
Supporting Information for

Enantioselective Synthesis of 5-Alkylated thiazolidinones via Palladium-Catalyzed Asymmetric Allylic C–H Alkylations of 1,4-Pentadienes with 5*H*-Thiazol-4-ones

Tian-Ci Wang, Zhi-Yong Han, Pu-Sheng Wang, Hua-Chen Lin, Shi-Wei Luo* and Liu-Zhu Gong*

[†]Hefei National Laboratory for Physical Sciences at the Microscale and Department of Chemistry, University of
Science and Technology of China, Hefei, 230026, China

[‡]Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), China

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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 (CDCl₃: δ H = 7.26 ppm, δ C = 77.16 ppm, DMSO: δ H = 2.50 ppm, δ C = 39.52 ppm).

The high resolution mass spectra were recorded on a Thermo LTQ Orbitrap XL (ESI+) or a P-SIMS-Gly of Bruker Daltonics Inc (EI+). Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer. Enantiomeric excesses were performed on Waters-Breeze (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump, UV detection monitored at 254 nm or 230nm). Chiralpak OD-H, IC, IE and ID columns were purchased from Daicel Chemical Industries, LTD.

The absolute configuration of **3da** was assigned by the X-ray analysis. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-343 polarimeter.

2. Materials:

Starting materials were purchased from commercial suppliers (Aldrich, Acros, TCI, J&K, etc.) and used as supplied unless otherwise stated.

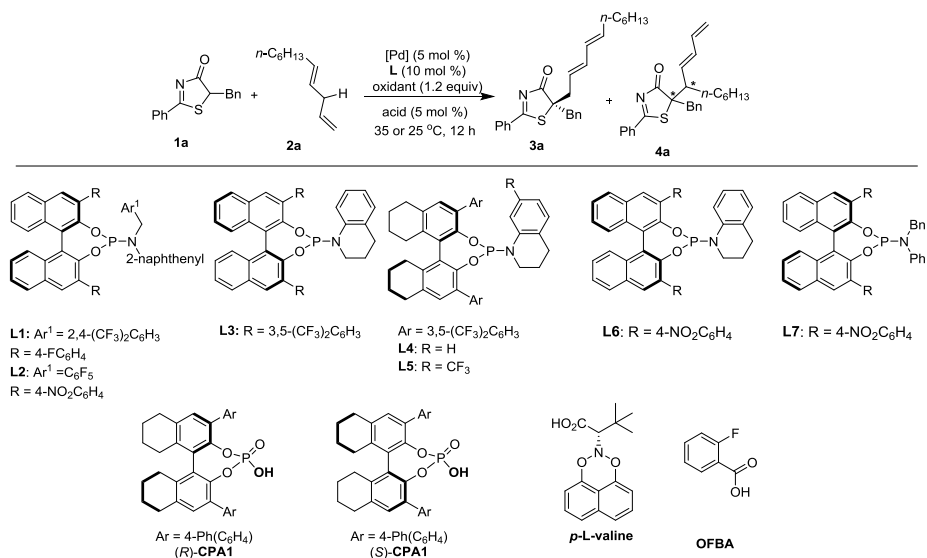
Pd₂(dba)₃, Pd (dba)₂ and Pd(OAc)₂ were purchased from Aldrich.

1, 4-Pentadiene and trans-1, 4-hexadiene were purchased from commercial suppliers (Aldrich and TCI). Other substituted 1, 4-pentadienes were prepared by following the literature report.¹

5H-thiazol-4-ones were prepared by following the literature report.²

All solvents were purified and dried according to standard methods prior to use, unless stated otherwise.

Table S1. Establishment of Optimal Conditions for the Allylic C-H Alkylation Reaction of 1,4-Pentadiene **2a with 5H-thiazol-4-ones **3a****

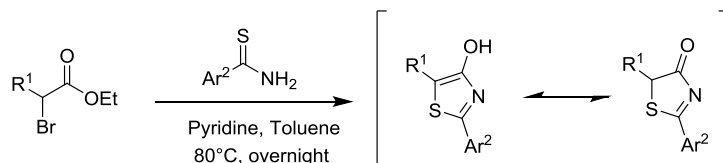


entry	[Pd]	L	acid	yield (%) ^b	3a/4aa ^c	ee (%) ^c
1 ^[d]	Pd(dba) ₂	L7	OFBA	trace	—	—
2	Pd ₂ (dba) ₃	PPh ₃	OFBA	trace	—	—
3	Pd ₂ (dba) ₃	L1	OFBA	67	13:1	-6
4	Pd ₂ (dba) ₃	L2	OFBA	44	15:1	57
5	Pd ₂ (dba) ₃	L3	OFBA	47	10:1	-58
6	Pd ₂ (dba) ₃	L4	OFBA	62	18:1	78
7	Pd ₂ (dba) ₃	L5	OFBA	91	17:1	88
8	Pd ₂ (dba) ₃	L6	OFBA	26	9:1	5
9 ^d	Pd ₂ (dba) ₃	L5	OFBA	77	17:1	88
10	Pd(dba) ₂	L5	OFBA	63	18:1	87
11	Pd(OAc) ₂	L5	OFBA	16	—	87
12	Pd ₂ (dba) ₃	L5	PhCOOH	50	17:1	87
13	Pd ₂ (dba) ₃	L5	CH ₃ COOH	92	18:1	86
14	Pd ₂ (dba) ₃	L5	Ph ₂ POOH	91	18:1	87
15	Pd ₂ (dba) ₃	L5	(PhO) ₂ POOH	trace	—	-
16	Pd ₂ (dba) ₃	L5	<i>p</i> -L-valine	68	23:1	86
17	Pd ₂ (dba) ₃	L5	(<i>R</i>)-CPA1	63	14:1	86
18	Pd ₂ (dba) ₃	L5	(<i>S</i>)-CPA1	50	17:1	88
19	Pd ₂ (dba) ₃	L5	TsOH·H ₂ O	trace	—	—
20	Pd ₂ (dba) ₃	L5	none	77	6:1	54
21 ^[e]	Pd ₂ (dba) ₃	L5	OFBA	95	20:1	90

^aReaction conditions: Unless indicated otherwise, reactions of **1a** (0.10 mmol), **2a** (0.20 mmol), Pd (0.005 mmol), ligand (0.01 mmol), OFBA (0.005 mmol), and 2,6-DMBQ (0.12 mmol) were carried out in toluene (2 mL) for 12 h. ^bThe yields and ratios of **3a/4a** were determined by ¹H NMR analysis of the crude reaction mixture. ^cThe ee value was determined by chiral HPLC analysis. ^d2,5-DMBQ (0.12 mmol) was used instead of 2,6-DMBQ. ^eThe reaction was carried out at 25 °C. 2,5(6)-DMBQ = 2,5(6)-dimethylquinone, OFBA = 2-fluorobenzoic acid, dba = dibenzylidene acetone.

3. Experimental procedures and characterization of new compounds.

Typical procedure for synthesis of 5H-thiazol-4-ones ^[2]



General procedure A:

Ethyl bromopropionate (3.96 g, 21.9 mmol) was added dropwise to a solution of thiobenzamide (3.00 g, 21.9 mmol) and pyridine (7 mL, 87.5 mmol) in toluene (200 mL) at 23 °C. The reaction mixture was heated to 80 °C for 6 h and allowed to be cooled down to 23 °C. The solvent was evaporated and the solid was recrystallized from ethanol to afford product (3.3 g, 81%).

3.1 Substrate 1a-1p can be prepared from General procedure A:

5-benzyl-2-phenylthiazol-4-ol (1a)

Faint yellow neat solid. 81% yield. ¹H NMR (400 MHz, DMSO-d₆) δ 10.59 (s, 1H), 7.78 (m, 2H), 7.43 (m, 3H), 7.34 – 7.24 (m, 4H), 7.21 (m, 1H), 3.98 (s, 2H). ¹³C NMR (101 MHz, DMSO-d₆) δ 159.4, 158.6, 140.5, 133.2, 129.5, 129.0, 128.4, 128.1, 126.2, 124.8, 107.5, 29.7. IR (KBr): γ 3435, 1589, 1503, 1492, 1454, 1407, 1242, 1148, 1074, 1052, 759, 710, 683 cm⁻¹. HRMS (ESI): m/z [M + H]⁺ calcd for [C₁₆H₁₄NOS]⁺ requires 268.0791, found 268.0800.

5-(4-fluorobenzyl)-2-phenylthiazol-4-ol (1b)

Yellow neat. 53% yield. ¹H NMR (400 MHz, DMSO-d₆) δ 10.62 (s, 1H), 7.78 (m, 2H), 7.43 (m, 3H), 7.32 – 7.25 (m, 1H), 7.12 (m, 2H), 3.98 (s, 2H). ¹³C NMR (101 MHz, DMSO-d₆) δ 162.0, 159.6, 159.5, 158.6, 136.7, 136.7, 133.2, 129.9, 129.8, 129.6, 129.1, 124.8, 115.2, 115.0. IR (KBr): γ 3444, 2916, 1585, 1511, 1435, 1041, 1243, 1150, 1111, 1055, 970, 808, 757, 683 cm⁻¹. HRMS (ESI): m/z [M + H]⁺ calcd for [C₁₆H₁₃FNOS]⁺ requires 286.0696, found 286.0706.

5-(3-methoxybenzyl)-2-phenylthiazol-4-ol (1c)

Yellow solid. 48% yield. ¹H NMR (400 MHz, DMSO-d₆) δ 10.58 (s, 1H), 7.90 – 7.64 (m, 2H), 7.57 – 7.36 (m, 3H), 7.22 (m, 2H), 6.99 – 6.64 (m, 1H), 3.95 (s, 2H), 3.72 (s, 3H). ¹³C NMR (101 MHz, DMSO-d₆) δ 159.4, 159.3, 158.6, 142.1, 133.3, 129.6, 129.5, 129.1, 124.8, 120.3, 113.9, 111.6, 107.4, 54.9, 29.7. IR (KBr): γ 3435, 2930, 2833, 2649, 1585, 1502, 1485, 1471, 1434, 1400, 1314, 1244, 1226, 1186, 1084, 1052, 1038, 791, 781, 763, 746, 732, 685 cm⁻¹. HRMS (ESI): m/z [M + H]⁺ calcd for [C₁₇H₁₆NO₂S]⁺ requires 298.0896, found 298.0901.

4-((4-hydroxy-2-phenylthiazol-5-yl) methyl) benzonitrile (1d)

Yellow solid. 79% yield. ¹H NMR (400 MHz, DMSO-d₆) δ 10.73 (s, 1H), 7.99 – 7.67 (m, 4H), 7.55 – 7.25 (m, 5H), 4.09 (s, 2H). ¹³C NMR (101 MHz, DMSO-d₆) δ 160.0, 159.0, 146.4, 133.1, 132.4, 129.7, 129.2, 129.1, 124.9, 118.8, 109.1, 105.6, 29.5. IR (KBr): γ 3431, 3069, 2652, 2225, 1606, 1585, 1503, 1482, 1439, 1410, 1307, 1240, 1178, 1140, 1043, 765, 758, 684 cm⁻¹. HRMS (ESI): m/z [M + H]⁺ calcd for [C₁₇H₁₃N₂OS]⁺ requires 293.0743, found 293.0752.

5-(naphthalen-2-ylmethyl)-2-phenylthiazol-4-ol (1e)

Light yellow solid. 75% yield. ¹H NMR (400 MHz, DMSO-d₆) δ 10.66 (s, 1H), 7.90 – 7.83 (m, 2H), 7.81 – 7.73 (m, 3H), 7.45 (m, 6H), 4.16 (s, 2H). ¹³C NMR (101 MHz, DMSO-d₆) δ 159.6, 158.6, 138.2, 133.2, 133.0, 131.7, 129.6, 129.0, 128.0, 127.4, 127.3, 126.9, 126.1, 126.1, 125.5, 124.8, 107.4, 29.9. IR (KBr): γ 3436, 3050, 2642, 1713, 1583, 1502, 1482, 1437, 1405, 1286, 1242, 1143, 1052, 823, 758, 683 cm⁻¹. HRMS (ESI): m/z [M + H]⁺ calcd for [C₂₀H₁₆NOS]⁺ requires 318.0947, found 318.0950.

5-(2-chlorobenzyl)-2-phenylthiazol-4-ol (1f)

Yellow powder. 47% yield. ¹H NMR (400 MHz, DMSO-d⁶) δ 10.66 (s, 1H), 7.78 (m, 2H), 7.48 – 7.40 (m, 4H), 7.37 (m, 1H), 7.31 (m, 2H), 4.08 (s, 2H). ¹³C NMR (101 MHz, DMSO-d⁶) δ 159.7, 158.9, 137.7, 133.1, 132.6, 130.5, 129.6, 129.3, 129.1, 128.4, 127.4, 124.8, 105.3, 27.7. IR (KBr): γ 3437, 1584, 1574, 1503, 1475, 1441, 1415, 1241, 1150, 1054, 758, 743, 710, 685 cm⁻¹. HRMS (ESI): m/z [M + H]⁺ calcd for [C₁₆H₁₃ClNOS]⁺ requires 302.0401, found 302.0411.

5-(3-chlorobenzyl)-2-phenylthiazol-4-ol (1g)

Yellow solid. 63% yield. ¹H NMR (400 MHz, DMSO-d⁶) δ 10.67 (s, 1H), 7.79 (m, 2H), 7.53 – 7.40 (m, 3H), 7.38 – 7.30 (m, 2H), 7.29 (m, 1H), 7.26 (m, 1H), 4.01 (s, 2H). ¹³C NMR (101 MHz, DMSO-d⁶) δ 159.8, 158.8, 143.1, 133.1, 133.0, 130.3, 129.7, 129.0, 127.9, 126.8, 126.2, 124.8, 106.4, 29.1. IR (KBr): γ 3437, 3061, 2660, 1587, 1574, 1503, 1474, 1435, 1407, 1242, 1189, 1148, 1079, 1054, 758, 781, 753, 683 cm⁻¹. HRMS (ESI): m/z [M + H]⁺ calcd for [C₁₆H₁₃ClNOS]⁺ requires 302.0401, found 302.0410.

5-(4-chlorobenzyl)-2-phenylthiazol-4-ol (1h)

Yellow neat. 56% yield. ¹H NMR (400 MHz, DMSO-d⁶) δ 10.64 (s, 1H), 7.78 (m, 2H), 7.48 – 7.40 (m, 3H), 7.36 (m, 2H), 7.28 (m, 2H), 3.98 (s, 2H). ¹³C NMR (101 MHz, DMSO-d⁶) δ 159.7, 158.7, 139.6, 133.2, 130.9, 130.0, 129.6, 129.1, 128.4, 124.8, 106.8, 28.9. IR (KBr): γ 3435, 2917, 2642, 1587, 1503, 1489, 1458, 1401, 1242, 1199, 1148, 1091, 1045, 823, 810, 756, 683 cm⁻¹. HRMS (ESI): m/z [M + H]⁺ calcd for [C₁₆H₁₃ClNOS]⁺ requires 302.0401, found 302.0408.

5-(3-methylbenzyl)-2-phenylthiazol-4-ol (1i)

Yellow solid. 65% yield. ¹H NMR (400 MHz, DMSO-d⁶) δ 10.57 (s, 1H), 7.88 – 7.73 (m, 2H), 7.55 – 7.36 (m, 3H), 7.18 (m, 1H), 7.03 (m, 3H), 3.94 (s, 3H), 2.26 (s, 2H). ¹³C NMR (101 MHz, DMSO-d⁶) δ 159.4, 158.5, 140.5, 137.5, 133.3, 129.6, 129.0, 128.7, 128.3, 126.9, 125.2, 124.8, 107.6, 29.6, 20.9. IR (KBr): γ 3434, 2926, 1585, 1503, 1437, 1402, 1242, 1155, 1058, 975, 755, 681 cm⁻¹. HRMS (ESI): m/z [M + H]⁺ calcd for [C₁₇H₁₆NOS]⁺ requires 282.0947, found 282.0958.

5-(2-methylbenzyl)-2-phenylthiazol-4-ol (1j)

Yellow solid. 71% yield. ¹H NMR (400 MHz, DMSO-d⁶) δ 10.59 (s, 1H), 7.84 – 7.70 (m, 2H), 7.51 – 7.33 (m, 2H), 7.26 – 7.03 (m, 4H), 3.95 (s, 2H), 2.28 (s, 3H). ¹³C NMR (101 MHz, DMSO-d⁶) δ 159.4, 158.3, 138.7, 135.6, 133.2, 130.1, 129.5, 129.0, 128.6, 126.5, 126.0, 124.8, 107.2, 27.7, 18.8. IR (KBr): γ 3438, 2285, 1587, 1420, 1241, 1147, 1111, 1052 cm⁻¹. HRMS (ESI): m/z [M + H]⁺ calcd for [C₁₇H₁₆NOS]⁺ requires 282.0947, found 282.0949.

5-(4-methylbenzyl)-2-phenylthiazol-4-ol (1k)

Yellow solid. 72% yield. ¹H NMR (400 MHz, DMSO-d⁶) δ 10.55 (s, 1H), 7.80 – 7.74 (m, 2H), 7.47 – 7.39 (m, 3H), 7.12 (q, *J* = 8.0 Hz, 4H), 3.94 (s, 2H), 2.25 (s, 3H). ¹³C NMR (101 MHz, DMSO-d⁶) δ 159.3, 158.4, 137.5, 135.2, 133.3, 129.5, 129.0, 129.0, 128.0, 124.8, 107.9, 29.3, 20.5. IR (KBr): γ 3444, 2916, 1585, 1511, 1435, 1401, 1243, 1150, 1111, 1055, 970, 808, 757, 683 cm⁻¹. HRMS (ESI): m/z [M + H]⁺ calcd for [C₁₇H₁₆NOS]⁺ requires 282.0947, found 282.0955.

5-(2-bromobenzyl)-2-phenylthiazol-4-ol (1l)

Yellow solid. 76% yield. ¹H NMR (400 MHz, DMSO-d⁶) δ 10.67 (s, 1H), 7.78 (m, 2H), 7.62 (m, 1H), 7.47 – 7.40 (m, 3H), 7.38 – 7.34 (m, 2H), 7.23 – 7.16 (m, 1H), 4.08 (s, 2H). ¹³C NMR (101 MHz, DMSO-d⁶) δ 159.7, 158.9, 139.4, 133.1, 132.6, 130.5, 129.6, 129.0, 128.6, 128.0, 124.8, 123.3, 105.4, 30.3. IR (KBr): γ 3435, 2361, 1571, 1500, 1475, 1396, 1238, 1144, 1070, 1042, 764, 688 cm⁻¹. HRMS (ESI): m/z [M + H]⁺ calcd for [C₁₆H₁₃BrNOS]⁺ requires 345.9896, found 345.9905.

5-(3-bromobenzyl)-2-phenylthiazol-4-ol (1m)

Yellow solid. 59% yield. ¹H NMR (400 MHz, DMSO-d⁶) δ 10.67 (s, 1H), 7.79 (m, 2H), 7.48 – 7.38 (m, 5H), 7.27 (m, 2H), 4.00 (s, 2H). ¹³C NMR (101 MHz, DMSO-d⁶) δ 159.8, 158.8, 143.4, 133.2, 130.8, 130.6, 129.7, 129.1, 129.0, 127.2, 124.8, 121.6, 106.4,

29.1. **IR** (KBr): γ 3435, 2361, 1571, 1500, 1475, 1396, 1238, 1144, 1070, 1042, 764, 688 cm^{-1} . **HRMS** (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{16}\text{H}_{13}\text{BrNOS}]^+$ requires 345.9896, found 345.9901.

5-(4-bromobenzyl)-2-phenylthiazol-4-ol (1n)

Yellow solid. 63% yield. **¹H NMR** (400 MHz, DMSO- d_6) δ 10.64 (s, 1H), 7.78 (m, 2H), 7.49 (m, 2H), 7.47 – 7.40 (m, 3H), 7.22 (m, 2H), 3.96 (s, 2H). **¹³C NMR** (101 MHz, DMSO- d_6) δ 159.7, 158.7, 140.0, 133.2, 131.3, 130.4, 129.6, 129.1, 124.8, 119.3, 106.7, 29.0. **IR** (KBr): γ 3442, 2360, 2341, 1584, 1441, 1419, 11149, 1041 cm^{-1} . **HRMS** (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{16}\text{H}_{13}\text{BrNOS}]^+$ requires 345.9896, found 345.9899.

5-methyl-2-phenylthiazol-4-ol (1o)

Yellow neat crystal. 81% yield. **¹H NMR** (400 MHz, DMSO- d_6) δ 10.30 (s, 1H), 7.78 (m, 2H), 7.64 – 7.28 (m, 4H), 2.21 (s, 3H). **¹³C NMR** (101 MHz, DMSO- d_6) δ 158.7, 158.2, 133.3, 129.4, 129.1, 124.7, 102.5, 9.1. **IR** (KBr): γ 3438, 1585, 1500, 1457, 1401, 1374, 1235, 1125, 1000, 981, 761, 683 cm^{-1} . **HRMS** (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{10}\text{H}_{10}\text{NOS}]^+$ requires 192.0478, found 192.0485.

3.2 Substrate 5a-5f can also be prepared from General procedure :

2,5-diphenylthiazol-4-ol (5a)

Yellow neat. 83% yield. **¹H NMR** (400 MHz, DMSO- d_6) δ 11.59 (s, 1H), 7.90 (dt, J = 4.0, 2.2 Hz, 2H), 7.81 – 7.68 (m, 2H), 7.58 – 7.45 (m, 3H), 7.45 – 7.35 (m, 2H), 7.28 – 7.12 (m, 1H). **¹³C NMR** (101 MHz, DMSO- d_6) δ 159.6, 158.4, 132.9, 131.7, 130.2, 129.2, 128.8, 126.0, 125.8, 125.1, 107.5. **IR** (KBr): γ 2919, 2569, 1571, 1489, 1455, 1420, 1332, 1047, 774, 758, 686 cm^{-1} . **HRMS** (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{15}\text{H}_{12}\text{NOS}]^+$ requires 254.0640, found 254.0636.

5-phenyl-2-(m-tolyl) thiazol-4-ol (5b)

Orange neat. 90% yield. **¹H NMR** (400 MHz, DMSO- d_6) δ 11.60 (s, 1H), 7.72 (t, J = 11.7 Hz, 4H), 7.40 (t, J = 7.4 Hz, 3H), 7.30 (d, J = 7.5 Hz, 1H), 7.22 (t, J = 7.3 Hz, 1H). **¹³C NMR** (101 MHz, DMSO- d_6) δ 160.2, 158.8, 139.0, 133.3, 132.2, 131.3, 129.6, 129.2, 126.5, 126.3, 126.1, 122.8, 107.8, 21.4. **IR** (KBr): γ 3085, 3058, 2963, 2924, 2854, 1717, 1602, 1586, 1514, 1477, 1445, 1376, 1266, 1181, 1152, 1090, 1004, 953, 907, 796, 759, 693 cm^{-1} . **HRMS** (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{16}\text{H}_{14}\text{NOS}]^+$ requires 268.0796, found 268.0789.

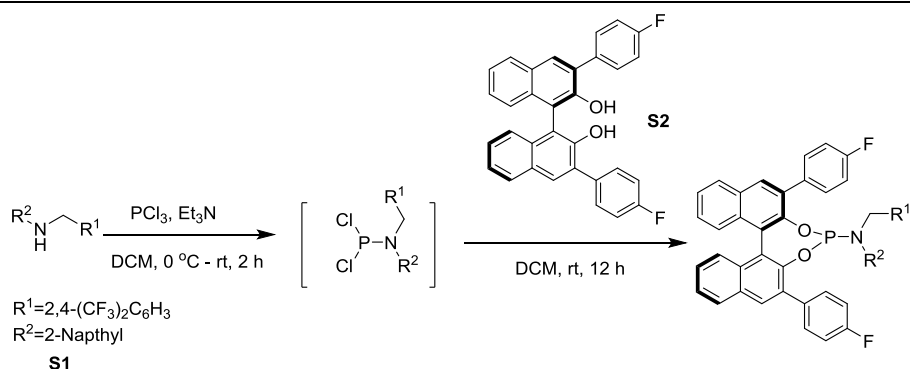
2-(4-bromophenyl)-5-phenylthiazol-4-ol (5c)

Yellow neat. 85% yield. **¹H NMR** (400 MHz, DMSO- d_6) δ 11.64 (s, 1H), 7.82 (d, J = 8.6 Hz, 2H), 7.72 (t, J = 8.6 Hz, 4H), 7.41 (t, J = 7.8 Hz, 2H), 7.24 (t, J = 7.4 Hz, 1H). **¹³C NMR** (101 MHz, DMSO- d_6) δ 158.5, 158.2, 132.2, 132.0, 131.5, 128.8, 127.0, 126.2, 125.9, 123.3, 108.1. **IR** (KBr): γ 3060, 3038, 2966, 2926, 2854, 1716, 1651, 1596, 1521, 1494, 1445, 1410, 1376, 1298, 1256, 1154, 1101, 1035, 1007, 947, 908, 843, 810, 763, 736, 697 cm^{-1} . **HRMS** (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{15}\text{H}_{11}\text{BrNOS}]^+$ requires 331.9745, found 331.9744.

2-(4-fluorophenyl)-5-phenylthiazol-4-ol (5d)

Yellow neat. 85% yield. **¹H NMR** (400 MHz, DMSO- d_6) δ 11.60 (s, 1H), 8.10 – 7.89 (m, 2H), 7.86 – 7.69 (m, 2H), 7.37 (ddd, J = 15.6, 12.2, 4.8 Hz, 4H), 7.23 (t, J = 7.4 Hz, 1H). **¹³C NMR** (101 MHz, DMSO- d_6) δ 164.3, 161.8, 158.4 (d, J = 9.1 Hz), 131.69, 129.5 (d, J = 3.1 Hz), 128.7, 127.49 (d, J = 8.7 Hz), 126.08, 125.8, 116.3 (d, J = 22.3 Hz), 107.62. **IR** (KBr): γ 3086, 3057, 2961, 1720, 1586, 1567, 1514, 1477, 1398, 1376, 1304, 1255, 1154, 1106, 1069, 1035, 1010, 947, 906, 834, 762, 696 cm^{-1} . **HRMS** (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{15}\text{H}_{11}\text{FNOS}]^+$ requires 272.0545, found 272.0544.

3.3 Chiral Ligand Preparation General procedure:

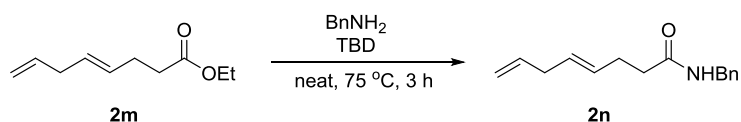


To a stirred solution of Et₃N (0.21 mL, 1.52 mmol, 8.0 equiv) and PCl₃ (0.15 mL (2M in CH₂Cl₂), 0.29 mmol, 1.5 equiv) in DCM (2 mL, dried over CaH₂) at 0 °C was slowly added amine S1 (0.29 mmol, 1.5 equiv) and the mixture was stirred at room temperature for 2 h. After the mixture was cooled down to 0 °C, S2 (100 mg, 0.19 mmol, 1.0 equiv) was added as solid in one portion. The mixture was further stirred at room temperature for 12 h. The mixture was concentrated in vacuo and the residue was purified by flash chromatography (SiO₂, light petroleum/dichloromethane) to provide the product L1.

N-(2,4-bis(trifluoromethyl)benzyl)-2,6-bis(4-fluorophenyl)-N-(naphthalen-2-yl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-amine (L1)

White neat solid. Yield: 90 %, 149.0 mg. ¹H NMR (400 MHz, CDCl₃) δ 8.12 (s, 1H), 8.04 – 7.94 (m, 3H), 7.80 – 7.73 (m, 2H), 7.68 – 7.60 (m, 2H), 7.60 – 7.53 (m, 3H), 7.52 – 7.43 (m, 5H), 7.37 (ddd, *J* = 9.7, 7.2, 4.8 Hz, 4H), 7.34 – 7.27 (m, 2H), 7.24 – 7.16 (m, 2H), 7.01 (dd, *J* = 14.7, 6.0 Hz, 2H), 6.59 (s, 1H), 6.50 (dd, *J* = 8.8, 1.4 Hz, 1H), 4.40 (d, *J* = 17.7 Hz, 1H), 4.26 (d, *J* = 17.5 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 163.8, 161.3, 146.5, 146.0, 143.0, 141.7, 141.2, 140.1, 136.8, 133.6, 133.4, 133.1, 132.4, 132.3, 132.1, 131.8, 131.3, 131.1, 130.6, 130.5, 130.3, 129.2, 128.7, 128.5, 128.4, 127.3, 127.2, 126.9, 126.7, 126.5, 126.4, 126.4, 125.7, 125.5, 125.1, 123.8, 121.8, 121.7, 121.1, 119.4, 119.3, 116.7, 115.5, 115.3, 115.1, 114.9, 113.8, 99.9, 46.0. ³¹P NMR (162 MHz, CDCl₃) 135.85. ¹⁹F NMR (376 MHz, CDCl₃) -61.42, -62.79, -114.27 (ddd), -114.51 (m). IR (KBr): γ 2389, 1771, 1629, 1506, 1344, 1265, 1130, 1052, 1015, 808, 753, 668, 511, 436, 418 cm⁻¹. HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₅₁H₃₁F₈NO₂P]⁺ requires 872.1965, found 872.1970.

(E)-N-benzyl octa-4, 7-dienamide



To the mixture of **2m** (537 mg, 3.20 mmol) and benzylamine (411 mg, 3.84 mmol) was added TBD (1,5,7-Triazabicyclo[4.4.0]dec-5-ene) (134 mg, 0.96 mmol) at room temperature. The mixture was stirred at 75 °C for 3 h. Then the reaction mixture was cooled down to room temperature and diluted with ether, washed with HCl (2 M), then extracted with ether (30 mL x3). The combined organic layers were dried over anhydrous Na₂SO₄. The mixture was filtered and concentrated in vacuo. The residue was purified by column chromatography on silica column.

White solid. Yield: 65%. ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.11 (m, 5H), 5.97 (s, 1H), 5.76 – 5.61 (m, 1H), 5.46 – 5.28 (m, 2H), 4.97 – 4.84 (m, 2H), 4.32 (d, *J* = 5.7 Hz, 2H), 2.64 (t, *J* = 5.6 Hz, 2H), 2.31 – 2.23 (m, 2H), 2.23 – 2.15 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 172.44, 138.45, 136.99, 129.65, 129.30, 128.73, 127.85, 127.52, 115.18, 43.60, 36.68, 36.48, 28.64. HRMS (ESI) *m/z* (M+H)⁺ calculated for C₁₅H₁₉NO: 230.1539, observed: 230.1549.

1. General experimental procedures for the control experiment of 1,4-pentadienes with 5H-thiazol-4-ones

To a flame-dried and Ar-purged Schlenk tube (10 mL) were added 5H-Thiazol-4-ones (0.10 mmol), Pd₂(dba)₃ (0.0025 mmol), phosphoramidite L5 (0.01 mmol), OFBA (0.005 mmol), 2,6-DMBQ (0.12 mmol) and a stirring bar. The schlenk tube was then

evacuated and filled with argon. This cycle was repeated three times and followed by the addition of toluene (2 mL) and 1, 4-pentadienes (0.20 mmol) via a syringe. The mixture was stirred at 25 °C for 72 h. The reaction mixture was purified by column chromatography on silica gel (petroleum/ethyl acetate = 20/1) to provide product **3**.

(R)-5-benzyl-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3aa)

Colorless oil. Yield: 95 %, 39.6 mg; l/b: 20:1. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 97/3, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 23.143 min (minor), t_R = 27.210 min (major). $[\alpha]_D^{20}$ = -34.1 (c 0.26, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 4.2 Hz, 4H), 7.21 – 7.15 (m, 1H), 6.12 (dd, *J* = 15.0, 10.4 Hz, 1H), 5.90 (dd, *J* = 15.0, 10.5 Hz, 1H), 5.67 – 5.57 (m, 1H), 5.41 (dt, *J* = 14.9, 7.4 Hz, 1H), 3.32 (d, *J* = 13.8 Hz, 1H), 3.23 (d, *J* = 13.8 Hz, 1H), 2.83 (dd, *J* = 14.1, 7.0 Hz, 1H), 2.72 (dd, *J* = 14.2, 7.8 Hz, 1H), 2.00 (q, *J* = 7.0 Hz, 2H), 1.38 – 1.14 (m, 8H), 0.86 (t, *J* = 6.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 195.2, 194.8, 136.1, 135.4, 134.8, 132.3, 130.4, 129.4, 128.9, 128.8, 128.2, 127.3, 123.3, 70.9, 44.3, 41.8, 32.6, 31.6, 29.1, 28.8, 22.6, 14.0. IR (KBr): γ 2959, 2925, 2854, 1598, 1720, 1513, 1484, 1446, 1261, 1165, 1093, 1028, 989, 800, 771, 700, 686 cm⁻¹. HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₂₇H₃₂NOS]⁺ requires 418.2199, found 418.2205. The absolute configuration was assigned tentatively by analogy.

