Supporting Information

Chiral Phosphoramidite Ligand-Modulated Palladium Auto-tandem Catalysis for Asymmetric Dehydrogenative Dienylation of Imines with α-Alkenes

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1. General information

Column chromatography was performed on silica gel (300-400 mesh) eluting with ethyl acetate (EtOAc) and petroleum ether. TLC was performed on glass-backed silica plates. UV light, I_2, and solution of potassium permanganate were used to visualize products or starting materials.

Reagents: Starting materials were purchased from commercial suppliers (Sigma-Aldrich, Acros, TCI, Energy Chemical, Adamas-Beta, J&K, etc.) and used as supplied unless otherwise stated. $Pd_2(dba)_3$ was purchased from Sigma-Aldrich. Toluene was dried according to standard methods and stored in Schlenk flasks under N_2 prior to use, unless stated otherwise. In addition, other solvents (THF, MTBE, 1,4-dioxane, AcOEt, CH_3CN, PhCl, DCM, DCE, and *p*-xylene) were purchased from commercial suppliers and dried over molecular sieves. N-sulfonylimines and phosphoramidite ligands were prepared according to the literature procedures.

Nuclear Magnetic Resonance Spectroscopy: ^{1}H, ^{13}C, ^{19}F, ^{31}P Nuclear magnetic resonance (NMR) spectra for compound characterization were recorded on a Bruker-400 or -500 MHz spectrometer in a suitable deuterated solvent. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, ddd = doublet of doublet of doublet, dt = double triplet; td = triple doublet; m = multiplet, br = broad, and coupling constants (J) are reported in Hertz (Hz).

Mass Spectrometry: The high-resolution mass spectra were recorded on a Thermo LTQ Orbitrap XL (ESI^+) or a P-SIMS-Gly of Bruker DaltonicsInc (EI^+). **Infrared spectra**: Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer.

Specific rotations: Specific rotations ($[\alpha]_D^{20}$) were determined at 589 nm (sodium D line) by using a Perkin-Elmer-343 polarimeter. Measurements were performed in an acid-resistant cell (100 mm length, diameter 3 mm) with concentrations (g/100 mL) reported in the corresponding solvent.

High Performance Liquid Chromatography: High Performance Liquid Chromatography (HPLC) analysis was performed on Waters-Breeze (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak IE, IF, IG, IC, IA, OD-H, AD-H, OJ columns were purchased from Daicel Chemical Industries, LTD.

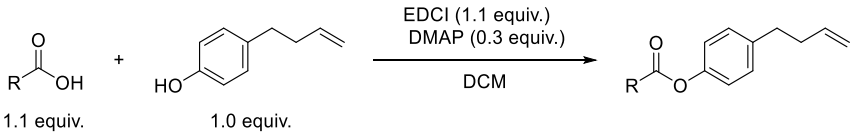
Infrared Spectra: Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer.

Melting Point: The melting point was obtained from SGW X-4A Mel-Temp apparatus.

The absolute configuration of **3** weas assigned by the X-ray analysis.

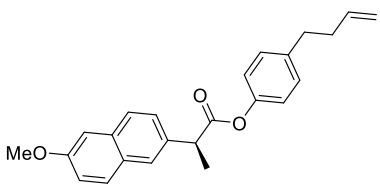
2. General procedures to prepare functionalized alkenes

Synthesis of alkene **s S1** and **S2**:



The alkenes **S1** and **S2** were prepared according to the literature procedure[1]: An oven-dried 10 mL round-bottom flask, equipped with a magnetic stirring bar, was charged with 4-(but-3-en-1-yl)phenol (148 mg, 1.0 mmol, 1.0 equiv.), acid (1.1 mmol, 1.1 equiv.), EDCI (211 mg, 1.1 mmol, 1.1 equiv.), DMAP(34 mg, 0.3 mmol, 0.3 equiv.) and anhydrous CH_2Cl_2 (2.5 mL). The mixture was stirred overnight at room temperature. The reaction was quenched with H_2O and extracted with CH_2Cl_2 (3 x 2 mL), dried over Na_2SO, filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (hexane/ EtOAc 10:1 to 2:1) to give the pure corresponding ester **S1** and **S2**.

4-(but-3-en-1-yl)phenyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (S1)



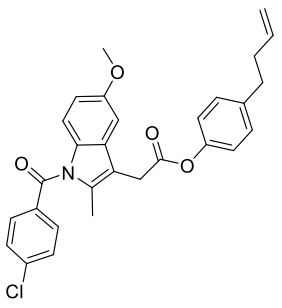
Colorless 1iquid. 0.32 g, 89% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.66 (m, 3H), 7.51 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.21 – 7.05 (m, 4H), 6.98 – 6.81 (m, 2H), 5.83 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.20 – 4.53 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 1H), 3.93 (s, 3H), 2.68 (dd, *J* = 8.9, 6.7 Hz, 2H), 2.34 (tdt, *J* = 7.9, 6.6, 1.5 Hz, 2H), 1.70 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.33, 157.77, 148.94, 139.34, 137.85, 135.27, 133.83, 129.35, 129.24, 129.03, 127.36, 126.18, 126.15, 121.11, 119.10, 115.08, 105.64, 55.34, 45.60, 35.45, 34.74, 18.56.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{24}H_{24}NaO_3]^+$ requires 383.1618, found 383.1619.

4-(but-3-en-1-yl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (S2)



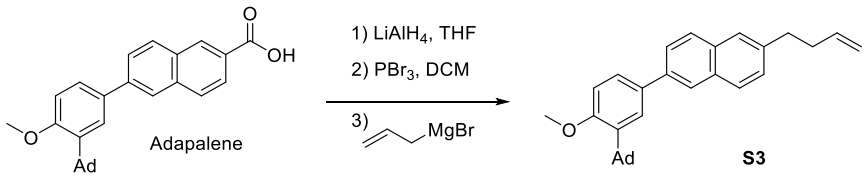
Colorless oil. 0.48 g, 98% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.55 (m, 2H), 7.55 – 7.39 (m, 2H), 7.23 – 7.13 (m, 2H), 7.11 (d, *J* = 2.5 Hz, 1H), 7.05 – 6.98 (m, 2H), 6.95 (dd, *J* = 9.0, 0.5 Hz, 1H), 6.73 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.86 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 1H), 5.16 – 4.81 (m, 2H), 3.91 (s, 2H), 3.85 (s, 3H), 2.80 – 2.65 (m, 2H), 2.47 (s, 3H), 2.36 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.47, 168.29, 156.20, 148.87, 139.57, 139.30, 137.83, 136.19, 133.94, 131.24, 130.92, 130.60, 129.36, 129.17, 121.16, 115.19, 115.07, 112.19, 111.87, 101.32, 55.74, 35.44, 34.74, 30.59, 13.48.

HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{29}H_{27}ClNO_4]^+$ requires 488.1623, found 488.1627.

Synthesis of alkene **S3**:



Under N_2 atmosphere, $LiAlH_4$ (57 mg, 1.5 mmol) was carefully added to a solution of adapalene (412 mg, 1.0 mmol) in anhydrous THF (10 mL) at 0 ℃. After being stirred for 20 min at 0 ℃ and 12 h at room temperature, the reaction was quenched with saturated sodium sulfate solution at 0 ℃, and the mixture was then filtered on celite, extracted with ethyl acetate (3 x 5 mL) and concentrated under reduced pressure. The resulting residue was applied to the next reaction without

further purification.

The above residue was dissolved in anhydrous methylene chloride (14 mL) and stirred for 10 minutes in an ice bath, then PBr_3 (0.11 mL, 1.15 mmol) was slowly added dropwise. After the addition was complete, the reaction mixture continued to react for 2 h at 0 ^oC. The reaction mixture was quenched with $NaHCO_3$ and extracted with methylene chloride (3 x 5 mL), washed with H_2O (5 mL) and saturated brine (5 mL), then dried over anhydrous sodium sulfate. The crude product was filtered, evaporated to dryness under reduced pressure and purified by column chromatography on silica gel (hexane) to give the pure corresponding bromide product.

To a 0 ℃ solution of allyl magnesium bromide (1.5 mL of a 1 M solution in THF, 1.5 mmol) was dropwise added a solution of the bromide product in THF (5 mL). The reaction was then allowed to slowly warm to rt and then stirred for 20 h under N_2. The reaction was carefully quenched with NH_4Cl and extracted with EtOAc (3 x 5 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane) to give the pure corresponding **S3**.

(3*r*,5*r*,7*r*)-1-(5-(6-(but-3-en-1-yl)naphthalen-2-yl)-2-methoxyphenyl)adamantane (S3)

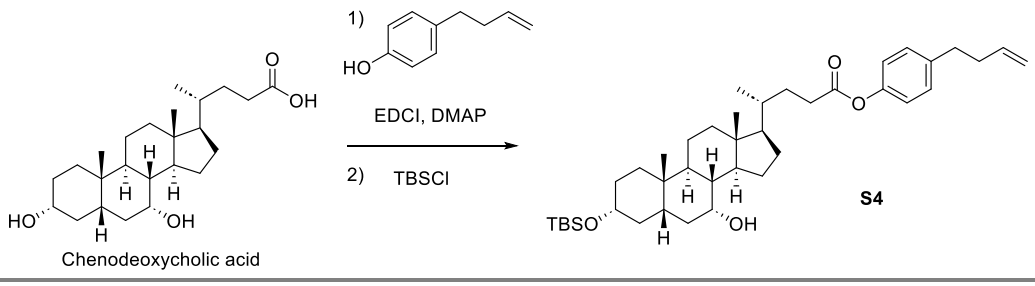
White solid. 0.25 g, 59% yield. m.p. 124-126 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 1.9 Hz, 1H), 7.87 – 7.79 (m, 2H), 7.72 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.53 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.36 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 5.93 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.39 – 4.78 (m, 2H), 3.91 (s, 3H), 2.97 – 2.78 (m, 2H), 2.64 – 2.40 (m, 2H), 2.31 – 2.18 (m, 6H), 2.17 – 2.01 (m, 3H), 1.90 – 1.74 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.50, 139.12, 138.85, 138.31, 138.09, 133.37, 132.44, 132.36, 128.01, 127.80, 127.69, 126.21, 125.88, 125.76, 125.54, 124.83, 115.06, 112.11, 55.19, 40.67, 37.21, 37.19, 35.59, 35.45, 29.18.

HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{31}H_{35}O]^+$ requires 423.2682, found 423.2685.

Synthesis of alkene **S4**:



An oven-dried 10 mL round-bottom flask, equipped with a magnetic stir bar, was charged with 4-(but-3-en-1-yl)phenol (148 mg, 1.0 mmol, 1.0 equiv.), chenodeoxycholic acid (432 mg, 1.1 mmol, 1.1 equiv.), EDCI (211 mg, 1.1 mmol, 1.1 equiv.), DMAP (34 mg, 0.3 mmol, 0.3 equiv.) and anhydrous CH_2Cl_2 (2.5 mL). The mixture was stirred overnight at room temperature. The reaction was quenched with H_2O and extracted with CH_2Cl_2 (3 x 2 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/ EtOAc 10:1) to give the pure corresponding ester. The ester was re-dissolved in DCM (5 mL) and then imidazole (0.2 g, 3.0 mmol) and TBSCl (0.45 g, 3.0 mmol) were added at ambient temperature. The reaction was stirred overnight. The reaction was diluted with DCM, then washed with saturated $NaHCO_3$, water, brine, dried (Na_2S0_4), filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (hexane/EtOAc 10:1) to give the pure corresponding alkene **S4**.

4-(but-3-en-1-yl)phenyl

(*R*)-4-((3*R*,5*R*,7*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-((tert-butyldimethylsilyl)oxy)-7-hydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)pentanoate (S4)

Colorless oil. 0.36 g, 56% yield.

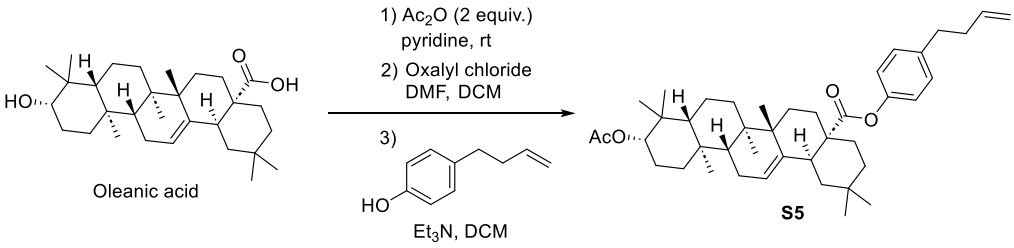
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.10 (m, 2H), 7.03 – 6.85 (m, 2H), 5.85 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.45 – 4.83 (m,

2H), 3.83 (s, 1H), 3.43 (td, *J* = 10.8, 5.3 Hz, 1H), 2.70 (dd, *J* = 9.0, 6.7 Hz, 2H), 2.59 (ddd, *J* = 14.9, 9.6, 5.0 Hz, 1H), 2.46 (ddd, *J* = 15.6, 9.0, 6.9 Hz, 1H), 2.36 (tdt, *J* = 7.7, 6.4, 1.3 Hz, 2H), 2.28 – 2.13 (m, 1H), 2.04 – 1.75 (m, 6H), 1.71 – 1.44 (m, 8H), 1.43 – 1.31 (m, 5H), 1.27 (d, *J* = 12.0 Hz, 1H), 1.23 – 1.11 (m, 4H), 0.99 (d, *J* = 6.3 Hz, 3H), 0.90 – 0.81 (m, 12H), 0.68 (s, 3H), 0.05 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.89, 148.86, 139.26, 137.90, 129.30, 121.29, 115.06, 72.90, 68.57, 55.83, 50.50, 42.75, 41.62, 40.11, 39.66, 39.49, 35.57, 35.45, 35.39, 35.09, 34.76, 34.67, 32.76, 31.37, 31.12, 30.99, 28.21, 25.99, 23.75, 22.82, 20.58, 18.32, 18.31, 11.82, -4.53, -4.59.

HRMS (ESI): m/z $[M+H]^+$ calcd for $[C_{40}H_{65}O_4Si]^+$ requires 637.4647, found 637.4653.

Synthesis of alkene **S5**:



The alkene **S5** was prepared according to the literature procedure[2]: To a 25 mL dried Schlenk flask were added oleanic acid (457 mg, 1.00 mmol, 1 .00 equiv.) in anhydrous pyridine (10 mL) and Ac_2O (2.0 equiv., 0.14 mL) at 0 °C. The reaction mixture was then slowly warmed to room temperature for 24 h. The reaction mixture was washed with water (3 x 10 mL) and extracted with ethyl acetate (3 x 5 mL). The combined organic layers were combined and dried over anhydrous Na_2SO_4. The filtrate was concentrated in vacuo to afford pure Ac-oleanic acid for further use in the next step.

To a 25 mL dried Schlenk flask were added a solution of Ac-oleanic acid anhydrous DCM (5.0 mL), oxalyl chloride (0.17 mL, 2.0 equiv.), and one drop of DMF. After the reaction mixture was stirred at room temperature for 3 hours, the solvent was removed in vacuo to afford Ac-oleanic chloride. Then, to the solution of 4-(but-3-en-1-yl)phenol (0.296 g, 2. 0 mmol, 2.0 equiv.), Et_3N (0.28 mL, 2.0 mmol, 2.0 equiv.) and DMAP (6.1 mg, 5 mol%) in anhydrous DCM (10.0 mL) was added Ac-oleanic chloride slowly at 0 ℃. The resulting mixture was warmed to 50 ℃ under N_2 and stirred for 24 hours. The reaction mixture was quenched with water and extracted with DCM (3 x 5.0 mL). The combined DCM phases were dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The residue was purified by flash column chromatography on silica gel with eluent (hexanes/EtOAc 4:1) to afford Ac-oleanic acid ester.

4-(but-3-en-1-yl)phenyl
(4*aS*,6*aS*,6b*R*,8*aR*,10*S*,12*aR*,12*bR*,14*bS*)-10-acetoxy-2,2,6a,6b,9,9,12a-heptamethyl-1,3,4,5,6,6*a*,6*b*,7,8,8a,9,10,11,12,12*a*, 12*b*,13,14*b*-octadecahydropicene-4a(2*H*)-carboxylate (S5)

White solid. 0.34 g, 54% yield. 87-89 ℃.

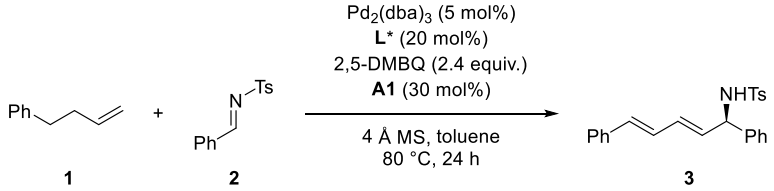
^{1}H NMR (400 MHz, CDCl3) δ 7.19 – 7.04 (m, 2H), 7.03 – 6.80 (m, 2H), 5.84 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1H), 5.34 (t, *J* = 3.7 Hz, 1H), 5.13 – 4.87 (m, 2H), 4.69 – 4.32 (m, 1H), 2.98 (dd, *J* = 13.8, 4.6 Hz, 1H), 2.69 (dd, *J* = 8.9, 6.6 Hz, 2H), 2.35 (tdt, *J* = 7.8, 6.5, 1.4 Hz, 2H), 2.05 (s, 4H), 1.95 – 1.70 (m, 7H), 1.68 – 1.47 (m, 7H), 1.46 – 1.31 (m, 3H), 1.30 – 1.22 (m, 2H), 1.18 (s, 4H), 1.10 – 1.01 (m, 1H), 0.99 – 0.92 (m, 9H), 0.89 – 0.83 (m, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.35, 171.01, 149.22, 143.38, 139.01, 137.91, 129.21, 122.75, 121.28, 115.05, 80.94, 55.34, 47.58, 47.09, 45.84, 41.86, 41.47, 39.56, 38.19, 37.72, 36.97, 35.50, 34.77, 33.92, 33.11, 32.82, 32.45, 30.76, 28.08, 27.80, 25.80, 23.63, 23.56, 23.48, 23.07, 21.32, 18.25, 17.47, 16.72, 15.44.

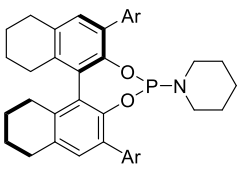
HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{42}H_{60}NaO_4]^+$ requires 651.4384, found 651.4387.

3. Development of suitable reaction conditions

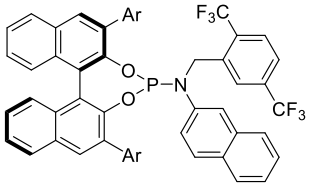
Supplementary Table 1. Ligand screenings[a]



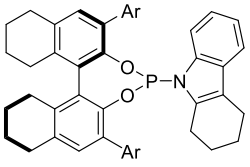
1 2 3



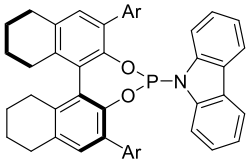
L1: Ar = 4-NO_2-C_6H_4
55%, 58% e.e., 93:7 *E/Z*



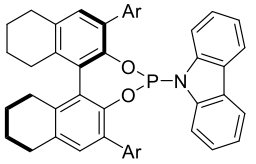
S-L1: Ar = 4-F-C_6H_4
N.R.



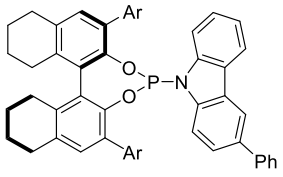
S-L2: Ar = 4-NO_2-C_6H_4
41%, 70% e.e., 93:7 *E/Z*



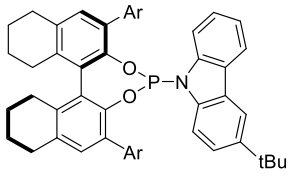
L2: Ar = 4-CF_3-C_6H_4
68%, 74% e.e., 93:7 *E/Z*



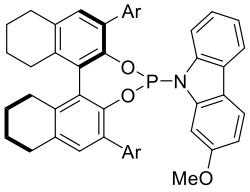
S-L3: Ar = 4-CHO-C_6H_4, 73%, 85% e.e., 94:6 *E/Z*
L3: Ar = Ph, 81%, 92% e.e., 95:5 *E/Z*
S-L4: Ar = 4-Ph-C_6H_4, 76%, 88% e.e., 95.5:4.5 *E/Z*
L4: Ar = 4-OMe-C_6H_4, 83%, 92% e.e., 95:5 *E/Z*
S-L5: Ar = 4-F-C_6H_4, 75%, 83% e.e., 93:7 *E/Z*
S-L6: Ar = 4-Cl-C_6H_4, 61%, 81% e.e., 94:6*E/Z*
S-L7: Ar = 3,5-$(OMe)_2$-C_6H_3, 80%, 89% e.e. 94:6 *E/Z*
S-L8: Ar = 4-CO_2Me-C_6H_4, 73%, 78% e.e. 94:6 *E/Z*
S-L9: Ar = 4-Me-C_6H_4, 93%, 90% e.e., 95:5 *E/Z*
S-L10: Ar = 4-tBu-C_6H_4, 84%, 91% e.e., 94:6 *E/Z*
S-L11: Ar = 3,5-$(Ph)_2$-C_6H_3, 36%, 69% e.e. 82:18 *E/Z*
L5: Ar = 1-Naphthalene, 57%, 92% e.e., 85:15 *E/Z*
L6: Ar = 9-Anthracene, 42%, 98% e.e., 77:23 *E/Z*



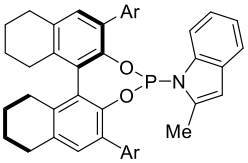
S-L12: Ar = 4-CF_3-C_6H_4
82%, 68% e.e., 92:8 *E/Z*
S-L13: Ar = 4-Me-C_6H_4
86%, 90% e.e., 95:5 *E/Z*



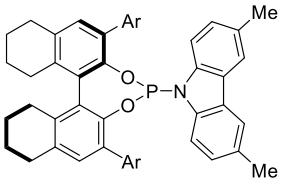
L7: Ar = 4-OMe-C_6H_4
87%, 91% e.e., 96:4 *E/Z*



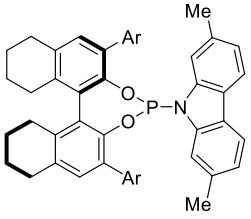
L8: Ar = 4-OMe-C_6H_4
72%, 95% e.e., 97:3 *E/Z*



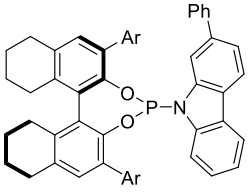
S-L14: Ar = 4-OMe-C_6H_4
59%, 86% e.e., 96:4 *E/Z*



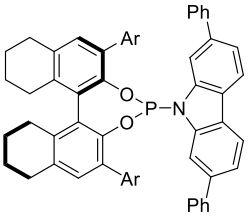
S-L15: Ar = 4-OMe-C_6H_4
77%, 90% e.e., 96:4 *E/Z*



S-L16: Ar = 4-OMe-C_6H_4
76%, 95% e.e., 97:3 *E/Z*



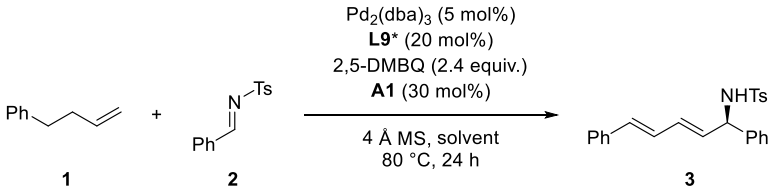
L9: Ar = 4-OMe-C_6H_4
82%, 95% e.e., 97:3 *E/Z*



L10: Ar = 4-OMe-C_6H_4
58%, 94% e.e., 97:3 *E/Z*

[a]Unless noted otherwise, reactions were carried out with **1** (0.1 mmol), **2** (0.05 mmol), $Pd_2(dba)_3$ (0.0025 mmol), **L*** (0.01 mmol), 2,5-DMBQ (0.12 mmol), **A1** (0.015 mmol) and 4 Å MS (30 mg) in toluene (0.5 mL) at 80 ℃ under N_2 for 24 h. The value of *E*/*Z* and yield which were determined by ^{1}H nuclear magnetic resonance (^{1}H NMR) analysis of the crude products based on trimethyl 1,3,5-benzenetricarboxylate as an internal standard. The value of e.e. was determined by high performance liquid chromatography using a chiral column.

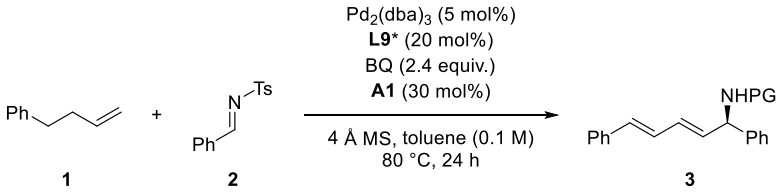
Supplementary Table 2. Solvent screening[a]



Entry	solvent	yield (%)[b]	e.e. (%)[c]	*E*/*Z*[d]
1	dioxane	54	88	>19:1
2	THF	64	88	>19:1
3	MTBE	81	92	>19:1
4	$^{i}Pr_2O$	96	93	>19:1
5	DCM	52	96	>19:1
6	DCE	18	96	>19:1
7	PhCl	56	96	>19:1
8	p-xylene	81	95	>19:1
9	o-xylene	91	94	>19:1
10	**toluene**	**82**	**95**	**>19:1**
11	toluene, 60 ℃	26	96	>19:1
12	toluene, 70 ℃	64	96	>19:1

[a]Unless noted otherwise, reactions were carried out with **1** (0.1 mmol), **2** (0.05 mmol), $Pd_2(dba)_3$ (0.0025 mmol), **L9*** (0.01 mmol), 2,5-DMBQ (0.12 mmol), **A1** (0.015 mmol) and 4 Å MS (30 mg) in solvent (0.5 mL) at 80 ℃ under N_2 for 24 h. [b,] [c]The value of *E*/*Z* and yield which were determined by ^{1}H nuclear magnetic resonance (^{1}H NMR) analysis of the crude products based on trimethyl 1,3,5-benzenetricarboxylate as an internal standard. [d]The value of e.e. was determined by high performance liquid chromatography using a chiral column.

Supplementary Table 3. Oxidant screening[a]

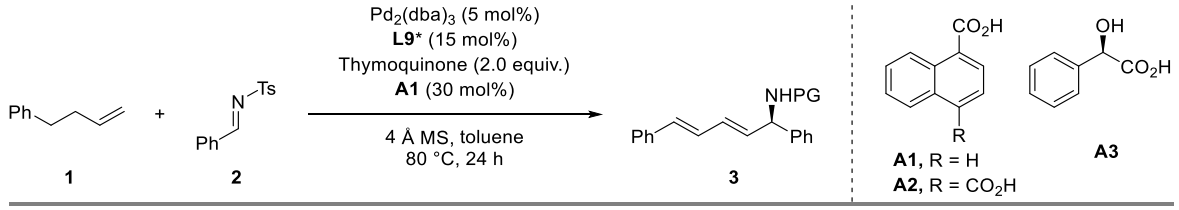


1 **2** **3**

2-Me-BQ	2,5-DMBQ	2,6-DMBQ	Thymoquinone	2,5-DTBQ	2,5-DPBQ
92%, 95% e.e. 94:6 *E/Z*	82%, 95% e.e. 97:3 *E/Z*	>95%, 95% e.e. 96:4 *E/Z*	>95%, 95% e.e. 97:3 *E/Z*	37%, 96% e.e. 97:3 *E/Z*	79%, 95% e.e. 98:2 *E/Z*

[a]Unless noted otherwise, reactions were carried out with **1** (0.1 mmol), **2** (0.05 mmol), $Pd_2(dba)_3$ (0.0025 mmol), **L9*** (0.01 mmol), BQ (0.12 mmol), **A1** (0.015 mmol) and 4 Å MS (30 mg) in toluene (0.5 mL) at 80 ℃ under N_2 for 24 h. [b, c]The value of *E*/*Z* and yield which were determined by ^{1}H nuclear magnetic resonance (^{1}H NMR) analysis of the crude products based on trimethyl 1,3,5-benzenetricarboxylate as an internal standard. [d]The value of e.e. was determined by high performance liquid chromatography using a chiral column.

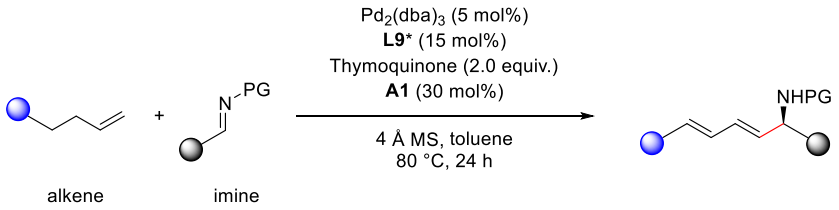
Supplementary Table 4. Further optimization of the reaction conditions[a]



Entry	yield (%)	e.e. (%)	*E/Z*	variation
1	81	95	>19:1	**L9** (11 mol %)
2	87	93	16:1	**L9** (15 mol %), Thymoquinone (1.5 equiv.)
3	93	93	19:1	**L9** (15 mol%), Thymoquinone (1.5 equiv.), **1** (1.5 equiv.)
4	>95	75	16:1	Without **A1**
5	90	88	>19:1	With **A2** instead of **A1**
6	89	94	>19:1	With **A3** instead of **A1**
7	91	94	>19:1	Without 4 Å MS
8	74	95	>19:1	[Pd] (5 mol%), **L9** (7.5 mol%), 24 h
9	92	94.6	>19:1	[Pd] (5 mol%), **L9** (7.5 mol%), 36 h
10	91	94.6	>19:1	[Pd] (5 mol%), **L9** (7.5 mol%), 48 h
11	>95	95	>19:1	toluene (0.2 M)
12	82	95	>19:1	toluene (0.05 M)
13	73	95	>19:1	70 ℃
14	69	94	19:1	70 ℃, 48 h
15	**>95 (95[b])**	**95**	**>19:1**	**none**

[a]Unless noted otherwise, reactions were carried out with **1** (0.1 mmol), **2** (0.05 mmol), $Pd_2(dba)_3$ (0.0025 mmol), **L9*** (0.0075 mmol), Thymoquinone (0.10 mmol), **A1** (0.015 mmol) and 4 Å MS (30 mg) in toluene (0.5 mL) at 80 ℃ under N_2 for 24 h. The value of *E*/*Z* and yield which were determined by ^{1}H nuclear magnetic resonance (^{1}H NMR) analysis of the crude products based on trimethyl 1,3,5-benzenetricarboxylate as an internal standard. The value of e.e. was determined by high performance liquid chromatography using a chiral column.

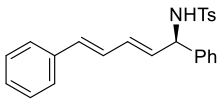
4. Substrates scope and characterization data



General procedure A: To a flame-dried and N_2-purged Schlenk tube (10 mL) were added imine (0.05 mmol, 1 equiv.), $Pd_2(dba)_3$ (0.0025 mmol, 2.3 mg), phosphoramidite (*R*)-**L9** (0.0075 mmol, 5.9 mg), **A1** (0.015 mmol, 2.6 mg), Thymoquinone (0.10 mmol, 16.4 mg), 4 Å MS (30 mg) and a stirring bar. The Schlenk tube was then evacuated and filled with nitrogen. This cycle was repeated three times and followed by the addition of anhydrous and degassed toluene (0.5 mL) and an alkene (0.1 mmol, 2 equiv.) via a syringe, then the resulting mixture was stirred at 80 ℃ for 24 h. The mixture was filtered through Celite and concentrated in *vacuo*, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to provide the desired product.

General procedure B: To a flame-dried and N_2-purged Schlenk tube (10 mL) were added imine (0.05 mmol, 1.0 equiv.), $Pd_2(dba)_3$ (0.0025 mmol, 2.3 mg), phosphoramidite (*R*)-**L9** (0.01 mmol, 7.9 mg), **A1** (0.015 mmol, 2.6 mg), Thymoquinone (0.10 mmol, 16.4 mg), 4 Å MS (30 mg) and a stirring bar. The Schlenk tube was then evacuated and filled with nitrogen. This cycle was repeated three times and followed by the addition of anhydrous and degassed toluene (0.5 mL) and an alkene (0.1 mmol, 2 equiv.) via a syringe, then the resulting mixture was stirred at 80 ℃ for 40 h. The mixture was filtered through Celite and concentrated in *vacuo*, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to provide the desired product.

***N*-((*R*,2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (3) (Known compound).**[3]



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) gave the product as a white solid. Yield: 95%, 18.5 mg. *E/Z* > 20:1. Enantiomeric excess: 95%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 15.178 min (major), t_R = 26.656 min (minor). $[\alpha]_D^{20}$ = -20.5 (c 0.93, $CHCl_3$). m.p. 86-88 ℃.

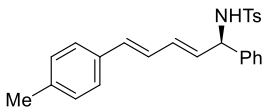
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.59 (m, 2H), 7.42 – 7.27 (m, 4H), 7.25 – 7.18 (m, 6H), 7.17 – 7.12 (m, 2H), 6.62 (ddd, *J* = 15.7, 10.4, 0.8 Hz, 1H), 6.42 (d, *J* = 15.6 Hz, 1H), 6.26 – 6.05 (m, 1H), 5.73 (ddt, *J* = 15.2, 6.7, 0.8 Hz, 1H), 5.04 (td, *J* = 6.9, 1.3 Hz, 1H), 4.96 (d, *J* = 7.2 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.34, 139.60, 137.60, 136.90, 133.63, 132.57, 132.03, 129.49, 128.74, 128.67, 127.87, 127.82, 127.51, 127.34, 127.07, 126.41, 59.57, 21.54.

IR (KBr): γ : 3273, 3029, 2961, 2924, 2856, 1449,1411,1352, 1263, 1156, 1092, 1024, 804, 761, 699, 669,560cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{24}H_{23}NNaO_2S]^+$ requires 412.1342, found 412.1348.

4-methyl-*N*-((*R*,2*E*,4*E*)-1-phenyl-5-(p-tolyl)penta-2,4-dien-1-yl)benzenesulfonamide (4) (Known compound).[4]



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 79%, 13.4 mg. *E/Z* = 19:1. Enantiomeric excess: 95%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 22.387 min (major), t_R = 29.306 min (minor). $[\alpha]_D^{20}$ = -33.6 (c 0.80, $CHCl_3$).

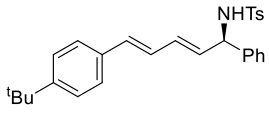
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.02 (m, 11H), 6.56 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 6.11 (ddd, *J* = 15.0, 10.4, 1.2 Hz, 1H), 5.69 (dd, *J* = 15.1, 6.5 Hz, 1H), 5.10 – 4.85 (m, 2H), 2.36 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.31, 139.69, 137.77, 137.63, 134.13, 133.62, 132.76, 131.41, 129.47, 129.38, 128.71, 127.82, 127.35, 127.07, 126.56, 126.34, 59.60, 21.53, 21.29.

IR (KBr): γ : 3272, 3026, 2960, 2924, 2857, 1601, 1506, 1450, 1424, 1326, 1261, 1157, 1092, 1024, 993, 913, 870, 808, 751, 700, 669, 560 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{25}NNaO_2S]^+$ requires 426.1498, found 426.1506.

***N*-((*R*,2*E*,4*E*)-5-(4-(*tert*-butyl)phenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (5) (Known compound).**[4]



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 84%, 18.7 mg. *E/Z* = 20:1. Enantiomeric excess: 94%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 13.723 min (major), t_R = 21.897 min (minor). $[\alpha]_D^{20}$ = -31.9 (c 0.94, $CHCl_3$).

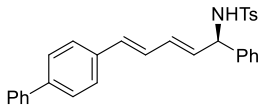
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.01 (m, 11H), 6.57 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.40 (d, *J* = 15.6 Hz, 1H), 6.24 – 5.99 (m, 1H), 5.70 (dd, *J* = 15.1, 6.5 Hz, 1H), 5.21 – 4.86 (m, 2H), 2.36 (s, 3H), 1.31 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.00, 143.30, 139.69, 137.65, 134.15, 133.52, 132.81, 131.44, 129.47, 128.71, 127.82, 127.34, 127.08, 126.77, 126.17, 125.60, 59.62, 34.65, 31.28, 21.54.

IR (KBr): γ : 3269, 3061, 3028, 2962, 2926, 2865,1656,1599,1513, 1494, 1453, 1363, 1327, 1262, 1203, 1159, 1093, 1028, 989, 927, 874, 812, 759, 668, 563 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{28}H_{31}NNaO_2S]^+$ requires 468.1968, found 468.1972.

***N*-((*R*,2*E*,4*E*)-5-([1,1'-biphenyl]-4-yl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (6) (Known compound).**[4]



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 82%, 19.0 mg. *E/Z* > 20:1. Enantiomeric excess: 96%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 21.142 min (major), t_R = 25.900 min (minor). $[\alpha]_D^{20}$ = -10.9 (c 0.95, $CHCl_3$). m.p. 100-102 ℃.

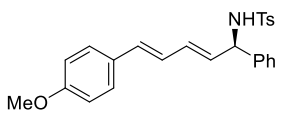
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.62 – 7.58 (m, 2H), 7.58 – 7.52 (m, 2H), 7.48 – 7.39 (m, 4H), 7.37 – 7.31 (m, 1H), 7.27 – 7.19 (m, 5H), 7.16 (dd, *J* = 7.3, 2.3 Hz, 2H), 6.66 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 6.18 (dd, *J* = 15.1, 10.5 Hz, 1H), 5.76 (dd, *J* = 15.1, 6.1 Hz, 1H), 5.22 – 4.79 (m, 2H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.35, 140.55, 140.49, 139.61, 137.63, 135.97, 133.15, 132.59, 132.15, 129.49, 128.84, 128.75, 127.88, 127.60, 127.42, 127.35, 127.33, 127.08, 126.95, 126.91, 126.86, 59.60, 21.55.

IR (KBr): γ : 3273, 3029, 2961, 2924, 2856, 1149, 1411, 1325, 1263, 1156, 1092, 1024, 804, 761, 699, 669, 560 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{30}H_{27}NNaO_2S]^+$ requires 488.1655, found 488.1659.

***N*-((*R*,2*E*,4*E*)-5-(4-methoxyphenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (7).**



According general procedure B: Rection run for 36 h, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 81%, 17.0 mg. *E/Z* =14:1. Enantiomeric excess: 96%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 18.049 min (major), t_R = 24.056 min (minor). $[\alpha]_D^{20}$ = -8.6 (c 1.55, $CHCl_3$).

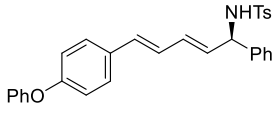
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.51 (m, 2H), 7.32 – 7.26 (m, 2H), 7.25 – 7.10 (m, 7H), 6.91 – 6.67 (m, 2H), 6.49 (ddd, *J* = 15.6, 10.2, 0.7 Hz, 1H), 6.37 (d, *J* = 15.6 Hz, 1H), 6.11 (ddd, *J* = 15.0, 10.2, 1.2 Hz, 1H), 5.67 (dd, *J* = 15.1, 6.7 Hz, 1H), 5.02 (td, *J* = 6.9, 1.2 Hz, 1H), 4.91 (d, *J* = 7.1 Hz, 1H), 3.81 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.40, 143.30, 139.74, 137.63, 133.23, 132.88, 130.81, 129.71, 129.46, 128.72, 128.70, 127.81, 127.66, 127.34, 127.06, 125.47, 114.10, 59.63, 55.33, 21.53.

IR (KBr): γ : 3275, 3030, 2926, 2845, 1686, 1603, 1507, 1457, 1327, 1265, 1157, 1094, 1031, 922, 817, 754, 699, 557 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{25}NNaO_3S]^+$ requires 442.1447, found 442.1452.

4-methyl-*N*-((*R*,2*E*,4*E*)-5-(4-phenoxyphenyl)-1-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (8) (Known compound).[4]



According general procedure A: Rection run for 36 h, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. 59%, 14.2 mg. *E/Z* = 16:1. Enantiomeric excess: 91%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 8.860 min (major), t_R = 13.497 min (minor). $[\alpha]_D^{20}$ = -21.3(c 0.72, $CHCl_3$). m.p. 128-130 ℃.

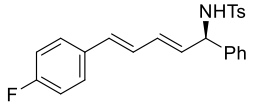
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.4 Hz, 2H), 7.38 – 7.28 (m, 4H), 7.25 – 7.18 (m, 5H), 7.18 – 7.06 (m, 3H), 7.06 – 6.98 (m, 2H), 6.94 (d, J = 8.7 Hz, 2H), 6.64 – 6.48 (m, 1H), 6.41 (d, J = 15.7 Hz, 1H), 6.15 (ddd, J = 15.1, 10.3, 1.3 Hz, 1H), 5.72 (dd, J = 15.1, 6.7 Hz, 1H), 5.20 – 4.98 (m, 1H), 4.82 (d, J = 6.9 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.1, 156.9, 143.3, 139.7, 137.7, 132.9, 132.7, 132.1, 131.6, 129.8, 129.5, 128.7, 127.9, 127.8, 127.3, 127.1, 126.6, 123.5, 119.1, 118.8, 59.6, 21.5.

IR (KBr): γ : 3447, 3289, 3063, 3035, 2961, 2925, 2857, 1641, 1594, 1494, 1452, 1326, 1255, 1158, 1093, 1025, 868, 803, 750, 697, 669, 557 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{30}H_{27}NNaO_3S]^+$ requires 504.1604, found 504.1614.

***N*-((*R*,2*E*,4*E*)-5-(4-fluorophenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (9) (Known compound).**[4]



According general procedure B: Rection run for 36 h, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 90%, 18.3 mg. *E/Z* > 20:1. Enantiomeric excess: 95%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 16.127 min (major), t_R = 30.023 min (minor). $[\alpha]_D^{20}$ = -26.6 (c 0.92, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.30 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.26 – 7.17 (m, 5H), 7.16 – 7.09 (m, 2H), 7.07 – 6.90 (m, 2H), 6.53 (dd, *J* = 15.7, 10.3 Hz, 1H), 6.39 (d, *J* = 15.7 Hz, 1H), 6.27 – 6.04 (m, 1H), 5.74 (dd, *J* = 15.2, 5.6 Hz, 1H), 5.01 (d, *J* = 4.6 Hz, 2H), 2.36 (s, 3H).

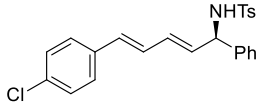
^{19}F NMR (376 MHz, $CDCl_3$) δ -113.78.

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.38 (d, J = 247.6 Hz), 143.33, 139.56, 137.59, 133.11 (d, J = 3.3 Hz), 132.33, 132.15, 129.47, 128.74, 127.93, 127.88, 127.85, 127.33, 127.30, 127.28, 127.05, 115.64 (d, J = 21.7 Hz), 59.54, 21.52.

IR (KBr): γ : 3273, 3032, 2959, 2925, 2854, 1599, 1507, 1454, 1326, 1262, 1230, 1184, 1157, 1093, 1025, 989, 930, 813, 759, 740, 701, 668, 562, 545 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{24}H_{22}FNNaO_2S]^+$ requires 430.1247, found 430.1248.

***N*-((*R*,2*E*,4*E*)-5-(4-chlorophenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (10) (Known compound).**[4]



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 75%, 15.8 mg. *E/Z* = 15:1. Enantiomeric excess: 96%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 15.074 min (major), t_R = 30.492 min (minor). $[\alpha]_D^{20}$ = -24.6 (c 1.33, $CHCl_3$). m.p. 108-110 ℃.

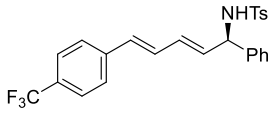
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.53 (m, 2H), 7.38 – 6.97 (m, 11H), 6.59 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.38 (d, *J* = 15.7 Hz, 1H), 6.26 – 6.06 (m, 1H), 5.76 (dd, *J* = 15.1, 6.5 Hz, 1H), 5.18 – 4.98 (m, 1H), 4.90 (d, *J* = 7.0 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.34, 139.50, 137.64, 135.43, 133.37, 132.73, 132.22, 129.46, 128.79 (d, *J* = 7.0 Hz), 128.11, 127.92, 127.53, 127.33, 127.04, 59.52, 21.50.

IR (KBr): γ : 3270, 3039, 2962, 2924, 2854, 1598, 1490, 1453, 1406, 1326, 1262, 1158, 1092, 1026, 989, 929, 813, 747, 701, 667, 564, 509 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{24}H_{22}ClNNaO_2S]^+$ requires 446.0952, found 446.0958.

4-methyl-*N*-((*R*,2*E*,4*E*)-1-phenyl-5-(4-(trifluoromethyl)phenyl)penta-2,4-dien-1-yl)benzenesulfonamide (11) (Known compound).[4]



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 78%, 17.8 mg. *E/Z* = 15:1. Enantiomeric excess: 97%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 7.766 min (major), t_R = 13.430 min (minor). $[\alpha]_D^{20}$ = -17.4 (c 0.89, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.17 (m, 5H), 7.15 – 7.08 (m, 2H), 6.71 (dd, *J* = 15.7, 10.5 Hz, 1H), 6.46 (d, *J* = 15.7 Hz, 1H), 6.30 – 6.15 (m, 1H), 5.84 (dd, *J* = 15.2, 6.5 Hz, 1H), 5.09 – 5.00 (m, 1H), 4.86 (d, *J* = 7.0 Hz, 1H), 2.37 (s, 3H).

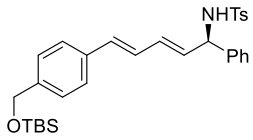
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.53.

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.39, 140.38, 139.34, 137.61, 133.96, 131.92, 129.92, 129.49, 129.41 (d, J = 32.5 Hz), 128.82, 128.02, 127.33, 127.04, 126.76 (d, J = 8.0 Hz), 126.45, 125.60 (q, J = 3.8 Hz), 122.79, 59.47, 21.50.

IR (KBr): γ : 3272, 3033, 2961, 2925, 2857, 1659, 1609, 1449, 1416, 1325, 1263, 1159, 1068, 1022, 807, 753, 700, 671, 560 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{22}F_3NNaO_2S]^+$ requires 480.1216, found 480.1224.

***N*-((*R*,2*E*,4*E*)-5-(4-(((*tert*-butyldimethylsilyl)oxy)methyl)phenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (12)**



According general procedure A: Rection run for 30 h, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 78%, 20.7 mg. *E/Z* = 20:1. Enantiomeric excess: 95%, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ℃, 298 nm): t_R = 23.969 min (major), t_R = 20.267 min (minor). $[\alpha]_D^{20}$ = -26.9 (c 1.04, $CHCl_3$).

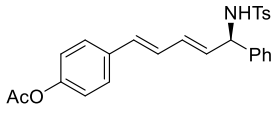
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.23 – 7.18 (m, 2H), 7.18 – 7.12 (m, 5H), 7.12 – 7.08 (m, 2H), 7.08 – 6.97 (m, 2H), 6.50 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.31 (d, *J* = 15.6 Hz, 1H), 6.12 – 5.94 (m, 1H), 5.61 (dd, *J* = 15.1, 6.6 Hz, 1H), 4.93 (t, *J* = 7.1 Hz, 1H), 4.85 (d, *J* = 7.1 Hz, 1H), 4.62 (s, 2H), 2.26 (s, 3H), 0.84 (s, 9H), -0.00 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.33, 141.20, 139.64, 137.62, 135.61, 133.54, 132.69, 131.70, 129.47, 128.72, 127.85, 127.35, 127.06, 126.35, 126.31, 64.76, 59.59, 25.98, 21.53, 18.45, -5.21.

IR (KBr): γ : 3273, 3028, 2928, 2856, 1602, 1501, 1460, 1414, 1326, 1258, 1209, 1156, 1025, 933, 805, 700, 669, 560 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{31}H_{39}NNaO_3SSi]^+$ requires 556.2312, found 556.2323.

4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)phenyl acetate (13)



According general procedure A: Rection run for 30 h, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 84%, 18.7 mg. *E/Z* = 20:1. Enantiomeric excess: 96%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 12.452 min (major), t_R = 20.986 min (minor). $[\alpha]_D^{20}$ = -25.0 (c 0.92, $CHCl_3$).

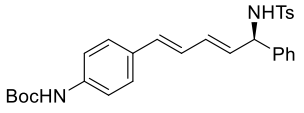
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.26 – 7.16 (m, 5H), 7.16 – 7.11 (m, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.55 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.39 (d, *J* = 15.6 Hz, 1H), 6.19 – 6.06 (m, 1H), 5.73 (dd, *J* = 15.1, 6.6 Hz, 1H), 5.03 (t, *J* = 6.8 Hz, 1H), 4.96 (d, *J* = 7.1 Hz, 1H), 2.36 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.46, 150.16, 143.32, 139.59, 137.69, 134.74, 132.53, 132.40, 132.30, 129.46, 128.73, 127.87, 127.74, 127.33, 127.06, 121.80, 59.55, 21.51, 21.16.

IR (KBr): γ : 3275, 3029, 2961, 2925, 2856, 1765, 1599, 1501, 1426, 1370, 1327, 1265, 1157, 1095, 1019, 910, 810, 753, 702, 669, 561 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{26}H_{25}NNaO_4S]^+$ requires 470.1397, found 470.1395.

***Tert*-butyl (4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)phenyl)carbamate (14)**



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 72%, 18.2 mg. *E*/*Z* > 20:1. Enantiomeric excess: 96%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 306 nm): t_R = 12.470 min (major), t_R = 24.114 min (minor). $[\alpha]_D^{20}$ = -19.7 (c 0.91, $CHCl_3$). m.p. 69-71 ℃.

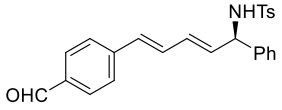
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 2H), 7.33 – 7.19 (m, 7H), 7.20 – 7.17 (m, 2H), 7.16 – 7.09 (m, 2H), 6.58 (s, 1H), 6.51 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.34 (d, *J* = 15.6 Hz, 1H), 6.10 (dd, *J* = 15.1, 10.4 Hz, 1H), 5.67 (dd, *J* = 15.1, 5.9 Hz, 1H), 5.07 – 4.95 (m, 2H), 2.35 (s, 3H), 1.51 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.67, 143.31, 139.70, 137.94, 137.64, 133.08, 132.71, 131.81, 131.30, 129.73, 129.46, 128.69, 127.81, 127.34, 127.10, 127.06, 126.48, 126.21, 118.54, 80.79, 59.60, 28.35, 21.53.

IR (KBr): γ : 3342, 2971, 2926, 1724, 1591, 1524, 1452, 1411, 1367, 1319, 1233, 1157, 1092, 1051, 990, 813, 738, 699, 669, 559 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{29}H_{32}N_2NaO_4S]^+$ requires 527.1975, found 527.1984.

***N*-((*R*,2*E*,4*E*)-5-(4-formylphenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (15)**



According general procedure B: Rection run for 36 h, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 48%, 10.0mg. *E*/*Z* = 19:1. Enantiomeric excess: 97%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 12.476 min (major), t_R = 19.837 min (minor). $[\alpha]_D^{20}$ = -29.2 (c 0.50, $CHCl_3$).

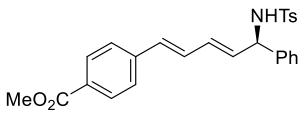
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.81 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.28 – 7.17 (m, 5H), 7.12 (dd, J = 6.7, 2.9 Hz, 2H), 6.77 (dd, J = 15.6, 10.5 Hz, 1H), 6.48 (d, J = 15.6 Hz, 1H), 6.24 (dd, J = 15.1, 10.5 Hz, 1H), 5.87 (dd, J = 15.1, 6.0 Hz, 1H), 5.18 – 4.82 (m, 2H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.64, 143.43, 142.99, 139.25, 137.53, 135.38, 134.62, 132.13, 131.86, 130.95, 130.21, 129.51, 128.83, 128.05, 127.32, 127.06, 126.79, 59.47, 21.53.

IR (KBr): γ : 3452, 3281, 2962, 2925, 1688, 1599, 1263, 1158, 1093, 1024, 803, 754, 701, 670 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{23}NNaO_3S]^+$ requires 440.1291, found 440.1296.

Methyl 4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)benzoate (16)



According general procedure A: Thymoquinone (2.4 equiv.), purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 71%, 15.8 mg. *E*/*Z* > 20:1. Enantiomeric excess: 97%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 10.430 min (major), t_R = 16.710 min (minor). $[\alpha]_D^{20}$ = -22.5 (c 0.80, $CHCl_3$). m.p. 103-105 ℃.

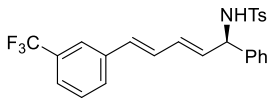
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.16 (m, 5H), 7.16 – 7.09 (m, 2H), 6.77 – 6.64 (m, 1H), 6.45 (d, *J* = 15.7 Hz, 1H), 6.20 (dd, *J* = 15.2, 10.5 Hz, 1H), 5.91 – 5.77 (m, 1H), 5.17 – 4.91 (m, 2H), 3.91 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.85, 143.38, 141.40, 139.37, 137.59, 133.89, 132.36, 132.02, 130.02, 129.99, 129.49, 129.02, 128.79, 127.97, 127.32, 127.05, 126.20, 59.48, 52.14, 21.52.

IR (KBr): γ : 3271, 2958, 2925, 1715, 1602, 1436, 1156, 1023, 807, 759, 700, 670, 560 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{26}H_{25}NNaO_4S]^+$ requires 470.1397, found 470.1397.

4-methyl-*N*-((*R*,2*E*,4*E*)-1-phenyl-5-(3-(trifluoromethyl)phenyl)penta-2,4-dien-1-yl)benzenesulfonamide (17)



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 72%, 16.4 mg. *E/Z* > 20:1. Enantiomeric excess: 96%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 14.097 min (major), t_R = 29.981 min (minor). $[\alpha]_D^{20}$ = -23.2 (c 0.83, $CHCl_3$). m.p. 125-127 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.60 (m, 2H), 7.56 (s, 1H), 7.52 – 7.36 (m, 3H), 7.29 – 7.17 (m, 5H), 7.16 – 7.06 (m, 2H), 6.73 – 6.62 (m, 1H), 6.45 (d, *J* = 15.7 Hz, 1H), 6.31 – 6.07 (m, 1H), 5.81 (dd, *J* = 15.2, 6.5 Hz, 1H), 5.12 – 5.00 (m, 1H), 4.95 (d, *J* = 7.1 Hz, 1H), 2.36 (s, 3H).

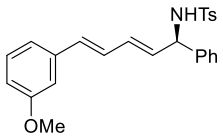
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.84.

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.37, 139.39, 137.72, 137.65, 133.63, 131.89, 131.85, 131.10 (d, J = 32.2 Hz), 129.48, 129.31, 129.11, 128.79, 127.98, 127.34, 127.05, 125.40, 124.19 (q, J = 3.7 Hz), 122.88 (q, J = 3.8 Hz), 122.70, 59.48, 21.47.

IR (KBr): γ : 3270, 3029, 2959, 2924, 2855, 1599, 1449, 1328, 1261, 1159, 1095, 1027, 904, 806, 753, 699, 669, 559 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{22}F_3NNaO_2S]^+$ requires 480.1216, found 480.1225.

***N*-((*R*,2*E*,4*E*)-5-(3-methoxyphenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (18)**



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 80%, 16.7 mg. *E/Z* = 16:1. Enantiomeric excess: 94%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 9.118 min (major), t_R = 14.229 min (minor). $[\alpha]_D^{20}$ = -18.9 (c 0.84, $CHCl_3$).

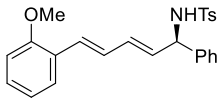
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.27 – 7.16 (m, 6H), 7.17 – 7.08 (m, 2H), 6.93 (dt, *J* = 7.7, 1.2 Hz, 1H), 6.87 (t, *J* = 2.1 Hz, 1H), 6.81 – 6.75 (m, 1H), 6.60 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.39 (d, *J* = 15.6 Hz, 1H), 6.23 – 6.06 (m, 1H), 5.73 (dd, *J* = 15.1, 6.7 Hz, 1H), 5.20 – 5.00 (m, 1H), 4.92 (d, *J* = 7.1 Hz, 1H), 3.80 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ159.8, 143.3, 139.6, 138.4, 137.6, 133.5, 132.5, 132.2, 129.6, 129.5, 128.7, 127.9, 127.8, 127.3, 127.1, 119.1, 113.4, 111.6, 59.6, 55.2, 21.5.167.08, 157.08, 152.30, 136.97, 130.63, 129.25, 128.52, 127.86, 125.84, 121.42, 120.96, 120.76, 118.98, 115.77, 111.15, 58.69, 55.57.

IR (KBr): γ : 3272, 3027, 2960, 2925, 2855, 1664, 1597, 1488, 1455, 1325, 1262, 1156, 1093, 1032, 926, 866, 808, 697, 559 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{25}NNaO_3S]^+$ requires 442.1447, found 442.1449.

***N*-((*R*,2*E*,4*E*)-5-(2-methoxyphenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (19)**



According general procedure A: Rection run for 36 h, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 81%, 16.8 mg. *E/Z* > 20:1. Enantiomeric excess: 98%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 8.474 min (major), t_R = 14.228 min (minor). $[\alpha]_D^{20}$ = -32.2 (c 0.86, $CHCl_3$). m.p. 138-140 ℃.

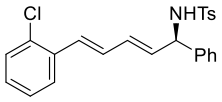
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.38 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.28 – 7.07 (m, 8H), 6.93 – 6.88 (m, 1H), 6.85 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.76 (d, *J* = 15.8 Hz, 1H), 6.63 (dd, *J* = 15.8, 10.4 Hz, 1H), 6.18 – 6.04 (m, 1H), 5.69 (dd, *J* = 15.1, 6.8 Hz, 1H), 5.05 – 4.98 (m, 1H), 4.86 (d, *J* = 7.0 Hz, 1H), 3.84 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.83, 143.30, 139.76, 137.67, 133.52, 131.33, 129.47, 128.85, 128.67, 128.60, 128.08, 127.78, 127.35, 127.08, 126.53, 125.92, 120.68, 110.91, 59.61, 55.45, 21.47.

IR (KBr): γ : 3452, 3281, 2962, 2927, 1637, 1599, 1488, 1458, 1324, 1258, 1155, 1094, 1024, 802, 752, 700, 670, 560 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{25}NNaO_3S]^+$ requires 442.1447, found 442.1453.

***N*-((*R*,2*E*,4*E*)-5-(2-chlorophenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (20)**



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 31%, 6.6 mg. *E/Z* = 20:1. Enantiomeric excess: 92%, determined by HPLC (CHIRALPAK IG, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 21.845 min (major), t_R = 19.885 min (minor). $[\alpha]_D^{20}$ = -18.2 (c 0.33, $CHCl_3$).

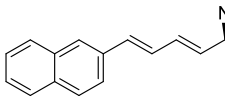
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.63 (m, 2H), 7.49 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.34 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.29 – 7.18 (m, 6H), 7.19 – 7.11 (m, 3H), 6.82 (d, *J* = 15.6 Hz, 1H), 6.60 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.28 – 6.08 (m, 1H), 5.86 – 5.64 (m, 1H), 5.04 (t, *J* = 7.0 Hz, 1H), 4.85 (d, *J* = 7.0 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.45, 139.44, 137.53, 134.85, 133.24, 133.20, 132.41, 129.89, 129.87, 129.53, 129.35, 128.80, 128.70, 127.98, 127.35, 127.06, 126.85, 126.24, 59.49, 21.51.

IR (KBr): γ : 3270, 2924, 2855, 1661, 1459, 1325, 1264, 1156, 1092, 1030, 808, 754, 699, 670, 560 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{24}H_{22}ClNNaO_2S]^+$ requires 446.0952, found 446.0956.

4-methyl-*N*-((*R*,2*E*,4*E*)-5-(naphthalen-2-yl)-1-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (21) (Known compound).[3]



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 76%, 16.7 mg. *E/Z* = 18:1. Enantiomeric excess: 96%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 15.074 min (major), t_R = 30.492 min (minor). $[\alpha]_D^{20}$ = -21.6 (c 0.83, $CHCl_3$).

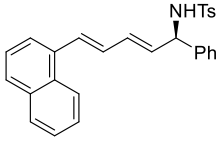
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.71 (m, 3H), 7.71 – 7.62 (m, 3H), 7.54 (dd, J = 8.6, 1.8 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.29 – 7.10 (m, 7H), 6.73 (dd, J = 15.6, 10.3 Hz, 1H), 6.58 (d, J = 15.6 Hz, 1H), 6.20 (ddd, J = 15.0, 10.3, 1.2 Hz, 1H), 5.77 (dd, J = 15.1, 6.4 Hz, 1H), 5.31 – 4.85 (m, 2H), 2.35 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.4, 139.6, 137.6, 134.4, 133.7, 133.6, 133.1, 132.6, 132.2, 129.5, 128.8, 128.3, 128.0, 127.9, 127.7, 127.4, 127.1, 126.6, 126.4, 126.1, 123.3, 59.6, 21.5.

IR (KBr): γ : 3272, 3056, 2961, 2924, 2856, 1599, 1449, 1325, 1263, 1157, 1092, 1024, 809, 742, 700, 669, 559 cm^{-1}.

HRMS (ESI): m/z $[M +Na]^+$ calcd for $[C_{28}H_{25}NNaO_2S]^+$ requires 462.1498, found 462.1500.

4-methyl-*N*-((*R*,2*E*,4*E*)-5-(naphthalen-1-yl)-1-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (22)



According general procedure A: Rection run for 36 h, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 65%, 14.2 mg. *E/Z* = 14:1. Enantiomeric excess: 95%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 15.074 min (major), t_R = 30.492 min (minor). $[\alpha]_D^{20}$ = -31.9 (c 0.72, $CHCl_3$). m.p. 128-130 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 1H), 7.84 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.71 – 7.63 (m, 2H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.35 – 7.11 (m, 8H), 6.67 (dd, *J* = 15.3, 10.6 Hz, 1H), 6.41 – 6.21 (m, 1H), 5.79 (dd, *J* = 15.1, 6.6 Hz, 1H), 5.51 – 5.04 (m, 1H), 4.97 (d, *J* = 7.1 Hz, 1H), 2.34 (s, 3H).

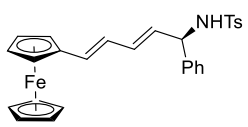
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.35, 139.60, 137.71, 134.28, 133.71, 132.80, 132.39, 131.08, 130.36, 130.32, 129.49, 128.77, 128.65, 128.21, 127.91, 127.37, 127.11, 126.16, 125.87, 125.59, 123.50, 123.36, 59.58, 21.53.

IR (KBr): γ : 3269, 3031, 2962, 2924, 2854, 1598, 1494, 1453, 1325, 1261, 1158, 1093, 1028, 989, 801, 764, 748, 701, 668,

565, 549 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{28}H_{25}NNaO_2S]^+$ requires 462.1498, found 462.1497.

4-methyl-*N*-((*S*,2*E*,4*E*)-1-phenyl-5-(Ferroceneyl)penta-2,4-dien-1-yl)benzenesulfonamide (23) (Known compound).[4]



According general procedure A: Rection run for 36 h, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a red solid. Yield: 76%, 18.8 mg. *E/Z* = 10:1. Enantiomeric excess: 87%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 7.199 min (major), t_R = 10.161 min (minor). $[\alpha]_D^{20}$ = -128.6 (c 0.95, $CHCl_3$). m.p. 152-154 ℃.

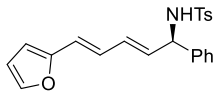
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.9 Hz, 2H), 7.24 – 7.08 (m, 7H), 6.28 – 6.13 (m, 2H), 6.08 – 5.91 (m, 1H), 5.58 (dd, *J* = 15.0, 6.6 Hz, 1H), 5.03 – 4.89 (m, 2H), 4.33 – 4.28 (m, 2H), 4.25 – 4.22 (m, 2H), 4.09 (s, 5H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.20, 139.81, 137.73, 133.02, 132.32, 129.42, 129.19, 128.66, 127.73, 127.31, 127.08, 125.30, 82.65, 69.31, 69.18, 69.16, 67.02, 66.74, 59.74, 21.57.

IR (KBr): γ : 3275, 3030, 2926, 2845, 1686, 1603, 1507, 1457, 1327, 1265, 1157, 1094, 1031, 922, 817, 754, 699, 557 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{28}H_{27}FeNNaO_2S]^+$ requires 520.1004, found 520.1006.

***N*-((*R*,2*E*,4*E*)-5-(furan-2-yl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (24)**



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 54%, 10.2 mg. *E/Z* = 12:1. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 28.123 min (major), t_R = 42.185 min (minor). $[\alpha]_D^{20}$ = -6.1 (c 0.51, $CHCl_3$).

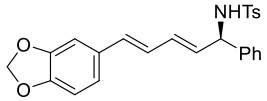
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H), 7.34 (d, *J* = 1.8 Hz, 1H), 7.25 – 7.11 (m, 7H), 6.51 (dd, *J* = 15.5, 10.8 Hz, 1H), 6.37 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.28 – 6.16 (m, 2H), 6.11 – 6.02 (m, 1H), 5.70 (dd, *J* = 15.1, 6.7 Hz, 1H), 5.02 (td, *J* = 6.9, 1.3 Hz, 1H), 4.87 (d, *J* = 7.1 Hz, 1H), 3.08 – 1.89 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 152.79, 143.32, 142.35, 139.61, 137.68, 132.17, 132.06, 129.47, 128.71, 127.85, 127.32, 127.06, 126.06, 121.07, 111.64, 108.85, 59.52, 21.46.

IR (KBr): γ : 3272, 2961, 2925, 2857, 1598, 1450, 1326, 1262, 1157, 1093, 1024, 930, 871, 804, 739, 700, 670, 559 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{22}H_{21}NNaO_3S]^+$ requires 402.1134, found 402.1129.

***N*-((*R*,2*E*,4*E*)-5-(benzo[*d*][1,3]dioxol-5-yl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (25)**



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 85%, 18.4 mg. *E/Z* = 20:1. Enantiomeric excess: 96%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 9.758 min (major), t_R = 14.546 min (minor). $[\alpha]_D^{20}$ = -19.0 (c 0.92, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.24 – 7.09 (m, 7H), 6.86 (d, *J* = 1.6 Hz, 1H), 6.81 – 6.69 (m, 2H), 6.44 (dd, *J* = 15.5, 10.2 Hz, 1H), 6.33 (d, *J* = 15.6 Hz, 1H), 6.10 (ddd, *J* = 15.1, 10.2, 1.3 Hz, 1H), 5.94 (s, 2H), 5.68 (dd, *J* = 15.1, 6.6 Hz, 1H), 5.01 (td, *J* = 6.9, 1.2 Hz, 1H), 4.94 (d, *J* = 7.1 Hz, 1H), 2.36 (s, 3H).

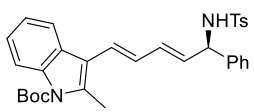
^{13}C NMR (126 MHz, $CDCl_3$) δ 148.11, 147.46, 143.28, 139.71, 137.69, 133.31, 132.60, 131.47, 131.31, 129.45, 128.70, 127.81, 127.34, 127.05, 125.89, 121.45, 108.41, 105.41, 101.16, 59.60, 21.51.

IR (KBr): γ : 3274,2961, 2923, 1493, 1444, 1326, 1256, 1156, 1094, 1036, 991, 929, 810, 752, 700, 669, 556 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{23}NNaO_4S]^+$ requires 456.1240 found 456.1241.

***Tert*-butyl**

2-methyl-3-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)-1H-indole-1-carboxylate (26)



According general procedure A: Purification by flash chromatography on silica gel (petroleum

ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 34%, 9.0 mg. *E/Z* = 18:1. Enantiomeric excess: 98%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 8.351 min (major), t_R = 10.274 min (minor). $[\alpha]_D^{20}$ = -28.0 (c 0.90, $CHCl_3$).

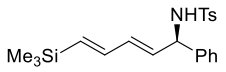
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 – 8.00 (m, 1H), 7.80 – 7.57 (m, 3H), 7.49 – 6.87 (m, 9H), 6.72 – 6.53 (m, 2H), 6.22 (ddd, *J* = 15.1, 9.6, 1.3 Hz, 1H), 5.69 (dd, *J* = 15.1, 6.8 Hz, 1H), 5.07 (td, *J* = 6.5, 1.2 Hz, 1H), 4.84 (d, *J* = 6.9 Hz, 1H), 2.60 (s, 3H), 2.36 (s, 3H), 1.68 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.50, 143.27, 139.78, 137.81, 136.13, 135.92, 133.79, 130.45, 129.44, 128.73, 128.56, 127.85, 127.81, 127.40, 127.07, 125.46, 123.78, 122.93, 119.18, 116.30, 115.46, 84.10, 59.72, 28.28, 21.50, 14.33.

IR (KBr): γ : 3275, 2966, 2926, 2857, 1730, 1453, 1323, 1263, 1224, 1094, 1025, 805, 753, 700, 670, 558 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{32}H_{34}N_2NaO_4S]^+$ requires 565.2132, found 565.2138.

4-methyl-*N*-((*R*,2*E*,4*E*)-1-phenyl-5-(trimethylsilyl)penta-2,4-dien-1-yl)benzenesulfonamide (27)



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 68%, 13.0 mg. *E/Z* = 9:1. Enantiomeric excess: 67%, determined by HPLC (CHIRALPAK IG, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 14.752 min (major), t_R = 17.001 min (minor). $[\alpha]_D^{20}$ = 7.4 (c 0.70, $CHCl_3$).

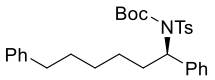
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 2H), 7.20 – 7.11 (m, 5H), 7.10 – 7.03 (m, 2H), 6.29 (ddd, *J* = 18.2, 10.0, 0.7 Hz, 1H), 5.93 (ddt, *J* = 15.2, 9.9, 1.0 Hz, 1H), 5.72 (d, *J* = 18.4 Hz, 1H), 5.63 – 5.38 (m, 1H), 5.03 – 4.86 (m, 1H), 4.79 (d, *J* = 7.0 Hz, 1H), 2.34 (s, 3H), -0.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.62, 143.87, 140.91, 138.94, 137.34, 136.38, 130.82, 130.08, 129.24, 128.73, 128.40, 60.75, 22.91, 0.00.

IR (KBr): γ : 3274, 2959, 2924, 1327, 1261, 1157, 1093, 1024, 863, 805, 755, 699, 670, 558 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{21}H_{27}NNaO_2SSi]^+$ require s 408.1424, found 408.1433.

***Tert*-butyl (*R*)-(1,6-diphenylhexyl)(tosyl)carbamate (28)**



To a flame-dried and N_2-purged Schlenk tube (10 mL) were added imine (0.05 mmol, 1 equiv.), $Pd_2(dba)_3$ (0.005 mmol, 2.3 mg), phosphoramidite (*R*)-**L9** (0.0075 mmol, 5.9 mg), **A1** (0.015 mmol, 2.6 mg), Thymoquinone (0.10 mmol, 16.4 mg), 4 Å MS (30 mg) and a stirring bar. The Schlenk tube was then evacuated and filled with nitrogen. This cycle was repeated three times and followed by the addition of anhydrous and degassed toluene (0.5 mL) and alkene (0.25 mmol, 5 equiv.) via a syringe, then the resulting mixture was stirred at 80 ℃ for 48 h. The mixture was filtered through Celite and concentrated in *vacuo*, and the residue was purified by column chromatography on silica gel (petroleum ether/ EtOAc = 10:1) to provide the desired product as a mixture of double bond migration and phosphoramidite. The mixture was dissolved in MeOH (1.0 mL), then 10% Pd/C (5.0 mg, 10 wt%) was added. The resulting solution was stirred at room temperature under an atmosphere of H_2 (balloon) overnight. After completion, the mixture was filtered through Celite and concentrated in *vacuo*, and the residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) to give the desired product as a white semisolid. The white semisolid was re-dissolved in anhydrous CH_2Cl_2 (0.5 mL), di-*tert*-butyl dicarbonate (0.15 mmol, 32.7 mg) and 2,4-dimethylaminopyridine (0.01 mmol, 1.2 mg) was added respectively. After the mixture was stirred for 12 h, the solvent was evaporated, the residue was purified by flash silica gel column chromatography (hexane/ethyl acetate = 20:1) to give the target product as a white semisolid. Yield: 49%, 12.4 mg. Enantiomeric excess: 56%, determined by HPLC (CHIRALPAK IG, hexane/isopropanol = 97/3, flow rate 1.0 mL/min, T = 30 ℃, 229 nm): t_R = 27.913 min (major), t_R = 25.360 min (minor). $[\alpha]_D^{20}$ = 10.2 (c 0.63, $CHCl_3$).

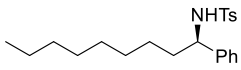
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 7.4 Hz, 2H), 7.37 – 7.23 (m, 5H), 7.23 – 7.06 (m, 5H), 5.64 – 5.59 (m, 1H), 2.61 (dd, *J* = 8.7, 6.8 Hz, 2H), 2.40 (s, 3H), 2.36 – 2.07 (m, 2H), 1.66 (dd, *J* = 10.2, 4.8 Hz, 2H), 1.56 – 1.39 (m, 4H), 1.22 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.97, 143.90, 142.68, 140.10, 137.38, 129.00, 128.42, 128.26, 128.14, 128.02, 127.33, 125.62, 84.08, 60.99, 35.83, 32.23, 31.30, 29.12, 27.82, 27.06, 21.57.

IR (KBr): γ : 3270, 2961, 2924, 1593, 1487, 1447, 1327, 1261, 1156, 1093, 1024, 870, 801, 752, 695, 552 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{30}H_{37}NNaO_4S]^+$ requires 530.2336, found 530.2346.

(*R*)-4-methyl-*N*-(1-phenylnonyl)benzenesulfonamide (29)



To a flame-dried and N_2-purged Schlenk tube (10 mL) were added imine (0.05 mmol, 1 equiv.), $Pd_2(dba)_3$ (0.005 mmol, 2.3 mg), phosphoramidite (*R*)-**L9** (0.0075 mmol, 5.9 mg), **A1** (0.015 mmol, 2.6 mg), Thymoquinone (0.10 mmol, 16.4 mg), 4 Å MS (30 mg) and a stirring bar. The Schlenk tube was then evacuated and filled with nitrogen. This cycle was repeated three times and followed by the addition of anhydrous and degassed toluene (0.5 mL) and alkene (0.25 mmol, 5 equiv.) via a syringe, then the resulting mixture was stirred at 80 ℃ for 48 h. The mixture was filtered through Celite and concentrated in *vacuo*, and the residue was purified by column chromatography on silica gel (petroleum ether/ EtOAc = 10:1) to provide the desired product as a mixture of double bond migration. The mixture was dissolved in MeOH (1.0 mL), then 10% Pd/C (5.0 mg, 10 wt%) was added. The resulting solution was stirred at room temperature under an atmosphere of H_2 (balloon) overnight. After completion, the mixture was filtered through Celite and concentrated in *vacuo*, and the residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc = 10/1) to give the desired product as a white semisolid. Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 24%, 4.5 mg. Enantiomeric excess: 64%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 99/1, flow rate 1.0 mL/min, T = 30 ℃, 228 nm): t_R = 41.948 min (major), t_R = 66.692 min (minor). $[\alpha]_D^{20}$ = 15.1 (c 0.23, $CHCl_3$).

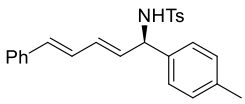
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.3 Hz, 2H), 7.20 – 7.08 (m, 5H), 7.05 – 6.96 (m, 2H), 4.73 (d, J = 7.1 Hz, 1H), 4.26 (q, J = 7.3 Hz, 1H), 2.35 (s, 3H), 1.81 – 1.61 (m, 1H), 1.18 (s, 13H), 0.86 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 141.1, 137.7, 129.3, 128.4, 127.3, 127.1, 126.5, 58.3, 37.7, 31.8, 29.3, 29.2, 29.1, 25.8, 22.6, 21.4, 14.1.

IR (KBr): γ : 3774, 2960, 2924, 2855, 1636, 1457, 1323, 1264, 1156, 1094, 1023, 801, 755, 700, 669, 557 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{22}H_{31}NNaO_2S]^+$ requires 396.1968, found 396.1975.

4-methyl-*N*-((*R*,2*E*,4*E*)-5-phenyl-1-(p-tolyl)penta-2,4-dien-1-yl)benzenesulfonamide (30)



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. 70%, 14.1 mg. *E/Z* = 20:1. Enantiomeric excess: 95%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 ℃, 290 nm): t_R = 29.174 min (major), t_R = 51.248 min (minor). $[\alpha]_D^{20}$ = -20.7 (c 0.71, $CHCl_3$).

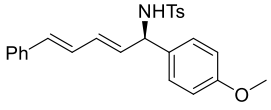
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.27 (m, 4H), 7.24 – 7.13 (m, 3H), 7.08 – 6.99 (m, 4H), 6.61 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.42 (d, *J* = 15.6 Hz, 1H), 6.15 (ddd, *J* = 15.2, 10.4, 1.2 Hz, 1H), 5.72 (dd, *J* = 15.1, 6.6 Hz, 1H), 4.98 (t, *J* = 6.8 Hz, 1H), 4.94 – 4.78 (m, 1H), 2.36 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.29, 137.69, 137.65, 136.95, 136.64, 133.47, 132.35, 132.27, 129.46, 129.39, 128.65, 127.77, 127.60, 127.37, 126.98, 126.39, 59.34, 21.53, 21.10.

IR (KBr): γ : 3283, 2962, 2924, 2858, 1642, 1445, 1325, 1265, 1155, 1092, 1028, 807, 753, 669, 553 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{25}NNaO_2S]^+$ requires 426.1498, found 426.1503.

***N*-((*R*,2*E*,4*E*)-1-(4-methoxyphenyl)-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (31)**



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 41%, 8.6 mg. *E/Z* = 18:1. Enantiomeric excess: 92%, determined by HPLC (CHIRALPAK IG, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 32.973 min (major), t_R = 46.903 min (minor). $[\alpha]_D^{20}$ = -18.9 (c 0.44, $CHCl_3$).

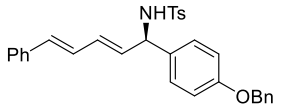
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.60 (m, 2H), 7.39 – 7.27 (m, 4H), 7.24 – 7.15 (m, 3H), 7.12 – 7.02 (m, 2H), 6.89 – 6.69 (m, 2H), 6.68 – 6.53 (m, 1H), 6.42 (d, *J* = 15.6 Hz, 1H), 6.14 (ddt, *J* = 15.2, 10.5, 0.9 Hz, 1H), 5.72 (dd, *J* = 15.2, 6.6 Hz, 1H), 4.98 (td, *J* = 6.8, 1.3 Hz, 1H), 4.81 (d, *J* = 6.9 Hz, 1H), 3.77 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.24, 143.25, 137.75, 136.96, 133.49, 132.33, 132.30, 131.75, 129.45, 128.65, 128.31, 127.77, 127.58, 127.36, 126.39, 114.07, 59.03, 55.31, 21.50.

IR (KBr): γ : 3272, 2961, 2925, 1606, 1509, 1446, 1325, 1258, 1155, 1091, 1030, 810, 755, 668, 555 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{25}NNaO_3S]^+$ requires 442.1447, found 442.1456.

***N*-((*R*,2*E*,4*E*)-1-(4-(benzyloxy)phenyl)-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (32)**



According general procedure A: Thymoquinone (2.4 equiv.), reaction run for 36 h, Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 64%, 15.8 mg. *E/Z* = 17:1. Enantiomeric excess: 86%, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 312 nm): t_R = 31.068 min (major), t_R = 36.649 min (minor). $[\alpha]_D^{20}$ = -5.9 (c 0.79, $CHCl_3$).

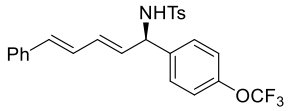
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.43 – 7.27 (m, 9H), 7.25 – 7.16 (m, 3H), 7.12 – 7.01 (m, 2H), 6.91 – 6.78 (m, 2H), 6.61 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.42 (d, *J* = 15.7 Hz, 1H), 6.15 (ddd, *J* = 15.1, 10.5, 1.3 Hz, 1H), 5.71 (dd, *J* = 15.1, 6.6 Hz, 1H), 5.02 (s, 2H), 4.98 (td, *J* = 6.7, 1.3 Hz, 1H), 4.81 (d, *J* = 6.8 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.43, 143.30, 137.67, 136.93, 136.77, 133.51, 132.35, 132.22, 131.98, 129.48, 128.66, 128.35, 128.09, 127.79, 127.55, 127.47, 127.37, 126.40, 114.98, 70.03, 59.03, 21.55.

IR (KBr): γ : 3272, 2961, 2924, 2857, 1605, 1507, 1450, 1324, 1260, 1154, 1092, 1023, 805, 736, 695, 668, 565 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{31}H_{29}NNaO_3S]^+$ requires 518.1760, found 518.1763.

4-methyl-*N*-((*R*,2*E*,4*E*)-5-phenyl-1-(4-(trifluoromethoxy)phenyl)penta-2,4-dien-1-yl)benzenesulfonamide (33)



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 59%, 13.9 mg. *E/Z* = 14:1. Enantiomeric excess: 95%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ℃, 254nm): t_R = 15.905 min (major), t_R = 33.943 min (minor). $[\alpha]_D^{20}$ = -28.7 (c 0.70, $CHCl_3$). m.p. 128-130 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 2H), 7.39 – 7.28 (m, 4H), 7.28 – 7.22 (m, 3H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.15 – 7.08 (m, 2H), 6.60 (dd, *J* = 15.7, 10.5 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 6.10 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.68 (dd, *J* = 15.2, 6.3 Hz, 1H), 5.17 – 4.98 (m, 2H), 2.36 (s, 3H).

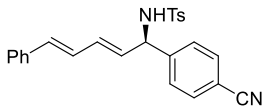
^{19}F NMR (471 MHz, $CDCl_3$) δ -72.87.

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.80, 143.77, 140.20, 137.32, 136.61, 134.55, 133.47, 130.62, 129.58, 129.04, 128.71, 128.08, 127.22, 126.95, 126.49, 121.52, 118.71 (d, J = 320.8 Hz), 58.78, 21.46.

IR (KBr): γ : 3271, 3028, 2961, 2925, 2857, 1599, 1497, 1421, 1327, 1257, 1213, 1138, 1093, 1023, 887, 805, 742, 669, 608, 564 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{22}F_3NNaO_3S]^+$ requires 496.1165, found 496.1172.

***N*-((*R*,2*E*,4*E*)-1-(4-cyanophenyl)-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (34)**



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 4:1) gave the product as a white solid. Yield: 89%, 18.4 mg. *E/Z* = 13:1. Enantiomeric excess: 92%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 26.619 min (major), t_R = 29.832 min (minor). $[\alpha]_D^{20}$ = -32.9 (c 0.92, $CHCl_3$).

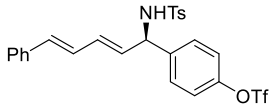
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.36 – 7.28 (m, 6H), 7.26 – 7.13 (m, 3H), 6.58 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.42 (d, *J* = 15.7 Hz, 1H), 6.06 (ddd, *J* = 14.8, 10.4, 1.2 Hz, 1H), 5.64 (dd, *J* = 15.1, 7.0 Hz, 1H), 5.31 (d, *J* = 7.2 Hz, 1H), 5.06 (t, *J* = 7.1 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.94, 143.84, 137.23, 136.54, 134.74, 133.79, 132.40, 130.07, 129.62, 128.73, 128.15, 127.90, 127.25, 126.86, 126.50, 118.52, 111.56, 59.19, 21.54.

IR (KBr): γ : 3267, 2961, 2924, 2856, 2229, 1602, 1442, 1328, 1263, 1157, 1092, 1025, 807, 742, 695, 668, 569 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{22}N_2NaO_2S]^+$ requires 437.1294, found 437.1300.

4-((*R*,2*E*,4*E*)-1-((4-methylphenyl)sulfonamido)-5-phenylpenta-2,4-dien-1-yl)phenyl trifluoromethanesulfonate (35)



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 68%, 18.2 mg. *E/Z* = 14:1. Enantiomeric excess: 94%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 10.967 min (major), t_R = 20.203 min (minor). $[\alpha]_D^{20}$ = -28.3 (c 0.92, $CHCl_3$). m.p. 125-127 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.3 Hz, 2H), 7.38 – 7.28 (m, 4H), 7.25 – 7.21 (m, 1H), 7.20 – 7.14 (m, 4H), 7.08 – 6.79 (m, 2H), 6.72 – 6.56 (m, 1H), 6.43 (d, J = 15.6 Hz, 1H), 6.12 (ddd, J = 15.0, 10.4, 1.3 Hz, 1H), 5.71 (dd, J = 15.2, 6.7 Hz, 1H), 5.22 (d, J = 7.3 Hz, 1H), 5.14 – 5.00 (m, 1H), 2.34 (s, 3H).

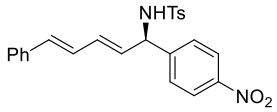
^{19}F NMR (376 MHz, $CDCl_3$) δ -57.90.

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.59 (q, *J* = 2.0 Hz), 143.55, 138.29, 137.46, 136.73, 134.18, 133.04, 131.20, 129.46, 128.68, 128.61, 127.96, 127.24, 127.18, 126.45, 121.07, 120.38 (d, J = 257.4 Hz), 58.90, 21.41.

IR (KBr): γ : 3270, 2960, 2925, 1505, 1442, 1326, 1261, 1219, 1159, 1092, 1024, 991, 808, 670, 566 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{25}H_{22}F_3NNaO_5S_2]^+$ requires 560.0784, found 560.0792.

4-methyl-*N*-((*R*,2*E*,4*E*)-1-(4-nitrophenyl)-5-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (36)



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 64%, 13.8 mg. *E/Z* = 11:1. Enantiomeric excess: 86%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ℃, 292 nm): t_R = 42.744 min (major), t_R = 46.079 min (minor). $[\alpha]_D^{20}$ = -23.0 (c 0.70, $CHCl_3$).

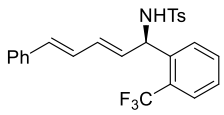
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.02 (m, 2H), 7.67 – 7.56 (m, 2H), 7.40 – 7.27 (m, 7H), 7.23 – 7.15 (m, 2H), 6.59 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.44 (d, *J* = 15.6 Hz, 1H), 6.08 (ddd, *J* = 15.0, 10.4, 1.2 Hz, 1H), 5.67 (dd, *J* = 15.1, 6.9 Hz, 1H), 5.22 (d, *J* = 6.8 Hz, 1H), 5.12 (t, *J* = 7.0 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.33, 146.85, 143.94, 137.18, 136.49, 134.93, 133.99, 129.87, 129.64, 128.72, 128.18, 128.04, 127.26, 126.77, 126.51, 123.80, 59.00, 21.50.

IR (KBr): γ : 3272, 2962, 2925, 1601, 1518, 1446, 1342, 1261, 1156, 1094, 1024, 802, 742, 696, 668, 563 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{24}H_{22}N_2NaO_4S]^+$ requires 457.1193, found 457.1198.

4-methyl-*N*-((*R*,2*E*,4*E*)-5-phenyl-1-(2-(trifluoromethyl)phenyl)penta-2,4-dien-1-yl)benzenesulfonamide (37)



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 87%, 19.8 mg. *E/Z* = 14:1. Enantiomeric excess: 93%, determined by HPLC (CHIRALPAK AD, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 7.469 min (major), t_R = 8.604 min (minor). $[\alpha]_D^{20}$ = -45.8 (c 1.00, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.63 (m, 2H), 7.59 – 7.52 (m, 1H), 7.51 – 7.37 (m, 2H), 7.37 – 7.27 (m, 5H), 7.24 – 7.12 (m, 3H), 6.59 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.40 (d, *J* = 15.6 Hz, 1H), 6.03 (dd, *J* = 15.2, 10.3 Hz, 1H), 5.87 – 5.66 (m, 1H), 5.46 – 5.28 (m, 2H), 2.35 (s, 3H).

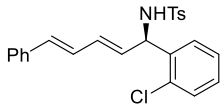
^{19}F NMR (376 MHz, $CDCl_3$) δ -58.24.

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.48, 138.72, 136.99, 136.75, 134.18, 132.81, 132.29, 131.73, 129.47, 128.90, 128.64, 127.89, 127.61, 127.51 (d, J = 13.3 Hz), 127.36, 127.31, 126.97 (d, J = 35.6 Hz), 126.44, 125.86 (q, J = 5.9 Hz), 124.00 (d, J = 274.4 Hz), 55.09 (d, J = 2.4 Hz), 21.50.

IR (KBr): γ : 3273, 2962, 2924, 1449, 1313, 1263, 1158, 1118, 1031, 991, 805, 668, 562 cm^{-1}.

HRMS (ESI): m/z [M + Na]$^+$ calcd for [$C_{25}H_{22}F_3NNaO_2S$]$^+$ requires 480.1216, found 480.1220.

***N*-((*R*,2*E*,4*E*)-1-(2-chlorophenyl)-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (38)**



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 82%, 17.3 mg. *E/Z* > 20:1. Enantiomeric excess: 92%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 15.429 min (major), t_R = 25.014 min (minor). $[\alpha]_D^{20}$ = -26.3 (c 0.87, $CHCl_3$). m.p. 111-113 ℃.

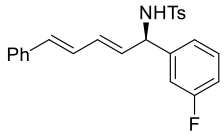
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.26 (m, 4H), 7.24 – 7.17 (m, 3H), 7.17 – 7.08 (m, 4H), 6.63 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.42 (d, *J* = 15.7 Hz, 1H), 6.10 (ddd, *J* = 15.0, 10.5, 1.4 Hz, 1H), 5.76 (dd, *J* = 15.2, 6.1 Hz, 1H), 5.47 – 5.39 (m, 1H), 5.32 (d, *J* = 7.7 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.34, 137.17, 136.81, 133.96, 132.81, 132.56, 130.70, 129.93, 129.42, 129.06, 128.88, 128.65, 127.86, 127.40, 127.21, 127.15, 126.44, 57.01, 21.51.

IR (KBr): γ : 3273, 2961, 2924, 1441, 1328, 1262, 1157, 1093, 1026, 803, 752, 697, 668, 563 cm^{-1}.

HRMS (ESI): m/z [M + Na]$^+$ calcd for [$C_{24}H_{22}ClNNaO_2S$]$^+$ requires 446.0952, found 446.0959.

***N*-((*R*,2*E*,4*E*)-1-(3-fluorophenyl)-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (39)**



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 60%, 12.2 mg. *E/Z* = 16:1. Enantiomeric excess: 91%, determined by HPLC (CHIRALPAK IG, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 17.618 min (major), t_R = 21.758 min (minor). $[\alpha]_D^{20}$ = -50.0 (c 0.61, $CHCl_3$). m.p. 124-126 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.3 Hz, 2H), 7.37 – 7.28 (m, 4H), 7.25 – 7.17 (m, 4H), 6.97 (dt, J = 7.8, 1.3 Hz, 1H), 6.91 (tdd, J = 8.3, 2.6, 1.0 Hz, 1H), 6.84 (dt, J = 9.8, 2.1 Hz, 1H), 6.60 (ddd, J = 15.7, 10.4, 0.8 Hz, 1H), 6.43 (d, J = 15.6 Hz, 1H), 6.24 – 5.96 (m, 1H), 5.68 (dd, J = 15.2, 6.3 Hz, 1H), 5.12 – 4.94 (m, 2H), 2.36 (s, 3H).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 2H), 7.36 – 7.27 (m, 4H), 7.25 – 7.16 (m, 4H), 6.96 (dt, *J* = 7.8, 1.3 Hz, 1H), 6.90 (tdd, *J* = 8.4, 2.6, 1.0 Hz, 1H), 6.83 (dt, *J* = 9.7, 2.1 Hz, 1H), 6.60 (dd, *J* = 15.7, 10.4 Hz, 1H), 6.43 (d, *J* = 15.6 Hz, 1H), 6.11 (dd, *J* = 14.4, 10.4 Hz, 1H), 5.68 (dd, *J* = 15.2, 6.3 Hz, 1H), 5.11 – 4.94 (m, 2H), 2.36 (s, 3H).

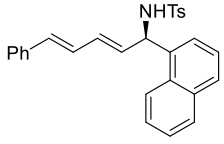
^{19}F NMR (376 MHz, $CDCl_3$) δ -112.36.

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.81 (d, J = 246.9 Hz), 143.56, 142.14 (d, J = 6.6 Hz), 137.43, 136.75, 134.12, 133.10, 131.09, 130.24 (d, J = 8.1 Hz), 129.53, 128.68, 127.94, 127.30, 127.21, 126.45, 122.73 (d, J = 2.9 Hz), 114.72 (d, J = 21.1 Hz), 114.11 (d, J = 22.4 Hz), 59.05 (d, J = 1.9 Hz), 21.51.

IR (KBr): γ : 3270, 2961, 2924, 1593, 1487, 1447, 1327, 1261, 1156, 1093, 1024, 870, 801, 752, 695, 552 cm^{-1}.

HRMS (ESI): m/z [M + Na]$^+$ calcd for [$C_{24}H_{22}FNNaO_2S$]$^+$ requires 430.1247, found 430.1251.

4-methyl-*N*-((*R*,2*E*,4*E*)-1-(naphthalen-1-yl)-5-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (40)



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 70%, 15.3 mg. *E/Z* = 20:1. Enantiomeric excess: 92%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 26.699 min (major), t_R = 43.885 min (minor). $[\alpha]_D^{20}$ = 22.9 (c 0.95, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dt, *J* = 7.0, 3.5 Hz, 1H), 7.81 (dt, *J* = 7.0, 3.5 Hz, 1H), 7.72 (dt, *J* = 7.4, 3.6 Hz, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.47 (dt, *J* = 6.4, 3.4 Hz, 2H), 7.37 – 7.26 (m, 6H), 7.24 – 7.14 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.63 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.35 (d, *J* = 15.6 Hz, 1H), 6.18 (ddd, *J* = 15.2, 10.4, 1.4 Hz, 1H), 5.94 (dd, *J* = 15.2, 5.9 Hz, 1H), 5.80 (t, *J* = 6.8 Hz, 1H), 5.09 (d, *J* = 6.9 Hz, 1H), 2.31 (s, 3H).

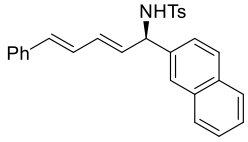
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.20, 137.50, 136.92, 135.00, 133.99, 133.58, 132.83, 132.06, 130.37, 129.29, 128.87,

128.78, 128.64, 127.78, 127.54, 127.25, 126.58, 126.39, 125.86, 125.52, 125.18, 123.30, 56.47, 21.45.

IR (KBr): γ : 3276, 2924, 1442, 1327, 1264, 1156, 1091, 1026, 991, 922, 804, 739, 695, 668, 566 cm^{-1}.

HRMS (ESI): m/z [M + Na]$^+$ calcd for $[C_{28}H_{25}NNaO_2S]^+$ requires 462.1498, found 462.1504.

4-methyl-*N*-((*R*,2*E*,4*E*)-1-(naphthalen-2-yl)-5-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (41)



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 66%, 12.9 mg. *E/Z* = 16:1. Enantiomeric excess: 74%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 10.365 min (major), t_R = 15.608 min (minor). $[\alpha]_D^{20}$ = -5.6 (c 0.72, $CHCl_3$). m.p. 139-141 ℃.

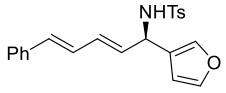
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 6.1, 3.4 Hz, 1H), 7.68 (dd, *J* = 9.1, 6.7 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.52 (s, 1H), 7.45 (dt, *J* = 6.2, 3.4 Hz, 2H), 7.38 – 7.17 (m, 6H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.64 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.42 (d, *J* = 15.7 Hz, 1H), 6.19 (ddd, *J* = 15.0, 10.4, 1.3 Hz, 1H), 5.82 (dd, *J* = 15.2, 6.4 Hz, 1H), 5.20 (t, *J* = 6.9 Hz, 1H), 5.11 (d, *J* = 7.4 Hz, 1H), 2.23 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.30, 137.61, 136.90, 136.67, 133.78, 133.13, 132.86, 132.83, 131.92, 129.35, 128.65, 128.62, 127.93, 127.83, 127.59, 127.51, 127.30, 126.43, 126.30, 126.21, 126.13, 124.88, 59.69, 21.36.

IR (KBr): γ : 3270, 2962, 2924, 2855, 1444, 1326, 1263, 1155, 1093, 1026, 863, 808, 751, 696, 669, 554 cm^{-1}.

