Supplementary Information

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

Shaotong Qiu, Xiang Gao, and Shifa Zhu*,†,‡

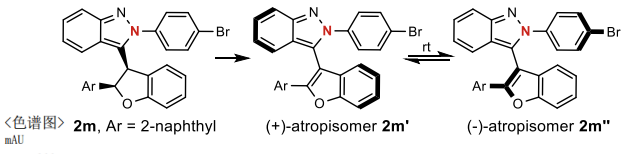
†Key Lab of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P. R. China

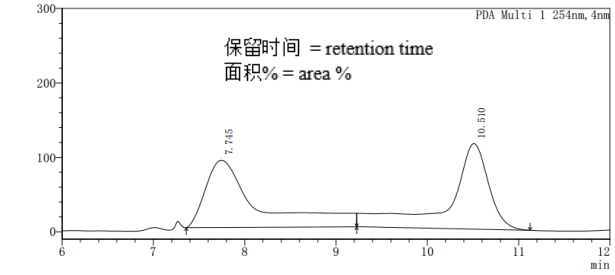
zhusf@scut.edu.cn

‡ Guangdong Youmei Institute of Intelligent Bio-manufacturing Co., Ltd.

Table of content

1. HPLC analysis of product 2m' and 2m''





〈峰表〉

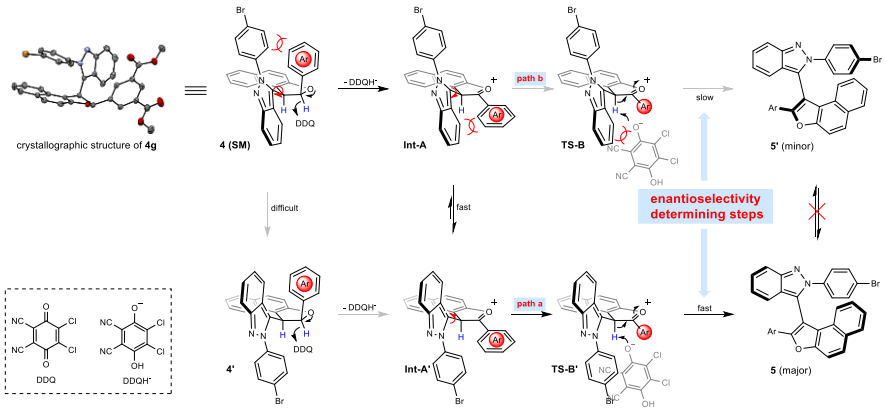
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.745	3643379	90295		44.002	50.331
2	10.510	3595512	114912		55.998	49.669
总计		7238891	205207		100.000	100.000

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.



Scheme 1S Proposed mechanism for central-to-axial chirality transfer of **4** to **5**

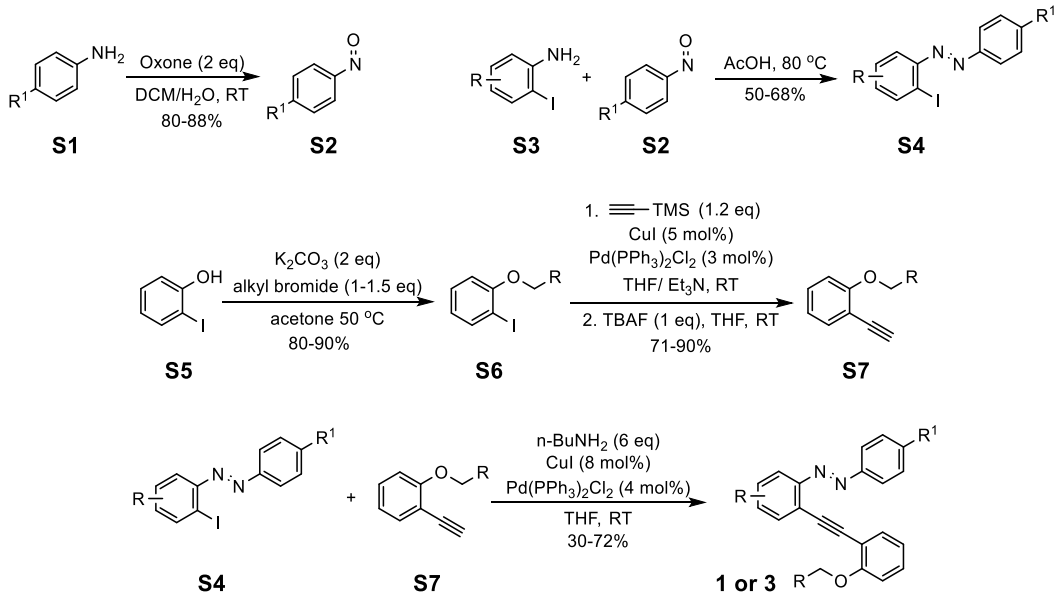
3. Experimental procedures and spectroscopic data

3.1 General information

All reactions were carried out under an inert atmosphere of dry N_2 in Schlenk tube, solvents were purified by standard method. ^1H, ^{13}C, ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ^1H; 101 MHz for ^{13}C; 376 MHz for ^{19}F) or Bruker AVANCE 500 (500 MHz for ^1H; 126 MHz for ^{13}C; 471 MHz for ^{19}F), ^1H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ 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



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[3]

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 ºC for 40 h. The resulting mixture was cooled to roomtemperature, diluted with DCM, and washed with brine and H_2O. The organic layer was dried through anhydrous Na_2SO_4, filtered over Celite, and concentrated in vacuo. Column chromatography onsilica gel gave thecorresponding 2-iodoazobenzenes **S4**.

Typical procedure for preparation of S7

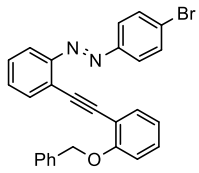
An oven-dried round bottom flask was charged with 2-iodophenols **S5** (1.0 equiv), K_2CO_3 (2.0 equiv), acetone (0.5 M) and alkyl bromide (1-1.5 equiv). The reaction mixture was stirred at 60 ºC in an oil bath for 10 h. After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, 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%), $Pd(PPh_3)_2Cl_2$ (3 mol%) were added to a schlenk tube, Et_3N (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 disppeared. 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 minites. The mixture was diluted with H_2O, and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$ 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. [4]

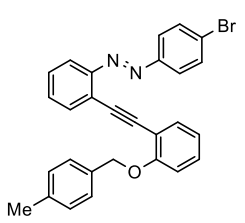
2-iodoazobenzene **S4** (1.0 equiv), $Pd(PPh_3)_2Cl_2$(0.04 equiv),CuI (0.08 equiv) and *n*$BuNH_2$ (6.0 mmol, 6.0 equiv) were dissolved in anhydrous THF (0.1 M) under N_2 atmosphere. To the resulting solution terminal alkyne **S7** (1.2 equiv) was added dropwise. The mixture was stirred at room temperature. After the reaction was completed (detected by TLC) (2-7 h), saturated NH_4Cl aqueous solutionwas added. The organic layer was separated, and the aqueous layer was extracted twice with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo (without heated). The crude residue was purified by columnchromatography on silica gel to afford **1**.

(E)-1-(2-((2-(benzyloxy)phenyl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (1a)



Yield 52% red solid, m. p. 96-97 ºC, R_f = 0.4 (EtOAc /petroleum ether = 1/20); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{27}H_{19}BrN_2NaO$ $(M+Na)^+$ 489.0573, Found 489.0565.

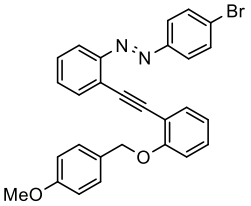
(E)-1-(4-bromophenyl)-2-(2-((2-((4-methylbenzyl)oxy)phenyl)ethynyl)phenyl)diazene (1b)



Yield 40%, red solid, m. p. 113-114 ºC, R_f = 0.5 (EtOAc/petroleum ether = 1/40); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.69 (m, 2H), 7.62 (ddd, *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 –

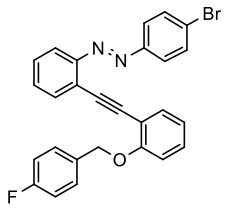
7.25 (m, 2H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.19 – 7.10 (m, 1H), 6.97 (d, *J* = 7.7 Hz, 2H), 6.90 – 6.78 (m, 2H), 5.07 (s, 2H), 2.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 152.7, 151.6, 137.4, 134.0, 133.64, 133.60, 132.2, 130.9, 130.0, 129.2, 128.7, 126.7, 125.6, 124.8, 124.7, 121.0, 115.9, 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 $C_{28}H_{22}BrN_2O$ $(M+H)^+$ 481.0910, Found 481.0907.

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



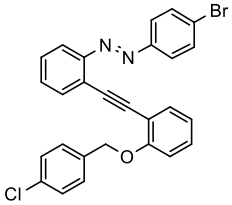
Yield 38%, red solid, m.p. 60-61 ^{o}C, R_f = 0.4 (DCM/petroleum ether = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.6 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.70 – 7.64 (m, 1H), 7.54 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 2H), 7.46 – 7.37 (m, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.29 – 7.23 (m, 1H), 6.98 – 6.89 (m, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 5.13 (s, 2H), 3.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 159.2, 152.6, 151.6, 133.62, 133.56, 132.3, 130.9, 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, 1612, 1587, 1572, 1513, 1463, 1493, 1444, 1227, 1241, 1033, 831; HRMS (ESI) Calcd for $C_{28}H_{22}BrN_2O_2$ $(M+H)^+$ 497.0859, Found 497.0855.

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



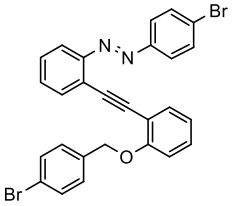
Yield 45%, red solid, m. p. 100-101 ^{o}C, R_f = 0.5 (DCM/petroleum ether = 1/10); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.30 (m, 4H), 7.19 (q, *J* = 7.3, 6.8 Hz, 1H), 6.92 – 6.83 (m, 4H), 5.06 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) 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; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.6; IR (KBr, cm^{-1}) 3060, 2955, 2853, 2215, 1604, 1573, 1510, 1494, 1447, 1278, 1225, 832, 749; HRMS (ESI) Calcd for $C_{27}H_{19}BrFN_2O$ $(M+H)^+$ 485.0659, Found 485.0663.

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



Yield 50%, red solid, m. p. 113-114 ^{o}C, R_f = 0.5 (DCM/petroleum ether = 1/5); ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{27}H1_8BrClN_2NaO$ $(M+Na)^+$ 523.0183, Found 523.0185.

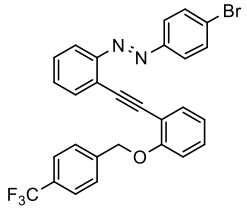
(E)-1-(2-((2-((4-bromobenzyl)oxy)phenyl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (1f)



Yield 50%, red solid, m. p. 122-123 ^{o}C, R_f = 0.5 (DCM/petroleum ether = 1/5); ^{1}H NMR (500 MHz, $CDCl_3$) 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

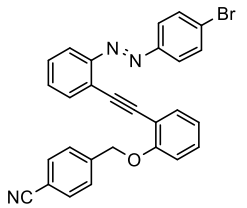
(m, 2H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 5.12 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 152.7, 151.5, 136.0, 133.6, 133.5, 132.2, 131.5, 130.9, 130.0, 128.8, 128.3, 125.6, 124.7, 124.5, 121.6, 121.3, 116.0, 113.6, 113.2, 92.3, 91.1, 69.9; IR (KBr, cm^{-1}) 3006, 2918, 2851, 2220, 1572, 1408, 1275, 1260, 833, 763, 750; HRMS (ESI) Calcd for $C_{27}H_{18}Br_2N_2NaO$ $(M+Na)^+$ 566.9678, Found 544.9855.

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



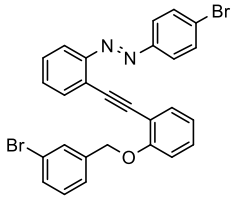
Yield 41%, red solid, m. p. 147-148 °C, R_f = 0.5 (DCM/petroleum ether = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.69 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.51 – 7.34 (m, 6H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 5.23 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) 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; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5**;** IR (KBr, cm^{-1}) 2926, 2217, 1573, 1469, 1445, 1421, 1325, 1280, 1164, 1115, 1066, 822, 762; HRMS (ESI) Calcd for $C_{28}H_{19}BrF_3N_2O$ $(M+H)^+$ 535.0627, Found 535.0625.

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



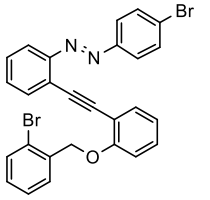
Yield 39%, red solid, m. p. 235-236 °C, R_f = 0.8 (DCM/petroleum ether = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.73 (m, 3H), 7.70 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.58 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.39 (m, 6H), 7.31 (td, *J* = 7.9, 1.8 Hz, 1H), 7.02 (td, *J* = 7.5, 1.0 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 5.21 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 152.7, 151.4, 142.3, 133.7, 133.4, 132.2, 131.0, 130.1, 129.0, 127.0, 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 $C_{28}H_{19}BrN_3O$ $(M+H)^+$ 492.0706, Found 492.0702.

(E)-1-(2-((2-((3-bromobenzyl)oxy)phenyl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (1i)



Yield 38%, red solid, m. p. 105-106 °C, R_f = 0.5 (DCM/petroleum ether = 1/10); ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{27}H_{19}Br_2N_2O$ $(M+H)^+$ 544.9859, Found 544.9852.

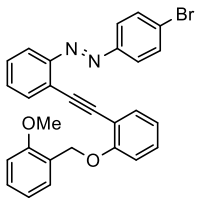
(E)-1-(2-((2-((2-bromobenzyl)oxy)phenyl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (1j)



Yield 45%, red solid, m. p. 115-116 °C, R_f = 0.4 (EtOAc/petroleum ether = 1/40); ^{1}H NMR (400 MHz, $CDCl_3$) 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

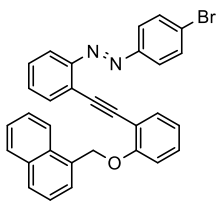
– 7.35 (m, 4H), 7.29 (td, *J* = 7.9, 1.7 Hz, 1H), 7.17 – 7.09 (m, 1H), 7.07 (dt, *J* = 7.6, 3.8 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 5.22 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1, 152.7, 151.5, 136.2, 133.6, 133.5, 132.3, 132.2, 130.9, 130.1, 128.9, 128.8, 128.3, 127.5, 125.7, 124.8, 124.6, 121.34, 121.25, 116.0, 113.4, 112.9, 92.4, 91.1, 69.8; IR (KBr, cm^{-1}) 3063, 2955, 2923, 2851, 2216, 1590, 1572, 1495, 1472, 1446, 1396, 1280, 1241, 1065, 1046, 1023, 749; HRMS (ESI) Calcd for $C_{27}H1_9Br_2N_2O$ $(M+H)^+$ 544.9859, Found 544.9855

(E)-1-(4-bromophenyl)-2-(2-((2-((2-methoxybenzyl)oxy)phenyl)ethynyl)phenyl)diazene (1k)



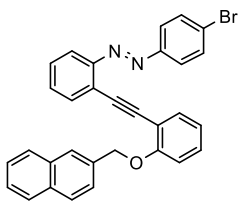
Yield 55%, red solid, m. p. 90-91 °C, R_f = 0.6 (EtOAc/petroleum ether = 1/20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 2H), 7.73 (ddd, *J* = 7.6, 4.5, 1.4 Hz, 2H), 7.57 (ddd, *J* = 9.8, 7.6, 1.7 Hz, 2H), 7.48 – 7.36 (m, 4H), 7.27 (td, *J* = 7.9, 1.7 Hz, 1H), 7.20 (td, *J* = 7.9, 1.7 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 2H), 6.88 – 6.79 (m, 2H), 5.25 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 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, 124.8, 120.7, 120.6, 115.9, 113.3, 112.9, 109.9, 92.7, 90.9, 65.6, 55.4; IR (KBr, cm^{-1}) 3059, 2959, 2928, 2857, 2216, 1734, 1590, 1573, 1495, 1278, 1244, 1048, 1031, 834, 740; HRMS (ESI) Calcd for $C_{28}H2_1BrN_2NaO_2$ $(M+Na)^+$ 519.0679, Found 519.0682.

(E)-1-(4-bromophenyl)-2-(2-((2-(naphthalen-1-ylmethoxy)phenyl)ethynyl)phenyl)diazene (1l)



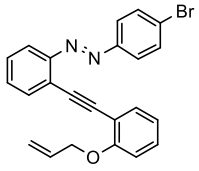
Yield 41%, red solid, m. p. 120-121 °C, R_f = 0.6 (DCM/petroleum ether = 1/10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 – 8.07 (m, 1H), 7.85 – 7.80 (m, 1H), 7.80 – 7.76 (m, 2H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.65 (d, *J* = 7.0 Hz, 1H), 7.56 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.46 – 7.38 (m, 4H), 7.38 – 7.30 (m, 3H), 7.27 (td, *J* = 7.8, 1.7 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 6.97 (t, J = 7.4 Hz, 1H), 5.63 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.5, 152.6, 151.5, 133.7, 133.61, 133.56, 132.2, 131.0, 130.8, 130.0, 128.71, 128.69, 128.6, 126.4, 125.8, 125.61, 125.59, 125.3, 124.7, 124.6, 123.5, 121.3, 115.9, 113.8, 113.6, 92.6, 91.2, 69.4; IR (KBr, cm^{-1}) 3059, 2924, 2215, 1590, 1573, 1494, 1478, 1446, 1278, 1265, 1234, 1065, 1006, 748; HRMS (ESI) Calcd for $C_{31}H_{22}BrN_2O$ $(M+H)^+$ 517.0910, Found 517.0901.

(E)-1-(4-bromophenyl)-2-(2-((2-(naphthalen-2-ylmethoxy)phenyl)ethynyl)phenyl)diazene (1m)



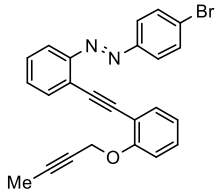
Yield 39%, red solid, m. p. 119-120 °C, R_f = 0.4 (DCM/petroleum ether = 1/5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.79 – 7.75 (m, 3H), 7.76 – 7.70 (m, 3H), 7.70 – 7.65 (m, 1H), 7.57 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.52 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.44 – 7.37 (m, 6H), 7.26 (td, *J* = 7.9, 1.8 Hz, 1H), 7.02 – 6.93 (m, 2H), 5.34 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 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; IR (KBr, cm^{-1}) 3057, 2924, 2853, 2215, 1590, 1573, 1494, 1479, 1446, 1278, 1239, 1148, 1007, 833, 814, 749; HRMS (ESI) Calcd for $C_{31}H_{22}BrN_2O$ $(M+H)^+$ 517.0910, Found 517.0908

(E)-1-(2-((2-(allyloxy)phenyl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (1n)



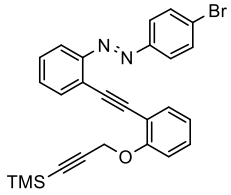
Yield 40%, red solid, m. p. 70-71 °C, R_f = 0.4 (EtOAc/petroleum ether = 1/20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.86 (m, 2H), 7.72 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.54 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.44 (td, *J* = 7.4, 1.5 Hz, 1H), 7.38 (td, *J* = 7.6, 1.6 Hz, 1H), 7.28 (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); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{23}H1_8BrN_2O$ $(M+H)^+$ 417.0597, Found 417.0602.

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



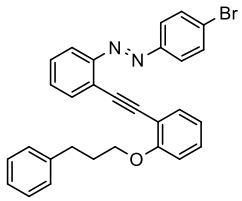
Yield 43%, red solid m. p. 60-61 °C; R_f = 0.4 (EtOAc/petroleum ether = 1/20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.90 (m, 2H), 7.73 (ddd, *J* = 7.7, 4.0, 1.4 Hz, 2H), 7.71 – 7.65 (m, 2H), 7.55 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.43 (td, *J* = 7.4, 1.4 Hz, 1H), 7.38 (td, *J* = 7.7, 1.6 Hz, 1H), 7.35 – 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 (t, *J* = 2.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{24}H1_7BrN_2NaO$ $(M+Na)^+$ 451.0416, Found 451.0408.

(E)-1-(4-bromophenyl)-2-(2-((2-((3-(trimethylsilyl)prop-2-yn-1-yl)oxy)phenyl)ethynyl)phenyl)-diazene (1p)



Yield 39%, red oil, R_f = 0.4 (EtOAc/petroleum ether = 1/20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.5 Hz, 2H), 7.61 – 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{26}H_{23}BrN_2OSi$ $(M+H)^+$ 487.0836, Found 487.0831.

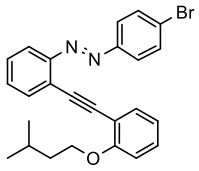
(E)-1-(4-bromophenyl)-2-(2-((2-(3-phenylpropoxy)phenyl)ethynyl)phenyl)diazene (1q)



Yield 58%, red solid, m. p. 110-111 °C, R_f = 0.6 (EtOAc/petroleum ether = 1/40); ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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,

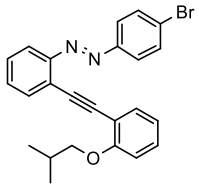
2215, 1589, 1573, 1494, 1277, 1241, 832, 739; HRMS (ESI) Calcd for $C_{29}H_{24}BrN_2O$ $(M+H)^+$ 495.1067, Found 495.1065.

(E)-1-(4-bromophenyl)-2-(2-((2-(isopentyloxy)phenyl)ethynyl)phenyl)diazene (1r)



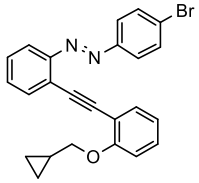
Yield 72%, red solid, m. p. 70-71 °C, R_f = 0.6 (petroleum ether); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.82 (m, 2H), 7.75 – 7.67 (m, 2H), 7.67 – 7.60 (m, 2H), 7.52 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.47 – 7.33 (m, 2H), 7.29 (td, *J* = 7.9, 1.8 Hz, 1H), 6.97 – 6.87 (m, 2H), 4.07 (t, *J* = 6.7 Hz, 2H), 1.91 – 1.78 (m, 1H), 1.67 (dd, *J* = 6.7, 6.3 Hz, 2H), 0.91 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{25}H_{23}BrN_2NaO$ $(M+Na)^+$ 469.0886, Found 469.0880.

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



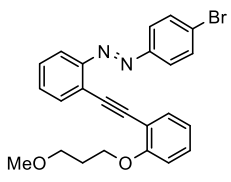
Yield 50%, red solid, m. p. 65-66 °C, R_f = 0.5 (EtOAc/petroleum ether = 1/50); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.74 – 7.68 (m, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.51 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.45 (td, *J* = 7.5, 1.3 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.33 – 7.27 (m, 1H), 6.97 – 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{24}H_{22}BrN_2O$ $(M+H)^+$ 433.0910, Found 433.0911.

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



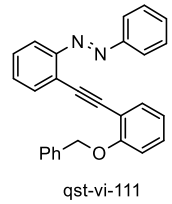
Yield 52%, red solid, m. p. 69-70 °C, R_f = 0.4 (EtOAc/petroleum ether = 1/50); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.84 (m, 2H), 7.76 – 7.68 (m, 2H), 7.65 – 7.60 (m, 2H), 7.52 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.40 – 7.34 (m, 1H), 7.27 (t, *J* = 7.8 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 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); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 152.7, 151.7, 133.63, 133.57, 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, 1480, 1446, 1279, 1241, 1108, 1022, 1007, 834, 750; HRMS (ESI) Calcd for $C_{24}H_{20}BrN_2O$ $(M+H)^+$ 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, R_f = 0.6 (EtOAc/petroleum ether = 1/20); ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{24}H_{22}BrN_2O_2$ $(M+H)^+$ 449.0859, Found 449.0862.

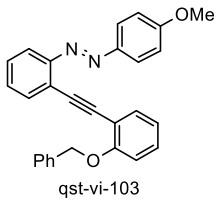
(E)-1-(2-((2-(benzyloxy)phenyl)ethynyl)phenyl)-2-phenyldiazene (1v)



qst-vi-111

Yield 42%, red solid, m. p. 110-111 °C, R_f = 0.6 (EtOAc/petroleum ether = 1/40); ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 153.0, 152.9, 137.1, 133.63, 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 $C_{27}H_{21}N_2O$ $(M+H)^+$ 389.1649, Found 389.1643.

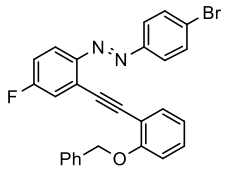
(E)-1-(2-((2-(benzyloxy)phenyl)ethynyl)phenyl)-2-(4-methoxyphenyl)diazene (1w)



qst-vi-103

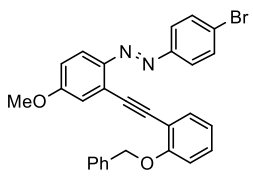
Yield 49%, red oil, R_f = 0.4 (DCM/petroleum ether = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.01 (m, 2H), 7.82 – 7.76 (m, 1H), 7.76 – 7.72 (m, 1H), 7.64 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.48 – 7.40 (m, 2H), 7.39 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 7.01 (td, *J* = 7.5, 0.8 Hz, 1H), 6.97 – 6.89 (m, 3H), 5.29 (s, 2H), 3.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 159.4, 153.1, 147.4, 137.2, 133.6, 133.5, 129.9, 129.8, 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 $C_{28}H_{23}N_2O_2$ $(M+H)^+$ 419.1754, Found 419.1749.

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



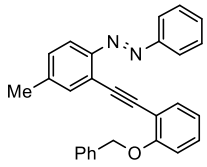
Yield 41%, red solid, m. p. 110-111 °C, R_f = 0.6 (DCM/petroleum ether = 1/5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.78 (dd, *J* = 9.1, 5.6 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.51 – 7.42 (m, 4H), 7.36 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.33 – 7.25 (m, 4H), 7.09 (td, *J* = 8.4, 2.8 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 5.22 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) 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; ^{19}F NMR (471 MHz, $CDCl_3$) δ -109.4; IR (KBr, cm^{-1}) 3744, 3153, 2199, 1574, 1510, 1279, 1174, 1132, 803, 689; HRMS (ESI) Calcd for $C_{27}H_{19}BrFN_2O$ $(M+H)^+$ 485.0659, Found 485.0654.

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



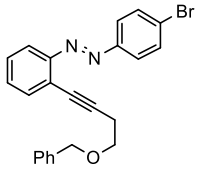
Yield 45%, red solid, m. p. 80-81 °C, R_f = 0.4 (DCM/petroleum ether = 1/5); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (t, *J* = 8.3 Hz, 3H), 7.62 – 7.54 (m, 1H), 7.47 (d, *J* = 8.0 Hz, 4H), 7.29 (t, *J* = 7.3 Hz, 3H), 7.25 – 7.21 (m, 1H), 7.16 (d, *J* = 2.9 Hz, 1H), 7.02 – 6.91 (m, 3H), 5.23 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{28}H_{22}BrN_2O_2$ $(M+H)^+$ 497.0859, Found 497.0863.

(E)-1-(2-((2-(benzyloxy)phenyl)ethynyl)-4-methylphenyl)-2-phenyldiazene (1z)



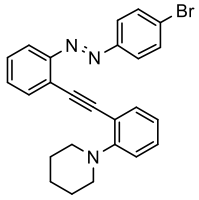
Yield 64%, red solid, m. p. 80-81 °C, R_f = 0.5 (EtOAc/petroleum ether = 1/20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.01 (m, 2H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 9.6 Hz, 3H), 7.44 (s, 2H), 7.39 – 7.15 (m, 6H), 7.04 – 6.94 (m, 2H), 5.28 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 152.9, 150.9, 141.1, 137.2, 133.9, 133.6, 130.9, 129.78, 129.76, 129.0, 128.5, 127.7, 126.8, 124.5, 123.3, 121.0, 115.8, 113.8, 113.2, 91.9, 91.4, 70.5, 21.3; IR (KBr, cm^{-1}) 3062, 3032, 2920, 2207, 1594, 1495, 1445, 1278, 1242, 1226, 769, 688; HRMS (ESI) Calcd for $C_{28}H2_3N_2O$ $(M+H)^+$ 403.1805, Found 403.1798.

(E)-1-(2-(4-(benzyloxy)but-1-yn-1-yl)phenyl)-2-(4-bromophenyl)diazene (1aa)



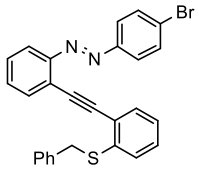
Yield 50%, red solid, m. p. 60-61 °C, R_f = 0.6 (EtOAc/petroleum ether = 1/40); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.66 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.57 (td, *J* = 5.7, 3.0 Hz, 3H), 7.39 – 7.25 (m, 7H), 4.59 (s, 2H), 3.72 (t, *J* = 7.0 Hz, 2H), 2.83 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 151.6, 138.1, 133.7, 132.3, 130.9, 128.49, 128.45, 127.8, 127.7, 125.7, 124.7, 124.5, 115.9, 93.8, 78.7, 73.1, 68.5, 21.4; IR (KBr, cm^{-1}) 3063, 3030, 2925, 2860, 2230, 1733, 1584, 1573, 1495, 1480, 1454, 1362, 1101, 1065, 763,743; HRMS (ESI) Calcd for $C_{23}H_{20}BrN_2O$ $(M+H)^+$ 419.0754, Found 419.0759.

(E)-1-(2-((2-((4-bromophenyl)diazenyl)phenyl)ethynyl)phenyl)piperidine (1ab)



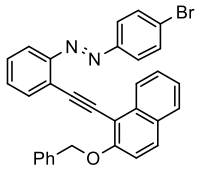
Yield 36%, red oil, R_f = 0.5 (DCM/petroleum ether = 1/10); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.6 Hz, 2H), 7.75 – 7.67 (m, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.55 – 7.49 (m, 1H), 7.46 – 7.41 (m, 1H), 7.41 – 7.35 (m, 1H), 7.29 – 7.25 (m, 1H), 6.94 (d, *J* = 7.7 Hz, 2H), 3.22 – 3.16 (m, 4H), 1.71 – 1.62 (m, 4H), 1.53 – 1.44 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 152.7, 151.6, 134.0, 133.4, 132.4, 130.9, 129.7, 128.6, 125.7, 124.8, 121.1, 117.9, 116.7, 116.1, 95.1, 91.7, 52.9, 26.3, 24.3; IR (KBr, cm^{-1}) 3064, 2928, 2851, 2805, 2209, 1572, 1559, 1540, 1457, 1382, 1275, 909, 833, 749; HRMS (ESI) Calcd for $C_{25}H_{23}BrN_3$ $(M+H)^+$ 444.1069, Found 444.1059.

(E)-1-(2-((2-(benzylthio)phenyl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (1ac)



Yield 30%, red solid, m. p. 88-89 °C, R_f = 0.35 (EtOAc/petroleum ether = 1/20); ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{27}H_{20}BrN_2S$ $(M+H)^+$ 483.0525, Found 483.0516.

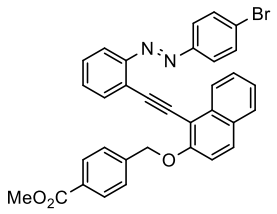
(E)-1-(2-((2-(benzyloxy)naphthalen-1-yl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (3a)



Yield 72%, red solid, m. p. 125-126 °C, R_f = 0.6 (DCM/petroleum ether = 1/2); ^{1}H NMR (500 MHz, $CDCl_3$) 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

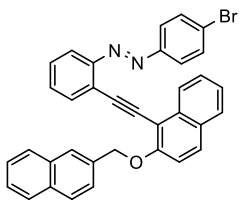
(s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.5, 152.8, 151.7, 137.2, 134.8, 133.5, 132.3, 131.0, 130.4, 128.9, 128.7, 128.6, 128.1, 127.9, 127.4, 127.0, 125.9, 125.7, 125.01, 124.99, 124.6, 116.0, 115.2, 107.9, 96.7, 91.0, 71.6; IR (KBr, cm^{-1}) 3053, 2193, 1592, 1451, 1269, 1147, 1071, 801, 749, 694; HRMS (ESI) Calcd for $C_{31}H_{22}BrN_2O$ $(M+H)^+$ 517.0910, Found 517.0901.

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



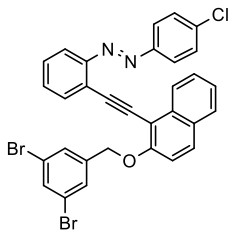
Yield 48%, red solid, m. p. 144-145 °C, R_f = 0.6 (DCM/petroleum ether = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 – 8.40 (m, 1H), 8.03 – 7.96 (m, 2H), 7.92 – 7.84 (m, 2H), 7.81 – 7.73 (m, 4H), 7.60 (d, J = 8.1 Hz, 2H), 7.57 – 7.51 (m, 2H), 7.48 (td, J = 7.5, 1.4 Hz, 1H), 7.46 – 7.36 (m, 3H), 7.21 (d, J = 9.1 Hz, 1H), 5.37 (s, 2H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 158.0, 152.8, 151.6, 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 $C_{33}H_{23}BrN_2NaO_3$ $(M+Na)^+$ 597.0784, Found 597.0781.

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



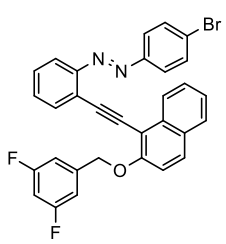
Yield 52%, red solid, m. p. 134-135 °C, R_f = 0.3 (DCM/petroleum ether = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 – 8.42 (m, 1H), 7.99 (s, 1H), 7.91 – 7.85 (m, 2H), 7.84 – 7.73 (m, 7H), 7.63 (dd, J = 8.5, 1.8 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.48 – 7.38 (m, 6H), 7.30 (d, J = 9.0 Hz, 1H), 5.51 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 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, 125.6, 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 $C_{35}H_{24}BrN_2O$ $(M+H)^+$ 567.1067, Found 567.1074.

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



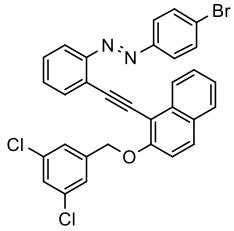
Yield 50%, red solid, m. p. 161-162 °C, R_f = 0.6 (DCM/petroleum ether = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 – 8.44 (m, 1H), 8.01 – 7.96 (m, 2H), 7.90 – 7.79 (m, 4H), 7.69 (s, 2H), 7.59 (s, 1H), 7.55 – 7.49 (m, 1H), 7.49 – 7.40 (m, 5H), 7.27 (s, 1H), 5.29 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 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 $C_{31}H_{20}Br_2ClN_2O$ $(M+H)^+$ 628.9626, Found 628.9619.

(E)-1-(4-bromophenyl)-2-(2-((2-((3,5-difluorobenzyl)oxy)naphthalen-1-yl)ethynyl)phenyl)diazene (3e)



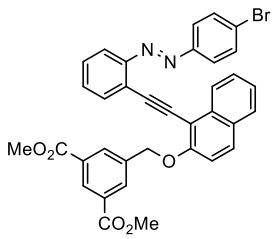
Yield 55%, red solid, m. p. 146-147 °C, R_f = 0.3 (DCM/petroleum ether = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, J = 7.5 Hz, 1H), 7.91 (d, J = 8.3 Hz, 2H), 7.88 – 7.74 (m, 5H), 7.59 (d, J = 8.3 Hz, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.13 (d, J = 7.0 Hz, 2H), 6.73 (t, J = 8.8 Hz, 1H), 5.33 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) 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, 132.3, 131.1, 130.5, 129.1, 128.9, 128.1, 127.5, 125.9, 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; ^{19}F NMR (471 MHz, $CDCl_3$) δ -109.3; IR (KBr, cm^{-1}) 3780, 3545, 1595, 1439, 1268, 1113, 755, 540; HRMS (ESI) Calcd for $C_{31}H_{20}BrF_2N_2O$ $(M+H)^+$ 553.0722, Found 553.0713.

(E)-1-(4-bromophenyl)-2-(2-((2-((3,5-dichlorobenzyl)oxy)naphthalen-1-yl)ethynyl)phenyl)diazene (3f)



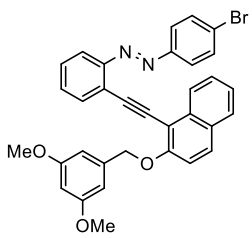
Yield 66%, red solid, m. p. 158-159 °C, R_f = 0.4 DCM/petroleum ether = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 – 8.43 (m, 1H), 7.91 (d, J = 8.6 Hz, 2H), 7.89 – 7.78 (m, 4H), 7.60 (d, J = 8.6 Hz, 2H), 7.55 – 7.47 (m, 3H), 7.47 – 7.40 (m, 3H), 7.30 – 7.26 (m, 2H), 5.29 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 152.8, 151.6, 140.6, 135.2, 134.7, 133.5, 132.3, 131.1, 130.5, 129.1, 128.9, 128.1, 128.0, 127.5, 125.9, 125.7, 125.2, 124.94, 124.90, 124.6, 116.1, 114.8, 108.3, 97.0, 90.4, 70.2; IR (KBr, cm^{-1}) 3077, 1574, 1497, 1475, 1267, 1236, 1146, 835, 790, 745, 696, 631; HRMS (ESI) Calcd for $C_{31}H_{19}BrCl_2N_2NaO$ $(M+Na)^+$ 606.9950, Found 606.9953.

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



Yield 68%, red solid, m. p. 140-141 °C, R_f = 0.6 (DCM/EtOAc /petroleum ether = 40/1/40); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.48 – 8.43 (m, 1H), 8.39 (s, 2H), 7.87 – 7.75 (m, 6H), 7.52 (d, 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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, 124.8, 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 $C_{35}H_{26}BrN_2O_5$ $(M+H)^+$ 633.1020, Found 633.1028.

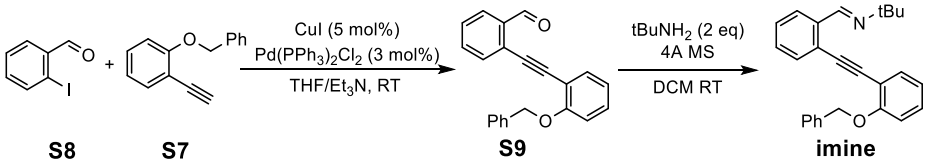
(E)-1-(4-bromophenyl)-2-(2-((2-((3,5-dimethoxybenzyl)oxy)naphthalen-1-yl)ethynyl)phenyl)diazene (3h)



Yield 45% red solid, m. p. 70-71 °C, R_f = 0.6 (DCM/petroleum ether = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) 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 (td, 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); ^{13}C

NMR (101 MHz, $CDCl_3$) 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, 125.7, 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, 1064, 1012, 824, 755; HRMS (ESI) Calcd for $C_{33}H_{25}BrN_2NaO_3$ $(M+Na)^+$ 599.0941, Found 599.0943.

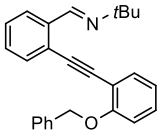
Procedure for preparation of azaenyene (imine)



In a Schlenk tube with a magnetic bar under nitrogen atmosphere, **S8** (1.0 eq.), **S7** (1.1 eq), CuI (5 mol%), $Pd(PPh_3)_2Cl_2$ (3 mol%) were added, and Et_3N (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.**

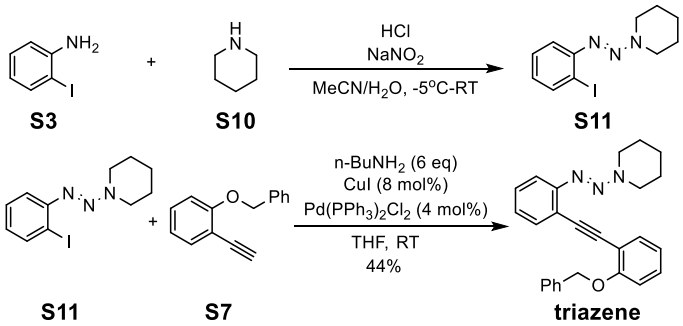
In a Schlenk tube with a magnetic bar under nitrogen atmosphere, 4 Å MS (100 mg) was activated by heat gun. After cooling the tube to room temperature, **S9** (1 eq), $tBuNH_2$ (2 eq), dry DCM (0.25 M) were added. The mixtures were stirred at room temperature until the starting material was comsumed. After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, and the residue was used as substrate directly.

(E)-1-(2-((2-(benzyloxy)phenyl)ethynyl)phenyl)-N-(tert-butyl)methanimine



Yield 80%, light yellow oil, R_f = 0.7 (EtOAc/petroleum ether = 1/20); ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{26}H_{26}NO$ $(M+H)^+$ 368.2009, Found 368.2011.

Procedure for preparation of azaenyene (triazene)

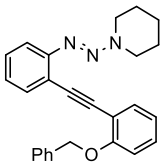


The *o*-iodoaniline **S3** (23 mmol, 1.0 eq.) was dissolved in a 2:1 mixture of acetonitrile–water (30 mL) and cooled to 0 °C. Concentrated aqueous HCl (7.6 mL, 91 mmol, 4.0 eq.) was added dropwise. The

reaction mixture was further cooled to −5 °C and aqueous solution of $NaNO_2$ (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 a2:1 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 Na_2SO_4, 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**.

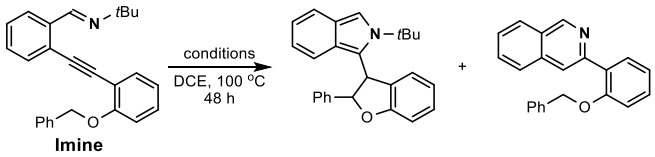
Ortho-iodo triazene substrate **S11** (1.0 eq), $Pd(PPh_3)_2Cl_2$ (0.04 equiv), CuI (0.08 equiv) and $nBuNH_2$ (6.0 mmol, 6.0 equiv) were dissolved in anhydrous THF (0.1 M) under N_2 atmosphere. To the resulting solution terminal alkyne **S7** (1.2 equiv) was added dropwise. The mixture was stirred at room temperature. After the reaction was completed (detected by TLC), saturated NH_4Cl aqueous solutionwas added. The organic layer was separated, and the aqueous layer was extracted twice with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude residue was purified by columnchromatography on silica gel to afford desired triazene product.

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



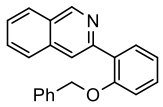
Yield 44%, white solid, m. p. 96-97 °C, R_f = 0.35 (EtOAc/petroleum ether = 1/20); ^1H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.42 (m, 5H), 7.32 (t, J = 7.4 Hz, 2H), 7.26 (t, J = 7.9 Hz, 2H), 7.22 – 7.17 (m, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.95 – 6.86 (m, 2H), 5.20 (s, 2H), 3.79 (s, 4H), 1.61 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{26}H_{26}N_3O$ $(M+H)^+$ 396.2071, Found 396.2075.

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

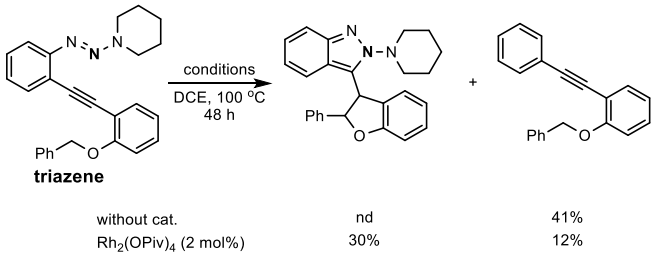


In a Schlenk tube with a magnetic bar under nitrogen atmosphere, imine (0.2 mmol, 73 mg), DCE (0.1 M, 2 ml) were added with or without $Rh_2(OAc)_4$ (2 mol%, 2.64 mg). The mixtures were stirred at 100 °C for 48 h. After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, 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

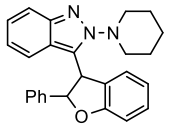


Yield 39%, white solid, m. p. 80-81 °C, R_f = 0.5 (EtOAc/petroleum ether = 1/10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.37 (s, 1H), 8.35 (s, 1H), 8.05 – 7.95 (m, 2H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.67 (t, *J* = 7.3 Hz, 1H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.41 (d, *J* = 7.3 Hz, 2H), 7.39 – 7.27 (m, 4H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 8.2 Hz, 1H), 5.19 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{22}H_{18}NO$ $(M+H)^+$ 312.1383, Found 312.1380.



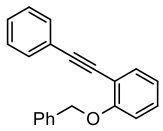
In a Schlenk tube with a magnetic bar under nitrogen atmosphere, triazene (0.2 mmol, 79 mg), DCE (0.1 M, 2 ml) were added with or without $Rh_2(OAc)_4$ (2 mol%, 2.64 mg). The mixtures were stirred at 100 °C for 48 h. After rapid filtration of silica gel, the solvent was evaporated by rotary evaporator, 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

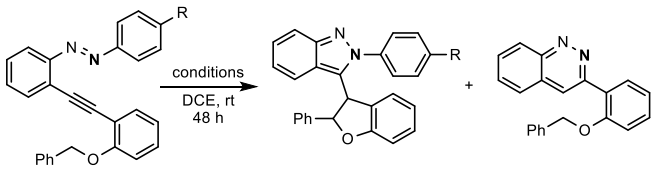


Yield 30%, white solid, m. p. 142-143 °C, R_f = 0.5 (EtOAc/petroleum ether = 1/20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.7 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.15 – 7.00 (m, 8H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.78 – 6.71 (m, 1H), 6.39 (d, *J* = 7.4 Hz, 1H), 6.01 (d, *J* = 8.1 Hz, 1H), 5.58 (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); ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{26}H2_6N_3O$ $(M+H)^+$ 396.2071, Found 396.2070.

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



Yield 41%, light yellow oil, R_f = 0.8 (EtOAc/petroleum ether = 1/20); ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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.

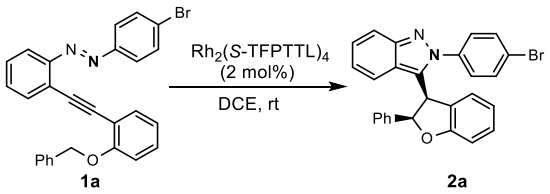


diazene

R = H, without cat.	10%	nd
R = OMe, without cat.	20%	nd
R = Br, without cat.	trace	nd
R = Br, $Rh_2(OPiv)_4$ (2 mol%)	90%	nd

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

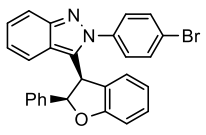


1a **2a**

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).

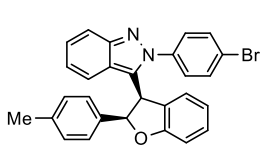
The procedures of other substrates **1**, were similar with that mentioned above.

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



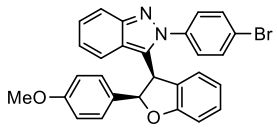
Yield 98%, > 99:1 dr, pale solid, m. p. 145-146 °C, R_f = 0.4 (EtOAc/petroleum ether = 1/10); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.8 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.12 – 7.06 (m, 2H), 7.01 (t, *J* = 7.6 Hz, 2H), 6.94 – 6.89 (m, 5H), 6.76 (d, *J* = 7.6 Hz, 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, $CDCl_3$) δ 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 $C_{27}H_{19}BrN_2NaO$ $(M+Na)^+$ 489.0573, Found 489.0579; HPLC: INA 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_2Cl_2).

2-(4-bromophenyl)-3-((2R,3R)-2-(p-tolyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2b)



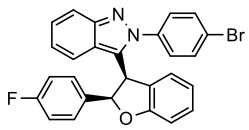
Yield 87%, > 99:1 dr, pale solid, m. p. 160-161 °C, R_f = 0.4 (EtOAc/petroleum ether = 1/10); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.7 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.11 – 7.07 (m, 2H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.95 – 6.82 (m, 3H), 6.79 – 6.69 (m, 3H), 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); ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{28}H_{22}BrN_2O$ $(M+H)^+$ 481.0910, Found 481.0906; HPLC: WHELK column, 90:10 hexanes:isopropanol, 0.80 mL/min, t_R = major: 20.1 min, minor: 18.1 min, 98:2 er; $[\alpha]_D^{24}$ 65.8° (c 0.29, CH_2Cl_2).

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



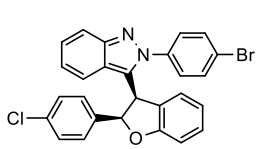
Yield 97%, > 99:1 dr, pale solid, m. p. 152-153 °C, R_f = 0.4 (EtOAc/petroleum ether = 1/8); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.9 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.1 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 1H), 7.02 – 6.89 (m, 3H), 6.82 – 6.75 (m, 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); ^{13}C NMR (101 MHz, $CDCl_3$) 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, 1380, 1302, 1252, 1175, 1013, 831, 750; HRMS (ESI) Calcd for $C_{28}H_{22}BrN_2O_2$ $(M+H)^+$ 497.0859, Found 497.0849; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 23.3 min, minor: 25.1 min, 97:3 er; $[\alpha]_D^{24}$ 34.8° (c 0.17, CH_2Cl_2).

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



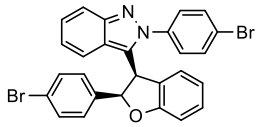
Yield 88%, > 99:1 dr, pale solid, m. p. 174-175 °C, R_f = 0.4 (EtOAc/petroleum ether = 1/10); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.13 – 7.07 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.98 – 6.87 (m, 3H), 6.75 – 6.70 (m, 3H), 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); ^{13}C NMR (101 MHz, $CDCl_3$) 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; ^{19}F NMR (376 MHz, $CDCl_3$) 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 $C_{27}H_{18}BrFN_2NaO$ $(M+Na)^+$ 507.0479, Found 507.0476; HPLC: WHELK column, 90:10 hexanes:isopropanol, 0.80 mL/min, t_R = major: 18.4 min, minor: 17.4 min, 99:1 er; $[\alpha]_D^{24}$ 60.8° (c 0.26, CH_2Cl_2).

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, R_f = 0.5 (DCM/petroleum ether = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{27}H_{19}BrClN_2O$ $(M+H)^+$ 501.0364 , Found 501.0366; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 17.8 min, minor: 20.1 min, > 99:1 er; $[\alpha]_D^{24}$ 32.4° (c 0.056, CH_2Cl_2).

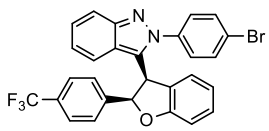
2-(4-bromophenyl)-3-((2R,3R)-2-(4-bromophenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2f)



Yield 96%, > 99:1 dr, pale solid, m. p. 193-194 °C, R_f = 0.5 (DCM/petroleum ether = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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, 1624, 1597, 1515, 1494, 1462, 1407, 1380, 1264, 1233, 1070, 1012, 831, 736; HRMS (ESI) Calcd for $C_{27}H_{19}Br_2N_2O$ $(M+H)^+$ 544.9859, Found 544.9853; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 17.9 min, minor: 21.2 min, > 99:1 er; $[\alpha]_D^{24}$ 6.0° (c 0.18, CH_2Cl_2).

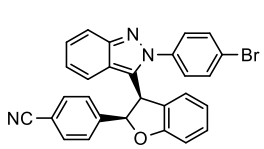
2-(4-bromophenyl)-3-((2R,3R)-2-(4-(trifluoromethyl)phenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2g)

Yield 95%, > 99:1 dr, pale solid, m. p. 180-181 °C, R_f = 0.45 (DCM/petroleum ether = 1/2); ^{1}H NMR



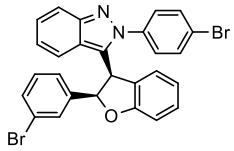
(400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 1H), 7.25 – 7.18 (m, 3H), 7.17 – 7.11 (m, 2H), 7.10 – 6.98 (m, 3H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.76 (t, *J* = 7.7 Hz, 1H), 6.42 (d, *J* = 8.7 Hz, 1H), 5.82 (d, *J* = 8.7 Hz, 1H), 5.41 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) 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; ^{19}F NMR (376 MHz, $CDCl_3$) 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 $C_{28}H_{19}BrF_3N_2O$ $(M+H)^+$ 535.0627, Found 535.0629; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 12.9 min, minor: 15.4 min, > 99:1 er; $[\alpha]_D^{24}$ 39.7° (c 0.35, CH_2Cl_2).

4-((2R,3R)-3-(2-(4-bromophenyl)-2H-indazol-3-yl)-2,3-dihydrobenzofuran-2-yl)benzonitrile (2h)



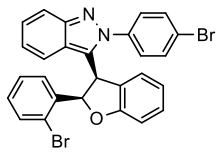
Yield 98%, > 99:1 dr, pale solid, m. p. 184-185 °C, R_f = 0.4 (EtOAc/petroleum ether = 1/5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 7.8 Hz, 2H), 7.21 – 7.12 (m, 5H), 7.04 – 6.95 (m, 3H), 6.76 (t, *J* = 7.7 Hz, 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); ^{13}C NMR (101 MHz, $CDCl_3$) 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, 122.2, 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 $C_{28}H_{19}BrN_3O$ $(M+H)^+$ 492.0706, Found 492.0706; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 45.4 min, minor: 36.8 min, > 99:1 er; $[\alpha]_D^{24}$ 14.4° (c 0.027, CH_2Cl_2).

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



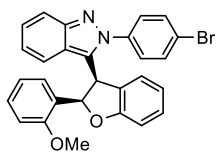
Yield 98%, > 99:1 dr, pale solid, m. p. 170-171 °C, R_f = 0.6 (EtOAc/petroleum ether = 1/10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.4 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.19 – 7.08 (m, 3H), 7.07 – 7.00 (m, 3H), 6.98 – 6.93 (m, 1H), 6.88 (s, 1H), 6.79 – 6.63 (m, 3H), 6.41 (d, *J* = 8.2 Hz, 1H), 5.66 (d, *J* = 8.4 Hz, 1H), 5.27 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{27}H_{19}Br_2N_2O$ $(M+H)^+$ 544.9859, Found 544.9855; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 18.4 min, minor: 22.3 min, 98:2 er; $[\alpha]_D^{24}$ 91.2° (c 0.38, CH_2Cl_2).

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



Yield 96%, 97:3 dr, pale solid, m. p. 188-189 °C, R_f = 0.6 (EtOAc/petroleum ether = 1/10); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{27}H_{19}Br_2N_2O$ $(M+H)^+$ 544.9859, Found 544.9857; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 11.9 min, minor: 17.6 min, 95:5 er; $[\alpha]_D^{24}$ 94.7° (c 0.10, CH_2Cl_2).

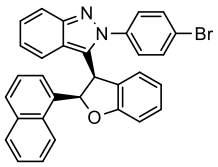
2-(4-bromophenyl)-3-((2R,3R)-2-(2-methoxyphenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2k)



Yield 83%, 98:2 dr, pale solid, m. p. 141-143 °C, R_f = 0.5 (EtOAc/petroleum ether = 1/10); ^{1}H NMR (500 MHz, $CDCl_3$) 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,

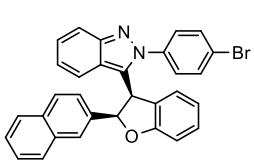
1H), 6.64 (q, *J* = 8.2 Hz, 2H), 6.44 (d, *J* = 8.2 Hz, 1H), 6.39 (d, *J* = 8.7 Hz, 1H), 6.26 (d, *J* = 8.5 Hz, 1H), 5.47 (d, *J* = 8.6 Hz, 1H), 3.30 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 155.6, 148.5, 138.9, 133.0, 132.3, 129.5, 129.1, 127.9, 127.4, 127.1, 126.4, 125.8, 124.9, 122.8, 121.6, 121.4, 121.2, 121.0, 120.3, 117.1, 110.1, 109.4, 83.2, 54.8, 45.0; IR (KBr, cm^{-1}) 3053, 2936, 2837, 1624, 1593, 1515, 1495, 1477, 1276, 1264, 1247, 833, 749; HRMS (ESI) Calcd for $C_{28}H_{22}BrN_2O_2$ $(M+H)^+$ 497.0859, Found 497.0860; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 16.4 min, minor: 12.9 min, 98:2 er; $[\alpha]_D^{24}$ 95.7° (c 0.3, CH_2Cl_2).

2-(4-bromophenyl)-3-((2R,3R)-2-(naphthalen-1-yl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2l)



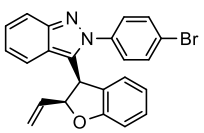
Yield 99%, > 99:1 dr, pale solid, m. p. 184-185 °C, R_f = 0.6 (EtOAc/petroleum ether = 1/10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.46 – 7.39 (m, 3H), 7.31 – 7.26 (m, 2H), 7.23 – 7.10 (m, 6H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.7 Hz, 1H), 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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, 126.4, 126.2, 125.3, 124.9, 124.4, 122.6, 122.2, 122.1, 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 $C_{31}H_{22}BrN_2O$ $(M+H)^+$ 517.0910, Found 517.0902; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 17.0 min, minor: 21.8 min, 99:1 er; $[\alpha]_D^{24}$ 167.2° (c 0.43, CH_2Cl_2).

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, R_f = 0.45 (DCM/petroleum ether = 1/2); ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3, 148.6, 138.4, 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, 126.2, 123.8, 123.2, 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 $C_{31}H2_2BrN_2O$ $(M+H)^+$ 517.0910, Found 517.0911; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 20.5 min, minor: 23.2 min, 98:2 er; $[\alpha]_D^{24}$ 54.0° (c 0.027, CH_2Cl_2).

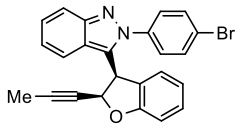
2-(4-bromophenyl)-3-((2S,3R)-2-vinyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2n)



Yield 80%, 97:3 dr, pale solid, m. p. 184-185 °C, R_f = 0.5 (EtOAc/petroleum ether = 1/10); ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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,

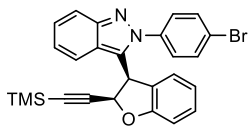
833; HRMS (ESI) Calcd for $C_{23}H_{18}BrN_2O$ $(M+H)^+$ 417.0597, Found 417.0595; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 13.8 min, minor: 16.3 min, 97:3 er; $[\alpha]_D^{24}$ 19.4° (c 0.28, CH_2Cl_2).

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



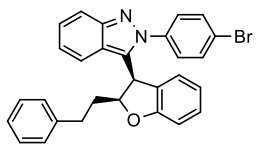
Yield 78%, > 99:1 dr, pale solid, m. p. 169-170 °C, R_f = 0.6 (EtOAc/petroleum ether = 1/10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.64 (m, 3H), 7.55 – 7.43 (m, 2H), 7.29 – 7.23 (m, 2H), 6.98 (d, *J* = 7.7 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 3H), 5.53 (d, *J* = 9.0 Hz, 1H), 5.14 (d, *J* = 9.2 Hz, 1H), 1.43 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 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, 121.3, 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 $C_{24}H_{18}BrN_2O$ $(M+H)^+$ 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_2Cl_2).

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



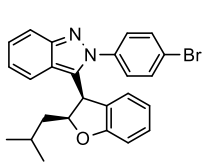
Yield 76%, > 99:1 dr, pale solid, m. p. 160-161 °C, R_f = 0.6 (EtOAc/petroleum ether = 1/10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.45 (m, 3H), 7.34 (d, *J* = 7.7 Hz, 2H), 7.13 – 7.08 (m, 1H), 7.07 – 7.02 (m, 1H), 6.82 (d, *J* = 7.3 Hz, 2H), 6.75 – 6.59 (m, 3H), 5.37 (d, *J* = 9.6 Hz, 1H), 5.06 – 4.94 (m, 1H), -0.45 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 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 $C_{26}H_{24}BrN_2OSi$ $(M+H)^+$ 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_2Cl_2).

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



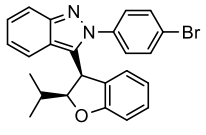
Yield 87%, 96:4 dr, pale solid, m. p. 175-176 °C, R_f = 0.5 (EtOAc/petroleum ether = 1/20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.7 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.25 (m, 3H), 7.24 – 7.13 (m, 4H), 7.04 – 6.95 (m, 4H), 6.94 – 6.81 (m, 3H), 5.00 (d, *J* = 9.2 Hz, 1H), 4.79 (td, *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, $CDCl_3$) δ 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 $C_{29}H_{24}BrN_2O$ $(M+H)^+$ 495.1067, Found 495.1064; 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_2Cl_2).

2-(4-bromophenyl)-3-((2S,3R)-2-isobutyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2r)



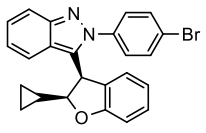
Yield 71%, 93:7 dr, pale solid, m. p. 110-111 °C, R_f = 0.6 (EtOAc/petroleum ether = 1/20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.62 (m, 3H), 7.43 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 7.4 Hz, 1H), 6.96 – 6.72 (m, 4H), 5.01 (d, *J* = 9.0 Hz, 1H), 4.93 (td, *J* = 9.5, 9.1, 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); ^{13}C NMR (101 MHz, $CDCl_3$) 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 $C_{25}H_{24}BrN_2O$ $(M+H)^+$ 447.1067, Found 447.1072; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 7.0 min, minor: 9.7 min, > 99:1 er; $[\alpha]_D^{24}$ 52.7° (c 0.22, CH_2Cl_2).

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



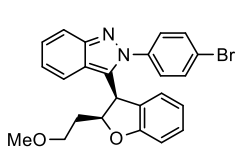
Yield 78%, 98:2 dr, pale solid, m. p. 200-201 °C, R_f = 0.6 (EtOAc/petroleum ether = 1/20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.6 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 1H), 7.54 – 7.46 (m, 2H), 7.27 (d, *J* = 8.7 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.07 (d, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{24}H_{22}BrN_2O$ $(M+H)^+$ 433.0910, Found 433.0908; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 7.9 min, minor: 19.7 min, > 99:1 er; $[\alpha]_D^{24}$ 169.0° (c 0.26, CH_2Cl_2).

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



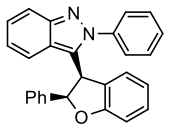
Yield 93%, 98:2 dr, pale solid, m. p. 166-167 °C, R_f = 0.6 (EtOAc/petroleum ether = 1/20); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.20 (m, 2H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.96 (dd, *J* = 10.7, 8.3 Hz, 2H), 6.90 – 6.82 (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); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{24}H_{20}BrN_2O$ $(M+H)^+$ 431.0754, Found 431.0750; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 11.3 min, minor: 17.0 min, 98:2 er; $[\alpha]_D^{24}$ 44.3° (c 0.34, CH_2Cl_2).

2-(4-bromophenyl)-3-((2S,3R)-2-(2-methoxyethyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2u)



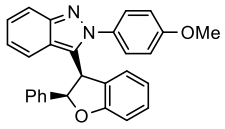
Yield 70%, 93:7 dr, pale solid, m. p. 78-79 °C, R_f = 0.4 (EtOAc/petroleum ether = 1/15); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 6.5 Hz, 2H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.91 – 6.81 (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); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{24}H_{22}BrN_2O_2$ $(M+H)^+$ 449.0859, Found 449.0854; HPLC: INC column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 6.9 min, minor: 6.6 min, 99:1 er; $[\alpha]_D^{24}$ 13.9° (c 0.24, CH_2Cl_2).

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



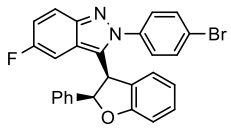
Yield 92%, > 99:1 dr, pale solid, m. p. 150-151 °C, R_f = 0.45 (EtOAc/petroleum ether = 1/10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 4H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.21 – 7.12 (m, 4H), 7.12 – 7.05 (m, 2H), 7.02 – 6.96 (m, 3H), 6.87 (d, *J* = 7.6 Hz, 2H), 6.76 (d, *J* = 7.4 Hz, 1H), 6.54 (d, *J* = 8.7 Hz, 1H), 5.79 (d, *J* = 8.7 Hz, 1H), 5.36 (d, *J* = 8.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) 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$C_{27}H_{21}N_2O$ $(M+H)^+$ 389.1649, Found 389.1649; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 15.4 min, minor: 12.0 min, 98:2 er; $[\alpha]_D^{24}$ 96.9° (c 0.15, CH_2Cl_2).

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, R_f = 0.5 (EtOAc/petroleum ether = 1/5); ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{28}H_{23}N_2O_2$ $(M+H)^+$ 419.1754, Found 419.1753; HPLC: INA column, 80:20 hexanes:isopropanol, 1.00 mL/min, t_R = major: 17.0 min, minor: 12.7 min, 96:4 er; $[\alpha]_D^{24}$ 76.9° (c 0.14, CH_2Cl_2).

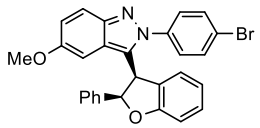
2-(4-bromophenyl)-5-fluoro-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2x)



Yield 80%, > 99:1 dr, pale solid, m. p. 171-172 °C, R_f = 0.6 (EtOAc/petroleum ether = 1/10); ^{1}H NMR (500 MHz, $CDCl_3$) 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,

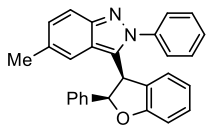
J = 7.4, 3.3 Hz, 2H), 7.02 (t, *J* = 7.3 Hz, 3H), 7.00 – 6.93 (m, 3H), 6.83 (d, *J* = 7.6 Hz, 2H), 6.02 (dd, *J* = 9.9, 2.4 Hz, 1H), 5.76 (d, *J* = 8.5 Hz, 1H), 5.26 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 157.9 (d, *J* = 240.6 Hz), 146.0, 138.2, 135.8, 133.3 (d, *J* = 8.7 Hz), 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 Hz), 119.6 (d, *J* = 9.7 Hz), 118.3 (d, *J* = 29.2 Hz), 110.5, 103.1 (d, *J* = 25.3 Hz), 88.0, 45.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ -118.8; IR (KBr, cm^{-1}) 3071, 2928, 1598, 1487, 1487, 1343, 1231, 1176, 1013, 837, 750; HRMS (ESI) Calcd for $C_{27}H_{19}BrFN_2O$ $(M+H)^+$ 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; $[\alpha]_D^{24}$ 61.8° (c 0.17, CH_2Cl_2).

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



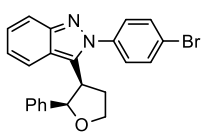
Yield 95%, > 99:1 dr, pale solid, m. p. 134-135 °C, R_f = 0.4 (EtOAc/petroleum ether = 1/10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 9.3 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 7.08 – 6.99 (m, 3H), 6.92 – 6.84 (m, 3H), 6.82 (d, *J* = 7.6 Hz, 2H), 5.74 (d, *J* = 8.3 Hz, 1H), 5.55 (s, 1H), 5.24 (d, *J* = 8.3 Hz, 1H), 3.46 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 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 $C_{28}H_{22}BrN_2O_2$ $(M+H)^+$ 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; $[\alpha]_D^{24}$ 54.7° (c 0.20, CH_2Cl_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 °C, R_f = 0.6 (EtOAc/petroleum ether = 1/10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 3H), 7.44 (d, *J* = 8.8 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 7.15 – 7.06 (m, 4H), 7.05 – 6.97 (m, 4H), 6.86 (d, *J* = 7.5 Hz, 2H), 6.18 (s, 1H), 5.76 (d, *J* = 8.6 Hz, 1H), 5.32 (d, *J* = 8.4 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 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 $C_{28}H_{23}N_2O$ $(M+H)^+$ 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; $[\alpha]_D^{24}$ 63.2° (c 0.15, CH_2Cl_2).

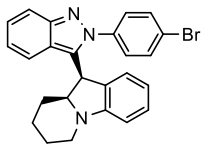
2-(4-bromophenyl)-3-((2R,3R)-2-phenyltetrahydrofuran-3-yl)-2H-indazole (2aa)



Yield 43%, > 99:1 dr, pale solid, m. p. 115-116 °C, R_f = 0.6 (EtOAc/petroleum ether = 1/15); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.38 (t, *J* = 7.1 Hz, 3H), 7.26 – 7.13 (m, 4H), 7.04 (d, *J* = 7.2 Hz, 2H), 6.58 (d, *J* = 8.2 Hz, 2H), 5.30 (d, *J* = 9.3 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); ^{13}C NMR (126 MHz, $CDCl_3$) δ 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,

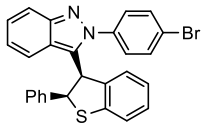
120.6, 117.5, 84.5, 67.5, 41.9, 32.0; IR (KBr, cm^{-1}) 3059, 2959, 2865, 1496, 1275, 1260, 1066, 1012, 836; HRMS (ESI) Calcd for $C_{23}H_{20}BrN_2O$ $(M+H)^+$ 419.0754, Found 419.0747; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 21.6 min, minor: 9.4 min, 90:10 er; $[\alpha]_D^{24}$ -10.9° (c 0.15, CH_2Cl_2).

(9aS,10S)-10-(2-(4-bromophenyl)-2H-indazol-3-yl)-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indole (2ab)



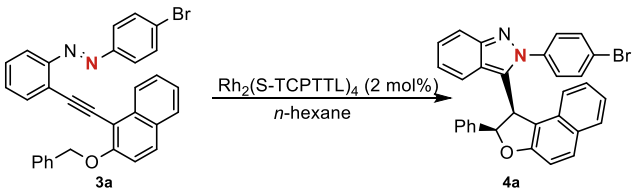
Yield 65%, 84:16 dr, pale solid, m. p. 218-225 °C, R_f = 0.4 (DCM/petroleum ether = 1/1); ^1H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.70 (m, 2H), 7.67 – 7.62 (m, 1H), 7.48 – 7.41 (m, 2H), 7.25 – 7.11 (m, 3H), 6.95 (d, J = 7.3 Hz, 1H), 6.89 – 6.80 (m, 1H), 6.70 – 6.54 (m, 2H), 4.77 (d, J = 7.8 Hz, 1H), 3.76 (d, J = 10.8 Hz, 1H), 3.42 (td, J = 8.7, 4.2 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); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.5, 149.3, 149.0, 139.0, 132.6, 132.5, 128.8, 128.6, 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}) 3683, 3305, 3053, 2937, 1654, 1609, 1488, 1361, 1147, 934, 733; HRMS (ESI) Calcd for$C_{25}H_{22}BrN_3Na$ $(M+Na)^+$ 466.0889, Found 466.0887; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 27.7 min, minor: 70.0 min, 93:7 er; $[\alpha]_D^{24}$ 98.7° (c 0.24, CH_2Cl_2).

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, R_f = 0.5 (EtOAc/petroleum ether = 1/10); ^1H NMR (500 MHz, $CDCl_3$) 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, 4H), 5.34 (d, J = 8.1 Hz, 1H), 5.17 (d, J = 8.1 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{27}H_{20}BrN_2S$ $(M+H)^+$ 483.0525, Found 483.0514; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 17.6 min, minor: 38.2 min, 81:19 er; $[\alpha]_D^{24}$ 27.0° (c 0.11, CH_2Cl_2).

3.5 General procedures for cycloisomerization of azaenyne 3

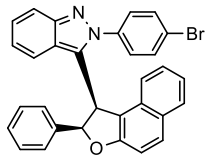


In a Schlenk tube with a magnetic bar under nitrogen atmosphere, **3a** (0.1 mmol, 51.7 mg), *n*-hexane (0.0035 M, 30 ml), Rh_2(*S*-TCPTTL)$_4$ (2 mol%, 3.9 mg) were added. The mixtures were stirred at room temperature until the starting material was consumed (TLC detected). After rapid filtration of 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).

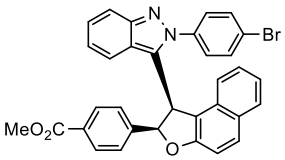
The procedures of other substrates **3**, were similar with that mentioned above.

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



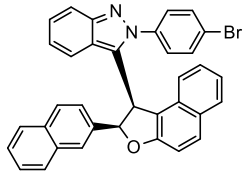
Yield 99%, > 99:1 dr, pale solid, m. p. 190-191 °C, R_f = 0.35 (DCM/petroleum ether = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, J = 8.8 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.60 – 7.54 (m, 2H), 7.41 (dd, J = 8.7, 1.1 Hz, 1H), 7.31 (d, J = 8.8 Hz, 1H), 7.28 – 7.19 (m, 3H), 7.14 – 7.07 (m, 1H), 7.05 – 6.95 (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); ^{13}C NMR (126 MHz, $CDCl_3$) 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, 1504, 1495, 1382, 1253, 1072, 1014, 958, 817, 732, 702; HRMS (ESI) Calcd for $C_{31}H_{22}BrN_2O$ $(M+H)^+$ 517.0910, Found 517.0902; HPLC: OD-H column, 70:30 hexanes:isopropanol, 0.80 mL/min, t_R = major: 10.7 min, minor: 16.0 min, 96:4 er; $[\alpha]_D^{24}$ 165.0° (c 0.067, CH_2Cl_2).

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, R_f = 0.5 (DCM/EtOAc/petroleum ether = 10/1/20); ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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, 1107, 1014, 965, 875, 817, 741; HRMS (ESI) Calcd for $C_{33}H_{24}BrN_2O_3$ $(M+H)^+$ 575.0965, Found 575.0955; HPLC: OD-H column, 80:20 hexanes:isopropanol, 1.00 mL/min, t_R = major: 20.8 min, minor: 10.8 min, 96:4 er; $[\alpha]_D^{24}$ 139.9° (c 0.15, CH_2Cl_2).

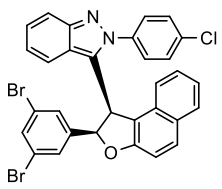
2-(4-bromophenyl)-3-((1R,2R)-2-(naphthalen-2-yl)-1,2-dihydronaphtho[2,1-b]furan-1-yl)-2H-indazole (4c)



Yield 82%, 92:8 dr, pale solid, m. p. 207-208 °C, R_f = 0.4 (EtOAc/petroleum ether = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (101 MHz, $CDCl_3$) 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, 126.50, 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,

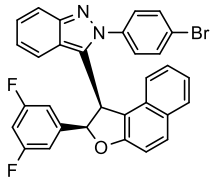
1628, 1591, 1501, 1379, 1251, 1070, 1015, 949, 808, 740; HRMS (ESI) Calcd for $C_{35}H2_3BrN_2NaO$ $(M+Na)^+$ 589.0886, Found 589.0880; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 27.4 min, minor: 37.4 min, 95:5 er; $[\alpha]_D^{24}$ 128.3° (c 0.095, CH_2Cl_2).

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



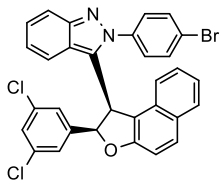
Yield 99%, 95:5 dr, pale solid, m. p. 95-96 °C, R_f = 0.5 (DCM/petroleum ether = 1/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, J = 8.9 Hz, 1H), 7.90 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.7 Hz, 1H), 7.42 – 7.35 (m, 4H), 7.34 – 7.26 (m, 3H), 7.14 – 7.07 (m, 1H), 6.91 (d, J = 1.7 Hz, 2H), 6.70 (dd, 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); ^{13}C NMR (101 MHz, $CDCl_3$) δ 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^{-1}) 3019, 2954, 2911, 1733, 1607, 1509, 1452, 1372, 1033, 818, 742, 584; HRMS (ESI) Calcd for $C_{31}H_{20}Br_2ClN_2O$ $(M+H)^+$ 628.9626, Found 628.9631; HPLC: OD-H column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 14.9 min, minor: 10.4 min, 99:1 er; $[\alpha]_D^{24}$ 156.9° (c 0.13, CH_2Cl_2).

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_f = 0.4 (DCM/petroleum ether = 1/2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 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); ^{13}C NMR (126 MHz, $CDCl_3$) δ 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; ^{19}F NMR (471 MHz, $CDCl_3$) δ -109.2; IR (KBr, cm^{-1}) 3064, 2935, 1626, 1588, 1501, 1381, 1278, 1174, 1137, 1013, 817, 744, 710; HRMS (ESI) Calcd for $C_{31}H_{20}BrF_2N_2O$ $(M+H)^+$ 553.0722, Found 553.0713; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 21.5 min, minor: 31.7 min, 96:4 er; $[\alpha]_D^{24}$ 112.4° (c 0.13, CH_2Cl_2).

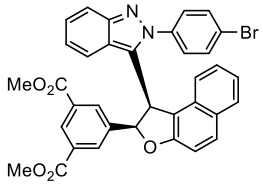
2-(4-bromophenyl)-3-((1R,2R)-2-(3,5-dichlorophenyl)-1,2-dihydronaphtho[2,1-b]furan-1-yl)-2H-indazole (4f)



Yield 99%, 96:4 dr, pale solid, m. p. 166-167 °C, R_f = 0.4 (DCM/petroleum ether = 1/2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 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); ^{13}C NMR (101 MHz, $CDCl_3$) δ 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, 122.5, 122.2, 119.7, 117.6, 112.1, 87.5, 45.0; IR (KBr, cm^{-1}) 3741, 3196, 3063, 2962, 1634, 1570, 1425, 1382, 1247, 1068, 1004,

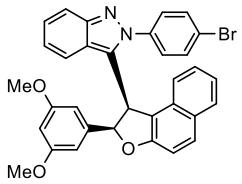
804, 742; HRMS (ESI) Calcd for $C_{31}H_{19}BrCl_2N_2NaO$ $(M+Na)^+$ 606.9950, Found 606.9956; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major:17.9 min, minor: 30.3 min, 98:2 er; $[\alpha]_D^{24}$ 200.8° (c 0.13, CH_2Cl_2).

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



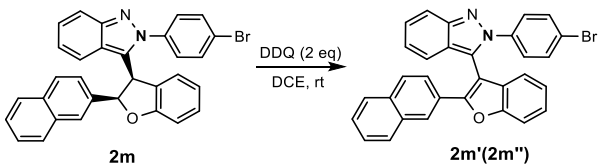
Yield 99%, 95:5 dr, pale solid, m. p. 271-272 °C, R_f = 0.5 (DCM/EtOAc/petroleum ether = 40/1/40); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.97 (d, J = 8.8 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.75 (s, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.44 – 7.38 (m, 2H), 7.37 – 7.31 (m, 3H), 7.11 – 7.05 (m, 3H), 6.72 – 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); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 157.8, 148.7, 138.2, 137.1, 132.6, 132.2, 131.5, 130.8, 130.6, 130.3, 130.1, 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 $C_{35}H2_5BrN_2NaO_5$ $(M+Na)^+$ 655.0839, Found 655.0844; HPLC: INA column, 80:20 hexanes:isopropanol, 1.00 mL/min, t_R = major: 20.9 min, minor: 30.9 min, 98:2 er; $[\alpha]_D^{24}$ 247.4° (c 0.13, CH_2Cl_2).

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



Yield 54%, > 99:1 dr, pale solid, m. p. 90-91 °C, R_f = 0.4 (DCMEtOAc/petroleum ether = 10/1/20); ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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, 121.1, 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 $C_{33}H_{25}BrN_2NaO_3$ $(M+Na)^+$ 599.0941, Found 599.0942; HPLC: INC column, 95:5 hexanes:isopropanol, 1.00 mL/min, t_R = major: 19.5 min, minor: 18.0 min, 96:4 er; $[\alpha]_D^{24}$ 289.6° (c 0.063, CH_2Cl_2).

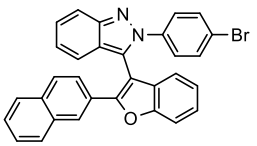
3.6 Procedures for central-to-axial chirality transfer reaction of 2m



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")



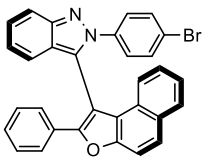
Yield 99%, pale solid, m. p. 226-227 °C, R_f = 0.6 (EtOAc/petroleum ether = 1/40); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.86 (m, 2H), 7.75 (d, J = 7.3 Hz, 1H), 7.70 (d, J = 8.6 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.51 – 7.44 (m, 3H), 7.44 – 7.37 (m, 2H), 7.31 – 7.27 (m, 2H), 7.23 (d, J = 7.5 Hz, 1H), 7.21 – 7.13 (m, 4H), 7.12 – 7.08 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) 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, 2857, 1730, 1495, 1458, 1364, 1265, 1084, 1017, 907, 818, 738; HRMS (ESI) Calcd for $C_{31}H_{20}BrN_2O$ $(M+H)^+$ 515.0754, Found 515.0759; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = isomer1: 7.7min, isomer2: 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).

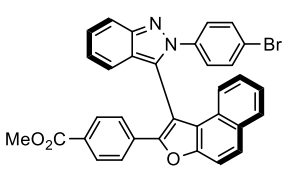
The procedures of other substrates **4**, were similar with that mentioned above.

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



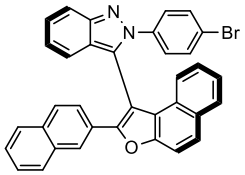
Yield 99%, pale solid, m. p. 170-171 °C, R_f = 0.7 (DCM/petroleum ether = 1/2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 8.4 Hz, 2H), 7.82 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 9.0 Hz, 1H), 7.49 – 7.38 (m, 3H), 7.30 (d, J = 8.2 Hz, 1H), 7.28 – 7.24 (m, 3H), 7.23 – 7.15 (m, 7H), 7.14 – 7.07 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2, 152.1, 149.6, 138.8, 131.8, 131.1, 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 $C_{31}H_{19}BrN_2NaO$ $(M+Na)^+$ 537.0573, Found 537.0567; HPLC: INA column, 95:5 hexanes:isopropanol, 1.00 mL/min, t_R = major: 10.0 min, minor: 7.6 min, 91:9 er; $[\alpha]_D^{24}$ -5.8° (c 0.069, CH_2Cl_2).

methyl 4-(1-(2-(4-bromophenyl)-2H-indazol-3-yl)naphtho[2,1-b]furan-2-yl)benzoate (5b)



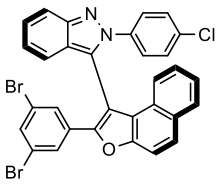
Yield 91%, pale solid, m. p. 224-225 °C, R_f = 0.6 (DCM/petroleum ether = 1/2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, J = 8.2 Hz, 2H), 7.88 (t, J = 9.3 Hz, 3H), 7.77 (dd, J = 9.0, 1.7 Hz, 1H), 7.49 – 7.41 (m, 3H), 7.33 – 7.25 (m, 5H), 7.22 (s, 1H), 7.18 (s, 2H), 7.11 (t, J = 7.5 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) 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, 804, 746; HRMS (ESI) Calcd for $C_{33}H_{21}BrN_2NaO_3$ $(M+Na)^+$ 595.0628, Found 595.0621; HPLC: INC column, 95:5 hexanes:isopropanol, 1.00 mL/min, t_R = major: 10.3 min, minor: 11.0 min, 91:9 er; $[\alpha]_D^{24}$ -17.8° (c 0.16, CH_2Cl_2).

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



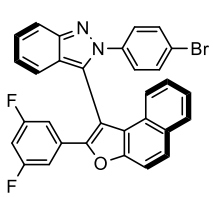
Yield 91%, , pale solid, m. p. 180-181 °C, R_f = 0.5 (EtOAc/petroleum ether = 1/10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 2H), 7.84 (d, J = 8.7 Hz, 2H), 7.79 (d, J = 9.0 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.68 – 7.61 (m, 2H), 7.52 – 7.39 (m, 5H), 7.33 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 7.6 Hz, 1H), 7.24 – 7.17 (m, 3H), 7.16 – 7.05 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{35}H_{21}BrN_2NaO$ $(M+Na)^+$ 587.0729, Found 587.0730; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 8.6 min, minor: 7.5 min, 90:10 er; $[\alpha]_D^{24}$ -101.9° (c 0.074, CH_2Cl_2).

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, R_f = 0.6 (DCM/petroleum ether = 1/4); ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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 $C_{31}H_{17}Br_2ClN_2NaO$ $(M+Na)^+$ 648.9288 , Found 648.9283; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 6.7 min, minor: 4.8 min, 91:9 er; $[\alpha]_D^{24}$ -57.3° (c 0.068, CH_2Cl_2).

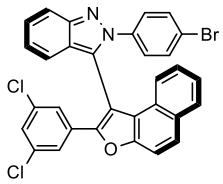
2-(4-bromophenyl)-3-(2-(3,5-difluorophenyl)naphtho[2,1-b]furan-1-yl)-2H-indazole (5e)



Yield 95%, pale solid, m. p. 184-185 °C, R_f = 0.6 (DCM/petroleum ether = 1/4); ^{1}H NMR (500 MHz, $CDCl_3$) 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,

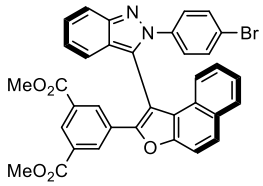
1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 8.9 Hz, 2H), 7.19 (d, *J* = 8.9 Hz, 2H), 7.16 – 7.10 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.7, 149.8, 149.4, 138.5, 132.3 (dd, *J* = 100.7, 35.6 Hz), 132.1, 131.4, 131.3, 129.3, 128.5, 127.9, 127.6, 126.0, 125.8, 125.5, 125.2 (dd, *J* = 3.7, 3.2 Hz), 123.9, 123.4, 123.2, 122.5, 122.5, 121.71, 121.68, 120.0, 118.5, 112.3, 109.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.4; IR (KBr, cm^{-1}) 3062, 2962, 2860, 1618, 1589, 1492, 1445, 1360, 1263, 1112, 1087, 1017, 803,741; HRMS (ESI) Calcd for $C_{31}H_{17}BrF_2N_2NaO$ $(M+Na)^+$ 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° (c 0.13, CH_2Cl_2).

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



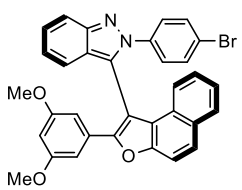
Yield 96%, pale solid, m. p. 225-226 °C, R_f = 0.6 (DCM/petroleum ether = 1/4); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 8.3, 4.1 Hz, 2H), 7.88 (d, *J* = 9.0 Hz, 1H), 7.75 (d, *J* = 9.0 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.43 – 7.36 (m, 2H), 7.32 – 7.25 (m, 3H), 7.25 – 7.18 (m, 3H), 7.16 – 7.09 (m, 1H), 7.03 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 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, 127.4, 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, 2963, 1586, 1494, 1409, 1365, 1262, 1211, 1099, 1010, 801, 742; HRMS (ESI) Calcd for $C_{31}H17BrCl_2N_2NaO$ $(M+Na)^+$ 604.9793, Found 604.9792; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 7.3 min, minor: 4.9 min, 93:7 er; $[\alpha]_D^{24}$ -54.4° (c 0.063, CH_2Cl_2).

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



Yield 99%, pale solid, m. p. 220-222 °C, R_f = 0.5 (DCM/EtOAc/petroleum ether = 40/1/40); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.07 – 7.93 (m, 4H), 7.89 (d, *J* = 8.9 Hz, 1H), 7.80 (d, J = 8.9 Hz, 1H), 7.51 – 7.41 (m, 4H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.18 (m, 4H), 7.12 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.86 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.4, 152.4, 150.8, 149.8, 138.7, 132.0, 131.3, 131.2, 130.33, 130.27, 130.25, 129.2, 127.7, 127.6, 127.4, 126.8, 126.0, 125.3, 123.6, 123.5, 123.4, 122.5, 122.4, 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 $C_{35}H_{24}BrN_2O_5$ $(M+H)^+$ 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° (c 0.047, CH_2Cl_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)naphtho[2,1-b]furan-1-yl)-2H-indazole (5h)

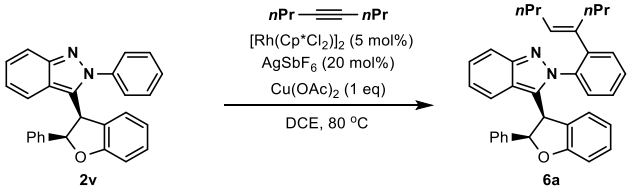


Yield 99%, pale solid, m. p. 78-79 °C R_f = 0.5 (EtOAc/petroleum ether = 1/10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 18.1, 8.5 Hz, 2H), 7.76 (d, *J* = 9.0 Hz, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.29 (d, *J* = 8.3 Hz, 1H), 7.21 (s, 1H), 7.18 – 7.11 (m, 4H), 7.04 (dd, *J* = 8.5, 6.6 Hz, 1H), 6.30 (d, *J* = 2.2 Hz, 2H), 6.27 (d, *J* = 2.3 Hz, 1H), 3.43 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 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,

111.3, 105.6, 102.3, 101.2, 54.2; IR (KBr, cm^{-1}) 3059, 2959, 2850, 1595, 1494, 1461, 1417, 1357, 1261, 1200, 1153, 1017, 802; HRMS (ESI) Calcd for $C_{33}H_{23}BrN_2NaO_3$ $(M+Na)^+$ 597.0784, Found 597.0783; HPLC: INC column, 95:5 hexanes:isopropanol, 1.00 mL/min, t_R = major: 8.0 min, minor: 8.6 min, 97:3 er; $[\alpha]_D^{24}$ -57.6° (c 0.035, CH_2Cl_2).

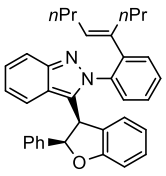
3.8 Procedures for late-modification of chiral isoindazoles

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



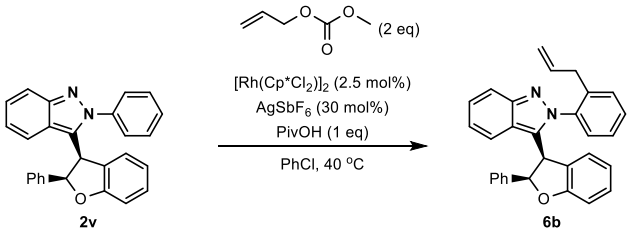
In a Schlenk tube with a magnetic bar under nitrogen atmosphere, **2v** (0.1 mmol, 38.8 mg), DCE (0.05 M, 2 ml), $[Rh(Cp^*Cl_2)]_2$ (5 mol%, 3.9 mg), $AgSbF_6$ (20 mol%, 6.86 mg), $Cu(OAc)_2$ (1 eq, 18.8 mg), alkyne (1.2 eq, 13.2 mg) were added. The mixtures were stirred at 80 °C until the starting material 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, R_f = 0.5 (EtOAc/petroleum ether = 1/40); ^1H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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, 127.2, 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 $C_{35}H_{35}N_2O$ $(M+H)^+$ 499.2744, Found 499.2738; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 4.4 min, minor: 4.1 min, 97:3 er; $[\alpha]_D^{24}$ 321.6° (c 0.083, CH_2Cl_2).

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

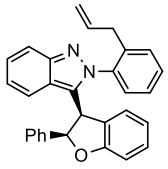


In a Schlenk tube with a magnetic bar under nitrogen atmosphere, **2v** (0.1 mmol, 38.8 mg), PhCl (0.1

M, 1 ml), $[Rh(Cp^*Cl_2)]_2$ (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).

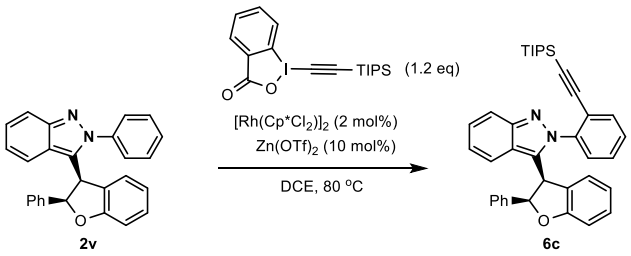
The procedures of the following substrate **4a** for accessing **6i** were similar with that mentioned above.

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



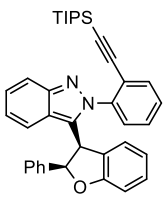
Yield 83%, > 99:1 dr, pale solid, m. p. 112-113 °C, R_f = 0.6 (EtOAc/petroleum ether = 1/20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.8 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.41 – 7.32 (m, 2H), 7.25 – 7.20 (m, 1H), 7.19 – 7.13 (m, 2H), 7.11 – 7.04 (m, 4H), 6.98 – 6.92 (m, 3H), 6.80 (dd, J = 8.6, 6.6 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); ^{13}C 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 $C_{30}H_{25}N_2O$ $(M+H)^+$ 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; $[\alpha]_D^{24}$ 93.7° (c 0.12, CH_2Cl_2).

Procedures for C-H alkynylation 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), $[Rh(Cp^*Cl_2)]_2$ (2 mol%, 1.6 mg), $Zn(OTf)_2$ (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).

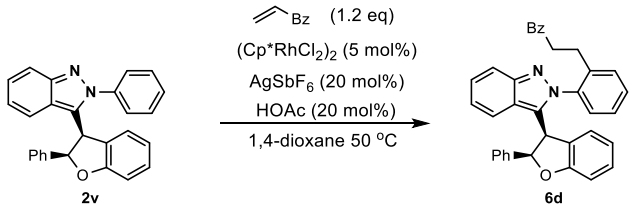
3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2-(2-((triisopropylsilyl)ethynyl)phenyl)-2H-indazole (6c)



Yield 78%, > 99:1 dr, pale solid, m. p. 134-135 °C, R_f = 0.7 (EtOAc/petroleum ether = 1/20); ^{1}H 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); ^{13}C 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, 128.6, 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 $C_{38}H_{41}N_2OSi$ $(M+H)^+$ 569.2983, Found 569.2990; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 7.3 min, minor: 4.6 min, 98:2 er; $[\alpha]_D^{24}$ 23.8° (c 0.14, CH_2Cl_2).

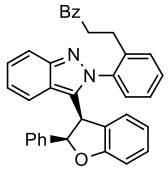
Procedures for C-H alkylation of chiral isoindazoles[8]



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), $[Rh(Cp^*Cl_2)]_2$ (5 mol%, 3.9 mg), $AgSbF_6$ (20 mol%, 6.86 mg), HOAc (20 mol%, 1.2 mg), 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).

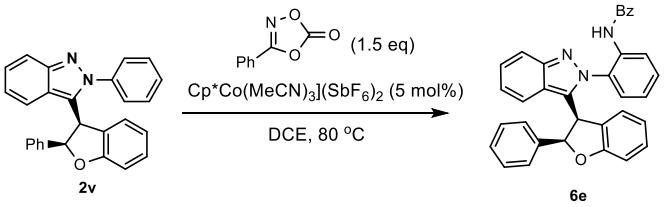
The procedures of the following substrate **4a** for accessing **6h** were similar with that mentioned above.

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



Yield 76%, > 99:1 dr, pale solid, m. p. 75-76 °C, R_f = 0.4 (EtOAc/petroleum ether = 1/20); ^1H NMR (400 MHz, $CDCl_3$) 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), 6.35 (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); ^{13}C NMR (101 MHz, $CDCl_3$) 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, 121.8, 121.5, 120.7, 117.6, 110.1, 88.2, 45.9, 39.5, 26.4; IR (KBr, cm^{-1}) 3061, 2927, 1718, 1683, 1596, 1496, 1457, 1379, 1231, 1160, 1018, 747, 696; HRMS (ESI) Calcd for $C_{36}H_{29}N_2O_2$ $(M+H)^+$ 521.2224, Found 521.2228; HPLC: INA column, 95:5 hexanes:isopropanol, 1.00 mL/min, t_R = major: 34.5 min, minor: 40.9 min, 98:2 er; $[\alpha]_D^{24}$ 90.2° (c 0.13, CH_2Cl_2).

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

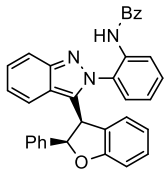


In a Schlenk tube with a magnetic bar under nitrogen atmosphere, **2v** (0.1 mmol, 38.8 mg), DCE (0.1

M, 1 ml), Cp*Co(MeCN)$_3$](SbF6)$_2$ (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).

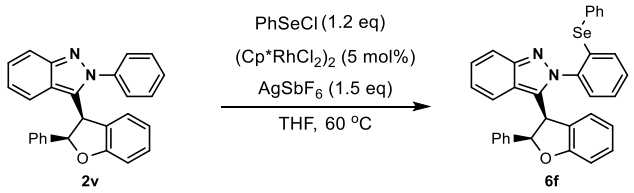
The procedures of the following substrate **4a** for accessing **6g** were similar with that mentioned above.

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



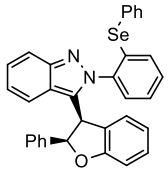
Yield 99%, > 99:1 dr, pale solid, m. p. 184-186 °C, R_f = 0.5 (DCM/petroleum ether = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (br, 1H), 8.77 (d, J = 8.0 Hz, 1H), 7.60 – 7.50 (m, 4H), 7.49 – 7.44 (m, 1H), 7.39 – 7.31 (m, 5H), 7.25 – 7.21 (m, 1H), 7.20 – 7.09 (m, 2H), 6.96 (t, J = 7.3 Hz, 1H), 6.87 – 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); ^{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^{-1}) 3310, 3060, 2961, 2927, 1679, 1596, 1527, 1461, 1309, 1263, 1099, 1024, 800, 750, 699; HRMS (ESI) Calcd for $C_{34}H_{26}N_3O_2$ $(M+H)^+$ 508.2020, Found 508.2020; HPLC: INA column, 80:20 hexanes:isopropanol, 1.00 mL/min, t_R = major: 9.5 min, minor: 43.8 min, 98:2 er; $[\alpha]_D^{24}$ 32.3° (c 0.17, CH_2Cl_2).

Procedures for C-H selenylation of chiral isoindazoles[10]



In a Schlenk tube with a magnetic bar under nitrogen atmosphere, **2v** (0.1 mmol, 38.8 mg), THF (0.1 M,1 ml), [Rh(Cp*Cl$_2$)]$_2$ (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).

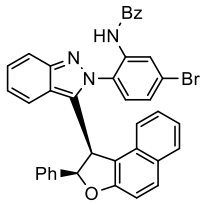
3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2-(2-(phenylselanyl)phenyl)-2H-indazole (6f)



Yield 76%, > 99:1 dr, pale solid, m. p. 196-198 °C, R_f = 0.3 (THF/petroleum ether = 1/20); ^{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); ^{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, 126.5, 126.3, 121.9, 121.8, 121.6, 120.7, 117.8, 110.0, 88.3, 46.0; IR (KBr, cm^{-1}) 3058, 2960, 2924, 2853, 1620, 1480, 1458, 1262, 1231, 1096, 1021, 801, 743; HRMS (ESI) Calcd for

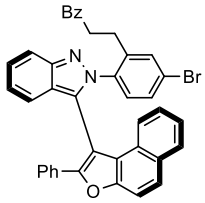
$C_{33}H_{25}N_2OSe$ $(M+H)^+$ 545.1127, Found 545.1129; HPLC: OD-H column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 8.9 min, minor: 17.8 min, 98:2 er; $[\alpha]_D^{24}$ 29.4° (c 0.13, CH_2Cl_2).

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)



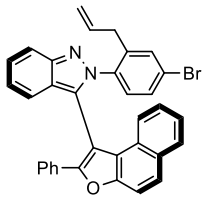
Yield 81%, > 99:1 dr, pale solid, m. p. 108-109 °C, R_f = 0.4 (EtOAc/petroleum ether = 1/10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.56 (s, 1H), 9.08 (s, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.46 (dd, *J* = 7.1, 3.4 Hz, 2H), 7.37 (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); ^{13}C NMR (126 MHz, $CDCl_3$) 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, 127.6, 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 $C_{38}H_{27}BrN_3O_2$ $(M+H)^+$ 636.1281, Found 636.1288; HPLC: OD-H column, 70:30 hexanes:isopropanol, 0.80 mL/min, t_R = major: 16.3 min, minor: 11.9 min, 96:4 er; $[\alpha]_D^{24}$ 80.5° (c 0.17, CH_2Cl_2).

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, R_f = 0.4 (EtOAc/petroleum ether = 1/20); ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) 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, 1453, 1261, 1023, 804, 745; HRMS (ESI) Calcd for $C_{40}H_{28}BrN_2O_2$ $(M+H)^+$ 647.1329, Found 647.1330; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 12.0 min, minor: 8.5 min, 91:9 er; $[\alpha]_D^{24}$ -1.7° (c 0.12, CH_2Cl_2).

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, R_f = 0.6 (EtOAc/petroleum ether = 1/20); ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.0, 152.0, 149.2, 139.2, 137.2, 134.8, 132.4, 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 $C_{34}H_{24}BrN_2O$ $(M+H)^+$ 555.1067, Found 555.1072; HPLC: INA column, 90:10 hexanes:isopropanol, 1.00 mL/min, t_R = major: 6.1 min, minor: 5.0 min, 91:9 er; $[\alpha]_D^{24}$ -1.3° (c 0.078, CH_2Cl_2).

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.; Schrçder, 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.

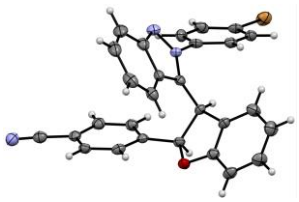
[8] Boerth, J. A.; Hummel, J. R. Ellman, J. A. *Angew. Chem. Int. Ed*., **2016**, *55*, 12650 –12654.

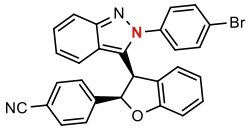
[9] Liang, Y.; Liang, Y.; Tang, C.; Yuan, Y.; Jiao, N. *Chem. Eur. J*., **2015**, *21*, 16395 – 16399.

[10] Yu, S.; Wan, B.; Li, X. *Org. Lett*., **2015**, *17*, 58−61.