(R)-5-(4-fluorobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ba)

Colorless oil. Yield: 56 %, 24.4 mg; l/b: 38:1. Enantiomeric excess: 86%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 10.509 min (minor), t_R = 11.409 min (major). $[\alpha]_D^{20}$ = -19.7 (c 0.06, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.18 (dd, *J* = 8.1, 5.6 Hz, 2H), 6.90 (t, *J* = 8.5 Hz, 2H), 6.14 (dd, *J* = 14.9, 10.4 Hz, 1H), 5.91 (dd, *J* = 15.1, 10.4 Hz, 1H), 5.68 – 5.59 (m, 1H), 5.42 (dt, *J* = 14.9, 7.3 Hz, 1H), 3.30 (d, *J* = 13.9 Hz, 1H), 3.19 (d, *J* = 13.9 Hz, 1H), 2.77 (ddd, *J* = 33.8, 14.1, 7.4 Hz, 2H), 2.01 (q, *J* = 7.1 Hz, 2H), 1.35 – 1.17 (m, 8H), 0.86 (t, *J* = 6.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 195.2, 194.6, 136.2, 135.6, 134.9, 132.1, 132.0, 131.9, 130.9, 129.3, 128.9, 128.8, 123.3, 115.2, 114.9, 43.2, 42.0, 32.6, 31.7, 29.1, 28.8, 22.6, 14.1. IR (KBr) γ 3448, 2924, 2854, 1720, 1509, 1484, 1446, 1260, 1158, 1026, 800, 686 cm⁻¹. HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₂₇H₃₁FNOS]⁺ requires 436.2105, found 436.2110. The absolute configuration was assigned tentatively by analogy.

(R)-5-(3-methylbenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ca)

Colorless oil. Yield: 91 %, 40.7 mg; l/b: 17:1. 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 = 16.297 min (minor), t_R = 18.723 min (major). $[\alpha]_D^{20}$ = -33.4 (c 0.27, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 7.3 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.86 – 6.70 (m, 3H), 6.12 (dd, *J* = 15.0, 10.4 Hz, 1H), 5.89 (dd, *J* = 15.1, 10.4 Hz, 1H), 5.68 – 5.56 (m, 1H), 5.40 (dt, *J* = 14.9, 7.4 Hz, 1H), 3.75 (s, 3H), 3.25 (dd, *J* = 31.8, 13.8 Hz, 2H), 2.81 (dd, *J* = 14.2, 7.0 Hz, 1H), 2.70 (dd, *J* = 14.1, 7.8 Hz, 1H), 2.00 (q, *J* = 7.0 Hz, 2H), 1.32 – 1.12 (m, 8H), 0.92 – 0.76 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 195.3, 194.8, 159.3, 137.0, 136.1, 135.4, 134.8, 132.2, 129.3, 129.2, 128.9, 128.8, 123.2, 122.7, 116.0, 112.8, 70.8, 55.2, 44.3, 41.8, 32.5, 31.6, 29.1, 28.8, 22.5, 14.0. IR (KBr) γ 2958, 2926, 2854, 1725, 1514, 1486, 1447, 1263, 1155, 1120, 1073, 1040 cm⁻¹. HRMS (ESI): *m/z* [M + H]⁺ calcd for [C₂₈H₃₄NO₂S]⁺ requires 448.2305, found 448.2314. The absolute configuration was assigned tentatively by analogy.

4-(((R)-4-oxo-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl)-4, 5-dihydrothiazol-5-yl) methyl) Benzonitrile (3da)

Colorless oil. Yield: 93 %, 41.1 mg; l/b: 23:1. Enantiomeric excess: 93%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 15.749 min (major), t_R = 18.413 min (minor). $[\alpha]_D^{20}$ = -20.0 (c 0.28, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 7.7 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.47 (dd, *J* = 17.6, 8.0 Hz, 4H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.16 (dd, *J* = 14.9, 10.5 Hz, 1H), 5.93 (dd, *J* = 15.0, 10.5 Hz, 1H), 5.71 – 5.60 (m, 1H), 5.44 (dt, *J* = 14.9, 7.4 Hz, 1H), 3.40 (d, *J* = 13.7 Hz, 1H), 3.26 (d, *J* = 13.7 Hz, 1H), 2.79 (qd, *J* = 14.1, 7.5 Hz, 2H), 2.02 (q, *J* = 7.0 Hz, 2H), 1.38 – 1.18 (m, 8H), 0.86 (t, *J* = 6.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 194.0, 193.1, 139.6, 135.5, 134.9, 134.2, 130.9, 130.8, 130.1, 128.1, 127.9, 127.8, 121.8, 117.6, 110.3, 69.2, 42.6, 41.4, 31.5, 30.6, 28.0, 27.8, 21.5, 13.0. IR (KBr) γ 3451, 2958, 2924, 2854, 1720,

1512, 1485, 1446, 1261, 1165, 1024, 991, 801, 773, 686 cm⁻¹ **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₈H₃₁N₂O]⁺ requires 443.2152, found 443.2157. The absolute configuration was assigned tentatively by analogy.

(R)-5-(naphthalen-2-ylmethyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ea)

Colorless oil. Yield: 37 %, 17.3 mg; l/b: 14:1. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 99/1, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 75.695 min (minor), t_R = 80.225 min (major). [α]_D²⁰ = -22.0 (c 0.25, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.01 (d, J = 7.4 Hz, 2H), 7.81 – 7.74 (m, 2H), 7.74 – 7.69 (m, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.47 – 7.39 (m, 4H), 7.36 (d, J = 8.5 Hz, 1H), 6.13 (dd, J = 14.9, 10.4 Hz, 1H), 5.91 (dd, J = 15.1, 10.4 Hz, 1H), 5.72 – 5.55 (m, 1H), 5.43 (dt, J = 14.9, 7.4 Hz, 1H), 3.50 (d, J = 13.9 Hz, 1H), 3.41 (d, J = 13.8 Hz, 1H), 2.88 (dd, J = 14.1, 7.0 Hz, 1H), 2.75 (dd, J = 14.1, 7.8 Hz, 1H), 2.01 (q, J = 7.0 Hz, 2H), 1.40 – 1.16 (m, 8H), 0.86 (t, J = 6.7 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.2, 194.8, 136.2, 135.4, 134.8, 133.2, 133.1, 132.5, 132.2, 129.3, 128.8, 128.3, 127.8, 127.8, 127.5, 126.0, 125.8, 123.2, 71.0, 44.3, 42.1, 32.6, 31.7, 29.1, 28.8, 22.6, 14.0. **IR** (KBr) γ 3462, 2958, 2924, 2854, 1719, 1510, 1484, 1445, 1260, 1151, 1096, 1027, 990, 817, 771, 685 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₃₁H₃₄NOS]⁺ requires 468.2356, found 468.2366. The absolute configuration was assigned tentatively by analogy.

(R)-5-(2-chlorobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3fa)

Colorless oil. Yield: 89 %, 30.4 mg; l/b: 13:1. Enantiomeric excess: 89%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 9.268 min (minor), t_R = 11.156 min (major). [α]_D²⁰ = +41.7 (c 0.51, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.98 (dd, J = 9.1, 8.0 Hz, 2H), 7.60 (dd, J = 13.3, 5.9 Hz, 1H), 7.42 (q, J = 8.2 Hz, 2H), 7.29 (dd, J = 5.4, 3.8 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.12 – 7.07 (m, 2H), 6.17 (dd, J = 14.9, 10.4 Hz, 1H), 5.92 (dd, J = 15.1, 10.4 Hz, 1H), 5.69 – 5.58 (m, 1H), 5.46 (dt, J = 14.9, 7.4 Hz, 1H), 3.70 (d, J = 14.0 Hz, 1H), 3.39 (t, J = 12.4 Hz, 1H), 2.86 (dd, J = 14.1, 7.0 Hz, 1H), 2.78 (dd, J = 14.1, 7.8 Hz, 1H), 2.01 (q, J = 7.0 Hz, 2H), 1.38 – 1.17 (m, 8H), 0.86 (t, J = 6.7 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 196.1, 195.1, 136.3, 135.5, 135.2, 134.8, 133.8, 132.2, 131.5, 129.5, 129.3, 128.8, 128.8, 128.7, 127.0, 123.2, 70.8, 42.7, 39.9, 32.6, 31.7, 29.1, 28.8, 22.6, 14.1. **IR** (KBr): γ 2957, 2925, 2854, 1720, 1597, 1511, 1484, 1445, 1314, 1261, 1155, 1094, 1054, 1039, 1027, 988, 800, 770, 754, 685 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₇H₃₁ClNOS]⁺ requires 342.1886, found 342.1892. The absolute configuration was assigned tentatively by analogy.

(R)-5-(3-chlorobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ga)

Colorless oil. Yield: 90 %, 40.6 mg; l/b: 12:1. Enantiomeric excess: 91%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 97/3, flow rate 0.5 mL/min, T = 30 °C, 254 nm): t_R = 42.023 min (minor), t_R = 43.785 min (major). [α]_D²⁰ = -20.1 (c 0.39, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.06 – 7.97 (m, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.45 (dd, J = 16.3, 8.7 Hz, 2H), 7.22 (s, 1H), 7.19 – 7.14 (m, 2H), 7.14 – 7.07 (m, 1H), 6.13 (dd, J = 14.9, 10.4 Hz, 1H), 5.90 (dt, J = 17.8, 8.9 Hz, 1H), 5.70 – 5.55 (m, 1H), 5.46 – 5.34 (m, 1H), 3.30 (d, J = 13.9 Hz, 1H), 3.20 (d, J = 13.8 Hz, 1H), 2.81 (dd, J = 14.1, 7.0 Hz, 1H), 2.71 (dd, J = 14.1, 7.8 Hz, 1H), 2.01 (q, J = 7.1 Hz, 2H), 1.39 – 1.15 (m, 8H), 0.86 (t, J = 6.7 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.2, 194.4, 137.3, 136.3, 135.6, 135.0, 133.9, 132.1, 130.5, 129.5, 129.3, 128.9, 128.86, 128.5, 127.6, 123.0, 70.5, 43.6, 42.0, 32.6, 31.7, 29.1, 28.8, 22.6, 14.1. **IR** (KBr) γ 3441, 2958, 2924, 2853, 1719, 1597, 1511, 1484, 1445, 1315, 1260, 1164, 1081, 1027, 989, 796, 771, 685 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₇H₃₁ClNOS]⁺ requires 452.1809, found 452.1815. The absolute configuration was assigned tentatively by analogy.

(R)-5-(4-chlorobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ha)

Colorless solid. Yield: 87 %, 39.3 mg; l/b: 12:1. Enantiomeric excess: 87%, determined by HPLC (CHIRALPAK IC, hexane/alcohol = 97/3, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 11.937 min (minor), t_R = 12.715 min (major). [α]_D²⁰ = -20.2 (c 0.17, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.94 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.7 Hz, 2H), 7.10 (q, J = 8.5 Hz, 4H), 6.07 (dd, J = 15.0, 10.4 Hz, 1H), 5.84 (dd, J = 15.1, 10.4 Hz, 1H), 5.61 – 5.50 (m, 1H), 5.35 (dt, J = 14.9, 7.3 Hz, 1H), 3.23 (d, J = 13.9 Hz, 1H), 3.12 (d, J = 13.8 Hz, 1H), 2.74 (dd, J = 14.2, 6.9 Hz, 1H), 2.65 (dd, J = 14.1, 7.8 Hz, 1H), 1.94 (q, J = 7.1 Hz, 1H), 1.30 –

1.10 (m, 8H), 0.79 (t, $J = 6.7$ Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.2, 194.5, 136.3, 135.6, 135.0, 133.8, 133.3, 132.1, 131.7, 129.3, 128.9, 128.8, 128.4, 123.1, 70.7, 43.3, 42.1, 32.6, 31.7, 29.1, 28.8, 22.6, 14.9. **IR** (KBr): γ 2956, 2925, 2854, 1720, 1513, 1485, 1446, 1260, 1164, 1094, 1016, 989, 801, 771, 771, 685 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₇H₃₁ClNOS]⁺ requires 452.1809, found 452.1818.

(R)-5-(3-methylbenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ia)

Colorless oil. Yield: 43 %, 18.5 mg; l/b: 10:1. Enantiomeric excess: 85%, (3ad) determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 11.298 min (minor), t_R = 13.384 min (major). $[\alpha]_D^{20}$ = -60.1 (c 0.48, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.07 – 8.01 (m, 2H), 7.65 – 7.58 (m, 1H), 7.50 – 7.42 (m, 2H), 7.16 – 7.09 (m, 1H), 7.08 – 6.97 (m, 3H), 6.11 (dd, $J = 15.0, 10.4$ Hz, 1H), 5.88 (dt, $J = 18.5, 9.3$ Hz, 1H), 5.67 – 5.51 (m, 1H), 5.40 (dt, $J = 14.9, 7.4$ Hz, 1H), 3.23 (q, $J = 13.8$ Hz, 2H), 2.81 (dd, $J = 14.2, 7.0$ Hz, 1H), 2.70 (dd, $J = 14.2, 7.8$ Hz, 1H), 2.28 (s, 3H), 2.00 (q, $J = 6.9$ Hz, 2H), 1.35 – 1.17 (m, 8H), 0.87 (dt, $J = 9.9, 4.6$ Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.2, 194.8, 137.8, 136.0, 135.4, 135.3, 134.7, 132.3, 131.1, 129.4, 128.8, 128.8, 128.1, 128.0, 127.4, 123.3, 70.9, 44.3, 41.7, 32.5, 31.6, 29.1, 28.8, 22.5, 21.3, 14.0. **IR** (KBr) γ 3440, 3019, 2958, 2924, 2854, 1720, 1598, 1512, 1485, 1446, 1314, 1260, 1154, 1096, 1027, 989, 771, 701, 686 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₈H₃₄NOS]⁺ requires 432.2356, found 432.2362. The absolute configuration was assigned tentatively by analogy.

(R)-5-(2-methylbenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ja)

Colorless oil. Yield: 52 %, 22.4 mg; l/b: 19:1. Enantiomeric excess: 86%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 97/3, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 23.972 min (minor), t_R = 34.278 min (major). $[\alpha]_D^{20}$ = -2.2 (c 0.27, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.00 (dd, $J = 8.3, 1.1$ Hz, 2H), 7.66 – 7.56 (m, 1H), 7.43 (dd, $J = 15.3, 7.6$ Hz, 2H), 7.18 (dd, $J = 8.0, 6.2$ Hz, 1H), 7.12 – 7.00 (m, 3H), 6.15 (dd, $J = 15.0, 10.3$ Hz, 1H), 5.91 (dd, $J = 14.1, 9.4$ Hz, 1H), 5.67 – 5.57 (m, 1H), 5.42 (dt, $J = 14.9, 7.4$ Hz, 1H), 3.36 (q, $J = 14.2$ Hz, 2H), 2.84 (dd, $J = 14.1, 6.9$ Hz, 1H), 2.76 (dd, $J = 14.1, 7.9$ Hz, 1H), 2.35 (s, 3H), 2.01 (q, $J = 7.0$ Hz, 2H), 1.38 – 1.15 (m, 8H), 0.97 – 0.77 (m, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.5, 195.3, 137.0, 136.2, 135.4, 134.8, 134.2, 132.2, 130.5, 130.3, 129.3, 128.8, 128.7, 127.3, 126.0, 123.4, 71.3, 42.2, 40.1, 32.5, 31.6, 29.1, 28.8, 22.6, 20.4, 14.0. **IR** (KBr) γ 2955, 2925, 1719, 1512, 1485, 1446, 1249, 1164, 988, 988, 770, 685 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₈H₃₄NOS]⁺ requires 432.2356, found 432.2362. The absolute configuration was assigned tentatively by analogy.

(R)-5-(4-methylbenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ka)

Colorless oil. Yield: 66 %, 28.5 mg; l/b: 11:1. Enantiomeric excess: 87%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 90/10, flow rate 0.5 mL/min, T = 30 °C, 254 nm): t_R = 24.565 min (minor), t_R = 26.558 min (major). $[\alpha]_D^{20}$ = -24.6 (c 0.31, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.08 – 7.99 (m, 2H), 7.66 – 7.56 (m, 1H), 7.46 (t, $J = 7.8$ Hz, 2H), 7.10 (t, $J = 10.0$ Hz, 2H), 7.04 (t, $J = 10.0$ Hz, 2H), 6.11 (dd, $J = 15.0, 10.4$ Hz, 1H), 5.89 (dd, $J = 15.1, 10.4$ Hz, 1H), 5.65 – 5.55 (m, 1H), 5.40 (dt, $J = 14.9, 7.4$ Hz, 1H), 3.23 (dd, $J = 32.7, 13.9$ Hz, 2H), 2.81 (dd, $J = 14.2, 7.0$ Hz, 1H), 2.70 (dd, $J = 14.1, 7.8$ Hz, 1H), 2.26 (s, 3H), 2.00 (q, $J = 7.0$ Hz, 2H), 1.36 – 1.18 (m, 8H), 0.90 – 0.81 (m, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.2, 194.8, 136.9, 136.0, 135.3, 134.7, 132.3, 130.2, 129.4, 128.9, 128.8, 128.8, 123.4, 71.1, 43.9, 41.7, 32.5, 31.6, 29.1, 28.8, 22.5, 21.0, 14.0. **IR** (KBr) γ 2957, 2924, 2853, 1720, 1513, 1484, 1446, 1261, 1096, 1026, 989, 805, 686 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₈H₃₄NOS]⁺ requires 432.2356, found 432.2361. The absolute configuration was assigned tentatively by analogy.

(R)-5-(2-bromobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3la)

Colorless oil. Yield: 66 %, 32.7 mg; l/b: 13:1. Enantiomeric excess: 88%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 97/3, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 17.715 min (minor), t_R = 22.299 min (major). $[\alpha]_D^{20}$ = +11.1 (c 0.04, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.99 (d, $J = 8.0$ Hz, 2H), 7.59 (t, $J = 7.5$ Hz, 1H), 7.50 – 7.39 (m, 3H), 7.24 (d, $J = 7.6$ Hz, 1H), 7.16 – 7.08 (m, 1H), 6.99 (dd, $J = 16.4, 8.7$ Hz, 1H), 6.18 (dd, $J = 15.0, 10.4$ Hz, 1H), 5.92 (dt, $J = 27.6, 13.8$ Hz, 1H), 5.71 – 5.59 (m, 1H), 5.53 – 5.41 (m, 1H), 3.69 (d, $J = 14.0$ Hz, 1H), 3.46 (d, $J = 14.0$ Hz, 1H), 2.93 – 2.72 (m, 2H), 2.02 (q, $J =$

7.0 Hz, 2H), 1.38 – 1.17 (m, 8H), 0.86 (t, $J = 6.7$ Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 196.2, 195.1, 136.3, 135.6, 135.5, 134.8, 132.7, 132.1, 131.3, 129.3, 128.9, 128.8, 128.8, 127.6, 12.6, 6.4, 123.2, 70.8, 42.8, 42.4, 32.6, 31.7, 29.1, 28.8, 22.6, 14.1. **IR** (KBr) γ 2957, 2924, 2853, 1720, 1597, 1511, 1484, 1445, 1314, 1251, 1155, 1095, 1027, 988, 800, 770, 753, 685 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₇H₃₁BrNOS]⁺ requires 496.1304, found 496.1320. The absolute configuration was assigned tentatively by analogy.

(R)-5-(3-bromobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ma)

Colorless oil. Yield: 89 %, 44.2 mg; l/b: 15:1. Enantiomeric excess: 89%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 99/1, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 54.043 min (minor), t_R = 56.947 min (major). $[\alpha]_D^{20} = -9.3$ (c 0.46, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.08 – 7.96 (m, 2H), 7.67 – 7.59 (m, 1H), 7.51 – 7.43 (m, 2H), 7.38 (t, $J = 1.7$ Hz, 1H), 7.34 – 7.29 (m, 1H), 7.16 (dd, $J = 6.4, 1.3$ Hz, 1H), 7.10 (dd, $J = 9.6, 5.8$ Hz, 1H), 6.12 (dt, $J = 21.0, 10.5$ Hz, 1H), 5.90 (dt, $J = 18.3, 9.2$ Hz, 1H), 5.71 – 5.56 (m, 1H), 5.41 (dt, $J = 14.9, 7.4$ Hz, 1H), 3.29 (d, $J = 13.8$ Hz, 1H), 3.19 (d, $J = 13.8$ Hz, 1H), 2.81 (dd, $J = 14.2, 7.1$ Hz, 1H), 2.71 (dd, $J = 14.2, 7.8$ Hz, 1H), 2.01 (q, $J = 7.0$ Hz, 2H), 1.29 (ddd, $J = 22.6, 10.6, 3.8$ Hz, 8H), 0.90 – 0.80 (m, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.1, 194.4, 137.6, 136.3, 135.6, 135.0, 133.4, 132.1, 130.5, 129.8, 129.2, 128.9, 128.8, 123.0, 122.1, 70.5, 43.6, 41.9, 32.5, 31.6, 29.1, 28.8, 22.5, 14.0. **IR** (KBr) γ 3465, 3018, 2956, 2923, 2852, 1719, 1511, 1484, 1446, 1260, 1164, 989, 796 771, 685 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₇H₃₁BrNOS]⁺ requires 496.1304, found 496.1316. The absolute configuration was assigned tentatively by analogy.

(R)-5-(4-bromobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3na)

Colorless oil. Yield: 92 %, 45.5 mg; l/b: 20:1. Enantiomeric excess: 91%, determined by HPLC (CHIRALPAK IC, hexane/alcohol = 97/3, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 13.261 min (minor), t_R = 14.027 min (major). $[\alpha]_D^{20} = -22.6$ (c 0.75, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.04 – 7.98 (m, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.8$ Hz, 2H), 7.34 (d, $J = 8.3$ Hz, 2H), 7.09 (d, $J = 8.3$ Hz, 2H), 6.13 (dd, $J = 15.0, 10.4$ Hz, 1H), 5.91 (dd, $J = 15.1, 10.4$ Hz, 1H), 5.69 – 5.58 (m, 1H), 5.42 (dt, $J = 14.9, 7.4$ Hz, 1H), 3.28 (d, $J = 13.9$ Hz, 1H), 3.17 (d, $J = 13.9$ Hz, 1H), 2.80 (dd, $J = 14.1, 7.0$ Hz, 1H), 2.72 (dd, $J = 14.1, 7.8$ Hz, 1H), 2.01 (q, $J = 7.0$ Hz, 1H), 1.41 – 1.11 (m, 8H), 0.86 (t, $J = 6.7$ Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 194.1, 193.4, 135.2, 134.6, 133.9, 133.2, 131.0, 130.3, 128.2, 127.9, 127.8, 122.0, 120.4, 69.5, 42.3, 41.1, 31.5, 30.6, 28.0, 27.8, 21.5, 13.0. **IR** (KBr) γ 2956, 2925, 2853, 1719, 1512, 1485, 1446, 1260, 1249, 1165, 1073, 1027, 1012, 988, 800, 685 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₇H₃₁BrNOS]⁺ requires 496.1304, found 496.1306. The absolute configuration was assigned tentatively by analogy.

(S)-5-methyl-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3oa)

Colorless oil. 94 %, 32.1 mg; l/b: 30:1. Enantiomeric excess: 83%, determined by HPLC (CHIRALPAK ID, hexane/isopropanol = 99/1, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 27.172 min (major), t_R = 30.835 min (minor). $[\alpha]_D^{20} = -65.2$ (c 0.30, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.13 (d, $J = 7.4$ Hz, 2H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.52 (t, $J = 7.8$ Hz, 2H), 6.14 (dd, $J = 14.8, 10.3$ Hz, 1H), 5.94 (dd, $J = 15.0, 10.7$ Hz, 1H), 5.70 – 5.58 (m, 1H), 5.46 (dt, $J = 14.9, 7.4$ Hz, 1H), 2.68 (d, $J = 7.6$ Hz, 2H), 2.03 (q, $J = 7.1$ Hz, 2H), 1.69 (s, 3H), 1.35 – 1.16 (m, 8H), 0.87 (t, $J = 6.7$ Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.5, 194.9, 135.9, 135.5, 134.9, 132.3, 129.3, 129.0, 128.8, 123.9, 64.9, 42.9, 32.6, 31.7, 29.1, 28.9, 25.1, 22.6, 14.1. **IR**: γ 2960, 2925, 2854, 1515, 1261, 1089, 801 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₁H₂₈NOS]⁺ requires 342.1886, found 342.1892. The absolute configuration was assigned tentatively by analogy.

4-(((R)-5-((2E, 4E)-hexa-2, 4-dien-1-yl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3db)

Colorless oil. Yield: 95 %, 35.4 mg; l/b: 20:1. Enantiomeric excess: 92%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 19.626 min (major), t_R = 23.835 min (minor). $[\alpha]_D^{20} = -21.6$ (c 0.32, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.98 (d, $J = 7.5$ Hz, 2H), 7.64 (t, $J = 7.4$ Hz, 1H), 7.48 (dd, $J = 17.7, 8.0$ Hz, 4H), 7.32 (d, $J = 8.1$ Hz, 2H), 6.16 (dd, $J = 14.9, 10.4$ Hz, 1H), 5.93 (dd, $J = 26.2, 15.2$ Hz, 1H), 5.67 (dq, $J = 13.6, 6.7$ Hz, 1H), 5.45 (tt, $J = 14.9, 7.4$ Hz, 1H), 3.46 – 3.34 (m, 1H), 3.27 (t, $J = 13.7$ Hz, 1H), 2.79 (qd, $J = 14.1, 7.5$ Hz, 2H), 1.68 (t, $J = 17.6$ Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 195.1, 194.1, 140.7, 136.4, 135.2, 131.9, 131.8, 131.2, 130.6, 130.3, 129.0, 128.8, 122.6, 118.6, 111.3, 70.2, 43.7, 42.4, 18.0. **IR** (KBr) γ 3465, 2924, 2853, 2228, 1719, 1597, 1510, 1484, 1445, 1261, 1167, 1097, 1025, 800, 685 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₃H₂₁N₂OS]⁺ requires 373.1369, found 373.1374. The absolute configuration was assigned tentatively by analogy.

4-(((R)-5-((2E, 4E)-octa-2, 4-dien-1-yl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3dc)

Colorless oil. Yield: 91 %, 36.4 mg; l/b: 23:1. Enantiomeric excess: 91%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 17.887 min (major), t_R = 21.645 min (minor). [α]_D²⁰ = -30.4 (c 0.38, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.01 – 7.94 (m, 2H), 7.66 – 7.59 (m, 1H), 7.53 – 7.42 (m, 4H), 7.31 (d, J = 8.4 Hz, 2H), 6.15 (dt, J = 18.5, 9.3 Hz, 1H), 5.93 (dd, J = 15.1, 10.4 Hz, 1H), 5.70 – 5.60 (m, 1H), 5.43 (dq, J = 14.5, 7.2 Hz, 1H), 3.40 (d, J = 13.7 Hz, 1H), 3.27 (t, J = 13.4 Hz, 1H), 2.79 (qd, J = 14.1, 7.4 Hz, 2H), 2.01 (q, J = 7.2 Hz, 2H), 1.45 – 1.30 (m, 2H), 0.86 (t, J = 7.4 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.1, 194.1, 140.7, 136.5, 135.7, 135.2, 131.9, 131.8, 131.1, 129.3, 129.0, 128.8, 122.8, 118.6, 111.3, 70.2, 43.6, 42.4, 34.6, 22.3, 13.7. **IR** (KBr) γ 3018, 2960, 2926, 2870, 2228, 1716, 1597, 1510, 1484, 1445, 1315, 1261, 1167, 1096, 1025, 990, 802, 772, 686 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₅H₂₅N₂OS]⁺ requires 401.1682, found 401.1686. The absolute configuration was assigned tentatively by analogy.

4-(((R)-4-oxo-2-phenyl-5-((2E, 4E)-tetradeca-2, 4-dien-1-yl)-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3dd)

Colorless oil. Yield: 90 %, 43.6 mg; l/b: 38:1. Enantiomeric excess: 93%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 14.042 min (major), t_R = 16.300 min (minor). [α]_D²⁰ = -20.3 (c 0.26, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.98 (d, J = 7.6 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.47 (dd, J = 17.6, 8.0 Hz, 4H), 7.32 (d, J = 8.1 Hz, 2H), 6.16 (dd, J = 15.0, 10.4 Hz, 1H), 5.93 (dd, J = 15.0, 10.4 Hz, 1H), 5.71 – 5.60 (m, 1H), 5.44 (dt, J = 14.9, 7.4 Hz, 1H), 3.40 (d, J = 13.7 Hz, 1H), 3.26 (d, J = 13.7 Hz, 1H), 2.79 (qd, J = 14.1, 7.5 Hz, 2H), 2.02 (q, J = 7.1 Hz, 2H), 1.38 – 1.14 (m, 14H), 0.87 (t, J = 6.7 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.0, 194.1, 140.6, 136.6, 136.0, 135.2, 131.9, 131.8, 131.2, 129.1, 129.0, 128.8, 122.8, 118.6, 111.3, 70.3, 43.6, 42.4, 32.6, 31.9, 29.5, 29.4, 29.3, 29.2, 29.1, 22.6, 14.1. **IR** (KBr) γ 3442, 2960, 2925, 2853, 2228, 1719, 1597, 1511, 1484, 1446, 1315, 1261, 1154, 1097, 1025, 990, 801, 773, 686 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₃₁H₃₇N₂OS]⁺ requires 485.2621, found 485.2622. The absolute configuration was assigned tentatively by analogy.

4-(((R)-4-oxo-2-phenyl-5-((2E, 4E)-5-(p-tolyl) penta-2, 4-dien-1-yl)-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3de)

Colorless oil. Yield: 91 %, 42.1 mg; l/b: 20:1. Enantiomeric excess: 93%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 23.393 min (major), t_R = 28.100 min (minor). [α]_D²⁰ = -23.8 (c 0.73, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.03 – 7.95 (m, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.49 (dd, J = 16.2, 7.9 Hz, 4H), 7.33 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 4.4 Hz, 1H), 7.24 (s, 1H), 7.16 (t, J = 8.6 Hz, 3H), 7.16 (t, J = 8.6 Hz, 1H), 6.17 (dd, J = 14.9, 10.4 Hz, 1H), 5.96 (dt, J = 22.9, 11.5 Hz, 1H), 5.76 – 5.65 (m, 1H), 5.46 (dt, J = 14.8, 7.4 Hz, 1H), 3.41 (d, J = 13.7 Hz, 1H), 3.26 (d, J = 13.7 Hz, 1H), 2.80 (ddd, J = 32.6, 14.1, 7.4 Hz, 2H), 2.67 (t, J = 7.8 Hz, 2H), 2.36 (dd, J = 15.0, 7.2 Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.1, 194.1, 141.6, 140.6, 136.3, 135.3, 134.5, 131.9, 131.8, 131.2, 129.8, 129.0, 128.8, 128.4, 128.3, 125.9, 123.4, 118.6, 111.4, 70.2, 43.7, 42.4, 35.5, 34.4. **IR** (KBr) γ 3023, 2924, 2853, 2228, 1716, 1510, 1484, 1445, 1414, 1251, 1156, 1027, 991, 699, 686 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₃₀H₂₇N₂OS]⁺ requires 463.1839, found 463.1846. The absolute configuration was assigned tentatively by analogy.

4-(((R)-5-((2E, 4E)-8-chloroocta-2, 4-dien-1-yl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3df)

Colorless oil. Yield: 81 %, 35.2 mg; l/b: 21:1. Enantiomeric excess: 89%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 29.384 min (major), t_R = 34.417 min (minor). [α]_D²⁰ =

-17.7 (c 0.28, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.01 – 7.94 (m, 2H), 7.69 – 7.61 (m, 1H), 7.53 – 7.42 (m, 4H), 7.32 (d, *J* = 8.3 Hz, 2H), 6.16 (dd, *J* = 15.0, 10.4 Hz, 1H), 5.98 (dd, *J* = 15.1, 10.5 Hz, 1H), 5.66 – 5.56 (m, 1H), 5.47 (dt, *J* = 14.9, 7.4 Hz, 1H), 3.49 (t, *J* = 6.6 Hz, 2H), 3.40 (d, *J* = 13.7 Hz, 1H), 3.26 (d, *J* = 13.7 Hz, 1H), 2.79 (ddd, *J* = 32.3, 14.2, 7.5 Hz, 2H), 2.19 (dd, *J* = 14.5, 7.5 Hz, 2H), 1.87 – 1.78 (m, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 194.0, 193.0, 139.6, 135.0, 134.2, 132.2, 130.9, 130.8, 130.1, 129.5, 128.0, 127.8, 122.8, 117.5, 110.3, 69.1, 43.2, 42.7, 41.3, 30.8, 28.5. **IR** (KBr) γ 2960, 2924, 2853, 2228, 1713, 1658, 1608, 1597, 1505, 1483, 1445, 1414, 1310, 1260, 1154, 1097, 1074, 1025, 801, 772, 685 cm⁻¹. **HRMS** (ESI): *m/z* [M + H]⁺ calcd for [C₂₅H₂₄ClN₂OS]⁺ requires 435.1292, found 435.1294. The absolute configuration was assigned tentatively by analogy.