HRMS (ESI): m/z [M + Na]$^+$ calcd for $[C_{28}H_{25}NNaO_2S]^+$ requires 462.1498, found 462.1502.

***N*-((*R*,2*E*,4*E*)-1-(furan-3-yl)-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (42)**



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 67%, 12.7 mg. *E/Z* = 19:1. Enantiomeric excess: 94%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 17.078 min (major), t_R = 22.867 min (minor). $[\alpha]_D^{20}$ = -34.2 (c 0.64, $CHCl_3$).

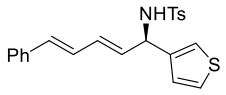
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.68 (m, 2H), 7.39 – 7.29 (m, 5H), 7.28 – 7.15 (m, 4H), 6.60 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.44 (d, *J* = 15.7 Hz, 1H), 6.27 – 6.13 (m, 2H), 5.67 (dd, *J* = 15.2, 6.8 Hz, 1H), 5.00 (t, *J* = 7.2 Hz, 1H), 4.82 (d, *J* = 7.7 Hz, 1H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.67, 143.50, 139.88, 137.77, 136.85, 133.83, 132.68, 130.86, 129.57, 128.67, 127.87, 127.32, 126.42, 125.00, 109.10, 51.82, 21.53.

IR (KBr): γ : 3270, 2961, 2924, 2856, 1442, 1326, 1262, 1156, 1093, 1025, 871, 801, 736, 694, 668, 556 cm^{-1}.

HRMS (ESI): m/z [M + Na]$^+$ calcd for $[C_{22}H_{21}NNaO_3S]^+$ requires 402.1134, found 402.1138.

4-methyl-*N*-((*R*,2*E*,4*E*)-5-phenyl-1-(thiophen-3-yl)penta-2,4-dien-1-yl)benzenesulfonamide (43)



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 77%, 15.2 mg. *E/Z* = 20:1. Enantiomeric excess: 96%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 298 nm): t_R = 12.353 min (major), t_R = 15.874 min (minor). $[\alpha]_D^{20}$ = -22.8 (c 0.76, $CHCl_3$).

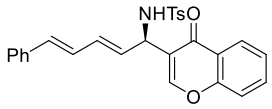
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H), 7.38 – 7.17 (m, 8H), 7.02 (dt, *J* = 2.8, 1.1 Hz, 1H), 6.85 (dd, *J* = 5.1, 1.3 Hz, 1H), 6.61 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.43 (d, *J* = 15.7 Hz, 1H), 6.16 (ddd, *J* = 15.0, 10.4, 1.2 Hz, 1H), 5.72 (dd, *J* = 15.1, 6.8 Hz, 1H), 5.12 (t, *J* = 7.2 Hz, 1H), 4.94 (dd, *J* = 7.7, 2.6 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.39, 140.75, 137.74, 136.89, 133.75, 132.58, 131.40, 129.52, 128.67, 127.84, 127.43, 127.29, 126.57, 126.42, 126.32, 122.34, 55.42, 21.52.

IR (KBr): γ : 3269, 3026, 2962, 2924, 2856, 1418, 1326, 1262, 1156, 1092, 1026, 915, 866, 802, 747, 667, 553 cm^{-1}.

HRMS (ESI): m/z [M + Na]$^+$ calcd for $[C_{22}H_{21}NNaO_2S_2]^+$ requires 418.0906, found 418.0910.

4-methyl-*N*-((*R*,2*E*,4*E*)-1-(4-oxo-4H-chromen-3-yl)-5-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (44)



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 72%, 16.4 mg. *E/Z* = 20:1. Enantiomeric excess: 80%, determined by HPLC (CHIRALPAK AD, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 29.065 min (major), t_R = 42.949 min (minor). $[\alpha]_D^{20}$ = -10.3 (c 0.83, $CHCl_3$). m.p. 57-59 ℃.

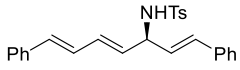
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.71 (s, 1H), 7.66 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.41 – 7.36 (m, 2H), 7.34 – 7.27 (m, 4H), 7.23 – 7.17 (m, 1H), 7.00 (dt, *J* = 8.0, 0.8 Hz, 2H), 6.61 (ddd, *J* = 15.7, 10.4, 0.8 Hz, 1H), 6.45 (d, *J* = 15.6 Hz, 1H), 6.35 – 6.15 (m, 2H), 5.99 – 5.87 (m, 1H), 4.81 (ddd, *J* = 9.5, 6.6, 1.3 Hz, 1H), 2.08 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.76, 155.97, 153.00, 143.12, 137.70, 136.87, 134.04, 133.85, 132.59, 130.14, 129.24, 128.62, 127.80, 127.46, 127.28, 126.43, 125.66, 125.36, 123.91, 121.61, 117.96, 55.61, 21.18.

IR (KBr): γ : 3259, 2962, 2924, 1638, 1464, 1408, 1330, 1262, 1158, 1093, 1026, 805, 738, 699, 670, 549 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{27}H_{23}NNaO_4S]^+$ requires 480.1240, found 480.1248.

***N*-((*R*,1*E*,4*E*,6*E*)-1,7-diphenylhepta-1,4,6-trien-3-yl)-4-methylbenzenesulfonamide (45)**



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 52%, 10.7 mg. *E/Z* = 12:1. Enantiomeric excess: 69%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 11.166 min (major), t_R = 21.045 min (minor). $[\alpha]_D^{20}$ = -11.1 (c 0.54, $CHCl_3$).

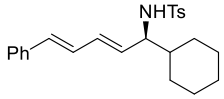
^{1}H NMR (400 MHz, Acetone-d_6) δ 8.28 (d, J = 8.8 Hz, 2H), 8.00 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.8 Hz, 1H), 7.40 (d, J = 7.4 Hz, 2H), 7.34 – 7.17 (m, 8H), 6.75 (dd, J = 15.7, 10.5 Hz, 1H), 6.50 (d, J = 15.7 Hz, 1H), 6.22 (dd, J = 15.2, 10.4 Hz, 1H), 5.86 (dd, J = 15.2, 7.1 Hz, 1H), 5.20 (ddd, J = 8.8, 7.2, 1.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.46, 137.96, 136.88, 136.07, 133.76, 132.66, 132.24, 130.96, 129.58, 128.66, 128.53, 127.99, 127.86, 127.50, 127.45, 127.14, 126.51, 126.44, 57.54, 21.45.

IR (KBr): γ : 3451, 3274, 2962, 2924, 1325, 1262, 1156, 1093, 1024, 803, 748, 696, 669 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{26}H_{25}NNaO_2S]^+$ requires 438.1498, found 438.1500.

***N*-((*S*,2*E*,4*E*)-1-cyclohexyl-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (46)**



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 77%, 15.2 mg. *E/Z* > 20:1. Enantiomeric excess: 94%, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 8.804 min (major), t_R = 10.207 min (minor). $[\alpha]_D^{20}$ = -63.0 (c 0.77, $CHCl_3$). m.p. 120-122 ℃.

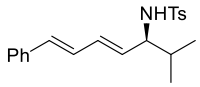
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.64 (m, 2H), 7.44 – 7.11 (m, 7H), 6.48 (dd, J = 15.7, 10.3 Hz, 1H), 6.29 (d, J = 15.7 Hz, 1H), 5.86 (dd, J = 15.2, 10.4 Hz, 1H), 5.36 (dd, J = 15.2, 7.9 Hz, 1H), 4.95 – 4.55 (m, 1H), 3.64 (td, J = 8.1, 5.9 Hz, 1H), 2.32 (s, 3H), 1.79 – 1.66 (m, 3H), 1.66 – 1.54 (m, 2H), 1.41 (tdt, J = 12.0, 6.3, 3.1 Hz, 1H), 1.23 – 1.05 (m, 3H), 0.95 (dtd, J = 14.5, 11.9, 9.1 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.18, 138.13, 137.08, 132.60, 132.46, 131.34, 129.46, 128.62, 127.81, 127.62, 127.35, 126.27, 61.06, 42.92, 29.00, 28.95, 26.25, 26.00, 25.98, 21.47.

IR (KBr): γ : 3274, 2926, 2854, 1444, 1324, 1261, 1156, 1093, 1026, 991, 808, 742, 669, 556 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{24}H_{29}NNaO_2S]^+$ requires 418.1811, found 418.1814.

4-methyl-*N*-((*S*,4*E*,6*E*)-2-methyl-7-phenylhepta-4,6-dien-3-yl)benzenesulfonamide (47)



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 66%, 11.7 mg. *E/Z* > 20:1.

Enantiomeric excess: 88%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 288 nm): t_R = 8.701 min (major), t_R = 9.546 min (minor). $[\alpha]_D^{20}$ = -79.7 (c 0.59, $CHCl_3$).

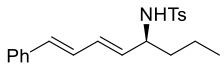
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.42 – 7.14 (m, 7H), 6.50 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.31 (d, *J* = 15.6 Hz, 1H), 5.91 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.38 (dd, *J* = 15.2, 7.7 Hz, 1H), 4.69 (d, *J* = 8.4 Hz, 1H), 3.65 (td, *J* = 8.0, 5.5 Hz, 1H), 2.33 (s, 3H), 1.77 (dq, *J* = 13.2, 6.7 Hz, 1H), 0.87 (dd, *J* = 11.4, 6.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.24, 138.04, 137.05, 132.69, 132.65, 130.94, 129.50, 128.63, 127.81, 127.65, 127.34, 126.28, 61.51, 33.16, 21.49, 18.42, 18.33.

IR (KBr): γ : 3274, 2962, 2925, 1441, 1323, 1262, 1156, 1094, 1028, 804, 745, 694, 668, 561 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{21}H_{25}NNaO_2S]^+$ requires 378.1498, found 378.1506.

4-methyl-*N*-((*S*,5*E*,7*E*)-8-phenylocta-5,7-dien-4-yl)benzenesulfonamide (48)



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 58%, 10.2 mg. *E/Z* >20:1. Enantiomeric excess: 83%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 9.242 min (major), t_R = 10.638 min (minor). $[\alpha]_D^{20}$ = -72.8 (c 0.52, $CHCl_3$).

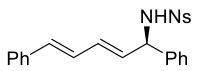
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.68 (m, 2H), 7.55 – 7.03 (m, 7H), 6.51 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.37 (d, *J* = 15.6 Hz, 1H), 6.02 (dd, *J* = 15.2, 10.3 Hz, 1H), 5.38 (dd, *J* = 15.2, 7.4 Hz, 1H), 4.53 (d, *J* = 7.8 Hz, 1H), 3.85 (p, *J* = 7.2 Hz, 1H), 2.36 (s, 3H), 1.56 – 1.41 (m, 2H), 1.37 – 1.23 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.28, 138.10, 137.04, 132.95, 132.85, 131.78, 129.53, 128.64, 127.78, 127.67, 127.33, 126.32, 55.78, 38.02, 21.51, 18.67, 13.67.

IR (KBr): γ : 3274, 3025, 2961, 2926, 2864, 1450, 1324, 1261, 1155, 1093, 1024, 804, 744, 668, 557 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{21}H_{25}NNaO_2S]^+$ requires 378.1498, found 378.1508.

***N*-((*R*,2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-yl)-4-nitrobenzenesulfonamide (49)**



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 83%, 17.4 mg. *E/Z* = 12:1. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 288 nm): t_R = 11.466 min (major), t_R = 9.451 min (minor). $[\alpha]_D^{20}$ = 3.3 (c 0.88, $CHCl_3$). m.p. 162-164 ℃.

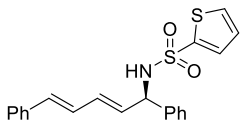
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 – 8.13 (m, 2H), 7.87 – 7.79 (m, 2H), 7.42 – 7.28 (m, 4H), 7.26 – 7.16 (m, 4H), 7.15 – 7.09 (m, 2H), 6.62 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.47 (d, *J* = 15.7 Hz, 1H), 6.20 (dd, *J* = 15.1, 10.4 Hz, 1H), 5.90 – 5.68 (m, 1H), 5.25 – 5.11 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.71, 146.55, 138.62, 136.54, 134.55, 133.37, 130.98, 128.87, 128.72, 128.43, 128.28, 128.11, 127.14, 126.90, 126.49, 123.95, 60.05.

IR (KBr): γ : 3283, 2961, 2924, 2856, 1529, 1452, 1345, 1309, 1263, 1160, 1095, 1023, 800, 753, 696 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{23}H_{20}N_2NaO_4S]^+$ requires 443.1036, found 443.1041.

***N*-((*R*,2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-yl)thiophene-2-sulfonamide (50)**



According general procedure A: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 92%, 17.5 mg. *E/Z* = 16:1. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ℃, 288 nm): t_R = 59.979 min (major), t_R = 34.769 min (minor). $[\alpha]_D^{20}$ = -16.1 (c 0.88, $CHCl_3$).

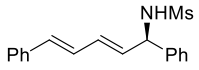
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.43 (m, 2H), 7.43 – 7.10 (m, 10H), 6.96 (dd, *J* = 5.0, 3.7 Hz, 1H), 6.66 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.48 (d, *J* = 15.7 Hz, 1H), 6.23 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.80 (dd, *J* = 15.1, 5.9 Hz, 1H), 5.19 – 5.03 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 141.64, 139.37, 136.86, 133.84, 132.70, 132.64, 131.99, 131.70, 128.82, 128.67, 128.03, 127.86, 127.44, 127.20, 127.03, 126.46, 59.84.

IR (KBr): γ : 3275, 2961, 2925, 2855, 1448, 1407, 1332, 1262, 1155, 1093, 1021, 799, 698, 588 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{21}H_{19}NNaO_2S_2]^+$ requires 404.0749, found 404.0747.

***N*-((*R*,2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-yl)methanesulfonamide (51)**



According general procedure A: Reaction run for 30 h, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 58%, 9.0 mg. *E/Z* = 14:1. Enantiomeric excess: 83%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 7.716 min (major), t_R = 9.015 min (minor). $[\alpha]_D^{20}$ = -12.5 (c 0.91, $CHCl_3$). m.p. 59-61 ℃.

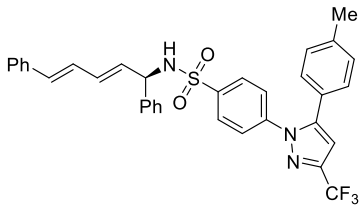
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 9H), 7.28 – 7.18 (m, 1H), 6.87 – 6.71 (m, 1H), 6.58 (d, *J* = 15.7 Hz, 1H), 6.47 – 6.34 (m, 1H), 5.94 (dd, *J* = 15.2, 6.8 Hz, 1H), 5.21 (td, *J* = 7.0, 1.3 Hz, 1H), 4.89 (d, *J* = 7.0 Hz, 1H), 2.77 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 139.83, 136.75, 134.26, 132.99, 132.09, 129.11, 128.70, 128.32, 127.98, 127.28, 127.19, 126.51, 59.62, 42.30.

IR (KBr): γ : 3273, 3026, 2961, 2925, 1447, 1319, 1264, 1150, 1095, 1026, 988, 800, 754, 698, 517 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{18}H_{19}NNaO_2S]^+$ requires 336.1029, found 336.1038.

***N*-((*R*,2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-yl)-4-(5-(p-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (52)**



According general procedure B: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 67%, 20.0 mg. *E/Z* > 20:1. Enantiomeric excess: 91%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 7.154 min (major), t_R = 11.364 min (minor). $[\alpha]_D^{20}$ = -17.4 (c 0.81, $CHCl_3$). m.p. 65-67 ℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.38 – 7.34 (m, 2H), 7.34 – 7.18 (m, 9H), 7.18 – 7.12 (m, 4H), 7.08 – 7.02 (m, 2H), 6.71 (s, 1H), 6.66 – 6.56 (m, 1H), 6.46 (d, *J* = 15.6 Hz, 1H), 6.19 (ddd, *J* = 14.9, 10.3, 1.2 Hz, 1H), 5.74 (dd, *J* = 15.2, 6.7 Hz, 1H), 5.08 (td, *J* = 6.7, 1.3 Hz, 1H), 4.95 (d, *J* = 6.7 Hz, 1H), 2.36 (s, 3H).

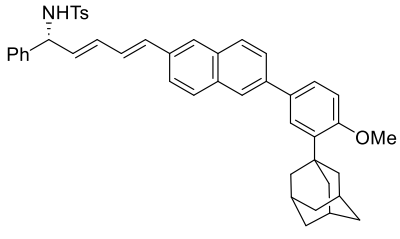
^{19}F NMR (376 MHz, CDCl3) δ -62.37.

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.2, 144.05 (d, J = 38.5 Hz), 142.3, 140.2, 139.7, 139.3, 136.7, 134.2, 133.0, 131.6, 129.7, 128.9, 128.7, 128.6, 128.2, 128.2, 127.9, 127.2, 127.1, 126.5, 125.8, 125.2, 121.12 (d, J = 269.2 Hz), 106.4, 59.8, 21.3.

IR (KBr): γ : 3257, 2961, 2924, 2856, 1596, 1495, 1466, 1411, 1311, 1265, 1236, 1159, 1069, 1024, 802, 744, 697, 622, 559 cm^{-1}.

HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{34}H_{29}F_3N_3O_2S]^+$ requires 600.1927, found 600.1927.

***N*-((*R*,2*E*,4*E*)-5-(6-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (53) (Known compound).[4]**



According general procedure B: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white solid. Yield: 88%, 29.9 mg. *E/Z* = 19:1. Enantiomeric excess: 95%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 10.813 min (major), t_R = 15.717 min (minor). $[\alpha]_D^{20}$ = -21.7 (c 1.50, $CHCl_3$). m.p. 100-102 ℃.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 1.9 Hz, 1H), 7.79 (t, *J* = 8.8 Hz, 2H), 7.74 – 7.62 (m, 4H), 7.57 (d, *J* = 2.4 Hz, 1H), 7.55 – 7.38 (m, 2H), 7.31 – 7.08 (m, 7H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.73 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.58 (d, *J* = 15.6 Hz, 1H), 6.20 (dd, *J* = 15.1, 10.4 Hz, 1H), 5.76 (dd, *J* = 15.1, 6.7 Hz, 1H), 5.06 (t, *J* = 6.9 Hz, 1H), 4.96 (d, *J* = 7.2 Hz, 1H), 3.88 (s, 3H), 2.35 (s, 3H), 2.18 (s, 6H), 2.10 (s, 3H), 1.80 (s, 6H).

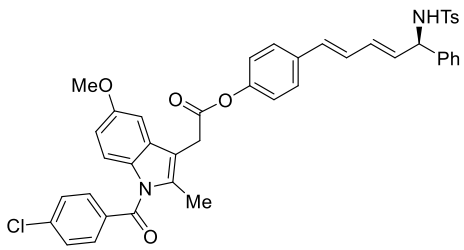
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.66, 143.33, 139.70, 139.18, 138.92, 137.74, 134.13, 133.83, 133.48, 133.01, 132.72, 132.39, 132.07, 129.49, 128.74, 128.45, 128.37, 127.87, 127.66, 127.38, 127.09, 126.38, 126.19, 125.84, 125.55, 124.82,

123.65, 112.13, 59.62, 55.19, 40.66, 37.22, 37.18, 29.16, 21.52.

IR (KBr): γ : 3270, 2907, 2851, 1496, 1453, 1325, 1265, 1237, 1157, 1093, 1027, 989, 810, 746, 701, 670, 560 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{45}H_{45}NNaO_3S]^+$ requires 702.3012, found 702.3012.

4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)phenyl 2-(1-(4-chlorobenzoyl)-2,5-dimethyl-1*H*-indol-3-yl)acetate (54)



According general procedure B: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 4:1) gave the product as a white solid. Yield: 81%, 30.1 mg. *E/Z* = 20:1. Enantiomeric excess: 96%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 46.828 min (major), t_R = 91.820 min (minor). $[\alpha]_D^{20}$ = -13.7 (c 1.52, $CHCl_3$). m.p. 159-161 ℃.

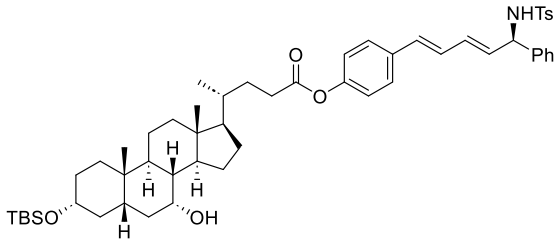
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.60 (m, 4H), 7.50 – 7.43 (m, 2H), 7.33 – 7.28 (m, 2H), 7.25 – 7.10 (m, 7H), 7.05 (d, *J* = 2.5 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 1H), 6.69 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.54 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 6.13 (ddd, *J* = 15.1, 10.4, 1.2 Hz, 1H), 5.72 (dd, *J* = 15.1, 6.6 Hz, 1H), 5.02 (t, *J* = 7.1 Hz, 1H), 4.95 (d, *J* = 7.1 Hz, 1H), 3.89 (s, 2H), 3.83 (s, 3H), 2.44 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.27, 168.33, 156.15, 150.17, 143.31, 139.57, 139.38, 137.68, 136.25, 134.86, 133.83, 132.42, 132.33, 131.22, 130.87, 129.45, 129.17, 128.73, 127.88, 127.83, 127.32, 127.29, 127.05, 121.62, 115.05, 111.95, 111.82, 101.26, 59.52, 55.76, 30.58, 21.50, 13.45.

IR (KBr): γ : 3276, 2960, 2925, 2855, 1755, 1681, 1598, 1474, 1403, 1322, 1262, 1217, 1158, 1126, 1092, 921, 804, 752, 700, 669, 560 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{43}H_{37}ClN_2NaO_6S]^+$ requires 767.1953, found 761.1957.

4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)phenyl (*R*)-4-((3*R*,5*R*,7*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-((tert-butyldimethylsilyl)oxy)-7-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (55)



According general procedure B: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 2:1) gave the product as a white semisolid. Yield: 65%, 29.0 mg. *E/Z* > 20:1. Diastereomeric excess: 95%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 291 nm): t_R = 11.699 min (major), t_R = 19.372 min (minor). $[\alpha]_D^{20}$ = -6.0 (c 1.63, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.56 (m, 2H), 7.30 – 7.26 (m, 2H), 7.21 – 7.12 (m, 5H), 7.12 – 7.06 (m, 2H), 7.03 – 6.94 (m, 2H), 6.51 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.35 (d, *J* = 15.6 Hz, 1H), 6.08 (ddd, *J* = 15.1, 10.4, 1.3 Hz, 1H), 5.67 (dd, *J* = 15.1, 6.6 Hz, 1H), 4.98 (t, *J* = 6.6 Hz, 1H), 4.87 (d, *J* = 7.1 Hz, 1H), 3.78 (q, *J* = 3.1 Hz, 1H), 3.45 – 3.33 (m, 1H), 2.54 (ddd, *J* = 14.9, 9.6, 4.9 Hz, 1H), 2.42 (ddd, *J* = 15.7, 9.0, 6.8 Hz, 1H), 2.31 (s, 3H), 2.15 (td, *J* = 13.3, 11.1 Hz, 1H), 1.96 – 1.70 (m, 6H), 1.65 – 1.02 (m, 18H), 0.94 (d, *J* = 6.2 Hz, 3H), 0.84 (d, *J* = 3.5 Hz, 12H), 0.62 (s, 3H), -0.00 (s, 6H).

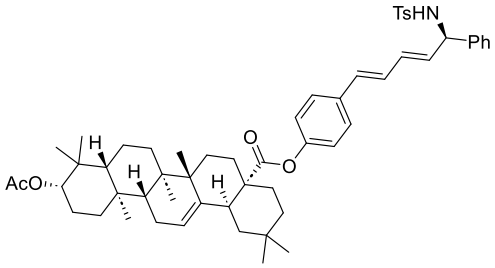
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.70, 150.30, 143.31, 139.59, 137.69, 134.58, 132.61, 132.45, 132.19, 129.45, 128.73, 127.87, 127.62, 127.33, 127.30, 127.06, 121.80, 72.90, 68.57, 59.54, 55.79, 50.50, 42.75, 41.60, 40.11, 39.65, 39.48, 35.56, 35.38, 35.09, 34.68, 32.76, 31.35, 31.12, 30.94, 28.22, 25.99, 23.74, 22.82, 21.51, 20.58, 18.33, 18.31, 11.82, -4.52.

IR (KBr): γ : 3554, 3275, 2929, 2858, 1755, 1501, 1485, 1374, 1327, 1261, 1202, 1158, 1091, 1022, 926, 869, 803, 754, 700, 669, 560 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{54}H_{75}NNaO_6SSi]^+$ requires 916.4977, found 916.4976.

4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)phenyl

(4*aS*,6*aS*,6*bR*,8*aR*,10*S*,12*aR*,12*bR*,14*bS*)-10-acetoxy-2,2,6*a*,6*b*,9,9,12*a*-heptamethyl-1,3,4,5,6,6*a*,6*b*,7,8,8*a*,9,10,11,12,12*a*,12*b*,13,14*b*-octadecahydropicene-4a(2*H*)-carboxylate (56)



According general procedure B: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 10:1) gave the product as a white semisolid. Yield: 66%, 29.2 mg. *E/Z* = 12:1. Diastereomeric excess: 94%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 8.720 min (major), t_R = 13.431 min (minor). $[\alpha]_D^{20}$ = 14.6 (c 1.76, $CHCl_3$).

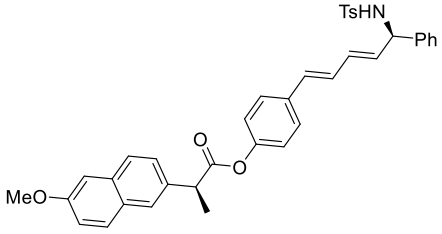
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.37 – 7.29 (m, 2H), 7.25 – 7.10 (m, 7H), 7.00 – 6.93 (m, 2H), 6.54 (dd, *J* = 15.5, 10.3 Hz, 1H), 6.39 (d, *J* = 15.6 Hz, 1H), 6.12 (ddd, *J* = 15.1, 10.4, 1.2 Hz, 1H), 5.72 (dd, *J* = 15.1, 6.6 Hz, 1H), 5.34 (t, *J* = 3.6 Hz, 1H), 5.05 – 5.00 (m, 1H), 4.96 (d, *J* = 7.1 Hz, 1H), 4.54 – 4.45 (m, 1H), 2.97 (dd, *J* = 13.9, 4.6 Hz, 1H), 2.36 (s, 2H), 2.05 (s, 4H), 1.93 – 1.86 (m, 3H), 1.82 – 1.21 (m, 16H), 1.18 (s, 4H), 1.10 – 1.00 (m, 1H), 0.97 – 0.92 (m, 9H), 0.89 – 0.80 (m, 10H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.19, 171.06, 150.70, 143.30, 139.62, 137.70, 134.36, 132.70, 132.47, 132.11, 129.45, 128.72, 127.85, 127.47, 127.33, 127.23, 127.05, 122.81, 121.79, 80.92, 59.55, 55.32, 47.55, 47.17, 45.79, 41.84, 41.46, 39.54, 38.17, 37.71, 36.95, 33.88, 33.09, 32.79, 32.41, 30.75, 28.07, 27.79, 25.80, 23.63, 23.54, 23.47, 23.06, 21.51, 21.33, 18.23, 17.43, 16.72, 15.43.

IR (KBr): γ : 3436, 3280, 2928, 2859, 1731, 1458, 1260, 1203, 1157, 1098, 1026, 808, 750, 702, 559 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{56}H_{71}NNaO_6S]^+$ requires 908.4894, found 908.4888.

4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)phenyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (57)



According general procedure B: Purification by flash chromatography on silica gel (petroleum ether/EtOAc = 4:1) gave the product as a white semisolid. Yield: 85%, 26.2 mg. *E/Z* = 20:1. Enantiomeric excess: 96%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 19.523 min (major), t_R = 36.333 min (minor). $[\alpha]_D^{20}$ = 62.8 (c 1.34, $CHCl_3$).

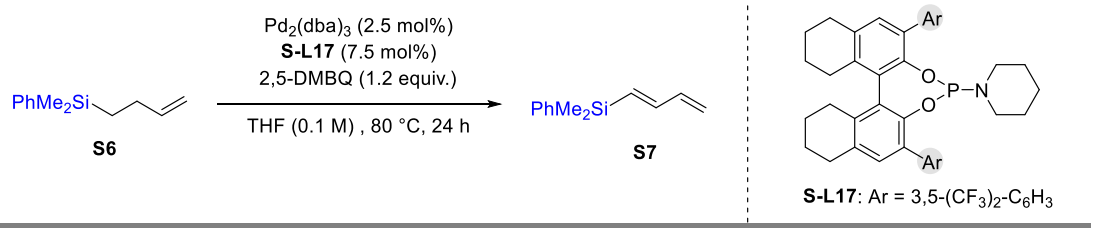
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.69 (m, 3H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.48 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.24 – 7.19 (m, 3H), 7.19 – 7.10 (m, 6H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.51 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.35 (d, *J* = 15.6 Hz, 1H), 6.10 (ddd, *J* = 15.0, 10.4, 1.2 Hz, 1H), 5.69 (dd, *J* = 15.1, 6.6 Hz, 1H), 5.09 – 4.97 (m, 1H), 4.93 (d, *J* = 7.1 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 1H), 3.91 (s, 3H), 2.34 (s, 3H), 1.68 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.15, 157.80, 150.35, 143.31, 139.59, 137.68, 135.08, 134.65, 133.85, 132.54, 132.39, 132.23, 129.45, 129.34, 129.01, 128.72, 127.86, 127.65, 127.42, 127.32, 127.22, 127.05, 126.17, 126.12, 121.64, 119.15, 105.65, 59.53, 55.36, 45.60, 21.50, 18.52.

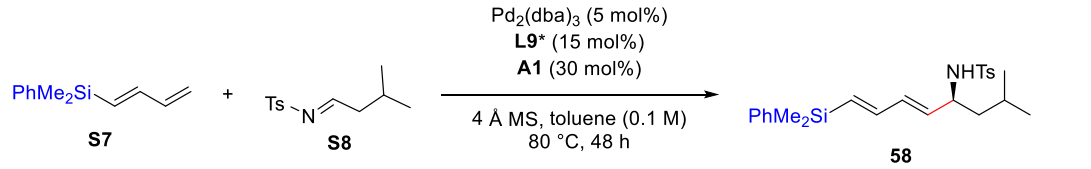
IR (KBr): γ : 3437, 2926, 1750, 1605, 1327, 1266, 1205, 1160, 1087, 1028, 810, 753, 700, 669, 559 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{38}H_{35}NNaO_5S]^+$ requires 640.2128, found 640.2134.

5. Synthetic applications



To a flame-dried and N_2-purged Schlenk tube (100 mL) were added $Pd_2(dba)_3$ (0.125 mmol, 115 mg), phosphoramidite **S-L17** (0.3 mmol, 0.65 g), 2,5-DMBQ (6.0 mmol, 815 mg) and a stirring bar. The Schlenk tube was then evacuated and filled with nitrogen. This cycle was repeated three times and followed by the addition of THF (25 mL) and alkene **S6** (5 mmol, 630 mg), then the resulting mixture was stirred at 60 ℃ for 24 h. The reaction mixture was filtered through a pad of Celite, and concentrated in vacuo, and the residue was purified by flash column chromatography on silica gel (petroleum) to provide the product **S7** as a colorless liquid, 0.94g, 99% yield. *E/Z* = 20:1. The spectroscopic data in accordance with the literature.[5] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 – 7.46 (m, 3H), 7.37 – 7.34 (m, 3H), 6.59 (ddt, *J* = 18.3, 10.1, 0.7 Hz, 1H), 6.40 (dtd, *J* = 17.0, 10.0, 0.7 Hz, 1H), 6.00 (dq, *J* = 18.2, 0.7 Hz, 1H), 5.25 (ddt, *J* = 17.0, 1.6, 0.7 Hz, 1H), 5.16 (ddt, *J* = 10.0, 1.6, 0.7 Hz, 1H), 0.37 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.20, 139.71, 138.53, 133.87, 132.33, 129.04, 127.82, 118.30, -2.62.



An oven-dried 5 mL test-tube equipped with a septum and a magnetic stir bar was charged with $Pd_2(dba)_3$ (4.6 mg, 5 mol%), ligand **L9** (11.8 mg, 15 mol%), N-sulfonylimine **S8** (0.1 mmol, 23.9 mg, 1.0 equiv.), **A1** (5.2 mg, 30 mol%) and 4 Å MS (60.0 mg). The tube was then evacuated and filled with N_2, this cycle was repeated three times, then toluene (0.5 mL) and diene **S7** (37.6 mg, 2.0 equiv.) was added via syringe. The resulting mixture was stirred at 80 ℃ for 36 h. After completion, purification by flash chromatography on silica gel (petroleum ether/EtOAc = 15/1) gave the product **58**.

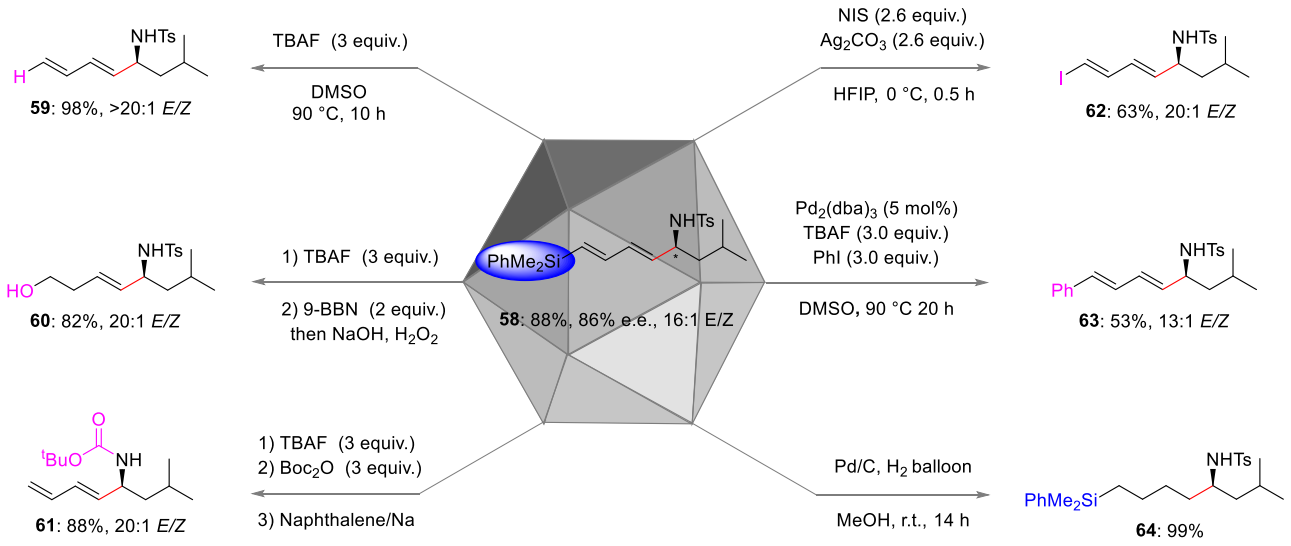
***N*-((*S*,5*E*,7*E*)-8-(dimethyl(phenyl)silyl)-2-methylocta-5,7-dien-4-yl)-4-methylbenzenesulfonamide (58)**: White semisolid. Yield: 61%, 25.9 mg. *E/Z* = 17:1. Enantiomeric excess: 82%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 97/3, flow rate 1.0 mL/min, T = 30 ℃, 254 nm): t_R = 28.386 min (major), t_R = 31.771 min (minor). $[\alpha]_D^{20}$ = -6.9 (c 0.95, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 – 7.66 (m, 2H), 7.55 – 7.47 (m, 2H), 7.42 – 7.28 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.28 (dd, *J* = 18.3, 10.0 Hz, 1H), 6.06 – 5.86 (m, 1H), 5.81 (d, *J* = 18.3 Hz, 1H), 5.27 (dd, *J* = 15.2, 7.6 Hz, 1H), 4.60 (d, *J* = 7.9 Hz, 1H), 3.84 (p, *J* = 7.5 Hz, 1H), 2.35 (s, 3H), 1.60 (dp, *J* = 13.4, 6.7 Hz, 1H), 1.36 (dt, *J* = 14.4, 7.3 Hz, 1H), 1.31 – 1.19 (m, 1H), 0.82 (dd, *J* = 11.4, 6.6 Hz, 7H), 0.38 – 0.23 (m, 6H).

^{13}C NMR (126 MHz, CDCl3) δ 144.43, 143.14, 138.41, 138.06, 133.99, 133.86, 133.82, 132.32, 129.46, 129.09, 127.84, 127.37, 54.11, 45.03, 24.32, 22.36, 22.29, 21.50, -2.60, -2.62.

IR (KBr): γ : 3283, 2961, 2924, 2856, 1529, 1452, 1345 ,1309, 1263, 1160, 1095, 1023, 800, 753, 696 cm^{-1}.

HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{24}H_{34}NO_2SSi]^+$ requires 450.1893, found 428.1883.



The compound **60** was synthesized following the literature[6]: To a solution of **58** (85.4 mg, 0.2 mmol, 1 equiv.) in DMSO (0.6 mL) was added TBAF (0.6 mL, 0.6 mmol, 1.0 equiv., 1.0 M solution in THF). The resulting mixture was stirred at 90 ℃ before complete conversion of the starting material as monitored by TLC. The reaction was quenched with sat aq. NH_4Cl and extracted with Et_2O (3 x 1.0 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: petroleum ether/EtOAc 10:1) afforded pure **59** as a white semisolid.

(*S*,*E*)-4-methyl-*N*-(2-methylocta-5,7-dien-4-yl)benzenesulfonamide (59): White semisolid. Yield: 98%, 57.5 mg. *E*/*Z* = 20:1. $[\alpha]_D^{20}$ = -24.3 (c 0.83, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 2H), 7.29 – 7.14 (m, 2H), 6.06 (dtd, *J* = 16.9, 10.2, 0.7 Hz, 1H), 5.86 (ddt, *J* = 15.3, 10.4, 0.8 Hz, 1H), 5.25 (ddd, *J* = 15.2, 7.6, 0.8 Hz, 1H), 5.12 – 4.89 (m, 2H), 4.51 (d, *J* = 7.9 Hz, 1H), 4.09 – 3.71 (m, 1H), 2.39 (s, 3H), 1.60 (dp, *J* = 13.4, 6.7 Hz, 1H), 1.42 – 1.23 (m, 2H), 0.89 – 0.74 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.16, 138.15, 135.90, 133.18, 131.96, 129.45, 127.32, 117.60, 54.11, 45.08, 24.32, 22.36, 22.26, 21.47.

IR (KBr): γ : 3434, 2962, 2924, 2855, 1726, 1455, 1265, 1090, 1023, 802, 755, 576 cm^{-1}.

HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{16}H_{24}NO_2S]^+$ requires 294.1522, found 294.1524.

The compound **60** was synthesized following the literature[7]: To a stirred solution of 9-BBN (0.5 M in THF, 0.24 mL, 2 equiv.) was slowly added a solution of **59** (17.4 mg, 0.0593 mmol) in THF (0.5 mL) at 0 ℃, then the mixture was stirred at room temperature for 12 h, another solution of 9-BBN (0.5 M in THF, 0.12 mL) was slowly added to the mixture at 0 ℃ and stirred at room temperature for 12 h. The reaction was cooled down to 0 ℃ and carefully quenched with H_2O (0.1 mL), sodium hydroxide (2 M, 0.4 mL) was added in one portion, then hydrogen peroxide (30% in H_2O, 0.4 mL) was slowly added. The resulting mixture was stirred at 0 ℃ for further l h. Saturated sodium sulfite (1.0 ml) was added to the mixture and extracted with ethyl acetate (1 mL x 3). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (light petroleum ether/ethyl acetate = 1:1) to obtain **60** as white semisolid.

(*S*,*E*)-*N*-(8-hydroxy-2-methyloct-5-en-4-yl)-4-methylbenzenesulfonamide (60): White semisolid. Yield: 84%, 15.6 mg. *E*/*Z* > 20:1. $[\alpha]_D^{20}$ = -12.4 (c 1.14, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.60 (m, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.36 (dt, J = 15.5, 6.8 Hz, 1H), 5.25 (ddt, J = 15.4, 7.4, 1.2 Hz, 1H), 4.53 (dd, J = 7.4, 3.8 Hz, 1H), 3.72 (p, J = 7.4 Hz, 1H), 3.51 (t, J = 6.4 Hz, 2H), 2.42 (s, 3H), 2.11 (q, J = 6.8, 6.4 Hz, 2H), 1.57 (dq, J = 13.3, 6.7 Hz, 1H), 1.42 – 1.20 (m, 3H), 0.80 (dd, J = 13.2, 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.34, 137.96, 133.40, 129.51, 128.34, 127.29, 61.51, 54.36, 45.13, 35.43, 24.33, 22.37,

22.18, 21.51.

IR (KBr): γ : 3466, 2959, 2924, 2862, 1646, 1460, 1267, 1154, 1027, 804, 755 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{16}H_{25}NNaO_3S]^+$ requires 334.1447, found 334.1447.

To a solution of **59** (0.16 mmol, 47 mg) and di-tert-butyl dicarbonate (0.48 mmol, 105 mg) in anhydrous CH_2Cl_2 (1.6 mL) was added 2,4-dimethylaminopyridine (0.032 mmol, 3.9 mg). After the mixture was stirred for 12 h, the solvent was evaporated, the residue was purified by flash silica gel column chromatography (hexane/ethyl acetate = 20:1) to give the target product **65** as a white semisolid (61.3 mg, 97% yield).

The compound **61** was synthesized following the literature[8]: To prepare the sodium-naphthalene reagent, a flame-dried 10 mL round bottom flask was charged with a stir bar, naphthalene (307.6 mg, 2.4 mmol), DME (2 mL), and small pieces of sodium metal (46 mg, 2 mmol). This mixture was allowed to be vigorously stirred for approximately 12 hours and became a dark green solution. This sodium-naphthalene reagent was used in next reaction.

The product **65** (34.2 mg, 0.083 mmol) was added to 10 mL round bottom flask containing a stirring bar. Dimethoxyethane (0.5 mL) was added via syringe, and the flask cooled down to -78 ℃. The dark, forest green solution of sodium naphthalide (0.6 mL, 1 M) was slowly added dropwise (via syringe) until the solution became a light forest green color that persisted for 2 min. After an additional 2.5 h at -78 ℃, the solution was quenched with saturated H_2O, allowed to warm to room temperature, and diluted with ethyl acetate (1 mL). The layers were separated, and the aqueous layer extracted with ethyl acetate (3 x 1 mL). Organic fractions were combined, dried over Na_2SO_4, and evaporated at reduced pressure. The residue was purified by flash silica gel column chromatography (hexane/ethyl acetate = 10:1) to give the target product **61** as a white semisolid.

***Tert*-butyl (*S*,*E*)-(2-methylocta-5,7-dien-4-yl)carbamate (61)**: White semisolid. Yield: 95%, 18.8 mg. *E*/*Z* = 20:1. $[\alpha]_D^{20}$ = -3.6 (c 0.11, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30 (dt, *J* = 16.8, 10.2 Hz, 1H), 6.15 (dd, *J* = 15.2, 10.5 Hz, 1H), 5.57 (dd, *J* = 15.2, 6.4 Hz, 1H), 5.18 (dd, *J* = 16.7, 1.7 Hz, 1H), 5.05 (dd, *J* = 10.1, 1.7 Hz, 1H), 4.39 (s, 1H), 4.19 (s, 1H), 1.64 (dq, *J* = 13.5, 6.8 Hz, 1H), 1.44 (s, 9H), 1.34 (h, *J* = 6.6 Hz, 2H), 0.91 (dd, *J* = 6.6, 2.4 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.17, 136.48, 135.19, 130.52, 116.93, 79.26, 50.34, 44.73, 28.42, 24.72, 22.64, 22.48.

IR (KBr): γ : 3437, 2961, 2924, 2855, 1639, 1265, 1096, 1022, 800, 755 cm^{-1}.

HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{14}H_{26}NO_2]^+$ requires 240.1958, found 240.1950.

The compound **62** was synthesized following the literature[9]: To an oven-dried 4-dram vial charged with a stirring bar, **58** (21.3 mg, 0.05 mmol) was added followed by distilled hexafluoro isopropanol (0.22 mL). The vial was protected from light with foil and the solution was stirred at room temperature for 10 min, then cooled down to 0 ℃ for 10 min. Ag_2CO_3 (4.1 mg, 0.0165 mmol) was added and then N-iodosuccinimide (26.1 mg, 0.13 mmol) was added in one portion. The reaction mixture was stirred at 0 ℃ for 5 minutes and then quenched with cold H_2O (3 mL). The suspension was diluted with dichloromethane (3 mL) and the organic layer was extracted with water (3 mL). The aqueous layer was next extracted with dichloromethane (3 x 2 mL) and the combined organic layers were dried over anhydrous magnesium sulfate and concentrated under vacuum. The residue was purified by flash silica gel column chromatography (hexane/ethyl acetate = 10:1) to give the target product **62** as a white semisolid.

***N*-((*S*,5*E*,7*E*)-8-iodo-2-methylocta-5,7-dien-4-yl)-4-methylbenzenesulfonamide (62)**: White semisolid. 13.2 mg, 63% yield. *E*/*Z* = 20:1. $[\alpha]_D^{20}$ = -23.9 (c 0.54, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.59 (m, 2H), 7.49 – 7.01 (m, 3H), 6.74 (ddd, *J* = 14.5, 10.6, 0.8 Hz, 1H), 6.18 (d, *J* = 14.4 Hz, 1H), 5.97 – 5.59 (m, 1H), 5.25 (ddt, *J* = 15.3, 7.5, 0.8 Hz, 1H), 4.50 (d, *J* = 7.9 Hz, 1H), 3.80 (p, *J* = 7.3 Hz, 1H), 2.42 (s, 3H), 1.57 (dp, *J* = 13.4, 6.7 Hz, 1H), 1.44 – 1.19 (m, 3H), 0.81 (dd, *J* = 10.0, 6.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.07, 143.46, 138.03, 133.67, 131.01, 129.54, 127.30, 79.63, 53.88, 44.81, 24.32, 22.35, 22.19, 21.57.

IR (KBr): γ : 3272, 2959, 2924, 2857, 1266, 1157, 1025, 803, 755, 558 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{16}H_{22}INNaO_2S]^+$ requires 442.0308, found 442.0306.

The compound **63** was synthesized following the literature[10]: PhI (62 mg, 0.15 mmol, 3 equiv.) and TBAF (3 equiv., 0.15 mL, 1.0 M in THF) were added sequentially to solution of **58** (21.3 mg, 0.05 mmol) in THF (0.6 mL) at 0 °C. The resulting solution was stirred for 15 min at 0 ℃ and then $Pd_2(dba)_3$ (2.3 mg, 0.005 mmol) was added. The reaction was removed from the ice bath and stirred at 90 ℃ for 24 h. The resulting solution was flushed through a plug of silica, eluting with ether, the filtrate was concentrated in vacuo. The resulting oily residue was purified via flash chromatography (silica, ether/petroleum ether gradient) to yield **63** as a white semisolid.

4-methyl-*N*-((*S*,5*E*,7*E*)-2-methyl-8-phenylocta-5,7-dien-4-yl)benzenesulfonamide (63): White semisolid. 9.8 mg, 53% yield. *E/Z* = 13:1. $[\alpha]_D^{20}$ = -11.2 (c 0.46, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.66 (m, 2H), 7.37 – 7.28 (m, 4H), 7.26 – 7.15 (m, 3H), 6.49 (dd, *J* = 15.6, 10.2 Hz, 1H), 6.37 (d, *J* = 15.7 Hz, 1H), 6.02 (ddd, *J* = 15.3, 10.2, 1.1 Hz, 1H), 5.35 (dd, *J* = 15.2, 7.6 Hz, 1H), 4.41 (d, *J* = 7.8 Hz, 1H), 3.90 (p, *J* = 7.5 Hz, 1H), 2.35 (s, 3H), 1.64 (dq, *J* = 13.4, 6.6 Hz, 1H), 1.46 – 1.25 (m, 2H), 0.84 (dd, *J* = 8.6, 6.6 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.26, 138.16, 137.05, 133.12, 132.87, 131.69, 129.50, 128.63, 127.77, 127.67, 127.36, 126.30, 54.38, 45.19, 24.39, 22.37, 22.32, 21.48.

IR (KBr): γ : 3442, 2961, 2924, 2858, 1659, 1456, 1265, 1155, 1023, 801,755, 553 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{22}H_{27}NNaO_2S]^+$ requires 392.1655, found 392.1662.

A mixture of **58** (21.3 mg, 0.05 mmol, 1.0 equiv.) and [10% Pd/C, 55% wet H_2O] (5 mg) in degassed MeOH (1 mL) under H_2 (1 atm) atmosphere was stirred at room temperature as the starting material was completely consumed (determined by TLC). Pd/C was then filtered through a pad of Celite, and the organic phase was concentrated. The residue was purified via flash column chromatography with petroleum ether/EtOAc = 4:1 to afford compound **64** as a white semisolid.

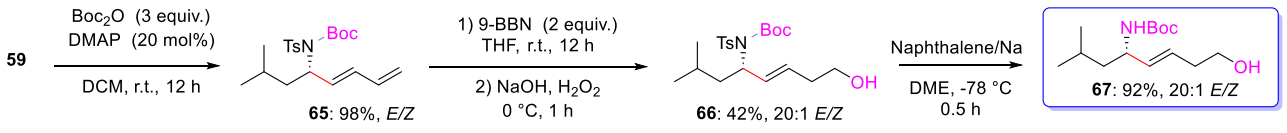
(*R*)-*N*-(8-(dimethyl(phenyl)silyl)-2-methyloctan-4-yl)-4-methylbenzenesulfonamide (64): White semisolid. 21.5 mg, 99% yield. $[\alpha]_D^{20}$ = -5.2 (c 1.05, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.70 (m, 2H), 7.53 – 7.45 (m, 2H), 7.35 (dd, *J* = 4.2, 2.1 Hz, 3H), 7.32 – 7.22 (m, 2H), 4.22 (d, *J* = 8.5 Hz, 1H), 3.29 – 3.14 (m, 1H), 2.39 (s, 3H), 1.58 – 1.46 (m, 1H), 1.38 – 1.30 (m, 1H), 1.16 (dt, *J* = 10.6, 7.1 Hz, 7H), 0.78 (d, *J* = 6.7 Hz, 3H), 0.71 (d, *J* = 6.6 Hz, 3H), 0.61 (t, *J* = 7.8 Hz, 2H), 0.23 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.05, 139.46, 138.50, 133.53, 129.52, 128.83, 127.74, 127.08, 52.25, 44.68, 34.98, 28.70, 24.45, 23.64, 22.74, 22.19, 21.48, 15.54, -3.09.

IR (KBr): γ : 3278, 2956, 2925, 2860, 1422, 1325, 1264, 1156, 1096, 1023, 809, 755, 702, 666, 551 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{24}H_{37}NNaO_2SSi]^+$ requires 454.2206, found 454.2211.



***Tert*-butyl (*S*,*E*)-(2-methylocta-5,7-dien-4-yl)(tosyl)carbamate (66)**: White semisolid. 61.3 mg, 97% yield. *E/Z* = 20:1. Enantiomeric excess: 86%, determined by **59**. $[\alpha]_D^{20}$ = 47.8 (c 0.59, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.31 – 7.24 (m, 2H), 6.42 – 6.17 (m, 2H), 6.02 (dd, *J* = 14.9, 8.0 Hz, 1H), 5.29 – 5.16 (m, 1H), 5.16 – 5.11 (m, 1H), 5.07 (qd, *J* = 7.7, 0.9 Hz, 1H), 2.41 (s, 3H), 1.89 (ddd, *J* = 13.6, 7.5, 6.8 Hz, 1H), 1.78 (ddd, *J* = 13.6, 7.7, 6.9 Hz, 1H), 1.61 (hept, *J* = 6.7 Hz, 1H), 1.31 (s, 9H), 1.03 – 0.90 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.63, 143.79, 137.77, 136.28, 133.87, 132.70, 129.13, 127.91, 118.12, 84.08, 59.01, 42.85, 27.91, 25.25, 22.67, 22.47, 21.56.

IR (KBr): γ : 3437, 2961, 1725, 1637, 1461, 1357, 1267, 1152, 1089, 1023, 803, 755, 670, 583 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{21}H_{31}NNaO_4S]^+$ requires 416.1866, found 416.1867.

To a stirred solution of **65** (59.2 mg, 0.15 mmol) in THF (0.3 mL) was slowly added 9-BBN (0.5 Min THF, 0.6 mL, 0.3 mmol)

at 0 ℃, then the mixture was stirred at room temperature for 12 h. The reaction was cooled down to 0 ℃ and carefully quenched with H_2O (0.1 mL), sodium hydroxide (2 M, 0.5 mL) was added in one portion, then hydrogen peroxide (30% in H_2O, 0.3 mL) was slowly added. The resulting mixture was stirred at room temperature for further l h. Saturated sodium sulfite (1.5 ml) was slowly added to the mixture and extracted with ethyl acetate (2 mL x 3). The organic layer was washed with brine, dried over Na_2SO_4, filtered, concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (light petroleum ether/ethyl acetate = 1:1) to obtain **66** as white semisolid.

***Tert*-butyl (*S*,*E*)-(8-hydroxy-2-methyloct-5-en-4-yl)(tosyl)carbamate (67)**: White semisolid. 25.9 mg, 42% yield. *E/Z* = 20:1. $[\alpha]_D^{20}$ = 23.3 (c 0.72, $CHCl_3$).

^{1}H NMR (400 MHz, CDCl3) δ 7.98 – 7.66 (m, 2H), 7.33 – 7.02 (m, 2H), 5.91 (ddt, J = 15.5, 7.4, 1.3 Hz, 1H), 5.72 (dtd, J = 15.3, 7.0, 1.0 Hz, 1H), 5.30 – 4.81 (m, 1H), 3.67 (td, J = 6.3, 1.8 Hz, 2H), 2.42 (s, 3H), 2.33 (qd, J = 6.3, 1.3 Hz, 2H), 1.87 (ddd, J = 14.0, 7.6, 6.7 Hz, 1H), 1.75 (dt, J = 13.6, 7.4 Hz, 1H), 1.60 (dt, J = 13.3, 6.6 Hz, 1H), 1.31 (s, 9H), 0.96 (dd, J = 11.6, 6.6 Hz, 6H).

^{13}C NMR (101 MHz, CDCl3) δ 150.69, 143.83, 137.84, 132.59, 130.13, 129.14, 127.85, 84.16, 61.72, 58.99, 42.71, 35.71, 27.91, 25.27, 22.67, 22.49, 21.57.

IR (KBr): γ : 3439, 2960, 2925, 2861, 1725, 1636, 1348, 1266, 1151, 1089, 1025, 801, 755, 584 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{21}H_{33}NNaO_5S]^+$ requires 434.1972, found 434.1980.

The product **66** (20.5 mg, 0.05 mmol) was added to 10 mL round bottom flask containing a stirring bar. Dimethoxyethane (0.4 mL) was added via syringe, and the flask was cooled down to -78 ℃. A dark, forest green solution of sodium naphthalide (0.4 mL) was slowly added dropwise (via syringe) until the solution became a light forest green color that persisted for 2 min. After an additional 30 min at -78 ℃, the solution was quenched with H_2O, allowed to warm to room temperature, and diluted with ethyl acetate (1 mL). The layers were separated, and the aqueous layer extracted with ethyl acetate (3 x 1 mL). Organic fractions were combined, dried over Na_2SO_4, and evaporated at reduced pressure. The residue was purified by flash silica gel column chromatography (hexane/ethyl acetate = 20:1) to give the target product **67** as a white semisolid and the spectroscopic data in accordance with the literature.[11]

***Tert*-butyl (*S*,*E*)-(8-hydroxy-2-methyloct-5-en-4-yl)carbamate (67)**: White semisolid. Yield: 92%, 11.8 mg. *E/Z* = 20:1. $[\alpha]_D^{20}$ = -6.2 (c 1.16, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.56 (dtd, *J* = 15.1, 7.0, 1.1 Hz, 1H), 5.40 (ddt, *J* = 15.4, 6.6, 1.2 Hz, 1H), 4.43 (s, 1H), 4.22 – 3.89 (m, 1H), 3.64 (t, *J* = 6.2 Hz, 2H), 2.34 – 2.17 (m, 2H), 1.88 (s, 1H), 1.65 (dt, *J* = 13.4, 6.7 Hz, 1H), 1.44 (s, 9H), 1.37 – 1.26 (m, 2H), 0.92 (dd, *J* = 6.6, 4.0 Hz, 6H).

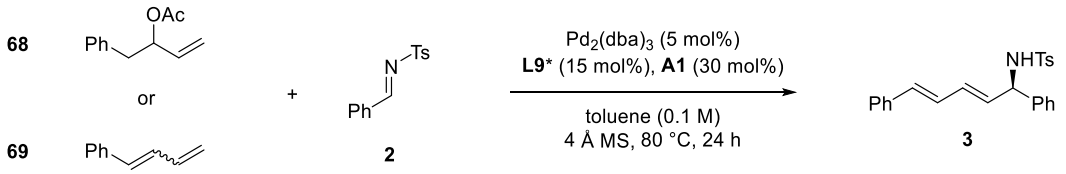
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.39, 134.63, 127.00, 79.31, 61.58, 51.09, 44.56, 35.67, 29.70, 28.41, 24.69, 22.55.

IR (KBr): γ : 3415, 2960, 2927, 2865, 1687, 1524, 1367, 1266, 1168, 1023, 800, 755 cm^{-1}.

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{14}H_{27}NNaO_3]^+$ requires 280.1883, found 280.1889.

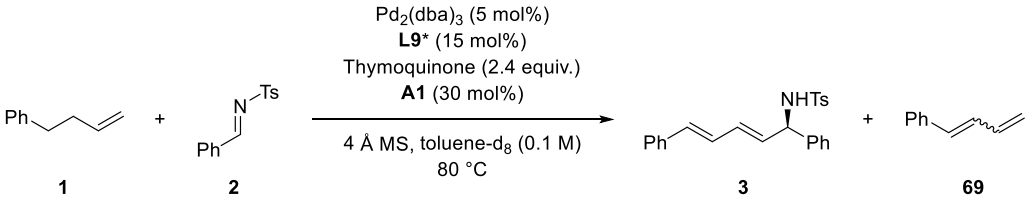
6. Mechanism study

(1) Control experiments

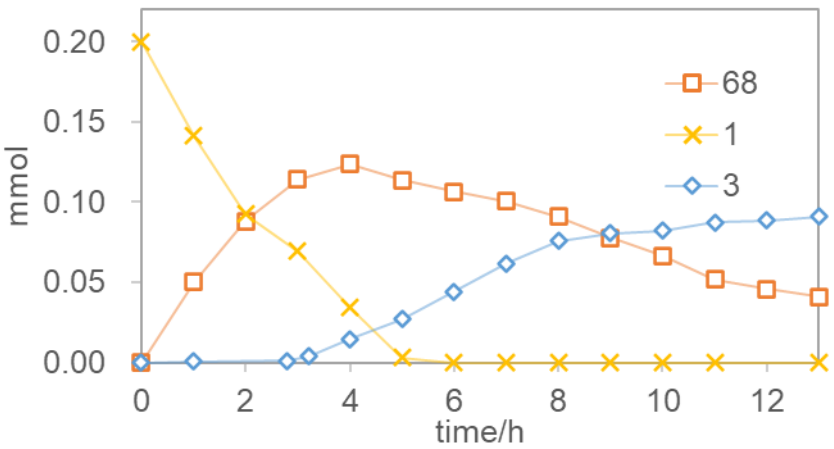


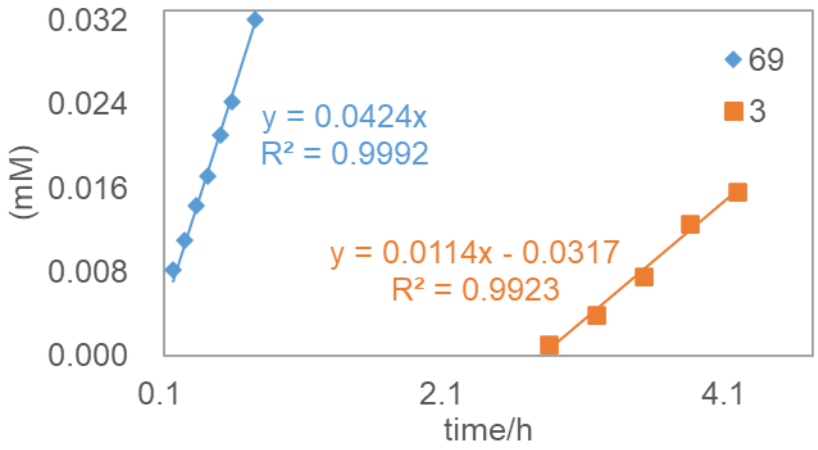
To a flame-dried and N_2-purged Schlenk tube (10 mL) were added imine **2** (0.05 mmol, 1 equiv.), $Pd_2(dba)_3$ (0.0025 mmol, 2.3 mg), phosphoramidite (*R*)-**L9** (0.0075 mmol, 5.9 mg), **A1** (0.015 mmol, 2.6 mg), 4 Å MS (30 mg) and a stirring bar. The Schlenk tube was then evacuated and filled with nitrogen. This cycle was repeated three times and followed by the addition of anhydrous toluene (0.5 mL) and the alkene **68** or **69** (0.1 mmol, 2 equiv.) via a syringe, then the resulting mixture was stirred at 80 ℃ for 24 h. The mixture was filtered through Celite and concentrated in *vacuo*, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to provide the desired product.

(2) Kinetic study

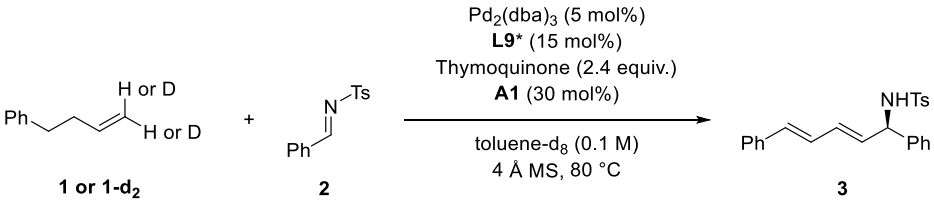


To a flame-dried and N_2-purged Schlenk tube (10 mL) were added imine **2** (0.1 mmol, 1 equiv.), $Pd_2(dba)_3$ (0.005 mmol, 4.6 mg), phosphoramidite (*R*)-**L9** (0.015 mmol, 11.8 mg), **A1** (0.03 mmol, 5.2 mg), Thymoquinone (0.2 mmol, 32.8 mg), 4 Å MS (60 mg) and a stirring bar. The Schlenk tube was then evacuated and filled with nitrogen. This cycle was repeated three times and followed by the addition of toluene-d_8 (1.0 mL) and the alkene **1** (0.2 mmol, 2 equiv.) via a syringe, then the resulting mixture was stirred at 80 ℃. The yield was determined by ^{1}H nuclear magnetic resonance (**^{1}H NMR**) analysis of the crude products based on trimethyl 1,3,5-benzenetricarboxylate as an internal standard.

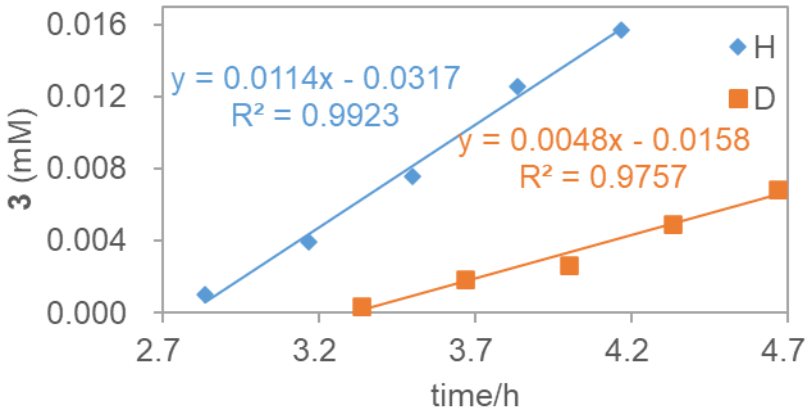


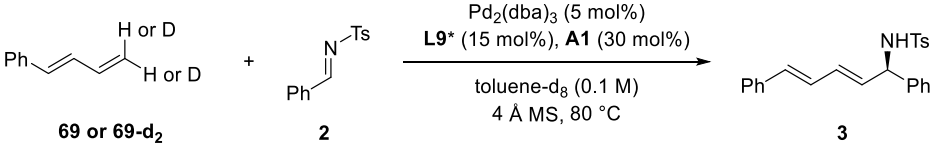


(3) Deuterium isotope effect (KIE)

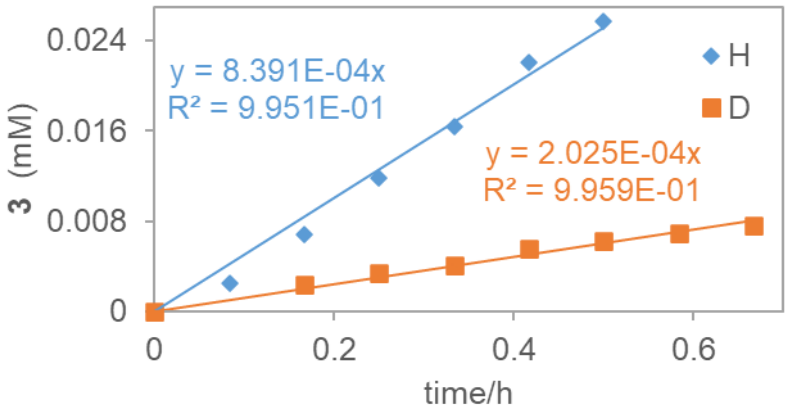


To a flame-dried and N_2-purged Schlenk tube (10 mL) were added imine **2** (0.1 mmol, 1 equiv.), $Pd_2(dba)_3$ (0.005 mmol, 4.6 mg), phosphoramidite (*R*)-**L9** (0.015 mmol, 11.8 mg), **A1** (0.03 mmol, 5.2 mg), Thymoquinone (0.2 mmol, 32.8 mg), 4 Å MS (60 mg) and a stirring bar. The Schlenk tube was then evacuated and filled with nitrogen. This cycle was repeated three times and followed by the addition of toluene-d_8 (1.0 mL) and alkene **1** or **1-d$_2$** (92% D-trans and 95% D-cis) (0.2 mmol, 2 equiv.) via a syringe, then the resulting mixture was stirred at 80 ℃. The yield was determined by ^{1}H nuclear magnetic resonance (**^{1}H NMR**) analysis of the crude products based on trimethyl 1,3,5-benzenetricarboxylate as an internal standard.



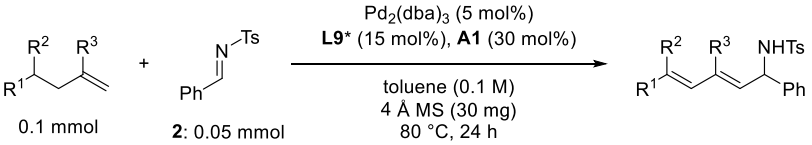


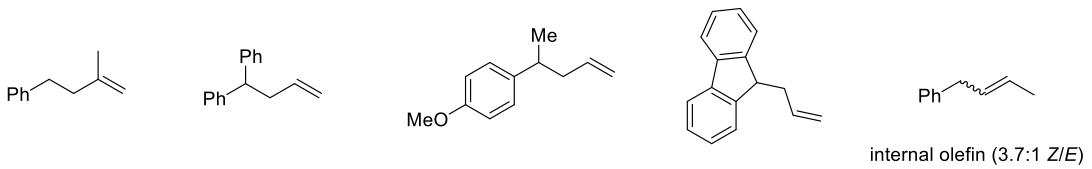
To a flame-dried and N_2-purged Schlenk tube (10 mL) were added imine **2** (0.1 mmol, 1 equiv.), $Pd_2(dba)_3$ (0.005 mmol, 4.6 mg), phosphoramidite (*R*)-**L9** (0.015 mmol, 11.8 mg), **A1** (0.03 mmol, 5.2 mg), 4 Å MS (60 mg) and a stirring bar. The Schlenk tube was then evacuated and filled with nitrogen. This cycle was repeated three times and followed by the addition of toluene-d_8 (1.0 mL) and alkene **69** or **69-d$_2$** (92% D-trans and 93% D-cis) (0.2 mmol, 2 equiv.) via a syringe, then the resulting mixture was stirred at 80 ℃. The yield was determined by ^{1}H nuclear magnetic resonance (**^{1}H NMR**) analysis of the crude products based on trimethyl 1,3,5-benzenetricarboxylate as an internal standard.

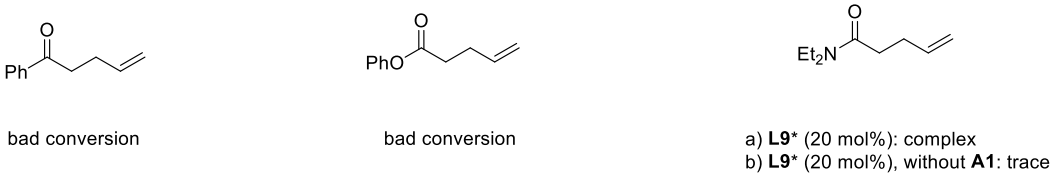


7. Unsuccessful attempt on the substrate scope

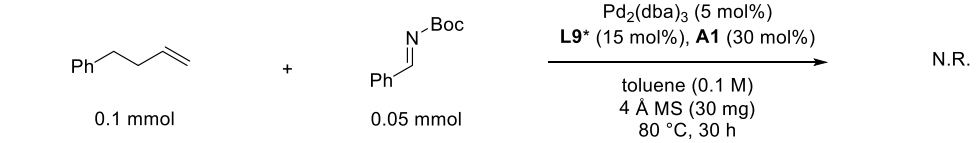
(1) Different alkenes



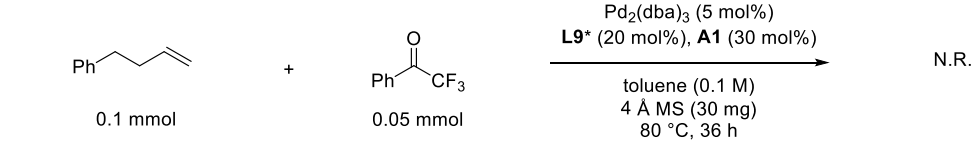




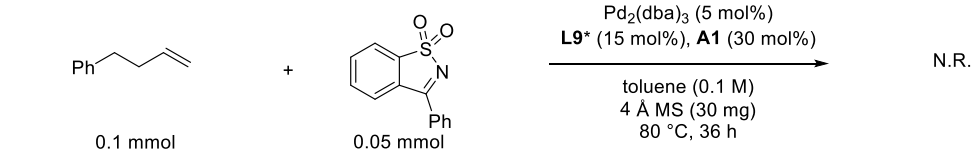
(2) Different electrophiles



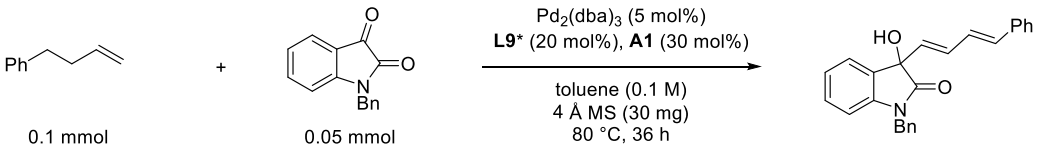
0.1 mmol 0.05 mmol



0.1 mmol 0.05 mmol



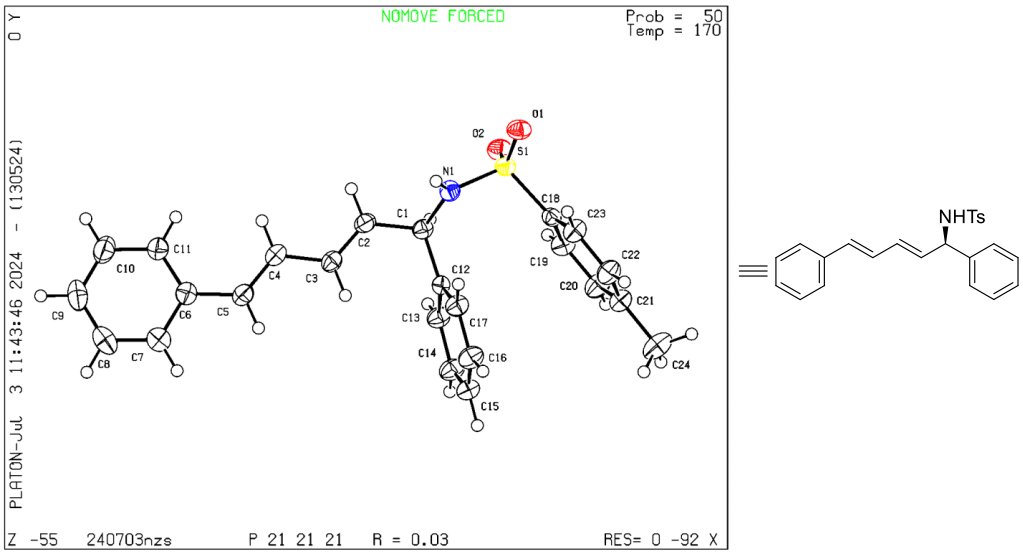
0.1 mmol 0.05 mmol



0.1 mmol 0.05 mmol >90%, 4% e.e., >20:1 *E*/*Z*

8. Crystal data and structure refinement

Preparation of the single crystals of compound 3: Compound **3** (19.0 mg) was dissolved in dichloromethane (5.0 mL) in a 25 mL tube and n-hexane (5.0 mL) was added. The tube was sealed with a piece of weighing paper with several tiny holes, thus allowing slow evaporation of the solvents at room temperature. After 72 h, several small particles could be observed at the bottom of the tube. The crystals were chosen, washed with n-hexane and subjected to the single crystal X-ray diffraction analysis for the determination of the absolute configuration of **3**. CCDC **2367672** (**3**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.



(Thermal ellipsoids shown at 50% probability)

Supplementary Table 7. Crystallographic data and structure refinement for 3.

Identification code	240703nzs
Empirical formula	$C_{24}H_{23}NO_2S$
Formula weight	389.49
Temperature/K	170.00
Crystal system	orthorhombic
Space group	P212121
a/Å	8.3944(2)
b/Å	9.6192(2)
c/Å	25.3546(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2047.32(8)
Z	4
ρ_{calc}g/cm^3	1.264
μ/mm^{-1}	1.011
F(000)	824.0
Crystal size/mm^3	0.17 × 0.17 × 0.05

Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/ °	8.554 to 109.894
Index ranges	$-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $-29 \leq l \leq 30$
Reflections collected	24083
Independent reflections	3885 [R_{int} = 0.0584, R_{sigma} = 0.0382]
Data/restraints/parameters	3885/0/254
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0336, wR_2 = 0.0815
Final R indexes [all data]	R_1 = 0.0396, wR_2 = 0.0844
Largest diff. peak/hole / e $Å^{-3}$	0.38/-0.39
Flack parameter	0.040(10)

Experimental:

Single crystals of $C_{24}H_{23}NO_2S$ **[**240703nzs**]** were **[]**. A suitable crystal was selected and **[]** on a **Bruker D8 Venture** diffractometer. The crystal was kept at 170.00 K during data collection. Using Olex2[12], the structure was solved with the SHELXT[13] structure solution program using Intrinsic Phasing and refined with the SHELXL[14] refinement package using Least Squares minimisation.

Crystal structure determination of [240703nzs**]:**

Crystal Data for $C_{24}H_{23}NO_2S$ (M =389.49 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 8.3944(2) Å, b = 9.6192(2) Å, c = 25.3546(6) Å, V = 2047.32(8) $Å^3$, Z = 4, T = 170.00 K, μ(GaKα) = 1.011 mm^{-1}, D_{calc} = 1.264 g/cm^3, 24083 reflections measured (8.554 ° ≤ 2Θ ≤ 109.894 °), 3885 unique (R_{int} = 0.0584, R_{sigma} = 0.0382) which were used in all calculations. The final R_1 was 0.0336 (I > 2σ(I)) and wR_2 was 0.0844 (all data).

Refinement model description:

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All N(H) groups

At 1.5 times of:

All C(H,H,H) groups

2.a Ternary CH refined with riding coordinates:

C1(H1A)

2.b Aromatic/amide H refined with riding coordinates:

N1(H1), C2(H2), C3(H3), C4(H4), C5(H5), C7(H7), C8(H8), C9(H9), C10(H10), C11(H11), C13(H13), C14(H14), C15(H15), C16(H16), C17(H17), C19(H19), C20(H20), C22(H22), C23(H23)

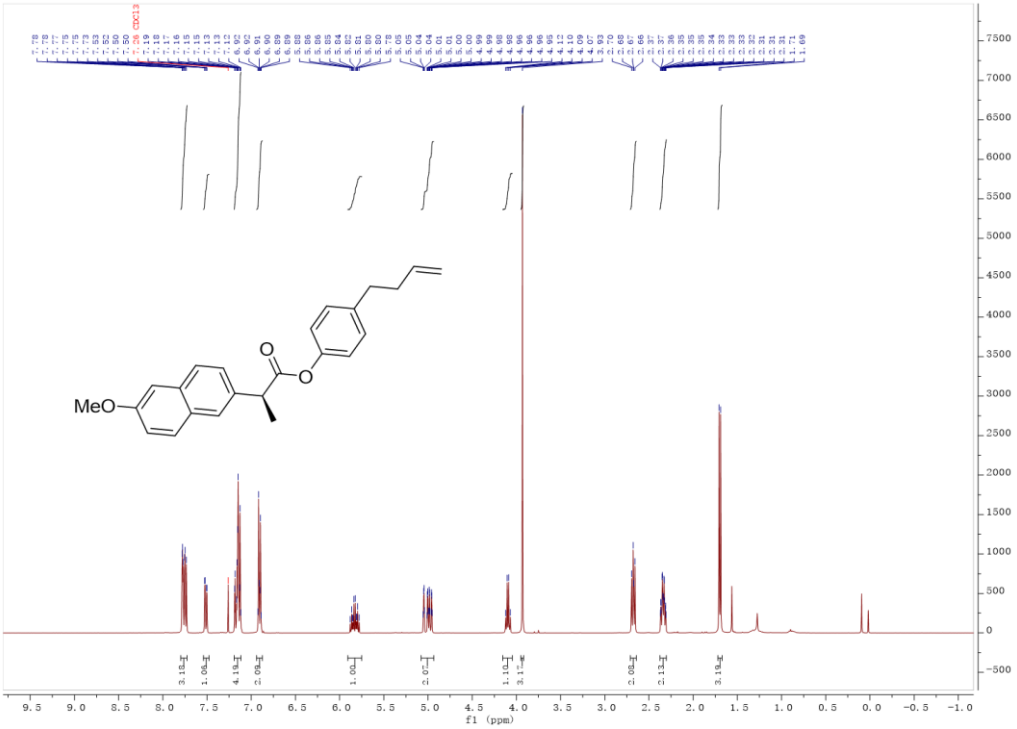
2.c Idealised Me refined as rotating group:

C24(H24A,H24B,H24C)

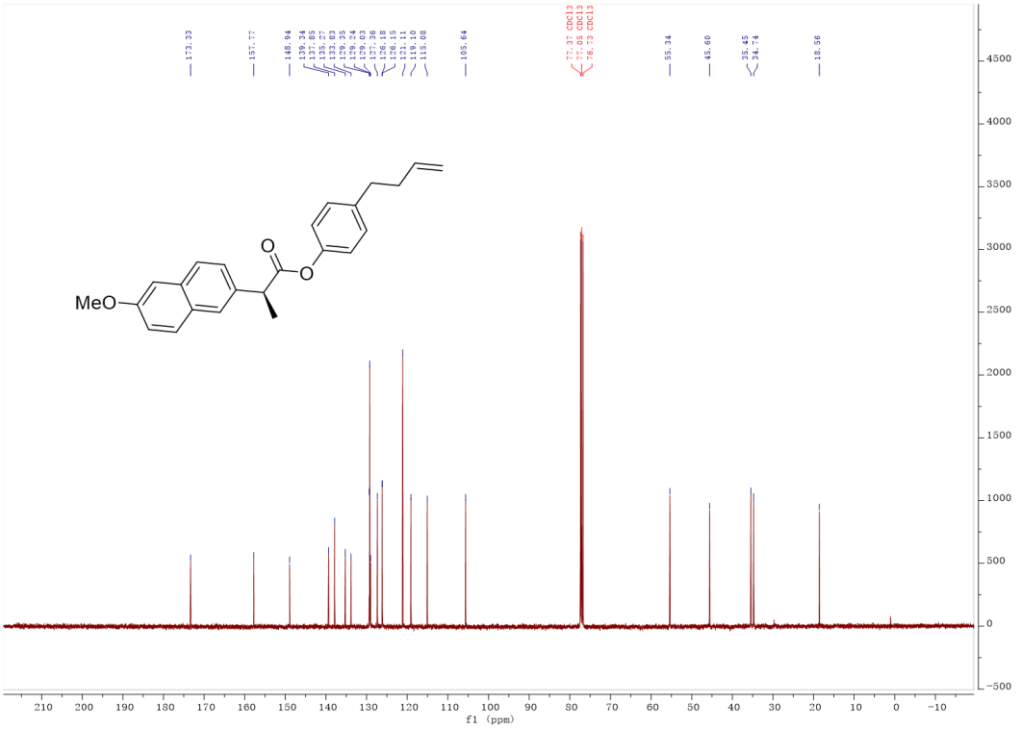
9. NMR spectra

4-(but-3-en-1-yl)phenyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (S1)

^{1}H NMR

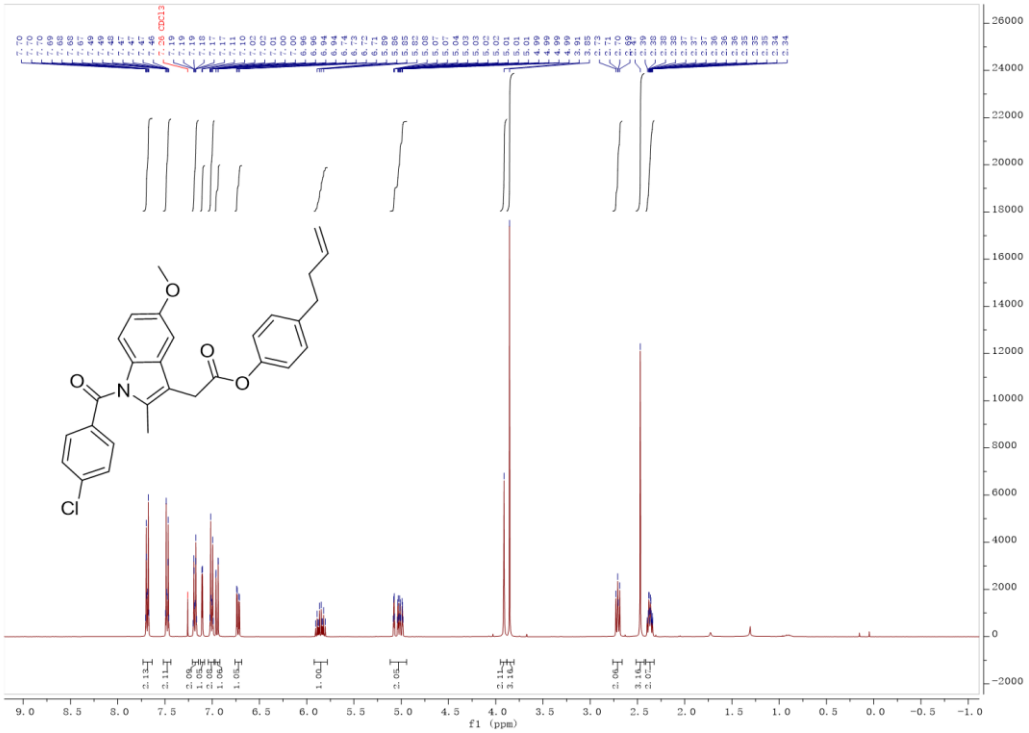


^{13}C NMR

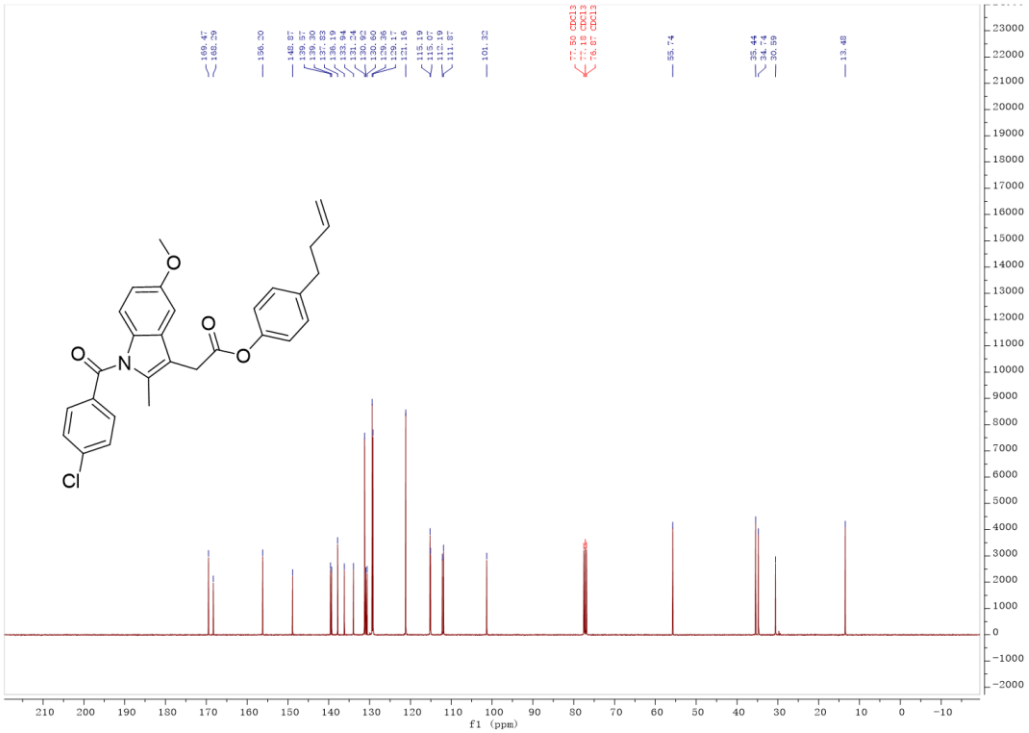


4-(but-3-en-1-yl)phenyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (S2)

^{1}H NMR

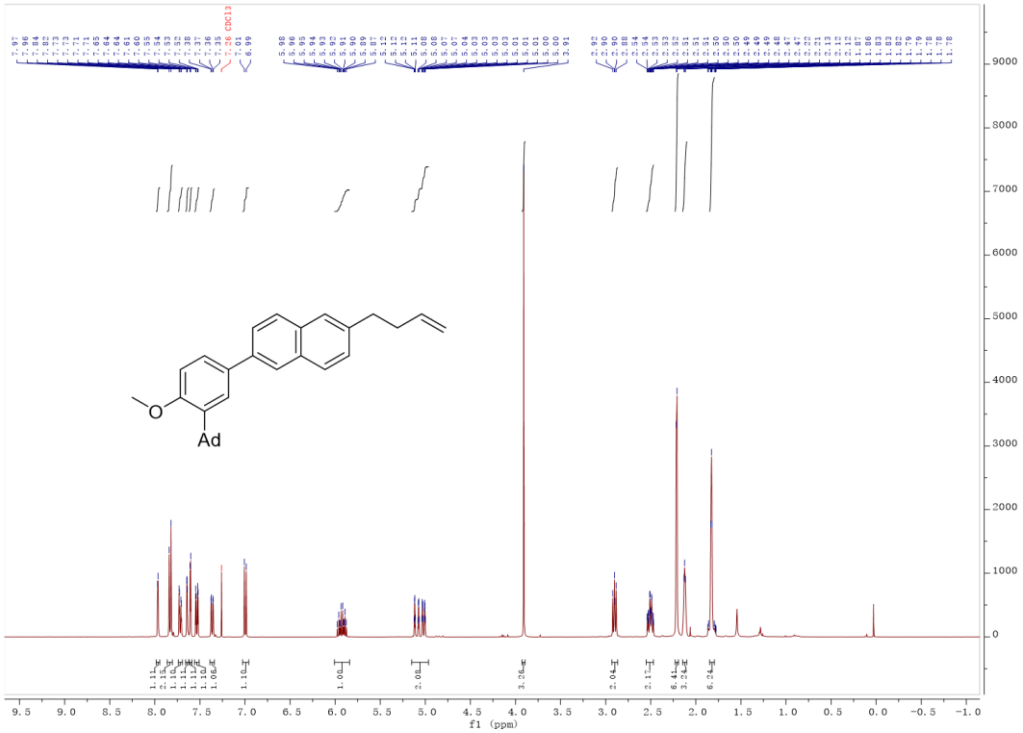


^{13}C NMR

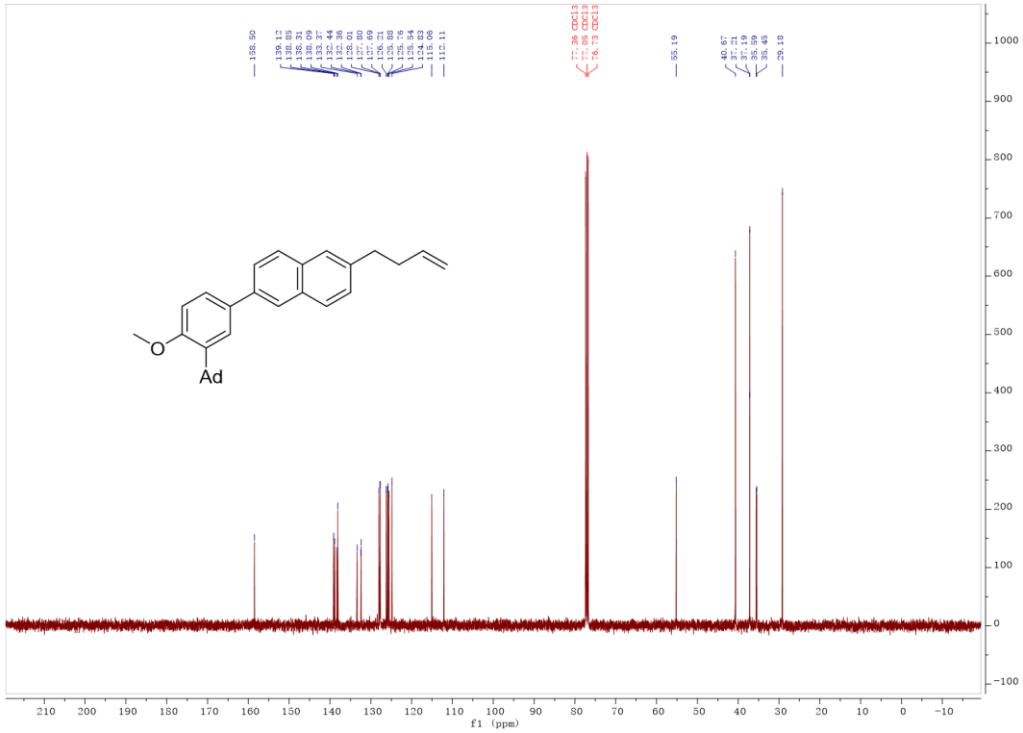


(3*r*,5*r*,7*r*)-1-(5-(6-(but-3-en-1-yl)naphthalen-2-yl)-2-methoxyphenyl)adamantane (S3)

^{1}H NMR



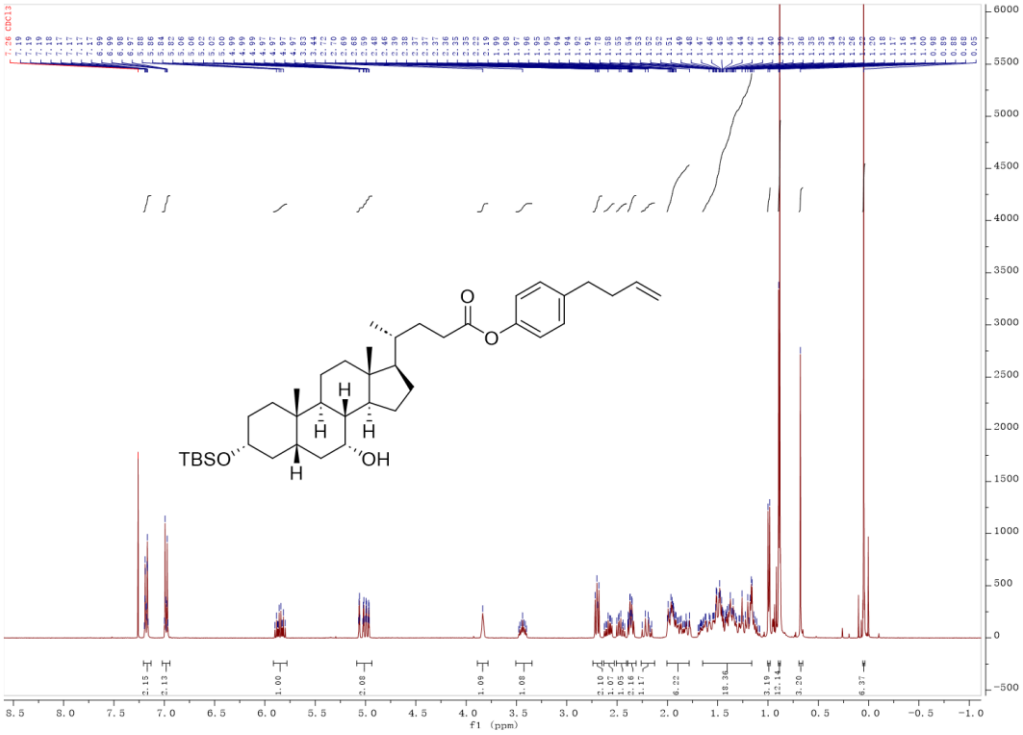
^{13}C NMR



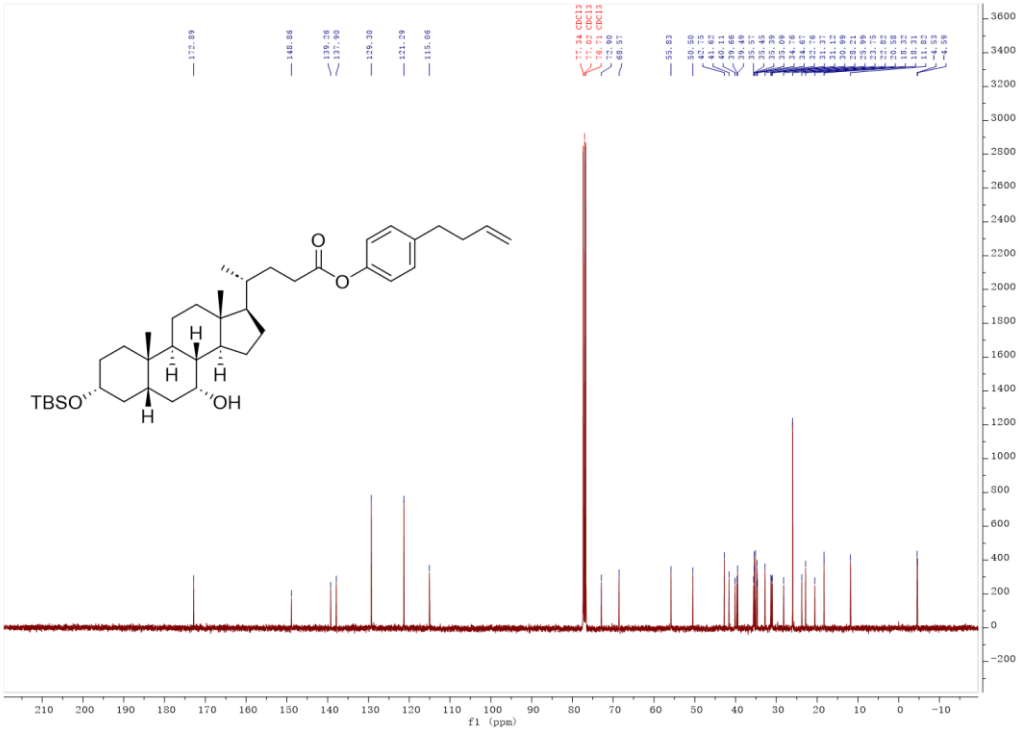
4-(but-3-en-1-yl)phenyl

(*R*)-4-((3*R*,5*R*,7*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-((tert-butyldimethylsilyl)oxy)-7-hydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[a]phenanthren-17-yl)pentanoate (S4)

