CH₂Cl₂).
2-(4-bromophenyl)-3-((2R,3R)-2-(4-chlorophenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2e)

Yield 97%, > 99:1 dr, pale solid, m. p. 168-169 °C, Rf = 0.5 (DCM/petroleum ether = 1/1); 1H NMR (500 MHz, CDCl3) δ 7.66 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 8.7 Hz, 1H), 7.38 (t, J = 7.9 Hz, 1H), 7.23 – 7.14 (m, 2H), 7.10 (d, J = 8.2 Hz, 1H), 7.07 – 6.93 (m, 5H), 6.86 – 6.71 (m, 3H), 6.46 (d, J = 8.7 Hz, 1H), 5.75 (d, J = 8.6 Hz, 1H), 5.31 (d, J = 8.6 Hz, 1H); 13C NMR (126 MHz, CDCl3) δ 159.9, 148.7, 138.4, 134.5, 134.2, 132.7, 132.5, 130.0, 128.4, 128.1, 128.0, 126.9, 126.6, 126.1, 123.4, 122.1, 122.0, 120.4, 117.6, 110.4, 87.3, 45.5; IR (KBr, cm⁻¹) 3053, 2925, 2853, 1598, 1515, 1494, 1477, 1380, 1233, 1090, 1013, 830, 746; HRMS (ESI) Calcd for C27H16BrCIN8O (M+H)+ 501.0364, Found 501.0366; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, tR = major: 17.8 min, minor: 20.1 min, > 99:1 er; [α]D²⁵ 32.4° (c 0.056, CH₂Cl₂).

2-(4-bromophenyl)-3-((2R,3R)-2-(4-bromophenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2f)

Yield 96%, > 99:1 dr, pale solid, m. p. 193-194 °C, Rf = 0.5 (DCM/petroleum ether = 1/1); 1H NMR (500 MHz, CDCl3) δ 7.66 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 8.8 Hz, 1H), 7.38 (t, J = 7.8 Hz, 1H), 7.19 (t, J = 8.5 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.1 Hz, 1H), 7.08 – 6.98 (m, 3H), 6.79 (t, J = 7.7 Hz, 1H), 6.71 (d, J = 8.1 Hz, 2H), 6.45 (d, J = 8.6 Hz, 1H), 5.73 (d, J = 8.6 Hz, 1H), 5.31 (d, J = 9.1 Hz, 1H); 13C NMR (126 MHz, CDCl3) δ 159.9, 148.7, 138.4, 135.0, 132.6, 132.5, 131.0, 130.0, 128.39, 128.35, 126.9, 126.6, 126.1, 123.4, 122.4, 122.1, 122.0, 120.3, 117.6, 110.4, 87.4, 45.4; IR (KBr, cm⁻¹) 3053, 2963, 2925, 2912, 1597, 1515, 1494, 1462, 1407, 1380, 1264, 1233, 1070, 1012, 831, 736; HRMS (ESI) Calcd for C27H16BrClN8O (M+H)+ 544.9859, Found 544.9853; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, tR = major: 17.9 min, minor: 21.2 min, > 99:1 er; [α]D²⁵ 6.0° (c 0.18, CH₂Cl₂).

2-(4-bromophenyl)-3-((2R,3R)-2-(4-(trifluoromethyl)phenyl)-3,3-dihydrobenzofuran-3-yl)-2H-indazole (2g)

Yield 95%, > 99:1 dr, pale solid, m. p. 180-181 °C, Rf = 0.45 (DCM/petroleum ether = 1/2); 1H NMR (400 MHz, CDCl3) δ 7.66 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 8.8 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H), 7.25 – 7.18 (m, 3H), 7.17 – 7.11 (m, 2H), 7.10 – 6.98 (m, 3H), 6.95 (d, J = 8.0 Hz, 2H), 6.76 (t, J = 7.7 Hz, 1H), 6.42 (d, J = 8.7 Hz, 1H), 5.82 (d, J = 8.7 Hz, 1H); 13C NMR (101 MHz, CDCl3) δ 159.9, 148.7, 140.1, 138.4, 132.6, 132.2, 130.5 (q, J = 32.3 Hz), 130.1, 128.2, 126.9, 126.7, 126.1, 124.8 (q, J = 4.0 Hz), 123.7 (q, J = 273.2 Hz), 123.4, 122.3, 122.2, 121.9, 120.3, 117.6, 110.4, 87.1, 45.6; 19F NMR (376 MHz, CDCl3) δ -62.7; IR (KBr, cm⁻¹) 3056, 2963, 2926, 1623, 1597, 1515, 1495, 1478, 1462, 1380, 1324, 1232, 1166, 1125, 1067, 1014, 831, 742; HRMS (ESI) Calcd for C28H19BrF3N8O (M+H)+ 535.0627, Found 535.0629; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, tR = major: 12.9 min, minor: 15.4 min, > 99:1 er; [α]D²⁵ 39.7° (c 0.35, CH₂Cl₂).
4-((2R,3R)-3-(2-(4-bromophenyl)-2H-indazol-3-yl)-2,3-dihydrobenzofuran-2-yl)benzonitrile (2h)

Yield 98%, > 99:1 dr, pale solid, m. p. 184-185 °C, Rf = 0.4 (EtOAc/petroleum ether = 1/5); 1H NMR (400 MHz, CDCl3) δ 7.71 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.8 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 7.27 (d, J = 7.8 Hz, 2H), 7.21 – 7.12 (m, 5H), 7.04 – 6.95 (m, 3H), 6.76 (t, J = 7.7 Hz, 1H), 6.46 (d, J = 8.7 Hz, 1H), 5.84 (d, J = 8.9 Hz, 1H), 5.46 (d, J = 8.9 Hz, 1H); 13C NMR (101 MHz, CDCl3) δ 159.6, 148.7, 141.7, 138.3, 132.7, 132.0, 131.5, 130.2, 128.2, 127.0, 126.8, 126.4, 126.0, 123.6, 122.4, 122.1, 121.8, 120.2, 118.2, 117.7, 112.0, 110.4, 86.7, 45.5; IR (KBr, cm−1) 3057, 2963, 2229, 1726, 1612, 1596, 1514, 1478, 1380, 1264, 1232, 1097, 1013, 832, 749; HRMS (ESI) Calcd for C28H18BrN3O (M+H)+ 492.0706; Found 492.0706; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, tR = major: 45.4 min, minor: 36.8 min, > 99:1 er; [α]D24 14.4° (c 0.027, CH2Cl2).

2-(4-bromophenyl)-3-((2R,3R)-2-(3-bromophenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2i)

Yield 98%, > 99:1 dr, pale solid, m. p. 170-171 °C, Rf = 0.6 (EtOAc/petroleum ether = 1/10); 1H NMR (500 MHz, CDCl3) δ 7.63 (d, J = 7.4 Hz, 2H), 7.45 (d, J = 8.5 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.19 – 7.08 (m, 3H), 7.07 – 7.00 (m, 3H), 6.98 – 6.93 (m, 1H), 6.88 (s, 1H), 6.79 – 6.63 (m, 3H), 6.41 (d, J = 8.2 Hz, 1H), 5.66 (d, J = 8.4 Hz, 1H), 5.27 (d, J = 8.5 Hz, 1H); 13C NMR (126 MHz, CDCl3) δ 159.9, 148.6, 138.4, 138.3, 132.6, 131.3, 130.1, 129.7, 129.5, 128.5, 126.7, 126.6, 126.1, 124.8, 123.4, 122.2, 122.1, 121.94, 121.89, 120.3, 117.6, 110.4, 87.0, 45.5; IR (KBr, cm−1) 3054, 1595, 1494, 1477, 1275, 1262, 1233, 1114, 1070, 833, 749; HRMS (ESI) Calcd for C27H16BrN3O (M+H)+ 544.9859, Found 544.9855; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, tR = major: 18.4 min, minor: 22.3 min, 98.2 er; [α]D24 91.2° (c 0.38, CH2Cl2).

2-(4-bromophenyl)-3-((2R,3R)-2-(2-bromophenyl)-2,3-dihydrobenzofuran-2-yl)-2H-indazole (2j)

Yield 96%, 97:3 dr, pale solid, m. p. 188-189 °C, Rf = 0.6 (EtOAc/petroleum ether = 1/10); 1H NMR (400 MHz, CDCl3) δ 7.64 (d, J = 8.2 Hz, 2H), 7.50 (d, J = 8.7 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 7.34 – 7.26 (m, 2H), 7.17 – 7.10 (m, 2H), 7.10 – 6.93 (m, 5H), 6.87 – 6.75 (m, 2H), 6.50 (d, J = 8.7 Hz, 1H), 6.12 (d, J = 8.0 Hz, 1H), 5.50 (d, J = 8.0 Hz, 1H); 13C NMR (101 MHz, CDCl3) δ 160.0, 148.6, 138.4, 135.1, 132.6, 132.5, 131.9, 130.0, 129.8, 128.52, 128.45, 127.4, 127.0, 126.5, 126.1, 123.2, 122.5, 122.3, 122.2, 122.0, 120.5, 117.6, 110.5, 87.3, 43.8; IR (KBr, cm−1) 2924, 1597, 1494, 1476, 1275, 1261, 1069, 1012, 749; HRMS (ESI) Calcd for C27H16Br2N2O (M+H)+ 544.9859, Found 544.9857; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, tR = major: 11.9 min, minor: 17.6 min, 95:5 er; [α]D24 94.7° (c 0.10, CH2Cl2).

2-(4-bromophenyl)-3-((2R,3R)-2-(2-methoxyphenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2k)

Yield 83%, 98:2 dr, pale solid, m. p. 141-143 °C, Rf = 0.5 (EtOAc/petroleum ether = 1/10); 1H NMR (500 MHz, CDCl3) δ 7.69 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 8.8 Hz, 1H), 7.39 (d, J = 8.2 Hz, 2H), 7.31 (t, J = 7.7 Hz, 1H), 7.16 (dd, J = 7.7, 1.7 Hz, 1H), 7.14 – 7.06 (m, 2H), 7.04 – 6.98 (m, 2H), 6.90 (t, J = 7.4 Hz,
2-(4-bromophenyl)-3-(((2R,3R)-2-(naphthalen-1-yl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2l)

Yield 99%, > 99:1 dr, pale solid, m. p. 184-185 °C, Rf = 0.6 (EtOAc/petroleum ether = 1/10); 1H NMR (500 MHz, CDCl3) δ 7.76 (d, J = 8.2 Hz, 1H), 7.58 (d, J = 8.2 Hz, 1H), 7.46 – 7.39 (m, 3H), 7.31 – 7.26 (m, 2H), 7.23 – 7.10 (m, 6H), 7.05 (t, J = 7.5 Hz, 1H), 6.99 (t, J = 7.7 Hz, 1H), 6.81 (dd, J = 8.7, 6.6 Hz, 1H), 6.55 (d, J = 8.3 Hz, 2H), 6.44 (d, J = 8.1 Hz, 2H), 5.55 (d, J = 8.0 Hz, 1H); 13C NMR (126 MHz, CDCl3) δ 160.3, 148.5, 137.9, 133.0, 132.8, 131.9, 130.9, 130.1, 129.9, 128.9, 128.5, 127.8, 127.6, 126.5, 126.2, 125.3, 124.9, 124.4, 122.6, 122.2, 121.9, 121.3, 120.7, 117.4, 110.7, 85.0, 44.9; IR (KBr, cm⁻¹) 3053, 2924, 1596, 1513, 1494, 1477, 1462, 1379, 1275, 1260, 833; HRMS (ESI) Calcd for C39H26BrN3O2 (M+H⁺) 497.0910, Found 497.0859; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, tR = major: 17.0 min, minor: 21.8 min, 99:1 er; [α]D²⁴ 167.2° (c 0.43, CH₂Cl₂).

2-(4-bromophenyl)-3-(((2R,3R)-2-(naphthalen-2-yl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2m)

Yield 98%, > 99:1 dr, pale solid, m. p. 204-205 °C, Rf = 0.45 (DCM/petroleum ether = 1/2); 1H NMR (500 MHz, CDCl3) δ 7.62 – 7.56 (m, 1H), 7.47 (d, J = 7.2 Hz, 1H), 7.44 – 7.37 (m, 3H), 7.34 (t, J = 8.3 Hz, 4H), 7.28 (s, 1H), 7.20 – 7.17 (m, 1H), 7.11 – 7.03 (m, 2H), 6.96 (t, J = 7.6 Hz, 1H), 6.76 – 6.63 (m, 4H), 6.42 (d, J = 8.6 Hz, 1H), 5.85 (d, J = 8.5 Hz, 1H), 5.30 (d, J = 8.5 Hz, 1H); 13C NMR (126 MHz, CDCl3) δ 160.3, 148.6, 138.4, 133.8, 133.3, 133.09, 133.06, 132.6, 132.2, 130.0, 128.4, 127.70, 127.67, 127.6, 127.2, 126.6, 126.5, 126.31, 126.28, 126.23, 123.8, 132.2, 122.1, 122.01, 121.98, 120.5, 117.5, 110.4, 88.4, 45.6; IR (KBr, cm⁻¹) 3054, 2965, 2925, 1623, 1596, 1513, 1495, 1477, 1462, 1378, 1232, 1070, 1013, 749; HRMS (ESI) Calcd for C39H26BrN3O2 (M+H⁺) 497.0910, Found 497.0911; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, tR = major: 20.5 min, minor: 23.2 min, 98:2 er; [α]D²⁴ 54.0° (c 0.027, CH₂Cl₂).

2-(4-bromophenyl)-3-(((2S,3R)-2-vinyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2n)

Yield 80%, 97:3 dr, pale solid, m. p. 184-185 °C, Rf = 0.5 (EtOAc/petroleum ether = 1/10); 1H NMR (500 MHz, CDCl3) δ 7.80 – 7.62 (m, 3H), 7.51 – 7.36 (m, 2H), 7.29 – 7.21 (m, 2H), 6.98 (d, J = 7.5 Hz, 2H), 6.87 (t, J = 7.4 Hz, 2H), 6.80 (d, J = 8.8 Hz, 1H), 5.60 (ddd, J = 17.7, 10.2, 8.0 Hz, 1H), 5.37 (d, J = 17.0 Hz, 1H), 5.29 (t, J = 8.7 Hz, 1H), 5.19 – 5.05 (m, 2H); 13C NMR (126 MHz, CDCl3) δ 159.4, 149.0, 138.6, 133.8, 133.4, 132.6, 129.7, 128.3, 127.1, 126.9, 125.7, 123.5, 122.1, 121.5, 120.8, 120.4, 117.6, 110.1, 86.8, 44.1; IR (KBr, cm⁻¹) 3059, 2924, 2853, 1596, 1516, 1495, 1478, 1380, 1275, 1262, 1233, 1013, 1004, 994, 977, 948, 865, 832, 806, 747, 705, 653, 584; HRMS (ESI) Calcd for C28H28BrN3O (M+H⁺) 547.0910, Found 547.0906; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, tR = major: 17.0 min, minor: 18.6 min, 97:3 er; [α]D²⁴ 17.0° (c 0.5, CH₂Cl₂).
833; HRMS (ESI) Calcd for C$_{23}$H$_{18}$BrN$_2$O (M+H)$^+$ 417.0597, Found 417.0595; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, $t_R$ = major: 13.8 min, minor: 16.3 min, 97:3 er; $[\alpha]_D^{24}$ 19.4° (c 0.28, CH$_2$Cl$_2$).