4-(((R)-5-((2E, 4E)-hexa-2, 4-dien-1-yl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3dg)

Colorless oil. Yield: 94 %, 35.0 mg; l/b: 34:1. Enantiomeric excess: 83%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t_R* = 19.351 min (major), *t_R* = 23.854 min (minor). [α]_D²⁰ = -28.3 (c 0.55, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.98 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.47 (dd, *J* = 17.7, 8.0 Hz, 4H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.15 (dd, *J* = 14.9, 10.4 Hz, 1H), 6.00 – 5.90 (m, 1H), 5.66 (dq, *J* = 13.6, 6.7 Hz, 1H), 5.42 (dt, *J* = 14.9, 7.4 Hz, 1H), 3.40 (d, *J* = 13.7 Hz, 1H), 3.25 (d, *J* = 13.7 Hz, 1H), 2.78 (qd, *J* = 14.1, 7.5 Hz, 2H), 1.71 (d, *J* = 6.7 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.0, 194.1, 140.7, 136.4, 135.2, 131.9, 131.8, 131.2, 130.6, 130.3, 129.0, 128.8, 122.6, 118.6, 111.3, 70.2, 43.7, 42.4, 18.0. **IR** (KBr) γ 2924, 2851, 2228, 1719, 1597, 1510, 1484, 1446, 1315, 1250, 1166, 1097, 1026, 990, 801, 757, 685 cm⁻¹. **HRMS** (ESI): *m/z* [M + H]⁺ calcd for [C₂₃H₂₁N₂OS]⁺ requires 373.1369, found 373.1374. The absolute configuration was assigned tentatively by analogy.

4-(((R)-4-oxo-2-phenyl-5-((2E, 4E)-5-phenylpenta-2, 4-dien-1-yl)-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3dh)

Colorless oil. Yield: 81 %, 35.2 mg; l/b: 24:1. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t_R* = 29.282 min (major), *t_R* = 32.718 min (minor). [α]_D²⁰ = -36.3 (c 0.39, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.01 – 7.94 (m, 2H), 7.67 – 7.60 (m, 1H), 7.54 – 7.49 (m, 2H), 7.49 – 7.43 (m, 2H), 7.37 – 7.31 (m, 4H), 7.31 – 7.26 (m, 2H), 7.24 – 7.17 (m, 1H), 6.66 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.50 (d, *J* = 15.7 Hz, 1H), 6.36 (dd, *J* = 14.9, 10.4 Hz, 1H), 5.68 (dt, *J* = 15.0, 7.5 Hz, 1H), 3.44 (d, *J* = 13.7 Hz, 1H), 3.29 (d, *J* = 13.7 Hz, 1H), 2.93 (dd, *J* = 14.7, 7.1 Hz, 1H), 2.84 (dd, *J* = 14.3, 8.1 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.1, 194.0, 140.5, 136.9, 136.4, 135.3, 133.0, 132.0, 131.8, 131.2, 129.0, 128.8, 128.6, 127.9, 127.7, 126.4, 126.0, 118.6, 111.4, 70.1, 43.8, 42.5. **IR** (KBr) γ 2960, 2924, 2853, 2228, 1713, 1658, 1608, 1597, 1505, 1483, 1445, 1414, 1310, 1260, 1154, 1097, 1074, 1025, 801, 772, 685 cm⁻¹. **HRMS** (ESI): *m/z* [M + H]⁺ calcd for [C₂₈H₂₃N₂OS]⁺ requires 435.1526, found 435.1535. The absolute configuration was assigned tentatively by analogy.

4-(((R)-4-oxo-2-phenyl-5-((2E, 4E)-5-(p-tolyl) penta-2, 4-dien-1-yl)-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3di)

Colorless oil. Yield: 54 %, 24.2 mg; l/b: 22:1. Enantiomeric excess: 91%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): *t_R* = 28.446 min (major), *t_R* = 34.048 min (minor). [α]_D²⁰ = -39.4 (c 0.28, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.62 (dd, *J* = 15.6, 10.3 Hz, 1H), 6.48 (d, *J* = 15.6 Hz, 1H), 6.35 (dd, *J* = 14.9, 10.4 Hz, 1H), 5.66 (dt, *J* = 15.0, 7.5 Hz, 1H), 3.44 (d, *J* = 13.7 Hz, 1H), 3.29 (d, *J* = 13.7 Hz, 1H), 2.88 (ddd, *J* = 35.6, 14.1, 7.6 Hz, 2H), 2.32 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.1, 194.0, 140.6, 137.6, 136.6, 135.3, 134.1, 133.0, 132.0, 131.8, 131.2, 129.3, 129.0, 128.8, 126.9, 126.3, 125.4, 118.6, 111.4, 70.1, 43.8, 42.5, 21.2. **IR** (KBr) γ 3021, 2962, 2924, 2854, 2228, 1716, 1608, 1597, 1510, 1484, 1445, 1414, 1315, 1261, 1166, 1022, 939, 851, 801, 758, 686 cm⁻¹. **HRMS** (ESI): *m/z* [M + H]⁺ calcd for [C₂₉H₂₅N₂OS]⁺ requires 449.1682, found 449.1686. The absolute configuration was assigned tentatively by analogy.

4-(((R)-5-((2E, 4E)-5-(4-methoxyphenyl) penta-2, 4-dien-1-yl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl)

benzonitrile (3dj)

Colorless oil. Yield: 50 %, 23.2 mg; l/b: 17:1. Enantiomeric excess: 92%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 54.883min (major), t_R = 63.218 min (minor). $[\alpha]_D^{20}$ = -33.5 (c 0.16, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.03 – 7.95 (m, 2H), 7.68 – 7.60 (m, 1H), 7.55 – 7.42 (m, 4H), 7.35 (t, J = 10.2 Hz, 2H), 7.30 – 7.27 (m, 2H), 6.88 – 6.76 (m, 2H), 6.51 (dt, J = 31.7, 12.8 Hz, 2H), 6.39 – 6.22 (m, 1H), 5.63 (dt, J = 15.0, 7.5 Hz, 1H), 3.79 (s, 3H), 3.43 (dd, J = 13.7, 5.1 Hz, 1H), 3.33 – 3.25 (m, 1H), 3.04 – 2.67 (m, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.1, 194.1, 159.4, 140.6, 136.7, 135.3, 132.5, 132.0, 131.8, 131.2, 129.7, 129.0, 128.8, 127.6, 125.9, 124.8, 118.6, 114.1, 111.4, 70.2, 55.3, 43.8, 42.5. **IR** (KBr) γ 3462, 2959, 2923, 2854, 1715, 1602, 1510, 1484, 1467, 1445, 1258, 1173, 1097, 1028, 803, 759, 686 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₉H₂₅N₂O₂S]⁺ requires 465.1631, found 465.1638. The absolute configuration was assigned tentatively by analogy.

4-(((R)-5-((2E, 4E)-5-(3-chlorophenyl) penta-2, 4-dien-1-yl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3dk)

Colorless oil. Yield: 86 %, 40.3 mg; l/b: 40:1. Enantiomeric excess: 93%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 72.866min (major), t_R = 80.912 min (minor). $[\alpha]_D^{20}$ = -29.8 (c 0.31, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.04 – 7.95 (m, 2H), 7.64 (t, J = 7.5 Hz, 1H), 7.56 – 7.43 (m, 2H), 7.33 (d, J = 8.3 Hz, 2H), 7.22 – 7.13 (m, 3H), 6.65 (dd, J = 15.6, 10.5 Hz, 3H), 6.42 (d, J = 15.6 Hz, 1H), 6.34 (dd, J = 14.9, 10.5 Hz, 1H), 5.71 (dt, J = 14.9, 7.5 Hz, 1H), 3.44 (d, J = 13.7 Hz, 1H), 3.28 (d, J = 13.7 Hz, 1H), 2.89 (ddd, J = 41.4, 14.1, 7.5 Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.0, 193.9, 140.5, 138.8, 136.0, 135.4, 134.6, 132.0, 131.7, 131.4, 131.2, 129.8, 129.3, 129.0, 128.9, 127.5, 127.2, 126.1, 124.6, 118.5, 111.4, 70.0, 43.9, 42.3. **IR** (KBr) γ 3018, 2961, 2925, 2854, 1713, 1608, 1504, 1483, 1482, 1445, 1415, 1260, 1094, 1022, 850, 799, 683, 667 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₈H₂₂ClN₂OS]⁺ requires 469.1136, found 469.1139. The absolute configuration was assigned tentatively by analogy.

(R, E)-4-((4-oxo-5-(penta-2, 4-dien-1-yl)-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzo-nitrile (3dl)

Colorless oil. Yield: 73 %, 26.1 mg; E/Z: 5:1. Enantiomeric excess: 84%/70%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): $t_{R,E}$ = 39.786 min (major), $t_{R,Z}$ = 41.761 min (major), $t_{R,E}$ = 48.924 min (minor), $t_{R,Z}$ = 51.992 min (minor). $[\alpha]_D^{20}$ = -22.4 (c 0.23, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.98 (d, J = 7.4 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.54 – 7.43 (m, 4H), 7.32 (d, J = 8.1 Hz, 2H), 6.60 (dt, J = 16.6, 10.6 Hz, 1H), 6.31 – 6.11 (m, 1H), 5.57 (td, J = 14.5, 7.4 Hz, 1H), 5.37 (dd, J = 18.4, 8.0 Hz, 1H), 5.25 (d, J = 5.5 Hz, 1H), 5.23 – 5.13 (m, 1H), 5.06 (d, J = 9.5 Hz, 1H), 3.43 (dd, J = 13.7, 8.3 Hz, 1H), 3.28 (t, J = 12.3 Hz, 1H), 2.94 (t, J = 6.7 Hz, 1H), 2.86 (dd, J = 14.1, 6.9 Hz, 1H), 2.78 (dd, J = 14.1, 7.9 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.0, 194.0, 140.5, 136.8, 136.0, 135.3, 134.3, 131.9, 131.8, 131.3, 131.2, 129.0, 128.8, 126.1, 123.6, 119.9, 118.6, 117.9, 111.4, 69.9, 43.8, 43.7, 42.2, 37.1. **IR** (KBr) γ 3436, 3013, 2961, 2924, 2854, 2228, 1715, 1597, 1505, 1483, 1445, 1414, 1314, 1260, 1153, 1097, 1022, 801, 773, 685 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₂H₁₉N₂O₂S]⁺ requires 359.1213, found 359.1219. The absolute configuration was assigned tentatively by analogy.

Ethyl (4E, 6E)-8-((R)-5-(4-cyanobenzyl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl)octa-4,6-dienoate (3dm)

Colorless oil. Yield: 91 %, 41.7 mg; l/b: 11:1. Enantiomeric excess: 84%, determined by HPLC (CHIRALPAK AD, hexane/isopropanol = 70/30, flow rate 1 mL/min, T = 30 °C, 254 nm): t_R = 12.533 min (major), t_R = 14.512 min (minor). $[\alpha]_D^{20}$ = -17.1 (c 0.69, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.97 (dd, J = 8.3, 1.1 Hz, 2H), 7.71 – 7.61 (m, 1H), 7.53 – 7.38 (m, 4H), 7.31 (d, J = 8.3 Hz, 2H), 6.12 (dt, J = 21.9, 10.9 Hz, 1H), 5.94 (dt, J = 19.0, 9.5 Hz, 1H), 5.69 – 5.57 (m, 1H), 5.45 (dt, J = 14.9, 7.4 Hz, 1H), 4.09 (p, J = 7.1 Hz, 2H), 3.45 – 3.35 (m, 1H), 3.28 – 3.16 (m, 1H), 2.82 (dd, J = 14.2, 7.1 Hz, 1H), 2.74 (dd, J = 14.2, 7.8 Hz, 1H), 2.34 (d, J = 2.9 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.0, 194.0, 172.8, 140.6, 136.0, 135.3, 132.9, 131.9, 131.8, 131.1, 130.3, 129.0, 128.8, 123.9, 118.6, 111.3, 70.1, 60.3, 43.7, 42.3, 33.7, 27.8, 14.2. **IR** (KBr) γ 2979, 2924, 2228, 1720, 1597, 1509, 1484, 1445, 1415, 1372, 1311, 1250, 1165, 1097, 1027, 992, 939, 803, 772, 758, 687 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₇H₂₇N₂O₂S]⁺ requires 459.1742, found 459.1741. The absolute configuration was assigned tentatively by analogy.

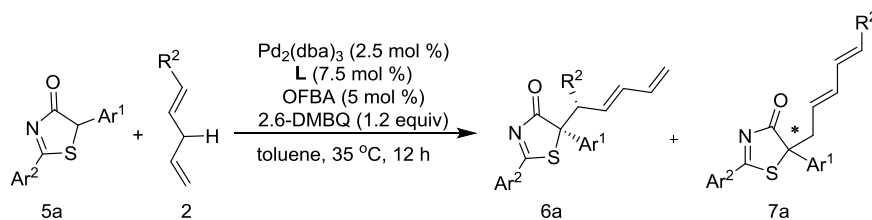
(4E, 6E)-N-benzyl-8-((R)-5-(4-cyanobenzyl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) octa-4,6-dienamide (3dn)

Colorless oil. Yield: 79 %, 41.0 mg; l/b: 11:1. Enantiomeric excess: 83%, determined by HPLC (CHIRALPAK AD, hexane/isopropanol = 70/30, flow rate 0.5 mL/min, T = 30 °C, 254 nm): t_R = 33.442 min (major), t_R = 44.467 min (minor). $[\alpha]_D^{20}$ = -3.9 (c 0.63, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.88 (ddd, J = 6.8, 5.6, 1.2 Hz, 2H), 7.56 (ddd, J = 8.6, 2.3, 1.2 Hz, 1H), 7.39 (ddd, J = 10.6, 6.5, 4.8 Hz, 4H), 7.26 – 7.20 (m, 4H), 7.19 – 7.12 (m, 3H), 6.06 (dd, J = 15.0, 10.4 Hz, 1H), 5.89 (dd, J = 15.1, 10.4 Hz, 1H), 5.78 (t, J = 5.1 Hz, 1H), 5.62 – 5.51 (m, 1H), 5.44 – 5.31 (m, 1H), 4.35 – 4.27 (m, 2H), 3.33 (dd, J = 13.7, 6.6 Hz, 1H), 3.18 (dd, J = 13.7, 6.5 Hz, 1H), 2.75 (dd, J = 14.2, 7.0 Hz, 1H), 2.68 (dd, J = 14.2, 7.8 Hz, 1H), 2.33 (h, J = 8.2 Hz, 2H), 2.18 (t, J = 7.3 Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.1, 194.0, 171.9, 140.6, 138.2, 136.0, 135.3, 133.2, 131.9, 131.7, 131.1, 130.4, 129.0, 128.8, 128.7, 127.8, 127.5, 124.0, 118.6, 111.3, 70.1, 43.7, 43.5, 42.3, 35.9, 28.5. **IR** (KBr) γ 3311, 2921, 2228, 1716, 1650, 1597, 1509, 1483, 1445, 1314, 1250, 1165, 991, 850, 823, 798, 773, 737, 700, 686, 668, 631, 572, 496 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₃₂H₃₀N₃O₂S]⁺ requires 520.2059, found 520.2056. The absolute configuration was assigned tentatively by analogy.

(4E, 6E)-8-((R)-5-(4-cyanobenzyl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) octa-4,6-dien-1-yl 4-methylbenzene sulfonate (3do)

Colorless oil. Yield: 92 %, 52.4 mg; l/b: 17:1. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK AD, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 40.762 min (major), t_R = 49.287 min (minor). $[\alpha]_D^{20}$ = -18.6 (c 0.77, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.08 – 7.90 (m, 2H), 7.83 – 7.72 (m, 2H), 7.69 – 7.58 (m, 1H), 7.55 – 7.41 (m, 4H), 7.37 – 7.31 (m, 4H), 6.10 (dt, J = 22.4, 11.2 Hz, 1H), 5.86 (dd, J = 15.1, 10.4 Hz, 1H), 5.62 – 5.47 (m, 1H), 5.42 (dd, J = 15.0, 7.4 Hz, 1H), 4.01 (dt, J = 19.5, 6.3 Hz, 2H), 3.47 – 3.36 (m, 1H), 3.27 (dd, J = 18.7, 10.7 Hz, 1H), 2.83 (dd, J = 14.2, 7.1 Hz, 1H), 2.75 (dd, J = 14.3, 7.8 Hz, 1H), 2.44 (s, 3H), 2.10 (dt, J = 13.5, 5.0 Hz, 2H), 1.81 – 1.58 (m, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 195.1, 194.0, 144.7, 140.6, 135.9, 135.3, 133.1, 132.8, 131.9, 131.8, 131.2, 130.6, 129.8, 129.0, 128.8, 127.8, 123.9, 118.6, 111.3, 70.1, 69.7, 43.7, 42.3, 28.2, 28.2, 21.6. **IR** (KBr) γ 2961, 2924, 2228, 1716, 1597, 1509, 1484, 1445, 1358, 1309, 1261, 1188, 1175, 1097, 1020, 993, 962, 925, 815, 773, 738, 687, 664, 574, 555 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₃₂H₃₁N₂O₄S₂]⁺ requires 571.1725, found 571.1727. The absolute configuration was assigned tentatively by analogy.

Table S2. Re-optimization of the Allylic C-H Alkylation Reaction of 1, 4- Pentadiene 2a with 2,5-diphenylthiazol-4(5H)-ones 6a



entry	[Pd]	L	OFBA	dr ^c	yield (%) ^b	6a/7a ^c	ee (%) ^d
1	Pd ₂ (dba) ₃	PPh ₃	5%	-	trace	-	-
2	Pd ₂ (dba) ₃	L7	5%	-	trace	-	-
3	Pd ₂ (dba) ₃	L6	5%	-	n.r	-	-
4	Pd ₂ (dba) ₃	L5	5%	6:1	60	6:1	0
5	Pd ₂ (dba) ₃	L2	5%	5:1	88	8:1	41
6	Pd ₂ (dba) ₃	L1	5%	3.6:1	91	10:1	84
7	Pd ₂ (dba) ₃	L1	none	-	n.r	-	-
8	Pd ₂ (dba) ₃	L1	10%	-	trace	-	-
9 ^e	Pd ₂ (dba) ₃	L1	5%	2.6:1	88	8:1	73
10 ^{e,f}	Pd ₂ (dba) ₃	L1	5%	3.7:1	92	13:1	87
11 ^f	Pd ₂ (dba) ₃	L1	5%	4.5:1	90	11:1	87

^aReaction conditions: Unless indicated otherwise, reactions of **1a** (0.10 mmol), **2a** (0.20 mmol), Pd (0.005 mmol), ligand (0.0075 mmol), OFBA (0.005 mmol), and 2,6-DMBQ (0.12 mmol) were carried out in toluene (2 mL) for 16 h. ^bIsolated yields of **6** with the ratios of E/Z >20:1. ^cThe dr and ratios of **6/7** were determined by ¹H NMR analysis of the crude reaction mixture. ^dThe ee value was determined by chiral HPLC analysis. ^e2,5-DMBQ (0.12 mmol) was used instead of 2,6-DMBQ. ^fThe reaction was carried out at 25 °C. 2,5(6)-DMBQ = 2,5(6)-dimethylquinone, OFBA = 2-fluorobenzoic acid, dba = dibenzylidene acetone.

General experimental procedures for the control experiment of 1,4-pentadienes with 2,5-diarylthiazol-4(5H)-ones

To a flame-dried and Ar-purged Schlenk tube (10 mL) were added 2,5-diarylthiazol-4(5H)-ones (0.10 mmol), Pd₂(dba)₃ (0.0025 mmol), phosphoramidite **L1** (0.0075 mmol), OFBA (0.005 mmol), 2,6-DMBQ (0.12 mmol) and a stirring bar. The schlenk tube was then evacuated and filled with argon. This cycle was repeated three times and followed by the addition of toluene (2 mL) and 1, 4-pentadienes (0.20 mmol) via a syringe. The mixture was stirred at 25 °C for 16 h. The reaction mixture was purified by column chromatography on silica gel (petroleum/ethyl acetate = 20/1) to provide product **6**.

(S)-5-((R, E)-hexa-3, 5-dien-2-yl)-2, 5-diphenylthiazol-4(5H)-one (6aa)

Colorless oil. Yield: 90 %, 30.0 mg; diastereomeric ratio: 5:1. Enantiomeric excess: 87%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 19.443 min (minor), t_R = 21.758 min (major). [α]_D²⁰ = 164.9 (c 0.28, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.22 – 8.15 (m, 2H), 7.79 – 7.76 (m, 2H), 7.71 – 7.64 (m, 2H), 7.57 – 7.50 (m, 2H), 7.42 – 7.28 (m, 4H), 6.28 – 6.10 (m, 2H), 5.67 – 5.58 (m, 1H), 5.17 – 5.08 (m, 1H), 5.02 – 4.96 (m, 1H), 3.48 (p, J = 7.1 Hz, 1H), 1.08 (t, J = 5.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 194.1, 192.6, 137.2, 136.5, 135.0, 134.4, 132.6, 132.1, 129.0, 128.8, 128.6, 128.3, 127.5, 117.3, 78.0, 46.5, 17.6. IR (KBr) γ 2963, 2925, 2854, 1719, 1596, 1517, 1486, 1446, 1376, 1250, 1153, 1098, 1027, 1003, 946, 908, 801, 773, 686 cm⁻¹. HRMS (ESI): m/z [M + H]⁺ calcd for [C₂₁H₂₀NOS]⁺ requires 334.1266, found 334.1260. The absolute configuration was assigned tentatively by analogy.

(S)-5-((R, E)-hexa-3, 5-dien-2-yl)-5-phenyl-2-(m-tolyl) thiazol-4(5H)-one (6ba)

Colorless oil. Yield: 70 %, 24.3 mg; diastereomeric ratio: 6:1. 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 = 22.936 min (minor), t_R = 33.535 min (major). $[\alpha]_D^{20}$ = 112.5 (c 0.46, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.02 (d, J = 7.9 Hz, 1H), 7.97 (d, J = 7.7 Hz, 1H), 7.78 – 7.73 (m, 2H), 7.52 – 7.46 (m, 1H), 7.41 (dd, J = 7.2, 5.3 Hz, 1H), 7.35 (dd, J = 6.2, 1.6 Hz, 2H), 7.33 – 7.30 (m, 1H), 6.34 – 6.09 (m, 2H), 5.77 – 5.57 (m, 1H), 5.22 – 5.09 (m, 1H), 4.98 (dt, J = 10.5, 4.5 Hz, 1H), 3.48 (p, J = 7.3 Hz, 1H), 2.44 (s, 3H), 1.06 (dd, J = 11.4, 6.7 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 194.3, 192.6, 139.0, 137.3, 136.6, 135.9, 134.3, 132.7, 132.1, 129.4, 128.9, 128.6, 128.5, 128.3, 127.6, 127.5, 126.0, 117.3, 77.8, 46.5, 21.2, 17.6. **IR** (KBr) γ 2910, 1572, 1491, 1456, 1405, 1345, 1215, 1061, 784, 756, 683 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₂H₂₂NOS]⁺ requires 348.1422, found 348.1425. The absolute configuration was assigned tentatively by analogy.

(S)-2-(4-bromophenyl)-5-((R, E)-hexa-3, 5-dien-2-yl)-5-phenylthiazol-4(5H)-one (6ca)

Colorless oil. Yield: 87 %, 35.8 mg; diastereomeric ratio: 4:1. Enantiomeric excess: 88%, determined by HPLC (CHIRALPAK IE, hexane/EtOH = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 16.621 min (minor), t_R = 17.829 min (major). $[\alpha]_D^{20}$ = 153.5 (c 0.24, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.08 – 7.98 (m, 2H), 7.76 – 7.73 (m, 1H), 7.70 – 7.64 (m, 2H), 7.39 – 7.28 (m, 3H), 6.26 – 6.09 (m, 2H), 5.68 – 5.52 (m, 1H), 5.18 – 5.10 (m, 1H), 4.99 (dt, J = 9.3, 4.6 Hz, 1H), 3.52 – 3.33 (m, 1H), 1.06 (dd, J = 11.3, 6.7 Hz, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 192.9, 192.4, 136.9, 136.4, 134.5, 132.4, 130.9, 130.3, 130.0, 128.7, 128.6, 128.4, 127.4, 117.5, 78.5, 46.6, 17.5. **IR** (KBr) γ 2965, 1572, 1557, 1489, 1409, 1388, 1048, 819, 753, 685 cm⁻¹. **HRMS** (ESI): m/z [M + H]⁺ calcd for [C₂₁H₁₉BrNOS]⁺ requires 412.0371, found 412.0367. The absolute configuration was assigned tentatively by analogy.

(S)-2-(4-fluorophenyl)-5-((R, E)-hexa-3, 5-dien-2-yl)-5-phenylthiazol-4(5H)-one (6da)

Colorless oil. Yield: 80 %, 29.9 mg; diastereomeric ratio: 5:1. Enantiomeric excess: 88%, determined by HPLC (CHIRALPAK IE, hexane/EtOH = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 14.929 min (minor), t_R = 15.846 min (major). $[\alpha]_D^{20}$ = 169.2 (c 0.36, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.26 – 8.11 (m, 2H), 7.81 – 7.74 (m, 2H), 7.42 – 7.30 (m, 3H), 7.24 – 7.11 (m, 2H), 6.33 – 6.05 (m, 2H), 5.69 – 5.54 (m, 1H), 5.26 – 5.10 (m, 1H), 4.99 (dt, J = 10.4, 4.4 Hz, 1H), 1.10 – 1.02 (m, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 192.5, 192.4, 137.0, 136.4, 134, 131.4 (d, J = 9.6 Hz), 131.4, 128.7, 128.6, 128.3, 127.5, 127.4, 117.4, 116.3 (d, J = 22.2 Hz), 78.5, 46.5, 17.5. **IR** (KBr) γ 2964, 2564, 1597, 1572, 1517, 1493, 1414, 1240, 1218, 1159, 1049, 830, 756, 686 cm⁻¹. **HRMS** (ESI): m/z [M + Na]⁺ calcd for [C₂₁H₁₉NaFNOS]⁺ requires 374.0991, found 374.0991. The absolute configuration was assigned tentatively by analogy.

(S, E)-5-(penta-2, 4-dien-1-yl)-2, 5-diphenylthiazol-4(5H)-one (6ab)

Yellow oil. Yield: 92 %, 31.4 mg; E/Z: 13:1. Enantiomeric excess: 89%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 254 nm): t_R = 19.176 min (minor), t_R = 20.432 min (major). $[\alpha]_D^{20}$ = -2.7 (c 0.55, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 8.17 (dt, J = 8.5, 1.5 Hz, 2H), 7.71 – 7.64 (m, 1H), 7.57 – 7.49 (m, 4H), 7.39 – 7.29 (m, 3H), 6.28 – 6.01 (m, 2H), 5.61 – 5.48 (m, 1H), 5.19 – 5.10 (m, 1H), 5.06 – 4.98 (m, 1H), 3.35 – 3.21 (m, 1H), 3.14 (dd, J = 14.3, 7.1 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 194.7, 192.9, 143.3, 138.0, 136.3, 136.2, 135.2, 132.1, 129.0, 128.9, 128.9, 128.3, 127.0, 117.5, 71.7, 42.9. **IR** (KBr) γ 2924, 1716, 1597, 1509, 1483, 1445, 1309, 1260, 1145, 1097, 1001, 904, 760, 685 cm⁻¹. **HRMS** (ESI): m/z [M + Na]⁺ calcd for [C₂₀H₁₇NaNOS]⁺ requires 342.0929, found 342.0925. The absolute configuration was assigned tentatively by analogy.

(S)-5-((R,E)-deca-1,3-dien-5-yl)-5-phenyl-2-(m-tolyl)thiazol-4(5H)-one(6bc)

Colorless oil. Yield: 57 %, 23.4 mg; diastereomeric ratio: 3:1. 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 = 7.870 min (minor), t_R = 9.978 min (major). $[\alpha]_D^{20}$ = 114.0 (c 0.26, CHCl₃). **¹H NMR** (400 MHz, CDCl₃) δ 7.98 (dd, J = 17.2, 9.5 Hz, 2H), 7.73 (t, J = 9.0 Hz, 2H), 7.48 (d, J = 7.6 Hz, 1H), 7.42 (dd, J = 7.6, 2.9 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.33 – 7.27 (m, 1H), 6.32 – 6.09 (m, 2H), 5.48 (dd, J = 14.8, 9.0 Hz, 1H), 5.19 –

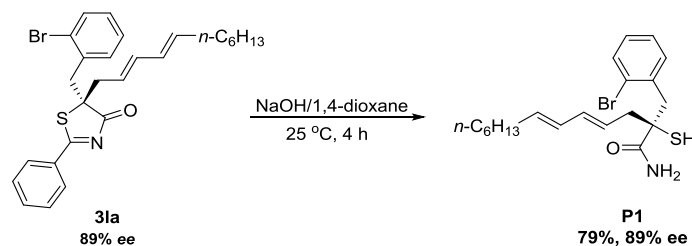
5.07 (m, 1H), 5.01 – 4.89 (m, 1H), 3.30 – 3.20 (m, 1H), 2.44 (s, 3H), 1.46 (ddd, $J = 9.2, 6.9, 3.1$ Hz, 1H), 1.35 – 1.19 (m, 3H), 1.17 – 1.06 (m, 2H), 0.78 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.1, 192.6, 139.0, 137.3, 136.4, 136.4, 135.8, 131.3, 129.3, 128.9, 128.6, 128.2, 127.4, 127.0, 126.1, 117.3, 77.5, 51.8, 31.4, 29.6, 22.2, 21.2, 13.8. **IR** (KBr) γ 2959, 2927, 1720, 1517, 1477, 1444, 1267, 1181, 1150, 1003, 796, 758, 693 cm^{-1} . **HRMS** (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{25}\text{H}_{27}\text{NNaOS}]^+$ requires 412.1711, found 412.1711. The absolute configuration was assigned tentatively by analogy.

(S)-5-((R, E)-nona-1, 3-dien-5-yl)-5-phenyl-2-(m-tolyl) thiazol-4(5H)-one (6bd)

Colorless oil. Yield: 75 %, 29.8 mg; diastereomeric ratio: 9:1. Enantiomeric excess: 91%, determined by HPLC (CHIRALPAK IE, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, $T = 30$ °C, 254 nm): $t_R = 12.092$ min (minor), $t_R = 15.939$ min (major). $[\alpha]_D^{20} = 153.0$ (c 0.34, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.98 (dd, $J = 17.2, 9.6$ Hz, 2H), 7.81 – 7.70 (m, 2H), 7.49 (d, $J = 7.6$ Hz, 1H), 7.44 – 7.41 (m, 1H), 7.39 – 7.33 (m, 2H), 7.31 (dt, $J = 5.0, 2.0$ Hz, 1H), 6.19 (ddt, $J = 20.5, 16.7, 10.4$ Hz, 2H), 5.54 – 5.42 (m, 1H), 5.19 – 5.11 (m, 1H), 4.98 (dd, $J = 9.6, 1.4$ Hz, 1H), 3.37 – 3.22 (m, 1H), 2.44 (s, 3H), 1.48 – 1.32 (m, 2H), 1.28 – 1.06 (m, 2H), 0.78 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 194.1, 192.6, 139.0, 137.2, 136.4, 136.4, 135.8, 132.1, 131.2, 129.4, 128.9, 128.6, 128.2, 127.5, 126.1, 117.3, 77.5, 51.6, 33.8, 21.2, 20.5, 13.6. **IR** (KBr) γ 2959, 2927, 1720, 1517, 1477, 1444, 1267, 1181, 1150, 1003, 796, 758, 693 cm^{-1} . **HRMS** (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{24}\text{H}_{25}\text{NNaOS}]^+$ requires 398.1555, found 398.1554. The absolute configuration was assigned tentatively by analogy.