4. X-Ray diffraction analysis

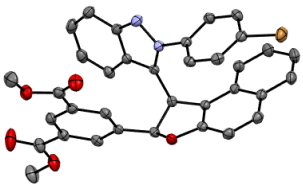
4.1 Crystal data and structure refinement for 2h

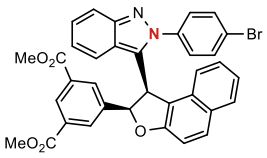




CCDC	2105966
Identification code	9st-147
Empirical formula	$C_{28}H_{18}BrN_3O$
Formula weight	492.36
Temperature/K	99.98(10)
Crystal system	monoclinic
Space group	I2
a/Å	20.2119(12)
b/Å	7.9865(4)
c/Å	28.5833(19)
α/°	90
β/°	99.590(6)
γ/°	90
Volume/Å^3	4549.5(5)
Z	8
ρ_{calc}g/cm^3	1.438
μ/mm^{-1}	2.664
F(000)	2000.0
Crystal size/mm^3	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 F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0447, wR_2 = 0.1145
Final R indexes [all data]	R_1 = 0.0456, wR_2 = 0.1160
Largest diff. peak/hole / e Å^{-3}	1.19/-0.80
Flack parameter	0.005(11)

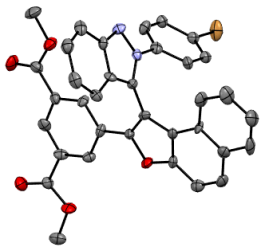
4.2 Crystal data and structure refinement for 4g

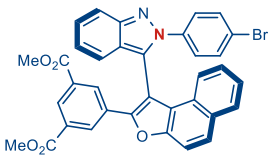




CCDC	2105967
Identification code	68-3
Empirical formula	$C_{35}H_{25}BrN_2O_5$
Formula weight	633.48
Temperature/K	199.99(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.00919(18)
b/Å	14.8084(3)
c/Å	13.4349(3)
α/°	90
β/°	92.747(2)
γ/°	90
Volume/Å^3	1392.88(6)
Z	2
ρ_{calc}g/cm^3	1.510
μ/mm^{-1}	2.416
F(000)	648.0
Crystal size/mm^3	0.12 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.586 to 147.578
Index ranges	$-8 \le h \le 6$, $-18 \le k \le 18$, $-16 \le l \le 16$
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

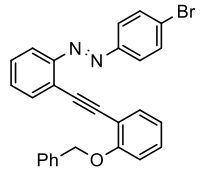


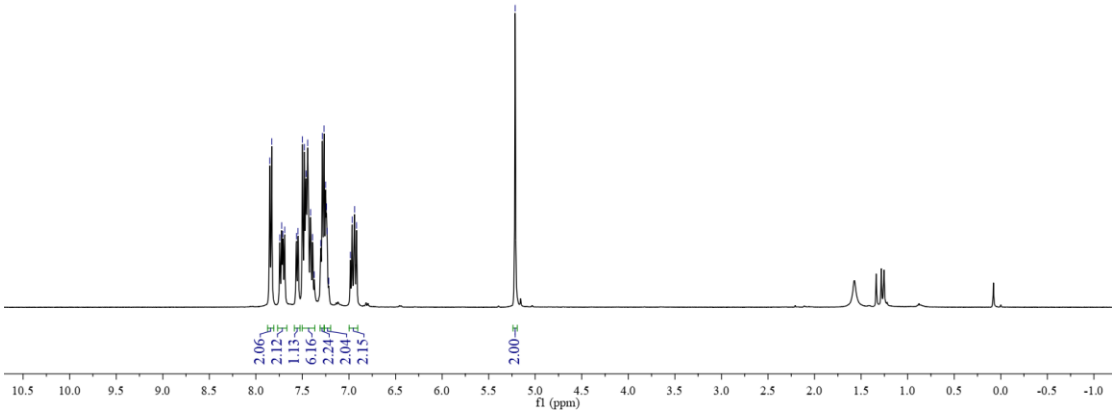


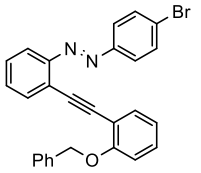
CCDC	2105968
Identification code	78-3
Empirical formula	$C_{35}H_{23}BrN_2O_5$
Formula weight	631.46
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.9824(12)
b/Å	10.3845(11)
c/Å	15.312(2)
α/°	90
β/°	92.079(13)
γ/°	90
Volume/Å^3	1427.4(3)
Z	2
ρ_{calc}g/cm^3	1.469
μ/mm^{-1}	1.488
F(000)	644.0
Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.538 to 59.082
Index ranges	$-9 \le h \le 11$, $-12 \le k \le 13$, $-19 \le l \le 14$
Reflections collected	11864
Independent reflections	6468 [R_{int} = 0.0899, R_{sigma} = 0.1693]
Data/restraints/parameters	6468/47/400
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0849, wR_2 = 0.1807
Final R indexes [all data]	R_1 = 0.1301, wR_2 = 0.2153
Largest diff. peak/hole / e Å^{-3}	1.44/-1.31
Flack/Hooft parameter	0.004(14)/0.031(12)

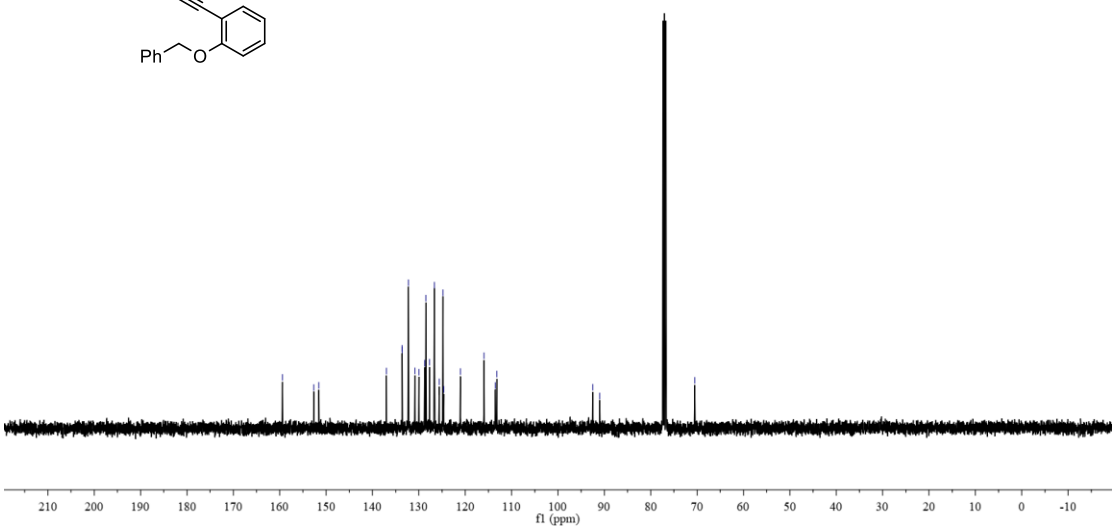
5. Copies of NMR spectrum

(E)-1-(2-((2-(benzyloxy)phenyl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (1a)

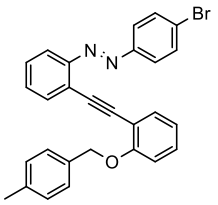


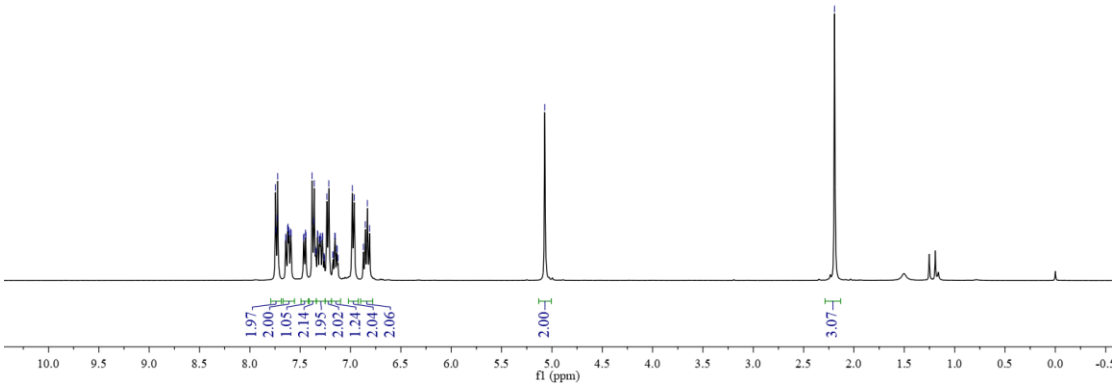


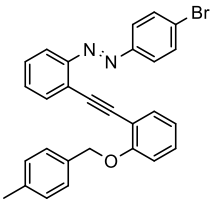


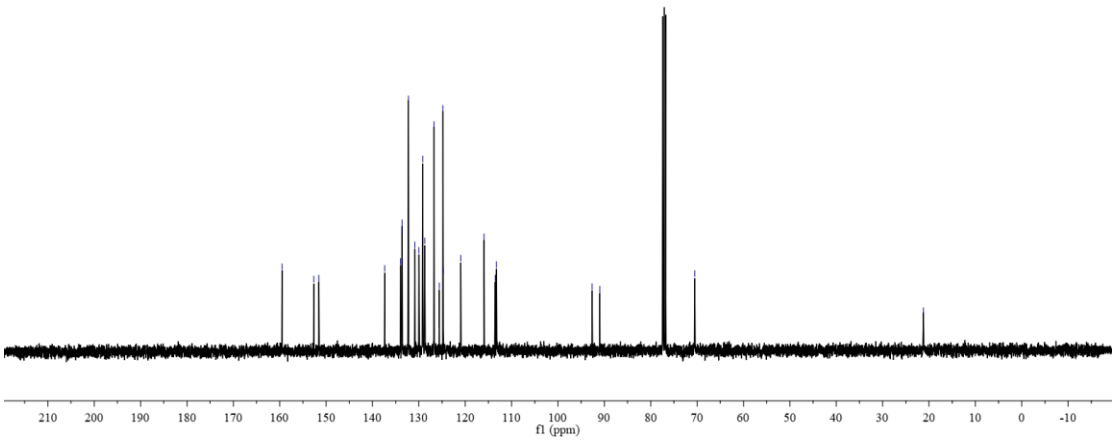


(E)-1-(4-bromophenyl)-2-(2-((2-((4-methylbenzyl)oxy)phenyl)ethynyl)phenyl)diazene ***(1b)***

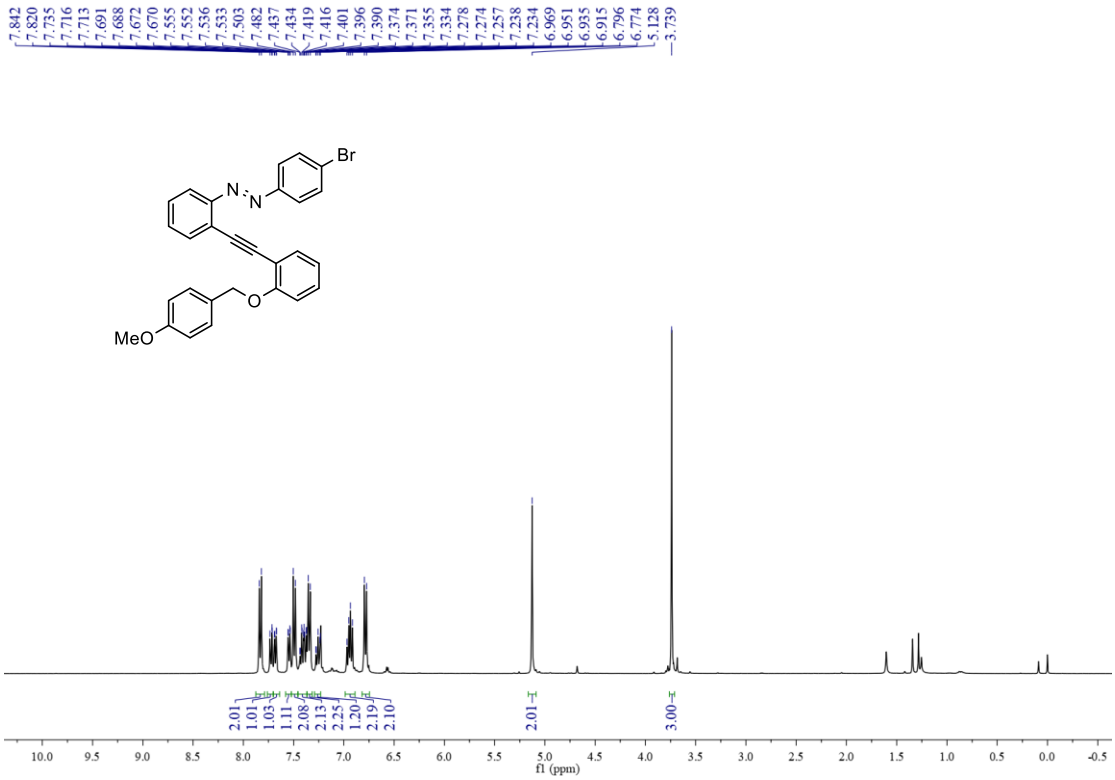


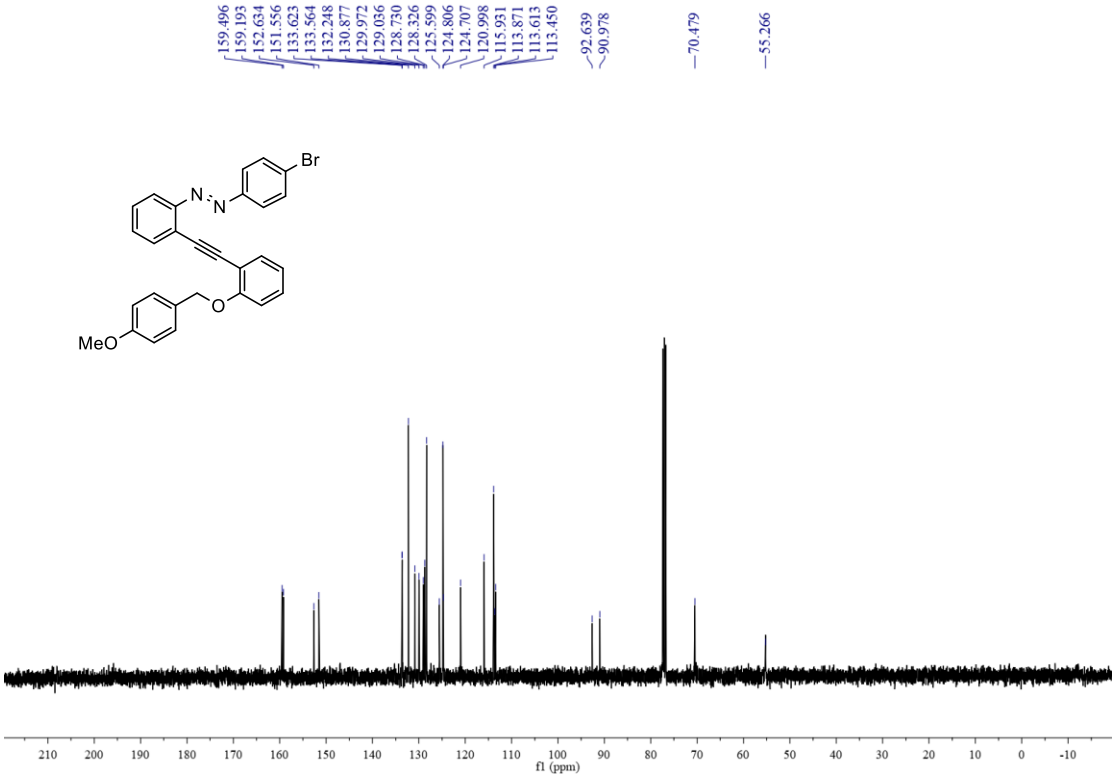




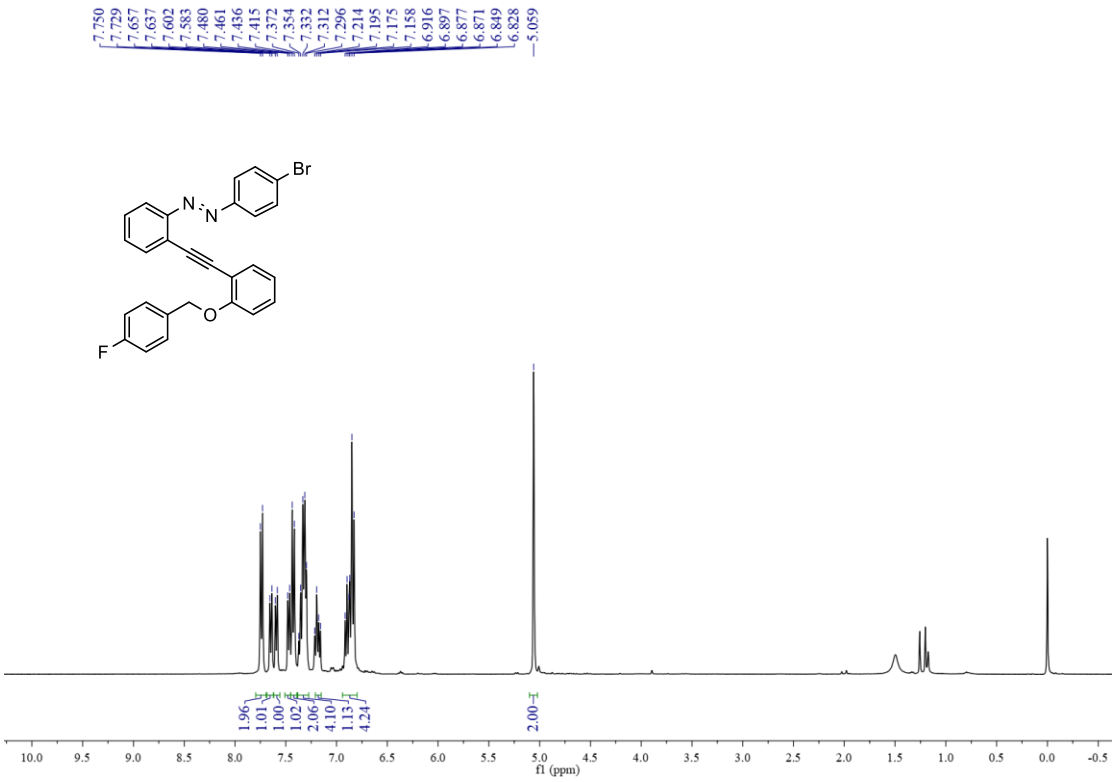


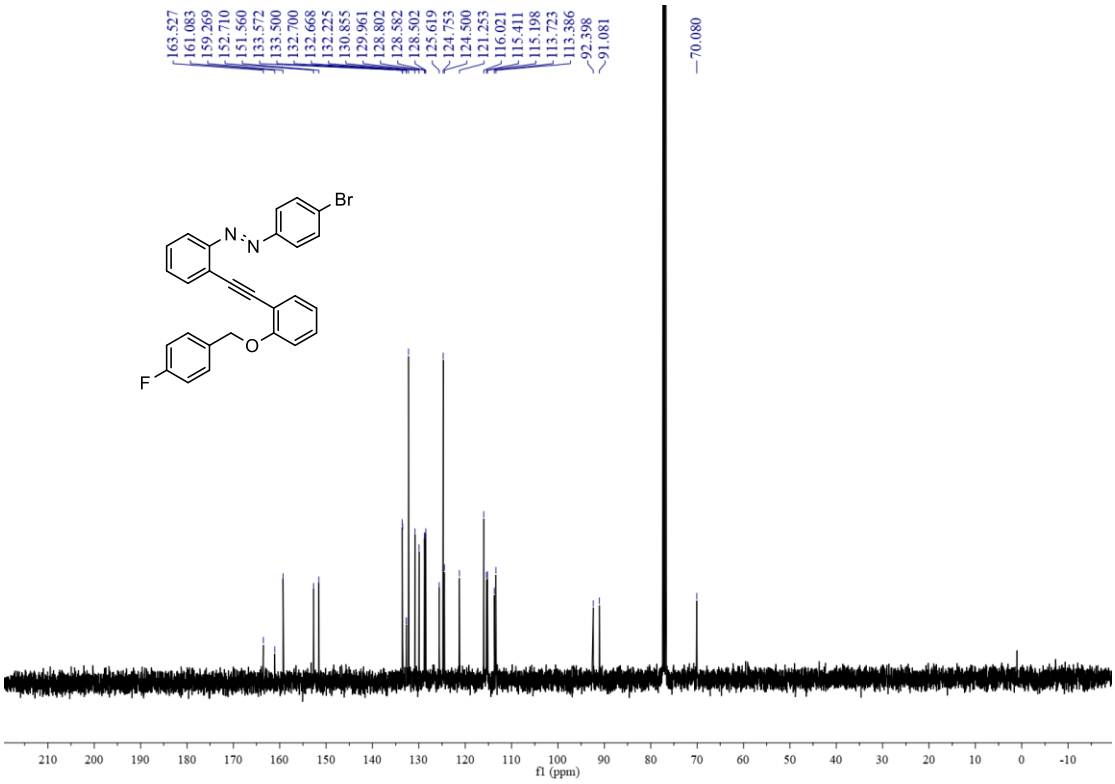
(E)-1-(4-bromophenyl)-2-(2-((2-((4-methoxybenzyl)oxy)phenyl)ethynyl)phenyl)diazene (1c)

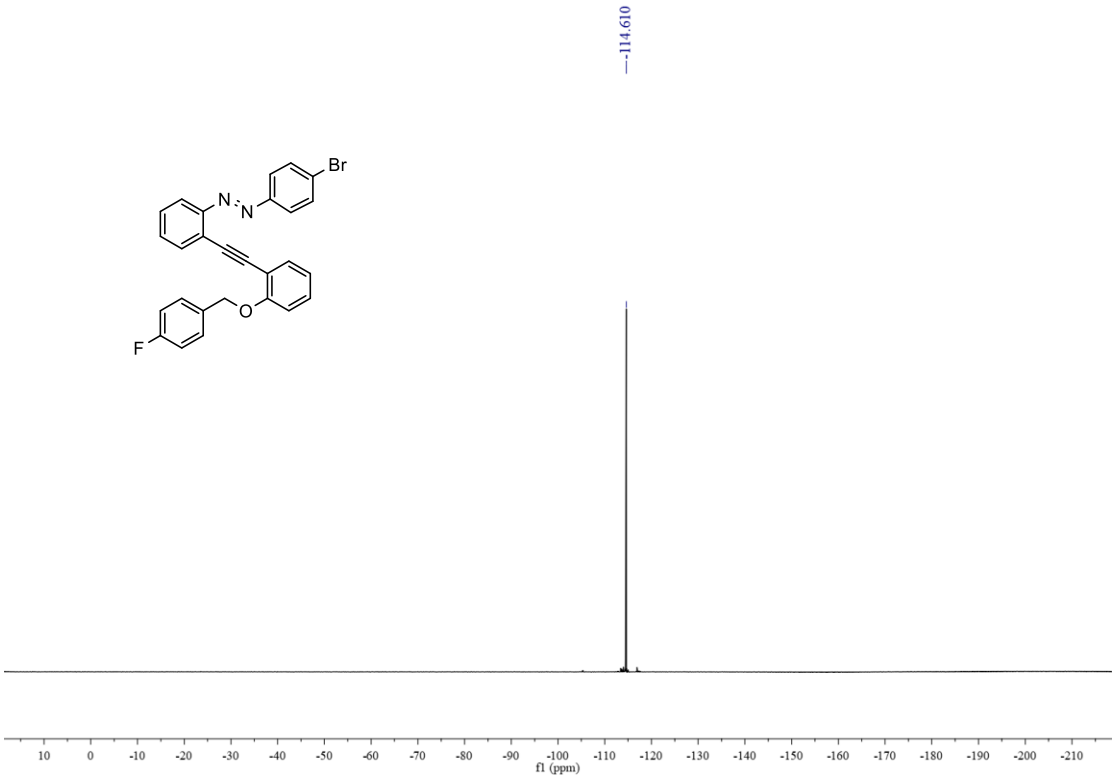




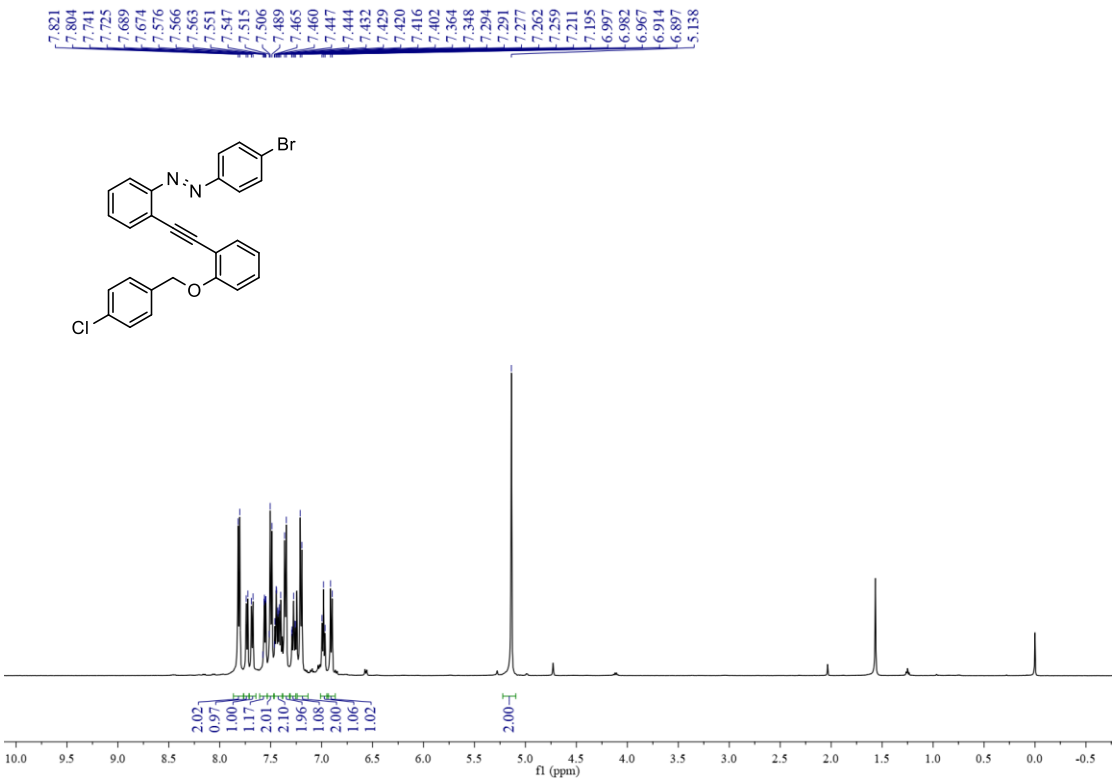
(E)-1-(4-bromophenyl)-2-(2-((2-((4-fluorobenzyl)oxy)phenyl)ethynyl)phenyl)diazene (1d)

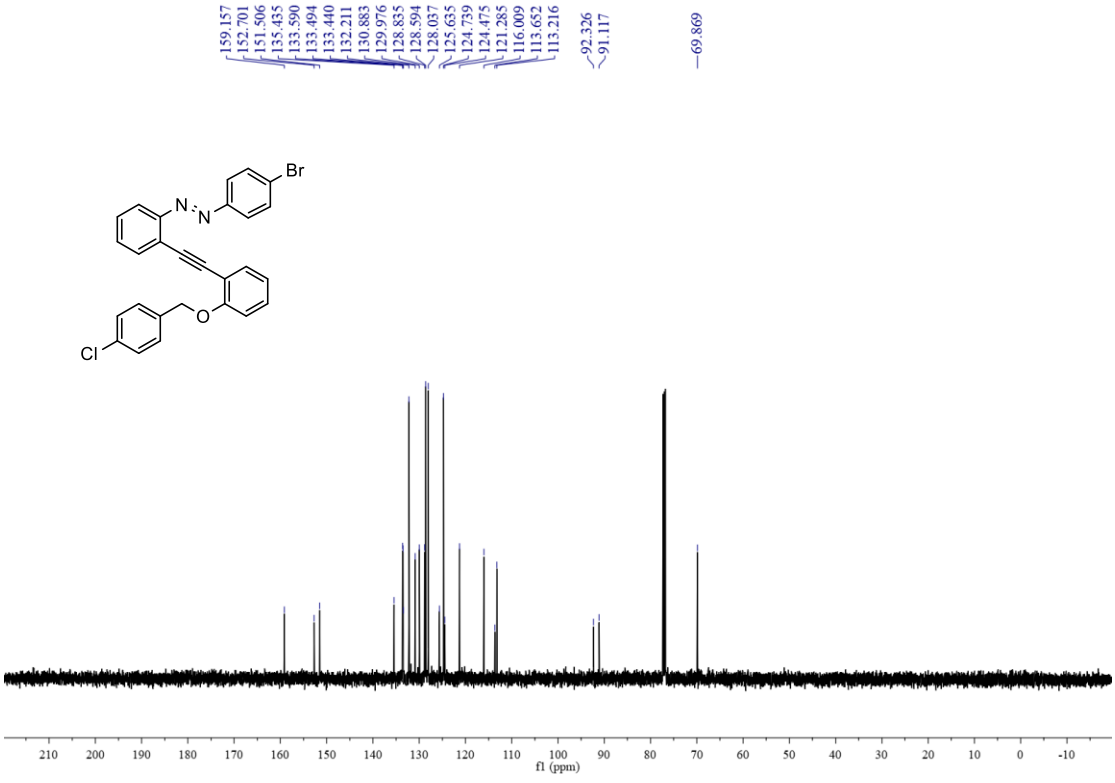




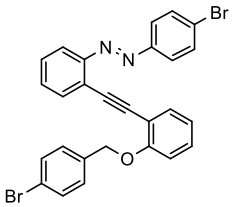

-114.610
Br
N
N
O
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

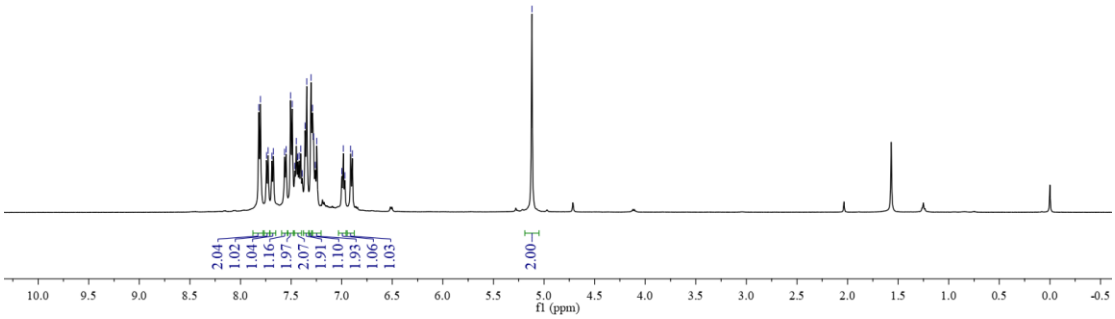
(E)-1-(4-bromophenyl)-2-(2-((2-((4-chlorobenzyl)oxy)phenyl)ethynyl)phenyl)diazene (1e)

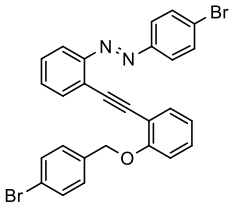


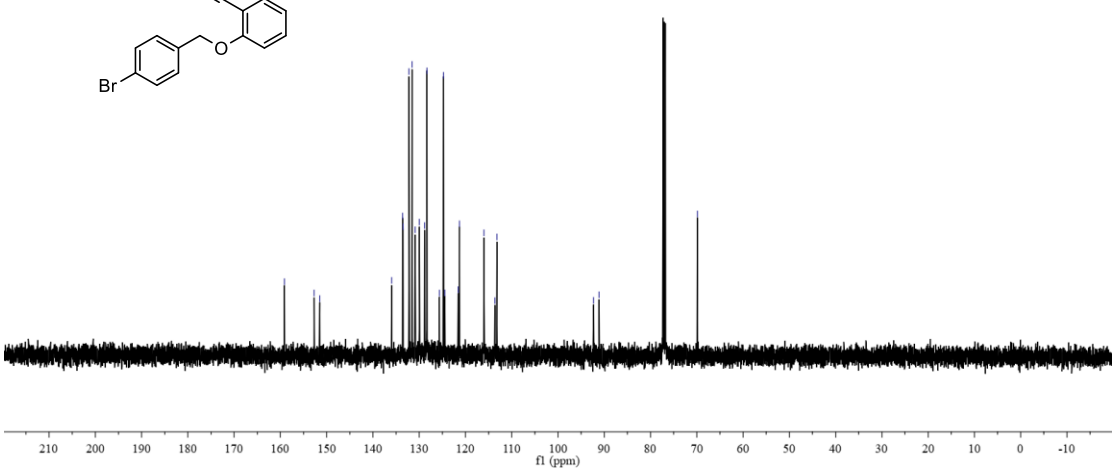


(E)-1-(2-((2-((4-bromobenzyl)oxy)phenyl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (1f)

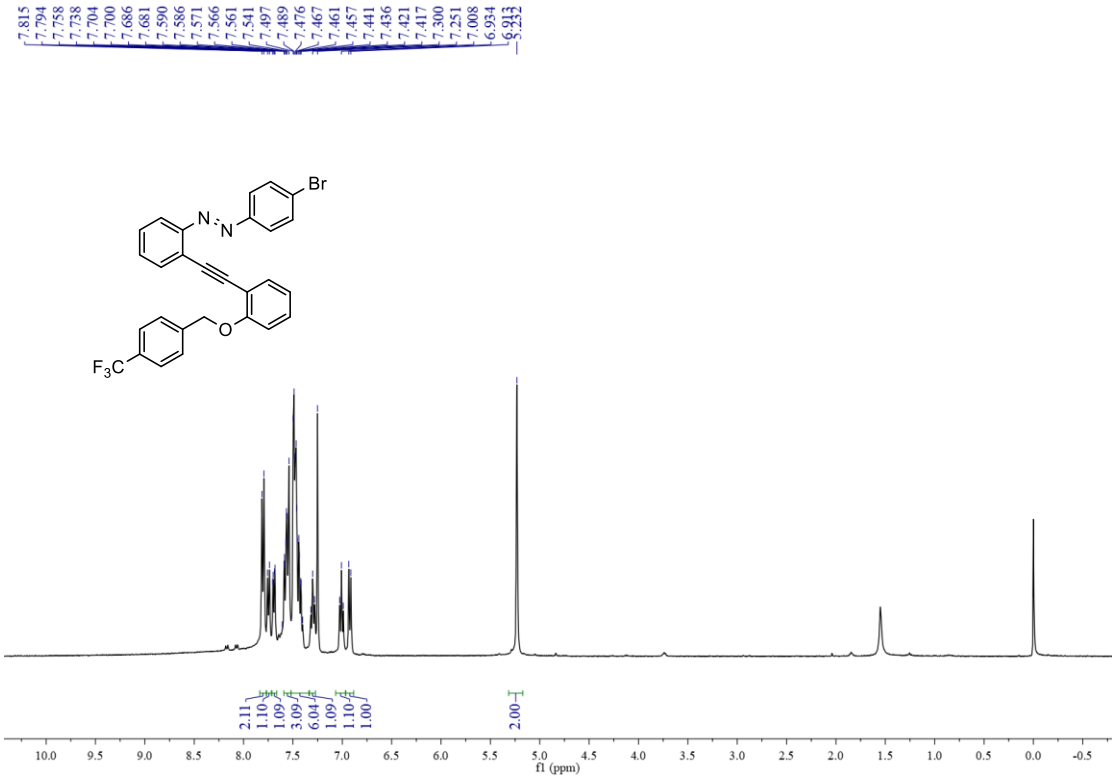


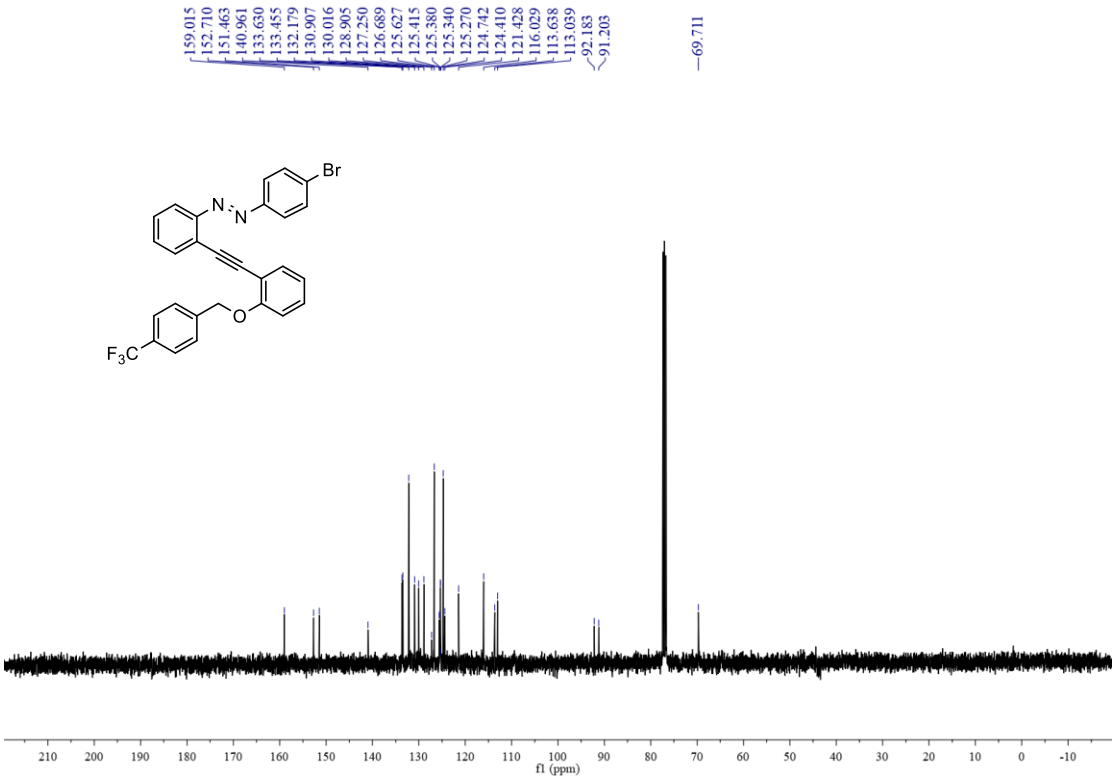


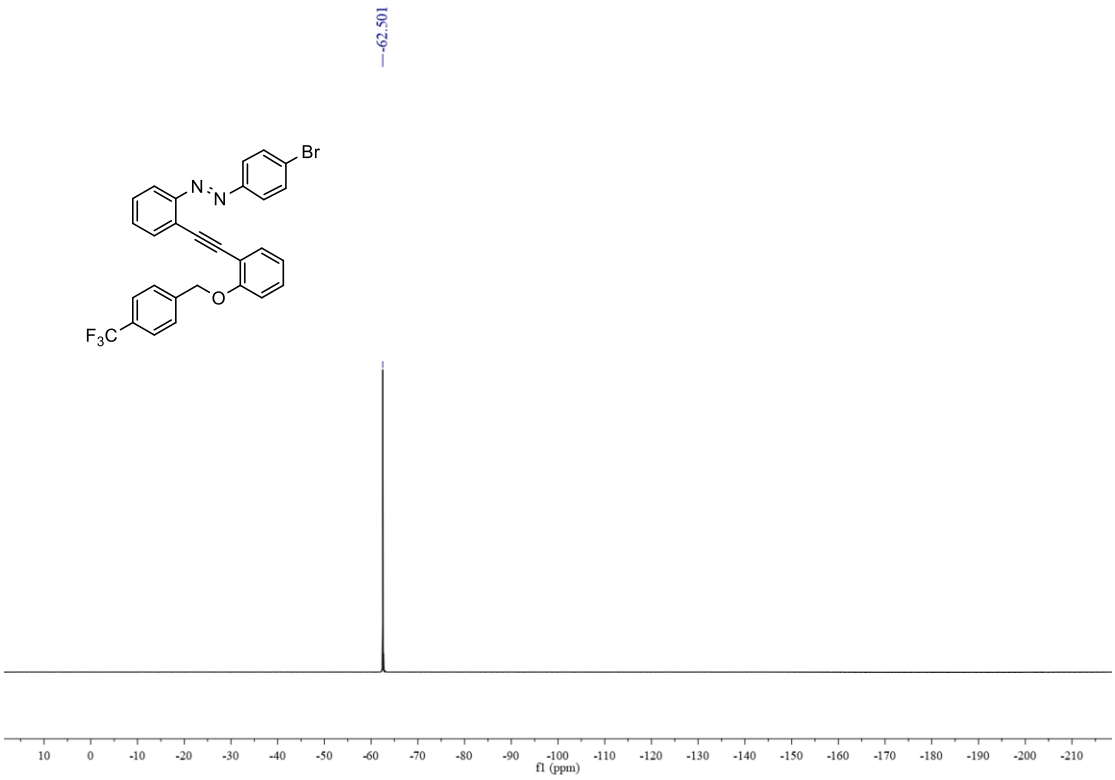




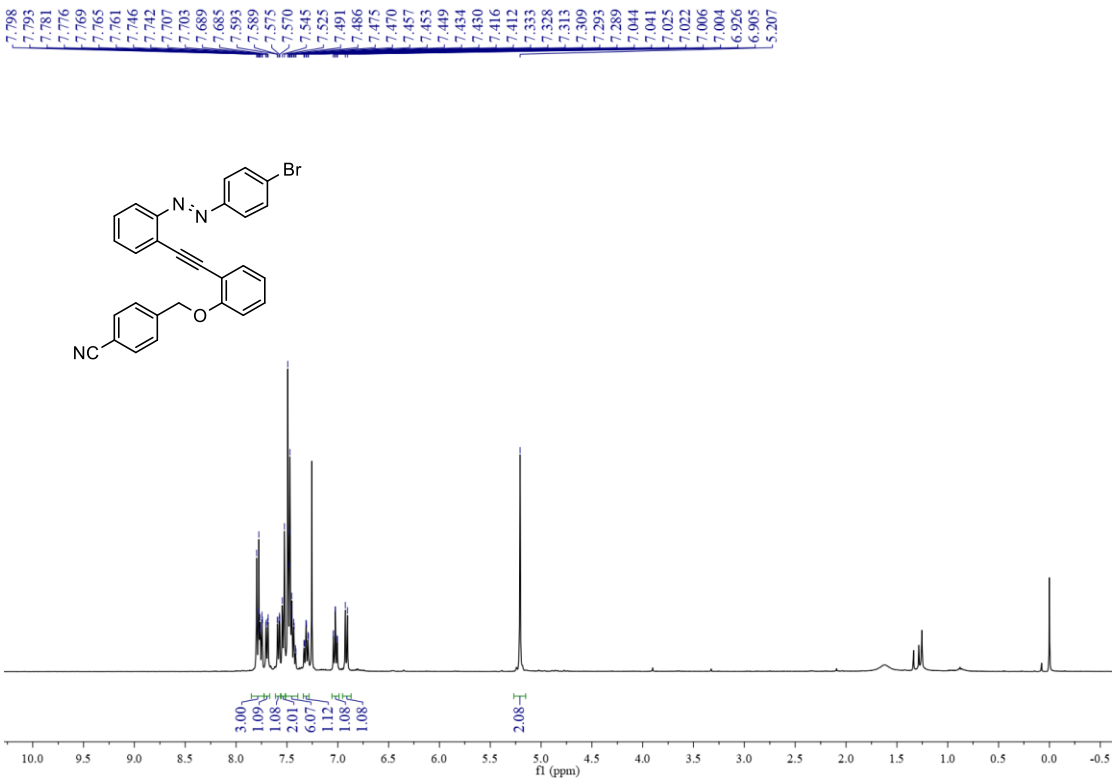
(E)-1-(4-bromophenyl)-2-(2-((2-((4-(trifluoromethyl)benzyl)oxy)phenyl)ethynyl)phenyl)diazene (1g)

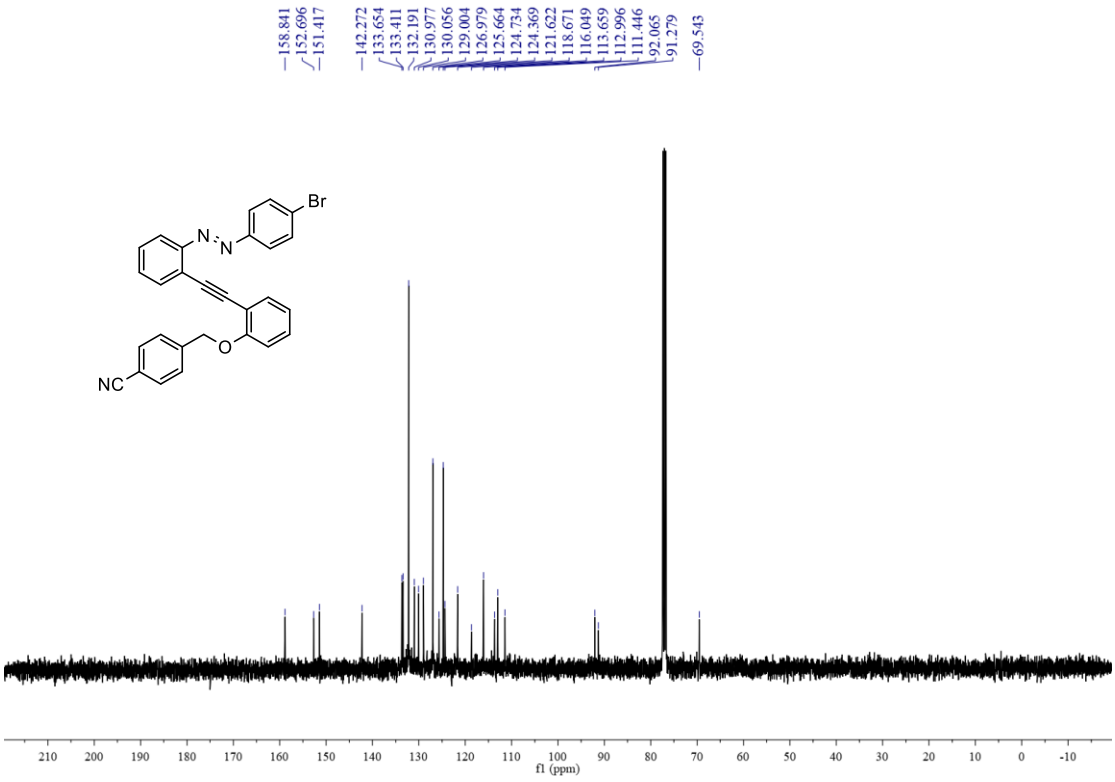




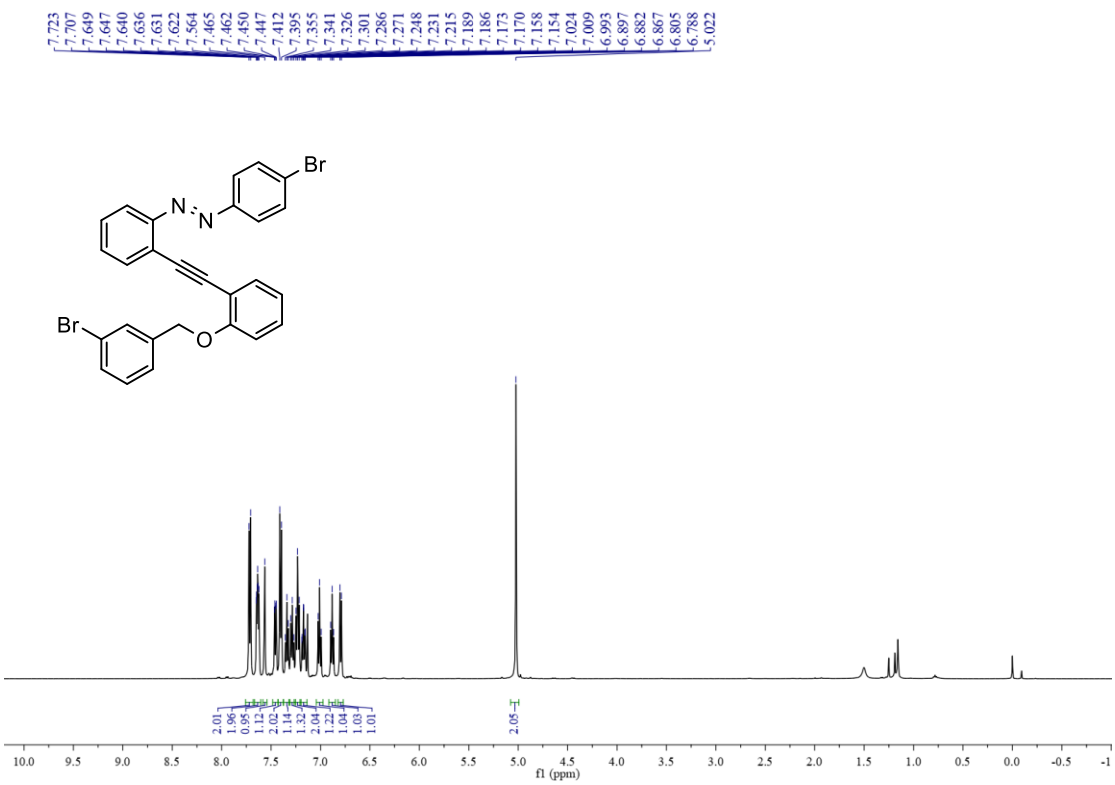

-62.501
Br
N
N
O
F3C
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

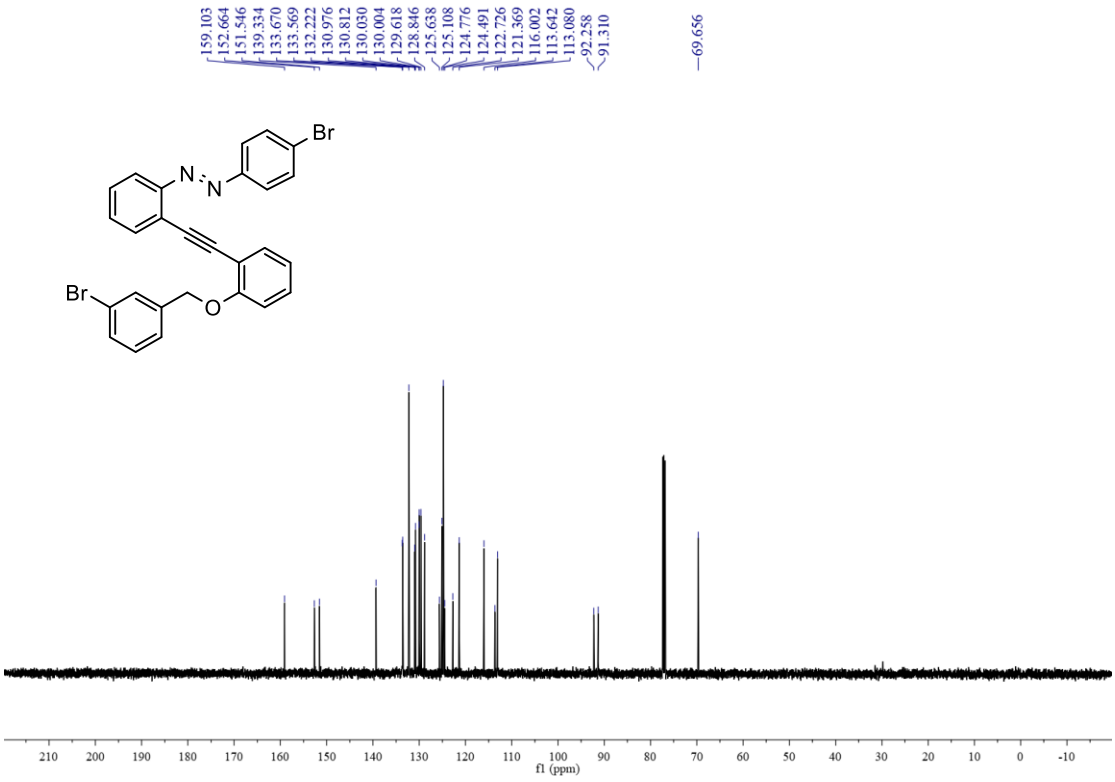
(E)-4-((2-((2-((4-bromophenyl)diazenyl)phenyl)ethynyl)phenoxy)methyl)benzonitrile (1h)



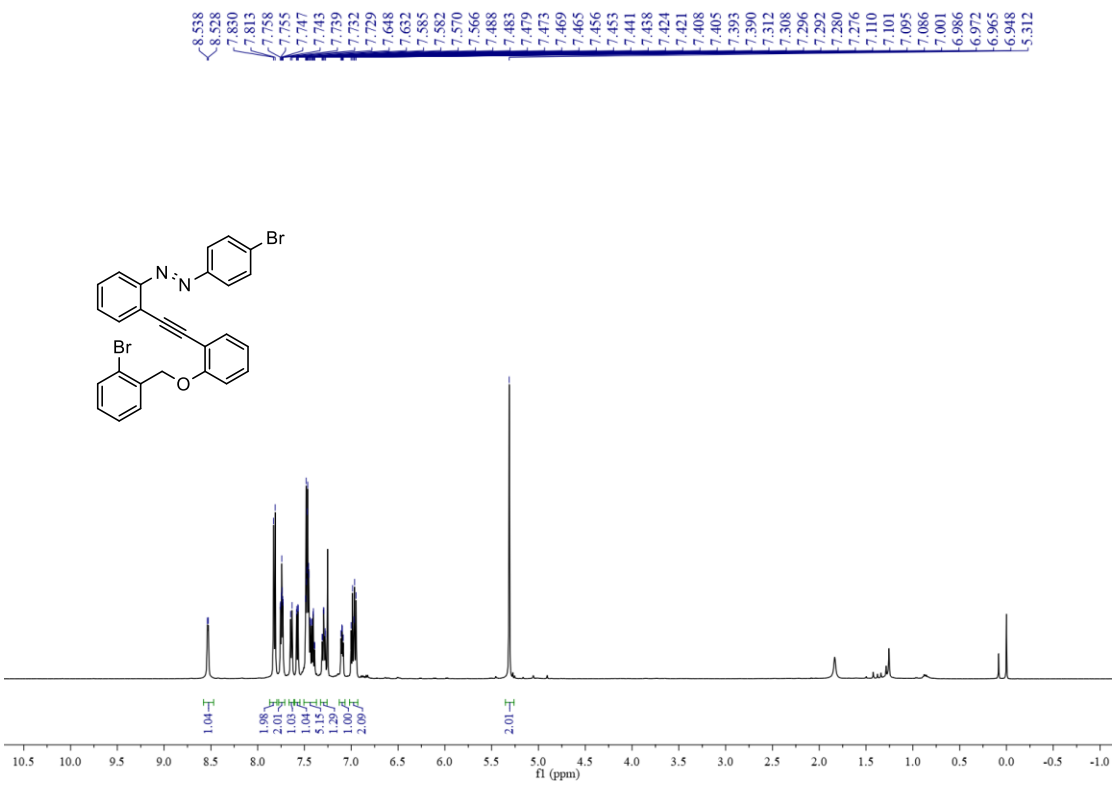


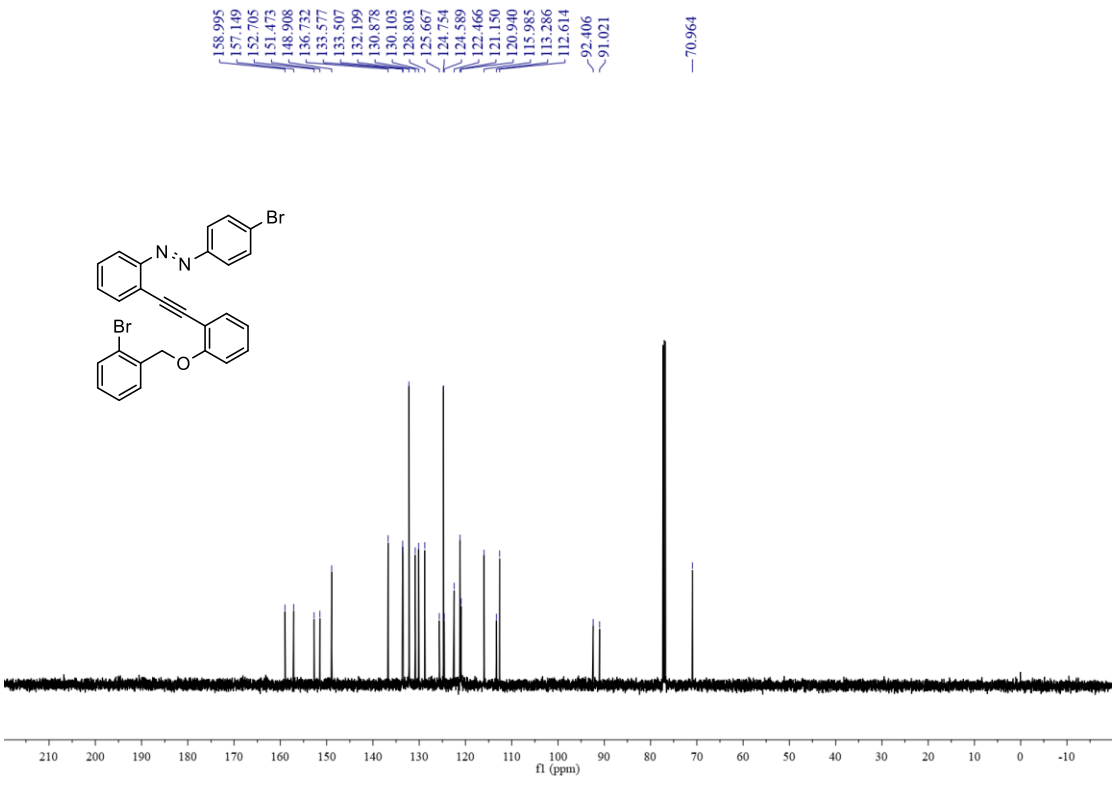
(E)-1-(2-((2-((3-bromobenzyl)oxy)phenyl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (1i)



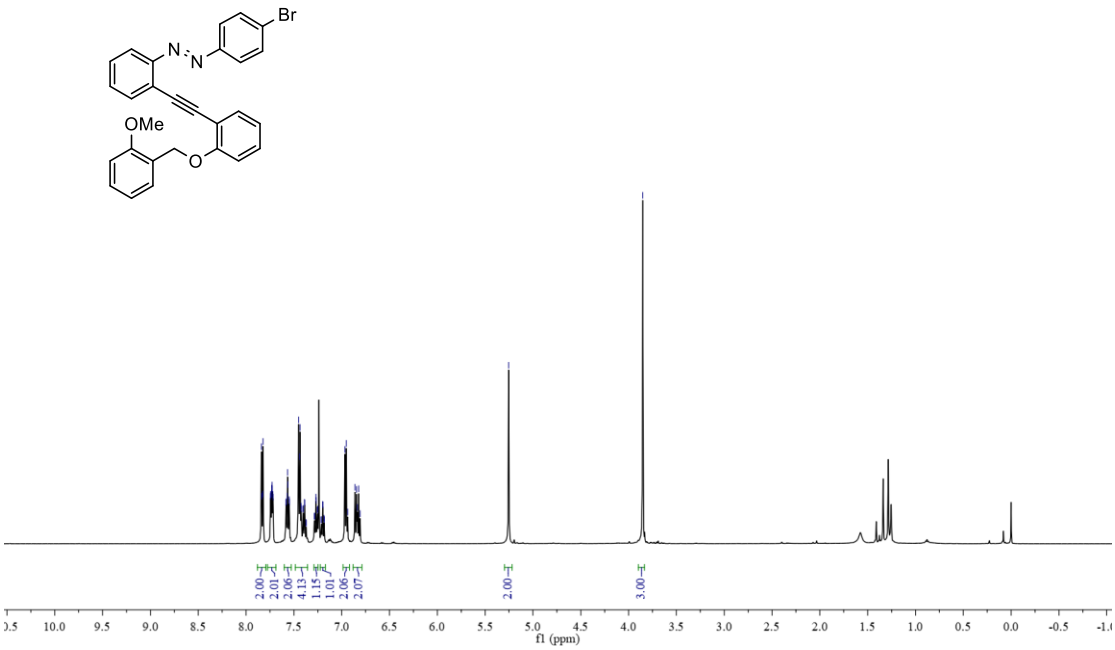


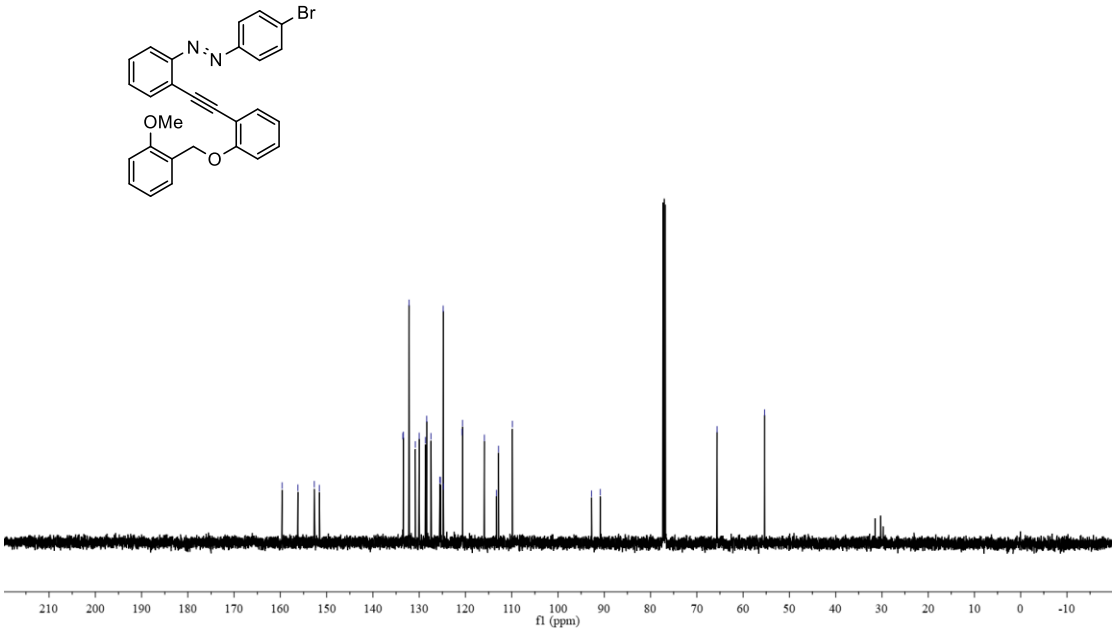
(E)-1-(2-((2-((2-bromobenzyl)oxy)phenyl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (1j)



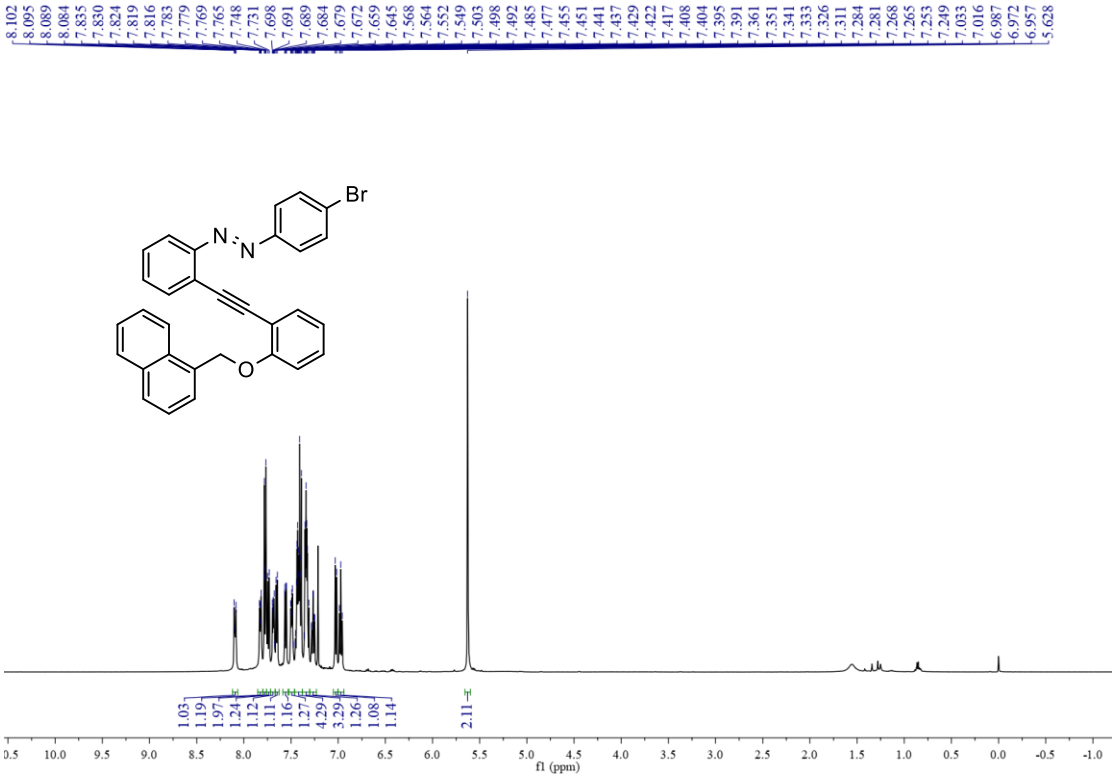


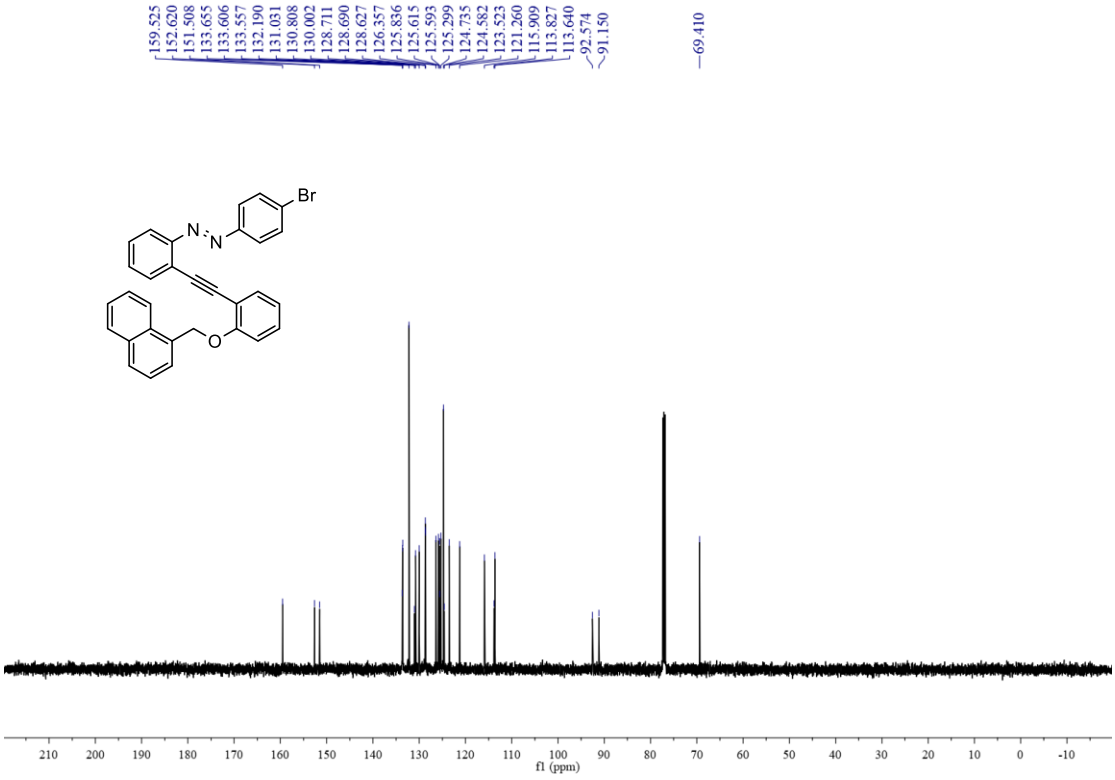
(E)-1-(4-bromophenyl)-2-(2-((2-((2-methoxybenzyl)oxy)phenyl)ethynyl)phenyl)diazene (1k)



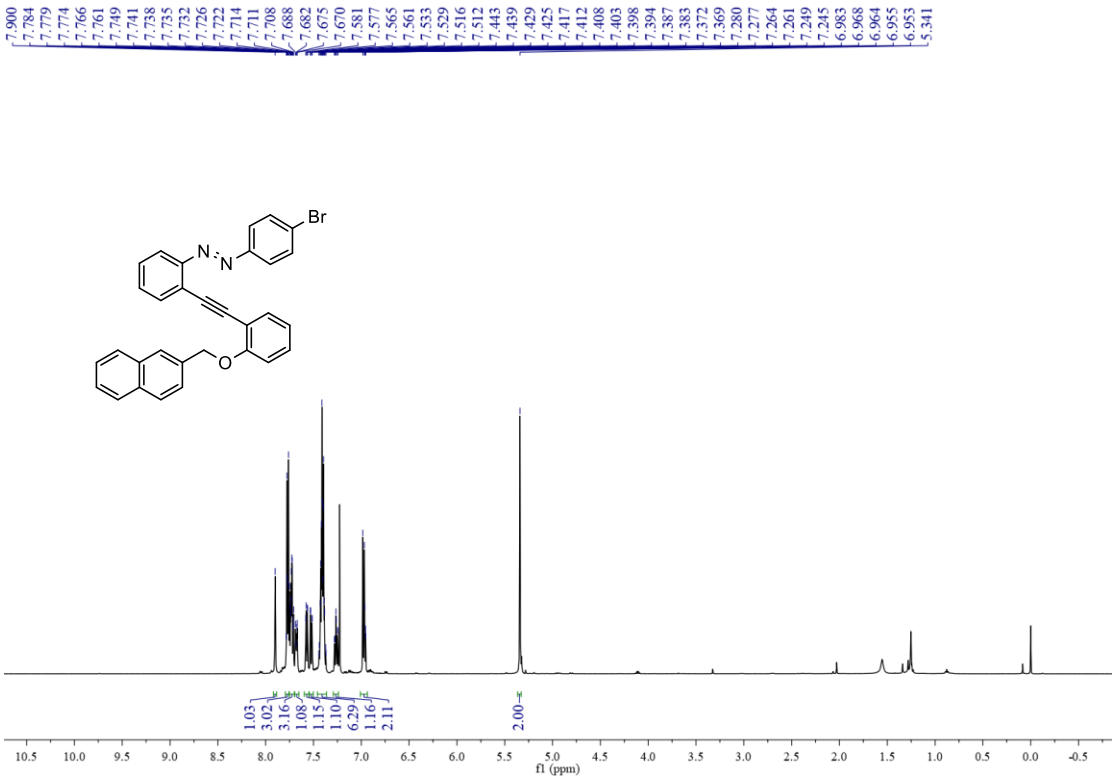


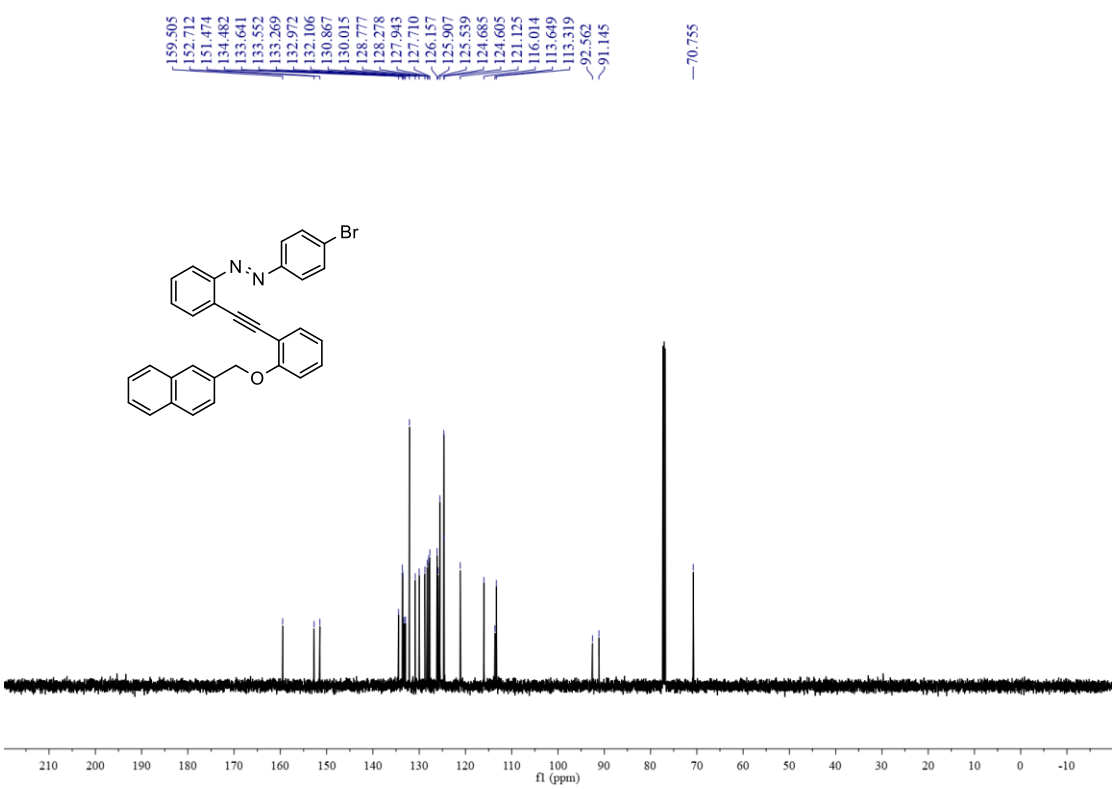
(E)-1-(4-bromophenyl)-2-(2-((2-(naphthalen-1-ylmethoxy)phenyl)ethynyl)phenyl)diazene (1l)



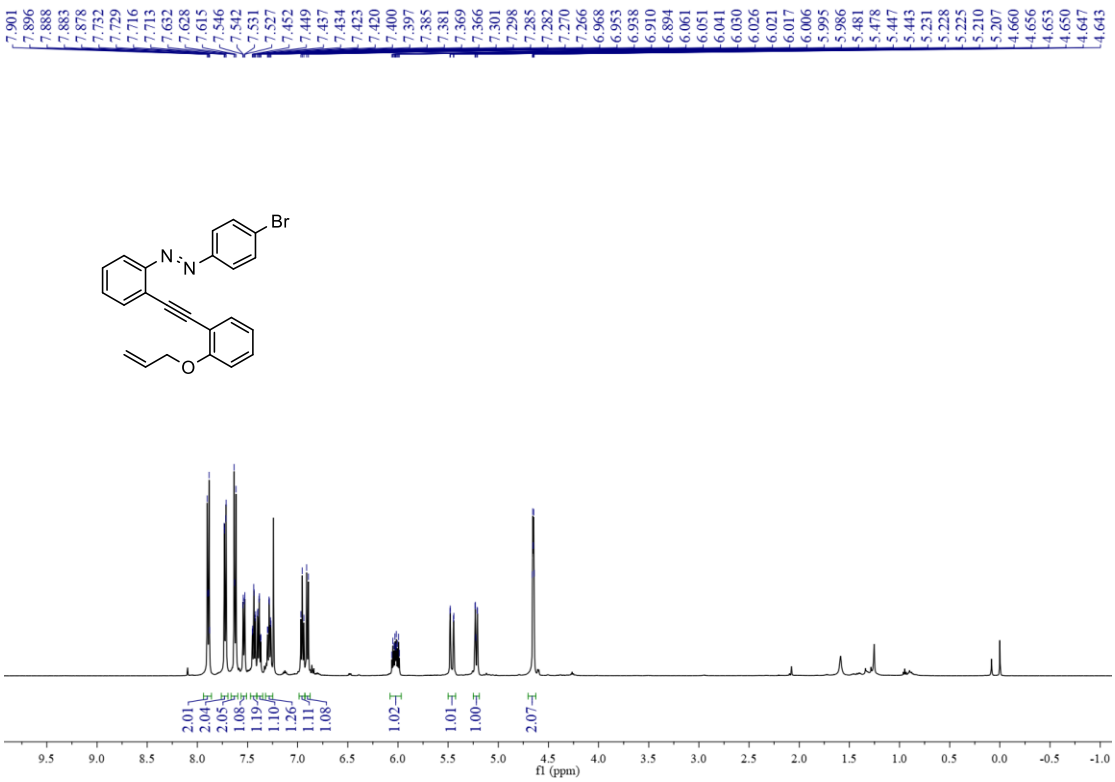


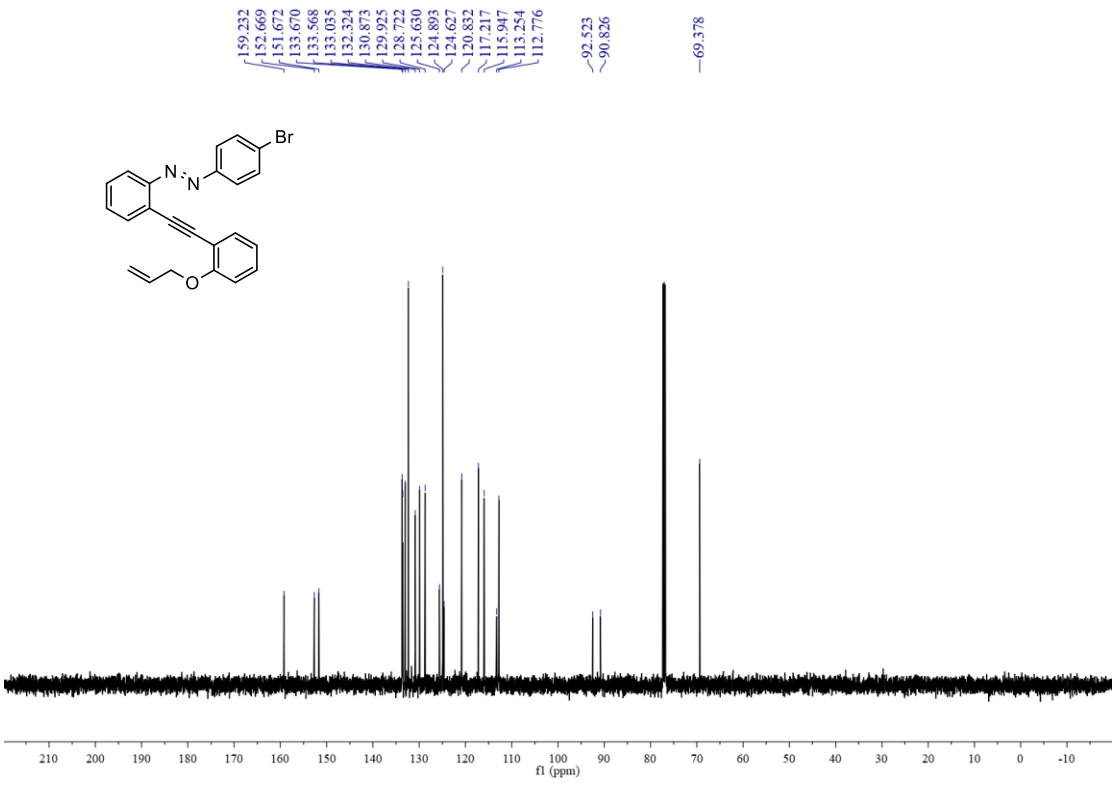
(E)-1-(4-bromophenyl)-2-(2-((2-(naphthalen-2-ylmethoxy)phenyl)ethynyl)phenyl)diazene (1m)



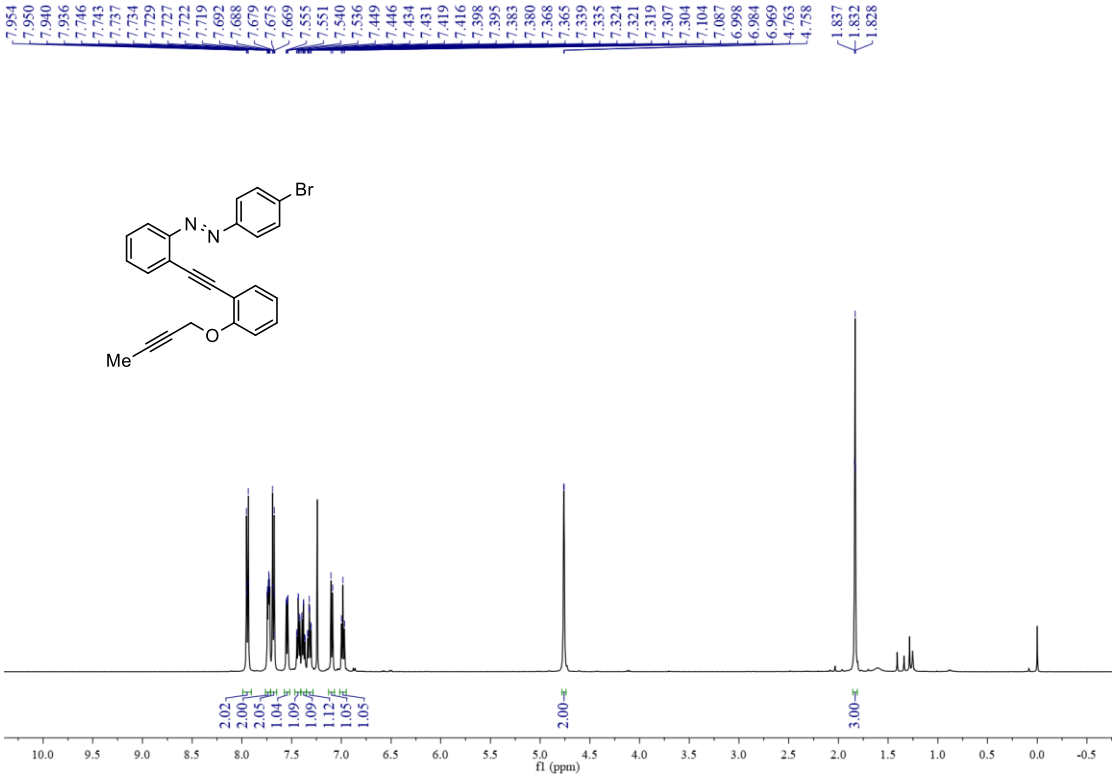


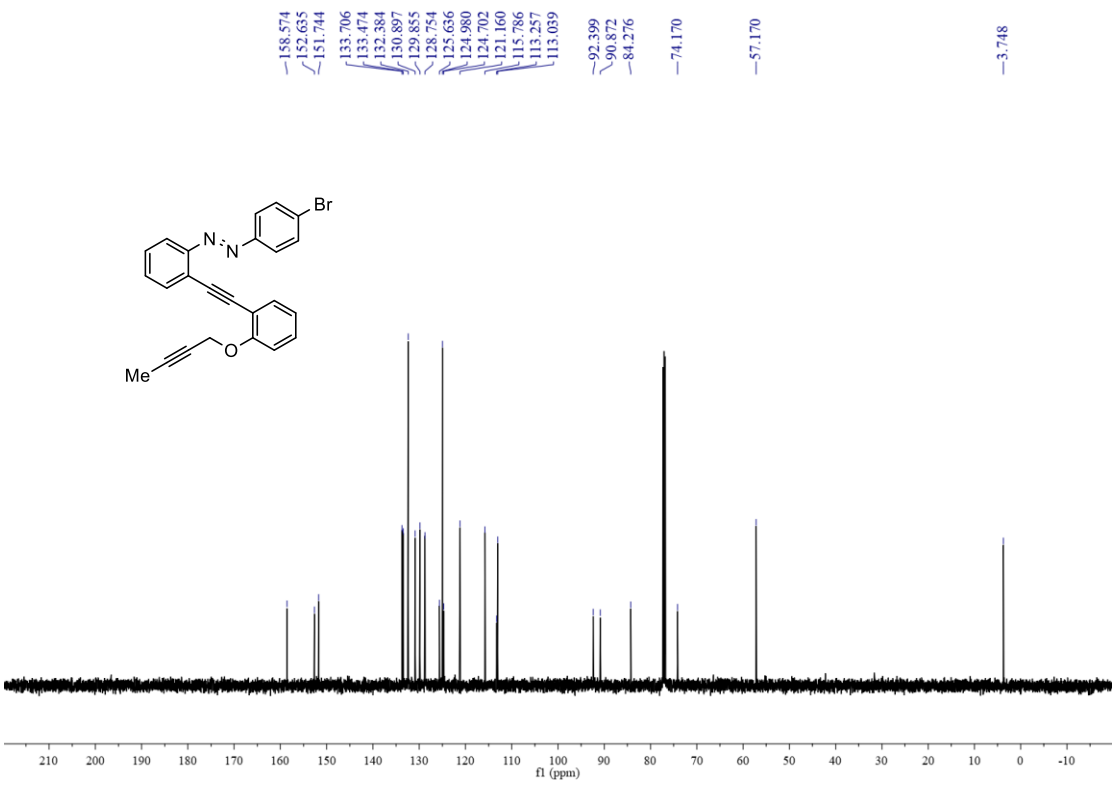
(E)-1-(2-((2-(allyloxy)phenyl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (1n)



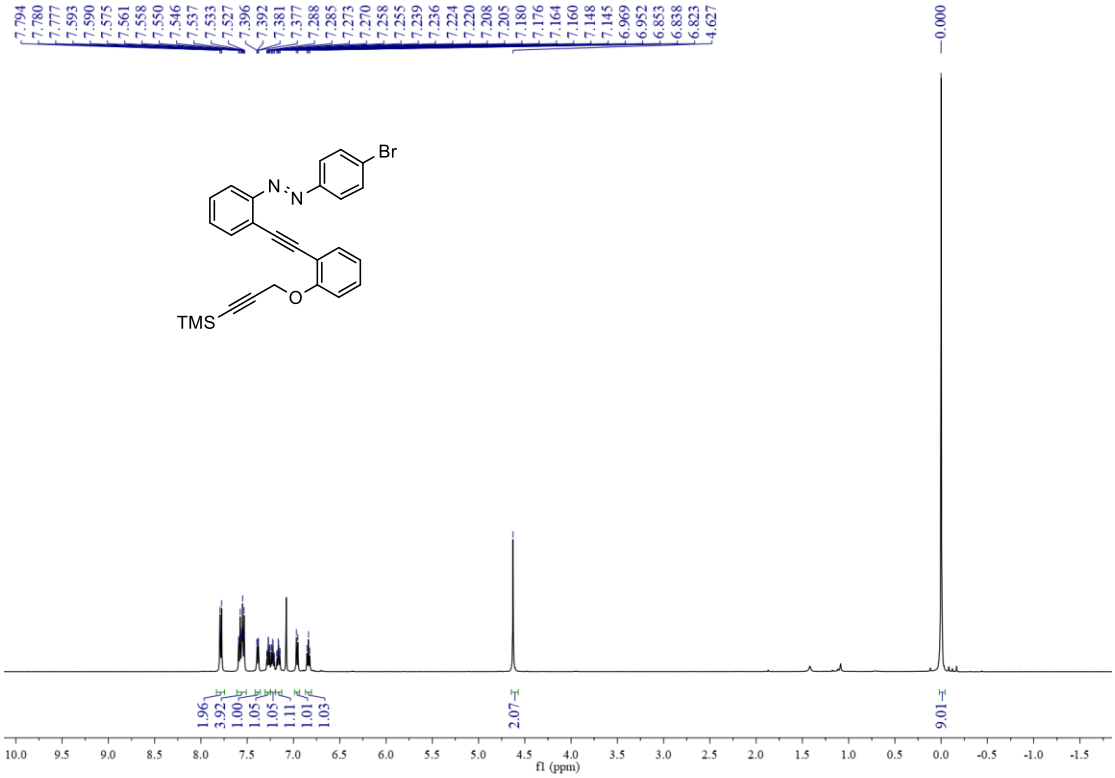


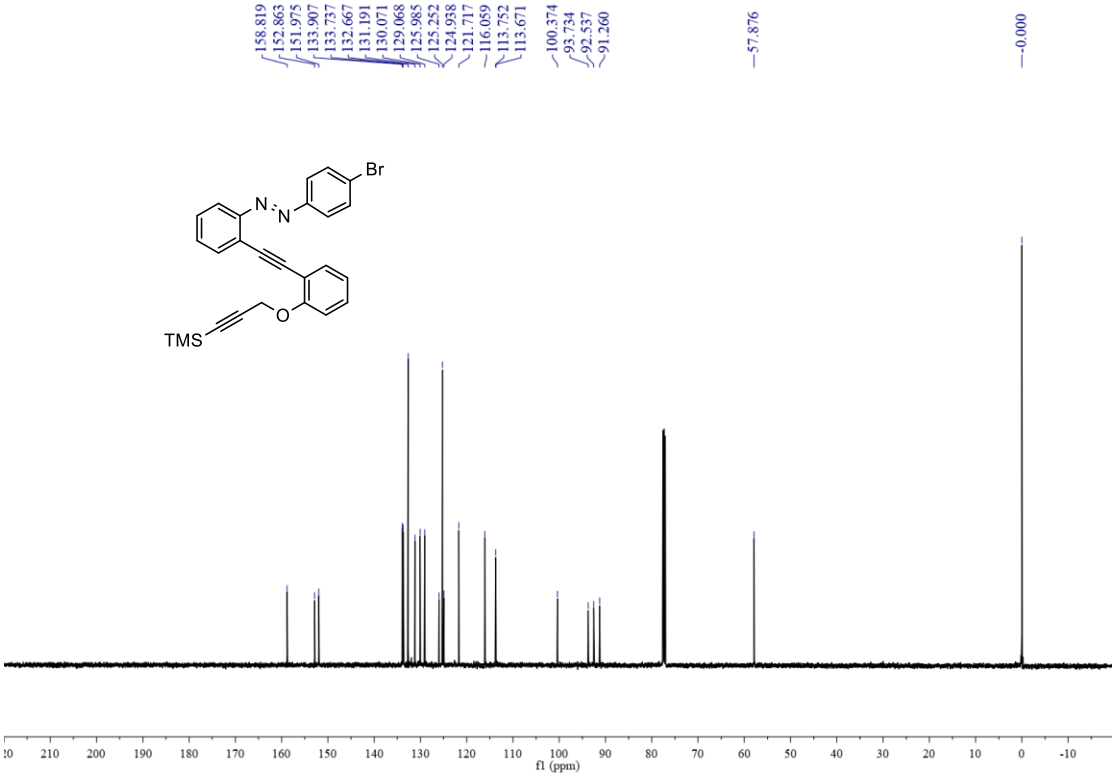
(E)-1-(4-bromophenyl)-2-(2-((2-(but-2-yn-1-yloxy)phenyl)ethynyl)phenyl)diazene (1o)



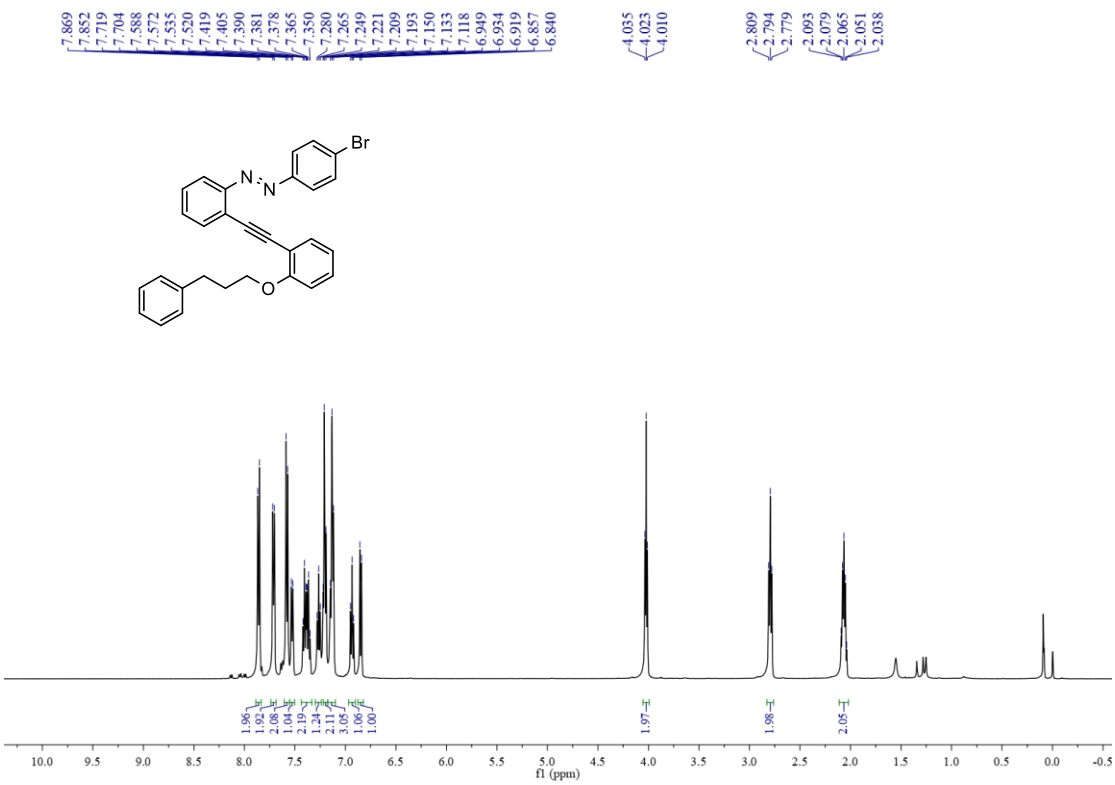


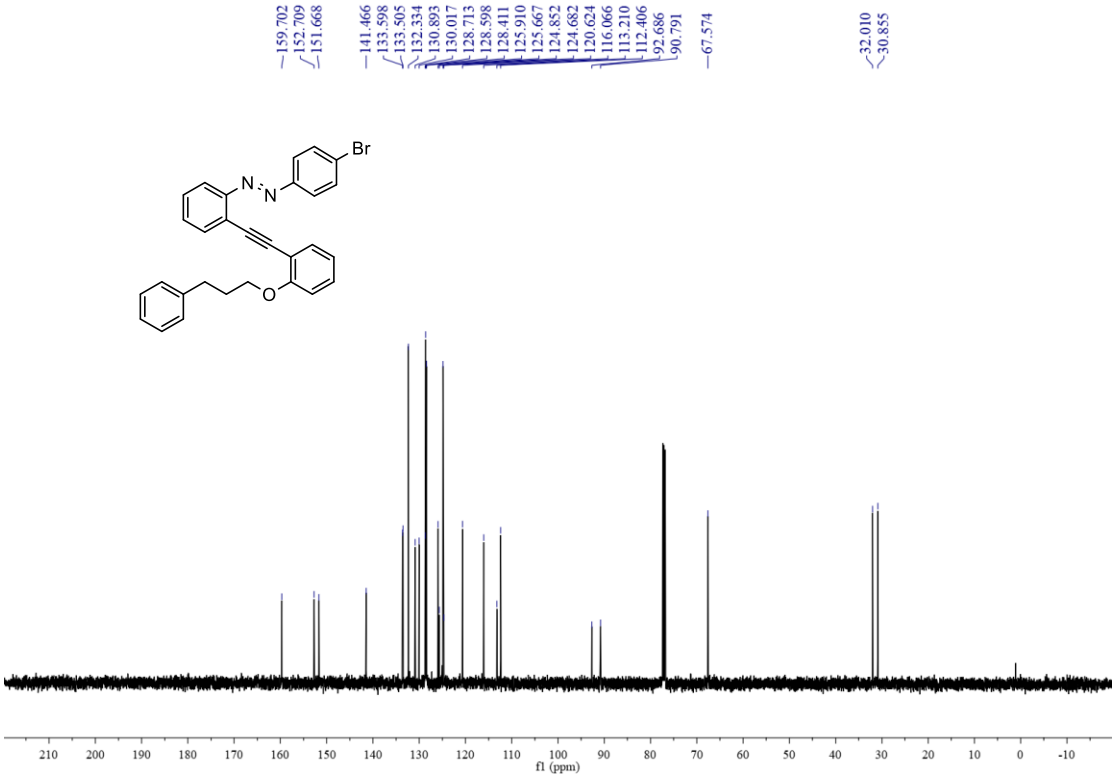
(E)-1-(4-bromophenyl)-2-(2-(2-((3-(trimethylsilyl)prop-2-yn-1-yl)oxy)phenyl)ethynyl)phenyl)-diazene (1p)



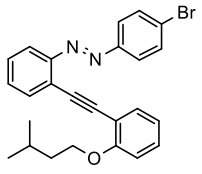


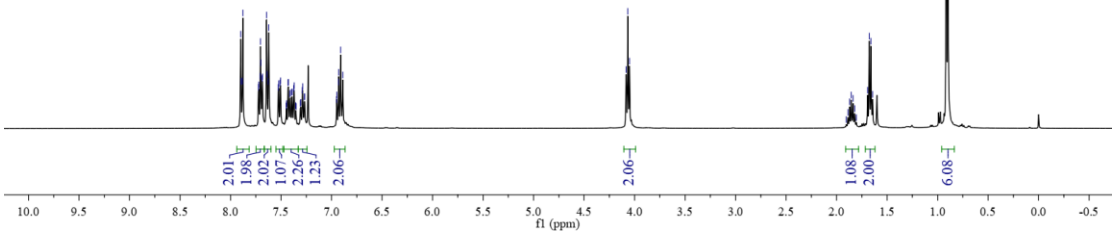
(E)-1-(4-bromophenyl)-2-(2-((2-(3-phenylpropoxy)phenyl)ethynyl)phenyl)diazene (1q)

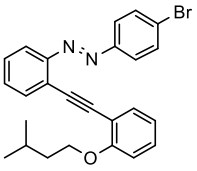


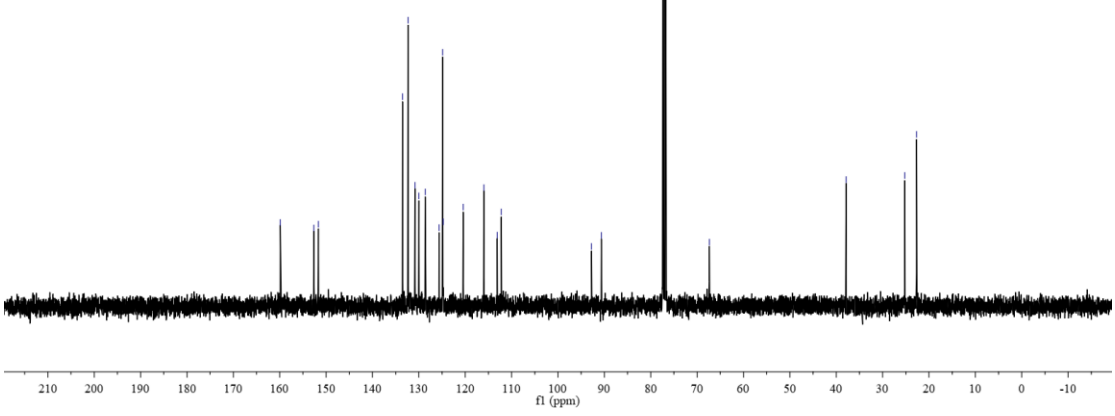


(E)-1-(4-bromophenyl)-2-(2-((2-(isopentyloxy)phenyl)ethynyl)phenyl)diazene (1r)

