
Supporting Information for

Branch- and Enantioselective Allylic C–H Alkylation Works Well for Almost All

Types of α -Alkenes

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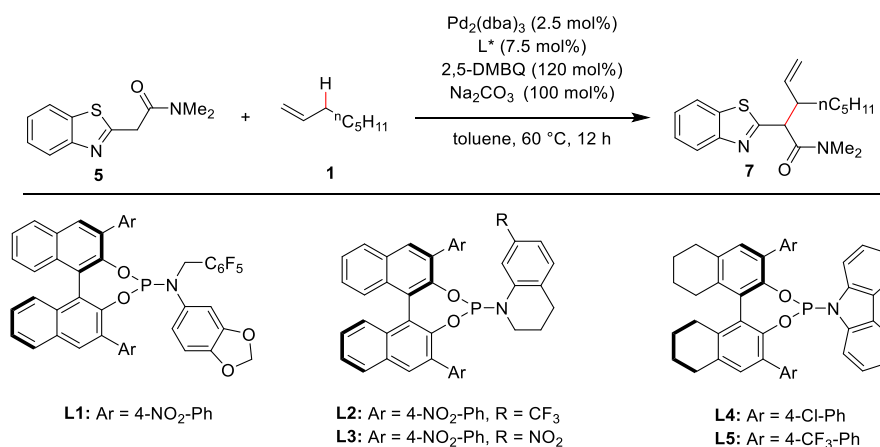
1. General information

NMR spectra were recorded on a Bruker-400 MHz spectrometer. 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 : $\delta\text{H} = 7.26$ ppm, $\delta\text{C} = 77.16$ ppm). Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-343 polarimeter. The high resolution mass spectra were recorded on a Thermo LTQ Orbitrap XL (ESI^+) or a P-SIMS-Gly of Bruker Daltonics Inc (EI^+). HPLC analysis was performed on Waters-Breeze (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump). Chiralpak IE, IF, IG, IC, OD-H, AD-H, OJ columns were purchased from Daicel Chemical Industries, LTD. Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer. The absolute configuration of **8** was assigned by the X-ray analysis.

Materials: Starting materials were purchased from commercial suppliers (Aldrich, Acros, TCI, Energy Chemical, Adamas-Beta, J&K, etc.) and used as supplied unless otherwise stated. $\text{Pd}_2(\text{dba})_3$ was purchased from Aldrich. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise.

2. Optimization of reaction conditions

2.1 Optimization of general conditions

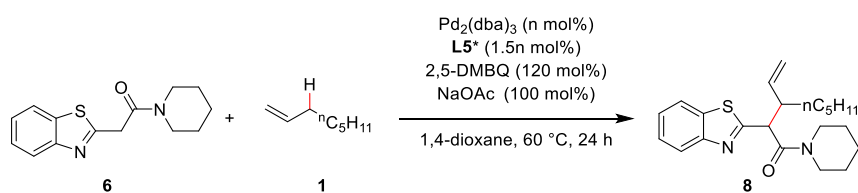


entry	L	solvent	base	temp.	yield (%) ^b	e.e. (%) ^c	d.r.	b/l
1	L1	toluene	Na_2CO_3	60 °C	18	9	10:1	8:1
2	L2	toluene	Na_2CO_3	60 °C	57	62	19:1	>20:1
3	L3	toluene	Na_2CO_3	60 °C	25	39	19:1	20:1
4	L4	toluene	Na_2CO_3	60 °C	88	76	12:1	>20:1
5	L5	toluene	Na_2CO_3	60 °C	75	84	15:1	>20:1
6	L5	THF	Na_2CO_3	60 °C	95	78	>20:1	20:1
7	L5	DCM	Na_2CO_3	60 °C	89	75	15:1	>20:1
8	L5	1,4-dioxane	Na_2CO_3	60 °C	89	86	>20:1	>20:1

9	L5	MTBE	Na ₂ CO ₃	60 °C	95	82	18:1	14:1
10	L5	p-xylene	Na ₂ CO ₃	60 °C	95	86	13:1	>20:1
11	L5	toluene	NaOAc	60 °C	95	85	14:1	>20:1
12	L5	toluene	K ₂ HPO ₄	60 °C	95	85	14:1	20:1
13	L5	toluene	Li ₂ CO ₃	60 °C	95	84	13:1	15:1
14	L5	toluene	Cs ₂ CO ₃	60 °C	48	69	10:1	13:1
15	L5	toluene	NaHCO ₃	60 °C	83	85	15:1	>20:1
16	L5	toluene	Et ₃ N	60 °C	79	84	17:1	10:1
17	L5	toluene	NaOAc	50 °C	30	88	21:1	>20:1
18	L5	1,4-dioxane	NaOAc	50 °C	65	87	>20:1	20:1
19	L5	1,4-dioxane	NaOAc	55 °C	94	86	>20:1	20:1
20	L5	1,4-dioxane	NaOAc	50 °C	95^d	87	>20:1	>20:1

^aReaction conditions: **5** (0.10 mmol), **1** (0.20 mmol), base (0.10 mmol), Pd₂(dba)₃(0.0025 mmol), **L** (0.0075 mmol), 2,5-DMBQ (0.12 mmol), toluene (1.0 mL), 60 °C, 12 h. >20:1 d.r., >20:1 b/l, which were determined by ¹H nuclear magnetic resonance (NMR) analysis of the crude products. The absolute stereochemistry of **3a** was assigned by analogy. ^bDetermined by ¹H NMR analysis of the crude products based on internal standard. ^cDetermined by high performance liquid chromatography using a chiral column. ^d24 h.

2.2 Screening of Pd catalytic capacity



Entry	n	yield (%) ^b	e.e. (%) ^c	d.r.	b/l
1	1	trace	-	-	-
2	1.5	18	90	18:1	18:1
3	2	59	91	>20:1	>20:1
4	2.5	93	90	>20:1	>20:1

^aReaction conditions: **6** (0.10 mmol), **1** (0.20 mmol), base (0.10 mmol), Pd₂(dba)₃(0.0025 mmol), **L5** (0.0075 mmol), 2,5-DMBQ (0.12 mmol), 1,4-dioxane (1.0 mL), 60 °C, 24 h. >20:1 d.r., >20:1 b/l, which were determined by ¹H nuclear magnetic resonance (¹H NMR) analysis of the crude products. The absolute stereochemistry of **3a** was assigned by analogy. ^bDetermined by ¹H NMR analysis of the crude products based on internal standard. ^cDetermined by high performance liquid chromatography using a chiral column.

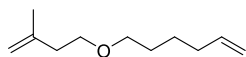
3. Experimental procedures for the synthesis of compounds s1, s2-s7 and L1-L7

3.1 Synthesis of s1



To a cooled suspension of NaH (0.48 g, 12 mmol, 60% in mineral oil) in DMF (10 ml) was slowly added 3-methyl-3-buten-1-ol (1.0 mL, 10 mmol) at 0 °C. Then 6-bromo-1-hexene (1.2 mL, 10 mmol) was added slowly and the reaction was allowed to warm to RT. After stirring at RT for 16 h, the resulting suspension was poured into saturated aqueous NH₄Cl at 0 °C and extracted with *n*-hexane (10 mL × 3). The *n*-hexane layer was washed with H₂O (10 mL × 3), brine (10 mL), dried over Na₂SO₄, filtered, and concentrated in vacuo. Purification of the residue by column chromatography (*n*-hexane) gave **s1**.¹

6-((3-methylbut-3-en-1-yl)oxy)hex-1-ene (**s1**).



Colorless liquid. Yield: 53%, 0.9 g.

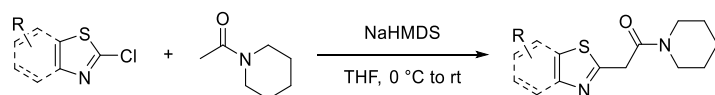
¹H NMR (400 MHz, CDCl₃) δ 5.92 – 5.69 (m, 1H), 5.10 – 4.89 (m, 2H), 4.82 – 4.66 (m, 2H), 3.52 (t, *J* = 7.0 Hz, 2H), 3.43 (t, *J* = 6.6 Hz, 2H), 2.30 (td, *J* = 7.0, 1.2 Hz, 2H), 2.14 – 2.02 (m, 2H), 1.75 (s, 3H), 1.64 – 1.54 (m, 2H), 1.50 – 1.40 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 142.99, 138.76, 114.45, 111.27, 70.75, 69.32, 37.81, 33.56, 29.17, 25.50, 22.76.

IR (KBr): γ : 3076, 2971, 2936, 2859, 1641, 1441, 1374, 1115, 993, 909, 748 cm⁻¹.

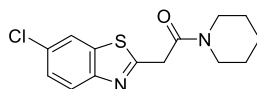
HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₁₁H₂₁O]⁺ requires 169.1587, found 169.1589.

3.2 Synthesis of s2-s7



General procedure I: To a solution of 2-chlorobenzothiazole (1 equiv.) and 1-(piperidin-1-yl)ethan-1-one (1.5 equiv.) in THF (0.67 M) at 0 °C was added NaHMDS (3 equiv., 2.0 M in THF) over 5 min. After stirring at 0 °C for 5 h, the reaction was warmed to room temperature and stirred for 18 h before being quenched carefully with 1 M aqueous NH₄Cl solution. The aqueous layer was separated and extracted with ethyl acetate (3 × 10 mL/10 mmol). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated in vacuo. Purification of the residue by column chromatography (CH₂Cl₂ to 2% MeOH/CH₂Cl₂) gave the corresponding product.²

2-(6-chlorobenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)ethan-1-one (**s2**).



Wheat solid. Yield: 96%.

¹H NMR (400 MHz, CDCl₃) δ 8.00 – 7.70 (m, 2H), 7.40 (dd, *J* = 8.7, 2.1 Hz, 1H), 4.21 (s, 2H), 3.72 – 3.39 (m, 4H), 1.72 – 1.42 (m, 6H).

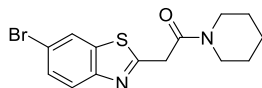
¹³C NMR (101 MHz, CDCl₃) δ 165.60, 165.50, 151.07, 137.10, 130.96, 126.70, 123.46, 121.16, 47.36, 43.28, 39.33,

26.36, 25.41, 24.34.

IR (KBr): γ : 2937, 2856, 1646, 1591, 1473, 1266, 1222, 1136, 1014, 952, 815, 765, 670 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{14}H_{16}ClN_2OS]^+$ requires 295.0666, found 295.0679.

2-(6-bromobenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)ethan-1-one (s3).



Beige solid. Yield: 94%.

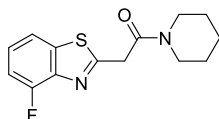
^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, J = 2.0 Hz, 1H), 7.82 (d, J = 8.7 Hz, 1H), 7.55 (dd, J = 8.7, 2.0 Hz, 1H), 4.22 (s, 2H), 3.64 – 3.32 (m, 4H), 1.90 – 1.39 (m, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 165.58, 165.56, 151.40, 137.60, 129.40, 124.10, 123.84, 118.65, 47.36, 43.29, 39.34, 26.37, 25.42, 24.35.

IR (KBr): γ : 2929, 2854, 1644, 1435, 1266, 1136, 1015, 813, 749 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{14}H_{16}BrN_2OS]^+$ requires 339.0161, found 339.0172.

2-(4-fluorobenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)ethan-1-one (s4).



Light yellow solid. Yield: 67%.

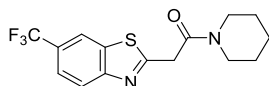
^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, J = 8.1 Hz, 1H), 7.33 (td, J = 8.0, 4.6 Hz, 1H), 7.16 (dd, J = 10.4, 8.1 Hz, 1H), 4.28 (s, 2H), 3.69 – 3.49 (m, 4H), 1.74 – 1.49 (m, 6H). **^{19}F NMR** (376 MHz, CDCl_3) δ -122.99.

^{13}C NMR (101 MHz, CDCl_3) δ 165.82, 165.64, 156.82, 154.28, 141.24, 141.11, 138.72, 138.68, 125.80, 125.73, 117.28, 117.24, 111.61, 111.43, 47.32, 43.28, 39.32, 26.34, 25.42, 24.34.

IR (KBr): γ : 2943, 2845, 1634, 1567, 1443, 1257, 1186, 1013, 776, 748 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{14}H_{16}FN_2OS]^+$ requires 279.0962, found 279.0967.

1-(piperidin-1-yl)-2-(6-(trifluoromethyl)benzo[d]thiazol-2-yl)ethan-1-one (s5).



Red solid. Yield: 52%.

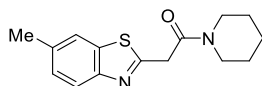
^1H NMR (400 MHz, CDCl_3) δ 8.18 (s, 1H), 8.06 (d, J = 8.5 Hz, 1H), 7.70 (d, J = 8.6, 1.7 Hz, 1H), 4.28 (s, 2H), 3.71 – 3.48 (m, 4H), 1.72 – 1.51 (m, 6H). **^{19}F NMR** (376 MHz, CDCl_3) δ -61.38.

^{13}C NMR (101 MHz, CDCl_3) δ 168.34, 165.42, 154.40, 136.00, 123.08, 122.92, 122.88, 119.27, 119.23, 47.34, 43.31, 39.35, 26.37, 25.40, 24.32.

IR (KBr): γ : 2937, 2858, 1644, 1510, 1445, 1412, 1320, 1275, 1164, 1122, 1082, 1050, 828 cm^{-1} .

HRMS (ESI): m/z $[M + Na]^+$ calcd for $[C_{15}H_{15}F_3N_2NaOS]^+$ requires 351.0749, found 351.0759.

2-(6-methylbenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)ethan-1-one (s6).



Yellow solid. Yield: 91%.

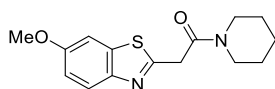
¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.3 Hz, 1H), 7.64 (s, 1H), 7.25 (d, *J* = 7.3 Hz, 1H), 4.20 (s, 2H), 3.77 – 3.41 (m, 4H), 2.47 (s, 3H), 1.66 – 1.38 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 165.94, 163.69, 150.72, 135.98, 135.11, 127.49, 122.19, 121.30, 47.41, 43.24, 39.75, 26.32, 25.42, 24.36, 21.51.

IR (KBr): γ : 2934, 2855, 1646, 1515, 1455, 1258, 1219, 1137, 1015, 952, 852, 814, 736, 619 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₁₅H₁₉N₂OS]⁺ requires 275.1213, found 275.1219.

2-(6-methoxybenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)ethan-1-one (s7).



Yellow solid. Yield: 90%.

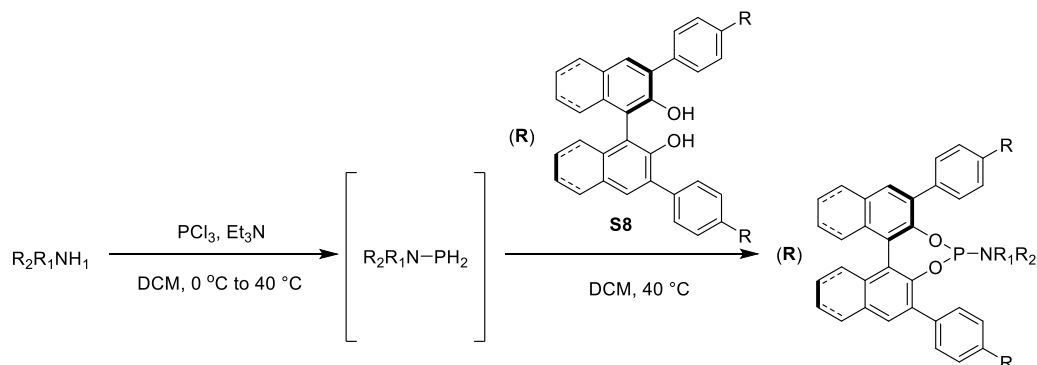
¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 8.9 Hz, 1H), 7.31 (d, *J* = 2.5 Hz, 1H), 7.05 (dd, *J* = 8.9, 2.5 Hz, 1H), 4.19 (s, 2H), 3.87 (s, 3H), 3.66 – 3.48 (m, 4H), 1.71 – 1.43 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 165.99, 162.15, 157.58, 147.09, 137.15, 123.16, 115.31, 103.96, 55.80, 47.40, 43.24, 39.62, 26.33, 25.42, 24.37.

IR (KBr): γ : 2926, 2854, 1638, 1603, 1465, 1260, 1226, 1055, 749 cm⁻¹.

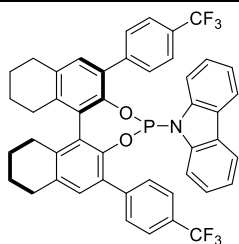
HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₁₅H₁₉N₂O₂S]⁺ requires 291.1162, found 291.1169.

3.3 Synthesis of L1-L7



General procedure II: To a stirred solution of Et₃N (5 equiv) and 9*H*-carbazole (1.5 equiv) in dichloromethane (0.1 M, dried over CaH₂) at 0 °C was slowly added PCl₃ (1.5 equiv, 2.0 M in DCM), and the mixture was stirred at 40 °C for 4 h. After the reaction mixture was cooled down to 0 °C, **S8** (1 equiv) was added as solid in one portion. The reaction mixture was further stirred at 40 °C overnight. The resulting mixture was cooled down to 0 °C and quenched carefully with water. The aqueous layer was separated and extracted with DCM. The combined organic layers were dried over Na₂SO₄, filtered, and concentrated in vacuo. Purification of the residue by column chromatography (SiO₂, light petroleum/dichloromethane 10:1 to 1:1) to provide **L**.³

9-(2,6-bis(4-(trifluoromethyl)phenyl)-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d':1',2'-f][1,3,2]dioxaphosphin-4-yl)-9*H*-carbazole (L1).



White solid. Yield: 81%, $[\alpha]_D^{20} = -320.7$ (c 0.34, CHCl_3).

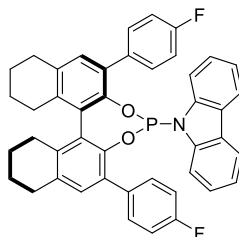
^1H NMR (400 MHz, CDCl_3) δ 7.93 – 7.76 (m, 2H), 7.72 (d, $J = 8.2$ Hz, 2H), 7.58 (d, $J = 8.2$ Hz, 2H), 7.29 (s, 1H), 7.25 – 6.79 (m, 8H), 6.64 (s, 1H), 6.52 (d, $J = 8.0$ Hz, 2H), 3.10 – 2.92 (m, 2H), 2.91 – 2.73 (m, 4H), 2.66 (dt, $J = 16.4$, 5.3 Hz, 1H), 2.55 (dt, $J = 16.9$, 5.7 Hz, 1H), 2.11 – 1.86 (m, 6H), 1.85 – 1.69 (m, 2H). **^{19}F NMR** (376 MHz, CDCl_3) δ -62.30, -62.51. **^{31}P NMR** (162 MHz, CDCl_3) δ 140.29.

^{13}C NMR (101 MHz, CDCl_3) δ 144.55, 144.03, 141.34, 140.91, 139.41, 139.02, 139.00, 138.69, 135.66, 135.64, 135.40, 131.06, 130.89, 130.82, 130.46, 130.41, 130.14, 129.84, 129.81, 129.45, 129.35, 129.33, 129.13, 128.66, 128.17, 127.84, 125.54, 125.24, 125.21, 123.82, 123.78, 122.84, 122.61, 121.30, 119.10, 29.34, 29.06, 28.03, 27.98, 22.84, 22.74, 22.74, 22.59.

IR (KBr): γ : 2927, 2856, 1617, 1441, 1324, 1260, 1209, 1190, 1164, 1125, 1067, 1018, 980, 944, 837, 796, 751 cm^{-1} .

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{46}\text{H}_{35}\text{F}_6\text{NO}_2\text{P}]^+$ requires 778.2304, found 778. 2299.

9-(2,6-bis(4-fluorophenyl)-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)-9H-carbazole (L2).



White solid. Yield: 86%. $[\alpha]_D^{20} = -211.4$ (c 0.57, CHCl_3).

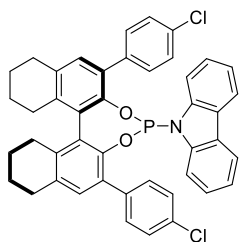
^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, $J = 7.7$ Hz, 2H), 7.61 (dd, $J = 8.7$, 5.4 Hz, 2H), 7.29 (s, 1H), 7.22 – 7.14 (m, 3H), 7.12 – 6.86 (m, 5H), 6.64 (s, 1H), 6.49 – 6.27 (m, 4H), 3.07 – 2.92 (m, 2H), 2.91 – 2.74 (m, 4H), 2.68 (dt, $J = 16.4$, 5.3 Hz, 1H), 2.55 (dt, $J = 17.0$, 5.7 Hz, 1H), 2.10 – 1.86 (m, 6H), 1.85 – 1.69 (m, 2H). **^{19}F NMR** (376 MHz, CDCl_3) δ -115.16, -116.78. **^{31}P NMR** (162 MHz, CDCl_3) δ 139.18.

^{13}C NMR (101 MHz, CDCl_3) δ 162.31, 161.45, 159.86, 159.01, 143.59, 143.56, 142.94, 140.46, 137.05, 137.03, 136.68, 134.28, 134.27, 133.99, 132.20, 132.17, 130.94, 130.91, 130.14, 130.12, 130.08, 130.05, 130.04, 129.90, 129.45, 129.40, 128.98, 128.90, 128.24, 128.22, 124.16, 119.95, 118.03, 114.21, 113.99, 112.73, 112.52, 28.27, 28.00, 26.91, 26.82, 21.86, 21.75, 21.59.

IR (KBr): γ : 2927, 2855, 1597, 1512, 1473, 1441, 1392, 1260, 1209, 1156, 1096, 1021, 944, 834, 804, 750 cm^{-1} .

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{44}\text{H}_{35}\text{F}_2\text{NO}_2\text{P}]^+$ requires 678.2368, found 678.2378.

9-(2,6-bis(4-chlorophenyl)-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)-9H-carbazole (L3).



White solid. Yield: 89%. $[\alpha]_D^{20} = -161.3$ (c 0.19, CHCl_3).

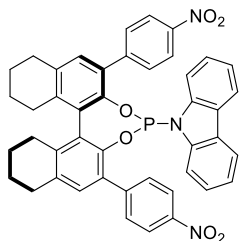
^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, $J = 7.7$ Hz, 2H), 7.58 (d, $J = 7.6$ Hz, 2H), 7.26 (t, $J = 3.9$ Hz, 2H), 7.18 (d, $J = 11.5$ Hz, 2H), 7.09 (t, $J = 7.4$ Hz, 2H), 6.96 (d, $J = 8.8$ Hz, 2H), 6.69 – 6.53 (m, 4H), 6.38 (d, $J = 7.2$ Hz, 2H), 3.03 – 2.86 (m, 2H), 2.86 – 2.70 (m, 4H), 2.63 (dt, $J = 16.4, 5.3$ Hz, 1H), 2.51 (dt, $J = 16.9, 5.8$ Hz, 1H), 1.91 (m, 6H), 1.79 – 1.64 (m, 2H). **^{31}P NMR** (202 MHz, CDCl_3) δ 138.92.

^{13}C NMR (101 MHz, CDCl_3) δ 144.84, 144.81, 144.20, 141.72, 138.01, 137.99, 137.63, 137.44, 136.14, 135.23, 135.22, 134.97, 132.37, 132.21, 132.18, 131.21, 130.59, 130.54, 130.38, 129.63, 129.60, 129.58, 129.43, 129.41, 128.48, 128.27, 127.23, 126.89, 125.89, 125.16, 120.86, 119.09, 29.45, 29.19, 28.07, 28.00, 23.07, 22.96, 22.80.

IR (KBr): γ : 2925, 2854, 1494, 1441, 1425, 1387, 1260, 1209, 1151, 1091, 1016, 979, 944, 795, 750 cm^{-1} .

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{44}\text{H}_{34}\text{Cl}_2\text{NO}_2\text{P}]^+$ requires 710.1777, found 710.1783.

9-(2,6-bis(4-nitrophenyl)-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)-9H-carbazole (L4).



Yellow solid. Yield: 78%. $[\alpha]_D^{20} = -190.9$ (c 0.49, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ 8.41 – 8.29 (m, 1H), 8.21 – 8.09 (m, 2H), 7.92 – 7.64 (m, 4H), 7.54 – 7.41 (m, 2H), 7.31 (s, 1H), 7.19 (d, $J = 8.3$ Hz, 2H), 7.09 – 6.79 (m, 3H), 6.68 (s, 1H), 6.59 – 6.44 (m, 2H), 3.05 – 2.93 (m, 2H), 2.89 – 2.72 (m, 4H), 2.64 (dt, $J = 16.5, 5.2$ Hz, 1H), 2.54 (dt, $J = 17.1, 5.7$ Hz, 1H), 2.09 – 1.85 (m, 6H), 1.83 – 1.66 (m, 2H).

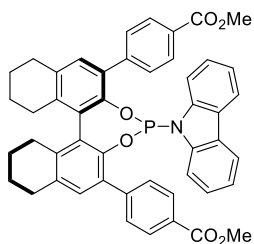
^{31}P NMR (162 MHz, CDCl_3) δ 140.47.

^{13}C NMR (101 MHz, CDCl_3) δ 148.07, 146.99, 145.43, 144.97, 144.48, 144.46, 143.95, 143.88, 142.33, 139.90, 139.88, 139.64, 136.06, 135.79, 130.97, 130.48, 130.43, 130.38, 130.36, 130.05, 130.02, 129.95, 129.31, 129.10, 128.33, 124.39, 123.59, 122.31, 121.45, 29.32, 29.03, 28.07, 28.03, 22.72, 22.63, 22.62, 22.48.

IR (KBr): γ : 2926, 2855, 1597, 1515, 1440, 1343, 1275, 1260, 1208, 1150, 1107, 750 cm^{-1} .

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{44}\text{H}_{35}\text{N}_3\text{O}_6\text{P}]^+$ requires 732.2258, found 732.2253.

Dimethyl 4,4'-(4-(9H-carbazol-9-yl)-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine-2,6-diyl)dibenzoate (L5).



White solid. Yield: 71%. $[\alpha]_D^{20} = -289.1$ (c 3.58, CHCl_3).

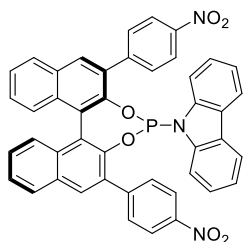
¹H NMR (600 MHz, Toluene-*d*₈, 80 °C) δ 7.96 – 7.85 (m, 2H), 7.61 (dt, *J* = 8.3, 1.6 Hz, 4H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.13 (m, 2H), 7.07 (s, 1H), 6.98 (t, *J* = 6.5 Hz, 2H), 6.85 (t, *J* = 7.7 Hz, 2H), 6.60 (s, 1H), 6.55 (dd, *J* = 8.3, 1.3 Hz, 2H), 3.55 (s, 3H), 3.45 (s, 3H), 2.79 – 2.66 (m, 4H), 2.63 – 2.51 (m, 3H), 2.42 (dt, *J* = 17.0, 5.8 Hz, 1H), 1.83 – 1.65 (m, 6H), 1.63 – 1.54 (m, 1H), 1.53 – 1.43 (m, 1H). **³¹P NMR** (162 MHz, CDCl₃) δ 139.74.

¹³C NMR (101 MHz, CDCl₃) ¹³C NMR (101 MHz, CDCl₃) δ 166.89, 166.66, 144.64, 144.08, 141.95, 141.34, 140.44, 138.92, 138.91, 138.62, 135.57, 135.31, 131.15, 130.94, 130.50, 130.45, 129.98, 129.57, 129.55, 129.52, 129.33, 129.31, 128.87, 128.33, 128.28, 127.19, 125.14, 120.94, 119.23, 51.98, 51.71, 29.34, 29.06, 28.02, 27.97, 22.84, 22.75, 22.60.

IR (KBr): γ : 2945, 2854, 1727, 1715, 1608, 1434, 1393, 1275, 1208, 1156, 1104, 1020, 980, 944, 750 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ + calcd for [C₄₈H₄₁NO₆P] + requires 758.2666, found 758.2662.

9-(2,6-bis(4-nitrophenyl)dinaphtho[2,1-d':1',2'-f][1,3,2]dioxaphosphepin-4-yl)-9H-carbazole (L6).



Yellow solid. Yield: 69%. [α]_D²⁰ = -9.5 (c 3.10, CHCl₃).

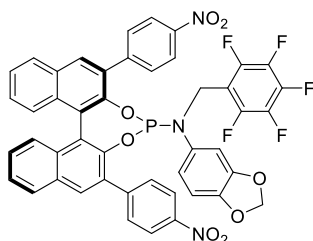
¹H NMR (600 MHz, Toluene-*d*₈, 80 °C) δ 7.82 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.77 – 7.72 (m, 2H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.50 (m, 4H), 7.49 – 7.45 (m, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.33 (s, 1H), 7.31 (ddd, *J* = 8.1, 6.8, 1.1 Hz, 1H), 7.26 (ddd, *J* = 8.1, 6.7, 1.1 Hz, 1H), 7.17 – 6.98 (m, 6H), 6.88 (t, *J* = 7.5 Hz, 2H), 6.52 (d, *J* = 8.5 Hz, 2H). **³¹P NMR** (162 MHz, CDCl₃) δ 147.73.

¹³C NMR (101 MHz, CDCl₃) δ 146.31, 145.87, 145.84, 144.78, 144.10, 142.59, 141.00, 139.90, 138.43, 131.99, 131.97, 131.80, 131.40, 131.38, 131.08, 130.62, 130.52, 130.45, 129.69, 129.67, 129.43, 128.57, 127.79, 126.48, 126.28, 126.08, 125.48, 125.40, 125.03, 124.96, 124.76, 123.29, 123.27, 122.65, 121.33, 120.66, 119.25, 118.36, 114.66, 109.52.

IR (KBr): γ : 2961, 2924, 2853, 1598, 1518, 1453, 1346, 1260, 1207, 1150, 1096, 1020, 959, 841, 799, 750 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ + calcd for [C₄₄H₂₇N₃O₆P]⁺ requires 724.1632, found 724.1636.

N-(benzo[d][1,3]dioxol-5-yl)-2,6-bis(4-nitrophenyl)-N-((perfluorophenyl)methyl) dinaphtho [2,1-d':1',2'-f][1,3,2]dioxaphosphepin-4-amine (L7).



Yellow solid. Yield: 62%, [α]_D²⁰ = -154.1 (c 2.45, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 8.48 – 8.41 (m, 2H), 8.38 (d, *J* = 8.5 Hz, 2H), 8.23 (s, 1H), 8.16 (s, 1H), 8.15 – 8.10 (m, 2H), 8.05 (dd, *J* = 8.2, 3.4 Hz, 2H), 7.99 (d, *J* = 8.6 Hz, 2H), 7.61 – 7.51 (m, 2H), 7.50 – 7.44 (m, 1H), 7.44 – 7.33 (m, 3H), 6.30 (d, *J* = 8.2 Hz, 1H), 5.78 (dd, *J* = 18.5, 1.5 Hz, 2H), 5.61 (dd, *J* = 8.2, 2.0 Hz, 1H), 5.07 (s, 1H), 4.45 (t, *J* = 12.2 Hz, 1H), 3.76 (d, *J* = 14.0 Hz, 1H). **¹⁹F NMR** δ -142.80 (dd, *J* = 22.6, 8.4 Hz), -153.74 (t, *J* = 20.8 Hz), -161.89 (td, *J* = 22.0, 8.5 Hz). **³¹P NMR** (162 MHz, CDCl₃) δ 135.27.

¹³C NMR (101 MHz, CDCl₃) ¹³C NMR (101 MHz, CDCl₃) δ 147.91, 147.54, 147.38, 146.28, 146.23, 146.20,

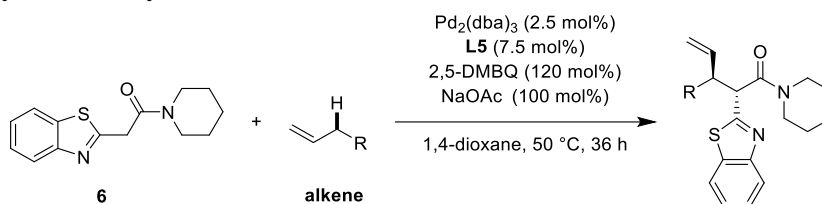
146.17, 145.72, 144.33, 143.91, 133.59, 133.35, 132.89, 132.41, 132.39, 131.37, 131.34, 131.31, 131.24, 131.11, 130.94, 130.70, 128.84, 128.81, 127.45, 127.26, 126.95, 126.80, 126.10, 125.93, 125.38, 125.32, 124.50, 124.47, 124.16, 124.11, 123.50, 123.46, 123.43, 120.67, 120.59, 107.77, 107.74, 106.95, 106.88, 101.66, 37.65.

IR (KBr): γ : 3057, 2900, 2855, 1655, 1600, 1505, 1454, 1346, 1260, 1207, 1192, 1126, 1020, 953, 8852, 835, 755 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[\text{C}_{46}\text{H}_{26}\text{F}_5\text{N}_3\text{O}_8\text{P}]^+$ requires 874.1372, found 874.1367.

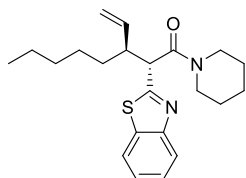
4. General procedure of products for asymmetric allylic C-H alkylation

4.1 Asymmetric allylic C-H alkylation of α -alkenes



General procedure III: To a flame-dried and N_2 -purged Schlenk tube (10 mL) were added 2-(benzo[d]thiazol-2-yl)-1-(piperidin-1-yl)ethan-1-one **6** (0.10 mmol, 26 mg), $\text{Pd}_2(\text{dba})_3$ (0.0025 mmol, 2.3 mg), phosphoramidite **L5** (0.0075 mmol, 5.8 mg), NaOAc (0.10 mmol, 8.2 mg), 2,5-DMBQ (0.12 mmol, 16.3 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 1,4-dioxane (0.5 mL) and alkene (0.15 mmol) via a syringe, then the resulting mixture was stirred at 50 °C for 36 h. The reaction mixture was concentrated in vacuo, and the residue was purified by column chromatography on silica gel (petroleum/ethyl acetate = 4/1) to provide the desired product.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-3-vinyloctan-1-one (**8**).



White solid. Yield: 93%, 34.5 mg. $b/\ell > 20/1$, $dr > 20/1$. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 9.514$ min (major), $t_R = 12.360$ min (minor). $[\alpha]_D^{20} = 9.0$ (c 0.32, CHCl_3).

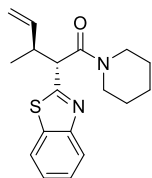
^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 8.1$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 1H), 7.37 (t, $J = 7.5$ Hz, 1H), 5.65 (dt, $J = 17.1, 9.5$ Hz, 1H), 5.26 – 5.06 (m, 2H), 4.51 (d, $J = 10.1$ Hz, 1H), 3.82 – 3.42 (m, 4H), 2.98 (qd, $J = 9.5, 4.1$ Hz, 1H), 1.67 – 1.38 (m, 6H), 1.35 – 1.03 (m, 8H), 0.78 (t, $J = 6.8$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.53, 168.52, 152.01, 139.10, 136.00, 125.72, 124.92, 122.71, 121.70, 117.53, 52.57, 48.63, 47.38, 43.53, 31.46, 26.56, 26.50, 25.63, 24.53, 22.50, 13.97.

IR (KBr): γ : 2960, 2926, 2854, 1641, 1435, 1261, 1095, 1017, 799 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[\text{C}_{22}\text{H}_{31}\text{N}_2\text{OS}]^+$ requires 371.2512, found 371.2514. The absolute configuration was assigned tentatively by the X-ray analysis.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-methyl-1-(piperidin-1-yl)pent-4-en-1-one (**9**).



White solid. Yield: 64%, 20 mg. *b/l* > 20/1, *dr* 17:1. Enantiomeric excess: 89%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t_R* = 12.470 min (major), *t_R* = 14.735 min (minor). $[\alpha]_D^{20} = 26.5$ (c 0.89, CHCl₃).

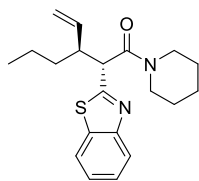
¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.87 (d, 1H), 7.46 (td, *J* = 7.6, 1.3 Hz, 1H), 7.37 (td, *J* = 7.7, 7.2, 1.2 Hz, 1H), 5.86 (ddd, *J* = 17.5, 10.4, 7.3 Hz, 1H), 5.25 – 5.03 (m, 2H), 4.39 (d, *J* = 10.2 Hz, 1H), 3.75 – 3.43 (m, 4H), 3.18 (dt, *J* = 10.1, 6.8 Hz, 1H), 1.69 – 1.45 (m, 5H), 1.43 – 1.31 (m, 1H), 0.95 (d, *J* = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 169.44, 168.45, 151.99, 140.68, 135.90, 125.81, 125.01, 122.73, 121.72, 115.42, 53.65, 47.35, 43.57, 42.44, 26.54, 25.64, 24.49, 17.34.

IR (KBr): γ : 3065, 2934, 2855, 1643, 1505, 1437, 1261, 1246, 1212, 1013, 760 cm⁻¹.

HRMS (ESI): *m/z* [M + Na]⁺ calcd for [C₁₈H₂₂N₂NaOS]⁺ requires 337.1345, found 337.1353. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-3-vinylhexan-1-one (10).



White solid. Yield: 95%, 32.5 mg. *b/l* > 20/1, *dr* > 20/1. Enantiomeric excess: 91%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t_R* = 6.005 min (major), *t_R* = 6.663 min (minor). $[\alpha]_D^{20} = 16.3$ (c 0.29, CHCl₃).

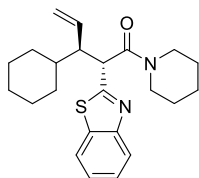
¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 5.64 (dt, *J* = 16.8, 9.5 Hz, 1H), 5.37 – 4.96 (m, 2H), 4.51 (d, *J* = 10.2 Hz, 1H), 3.79 – 3.37 (m, 4H), 3.00 (qd, *J* = 9.9, 2.9 Hz, 1H), 1.76 – 1.06 (m, 10H), 0.76 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 169.44, 168.45, 151.99, 140.68, 135.90, 125.81, 125.01, 122.73, 121.72, 115.42, 53.65, 47.35, 43.57, 42.44, 26.54, 25.64, 24.49, 17.34.

IR (KBr): γ : 3072, 2933, 2856, 1643, 1504, 1437, 1261, 1246, 1135, 1124, 1066, 1014, 803, 760, 730 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₂₀H₂₇N₂OS]⁺ requires 343.1839, found 343.1849. The absolute configuration was assigned tentatively by analogy.

(2R,3R)-2-(benzo[d]thiazol-2-yl)-3-cyclohexyl-1-(piperidin-1-yl)pent-4-en-1-one (11).



White solid. Yield: 51%, 19.4 mg. *b/l* > 20/1, *dr* > 20/1. Enantiomeric excess: 94%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t_R* = 14.163 min (major), *t_R* = 17.825 min (minor). $[\alpha]_D^{20} = 19.3$ (c 0.69, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.87 (d, 1H), 7.45 (m, 1H), 7.38 (m, 1H), 5.73 (ddd, *J* =

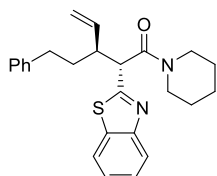
16.6, 10.9, 9.4 Hz, 1H), 5.28 – 5.04 (m, 2H), 4.80 (d, $J = 10.6$ Hz, 1H), 3.86 – 3.32 (m, 4H), 2.94 (td, $J = 10.1$, 2.4 Hz, 1H), 2.01 – 1.85 (m, 1H), 1.71 – 1.34 (m, 10H), 1.19 – 0.91 (m, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.57, 168.63, 152.11, 135.96, 135.81, 125.70, 124.91, 122.71, 121.70, 118.61, 54.37, 49.10, 47.35, 43.53, 38.21, 32.08, 26.91, 26.57, 26.43, 26.24, 25.59, 24.53.

IR (KBr): γ : 3072, 3000, 2924, 2852, 1644, 1503, 1436, 1261, 1246, 1209, 1135, 1092, 1014, 801, 759, 729 cm^{-1} .

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{23}\text{H}_{31}\text{N}_2\text{OS}]^+$ requires 383.2152, found 383.2154. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-phenethyl-1-(piperidin-1-yl)pent-4-en-1-one (12).



White solid. Yield: 69%, 27.9 mg. $b/l > 20/1$, $dr > 20/1$. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 15.628$ min (major), $t_R = 18.747$ min (minor). $[\alpha]_D^{20} = 16.6$ (c 1.54, CHCl_3).

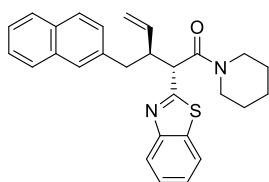
^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.1$ Hz, 1H), 7.88 – 7.79 (m, 1H), 7.51 – 7.41 (m, 1H), 7.40 – 7.33 (m, 1H), 7.17 (dd, $J = 8.0$, 6.5 Hz, 2H), 7.13 – 7.06 (m, 1H), 7.04 – 6.90 (m, 2H), 5.74 (ddd, $J = 17.1$, 10.2, 8.8 Hz, 1H), 5.37 – 5.06 (m, 2H), 4.56 (d, $J = 9.9$ Hz, 1H), 3.77 – 3.36 (m, 4H), 3.04 (qd, $J = 9.7$, 3.7 Hz, 1H), 2.71 (ddd, $J = 14.4$, 9.7, 5.2 Hz, 1H), 2.41 (ddd, $J = 13.9$, 9.7, 7.2 Hz, 1H), 1.73 – 1.34 (m, 8H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.10, 168.31, 151.98, 141.75, 138.72, 135.98, 128.40, 128.23, 125.80, 125.71, 125.02, 122.77, 121.72, 118.25, 52.37, 48.10, 47.40, 43.57, 33.08, 33.03, 26.56, 25.63, 24.51.

IR (KBr): γ : 3061, 3025, 2935, 2855, 1644, 1496, 1436, 1261, 1245, 1014, 760, 731, 699 cm^{-1} .

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{25}\text{H}_{29}\text{N}_2\text{OS}]^+$ requires 405.1995, found 405.2001. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-(naphthalen-2-ylmethyl)-1-(piperidin-1-yl)pent-4-en-1-one (13).



White solid. Yield: 46%, 20.2 mg. b/l 10/1, $dr > 20/1$. Enantiomeric excess: 92%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 9.533$ min (major), $t_R = 10.505$ min (minor). $[\alpha]_D^{20} = 1.9$ (c 0.97, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, $J = 8.1$ Hz, 1H), 7.89 (d, $J = 8.0$, 1.1 Hz, 1H), 7.78 – 7.73 (m, 1H), 7.73 – 7.66 (m, 2H), 7.52 – 7.45 (m, 2H), 7.43 – 7.34 (m, 3H), 7.24 (dd, $J = 8.4$, 1.8 Hz, 1H), 5.74 (ddd, $J = 16.8$, 10.6, 8.6 Hz, 1H), 5.12 – 4.89 (m, 2H), 4.68 (d, $J = 9.9$ Hz, 1H), 3.75 – 3.37 (m, 5H), 2.85 (dd, $J = 13.7$, 4.0 Hz, 1H), 2.68 (dd, $J = 13.7$, 10.4 Hz, 1H), 1.66 – 1.45 (m, 5H), 1.44 – 1.33 (m, 1H).

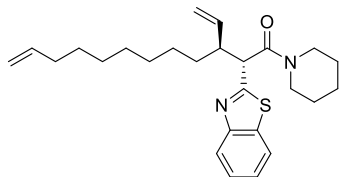
^{13}C NMR (101 MHz, CDCl_3) δ 169.23, 168.15, 152.12, 138.05, 136.90, 135.97, 133.34, 132.00, 127.75, 127.63, 127.62, 127.57, 127.47, 125.95, 125.78, 125.18, 122.84, 121.80, 118.12, 52.24, 50.13, 47.40, 43.59, 38.63, 26.52, 25.63, 24.50.

IR (KBr): γ : 3056, 3006, 2935, 2855, 1635, 1506, 1436, 1264, 1245, 1216, 1135, 1123, 1014, 814, 759, 730 cm^{-1} .

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{28}\text{H}_{29}\text{N}_2\text{OS}]^+$ requires 441.1995, found 441.2002. The absolute

configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-3-vinyldodec-11-en-1-one (14).



White solid. Yield: 71%, 30.1 mg. *b/l* > 20/1, *dr* > 20/1. Enantiomeric excess: 87%, determined by HPLC (CHIRALPAK IF, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t*_R = 6.251 min (major), *t*_R = 7.727 min (minor). [α]_D²⁰ = 7.6 (c 0.31, CHCl₃).

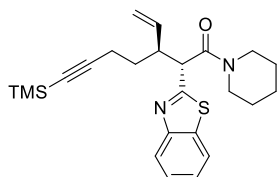
¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 5.85 – 5.71 (m, 1H), 5.64 (dt, *J* = 17.6, 9.5 Hz, 1H), 5.28 – 5.07 (m, 2H), 5.00 – 4.83 (m, 2H), 4.50 (d, *J* = 10.1 Hz, 1H), 3.77 – 3.40 (m, 4H), 2.98 (qd, *J* = 9.3, 4.2 Hz, 1H), 1.96 (q, *J* = 6.9 Hz, 2H), 1.74 – 1.37 (m, 8H), 1.35 – 1.05 (m, 10H).

¹³C NMR (101 MHz, CDCl₃) δ 169.53, 168.52, 151.99, 139.21, 139.08, 135.99, 125.74, 124.95, 122.72, 121.71, 117.57, 114.05, 52.55, 48.62, 47.40, 43.54, 33.73, 31.44, 29.27, 29.14, 28.97, 28.84, 26.76, 26.56, 25.64, 24.53.

IR (KBr): γ : 3074, 2926, 2854, 1639, 1505, 1455, 1260, 1246, 1134, 1014, 852, 800, 759, 729, 546, 463 cm⁻¹.

HRMS (ESI): *m/z* [M + Na]⁺ calcd for [C₂₆H₃₆N₂NaOS]⁺ requires 447.244, found 447.2445. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-7-(trimethylsilyl)-3-vinylhept-6-yn-1-one(15).



White solid. Yield: 81%, 34.1 mg. *b/l* 10/1, *d.r.* 20/1. Enantiomeric excess: 85%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t*_R = 4.588 min (major), *t*_R = 5.190 min (minor). [α]_D²⁰ = 10.0 (c 1.50, CHCl₃).

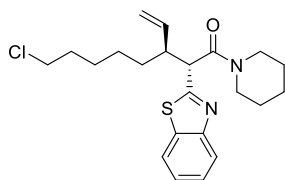
¹H NMR (400 MHz, CDCl₃) δ 7.86 (ddd, *J* = 8.1, 1.2, 0.6 Hz, 1H), 7.75 (ddd, *J* = 8.0, 1.3, 0.7 Hz, 1H), 7.34 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.26 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 5.50 (ddd, *J* = 17.1, 10.2, 8.9 Hz, 1H), 5.19 – 5.01 (m, 2H), 4.40 (d, *J* = 10.2 Hz, 1H), 3.73 – 3.27 (m, 4H), 3.02 (qd, *J* = 10.4, 3.4 Hz, 1H), 2.12 (ddd, *J* = 17.0, 7.7, 4.8 Hz, 1H), 1.97 (dt, *J* = 16.9, 8.3 Hz, 1H), 1.56 – 1.21 (m, 8H), -0.00 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 168.91, 167.99, 151.87, 137.63, 135.93, 125.64, 124.89, 122.61, 121.56, 118.62, 106.30, 84.83, 52.15, 47.61, 47.25, 43.43, 30.22, 26.44, 25.48, 24.36, 17.39, -0.00.

IR (KBr): γ : 3066, 2938, 2856, 2173, 1651, 1644, 1634, 1505, 1434, 1246, 1135, 1013, 921, 840, 760, 730, 638 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₂₄H₃₃N₂OSSi]⁺ requires 425.2077, found 425.2083. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-8-chloro-1-(piperidin-1-yl)-3-vinyloctan-1-one (16).



White solid. Yield: 95%, 38.4 mg. *b/l* > 20/1, *dr* > 20/1. Enantiomeric excess: 91%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 97/3, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t*_R = 39.893 min (minor), *t*_R = 50.079 min (major). [α]_D²⁰ = 13.9 (c 0.98, CHCl₃).

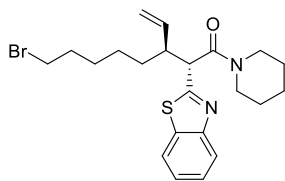
¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, 1H), 7.86 (d, 1H), 7.45 (ddd, *J* = 8.2, 7.2, 1.3 Hz, 1H), 7.37 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 5.64 (ddd, *J* = 17.1, 10.2, 8.8 Hz, 1H), 5.28 – 5.04 (m, 2H), 4.49 (d, *J* = 10.0 Hz, 1H), 3.69 – 3.44 (m, 4H), 3.42 (t, *J* = 6.7 Hz, 2H), 2.99 (qd, *J* = 9.1, 4.7 Hz, 1H), 1.68 – 1.07 (m, 14H).

¹³C NMR (101 MHz, CDCl₃) δ 169.31, 168.40, 151.99, 138.86, 135.93, 125.81, 125.03, 122.74, 121.74, 117.82, 52.48, 48.49, 47.39, 44.97, 43.56, 32.44, 31.27, 26.57, 26.50, 26.10, 25.63, 24.51.

IR (KBr): γ : 3067, 2933, 2856, 1635, 1503, 1436, 1313, 1262, 1245, 1214, 1134, 1014, 802, 760, 730 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₂₂H₃₀ClN₂OS]⁺ requires 405.1762, found 405.1769. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-8-bromo-1-(piperidin-1-yl)-3-vinyloctan-1-one (17).



White solid. Yield: 90%, 40.3 mg. *b/l* > 20/1, *dr* > 20/1. Enantiomeric excess: 91%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 97/3, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t*_R = 42.144 min (major), *t*_R = 52.286 min (minor). [α]_D²⁰ = 13.8 (c 0.36, CHCl₃).

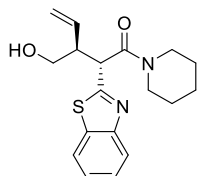
¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 5.64 (dt, *J* = 18.0, 9.5 Hz, 1H), 5.25 – 5.06 (m, 2H), 4.50 (d, *J* = 10.1 Hz, 1H), 3.72 – 3.43 (m, 4H), 3.30 (t, *J* = 6.8 Hz, 2H), 2.99 (qd, *J* = 9.3, 4.2 Hz, 1H), 1.83 – 1.11 (m, 14H).

¹³C NMR (101 MHz, CDCl₃) δ 169.30, 168.40, 151.99, 138.85, 135.94, 125.82, 125.03, 122.75, 121.74, 117.84, 52.48, 48.49, 47.40, 43.57, 33.79, 32.63, 31.23, 27.78, 26.57, 25.98, 25.63, 24.51.

IR (KBr): γ : 3067, 2961, 2930, 2855, 1635, 1504, 1435, 1261, 1096, 1015, 852, 800, 760, 730 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₂₂H₃₀BrN₂OS]⁺ requires 451.1236, found 451.1238. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-(hydroxymethyl)-1-(piperidin-1-yl)pent-4-en-1-one (18).



(SiO₂, petroleum/ethyl acetate = 1/1). White solid. Yield: 55%, 18.2 mg. *b/l* > 20/1, *dr* 20/1. Enantiomeric excess: 88%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t*_R = 35.221 min (major), *t*_R = 44.262 min (minor). [α]_D²⁰ = 34.5 (c 0.44, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.46 (t, 1H), 7.39 (t, *J* = 7.5 Hz,

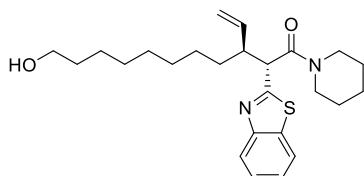
1H), 5.98 (ddd, $J = 17.5, 10.3, 8.5$ Hz, 1H), 5.37 – 5.18 (m, 2H), 4.83 (d, $J = 10.0$ Hz, 1H), 3.75 – 3.50 (m, 5H), 3.44 (dt, $J = 11.7, 3.3$ Hz, 1H), 3.24 – 2.75 (m, 1H), 2.79 (s, 1H), 1.70 – 1.47 (m, 5H), 1.44 – 1.31 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 168.84, 168.32, 151.98, 136.68, 135.70, 126.04, 125.25, 122.76, 121.75, 118.31, 63.04, 50.36, 48.35, 47.47, 43.67, 26.51, 25.59, 24.45.

IR (KBr): γ : 3419, 3069, 2961, 2926, 2855, 1633, 1435, 1261, 1016, 800, 762 cm^{-1} .

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{18}\text{H}_{23}\text{N}_2\text{O}_2\text{S}]^+$ requires 331.1475, found 331.1482. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-11-hydroxy-1-(piperidin-1-yl)-3-vinylundecan-1-one (19).



(petroleum/ethyl acetate = 1/1). White solid. Yield: 64%, 27.6 mg. $b/l > 20/1$, $dr > 20/1$. Enantiomeric excess: 84%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 9.128$ min (major), $t_R = 10.742$ min (minor). $[\alpha]_D^{20} = 9.9$ (c 0.99, CHCl_3).

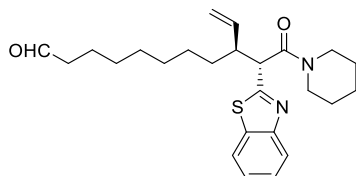
^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.1$ Hz, 1H), 7.86 (d, $J = 7.9$ Hz, 1H), 7.44 (t, $J = 7.7$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 1H), 5.62 (dt, $J = 17.3, 9.6$ Hz, 1H), 5.30 – 5.05 (m, 2H), 4.49 (d, $J = 10.2$ Hz, 1H), 3.94 – 3.29 (m, 6H), 2.97 (qd, $J = 9.4, 3.9$ Hz, 1H), 1.70 – 0.90 (m, 21H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.58, 168.50, 151.88, 138.99, 135.92, 125.77, 124.98, 122.67, 121.72, 117.67, 62.88, 52.46, 48.64, 47.40, 43.55, 32.72, 31.38, 29.33, 29.23, 29.05, 26.71, 26.55, 25.64, 25.62, 24.49.

IR (KBr): γ : 3419, 3065, 2926, 2854, 1633, 1435, 1261, 1016, 801, 761 cm^{-1} .

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{25}\text{H}_{37}\text{N}_2\text{O}_2\text{S}]^+$ requires 429.2570, found 429.2577. The absolute configuration was assigned tentatively by analogy.

(S)-9-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)undec-10-enal (20).



White solid. Yield: 64%, 27.3 mg. b/l 13/1, dr 20/1. Enantiomeric excess: 85%, determined by HPLC analysis of the OH derivative (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 9.120$ min (major), $t_R = 10.681$ min (minor). $[\alpha]_D^{20} = 12.5$ (c 0.96, CHCl_3).

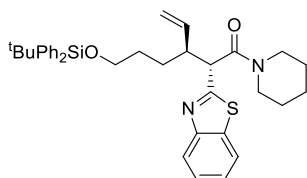
^1H NMR (400 MHz, CDCl_3) δ 9.71 (s, 1H), 7.98 (d, $J = 8.1$ Hz, 1H), 7.88 (d, $J = 7.9$ Hz, 1H), 7.52 – 7.42 (m, 1H), 7.37 (t, $J = 7.5$ Hz, 1H), 5.64 (ddd, $J = 17.1, 10.2, 8.8$ Hz, 1H), 5.31 – 5.01 (m, 2H), 4.50 (d, $J = 10.1$ Hz, 1H), 3.83 – 3.35 (m, 4H), 2.98 (qd, $J = 9.3, 4.1$ Hz, 1H), 2.33 (td, $J = 7.4, 1.9$ Hz, 2H), 1.75 – 0.95 (m, 18H).

^{13}C NMR (101 MHz, CDCl_3) δ 202.94, 169.49, 168.47, 151.97, 139.01, 135.96, 125.77, 124.98, 122.72, 121.72, 117.66, 52.51, 48.60, 47.40, 43.82, 43.54, 31.35, 29.09, 28.96, 28.92, 26.65, 26.56, 25.64, 24.52, 21.98.

IR (KBr): γ : 3073, 2929, 2855, 2719, 1723, 1635, 1437, 1245, 1196, 1135, 1014, 801 cm^{-1} .

HRMS (ESI): m/z $[\text{M} + \text{Na}]^+$ calcd for $[\text{C}_{25}\text{H}_{34}\text{N}_2\text{NaO}_2\text{S}]^+$ requires 449.2233, found 449.2234. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-6-((tert-butyldiphenylsilyl)oxy)-1-(piperidin-1-yl)-3-vinylhexan-1-one (21).



White solid. Yield: 51%, 30.5 mg. *b/l* 20/1, *dr* > 20/1. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 97/3, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 18.605 min (major), t_R = 31.534 min (minor). $[\alpha]_D^{20}$ = 13.8 (c 1.30, CHCl₃).

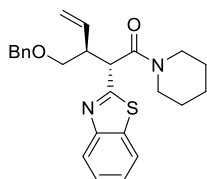
¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.84 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.59 – 7.52 (m, 4H), 7.49 – 7.41 (m, 1H), 7.40 – 7.28 (m, 7H), 5.64 (ddd, *J* = 17.1, 10.2, 8.8 Hz, 1H), 5.32 – 5.07 (m, 2H), 4.53 (d, *J* = 10.2 Hz, 1H), 3.75 – 3.36 (m, 6H), 3.13 – 2.91 (m, 1H), 1.70 – 1.22 (m, 10H), 0.85 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 169.33, 168.46, 152.03, 138.93, 135.99, 135.52, 135.49, 133.93, 133.90, 129.44, 127.54, 125.77, 124.98, 122.77, 121.74, 117.84, 63.40, 52.66, 48.62, 47.42, 43.58, 30.12, 27.86, 26.62, 26.60, 25.66, 24.54, 19.01.

IR (KBr): γ : 3070, 2999, 2932, 2856, 1643, 1436, 1261, 1245, 1110, 1013, 822, 759, 730, 702, 505 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₃₆H₄₅N₂O₂SSi]⁺ requires 597.2966, found 597.2967. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-((benzyloxy)methyl)-1-(piperidin-1-yl)pent-4-en-1-one (22).



White solid. Yield: 46%, 19.5 mg. *b/l* > 20/1, *dr* 15/1. Enantiomeric excess: 92%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 9.031 min (major), t_R = 10.111 min (minor). $[\alpha]_D^{20}$ = 52.2 (c 0.14, CHCl₃).

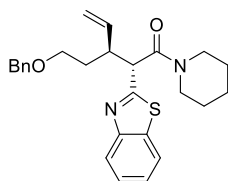
¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.85 (d, 1H), 7.46 (m, 1H), 7.37 (td, *J* = 7.6, 7.2, 1.2 Hz, 1H), 7.24 – 7.17 (m, 5H), 5.98 (ddd, *J* = 17.4, 10.4, 8.2 Hz, 1H), 5.36 – 5.06 (m, 2H), 4.85 (d, *J* = 9.7 Hz, 1H), 4.38 (s, 2H), 3.96 – 3.48 (m, 4H), 3.46 – 3.26 (m, 3H), 1.68 – 1.30 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 168.67, 168.04, 152.23, 138.13, 136.82, 135.89, 128.17, 127.54, 127.39, 125.80, 125.01, 122.87, 121.67, 118.04, 70.82, 48.74, 48.47, 47.39, 43.59, 26.54, 25.62, 24.50.

IR (KBr): γ : 3446, 3062, 2924, 2854, 1636, 1497, 1436, 1261, 1098, 1014, 801, 760, 731, 697 cm⁻¹.

HRMS (ESI): *m/z* [M + Na]⁺ calcd for [C₂₅H₂₈N₂NaO₂S]⁺ requires 443.1764, found 443.1766. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-(2-(benzyloxy)ethyl)-1-(piperidin-1-yl)pent-4-en-1-one (23).



White solid. Yield: 83%, 36.1 mg. *b/l* > 20/1, *dr* 20/1. Enantiomeric excess: 89%, determined by HPLC (CHIRALPAK IG, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 8.630 min (major), t_R = 10.999 min (minor). $[\alpha]_D^{20}$ = 9.6 (c 1.06, CHCl₃).

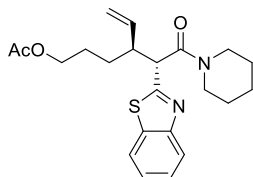
¹H NMR (400 MHz, CDCl₃) δ 7.96 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.85 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.44 (ddd, *J* = 8.2, 7.2, 1.3 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.31 – 7.20 (m, 5H), 5.69 (ddd, *J* = 17.1, 10.2, 8.9 Hz, 1H), 5.30 – 4.97 (m, 2H), 4.54 (d, *J* = 10.0 Hz, 1H), 4.44 – 4.27 (m, 2H), 3.73 – 3.32 (m, 6H), 3.19 (qd, 1H), 1.70 – 1.43 (m, 7H), 1.42 – 1.32 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 168.99, 168.26, 152.08, 138.43, 136.02, 128.28, 127.60, 127.44, 125.80, 125.02, 122.78, 121.72, 118.02, 72.81, 68.00, 52.44, 47.37, 45.69, 43.56, 31.50, 26.56, 25.63, 24.50.

IR (KBr): γ : 3063, 2930, 2854, 1634, 1497, 1435, 1314, 1261, 1016, 921, 852, 799, 760, 730, 697 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₂₆H₃₁N₂O₂S]⁺ requires 435.2101, found 435.2112. The absolute configuration was assigned tentatively by analogy.

(S)-4-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)hex-5-en-1-yl acetate (24).



White solid. Yield: 86%, 34.3 mg. *b/l* 17/1, *dr* > 20/1. Enantiomeric excess: 92%, determined by HPLC (CHIRALPAK IF, hexane/isopropanol = 97/3, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t_R* = 55.867 min (major), *t_R* = 65.512 min (minor). [α]_D²⁰ = 15.0 (c 0.64, CHCl₃).

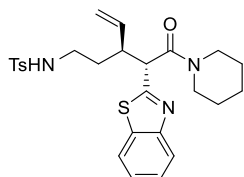
¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.46 (t, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 5.70 – 5.58 (m, 1H), 5.27 – 5.07 (m, 2H), 4.50 (d, *J* = 10.1 Hz, 1H), 3.99 – 3.81 (m, 2H), 3.70 – 3.40 (m, 4H), 3.01 (p, *J* = 8.4 Hz, 1H), 1.87 (s, 3H), 1.74 – 1.35 (m, 8H), 1.28 (dt, *J* = 11.4, 5.2 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 171.05, 169.07, 168.21, 151.94, 138.40, 135.88, 125.86, 125.10, 122.76, 121.71, 118.28, 64.00, 52.38, 48.27, 47.39, 43.58, 27.64, 26.56, 25.89, 25.62, 24.48, 20.83.

IR (KBr): γ : 3065, 2962, 2855, 1733, 1635, 1505, 1435, 1364, 1313, 1260, 1094, 1018, 852, 799, 731, 686, 666 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₂₂H₂₉N₂O₃S]⁺ requires 401.1893, found 401.1900. The absolute configuration was assigned tentatively by analogy.

N-((S)-3-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)pent-4-en-1-yl)-4-methylbenzenesulfonamide (25).



(petroleum/ethyl acetate = 1/1). White solid. Yield: 59%, 29.1 mg. *b/l* > 20/1, *dr* > 20/1. Enantiomeric excess: 86%, determined by HPLC (CHIRALPAK IF, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t_R* = 25.193 min (minor), *t_R* = 32.228 min (major). [α]_D²⁰ = 18.5 (c 0.40, CHCl₃).

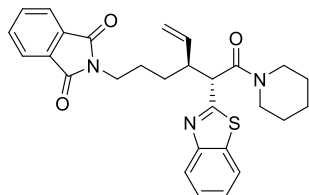
¹H NMR (400 MHz, CDCl₃) δ 7.76 – 7.67 (m, 2H), 7.67 – 7.61 (m, 2H), 7.39 (ddd, *J* = 8.2, 7.2, 1.4 Hz, 1H), 7.33 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.20 – 7.14 (m, 2H), 5.70 – 5.53 (m, 2H), 5.70 – 5.53 (m, 2H), 4.54 (d, *J* = 9.9 Hz, 1H), 3.68 – 3.41 (m, 4H), 3.14 – 2.91 (m, 2H), 2.81 – 2.68 (m, 1H), 2.37 (s, 3H), 1.69 – 1.42 (m, 6H), 1.39 – 1.28 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 169.34, 168.22, 150.94, 143.02, 137.59, 136.91, 135.23, 129.57, 126.99, 125.88, 125.02, 122.01, 121.65, 118.98, 51.65, 47.36, 46.93, 43.63, 41.63, 31.34, 26.58, 25.64, 24.46, 21.50.

IR (KBr): γ : 3079, 2927, 2856, 1634, 1437, 1330, 1261, 1157, 1094, 1017, 812, 760, 730, 660, 551 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[\text{C}_{26}\text{H}_{32}\text{N}_3\text{O}_3\text{S}_2]^+$ requires 498.1880, found 498.1885. The absolute configuration was assigned tentatively by analogy.

2-((S)-4-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)hex-5-en-1-yl)isoindoline-1,3-dione (26).



(dichloromethane/ethyl acetate = 3/7). White solid. Yield: 58%, 28.3 mg. b/l 20/1, $dr > 20/1$. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 47.137$ min (minor), $t_R = 33.068$ min (major). $[\alpha]_D^{20} = 13.6$ (c 0.45, CHCl_3).

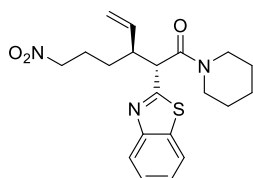
^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.1$ Hz, 1H), 7.83 (d, $J = 7.9$ Hz, 1H), 7.79 – 7.72 (m, 2H), 7.70 – 7.61 (m, 2H), 7.49 – 7.41 (m, 1H), 7.39 – 7.32 (m, 1H), 5.65 (ddd, $J = 17.0, 10.2, 8.9$ Hz, 1H), 5.30 – 5.03 (m, 2H), 4.51 (d, $J = 10.0$ Hz, 1H), 4.05 – 3.33 (m, 6H), 3.16 – 2.93 (m, 1H), 1.84 – 1.18 (m, 10H).

^{13}C NMR (101 MHz, CDCl_3) δ 168.91, 168.21, 168.19, 151.95, 138.26, 135.87, 133.77, 132.00, 125.79, 125.01, 123.08, 122.74, 121.70, 118.33, 52.25, 48.35, 47.38, 43.55, 37.69, 28.71, 26.55, 25.99, 25.61, 24.49.

IR (KBr): γ : 3064, 3004, 2935, 2855, 1771, 1715, 1635, 1503, 1437, 1396, 1372, 1245, 1014, 759, 720, 666, 530 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[\text{C}_{28}\text{H}_{30}\text{N}_3\text{O}_3\text{S}]^+$ requires 488.2002, found 488.2011. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-6-nitro-1-(piperidin-1-yl)-3-vinylhexan-1-one (27).



Yellow oil. Yield: 93%, 36 mg. $b/l > 20/1$, dr 20/1. Enantiomeric excess: 92%, determined by HPLC (CHIRALPAK IF, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 20.646$ min (major), $t_R = 23.521$ min (minor). $[\alpha]_D^{20} = 64.8$ (c 0.16, CHCl_3).

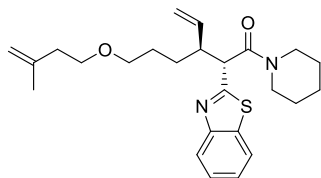
^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 8.1$ Hz, 1H), 7.91 – 7.84 (m, 1H), 7.50 – 7.43 (m, 1H), 7.42 – 7.35 (m, 1H), 5.66 (ddd, $J = 17.1, 10.2, 8.9$ Hz, 1H), 5.34 – 5.09 (m, 2H), 4.50 (d, $J = 9.9$ Hz, 1H), 4.33 – 4.14 (m, 2H), 3.75 – 3.39 (m, 4H), 3.04 (qd, $J = 14.5, 11.6, 7.4$ Hz, 1H), 2.12 (dp, $J = 15.1, 7.5$ Hz, 1H), 1.82 (dp, $J = 14.5, 7.5$ Hz, 1H), 1.66 – 1.45 (m, 5H), 1.43 – 1.29 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 168.44, 167.93, 152.00, 137.78, 135.78, 126.01, 125.26, 122.86, 121.79, 118.97, 75.08, 52.26, 47.93, 47.39, 43.64, 27.99, 26.56, 25.62, 24.90, 24.46.

IR (KBr): γ : 3065, 2925, 2855, 1635, 1549, 1435, 1261, 1095, 1015, 801, 761 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[\text{C}_{20}\text{H}_{26}\text{N}_3\text{O}_3\text{S}]^+$ requires 388.1689, found 388.1698. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-6-((3-methylbut-3-en-1-yl)oxy)-1-(piperidin-1-yl)-3-vinylhexan-1-one (28).



Colourless oil. Yield: 61%, 26.0 mg. *b/l* > 20/1, *dr* > 20/1. Enantiomeric excess: 89%, determined by HPLC (CHIRALPAK IF, hexane/isopropanol = 97/3, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t_R* = 17.304 min (major), *t_R* = 24.077 min (minor). $[\alpha]_{\text{D}}^{20} = 13.9$ (c 1.05, CHCl₃).

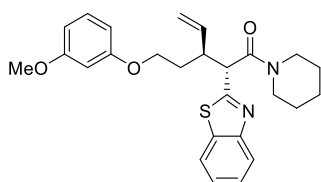
¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.51 – 7.42 (m, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 5.65 (ddd, *J* = 17.4, 10.2, 8.8 Hz, 1H), 5.29 – 5.09 (m, 2H), 4.79 – 4.58 (m, 2H), 4.51 (d, *J* = 10.1 Hz, 1H), 3.70 – 3.44 (m, 4H), 3.39 (t, *J* = 7.0 Hz, 2H), 3.27 (q, *J* = 6.6 Hz, 2H), 3.00 (qd, *J* = 9.5, 4.6 Hz, 1H), 2.15 (t, *J* = 6.9 Hz, 2H), 1.69 – 1.20 (m, 13H).

¹³C NMR (101 MHz, CDCl₃) δ 169.28, 168.37, 152.00, 142.94, 138.71, 135.98, 125.76, 124.99, 122.75, 121.70, 118.03, 111.22, 70.34, 69.16, 52.52, 48.53, 47.40, 43.54, 37.69, 27.97, 27.05, 26.56, 25.64, 24.52, 22.69.

IR (KBr): γ : 3073, 2934, 2855, 1644, 1504, 1436, 1261, 1245, 1215, 1112, 1014, 801, 760, 730 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₂₅H₃₅N₂O₂S]⁺ requires 427.2414, found 427.2422. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-(2-(3-methoxyphenoxy)ethyl)-1-(piperidin-1-yl)pent-4-en-1-one (29).



White solid. Yield: 83%, 37.4 mg. *b/l* 11/1, *dr* 20/1. Enantiomeric excess: 89%, determined by HPLC (CHIRALPAK OD, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t_R* = 7.245 min (minor), *t_R* = 8.790 min (major). $[\alpha]_{\text{D}}^{20} = 3.9$ (c 1.12, CHCl₃).

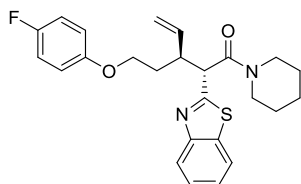
¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.87 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.46 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.41 – 7.35 (m, 1H), 7.09 (t, *J* = 8.2 Hz, 1H), 6.53 – 6.30 (m, 3H), 5.73 (ddd, *J* = 17.1, 10.2, 8.9 Hz, 1H), 5.34 – 5.04 (m, 2H), 4.58 (d, *J* = 10.0 Hz, 1H), 3.96 – 3.79 (m, 2H), 3.74 (s, 3H), 3.68 – 3.47 (m, 4H), 3.29 (qd, *J* = 10.3, 3.2 Hz, 1H), 1.91 – 1.34 (m, 8H).

¹³C NMR (101 MHz, CDCl₃) δ 168.81, 168.12, 160.70, 160.01, 152.03, 138.01, 135.98, 129.73, 125.86, 125.10, 122.80, 121.76, 118.56, 106.61, 106.23, 100.88, 65.39, 55.22, 52.40, 47.41, 45.45, 43.62, 30.98, 26.59, 25.64, 24.50.

IR (KBr): γ : 3065, 2998, 2936, 2855, 1639, 1601, 1492, 1437, 1286, 1245, 1200, 1169, 1152, 1045, 1015, 761, 731 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₂₆H₃₁N₂O₃S]⁺ requires 451.2050, found 451.2057. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-(2-(4-fluorophenoxy)ethyl)-1-(piperidin-1-yl)pent-4-en-1-one (30).



White solid. Yield: 87%, 38.0 mg. *b/l* > 20/1, *dr* > 20/1. Enantiomeric excess: 90%, determined by HPLC

(CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 7.858 min (major), t_R = 9.048 min (minor). $[\alpha]_D^{20}$ = 0.7 (c 1.02, CHCl₃).

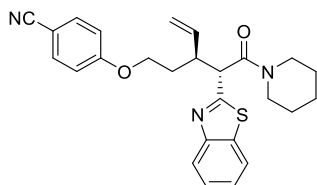
¹H NMR (400 MHz, CDCl₃) δ 7.97 (dd, J = 8.1, 2.7 Hz, 1H), 7.86 (dd, J = 8.0, 2.7 Hz, 1H), 7.45 (td, J = 8.1, 4.0 Hz, 1H), 7.37 (td, J = 7.8, 2.6 Hz, 1H), 6.94 – 6.82 (m, 2H), 6.77 – 6.64 (m, 2H), 5.72 (ddd, J = 17.0, 9.4, 2.7 Hz, 1H), 5.38 – 5.10 (m, 2H), 4.56 (d, J = 10.1, 2.8 Hz, 1H), 4.07 – 3.74 (m, 2H), 3.71 – 3.45 (m, 4H), 3.27 (q, J = 10.2 Hz, 1H), 1.88 – 1.29 (m, 8H). **¹⁹F NMR** (376 MHz, CDCl₃) δ -124.32.

¹³C NMR (101 MHz, CDCl₃) δ 168.78, 168.08, 158.28, 155.92, 154.81, 152.03, 138.03, 135.98, 125.87, 125.11, 122.78, 121.74, 118.52, 115.72, 115.49, 115.46, 115.38, 65.98, 52.41, 47.39, 45.37, 43.61, 30.94, 26.58, 25.63, 24.49.

IR (KBr): γ : 3066, 2936, 2856, 1636, 1505, 1468, 1436, 1246, 1208, 1134, 1096, 1015, 827, 801, 760 cm⁻¹.

HRMS (ESI): m/z [M + H]⁺ calcd for [C₂₅H₂₈FN₂O₂S]⁺ requires 439.1850 found 439.1859. The absolute configuration was assigned tentatively by analogy.

4-(((S)-3-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)pent-4-en-1-yl)oxy)benzo nitrile (31).



White solid. Yield: 85%, 38.0 mg. b/l 11/1, dr 18/1. Enantiomeric excess: 89%, determined by HPLC (CHIRALPAK AD, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 7.659 min (minor), t_R = 8.484 min (major). $[\alpha]_D^{20}$ = -18.7 (c 0.58, CHCl₃).

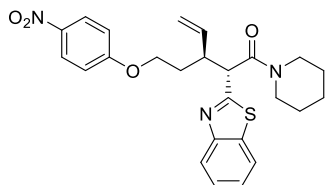
¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 8.0 Hz, 1H), 7.87 (dd, J = 8.0, 1.2 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.39 (td, J = 7.7, 7.2, 1.2 Hz, 1H), 6.81 (d, J = 8.8 Hz, 2H), 5.72 (ddd, J = 17.1, 10.2, 8.9 Hz, 1H), 5.34 – 5.15 (m, 2H), 4.56 (d, J = 10.1 Hz, 1H), 4.02 – 3.84 (m, 2H), 3.77 – 3.46 (m, 4H), 3.38 – 3.18 (m, 1H), 1.93 – 1.32 (m, 8H).

¹³C NMR (101 MHz, CDCl₃) δ 168.60, 167.95, 161.92, 151.95, 137.75, 135.88, 133.85, 125.99, 125.26, 122.78, 121.78, 119.31, 118.87, 115.14, 103.69, 65.65, 52.33, 47.41, 45.24, 43.65, 30.55, 26.59, 25.63, 24.46.

IR (KBr): γ : 2934, 2855, 2223, 1637, 1605, 1508, 1437, 1301, 1259, 1171, 1094, 1014, 834, 801, 760, 548 cm⁻¹.

HRMS (ESI): m/z [M + H]⁺ calcd for [C₂₆H₂₈N₃O₂S]⁺ requires 446.1897, found 446.1908. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-(2-(4-nitrophenoxy)ethyl)-1-(piperidin-1-yl)pent-4-en-1-one (32).



White solid. Yield: 72%, 31.5 mg. b/l > 20/1, dr > 20/1. Enantiomeric excess: 92%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 41.409 min (major), t_R = 47.865 min (minor). $[\alpha]_D^{20}$ = -29.3 (c 0.11, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 8.09 (dd, J = 9.8, 2.7 Hz, 2H), 7.97 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.47 (t, J = 7.8 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 6.99 – 6.74 (m, 2H), 5.72 (dt, J = 17.3, 9.6 Hz, 1H), 5.36 – 5.08 (m, 2H), 4.56 (d, J = 10.2 Hz, 1H), 4.09 – 3.81 (m, 2H), 3.73 – 3.41 (m, 4H), 3.29 (qd, J = 10.6, 9.8, 3.0 Hz, 1H), 1.91 – 1.78 (m, 1H), 1.76 – 1.66 (m, 1H), 1.66 – 1.44 (m, 5H), 1.44 – 1.32 (m, 1H).

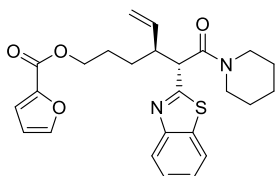
¹³C NMR (101 MHz, CDCl₃) δ 168.55, 167.93, 163.69, 151.99, 141.34, 137.76, 135.87, 125.98, 125.78, 125.24,

122.79, 121.75, 118.87, 114.39, 66.12, 52.35, 47.40, 45.21, 43.65, 30.54, 26.59, 25.62, 24.46.

IR (KBr): γ : 3077, 2925, 2854, 1635, 1607, 1592, 1508, 1497, 1455, 1436, 1339, 1261, 1172, 1110, 1014, 845, 800, 761 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[\text{C}_{25}\text{H}_{28}\text{N}_3\text{O}_4\text{S}]^+$ requires 466.1795, found 466.1797. The absolute configuration was assigned tentatively by analogy.

(S)-4-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)hex-5-en-1-yl furan-2-carboxylate (33).



White solid. Yield: 70%, 31.8 mg. $b/l > 20/1$, dr 15/1. Enantiomeric excess: 88%, determined by HPLC (CHIRALPAK IF, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 10.380$ min (major), $t_R = 11.349$ min (minor). $[\alpha]_D^{20} = 19.4$ (c 0.41, CHCl_3).

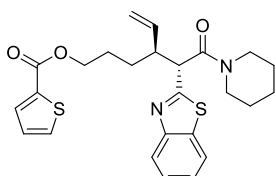
^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.0$ Hz, 1H), 7.85 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.55 – 7.43 (m, 2H), 7.37 (td, $J = 7.6, 1.2$ Hz, 1H), 6.88 (dd, $J = 3.5, 0.8$ Hz, 1H), 6.39 (dd, $J = 3.5, 1.7$ Hz, 1H), 5.67 (ddd, $J = 17.1, 10.2, 8.8$ Hz, 1H), 5.38 – 5.09 (m, 2H), 4.52 (d, $J = 10.2$ Hz, 1H), 4.16 (tt, $J = 6.8, 3.9$ Hz, 2H), 3.77 – 3.43 (m, 4H), 3.06 (qd, $J = 9.4, 4.3$ Hz, 1H), 1.87 – 1.77 (m, 1H), 1.64 – 1.46 (m, 6H), 1.44 – 1.33 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.09, 168.19, 158.60, 151.94, 146.12, 144.57, 138.35, 135.88, 125.84, 125.06, 122.78, 121.73, 118.39, 117.59, 111.70, 64.36, 52.39, 48.27, 47.40, 43.59, 27.62, 26.57, 26.03, 25.63, 24.49.

IR (KBr): γ : 3066, 2935, 2855, 1721, 1635, 1473, 1437, 1295, 1261, 1245, 1229, 1179, 1119, 1014, 801, 761 cm^{-1} .

HRMS (ESI): m/z $[M + \text{Na}]^+$ calcd for $[\text{C}_{25}\text{H}_{28}\text{N}_2\text{NaO}_4\text{S}]^+$ requires 475.1662, found 475.1670. The absolute configuration was assigned tentatively by analogy.

(S)-4-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)hex-5-en-1-yl thiophene-2-carboxylate (34).



White solid. Yield: 72%, 33.8 mg. b/l 14/1, $dr > 20/1$. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 17.512$ min (minor), $t_R = 18.417$ min (major). $[\alpha]_D^{20} = 13.4$ (c 0.42, CHCl_3).

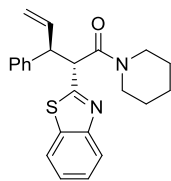
^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.0$ Hz, 1H), 7.84 (d, 1H), 7.56 (dd, $J = 3.7, 1.3$ Hz, 1H), 7.49 – 7.33 (m, 3H), 6.97 (dd, $J = 5.0, 3.7$ Hz, 1H), 5.67 (ddd, $J = 17.0, 10.2, 8.8$ Hz, 1H), 5.36 – 5.14 (m, 2H), 4.53 (d, $J = 10.2$ Hz, 1H), 4.15 (t, $J = 6.4$ Hz, 2H), 3.91 – 3.41 (m, 4H), 3.07 (qd, $J = 10.1, 3.4$ Hz, 1H), 1.89 – 1.75 (m, 1H), 1.68 – 1.33 (m, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.20, 168.21, 162.09, 151.93, 138.39, 135.94, 133.77, 133.12, 132.18, 127.57, 125.83, 125.05, 122.80, 121.75, 118.40, 64.48, 52.40, 48.31, 47.41, 43.61, 27.68, 26.58, 26.09, 25.64, 24.49.

IR (KBr): γ : 3075, 2932, 2855, 1708, 1635, 1436, 1418, 1260, 1224, 1095, 1014, 801, 759, 730 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[\text{C}_{25}\text{H}_{29}\text{N}_2\text{O}_3\text{S}_2]^+$ requires 469.1620, found 469.1614. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-phenyl-1-(piperidin-1-yl)pent-4-en-1-one (35).



40 °C, 48 h. White solid. Yield: 93%, 35.0 mg. *b/l* > 20/1, *dr* > 20/1. Enantiomeric excess: 79%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t*_R = 18.254 min (minor), *t*_R = 20.929 min (major). [α]_D²⁰ = 50.9 (c 1.42, CHCl₃).

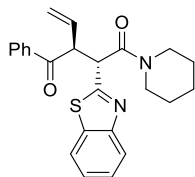
¹H NMR (400 MHz, CDCl₃) δ 7.92 – 7.60 (m, 2H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 15.2 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.14 (ddd, *J* = 17.4, 10.5, 7.3 Hz, 1H), 5.23 – 4.86 (m, 3H), 4.42 (dd, *J* = 10.6, 7.5 Hz, 1H), 3.94 – 3.54 (m, 4H), 1.70 – 1.43 (m, 5H), 1.41 – 1.29 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 168.36, 167.72, 151.93, 139.66, 138.89, 135.62, 128.57, 128.40, 126.80, 125.60, 124.79, 122.61, 121.58, 116.60, 53.82, 52.25, 47.35, 43.74, 26.49, 25.63, 24.47.

IR (KBr): γ : 3060, 3027, 2936, 2855, 1635, 1503, 1435, 1263, 1245, 1207, 1135, 1113, 1067, 1013, 759, 730, 700 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₂₃H₂₄N₂OS]⁺ requires 377.1682, found 377.1690. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-4-phenyl-1-(piperidin-1-yl)-3-vinylbutane-1,4-dione (36).



40 °C, 48 h. Yellow oil. Yield: 83%, 33.5 mg. *b/l* > 20/1, *dr* 12/1. Enantiomeric excess: 92%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t*_R = 13.324 min (major), *t*_R = 14.324 min (minor). [α]_D²⁰ = -162.9 (c 0.5, CHCl₃).

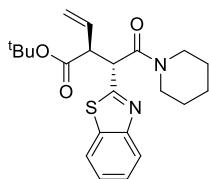
¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.96 (m, 2H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.45 – 7.34 (m, 3H), 7.29 (d, *J* = 8.2 Hz, 1H), 5.99 (ddd, *J* = 17.7, 10.2, 7.5 Hz, 1H), 5.61 – 5.14 (m, 4H), 4.06 – 3.41 (m, 4H), 1.76 – 1.43 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 198.13, 167.12, 166.87, 152.49, 136.38, 135.23, 133.76, 133.19, 128.77, 128.50, 125.80, 124.98, 123.27, 121.43, 120.87, 54.02, 48.94, 47.68, 43.76, 26.66, 25.75, 24.54.

IR (KBr): γ : 3061, 3003, 2935, 2855, 1682, 1635, 1596, 1507, 1435, 1313, 1267, 1191, 1099, 1013, 932, 801, 759, 730, 705, 686 cm⁻¹.

HRMS (ESI): *m/z* [M + Na]⁺ calcd for [C₂₄H₂₄N₂NaO₂S]⁺ requires 427.1451, found 427.1459. The absolute configuration was assigned tentatively by analogy.

Tert-butyl (S)-2-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)but-3-enoate (37).



40 °C, 48 h. White solid. Yield: 81%, 32.2 mg. *b/l* > 20/1, *dr* 4/1. Enantiomeric excess: 89%, determined by HPLC

(CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 10.425 min (minor), t_R = 11.710 min (major). $[\alpha]_D^{20}$ = -9.6 (c 0.30, CHCl₃).

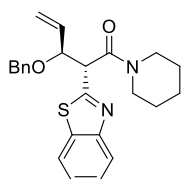
¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 8.1 Hz, 1H), 7.88 – 7.81 (m, 1H), 7.50 – 7.41 (m, 1H), 7.36 (td, J = 7.6, 7.2, 1.2 Hz, 1H), 5.94 (ddd, J = 17.3, 10.3, 8.4 Hz, 1H), 5.41 – 5.16 (m, 2H), 4.95 (d, J = 10.6 Hz, 1H), 4.02 (dd, J = 10.6, 8.4 Hz, 1H), 3.81 – 3.41 (m, 4H), 1.79 – 1.38 (m, 6H), 1.21 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 170.56, 167.23, 166.65, 152.28, 135.62, 133.36, 125.89, 125.09, 123.02, 121.59, 119.63, 81.28, 54.69, 49.75, 47.46, 43.70, 27.67, 26.55, 25.65, 24.47.

IR (KBr): γ : 3064, 2933, 2856, 1727, 1646, 1436, 1367, 1313, 1260, 1149, 1013, 802, 761 cm⁻¹.

HRMS (ESI): m/z [M + Na]⁺ calcd for [C₂₂H₂₈N₂NaO₃S]⁺ requires 423.1713, found 423.1720. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-(benzyloxy)-1-(piperidin-1-yl)pent-4-en-1-one (38).



40 °C, 48 h. White solid. Yield: 94%, 38.5 mg. $b/l > 20/1$, dr 10/1. Enantiomeric excess: 87%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 8.529 min (major), t_R = 10.810 min (minor). $[\alpha]_D^{20}$ = 32.4 (c 0.70, CHCl₃).

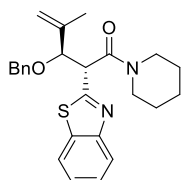
¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, J = 8.1 Hz, 1H), 7.87 – 7.76 (m, 1H), 7.46 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H), 7.37 (td, J = 7.7, 7.2, 1.3 Hz, 1H), 7.16 – 7.10 (m, 1H), 7.09 – 7.03 (m, 2H), 6.97 – 6.90 (m, 2H), 5.92 (ddd, J = 17.2, 10.4, 6.7 Hz, 1H), 5.61 – 5.26 (m, 2H), 4.74 (d, J = 9.1 Hz, 1H), 4.68 – 4.51 (m, 2H), 4.27 (d, J = 11.9 Hz, 1H), 3.74 – 3.40 (m, 4H), 1.67 – 1.43 (m, 5H), 1.41 – 1.30 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 167.64, 166.64, 152.32, 137.72, 135.89, 135.57, 128.04, 127.68, 127.36, 125.70, 124.89, 122.96, 121.58, 119.55, 81.97, 70.84, 53.60, 47.49, 43.48, 26.46, 25.59, 24.45.

IR (KBr): γ : 3062, 3029, 3004, 2934, 2855, 1639, 1507, 1497, 1436, 1261, 1247, 1208, 1156, 1067, 1013, 951, 802, 760, 731, 698 cm⁻¹.

HRMS (ESI): m/z [M + H]⁺ calcd for [C₂₄H₂₇N₂O₂S]⁺ requires 407.1788, found 407.1791. The absolute configuration was assigned tentatively by analogy.

(2R,3R)-2-(benzo[d]thiazol-2-yl)-3-(benzyloxy)-4-methyl-1-(piperidin-1-yl)pent-4-en-1-one (39).



40 °C, 48 h. White solid. Yield: 44%, 18.6 mg. $b/l > 20/1$, dr 5/1. Enantiomeric excess: 71%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 8.092 min (major), t_R = 9.225 min (minor). $[\alpha]_D^{20}$ = 7.6 (c 0.69, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, J = 8.1 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.52 – 7.40 (m, 1H), 7.41 – 7.34 (m, 1H), 7.15 – 7.09 (m, 1H), 7.04 (dd, J = 8.2, 6.7 Hz, 2H), 6.88 (d, J = 7.2 Hz, 2H), 5.26 – 5.08 (m, 2H), 4.88 (d, J = 9.8 Hz, 1H), 4.60 (d, J = 9.8 Hz, 1H), 4.47 (d, J = 12.0 Hz, 1H), 4.19 (d, J = 12.0 Hz, 1H), 3.76 – 3.32 (m, 4H), 1.82 (s, 3H), 1.63 – 1.34 (m, 6H).

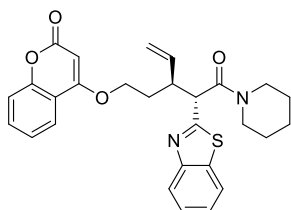
¹³C NMR (101 MHz, CDCl₃) δ 168.21, 166.67, 152.29, 141.21, 137.73, 135.89, 127.97, 127.60, 127.27, 125.65,

124.85, 122.93, 121.58, 117.64, 84.84, 70.15, 51.65, 47.43, 43.41, 26.51, 25.58, 24.45, 17.40.

IR (KBr): γ : 3063, 3029, 2933, 2855, 1643, 1505, 1436, 1261, 2246, 1206, 1155, 1069, 1014, 802, 760, 731, 697 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{25}H_{29}N_2O_2S]^+$ requires 421.1944, found 421.1954. The absolute configuration was assigned tentatively by analogy.

4-(((S)-3-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)pent-4-en-1-yl)oxy)-2H-chromen-2-one (40).



White solid. Yield: 54%, 26.3 mg. *b/l* 20/1, *dr* 13/1. Enantiomeric excess: 88%, determined by HPLC (CHIRALPAK AD, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 16.569 min (minor), t_R = 18.480 min (major). $[\alpha]_D^{20}$ = -9.5 (c 0.24, CHCl_3).

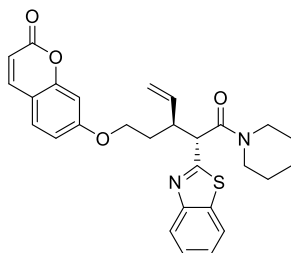
^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, J = 8.1 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.78 (dd, J = 7.9, 1.6 Hz, 1H), 7.56 – 7.45 (m, 2H), 7.44 – 7.36 (m, 1H), 7.28 (d, J = 12.3 Hz, 2H), 5.72 (ddd, J = 17.1, 10.2, 8.9 Hz, 1H), 5.56 (s, 1H), 5.33 – 5.12 (m, 2H), 4.59 (d, J = 10.1 Hz, 1H), 4.28 – 3.93 (m, 2H), 3.84 – 3.45 (m, 4H), 3.35 (q, J = 11.6 Hz, 1H), 1.99 – 1.88 (m, 1H), 1.79 (ddd, J = 14.3, 10.6, 5.3 Hz, 1H), 1.69 – 1.46 (m, 5H), 1.45 – 1.35 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 168.46, 167.87, 165.44, 162.91, 153.29, 152.06, 137.40, 135.86, 132.34, 126.07, 125.35, 123.91, 123.17, 122.92, 121.77, 119.29, 116.71, 115.63, 90.44, 66.75, 52.33, 47.42, 45.46, 43.69, 30.24, 26.60, 25.62, 24.46.

IR (KBr): γ : 3065, 2926, 2854, 1731, 1613, 1506, 1436, 1279, 1262, 1230, 1200, 1156, 1121, 1095, 1014, 834, 801, 760 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{28}H_{29}N_2O_4S]^+$ requires 489.1843, found 489.1850. The absolute configuration was assigned tentatively by analogy.

7-(((S)-3-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)pent-4-en-1-yl)oxy)-2H-chromen-2-one (41).



White solid. Yield: 52%, 25.4 mg. *b/l* 14/1, *dr* 15/1. Enantiomeric excess: 88%, determined by HPLC (CHIRALPAK OD, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 12.540 min (minor), t_R = 14.347 min (major). $[\alpha]_D^{20}$ = -7.8 (c 0.16, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 9.4 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.40 – 7.34 (m, 1H), 7.28 (d, J = 8.7 Hz, 1H), 6.74 (dd, J = 8.6, 2.4 Hz, 1H), 6.68 (d, J = 2.4 Hz, 1H), 6.22 (d, J = 9.4 Hz, 1H), 5.72 (ddd, J = 17.0, 10.2, 8.9 Hz, 1H), 5.34 – 5.07 (m, 2H), 4.57 (d, J = 10.0 Hz, 1H), 4.05 – 3.83 (m, 2H), 3.73 – 3.44 (m, 4H), 3.37 – 3.23 (m, 1H), 1.91 – 1.78 (m, 1H), 1.76 – 1.68 (m, 1H), 1.65 – 1.46 (m,

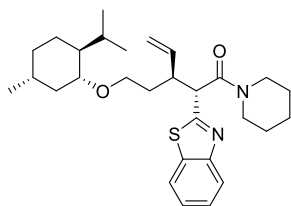
5H), 1.43 – 1.35 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 168.64, 167.99, 161.92, 161.25, 155.76, 151.98, 143.43, 137.76, 135.90, 128.62, 125.92, 125.17, 122.81, 121.75, 118.88, 113.01, 112.95, 112.39, 101.25, 65.91, 52.34, 47.41, 45.33, 43.64, 30.56, 26.59, 25.63, 24.47.

IR (KBr): γ : 3075, 3004, 2928, 2855, 1723, 1622, 1566, 1437, 1373, 1272, 1261, 1238, 1182, 1139, 1107, 1013, 930, 761 cm⁻¹.

HRMS (ESI): m/z [M + Na]⁺ calcd for [C₂₈H₂₈N₂NaO₄S]⁺ requires 511.1662, found 511.1672. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-(2-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)ethy l)-1-(piperidin-1-yl)pent-4-en-1-one (42).



White solid. Yield: 60%, 29.0 mg. *b/l*> 20/1, *dr*> 20/1. Enantiomeric excess: 84%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t_R* = 6.056 min (major), *t_R* = 6.648 min (minor). [α]_D²⁰ = -38.1 (c 0.50, CHCl₃).

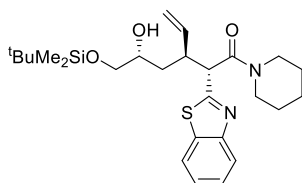
¹H NMR (400 MHz, CDCl₃) δ 7.96 (ddd, *J* = 8.1, 1.2, 0.6 Hz, 1H), 7.85 (ddd, *J* = 7.9, 1.3, 0.6 Hz, 1H), 7.44 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.35 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 5.69 (ddd, *J* = 17.2, 10.3, 8.9 Hz, 1H), 5.33 – 5.04 (m, 2H), 4.53 (d, *J* = 9.9 Hz, 1H), 3.74 – 3.41 (m, 5H), 3.27 – 3.07 (m, 2H), 2.87 (td, *J* = 10.5, 4.1 Hz, 1H), 2.31 – 2.10 (m, 1H), 2.03 – 1.88 (m, 1H), 1.78 – 1.17 (m, 11H), 1.17 – 1.02 (m, 1H), 0.91 – 0.61 (m, 12H).

¹³C NMR (101 MHz, CDCl₃) δ 169.03, 168.32, 152.04, 138.60, 136.06, 125.73, 124.94, 122.72, 121.69, 118.02, 79.21, 65.74, 52.52, 48.24, 47.39, 45.64, 43.55, 40.46, 34.55, 32.29, 31.47, 26.56, 25.64, 25.29, 24.52, 23.17, 22.33, 21.02, 16.12.

IR (KBr): γ : 3068, 2958, 2856, 1645, 1503, 1435, 1367, 1314, 1287, 1269, 1245, 1216, 1111, 851, 802, 730 cm⁻¹.

HRMS (ESI): m/z [M + H]⁺ calcd for [C₂₉H₄₃N₂O₂S]⁺ requires 483.3040, found 483.3048. The absolute configuration was assigned tentatively by analogy.

(2R,3S,5R)-2-(benzo[d]thiazol-2-yl)-6-((tert-butyldimethylsilyl)oxy)-5-hydroxy-1-(piperidin-1-yl)-3-vinylhexan-1-one (43).



(petroleum/ethyl acetate = 1/1). White solid. Yield: 64%, 37.9 mg. *b/l*> 20/1, *dr*> 20/1. Enantiomeric excess: 91%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t_R* = 17.766 min (minor), *t_R* = 39.182 min (major). [α]_D²⁰ = 16.8 (c 0.98, CHCl₃).

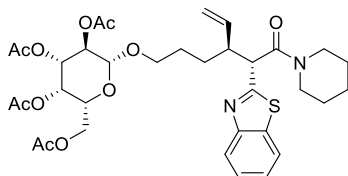
¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.1 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.48 – 7.41 (t, 1H), 7.38 – 7.31 (m, 1H), 5.70 (ddd, 1H), 5.42 – 5.11 (m, 2H), 4.53 (d, *J* = 9.9 Hz, 1H), 3.78 – 3.16 (m, 8H), 2.20 (d, *J* = 4.8 Hz, 1H), 1.69 – 1.18 (m, 9H), 0.74 (s, 9H), -0.05 (s, 3H), -0.08 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 169.20, 168.25, 151.88, 138.44, 136.04, 125.75, 125.00, 122.66, 121.82, 118.45, 68.87, 67.33, 52.51, 47.39, 45.05, 43.57, 34.88, 26.55, 25.70, 25.63, 24.50, 18.10, -5.45, -5.54.

IR (KBr): γ : 3443, 3068, 2928, 2856, 1634, 1437, 1259, 1096, 1016, 836, 802, 760, 730 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[\text{C}_{26}\text{H}_{41}\text{N}_2\text{O}_3\text{SSi}]^+$ requires 489.2602, found 489.2608. The absolute configuration was assigned tentatively by analogy.

(2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(((S)-4-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)hex-5-en-1-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (44).



(petroleum/ethyl acetate = 1/1). White solid. Yield: 62%, 42.5 mg. b/l 20/1, $dr > 20/1$. Enantiomeric excess: 91%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 20.631$ min (major), $t_R = 25.492$ min (minor). $[\alpha]_D^{20} = 0.3$ (c 1.09, CHCl_3).

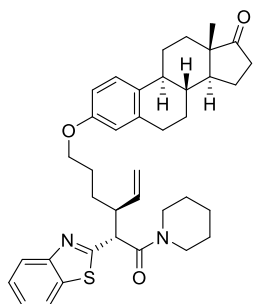
^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.0$ Hz, 1H), 7.89 (dd, $J = 7.9, 1.2$ Hz, 1H), 7.49 – 7.43 (m, 1H), 7.38 (td, $J = 7.6, 7.2, 1.2$ Hz, 1H), 5.63 (ddd, $J = 17.1, 10.2, 8.8$ Hz, 1H), 5.39 – 5.32 (m, 1H), 5.26 – 5.07 (m, 3H), 4.92 (dd, $J = 10.5, 3.5$ Hz, 1H), 4.49 (d, $J = 10.1$ Hz, 1H), 4.32 (d, $J = 7.9$ Hz, 1H), 4.11 (dd, $J = 6.7, 4.5$ Hz, 2H), 3.90 – 3.73 (m, 2H), 3.70 – 3.41 (m, 4H), 3.39 – 3.22 (m, 1H), 2.98 (qd, $J = 10.1, 3.3$ Hz, 1H), 2.12 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H), 1.94 (s, 3H), 1.73 – 1.17 (m, 10H).

^{13}C NMR (101 MHz, CDCl_3) δ 170.41, 170.29, 170.18, 169.42, 169.03, 168.25, 152.00, 138.48, 135.91, 125.84, 125.09, 122.74, 121.76, 118.23, 101.30, 70.89, 70.49, 69.82, 68.71, 66.99, 61.22, 52.49, 48.47, 47.39, 43.56, 27.57, 27.07, 26.55, 25.61, 24.48, 20.71, 20.69, 20.62.

IR (KBr): γ : 2934, 2856, 1750, 1636, 1437, 1396, 1222, 1172, 1135, 1056, 955, 801, 762, 733, 544 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[\text{C}_{34}\text{H}_{45}\text{N}_2\text{O}_{11}\text{S}]^+$ requires 689.2739, found 689.2742. The absolute configuration was assigned tentatively by analogy.

(8R,9S,13S,14S)-3-(((S)-4-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)hex-5-en-1-yl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (45).



White solid. Yield: 67%, 40.1 mg. $b/l > 20/1$, $dr > 20/1$. Enantiomeric excess: 87%, determined by HPLC (CHIRALPAK IF, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 14.843$ min (major), $t_R = 16.975$ min (minor). $[\alpha]_D^{20} = 66.2$ (c 1.77, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ 8.05 – 7.93 (m, 1H), 7.90 – 7.79 (m, 1H), 7.48 – 7.42 (m, 1H), 7.41 – 7.33 (m, 1H), 7.11 (d, $J = 8.6$ Hz, 1H), 6.55 (dd, $J = 8.6, 2.7$ Hz, 1H), 6.49 (d, $J = 2.8$ Hz, 1H), 5.68 (ddd, $J = 17.0, 10.2, 8.8$ Hz, 1H), 5.38 – 5.08 (m, 2H), 4.53 (d, $J = 10.1$ Hz, 1H), 3.90 – 3.42 (m, 6H), 3.17 – 2.98 (m, 1H), 2.91 – 2.73 (m, 2H), 2.49 (dd, $J = 18.9, 8.6$ Hz, 1H), 2.41 – 2.32 (m, 1H), 2.27 – 1.77 (m, 7H), 1.65 – 1.33 (m, 14H), 0.89 (s, 3H).

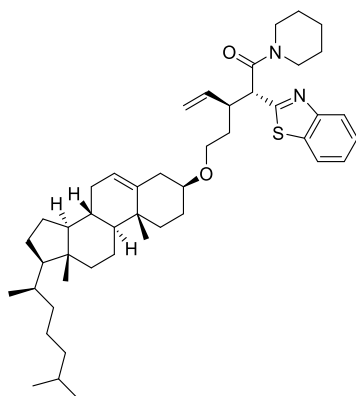
^{13}C NMR (101 MHz, CDCl_3) δ 169.16, 168.30, 156.89, 152.00, 138.59, 137.56, 135.95, 131.75, 126.19, 125.80, 125.03, 122.80, 121.73, 118.22, 114.41, 112.09, 67.24, 52.48, 50.37, 48.40, 48.02, 47.41, 43.95, 43.58, 38.34, 35.90,

31.57, 29.63, 27.83, 26.71, 26.58, 26.56, 25.91, 25.65, 24.51, 21.60, 13.87.

IR (KBr): γ : 3058, 2931, 2857, 1737, 1634, 1499, 1436, 1258, 1055, 1013, 759, 732 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[\text{C}_{38}\text{H}_{47}\text{N}_2\text{O}_3\text{S}]^+$ requires 611.3302, found 611.3300. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-6-(((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)-1-(piperidin-1-yl)-3-vinylhexan-1-one (46).



White solid. Yield: 46%, 32.7 mg. $b/l > 10/1$, $dr > 20/1$. Enantiomeric excess: 85%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 6.313$ min (major), $t_R = 7.995$ min (minor). $[\alpha]_D^{20} = -14.3$ (c 0.88, CHCl_3).

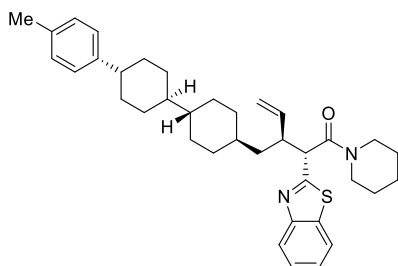
^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.1$ Hz, 1H), 7.85 (d, $J = 7.9$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 1H), 7.36 (t, $J = 7.5$ Hz, 1H), 5.68 (dt, $J = 17.3, 9.6$ Hz, 1H), 5.39 – 5.08 (m, 3H), 4.54 (d, $J = 10.1$ Hz, 1H), 3.72 – 3.38 (m, 5H), 3.37 – 3.28 (m, 1H), 3.14 (qd, $J = 10.2, 3.3$ Hz, 1H), 3.00 (tt, $J = 11.2, 4.3$ Hz, 1H), 2.24 (ddd, $J = 13.3, 4.9, 2.0$ Hz, 1H), 2.16 – 2.05 (m, 1H), 2.03 – 1.90 (m, 2H), 1.80 (tq, $J = 11.6, 3.7, 3.0$ Hz, 3H), 1.67 – 0.80 (m, 41H), 0.66 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 168.97, 168.29, 152.03, 141.03, 138.53, 136.03, 125.76, 124.98, 122.75, 121.70, 121.36, 118.00, 78.92, 65.54, 56.76, 56.12, 52.41, 50.14, 47.40, 45.74, 43.56, 42.30, 39.77, 39.52, 39.18, 37.18, 36.83, 36.19, 35.79, 31.94, 31.86, 31.80, 28.25, 28.23, 28.03, 26.57, 25.64, 24.52, 24.30, 23.82, 22.85, 22.59, 21.04, 19.36, 18.72, 11.86.

IR (KBr): γ : 2934, 2856, 1644, 1435, 1437, 1261, 1246, 1104, 1018, 800, 759 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[\text{C}_{46}\text{H}_{69}\text{N}_2\text{O}_2\text{S}]^+$ requires 713.5074, found 713.5076. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-3-(((1S,1'R,4R,4'S)-4'-(p-tolyl)-[1,1'-bi(cyclohexan)]-4-yl)methyl)pent-4-en-1-one (47).



White solid. Yield: 30%, 17.3 mg. $b/l > 20/1$, $dr > 20/1$. Enantiomeric excess: 80%, determined by HPLC (CHIRALPAK IG, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 8.453$ min (minor),

$t_R = 12.278$ min (major). $[\alpha]_D^{20} = 0.8$ (c 0.59, CHCl_3).

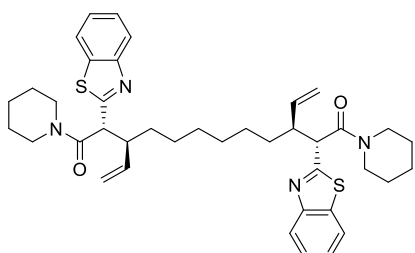
^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 8.1$ Hz, 1H), 7.88 (d, $J = 7.9$ Hz, 1H), 7.46 (ddd, $J = 8.2, 7.2, 1.3$ Hz, 1H), 7.41 – 7.34 (m, 1H), 7.08 (d, 4H), 5.62 (ddd, $J = 17.1, 10.2, 8.9$ Hz, 1H), 5.37 – 5.00 (m, 2H), 4.47 (d, $J = 10.1$ Hz, 1H), 3.80 – 3.38 (m, 4H), 3.13 (qd, 1H), 2.37 (tt, $J = 12.1, 3.4$ Hz, 1H), 2.30 (s, 3H), 1.93 – 1.81 (m, 3H), 1.80 – 1.72 (m, 2H), 1.66 – 0.74 (m, 21H), 0.58 (dd, $J = 13.7, 10.2$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.67, 168.50, 151.92, 144.92, 139.19, 136.05, 135.17, 128.93, 126.67, 125.72, 124.94, 122.73, 121.76, 117.62, 52.95, 47.43, 46.27, 44.19, 43.53, 43.23, 42.82, 39.25, 34.77, 34.73, 34.66, 31.64, 30.33, 30.29, 29.97, 29.65, 26.57, 25.67, 24.55, 21.00.

IR (KBr): γ : 2920, 2850, 2359, 1627, 1506, 1438, 1260, 1245, 1091, 1014, 916 cm^{-1} .

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{37}\text{H}_{49}\text{N}_2\text{OS}]^+$ requires 569.3560, found 569.3560. The absolute configuration was assigned tentatively by analogy.

(2R,3S,10S,11R)-2,11-bis(benzo[d]thiazol-2-yl)-1,12-di(piperidin-1-yl)-3,10-divinyldodecane-1,12-dione (48).



(petroleum/ethyl acetate = 1/1). White solid. Yield: 64%, 43.8 mg. $b/\lambda > 20/1$, dr 20/1. Enantiomeric excess: 86%, determined by HPLC (CHIRALPAK IG, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_R = 35.413$ min (major), $t_R = 40.802$ min (minor). $[\alpha]_D^{20} = 18.0$ (c 0.62, CHCl_3).

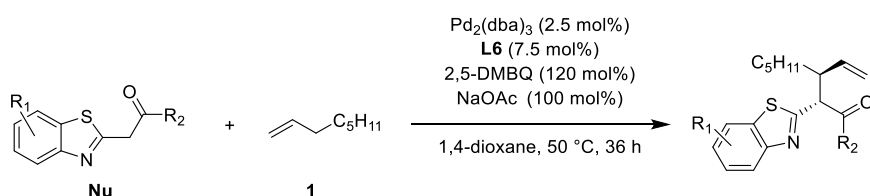
^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 8.2$ Hz, 2H), 7.85 (d, $J = 8.0$ Hz, 2H), 7.55 – 7.40 (m, 2H), 7.39 – 7.32 (m, 2H), 5.59 (ddd, $J = 17.0, 10.2, 8.8$ Hz, 2H), 5.30 – 4.97 (m, 4H), 4.46 (d, $J = 10.1$ Hz, 2H), 3.92 – 3.28 (m, 8H), 2.92 (qd, $J = 9.4, 4.0$ Hz, 2H), 1.70 – 1.35 (m, 12H), 1.24 – 0.90 (m, 12H).

^{13}C NMR (101 MHz, CDCl_3) δ 169.50, 168.50, 151.97, 139.01, 135.96, 125.73, 124.93, 122.70, 121.70, 117.56, 52.48, 48.60, 47.38, 43.52, 31.42, 29.11, 26.70, 26.55, 25.62, 24.51.

IR (KBr): γ : 3067, 3001, 2932, 2855, 1638, 1503, 1436, 1261, 1245, 1215, 1135, 1123, 1014, 952, 920, 759, 739 cm^{-1} .

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{40}\text{H}_{51}\text{N}_4\text{O}_2\text{S}_2]^+$ requires 683.3443, found 683.3455. The absolute configuration was assigned tentatively by analogy.

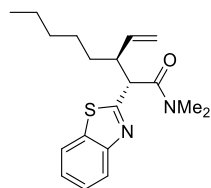
4.2 Asymmetric functionalized coordinating nucleophiles of oct-1-ene



General procedure IV: To a flame-dried and N_2 -purged Schlenk tube (10 mL) were added **Nu** (0.1 mmol), $\text{Pd}_2(\text{dba})_3$ (0.0025 mmol, 2.3 mg), phosphoramidite **L6** (0.0075 mmol, 5.8 mg), NaOAc (0.10 mmol, 8.2 mg) 2,5-DMBQ (0.12 mmol, 16.3 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 1,4-dioxane (0.5 mL) and oct-1-ene **1** (0.15 mmol, 16.8 mg), via a syringe, then the resulting mixture was stirred at 50 °C for 36 h. The reaction mixture was

concentrated in vacuo, and the residue was purified by column chromatography on silica gel (petroleum/ethyl acetate = 4/1) to provide the desired product.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-N,N-dimethyl-3-vinyloctanamide (7).



White solid. Yield: 63%, 20.9 mg. *b/l* > 20/1, *dr* > 20/1. Enantiomeric excess: 86%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t*_R = 9.137 min (major), *t*_R = 13.064 min (minor). [α]_D²⁰ = 23.1 (c 0.32, CHCl₃).

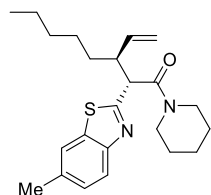
¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.41 (t, 1H), 7.41 – 7.34 (t, 1H), 5.65 (ddd, *J* = 17.1, 10.5, 8.8, 1.6 Hz, 1H), 5.30 – 4.99 (m, 2H), 4.51 (dd, *J* = 10.3, 1.6 Hz, 1H), 3.16 (s, 3H), 3.01 – 2.95 (m, 3H), 2.94 (s, 1H), 1.51 – 0.96 (m, 8H), 0.78 (t, *J* = 7.0, 1.7 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 170.41, 169.29, 151.91, 138.70, 135.98, 125.77, 124.98, 122.72, 121.72, 117.76, 53.03, 48.94, 37.87, 36.03, 31.44, 26.54, 22.53, 14.00.

IR (KBr): γ : 3447, 3067, 2958, 2927, 2856, 1644, 1503, 1456, 1436, 1261, 1245, 1115, 1068, 1031, 761 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₁₉H₂₇N₂OS]⁺ requires 331.1839, found 331.1848. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(6-methylbenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-3-vinyloctan-1-one (49).



White solid. Yield: 83%, 31.8 mg. *b/l* > 20/1, *dr* > 20/1. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t*_R = 4.862 min (major), *t*_R = 7.174 min (minor). [α]_D²⁰ = 3.5 (c 0.53, CHCl₃).

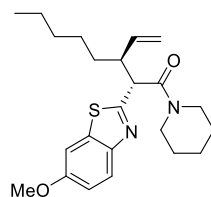
¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.3 Hz, 1H), 7.66 (s, 1H), 7.26 (d, *J* = 6.4 Hz, 1H), 5.64 (ddd, *J* = 17.2, 10.2, 8.8 Hz, 1H), 5.30 – 5.06 (m, 2H), 4.47 (d, *J* = 10.1 Hz, 1H), 3.80 – 3.38 (m, 4H), 2.97 (qd, *J* = 9.4, 4.3 Hz, 1H), 2.48 (s, 3H), 1.66 – 1.00 (m, 14H), 0.78 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 168.55, 168.36, 150.12, 139.19, 136.15, 135.04, 127.32, 122.19, 121.43, 117.47, 52.52, 48.52, 47.36, 43.51, 31.47, 31.44, 26.55, 26.50, 25.64, 24.53, 22.52, 21.50, 13.99.

IR (KBr): γ : 3077, 2930, 2856, 1644, 1507, 1442, 1260, 1248, 1216, 1162, 1135, 1090, 1014, 919, 814, 754 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₂₃H₃₃N₂OS]⁺ requires 385.2308, found 385.2312. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(6-methoxybenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-3-vinyloctan-1-one (50).



White solid. Yield: 73%, 29.3 mg. *b/l*> 20/1, *dr* 10/1. Enantiomeric excess: 91%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t_R* = 6.145 min (major), *t_R* = 8.225 min (minor). [α]_D²⁰ = -8.0 (c 2.23, CHCl₃).

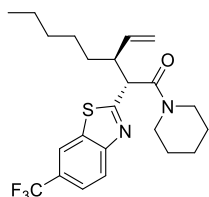
¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 8.9 Hz, 1H), 7.32 (d, *J* = 2.6 Hz, 1H), 7.05 (dd, *J* = 8.9, 2.6 Hz, 1H), 5.63 (ddd, *J* = 17.1, 10.2, 8.8 Hz, 1H), 5.29 – 5.00 (m, 2H), 4.45 (d, *J* = 10.1 Hz, 1H), 3.87 (s, 3H), 3.71 – 3.42 (m, 4H), 2.96 (qd, *J* = 9.0, 4.8 Hz, 1H), 1.71 – 1.00 (m, 14H), 0.79 (t, *J* = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 168.62, 166.81, 157.57, 146.49, 139.18, 137.34, 123.16, 117.46, 115.19, 104.03, 55.80, 52.42, 48.51, 47.36, 43.49, 31.47, 31.44, 26.55, 26.50, 25.63, 24.53, 22.51, 13.99.

IR (KBr): γ : 3076, 2931, 2856, 1636, 1602, 1558, 1508, 1435, 1261, 1229, 1135, 1058, 1025, 810 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₂₃H₃₃N₂O₂S]⁺ requires 401.2257, found 401.2264. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-1-(piperidin-1-yl)-2-(6-(trifluoromethyl)benzo[d]thiazol-2-yl)-3-vinyloctan-1-one (51).



White solid. Yield: 95%, 49.6 mg. *b/l*> 20/1, *dr*> 20/1. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK IF, hexane/isopropanol = 99/1, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t_R* = 16.057 min (major), *t_R* = 26.098 min (minor). [α]_D²⁰ = -0.7 (c 0.78, CHCl₃).

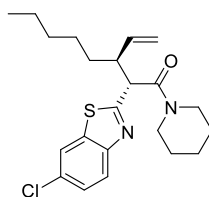
¹H NMR (400 MHz, CDCl₃) δ 8.17 (s, 1H), 8.06 (d, *J* = 8.6 Hz, 1H), 7.69 (dd, *J* = 8.6, 1.7 Hz, 1H), 5.64 (ddd, *J* = 17.2, 9.6 Hz, 1H), 5.37 – 4.97 (m, 2H), 4.54 (d, *J* = 9.9 Hz, 1H), 3.87 – 3.32 (m, 4H), 2.96 (qd, *J* = 9.7, 3.2 Hz, 1H), 1.79 – 1.01 (m, 14H), 0.79 (t, *J* = 6.9 Hz, 3H). **¹⁹F NMR** (376 MHz, CDCl₃) δ -61.35.

¹³C NMR (101 MHz, CDCl₃) δ 173.02, 168.29, 153.90, 138.68, 136.18, 123.10, 122.76, 122.73, 119.37, 119.33, 117.91, 52.54, 49.16, 47.46, 43.58, 31.48, 31.42, 26.57, 26.46, 25.60, 24.47, 22.47, 13.95.

IR (KBr): γ : 3076, 2930, 2856, 1635, 1569, 1499, 1471, 1442, 1258, 1247, 1135, 1014, 924, 776, 737 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₂₃H₃₀F₃N₂OS]⁺ requires 439.2025, found 439.2029. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(6-chlorobenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-3-vinyloctan-1-one (52).