2-(4-bromophenyl)-3-((2R,3R)-2-(prop-1-yn-1-yl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2o)

Yield 78%; > 99:1 dr, pale solid, m. p. 169-170 °C, $R_f$ = 0.6 (EtOAc/petroleum ether = 1/10); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.78 – 7.64 (m, 3H), 7.55 – 7.43 (m, 2H), 7.29 – 7.23 (m, 2H), 6.98 (d, $J$ = 7.7 Hz, 2H), 6.87 (d, $J$ = 8.5 Hz, 3H), 5.53 (d, $J$ = 9.0 Hz, 1H), 5.14 (d, $J$ = 9.2 Hz, 1H), 1.43 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 158.9, 149.0, 138.8, 133.6, 132.6, 129.7, 128.3, 126.7, 126.0, 125.7, 123.5, 121.8, 121.7, 117.4, 110.4, 87.6, 76.4, 74.1, 45.1, 3.4; IR (KBr, cm$^{-1}$) 3058, 2962, 2924, 2857, 2243, 1595, 1487, 1382, 1266, 1227, 1162, 1100, 1018, 750; HRMS (ESI) Calcd for C$_{23}$H$_{18}$BrN$_2$O (M+H)$^+$ 429.0597, Found 429.0601; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, $t_R$ = major: 15.3 min, minor: 16.4 min, 97:3 er; $[\alpha]_D^{24}$ -51.0° (c 0.17, CH$_2$Cl$_2$).

2-(4-bromophenyl)-3-((2R,3R)-2-(trimethylsilyl)ethynyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2p)

Yield 76%, > 99:1 dr, pale solid, m. p. 160-161 °C, $R_f$ = 0.6 (EtOAc/petroleum ether = 1/10); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.64 – 7.45 (m, 3H), 7.34 (d, $J$ = 7.7 Hz, 2H), 7.13 – 7.08 (m, 1H), 7.07 – 7.02 (m, 1H), 6.82 (d, $J$ = 7.3 Hz, 2H), 6.75 – 6.59 (m, 3H), 5.37 (d, $J$ = 9.6 Hz, 1H), 5.06 – 4.94 (m, 1H), -0.45 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 159.9, 150.1, 139.9, 134.8, 133.8, 130.9, 129.4, 127.8, 126.9, 126.7, 124.6, 122.92, 122.85, 122.3, 118.6, 111.5, 100.3, 97.7, 77.2, 46.2, 0.0; IR (KBr, cm$^{-1}$) 3060, 2961, 1593, 1488, 1383, 1261, 1078, 1020, 846, 804, 753; HRMS (ESI) Calcd for C$_{23}$H$_{22}$BrN$_2$Si (M+H)$^+$ 487.0836, Found 487.0826; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, $t_R$ = major: 9.8 min, minor: 11.3 min, 90:10 er; $[\alpha]_D^{24}$ -14.4° (c 0.014, CH$_2$Cl$_2$).

2-(4-bromophenyl)-3-((2S,3R)-2-phenethyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2q)

Yield 87%, 96:4 dr, pale solid, m. p. 175-176 °C, $R_f$ = 0.5 (EtOAc/petroleum ether = 1/20); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.68 (d, $J$ = 8.7 Hz, 1H), 7.63 (d, $J$ = 8.4 Hz, 2H), 7.37 – 7.25 (m, 3H), 7.24 – 7.13 (m, 4H), 7.04 – 6.95 (m, 4H), 6.94 – 6.81 (m, 3H), 5.00 (d, $J$ = 9.2 Hz, 1H), 4.79 (td, $J$ = 9.6, 3.5 Hz, 1H), 2.81 – 2.70 (m, 1H), 2.67 – 2.55 (m, 1H), 1.97 – 1.83 (m, 1H), 1.45 – 1.35 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.4, 149.1, 140.8, 138.6, 133.7, 132.7, 129.5, 128.6, 128.5, 128.1, 127.2, 127.0, 126.2, 125.7, 123.5, 122.2, 121.4, 121.1, 117.7, 110.2, 84.7, 43.4, 33.6, 32.1; IR (KBr, cm$^{-1}$) 3060, 3027, 2951, 1732, 1624, 1597, 1543, 1516, 1495, 1479, 1461, 1264, 1234, 832, 749; HRMS (ESI) Calcd for C$_{26}$H$_{22}$BrN$_2$O (M+H)$^+$ 495.067; Found 495.066; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, $t_R$ = major: 10.1 min, minor: 15.6 min, > 99:1 er; $[\alpha]_D^{24}$ -13.7° (c 0.29, CH$_2$Cl$_2$).
2-(4-bromophenyl)-3-((2S,3R)-2-isobutyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2r)

Yield 71%, 93:7 dr, pale solid, m. p. 110-111 °C, Rf = 0.6 (EtOAc/petroleum ether = 1/20); 1H NMR (400 MHz, CDCl₃) δ 7.80 – 7.62 (m, 3H), 7.43 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 6.99 (d, J = 7.4 Hz, 1H), 6.96 – 6.72 (m, 4H), 5.01 (d, J = 9.0 Hz, 1H), 4.93 (dd, J = 9.5, 9.1, 3.4 Hz, 1H), 1.78 – 1.68 (m, 1H), 1.58 – 1.46 (m, 1H), 0.98 – 0.87 (m, 1H), 0.86 – 0.71 (m, 6H); 13C NMR (101 MHz, CDCl₃) δ 159.5, 149.1, 138.7, 134.1, 132.8, 129.5, 128.2, 127.5, 127.0, 125.6, 123.6, 122.1, 121.4, 121.2, 121.1, 117.6, 110.2, 84.5, 43.6, 40.6, 25.2, 23.4, 21.8; IR (KBr, cm⁻¹) 3055, 2956, 2930, 2870, 1625, 1597, 1516, 1495, 1479, 1381, 1275, 1264, 1234, 1069, 749; HRMS (ESI) Calcd for C₂₅H₂₃BrN₂O (M+H)⁺ 447.1067. Found 447.1072; HPLC: INIA column, 90:10 hexanes:isopropanol, 1.00 mL/min, tᵣ = major: 7.0 min, minor: 9.7 min, > 99:1 er; [α]D²⁴ 52.7° (c 0.22, CH₂Cl₂).

2-(4-bromophenyl)-3-((2S,3R)-2-isopropyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2s)

Yield 78%, 98:2 dr, pale solid, m. p. 200-201 °C, Rf = 0.6 (EtOAc/petroleum ether = 1/20); 1H NMR (500 MHz, CDCl₃) δ 7.76 (d, J = 8.6 Hz, 2H), 7.65 (d, J = 8.8 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.27 (d, J = 8.7 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.07 (d, J = 7.4 Hz, 1H), 6.98 (d, J = 8.1 Hz, 1H), 6.91 (dd, J = 8.7, 6.6 Hz, 1H), 6.83 (t, J = 7.5 Hz, 1H), 4.92 (d, J = 8.1 Hz, 1H), 4.34 (dd, J = 10.4, 8.1 Hz, 1H), 1.89 – 1.78 (m, 1H), 1.07 (d, J = 6.5 Hz, 3H), 0.48 (d, J = 6.6 Hz, 3H); 13C NMR (126 MHz, CDCl₃) δ 159.1, 149.1, 138.7, 134.6, 132.8, 129.4, 128.9, 128.6, 126.9, 125.0, 123.6, 122.1, 121.4, 121.2, 120.9, 117.6, 110.4, 92.1, 42.1, 28.8, 20.1, 18.9; IR (KBr, cm⁻¹) 2967, 2870, 1514, 1493, 1275, 1261, 1010, 749; HRMS (ESI) Calcd for C₂₅H₂₃BrN₂O (M+H)⁺ 433.0910. Found 433.0908; HPLC: INIA column, 90:10 hexanes:isopropanol, 1.00 mL/min, tᵣ = major: 7.9 min, minor: 19.7 min, > 99:1 er; [α]D²⁴ 169.0° (c 0.26, CH₂Cl₂).

2-(4-bromophenyl)-3-((2S,3R)-2-cyclopropyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2t)

Yield 93%, 98:2 dr, pale solid, m. p. 166-167 °C, Rf = 0.6 (EtOAc/petroleum ether = 1/20); 1H NMR (500 MHz, CDCl₃) δ 7.74 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.8 Hz, 1H), 7.51 (d, J = 8.2 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.02 (d, J = 7.4 Hz, 1H), 6.96 (dd, J = 10.7, 8.3 Hz, 2H), 6.90 – 6.82 (m, 2H), 5.06 (d, J = 8.9 Hz, 1H), 4.07 (t, J = 9.2 Hz, 1H), 0.81 – 0.71 (m, 1H), 0.58 – 0.45 (m, 2H), 0.24 – 0.18 (m, 1H), 0.04 – 0.03 (m, 1H); 13C NMR (126 MHz, CDCl₃) δ 159.4, 149.0, 138.7, 134.4, 132.7, 129.6, 128.4, 127.7, 126.9, 125.6, 123.5, 122.1, 121.5, 121.3, 121.0, 117.6, 110.0, 91.4, 43.4, 11.5, 4.2, 2.6; IR (KBr, cm⁻¹) 3055, 3006, 2924, 1596, 1515, 1495, 1478, 1461, 1275, 1263, 1234, 972, 749; HRMS (ESI) Calcd for C₂₅H₂₃BrN₂O (M+H)⁺ 431.0754. Found 431.0750; HPLC: INIA column, 90:10 hexanes:isopropanol, 1.00 mL/min, tᵣ = major: 11.3 min, minor: 17.0 min, 98.2 er; [α]D²⁴ 44.3° (c 0.34, CH₂Cl₂).
2-(4-bromophenyl)-3-((2S,3R)-2-(2-methoxyethyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2u)

Yield 70%, 93:7 dr, pale solid, m. p. 78-79 °C, Rf = 0.4 (EtOAc/petroleum ether = 1/15); 1H NMR (500 MHz, CDCl3) δ 7.73 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.8 Hz, 1H), 7.47 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 6.5 Hz, 2H), 7.00 (d, J = 7.4 Hz, 1H), 6.95 (d, J = 8.1 Hz, 1H), 6.91 – 6.81 (m, 3H), 5.11 – 5.00 (m, 2H), 3.52 (td, J = 9.2, 4.9 Hz, 1H), 3.35 (dt, J = 9.9, 5.2 Hz, 1H), 3.27 (s, 3H), 1.80 – 1.72 (m, 1H), 1.52 – 1.42 (m, 1H); 13C NMR (126 MHz, CDCl3) δ 159.3, 149.1, 138.6, 133.8, 132.8, 132.6, 129.5, 128.4, 128.2, 127.3, 126.9, 125.6, 122.2, 121.2, 121.0, 117.7, 110.2, 82.9, 69.0, 58.8, 43.3, 32.4; IR (KBr, cm⁻¹) 2924, 2891, 1624, 1597, 1516, 1495, 1479, 1461, 1381, 1275, 1262, 1115, 1069, 1012, 833; HRMS (ESI) Calcd for C28H22BrN3O2 (M+H)+ 449.0859, Found 449.0854; HPLC: INC column, 90:10 hexanes/isopropanol, 1.00 mL/min, tR = major: 6.9 min, minor: 6.6 min, 99:1 er; [α]D²⁴ 13.9° (c 0.24, CH₂Cl₂).

2-phenyl-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2v)

Yield 92%, > 99:1 dr, pale solid, m. p. 150-151 °C, Rf = 0.45 (EtOAc/petroleum ether = 1/10); 1H NMR (500 MHz, CDCl3) δ 7.56 – 7.48 (m, 4H), 7.36 (t, J = 7.7 Hz, 1H), 7.21 – 7.12 (m, 4H), 7.12 – 7.05 (m, 2H), 7.02 – 6.96 (m, 3H), 6.87 (d, J = 7.6 Hz, 2H), 6.76 (d, J = 7.4 Hz, 1H), 6.54 (d, J = 8.7 Hz, 1H), 5.79 (d, J = 8.7 Hz, 1H), 5.36 (d, J = 8.7 Hz, 1H); 13C NMR (126 MHz, CDCl3) δ 160.1, 148.4, 139.4, 136.0, 133.0, 129.8, 129.3, 129.2, 128.3, 127.9, 127.4, 127.0, 126.7, 126.3, 126.1, 121.9, 121.8, 121.6, 120.7, 117.4, 110.2, 88.0, 45.6; IR (KBr, cm⁻¹) 3057, 2961, 2927, 1592, 1468, 1411, 1267, 1228, 1267, 1228, 1089, 1022, 749, 695; HRMS (ESI) Calcd for C27H16N2O2 (M+H)+ 389.1649, Found 389.1649; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, tR = major: 15.4 min, minor: 12.0 min, 98:2 er; [α]D²⁴ 96.9° (c 0.15, CH₂Cl₂).

2-(4-methoxyphenyl)-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2w)

Yield 85%, > 99:1 dr, pale solid, m. p. 162-163 °C, Rf = 0.5 (EtOAc/petroleum ether = 1/5); 1H NMR (500 MHz, CDCl3) δ 7.53 (d, J = 8.7 Hz, 1H), 7.35 (t, J = 7.8 Hz, 1H), 7.19 – 7.13 (m, 2H), 7.10 (d, J = 7.8 Hz, 1H), 7.09 – 7.03 (m, 3H), 7.03 – 6.94 (m, 5H), 6.89 (d, J = 7.6 Hz, 2H), 6.77 (t, J = 7.7 Hz, 1H), 6.54 (d, J = 8.7 Hz, 1H), 5.79 (d, J = 8.7 Hz, 1H), 5.31 (d, J = 8.7 Hz, 1H), 3.90 (s, 3H); 13C NMR (126 MHz, CDCl3) δ 160.2, 160.1, 148.1, 136.0, 133.4, 132.1, 129.8, 128.3, 128.2, 127.9, 127.4, 126.7, 126.3, 126.1, 121.8, 121.5, 120.6, 117.3, 114.3, 110.2, 88.0, 55.7, 45.6; IR (KBr, cm⁻¹) 3749, 2963, 1517, 1458, 1377, 1259, 1026, 800, 745, 697; HRMS (ESI) Calcd for C26H19N3O2 (M+H)+ 419.1754, Found 419.1753; HPLC: INA column, 80:20 hexanes/isopropanol, 1.00 mL/min, tR = major: 17.0 min, minor: 12.7 min, 96:4 er; [α]D₂⁴ 76.9° (c 0.14, CH₂Cl₂).

2-(4-bromophenyl)-5-fluoro-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2x)

Yield 80%, > 99:1 dr, pale solid, m. p. 171-172 °C, Rf = 0.6 (EtOAc/petroleum ether = 1/10); 1H NMR (500 MHz, CDCl3) δ 7.63 (d, J = 8.2 Hz, 2H), 7.49 (dd, J = 9.4, 4.8 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 7.18 (d, J = 7.4 Hz, 1H), 7.11 (dt, J = 9.2, 4.9 Hz, 1H), 7.09 (s, 1H), 6.95 – 6.85 (m, 2H), 6.84 – 6.74 (m, 4H), 6.66 (d, J = 7.5 Hz, 1H), 6.56 (d, J = 7.7 Hz, 1H), 5.73 (d, J = 8.0 Hz, 1H), 5.29 (d, J = 8.0 Hz, 1H), 3.90 (s, 3H); 13C NMR (126 MHz, CDCl3) δ 160.2, 159.1, 148.1, 136.0, 133.4, 132.1, 129.8, 128.3, 128.2, 127.9, 127.4, 126.7, 126.3, 126.1, 121.8, 121.5, 120.6, 117.3, 114.3, 110.2, 88.0, 55.7, 45.6; IR (KBr, cm⁻¹) 3749, 2963, 1517, 1458, 1377, 1259, 1026, 800, 745, 697; HRMS (ESI) Calcd for C26H19N3O2 (M+H)+ 419.1754, Found 419.1753; HPLC: INA column, 80:20 hexanes/isopropanol, 1.00 mL/min, tR = major: 17.0 min, minor: 12.7 min, 96:4 er; [α]D₂⁴ 76.9° (c 0.14, CH₂Cl₂).
$J = 7.4, 3.3 \text{ Hz, 2H}$, 7.02 (t, $J = 7.3 \text{ Hz, 3H}$), 7.00 – 6.93 (m, 3H), 6.83 (d, $J = 7.6 \text{ Hz, 2H}$), 6.02 (dd, $J = 9.9, 2.4 \text{ Hz, 1H}$), 5.76 (d, $J = 8.5 \text{ Hz, 1H}$), 5.26 (d, $J = 8.5 \text{ Hz, 1H}$); $^1\text{C NMR}$ (126 MHz, CDCl$_3$) $\delta$ 160.1, 157.9 (d, $J = 240.6 \text{ Hz}$), 146.0, 138.2, 135.8, 133.3 (d, $J = 8.7 \text{ Hz}$), 132.4, 130.2, 128.5, 128.4, 128.0, 126.7, 126.6, 126.0, 123.5, 122.1, 121.3 (d, $J = 11.4 \text{ Hz}$), 119.6 (d, $J = 9.7 \text{ Hz}$), 118.3 (d, $J = 29.2 \text{ Hz}$), 110.5, 103.1 (d, $J = 25.3 \text{ Hz}$), 88.0, 45.5; $^1\text{F NMR}$ (471 MHz, CDCl$_3$) $\delta$ -118.8; IR (KBr, cm$^{-1}$) 3071, 2928, 1598, 1487, 1487, 1343, 1231, 1176, 1013, 837, 750; HRMS (ESI) Calcd for C$_7$H$_7$BrN$_2$O (M+H)$^+$ 485.0660 , Found 485.0653; HPLC: WHELK column, 90:10 hexanes:isopropanol, 0.80 mL/min, $t_{R}$ = major: 18.0 min, minor: 17.0 min, 97:3 er; $[\alpha]_D^{21} 61.8^o$ (c 0.17, CH$_2$Cl$_2$).