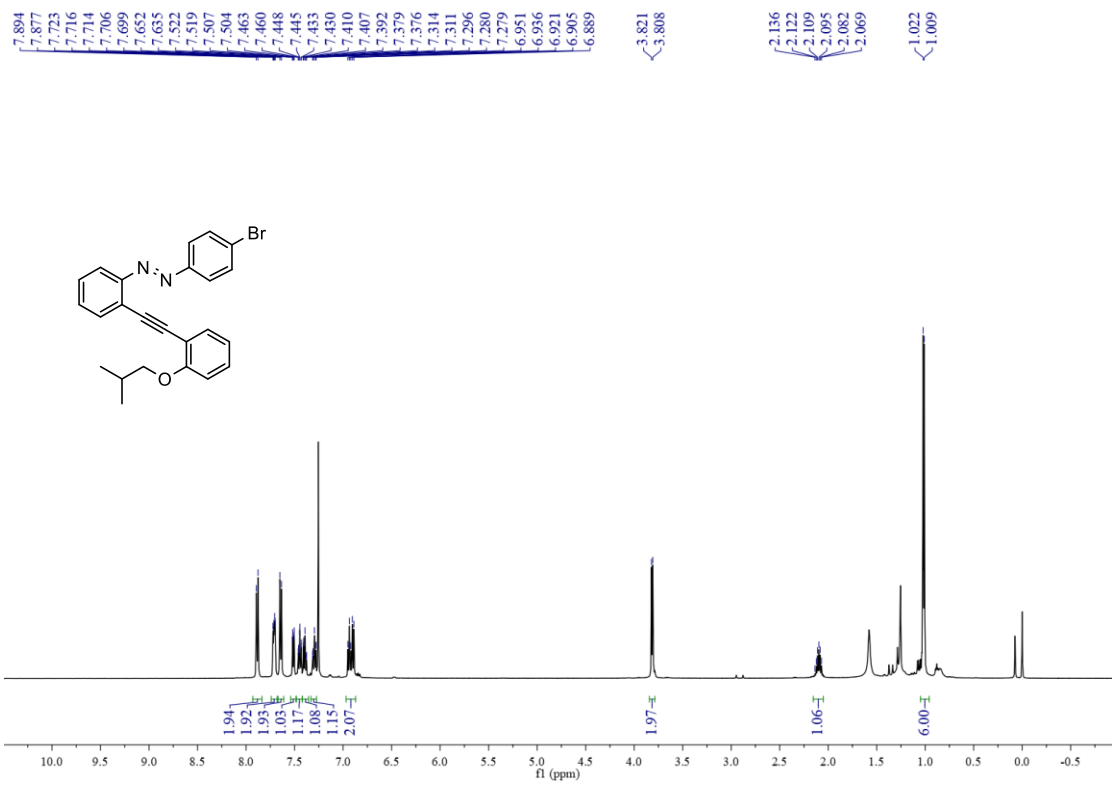


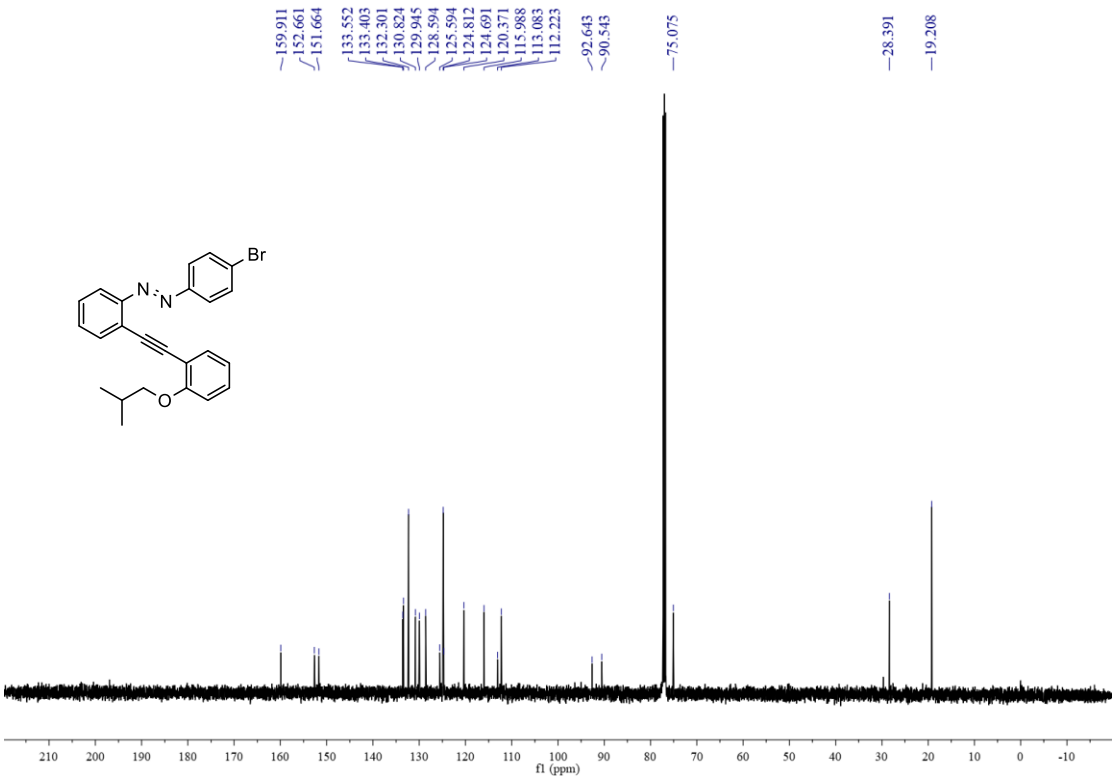




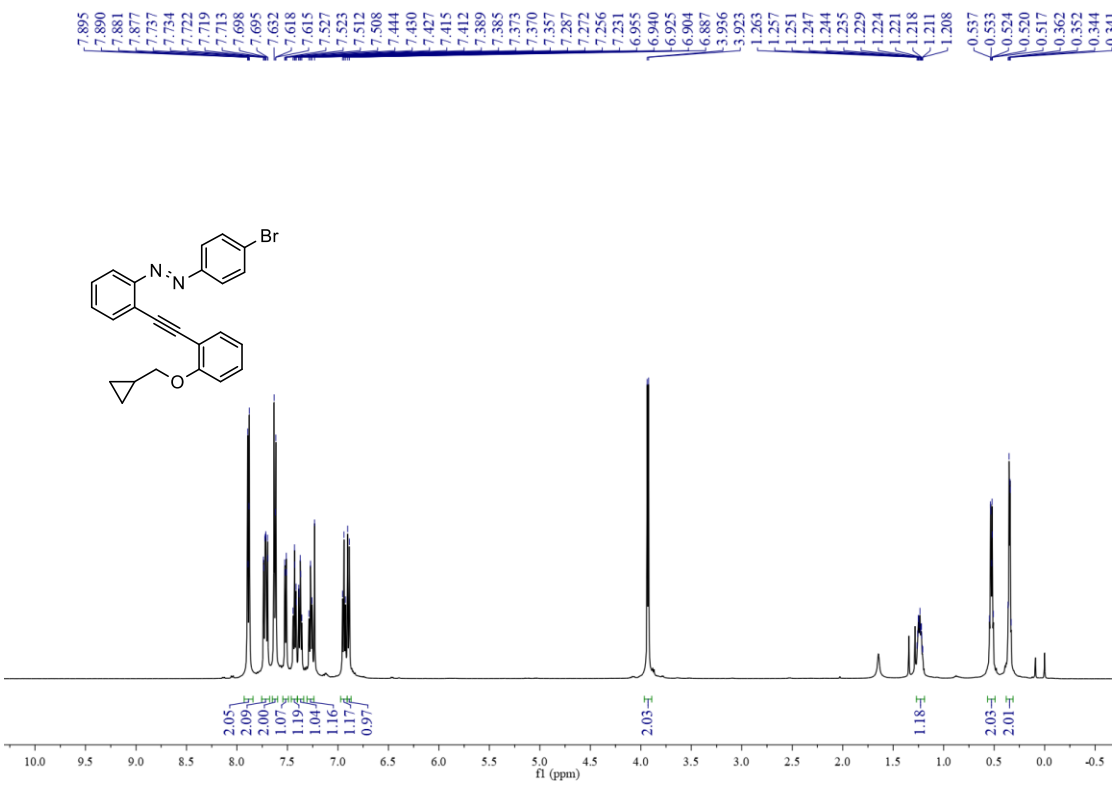


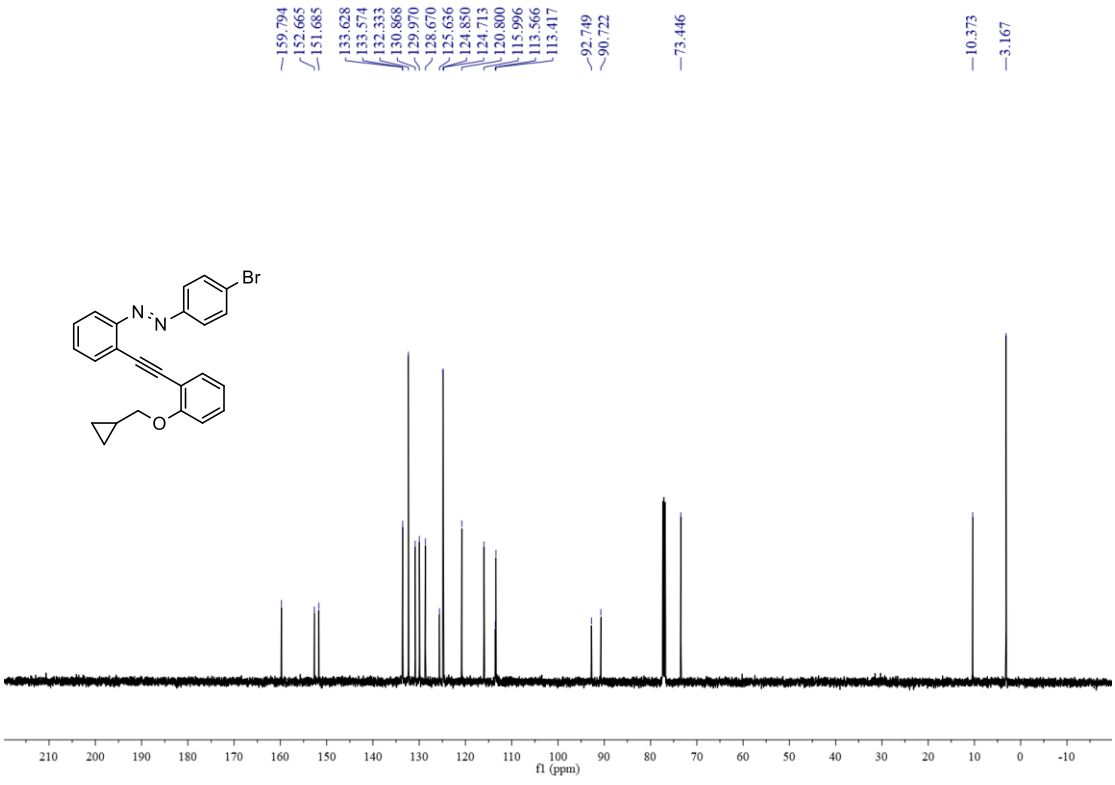
(E)-1-(4-bromophenyl)-2-(2-((2-isobutoxyphenyl)ethynyl)phenyl)diazene (1s)



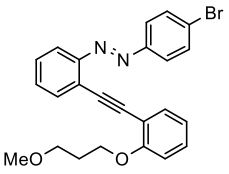


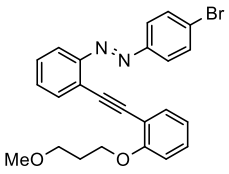
(E)-1-(4-bromophenyl)-2-(2-((2-(cyclopropylmethoxy)phenyl)ethynyl)phenyl)diazene (1t)

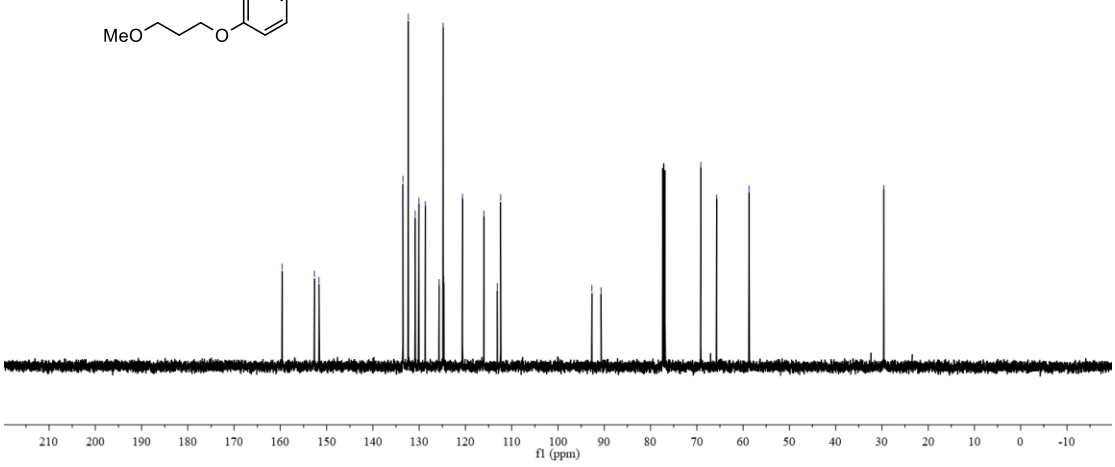




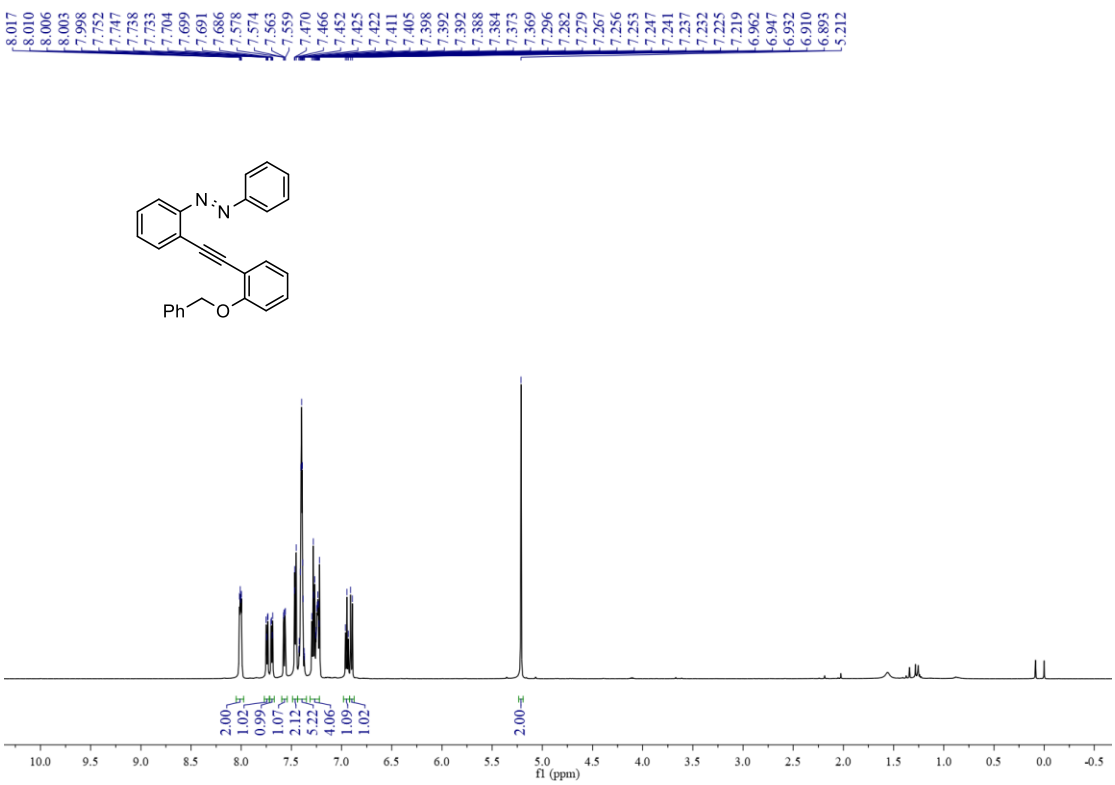
(E)-1-(4-bromophenyl)-2-(2-((2-(3-methoxypropoxy)phenyl)ethynyl)phenyl)diazene (1u)

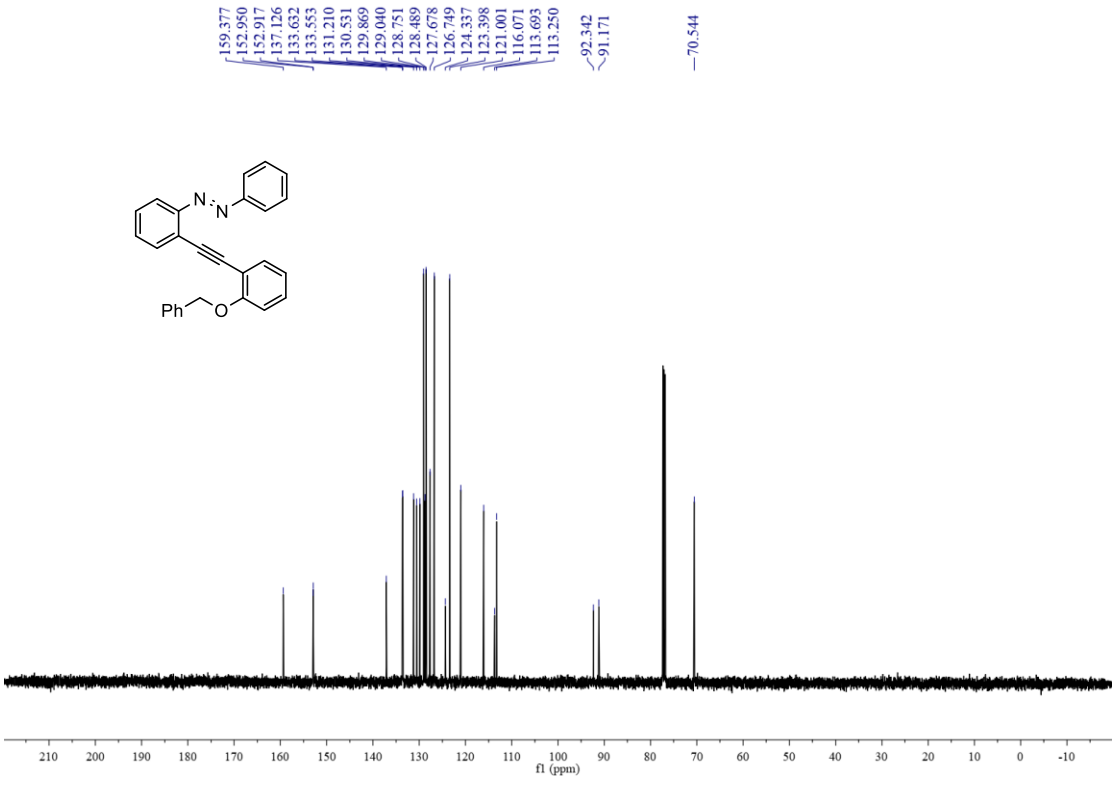




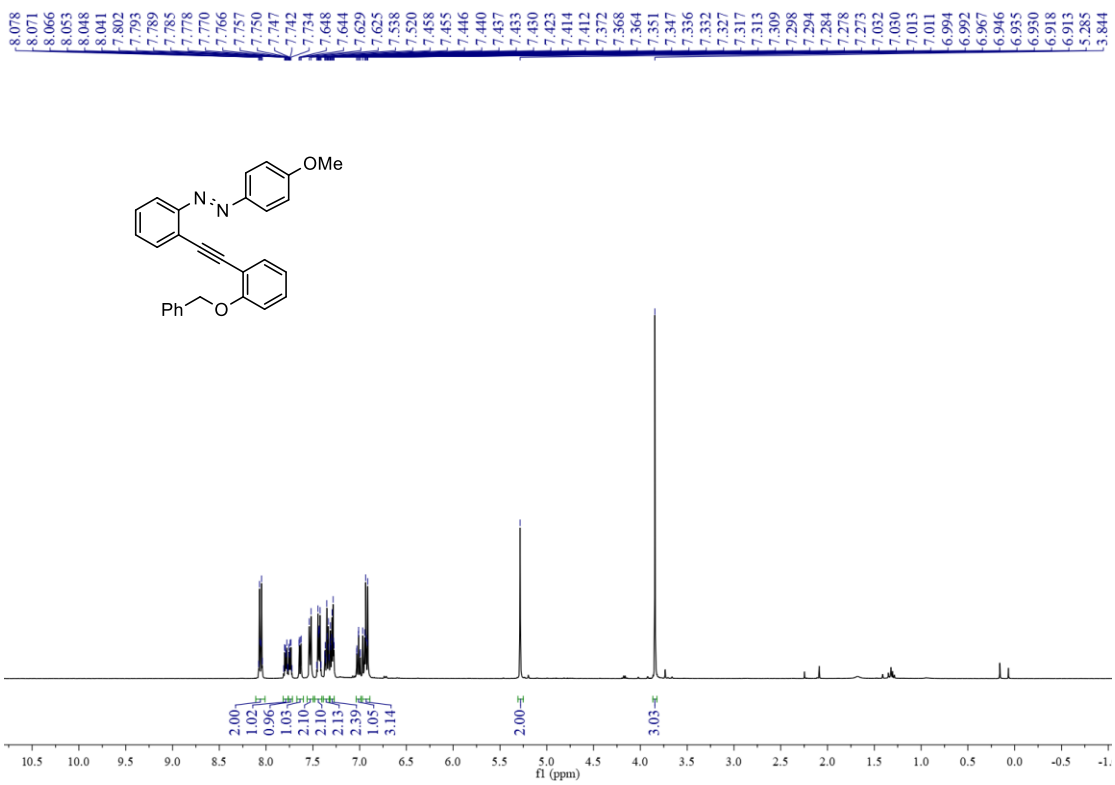


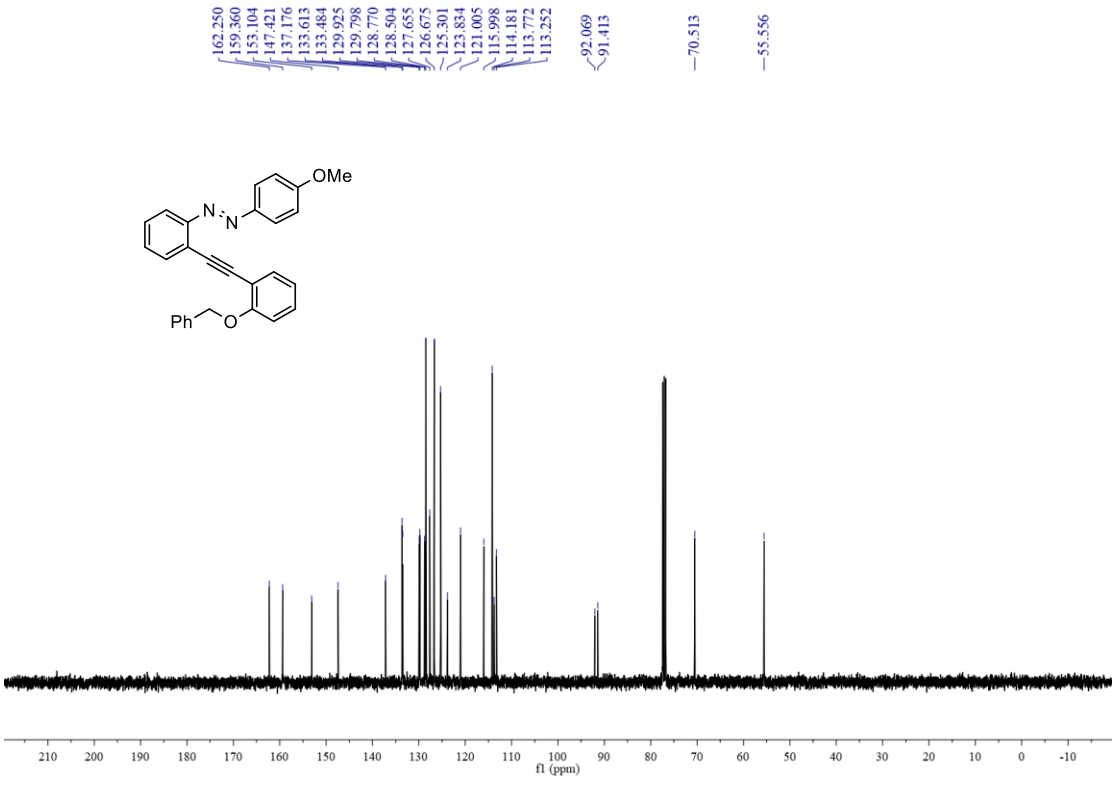
(E)-1-(2-((2-(benzyloxy)phenyl)ethynyl)phenyl)-2-phenyldiazene (1v)



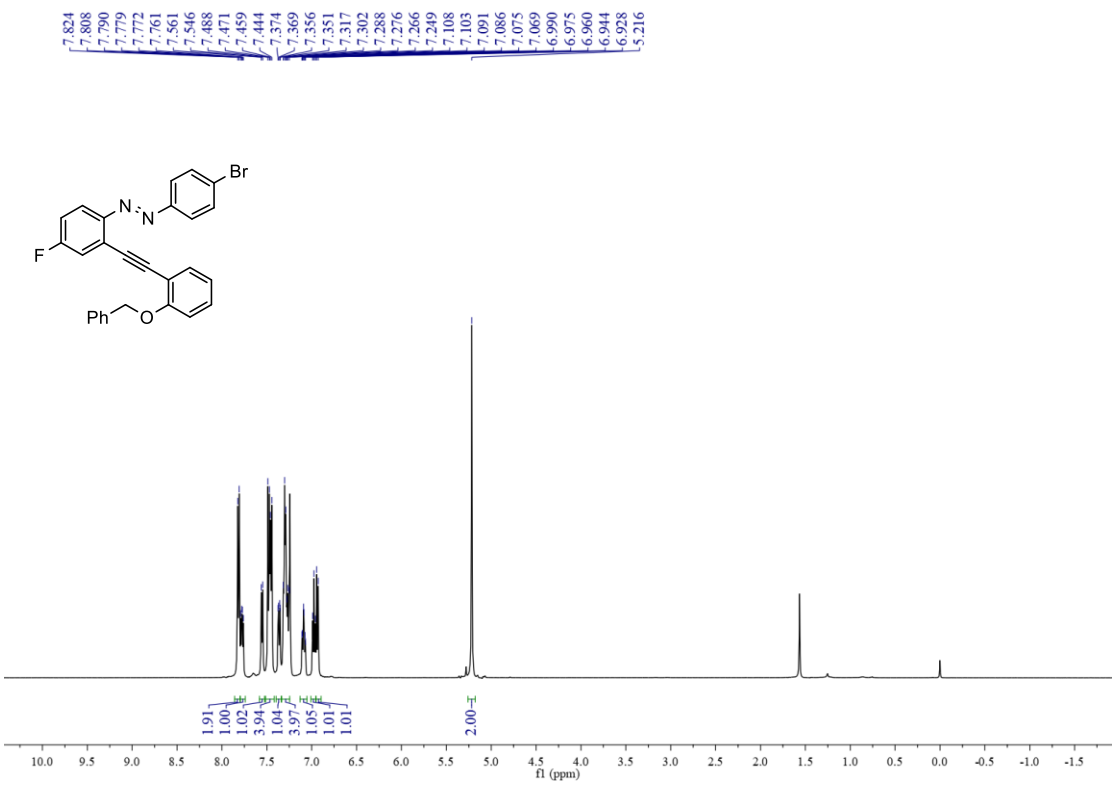


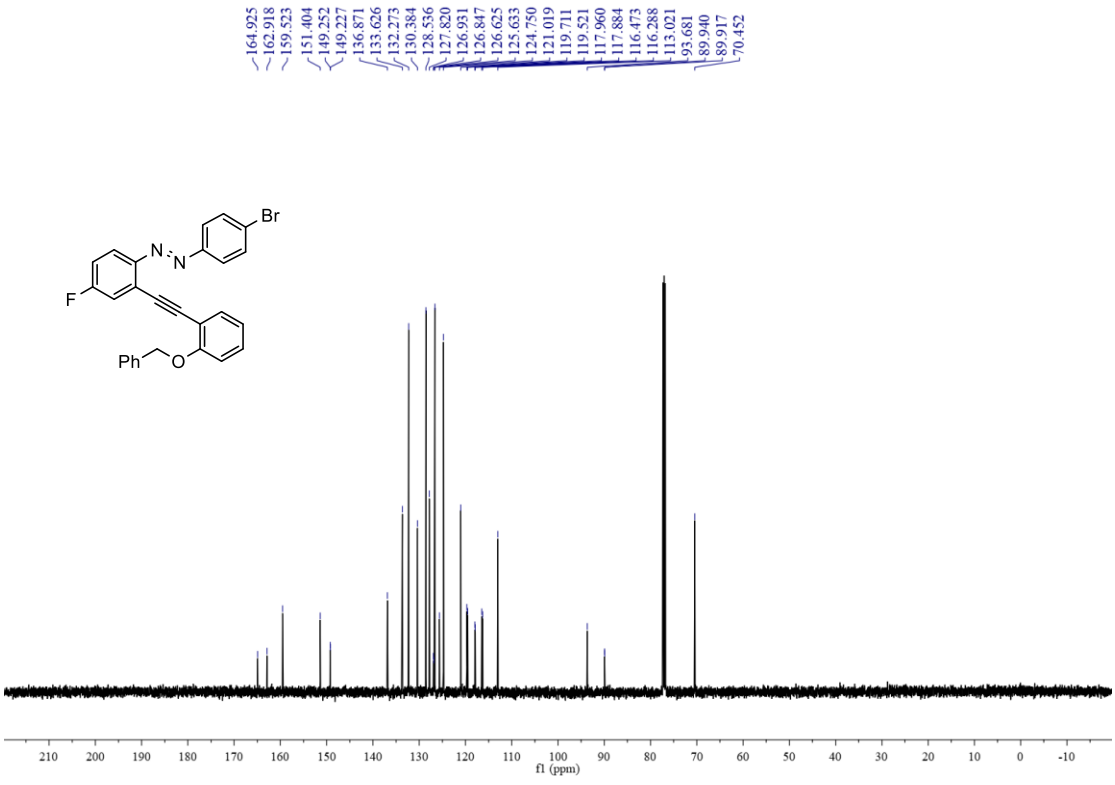
(E)-1-(2-((2-(benzyloxy)phenyl)ethynyl)phenyl)-2-(4-methoxyphenyl)diazene (1w)





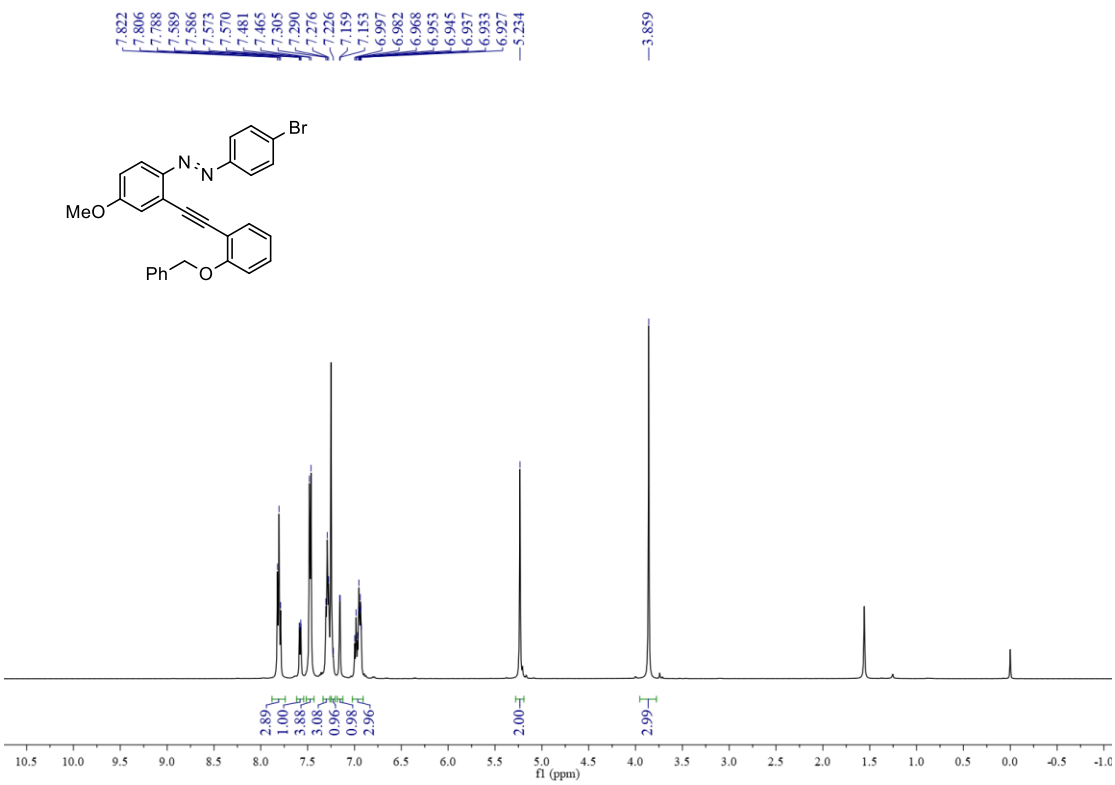
(E)-1-(2-((2-(benzyloxy)phenyl)ethynyl)-4-fluorophenyl)-2-(4-bromophenyl)diazene (1x)

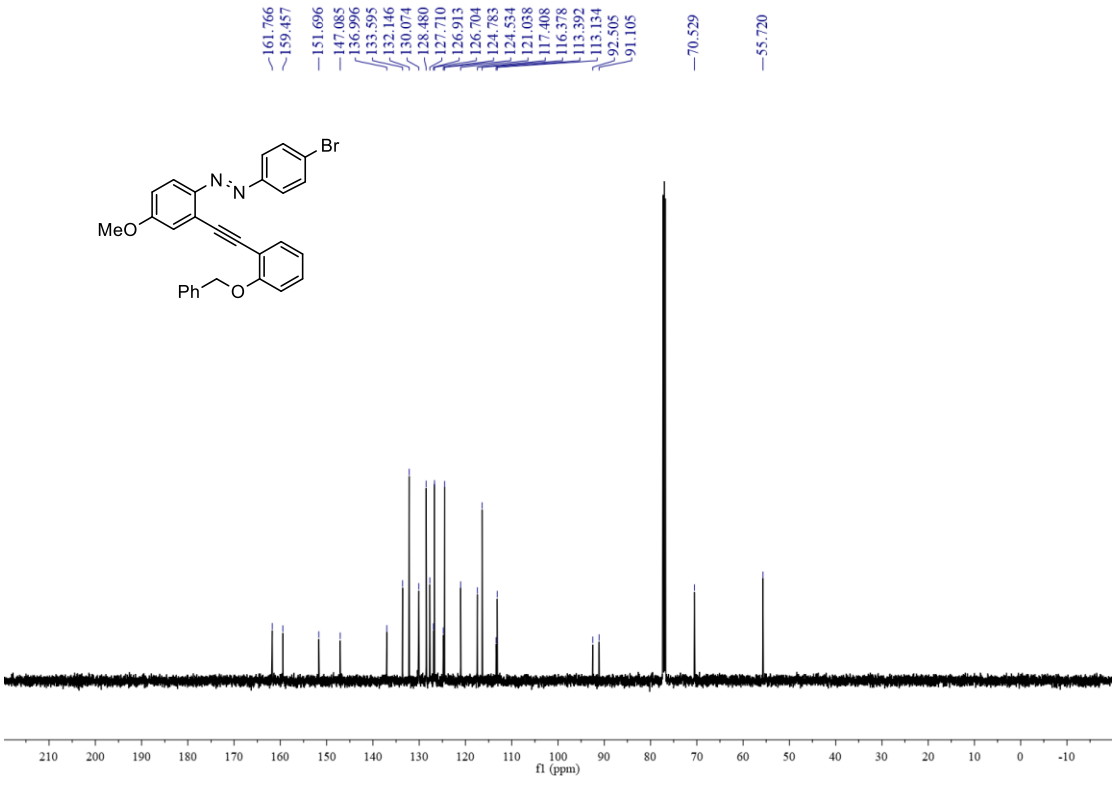




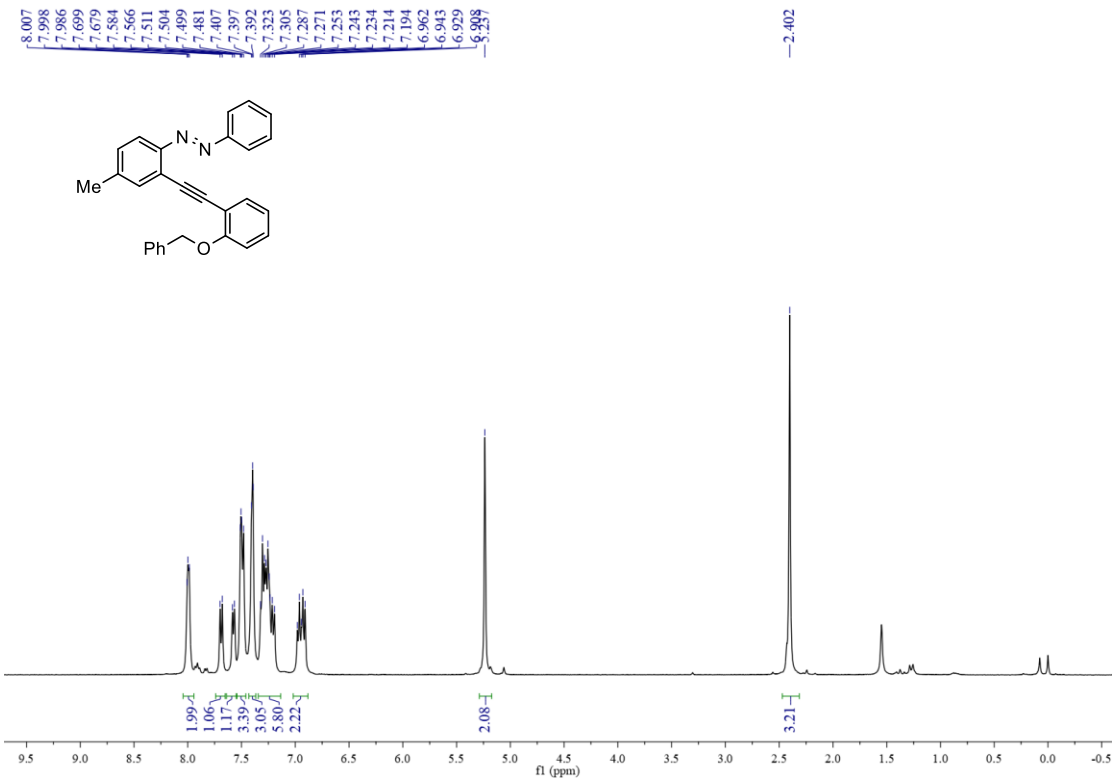

-109.398
Br
N
N
F
Ph
O
f1 (ppm)

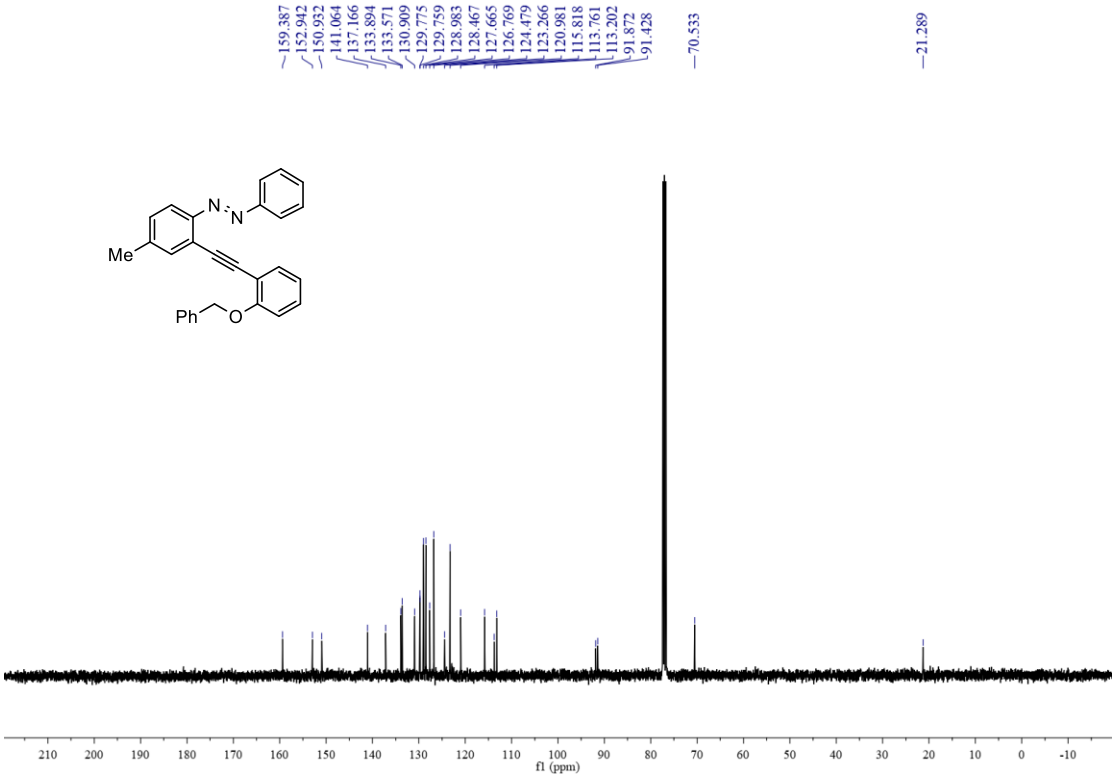
(E)-1-(2-((2-(benzyloxy)phenyl)ethynyl)-4-methoxyphenyl)-2-(4-bromophenyl)diazene (1y)



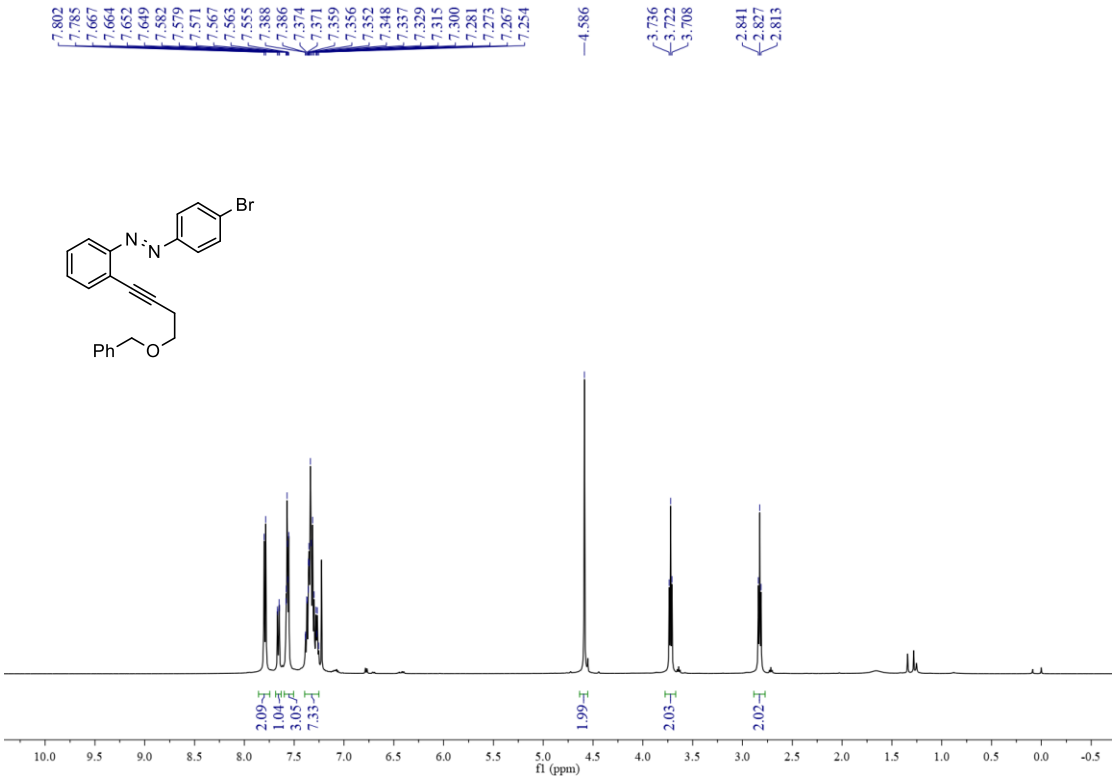


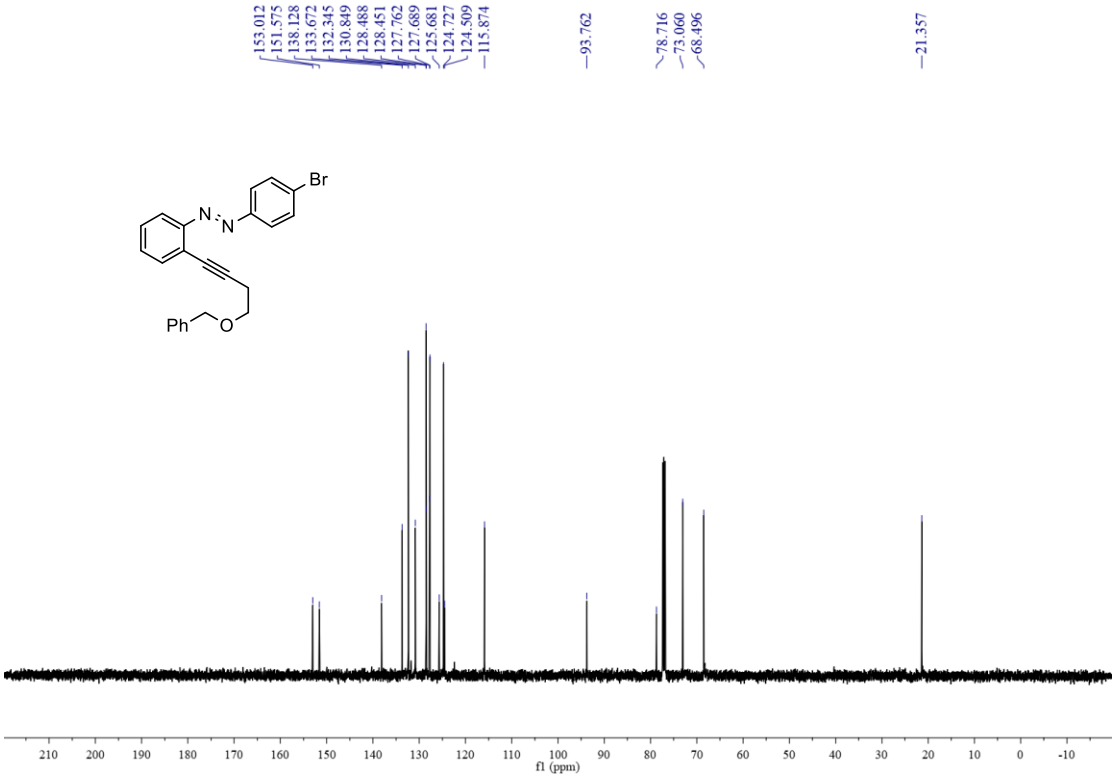
(E)-1-(2-((2-(benzyloxy)phenyl)ethynyl)-4-methylphenyl)-2-phenyldiazene (1z)



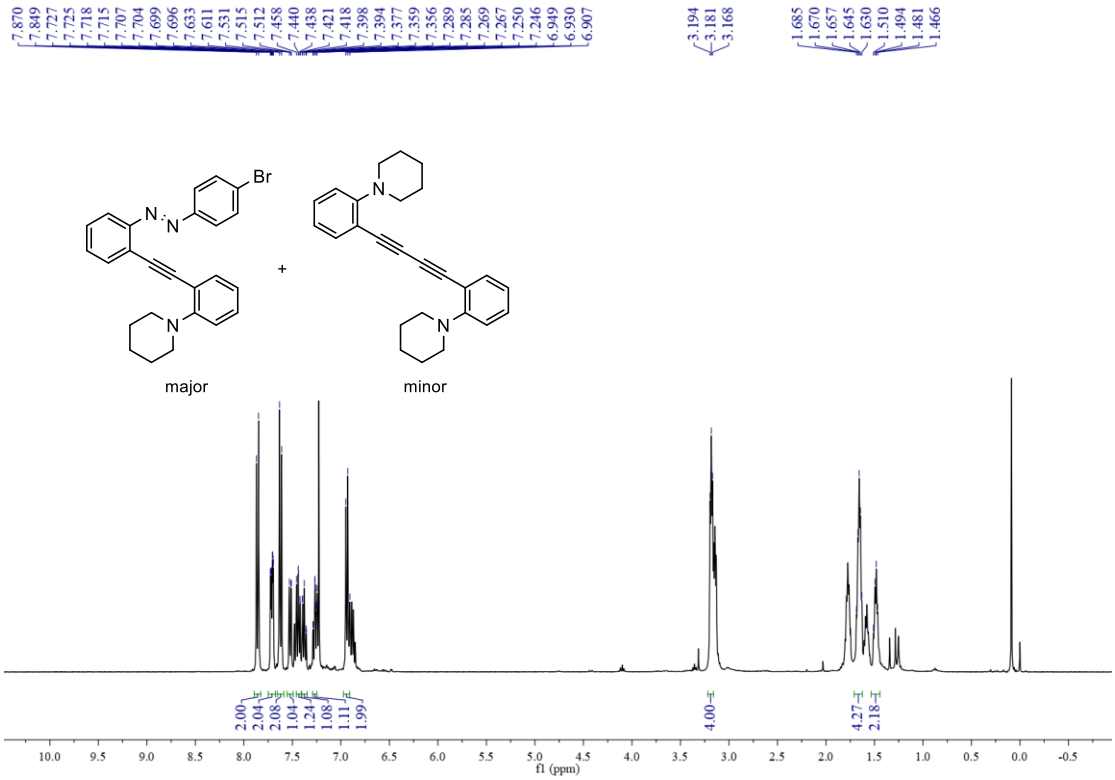


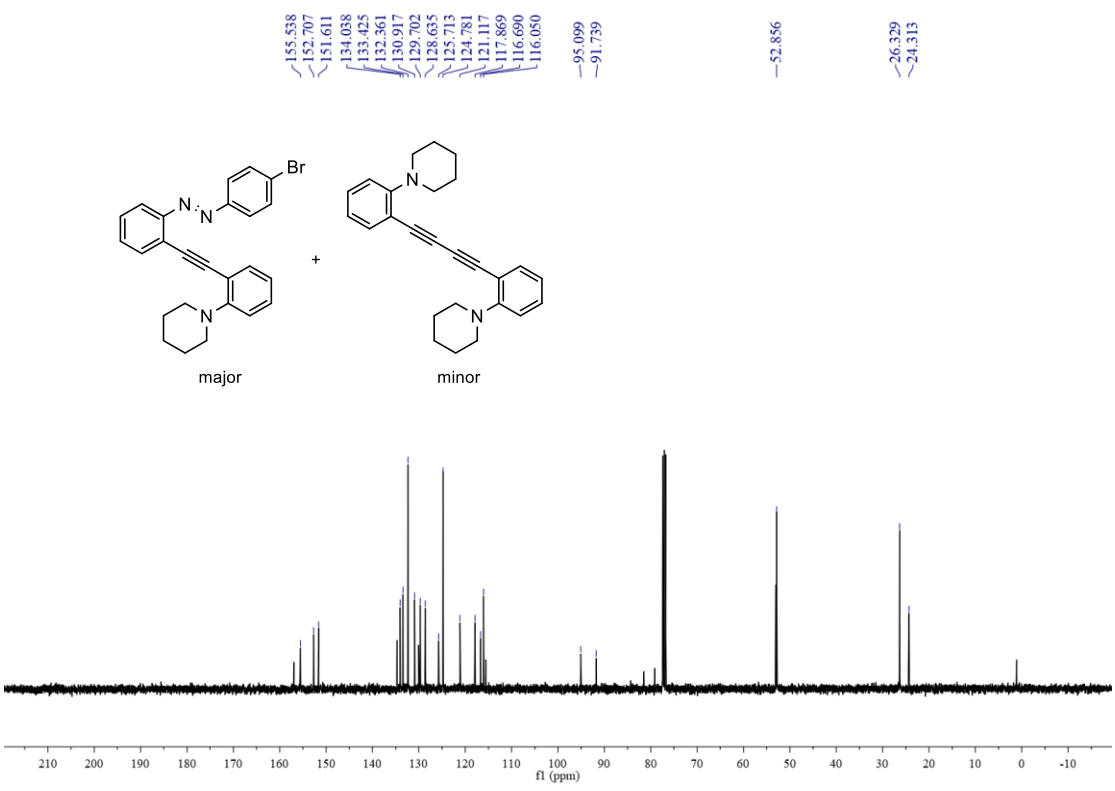
(E)-1-(2-(4-(benzyloxy)but-1-yn-1-yl)phenyl)-2-(4-bromophenyl)diazene (1aa)

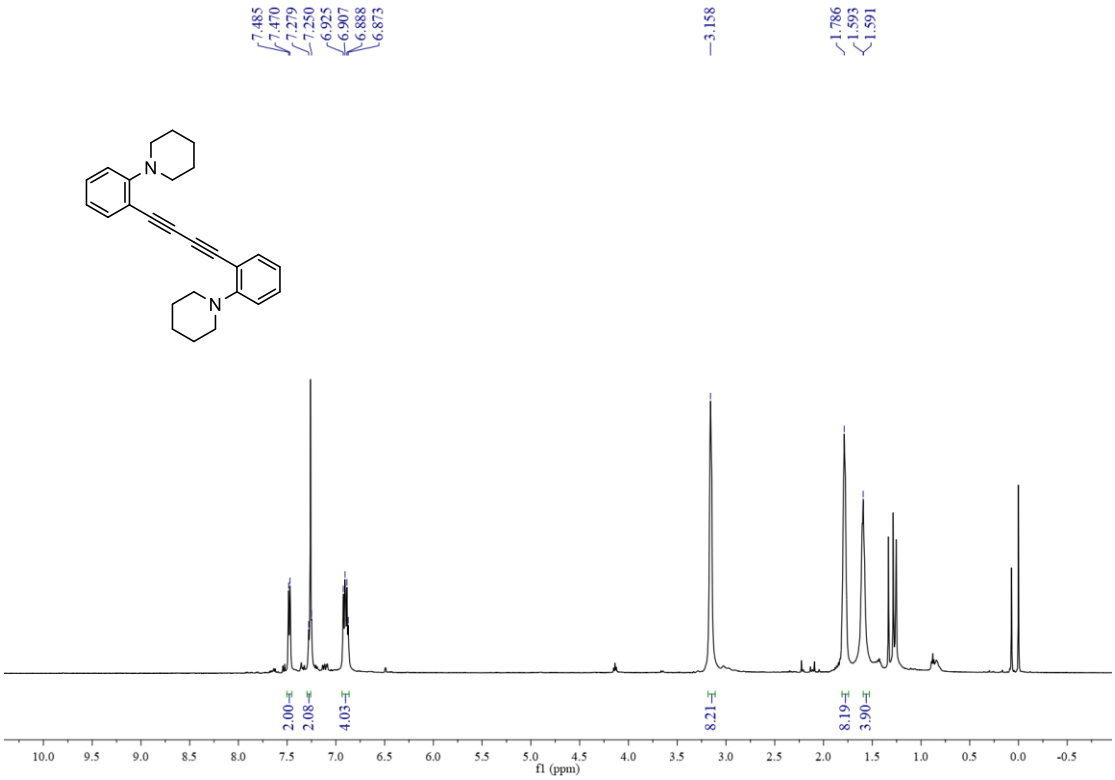


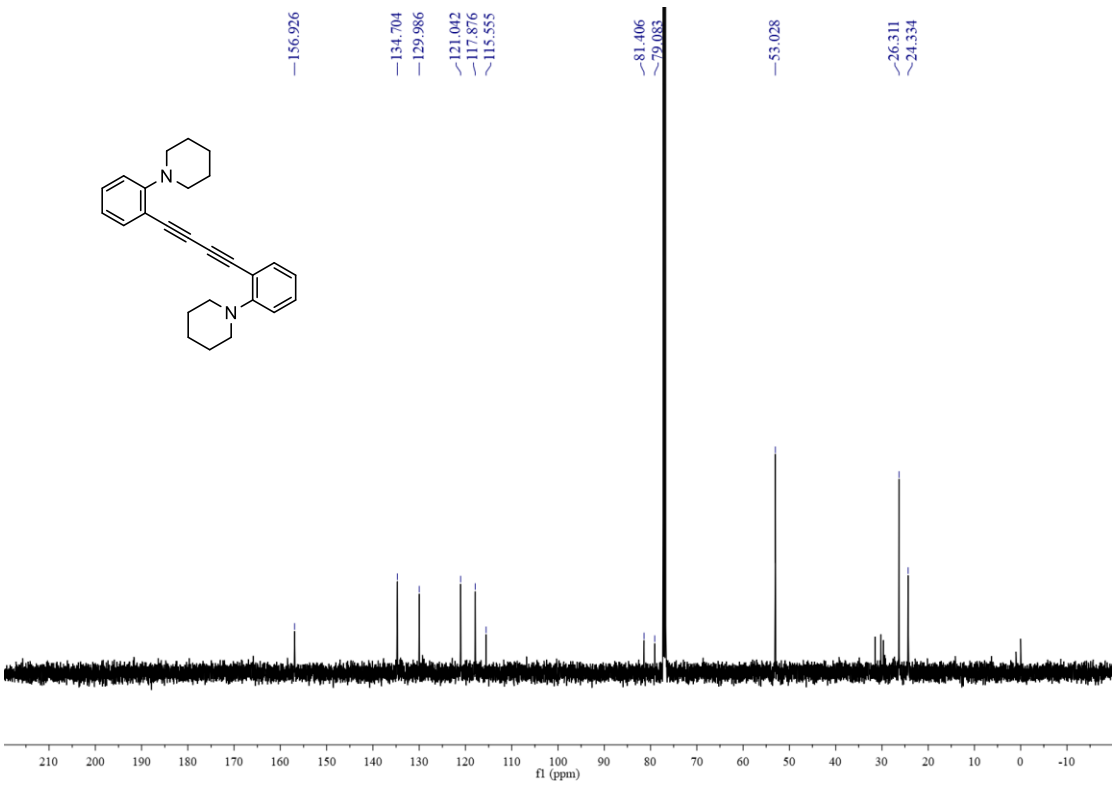


(E)-1-(2-((2-((4-bromophenyl)diazenyl)phenyl)ethynyl)phenyl)piperidine (1ab)

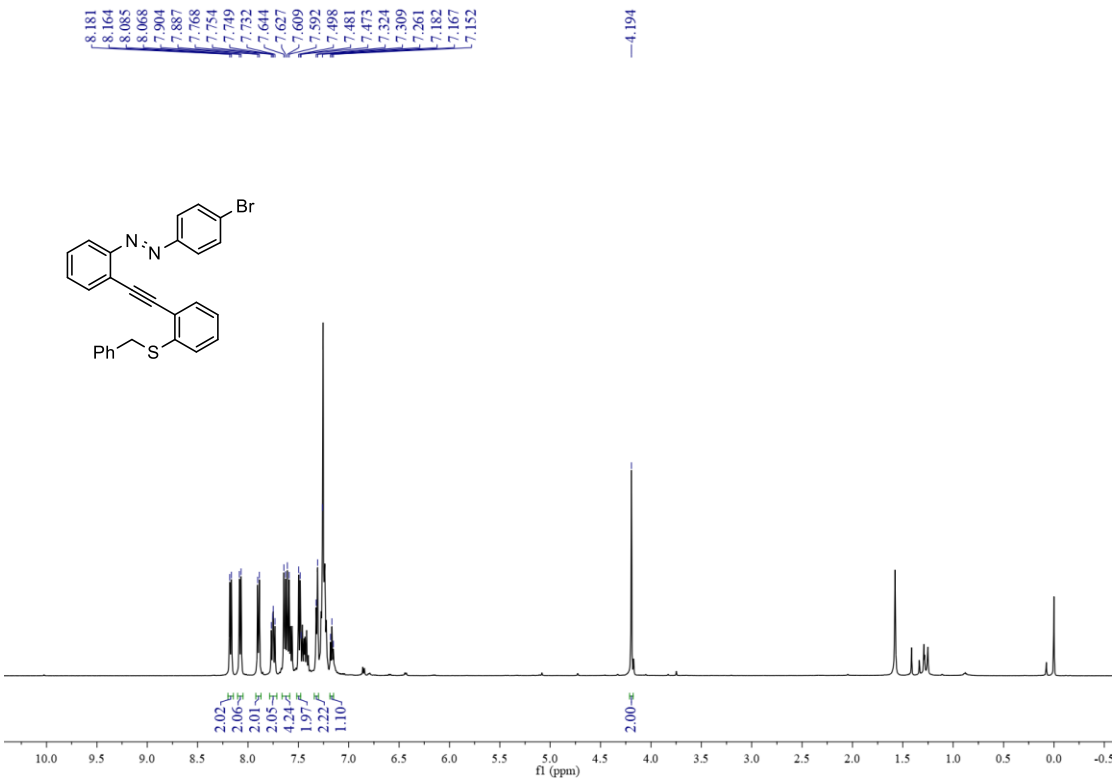


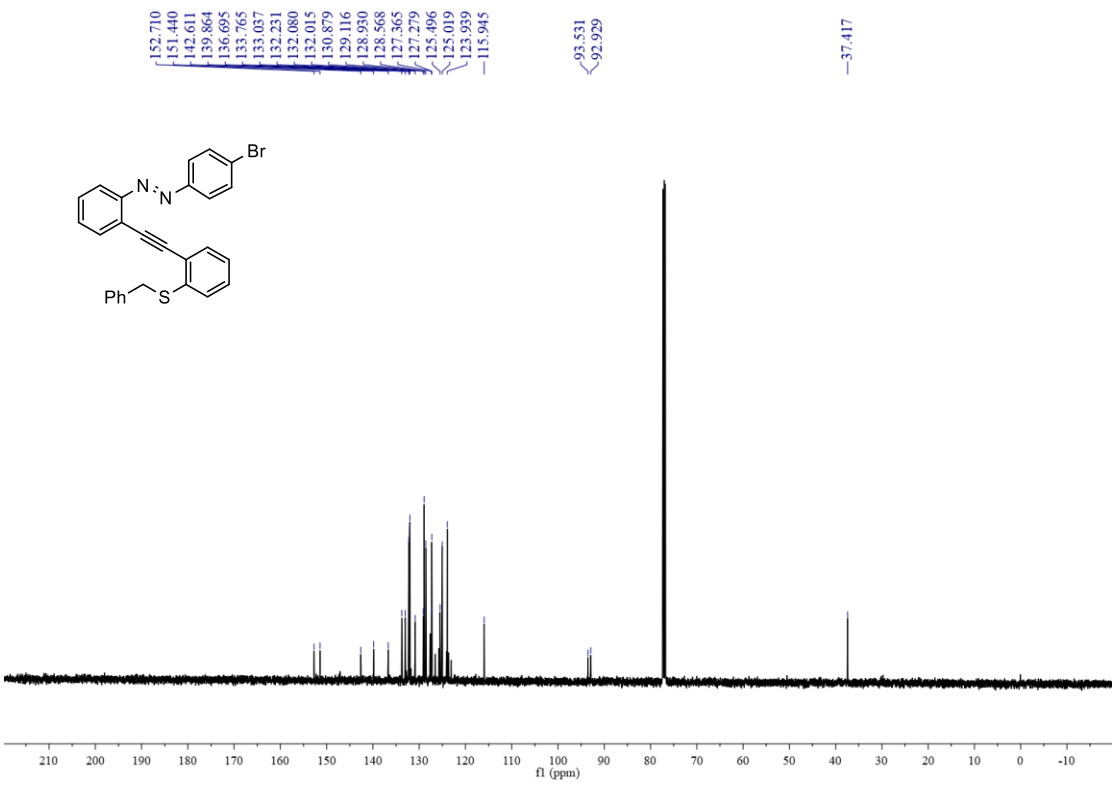



7.485
7.470
7.279
7.250
6.925
6.907
6.888
6.873
3.158
1.786
1.593
1.591
2.00
2.08
4.03
8.21
8.19
3.90
f1 (ppm)

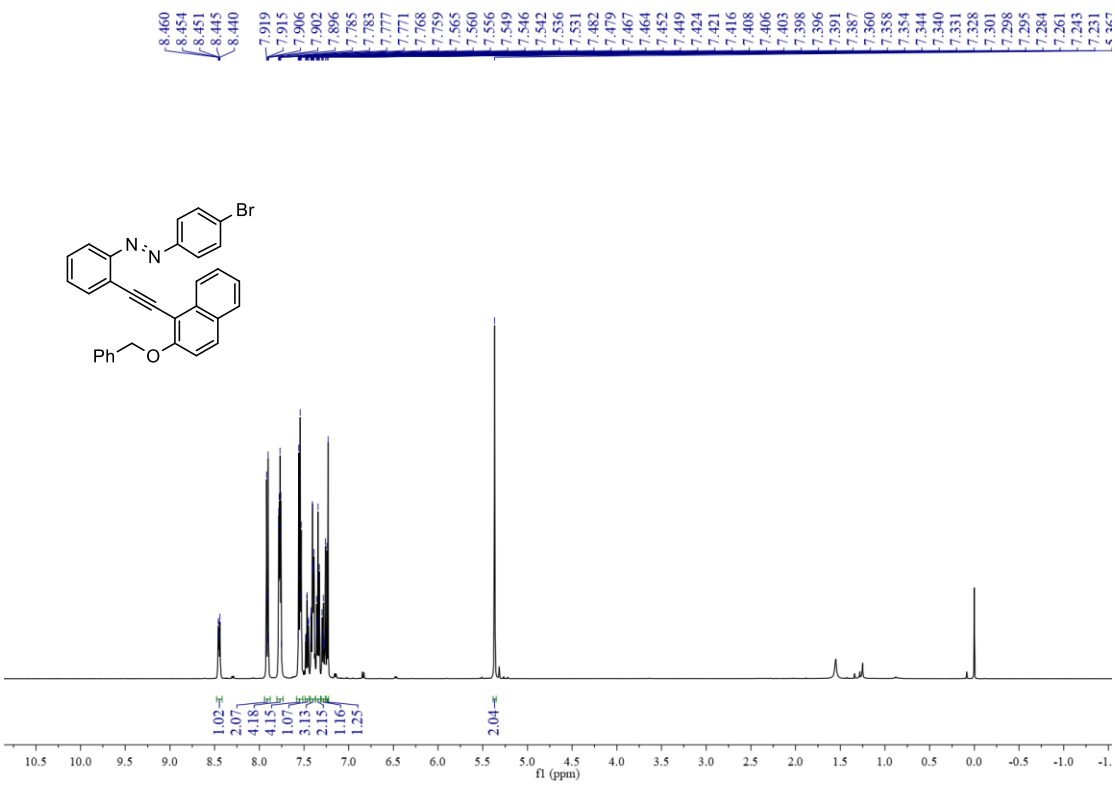

156.926
134.704
129.986
121.042
117.876
115.555
81.406
79.083
53.028
26.311
24.334
f1 (ppm)

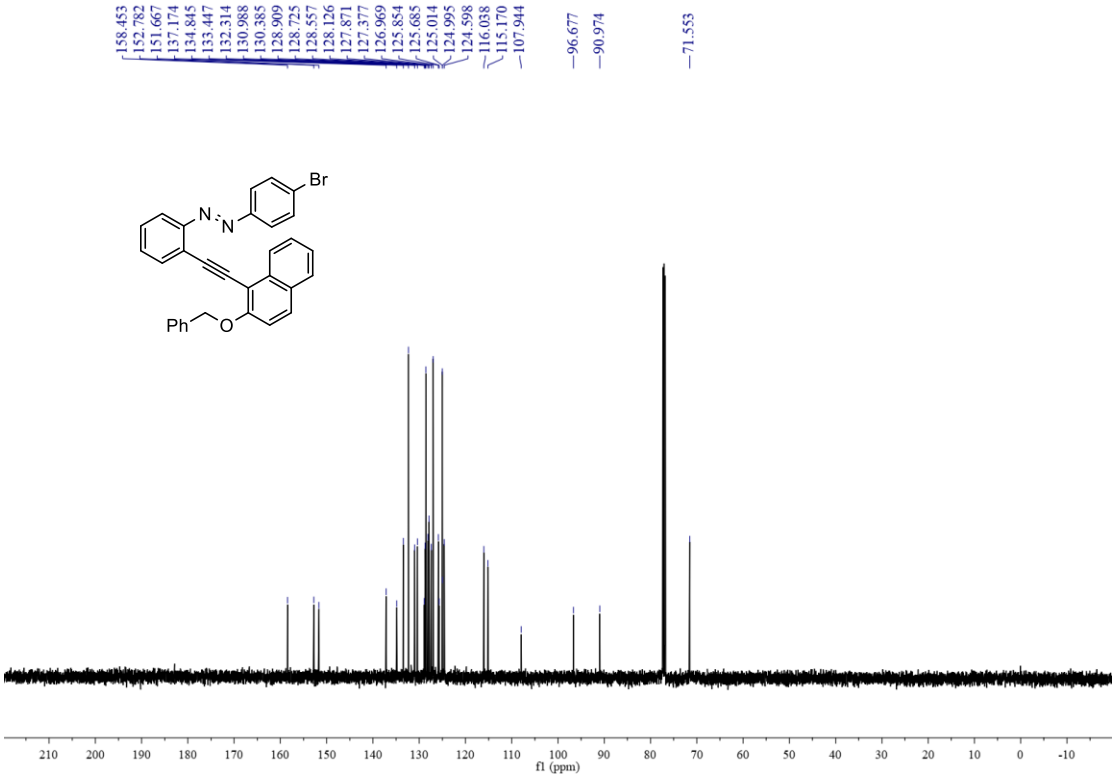
(E)-1-(2-((2-(benzylthio)phenyl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (1ac)



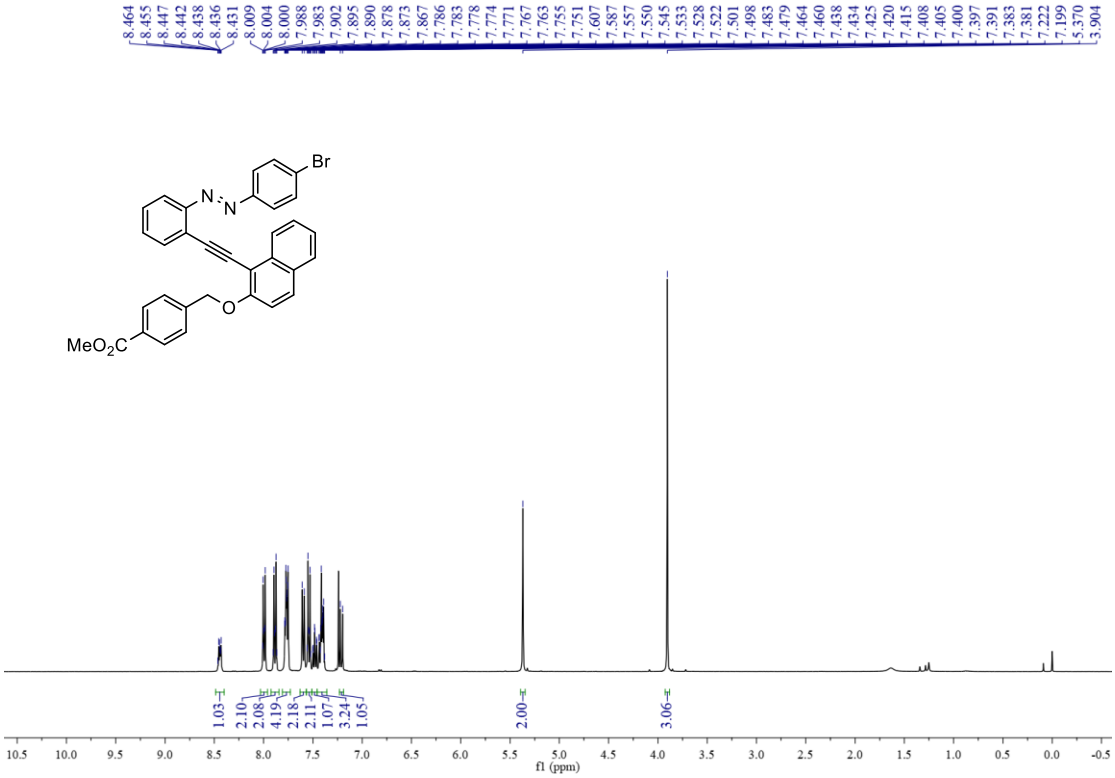


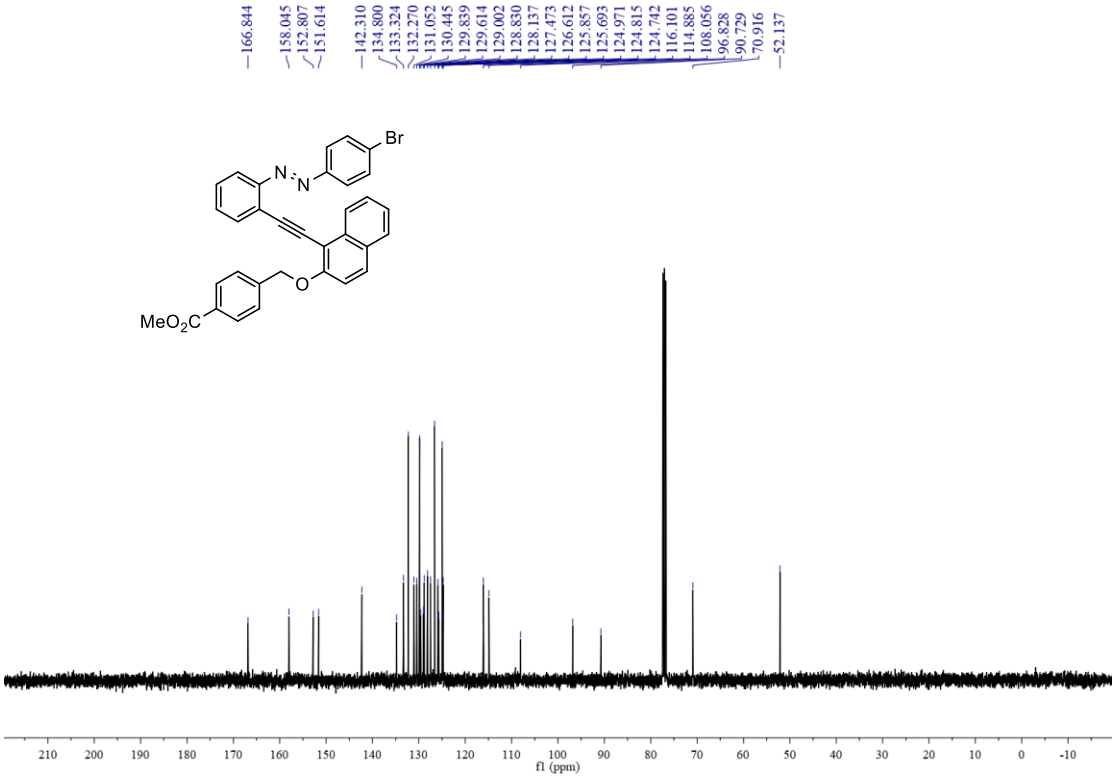
(E)-1-(2-((2-(benzyloxy)naphthalen-1-yl)ethynyl)phenyl)-2-(4-bromophenyl)diazene (3a)



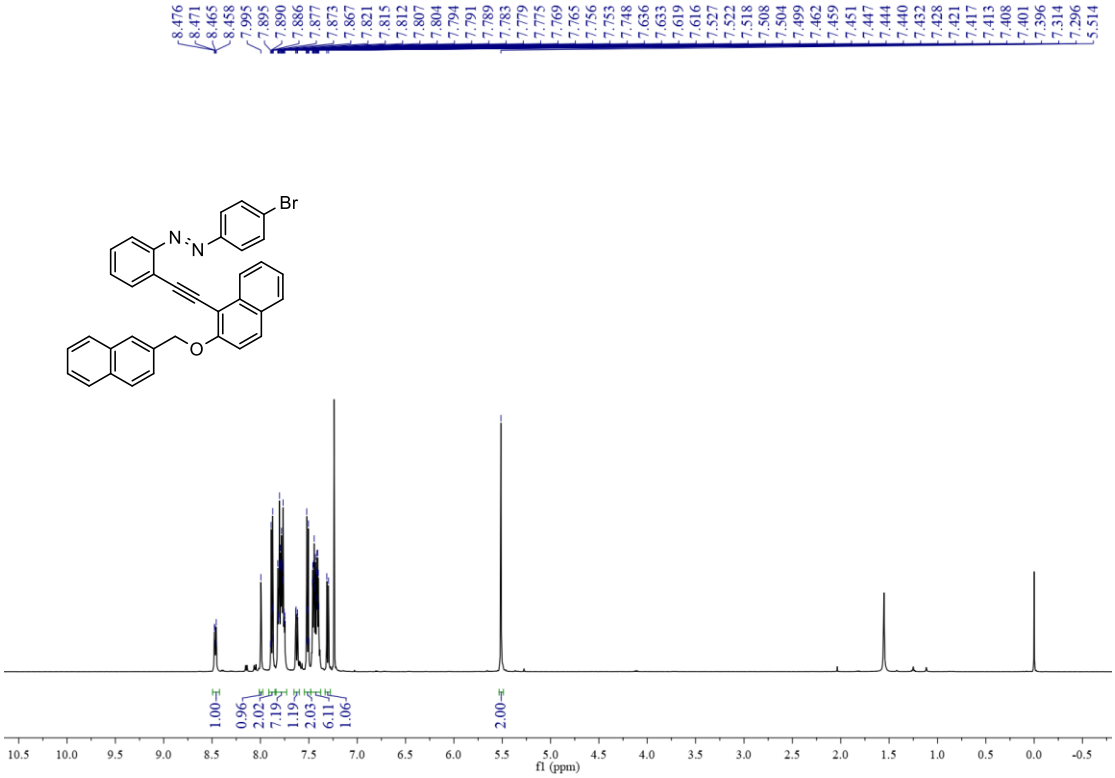


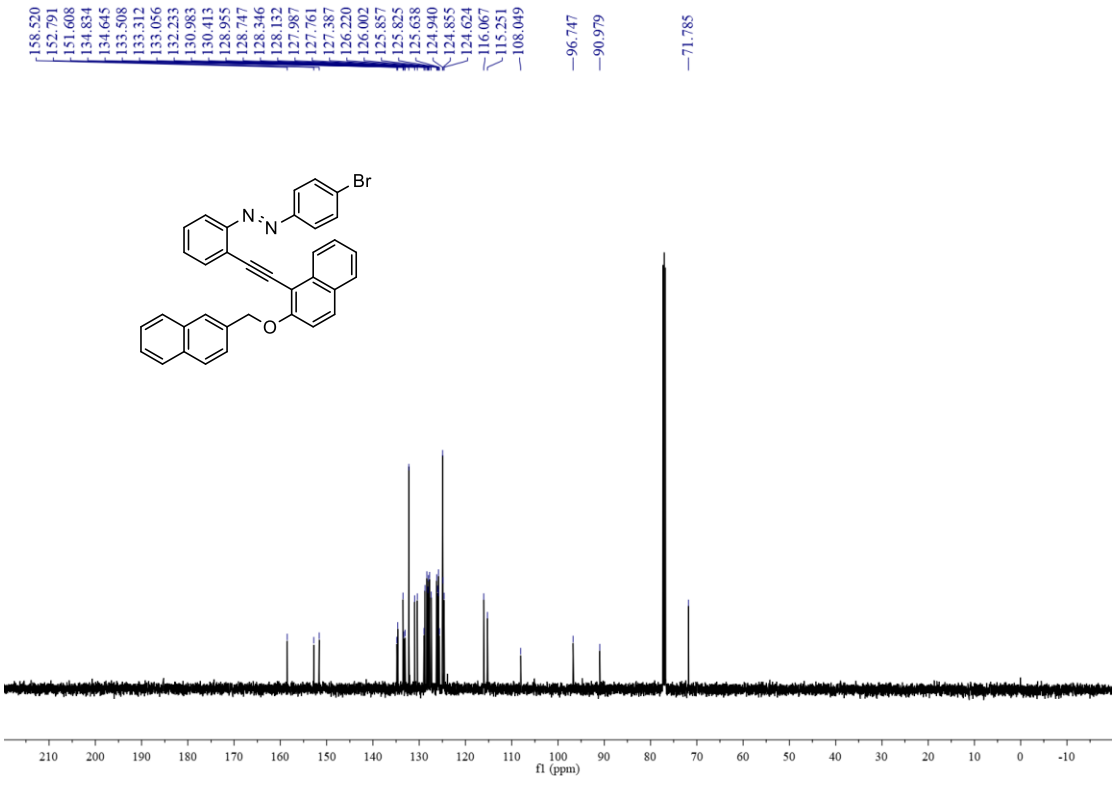
Methyl (E)-4-(((1-((2-((4-bromophenyl)diazenyl)phenyl)ethynyl)naphthalen-2-yl)oxy)methyl)-benzoate (3b)



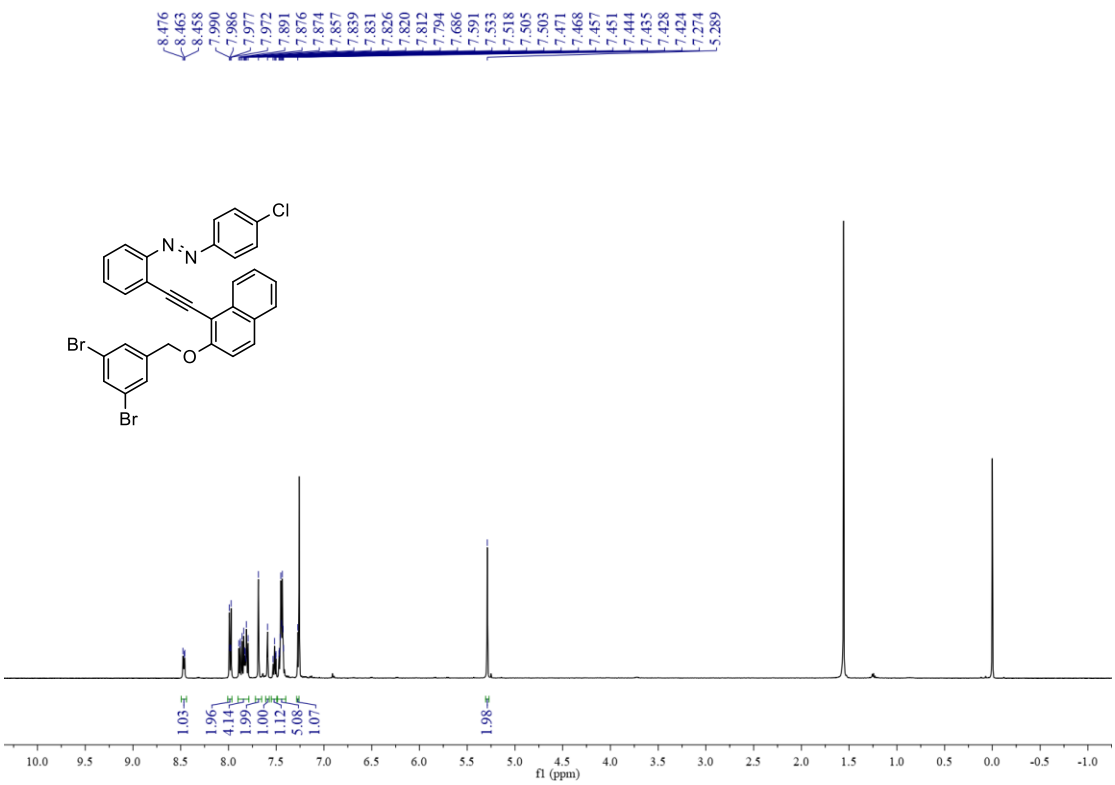


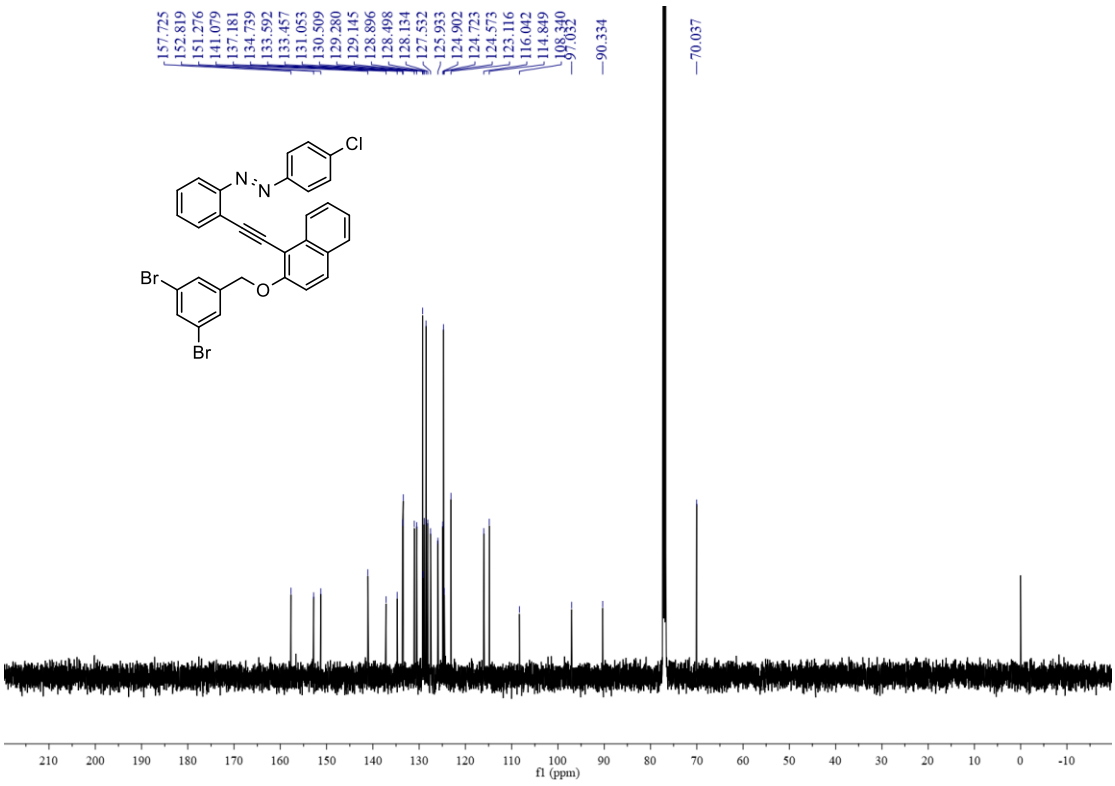
(E)-1-(4-bromophenyl)-2-(2-((2-(naphthalen-2-ylmethoxy)naphthalen-1-yl)ethynyl)phenyl)diazene (3c)



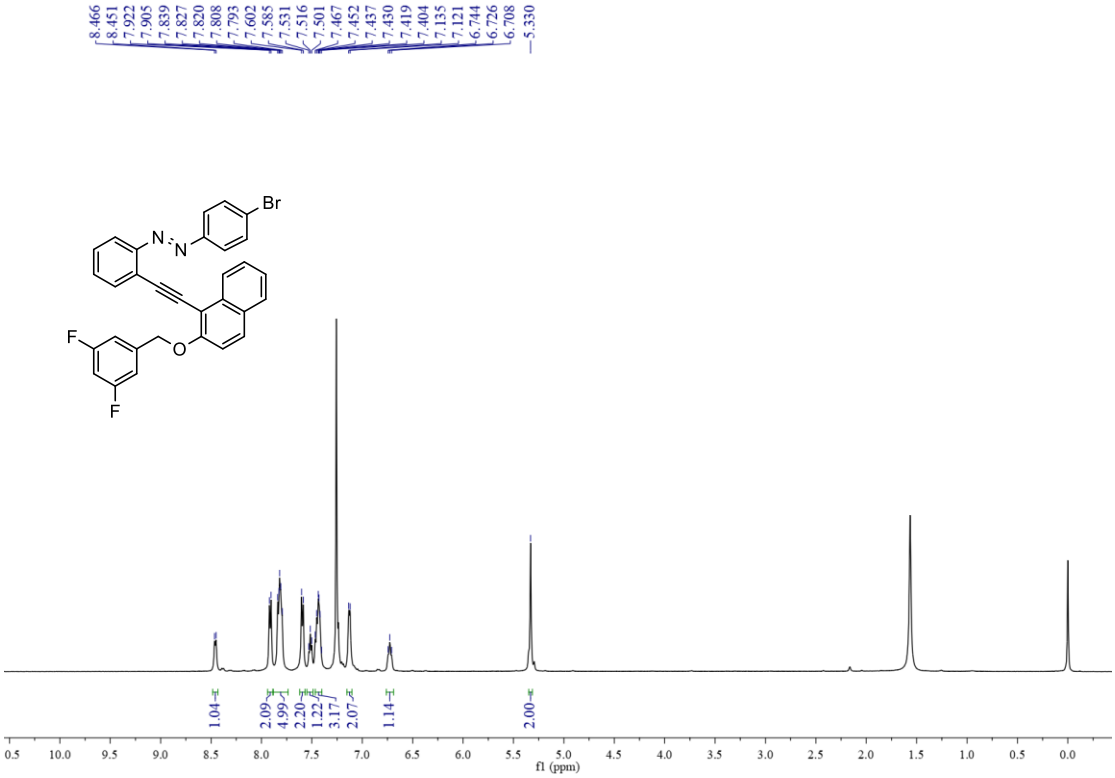


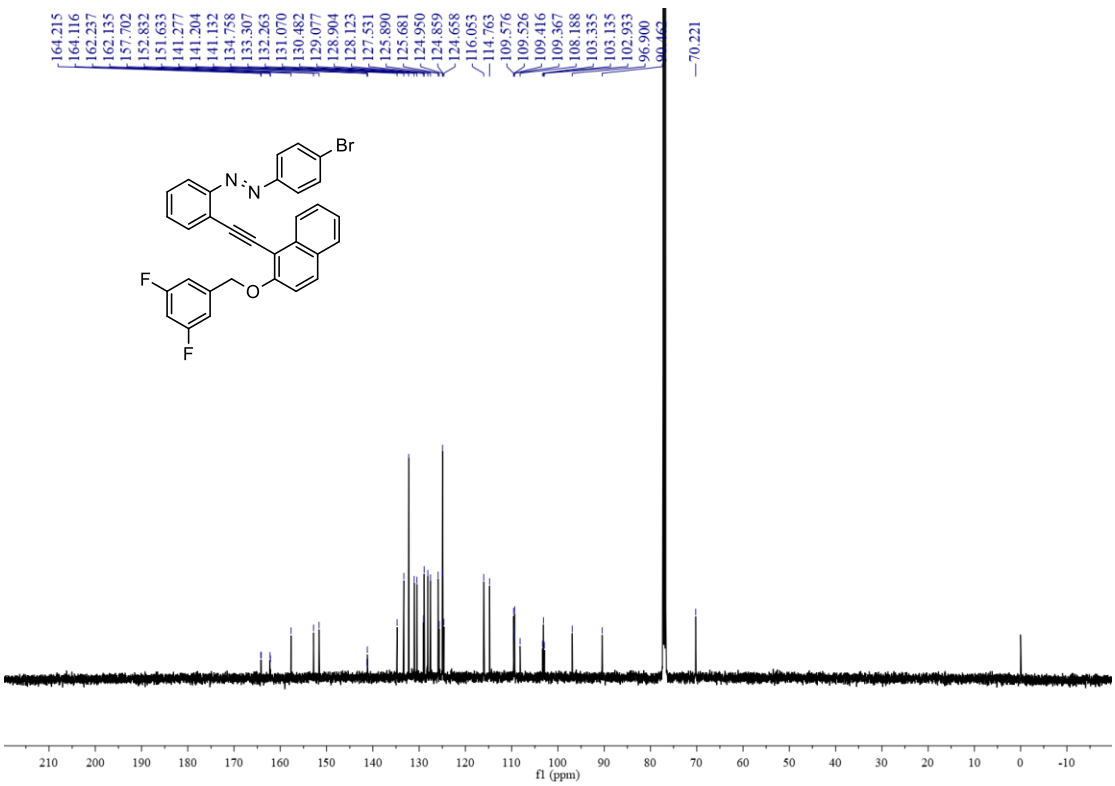
(E)-1-(4-chlorophenyl)-2-(2-((2-((3,5-dibromobenzyl)oxy)naphthalen-1-yl)ethynyl)phenyl)diazene (3d)

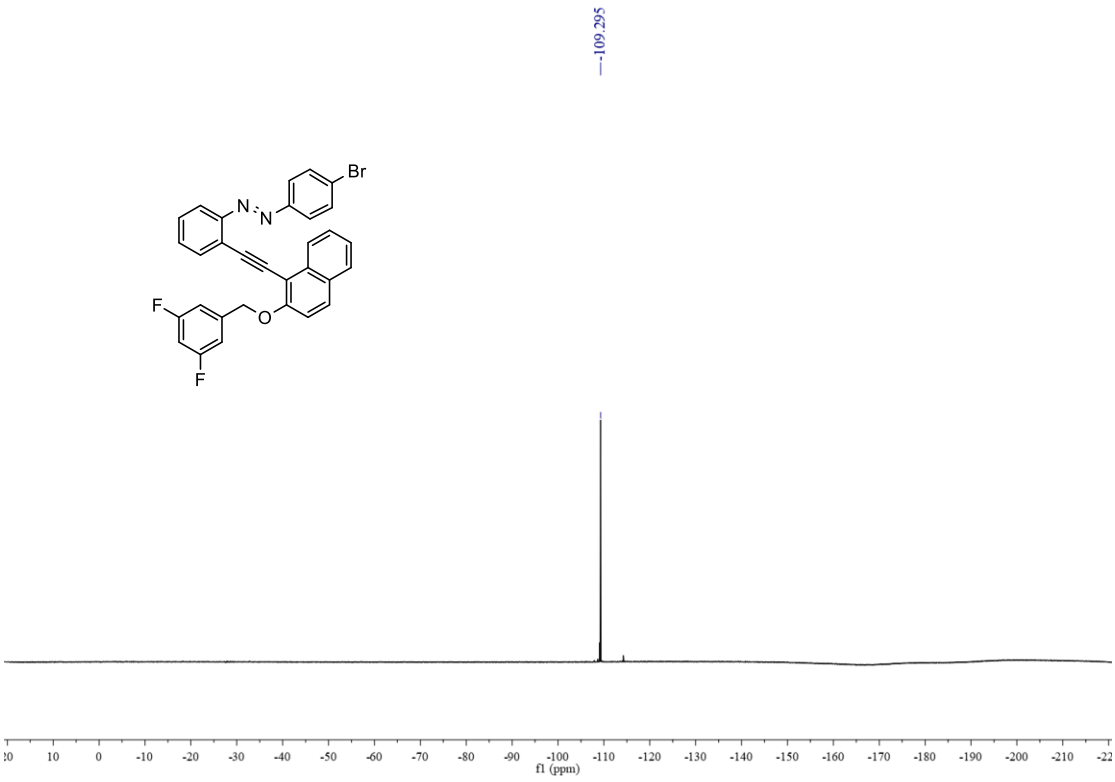




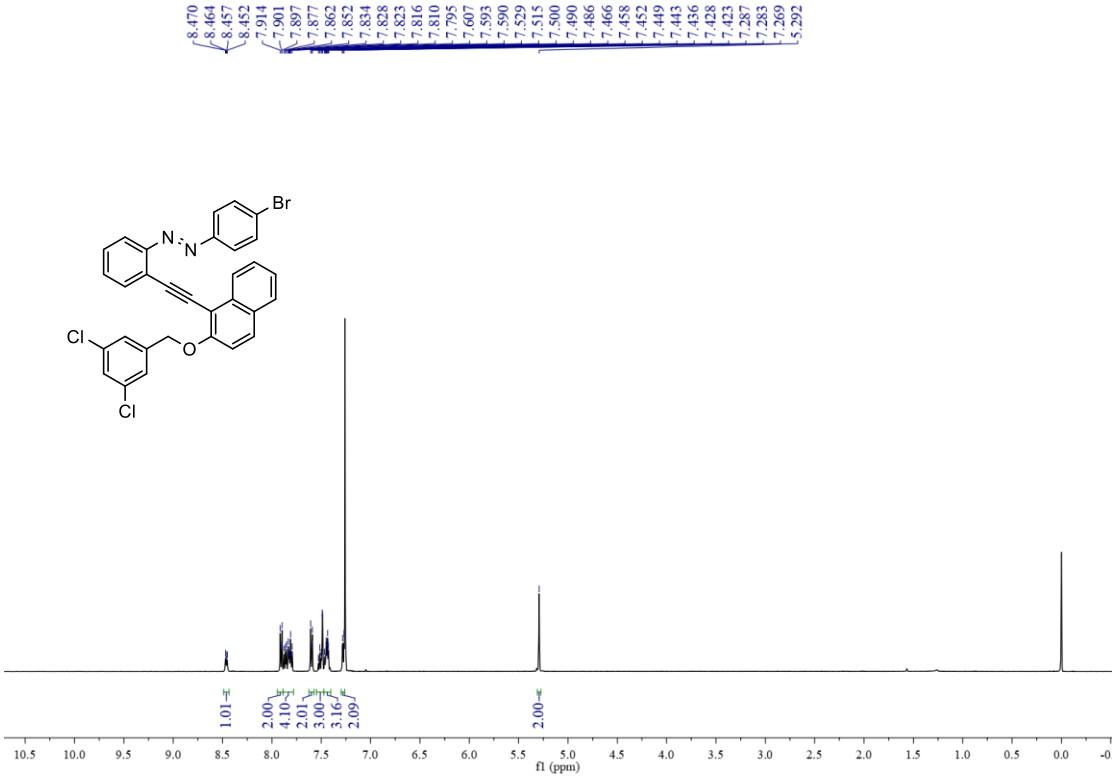
(E)-1-(4-bromophenyl)-2-(2-((2-((3,5-difluorobenzyl)oxy)naphthalen-1-yl)ethynyl)phenyl)diazene (3e)

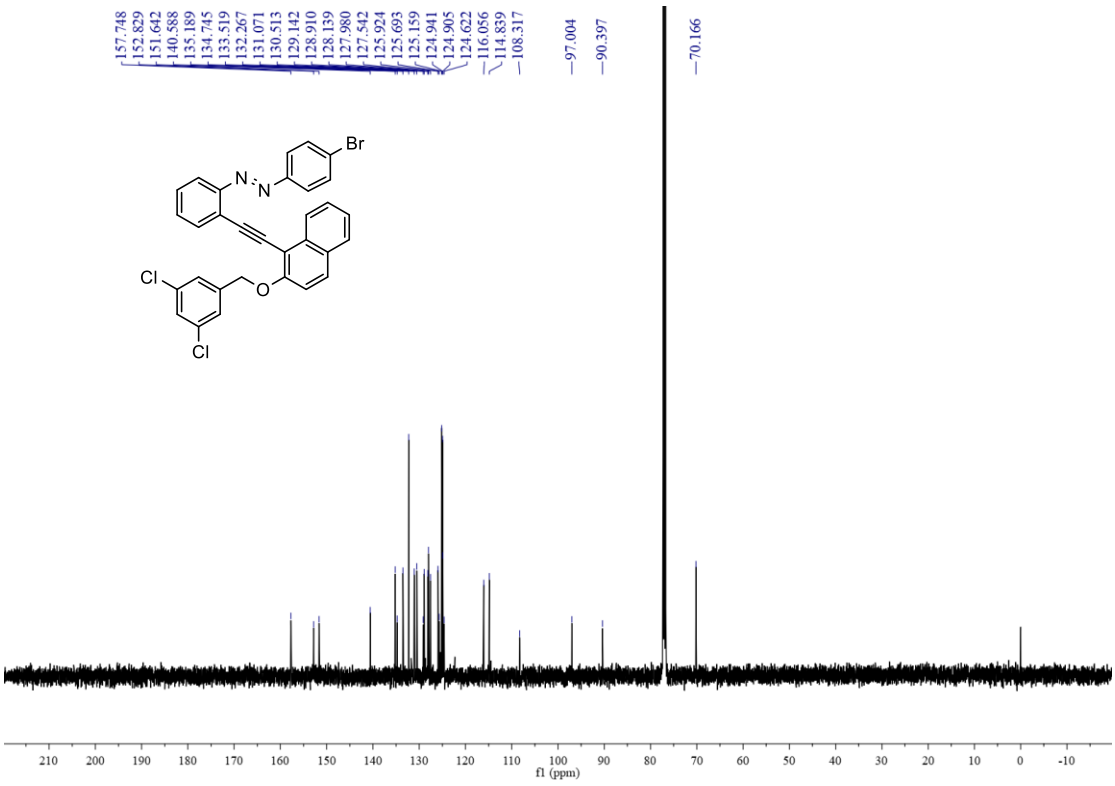




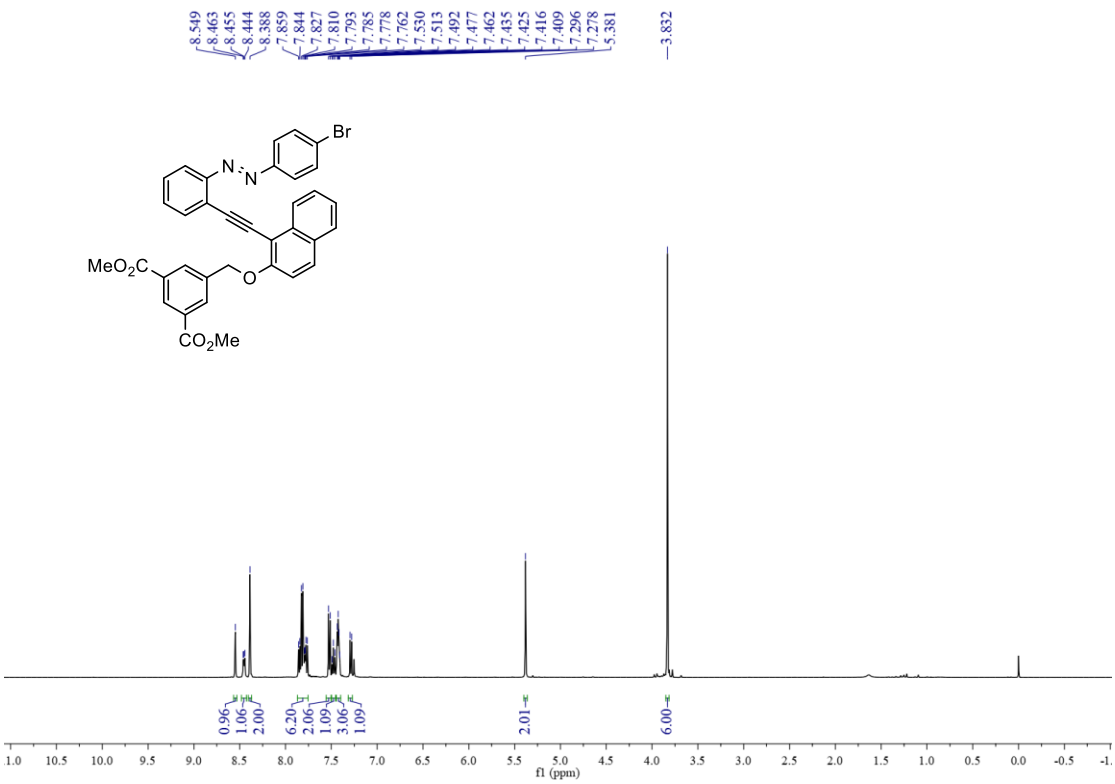

-109.295
Br
N
N
F
O
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

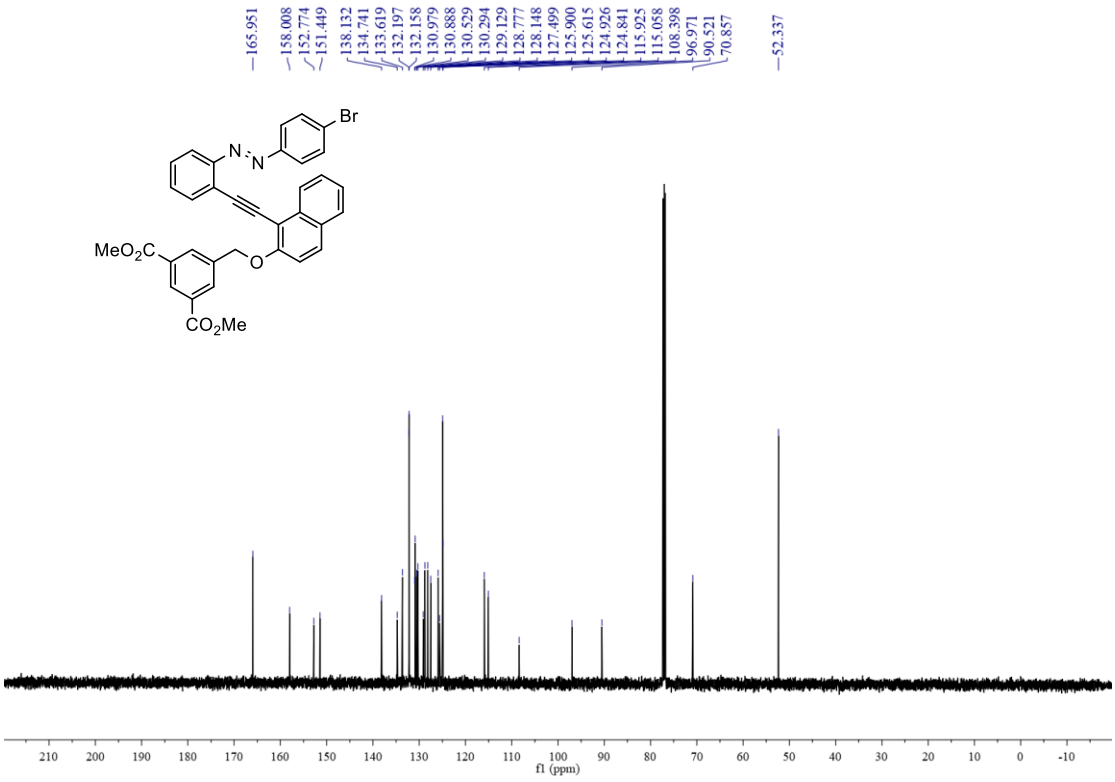
(E)-1-(4-bromophenyl)-2-(2-((2-((3,5-dichlorobenzyl)oxy)naphthalen-1-yl)ethynyl)phenyl)diazene (3f)