^{1}H NMR

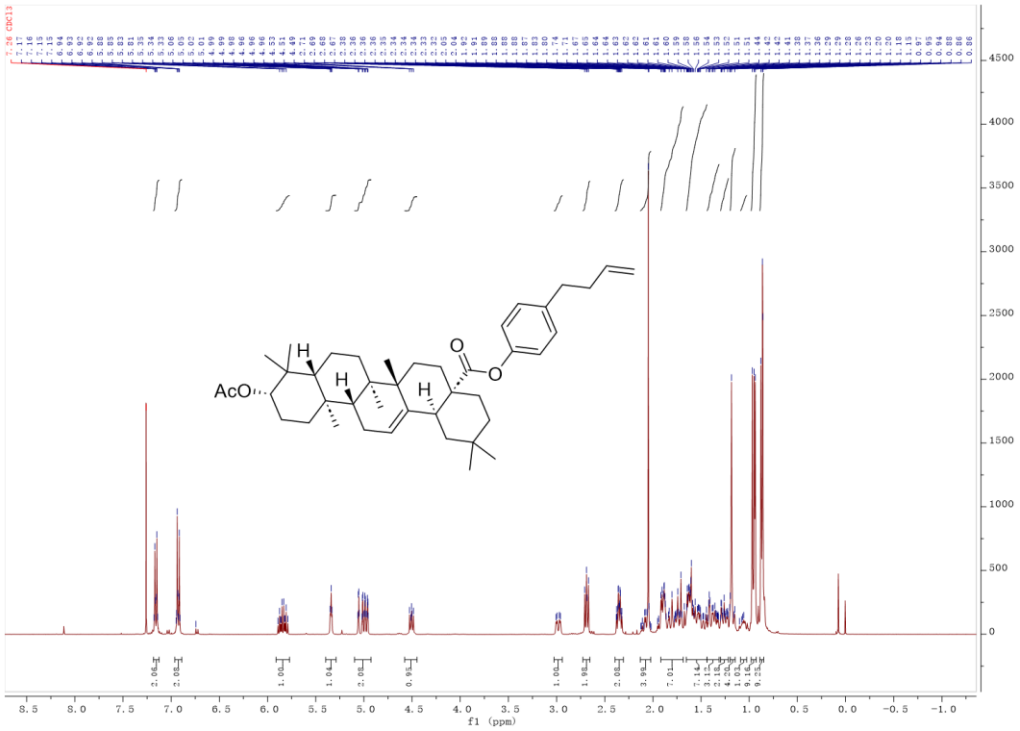


^{13}C NMR

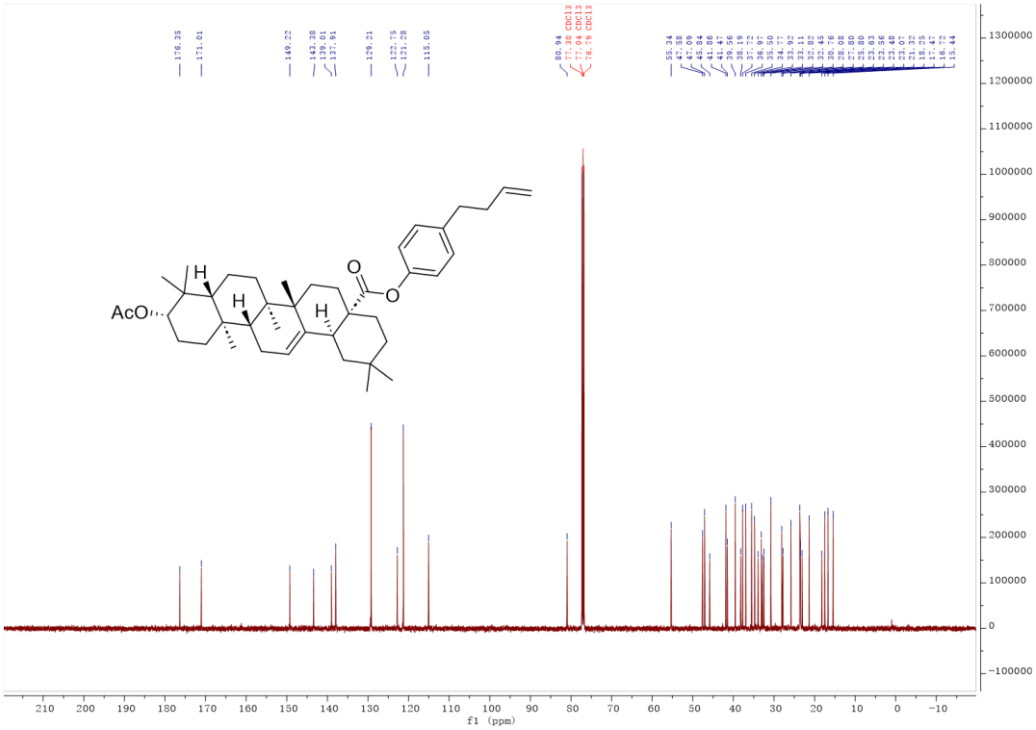


4-(but-3-en-1-yl)phenyl
(*4aS*,6*aS*,6b*R*,8*aR*,10*S*,12*aR*,12*bR*,14*bS*)-10-acetoxy-2,2,6a,6b,9,9,12a-heptamethyl-1,3,4,5,6,6*a*,6*b*,7,8,8a,9,10,11,12,12*a*,12*b*,13,14*b*-octadecahydropicene-4a(2*H*)-carboxylate (S5)

^{1}H NMR

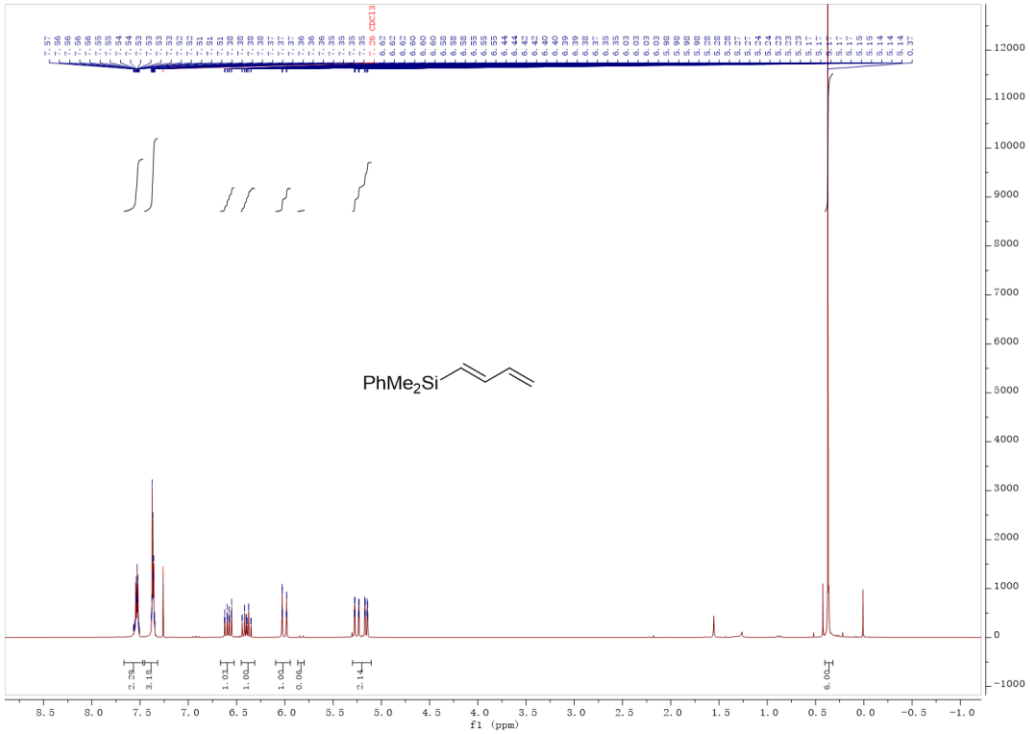


^{13}C NMR

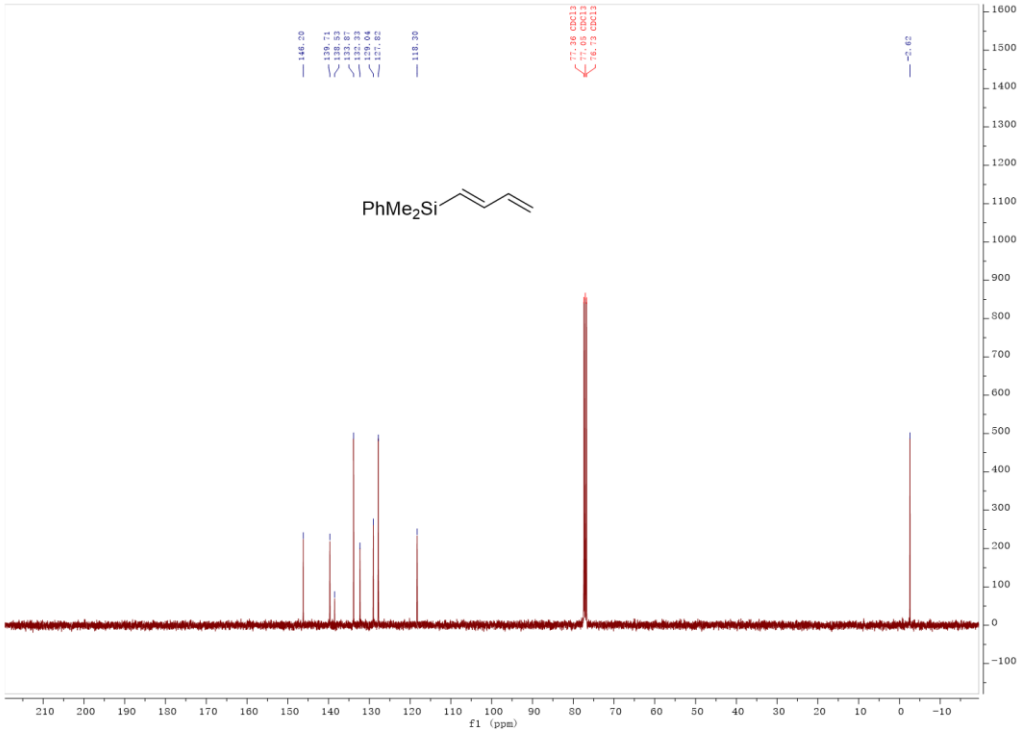


***(E)*-buta-1,3-dien-1-yldimethyl(phenyl)silane (S7)**

^{1}H NMR



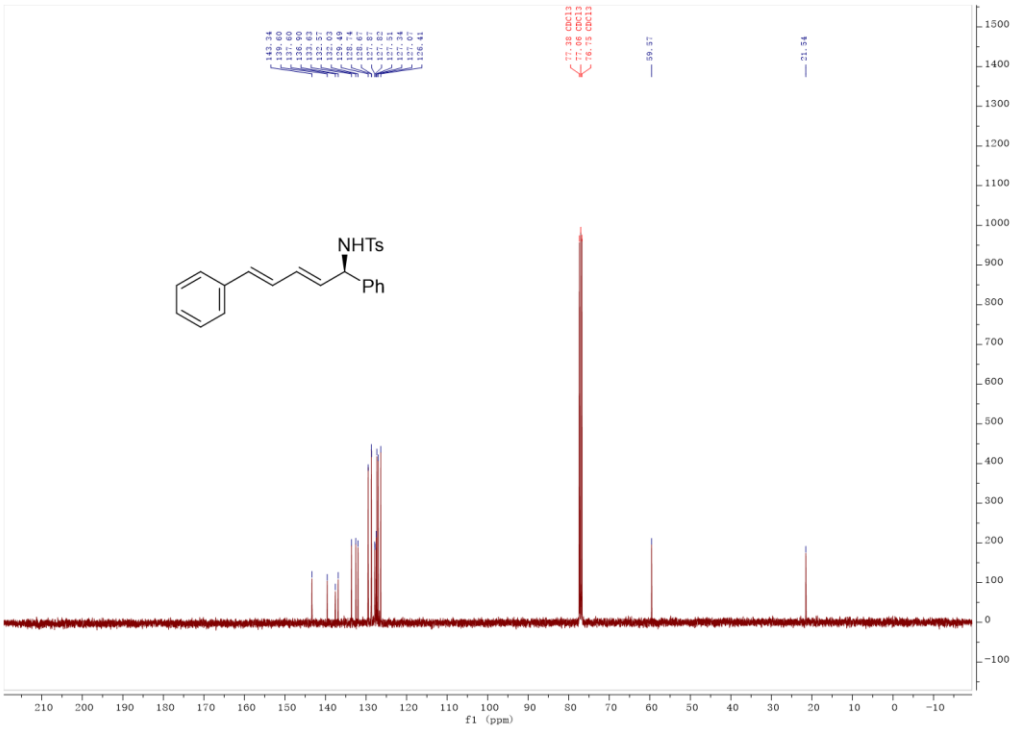
^{13}C NMR



***N*-((*R*,2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (3)**

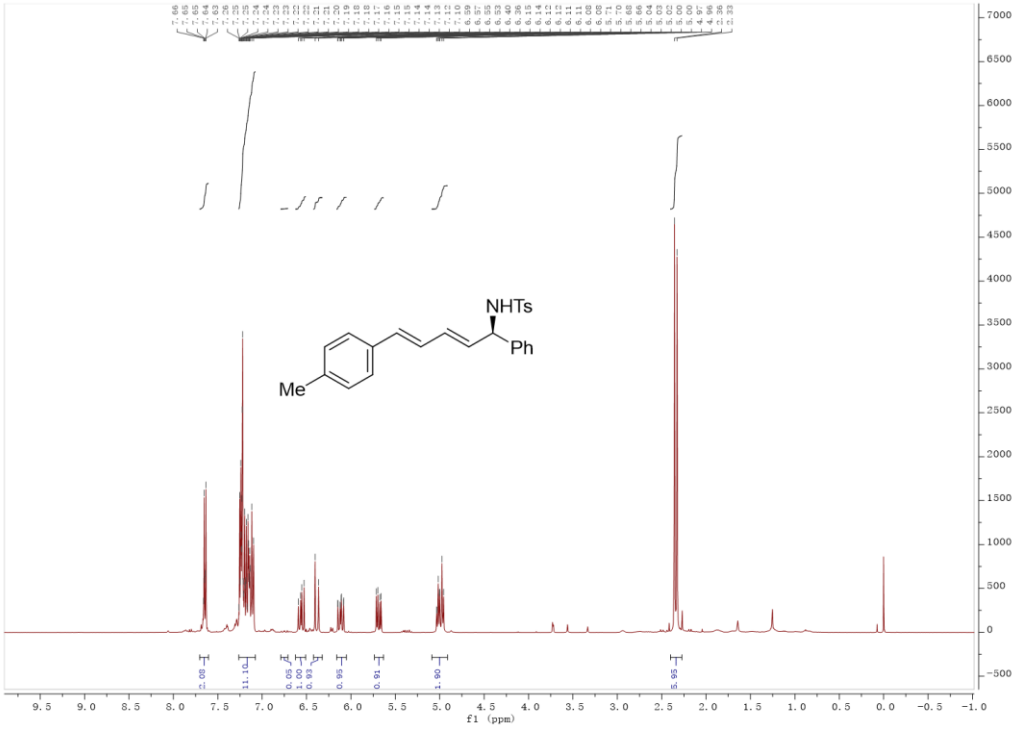
^{1}H NMR

^{13}C NMR

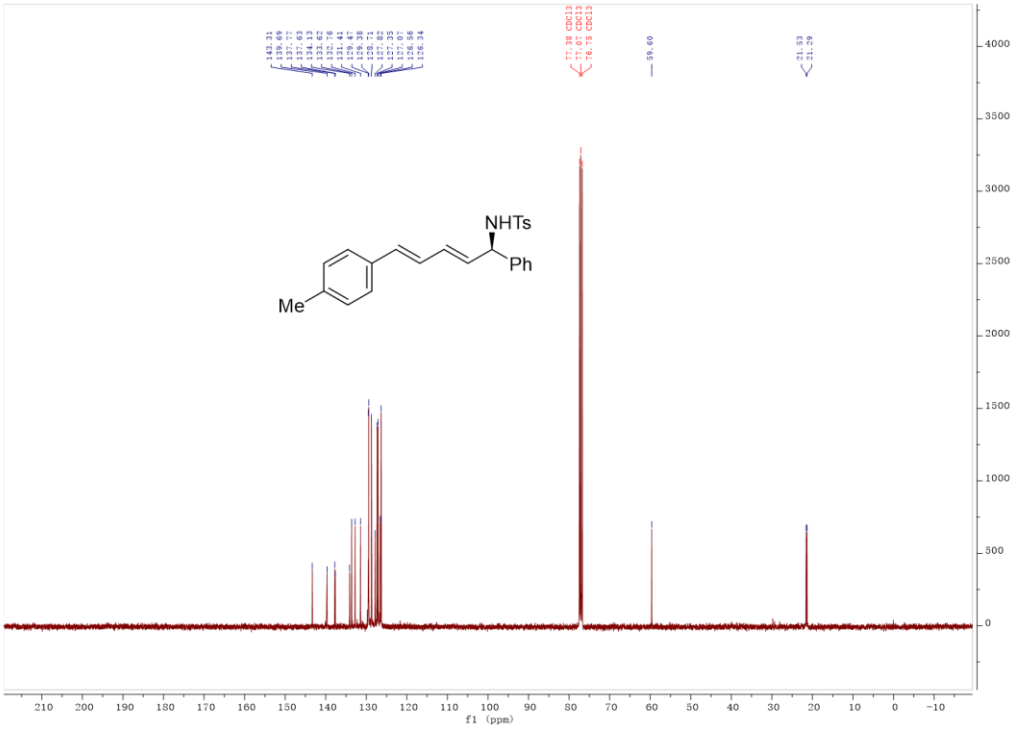


4-methyl-*N*-((*R*,2*E*,4*E*)-1-phenyl-5-(p-tolyl)penta-2,4-dien-1-yl)benzenesulfonamide (4)

^{1}H NMR

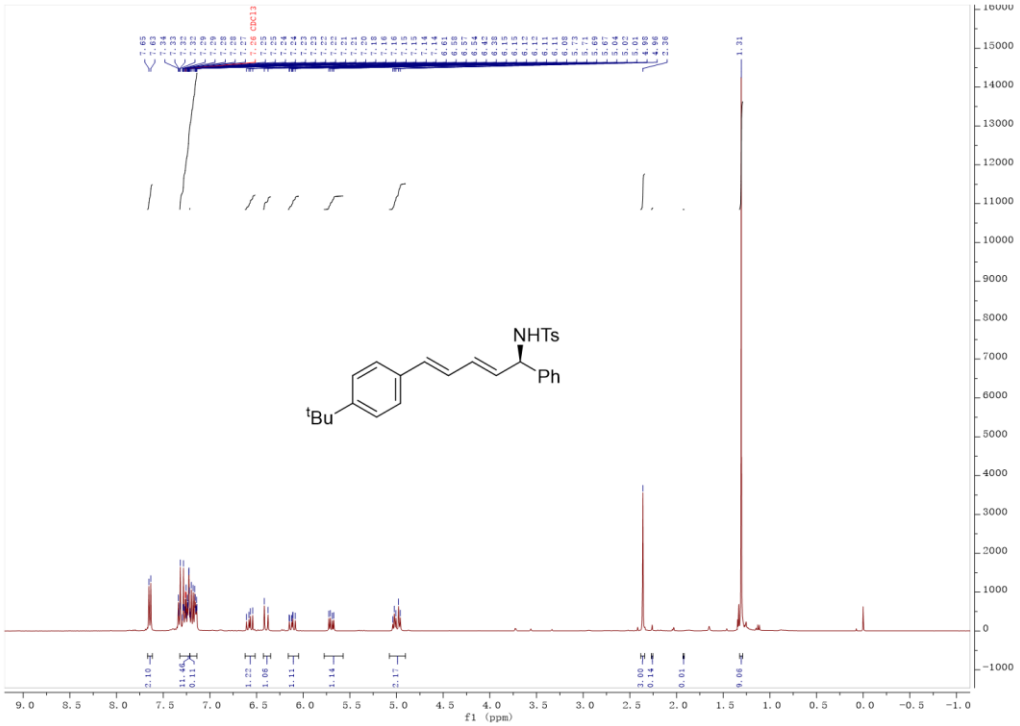


^{13}C NMR

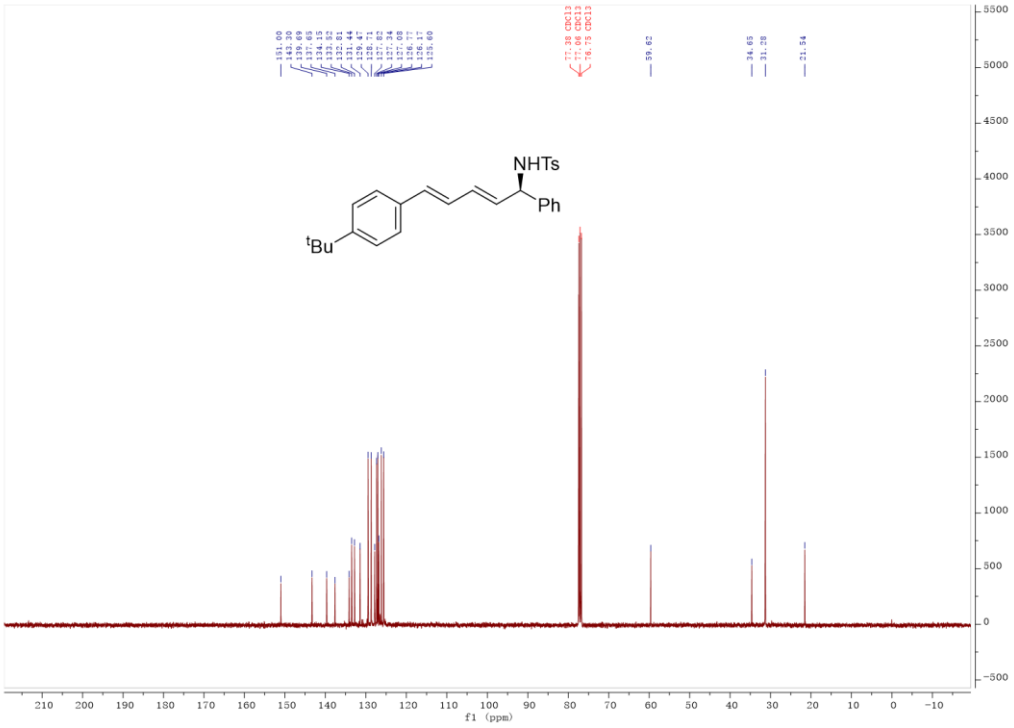


***N*-((*R*,2*E*,4*E*)-5-(4-(*tert*-butyl)phenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (5)**

^{1}H NMR

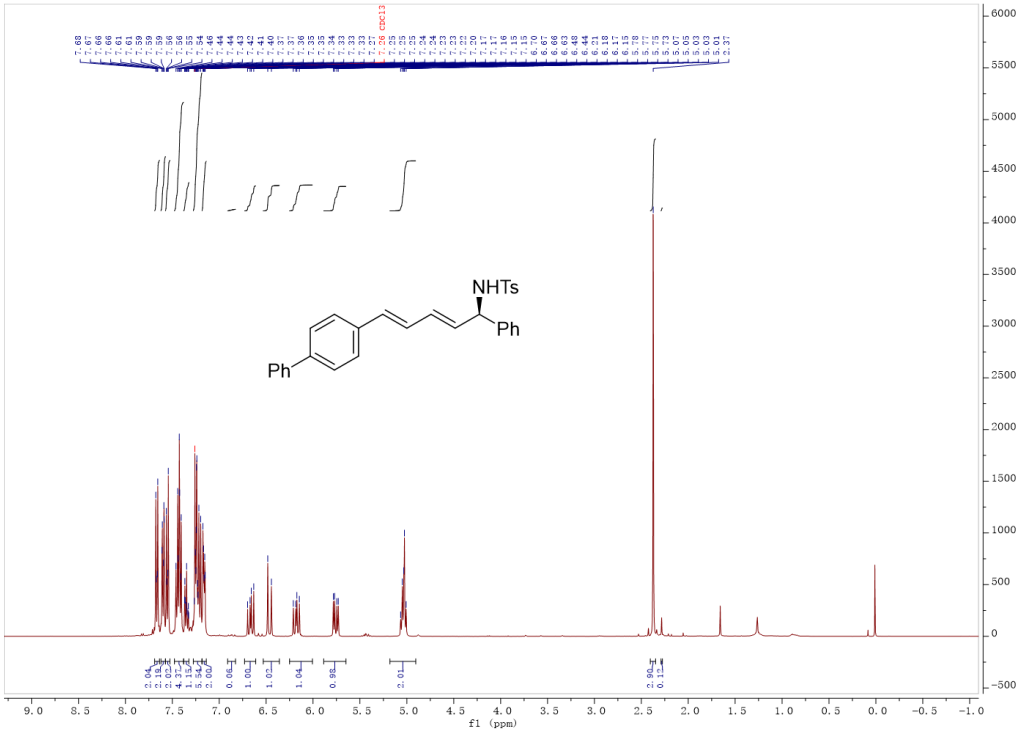


^{13}C NMR

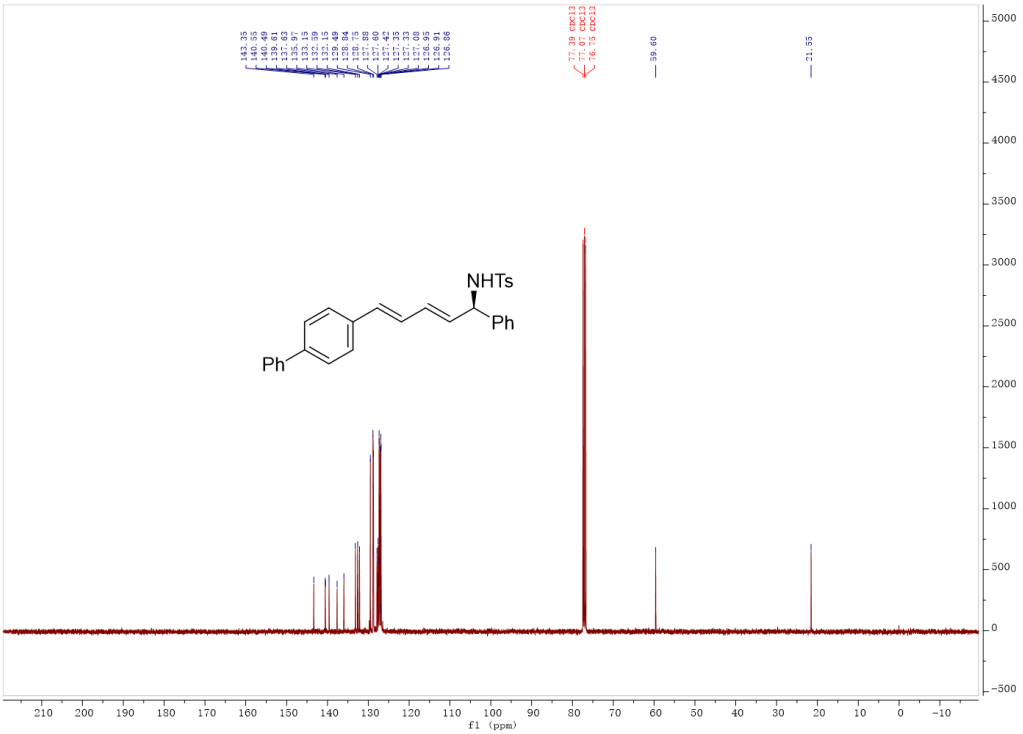


***N*-((*R*,2*E*,4*E*)-5-([1,1'-biphenyl]-4-yl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (6)**

^{1}H NMR

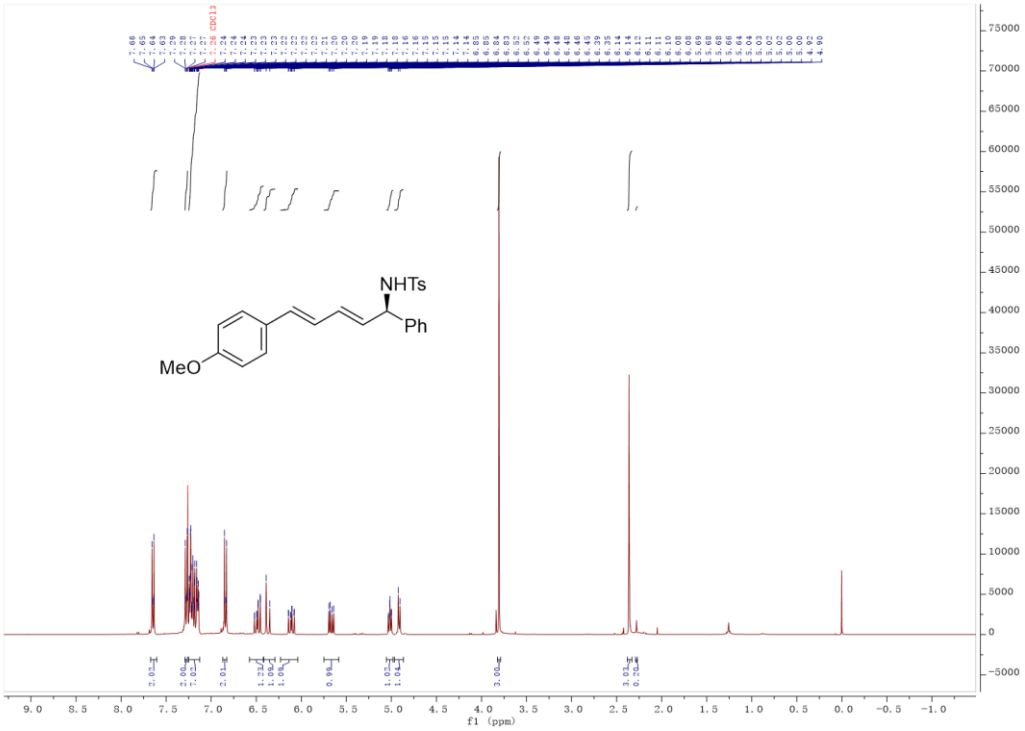


^{13}C NMR

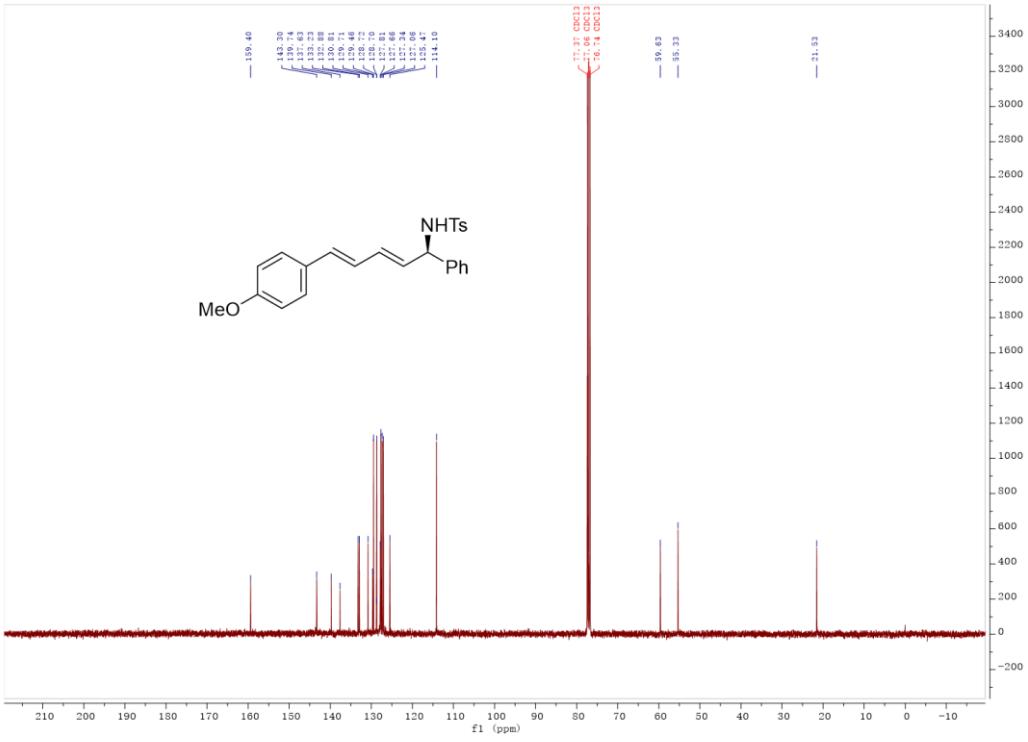


***N*-((*R*,2*E*,4*E*)-5-(4-methoxyphenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (7)**

^{1}H NMR

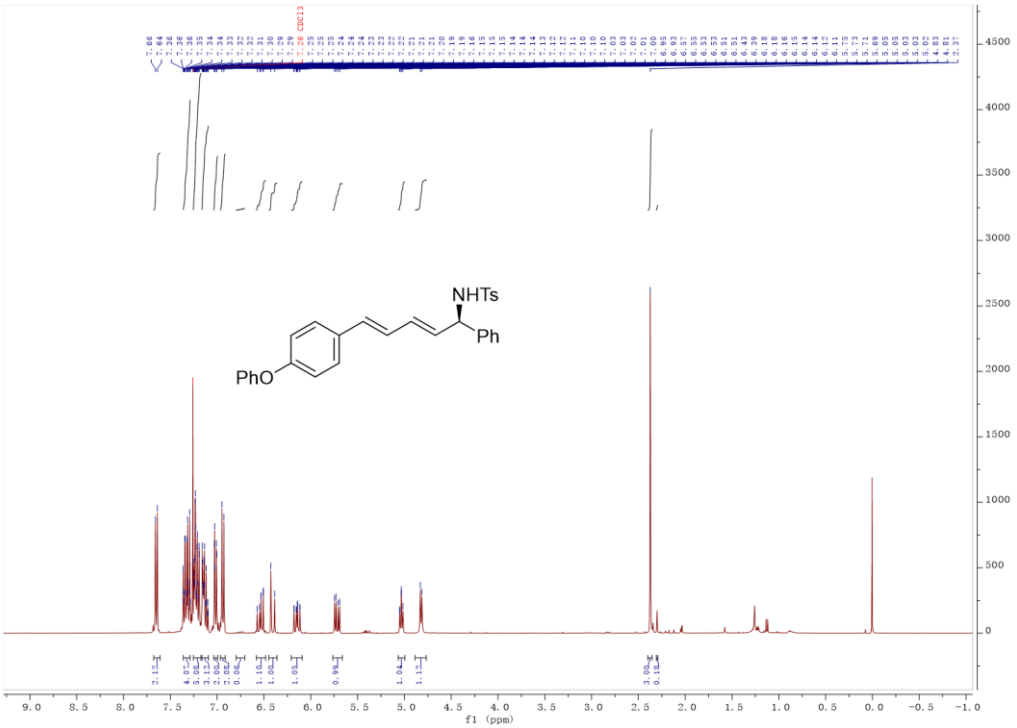


^{13}C NMR

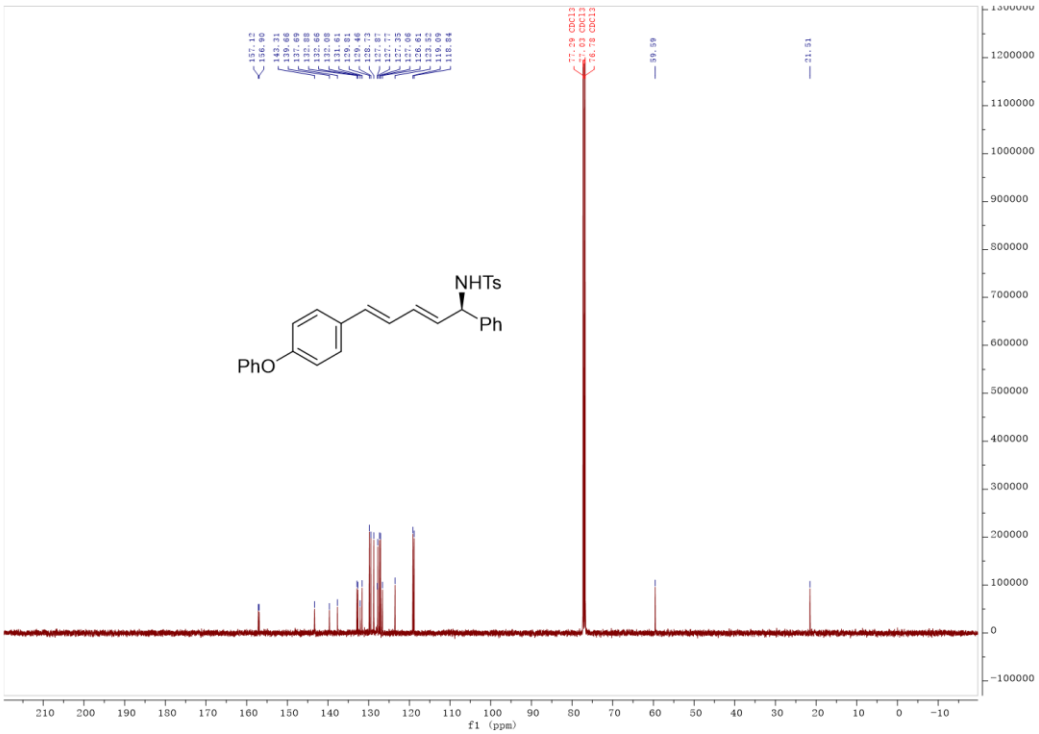


4-methyl-*N*-((*R*,2*E*,4*E*)-5-(4-phenoxyphenyl)-1-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (8)

^{1}H NMR

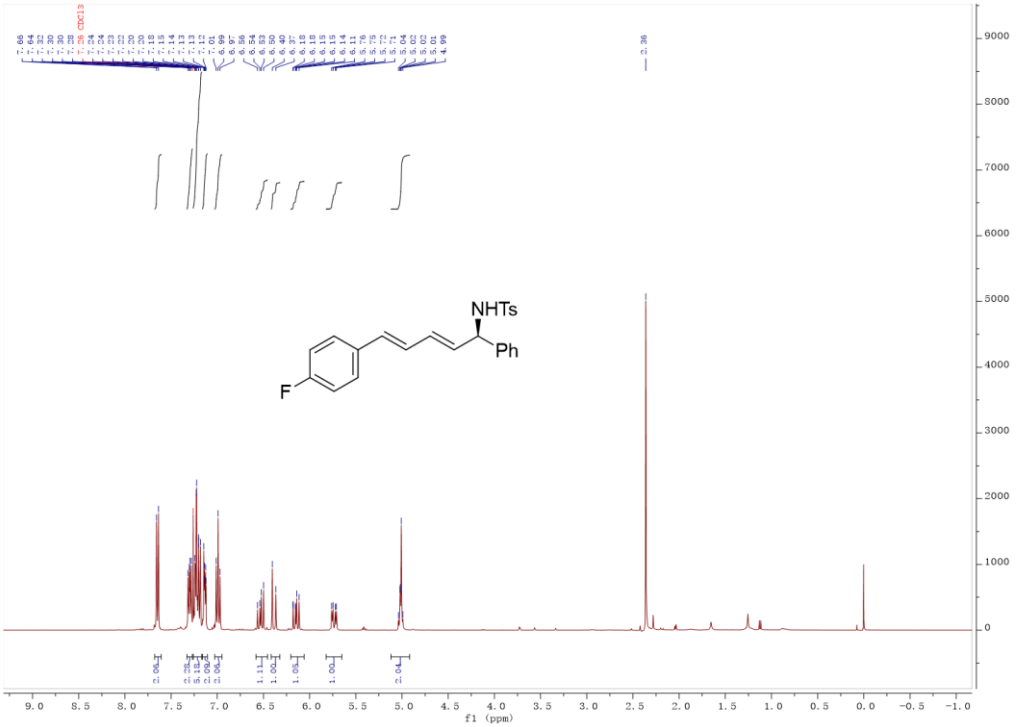


^{13}C NMR

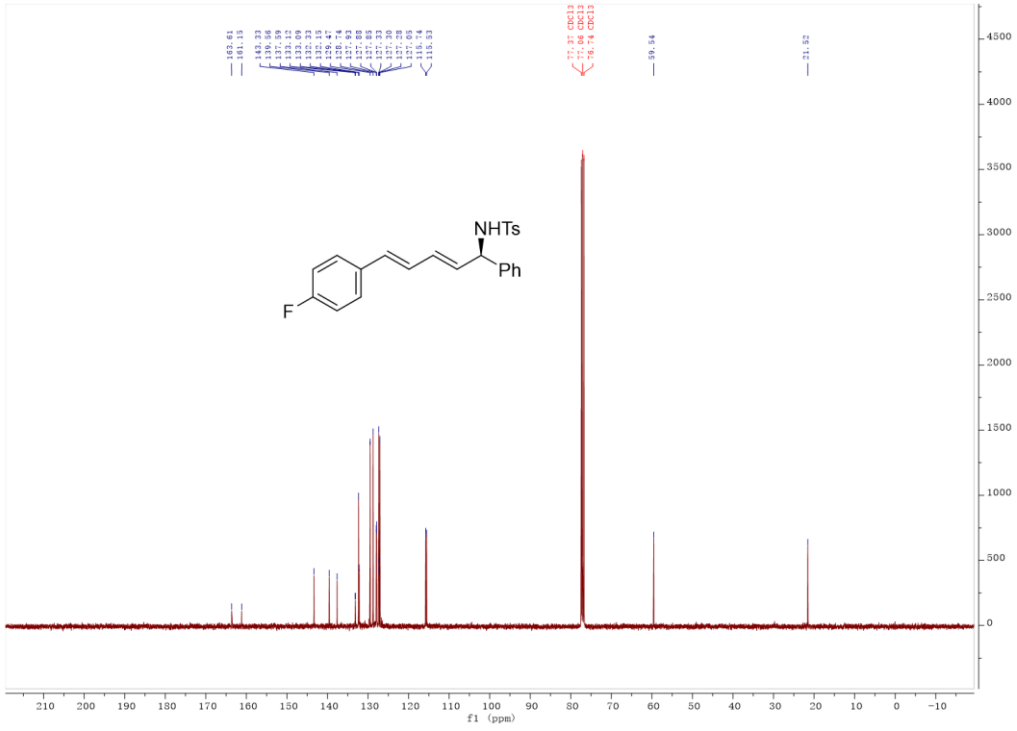


***N*-((*R*,2*E*,4*E*)-5-(4-fluorophenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (9)**

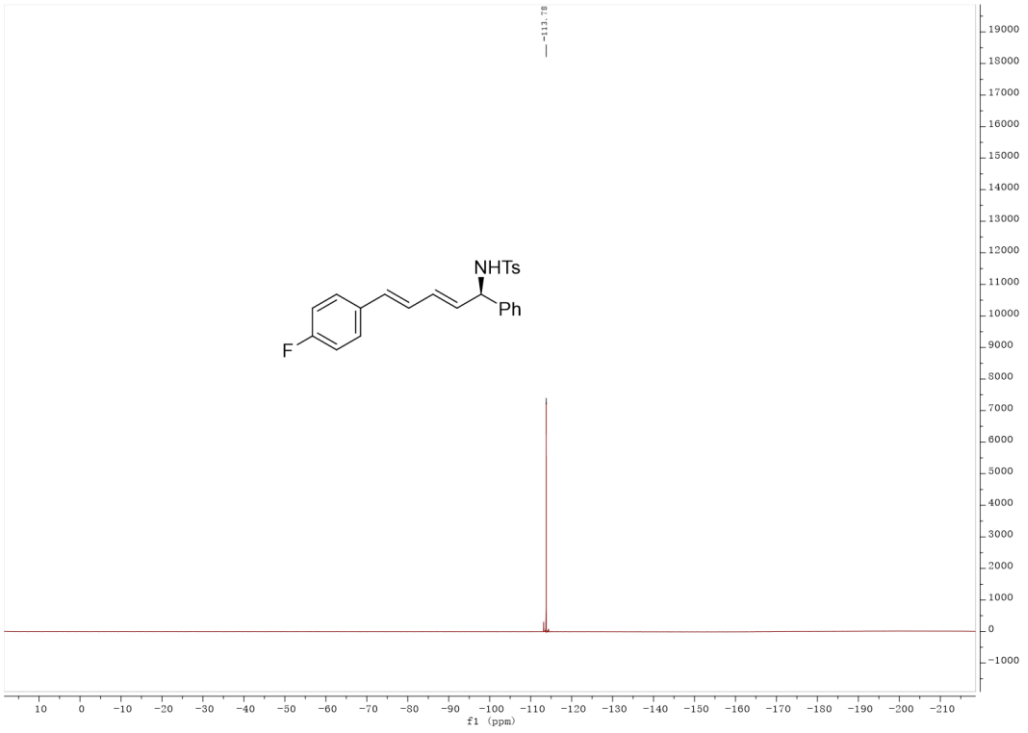
^{1}H NMR



^{13}C NMR

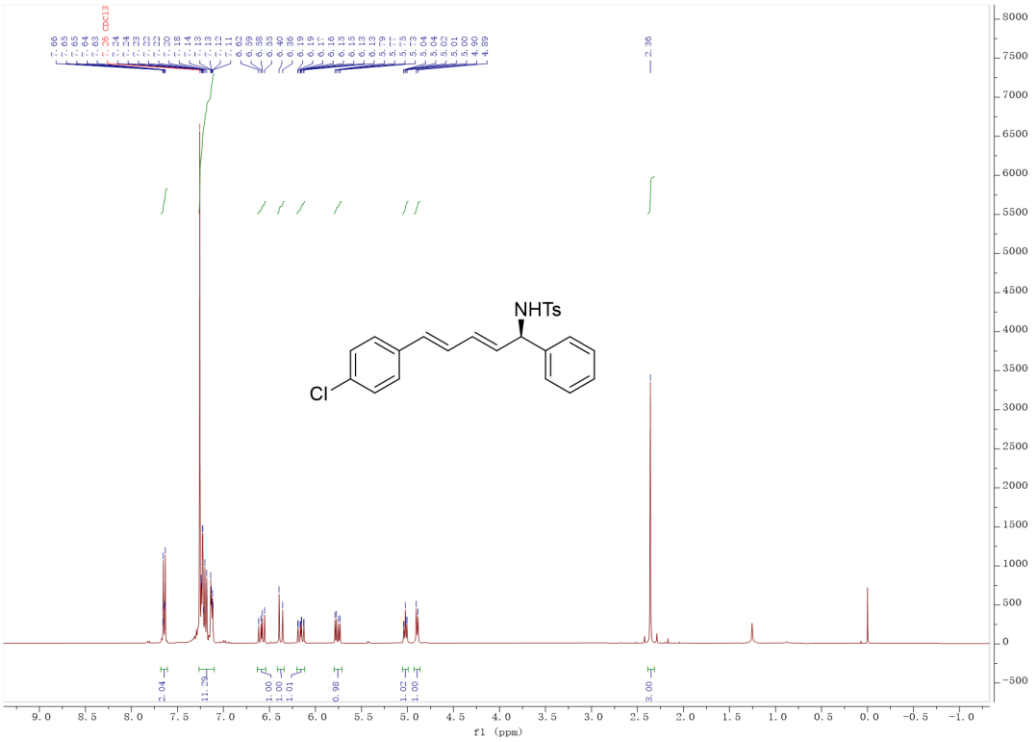


^{19}F NMR

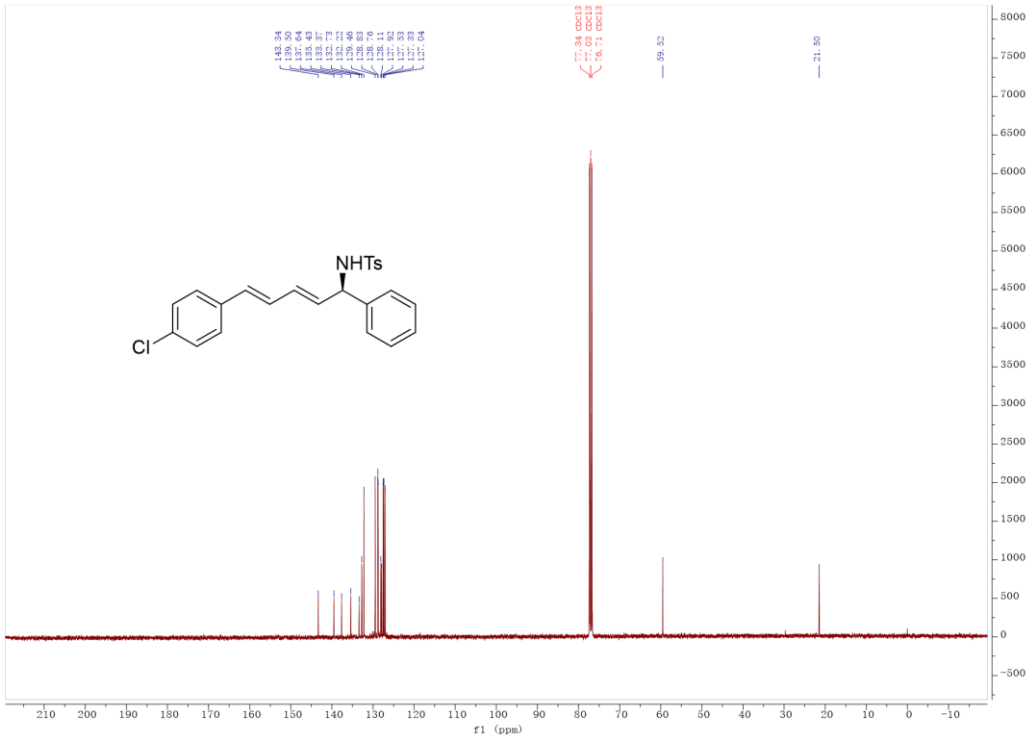


***N*-((*R*,2*E*,4*E*)-5-(4-chlorophenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (10)**

^{1}H NMR

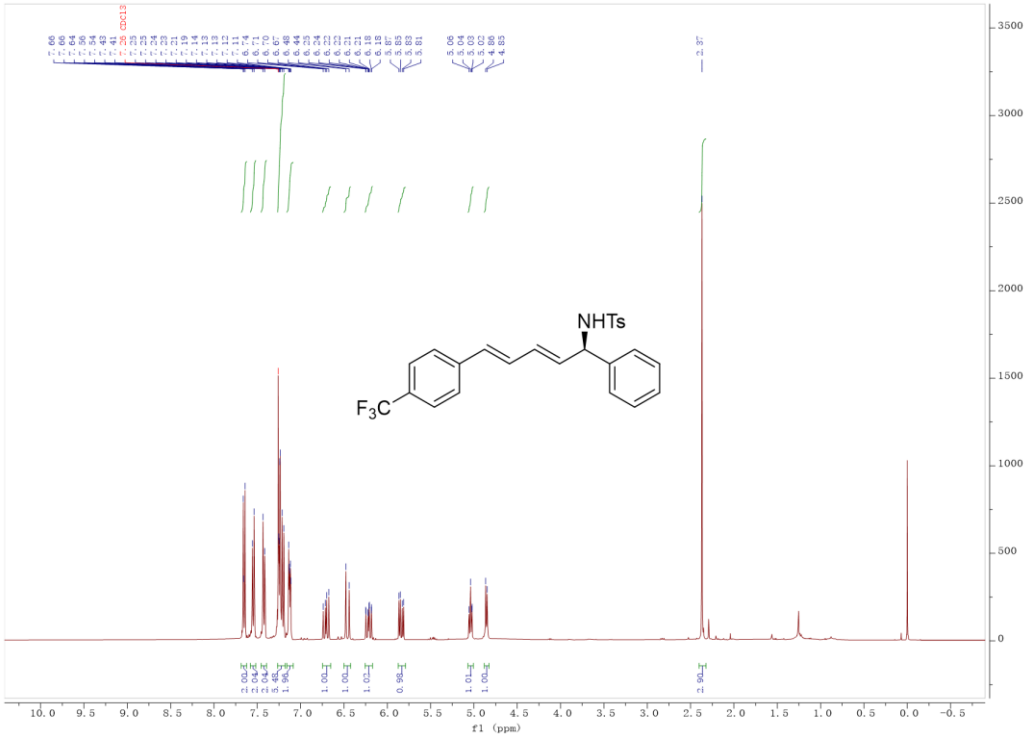


^{13}C NMR

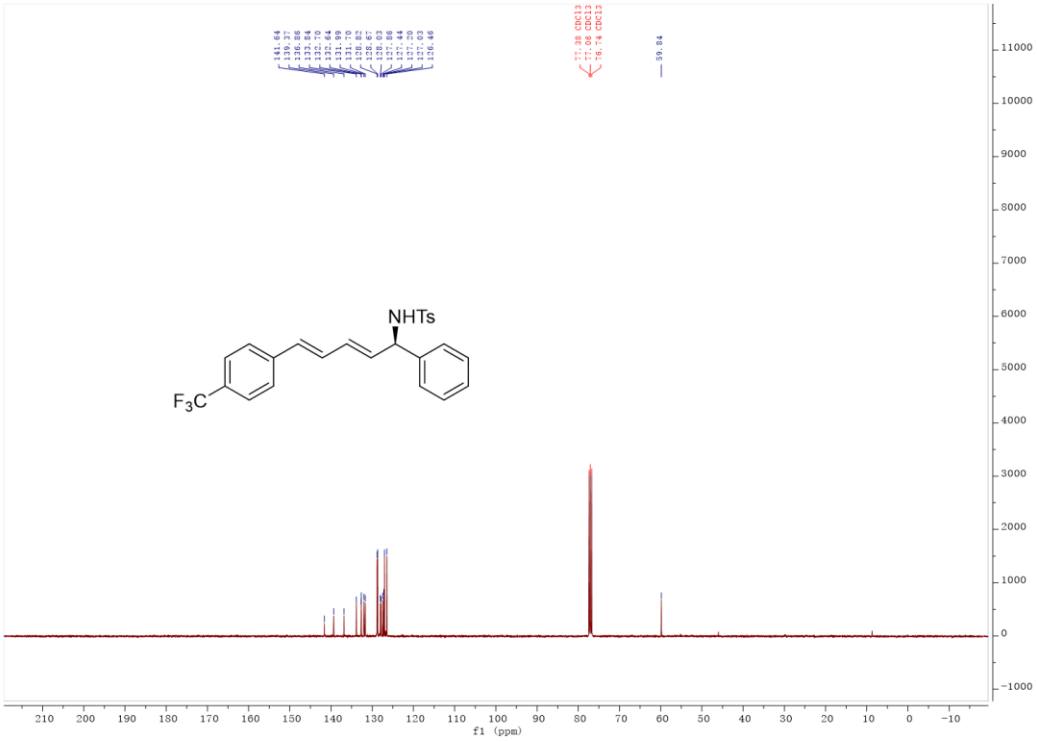


4-methyl-*N*-((*R*,2*E*,4*E*)-1-phenyl-5-(4-(trifluoromethyl)phenyl)penta-2,4-dien-1-yl)benzenesulfonamide (11)

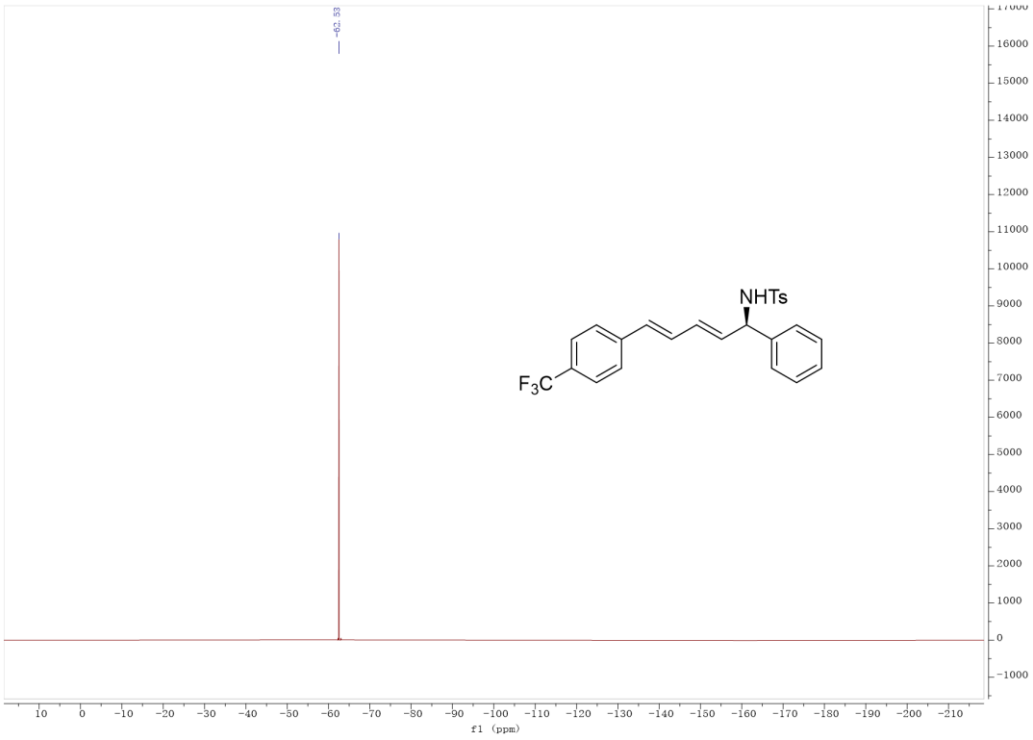
^{1}H NMR



^{13}C NMR

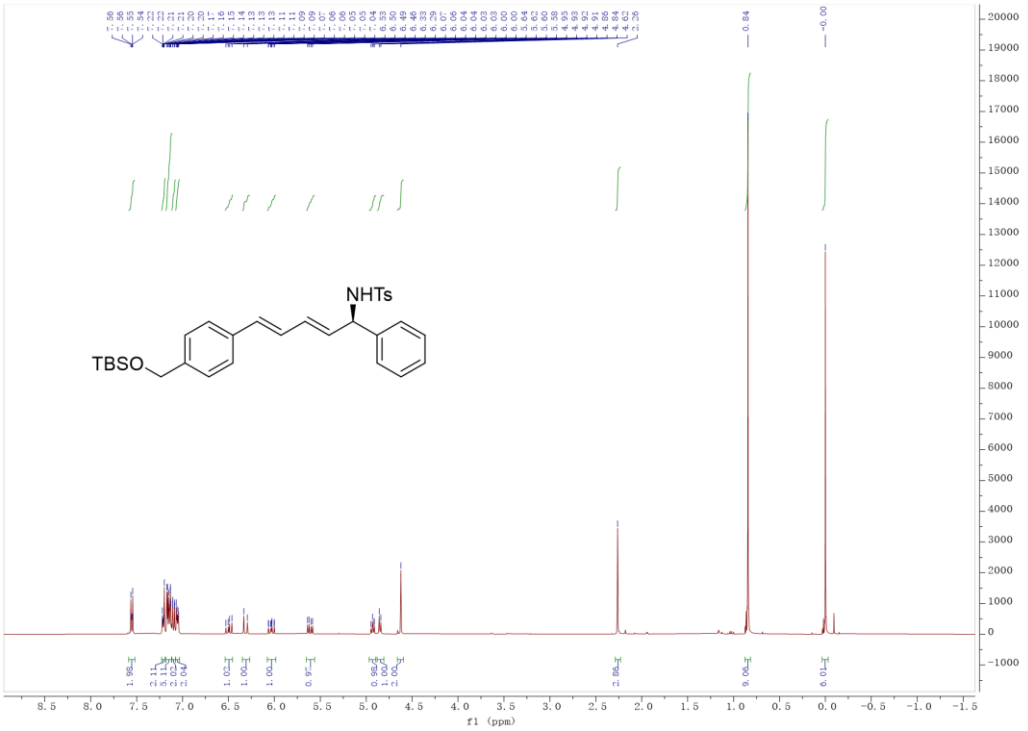


^{19}F NMR

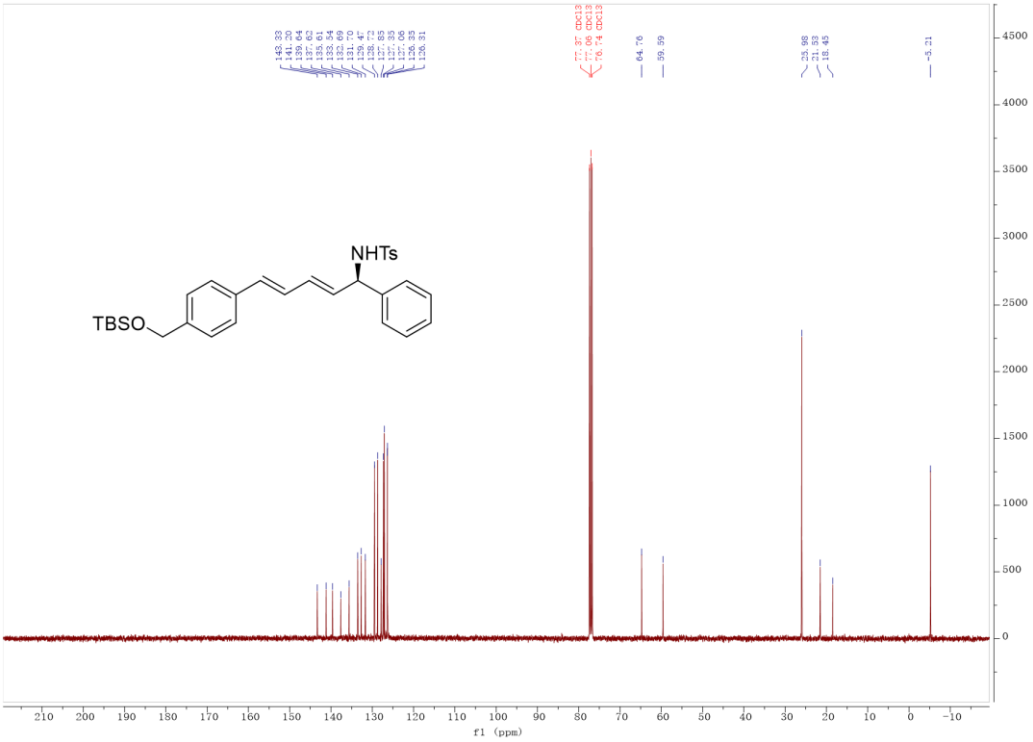

-62.53
NHTs
F3C
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

***N*-((*R*,2*E*,4*E*)-5-(4-(((*tert*-butyldimethylsilyl)oxy)methyl)phenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (12)**

^{1}H NMR

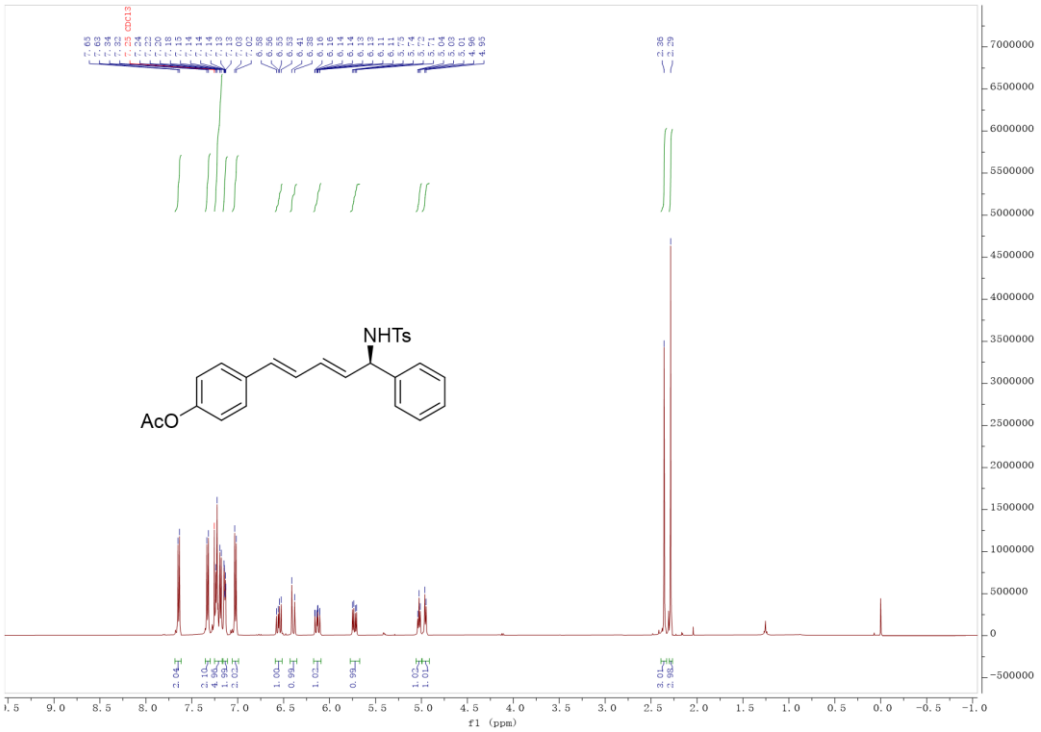


^{13}C NMR

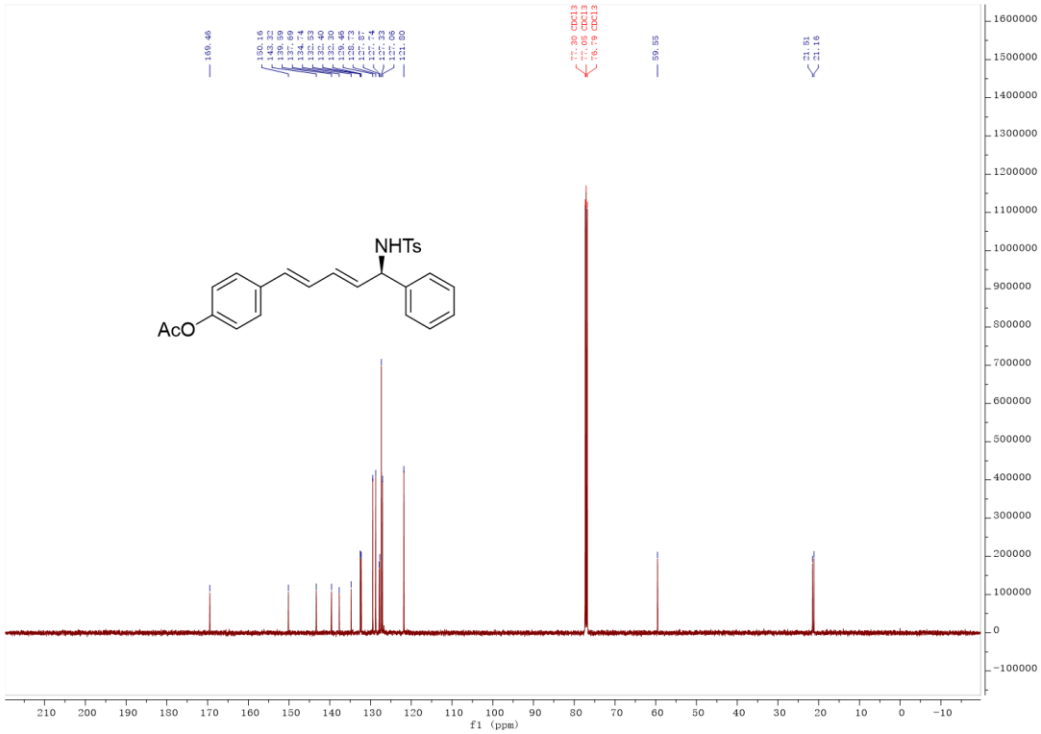


4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)phenyl acetate (13)

^{1}H NMR

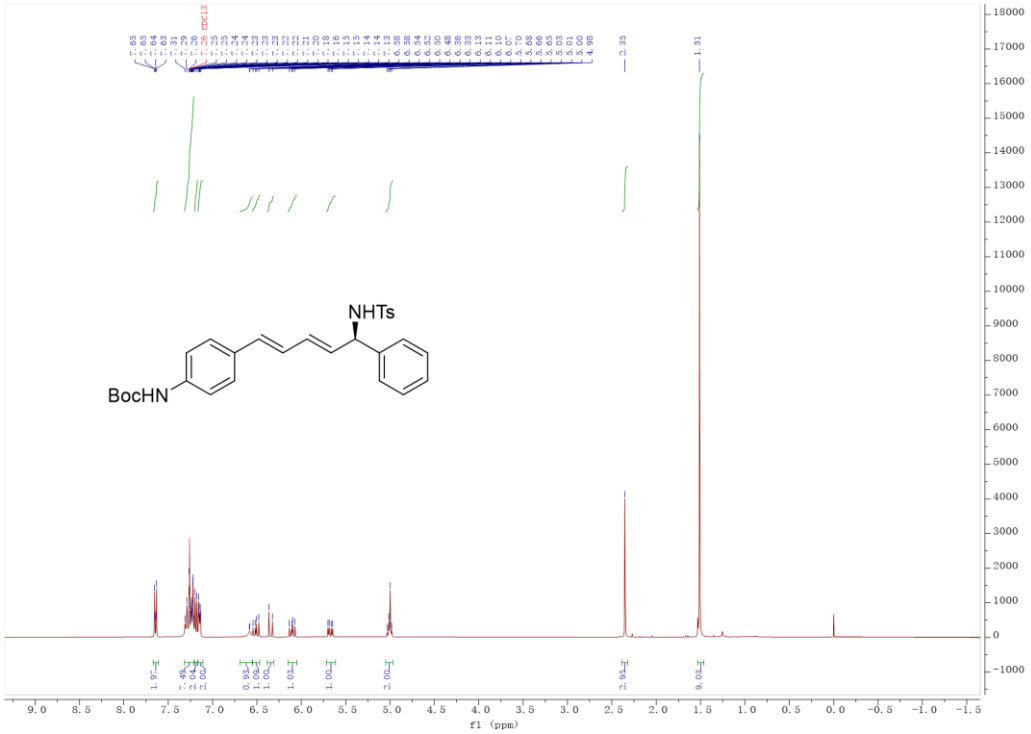


^{13}C NMR

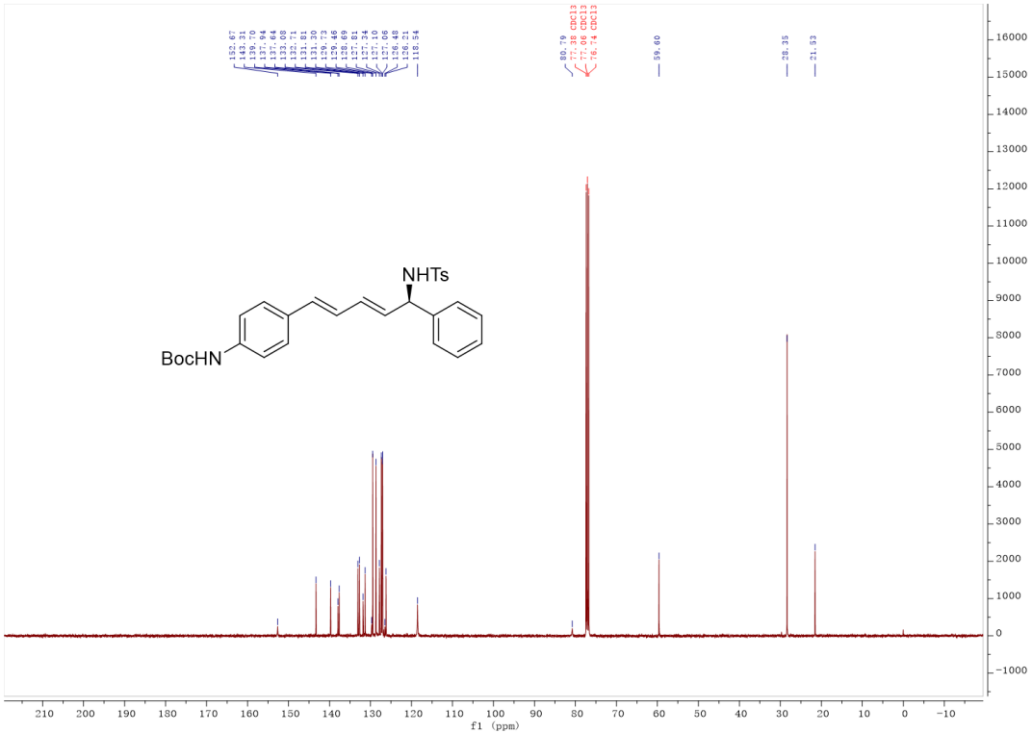


***Tert*-butyl (4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)phenyl)carbamate (14)**

^{1}H NMR

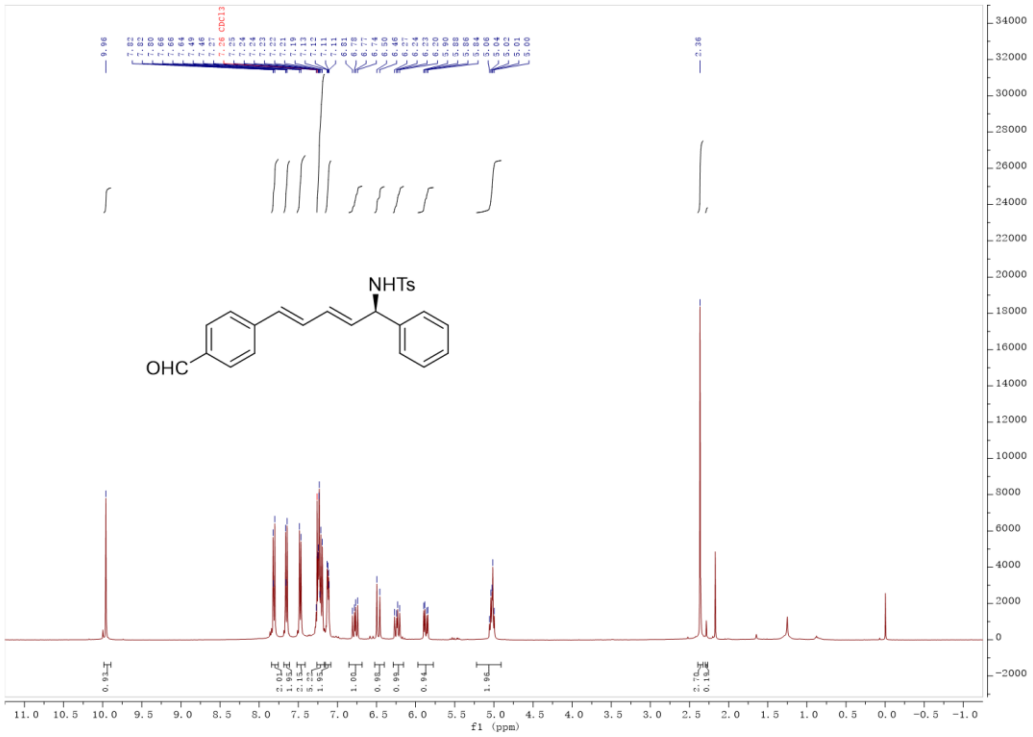


^{13}C NMR

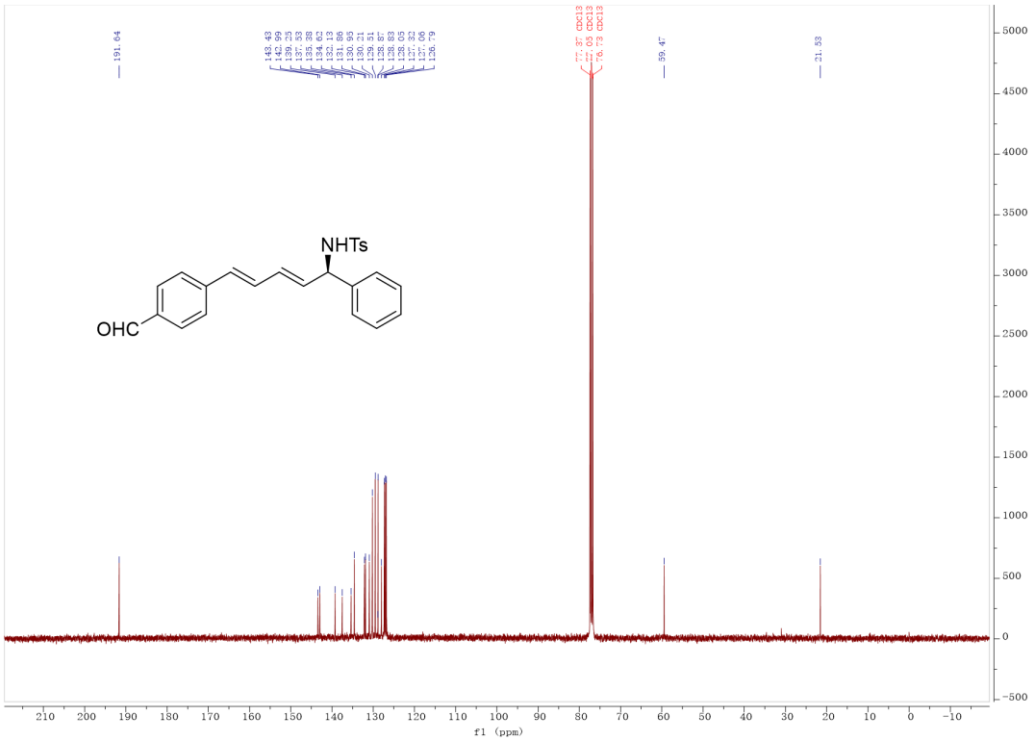


***N*-((*R*,2*E*,4*E*)-5-(4-formylphenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (15)**.

^{1}H NMR

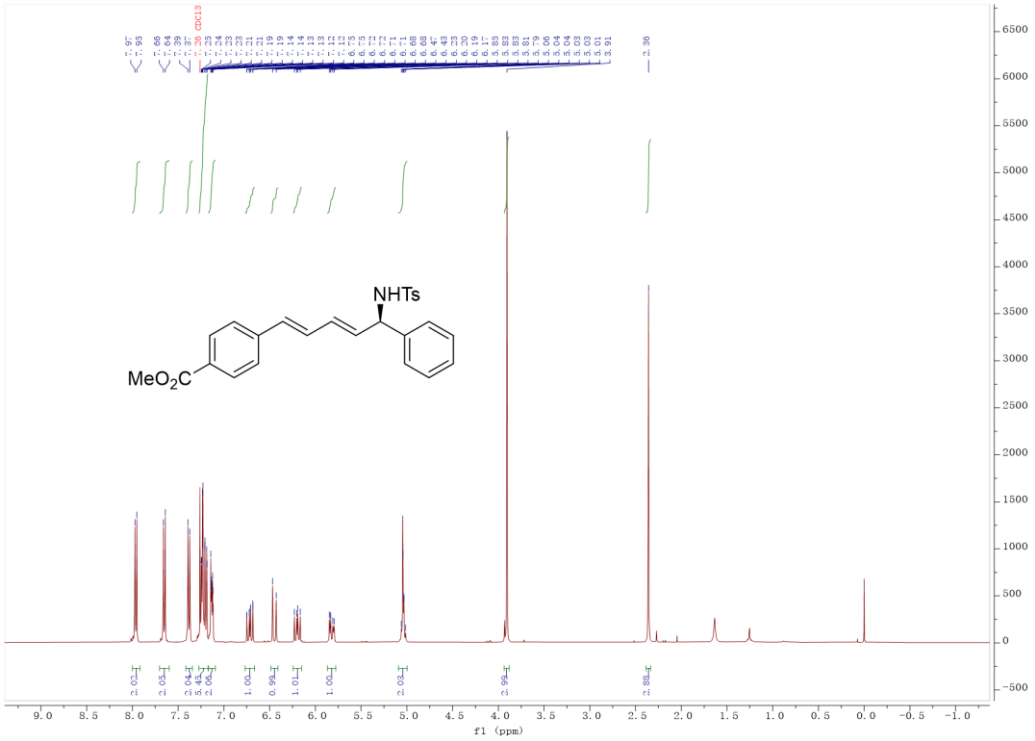


^{13}C NMR

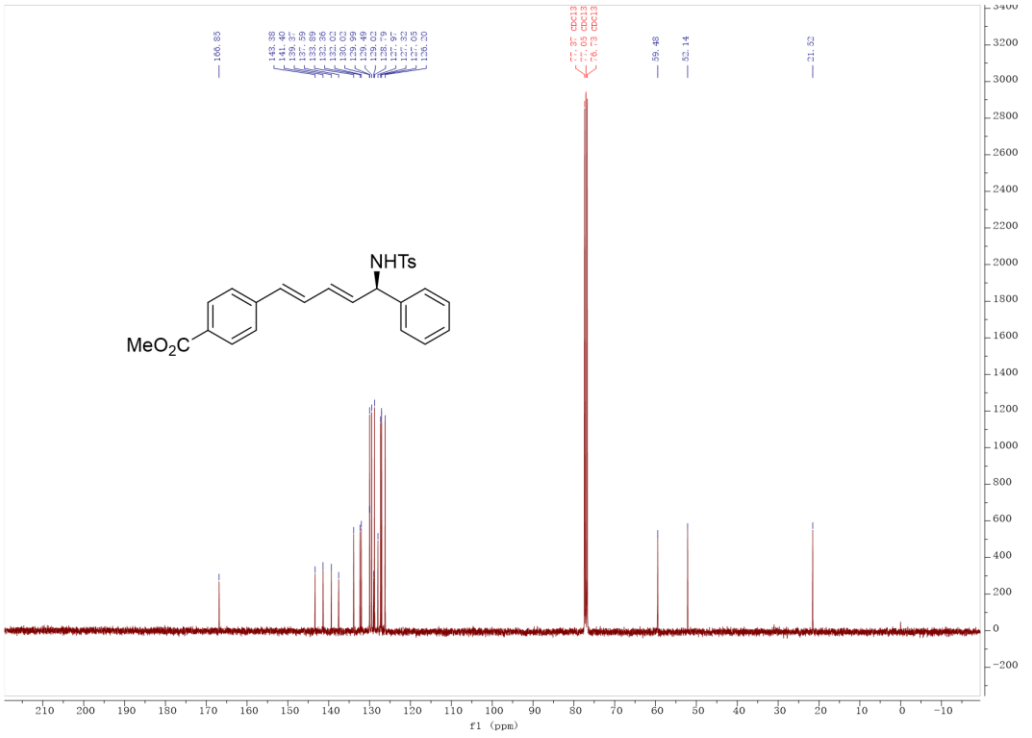


Methyl 4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)benzoate (16)

^{1}H NMR

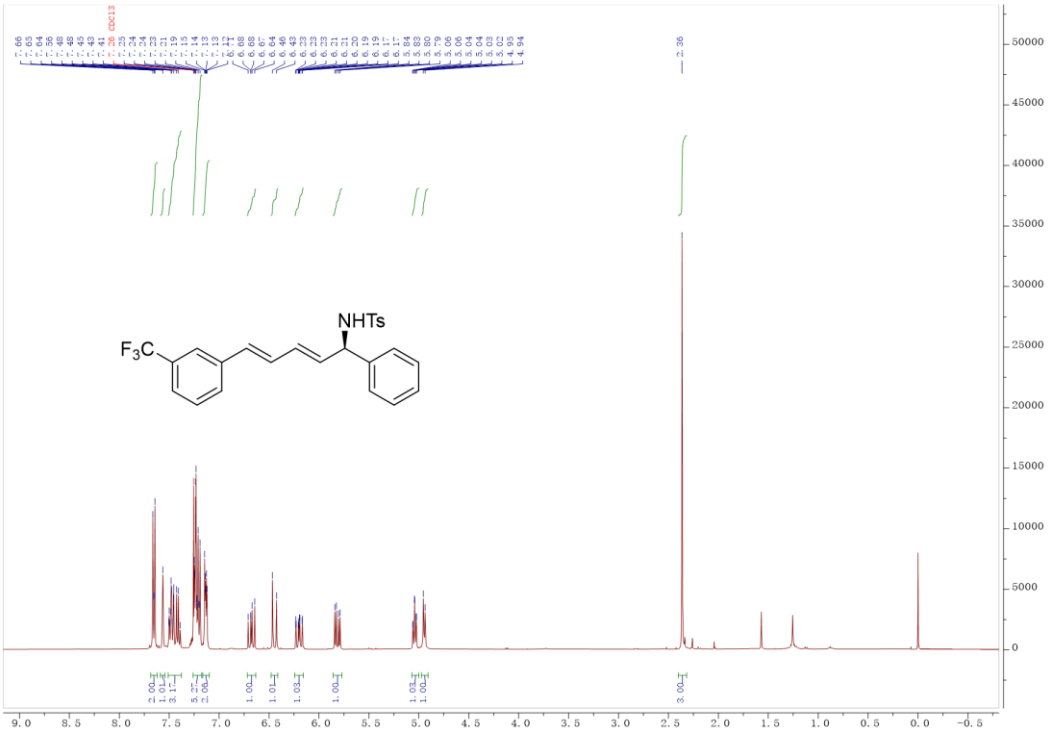


^{13}C NMR

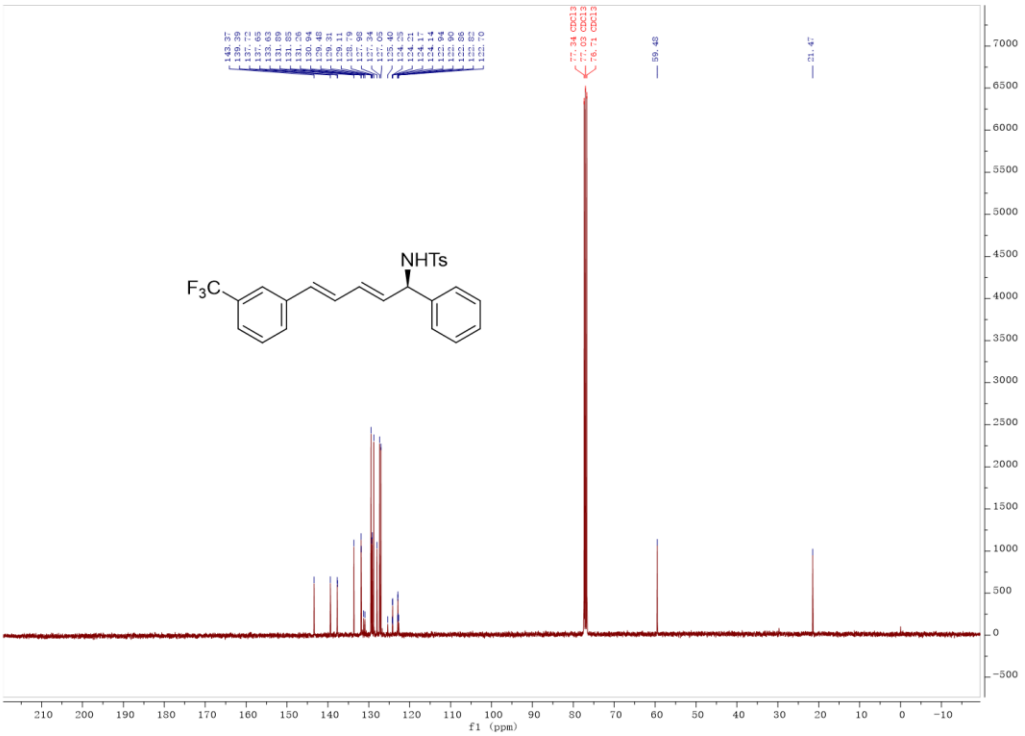


4-methyl-*N*-((*R*,2*E*,4*E*)-1-phenyl-5-(3-(trifluoromethyl)phenyl)penta-2,4-dien-1-yl)benzenesulfonamide (17)