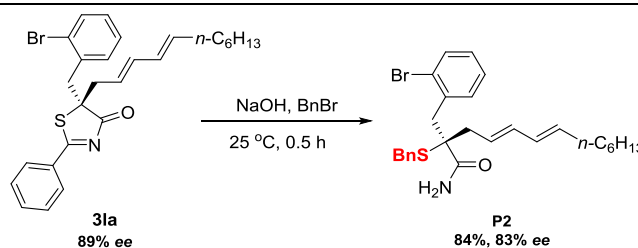
Chemical Transformations of 3la and 6ba

4. 1 Chemical Transformations of 3la



To a solution of (R)-5-(4-bromobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one $^{[3]}$ **3la** (1.0 eq, 49.6 mg, 0.10 mmol) in dioxane (1 mL) at 0 °C was added dropwise aqueous solution of NaOH (2.5 M, 0.1 mL, 0.25 mmol). The resulting mixture was stirred at room temperature for 4 h and afterwards the reaction was quenched with 2 M aq. NaHSO_4 . The combined organic phases were washed with an aqueous solution of saturated NaHCO_3 , and brine and dried over MgSO_4 . Evaporation of the solvent under reduced pressure gave 32.4 mg (0.08 mmol, yield: 79%) of the pure product as a colorless oil.

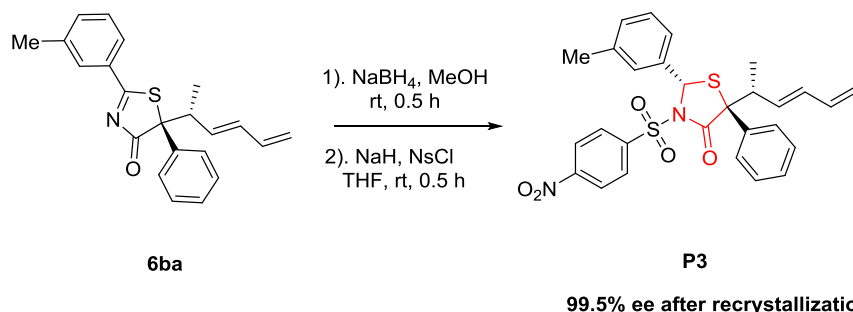
(S, 4E, 6E)-2-(2-bromobenzyl)-2-mercaptotrideca-4, 6-dienamide (P1): Enantiomeric excess: 89%, determined by HPLC (CHIRALPAK OD-H, hexane/isopropanol = 97/3, flow rate 1.0 mL/min, $T = 30$ °C, 210 nm): $t_R = 8.295$ min (major), $t_R = 9.103$ min (minor). $[\alpha]_D^{20} = -22.7$ (c 0.17, CHCl_3). ^1H NMR (400 MHz, CDCl_3) δ 7.57 (dd, $J = 8.0, 1.3$ Hz, 1H), 7.35 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.23 (td, $J = 7.5, 1.3$ Hz, 1H), 7.14 – 7.08 (m, 1H), 6.17 (dd, $J = 15.0, 10.4$ Hz, 1H), 6.02 (dd, $J = 15.0, 10.4$ Hz, 1H), 5.73 – 5.62 (m, 2H), 5.50 (ddd, $J = 15.0, 9.0, 6.0$ Hz, 1H), 3.59 (d, $J = 14.0$ Hz, 1H), 3.38 (d, $J = 14.0$ Hz, 1H), 3.08 (dt, $J = 16.6, 8.3$ Hz, 1H), 2.44 (dd, $J = 13.8, 9.1$ Hz, 1H), 2.06 (dd, $J = 14.0, 7.0$ Hz, 2H), 1.36 (dd, $J = 13.7, 6.5$ Hz, 2H), 1.32 – 1.22 (m, 6H), 0.88 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 175.8, 136.3, 135.9, 135.3, 133.2, 131.7, 129.5, 128.7, 127.4, 126.4, 124.6, 58.0, 45.4, 44.5, 32.6, 31.7, 29.2, 28.9, 22.6, 14.1. **IR** (KBr) γ 3444, 3333, 2925, 2854, 1671, 1566, 1466, 1439, 1377, 1261, 1093, 1025, 863, 800, 725, 659 cm^{-1} . **HRMS** (ESI): m/z $[\text{M} + \text{Na}]^+$ calcd for $[\text{C}_{23}\text{H}_{21}\text{N}_2\text{OS}]^+$ requires 432.0967, found 432.0975. The absolute configuration was assigned tentatively by analogy.



(R)-5-(4-bromobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one ^[4] (0.1 mmol) was dissolved in EtOH (1 mL). Then benzyl bromide (0.25 mmol) and 2.5 N NaOH (0.05 mL) were added to the reaction vessel. The reaction was complete after stirring for 0.5 hour at rt. After adjusting pH to 2 with 1 N KHSO₄, extraction with DCM followed. The combined organic layers were then dried over NaSO₄. After removal of the solvent, the residue was subjected to flash chromatography (1:2 EA/hexane) to afford the titled product as colorless oil (41.9 mg, 84% yield).

(S, 4E, 6E)-2-(benzylthio)-2-(2-bromobenzyl) trideca-4, 6-dienamide (P2): Enantiomeric excess: 83%, determined by HPLC (CHIRALPAK OD-H, hexane/isopropanol = 85/15, flow rate 1.0 mL/min, T = 30 °C, 210 nm): t_R = 8.295 min (major), t_R = 9.103 min (minor). [α]_D²⁰ = -23.8 (c 0.17, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.60 – 7.45 (m, 1H), 7.45 – 7.36 (m, 1H), 7.32 – 7.26 (m, 2H), 7.26 – 7.18 (m, 4H), 7.08 (td, J = 7.7, 1.7 Hz, 1H), 6.20 – 5.98 (m, 1H), 5.74 (dt, J = 14.5, 7.2 Hz, 1H), 5.64 (dt, J = 13.9, 6.9 Hz, 1H), 3.77 (d, J = 11.5 Hz, 1H), 3.64 (d, J = 11.5 Hz, 1H), 3.41 (q, J = 14.5 Hz, 2H), 2.76 (qd, J = 15.4, 7.3 Hz, 2H), 2.07 (dd, J = 14.1, 7.0 Hz, 2H), 1.37 (dd, J = 13.4, 6.4 Hz, 2H), 1.33 – 1.24 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 174.8, 136.6, 136.1, 134.7, 134.5, 133.0, 132.2, 129.8, 129.1, 128.7, 128.5, 127.4, 127.0, 126.5, 125.5, 59.2, 41.5, 39.0, 34.5, 32.6, 31.7, 29.2, 28.9, 22.6, 14.1. IR (KBr) γ 3443, 3025, 2924, 2853, 1676, 1585, 1496, 1453, 1437, 1376, 1260, 1095, 1026, 989, 800, 749, 709 cm⁻¹. HRMS (ESI): m/z [M + H]⁺ calcd for [C₂₃H₂₁N₂OS]⁺ requires 500.1617, found 500.1621. The absolute configuration was assigned tentatively by analogy.

4.2 Chemical Transformations of 6ba



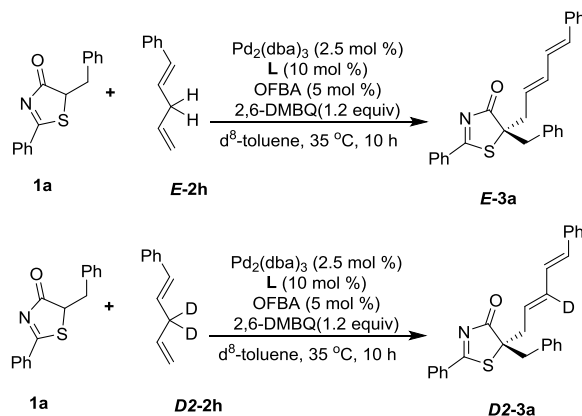
A solution of **(S)-5-((R, E)-hexa-3, 5-dien-2-yl)-5-phenyl-2-(m-tolyl) thiazol-4(5H)-one 6ba** ^[5] (347 mg, 1 mmol) in methanol (5 mL) was added to an ice-cooled solution of NaBH₄ (0.02 g, 0.53 mmol) in methanol (10 mL) with stirring. The reaction mixture was stirred for 0.5 h at room temperature, concentrated under reduced pressure, and then extracted with CHCl₃. The CHCl₃ layer was dried over K₂CO₃, filtered, and concentrated. The residue was dissolved in dried THF (1 mL) and dropwise to an ice-cooled solution of NaH (40 mg, 60% in oil, 1.5 mmol). After reaction 5 min at 0 °C, the NsCl (331.5 mg, 1.5 mmol) in THF (1 mL) was added dropwise to the mixture at 0 °C. The reaction mixture was stirred for 0.5 h at room temperature. And quenched by NH₄Cl (sat), extracted with CHCl₃, dried over Na₂SO₄. After removal of the solvent, the residue was subjected to flash chromatography (1:10 EA/hexane) and recrystallization from the mixture solvent of (CHCl₃/MeOH) to afford the titled product as a white solid (368 mg, 69% yield, 99.5% ee).

(2S, 5S)-5-((R, E)-hexa-3, 5-dien-2-yl)-3-((4-nitrophenyl)sulfonyl)-2,5-diphenylthiazolidin-4-one (P3): Enantiomeric excess: 99.5%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C, 210 nm): t_R = 15.228 min (major), t_R = 28.315 min (minor). [α]_D²⁵ = -61.1 (c 0.17, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 8.12 – 7.98 (m, 2H), 7.84 – 7.69 (m, 2H), 7.71 – 7.61 (m, 2H), 7.41 – 7.34 (m, 3H), 7.23 – 7.13 (m, 2H), 7.11 (d, J = 7.0 Hz, 1H), 7.01 (s, 1H), 6.34 – 6.11 (m, 2H),

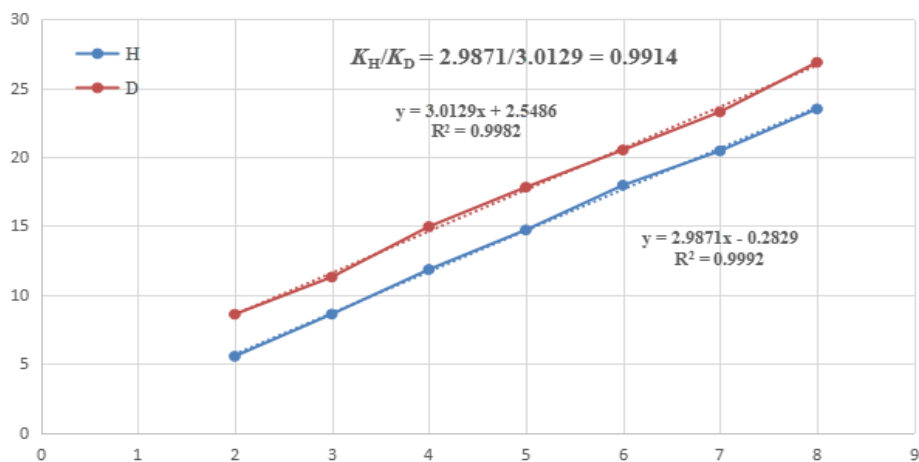
5.85 (s, 1H), 5.83 – 5.71 (m, 1H), 5.15 (dd, $J = 11.8, 5.1$ Hz, 1H), 5.09 – 5.01 (m, 1H), 3.37 – 3.25 (m, 1H), 2.22 (d, $J = 11.1$ Hz, 3H), 0.76 (d, $J = 6.9$ Hz, 3H). **^{13}C NMR** (101 MHz, CDCl_3) δ 171.7, 150.4, 143.0, 138.3, 137.3, 136.6, 135.9, 135.0, 133.7, 130.3, 129.4, 128.8, 128.7, 128.5, 128.5, 127.2, 125.6, 123.4, 117.3, 69.0, 60.0, 44.6, 21.3, 16.0. **IR** (KBr) γ 3729, 3427, 3106, 2962, 2924, 2853, 2358, 1722, 1605, 1531, 1379, 1347, 1260, 1181, 1150, 1087, 1013, 796, 422 cm^{-1} . **HRMS** (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_2\text{S}_2\text{Na}]^+$ requires 557.1181, found 557.1178.

5. Mechanistic studies

5.1 Kinetic Isotope Effect (KIE)



General procedure: To a Ar-purged NMR tube were added $\text{Pd}_2(\text{dba})_3$ (0.58 mg), **L5** (2.4 mg), OFBA (0.2 mg), DMBQ (4.1 mg) and degassed $\text{d}^8\text{-toluene}$ (0.6 mL). Then **E-2h** or **D2-2h** (0.05 mmol) was added and the NMR tube was immediately placed at 35 °C, ^1H -NMR scan was conducted every 1 hours for 9 hours.



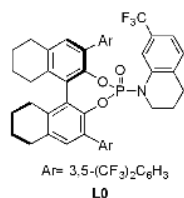
R-5-benzyl-2-phenyl-5-((2E, 4E)-5-phenylpenta-2, 4-dien-1-yl-3-d) thiazol-4(5H)-one (D2-3a).

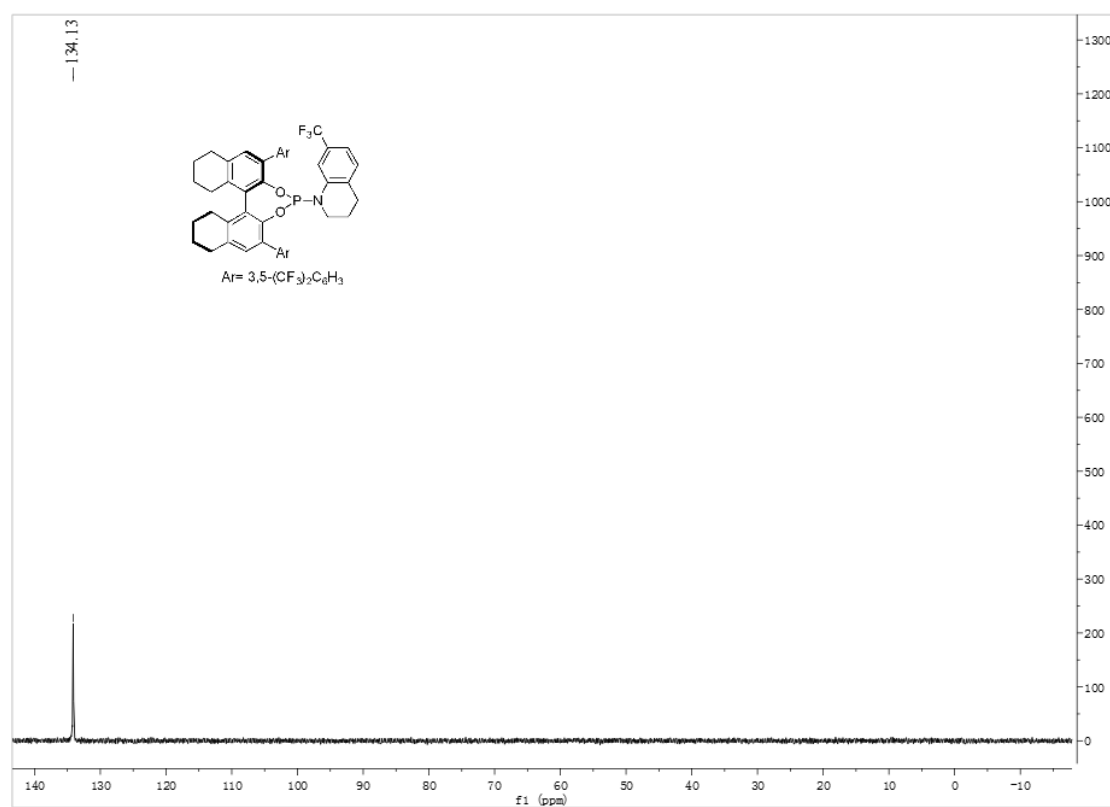
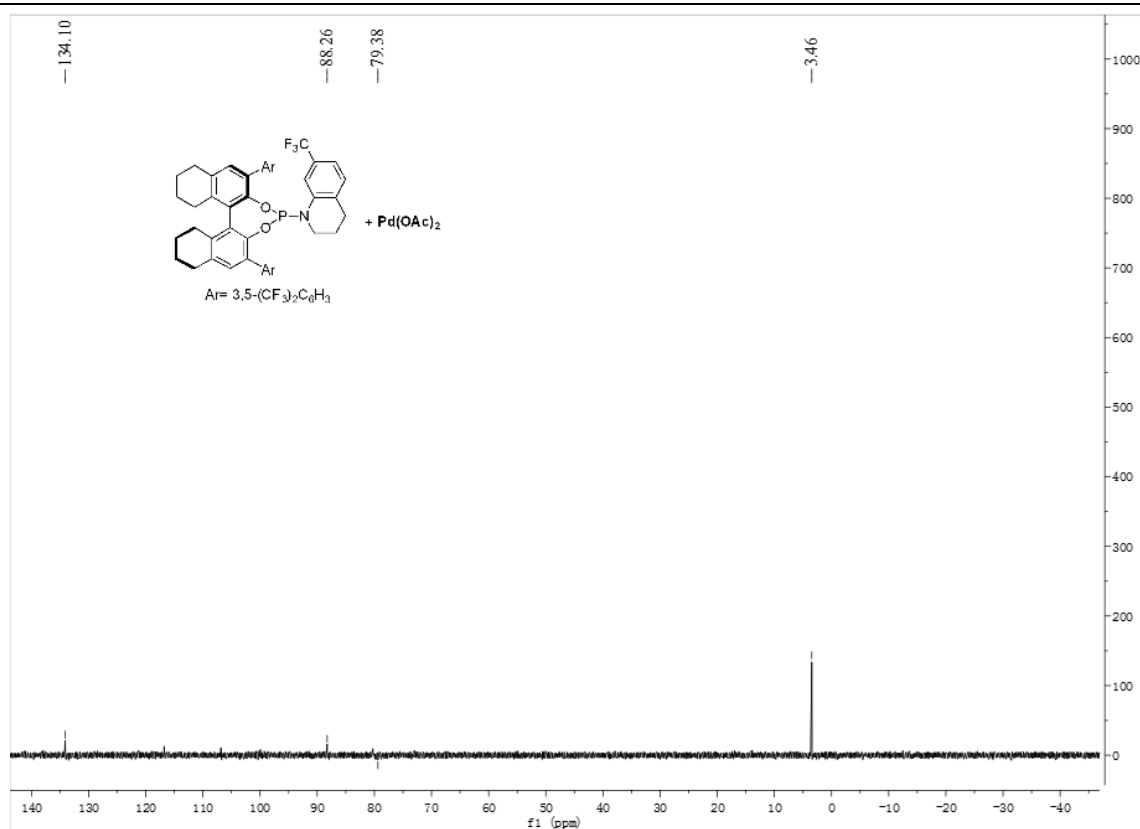
^1H NMR (400 MHz, CDCl_3) δ 8.12 – 7.97 (m, 1H), 7.76 – 7.58 (m, 1H), 7.54 – 7.41 (m, 1H), 7.36 – 7.31 (m, 1H), 7.28 (dd, $J = 7.1, 1.7$ Hz, 1H), 7.25 – 7.13 (m, 2H), 3.45 – 3.31 (m, 1H), 3.26 (d, $J = 13.8$ Hz, 1H), 2.93 (dd, $J = 14.2, 7.1$ Hz, 1H), 2.80 (dd, $J = 14.1, 7.9$ Hz, 1H). **^{13}C NMR** (101 MHz, CDCl_3) δ 195.3, 194.7, 137.0, 135.3, 134.9, 132.4, 132.1, 130.4, 128.9, 128.8, 128.5, 128.3, 128.1, 127.5, 127.4, 126.5, 126.3, 70.8, 44.5, 41.7. **HRMS** (ESI): m/z $[\text{M} + \text{H}]^+$ calcd for $[\text{C}_{27}\text{H}_{23}\text{DNOS}]^+$ requires 411.1641, found 411.1642.

5.2 ^{31}P NMR and HRMS Studies

5.2.1 ^{31}P NMR Studies:

Figure 1 displays ^{13}C NMR spectra. The top panel shows four stacked spectra (purple, blue, green, yellow) with two new peaks indicated by arrows. The bottom panel shows a zoomed-in view of the L5 (red) and L0 (black) spectra, with peaks labeled L5, Pd + L5, and L0.

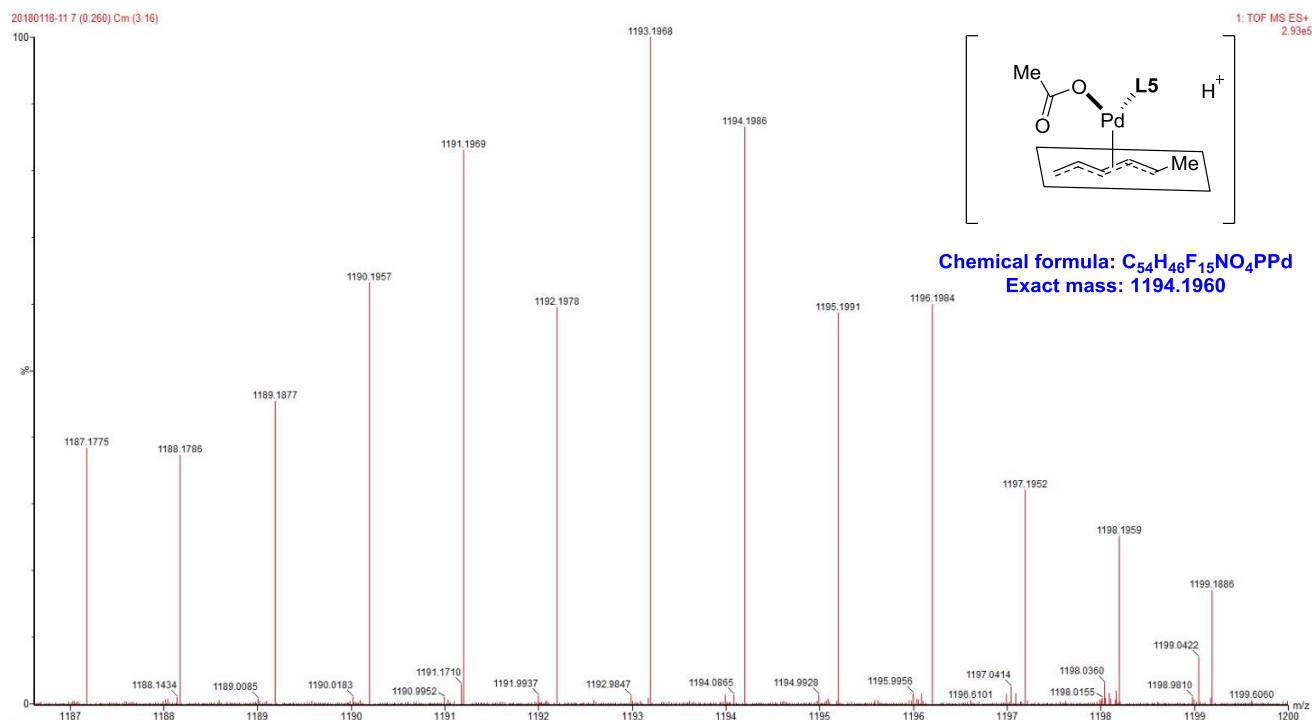
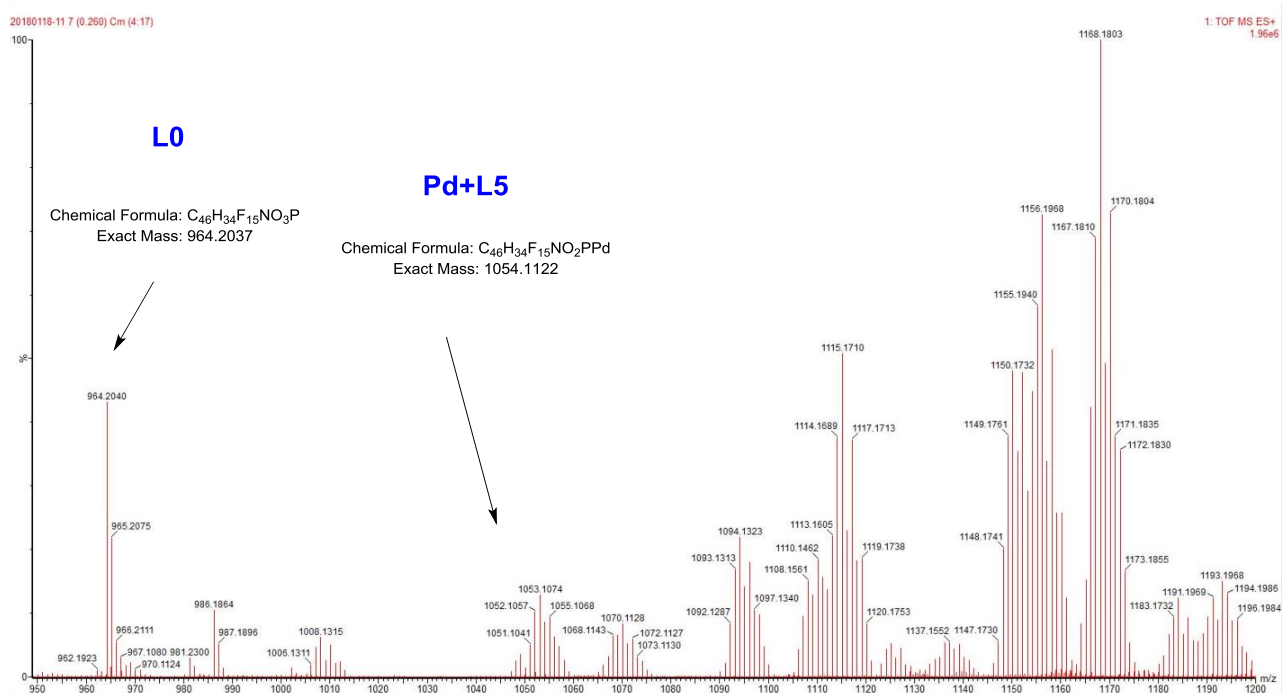


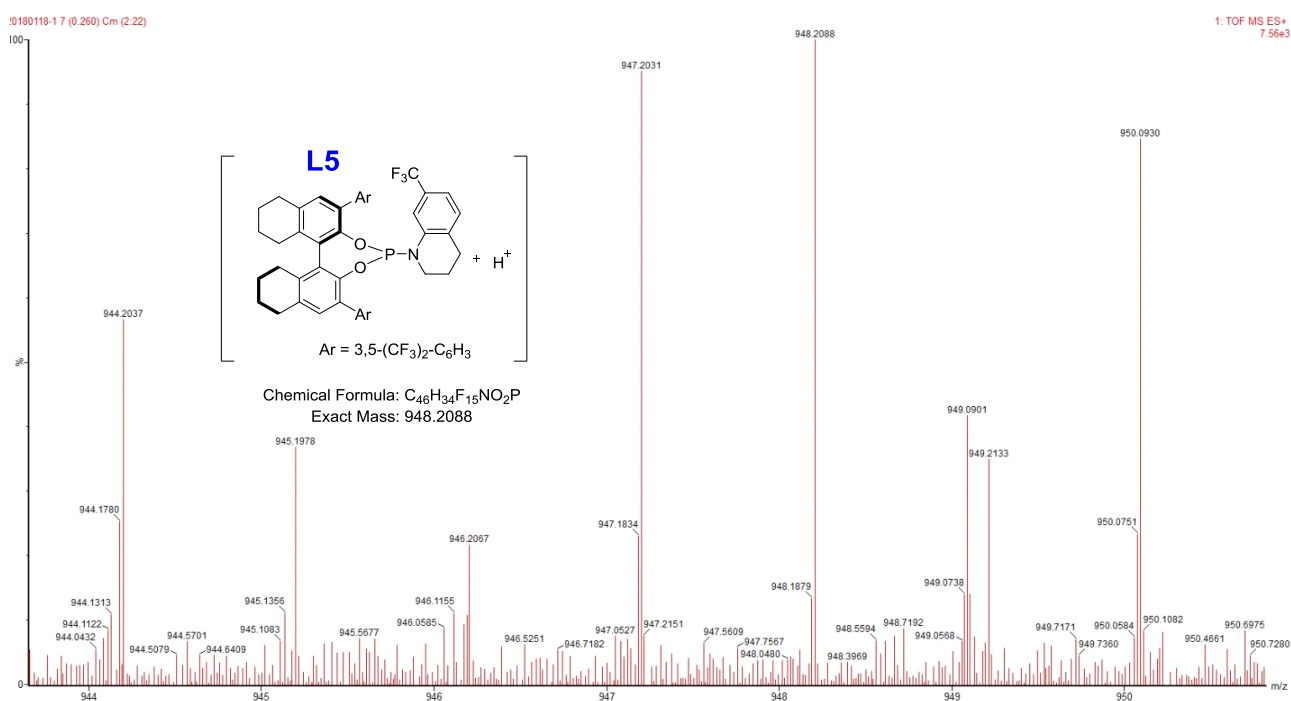
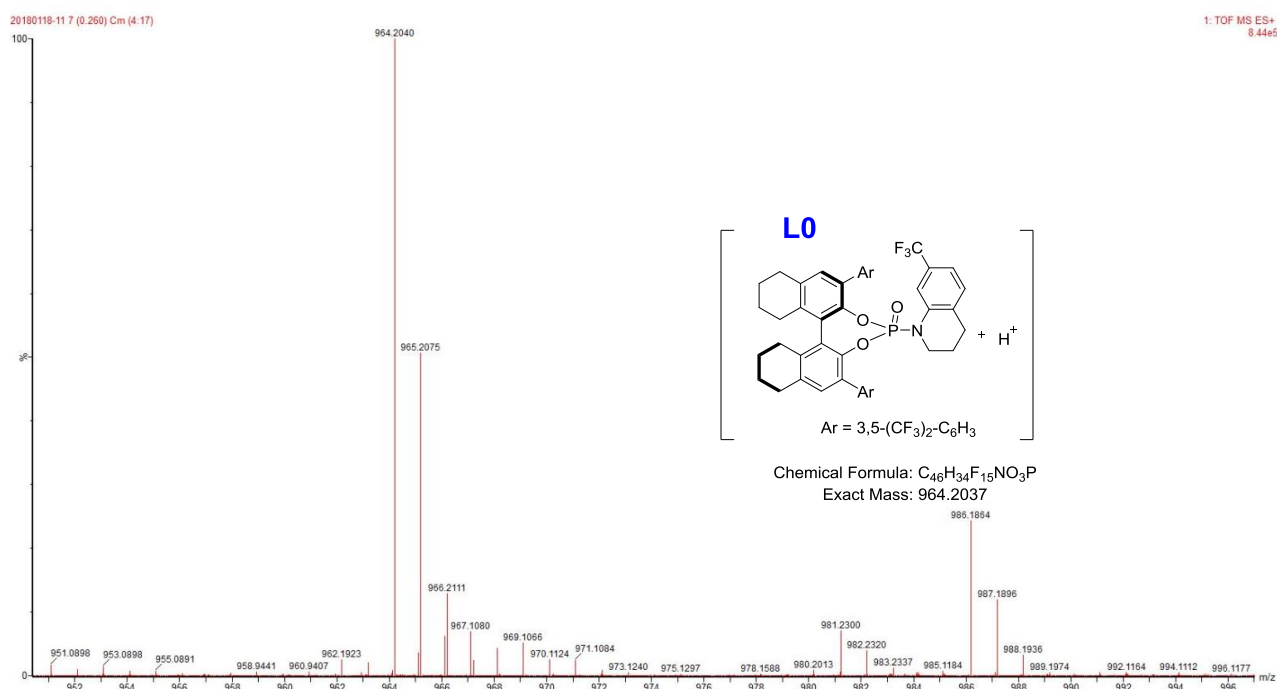


5.2.2 HRMS Studies

Under an atmosphere of N_2 , Pd(OAc)_2 (2.4 mg, 0.02 mmol, 1 equiv), L5 (19.2 mg, 0.02 mmol, 1 equiv) and the 1,4-hexadiene (8.2 mg, 0.1 mmol, 5 eq.) were added to a glass vial, then Acetone- d_6 (0.50 mL) was added and the mixture was stirred for 30 min at 25

°C . Then the solution (0.01 mL) was diluted with CH₃CN (1.0 mL) and the diluted solution was subjected to run ESI-MS analysis. Middle peaks corresponding to Allylic Pd^{II} intermediate were observed.





X-ray Single Crystal Data - Determination of the Absolute Configuration

(1) Determination of the Absolute Configuration of Product 3da and P3.