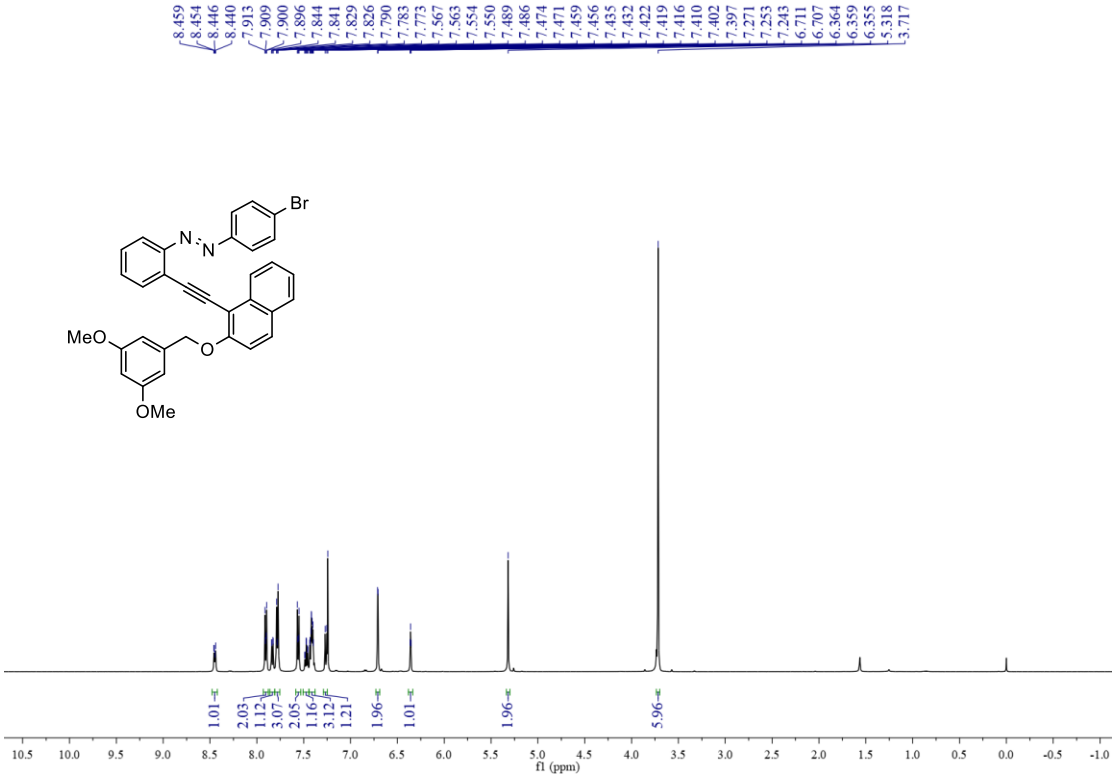


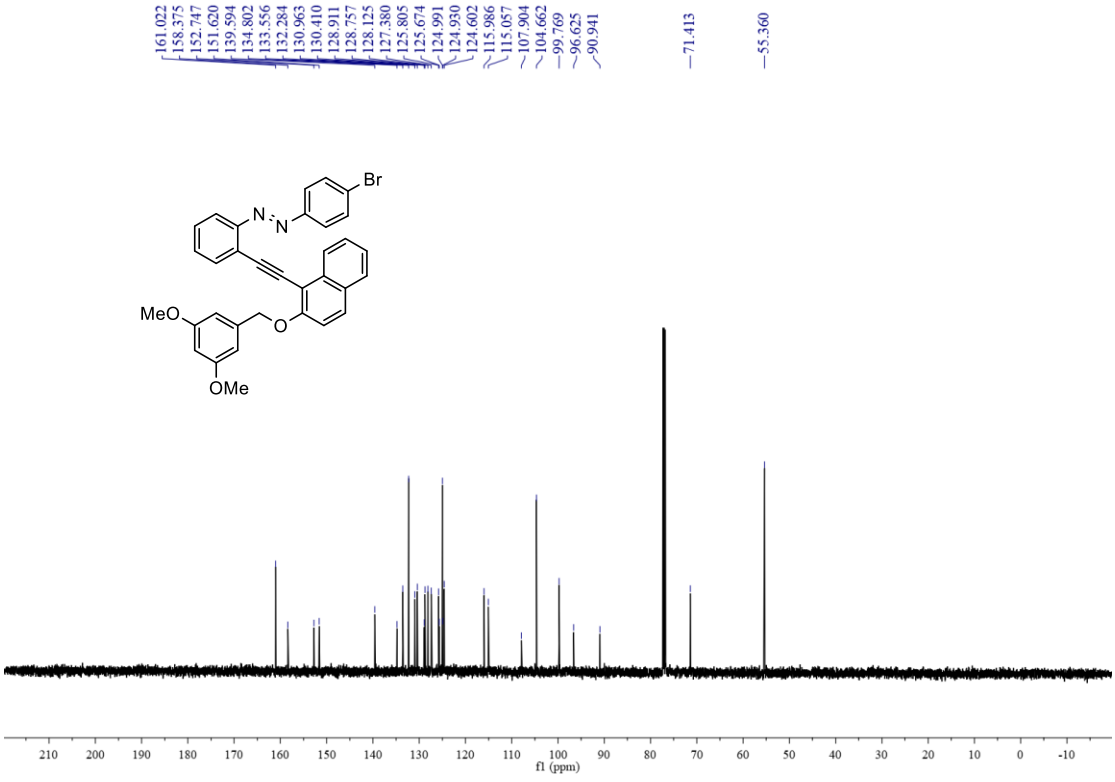
dimethyl (E)-5-(((1-((2-((4-bromophenyl)diazenyl)phenyl)ethynyl)naphthalen-2-yl)oxy)methyl)-isophthalate (3g)



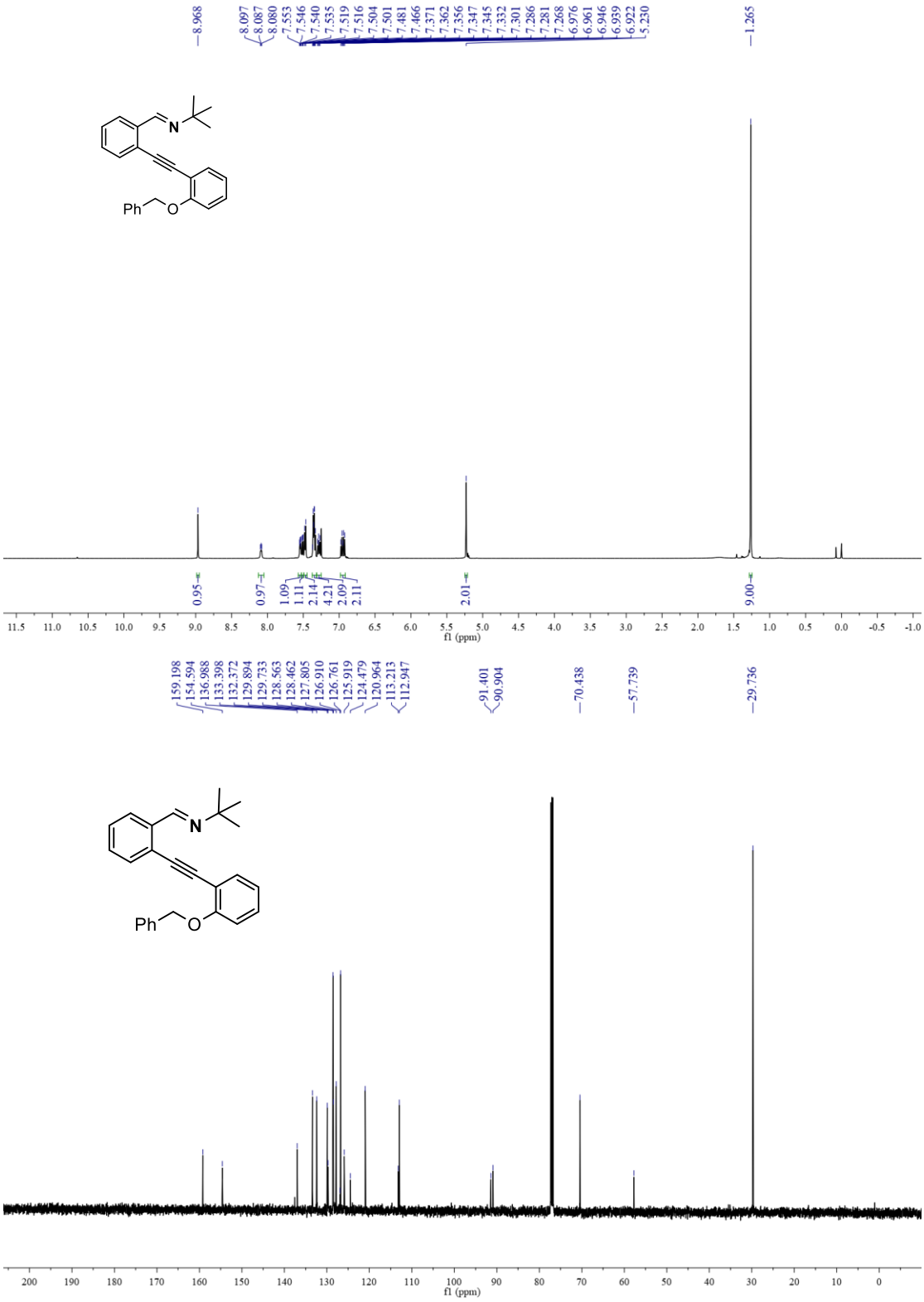


(E)-1-(4-bromophenyl)-2-(2-((2-((3,5-dimethoxybenzyl)oxy)naphthalen-1-yl)ethynyl)phenyl)diazene (3h)

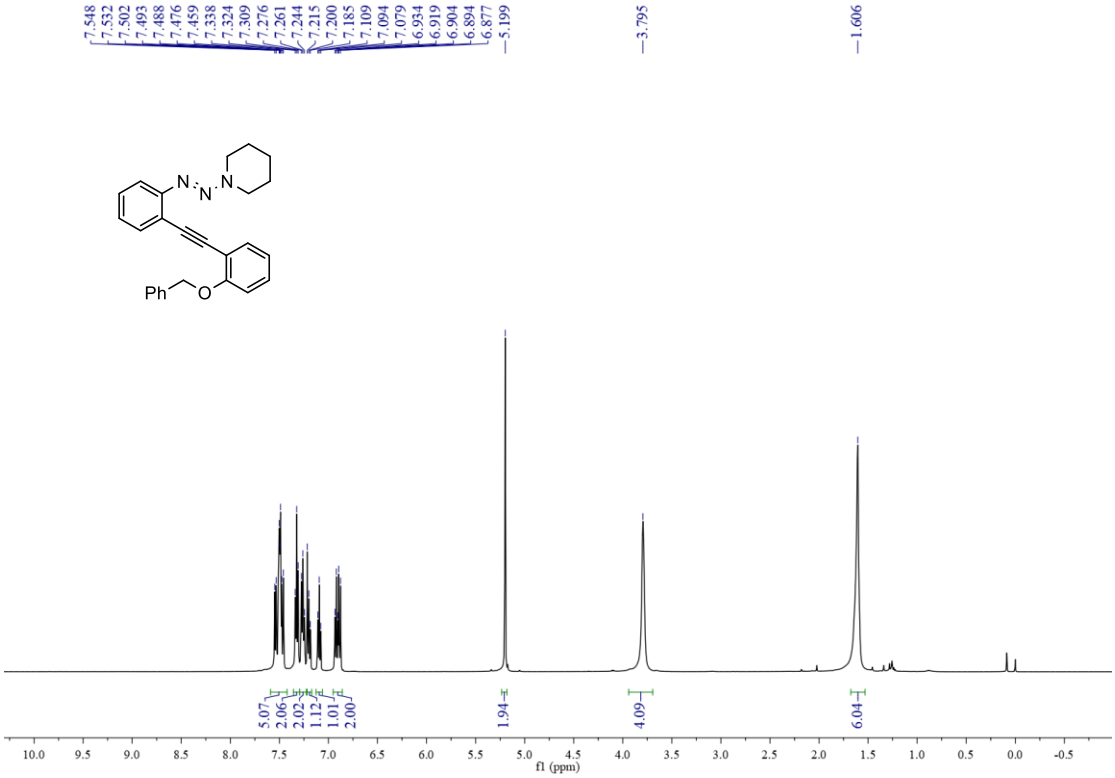


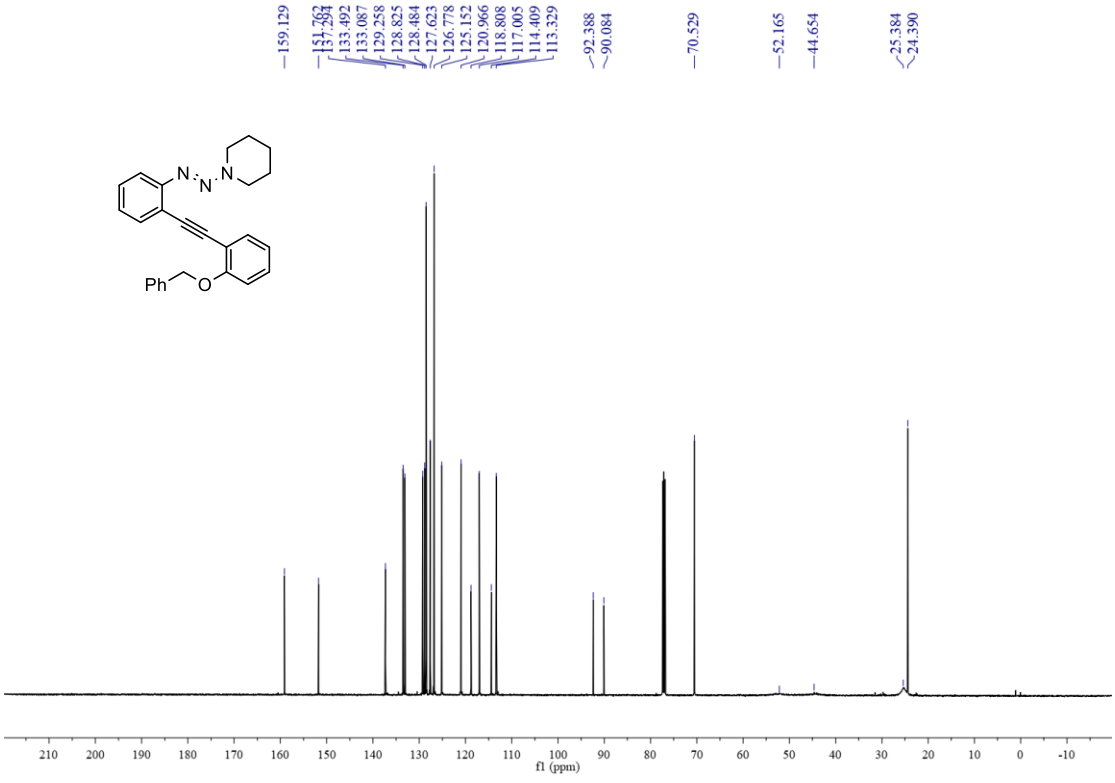


(E)-1-(2-((2-(benzyloxy)phenyl)ethynyl)phenyl)-N-(tert-butyl)methanimine

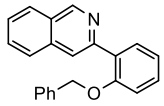


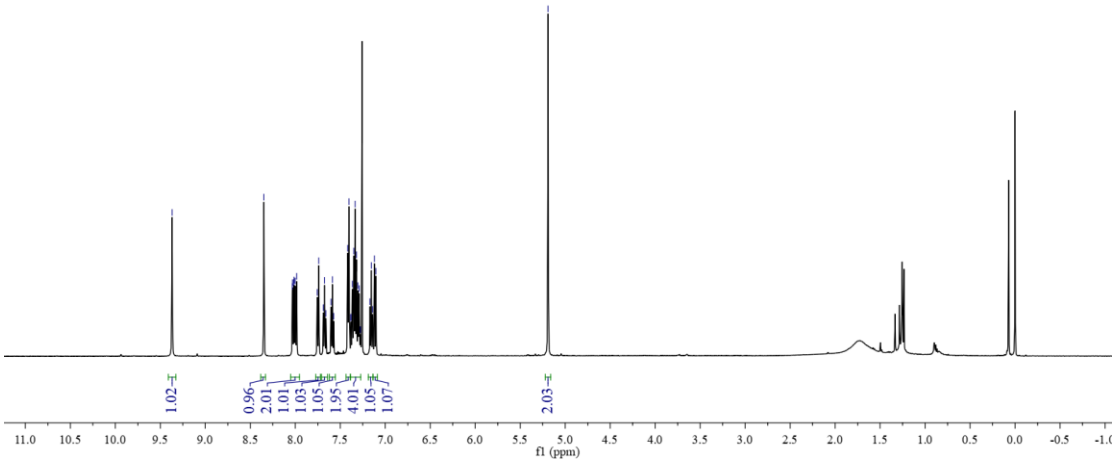
(E)-1-((2-((2-(benzyloxy)phenyl)ethynyl)phenyl)diazenyl)piperidine

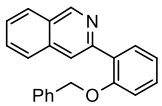


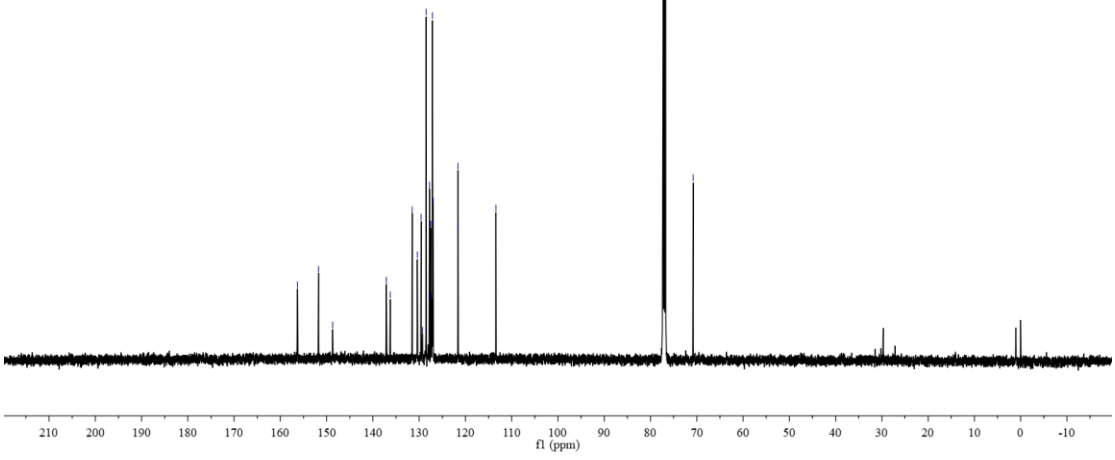


3-(2-(benzyloxy)phenyl)isoquinoline

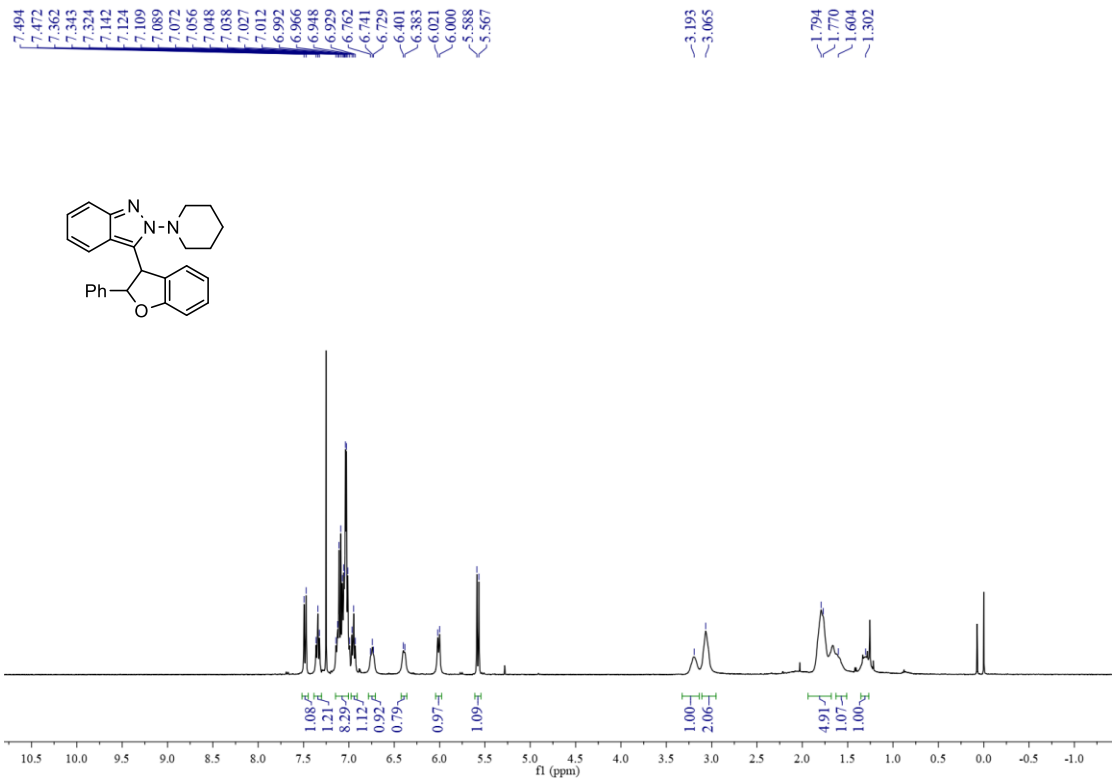


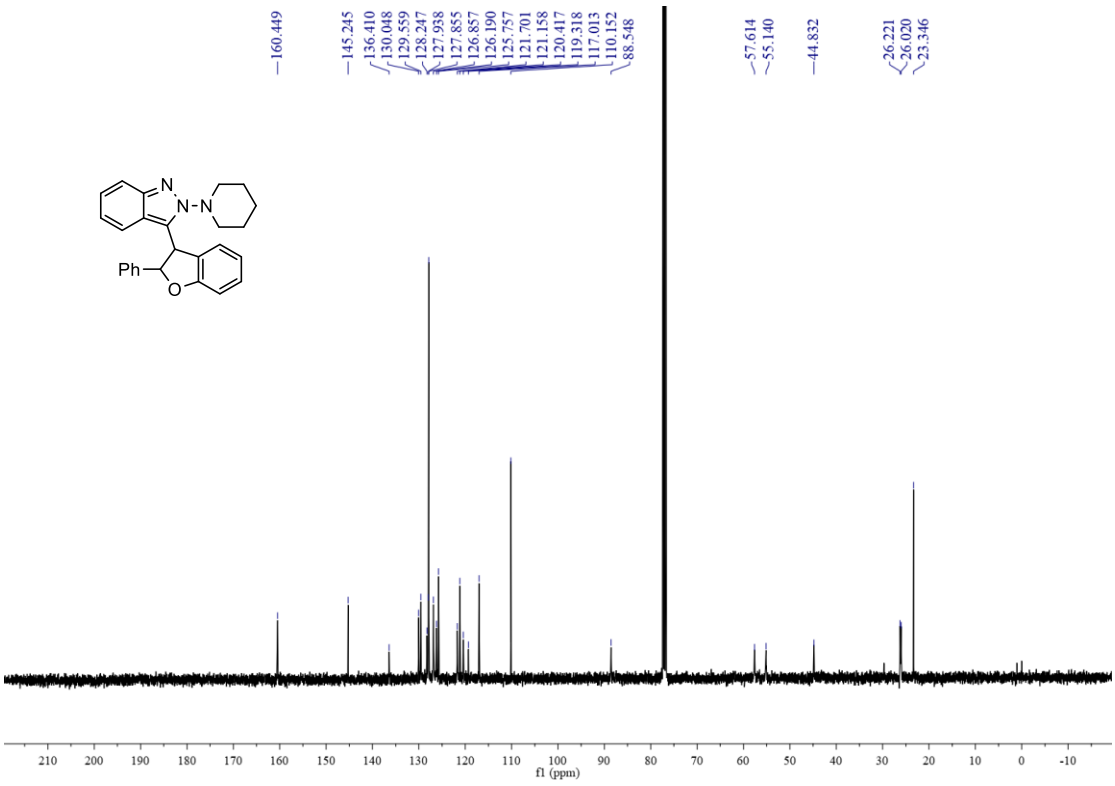




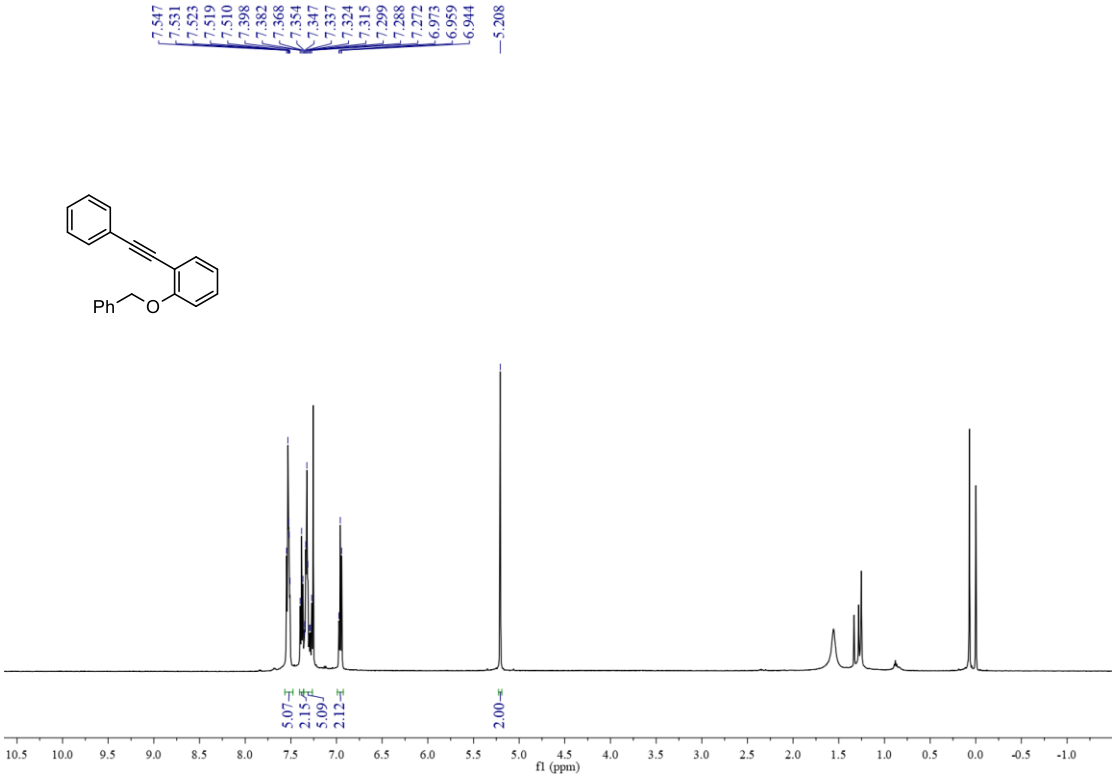


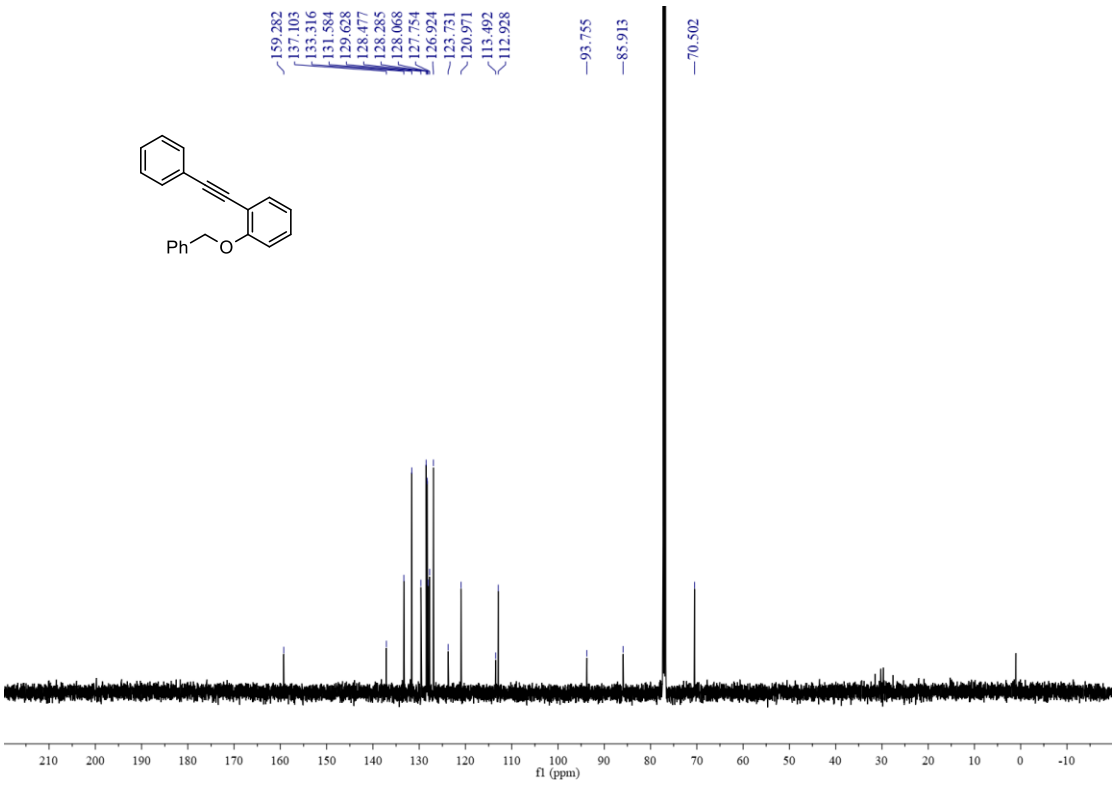
3-(2-phenyl-2,3-dihydrobenzofuran-3-yl)-2-(piperidin-1-yl)-2H-indazole



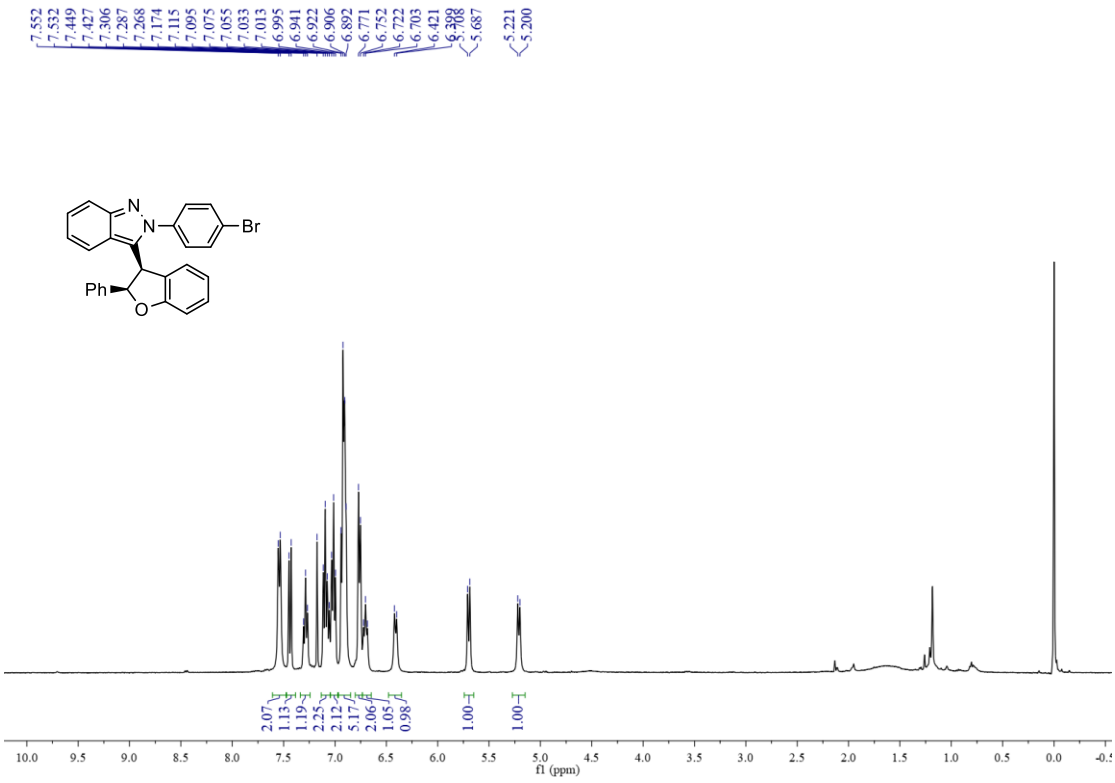


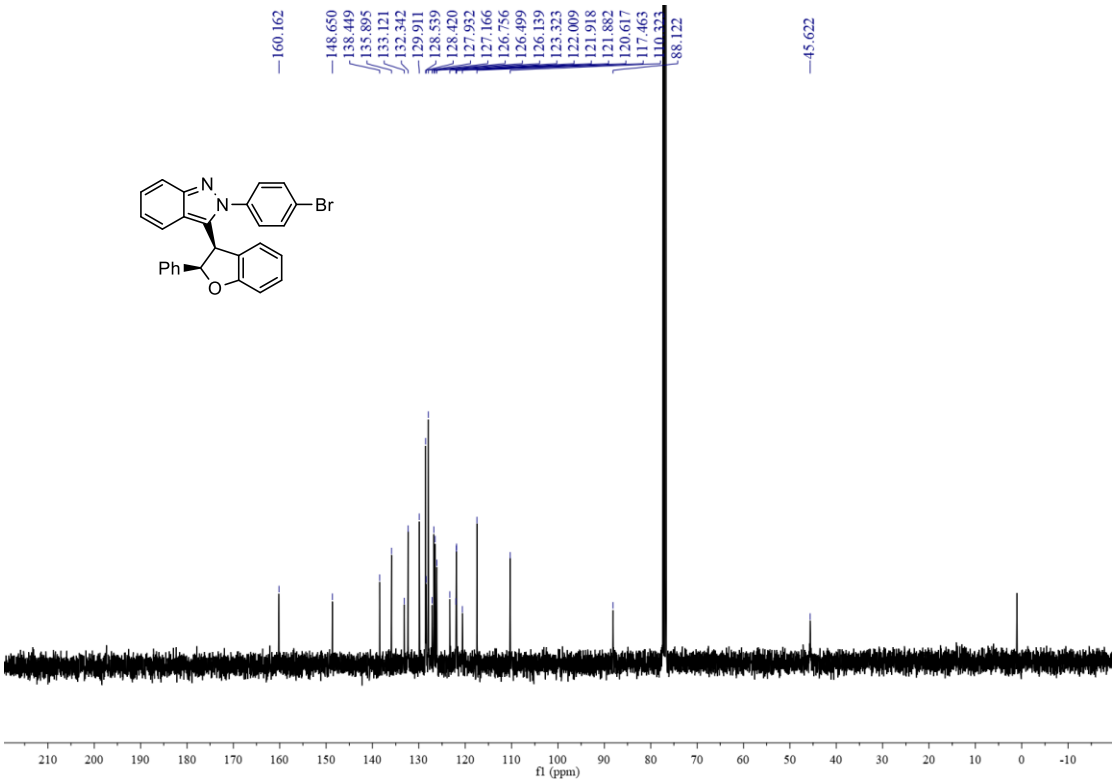
1-(benzyloxy)-2-(phenylethynyl)benzene



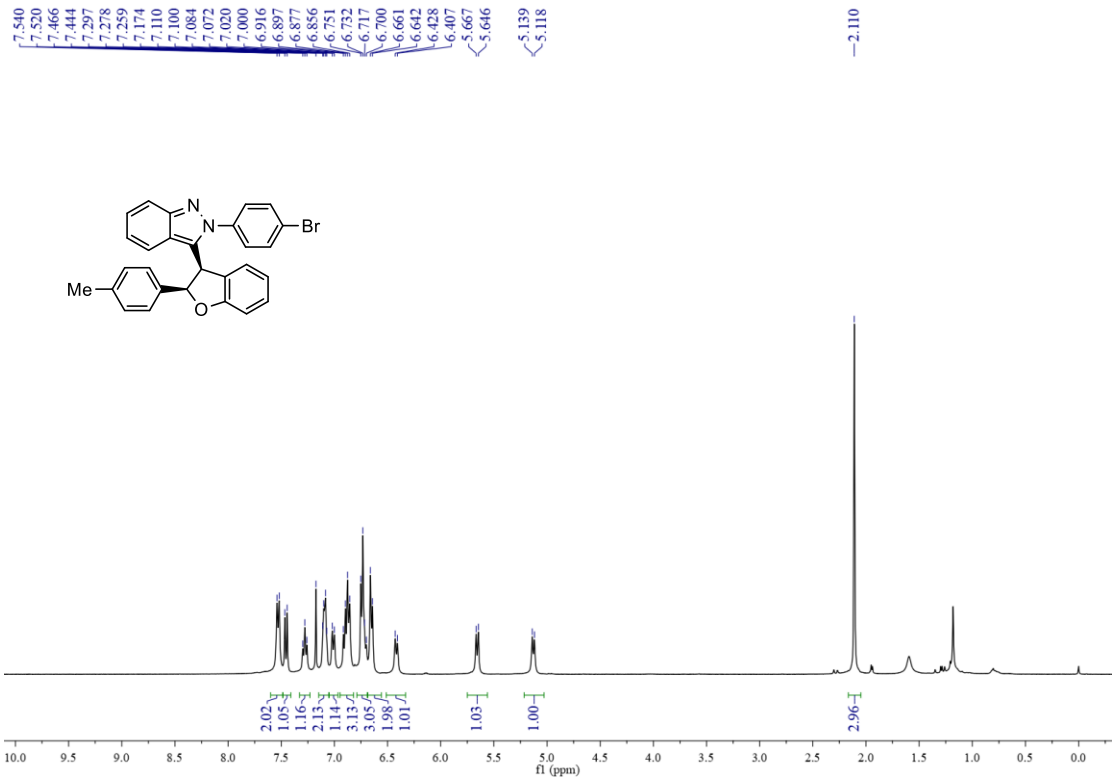


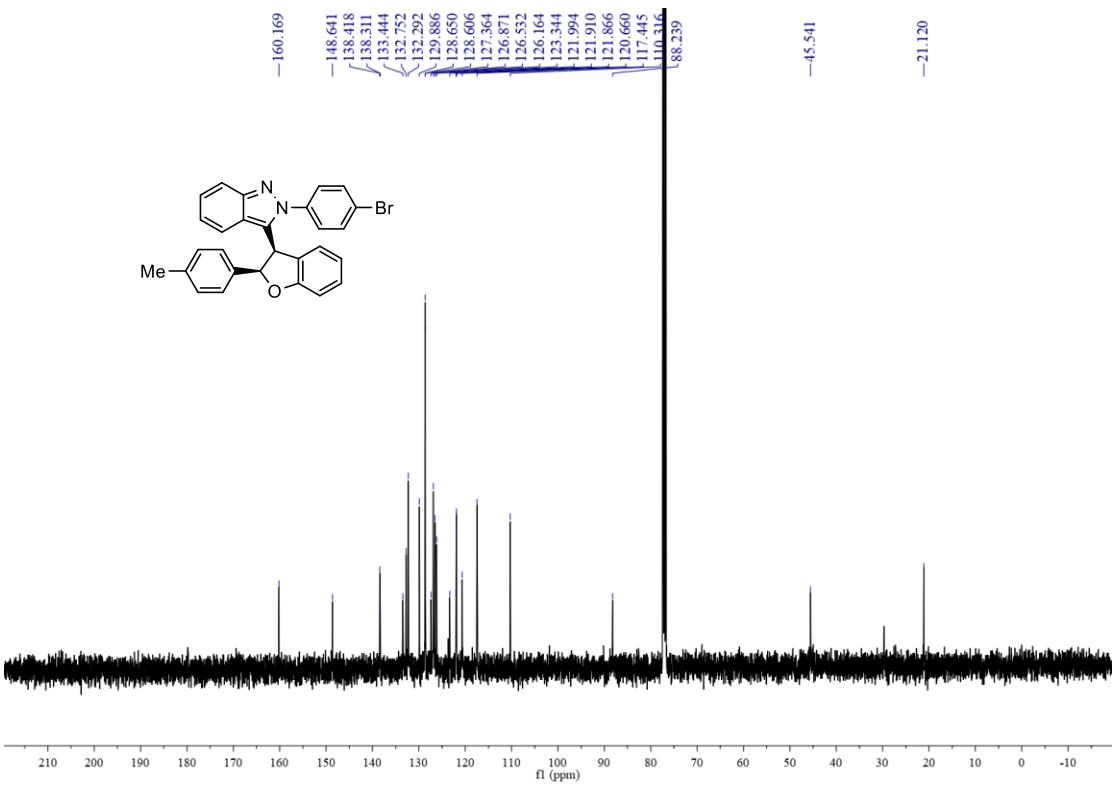
2-(4-bromophenyl)-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2a)



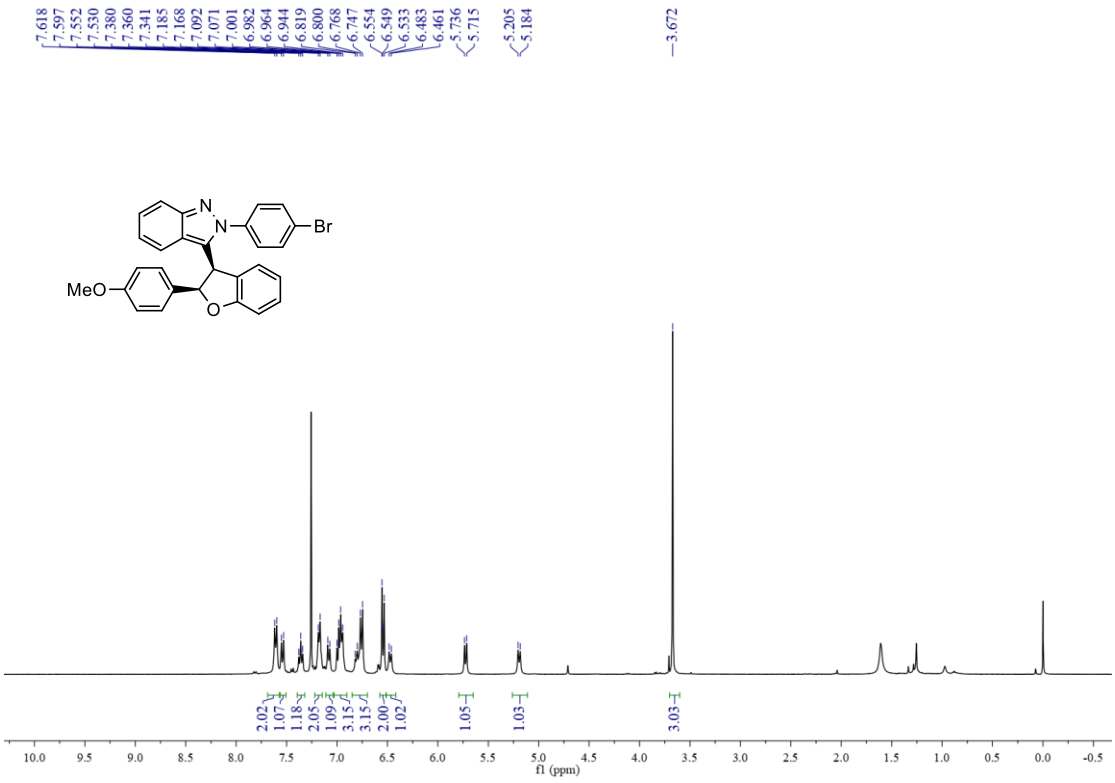


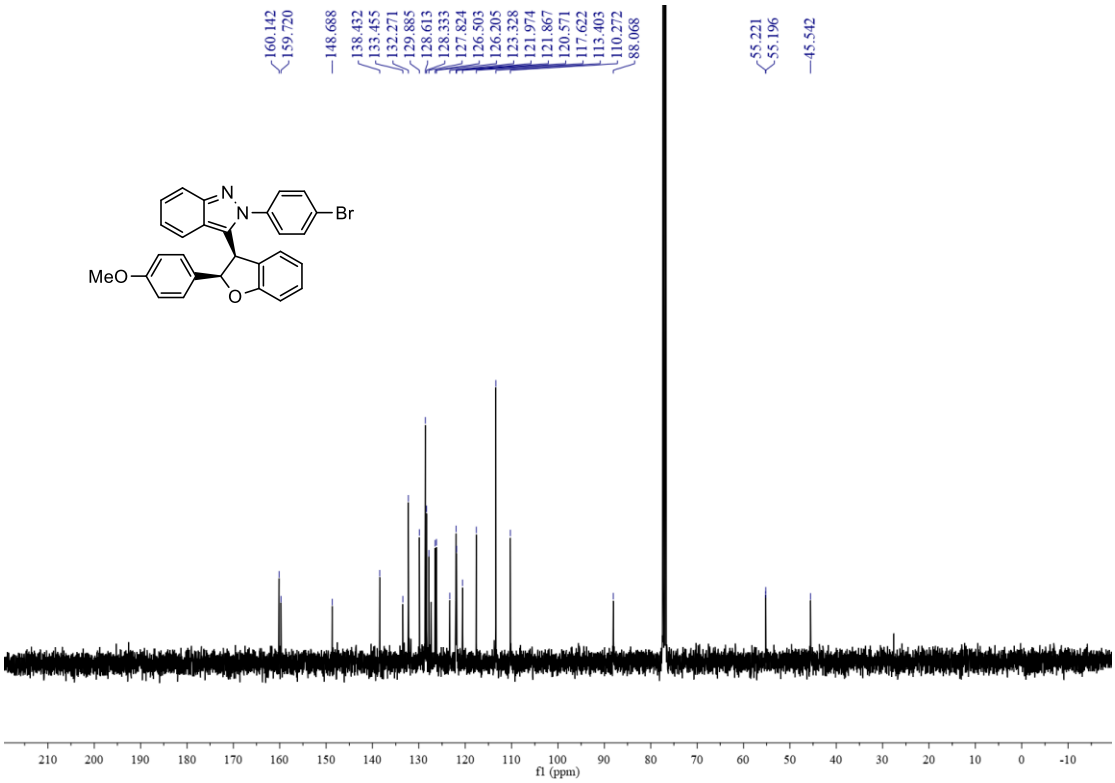
2-(4-bromophenyl)-3-((2R,3R)-2-(p-tolyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2b)



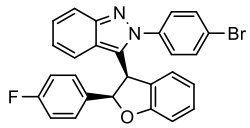


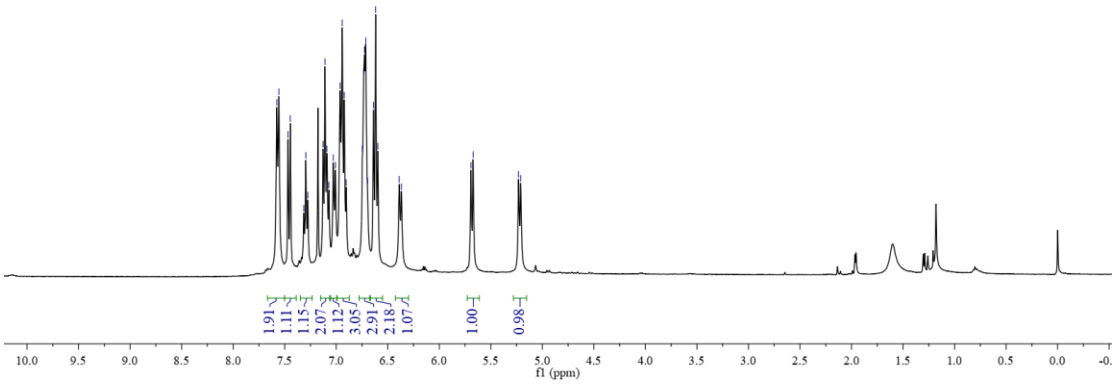
2-(4-bromophenyl)-3-((2R,3R)-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2c)

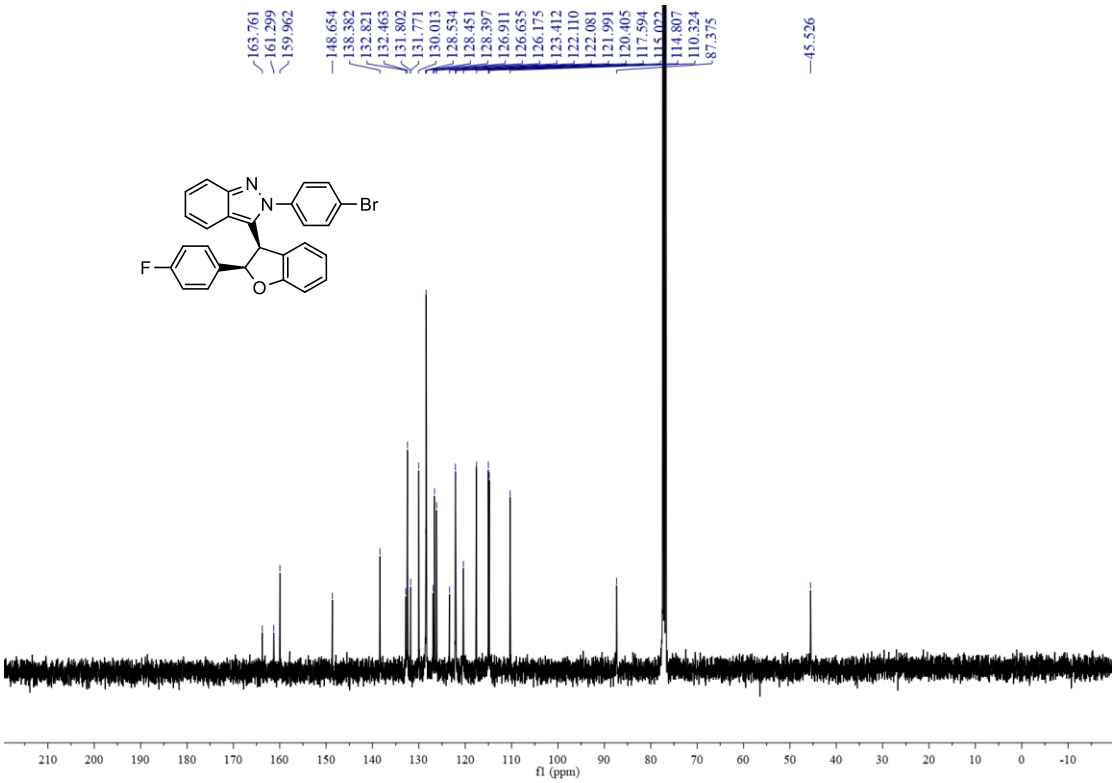




2-(4-bromophenyl)-3-((2R,3R)-2-(4-fluorophenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2d)

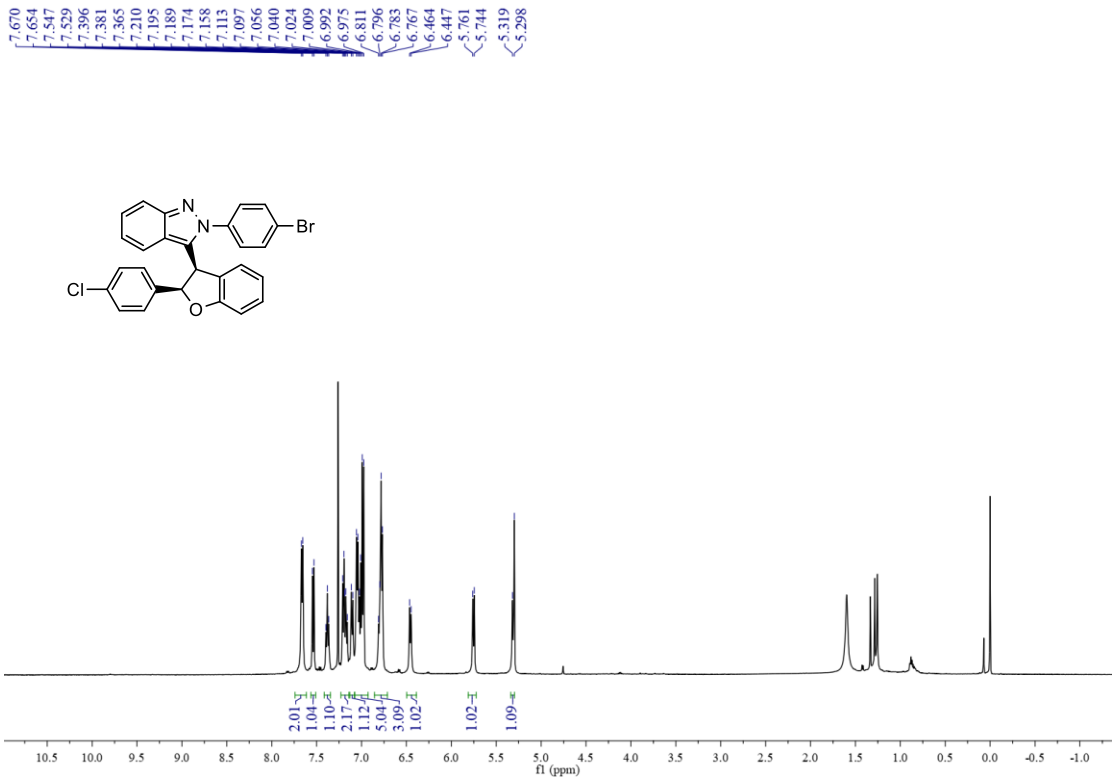


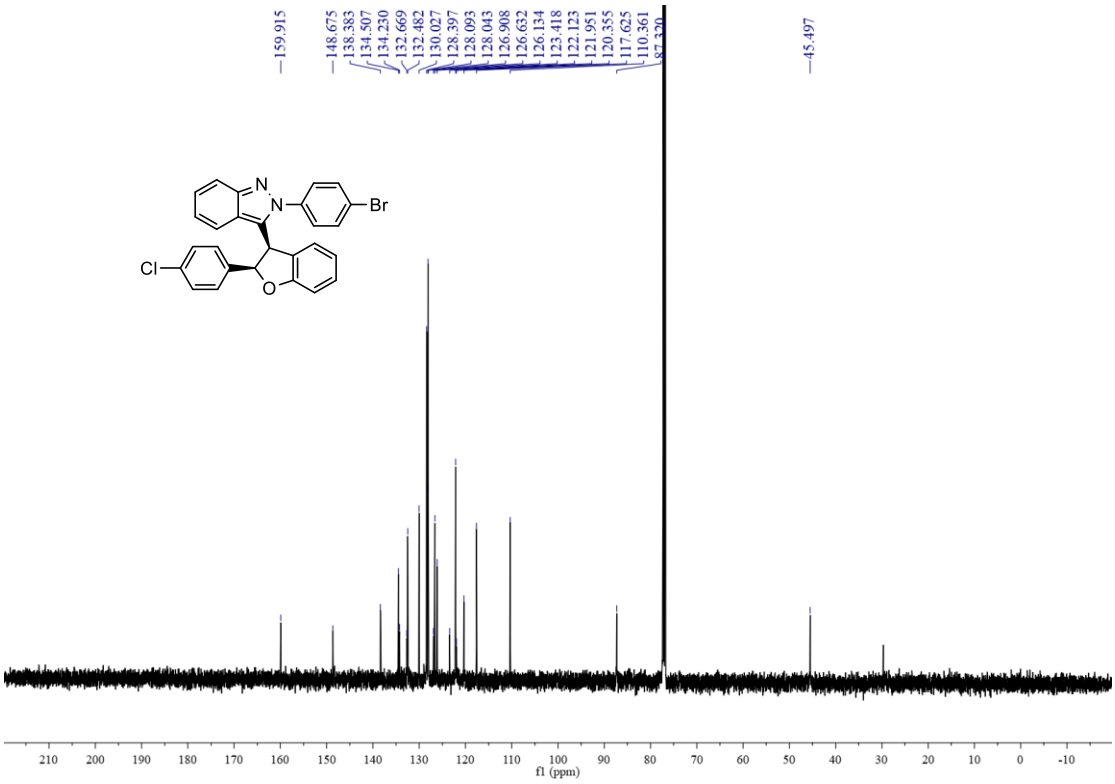




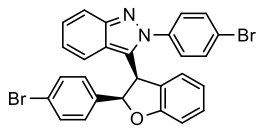

-112.893
N
N
Br
F
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

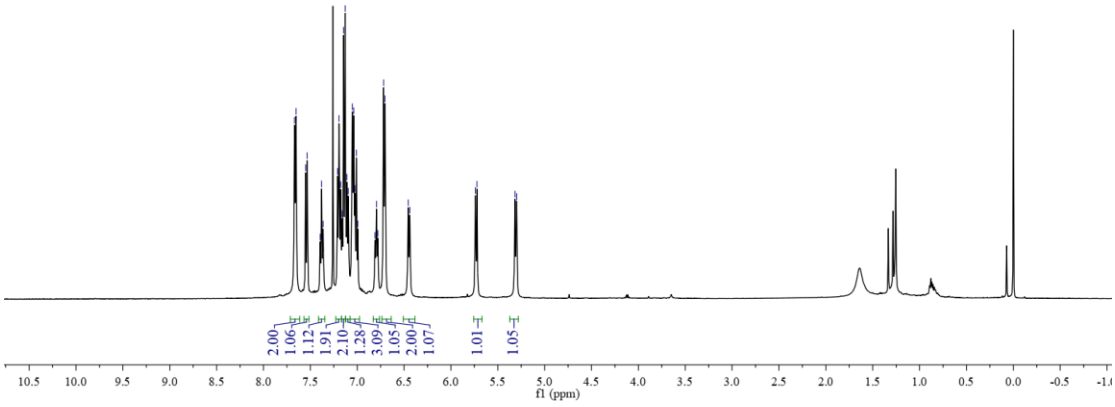
2-(4-bromophenyl)-3-((2R,3R)-2-(4-chlorophenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2e)

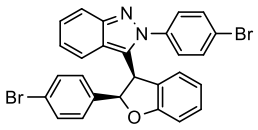




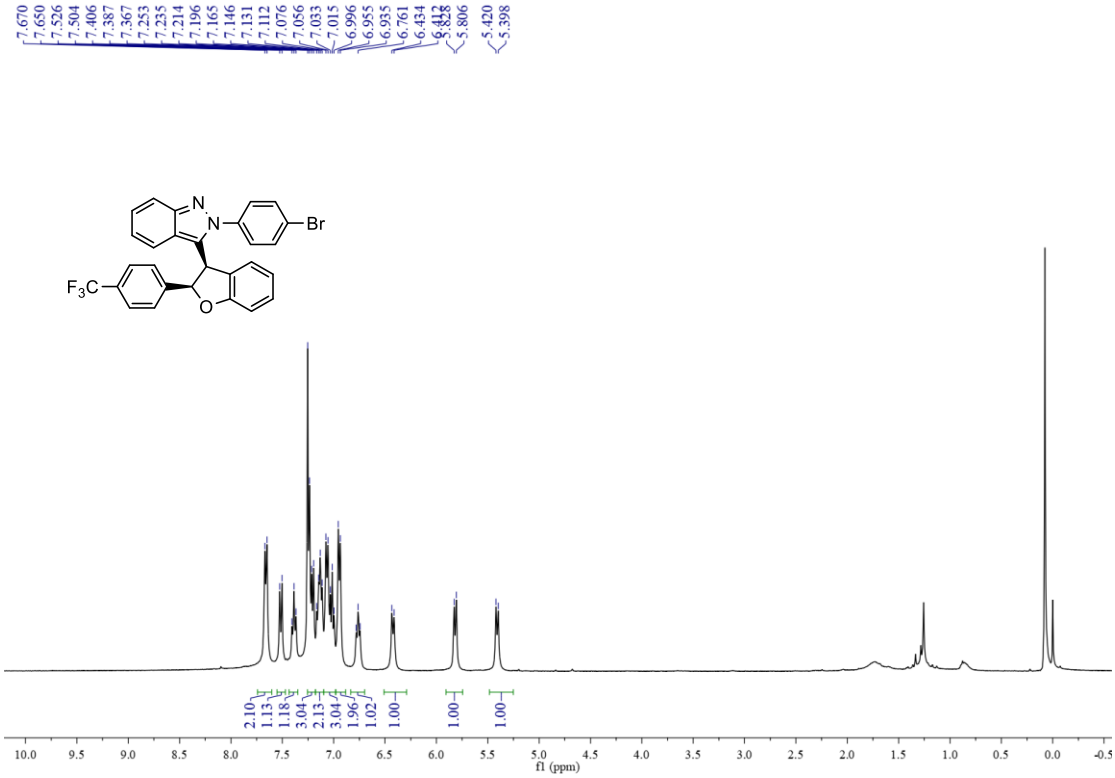
2-(4-bromophenyl)-3-((2R,3R)-2-(4-bromophenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2f)

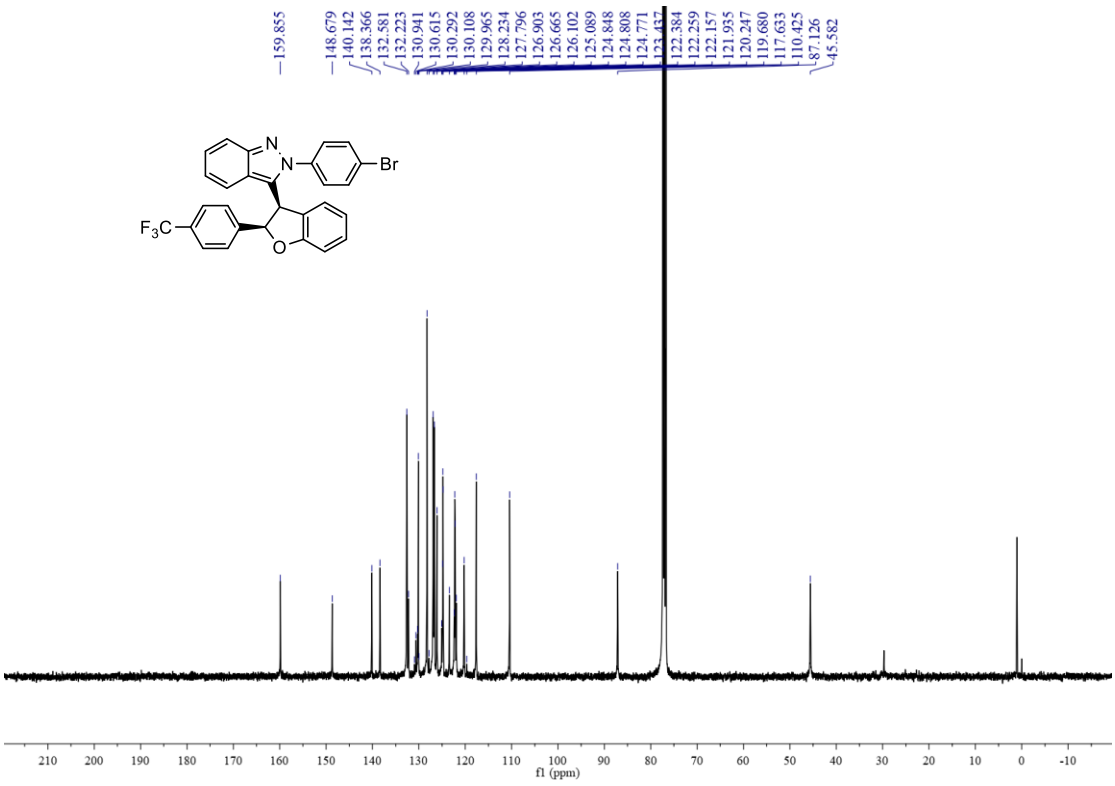


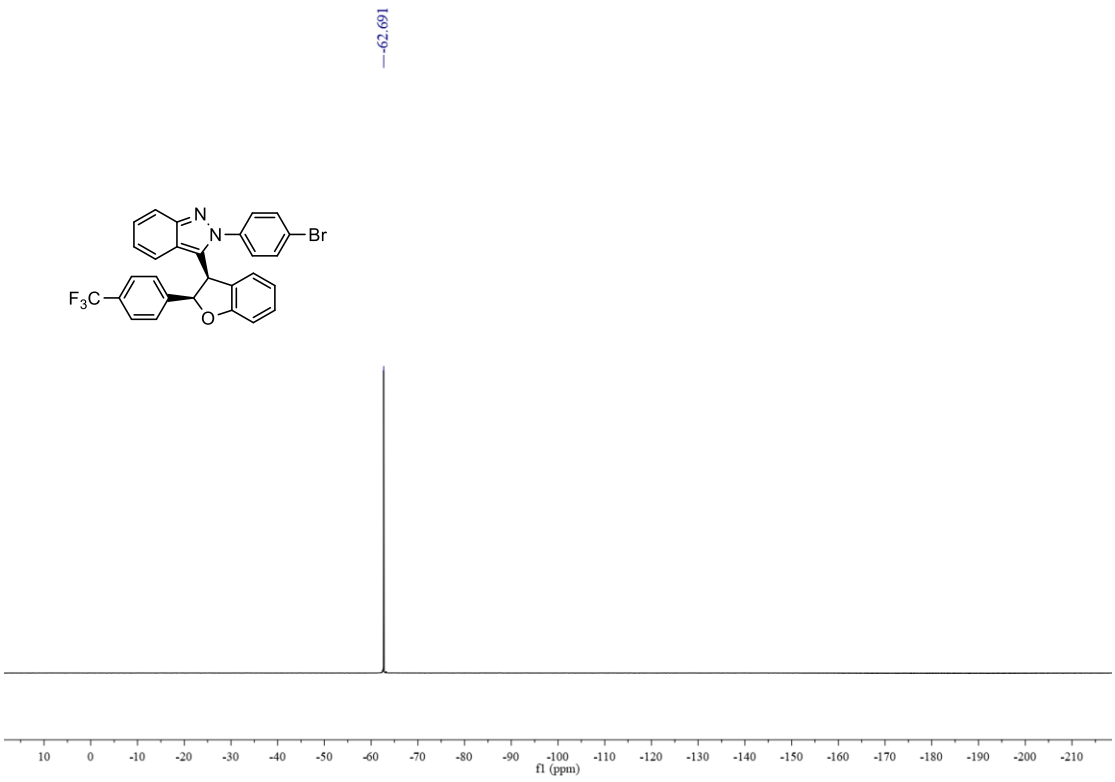




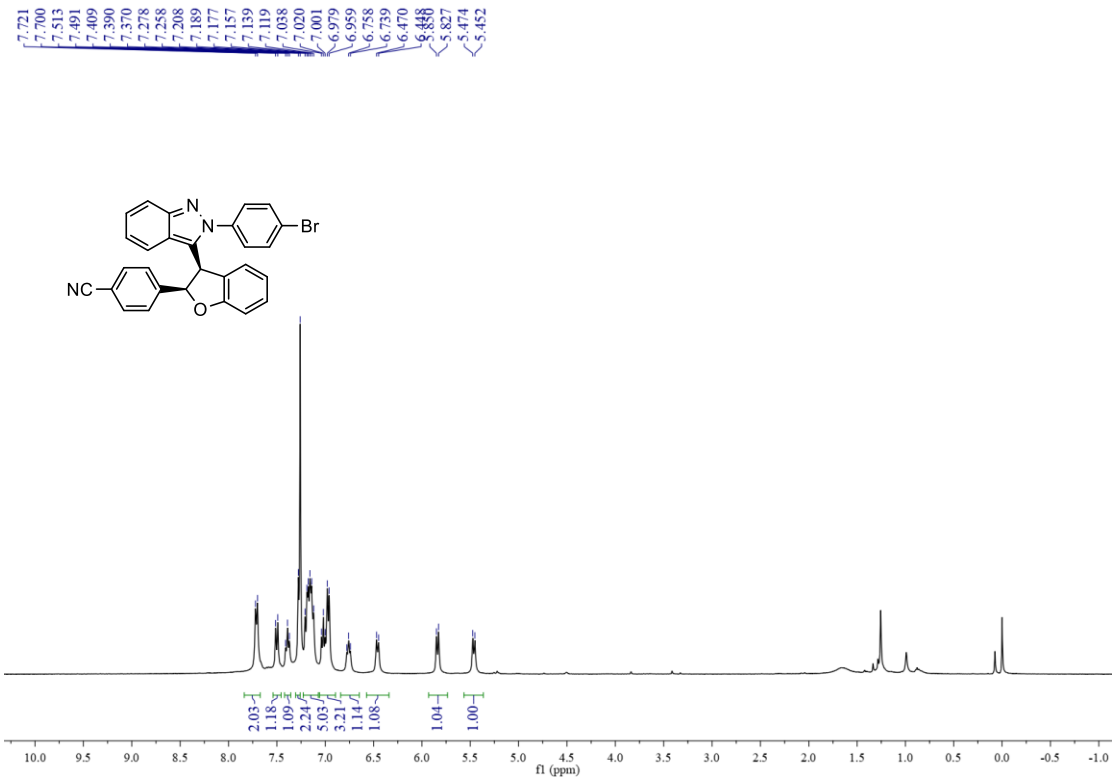
2-(4-bromophenyl)-3-((2R,3R)-2-(4-(trifluoromethyl)phenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2g)

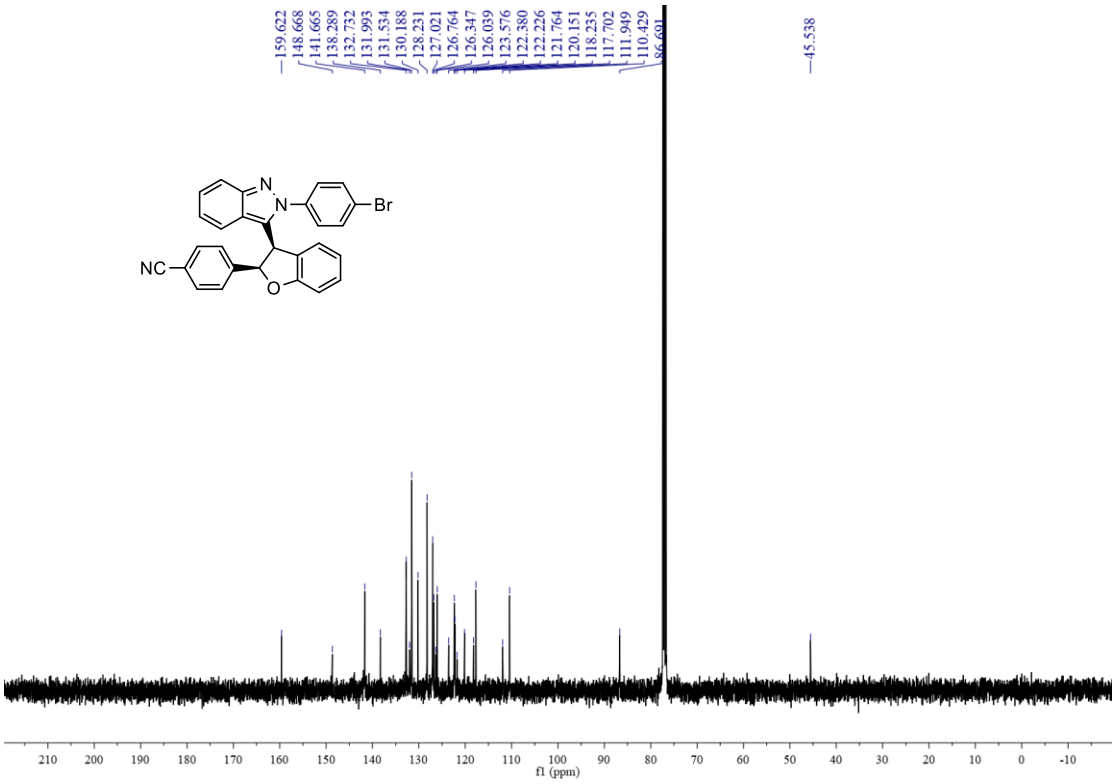




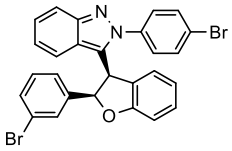

-62.691
N
N
Br
F3C
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

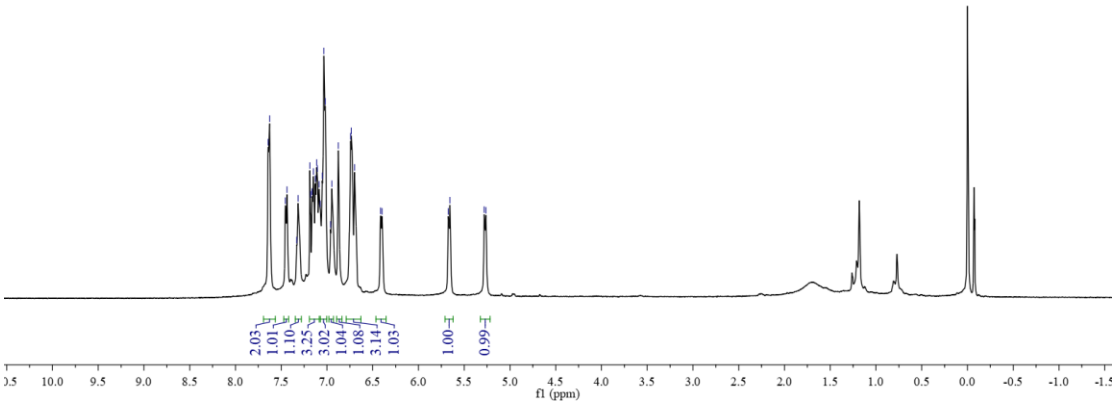
4-((2R,3R)-3-(2-(4-bromophenyl)-2H-indazol-3-yl)-2,3-dihydrobenzofuran-2-yl)benzonitrile (2h)

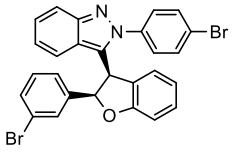


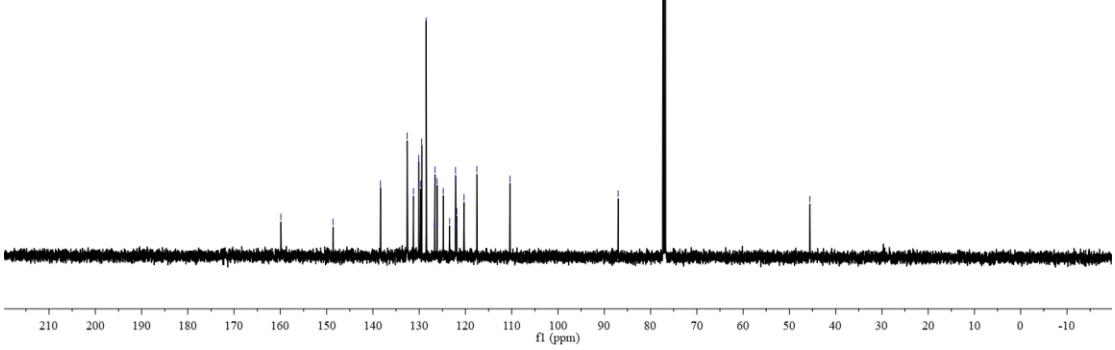


2-(4-bromophenyl)-3-((2R,3R)-2-(3-bromophenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2i)

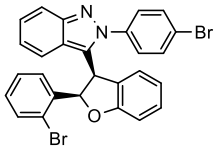


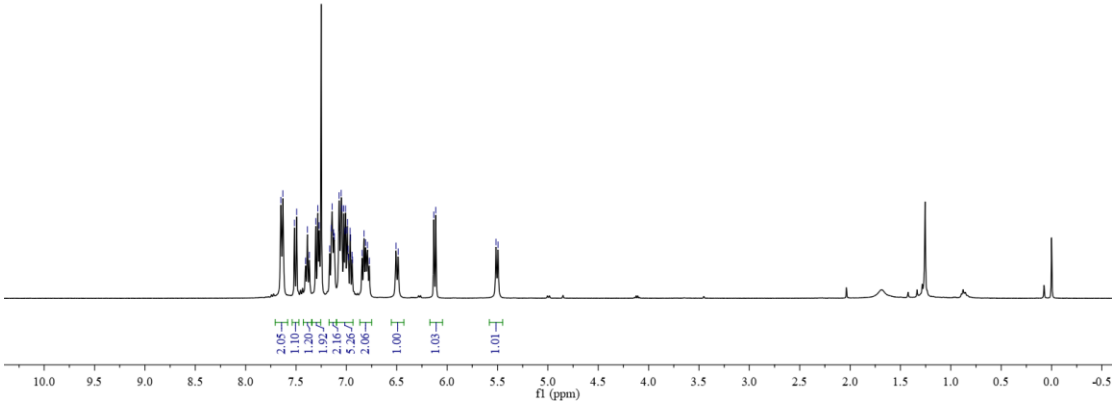


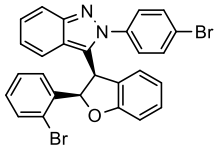


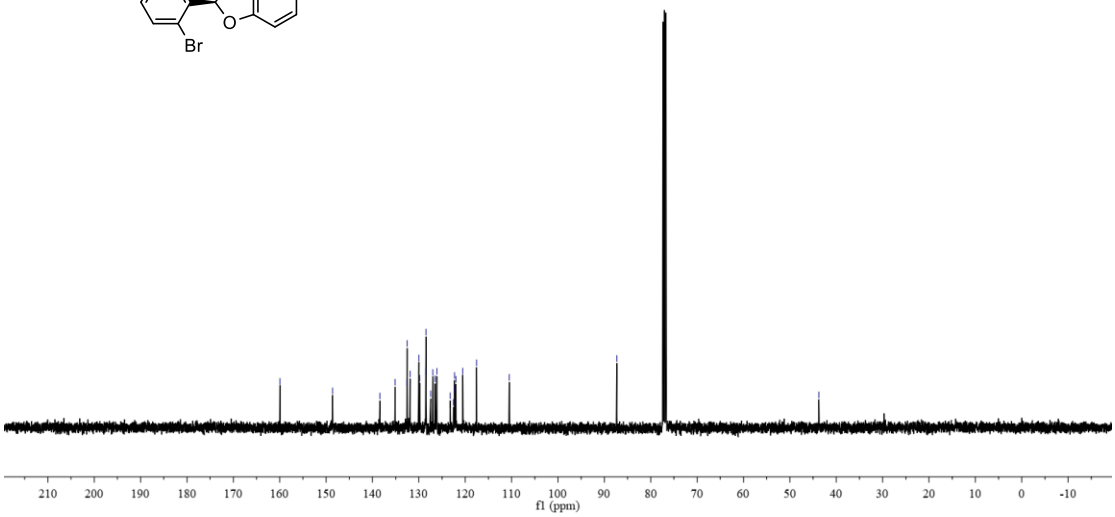


2-(4-bromophenyl)-3-((2R,3R)-2-(2-bromophenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2j)

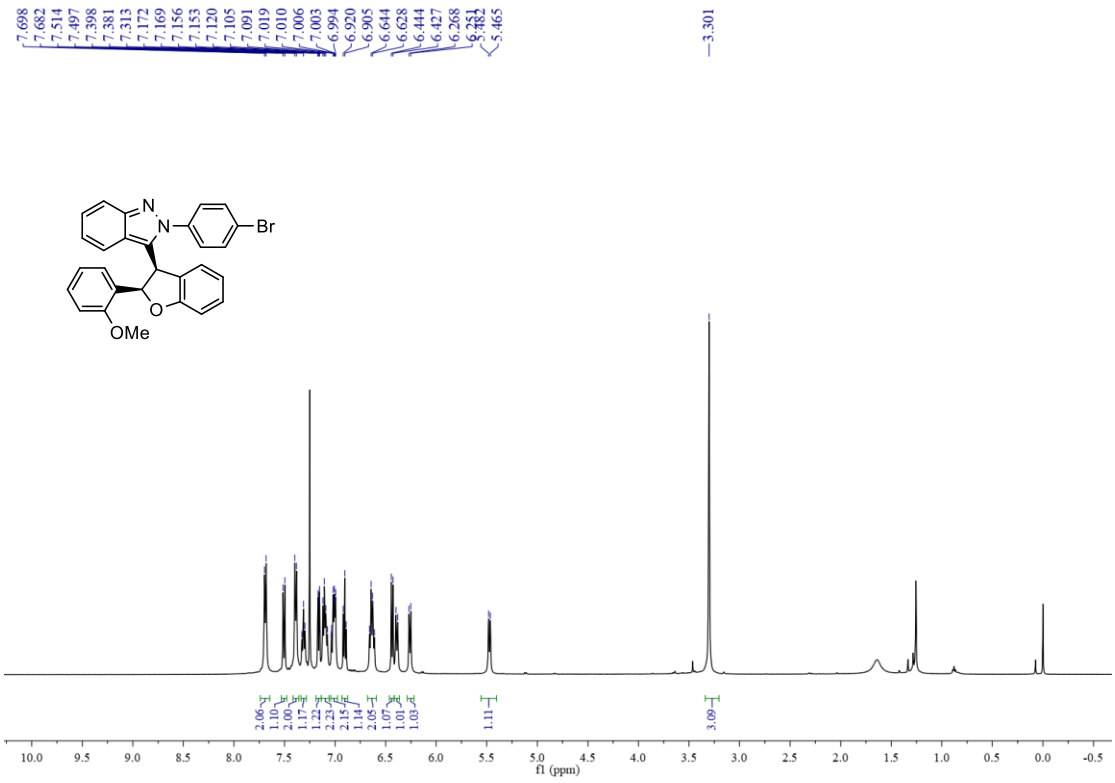


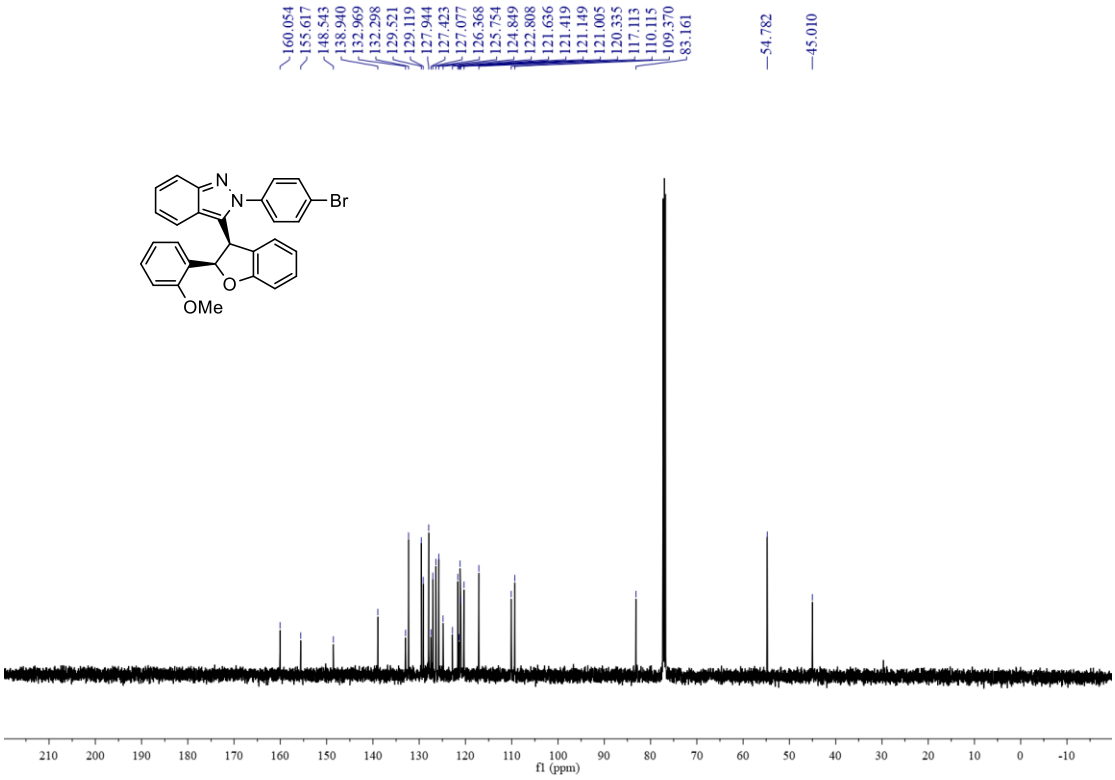




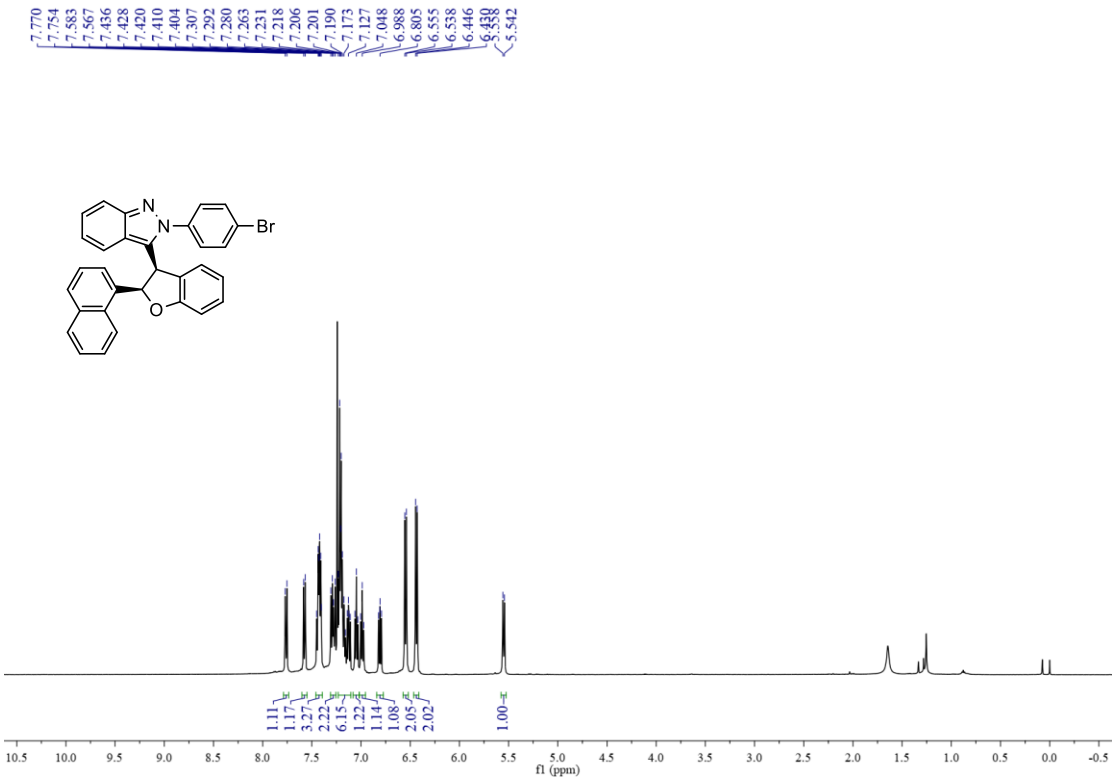


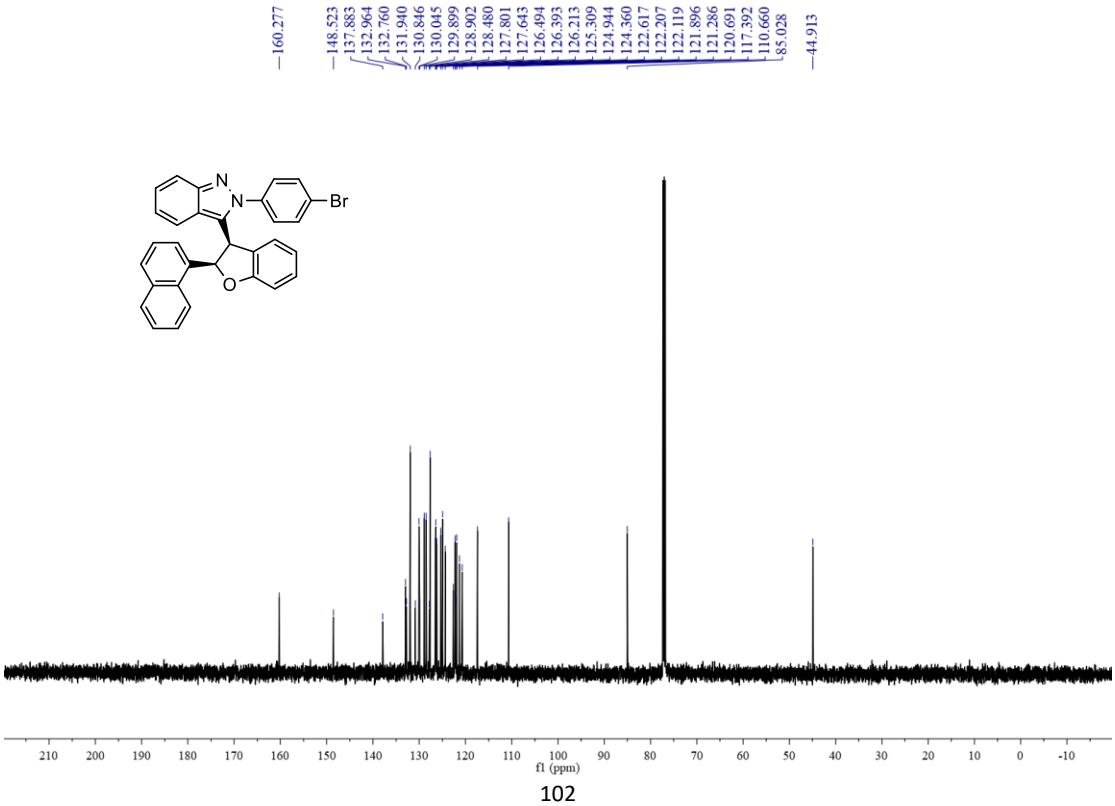
2-(4-bromophenyl)-3-((2R,3R)-2-(2-methoxyphenyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2k)



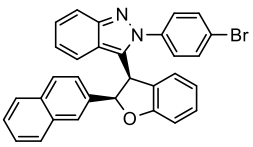


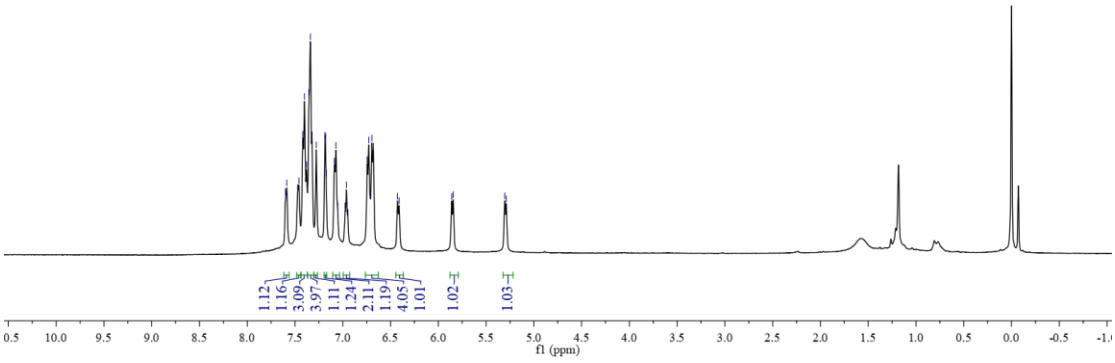
2-(4-bromophenyl)-3-((2R,3R)-2-(naphthalen-1-yl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2l)

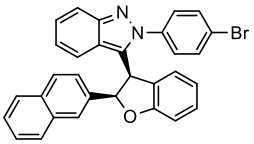




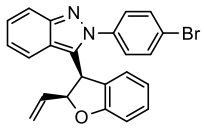
2-(4-bromophenyl)-3-((2R,3R)-2-(naphthalen-2-yl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2m)



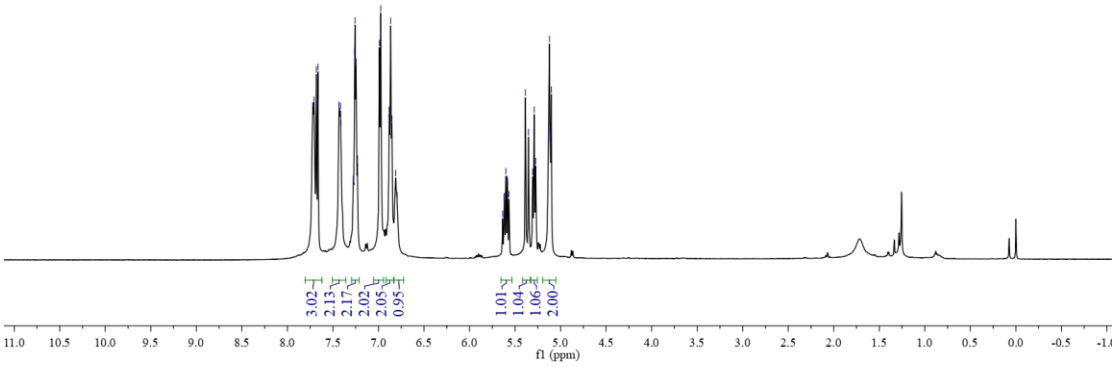


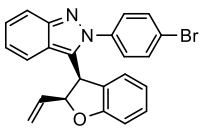


2-(4-bromophenyl)-3-((2S,3R)-2-vinyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2n)



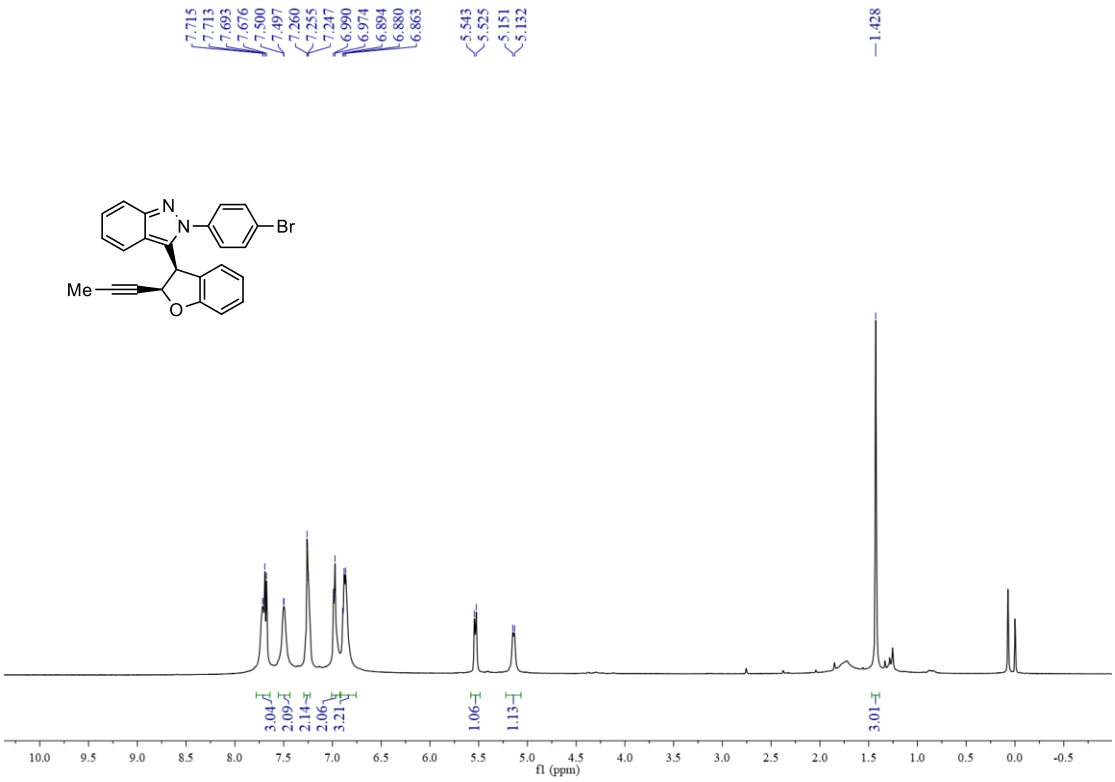
97:3 d.r.

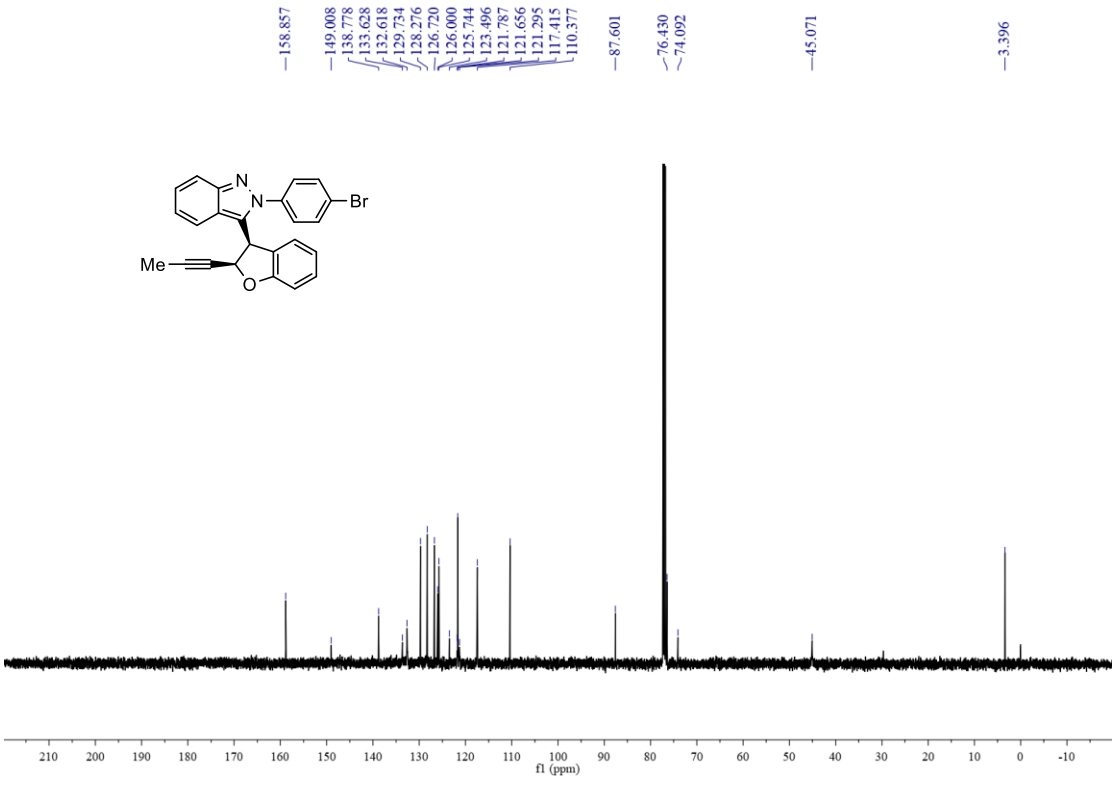




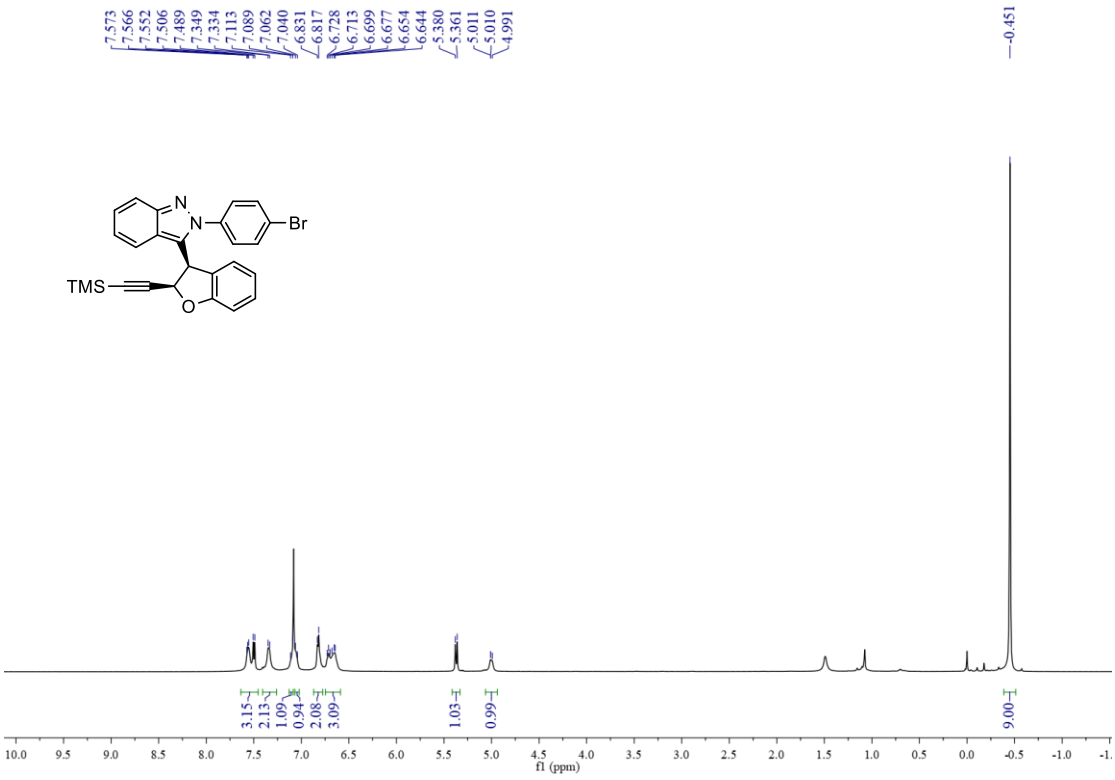
97:3 d.r.