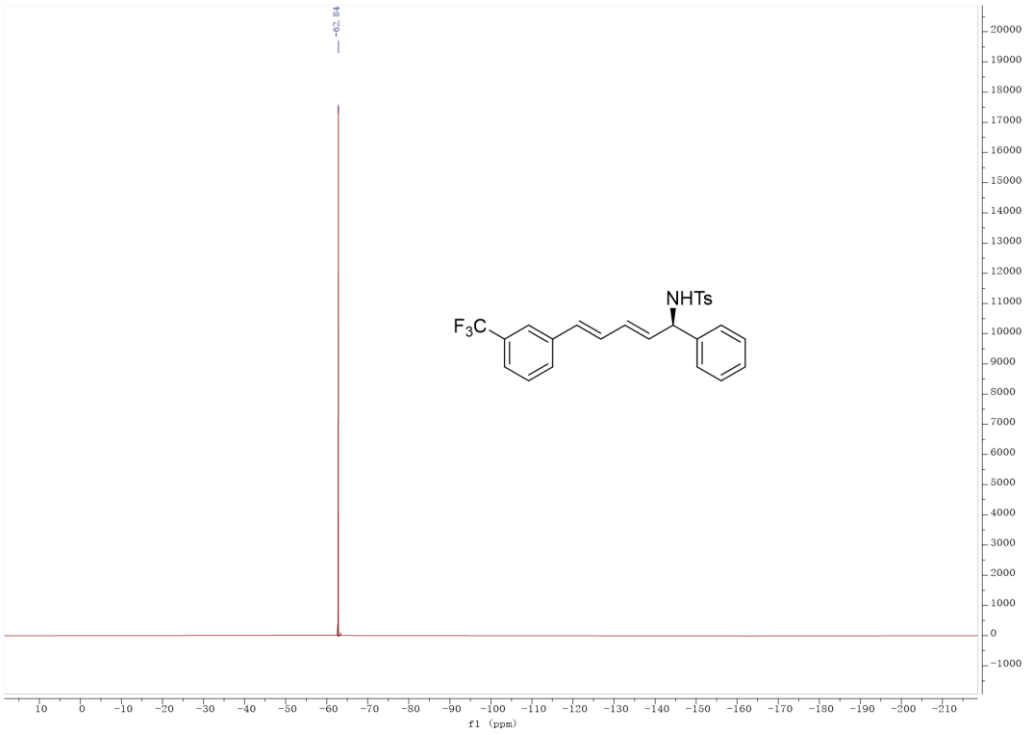
^{1}H NMR



^{13}C NMR

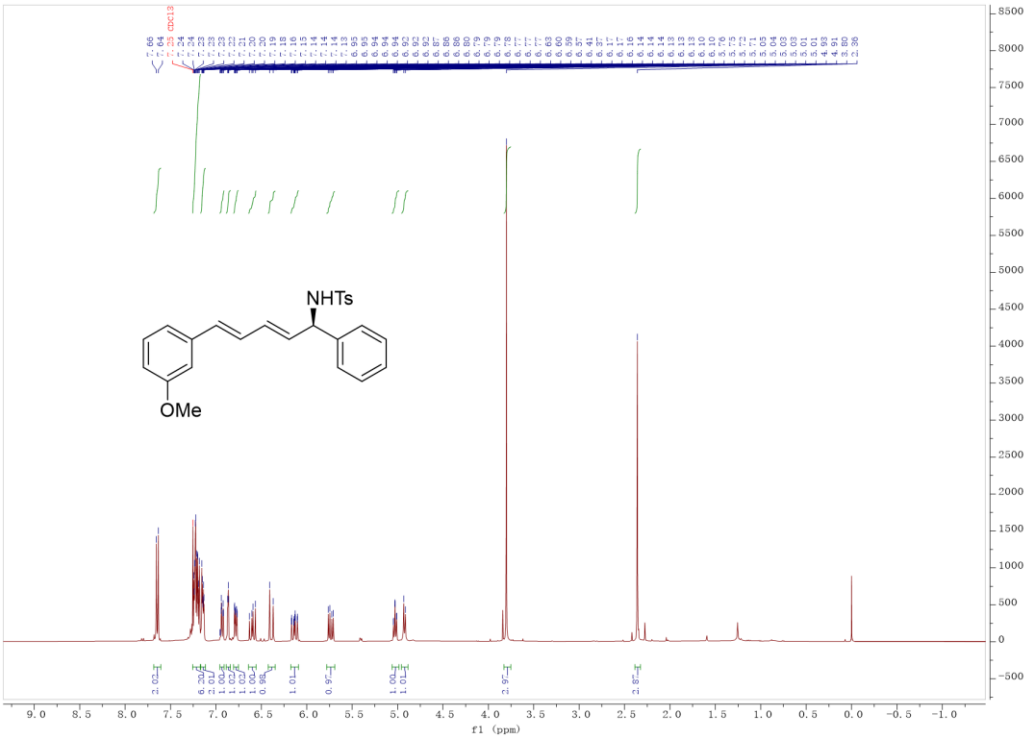


^{19}F NMR

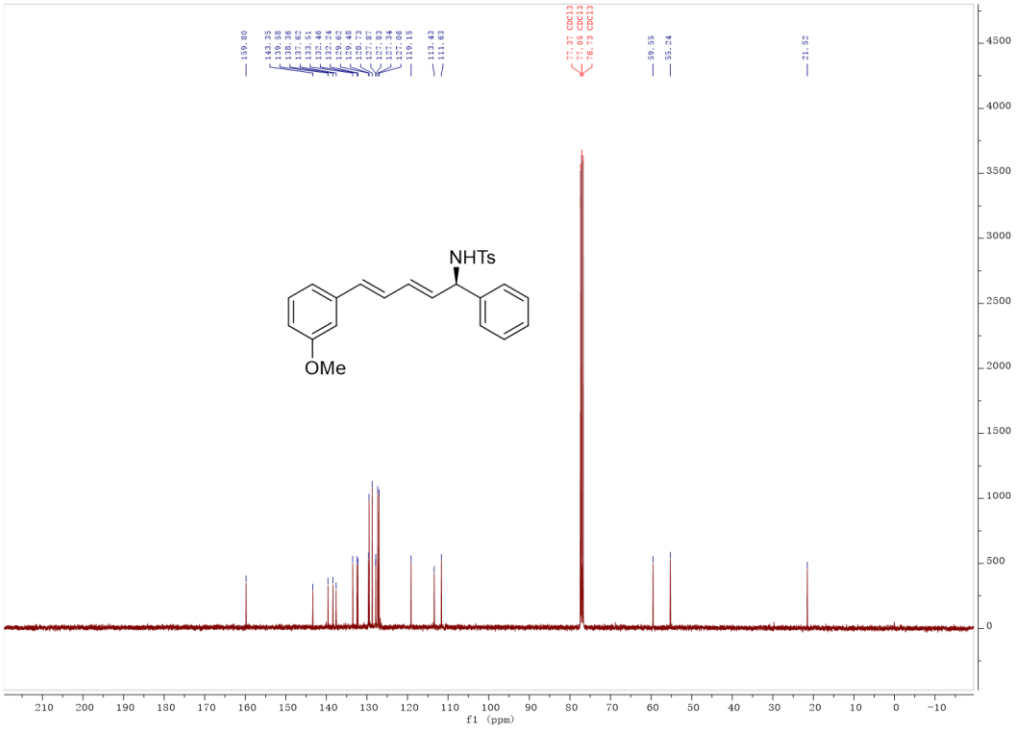

-62.84
NHTs
F3C
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

***N*-((*R*,2*E*,4*E*)-5-(3-methoxyphenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (18)**

^{1}H NMR

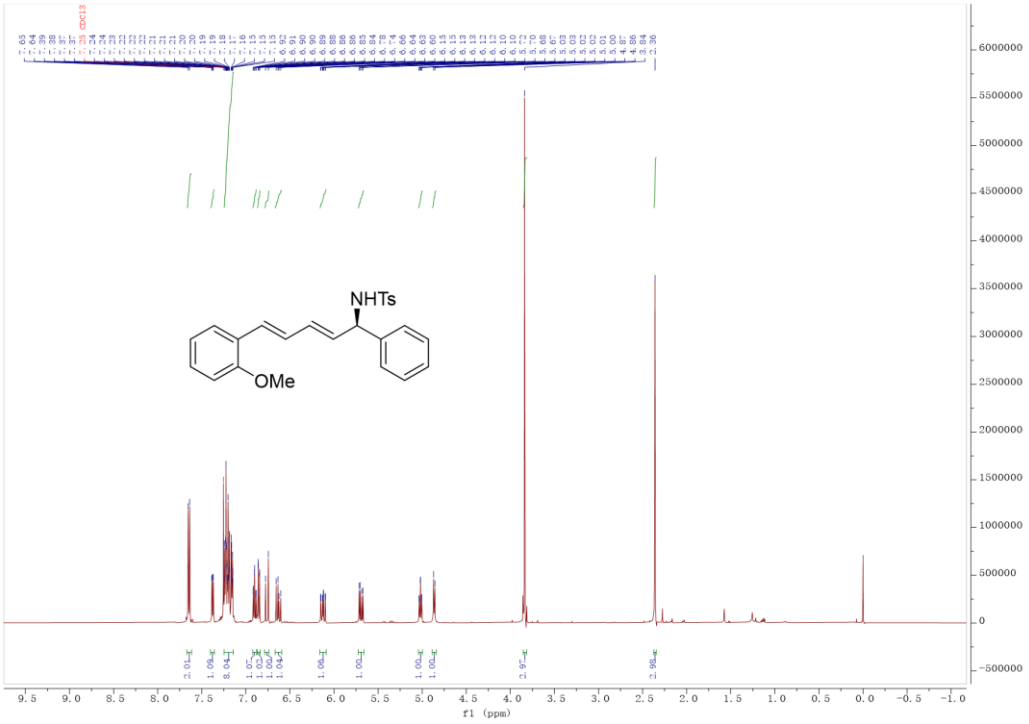


^{13}C NMR

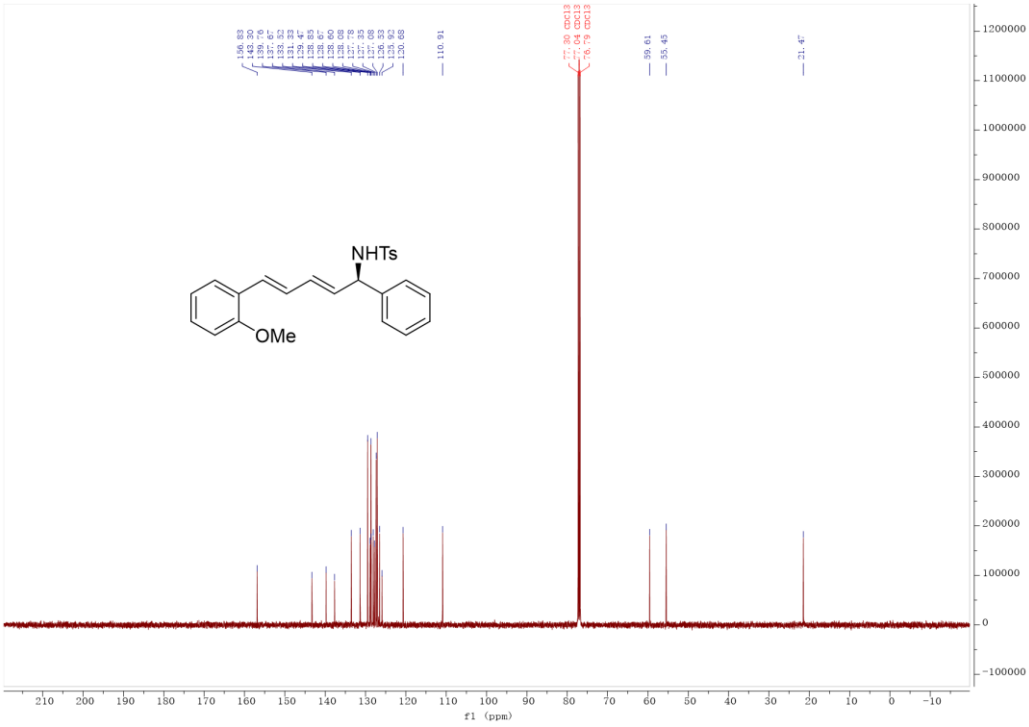


***N*-((*R*,2*E*,4*E*)-5-(2-methoxyphenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (19)**

^{1}H NMR

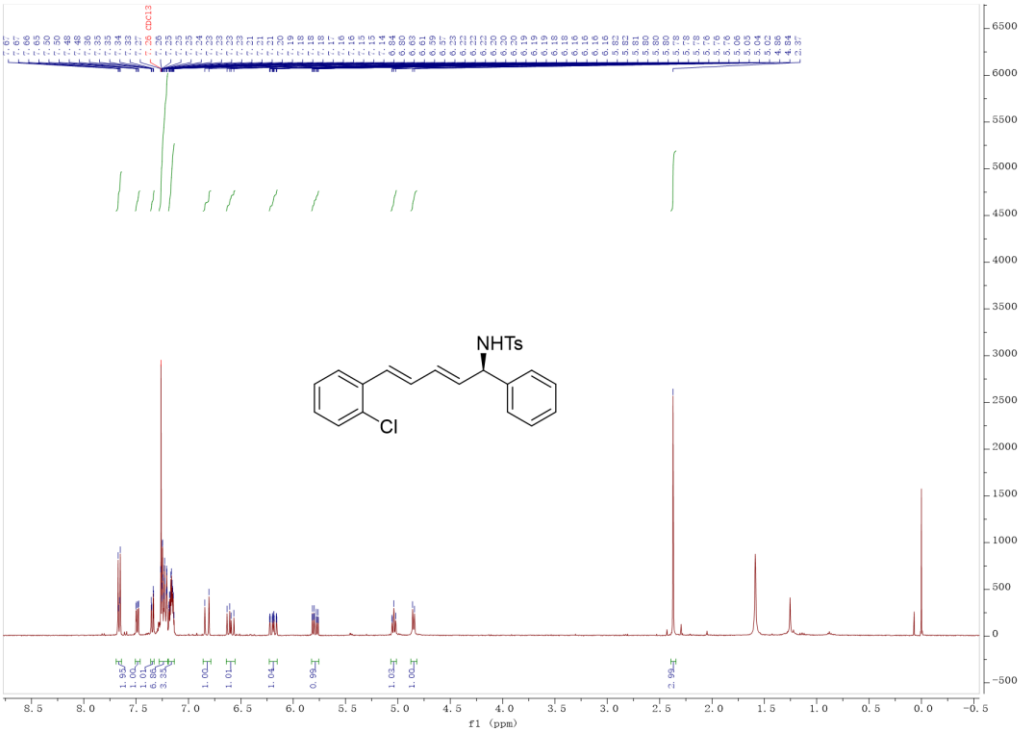


^{13}C NMR

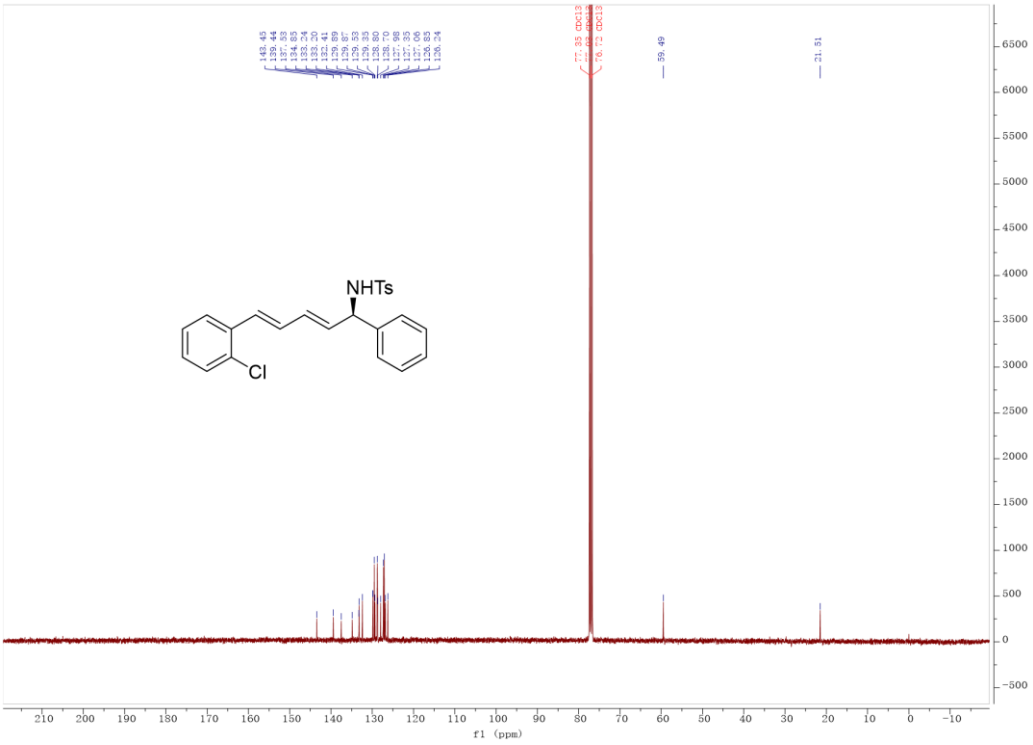


***N*-((*R*,2*E*,4*E*)-5-(2-chlorophenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (20)**

^{1}H NMR



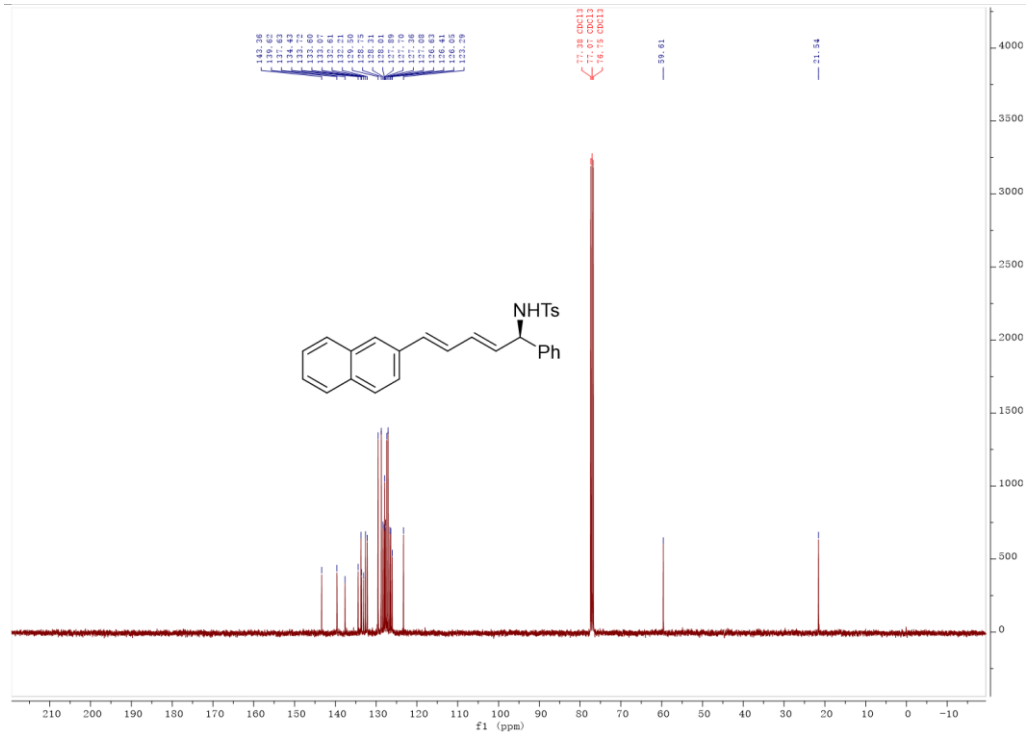
^{13}C NMR



4-methyl-N-((*R*,2*E*,4*E*)-5-(naphthalen-2-yl)-1-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (21)

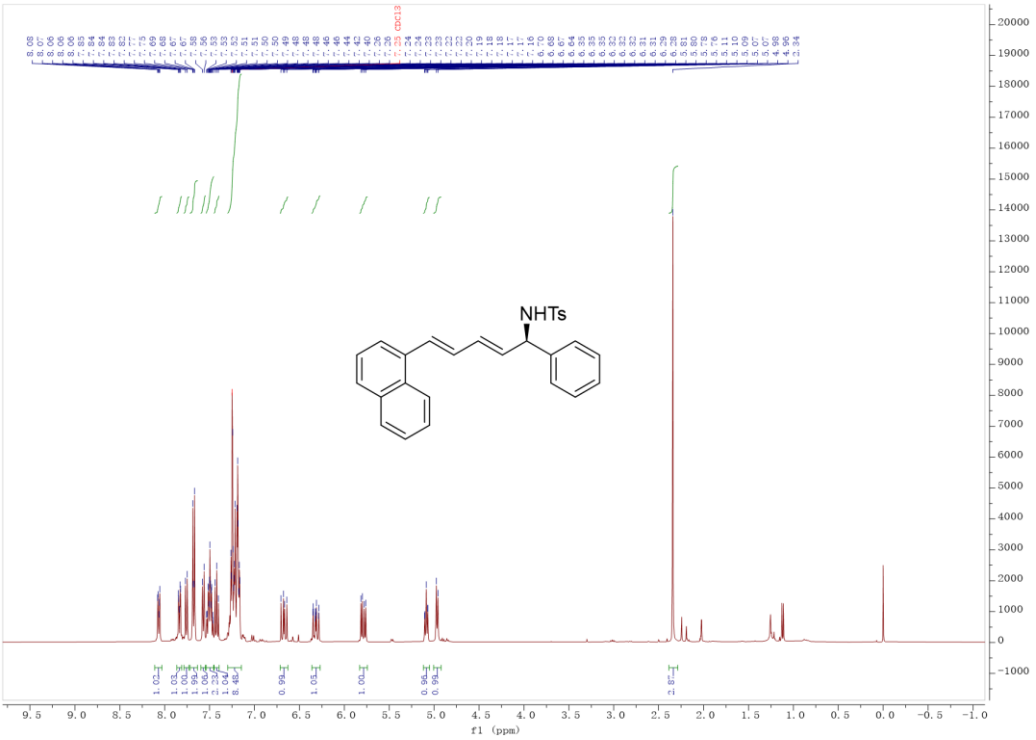
^{1}H NMR

^{13}C NMR

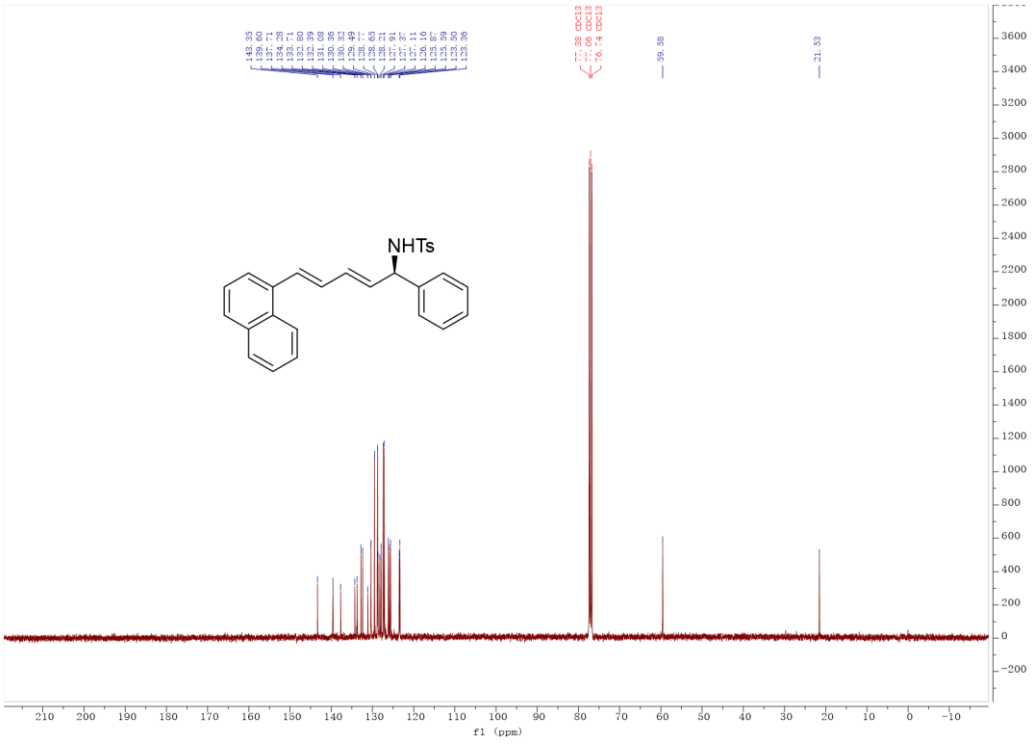


4-methyl-*N*-((*R*,2*E*,4*E*)-5-(naphthalen-1-yl)-1-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (22)

^{1}H NMR

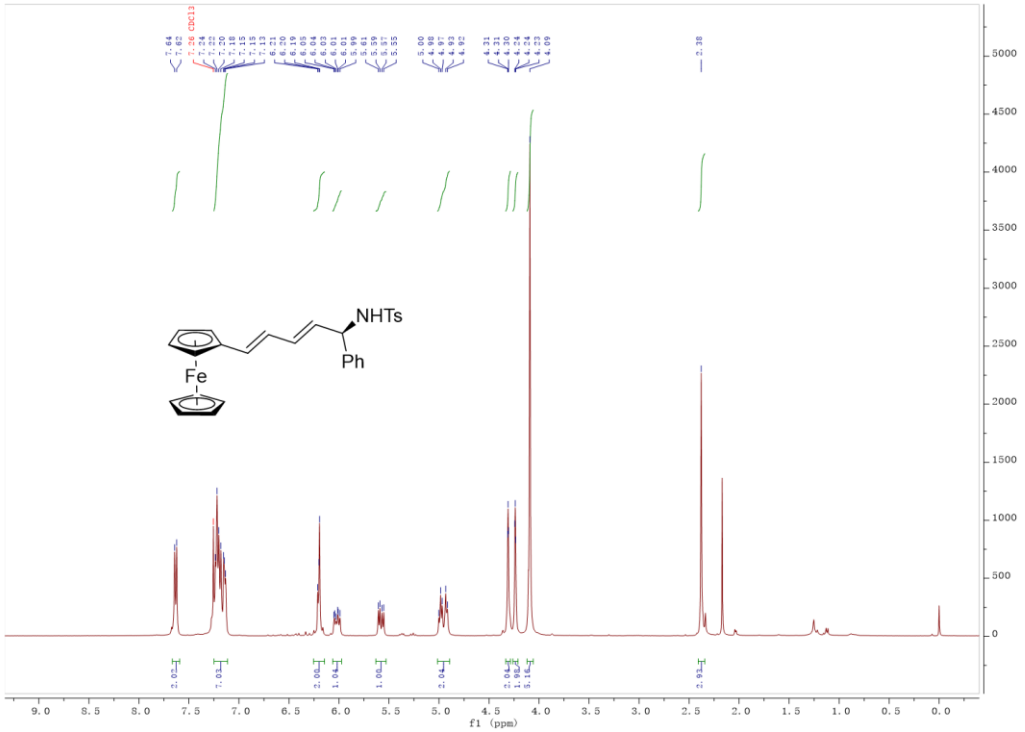


^{13}C NMR

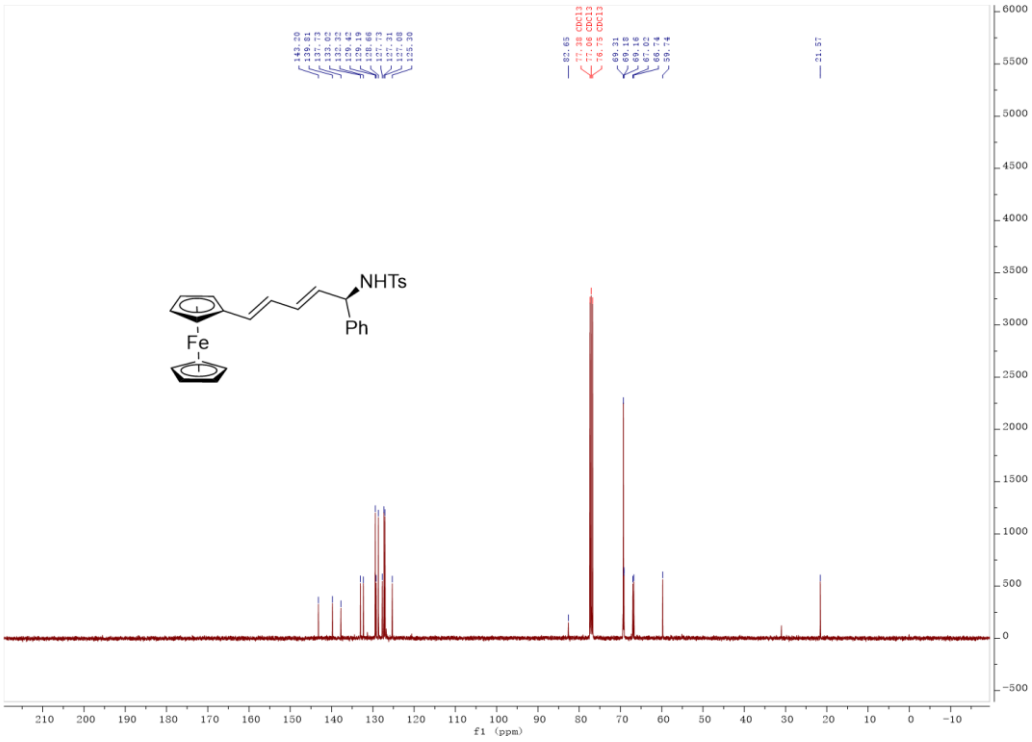


4-methyl-*N*-((*S*,2*E*,4*E*)-1-phenyl-5-(Ferroceneyl)penta-2,4-dien-1-yl)benzenesulfonamide (23)

^{1}H NMR

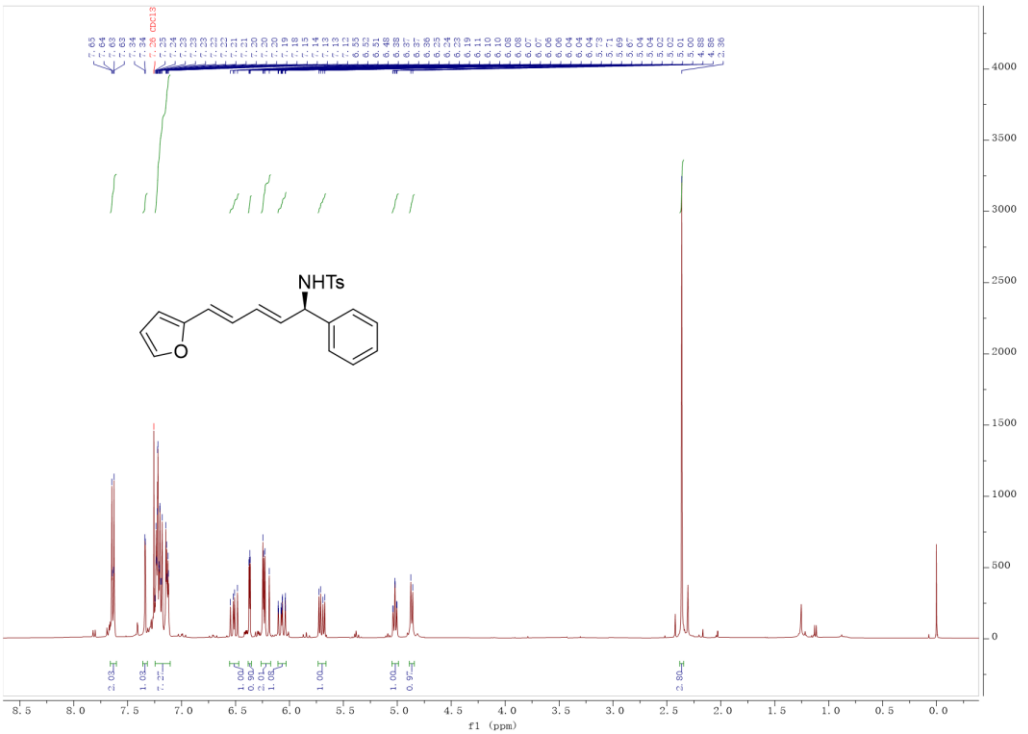


^{13}C NMR

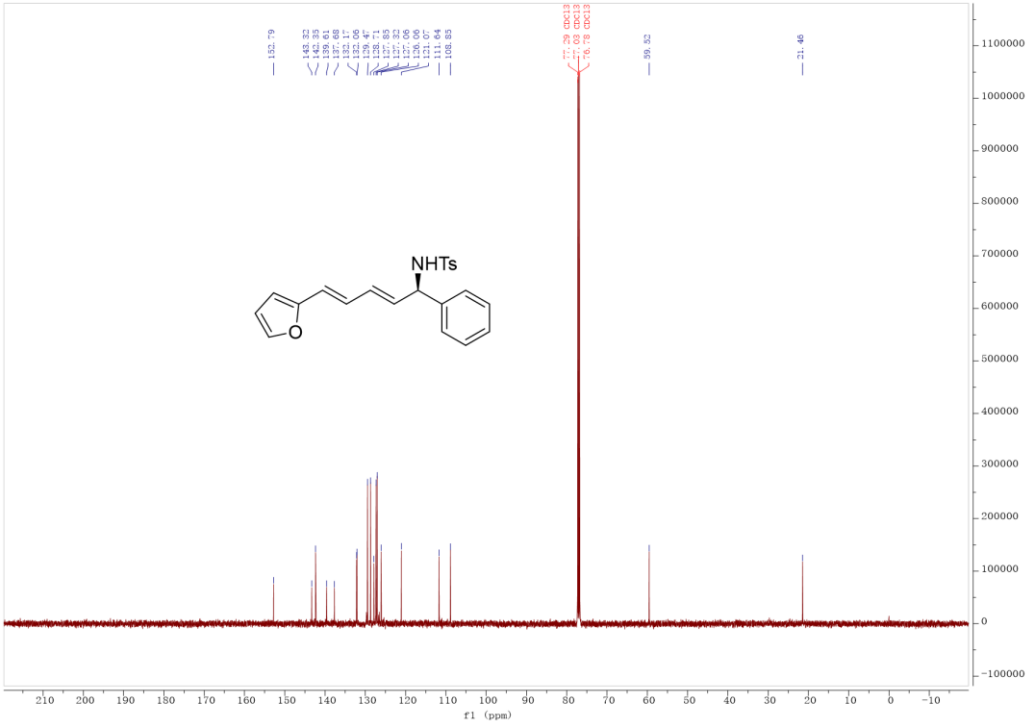


***N*-((*R*,2*E*,4*E*)-5-(furan-2-yl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (24)**

^{1}H NMR

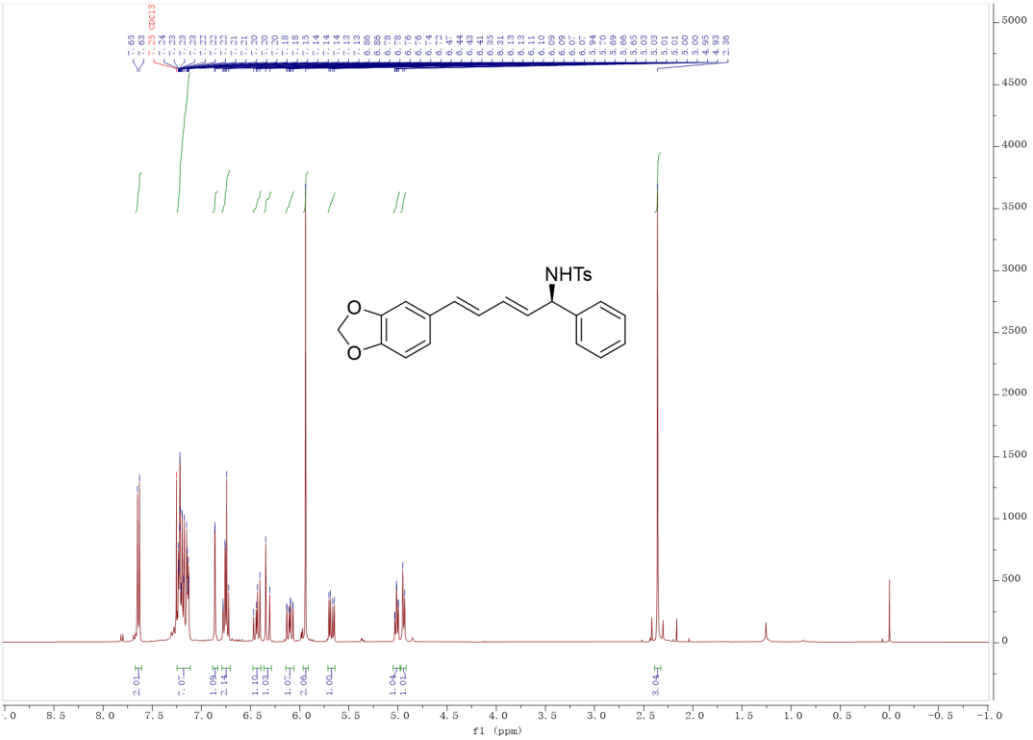


^{13}C NMR

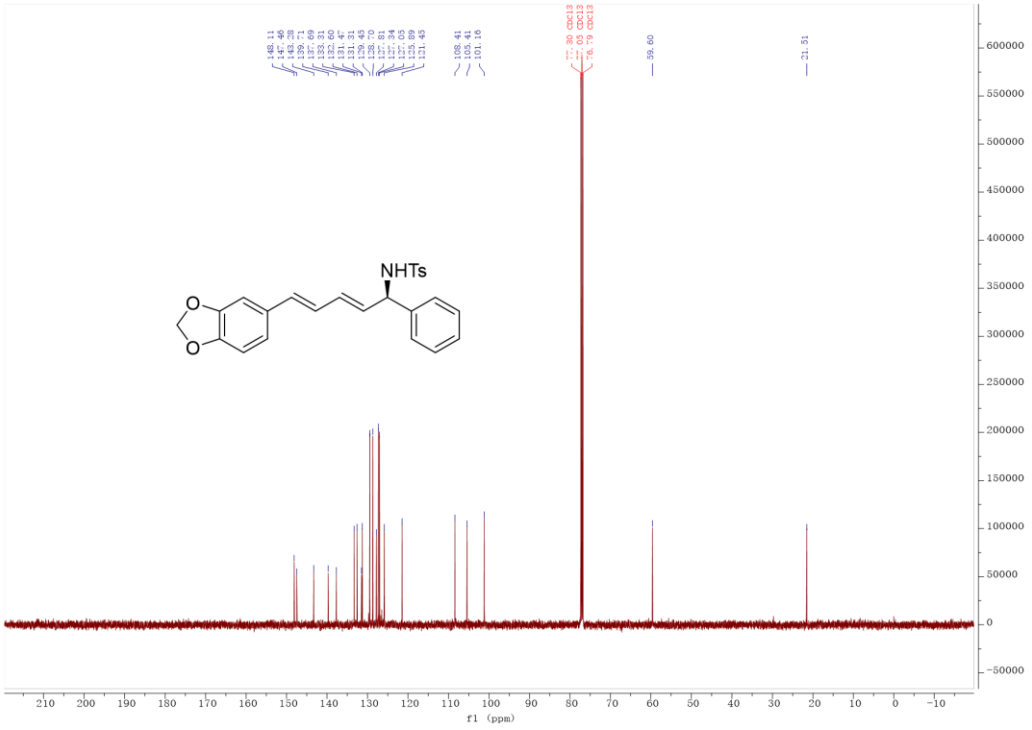


***N*-((*R*,2*E*,4*E*)-5-(benzo[*d*][1,3]dioxol-5-yl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (25)**

^{1}H NMR



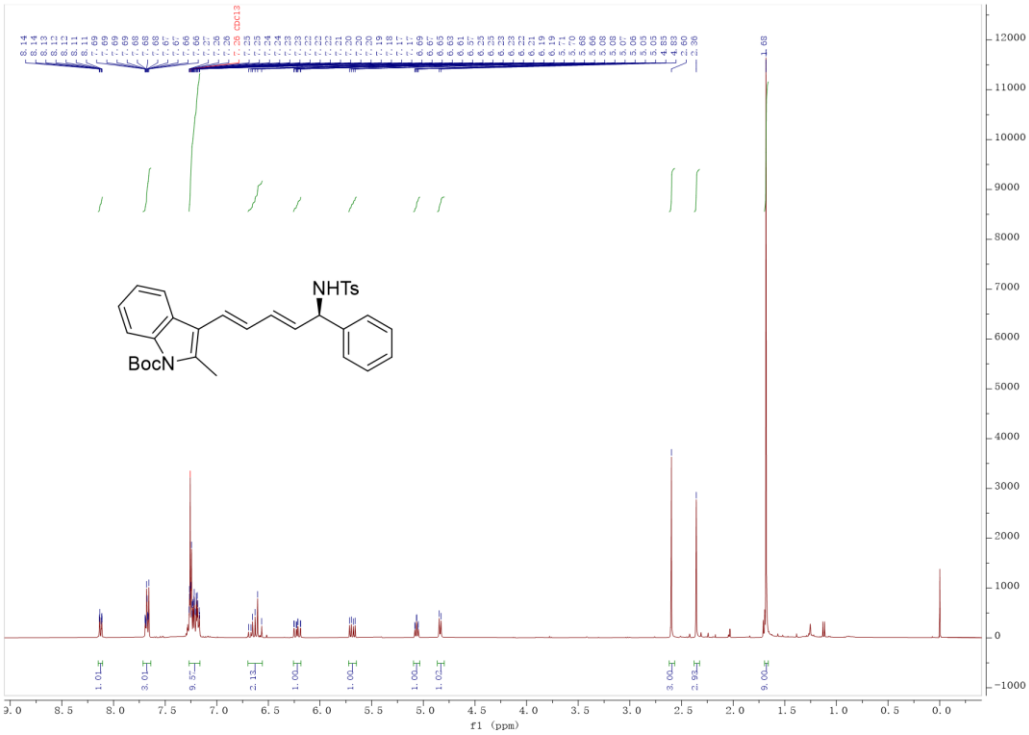
^{13}C NMR



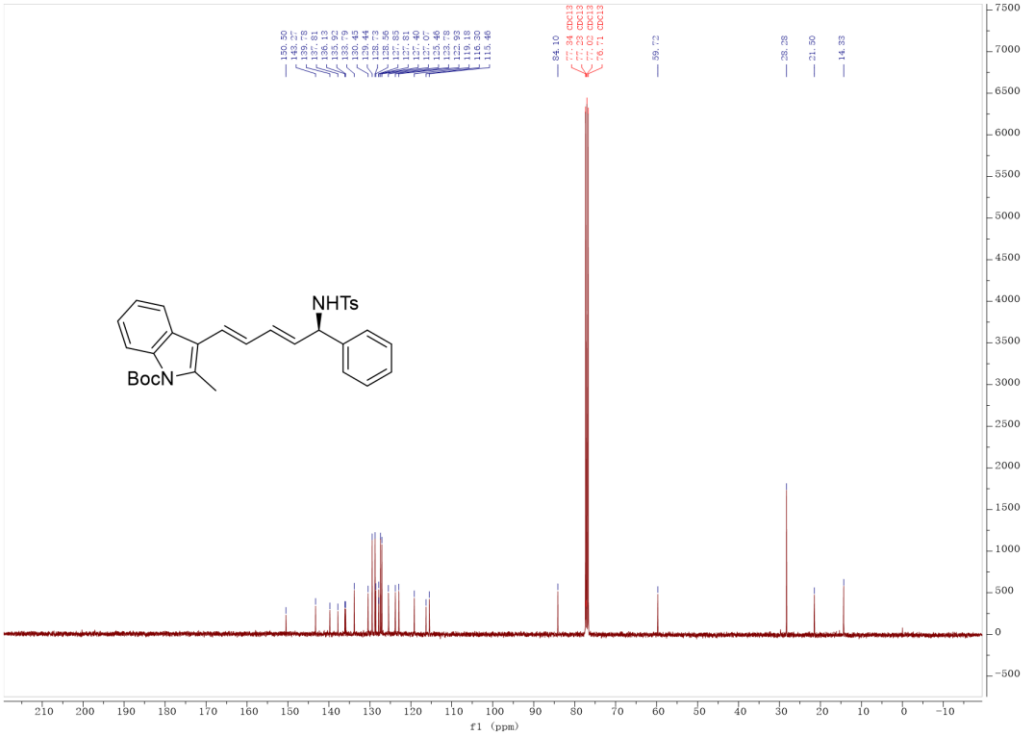
***Tert*-butyl**

2-methyl-3-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)-1*H*-indole-1-carboxylate (26)

^{1}H NMR

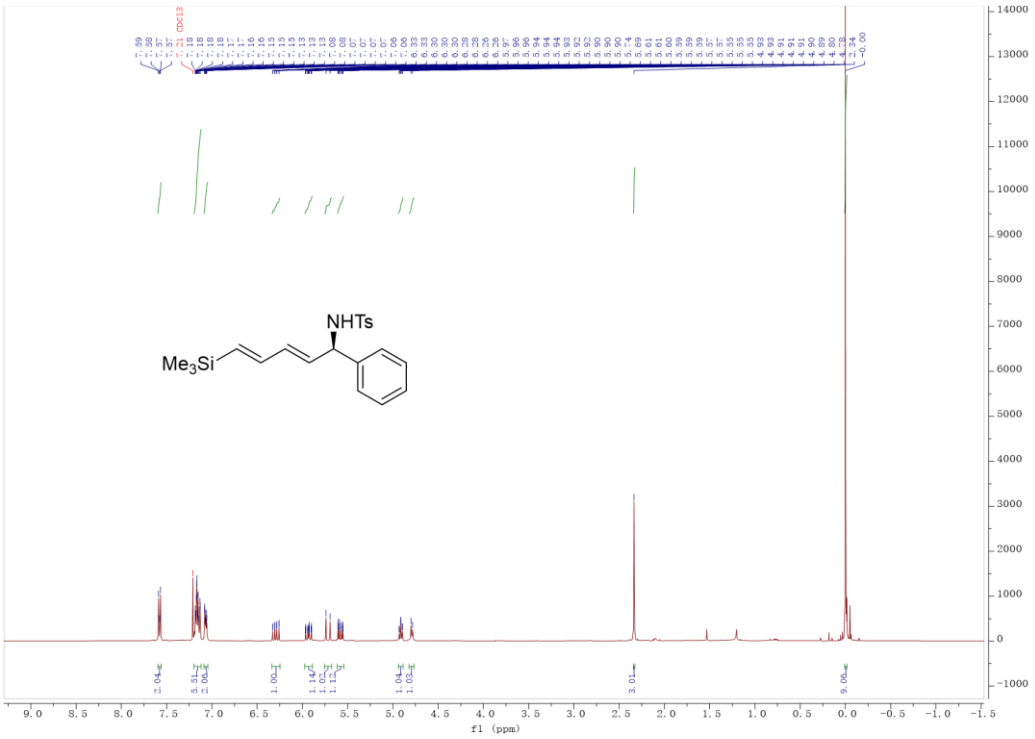


^{13}C NMR

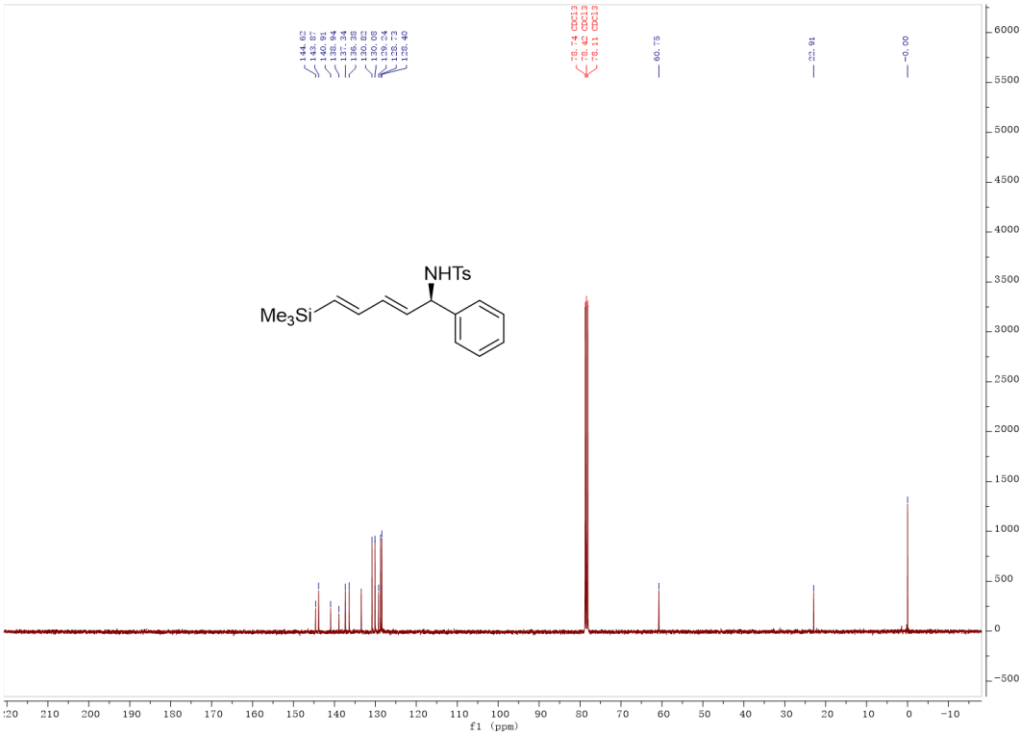


4-methyl-*N*-((*R*,2*E*,4*E*)-1-phenyl-5-(trimethylsilyl)penta-2,4-dien-1-yl)benzenesulfonamide (27)

^{1}H NMR

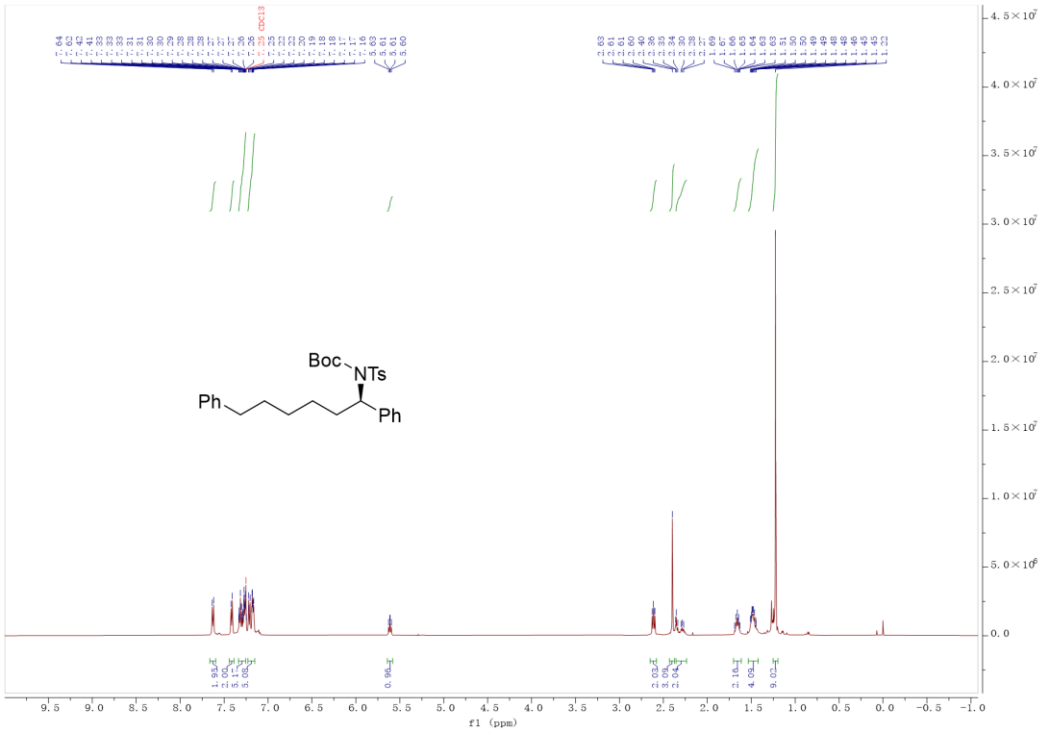


^{13}C NMR

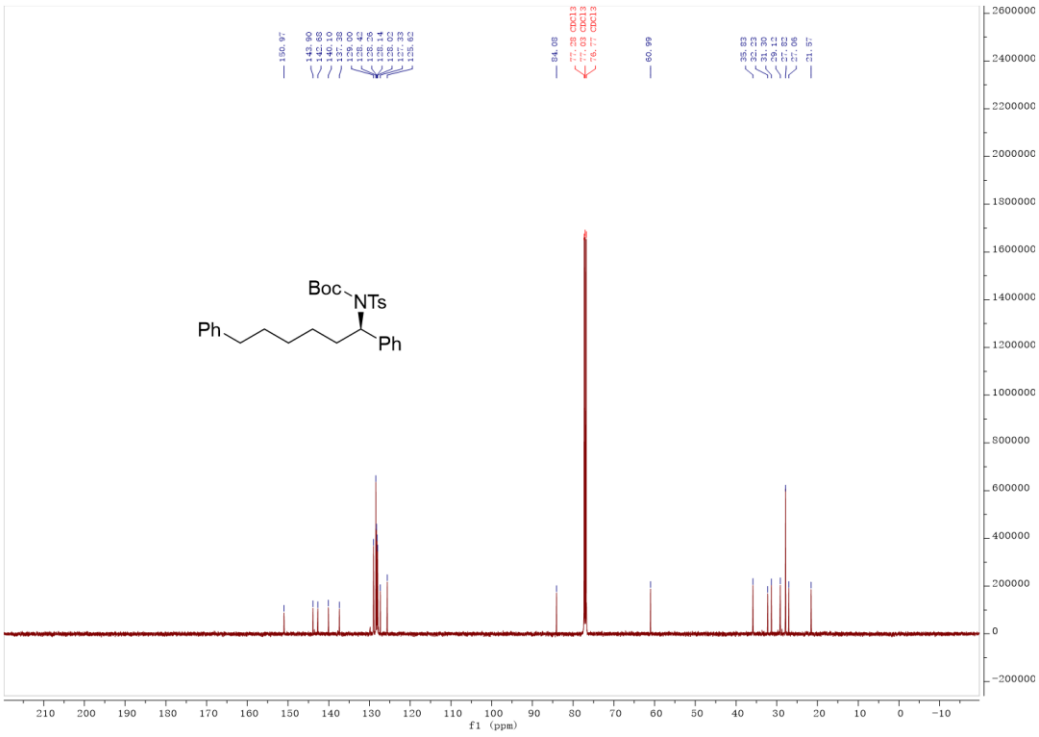


***Tert*-butyl (*R*)-(1,6-diphenylhexyl)(tosyl)carbamate (28)**

^{1}H NMR

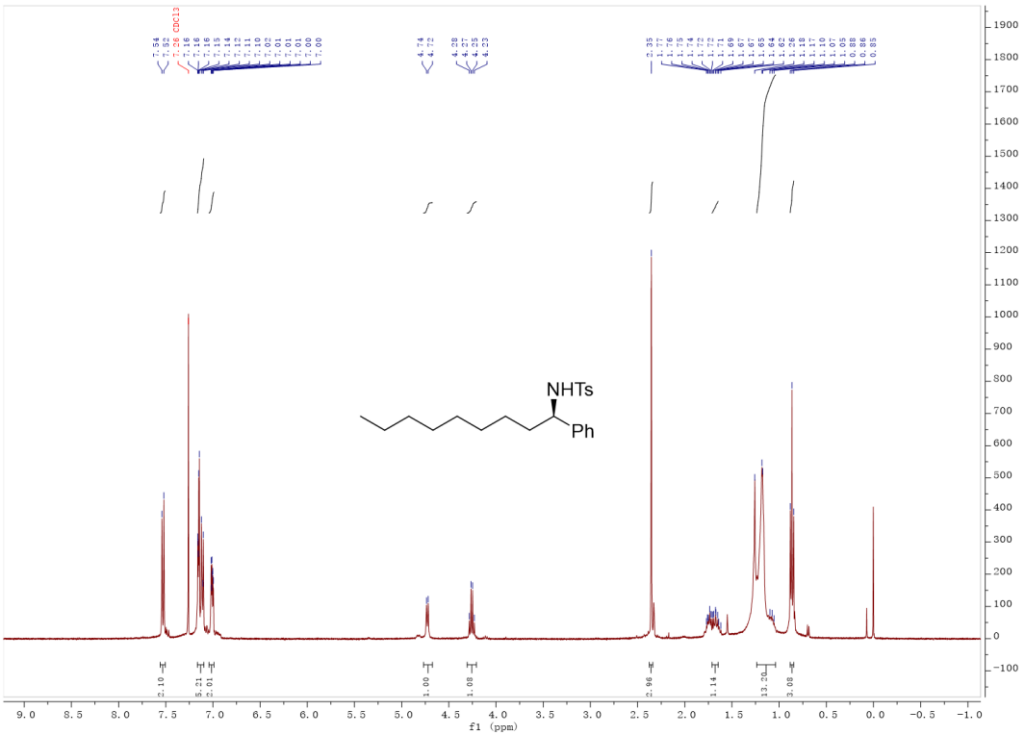


^{13}C NMR

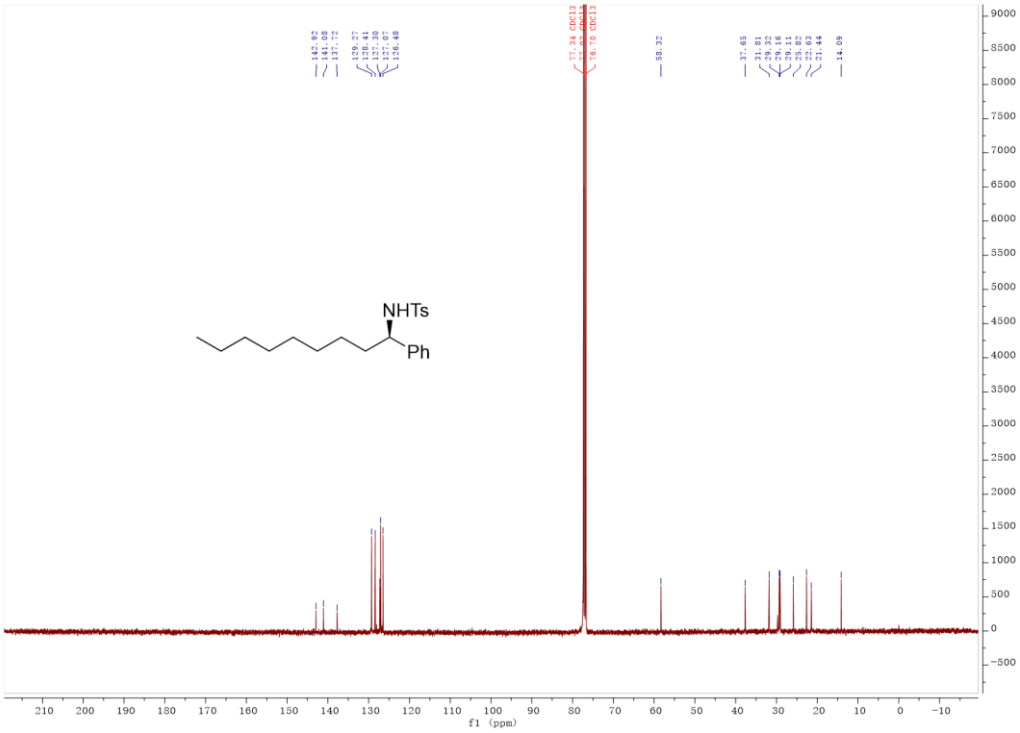


(*R*)-4-methyl-*N*-(1-phenylnonyl)benzenesulfonamide (29)

^{1}H NMR

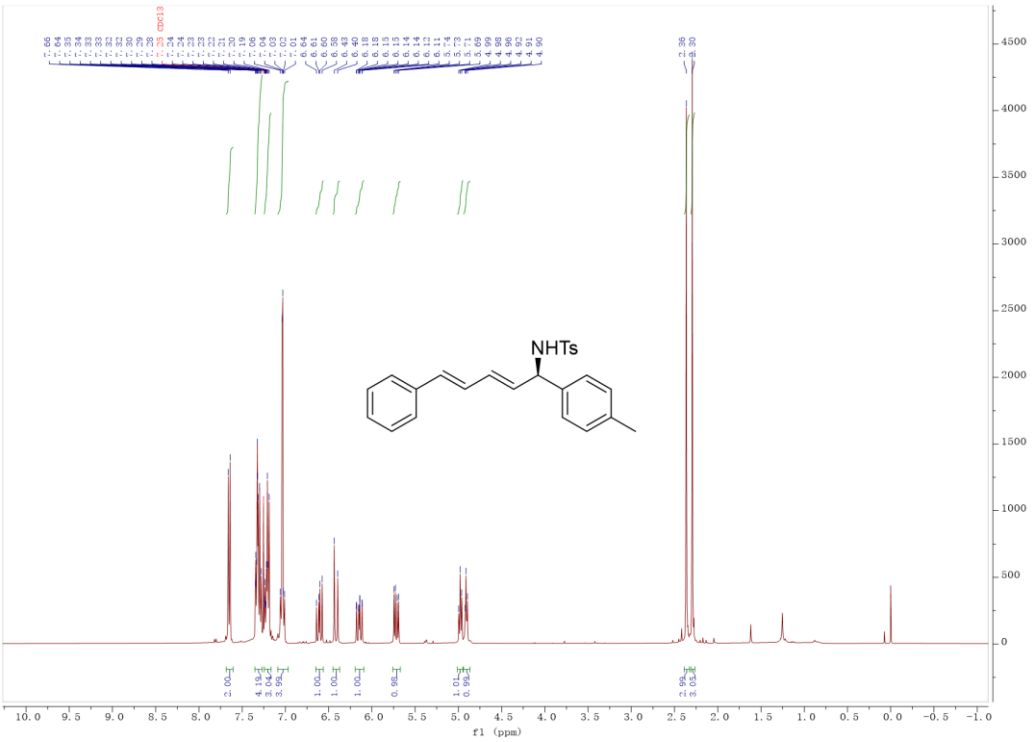


^{13}C NMR

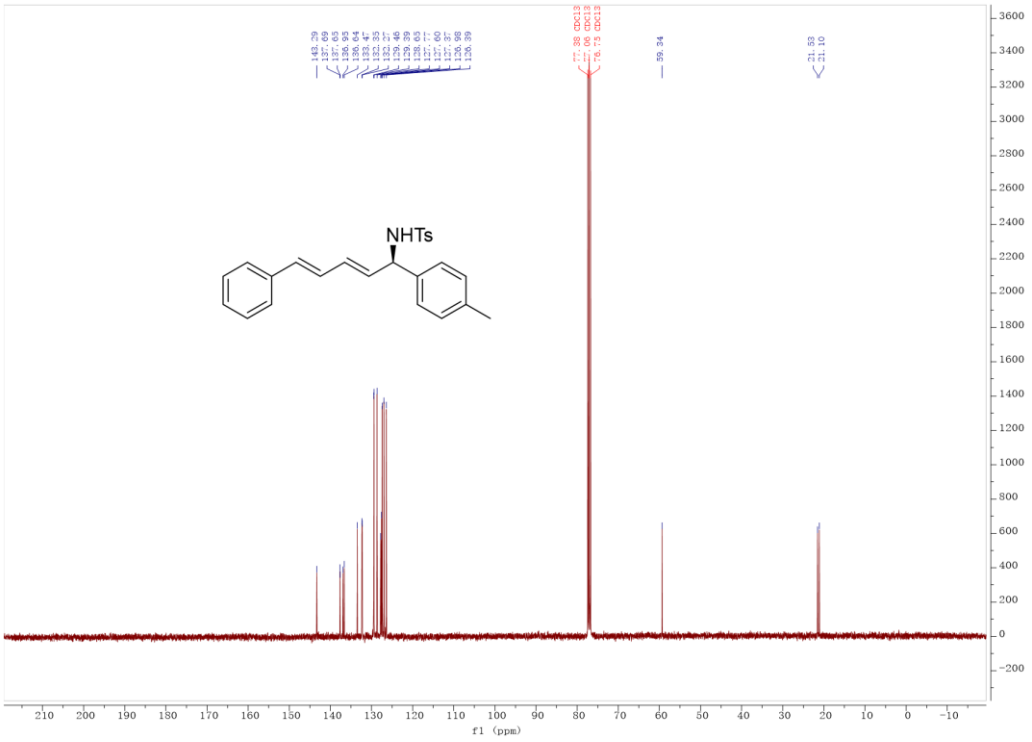


4-methyl-*N*-((*R*,2*E*,4*E*)-5-phenyl-1-(p-tolyl)penta-2,4-dien-1-yl)benzenesulfonamide (30)

^{1}H NMR

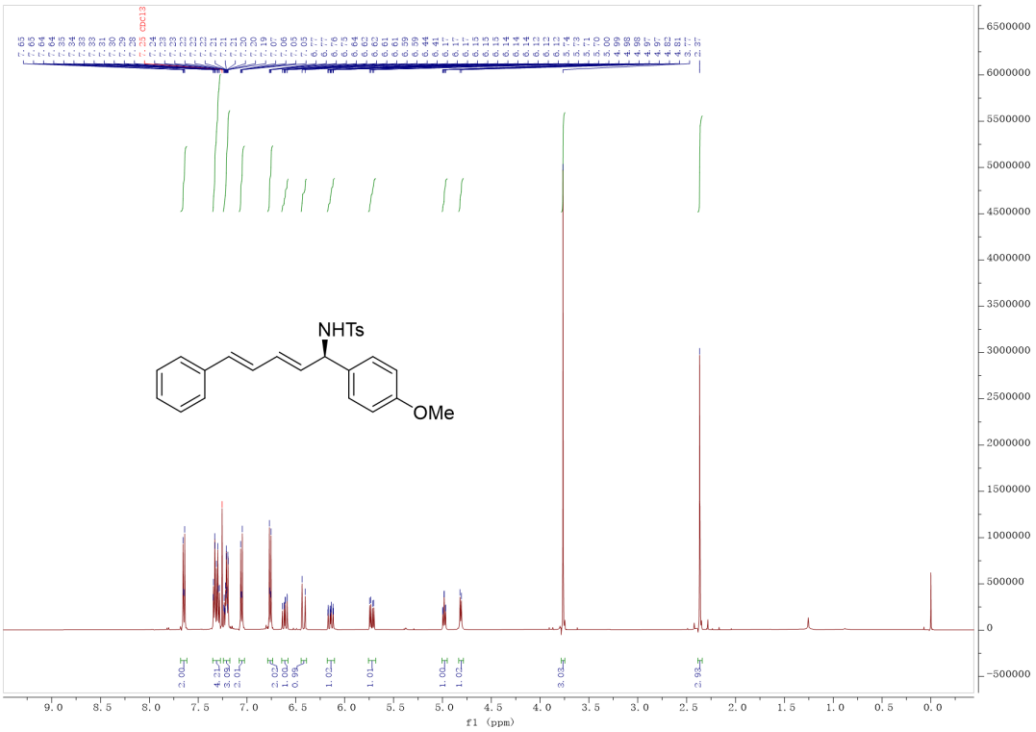


^{13}C NMR

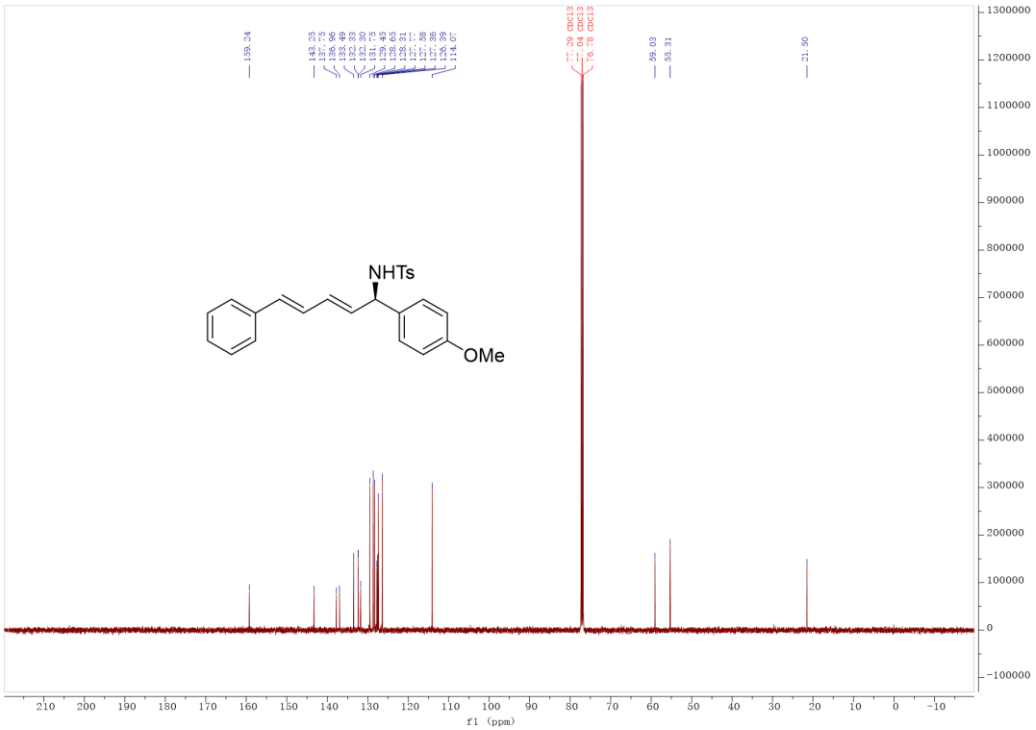


***N*-((*R*,2*E*,4*E*)-1-(4-methoxyphenyl)-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (31)**

^{1}H NMR

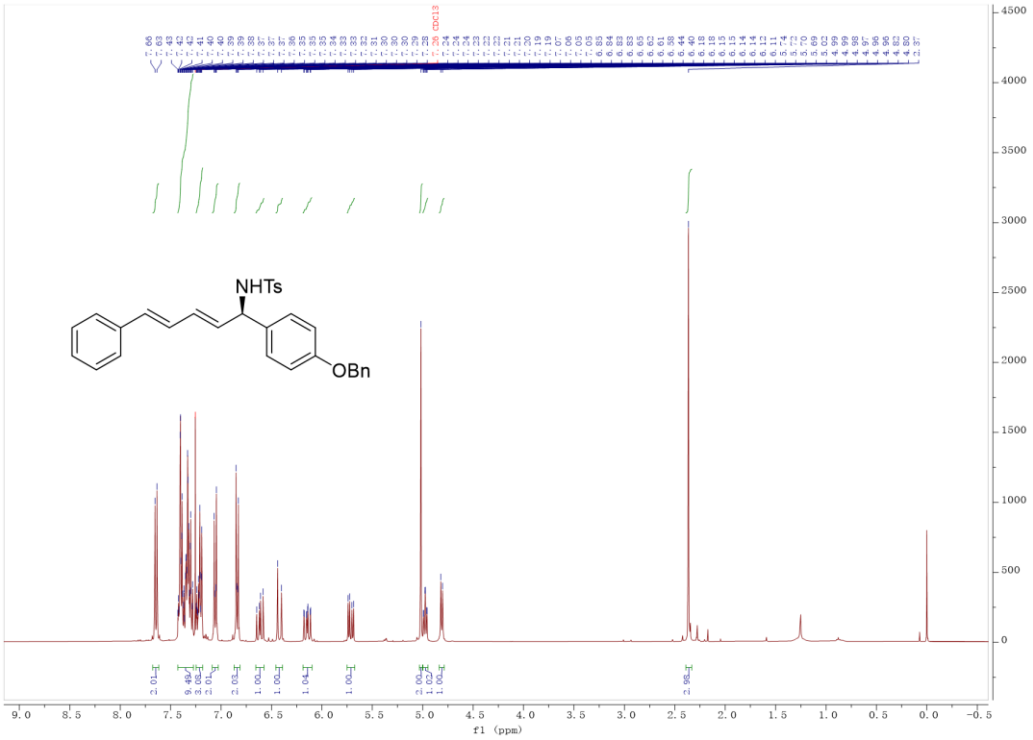


^{13}C NMR

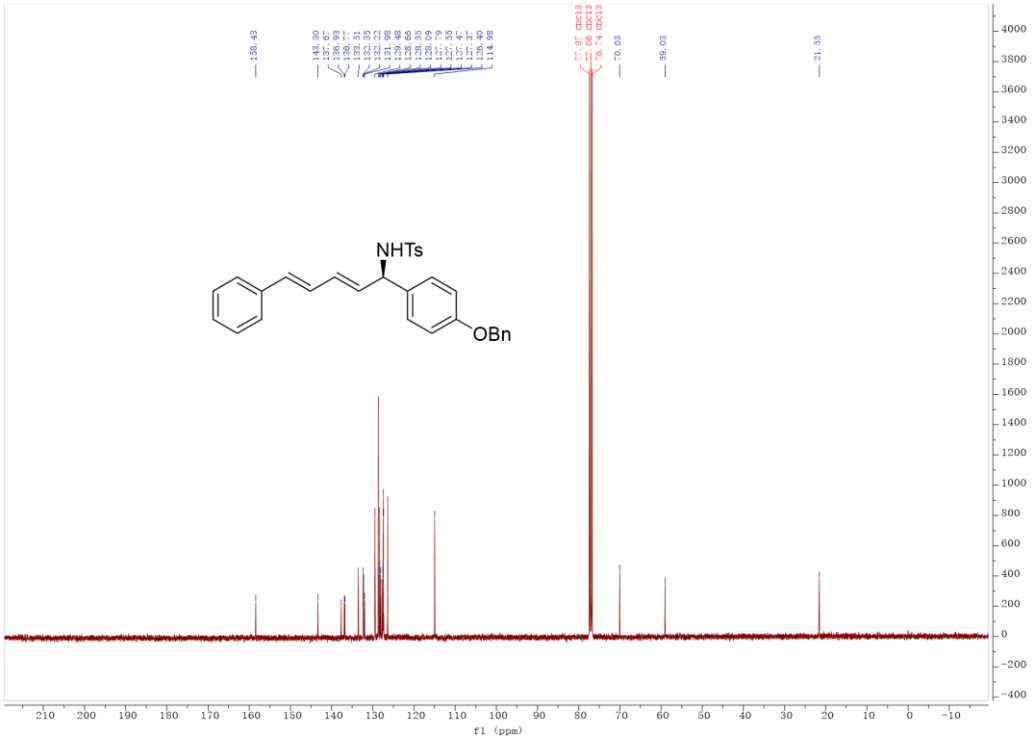


***N*-((*R*,2*E*,4*E*)-1-(4-(benzyloxy)phenyl)-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (32)**

^{1}H NMR

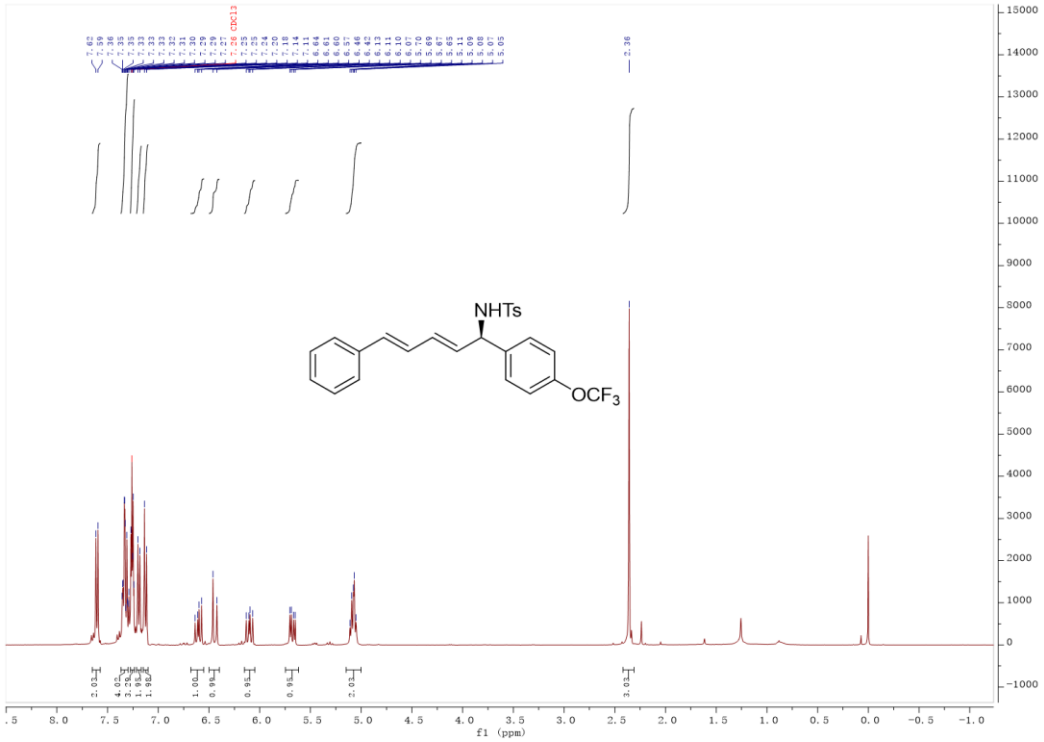


^{13}C NMR

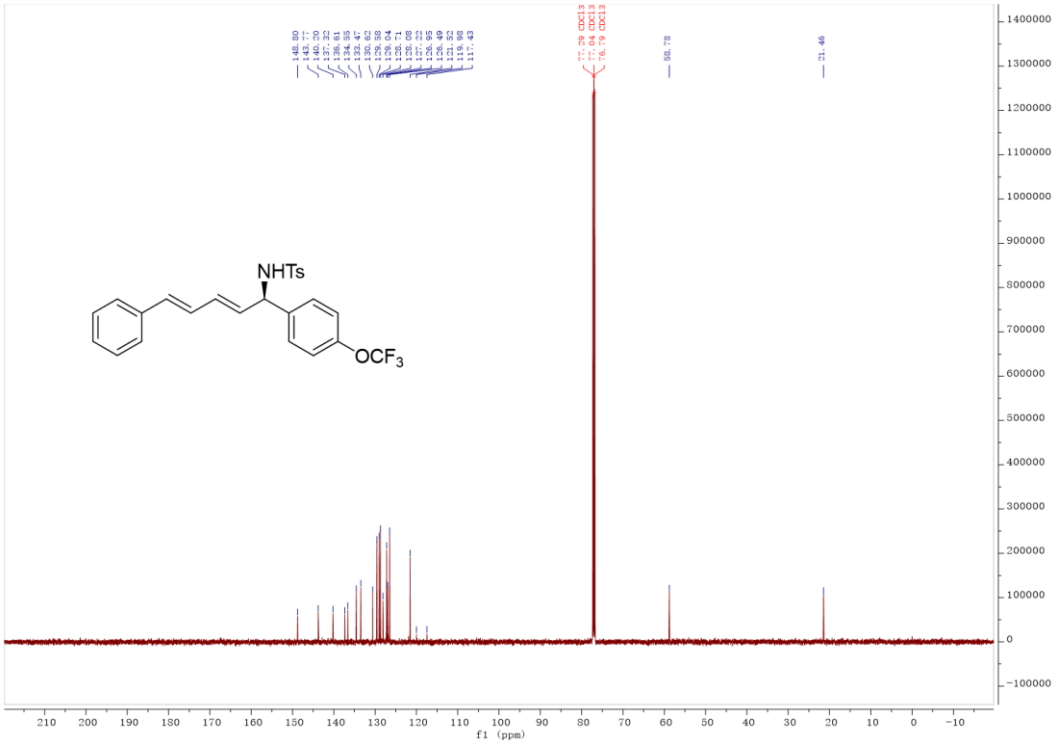


4-methyl-*N*-((*R*,2*E*,4*E*)-5-phenyl-1-(4-(trifluoromethoxy)phenyl)penta-2,4-dien-1-yl)benzenesulfonamide (33)

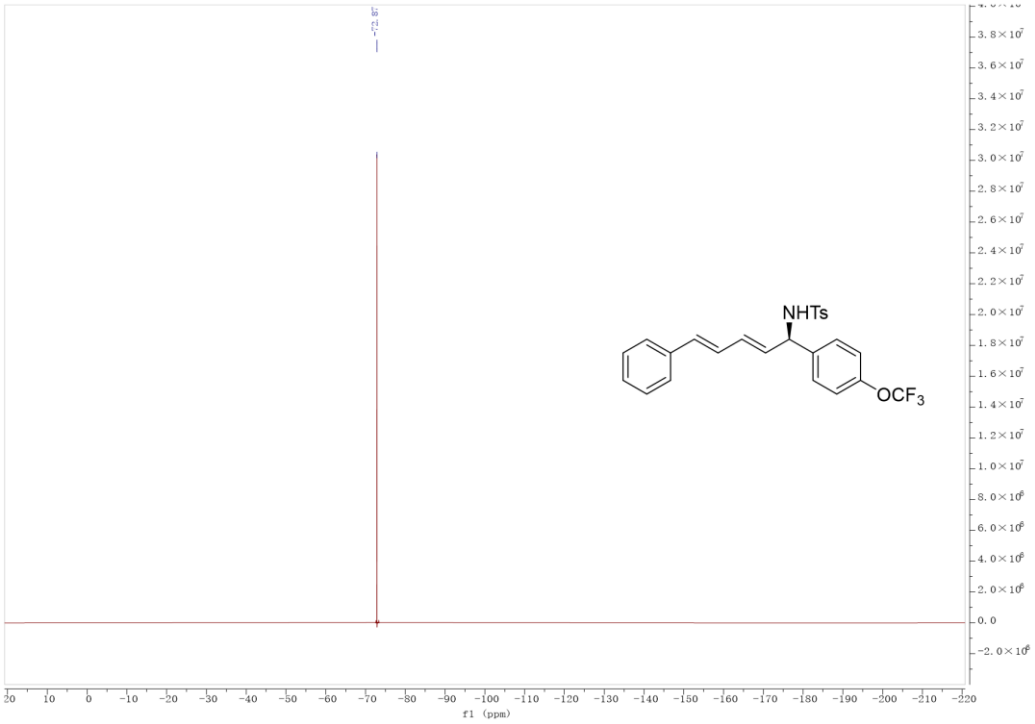
^{1}H NMR



^{13}C NMR

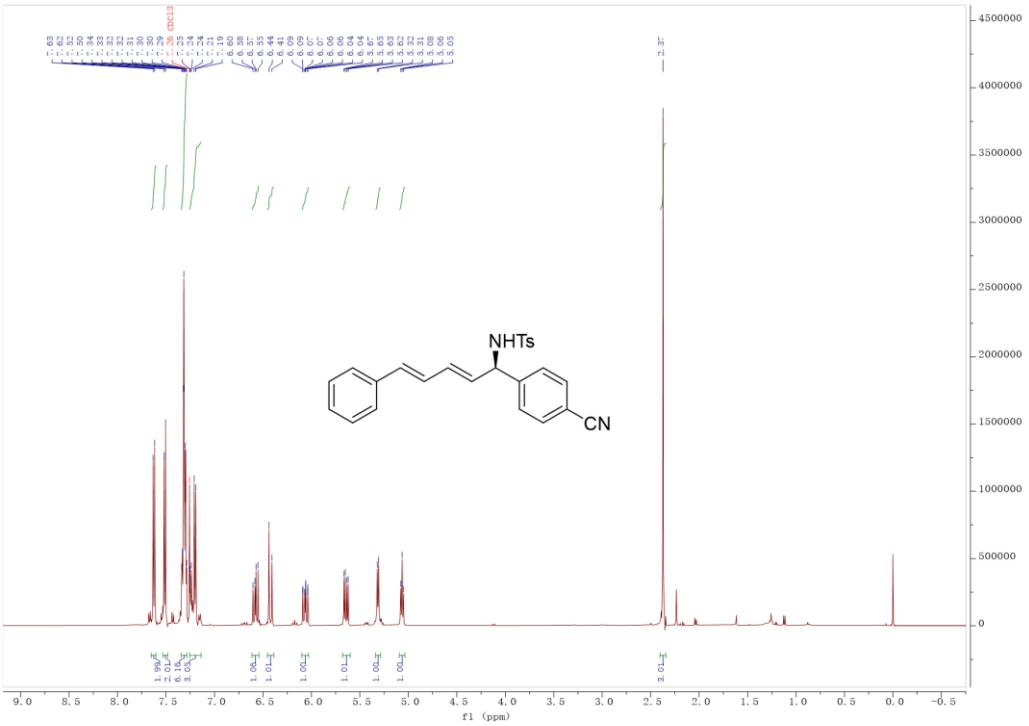


^{19}F NMR

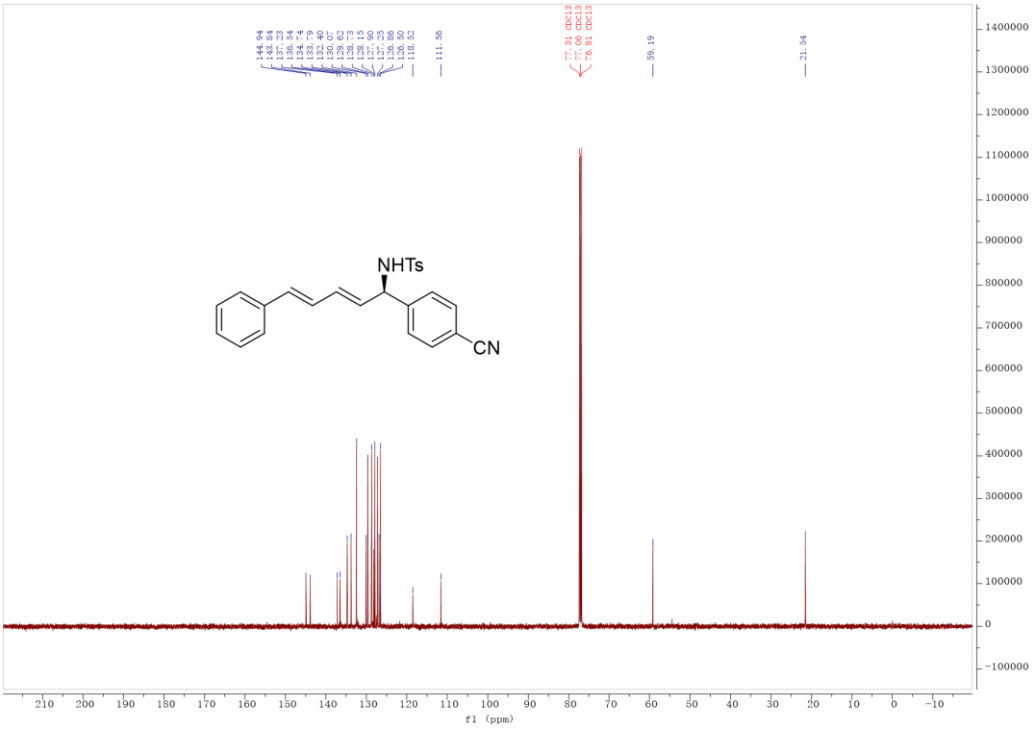


***N*-((*R*,2*E*,4*E*)-1-(4-cyanophenyl)-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (34)**

^{1}H NMR

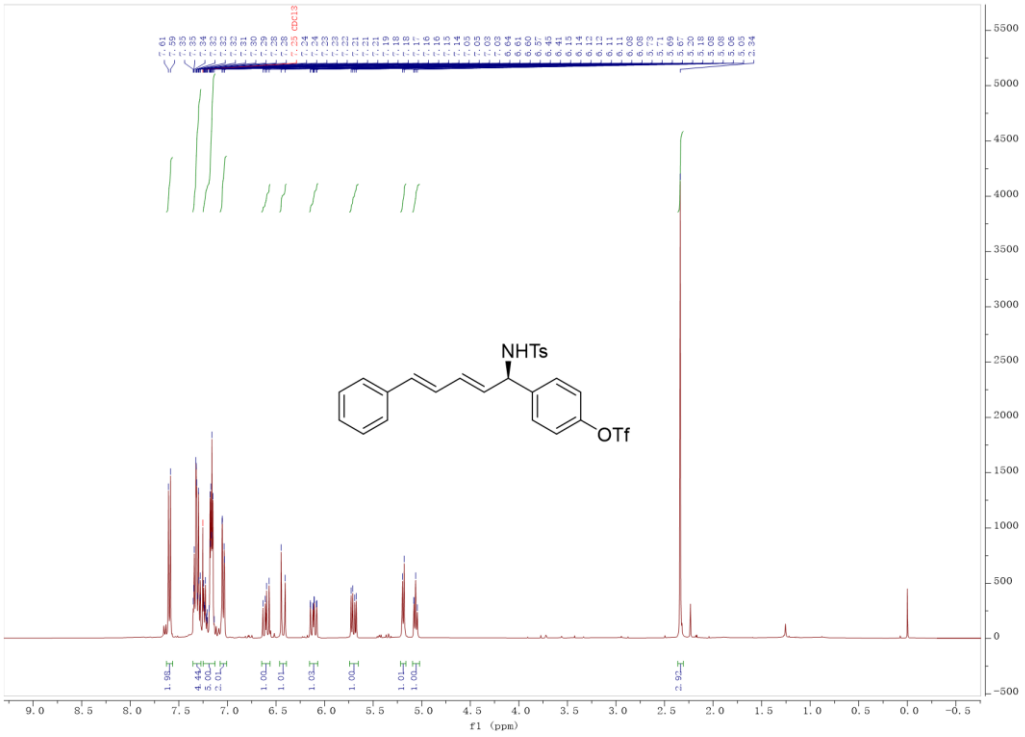


^{13}C NMR

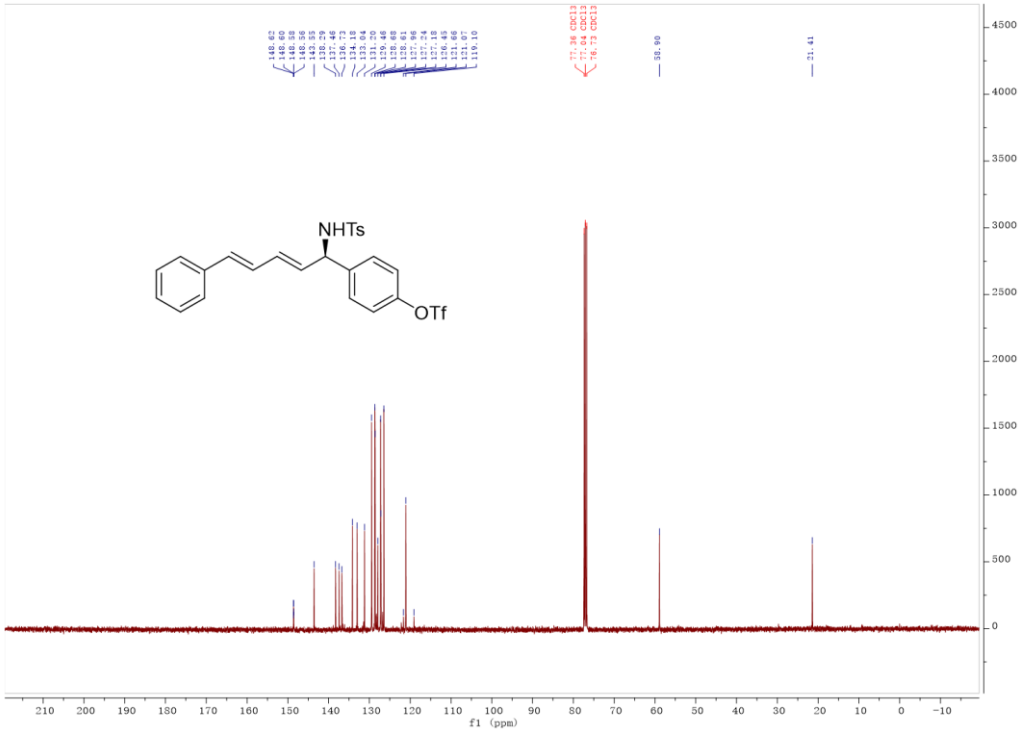


4-((*R*,2*E*,4*E*)-1-((4-methylphenyl)sulfonamido)-5-phenylpenta-2,4-dien-1-yl)phenyl trifluoromethanesulfonate (35)

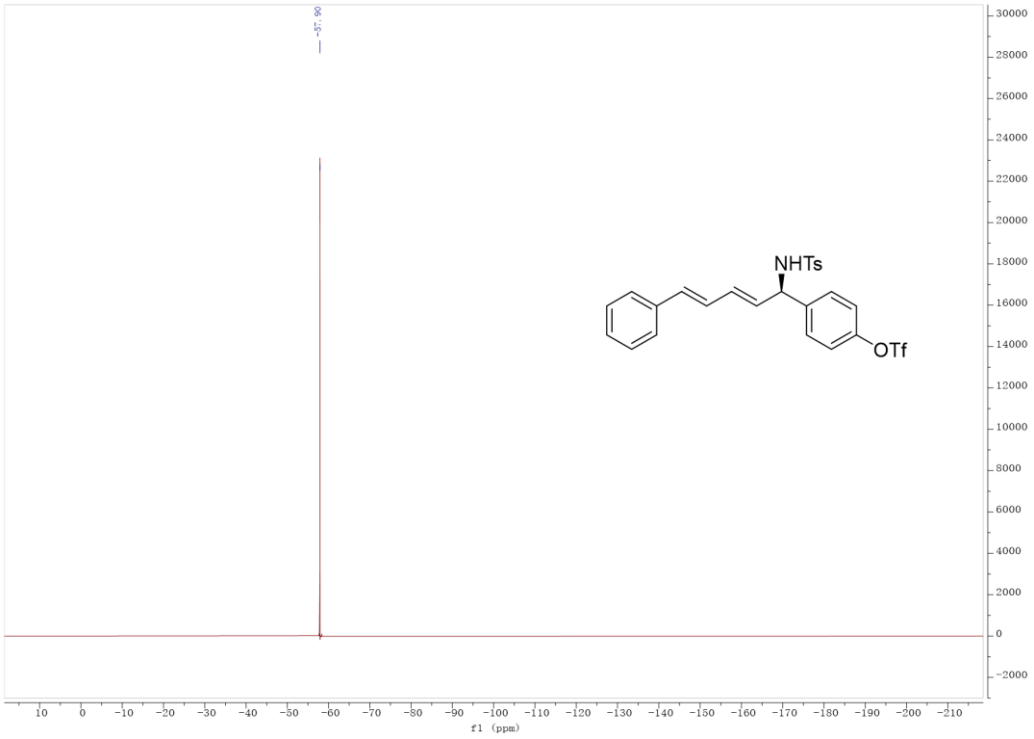
^{1}H NMR



^{13}C NMR

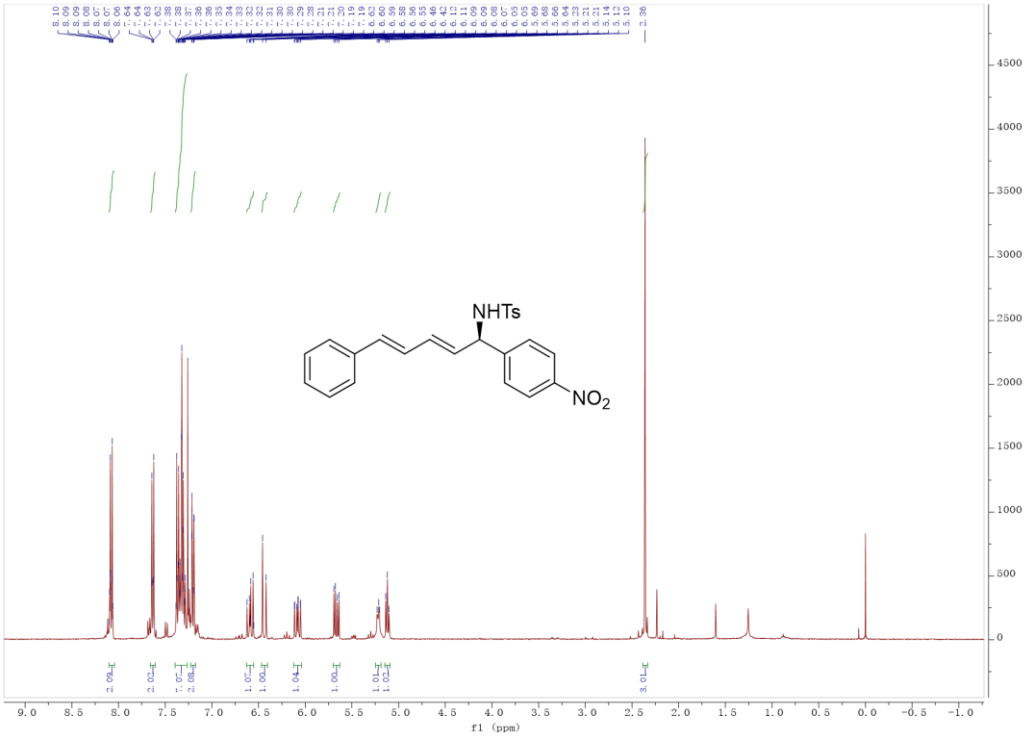


^{19}F NMR

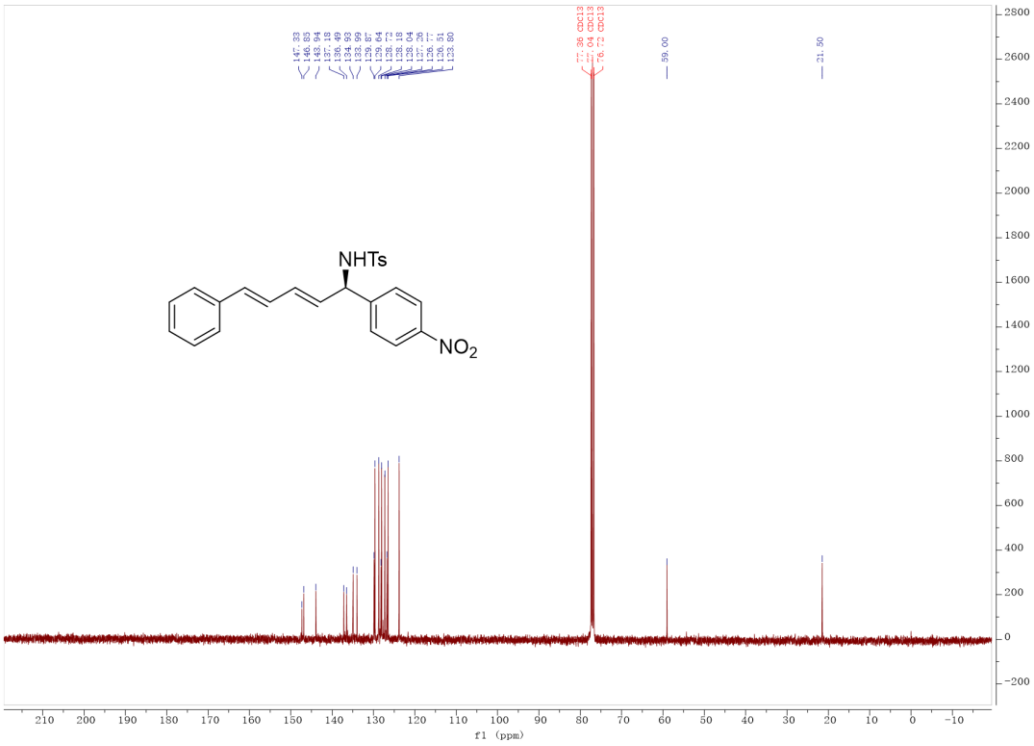

-57.90
NHTs
OTf
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

4-methyl-*N*-((*R*,2*E*,4*E*)-1-(4-nitrophenyl)-5-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (36)

^{1}H NMR

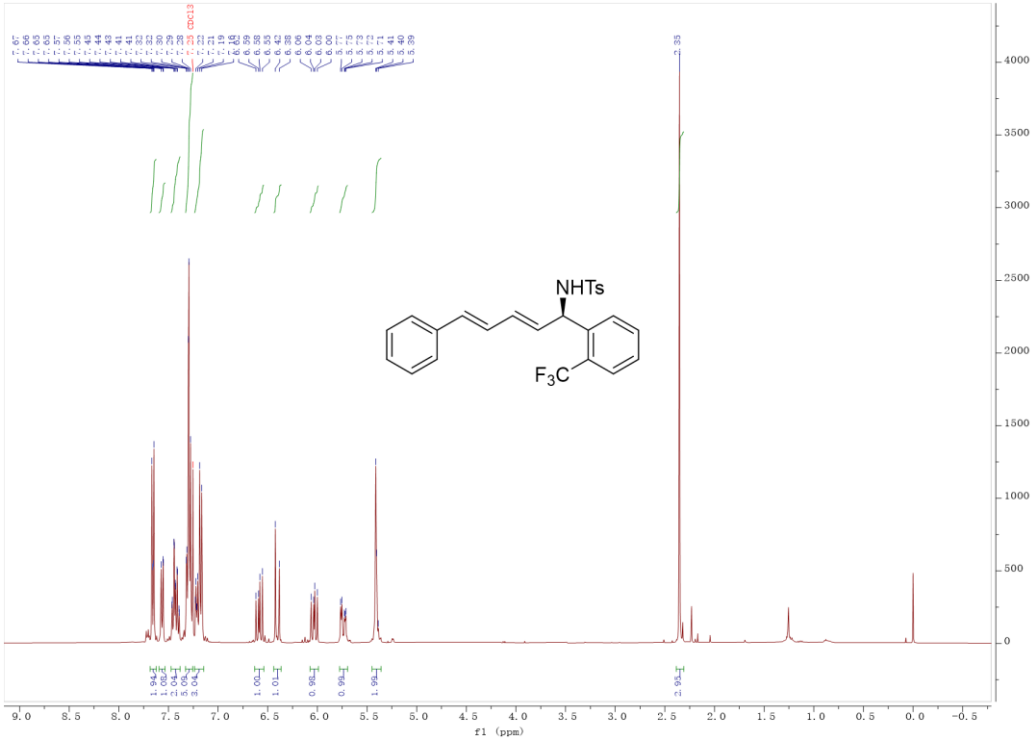


^{13}C NMR

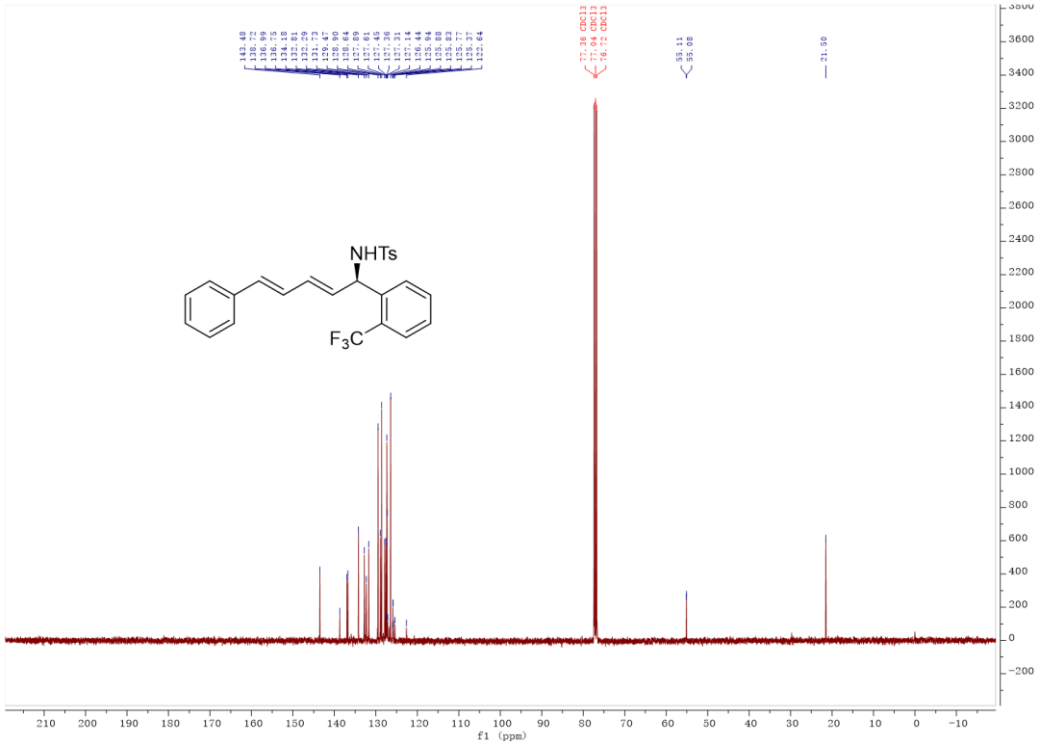


4-methyl-*N*-((*R*,2*E*,4*E*)-5-phenyl-1-(2-(trifluoromethyl)phenyl)penta-2,4-dien-1-yl)benzenesulfonamide (37)