CCDC Number: 1836280

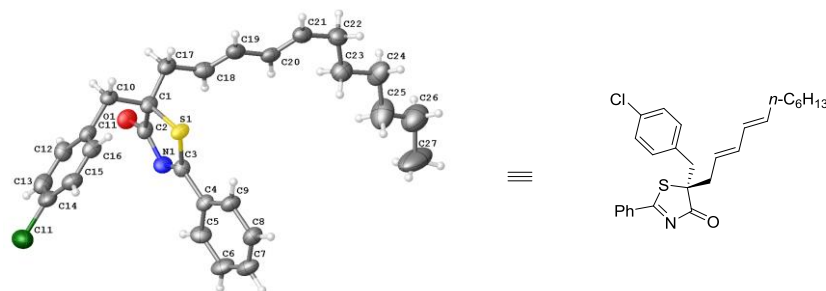


Table 1. Crystal data and structure refinement for cu_dm17049_0m.	
Identification code	cu_dm17049_0m
Empirical formula	C ₂₇ H ₃₀ Cl N O S
Formula weight	452.03
Temperature	130 K
Wavelength/Å	1.54178
Crystal system	Orthorhombic
Space group	P 21 21 21
a/Å	5.9641(4)
b/Å	17.2956(13)
c/ Å	24.3231(16)
α / °	90
β / °	90
γ / °	90
Volume/ Å ³	2509.0(3)
Z	4
Density (calculated) / mg/cm ³	1.197
μ / mm ⁻¹	2.253
F(000)	960
Crystal size/ mm ³	0.15 x 0.1 x 0.06
2 θ range for data collection/ °	3.135 to 69.650
Index ranges	-6<= <i>h</i> <=5, -20<= <i>k</i> <=20, -28<= <i>l</i> <=29
Reflections collected	15303
Independent reflections	4410 [R(int) = 0.1048]
Data / restraints / parameters	4410 / 12 / 281
Goodness-of-fit on F ²	1.051
Final R indices [I>2 σ (I)]	R1 = 0.0703, wR2 = 0.1843
R indices (all data)	R1 = 0.0941, wR2 = 0.2025
Extinction coefficient	n/a
Largest diff. peak and hole/ e.Å ⁻³	0.714 and -0.499

(2) Determination of the Absolute Configuration of Product P3.

CCDC Number: 1836281

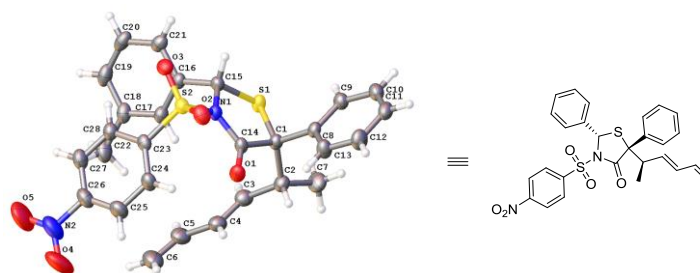
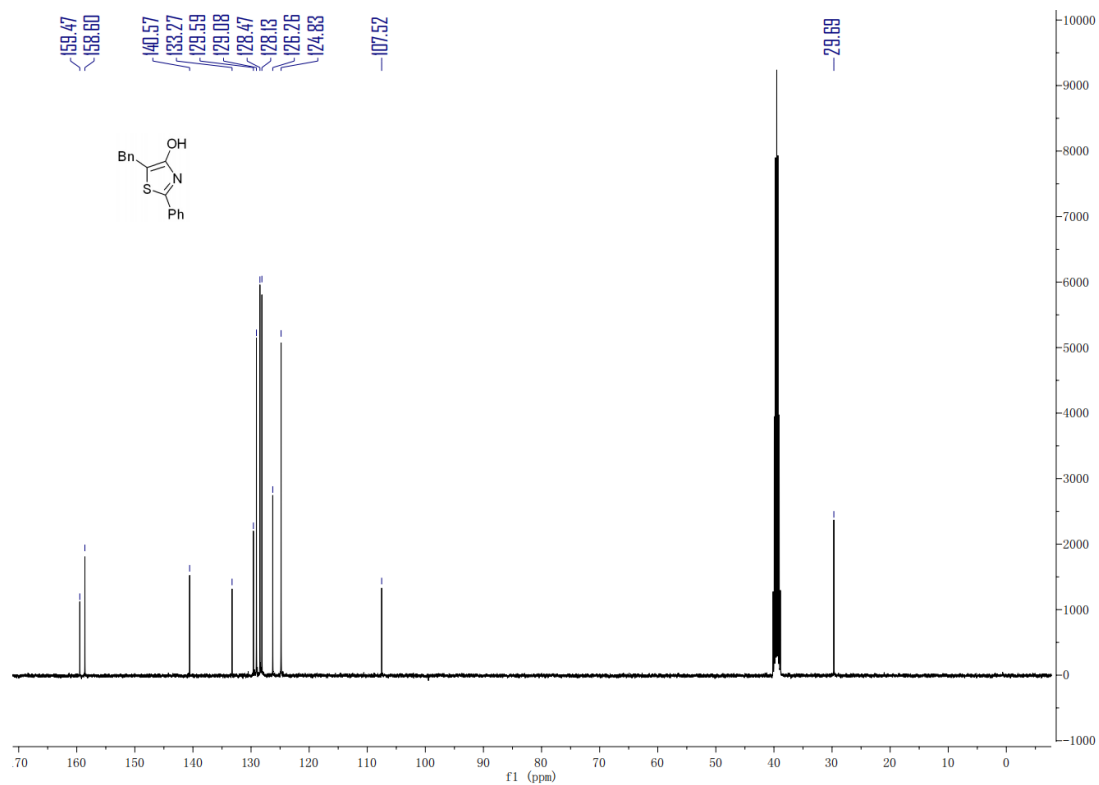
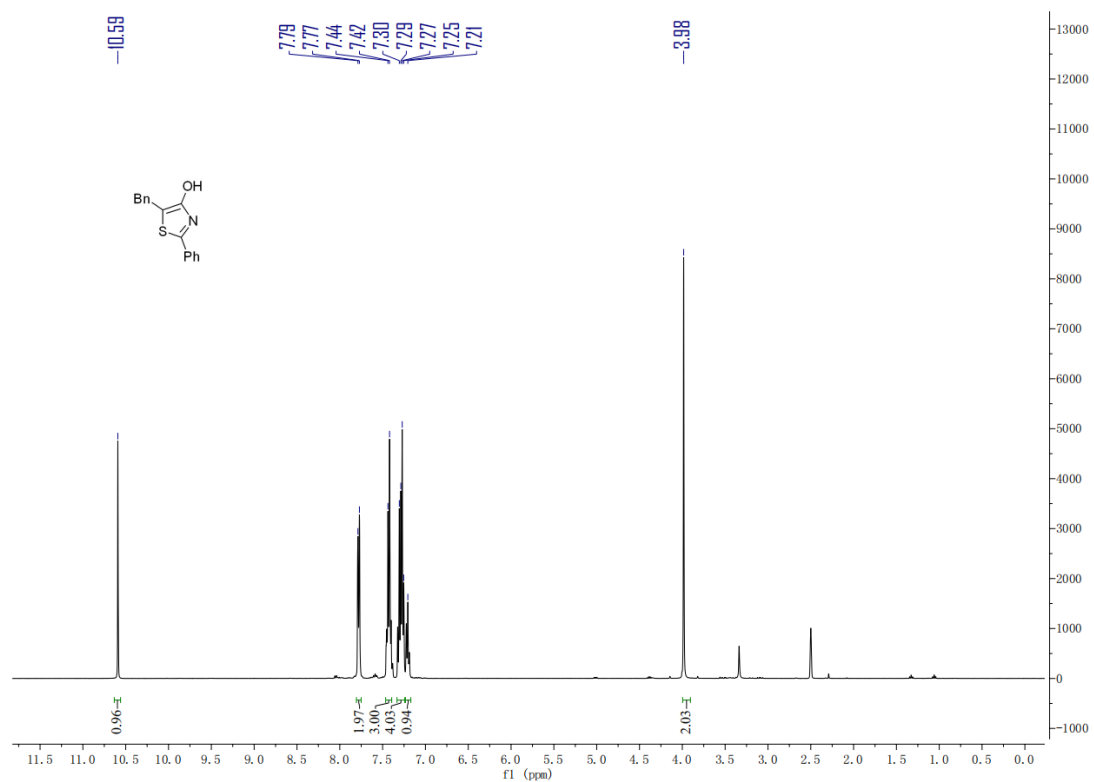


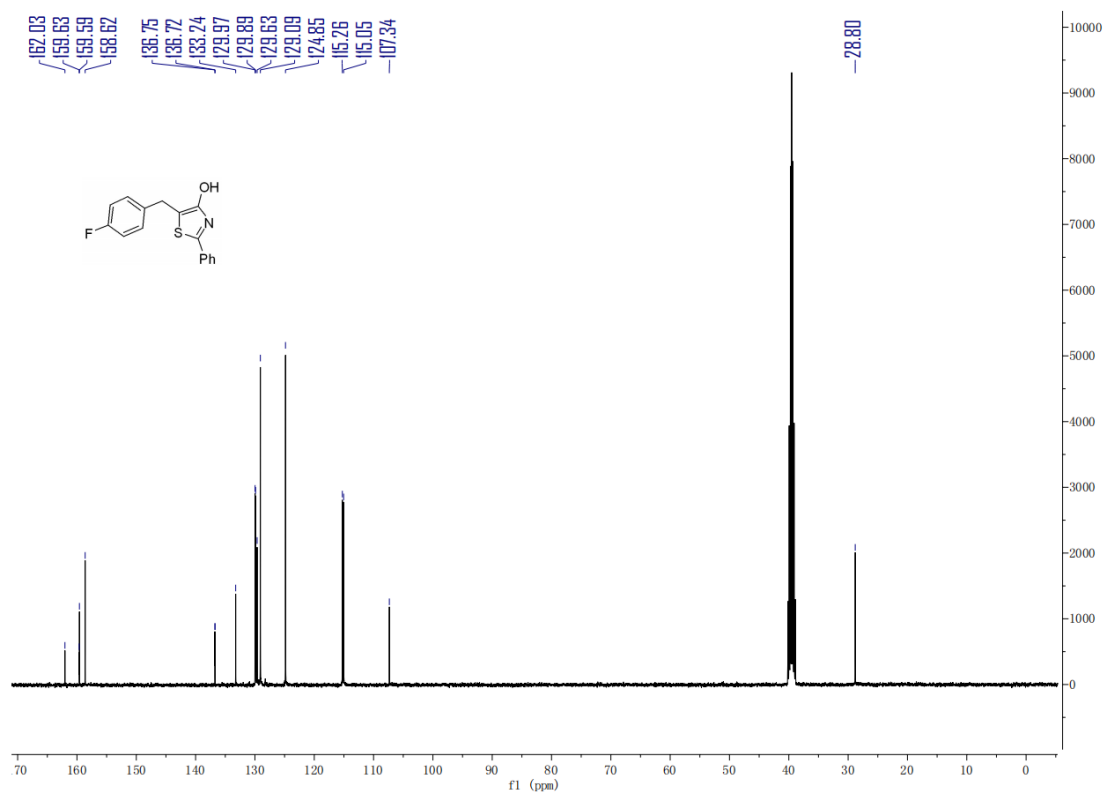
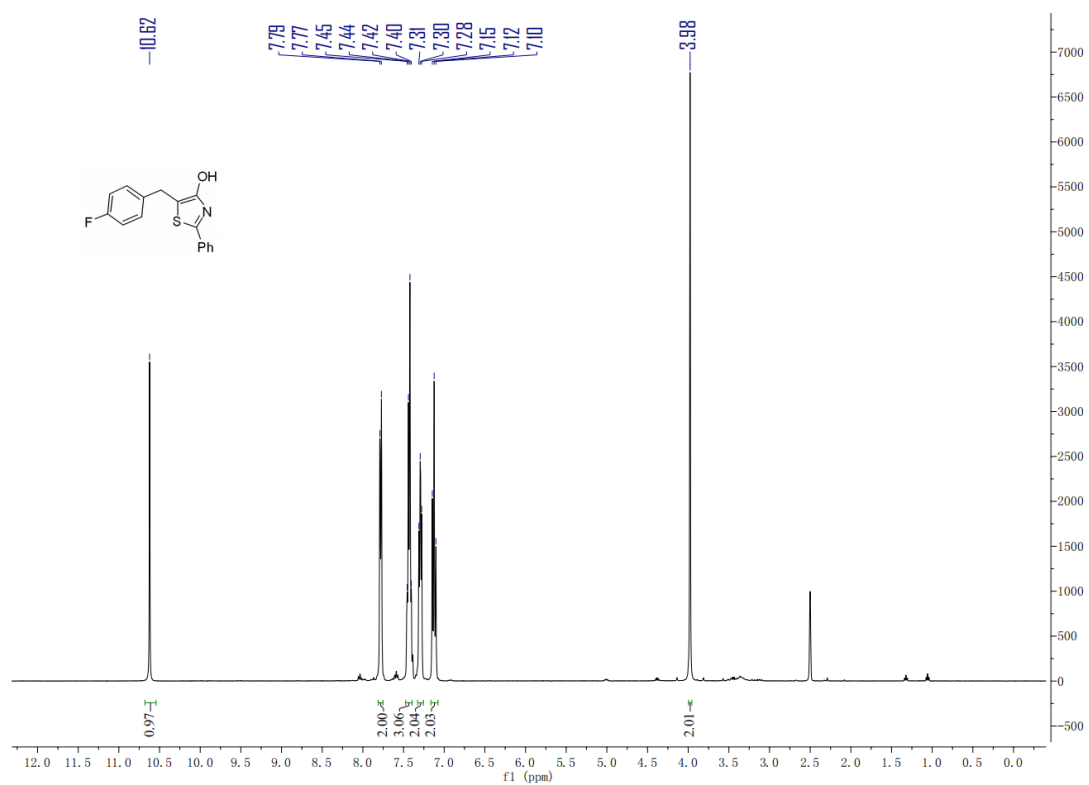
Table 2. Crystal data and structure refinement for cu_dm17049_0m.	
Identification code	wmj18024_0m
Empirical formula	C ₂₈ H ₂₆ N ₂ O ₅ S ₂
Formula weight	534.63
Temperature	306.49 K
Wavelength	1.34139 Å
Crystal system	Monoclinic
Space group	P 1 21 1
Unit cell dimensions	a = 11.1699(2) Å
	b = 8.2022(2) Å
	c = 14.7242(3) Å
Volume	1321.78(5) Å ³
Z	2
Density (calculated)	1.343 Mg/m ³
Absorption coefficient	1.408 mm ⁻¹
F(000)	560
Crystal size	0.1 x 0.08 x 0.06 mm ³
Theta range for data collection	7.013 to 57.027 °
Index ranges	-13 ≤ h ≤ 13, -10 ≤ k ≤ 9, -18 ≤ l ≤ 18
Reflections collected	13543
Independent reflections	5024 [R(int) = 0.0349]
Completeness to theta = 53.594 °	96.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7512 and 0.5842
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5024 / 1 / 336
Goodness-of-fit on F ²	1.053
Final R indices [I > 2σ(I)]	R1 = 0.0279, wR2 = 0.0770
R indices (all data)	R1 = 0.0285, wR2 = 0.0777
Absolute structure parameter	0.048(6)

-
1. (a) Lynd, R. A.; Zweifel, G. *Synthesis* **1974**, 658. (b) Wang, P.-S.; Lin, H.-C.; Zhou, X.-L.; Gong, L.-Z. *Org. Lett.* **2014**, 16, 3332.
 2. Kerdesky, F. A. J.; Holms, J. H.; Moore, J. L.; Bell, R. L.; Dyer, R. D.; Carter, G. W.; Brooks, D. W. *J. Med. Chem.*, **1991**, 34, 2158.
 3. Diosdado, S.; Etxabe, J.; Izquierdo, J.; Landa, A.; Mielgo, A.; Olaizola, I.; Lopez, R.; Palomo, C. *Angew. Chem. Int. Ed.* **2013**, 52, 11846.
 4. Chen, W.; Hartwig, J. F. *J. Am. Chem. Soc.* **2014**, 136, 377.
 5. Yamamoto, Y.; Ohnishi, S.; Azuma, Y. *Pharmaceutical Bulletin*, **1983**, 31, 6, 1929 .

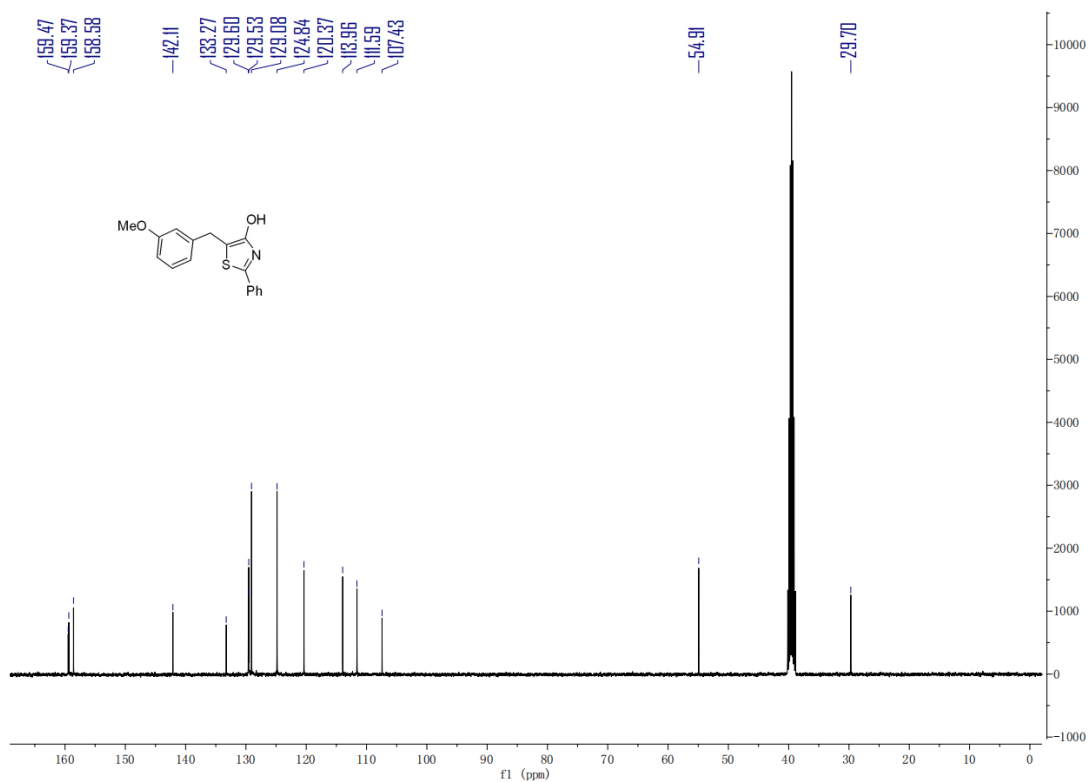
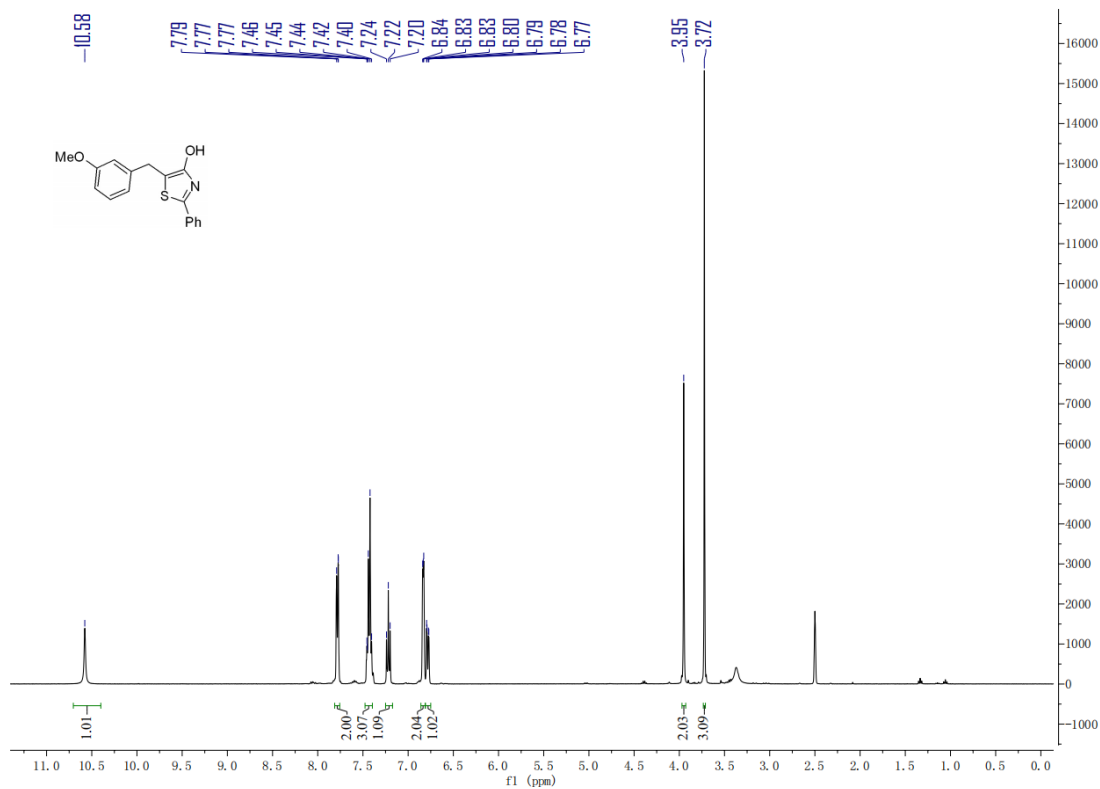
5-benzyl-2-phenylthiazol-4-ol (1a)



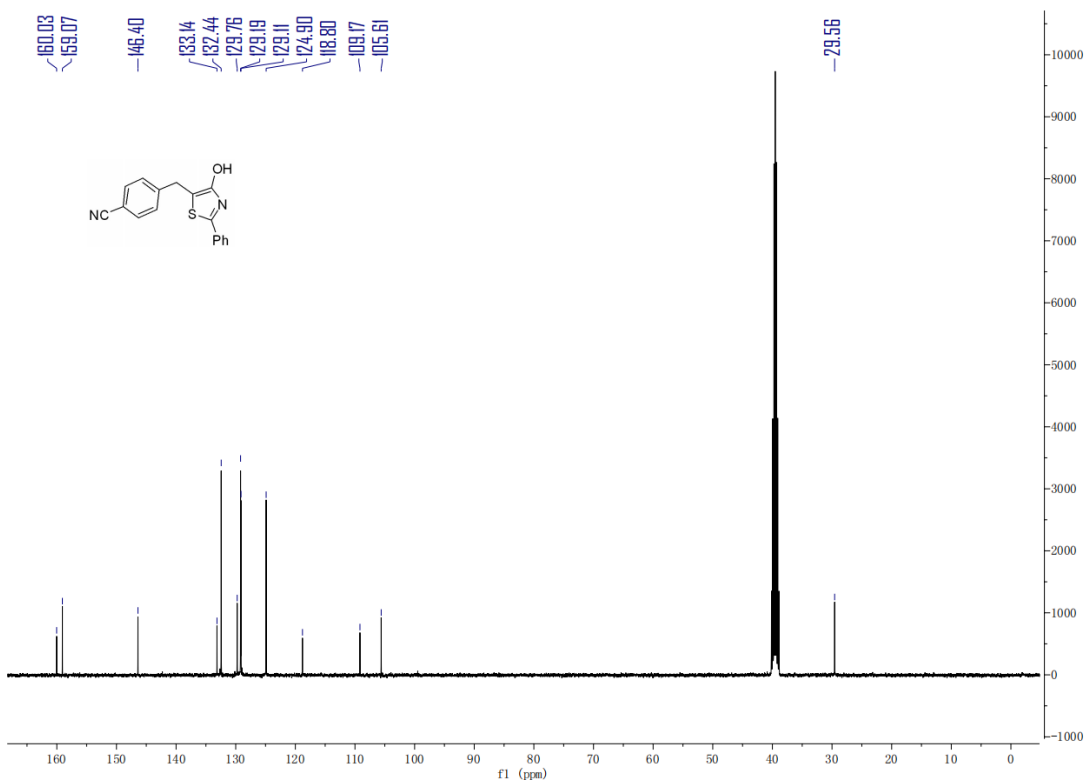
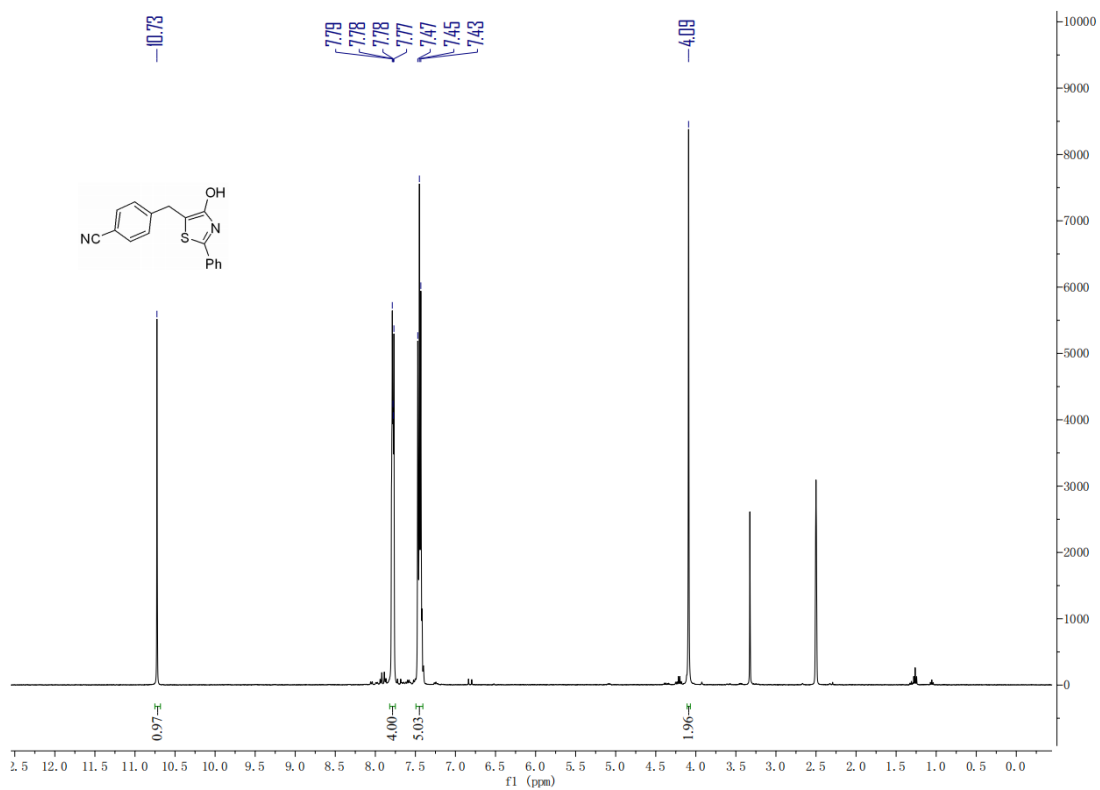
5-(4-fluorobenzyl)-2-phenylthiazol-4-ol (1b)



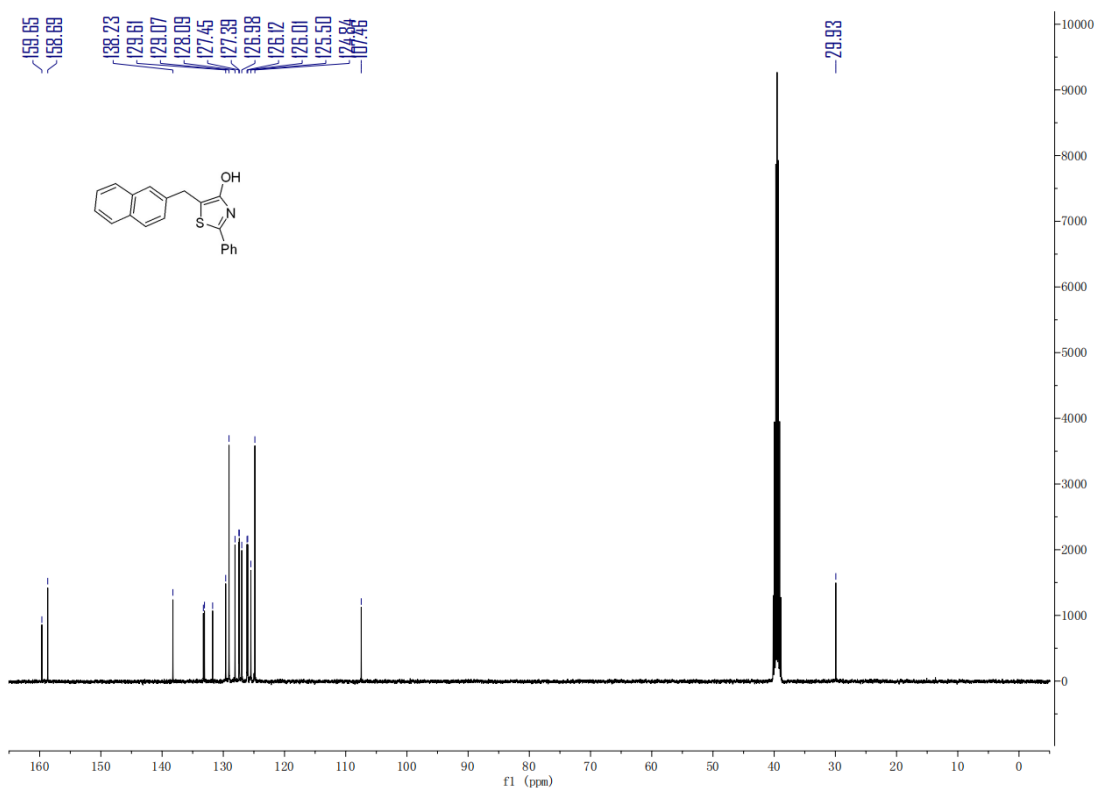
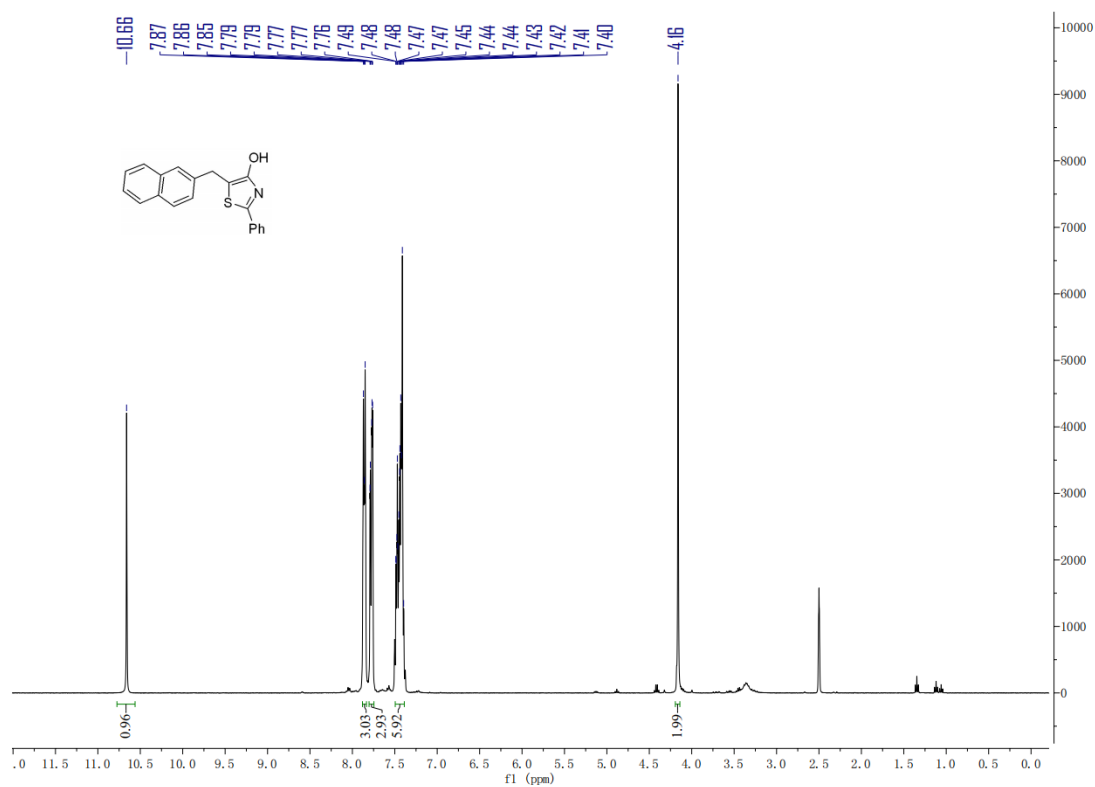
5-(3-methoxybenzyl)-2-phenylthiazol-4-ol (1c)