White solid. Yield: 90%, 36.5 mg. *b/l*> 20/1, *dr*> 20/1. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t_R* = 5.252 min (major), *t_R* = 6.016 min (minor). [α]_D²⁰ = -12.4 (c 1.20, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.80 (m, 2H), 7.40 (dd, *J* = 8.7, 2.1 Hz, 1H), 5.61 (ddd, *J* = 17.1, 10.2, 8.9 Hz, 1H), 5.28 – 5.03 (m, 2H), 4.47 (d, *J* = 10.0 Hz, 1H), 3.70 – 3.32 (m, 4H), 3.05 – 2.81 (m, 1H), 1.66 – 1.38 (m, 6H), 1.33 – 1.02 (m, 8H), 0.77 (t, *J* = 6.9 Hz, 3H).

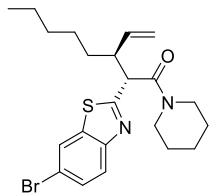
¹³C NMR (101 MHz, CDCl₃) δ 170.16, 168.40, 150.47, 138.81, 137.27, 130.93, 126.54, 123.47, 121.26, 117.81, 52.38, 48.98, 47.43, 43.53, 31.45, 31.43, 26.56, 26.48, 25.62, 24.49, 22.50, 14.00.

IR (KBr): γ : 3077, 2930, 2855, 1635, 1591, 1504, 1439, 1304, 1263, 1214, 1164, 1134, 1097, 1014, 920, 853, 814,

758, 680, 659 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[\text{C}_{22}\text{H}_{30}\text{ClN}_2\text{OS}]^+$ requires 405.1762, found 405.1768. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(6-bromobenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-3-vinyloctan-1-one (53).



White solid. Yield: 69%, 31.2 mg. *b/l* 20/1, *dr* > 20/1. Enantiomeric excess: 92%, determined by HPLC (CHIRALPAK IE10, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 8.468$ min (major), $t_R = 11.221$ min (minor). $[\alpha]_D^{20} = -17.7$ (c 1.17, CHCl_3).

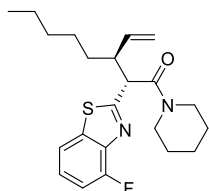
^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 1.9$ Hz, 1H), 7.80 (d, $J = 8.7$ Hz, 1H), 7.53 (dd, $J = 8.7, 2.0$ Hz, 1H), 5.61 (ddd, $J = 17.2, 9.6$ Hz, 1H), 5.26 – 5.01 (m, 2H), 4.47 (d, $J = 10.0$ Hz, 1H), 3.78 – 3.39 (m, 4H), 2.92 (qd, $J = 9.7, 3.4$ Hz, 1H), 1.68 – 1.38 (m, 6H), 1.35 – 1.00 (m, 8H), 0.77 (t, $J = 6.9$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 170.21, 168.37, 150.79, 138.79, 137.75, 129.23, 124.19, 123.84, 118.63, 117.82, 52.37, 48.98, 47.43, 43.54, 31.45, 31.43, 26.56, 26.47, 25.61, 24.49, 22.49, 14.00.

IR (KBr): γ : 3077, 2931, 2856, 1635, 1585, 1503, 1436, 1303, 1263, 1241, 1214, 1135, 1084, 1047, 1013, 921, 814, 754, 666 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[\text{C}_{22}\text{H}_{30}\text{BrN}_2\text{OS}]^+$ requires 449.1257, found 449.1266. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(4-fluorobenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-3-vinyloctan-1-one (54).



White solid. Yield: 82%, 31.7 mg. *b/l* > 20/1, *dr* > 20/1. Enantiomeric excess: 72%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 4.967$ min (major), $t_R = 5.442$ min (minor). $[\alpha]_D^{20} = 2.5$ (c 0.59, CHCl_3).

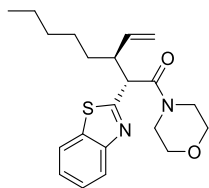
^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 8.0$ Hz, 1H), 7.39 – 7.29 (m, 1H), 7.15 (dd, $J = 10.5, 8.0$ Hz, 1H), 5.62 (dt, $J = 17.1, 9.6$ Hz, 1H), 5.39 – 4.95 (m, 2H), 4.59 (d, $J = 10.0$ Hz, 1H), 3.78 – 3.30 (m, 4H), 2.94 (qd, $J = 10.0, 3.0$ Hz, 1H), 1.75 – 1.40 (m, 6H), 1.37 – 1.01 (m, 8H), 0.79 (t, $J = 6.9$ Hz, 3H). **^{19}F NMR** (376 MHz, CDCl_3) δ -122.86.

^{13}C NMR (101 MHz, CDCl_3) δ 170.49, 168.55, 156.83, 154.29, 140.75, 140.62, 138.91, 138.87, 138.82, 125.74, 125.67, 117.80, 117.41, 117.37, 111.45, 111.27, 52.46, 49.27, 47.48, 43.54, 31.45, 31.41, 26.54, 25.63, 24.49, 22.50, 13.97.

IR (KBr): γ : 3078, 2932, 2857, 1646, 1635, 1505, 1456, 1412, 1319, 1272, 1226, 1165, 1125, 1084, 1050, 1015, 921, 882, 827, 797, 720, 650 cm^{-1} .

HRMS (ESI): m/z $[M + \text{Na}]^+$ calcd for $[\text{C}_{22}\text{H}_{29}\text{FN}_2\text{NaOS}]^+$ requires 411.1877, found 411.1888. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-1-morpholino-3-vinyloctan-1-one (55).



White solid. Yield: 94%, 35.6 mg. *b/l* > 20/1, *dr* > 20/1. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t*_R = 9.621 min (major), *t*_R = 11.471 min (minor). [α]_D²⁰ = 19.4 (c 0.53, CHCl₃).

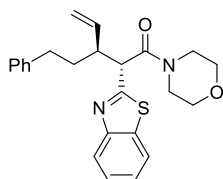
¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.91 – 7.85 (m, 1H), 7.51 – 7.43 (m, 1H), 7.42 – 7.34 (m, 1H), 5.64 (ddd, *J* = 17.3, 10.2, 8.8 Hz, 1H), 5.37 – 5.01 (m, 2H), 4.45 (d, *J* = 10.2 Hz, 1H), 3.80 – 3.37 (m, 8H), 3.00 (qd, *J* = 9.1, 4.7 Hz, 1H), 1.43 – 0.98 (m, 8H), 0.79 (t, *J* = 6.9 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 169.00, 168.85, 151.95, 138.84, 135.89, 125.89, 125.13, 122.79, 121.74, 117.91, 66.80, 66.66, 52.49, 48.57, 46.65, 42.64, 31.49, 31.42, 26.45, 22.50, 13.97.

IR (KBr): γ : 3066, 2928, 2856, 1646, 1505, 1436, 1450, 1397, 1314, 1260, 1128, 1066, 1014, 920, 802, 760, 730 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₂₁H₂₉N₂O₂S]⁺ requires 373.1944, found 373.1951. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-1-morpholino-3-phenethylpent-4-en-1-one (56).



White solid. Yield: 80%, 32.4 mg. *b/l* > 20/1, *dr* 18/1. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t*_R = 14.854 min (major), *t*_R = 18.324 min (minor). [α]_D²⁰ = 21.2 (c 0.24, CHCl₃).

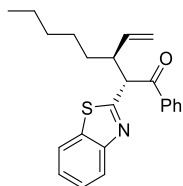
¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.0, 1.2 Hz, 1H), 7.46 (ddd, *J* = 8.2, 7.1, 1.3 Hz, 1H), 7.38 (td, *J* = 7.7, 1.2 Hz, 1H), 7.21 – 7.15 (m, 2H), 7.14 – 7.08 (m, 1H), 7.04 – 6.96 (m, 2H), 5.87 – 5.61 (m, 1H), 5.31 – 5.16 (m, 2H), 4.50 (d, *J* = 10.1 Hz, 1H), 3.87 – 3.40 (m, 8H), 3.04 (qd, *J* = 9.8, 3.6 Hz, 1H), 2.72 (ddd, *J* = 14.4, 9.6, 5.2 Hz, 1H), 2.42 (ddd, *J* = 13.8, 9.7, 7.3 Hz, 1H), 1.71 – 1.49 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 168.79, 168.44, 151.94, 141.57, 138.46, 135.87, 128.37, 128.24, 125.94, 125.78, 125.19, 122.83, 121.73, 118.54, 66.77, 66.64, 52.33, 47.96, 46.65, 42.66, 33.10, 32.97.

IR (KBr): γ : 3062, 3025, 2962, 2922, 2855, 1646, 1497, 1455, 1435, 1262, 1241, 1115, 1068, 1031, 801, 760, 730, 699 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₂₄H₂₇N₂O₂S]⁺ requires 407.1788, found 407.1790. The absolute configuration was assigned tentatively by analogy.

(2R,3S)-2-(benzo[d]thiazol-2-yl)-1-phenyl-3-vinyloctan-1-one (57).



(petroleum/ethyl acetate = 10/1). Yellow oil. Yield: 79%, 28.6 mg. *b/l* > 20/1, *dr* > 1/1. Enantiomeric excess: 80/83%,

determined by HPLC (CHIRALPAK IF, hexane/isopropanol = 99/1, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 9.110 min (minor), t_R = 9.843 min (major)/ t_R = 13.928 min (major), t_R = 15.410 min (minor).. $[\alpha]_D^{20}$ = -17.2 (c 0.60, CHCl₃).

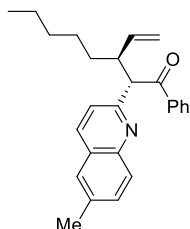
¹H NMR (400 MHz, CDCl₃) δ 8.17 – 8.10 (m, 1H), 8.09 – 8.05 (m, 1H), 8.00 (dd, J = 13.0, 8.1 Hz, 1H), 7.84 (dd, J = 16.1, 7.9 Hz, 1H), 7.65 – 7.51 (m, 1H), 7.50 – 7.40 (m, 3H), 7.34 (dt, J = 14.1, 7.6 Hz, 1H), 5.58 (ddd, J = 16.9, 9.7, 4.8 Hz, 1H), 5.32 (d, J = 10.0 Hz, 1H), 5.16 – 4.99 (m, 1H), 4.97 – 4.85 (m, 1H), 3.12 (qt, J = 13.6, 5.7 Hz, 1H), 1.42 – 1.01 (m, 8H), 0.90 – 0.71 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 197.84, 197.73, 168.23, 168.14, 152.35, 138.56, 137.78, 137.07, 136.83, 135.92, 135.86, 133.80, 133.59, 128.91, 128.87, 128.83, 128.77, 125.97, 125.84, 125.13, 124.99, 122.98, 122.93, 121.69, 121.63, 118.19, 117.95, 57.30, 57.28, 49.02, 48.80, 33.30, 31.70, 31.53, 31.45, 26.80, 26.37, 22.53, 14.03, 14.01.

IR (KBr): γ : 3065, 2956, 2928, 2856, 1685, 1595, 1500, 1456, 1447, 1436, 1314, 1261, 1208, 1182, 1157, 1066, 1014, 1000, 921, 800, 759, 729, 687 cm⁻¹.

HRMS (ESI): m/z [M + H]⁺ calcd for [C₂₃H₂₆NOS]⁺ requires 364.1730, found 364.1738. The absolute configuration was assigned tentatively by analogy.

(2S,3S)-2-(6-methylquinolin-2-yl)-1-phenyl-3-vinyloctan-1-one (58).



(petroleum/ethyl acetate = 10/1). Yellow oil. Yield: 88%, 32.5 mg. b/λ 20/1, dr 20/1. Enantiomeric excess: 66%, determined by HPLC (CHIRALPAK IF, hexane/isopropanol = 99/1, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 8.791 min (major), t_R = 13.870 min (minor). $[\alpha]_D^{20}$ = -18.6 (c 0.79, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 8.14 – 8.10 (m, 2H), 7.99 (dd, J = 8.9, 3.1 Hz, 2H), 7.57 – 7.50 (m, 3H), 7.48 – 7.43 (m, 1H), 7.38 (dd, J = 8.4, 7.0 Hz, 2H), 5.67 (ddd, J = 17.2, 10.3, 8.7 Hz, 1H), 5.13 – 5.07 (m, 2H), 5.00 (dd, J = 10.4, 1.7 Hz, 1H), 3.24 (qd, J = 10.5, 2.9 Hz, 1H), 2.50 (s, 3H), 1.38 – 1.21 (m, 3H), 1.18 – 1.00 (m, 5H), 0.77 (t, J = 7.0 Hz, 3H).

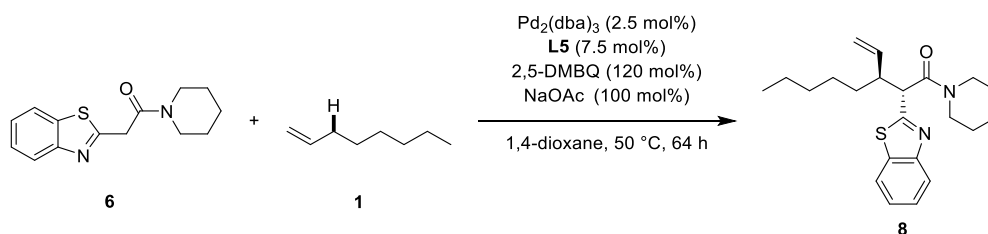
¹³C NMR (101 MHz, CDCl₃) δ 199.30, 157.26, 146.60, 139.93, 137.81, 136.24, 136.08, 132.90, 131.70, 128.93, 128.87, 128.47, 127.19, 126.41, 120.21, 116.97, 61.97, 46.52, 31.64, 31.56, 26.40, 22.48, 21.52, 13.98.

IR (KBr): γ : 3061, 2961, 2855, 1682, 1596, 1579, 1561, 1497, 1447, 1376, 1288, 1263, 1182, 1093, 1019 cm⁻¹.

HRMS (ESI): m/z [M + Na]⁺ calcd for [C₂₆H₂₉NNaO]⁺ requires 394.2141, found 394.2148. The absolute configuration was assigned tentatively by analogy.

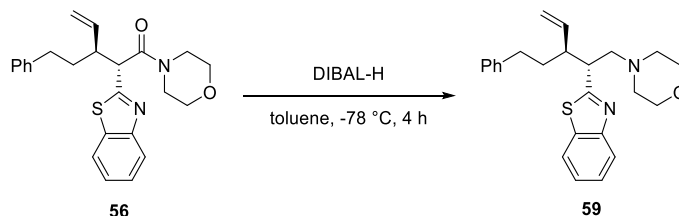
5. Synthetic applications

5.1 Procedure for gram-scale reaction



To a flame-dried and N_2 -purged Schlenk tube (100 mL) were added 2-(benzo[d]thiazol-2-yl)-1-(piperidin-1-yl)ethan-1-one **6** (4.0 mmol, 1.04 g), $\text{Pd}_2(\text{dba})_3$ (0.1 mmol, 91.6 mg), phosphoramidite **L5** (0.3 mmol, 232.8 mg), NaOAc (4.0 mmol, 328 mg), 2,5-DMBQ (4.8 mmol, 652 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 1,4-dioxane (20 mL) and oct-1-ene **1** (6.0 mmol, 673.3 mg) via a syringe, then the resulting mixture was stirred at 50 °C for 64 h (monitored by TLC). The reaction mixture was filtered through a pad of Celite, and concentrated in vacuo, and the residue was purified by column chromatography on silica gel (petroleum/ethyl acetate = 4/1) to provide the product **8** (1.29 g, 87%, 91% ee, >20:1 dr, >20:1 b/l).

5.2 Synthetic transformation of α -benzothiazylacetamide



To a solution of **56** (0.05 mmol, 20.3 mg) in toluene (1 mL) at -78 °C was slowly added DIBAL-H (1.5 M in toluene, 0.3 mmol, 0.2 mL), then the resulting mixture was stirred at -78 °C for 4 h. The reaction was quenched by a saturated aqueous solution of Seignette salt (1 mL) and extracted with ethyl acetate (1 mL $\times$ 3). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered, concentrated in vacuo, and the crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford the desired product **59**.⁴

4-((2R,3S)-2-(benzo[d]thiazol-2-yl)-3-phenethylpent-4-en-1-yl)morpholine (**59**).

Colorless oil. Yield: 58%, 11.5 mg. *dr* 12/1. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK IG, hexane/isopropanol = 97/3, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 8.980 min (minor), t_R = 9.929 min (major). $[\alpha]_D^{20}$ = -12.2 (c 1.51, CHCl_3).

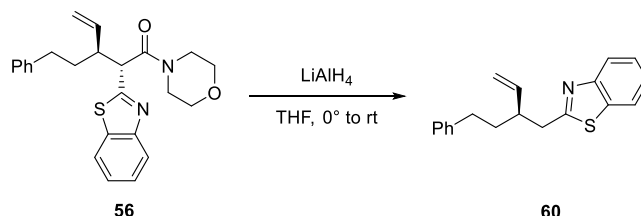
¹H NMR (400 MHz, CDCl_3) δ 7.98 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 7.9, 1.2 Hz, 1H), 7.46 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H), 7.36 (td, J = 7.6, 1.2 Hz, 1H), 7.23 – 7.17 (m, 2H), 7.16 – 7.10 (m, 1H), 7.07 – 6.99 (m, 2H), 5.69 (dt, J = 17.0, 9.8 Hz, 1H), 5.31 – 5.00 (m, 2H), 3.61 – 3.48 (m, 4H), 3.43 – 3.33 (m, 1H), 2.82 – 2.74 (m, 2H), 2.73 – 2.65 (m, 1H), 2.63 – 2.55 (m, 1H), 2.54 – 2.38 (m, 3H), 2.37 – 2.26 (m, 2H), 1.78 – 1.66 (m, 1H), 1.57 (ddd, J = 13.4, 10.0, 4.7 Hz, 1H).

¹³C NMR (101 MHz, CDCl_3) δ 174.11, 152.80, 141.97, 139.59, 134.94, 128.42, 128.22, 125.72, 125.69, 124.63,

122.69, 121.50, 117.69, 66.91, 61.82, 53.70, 47.67, 46.92, 33.59, 33.22.

IR (KBr): γ : 3062, 2962, 2853, 1637, 1603, 1507, 1455, 1436, 1261, 1115, 1014, 914, 866, 799, 759, 699 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[\text{C}_{24}\text{H}_{29}\text{N}_2\text{OS}]^+$ requires 393.1995, found 393.2003. The absolute configuration was assigned tentatively by analogy.



To a solution of **56** (0.345 mmol, 140 mg) in anhydrous THF (2.0 mL) at 0 °C was carefully added LiAlH_4 (0.69 mmol, 2.5 M in THF, 0.28 mL). The reaction mixture was then warmed to RT and stirred for overnight. The reaction was quenched with water (5 mL) and extracted with ethyl acetate (5 mL $\times$ 3). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered, concentrated in vacuo, and the crude product was purified by flash column chromatography (petroleum ether/ethyl acetate 10:1) to afford product **60**.⁵

(R)-2-(2-phenethylbut-3-en-1-yl)benzo[d]thiazole (60).

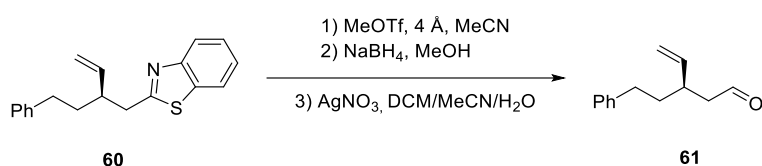
Colorless oil. Yield: 62%, 62.7 mg. Enantiomeric excess: 87%, determined by HPLC (CHIRALPAK OD, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, $T = 30^\circ\text{C}$, 254 nm): $t_R = 4.538$ min (minor), $t_R = 6.311$ min (major). $[\alpha]_D^{20} = 11.4$ (c 1.04, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, $J = 8.1$ Hz, 1H), 7.83 (d, $J = 8.0, 1.2$ Hz, 1H), 7.45 (t, 1H), 7.36 (t, 1H), 7.31 – 7.23 (m, 2H), 7.21 – 7.14 (m, 3H), 5.75 (ddd, $J = 16.9, 10.4, 8.6$ Hz, 1H), 5.34 – 4.99 (m, 2H), 3.19 (qd, $J = 14.5, 7.2$ Hz, 2H), 2.85 – 2.65 (m, 2H), 2.59 (ddd, $J = 13.8, 10.3, 6.5$ Hz, 1H), 2.01 – 1.80 (m, 1H), 1.81 – 1.57 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 170.12, 153.13, 142.05, 140.42, 135.29, 128.41, 128.35, 125.86, 125.80, 124.70, 122.61, 121.46, 116.62, 44.14, 39.93, 36.14, 33.30.

IR (KBr): 3062, 2962, 2923, 2854, 1515, 1434, 1261, 1095, 1015, 799, 758, 698 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[\text{C}_{19}\text{H}_{20}\text{NS}]^+$ requires 294.1311, found 294.1317. The absolute configuration was assigned tentatively by analogy.



A mixture of **60** (156.8 mg, 0.53 mmol), activated 4 Å molecular sieves (0.53 g), and anhydrous CH_3CN (5.4 mL) was stirred at room temperature for 10 min, then methyl triflate (91 μL , 0.80 mmol) was added to the suspension. The suspension was stirred at room temperature for 15 min (monitored by TLC). The mixture was filtered through a pad of Celite. The filtrate was concentrated in vacuo to give the crude *N*-methylbenzothiazolium salt.

The residue was dissolved in MeOH (5.4 mL) at 0 °C and added NaBH_4 (1.59 mmol, 60.1 mg) to the reaction until the starting material had been consumed as determined by TLC. The mixture was quenched by acetone and concentrated in vacuo, then DCM (10 mL) and water (10 mL) were added. The organic phase was separated, and the aqueous phase was extracted with DCM (10 mL $\times$ 3). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered and concentrated in vacuo to give the crude benzothiazoline.

To a vigorously stirred solution of the crude benzothiazoline in DCM (0.6 mL) and CH_3CN (3 mL) were added H_2O (0.36 mL) followed by AgNO_3 (0.6 mmol, 102 mg). The mixture was stirred at RT (monitored by TLC until benzothiazoline was fully consumed), then diluted with phosphate buffer (1 M, pH = 7, 0.5 mL). After stirred for

15 min, the reaction mixture was further diluted with phosphate buffer (1 M, pH = 7, 13 mL). The suspension was filtered through a pad of Celite, extracted with ethyl acetate (10 mL $\times$ 3), and the combined organic layers were dried over Na₂SO₄, filtered through a pad of Celite, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1) to afford product **61**.^{6,7}

(R)-3-phenethylpent-4-enal (61).

Colorless oil. Yield: 74%, 74.2 mg. Enantiomeric excess: 87%, determined by **60**. $[\alpha]_D^{20} = 1.8$ (c 0.48, CHCl₃).

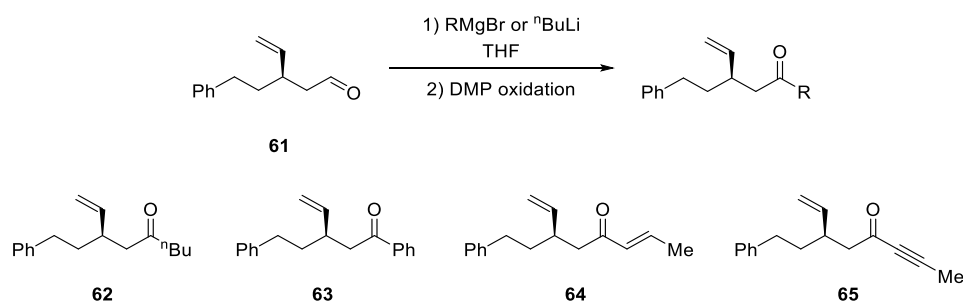
¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, J = 8.1 Hz, 1H), 7.83 (dd, J = 8.0, 1.2 Hz, 1H), 7.52 – 7.42 (m, 1H), 7.38 – 7.33 (m, 1H), 7.31 – 7.23 (m, 2H), 7.21 – 7.14 (m, 3H), 5.75 (ddd, J = 16.9, 10.4, 8.6 Hz, 1H), 5.34 – 4.99 (m, 2H), 3.19 (qd, J = 14.5, 7.2 Hz, 2H), 2.85 – 2.65 (m, 2H), 2.59 (ddd, J = 13.8, 10.3, 6.5 Hz, 1H), 2.01 – 1.80 (m, 1H), 1.81 – 1.57 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 202.10, 141.84, 140.47, 128.41, 128.37, 125.89, 116.11, 48.59, 37.99, 36.40, 33.18.

IR (KBr): γ : 3063, 3026, 2961, 2924, 2854, 2718, 1726, 1496, 1454, 1412, 1260, 1093, 1021, 918, 800, 749, 699 cm⁻¹.

HRMS (ESI): m/z [M + H]⁺ calcd for [C₁₃H₁₇O]⁺ requires 189.1274, found 189.1281. The absolute configuration was assigned tentatively by analogy.

5.3 General procedure synthesis of carbonyl compounds from compound **61**



To a solution of **61** (18.8 mg, 0.1 mmol) in THF (1 mL) was slowly added phenylmagnesium bromide (0.31 mmol, 1 M in THF, 0.31 mL) at 0° C. The resulting solution was allowed to stir overnight at room temperature. After the reaction was completed (monitored by TLC), the mixture was cooled to 0° C and saturated aq. NH₄Cl (1 mL) was added dropwise, then diluted with ethyl acetate (1 mL $\times$ 3) and washed with aq. NaHCO₃, brine, and water, respectively. The organic layer was dried with anhydrous Na₂SO₄, filtered and concentrated. The crude product was directly used in the next step without further purification.⁸

The residue was re-dissolved in dry DCM (1.0 mL), then Dess-Martin periodinane (63.6 mg, 0.15 mmol) was added at room temperature. After the reaction was completed (monitored by TLC), the reaction mixture was diluted with DCM, poured slowly into a solution of Na₂S₂O₃:NaHCO₃ (1:1) and stirred for 5 minutes. DCM (1 mL $\times$ 3) was used in the extraction and the combined organic extracts were washed with saturated aq. NaHCO₃, brine. The organic phase was dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by flash chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to afford the desired product ketone **63**.⁹ Ketone **62**, **64** and **65** were synthesized according to similar process.

(R)-3-phenethylnon-1-en-5-one (62).

Colorless oil. Yield: 90%, 28.6 mg. Enantiomeric excess: 87%, determined by **60**. $[\alpha]_D^{20} = 9.3$ (c 0.89, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.22 (m, 2H), 7.21 – 7.11 (m, 3H), 5.66 (ddd, J = 17.9, 9.8, 8.4 Hz, 1H), 5.15 – 4.98 (m, 2H), 2.71 – 2.59 (m, 2H), 2.54 (ddd, J = 13.8, 10.3, 6.5 Hz, 1H), 2.44 (d, J = 7.0 Hz, 2H), 2.35 (t, J = 7.4 Hz, 2H), 1.71 (dddd, J = 13.4, 10.4, 6.5, 4.6 Hz, 1H), 1.63 – 1.47 (m, 3H), 1.36 – 1.22 (m, 2H), 0.89 (t, J = 7.3 Hz,

3H).

¹³C NMR (101 MHz, CDCl₃) δ 210.11, 142.22, 141.07, 128.38, 128.34, 125.76, 115.46, 48.20, 43.21, 39.25, 36.41, 33.41, 25.72, 22.33, 13.87.

IR (KBr): γ : 3063, 2959, 2859, 1716, 1638, 1603, 1496, 1454, 1410, 1364, 1261, 1091, 1030, 915, 800, 735, 699 cm⁻¹.

HRMS (ESI): m/z [M + Na]⁺ calcd for [C₁₇H₂₄NaO]⁺ requires 267.1719, found 267.1724. The absolute configuration was assigned tentatively by analogy.

(R)-3-phenethyl-1-phenylpent-4-en-1-one (63).

Colorless oil. Yield: 92%, 24.2 mg. Enantiomeric excess: 87%, determined by **60**. [α]_D²⁰ = 10.4 (c 0.93, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.82 (m, 2H), 7.57 – 7.49 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.18 – 7.10 (m, 3H), 5.84 – 5.61 (m, 1H), 5.15 – 4.93 (m, 2H), 3.07 – 2.94 (m, 2H), 2.80 (q, *J* = 7.2 Hz, 1H), 2.68 (ddd, *J* = 13.8, 10.5, 5.3 Hz, 1H), 2.56 (ddd, *J* = 13.8, 10.4, 6.3 Hz, 1H), 1.91 – 1.74 (m, 1H), 1.72 – 1.61 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 199.23, 142.24, 141.13, 137.32, 132.97, 128.59, 128.38, 128.34, 128.12, 125.76, 115.49, 43.94, 39.55, 36.41, 33.47.

IR (KBr): γ : 2962, 2923, 2854, 1685, 1448, 1416, 1356, 1261, 1094, 1018, 915, 865, 800, 697 cm⁻¹.

HRMS (ESI): m/z [M + Na]⁺ calcd for [C₁₉H₂₂NaO]⁺ requires 287.1406, found 287.1416. The absolute configuration was assigned tentatively by analogy.

(R,E)-6-phenethylocta-2,7-dien-4-one (64).

Colorless oil. Yield: 88%, 20.3 mg. Enantiomeric excess: 87%, determined by **60**. [α]_D²⁰ = 16.3 (c 0.27, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.23 (m, 2H), 7.21 – 7.13 (m, 3H), 6.25 – 6.05 (m, 2H), 5.80 – 5.55 (m, 1H), 5.14 – 4.89 (m, 2H), 2.75 – 2.60 (m, 2H), 2.59 – 2.44 (m, 3H), 2.09 (d, 3H), 1.80 – 1.67 (m, 1H), 1.66 – 1.53 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 200.71, 142.93, 142.28, 141.13, 128.38, 128.32, 127.93, 125.73, 115.32, 49.53, 39.46, 36.41, 33.40, 15.91.

IR (KBr): γ : 3026, 2961, 2924, 2854, 1692, 1619, 1496, 1455, 1417, 1336, 1261, 1098, 1029, 915, 800, 698 cm⁻¹.

HRMS (ESI): m/z [M + Na]⁺ calcd for [C₁₆H₂₀NaO]⁺ requires 251.1406, found 251.1411. The absolute configuration was assigned tentatively by analogy.

(R)-6-phenethyloct-7-en-2-yn-4-one (65).

Colorless oil. Yield: 87%, 25.6 mg. Enantiomeric excess: 87%, determined by **60**. [α]_D²⁰ = 15.6 (c 1.04, CHCl₃).

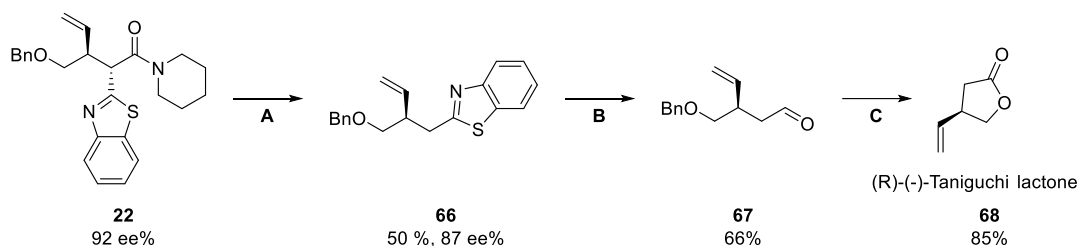
¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.23 (m, 2H), 7.21 – 7.12 (m, 3H), 5.74 – 5.58 (m, 1H), 5.14 – 4.97 (m, 2H), 2.79 – 2.61 (m, 2H), 2.61 – 2.49 (m, 3H), 1.98 (s, 3H), 1.79 – 1.69 (m, 1H), 1.67 – 1.56 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 186.96, 142.03, 140.39, 128.41, 128.34, 125.79, 115.85, 90.36, 80.45, 50.63, 39.35, 36.11, 33.25, 4.08.

IR (KBr): γ : 2962, 2217, 1675, 1454, 1416, 1261, 1096, 1018, 916, 856, 799, 698 cm⁻¹.

HRMS (ESI): m/z [M + Na]⁺ calcd for [C₁₆H₁₈NaO]⁺ requires 249.1250, found 249.1258. The absolute configuration was assigned tentatively by analogy.

5.4 Asymmetry synthesis of (R)-(-)-Taniguchi lactone (68)



Conditions: **A:** LiAlH₄, THF, 0 °C to rt. **B:** 1) MeOTf, 4 Å, MeCN. 2) NaBH₄, MeOH. 3) AgNO₃, DCM/MeCN/H₂O. **C:** 1) I₂, KOH, MeOH. 2) a. DDQ, DCM/H₂O; b. TFA.

A: To a solution of **22** (0.58 mmol, 243 mg) in anhydrous THF (2.6 mL) were carefully added LiAlH₄ (1.74 mmol, 2.5 M in THF, 0.70 mL) at 0 °C. The reaction mixture was then warm to RT and stirred overnight. The reaction was quenched with water (5 mL) and extracted with ethyl acetate (5 mL × 3), the combined organic phases were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo, and the crude product was purified by flash column chromatography (petroleum ether/ethyl acetate 10:1, visualized with UV) to afford product **66**.

(R)-2-(2-((benzyloxy)methyl)but-3-en-1-yl)benzo[d]thiazole (**66**).

Colorless oil. Yield: 50%, 90 mg. Enantiomeric excess: 87%, determined by HPLC (CHIRALPAK OD, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 5.222 min (minor), t_R = 7.302 min (major). [α]_D²⁰ = 1.3 (c 0.24, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, 1H), 7.81 (d, *J* = 8.0, 1.2 Hz, 1H), 7.47 – 7.39 (m, 1H), 7.37 – 7.22 (m, 6H), 5.84 (ddd, *J* = 17.7, 10.4, 7.9 Hz, 1H), 5.31 – 5.00 (m, 2H), 4.52 (s, 2H), 3.67 – 3.46 (m, 2H), 3.40 (dd, *J* = 14.6, 6.1 Hz, 1H), 3.17 (dd, *J* = 14.6, 8.3 Hz, 1H), 3.08 – 2.96 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 170.07, 153.22, 138.29, 137.90, 135.37, 128.39, 127.63, 127.62, 125.87, 124.72, 122.63, 121.49, 117.04, 73.14, 72.58, 44.29, 36.23.

IR (KBr): γ : 3063, 2962, 2924, 2854, 2716, 1683, 1519, 1495, 1455, 1435, 1416, 1360, 1261, 1096, 1018, 864, 800, 759, 697 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₁₉H₂₀NOS]⁺ requires 310.1260, found 310.1269. The absolute configuration was assigned tentatively by analogy.

B: 1) A mixture of **66** (88.5 mg, 0.29 mmol), activated 4-Å powdered molecular sieves (0.29 g), and anhydrous CH₃CN (2.9 mL) was stirred at room temperature for 10 min, and then methyl triflate (49.3 μL, 0.435 mmol) was added to the suspension. The suspension was stirred at room temperature for 15 min (monitored by TLC), filtered through a pad of Celite, and concentrated to give the *N*-methylbenzothiazolium salt. The crude product was directly used in the next step without further purification.

2) The residue was dissolved in MeOH (2.9 mL) at 0 °C, then NaBH₄ (0.87 mmol, 32.9 mg) was added. The reaction was warmed to room temperature until the starting material was completely consumed as determined by TLC. The mixture was quenched by acetone and concentrated in vacuo, then DCM (10 mL) and water (10 mL) were added. The organic phase was separated, and the aqueous phase was extracted with DCM (10 mL × 3). The combined organic phases were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo to give the crude benzothiazoline.

3) To a vigorously stirred solution of the crude benzothiazoline in DCM (0.87 mL) and CH₃CN (4.3 mL) was added H₂O (0.52 mL) and followed by the addition of AgNO₃ (0.87 mmol, 147.8 mg). The mixture was stirred at RT (monitored by TLC until benzothiazoline was fully consumed), then diluted with phosphate buffer (1 M, pH = 7, 0.3 mL). After being stirred for 15 min, the reaction mixture was diluted with phosphate buffer (1 M, pH = 7, 7 mL). The suspension was filtered through a pad of Celite, extracted with ethyl acetate (5 mL × 3), and the combined organic layers were dried over anhydrous Na₂SO₄, filtered through a pad of Celite, and concentrated in vacuo. The

residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1) to afford product **67**.

2-((R)-2-((benzyloxy)methyl)but-3-en-1-yl)-3-methyl-2,3-dihydrobenzo[d]thiazole (**67**).

Colorless oil. Yield: 66%, 38.9 mg. Enantiomeric excess: 87%, determined by **66**. $[\alpha]_{\text{D}}^{20} = 17.5$ (c 0.55, CHCl_3).

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.66 (s, 1H), 7.50 – 7.04 (m, 5H), 5.69 (ddd, $J = 17.6, 10.5, 7.4$ Hz, 1H), 5.20 – 4.82 (m, 2H), 4.42 (s, 2H), 3.44 (dd, $J = 9.2, 5.2$ Hz, 1H), 3.28 (dd, $J = 9.2, 7.7$ Hz, 1H), 2.93 (h, $J = 6.9$ Hz, 1H), 2.55 (ddd, $J = 16.5, 6.4, 2.2$ Hz, 1H), 2.39 (ddd, $J = 16.6, 7.4, 2.1$ Hz, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 201.78, 138.09, 137.61, 128.43, 127.69, 127.63, 116.48, 73.15, 72.85, 45.70, 38.54.

IR (KBr): γ : 2962, 2924, 2854, 1727, 1454, 1411, 1260, 1094, 1026, 864, 799, 698 cm^{-1} .

HRMS (ESI): m/z $[\text{M} + \text{Na}]^+$ calcd for $[\text{C}_{13}\text{H}_{16}\text{NaO}_2]^+$ requires 227.1043, found 227.1048. The absolute configuration was assigned tentatively by analogy.

C: 1) Aldehyde **67** (16.8 mg, 0.082 mmol) was dissolved in MeOH (1.3 mL), then KOH (45.7 mg, 0.82 mmol) and I_2 (208.1 g, 0.82 mmol) were added at 0 °C. The reaction was stirred at room temperature for 30 min then was quenched with saturated $\text{Na}_2\text{S}_2\text{O}_3$ (aq., 1mL) and diluted with H_2O (1 mL). The mixture was extracted with CH_2Cl_2 (1 mL $\times$ 3) and the combined organic layers were washed with saturated brine, dried over anhydrous Na_2SO_4 , filtered and concentrated under reduced pressure.¹⁰

2) The residue was dissolved in $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$ (20/1, 1.7 mL), and then DDQ (74 mg, 0.328 mmol) was added. The reaction was stirred at 40 °C for 5 h (monitored by TLC), and then TFA (0.123 mmol, 9 μL) was added, and the mixture was stirred at 40 °C for 5 h again. The mixture was partitioned between CHCl_3 (1 mL $\times$ 3) and sat. aq. NaHCO_3 . The organic layer was washed with brine, dried over Na_2SO_4 , filtered and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexanes/ethyl acetate = 2:1) to give **68** as a colorless oil. The spectroscopic data of the compound matched with the previously reported data.¹¹

(R)-4-vinyldihydrofuran-2(3H)-one (**68**).

Colorless oil. Yield: 85%, 7.8 mg. Enantiomeric excess: 87%, determined by **66**. $[\alpha]_{\text{D}}^{20} = -12.0$ (c 0.25, CHCl_3).

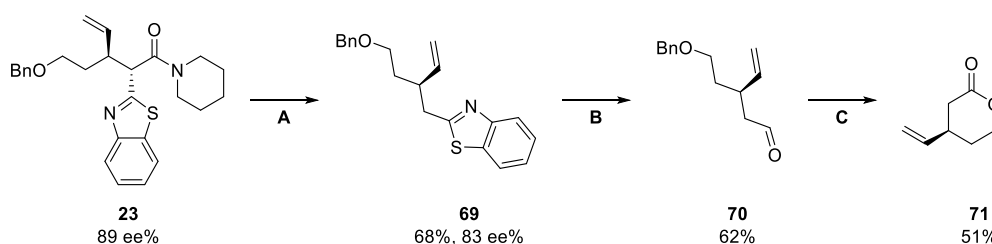
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 5.78 (ddd, $J = 17.4, 10.3, 7.6$ Hz, 1H), 5.29 – 5.08 (m, 2H), 4.45 (dd, $J = 9.1, 7.7$ Hz, 1H), 4.03 (dd, $J = 9.0, 7.9$ Hz, 1H), 3.23 (h, $J = 8.1$ Hz, 1H), 2.68 (dd, $J = 17.4, 8.4$ Hz, 1H), 2.39 (dd, $J = 17.4, 9.0$ Hz, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 176.42, 135.77, 117.53, 72.21, 39.83, 34.16.

IR (KBr): γ : 2961, 2923, 2852, 1260, 1091, 1019, 799 cm^{-1} .

HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_6\text{H}_9\text{O}_2]^+$ requires 113.0597, found 113.0600. The absolute configuration was assigned tentatively by analogy.

5.5 Asymmetry synthesis of (R)-4-vinyltetrahydro-2H-pyran-2-one (**71**)



Conditions: **A:** LiAlH_4 , THF, 0°C to rt. **B:** 1) MeOTf , 4 Å, MeCN. 2) NaBH_4 , MeOH. 3) AgNO_3 , DCM/MeCN/ H_2O . **C:** 1) I_2 , KOH, MeOH. 2) a. DDQ, DCM/ H_2O ; b. TFA.

A: To a solution of **23** (0.63 mmol, 272 mg) in anhydrous THF (2.8 mL) was carefully added LiAlH_4 (1.89 mmol, 2.5 M in THF, 0.76 mL) at 0 °C. The reaction mixture was then warmed to RT and stirred overnight. The reaction

was quenched with water (5 mL) and extracted with ethyl acetate (5 mL $\times$ 3), the combined organic phases were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo, and the crude product was purified by flash column chromatography (petroleum ether/ethyl acetate 10:1, visualized with UV) to afford product **69**.

(R)-2-(2-(2-(benzyloxy)ethyl)but-3-en-1-yl)benzo[d]thiazole (69).

Colorless oil. Yield: 68%, 138.1 mg. Enantiomeric excess: 83%, determined by HPLC (CHIRALPAK OD, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 5.190 min (minor), t_R = 6.677 min (major). $[\alpha]_D^{20}$ = 1.8 (c 0.17, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.93 (m, 1H), 7.81 (dd, J = 7.9, 1.3 Hz, 1H), 7.42 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H), 7.35 – 7.29 (m, 5H), 7.28 – 7.23 (m, 1H), 5.68 (ddd, J = 17.0, 10.3, 8.6 Hz, 1H), 5.12 – 4.87 (m, 2H), 4.46 (d, J = 2.6 Hz, 2H), 3.61 – 3.40 (m, 2H), 3.31 – 3.04 (m, 2H), 2.93 – 2.75 (m, 1H), 1.90 (dtd, J = 14.2, 7.2, 4.7 Hz, 1H), 1.67 (ddt, J = 14.0, 9.3, 5.8 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 170.13, 153.15, 140.13, 138.50, 135.39, 128.39, 127.71, 127.58, 125.88, 124.73, 122.65, 121.50, 116.50, 73.00, 67.93, 41.45, 39.92, 34.27.

IR (KBr): γ : 2962, 2922, 2853, 2718, 1457, 1437, 1412, 1363, 1260, 1093, 1018, 856, 800, 697 cm⁻¹.

HRMS (ESI): m/z [M + H]⁺ calcd for [C₂₀H₂₂NOS]⁺ requires 324.1417, found 324.1428. The absolute configuration was assigned tentatively by analogy.

B: 1) A mixture of **69** (55 mg, 0.17 mmol), activated 4-Å powdered molecular sieves (0.17 g), and anhydrous CH₃CN (1.7 mL) was stirred at room temperature for 10 min, and then methyl triflate (28.9 μ L, 0.255 mmol) was added to the suspension. The suspension was stirred at room temperature for 15 min (monitored by TLC), filtered through a pad of Celite, and concentrated to give the *N*-methylbenzothiazolium salt. The crude product was directly used in the next step without further purification.

2) The residue was dissolved in MeOH (1.7 mL) at 0 °C, and then NaBH₄ (0.51 mmol, 19.3 mg) was added. The reaction was warmed up to room temperature until the starting material was completely consumed as determined by TLC. The mixture was quenched by acetone and concentrated in vacuo, then DCM (5 mL) and water (5 mL) were added. The organic phase was separated, and the aqueous phase was extracted with DCM (5 mL $\times$ 3). The combined organic phases were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo to give the crude benzothiazoline.

3) To a vigorously stirred solution of the crude benzothiazoline in DCM (0.5 mL) and CH₃CN (2.6 mL) were added H₂O (0.3 mL) and followed by addition of AgNO₃ (0.51 mmol, 86.6 mg). The mixture was stirred at RT (monitored by TLC until benzothiazoline was fully consumed), then diluted with phosphate buffer (1 M, pH = 7, 0.17 mL). After being stirred for 15 min, the reaction mixture was further diluted with phosphate buffer (1 M, pH = 7, 4.3 mL). The suspension was filtered through a pad of Celite, extracted with ethyl acetate (5 mL $\times$ 3), and the combined organic layers were dried over Na₂SO₄, filtered through a pad of Celite, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1) to afford product **70**.

(R)-3-(2-(benzyloxy)ethyl)pent-4-enal (70).

Colorless oil. Yield: 62%, 23 mg. Enantiomeric excess: 83%, determined by the **69**. $[\alpha]_D^{20}$ = 11.9 (c 0.30, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 9.69 (t, J = 2.3 Hz, 1H), 7.44 – 7.14 (m, 5H), 5.74 – 5.59 (m, 1H), 5.15 – 4.88 (m, 2H), 4.47 (s, 2H), 3.58 – 3.40 (m, 2H), 2.85 (ddd, J = 14.1, 8.4, 5.7 Hz, 1H), 2.58 – 2.33 (m, 2H), 1.76 (ddt, J = 11.9, 7.5, 5.9 Hz, 1H), 1.64 (ddt, J = 14.2, 8.7, 5.7 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 202.13, 140.32, 138.40, 128.40, 127.70, 127.63, 115.83, 73.02, 67.66, 48.39, 35.34, 34.48.

IR (KBr): γ : 2962, 2923, 2853, 1723, 1455, 1260, 1049, 1019, 799 cm⁻¹.

HRMS (ESI): m/z [M + Na]⁺ calcd for [C₁₄H₁₈NaO₂]⁺ requires 241.1199, found 241.1204. The absolute

configuration was assigned tentatively by analogy.

C: 1) Aldehyde **70** (17 mg, 0.078 mmol, 1.0 equiv) was dissolved in MeOH (1.2 mL), and then KOH (43.7 mg, 0.78 mmol) and I₂ (198 mg, 0.78 mmol) were added at 0 °C. The reaction was stirred at room temperature for 30 min and then was quenched with saturated Na₂S₂O₃ (aq., 1 mL) and diluted with H₂O (1 mL). The mixture was extracted with CH₂Cl₂ (1 mL × 3) and the combined organic layers were washed with saturated brine, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure.

2) The residue was dissolved in CH₂Cl₂/H₂O (20/1, 1.7 mL), and then DDQ (70.4 mg, 0.31 mmol) was added. The reaction was stirred at 40 °C for 5 h (monitored by TLC), and then TFA (0.12 mmol, 8.6 μL) was added, and the mixture was stirred at 40 °C for 5 h again. The mixture was partitioned between CHCl₃ (1.5 mL × 3) and sat. aq. NaHCO₃. The organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexanes/ethyl acetate = 2:1) to give **71** as a colorless oil. The spectroscopic data of the compound matched with the previously reported data.¹²

(R)-4-vinyltetrahydro-2H-pyran-2-one (**71**).

Colorless oil. Yield: 51%, 5 mg. Enantiomeric excess: 83%, determined by **69**. [α]_D²⁰ = 25.2 (c 0.25, CHCl₃).

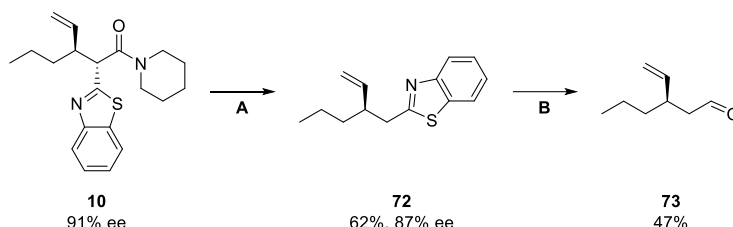
¹H NMR (400 MHz, CDCl₃) δ 5.84 – 5.58 (m, 1H), 5.21 – 4.83 (m, 2H), 4.38 (dt, *J* = 11.4, 4.7 Hz, 1H), 4.26 (ddd, *J* = 11.3, 9.9, 3.9 Hz, 1H), 2.71 – 2.57 (m, 2H), 2.38 – 2.26 (m, 1H), 2.06 – 1.90 (m, 1H), 1.75 – 1.61 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 170.53, 139.44, 115.12, 68.24, 35.43, 35.08, 28.50.

IR (KBr): γ : 2960, 2923, 2853, 1260, 1092, 1018, 799 cm⁻¹.

HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₇H₁₁O₂]⁺ requires 127.0754, found 127.0756. The absolute configuration was assigned tentatively by analogy.

5.6 Asymmetry synthesis of (R)-3-vinylhexanal (**73**)



Conditions: **A:** LiAlH₄, THF, 0 °C to rt. **B:** 1) MeOTf, 4 Å, MeCN. 2) NaBH₄, MeOH. 3) AgNO₃, DCM/MeCN/H₂O.

A: To a solution of **10** (0.26 mmol, 89 mg) in anhydrous THF (1.1 mL) were carefully added LiAlH₄ (0.78 mmol, 2.5 M in THF, 0.31 mL) at 0 °C. The reaction mixture was then warmed up to RT and stirred overnight. The reaction was quenched with water (3 mL) and extracted with ethyl acetate (3 mL × 3), the combined organic phases were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo, and the crude product was purified by flash column chromatography (petroleum ether/ethyl acetate 10:1, visualized with UV) to afford product **72**.

(R)-2-(2-vinylpentyl)benzo[d]thiazole (**72**).

Colorless oil. Yield: 62%, 37.1 mg. Enantiomeric excess: 87%, determined by HPLC (CHIRALPAK OD, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t*_R = 3.763 min (minor), *t*_R = 3.965 min (major). [α]_D²⁰ = -11 (c 0.24, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ 7.98 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.83 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.44 (ddd, *J* = 8.2, 7.2, 1.3 Hz, 1H), 7.34 (td, *J* = 7.6, 1.2 Hz, 1H), 5.67 (ddd, *J* = 18.1, 9.9, 8.6 Hz, 1H), 5.17 – 4.83 (m, 2H), 3.33 – 2.88 (m, 2H), 2.73 – 2.56 (m, 1H), 1.55 – 1.20 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 170.60, 153.15, 140.87, 135.31, 125.82, 124.65, 122.59, 121.45, 115.85, 44.34, 39.99,

36.66, 20.13, 14.00.

IR (KBr): γ : 2962, 2925, 2853, 1658, 1632, 1456, 1412, 1260, 1094, 865, 800, 758, 728, 701 cm^{-1} .

HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{14}H_{18}NS]^+$ requires 232.1154, found 232.1147. The absolute configuration was assigned tentatively by analogy.

B: 1) A mixture of **72** (70 mg, 0.30 mmol), activated 4-Å powdered molecular sieves (0.3 g), and anhydrous CH_3CN (3 mL) was stirred at room temperature for 10 min, and then methyl triflate (51 μL , 0.45 mmol) was added to the suspension. The suspension was stirred at room temperature for 15 min (monitored by TLC), filtered through a pad of Celite, and concentrated to give the *N*-methylbenzothiazolium salt. The crude product was directly used in the next step without further purification.

2) The residue was dissolved in MeOH (3 mL) at 0 °C, and then NaBH_4 (0.9 mmol, 34 mg) was added. The reaction was warmed up to room temperature until the starting material was completely consumed as determined by TLC. The mixture was quenched by acetone and concentrated in vacuo, and then DCM (10 mL) and water (10 mL) were added. The organic phase was separated, and the aqueous phase was extracted with DCM (10 mL $\times$ 3). The combined organic phases were dried over anhydrous Na_2SO_4 , filtered and concentrated in vacuo to give the crude benzothiazoline.

3) To a vigorously stirred solution of the crude benzothiazoline in DCM (0.9 mL) and CH_3CN (4.5 mL) was added H_2O (0.48 mL) and followed by the addition of AgNO_3 (0.9 mmol, 153 mg). The mixture was stirred at RT (monitored by TLC until benzothiazoline was fully consumed), then diluted with phosphate buffer (1 M, pH = 7, 0.3 mL). After being stirred for 15 min, the reaction mixture was further diluted with phosphate buffer (1 M, pH = 7, 7.5 mL). The suspension was filtered through a pad of Celite, extracted with ethyl acetate (5 mL $\times$ 3), and the combined organic layers were dried over Na_2SO_4 , filtered through a pad of Celite, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1) to afford product **73**.

(R)-3-vinylhexanal (73).

Colorless oil. Yield: 47%, 17.7 mg. Enantiomeric excess: 87%, determined by **72**. $[\alpha]_D^{20} = -19.3$ (c 0.27, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ 9.72 (d, $J = 2.3$ Hz, 1H), 5.65 (ddd, $J = 17.8, 9.9, 8.2$ Hz, 1H), 5.19 – 4.82 (m, 2H), 2.63 (q, $J = 6.7$ Hz, 1H), 2.45 – 2.35 (m, 2H), 1.40 – 1.26 (m, 4H), 0.89 (t, 3H).

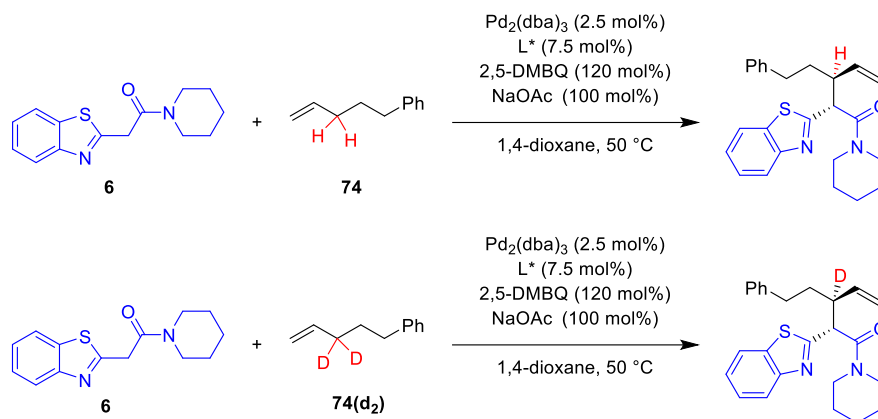
^{13}C NMR (101 MHz, CDCl_3) δ 202.55, 140.96, 115.27, 48.56, 38.15, 36.93, 20.04, 13.95.

IR (KBr): γ : 2961, 2924, 2853, 2717, 1261, 1094, 1024, 864, 800, 738, 700 cm^{-1} .

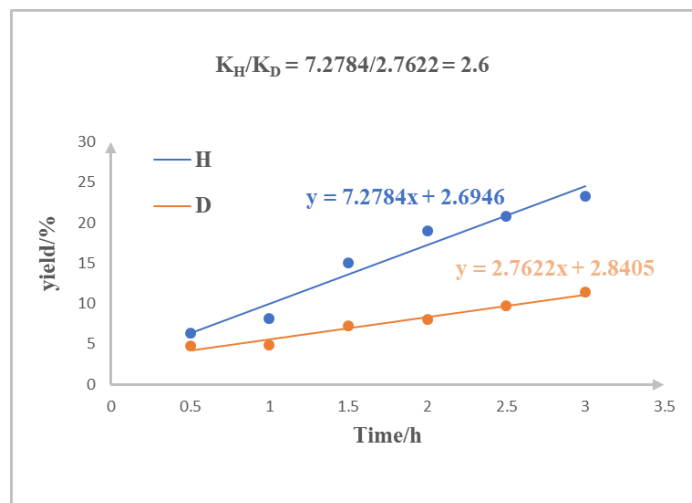
HRMS (ESI): m/z $[M + \text{Na}]^+$ calcd for $[C_8H_{14}\text{NaO}]^+$ requires 149.0937, found 149.0928. The absolute configuration was assigned tentatively by analogy.

6. Mechanistic studies

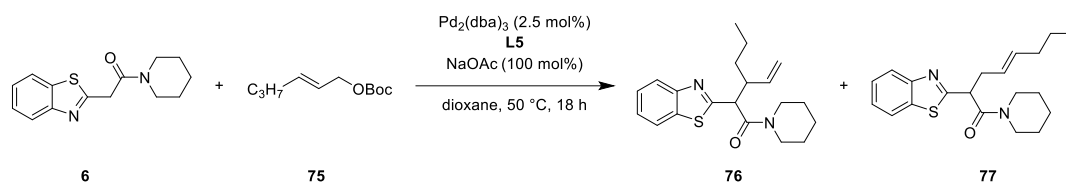
6.1 Kinetic Isotope Effect (KIE)



General procedure: To a flame-dried and N_2 -purged Schlenk tube (10 mL) were added **6** (0.10 mmol), $\text{Pd}_2(\text{dba})_3$ (0.0025 mmol), phosphoramidite **L5** (0.0075 mmol), NaOAc (0.10 mmol), 2,5-DMBQ (0.12 mmol), 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 1,4-dioxane (0.5 mL) and **74** or **74(d₂)** (0.15 mmol) via a syringe, then the resulting mixture was stirred at 50 °C for 0.5 h. The yield was determined by ^1H NMR analysis of the crude mixture based on trimethyl 1,3,5-benzenetricarboxylate as an internal standard. Similar reactions were conducted for 1 h, 1.5 h, 2 h, 2.5 h and 3 h.



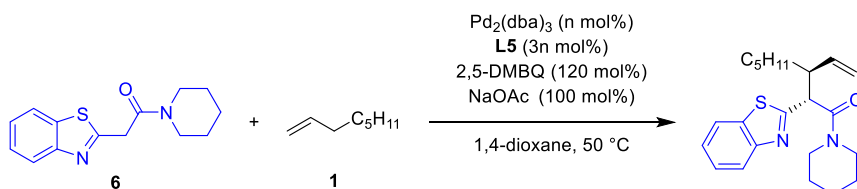
6.2 Effect of ligand capacity



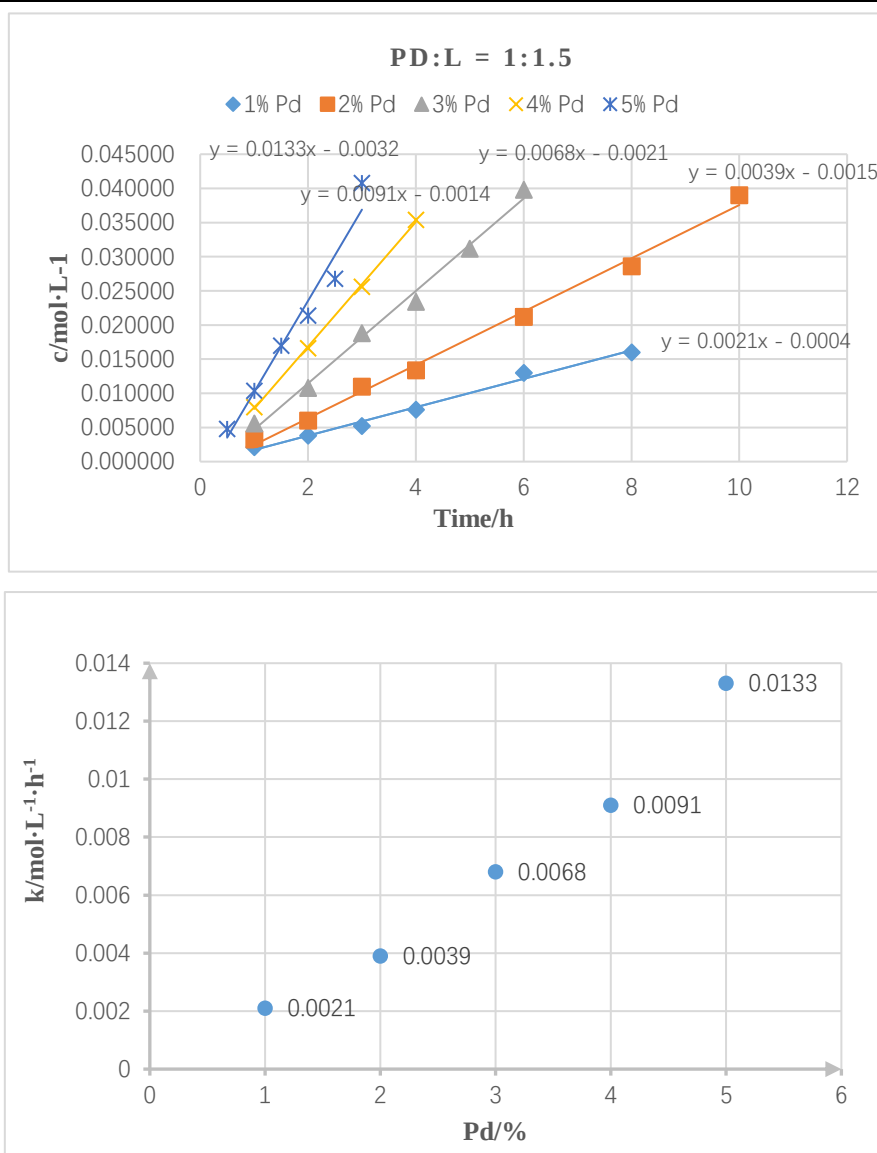
General procedure: To a flame-dried and N₂-purged Schlenk tube (10 mL) were added Pd₂(dba)₃ (0.0025 mmol), PPh₃ or **L5** (0.005 mmol), and a stirring bar. The Schlenk tube was then evacuated and filled with nitrogen. This cycle was repeated three times and followed by the addition of 1,4-dioxane (1.0 mL) via a syringe, then the resulting mixture was stirred at 50 °C for 2 h. After with N₂-purged Schlenk tube were added **6** (0.10 mmol), NaOAc (0.10 mmol), and **75** (0.15 mmol) via a syringe, then the resulting mixture was stirred at 50 °C for 18 h. The yield was determined by ¹H NMR analysis of the crude mixture based on trimethyl 1,3,5-benzenetricarboxylate as an internal standard and e.e. was determined by high performance liquid chromatography using a chiral column. Similar reactions were conducted for 0.010 mmol, 0.020 mmol, 0.030 mmol and 0.040 mmol of ligand.

entry	L	L (mmol%)	yield %	e.e. %	d.r.	b/l
1	PPh ₃	5	88	-	>20:1	4.5:1
2	PPh ₃	10	87	-	12:1	2.6:1
3	PPh ₃	20	95	-	-	1:1.01
4	PPh ₃	30	90	-	-	1:1.25
5	PPh ₃	40	84	-	-	1:16
6	L5	5	91	90	>20:1	>20:1
7	L5	10	95	91	>20:1	>20:1
8	L5	20	95	90	>20:1	>20:1
9	L5	30	94	90	>20:1	>20:1
10	L5	40	91	91	>20:1	>20:1

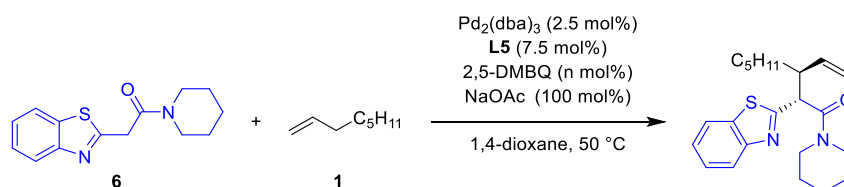
6.3 Kinetic studies of Pd



General procedure: To a flame-dried and N₂-purged Schlenk tube (10 mL) were added **6** (0.20 mmol), Pd₂(dba)₃ (0.001 mmol), phosphoramidite **L5** (0.003-0.015 mmol), NaOAc (0.20 mmol) 2,5-DMBQ (0.24 mmol), 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 1,4-dioxane (1.0 mL) and **1** (0.30 mmol) via a syringe, then the resulting mixture was stirred at 50 °C. The yield was determined by ¹H NMR analysis of the crude mixture based on trimethyl 1,3,5-benzenetricarboxylate as an internal standard.

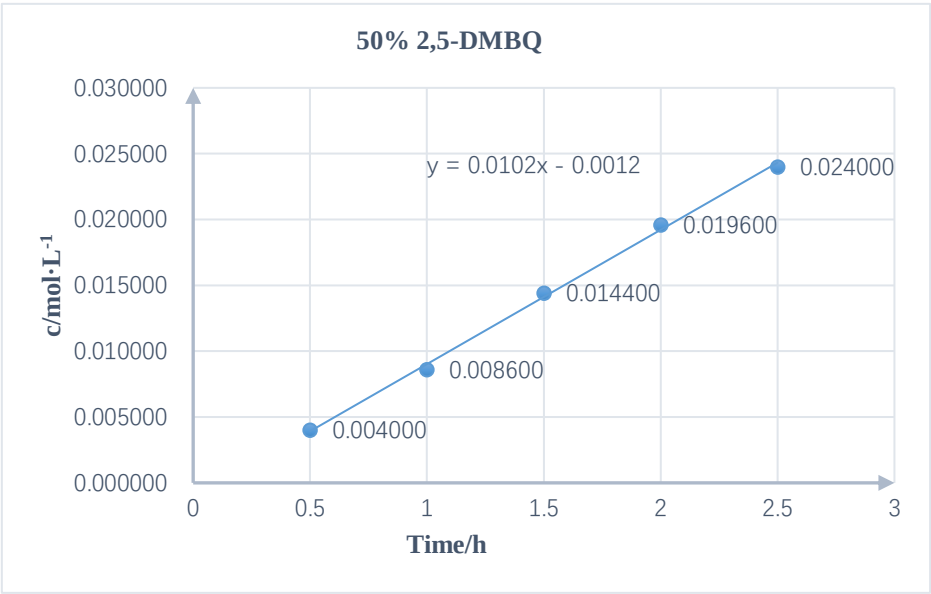


6.4 Kinetic studies of 2,5-DMBQ

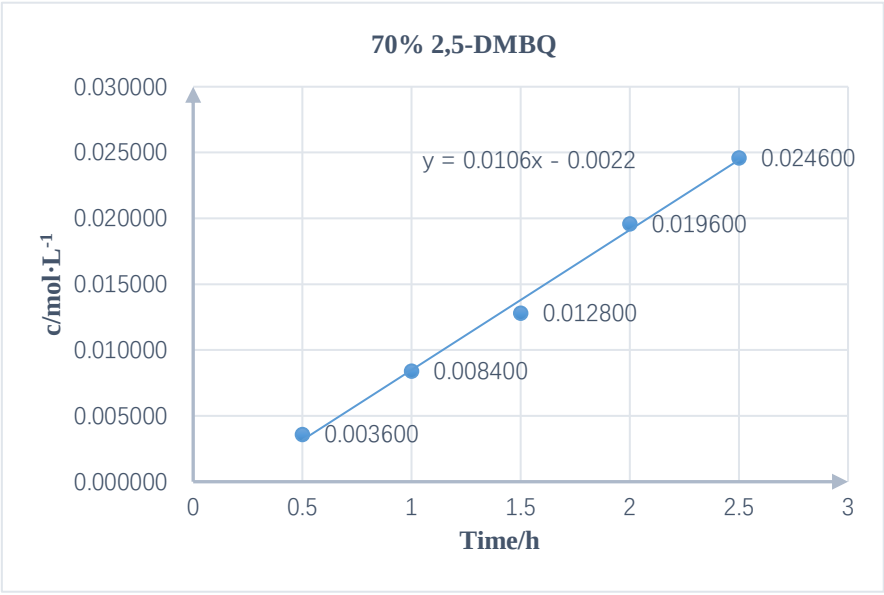


To a flame-dried and N_2 -purged Schlenk tube (10 mL) were added **6** (0.20 mmol), $\text{Pd}_2(\text{dba})_3$ (0.005 mmol), phosphoramidite **L5** (0.015 mmol), NaOAc (0.20 mmol), 2,5-DMBQ (0.10 mmol), and a stirring bar. The Schlenk tube was then evacuated and filled with nitrogen. This cycle was repeated three times and followed by the addition of 1,4-dioxane (1.0 mL) and **1** (0.30 mmol) via a syringe, then the resulting mixture was stirred at 50 °C. The yield was determined by ^1H NMR analysis of the crude mixture based on trimethyl 1,3,5-benzenetricarboxylate as an internal standard. Similar reactions were conducted for 0.014 mmol, 0.018 mmol, 0.020 mmol and 0.024 mmol of 2,5-DMBQ.

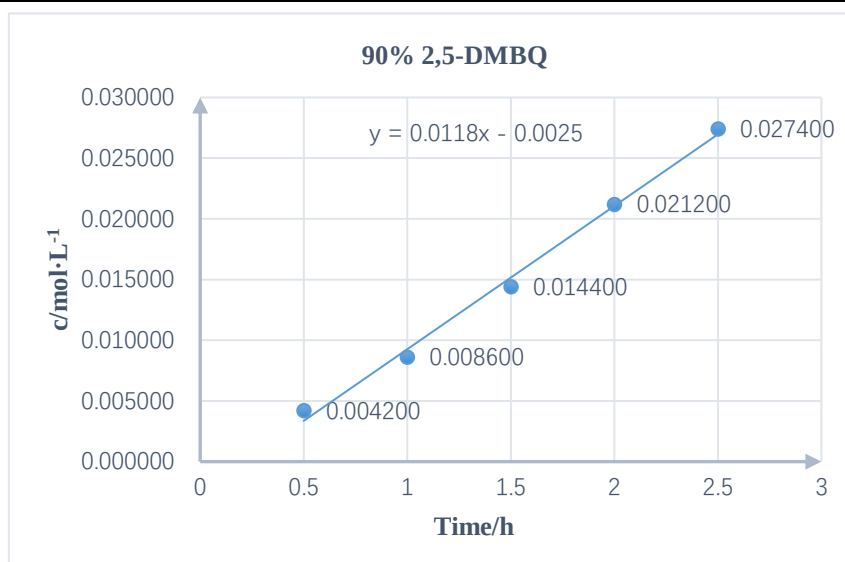
50% 2,5-DMBQ



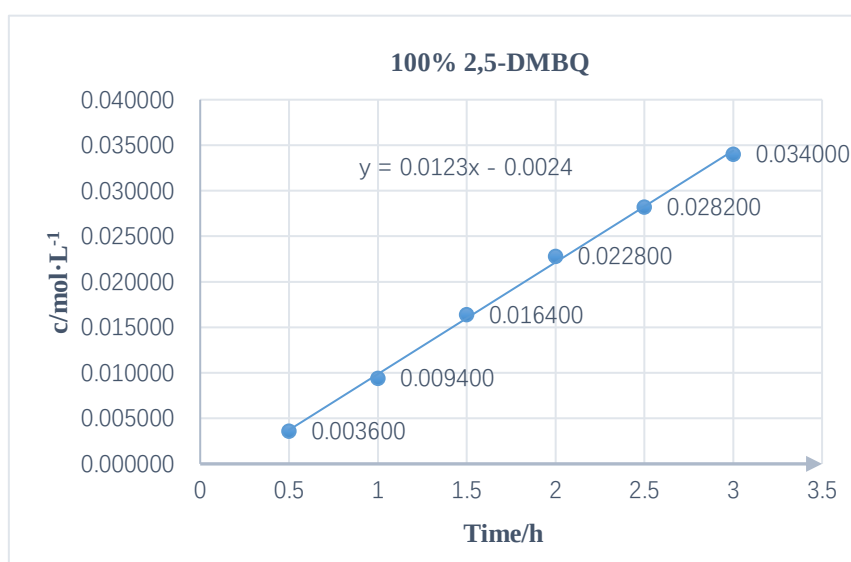
70% 2,5-DMBQ



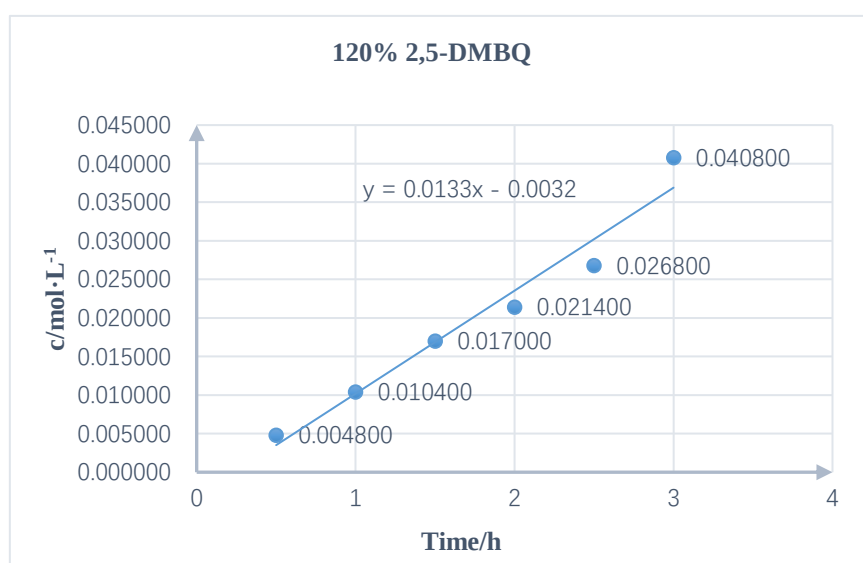
90% 2,5-DMBQ

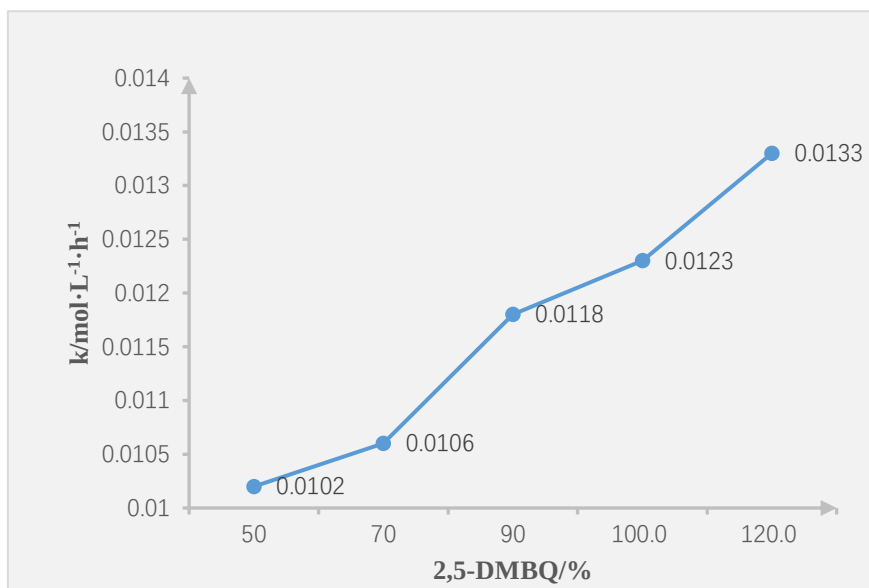


100% 2,5-DMBQ

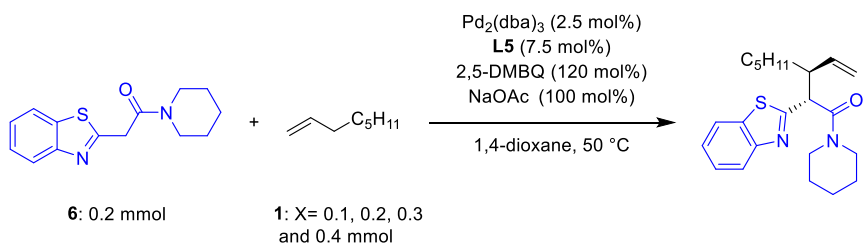


120% 2,5-DMBQ

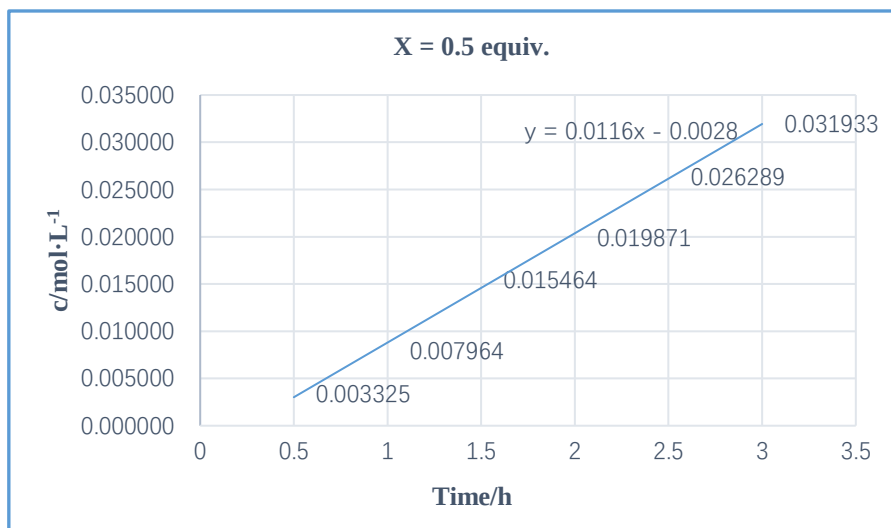


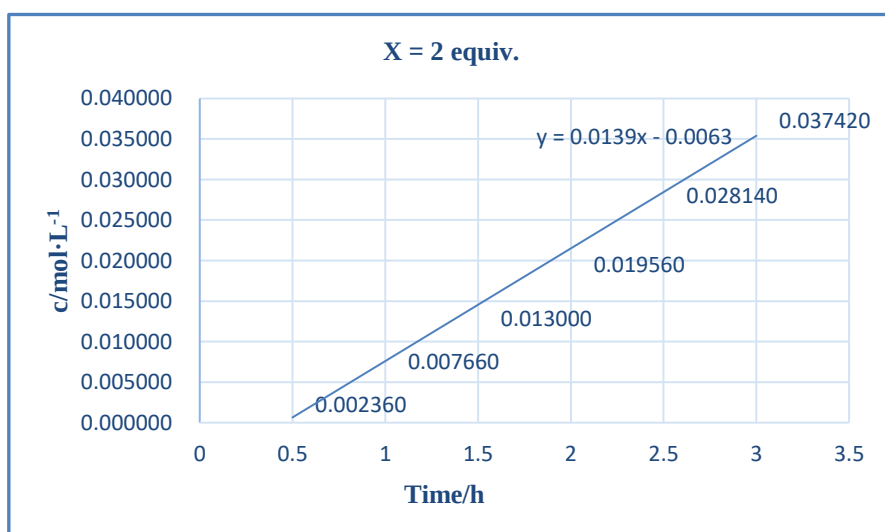
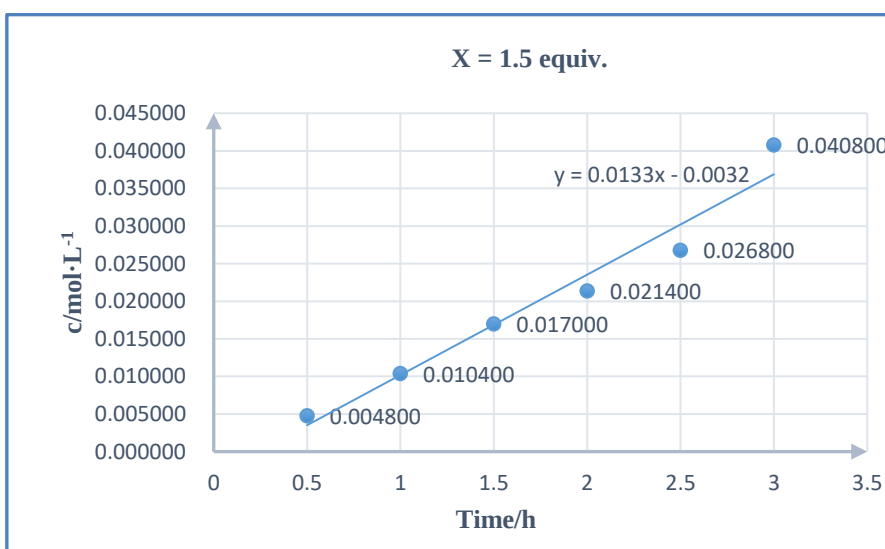
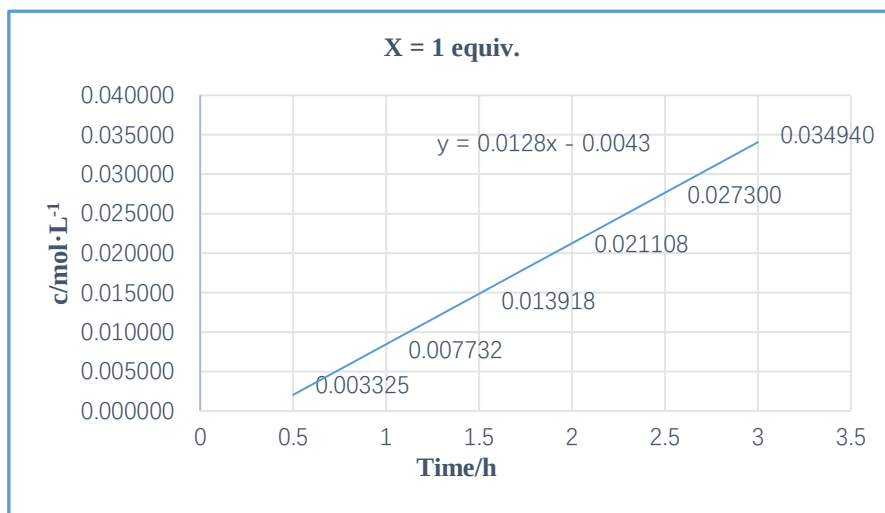


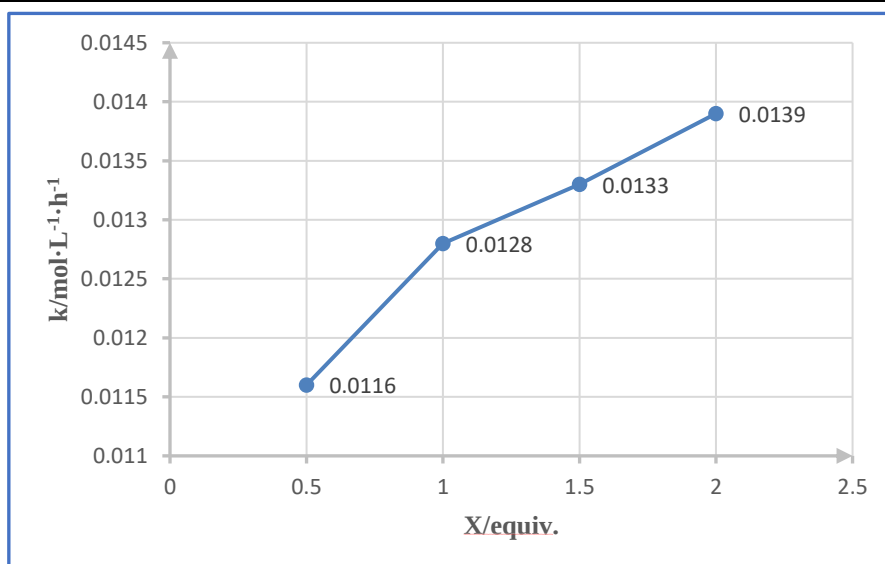
6.5 Kinetic studies of α -alkenes



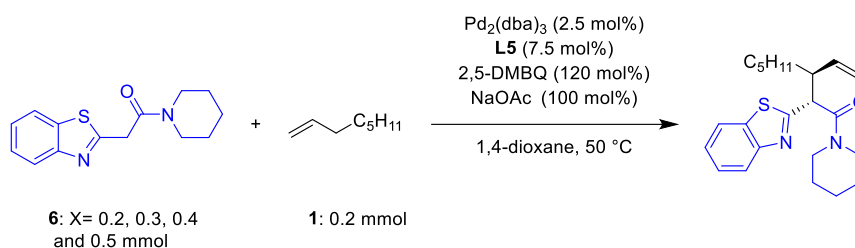
General procedure: 1. To a flame-dried and N_2 -purged Schlenk tube (10 mL) were added **6** (0.20 mmol), $\text{Pd}_2(\text{dba})_3$ (0.001 mmol), phosphoramidite **L5** (0.003 mmol), NaOAc (0.20 mmol), 2,5-DMBQ (0.24 mmol), and a stirring bar. The Schlenk tube was then evacuated and filled with nitrogen. This cycle was repeated three times and followed by the addition of 1,4-dioxane (1.0 mL) and **1** (X = 0.1 mmol) via a syringe, then the resulting mixture was stirred at 50 °C. The yield was determined by ^1H NMR analysis of the crude mixture based on trimethyl 1,3,5-benzenetricarboxylate as an internal standard. Similar reactions were conducted for 0.2 mmol, 0.3 mmol and 0.4 mmol of **1**.



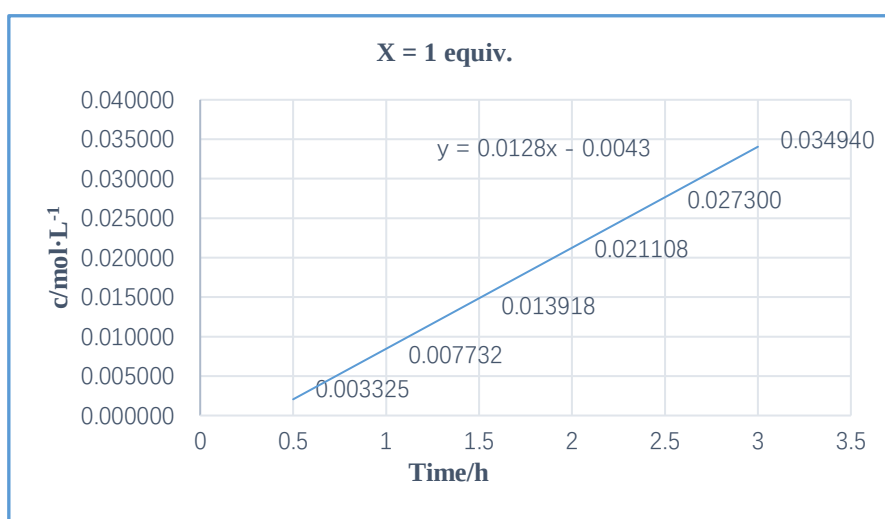


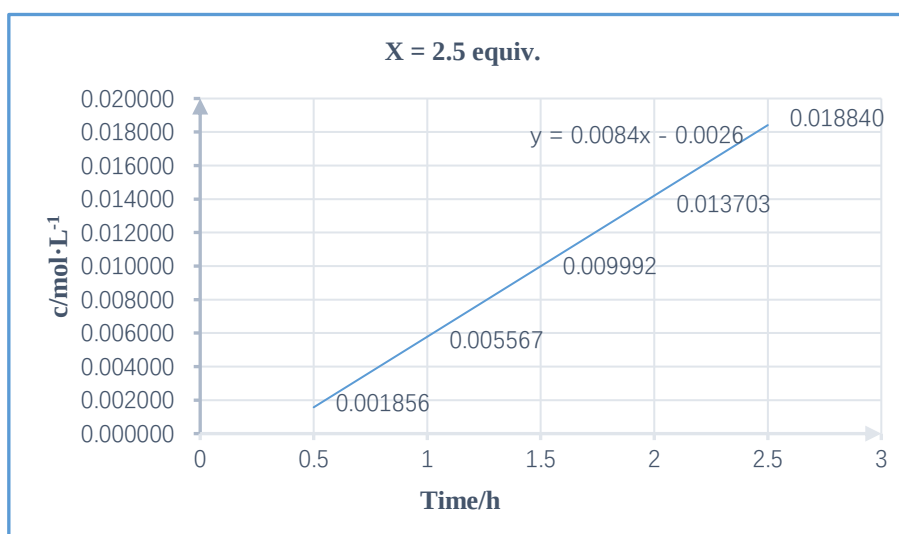
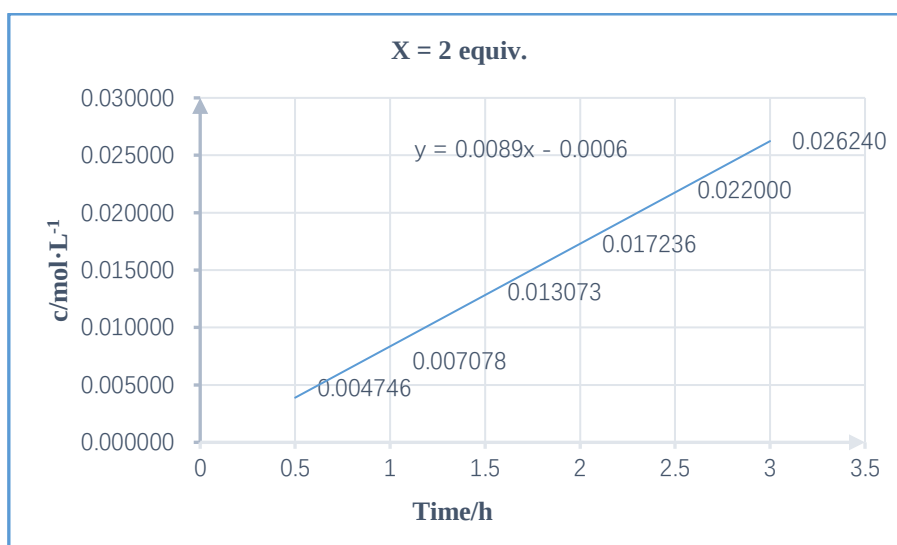
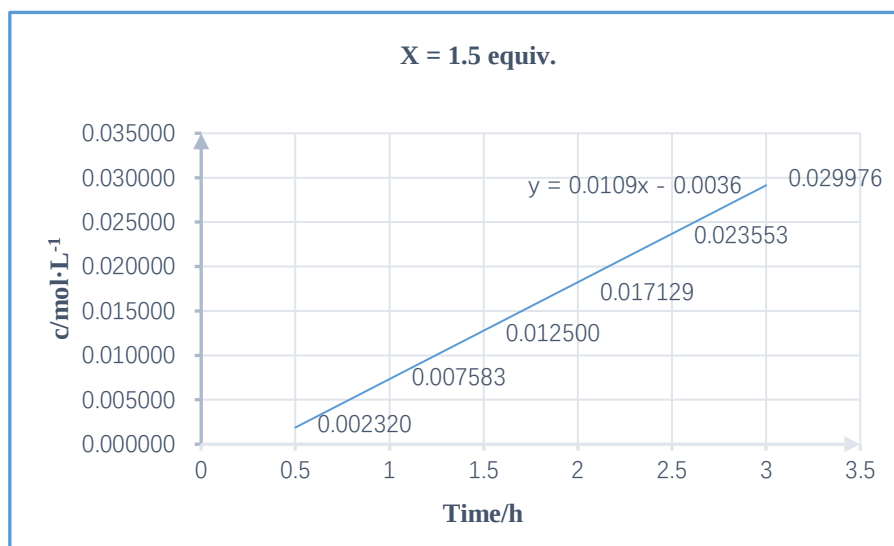


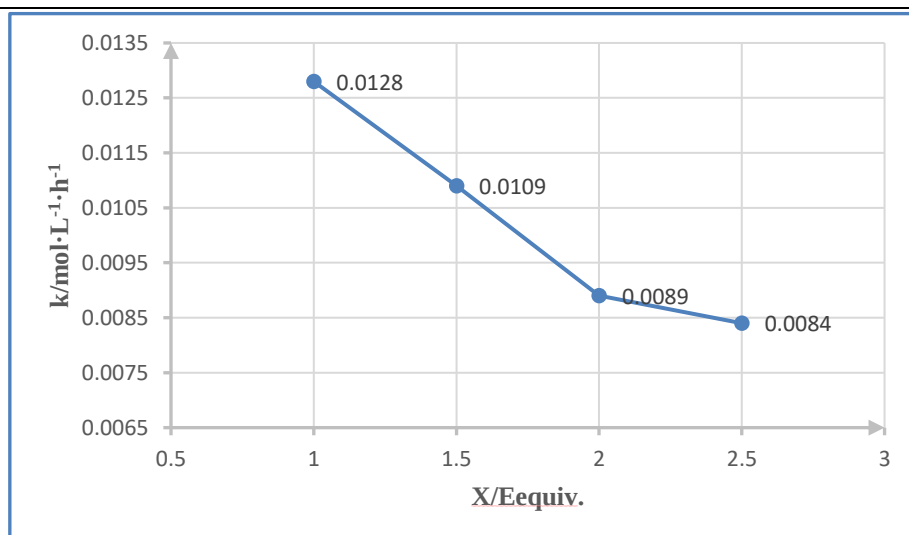
6.6 Kinetic studies of nucleophile



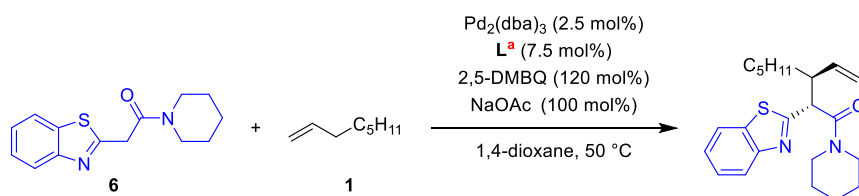
General procedure: To a flame-dried and N_2 -purged Schlenk tube (10 mL) were added **6** (0.20 mmol), $\text{Pd}_2(\text{dba})_3$ (0.001 mmol), phosphoramidite **L5** (0.003 mmol), NaOAc (0.20 mmol), 2,5-DMBQ (0.24 mmol), and a stirring bar. The Schlenk tube was then evacuated and filled with nitrogen. This cycle was repeated three times and followed by the addition of 1,4-dioxane (1.0 mL) and **1** (0.2 mmol) via a syringe, then the resulting mixture was stirred at 50 °C. The yield was determined by ^1H NMR analysis of the crude mixture based on trimethyl 1,3,5-benzenetricarboxylate as an internal standard. Similar reactions were conducted for 0.3 mmol, 0.4 mmol and 0.5 mmol of **6**.



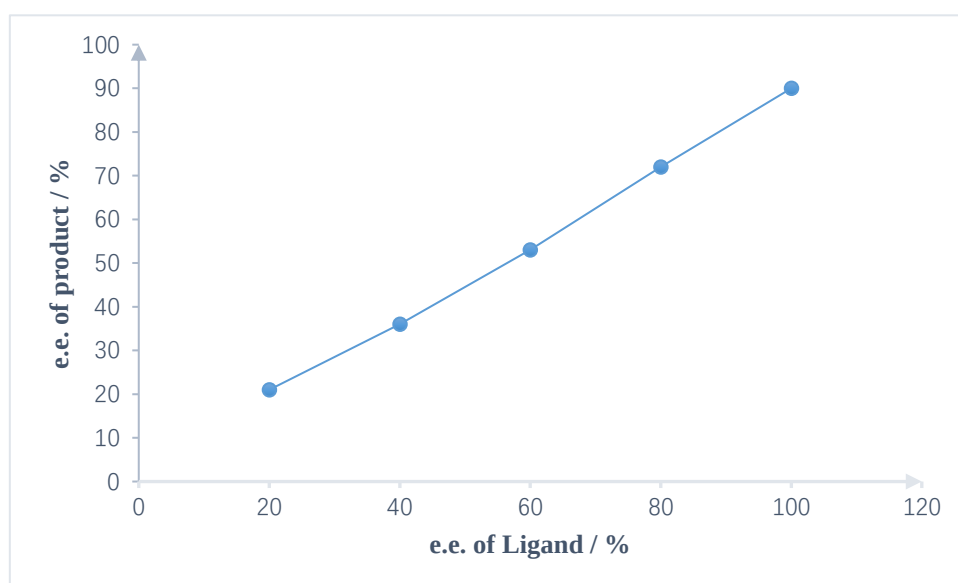




6.7 Non-linear effect studies

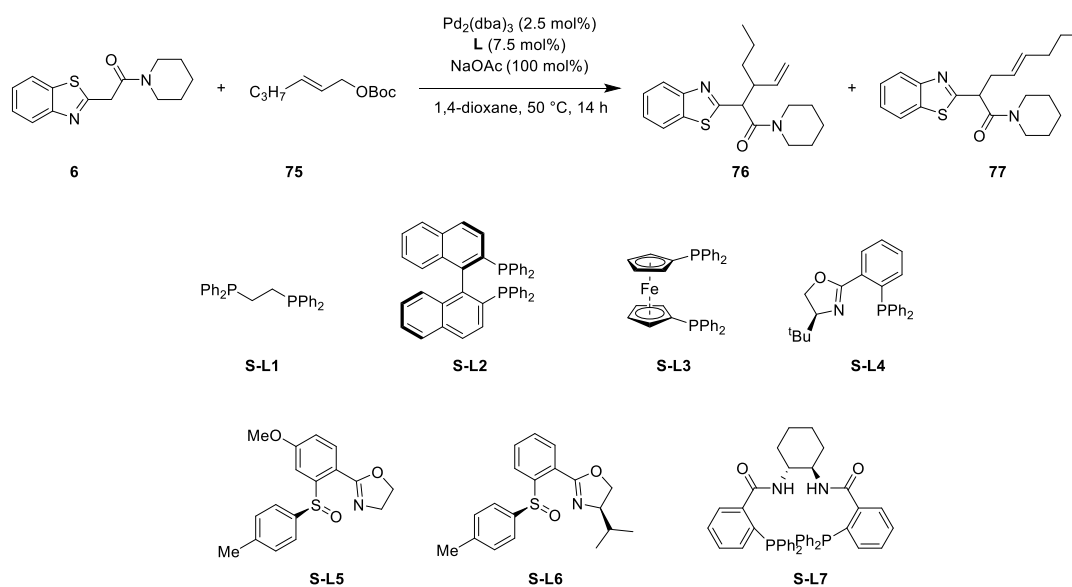


General procedure: To a flame-dried and N_2 -purged Schlenk tube (10 mL) were added **6** (0.10 mmol), $\text{Pd}_2(\text{dba})_3$ (0.0025 mmol), phosphoramidite L^{a} (0.0075 mmol), NaOAc (0.10 mmol) 2,5-DMBQ (0.12 mmol), and a stirring bar. The Schlenk tube was then evacuated and filled with nitrogen. This cycle was repeated three times and followed by the addition of 1,4-dioxane (0.5 mL) and **1** (0.15 mmol) via a syringe, then the resulting mixture was stirred at 50 °C for 36 h. The reaction mixture was concentrated in vacuo, and the residue was purified by column chromatography on silica gel (petroleum/ethyl acetate = 4/1) to provide product.



Entry	$L^a = [R(L) + S(L)] / \text{mg}$	R(L) /mg	S(L) /mg	e.e. of L^a / %	e.e. of product / %
1	20	12	8	20	21
2	20	14	6	40	36
3	20	16	4	60	53
4	20	18	2	80	72
5	20	20	0	100	90

6.8 Effect of bidentate phosphine ligand



General procedure: To a flame-dried and N_2 -purged Schlenk tube (10 mL) were added **6** (0.10 mmol), $\text{Pd}_2(\text{dba})_3$ (0.0025 mmol), PPh_3 or **S-L** (0.0075 mmol), NaOAc (0.10 mmol), 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 1,4-dioxane (1.0 mL) and **75** (0.15 mmol) via a syringe, then the resulting mixture was stirred at 50 °C for 14 h. The yield was determined by ^1H NMR analysis of the crude mixture based on trimethyl 1,3,5-benzenetricarboxylate as an internal standard.

Entry	L	yield % ^b	b/l
1	S-L1	95	1:25
2	S-L2	95	1:18
3	S-L3	95 ^c	1:1.05
4	S-L4	78	1:9
5	S-L5	n.r.	-
6	S-L6	n.r.	-
7	S-L7	86 ^c	1:1.1

7. X-Ray single crystal data for 8

CCDC Number: 2113198

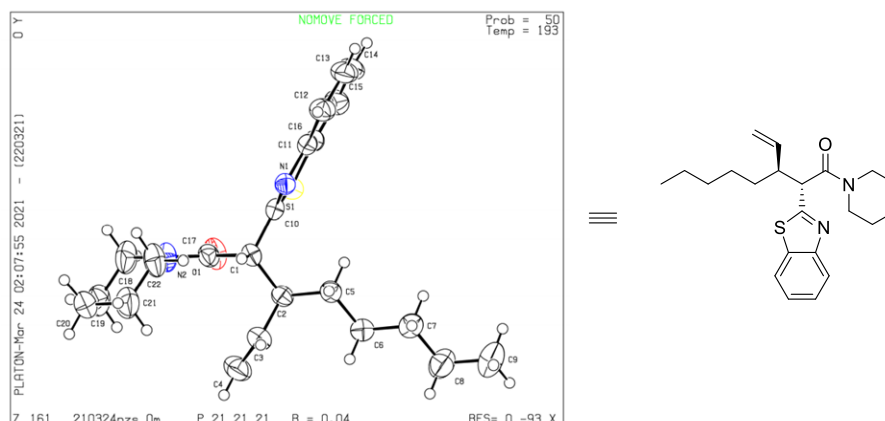


Table 1. Crystal data and structure refinement for 210324nzs_0m.

Table 1. Crystal data and structure refinement for 210324nzs_0m.	
Identification code	210324nzs_0m
Empirical formula	C ₂₂ H ₃₀ N ₂ O ₂ S
Formula weight	370.54
Temperature	192.99 K
Wavelength/Å	1.34139
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	10.5952(2)
b/Å	10.6652(2)
c/ Å	19.0947(3)
α/ °	90
β/ °	90
γ/ °	90
Volume/ Å ³	2157.70(7)
Z	2
Density (calculated) / mg/cm ³	1.141
μ/ mm ⁻¹	0.917
F(000)	800
Crystal size/ mm ³	0.07 x 0.06 x 0.05
2θ range for data collection/ °	4.131 to 54.922°
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -23 ≤ l ≤ 17
Reflections collected	23454
Independent reflections	4075 [R(int) = 0.0606]
Completeness to theta = 53.594°	99.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.5433

Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4075 / 1 / 236
Goodness-of-fit on F ²	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.0874
R indices (all data)	R1 = 0.0468, wR2 = 0.0922
Absolute structure parameter	0.021(10)
Extinction coefficient	n/a
Largest diff. peak and hole/ e.Å ⁻³	0.182 and -0.145

8. Computational details

All DFT calculations were performed at B3LYP-D3(BJ)/6-31G(d)-LANL2DZ level using Gaussian 09 program.¹³ BSI denotes the LANL2DZ basis set based on effective core potential (ECP) was used for the Pd atom and 6-31G (d) basis sets for C, H, O, N, P and S atoms.^{14,15} Free energies were calculated at 298.15 K, 1 atm (unit: kcal/mol). All geometric structures are visualized using CYLview.¹⁶

8.1 Table of energies

Table S1. Zero-point correction (ZPE), thermal correction to enthalpy (TCH), thermal correction to Gibbs free energy (TCG), energies (E), enthalpies (H), and Gibbs free energies (G) (in Hartree) of the structures calculated at the B3LYP-D3(BJ)/6-31G(d) -LANL2DZ level of theory.