**2-(4-bromophenyl)-5-methoxy-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2y)**

Yield 95%, > 99:1 dr, pale solid, m. p. 134-135$\degree$C, $R_t = 0.4$ (EtOAc/petroleum ether = 1/10); $^1\text{H NMR}$ (500 MHz, CDCl$_3$) $\delta$ 7.58 (d, $J = 8.2 \text{ Hz, 2H}$), 7.42 (d, $J = 9.3 \text{ Hz, 1H}$), 7.36 (t, $J = 7.7 \text{ Hz, 1H}$), 7.26 – 7.22 (m, 1H), 7.14 (t, $J = 7.4 \text{ Hz, 1H}$), 7.10 (d, $J = 8.1 \text{ Hz, 1H}$), 7.08 – 6.99 (m, 3H), 6.92 – 6.84 (m, 3H), 6.82 (d, $J = 7.6 \text{ Hz, 2H}$), 5.74 (d, $J = 8.3 \text{ Hz, 1H}$), 5.55 (s, 1H), 5.24 (d, $J = 8.3 \text{ Hz, 1H}$), 3.46 (s, 3H); $^1\text{C NMR}$ (126 MHz, CDCl$_3$) $\delta$ 160.3, 154.7, 145.6, 138.5, 135.8, 132.2, 131.5, 129.8, 128.5, 128.4, 128.0, 127.4, 127.0, 126.5, 123.0, 122.2, 122.0, 121.6, 118.8, 110.0, 96.4, 88.4, 54.9, 45.6; IR (KBr, cm$^{-1}$) 3748, 3063, 2927, 1523, 1494, 1476, 1459, 1263, 1219, 1178, 1099, 1067, 1014, 833, 810, 699; HRMS (ESI) Calcd for C$_{25}$H$_{25}$BrN$_2$O$_2$ (M+H)$^+$ 497.0859; Found 497.0863; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, $t_{R}$ = major: 24.2 min, minor: 22.8 min, 97:3 er; $[\alpha]_D^{21} 54.7^o$ (c 0.20, CH$_2$Cl$_2$).

**5-methyl-2-phenyl-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2z)**

Yield 99%, > 99:1 dr, pale solid, m. p. 145-146$\degree$C, $R_t = 0.6$ (EtOAc/petroleum ether = 1/10); $^1\text{H NMR}$ (500 MHz, CDCl$_3$) $\delta$ 7.55 – 7.45 (m, 3H), 7.44 (d, $J = 8.8 \text{ Hz, 1H}$), 7.37 (t, $J = 7.6 \text{ Hz, 1H}$), 7.19 (d, $J = 7.3 \text{ Hz, 1H}$), 7.15 – 7.06 (m, 4H), 7.05 – 6.97 (m, 4H), 6.86 (d, $J = 7.5 \text{ Hz, 2H}$), 6.18 (s, 1H), 5.76 (d, $J = 8.6 \text{ Hz, 1H}$), 5.32 (d, $J = 8.4 \text{ Hz, 1H}$), 2.17 (s, 3H); $^1\text{C NMR}$ (126 MHz, CDCl$_3$) $\delta$ 160.1, 147.5, 139.5, 136.1, 131.9, 130.7, 129.7, 129.1, 128.3, 127.8, 127.4, 127.0, 126.8, 126.2, 122.1, 121.8, 118.6, 117.1, 110.1, 88.1, 45.6, 21.9; IR (KBr, cm$^{-1}$) 3059, 2918, 1227, 1597, 1524, 1499, 1478, 1455, 1232, 802, 754, 696; HRMS (ESI) Calcd for C$_{28}$H$_{28}$N$_2$O (M+H)$^+$ 403.1805; Found 403.1801; HPLC: OD-H column, 80:20 hexanes/isopropanol, 1.00 mL/min, $t_{R}$ = major: 23.8 min, minor: 7.5 min, 95:5 er; $[\alpha]_D^{21} 63.2^o$ (c 0.15, CH$_2$Cl$_2$).

**2-(4-bromophenyl)-3-((2R,3R)-2-phenyltetrahydrofuran-3-yl)-2H-indazole (2aa)**

Yield 43%, > 99:1 dr, pale solid, m. p. 115-116$\degree$C, $R_t = 0.6$ (EtOAc/petroleum ether = 1/15); $^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 7.92 (d, $J = 8.6 \text{ Hz, 1H}$), 7.75 (d, $J = 8.8 \text{ Hz, 1H}$), 7.38 (t, $J = 7.1 \text{ Hz, 3H}$), 7.26 – 7.13 (m, 4H), 7.04 (d, $J = 7.2 \text{ Hz, 2H}$), 6.58 (d, $J = 8.2 \text{ Hz, 2H}$), 5.30 (d, $J = 9.3 \text{ Hz, 1H}$), 4.44 – 4.35 (m, 1H), 4.35 – 4.25 (m, 1H), 3.49 – 3.38 (m, 1H), 2.76 – 2.64 (m, 1H), 2.49 – 2.39 (m, 1H); $^1\text{C NMR}$ (126 MHz, CDCl$_3$) $\delta$ 148.7, 138.7, 137.5, 136.6, 132.2, 128.6, 127.8, 127.6, 126.5, 126.3, 123.3, 121.5, 121.2,
(9aS,10S)-10-(2-(4-bromophenyl)-2H-indazol-3-yl)-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indole (2ab)

Yield 65%, 84:16 dr, pale solid, m. p. 218-225 °C, Rf = 0.4 (DCM/petroleum ether = 1/1); 1H NMR (500 MHz, CDCl3) δ 7.78 – 7.70 (m, 2H), 7.67 – 7.62 (m, 1H), 7.48 – 7.41 (m, 2H), 7.25 – 7.11 (m, 3H), 6.95 (d, J = 7.3 Hz, 1H), 6.89 – 6.80 (m, 1H), 6.70 – 6.54 (m, 2H), 4.77 (d, J = 7.8 Hz, 1H), 3.76 (d, J = 10.8 Hz, 1H), 3.42 (td, J = 8.1 Hz, 1H), 2.71 (t, J = 11.5 Hz, 1H), 1.82 – 1.71 (m, 2H), 1.70 – 1.62 (m, 1H), 1.54 – 1.44 (m, 1H), 1.38 – 1.31 (m, 1H), 1.19 – 1.08 (m, 1H); 13C NMR (126 MHz, CDCl3) δ 151.5, 149.3, 149.0, 139.0, 132.6, 132.5, 128.8, 128.3, 126.8, 125.4, 121.6, 118.3, 117.3, 106.7, 67.8, 45.3, 42.6, 26.8, 24.2, 24.1; IR (KBr, cm⁻¹) 3606, 3305, 3053, 2937, 1654, 1609, 1488, 1361, 1147, 934, 733; HRMS (ESI) Calcd for C32H28Br2N2S (M+H)⁺ 483.0514, Found 483.0514; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, tR = major: 27.7 min, minor: 70.0 min, 93.7 er; [α]D24 27.0° (c 0.24, CH2Cl2).

2-(4-bromophenyl)-3-((2R,3R)-2-phenyl-2,3-dihydrobenzo[b]thiophen-3-yl)-2H-indazole (2ac)

Yield 46%, > 99:1 dr, pale solid, m. p. 150-151 °C, Rf = 0.5 (EtOAc/petroleum ether = 1/10); 1H NMR (500 MHz, CDCl3) δ 7.61 – 7.53 (m, 3H), 7.41 (d, J = 7.8 Hz, 1H), 7.32 (td, J = 7.5, 1.5 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.14 – 7.04 (m, 3H), 6.98 (t, J = 7.8 Hz, 2H), 6.89 – 6.83 (m, 2H), 6.82 – 6.76 (m, 2H), 5.34 (d, J = 8.1 Hz, 1H), 5.17 (d, J = 8.1 Hz, 1H); 13C NMR (126 MHz, CDCl3) δ 148.7, 142.0, 138.5, 138.1, 136.1, 133.2, 132.3, 129.1, 128.8, 128.5, 128.3, 128.2, 126.5, 126.2, 125.4, 123.4, 122.3, 121.9, 121.8, 121.4, 117.4, 58.2, 51.2; IR (KBr, cm⁻¹) 3059, 2960, 2924, 2856, 1590, 1492, 1452, 1297, 1070, 1018, 800, 742, 700; HRMS (ESI) Calcd for C27H26Br2N2S (M+H)⁺ 483.0525, Found 483.0514; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, tR = major: 17.6 min, minor: 38.2 min, 81:19 er; [α]D24 27.0° (c 0.11, CH2Cl2).

3.5 General procedures for cycloisomerization of azaenyne 3

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, 3a (0.1 mmol, 51.7 mg), n-hexane (0.0035 M, 30 ml), Rh2(S-TCPITTL)₄ (2 mol%, 3.9 mg) were added. The mixtures were stirred at room temperature until the starting material was consumed (TLC detected). After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using DCM/petroleum ether as eluent to afford the product 4a (0.1 mmol,
51.5 mg).

The procedures of other substrates 3, were similar with that mentioned above.

2-(4-bromophenyl)-3-((1R,2R)-2-phenyl-1,2-dihydronaphtho[2,1-b]furan-1-yl)-2H-indazole (4a)

Yield 99%, > 99:1 dr, pale solid, m. p. 190-191 °C, Rf = 0.35 (DCM/petroleum ether = 1/1); 1H NMR (500 MHz, CDCl3) δ 7.87 (d, J = 8.8 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.60 – 7.54 (m, 2H), 7.41 (dd, J = 8.7, 1.1 Hz, 1H), 7.31 (d, J = 8.8 Hz, 1H), 7.28 – 7.19 (m, 3H), 7.14 – 7.07 (m, 1H), 7.05 – 6.95 (m, 3H), 6.92 – 6.86 (m, 2H), 6.83 (dd, J = 8.0, 1.4 Hz, 2H), 6.58 (ddd, J = 8.7, 6.6, 0.9 Hz, 1H), 6.22 (dt, J = 8.8, 1.1 Hz, 1H), 5.85 (d, J = 8.5 Hz, 1H), 5.48 (d, J = 8.6 Hz, 1H); 13C NMR (126 MHz, CDCl3) δ 157.0, 147.6, 137.4, 134.5, 131.5, 131.3, 130.2, 129.6, 128.9, 128.1, 127.8, 127.5, 127.0, 126.5, 125.4, 122.5, 122.4, 121.4, 121.2, 121.0, 119.2, 117.7, 116.4, 111.2, 88.5, 43.8; IR (KBr, cm⁻¹) 3059, 2962, 1627, 1588, 1495, 1382, 1253, 1072, 1014, 958, 817, 732, 702; HRMS (ESI) Calcd for C31H28BrN10O (M+H)+ 517.0910, Found 517.0902; HPLC: OD-H column, 70:30 hexanes/isopropanol, 0.80 mL/min, tR = major: 10.7 min, minor: 16.0 min, 96.4 ε; [α]D⁺ 24 165.0° (c 0.067, CH2Cl2).

methyl 4-((1R,2R)-1-(2-(4-bromophenyl)-2H-indazol-3-yl)-1,2-dihydronaphtho[2,1-b]furan-2-yl)benzoate (4b)

Yield 99%, 96:4 dr, pale solid, m. p. 150-151 °C, Rf = 0.5 (DCM/EtOAc/petroleum ether = 10/1/20); 1H NMR (500 MHz, CDCl3) δ 7.95 (d, J = 8.8 Hz, 1H), 7.88 (d, J = 8.1 Hz, 1H), 7.72 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.46 (s, 1H), 7.39 (d, J = 8.8 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.12 – 7.06 (m, 1H), 7.05 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 8.3 Hz, 2H), 6.67 (dd, J = 8.7, 6.5 Hz, 1H), 6.32 (d, J = 8.7 Hz, 1H), 5.98 (d, J = 8.7 Hz, 1H), 5.64 (d, J = 8.7 Hz, 1H), 3.86 (s, 3H); 13C NMR (126 MHz, CDCl3) δ 166.5, 157.9, 148.6, 140.7, 138.3, 132.6, 132.1, 131.5, 130.6, 130.4, 130.1, 129.2, 128.5, 127.6, 127.3, 126.7, 123.8, 123.6, 122.31, 122.28, 122.2, 120.0, 118.4, 117.6, 112.1, 88.7, 52.2, 44.9; IR (KBr, cm⁻¹) 3059, 2921, 2852, 1721, 1626, 1502, 1431, 1381, 1277, 1104, 965, 875, 817, 741; HRMS (ESI) Calcd for C33H29BrN10O (M+H)+ 575.0965, Found 575.0955; HPLC: OD-H column, 80:20 hexanes/isopropanol, 1.00 mL/min, tR = major: 20.8 min, minor: 10.8 min, 96.4 ε; [α]D⁺ 24 139.9° (c 0.15, CH2Cl2).