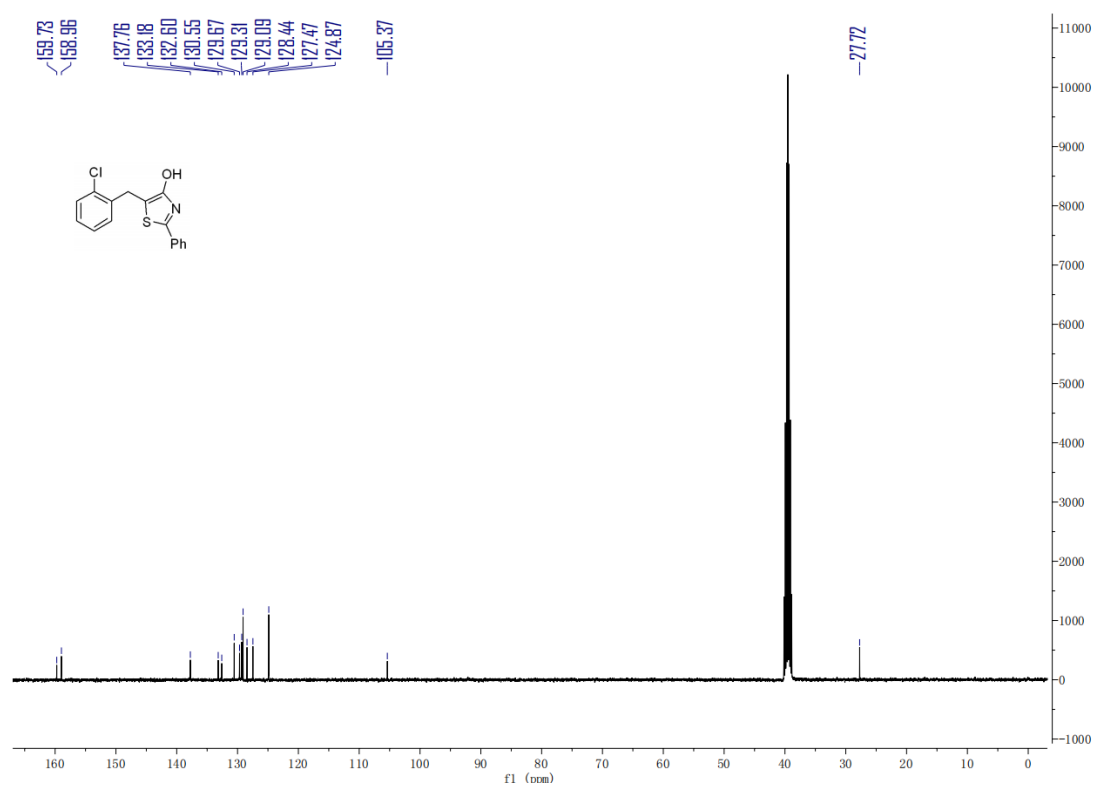
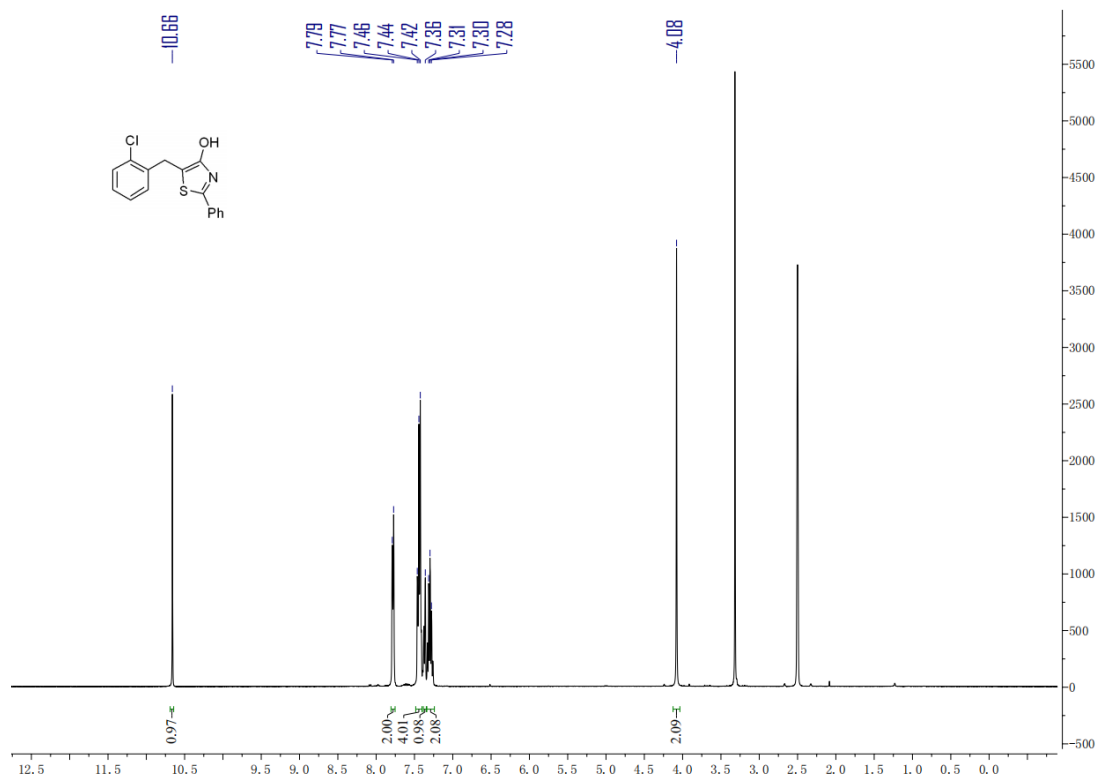
4-((4-hydroxy-2-phenylthiazol-5-yl) methyl) benzonitrile (1d)



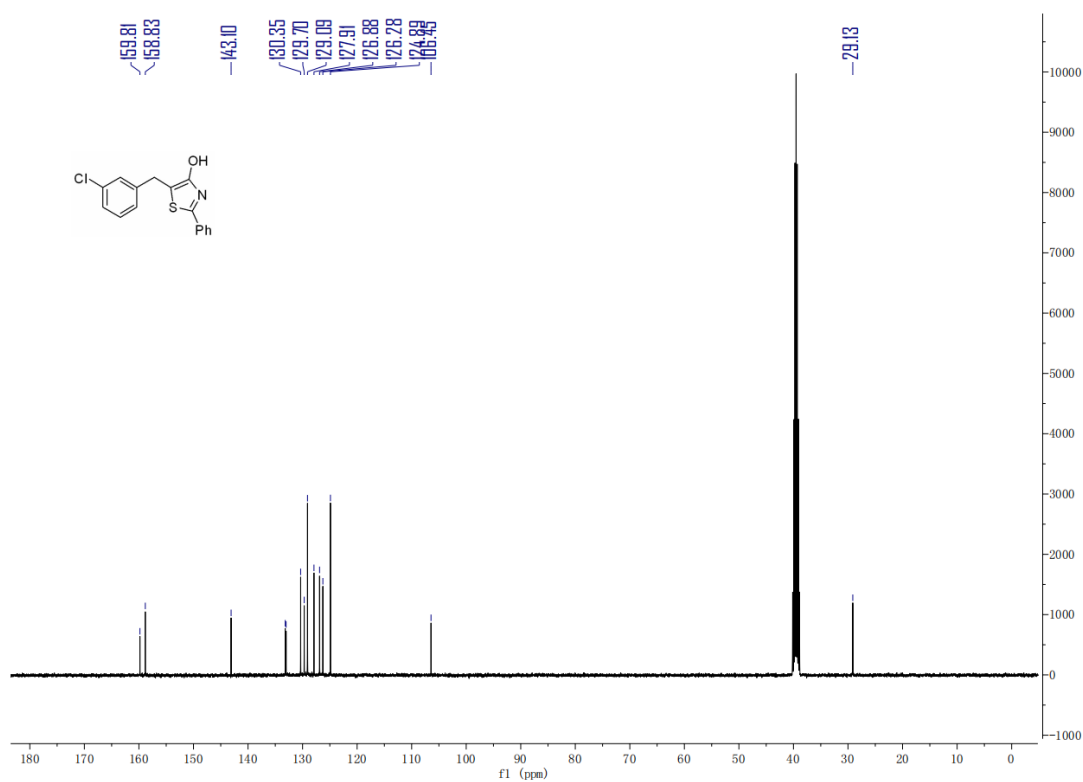
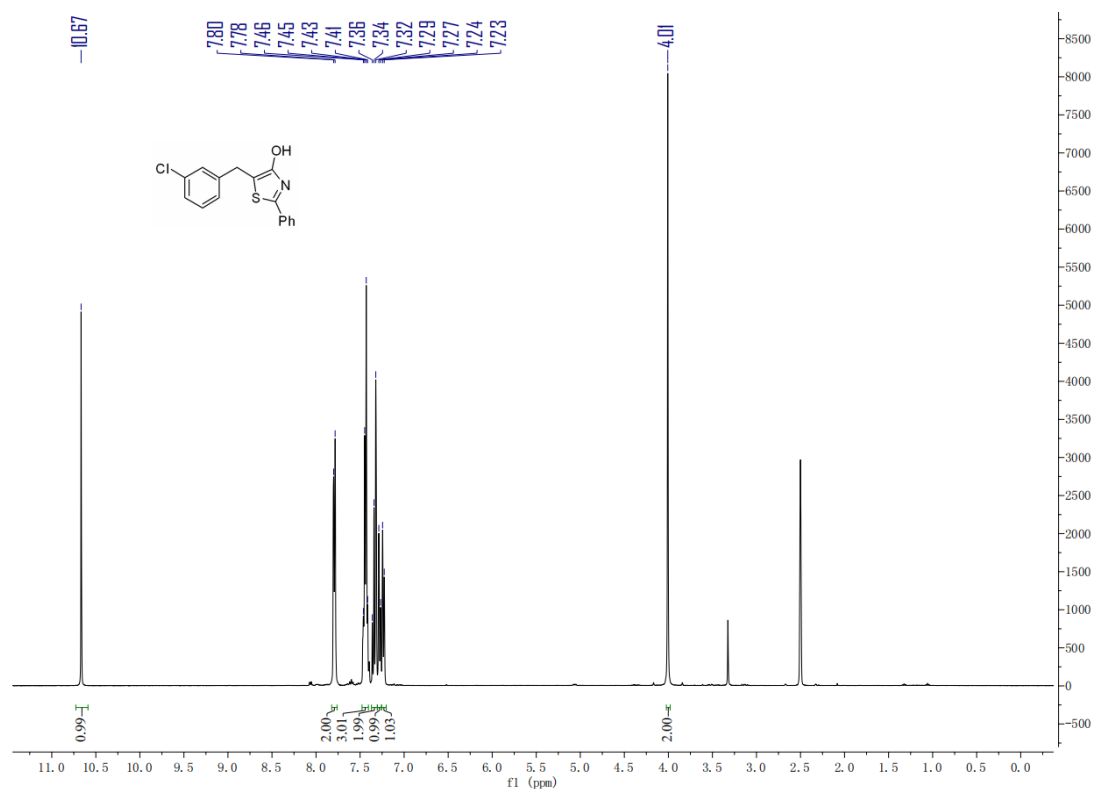
5-(naphthalen-2-ylmethyl)-2-phenylthiazol-4-ol (1e)



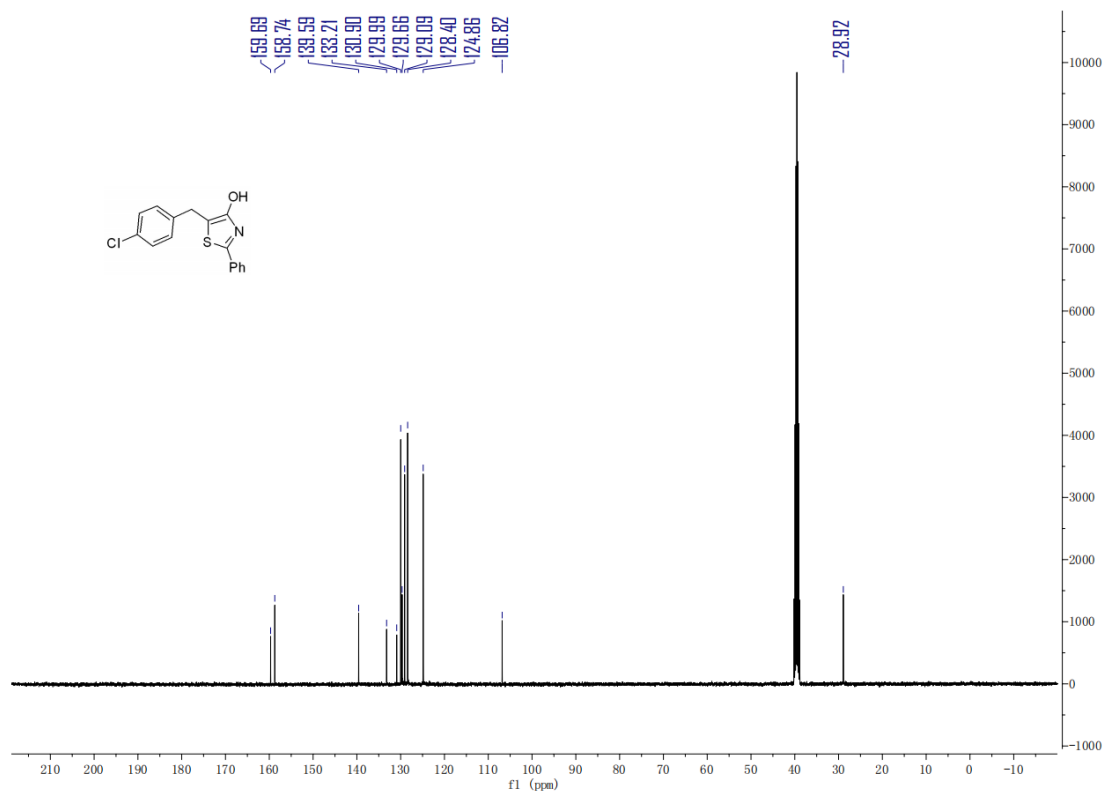
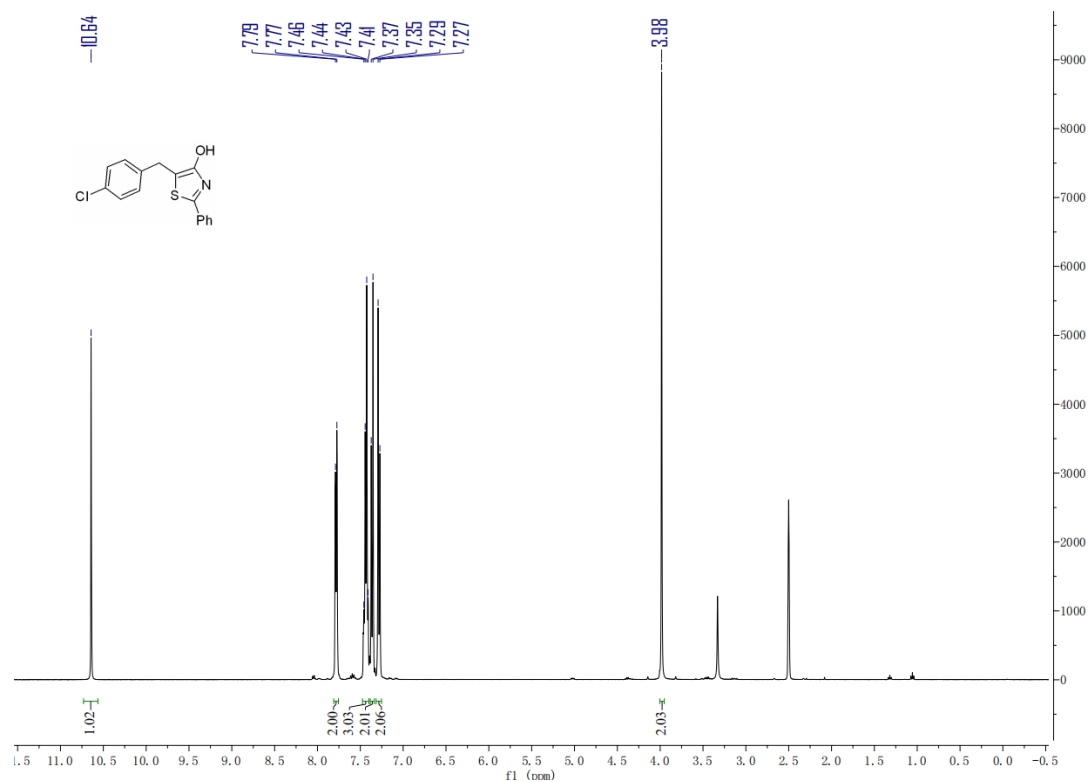
5-(2-chlorobenzyl)-2-phenylthiazol-4-ol (1f)



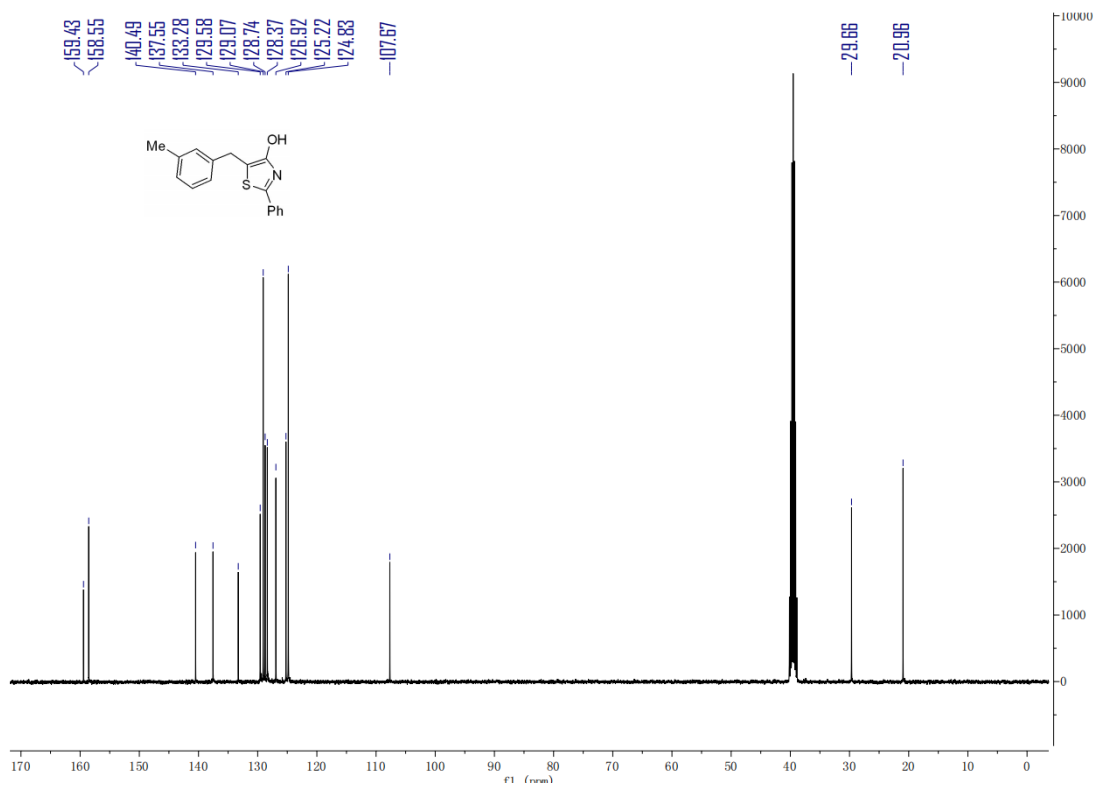
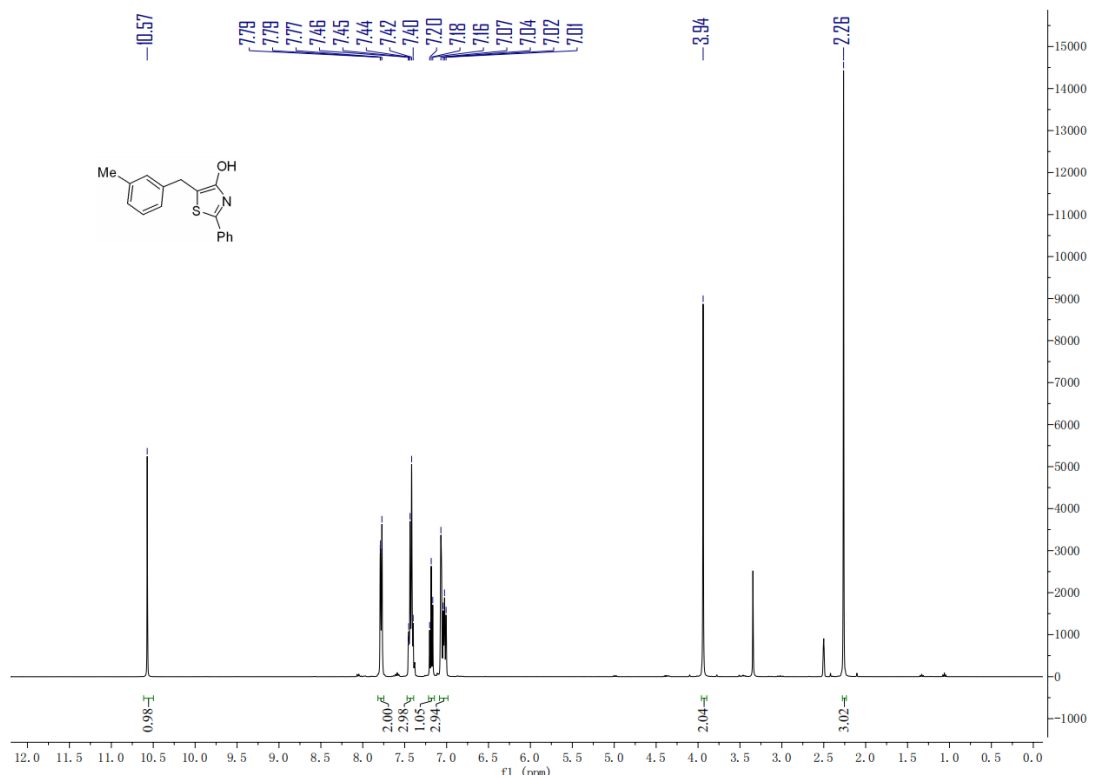
5-(3-chlorobenzyl)-2-phenylthiazol-4-ol (1g)



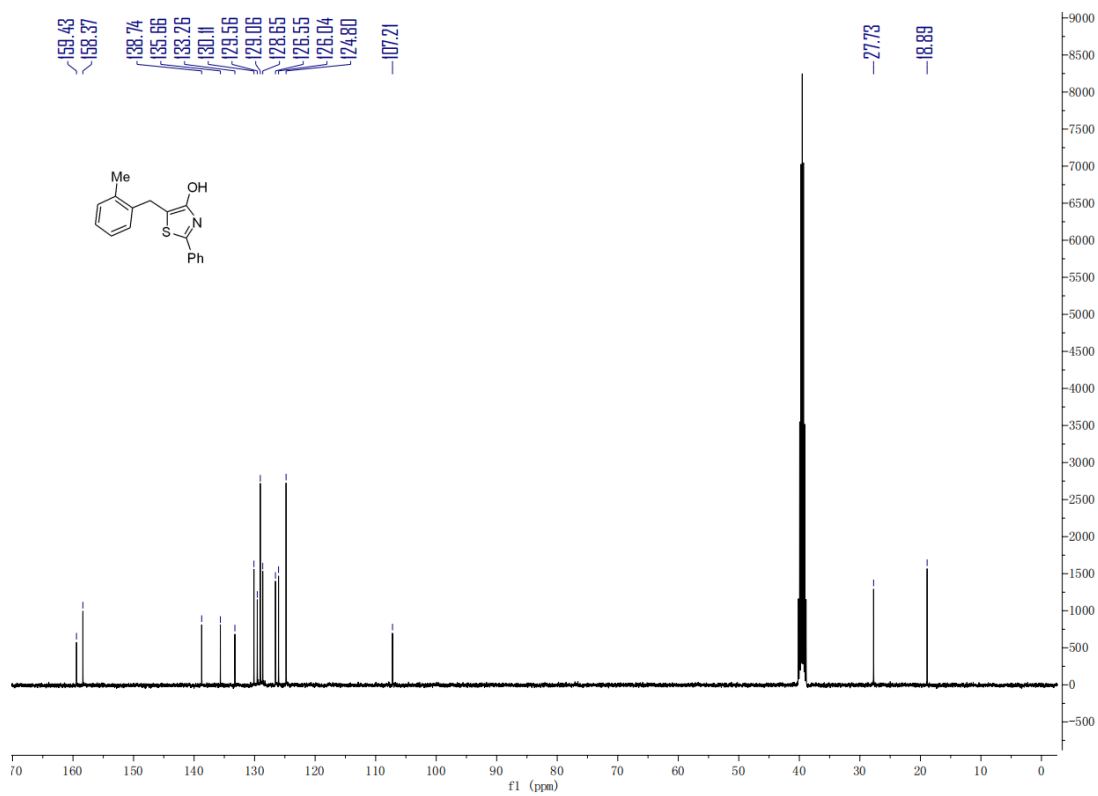
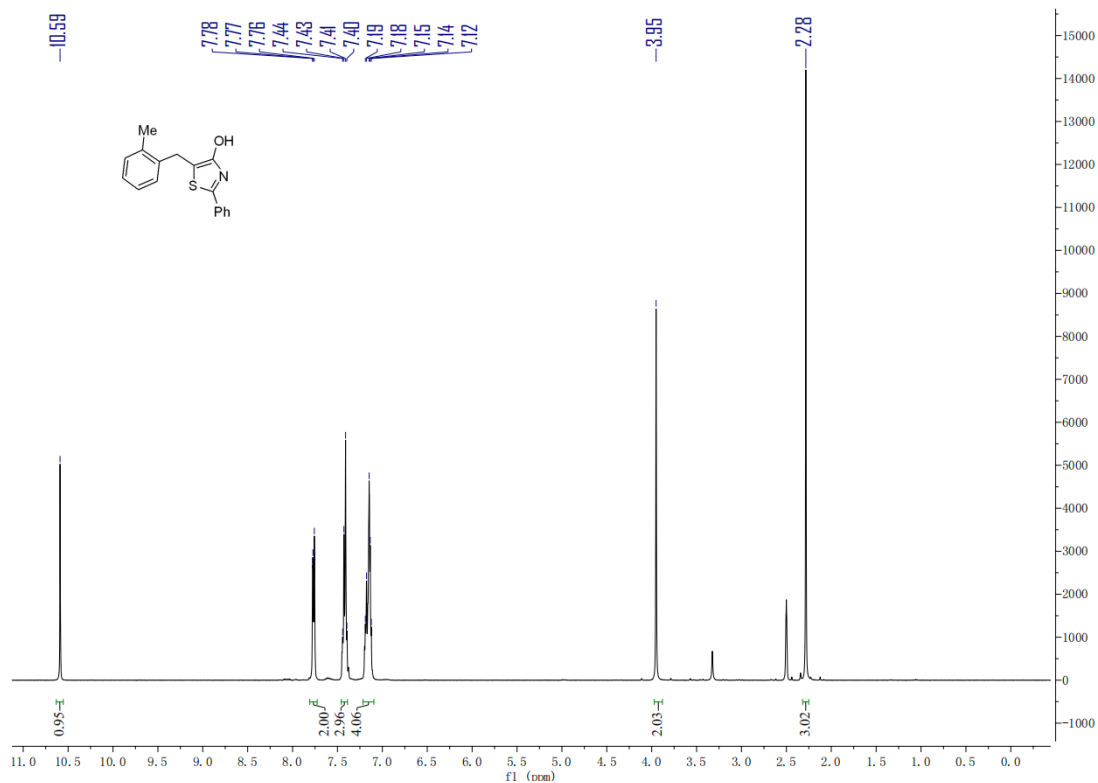
5-(4-chlorobenzyl)-2-phenylthiazol-4-ol (1h)



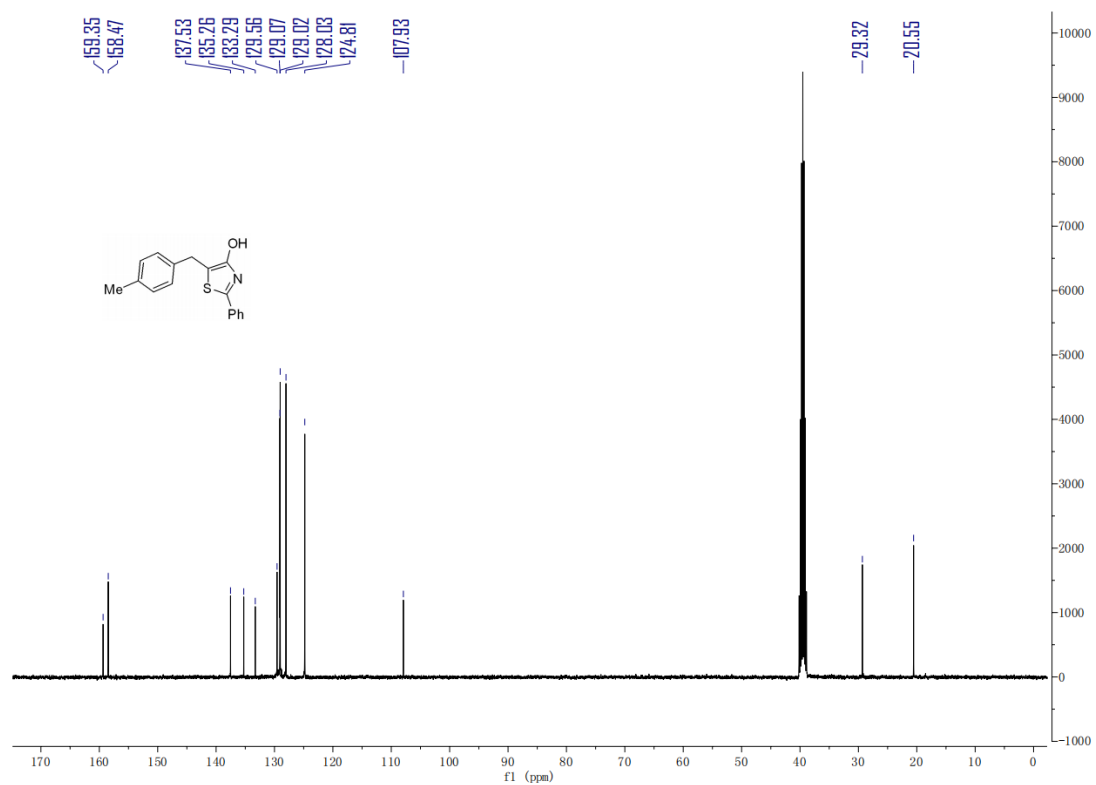
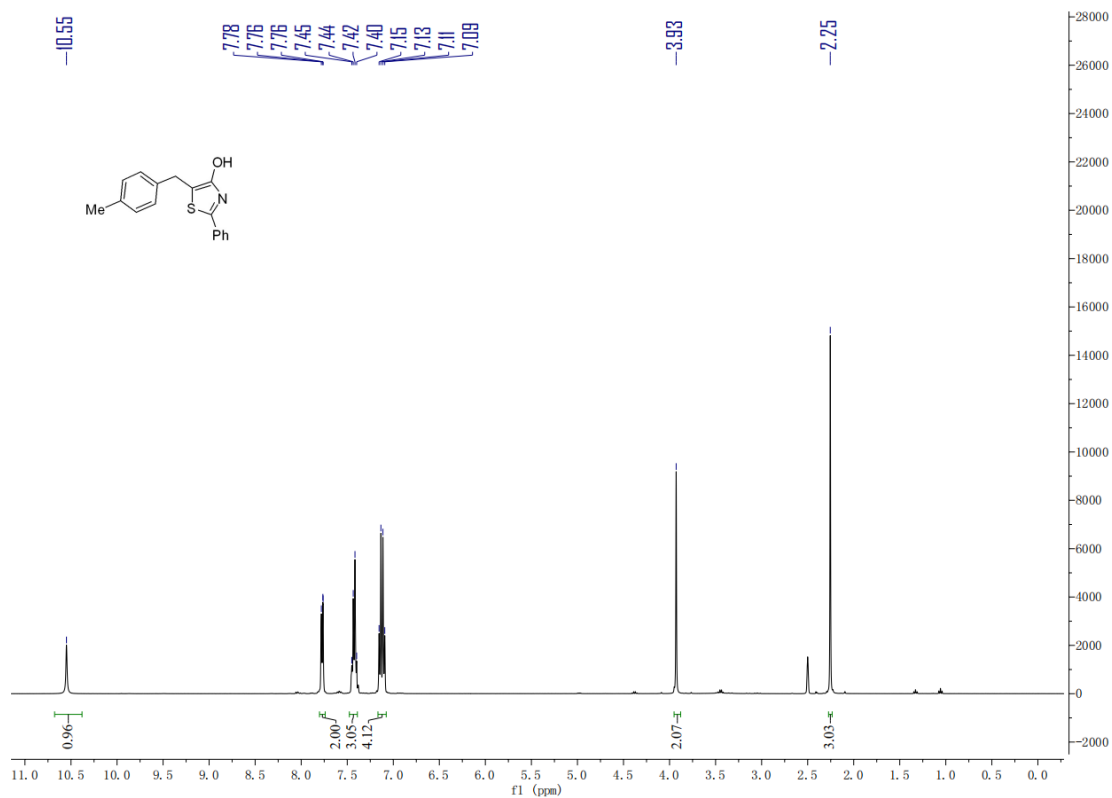
5-(3-methylbenzyl)-2-phenylthiazol-4-ol (1i)