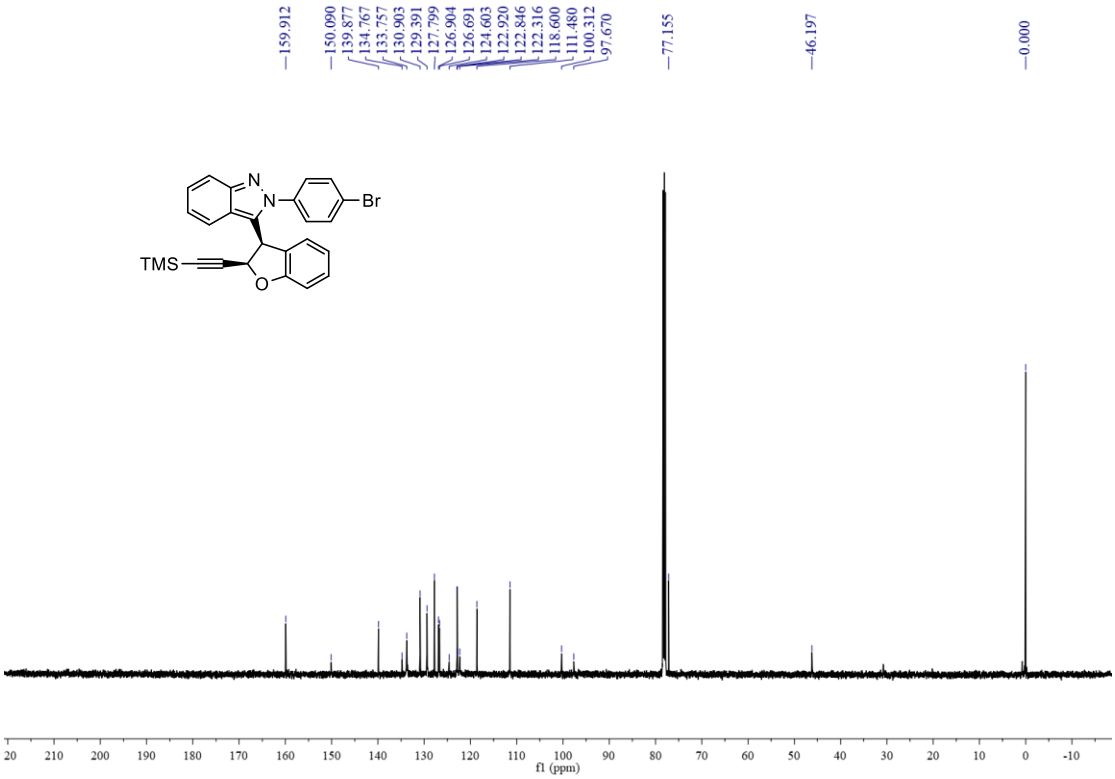
2-(4-bromophenyl)-3-((2R,3R)-2-(prop-1-yn-1-yl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2o)



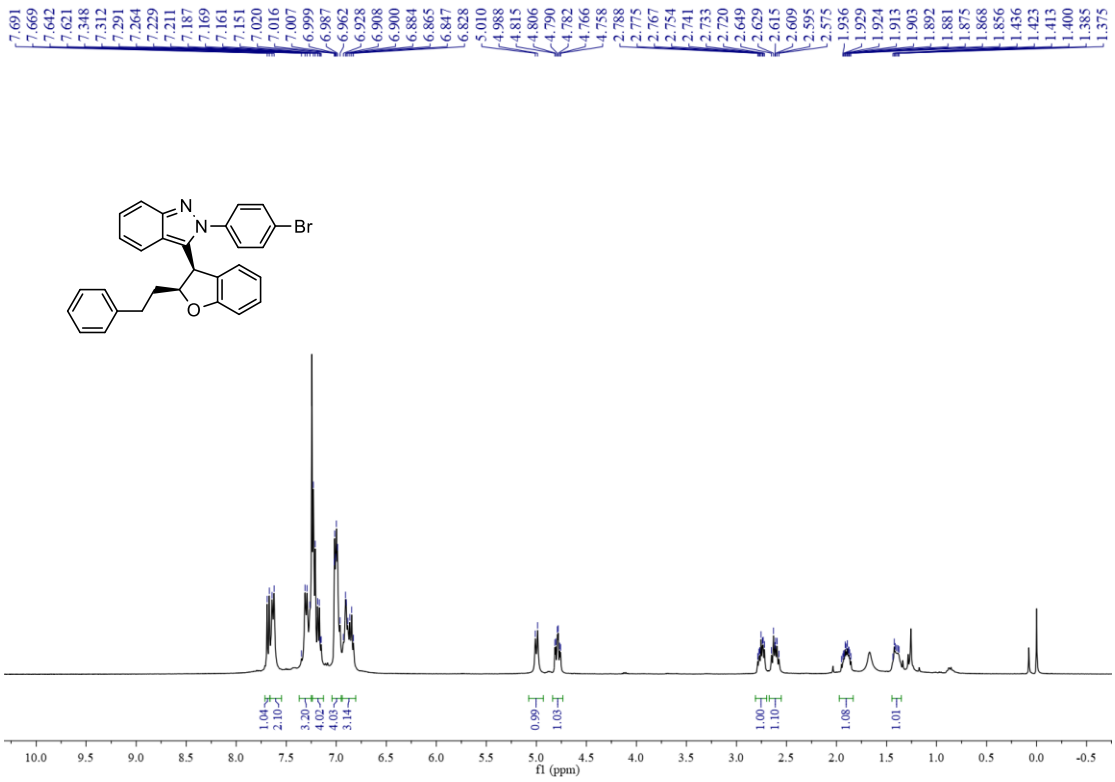


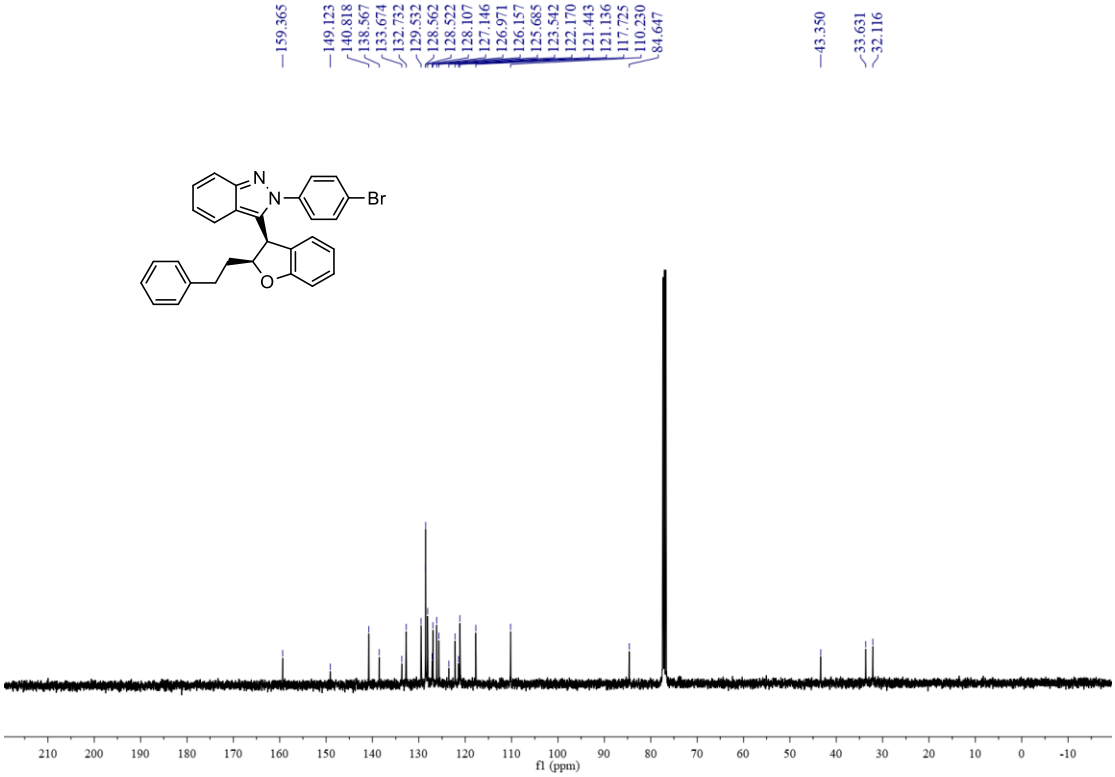
2-(4-bromophenyl)-3-((2R,3R)-2-((trimethylsilyl)ethynyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2p)



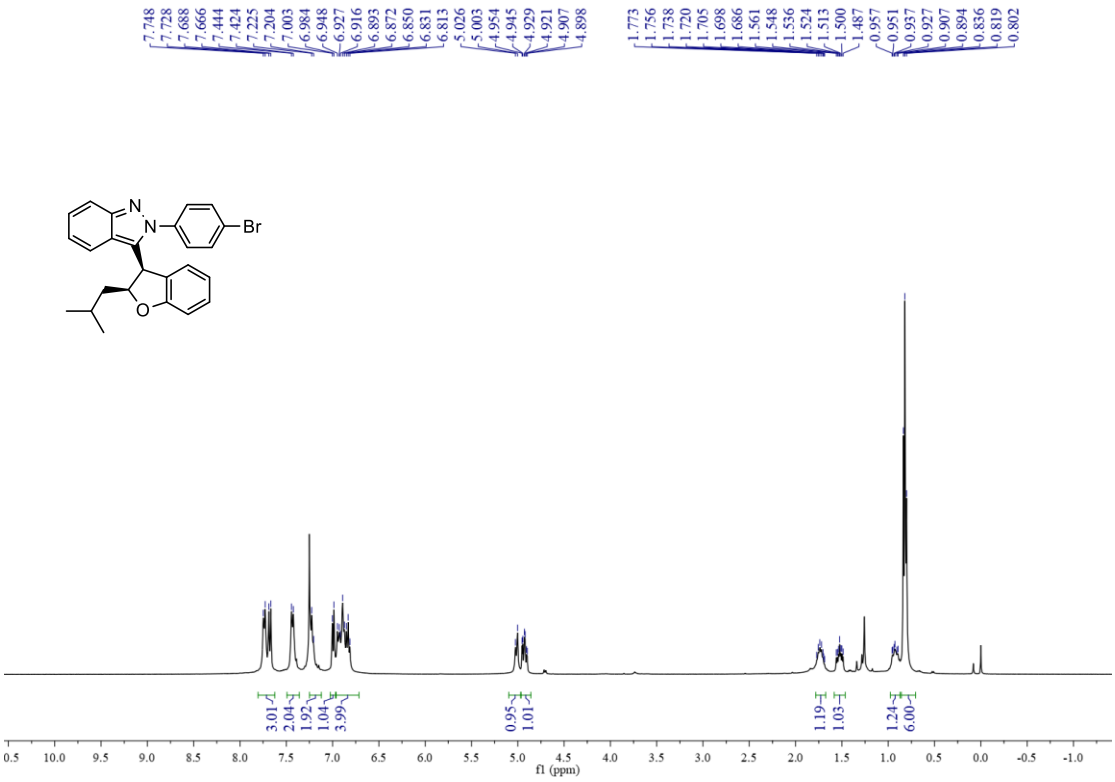


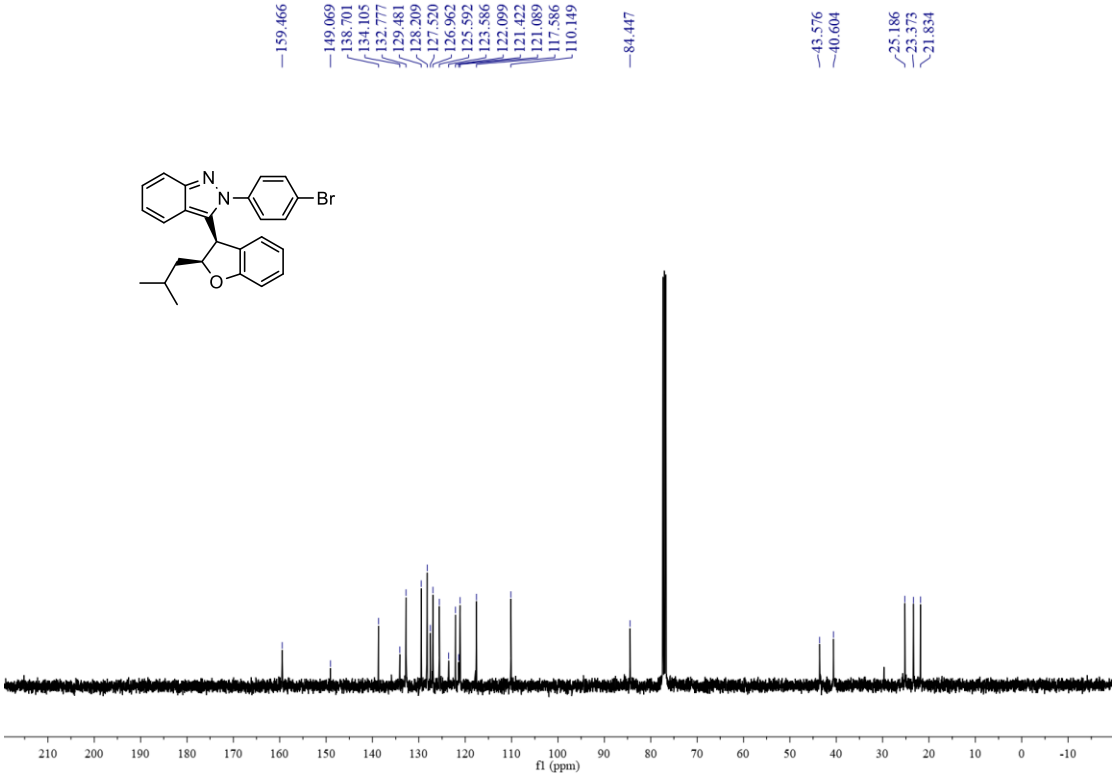
2-(4-bromophenyl)-3-((2S,3R)-2-phenethyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2q)



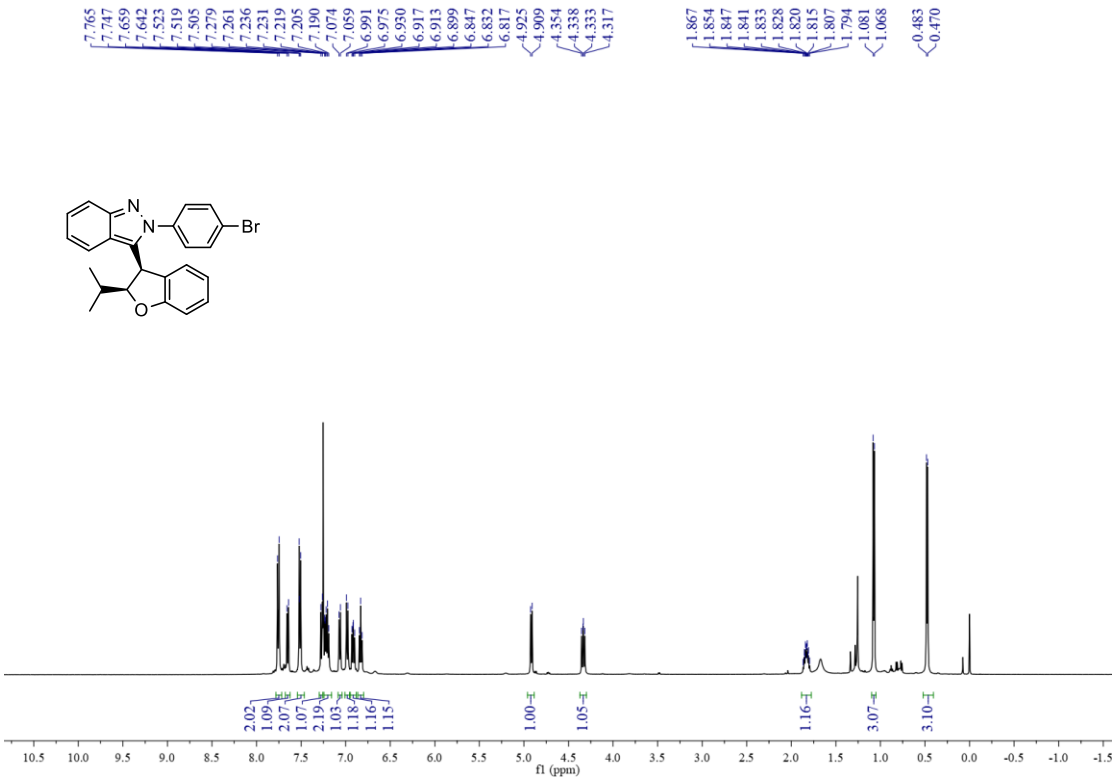


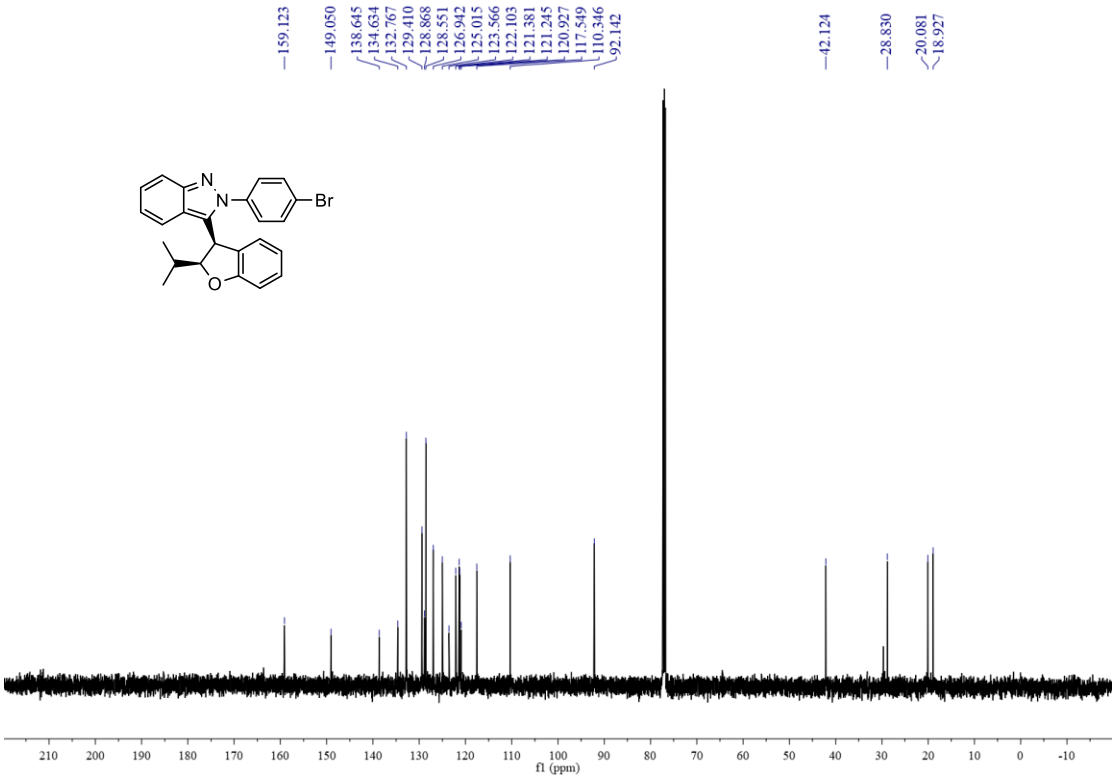
2-(4-bromophenyl)-3-((2S,3R)-2-isobutyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2r)



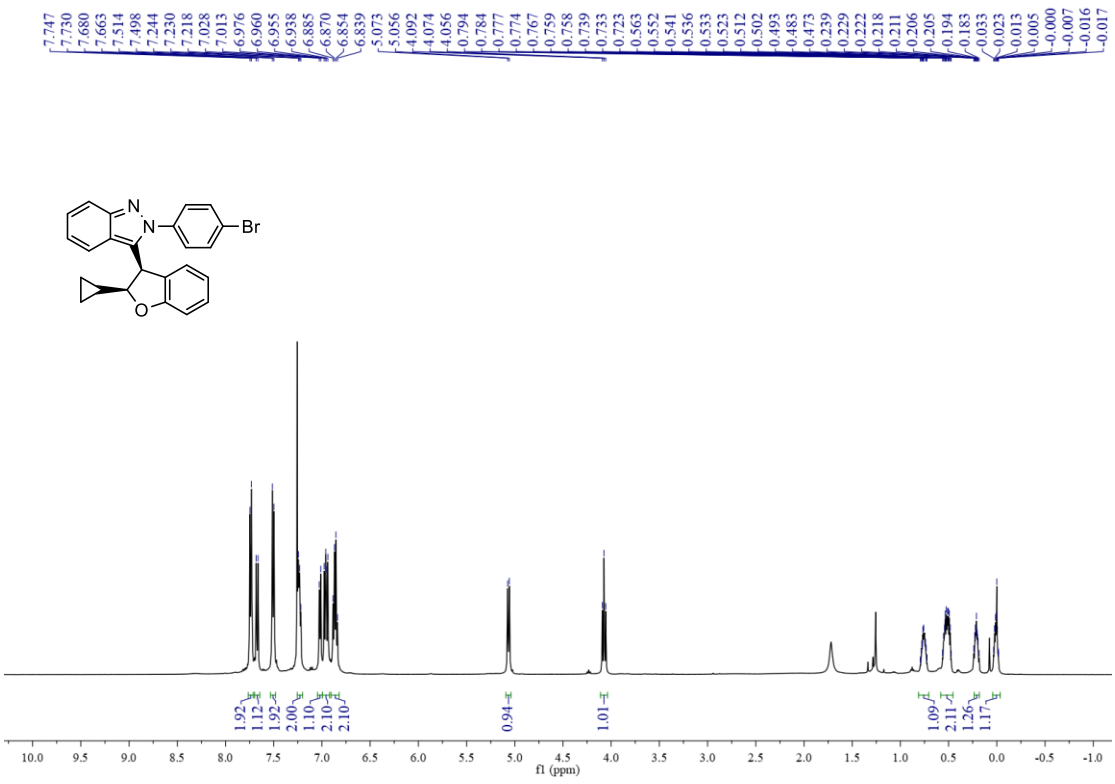


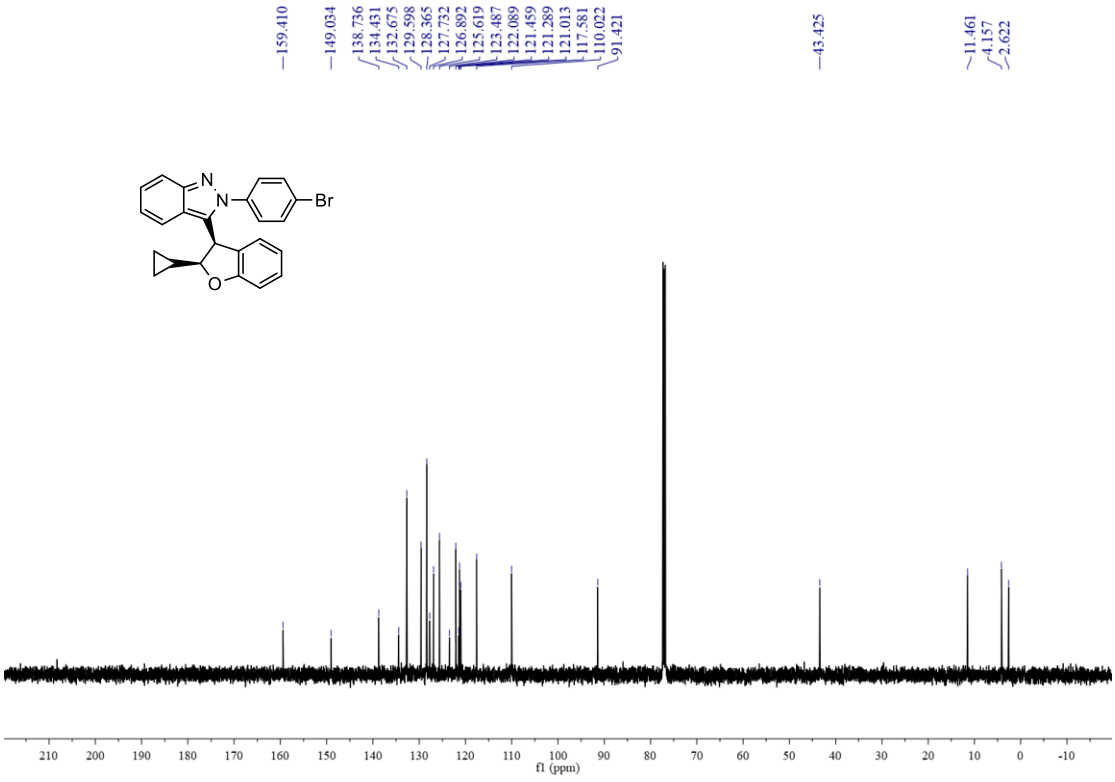
2-(4-bromophenyl)-3-((2S,3R)-2-isopropyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2s)



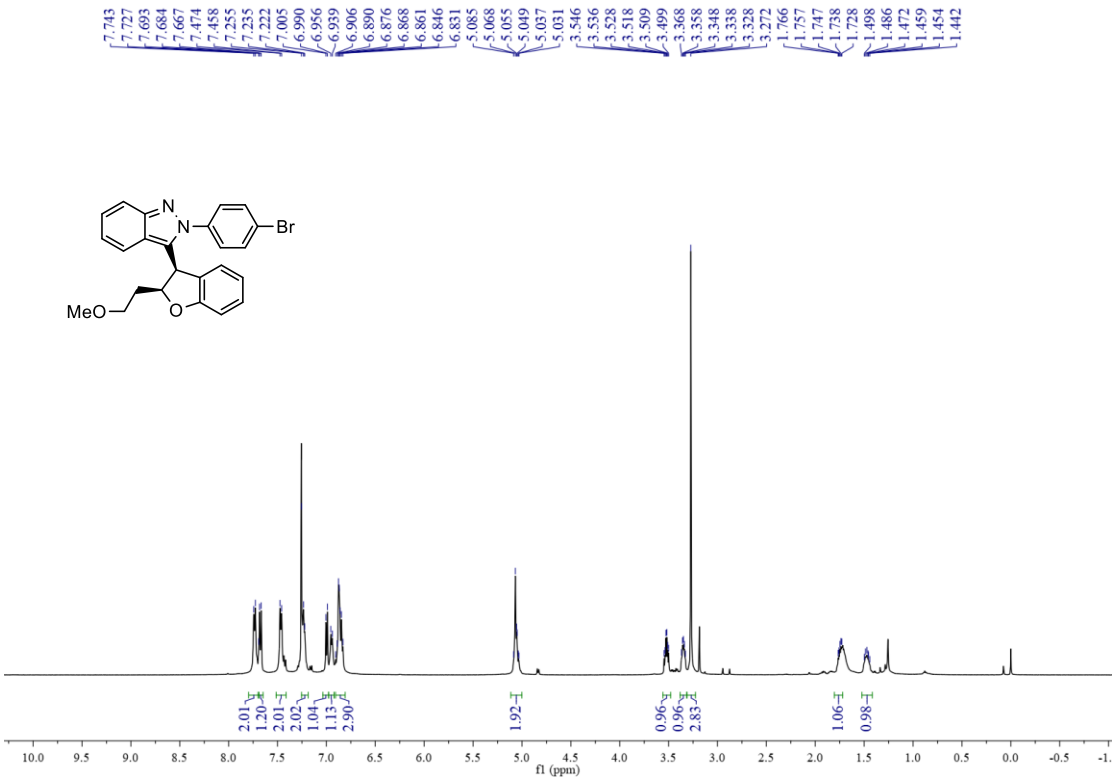


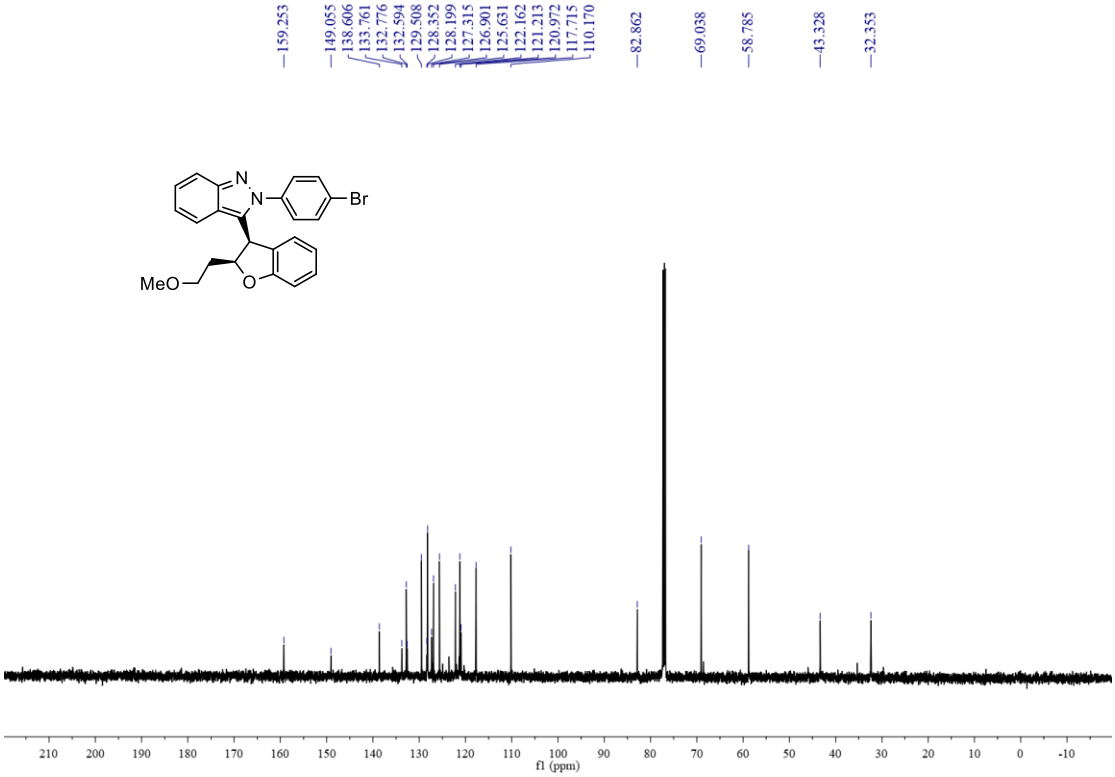
2-(4-bromophenyl)-3-((2S,3R)-2-cyclopropyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2t)



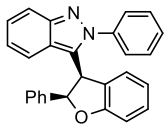


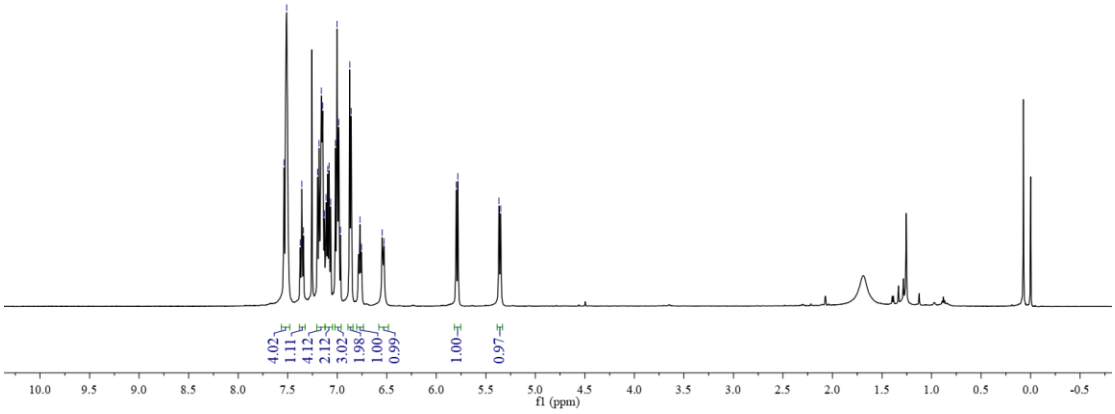
2-(4-bromophenyl)-3-((2S,3R)-2-(2-methoxyethyl)-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2u)

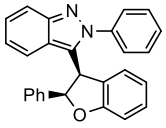




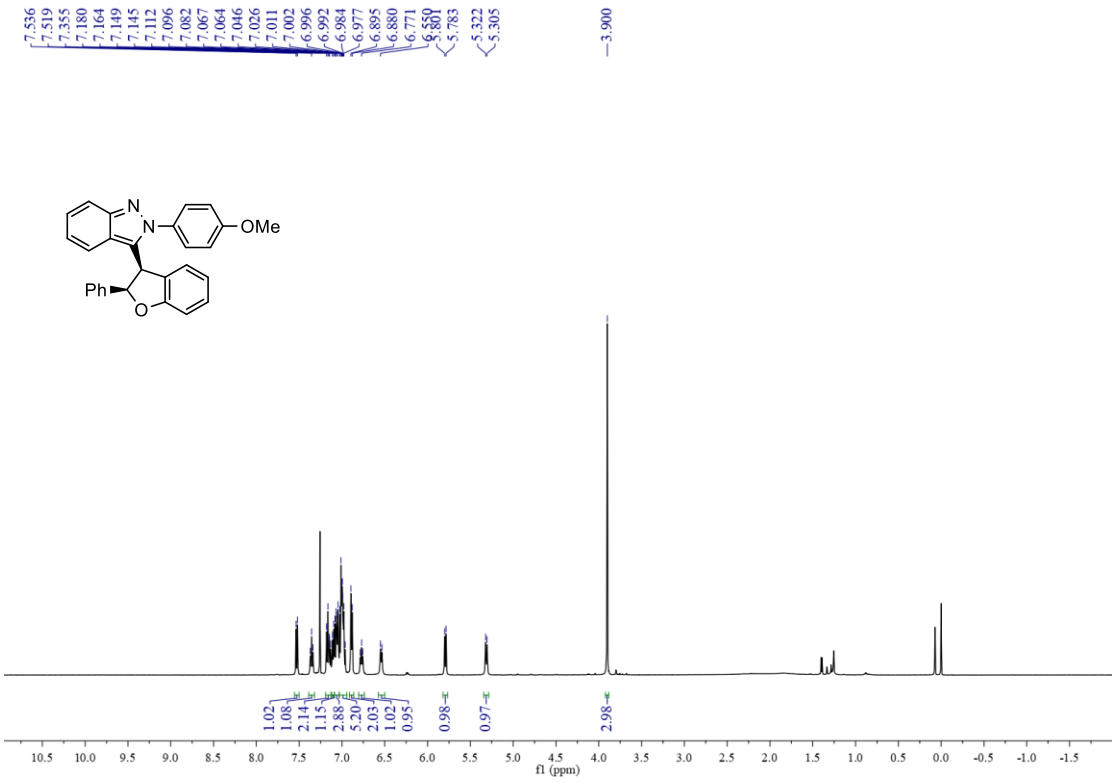
2-phenyl-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2v)

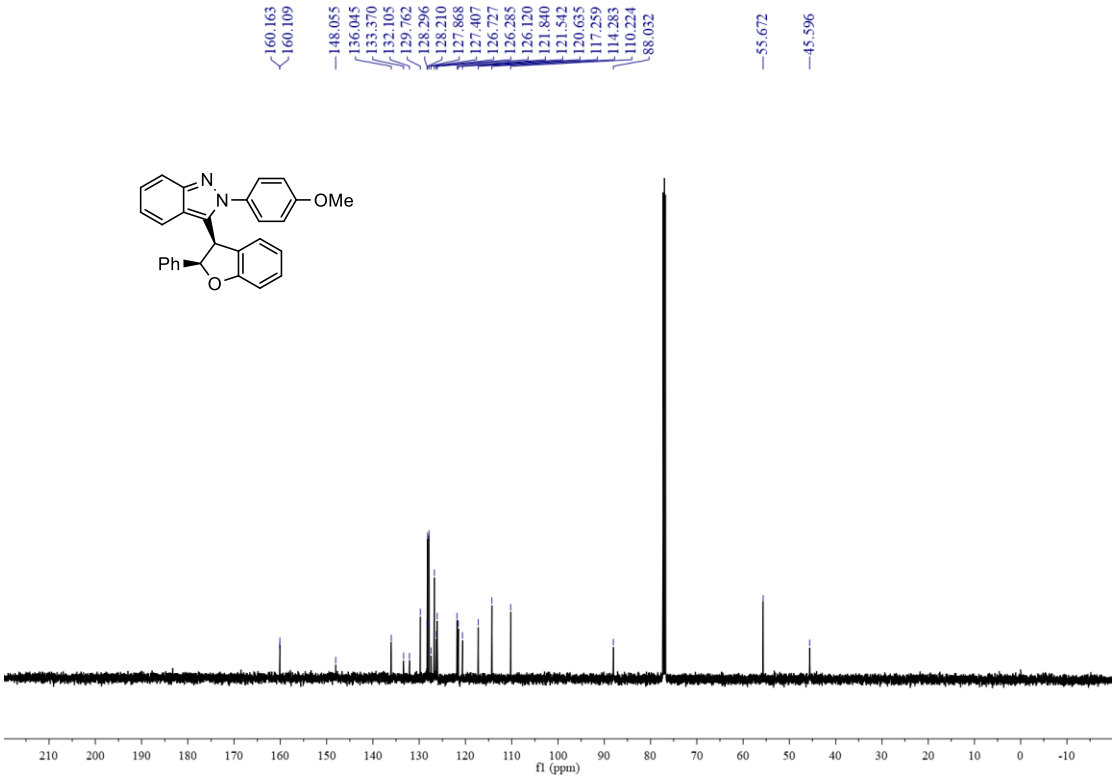




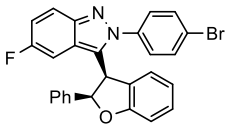


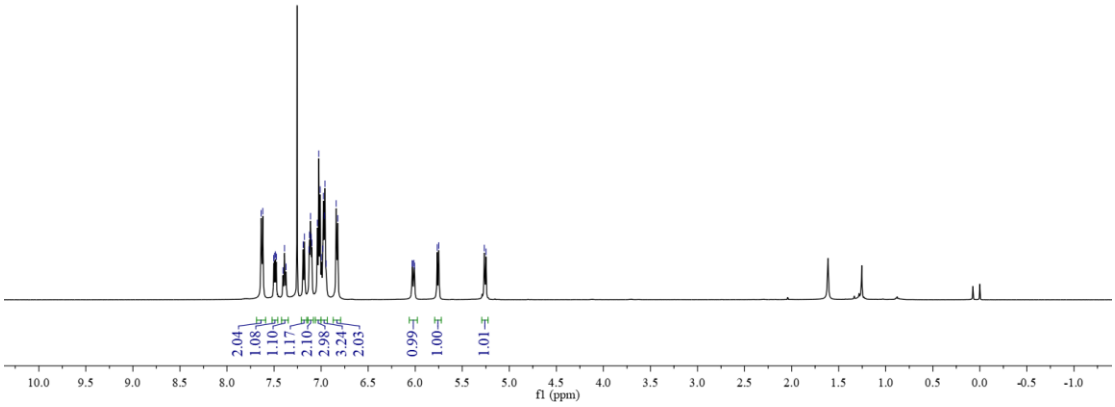
2-(4-methoxyphenyl)-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2w)

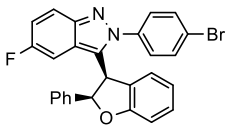


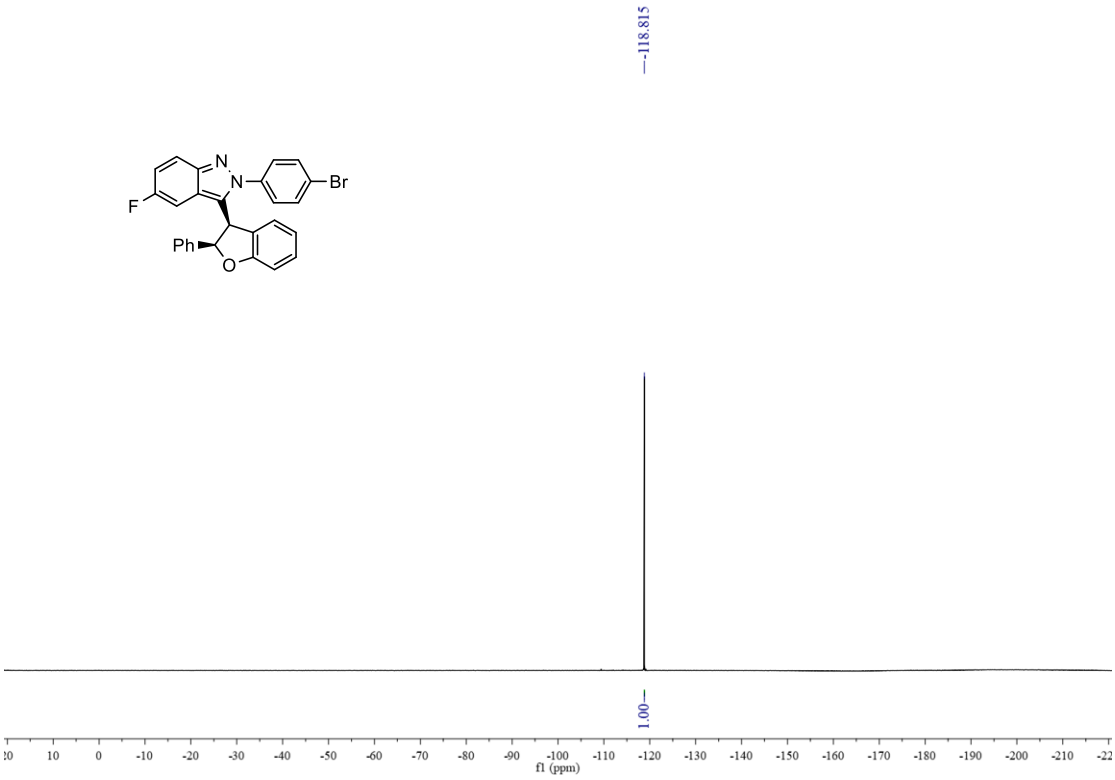


2-(4-bromophenyl)-5-fluoro-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2x)

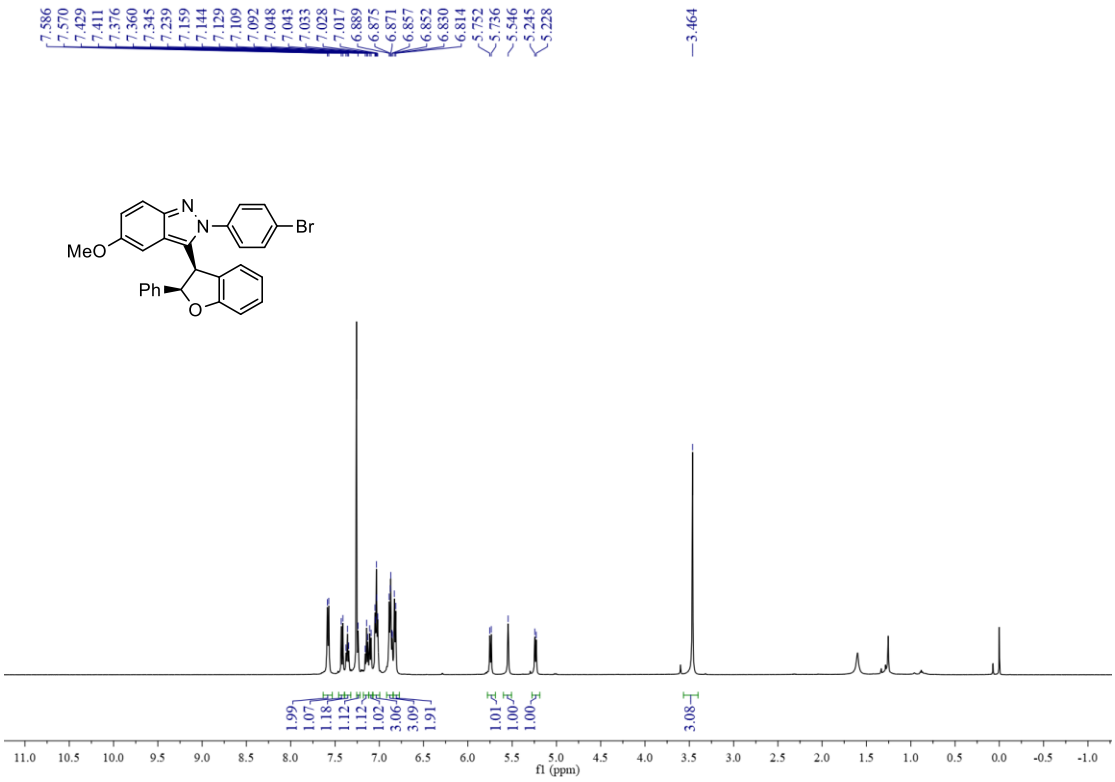


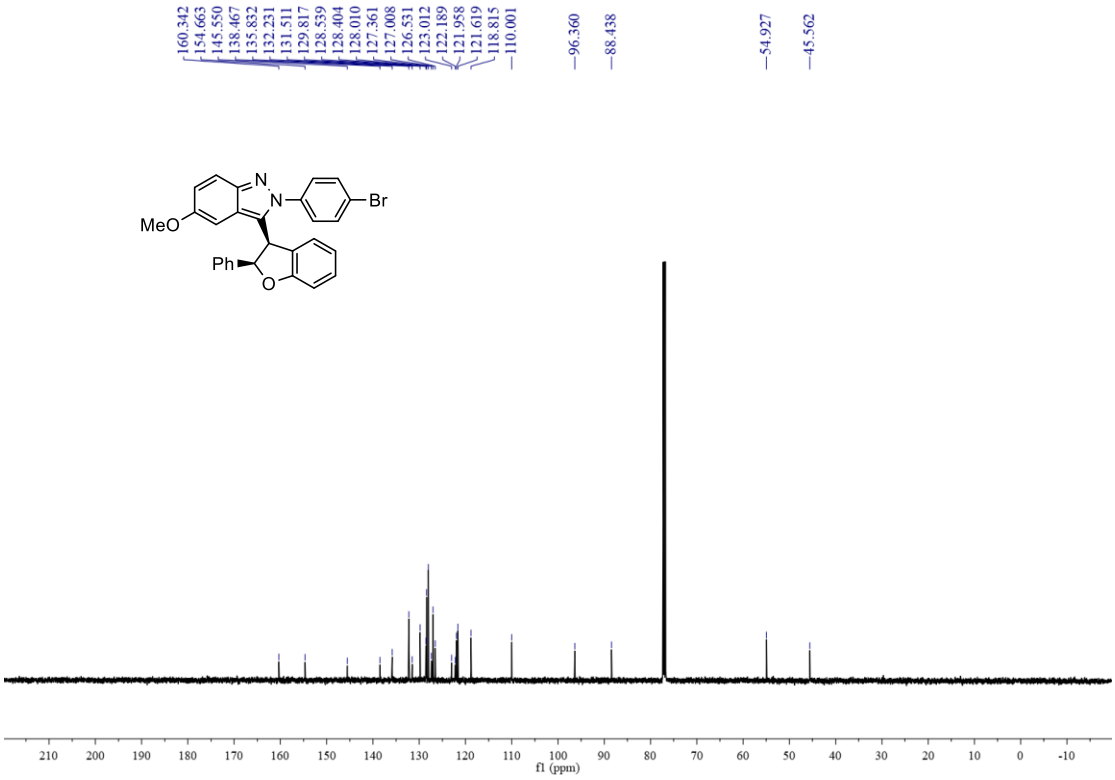




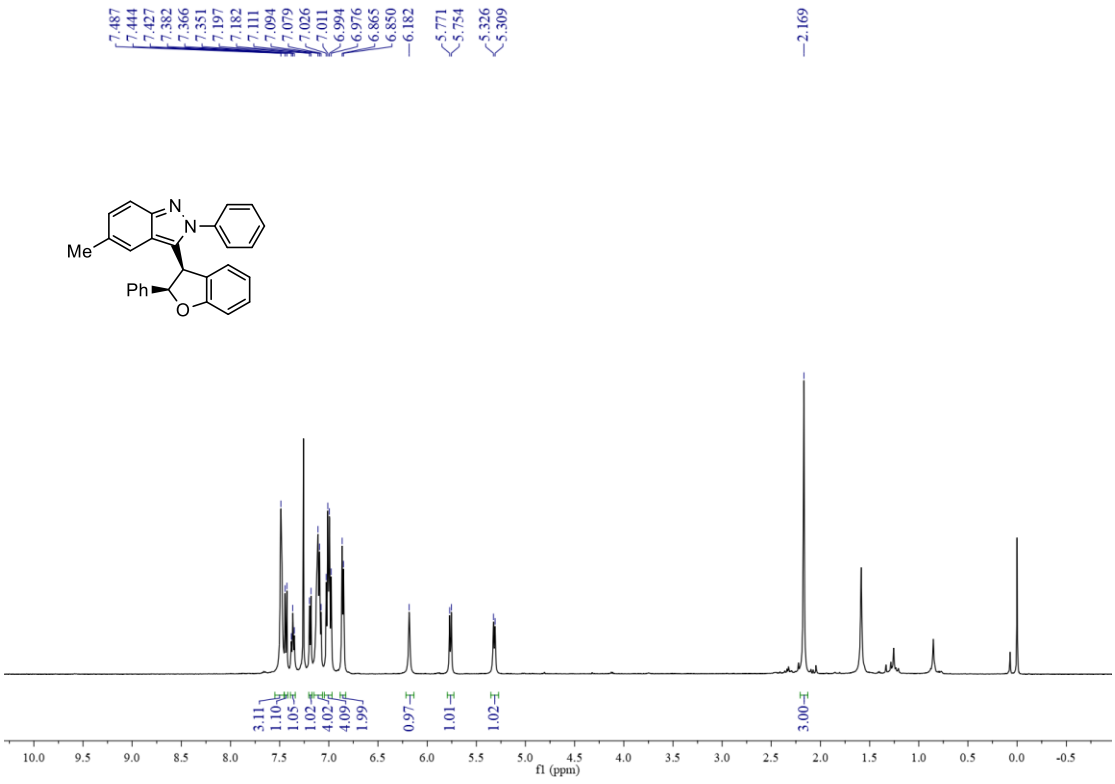

-118.815
N
N
Br
F
Ph
O
1.00
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

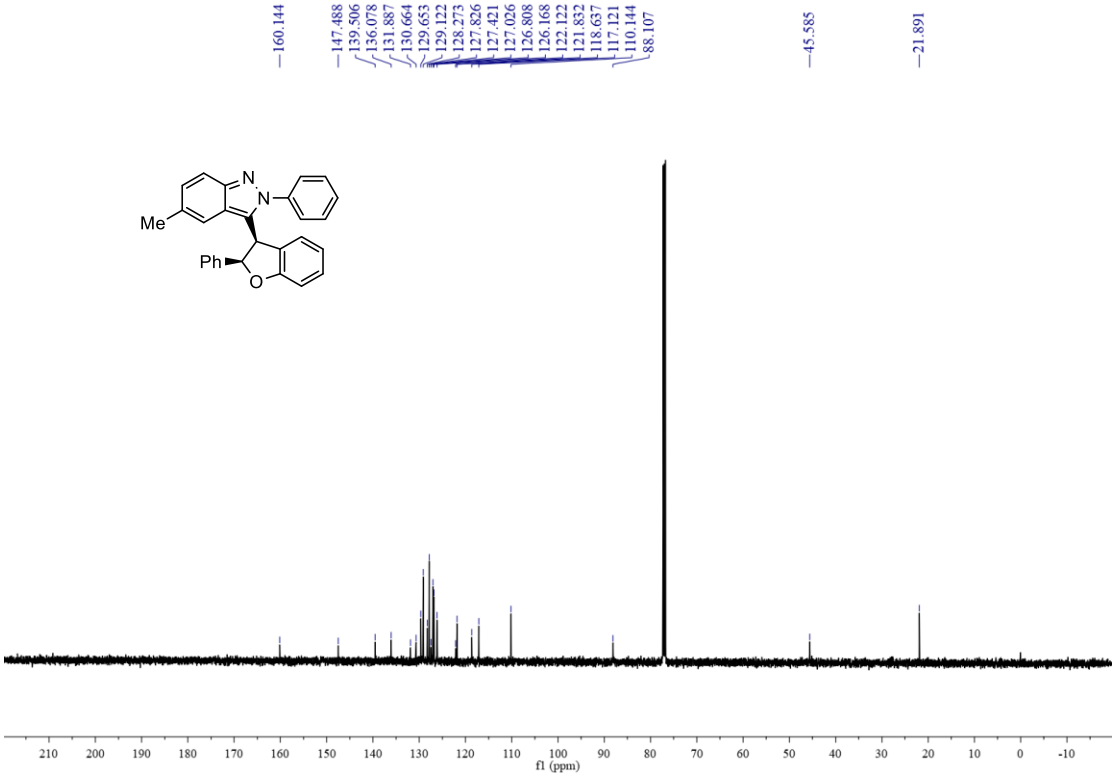
2-(4-bromophenyl)-5-methoxy-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2y)



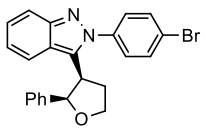


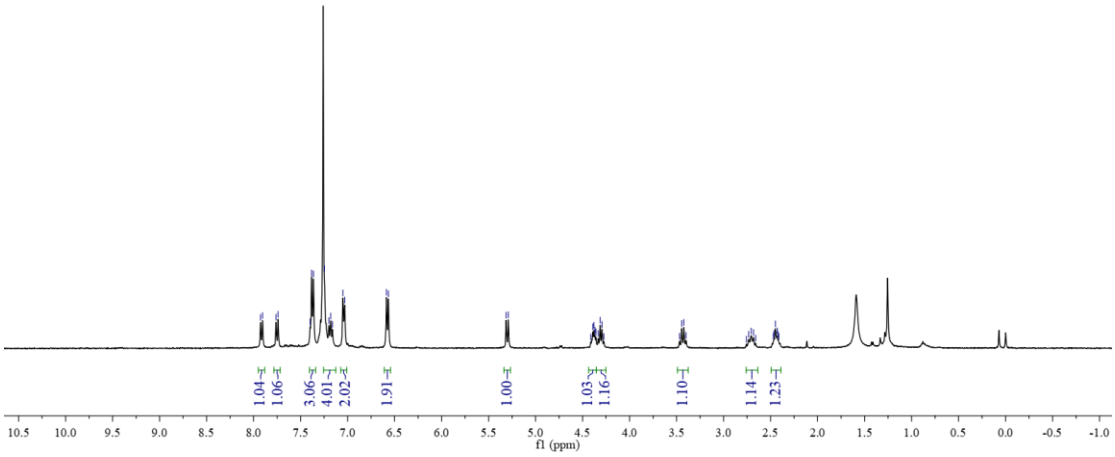
5-methyl-2-phenyl-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (2z)

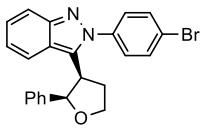


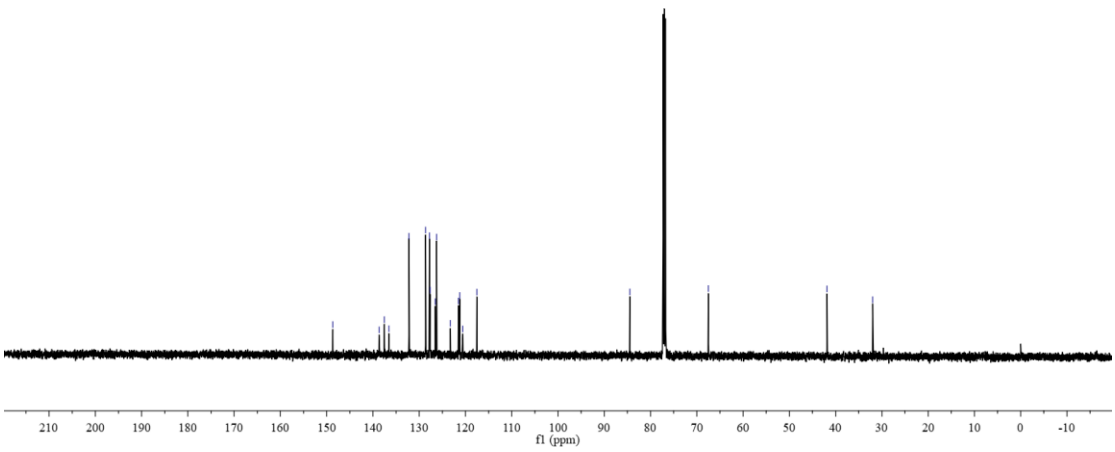


2-(4-bromophenyl)-3-((2R,3R)-2-phenyltetrahydrofuran-3-yl)-2H-indazole (2aa)

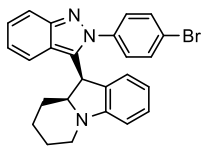




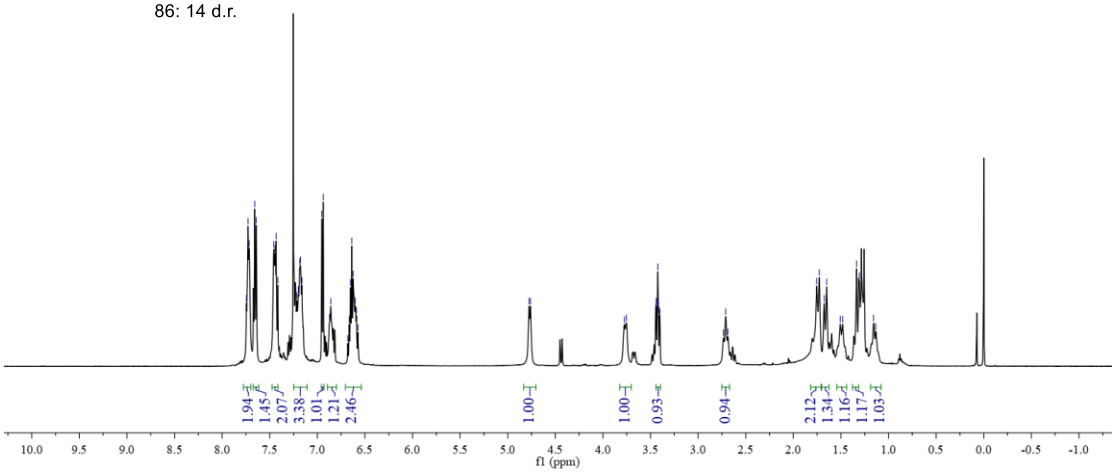


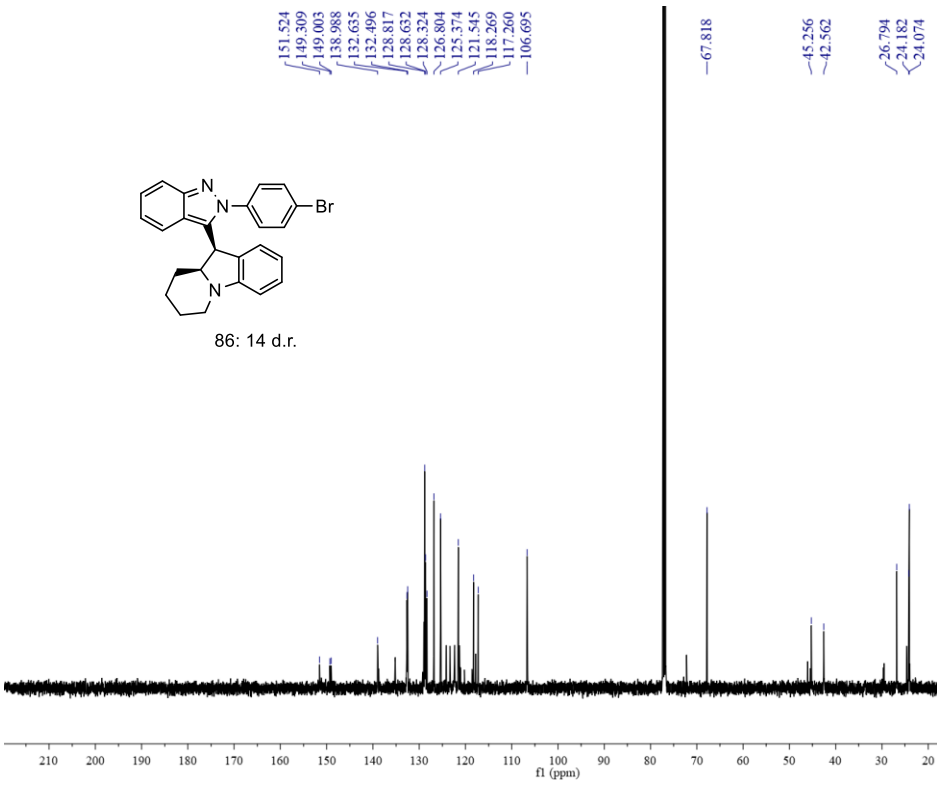


(9aS,10S)-10-(2-(4-bromophenyl)-2H-indazol-3-yl)-6,7,8,9,9a,10-hexahydropyrido[1,2-a]indole (2ab)



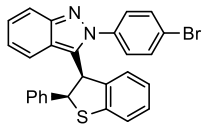
86: 14 d.r.

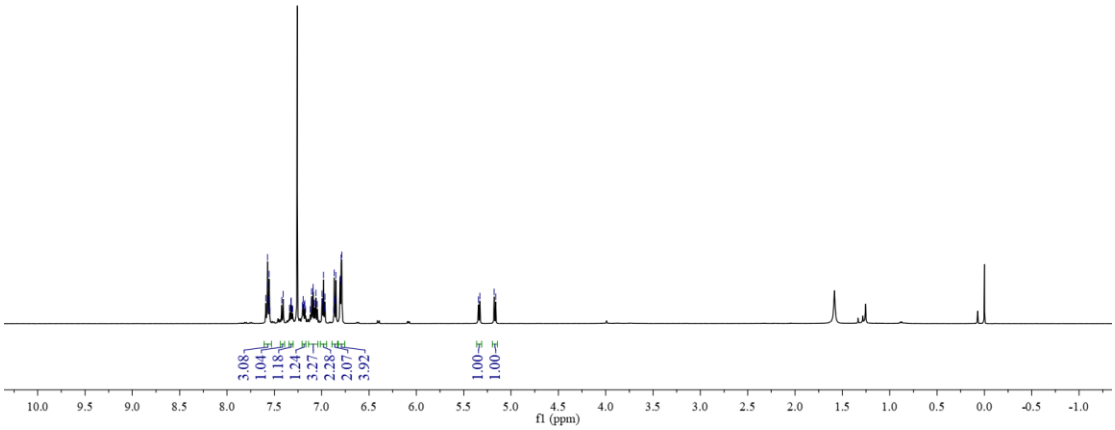


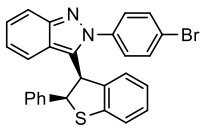


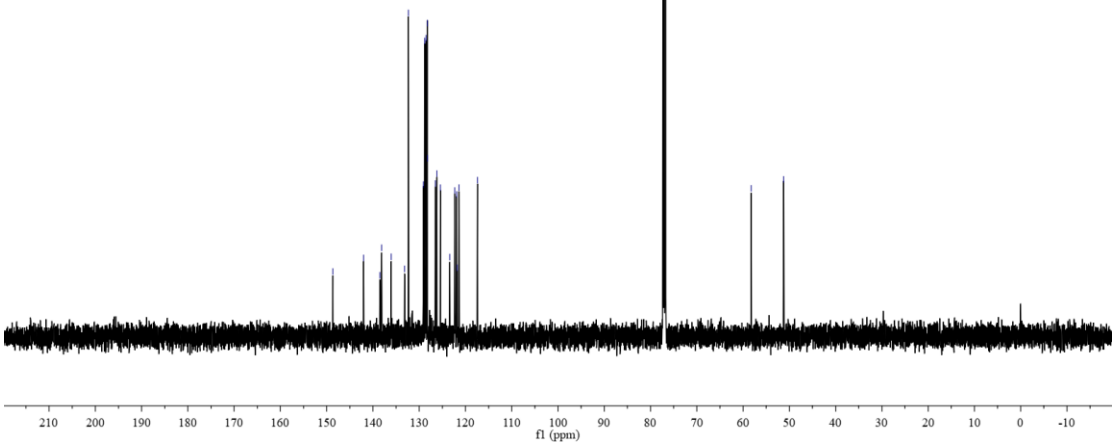
86: 14 d.r.

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

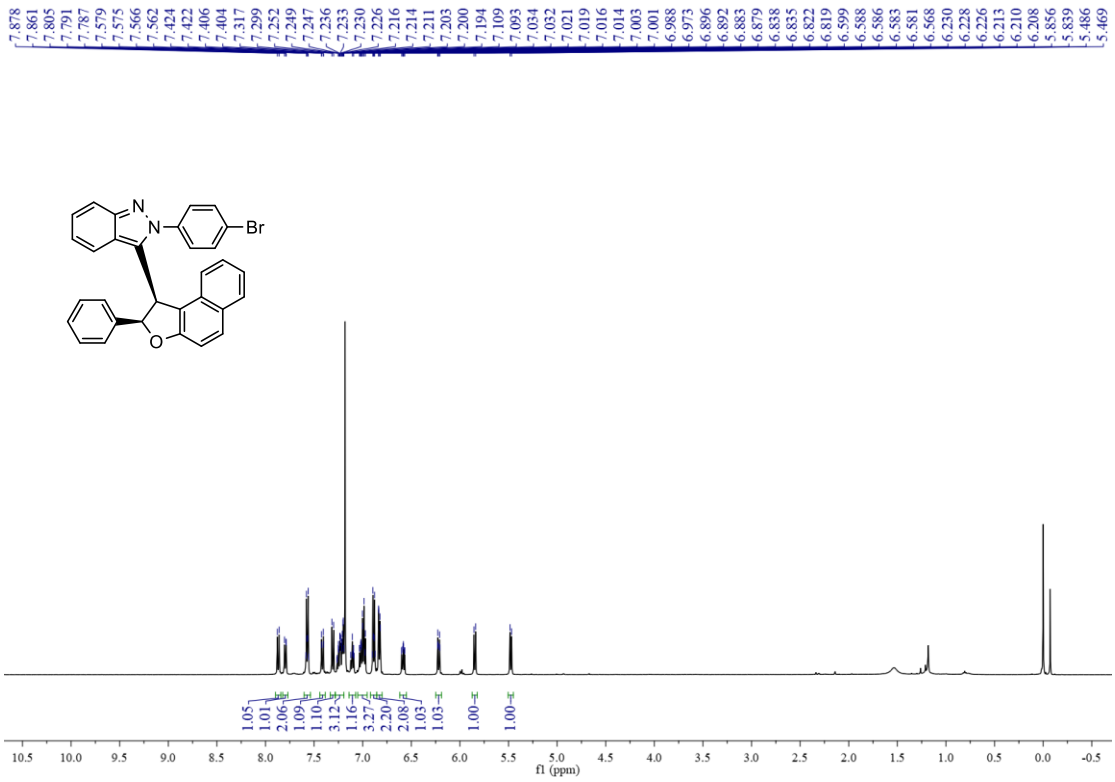


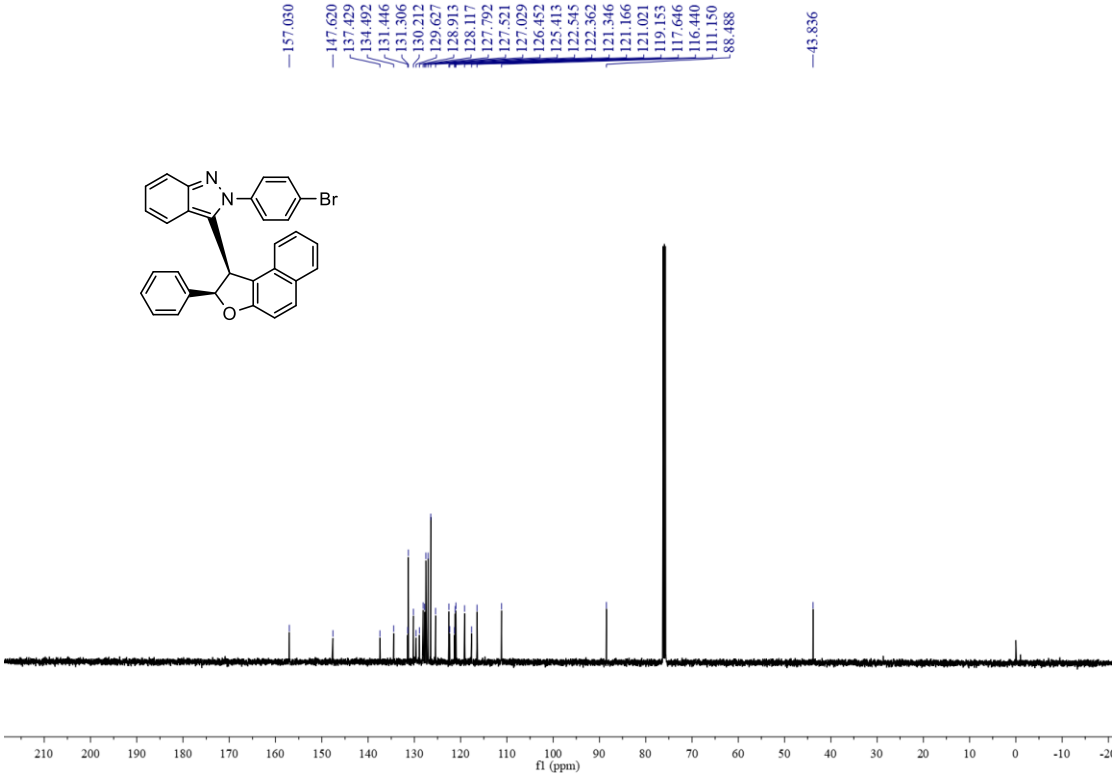




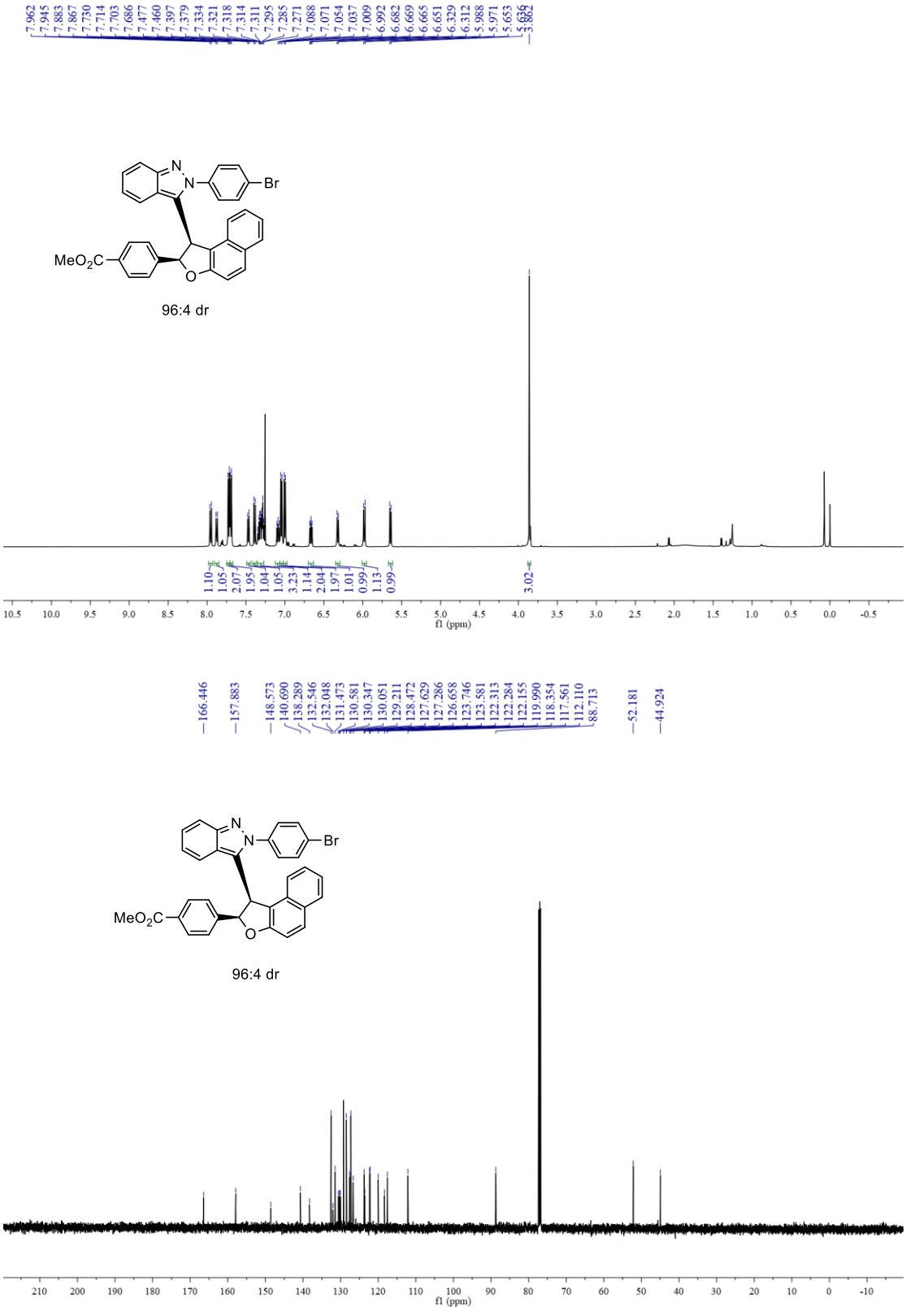


2-(4-bromophenyl)-3-((1R,2R)-2-phenyl-1,2-dihydronaphtho[2,1-b]furan-1-yl)-2H-indazole (4a)

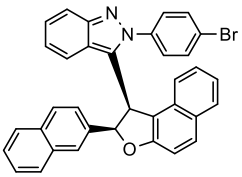




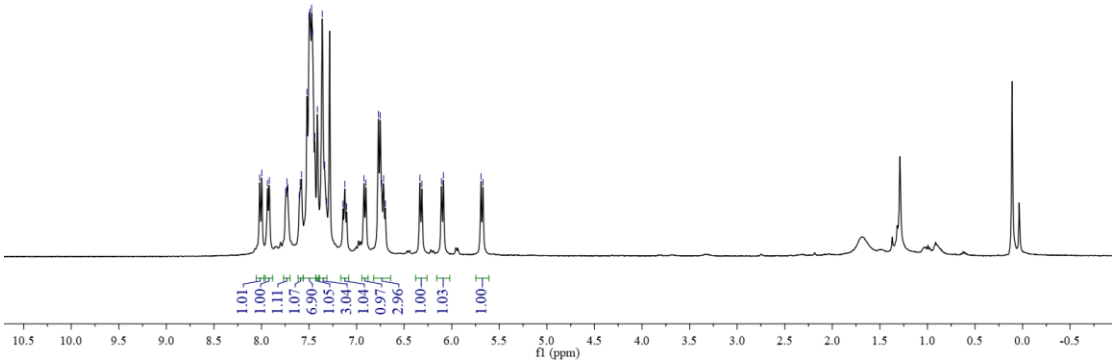
methyl 4-((1R,2R)-1-(2-(4-bromophenyl)-2H-indazol-3-yl)-1,2-dihydronaphtho[2,1-b]furan-2-yl)-benzoate (4b)

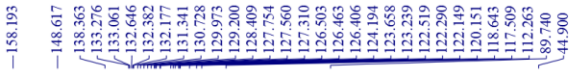


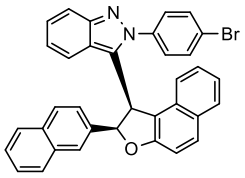
2-(4-bromophenyl)-3-((1R,2R)-2-(naphthalen-2-yl)-1,2-dihydronaphtho[2,1-b]furan-1-yl)-2H-indazole (4c)



92:8 d.r.

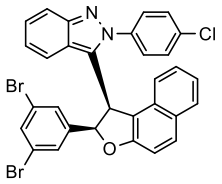




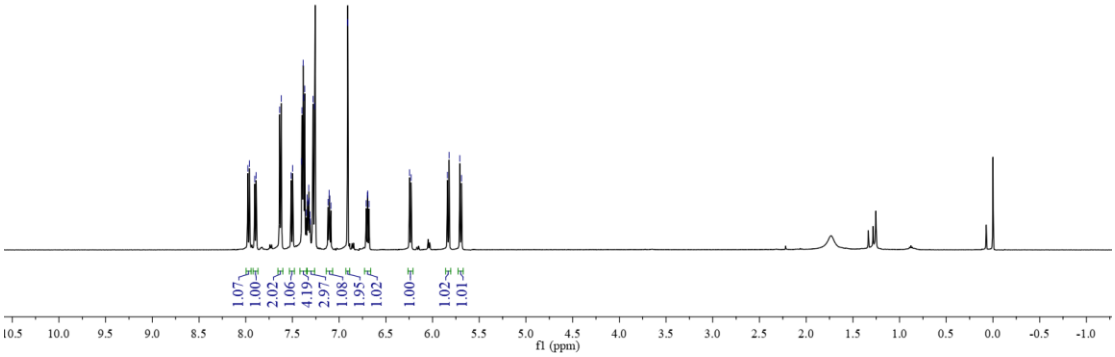


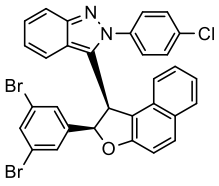
92:8 d.r.

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

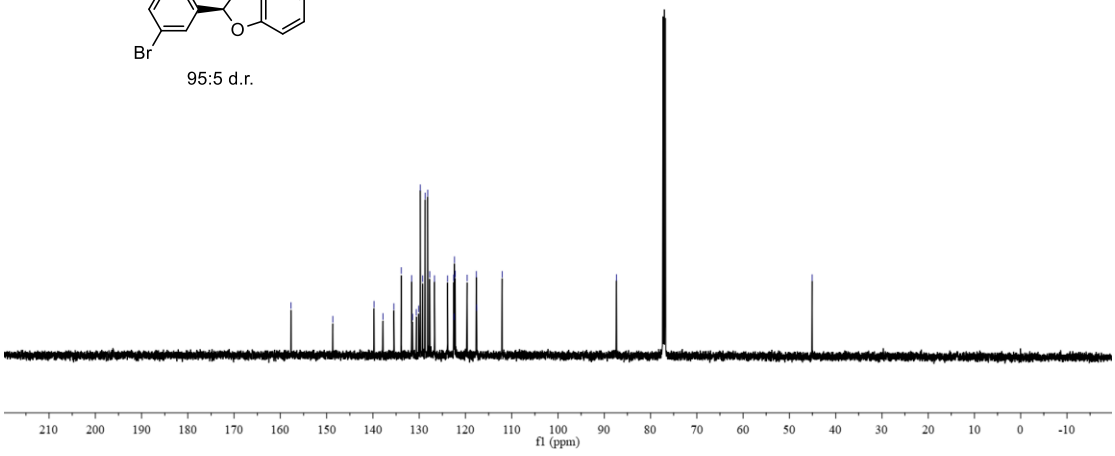


95:5 d.r.

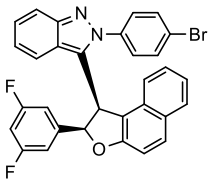




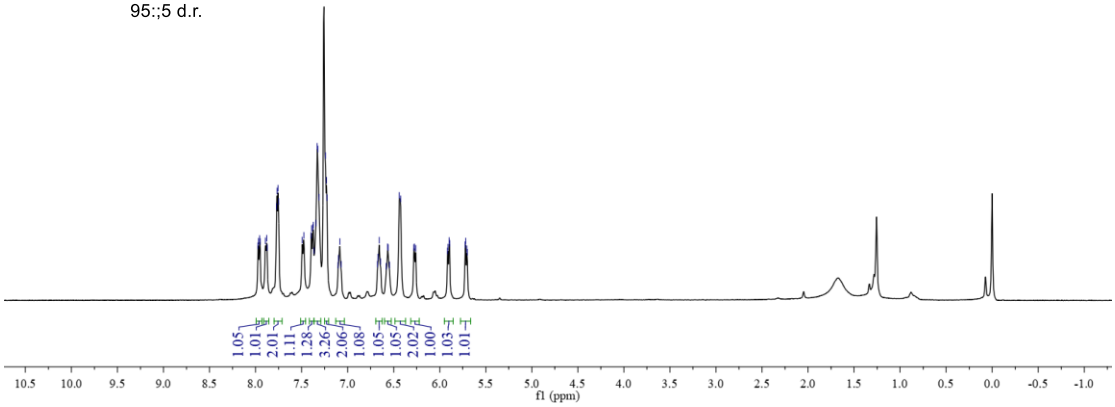
95:5 d.r.

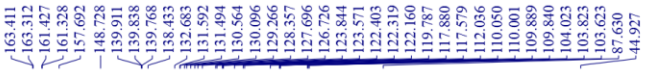


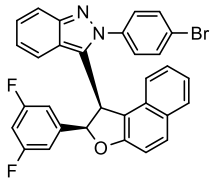
2-(4-bromophenyl)-3-((1R,2R)-2-(3,5-difluorophenyl)-1,2-dihydronaphtho[2,1-b]furan-1-yl)-2H-indazole (4e)



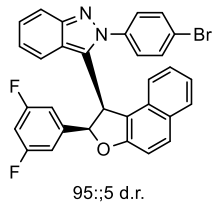
95:;5 d.r.







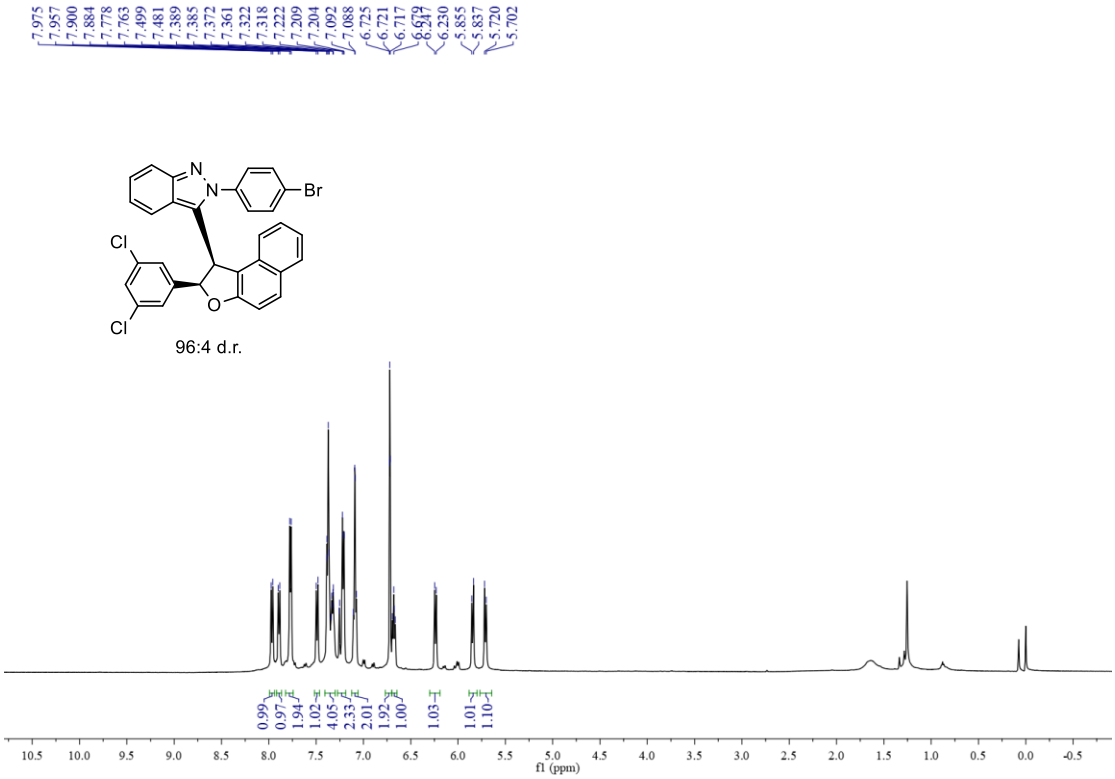
95:;5 d.r.

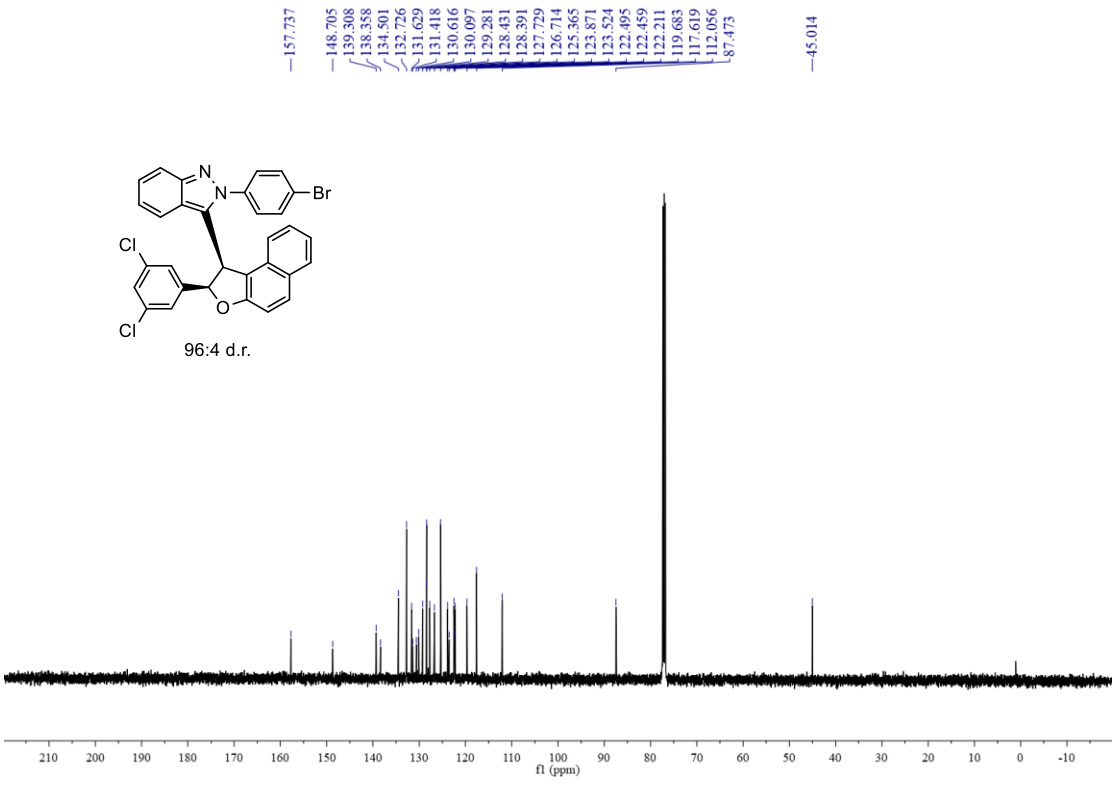

N
N
Br
F
F
O

95:;5 d.r.