2-(4-bromophenyl)-3-((1R,2R)-2-(naphthalen-2-yl)-1,2-dihydronaphtho[2,1-b]furan-1-yl)-2H-indazole (4c)

Yield 82%, 92:8 dr, pale solid, m. p. 207-208 °C, Rf = 0.4 (EtOAc/petroleum ether = 1/2); 1H NMR (400 MHz, CDCl3) δ 8.01 (d, J = 8.8 Hz, 1H), 7.93 (d, J = 7.7 Hz, 1H), 7.77 – 7.70 (m, 1H), 7.62 – 7.56 (m, 1H), 7.56 – 7.43 (m, 7H), 7.41 (s, 1H), 7.39 – 7.31 (m, 3H), 7.12 (t, J = 7.7 Hz, 1H), 6.91 (d, J = 8.5 Hz, 1H), 6.82 – 6.64 (m, 3H), 6.32 (d, J = 8.7 Hz, 1H), 6.10 (d, J = 8.6 Hz, 1H), 5.68 (d, J = 8.6 Hz, 1H); 13C NMR (101 MHz, CDCl3) δ 158.2, 148.6, 138.4, 133.3, 133.1, 132.7, 132.4, 132.2, 131.3, 130.7, 130.0, 129.2, 128.4, 127.8, 127.6, 127.3, 126.5, 126.46, 126.41, 124.2, 123.7, 123.2, 122.5, 122.3, 122.2, 120.2, 118.6, 117.5, 112.3, 89.7, 44.9; IR (KBr, cm⁻¹) 3057, 2928,
2-(4-chlorophenyl)-3-((1R,2R)-2-(3,5-dibromophenyl)-1,2-dihydronaphtho[2,1-b]furan-1-yl)-2H-indazole (4d)

Yield 99%, 95:5 dr, pale solid, m. p. 95-96 °C, R<sub>t</sub> = 0.5 (DCM/petroleum ether = 1/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) &delta; 7.97 (d, J = 8.9 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.7 Hz, 1H), 7.42 – 7.35 (m, 4H), 7.34 – 7.26 (m, 3H), 7.14 – 7.07 (m, 1H), 6.91 (d, J = 1.7 Hz, 2H), 6.70 (d, J = 8.7, 6.6 Hz, 1H), 6.24 (d, J = 8.7 Hz, 1H), 5.83 (d, J = 9.0 Hz, 1H), 5.70 (d, J = 9.0 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) &delta; 157.7, 148.7, 139.8, 137.8, 135.5, 133.9, 131.6, 131.5, 130.6, 130.1, 129.8, 129.3, 128.7, 128.2, 127.7, 126.7, 123.9, 122.6, 122.5, 122.4, 122.2, 119.6, 117.7, 117.6, 112.1, 87.4, 45.1; IR (KBr, cm<sup>-1</sup>) 3019, 2954, 2911, 1733, 1609, 1505, 1452, 1372, 1033, 818, 742, 584; HRMS (ESI) Calcd for C<sub>33</sub>H<sub>20</sub>Br<sub>2</sub>N<sub>2</sub>O (M+H)<sup>+</sup> 628.9626, Found 628.9631; HPLC: OD-H column, 90:10 hexanes/isopropanol, 1.00 mL/min, t<sub>R</sub> = major: 14.9 min, minor: 10.4 min, 99.1 er; [α]<sub>D</sub><sup>24</sup> 156.9° (c 0.13, CH<sub>2</sub>Cl<sub>2</sub>).

2-(4-bromophenyl)-3-((1R,2R)-2-(3,5-difluorophenyl)-1,2-dihydronaphtho[2,1-b]furan-1-yl)-2H-indazole (4e)

Yield 95%, 95:5 dr, pale solid, m. p. 186-187 °C, R<sub>t</sub> = 0.4 (DCM/petroleum ether = 1/2); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) &delta; 7.96 (dd, J = 8.8, 3.0 Hz, 1H), 7.91 – 7.86 (m, 1H), 7.76 (dd, J = 8.6, 3.0 Hz, 2H), 7.48 (d, J = 8.9 Hz, 1H), 7.39 (dd, J = 8.8, 3.0 Hz, 1H), 7.36 – 7.29 (m, 3H), 7.25 – 7.21 (m, 2H), 7.13 – 7.04 (m, 1H), 6.69 – 6.62 (m, 1H), 6.60 – 6.53 (m, 1H), 6.43 (d, J = 7.1 Hz, 2H), 6.32 – 6.22 (m, 1H), 5.90 (dd, J = 8.9, 3.0 Hz, 1H), 5.71 (dd, J = 9.0, 3.0 Hz, 1H); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) &delta; 162.4 (dd, J = 250.0, 12.5 Hz), 157.7, 148.73, 139.8 (t, J = 9.0 Hz), 138.4, 132.7, 131.6, 131.5, 130.6, 130.1, 129.3, 128.4, 127.7, 126.7, 123.8, 123.6, 122.4, 122.3, 122.2, 119.8, 117.9, 117.6, 112.0, 109.9 (dd, J = 20.2, 6.2 Hz), 103.8 (t, J = 25.2 Hz), 87.6, 44.9; <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) &delta; -109.2; IR (KBr, cm<sup>-1</sup>) 3064, 2935, 1626, 1588, 1501, 1381, 1278, 1174, 1137, 1013, 817, 744, 710; HRMS (ESI) Calcd for C<sub>24</sub>H<sub>16</sub>Br<sub>2</sub>F<sub>2</sub>N<sub>2</sub>O (M+H)<sup>+</sup> 553.0722, Found 553.0713; HPLC: OD-H column, 90:10 hexanes/isopropanol, 1.00 mL/min, t<sub>R</sub> = major: 21.5 min, minor: 31.7 min, 96.4 er; [α]<sub>D</sub><sup>24</sup> 112.4° (c 0.13, CH<sub>2</sub>Cl<sub>2</sub>).

2-(4-bromophenyl)-3-((1R,2R)-2-(3,5-dichlorophenyl)-1,2-dihydronaphtho[2,1-b]furan-1-yl)-2H-indazole (4f)

Yield 99%, 96:4 dr, pale solid, m. p. 166-167 °C, R<sub>t</sub> = 0.4 (DCM/petroleum ether = 1/2); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) &delta; 7.96 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.8 Hz, 1H), 7.40 – 7.30 (m, 4H), 7.21 (d, J = 8.1 Hz, 2H), 7.08 (t, J = 7.7 Hz, 2H), 6.72 (s, 2H), 6.68 (t, J = 8.7, 6.6 Hz, 1H), 6.24 (d, J = 8.7 Hz, 1H), 5.85 (d, J = 9.0 Hz, 1H), 5.71 (d, J = 9.0 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) &delta; 157.7, 148.7, 139.3, 138.4, 134.5, 132.7, 131.6, 131.4, 130.6, 130.1, 129.3, 128.4, 128.4, 127.7, 126.7, 125.4, 123.9, 123.5, 122.5, 122.2, 119.7, 117.6, 112.1, 87.5, 45.0; IR (KBr, cm<sup>-1</sup>) 3741, 3196, 3063, 2962, 1634, 1570, 1425, 1382, 1247, 1068, 1004,
804, 742; HRMS (ESI) Calcd for C₁₉H₁₉BrCl₂N₂O₅ (M+Na)⁺ 606.9950, Found 606.9956; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, tᵣ = major:17.9 min, minor: 30.3 min, 98.2 er; [α]₀²⁴ 200.8° (c 0.13, CH₂Cl₂).

dimethyl 5-((1R,2R)-1-(2-(4-bromophenyl)-2H-indazol-3-yl)-1,2-dihyronaphtho[2,1-b]furan-2-yl)isophthalate (4g)

Yield 99%, 95:5 dr, pale solid, m. p. 271-272 °C, Rᵣ = 0.5 (DCM/EtOAc/petroleum ether = 40/1/40); ¹H NMR (500 MHz, CDCl₃) δ 8.43 (s, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.75 (s, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.44 – 7.38 (m, 2H), 7.37 – 7.31 (m, 3H), 7.11 – 7.05 (m, 3H), 6.72 – 6.65 (m, 1H), 6.34 (d, J = 8.7 Hz, 1H), 6.04 (d, J = 9.0 Hz, 1H), 5.74 (d, J = 9.0 Hz, 1H), 3.82 (s, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 165.4, 157.8, 148.7, 138.2, 137.1, 132.6, 132.2, 131.5, 130.8, 130.6, 130.3, 129.2, 128.3, 127.7, 126.5, 123.8, 123.6, 122.4, 122.3, 122.2, 120.0, 117.8, 117.5, 112.2, 87.8, 52.3, 45.0; IR (KBr, cm⁻¹) 2962, 1722, 1629, 1498, 1254, 1206, 1095, 1021, 802; HRMS (ESI) Calcd for C₉₃H₇₃Br₈NaO₂ (M+Na)⁺ 655.0839, Found 655.0844; HPLC: INA column, 80:20 hexanes:isopropanol, 1.00 mL/min, tᵣ = major: 20.9 min, minor: 30.9 min, 98.2 er; [α]₀²⁴ 247.4° (c 0.13, CH₂Cl₂).

2-(4-bromophenyl)-3-((1R,2R)-2-(3,5-dimethoxyphenyl)-1,2-dihyronaphtho[2,1-b]furan-1-yl)-2H-indazole (4h)

Yield 54%, > 99:1 dr, pale solid, m. p. 90-91 °C, Rᵣ = 0.4 (DCE/MeOAc/petroleum ether = 10/1/20); ¹H NMR (500 MHz, CDCl₃) δ 7.88 (d, J = 8.8 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.8 Hz, 1H), 7.32 (d, J = 8.8 Hz, 1H), 7.29 – 7.22 (m, 3H), 7.01 (d, J = 7.6 Hz, 1H), 6.96 (d, J = 8.2 Hz, 2H), 6.59 (t, J = 7.6 Hz, 1H), 6.25 (d, J = 8.7 Hz, 1H), 6.19 (s, 1H), 6.00 – 5.91 (m, 2H), 5.75 (d, J = 8.5 Hz, 1H), 5.44 (d, J = 8.4 Hz, 1H), 3.27 (s, 6H); ¹³C NMR (126 MHz, CDCl₃) δ 159.3, 157.0, 147.6, 137.3, 136.4, 131.2, 130.3, 129.6, 128.9, 128.1, 127.6, 126.5, 125.3, 122.6, 122.4, 121.6, 121.2, 119.1, 117.6, 116.7, 111.2, 104.0, 100.8, 88.5, 53.9, 43.8; IR (KBr, cm⁻¹) 2920, 2854, 1735, 1634, 1557, 1376, 1258, 1092, 1020, 800, 694; HRMS (ESI) Calcd for C₃₃H₂₅BrN₂O₅ (M+Na)⁺ 606.9941, Found 599.0942; HPLC: INC column, 95.5 hexanes:isopropanol, 1.00 mL/min, tᵣ = major: 19.5 min, minor: 18.0 min, 96:4 er; [α]₀²⁴ 289.6° (c 0.063, CH₂Cl₂).

3.6 Procedures for central-to-axial chirality transfer reaction of 2m

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, 2m (0.1 mmol, 51.7 mg), DCE (0.05 M, 2 mL), DDQ (2 eq, 45 mg) were added. The mixtures were stirred at room temperature until the starting material was consumed (TLC detected). After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on
silica gel using EtOAc/petroleum ether as eluent to afford the product (0.099 mmol, 51.0 mg).

2-(4-bromophenyl)-3-(2-(naphthalen-2-yl)benzofuran-3-yl)-2H-indazole (2m' and 2m")

Yield 99%, pale solid, m. p. 226-227 °C, Rf = 0.6 (EtOAc/petroleum ether = 1/40); 1H NMR (500 MHz, CDCl₃) δ 7.92 – 7.86 (m, 2H), 7.75 (d, J = 7.3 Hz, 1H), 7.70 (d, J = 8.6 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.51 – 7.44 (m, 3H), 7.44 – 7.37 (m, 2H), 7.31 – 7.27 (m, 2H), 7.23 (d, J = 7.5 Hz, 1H), 7.21 – 7.13 (m, 4H), 7.12 – 7.08 (m, 1H); 13C NMR (126 MHz, CDCl₃) δ 153.3, 152.5, 148.6, 137.9, 132.2, 132.0, 130.8, 128.2, 127.5, 127.4, 126.6, 126.5, 126.0, 125.9, 125.8, 125.7, 125.3, 125.1, 124.4, 122.7, 122.4, 122.1, 121.8, 121.0, 119.7, 119.1, 117.1, 110.6, 104.8; IR (KBr, cm⁻¹) 3058, 2922, 2861, 1589, 1493, 1404, 1261, 1082, 1015, 802, 744, 703; HRMS (ESI) Calcd for C₃₂H₂₁BrN₂O (M+Na)+ 537.0573, Found 537.0579; HPLC: INIA column, 90:10 hexanes:isopropanol, 1.00 mL/min, tᵣ = 7.7 min, isomer 1: 10.5 min.

3.7 General procedures for central-to-axial chirality transfer reactions of 4

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, 4a (0.1 mmol, 51.7 mg), DCE (0.05 M, 2 ml), DDQ (2 eq, 45 mg) were added. The mixtures were stirred at -20 °C until the starting material was consumed (TLC detected). After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using DCM/petroleum ether as eluent to afford the product 5a (0.099 mmol, 51.0 mg).

The procedures of other substrates 4, were similar with that mentioned above.

2-(4-bromophenyl)-3-(2-phenyl)naphtho[2,1-b]furan-1-yl)-2H-indazole (5a)

Yield 99%, pale solid, m. p. 170-171 °C, Rf = 0.7 (DCM/petroleum ether = 1/2); 1H NMR (500 MHz, CDCl₃) δ 7.94 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 9.0 Hz, 1H), 7.49 – 7.38 (m, 3H), 7.30 (d, J = 8.2 Hz, 1H), 7.28 – 7.24 (m, 3H), 7.23 – 7.15 (m, 7H), 7.14 – 7.07 (m, 1H); 13C NMR (126 MHz, CDCl₃) δ 153.2, 152.1, 149.6, 138.8, 131.8, 131.8, 129.6, 129.1, 128.9, 128.8, 128.0, 127.7, 127.6, 127.0, 126.8, 126.1, 125.8, 124.9, 123.6, 123.4, 123.2, 122.5, 122.1, 120.7, 118.2, 112.3, 106.2; IR (KBr, cm⁻¹) 3058, 2962, 2861, 1589, 1493, 1404, 1261, 1082, 1015, 802, 744, 703; HRMS (ESI) Calcd for C₃₂H₂₁BrN₂O+N⁺ 537.0573, Found 537.0567; HPLC: INIA column, 95:5 hexanes:isopropanol, 1.00 mL/min, tᵣ = major: 10.0 min, minor: 7.6 min, [α]D = -5.8° (c 0.069, CH₂Cl₂).
methyl 4-(1-(2-(4-bromophenyl)-2H-indazol-3-yl)naphtho[2,1-b]furan-2-yl)benzoate (5b)

Yield 91%, pale solid, m. p. 224-225 °C, Rf = 0.6 (DCM/petroleum ether = 1:2); 1H NMR (500 MHz, CDCl3) δ 7.96 (d, J = 8.2 Hz, 2H), 7.88 (t, J = 9.3 Hz, 3H), 7.77 (dd, J = 9.0, 1.7 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.33 – 7.25 (m, 5H), 7.22 (s, 1H), 7.18 (s, 2H), 7.11 (t, J = 7.5 Hz, 1H), 3.89 (s, 3H); 13C NMR (126 MHz, CDCl3) δ 166.4, 152.5, 151.8, 149.7, 138.7, 133.5, 132.0, 131.1, 130.0, 129.9, 129.2, 127.8, 127.7, 127.6, 127.31, 127.26, 126.0, 125.4, 125.2, 123.5, 123.3, 122.4, 122.3, 120.4, 118.3, 112.3, 108.2, 52.2; IR (KBr, cm⁻¹) 3058, 2957, 1721, 1604, 1494, 1437, 1274, 1188, 1104, 1014, 1004, 746; HRMS (ESI) Calcd for C53H53Br2N6O4 (M+Na)+ 955.0628, Found 955.0621; HPLC: IN column, 95.5 hexanes/isopropanol, 1.00 mL/min, tR = major: 10.3 min, minor: 11.0 min, 91.9 er: [α]D24 -17.8° (c 0.16, CH2Cl2).

2-(4-bromophenyl)-3-(2-(naphthalen-2-yl)naphtho[2,1-b]furan-1-yl)-2H-indazole (5c)

Yield 91%, pale solid, m. p. 180-181 °C, Rf = 0.5 (EtOAc/petroleum ether = 1:10); 1H NMR (500 MHz, CDCl3) δ 8.00 – 7.92 (m, 2H), 7.84 (d, J = 8.7 Hz, 2H), 7.79 (d, J = 9.0 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.68 – 7.61 (m, 2H), 7.52 – 7.39 (m, 5H), 7.33 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 7.6 Hz, 1H), 7.24 – 7.17 (m, 3H), 7.16 – 7.05 (m, 3H); 13C NMR (126 MHz, CDCl3) δ 153.3, 152.2, 149.7, 138.9, 133.12, 133.07, 131.9, 131.1, 129.1, 128.6, 128.5, 128.0, 127.73, 127.65, 127.6, 127.03, 126.95, 126.9, 126.7, 126.1, 125.6, 125.0, 123.7, 123.6, 123.3, 122.7, 122.5, 122.2, 120.7, 118.2, 112.3, 106.6; IR (KBr, cm⁻¹) 3056, 2935, 1615, 1496, 1405, 1365, 1264, 1084, 1011, 947, 809, 742; HRMS (ESI) Calcd for C35H28Br2N4O (M+Na)+ 587.0729, Found 587.0730; HPLC: IN column, 90:10 hexanes/isopropanol, 1.00 mL/min, tR = major: 8.6 min, minor: 7.5 min, 90:10 er; [α]D24 -101.9° (c 0.074, CH2Cl2).