Structures	ZPE	TCH	TCG	E	H	G	Imaginary Frequency
67	0.201791	0.216659	0.159179	-1008.538051	-1008.537107	-1008.594587	
68	0.20181	0.216549	0.159851	-1008.531754	-1008.53081	-1008.587509	
69	0.201622	0.216353	0.159728	-1008.531364	-1008.53042	-1008.587045	
(R,S)-TS-N	0.871725	0.934826	0.772457	-3977.10775	-3977.106806	-3977.269174	-98.39
(S,R)-TS-N	0.872199	0.935053	0.772552	-3977.102252	-3977.101308	-3977.263809	-123.23
(R,R)-TS-N	0.872112	0.935327	0.771194	-3977.103321	-3977.102377	-3977.266509	-157.1
(S,S)-TS-N	0.872205	0.93535	0.773696	-3977.101249	-3977.100305	-3977.261958	-56.64
(S,S)-TS-O	0.871995	0.934681	0.773784	-3977.101924	-3977.100979	-3977.261876	-216.29
(S,R)-TS-O	0.871476	0.934572	0.772538	-3977.093574	-3977.09263	-3977.254664	-186.53
(R,S)-TS-O	0.87196	0.935038	0.773365	-3977.098308	-3977.097364	-3977.259036	-169.92
(R,R)-TS-O	0.872219	0.935271	0.773636	-3977.099766	-3977.098821	-3977.260457	-109.4

8.2 Atomic cartesian coordinates of intermediates and transition states in the most favored path A (presented in Å).

67

Coordinates (Angstroms)			
	X	Y	Z
C	1.42758600	0.77973600	0.00281200
H	1.63585700	1.84064400	0.03791200
C	2.48783100	-0.23119700	-0.01233400
C	0.07513900	0.44100000	0.00598600

N	-0.88179400	1.37716400	0.02411900
O	2.20669600	-1.43864200	0.01865900
S	-0.52079200	-1.24980200	-0.01848600
C	-2.11988500	0.81449800	0.01431700
C	-2.14898400	-0.61271700	-0.01092100
C	-3.33245100	1.53767900	0.02722000
H	-3.29814800	2.62193700	0.04614500
C	-3.36107600	-1.30431300	-0.02246200
H	-3.38406900	-2.38944900	-0.04121300
C	-4.52799200	0.84207000	0.01514100
H	-5.46882700	1.38407000	0.02472100
C	-4.54299000	-0.56885300	-0.00955100
H	-5.49508000	-1.09141100	-0.01861900
N	3.79166200	0.20696500	-0.05937500
C	4.85889800	-0.77292100	0.07157000
H	5.57538200	-0.66504100	-0.75155600
H	5.39642300	-0.64103900	1.02062800
H	4.41579000	-1.76681800	0.04401800
C	4.18552300	1.60762600	-0.04805700
H	3.55371800	2.20432800	-0.70925900
H	4.15930400	2.04398600	0.96049300
H	5.21007200	1.68020600	-0.42229400

68

Coordinates (Angstroms)			
	X	Y	Z
C	-1.56007100	-1.32717200	0.08703300
H	-1.72058400	-2.39545700	0.18177400
C	-2.76485400	-0.55445200	-0.32298000
C	-0.25477400	-0.84098300	0.04029300
N	0.09797000	0.42007100	-0.20047800
O	-3.44704200	-1.04178400	-1.22815900
S	1.13843900	-1.95885300	0.30793700
C	1.45228500	0.57467700	-0.18639000
C	2.21507300	-0.60397300	0.07656600
C	2.12409800	1.79382200	-0.40740500
H	1.54005400	2.68543400	-0.60964500
C	3.60819300	-0.56972100	0.12134300
H	4.18312500	-1.46800200	0.32170200
C	3.50818600	1.81998300	-0.36239400
H	4.03490000	2.75417200	-0.53190200
C	4.24557900	0.64877500	-0.10021800
H	5.33007200	0.69453800	-0.07093800
N	-3.05773300	0.62766600	0.28791700

C	-4.13644500	1.44417600	-0.24306600
H	-4.91481200	1.59316700	0.51604000
H	-3.75360000	2.42707900	-0.54640500
H	-4.56284000	0.93455600	-1.10595200
C	-2.35637000	1.15598400	1.44392100
H	-1.77400800	0.36944900	1.92339600
H	-1.67586600	1.96741200	1.16335200
H	-3.09218000	1.53270500	2.16456100

69

Coordinates (Angstroms)			
	X	Y	Z
C	1.44105800	1.43179100	0.13943100
H	1.48104500	2.50442000	0.29392400
C	2.70643900	0.77775400	-0.27592100
C	0.17196400	0.85979900	0.07718800
N	-0.94849600	1.54116000	0.32151900
O	3.38669100	1.32180700	-1.14489400
S	-0.09824400	-0.86448500	-0.39049400
C	-2.05452000	0.76116200	0.16506800
C	-1.81611100	-0.59103900	-0.22559400
C	-3.38070000	1.19967900	0.35734900
H	-3.55503400	2.22868500	0.65318500
C	-2.86832000	-1.48397700	-0.42142200
H	-2.68267100	-2.51073000	-0.71998000
C	-4.42122000	0.30686000	0.16147900
H	-5.44634600	0.63417500	0.30582500
C	-4.16877000	-1.02414200	-0.22484100
H	-5.00145200	-1.70524800	-0.37292900
N	3.02731600	-0.44232900	0.27016300
C	2.57907400	-0.87529100	1.58560900
H	2.15678900	-1.88499500	1.53966100
H	3.42529000	-0.88068500	2.28666800
H	1.81800500	-0.19597100	1.96838200
C	4.19017100	-1.14022200	-0.25718600
H	4.37302900	-0.80203200	-1.27610900
H	5.08511300	-0.93785100	0.34783300
H	3.99847700	-2.21853300	-0.24813800

(R,S)-TS-N

Coordinates (Angstroms)			
	X	Y	Z
C	1.47777500	-3.51248900	-1.66188900

C	0.00598600	-3.73531000	-1.54511000
C	-0.67012700	-3.23851900	-0.41379500
C	-2.05122700	-3.36444500	-0.23051900
C	-2.76595000	-4.05719000	-1.21850100
C	-2.12743400	-4.53993200	-2.35239200
C	-0.75032200	-4.36976000	-2.55196300
C	1.96513200	-2.19879700	-1.56082000
C	3.32457500	-1.86903500	-1.62346500
C	4.22299300	-2.93007300	-1.79690300
C	3.77207100	-4.24229300	-1.86893200
C	2.40966000	-4.56272800	-1.79502500
C	3.78598800	-0.47640100	-1.41350900
C	-2.75523900	-2.71273000	0.89861500
O	0.06941200	-2.55692000	0.55292900
O	1.04821900	-1.18058900	-1.32041000
P	0.45921500	-0.97572600	0.21956800
N	1.83848200	-0.89539700	1.24189100
Pd	-1.17291000	0.51177000	0.24898800
C	-1.35699300	0.94331300	2.31357200
C	-2.46367300	1.68301600	1.78645000
C	-2.43391000	3.01286300	1.36060800
H	-1.57838700	0.05134700	2.89115400
H	-0.46153700	1.47744000	2.62599600
H	-3.42271300	1.17464800	1.73270200
H	-1.55487500	3.61248800	1.57828800
C	-1.31924300	3.37927300	-1.03776100
H	-0.44235500	2.92782000	-0.59560300
C	-1.45161900	4.81375300	-1.15744100
C	-2.15327000	2.50444700	-1.73805500
N	-2.06264300	1.16868700	-1.61904200
C	3.13773900	0.61345100	-2.02160600
C	3.53422600	1.91527200	-1.74654500
C	4.58611600	2.15361600	-0.85607200
C	5.25724500	1.08317500	-0.26916400
C	4.85879500	-0.22253500	-0.54856200
C	-3.89451300	-1.93565300	0.63554500
C	-4.57715100	-1.30468300	1.67148700
C	-4.12737700	-1.44186200	2.98570500
C	-2.99832100	-2.21860100	3.26158600
C	-2.31729300	-2.84770600	2.22488900
O	-2.47619800	5.32824300	-1.65201100
H	-3.83746000	-4.18284700	-1.10029700
H	5.28578200	-2.71667900	-1.85561100
H	2.30960700	0.43749800	-2.69708500
H	5.34402600	-1.05049400	-0.04257300

H	3.01669200	2.74856700	-2.21092700
H	6.05827800	1.26861100	0.43608500
H	-1.44034000	-3.44664400	2.44087500
H	-4.22217900	-1.79756200	-0.38953800
H	-2.65982500	-2.33327800	4.28575500
H	-5.45296300	-0.70114400	1.45786400
H	4.49420400	-5.04828100	-1.96784400
H	-2.71044400	-5.03907900	-3.12174900
C	-3.69077100	3.72019600	0.97012000
H	-3.53203100	4.50019300	0.22131400
H	-4.42700900	3.01049000	0.57860700
H	-4.12900600	4.19321600	1.86317500
S	-3.46250500	3.02737100	-2.82607300
C	-2.91418800	0.49567700	-2.47270900
C	-3.77991100	1.33447900	-3.20953400
C	-2.96340000	-0.89187600	-2.65015000
H	-2.26158200	-1.52205700	-2.11797400
C	-4.72191900	0.79641700	-4.08539300
H	-5.39156500	1.44312200	-4.64483200
C	-3.90035300	-1.42455600	-3.53189100
H	-3.93906000	-2.50007800	-3.67801900
C	-4.78043300	-0.59037100	-4.23857100
H	-5.50538400	-1.02338800	-4.92165100
N	-0.43517300	5.60935800	-0.65936300
C	-0.64028500	7.04438300	-0.57596600
H	-0.68262200	7.38043300	0.47051100
H	0.17630600	7.58039100	-1.07618700
H	-1.58365700	7.27821500	-1.06728800
C	0.77884200	5.07778800	-0.07287200
H	1.17590100	4.24349800	-0.65569600
H	1.54402100	5.85857800	-0.06604000
H	0.63334000	4.73933300	0.96511900
C	2.69906000	-1.92451100	1.73128700
C	3.71678300	-1.32587500	2.51320800
C	2.67061900	-3.30809600	1.54384100
C	4.71563100	-2.11079900	3.09766400
C	3.67929600	-4.07140200	2.12925600
H	1.90431400	-3.78203800	0.95415200
C	4.69560700	-3.48729100	2.89941200
H	5.49639900	-1.64521700	3.69251300
H	3.67162200	-5.14691000	1.97756300
H	5.46656800	-4.11143000	3.34116400
C	2.36252600	0.34909200	1.69704800
C	1.95324000	1.65336900	1.41593900
C	3.49852600	0.10384800	2.50057300

C	2.67250700	2.70153200	1.98988000
H	1.11569900	1.85268300	0.75883700
C	4.20775600	1.16778100	3.06421300
C	3.78641600	2.46820000	2.80870400
H	2.37922800	3.72170100	1.77412700
H	5.08307100	0.97741300	3.67875600
H	4.33309300	3.30892100	3.22326200
C	-0.14475600	-4.82247100	-3.85821600
H	0.82247800	-4.35094400	-4.04379700
H	0.00108900	-5.90907200	-3.87976500
H	-0.81266400	-4.56953900	-4.68799700
C	2.00062300	-6.01573400	-1.79583200
H	1.98668800	-6.43077700	-2.81064700
H	2.71470300	-6.60930700	-1.21552700
H	1.00656100	-6.15966100	-1.36595800
C	-4.80059400	-0.68082300	4.09041700
C	4.98918100	3.56852000	-0.56398200
F	-4.25121400	0.55143100	4.24382800
F	-4.68776900	-1.30748100	5.28134000
F	-6.11565800	-0.49229100	3.84884700
F	5.70587900	4.10844400	-1.57707900
F	5.74149200	3.67282400	0.55223800
F	3.90612900	4.37245900	-0.39525000

(S,R)-TS-N

Coordinates (Angstroms)			
	X	Y	Z
C	1.08032300	-2.93380600	-2.49236800
C	-0.40936700	-2.84491400	-2.47539600
C	-1.06611000	-2.59111700	-1.25500500
C	-2.46224400	-2.56009000	-1.13480300
C	-3.20638500	-2.76156800	-2.30752500
C	-2.58116800	-2.94164400	-3.53308700
C	-1.18521700	-2.98156400	-3.64464700
C	1.82258900	-1.85031900	-1.99929300
C	3.22174300	-1.82848300	-1.95062600
C	3.88625700	-2.97250900	-2.41065600
C	3.17562400	-4.07633900	-2.86611900
C	1.77505000	-4.08713400	-2.91283400
C	3.94916400	-0.68466800	-1.35401800
C	-3.15807100	-2.34452900	0.15567700
O	-0.28929900	-2.36447800	-0.12031000
O	1.12159400	-0.76570200	-1.48572900
P	0.42852800	-0.86329300	0.02244100

N	1.67880700	-1.34051900	1.09796200
Pd	-0.74475300	0.95299200	0.45209800
C	-1.77935900	0.41516300	2.22059900
C	-2.28270800	1.73751100	2.02566800
C	-3.44420100	2.07143500	1.31323300
H	-2.41412800	-0.43274300	1.99435600
H	-1.07276100	0.24968700	3.03052500
H	-1.75312900	2.55918500	2.50623200
H	-4.09247900	1.26871600	0.97862100
C	-3.03281300	2.15923300	-1.25587000
H	-2.72558600	1.12254700	-1.18676600
C	-4.35143700	2.50016700	-1.73928600
C	-1.99255800	3.09581300	-1.18766600
N	-0.77046900	2.76931600	-0.74580200
C	3.60073200	0.64310700	-1.65764900
C	4.24227400	1.70271200	-1.03183000
C	5.23231800	1.45423800	-0.07567500
C	5.61223100	0.14496700	0.21007800
C	4.97796100	-0.91697200	-0.43206200
C	-2.75459500	-3.00778600	1.32551500
C	-3.45196300	-2.83576000	2.51807700
C	-4.56375400	-1.99198300	2.56293400
C	-4.97726000	-1.32522000	1.40771200
C	-4.27832000	-1.49871700	0.21715200
O	-4.78556700	3.66460200	-1.70476100
H	-4.28955500	-2.77182800	-2.24392400
H	4.97141100	-2.99492800	-2.39028400
H	2.81255800	0.84326200	-2.37328100
H	5.23729800	-1.93624100	-0.16672100
H	3.95679100	2.72125700	-1.27026400
H	6.37053400	-0.04663200	0.95937700
H	-4.58851900	-0.94407300	-0.66082100
H	-1.88853800	-3.65797500	1.30003200
H	-5.82965000	-0.65499900	1.44438500
H	-3.12644700	-3.34752600	3.41680100
H	3.71654400	-4.96359000	-3.18412400
H	-3.18436200	-3.05711000	-4.42962100
C	-4.00949400	3.45135200	1.38884000
H	-4.71182100	3.50291600	2.23596500
H	-3.21890400	4.18683400	1.57077100
H	-4.55237800	3.74127100	0.48549900
S	-2.16300200	4.82065400	-1.59038500
C	0.11210900	3.83372800	-0.76833400
C	-0.45511100	5.04821600	-1.21414400
C	1.45594300	3.79258200	-0.37648700

H	1.88951200	2.85805700	-0.04022800
C	0.30529800	6.21599400	-1.27247400
H	-0.13487500	7.14830800	-1.61353100
C	2.21283800	4.95961600	-0.43366700
H	3.25175200	4.93372800	-0.11965500
C	1.64384400	6.16259000	-0.88096100
H	2.24872800	7.06364600	-0.92003500
N	-5.18363300	1.45185800	-2.15750800
C	-6.53844700	1.83813400	-2.53107700
H	-6.58259800	2.26729400	-3.54366600
H	-7.18057200	0.95147600	-2.49773100
H	-6.90545900	2.58822900	-1.83179200
C	-4.64375800	0.37494000	-2.97875300
H	-3.64548700	0.08657600	-2.65430100
H	-5.29493800	-0.50313100	-2.90571400
H	-4.58709900	0.66540700	-4.04045400
C	2.35480700	-2.58937500	1.23993900
C	3.44675400	-2.41480500	2.12487800
C	2.09811700	-3.83519700	0.66400400
C	4.29603000	-3.48616300	2.41852800
C	2.96175500	-4.88742700	0.96330000
H	1.26881100	-3.98551300	-0.00718500
C	4.05298100	-4.72274000	1.82922000
H	5.13525100	-3.34710900	3.09428900
H	2.77873400	-5.85653000	0.50830900
H	4.70631200	-5.56362400	2.04192100
C	2.38470300	-0.38443100	1.89029700
C	2.17215300	0.98569100	2.04783900
C	3.46400500	-1.02753900	2.53492200
C	3.05901100	1.70218200	2.85024700
H	1.34780600	1.49172400	1.55849400
C	4.33454800	-0.29594100	3.34827900
C	4.13261600	1.07240200	3.49699100
H	2.91824200	2.77281100	2.95683100
H	5.16838500	-0.79001100	3.83909600
H	4.81510600	1.65944100	4.10296000
C	-0.56753400	-3.12840500	-5.01403100
H	0.48266400	-2.82966600	-5.02190400
H	-0.62509600	-4.16315700	-5.37229500
H	-1.10593600	-2.50724300	-5.73742000
C	1.06883100	-5.34660200	-3.35305700
H	1.04762000	-5.43656900	-4.44575600
H	1.59314600	-6.22769200	-2.96873300
H	0.03595600	-5.38108400	-2.99860700
C	-5.33785300	-1.81321600	3.83748900

C	5.87182000	2.61753700	0.62191500
F	-6.43075300	-2.61075100	3.87431800
F	-5.77851600	-0.54186700	3.97493600
F	-4.59581400	-2.10770400	4.92623800
F	6.69229400	3.31178700	-0.20081200
F	6.60422100	2.24205100	1.69188700
F	4.94200300	3.50469100	1.06606100

(R,R)-TS-N

Coordinates (Angstroms)			
	X	Y	Z
C	2.98758100	-3.34793300	-1.10164400
C	1.65544300	-4.00854600	-1.23812700
C	0.59674100	-3.58222100	-0.41284700
C	-0.68404900	-4.14377300	-0.46250500
C	-0.89601800	-5.16740100	-1.39743300
C	0.12004900	-5.57883300	-2.24947100
C	1.39957400	-5.00972400	-2.19721300
C	3.05703500	-1.95154800	-1.23219100
C	4.24211900	-1.21870800	-1.08877300
C	5.40320700	-1.94789300	-0.79968400
C	5.35839400	-3.32679000	-0.63604600
C	4.16562400	-4.04973700	-0.77208900
C	4.24418200	0.26220100	-1.14650700
C	-1.79601000	-3.64663700	0.38190000
O	0.83332900	-2.53879700	0.48106900
O	1.86755900	-1.25985300	-1.44576400
P	0.85764100	-0.99597700	-0.14901700
N	1.86393000	-0.31936900	1.07643100
Pd	-1.05348400	0.00846500	-0.66823800
C	-1.90777200	0.11613900	1.40787100
C	-1.58382500	1.40498600	1.86057700
C	-2.41298000	2.51335600	1.75524000
H	-2.94123800	-0.09407800	1.14704800
H	-1.37262800	-0.72673200	1.83098500
H	-0.59769700	1.55561900	2.29072300
H	-3.45469600	2.36172800	1.48982800
C	-2.27135800	3.13983100	-0.61691300
H	-1.22345300	2.90534000	-0.73215200
C	-2.72012300	4.51446700	-0.43621200
C	-3.15109500	2.16152000	-1.08189100
N	-2.74820700	0.94710200	-1.50883900
C	3.53137000	0.95912500	-2.13762700

C	3.47678800	2.34626700	-2.12711400
C	4.13447200	3.06528300	-1.12419000
C	4.87296600	2.39052000	-0.15451800
C	4.92624600	0.99805600	-0.16811600
C	-1.66397100	-3.47729000	1.76824600
C	-2.72741100	-2.99236500	2.52461100
C	-3.93209700	-2.65602100	1.90173600
C	-4.08208200	-2.83123300	0.52515500
C	-3.02354400	-3.33700800	-0.22032600
O	-3.90590100	4.76861900	-0.16842500
H	-1.87609400	-5.63128600	-1.45331300
H	6.34348300	-1.41736500	-0.68563000
H	3.00342600	0.40732700	-2.90568800
H	5.44922400	0.47438300	0.62520700
H	2.90562300	2.87300000	-2.88468300
H	5.36394600	2.94600200	0.63532400
H	-3.13526900	-3.45430100	-1.29070000
H	-0.72333600	-3.71777700	2.25089900
H	-5.00723000	-2.55335600	0.03134700
H	-2.61961000	-2.86003400	3.59539600
H	6.26815200	-3.86186700	-0.37730500
H	-0.08029100	-6.35303900	-2.98535600
C	-2.08036700	3.79470900	2.46090800
H	-2.32520100	3.69686900	3.52908600
H	-1.01282100	4.02694500	2.38776600
H	-2.66577100	4.62980800	2.07287700
S	-4.92260700	2.35909600	-1.04642300
C	-3.81760700	0.15850000	-1.92207300
C	-5.08662400	0.74041500	-1.72263600
C	-3.71195500	-1.09855500	-2.52738100
H	-2.72704600	-1.51602700	-2.71266700
C	-6.25183000	0.05367000	-2.06332400
H	-7.22746600	0.49950300	-1.89541300
C	-4.87564700	-1.78028200	-2.87395400
H	-4.80557900	-2.75653800	-3.34574600
C	-6.13786800	-1.21655900	-2.63060500
H	-7.03544600	-1.76321400	-2.90423200
N	-1.77559300	5.52881500	-0.49008200
C	-0.55508200	5.46010700	-1.27821900
H	-0.69299000	5.93773300	-2.26058900
H	0.25853700	5.98363800	-0.76379500
H	-0.24331300	4.43186600	-1.44819200
C	-2.24219100	6.88365700	-0.23856000
H	-3.11092200	6.84535500	0.41651400
H	-1.43833900	7.45979700	0.23336800

H	-2.53369800	7.39157700	-1.17017300
C	2.77052100	-0.93136000	1.99306800
C	3.33485900	0.07873100	2.81160000
C	3.14562200	-2.26678200	2.15836100
C	4.27816400	-0.24647700	3.79120100
C	4.09245200	-2.56815100	3.13596100
H	2.73216800	-3.04853100	1.54413800
C	4.65769900	-1.57513400	3.94924400
H	4.70930300	0.53348100	4.41253600
H	4.39758100	-3.60298200	3.26233300
H	5.39307100	-1.84486400	4.70130000
C	1.92023300	1.08596900	1.30130100
C	1.30603300	2.12754600	0.60765000
C	2.78610400	1.34786200	2.38609800
C	1.52121600	3.42934100	1.05614600
H	0.67368600	1.93193100	-0.25051600
C	2.99873600	2.66098700	2.81632600
C	2.35535300	3.69964800	2.15092400
H	1.04608000	4.24957600	0.53394100
H	3.66435100	2.86298000	3.65072200
H	2.51414900	4.72678700	2.46327100
C	2.43692500	-5.45497300	-3.19957600
H	3.24198500	-4.72436900	-3.30454500
H	2.88926000	-6.41196000	-2.91302900
H	1.97484500	-5.59904000	-4.18165200
C	4.17617000	-5.53391200	-0.49727400
H	4.55652900	-6.10072600	-1.35548000
H	4.83217400	-5.75620900	0.35085100
H	3.17771900	-5.91272000	-0.26672400
C	-5.03902300	-2.00505500	2.67810400
C	4.04029600	4.56240000	-1.12095500
F	-6.25552500	-2.44075200	2.28330500
F	-5.03499900	-0.65873500	2.50279300
F	-4.93577200	-2.22874400	4.00577100
F	4.84734000	5.12169900	-2.05280000
F	4.37912100	5.10055700	0.06963700
F	2.78000400	4.98359000	-1.40936300

(S,S)-TS-N

Coordinates (Angstroms)			
	X	Y	Z
C	2.23370100	-3.36545400	-1.80733100
C	0.77800800	-3.60214100	-2.03546400

C	-0.13929800	-3.17662500	-1.05597100
C	-1.51927700	-3.39059300	-1.15749500
C	-1.97735500	-4.03362900	-2.31834200
C	-1.09903200	-4.40926300	-3.32491000
C	0.28187800	-4.20191000	-3.21030300
C	2.66577000	-2.05229100	-1.56648200
C	3.99883700	-1.71161300	-1.30903400
C	4.92530800	-2.76286700	-1.29068200
C	4.52010600	-4.07640100	-1.49230200
C	3.18200100	-4.40710600	-1.74554500
C	4.39087100	-0.32086300	-0.98387600
C	-2.47704800	-2.99126500	-0.10011700
O	0.35506300	-2.50222500	0.05946100
O	1.70018200	-1.05109100	-1.52335700
P	0.75255100	-0.89787800	-0.16368900
N	1.84863900	-0.78710800	1.15705400
Pd	-0.74583400	0.70780200	-0.48632100
C	-1.32729200	1.05519800	1.61230000
C	-2.71045300	0.76201500	1.64177300
C	-3.69752000	1.70912600	1.46121200
H	-0.65998800	0.37824700	2.13791600
H	-1.03157500	2.10189600	1.67242800
H	-3.00388200	-0.26703900	1.81972400
H	-3.38877900	2.74553200	1.34919800
C	-3.90720500	1.77793900	-1.10088600
H	-3.55820400	0.75787600	-1.19032000
C	-5.31923200	2.10722500	-1.16505100
C	-2.92785400	2.76195700	-1.18977700
N	-1.61017700	2.48113600	-1.25846100
C	3.89865800	0.77321600	-1.71724900
C	4.23087400	2.07255400	-1.35847300
C	5.05957400	2.30356300	-0.25566400
C	5.57370900	1.22860600	0.46564800
C	5.24164700	-0.07441800	0.10130200
C	-2.20591700	-3.21468700	1.26167800
C	-3.16188600	-2.93108700	2.22896300
C	-4.40498100	-2.40822300	1.85659800
C	-4.68091000	-2.15902600	0.51329600
C	-3.72162800	-2.44992000	-0.45326700
O	-5.72904600	3.25608000	-0.92920800
H	-3.03803200	-4.24016600	-2.42073400
H	5.97025900	-2.54007100	-1.09864600
H	3.24433500	0.60076300	-2.56309300
H	5.59800000	-0.90596400	0.69994000
H	3.83787500	2.90857900	-1.92784500

H	6.19826600	1.40905100	1.33198700
H	-3.93664200	-2.24956000	-1.49728300
H	-1.24846800	-3.62628600	1.55651500
H	-5.63300700	-1.72921400	0.22638800
H	-2.94738600	-3.11861900	3.27634600
H	5.25558400	-4.87458400	-1.43869600
H	-1.48743100	-4.87675800	-4.22574100
C	-5.13870100	1.48603100	1.80147800
H	-5.76634200	2.25855500	1.35311300
H	-5.49404800	0.50592400	1.47766800
H	-5.27259000	1.53443700	2.89144600
S	-3.28515900	4.50470500	-1.06904600
C	-0.82581400	3.63289800	-1.26143900
C	-1.55462900	4.83503000	-1.15552900
C	0.57167400	3.67303400	-1.35877100
H	1.12788200	2.74908600	-1.48296600
C	-0.90477000	6.06808900	-1.11135500
H	-1.47225400	6.98986900	-1.02419900
C	1.22147800	4.90323900	-1.29259700
H	2.30511300	4.93928400	-1.33167200
C	0.48940500	6.09334200	-1.16738900
H	1.01062000	7.04487800	-1.12053000
N	-6.22577700	1.07771200	-1.40641900
C	-7.63812900	1.42573200	-1.37649700
H	-7.99508700	1.77201600	-2.35840100
H	-8.21848400	0.54268100	-1.08669400
H	-7.79342000	2.22671000	-0.65573000
C	-5.91573800	-0.06307000	-2.25042400
H	-4.84436400	-0.24984800	-2.27947600
H	-6.41824400	-0.96204400	-1.87210700
H	-6.25862600	0.10261000	-3.28392900
C	2.61455400	-1.79575000	1.81879300
C	3.43516200	-1.17387200	2.79223100
C	2.66345300	-3.17899600	1.63059900
C	4.30773900	-1.93645800	3.57454900
C	3.54638800	-3.91933100	2.41547600
H	2.05428900	-3.66951500	0.89009900
C	4.36284400	-3.31289900	3.38085200
H	4.93682800	-1.45310600	4.31674400
H	3.59931200	-4.99387300	2.26577700
H	5.03940100	-3.91900100	3.97590200
C	2.25420500	0.47274900	1.69889700
C	1.89749800	1.76694600	1.32417200
C	3.20147100	0.25224300	2.72196000
C	2.47325100	2.83620000	2.00739000

H	1.20255900	1.95299900	0.51775200
C	3.76590500	1.33549700	3.40273100
C	3.39688800	2.62793200	3.04224500
H	2.21296000	3.84488700	1.70415400
H	4.49702600	1.16599000	4.18827100
H	3.84148300	3.47979400	3.54662600
C	1.17749400	-4.58823900	-4.36205100
H	2.14461800	-4.08325500	-4.31309200
H	1.36450300	-5.66863400	-4.38093400
H	0.70205300	-4.32739000	-5.31321200
C	2.80079800	-5.86111800	-1.88296700
H	3.02076700	-6.24249900	-2.88734100
H	3.37264200	-6.47060300	-1.17556900
H	1.73710300	-6.02356800	-1.69350300
C	-5.39913900	-2.07897300	2.93141700
C	5.40784100	3.71406900	0.11758800
F	-6.57019600	-1.63097000	2.42897300
F	-4.92452700	-1.11783600	3.76171800
F	-5.67329400	-3.15328400	3.70472000
F	6.33263200	4.24061800	-0.71986700
F	5.90664000	3.80918900	1.36839000
F	4.32725100	4.53356900	0.05370700

(R,S)-TS-O

Coordinates (Angstroms)			
	X	Y	Z
C	-1.18976800	3.91854700	-1.47247400
C	0.26770500	3.92331600	-1.78593500
C	1.14025300	3.29835400	-0.87743600
C	2.52274900	3.22550500	-1.07431400
C	3.03432000	3.82458200	-2.23472600
C	2.19108800	4.42841300	-3.15770800
C	0.80375200	4.47884000	-2.96419500
C	-1.82155500	2.68181300	-1.24023700
C	-3.16342700	2.57248000	-0.85073000
C	-3.88750100	3.77143900	-0.75157300
C	-3.28514200	5.00203600	-0.96694700
C	-1.93018400	5.10566800	-1.30666400
C	-3.78761400	1.29388700	-0.43734100
C	3.41235400	2.48713100	-0.14865700
O	0.57583400	2.66274000	0.23235000
O	-1.04172100	1.52987800	-1.35524700
P	0.00375400	1.13413600	-0.11830800

N	-1.01565900	0.94109100	1.24809100
Pd	1.54477500	-0.39145800	-0.53077000
C	1.91036800	-0.73272900	1.58115800
C	2.71123900	-1.89012800	1.47609200
C	2.19607700	-3.17858200	1.42272700
H	2.39678000	0.19289200	1.87513200
H	0.90682600	-0.85807900	1.97297800
H	3.79068000	-1.76648500	1.42232500
H	1.11802800	-3.30147500	1.49247800
C	2.01192200	-3.83076600	-0.95765700
H	2.20115800	-4.84380400	-0.63650600
C	3.08746400	-2.98428700	-1.34290100
C	0.66226100	-3.62205300	-1.39535000
N	-0.33545200	-4.39480700	-1.03464700
C	-3.56404200	0.08169100	-1.10720200
C	-4.13959200	-1.09840600	-0.64784500
C	-4.95820700	-1.08594500	0.48155800
C	-5.19898200	0.11261200	1.15363100
C	-4.61376400	1.28882600	0.70016300
C	3.38506900	2.70034800	1.23698100
C	4.22713000	1.98143000	2.08208600
C	5.10627000	1.03559700	1.54909900
C	5.15458200	0.82655000	0.17004100
C	4.30979500	1.54174900	-0.67025000
O	2.90675300	-1.75319500	-1.61807800
H	4.10534700	3.79725200	-2.41099800
H	-4.93645500	3.72532200	-0.47758300
H	-2.92399000	0.05277400	-1.98027100
H	-4.75018400	2.20425700	1.26558700
H	-3.93862500	-2.02861400	-1.16009000
H	-5.80818500	0.11928500	2.05072900
H	4.31424700	1.34297200	-1.73678800
H	2.69105800	3.42158100	1.65330200
H	5.82959700	0.08538500	-0.23959800
H	4.19046100	2.14168700	3.15394600
H	-3.86862300	5.91097200	-0.84643800
H	2.61088400	4.85762700	-4.06357600
C	3.04446200	-4.35705500	1.80350400
H	3.07611000	-4.44010500	2.89997900
H	2.65215300	-5.30232000	1.42005900
H	4.07530000	-4.22923900	1.45889800
S	0.21662400	-2.36563300	-2.61437100
C	-1.50111200	-4.09166500	-1.71220100
C	-1.40723200	-3.01901200	-2.63669100
C	-2.72242600	-4.76395000	-1.56386900

H	-2.79691900	-5.57825000	-0.85048700
C	-2.49581600	-2.63610600	-3.41958100
H	-2.41128700	-1.82143600	-4.13249000
C	-3.80847500	-4.38351300	-2.34723700
H	-4.75710500	-4.89920100	-2.23406600
C	-3.69602100	-3.33460500	-3.27392200
H	-4.55517900	-3.05185300	-3.87488300
N	4.38010300	-3.46537500	-1.32648600
C	5.49752100	-2.54218900	-1.38948900
H	6.08970800	-2.56970600	-0.46362900
H	6.15768800	-2.79220500	-2.23032400
H	5.09928100	-1.54059500	-1.53410300
C	4.70417900	-4.87974700	-1.33935800
H	4.94960900	-5.27069200	-0.34231100
H	3.87042100	-5.45565200	-1.74471300
H	5.57334300	-5.04061400	-1.98792600
C	-1.61050700	1.89531200	2.12120000
C	-2.37925500	1.20227100	3.08903700
C	-1.56437900	3.29060000	2.10655300
C	-3.09590200	1.91228000	4.05649300
C	-2.29513800	3.97800900	3.07501600
H	-1.00192900	3.82772900	1.35881300
C	-3.05185800	3.30318700	4.04512000
H	-3.69008600	1.38034900	4.79420400
H	-2.27838500	5.06406400	3.06763600
H	-3.60946000	3.86970900	4.78508100
C	-1.49074700	-0.34741300	1.63635600
C	-1.29666900	-1.59144700	1.03246800
C	-2.29464000	-0.21165300	2.78863600
C	-1.87584400	-2.70798000	1.63296500
H	-0.72031500	-1.70038100	0.12278900
C	-2.87755900	-1.34211400	3.36958700
C	-2.65545900	-2.58868500	2.79316600
H	-1.72670100	-3.67693900	1.16924700
H	-3.51149100	-1.24256600	4.24575200
H	-3.11708800	-3.47176600	3.22276500
C	-0.06494900	5.07496900	-4.04493300
H	-1.10559000	4.75715100	-3.95040500
H	-0.04544700	6.17111100	-4.01781400
H	0.29814200	4.77061600	-5.03205400
C	-1.31033400	6.47647000	-1.43169000
H	-1.51572100	6.92433400	-2.41142400
H	-1.72790100	7.15049700	-0.67661800
H	-0.22582700	6.44753200	-1.30262500
C	6.02082300	0.24371500	2.43603800

C	-5.61268100	-2.35332900	0.94551800
F	7.28190100	0.73225200	2.43300900
F	6.11253400	-1.04956300	2.02167600
F	5.60292900	0.22461600	3.71787400
F	-5.82720000	-2.35590600	2.28324900
F	-4.87983400	-3.44993800	0.65151600
F	-6.82519200	-2.53204900	0.36252300

(S,R)-TS-O

Coordinates (Angstroms)			
	X	Y	Z
C	-0.82357700	3.50633000	-1.41304100
C	0.66765600	3.45015100	-1.47574500
C	1.39944600	2.75848800	-0.48968000
C	2.79230700	2.61731200	-0.53631100
C	3.46639700	3.22996800	-1.59959400
C	2.76948900	3.90630200	-2.59114600
C	1.37331000	4.00537600	-2.56780800
C	-1.52722400	2.29596200	-1.32518500
C	-2.92455800	2.19853900	-1.34960200
C	-3.62943900	3.40839200	-1.43428800
C	-2.96164300	4.62640400	-1.44643700
C	-1.56293400	4.70544900	-1.42906600
C	-3.61666100	0.89192000	-1.23545000
C	3.54338800	1.80403400	0.45031600
O	0.73216900	2.20141300	0.59756000
O	-0.79067100	1.13795800	-1.11396400
P	-0.22697300	0.85637500	0.42620700
N	-1.49115100	1.37975900	1.47561900
Pd	0.42570000	-1.27088700	0.62687800
C	1.96207400	-1.33916400	2.02526000
C	1.55292300	-2.70929400	1.96947000
C	2.07624000	-3.66511300	1.08433400
H	2.85629300	-1.03602400	1.48888100
H	1.76481100	-0.77664400	2.93285400
H	0.83437900	-3.05853100	2.71060500
H	2.92155000	-3.38747200	0.46112500
C	1.14124200	-3.88414900	-1.25083400
H	1.61467000	-4.85059800	-1.34747100
C	-0.25255800	-3.80228100	-0.94018100
C	1.89750900	-2.81538000	-1.81721100
N	3.20239300	-2.86732700	-1.97969800
C	-3.09934800	-0.26868700	-1.83578000

C	-3.74546400	-1.49114600	-1.69866100
C	-4.93312300	-1.57584900	-0.97062100
C	-5.46462800	-0.43208600	-0.36988300
C	-4.80838300	0.78711900	-0.49930300
C	3.38932100	1.97842200	1.83423300
C	4.13226300	1.21560700	2.72942700
C	5.03173800	0.25782000	2.25292500
C	5.19321800	0.07349200	0.87824100
C	4.45717300	0.84618700	-0.01570900
O	-0.82875800	-2.70840400	-0.62598100
H	4.54619200	3.14211800	-1.65422900
H	-4.71398900	3.38698500	-1.47139400
H	-2.17885200	-0.22334700	-2.40145100
H	-5.20044100	1.65955800	0.01220000
H	-3.31384400	-2.37561700	-2.15058300
H	-6.37488500	-0.49921800	0.21463900
H	4.57308100	0.68902200	-1.08108100
H	2.68762800	2.71582300	2.20657300
H	5.88047000	-0.67756400	0.50430700
H	4.01308600	1.35861200	3.79808700
H	-3.53727800	5.54811600	-1.45668600
H	3.31336400	4.34151400	-3.42529000
C	1.82421000	-5.12145700	1.34476400
H	2.26726000	-5.76038200	0.57930900
H	2.25605000	-5.40031700	2.31735800
H	0.74917300	-5.32974600	1.39701200
S	1.14321000	-1.27812900	-2.37685600
C	3.69442700	-1.72131300	-2.56681900
C	2.72739000	-0.72554400	-2.87041700
C	5.04240200	-1.47519800	-2.86842300
H	5.78298500	-2.23530400	-2.64034500
C	3.08415600	0.48629900	-3.45636300
H	2.33833400	1.24633100	-3.66293000
C	5.39835800	-0.26574200	-3.46178000
H	6.44058400	-0.07302900	-3.70034800
C	4.42964100	0.70749400	-3.75564200
H	4.72694500	1.64623000	-4.21368100
N	-1.00249700	-4.95225200	-0.89433100
C	-2.35206600	-4.91517000	-0.35144500
H	-3.10749200	-4.96358600	-1.14613100
H	-2.50637900	-5.76730400	0.32160300
H	-2.49056400	-3.98587700	0.19504400
C	-0.58797800	-6.20351500	-1.50717700
H	0.13074800	-6.01738000	-2.30664700
H	-0.13949700	-6.89464200	-0.77970800

H	-1.46408200	-6.69367000	-1.94582600
C	-1.85343700	2.68656400	1.92797000
C	-3.06513100	2.59059300	2.65577500
C	-1.21523800	3.92218700	1.78805600
C	-3.65627100	3.73016000	3.20913000
C	-1.82164800	5.04697100	2.34669800
H	-0.27772200	4.01966600	1.26772800
C	-3.03402200	4.96283800	3.04526000
H	-4.58820000	3.64592700	3.76118200
H	-1.33011400	6.00975000	2.23766200
H	-3.48019200	5.85863700	3.46691100
C	-2.49661300	0.47651700	1.93497300
C	-2.63933900	-0.89659200	1.72421800
C	-3.46272100	1.19994000	2.66915100
C	-3.73371500	-1.53496900	2.30562900
H	-1.95880100	-1.46404600	1.10190300
C	-4.55950000	0.54299200	3.23490900
C	-4.68554900	-0.83059400	3.05758400
H	-3.86635600	-2.59699600	2.13723400
H	-5.29948400	1.10231700	3.80064200
H	-5.53019600	-1.35980400	3.48876400
C	0.67424000	4.66231900	-3.73441800
H	-0.33813200	4.27553200	-3.87229200
H	0.59581700	5.74786300	-3.60311500
H	1.23797700	4.48890500	-4.65635000
C	-0.91280600	6.06324200	-1.32859300
H	-1.06260100	6.65563700	-2.23892800
H	-1.36169700	6.62312400	-0.50018200
H	0.16074900	5.99076500	-1.14336800
C	5.72645900	-0.65596900	3.21798400
C	-5.59802200	-2.90550800	-0.78161000
F	6.90487300	-1.10722400	2.73645900
F	4.96969100	-1.75120300	3.48755100
F	5.97232100	-0.05461200	4.40309400
F	-6.93192300	-2.79149500	-0.60668100
F	-5.12600100	-3.57226900	0.31023700
F	-5.39382000	-3.73087800	-1.83598500

(R,R)-TS-O

Coordinates (Angstroms)			
	X	Y	Z
C	-0.98534100	4.13987700	-1.40575700
C	0.47176000	4.06940700	-1.71328000

C	1.29670200	3.33183700	-0.84396900
C	2.68986100	3.27747200	-0.97428900
C	3.25069400	3.99318300	-2.04511100
C	2.45247900	4.67469400	-2.95214900
C	1.05843400	4.71918500	-2.81576100
C	-1.71339700	2.94505000	-1.26415300
C	-3.05569100	2.91525300	-0.86324000
C	-3.67910300	4.15376300	-0.64899300
C	-2.98018800	5.34529500	-0.77501200
C	-1.62615100	5.36634100	-1.13097100
C	-3.78160000	1.66144800	-0.55640000
C	3.54677200	2.48041000	-0.06812000
O	0.67888300	2.61652700	0.18037900
O	-1.03314400	1.74386300	-1.47453100
P	-0.02577400	1.17375300	-0.27386800
N	-1.04475500	1.01559900	1.10127300
Pd	1.33884500	-0.50560900	-0.76222200
C	1.90485300	-0.89751500	1.31321500
C	1.49284900	-2.23468400	1.50386300
C	2.33140400	-3.32798200	1.37685300
H	2.97297600	-0.70938600	1.22386500
H	1.36106400	-0.12432500	1.84839000
H	0.45521200	-2.41588100	1.76950200
H	3.39185900	-3.13303500	1.24051200
C	2.34532500	-4.04366700	-1.00096500
H	2.73458800	-4.99070500	-0.65979200
C	3.22053800	-2.98292400	-1.34358500
C	0.95686600	-4.06924100	-1.31884400
N	0.14449700	-5.01832300	-0.90977400
C	-3.71566800	0.52381200	-1.37546400
C	-4.39958900	-0.63627100	-1.02924000
C	-5.15811300	-0.68102400	0.14255700
C	-5.23462700	0.44247200	0.96412500
C	-4.55147400	1.60266500	0.61604000
C	3.30218000	2.39279300	1.31285300
C	4.10979400	1.60791400	2.12921100
C	5.19056200	0.91295100	1.58253300
C	5.47918900	1.03452500	0.22227700
C	4.65762100	1.80072100	-0.59406500
O	2.79254500	-1.83288300	-1.69859700
H	4.32934900	4.00373200	-2.16385600
H	-4.72431600	4.16762900	-0.35731700
H	-3.11609700	0.54640100	-2.27791200
H	-4.56936800	2.45542300	1.28596300
H	-4.31876500	-1.51999300	-1.64947300

H	-5.79725900	0.39915500	1.88954600
H	4.85656500	1.84504200	-1.65952200
H	2.46493600	2.92578100	1.74483800
H	6.33117200	0.51317700	-0.19736200
H	3.89539300	1.52588200	3.18914900
H	-3.48449500	6.28525300	-0.56759000
H	2.91552200	5.18640600	-3.79173800
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H	1.70105400	-4.65870000	2.93869400
H	1.00919400	-5.02355600	1.34352100
H	2.69785200	-5.43348300	1.69526400
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C	-1.34818000	-3.66482500	-2.14970700
C	-2.24730900	-5.63132500	-1.03220800
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C	-2.60535700	-3.34089100	-2.65834900
H	-2.74105300	-2.46722400	-3.28931300
C	-3.50429400	-5.29628000	-1.52550000
H	-4.36052600	-5.91753100	-1.28055800
C	-3.68353400	-4.16560900	-2.33872400
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H	5.06054600	-4.71930500	0.16790000
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C	-1.64494900	-0.23551800	1.43470000
C	-1.65720200	-1.43520700	0.72382300
C	-2.36854100	-0.09221900	2.63849800
C	-2.36119600	-2.51051600	1.26511400

H	-1.14977400	-1.54189900	-0.22533400
C	-3.06389600	-1.18243300	3.17012000
C	-3.04919000	-2.39173700	2.48177300
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H	-3.62889000	-1.07563200	4.09173300
H	-3.60564100	-3.24003400	2.86696900
C	0.24099200	5.42167900	-3.87225400
H	-0.82267900	5.19160400	-3.78445500
H	0.35855500	6.51038800	-3.81454800
H	0.57465900	5.11523000	-4.86962700
C	-0.89963200	6.68965300	-1.15186600
H	-1.02392800	7.20428300	-2.11207900
H	-1.30013300	7.35187800	-0.37777600
H	0.17282900	6.57018900	-0.98035500
C	5.96300800	-0.06846300	2.40955600
C	-5.92155700	-1.92486300	0.49169900
F	7.26170100	-0.13725700	2.04295800
F	5.45840400	-1.32826900	2.26106300
F	5.92017400	0.21275600	3.72666400
F	-6.16318700	-2.01996600	1.81942000
F	-5.27018900	-3.04845500	0.11745500
F	-7.12943600	-1.95699200	-0.12595100

(S,S)-TS-O

Coordinates (Angstroms)			
	X	Y	Z
C	-1.16423500	3.69890600	-1.24941400
C	0.32624100	3.79047600	-1.21053500
C	1.02229800	3.10975400	-0.19269900
C	2.41934800	3.02701600	-0.14354600
C	3.13282900	3.73596200	-1.12067200
C	2.47235000	4.43104200	-2.12432300
C	1.07325100	4.44566300	-2.21227800
C	-1.74320900	2.41800200	-1.25000300
C	-3.12348500	2.18613100	-1.28879100
C	-3.94677900	3.32046600	-1.32056400
C	-3.40462700	4.59918200	-1.27906100
C	-2.02077300	4.81774800	-1.23640000
C	-3.67966400	0.81250300	-1.23312800
C	3.12376000	2.14169400	0.81442600
O	0.27569200	2.45496500	0.78706400
O	-0.89649400	1.32273600	-1.12682200
P	-0.31986800	0.95188100	0.39042500

N	-1.68263400	0.97540800	1.42795200
Pd	1.09538500	-0.78119200	0.24991300
C	1.32152000	-1.61877800	2.15741200
C	2.35880400	-2.28151400	1.42698100
C	2.26864000	-3.56350500	0.85668900
H	1.61598000	-0.87002100	2.88717200
H	0.40441600	-2.15561000	2.39380900
H	3.34767000	-1.83441800	1.44007800
H	1.35152100	-4.12832300	0.99238300
C	1.54227300	-3.79079600	-1.57496300
H	2.07835300	-4.72198600	-1.67400000
C	0.13159100	-3.76043100	-1.30368700
C	2.23489800	-2.65065500	-2.04390700
N	3.52227000	-2.59551200	-2.29839600
C	-3.09397000	-0.24547500	-1.94748300
C	-3.62193000	-1.52927300	-1.88028500
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C	-5.33974400	-0.74102100	-0.37235900
C	-4.80453800	0.54169500	-0.43750000
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C	3.44842400	1.21392500	3.03304000
C	4.43223500	0.35508200	2.53447200
C	4.78422900	0.40675800	1.18453600
C	4.13280900	1.29141300	0.33199300
O	-0.51667400	-2.68325100	-1.30882300
H	4.21727500	3.70737200	-1.10165000
H	-5.02362800	3.18971100	-1.36050300
H	-2.21422200	-0.07058700	-2.55251300
H	-5.23911800	1.33524600	0.16163700
H	-3.14049900	-2.33141900	-2.42548900
H	-6.20425800	-0.93826000	0.25165900
H	4.37783400	1.29242000	-0.72327200
H	2.02361500	2.74897800	2.56675400
H	5.53537600	-0.26830400	0.78900600
H	3.18084200	1.17688900	4.08374200
H	-4.07015000	5.45822100	-1.26404800
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H	3.36474300	-5.31413100	0.21909200
H	4.01838200	-3.76193400	-0.35588500
H	4.23600400	-4.23104400	1.33769800
S	1.37431800	-1.05125400	-2.25887700
C	3.93765900	-1.32274300	-2.65597500
C	2.92249800	-0.33679400	-2.70882400
C	5.25617300	-0.95346400	-2.95224300

H	6.04066700	-1.70247200	-2.91080300
C	3.18705500	0.97598700	-3.07670000
H	2.39519900	1.71683800	-3.10869900
C	5.53031500	0.36895200	-3.30464000
H	6.55160200	0.65790800	-3.53646200
C	4.50812400	1.32595800	-3.37544500
H	4.73974200	2.34880200	-3.65766400
N	-0.50582400	-4.93744300	-0.93582800
C	-1.95935400	-4.92555200	-0.85452400
H	-2.43175800	-5.23312700	-1.79964400
H	-2.29254300	-5.60872400	-0.06613700
H	-2.28891000	-3.91794400	-0.62075300
C	0.11723500	-6.23719000	-1.12756500
H	1.10436200	-6.27431600	-0.65923400
H	-0.50473200	-6.99543200	-0.64476900
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C	-4.32682000	2.36514800	3.49148000
C	-3.06201300	4.26062100	2.67512000
H	-1.36608100	3.85592000	1.41683000
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H	-4.79886300	4.41314800	3.94911800
C	-2.34584900	-0.23347300	1.79496900
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C	-2.90627800	-2.54683300	1.92179400
H	-1.35504800	-1.79159400	0.63548300
C	-4.22448300	-0.94358800	3.17192600
C	-3.95410300	-2.25867700	2.80894700
H	-2.73400300	-3.57259900	1.61776100
H	-5.05172600	-0.70724700	3.83541500
H	-4.57025600	-3.06623900	3.19231100
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H	-0.57478300	4.71990600	-3.59258500
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H	1.03348600	4.96199500	-4.29778300
C	-1.50736300	6.23085600	-1.10247800
H	-1.56261100	6.77428800	-2.05334900
H	-2.11589400	6.78526000	-0.37988700
H	-0.46908800	6.25617900	-0.76354100
C	5.11592200	-0.61512100	3.45254400

C	-5.32014000	-3.16529700	-1.01646400
F	6.21680100	-0.08646000	4.03252400
F	5.52017100	-1.72877200	2.79125700
F	4.29934500	-1.01832200	4.45277900
F	-6.66654800	-3.15245700	-0.89276700
F	-4.84764600	-3.86085800	0.05190000
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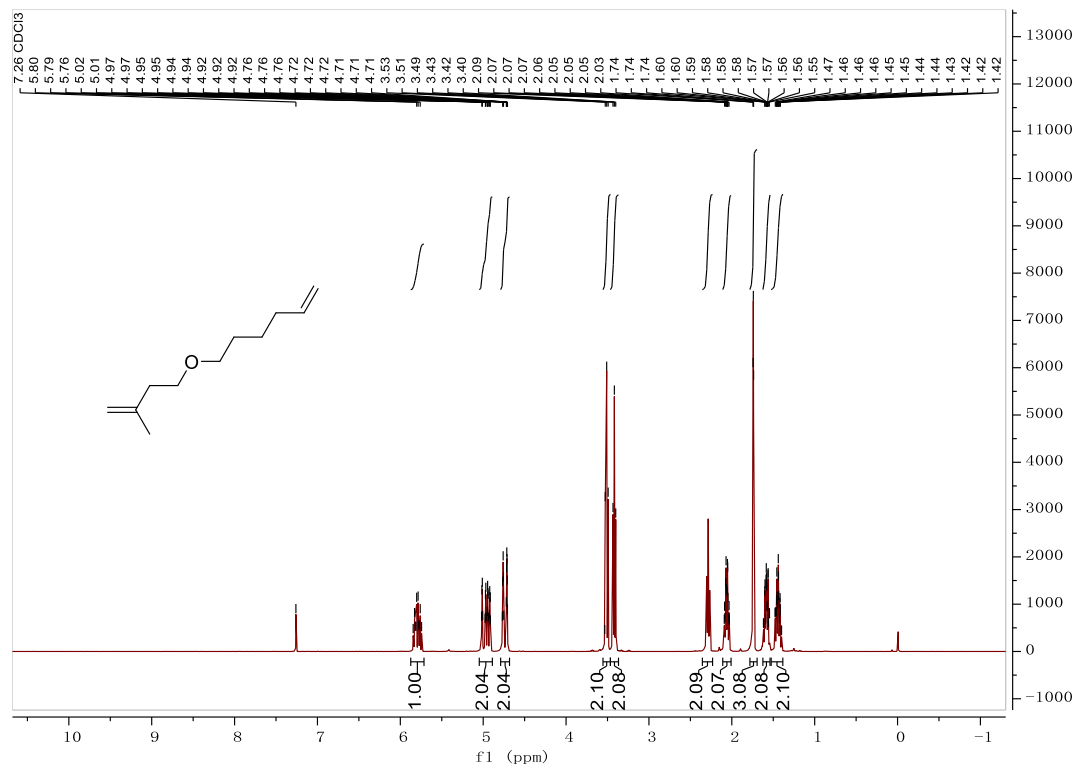
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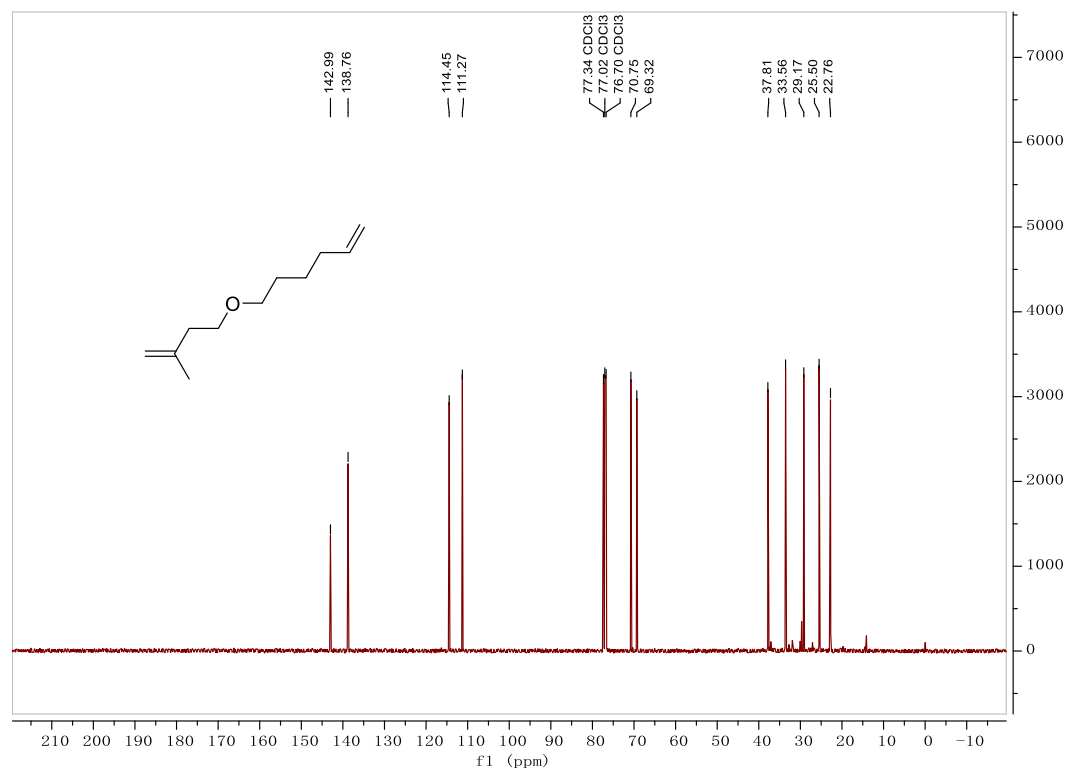
10. NMR spectra

6-((3-methylbut-3-en-1-yl)oxy)hex-1-ene (s1)

^1H NMR, CDCl_3 , 400 MHz

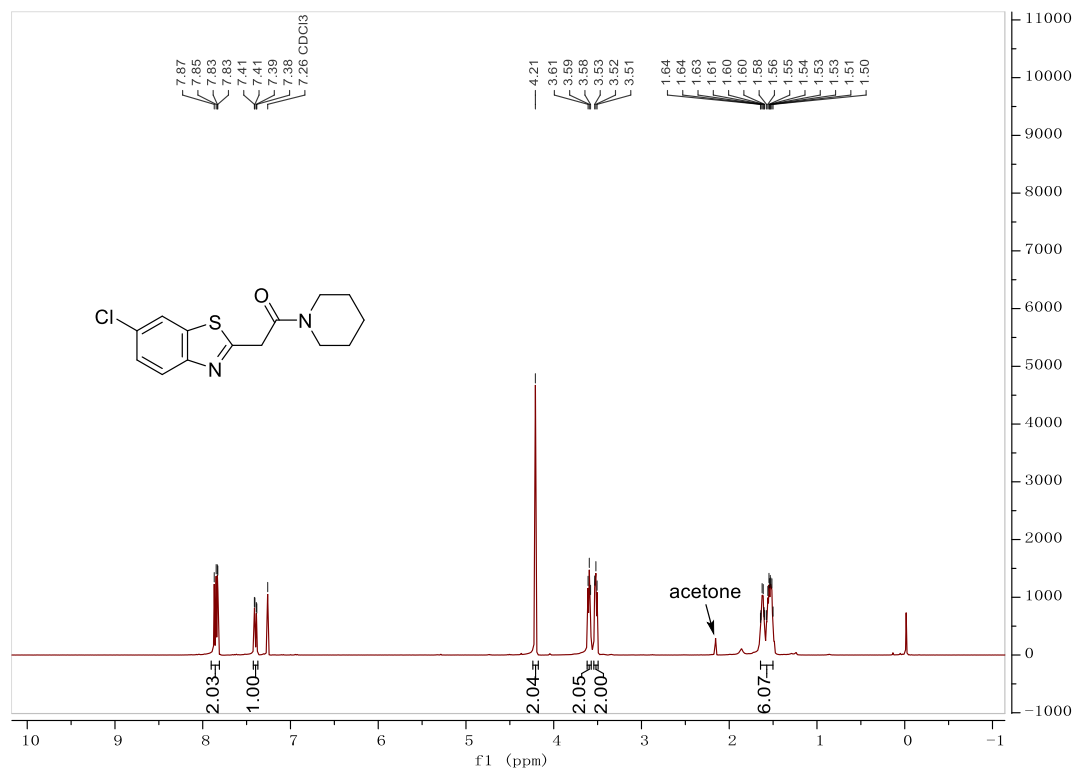


^{13}C NMR, CDCl_3 , 101 MHz

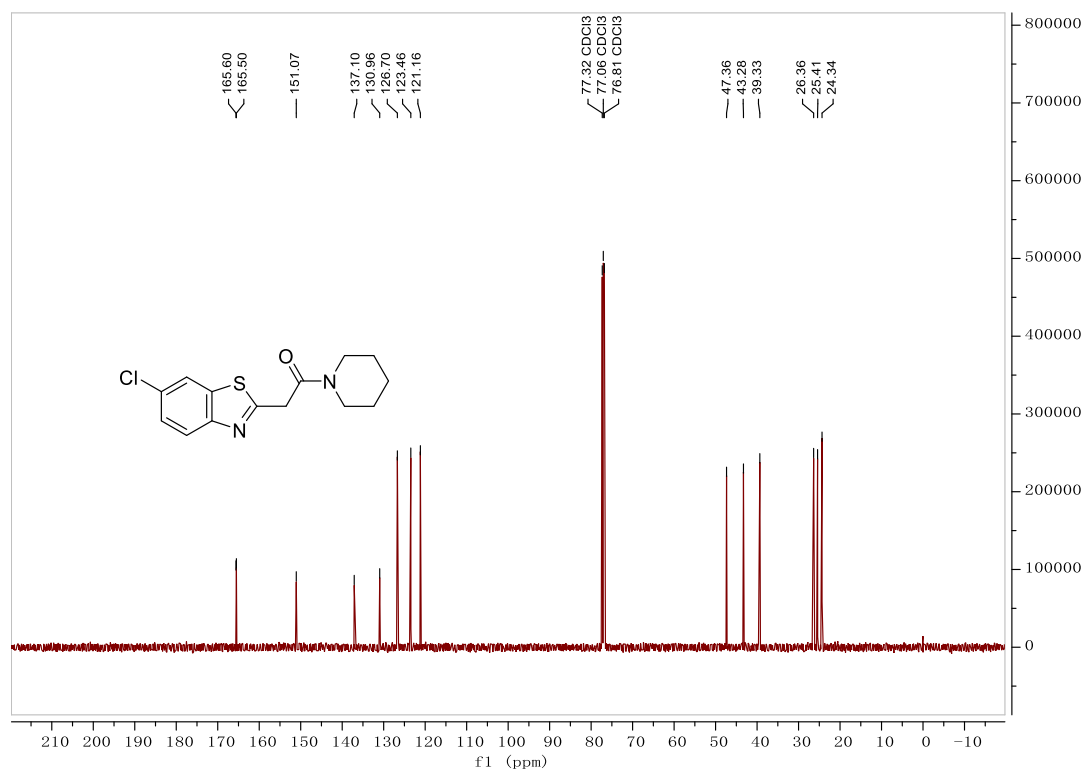


2-(6-chlorobenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)ethan-1-one (s2)

¹H NMR, CDCl₃, 400 MHz

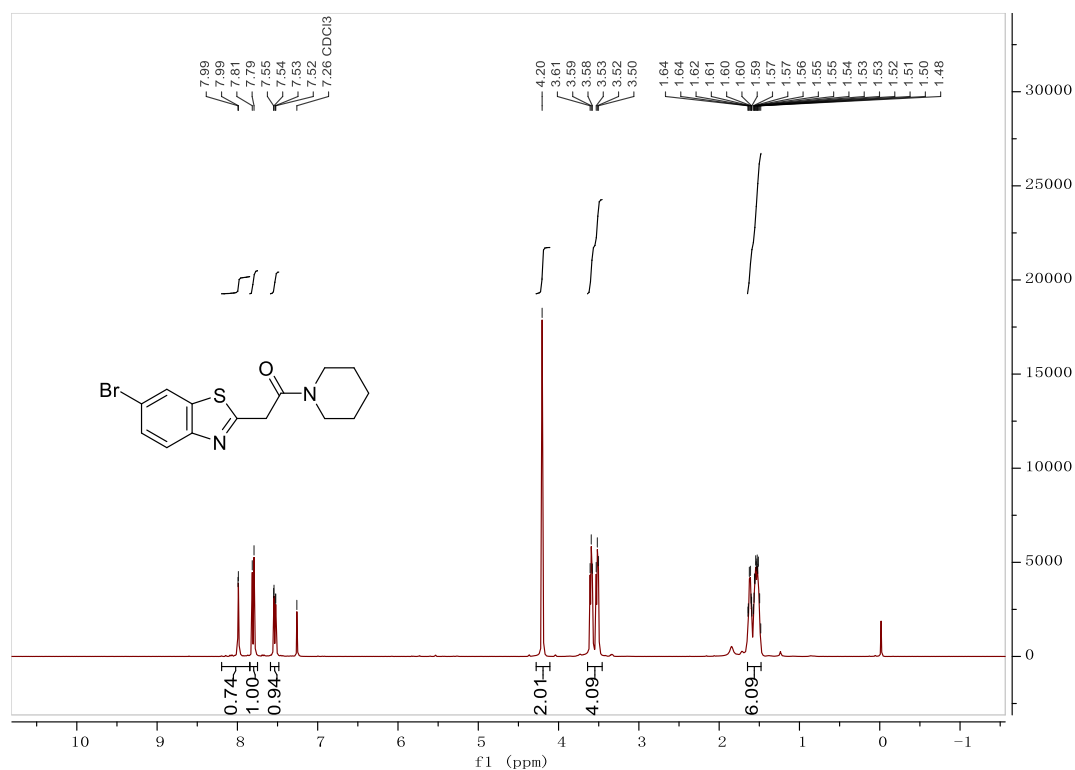


¹³C NMR, CDCl₃, 101 MHz

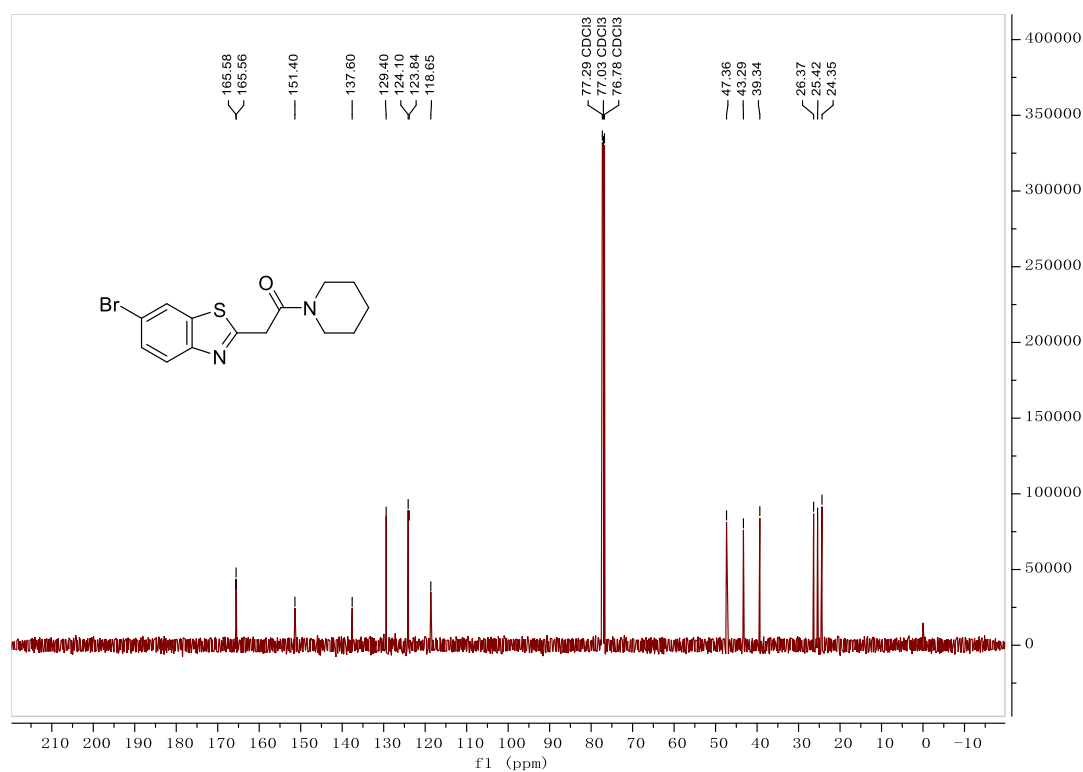


2-(6-bromobenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)ethan-1-one (s3)

¹H NMR, CDCl₃, 400 MHz

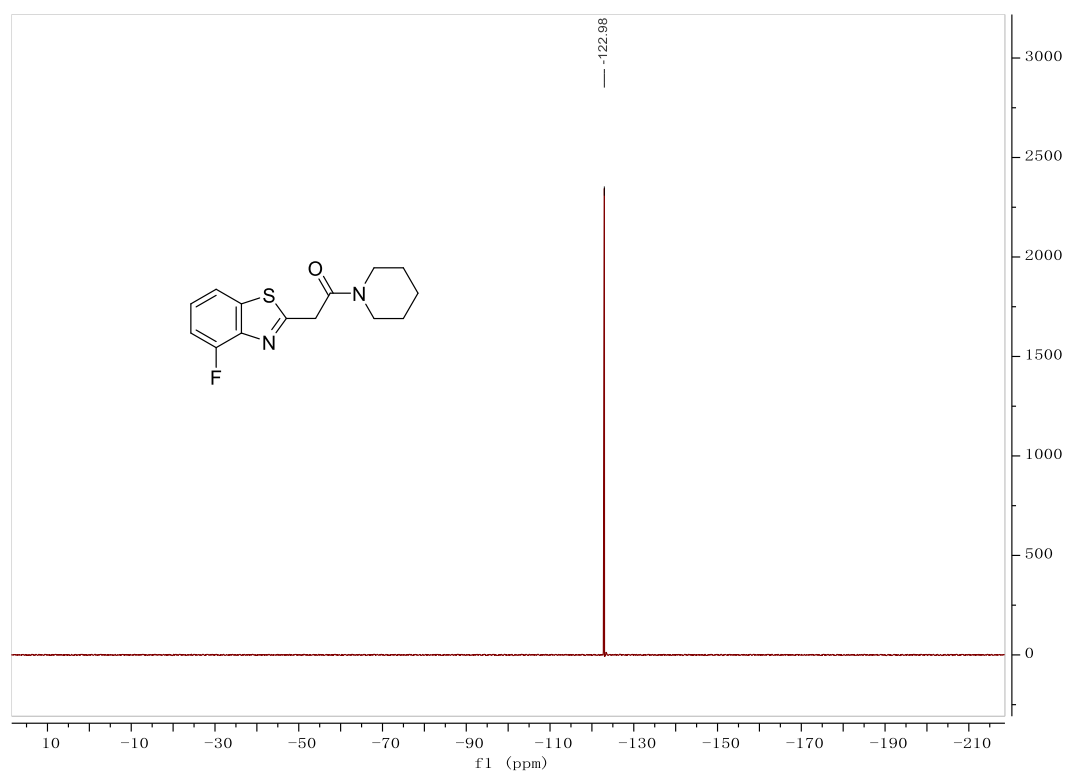
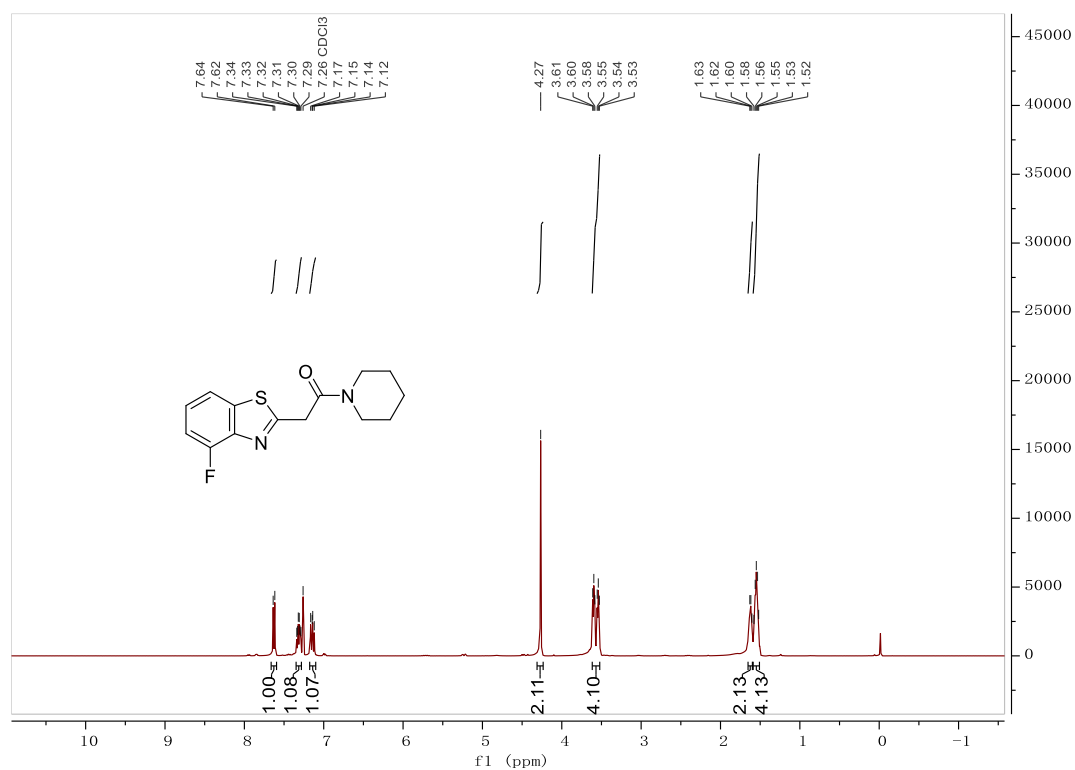


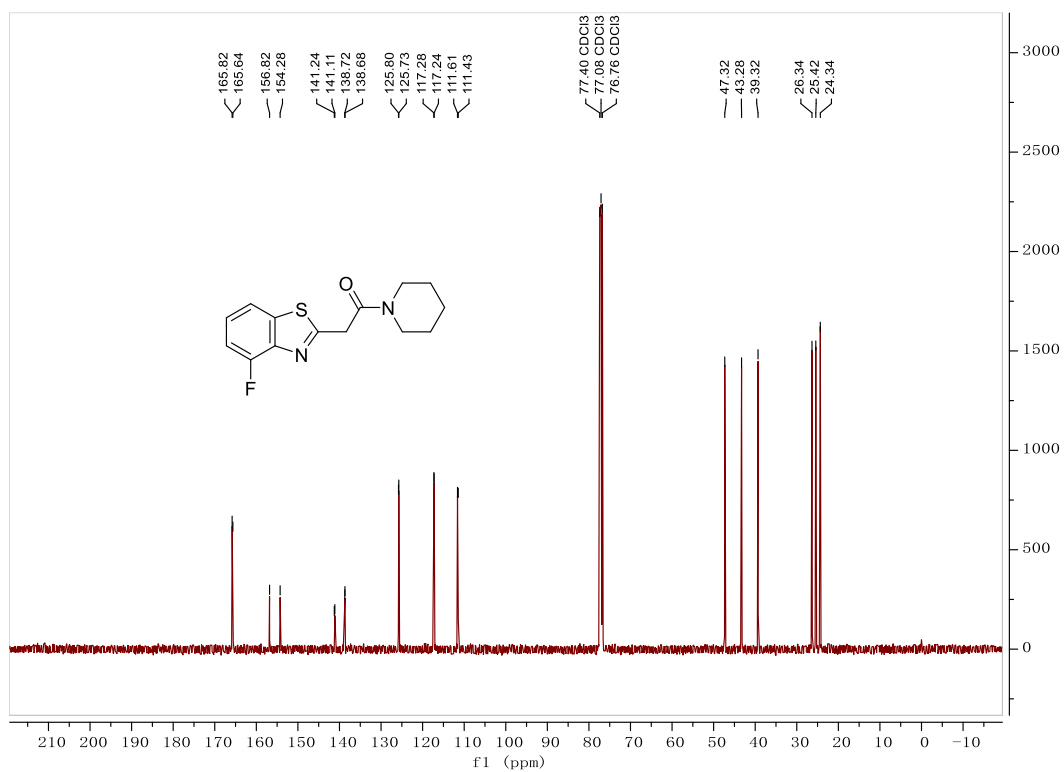
¹³C NMR, CDCl₃, 101 MHz



2-(4-fluorobenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)ethan-1-one (s4)

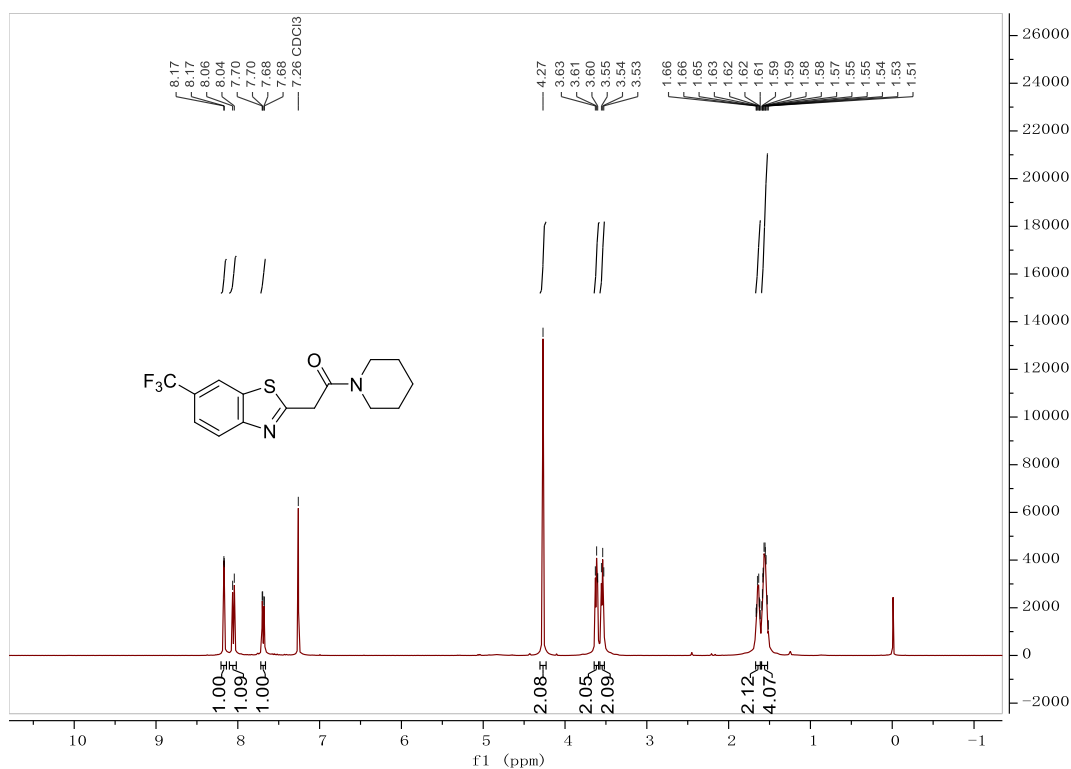
¹H NMR, CDCl₃, 400 MHz



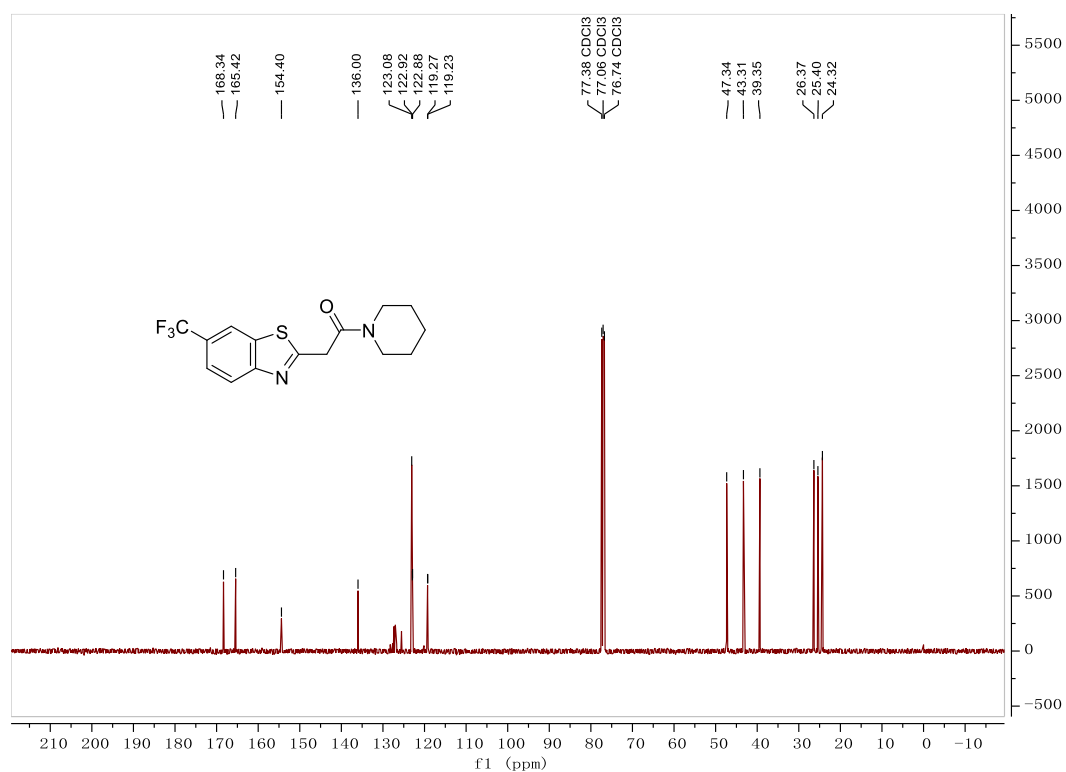
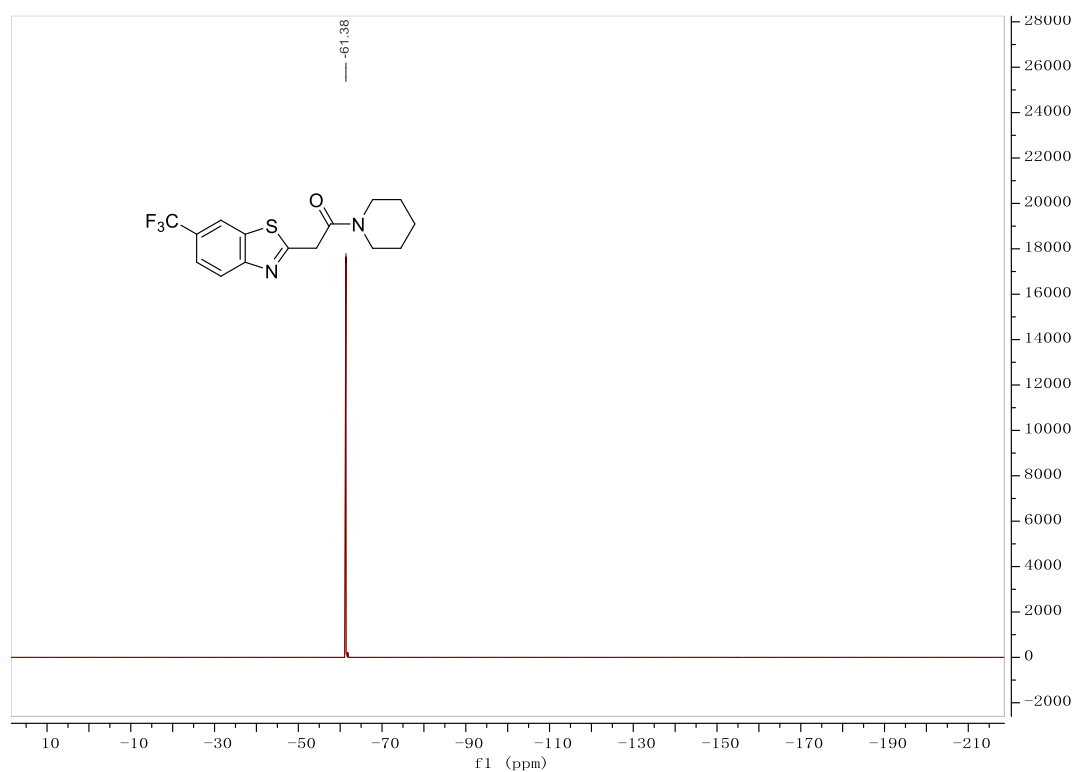


1-(piperidin-1-yl)-2-(6-(trifluoromethyl)benzo[d]thiazol-2-yl)ethan-1-one (s5)

¹H NMR, CDCl₃, 400 MHz

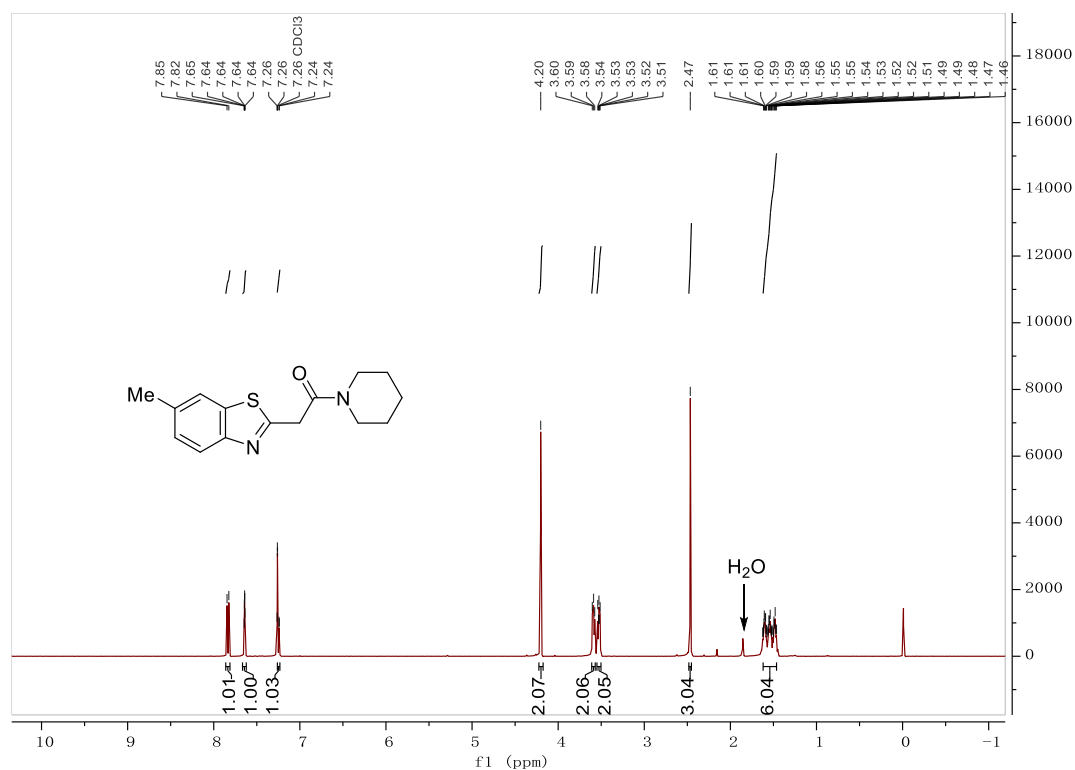


¹⁹F NMR, CDCl₃, 376 MHz

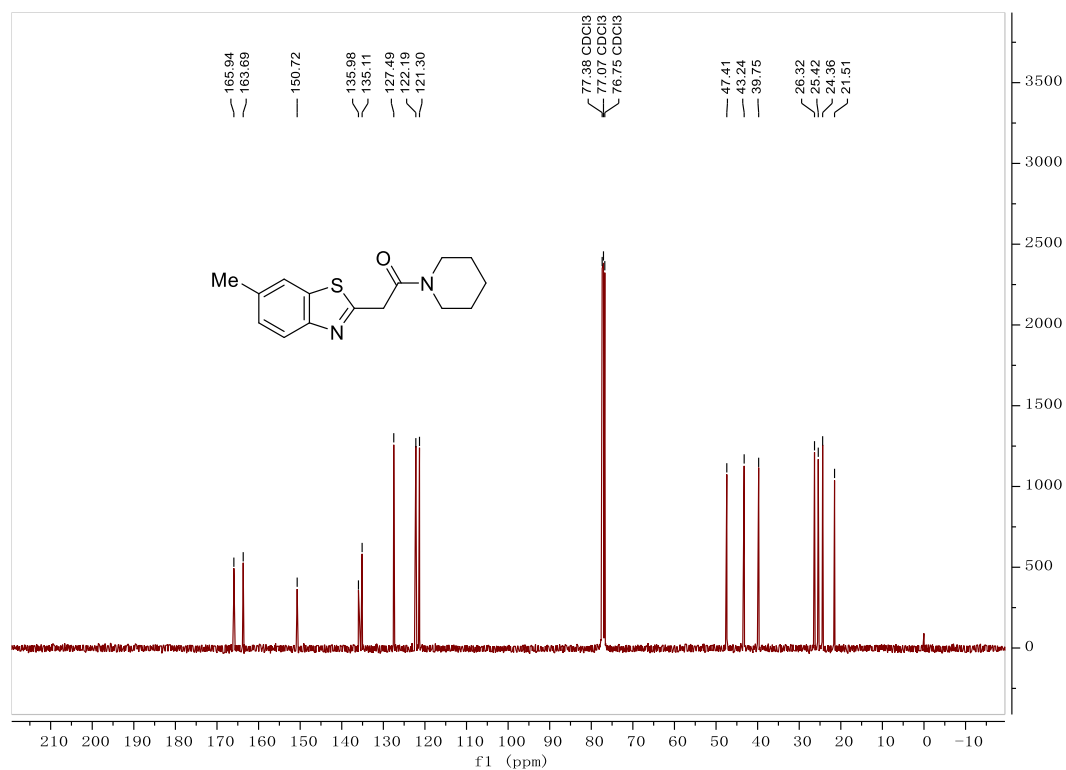


2-(6-methylbenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)ethan-1-one (s6)

¹H NMR, CDCl₃, 400 MHz

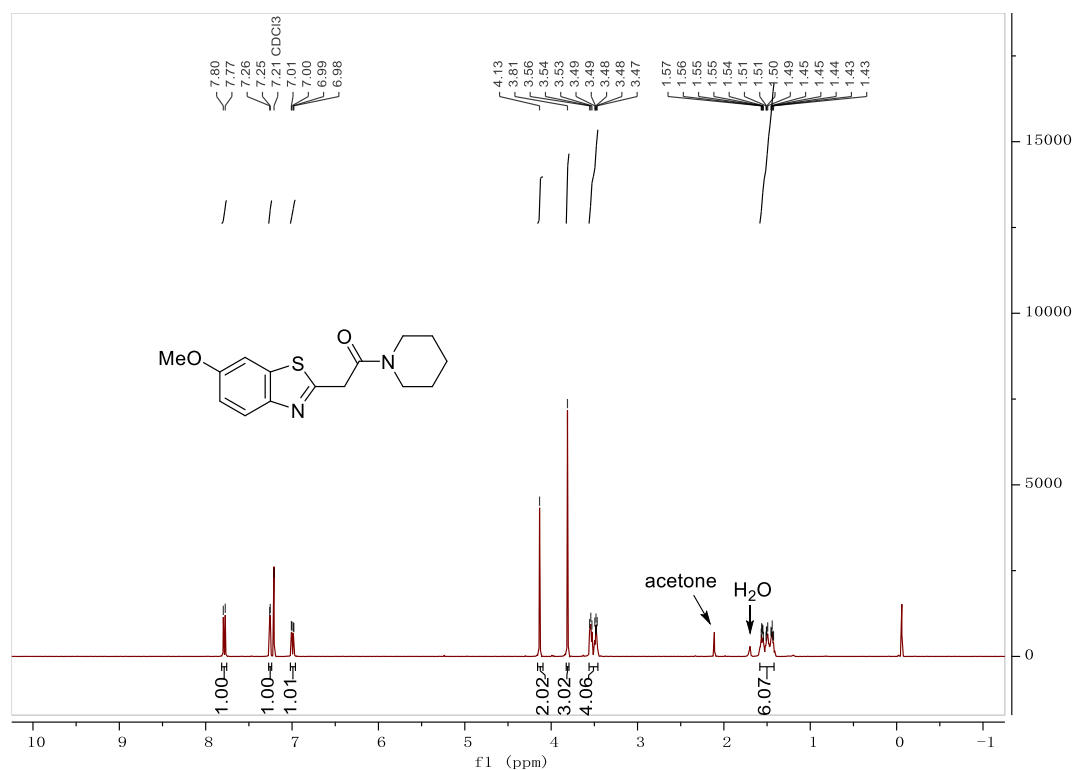


¹³C NMR, CDCl₃, 101 MHz

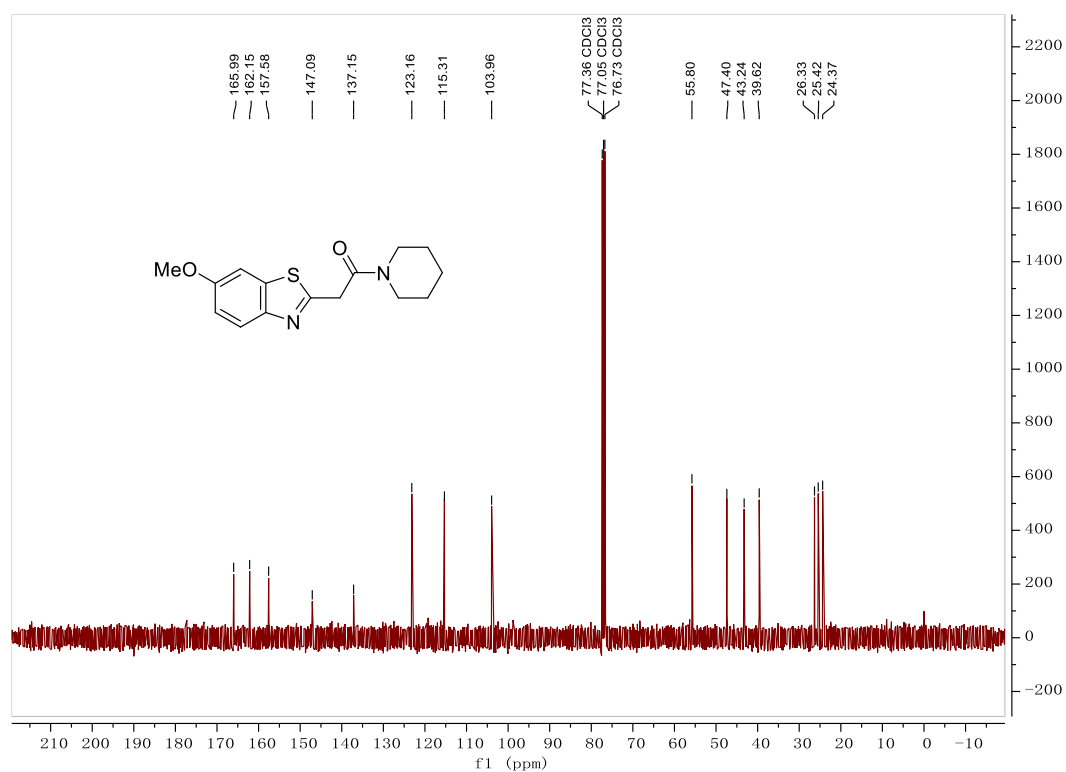


2-(6-methoxybenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)ethan-1-one (s7)

¹H NMR, CDCl₃, 400 MHz

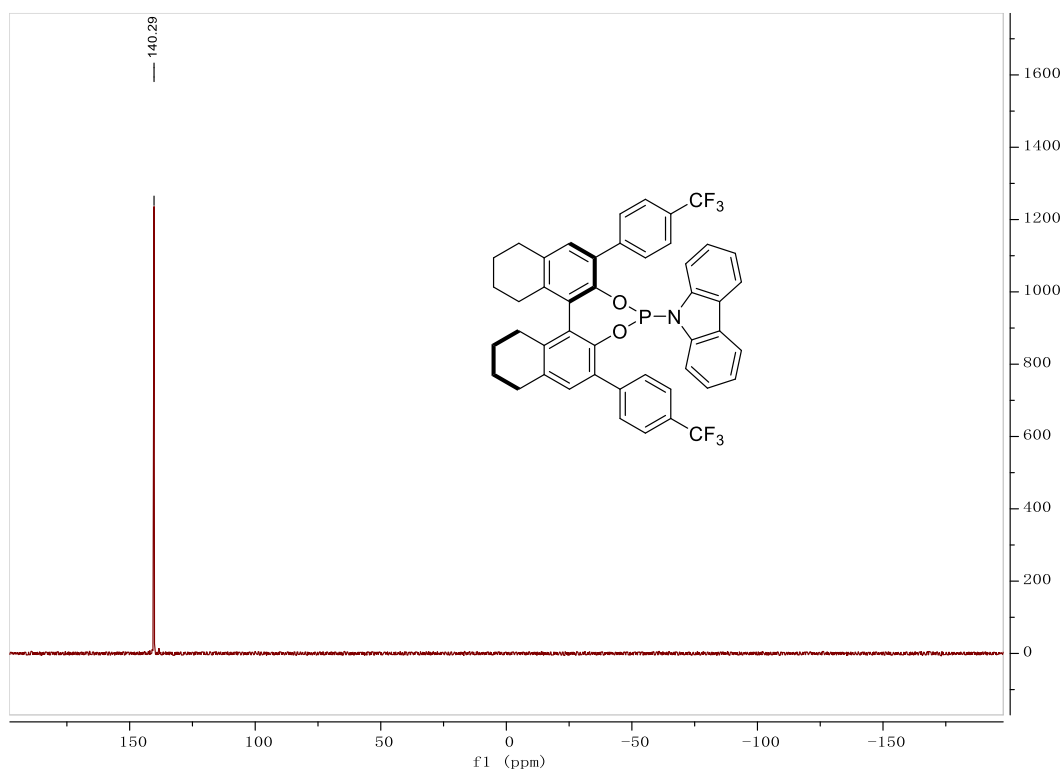


¹³C NMR, CDCl₃, 101 MHz

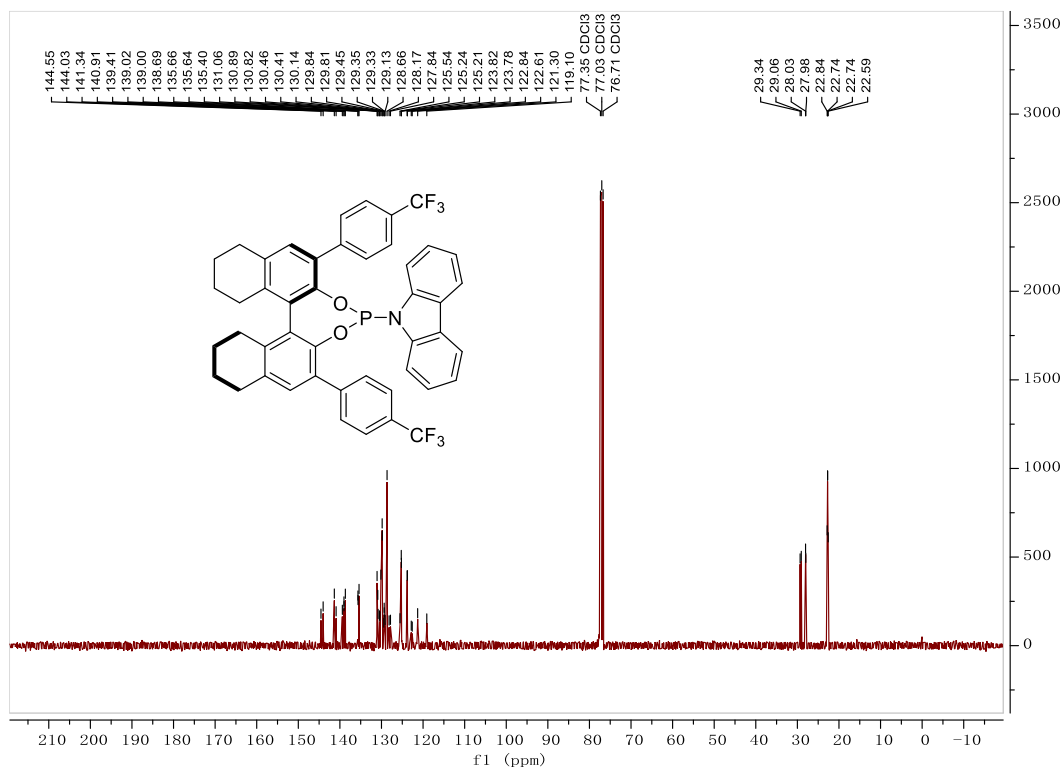


9-(2,6-bis(4-(trifluoromethyl)phenyl)-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d':2'-f][1,3,2]dioxaphosphepin-4-yl)-9H-carbazole (L1)

¹H NMR, CDCl₃, 400 MHz

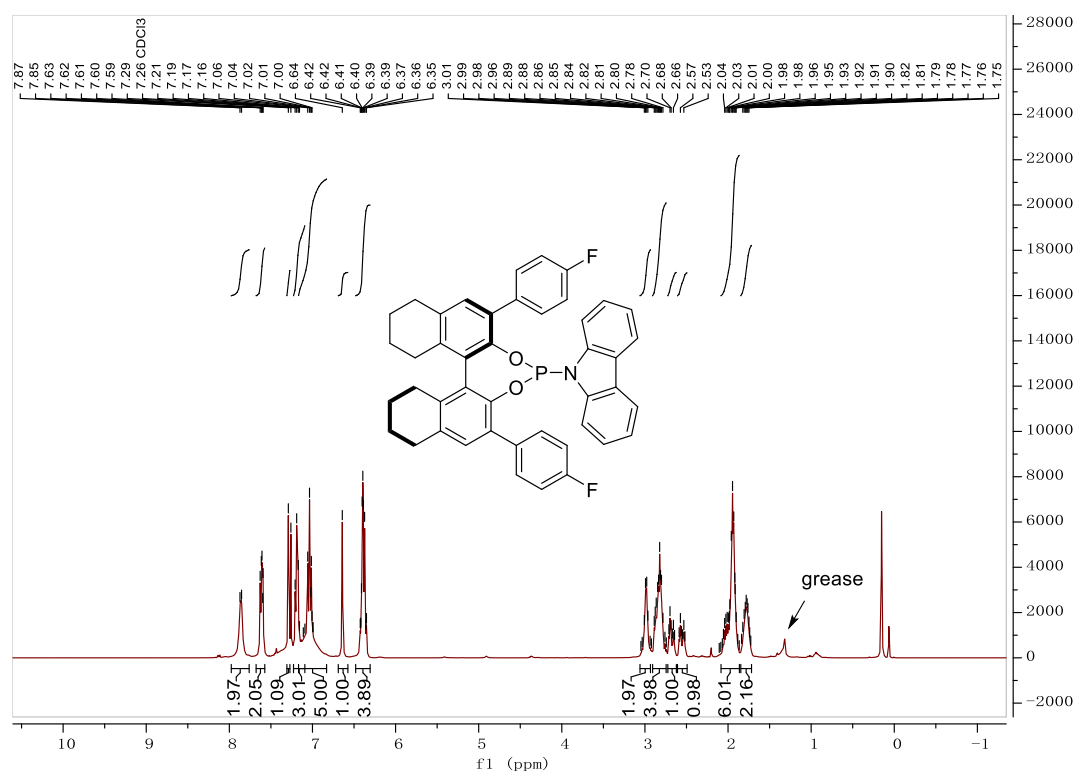


^{13}C NMR, CDCl₃, 101 MHz

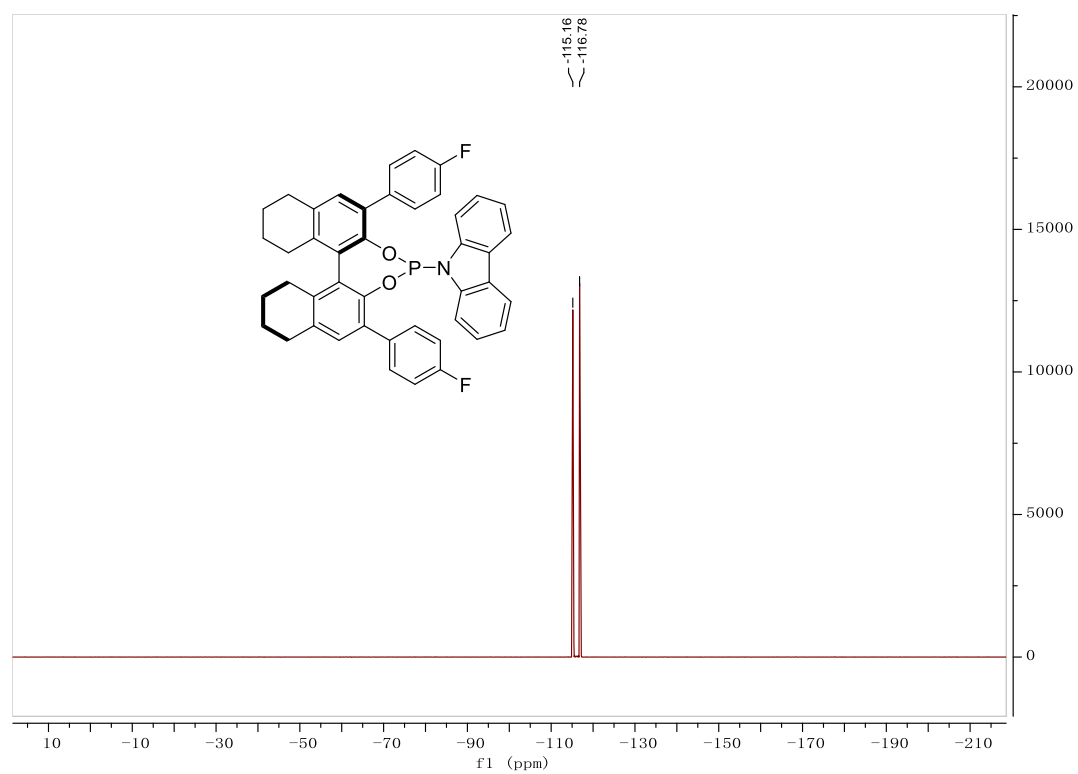


9-(2,6-bis(4-fluorophenyl)-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d':1',2'-f][1,3,2]dioxaphosphin-4-yl)-9H-carbazole (L2)

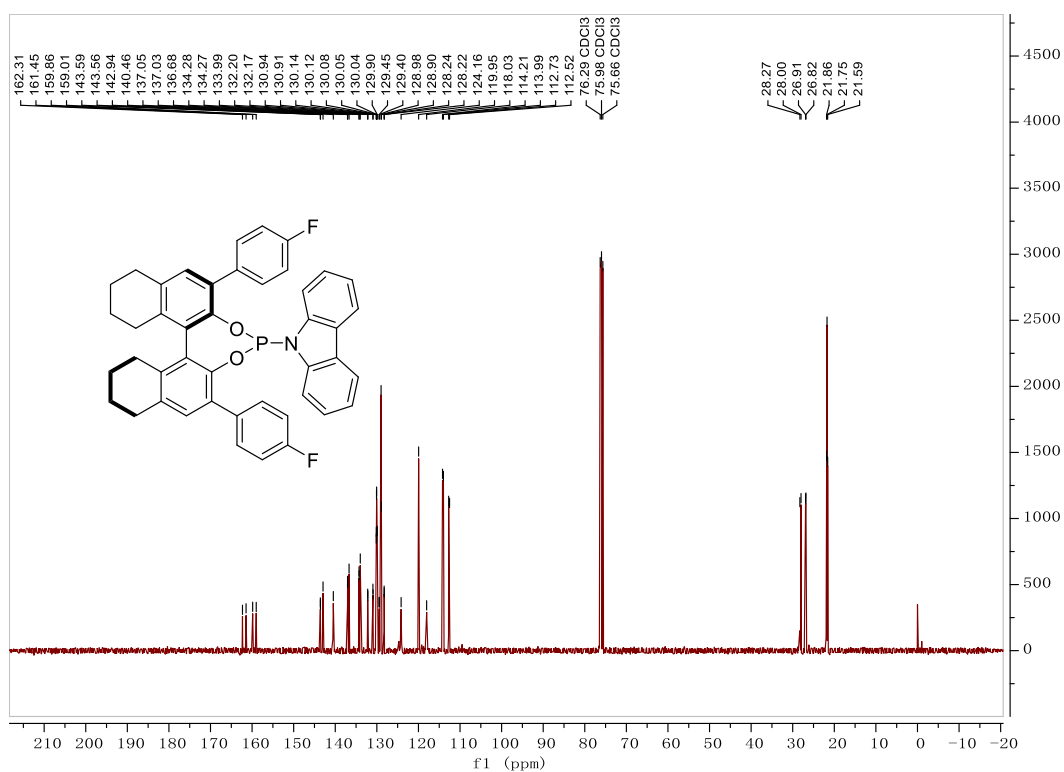
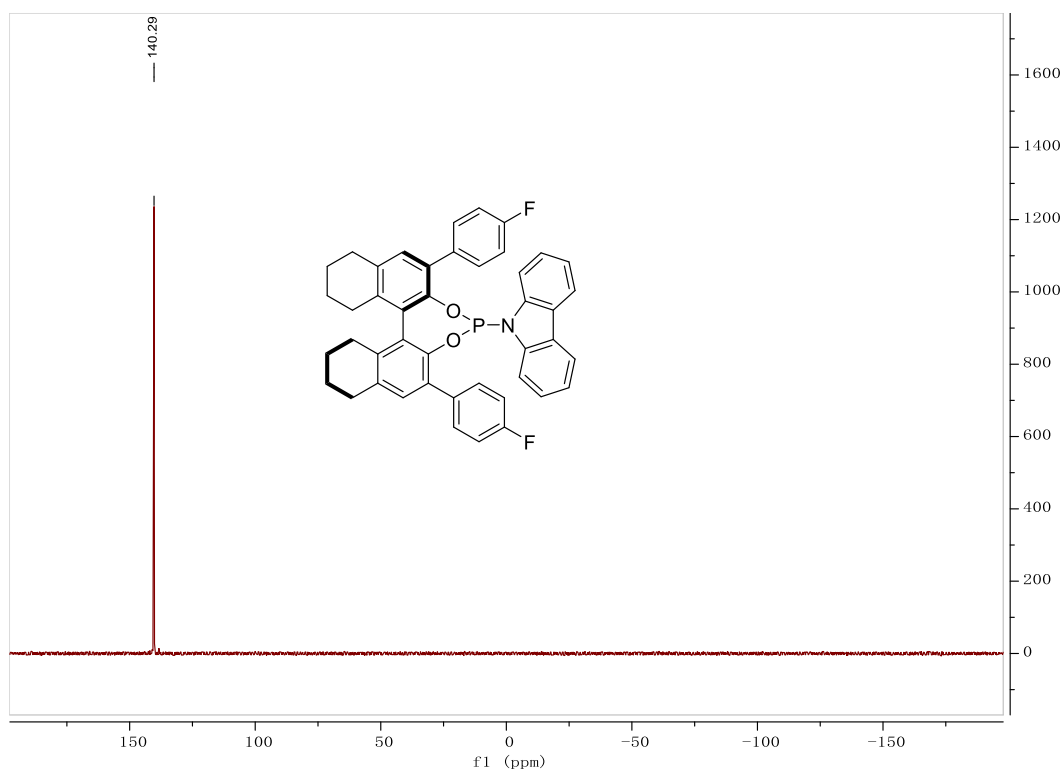
^1H NMR, CDCl₃, 400 MHz



¹H NMR, CDCl₃, 376 MHz

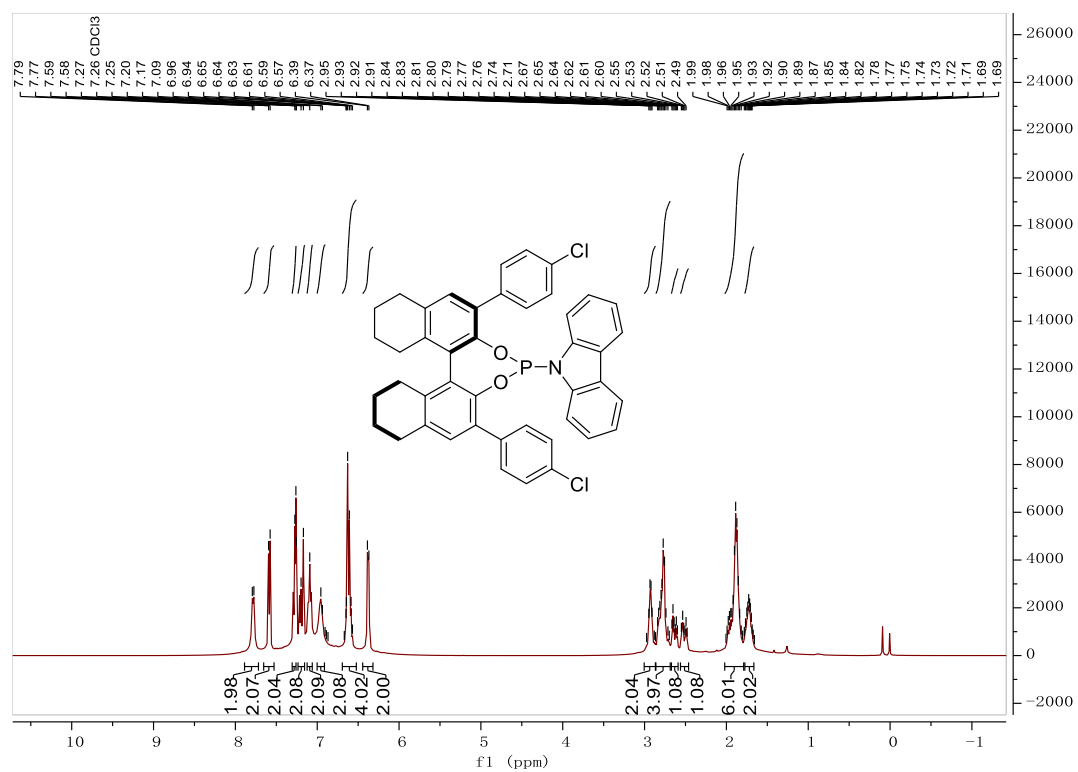


³¹P NMR, CDCl₃, 202 MHz

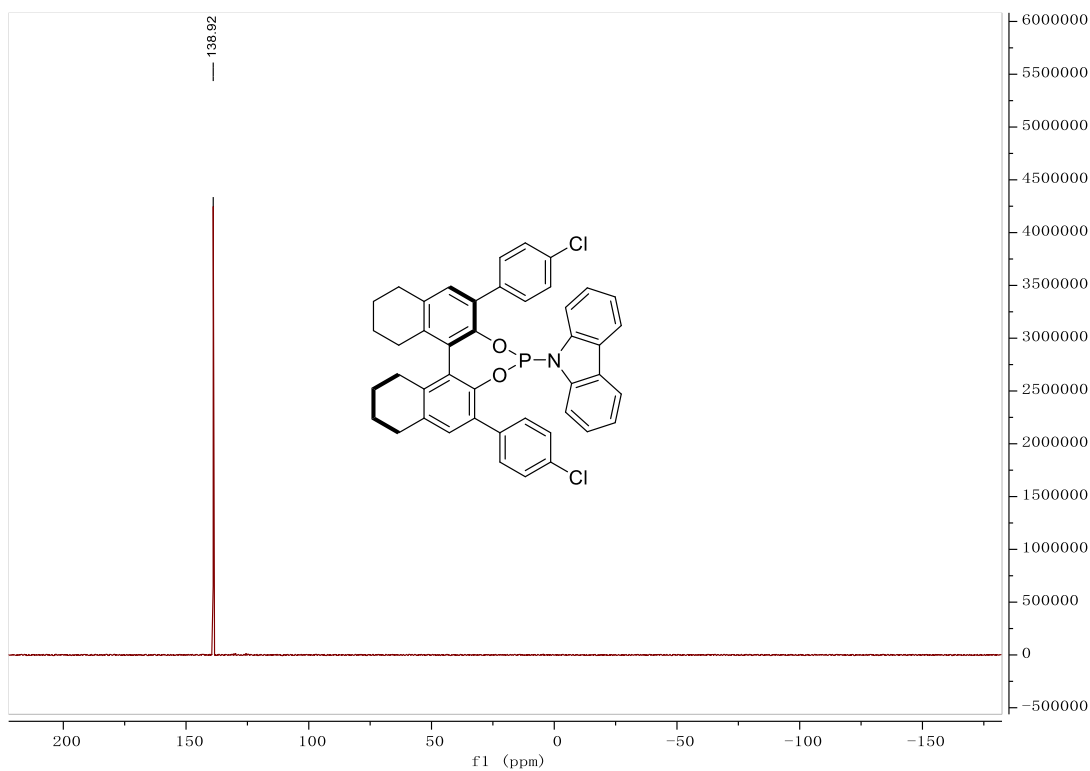


9-(2,6-bis(4-chlorophenyl)-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d':1',2'-f][1,3,2]dioxaphosphin-4-yl)-9H-carbazole (L3)

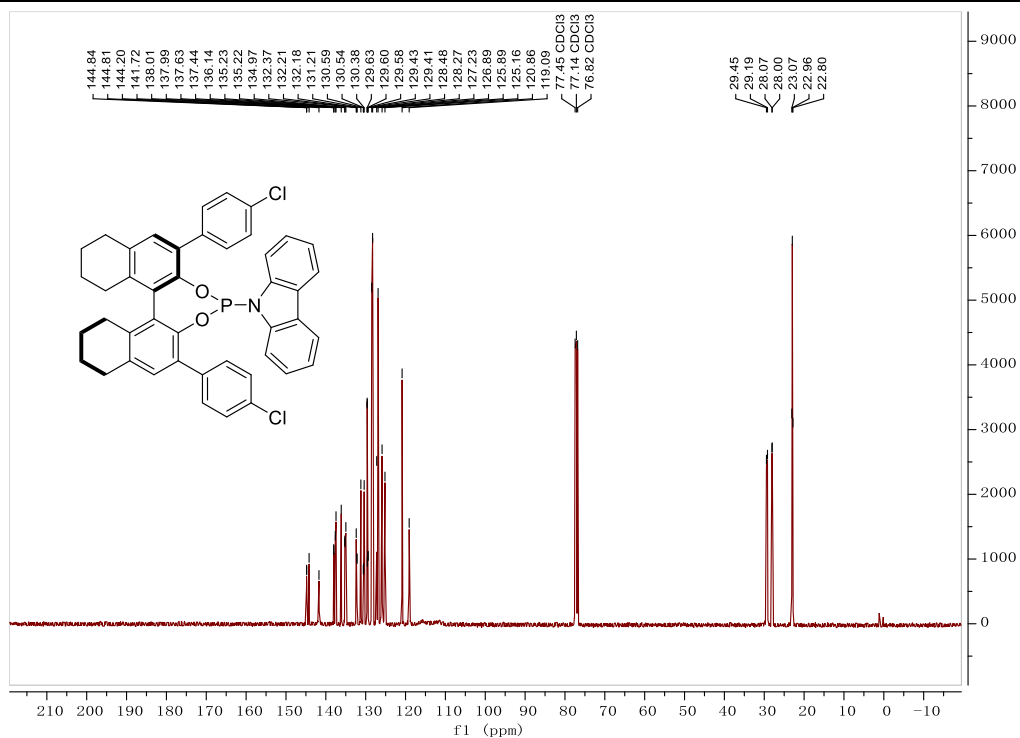
¹H NMR, CDCl₃, 400 MHz



³¹P NMR, CDCl₃, 202 MHz

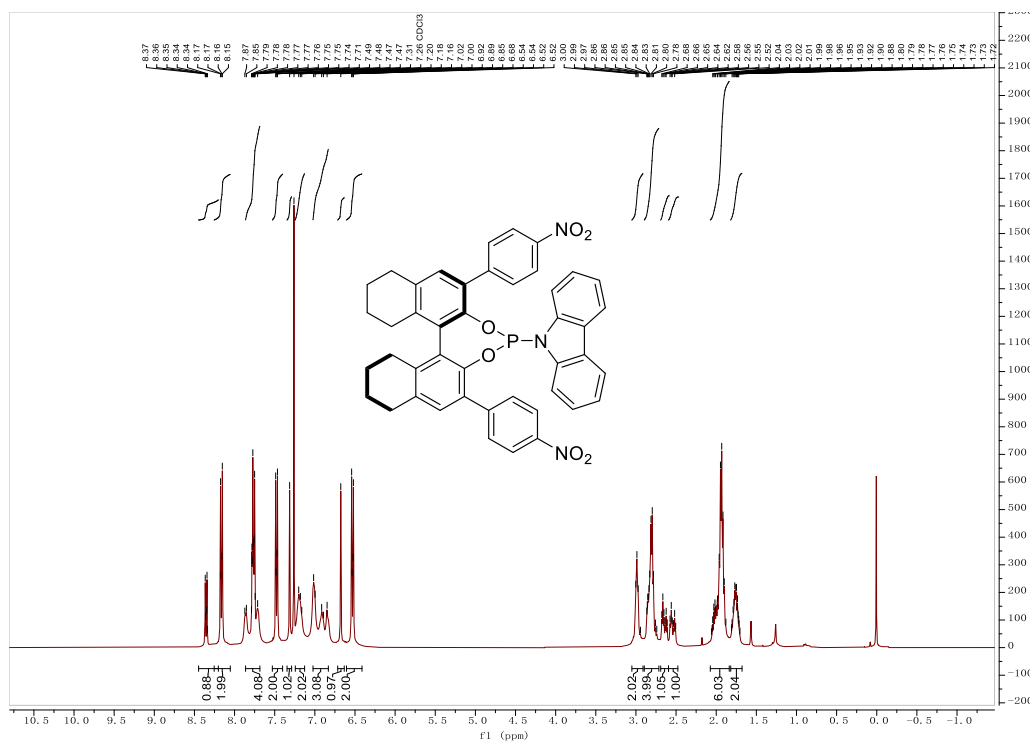


¹³C NMR, CDCl₃, 101 MHz

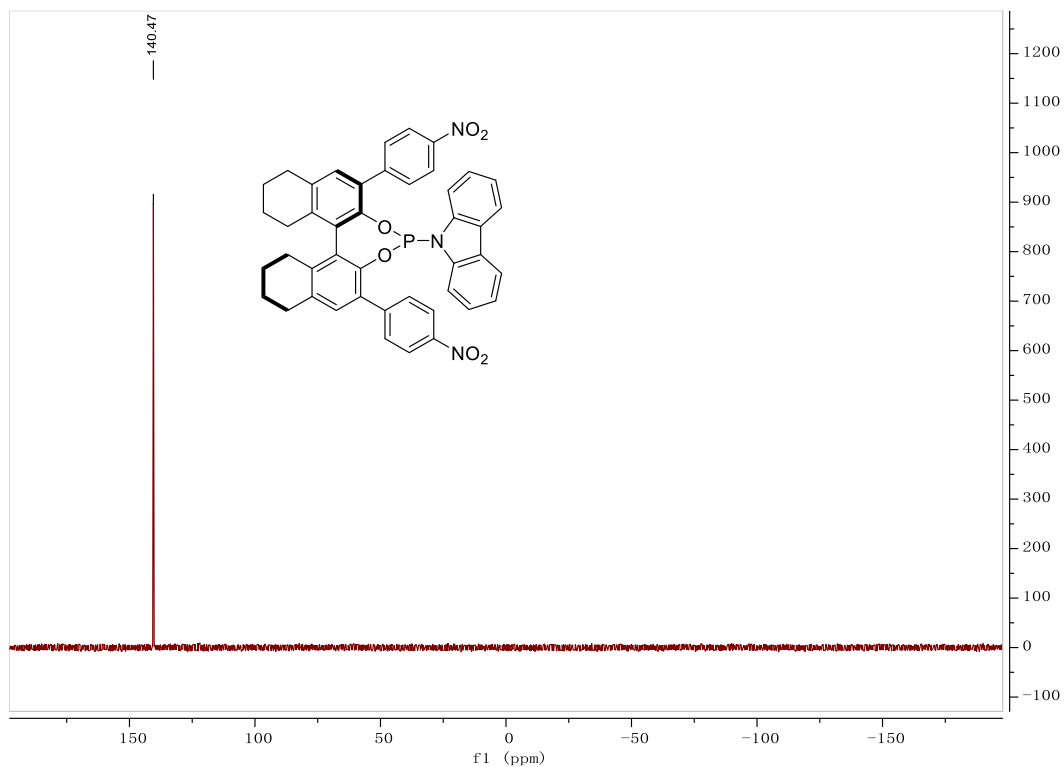


9-(2,6-bis(4-nitrophenyl)-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)-9H-carbazole (L4)

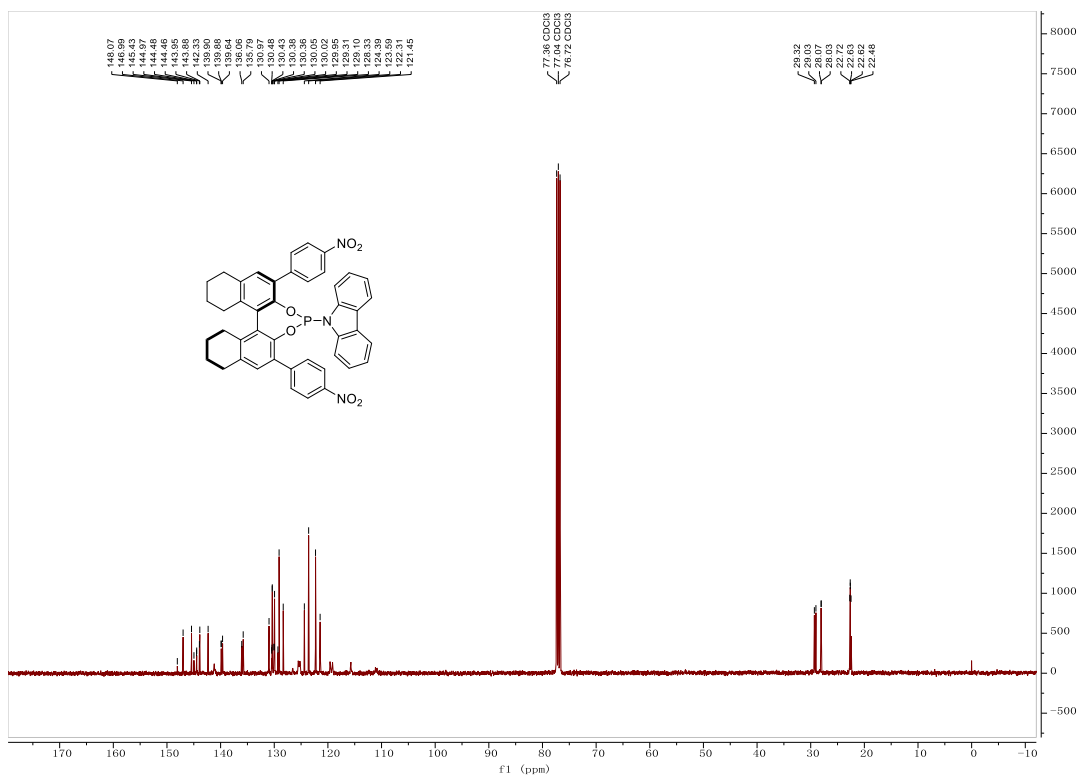
¹H NMR, CDCl₃, 400 MHz



³¹P NMR, CDCl₃, 202 MHz

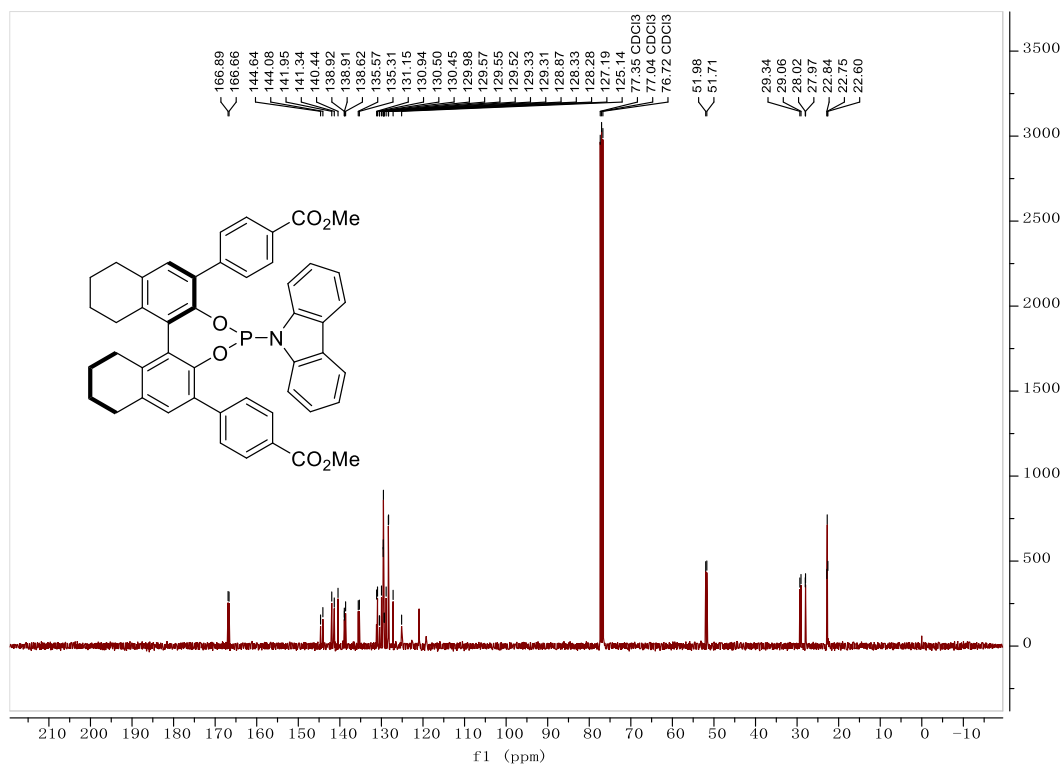


^{13}C NMR, CDCl_3 , 101 MHz

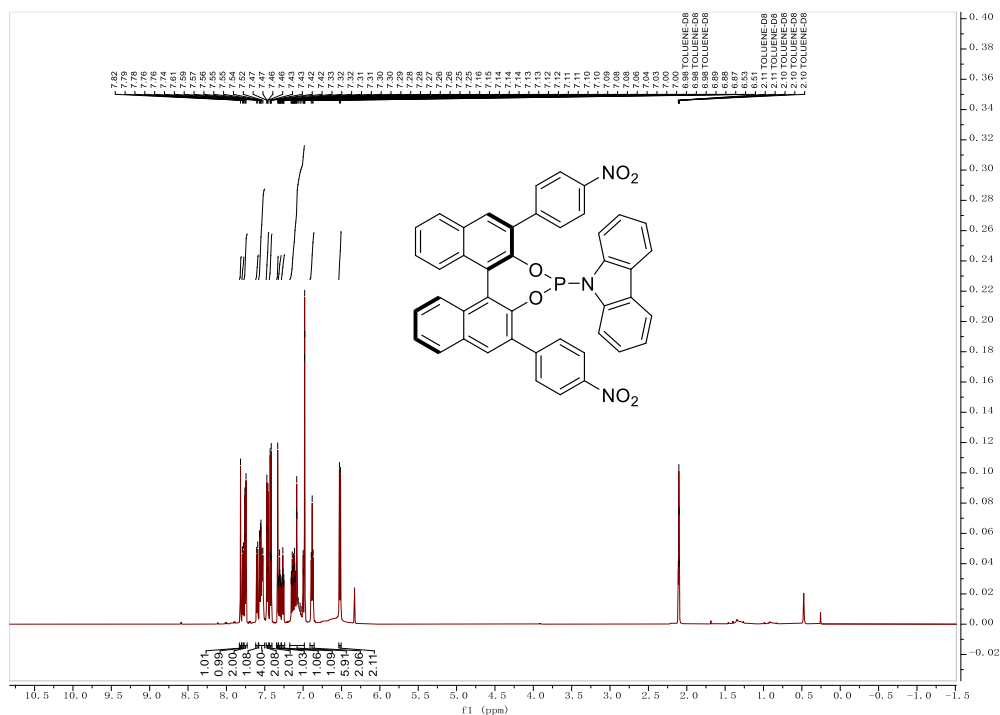


dimethyl 4,4'-(4-(9H-carbazol-9-yl)-8,9,10,11,12,13,14,15-octahydrodinaphtho[2,1-d':1',2'-f][1,3,2]dioxaphosphine-2,6-diyl)dibenzoate (L5)

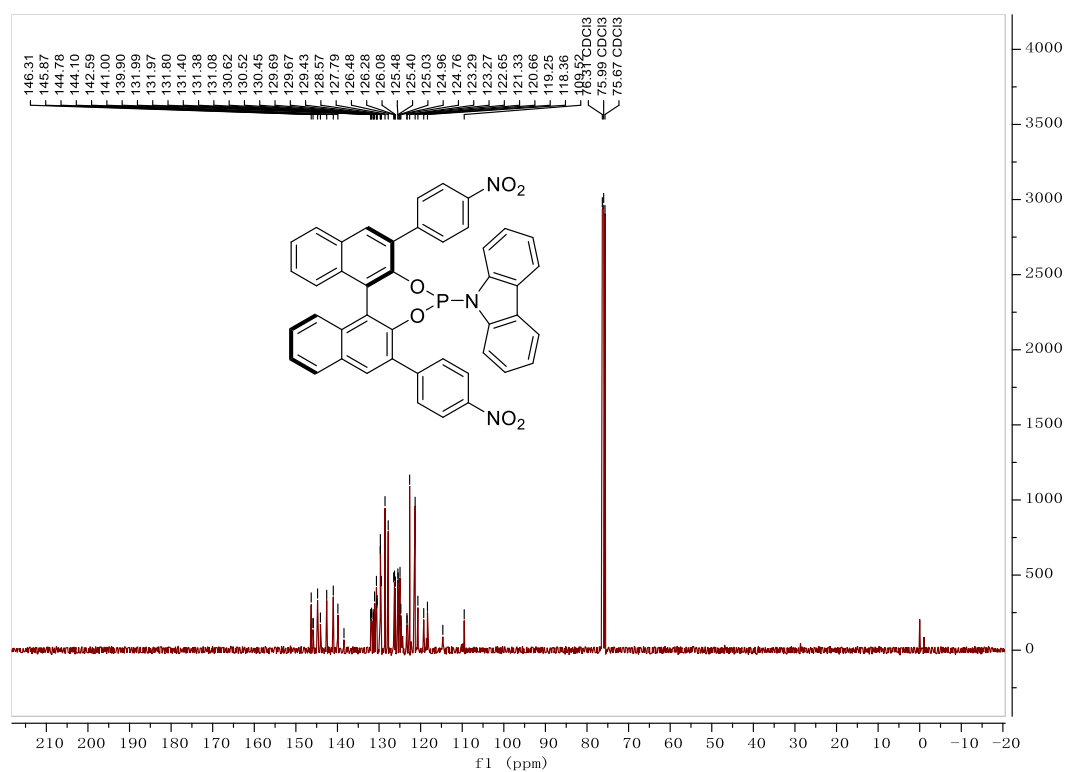
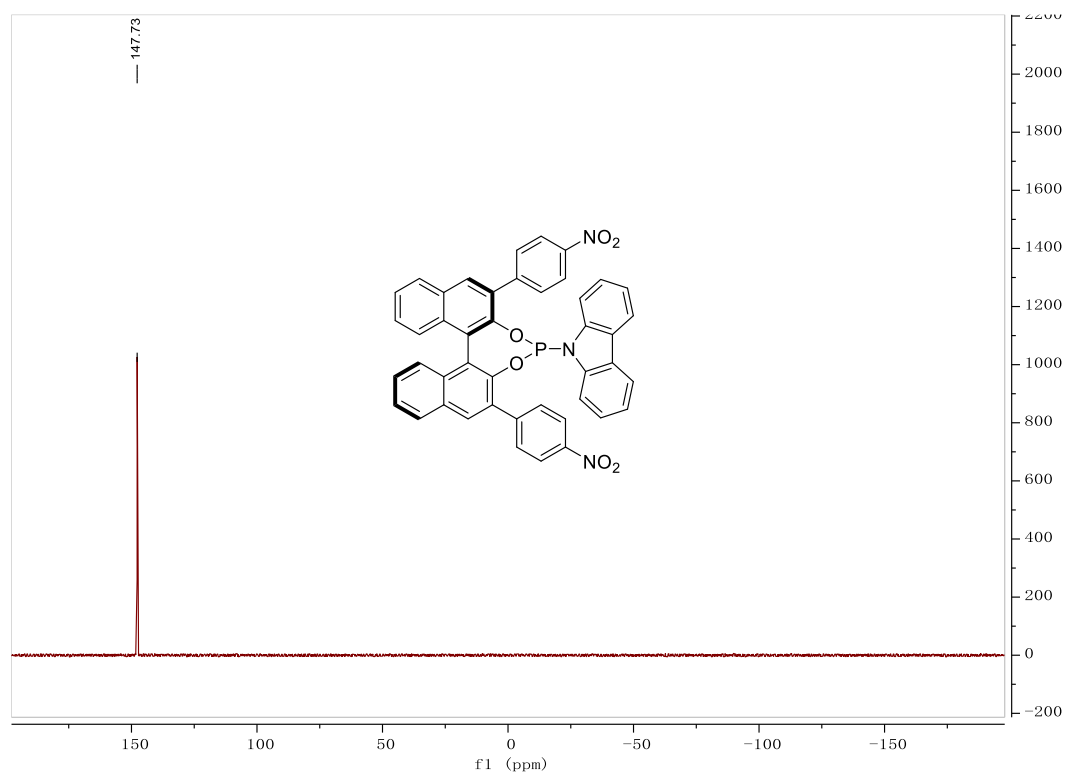
^1H NMR, CDCl_3 , 400 MHz