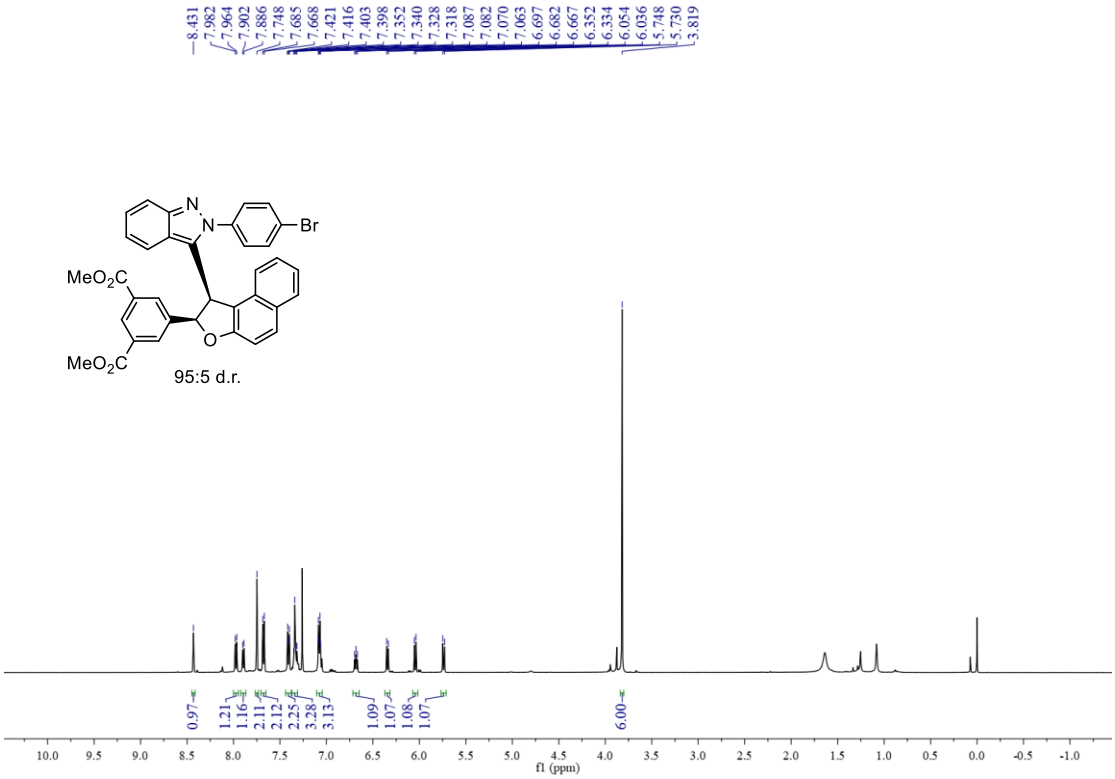
-109.203
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

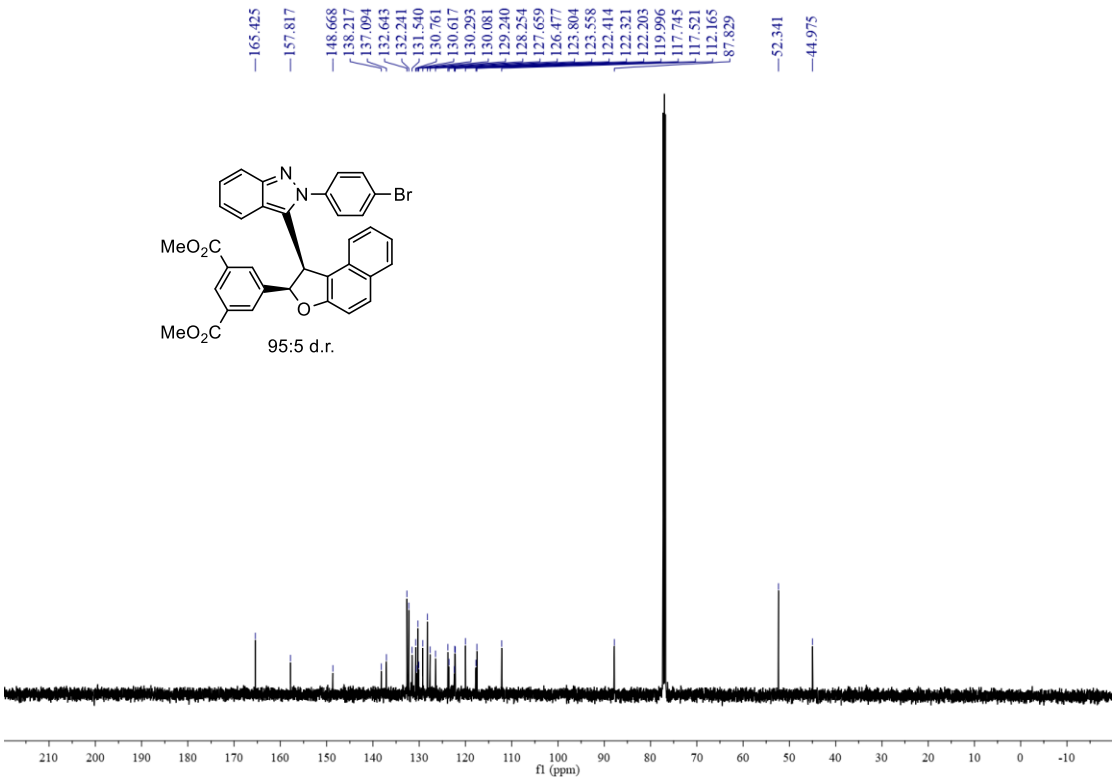
2-(4-bromophenyl)-3-((1R,2R)-2-(3,5-dichlorophenyl)-1,2-dihydronaphtho[2,1-b]furan-1-yl)-2H-indazole (4f)



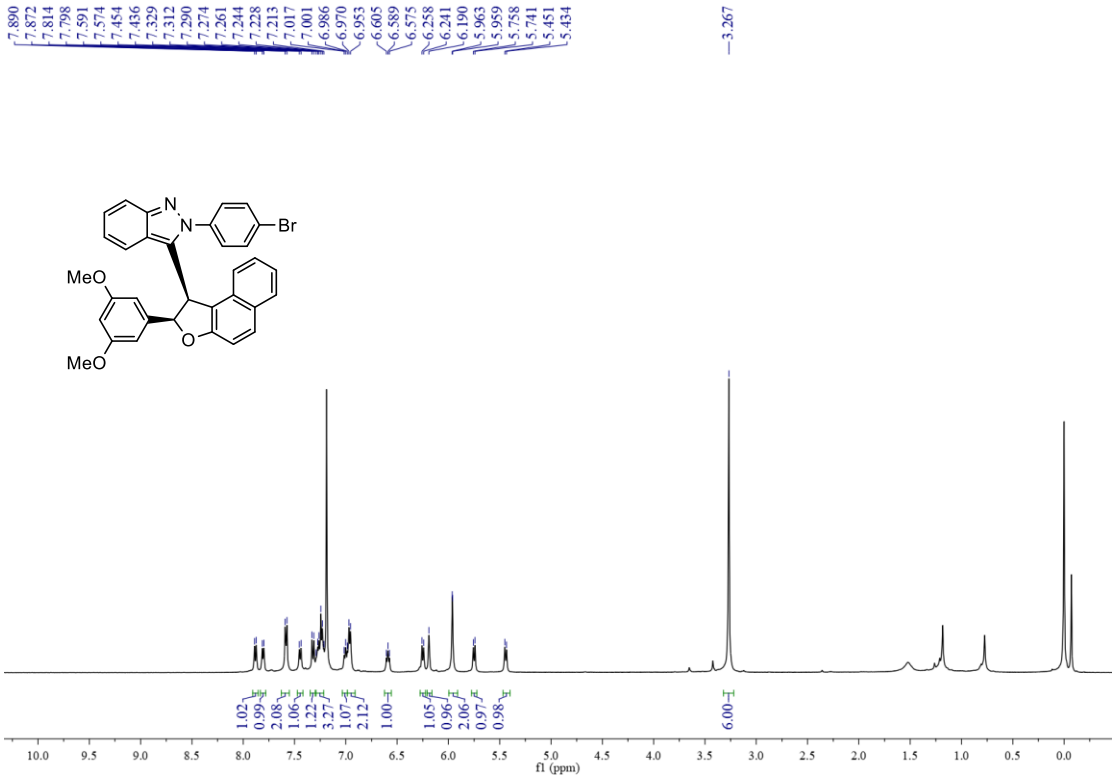


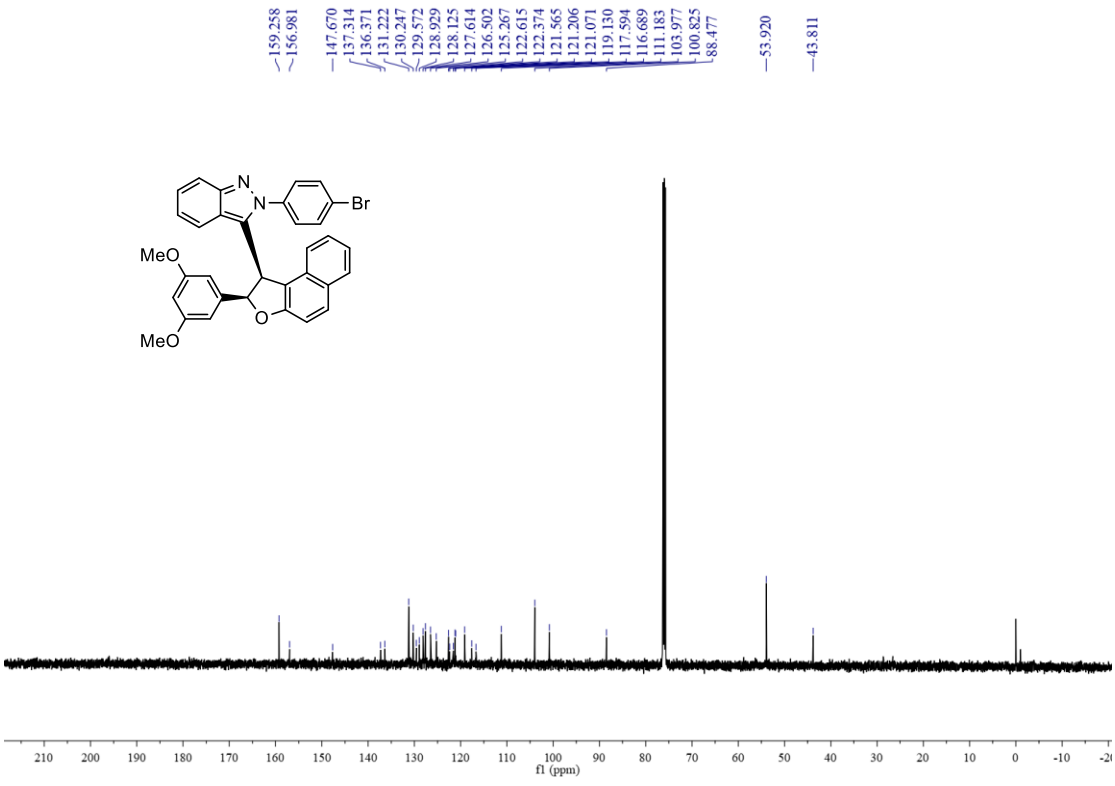
dimethyl 5-((1R,2R)-1-(2-(4-bromophenyl)-2H-indazol-3-yl)-1,2-dihydronaphtho[2,1-b]furan-2-yl)-isophthalate (4g)



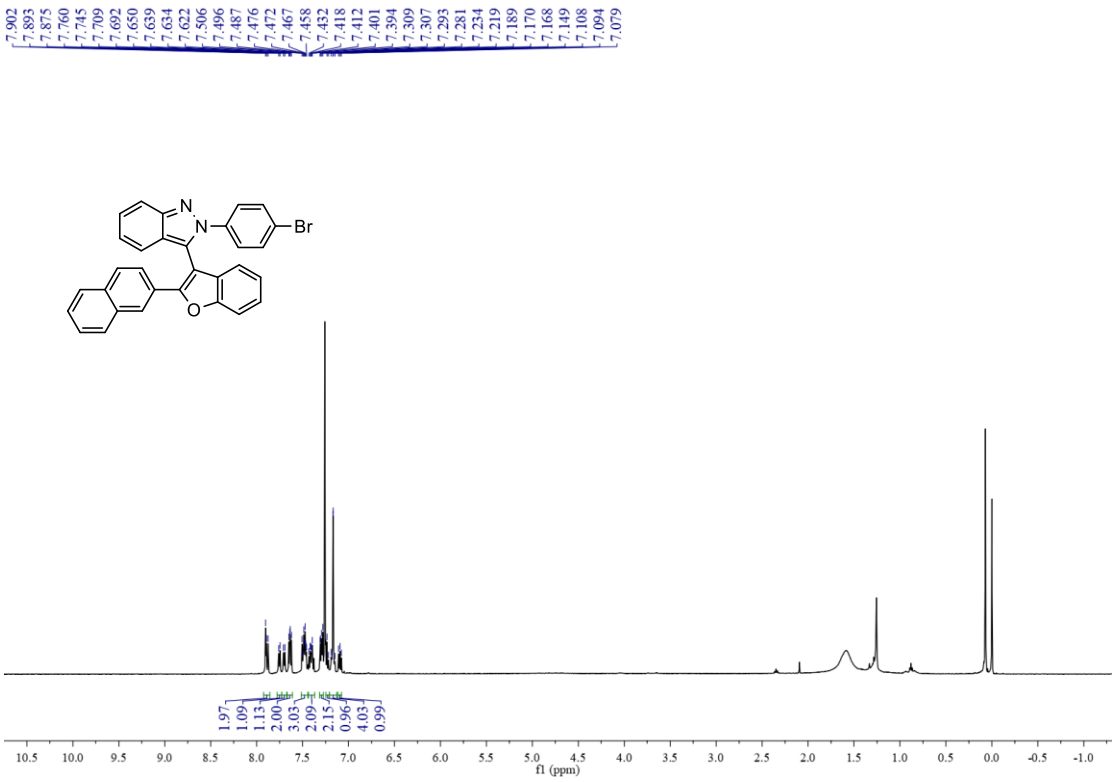


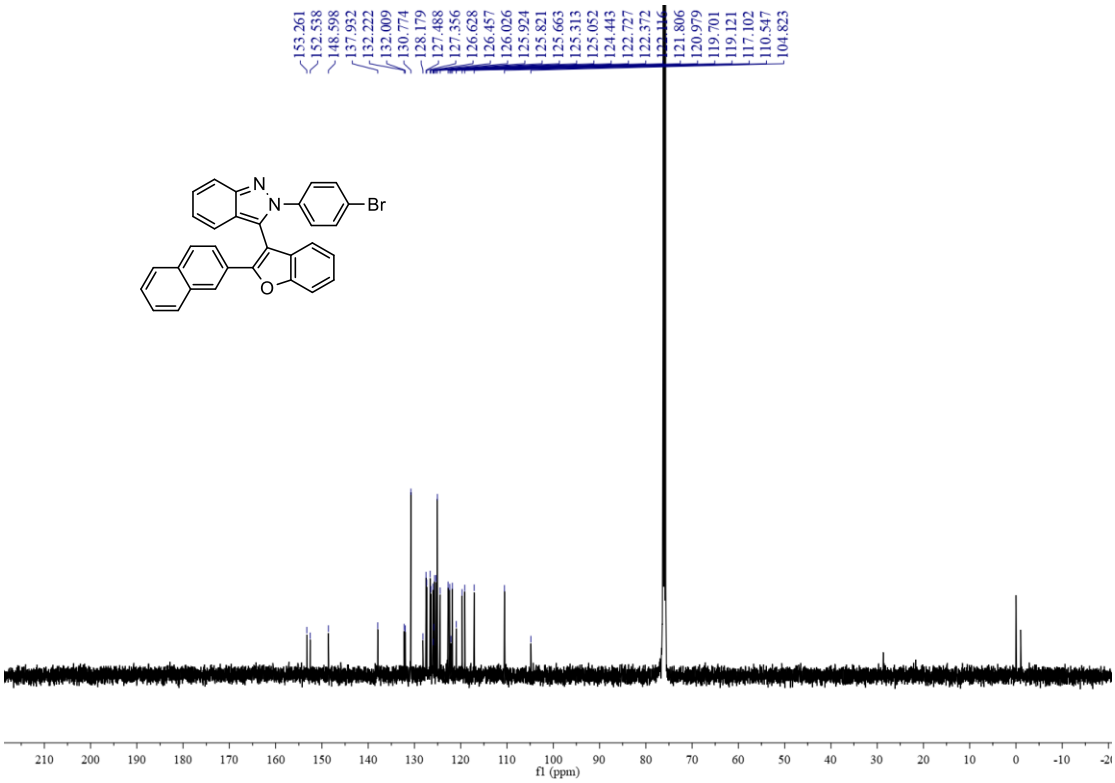
2-(4-bromophenyl)-3-((1R,2R)-2-(3,5-dimethoxyphenyl)-1,2-dihydronaphtho[2,1-b]furan-1-yl)-2H-indazole (4h)



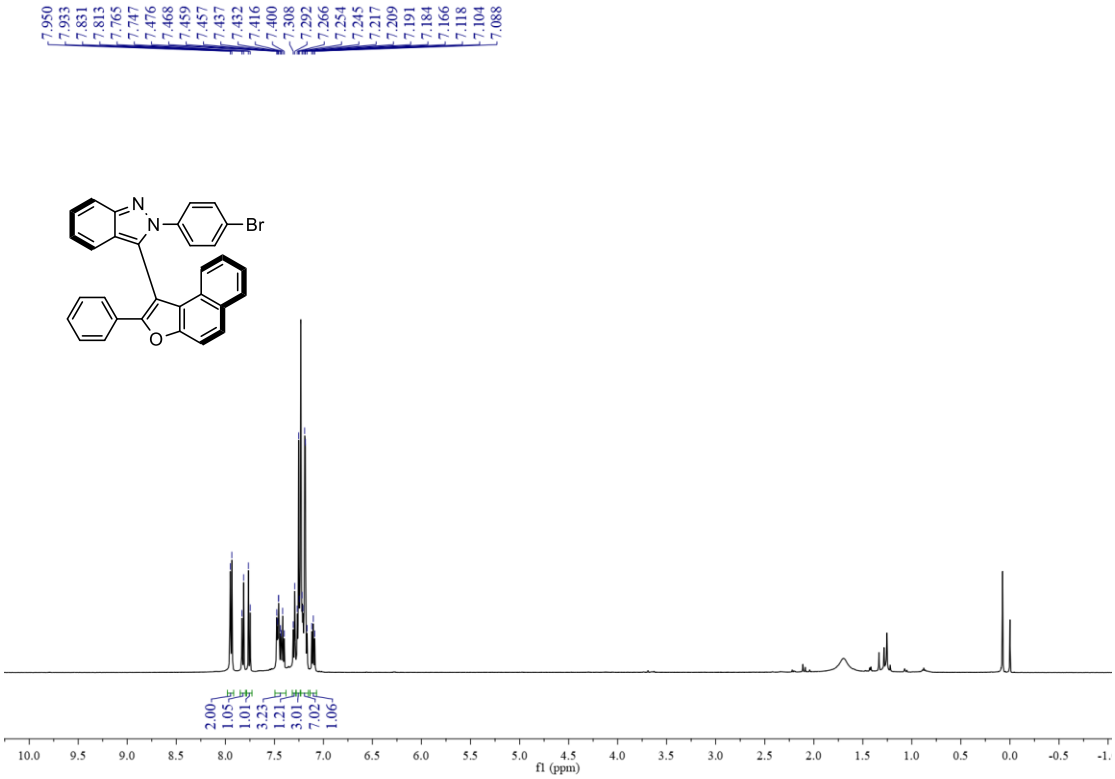


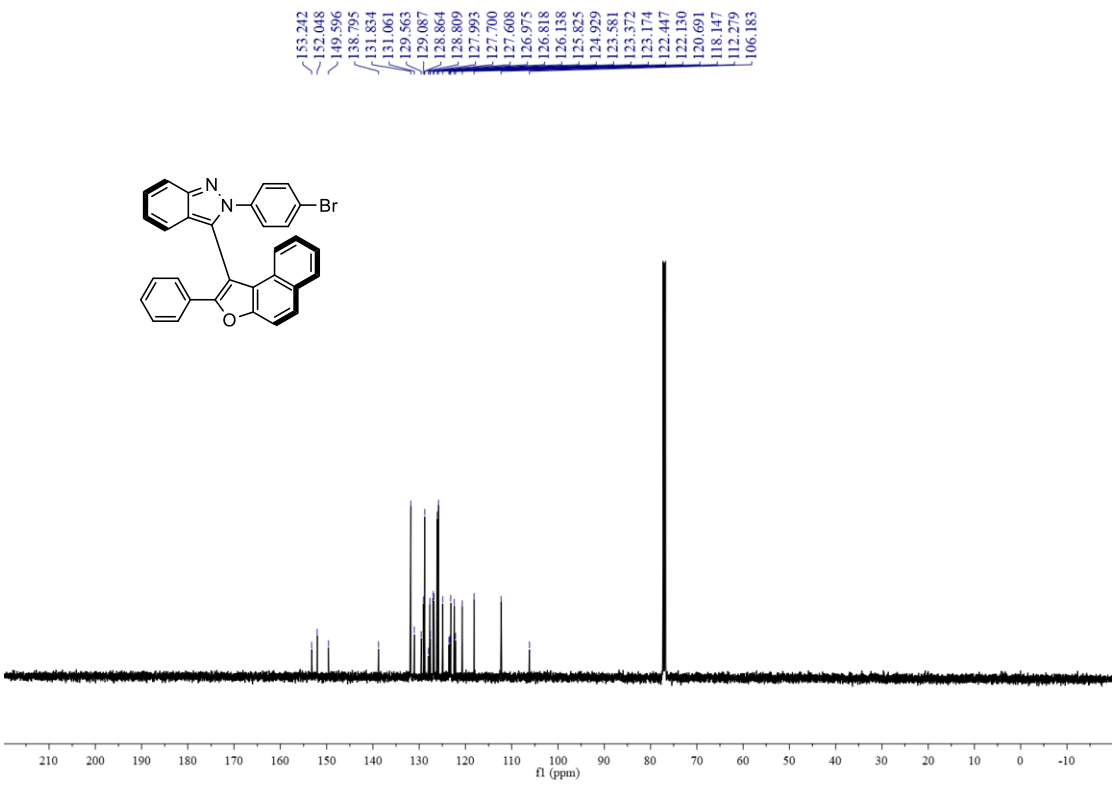
2-(4-bromophenyl)-3-(2-(naphthalen-2-yl)benzofuran-3-yl)-2H-indazole



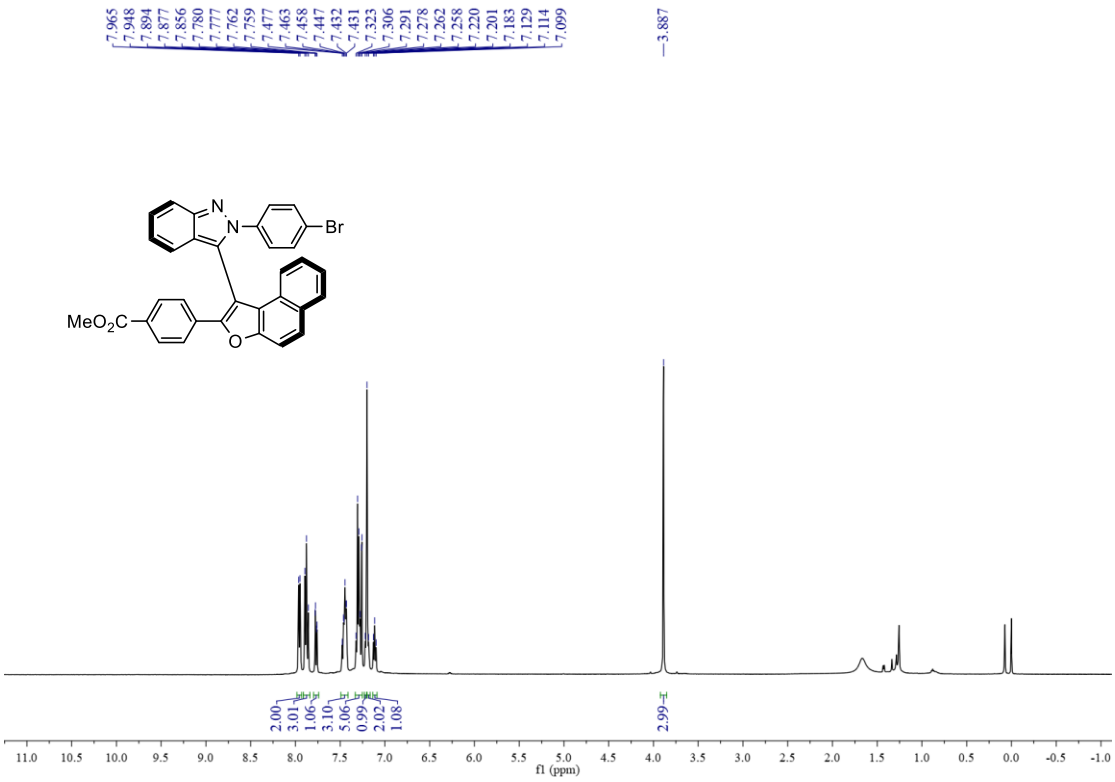


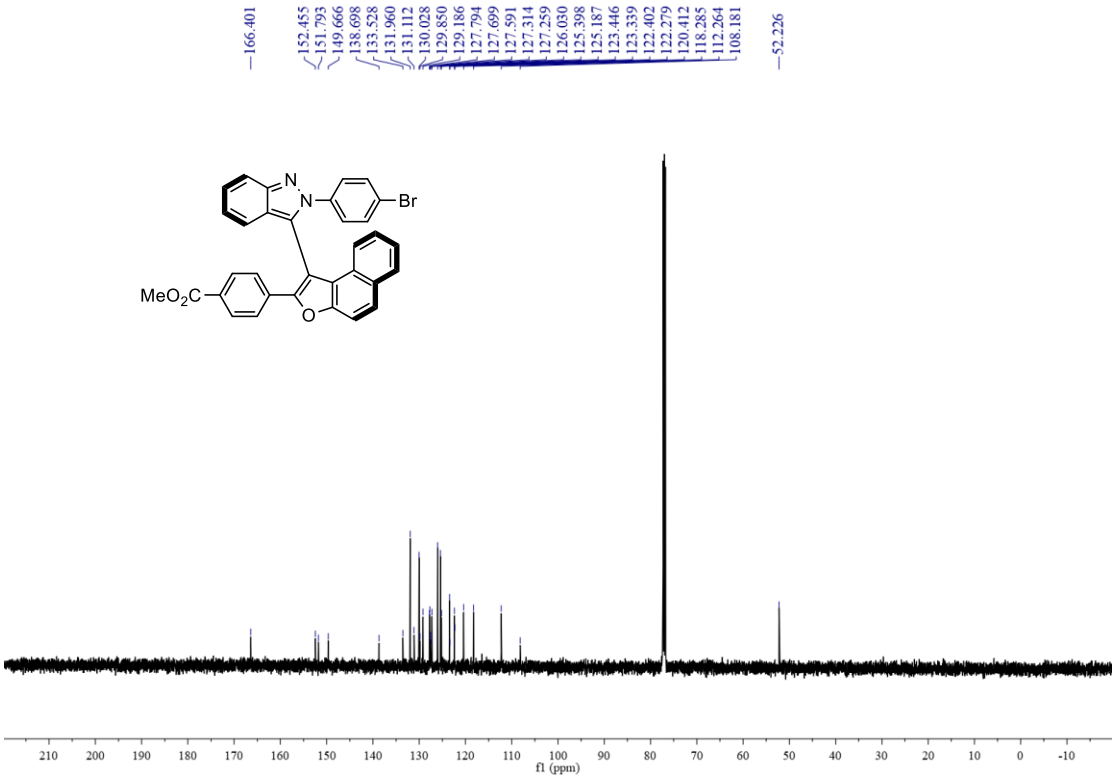
2-(4-bromophenyl)-3-(2-phenylnaphtho[2,1-b]furan-1-yl)-2H-indazole (5a)



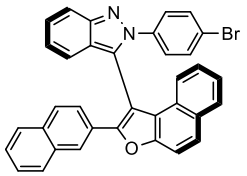


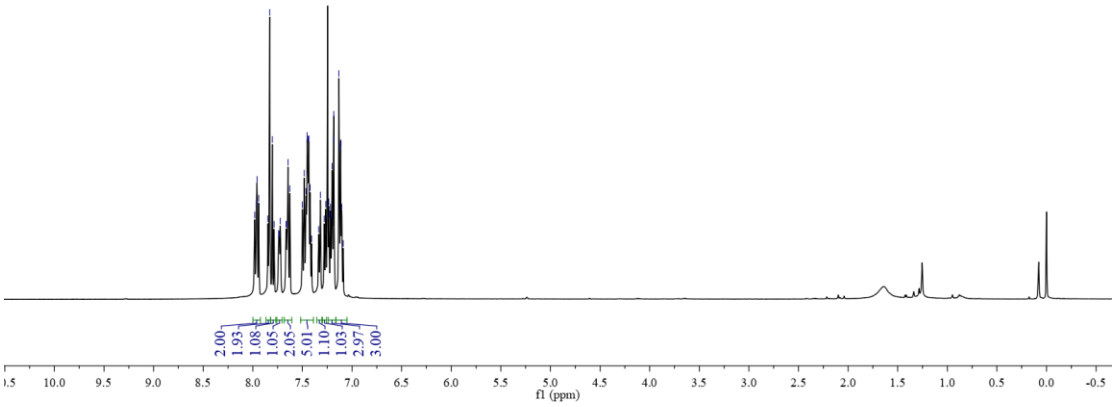
methyl 4-(1-(2-(4-bromophenyl)-2H-indazol-3-yl)naphtho[2,1-b]furan-2-yl)benzoate (5b)

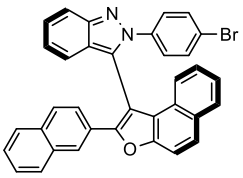




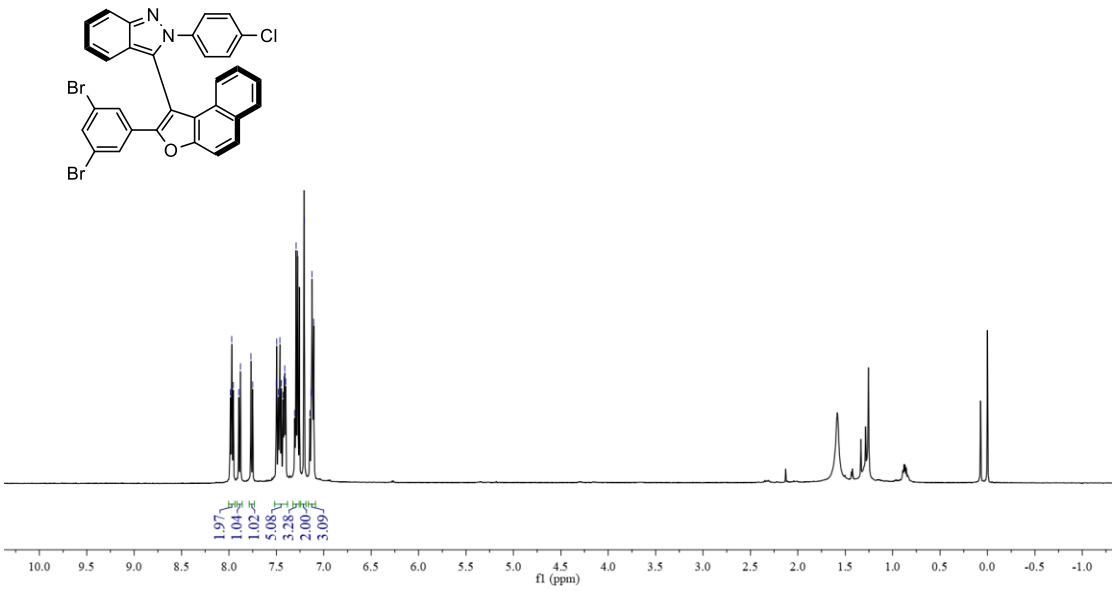
2-(4-bromophenyl)-3-(2-(naphthalen-2-yl)naphtho[2,1-b]furan-1-yl)-2H-indazole (5c)

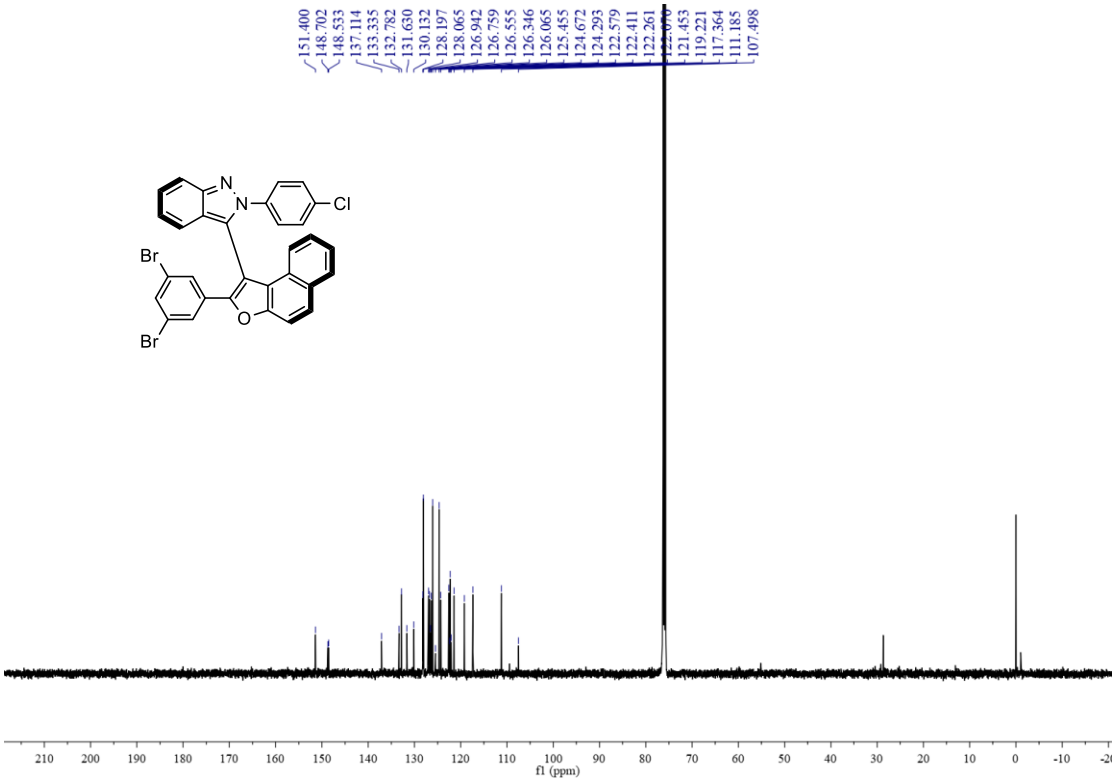




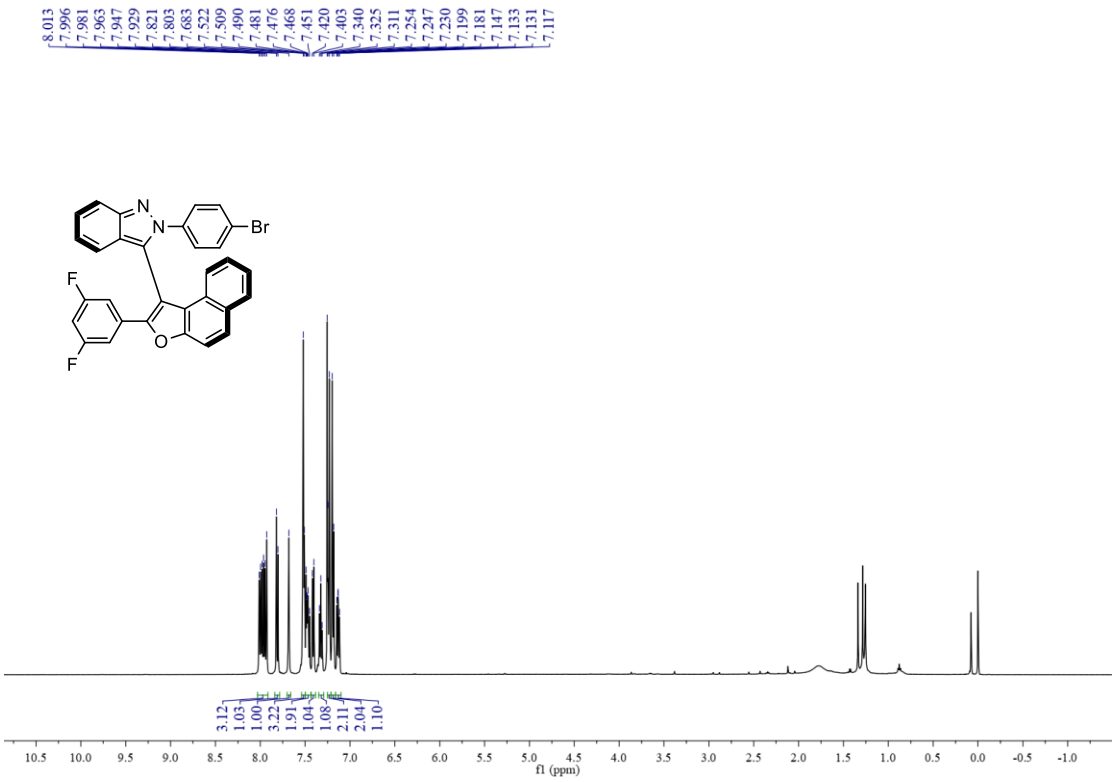


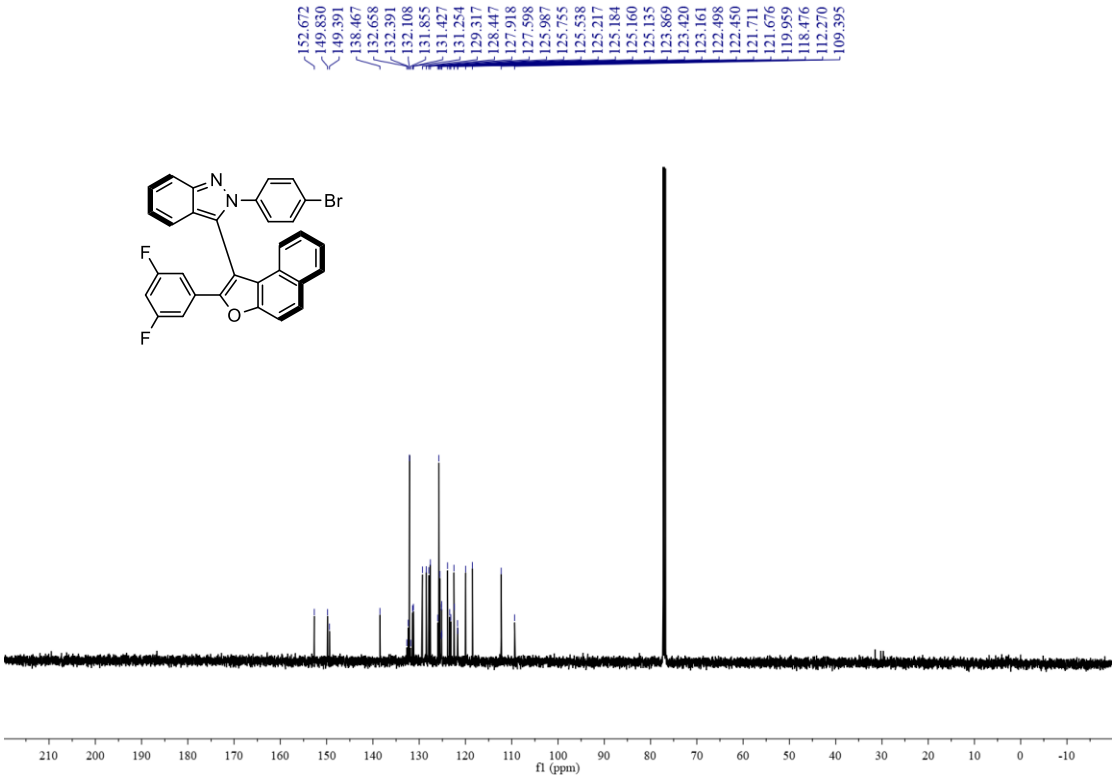
2-(4-chlorophenyl)-3-(2-(3,5-dibromophenyl)naphtho[2,1-b]furan-1-yl)-2H-indazole (5d)

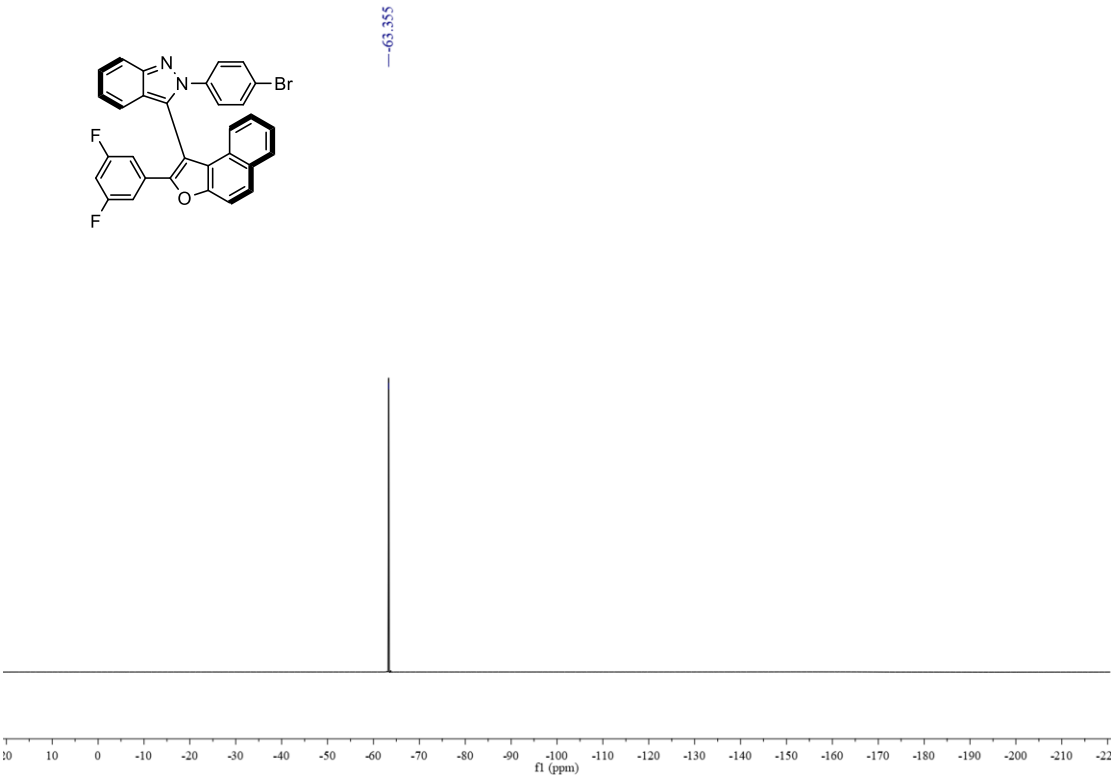




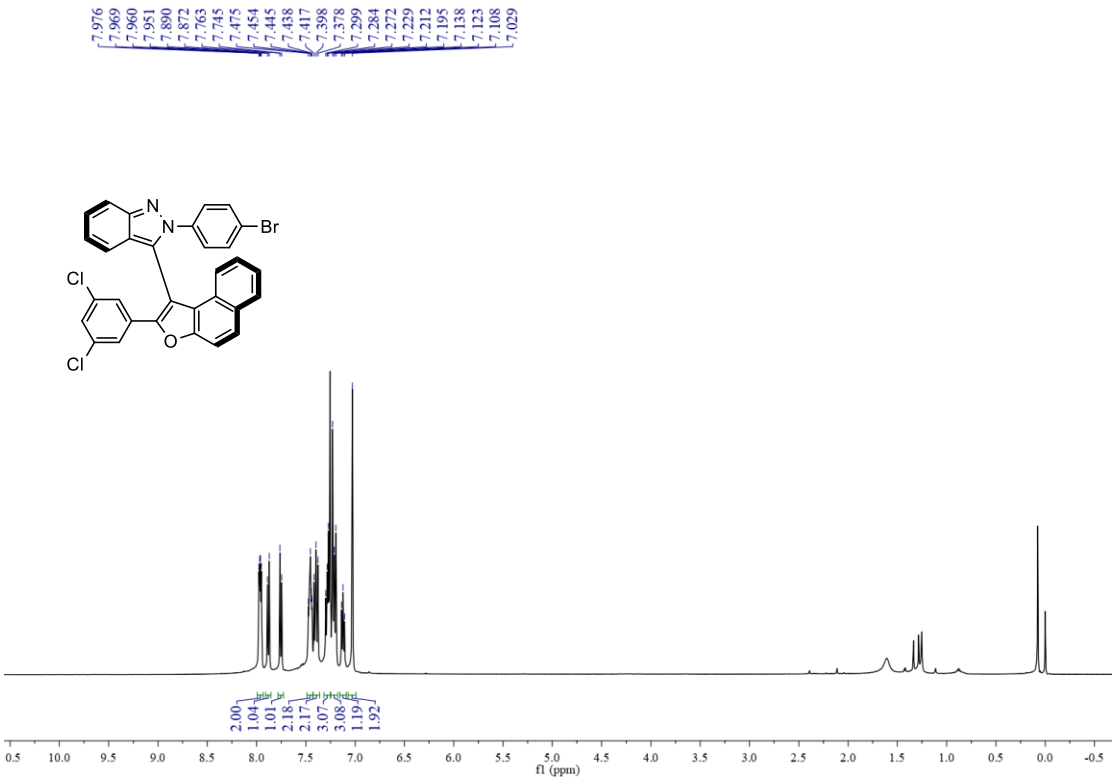
2-(4-bromophenyl)-3-(2-(3,5-difluorophenyl)naphtho[2,1-b]furan-1-yl)-2H-indazole (5e)

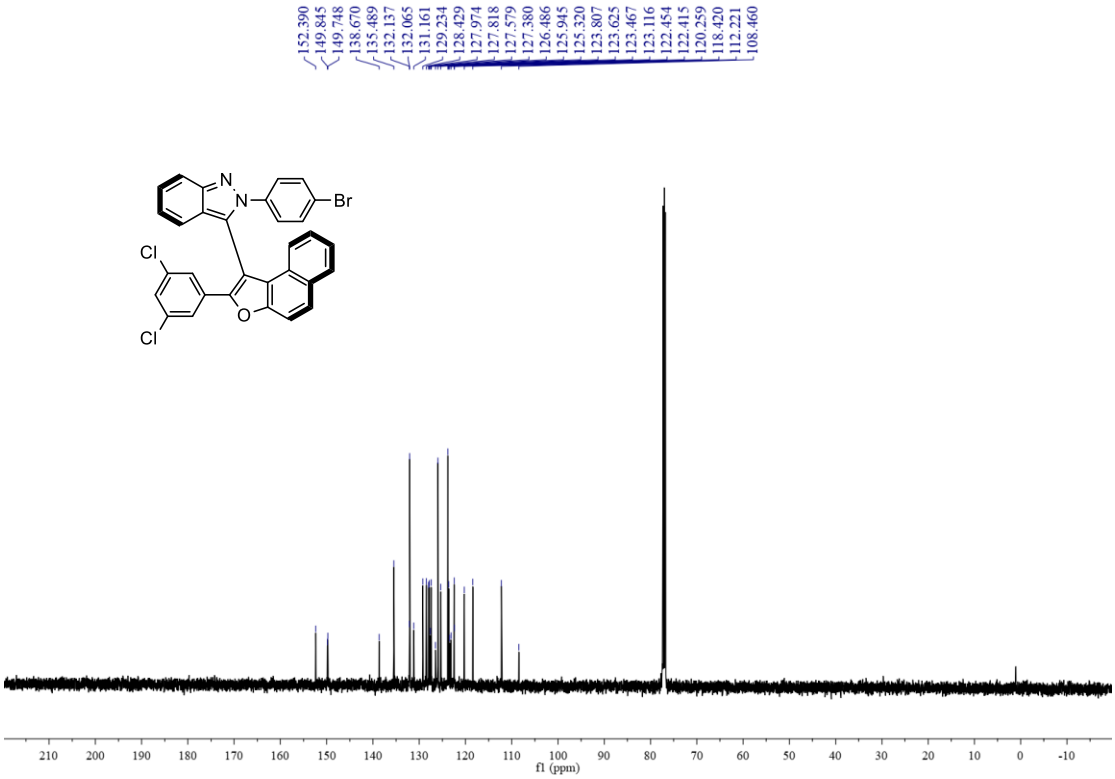




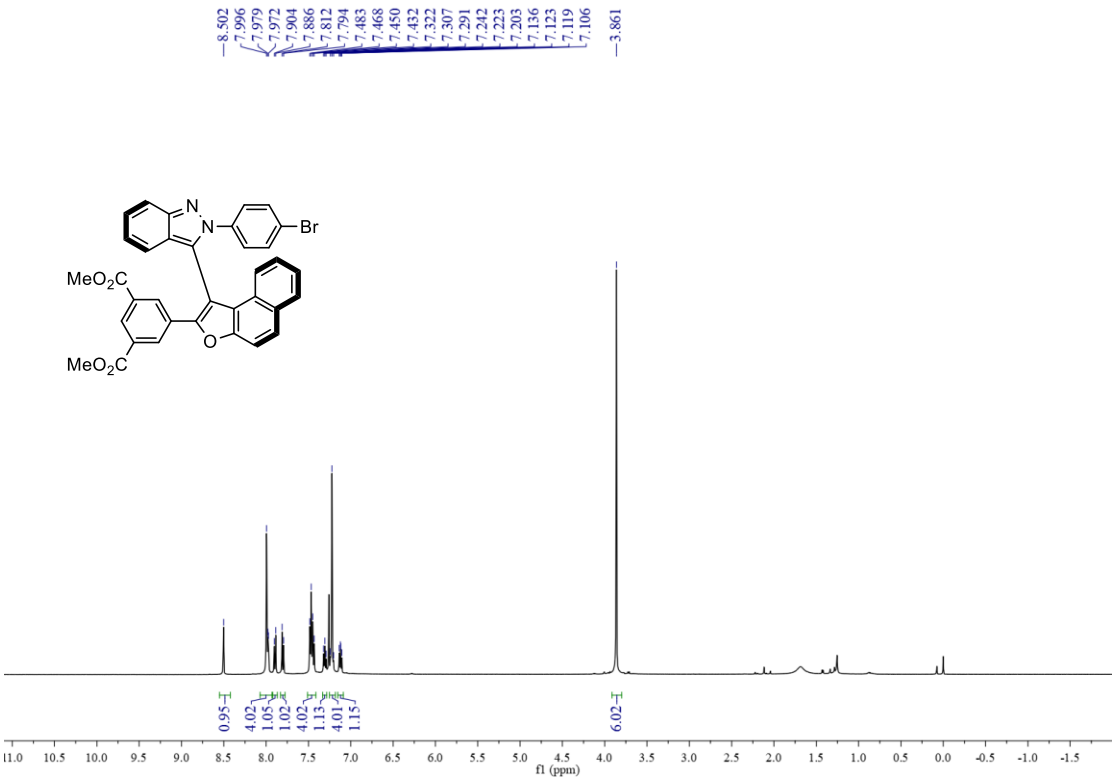

-63.355
N
N
Br
F
F
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

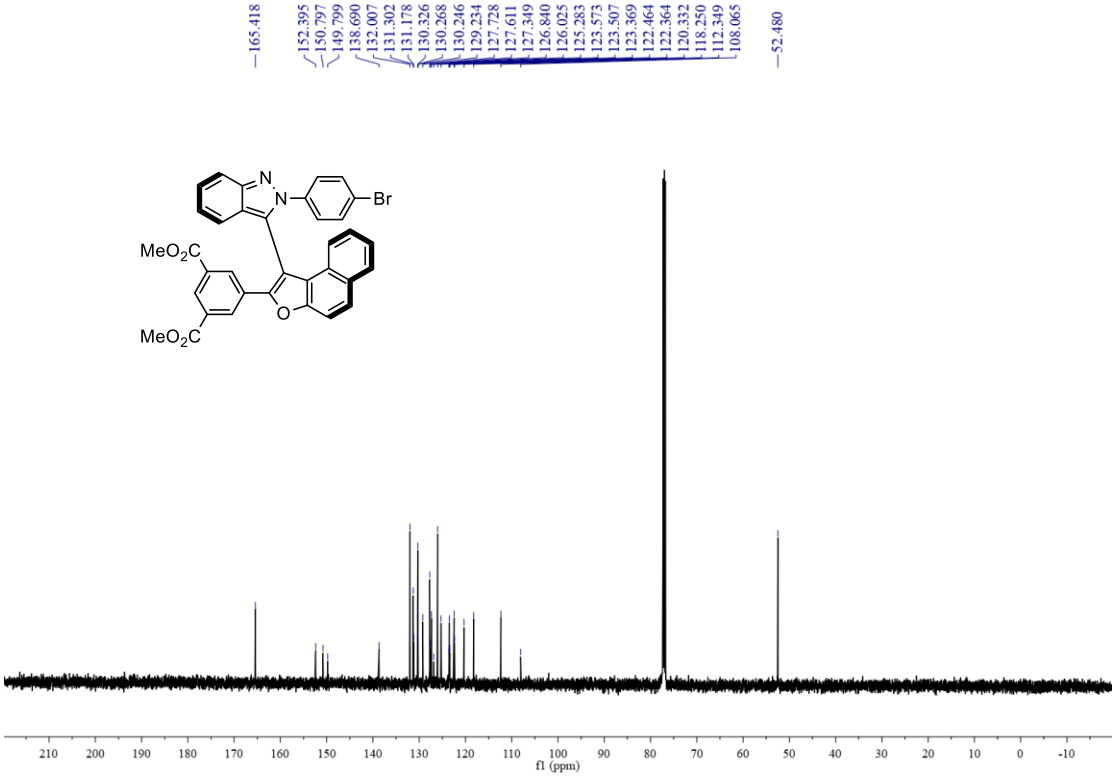
2-(4-bromophenyl)-3-(2-(3,5-dichlorophenyl)naphtho[2,1-b]furan-1-yl)-2H-indazole (5f)



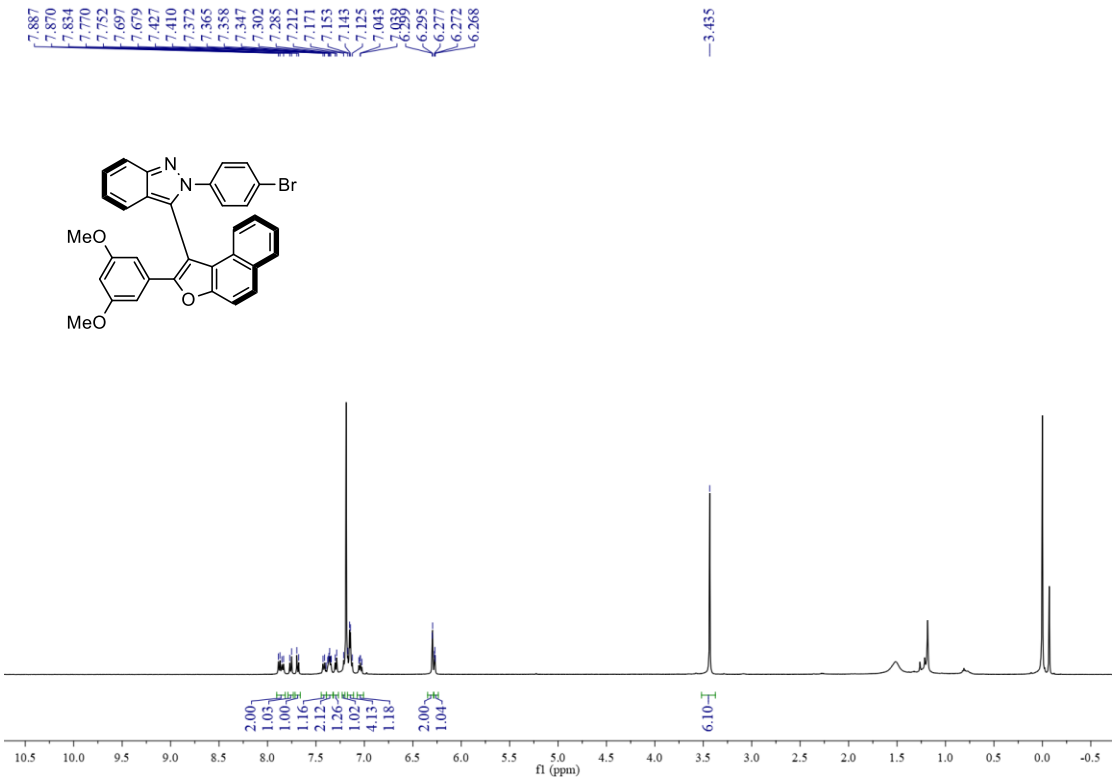


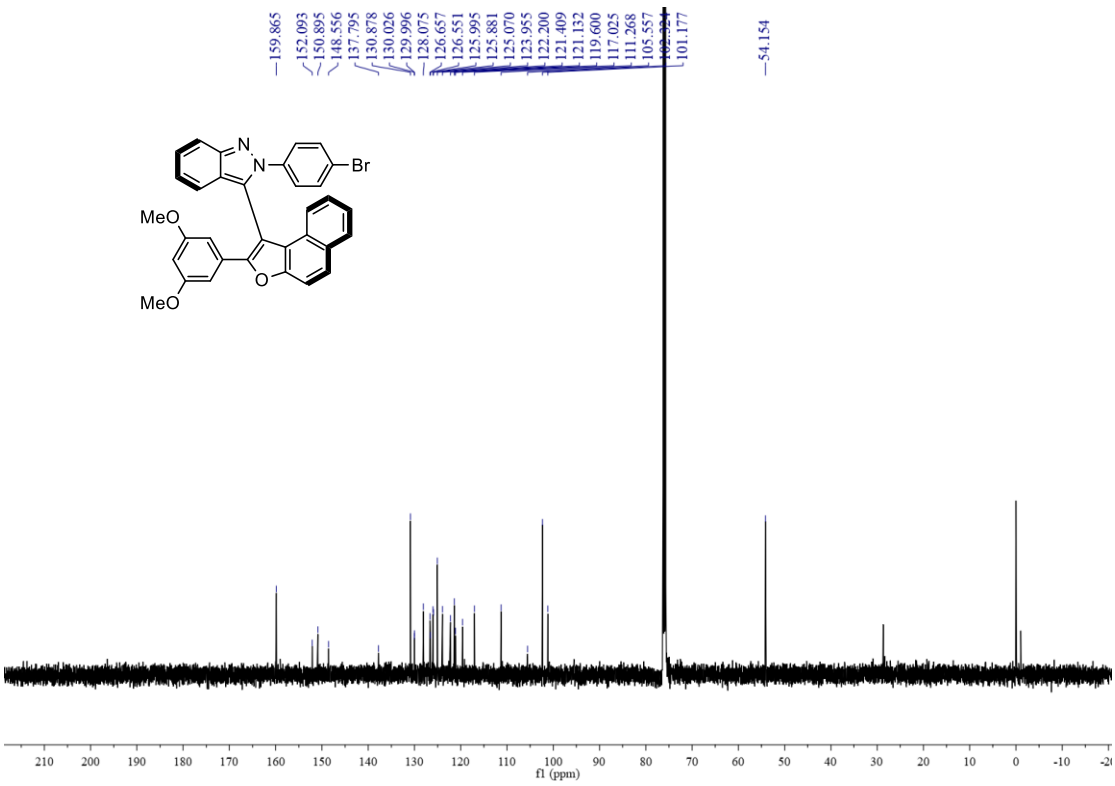
dimethyl 5-(1-(2-(4-bromophenyl)-2H-indazol-3-yl)naphtho[2,1-b]furan-2-yl)isophthalate (5g)



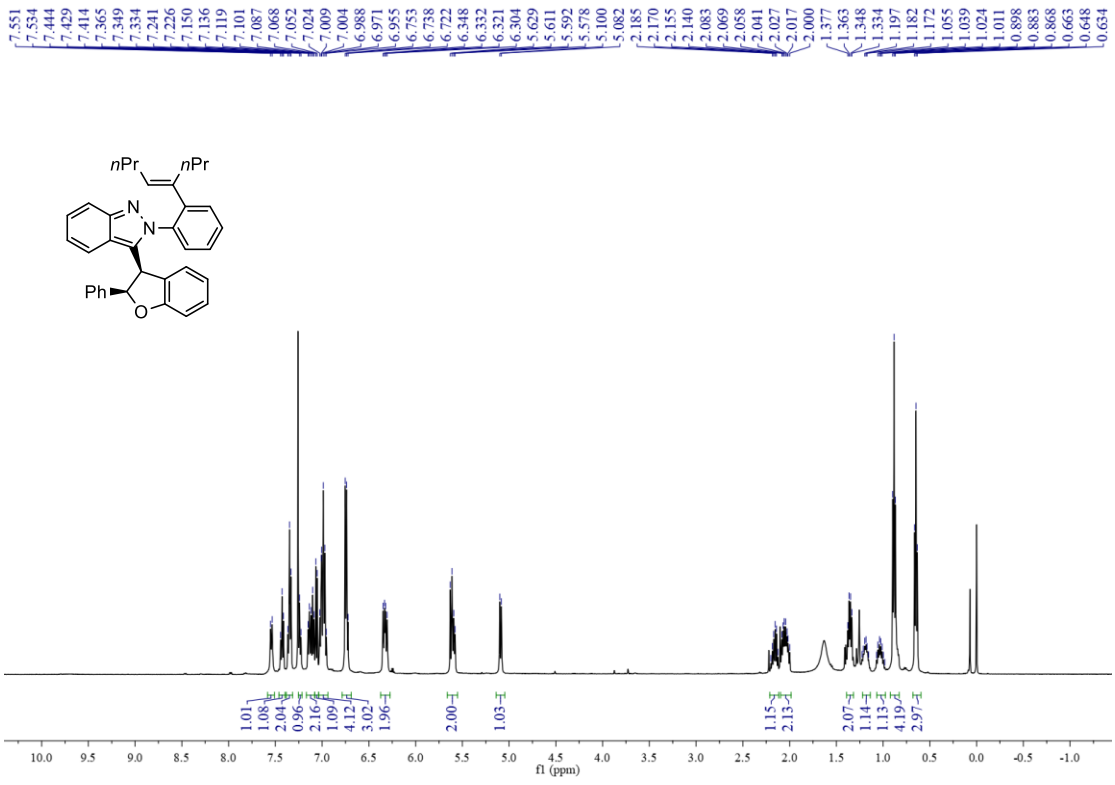


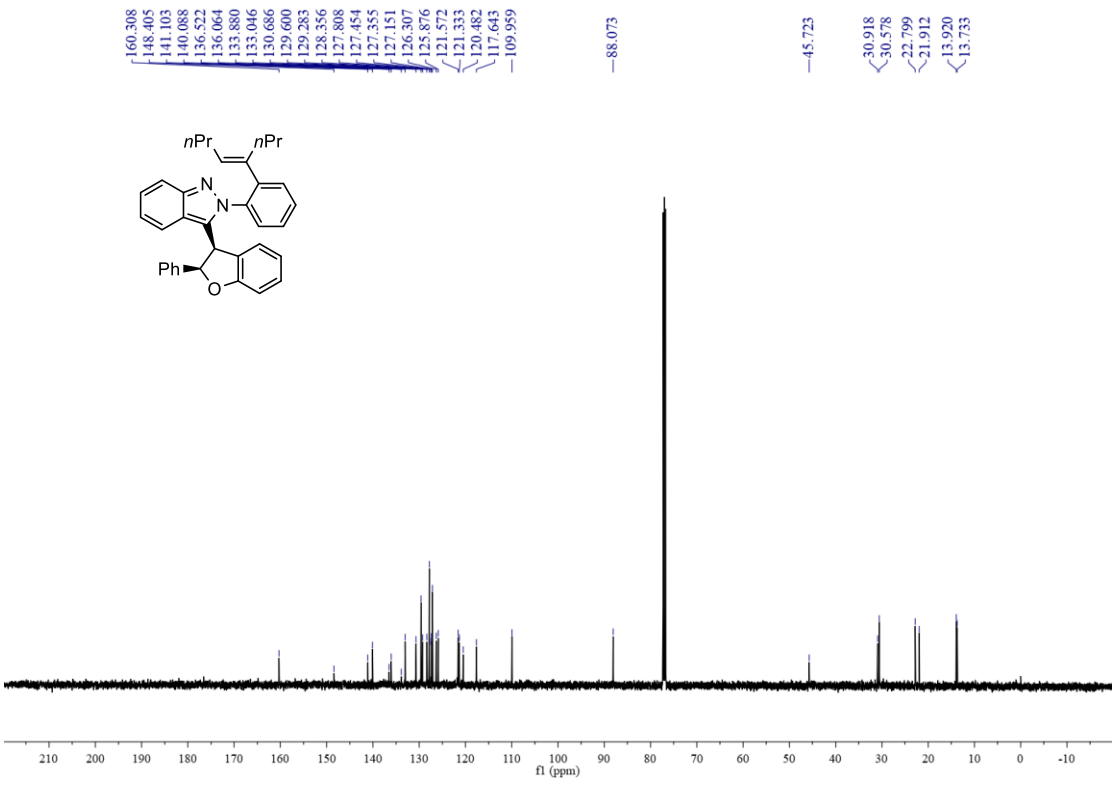
2-(4-bromophenyl)-3-(2-(3,5-dimethoxyphenyl)naphtho[2,1-b]furan-1-yl)-2H-indazole (5h)



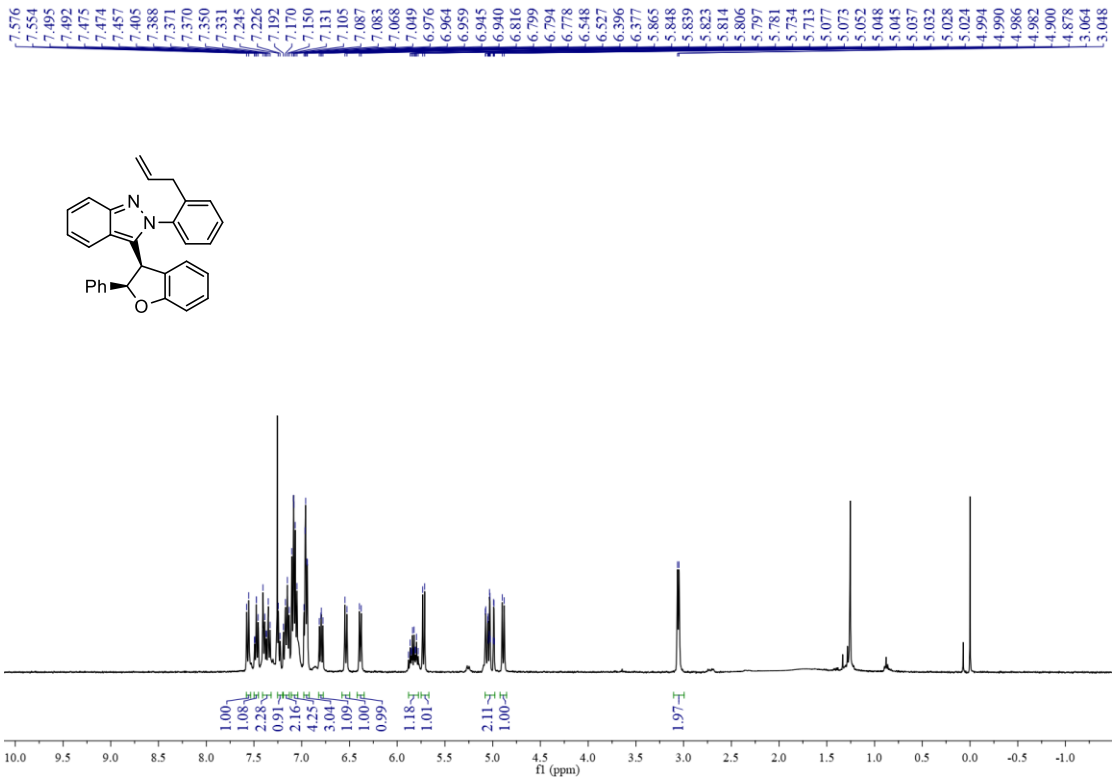


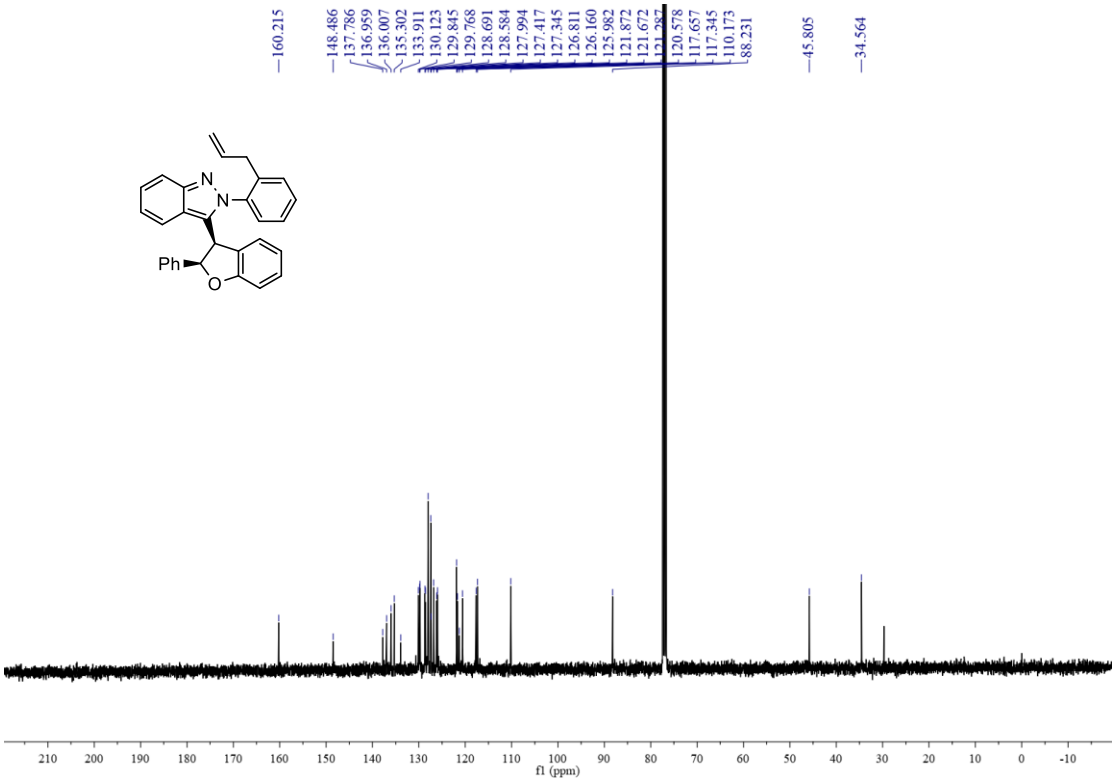
2-(2-((E)-oct-4-en-4-yl)phenyl)-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (6a)



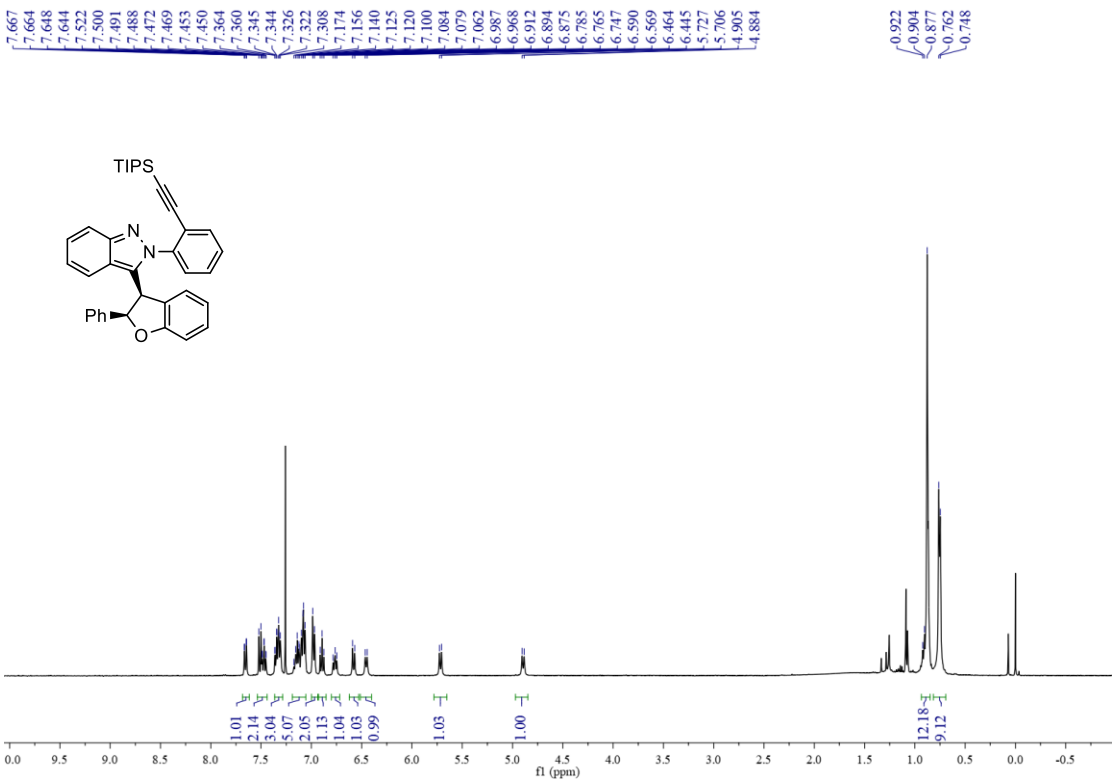


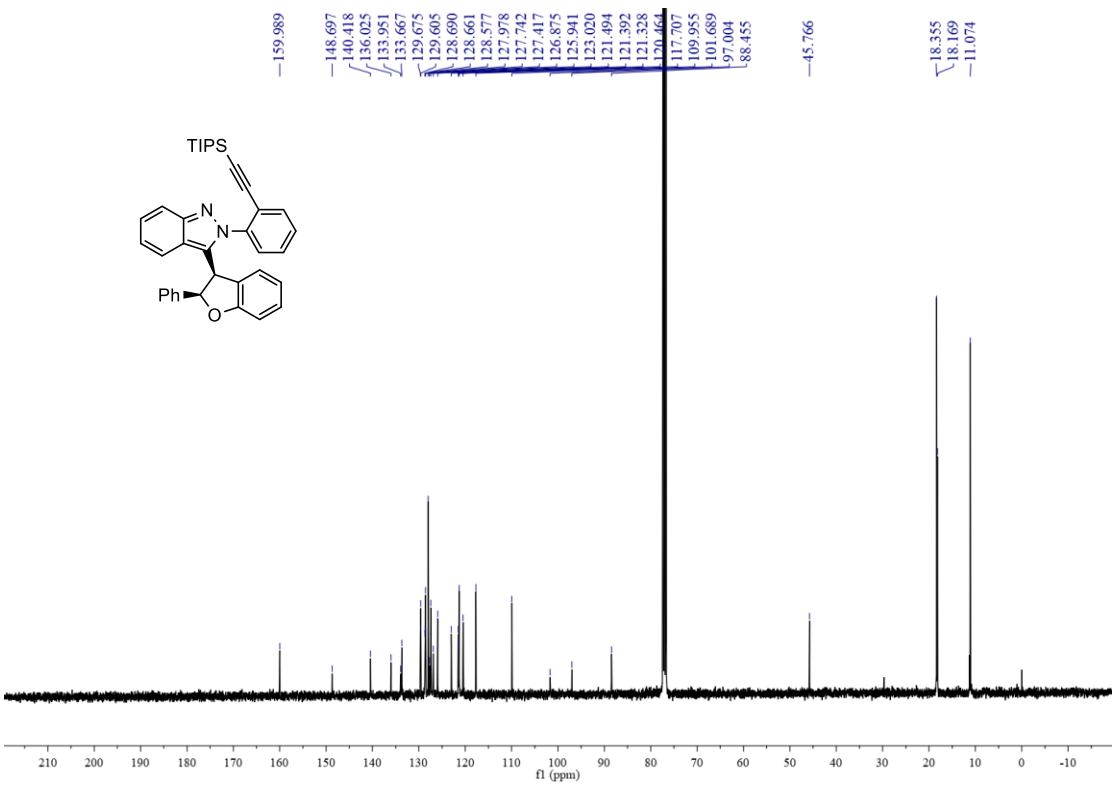
2-(2-allylphenyl)-3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazole (6b)



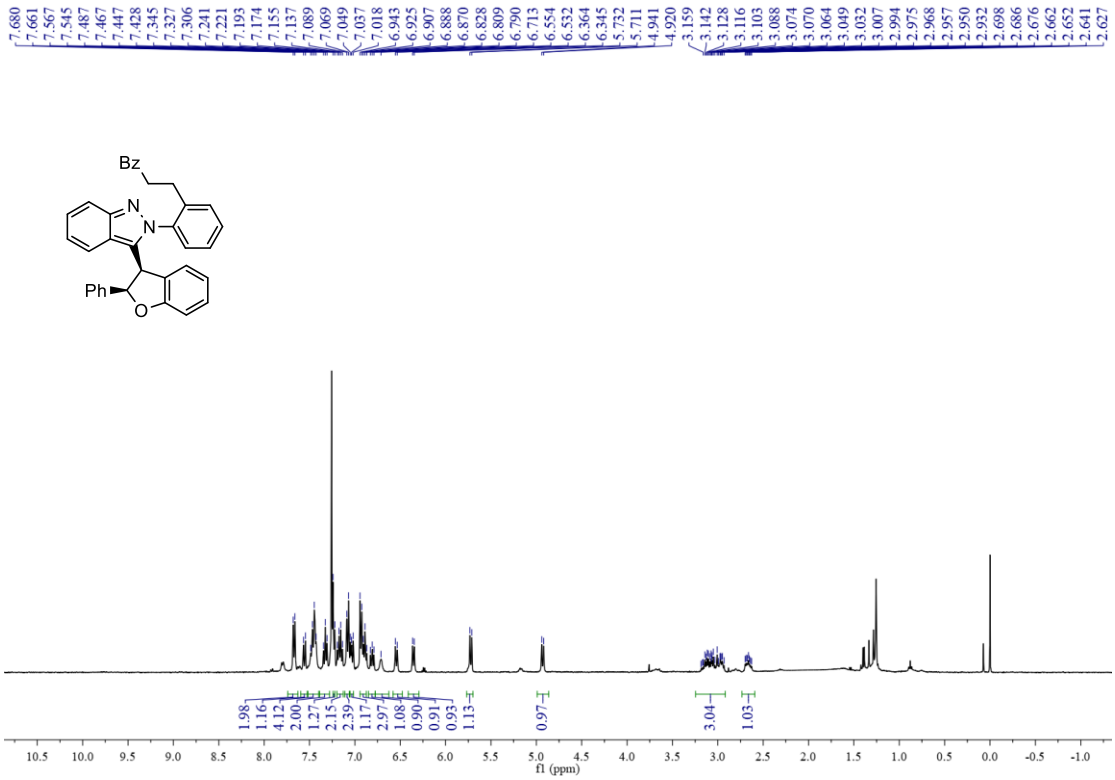


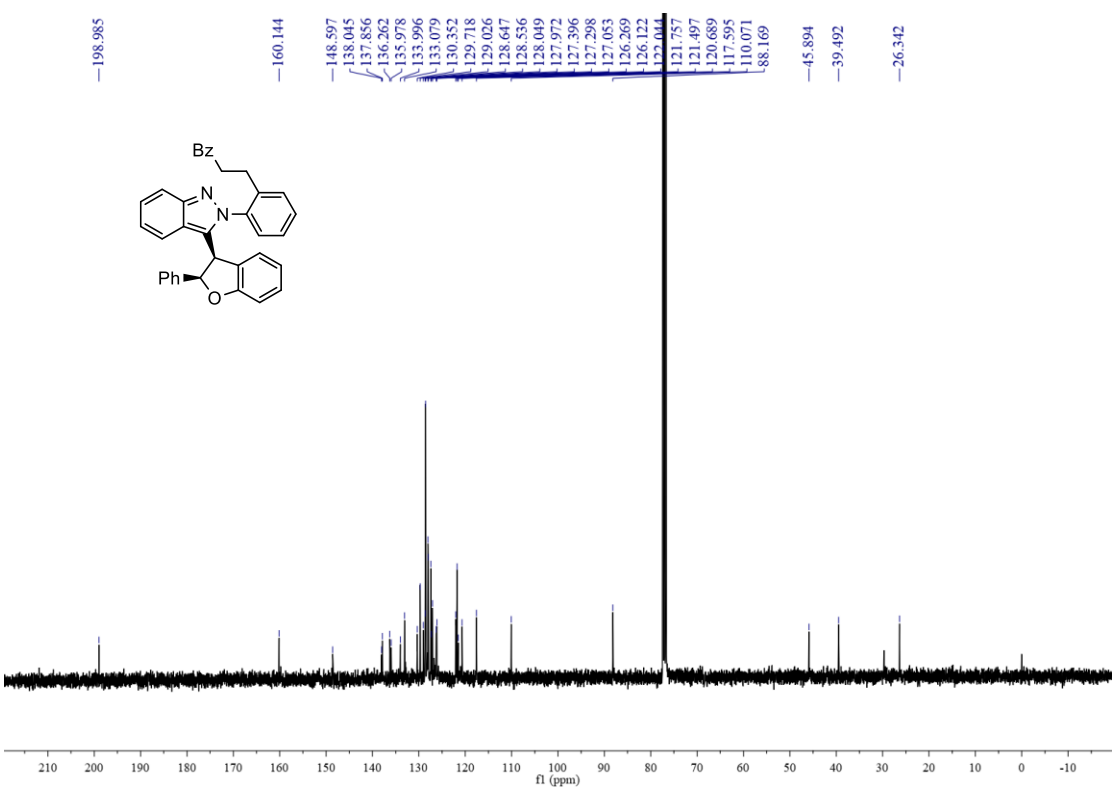
3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2-(2-((triisopropylsilyl)ethynyl)phenyl)-2H-indazole (6c)



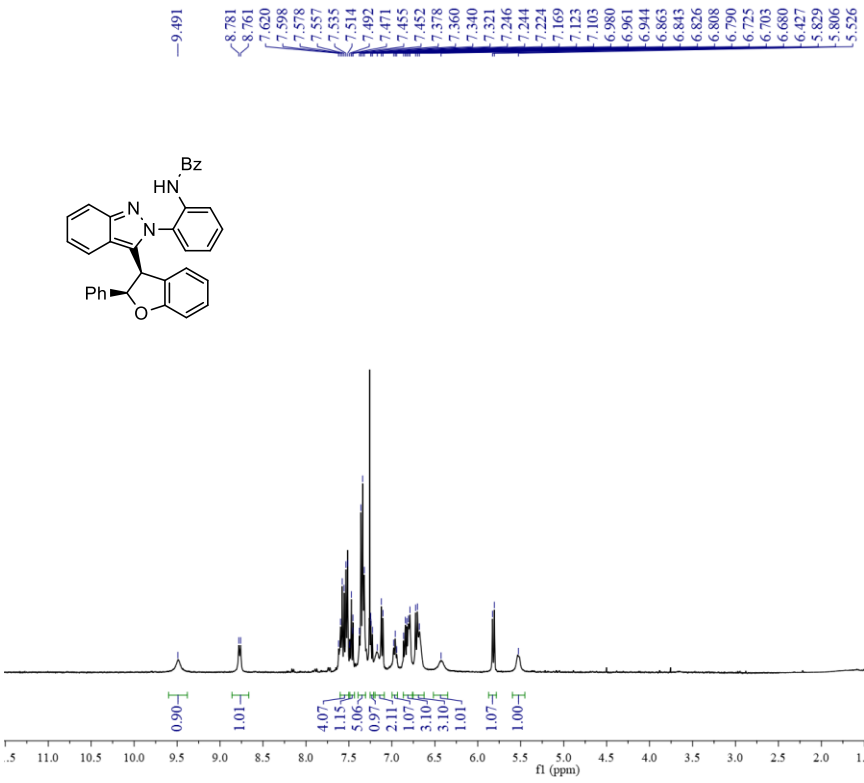


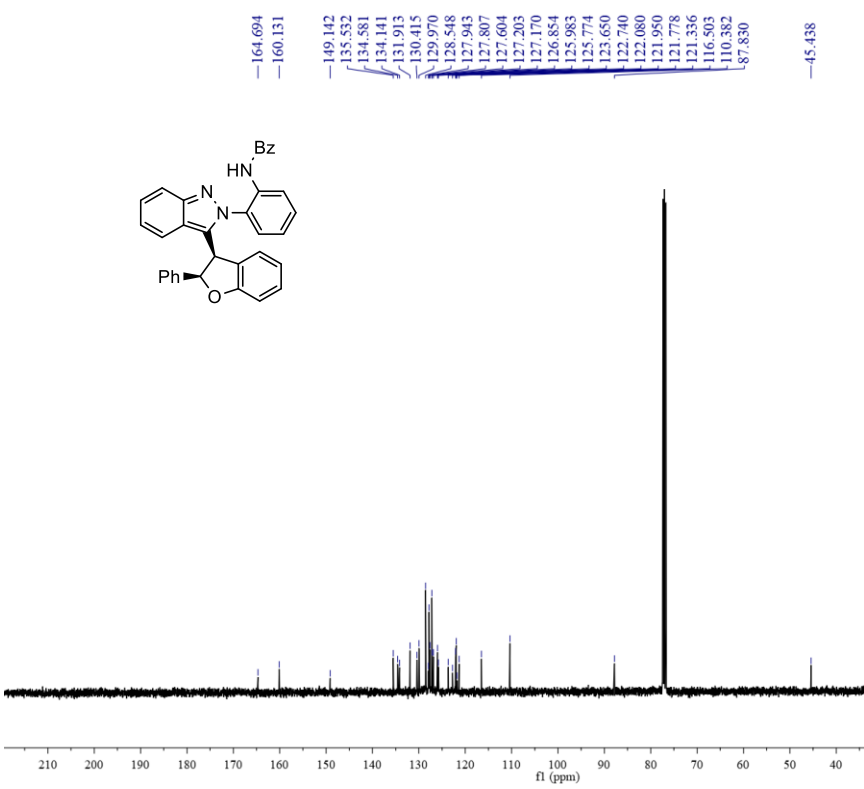
1-phenyl-3-(2-(3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazol-2-yl)phenyl)propan-1-one (6d)



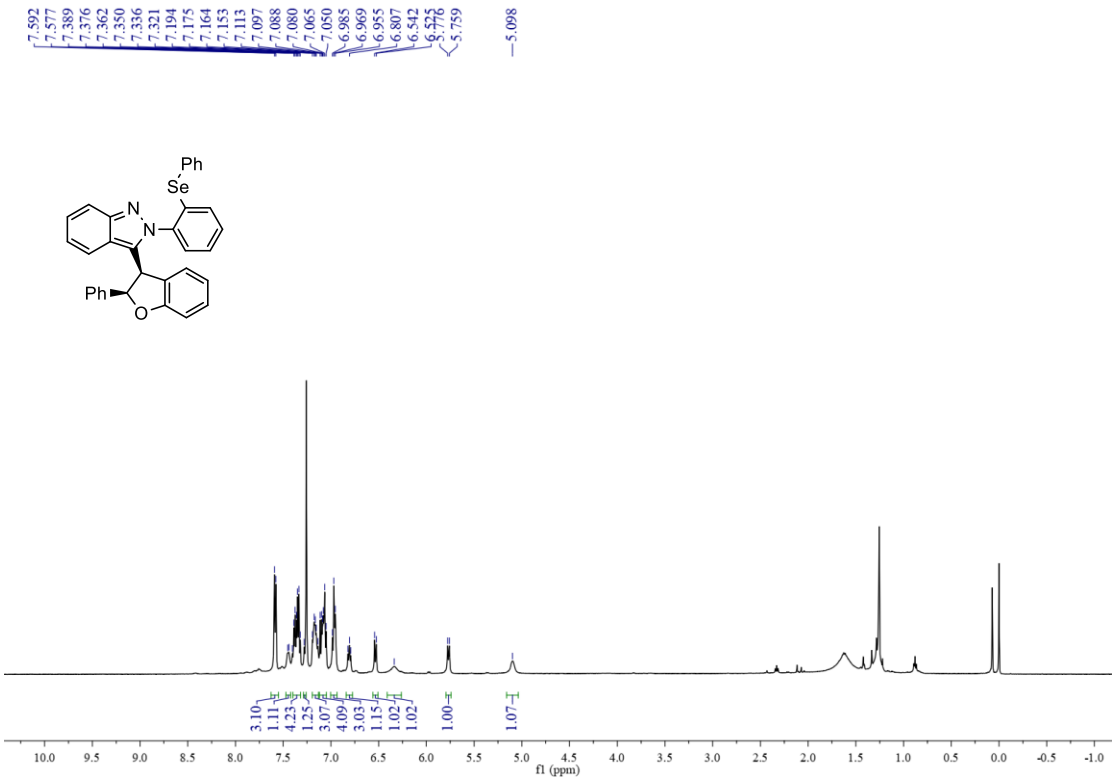


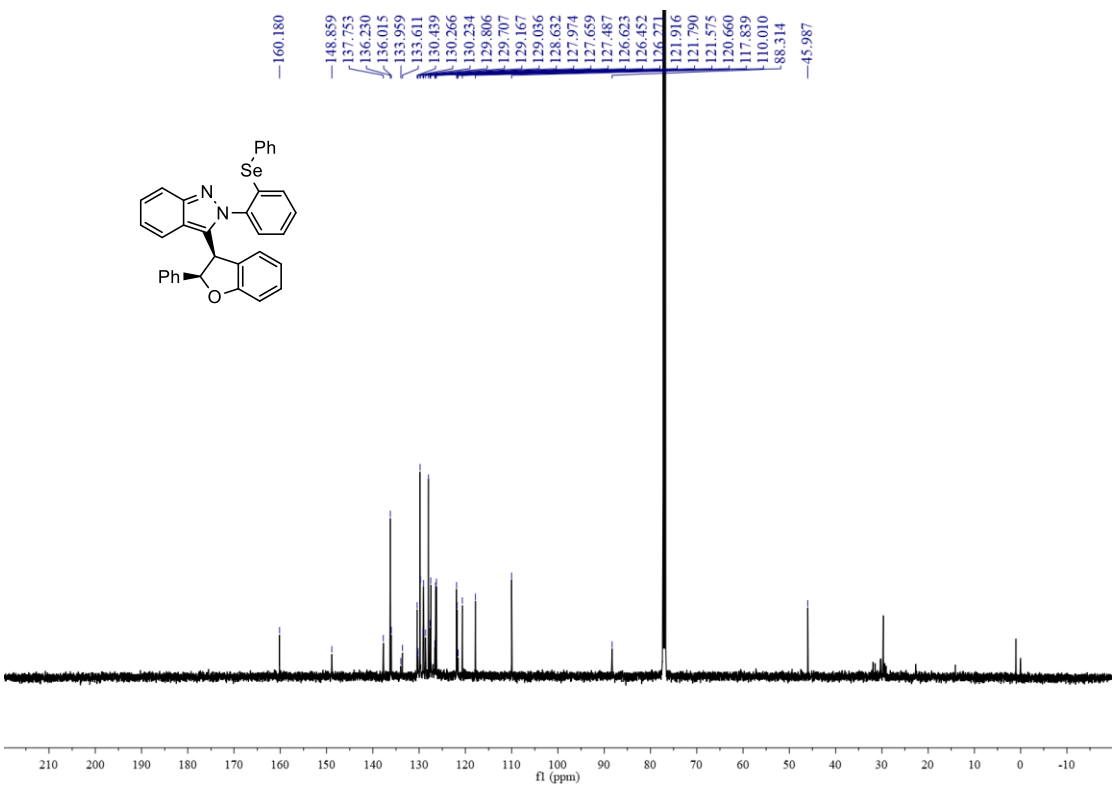
N-(2-(3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2H-indazol-2-yl)phenyl)benzamide (6e)



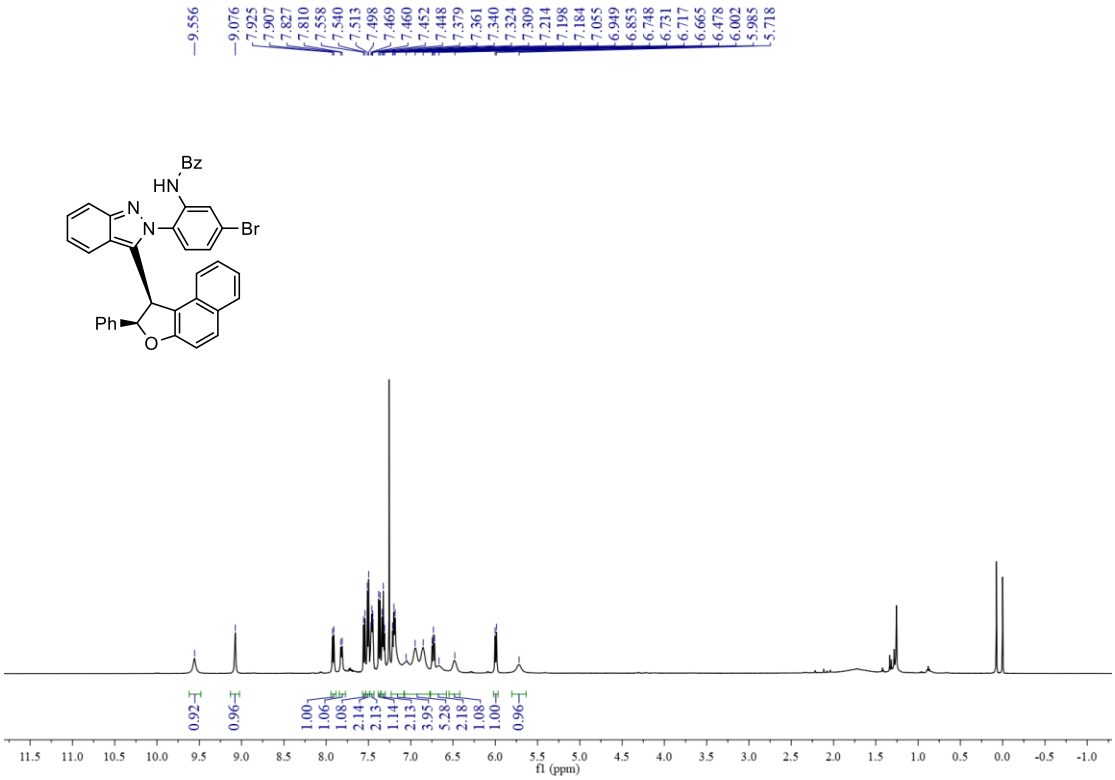


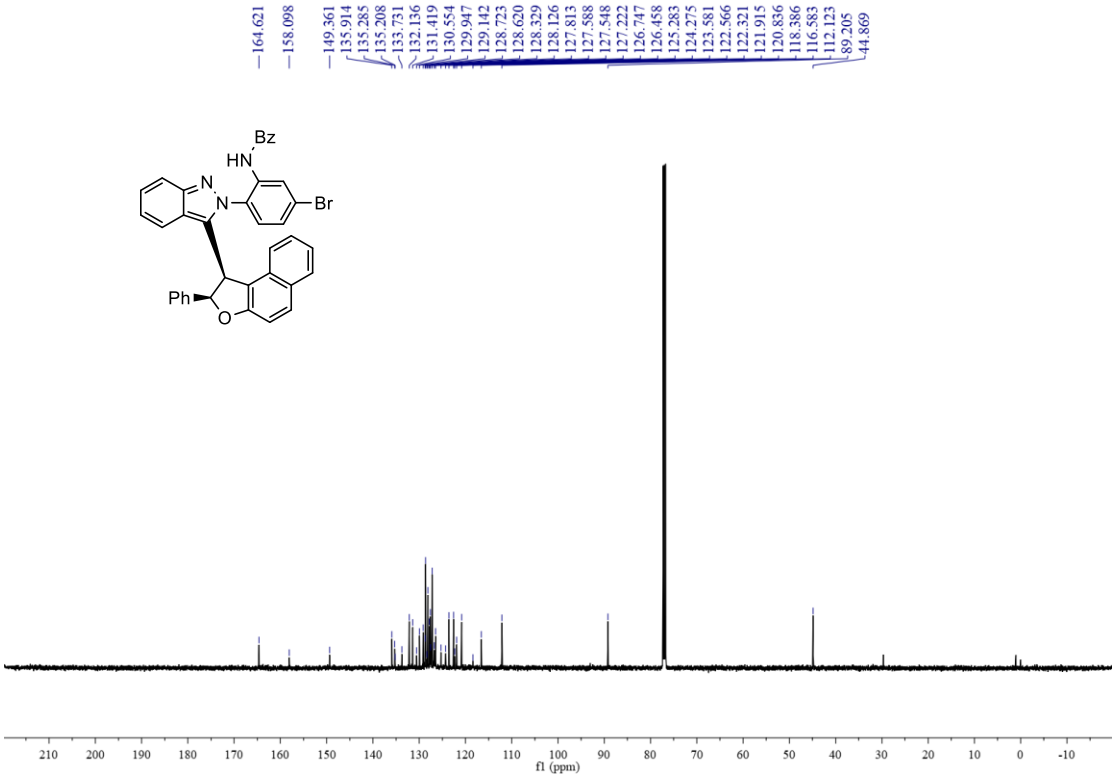
3-((2R,3R)-2-phenyl-2,3-dihydrobenzofuran-3-yl)-2-(2-(phenylselanyl)phenyl)-2H-indazole (6f)



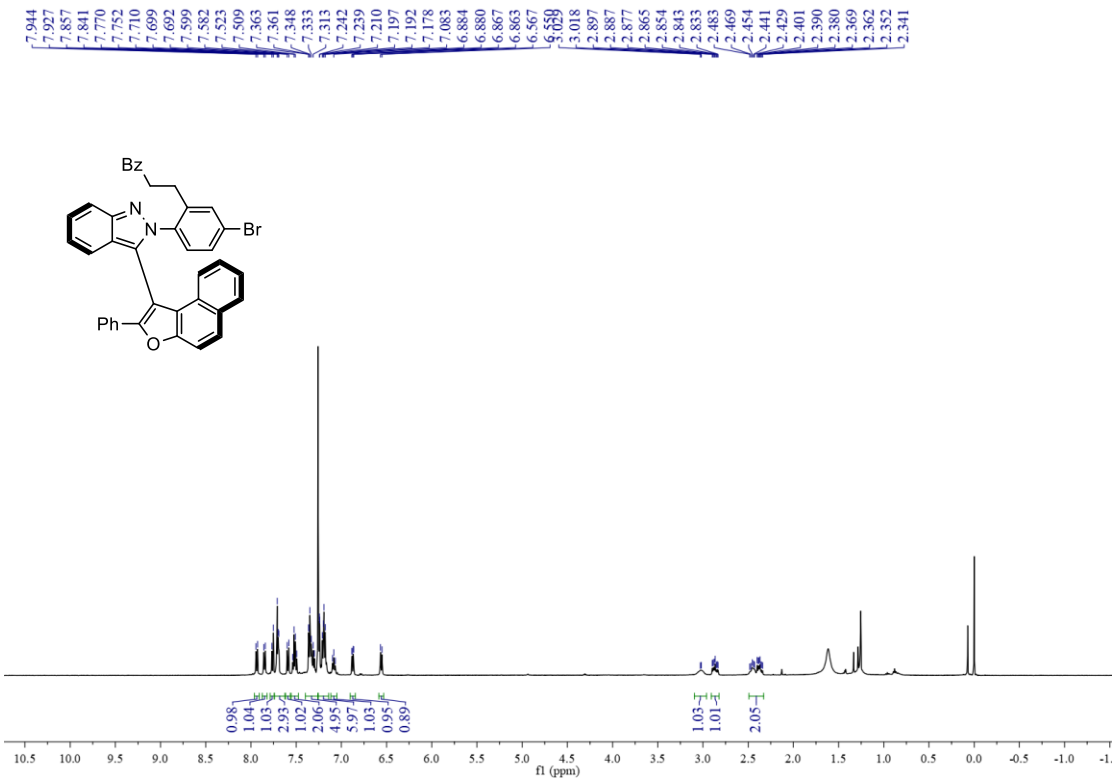


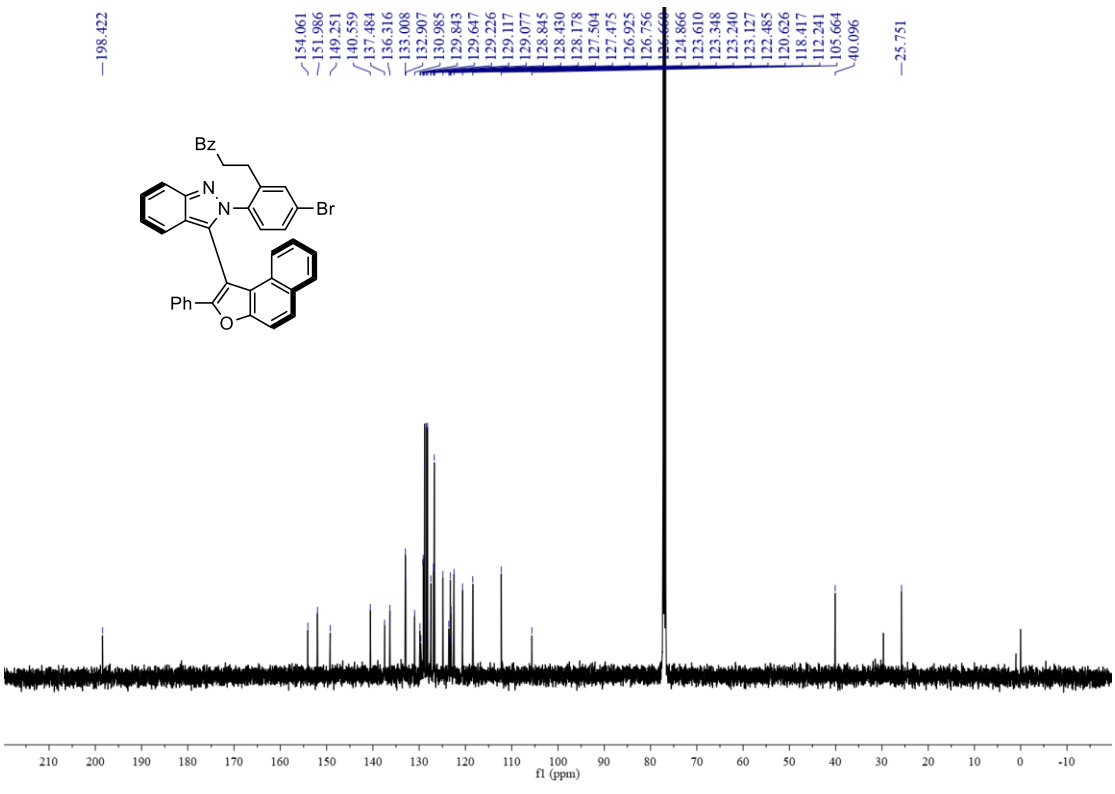
N-(5-bromo-2-(3-((1R,2R)-2-phenyl-1,2-dihydronaphtho[2,1-b]furan-1-yl)-2H-indazol-2-yl)phenyl)-benzamide (6g)



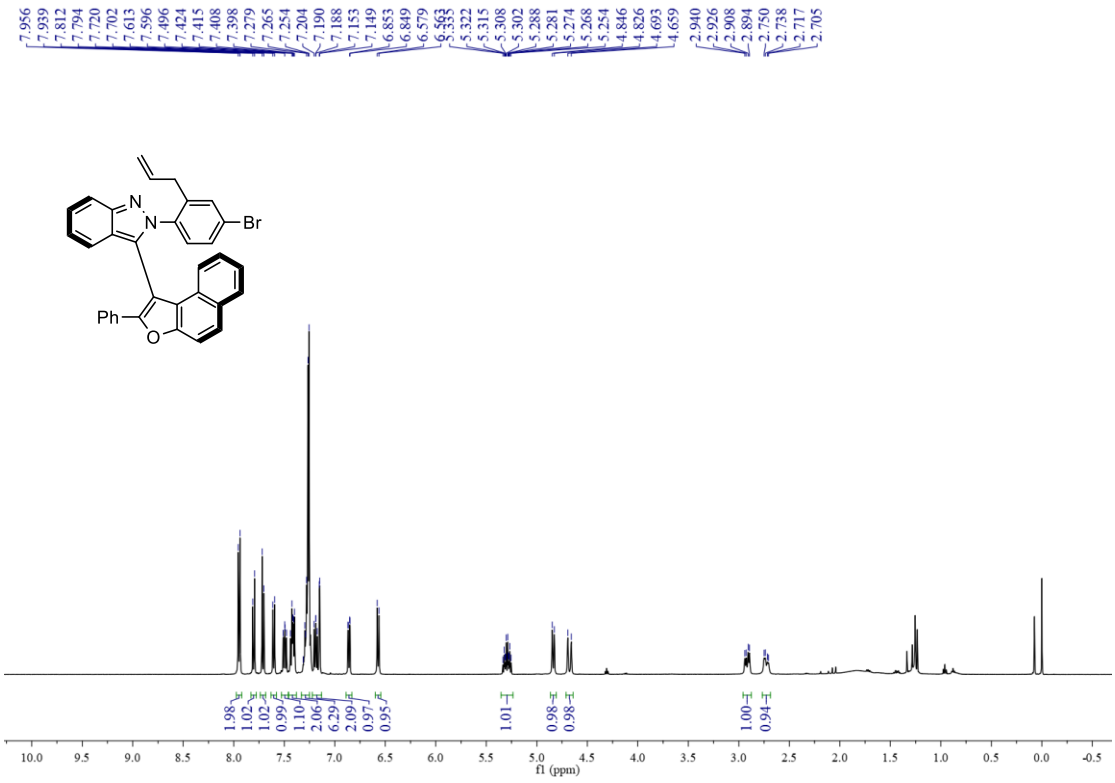


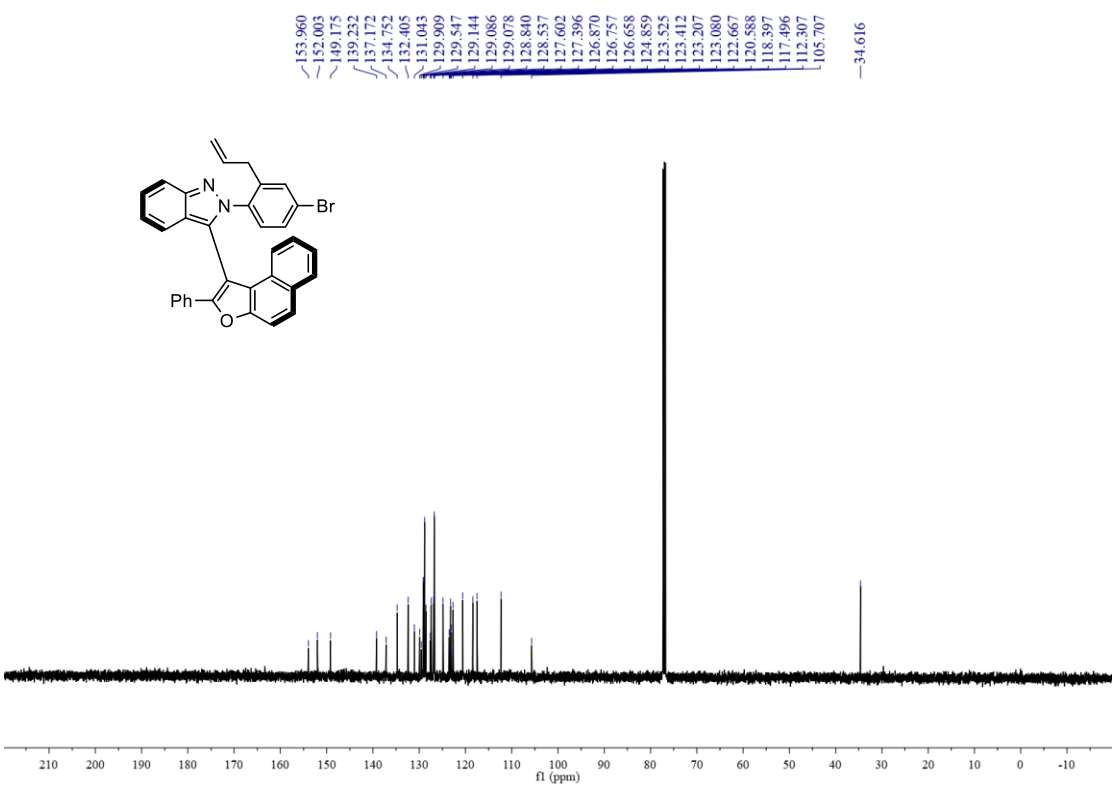
3-(5-bromo-2-(3-(2-phenylnaphtho[2,1-b]furan-1-yl)-2H-indazol-2-yl)phenyl)-1-phenylpropan-1-one (6h)



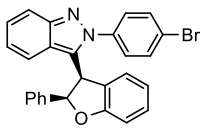


2-(2-allyl-4-bromophenyl)-3-(2-phenylnaphtho[2,1-b]furan-1-yl)-2H-indazole (6i)



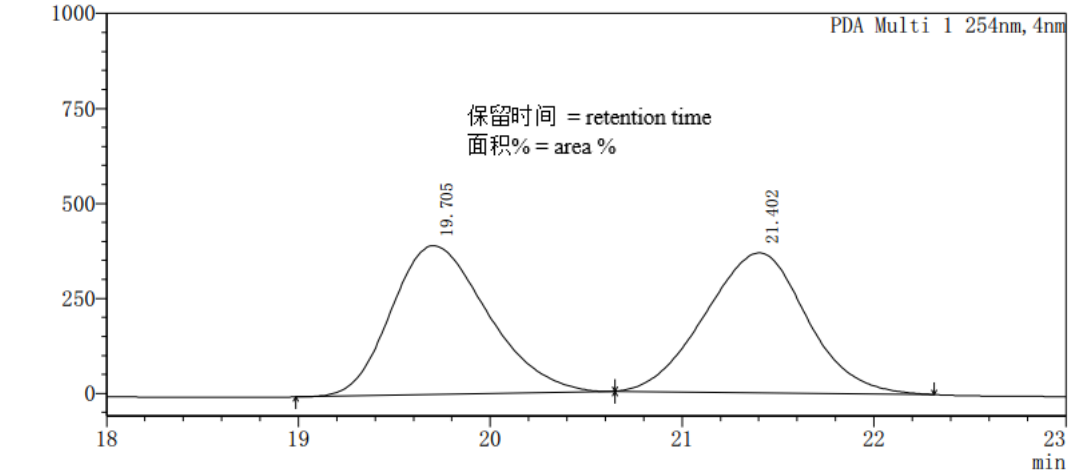


6. Data of HPLC



3a

〈色谱图〉

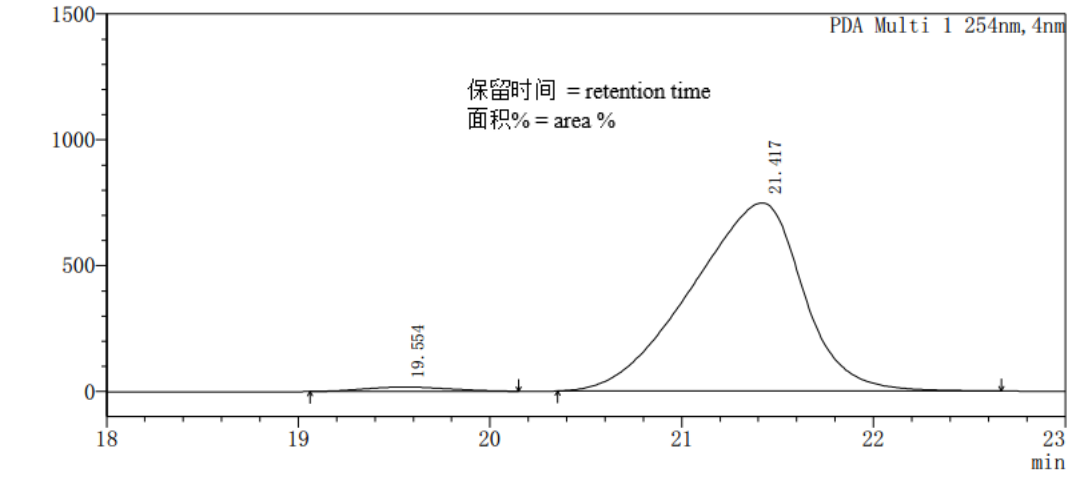


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	19.705	13671576	391701		51.558	50.174
2	21.402	13576772	368033		48.442	49.826
总计		27248349	759734		100.000	100.000

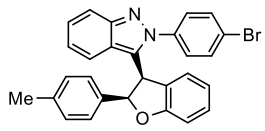
〈色谱图〉



〈峰表〉

PDA Ch1 254nm

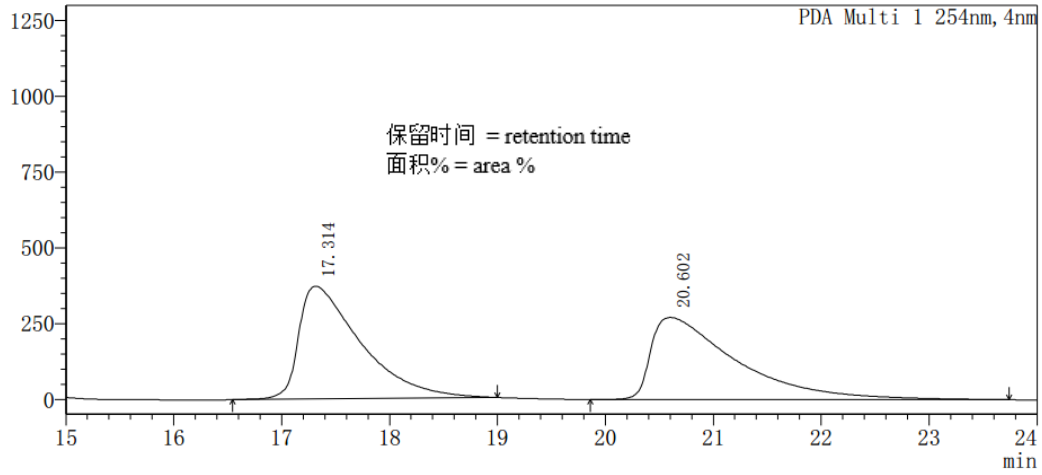
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	19.554	545481	17332		2.266	1.766
2	21.417	30335364	747585		97.734	98.234
总计		30880845	764917		100.000	100.000