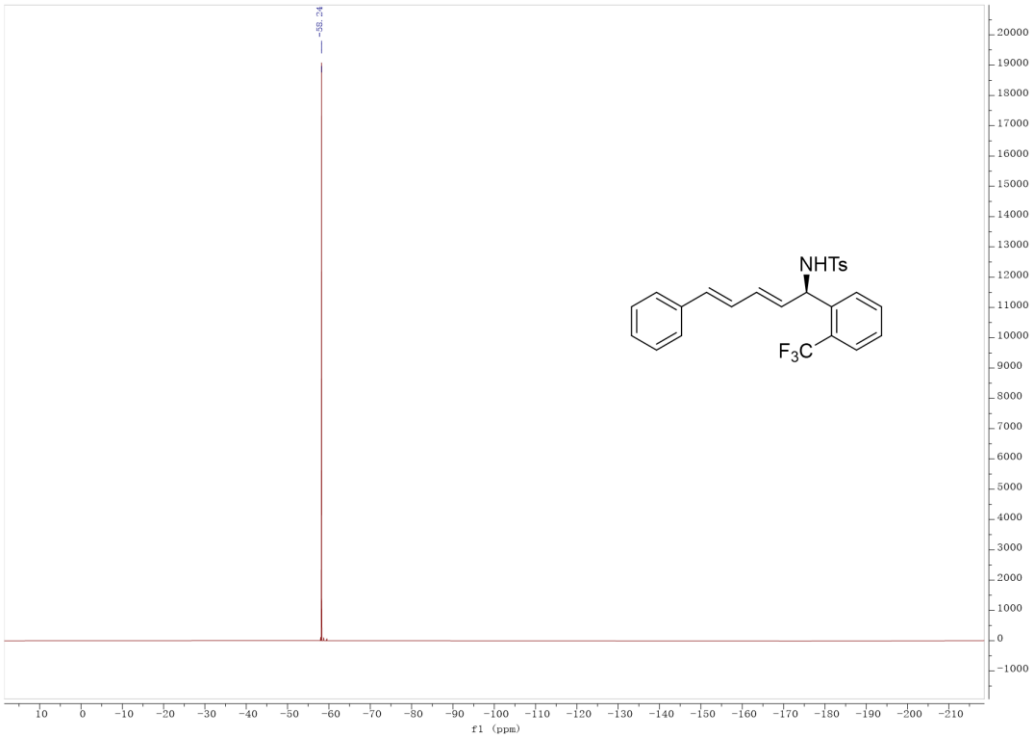
^{1}H NMR



^{13}C NMR

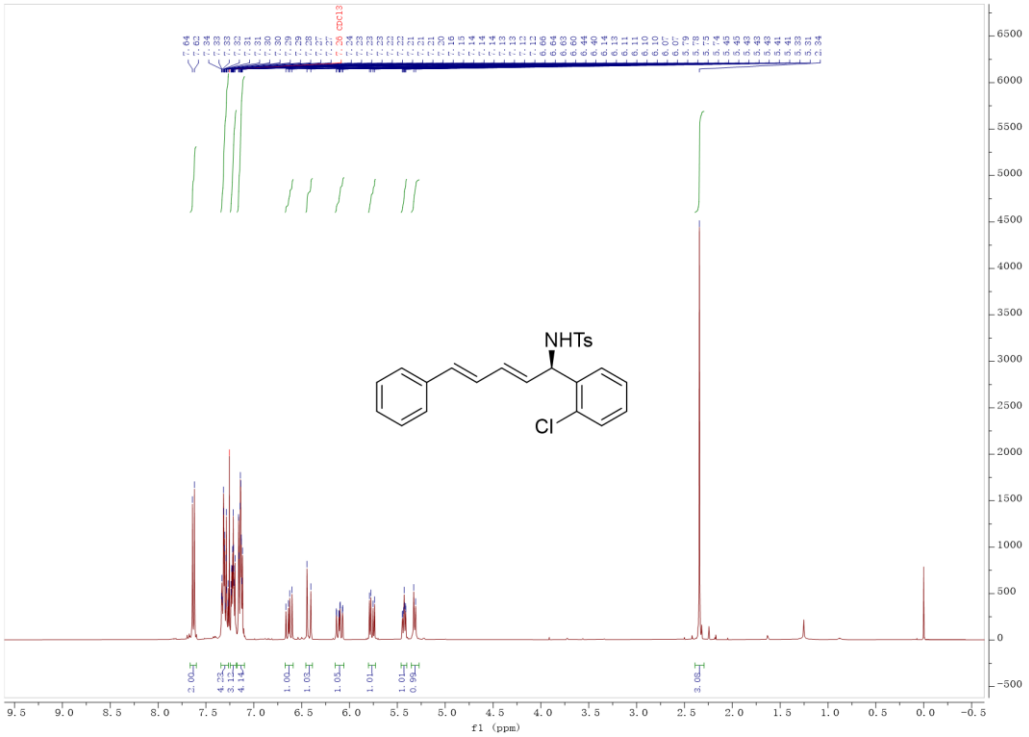


^{19}F NMR

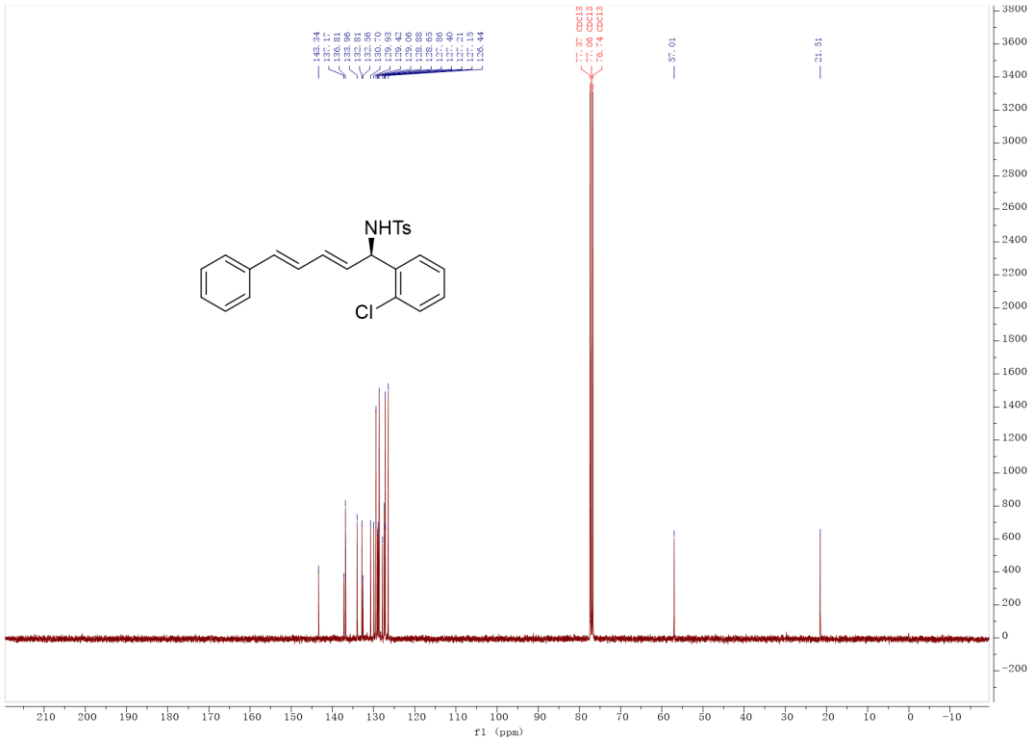

-58.24
NHTs
F3C
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

***N*-((*R*,2*E*,4*E*)-1-(2-chlorophenyl)-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (38)**

^{1}H NMR

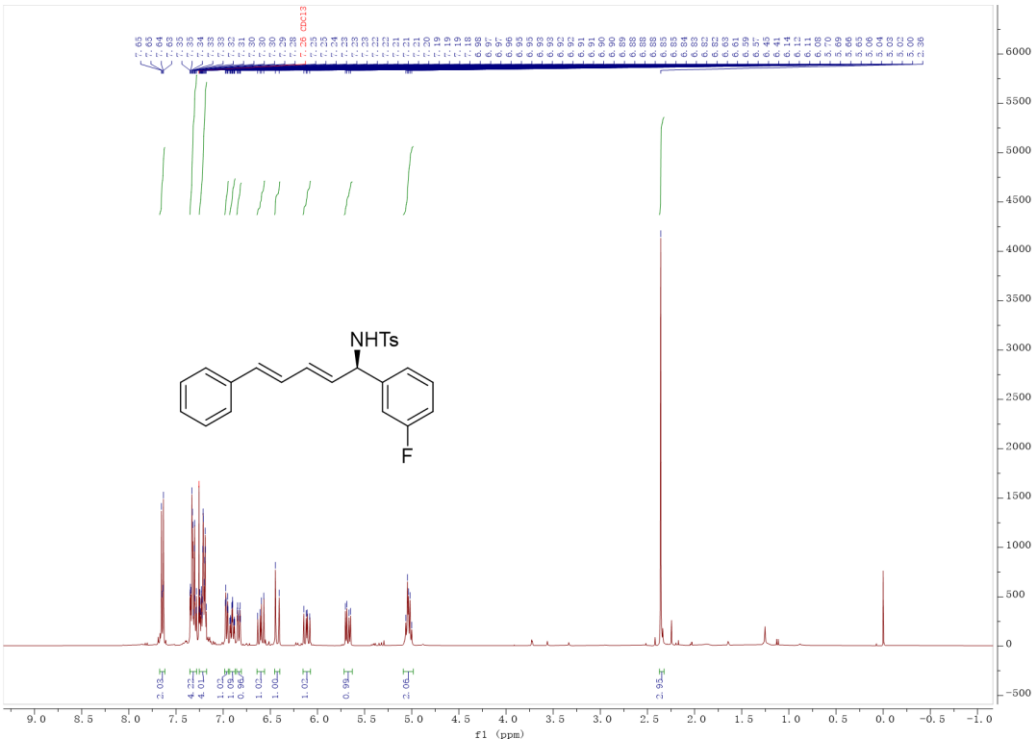


^{13}C NMR

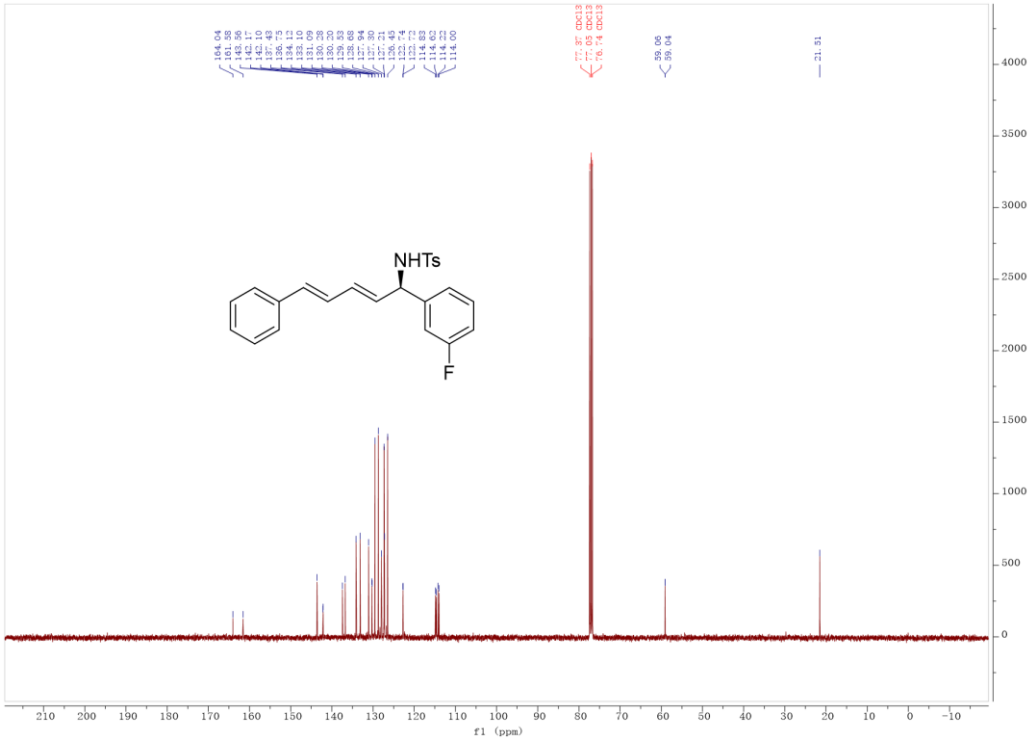


***N*-((*R*,2*E*,4*E*)-1-(3-fluorophenyl)-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (39)**

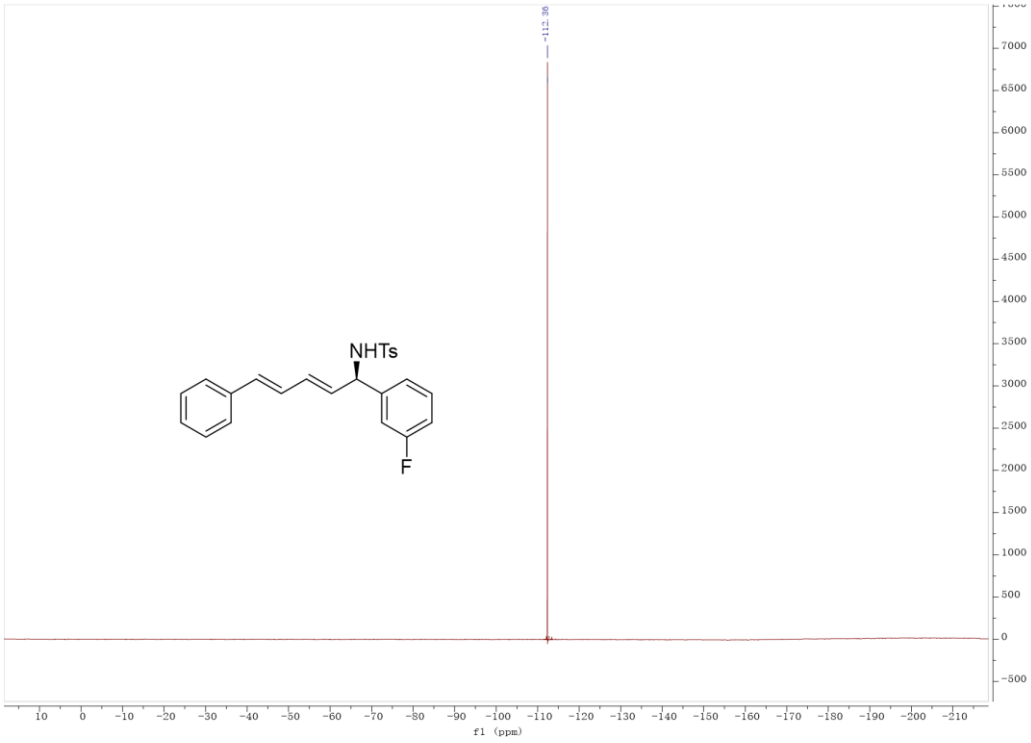
^{1}H NMR



^{13}C NMR

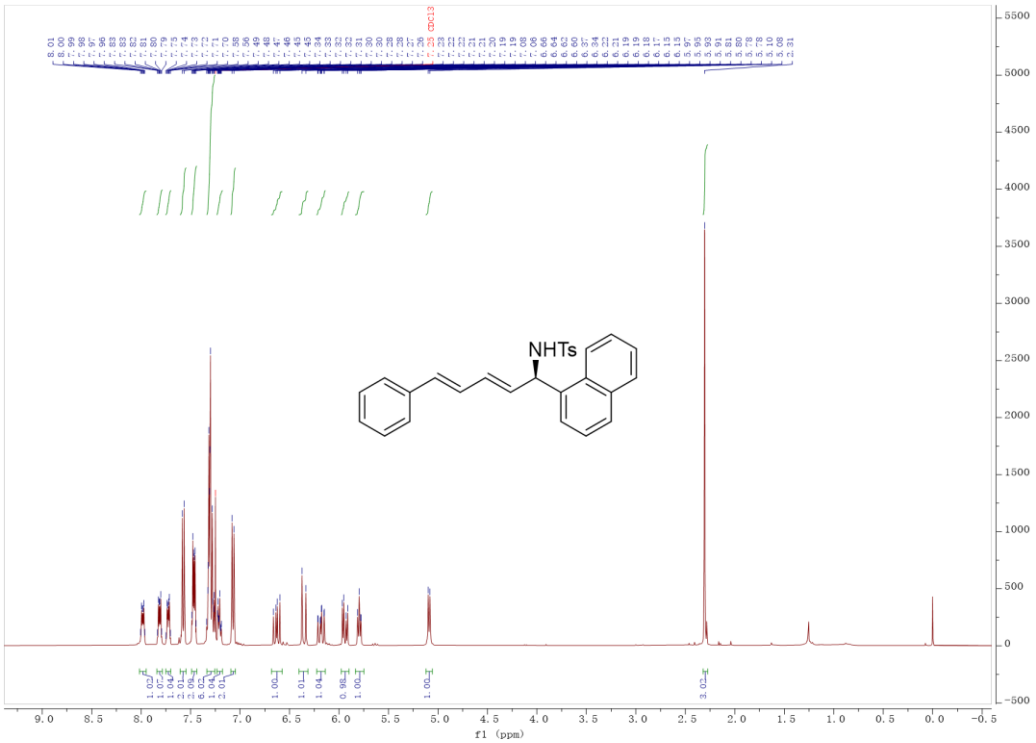


^{19}F NMR

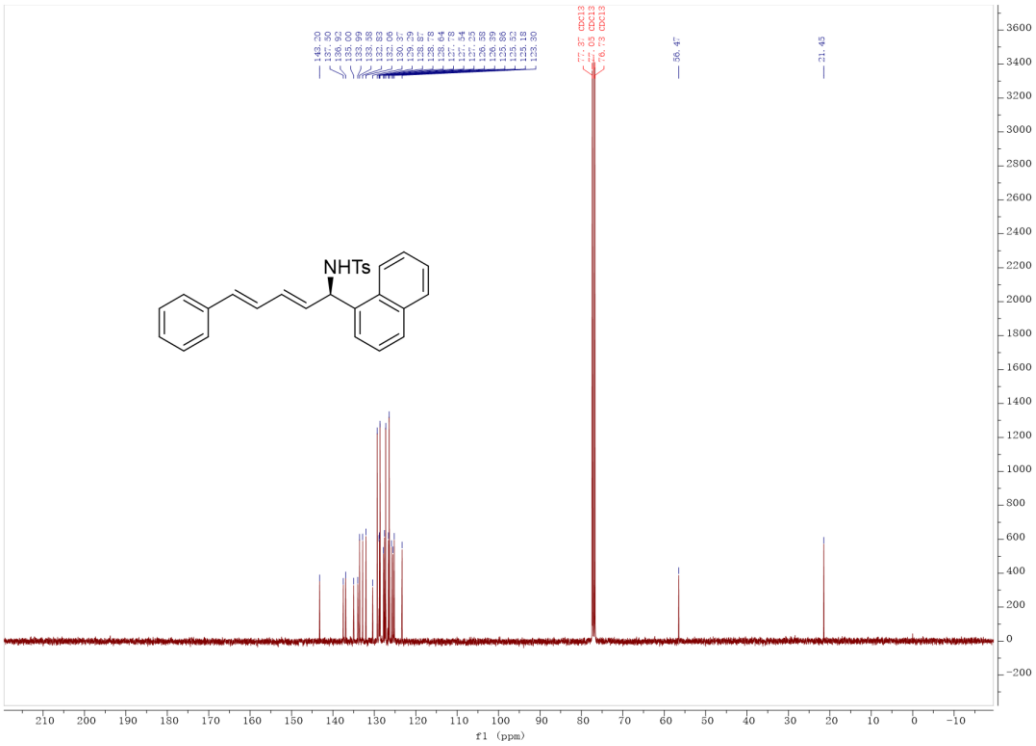

-112.30
NHTs
F
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

4-methyl-*N*-((*R*,2*E*,4*E*)-1-(naphthalen-1-yl)-5-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (40)

^{1}H NMR

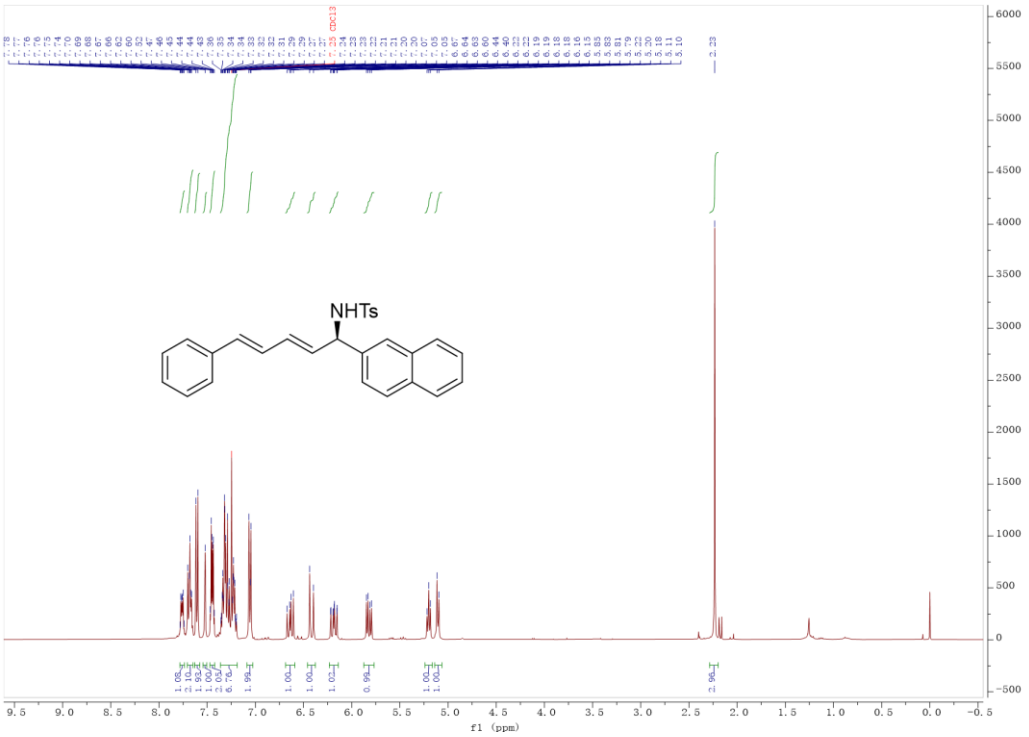


^{13}C NMR

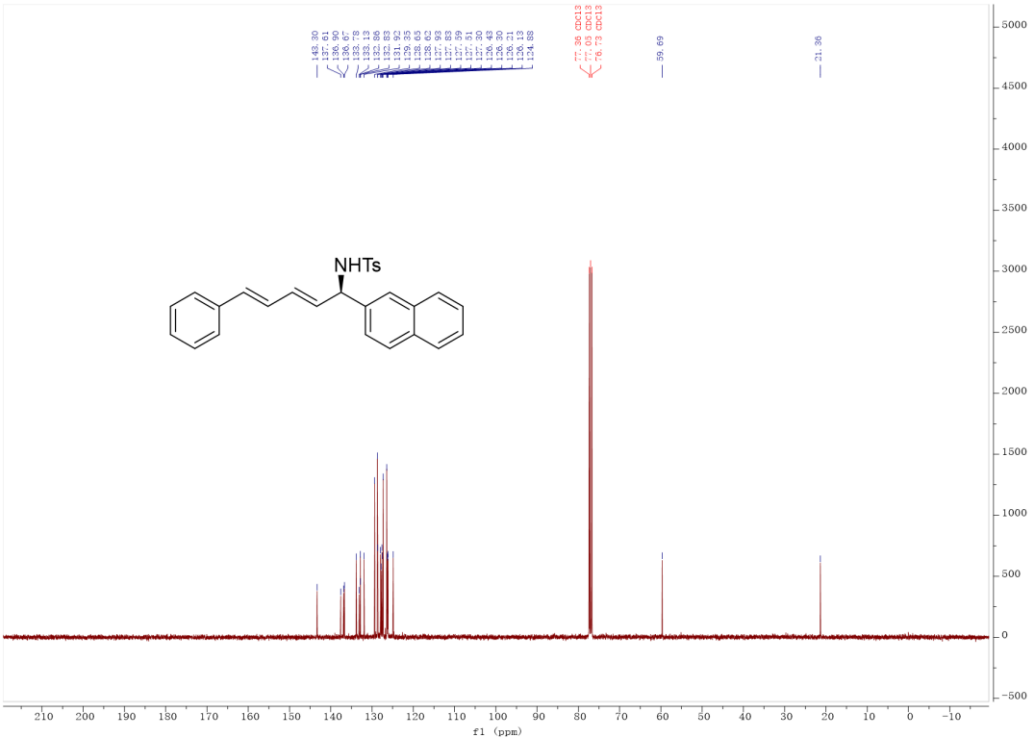


4-methyl-*N*-((*R*,2*E*,4*E*)-1-(naphthalen-2-yl)-5-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (41)

^{1}H NMR

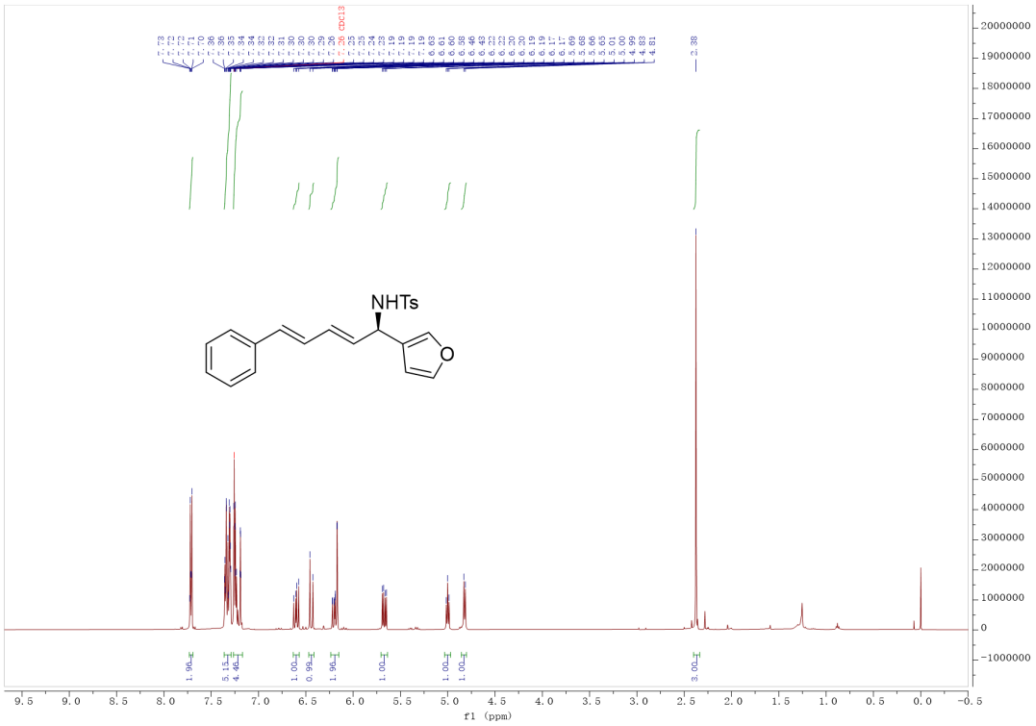


^{13}C NMR

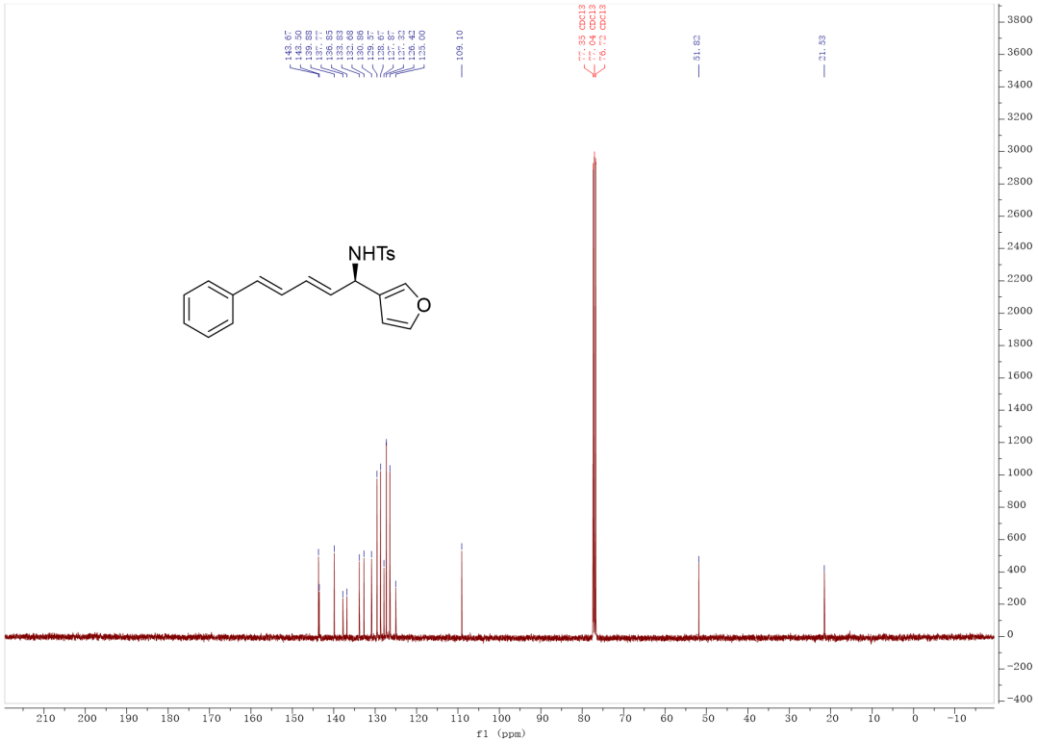


***N*-((*R*,2*E*,4*E*)-1-(furan-3-yl)-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (42)**

^{1}H NMR

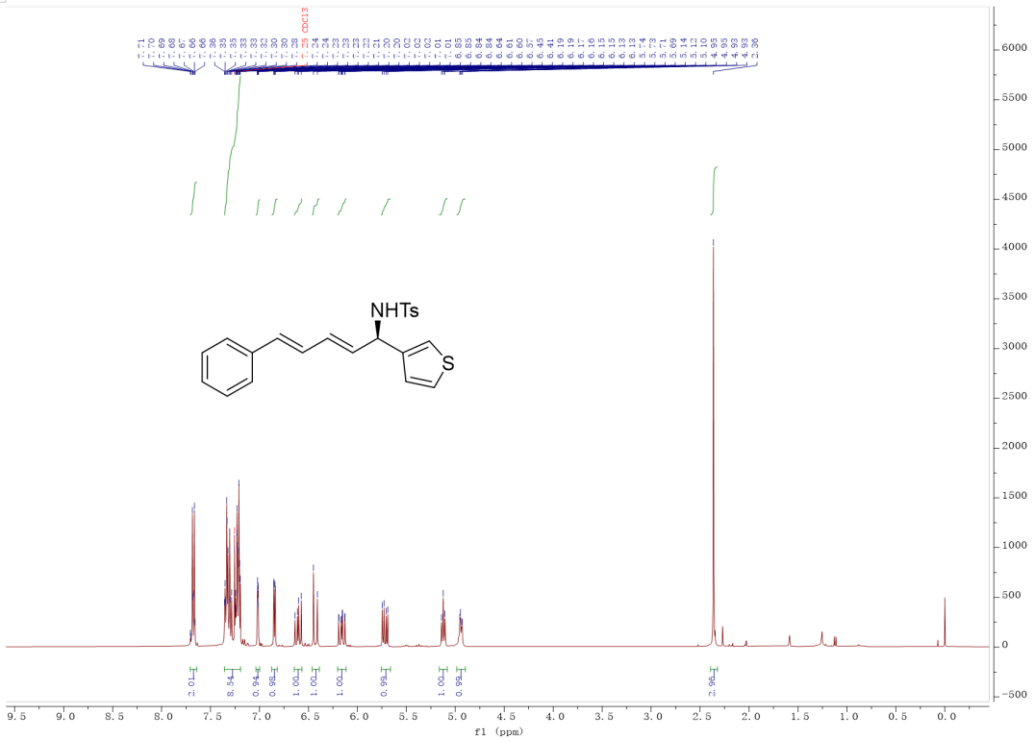


^{13}C NMR

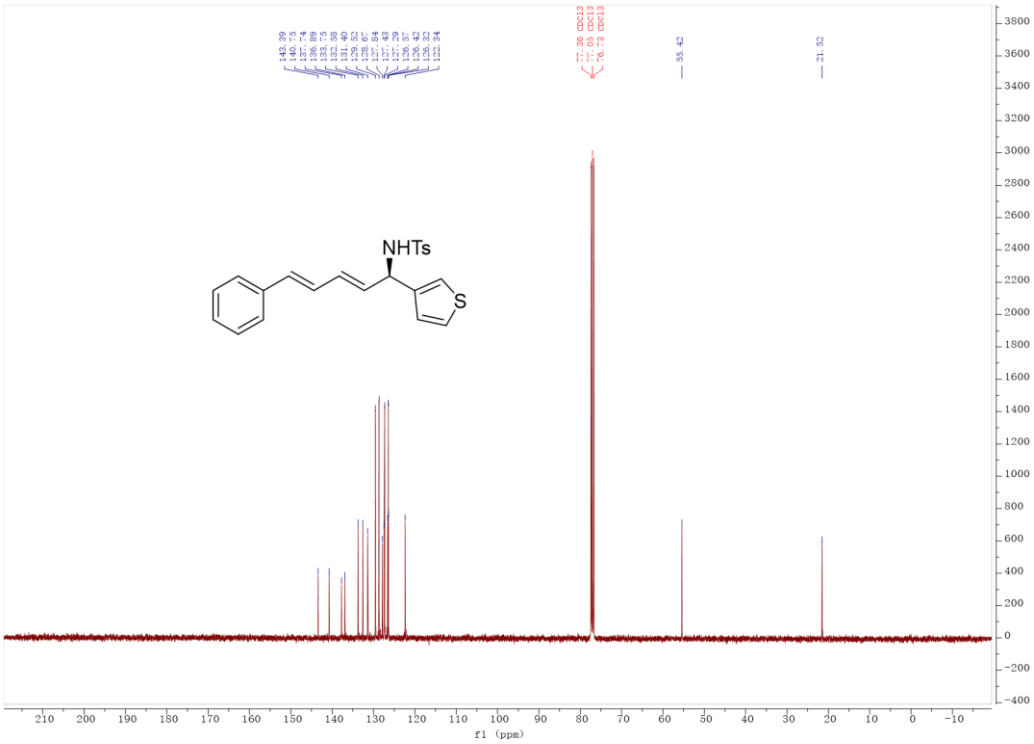


4-methyl-*N*-((*R*,2*E*,4*E*)-5-phenyl-1-(thiophen-3-yl)penta-2,4-dien-1-yl)benzenesulfonamide (43)

^{1}H NMR

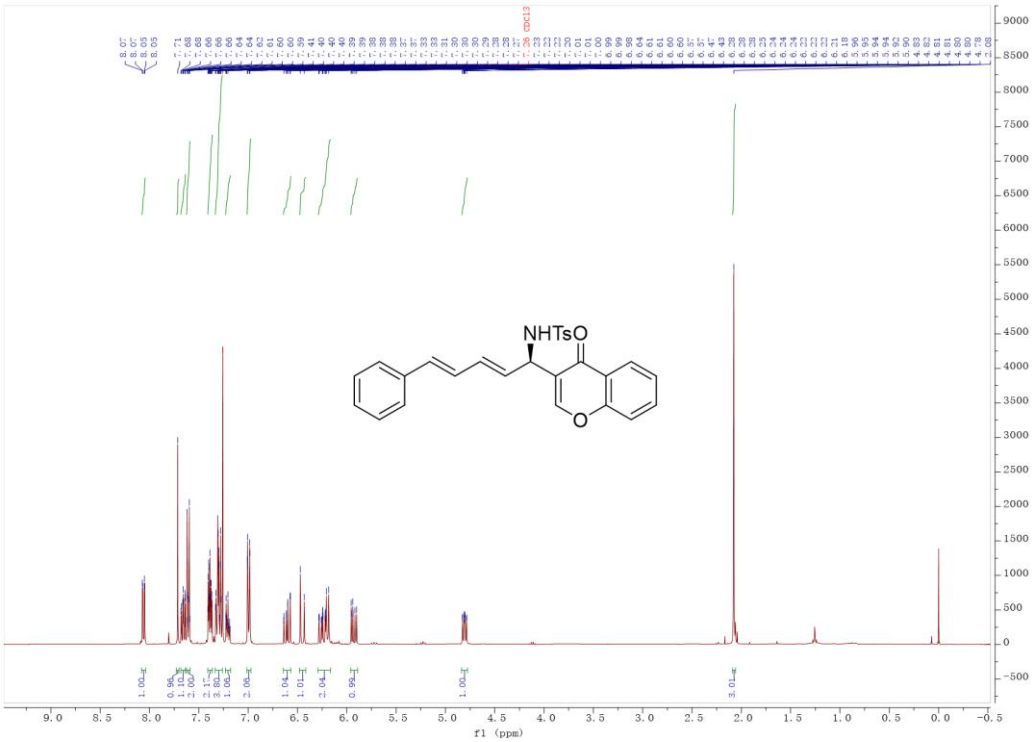


^{13}C NMR

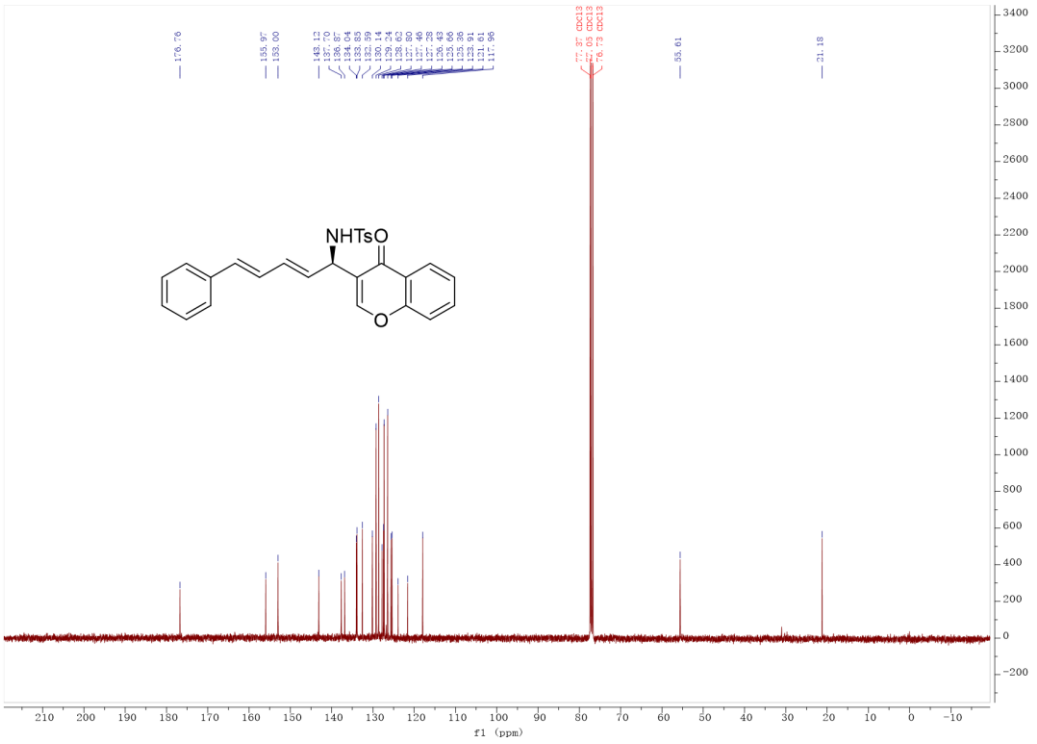


4-methyl-*N*-((*R*,2*E*,4*E*)-1-(4-oxo-4*H*-chromen-3-yl)-5-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (44)

^{1}H NMR

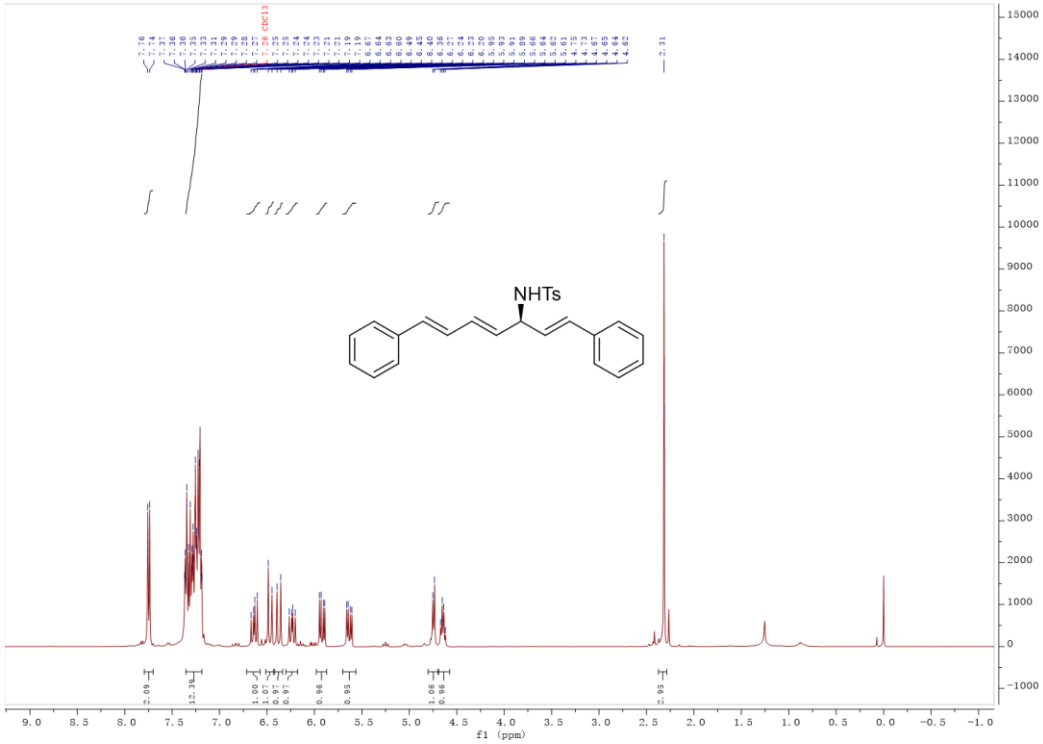


^{13}C NMR

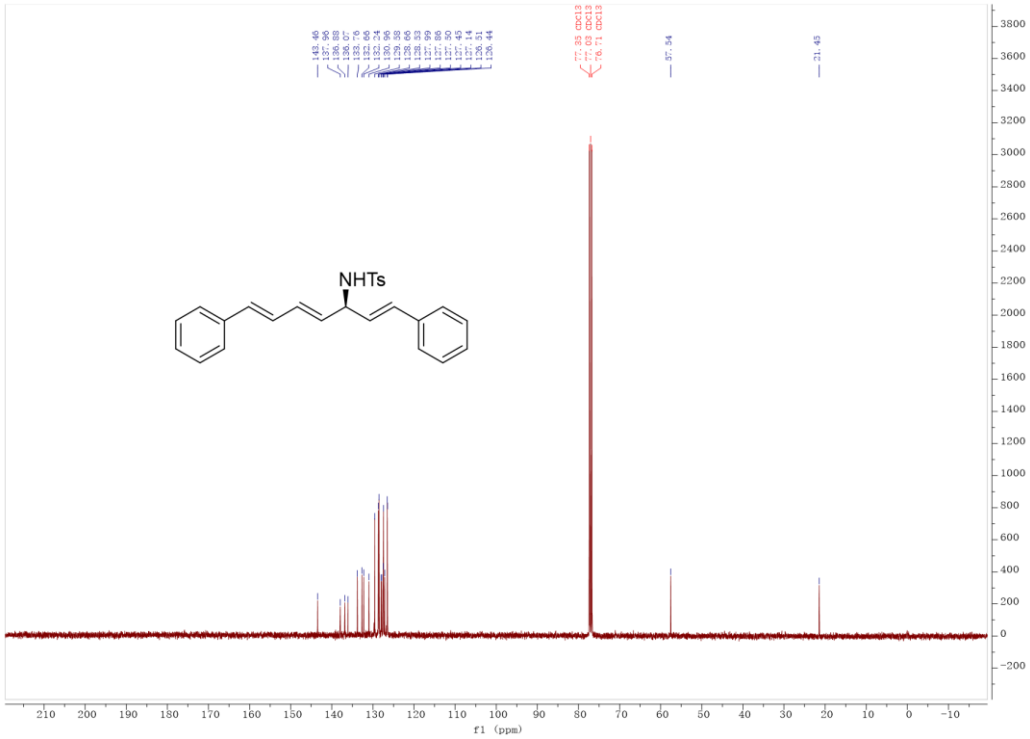


***N*-((*R*,1*E*,4*E*,6*E*)-1,7-diphenylhepta-1,4,6-trien-3-yl)-4-methylbenzenesulfonamide (45)**

^{1}H NMR

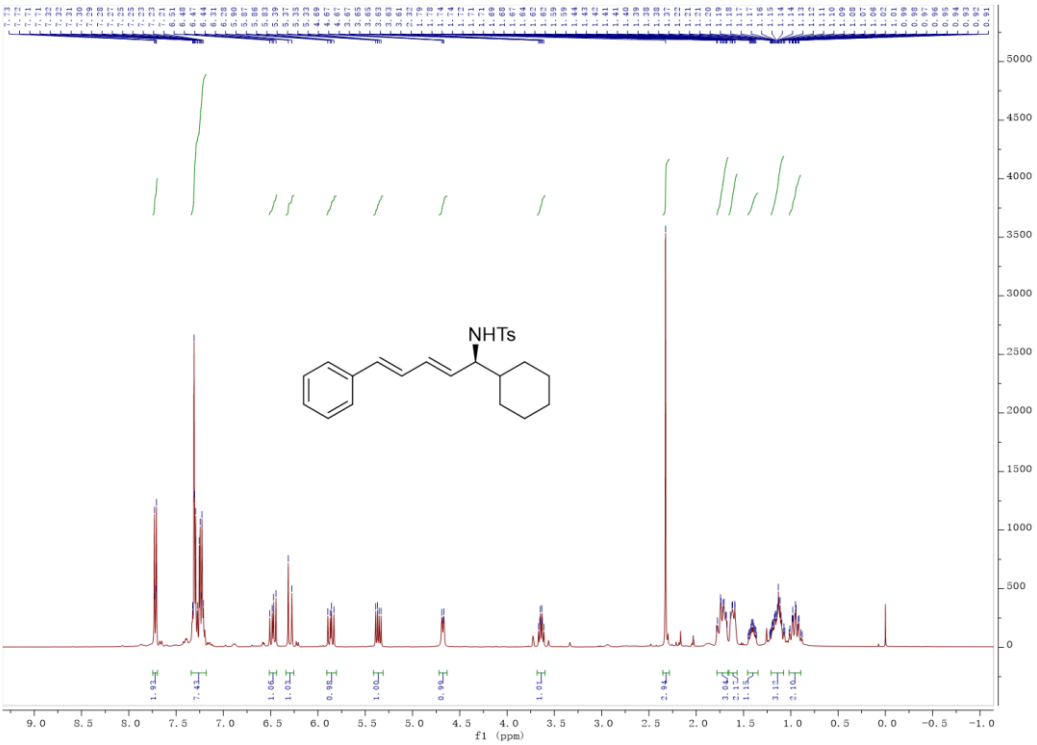


^{13}C NMR

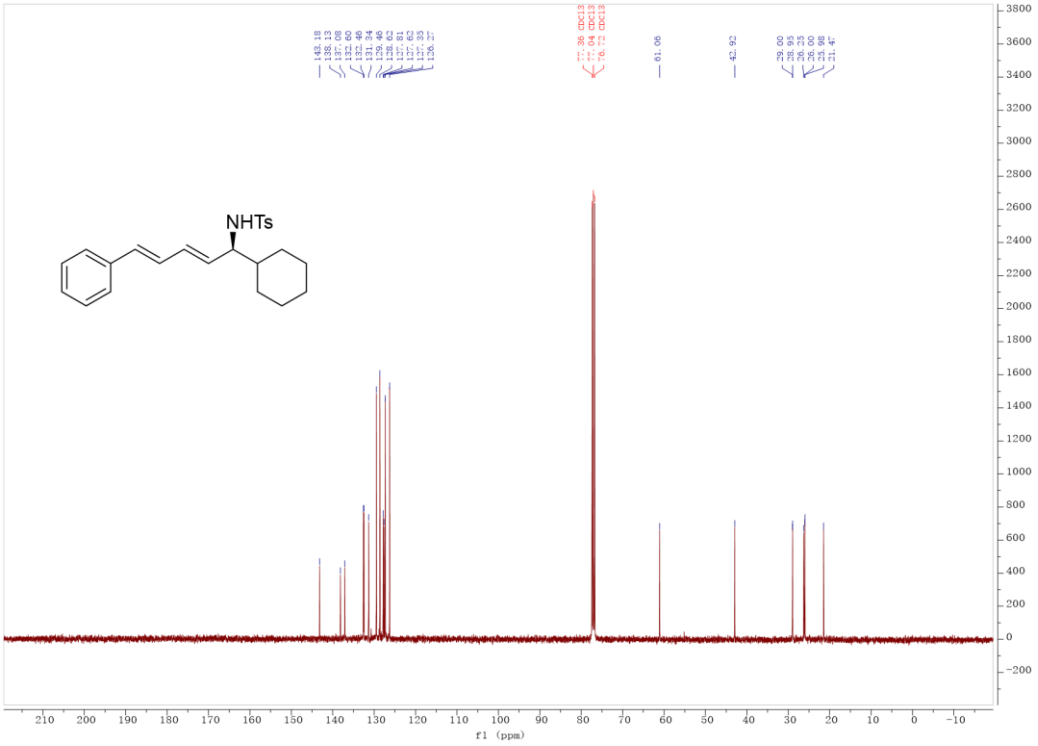


***N*-((*S*,2*E*,4*E*)-1-cyclohexyl-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (46)**

^{1}H NMR

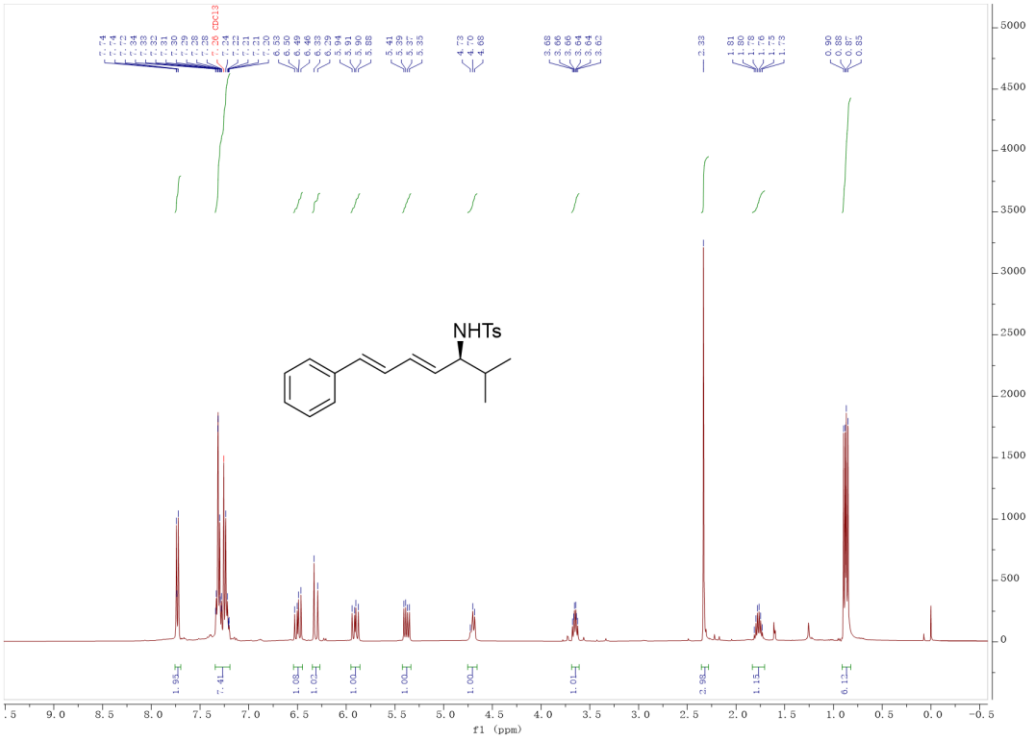


^{13}C NMR

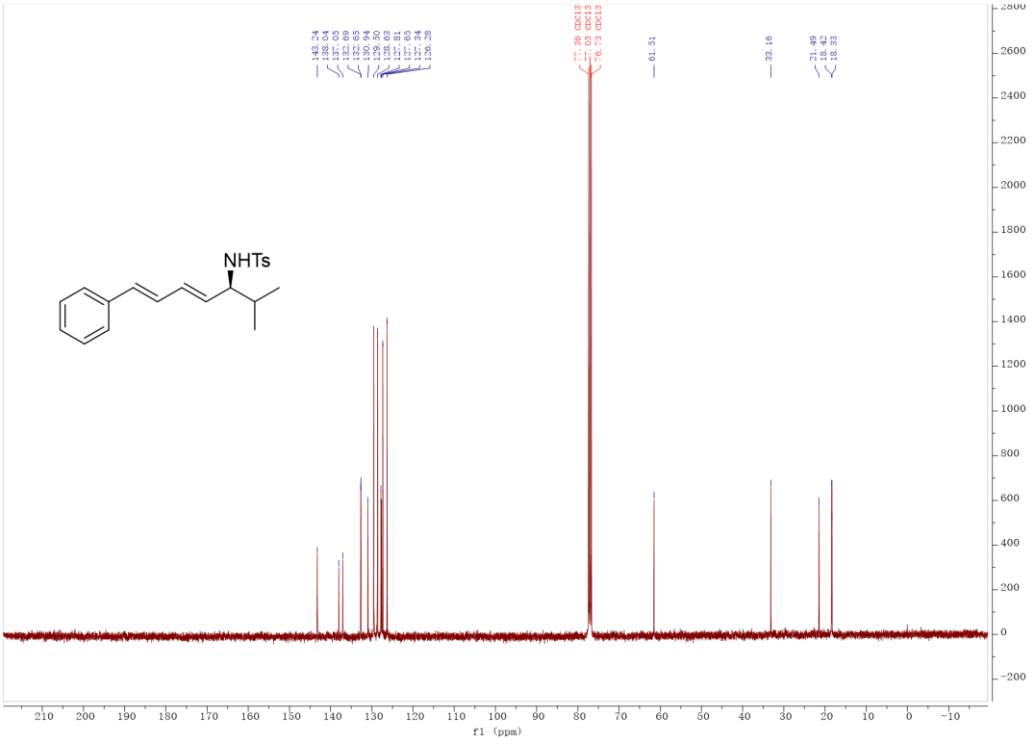


4-methyl-*N*-((*S*,4*E*,6*E*)-2-methyl-7-phenylhepta-4,6-dien-3-yl)benzenesulfonamide (47)

^{1}H NMR

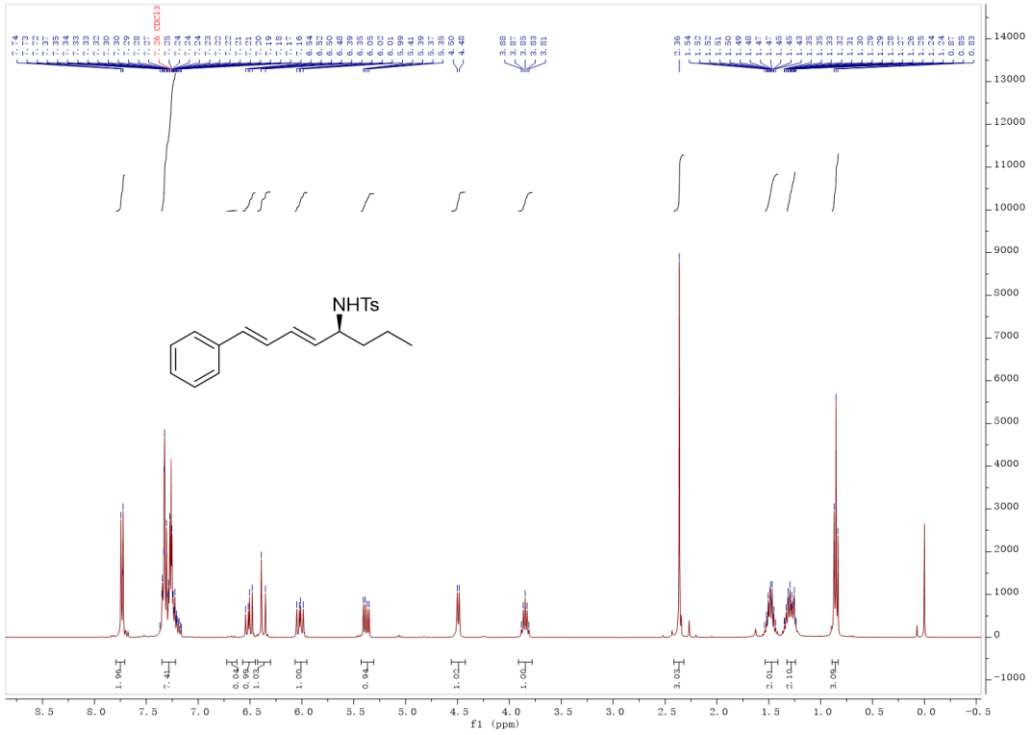


^{13}C NMR

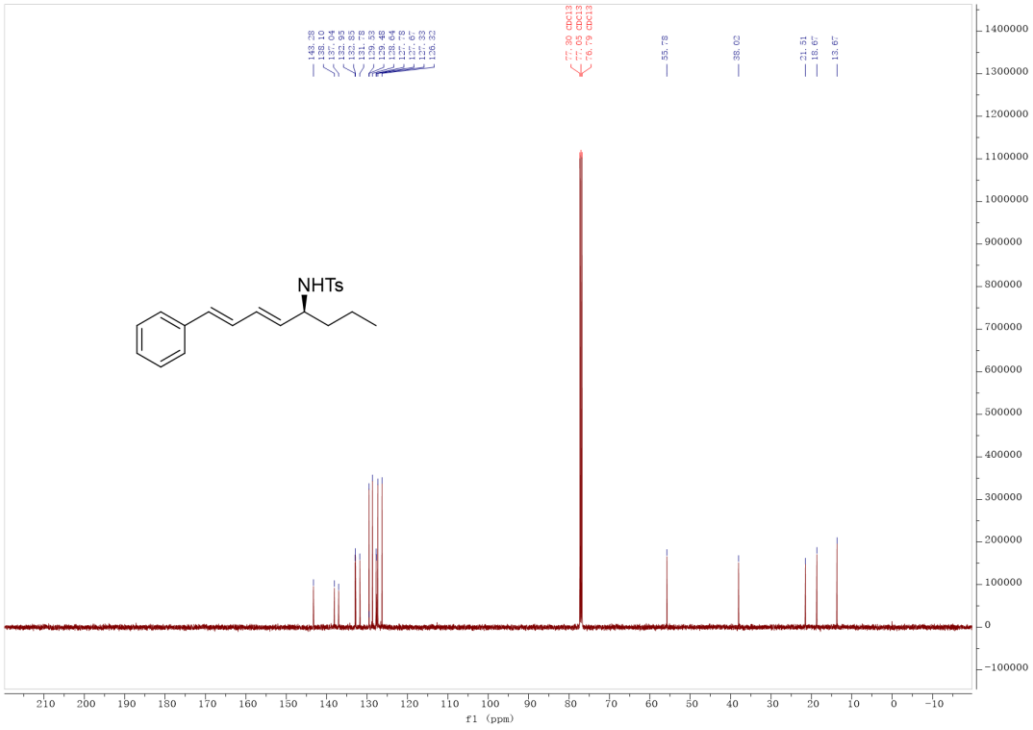


4-methyl-*N*-((*S*,5*E*,7*E*)-8-phenylocta-5,7-dien-4-yl)benzenesulfonamide (48)

^{1}H NMR

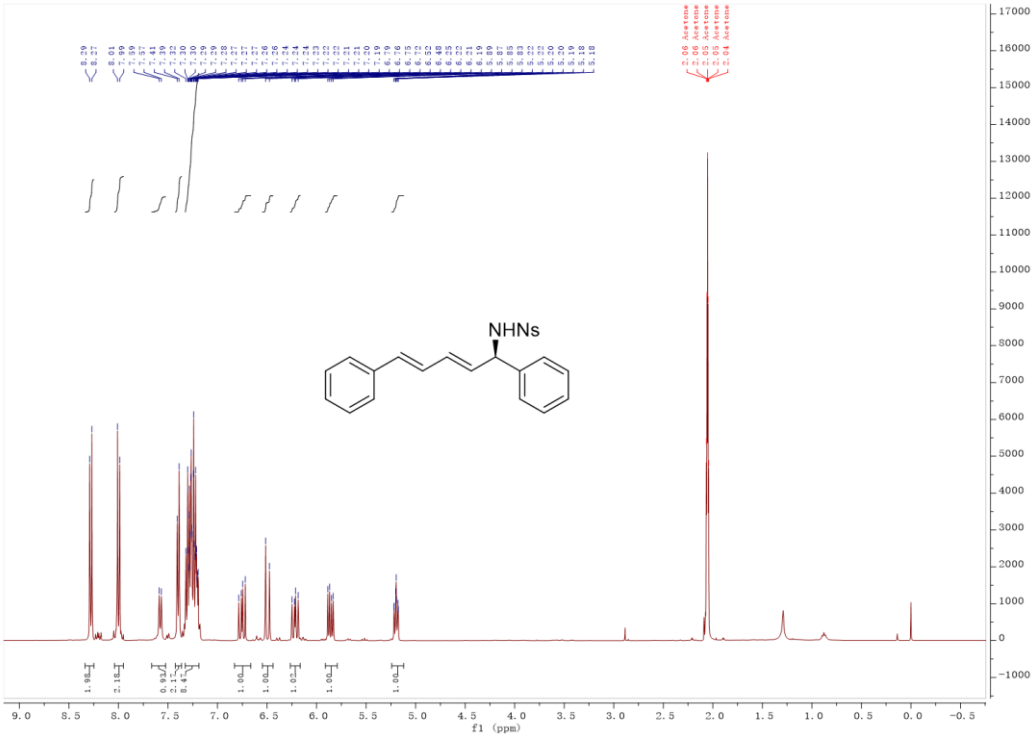


^{13}C NMR

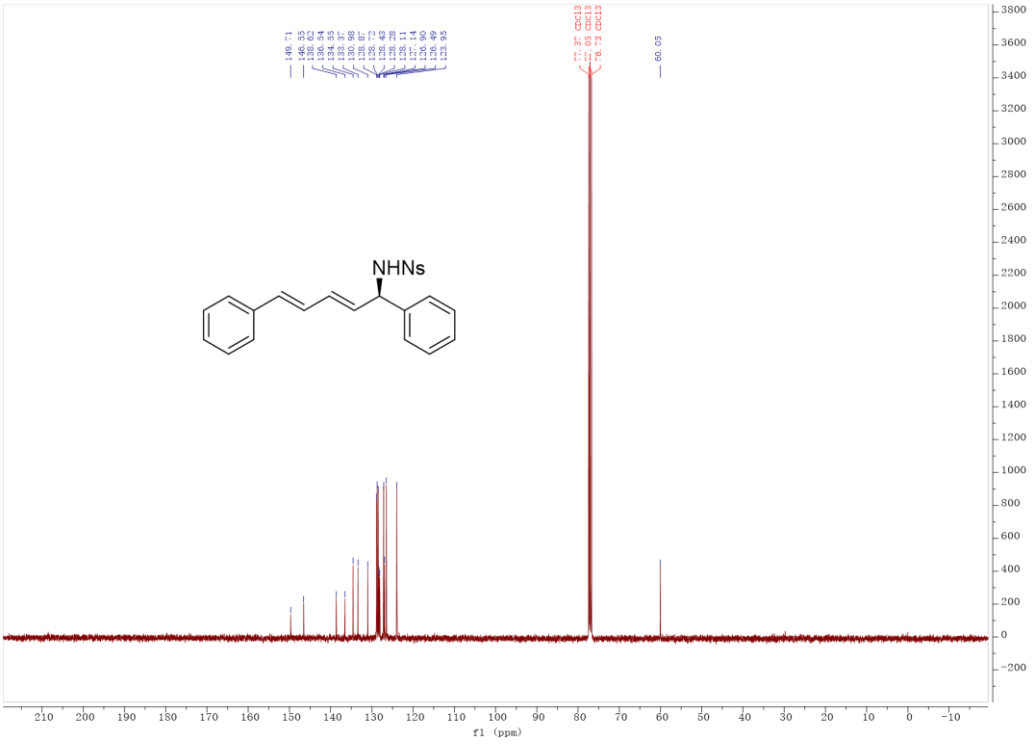


***N*-((*R*,2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-yl)-4-nitrobenzenesulfonamide (49)**

^{1}H NMR

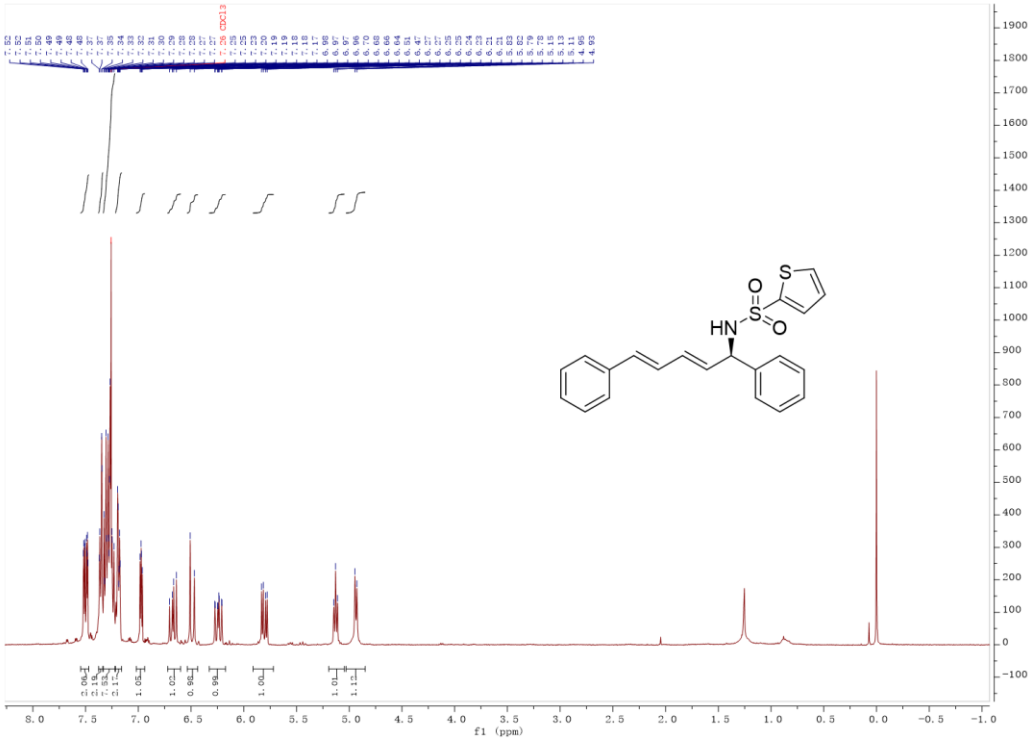


^{13}C NMR

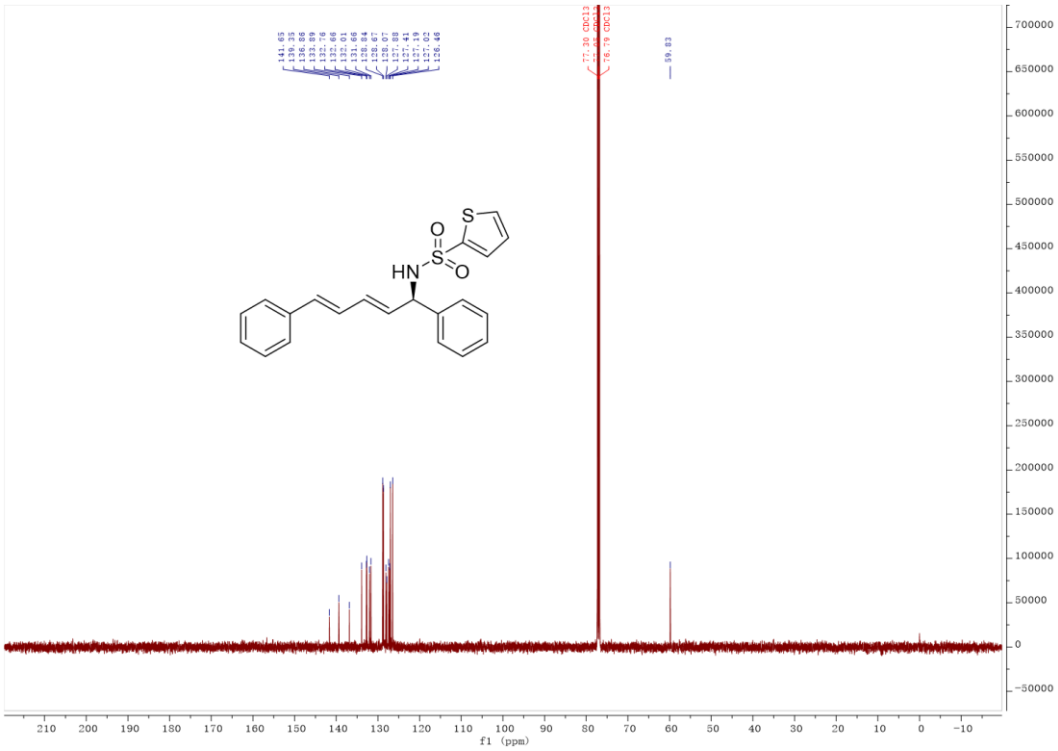


***N*-((*R*,2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-yl)thiophene-2-sulfonamide (50)**

^{1}H NMR

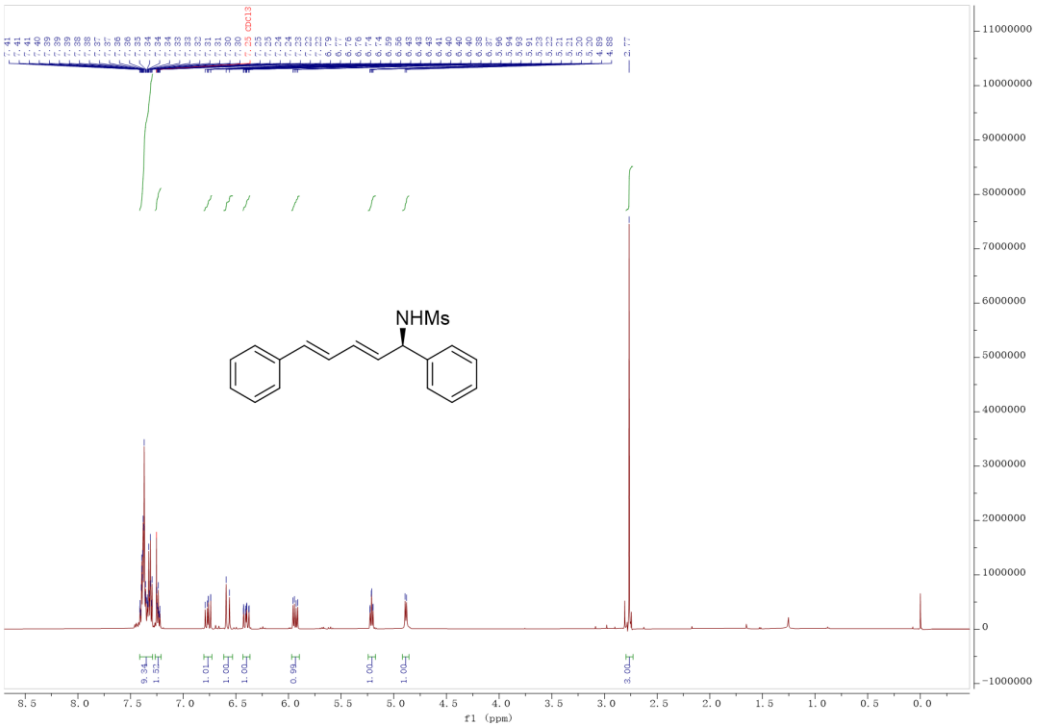


^{13}C NMR

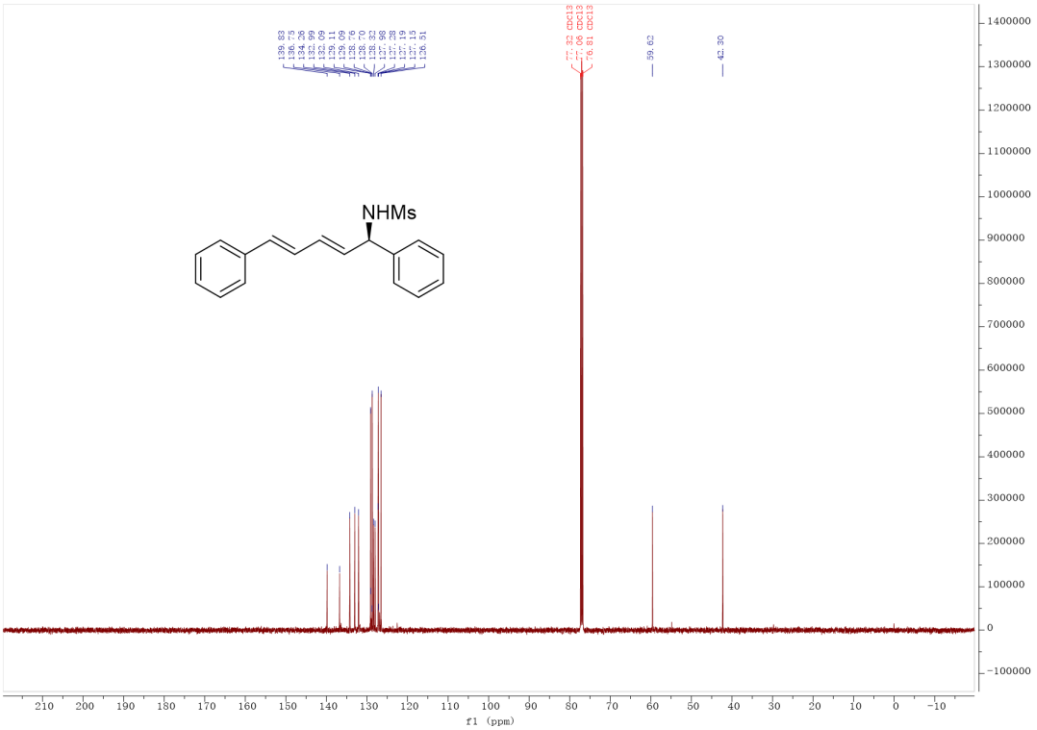


***N*-((*R*,2E,4E)-1,5-diphenylpenta-2,4-dien-1-yl)methanesulfonamide (51)**

^{1}H NMR

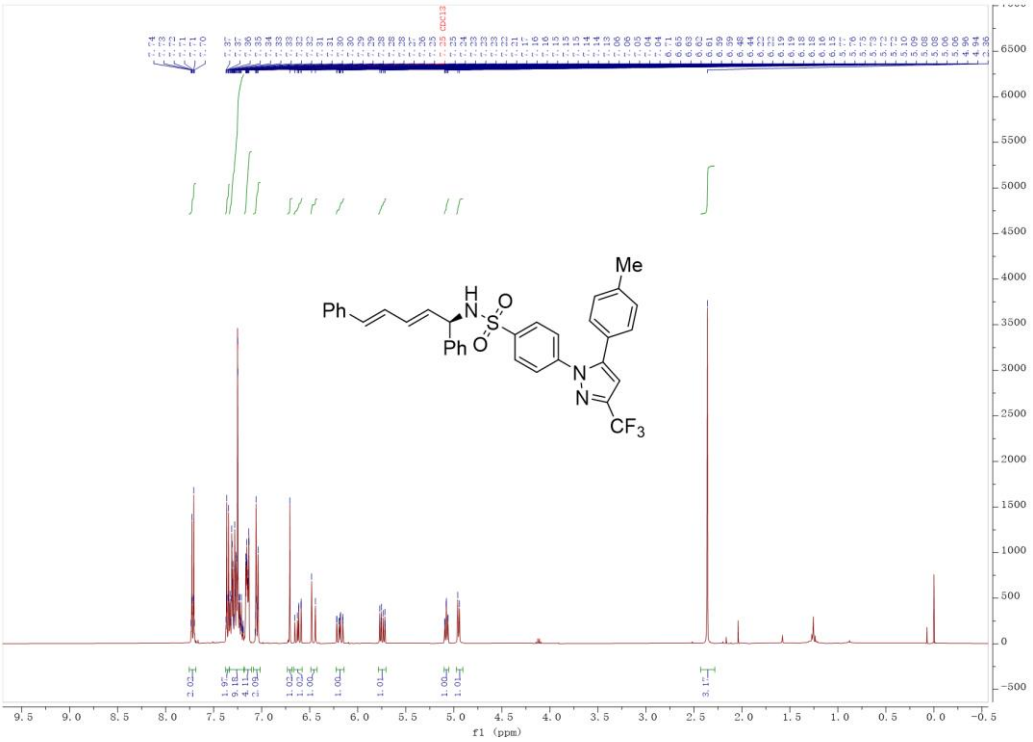


^{13}C NMR

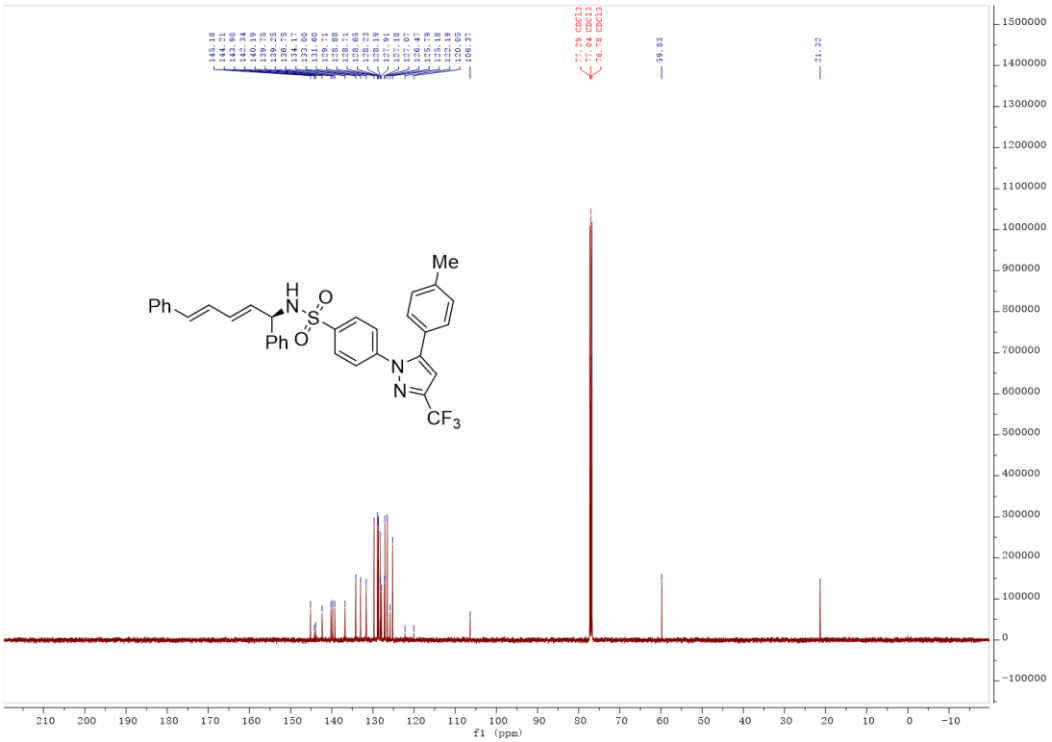


***N*-((*R*,2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-yl)-4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (52)**

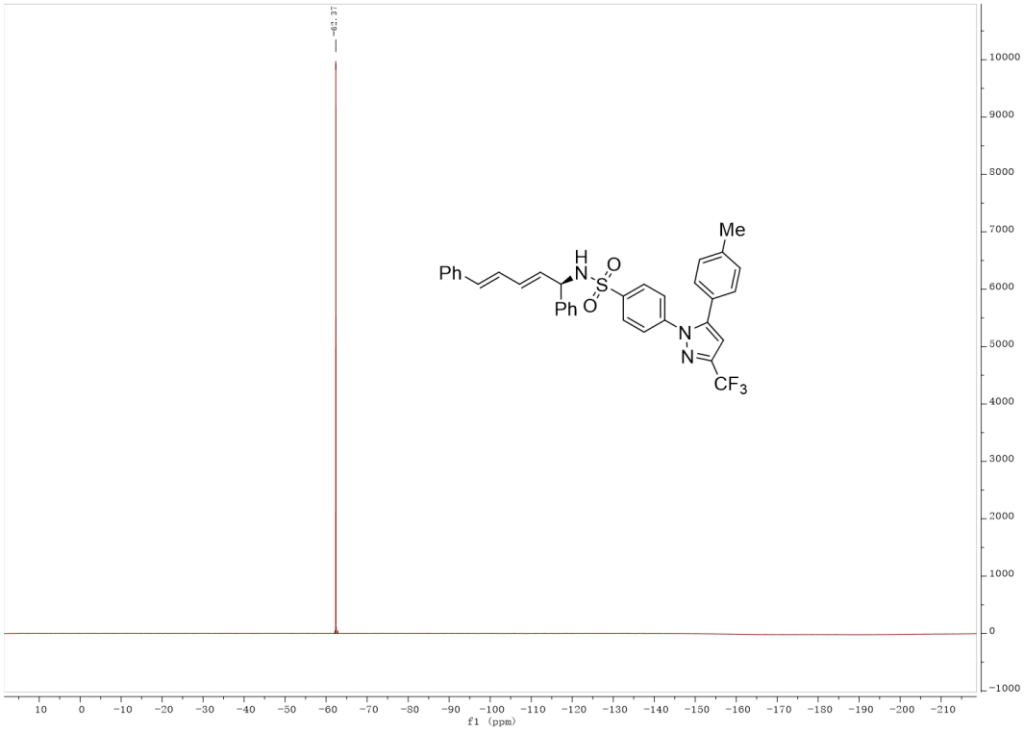
^{1}H NMR



^{13}C NMR

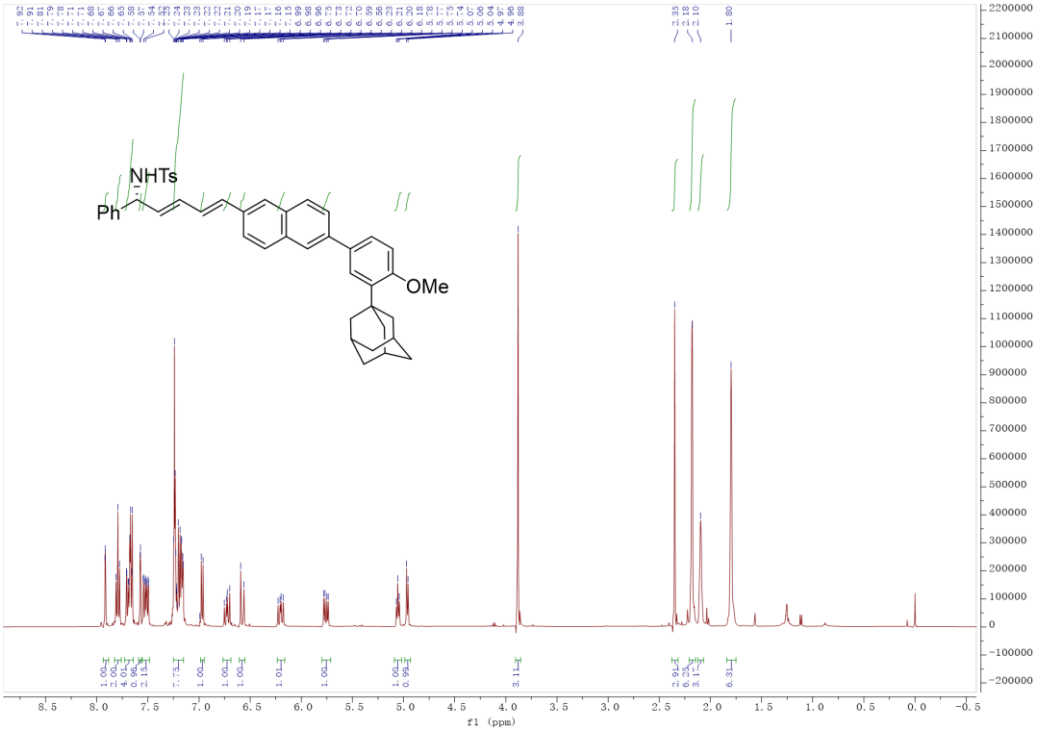


^{19}F NMR

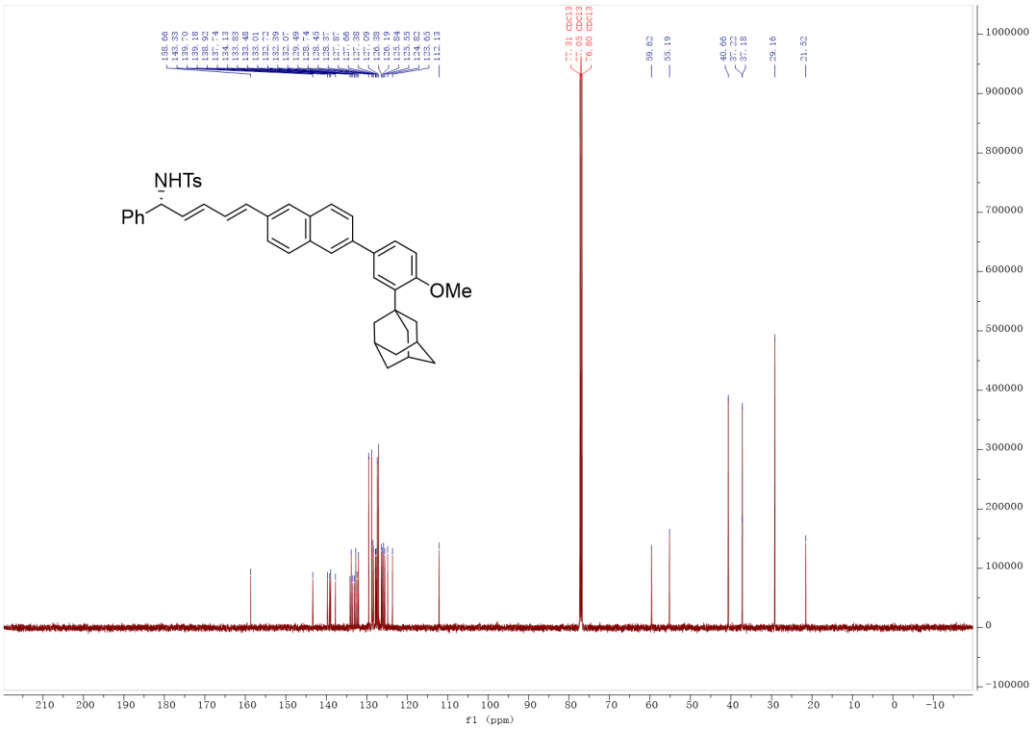

-62.37
Me
Ph
H
N
O
S
O
Ph
N
N
CF3
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

***N*-((*R*,2*E*,4*E*)-5-(6-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (53)**

^{1}H NMR

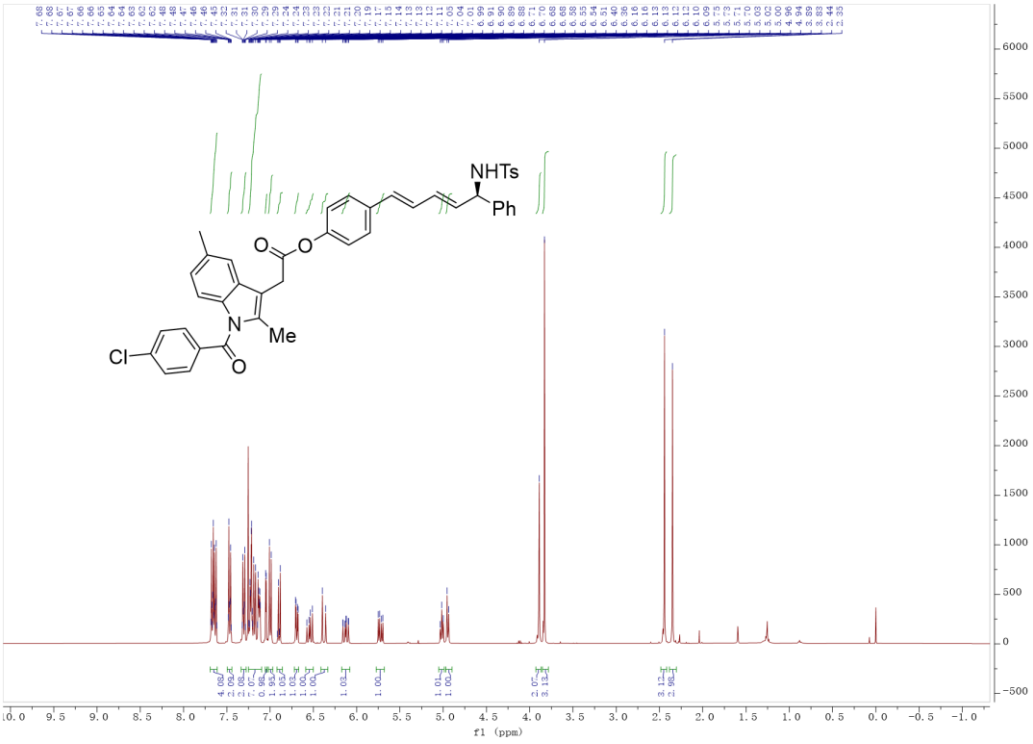


^{13}C NMR

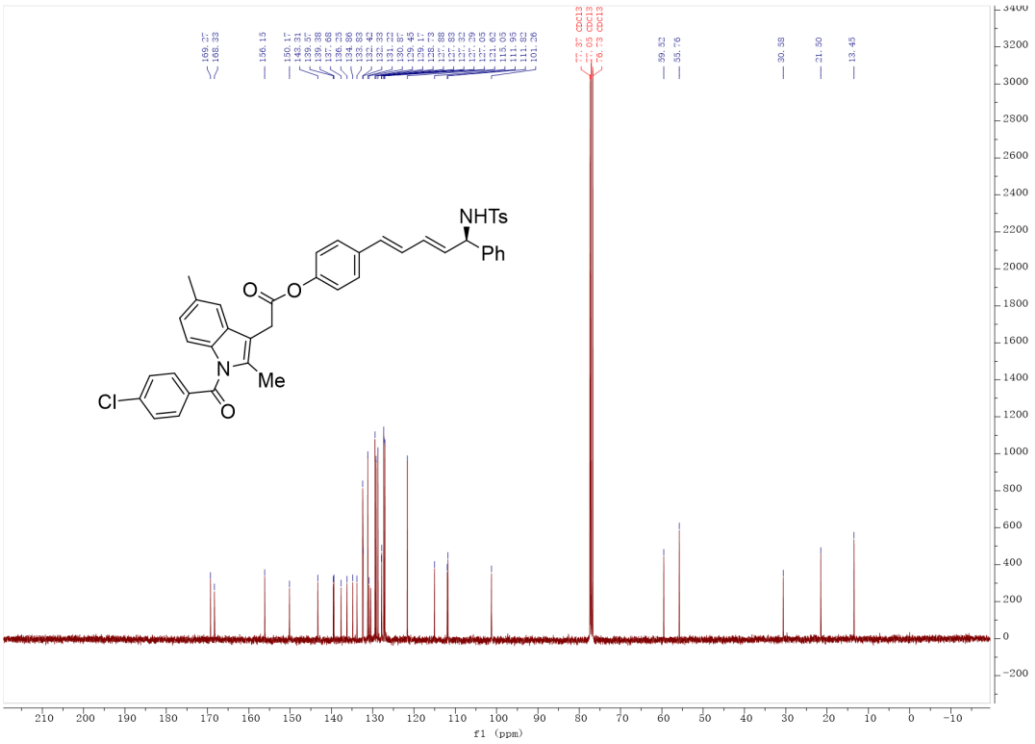


4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)phenyl 2-(1-(4-chlorobenzoyl)-2,5-dimethyl-1H-indol-3-yl)acetate (54)

^{1}H NMR

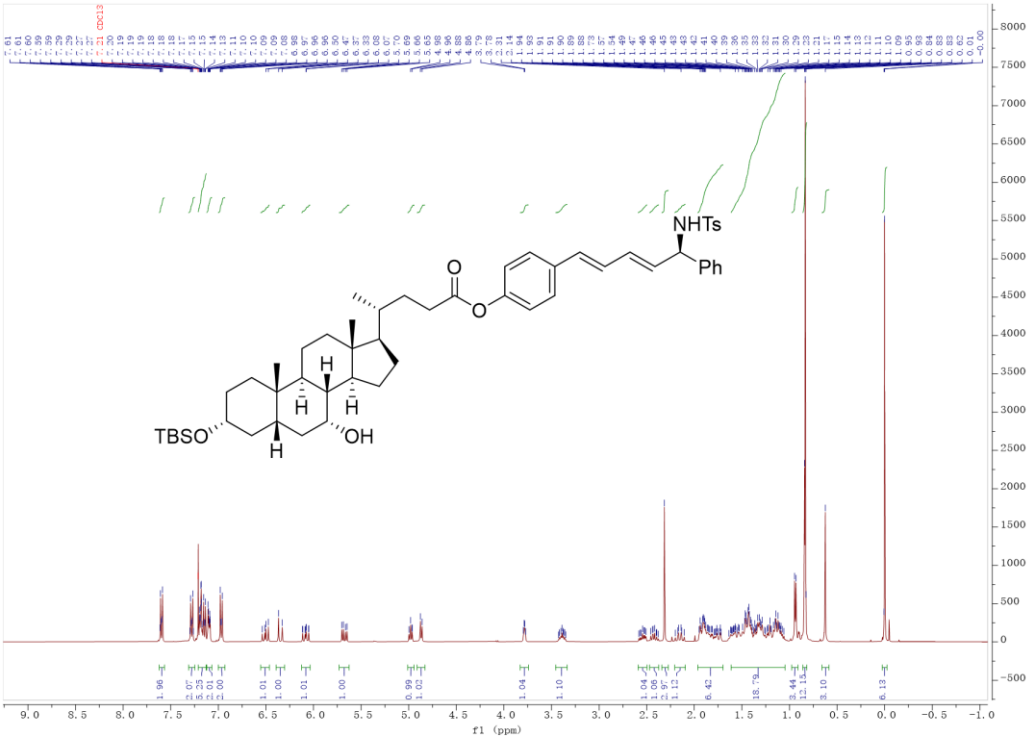


^{13}C NMR

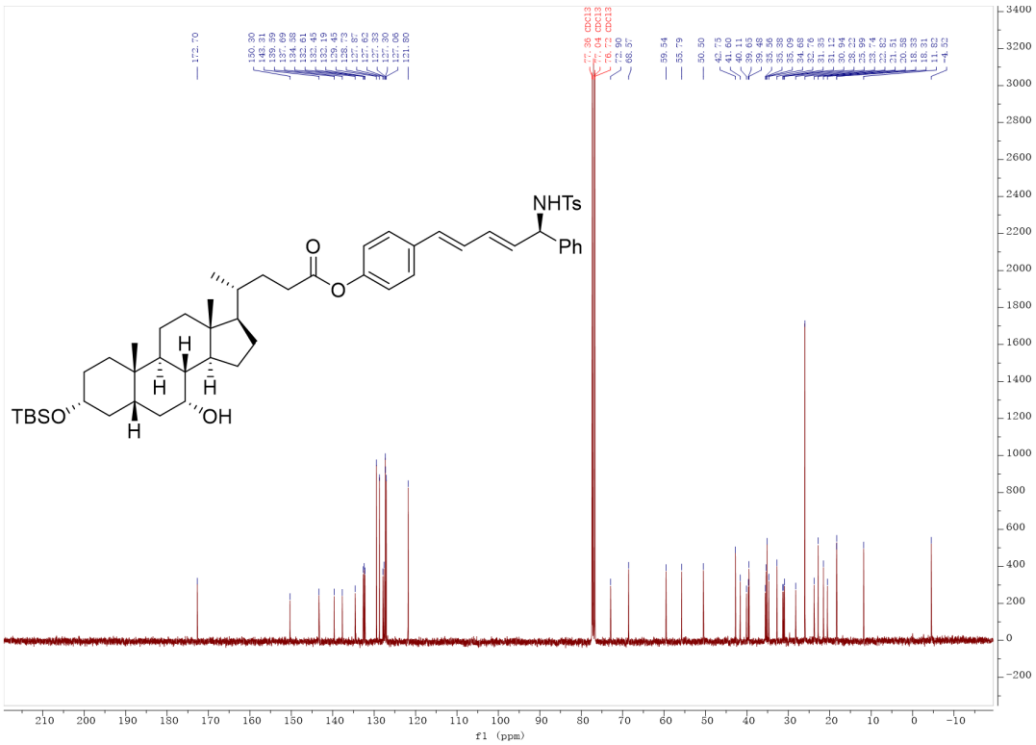


4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)phenyl (*R*)-4-((3*R*,5*R*,7*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-((*tert*-butyldimethylsilyl)oxy)-7-hydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoate (55)