9-(2,6-bis(4-nitrophenyl)dinaphtho[2,1-d':1',2'-f][1,3,2]dioxaphosphepin-4-yl)-9H-carbazole (L6)
¹H NMR, CDCl₃, 400 MHz

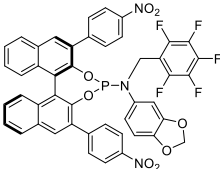


³¹P NMR, CDCl₃, 202 MHz

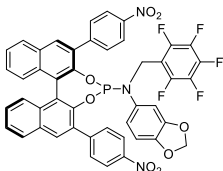


N-(benzo[d][1,3]dioxol-5-yl)-2,6-bis(4-nitrophenyl)-N-((perfluorophenyl)methyl) dinaphtho [2,1-d':1',2'-f][1,3,2]dioxaphosphepin-4-amine (L7)

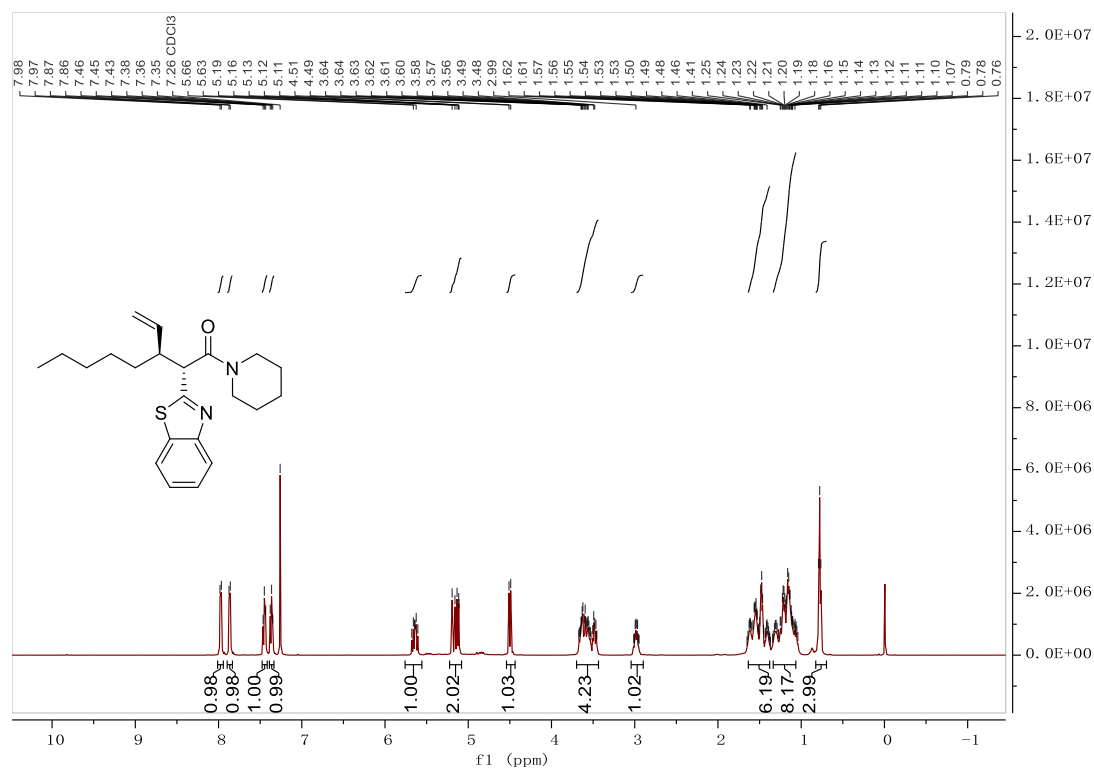
¹H NMR, CDCl₃, 400 MHz



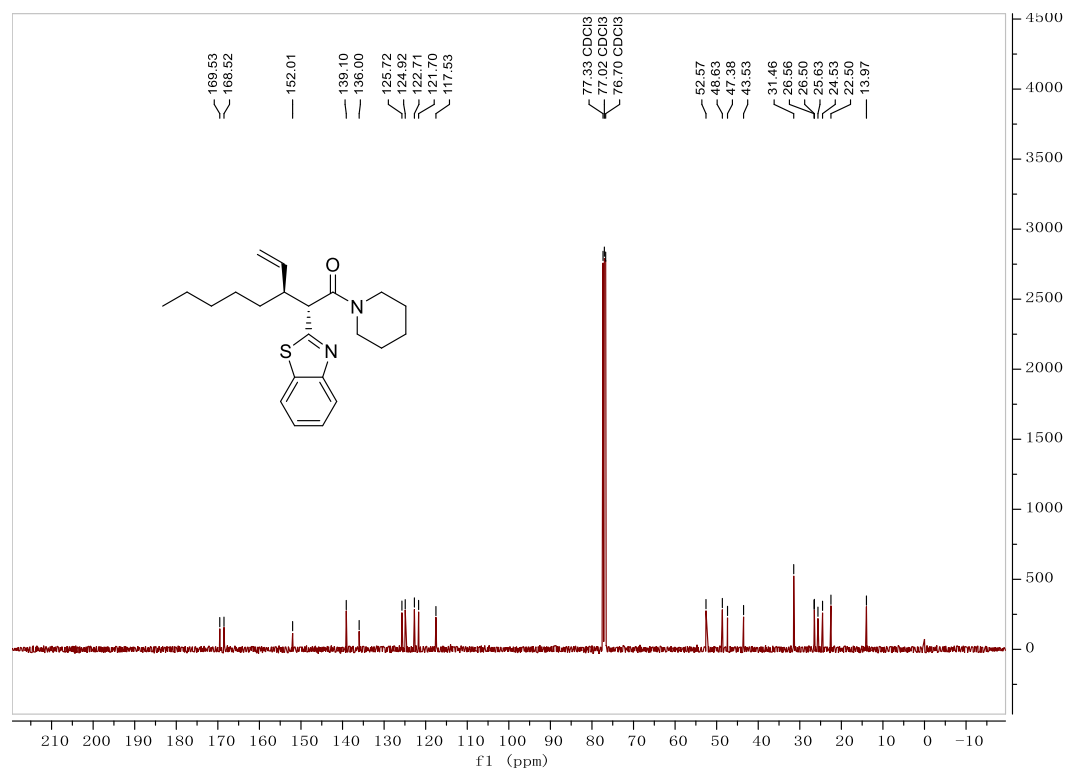
¹⁹F NMR, CDCl₃, 376 MHz

³¹P NMR, CDCl₃, 202 MHz

¹H NMR, CDCl₃, 400 MHz

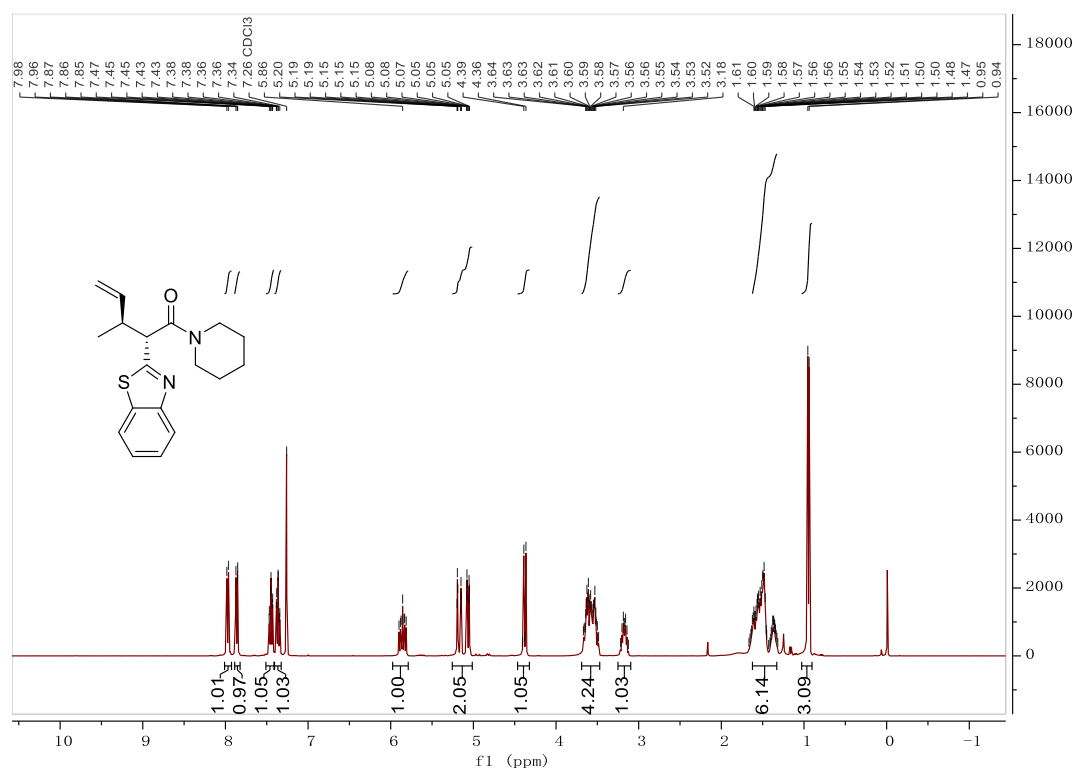


¹³C NMR, CDCl₃, 101 MHz

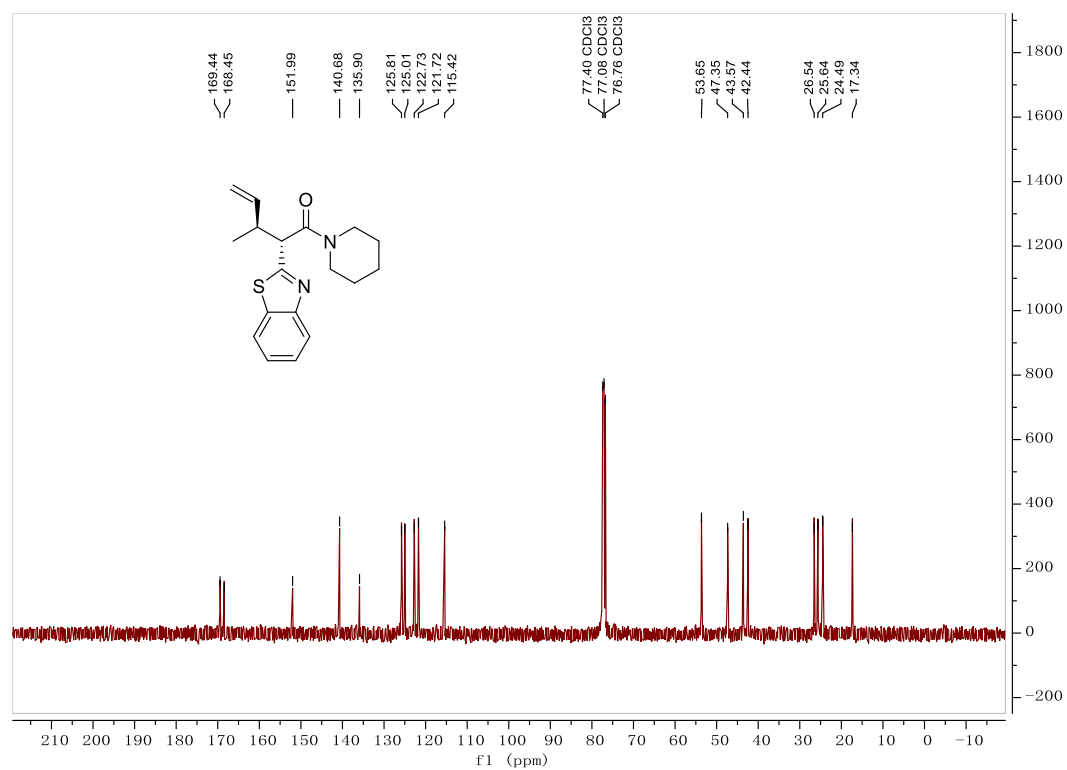


(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-methyl-1-(piperidin-1-yl)pent-4-en-1-one (9)

¹H NMR, CDCl₃, 400 MHz

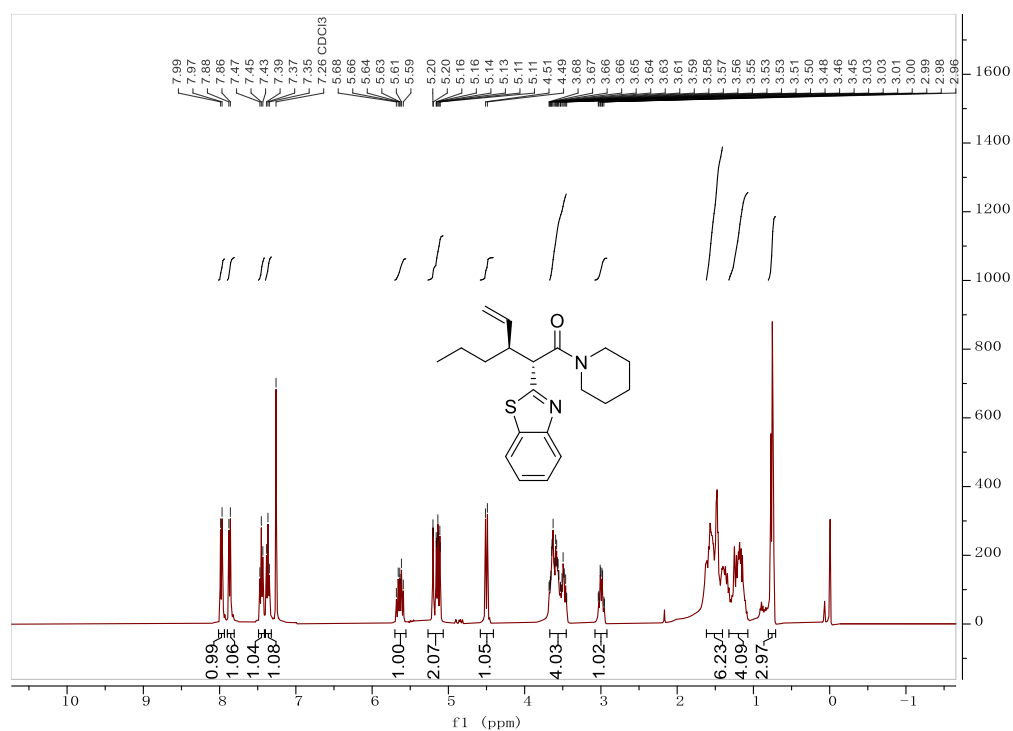


¹³C NMR, CDCl₃, 101 MHz

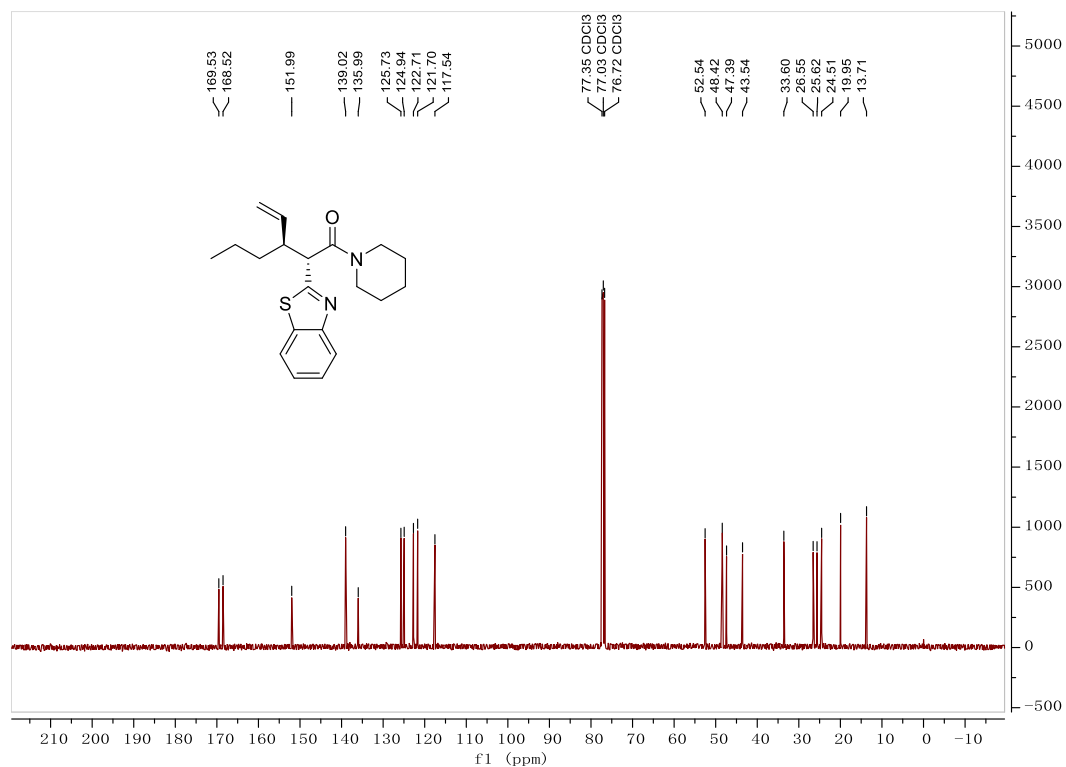


(2R,3S)-2-(benzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-3-vinylhexan-1-one (10)

¹H NMR, CDCl₃, 400 MHz

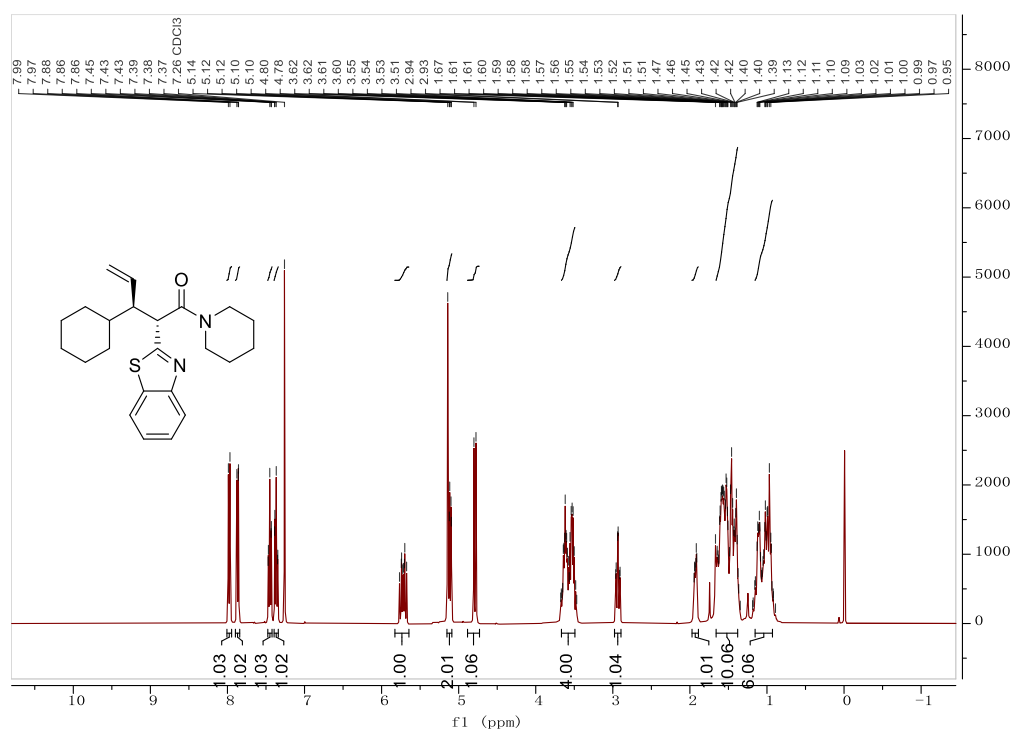


¹³C NMR, CDCl₃, 101 MHz

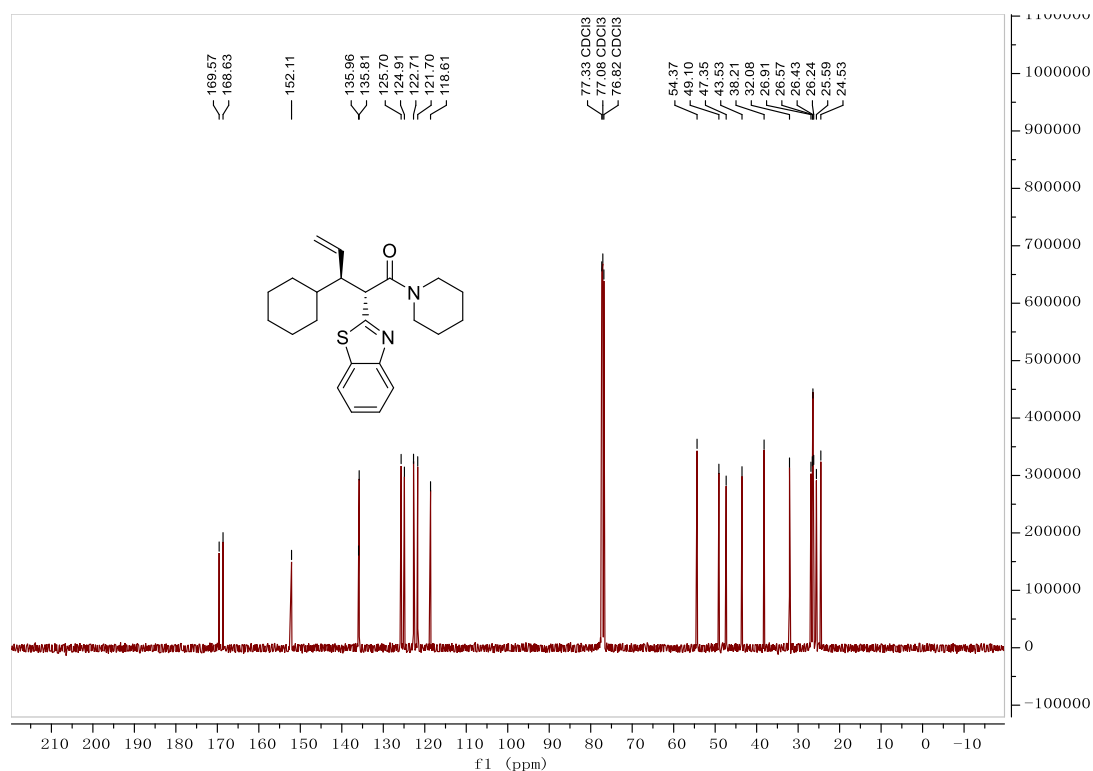


(2R,3R)-2-(benzo[d]thiazol-2-yl)-3-cyclohexyl-1-(piperidin-1-yl)pent-4-en-1-one (11)

¹H NMR, CDCl₃, 400 MHz

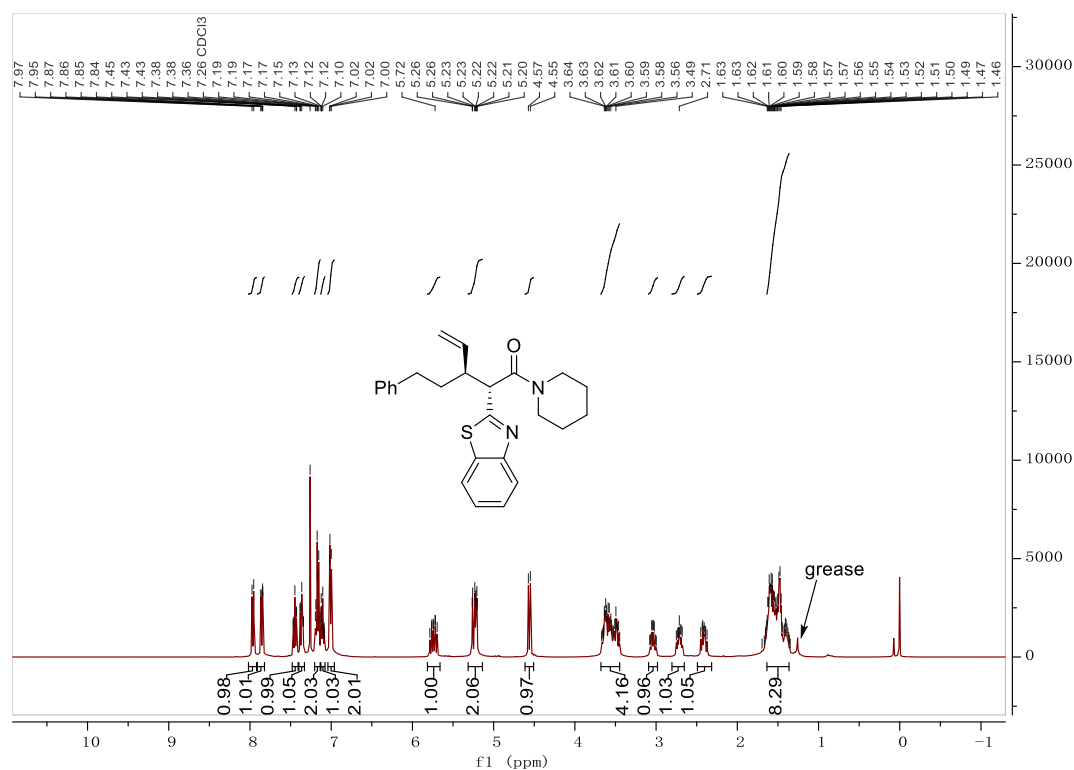


¹³C NMR, CDCl₃, 101 MHz

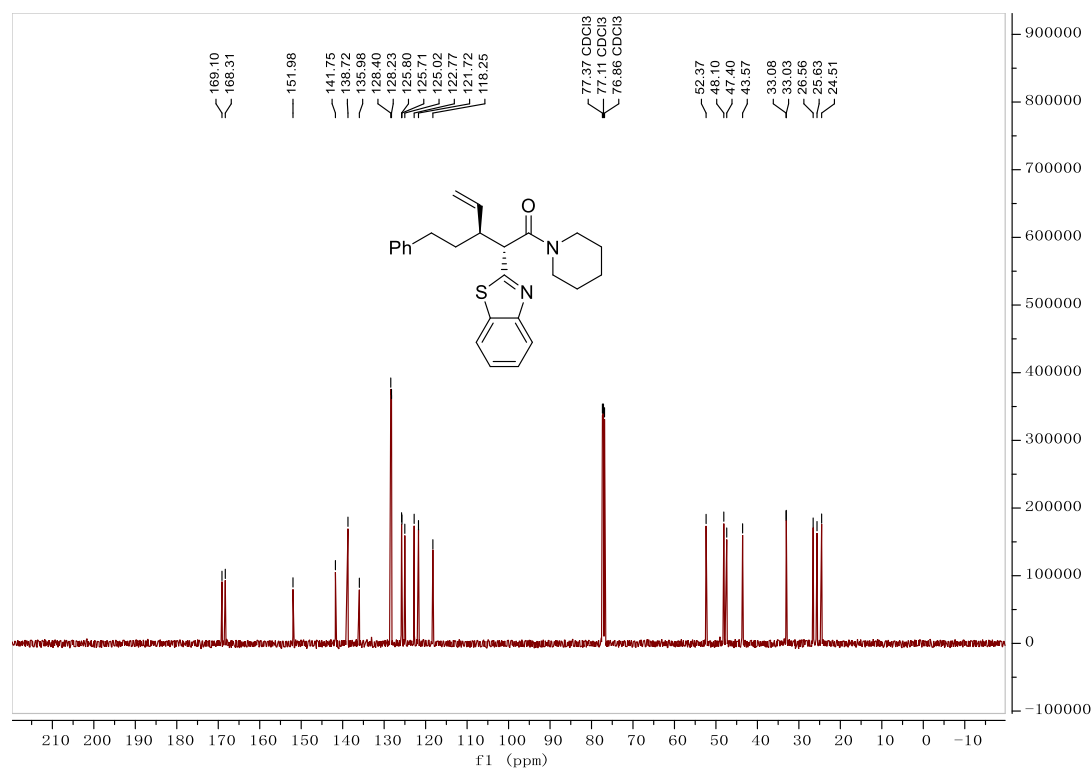


(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-phenethyl-1-(piperidin-1-yl)pent-4-en-1-one (12)

¹H NMR, CDCl₃, 400 MHz

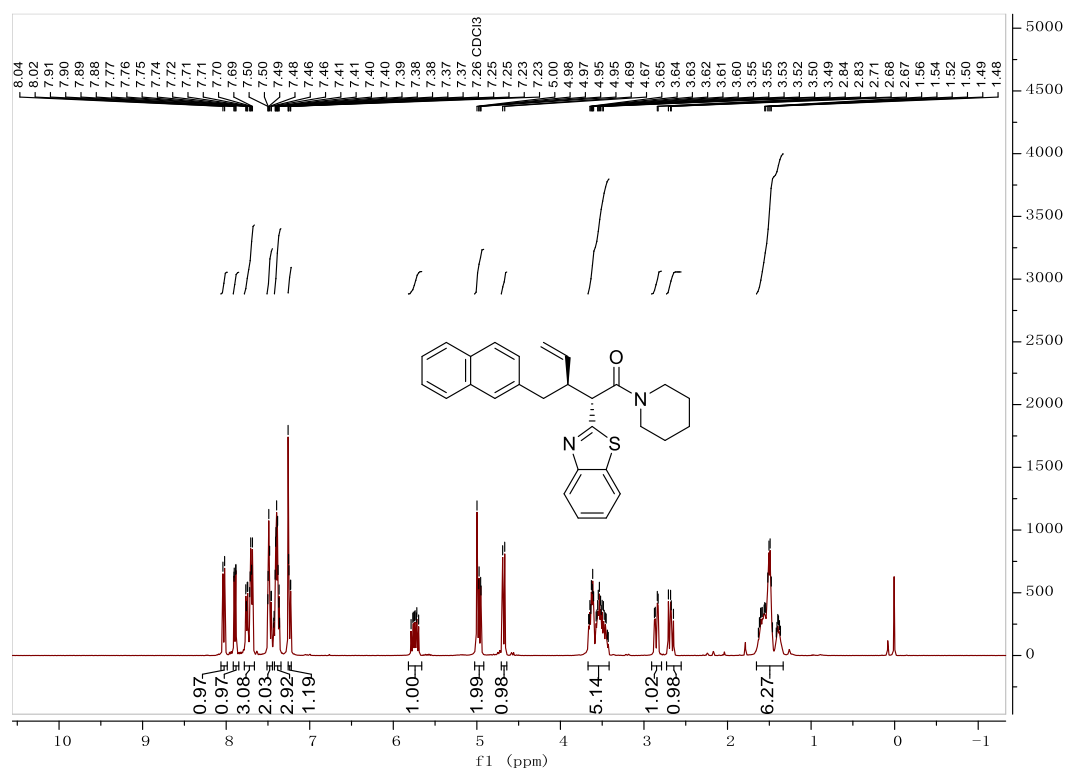


¹³C NMR, CDCl₃, 101 MHz

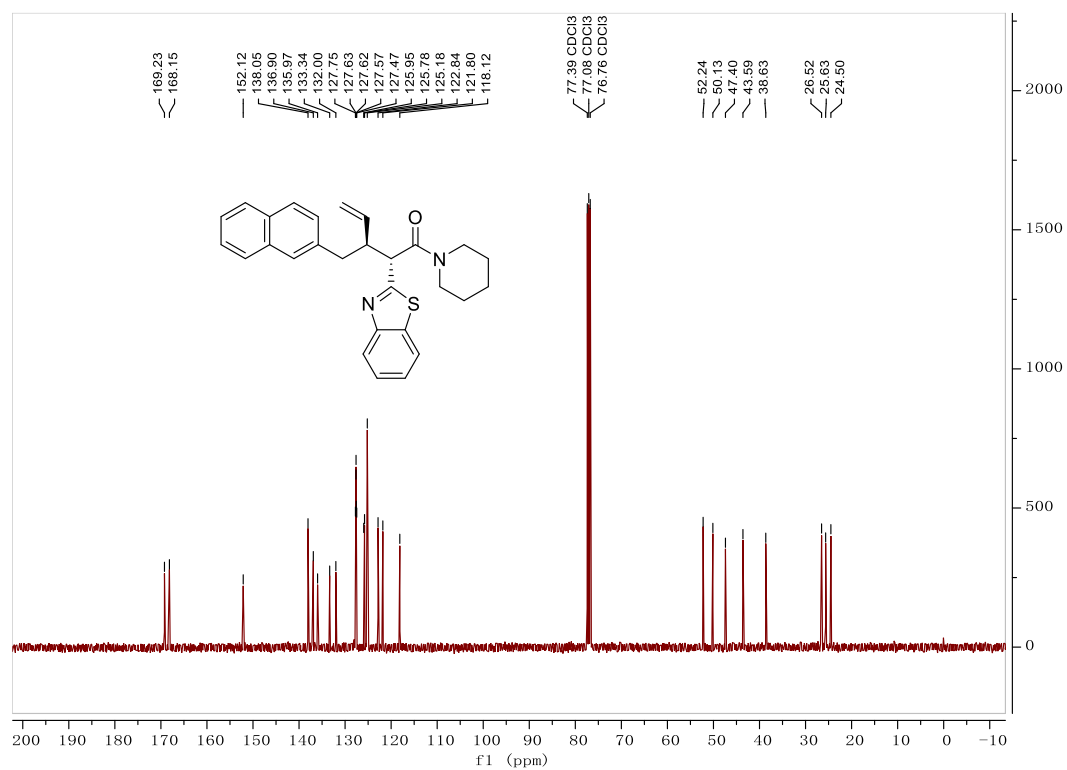


(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-(naphthalen-2-ylmethyl)-1-(piperidin-1-yl)pent-4-en-1-one (13)

¹H NMR, CDCl₃, 400 MHz

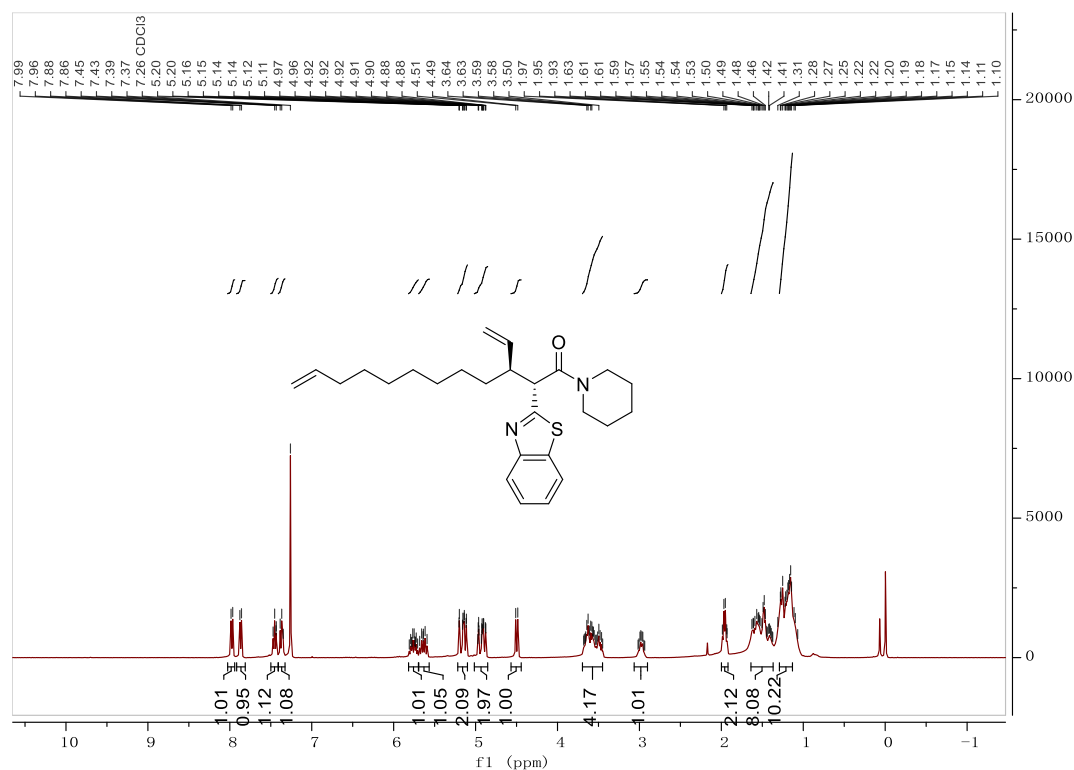


¹³C NMR, CDCl₃, 101 MHz

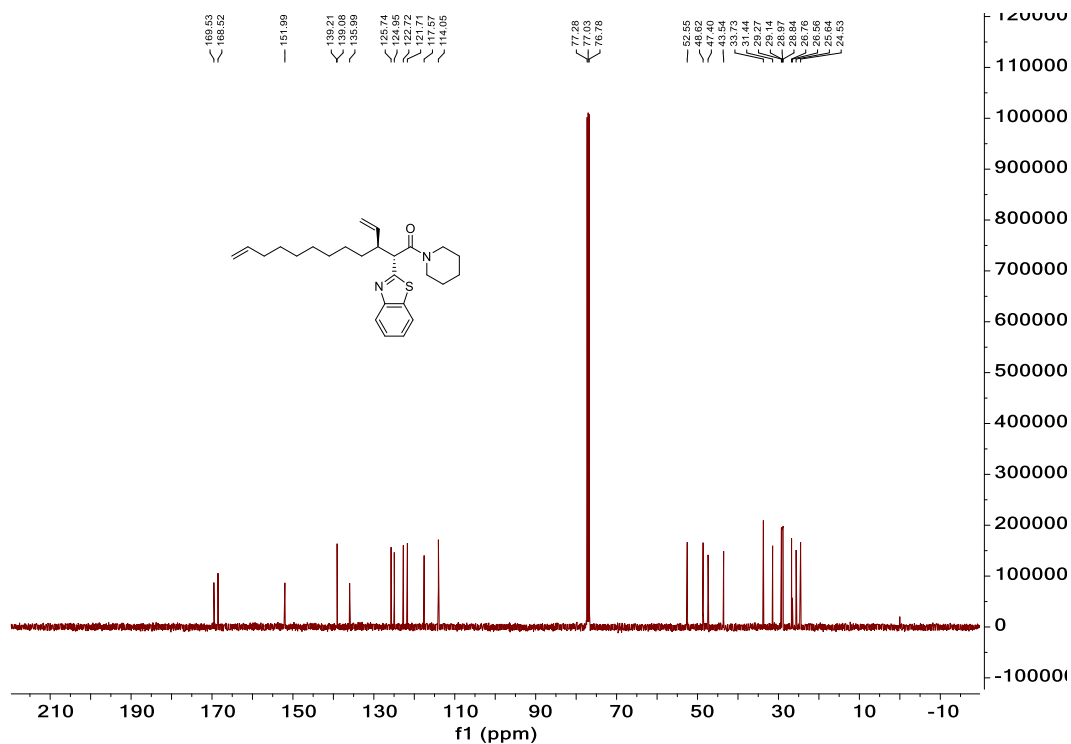


(2R,3S)-2-(benzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-3-vinyldodec-11-en-1-one (14)

¹H NMR, CDCl₃, 400 MHz

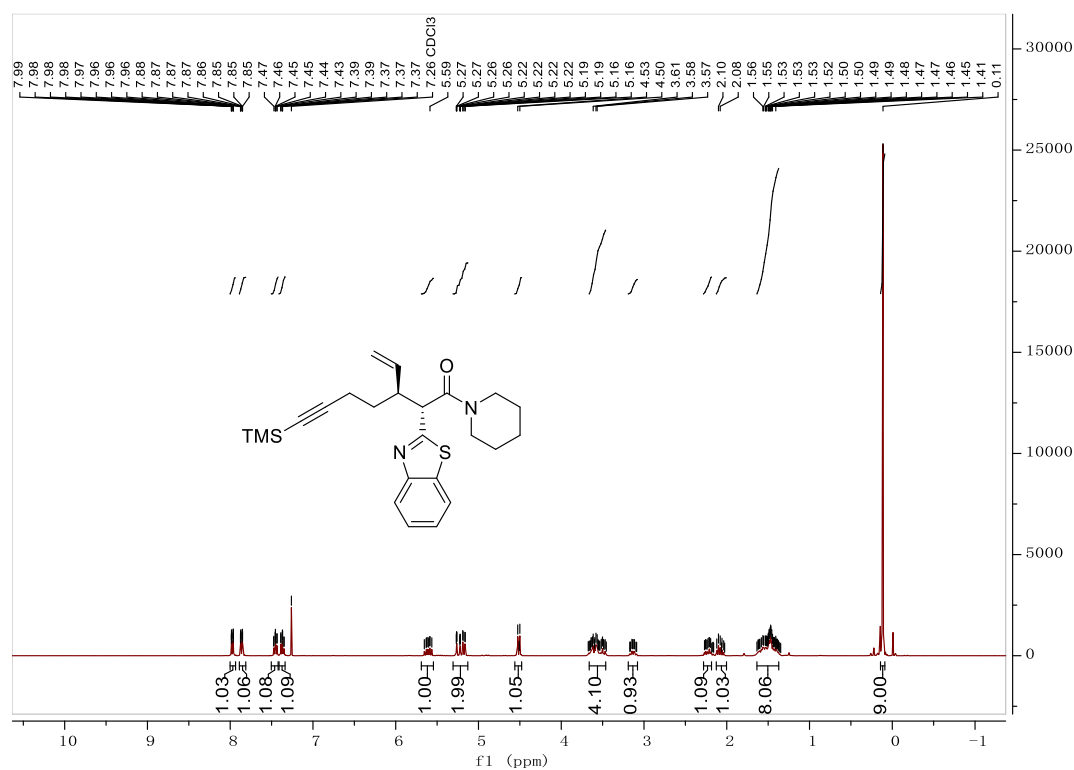


^{13}C NMR, CDCl_3 , 101 MHz

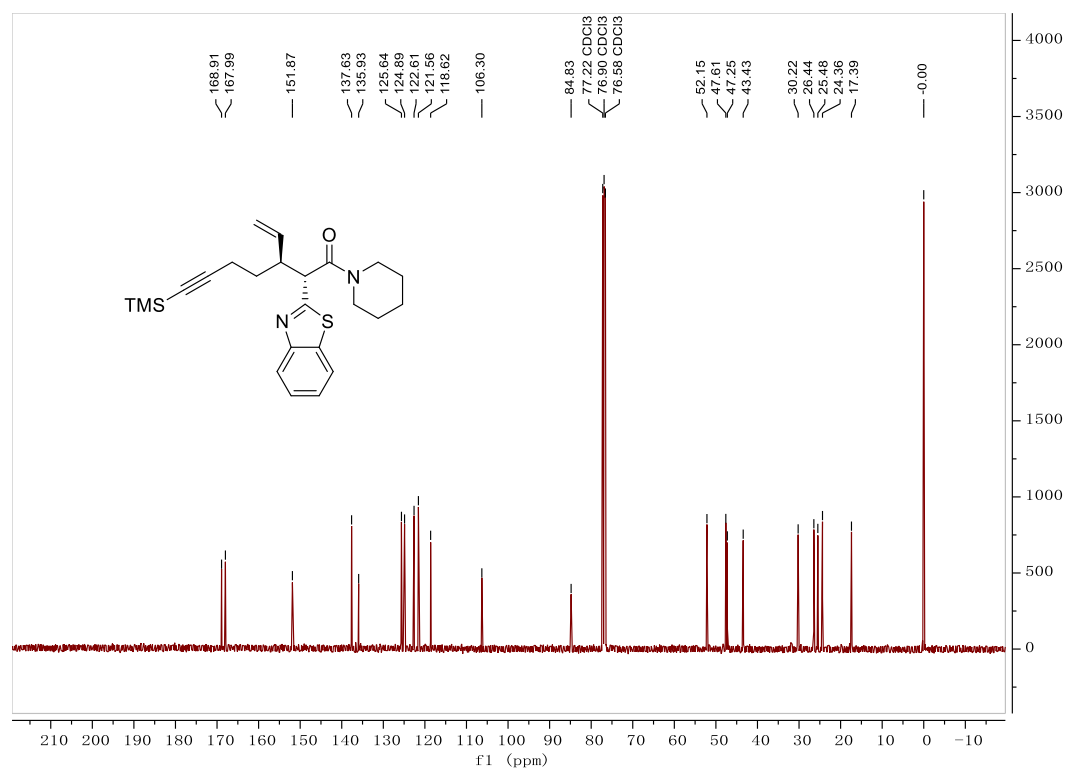


(2R,3S)-2-(benzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-7-(trimethylsilyl)-3-vinylhept-6-yn-1-one (15)

^1H NMR, CDCl_3 , 400 MHz

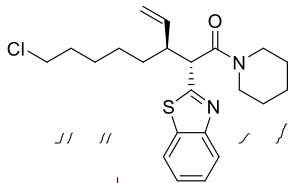


¹³C NMR, CDCl₃, 101 MHz



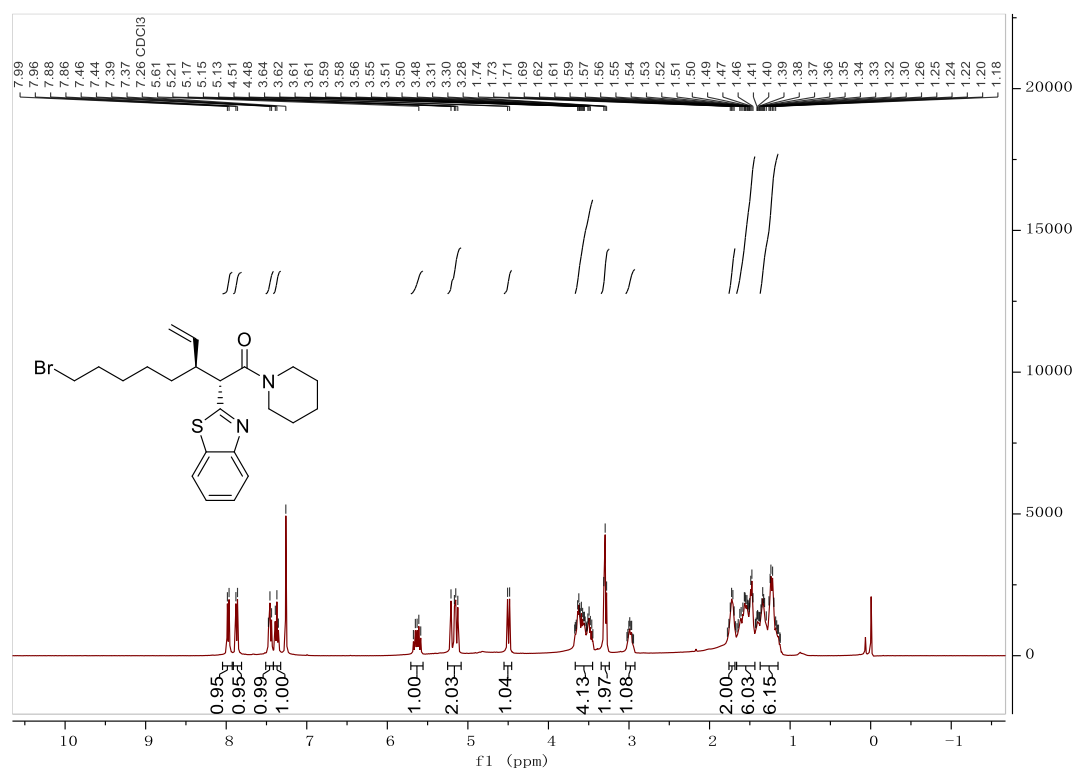
(2R,3S)-2-(benzo[d]thiazol-2-yl)-8-chloro-1-(piperidin-1-yl)-3-vinyloctan-1-one (16)

¹H NMR, CDCl₃, 400 MHz

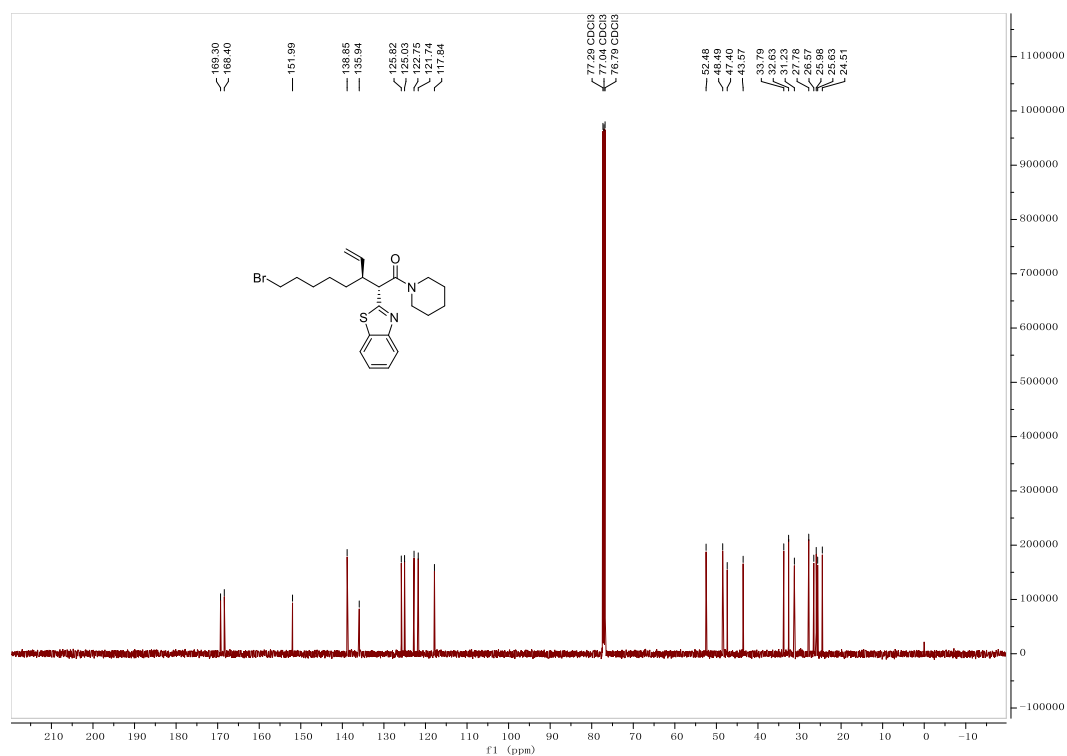


(2R,3S)-2-(benzo[d]thiazol-2-yl)-8-bromo-1-(piperidin-1-yl)-3-vinyloctan-1-one (17)

S108

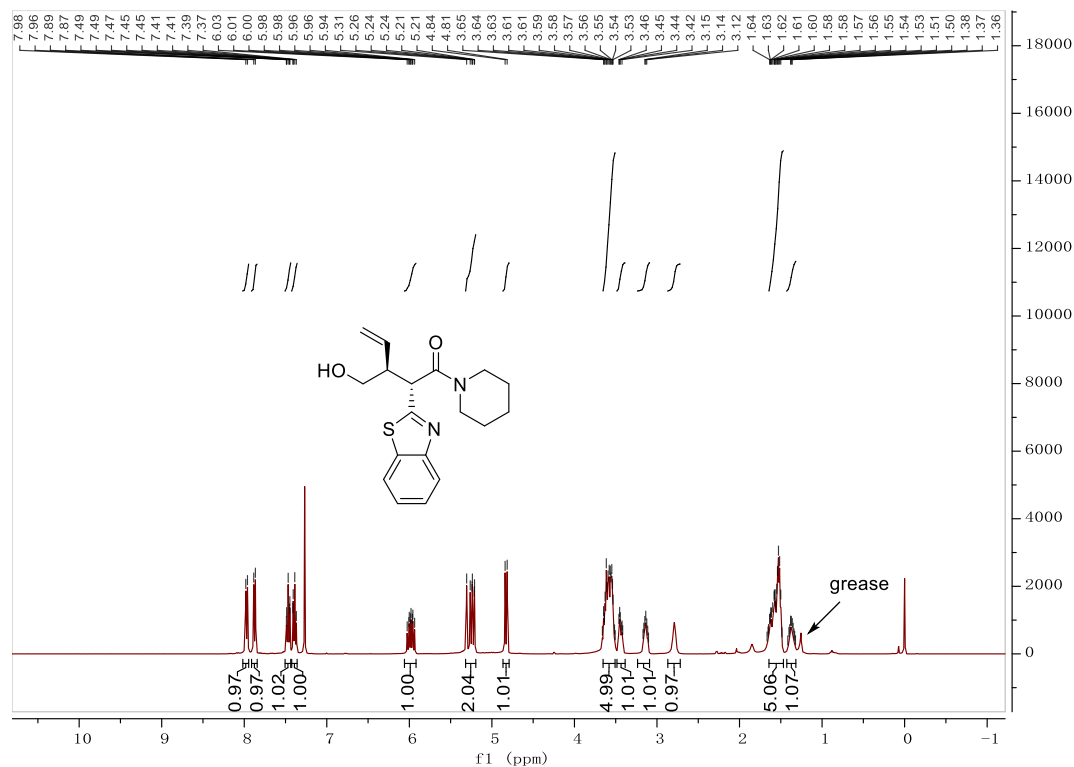


¹³C NMR, CDCl₃, 101 MHz

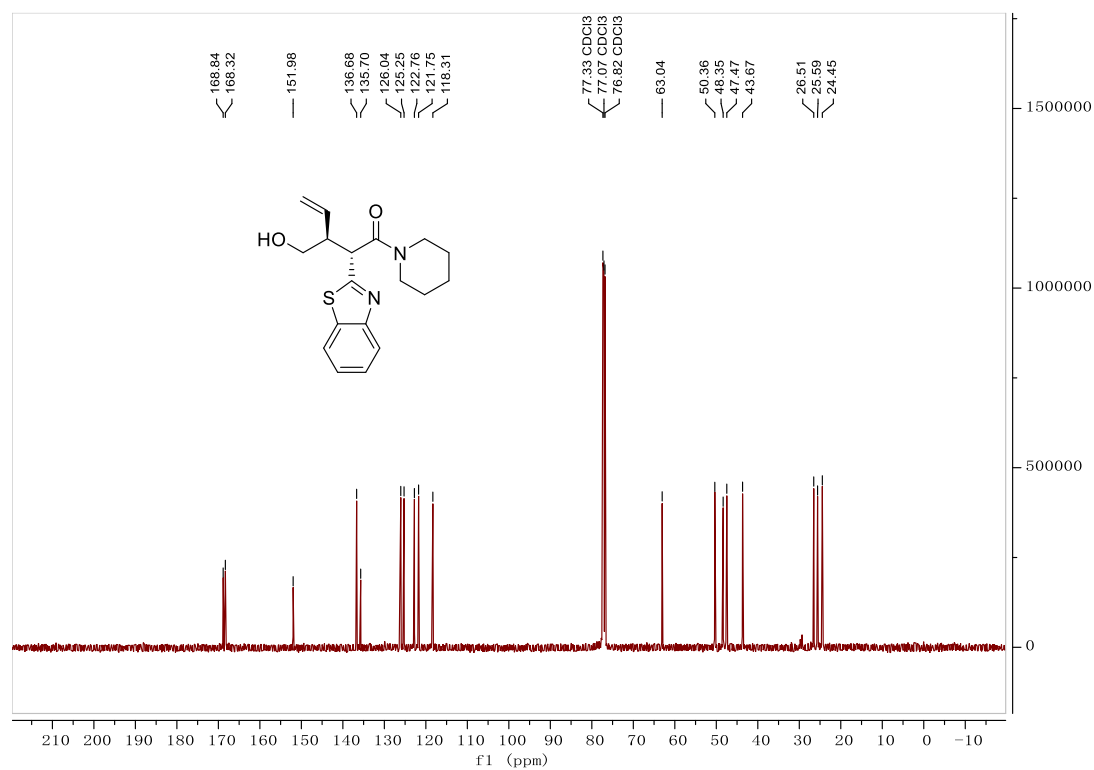


(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-(hydroxymethyl)-1-(piperidin-1-yl)pent-4-en-1-one (18)

¹H NMR, CDCl₃, 400 MHz

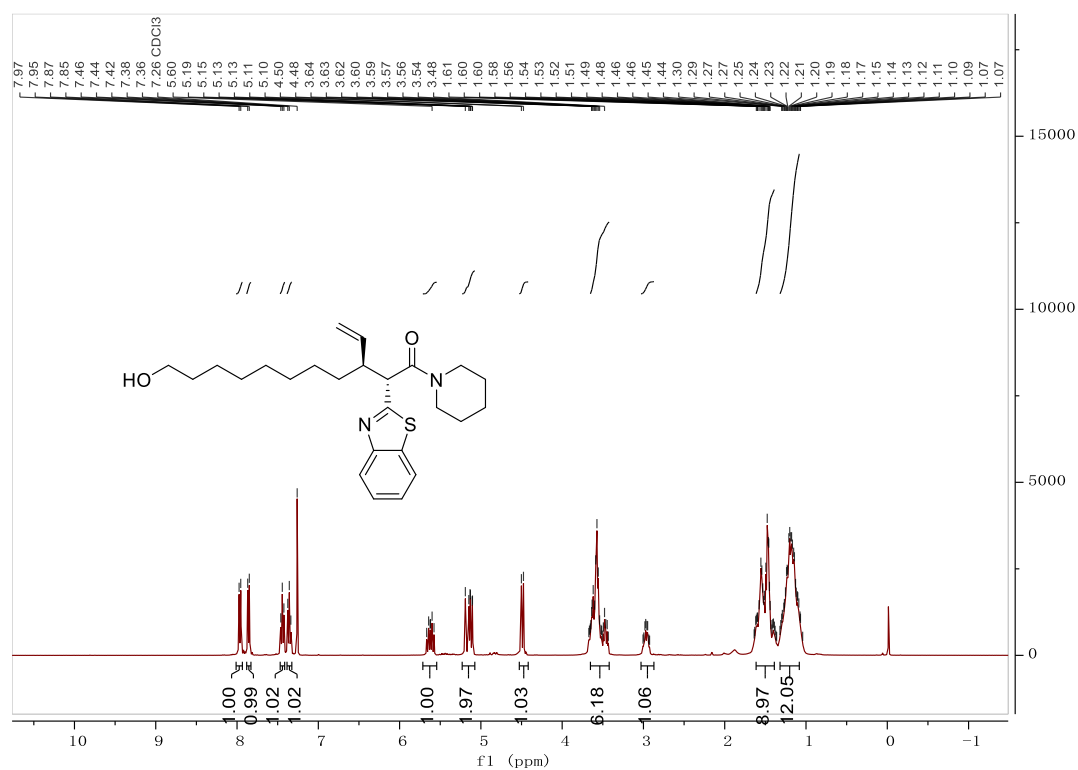


¹³C NMR, CDCl₃, 101 MHz

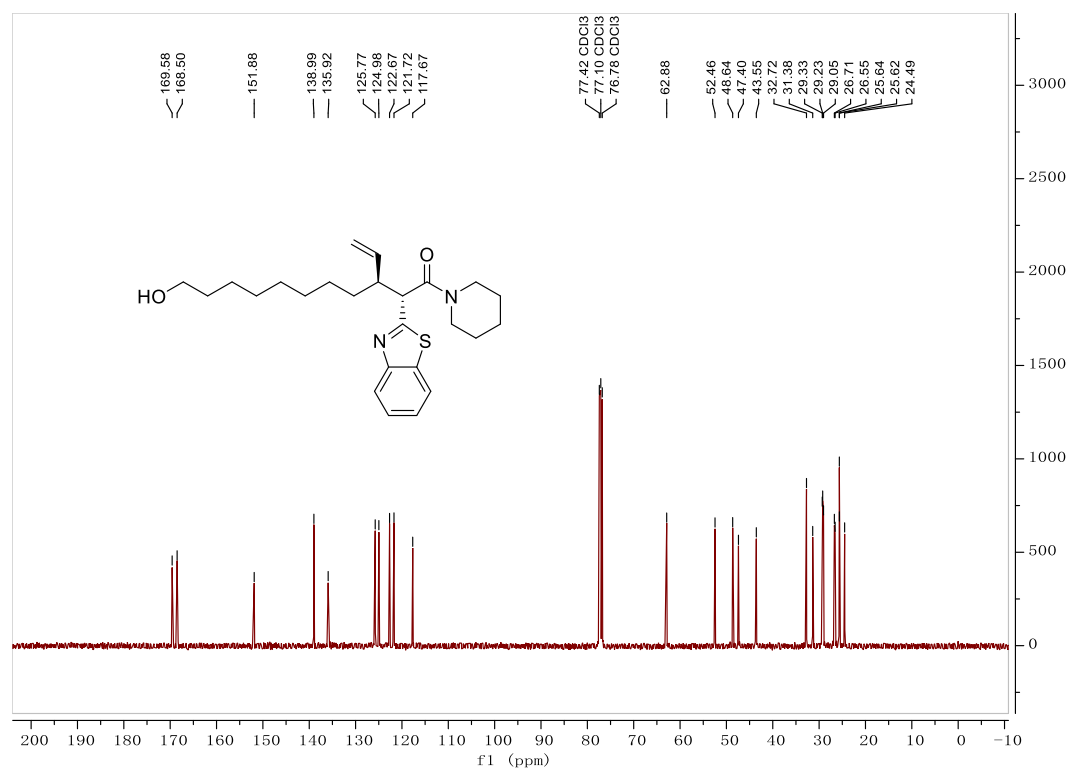


(2R,3S)-2-(benzo[d]thiazol-2-yl)-11-hydroxy-1-(piperidin-1-yl)-3-vinylundecan-1-one (19)

¹H NMR, CDCl₃, 400 MHz

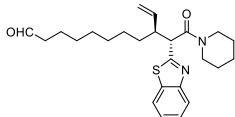


¹³C NMR, CDCl₃, 101 MHz



(S)-9-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)undec-10-enal (20)

¹H NMR, CDCl₃, 400 MHz

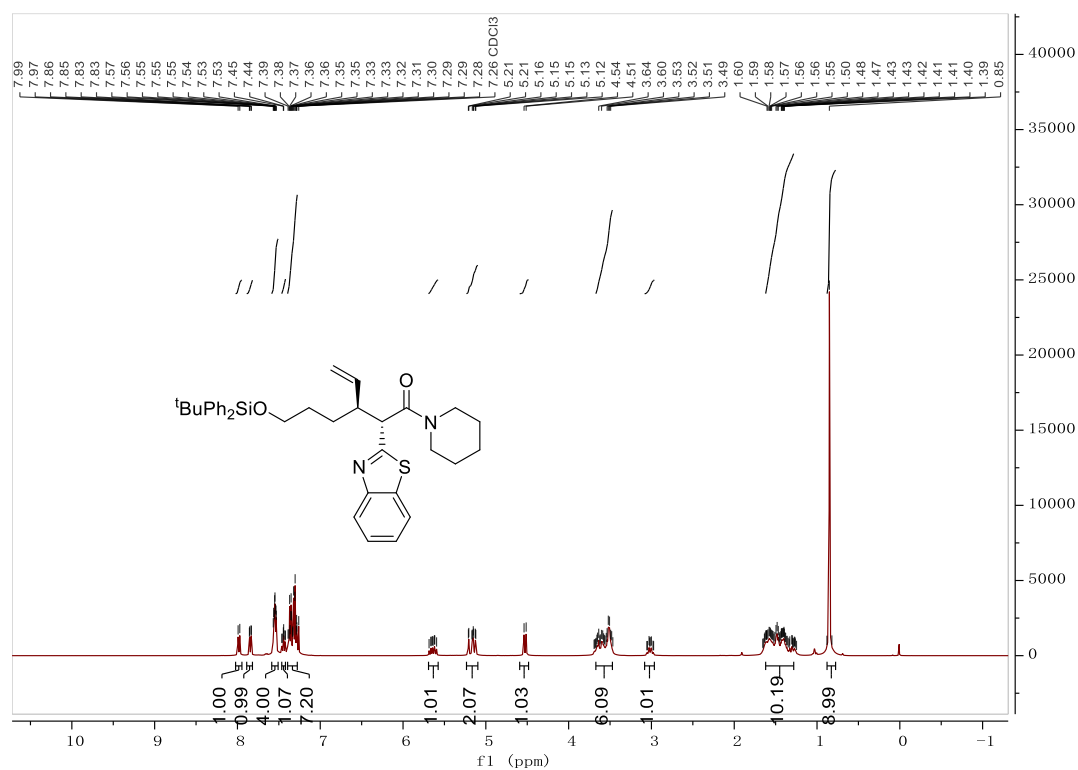


Chemical structure of compound 10 is shown above the spectrum. The structure is a 2-(2-((2-methyl-6-oxohept-5-en-2-ylideneamino)pyridin-3-ylthio)pyridine)pyridine.

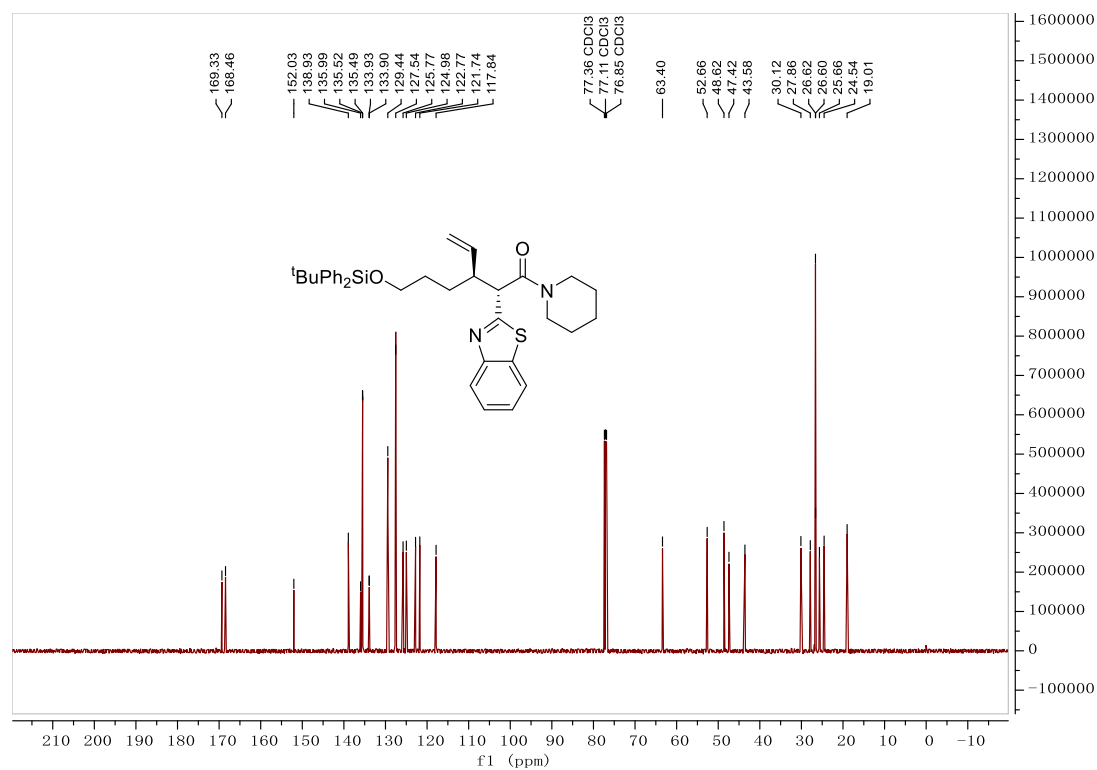
¹³C NMR spectrum (CDCl₃) showing peaks (ppm):

- 202.94
- 169.49, 168.47
- 151.97
- 139.01, 135.96
- 125.77, 124.98, 122.72, 121.72, 117.66
- 77.38, 77.06, 76.75 (CDCl₃)
- 52.51, 48.60, 47.40, 43.82, 43.54, 31.35, 29.09, 28.96, 28.92, 26.65, 26.56, 25.64, 24.52, 21.98

¹H NMR, CDCl₃, 400 MHz

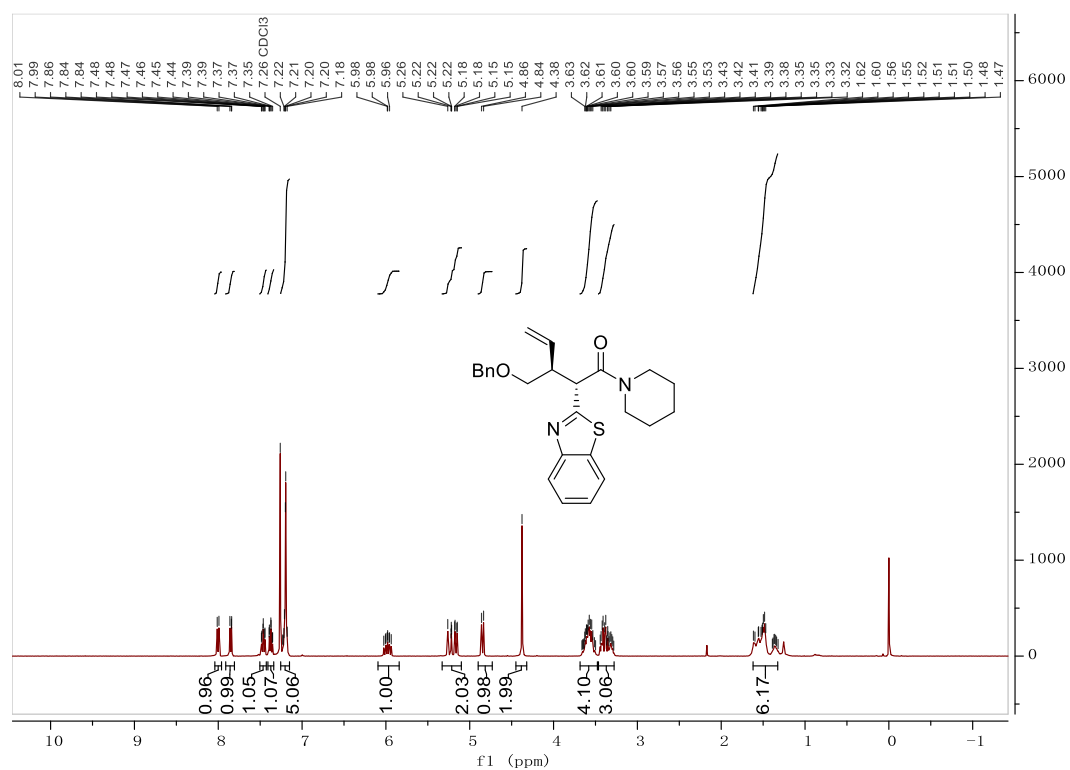


¹³C NMR, CDCl₃, 101 MHz

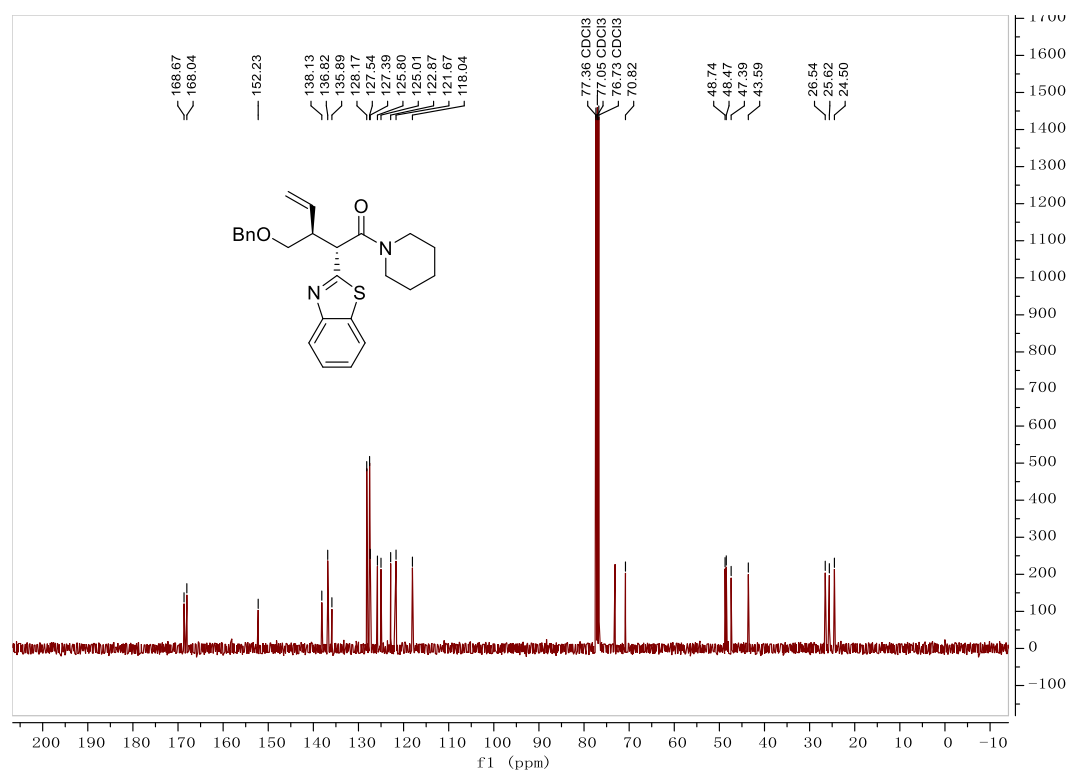


(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-((benzyloxy)methyl)-1-(piperidin-1-yl)pent-4-en-1-one (22)

¹H NMR, CDCl₃, 400 MHz

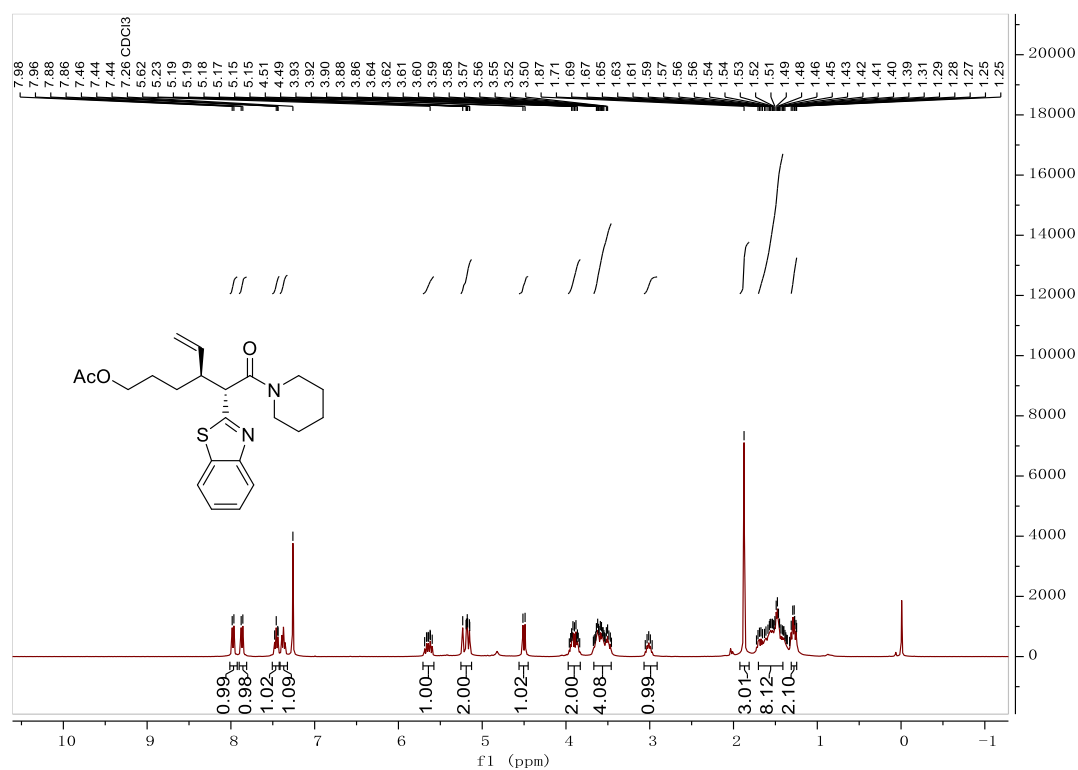


¹³C NMR, CDCl₃, 101 MHz

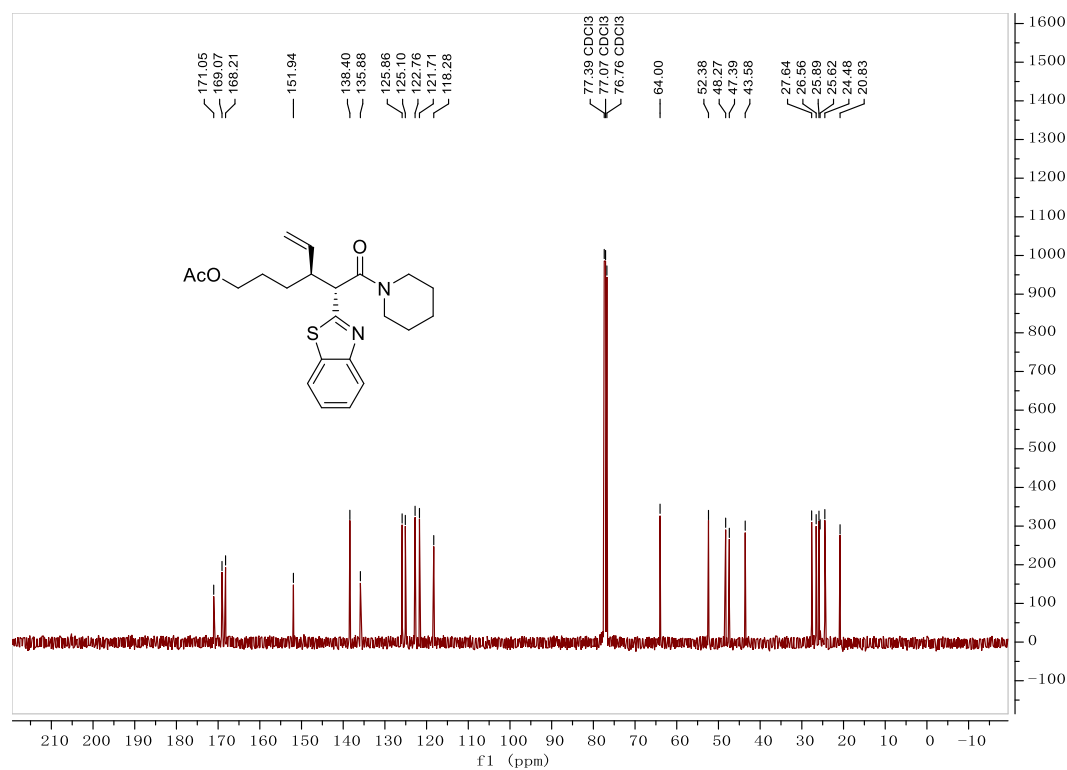


(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-(2-(benzyloxy)ethyl)-1-(piperidin-1-yl)pent-4-en-1-one (23)

¹H NMR, CDCl₃, 400 MHz

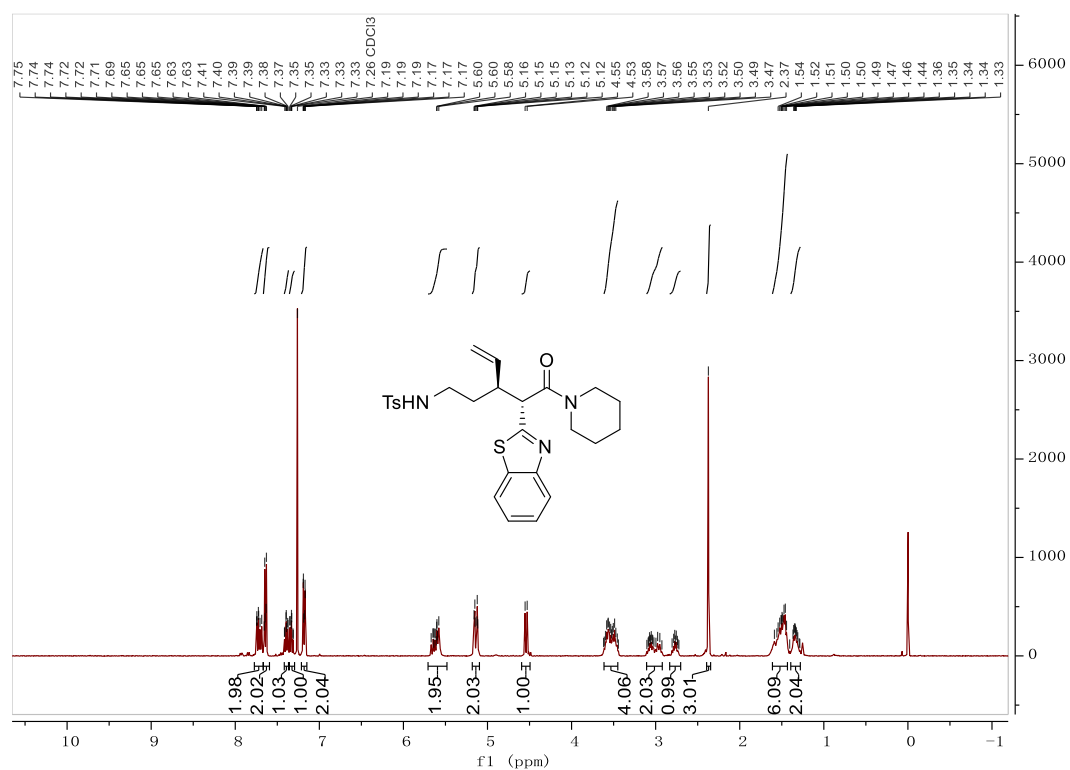


¹³C NMR, CDCl₃, 101 MHz

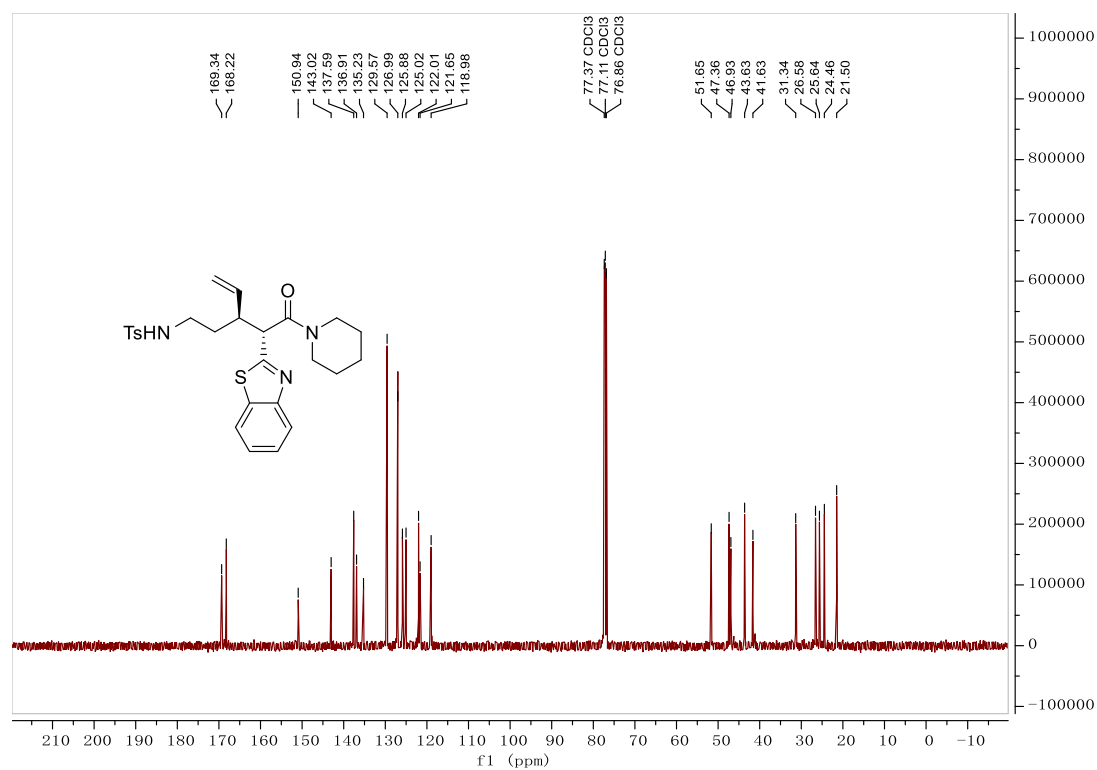


N-((S)-3-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)pent-4-en-1-yl)-4-methylbenzenesulfonamide (25)

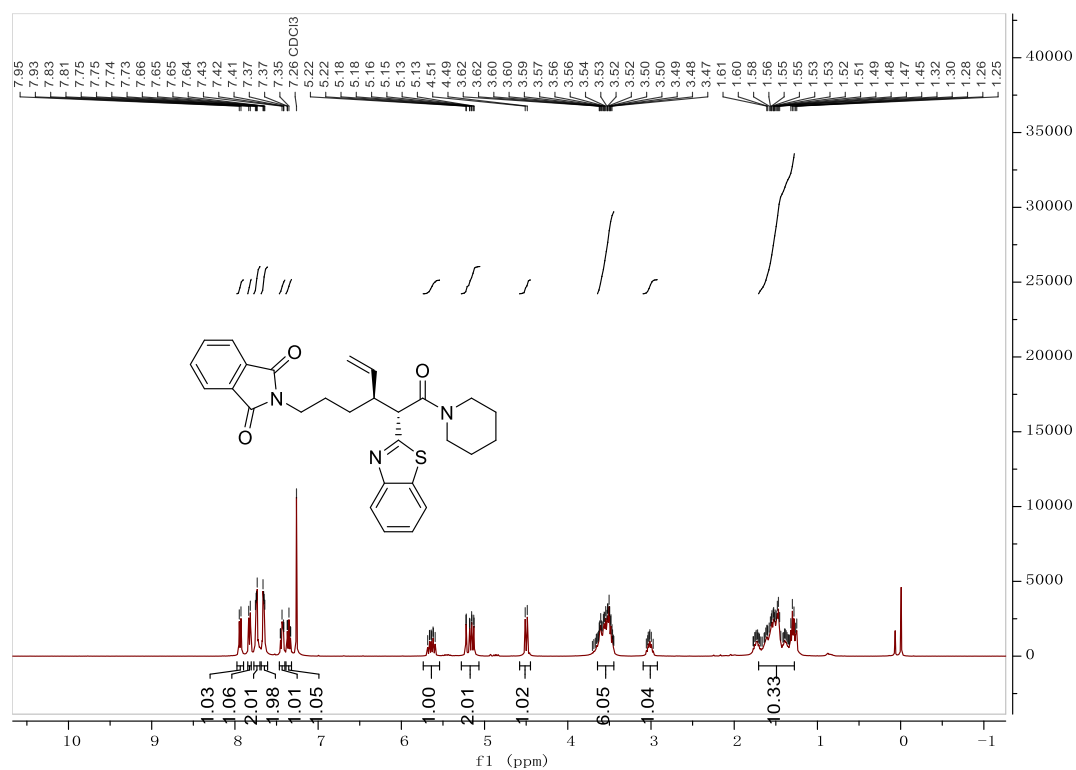
¹H NMR, CDCl₃, 400 MHz



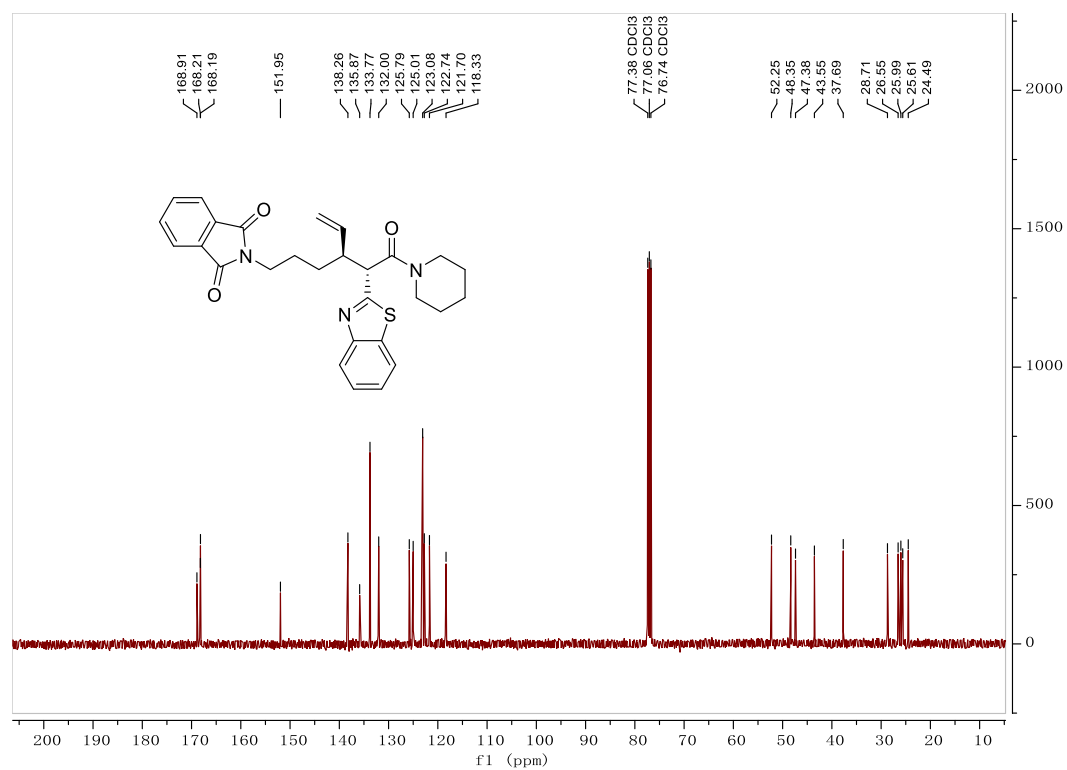
¹³C NMR, CDCl₃, 101 MHz



2-((S)-4-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)hex-5-en-1-yl)isoindoline-1,3-dione (26)
¹H NMR, CDCl₃, 400 MHz

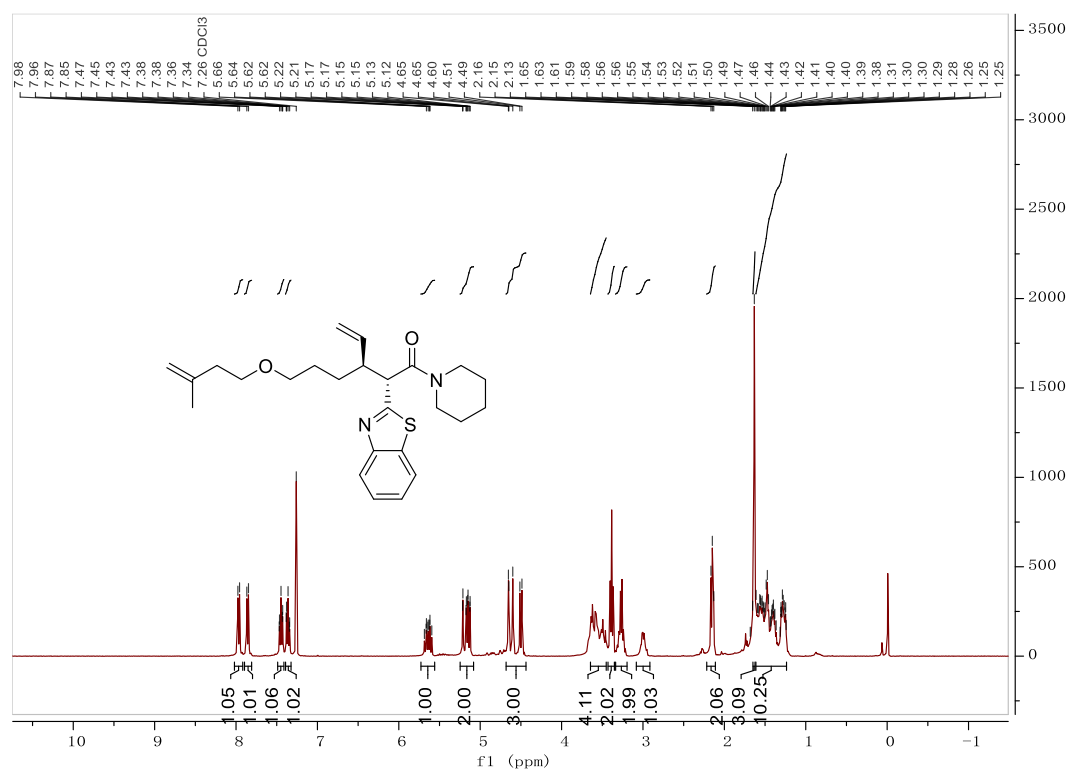


¹³C NMR, CDCl₃, 101 MHz

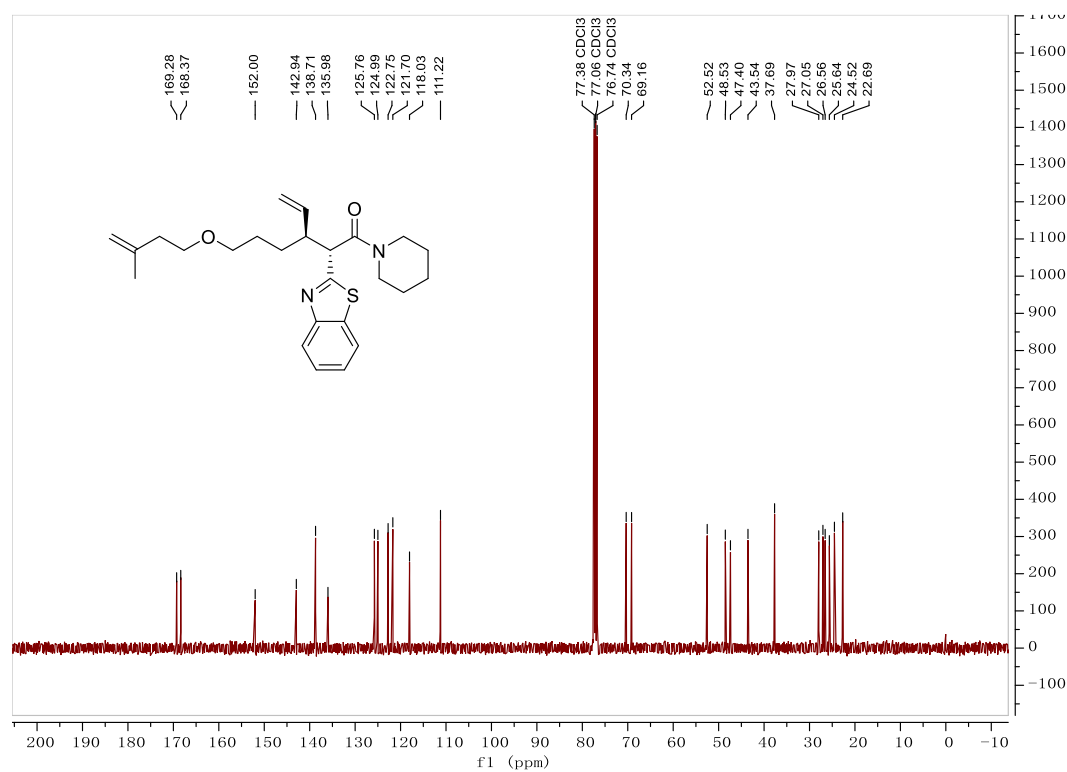


(2R,3S)-2-(benzo[d]thiazol-2-yl)-6-nitro-1-(piperidin-1-yl)-3-vinylhexan-1-one (27)

¹H NMR, CDCl₃, 400 MHz

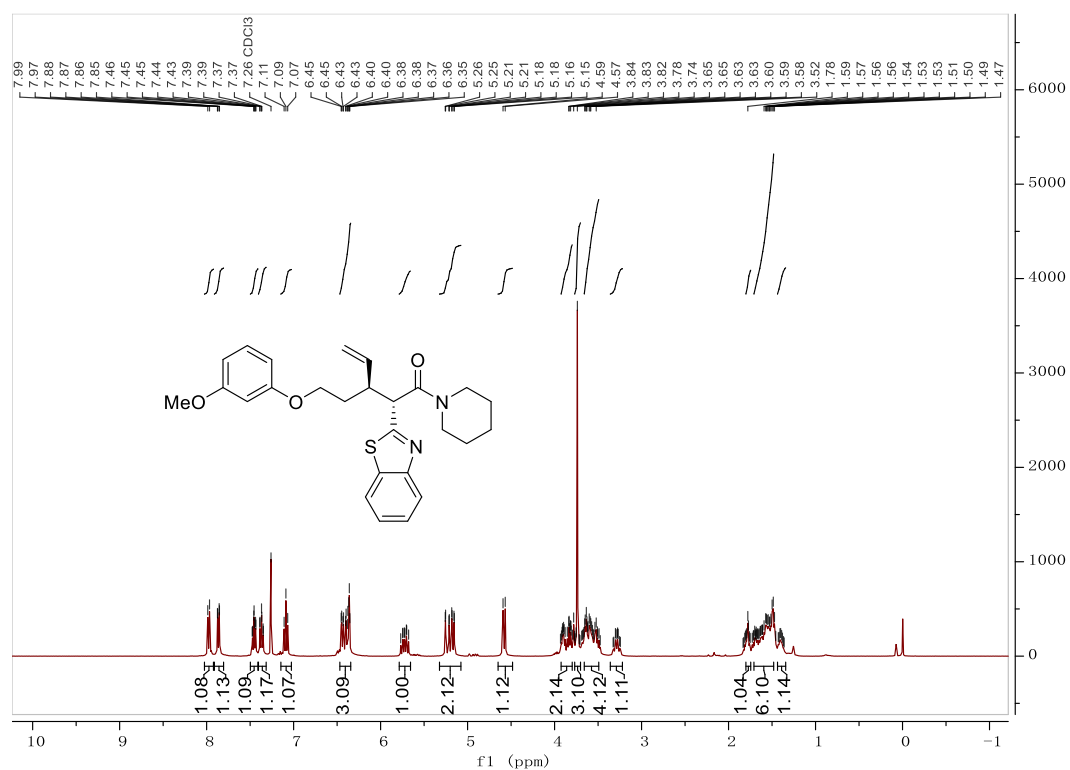


¹³C NMR, CDCl₃, 101 MHz

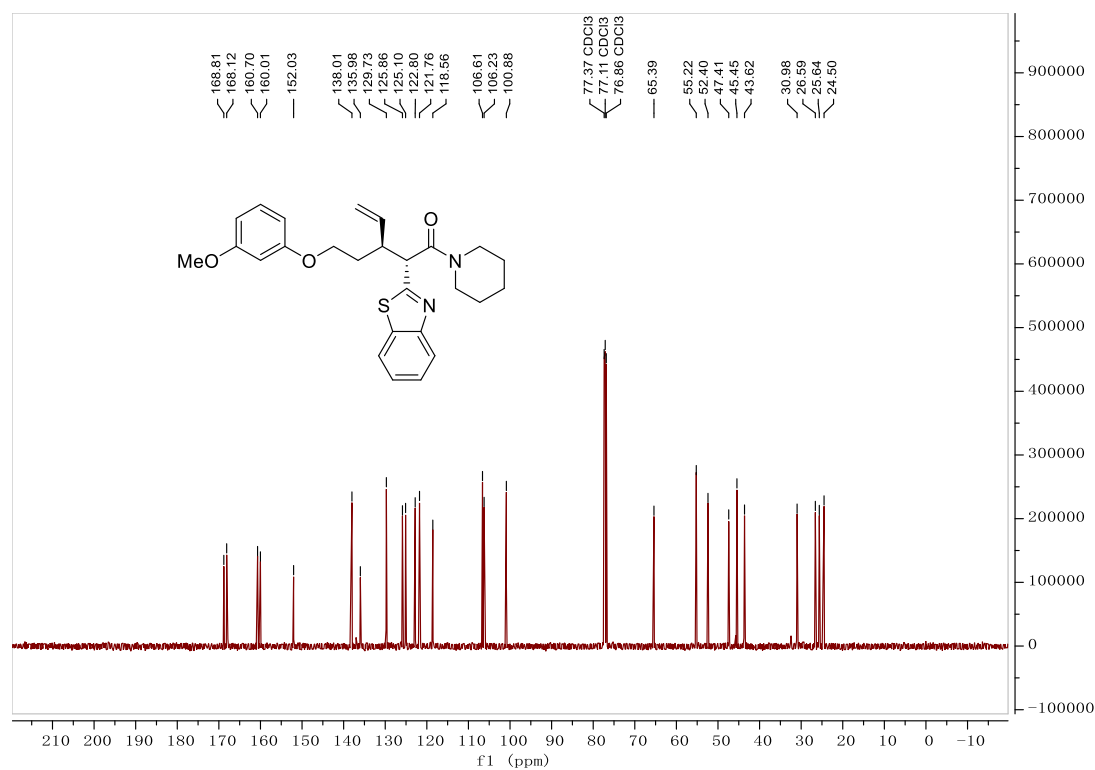


(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-(2-(3-methoxyphenoxy)ethyl)-1-(piperidin-1-yl)pent-4-en-1-one (29)

¹H NMR, CDCl₃, 400 MHz

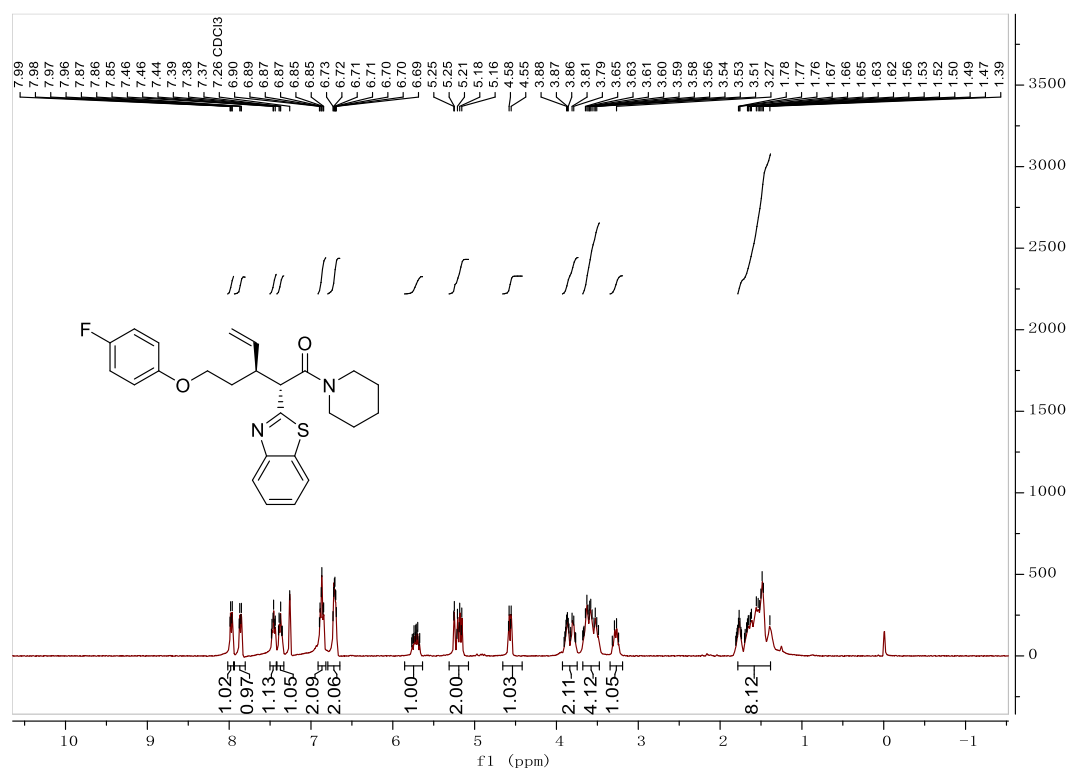


¹³C NMR, CDCl₃, 101 MHz

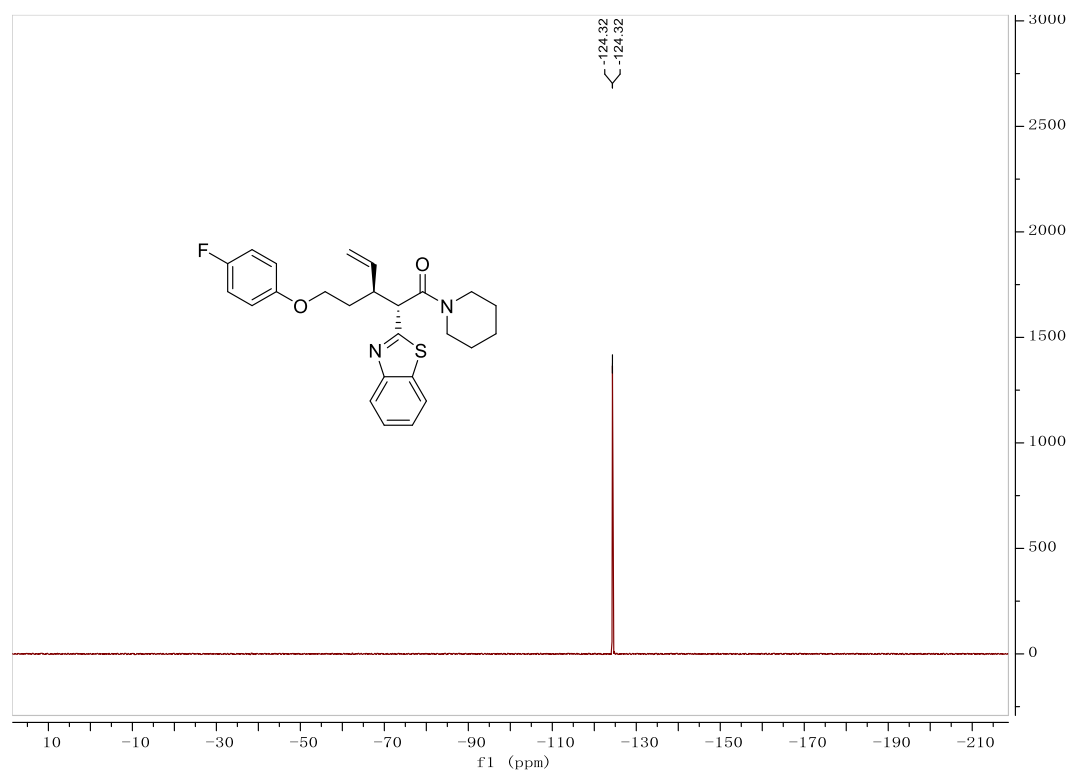


(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-(2-(4-fluorophenoxy)ethyl)-1-(piperidin-1-yl)pent-4-en-1-one (30)

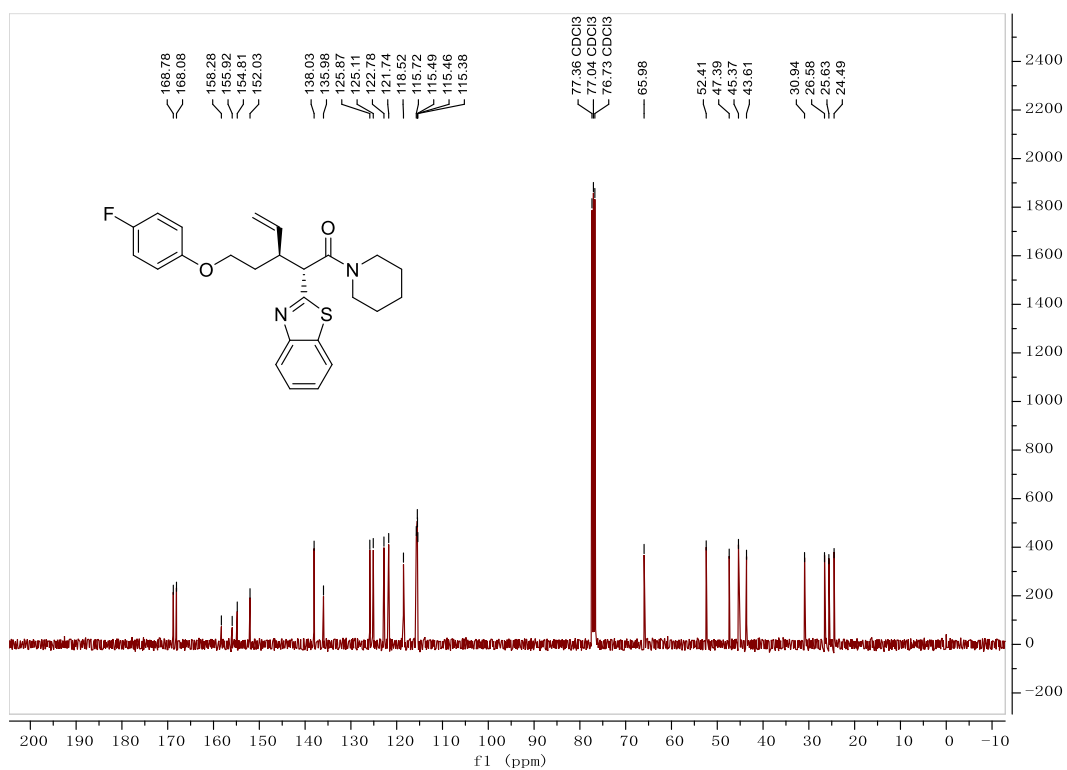
¹H NMR, CDCl₃, 400 MHz



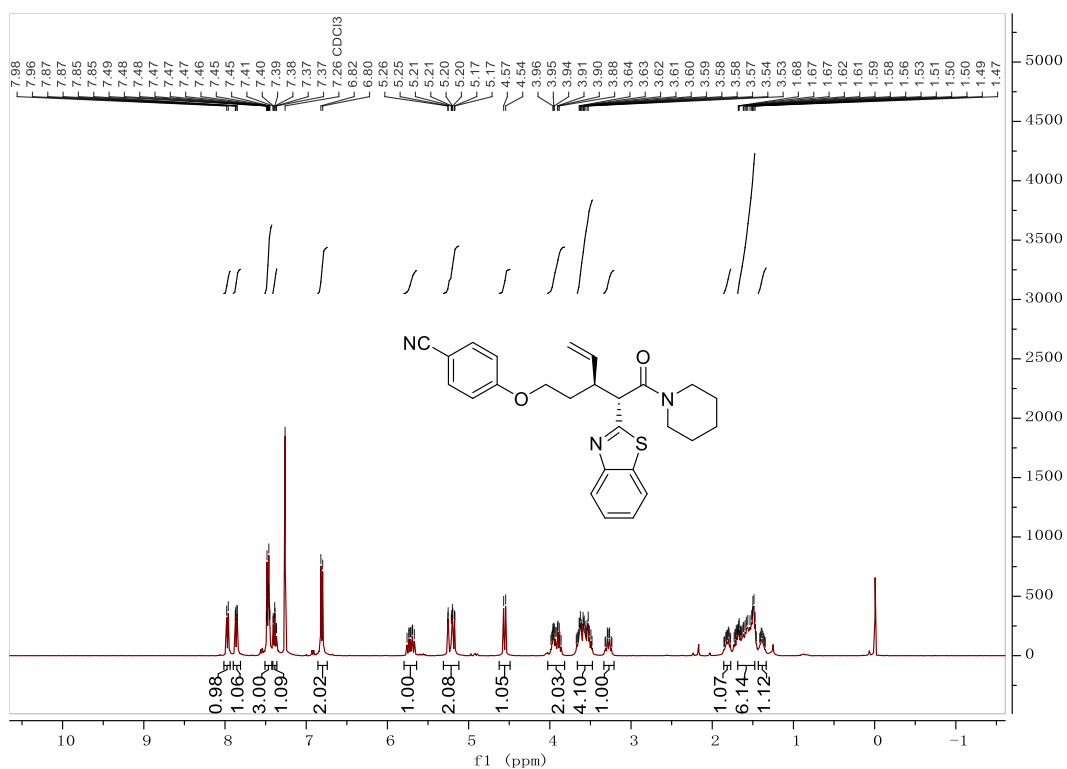
¹⁹F NMR, CDCl₃, 376 MHz



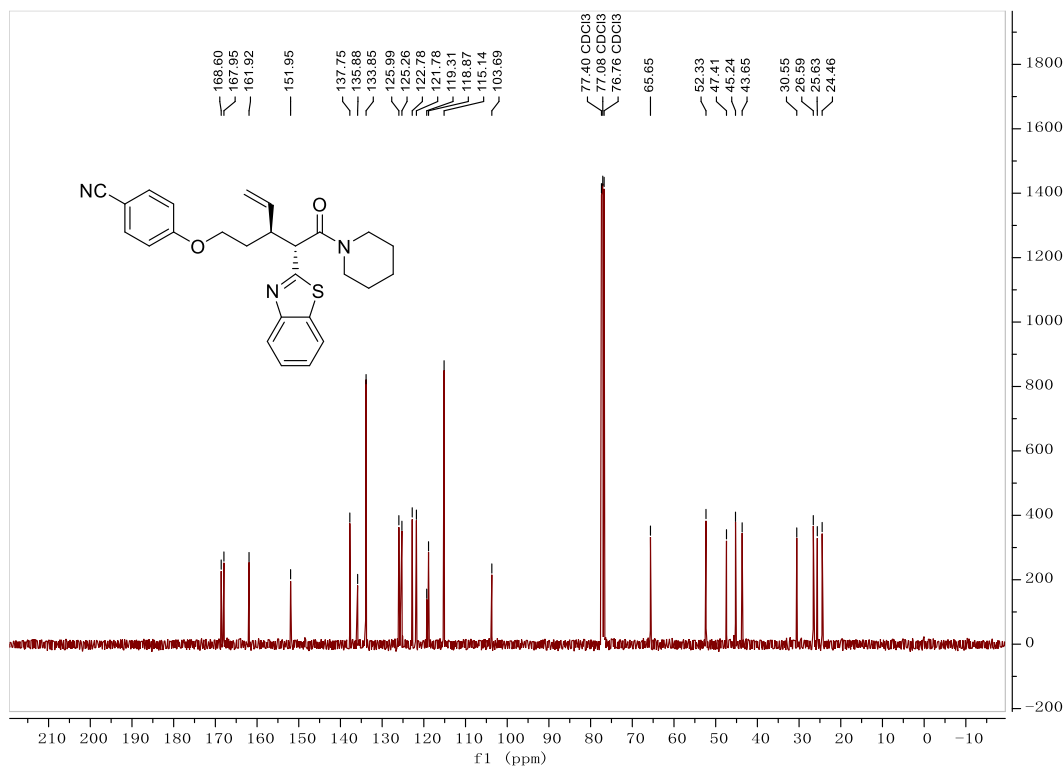
¹³C NMR, CDCl₃, 101 MHz



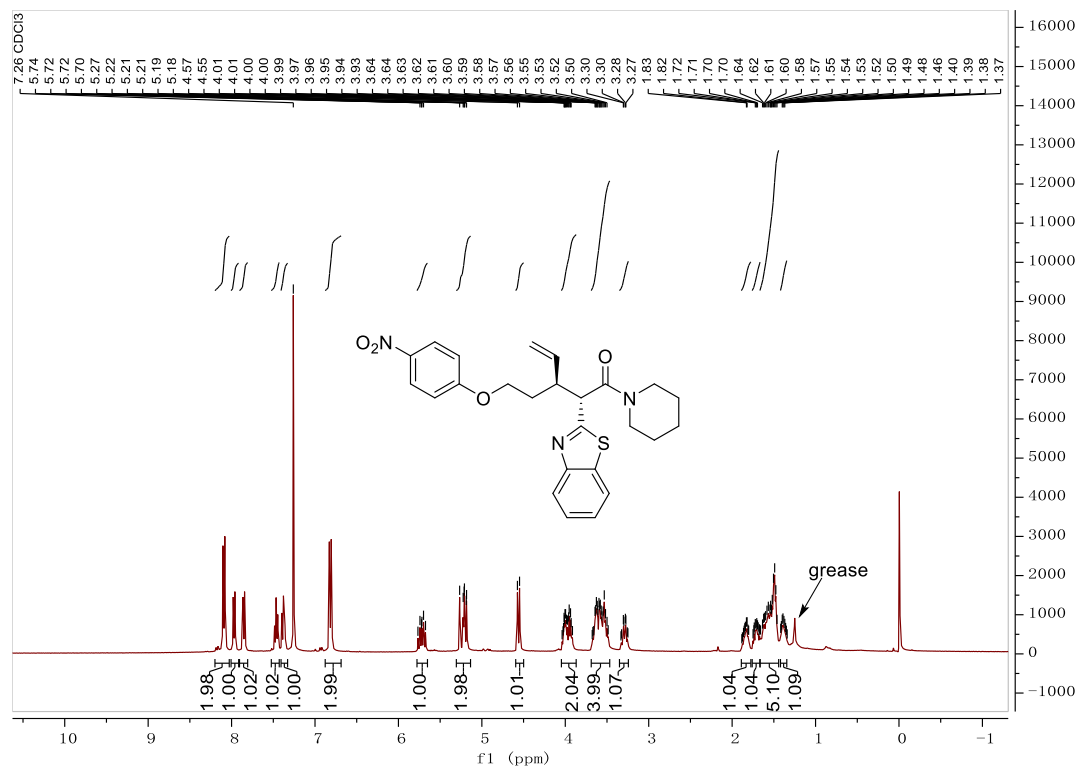
4-(((S)-3-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)pent-4-en-1-yl)oxy)benz onitrile (31)
¹H NMR, CDCl₃, 400 MHz