2-(4-chlorophenyl)-3-(2-(3,5-dibromophenyl)naphtho[2,1-b]furan-1-yl)-2H-indazole (5d)

Yield 90%, pale solid, m. p. 201-202 °C, Rf = 0.6 (DCM/petroleum ether = 1:4); 1H NMR (500 MHz, CDCl3) δ 7.97 (t, J = 7.6 Hz, 2H), 7.89 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 8.9 Hz, 1H), 7.52 – 7.38 (m, 5H), 7.33 – 7.26 (m, 3H), 7.21 (s, 2H), 7.16 – 7.09 (m, 3H); 13C NMR (126 MHz, CDCl3) δ 151.4, 148.7, 148.5, 137.1, 133.3, 132.8, 131.6, 130.1, 128.2, 128.1, 126.9, 126.8, 126.6, 126.4, 126.1, 125.5, 124.7, 124.3, 122.6, 122.4, 122.3, 122.1, 121.5, 119.2, 117.4, 111.2, 107.5; IR (KBr, cm⁻¹) 3747, 3525, 3446, 2962, 2922, 2851, 1670, 1520, 1340, 1260, 1123, 1014, 944, 803, 746; HRMS (ESI) Calcd for C35H24Br2ClN4NaO (M+Na)+ 648.9288. Found 648.9283; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, tR = major: 6.7 min, minor: 4.8 min, 91.9 er; [α]D24 -57.3° (c 0.068, CH2Cl2).

2-(4-bromophenyl)-3-(2-(3,5-difluorophenyl)naphtho[2,1-b]furan-1-yl)-2H-indazole (5e)

Yield 95%, pale solid, m. p. 184-185 °C, Rf = 0.6 (DCM/petroleum ether = 1:4); 1H NMR (500 MHz, CDCl3) δ 8.03 – 7.91 (m, 3H), 7.81 (d, J = 9.0 Hz, 1H), 7.68 (s, 1H), 7.52 (d, J = 6.3 Hz, 3H), 7.50 – 7.44 (m, 2H), 7.41 (d, J = 8.5 Hz, 2H).
2-(4-bromophenyl)-3-(2-(3,5-dichlorophenyl)naptho[2,1-b]furan-1-yl)-2H-indazole (5f)

Yield 96%, pale solid, m. p. 225-226 °C, Rf = 0.6 (DCM/petroleum ether = 1/4);

\[ ^{1}H \text{NMR (500 MHz, CDCl}_{3} \] \( \delta \) 7.96 (dd, \( J = 8.3, 4.1 \text{ Hz, 2H} \), 7.88 (d, \( J = 9.0 \text{ Hz, 1H} \), 7.75 (d, \( J = 9.0 \text{ Hz, 1H} \)), 7.49 - 7.43 (m, 2H), 7.43 - 7.36 (m, 2H), 7.32 - 7.25 (m, 3H), 7.25 - 7.18 (m, 3H), 7.16 - 7.09 (m, 1H), 7.03 (s, 2H); \)

\[ ^{13}C \text{NMR (126 MHz, CDCl}_{3} \] \( \delta \) 152.4, 149.84, 149.75, 138.7, 135.5, 132.14, 132.07, 131.2, 129.2, 128.4, 128.0, 127.8, 127.6, 126.5, 126.0, 125.3, 123.8, 123.6, 123.5, 123.1, 122.5, 122.4, 120.3, 118.4, 112.2, 108.5; \)

IR (KBr, cm\(^{-1}\)) 3063, 2962, 2860, 1618, 1589, 1492, 1445, 1360, 1263, 1112, 1087, 1017, 803,741; HRMS (ESI) Calcd for C\(_{31}\)H\(_{27}\)BrF\(_{2}\)N\(_{2}\)O\(_{3}\) (M+Na\(^{+}\)) 573.0384, Found 573.0377; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, \( t_{R} \) = major: 7.4 min, minor: 5.4 min, 91.9 er; \( [\alpha]_{D}^{24} -7.2^\circ \) (c 0.13, CH\(_{2}\)Cl\(_{2}\)).

dimethyl 5-(1-(2-(4-bromophenyl)-2H-indazol-3-yl)naptho[2,1-b]furan-2-yl)isophthalate (5g)

Yield 99%, pale solid, m. p. 220-222 °C, Rf = 0.5 (DCM/ EtOAc/petroleum ether = 40/1/40); \( ^{1}H \text{NMR (500 MHz, CDCl}_{3} \] \( \delta \) 8.50 (s, 1H), 8.07 - 7.93 (m, 4H), 7.89 (d, \( J = 8.9 \text{ Hz, 1H} \), 7.80 (d, \( J = 8.9 \text{ Hz, 1H} \), 7.51 - 7.41 (m, 4H), 7.31 (t, \( J = 7.6 \text{ Hz, 1H} \), 7.25 - 7.18 (m, 4H), 7.12 (dd, \( J = 8.5, 6.5 \text{ Hz, 1H} \), 3.86 (s, 6H); \)

\[ ^{13}C \text{NMR (126 MHz, CDCl}_{3} \] \( \delta \) 165.4, 152.4, 150.8, 149.8, 138.7, 132.0, 131.3, 132.1, 132.4, 132.0, 132.3, 125.3, 126.0, 126.3, 123.5, 124.2, 122.4, 122.0, 120.3, 118.3, 112.4, 108.1, 52.45; IR (KBr, cm\(^{-1}\)) 3059, 2952, 1729, 1598, 1495, 1439, 1302, 1246, 1005, 815, 749; HRMS (ESI) Calcd for C\(_{35}\)H\(_{33}\)BrF\(_{2}\)N\(_{2}\)O\(_{5}\) (M+H\(^{+}\)) 631.0863, Found 631.0870; HPLC: INA column, 80:20 hexanes/isopropanol, 1.00 mL/min, \( t_{R} \) = major: 9.9 min, minor: 6.3 min, 92.8 er; \( [\alpha]_{D}^{24} -101.6^\circ \) (c 0.047, CH\(_{2}\)Cl\(_{2}\)). For HPLC data after recrystallization: \( t_{R} \) = major: 10.8 min, minor: 7.3 min, > 99:1 er.

2-(4-bromophenyl)-3-(2-(3,5-dimethoxyphenyl)naptho[2,1-b]furan-1-yl)-2H-indazole (5h)

Yield 99%, pale solid, m. p. 78-79 °C Rf = 0.5 (EtOAc/petroleum ether = 1/10);

\[ ^{1}H \text{NMR (500 MHz, CDCl}_{3} \] \( \delta \) 7.86 (dd, \( J = 18.1, 8.5 \text{ Hz, 2H} \), 7.76 (d, \( J = 9.0 \text{ Hz, 1H} \)), 7.69 (d, \( J = 8.9 \text{ Hz, 1H} \), 7.42 (d, \( J = 8.4 \text{ Hz, 1H} \), 7.39 - 7.32 (m, 2H), 7.29 (d, \( J = 8.3 \text{ Hz, 1H} \), 7.21 (s, 1H), 7.18 - 7.11 (m, 4H), 7.04 (dd, \( J = 8.5, 6.6 \text{ Hz, 1H} \), 6.30 (d, \( J = 2.2 \text{ Hz, 2H} \), 6.27 (d, \( J = 2.3 \text{ Hz, 1H} \), 3.43 (s, 6H); \)

\[ ^{13}C \text{NMR (126 MHz, CDCl}_{3} \] \( \delta \) 159.9, 152.1, 150.9, 148.6, 137.8, 130.9, 130.03, 130.00, 128.1, 126.7, 126.6, 126.0, 125.9, 125.1, 124.0, 122.2, 121.4, 121.1, 119.6, 117.0,
3.8 Procedures for late-modification of chiral isoindazoles

Procedures for C-H alkenylation of chiral isoindazoles[5]

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, 2v (0.1 mmol, 38.8 mg), DCE (0.05 M, 2 ml), [Rh(Cp*Cl)2]2 (5 mol%, 3.9 mg), AgSbF6 (20 mol%, 6.86 mg), Cu(OAc)2 (1 eq, 18.8 mg), alkyne (1.2 eq, 13.2 mg) were added. The mixtures were stirred at 80 °C until the starting material was consumed (TLC detected). After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the product 6a (0.076 mmol, 37.8 mg).

2-(2-((E)-oct-4-en-4-yl)phenyl)-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (6a)

Yield 76%, > 99:1 dr, pale solid, m. p. 150-151 °C, Rf = 0.5 (EtOAc/petroleum ether = 1/40); 1H NMR (500 MHz, CDCl3) δ 7.54 (d, J = 8.6 Hz, 1H), 7.43 (t, J = 7.5 Hz, 1H), 7.35 (t, J = 7.9 Hz, 2H), 7.23 (d, J = 7.3 Hz, 1H), 7.17 – 7.08 (m, 2H), 7.06 (d, J = 8.0 Hz, 1H), 7.04 – 6.94 (m, 4H), 6.74 (t, J = 7.7 Hz, 3H), 6.37 – 6.27 (m, 2H), 5.66 – 5.55 (m, 2H), 5.09 (d, J = 8.8 Hz, 1H), 2.21 – 2.12 (m, 1H), 2.10 – 1.98 (m, 2H), 1.39 – 1.32 (m, 2H), 1.22 – 1.14 (m, 1H), 1.07 – 0.97 (m, 1H), 0.92 – 0.83 (m, 4H), 0.65 (t, J = 7.3 Hz, 3H); 13C NMR (126 MHz, CDCl3) δ 160.3, 148.4, 141.1, 140.1, 136.5, 136.1, 133.9, 133.1, 130.7, 129.6, 129.3, 128.4, 127.8, 127.5, 127.4, 126.3, 125.9, 121.6, 121.3, 120.5, 117.6, 110.0, 88.1, 45.7, 31.0, 30.6, 22.8, 21.9, 13.9, 13.7; IR (KBr, cm⁻¹) 3060, 2959, 2868, 1730, 1599, 1552, 1464, 1378, 1268, 1229, 1092, 1023, 803, 750; HRMS (ESI) Calcd for C33H35N2O (M+H)⁺ 499.2744, Found 499.2738; HPLC: IN column, 95:5 hexanes/isopropanol, 1.00 mL/min, tR = major: 4.4 min, minor: 4.1 min, 97:3 er; [α]D⁺24 321.6° (c 0.083, CH₂Cl₂).

Procedures for C-H allylation of chiral isoindazoles[6]

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, 2v (0.1 mmol, 38.8 mg), PhCl (0.1
M, 1 ml), [Rh(Cp^*Cl)]_2 (2.5 mol%, 1.9 mg), AgSbF_6 (30 mol%, 10.3 mg), PivOH (1 eq, 10.2 mg), allyl carbonic ester (2 eq, 23.2 mg) were added. The mixtures were stirred at 40 °C until the starting material was consumed (TLC detected). After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the product 6b (0.083 mmol, 35.5 mg).

The procedures of the following substrate 4a for accessing 6i were similar with that mentioned above.

2-(2-allylphenyl)-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (6b)

Yield 83%, > 99:1 dr, pale solid, m. p. 112-113 °C, R_t = 0.6 (EtOAc/petroleum ether = 1/20); 

1H NMR (400 MHz, CDCl_3) δ 7.57 (d, J = 8.8 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.41 – 7.32 (m, 2H), 7.25 – 7.20 (m, 1H), 7.19 – 7.13 (m, 2H), 7.11 – 7.04 (m, 4H), 6.98 – 6.92 (m, 3H), 6.80 (dd, J = 8.6, 6.6 Hz, 1H), 6.54 (d, J = 8.6 Hz, 1H), 6.39 (d, J = 7.8 Hz, 1H), 5.88 – 5.78 (m, 1H), 5.72 (d, J = 8.5 Hz, 1H), 5.08 – 4.98 (m, 2H), 4.89 (d, J = 8.5 Hz, 1H), 3.06 (d, J = 6.6 Hz, 2H); 

13C NMR (101 MHz, CDCl_3) δ 160.2, 148.5, 137.8, 137.0, 136.0, 135.3, 133.9, 130.1, 129.84, 129.77, 128.7, 128.6, 128.0, 127.4, 127.3, 126.8, 126.2, 126.0, 121.9, 121.7, 121.3, 120.6, 117.6, 117.3, 110.2, 88.2, 45.8, 34.6; IR (KBr, cm\(^{-1}\)) 3063, 2928, 1597, 1467, 1381, 1272, 1227, 1159, 1095, 988, 962, 749, 695; HRMS (ESI) Calcd for C_{36}H_{23}N_{2}O (M+)\(^{+}\) 429.1962, Found 429.1966; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, t_R = major: 9.2 min, minor: 7.2 min, 98.2 er; [α]_D\(^{24}\) 93.7º (c 0.12, CH_2Cl_2).

Procedures for C-H alkylation of chiral isoindazoles[7]

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, 2v (0.1 mmol, 38.8 mg), DCE (0.1 M, 1 ml), [Rh(Cp^*Cl)]_2 (2 mol%, 1.6 mg), Zn(OtBu)_2 (10 mol%, 3.6 mg), alkyne (1.2 eq, 51.3 mg) were added. The mixtures were stirred at 80 °C until the starting material was consumed (TLC detected). After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the product 6c (0.078 mmol, 44.3 mg).

3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2-(2-((triisopropylsilyl)ethynyl)phenyl)-2H-indazole (6c)

Yield 78%, > 99:1 dr, pale solid, m. p. 134-135 °C, R_t = 0.7 (EtOAc/petroleum ether = 1/20); 

1H NMR (400 MHz, CDCl_3) δ 7.66 (dd, J = 7.7, 1.5 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.36 – 7.29 (m, 3H), 7.19 – 7.06 (m, 5H), 6.98 (d, J = 7.2 Hz, 2H), 6.89 (t, J = 7.4 Hz, 1H), 6.77 (t, J = 7.6 Hz, 1H), 6.58 (d, J = 8.6 Hz, 1H), 6.45 (d, J = 7.9 Hz, 1H), 5.72 (d, J = 8.4 Hz, 1H), 4.89 (d, J = 8.4 Hz, 1H), 0.93 – 0.85 (m, 12H), 0.75 (d, J = 5.6 Hz, 9H); 

13C NMR (101 MHz, CDCl_3) δ 160.0, 148.7, 140.4, 136.0, 134.0,
133.7, 129.7, 129.6, 128.69, 128.66, 128.0, 127.7, 127.4, 126.9, 125.9, 123.0, 121.5, 121.4, 121.3, 120.5, 117.7, 110.0, 101.7, 97.0, 88.5, 45.8, 18.4, 18.2, 11.1; IR (KBr, cm⁻¹) 3061, 2942, 2892, 2864, 2156, 1599, 1540, 1459, 1231, 1094, 1018, 801, 746; HRMS (ESI) Calcd for C₃₉H₃₇N₂O₇Si (M+H)⁺ 569.2983, Found 569.2990; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, tᵣ = major: 7.3 min, minor: 4.6 min, 98:2 er; [α]D 24 23.8° (c 0.14, CH₃Cl₂).