2b

〈色谱图〉

mAU



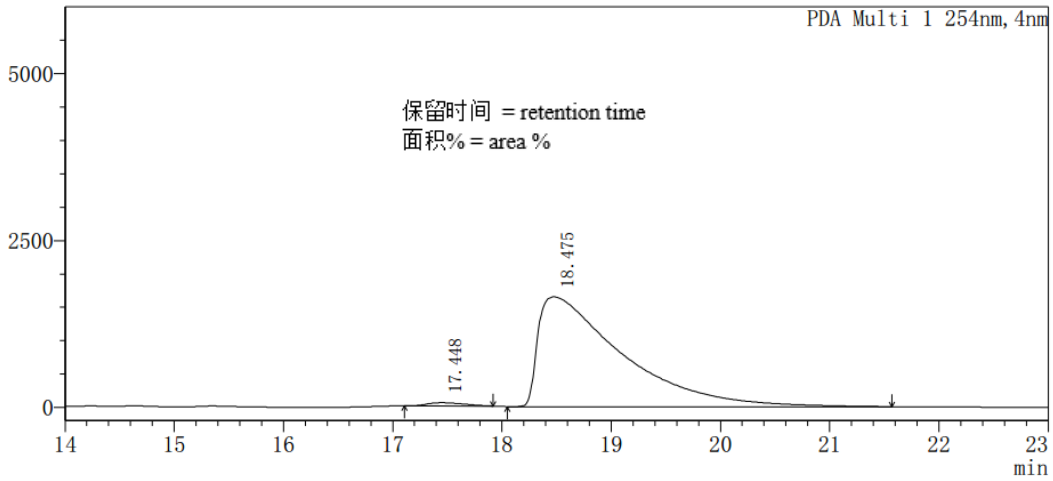
〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	17.314	14900818	372436		57.841	49.934
2	20.602	14939986	271458		42.159	50.066
总计		29840805	643894		100.000	100.000

〈色谱图〉

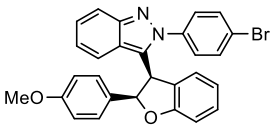
mAU



〈峰表〉

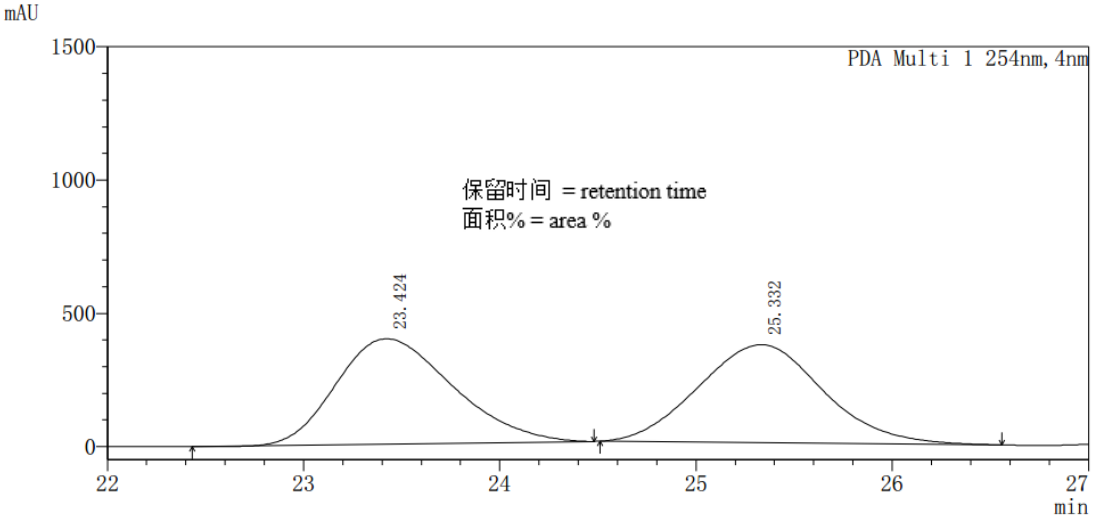
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	17.448	1202346	50033		2.952	1.352
2	18.475	87729287	1644596		97.048	98.648
总计		88931633	1694629		100.000	100.000



2c

〈色谱图〉

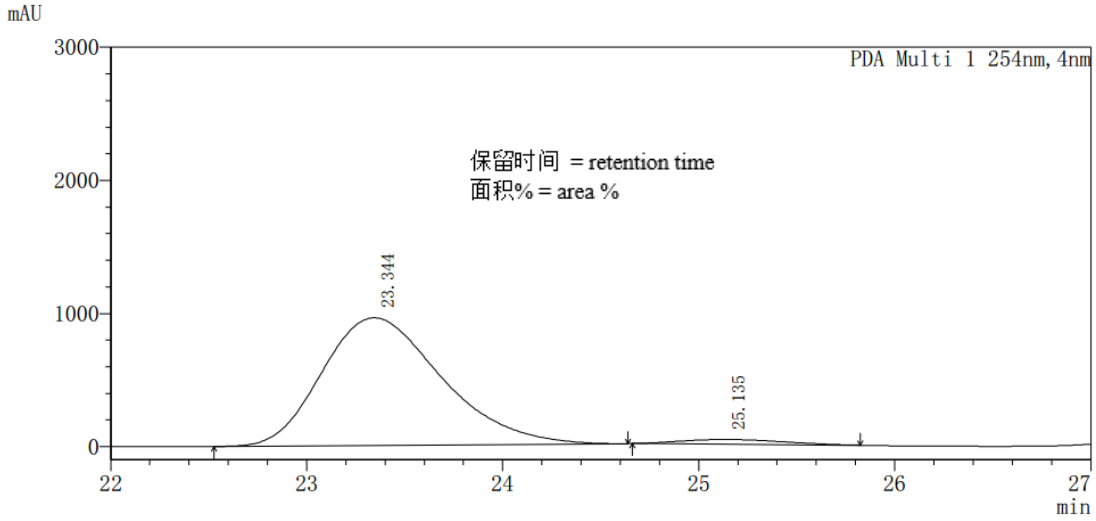


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	23.424	16304655	395324		51.824	50.103
2	25.332	16237423	367503		48.176	49.897
总计		32542078	762827		100.000	100.000

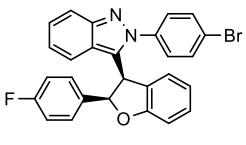
〈色谱图〉



〈峰表〉

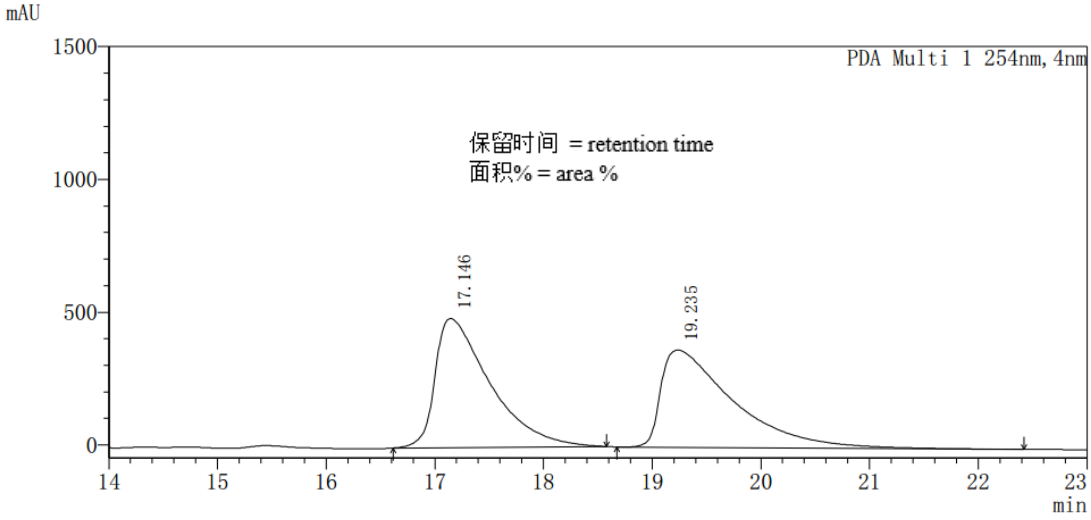
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	23.344	40727343	958783		96.413	96.912
2	25.135	1297916	35673		3.587	3.088
总计		42025259	994457		100.000	100.000



2d

〈色谱图〉

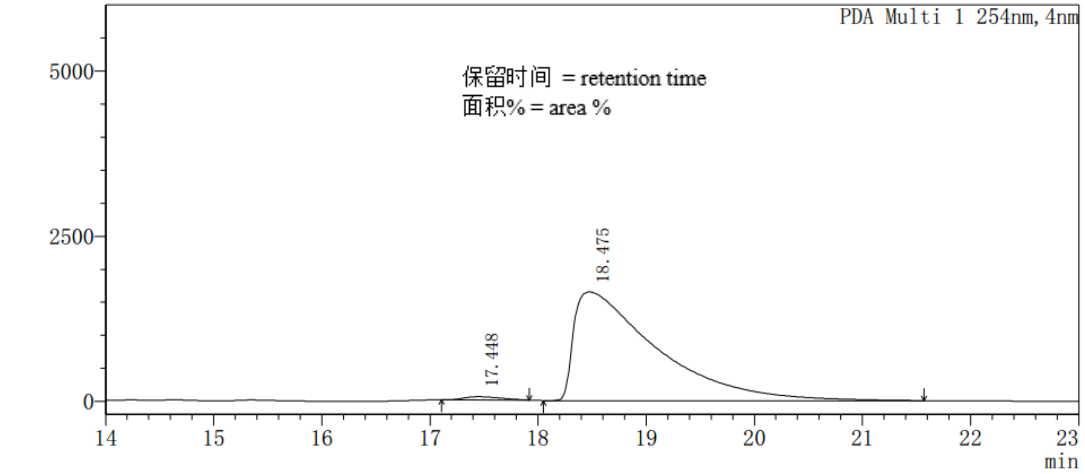


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	17.146	17086781	486420		57.028	50.280
2	19.235	16896656	366534		42.972	49.720
总计		33983437	852955		100.000	100.000

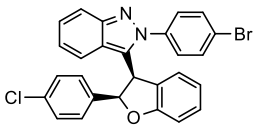
〈色谱图〉



〈峰表〉

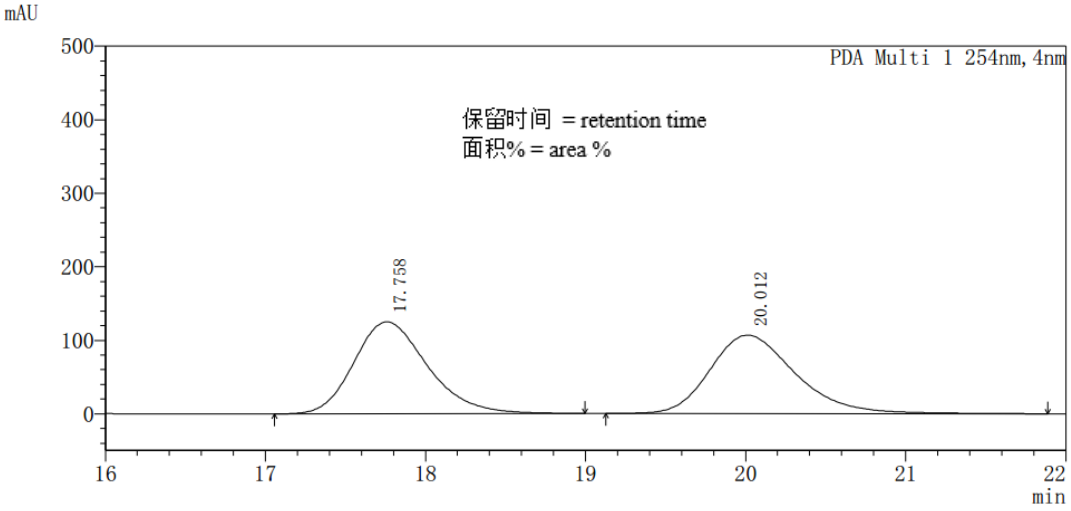
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	17.448	1202346	50033		2.952	1.352
2	18.475	87729287	1644596		97.048	98.648
总计		88931633	1694629		100.000	100.000



2e

〈色谱图〉

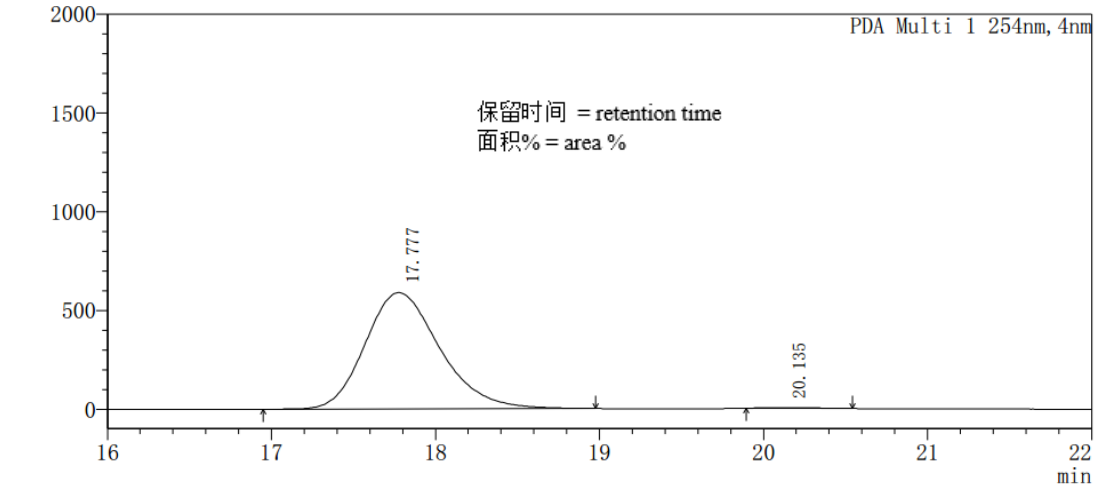


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	17.758	4008657	125019		53.954	50.266
2	20.012	3966246	106695		46.046	49.734
总计		7974903	231714		100.000	100.000

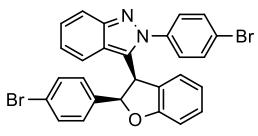
〈色谱图〉



〈峰表〉

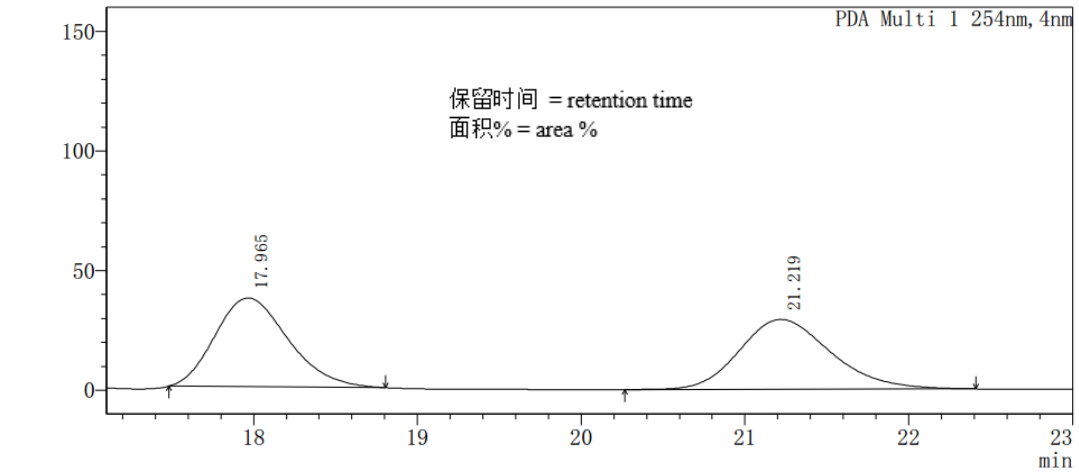
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	17.777	18674030	589110		99.412	99.577
2	20.135	79299	3483		0.588	0.423
总计		18753328	592593		100.000	100.000



2f

〈色谱图〉

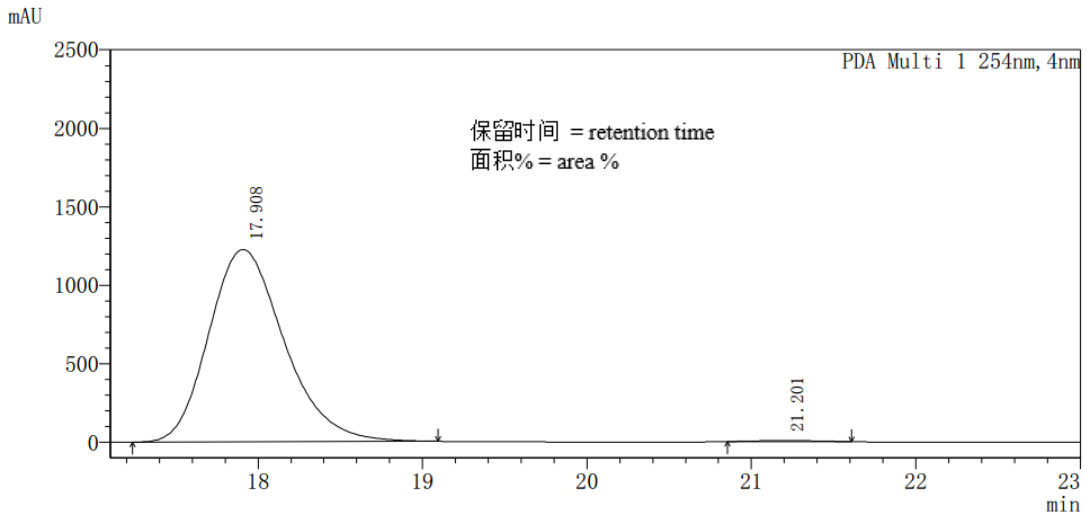


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	17.965	1154843	37114		55.971	50.472
2	21.219	1133254	29195		44.029	49.528
总计		2288097	66308		100.000	100.000

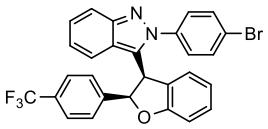
〈色谱图〉



〈峰表〉

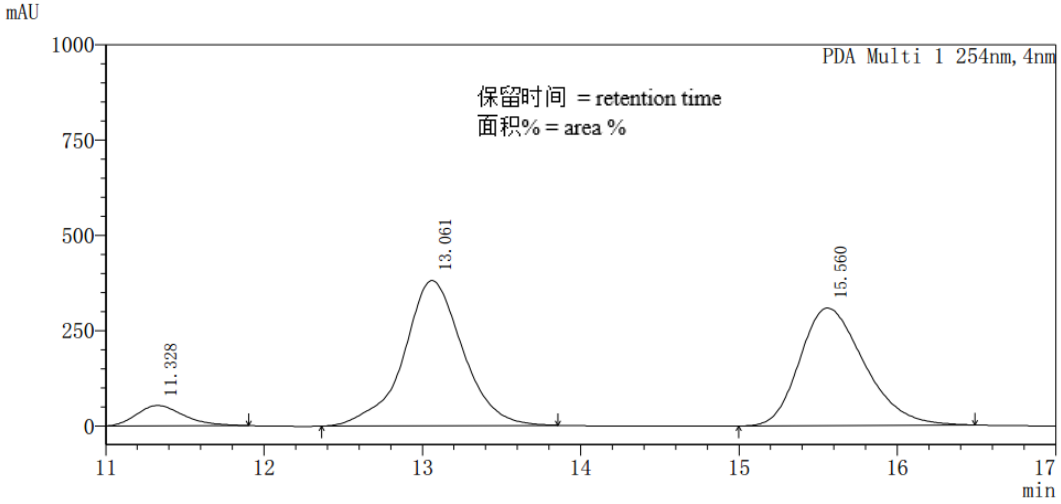
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	17.908	39141053	1225879		99.441	99.535
2	21.201	183039	6889		0.559	0.465
总计		39324092	1232768		100.000	100.000



2g

〈色谱图〉

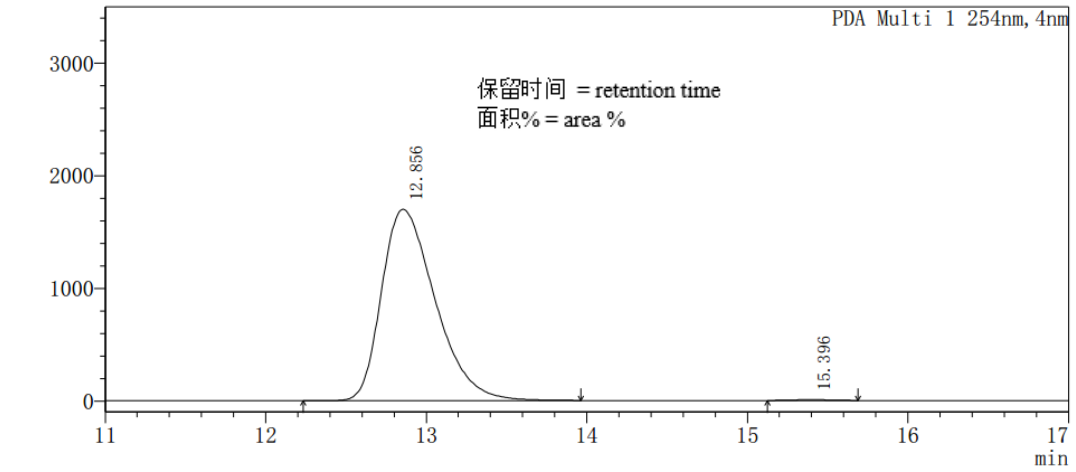


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	11.328	1120018	53665		7.219	5.666
2	13.061	9899713	380881		51.236	50.079
3	15.560	8748559	308845		41.545	44.256
总计		19768290	743391		100.000	100.000

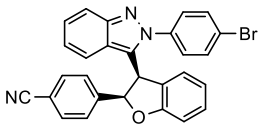
〈色谱图〉



〈峰表〉

PDA Ch1 254nm

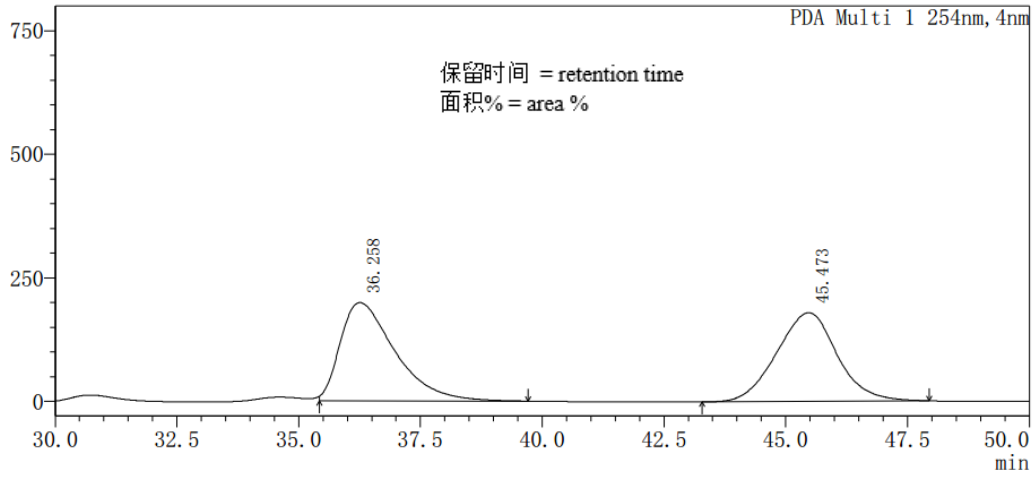
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	12.856	39583445	1700815		99.580	99.650
2	15.396	139208	7170		0.420	0.350
总计		39722653	1707985		100.000	100.000



2h

〈色谱图〉

mAU



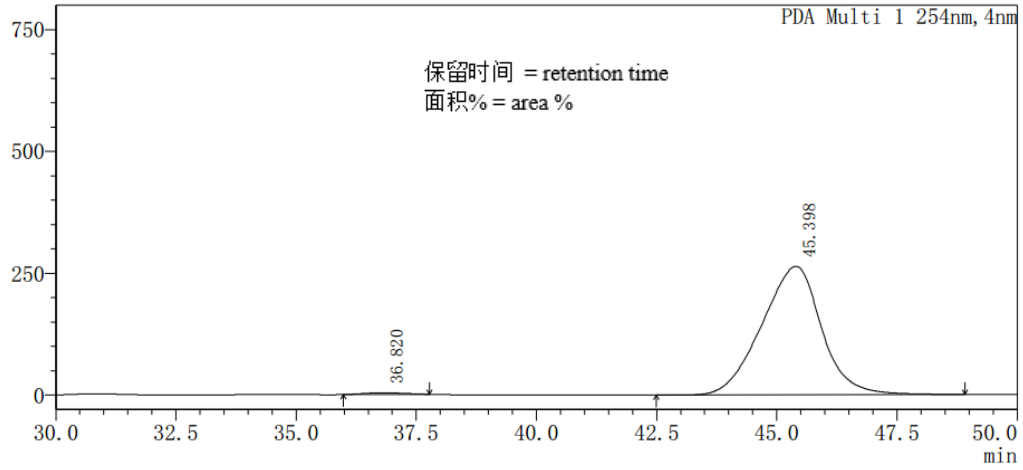
〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	36.258	15534211	198804		52.537	50.012
2	45.473	15526873	179606		47.463	49.988
总计		31061084	378410		100.000	100.000

〈色谱图〉

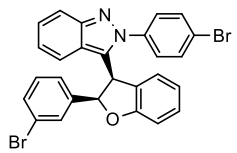
mAU



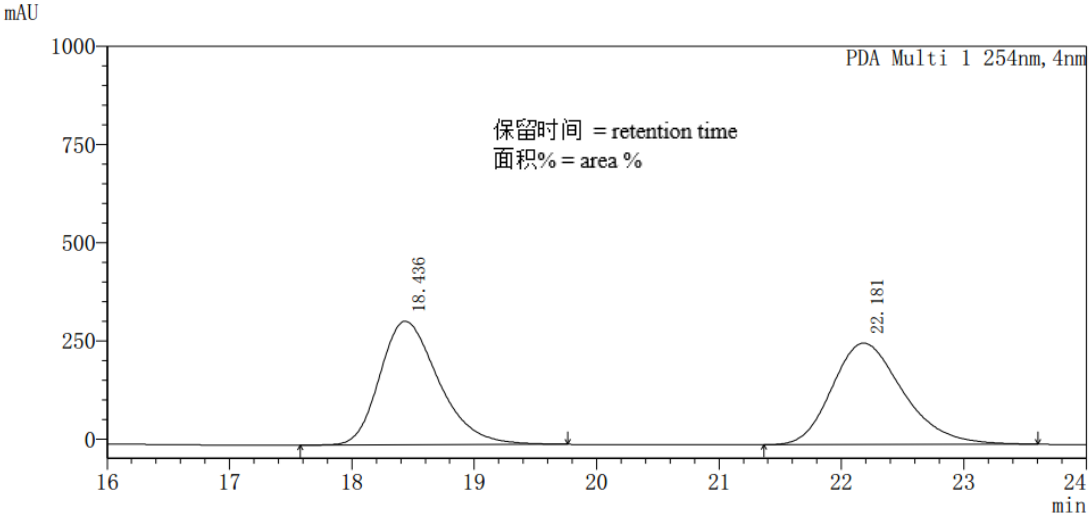
〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	36.820	208910	3539		1.324	0.903
2	45.398	22917001	263835		98.676	99.097
总计		23125911	267374		100.000	100.000



〈色谱图〉

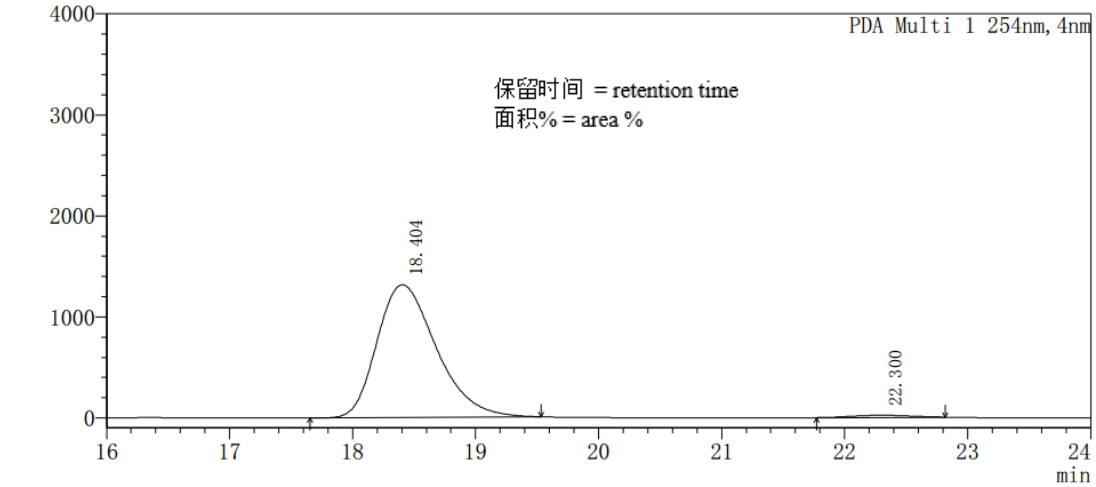


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	18.436	10522000	314745		54.913	50.171
2	22.181	10450293	258425		45.087	49.829
总计		20972293	573171		100.000	100.000

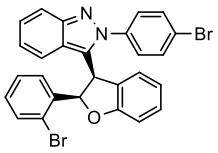
〈色谱图〉



〈峰表〉

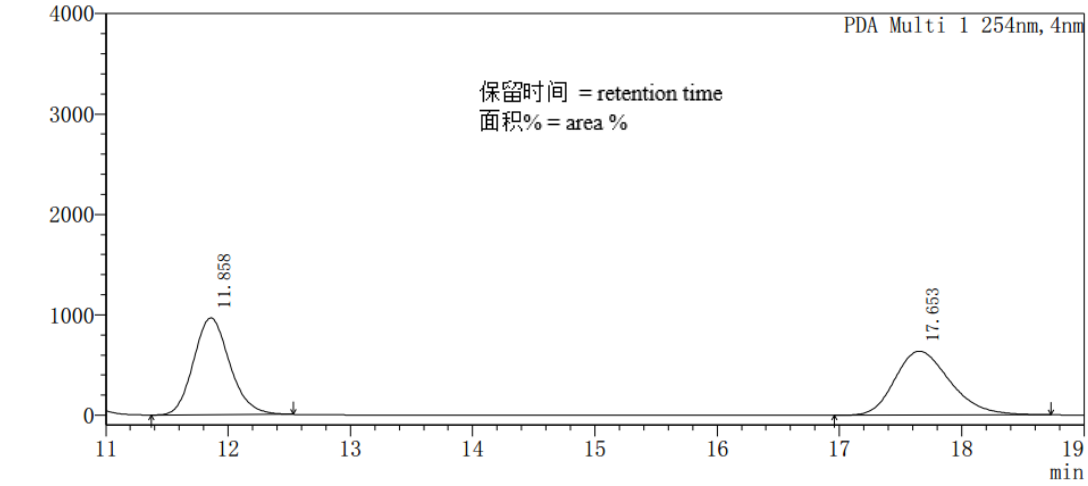
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	18.404	44075472	1314811		98.381	98.405
2	22.300	714552	21639		1.619	1.595
总计		44790025	1336450		100.000	100.000



2j

〈色谱图〉

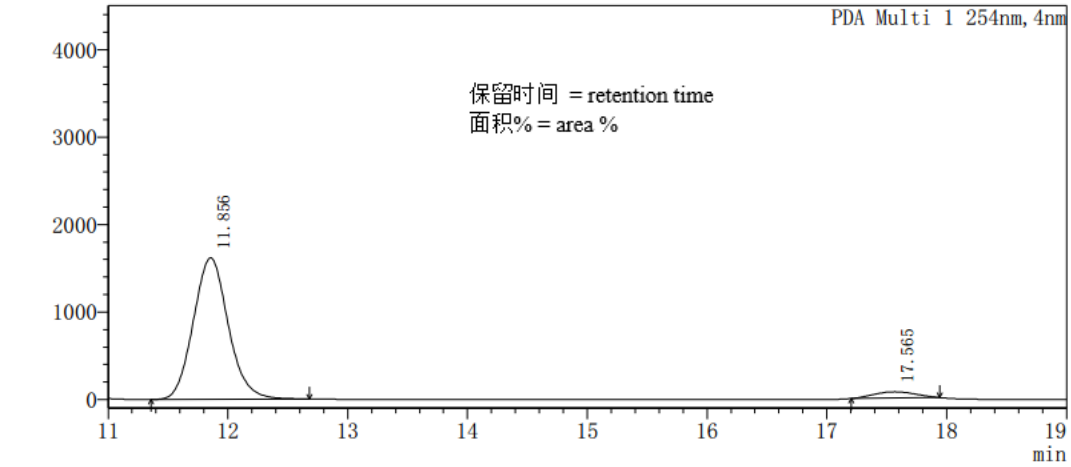


〈峰表〉

PDA Ch1 254nm

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

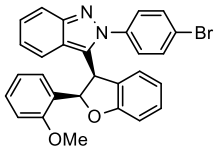
〈色谱图〉



〈峰表〉

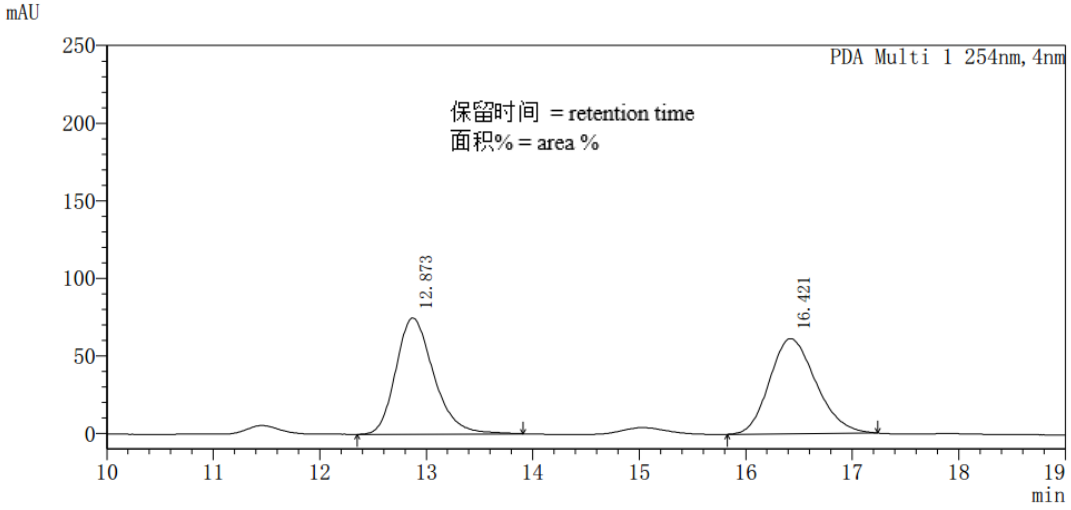
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	11.856	32799699	1616080		95.759	95.001
2	17.565	1725819	71579		4.241	4.999
总计		34525518	1687658		100.000	100.000



2k

〈色谱图〉

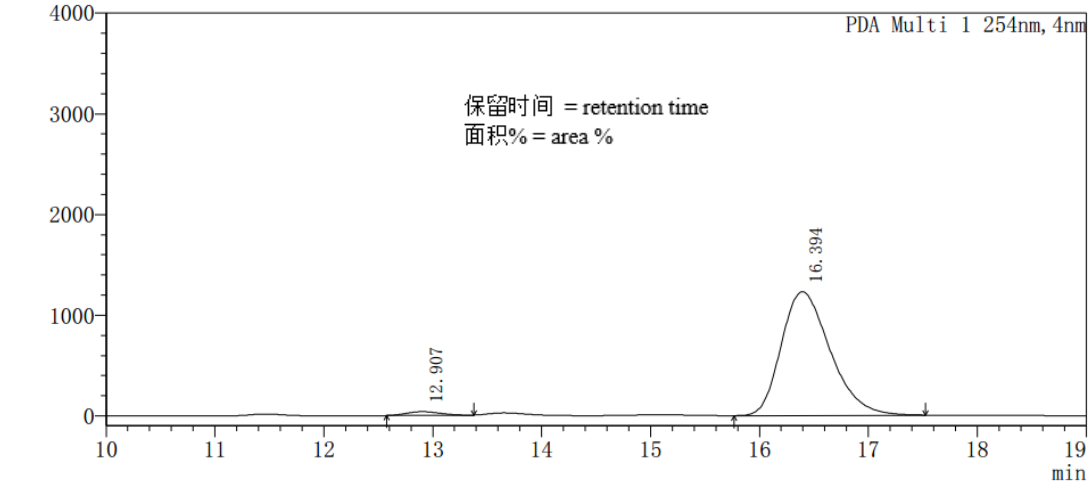


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	12.873	1849927	74825		54.997	49.907
2	16.421	1856826	61227		45.003	50.093
总计		3706753	136052		100.000	100.000

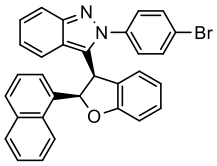
〈色谱图〉



〈峰表〉

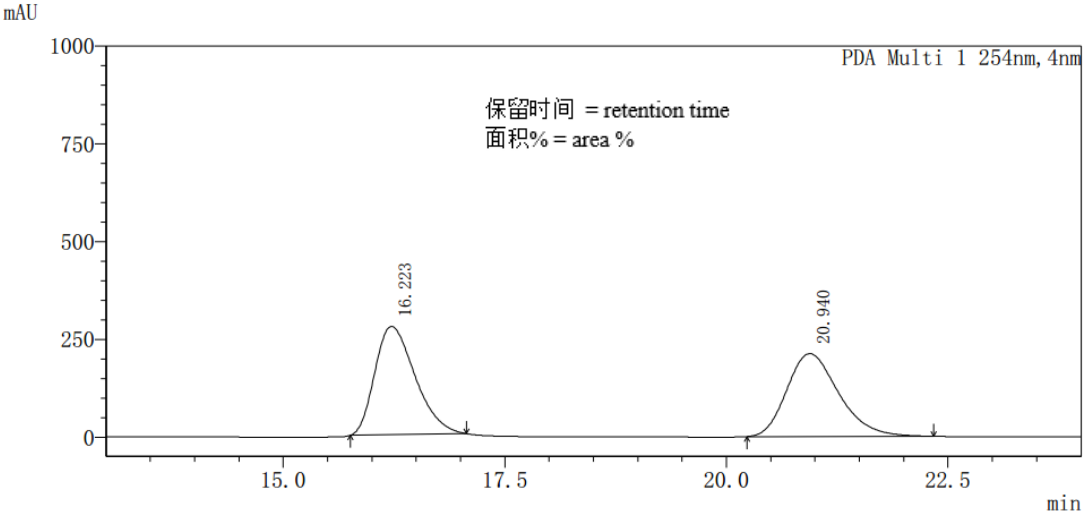
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	12.907	775285	36854		2.910	1.980
2	16.394	38381008	1229444		97.090	98.020
总计		39156293	1266299		100.000	100.000



2l

〈色谱图〉

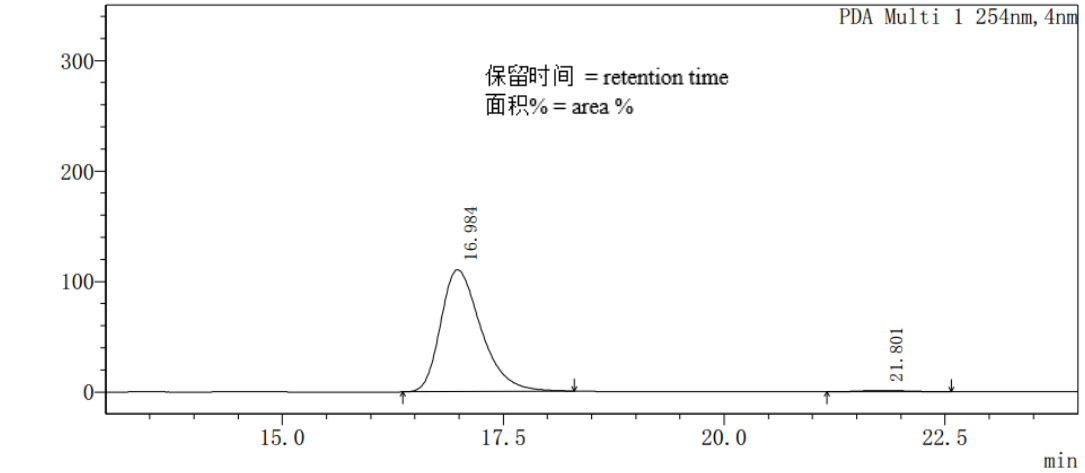


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	16.223	8778339	277519		56.693	50.420
2	20.940	8632244	211992		43.307	49.580
总计		17410583	489511		100.000	100.000

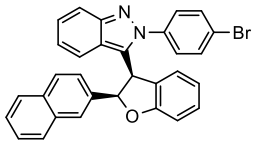
〈色谱图〉



〈峰表〉

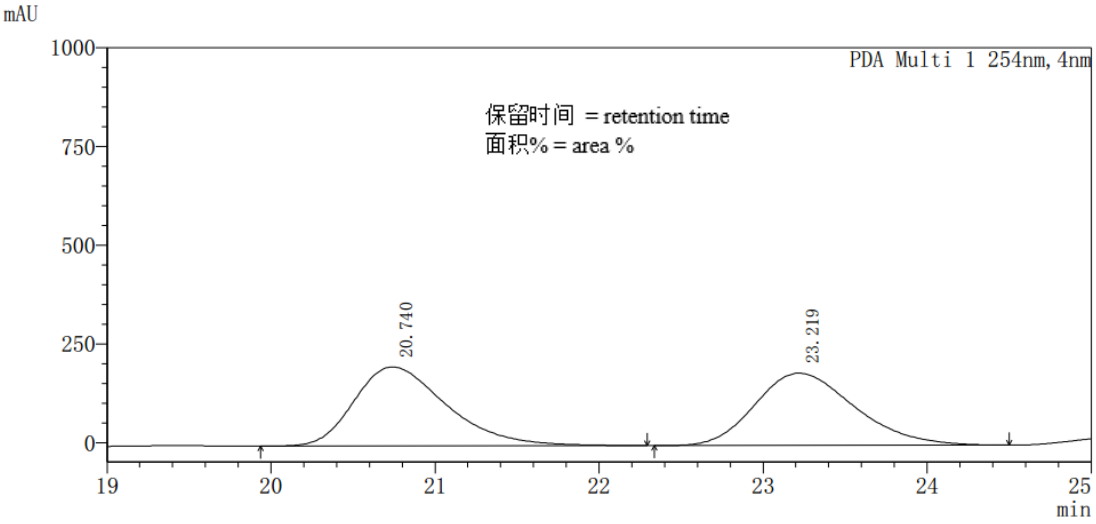
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	16.984	3518033	110341		98.817	98.586
2	21.801	50454	1321		1.183	1.414
总计		3568486	111662		100.000	100.000



2m

〈色谱图〉

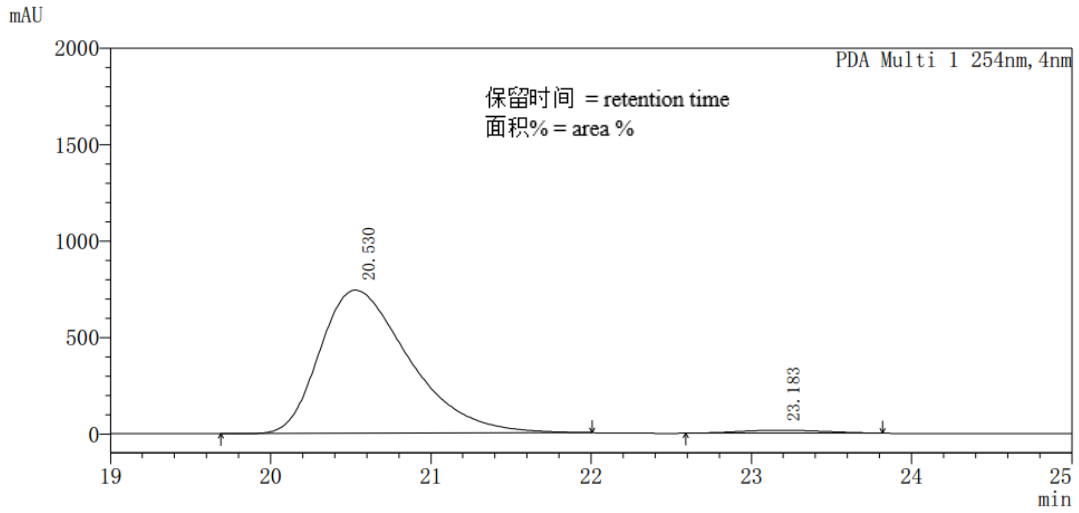


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	20.740	7872435	200267		52.216	50.329
2	23.219	7769449	183271		47.784	49.671
总计		15641884	383538		100.000	100.000

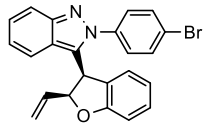
〈色谱图〉



〈峰表〉

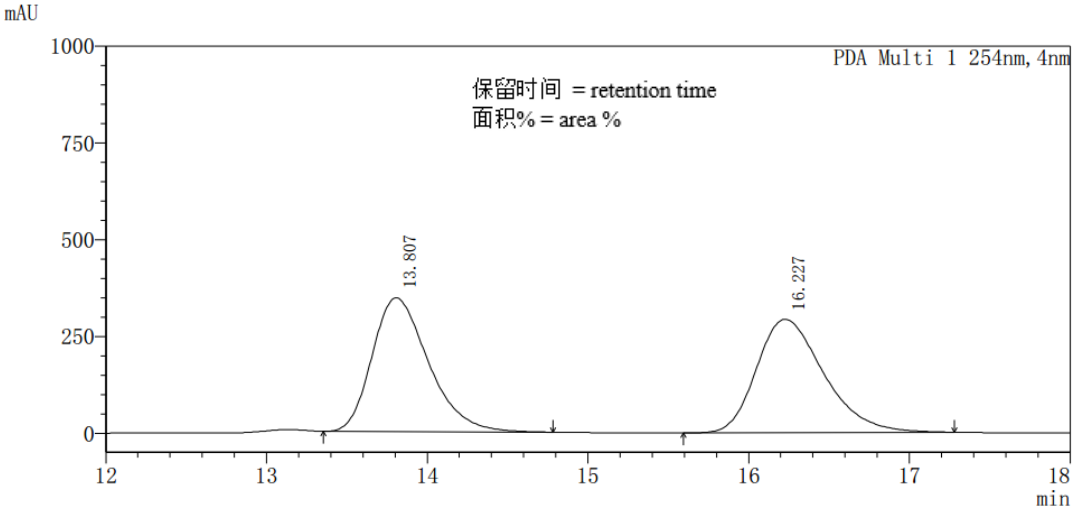
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	20.530	28939489	743544		97.890	98.000
2	23.183	590502	16026		2.110	2.000
总计		29529992	759570		100.000	100.000



2n

〈色谱图〉

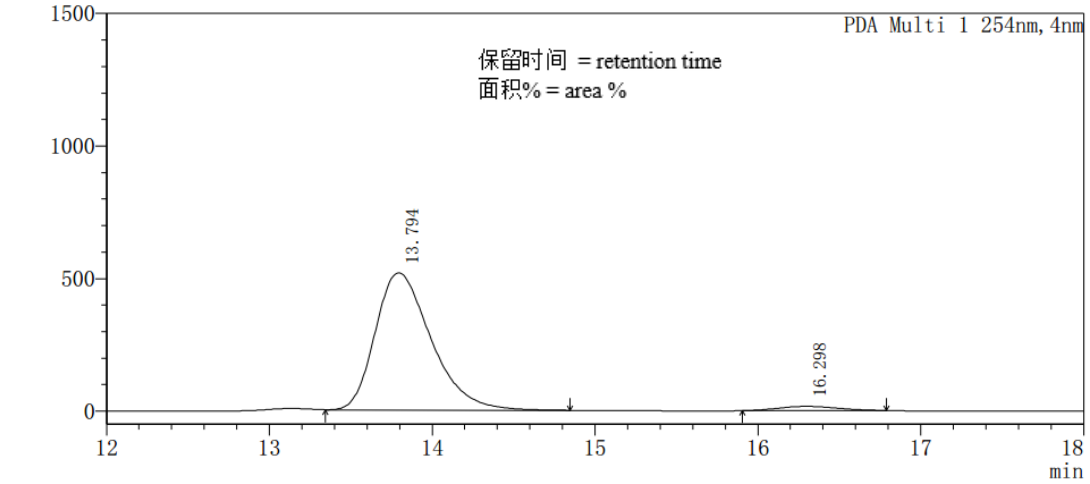


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	13.807	8443416	345701		54.104	49.687
2	16.227	8549670	293253		45.896	50.313
总计		16993086	638954		100.000	100.000

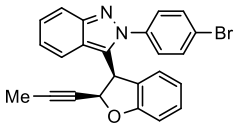
〈色谱图〉



〈峰表〉

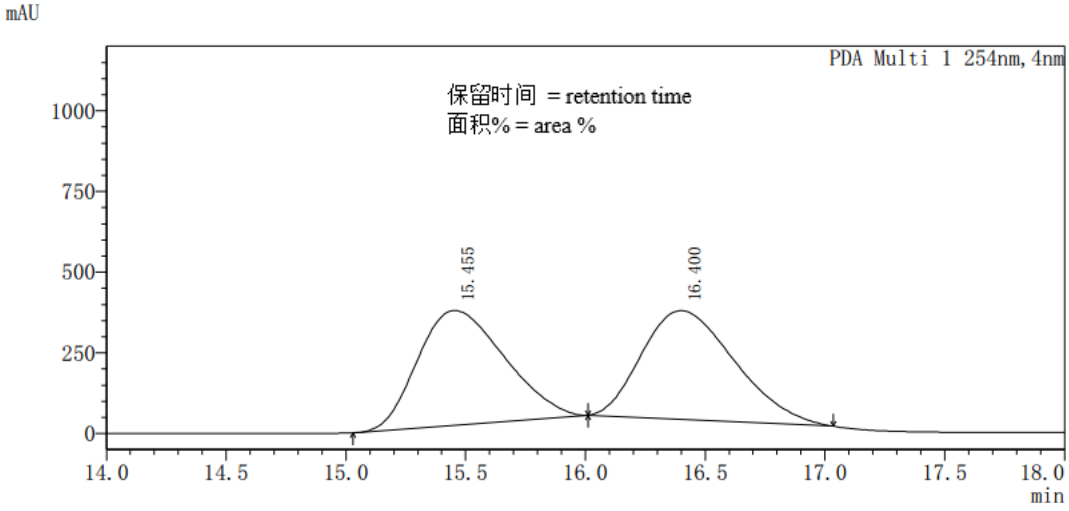
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	13.794	12343901	517667		96.989	96.783
2	16.298	410282	16072		3.011	3.217
总计		12754182	533739		100.000	100.000



2o

〈色谱图〉

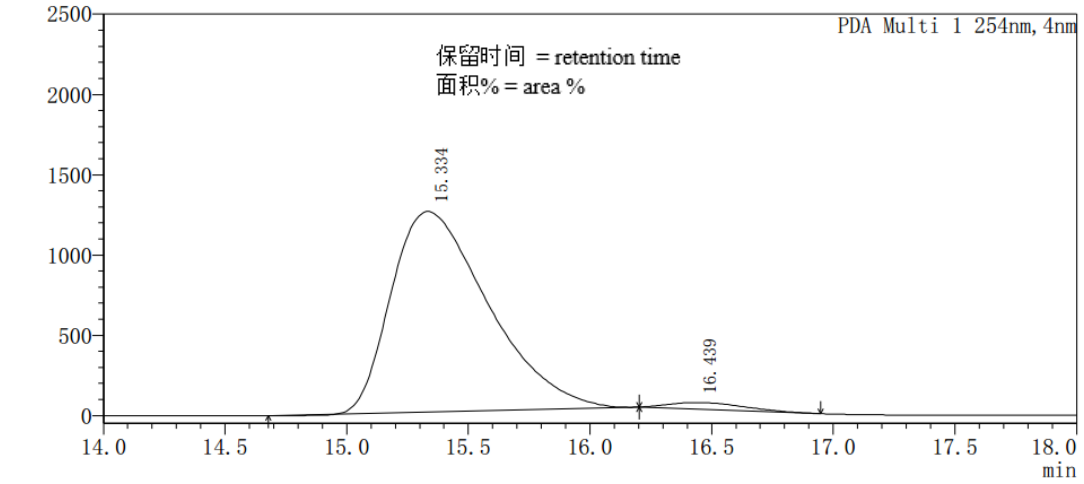


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	15.455	8964325	355140		51.326	49.652
2	16.400	9090158	336791		48.674	50.348
总计		18054483	691931		100.000	100.000

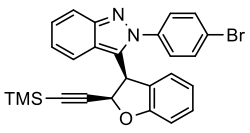
〈色谱图〉



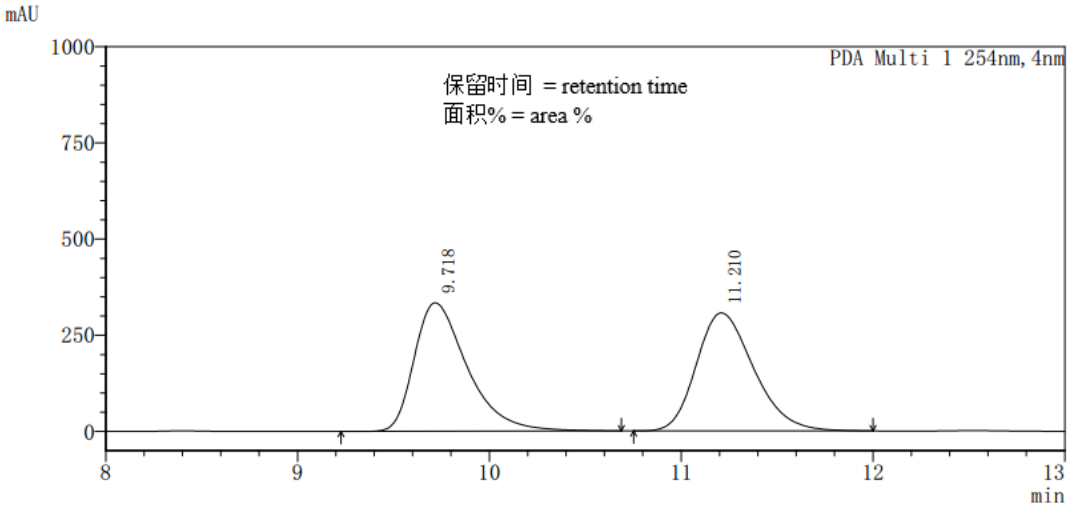
〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	15.334	34627961	1248297		96.794	97.467
2	16.439	899748	41351		3.206	2.533
总计		35527709	1289648		100.000	100.000



〈色谱图〉

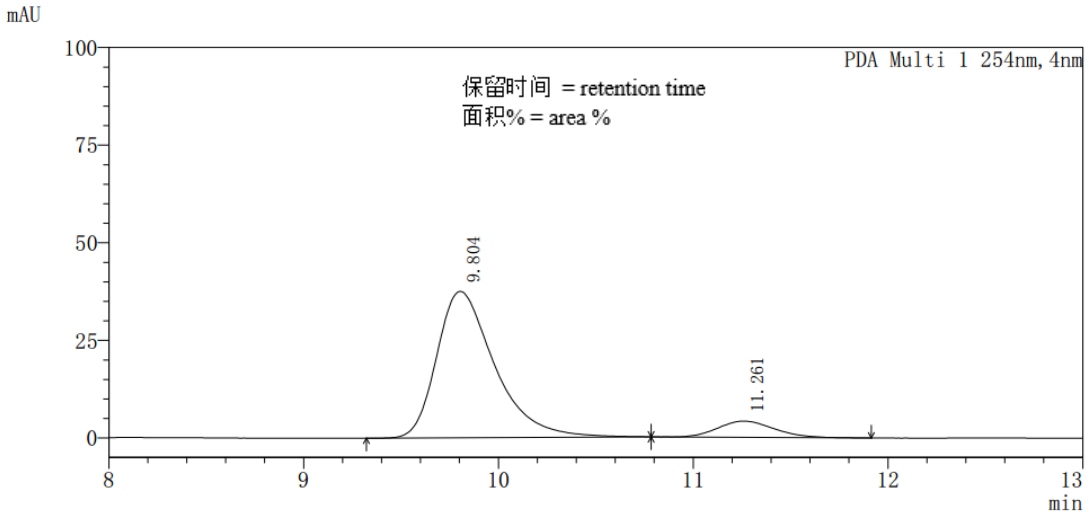


〈峰表〉

PDA Ch1 254nm

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

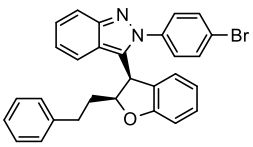
〈色谱图〉



〈峰表〉

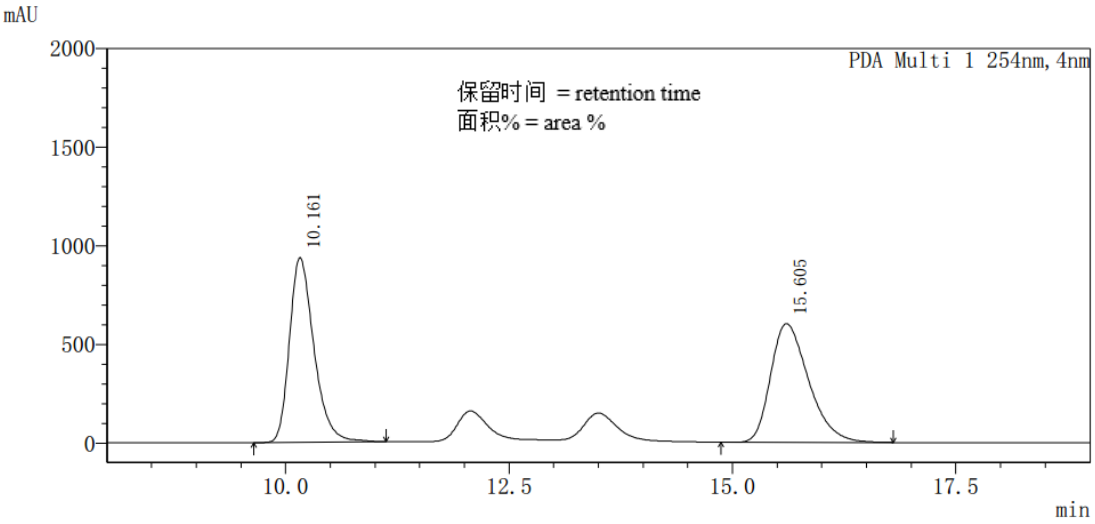
PDA Ch1 254nm

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



2q

〈色谱图〉

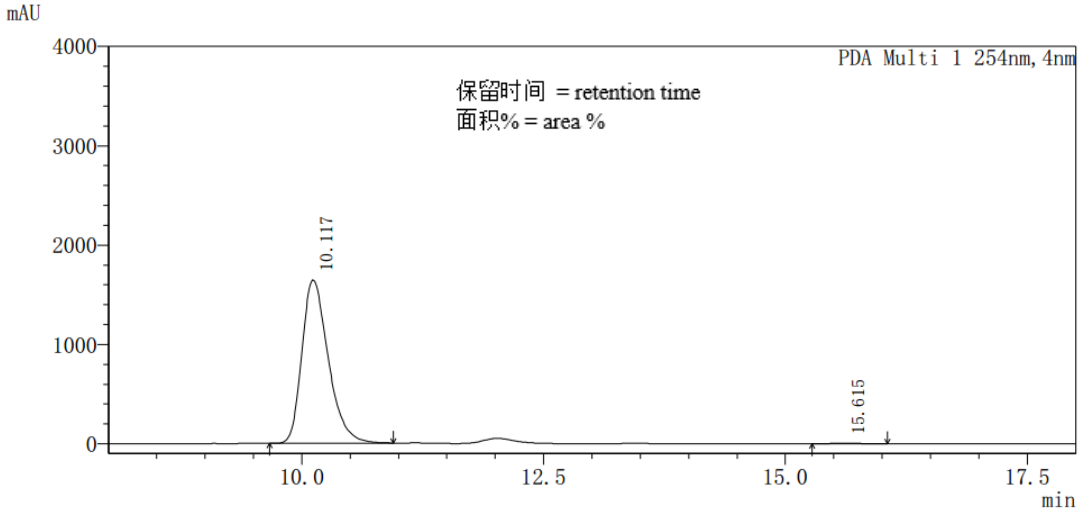


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.161	17887190	937181		60.904	50.097
2	15.605	17817905	601597		39.096	49.903
总计		35705096	1538778		100.000	100.000

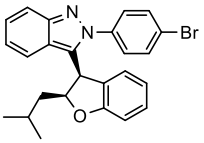
〈色谱图〉



〈峰表〉

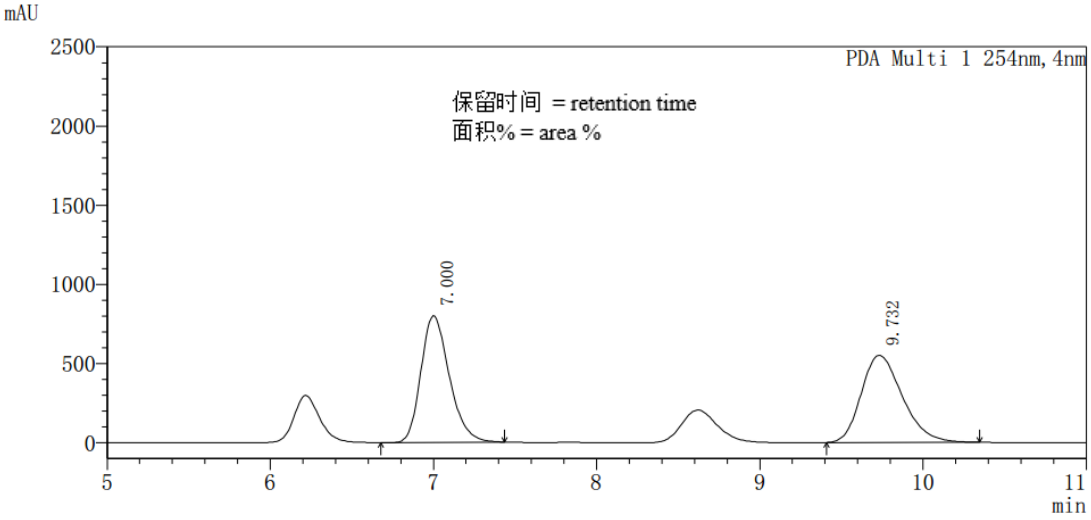
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.117	31176387	1643393		99.814	99.764
2	15.615	73743	3059		0.186	0.236
总计		31250129	1646452		100.000	100.000



2r

〈色谱图〉

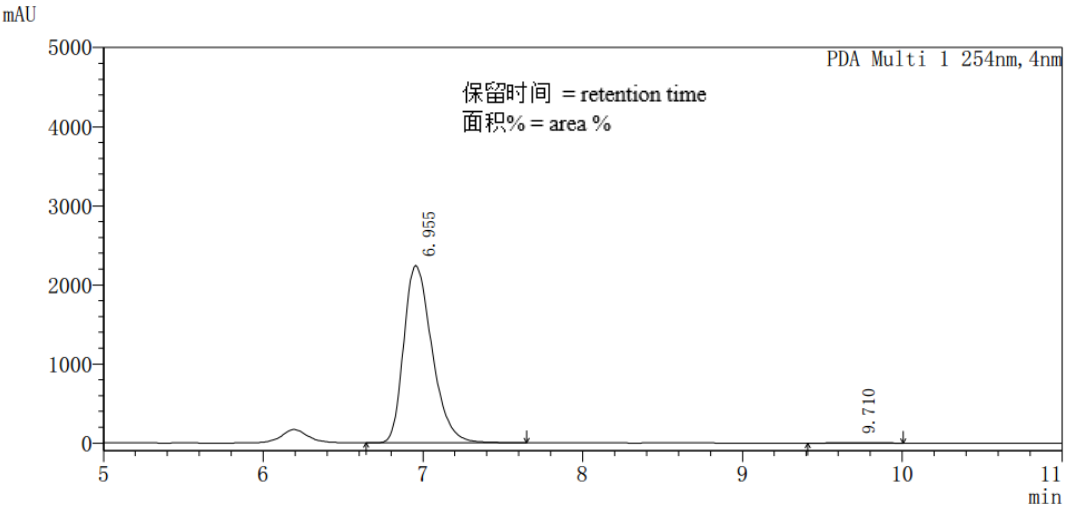


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.000	9698675	800222		59.250	50.116
2	9.732	9653967	550361		40.750	49.884
总计		19352642	1350584		100.000	100.000

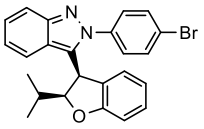
〈色谱图〉



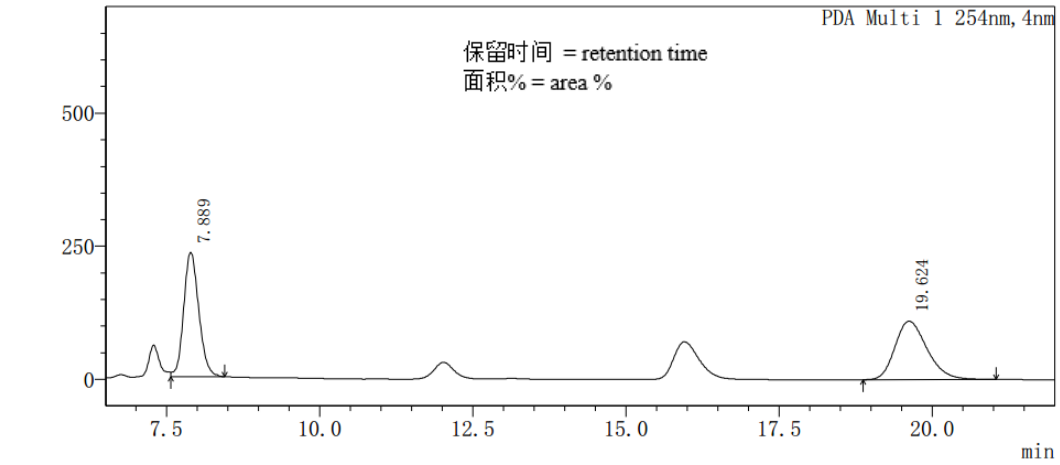
〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	6.955	27691151	2243402		99.793	99.730
2	9.710	75025	4645		0.207	0.270
总计		27766176	2248047		100.000	100.000



〈色谱图〉

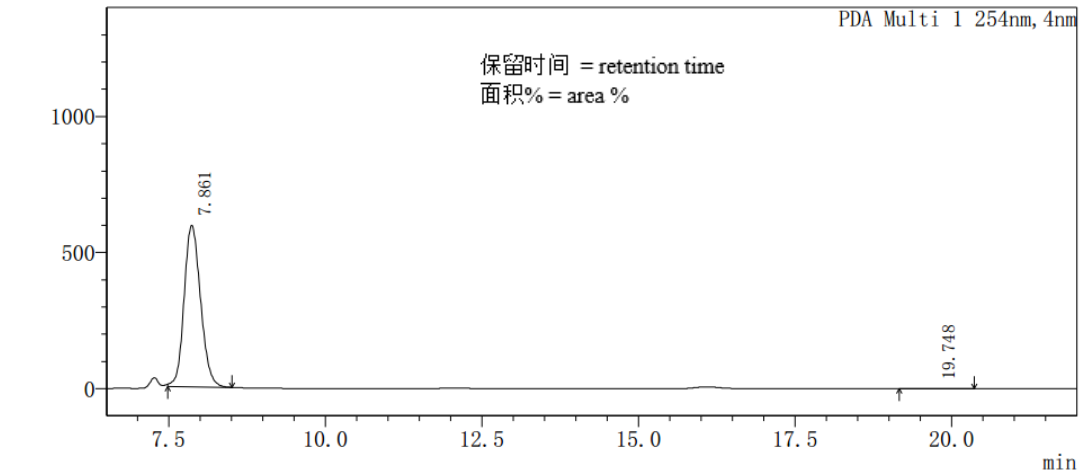


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.889	4006538	233656		68.024	49.993
2	19.624	4007615	109833		31.976	50.007
总计		8014154	343489		100.000	100.000

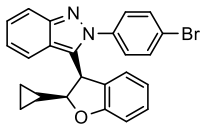
〈色谱图〉



〈峰表〉

PDA Ch1 254nm

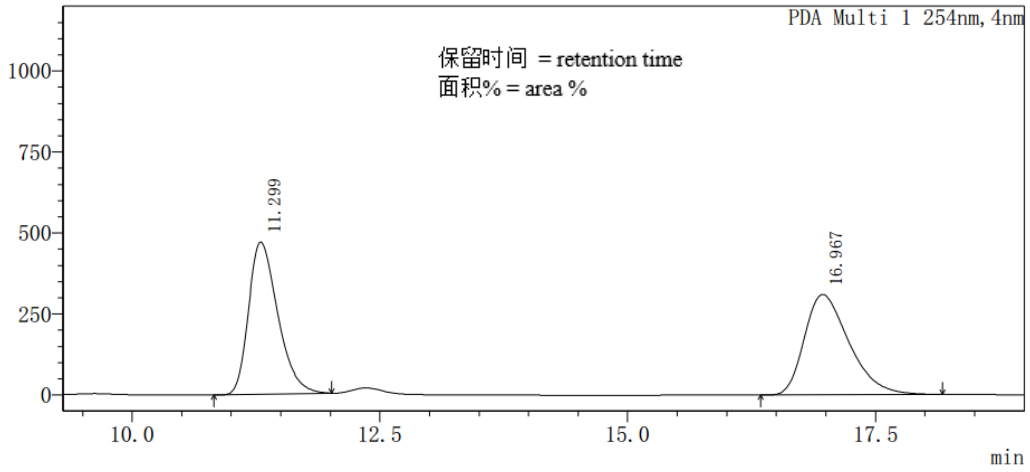
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.861	10874405	593557		99.820	99.677
2	19.748	35288	1068		0.180	0.323
总计		10909692	594625		100.000	100.000



2t

〈色谱图〉

mAU



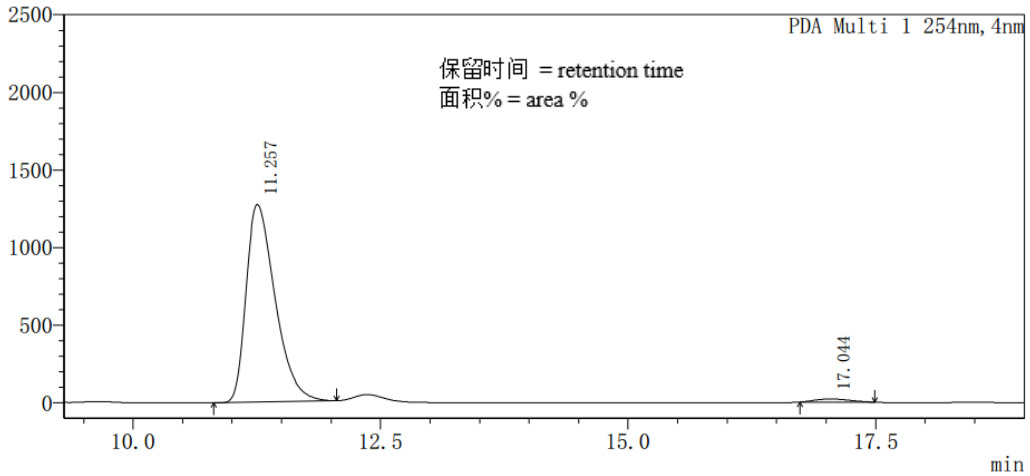
〈峰表〉

PDA Ch1 254nm

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〉

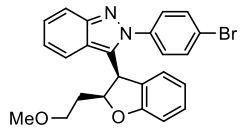
mAU



〈峰表〉

PDA Ch1 254nm

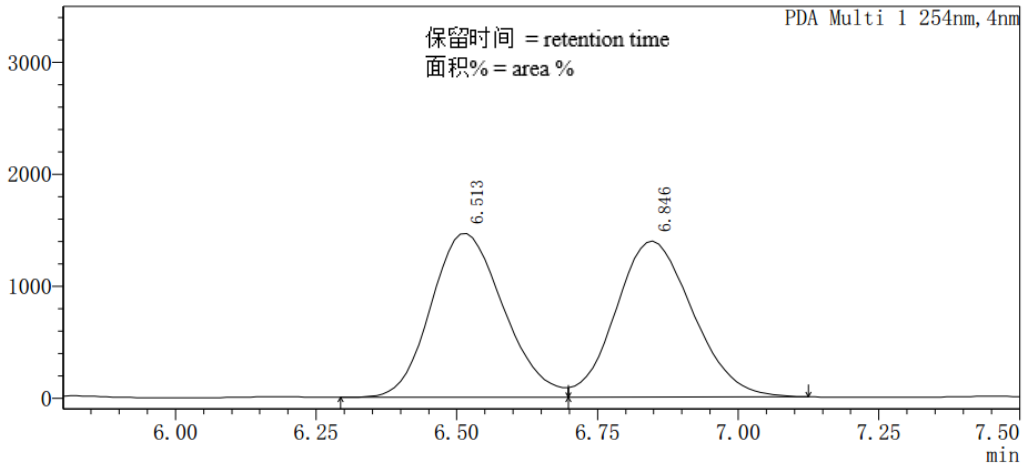
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	11.257	26049881	1273051		98.463	98.174
2	17.044	484518	19869		1.537	1.826
总计		26534400	1292920		100.000	100.000



2u

〈色谱图〉

mAU



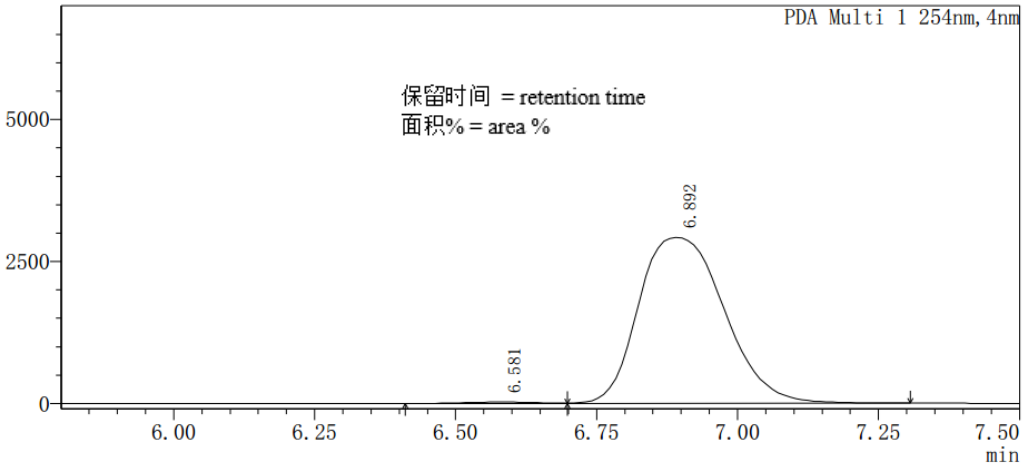
〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	6.513	13148989	1464044		51.248	49.905
2	6.846	13199202	1392746		48.752	50.095
总计		26348191	2856790		100.000	100.000

〈色谱图〉

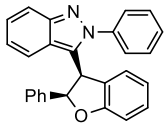
mAU



〈峰表〉

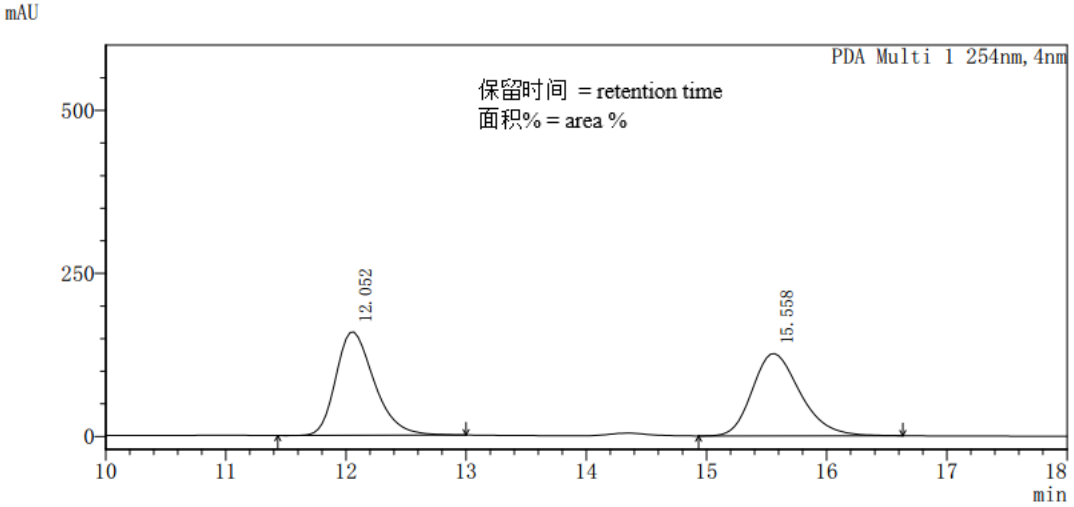
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	6.581	195480	24298		0.826	0.631
2	6.892	30785184	2917853		99.174	99.369
总计		30980664	2942151		100.000	100.000



2v

〈色谱图〉

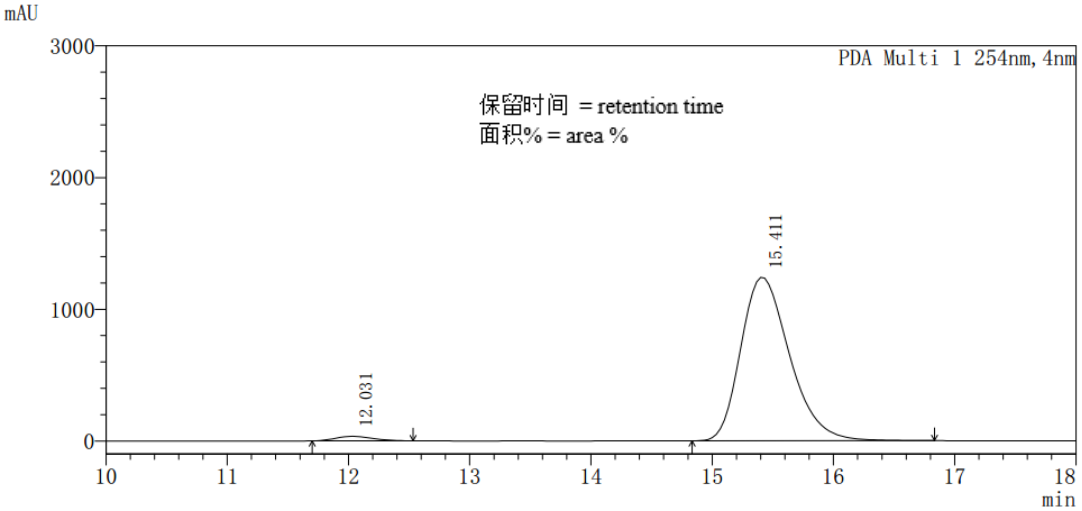


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	12.052	3536481	158466		55.654	50.269
2	15.558	3498684	126268		44.346	49.731
总计		7035165	284734		100.000	100.000

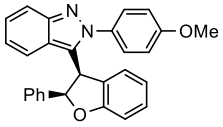
〈色谱图〉



〈峰表〉

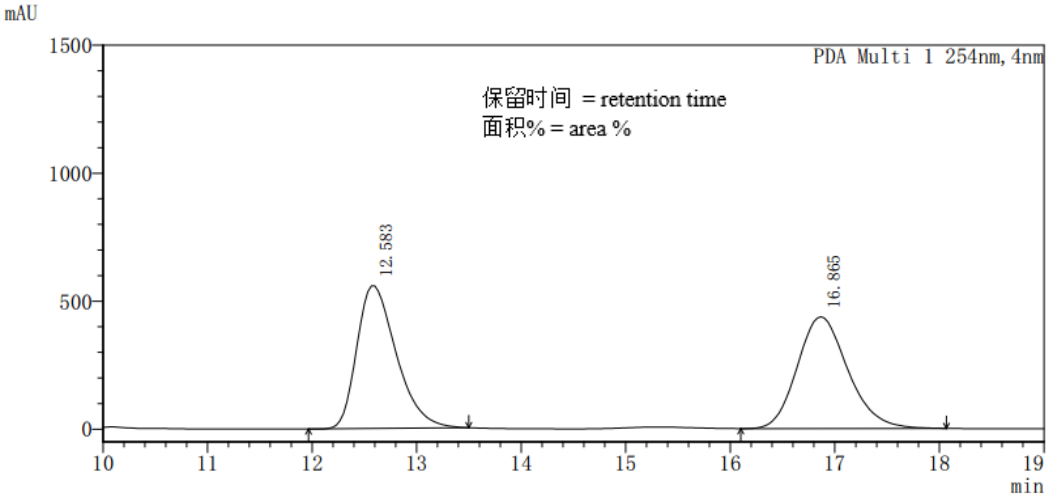
PDA Ch1 254nm

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



2w

〈色谱图〉

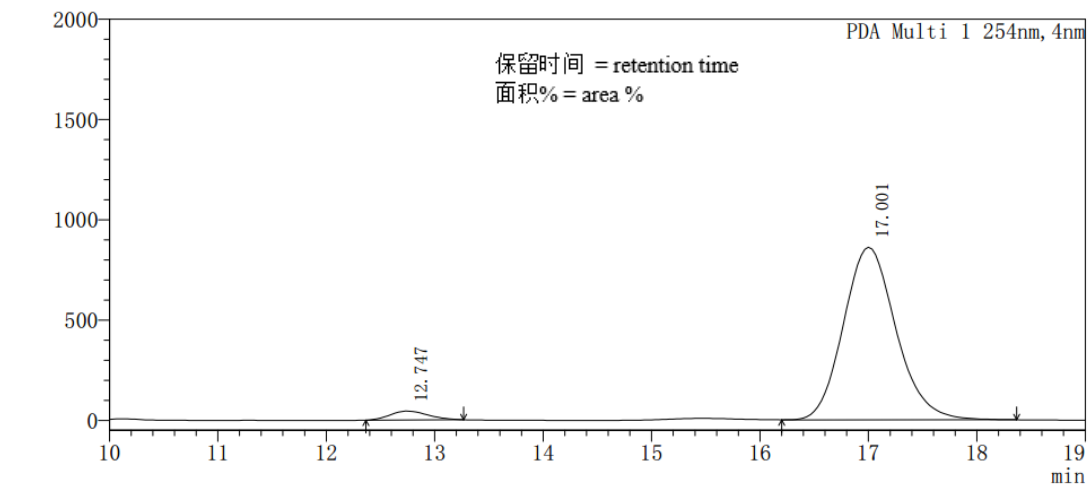


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	12.583	14652850	557456		56.056	49.931
2	16.865	14693231	437009		43.944	50.069
总计		29346082	994465		100.000	100.000

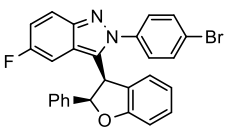
〈色谱图〉



〈峰表〉

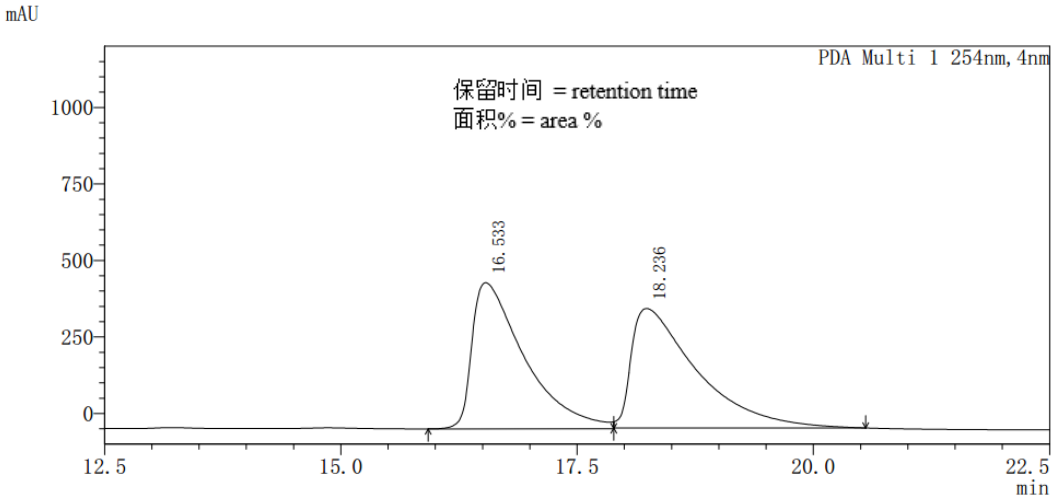
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	12.747	1064642	44030		4.864	3.543
2	17.001	28986600	861277		95.136	96.457
总计		30051242	905307		100.000	100.000



2x

〈色谱图〉

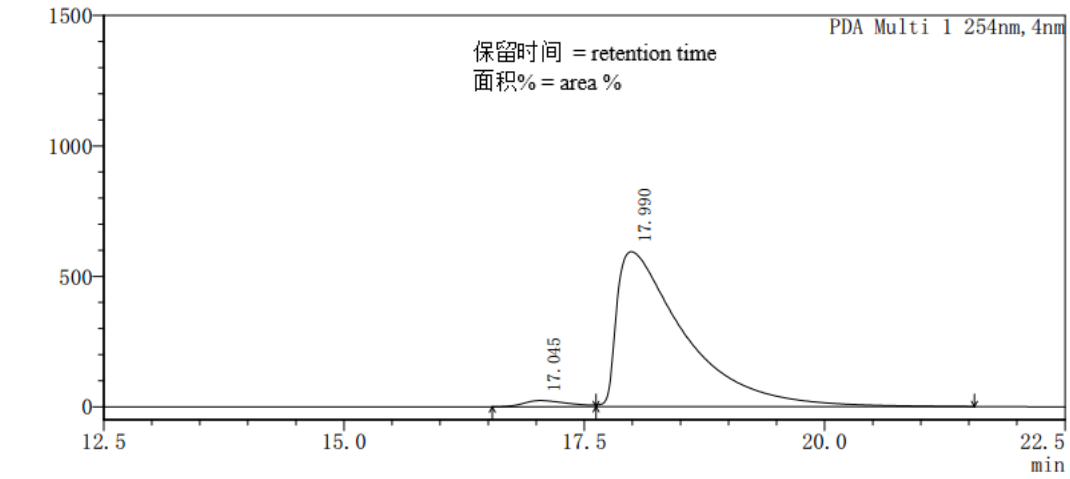


〈峰表〉

PDA Ch1 254nm

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

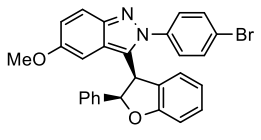
〈色谱图〉



〈峰表〉

PDA Ch1 254nm

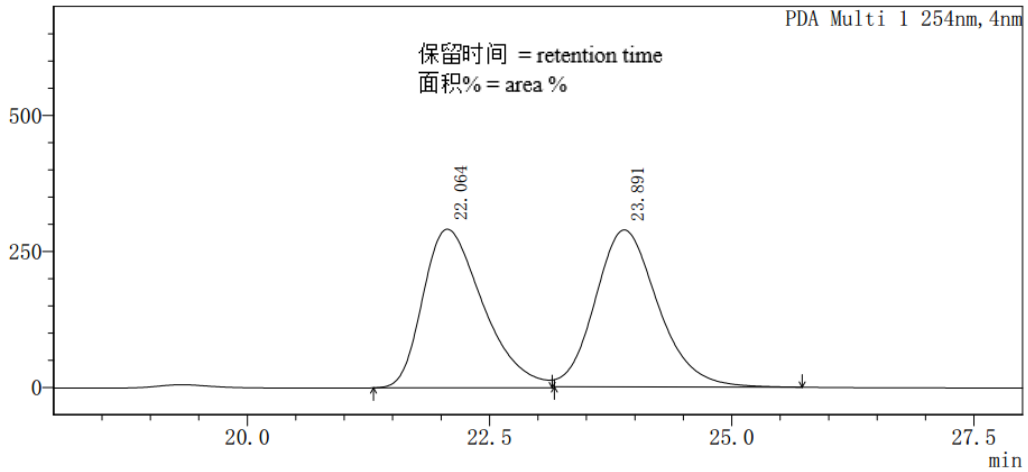
峰号	保留时间	高度	面积	化合物名	高度%	面积%
1	17.045	23804	781965		3.855	2.599
2	17.990	593711	29308018		96.145	97.401
总计		617514	30089982		100.000	100.000



2y

〈色谱图〉

mAU



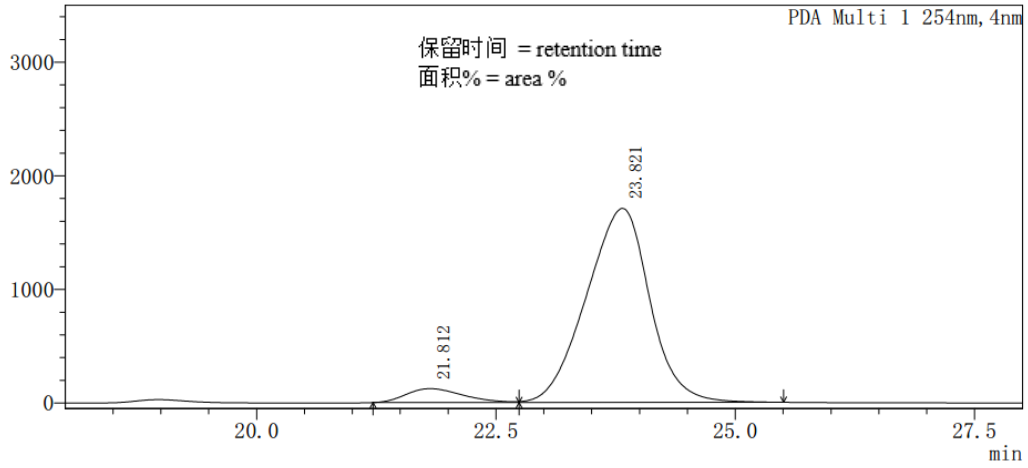
〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	22.064	12597757	291251		50.252	49.165
2	23.891	13025887	288332		49.748	50.835
总计		25623644	579583		100.000	100.000

〈色谱图〉

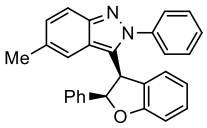
mAU



〈峰表〉

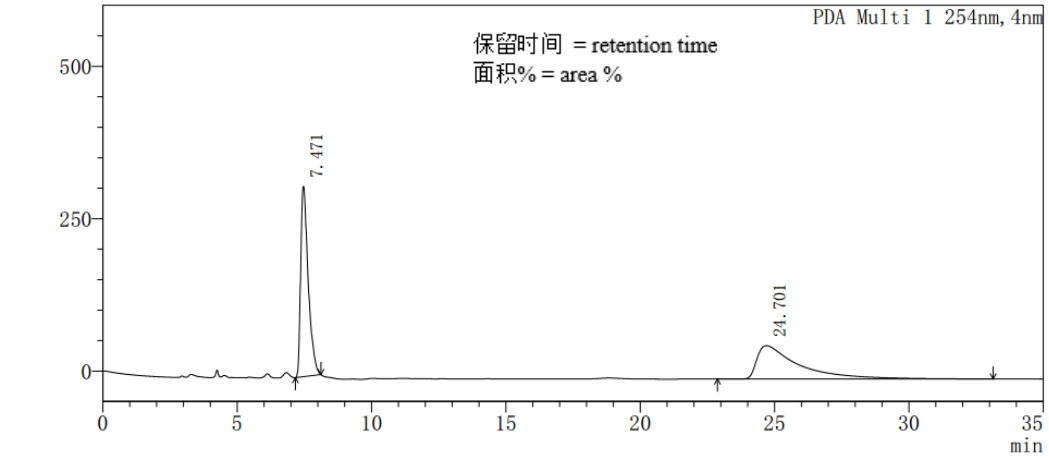
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	21.812	5077916	122744		6.702	6.058
2	23.821	78744892	1708814		93.298	93.942
总计		83822808	1831558		100.000	100.000



2z

〈色谱图〉

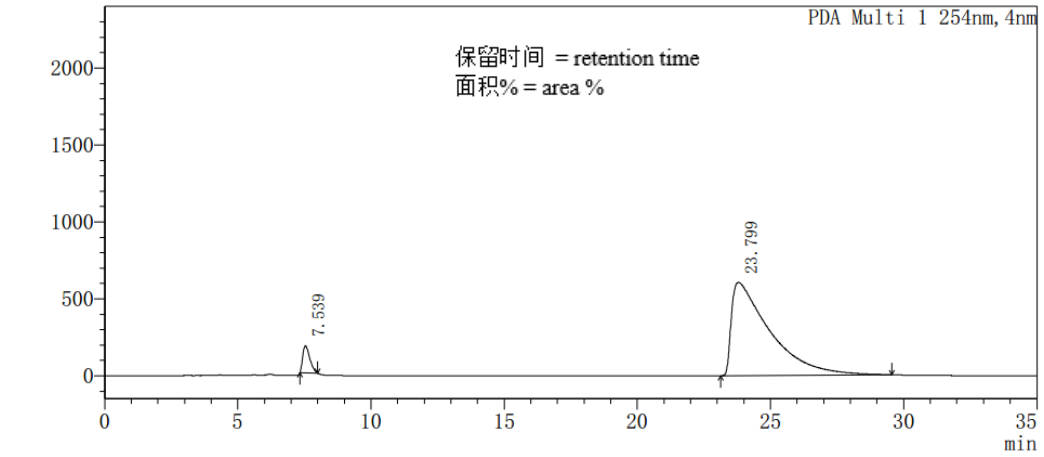


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.471	6072926	312419		85.086	50.570
2	24.701	5935995	54762		14.914	49.430
总计		12008920	367181		100.000	100.000

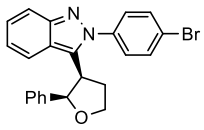
〈色谱图〉



〈峰表〉

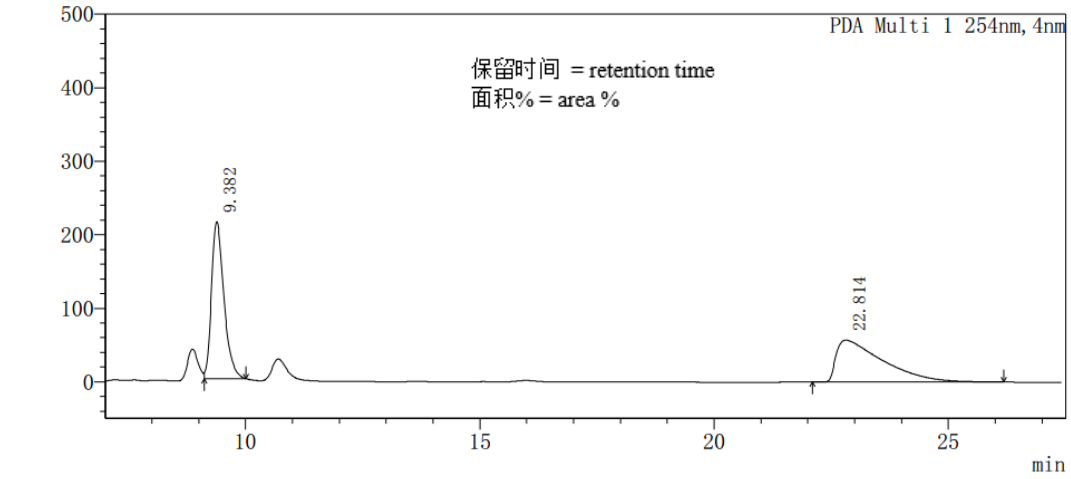
PDA Ch1 254nm

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		63991363	780525		100.000	100.000



2aa

〈色谱图〉

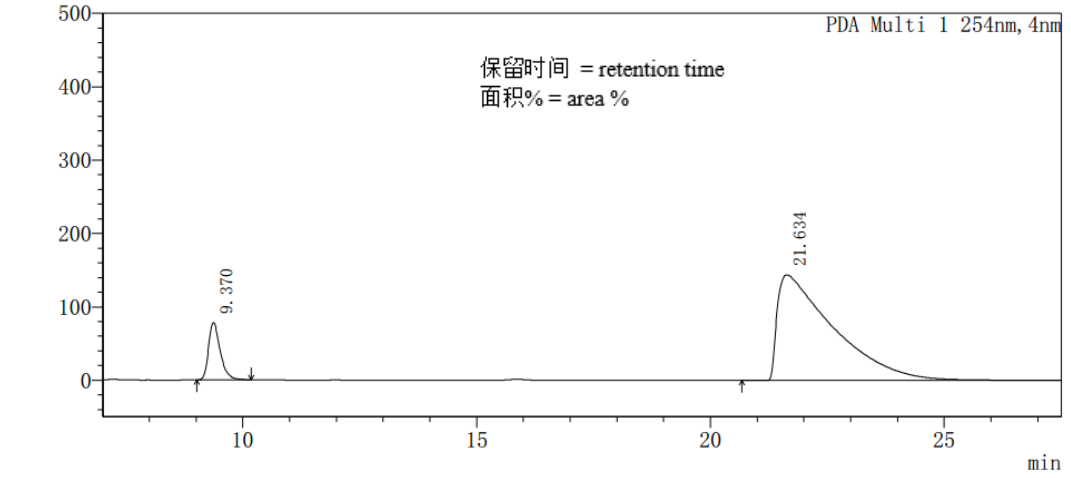


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	9.382	3957128	213849		78.981	50.100
2	22.814	3941378	56912		21.019	49.900
总计		7898506	270761		100.000	100.000

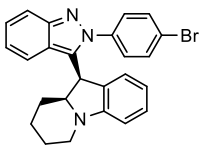
〈色谱图〉



〈峰表〉

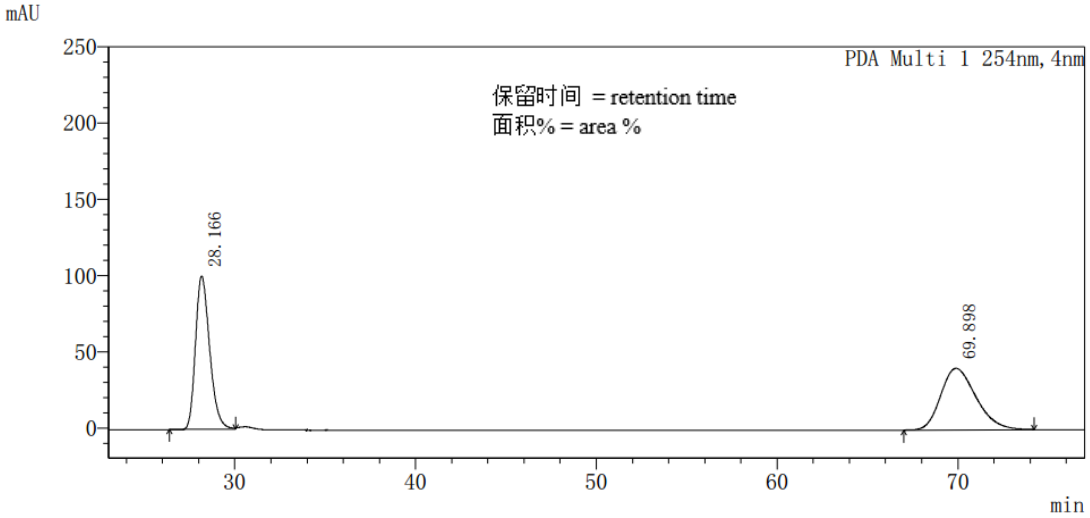
PDA Ch1 254nm

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

〈色谱图〉

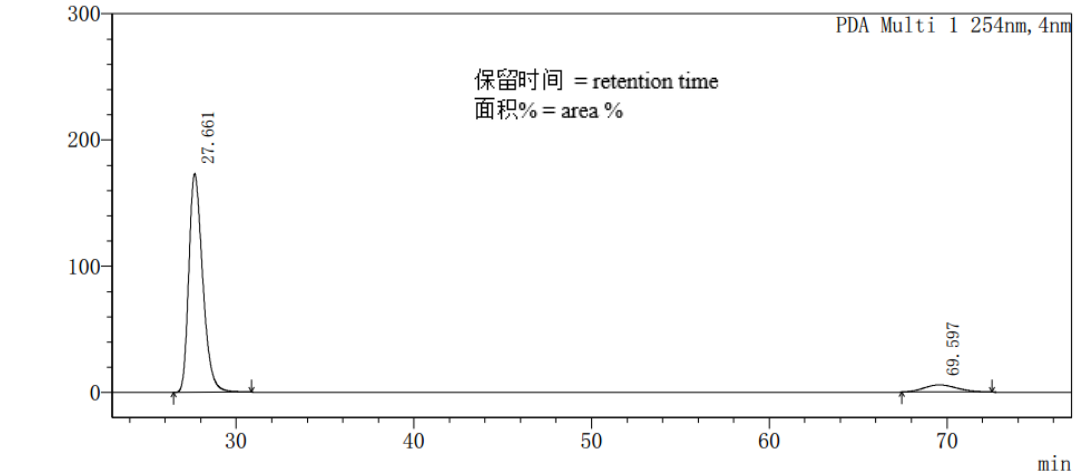


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	28.166	5475580	100702		71.372	49.984
2	69.898	5478986	40393		28.628	50.016
总计		10954566	141095		100.000	100.000