^{1}H NMR

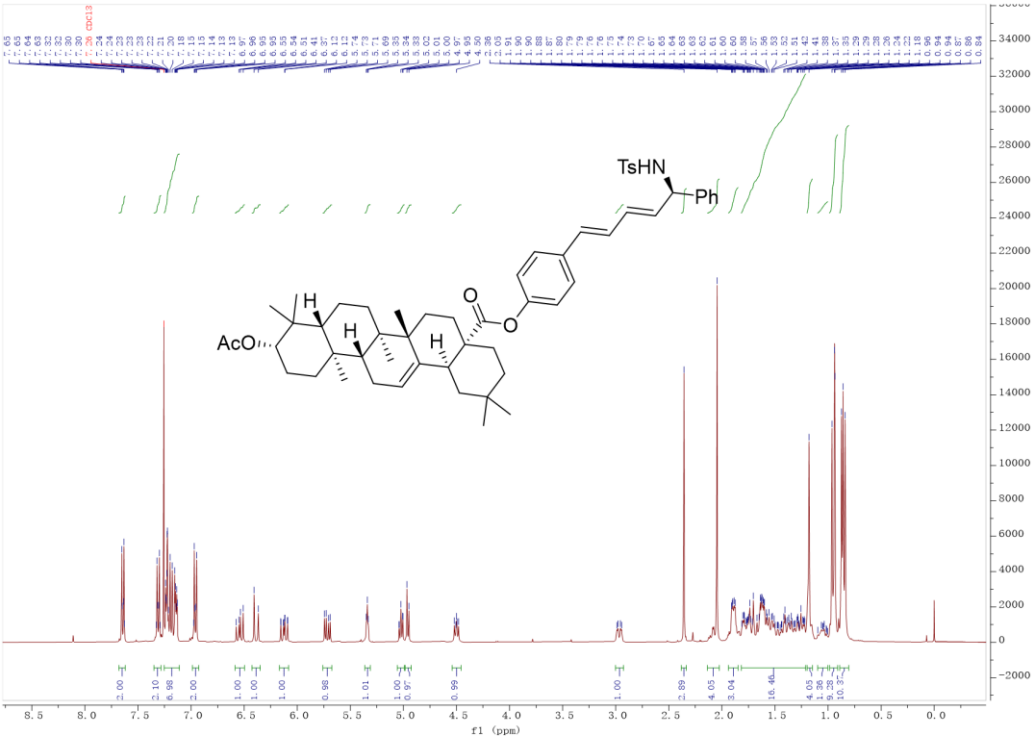


^{13}C NMR

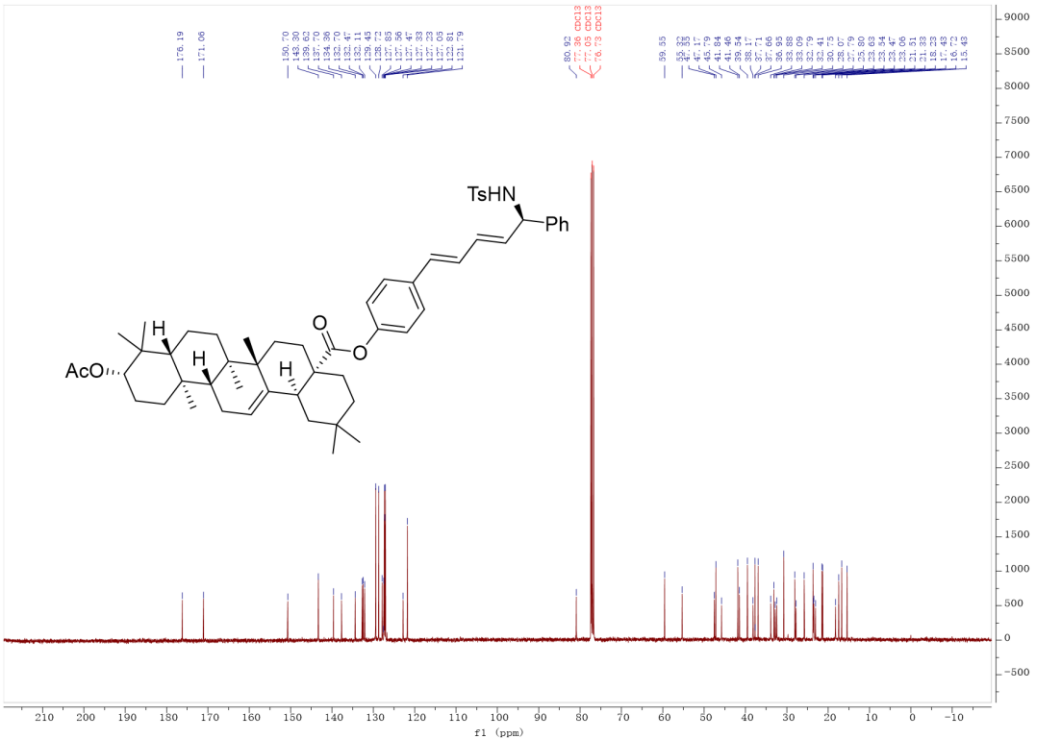


4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)phenyl (4a*S*,6a*S*,6b*R*,8a*R*,10*S*,12a*R*,12b*R*,14b*S*)-10-acetoxy-2,2,6a,6b,9,9,12a-heptamethyl-1,3,4,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-octadecahydropicene-4a(2*H*)-carboxylate (56)

^{1}H NMR

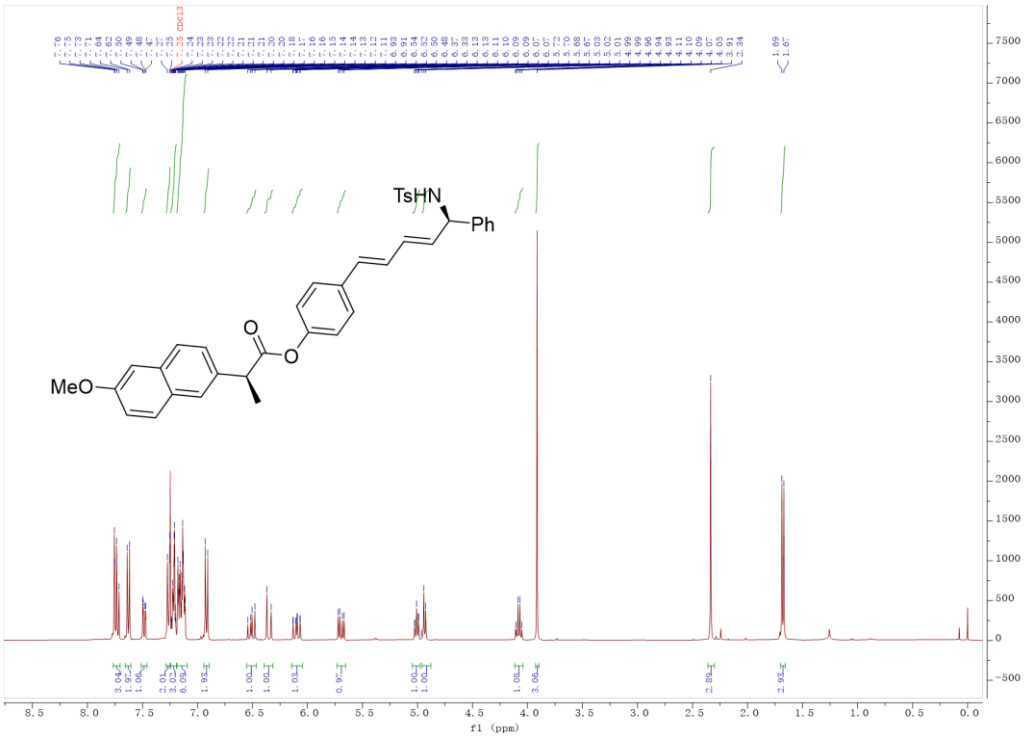


^{13}C NMR

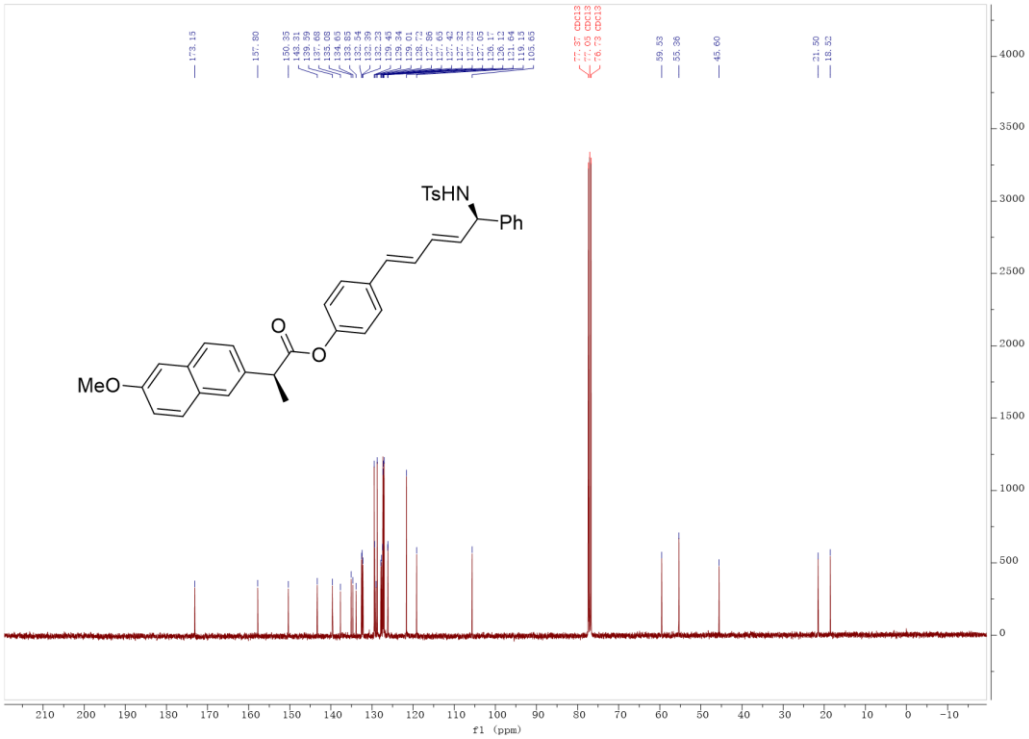


4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)phenyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (57)

^{1}H NMR

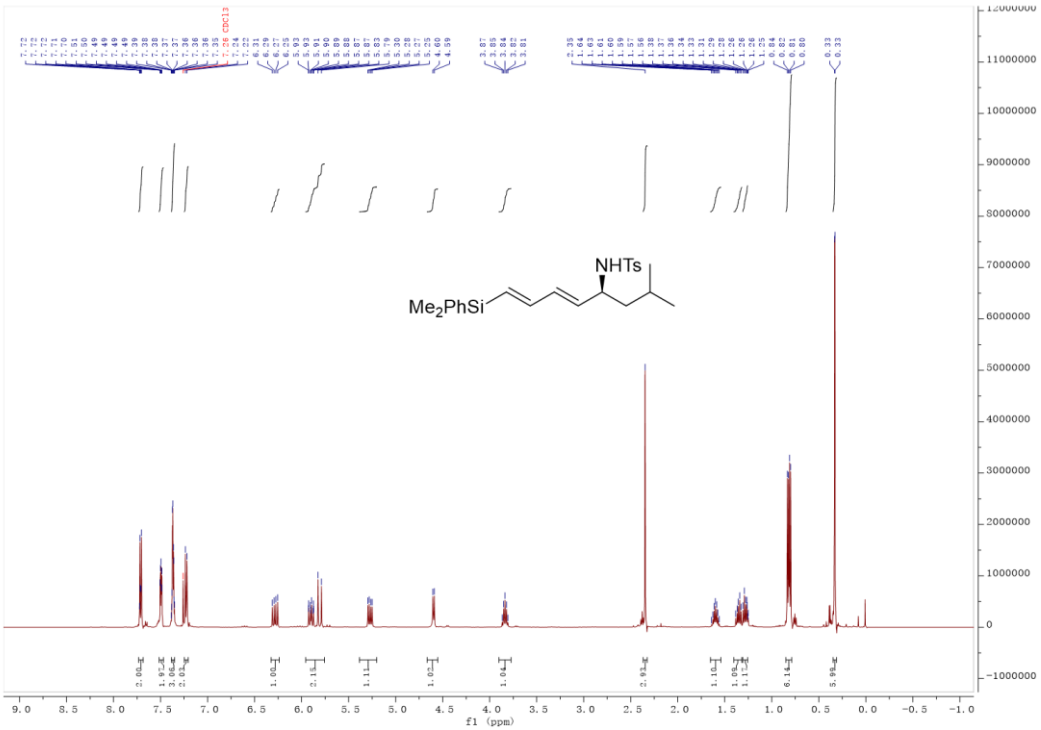


^{13}C NMR

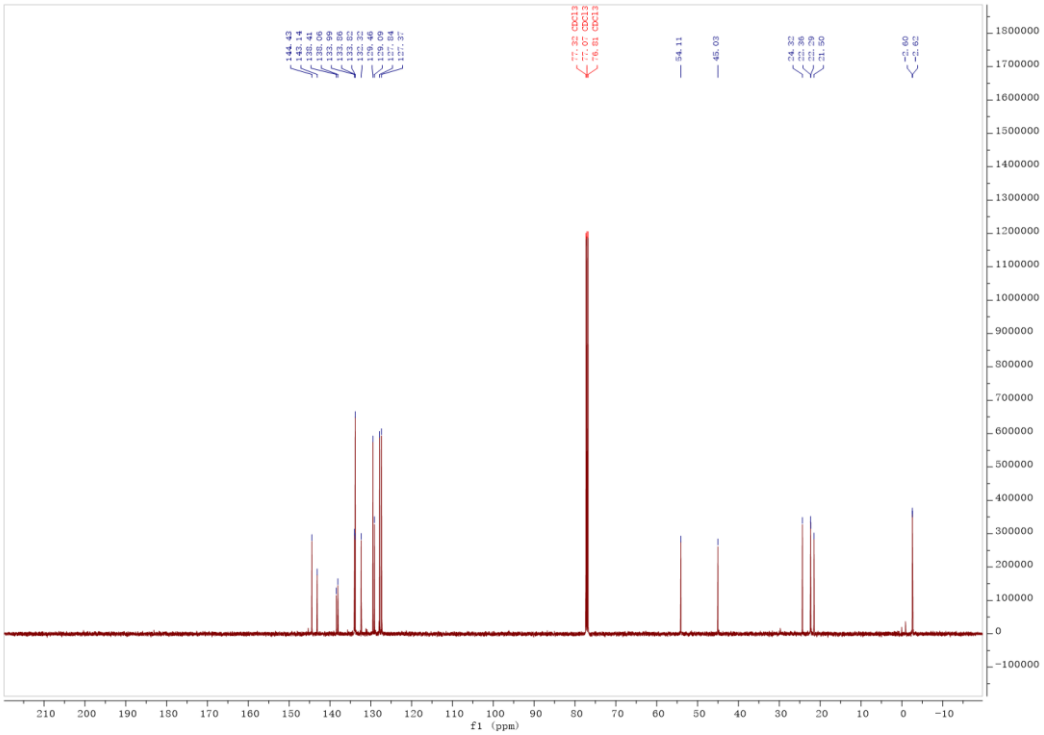


***N*-((*S*,5*E*,7*E*)-8-(dimethyl(phenyl)silyl)-2-methylocta-5,7-dien-4-yl)-4-methylbenzenesulfonamide (58)**

^{1}H NMR

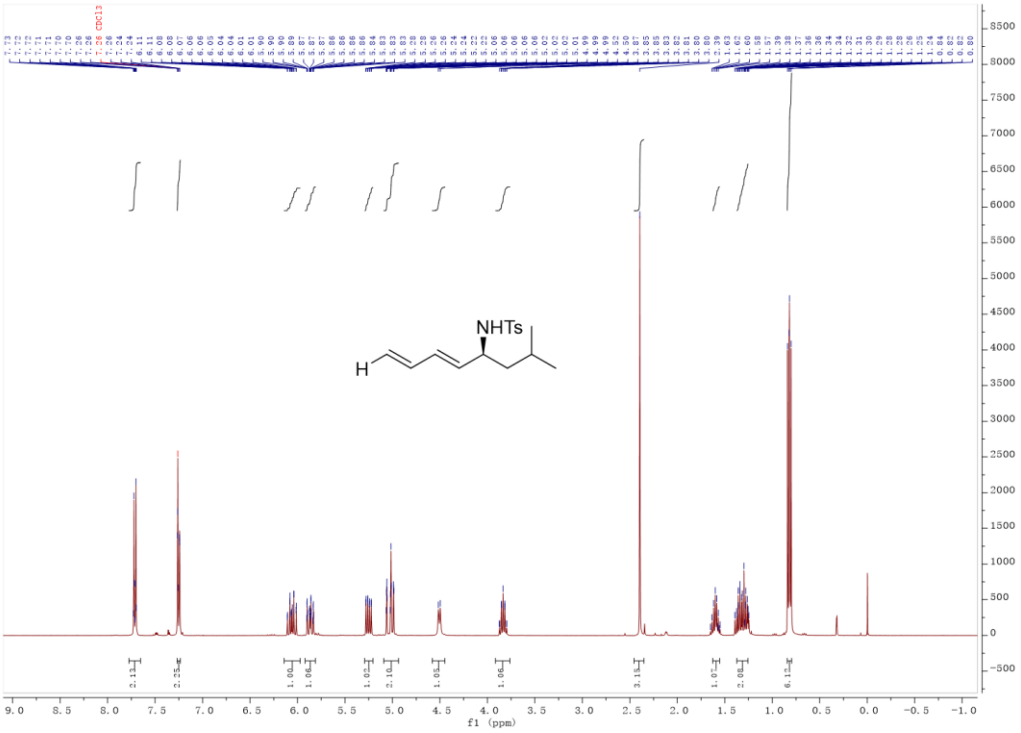


^{13}C NMR

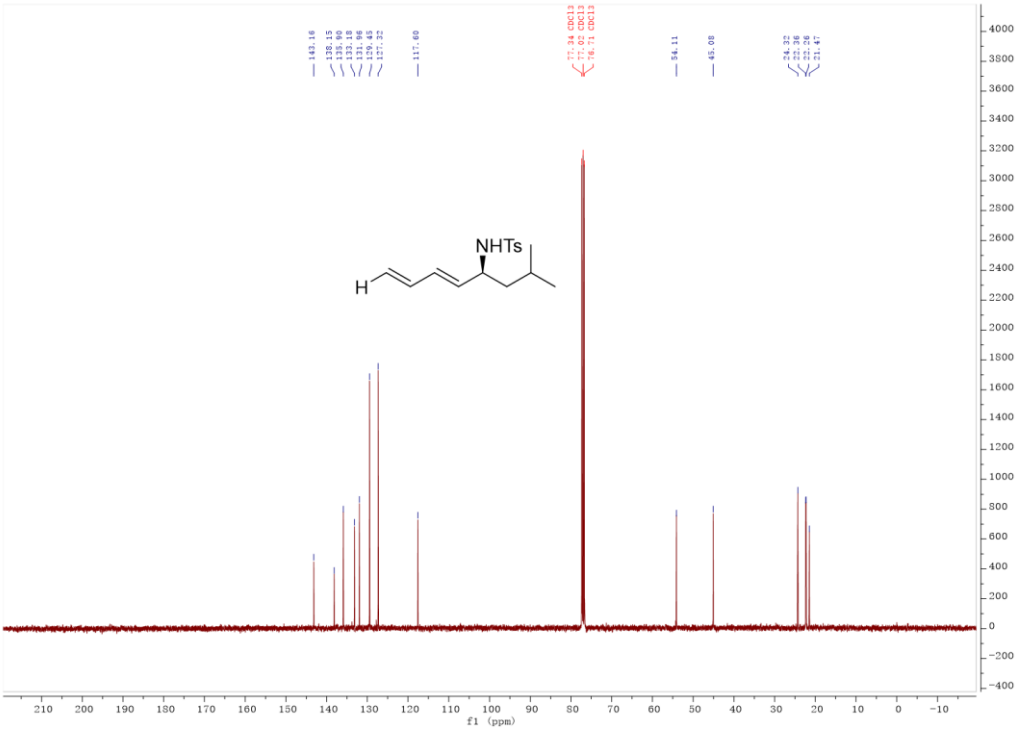


(*S*,*E*)-4-methyl-*N*-(2-methylocta-5,7-dien-4-yl)benzenesulfonamide (59)

^{1}H NMR

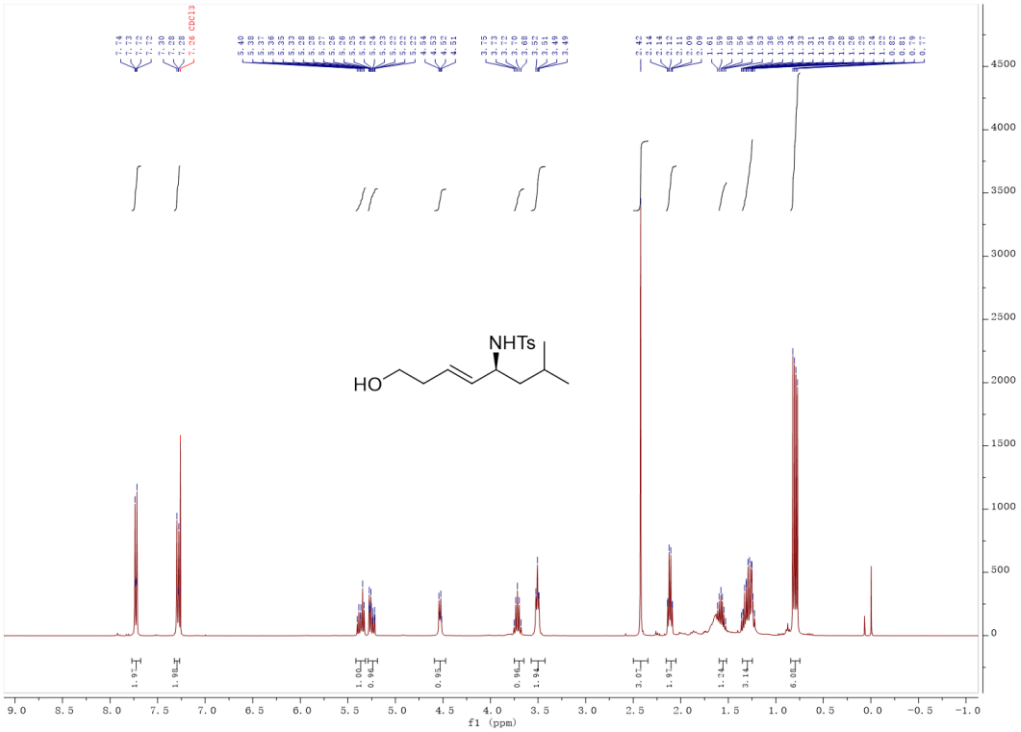


^{13}C NMR

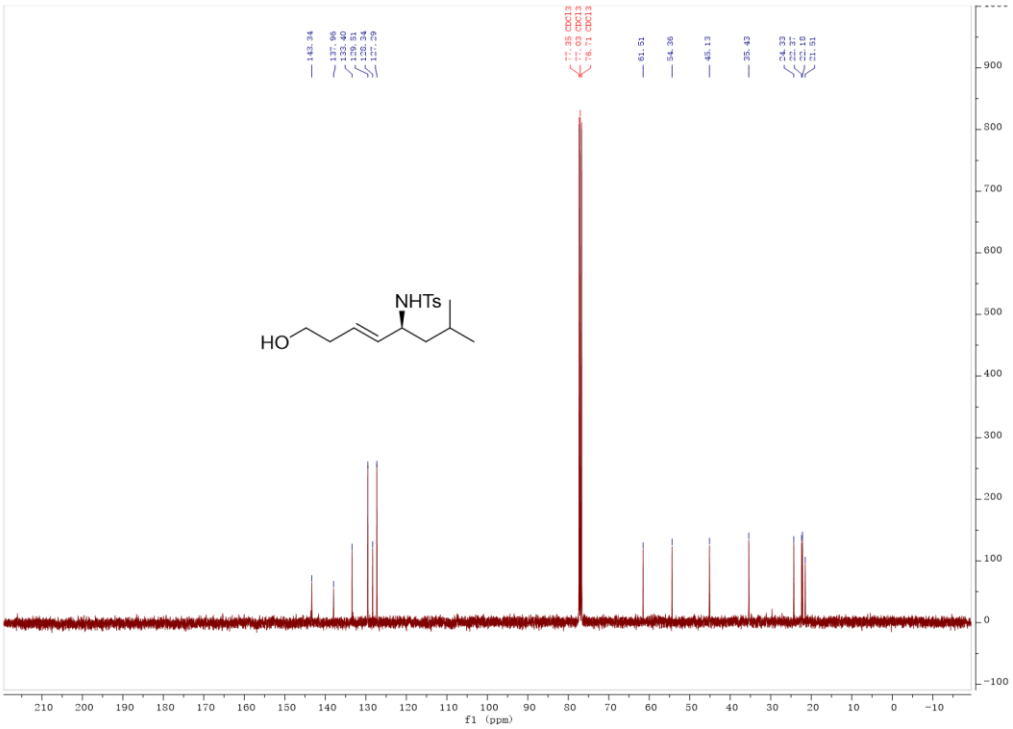


(*S*,*E*)-*N*-(8-hydroxy-2-methyloct-5-en-4-yl)-4-methylbenzenesulfonamide (60)

^{1}H NMR

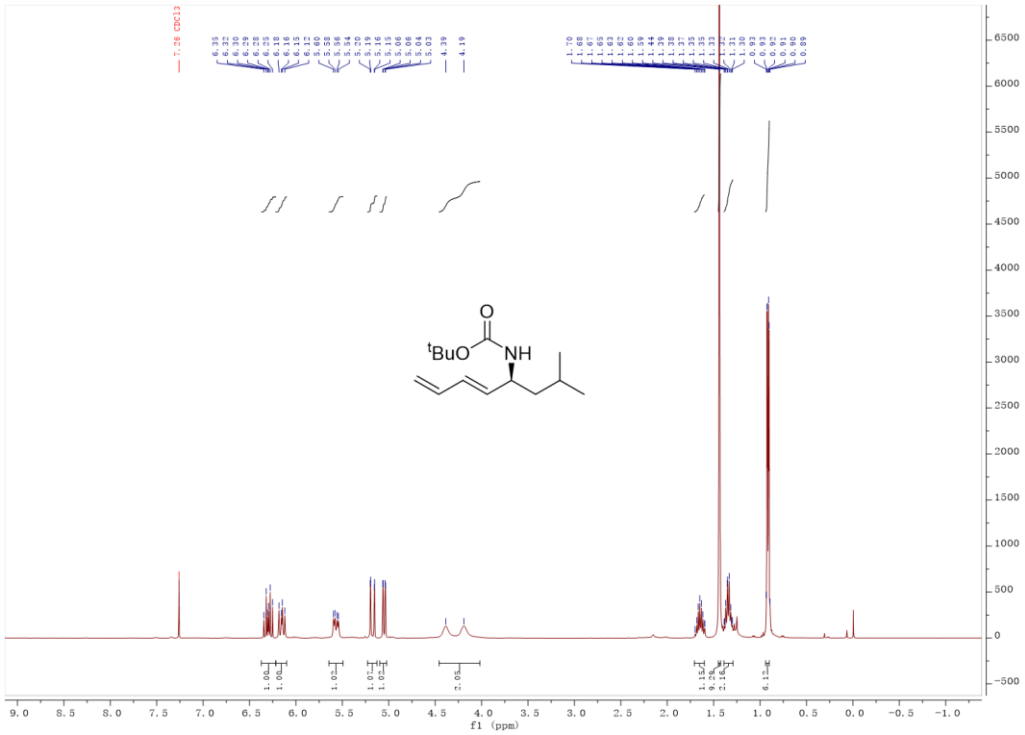


^{13}C NMR

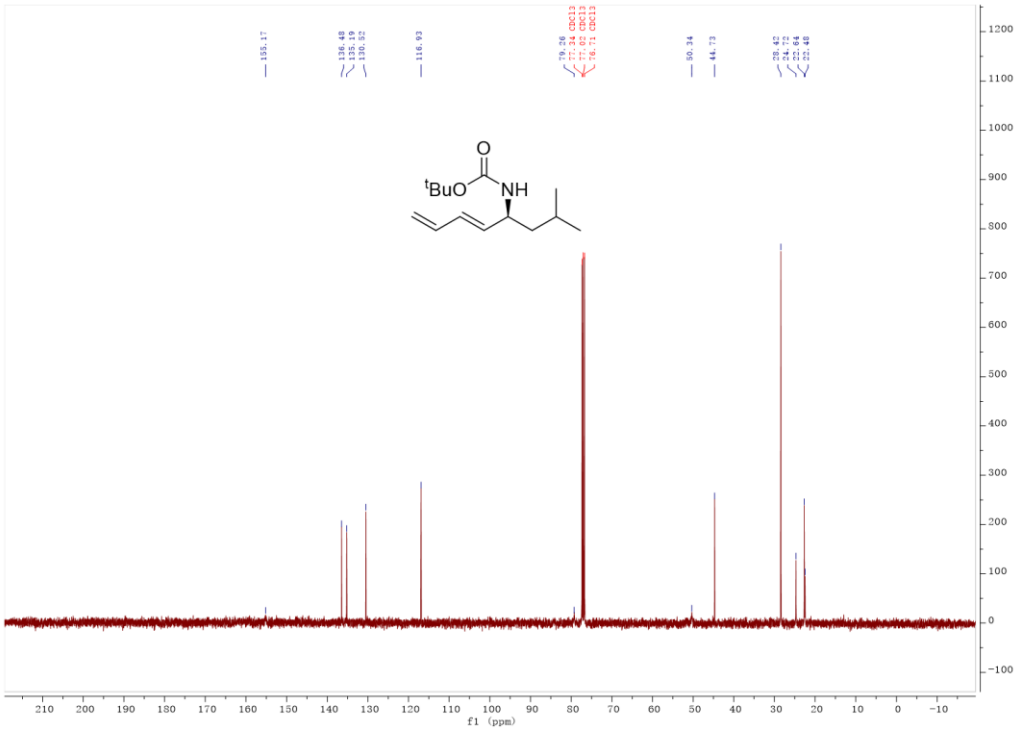


***Tert*-butyl (*S*,*E*)-(2-methylocta-5,7-dien-4-yl)carbamate (61)**

^{1}H NMR

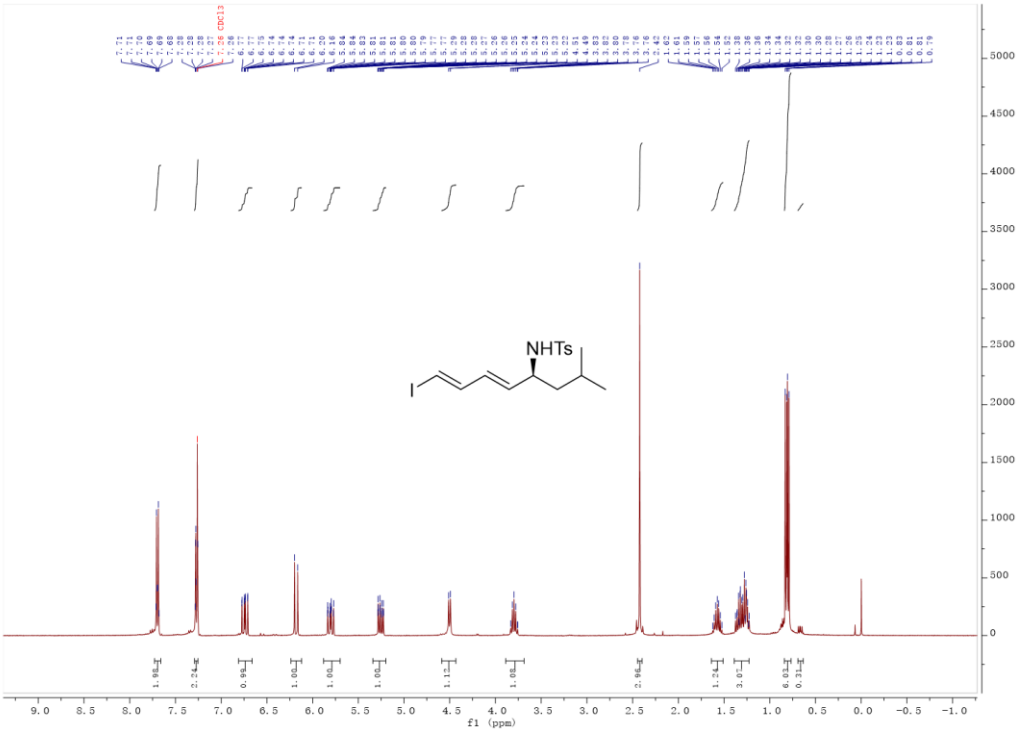


^{13}C NMR

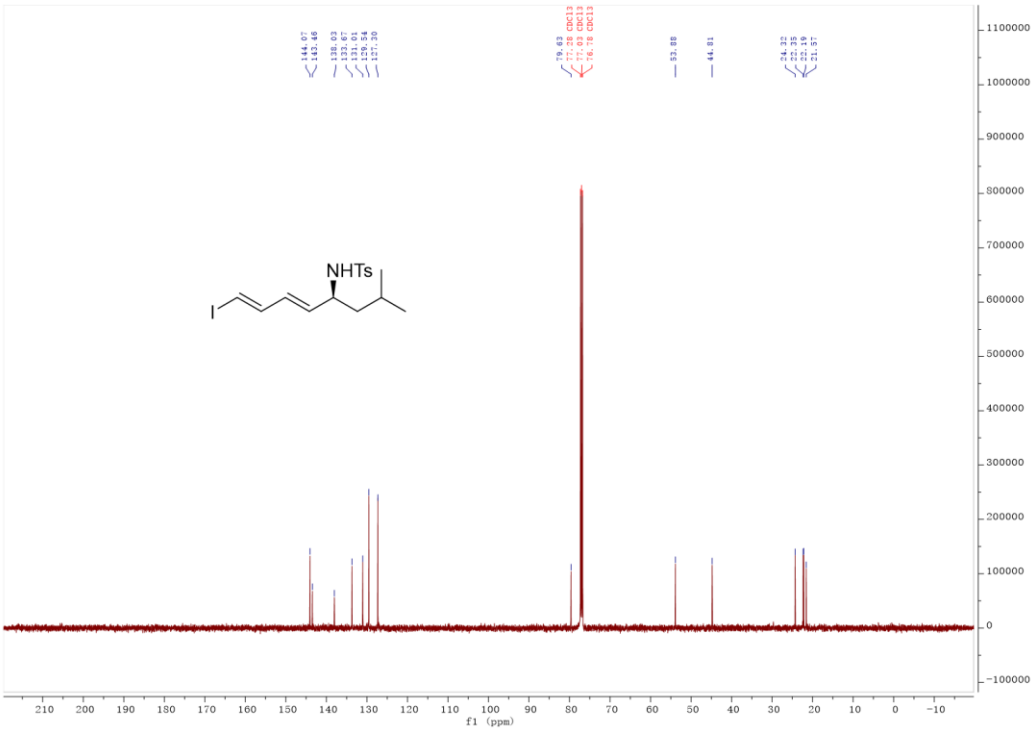


***N*-((*S*,5*E*,7*E*)-8-iodo-2-methylocta-5,7-dien-4-yl)-4-methylbenzenesulfonamide (62)**

^{1}H NMR

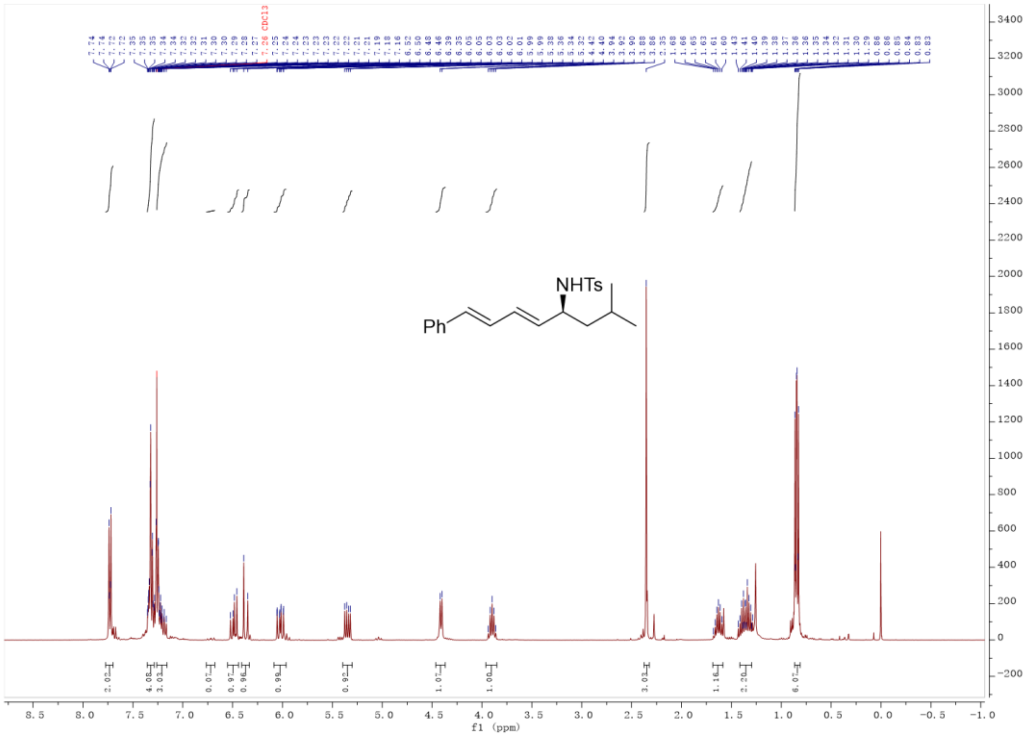


^{13}C NMR

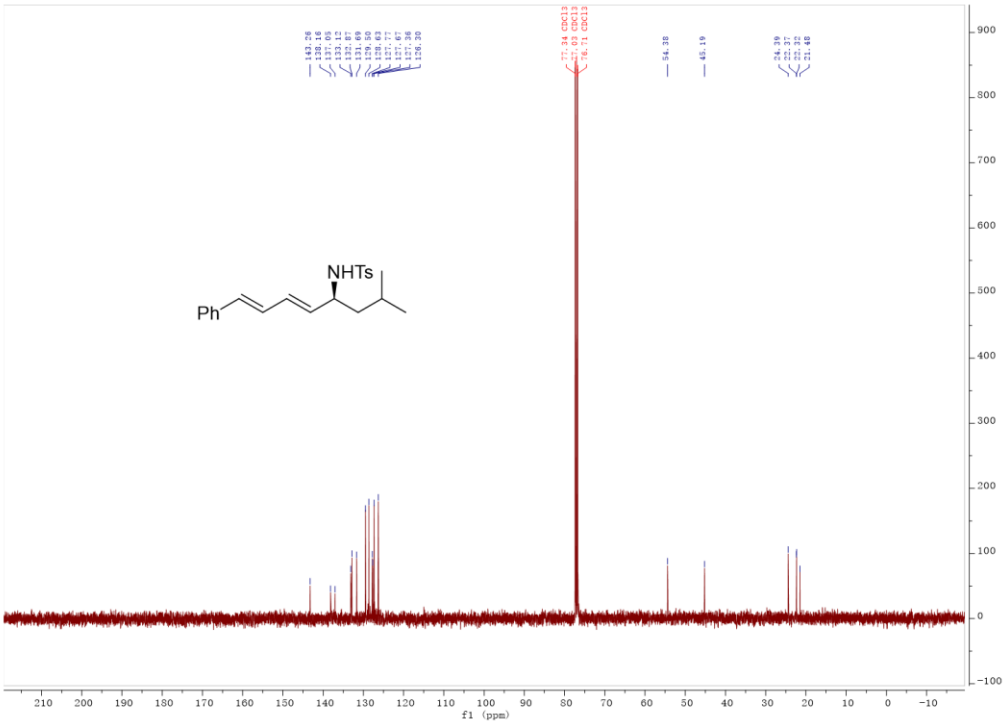


4-methyl-*N*-((*S*,5*E*,7*E*)-2-methyl-8-phenylocta-5,7-dien-4-yl)benzenesulfonamide (63)

^{1}H NMR

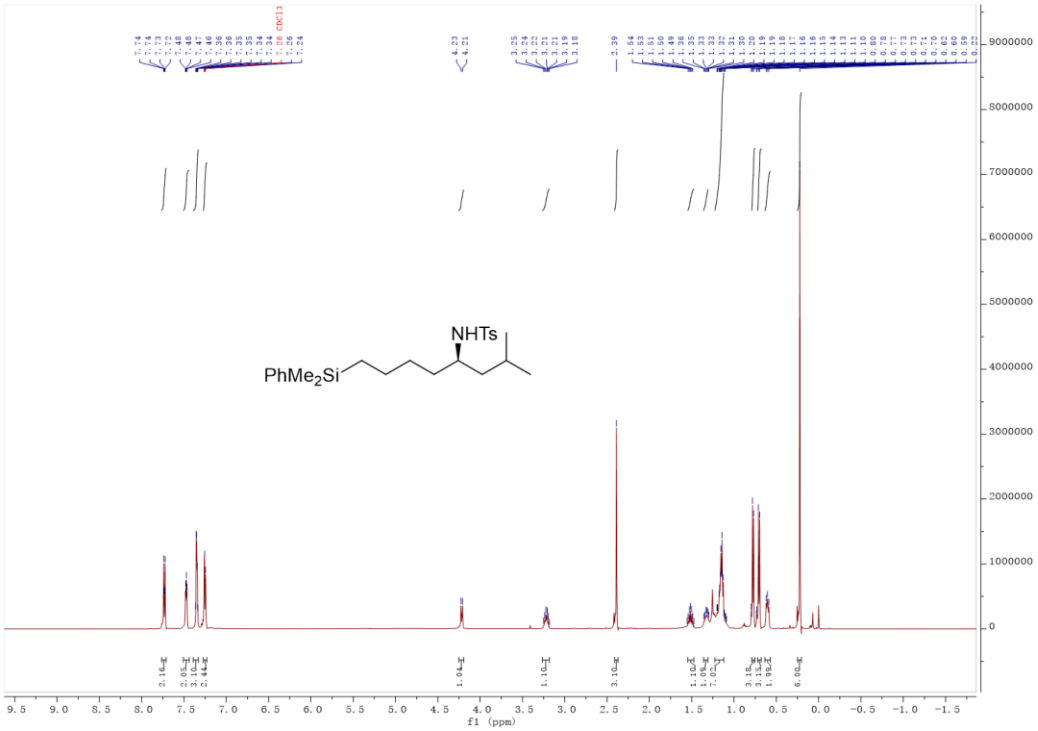


^{13}C NMR

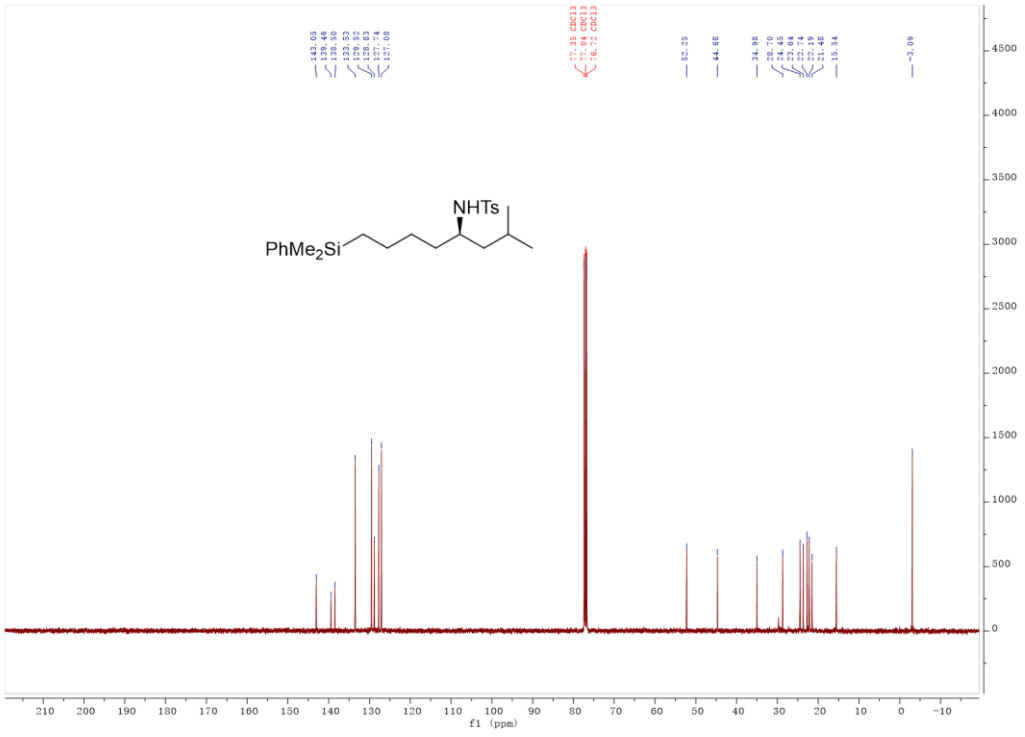


(*R*)-*N*-(8-(dimethyl(phenyl)silyl)-2-methyloctan-4-yl)-4-methylbenzenesulfonamide (64)

^{1}H NMR

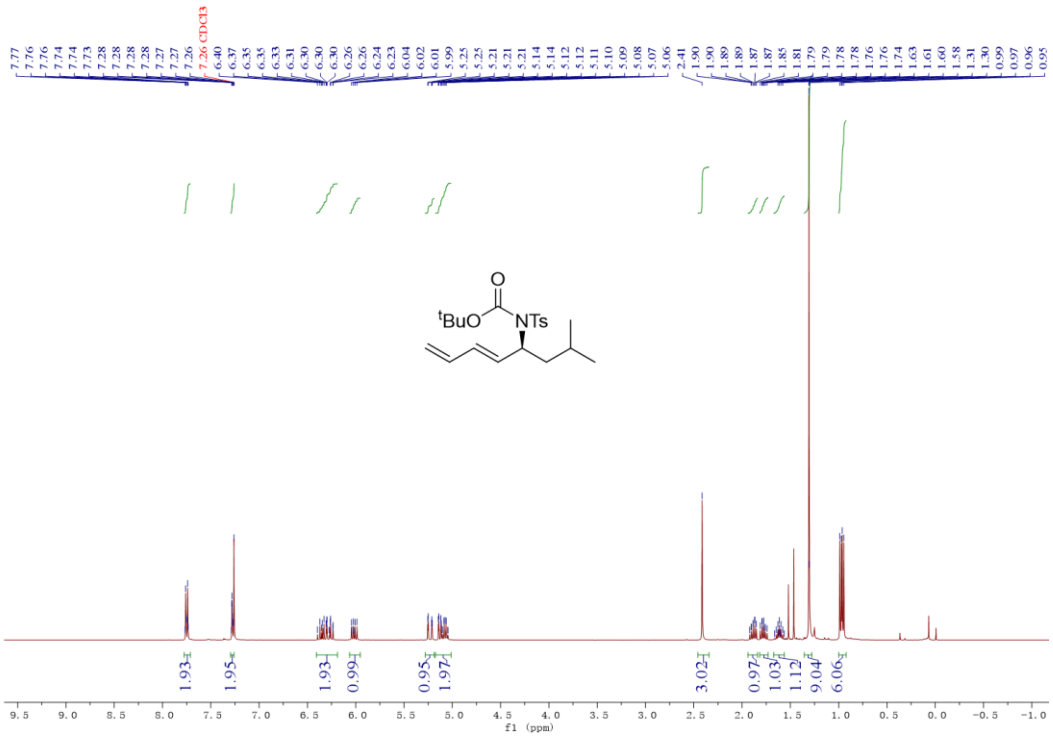


^{13}C NMR

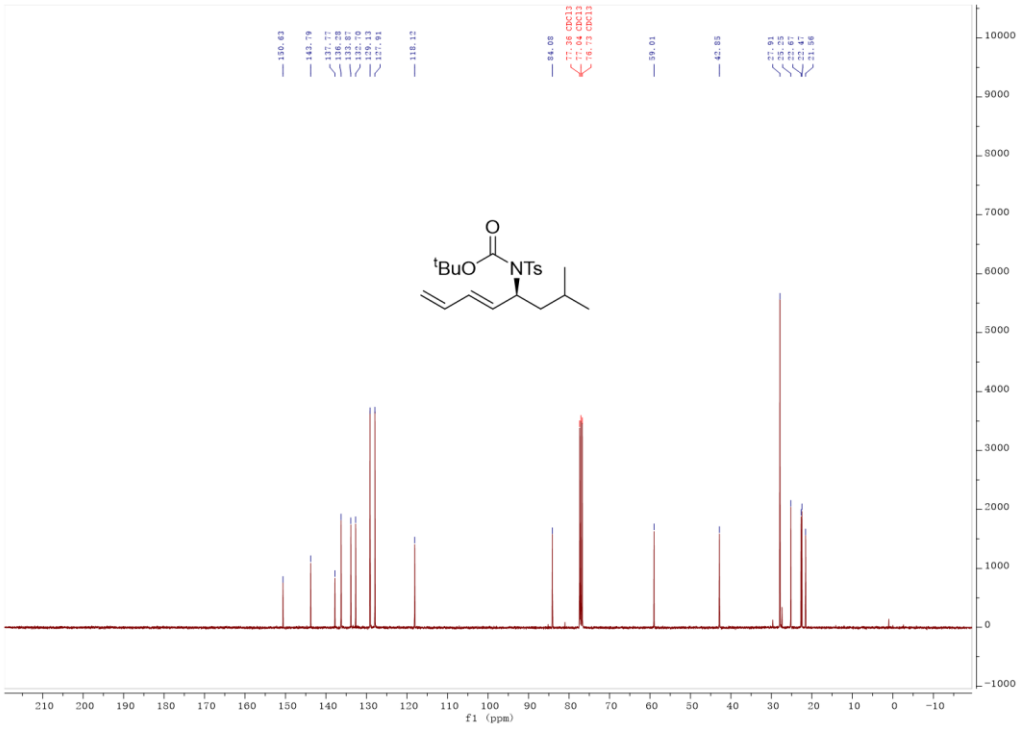


***Tert*-butyl (*S*,*E*)-(2-methylocta-5,7-dien-4-yl)(tosyl)carbamate (65)**

^{1}H NMR

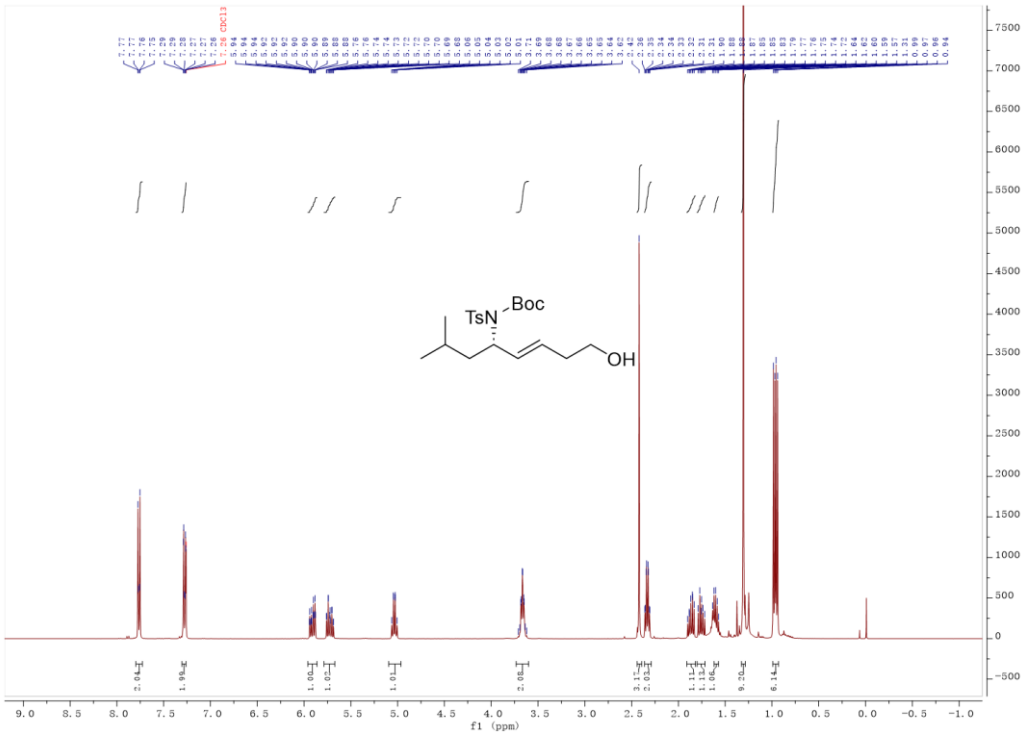


^{13}C NMR

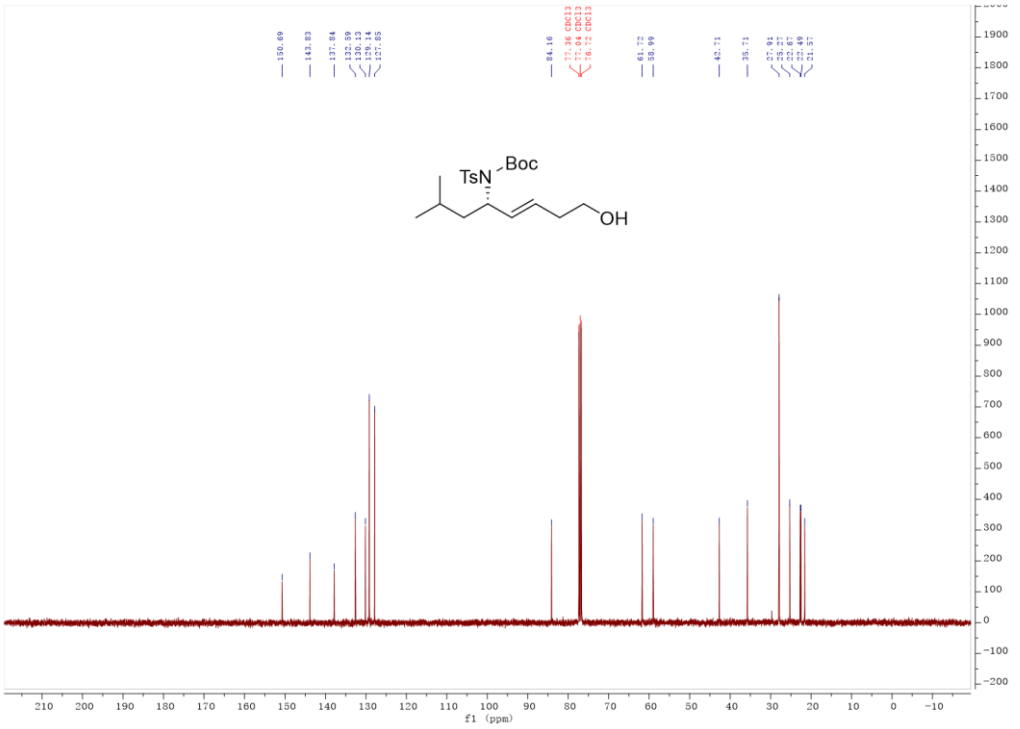


***Tert*-butyl (*S*,*E*)-(8-hydroxy-2-methyloct-5-en-4-yl)(tosyl)carbamate (66)**

^{1}H NMR

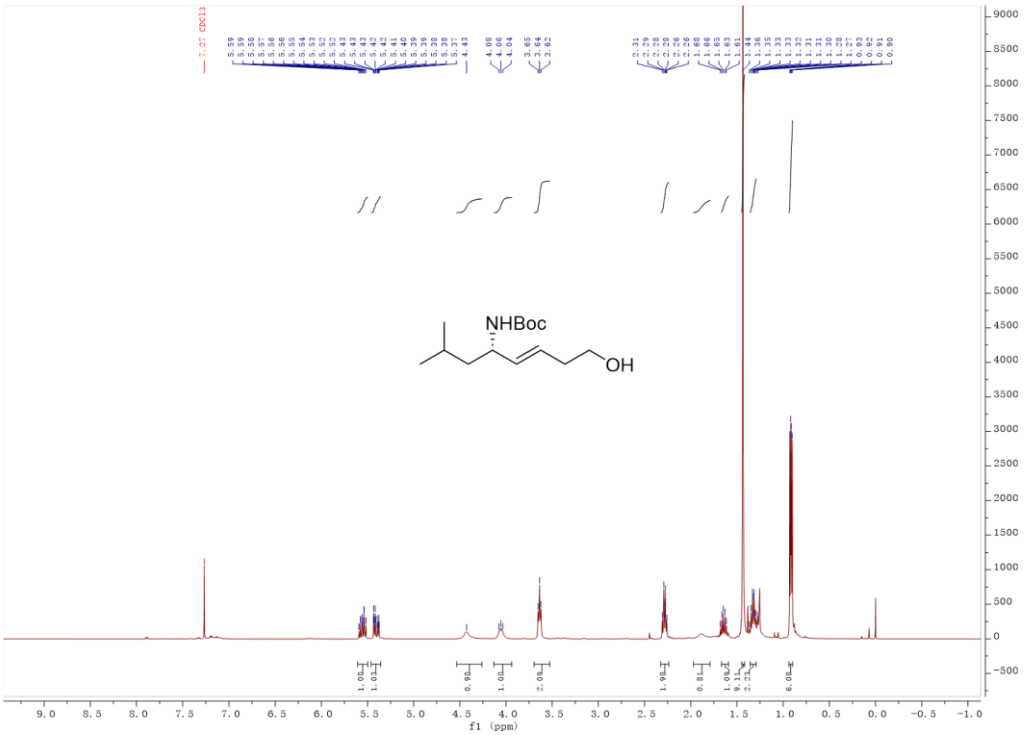


^{13}C NMR

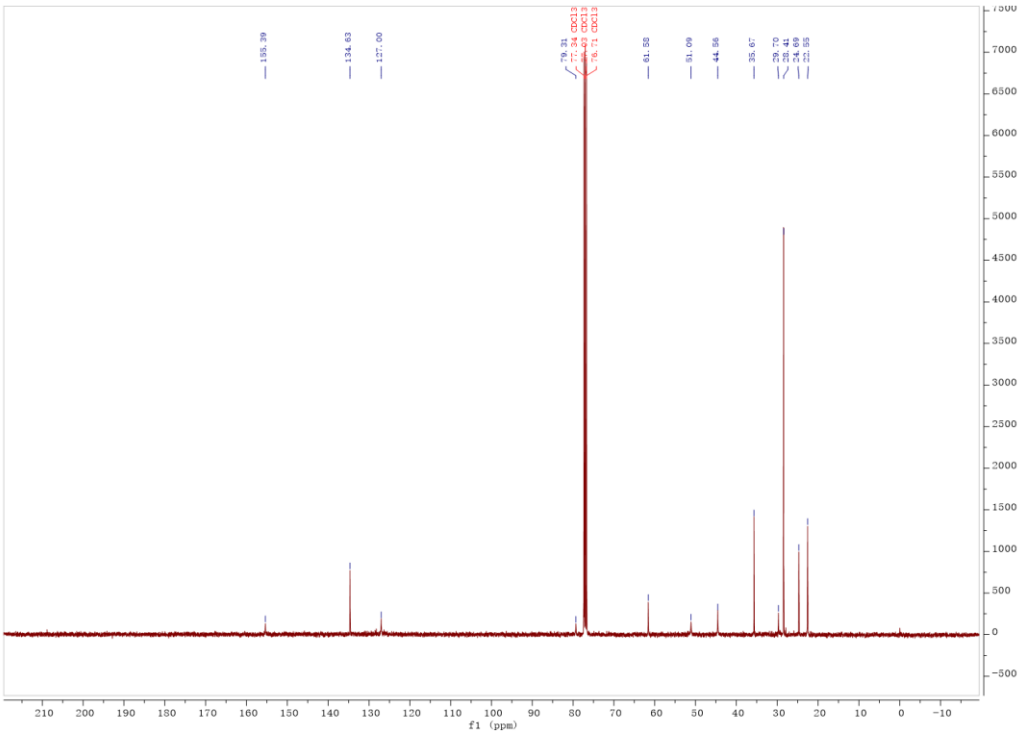


***Tert*-butyl (*S*,*E*)-(8-hydroxy-2-methyloct-5-en-4-yl)carbamate (67)**

^{1}H NMR



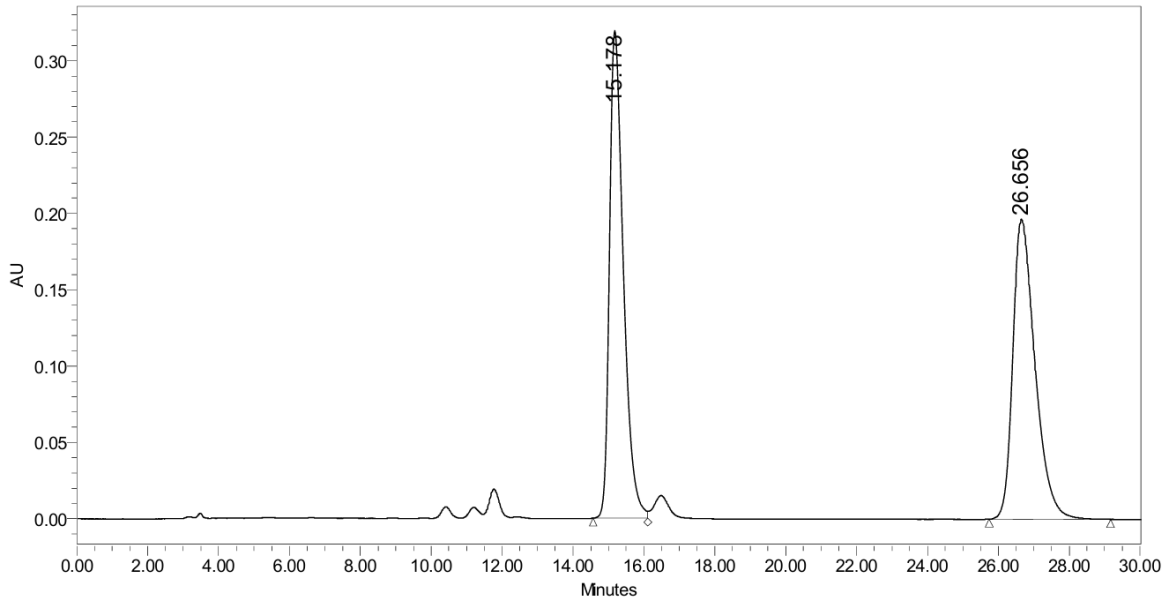
^{13}C NMR



10. HPLC spectra

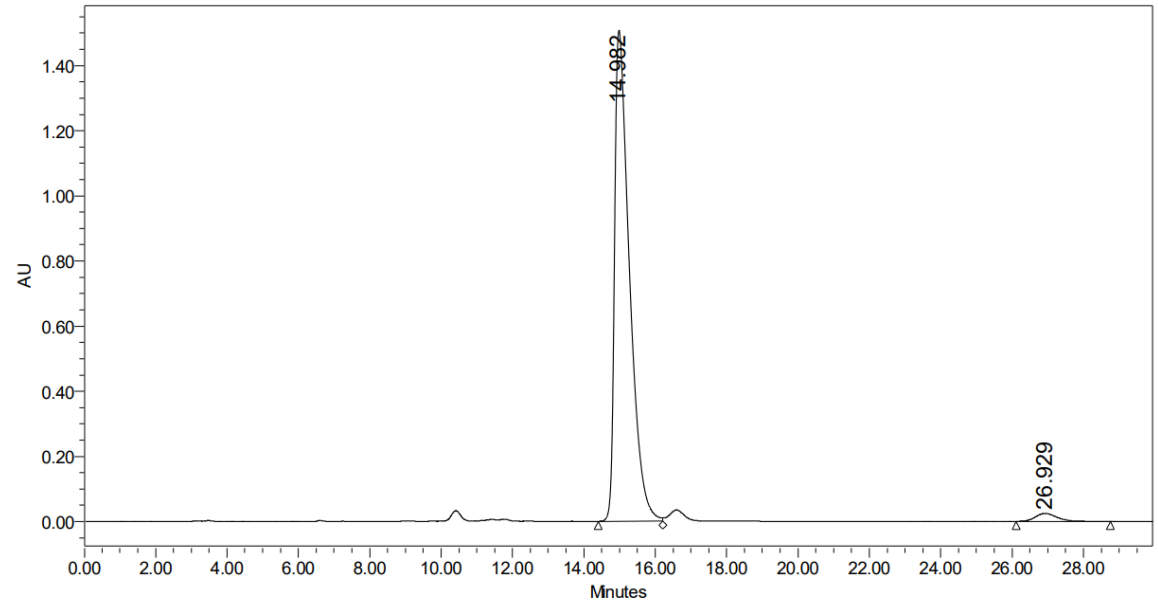
***N*-((*R*,2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (3)**

Racemic



	RT	Area	% Area	Height
1	15.178	8716598	50.67	319268
2	26.656	8485972	49.33	196518

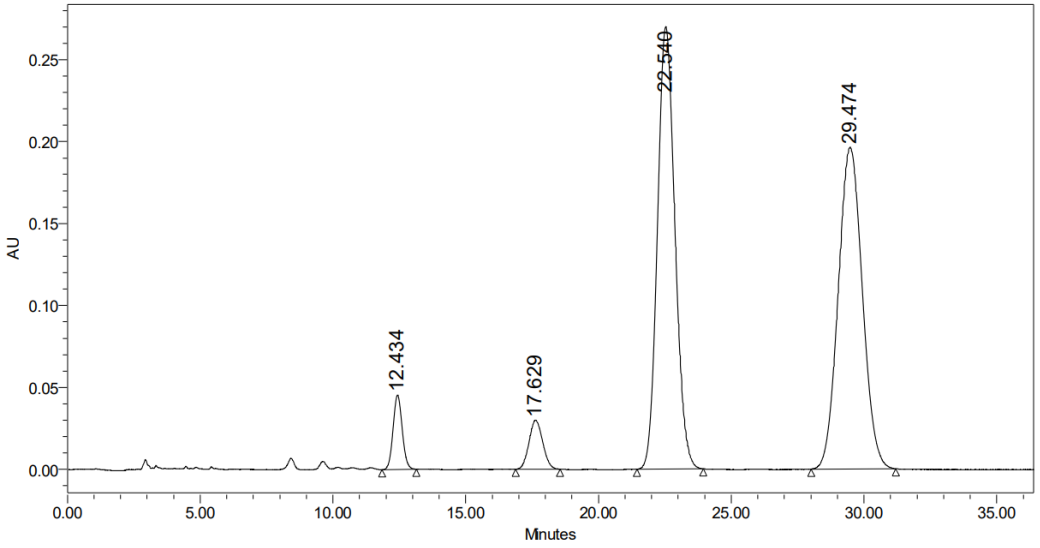
Enantioenriched



	RT	Area	% Area	Height
1	14.982	43728529	97.66	1507344
2	26.929	1049697	2.34	24691

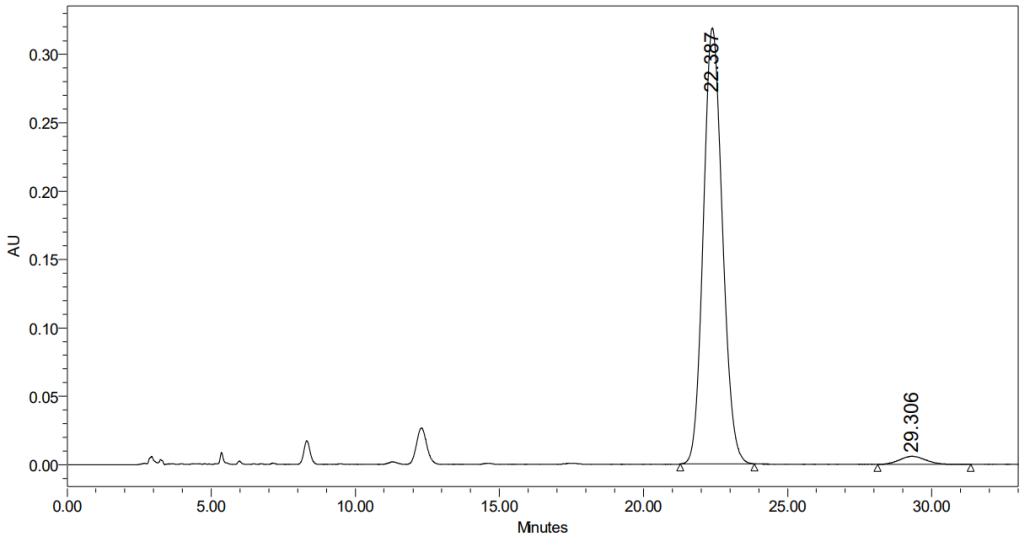
4-methyl-*N*-((*R*,2*E*,4*E*)-1-phenyl-5-(p-tolyl)penta-2,4-dien-1-yl)benzenesulfonamide (4)

Racemic



	RT	Area	% Area	Height
1	12.434	1091238	4.07	45471
2	17.629	1076114	4.01	29939
3	22.540	12347401	46.01	269951
4	29.474	12319252	45.91	196257

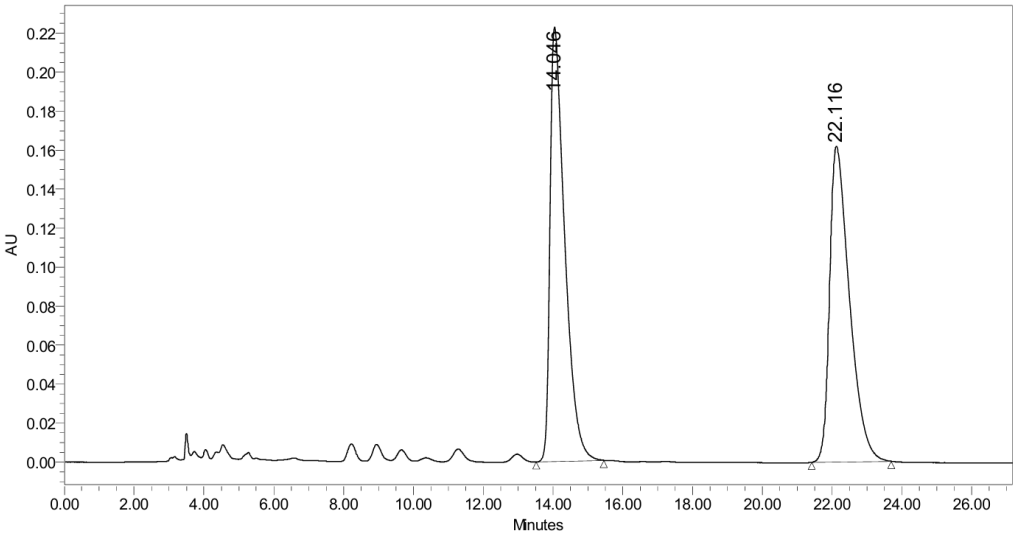
Enantioenriched



	RT	Area	% Area	Height
1	22.387	14741524	97.49	318791
2	29.306	379374	2.51	5904

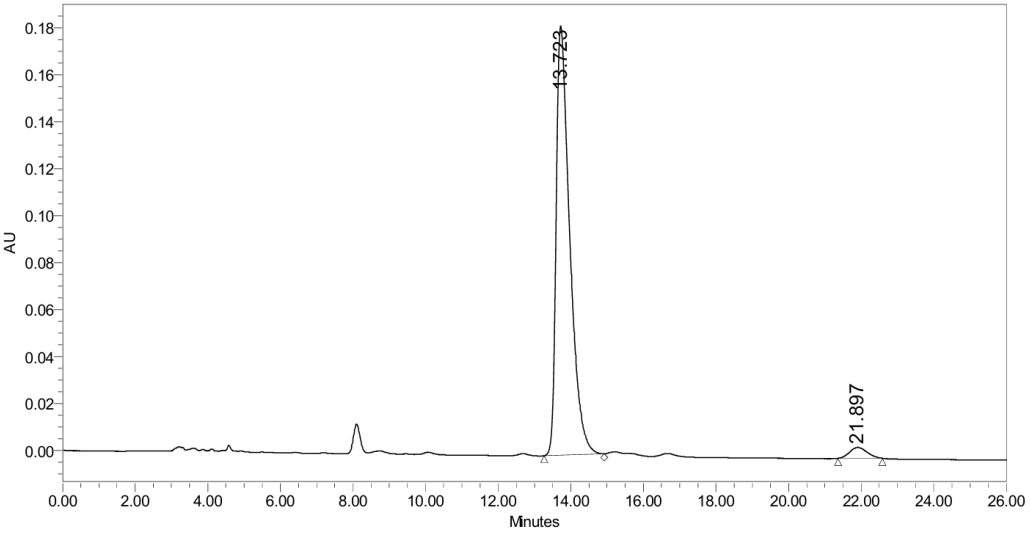
***N*-((*R*,2*E*,4*E*)-5-(4-(*tert*-butyl)phenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (5)**

Racemic



	RT	Area	% Area	Height
1	14.046	6552718	50.64	222752
2	22.116	6386228	49.36	161899

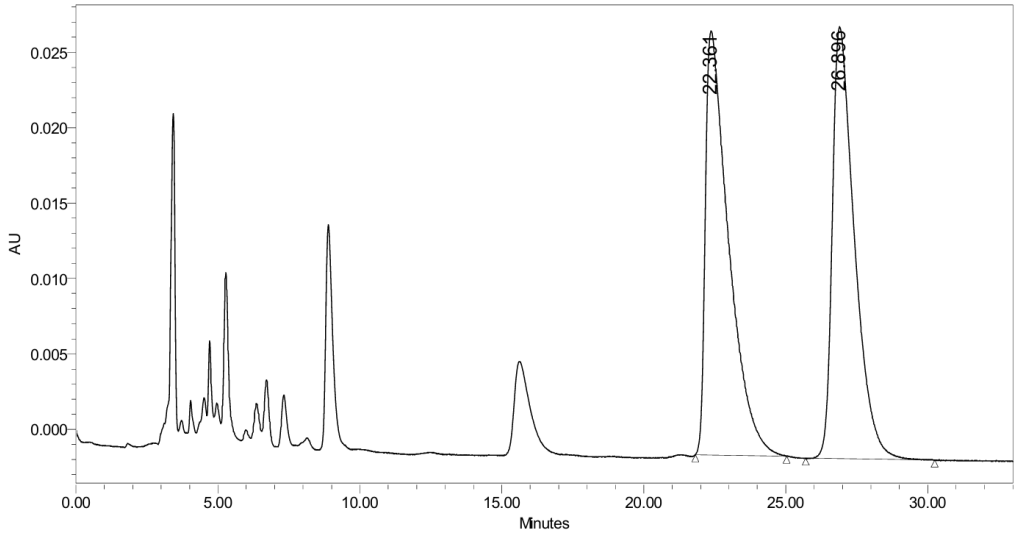
Enantioenriched



	RT	Area	% Area	Height
1	13.723	4746767	96.85	182617
2	21.897	154275	3.15	4655

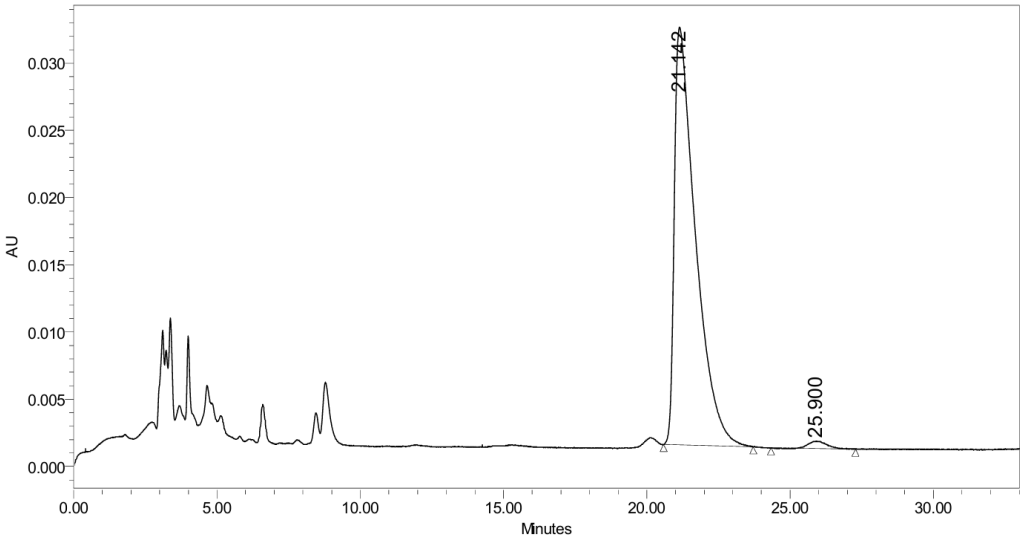
***N*-((*R*,2*E*,4*E*)-([1,1'-biphenyl]-4-yl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (6)**

Racemic



	RT	Area	% Area	Height
1	22.361	1604389	50.90	28140
2	26.896	1547942	49.10	28640

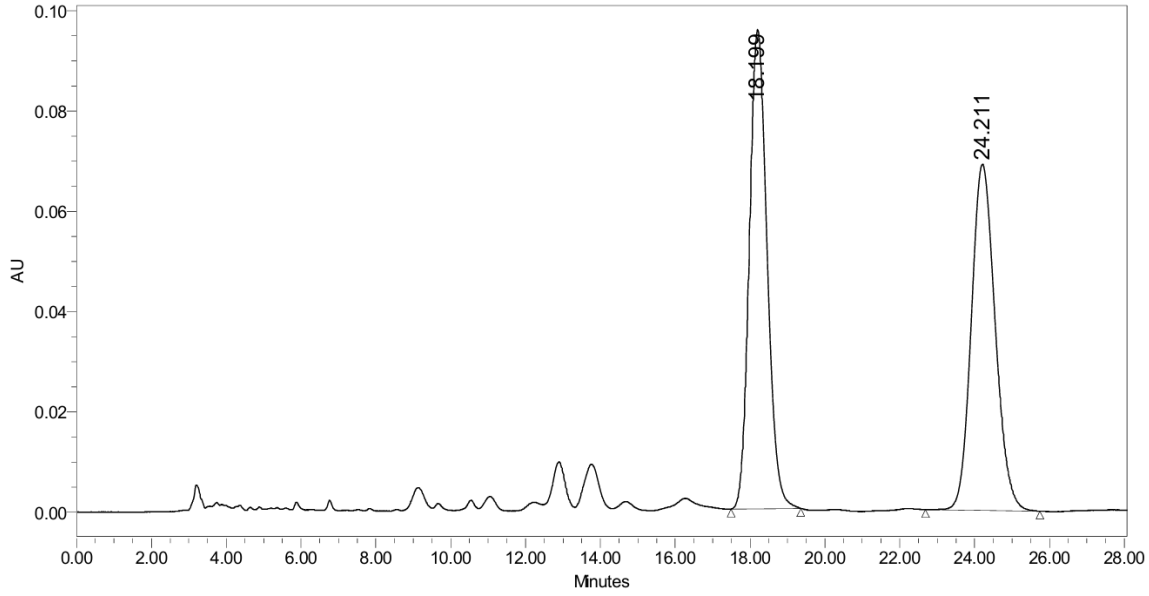
Enantioenriched



	RT	Area	% Area	Height
1	21.142	1588717	98.40	31075
2	25.900	25772	1.60	547

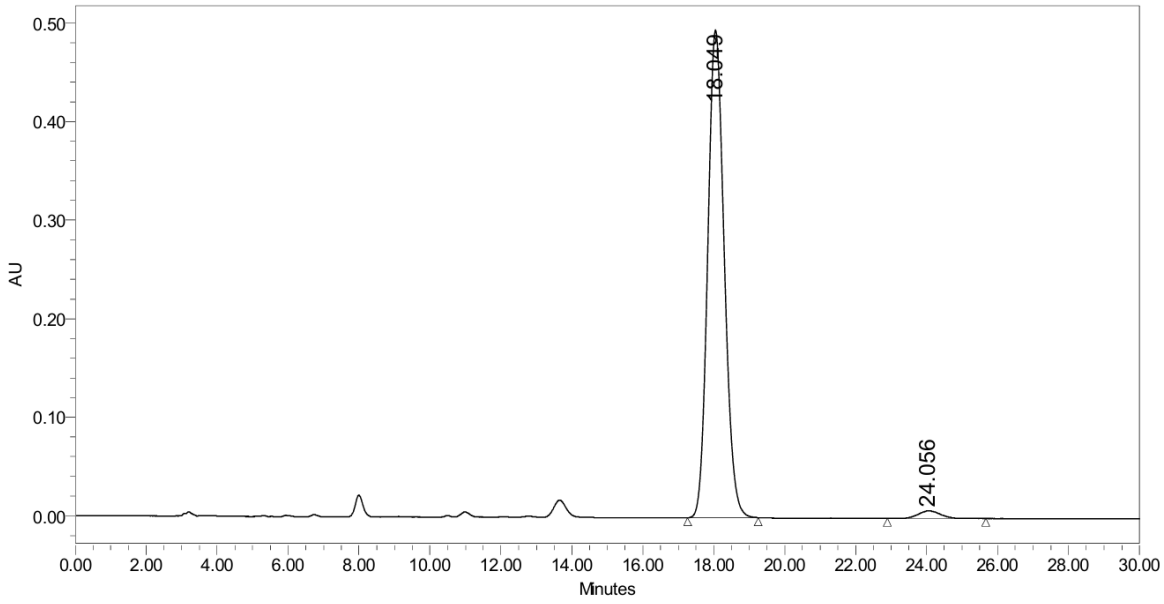
***N*-((*R*,2*E*,4*E*)-5-(4-methoxyphenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (7)**

Racemic



	RT	Area	% Area	Height
1	18.199	3122125	50.45	95529
2	24.211	3067003	49.55	69049

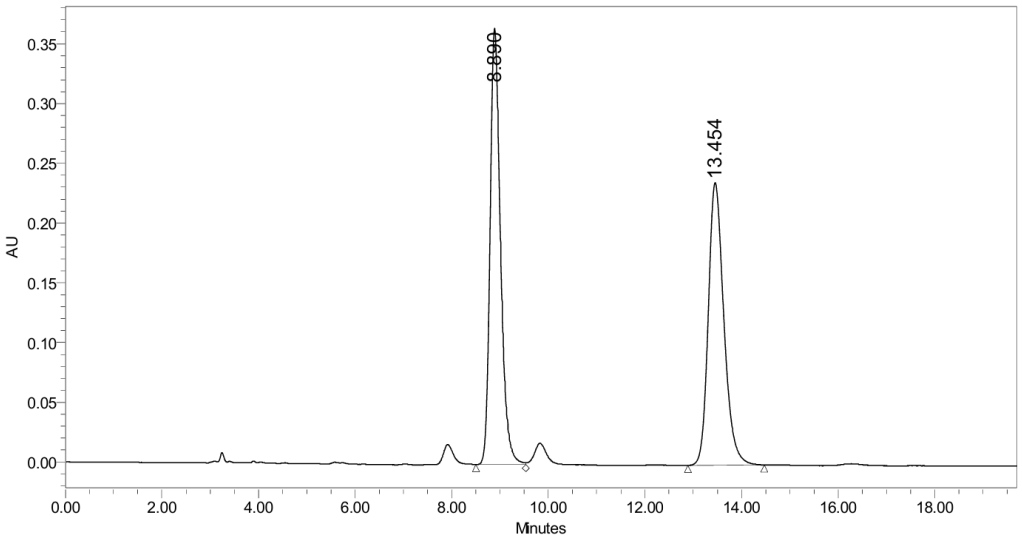
Enantioenriched



	RT	Area	% Area	Height
1	18.049	16037418	97.93	494579
2	24.056	338639	2.07	7697

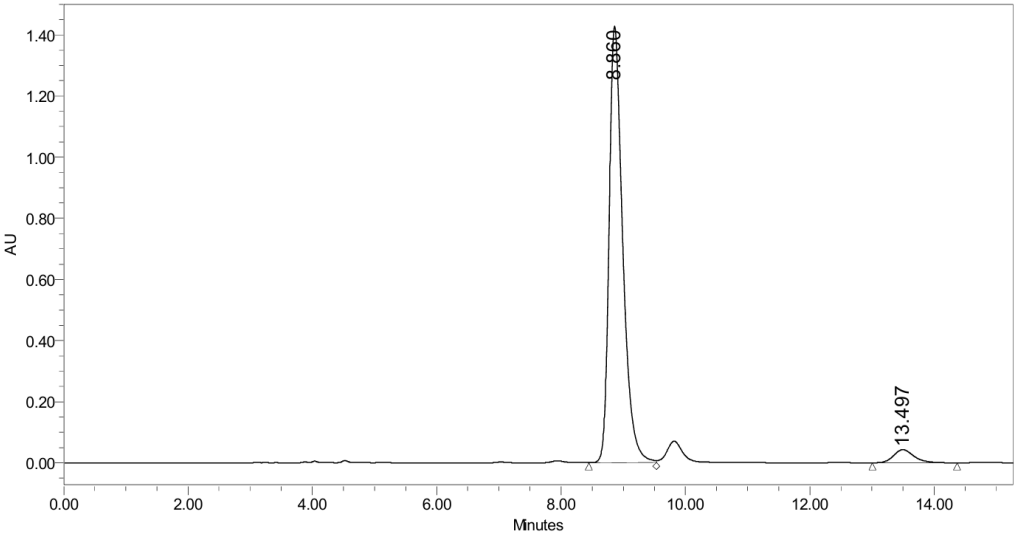
4-methyl-*N*-((*R*,2*E*,4*E*)-5-(4-phenoxyphenyl)-1-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (8)

Racemic



	RT	Area	% Area	Height
1	8.890	5454469	50.65	365024
2	13.454	5315150	49.35	236586

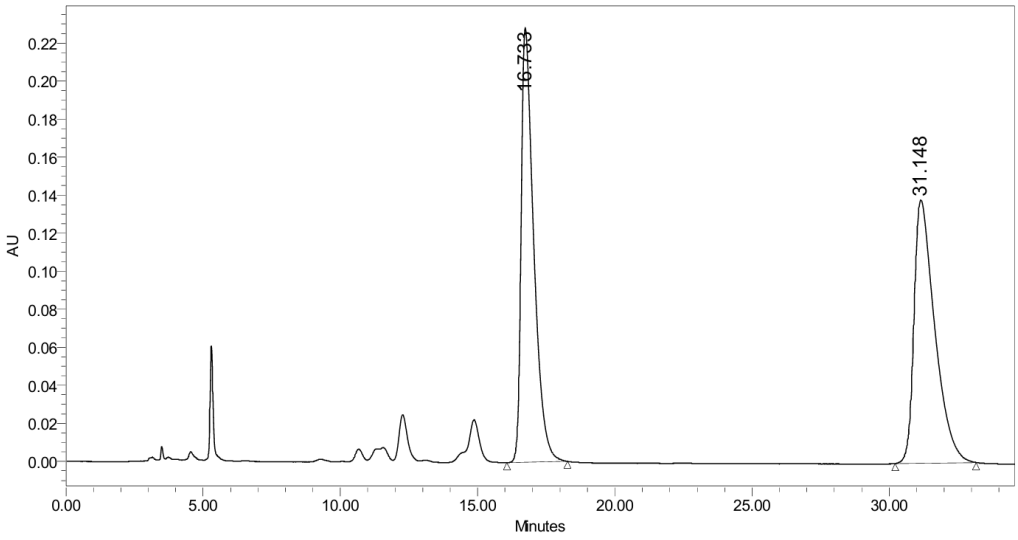
Enantioenriched



	RT	Area	% Area	Height
1	8.860	21757380	95.64	1426986
2	13.497	992630	4.36	42980

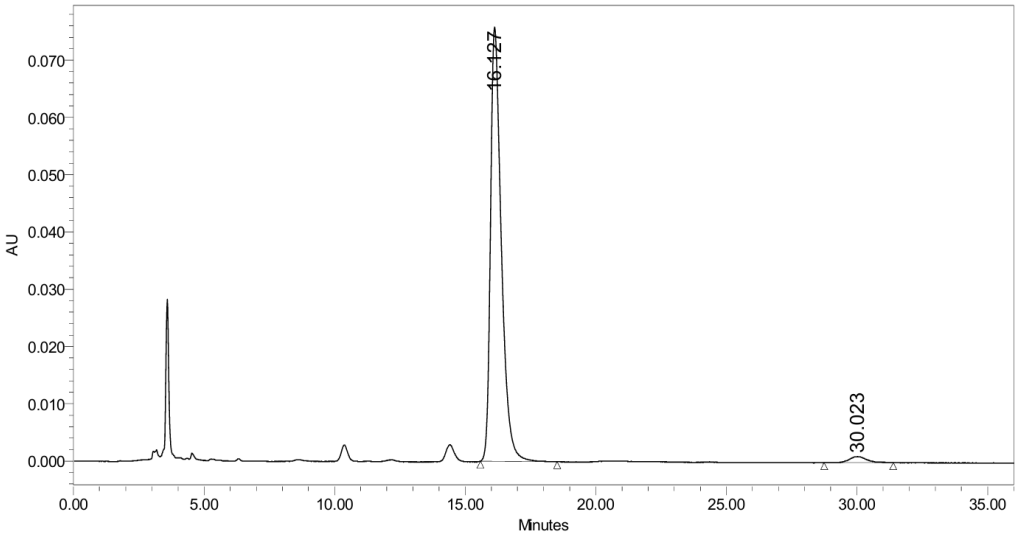
***N*-((*R*,2*E*,4*E*)-5-(4-fluorophenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (9)**

Racemic



	RT	Area	% Area	Height
1	16.733	7276098	50.08	228519
2	31.148	7253207	49.92	138459

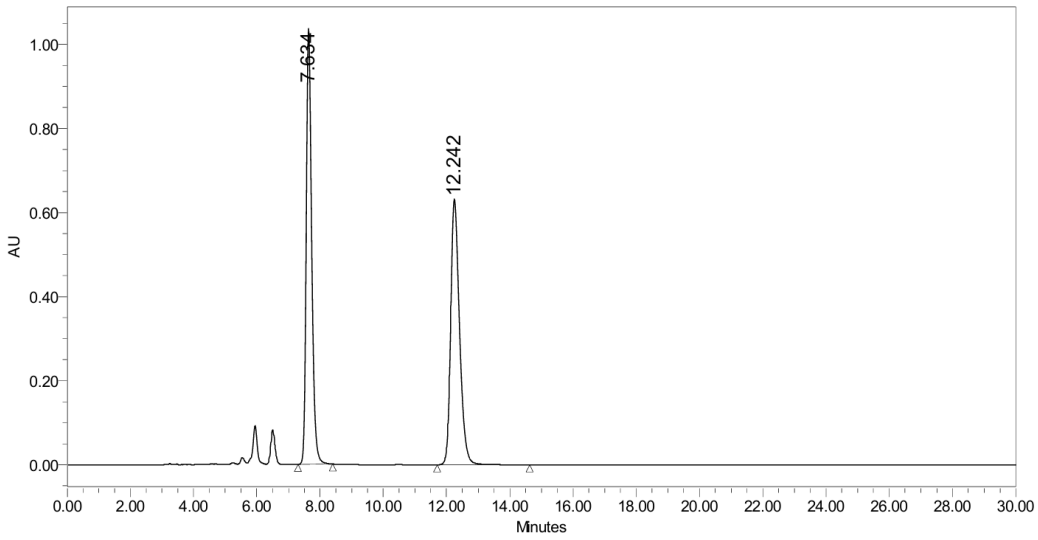
Enantioenriched



	RT	Area	% Area	Height
1	16.127	2168772	97.77	75787
2	30.023	49470	2.23	1085

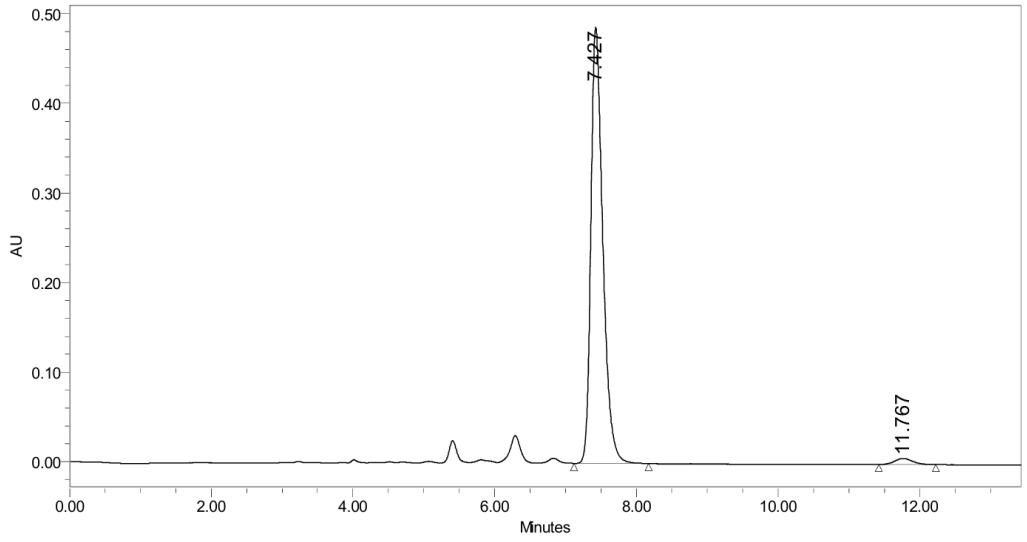
***N*-((*R*,2*E*,4*E*)-5-(4-chlorophenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (10)**

Racemic



	RT	Area	% Area	Height
1	7.634	12420193	50.34	1035688
2	12.242	12251922	49.66	631212

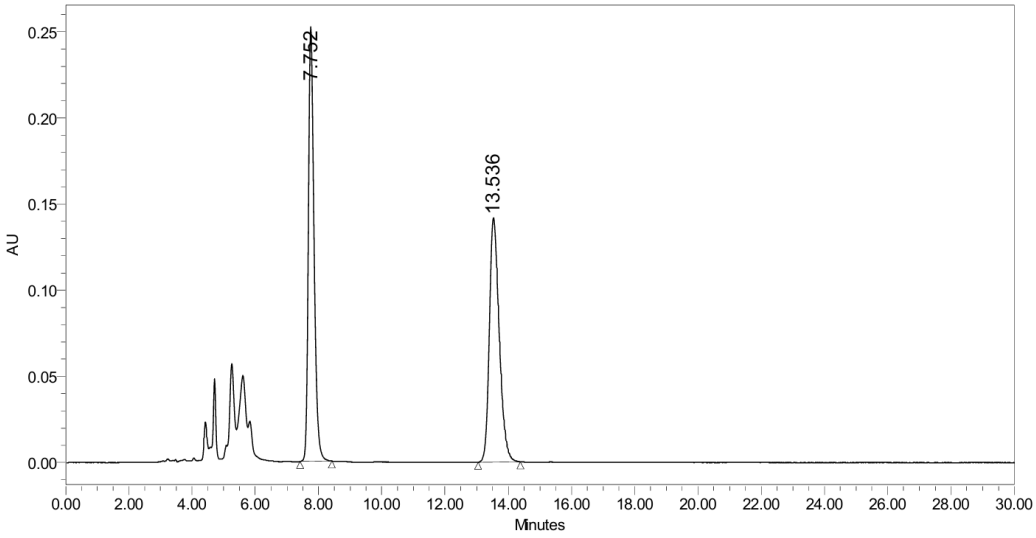
Enantioenriched



	RT	Area	% Area	Height
1	7.427	5655443	97.91	486658
2	11.767	120977	2.09	6785

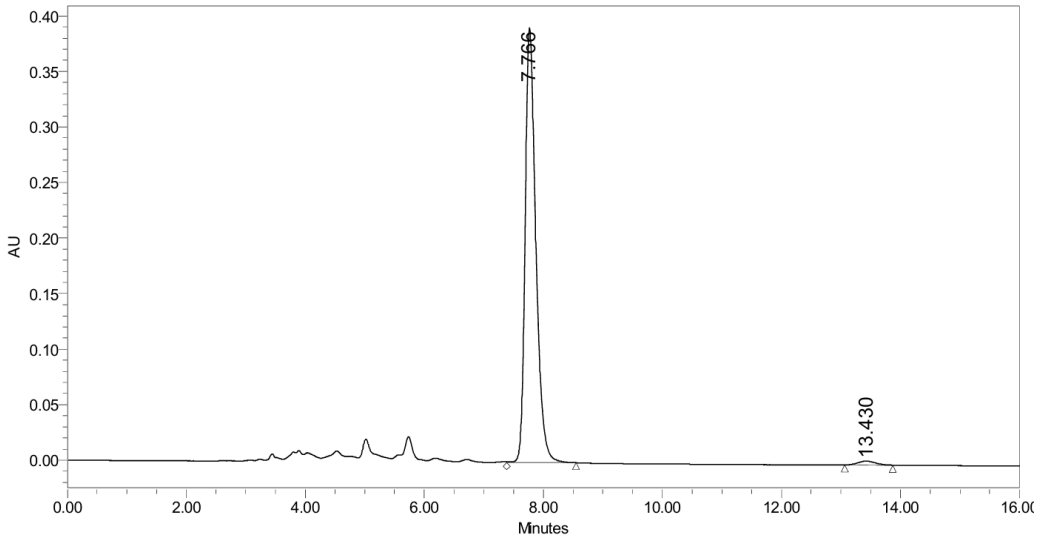
4-methyl-*N*-((*R*,2*E*,4*E*)-1-phenyl-5-(4-(trifluoromethyl)phenyl)penta-2,4-dien-1-yl)benzenesulfonamide (11)