Procedures for C-H alkylation of chiral isoindazoles[8]

![Diagram](image)

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, 2v (0.1 mmol, 38.8 mg), 1,4-dioxane (0.1 M, 1 ml), [Rh(Cp*Cl₂)]₂ (5 mol%), AgSbF₆ (20 mol%), HOAc (20 mol%), alkene (1.2 eq, 15.8 mg) were added. The mixtures were stirred at 50 °C until the starting material was consumed (TLC detected). After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the product 6d (0.076 mmol, 39.5 mg).

The procedures of the following substrate 4a for accessing 6h were similar with that mentioned above.

1-phenyl-3-(2-(2-(3R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazol-2-yl)phenyl)propan-1-one (6d)

![Diagram](image)

Yield 76%, > 99:1 dr, pale solid, m. p. 75-76 °C, Rᵣ = 0.4 (EtOAc/petroleum ether = 1/20); ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 7.6 Hz, 2H), 7.56 (d, J = 8.8 Hz, 1H), 7.52 – 7.40 (m, 4H), 7.33 (t, J = 7.8 Hz, 2H), 7.23 (d, J = 7.8 Hz, 1H), 7.20 – 7.13 (m, 2H), 7.08 (d, J = 8.3 Hz, 2H), 7.05 – 7.01 (m, 1H), 6.94 – 6.87 (m, 3H), 6.85 – 6.77 (m, 1H), 6.71 (s, 1H), 6.54 (d, J = 8.6 Hz, 1H), 6.55 (d, J = 7.7 Hz, 1H), 5.72 (d, J = 8.5 Hz, 1H), 4.93 (d, J = 8.6 Hz, 1H), 3.24 – 2.92 (m, 3H), 2.73 – 2.59 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 199.0, 160.1, 148.6, 138.0, 137.9, 136.3, 136.0, 134.0, 133.1, 130.4, 129.7, 129.0, 128.7, 128.5, 128.1, 128.0, 127.4, 127.3, 127.0, 126.3, 126.1, 122.0, 121.5, 120.7, 117.6, 110.1, 88.2, 45.9, 39.5, 26.4; IR (KBr, cm⁻¹) 3061, 2927, 2878, 1683, 1596, 1580, 1379, 1231, 1160, 1018, 747, 696; HRMS (ESI) Calcd for C₃₉H₃₇N₂O₇Si (M+H)⁺ 569.2983, Found 569.2990; HPLC: INA column, 90:10 hexanes/isopropanol, 1.00 mL/min, tᵣ = major: 34.5 min, minor: 40.9 min, 98:2 er; [α]D 24 90.2° (c 0.13, CH₃Cl₂).

Procedures for C-H amidation of chiral isoindazoles[9]

![Diagram](image)

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, 2v (0.1 mmol, 38.8 mg), DCE (0.1
M, 1 ml), Cp*Co(MeCN)_{3}[(SbF_{6})_{2}] (5 mol%, 2.7 mg), amination reagent (1.5 eq, 24.5 mg) were added. The mixtures were stirred at 80 °C until the starting material was consumed (TLC detected). After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the product 6e (0.099 mmol, 50.2 mg).

The procedures of the following substrate 4a for accessing 6g were similar with that mentioned above.

**N-(2-(3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazol-2-yl)phenyl)benzamido (6e)**

Yield 99%, > 99:1 dr, pale solid, m. p. 184-186 °C, R_{f} = 0.5 (DCM/petroleum ether = 1/1); {\textsuperscript{1}}H NMR (400 MHz, CDCl_{3}) δ 9.49 (br, 1H), 8.77 (d, J = 8.0 Hz, 1H), 7.60 – 7.50 (m, 4H), 7.49 – 7.44 (m, 1H), 7.39 – 7.31 (m, 5H), 7.25 – 7.21 (m, 1H), 7.20 – 7.09 (m, 2H), 6.96 (t, J = 7.3 Hz, 1H), 6.87 – 6.76 (m, 3H), 6.75 – 6.62 (m, 3H), 6.43 (br, 1H), 5.82 (d, J = 9.0 Hz, 1H), 5.53 (br, 1H); {\textsuperscript{13}}C NMR (101 MHz, CDCl_{3}) δ 164.7, 160.1, 149.1, 135.5, 134.6, 134.1, 131.9, 130.4, 130.0, 128.6, 127.9, 127.8, 127.6, 127.20, 127.17, 126.9, 126.0, 125.8, 123.7, 122.7, 122.1, 122.0, 121.8, 121.3, 116.5, 110.4, 87.8, 45.4; IR (KBr, cm\textsuperscript{-1}) 3310, 3060, 2961, 2927, 1679, 1596, 1527, 1461, 1461, 1309, 1263, 1099, 1024, 800, 750, 699; HRMS (ESI) Calcd for C_{36}H_{28}N_{2}O (M+H){\textsuperscript{+}} 508.202; Found 508.202; HPLC: INN column, 80:20 hexanes/isopropanol, 1.00 mL/min, t_{R} = major: 9.5 min, minor: 43.8 min, 98:2 er; [α]{\textsubscript{D}}{\textsuperscript{24}} 32.3° (c 0.17, CH_{2}Cl_{2}).

**Procedures for C-H selenylation of chiral isindazoles{\textsuperscript{[10]}}**

![Diagram](https://via.placeholder.com/150)

In a Schlenk tube with a magnetic bar under nitrogen atmosphere, 2\textsuperscript{v} (0.1 mmol, 38.8 mg), THF (0.1 M, 1 ml), [Rh(Cp*Cl){\textsubscript{2}}] (5 mol%, 3.9 mg), AgSbF_{6} (1.5 eq, 17.2 mg), PhSeCl (1.2 eq, 22.9 mg) were added. The mixtures were stirred at 60 °C until the starting material was consumed. After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using THF/petroleum ether as eluent to afford the product 6f (0.076 mmol, 41.3 mg).

**3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2-((phenylselenyl)phenyl)-2H-indazole (6f)**

Yield 76%, > 99:1 dr, pale solid, m. p. 196-198 °C, R_{f} = 0.3 (THF/petroleum ether = 1/20); {\textsuperscript{1}}H NMR (500 MHz, CDCl_{3}) δ 7.58 (d, J = 7.8 Hz, 3H), 7.45 (d, J = 5.9 Hz, 1H), 7.40 – 7.32 (m, 4H), 7.29 – 7.26 (m, 1H), 7.19 – 7.13 (m, 3H), 7.12 – 7.05 (m, 4H), 7.00 – 6.94 (m, 3H), 6.84 – 6.77 (m, 1H), 6.53 (d, J = 8.6 Hz, 1H), 6.34 (s, 1H), 5.77 (d, J = 8.4 Hz, 1H), 5.10 (s, 1H); {\textsuperscript{13}}C NMR (126 MHz, CDCl_{3}) δ 160.2, 148.9, 137.8, 136.2, 136.0, 134.0, 133.6, 130.4, 130.3, 130.2, 129.8, 129.7, 129.2, 129.0, 128.6, 128.0, 127.7, 127.5, 126.6, 126.3, 121.9, 121.8, 121.6, 120.7, 117.8, 110.0, 88.3, 46.0; IR (KBr, cm\textsuperscript{-1}) 3058, 2960, 2924, 2853, 1620, 1480, 1458, 1262, 1231, 1096, 1021, 801, 743; HRMS (ESI) Calcd for
C₃₃H₃₂N₂OSe (M+H)+ 545.1127, Found 545.1129; HPLC: OD-H column, 90:10 hexanes:isopropanol, 1.00 mL/min, tᵣ = major: 8.9 min, minor: 17.8 min, 98:2 er; [α]D²⁴ 29.4° (c 0.13, CH₂Cl₂).

N-(5-bromo-2-(3-((1R,2R)-2-phenyl-1,2-dihydrophto[2,1-b]furan-1-yl)-2H-indazol-2-yl)phenyl)-benzamide (6g)

Yield 81%, > 99:1 dr, pale solid, m. p. 108-109 °C, Rf = 0.4 (EtOAc/petroleum ether = 1/10); ¹H NMR (500 MHz, CDCl₃) δ 9.56 (s, 1H), 9.08 (s, 1H), 7.92 (d, J = 8.8 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.55 (d, J = 8.8 Hz, 1H), 7.51 (d, J = 7.4 Hz, 2H), 7.46 (dd, J = 7.1, 3.4 Hz, 2H), 7.37 (d, J = 8.8 Hz, 1H), 7.32 (t, J = 7.7 Hz, 2H), 7.23 – 7.08 (m, 4H), 7.07 – 6.77 (m, 5H), 6.77 – 6.58 (m, 2H), 6.48 (s, 1H), 5.99 (d, J = 8.9 Hz, 1H), 5.72 (s, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 164.6, 158.1, 149.4, 135.9, 135.3, 135.2, 133.7, 132.1, 131.4, 130.6, 130.0, 129.1, 128.7, 128.6, 128.3, 128.1, 127.8, 127.6, 127.2, 126.8, 126.5, 125.3, 124.2, 123.6, 122.6, 122.3, 121.9, 120.8, 118.4, 116.6, 112.1, 89.2, 44.9; IR (KBr, cm⁻¹) 3316, 2961, 2929, 1771, 1650, 1539, 1263, 1022, 802, 743, 702; HRMS (ESI) Calcd for C₃₂H₂₂BrN₂O₂ (M+H)+ 636.1281, Found 636.1288; HPLC: OD-H column, 70:30 hexanes:isopropanol, 0.80 mL/min, tᵣ = major: 16.3 min, minor: 11.9 min, 96:4 er; [α]D²⁴ 80.5° (c 0.17, CH₂Cl₂).

3-(5-bromo-2-(3-(2-phenylnaphtho[2,1-b]furan-1-yl)-2H-indazol-2-yl)phenyl)-1-phenylpropan-1-one (6h)

Yield 80%, pale solid, m. p. 81-82 °C, Rf = 0.4 (EtOAc/petroleum ether = 1/20); ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, J = 8.8 Hz, 1H), 7.85 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 9.0 Hz, 1H), 7.74 – 7.62 (m, 3H), 7.59 (d, J = 8.4 Hz, 1H), 7.52 (dd, J = 7.8, 7.3 Hz, 2H), 7.40 – 7.26 (m, 5H), 7.26 – 7.14 (m, 6H), 7.08 (t, J = 7.7 Hz, 1H), 6.87 (dd, J = 8.5, 2.2 Hz, 1H), 6.56 (d, J = 8.5 Hz, 1H), 3.10 – 2.96 (m, 1H), 2.91 – 2.82 (m, 1H), 2.49 – 2.33 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 198.4, 154.1, 152.0, 149.3, 140.6, 137.5, 136.3, 133.0, 132.9, 131.0, 129.8, 129.7, 129.2, 129.1, 129.1, 128.8, 128.4, 128.2, 127.5, 127.5, 126.9, 126.8, 126.7, 124.9, 123.6, 123.4, 123.2, 123.1, 122.5, 120.6, 118.4, 112.2, 105.7, 40.1, 25.8; IR (KBr, cm⁻¹) 3059, 2966, 2927, 1683, 1651, 1540, 1543, 1261, 1023, 804, 745; HRMS (ESI) Calcd for C₃₀H₂₀BrN₂O₂ (M+H)+ 647.1329, Found 647.1330; HPLC: INAg column, 90:10 hexanes:isopropanol, 1.00 mL/min, tᵣ = major: 12.0 min, minor: 8.5 min, 91:9 er; [α]D²⁴ -1.7° (c 0.12, CH₂Cl₂).

2-(2-allyl-4-bromophenyl)-3-(2-phenylnaphtho[2,1-b]furan-1-yl)-2H-indazole (6i)

Yield 85%, pale solid, m. p. 94-95 °C, Rf = 0.6 (EtOAc/petroleum ether = 1/20); ¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, J = 8.7 Hz, 2H), 7.80 (d, J = 9.0 Hz, 1H), 7.71 (d, J = 8.9 Hz, 1H), 7.60 (d, J = 8.4 Hz, 1H), 7.49 (dd, J = 8.6, 7.5 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.33 – 7.25 (m, 6H), 7.22 – 7.13 (m, 2H), 6.86 (dd, J = 8.5, 2.2 Hz, 1H), 6.57 (d, J = 8.5 Hz, 1H), 5.29 (ddt, J = 16.9, 10.1, 6.8 Hz, 1H), 4.84 (d, J = 10.0 Hz, 1H), 4.68 (d, J = 17.2 Hz, 1H), 2.92 (dd, J = 16.1, 7.0 Hz, 1H), 2.73 (dd, J = 16.2, 6.0 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 154.0, 152.0, 149.2, 139.2, 137.2, 134.8, 133.4, 131.0, 129.9, 129.6, 129.1, 129.09, 129.08, 128.8, 128.5, 127.6, 127.4, 126.9, 126.8,
126.7, 124.9, 123.5, 123.4, 123.2, 123.1, 122.7, 120.6, 118.4, 117.5, 112.3, 105.7, 34.6; IR (KBr, cm⁻¹): 3060, 2961, 2927, 1736, 1680, 1491, 1261, 920, 745, 712; HRMS (ESI) Calcd for C₃₄H₂₄BrN₂O (M+H)+ 555.1067, Found 555.1072; HPLC: INAg column, 90:10 hexanes:isopropanol, 1.00 mL/min, tᵣ = major: 6.1 min, minor: 5.0 min, 91.9 er; [α]D²⁴ =-1.3° (c 0.078, CH₂Cl₂).

3.9. Reference

[1] a) Hu, Y.; Wang, Z.; Yang, H.; Chen, J.; Zhou, L.; Wu, Z.; Lei, Y. Chem. Sci., 2019, 10, 6777–6784. b) Morales-Rivera, C. A.; Floreancig, P.; Liu, P. J. Am. Chem. Soc. 2017, 139, 17935–17944.
[2] Priewisch, B.; Rück-Braun, K. J. Org. Chem., 2005, 70, 2350-2352.
[3] Fang, Y.; Wang, C.; Su, S.; Yu, H.; Huang, Y. Org. Biomol. Chem., 2014, 12, 1061–1071.
[4] Wei, W.; Li, X.; Gu, M.; Yao, H.; Lin, A. Org. Biomol. Chem., 2017, 15, 8458-8462.
[5] Davies, D. L.; Ellul, C. E.; Macgregor, S. A.; McMullin, C. L.; Singh, K. J. Am. Chem. Soc., 2015, 137, 9659–9669.
[6] Wang, H.; Schröder, N.; Glorius, F. Angew. Chem., Int. Ed., 2013, 52, 5386 –5389.
[7] Xie, F.; Qi, Z.; Yu, S.; Li, X. J. Am. Chem. Soc., 2014, 136, 4780–4787.
[8] Boerth, J. A.; Hummel, J. R. Ellman, J. A. Angew. Chem. Int. Ed., 2016, 55, 12650 –12654.
[9] Liang, Y.; Liang, Y.; Tang, C.; Yuan, Y.; Jiao, N. Chem. Eur. J., 2015, 21, 16395 –16399.
[10] Yu, S.; Wan, B.; Li, X. Org. Lett., 2015, 17, 58–61.
4. X-Ray diffraction analysis

4.1 Crystal data and structure refinement for 2h

CCDC 2105966
Identification code 9st-147
Empirical formula C_{28}H_{18}BrN_{3}O
Formula weight 492.36
Temperature/K 99.98(10)
Crystal system monoclinic
Space group I2
a/Å 20.2119(12)
b/Å 7.9865(4)
c/Å 28.5833(19)
α/° 90
β/° 99.590(6)
γ/° 90
Volume/Å³ 4549.5(5)
Z 8
ρ_{calc} g/cm³ 1.438
μ/mm⁻¹ 2.664
F(000) 2000.0
Crystal size/mm³ 0.13 × 0.11 × 0.1
Radiation Cu Kα (λ = 1.54184)
2Θ range for data collection/° 4.986 to 147.196
Index ranges -19 ≤ h ≤ 24, -9 ≤ k ≤ 8, -35 ≤ l ≤ 33
Reflections collected 14962
Independent reflections 7084 [R_{int} = 0.0537, R_{sigma} = 0.0534]
Data/restraints/parameters 7084/1/595
Goodness-of-fit on F² 1.056
Final R indexes [I>2σ (I)] R₁ = 0.0447, wR₂ = 0.1145
Final R indexes [all data] R₁ = 0.0456, wR₂ = 0.1160
Largest diff. peak/hole / e Å⁻³ 1.19/-0.80
Flack parameter 0.005(11)
4.2 Crystal data and structure refinement for 4g