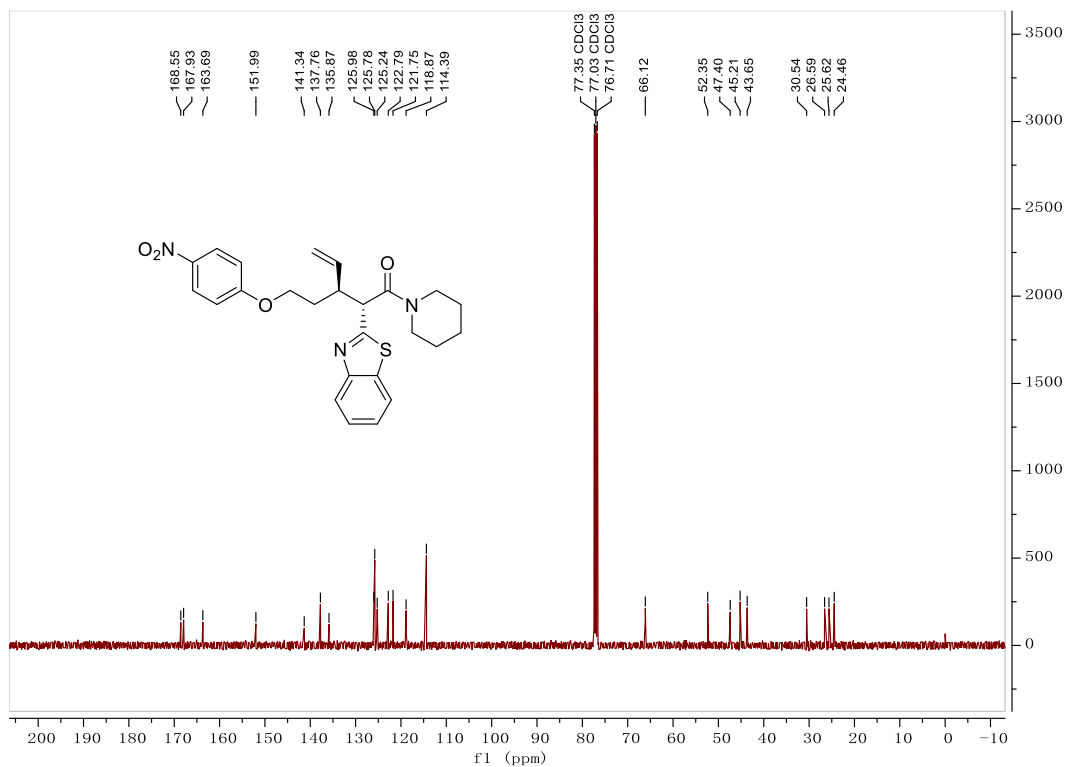
¹³C NMR, CDCl₃, 101 MHz



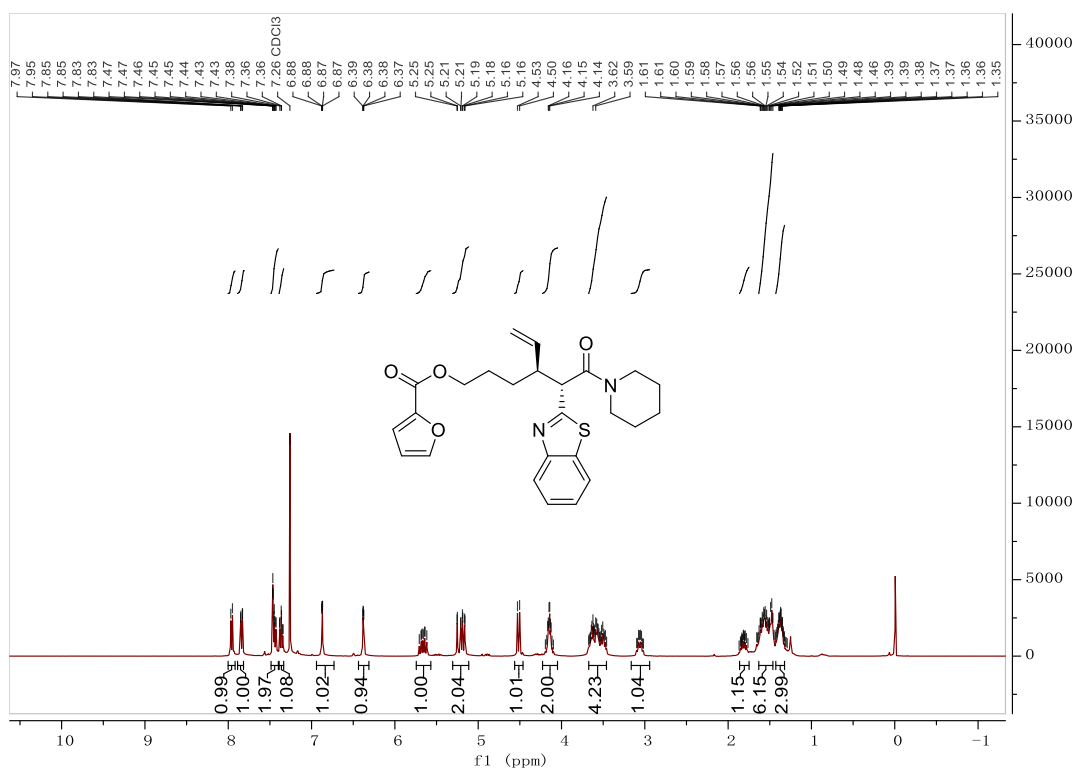
(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-(2-(4-nitrophenoxy)ethyl)-1-(piperidin-1-yl)pent-4-en-1-one (32)
 ^1H NMR, CDCl_3 , 400 MHz



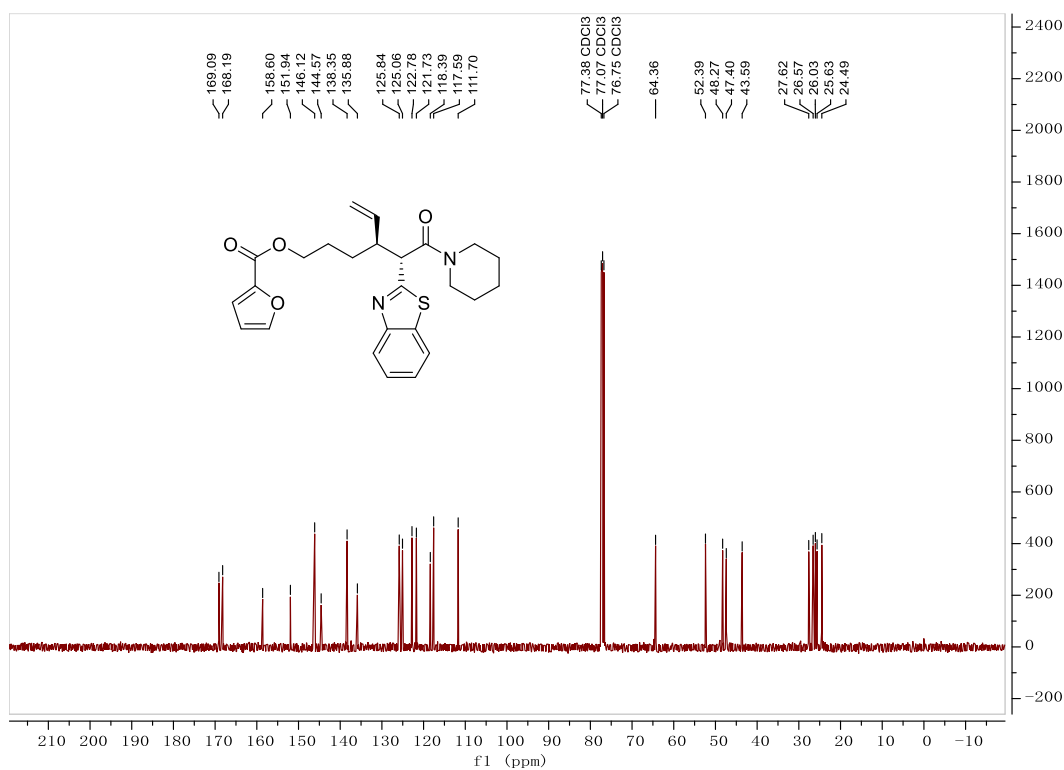
^{13}C NMR, CDCl_3 , 101 MHz



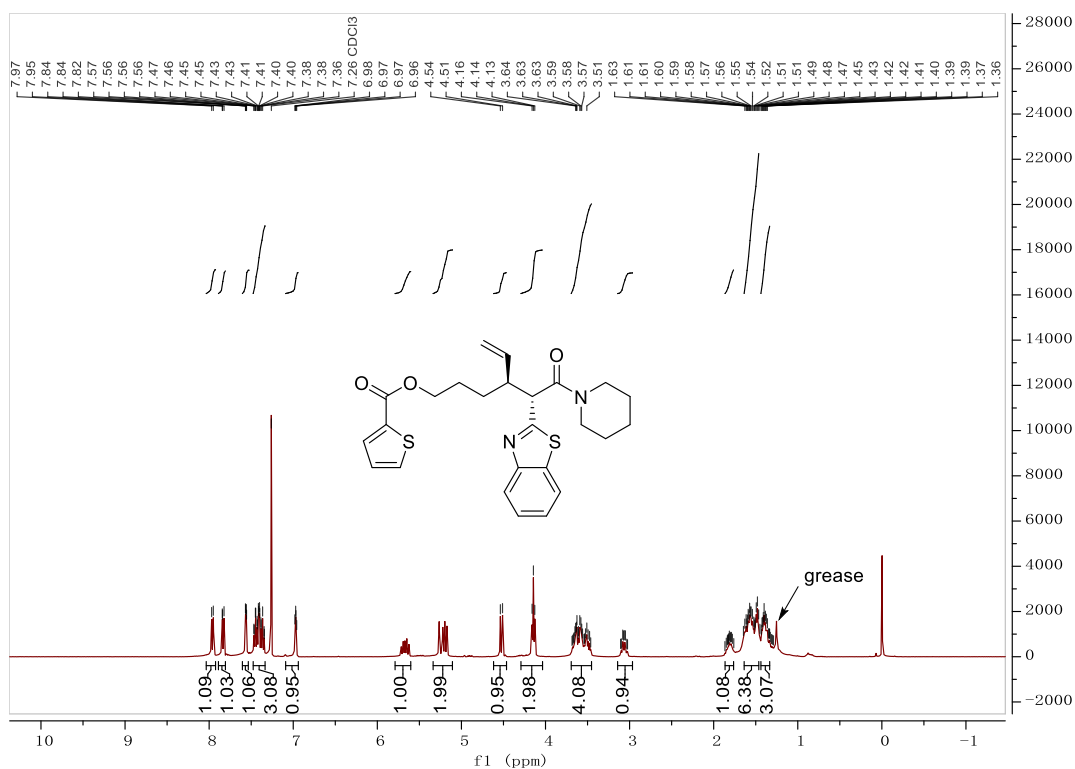
(S)-4-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)hex-5-en-1-yl furan-2-carboxylate (33)
¹H NMR, CDCl₃, 400 MHz



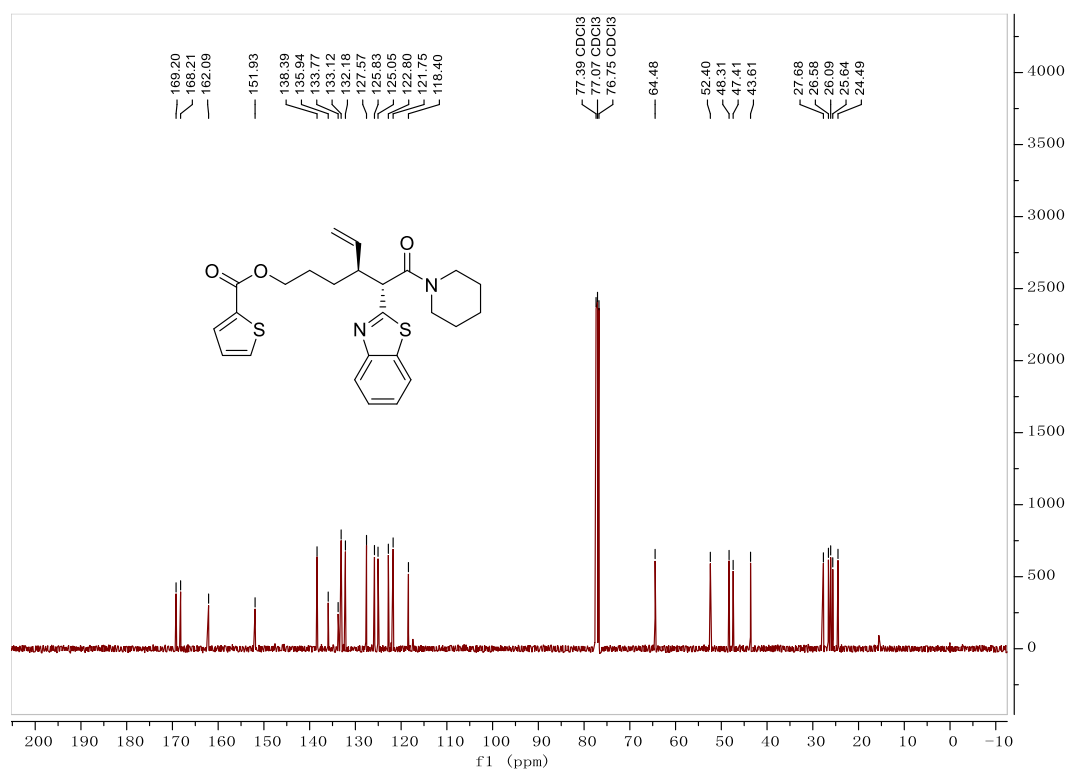
¹³C NMR, CDCl₃, 101 MHz



(S)-4-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)hex-5-en-1-yl thiophene-2-carboxylate (34)
¹H NMR, CDCl₃, 400 MHz

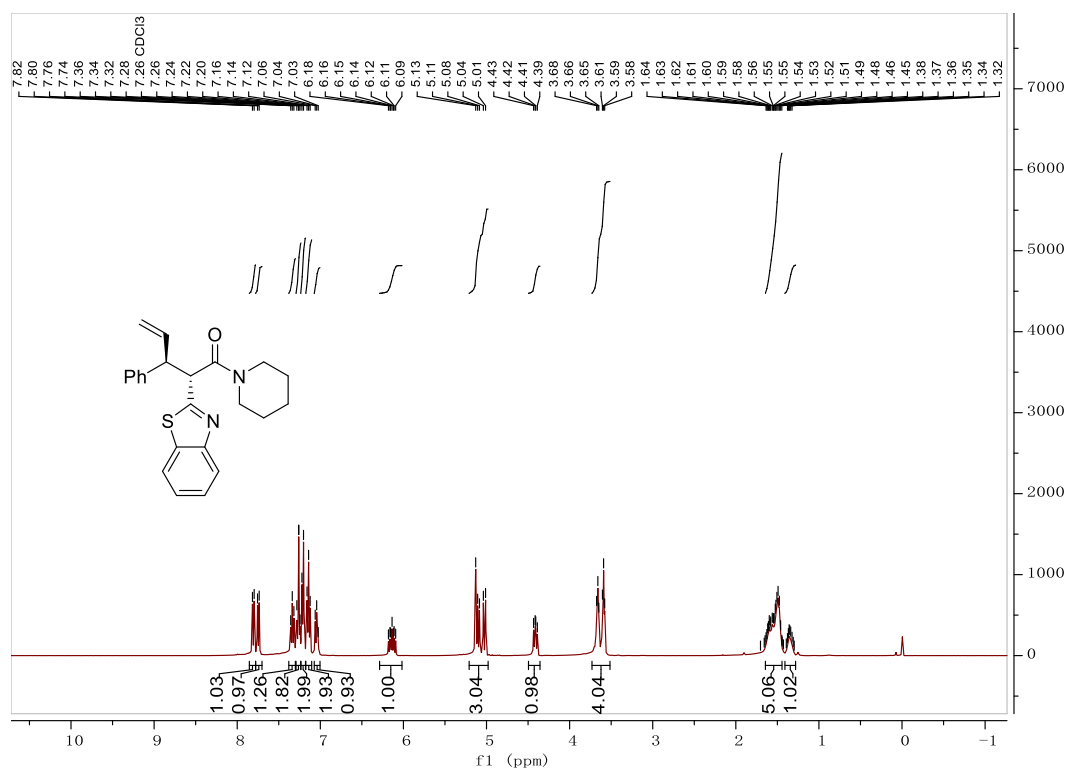


¹³C NMR, CDCl₃, 101 MHz

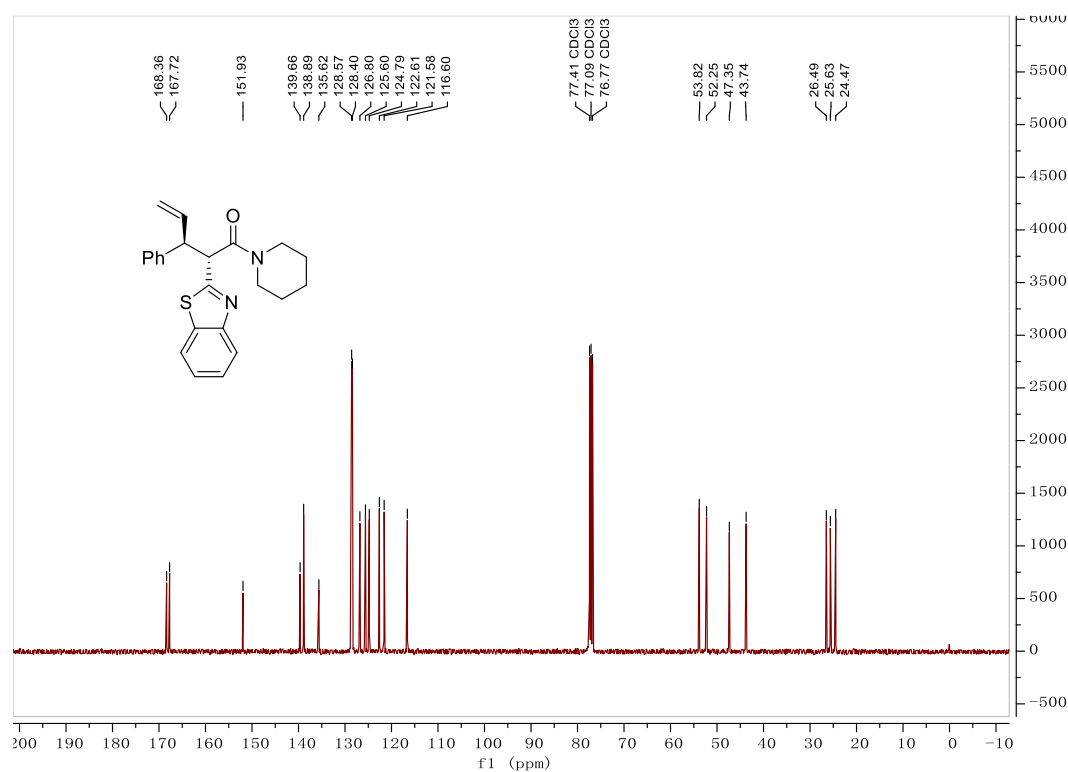


(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-phenyl-1-(piperidin-1-yl)pent-4-en-1-one (35)

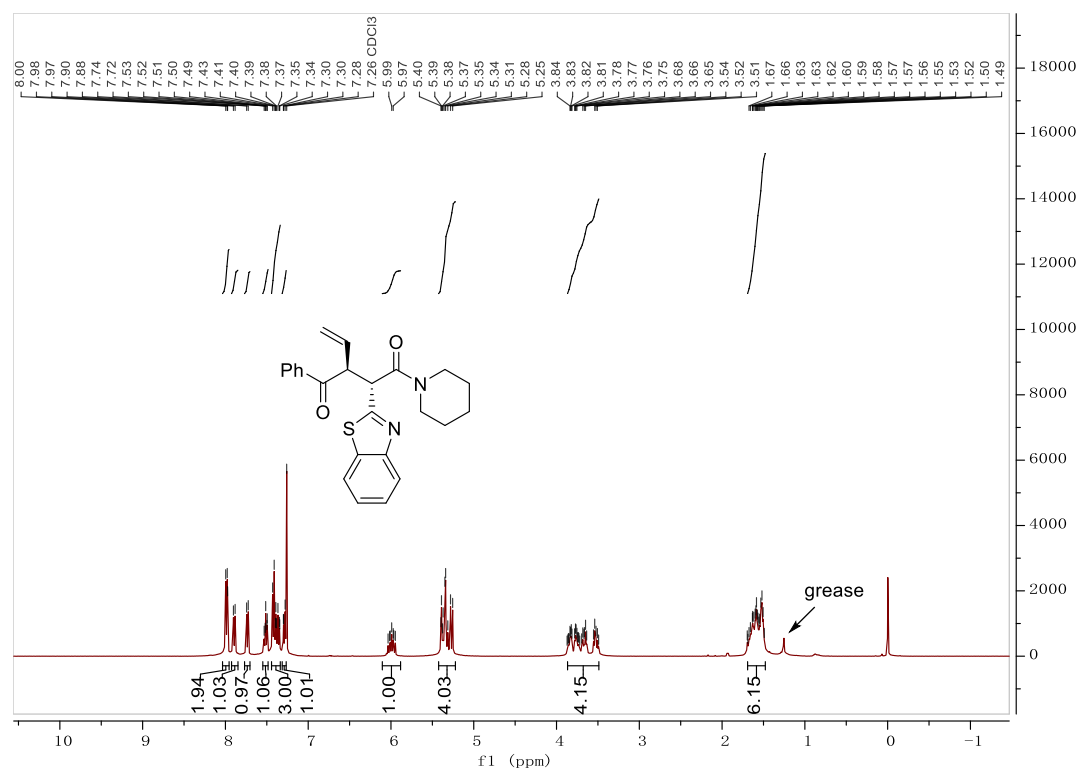
¹H NMR, CDCl₃, 400 MHz



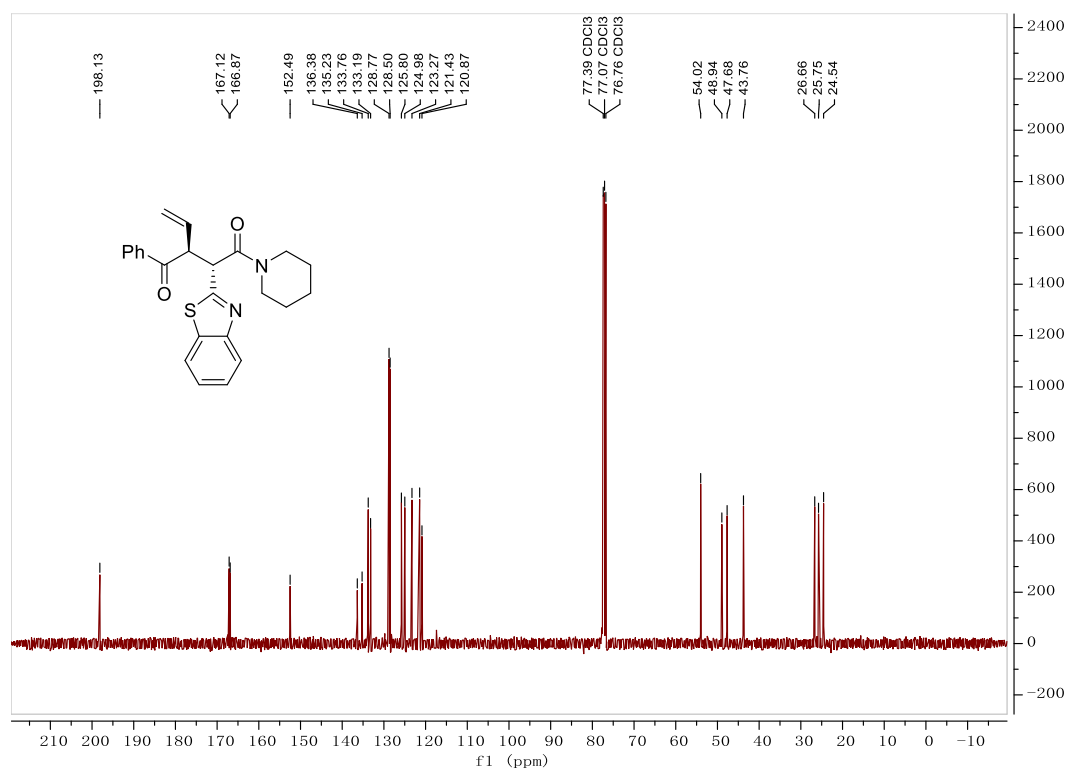
¹³C NMR, CDCl₃, 101 MHz



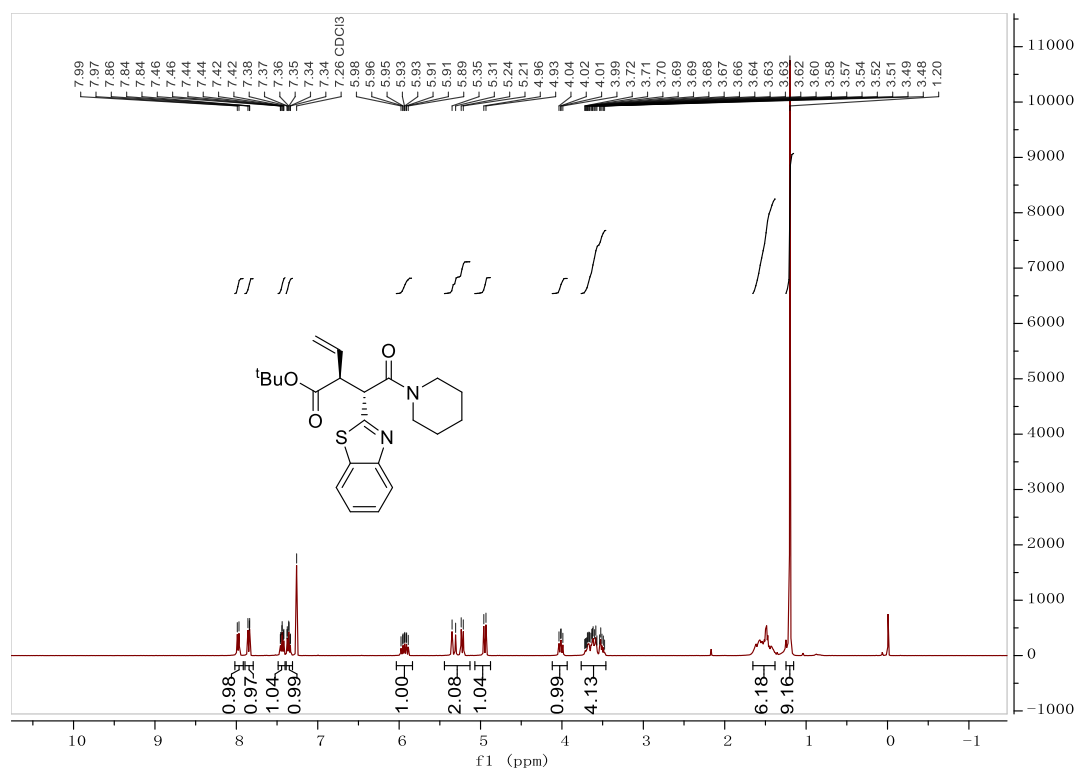
(2R,3S)-2-(benzo[d]thiazol-2-yl)-4-phenyl-1-(piperidin-1-yl)-3-vinylbutane-1,4-dione (36)
¹H NMR, CDCl₃, 400 MHz



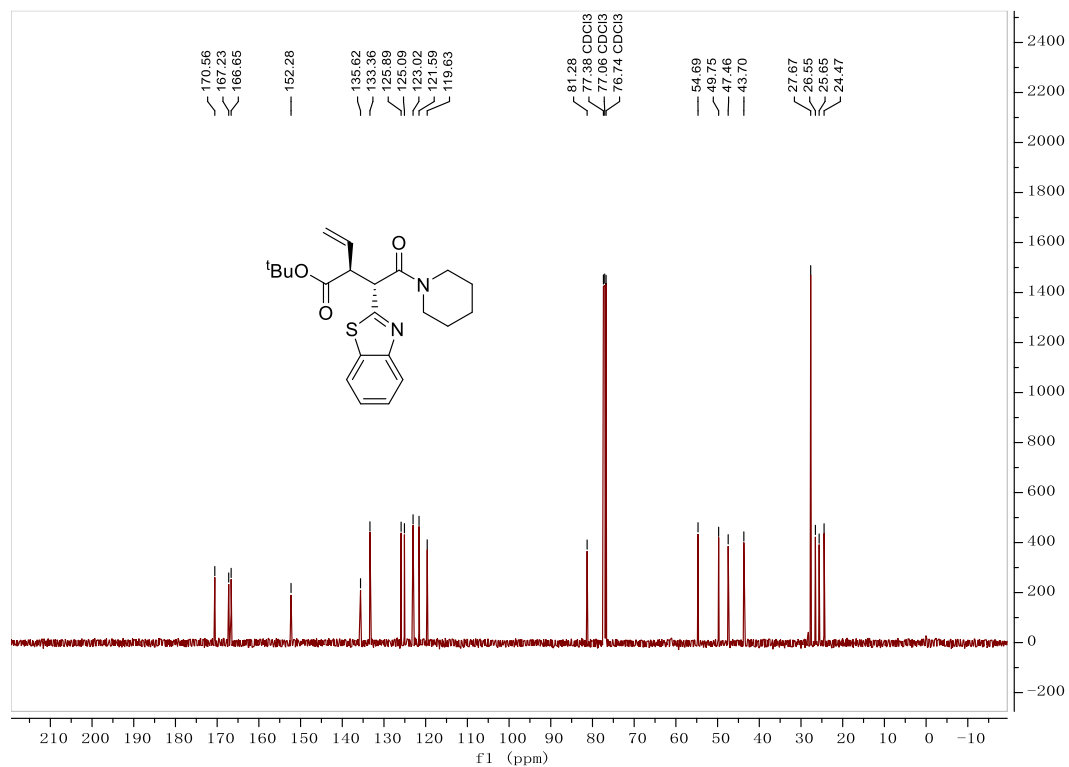
¹³C NMR, CDCl₃, 101 MHz



Tert-butyl (S)-2-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)but-3-enoate (37)
¹H NMR, CDCl₃, 400 MHz

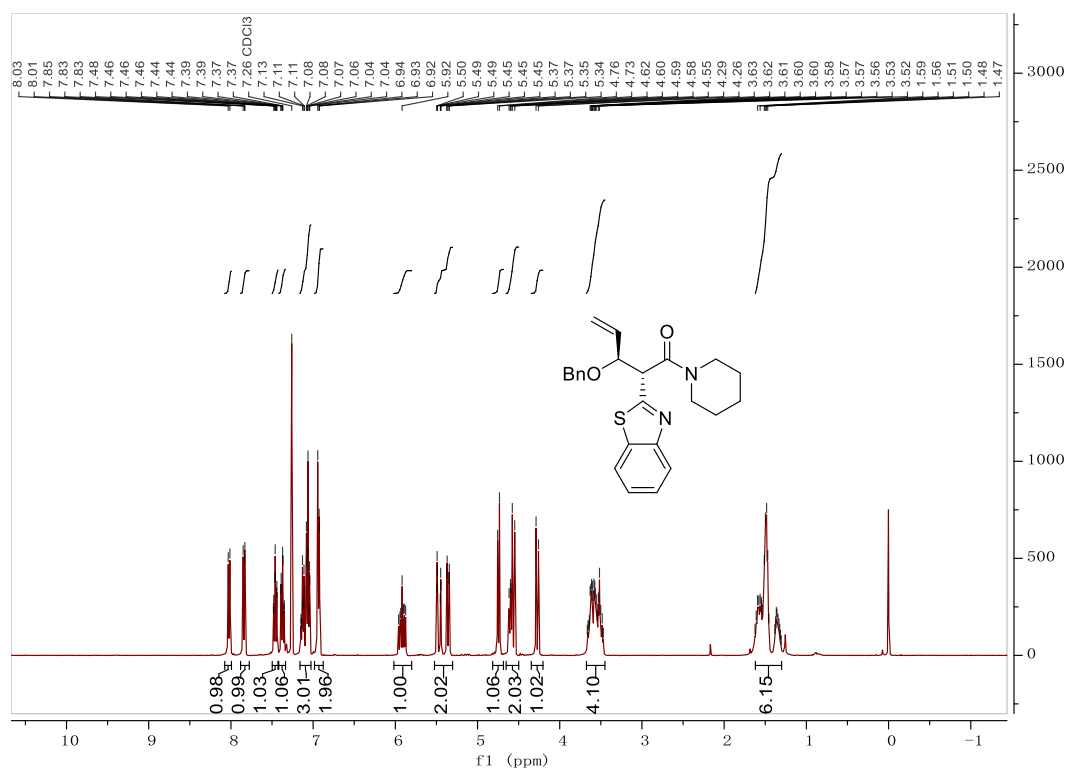


¹³C NMR, CDCl₃, 101 MHz

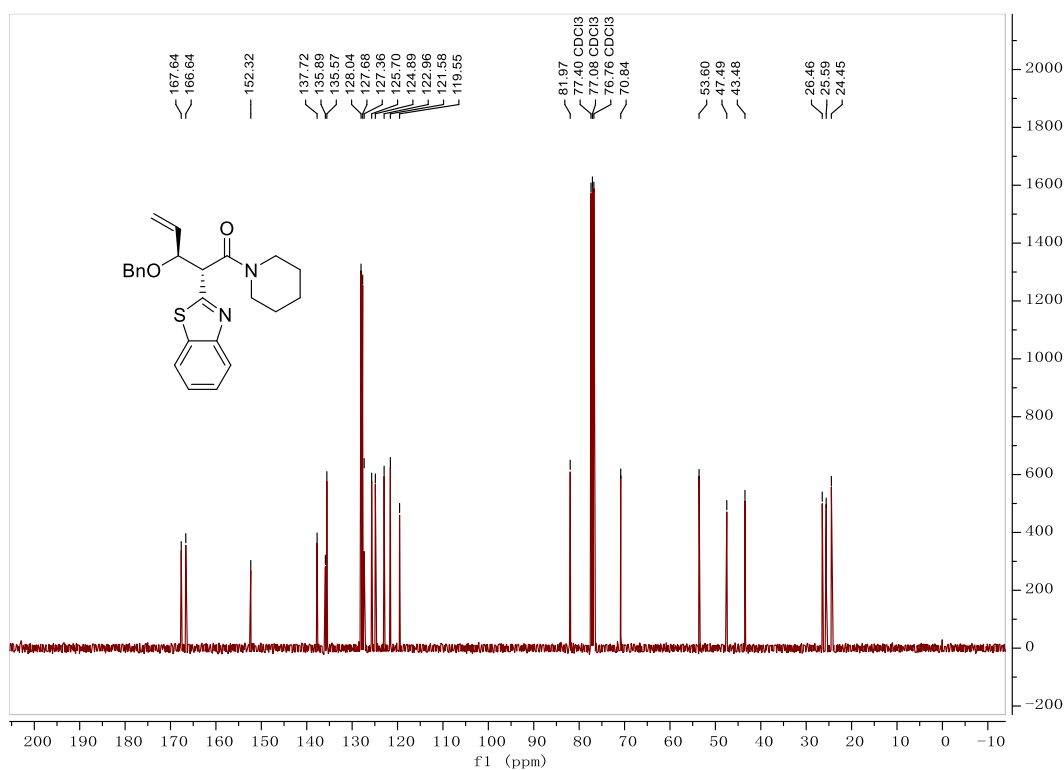


(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-(benzyloxy)-1-(piperidin-1-yl)pent-4-en-1-one (38)

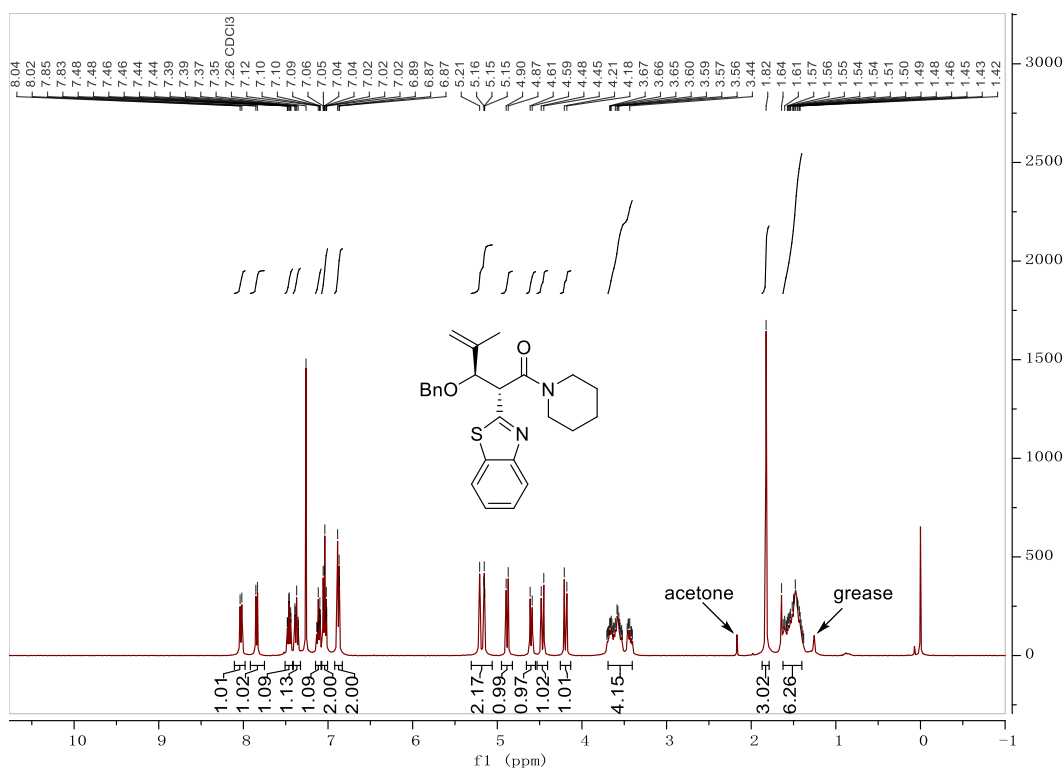
¹H NMR, CDCl₃, 400 MHz



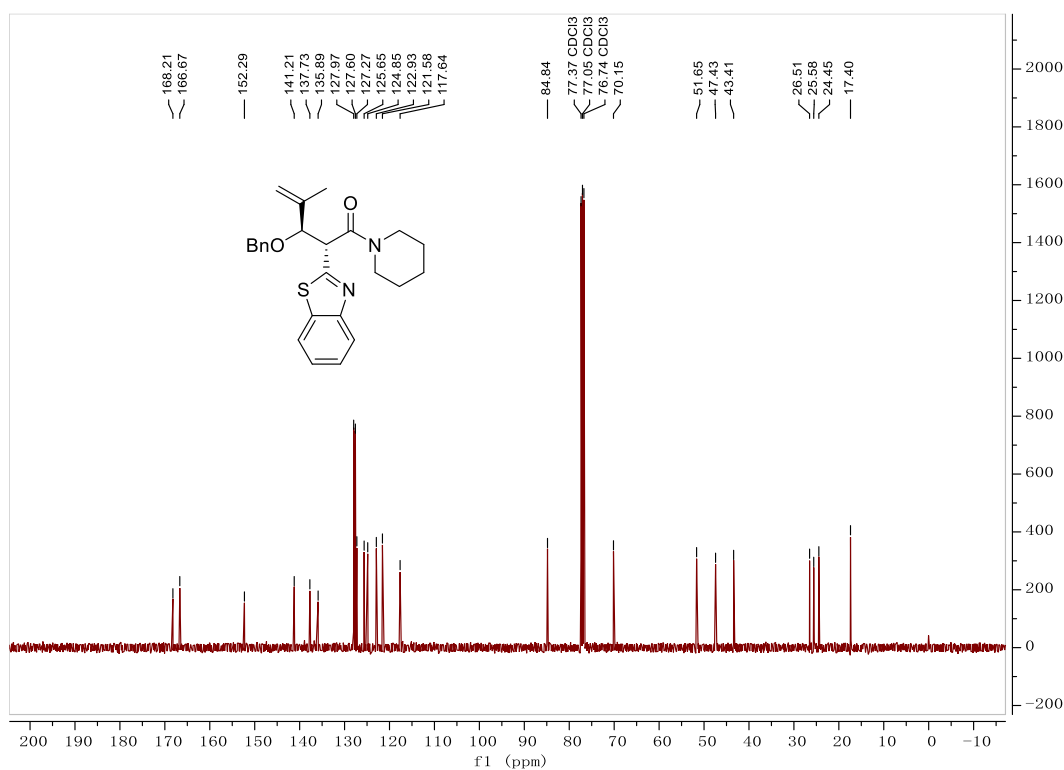
¹³C NMR, CDCl₃, 101 MHz



(2R,3R)-2-(benzo[d]thiazol-2-yl)-3-(benzyloxy)-4-methyl-1-(piperidin-1-yl)pent-4-en-1-one (39)
¹H NMR, CDCl₃, 400 MHz

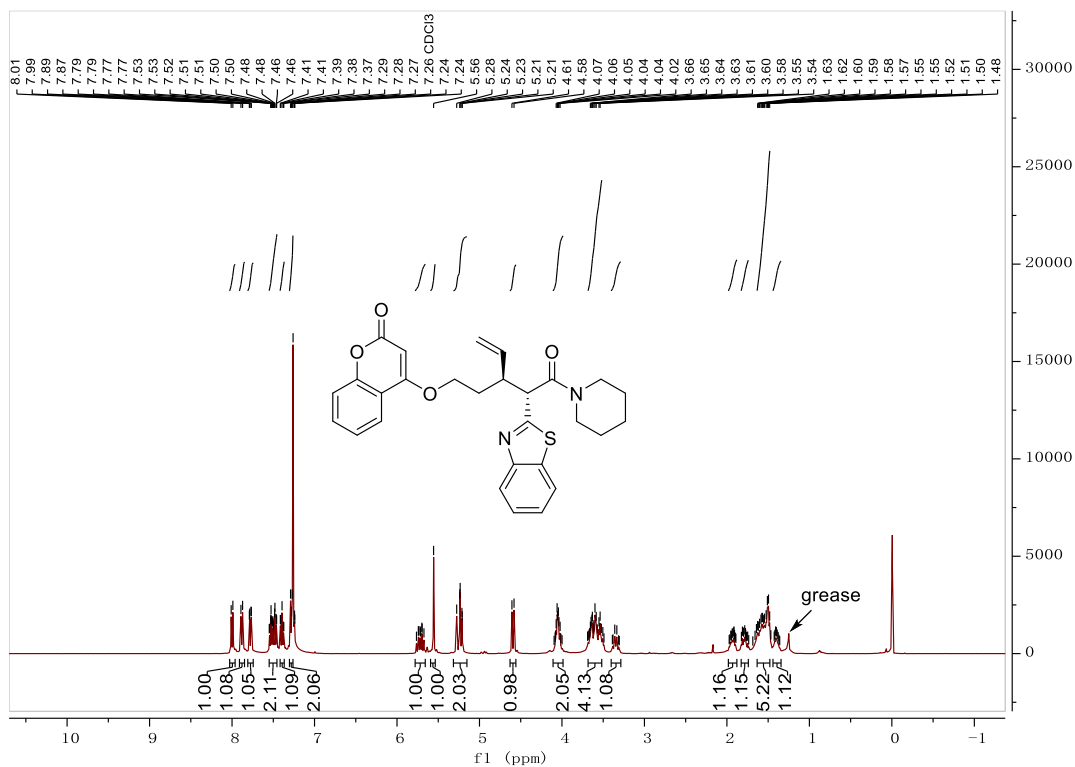


¹³C NMR, CDCl₃, 101 MHz

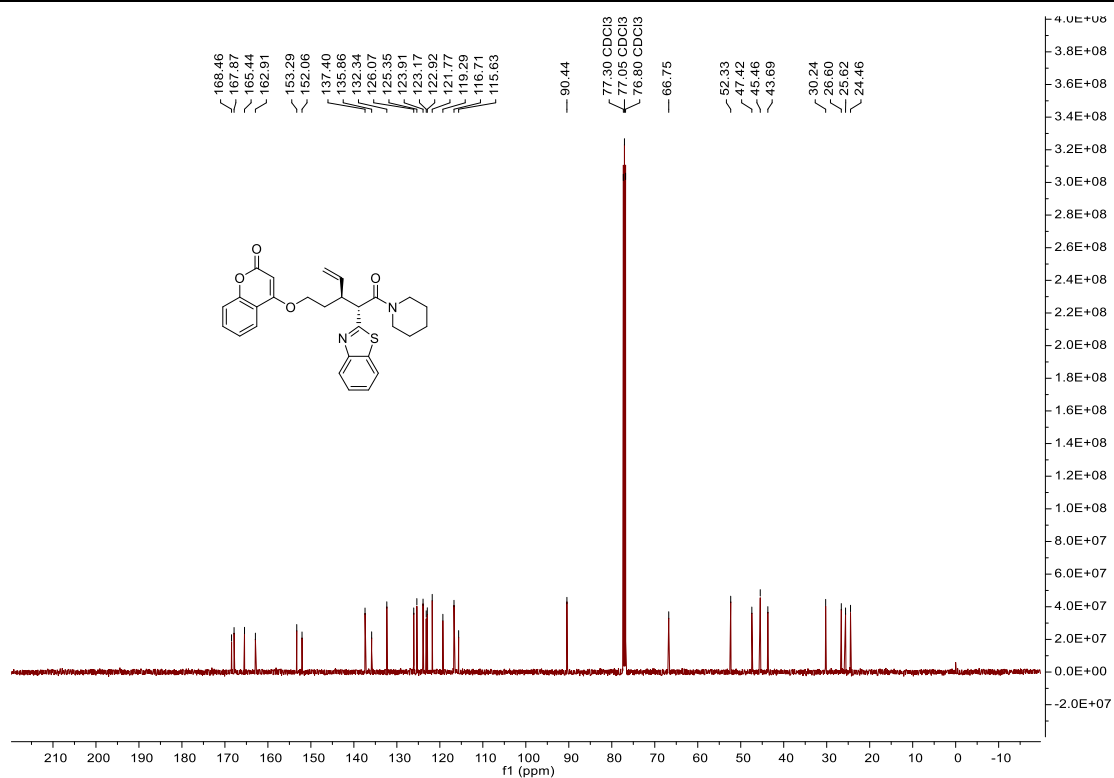


4-(((S)-3-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)pent-4-en-1-yl)oxy)-2H-chromen-2-one (40)

^1H NMR, CDCl_3 , 400 MHz

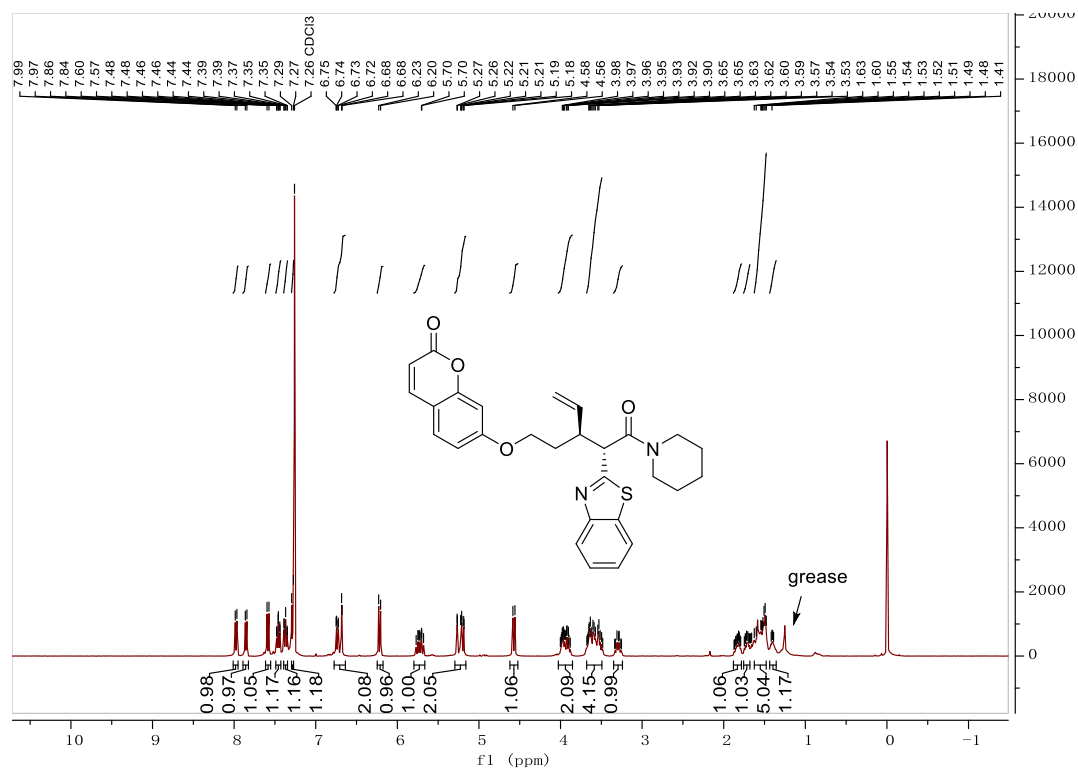


^{13}C NMR, CDCl_3 , 101 MHz

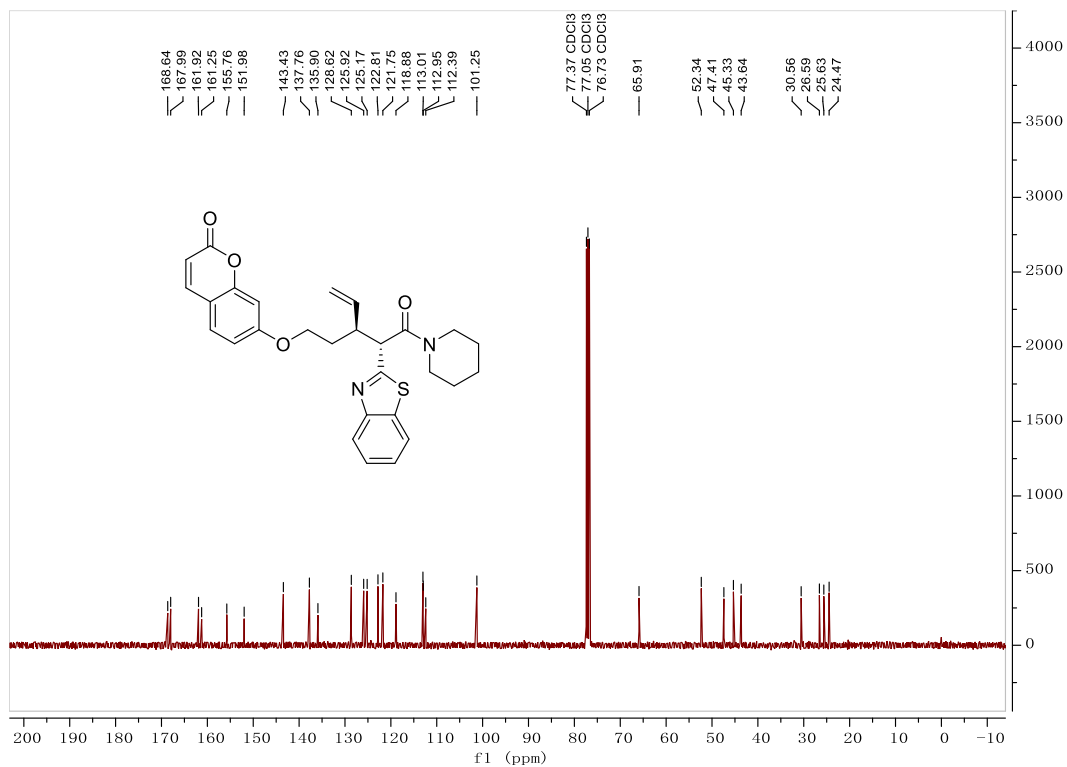


7-(((S)-3-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)pent-4-en-1-yl)oxy)-2H-chromen-2-one (41)

¹H NMR, CDCl₃, 400 MHz

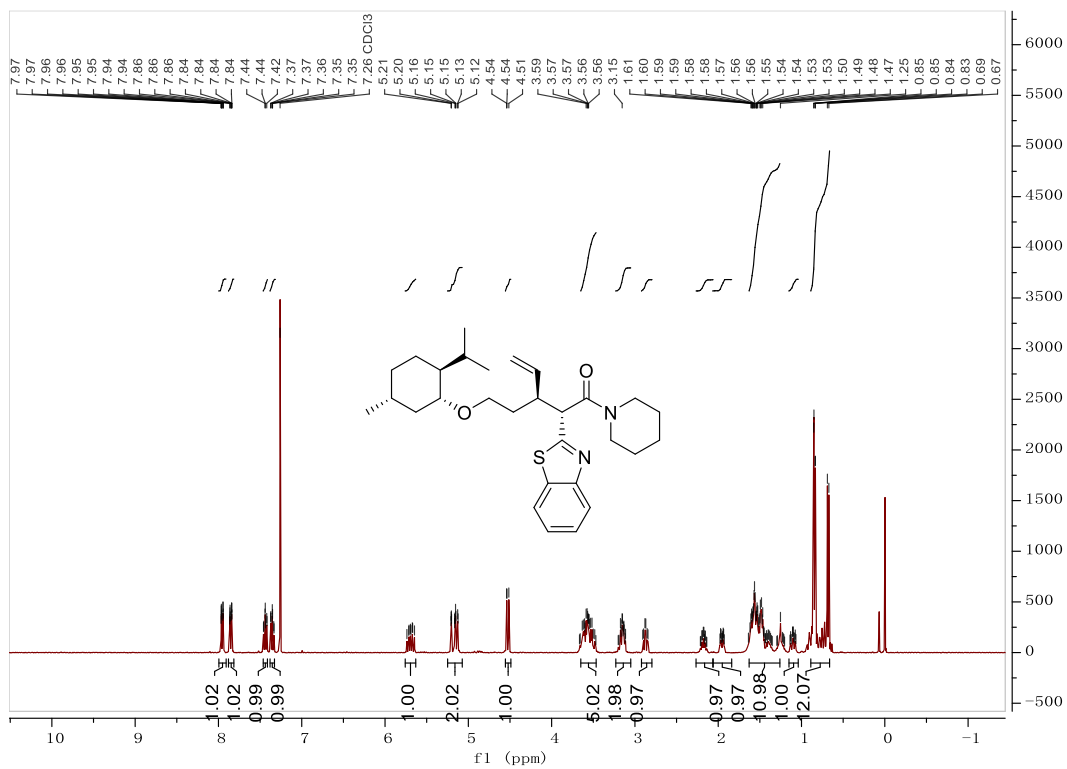


¹³C NMR, CDCl₃, 101 MHz

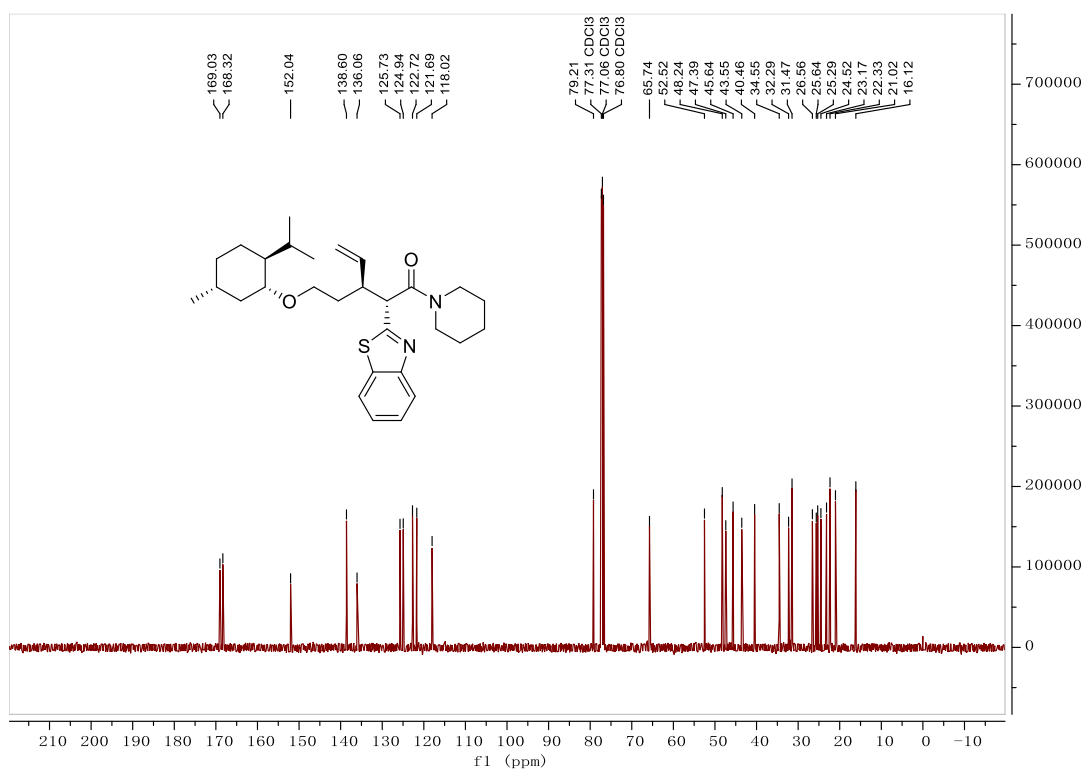


(2R,3S)-2-(benzo[d]thiazol-2-yl)-3-(2-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)ethyl)-1-(piperidin-1-yl)pent-4-en-1-one (42)

¹H NMR, CDCl₃, 400 MHz

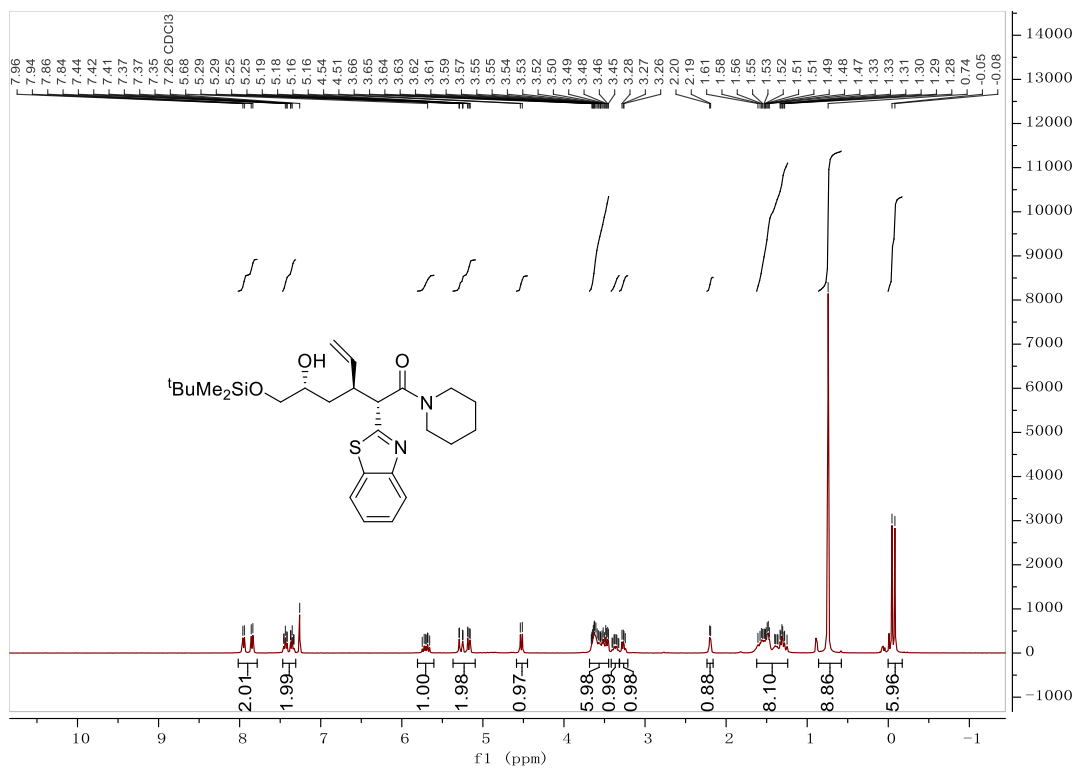


¹³C NMR, CDCl₃, 101 MHz

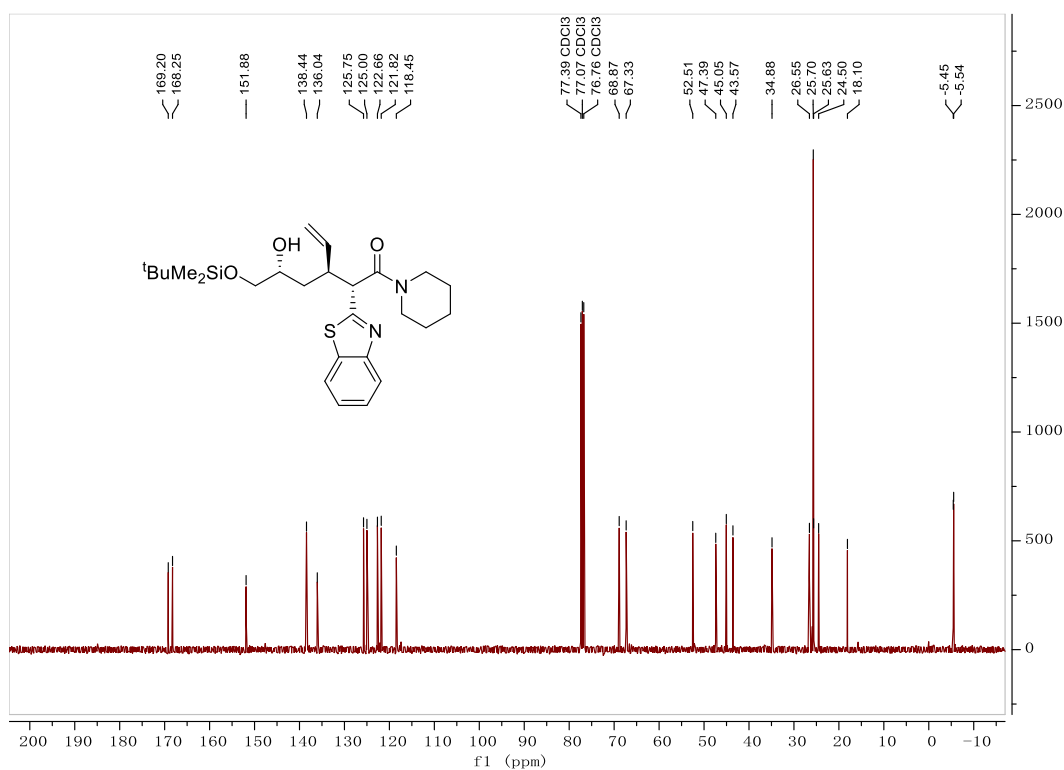


(2R,3S,5R)-2-(benzo[d]thiazol-2-yl)-6-((tert-butyl dimethylsilyl)oxy)-5-hydroxy-1-(piperidin-1-yl)-3-vinylhexan-1-one (43)

^1H NMR, CDCl₃, 400 MHz

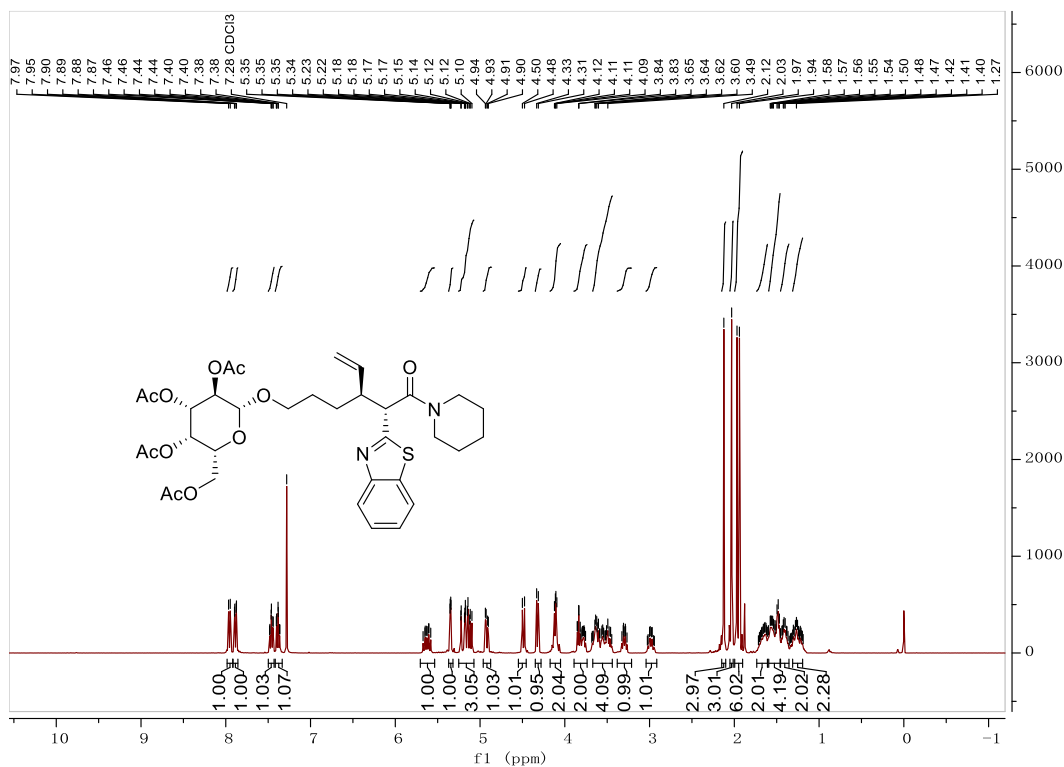


^{13}C NMR, CDCl₃, 101 MHz

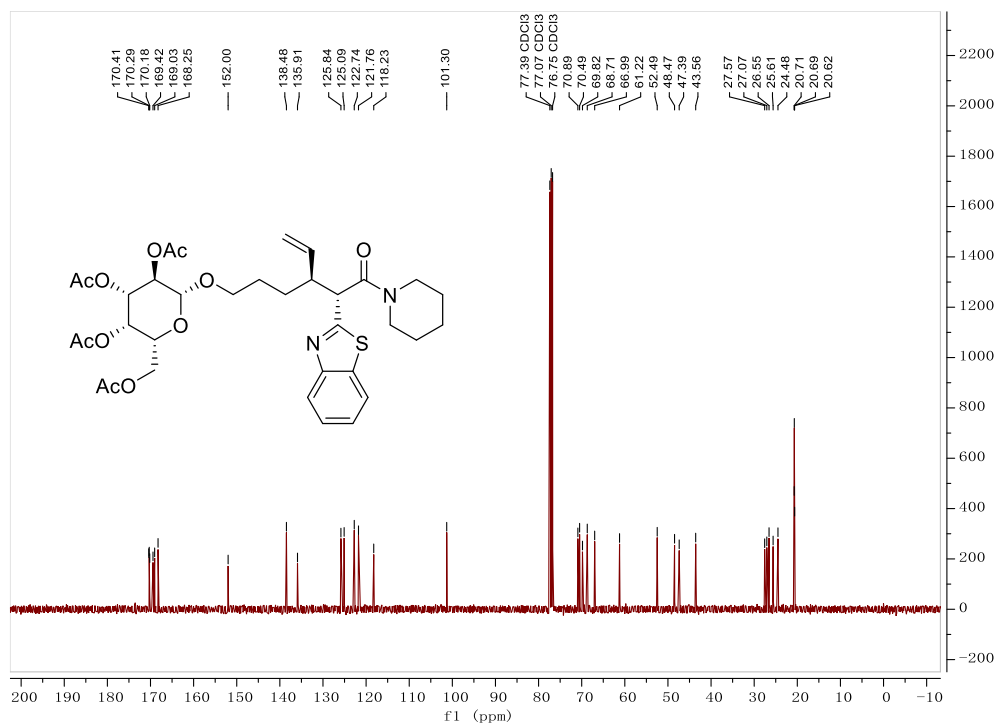


(2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-(((S)-4-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)hex-5-en-1-yl)oxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (44)

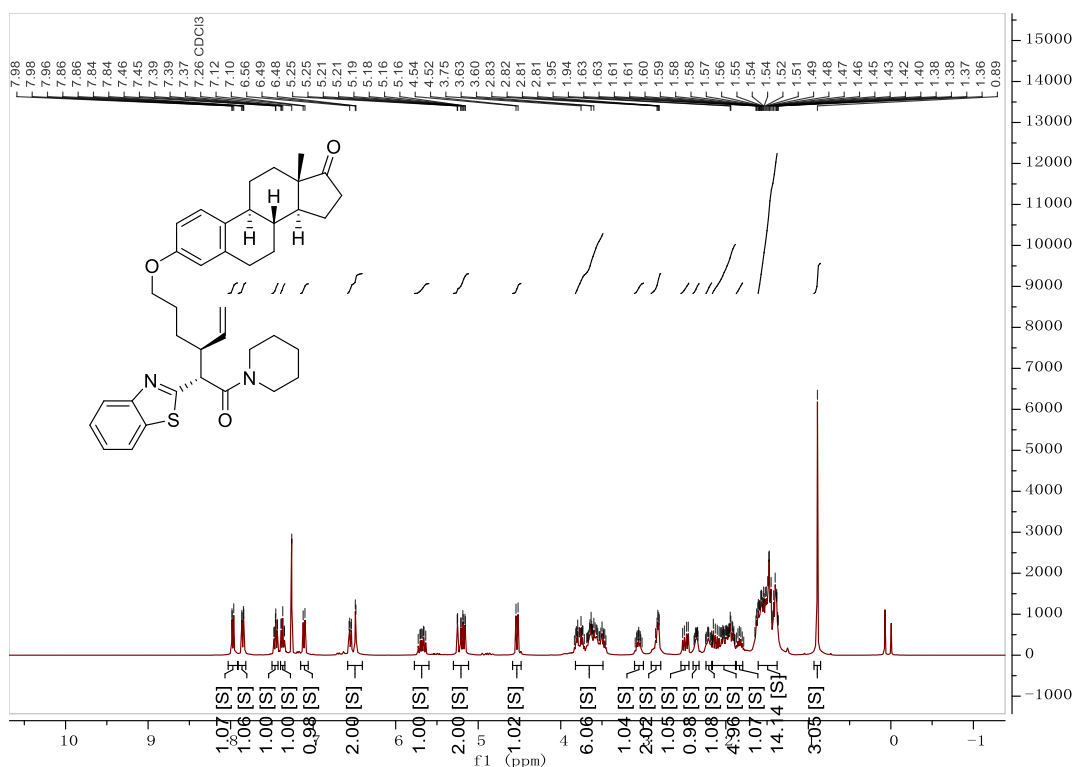
¹H NMR, CDCl₃, 400 MHz



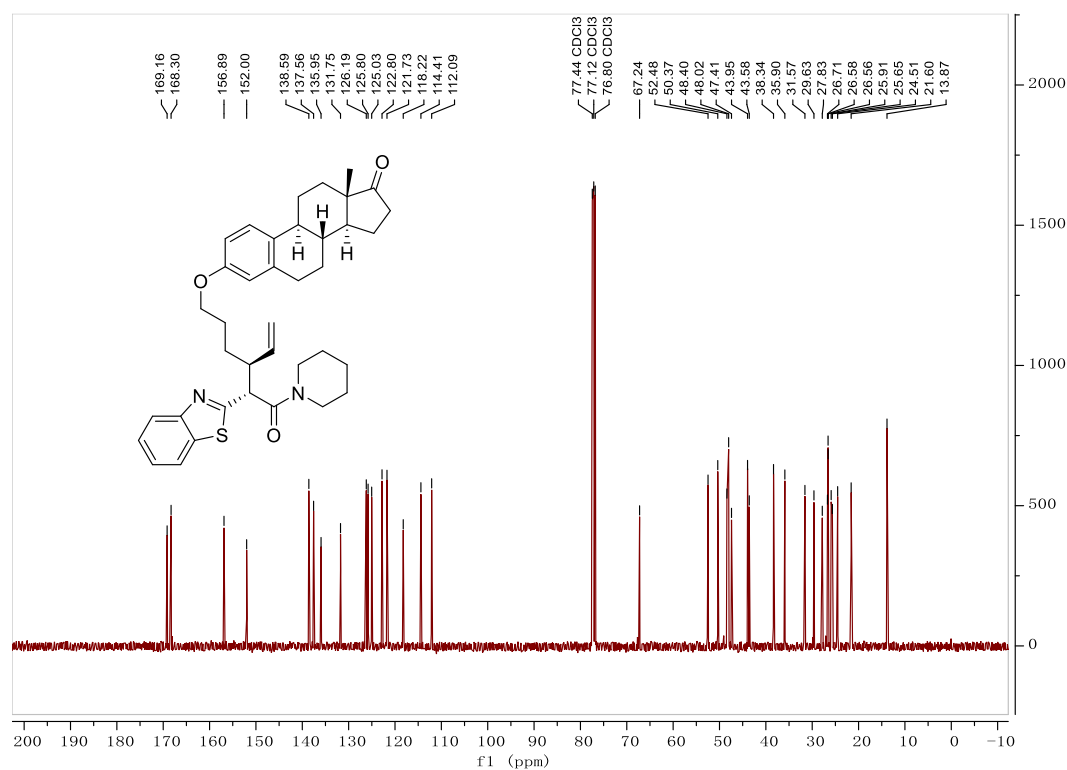
¹³C NMR, CDCl₃, 101 MHz



(8R,9S,13S,14S)-3-(((S)-4-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)hex-5-en-1-yl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (45)
¹H NMR, CDCl₃, 400 MHz

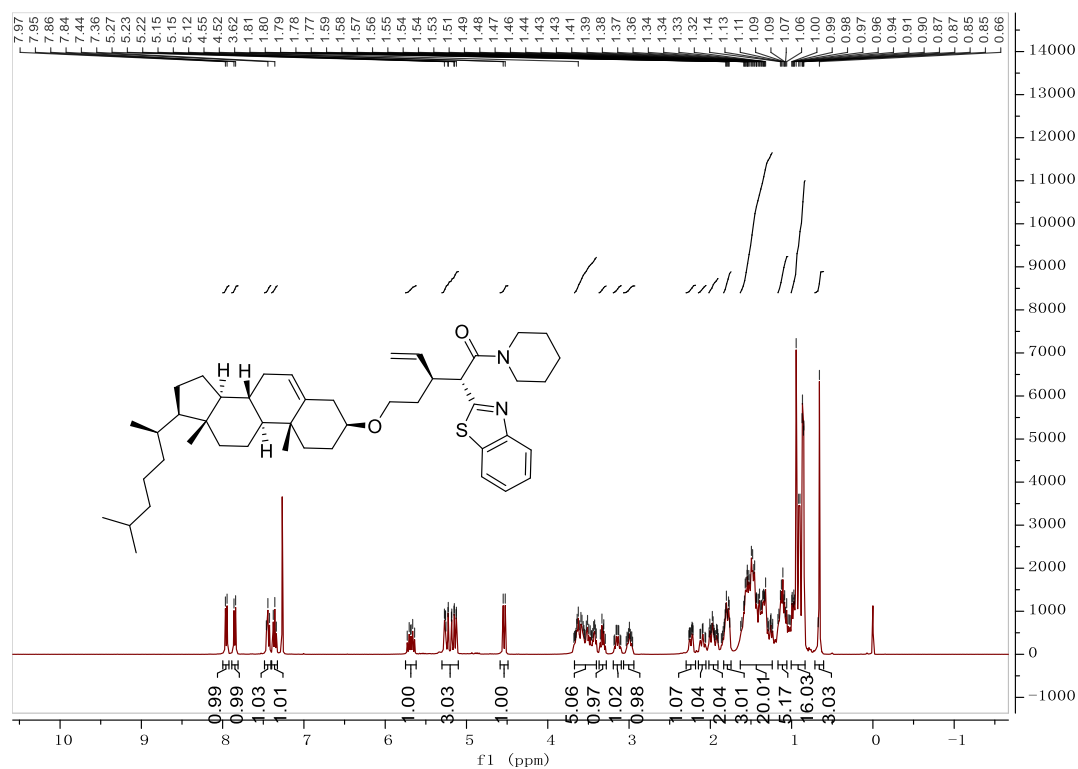


(8R,9S,13S,14S)-3-(((S)-4-((R)-1-(benzo[d]thiazol-2-yl)-2-oxo-2-(piperidin-1-yl)ethyl)hex-5-en-1-yl)oxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (45)
¹³C NMR, CDCl₃, 101 MHz

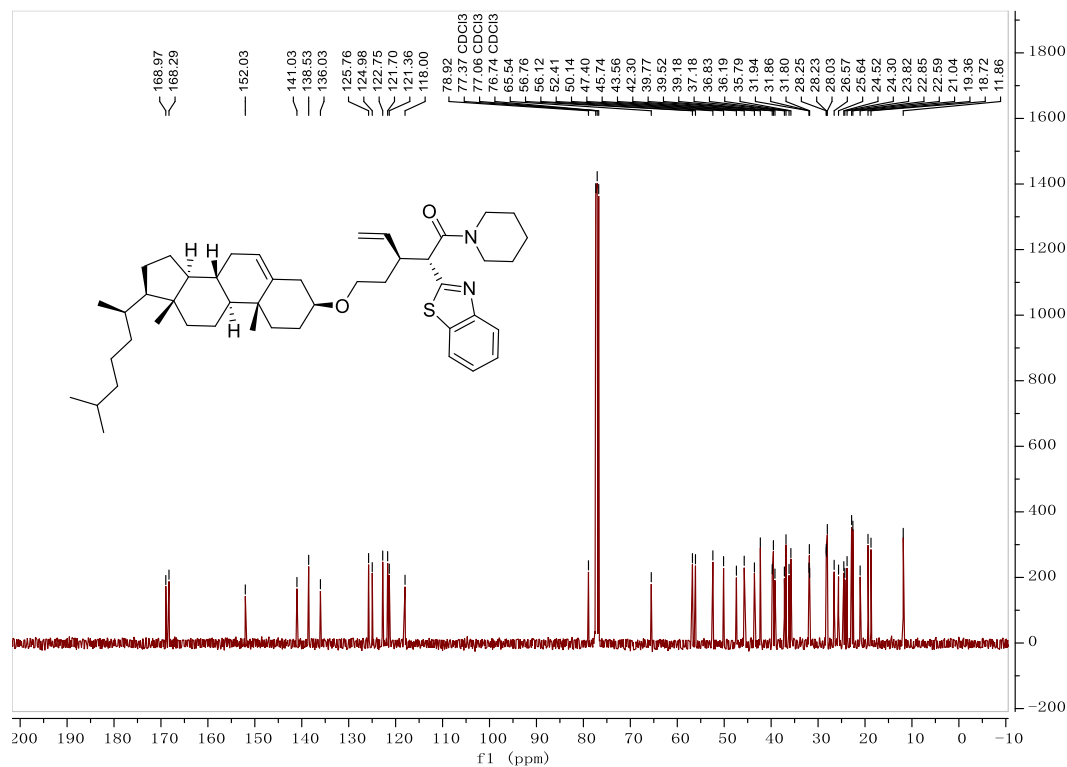


(2R,3S)-2-(benzo[d]thiazol-2-yl)-6-(((3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)-1-(piperidin-1-yl)-3-vinylhexan-1-one (46)

¹H NMR, CDCl₃, 400 MHz

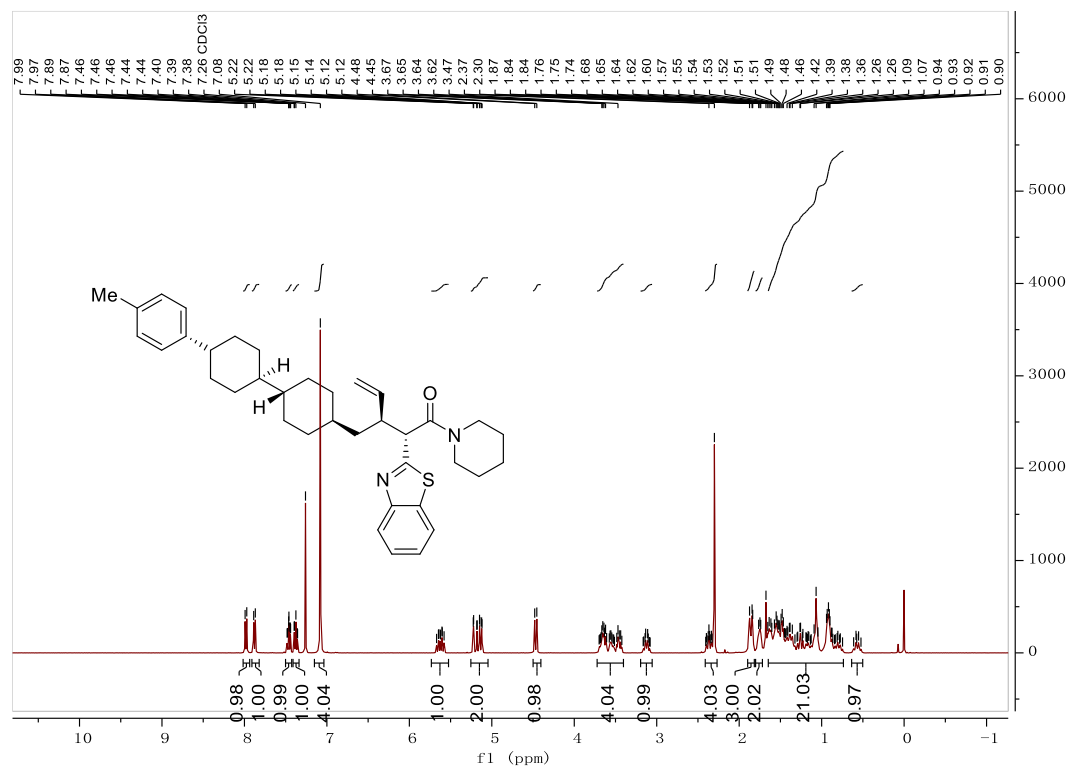


¹³C NMR, CDCl₃, 101 MHz

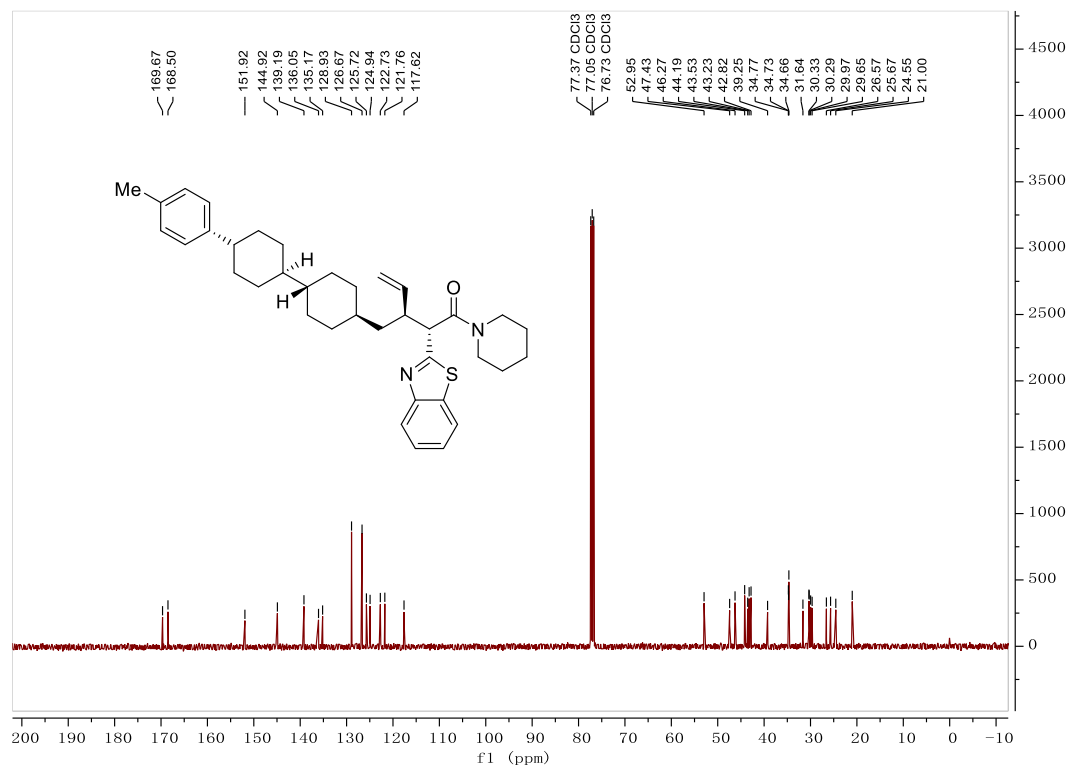


(2R,3S)-2-(benzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-3-(((1S,1'r,4R,4'S)-4'-(p-tolyl)-[1,1'-bi(cyclohexan)]-4-yl)methyl)pent-4-en-1-one (47)

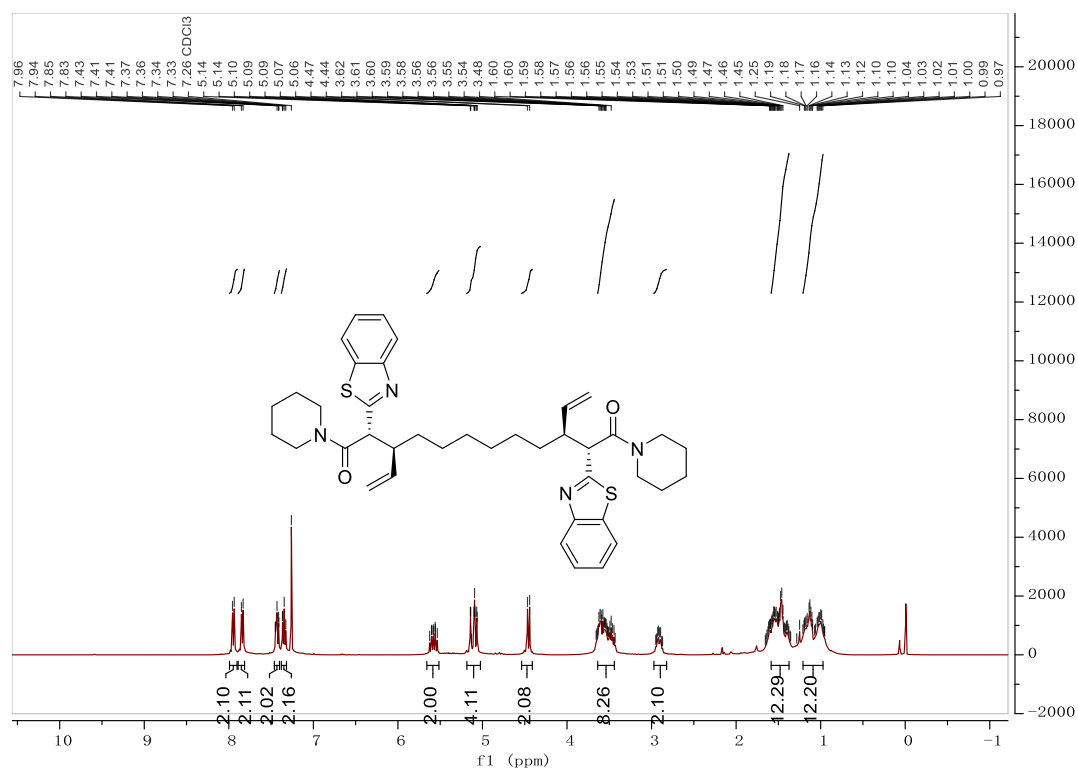
¹H NMR, CDCl₃, 400 MHz



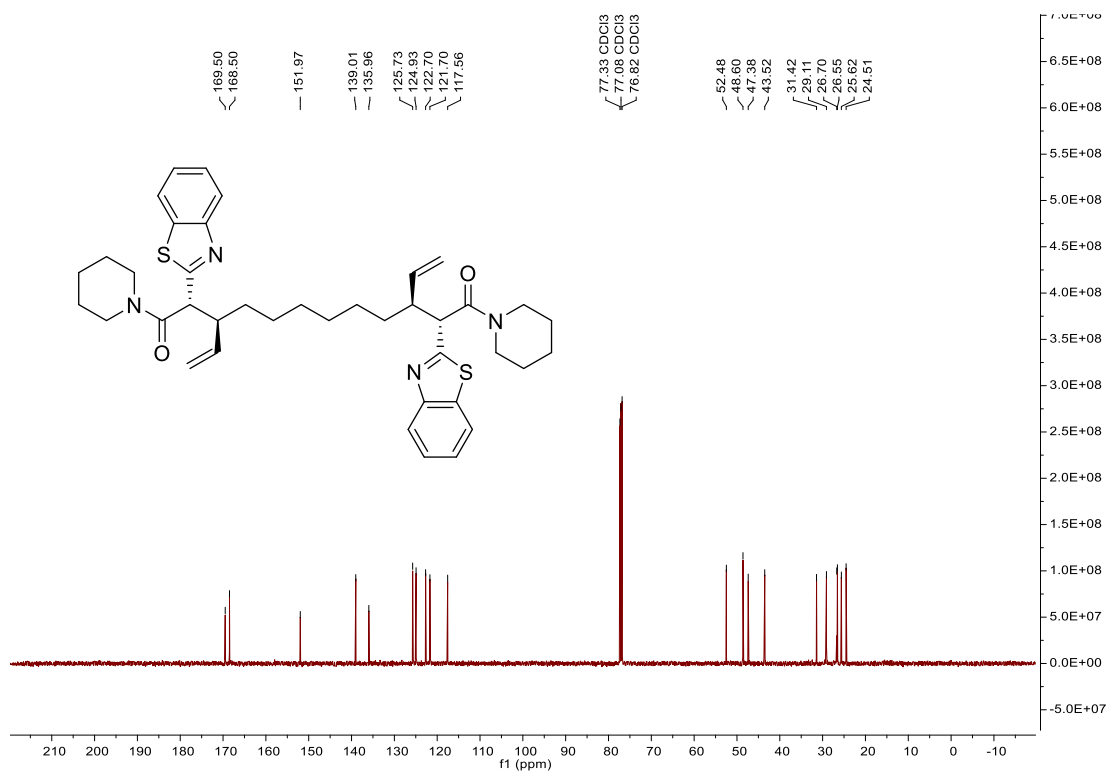
¹³C NMR, CDCl₃, 101 MHz



(2R,3S,10S,11R)-2,11-bis(benzo[d]thiazol-2-yl)-1,12-di(piperidin-1-yl)-3,10-divinyldodecane-1,12-dione (48)
 ^1H NMR, CDCl₃, 400 MHz

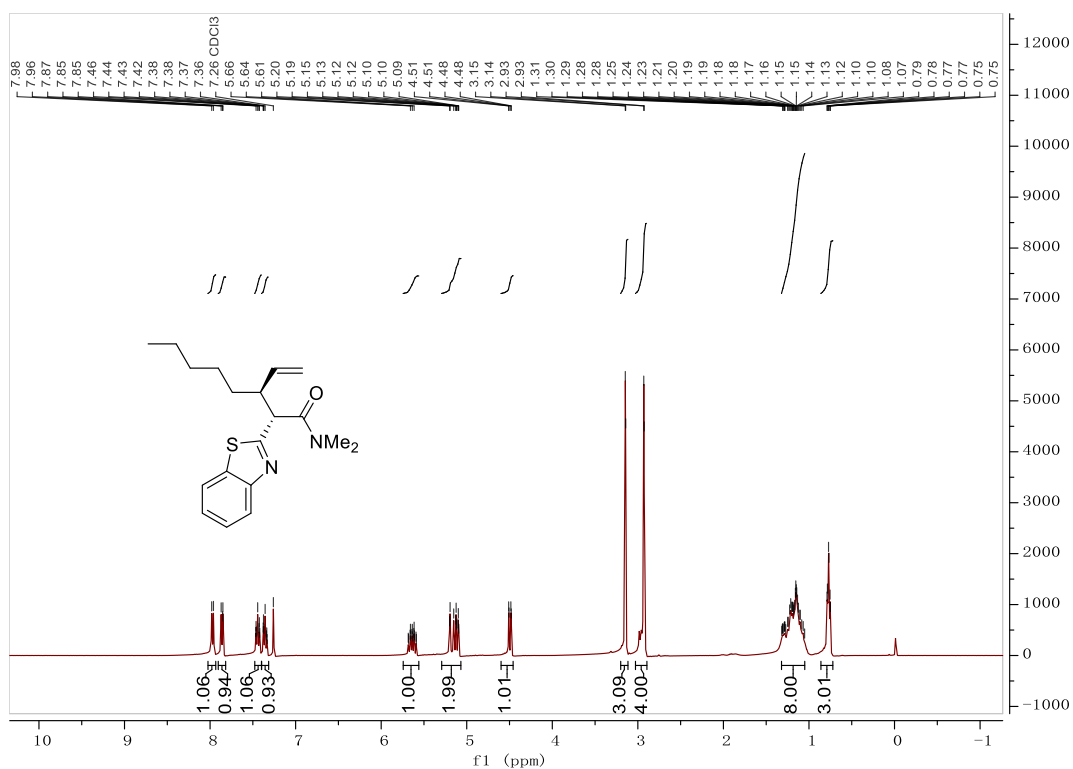


^{13}C NMR, CDCl₃, 101 MHz

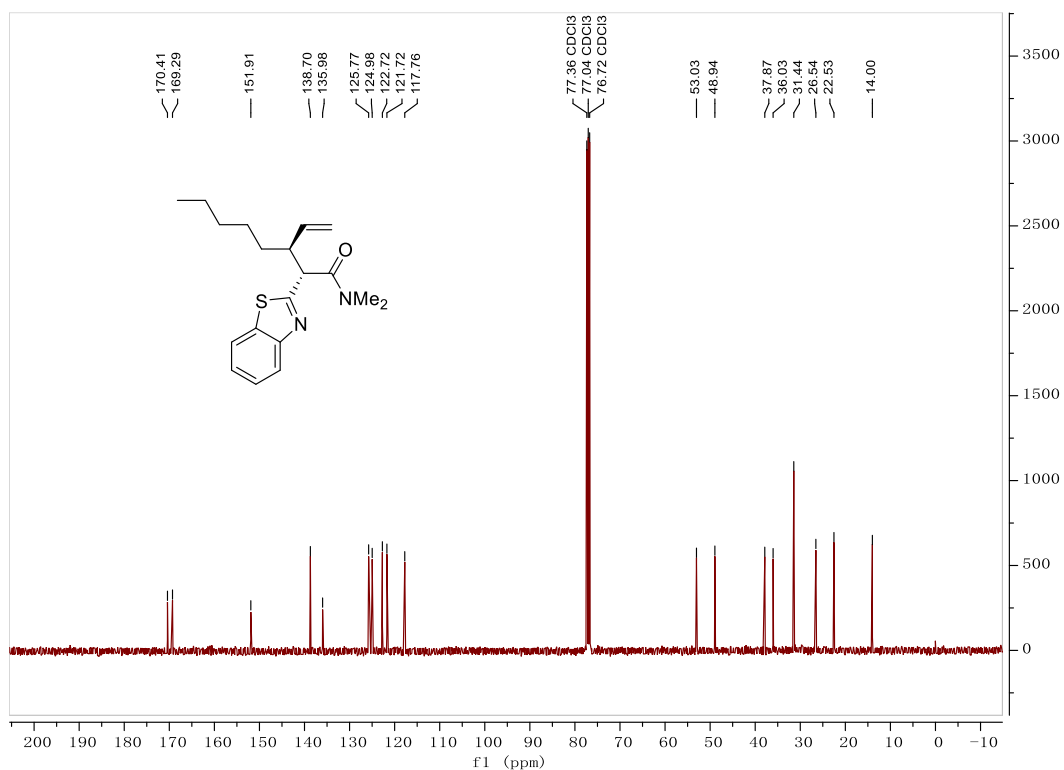


(2R,3S)-2-(benzo[d]thiazol-2-yl)-N,N-dimethyl-3-vinyloctanamide (7)

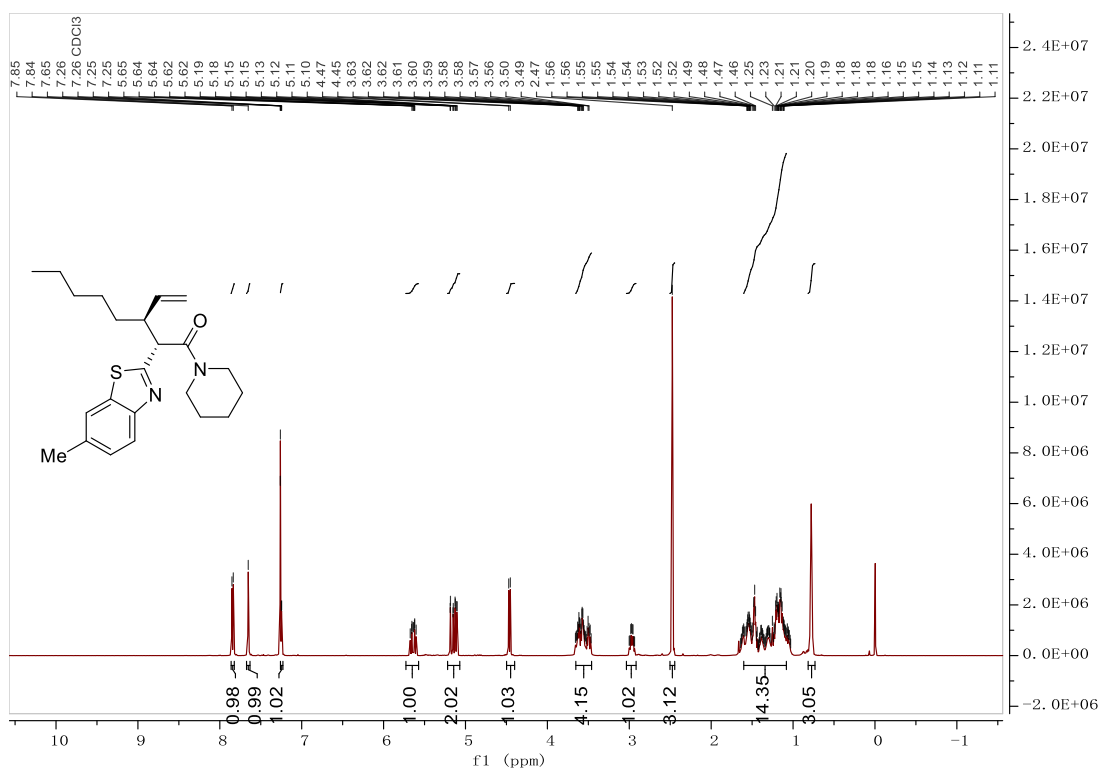
¹H NMR, CDCl₃, 400 MHz



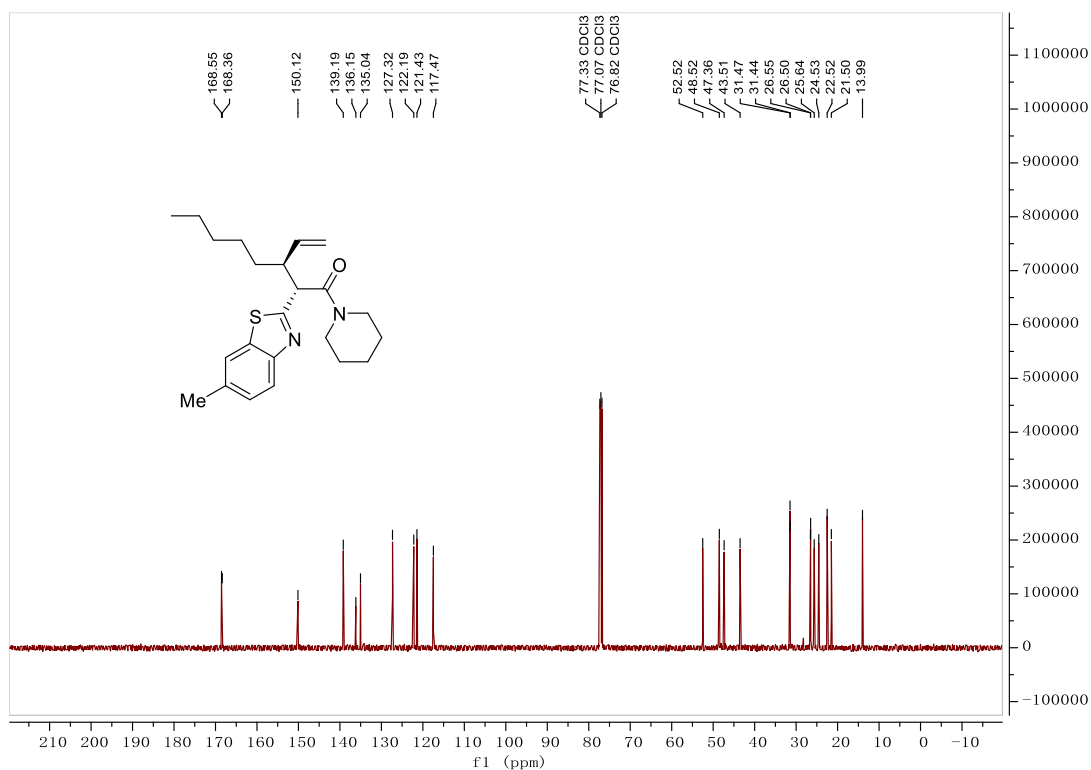
¹³C NMR, CDCl₃, 101 MHz



(2R,3S)-2-(6-methylbenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-3-vinyloctan-1-one (49)
¹H NMR, CDCl₃, 400 MHz

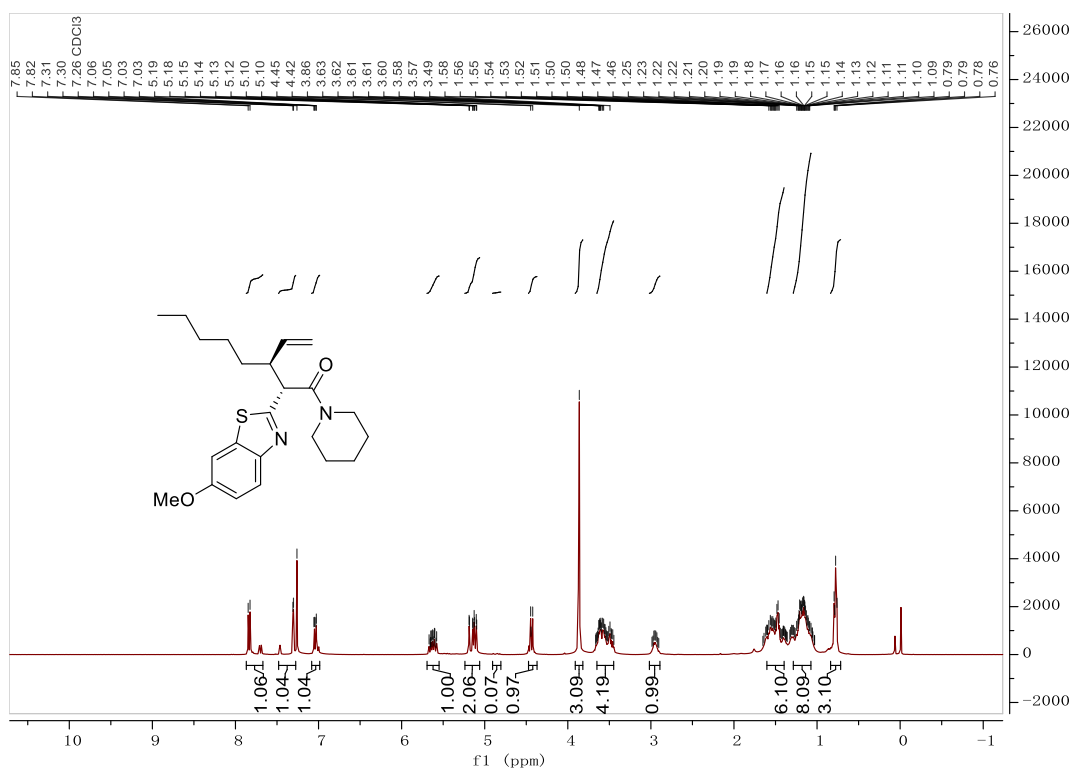


¹³C NMR, CDCl₃, 101 MHz

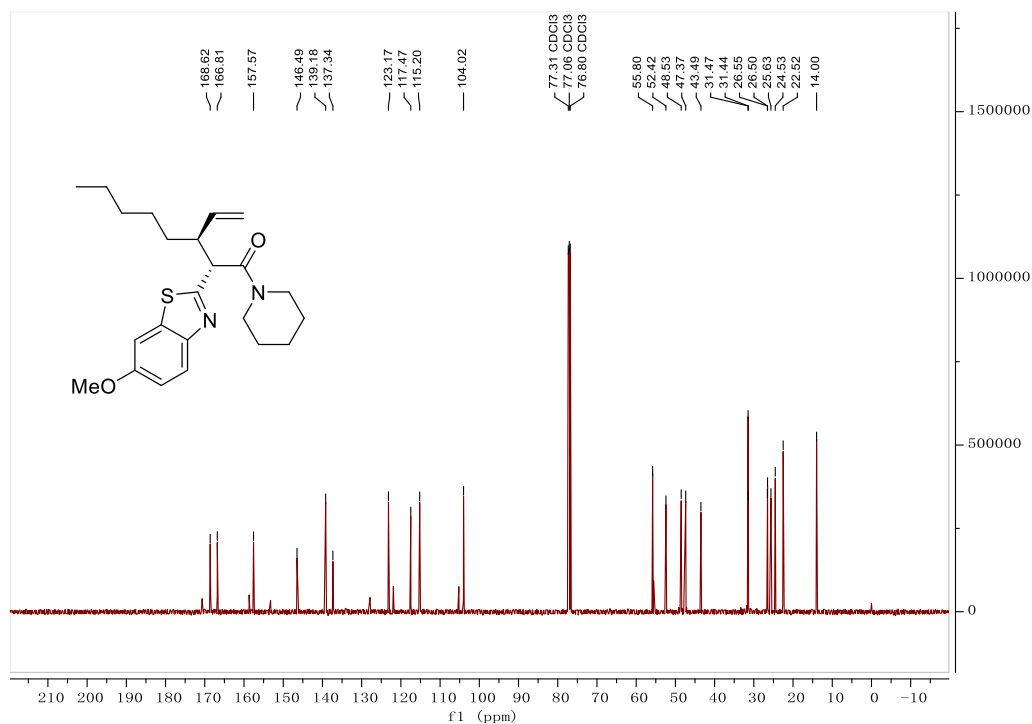


(2R,3S)-2-(6-methoxybenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-3-vinyloctan-1-one (50)

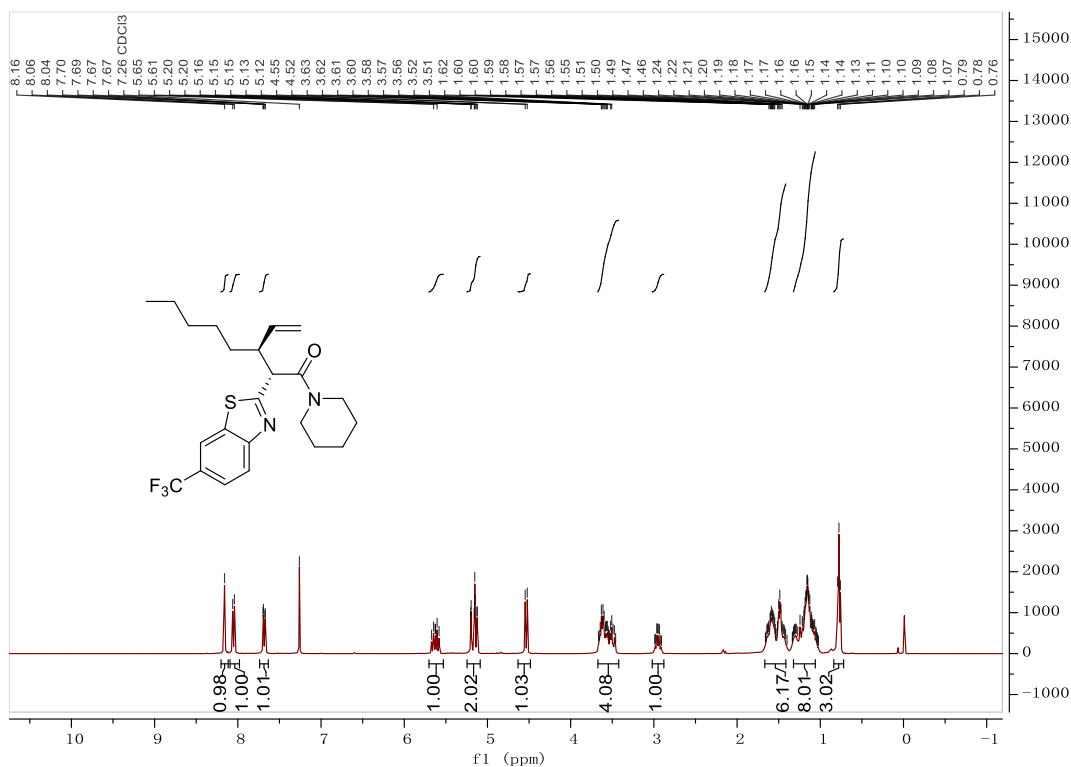
¹H NMR, CDCl₃, 400 MHz



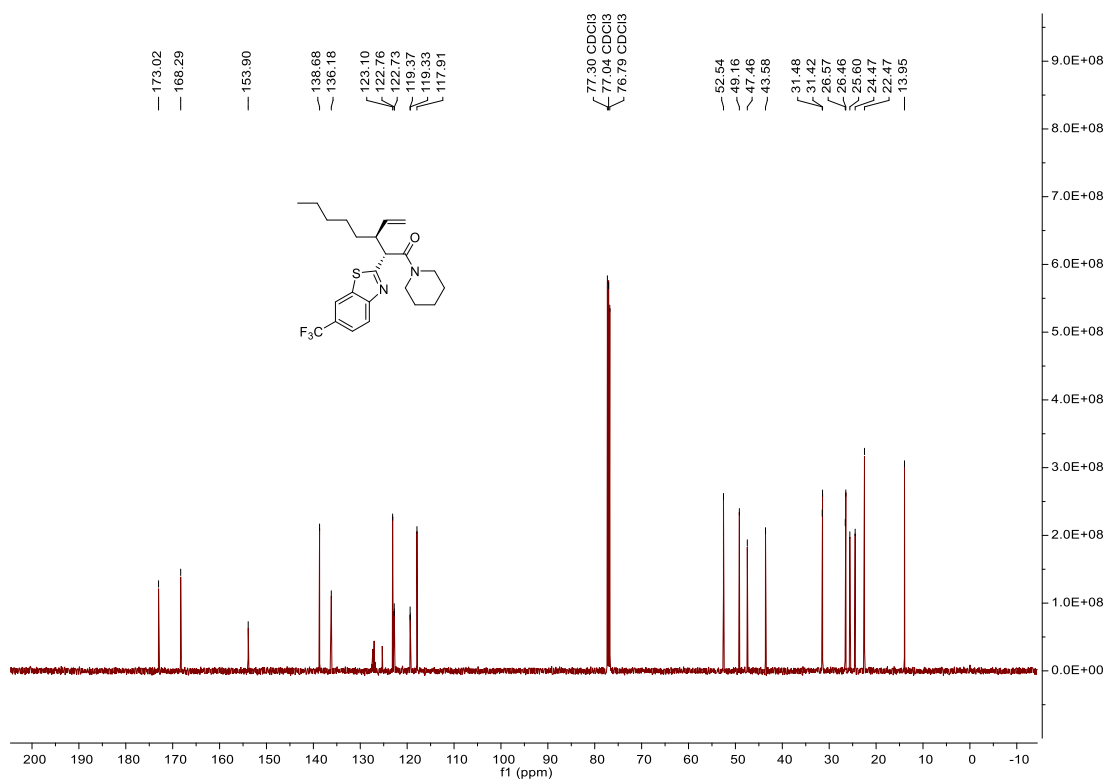
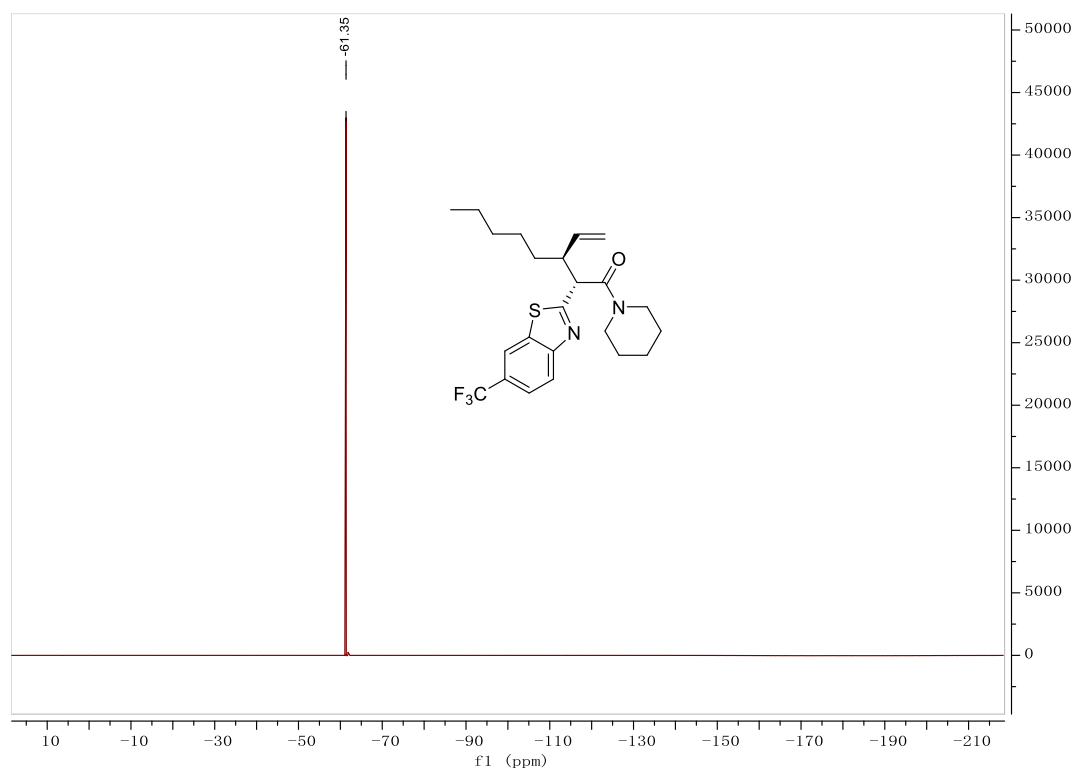
¹³C NMR, CDCl₃, 101 MHz



(2R,3S)-1-(piperidin-1-yl)-2-(6-(trifluoromethyl)benzo[d]thiazol-2-yl)-3-vinyloctan-1-one (51)
¹H NMR, CDCl₃, 400 MHz

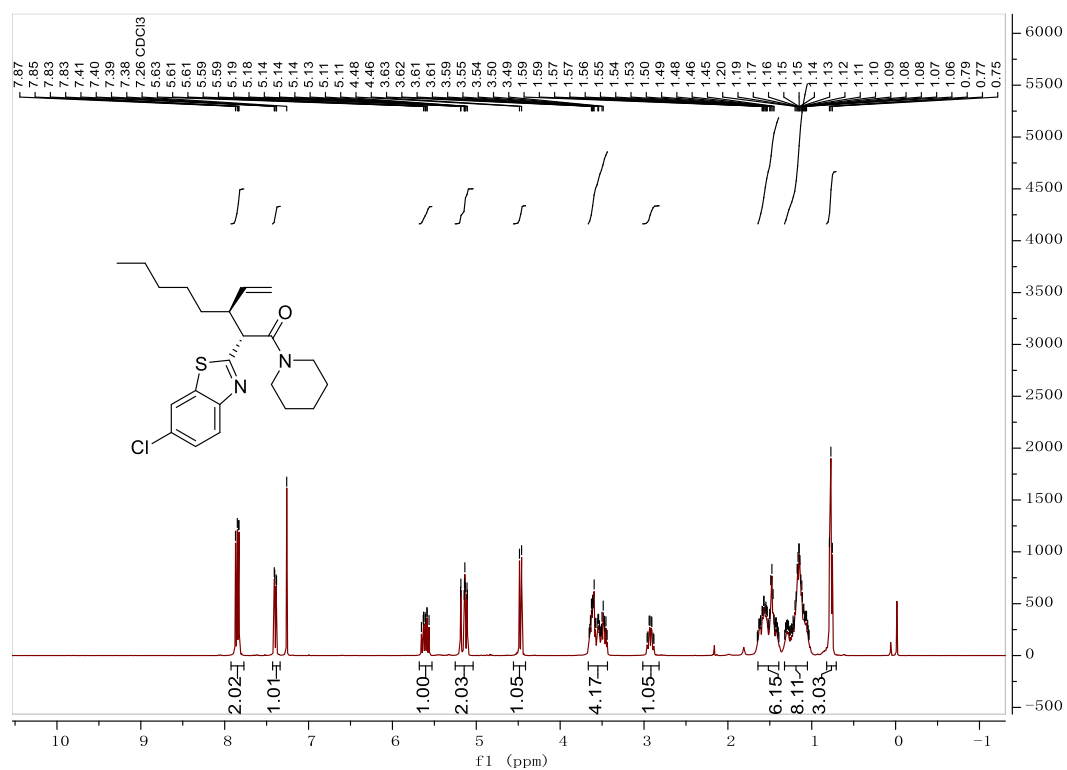


¹⁹F NMR, CDCl₃, 376 MHz

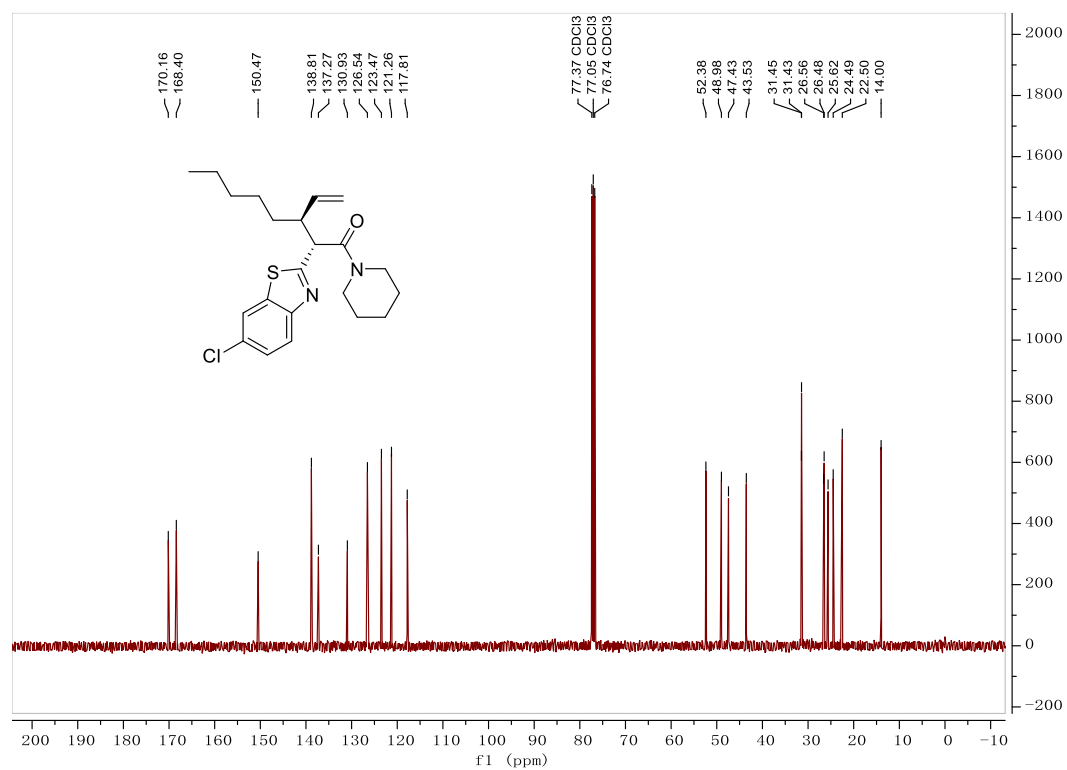


(2R,3S)-2-(6-chlorobenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-3-vinyloctan-1-one (52)