Racemic



	RT	Area	% Area	Height
1	7.752	3135706	50.63	252111
2	13.536	3057630	49.37	141684

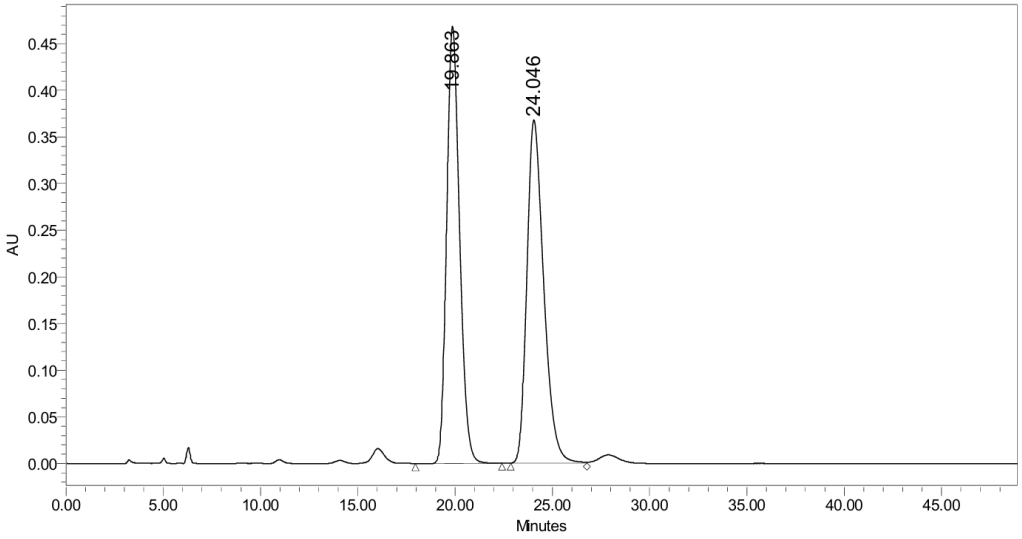
Enantioenriched



	RT	Area	% Area	Height
1	7.766	4891146	98.53	391304
2	13.430	73120	1.47	3543

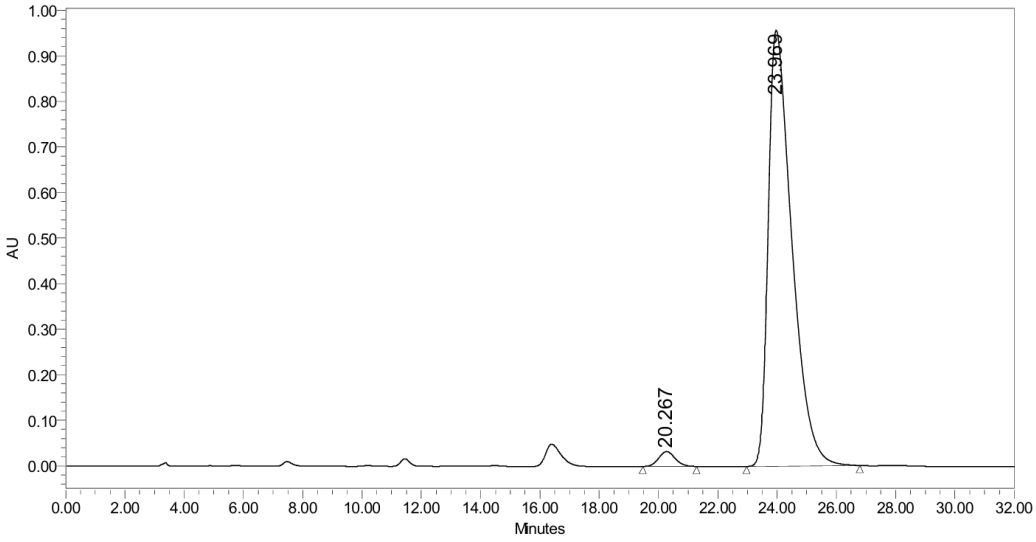
***N*-((*R*,2*E*,4*E*)-5-(4-(((*tert*-butyldimethylsilyl)oxy)methyl)phenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (12)**

Racemic



	RT	Area	% Area	Height
1	19.863	21605294	49.37	468504
2	24.046	22154243	50.63	367731

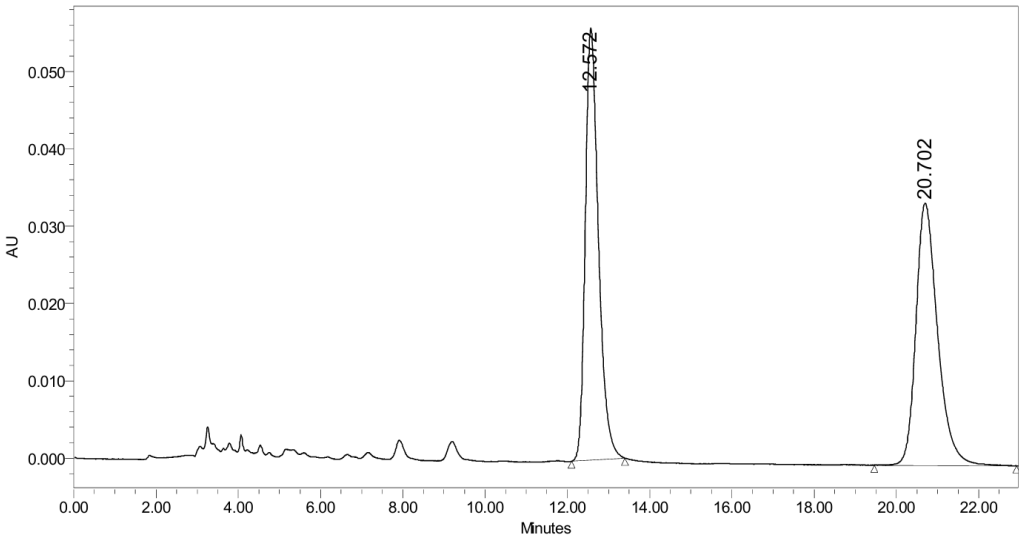
Enantioenriched



	RT	Area	% Area	Height
1	20.267	1270407	2.34	32692
2	23.969	53029304	97.66	956787

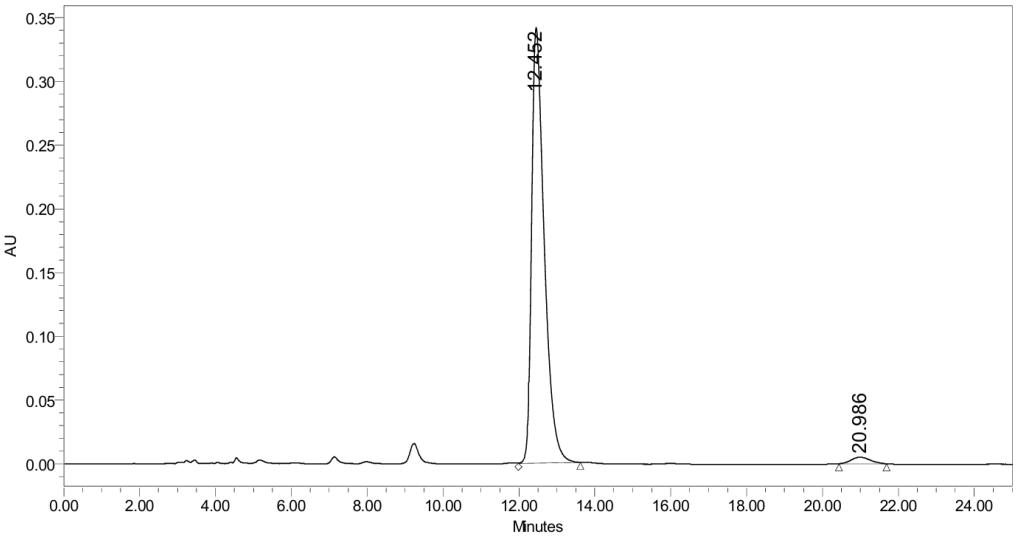
4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)phenyl acetate (13)

Racemic



	RT	Area	% Area	Height
1	12.572	1242204	49.96	55853
2	20.702	1243982	50.04	33903

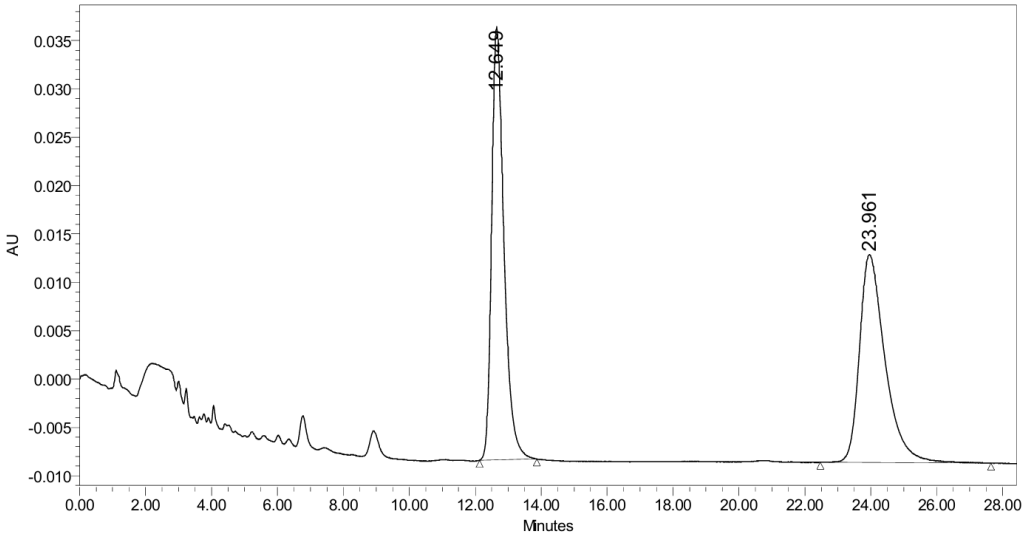
Enantioenriched



	RT	Area	% Area	Height
1	12.452	7892724	97.81	341383
2	20.986	177088	2.19	5157

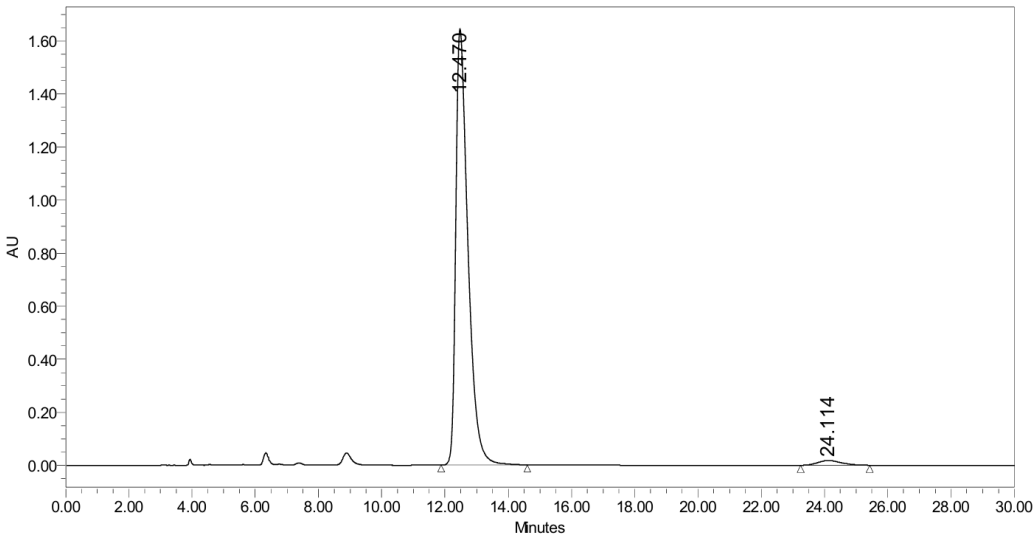
***Tert*-butyl (4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)phenyl)carbamate (14)**

Racemic



	RT	Area	% Area	Height
1	12.649	1174455	50.21	44798
2	23.961	1164429	49.79	21498

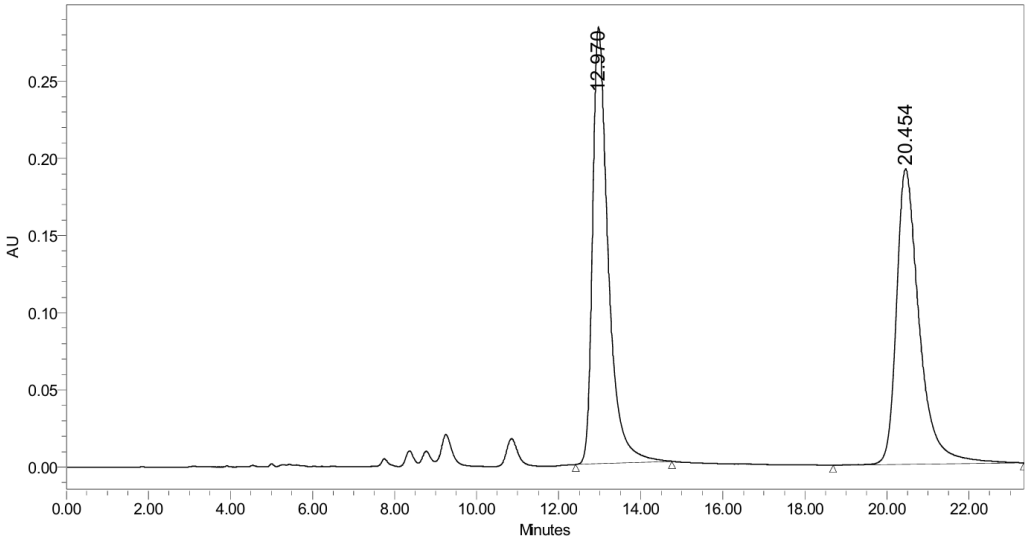
Enantioenriched



	RT	Area	% Area	Height
1	12.470	44140573	97.92	1644219
2	24.114	939195	2.08	18037

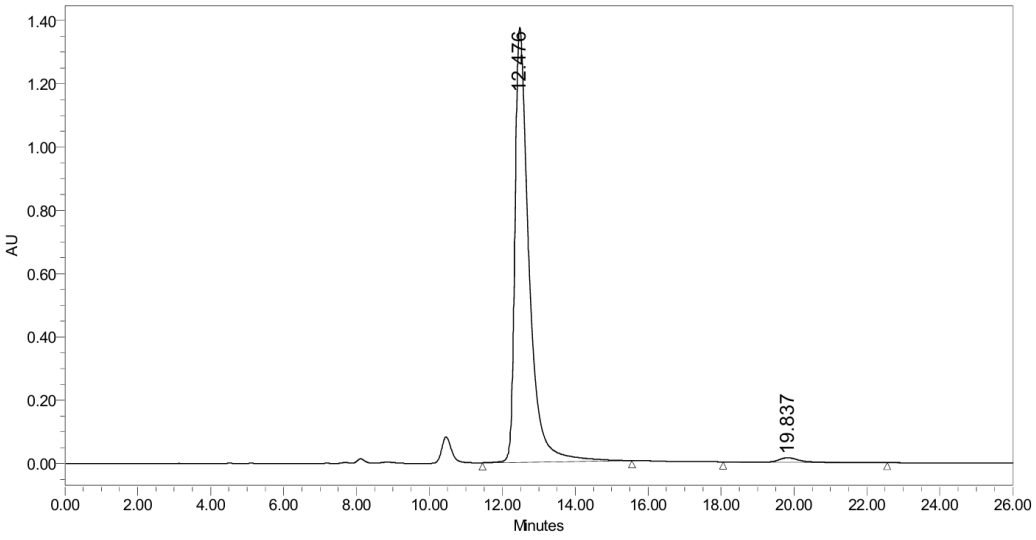
***N*-((*R*,2*E*,4*E*)-5-(4-formylphenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (15)**

Racemic



	RT	Area	% Area	Height
1	12.970	7415941	50.13	282968
2	20.454	7378039	49.87	191343

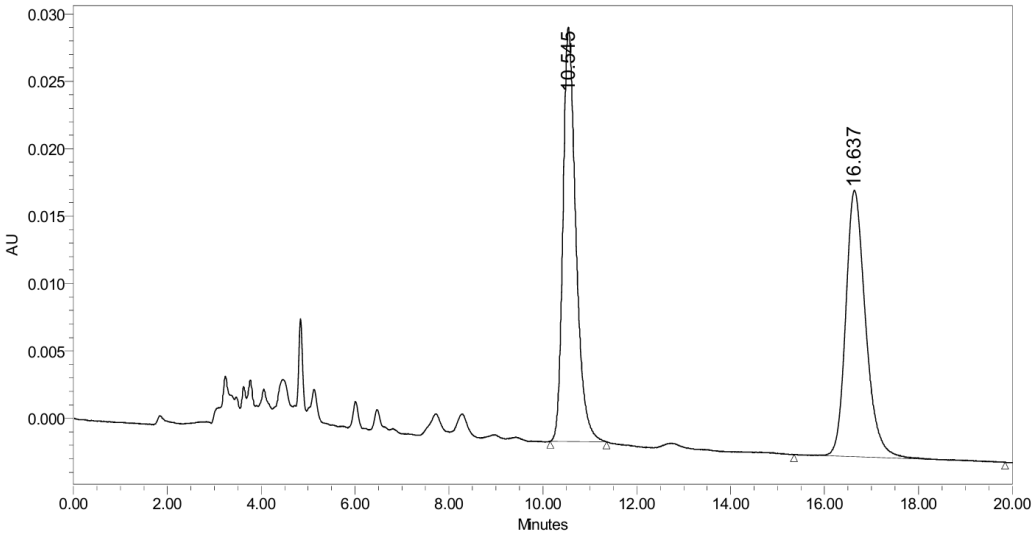
Enantioenriched



	RT	Area	% Area	Height
1	12.476	36635791	98.53	1373217
2	19.837	544713	1.47	14301

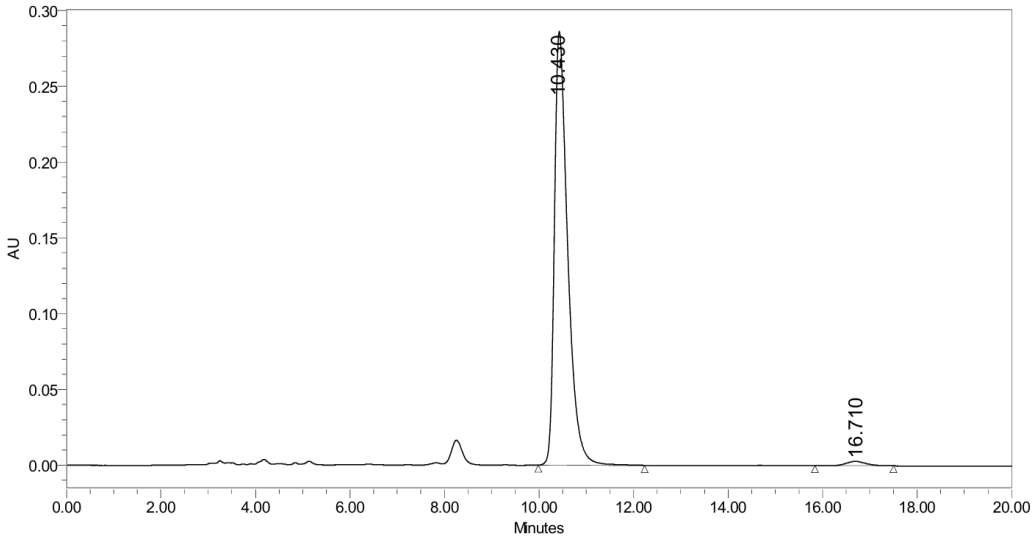
Methyl 4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)benzoate (16)

Racemic



	RT	Area	% Area	Height
1	10.545	588853	50.40	30711
2	16.637	579590	49.60	19736

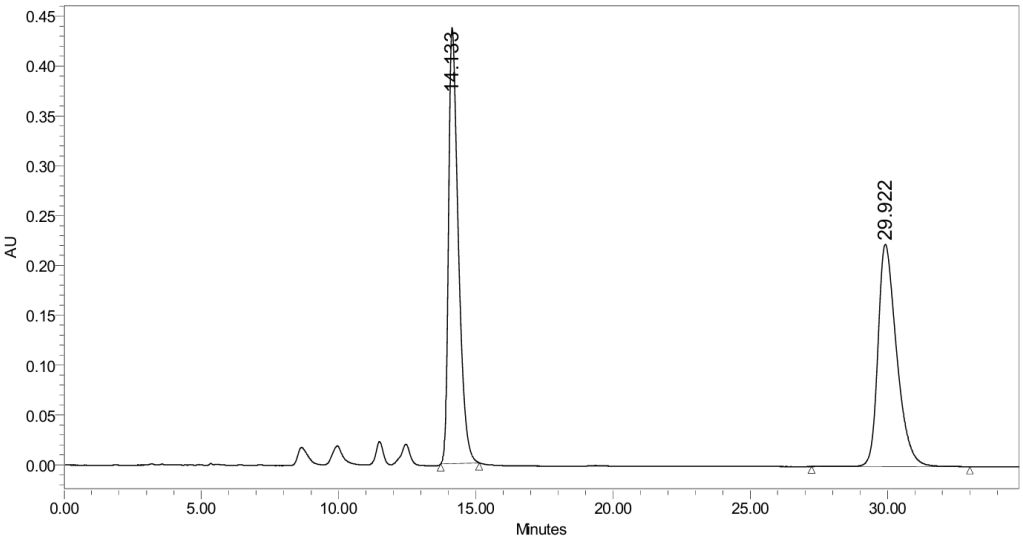
Enantioenriched



	RT	Area	% Area	Height
1	10.430	5612065	98.60	286222
2	16.710	79952	1.40	2809

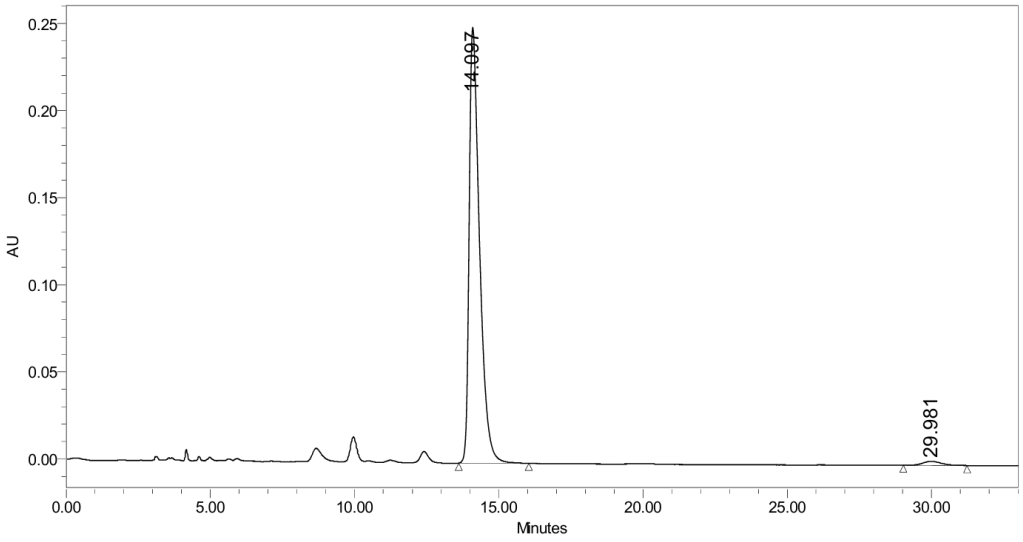
4-methyl-*N*-((*R*,2*E*,4*E*)-1-phenyl-5-(3-(trifluoromethyl)phenyl)penta-2,4-dien-1-yl)benzenesulfonamide (17)

Racemic



	RT	Area	% Area	Height
1	14.133	10846771	50.65	436603
2	29.922	10566731	49.35	222820

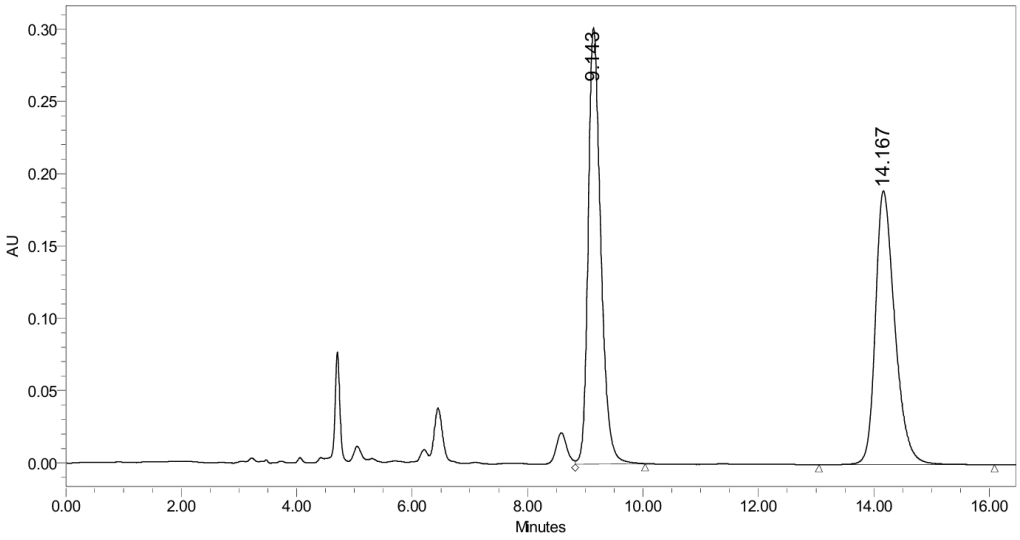
Enantioenriched



	RT	Area	% Area	Height
1	14.097	6268446	98.34	250105
2	29.981	105639	1.66	2374

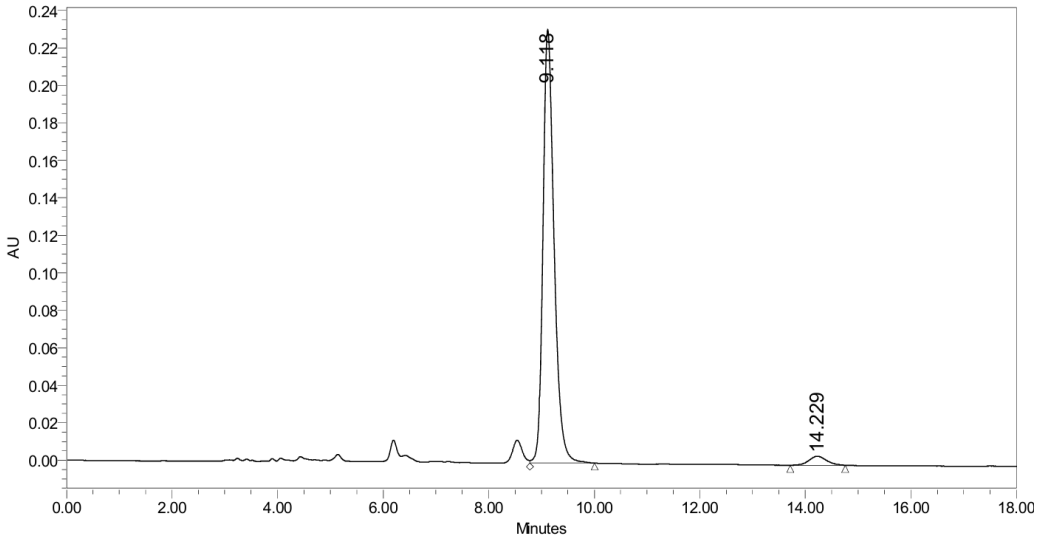
***N*-((*R*,2*E*,4*E*)-5-(3-methoxyphenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (18)**

Racemic



	RT	Area	% Area	Height
1	9.143	4510267	50.44	301648
2	14.167	4431878	49.56	189373

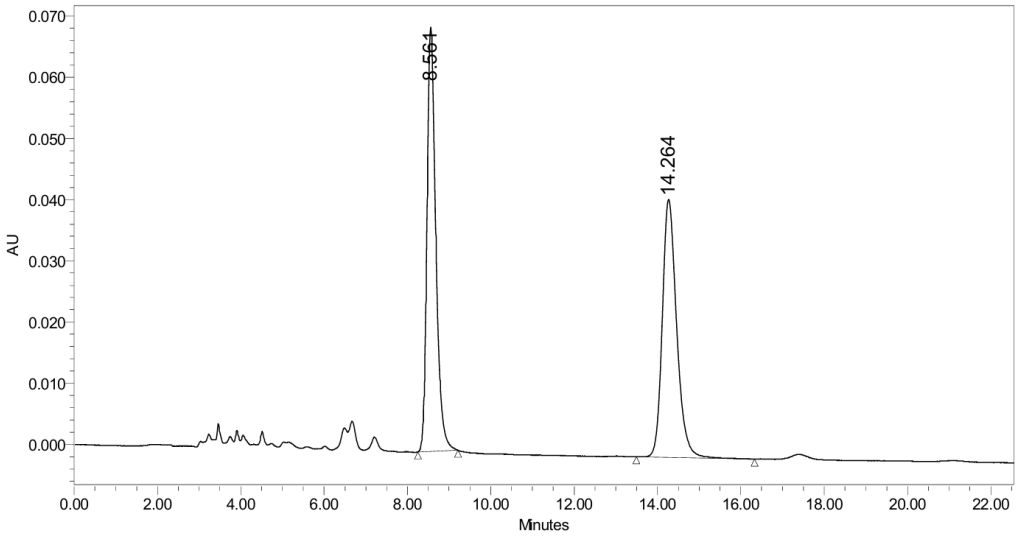
Enantioenriched



	RT	Area	% Area	Height
1	9.118	3396934	96.84	231394
2	14.229	110691	3.16	4795

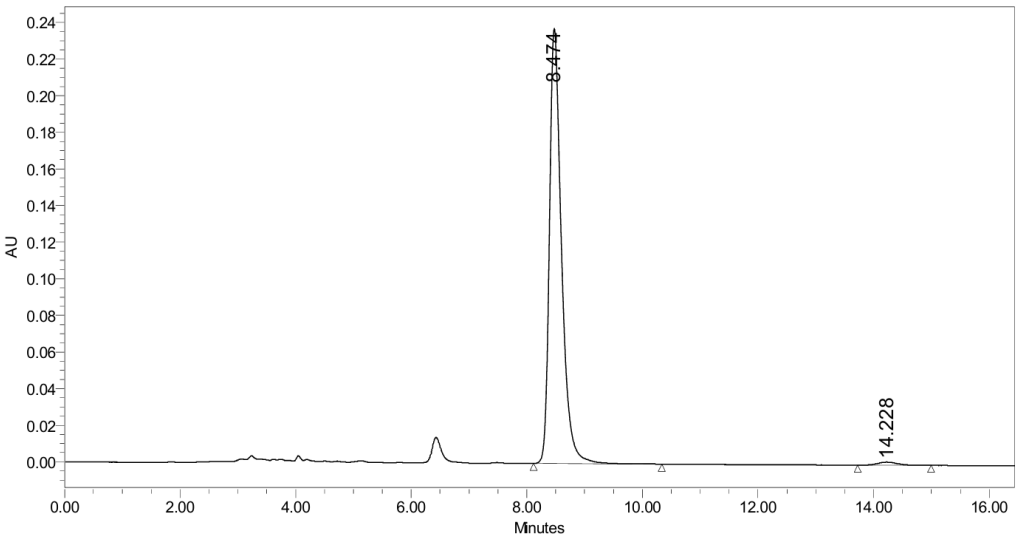
***N*-((*R*,2*E*,4*E*)-5-(2-methoxyphenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (19)**

Racemic



	RT	Area	% Area	Height
1	8.561	1016330	50.34	69245
2	14.264	1002702	49.66	42165

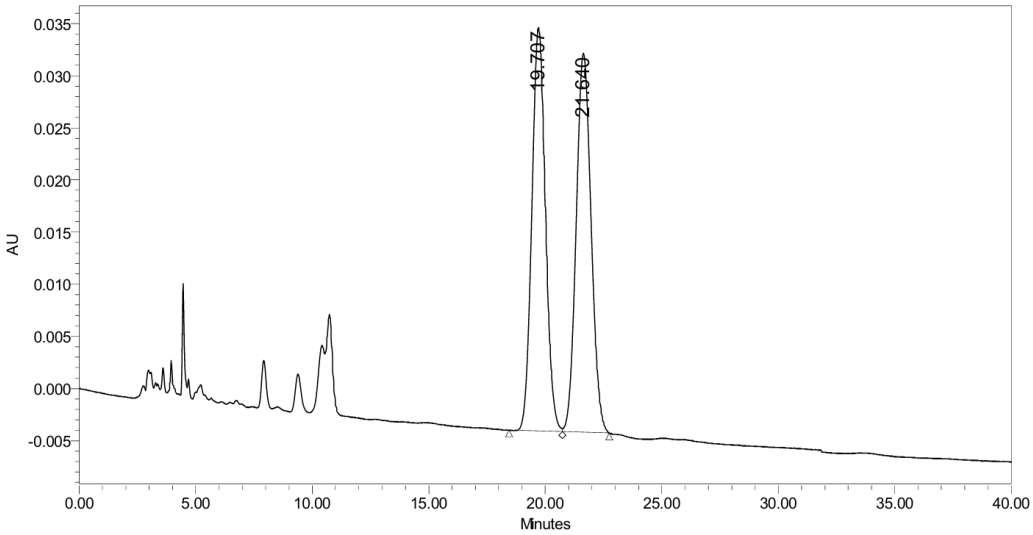
Enantioenriched



	RT	Area	% Area	Height
1	8.474	3451860	98.84	237481
2	14.228	40626	1.16	1735

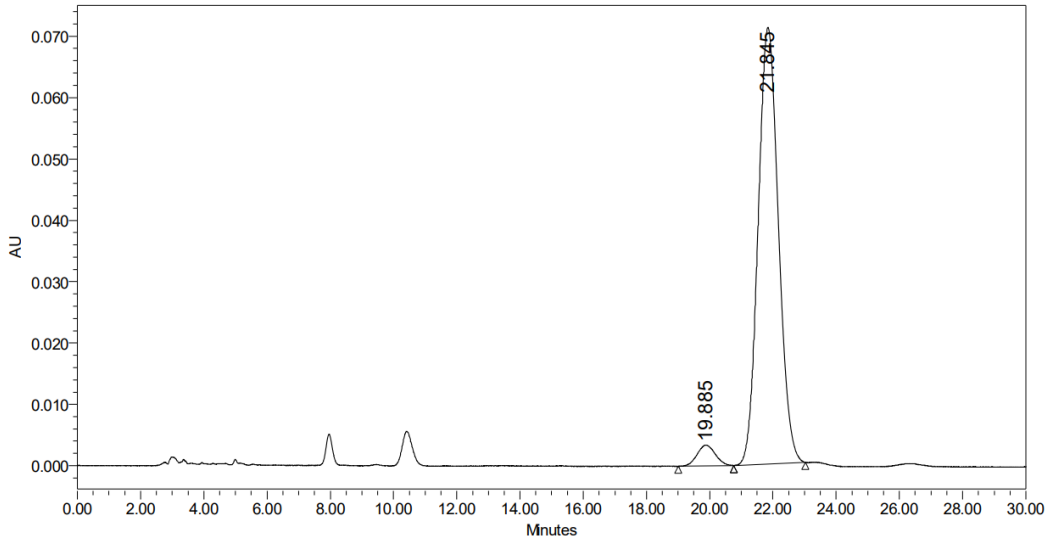
***N*-((*R*,2*E*,4*E*)-5-(2-chlorophenyl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (20)**

Racemic



	RT	Area	% Area	Height
1	19.707	1577167	49.53	38678
2	21.640	1607123	50.47	36328

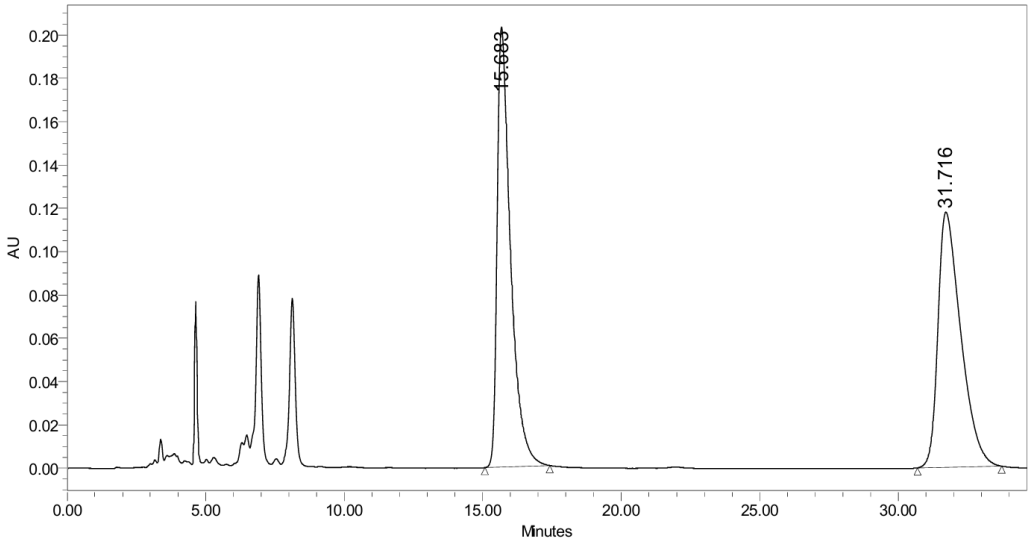
Enantioenriched



	RT	Area	% Area	Height
1	19.885	135799	4.10	3401
2	21.845	3179915	95.90	71151

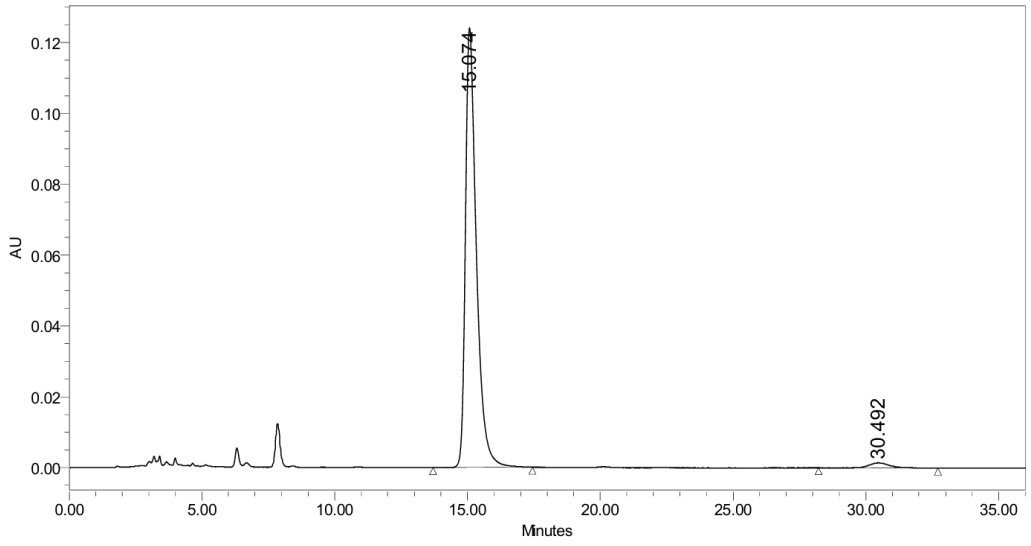
4-methyl-*N*-((*R*,2*E*,4*E*)-5-(naphthalen-2-yl)-1-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (21)

Racemic



	RT	Area	% Area	Height
1	15.683	6808203	50.07	203125
2	31.716	6789981	49.93	117898

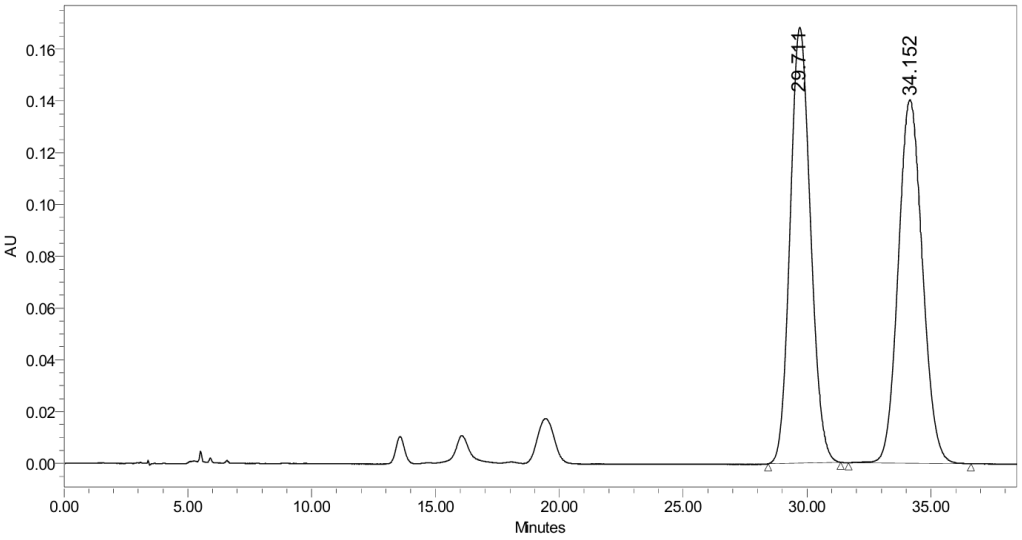
Enantioenriched



	RT	Area	% Area	Height
1	15.074	3564876	97.89	124061
2	30.492	76675	2.11	1439

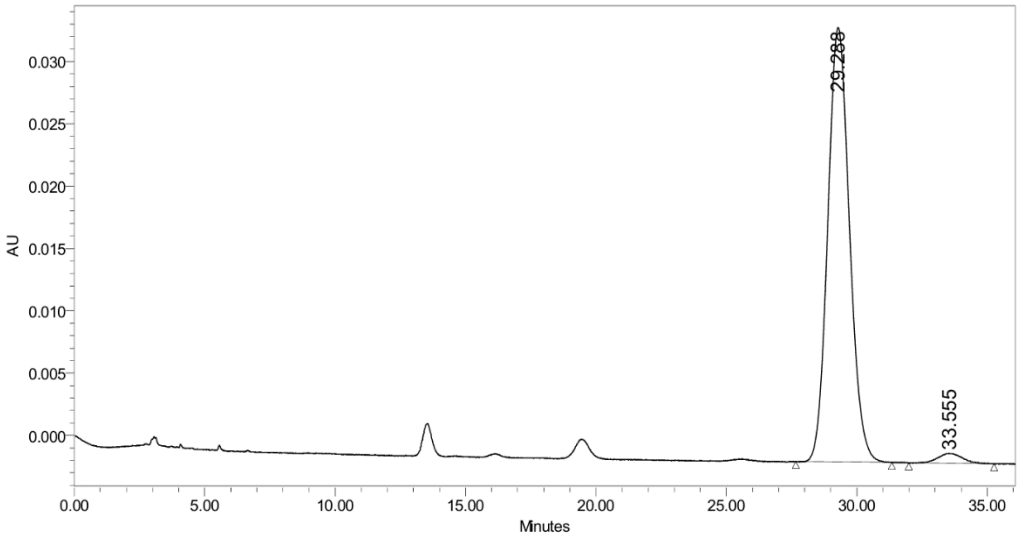
4-methyl-*N*-((*R*,2*E*,4*E*)-5-(naphthalen-1-yl)-1-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (22)

Racemic



	RT	Area	% Area	Height
1	29.711	9674620	50.62	168266
2	34.152	9438322	49.38	140329

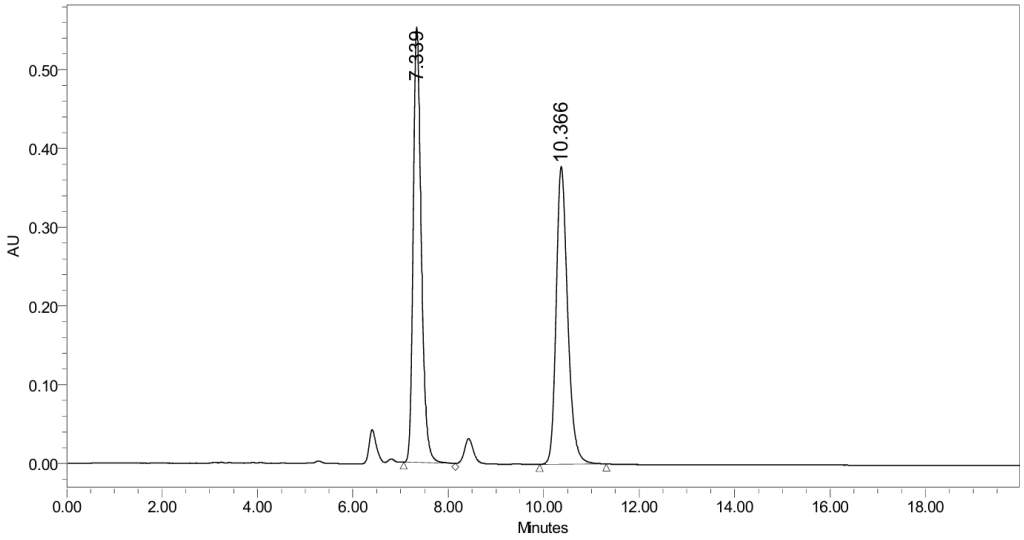
Enantioenriched



	RT	Area	% Area	Height
1	29.288	2007636	97.48	34847
2	33.555	51949	2.52	792

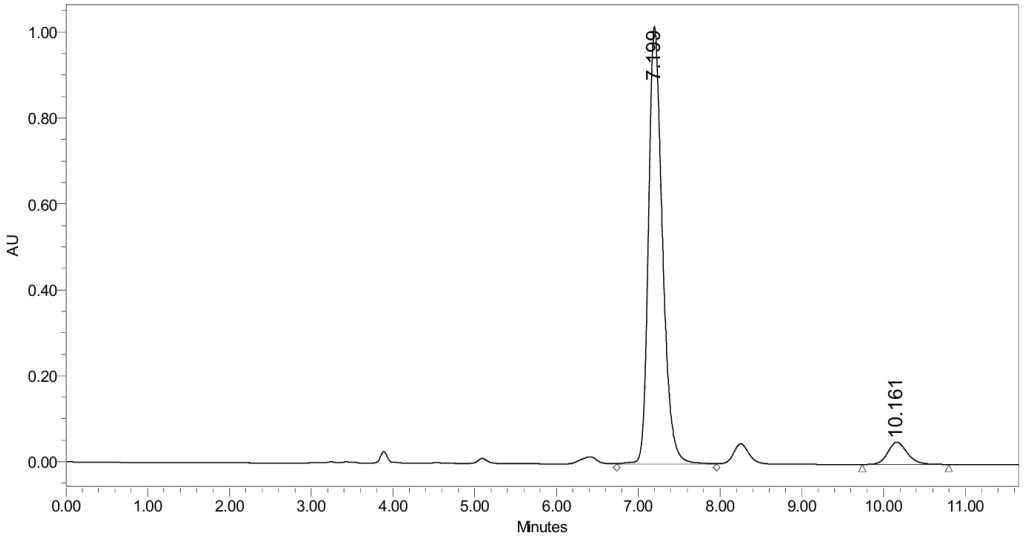
4-methyl-*N*-((*S*,2*E*,4*E*)-1-phenyl-5-(Ferroceneyl)penta-2,4-dien-1-yl)benzenesulfonamide (23)

Racemic



	RT	Area	% Area	Height
1	7.339	6482243	50.50	552918
2	10.366	6353400	49.50	378159

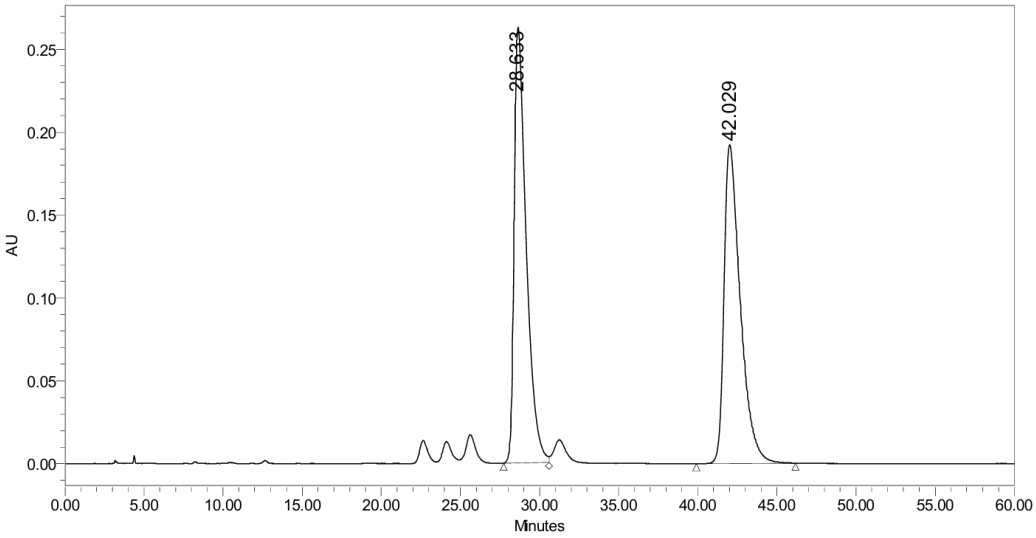
Enantioenriched



	RT	Area	% Area	Height
1	7.199	12084122	93.37	1017617
2	10.161	857454	6.63	51722

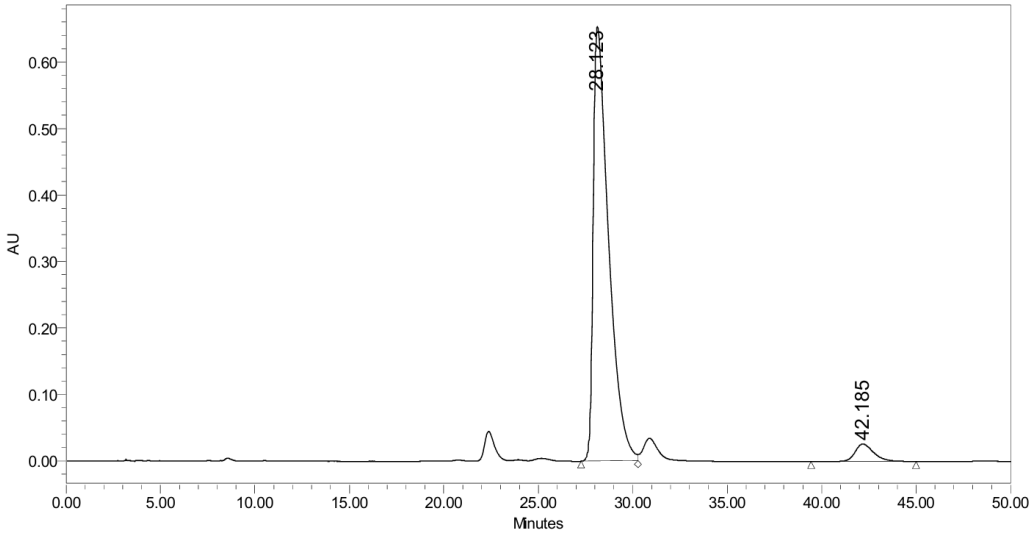
***N*-((*R*,2*E*,4*E*)-5-(furan-2-yl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (24)**

Racemic



	RT	Area	% Area	Height
1	28.633	13859180	50.25	262835
2	42.029	13722116	49.75	192387

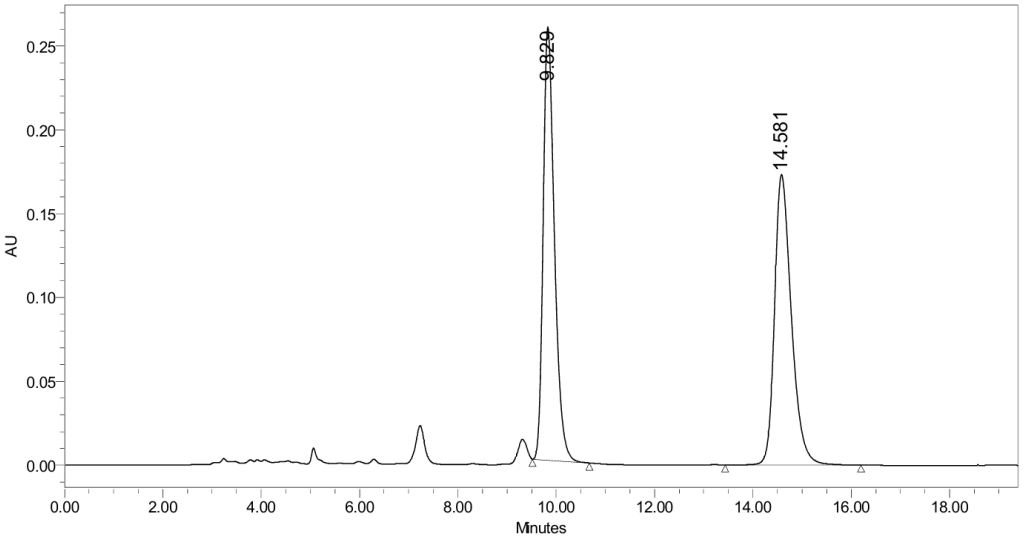
Enantioenriched



	RT	Area	% Area	Height
1	28.123	36807082	95.34	653304
2	42.185	1797822	4.66	26273

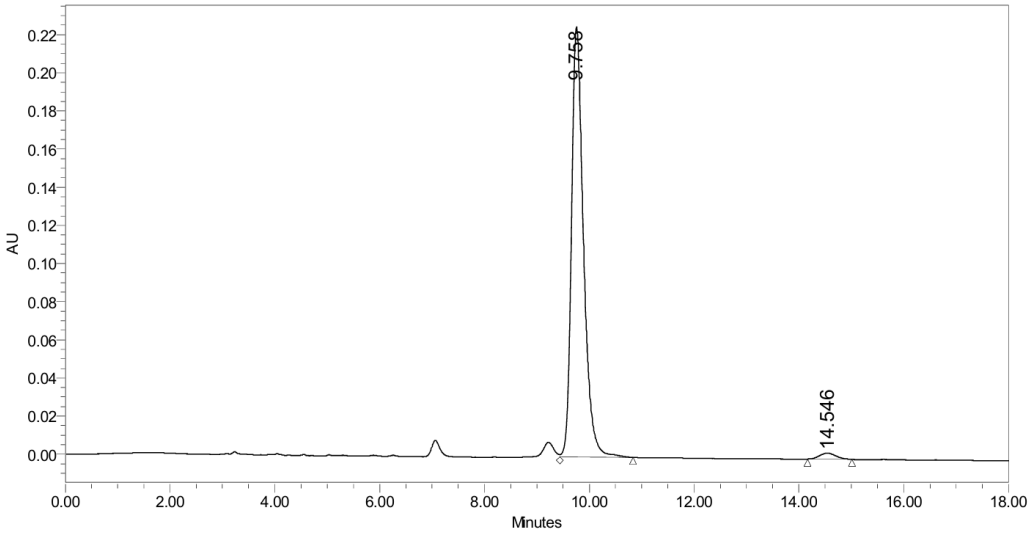
***N*-((*R*,2*E*,4*E*)-5-(benzo[*d*][1,3]dioxol-5-yl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (25)**

Racemic



	RT	Area	% Area	Height
1	9.829	4113326	49.83	258295
2	14.581	4140893	50.17	173155

Enantioenriched

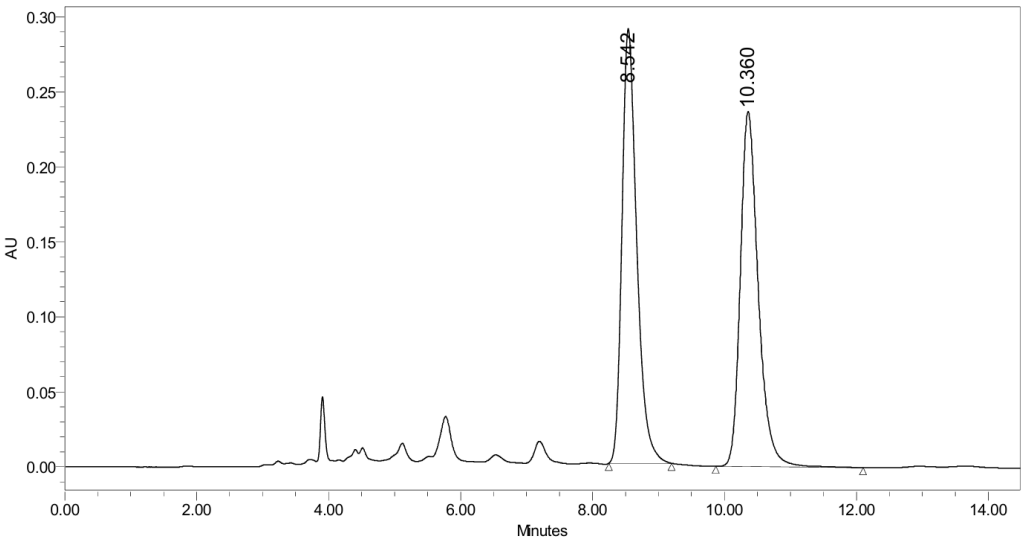


	RT	Area	% Area	Height
1	9.758	3562145	98.08	225436
2	14.546	69800	1.92	3224

***Tert*-butyl**

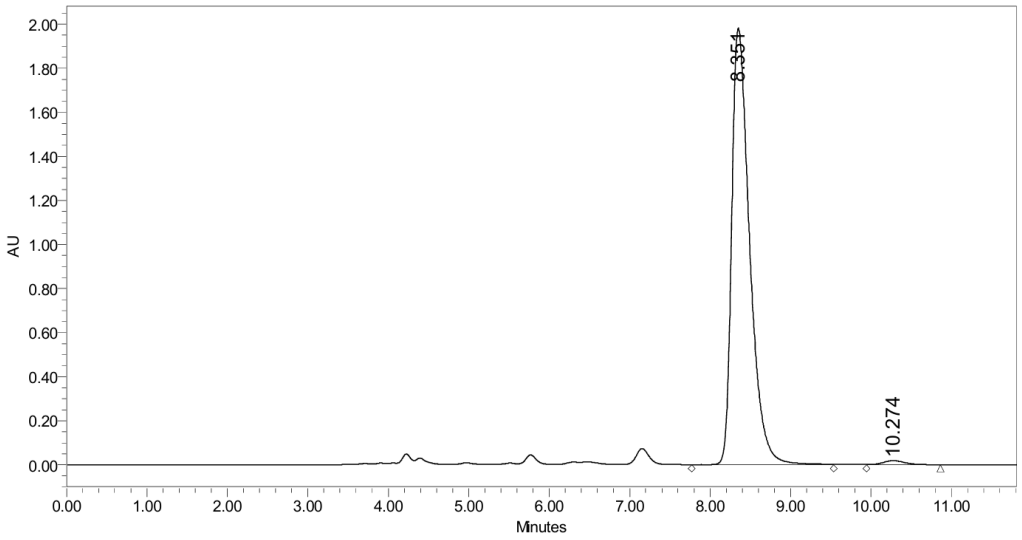
2-methyl-3-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)-1H-indole-1-carboxylate (26)

Racemic



	RT	Area	% Area	Height
1	8.542	4527311	50.28	289751
2	10.360	4476384	49.72	236937

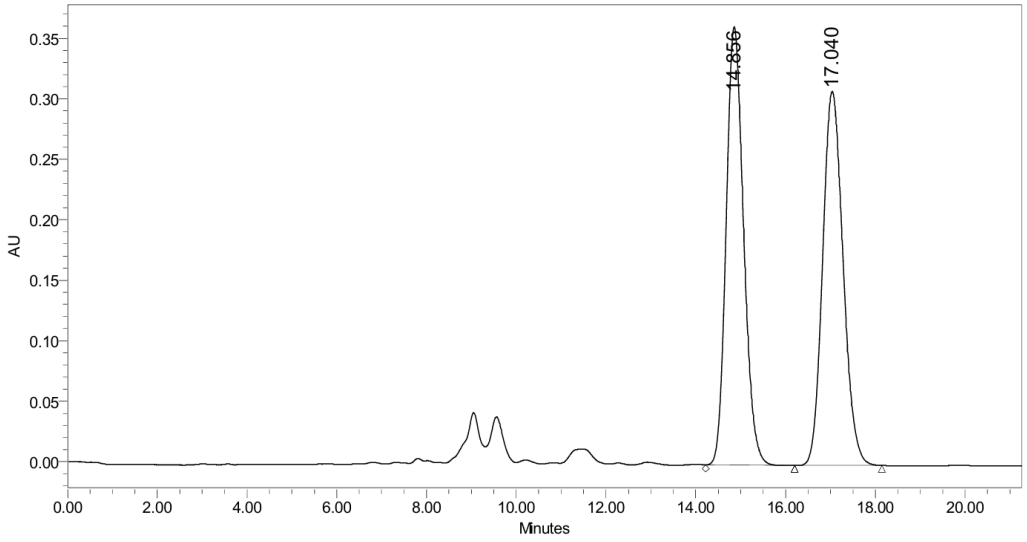
Enantioenriched



	RT	Area	% Area	Height
1	8.351	30666629	98.85	1981715
2	10.274	357200	1.15	19105

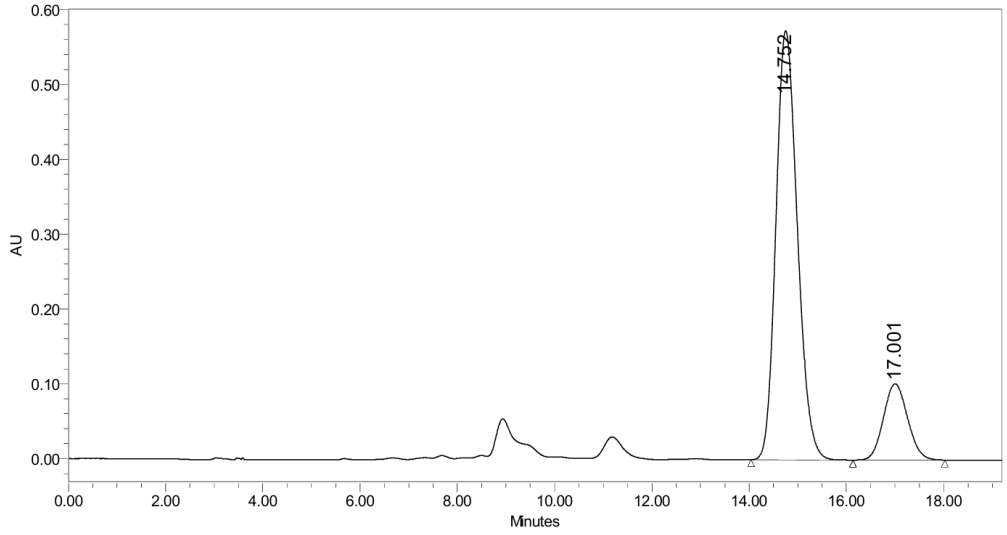
4-methyl-*N*-((*R*,2*E*,4*E*)-1-phenyl-5-(trimethylsilyl)penta-2,4-dien-1-yl)benzenesulfonamide (27)

Racemic



	RT	Area	% Area	Height
1	14.856	9783202	50.24	362353
2	17.040	9691590	49.76	309213

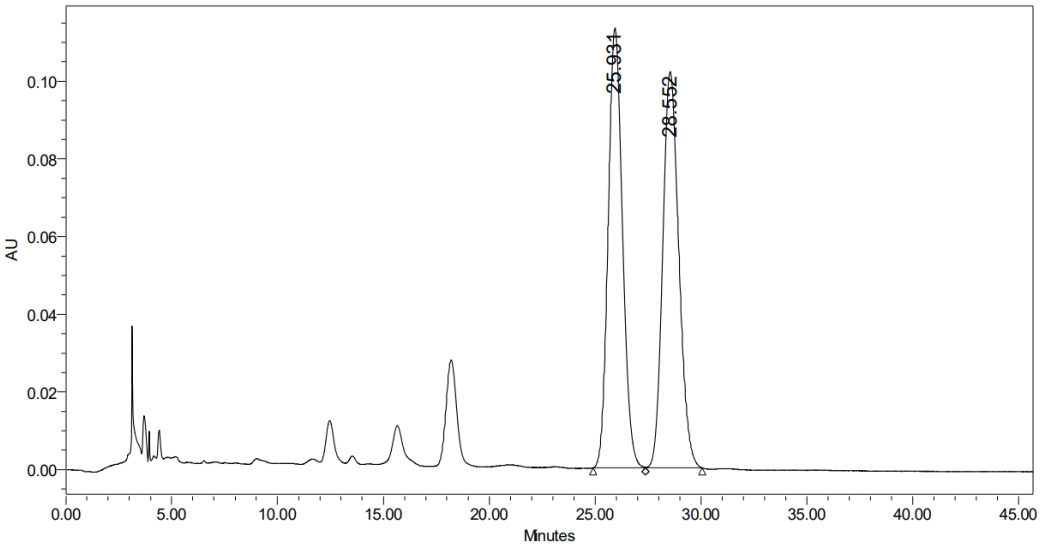
Enantioenriched



	RT	Area	% Area	Height
1	14.752	17627939	83.42	573435
2	17.001	3504773	16.58	101951

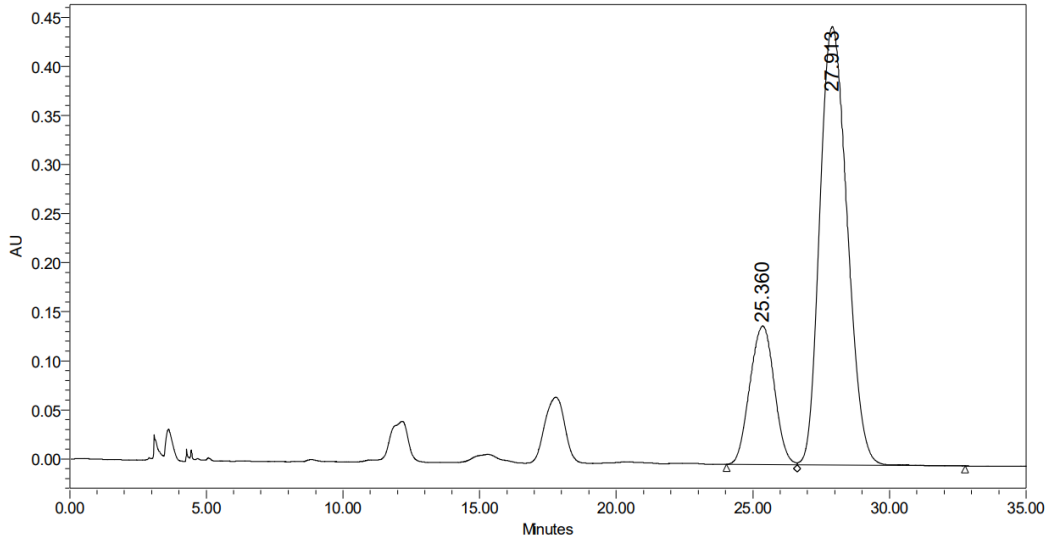
***Tert*-butyl (*R*)-(1,6-diphenylhexyl)(tosyl)carbamate (28)**

Racemic



	RT	Area	% Area	Height
1	25.931	5316444	49.69	113219
2	28.552	5383636	50.31	102002

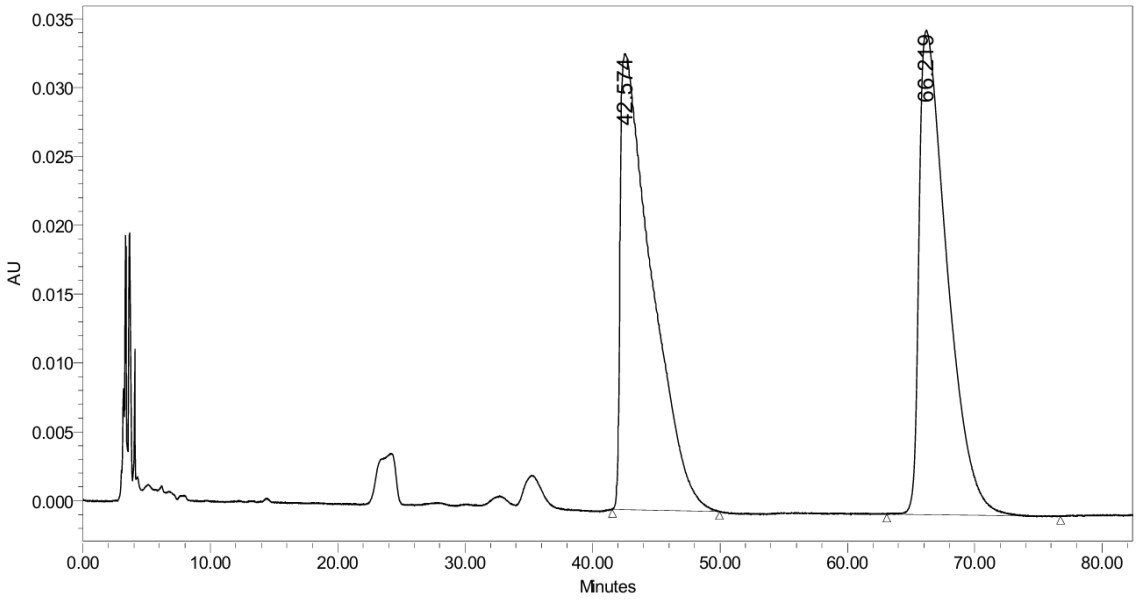
Enantioenriched



	RT	Area	% Area	Height
1	25.360	8772553	22.08	141169
2	27.913	30954839	77.92	446764

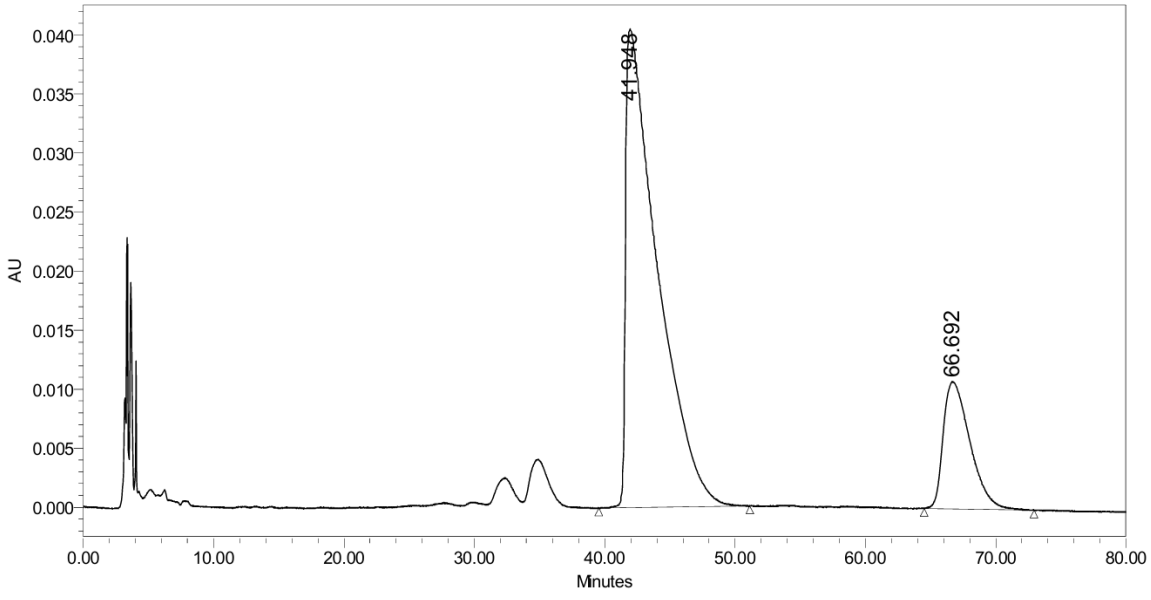
(*R*)-4-methyl-*N*-(1-phenylnonyl)benzenesulfonamide (29)

Racemic



	RT	Area	% Area	Height
1	42.574	5658932	51.32	33139
2	66.219	5367467	48.68	35183

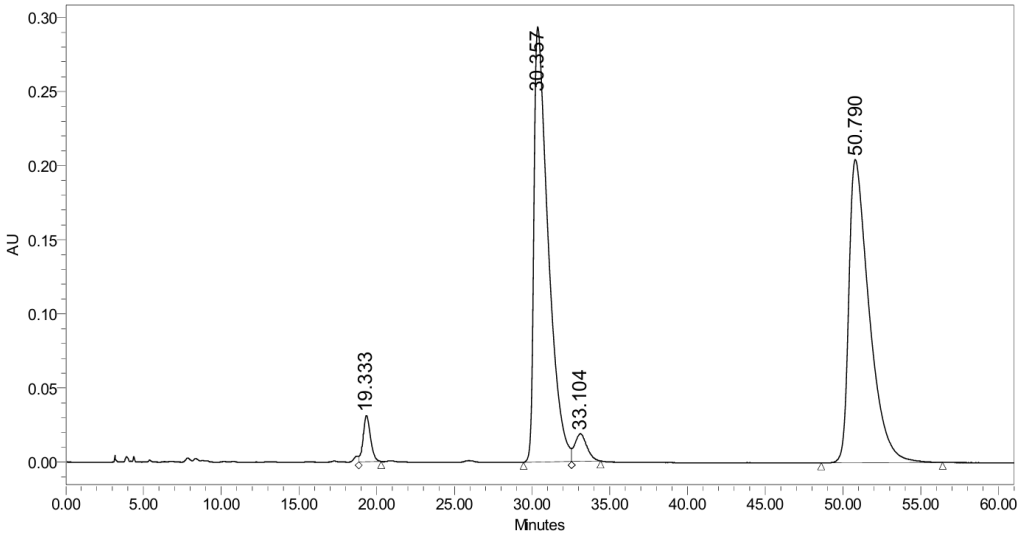
Enantioenriched



	RT	Area	% Area	Height
1	41.948	6891310	81.80	40521
2	66.692	1533600	18.20	10783

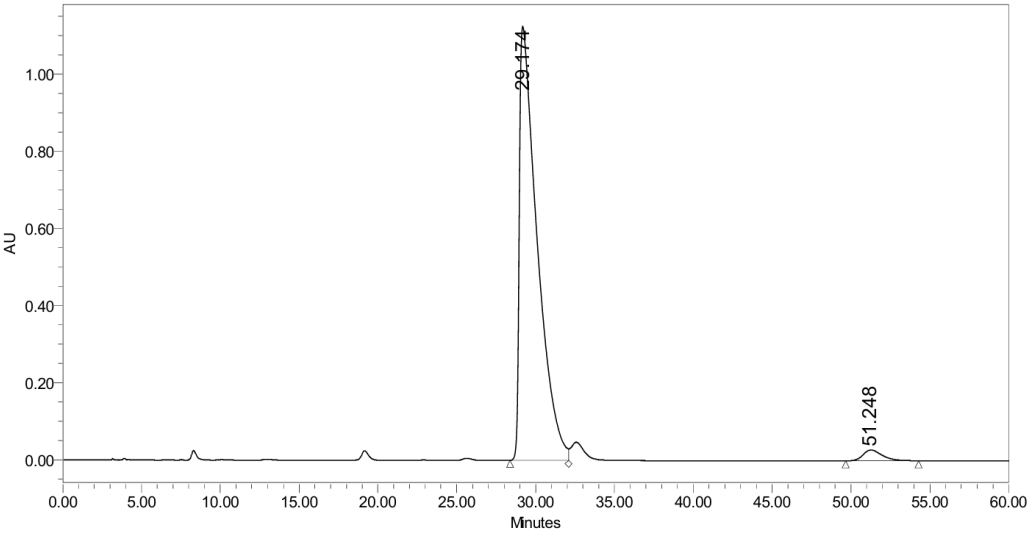
4-methyl-*N*-((*R*,2*E*,4*E*)-5-phenyl-1-(p-tolyl)penta-2,4-dien-1-yl)benzenesulfonamide (30)

Racemic



	RT	Area	% Area	Height
1	19.333	1022947	2.59	31139
2	30.357	18836917	47.64	293570
3	33.104	1012950	2.56	18615
4	50.790	18664607	47.21	204634

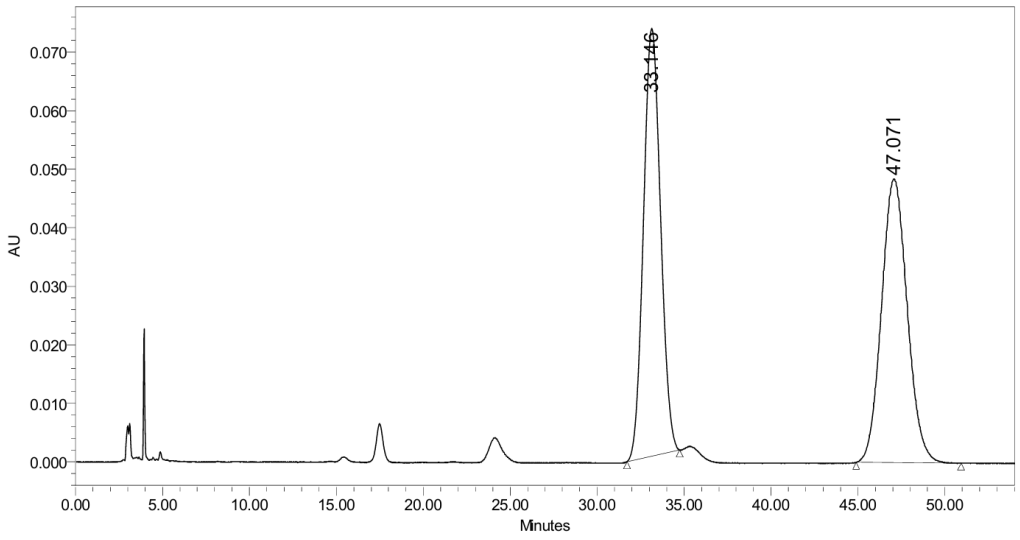
Enantioenriched



	RT	Area	% Area	Height
1	29.174	88434344	97.41	1124544
2	51.248	2355244	2.59	28049

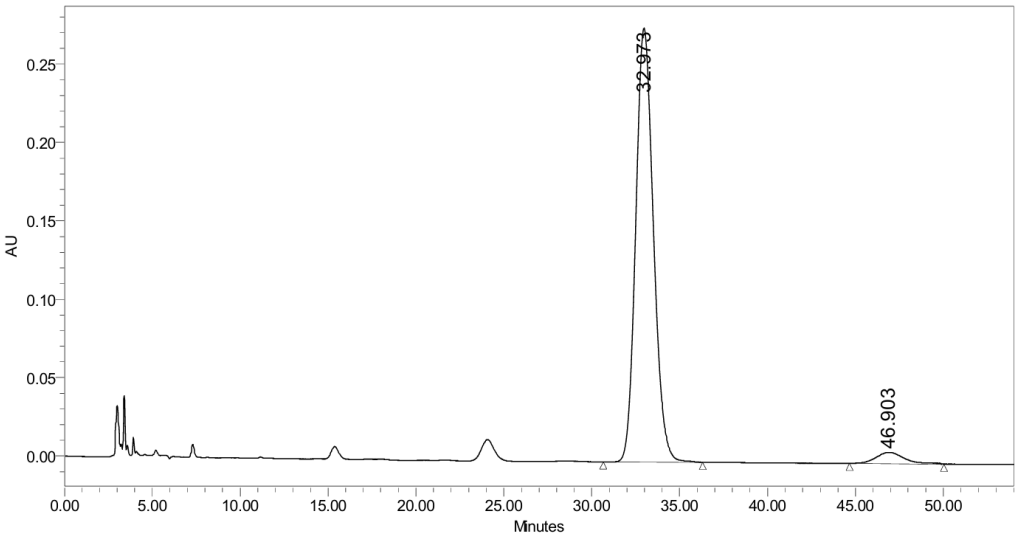
***N*-((*R*,2*E*,4*E*)-1-(4-methoxyphenyl)-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (31)**

Racemic



	RT	Area	% Area	Height
1	33.146	4969455	49.84	73021
2	47.071	5001956	50.16	48440

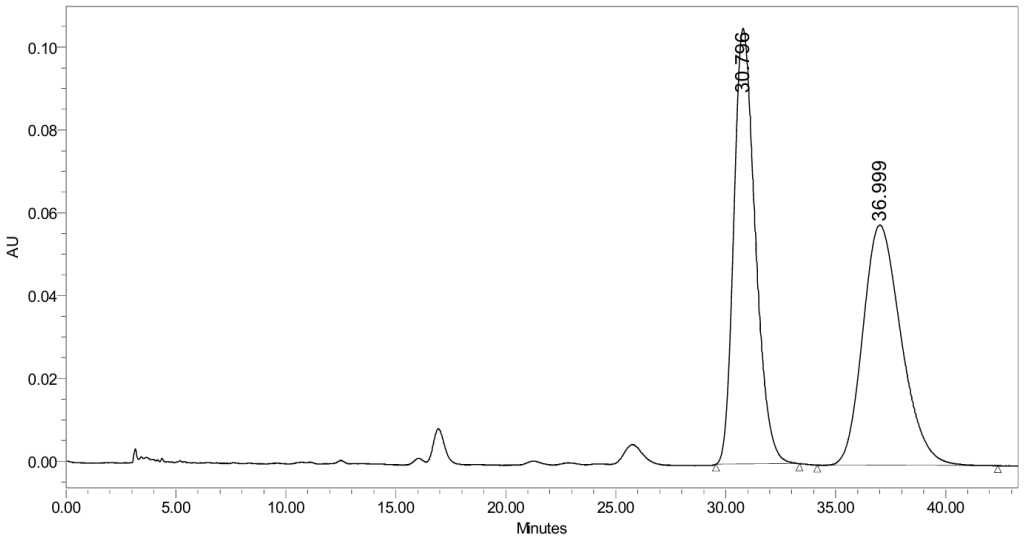
Enantioenriched



	RT	Area	% Area	Height
1	32.973	19413613	96.03	276748
2	46.903	801767	3.97	7219

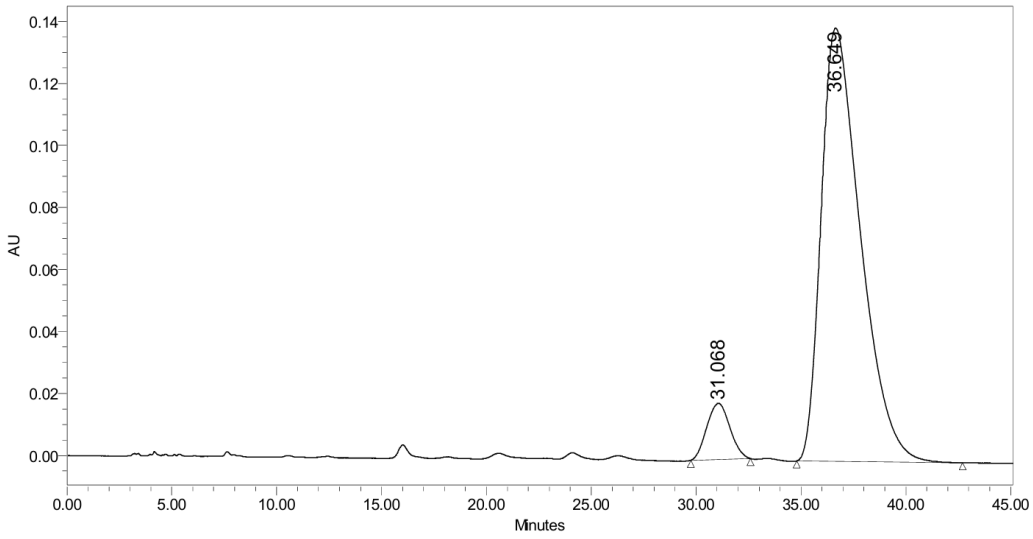
***N*-((*R*,2*E*,4*E*)-1-(4-(benzyloxy)phenyl)-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (32)**

Racemic



	RT	Area	% Area	Height
1	30.796	7110314	50.19	105234
2	36.999	7055330	49.81	58047

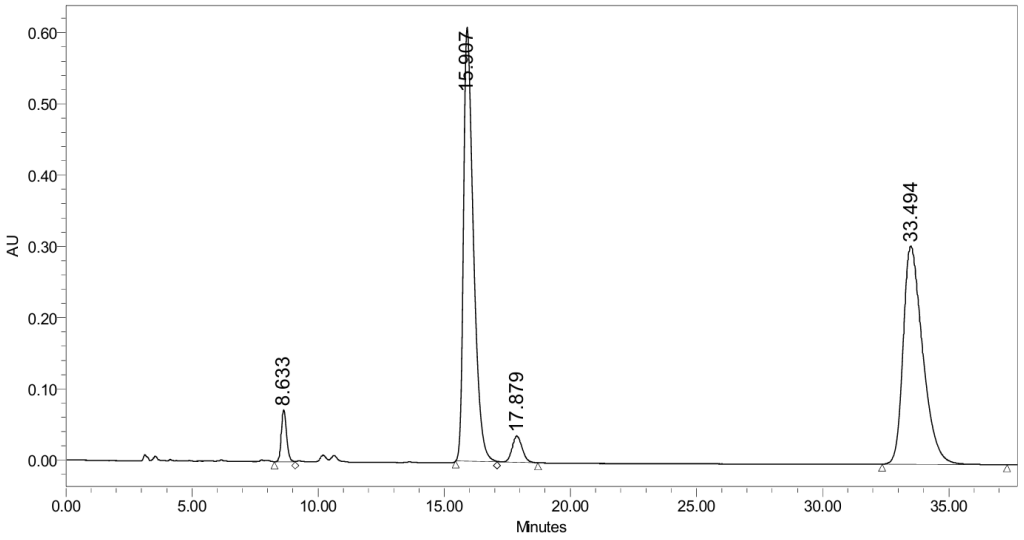
Enantioenriched



	RT	Area	% Area	Height
1	31.068	1391485	7.11	18126
2	36.649	18174184	92.89	139747

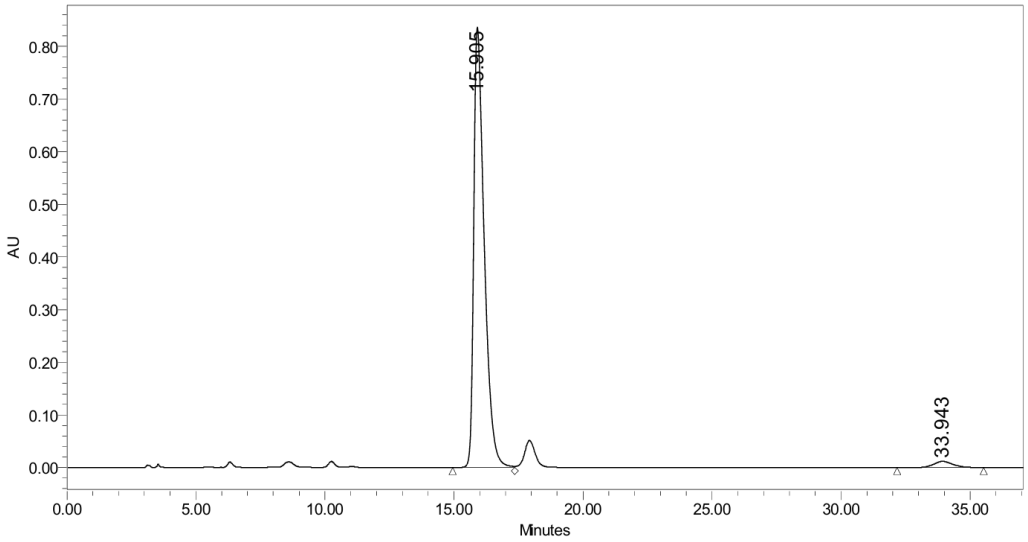
4-methyl-*N*-((*R*,2*E*,4*E*)-5-phenyl-1-(4-(trifluoromethoxy)phenyl)penta-2,4-dien-1-yl)benzenesulfonamide (33)

Racemic



	RT	Area	% Area	Height
1	8.633	1044680	2.97	73126
2	15.907	16721598	47.56	609210
3	17.879	1021067	2.90	36921
4	33.494	16375301	46.57	306585

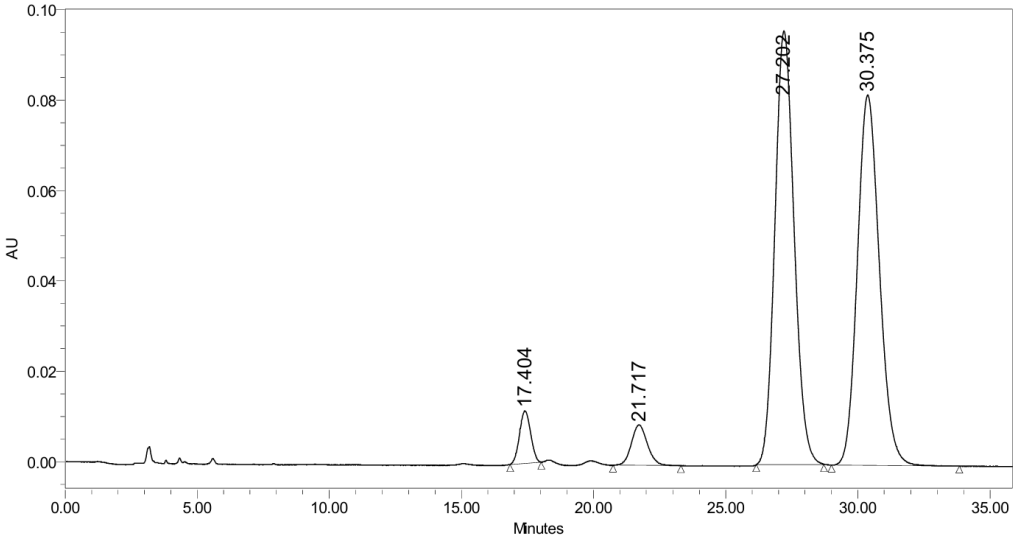
Enantioenriched



	RT	Area	% Area	Height
1	15.905	23689826	97.50	835999
2	33.943	606806	2.50	11626

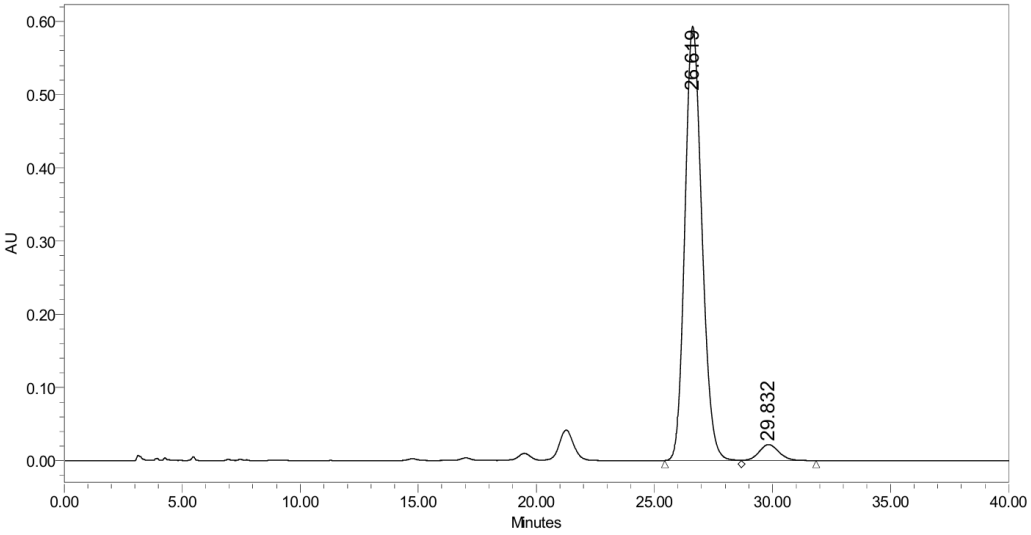
***N*-((*R*,2*E*,4*E*)-1-(4-cyanophenyl)-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (34)**

Racemic



	RT	Area	% Area	Height
1	17.404	340023	3.28	11595
2	21.717	377260	3.64	8932
3	27.202	4865860	46.96	95902
4	30.375	4778164	46.12	81895

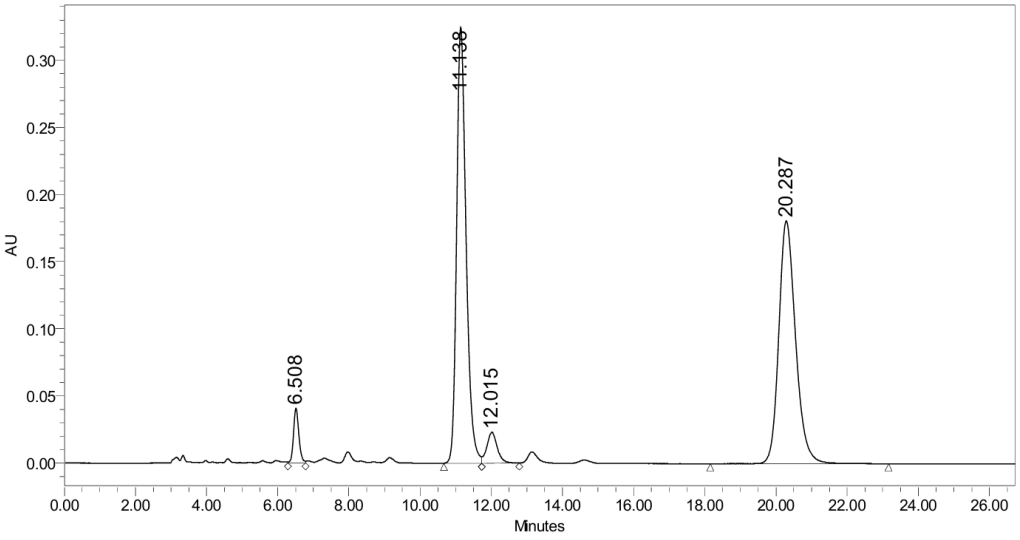
Enantioenriched



	RT	Area	% Area	Height
1	26.619	29829766	95.89	593139
2	29.832	1277739	4.11	21849

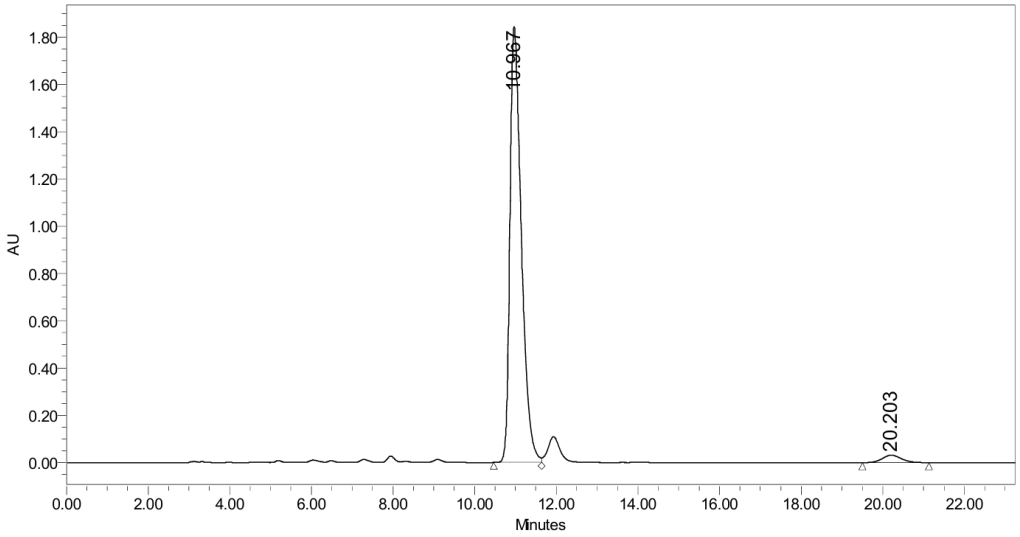
4-((*R*,2*E*,4*E*)-1-((4-methylphenyl)sulfonamido)-5-phenylpenta-2,4-dien-1-yl)phenyl trifluoromethanesulfonate (35)