CCDC 2105967
Identification code 68-3
Empirical formula C_{35}H_{25}BrN_{2}O_{5}
Formula weight 633.48
Temperature/K 199.99(10)
Crystal system monoclinic
Space group P2_{1}
a/Å 7.00919(18)
b/Å 14.8084(3)
c/Å 13.4349(3)
α/° 90
β/° 92.747(2)
γ/° 90
Volume/Å^{3} 1392.88(6)
Z 2
ρ_{calc} g/cm^{3} 1.510
μ/mm^{-1} 2.416
F(000) 648.0
Crystal size/mm^{3} 0.12 \times 0.1 \times 0.08
Radiation Cu Kα (λ = 1.54184)
2Θ range for data collection/° 6.586 to 147.578
Index ranges -8 \leq h \leq 6, -18 \leq k \leq 18, -16 \leq l \leq 16
Reflections collected 10046
Independent reflections 5469 [R_{int} = 0.0250, R_{sigma} = 0.0335]
Data/restraints/parameters 5469/1/390
Goodness-of-fit on F^{2} 1.027
Final R indexes [I>2σ (I)] R_{1} = 0.0273, wR_{2} = 0.0681
Final R indexes [all data] R_{1} = 0.0281, wR_{2} = 0.0685
Largest diff. peak/hole / e Å^{-3} 0.20/-0.52
Flack/Hooft parameter -0.019(7)/-0.001(6)
4.3 Crystal data and structure refinement for 5g

CCDC 2105968
Identification code 78-3
Empirical formula C_{35}H_{23}BrN_{2}O_{5}
Formula weight 631.46
Temperature/K 150.00(10)
Crystal system monoclinic
Space group P2_1
a/Å 8.9824(12)
b/Å 10.3845(11)
c/Å 15.312(2)
α/° 90
β/° 92.079(13)
γ/° 90
Volume/Å³ 1427.4(3)
Z 2
ρ calc g/cm³ 1.469
μ/mm⁻¹ 1.488
F(000) 644.0
Crystal size/mm³ 0.14 × 0.12 × 0.1
Radiation Mo Kα (λ = 0.71073)
2θ range for data collection/° 4.538 to 59.082
Index ranges -9 ≤ h ≤ 11, -12 ≤ k ≤ 13, -19 ≤ l ≤ 14
Reflections collected 11864
Independent reflections 6468 [R_{int} = 0.0899, R_{sigma} = 0.1693]
Data/restraints/parameters 6468/47/400
Goodness-of-fit on F² 1.037
Final R indexes [I>2σ (I)] R₁ = 0.0849, wR₂ = 0.1807
Final R indexes [all data] R₁ = 0.1301, wR₂ = 0.2153
Largest diff. peak/hole / e Å⁻³ 1.44/-1.31
Flack/Hooft parameter 0.004(14)/0.031(12)
5. Copies of NMR spectrum

\textit{(E)-1-(2-((2-benzyloxy)phenyl)ethynyl)phenyl-2-(4-bromophenyl)diazene (1a)}
(E)-1-(4-bromophenyl)-2-((2-((2-((4-methylbenzyl)oxy)phenyl)ethynyl)phenyl)diazene (1b)
(E)-1-(4-bromophenyl)-2-((2-((4-methoxybenzyl)oxy)phenyl)ethynyl)phenyl)diazene (1c)
(E)-1-(4-bromophenyl)-2-((2-((4-fluorobenzyl)oxy)phenyl)ethynyl)phenyl)diazene (1d)
(E)-1-(4-bromophenyl)-2-((2-((4-chlorobenzyl)oxy)phenyl)ethynyl)phenyl)diazene (1e)
(E)-1-(2-((2-((4-bromobenzyl)oxy)phenyl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (1f)
(E)-1-(4-bromophenyl)-2-((2-((4-(trifluoromethyl)benzyl)oxy)phenyl)ethynyl)phenyl)diazene (1g)
(E)-4-((2-((4-bromophenyl)diazenyl)phenyl)ethynyl)phenoxy)methyl)benzonitrile (1h)
(E)-1-(2-(((3-bromobenzyl)oxy)phenyl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (Ii)
(E)-1-(2-((2-bromobenzyl)oxy)phenyl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (1j)
(E)-1-(4-bromophenyl)-2-(2-((2-methoxybenzyl)oxy)phenyl)ethynyl)phenyl)diazene (1k)
(E)-1-(4-bromophenyl)-2-(2-((2-naphthalen-1-ylmethoxy)phenyl)ethyl)phenyl)diazene (1I)
(E)-1-(4-bromophenyl)-2-(2-((2-(naphthalen-2-ylmethoxy)phenyl)ethynyl)phenyl)diazene (1m)
(E)-1-(2-((2-allyloxy)phenyl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (1n)
(E)-1-(4-bromophenyl)-2-((2-(but-2-yn-1-yl)oxy)phenyl)ethynyl)phenyl)diazene (1o)
(E)-1-(4-bromophenyl)-2-[(2-((3-(trimethylsilyl)prop-2-yn-1-yl)oxy)phenyl)ethynyl]phenyl)diazene (1p)
(E)-1-(4-bromophenyl)-2-[(2-(3-phenylpropoxy)phenyl)ethynyl]phenyl)diazene (1q)
(E)-1-(4-bromophenyl)-2-((2-(isopentyloxy)phenyl)ethynyl)phenyl)diazene (1r)
(E)-1-(4-bromophenyl)-2-((2-isobutoxyphenyl)ethynyl)phenyl)diazene (1s)
(E)-1-(4-bromophenyl)-2-(2-((2-(cyclopropylmethoxy)phenyl)ethynyl)phenyl)diazene (1t)
(E)-1-(4-bromophenyl)-2-(2-((2-(3-methoxypropoxy)phenyl)ethynyl)phenyl)dizene (1u)
(E)-1-(2-((2-benzyloxy)phenyl)ethynyl)phenyl)-2-phenyldiazene (1v)
(E)-1-(2-((2-benzylxoy)phenyl)ethynyl)phenyl)-2-(4-methoxyphenyl)diazene (1w)
(E)-1-(2-((2-(benzyloxy)phenyl)ethynyl)-4-fluorophenyl)-2-(4-bromophenyl)diazene (1x)
(E)-1-(2-((2-benzyl oxy)phenyl)ethynyl)-4-methoxyphenyl)-2-(4-bromophenyl)diazen e (1y)
(E)-1-(2-((2-(benzyloxy)phenyl)ethynyl)-4-methylphenyl)-2-phenyldiazene (1z)
(E)-1-(2-(4-(benzyl oxy)but-1-yn-1-yl)phenyl)-2-(4-bromophenyl)diazene (1aa)
(E)-1-{2-[(4-bromophenyl)diazenyl]phenyl}ethynyl]phenyl)piperidine (1ab)
(E)-1-((2-(benzylthio)phenyl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (Iac)
(E)-1-(2-((2-(benzyloxy)naphthalen-1-yl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (3a)
**Methyl (E)-4-(((1-(((2-((4-bromophenyl)diazenny1)phenyl)ethyny1)naphthalen-2-yl)oxy)methyl)benzoate (3b)**
(E)-1-(4-chlorophenyl)-2-(2-((2-(3-(3,5-dibromobenzyl)oxy)naphthalen-1-yl)ethynyl)phenyl)diazene (3d)
(E)-1-(4-bromophenyl)-2-((2-((3,5-difluorobenzyl)oxy)naphthalen-1-yl)ethynyl)phenyl)diazene (3e)
(E)-1-(4-bromophenyl)-2-(2-(((3,5-dichlorobenzyl)oxy)naphthalen-1-yl)ethynyl)phenyl)diazene (3f)
dimethyl (E)-5-((((1-((2-((4-bromophenyl)diazenyl)phenyl)ethyl)phenyl)ethynyl)napthalen-2-yl)oxy)methyl)-isophthalate (3g)
(E)-1-(4-bromophenyl)-2-[(2-((3,5-dimethoxybenzyl)oxy)naphthalen-1-yl)ethynyl]phenyl)diazene (3h)
(E)-1-((2-(benzyloxy)phenyl)ethynyl)phenyl-N-(tert-butyl) methanimine
(E)-1-((2-(benzyloxy)phenyl)ethyl)phenyl)diazene)piperidine
3-(2-(benzyl oxy)phenyl)isoquinoline
3-(2-phenyl-2,3-dihydrobenzofuran-3-yl)-2-(piperidin-1-yl)-2H-indazole
1-(benzyloxy)-2-(phenylethynyl)benzene
2-(4-bromophenyl)-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2a)
2-((4-bromophenyl)-3-((2R,3R)-2-(p-tolyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2b)
2-((4-bromophenyl)-3-((2R,3R)-2-((4-methoxyphenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2c)
2-(4-bromophenyl)-3-((2R,3R)-2-(4-fluorophenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2d)
2-(4-bromophenyl)-3-((2R,3R)-2-(4-chlorophenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2e)
2-(4-bromophenyl)-3-((2R,3R)-2-(4-bromophenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2f)
2-(4-bromophenyl)-3-((2R,3R)-2-(4-(trifluoromethyl)phenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2g)
4-((2R,3R)-3-(2-(4-bromophenyl)-2H-indazol-3-yl)-2,3-dihydrobenzofuran-2-yl)benzonitrile (2h)
2-(4-bromophenyl)-3-((2R,3R)-2-(3-bromophenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2i)
2-(4-bromophenyl)-3-((2R,3R)-2-(2-bromophenyl)-3,2-dihydrobenzofuran-3-yl)-2H-indazole (2j)
2-(4-bromophenyl)-3-((2R,3R)-2-(2-methoxyphenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2k)
2-(4-bromophenyl)-3-(((2R,3R)-2-(naphthalen-1-yl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2l)
2-(4-bromophenyl)-3-((2R,3R)-2-(naphthalen-2-yl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2m)
2-((4-bromophenyl)-3-((2S,3R)-2-vinyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2n)

97.3 d.r.

97.3 d.r.
2-(4-bromophenyl)-3-((2R,3R)-2-(prop-1-yn-1-yl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2o)
2-(4-bromophenyl)-3-((2R,3R)-2-((trimethylsilyl)ethynyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2p)
2-(4-bromophenyl)-3-((2S,3R)-2-phenethyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2q)
2-(4-bromophenyl)-3-((2S,3R)-2-isobutyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2r)
2-((4-bromophenyl)-3-((2S,3R)-2-isopropyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2s)
2-(4-bromophenyl)-3-((2S,3R)-2-cyclopropyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2t)
2-(4-bromophenyl)-3-((2S,3R)-2-(2-methoxyethyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2u)
2-phenyl-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2v)
2-(4-methoxyphenyl)-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2w)
2-(4-bromophenyl)-5-fluoro-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2x)
2-(4-bromophenyl)-5-methoxy-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2y)
5-methyl-2-phenyl-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2z)
2-(4-bromophenyl)-3-((2R,3R)-2-phenyltetrahydrofuran-3-yl)-2H-indazole (2aa)
(9aS,10S)-10-(2-(4-bromophenyl)-2H-indazol-3-yl)-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indole (2ab)
2-(4-bromophenyl)-3-((2R,3R)-2-phenyl-2,3-dihydrobenzo[b]thiophen-3-yl)-2H-indazole(2ac)
2-(4-bromophenyl)-3-((1R,2R)-2-phenyl-1,2-dihyronaphtho[2,1-b]furan-1-yl)-2H-indazole (4a)
methyl 4-((1R,2R)-1-(2-(4-bromophenyl)-2H-indazol-3-yl)-1,2-dihydranaptho[2,1-b]furan-2-yl)-benzoate (4b)
2-(4-bromophenyl)-3-((1R,2R)-2-(naphthalen-2-yl)-1,2-dihyronaphtho[2,1-b]furan-1-yl)-2H-indazole (4c)
2-(4-chlorophenyl)-3-((1R,2R)-2-(3,5-dibromophenyl)-1,2-dihydroronaph[2,1-b]furan-1-yl)-2H-indazole (4d)

95:5 d.r.
2-(4-bromophenyl)-3-((1R,2R)-2-(3,5-difluorophenyl)-1,2-dihydropthof[2,1-b]furan-1-yl)-2H-indazole (4e)
2-((4-bromophenyl)-3-((1R,2R)-2-(3,5-dichlorophenyl)-1,2-dihydroronaphtho[2,1-b]furan-1-yl)-2H-indazole (4f)
dimethyl 5-(((1R,2R)-1-(2-(4-bromophenyl)-2H-indazol-3-yl)-1,2-dihydronaphtho[2,1-b]furan-2-yl)-isophthalate (4g)
2-(4-bromophenyl)-3-((1R,2R)-2-(3,5-dimethoxyphenyl)-1,2-dihydrophto[2,1-b]furan-1-yl)-2H-indazole (4h)
2-(4-bromophenyl)-3-(2-(naphthalen-2-yl)benzofuran-3-yl)-2H-indazole
2-(4-bromophenyl)-3-(2-phenylnaphtho[2,1-b]furan-1-yl)-2H-indazole (5a)
methyl 4-(1-(2-(4-bromophenyl)-2H-indazol-3-yl)naphtho[2,1-b]furan-2-yl)benzoate (5b)
2-(4-bromophenyl)-3-(2-(naphthalen-2-yl)naphtho[2,1-b]furan-1-yl)-2H-indazole (5c)
2-(4-chlorophenyl)-3-(2-(3,5-dibromophenyl)naphtho[2,1-b]furan-1-yl)-2H-indazole (5d)
2-(4-bromophenyl)-3-(2-(3,5-difluorophenyl)naphtho[2,1-b]furan-1-yl)-2H-indazole (5e)
2-(4-bromophenyl)-3-(2-(3,5-dichlorophenyl)naphtho[2,1-b][furan-1-yl]-2H-indazole (5f)
dimethyl 5-(1-(2-(4-bromophenyl)-2H-indazol-3-yl)naphtho[2,1-b]furan-2-yl)isophthalate (5g)
2-(4-bromophenyl)-3-(2-(3,5-dimethoxyphenyl)naphtho[2,1-b]furan-1-yl)-2H-indazole (5h)
2-(2-(((E)-oct-4-en-4-yl)phenyl)-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (6a)
2-(2-allylphenyl)-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (6b)
3-\(((2R,3R)-2\text{-phenyl}-2,3\text{-dihydrobenzofuran-3-yl})-2-\text{-}((\text{triisopropylsilyl})\text{ethynyl})\text{phenyl})\text{-}2H\text{-}\text{indazole} \ (6c) \)
1-phenyl-3-(2-(3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazol-2-yl)phenyl)propan-1-one (6d)
$N$-(2-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazol-2-yl)phenyl)benzamide (6e)
3-(((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2-(2-(phenylselanyl)phenyl)-2H-indazole (6f)
N-(5-bromo-2-(3-((1R,2R)-2-phenyl-1,2-dihydronaphtho[2,1-b]furan-1-yl)-2H-indazol-2-yl)phenyl)-benzamide (6g)
$\text{3-(5-bromo-2-(3-(2-phenylnaphto[2,1-b]furan-1-yl)-2H-indazol-2-yl)phenyl)-1-phenylpropan-1-one (6h)}$
2-(2-allyl-4-bromophenyl)-3-(2-phenyl-naphtho[2,1-b]furan-1-yl)-2H-indazole (6i)
6. Data of HPLC

![Chemical structure of 3a]

**Retention Time**: The retention time of each peak is measured in minutes. It is the time interval between the injection of the sample and the elution of the peak from the column.