^1H NMR, CDCl_3 , 400 MHz

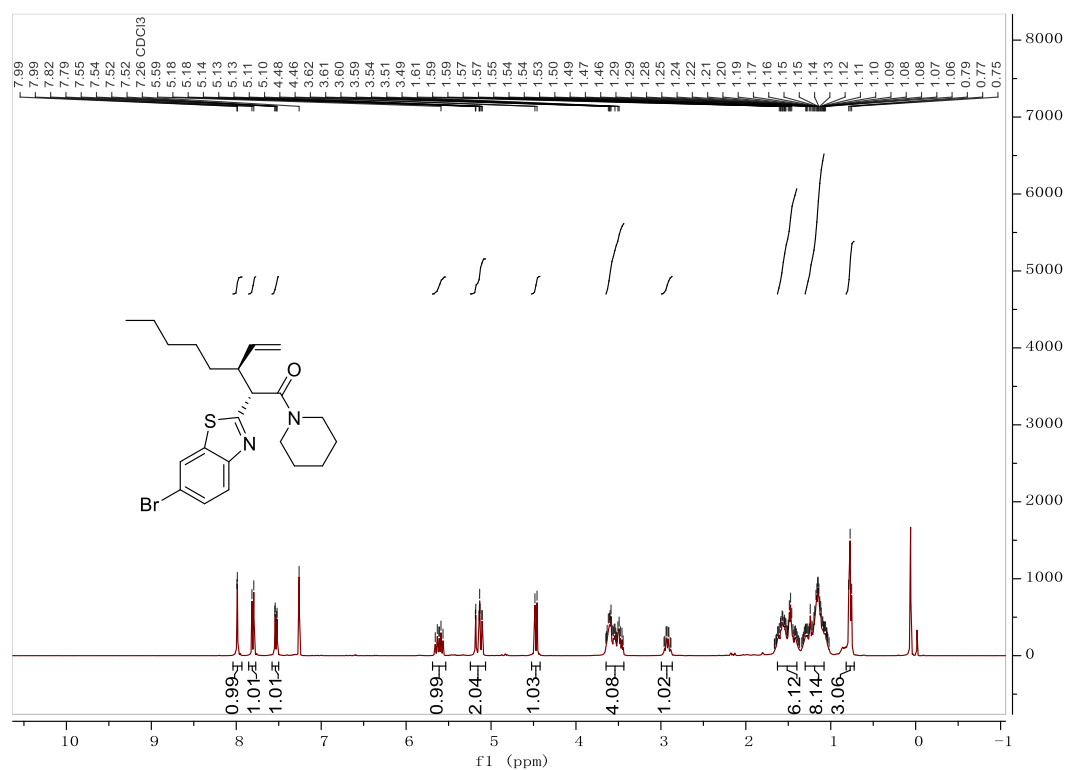


¹³C NMR, CDCl₃, 101 MHz

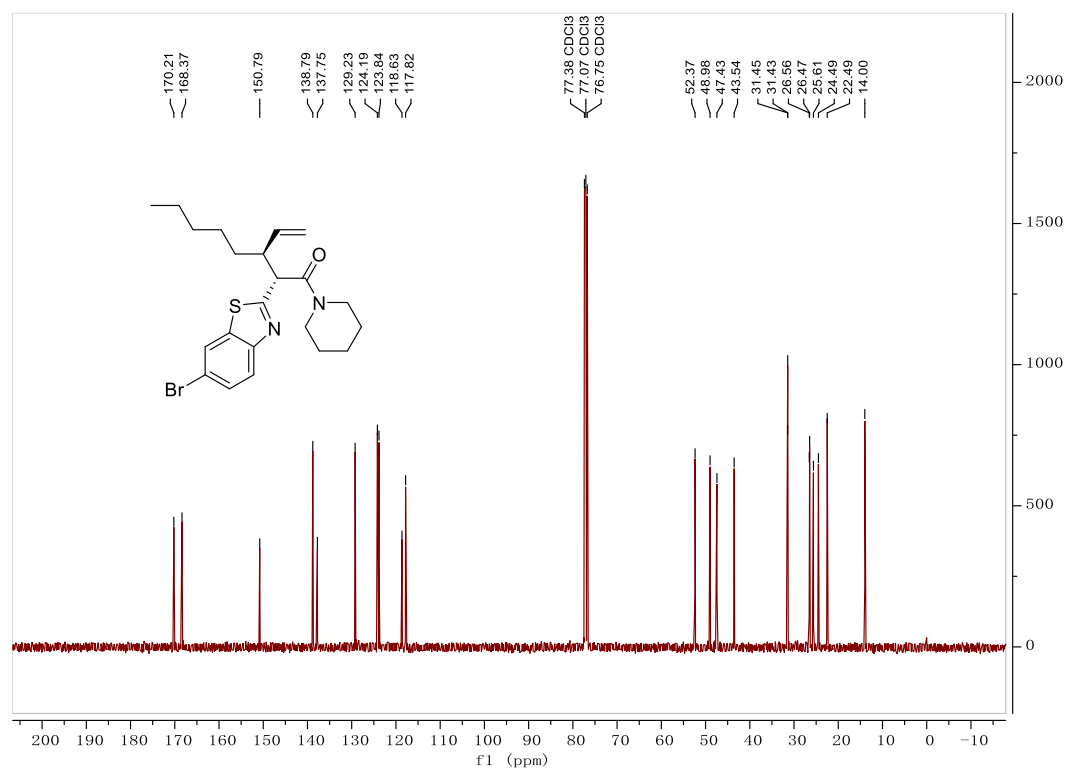


(2R,3S)-2-(6-bromobenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-3-vinyloctan-1-one (53)

¹H NMR, CDCl₃, 400 MHz

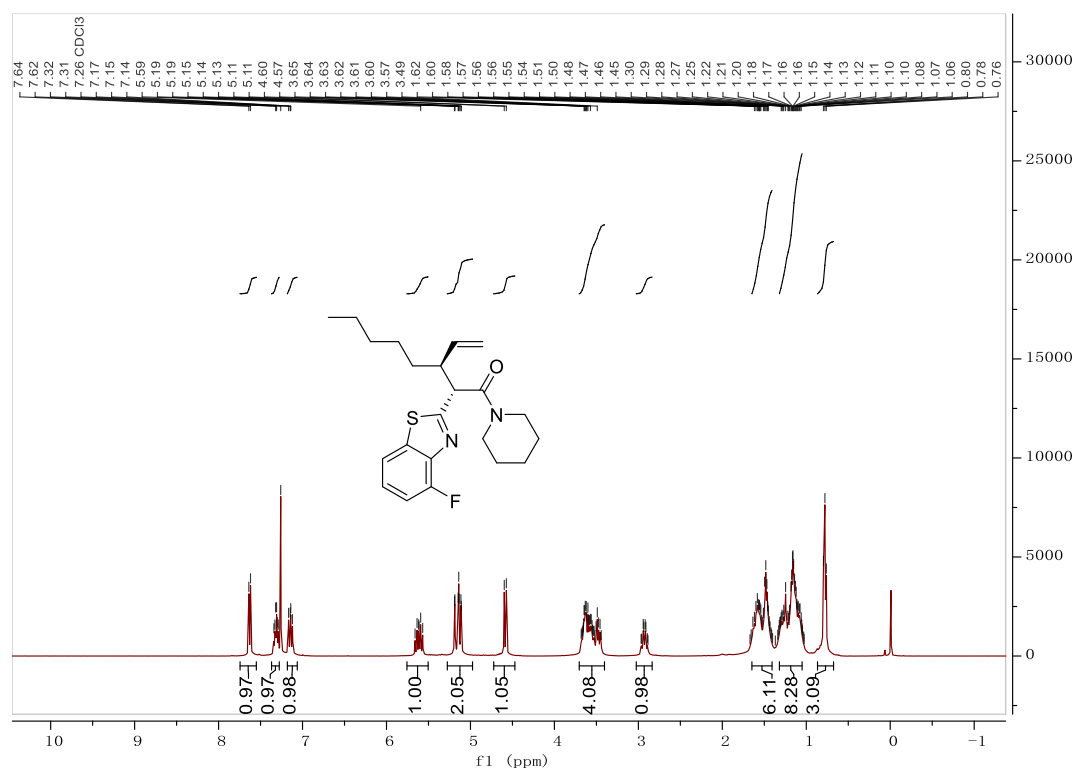


¹³C NMR, CDCl₃, 101 MHz

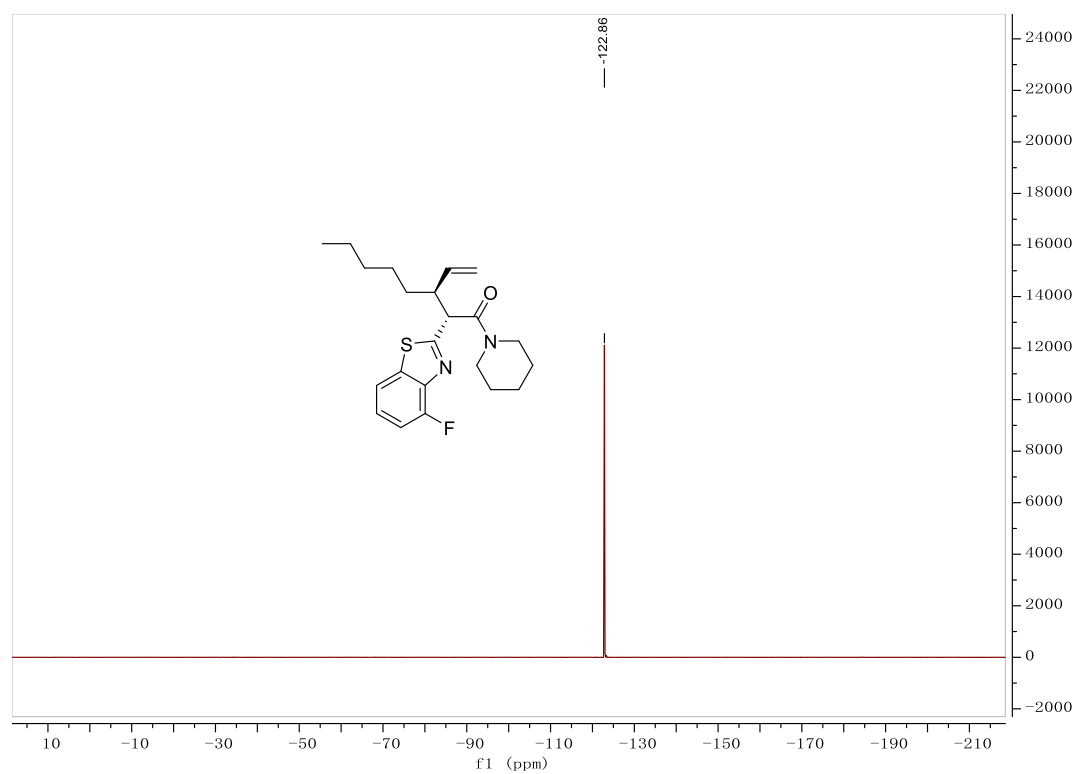


(2R,3S)-2-(4-fluorobenzo[d]thiazol-2-yl)-1-(piperidin-1-yl)-3-vinyloctan-1-one (54)

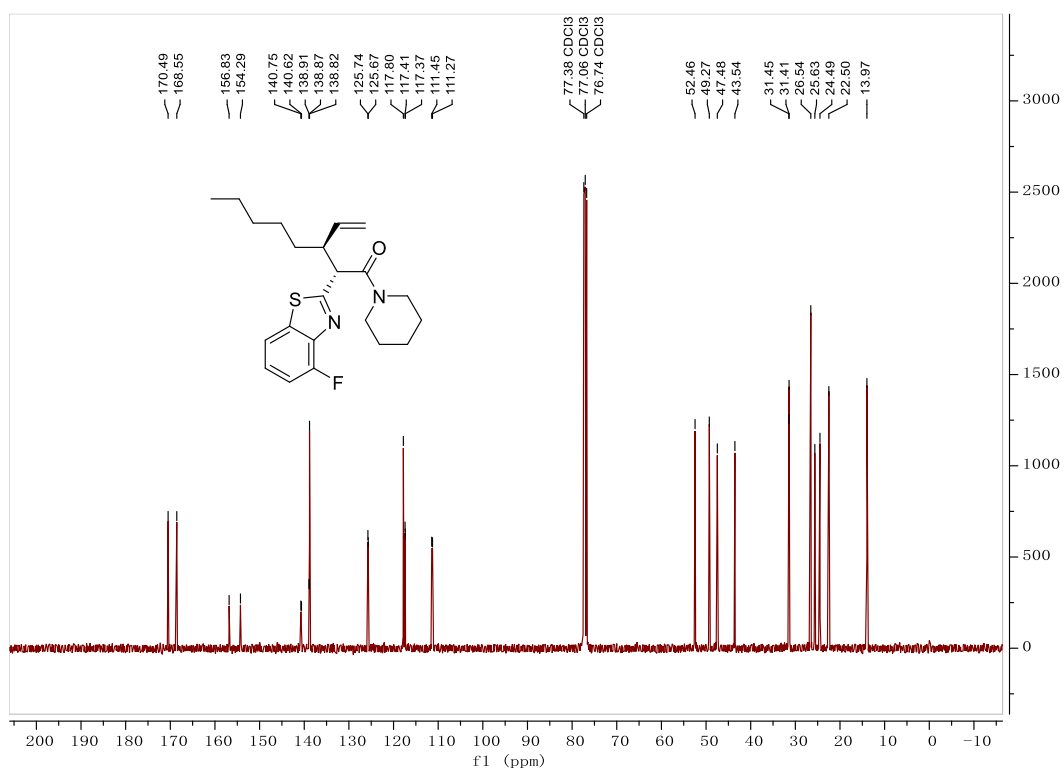
¹H NMR, CDCl₃, 400 MHz



¹⁹F NMR, CDCl₃, 376 MHz

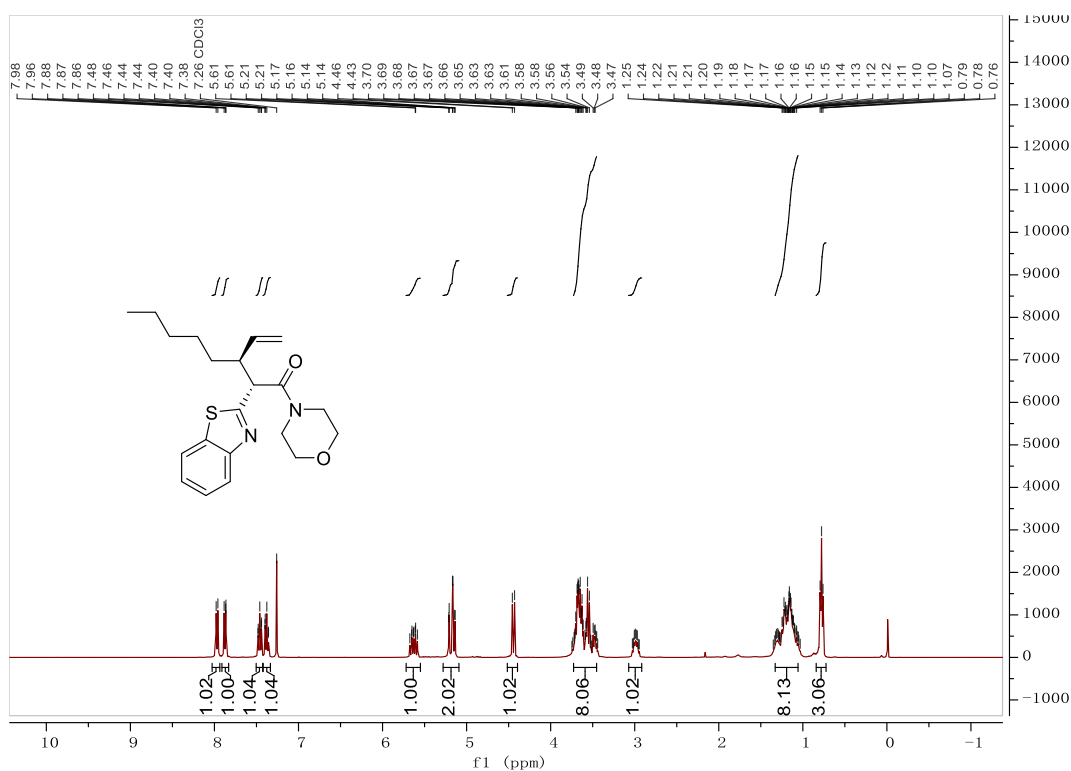


¹³C NMR, CDCl₃, 101 MHz

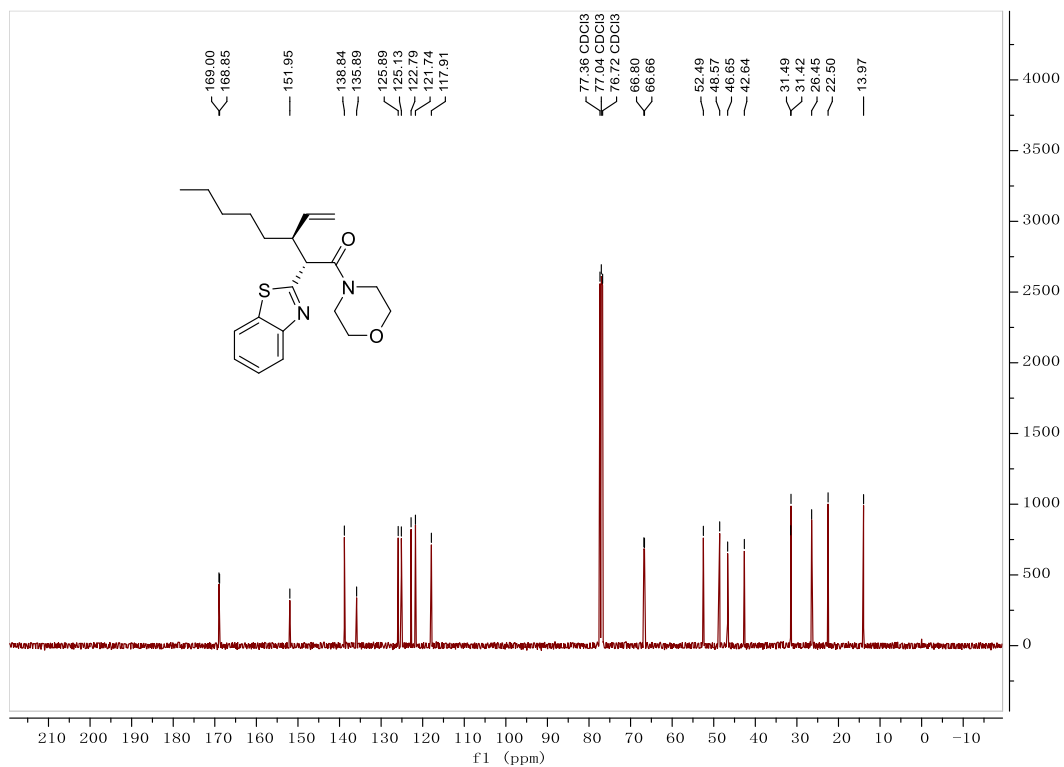


(2R,3S)-2-(benzo[d]thiazol-2-yl)-1-morpholino-3-vinyloctan-1-one (55)

¹H NMR, CDCl₃, 400 MHz

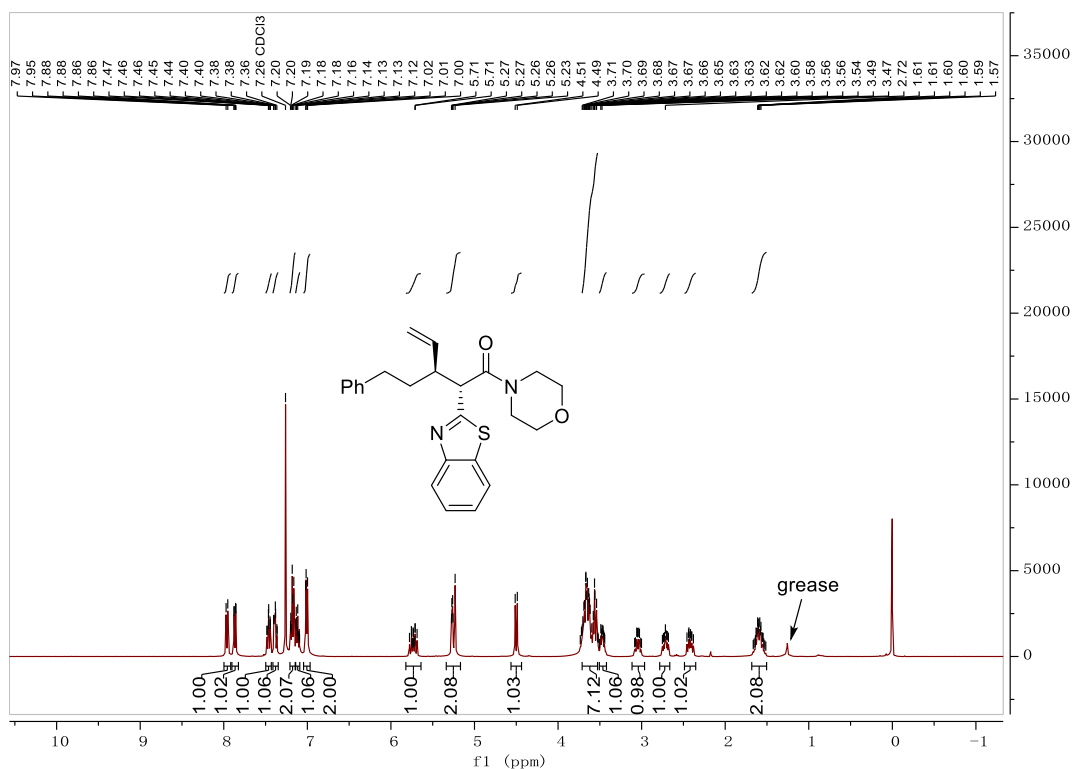


¹³C NMR, CDCl₃, 101 MHz

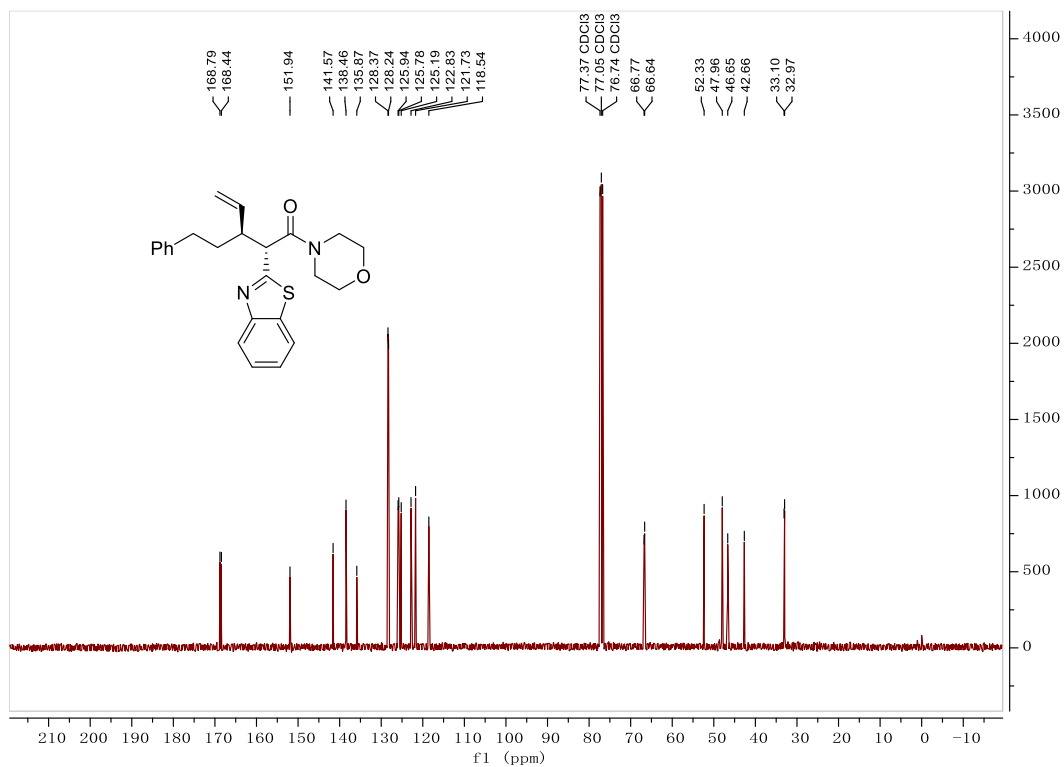


(2R,3S)-2-(benzo[d]thiazol-2-yl)-1-morpholino-3-phenethylpent-4-en-1-one (56)

¹H NMR, CDCl₃, 400 MHz

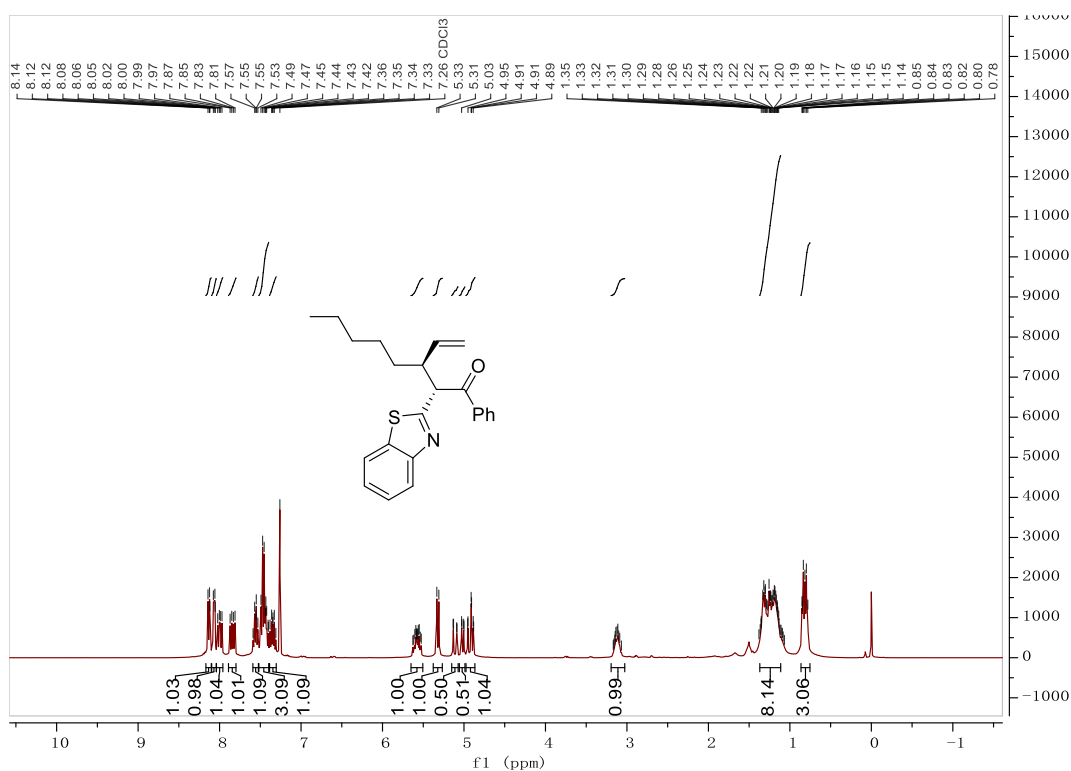


¹³C NMR, CDCl₃, 101 MHz

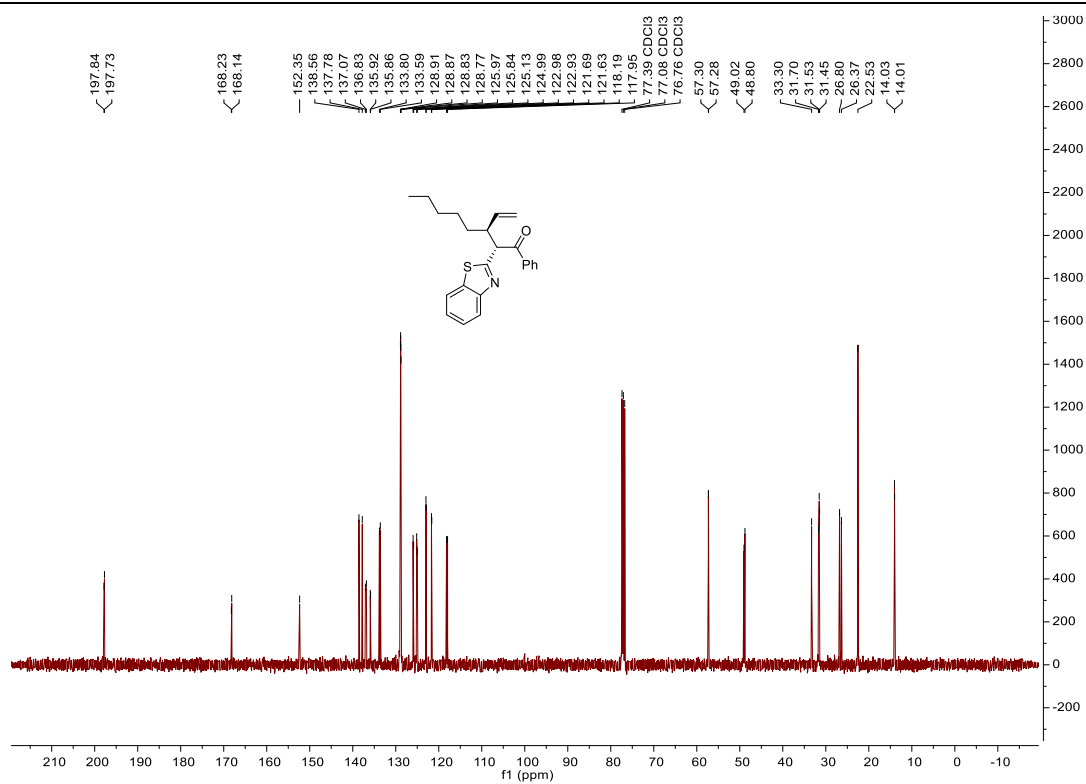


(2R,3S)-2-(benzo[d]thiazol-2-yl)-1-phenyl-3-vinyloctan-1-one (57)

¹H NMR, CDCl₃, 400 MHz

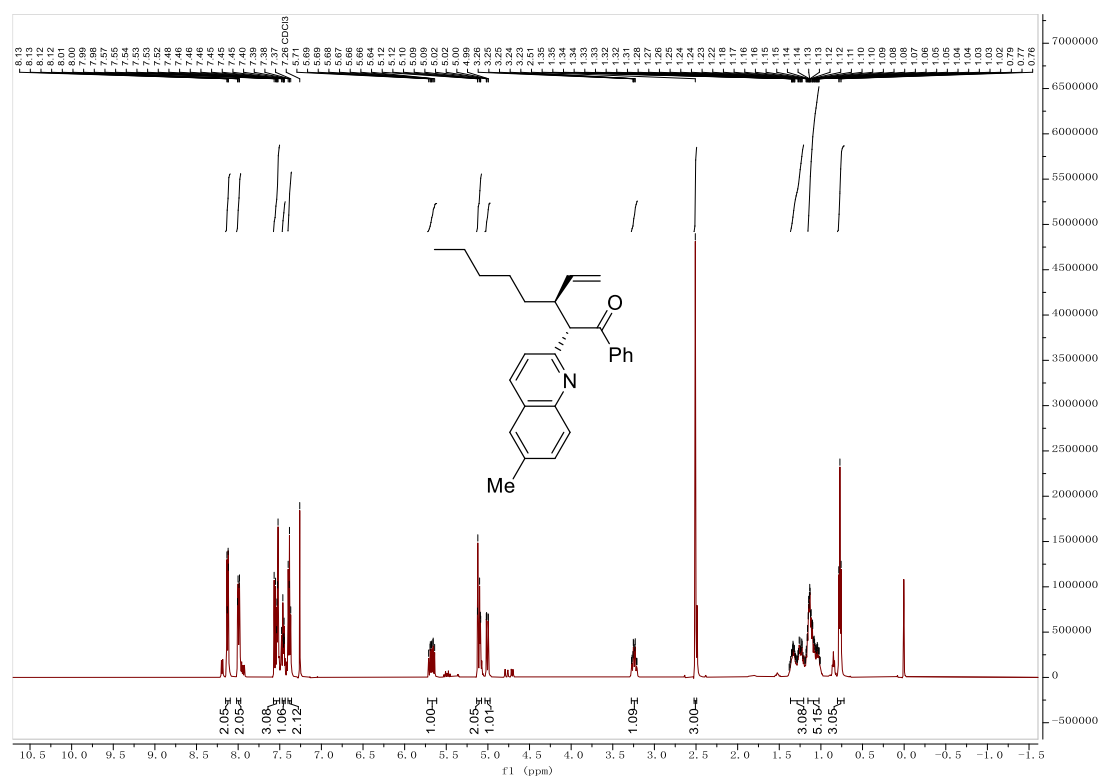


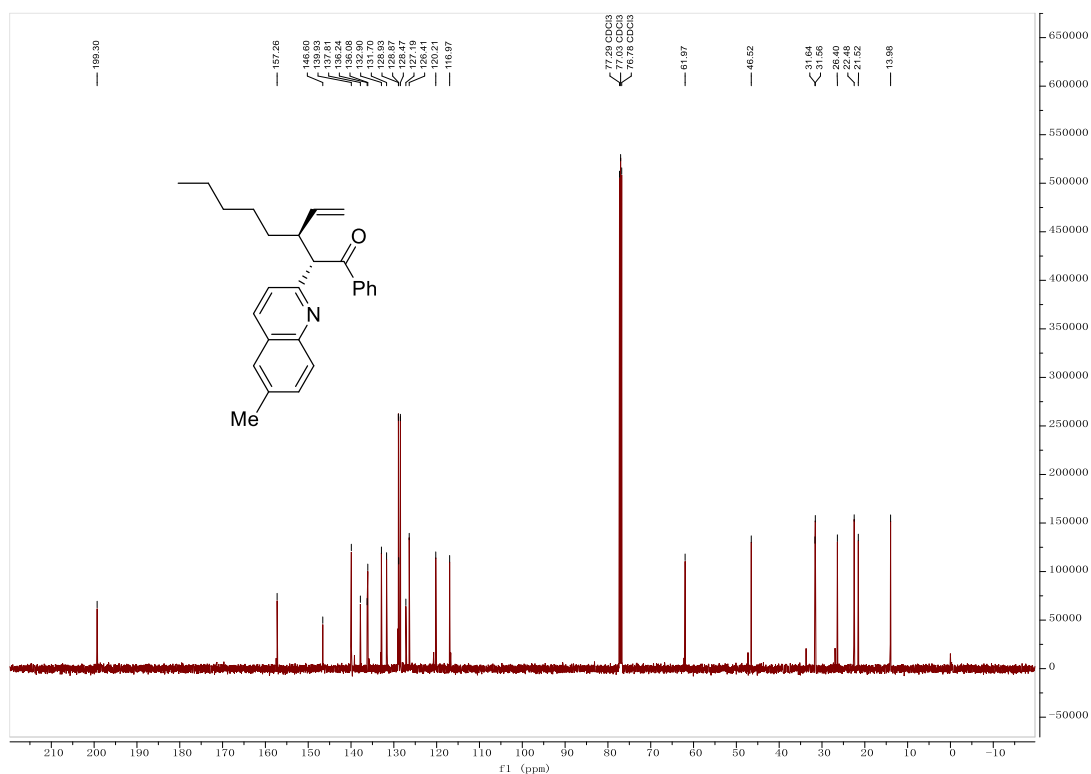
¹³C NMR, CDCl₃, 101 MHz



(2S,3S)-2-(6-methylquinolin-2-yl)-1-phenyl-3-vinyloctan-1-one (58)

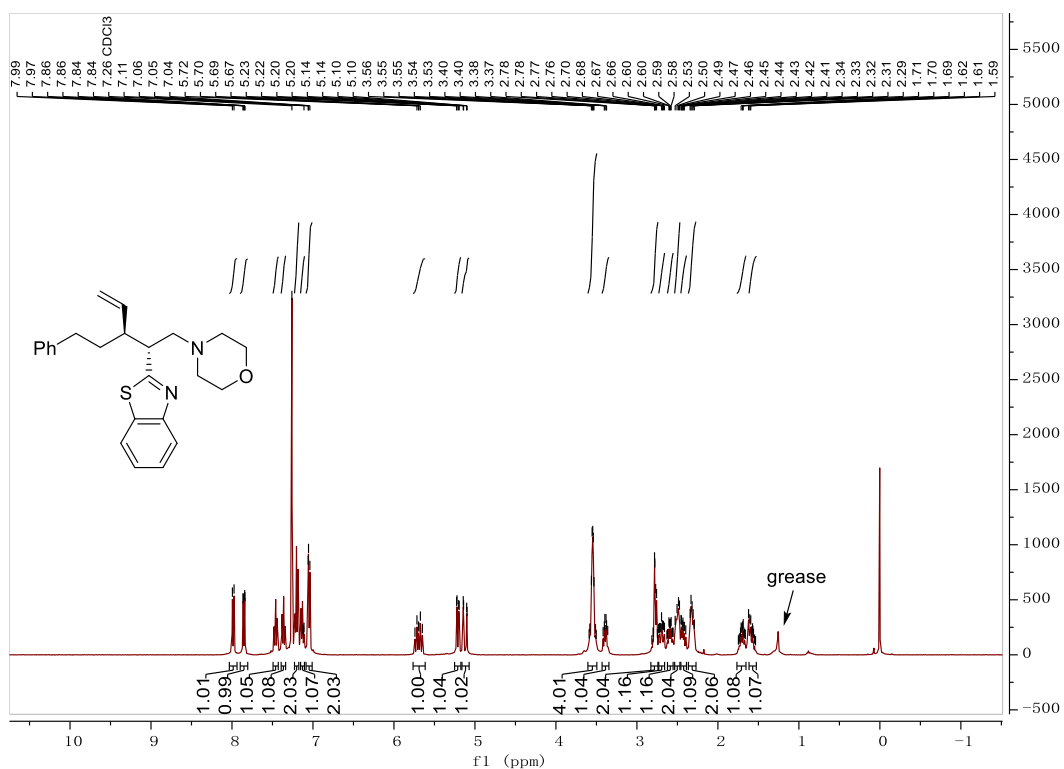
¹H NMR, CDCl₃, 400 MHz



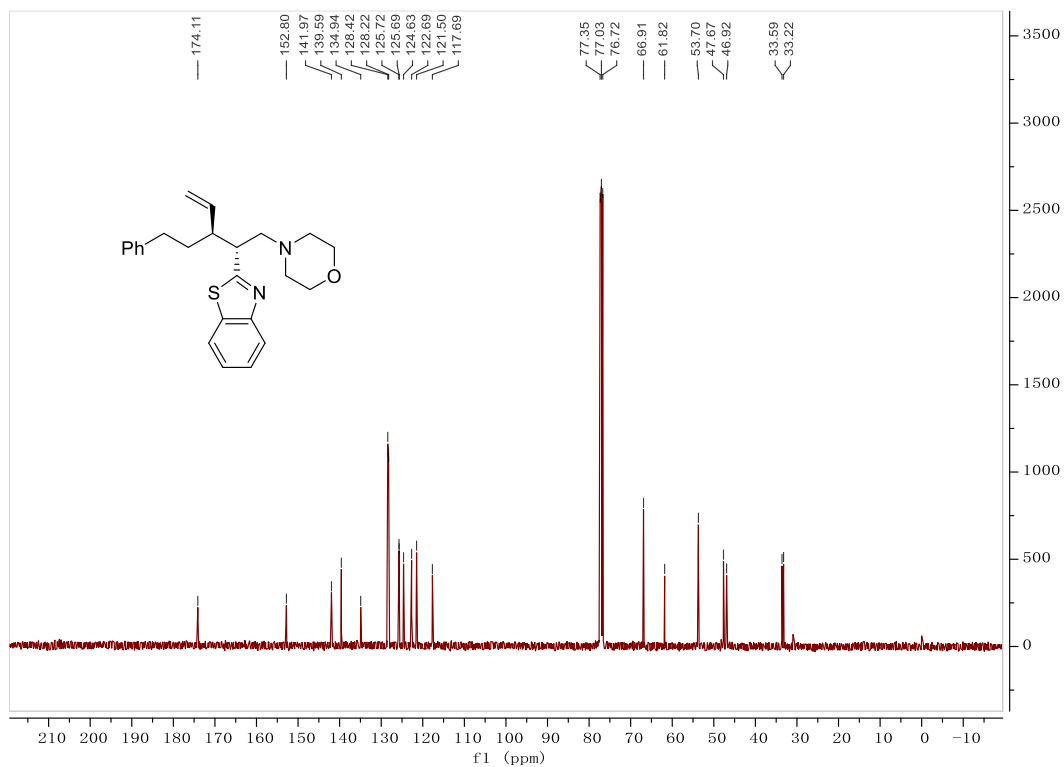


4-((2R,3S)-2-(benzo[d]thiazol-2-yl)-3-phenethylpent-4-en-1-yl)morpholine (59)

¹H NMR, CDCl₃, 400 MHz

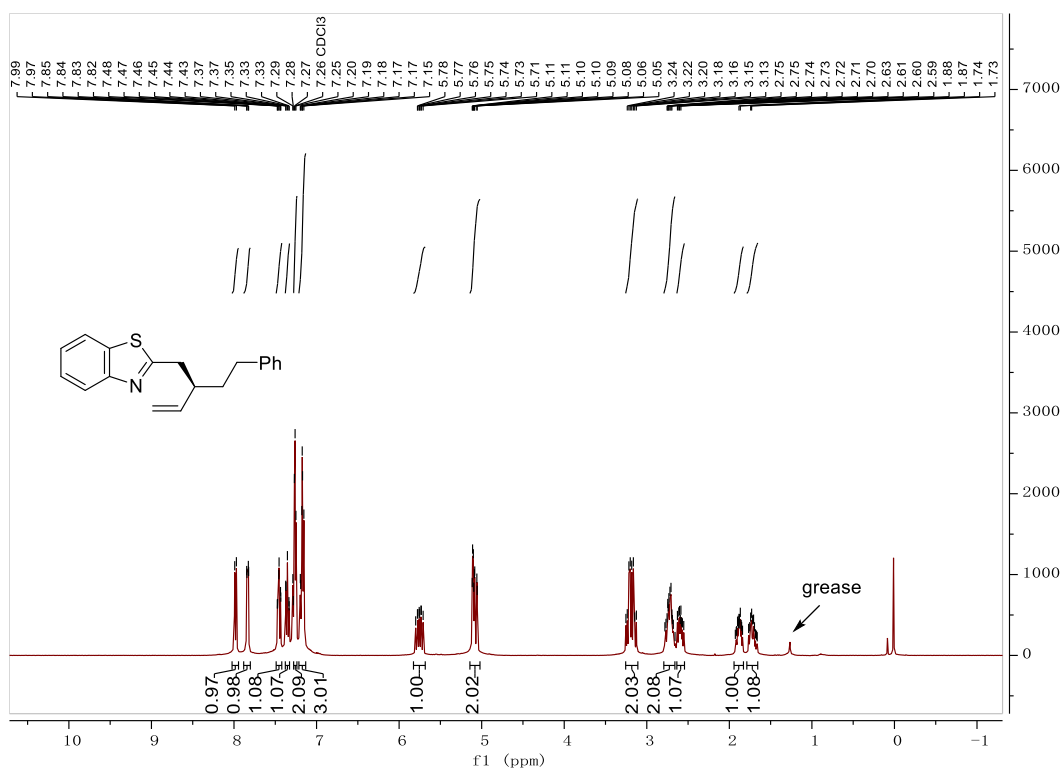


¹³C NMR, CDCl₃, 101 MHz

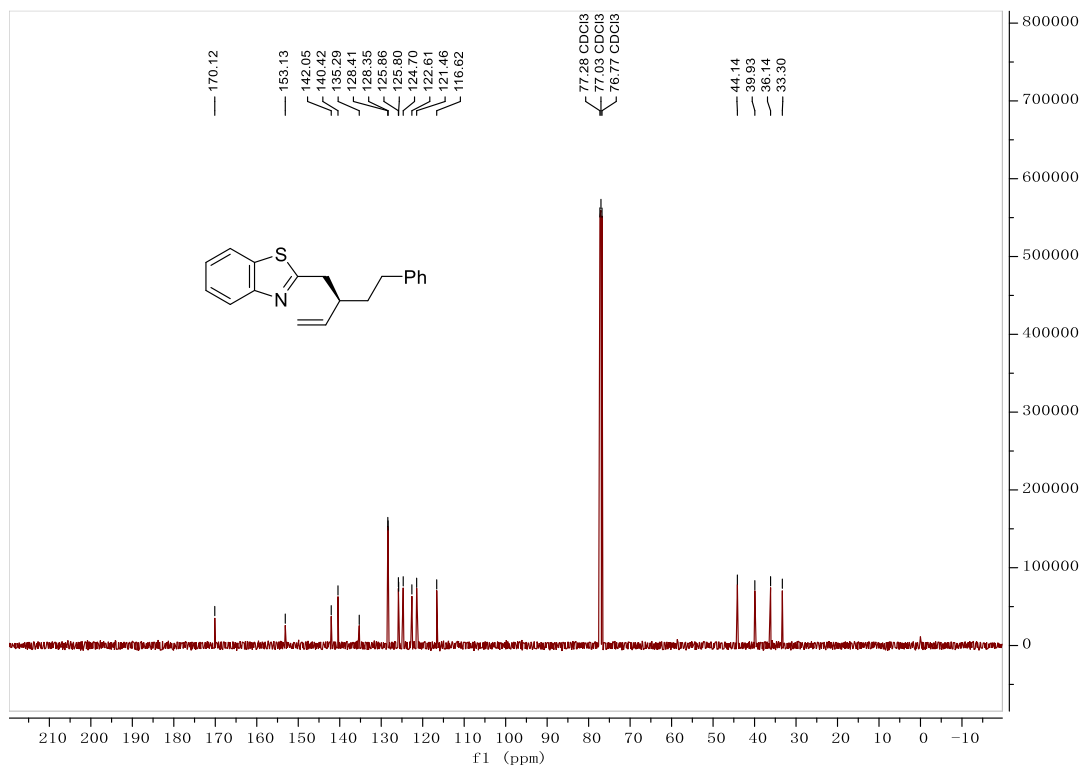


(R)-2-(2-phenethylbut-3-en-1-yl)benzo[d]thiazole (60)

¹H NMR, CDCl₃, 400 MHz

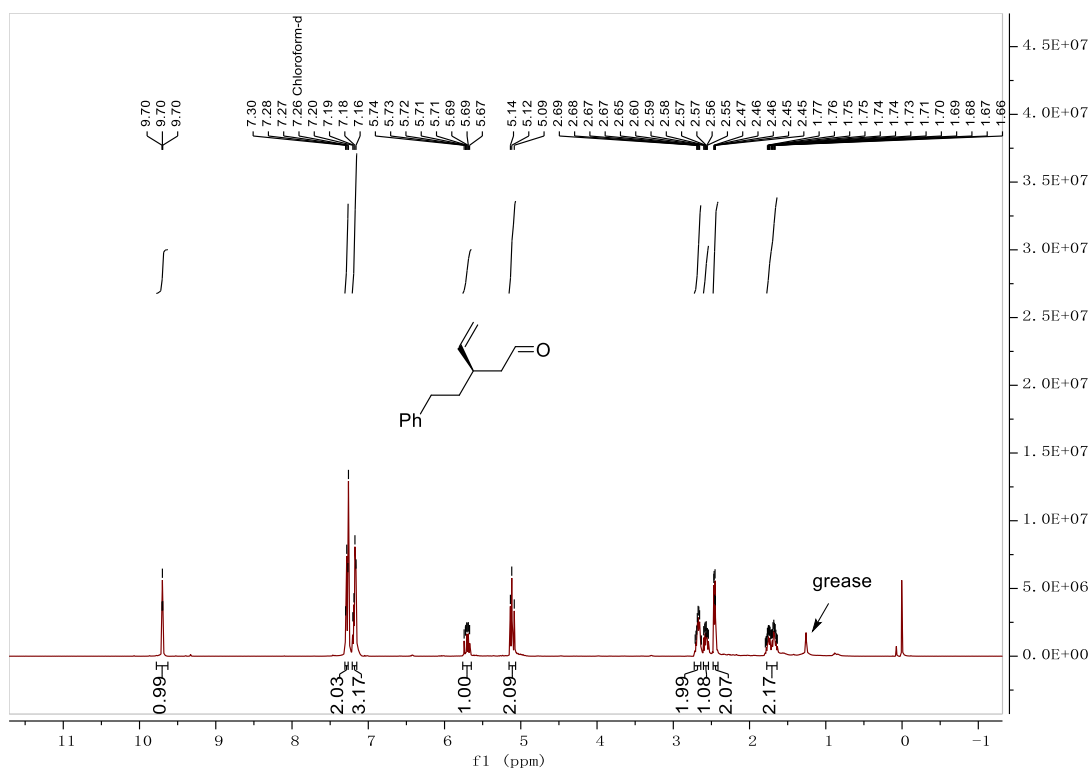


¹³C NMR, CDCl₃, 101 MHz

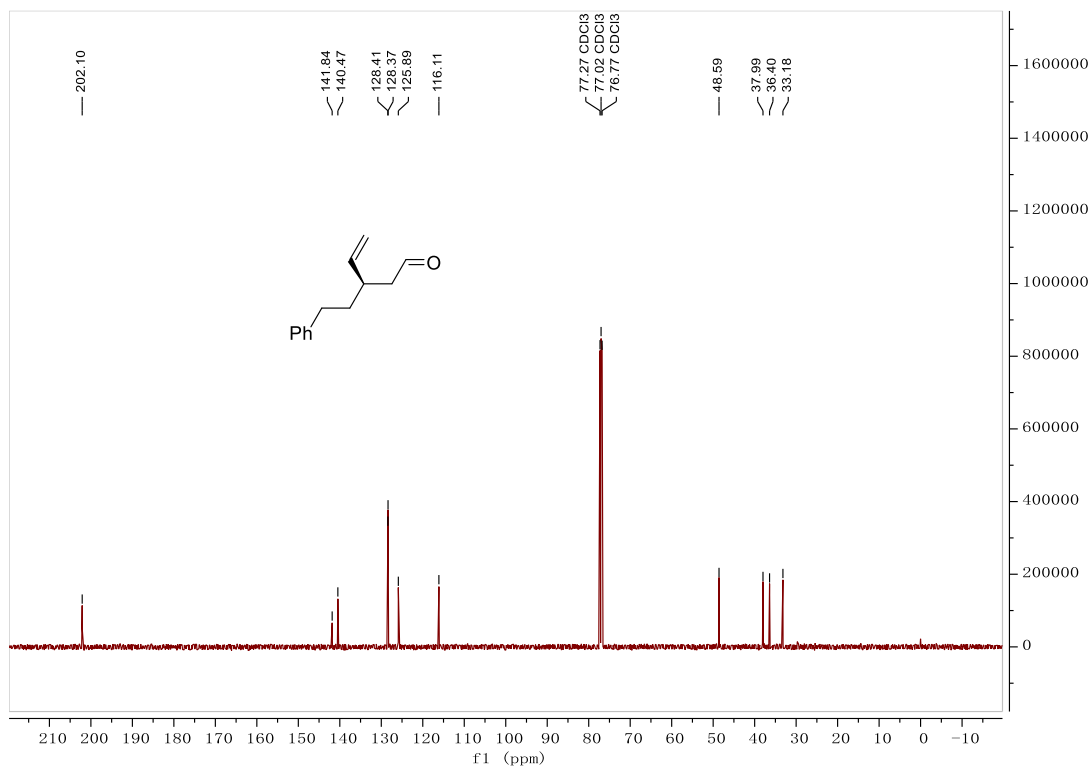


(R)-3-phenethylpent-4-enal (61)

¹H NMR, CDCl₃, 400 MHz

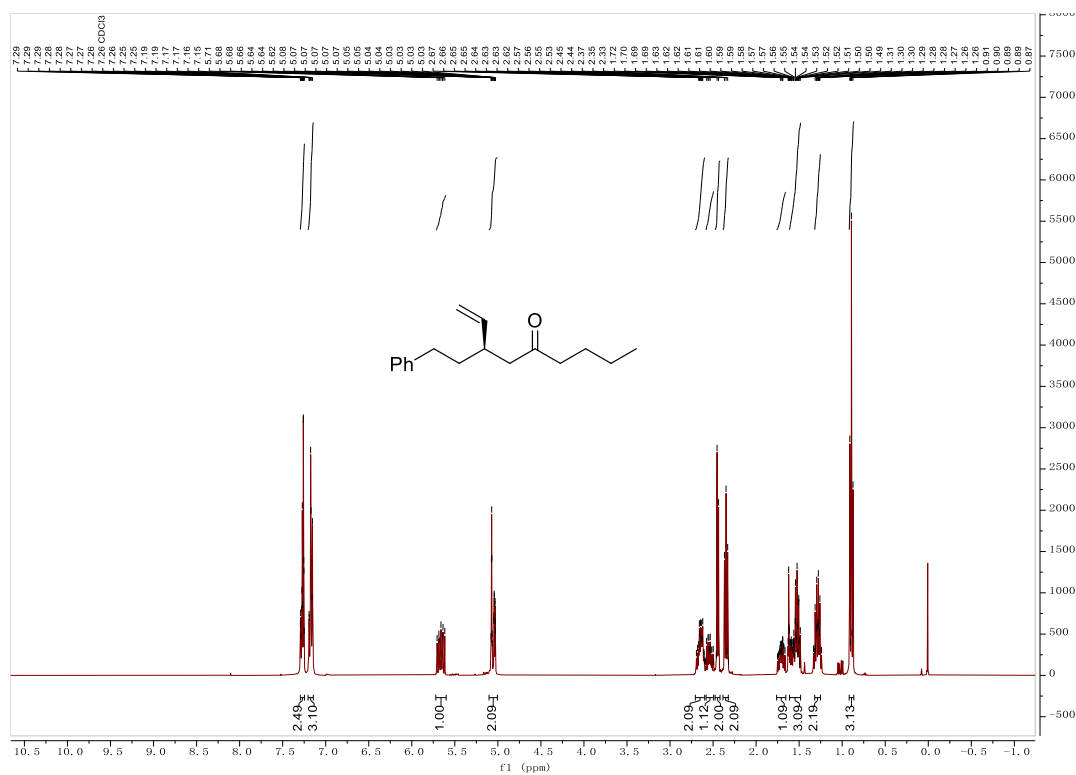


¹³C NMR, CDCl₃, 101 MHz

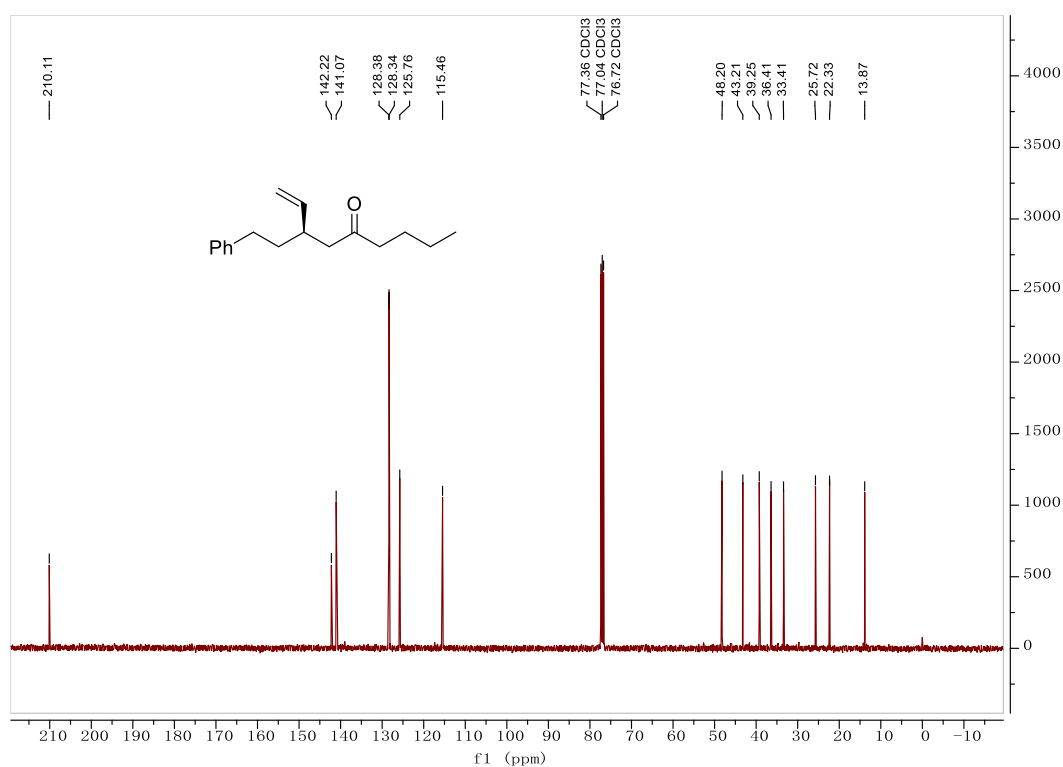


(R)-3-phenethylnon-1-en-5-one (62)

¹H NMR, CDCl₃, 400 MHz

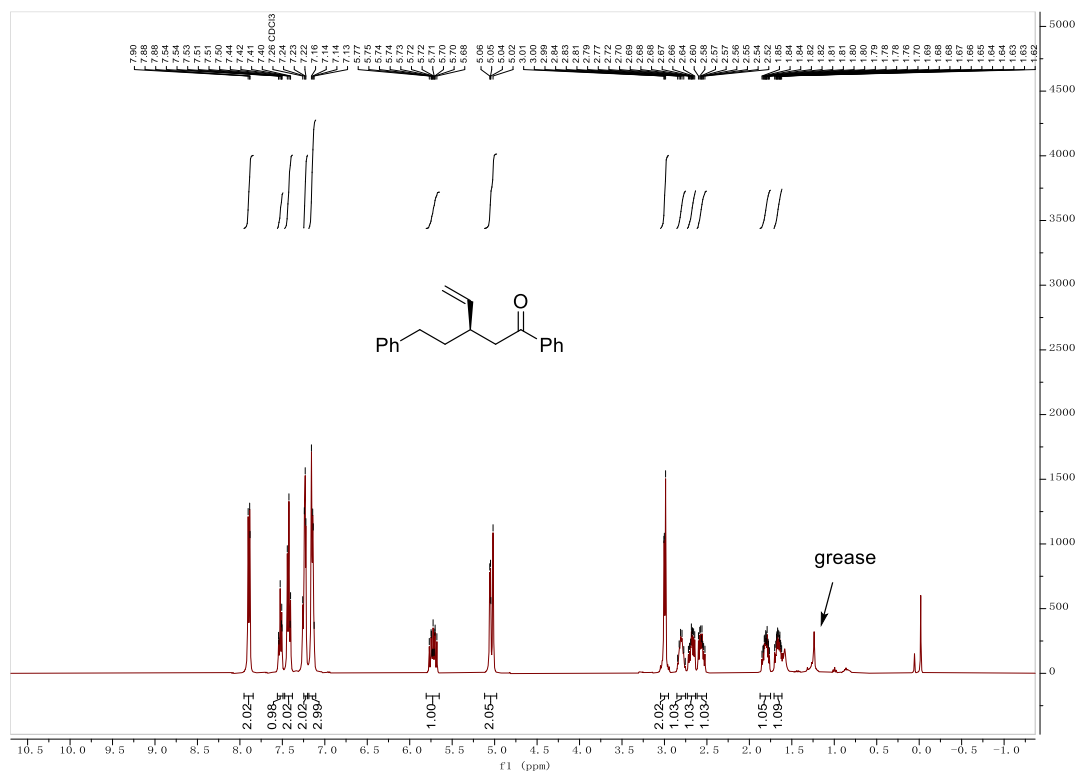


¹³C NMR, CDCl₃, 101 MHz

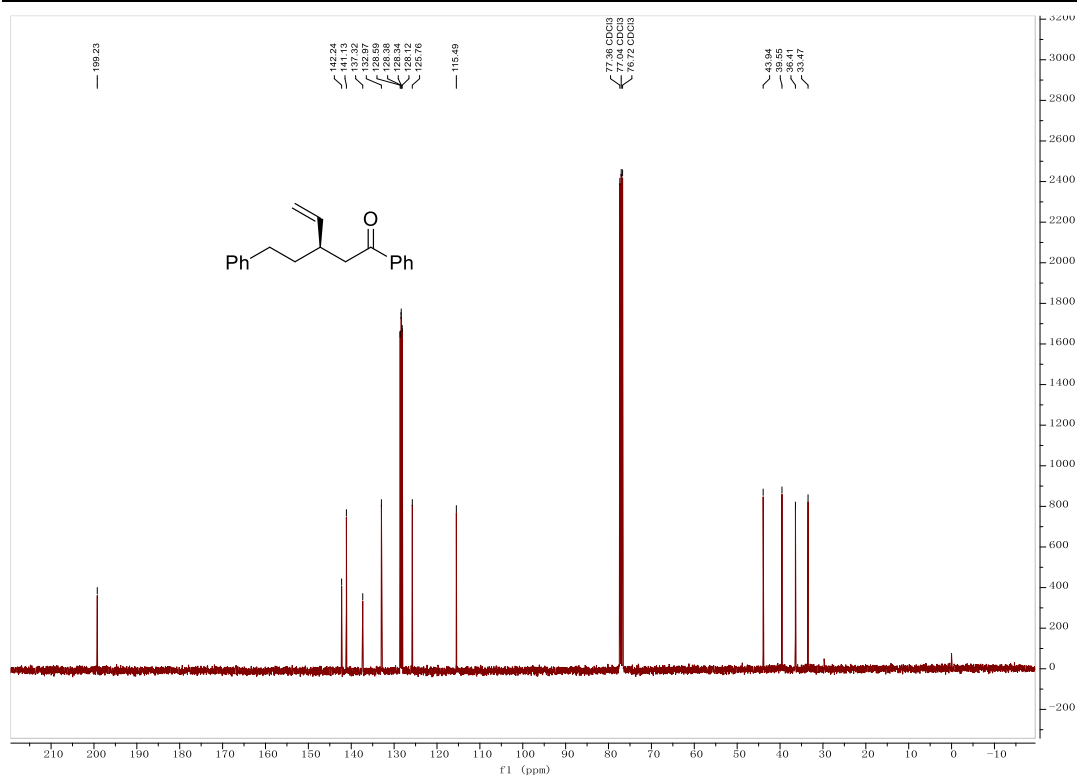


(R)-3-phenethyl-1-phenylpent-4-en-1-one (63)

¹H NMR, CDCl₃, 400 MHz

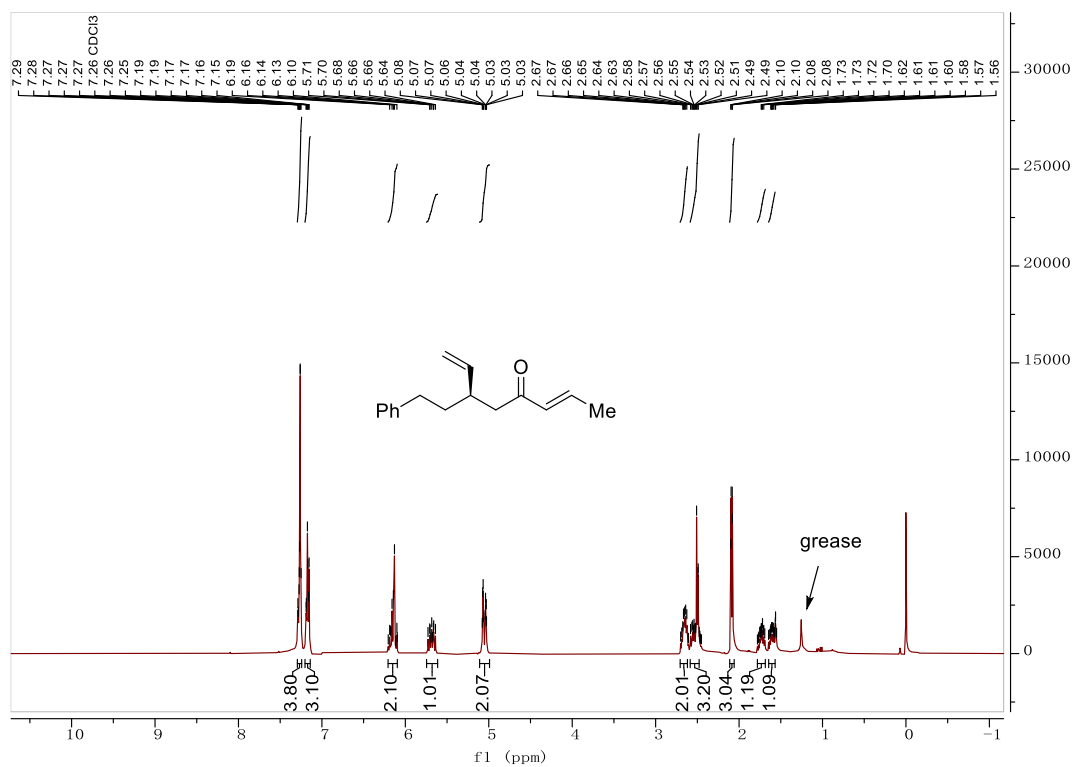


¹³C NMR, CDCl₃, 101 MHz

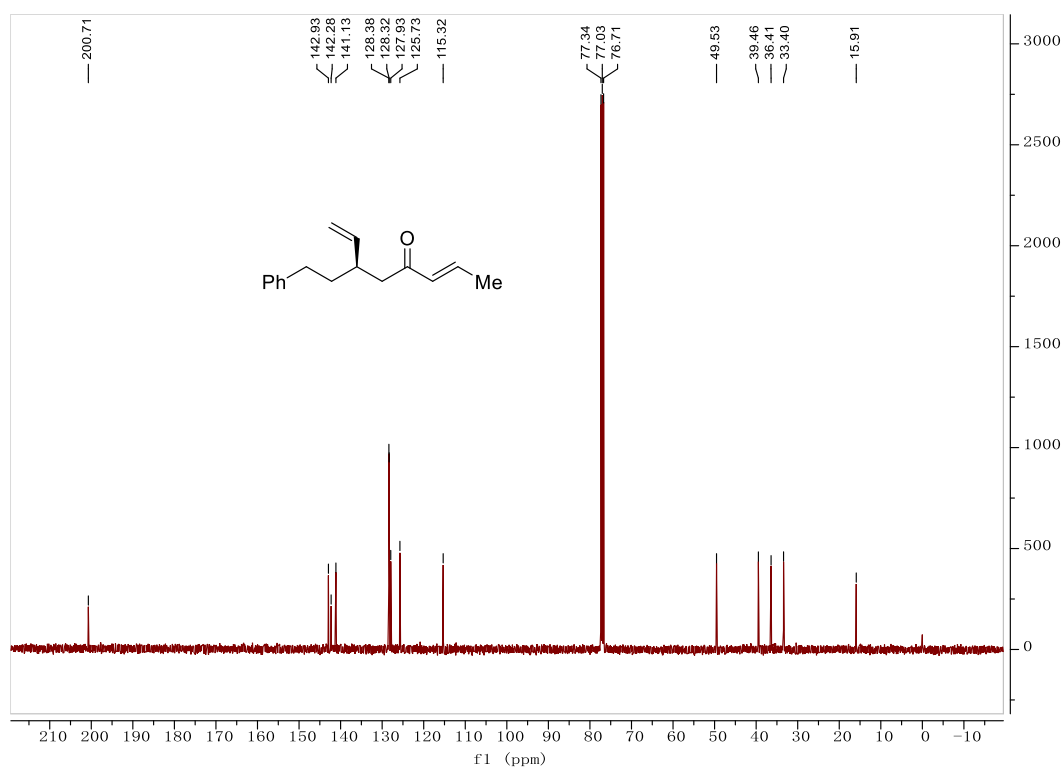


(R,E)-6-phenethylocta-2,7-dien-4-one (64)

¹H NMR, CDCl₃, 400 MHz

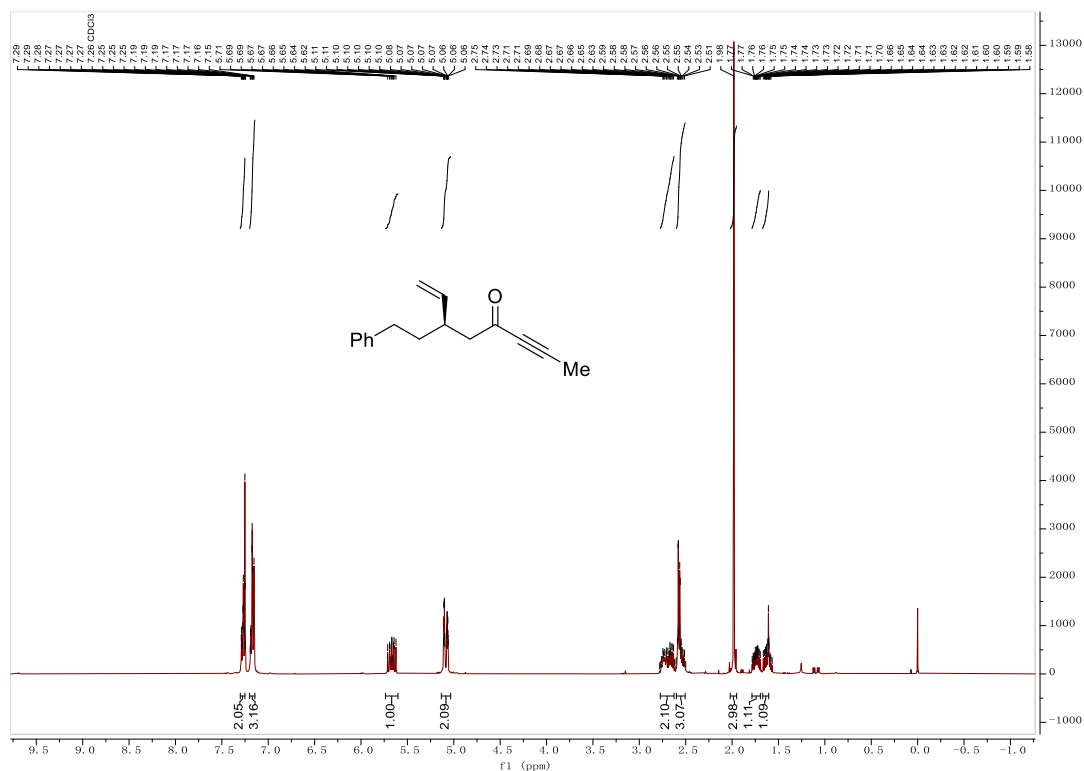


¹³C NMR, CDCl₃, 101 MHz

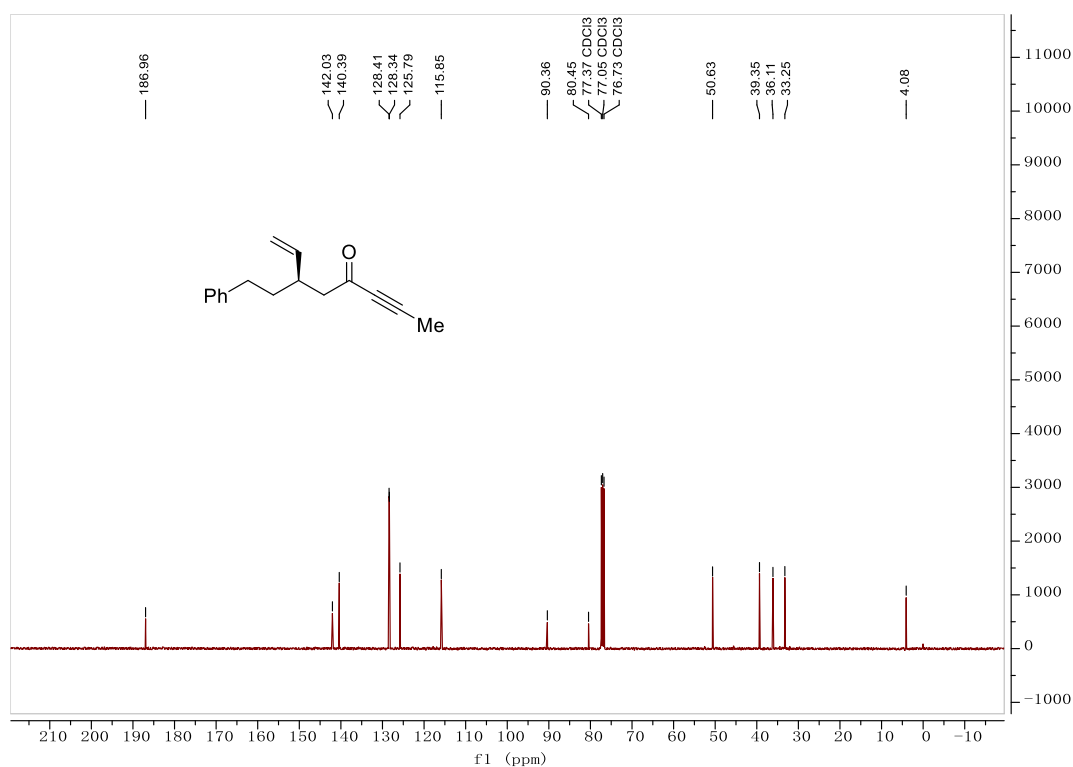


(R)-6-phenethyloct-7-en-2-yn-4-one (65)

¹H NMR, CDCl₃, 400 MHz

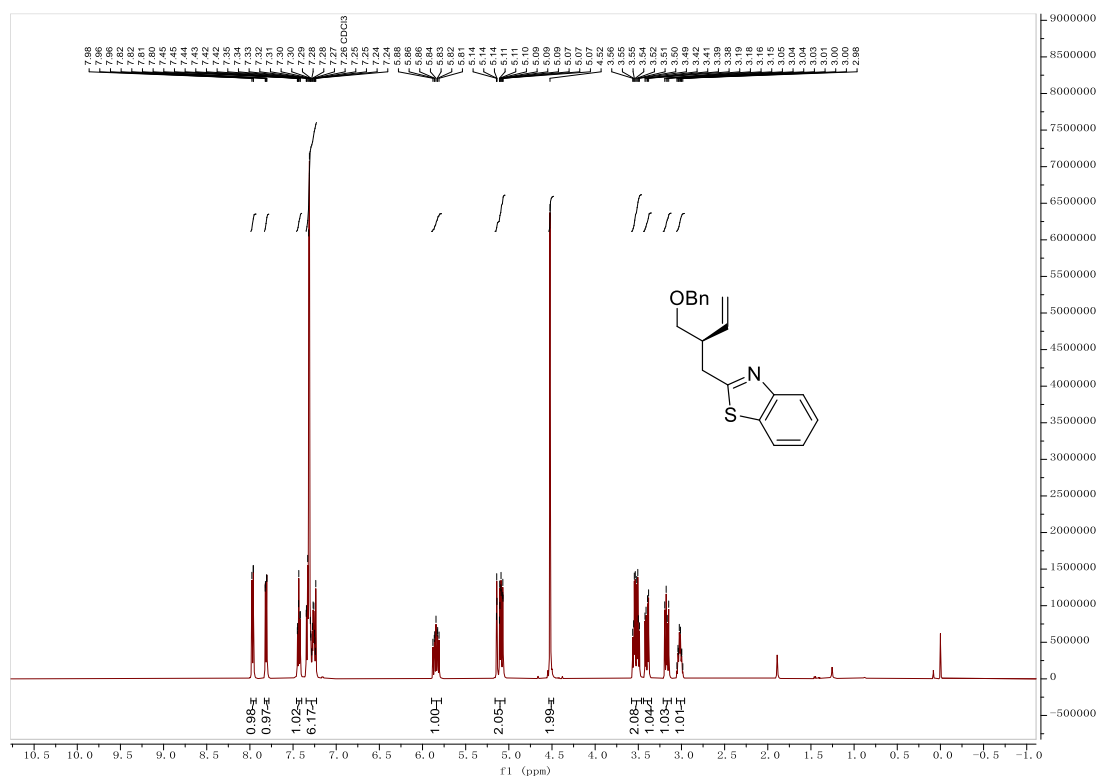


¹³C NMR, CDCl₃, 101 MHz

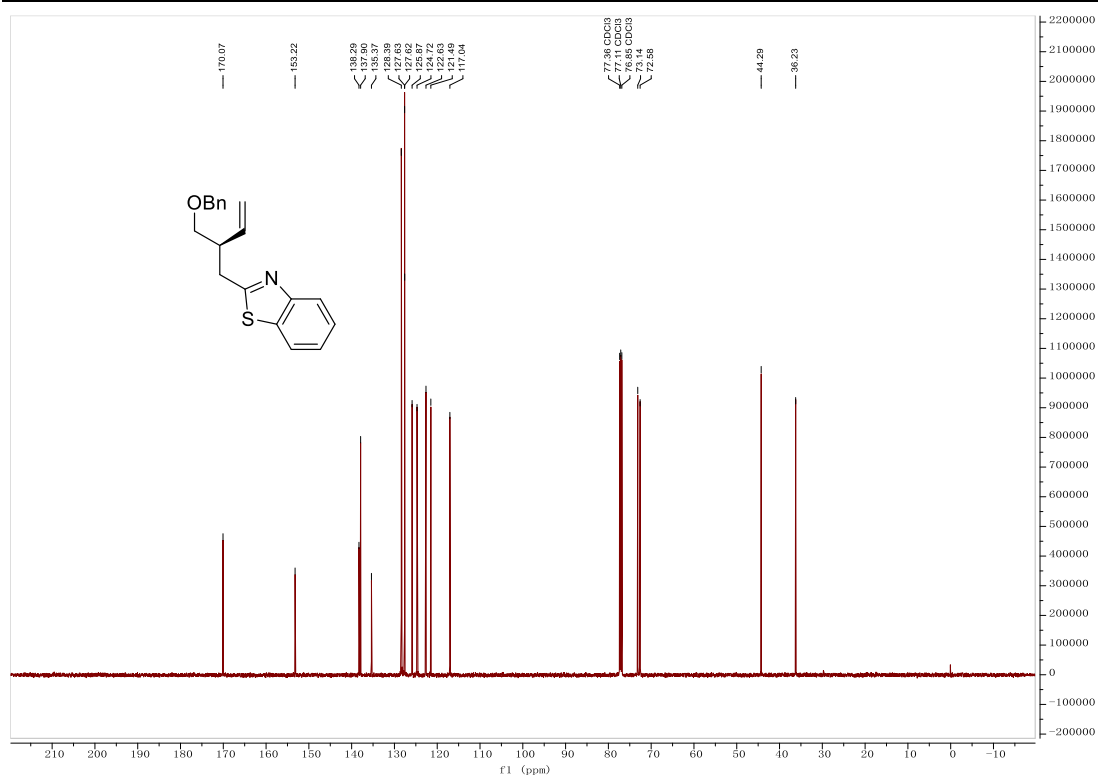


(R)-2-(2-((benzyloxy)methyl)but-3-en-1-yl)benzo[d]thiazole (66)

¹H NMR, CDCl₃, 400 MHz

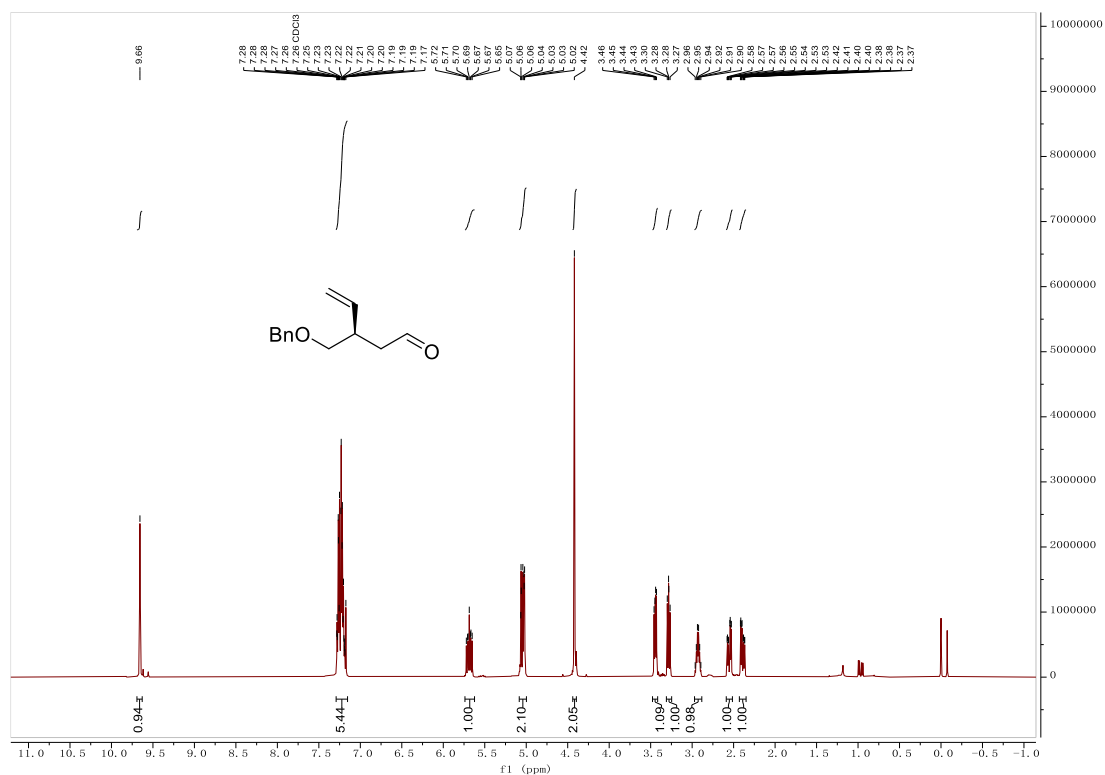


¹³C NMR, CDCl₃, 101 MHz

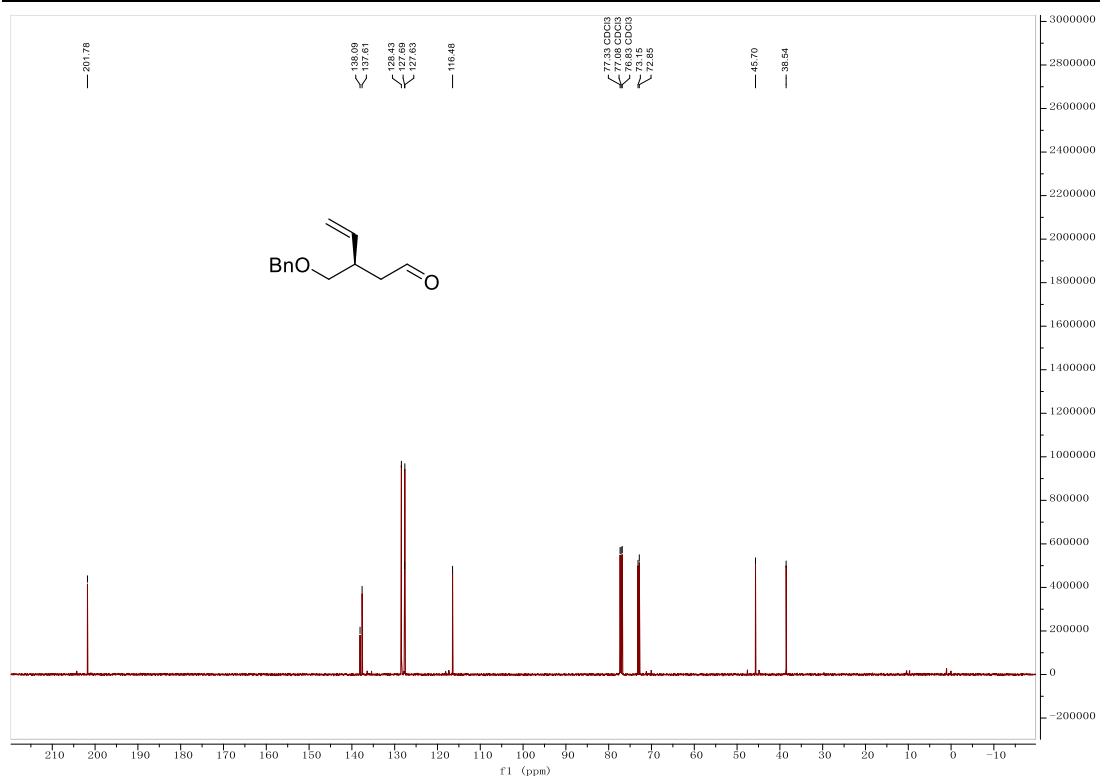


(R)-3-((benzyloxy)methyl)pent-4-enal (67)

¹H NMR, CDCl₃, 400 MHz

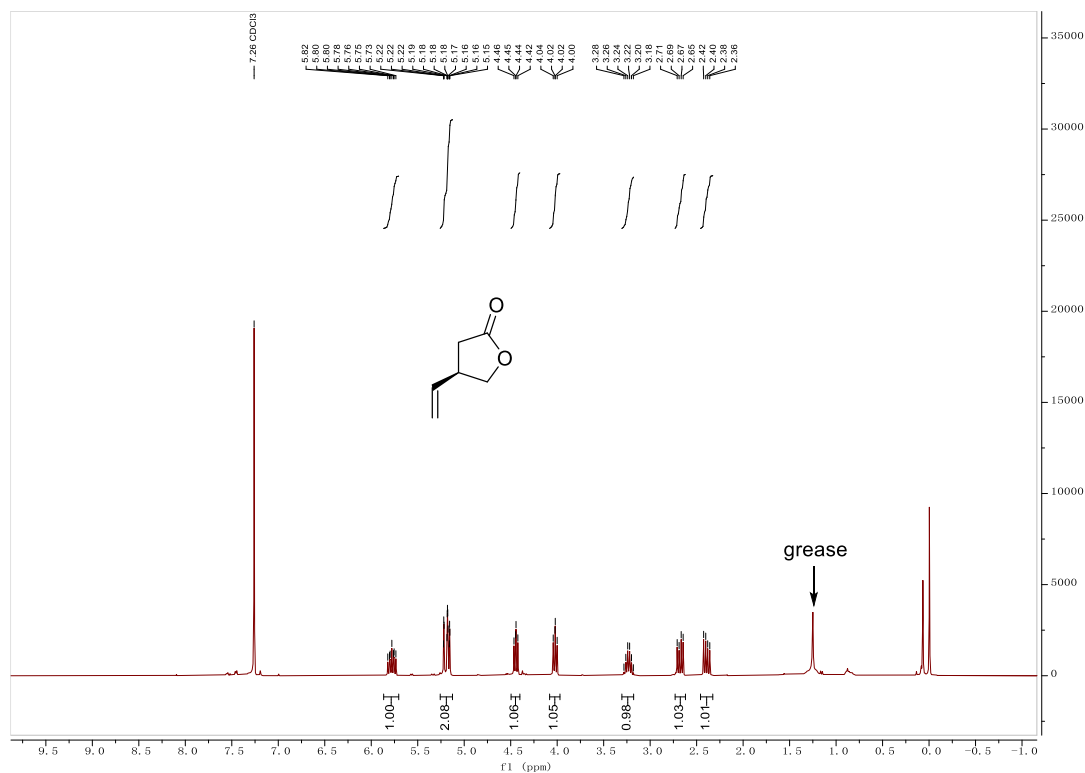


¹³C NMR, CDCl₃, 101 MHz

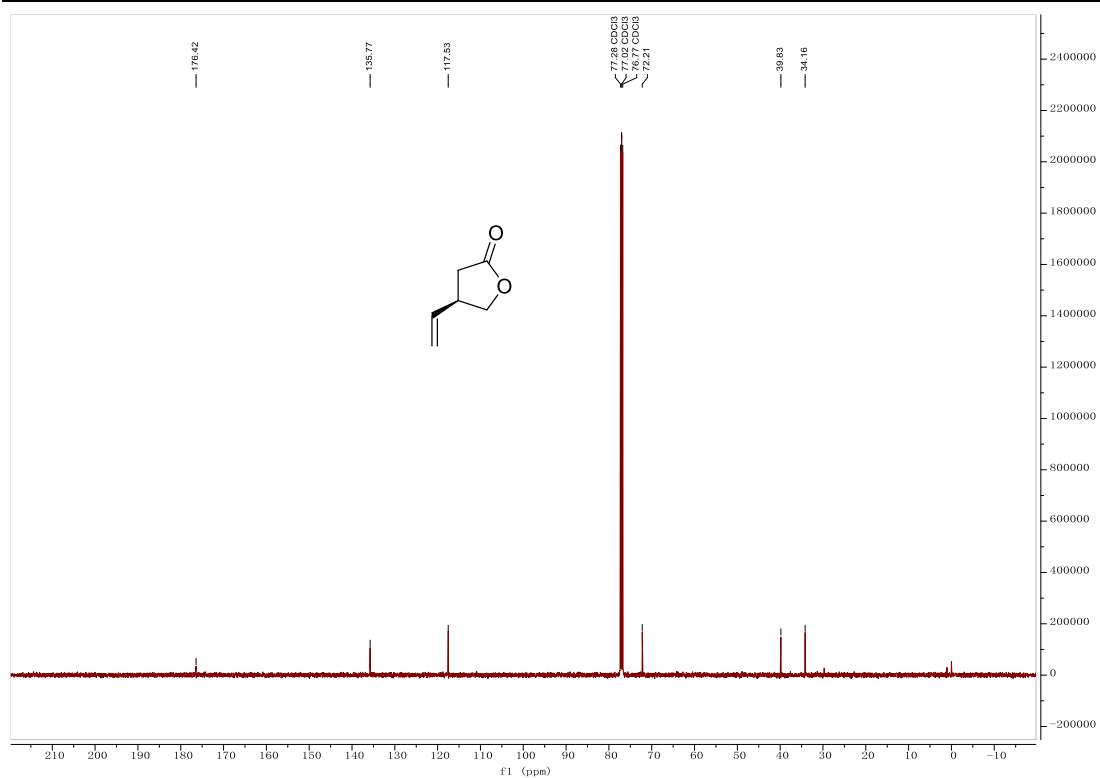


(R)-4-vinyldihydrofuran-2(3H)-one (68)

¹H NMR, CDCl₃, 400 MHz

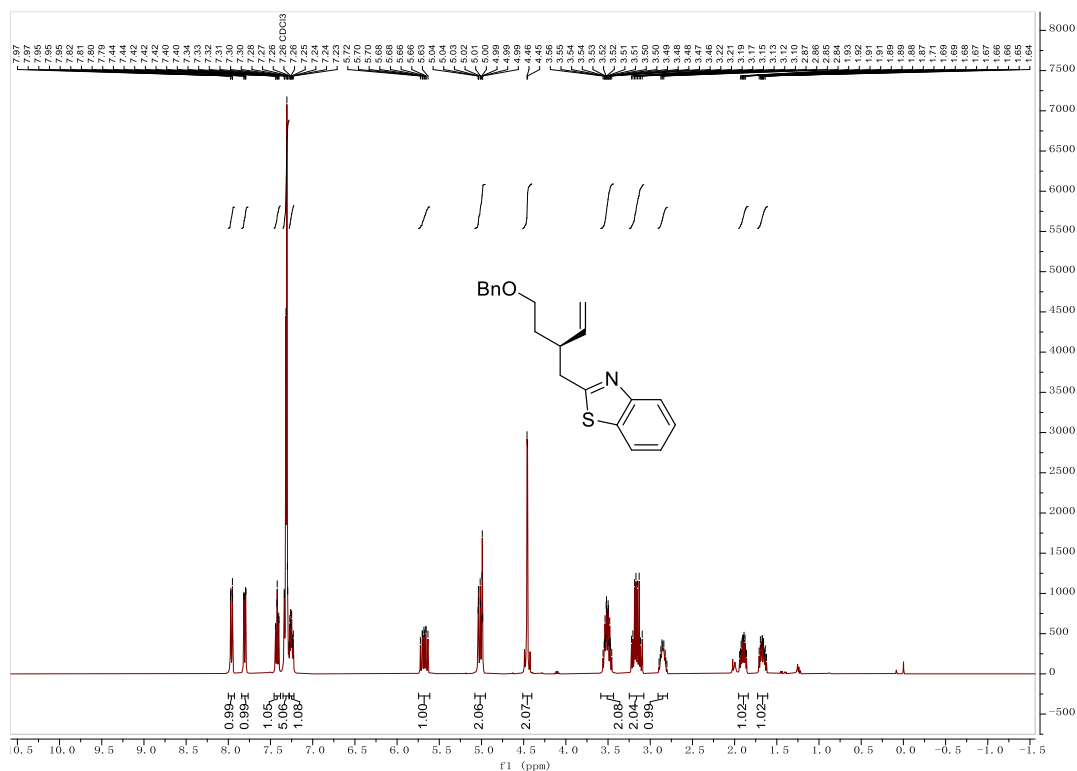


¹³C NMR, CDCl₃, 101 MHz

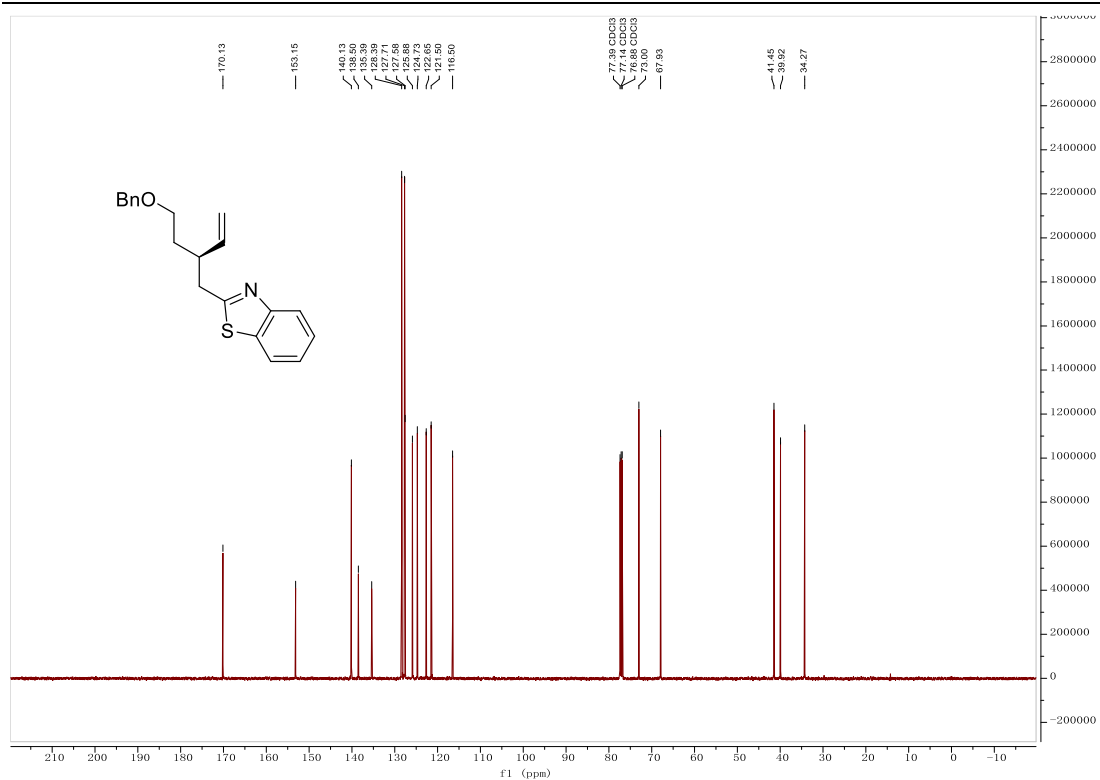


(R)-2-(2-(2-(benzyloxy)ethyl)but-3-en-1-yl)benzo[d]thiazole (69)

¹H NMR, CDCl₃, 400 MHz

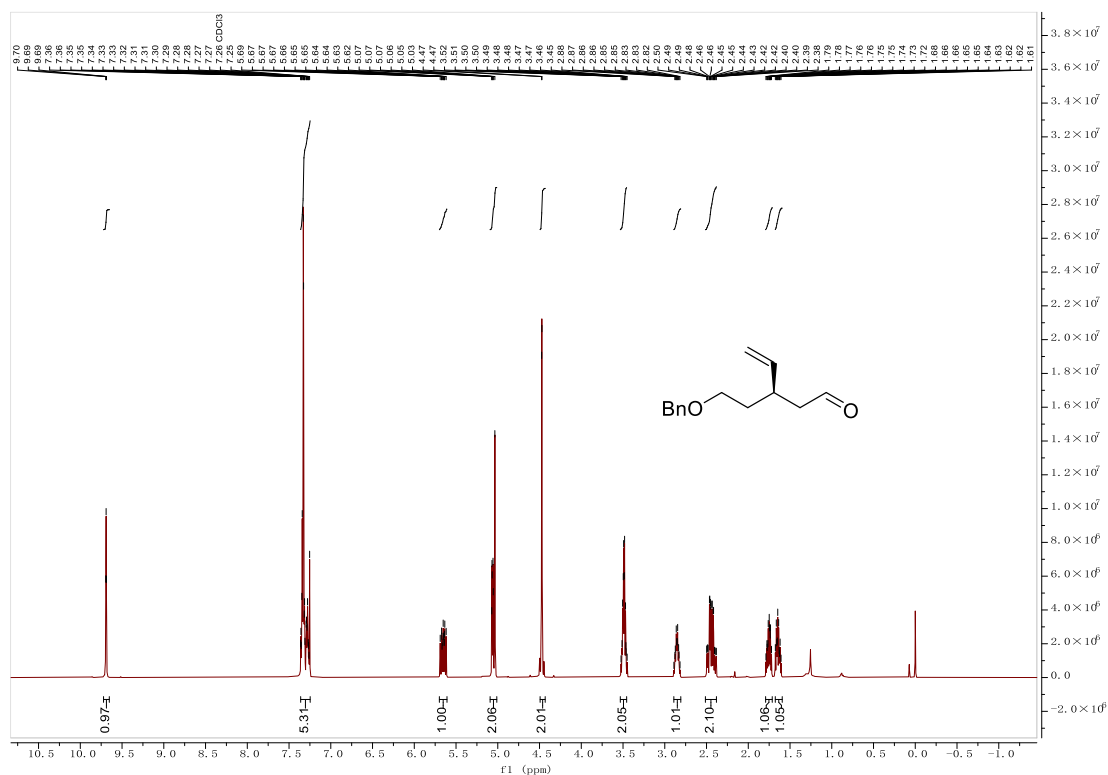


¹³C NMR, CDCl₃, 101 MHz

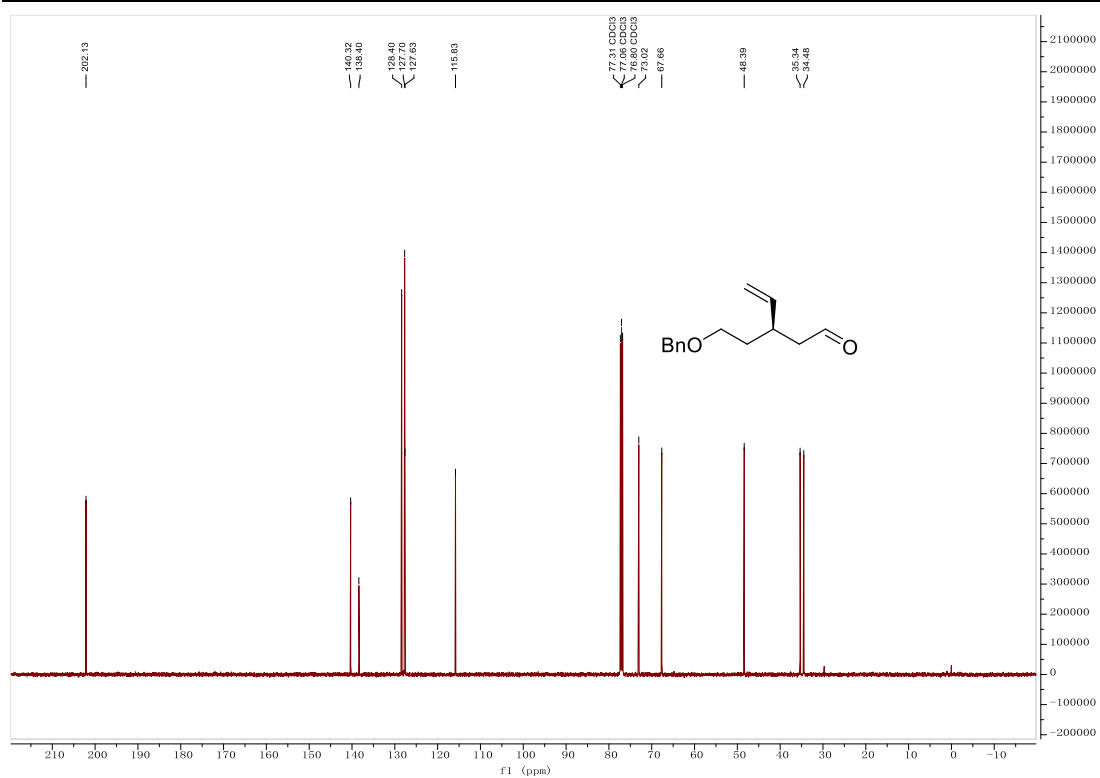


(R)-3-(2-(benzyloxy)ethyl)pent-4-enal (70)

¹H NMR, CDCl₃, 400 MHz

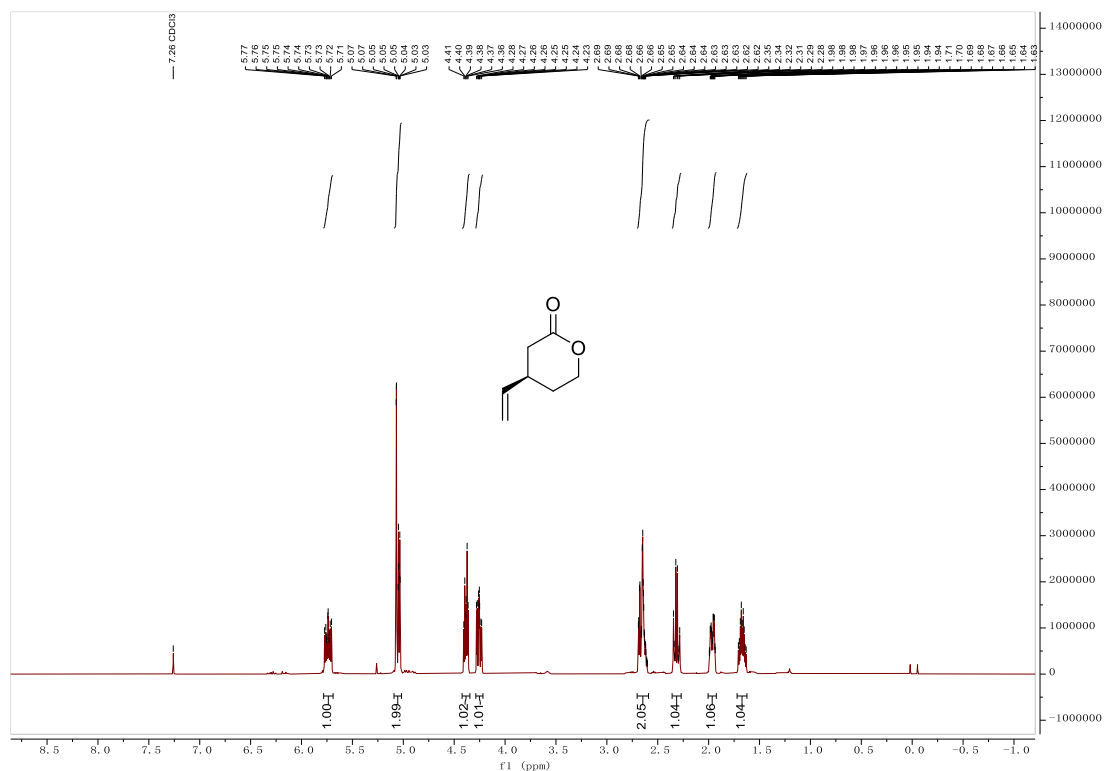


¹³C NMR, CDCl₃, 101 MHz

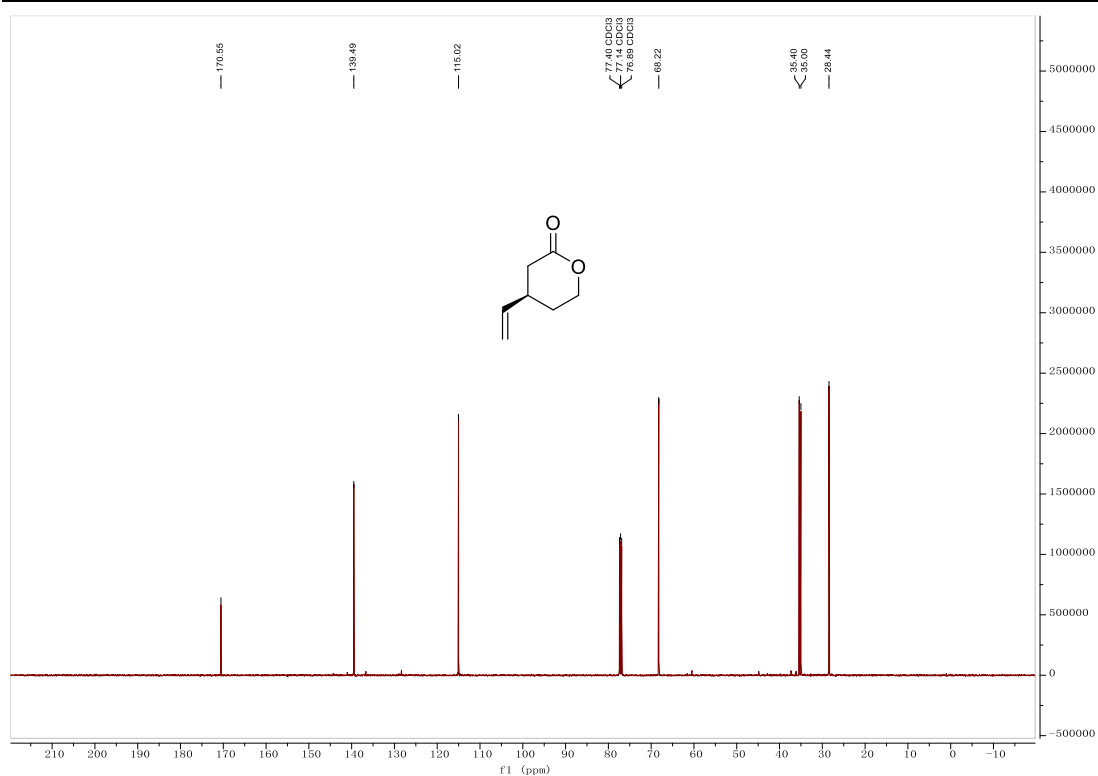


(R)-4-vinyltetrahydro-2H-pyran-2-one (71)

^1H NMR, CDCl_3 , 400 MHz

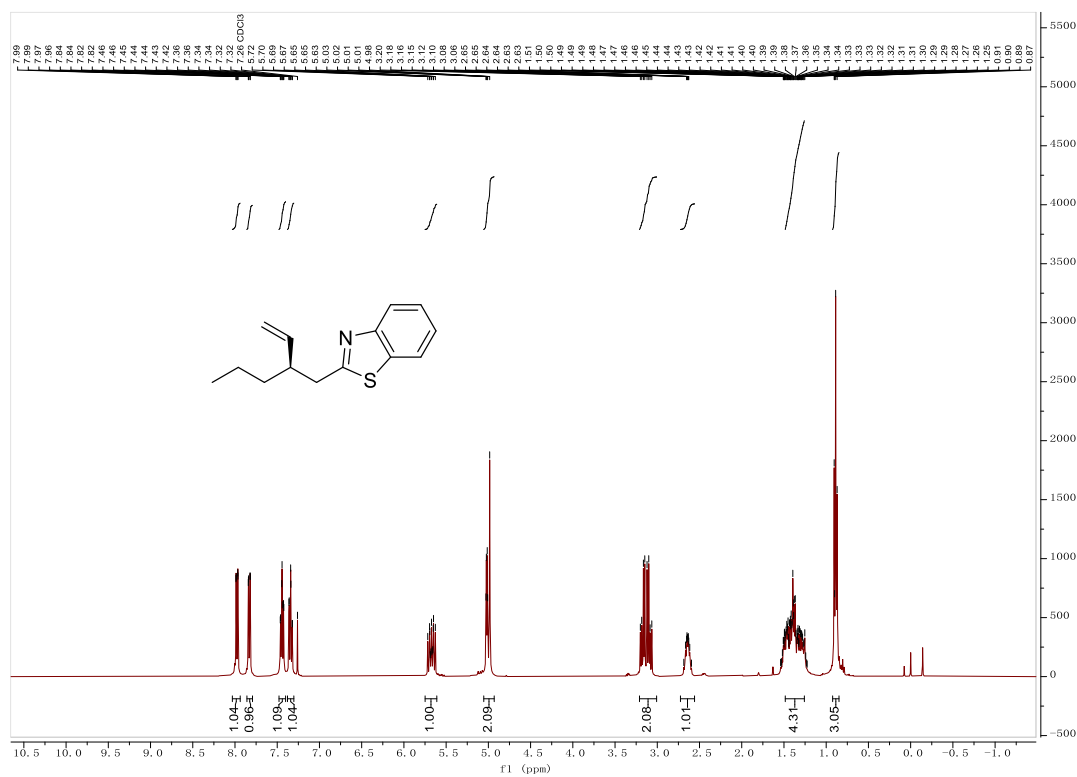


^{13}C NMR, CDCl_3 , 101 MHz

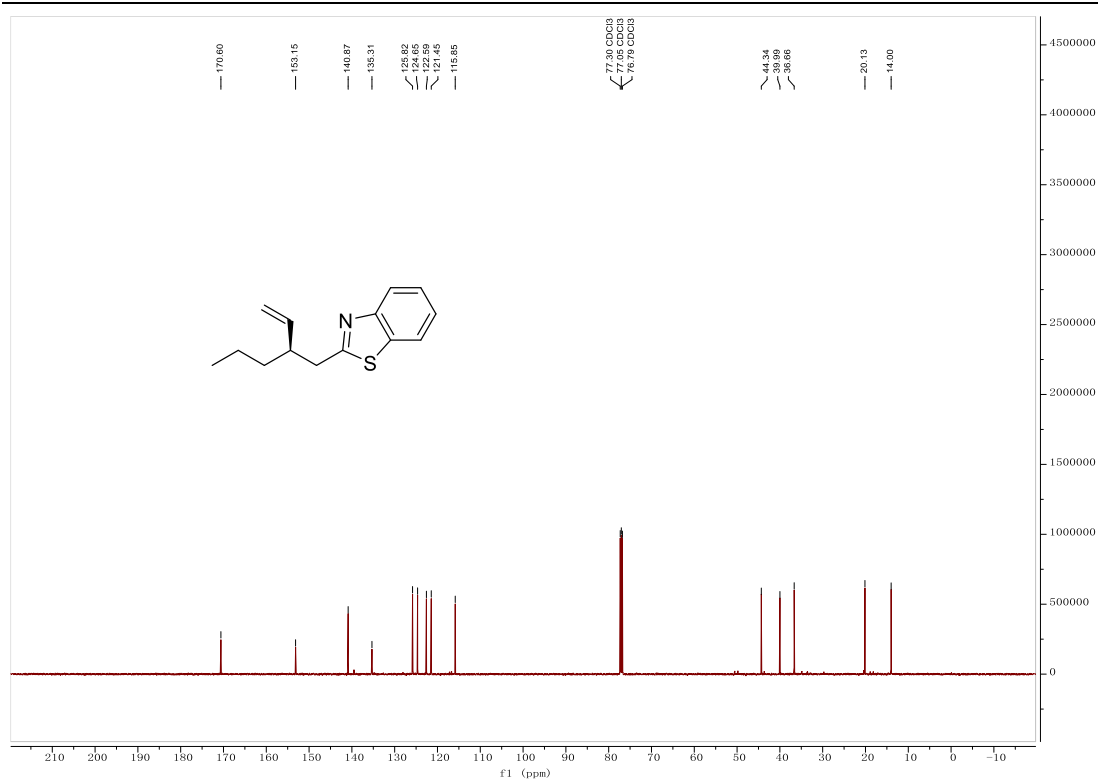


(R)-2-(2-vinylpentyl)benzo[d]thiazole (72)

¹H NMR, CDCl₃, 400 MHz

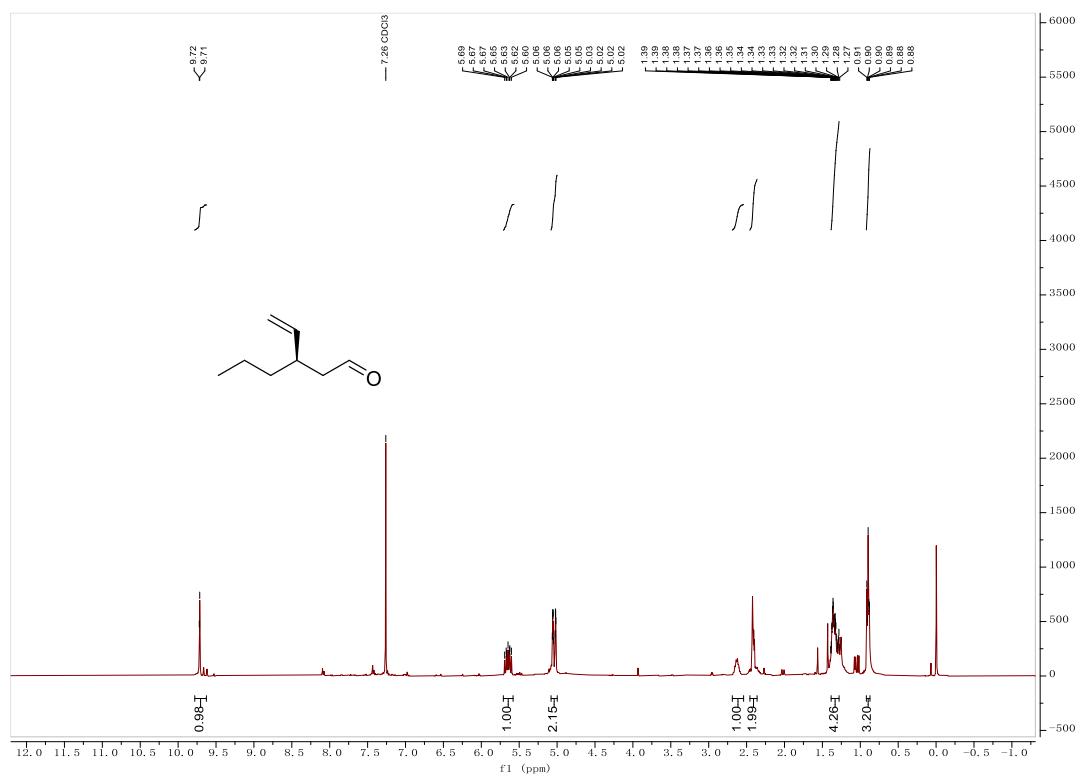


¹³C NMR, CDCl₃, 101 MHz

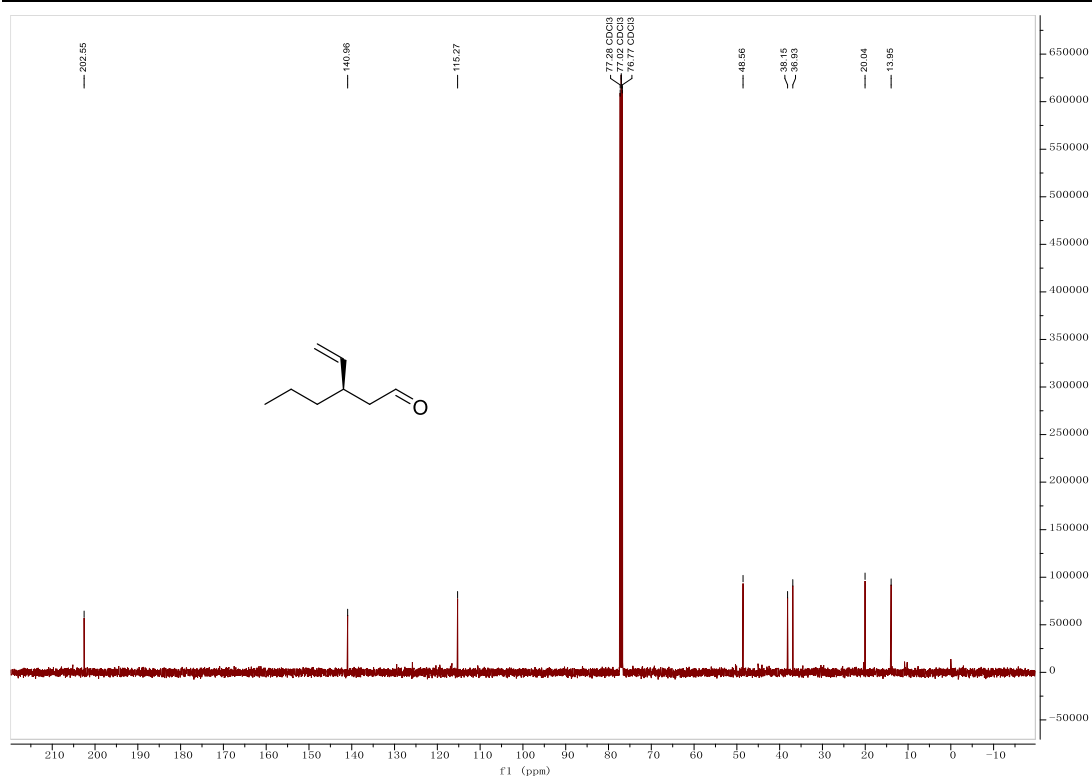


(R)-3-vinylhexanal (73)