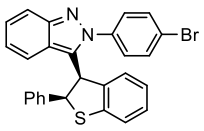
〈色谱图〉



〈峰表〉

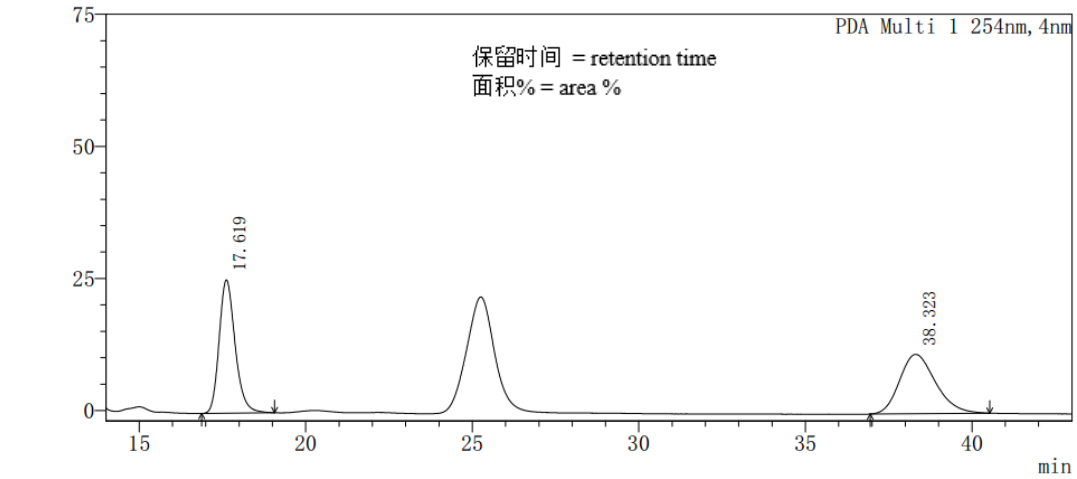
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	27.661	9434579	173235		96.814	92.733
2	69.597	739324	5700		3.186	7.267
总计		10173903	178935		100.000	100.000



2ac

〈色谱图〉

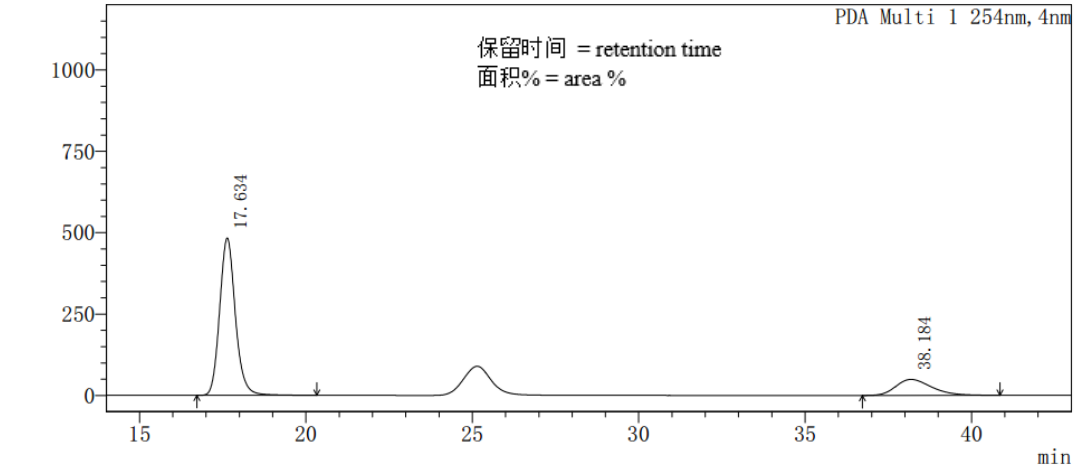


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	17.619	844592	25264		69.228	50.118
2	38.323	840604	11230		30.772	49.882
总计		1685196	36494		100.000	100.000

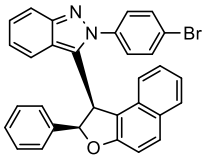
〈色谱图〉



〈峰表〉

PDA Ch1 254nm

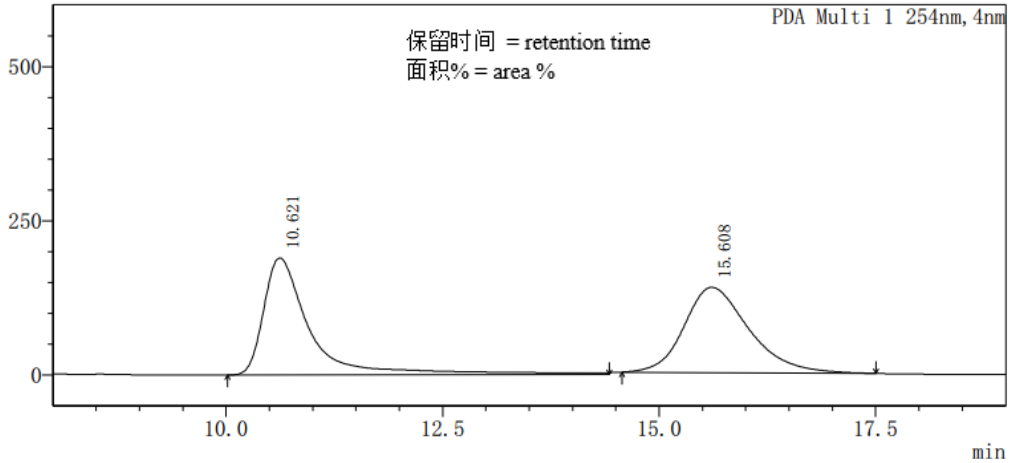
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	17.634	15870465	483579		90.788	81.206
2	38.184	3672968	49069		9.212	18.794
总计		19543432	532648		100.000	100.000



4a

〈色谱图〉

mAU



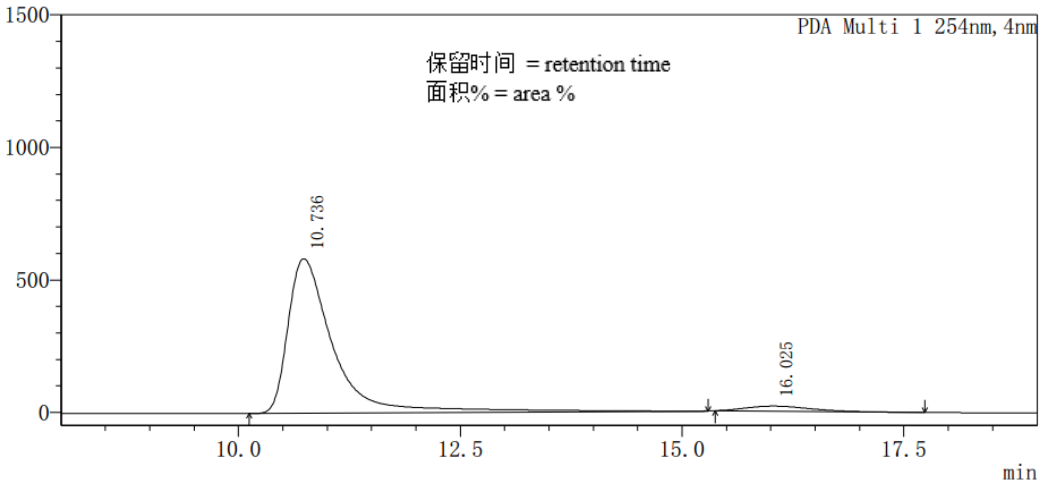
〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.621	7208166	189535		57.824	49.956
2	15.608	7220831	138243		42.176	50.044
总计		14428997	327778		100.000	100.000

〈色谱图〉

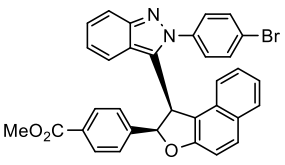
mAU



〈峰表〉

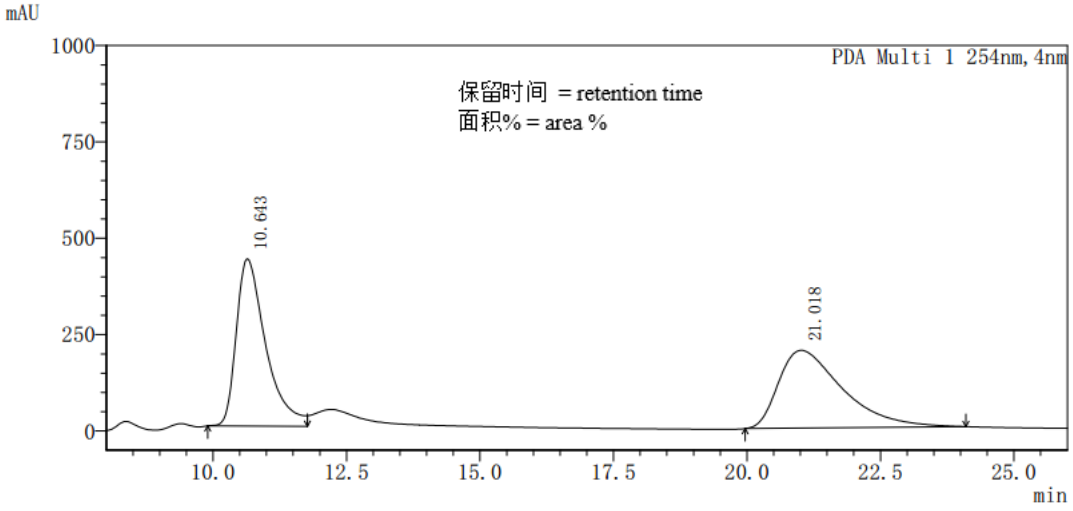
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.736	21158178	583360		96.809	95.610
2	16.025	971410	19231		3.191	4.390
总计		22129588	602591		100.000	100.000



4b

〈色谱图〉

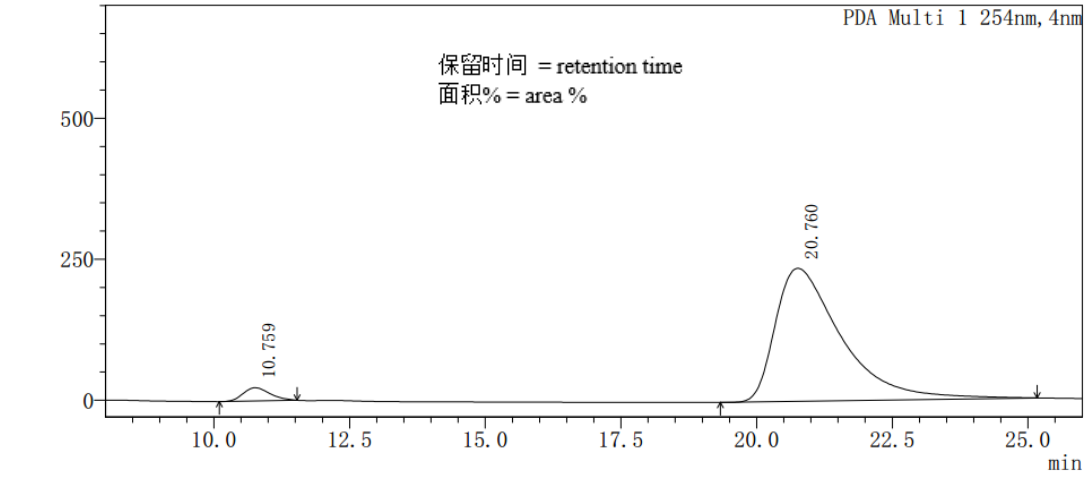


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.643	16657792	433969		68.254	49.757
2	21.018	16820642	201850		31.746	50.243
总计		33478434	635819		100.000	100.000

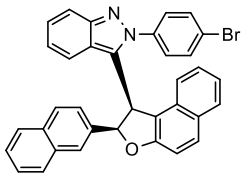
〈色谱图〉



〈峰表〉

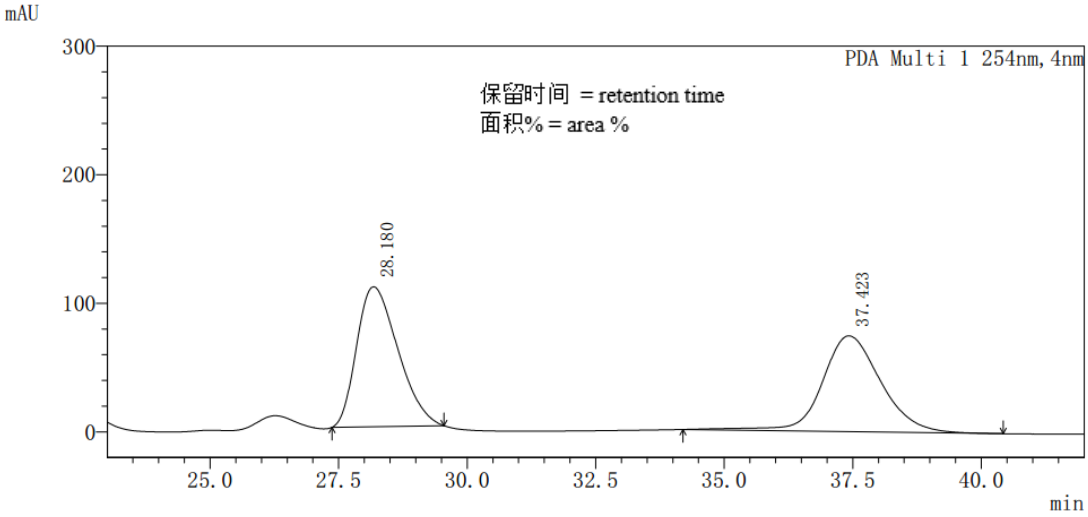
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.759	817262	23567		9.079	3.928
2	20.760	19990281	236004		90.921	96.072
总计		20807543	259571		100.000	100.000



4c

〈色谱图〉

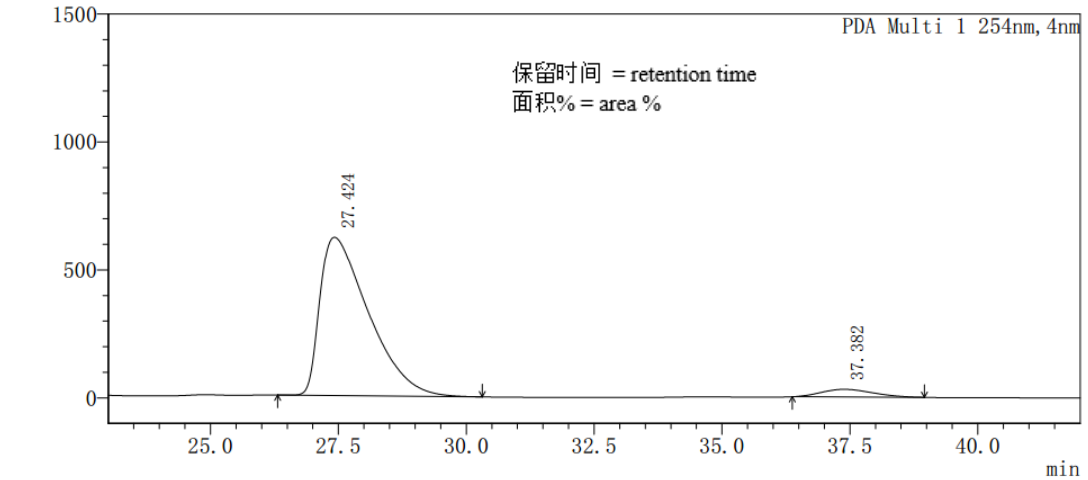


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	28.180	6076728	108799		59.339	50.682
2	37.423	5913241	74553		40.661	49.318
总计		11989969	183352		100.000	100.000

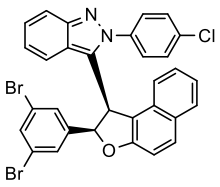
〈色谱图〉



〈峰表〉

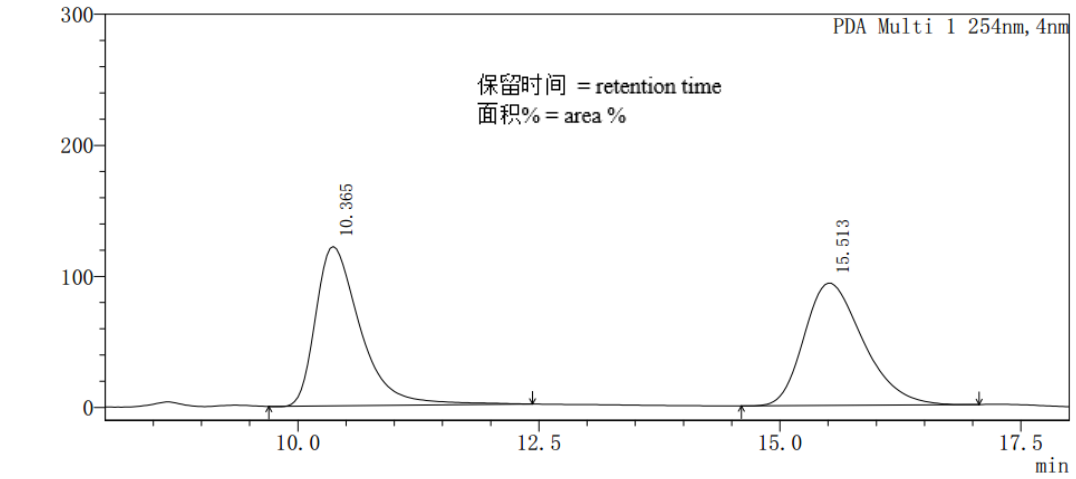
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	27.424	40950208	618287		95.386	95.138
2	37.382	2092658	29910		4.614	4.862
总计		43042866	648197		100.000	100.000



4d

〈色谱图〉

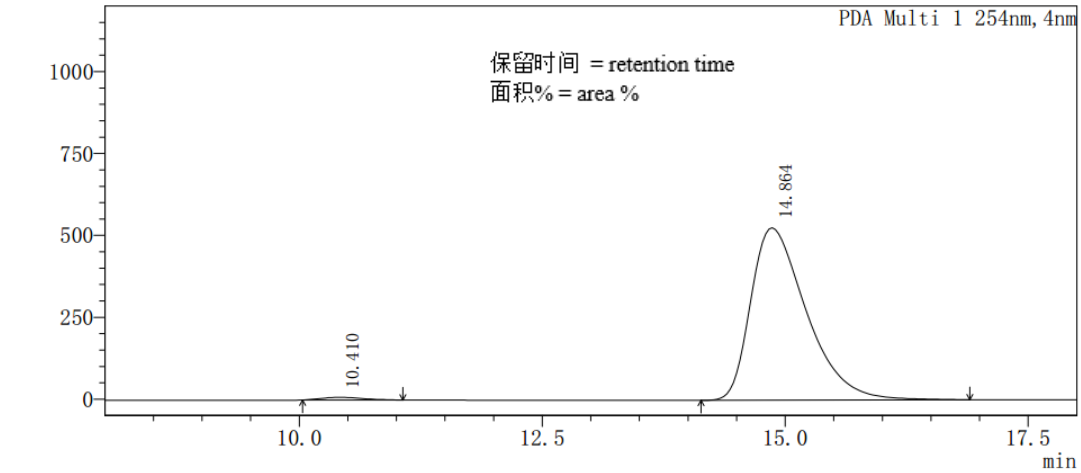


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.365	3933267	121763		56.596	49.749
2	15.513	3972880	93381		43.404	50.251
总计		7906146	215144		100.000	100.000

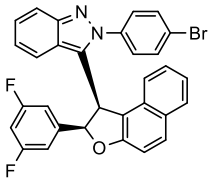
〈色谱图〉



〈峰表〉

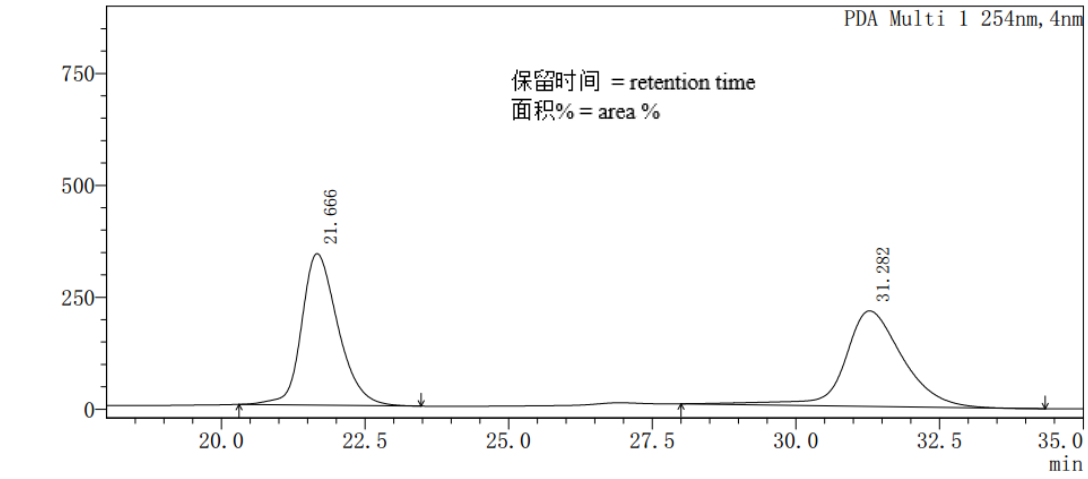
PDA Ch1 254nm

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	21011195	526074		98.443	98.870
总计		21251325	534397		100.000	100.000



4e

〈色谱图〉

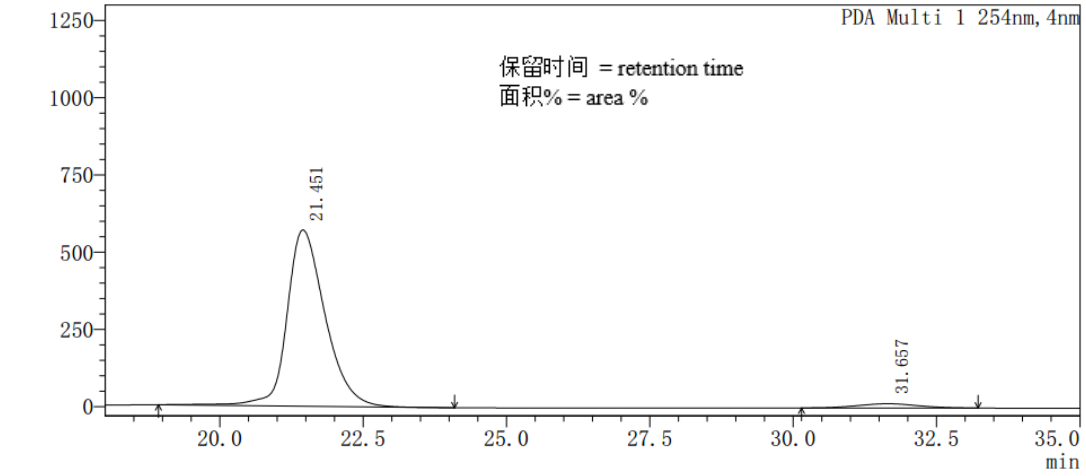


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	21.666	14950081	338484		61.348	50.033
2	31.282	14930244	213263		38.652	49.967
总计		29880325	551747		100.000	100.000

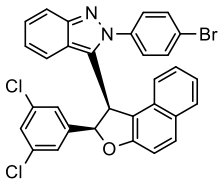
〈色谱图〉



〈峰表〉

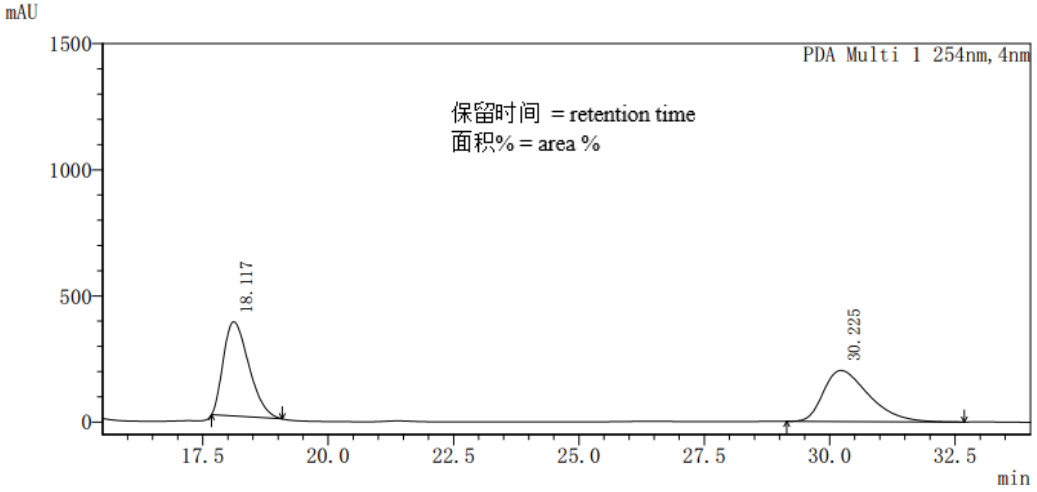
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	21.451	26418935	570575		97.628	96.298
2	31.657	1015678	13861		2.372	3.702
总计		27434613	584436		100.000	100.000



4f

〈色谱图〉

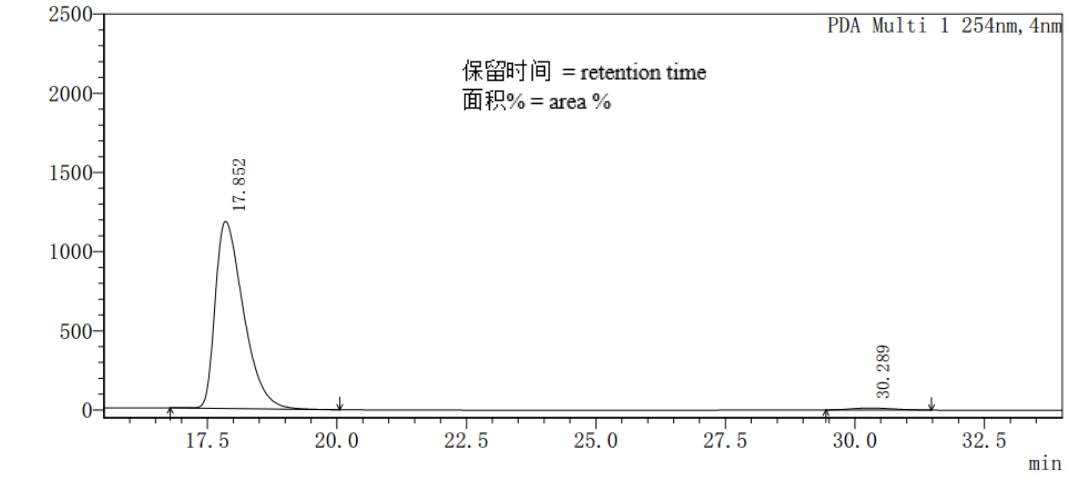


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	18.117	13228608	373370		64.801	50.916
2	30.225	12752552	202807		35.199	49.084
总计		25981159	576177		100.000	100.000

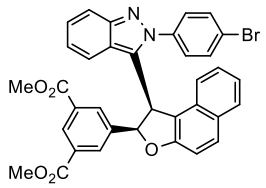
〈色谱图〉



〈峰表〉

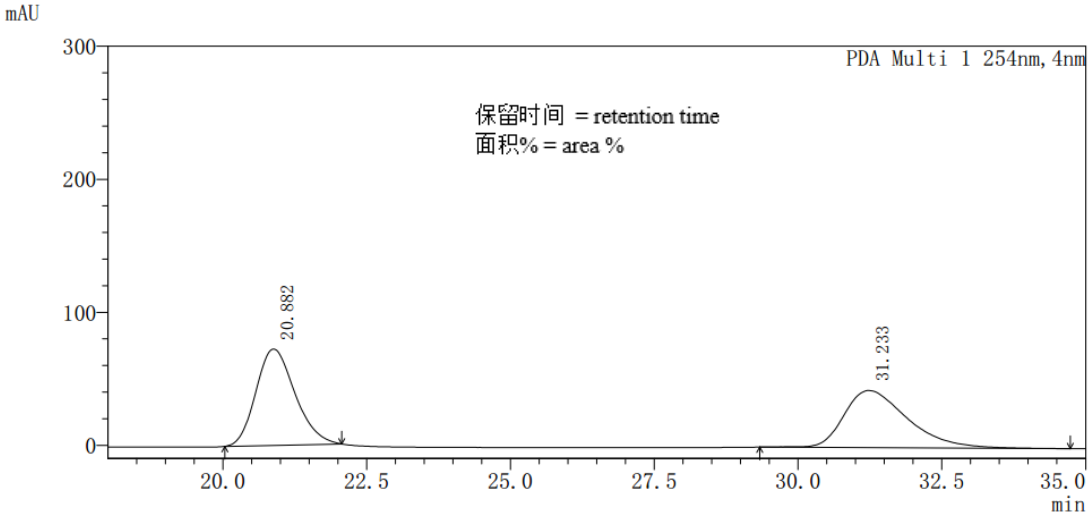
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	17.852	44791209	1181162		98.965	98.461
2	30.289	700292	12349		1.035	1.539
总计		45491501	1193511		100.000	100.000



4g

〈色谱图〉

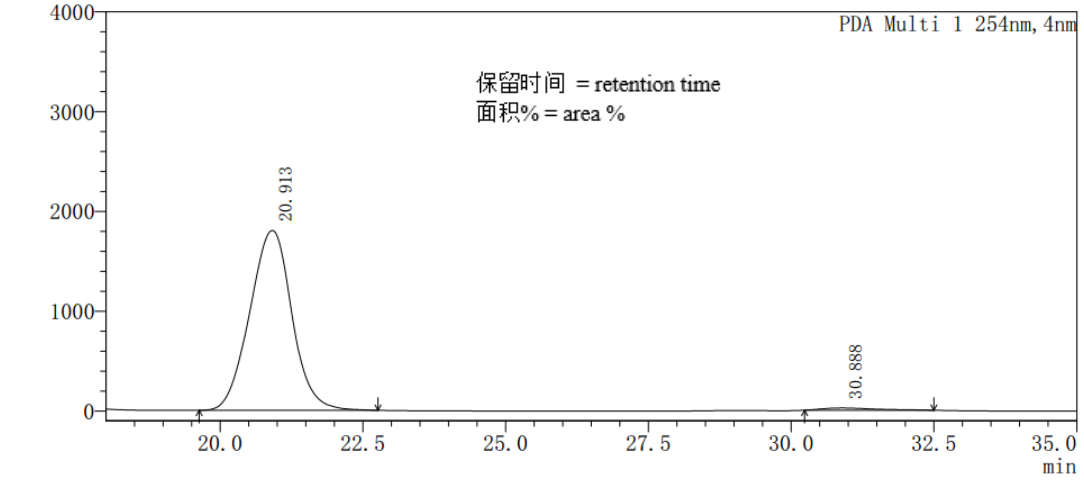


〈峰表〉

PDA Ch1 254nm

峰号	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

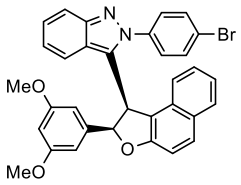
〈色谱图〉



〈峰表〉

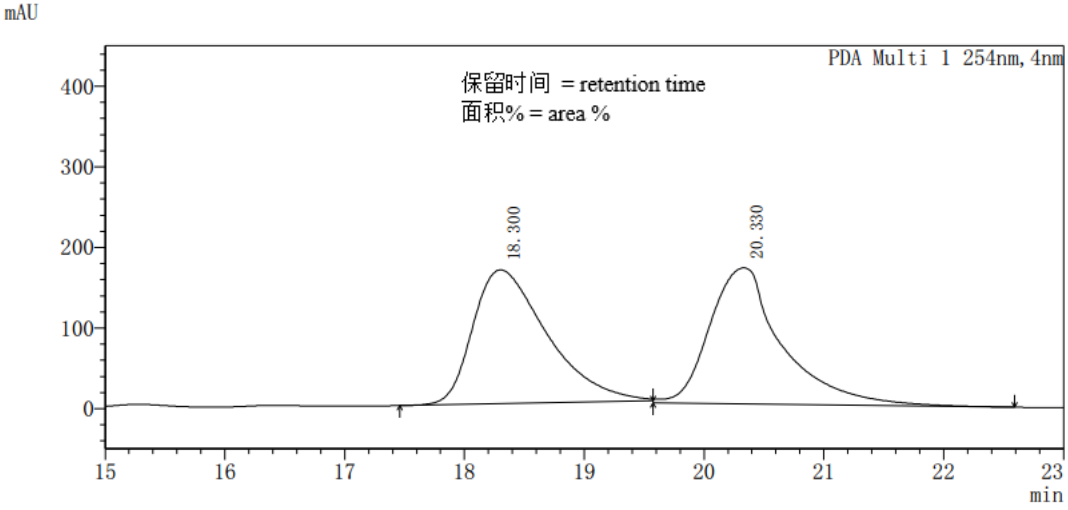
PDA Ch1 254nm

峰号	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



4h

〈色谱图〉

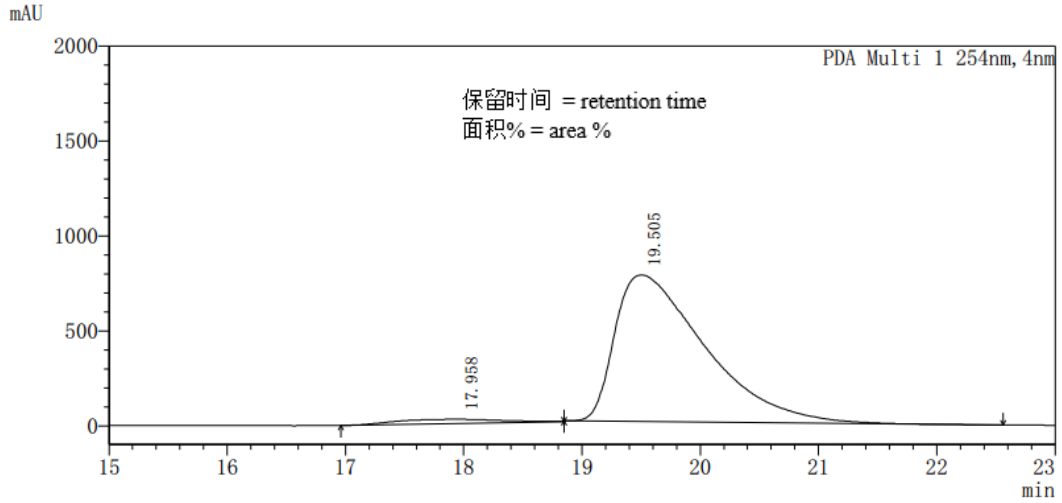


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	18.300	7136968	165786		49.574	50.121
2	20.330	7102574	168633		50.426	49.879
总计		14239542	334419		100.000	100.000

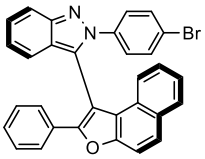
〈色谱图〉



〈峰表〉

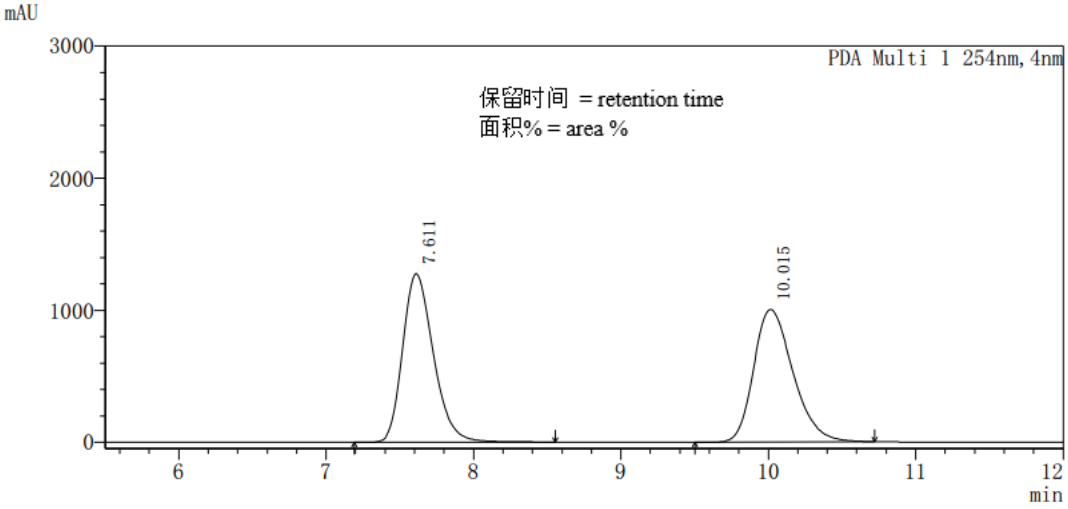
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	17.958	1570269	22901		2.876	3.682
2	19.505	41077592	773442		97.124	96.318
总计		42647862	796343		100.000	100.000



5a

〈色谱图〉

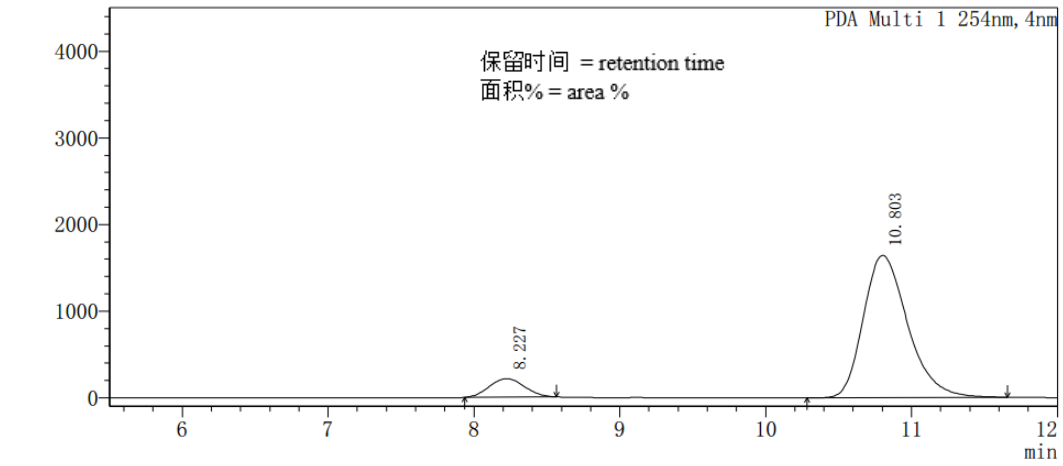


〈峰表〉

PDA Ch1 254nm

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

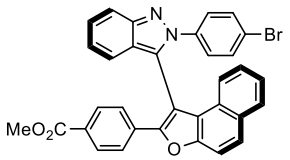
〈色谱图〉



〈峰表〉

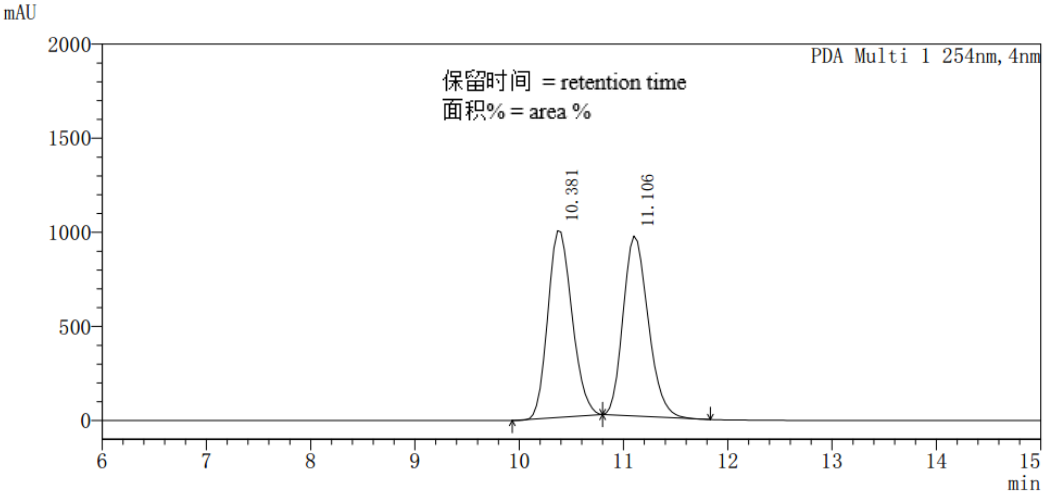
PDA Ch1 254nm

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		38255871	1854504		100.000	100.000



5b

〈色谱图〉

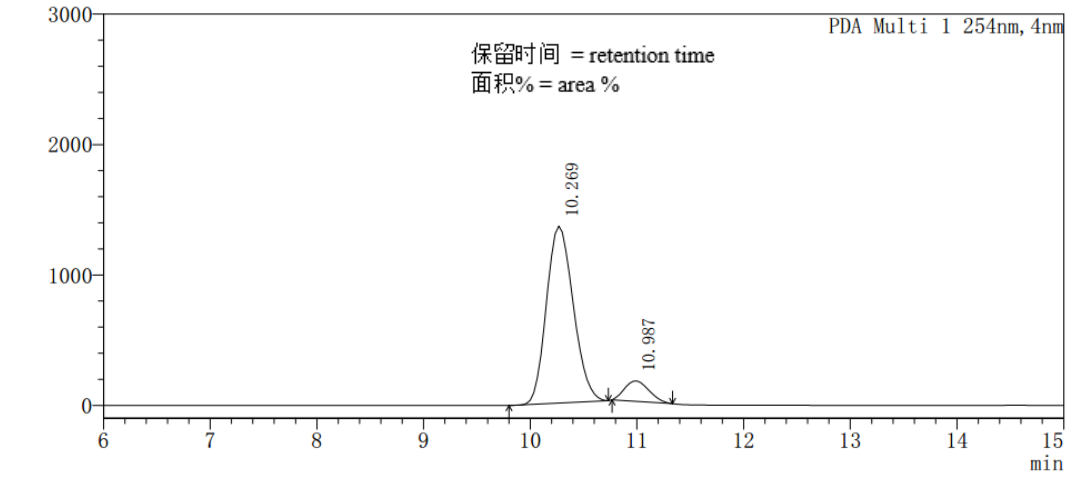


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.381	16047241	992676		50.907	50.098
2	11.106	15984535	957311		49.093	49.902
总计		32031776	1949987		100.000	100.000

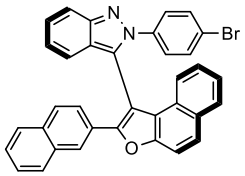
〈色谱图〉



〈峰表〉

PDA Ch1 254nm

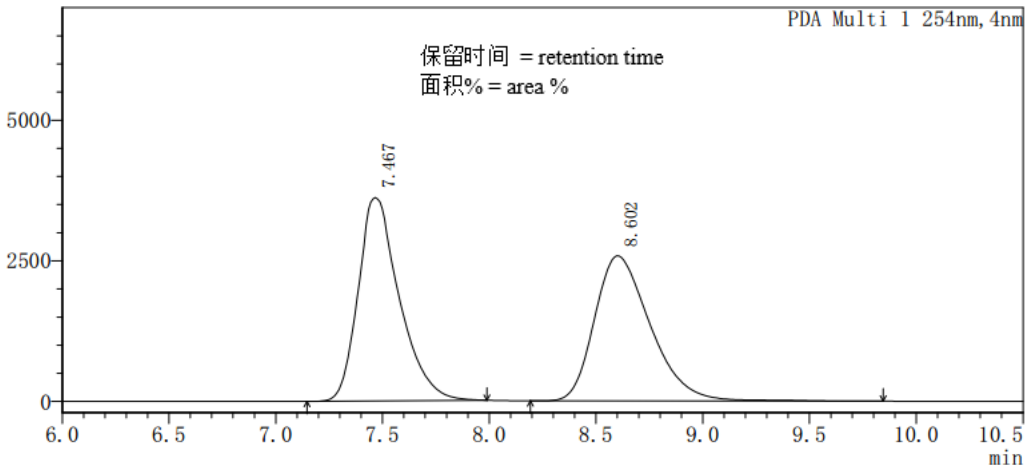
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	10.269	23685629	1357457		89.666	90.558
2	10.987	2469682	156454		10.334	9.442
总计		26155311	1513911		100.000	100.000



5c

<色谱图>

mAU



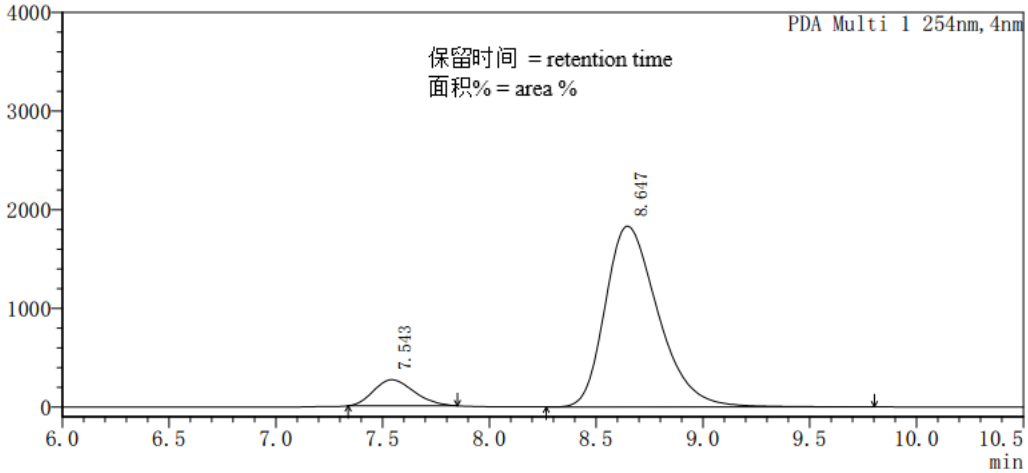
<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.467	48445377	3615229		58.361	50.752
2	8.602	47010325	2579389		41.639	49.248
总计		95455701	6194618		100.000	100.000

<色谱图>

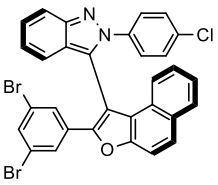
mAU



<峰表>

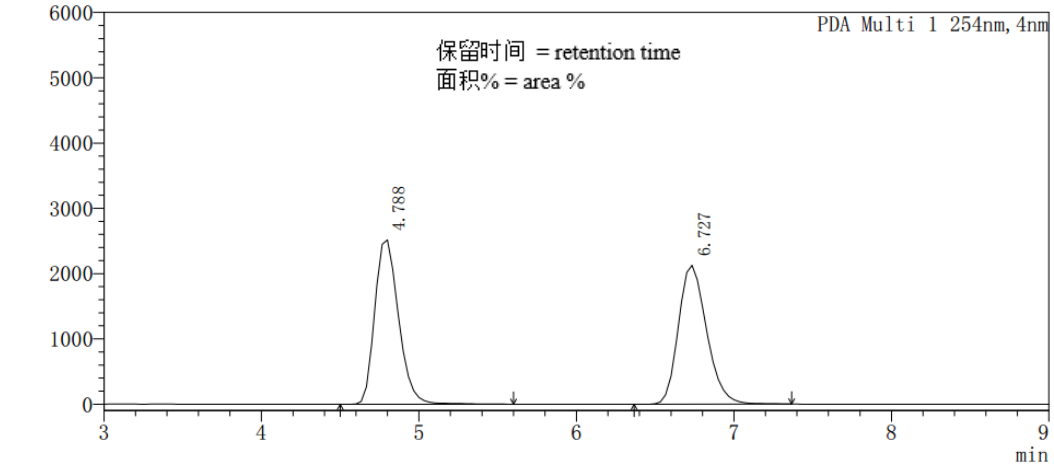
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.543	3484751	265274		12.634	9.921
2	8.647	31639172	1834483		87.366	90.079
总计		35123923	2099757		100.000	100.000



5d

〈色谱图〉

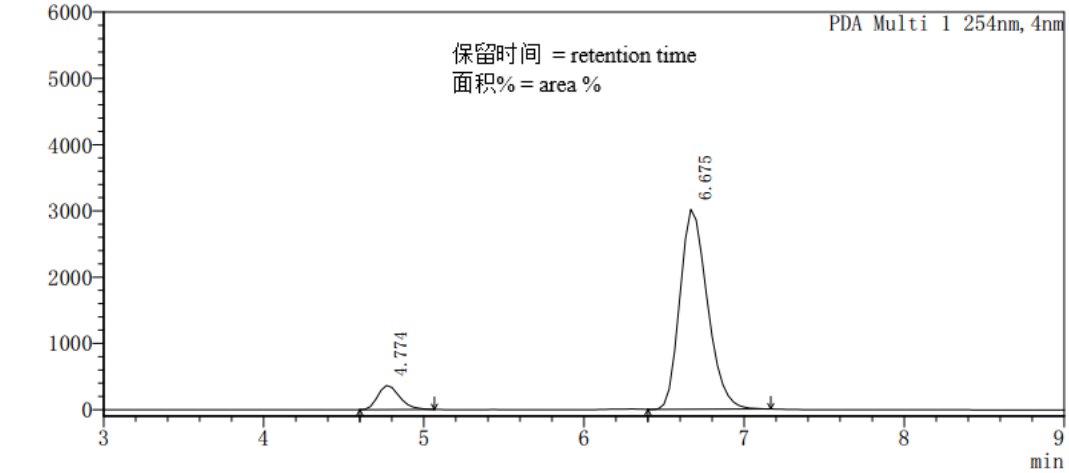


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.788	26481087	2517354		54.218	49.931
2	6.727	26554014	2125651		45.782	50.069
总计		53035101	4643005		100.000	100.000

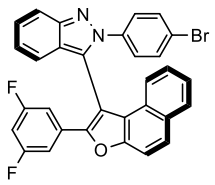
〈色谱图〉



〈峰表〉

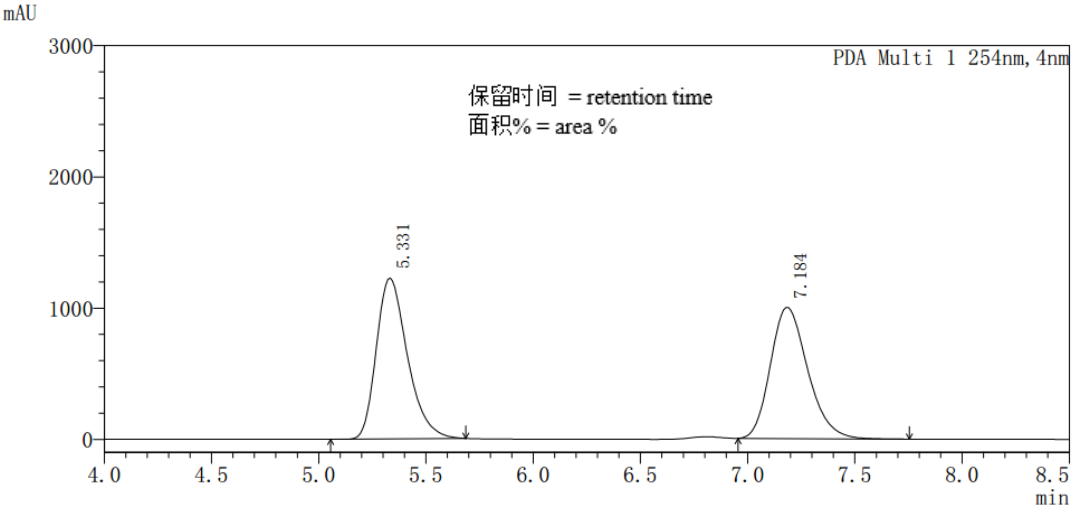
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.774	3462117	365354		10.801	8.761
2	6.675	36054457	3017248		89.199	91.239
总计		39516573	3382602		100.000	100.000



5e

〈色谱图〉

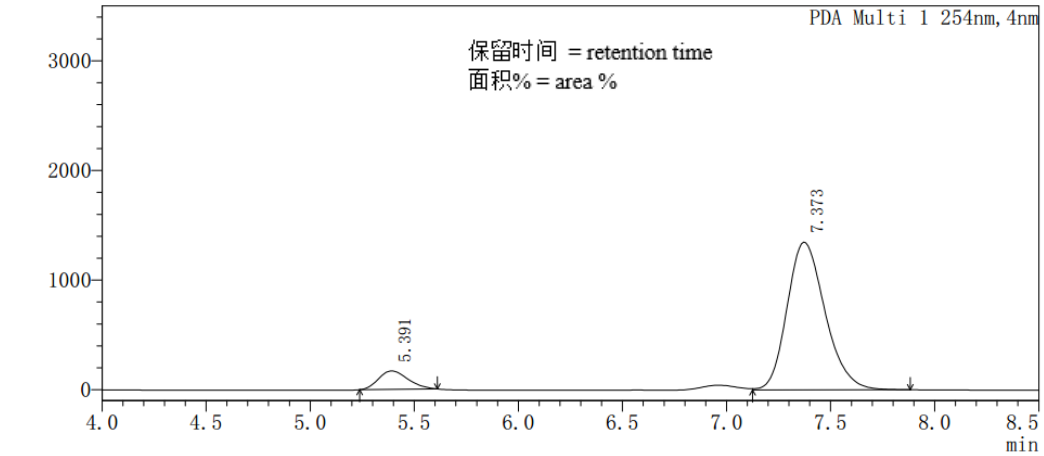


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	5.331	12336824	1226888		55.126	50.486
2	7.184	12099544	998716		44.874	49.514
总计		24436367	2225604		100.000	100.000

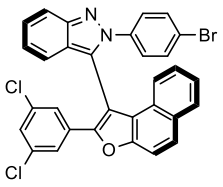
〈色谱图〉



〈峰表〉

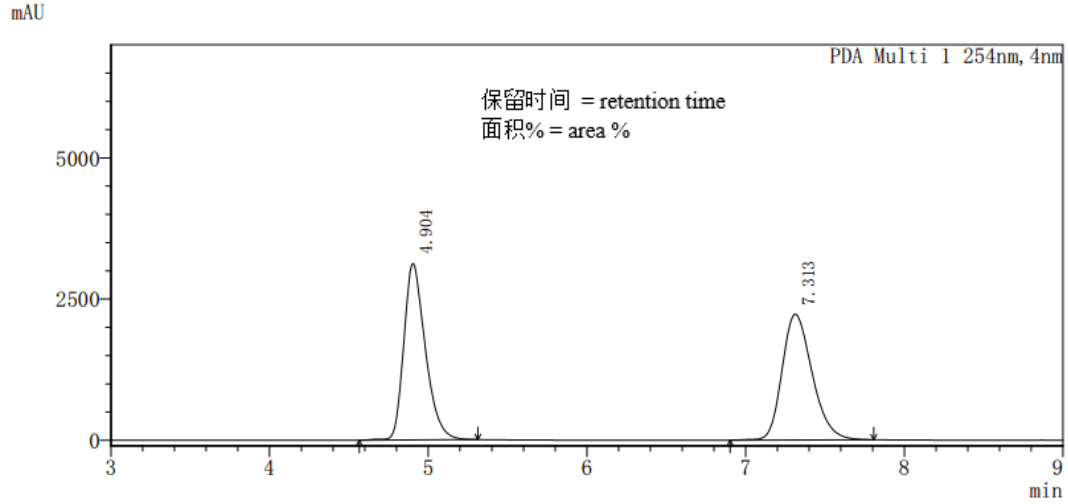
PDA Ch1 254nm

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



5f

〈色谱图〉

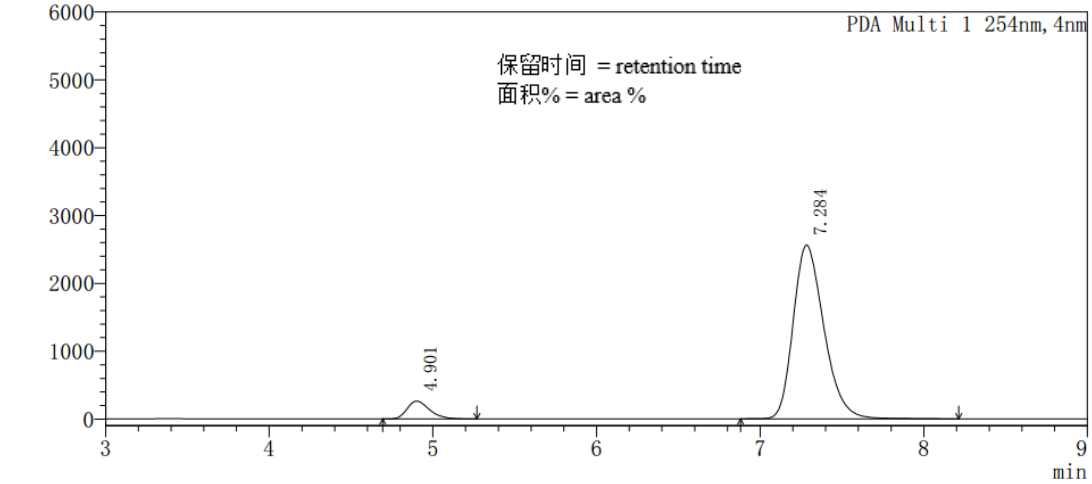


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.904	29483994	3126687		58.422	50.116
2	7.313	29347914	2225231		41.578	49.884
总计		58831908	5351919		100.000	100.000

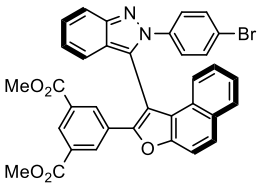
〈色谱图〉



〈峰表〉

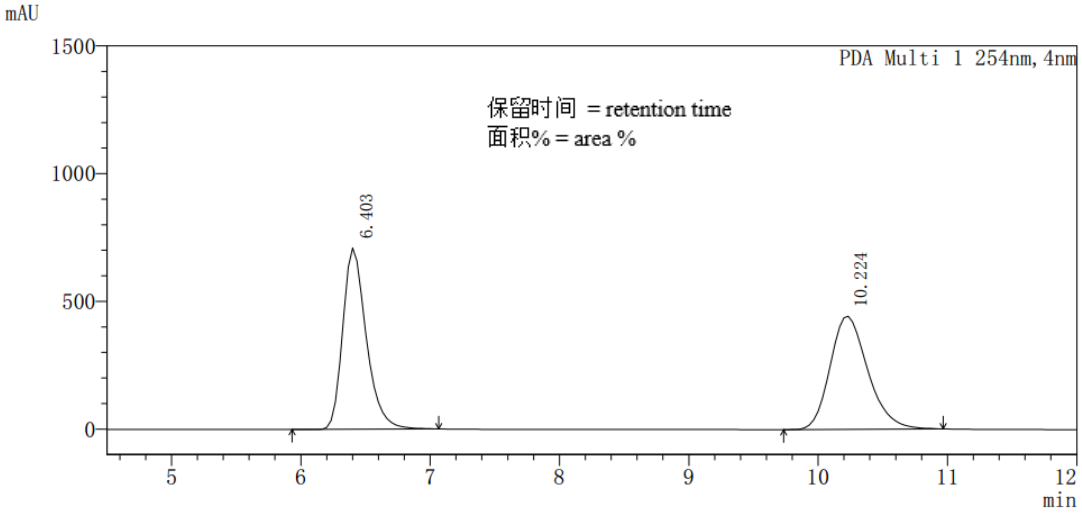
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.901	2500654	262525		9.283	6.940
2	7.284	33533654	2565514		90.717	93.060
总计		36034308	2828039		100.000	100.000



5g

〈色谱图〉

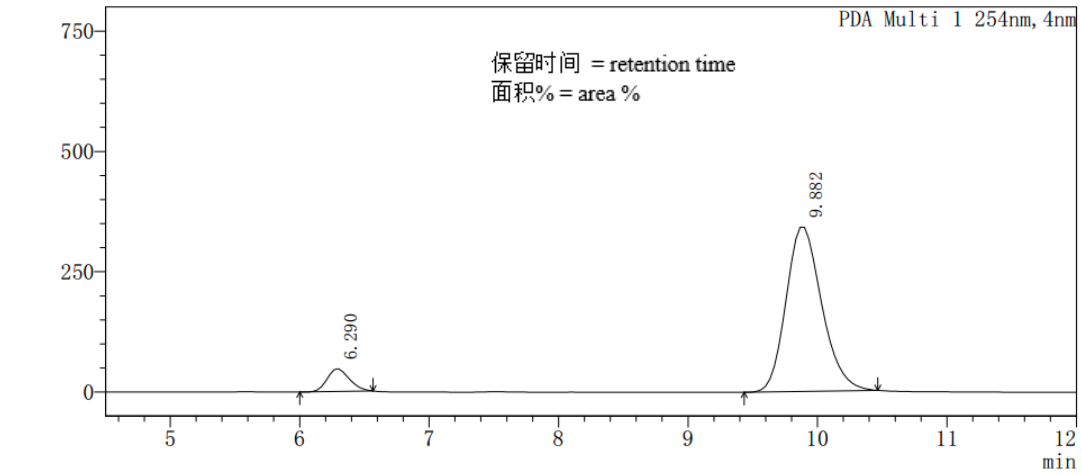


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	6.403	8974598	709167		61.549	49.993
2	10.224	8977140	443031		38.451	50.007
总计		17951737	1152197		100.000	100.000

〈色谱图〉



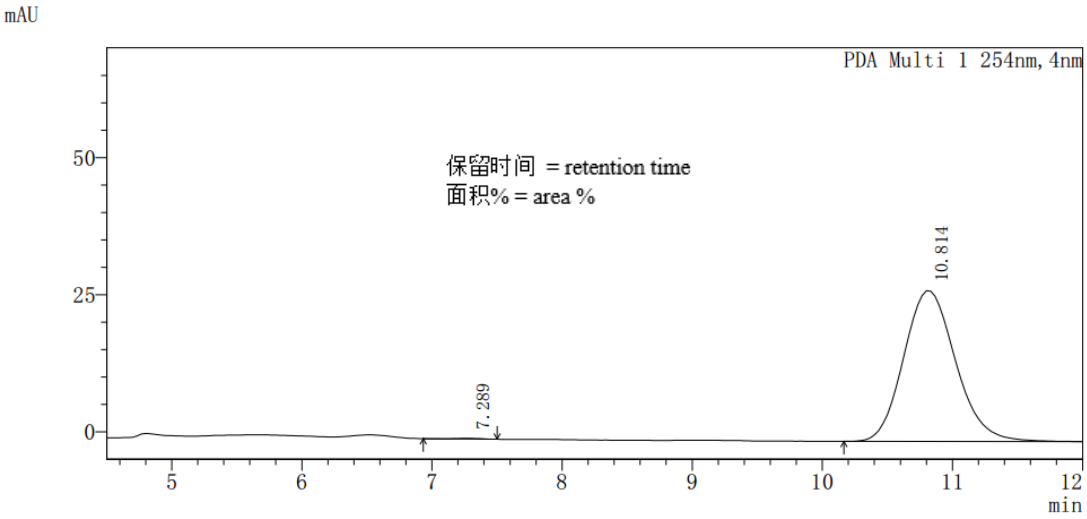
〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	6.290	566092	47206		12.139	7.927
2	9.882	6575143	341676		87.861	92.073
总计		7141235	388882		100.000	100.000

HPLC data of 5g after recrystallization.

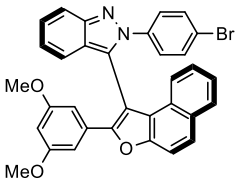
〈色谱图〉



〈峰表〉

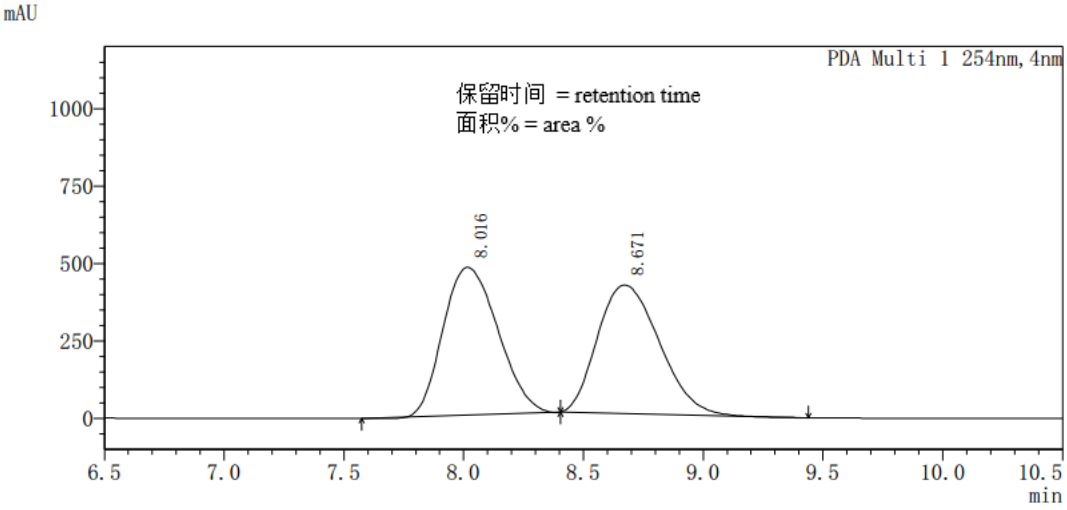
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.289	1400	135		0.490	0.183
2	10.814	764385	27483		99.510	99.817
总计		765785	27618		100.000	100.000



5h

〈色谱图〉

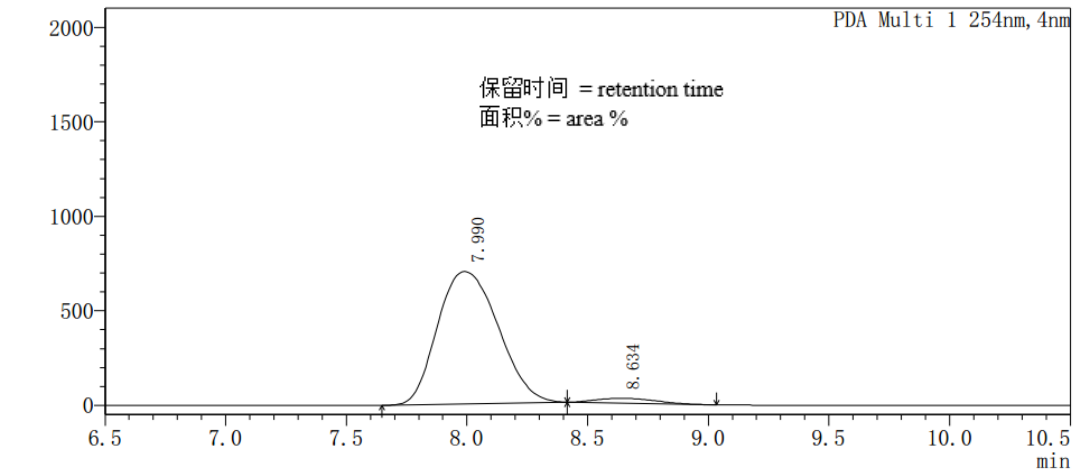


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	8.016	7568666	475511		53.440	50.436
2	8.671	7437942	414291		46.560	49.564
总计		15006609	889802		100.000	100.000

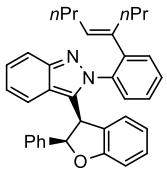
〈色谱图〉



〈峰表〉

PDA Ch1 254nm

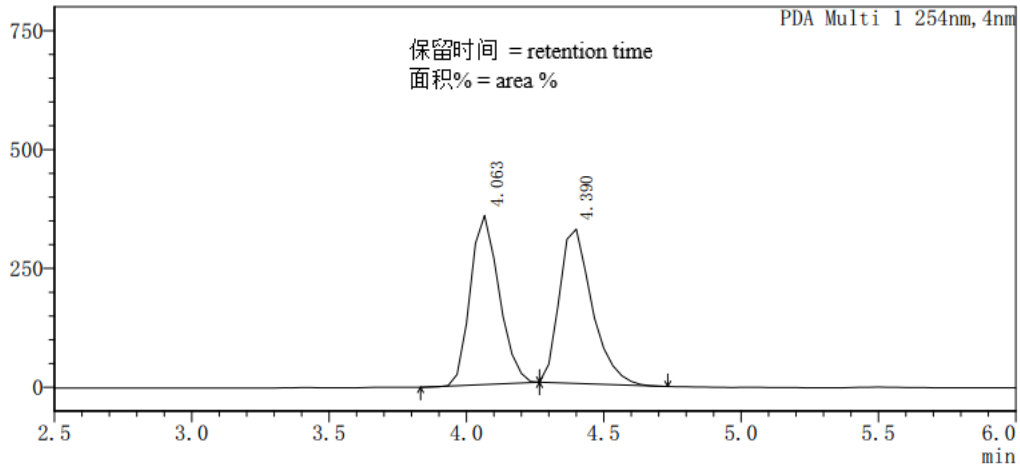
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.990	12271329	700664		96.527	96.600
2	8.634	431944	25207		3.473	3.400
总计		12703273	725871		100.000	100.000



6a

〈色谱图〉

mAU



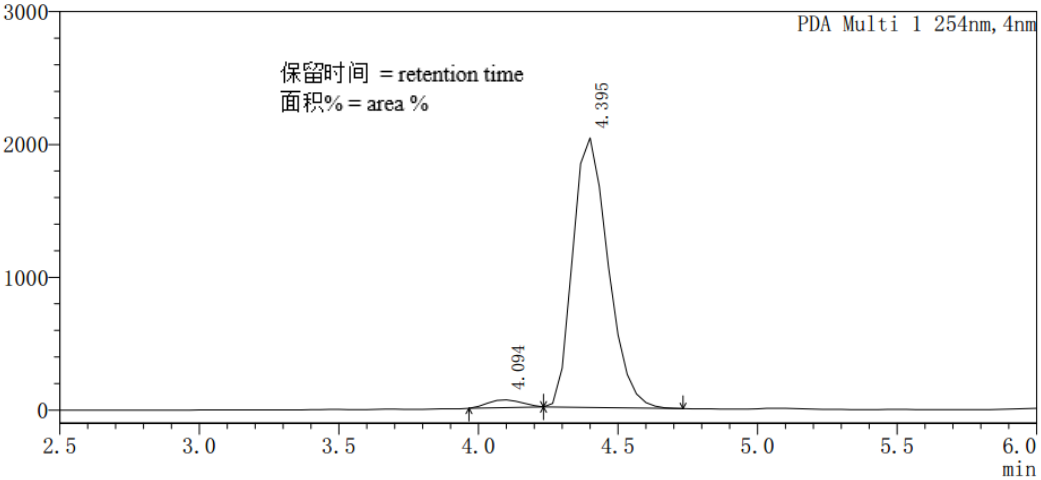
〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.063	2605209	355518		52.296	49.217
2	4.390	2688077	324296		47.704	50.783
总计		5293286	679814		100.000	100.000

〈色谱图〉

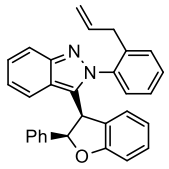
mAU



〈峰表〉

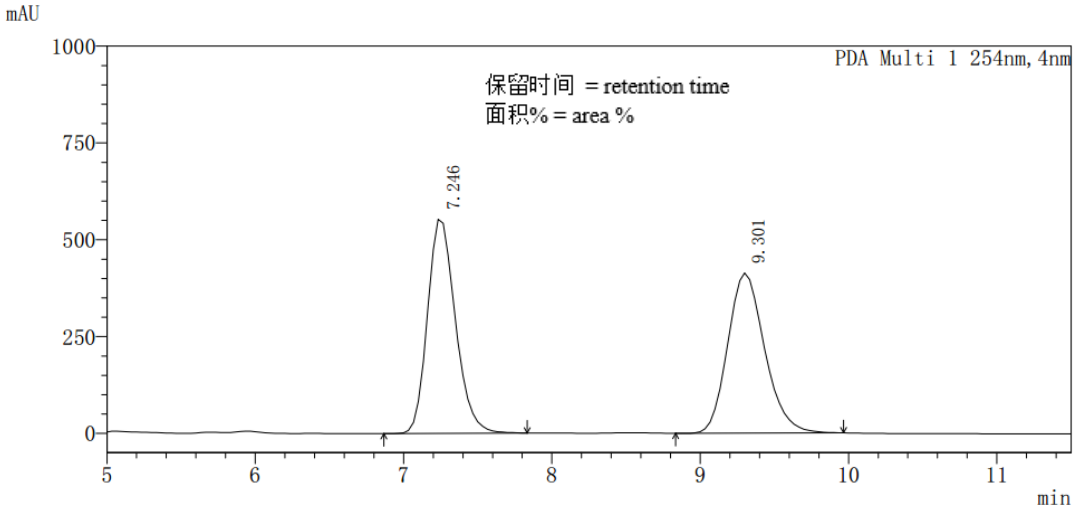
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.094	519331	58540		2.801	2.823
2	4.395	17877290	2031279		97.199	97.177
总计		18396621	2089819		100.000	100.000



6b

〈色谱图〉

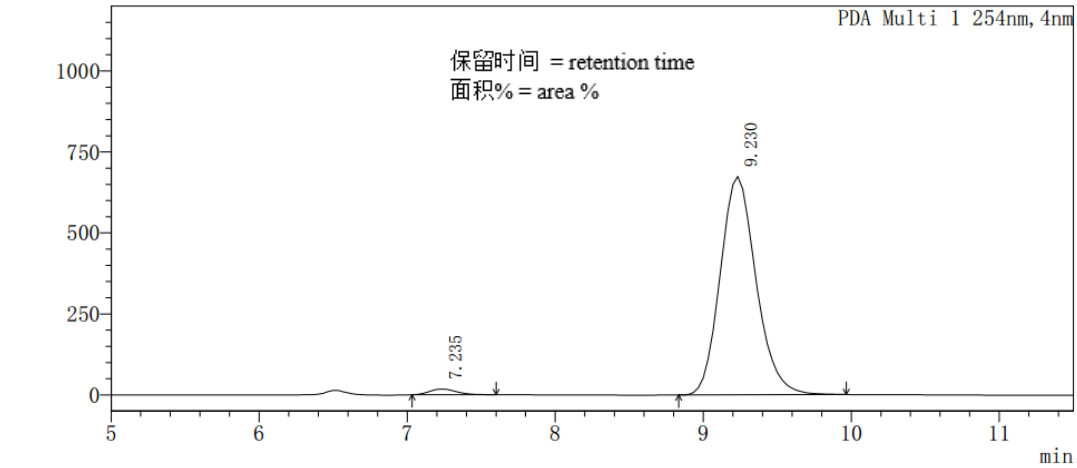


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.246	7238292	552985		57.208	50.314
2	9.301	7147866	413637		42.792	49.686
总计		14386158	966622		100.000	100.000

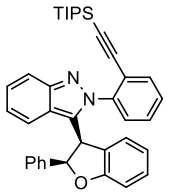
〈色谱图〉



〈峰表〉

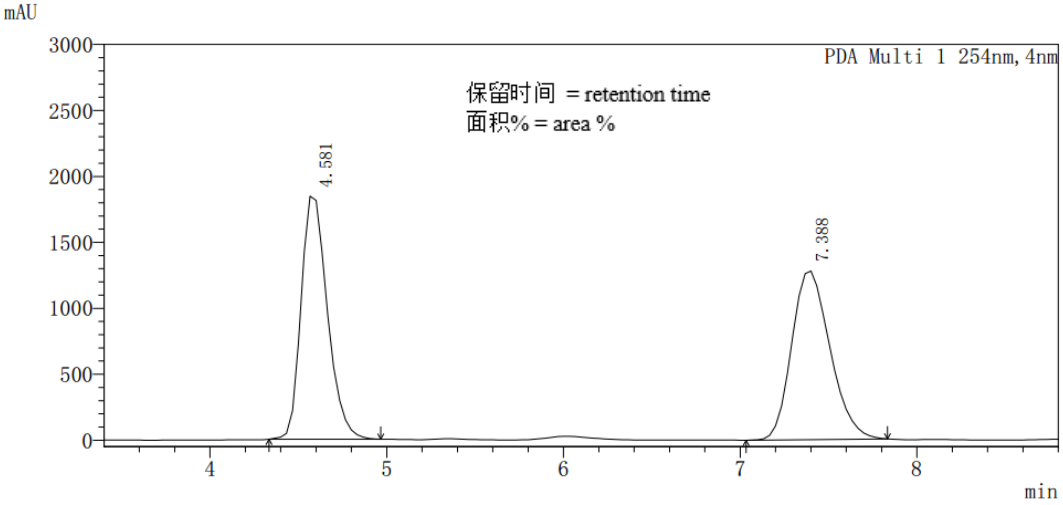
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	7.235	225717	17817		2.576	1.948
2	9.230	11358755	673950		97.424	98.052
总计		11584472	691767		100.000	100.000



6c

〈色谱图〉

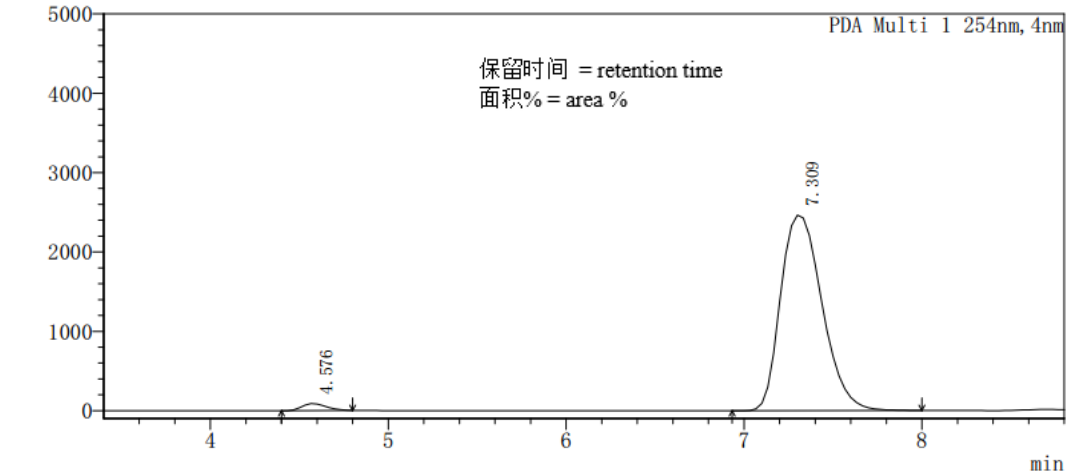


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.581	19106157	1843108		59.039	49.737
2	7.388	19308460	1278740		40.961	50.263
总计		38414617	3121848		100.000	100.000

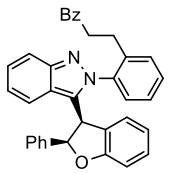
〈色谱图〉



〈峰表〉

PDA Ch1 254nm

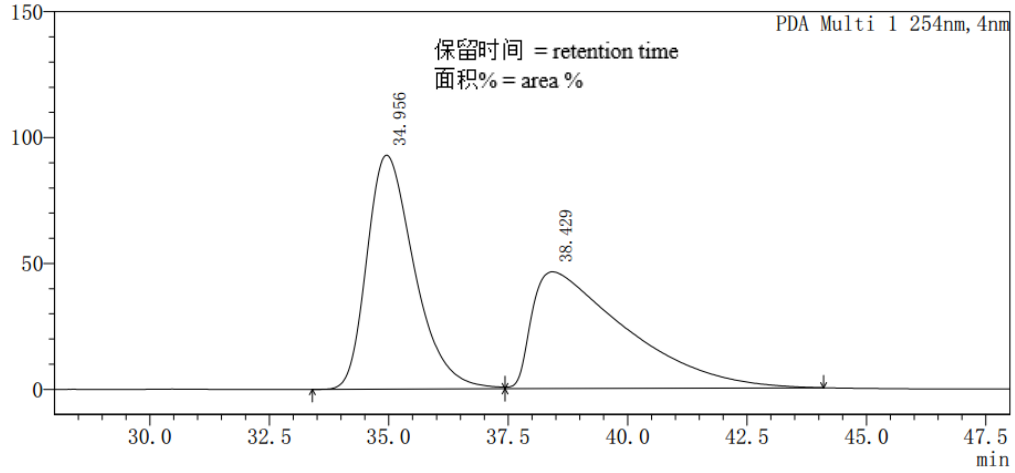
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.576	836811	88194		3.451	2.049
2	7.309	40000534	2467435		96.549	97.951
总计		40837345	2555628		100.000	100.000



6d

〈色谱图〉

mAU



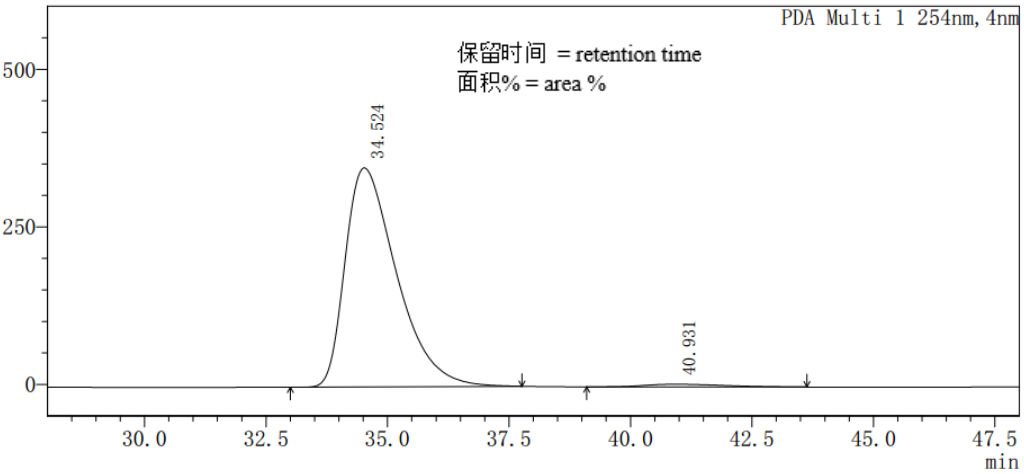
〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	34.956	6439642	92992		66.706	50.222
2	38.429	6382682	46414		33.294	49.778
总计		12822324	139405		100.000	100.000

〈色谱图〉

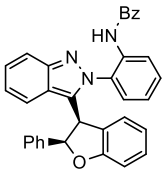
mAU



〈峰表〉

PDA Ch1 254nm

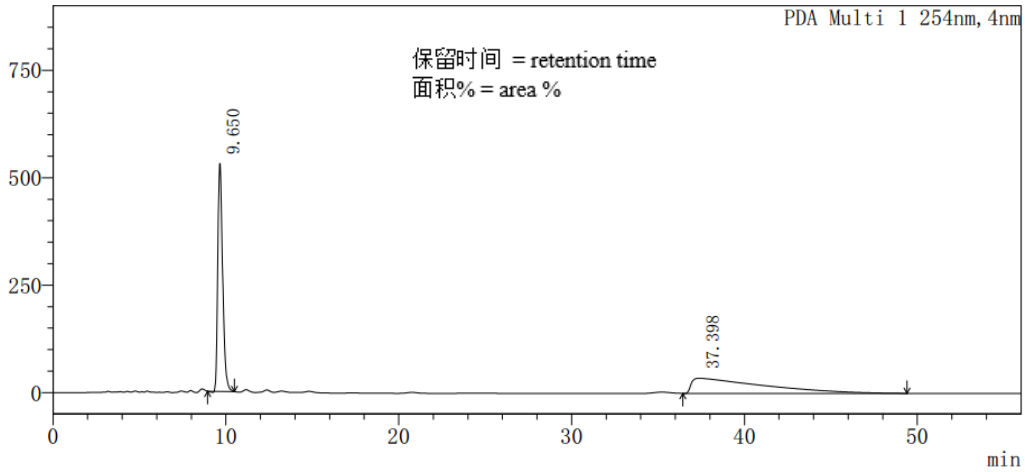
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	34.524	25614317	347604		98.776	98.103
2	40.931	495284	4306		1.224	1.897
总计		26109600	351910		100.000	100.000



6e

〈色谱图〉

mAU



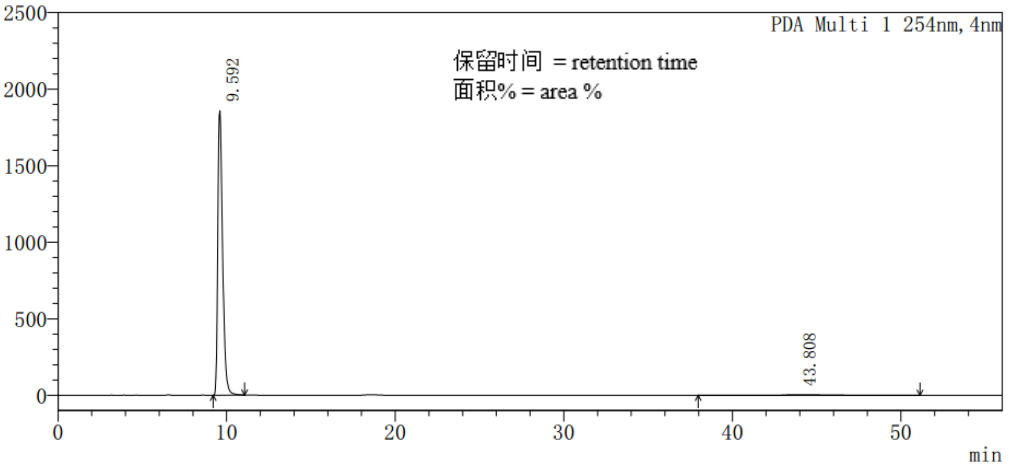
〈峰表〉

PDA Ch1 254nm

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	10206584	35026		6.198	49.692
总计		20539605	565166		100.000	100.000

〈色谱图〉

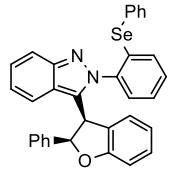
mAU



〈峰表〉

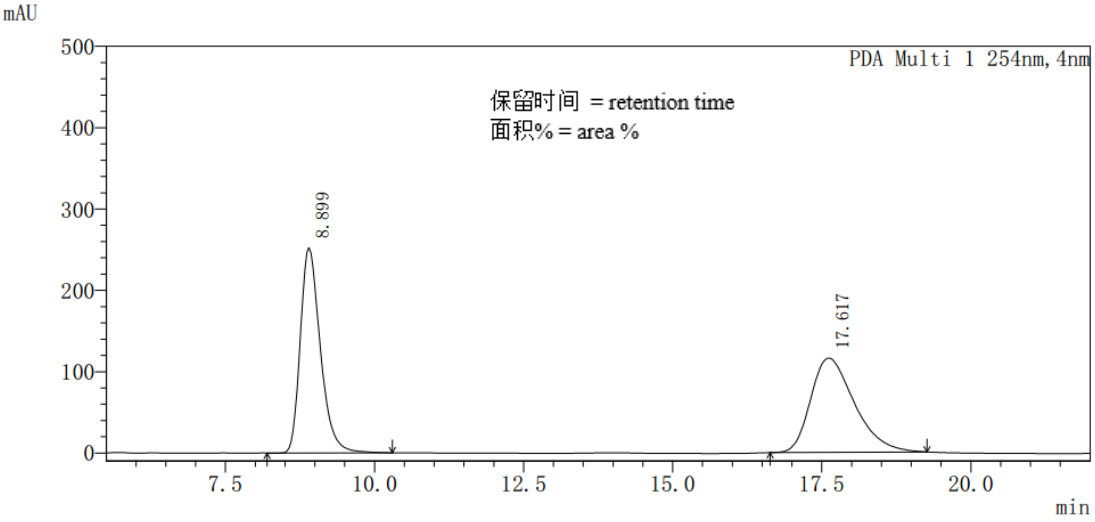
PDA Ch1 254nm

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



6f

〈色谱图〉

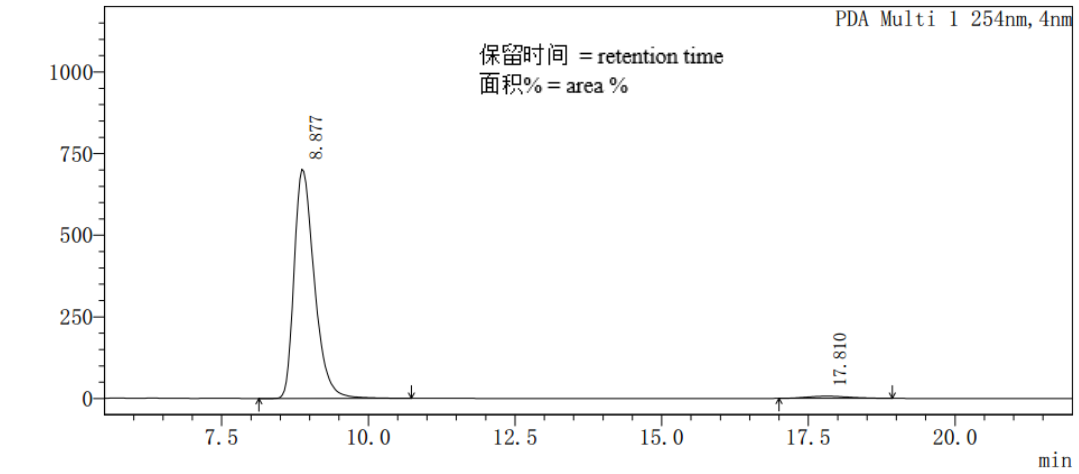


〈峰表〉

PDA Ch1 254nm

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		11828649	368422		100.000	100.000

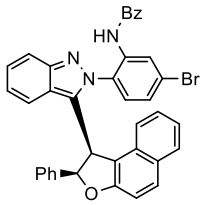
〈色谱图〉



〈峰表〉

PDA Ch1 254nm

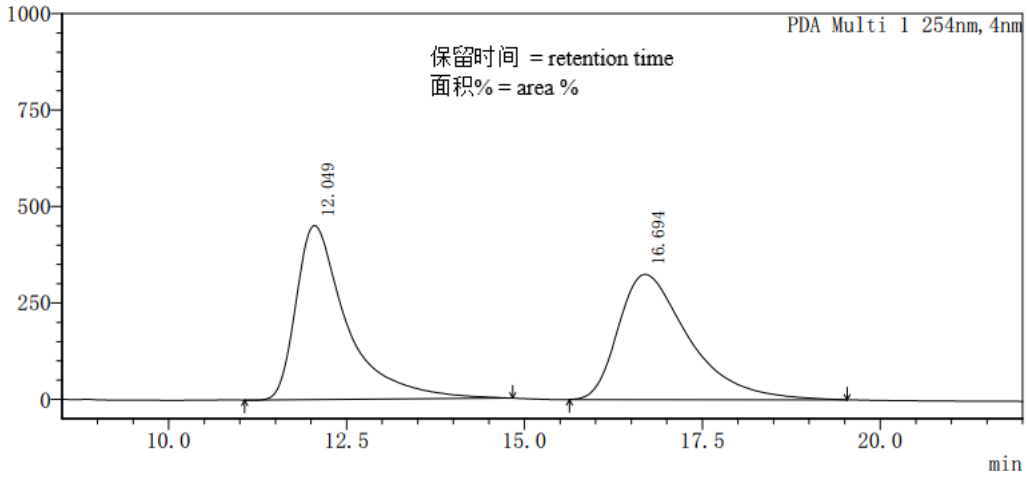
峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	8.877	16833938	701885		99.059	98.031
2	17.810	338032	6668		0.941	1.969
总计		17171970	708553		100.000	100.000



6g

〈色谱图〉

mAU



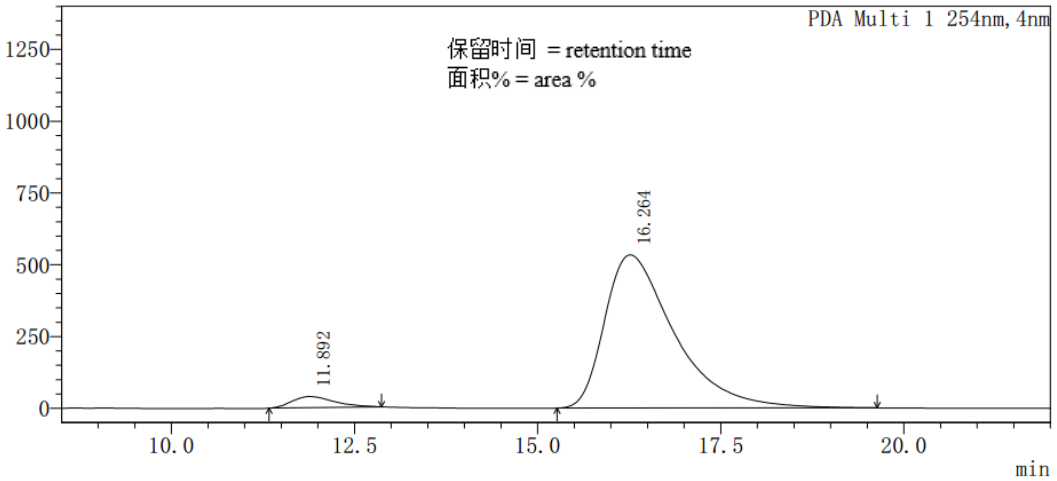
〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	12.049	22462409	450843		58.127	50.057
2	16.694	22410940	324771		41.873	49.943
总计		44873349	775615		100.000	100.000

〈色谱图〉

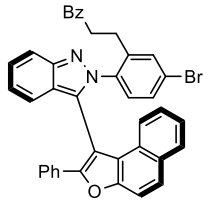
mAU



〈峰表〉

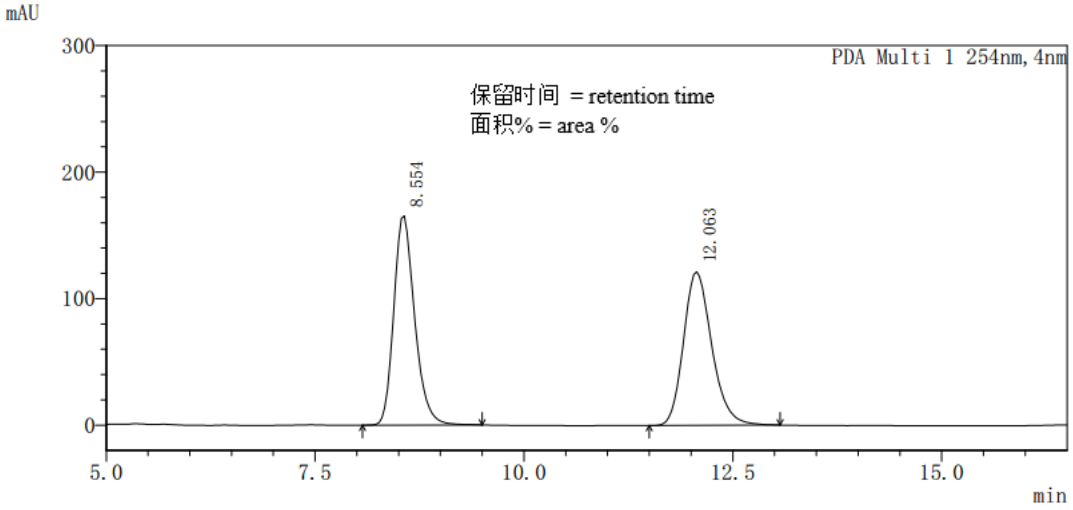
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	11.892	1554251	38858		6.783	4.222
2	16.264	35254891	533998		93.217	95.778
总计		36809142	572856		100.000	100.000



6h

〈色谱图〉

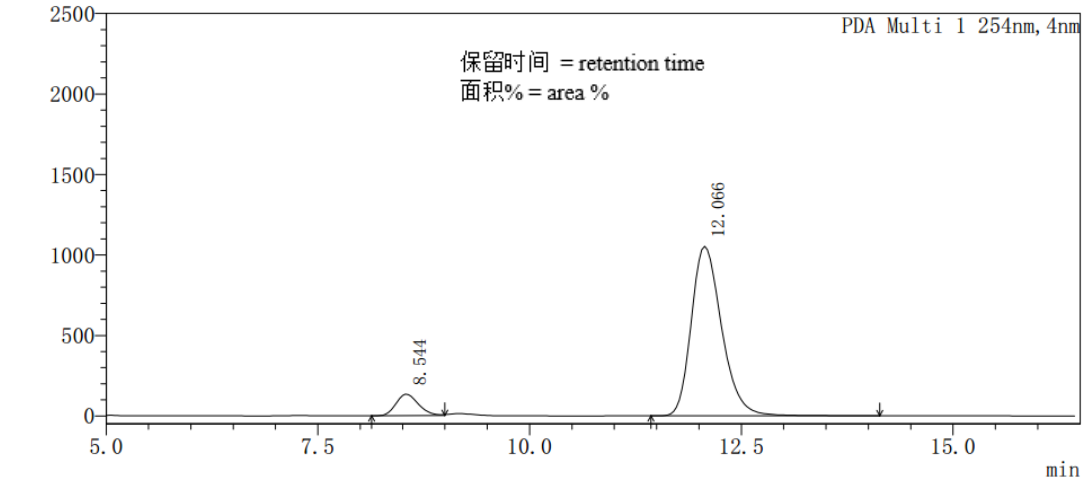


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	8.554	2879139	165287		57.635	50.174
2	12.063	2859155	121497		42.365	49.826
总计		5738293	286784		100.000	100.000

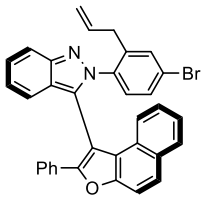
〈色谱图〉



〈峰表〉

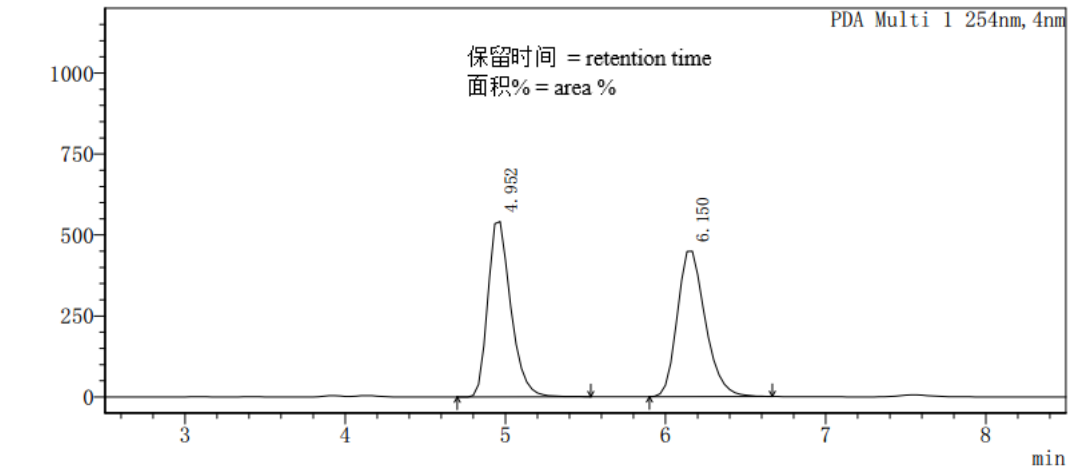
PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	8.544	2494761	133452		11.241	8.659
2	12.066	26316935	1053705		88.759	91.341
总计		28811696	1187157		100.000	100.000



6i

〈色谱图〉

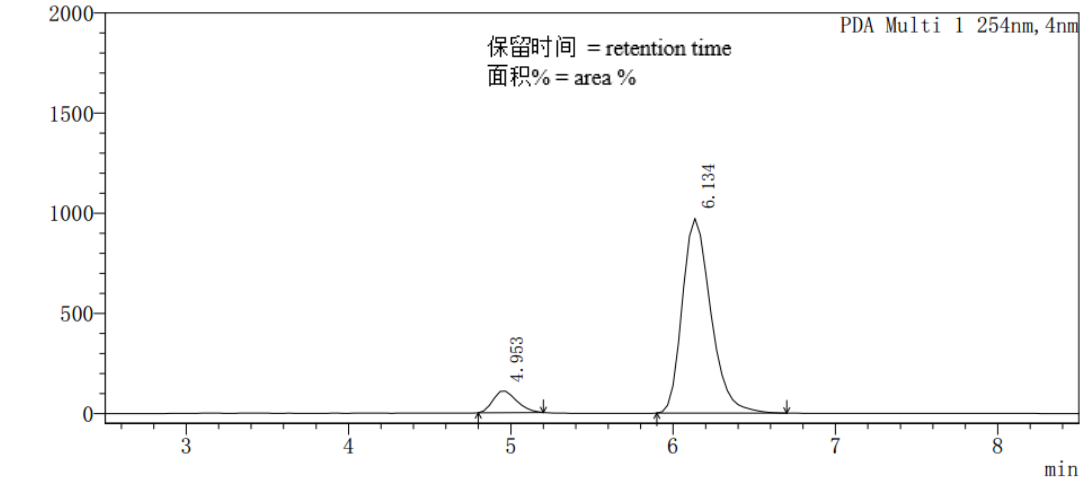


〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.952	5377926	541237		54.707	49.607
2	6.150	5463058	448107		45.293	50.393
总计		10840985	989343		100.000	100.000

〈色谱图〉



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	化合物名	高度%	面积%
1	4.953	1103533	108177		10.010	8.516
2	6.134	11854932	972494		89.990	91.484
总计		12958465	1080672		100.000	100.000