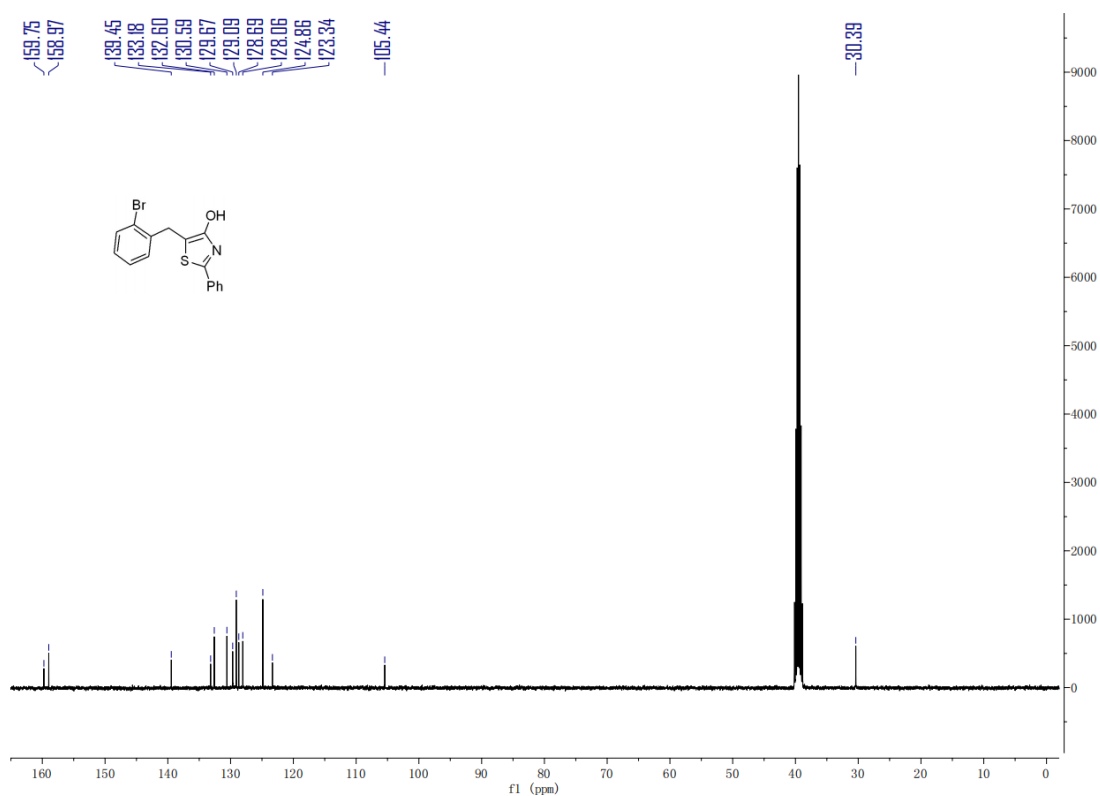
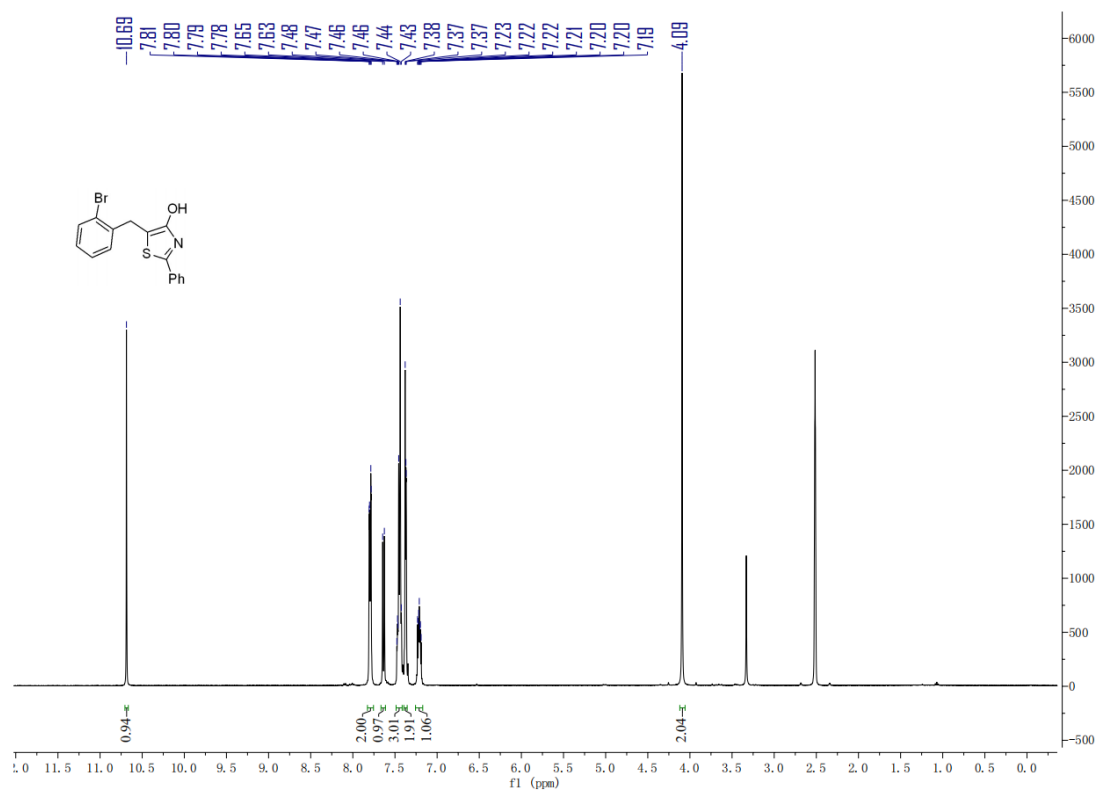
5-(2-methylbenzyl)-2-phenylthiazol-4-ol (1j)



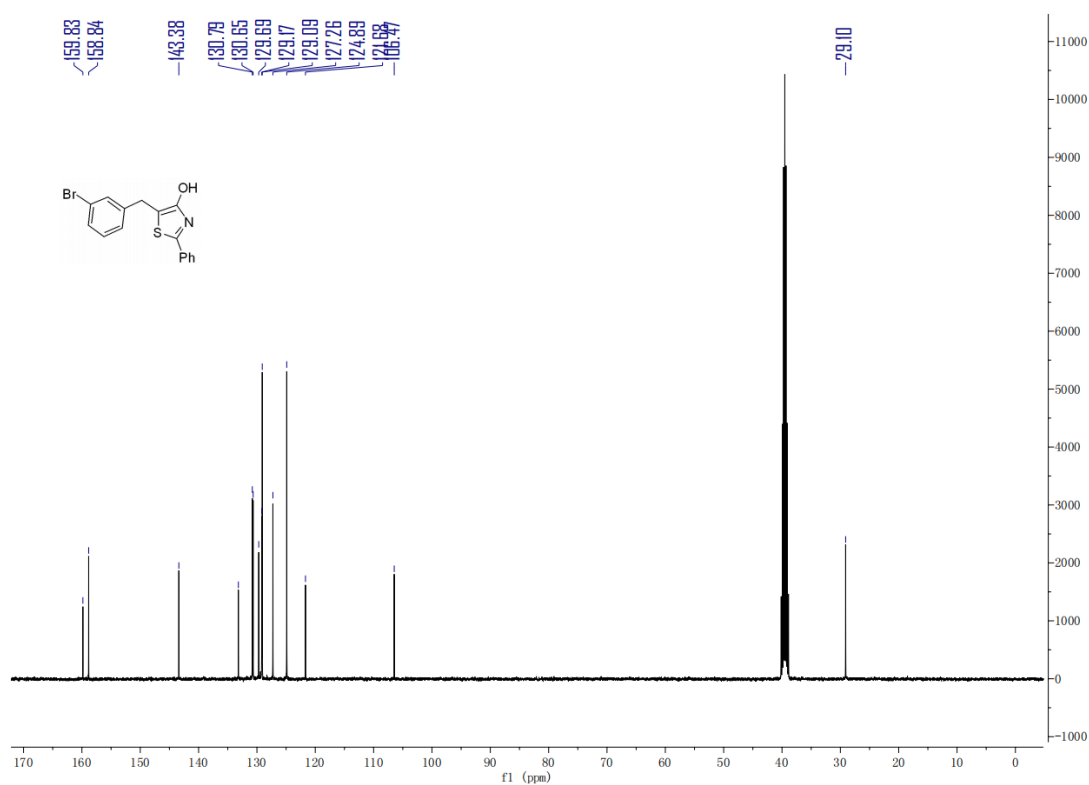
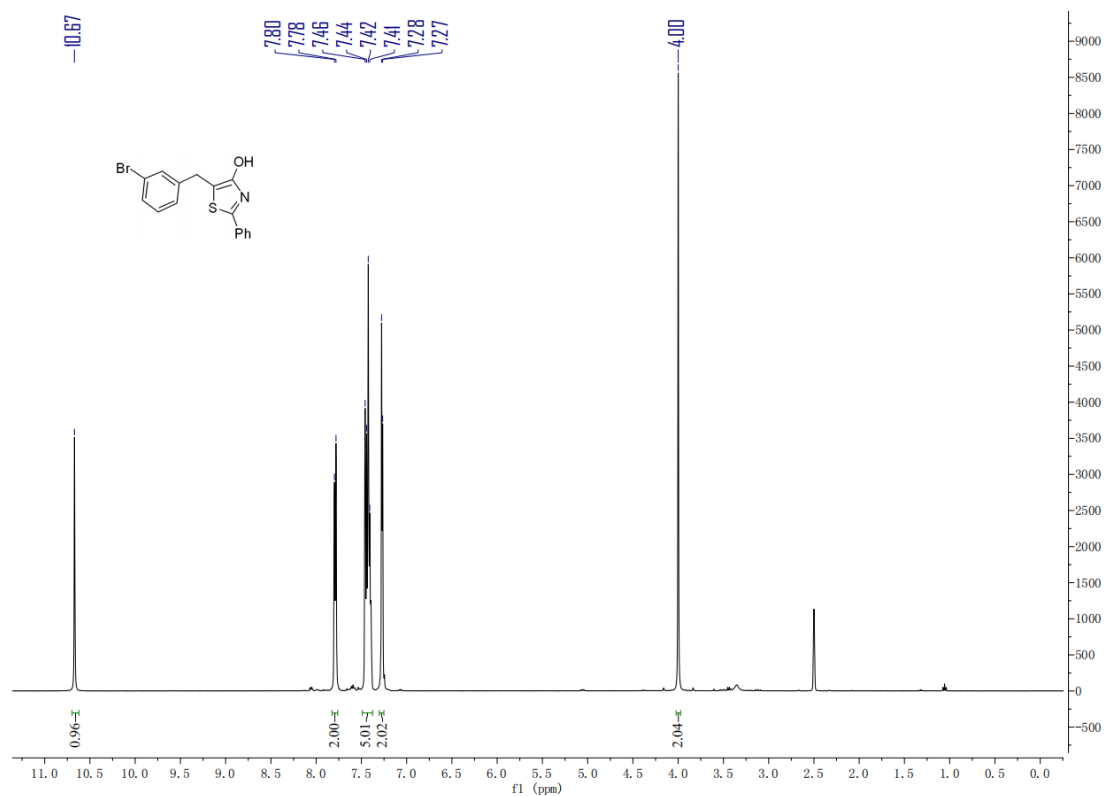
5-(4-methylbenzyl)-2-phenylthiazol-4-ol (1k)



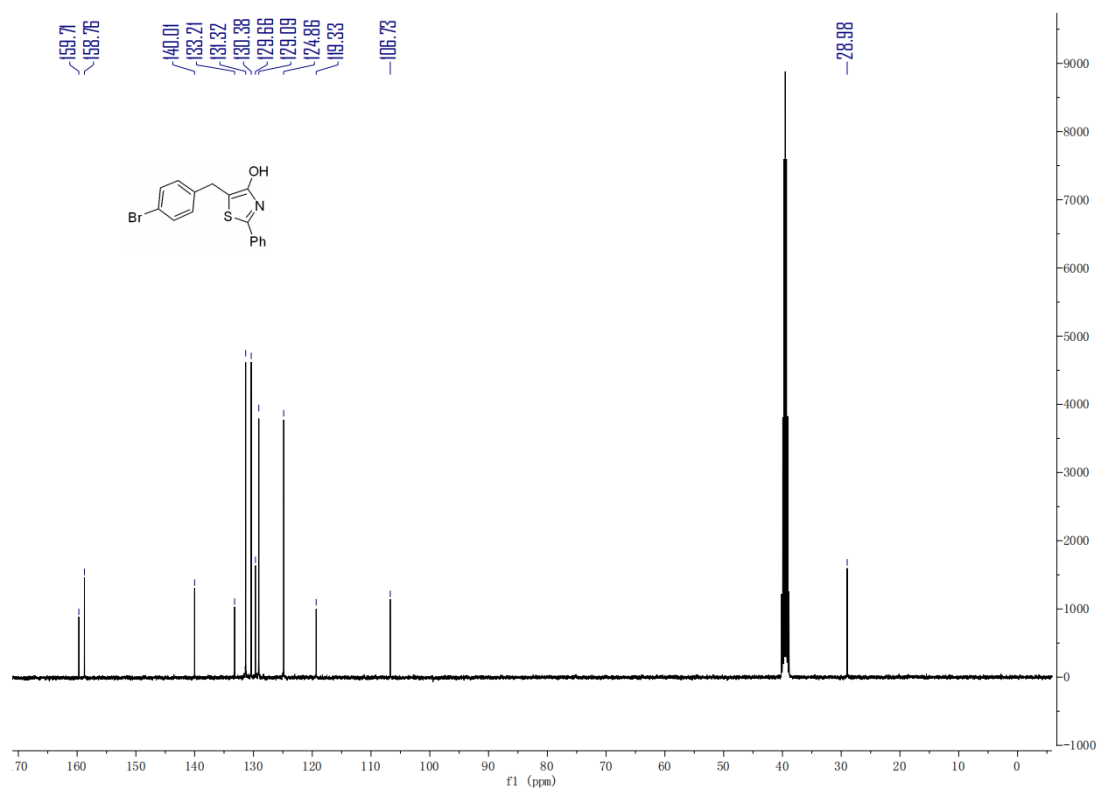
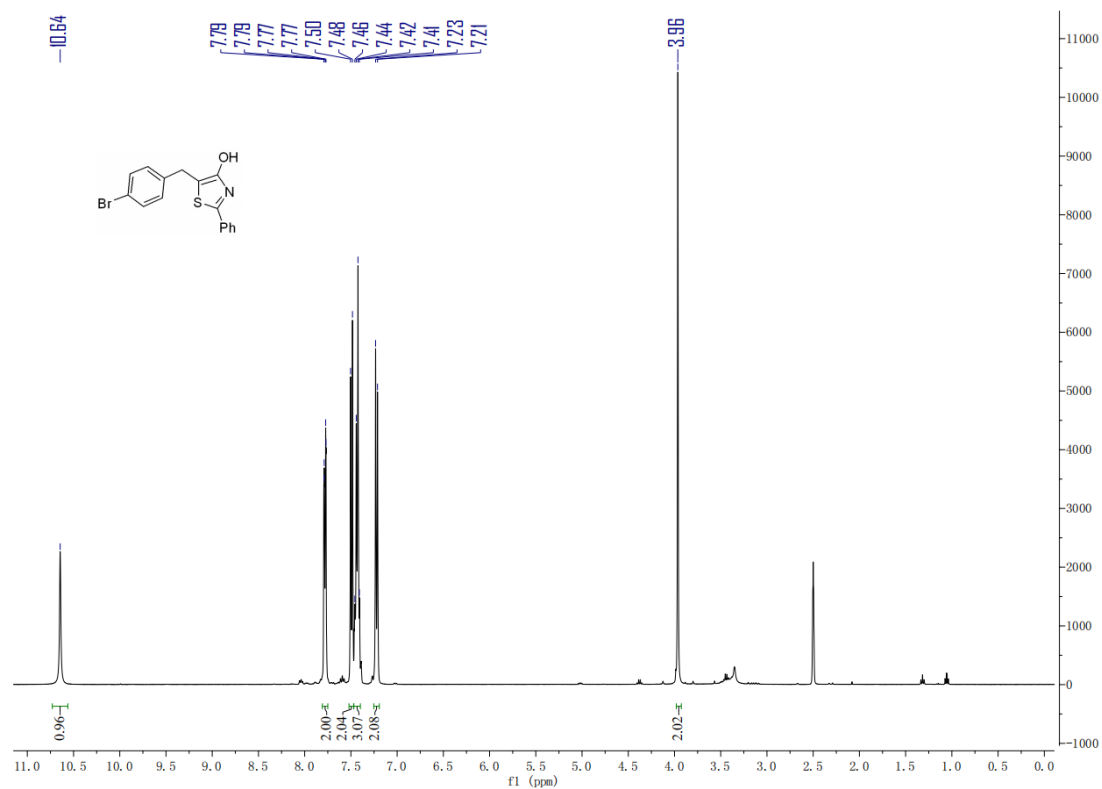
5-(2-bromobenzyl)-2-phenylthiazol-4-ol (11)



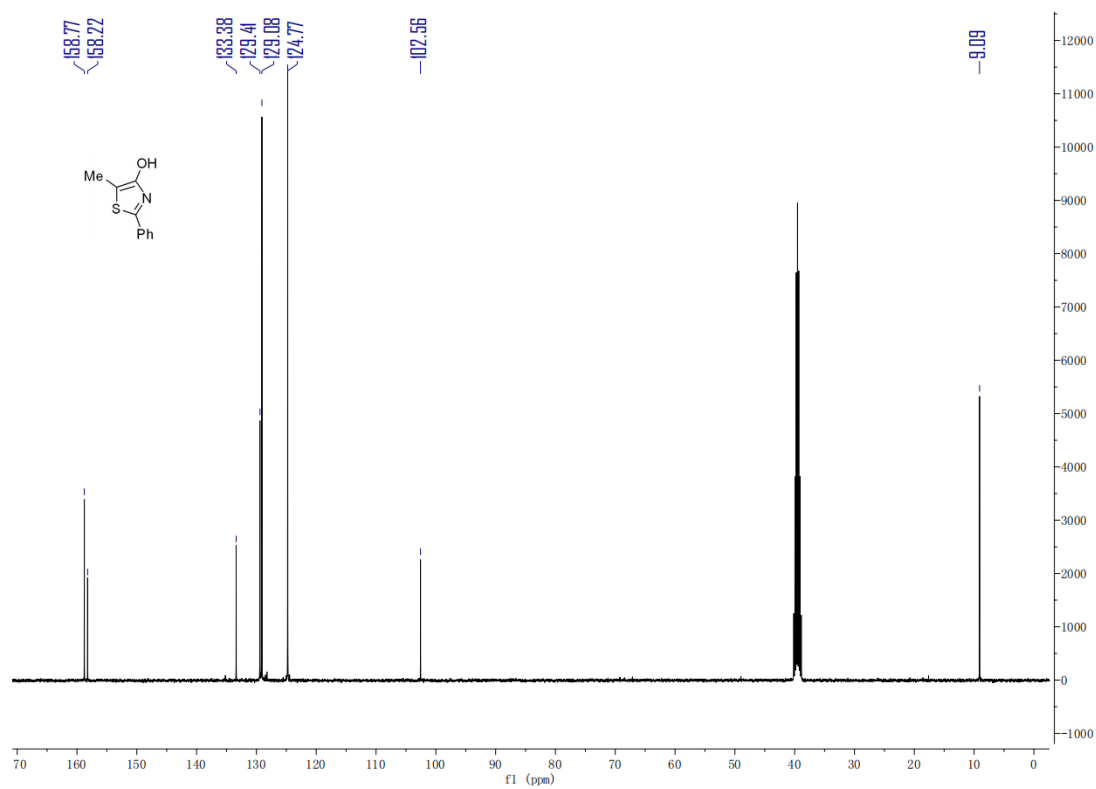
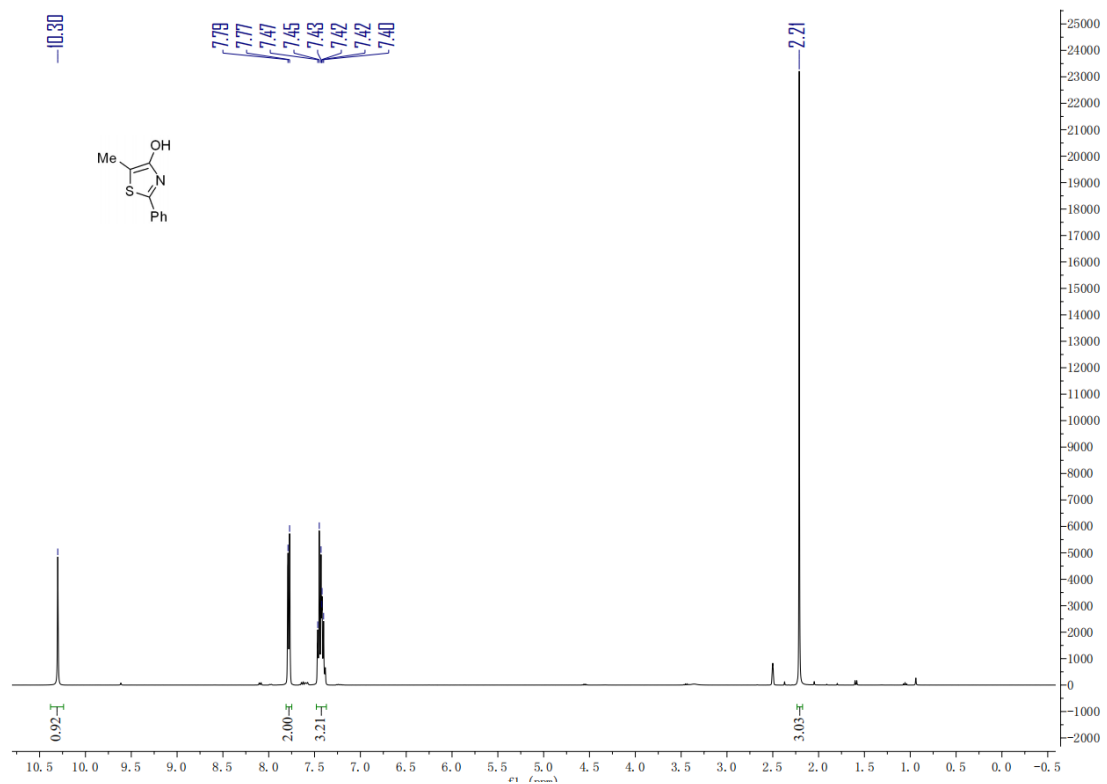
5-(3-bromobenzyl)-2-phenylthiazol-4-ol (1m)



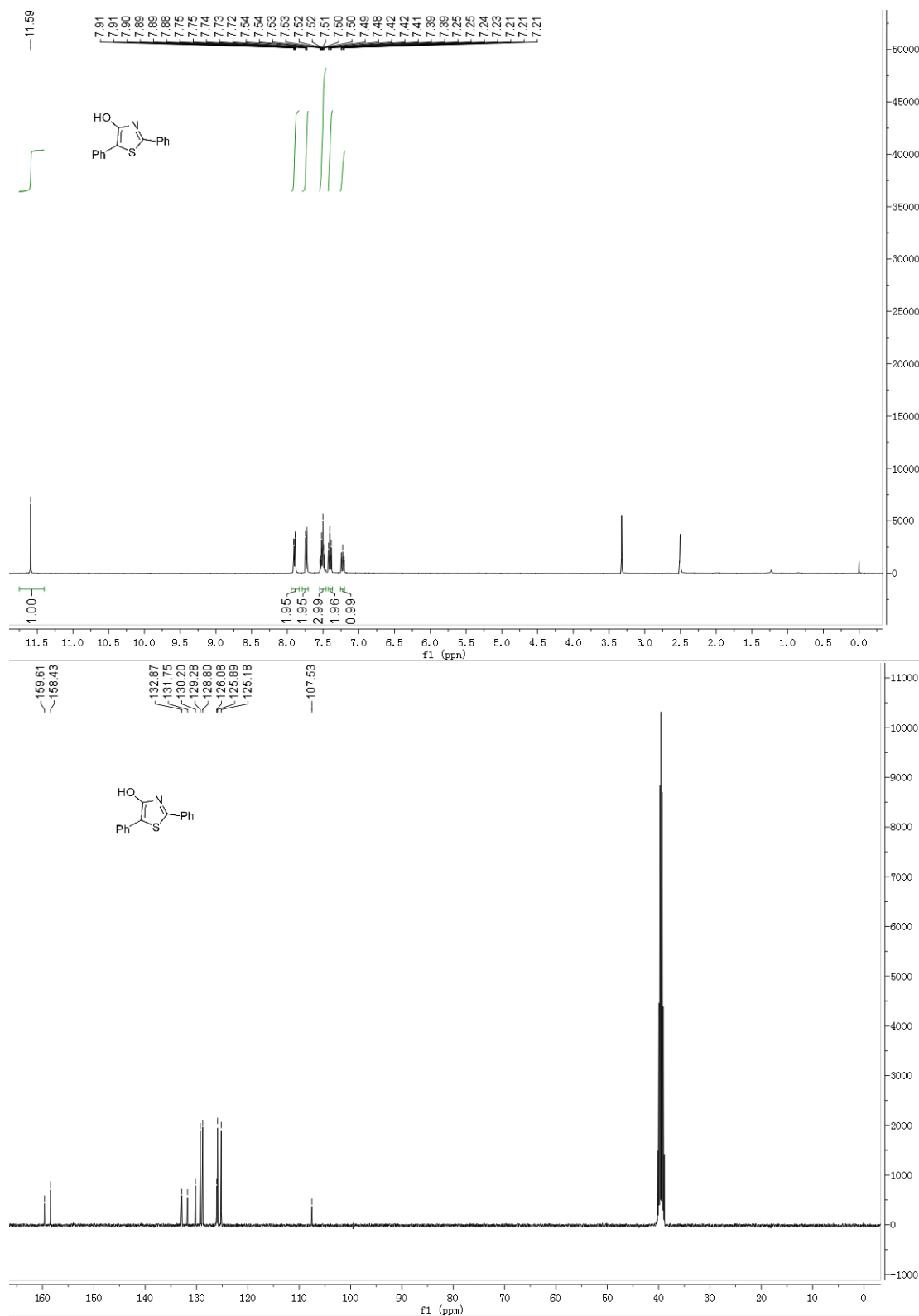
5-(4-bromobenzyl)-2-phenylthiazol-4-ol (1n)

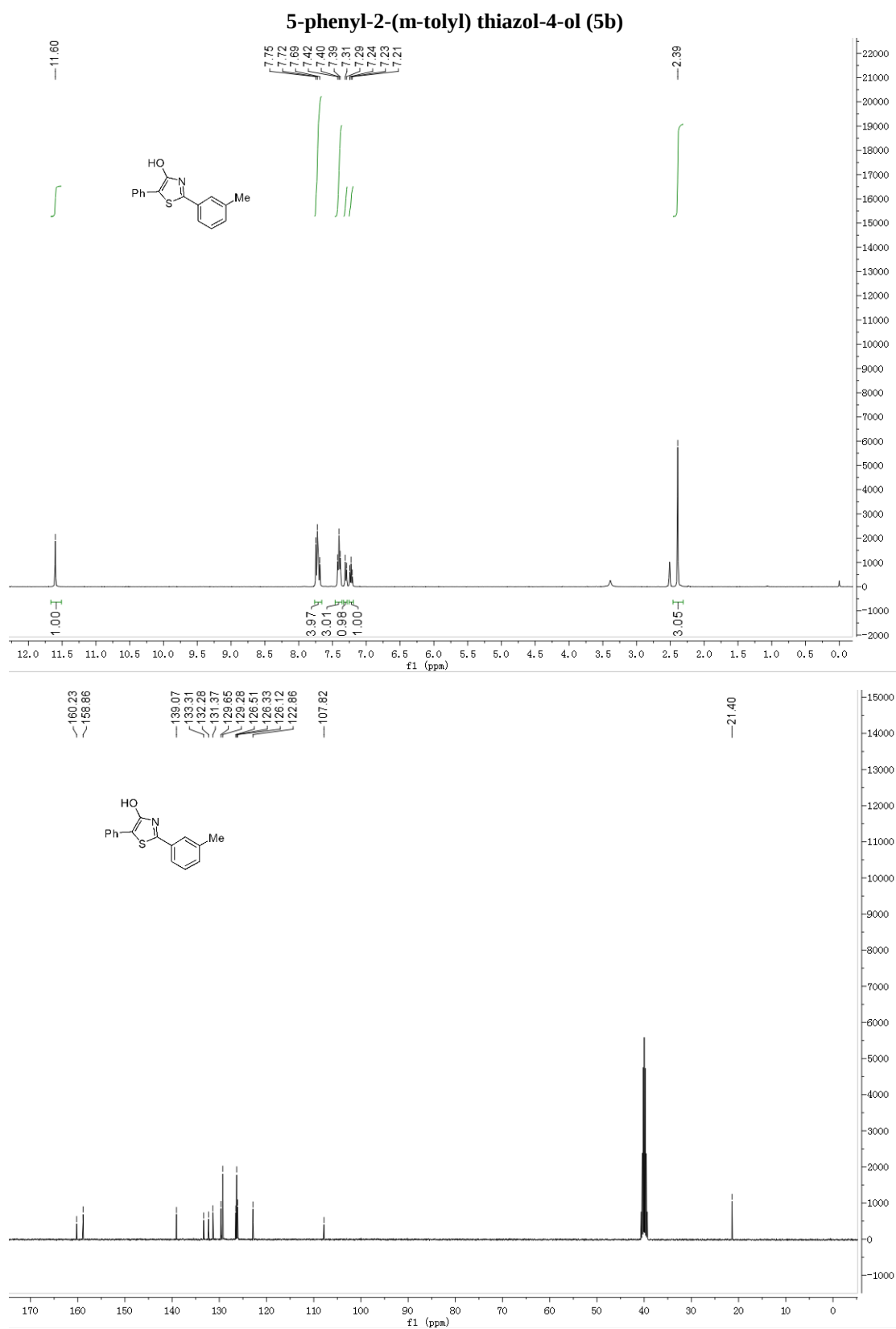


5-methyl-2-phenylthiazol-4-ol (1o)