Racemic



	RT	Area	% Area	Height
1	6.508	423654	3.30	40774
2	11.138	6015234	46.79	325000
3	12.015	468793	3.65	22938
4	20.287	5949291	46.27	180887

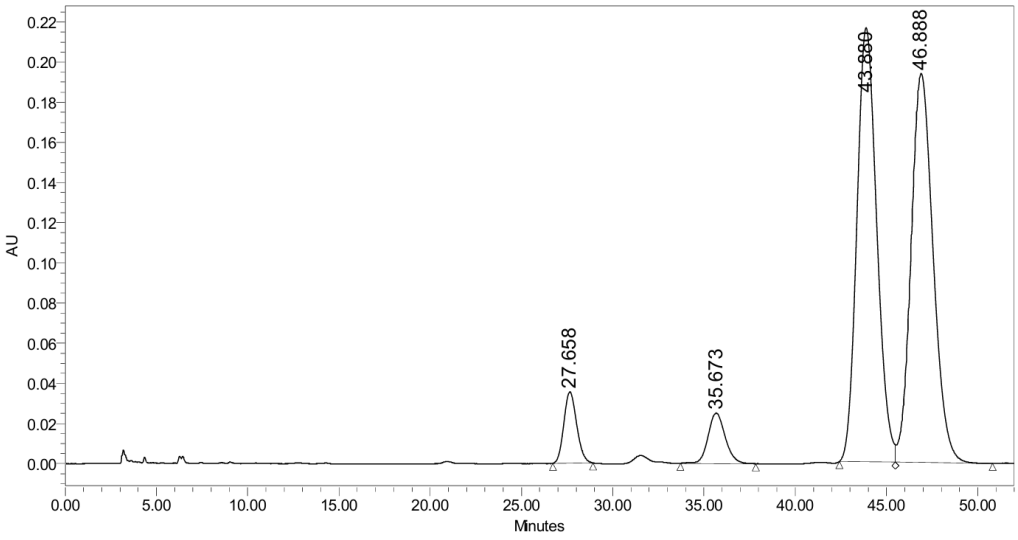
Enantioenriched



	RT	Area	% Area	Height
1	10.967	35566656	97.15	1842739
2	20.203	1043094	2.85	31745

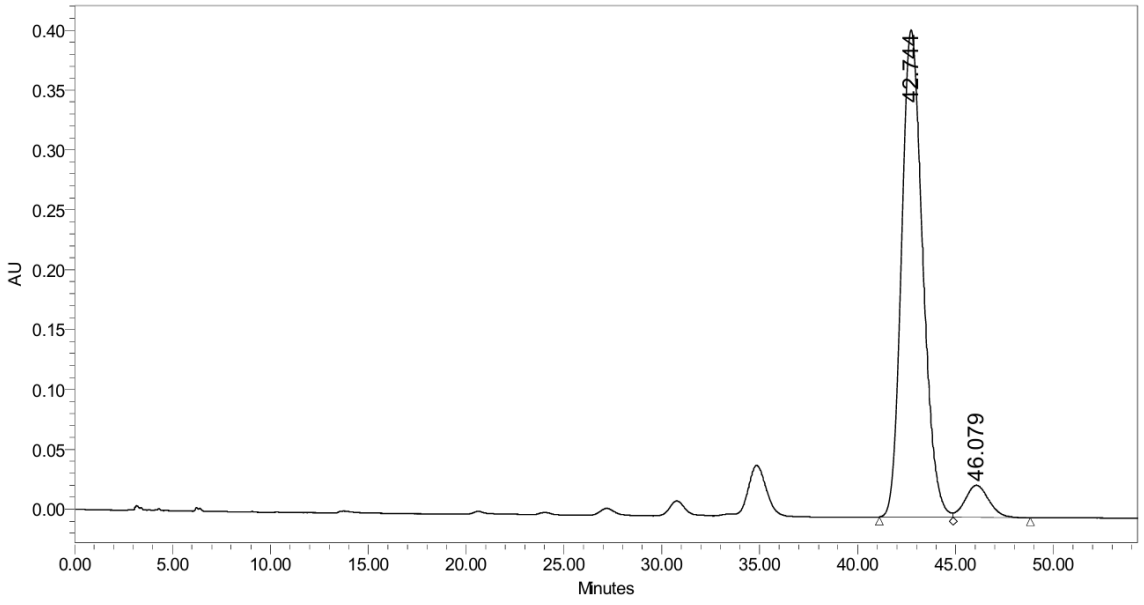
4-methyl-*N*-((*R*,2*E*,4*E*)-1-(4-nitrophenyl)-5-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (36)

Racemic



	RT	Area	% Area	Height
1	27.658	1743458	4.84	35509
2	35.673	1637694	4.54	25094
3	43.880	16431522	45.58	216094
4	46.888	16239995	45.05	193689

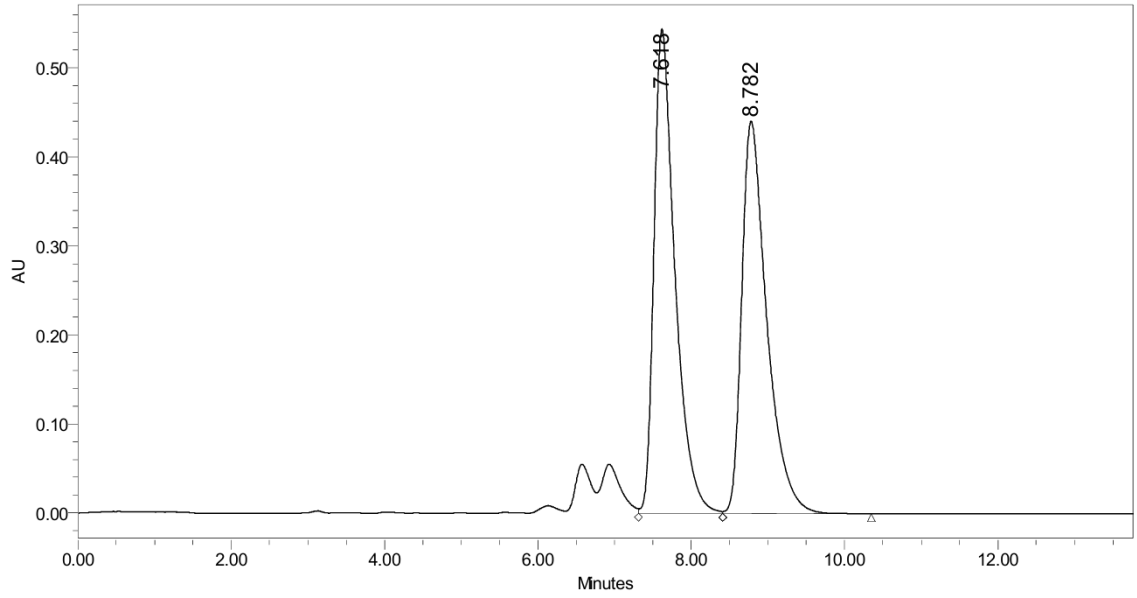
Enantioenriched



	RT	Area	% Area	Height
1	42.744	30586973	93.15	406698
2	46.079	2247669	6.85	26937

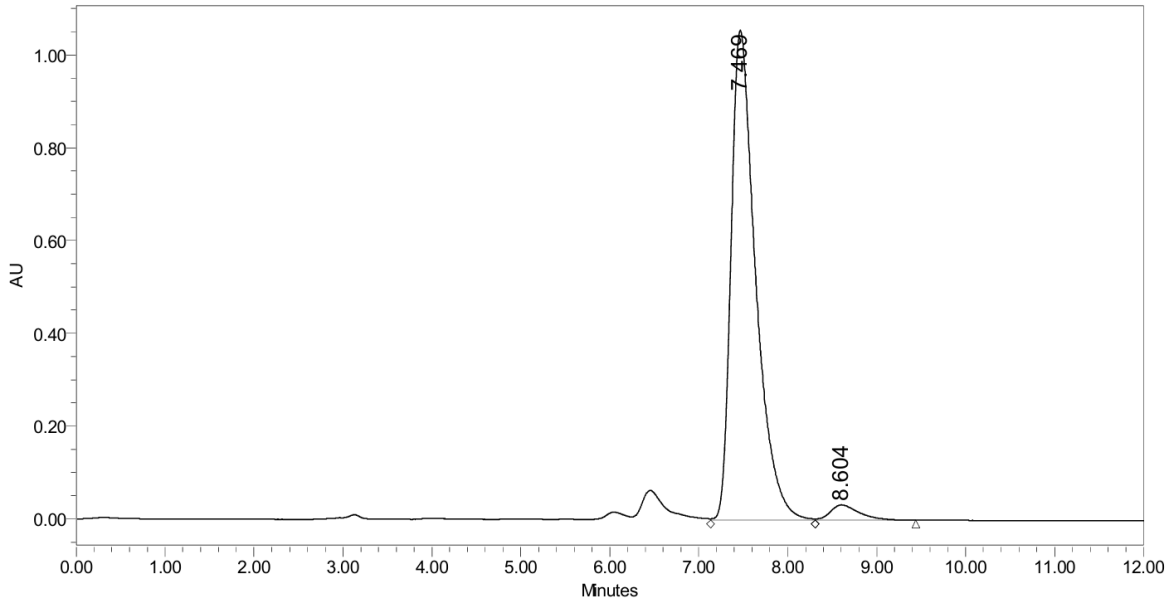
4-methyl-*N*-((*R*,2*E*,4*E*)-5-phenyl-1-(2-(trifluoromethyl)phenyl)penta-2,4-dien-1-yl)benzenesulfonamide (37)

Racemic



	RT	Area	% Area	Height
1	7.618	10300464	50.87	544059
2	8.782	9949562	49.13	440817

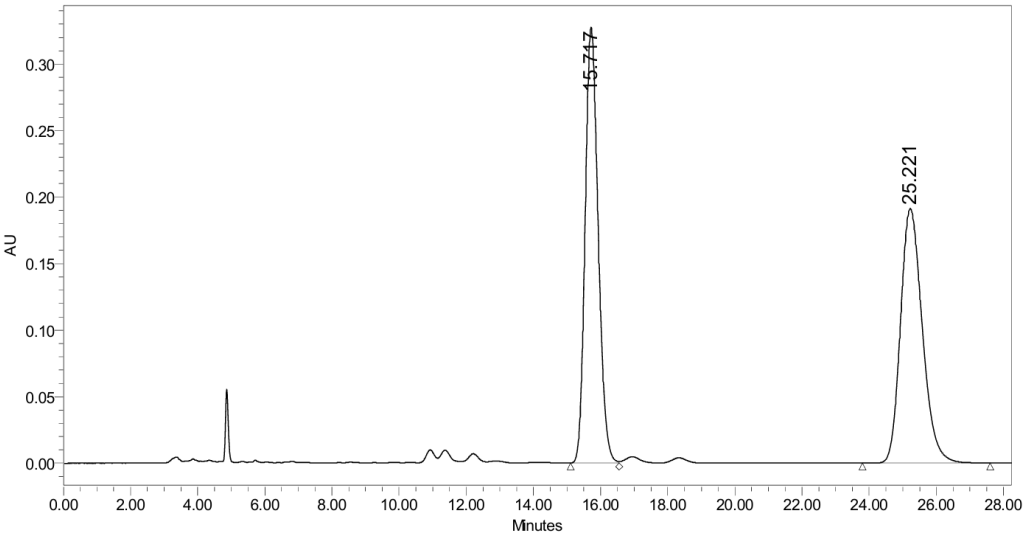
Enantioenriched



	RT	Area	% Area	Height
1	7.469	20180896	96.46	1055279
2	8.604	741625	3.54	32731

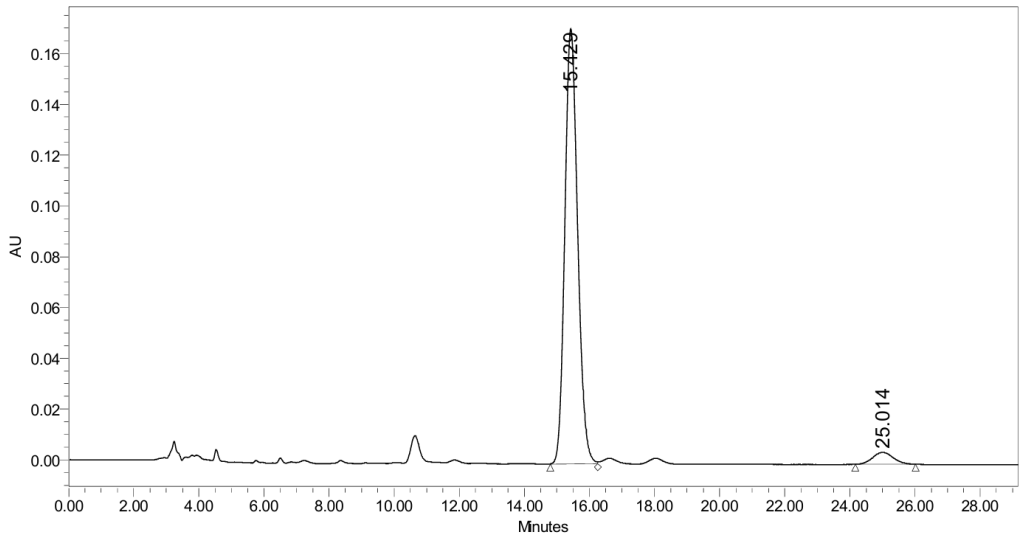
***N*-((*R*,2*E*,4*E*)-1-(2-chlorophenyl)-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (38)**

Racemic



	RT	Area	% Area	Height
1	15.717	8693775	50.38	327332
2	25.221	8561784	49.62	191357

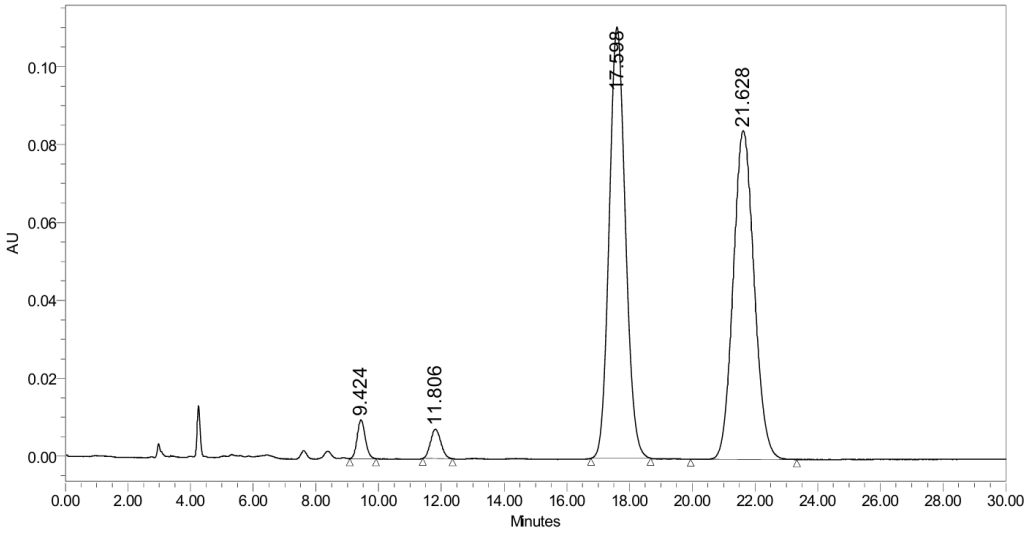
Enantioenriched



	RT	Area	% Area	Height
1	15.429	4693971	95.81	171344
2	25.014	205211	4.19	4723

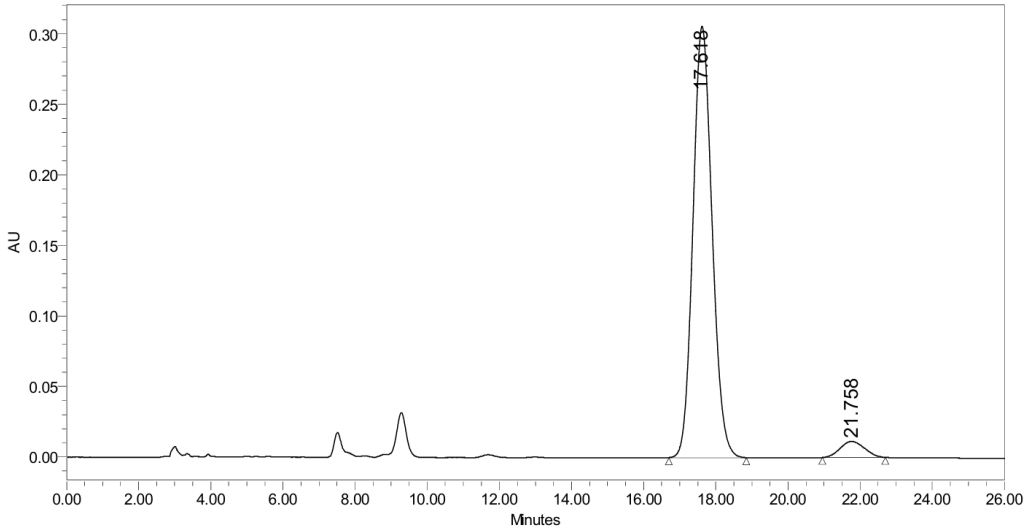
***N*-((*R*,2*E*,4*E*)-1-(3-fluorophenyl)-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (39)**

Racemic



	RT	Area	% Area	Height
1	9.424	177618	2.16	9952
2	11.806	171891	2.09	7537
3	17.598	3993084	48.46	110728
4	21.628	3898104	47.30	84381

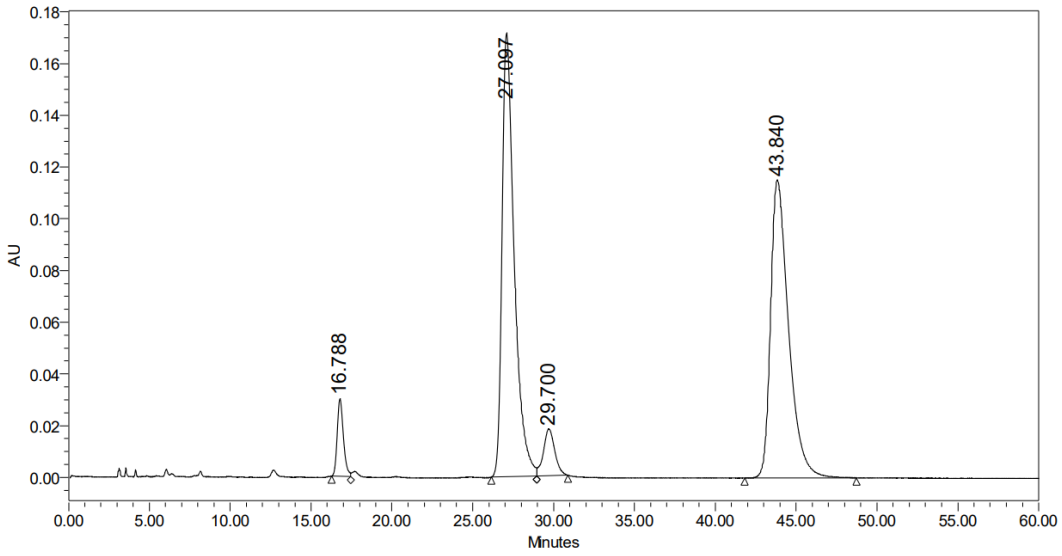
Enantioenriched



	RT	Area	% Area	Height
1	17.618	11302026	95.53	305649
2	21.758	528476	4.47	11363

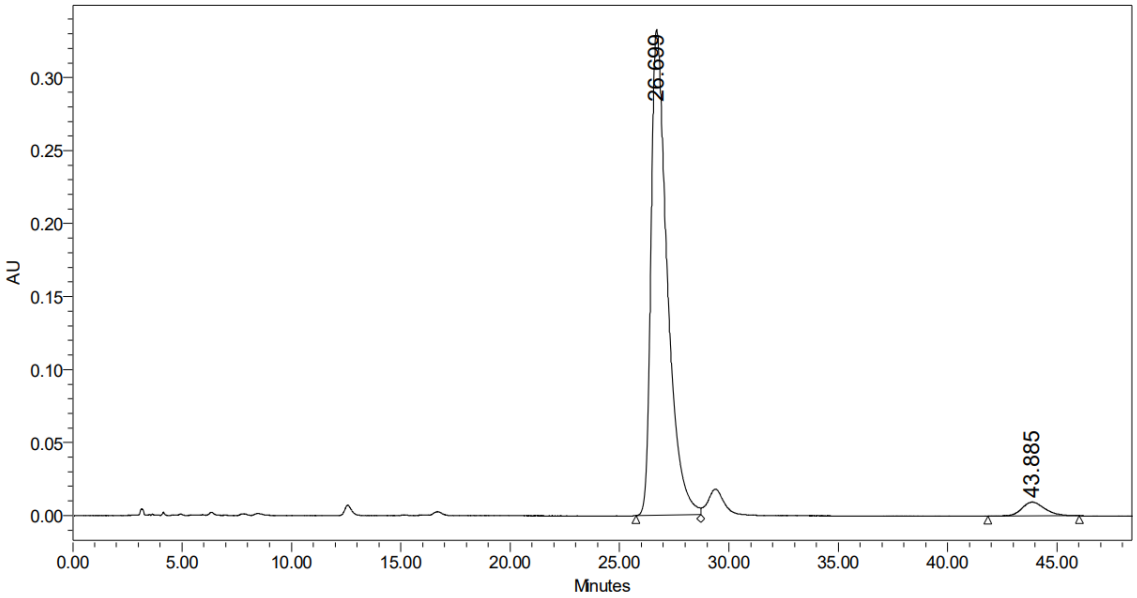
4-methyl-*N*-((*R*,2*E*,4*E*)-1-(naphthalen-1-yl)-5-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (40)

Racemic



	RT	Area	% Area	Height
1	16.788	798491	4.10	29947
2	27.097	8965933	45.99	171528
3	29.700	882113	4.52	18123
4	43.840	8850359	45.39	115250

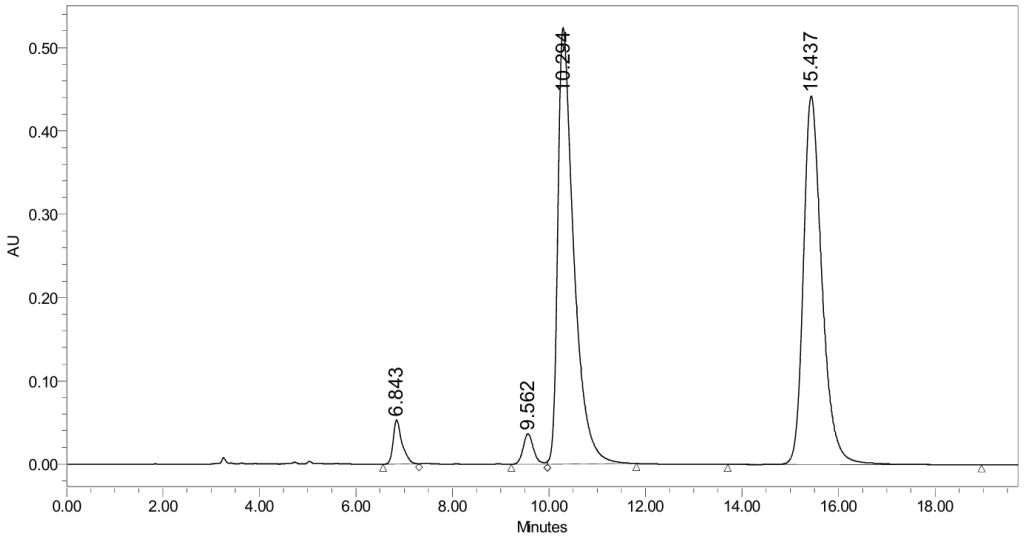
Enantioenriched



	RT	Area	% Area	Height
1	26.699	17017592	96.08	332675
2	43.885	694281	3.92	9491

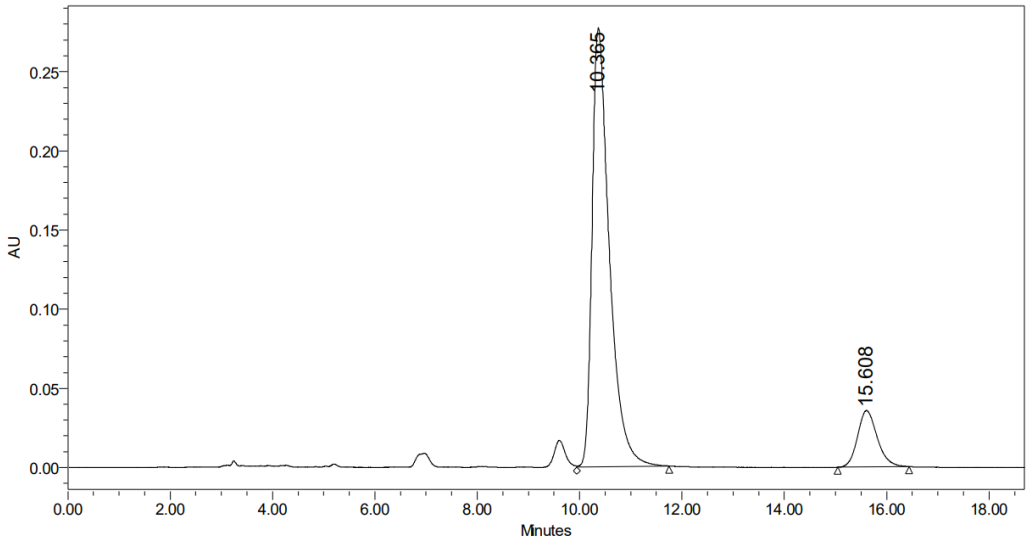
4-methyl-*N*-((*R*,2*E*,4*E*)-1-(naphthalen-2-yl)-5-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (41)

Racemic



	RT	Area	% Area	Height
1	6.843	677172	2.70	52972
2	9.562	551930	2.20	36586
3	10.294	12053584	47.97	523621
4	15.437	11843442	47.14	442452

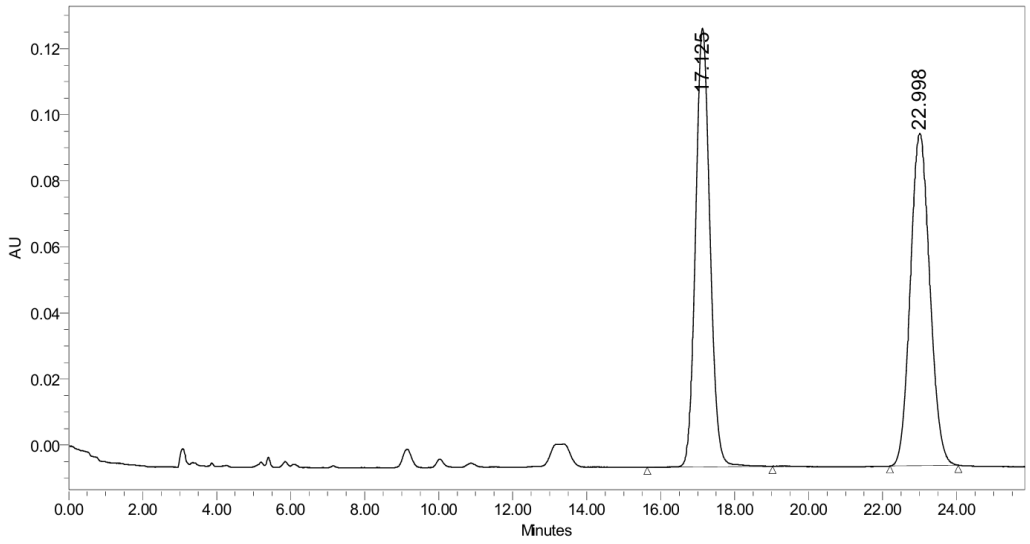
Enantioenriched



	RT	Area	% Area	Height
1	10.365	6450106	87.10	277180
2	15.608	955207	12.90	35668

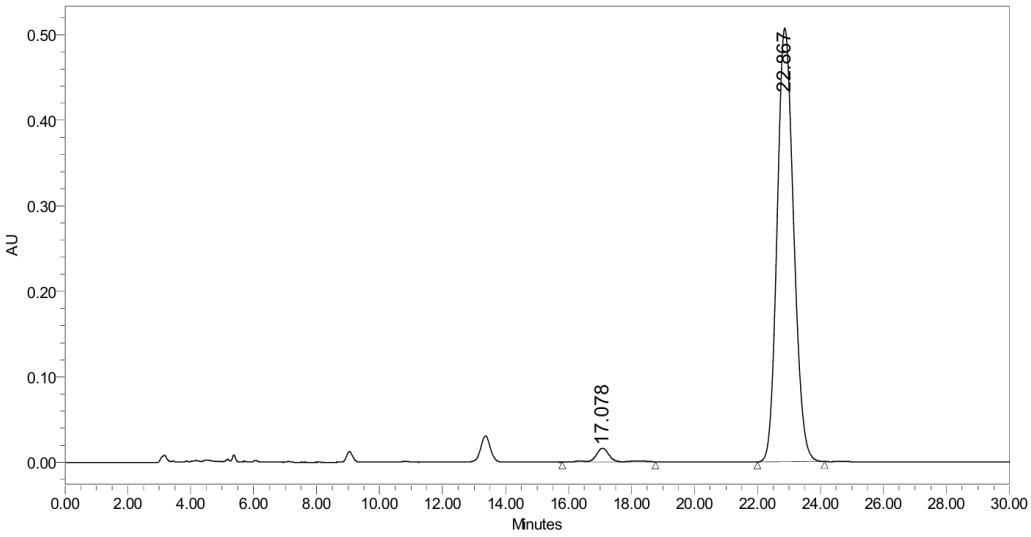
***N*-((*R*,2*E*,4*E*)-1-(furan-3-yl)-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (42)**

Racemic



	RT	Area	% Area	Height
1	17.125	3591123	49.64	132649
2	22.998	3642847	50.36	100573

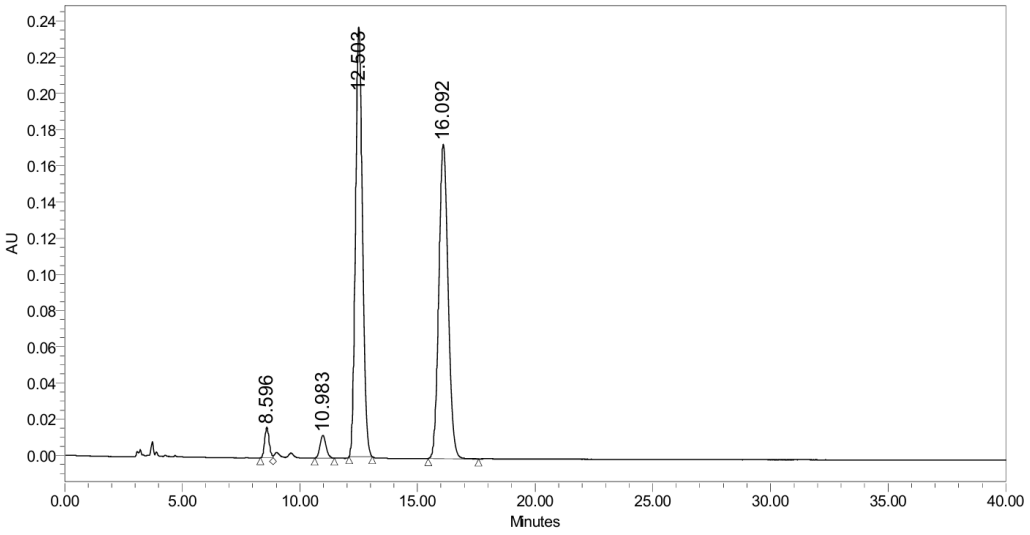
Enantioenriched



	RT	Area	% Area	Height
1	17.078	515724	2.71	16089
2	22.867	18541287	97.29	507156

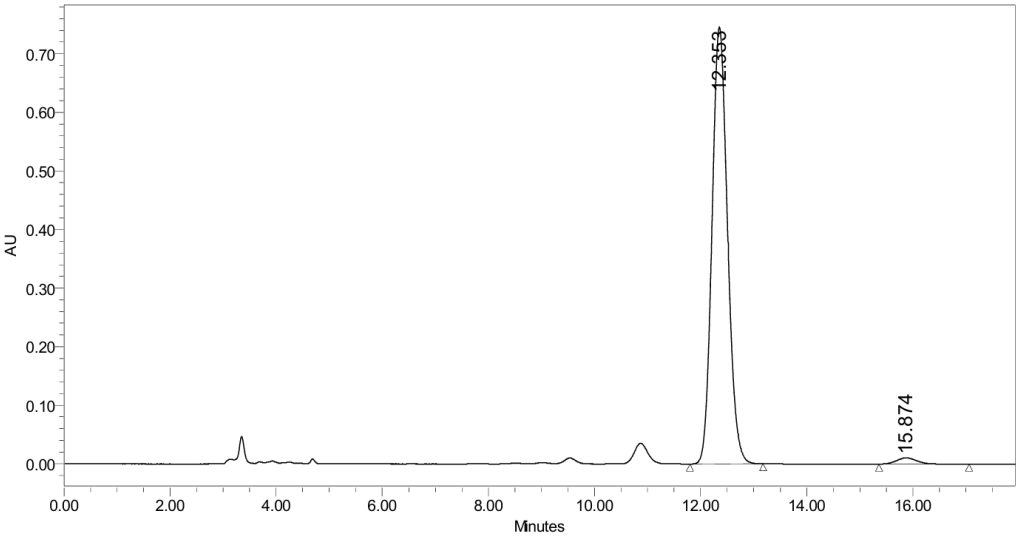
4-methyl-*N*-((*R*,2*E*,4*E*)-5-phenyl-1-(thiophen-3-yl)penta-2,4-dien-1-yl)benzenesulfonamide (43)

Racemic



	RT	Area	% Area	Height
1	8.596	220145	2.20	16811
2	10.983	223335	2.23	12577
3	12.503	4824746	48.16	237116
4	16.092	4749964	47.41	173782

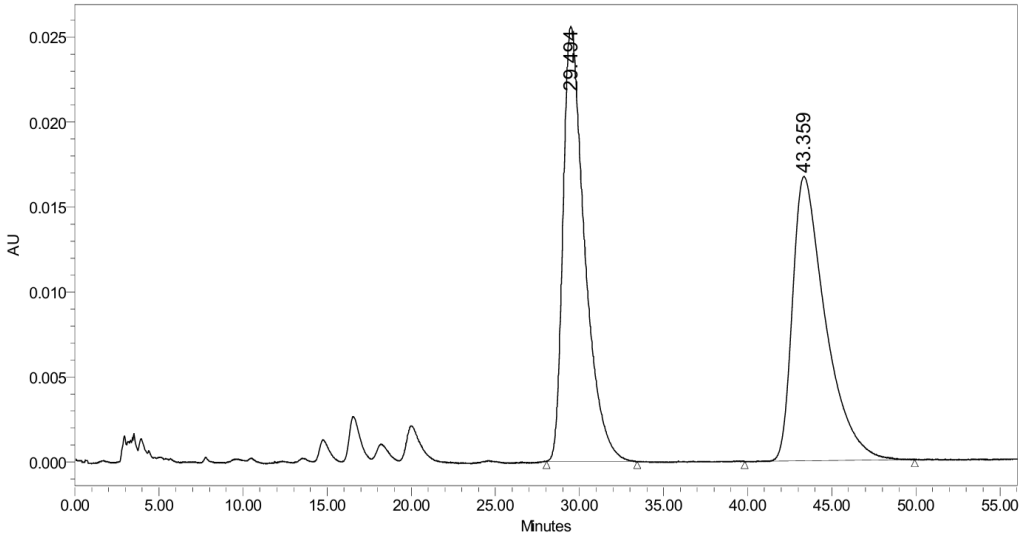
Enantioenriched



	RT	Area	% Area	Height
1	12.353	15188848	98.12	745939
2	15.874	290588	1.88	10585

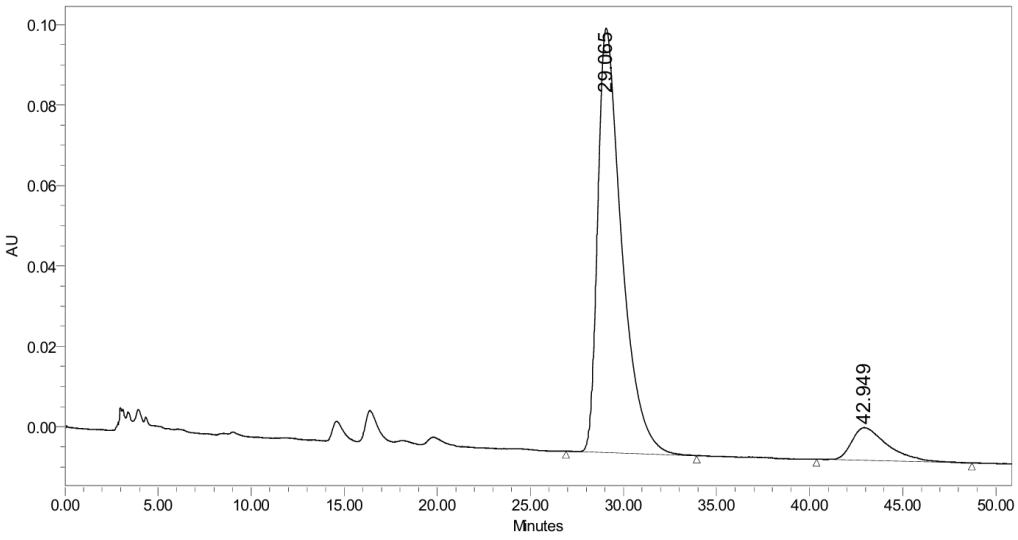
4-methyl-*N*-((*R*,2*E*,4*E*)-1-(4-oxo-4H-chromen-3-yl)-5-phenylpenta-2,4-dien-1-yl)benzenesulfonamide (44)

Racemic



	RT	Area	% Area	Height
1	29.494	2295030	50.32	25604
2	43.359	2265397	49.68	16733

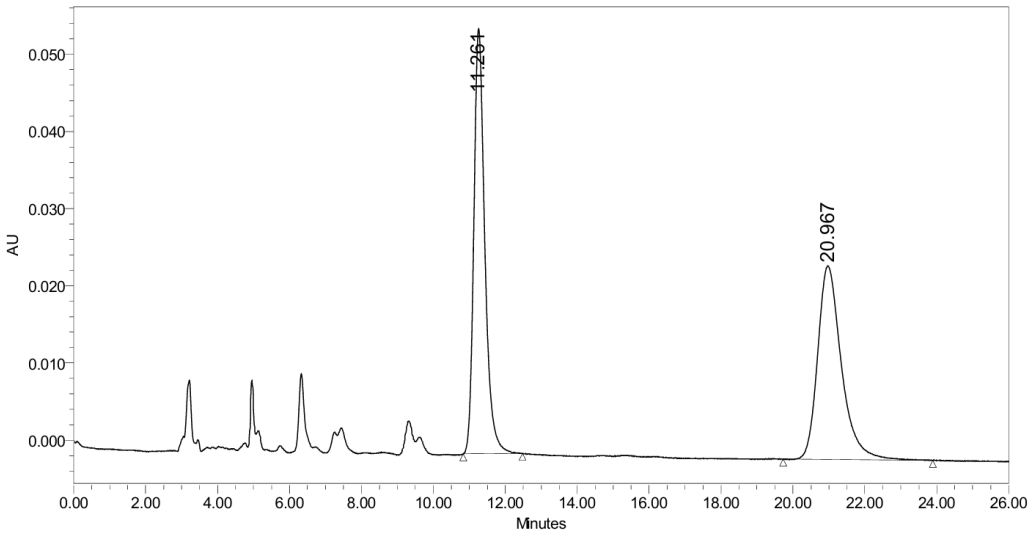
Enantioenriched



	RT	Area	% Area	Height
1	29.065	9453878	89.79	105520
2	42.949	1074869	10.21	8124

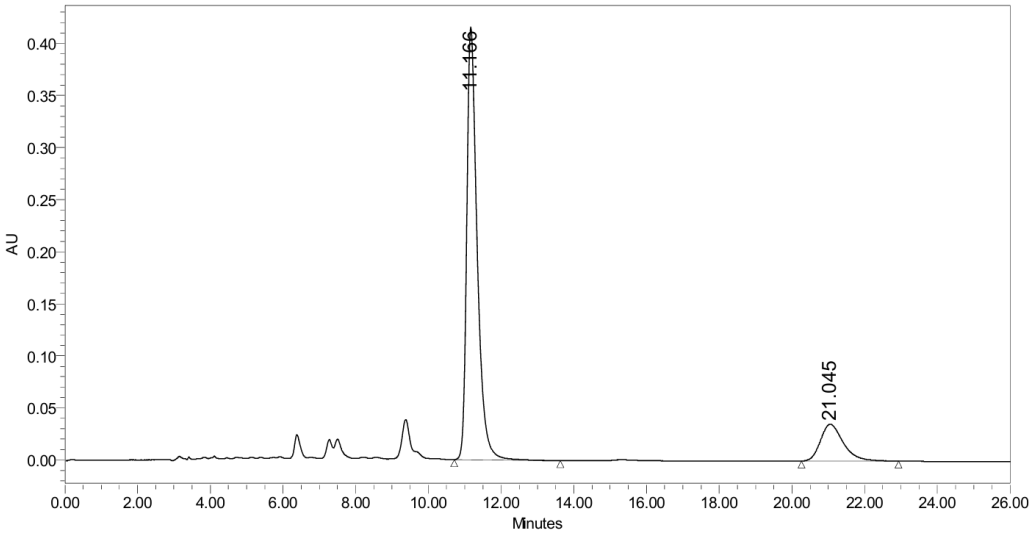
***N*-((*R*,1*E*,4*E*,6*E*)-1,7-diphenylhepta-1,4,6-trien-3-yl)-4-methylbenzenesulfonamide (45)**

Racemic



	RT	Area	% Area	Height
1	11.261	1157537	50.26	55082
2	20.967	1145570	49.74	25095

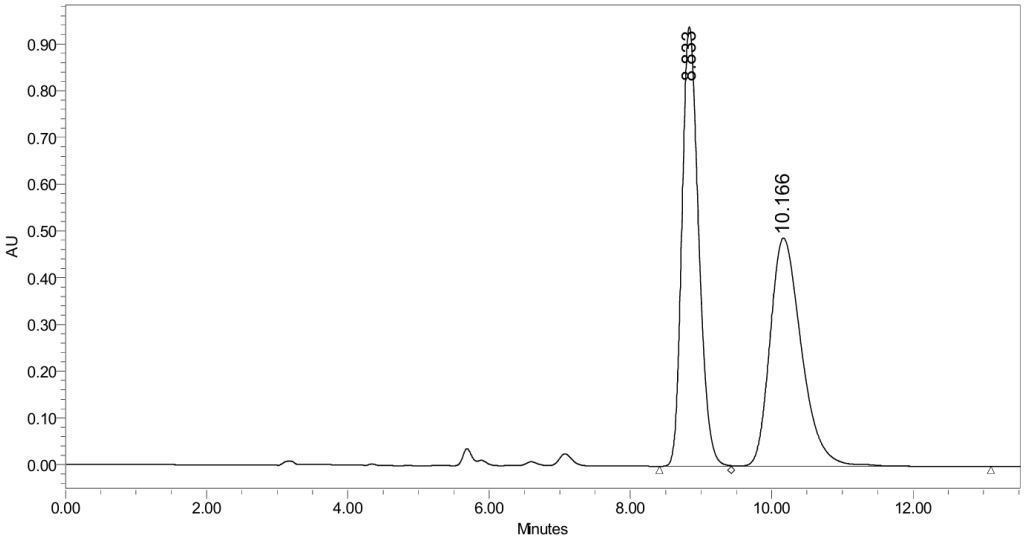
Enantioenriched



	RT	Area	% Area	Height
1	11.166	8312897	84.26	415400
2	21.045	1553360	15.74	35395

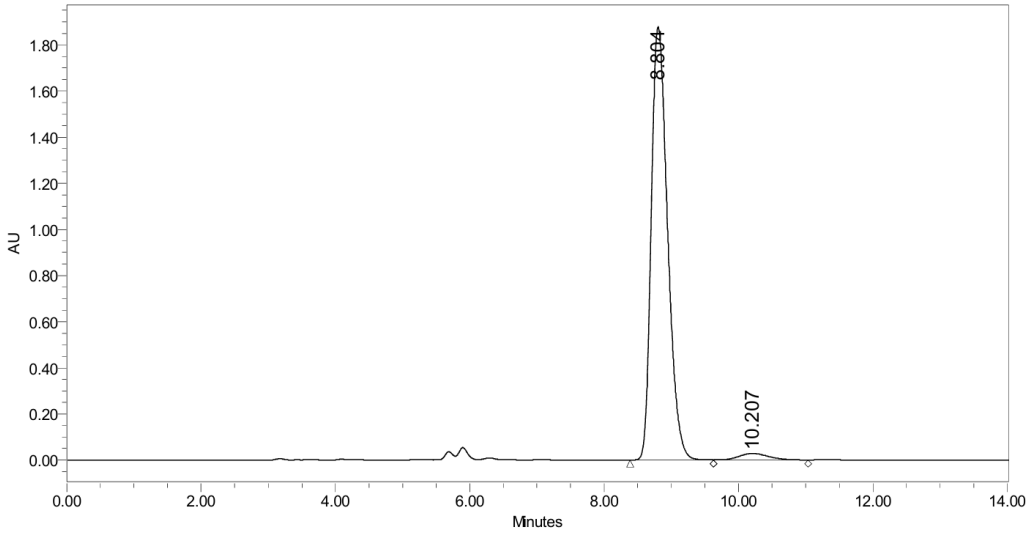
***N*-((*S*,2*E*,4*E*)-1-cyclohexyl-5-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (46)**

Racemic



	RT	Area	% Area	Height
1	8.833	15412585	50.45	939459
2	10.166	15136712	49.55	488446

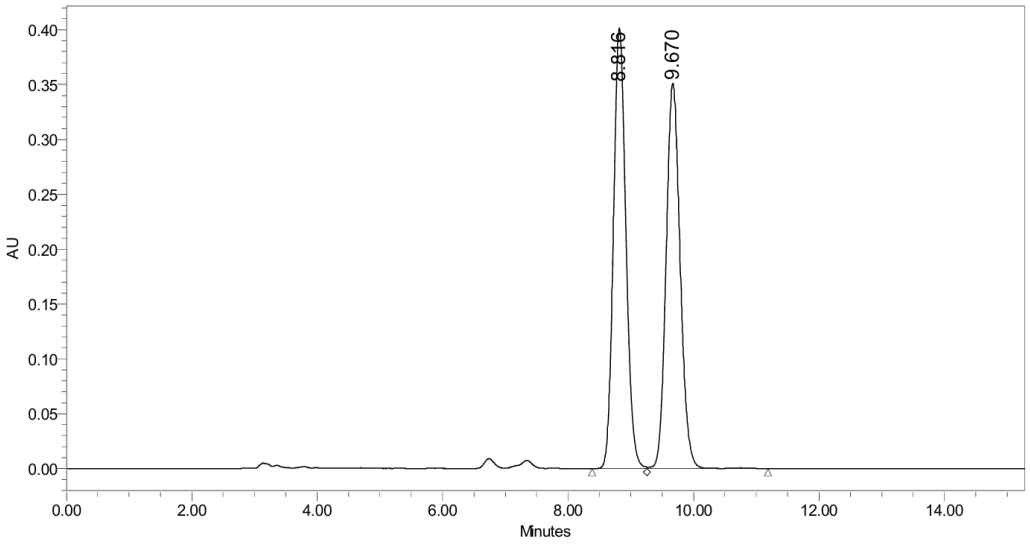
Enantioenriched



	RT	Area	% Area	Height
1	8.804	31532175	97.21	1878710
2	10.207	903878	2.79	28693

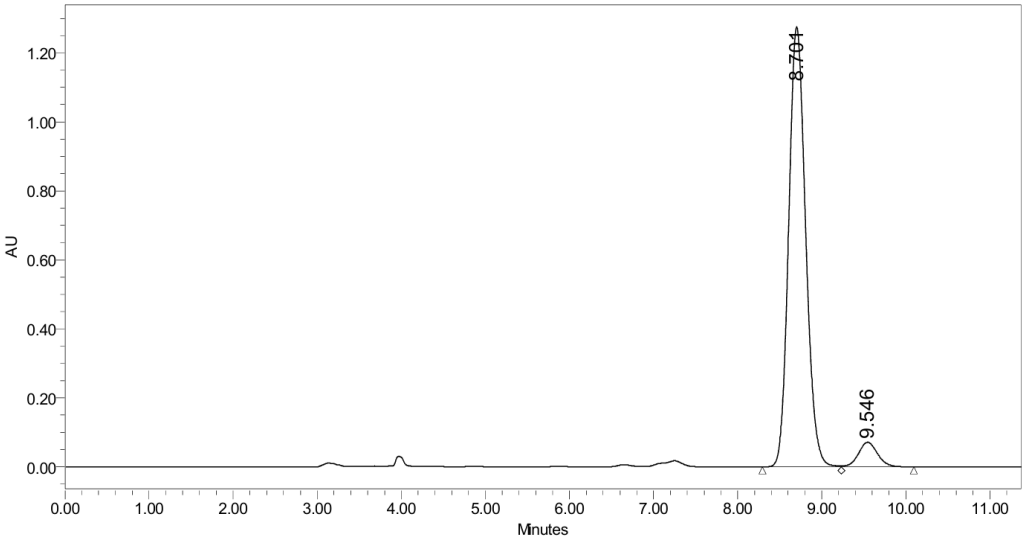
4-methyl-*N*-((*S*,4*E*,6*E*)-2-methyl-7-phenylhepta-4,6-dien-3-yl)benzenesulfonamide (47)

Racemic



	RT	Area	% Area	Height
1	8.816	5551161	50.55	401391
2	9.670	5430754	49.45	351151

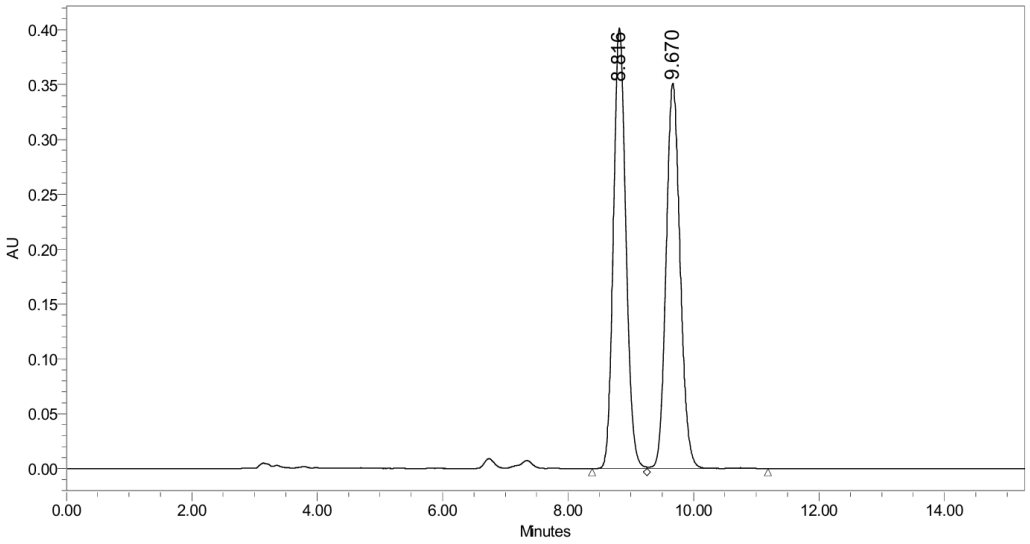
Enantioenriched



	RT	Area	% Area	Height
1	8.701	17928244	94.10	1275041
2	9.546	1123233	5.90	71058

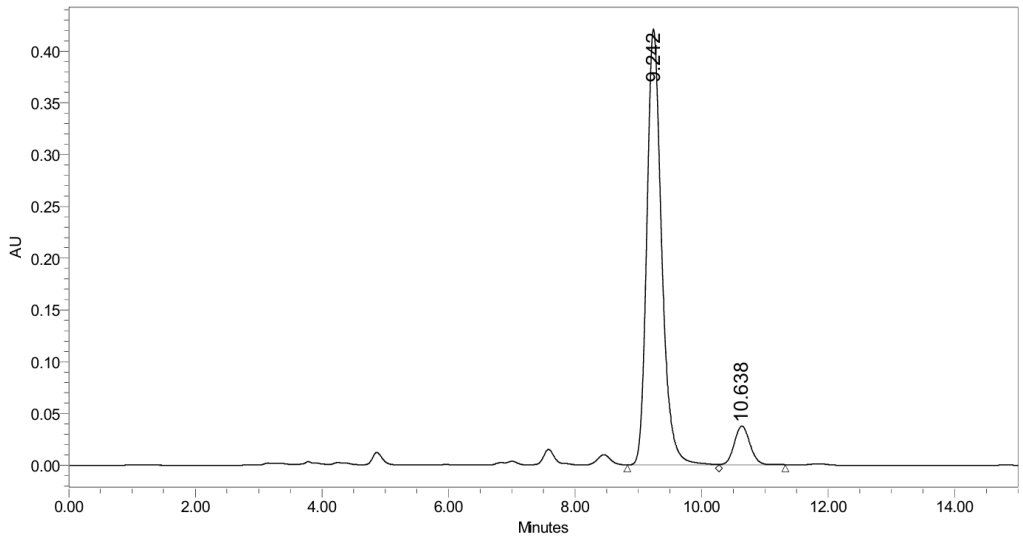
4-methyl-*N*-((*S*,5*E*,7*E*)-8-phenylocta-5,7-dien-4-yl)benzenesulfonamide (48)

Racemic



	RT	Area	% Area	Height
1	8.816	5551161	50.55	401391
2	9.670	5430754	49.45	351151

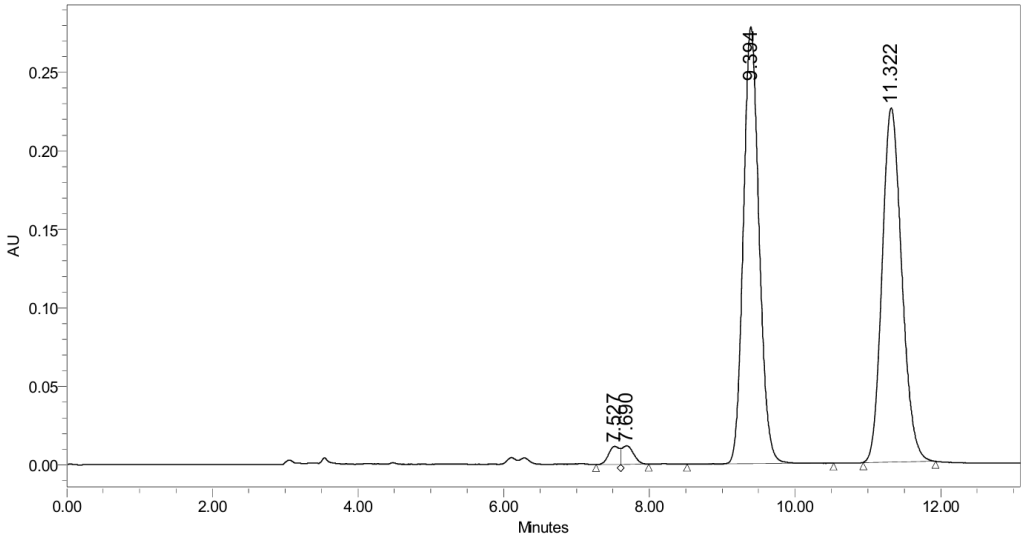
Enantioenriched



	RT	Area	% Area	Height
1	9.242	6859309	91.46	420668
2	10.638	640145	8.54	37357

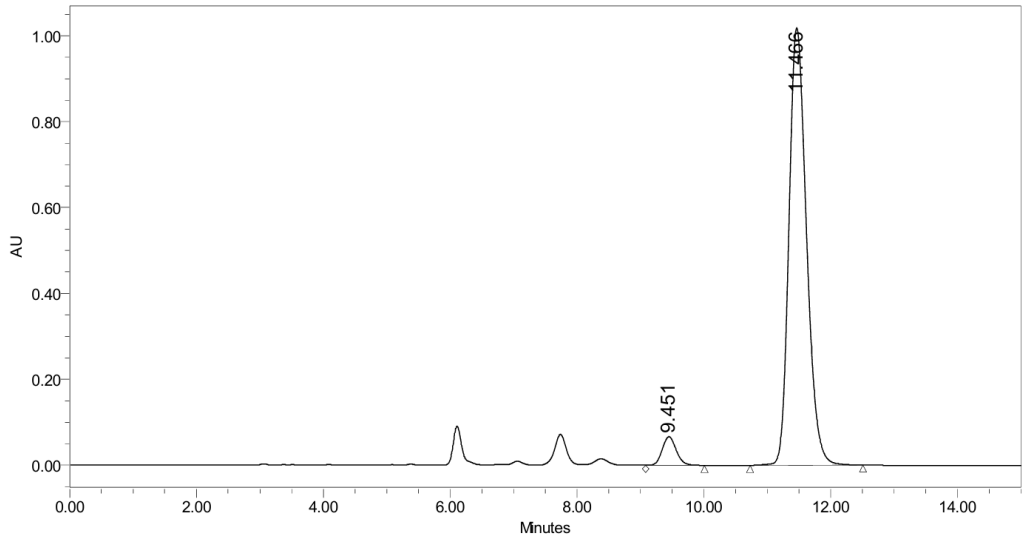
***N*-((*R*,2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-yl)-4-nitrobenzenesulfonamide (49)**

Racemic



	RT	Area	% Area	Height
1	7.527	120233	1.39	11535
2	7.690	132325	1.53	11849
3	9.394	4166089	48.11	278121
4	11.322	4240959	48.97	225479

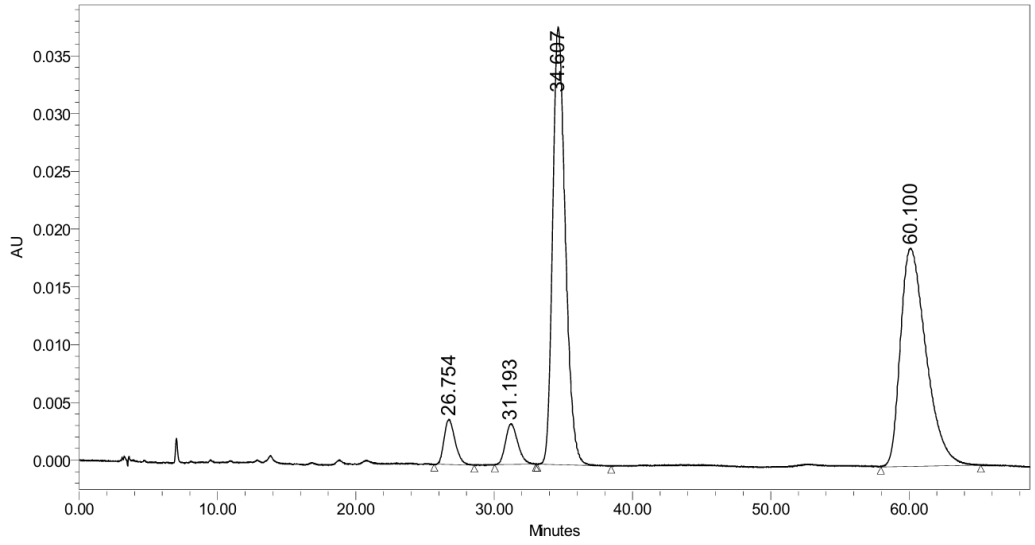
Enantioenriched



	RT	Area	% Area	Height
1	9.451	1012728	4.91	66450
2	11.466	19619860	95.09	1018809

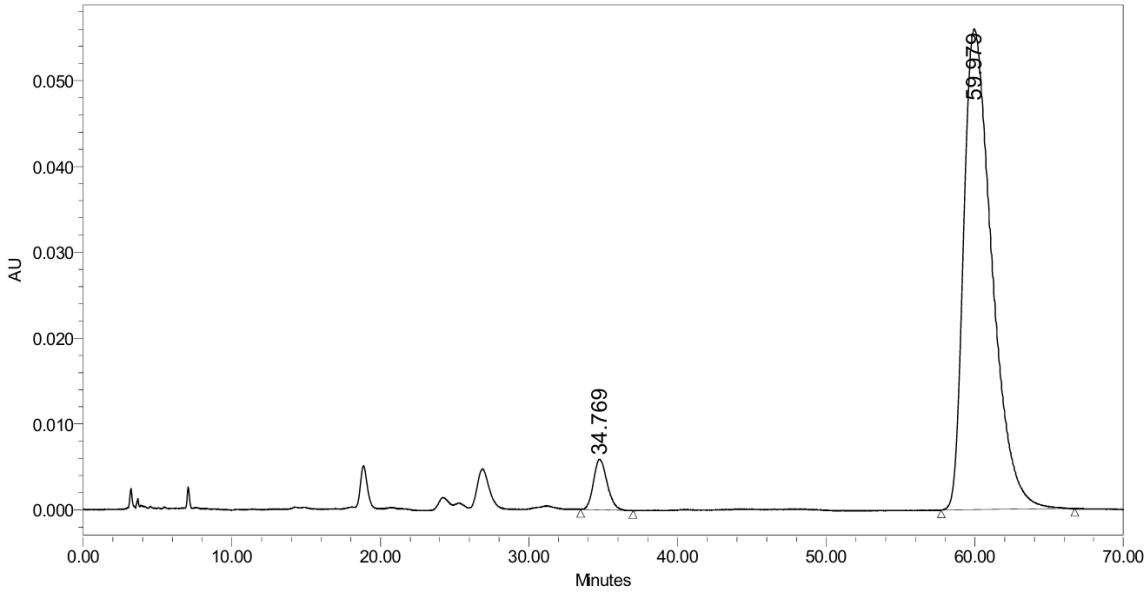
***N*-((*R*,2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-yl)thiophene-2-sulfonamide (50)**

Racemic



	RT	Area	% Area	Height
1	26.754	214782	4.06	3911
2	31.193	218401	4.12	3535
3	34.607	2427851	45.84	37890
4	60.100	2435198	45.98	18872

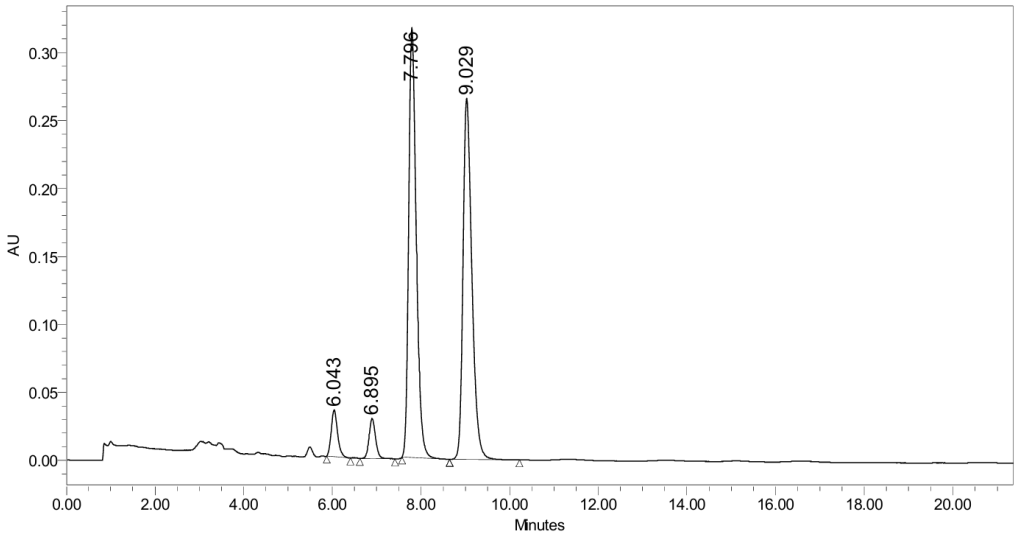
Enantioenriched



	RT	Area	% Area	Height
1	34.769	372986	4.79	5881
2	59.979	7410501	95.21	55978

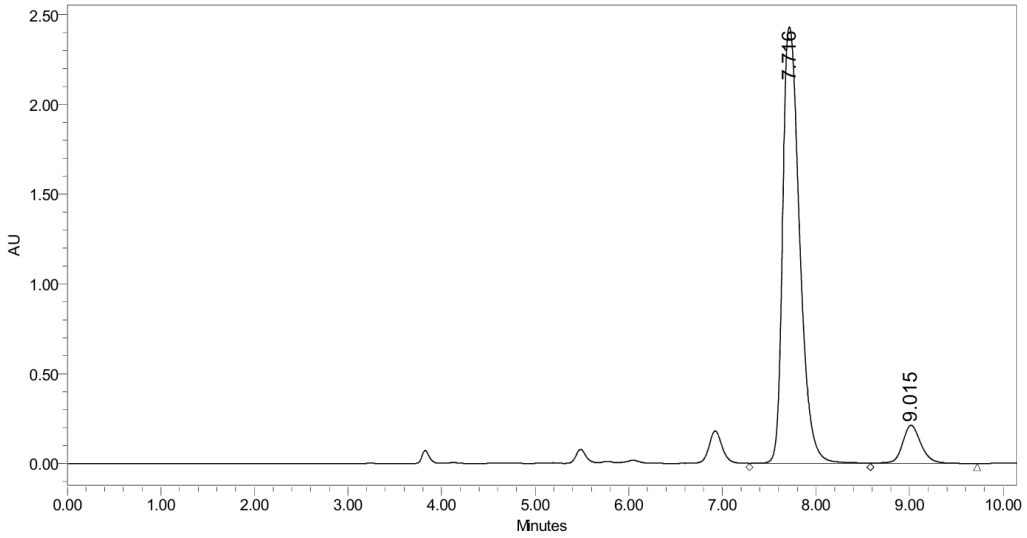
***N*-((*R*,2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-yl)methanesulfonamide (51)**

Racemic



	RT	Area	% Area	Height
1	6.043	340952	4.20	34379
2	6.895	298784	3.68	29439
3	7.796	3760523	46.37	316085
4	9.029	3709910	45.74	265597

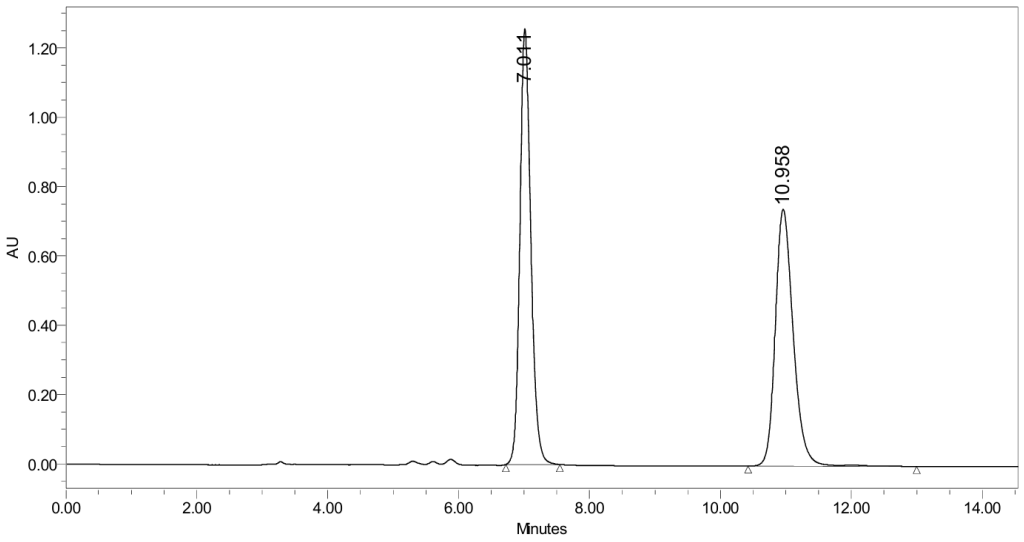
Enantioenriched



	RT	Area	% Area	Height
1	7.716	30760016	91.28	2430685
2	9.015	2938827	8.72	212883

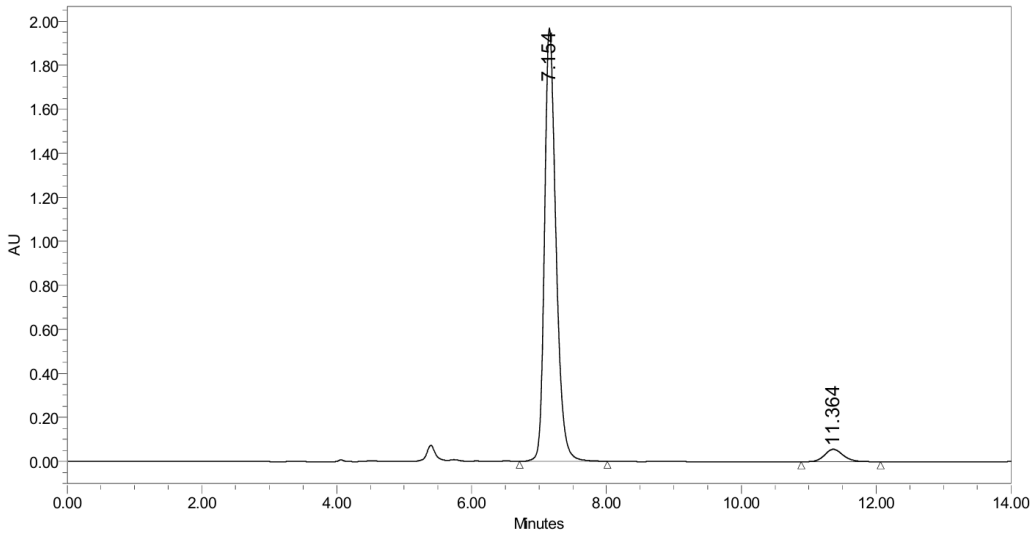
***N*-((*R*,2*E*,4*E*)-1,5-diphenylpenta-2,4-dien-1-yl)-4-(5-(p-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)benzenesulfonamide (52)**

Racemic



	RT	Area	% Area	Height
1	7.011	14504245	50.65	1255921
2	10.958	14131733	49.35	740554

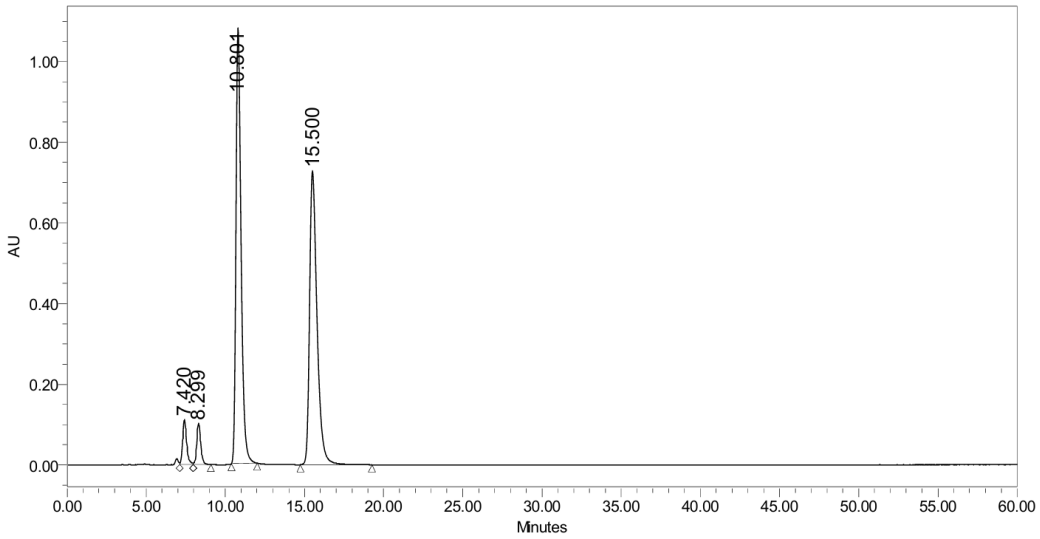
Enantioenriched



	RT	Area	% Area	Height
1	7.154	23309149	95.48	1968092
2	11.364	1103797	4.52	56777

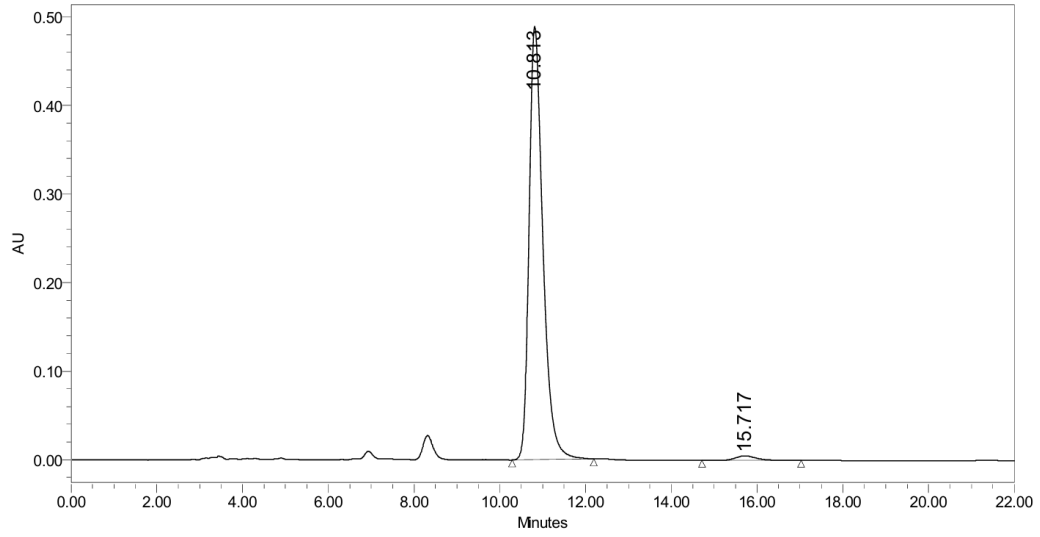
***N*-((*R*,2*E*,4*E*)-5-(6-(3-((3*r*,5*r*,7*r*)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)-1-phenylpenta-2,4-dien-1-yl)-4-methylbenzenesulfonamide (53)**

Racemic



	RT	Area	% Area	Height
1	7.420	1947095	3.76	111739
2	8.299	1773376	3.42	102395
3	10.801	24262721	46.81	1079417
4	15.500	23850395	46.01	728111

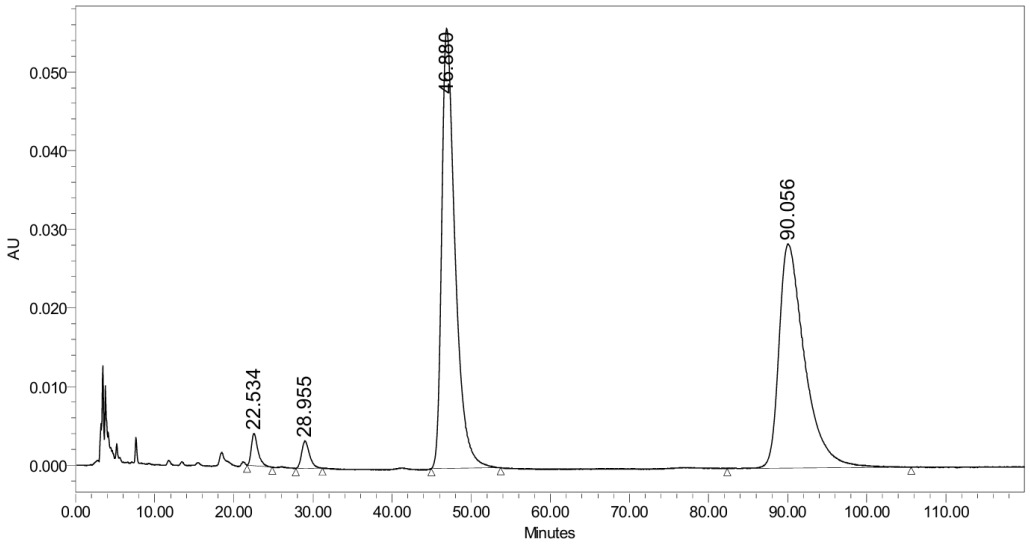
Enantioenriched



	RT	Area	% Area	Height
1	10.813	10955681	98.37	489110
2	15.717	181049	1.63	5150

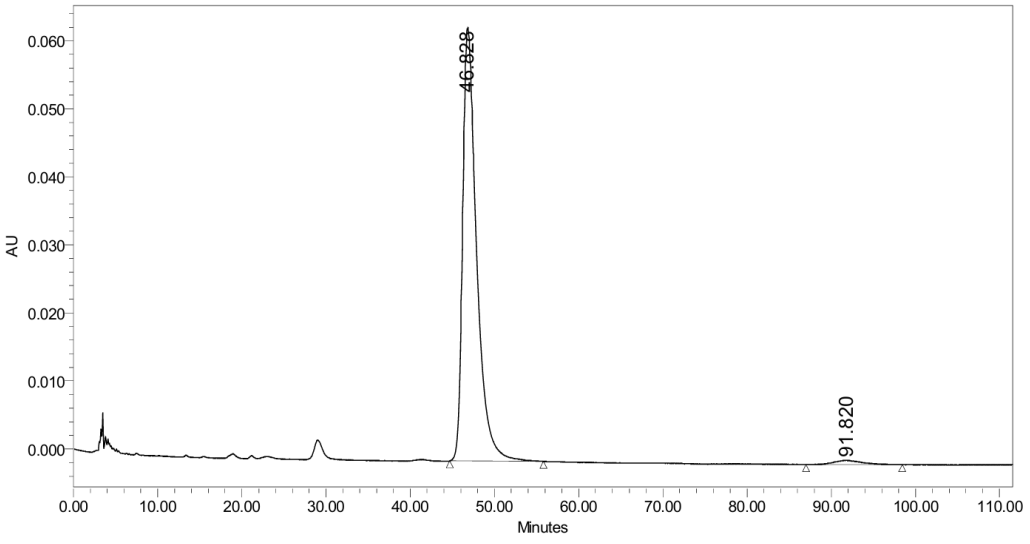
4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)phenyl 2-(1-(4-chlorobenzoyl)-2,5-dimethyl-1*H*-indol-3-yl)acetate (54)

Racemic



	RT	Area	% Area	Height
1	22.534	236916	1.76	4098
2	28.955	238505	1.77	3472
3	46.880	6525263	48.56	55937
4	90.056	6436913	47.90	28480

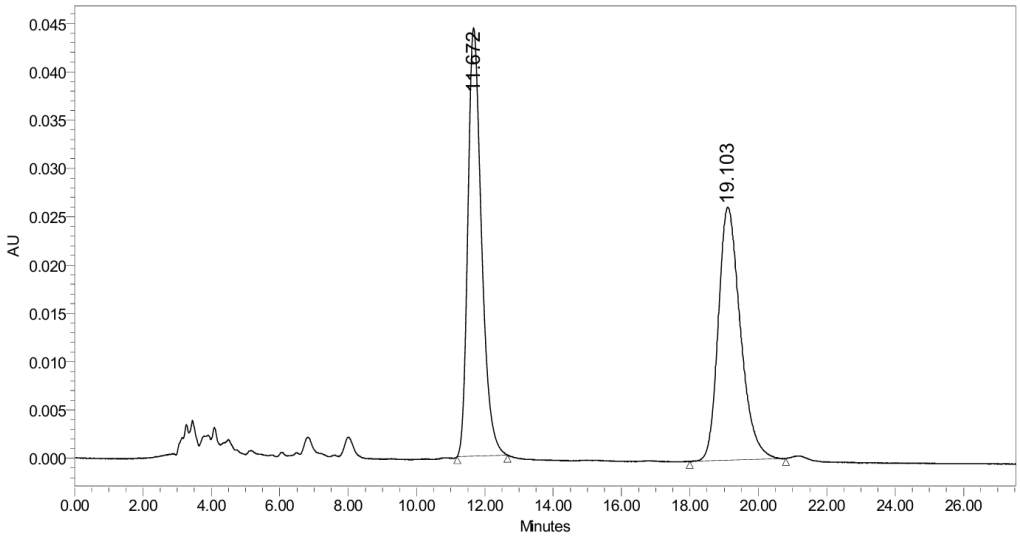
Enantioenriched



	RT	Area	% Area	Height
1	46.828	7405877	98.17	63690
2	91.820	138194	1.83	610

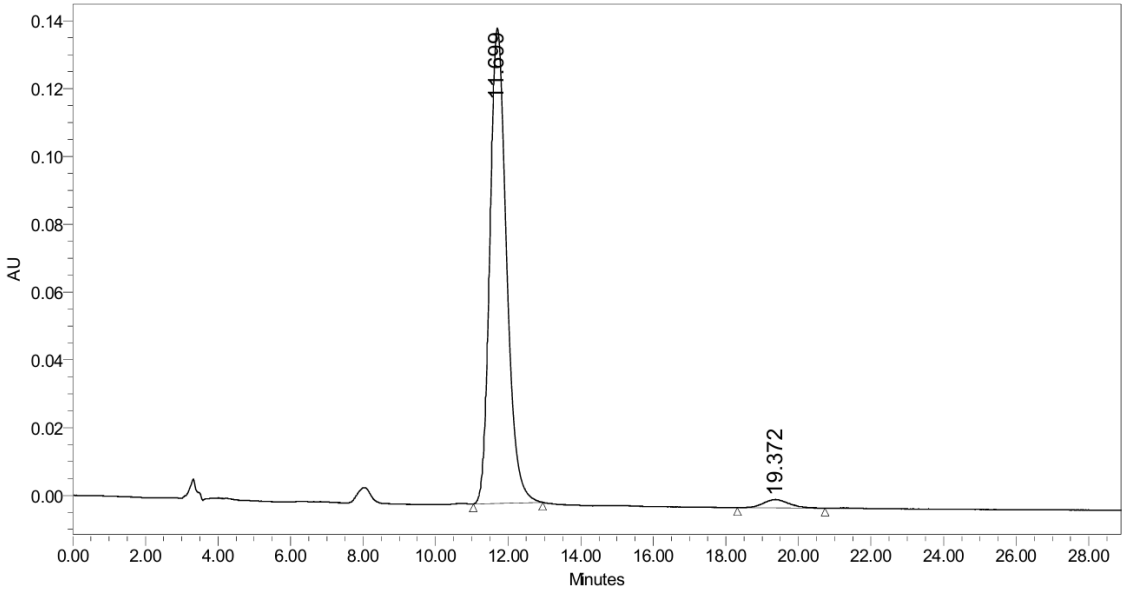
4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)phenyl (*R*)-4-((3*R*,5*R*,7*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-((tert-butyldimethylsilyl)oxy)-7-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (55)

Racemic



	RT	Area	% Area	Height
1	11.672	1221764	50.89	44312
2	19.103	1179007	49.11	26193

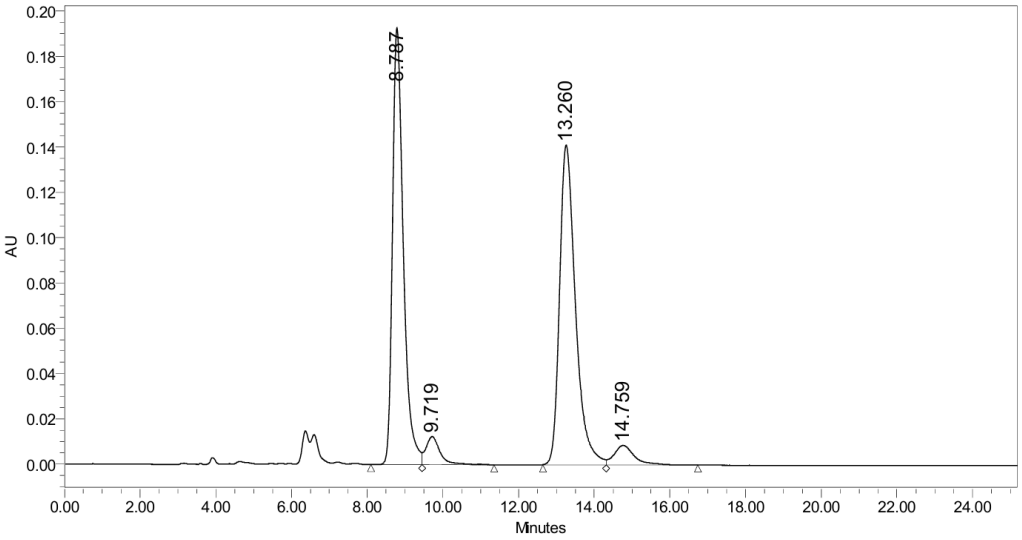
Enantioenriched



	RT	Area	% Area	Height
1	11.699	4466449	97.46	140140
2	19.372	116343	2.54	2431

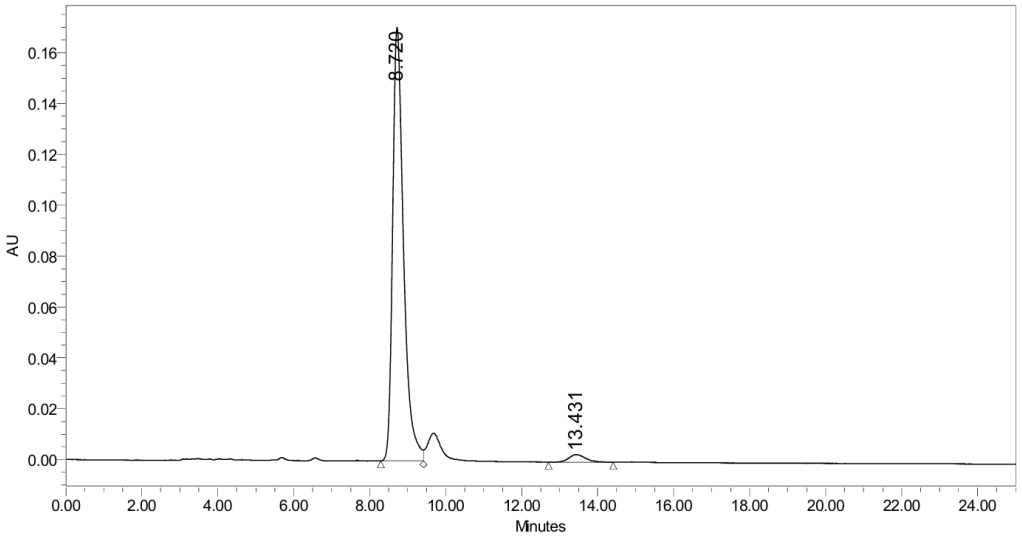
4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)phenyl (4*aS*,6*aS*,6*bR*,8*aR*,10*S*,12*aR*,12*bR*,14*bS*)-10-acetoxy-2,2,6*a*,6*b*,9,9,12*a*-heptamethyl-1,3,4,5,6,6*a*,6*b*,7,8,8*a*,9,10,11,12,12*a*,12*b*,13,14*b*-octadecahydropicene-4a(2*H*)-carboxylate (56)

Racemic



	RT	Area	% Area	Height
1	8.787	3841193	44.59	192814
2	9.719	322937	3.75	12413
3	13.260	4130099	47.95	141159
4	14.759	319766	3.71	8639

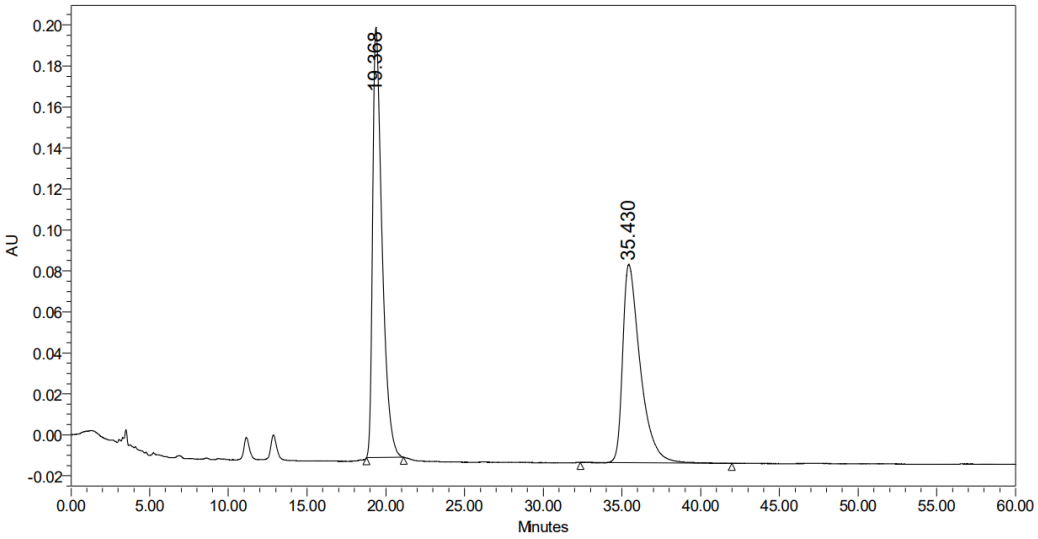
Enantioenriched



	RT	Area	% Area	Height
1	8.720	3406373	97.37	170428
2	13.431	91894	2.63	2970

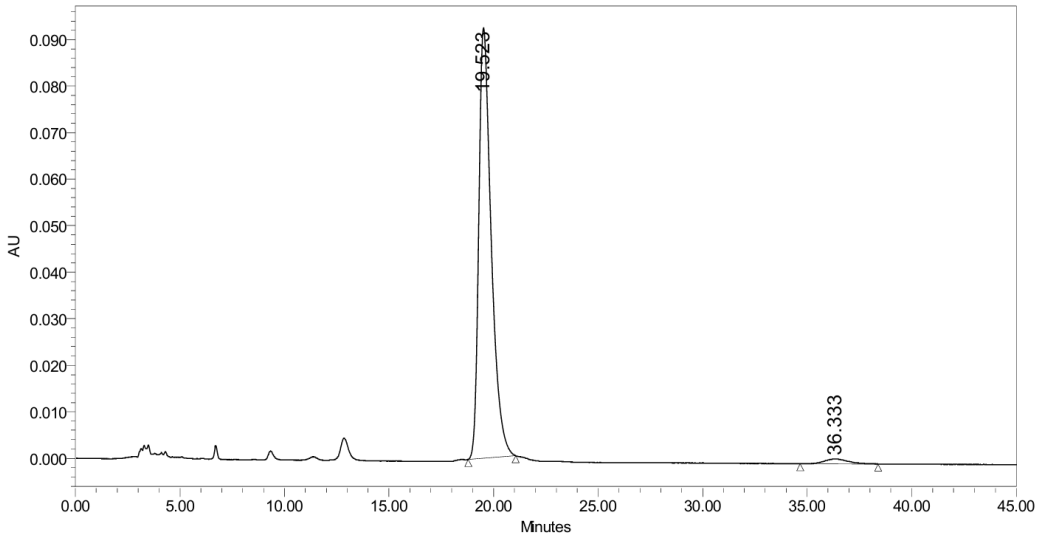
4-((*R*,1*E*,3*E*)-5-((4-methylphenyl)sulfonamido)-5-phenylpenta-1,3-dien-1-yl)phenyl (*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (57)

Racemic



	RT	Area	% Area	Height
1	19.368	8737610	53.78	209921
2	35.430	7508863	46.22	96859

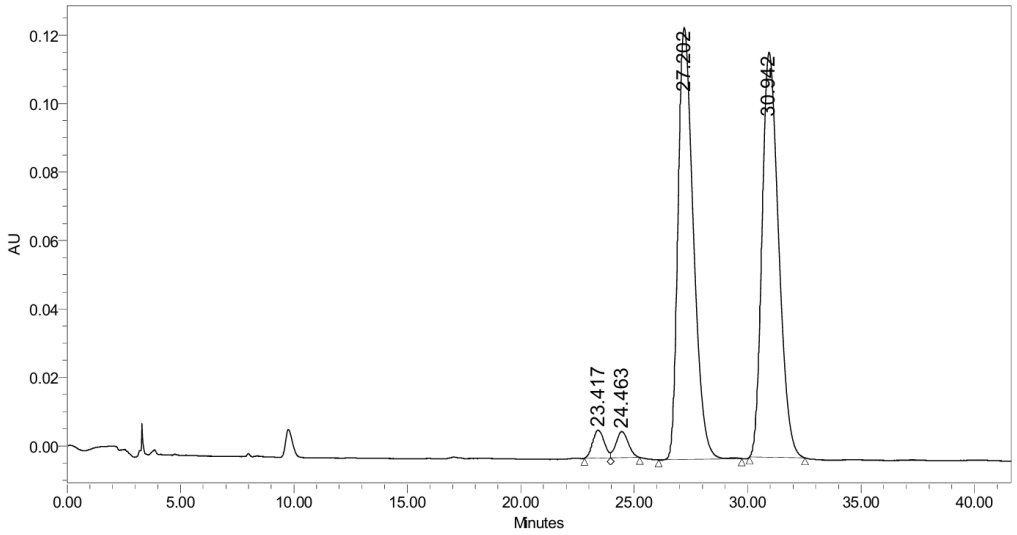
Enantioenriched



	RT	Area	% Area	Height
1	19.523	3796969	97.91	92454
2	36.333	81207	2.09	1058

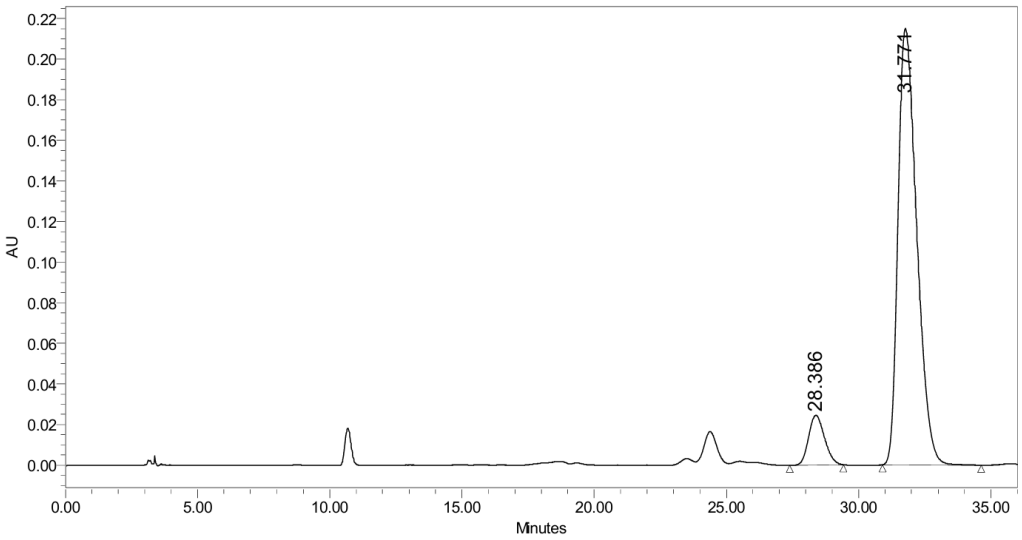
***N*-((*S*,5*E*,7*E*)-8-(dimethyl(phenyl)silyl)-2-methylocta-5,7-dien-4-yl)-4-methylbenzenesulfonamide (58)**

Racemic



	RT	Area	% Area	Height
1	23.417	287486	2.30	8156
2	24.463	285552	2.28	7621
3	27.202	5935394	47.47	126260
4	30.942	5995603	47.95	118323

Enantioenriched



	RT	Area	% Area	Height
1	28.386	1027162	8.92	24537
2	31.771	10482358	91.08	214859

11. References

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