¹H NMR, CDCl₃, 400 MHz

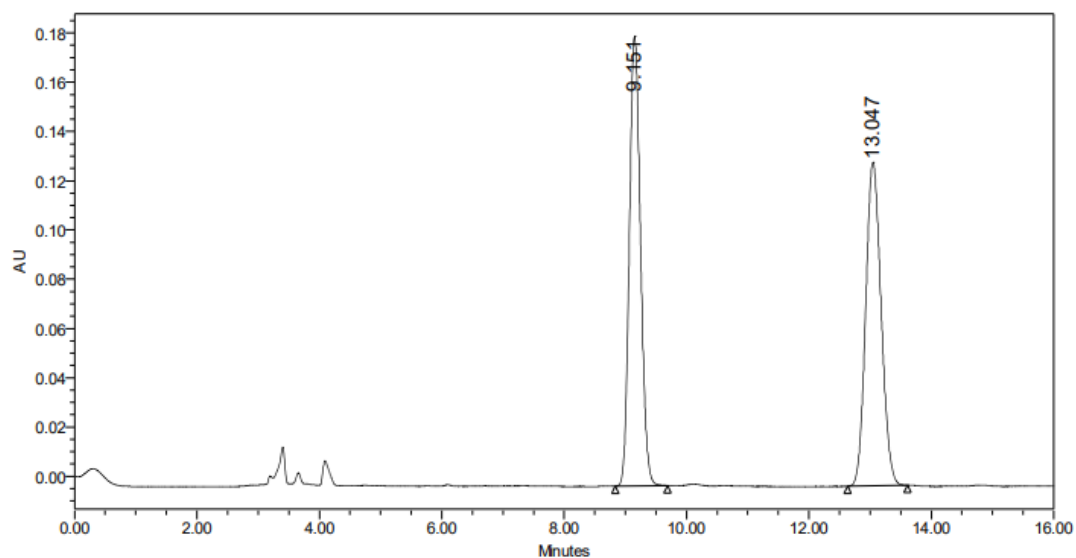


¹³C NMR, CDCl₃, 101 MHz



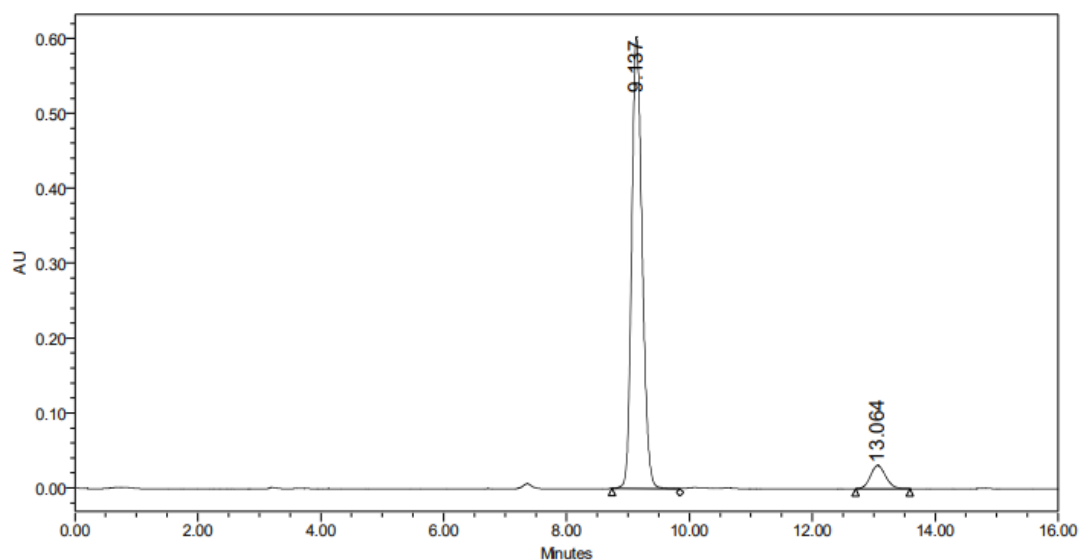
11. HPLC spectra

Racemic 7



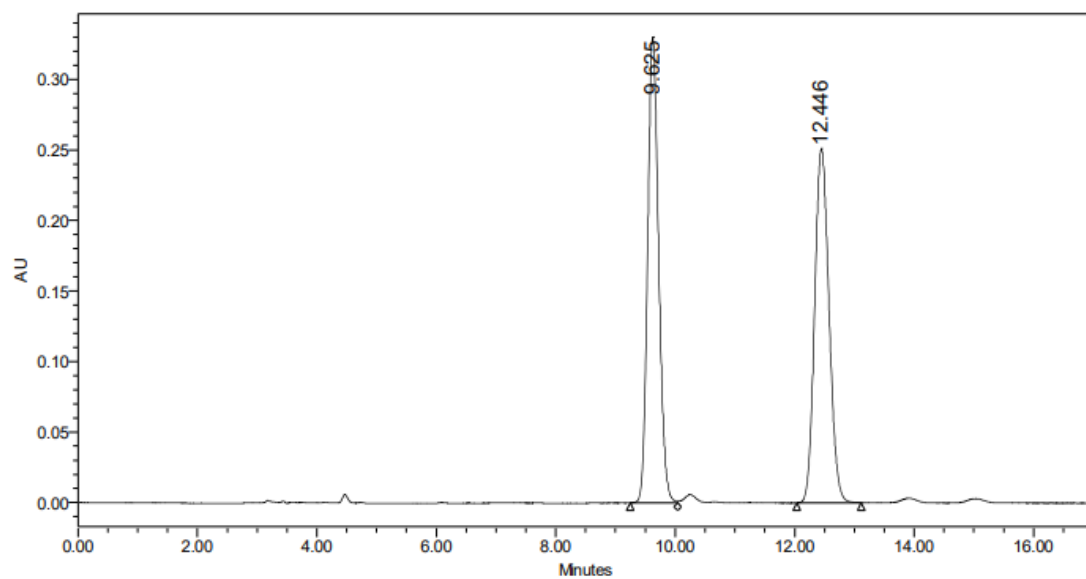
	RT	Area	% Area	Height
1	9.151	2289045	49.99	182572
2	13.047	2290234	50.01	131341

Enantioenriched 7



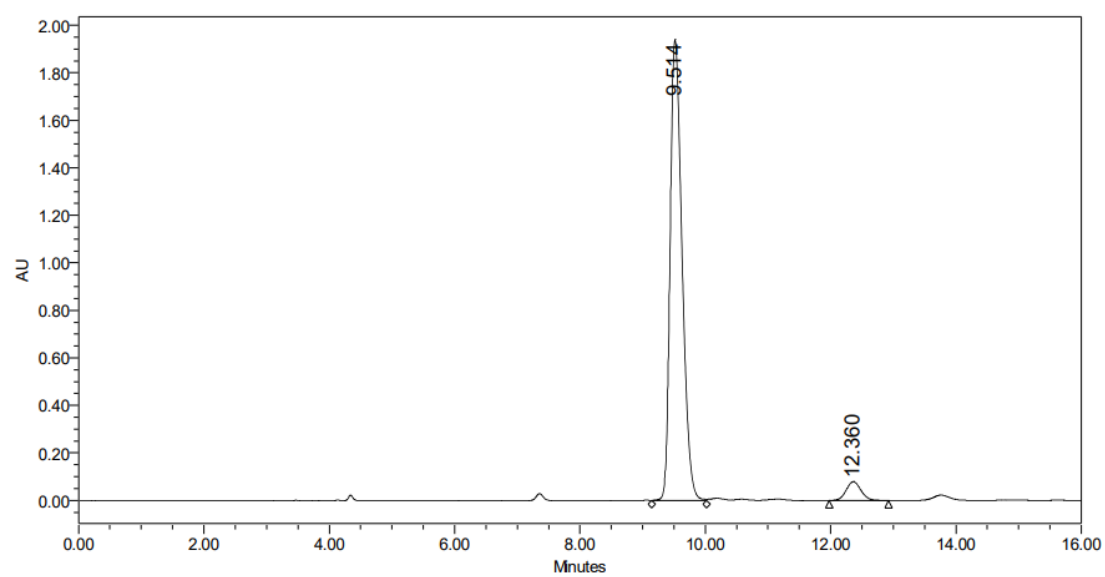
	RT	Area	% Area	Height
1	9.137	7069857	93.06	602714
2	13.064	527498	6.94	30793

Racemic 8



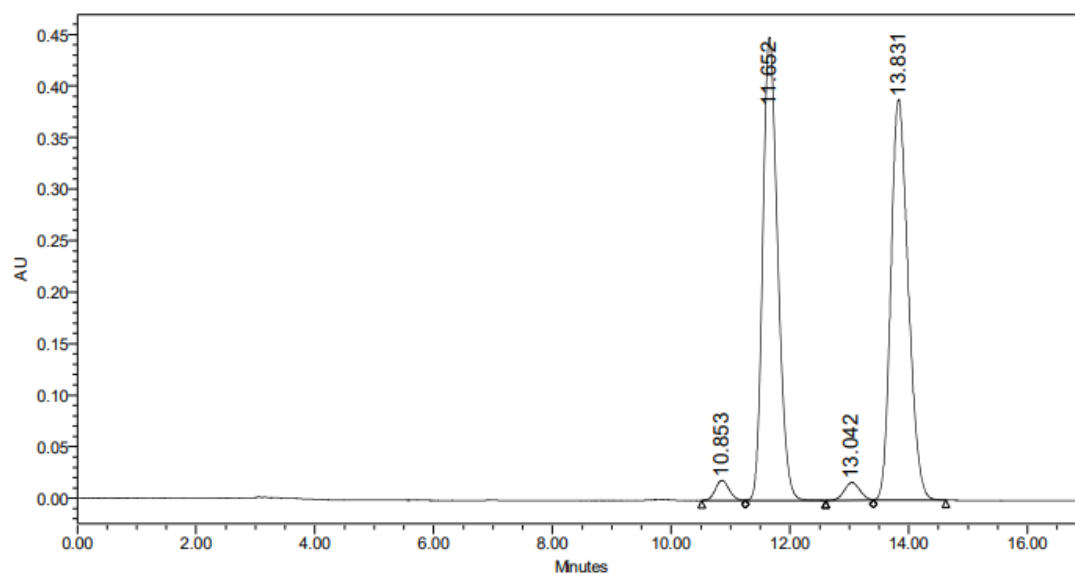
	RT	Area	% Area	Height
1	9.625	4217345	50.43	330188
2	12.446	4145126	49.57	251121

Enantioenriched 8



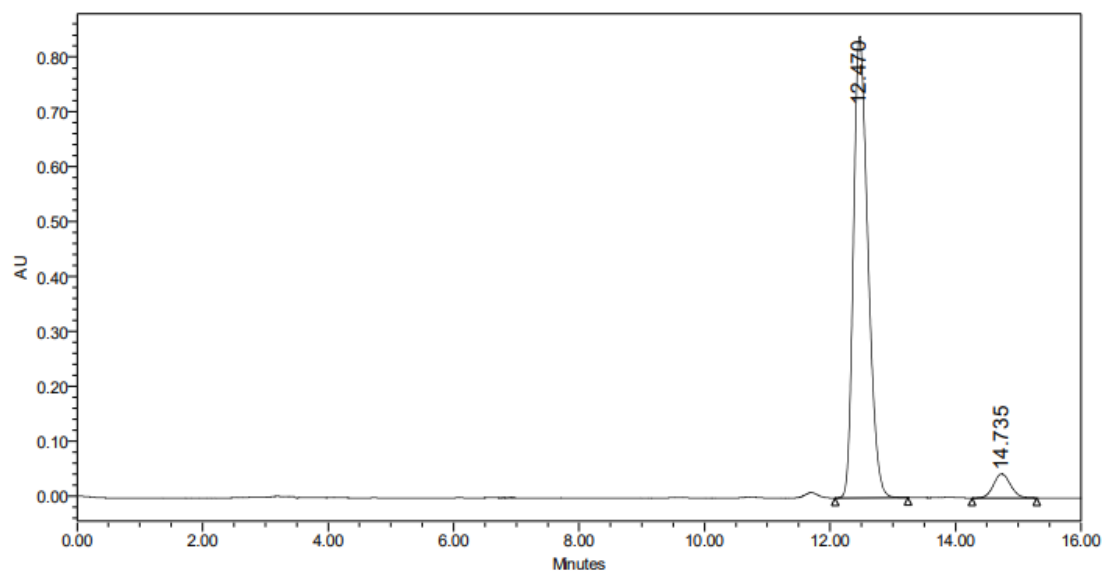
	RT	Area	% Area	Height
1	9.514	25436493	95.24	1938875
2	12.360	1271422	4.76	78549

Racemic 9



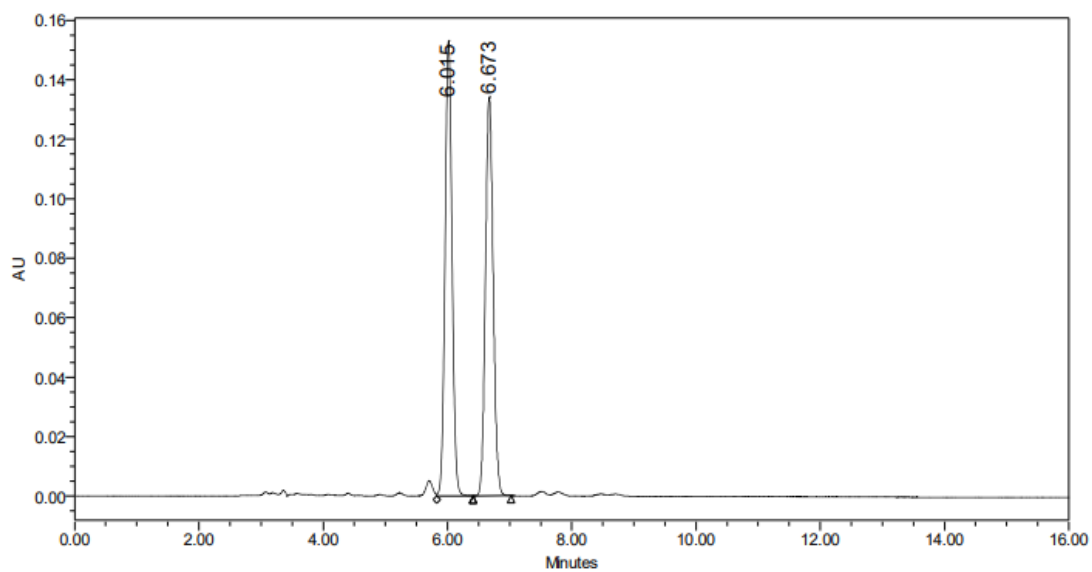
	RT	Area	% Area	Height
1	10.853	313215	1.91	19411
2	11.652	7893383	48.10	448874
3	13.042	318161	1.94	17173
4	13.831	7884711	48.05	388732

Enantioenriched 9



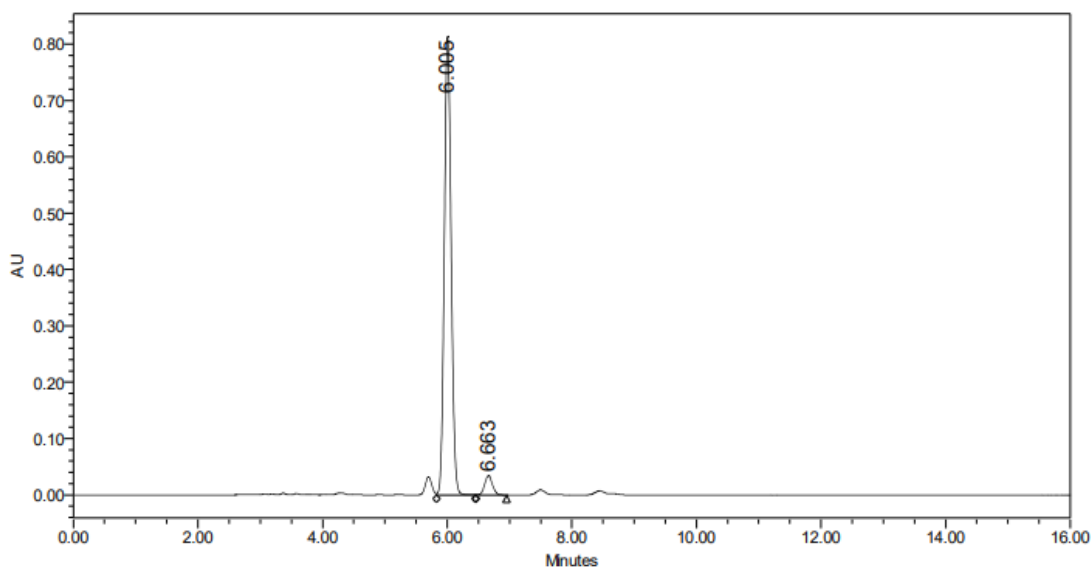
	RT	Area	% Area	Height
1	12.470	13547658	94.33	839721
2	14.735	814270	5.67	43700

Racemic 10



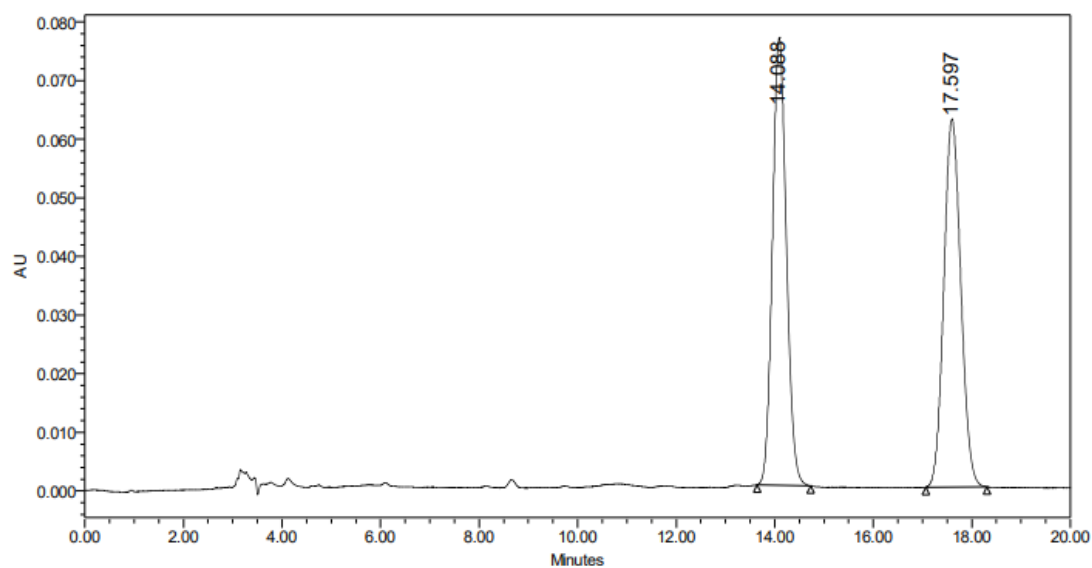
	RT	Area	% Area	Height
1	6.015	1200064	50.88	152997
2	6.673	1158609	49.12	134066

Enantioenriched 10



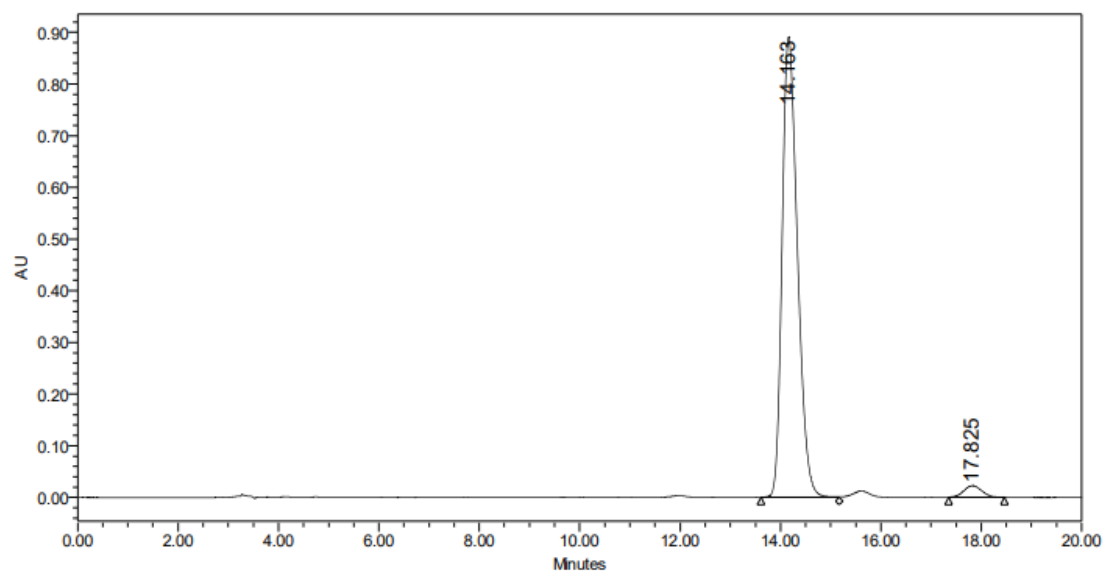
	RT	Area	% Area	Height
1	6.005	6230062	95.52	812971
2	6.663	292346	4.48	33844

Racemic 11



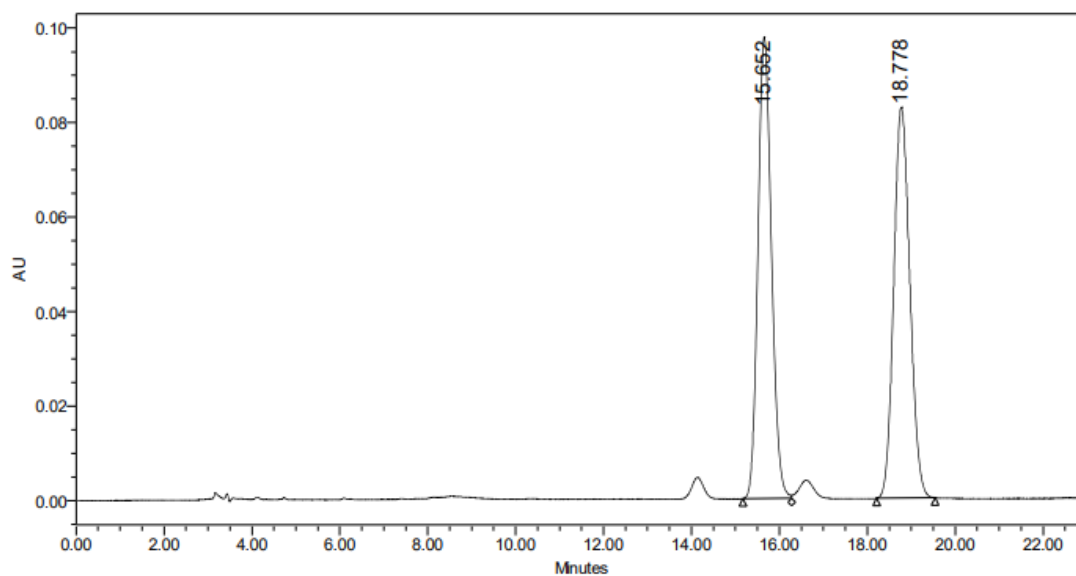
	RT	Area	% Area	Height
1	14.088	1501013	49.81	76335
2	17.597	1512615	50.19	62767

Enantioenriched 11



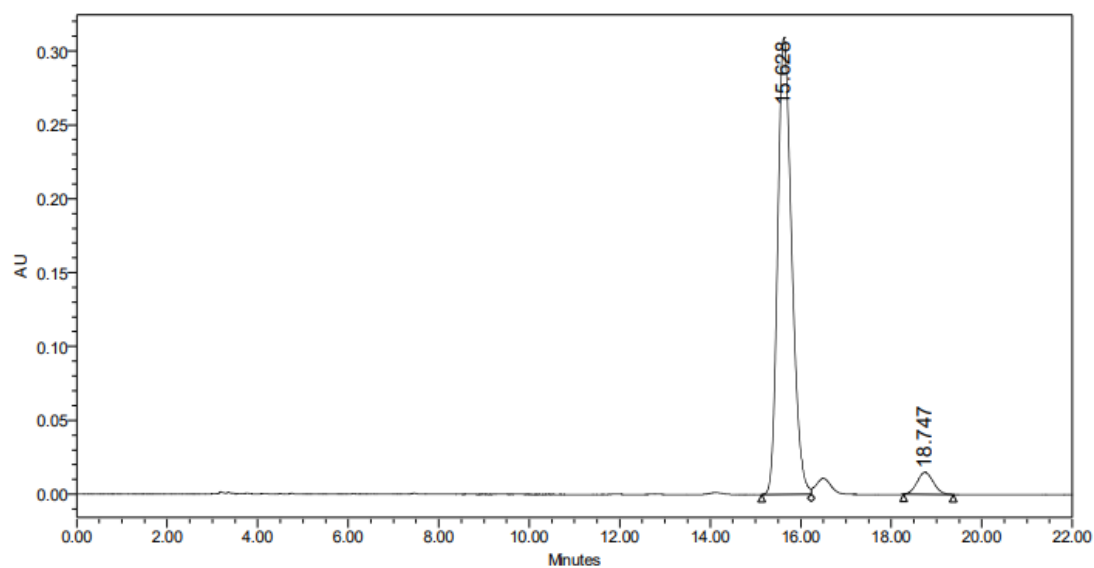
	RT	Area	% Area	Height
1	14.163	18925641	97.12	889957
2	17.825	560470	2.88	22450

Racemic 12



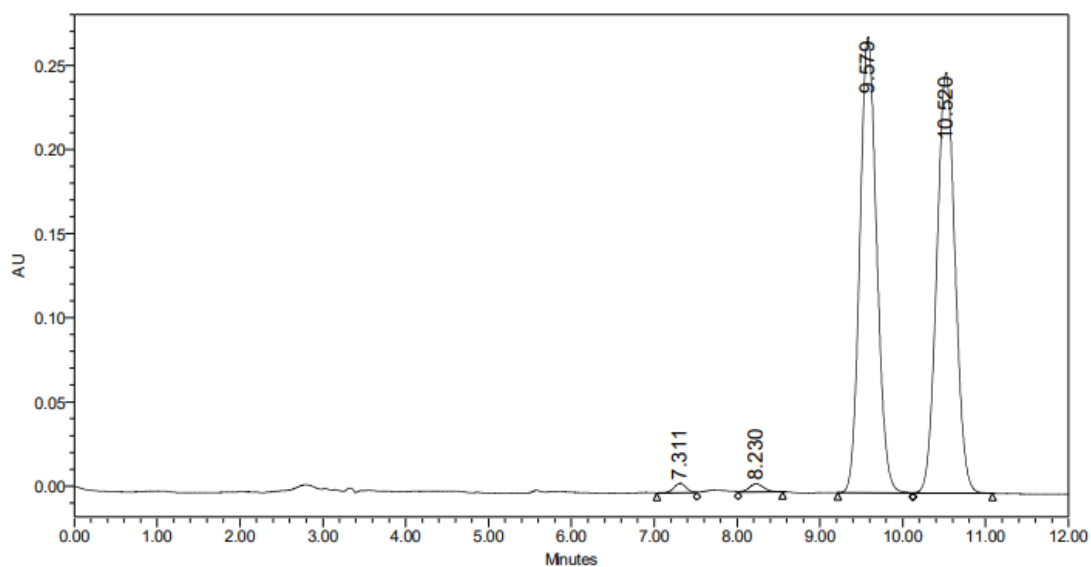
	RT	Area	% Area	Height
1	15.652	2091719	50.03	97662
2	18.778	2088842	49.97	82732

Enantioenriched 12



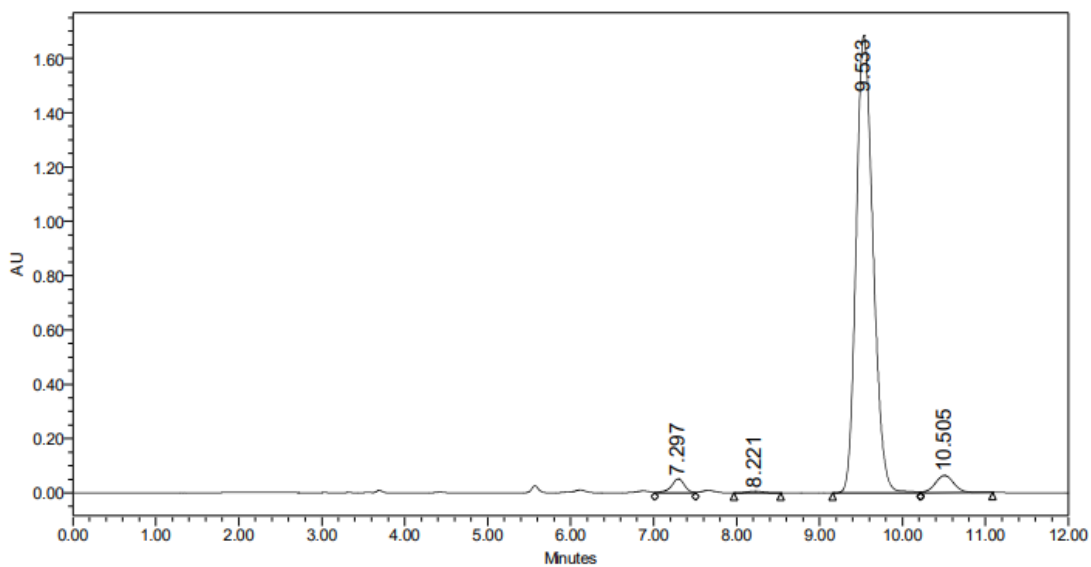
	RT	Area	% Area	Height
1	15.628	6709017	94.81	309157
2	18.747	367629	5.19	14793

Racemic 13

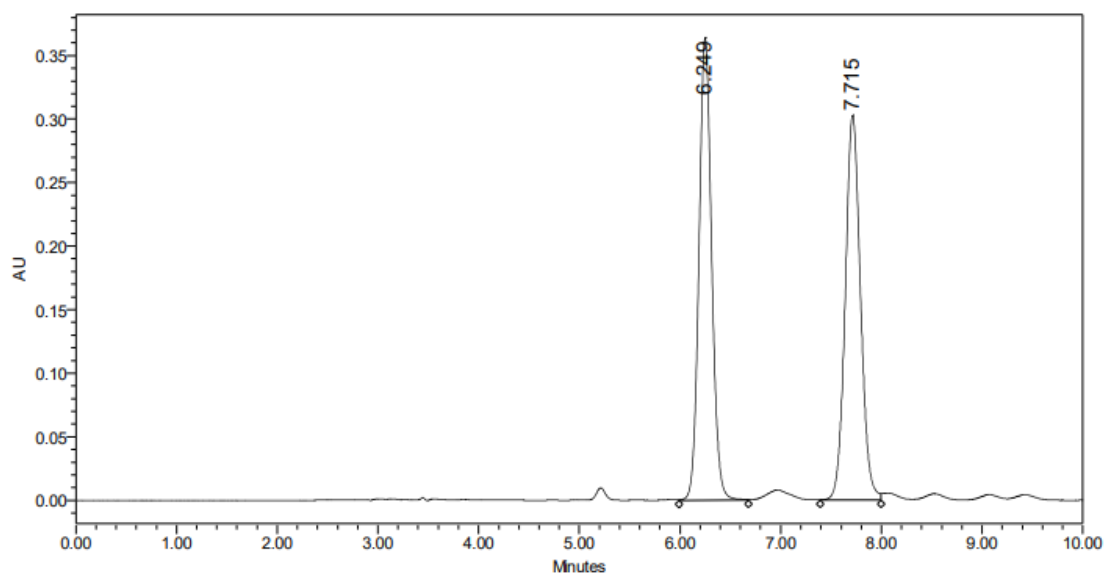


	RT	Area	% Area	Height
1	7.311	57862	0.74	5580
2	8.230	60992	0.78	4879
3	9.579	3832270	49.19	270589
4	10.520	3839835	49.29	249766

Enantioenriched 13



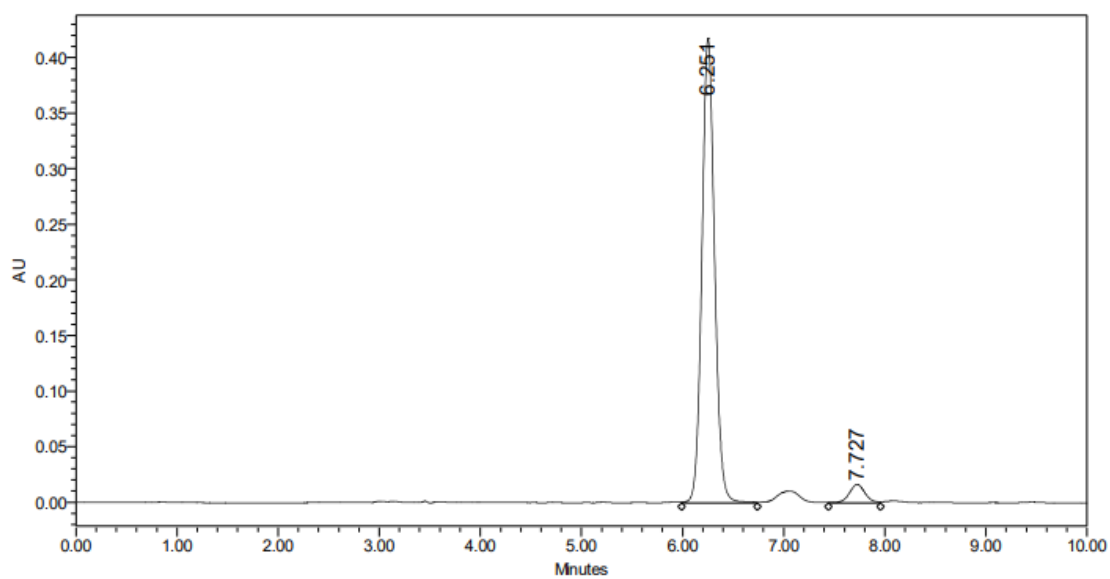
	RT	Area	% Area	Height
1	7.297	560429	2.20	51137
2	8.221	67626	0.27	5834
3	9.533	23904160	93.69	1683861
4	10.505	981395	3.85	63321



	RT	Area	% Area	Height
1	6.249	3197201	49.94	363878
2	7.715	3204848	50.06	302873

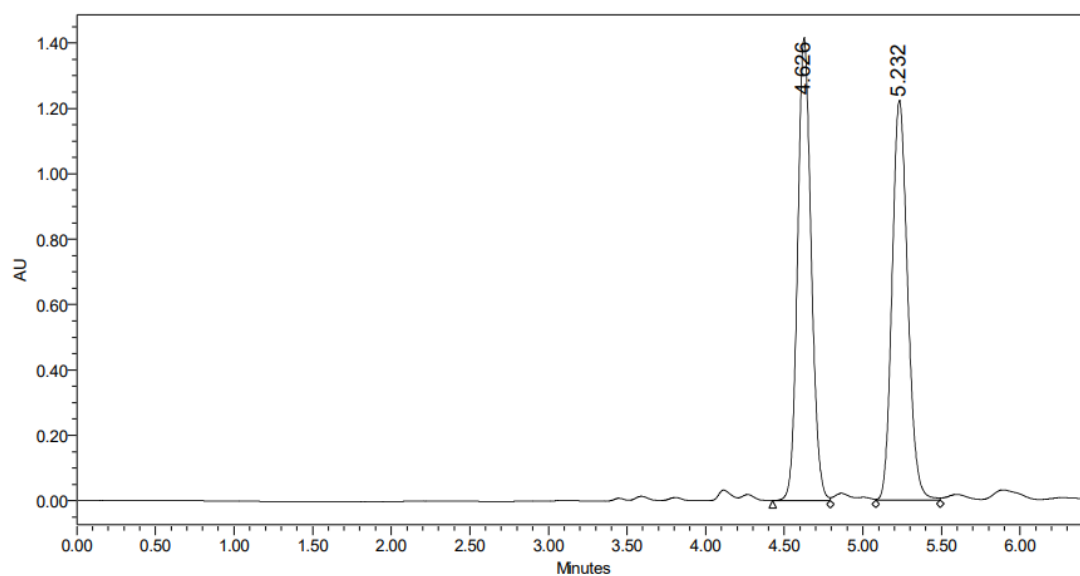
Racemic 14

Enantioenriched 14



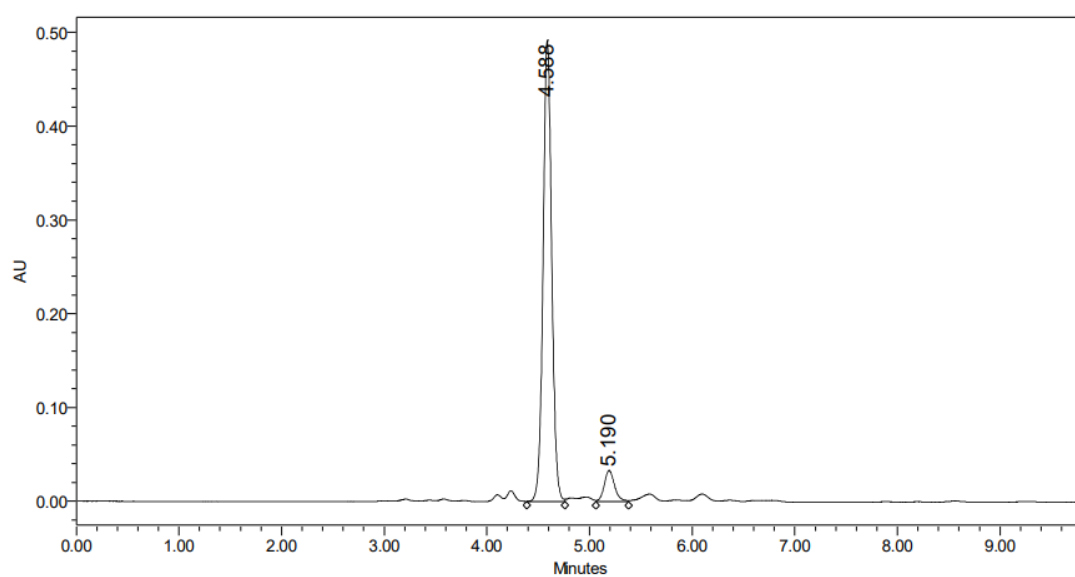
	RT	Area	% Area	Height
1	6.251	3644135	95.47	417623
2	7.727	173093	4.53	16302

Racemic 15



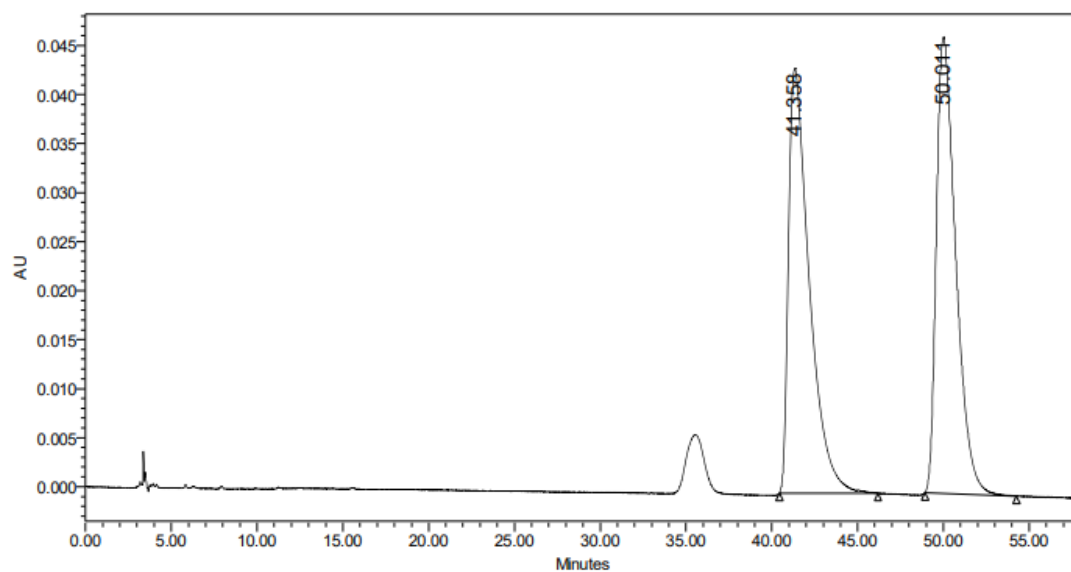
	RT	Area	% Area	Height
1	4.626	8537310	50.31	1415210
2	5.232	8432208	49.69	1222912

Enantioenriched 15



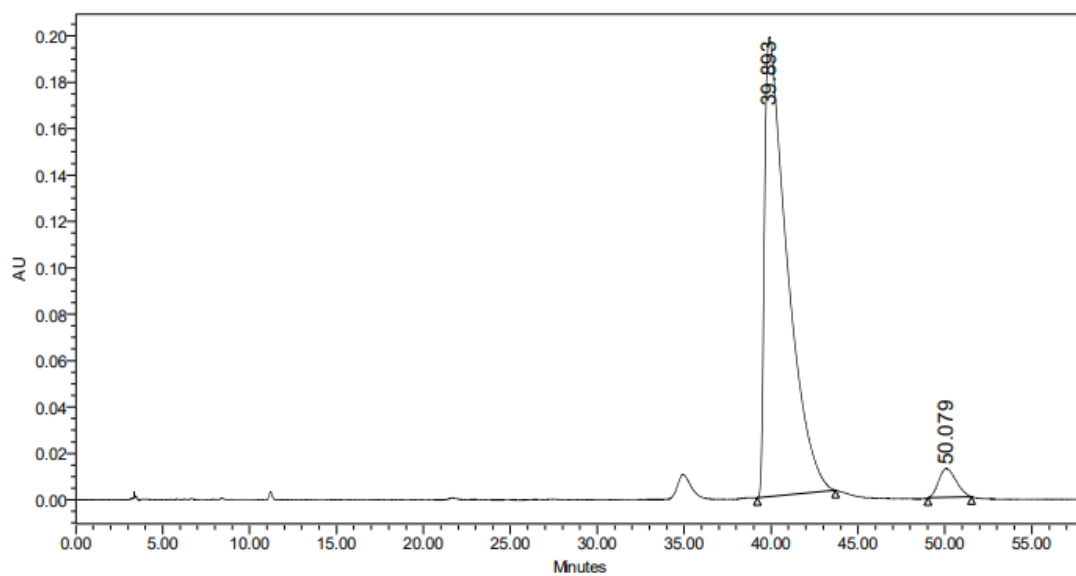
	RT	Area	% Area	Height
1	4.588	2867617	92.44	491701
2	5.190	234422	7.56	33321

Racemic 16



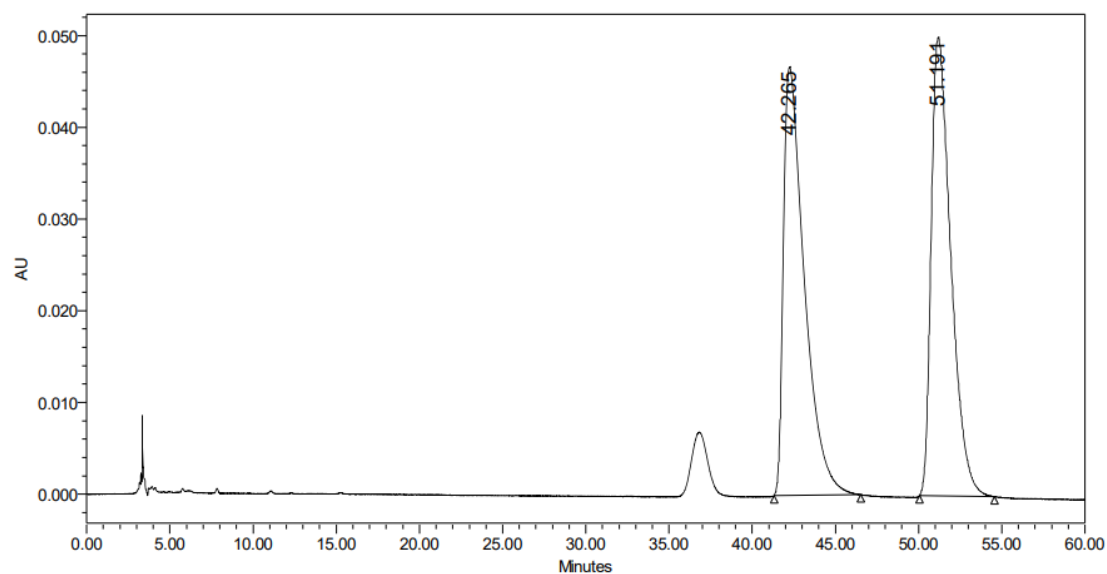
	RT	Area	% Area	Height
1	41.358	3641041	49.95	43330
2	50.011	3647858	50.05	46539

Enantioenriched 16



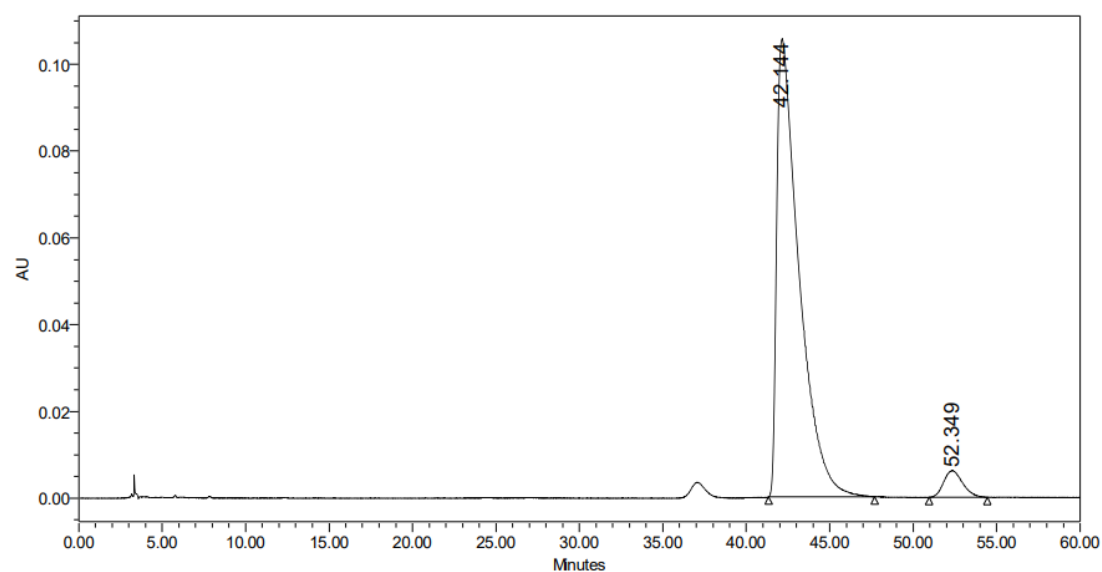
	RT	Area	% Area	Height
1	39.893	18097908	95.43	198060
2	50.079	866041	4.57	12405

Racemic 17



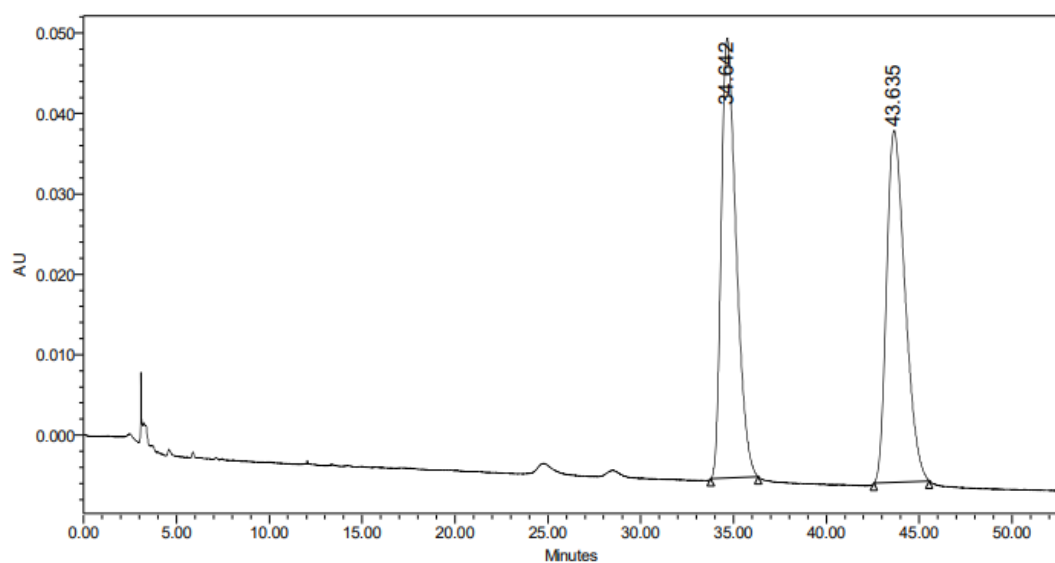
	RT	Area	% Area	Height
1	42.265	4083613	49.82	46723
2	51.191	4113600	50.18	49964

Enantioenriched 17



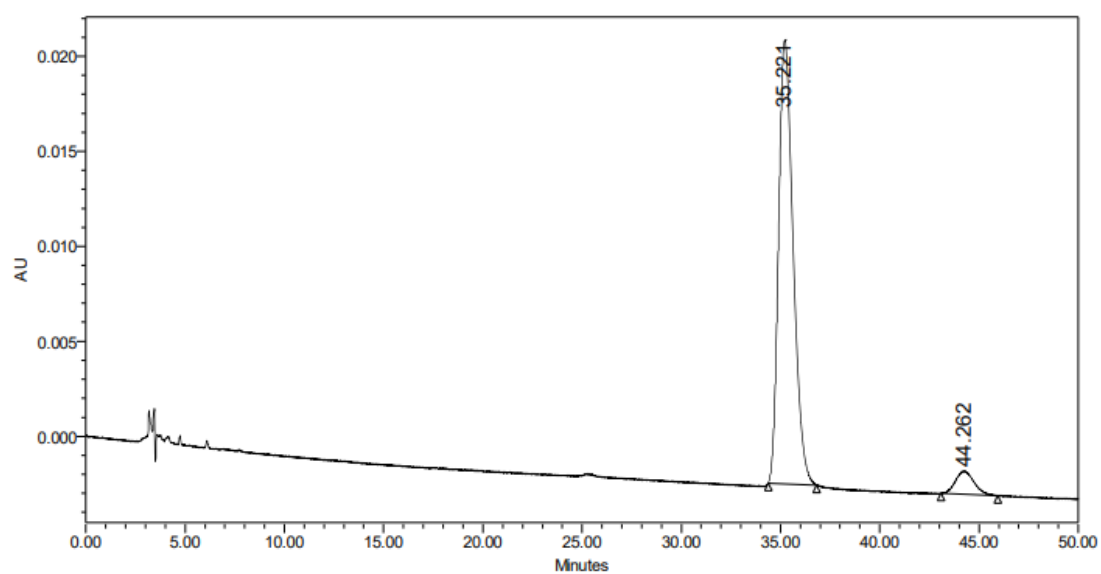
	RT	Area	% Area	Height
1	42.144	9786571	95.27	105536
2	52.349	486124	4.73	6157

Racemic 18



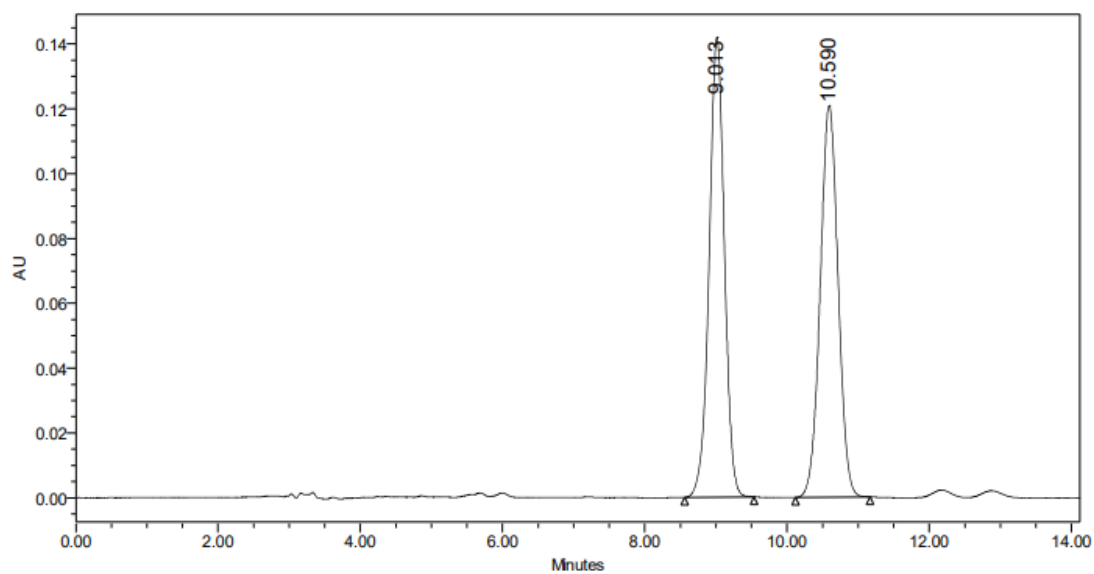
	RT	Area	% Area	Height
1	34.642	3094293	50.44	54671
2	43.635	3040161	49.56	43737

Enantioenriched 18



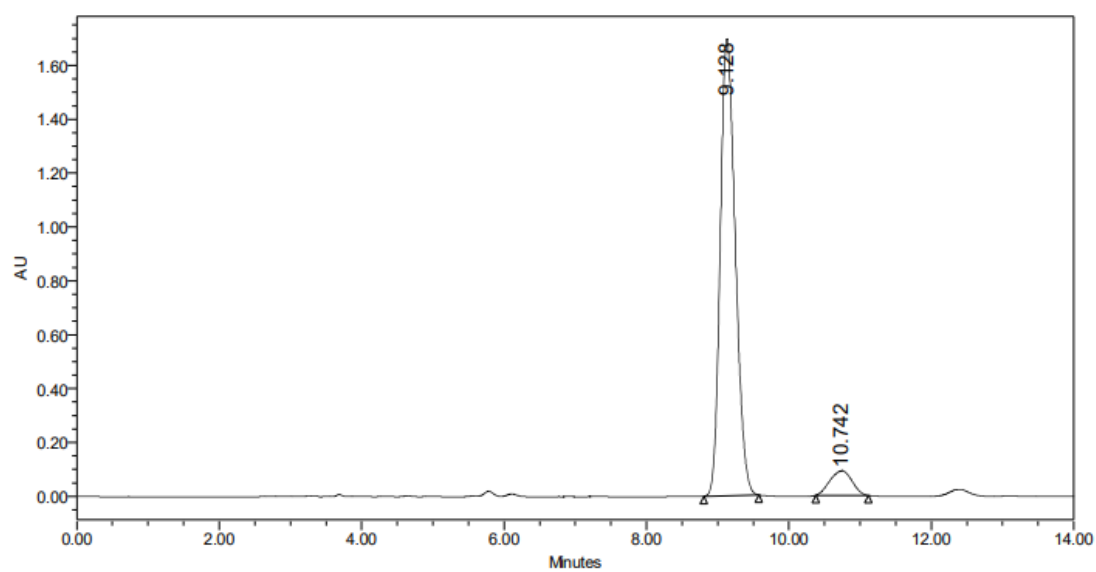
	RT	Area	% Area	Height
1	35.221	1195035	93.87	23369
2	44.262	77998	6.13	1224

Racemic 19



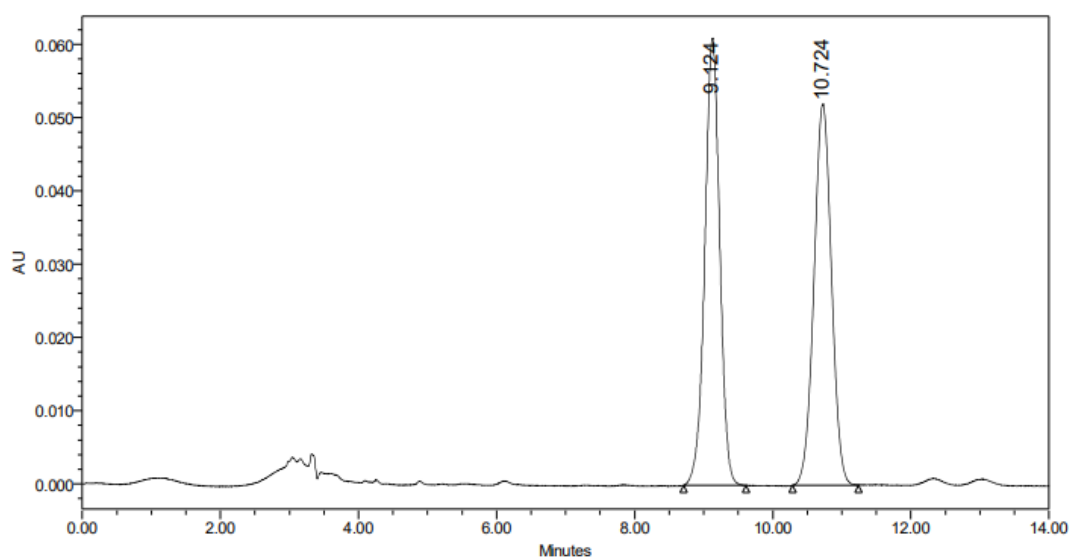
	RT	Area	% Area	Height
1	9.013	2111378	49.95	141859
2	10.590	2115798	50.05	120832

Enantioenriched 19



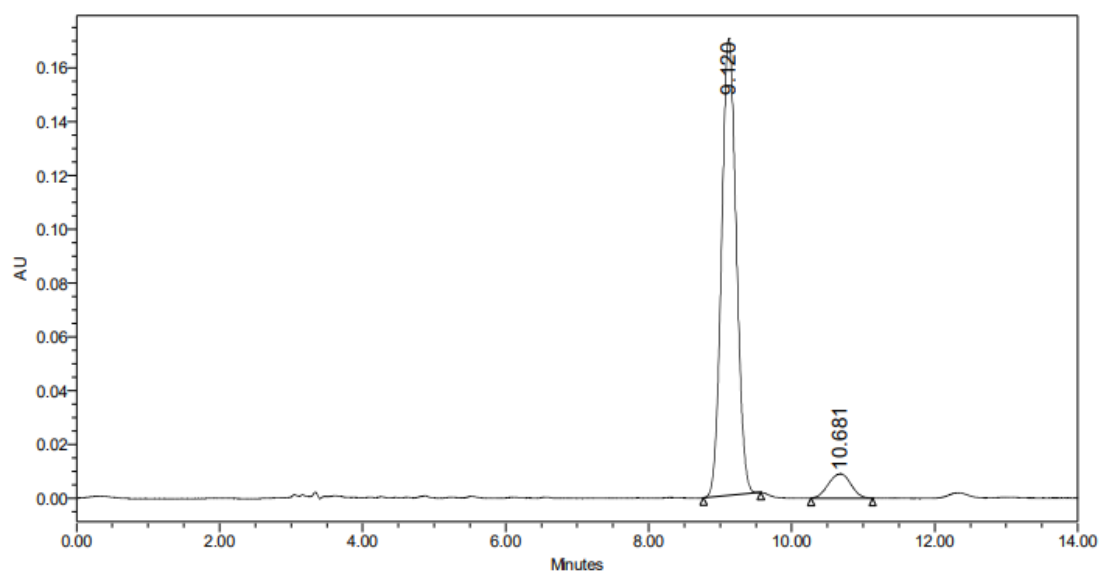
	RT	Area	% Area	Height
1	9.128	24741023	92.64	1694979
2	10.742	1964344	7.36	91391

Racemic 20



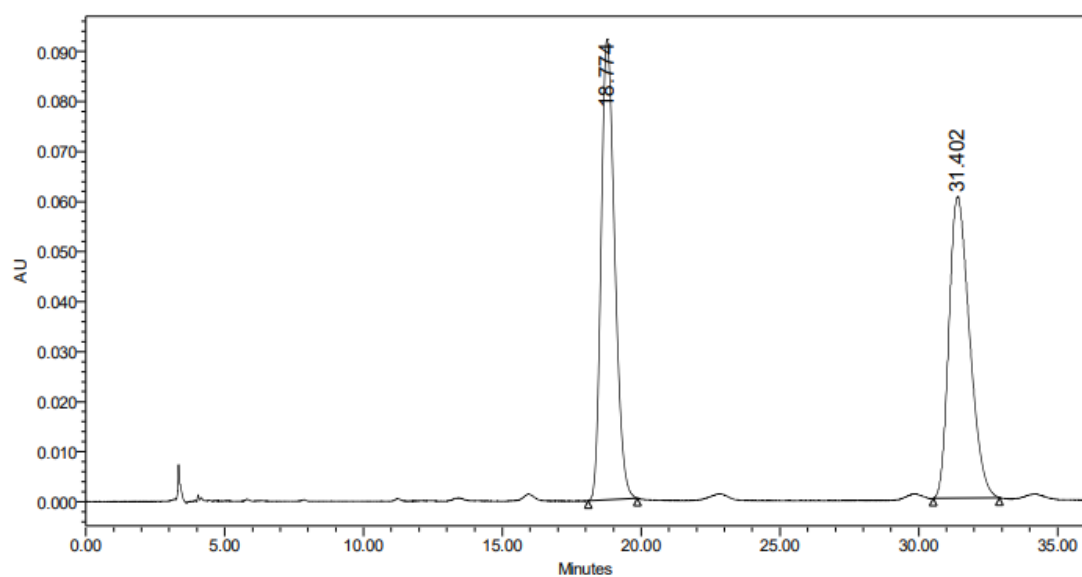
	RT	Area	% Area	Height
1	9.124	915564	50.00	61007
2	10.724	915551	50.00	52020

Enantioenriched 20



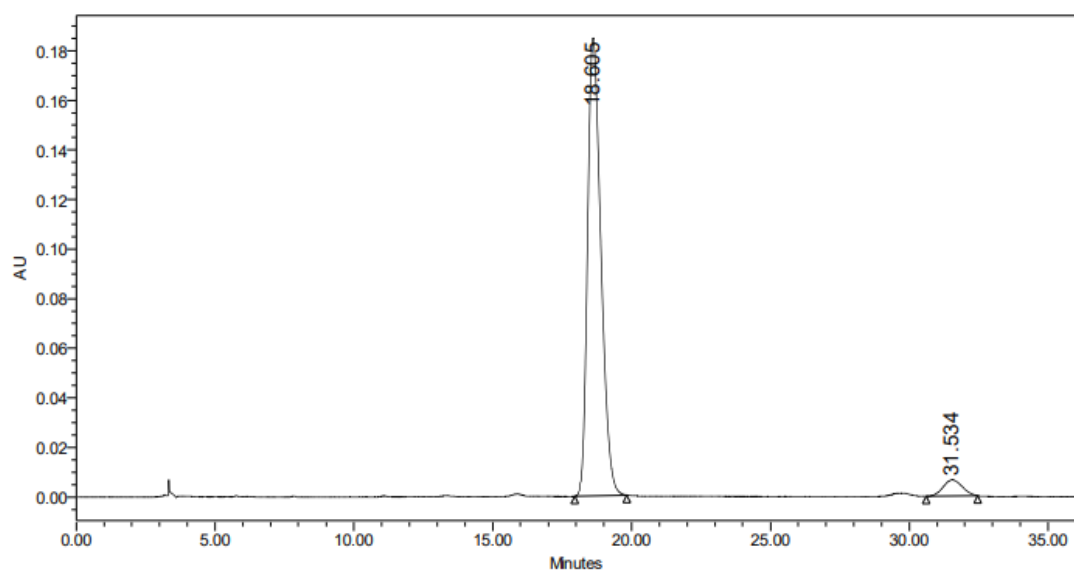
	RT	Area	% Area	Height
1	9.120	2407124	92.45	169757
2	10.681	196497	7.55	9026

Racemic 21



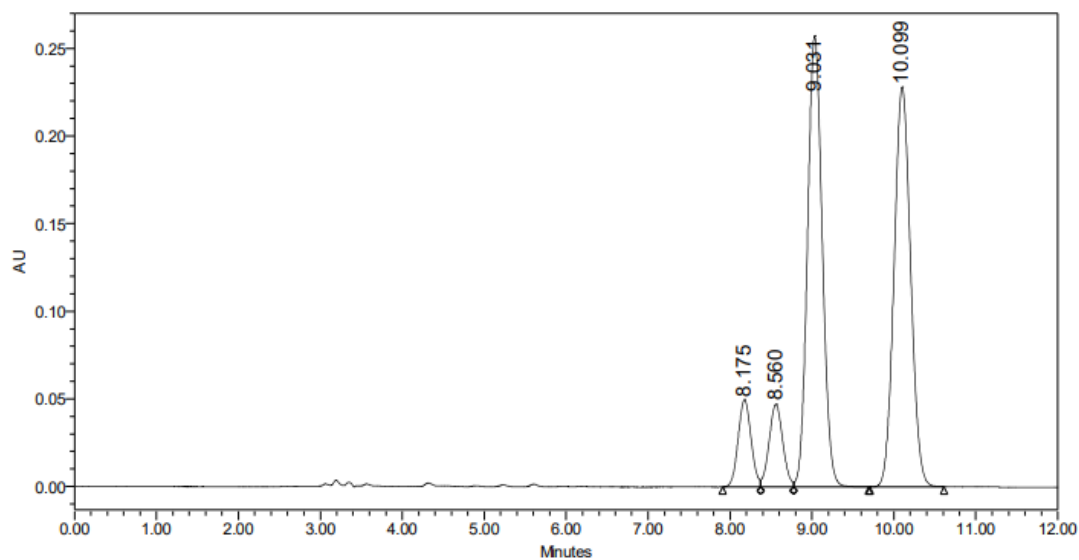
	RT	Area	% Area	Height
1	18.774	3129071	50.18	91965
2	31.402	3107222	49.82	60206

Enantioenriched 21



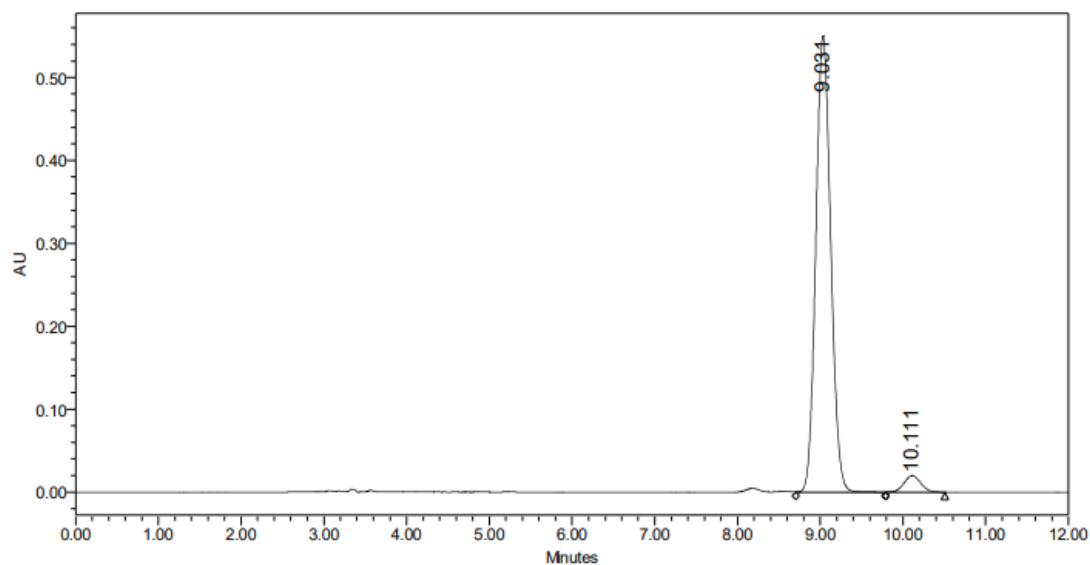
	RT	Area	% Area	Height
1	18.605	6190795	95.19	184453
2	31.534	313097	4.81	6520

Racemic 22



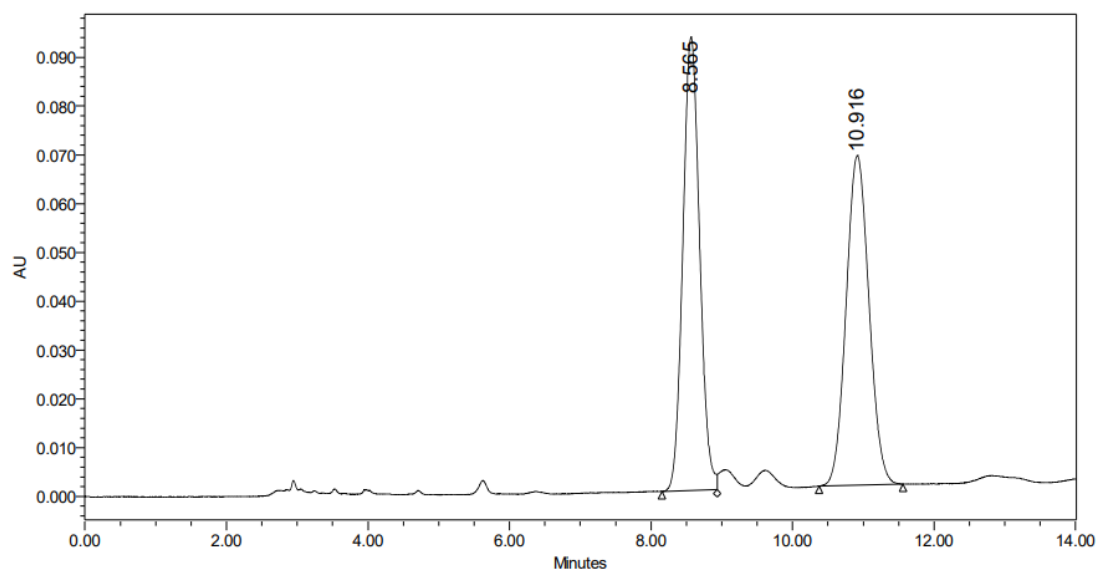
	RT	Area	% Area	Height
1	8.175	548421	7.28	49745
2	8.560	548982	7.29	47143
3	9.031	3221687	42.78	257422
4	10.099	3210867	42.64	228138

Enantioenriched 22



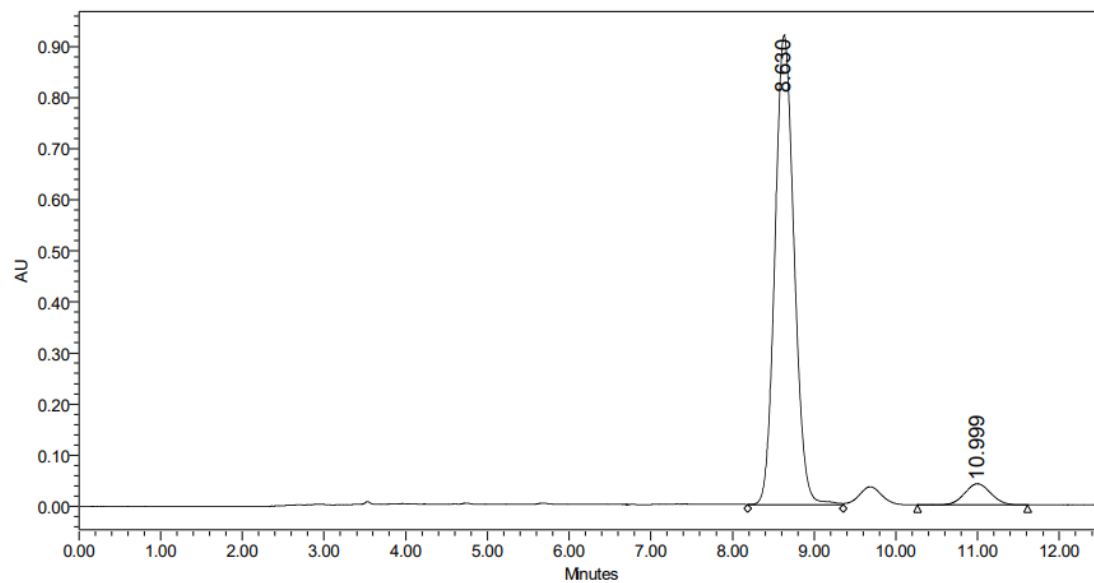
	RT	Area	% Area	Height
1	9.031	6888033	96.08	549983
2	10.111	280720	3.92	19860

Racemic 23



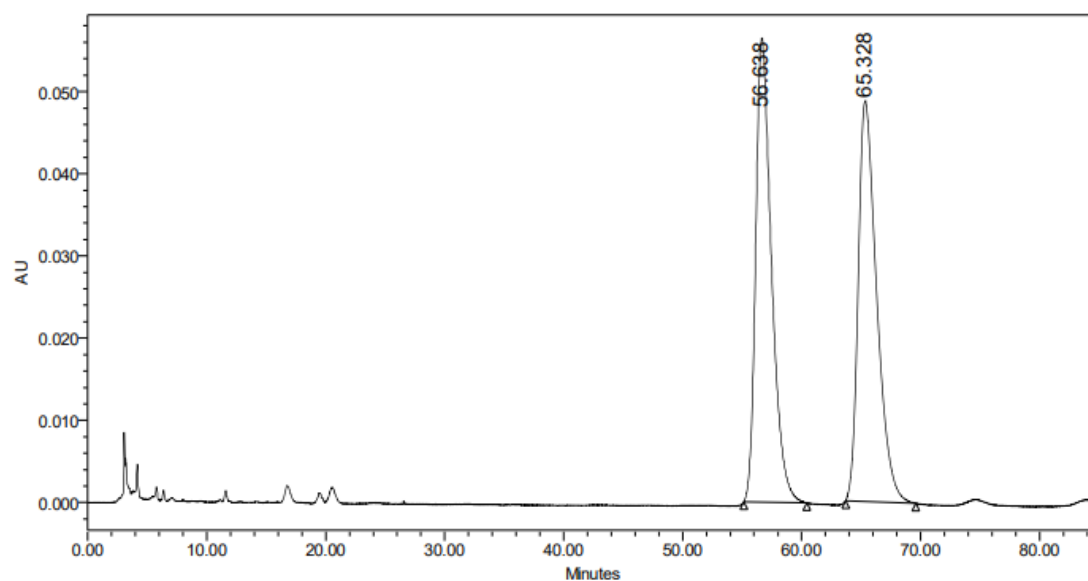
	RT	Area	% Area	Height
1	8.565	1525664	50.19	92926
2	10.916	1514094	49.81	67561

Enantioenriched 23



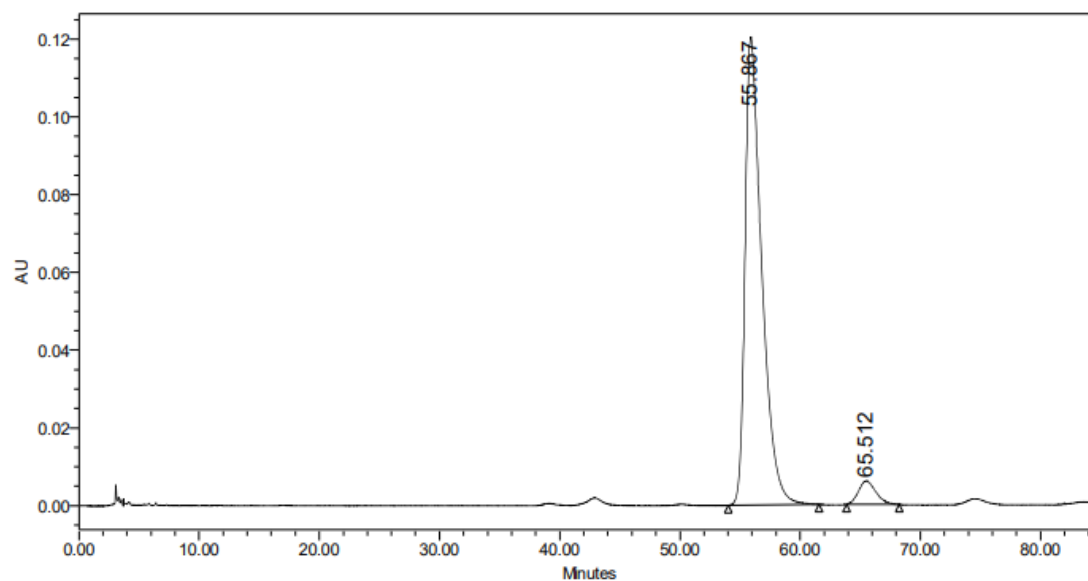
	RT	Area	% Area	Height
1	8.630	15017404	94.25	919076
2	10.999	916980	5.75	41144

Racemic 24



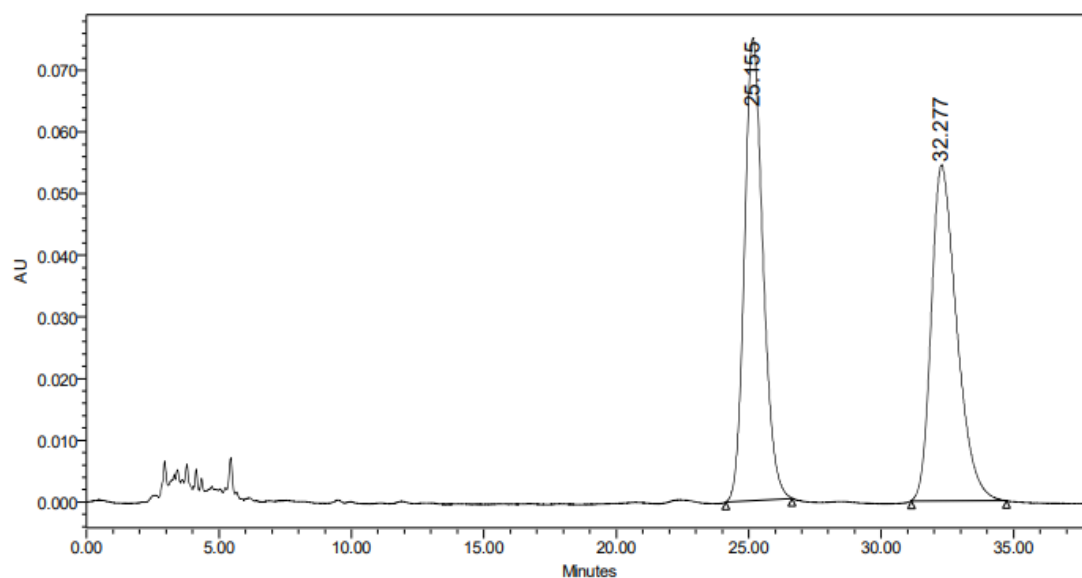
	RT	Area	% Area	Height
1	56.638	5253636	50.08	56392
2	65.328	5237467	49.92	48696

Enantioenriched 24



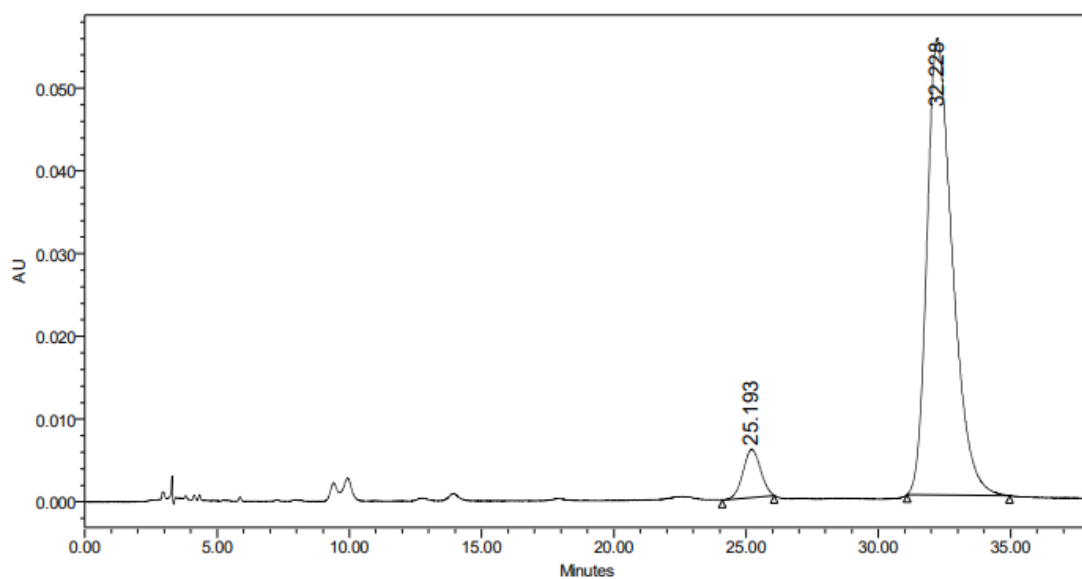
	RT	Area	% Area	Height
1	55.867	11486952	95.04	120368
2	65.512	599647	4.96	5997

Racemic 25



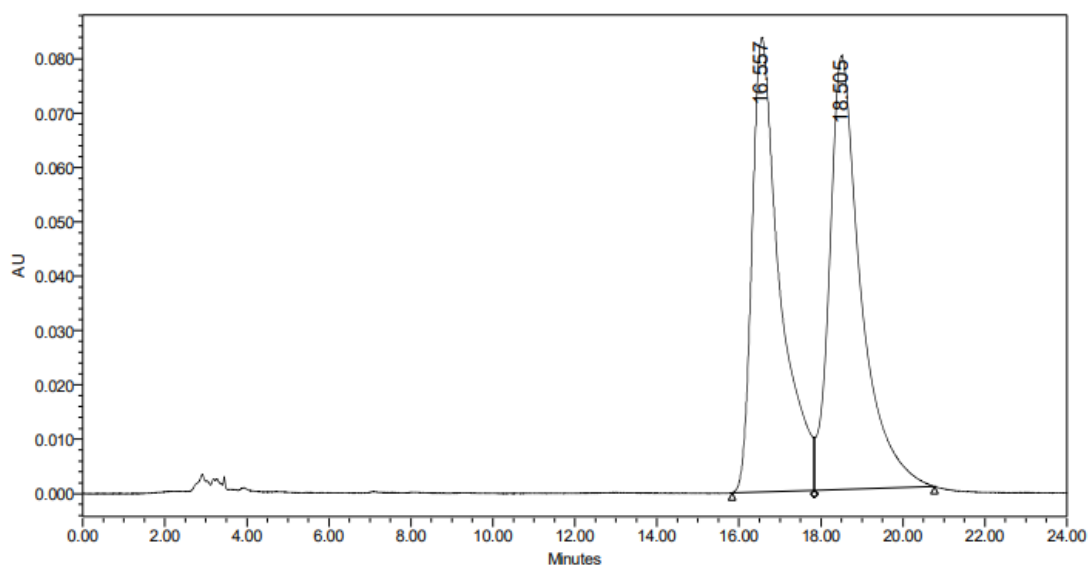
	RT	Area	% Area	Height
1	25.155	3676574	50.14	75015
2	32.277	3656598	49.86	54410

Enantioenriched 25



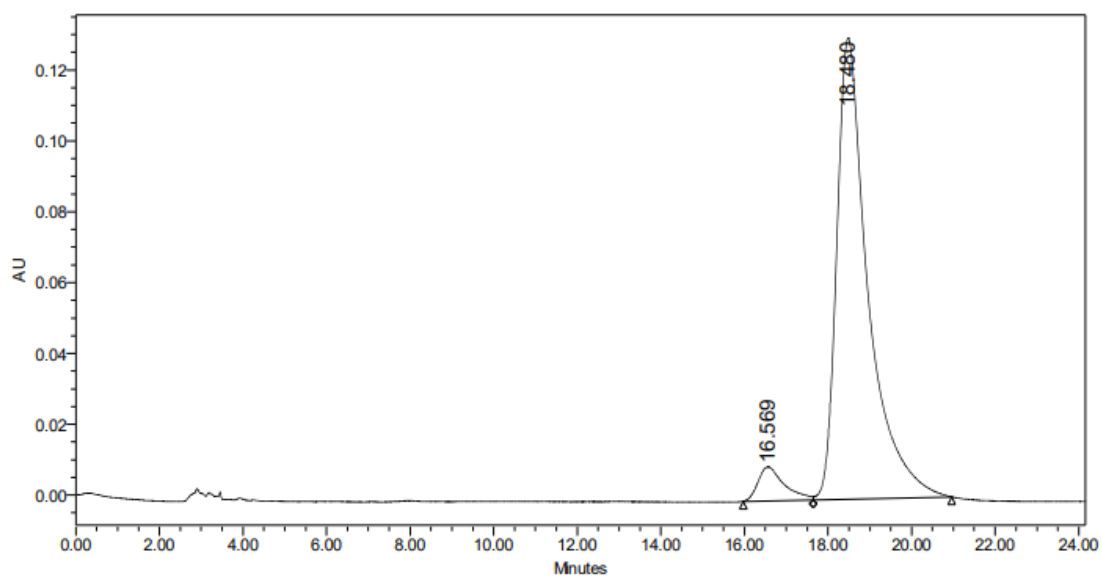
	RT	Area	% Area	Height
1	25.193	271251	6.81	5848
2	32.228	3709188	93.19	55177

Racemic 26



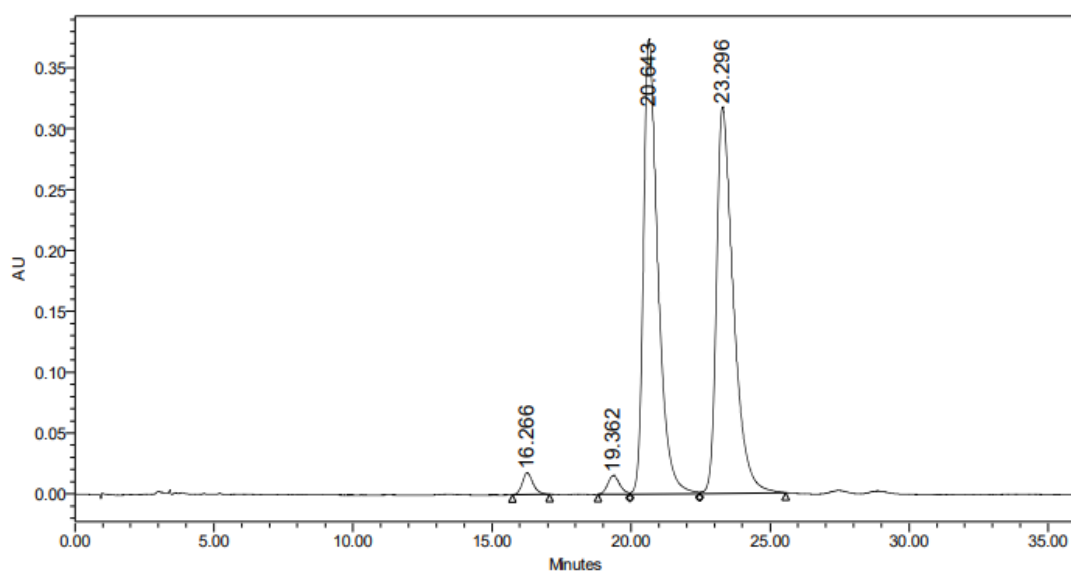
	RT	Area	% Area	Height
1	16.557	3950375	48.21	83528
2	18.505	4244317	51.79	79787

Enantioenriched 26



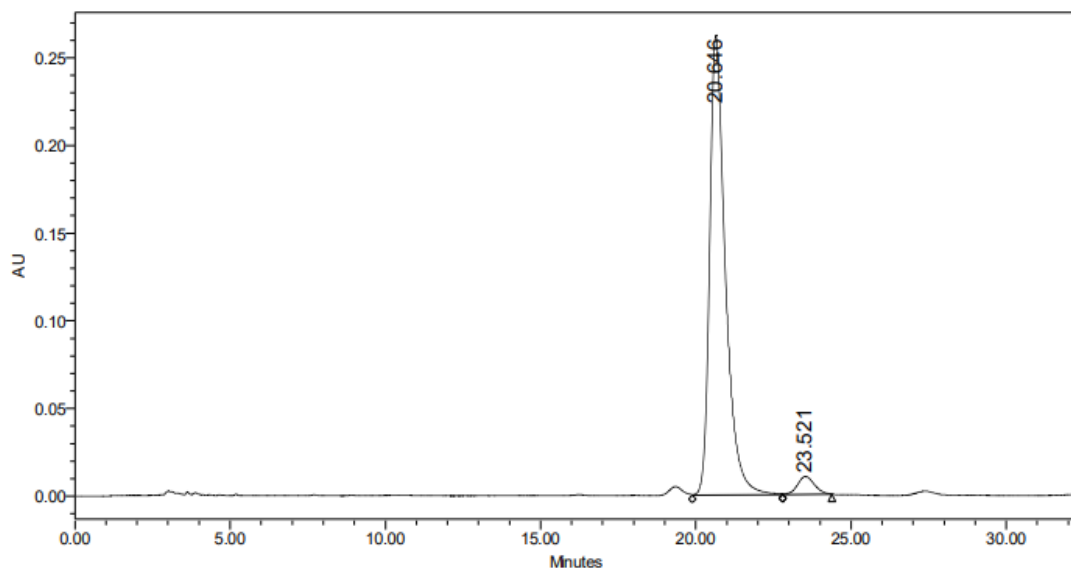
	RT	Area	% Area	Height
1	16.569	416571	5.77	9553
2	18.480	6798593	94.23	130097

Racemic 27



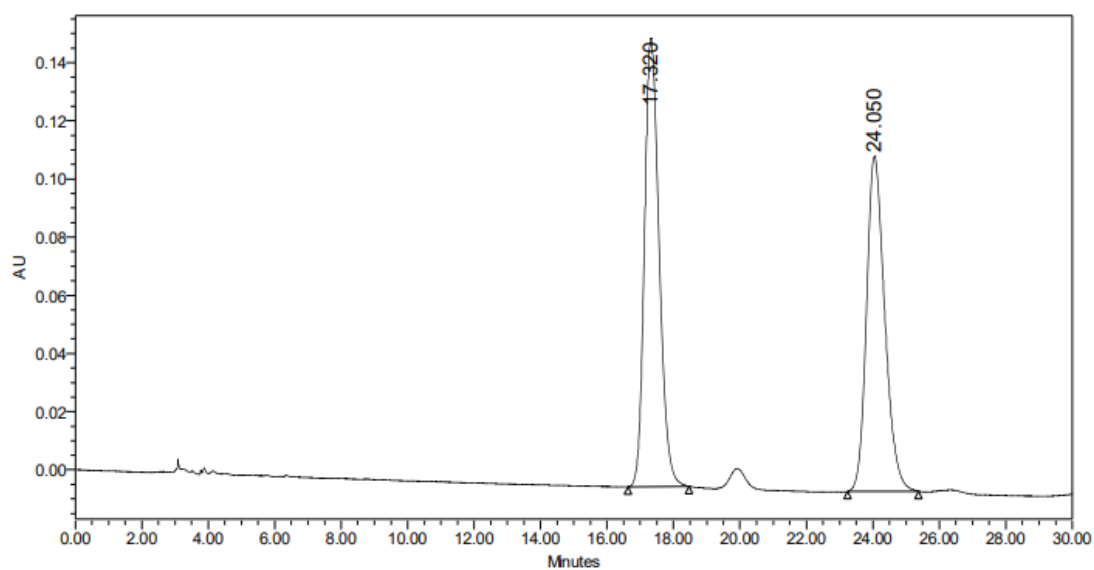
	RT	Area	% Area	Height
1	16.266	483005	1.75	17884
2	19.362	461967	1.68	15429
3	20.643	13321511	48.33	373791
4	23.296	13294976	48.24	317233

Enantioenriched 27



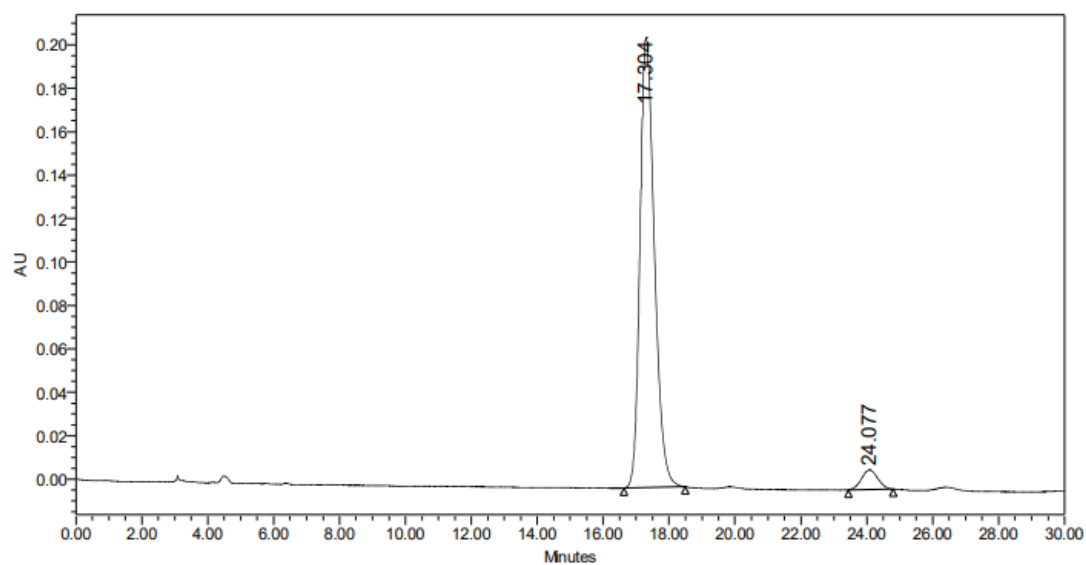
	RT	Area	% Area	Height
1	20.646	9207676	95.97	262106
2	23.521	386466	4.03	10205

Racemic 28



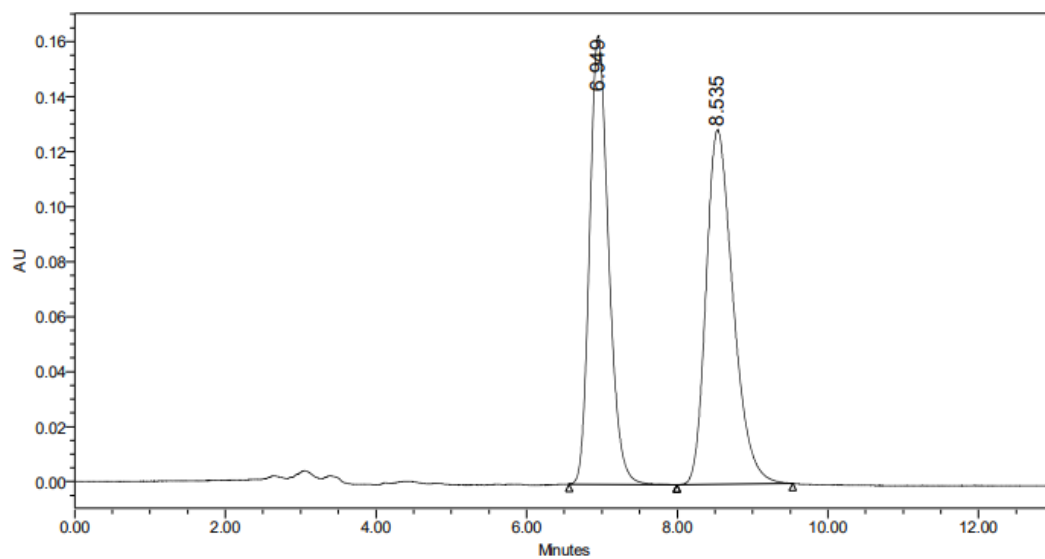
	RT	Area	% Area	Height
1	17.320	4654268	51.44	154052
2	24.050	4392879	48.56	115231

Enantioenriched 28



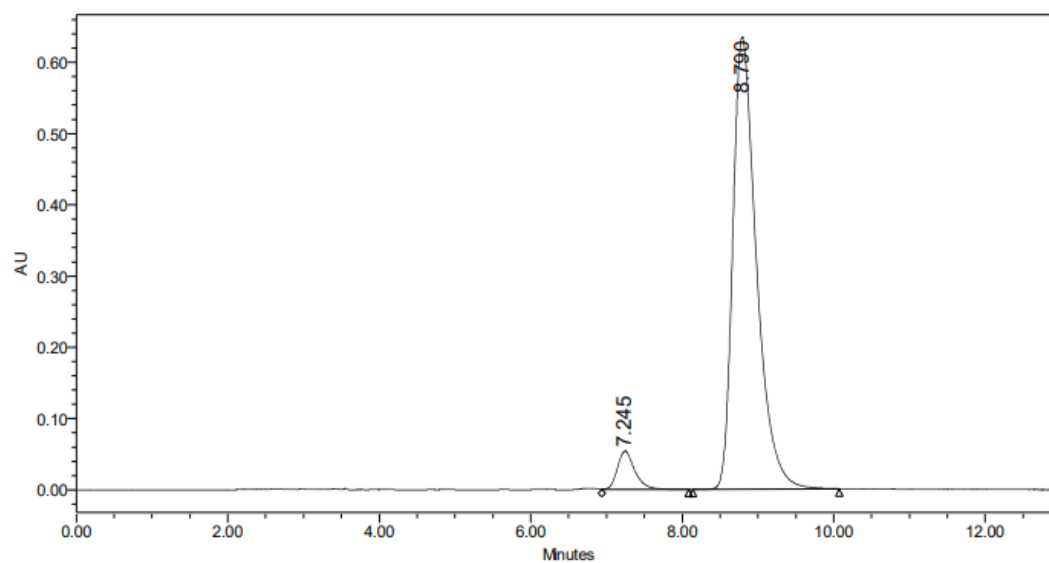
	RT	Area	% Area	Height
1	17.304	6180228	95.20	207175
2	24.077	311697	4.80	8989

Racemic 29



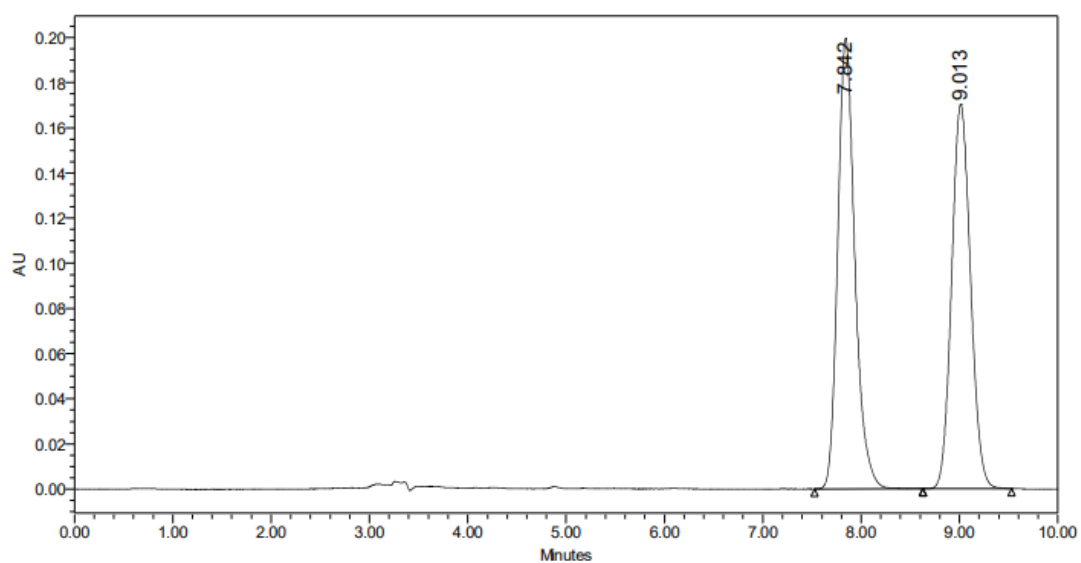
	RT	Area	% Area	Height
1	6.949	2866601	47.25	163010
2	8.535	3200299	52.75	128865

Enantioenriched 29



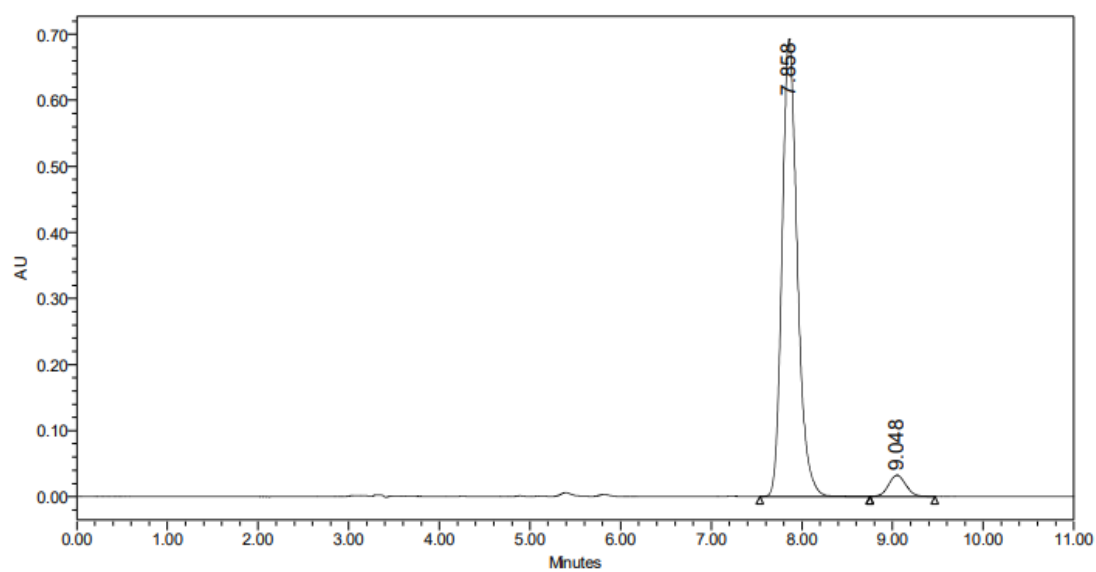
	RT	Area	% Area	Height
1	7.245	869556	5.93	53938
2	8.790	13786436	94.07	634056

Racemic 30



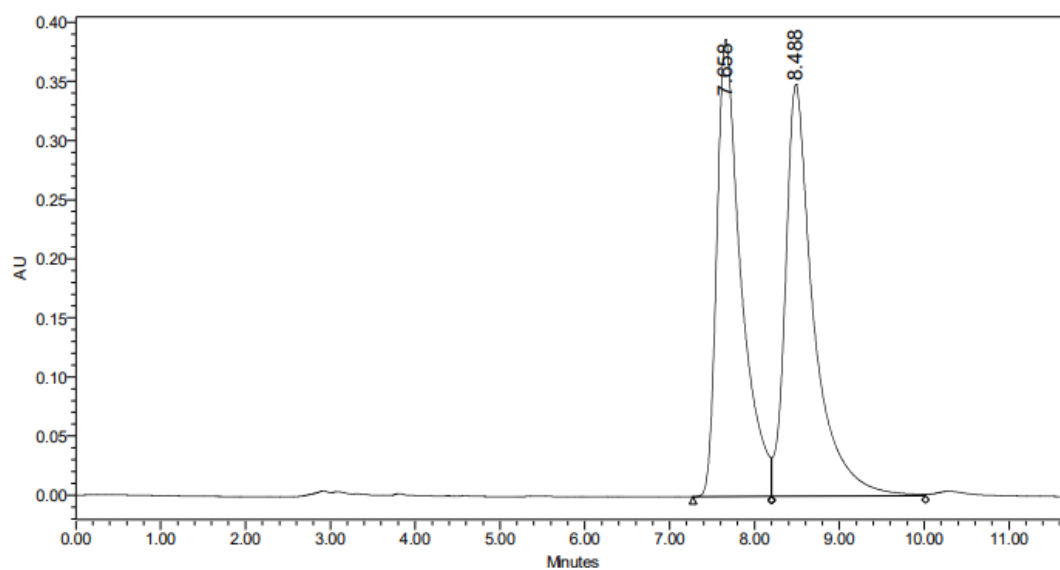
	RT	Area	% Area	Height
1	7.842	2408026	51.56	199359
2	9.013	2262704	48.44	170236

Enantioenriched 30



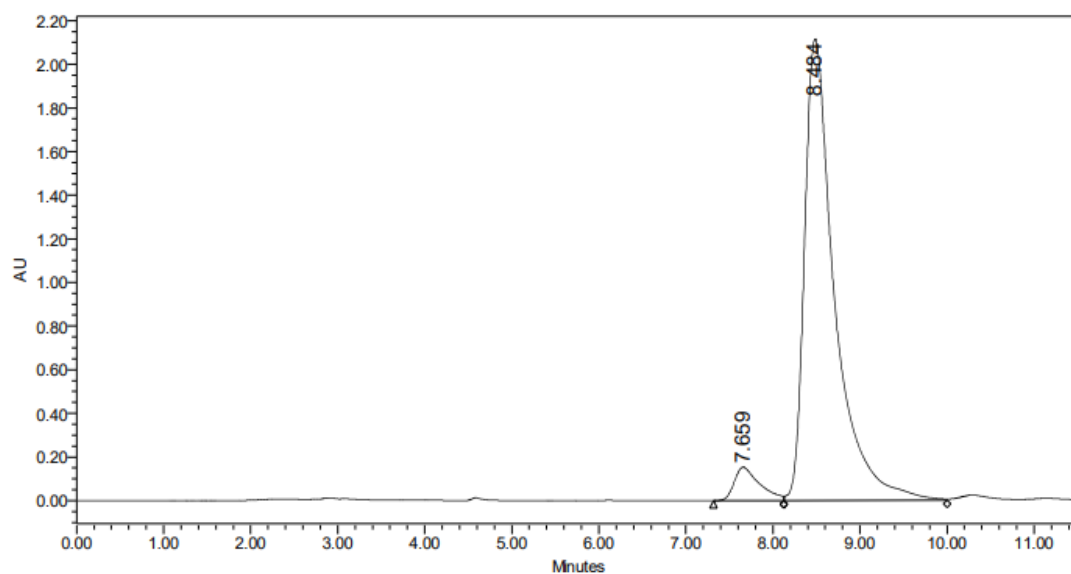
	RT	Area	% Area	Height
1	7.858	8098722	95.01	692231
2	9.048	425062	4.99	32193

Racemic 31



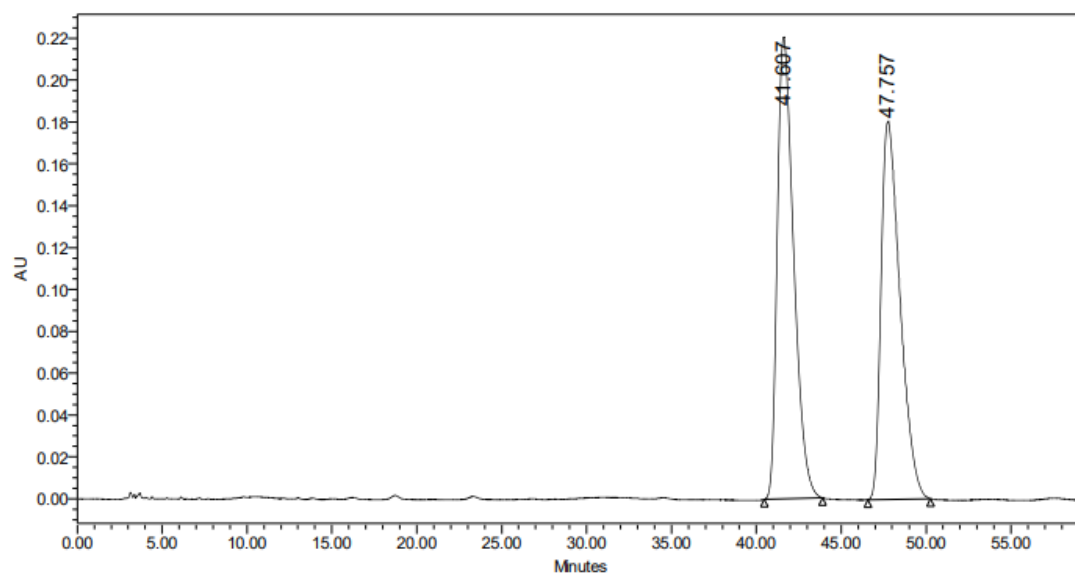
	RT	Area	% Area	Height
1	7.658	7629857	48.76	386450
2	8.488	8016900	51.24	348412

Enantioenriched 31



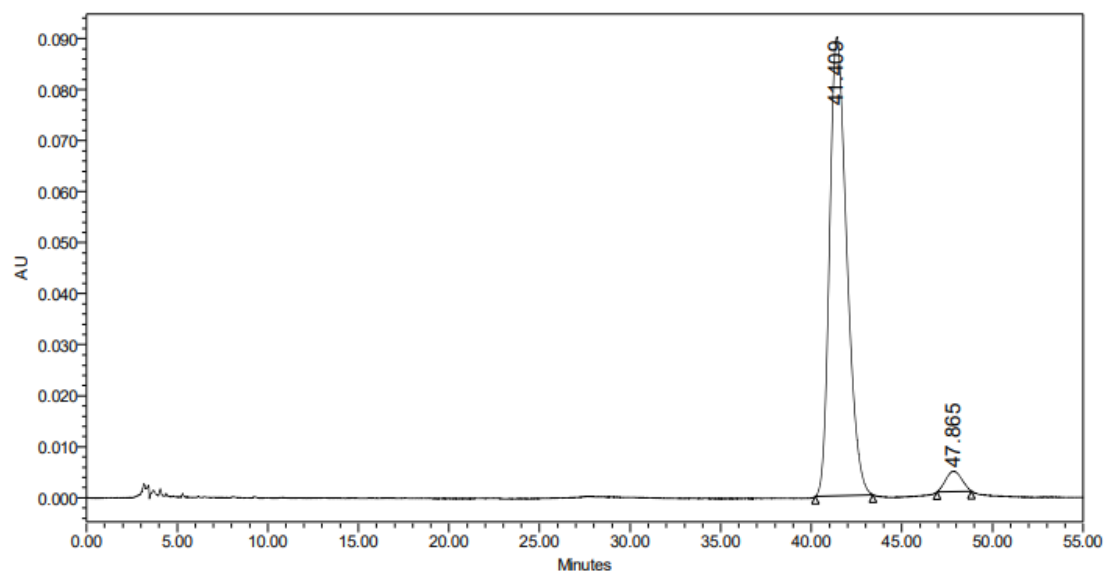
	RT	Area	% Area	Height
1	7.659	3073207	5.74	152510
2	8.484	50490796	94.26	2112692

Racemic 32



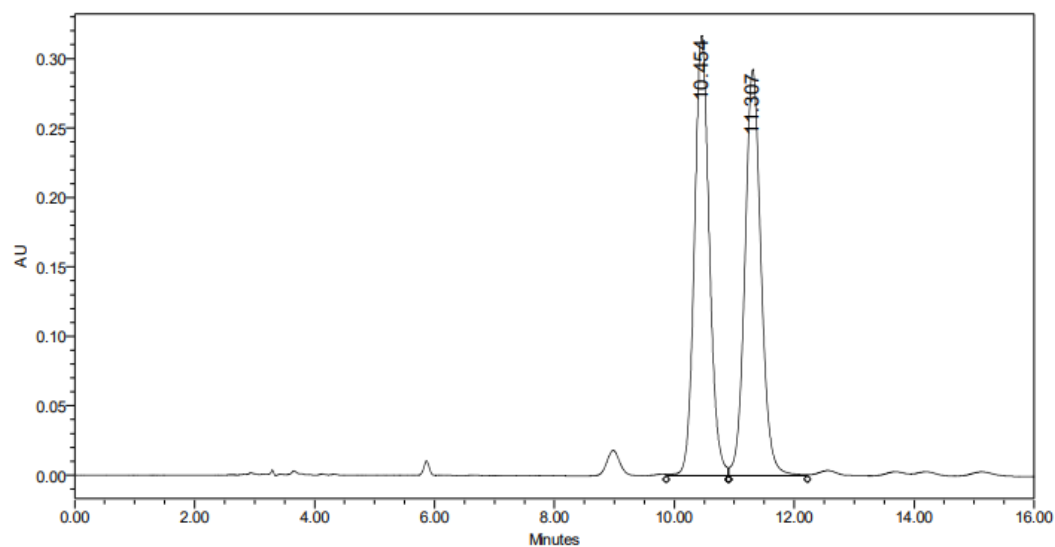
	RT	Area	% Area	Height
1	41.607	14883819	51.63	220469
2	47.757	13942537	48.37	180597

Enantioenriched 32



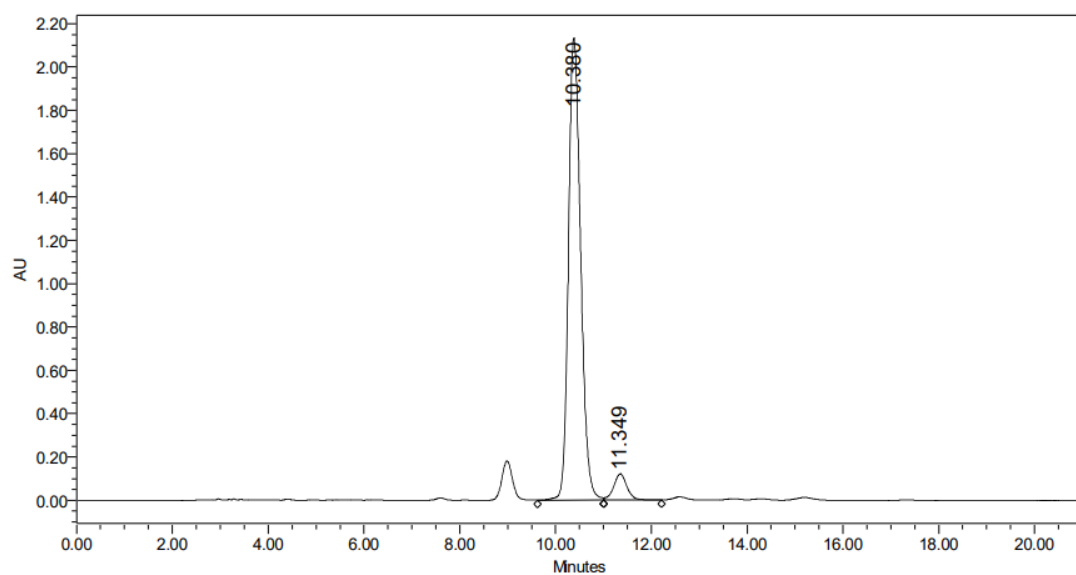
	RT	Area	% Area	Height
1	41.409	5919033	96.06	89898
2	47.865	242673	3.94	3997

Racemic 33



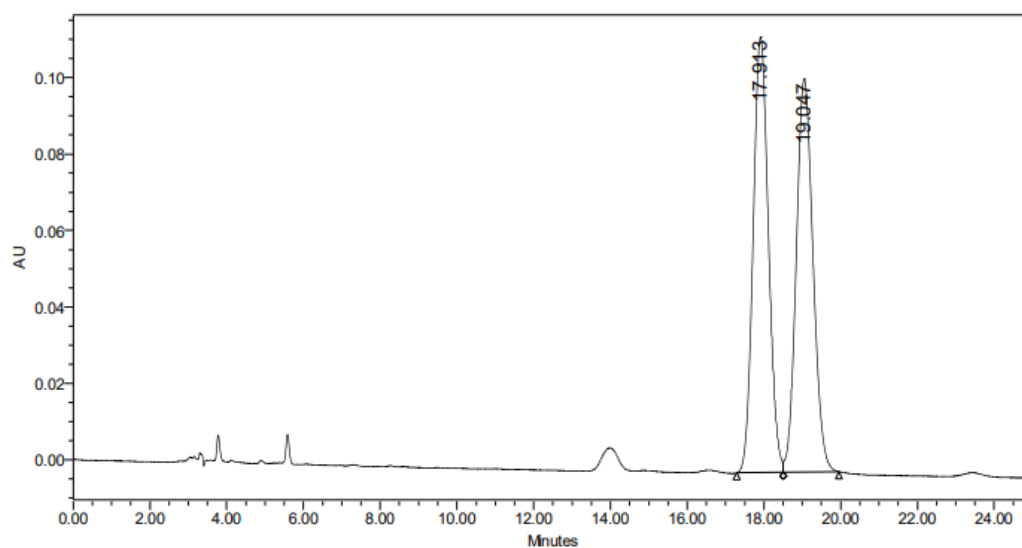
	RT	Area	% Area	Height
1	10.454	5413216	49.69	316661
2	11.307	5480491	50.31	292391

Enantioenriched 33



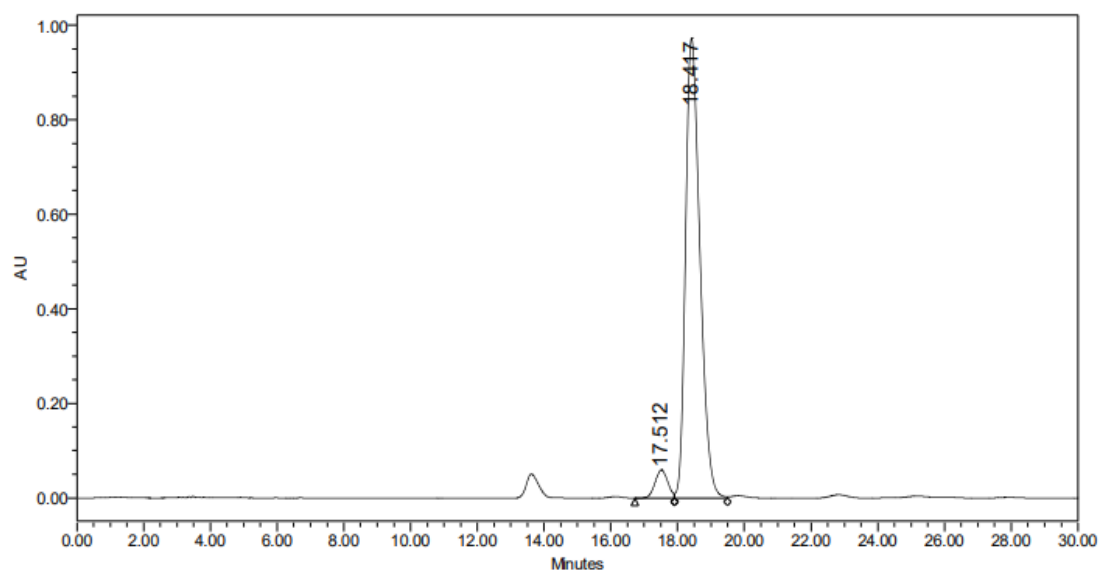
	RT	Area	% Area	Height
1	10.380	37384004	94.14	2131029
2	11.349	2326264	5.86	120742

Racemic 34



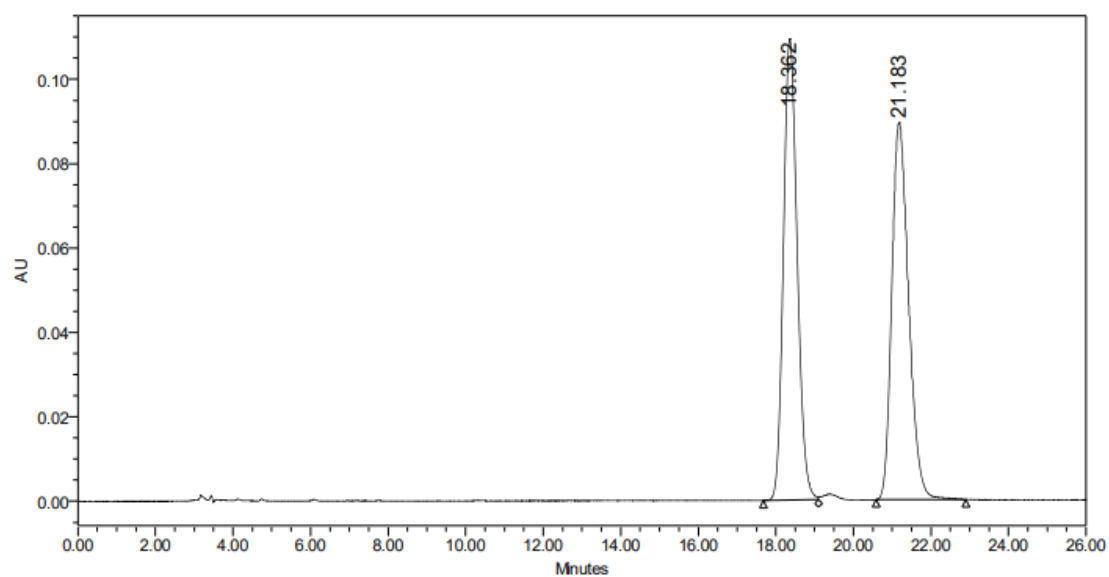
	RT	Area	% Area	Height
1	17.913	3144904	50.13	113979
2	19.047	3128446	49.87	102907

Enantioenriched 34



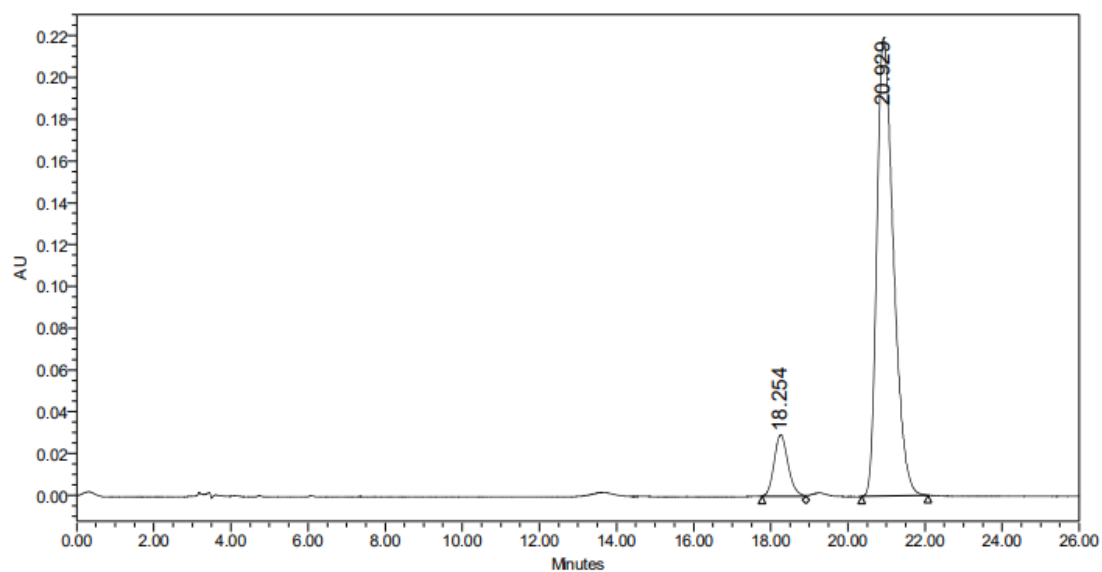
	RT	Area	% Area	Height
1	17.512	1548499	5.03	59209
2	18.417	29261728	94.97	972741