**Area %**: The area under the peak is normalized to give the area percentage (% area). It is a measure of the amount of substance present in the sample.
色谱图

保留时间 = retention time
面积% = area %

峰表

| 峰号 | 保留时间 | 面积     | 高度     | 化合物名 | 高度% | 面积% |
|------|-----------|----------|----------|----------|-------|-------|
| 1    | 17.314    | 14900818 | 372436   |          |       |       |
| 2    | 20.602    | 14939986 | 271438   |          | 57.841| 49.934|
| 总计 |           | 29840805 | 643884   |          | 100.000| 100.000|
保留时间 = retention time
面积% = area %
色谱图

保留时间 = retention time
面积% = area %

峰表

| 峰号 | 保留时间 | 面积   | 高度   | 化合物名 | 高度% | 面积%   |
|------|-----------|--------|--------|----------|-------|----------|
| 1    | 11.858    | 19861953 | 965589 | 不同化合物 | 60.254 | 49.829   |
| 2    | 17.653    | 19998658 | 636944 | 不同化合物 | 39.746 | 50.171   |
| 总计 | 39860611  | 1602533 |        | 表面 | 100.000 | 100.000 |

色谱图

保留时间 = retention time
面积% = area %

峰表

| 峰号 | 保留时间 | 面积   | 高度   | 化合物名 | 高度% | 面积%   |
|------|-----------|--------|--------|----------|-------|----------|
| 1    | 11.896    | 327999999 | 1816080 | 不同化合物 | 95.759 | 95.001   |
| 2    | 17.565    | 1725619  | 71579  | 不同化合物 | 4.241  | 4.999    |
| 总计 | 34327518 | 1687658 |        | 表面 | 100.000 | 100.000 |

158
色谱图

保留时间 = retention time
面积% = area %

峰表

| 峰号 | 保留时间 | 面积     | 高度     | 化合物名 | 高度% | 面积% |
|------|---------|---------|---------|---------|-------|-------|
| 1    | 12.873  | 1840927 | 73825   |         |       |       |
| 2    | 16.421  | 1856826 | 61227   |         | 45.003| 50.093|
| 总计 |         | 3706753 | 136052  |         | 100.00| 100.00|

色谱图

保留时间 = retention time
面积% = area %

峰表

| 峰号 | 保留时间 | 面积     | 高度     | 化合物名 | 高度% | 面积% |
|------|---------|---------|---------|---------|-------|-------|
| 1    | 12.907  | 773285  | 36854   |         | 2.910 | 1.980 |
| 2    | 16.394  | 38381008| 1229444 |         | 97.090| 98.020|
| 总计 |         | 39156293| 1266299 |         | 100.00| 100.00|

159
色谱图

保留时间 = retention time
面积% = area %

峰表

| 峰号 | 保留时间 | 高度 | 面积   | 化合物名 | 高度% | 面积% |
|------|----------|------|--------|----------|-------|-------|
| 1    | 9.718    | 334137 | 6414287 |          | 52.115 | 50.132 |
| 2    | 11.210   | 307022 | 6380622 |          | 47.885 | 49.868 |
| 总计 |          | 641158 | 12794909 |          | 100.000 | 100.000 |

色谱图

保留时间 = retention time
面积% = area %

峰表

| 峰号 | 保留时间 | 高度 | 面积   | 化合物名 | 高度% | 面积% |
|------|----------|------|--------|----------|-------|-------|
| 1    | 9.804    | 37509 | 775119 |          | 90.050 | 90.266 |
| 2    | 11.261   | 4144  | 83582  |          | 9.950  | 9.734 |
| 总计 |          | 41653 | 858701 |          | 100.000 | 100.000 |
保留时间 = retention time
面积% = area %
色谱图

保留时间 = retention time
面积% = area %

峰表

| 峰号 | 保留时间 | 面积   | 高度   | 化合物名 | 高度% | 面积% |
|------|----------|--------|--------|----------|-------|-------|
| 1    | 11.299   | 9663913| 470240 |          | 60.244| 49.820|
| 2    | 16.967   | 9733629| 310316 |          | 39.756| 50.180|
| 总计 |          | 19397542| 780556 |          | 100.000 | 100.000 |

色谱图

保留时间 = retention time
面积% = area %

峰表

| 峰号 | 保留时间 | 面积   | 高度   | 化合物名 | 高度% | 面积% |
|------|----------|--------|--------|----------|-------|-------|
| 1    | 11.257   | 28649881| 1273051|          | 98.463| 98.174|
| 2    | 17.044   | 484518  | 19869  |          | 1.537 | 1.826 |
| 总计 |          | 28534400| 1292920|          | 100.000 | 100.000 |
色谱图

保留时间 = retention time
面积% = area %

色谱图

保留时间 = retention time
面积% = area %

峰表

| 峰号 | 保留时间 | 面积  | 高度  | 化合物名 | 高度% | 面积% |
|------|----------|-------|-------|----------|-------|-------|
| 1    | 12.031   | 707435| 34090 |          | 2.673 | 1.989 |
| 2    | 15.411   | 34858944| 1241496|          | 97.327 | 98.011 |
| 总计 |          | 35566379| 1275587|          | 100.000 | 100.000 |
保留时间 = retention time
面积% = area %
### 色谱图

保留时间 = retention time
面积% = area %

| 峰号 | 保留时间 | 面积   | 高度   | 化合物名 | 高度% | 面积% |
|------|---------|--------|--------|----------|-------|-------|
| 1    | 16.533  | 18534804 | 477636 |           | 55.016 | 49.582 |
| 2    | 18.236  | 18847588 | 390548 |           | 44.984 | 50.418 |
| 总计 |         | 37382392 | 868184 | 100.000  | 100.000 |       |

### 色谱图

保留时间 = retention time
面积% = area %

| 峰号 | 保留时间 | 高度   | 面积   | 化合物名 | 高度% | 面积% |
|------|---------|--------|--------|----------|-------|-------|
| 1    | 17.045  | 23804  | 781965 | 3.885    | 2.599 |
| 2    | 17.990  | 58711  | 29308018 | 96.145  | 97.401 |
| 总计 |         | 617811 | 30889982 | 100.000  | 100.000 |
### 色谱图

**PDA Multi I 254nm, 4nm**

| 保留时间 | 面积  | 高度  | 化合物名 | 高度%  | 面积%  |
|---------|-------|-------|----------|--------|--------|
| 7.471   | 6672926 | 312419 |          | 85.086 | 50.570 |
| 8.701   | 5935996 | 54762  |          | 14.914 | 49.430 |
| 总计    | 12008920 | 367181 |          | 100.000 | 100.000 |

### 峰表

**PDA Ch1 254nm**

| 峰号 | 保留时间 | 面积  | 高度  | 化合物名 | 高度%  | 面积%  |
|------|-----------|-------|-------|----------|--------|--------|
| 1    | 7.539     | 3181488 | 174744 |          | 22.388 | 4.972 |
| 2    | 23.799    | 60809875 | 605781 |          | 77.612 | 95.028 |
| 总计 |           | 63991863 | 780525 |          | 100.000 | 100.000 |
色谱图

保留时间 = retention time
面积% = area %

峰表

| 峰号 | 保留时间 | 面积  | 高度  | 化合物名 | 高度% | 面积%  |
|------|----------|-------|-------|----------|-------|--------|
| 1    | 9.382    | 3957128| 213849|          | 78.091| 50.100 |
| 2    | 22.814   | 3941378| 56912 |          | 21.019| 49.900 |
| 总计 |          | 7898506| 270761|          | 100.000| 100.000|

色谱图

保留时间 = retention time
面积% = area %

峰表

| 峰号 | 保留时间 | 面积  | 高度  | 化合物名 | 高度% | 面积%  |
|------|----------|-------|-------|----------|-------|--------|
| 1    | 9.370    | 1360245| 78379 |          | 35.252| 10.170 |
| 2    | 21.634   | 12014372| 143961|          | 64.748| 89.830 |
| 总计 |          | 13374617| 222341|          | 100.000| 100.000|
2ab
4d

**<色谱图>**

**nAU**

保留时间 = retention time  
面积% = area %

**<峰表>**

| 峰号 | 保留时间 | 面积    | 高度    | 化合物名 | 高度% | 面积% |
|------|----------|---------|---------|----------|-------|-------|
| 1    | 10.365   | 2932267 | 121763  |          | 56.596| 49.749|
| 2    | 15.513   | 3972880 | 93381   |          | 43.404| 50.251|
| 总计 |          | 7906146 | 215144  |          | 100.000| 100.000|

**<色谱图>**

**nAU**

保留时间 = retention time  
面积% = area %

**<峰表>**

| 峰号 | 保留时间 | 面积    | 高度    | 化合物名 | 高度% | 面积% |
|------|----------|---------|---------|----------|-------|-------|
| 1    | 10.410   | 240130  | 8323    |          | 1.557 | 1.130 |
| 2    | 14.864   | 2101195 | 526074  |          | 98.443| 98.870|
| 总计 |          | 21251325| 534397  |          | 100.000| 100.000|
色谱图
nAU
保留时间 = retention time
面积 % = area %

峰表
PDA Ch 1 254nm
保留时间 | 面积 | 高度 | 化合物名 | 高度% | 面积%
--- | --- | --- | --- | --- | ---
1 | 20.882 | 3423346 | 72379 | 62.729 | 50.926
2 | 31.233 | 3298851 | 43004 | 37.271 | 49.074
总计 | 6722197 | 115382 | | 100.000 | 100.000

色谱图
nAU
保留时间 = retention time
面积 % = area %

峰表
PDA Ch 1 254nm
保留时间 | 面积 | 高度 | 化合物名 | 高度% | 面积%
--- | --- | --- | --- | --- | ---
1 | 20.913 | 92555142 | 1802431 | 98.772 | 98.430
2 | 30.888 | 1476134 | 22407 | 1.228 | 1.570
总计 | 94031276 | 1824838 | | 100.000 | 100.000
<色谱图>

保留时间 = retention time
面积% = area %

<峰表>

| 峰号 | 保留时间 | 面积  | 高度  | 化合物名 | 高度% | 面积% |
|------|-----------|-------|-------|----------|-------|-------|
| 1    | 7.611     | 18515879 | 1276885 |          | 55.972 | 49.876 |
| 2    | 10.015    | 18607943 | 1004420 |          | 44.028 | 50.124 |
| 总计 |           | 37123822 | 2281305 |          | 100.000 | 100.000 |

<色谱图>

保留时间 = retention time
面积% = area %

<峰表>

| 峰号 | 保留时间 | 面积  | 高度  | 化合物名 | 高度% | 面积% |
|------|-----------|-------|-------|----------|-------|-------|
| 1    | 8.227     | 3579529  | 212975 |          | 11.484 | 9.357 |
| 2    | 10.803    | 34676341 | 1641529 |          | 88.516 | 90.643 |
| 总计 |           | 38253371 | 1851504 |          | 100.000 | 100.000 |
<色谱图>

保留时间 = retention time
面积% = area %

<峰表>

| 峰号 | 保留时间 | 面积   | 高度   | 化合物名 | 高度% | 面积% |
|------|-----------|--------|--------|----------|-------|-------|
| 1    | 5.331     | 12339824 | 1228888 |          | 55.126 | 50.486 |
| 2    | 7.184     | 12099544 | 998716  |          | 44.874 | 49.514 |
| 总计 |           | 24436367 | 2225604 |          | 100.000 | 100.000 |

<色谱图>

保留时间 = retention time
面积% = area %

<峰表>

| 峰号 | 保留时间 | 面积   | 高度   | 化合物名 | 高度% | 面积% |
|------|-----------|--------|--------|----------|-------|-------|
| 1    | 5.391     | 1665261 | 168978  |          | 11.141 | 8.878 |
| 2    | 7.373     | 17091542 | 1347709 |          | 88.859 | 91.122 |
| 总计 |           | 18756802 | 1516687 |          | 100.000 | 100.000 |
### 色谱图

PDA Multi 1 254nm, 4mm

保留时间 = retention time
面积% = area %

### 峰表

| 峰号 | 保留时间 | 面积   | 高度     | 化合物名 | 高度% | 面积% |
|------|----------|--------|----------|----------|-------|-------|
| 1    | 4.901    | 804424 | 5126887  | 68.422   | 50.116|       |
| 2    | 7.313    | 29347911 | 2225231  | 41.578   | 49.884|       |
| 总计 |          | 88831908 | 5351919  | 100.000  | 100.000|       |

### 色谱图

PDA Multi 1 254nm, 4mm

保留时间 = retention time
面积% = area %

### 峰表

| 峰号 | 保留时间 | 面积   | 高度     | 化合物名 | 高度% | 面积% |
|------|----------|--------|----------|----------|-------|-------|
| 1    | 4.901    | 2500654 | 282525   | 9.983    | 6.940 |       |
| 2    | 7.284    | 33533654 | 2565514  | 90.717   | 93.060|       |
| 总计 |          | 36034308 | 2828039  | 100.000  | 100.000|       |
HPLC data of 5g after recrystallization.
图1：
保留时间 = retention time
面积% = area %

表1：

| 峰号 | 保留时间 | 面积  | 高度   | 化合物名 | 高度% | 面积% |
|------|----------|-------|--------|----------|-------|-------|
| 1    | 4.581    | 11906157 | 184108 |          | 59.039 | 49.737 |
| 2    | 7.388    | 19308460 | 1278740|          | 40.961 | 50.263 |
| 总计 |          | 38414617 | 3121848|          | 100.000 | 100.000 |

图2：
保留时间 = retention time
面积% = area %

表2：

| 峰号 | 保留时间 | 面积  | 高度   | 化合物名 | 高度% | 面积% |
|------|----------|-------|--------|----------|-------|-------|
| 1    | 4.576    | 838811 | 88194  |          | 3.451 | 2.049 |
| 2    | 7.309    | 40000534 | 2467435|          | 96.549 | 97.951 |
| 总计 |          | 40837345 | 2555628|          | 100.000 | 100.000 |

197
<色谱图>

保留时间 = retention time
面积% = area %

| 峰号 | 保留时间 | 面积   | 高度   | 化合物名 | 高度% | 面积% |
|------|----------|--------|--------|----------|-------|-------|
| 1    | 9.650    | 10333021 | 530140 | 93.802   | 50.308 |
| 2    | 37.398   | 10206854 | 33026  | 6.198    | 49.692 |
| 总计 |          | 20539605 | 565166 | 100.000  | 100.000 |

<峰表>

保留时间 = retention time
面积% = area %

| 峰号 | 保留时间 | 面积   | 高度   | 化合物名 | 高度% | 面积% |
|------|----------|--------|--------|----------|-------|-------|
| 1    | 9.592    | 36818160 | 1857662 | 99.756   | 97.898 |
| 2    | 43.808   | 790640  | 4542   | 0.244    | 2.102 |
| 总计 |          | 37608800 | 1862204 | 100.000  | 100.000 |
<色谱图>

保留时间 = retention time
面积% = area %

| 峰号 | 保留时间 | 面积    | 高度   | 化合物名       | 高度% | 面积%    |
|------|----------|--------|--------|----------------|-------|----------|
| 1    | 8.899    | 5910573| 252559 |                | 68.552| 49.968   |
| 2    | 17.617   | 5918076| 115863 |                | 31.448| 50.032   |
| 总计 |          | 11823649| 368422 |                | 100.000| 100.000 |

<色谱图>

保留时间 = retention time
面积% = area %

| 峰号 | 保留时间 | 面积    | 高度   | 化合物名       | 高度% | 面积%    |
|------|----------|--------|--------|----------------|-------|----------|
| 1    | 8.877    | 16833938| 701885 |                | 99.059| 98.031   |
| 2    | 17.810   | 338032  | 6668   |                | 0.941 | 1.969    |
| 总计 |          | 17171970| 708553 |                | 100.000| 100.000 |