Racemic 35



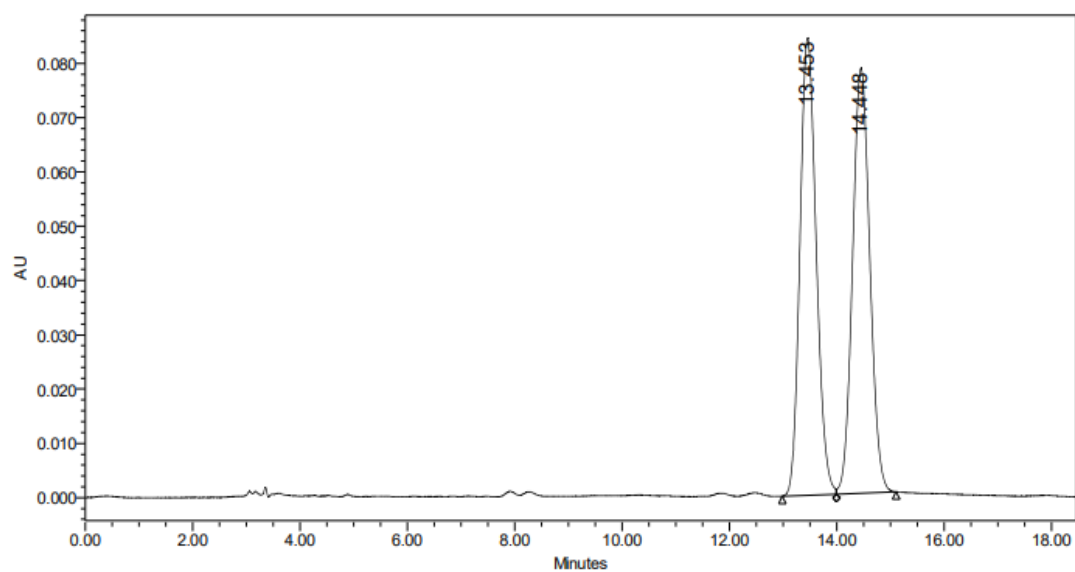
	RT	Area	% Area	Height
1	18.362	2706733	50.29	109255
2	21.183	2675889	49.71	89346

Enantioenriched 35



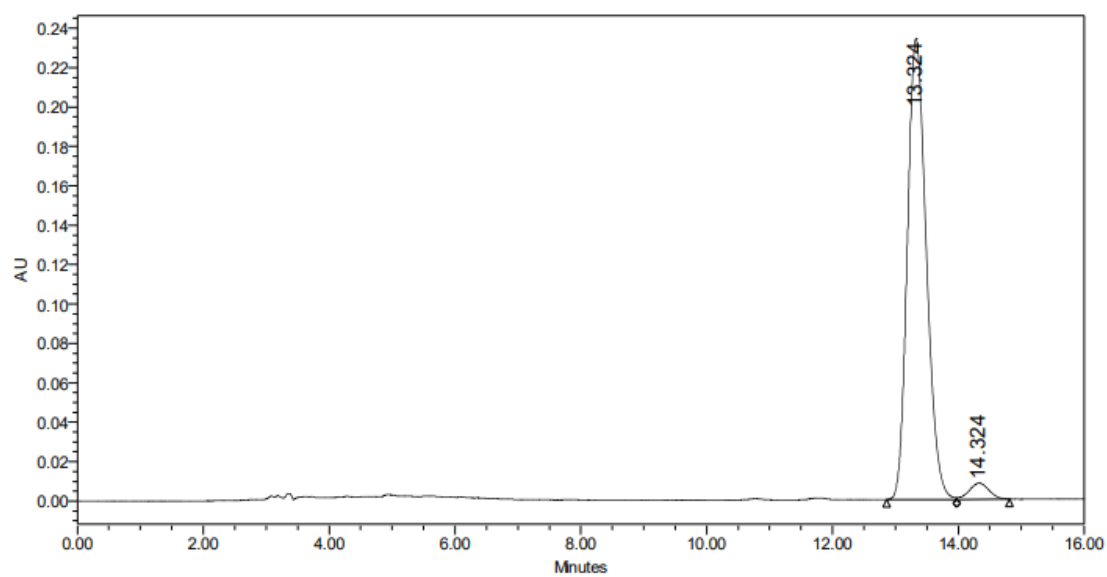
	RT	Area	% Area	Height
1	18.254	736020	10.10	29393
2	20.929	6549020	89.90	219325

Racemic 36



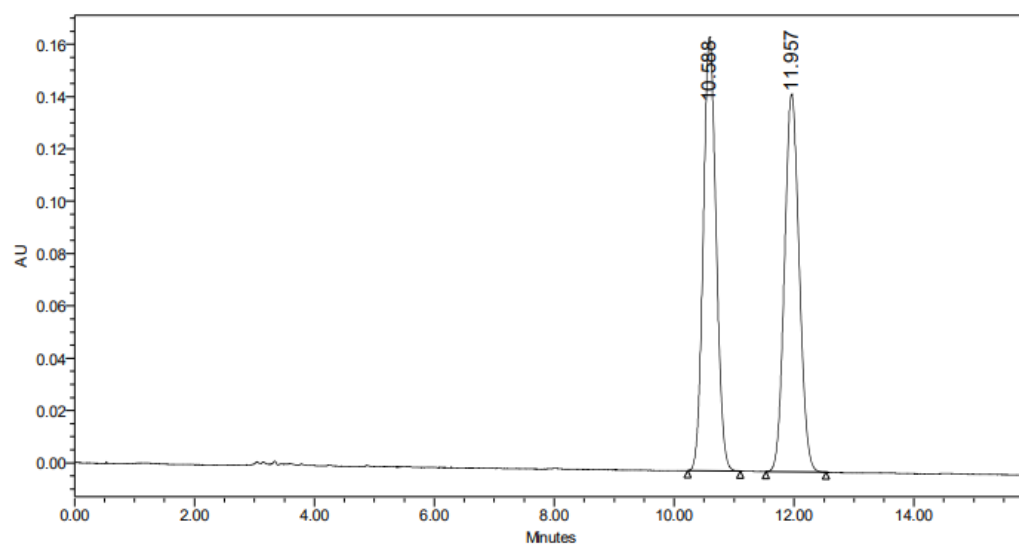
	RT	Area	% Area	Height
1	13.453	1767764	50.31	84182
2	14.448	1746282	49.69	78339

Enantioenriched 36



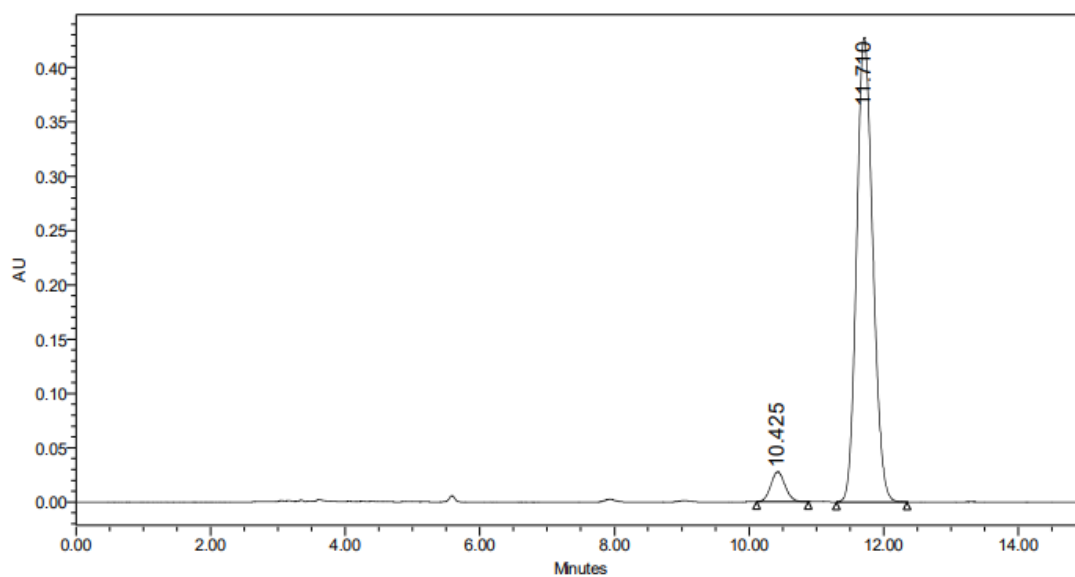
	RT	Area	% Area	Height
1	13.324	4853499	96.40	233874
2	14.324	181224	3.60	8225

Racemic 37



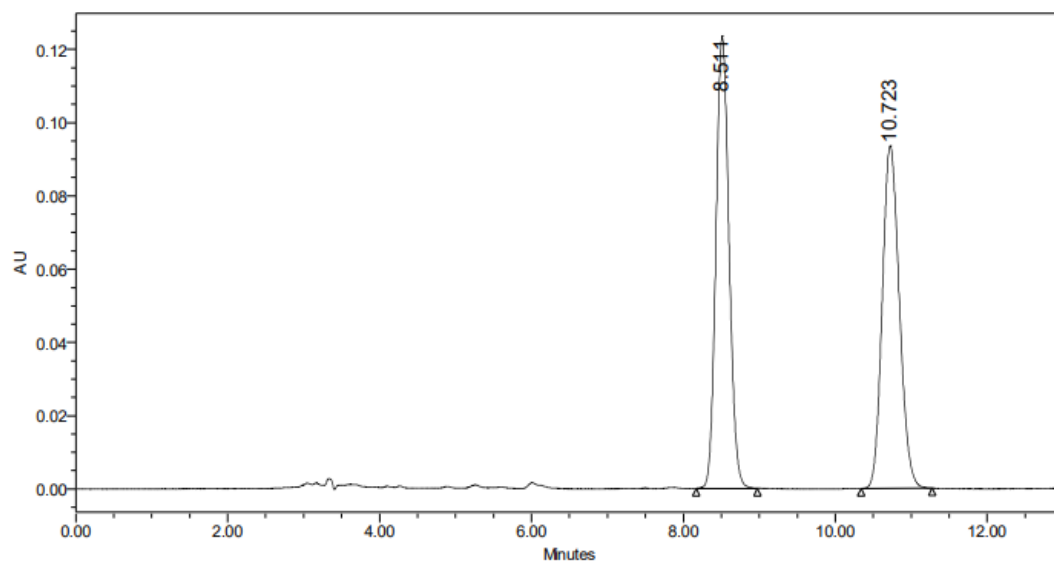
	RT	Area	% Area	Height
1	10.588	2465654	50.01	165699
2	11.957	2464954	49.99	144351

Enantioenriched 37



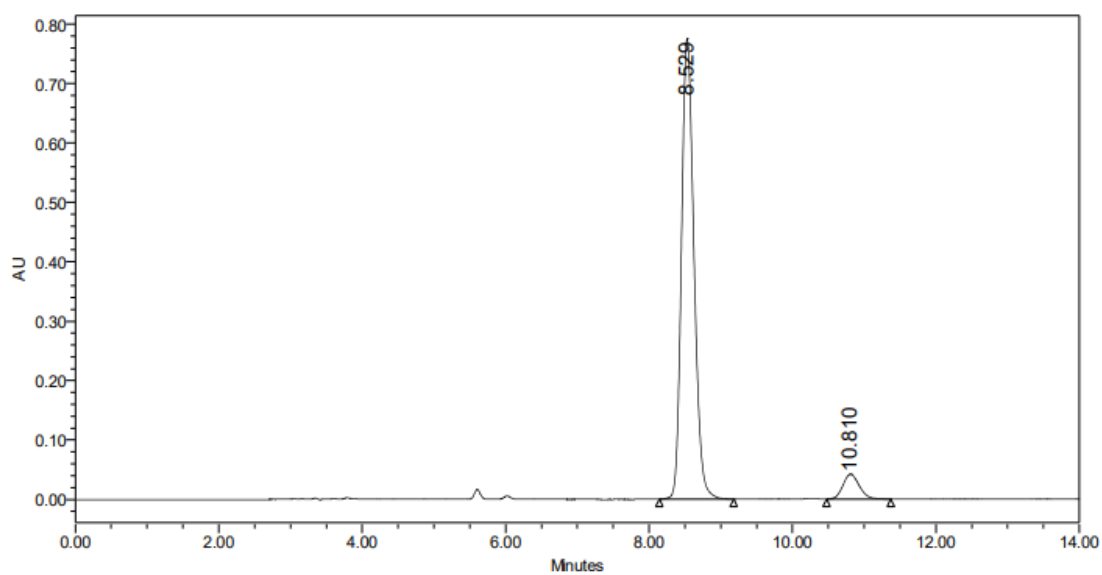
	RT	Area	% Area	Height
1	10.425	406686	5.35	27509
2	11.710	7194034	94.65	427093

Racemic 38



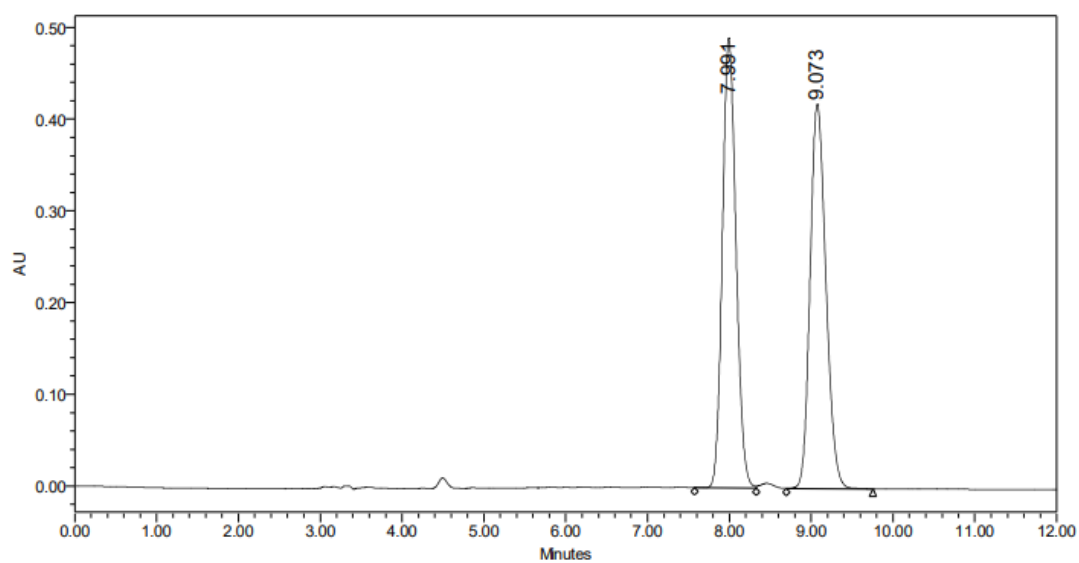
	RT	Area	% Area	Height
1	8.511	1463636	50.19	123479
2	10.723	1452566	49.81	93538

Enantioenriched 38



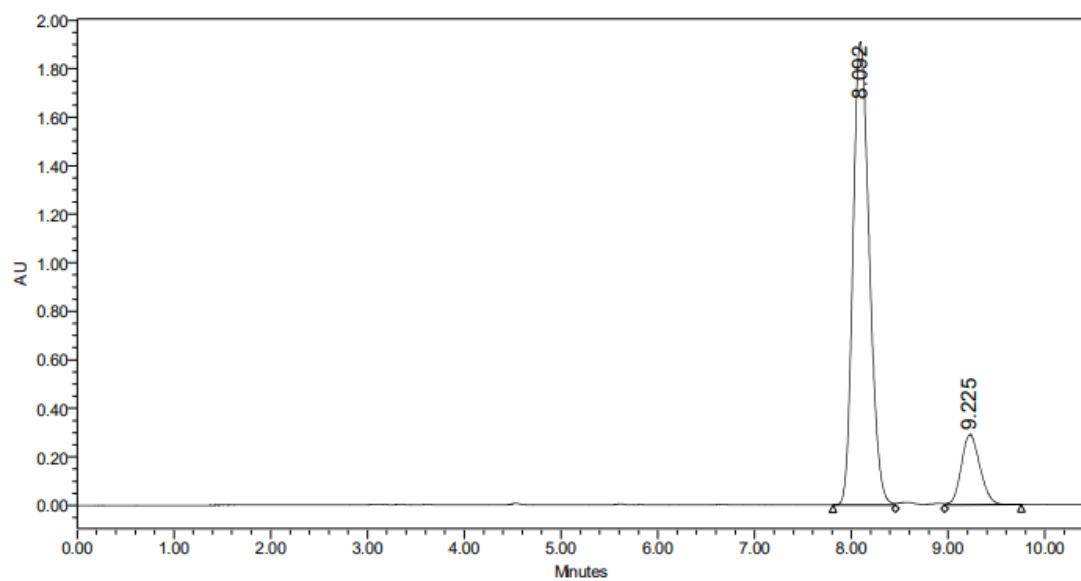
	RT	Area	% Area	Height
1	8.529	9412688	93.42	775293
2	10.810	662718	6.58	41828

Racemic 39



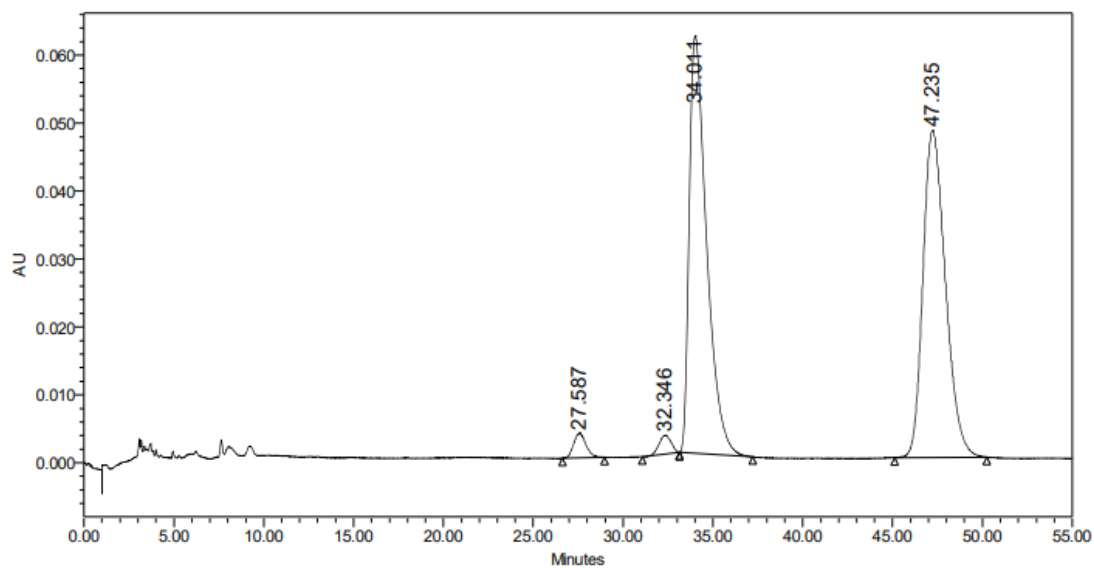
	RT	Area	% Area	Height
1	7.991	5660747	50.11	490078
2	9.073	5636031	49.89	418727

Enantioenriched 39



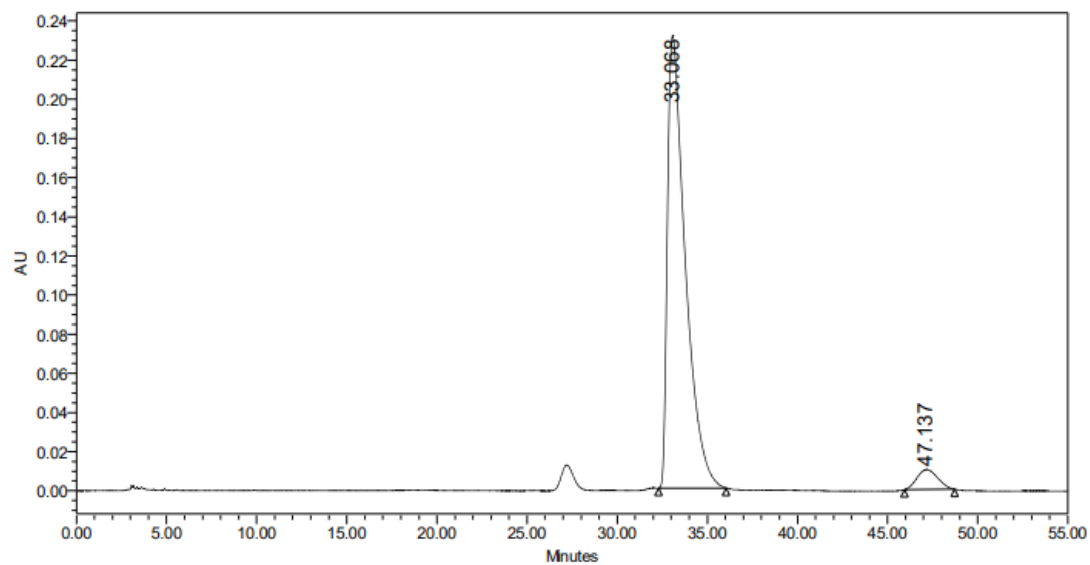
	RT	Area	% Area	Height
1	8.092	22475005	85.31	1908081
2	9.225	3871473	14.69	289309

Racemic 40



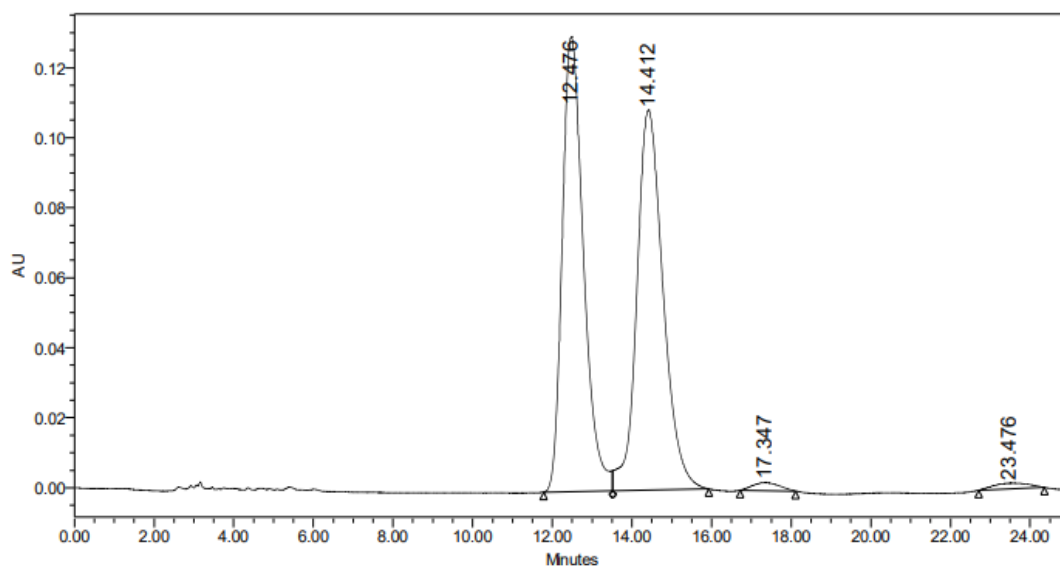
	RT	Area	% Area	Height
1	27.587	171555	1.99	3627
2	32.346	130717	1.52	2743
3	34.011	4117101	47.82	61457
4	47.235	4190570	48.67	48132

Enantioenriched 40



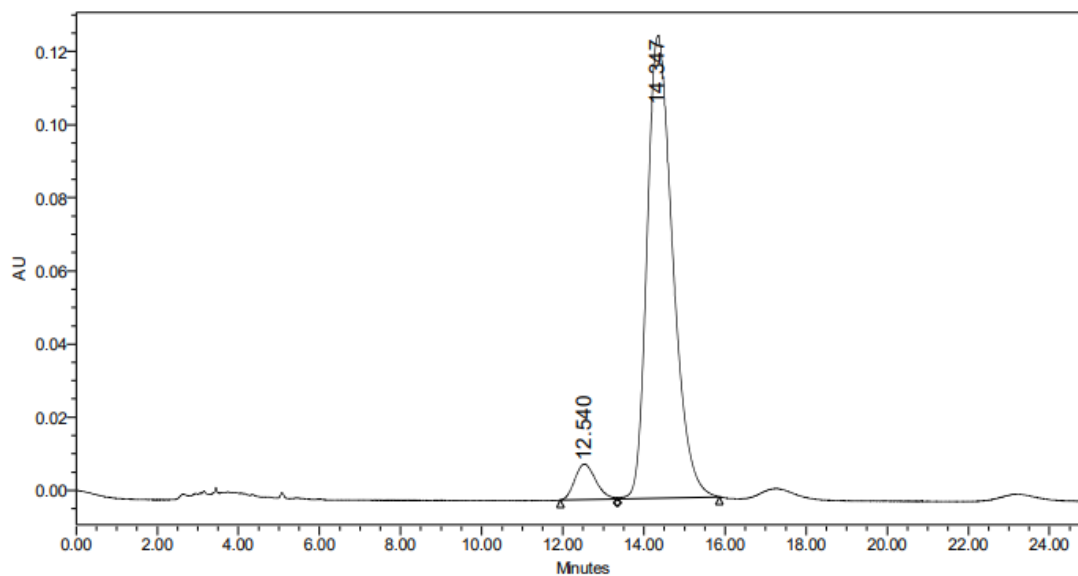
	RT	Area	% Area	Height
1	33.068	15952829	95.18	231117
2	47.137	807025	4.82	10176

Racemic 41



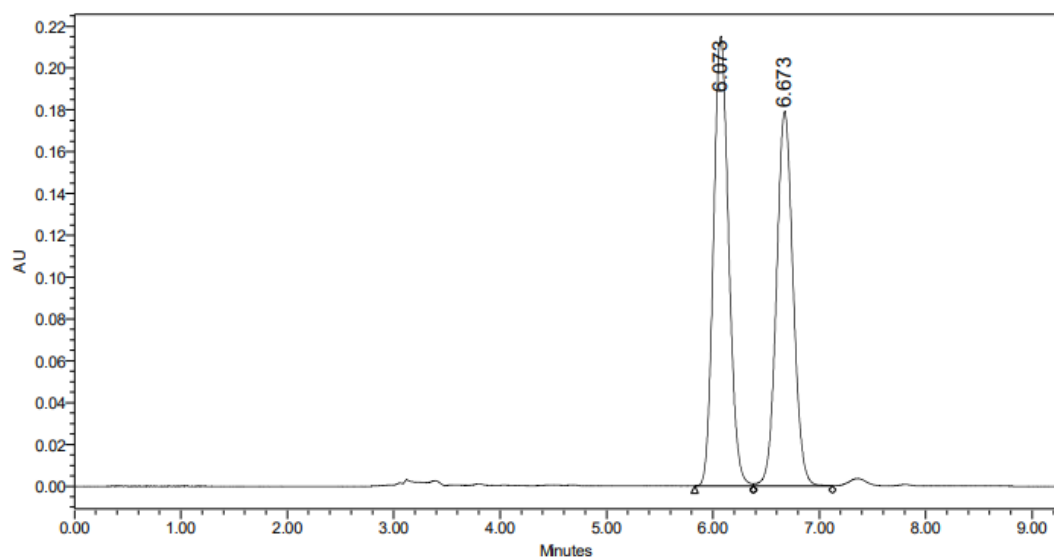
	RT	Area	% Area	Height
1	12.476	4768031	48.05	129879
2	14.412	4947730	49.86	108574
3	17.347	107703	1.09	2307
4	23.476	99979	1.01	1636

Enantioenriched 41



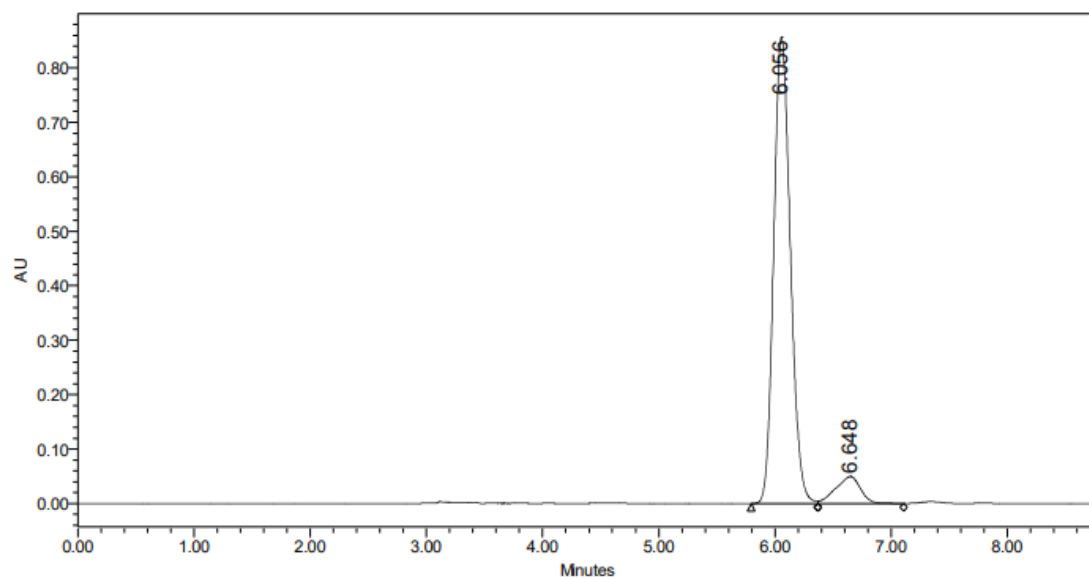
	RT	Area	% Area	Height
1	12.540	346416	5.93	9701
2	14.347	5497093	94.07	126423

Racemic 42



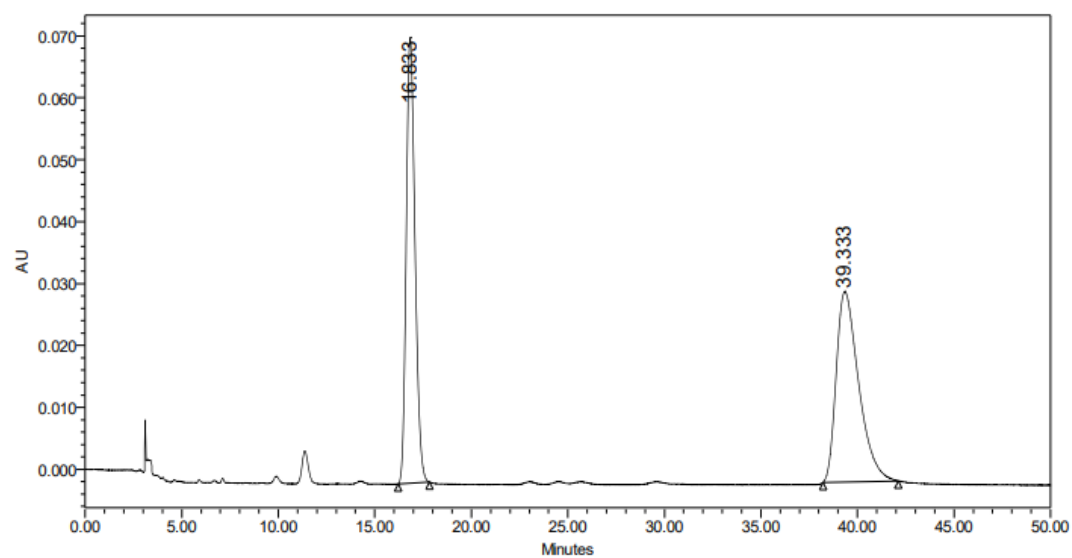
	RT	Area	% Area	Height
1	6.073	2120685	52.11	214837
2	6.673	1949098	47.89	178962

Enantioenriched 42



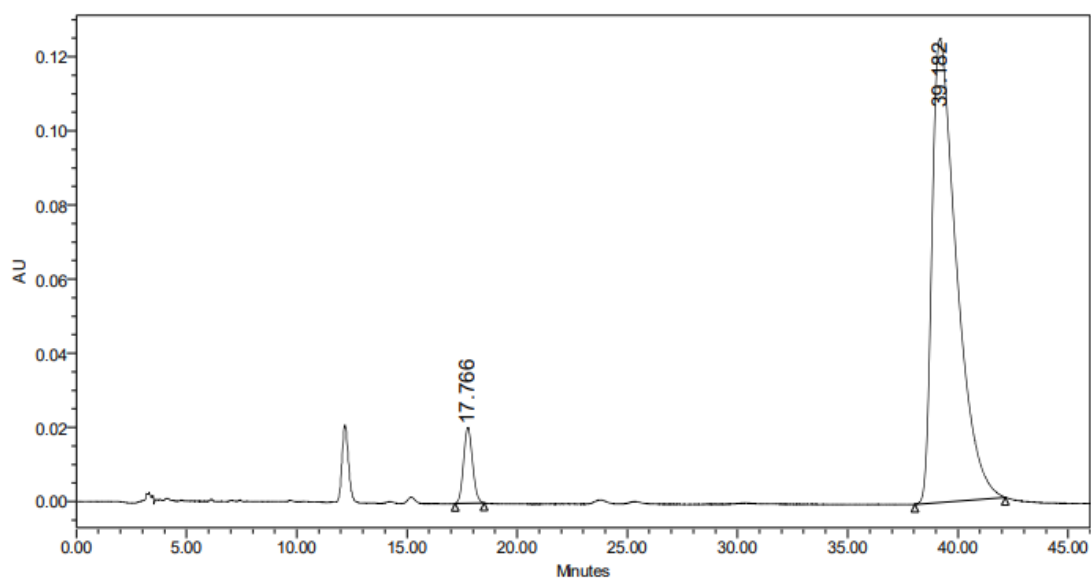
	RT	Area	% Area	Height
1	6.056	8531517	92.04	856449
2	6.648	738194	7.96	49451

Racemic 43



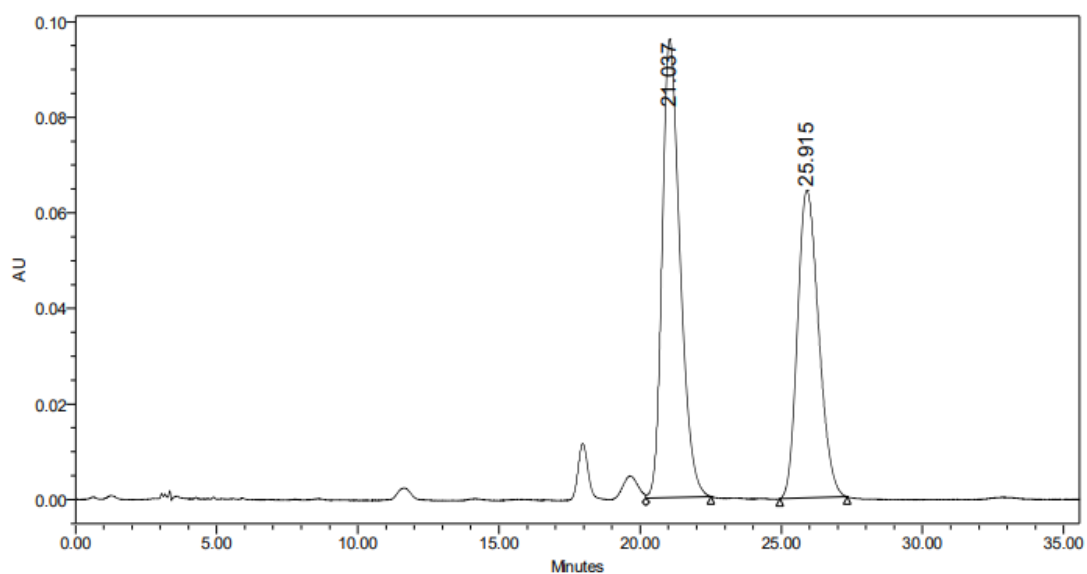
	RT	Area	% Area	Height
1	16.833	2255812	47.59	71960
2	39.333	2484692	52.41	30776

Enantioenriched 43



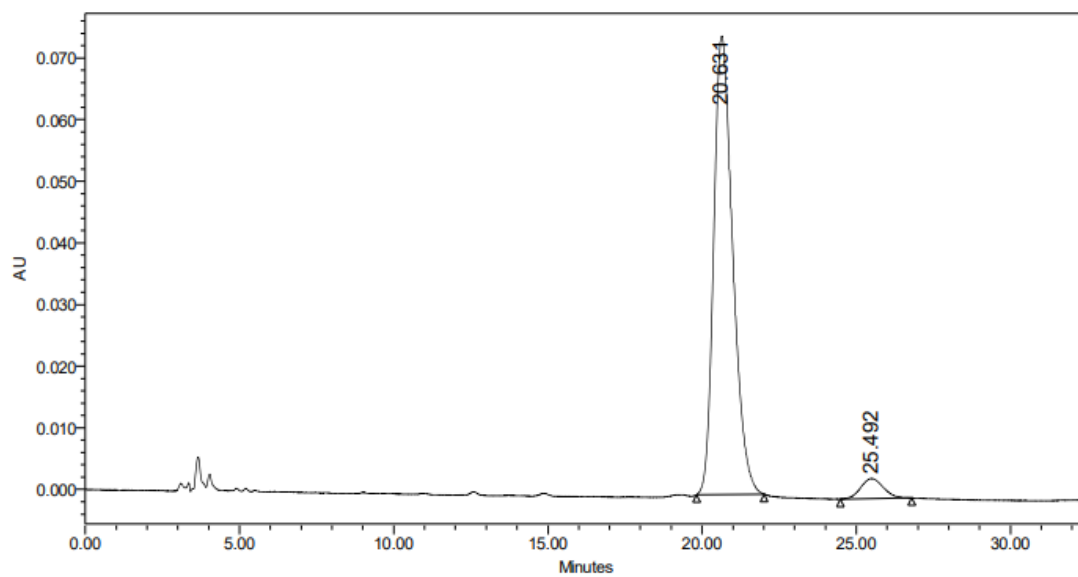
	RT	Area	% Area	Height
1	17.766	578915	5.61	20378
2	39.182	9735164	94.39	125130

Racemic 44



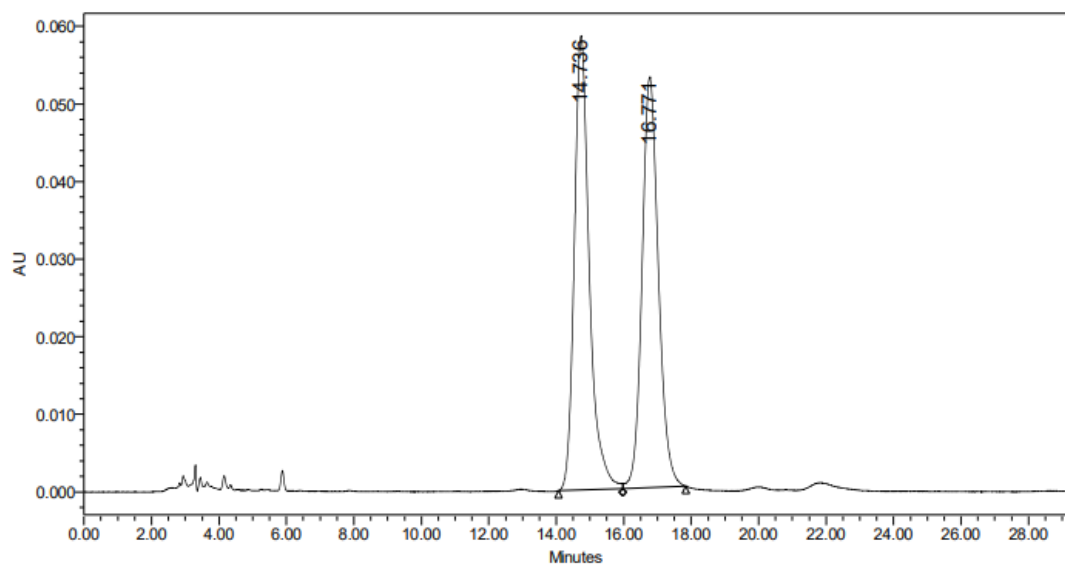
	RT	Area	% Area	Height
1	21.037	4229338	55.99	95960
2	25.915	3324653	44.01	64367

Enantioenriched 44



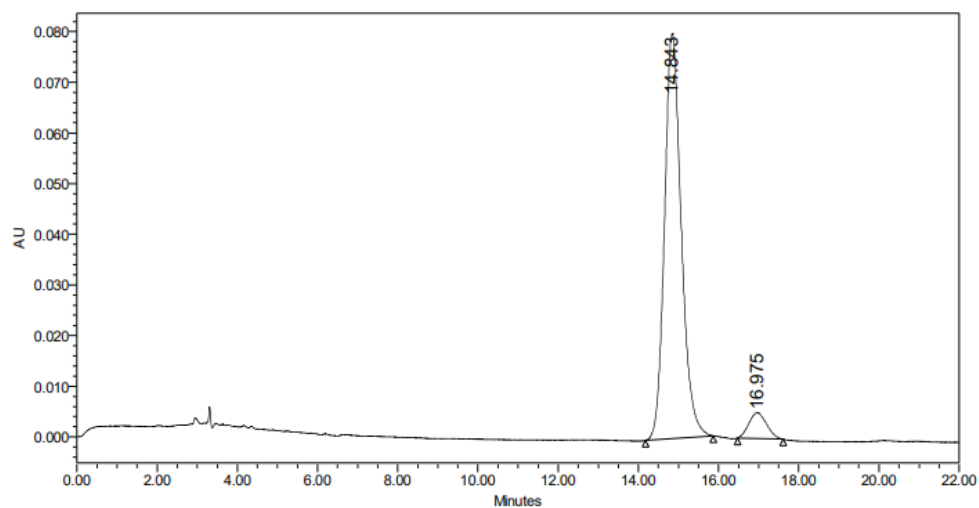
	RT	Area	% Area	Height
1	20.631	3188488	95.05	74323
2	25.492	165920	4.95	3260

Racemic 45



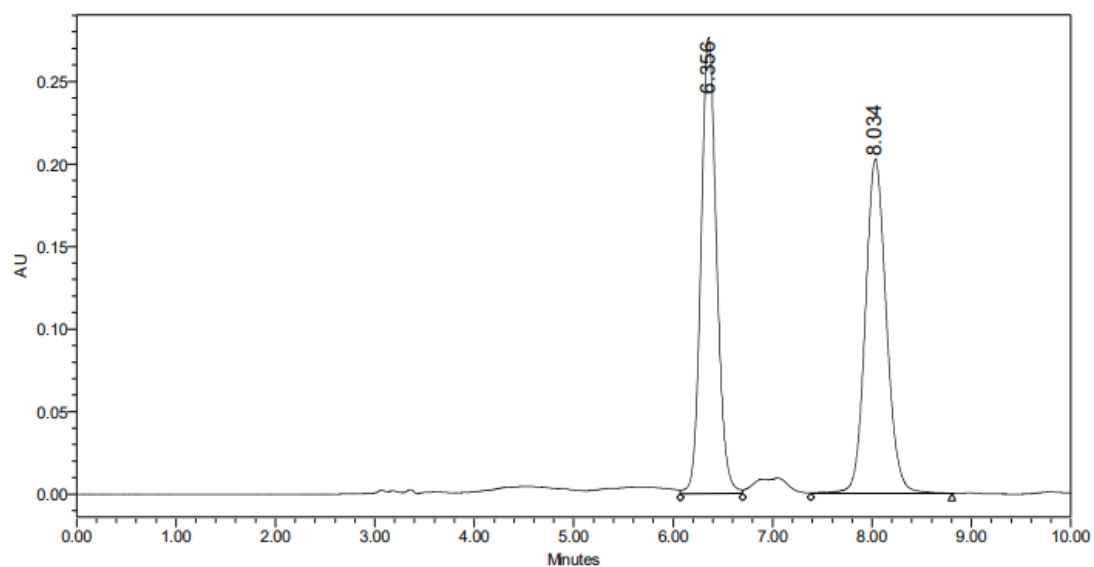
	RT	Area	% Area	Height
1	14.736	1802044	50.40	58446
2	16.771	1773245	49.60	52852

Enantioenriched 45



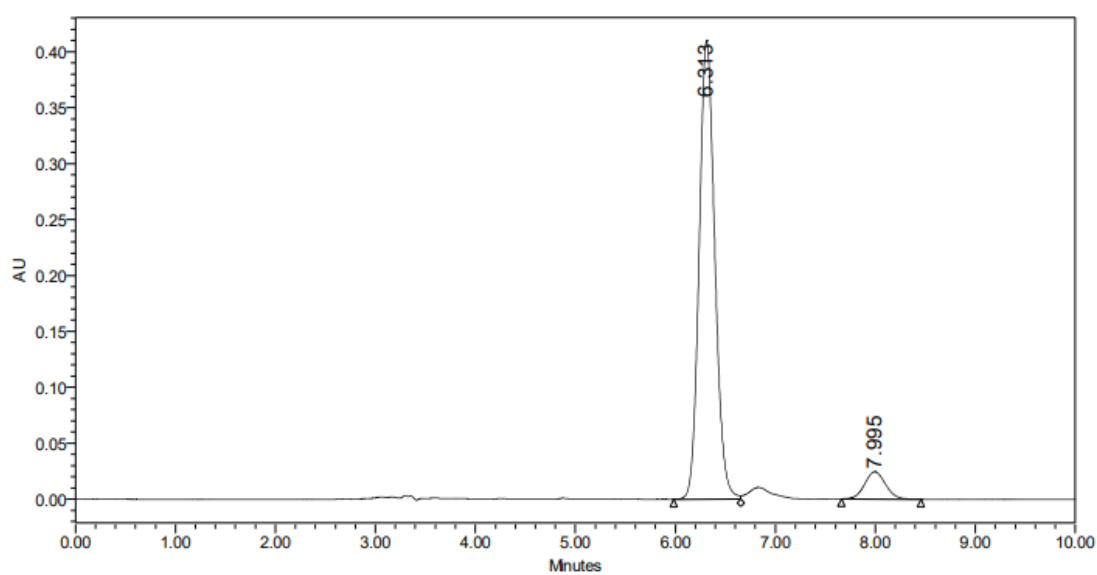
	RT	Area	% Area	Height
1	14.843	2335050	93.71	79931
2	16.975	156820	6.29	5072

Racemic 46



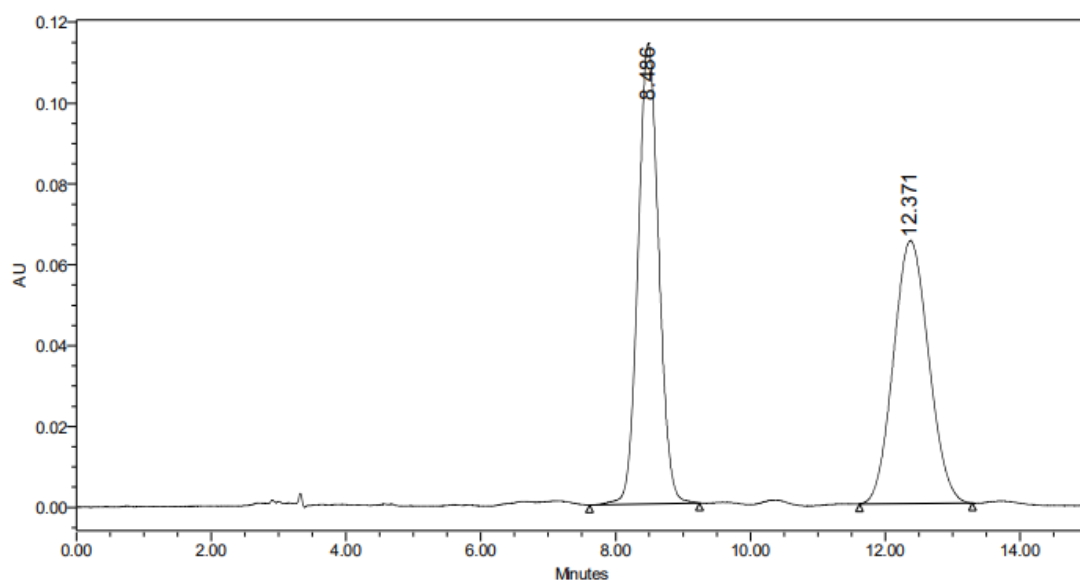
	RT	Area	% Area	Height
1	6.356	3016393	50.30	276120
2	8.034	2980517	49.70	202311

Enantioenriched 46



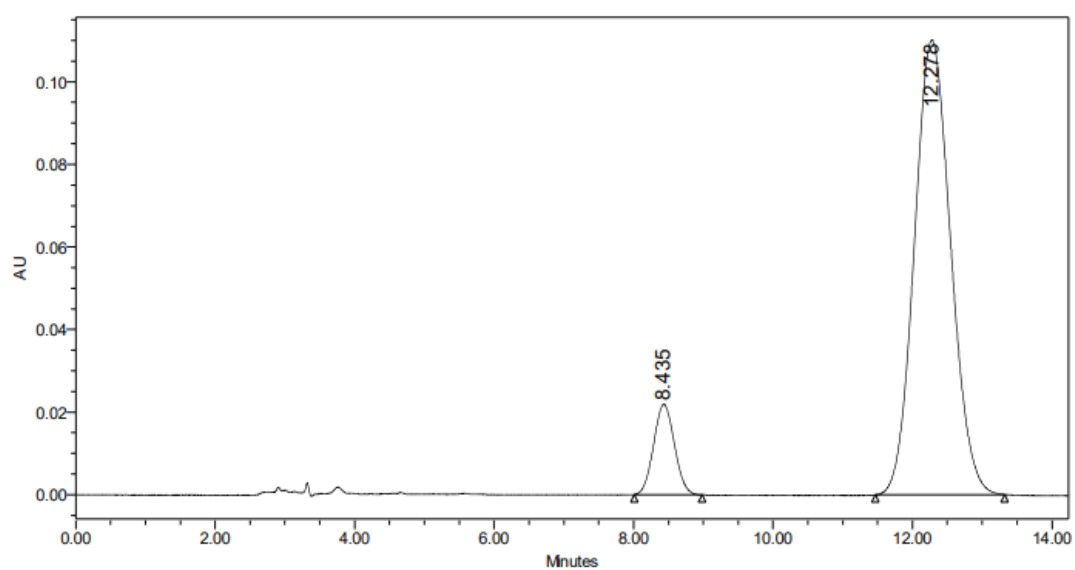
	RT	Area	% Area	Height
1	6.313	4469852	92.66	410086
2	7.995	354091	7.34	24402

Racemic 47



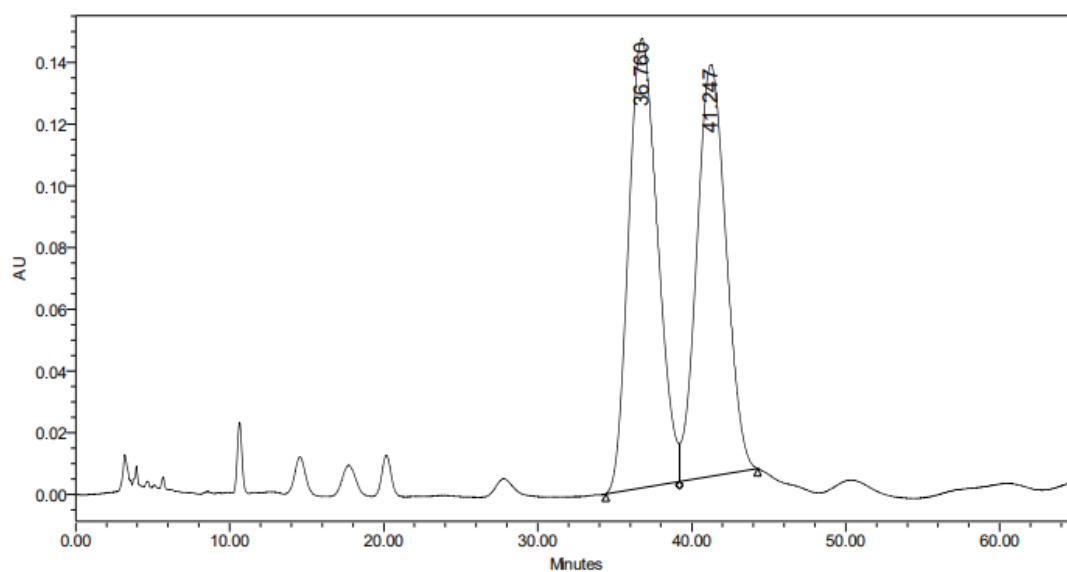
	RT	Area	% Area	Height
1	8.486	2426702	50.70	114007
2	12.371	2359776	49.30	65041

Enantioenriched 47



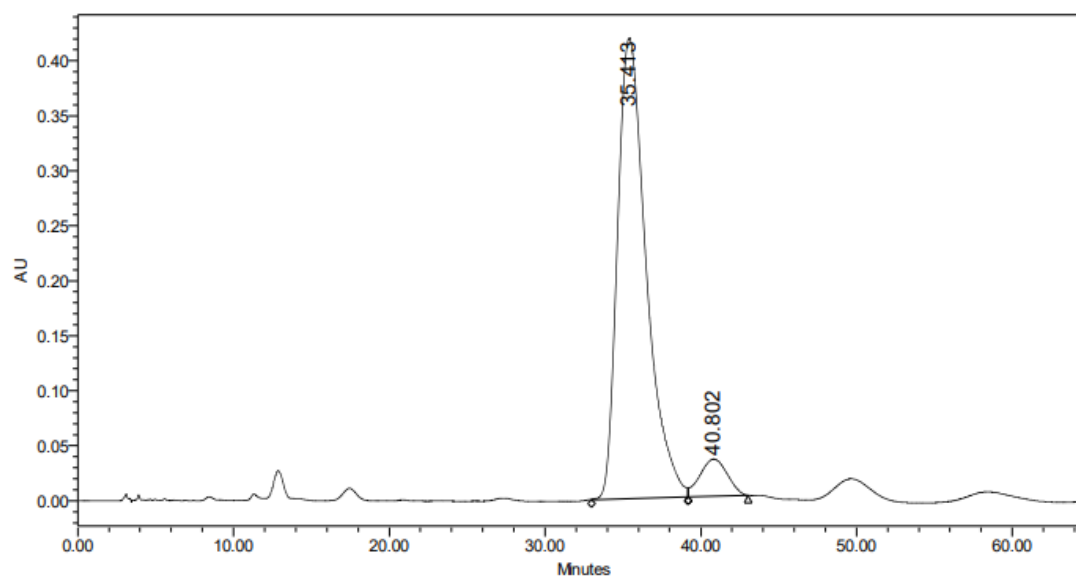
	RT	Area	% Area	Height
1	8.435	454562	10.21	21894
2	12.278	3996932	89.79	110126

Racemic 48



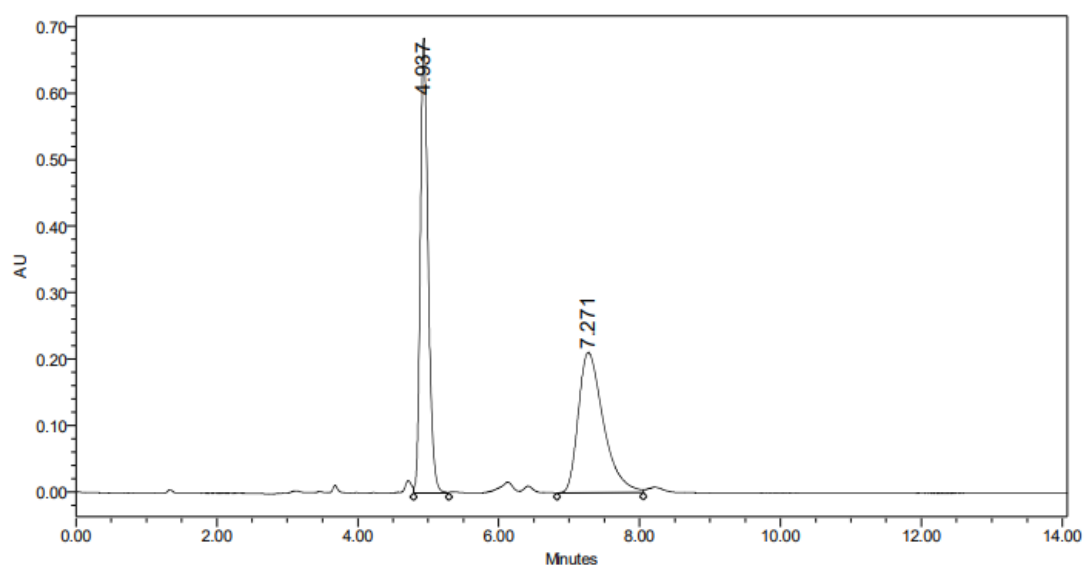
	RT	Area	% Area	Height
1	36.760	18962251	51.76	145541
2	41.247	17674578	48.24	133411

Enantioenriched 48



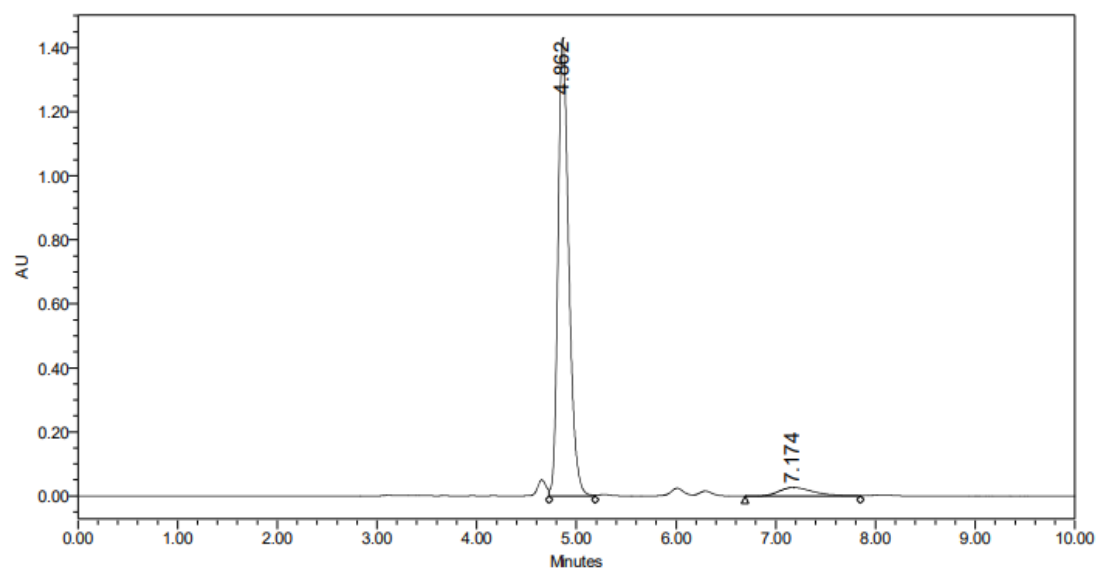
	RT	Area	% Area	Height
1	35.413	53835615	92.85	418652
2	40.802	4144295	7.15	33830

Racemic 49



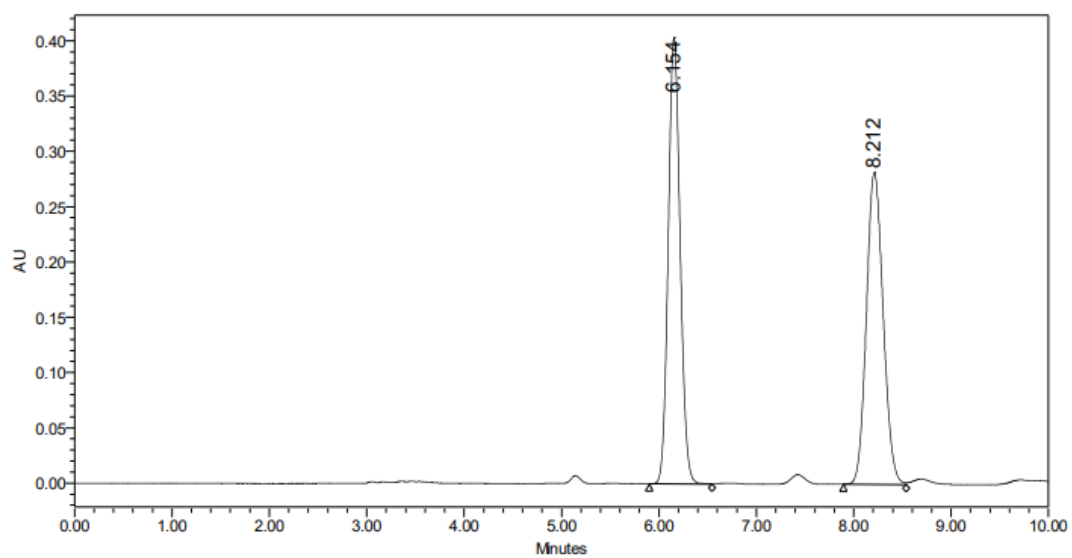
	RT	Area	% Area	Height
1	4.937	5249841	50.05	683290
2	7.271	5239303	49.95	211126

Enantioenriched 49



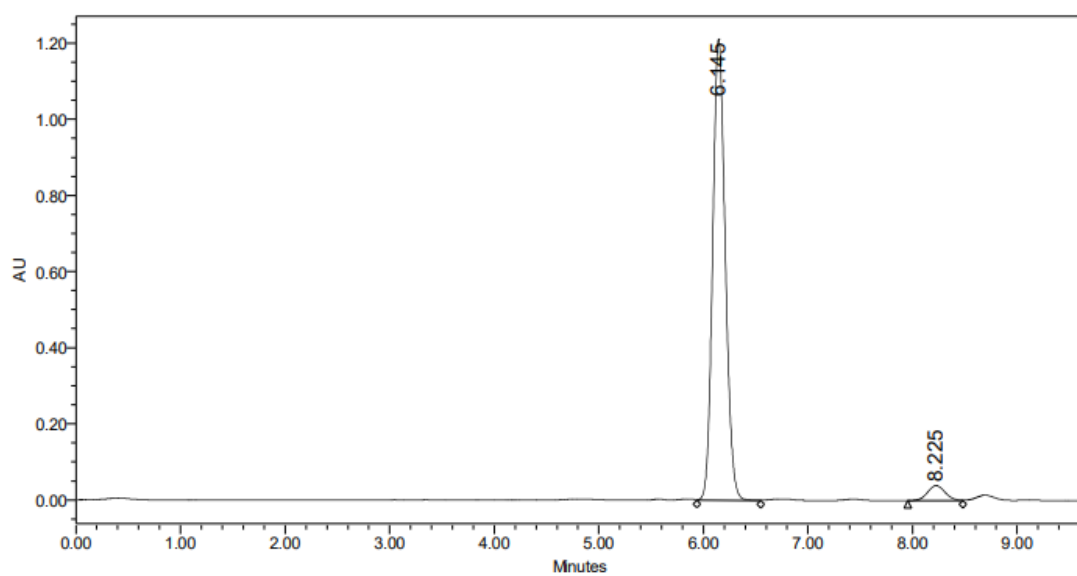
	RT	Area	% Area	Height
1	4.862	10703744	94.40	1429955
2	7.174	635273	5.60	26564

Racemic 50



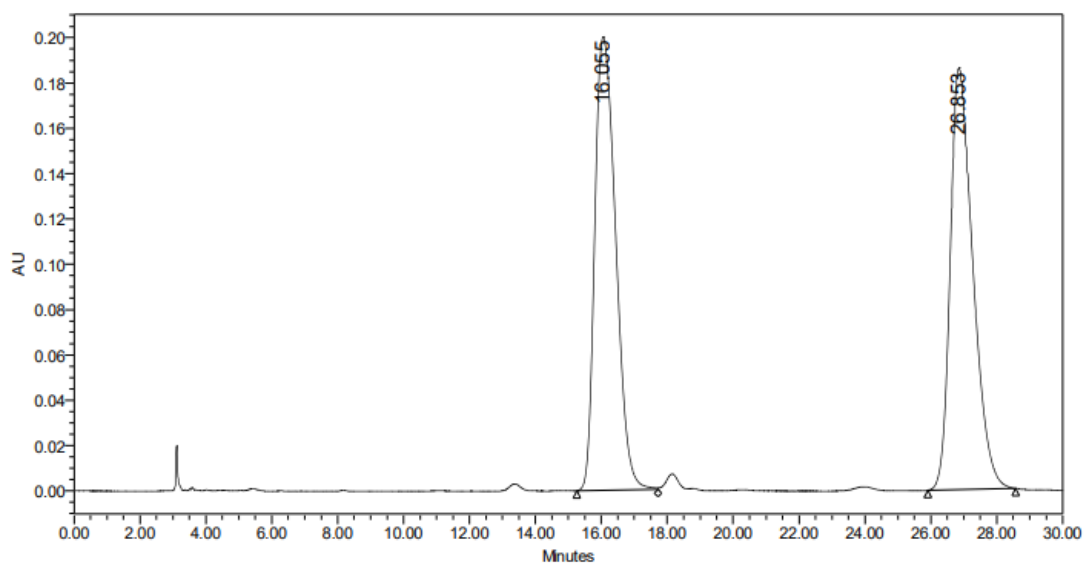
	RT	Area	% Area	Height
1	6.154	3434417	50.60	403564
2	8.212	3353239	49.40	281908

Enantioenriched 50



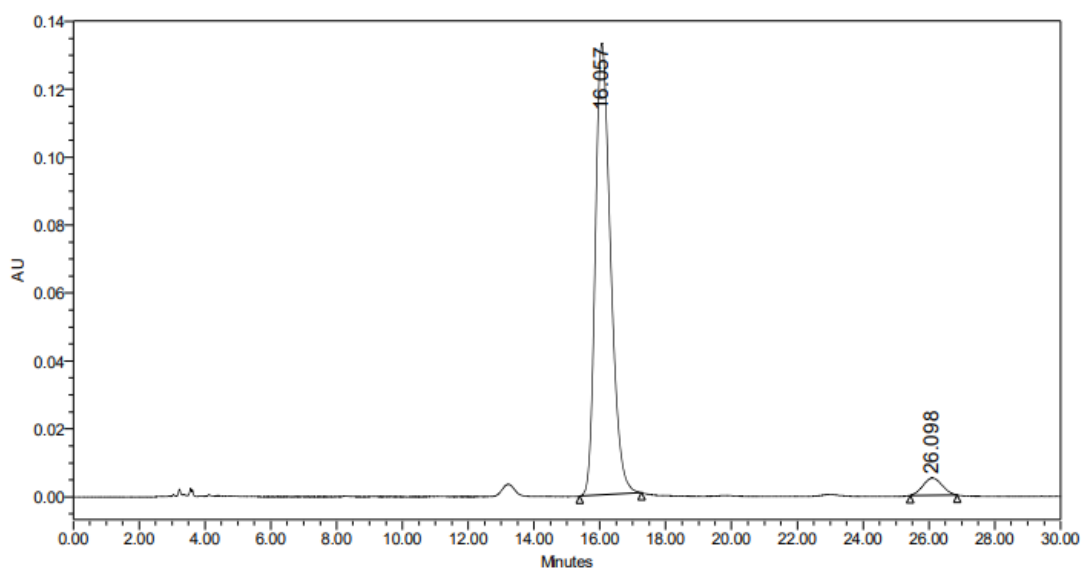
	RT	Area	% Area	Height
1	6.145	10192868	95.69	1211203
2	8.225	459038	4.31	39161

Racemic 51



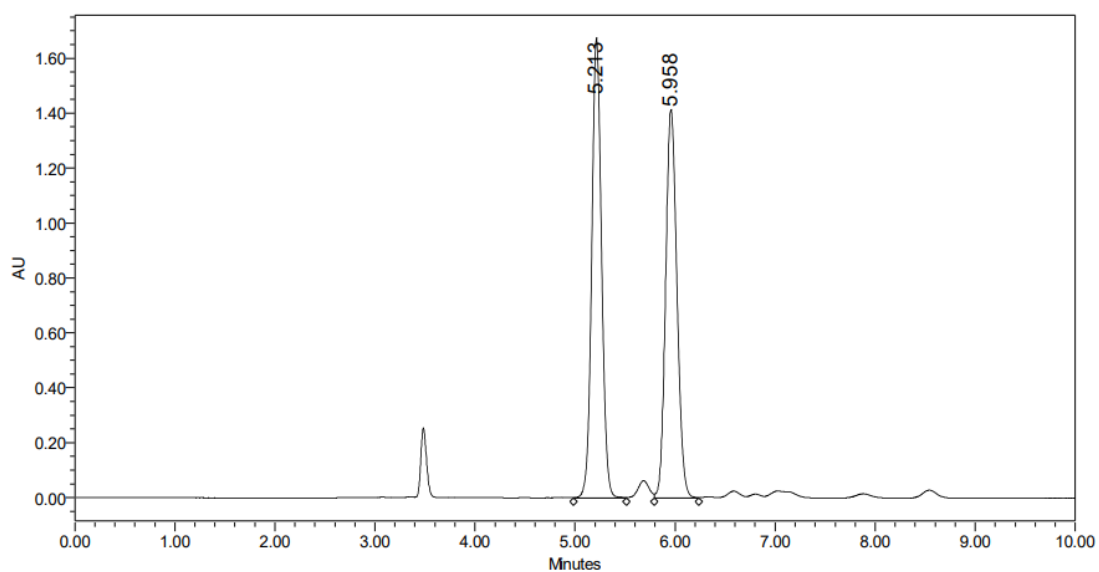
	RT	Area	% Area	Height
1	16.055	8856672	50.16	200041
2	26.853	8798732	49.84	186067

Enantioenriched 51



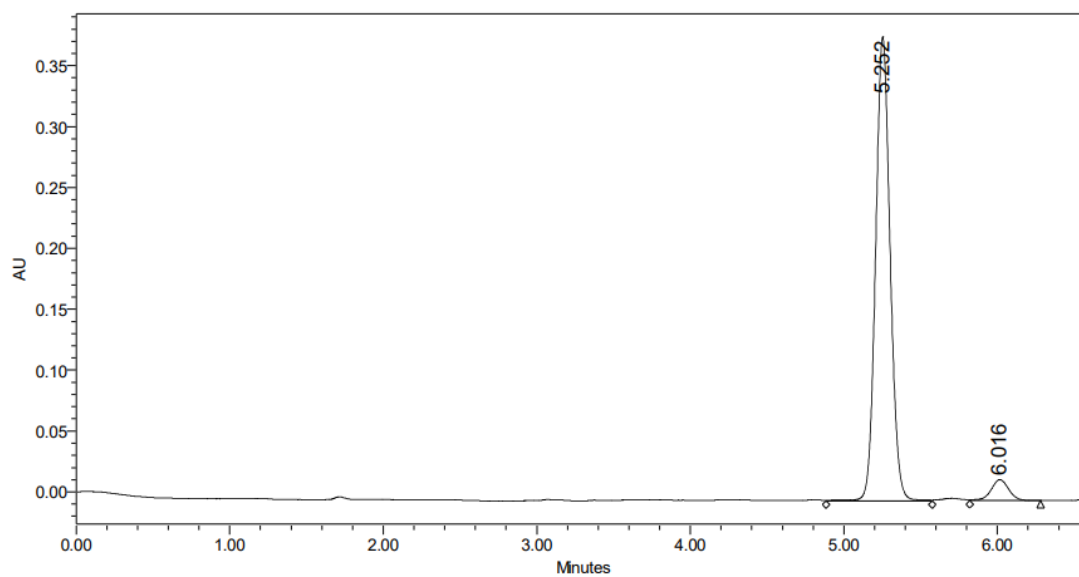
	RT	Area	% Area	Height
1	16.057	4312773	95.46	132910
2	26.098	204988	4.54	5096

Racemic 52



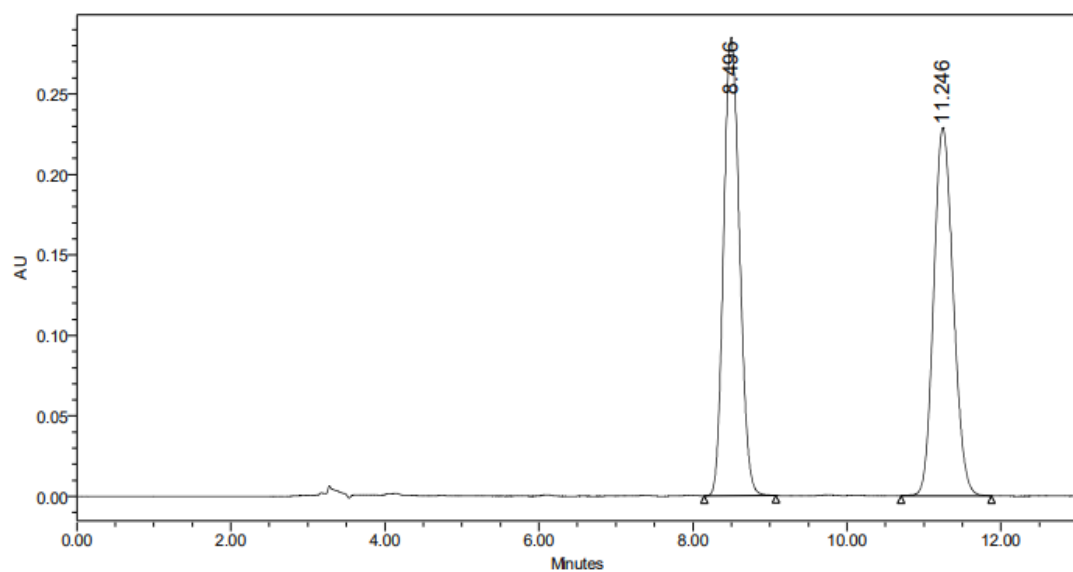
	RT	Area	% Area	Height
1	5.213	11427943	50.77	1673554
2	5.958	11081486	49.23	1413191

Enantioenriched 52



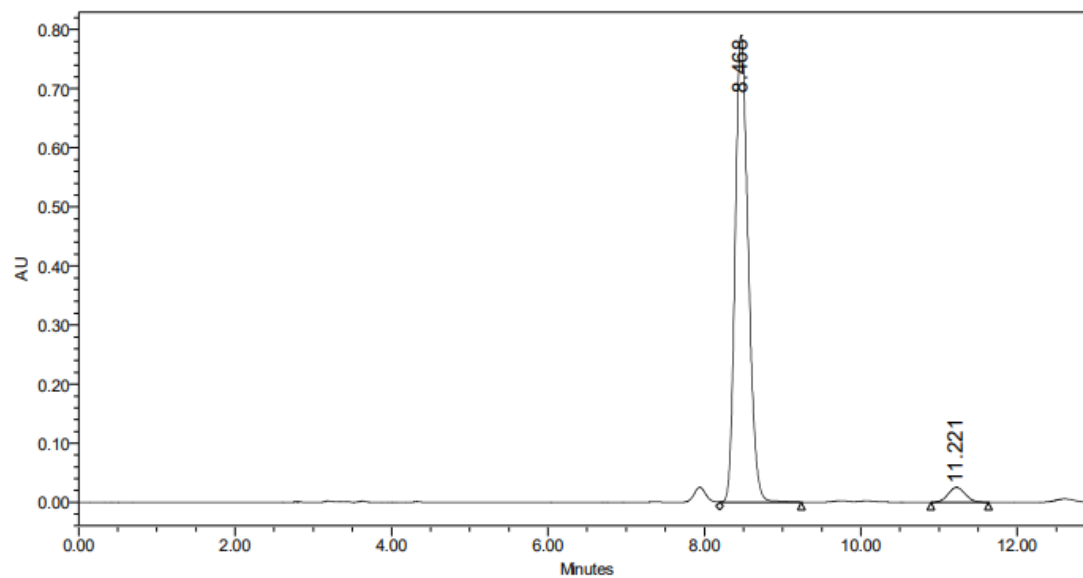
	RT	Area	% Area	Height
1	5.252	2503731	94.77	380793
2	6.016	138182	5.23	17200

Racemic 53



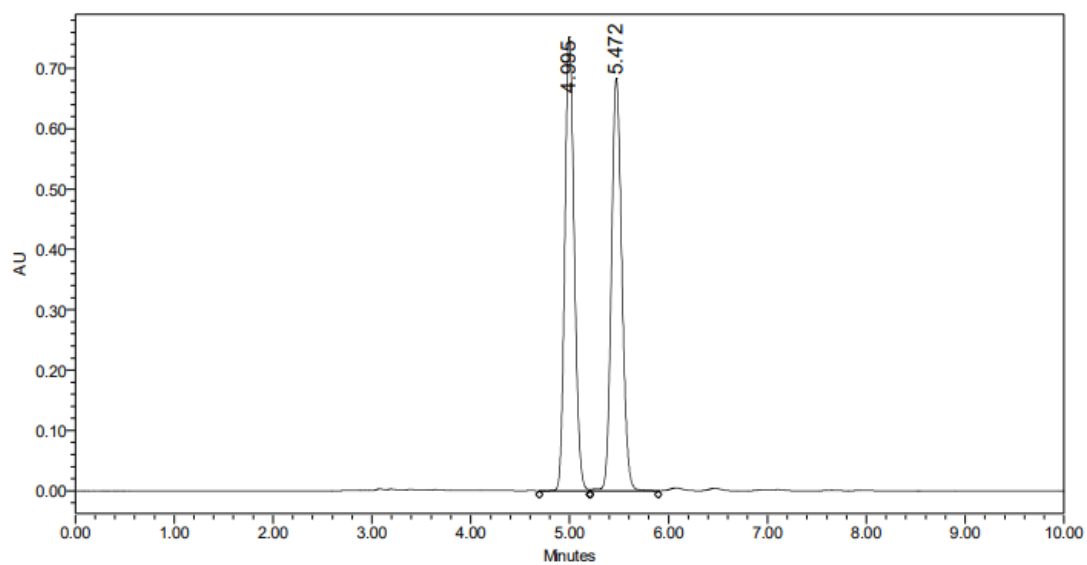
	RT	Area	% Area	Height
1	8.496	4054787	50.05	284497
2	11.246	4046597	49.95	228630

Enantioenriched 53



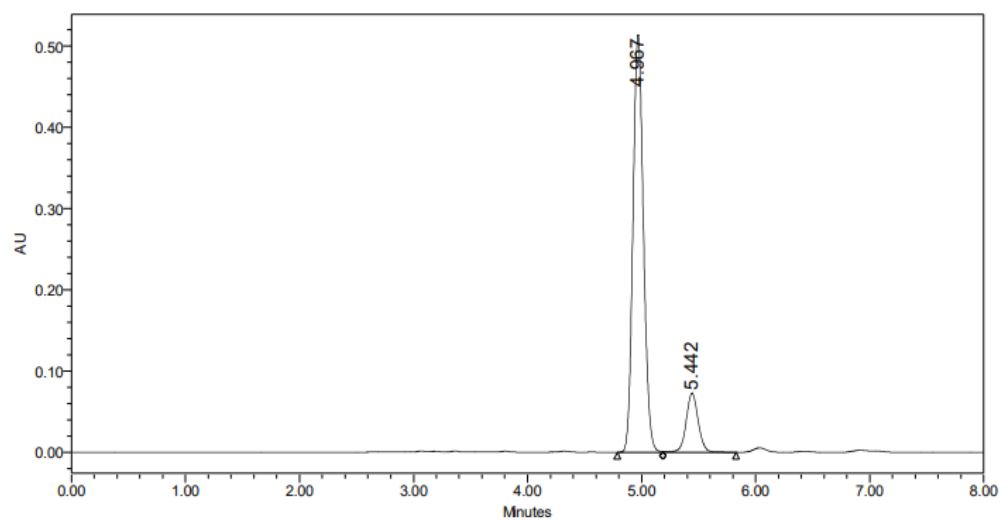
	RT	Area	% Area	Height
1	8.468	9082658	96.00	789576
2	11.221	378828	4.00	25059

Racemic 54



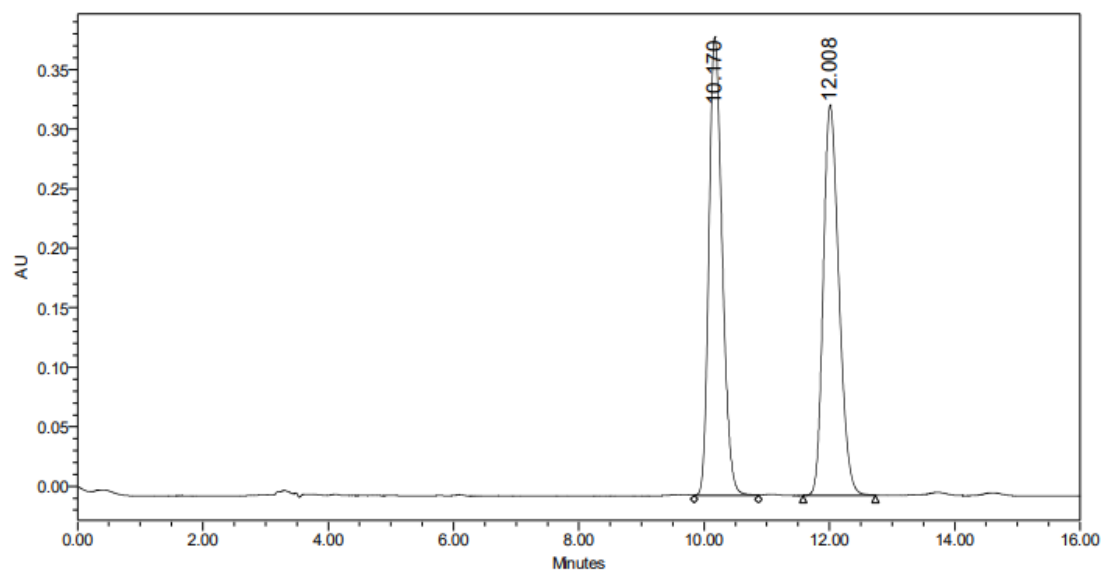
	RT	Area	% Area	Height
1	4.995	4938254	49.74	752077
2	5.472	4989770	50.26	683695

Enantioenriched 54



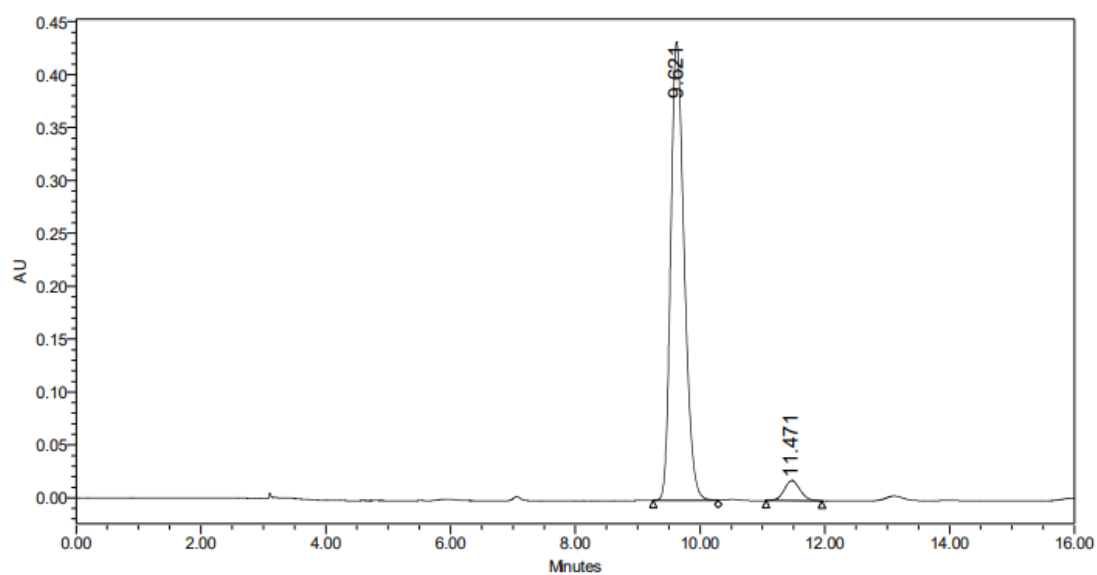
	RT	Area	% Area	Height
1	4.967	3258901	85.87	513431
2	5.442	536401	14.13	72700

Racemic 55



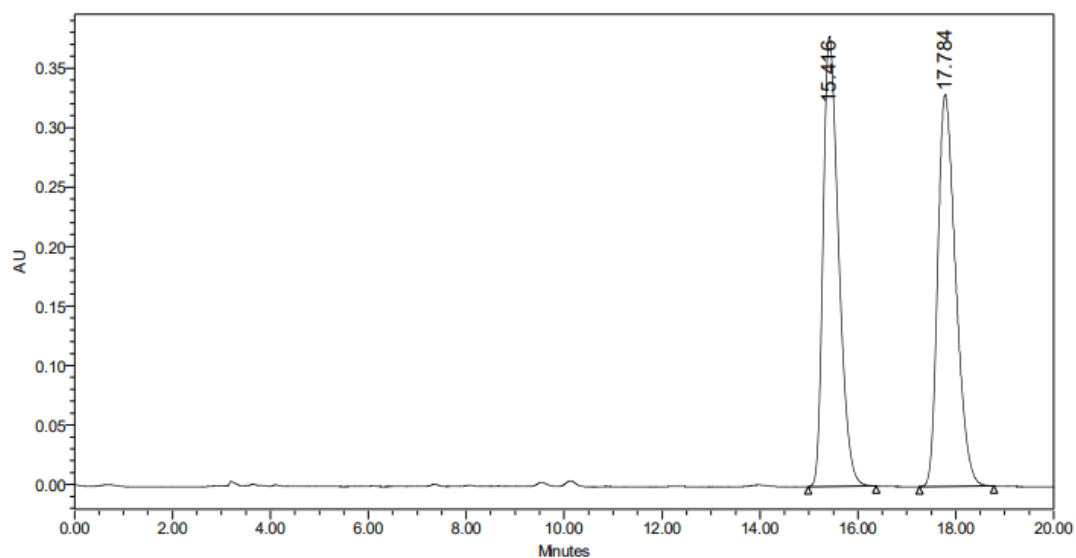
	RT	Area	% Area	Height
1	10.170	5681408	49.98	385212
2	12.008	5685936	50.02	327864

Enantioenriched 55



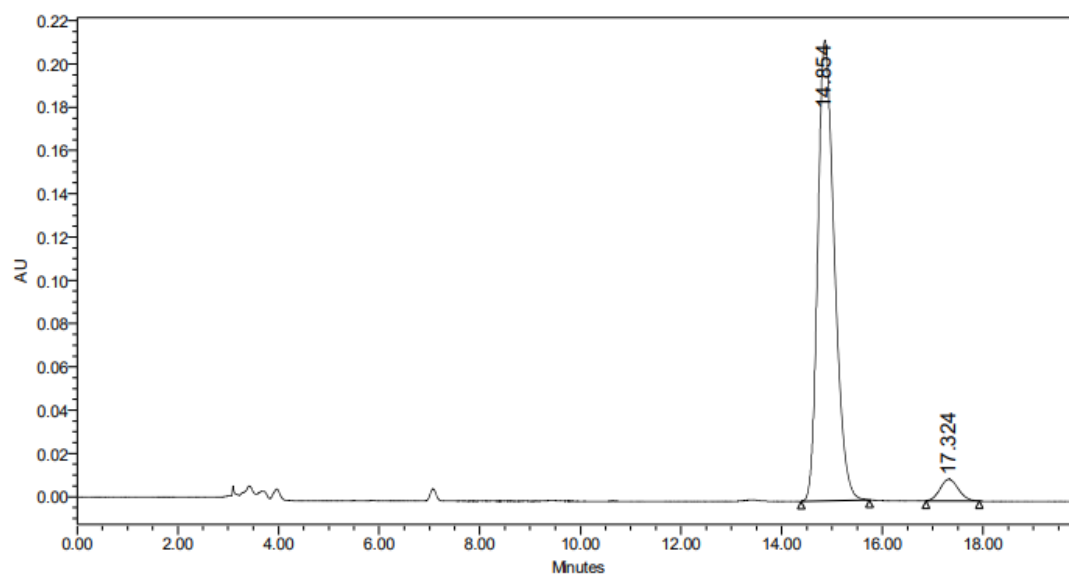
	RT	Area	% Area	Height
1	9.621	6524663	95.14	433332
2	11.471	333397	4.86	18885

Racemic 56



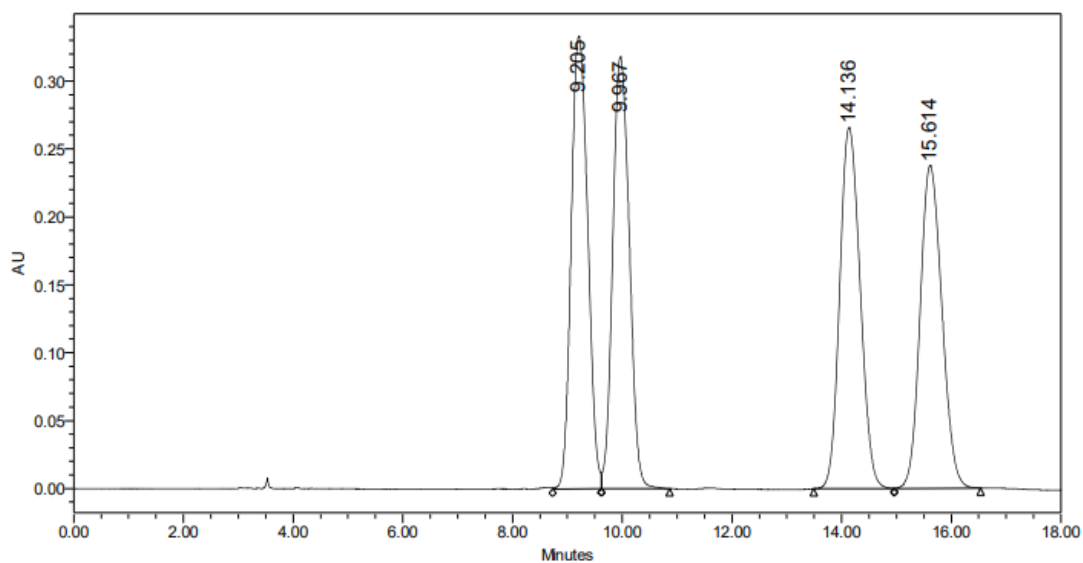
	RT	Area	% Area	Height
1	15.416	8363420	50.07	378011
2	17.784	8341099	49.93	329027

Enantioenriched 56



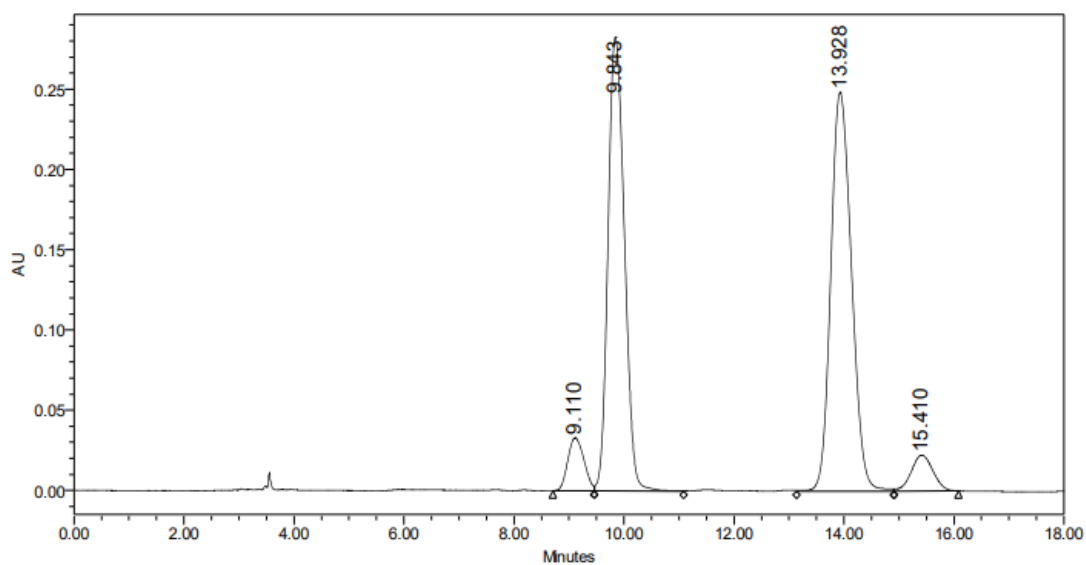
	RT	Area	% Area	Height
1	14.854	4870615	95.09	212617
2	17.324	251395	4.91	10019

Racemic 57



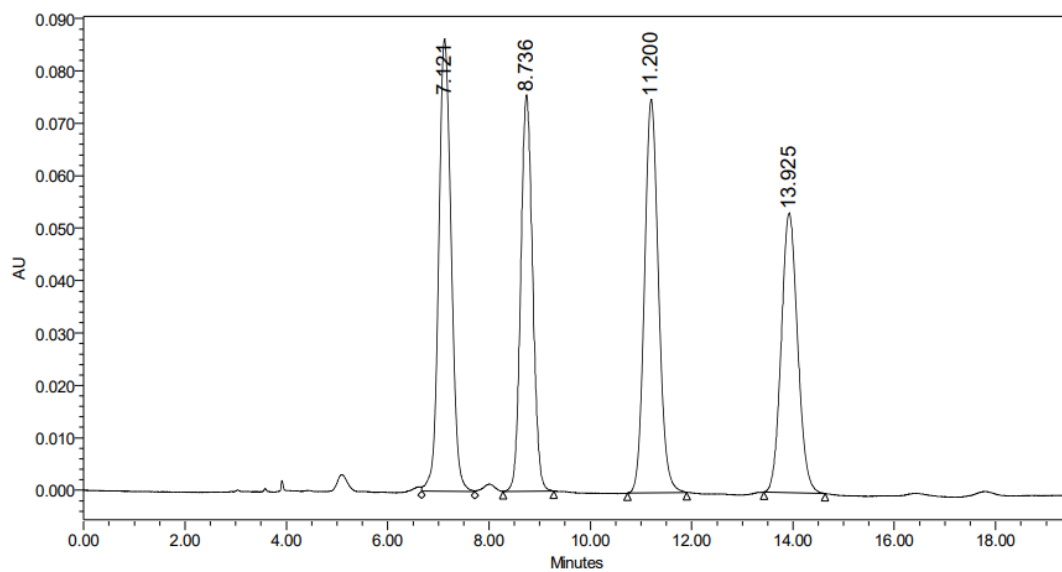
	RT	Area	% Area	Height
1	9.205	6952103	25.60	333122
2	9.967	6710255	24.71	317979
3	14.136	6905561	25.43	265851
4	15.614	6588081	24.26	237590

Enantioenriched 57



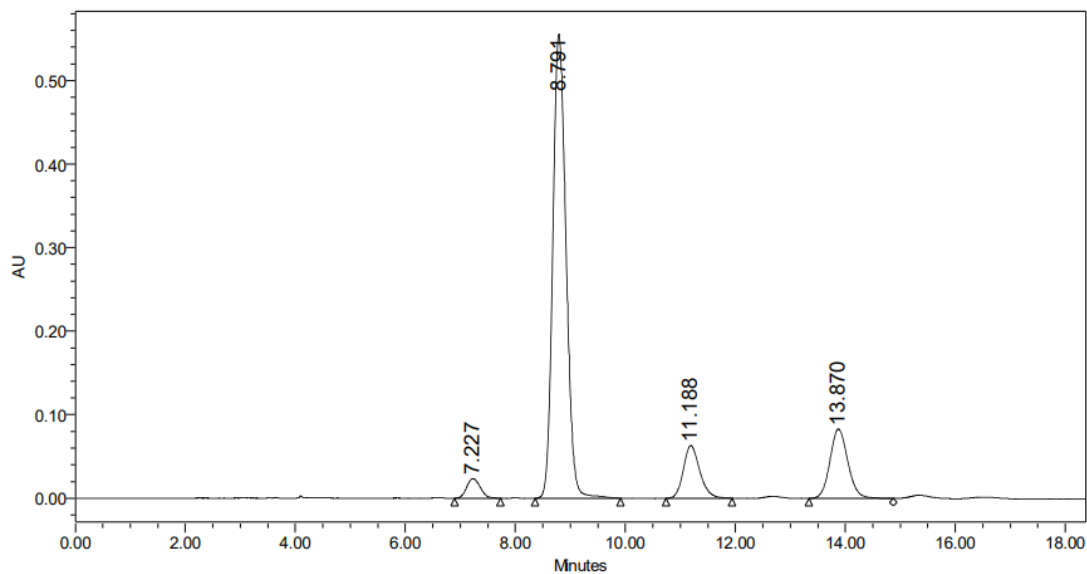
	RT	Area	% Area	Height
1	9.110	672651	4.91	33091
2	9.843	5873902	42.87	282693
3	13.928	6539547	47.73	248474
4	15.410	615074	4.49	22362

Racemic 58



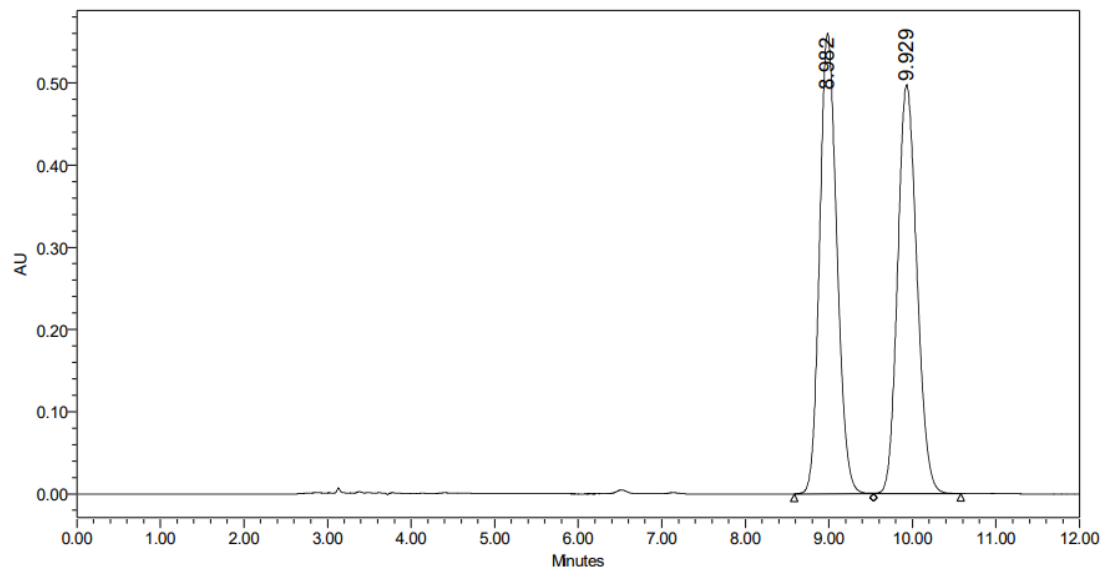
	RT	Area	% Area	Height
1	7.121	1467356	27.50	86260
2	8.736	1232332	23.10	75625
3	11.200	1439626	26.98	75010
4	13.925	1196152	22.42	53294

Enantioenriched 58



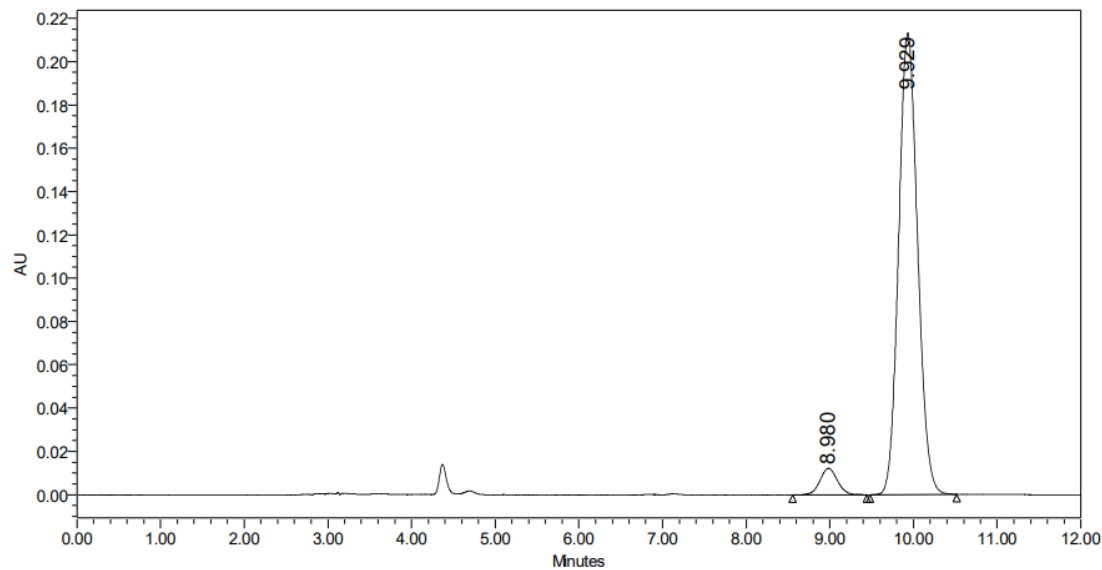
	RT	Area	% Area	Height
1	7.227	400306	3.10	23501
2	8.791	9298748	72.08	555126
3	11.188	1314831	10.19	63077
4	13.870	1886831	14.63	83126

Racemic 59



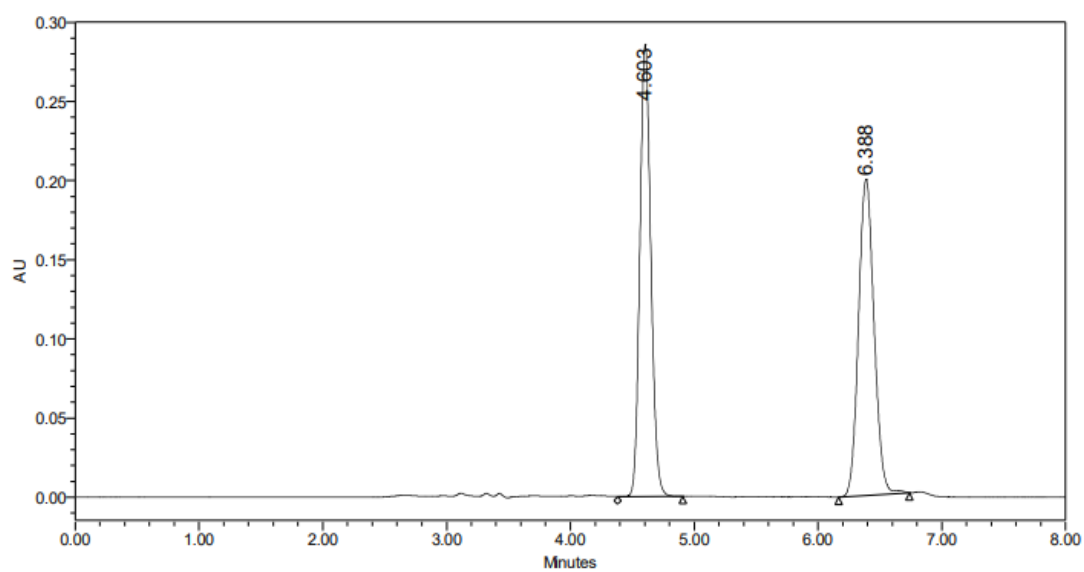
	RT	Area	% Area	Height
1	8.982	8013537	50.22	559916
2	9.929	7942023	49.78	497285

Enantioenriched 59



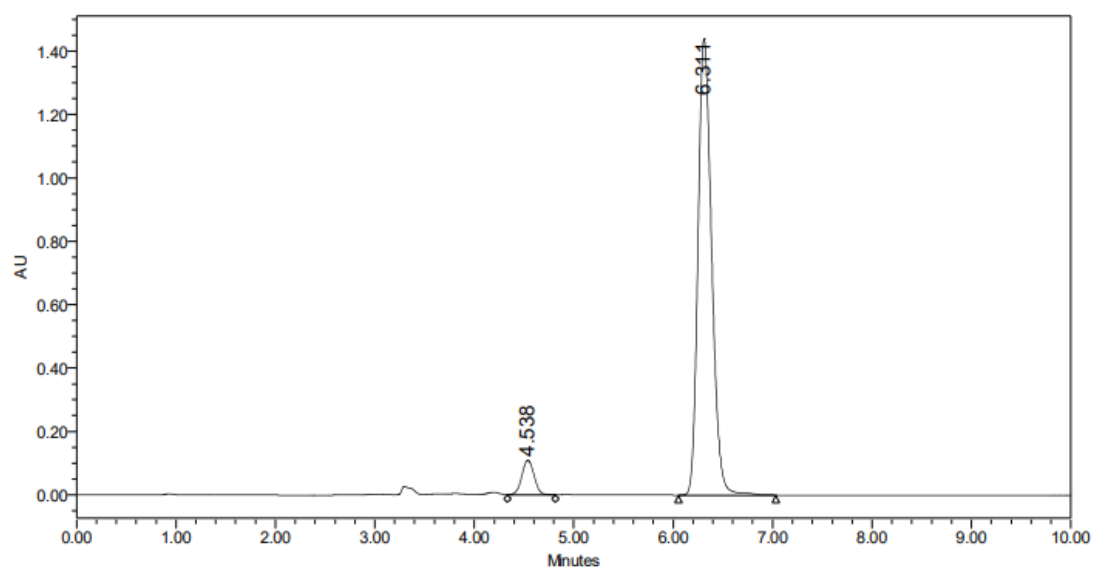
	RT	Area	% Area	Height
1	8.980	176004	5.01	12193
2	9.929	3336818	94.99	212935

Racemic 60



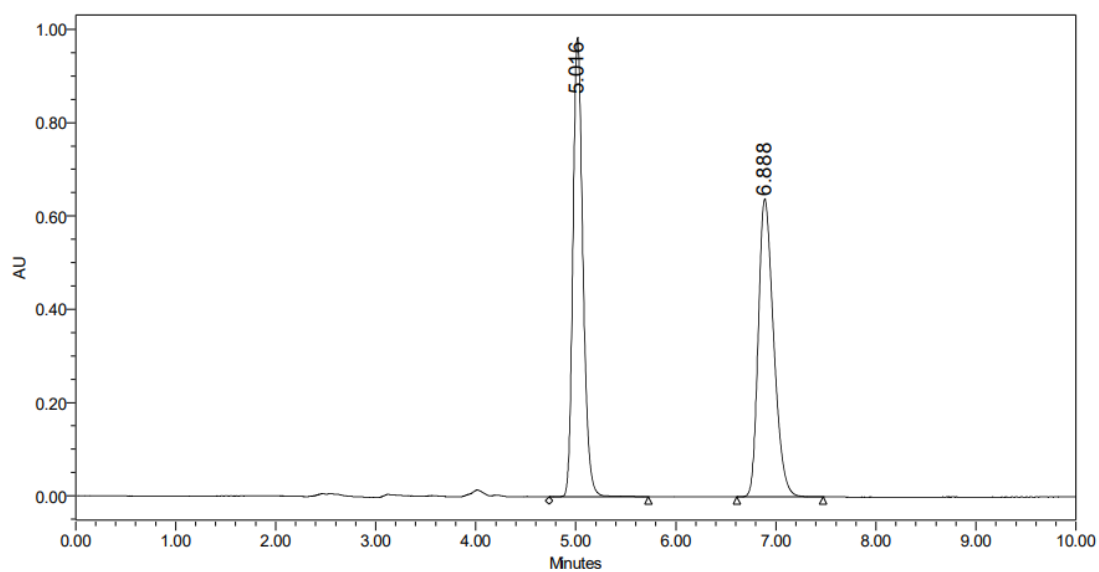
	RT	Area	% Area	Height
1	4.603	1756116	50.28	285669
2	6.388	1736868	49.72	199770

Enantioenriched 60



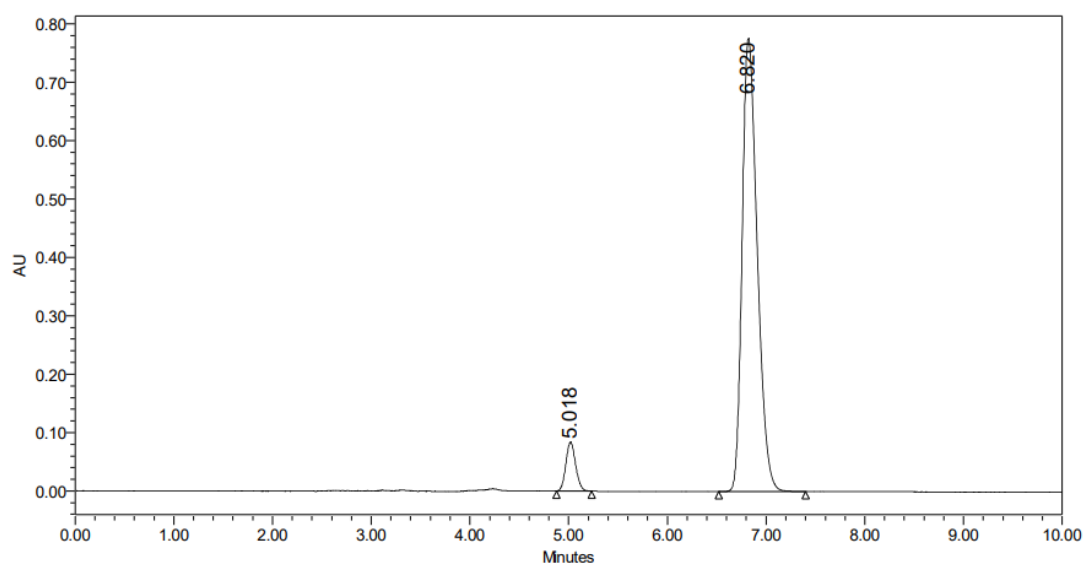
	RT	Area	% Area	Height
1	4.538	954662	6.50	109732
2	6.311	13731392	93.50	1439559

Racemic 66



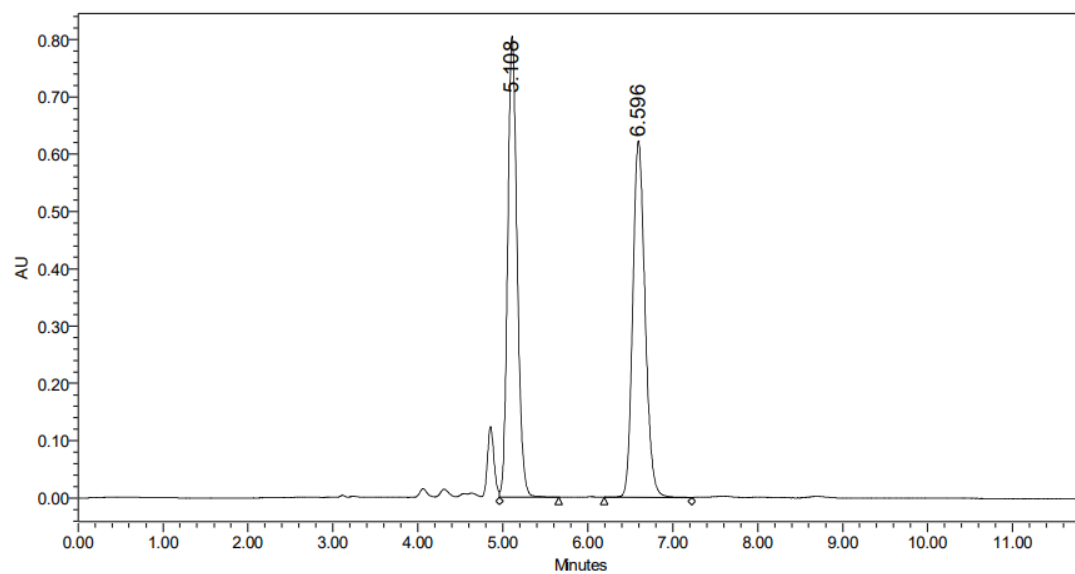
	RT	Area	% Area	Height
1	5.016	6832857	50.02	983912
2	6.888	6828621	49.98	638678

Enantioenriched 66



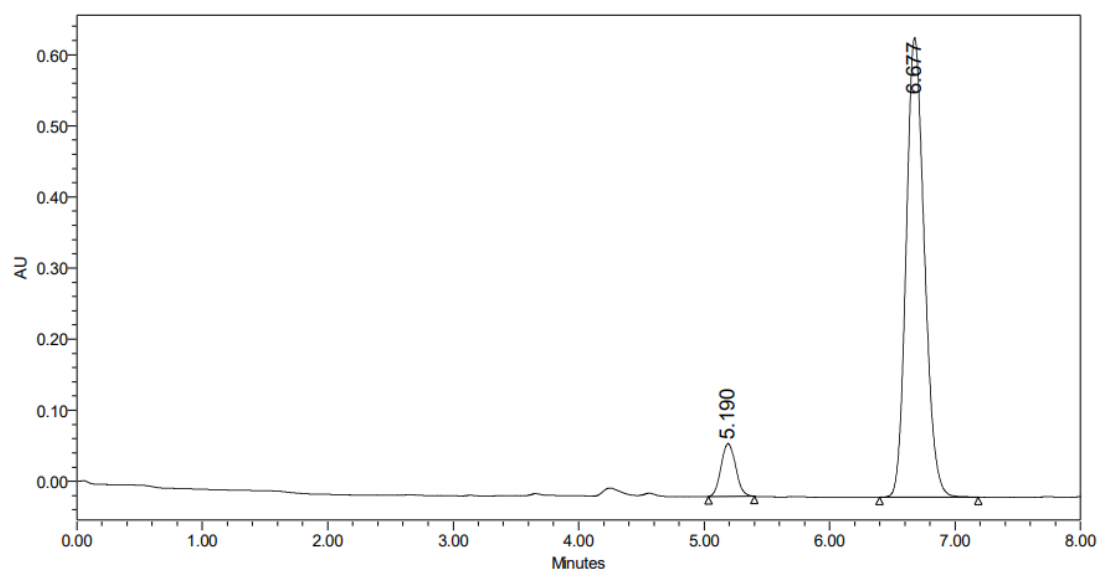
	RT	Area	% Area	Height
1	5.018	575890	6.54	83693
2	6.820	8228960	93.46	775438

Racemic 69



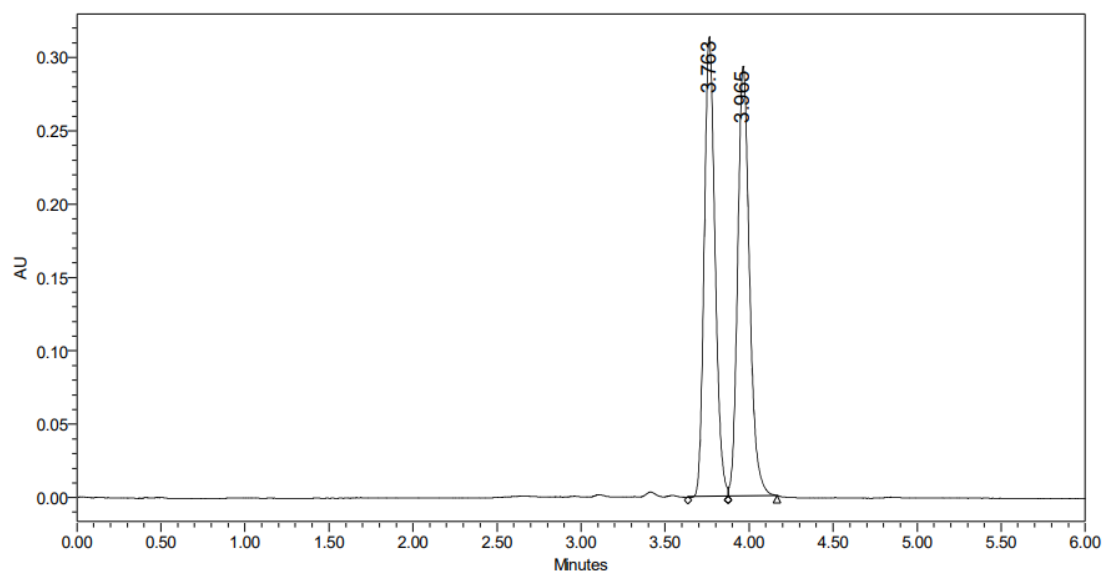
	RT	Area	% Area	Height
1	5.108	6209802	49.83	803915
2	6.596	6251793	50.17	622277

Enantioenriched 69



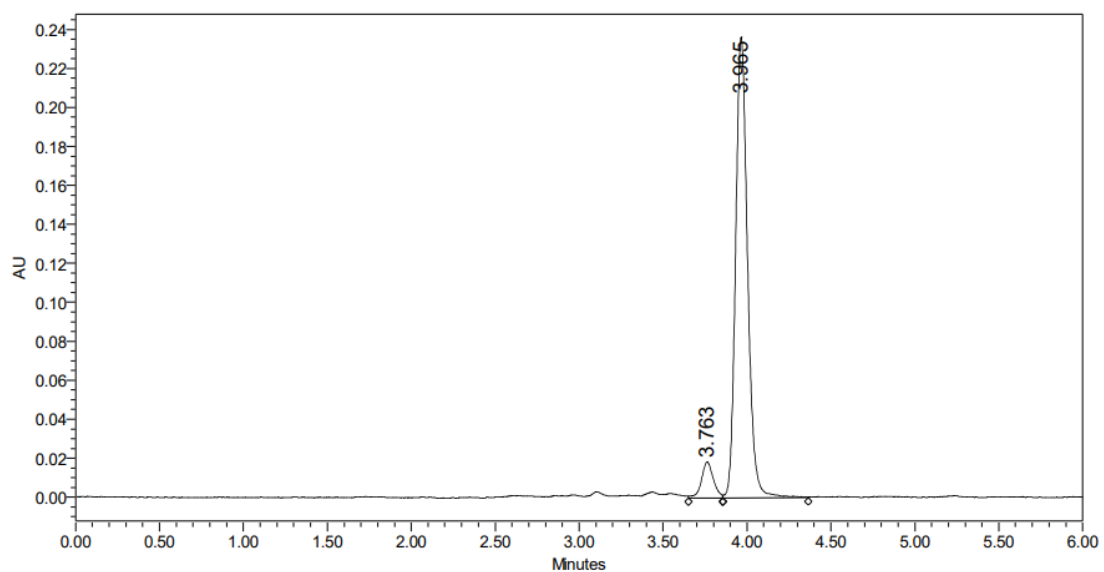
	RT	Area	% Area	Height
1	5.190	601650	8.45	74126
2	6.677	6514377	91.55	645518

Racemic 72



	RT	Area	% Area	Height
1	3.763	1398208	49.36	312969
2	3.965	1434475	50.64	292880

Enantioenriched 72



	RT	Area	% Area	Height
1	3.763	90019	7.16	18342
2	3.965	1166385	92.84	236358