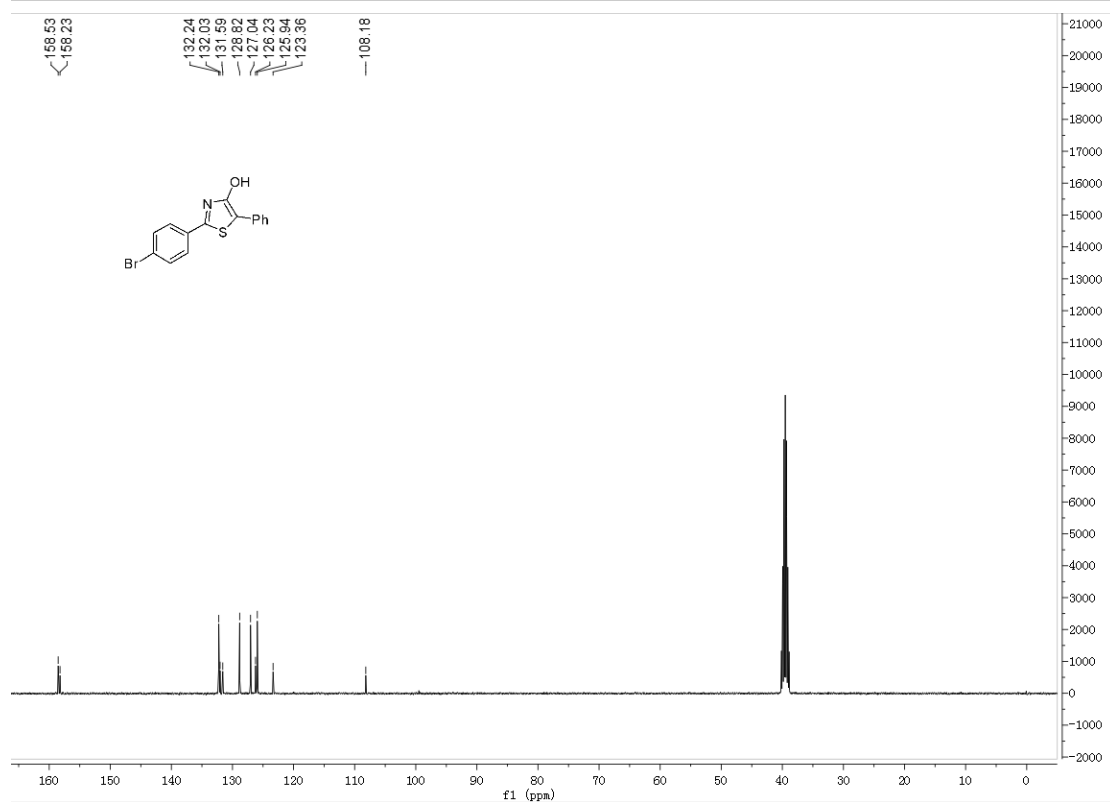
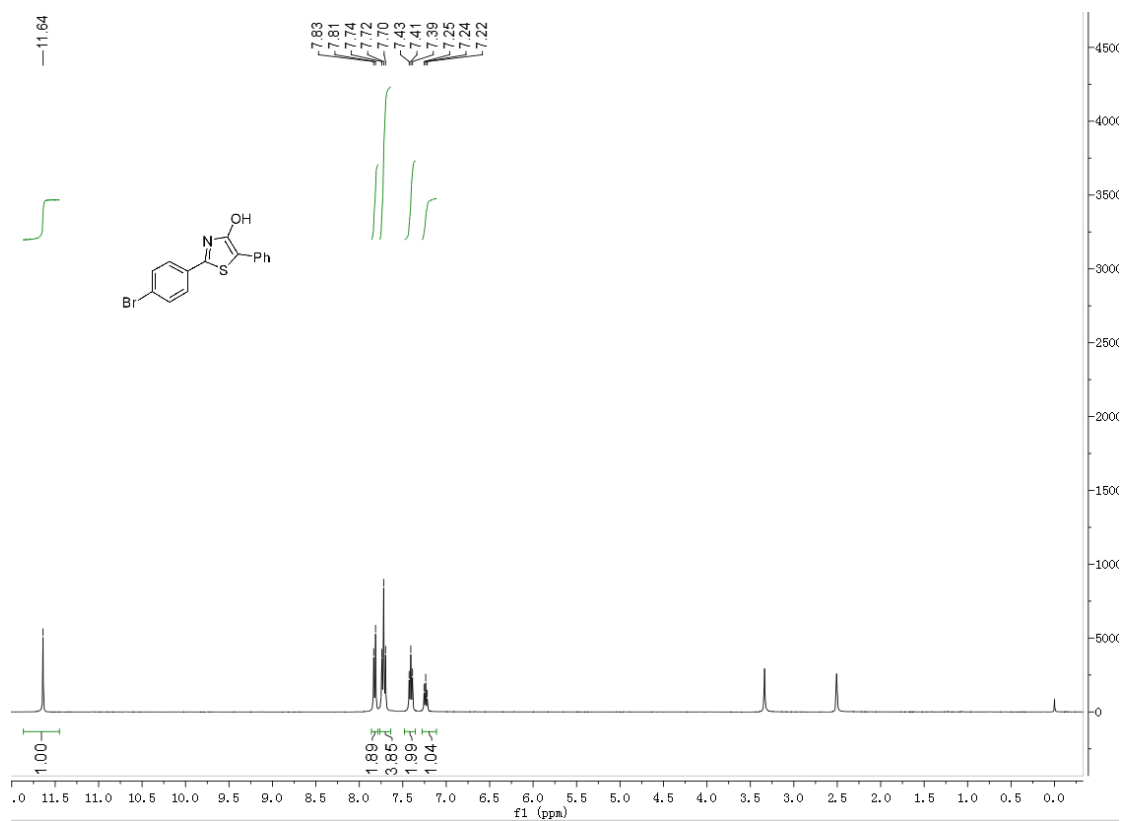


2,5-diphenylthiazol-4-ol (5a)

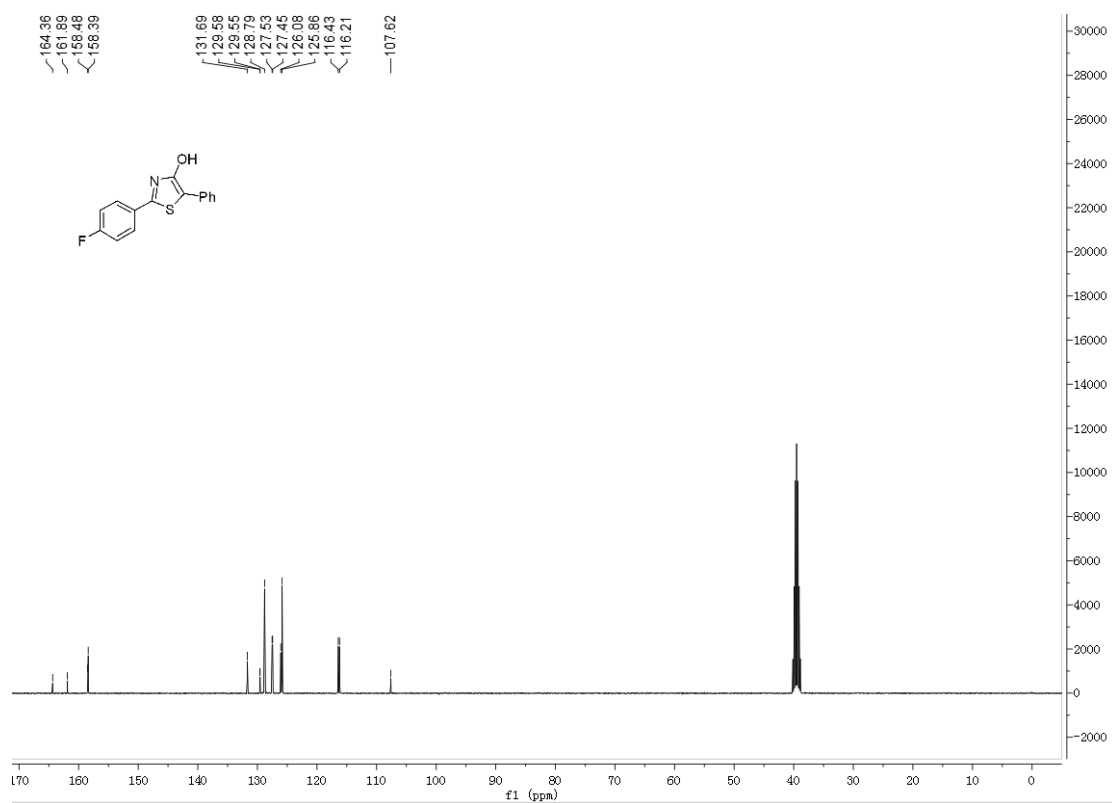
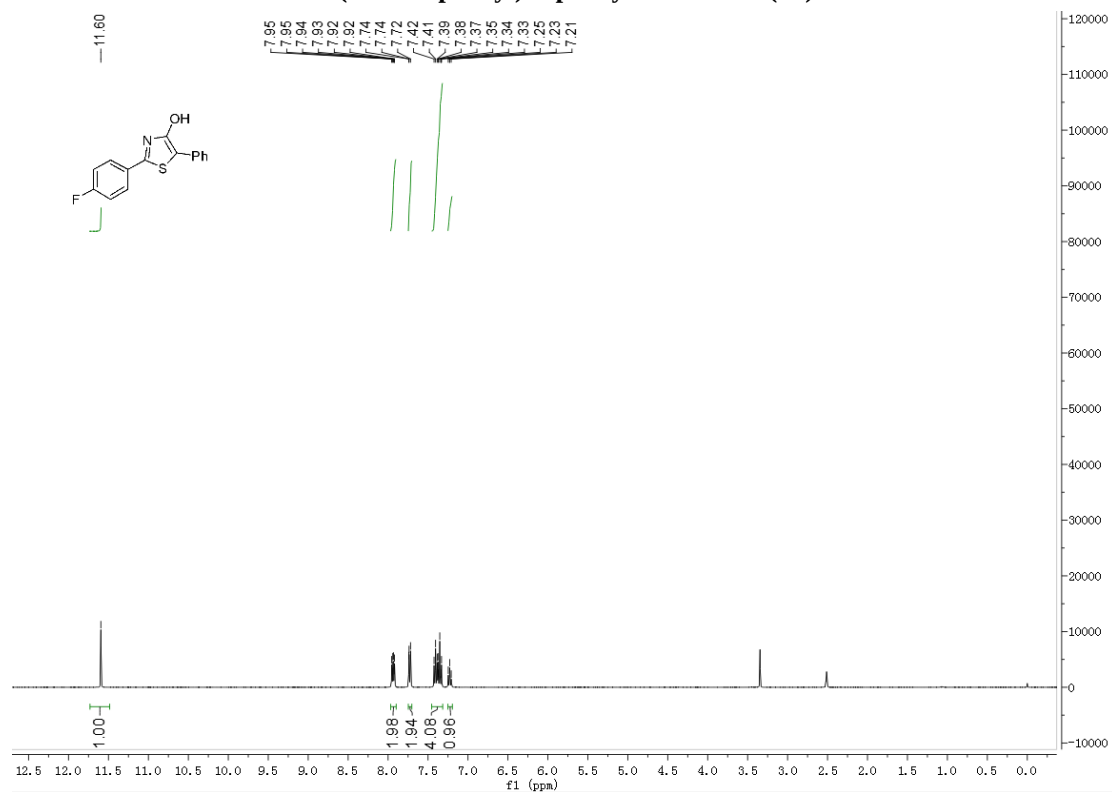




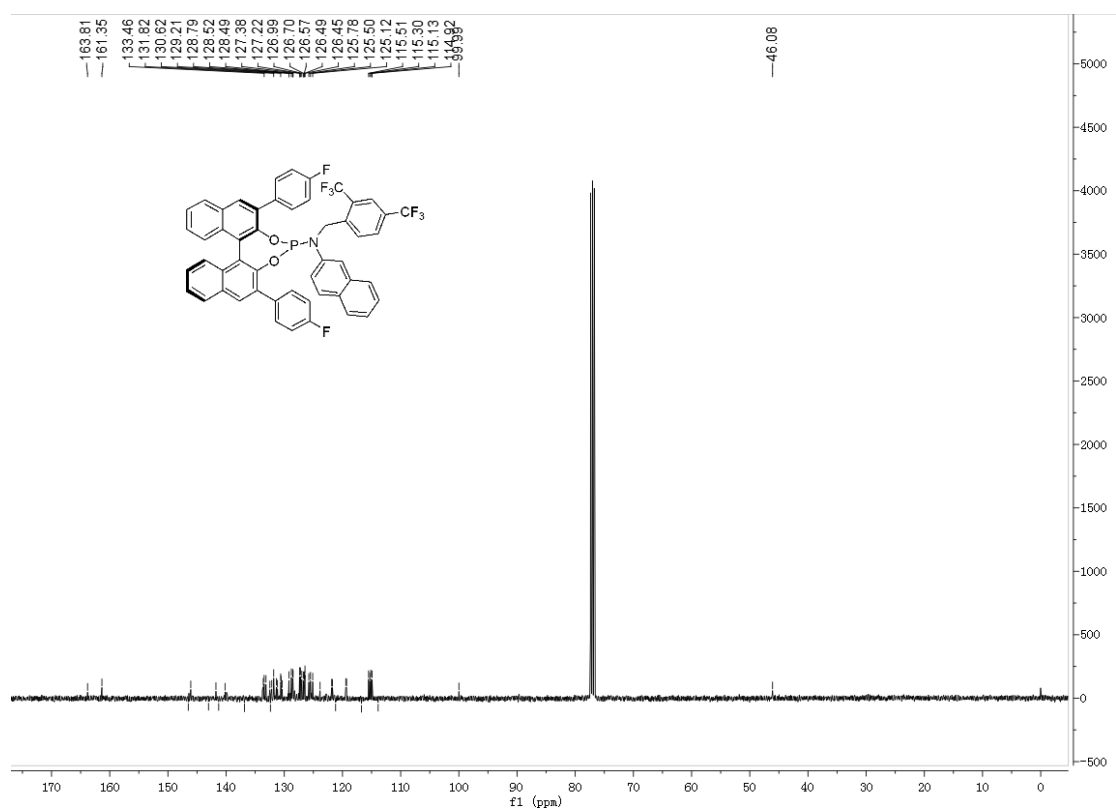
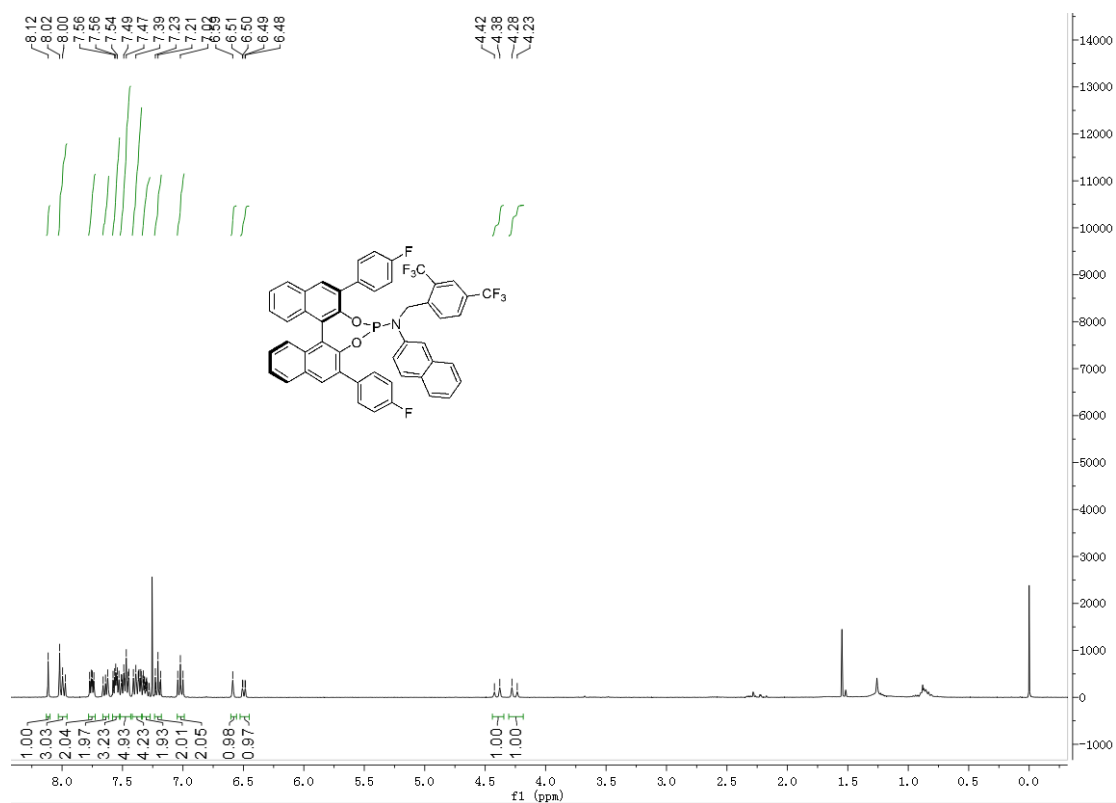
2-(4-bromophenyl)-5-phenylthiazol-4-ol (5c)

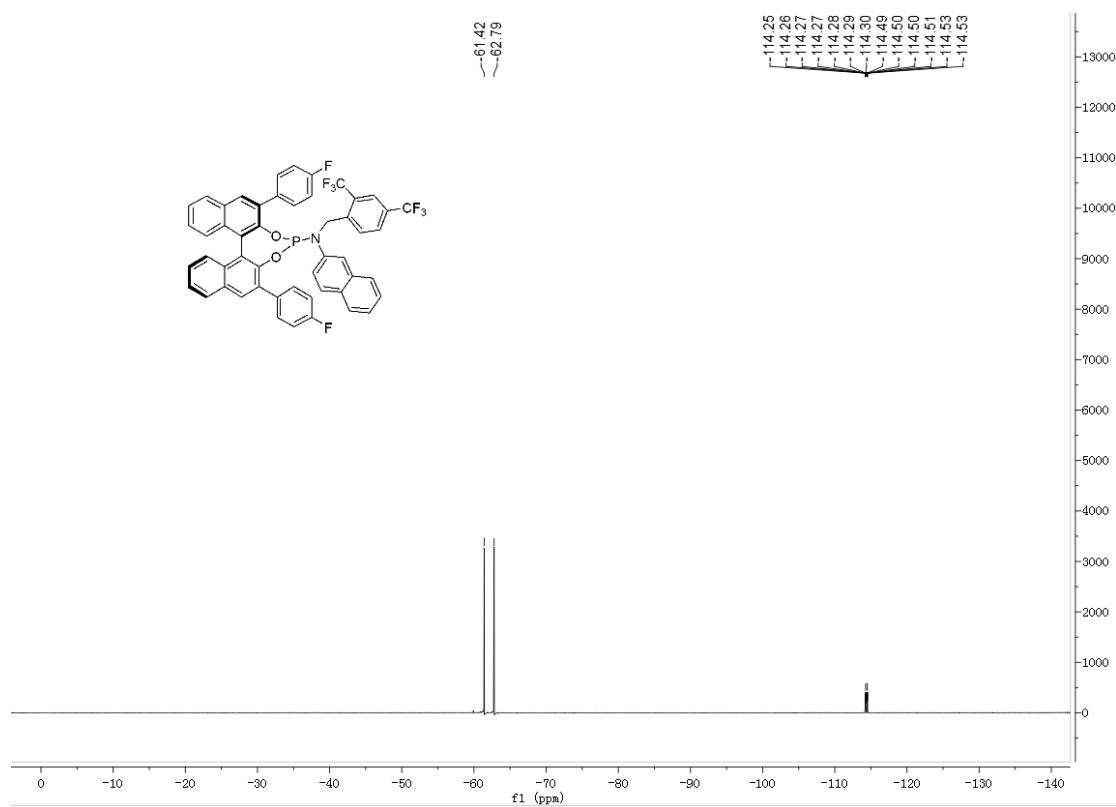
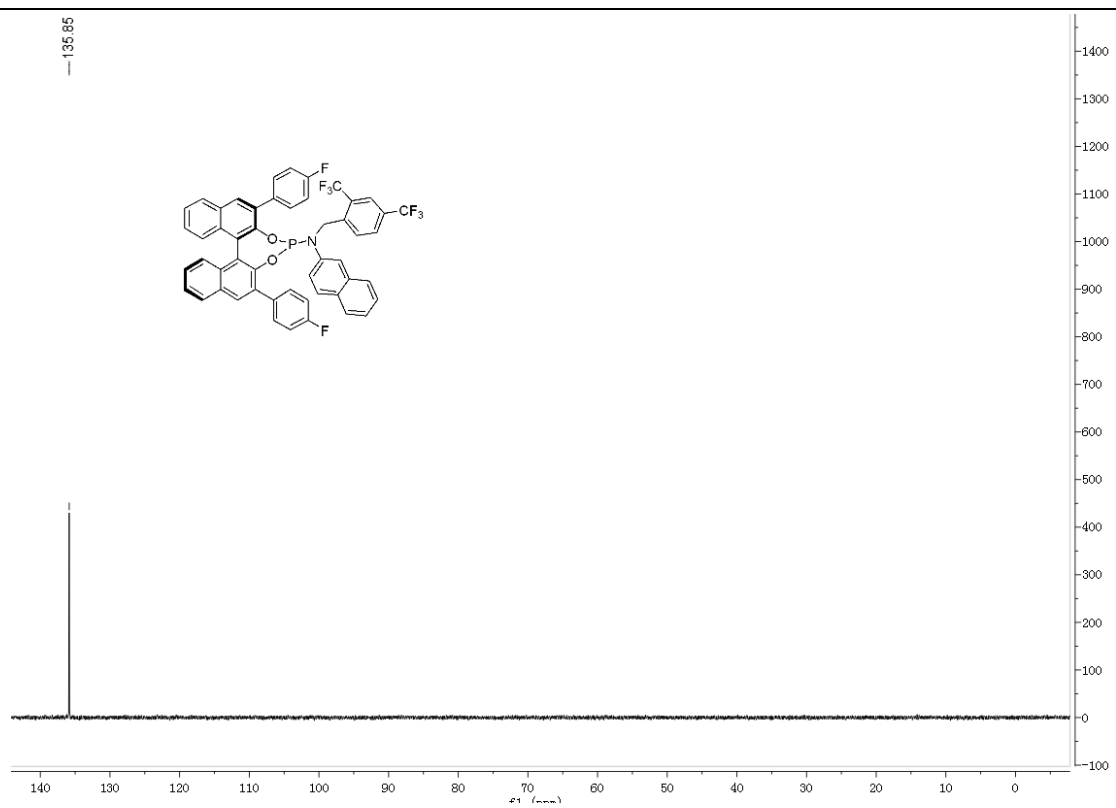


2-(4-fluorophenyl)-5-phenylthiazol-4-ol (5d)

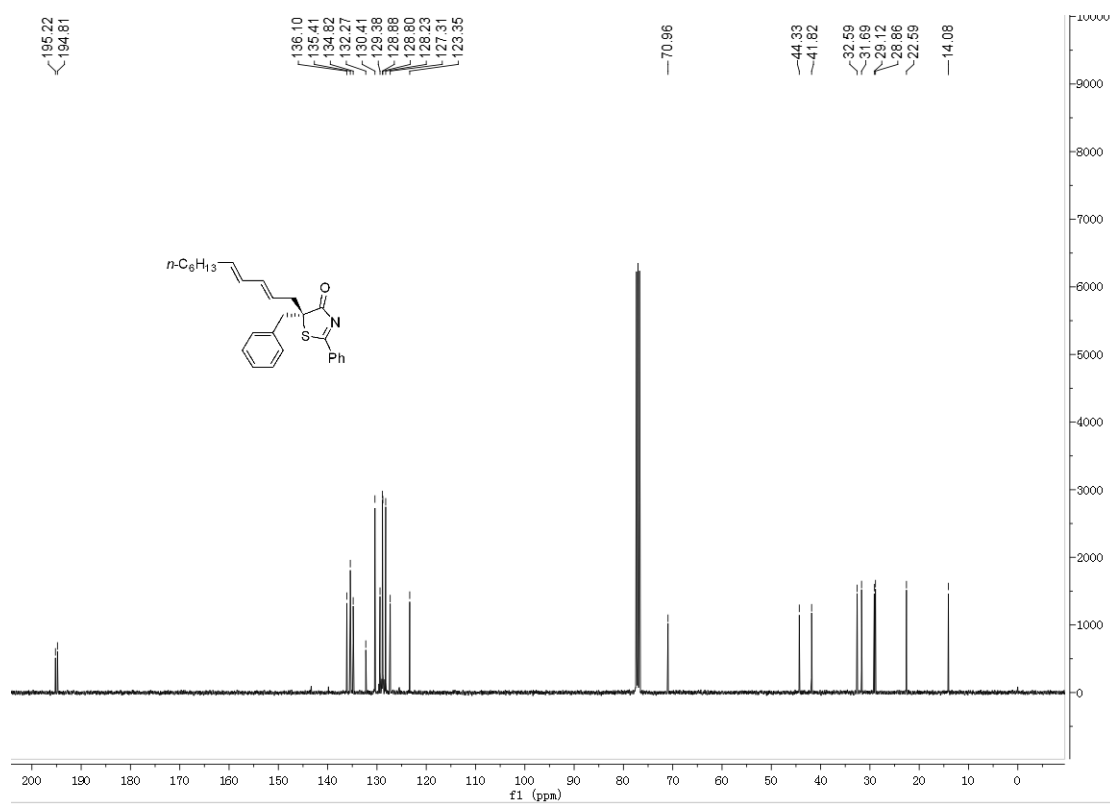
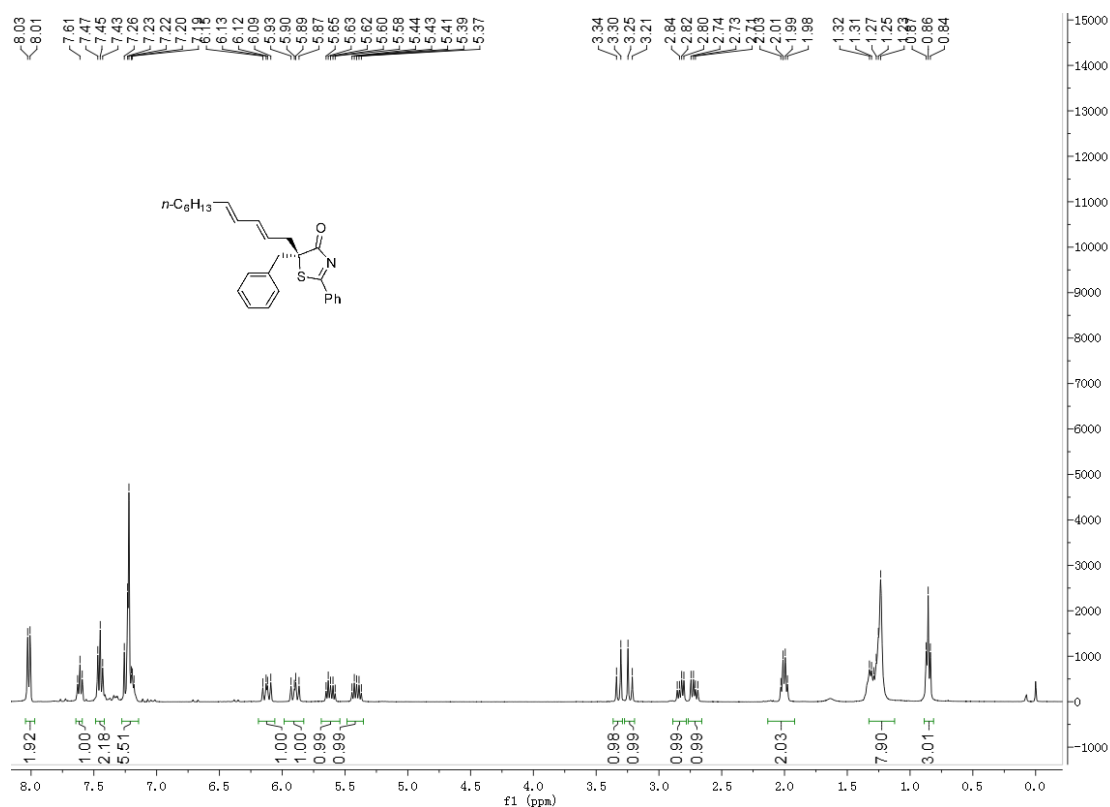


N-(2,4-bis(trifluoromethyl)benzyl)-2,6-bis(4-fluorophenyl)-N-(naphthalen-2-yl)dinaphtho[2,1-d':1',2'-f][1,3,2]dioxaphosphepin-4-amine (L1)

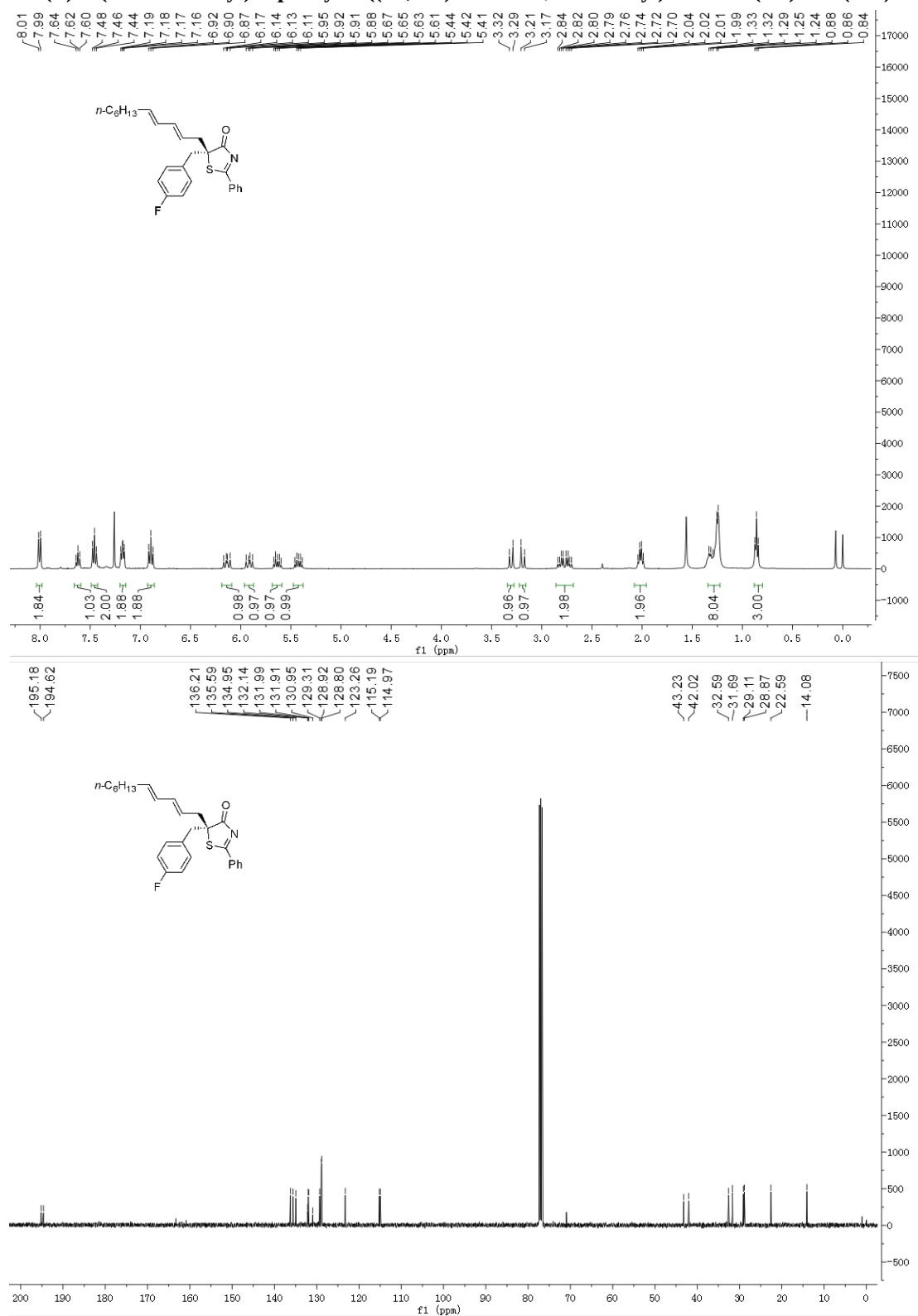




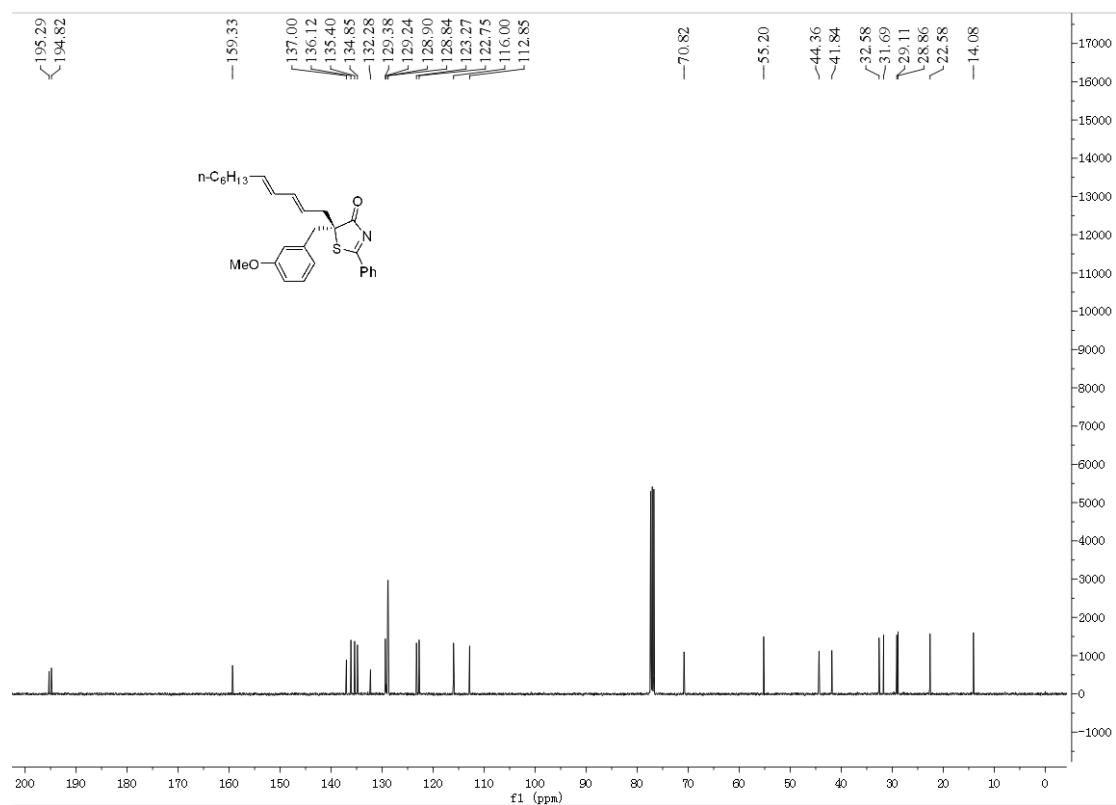
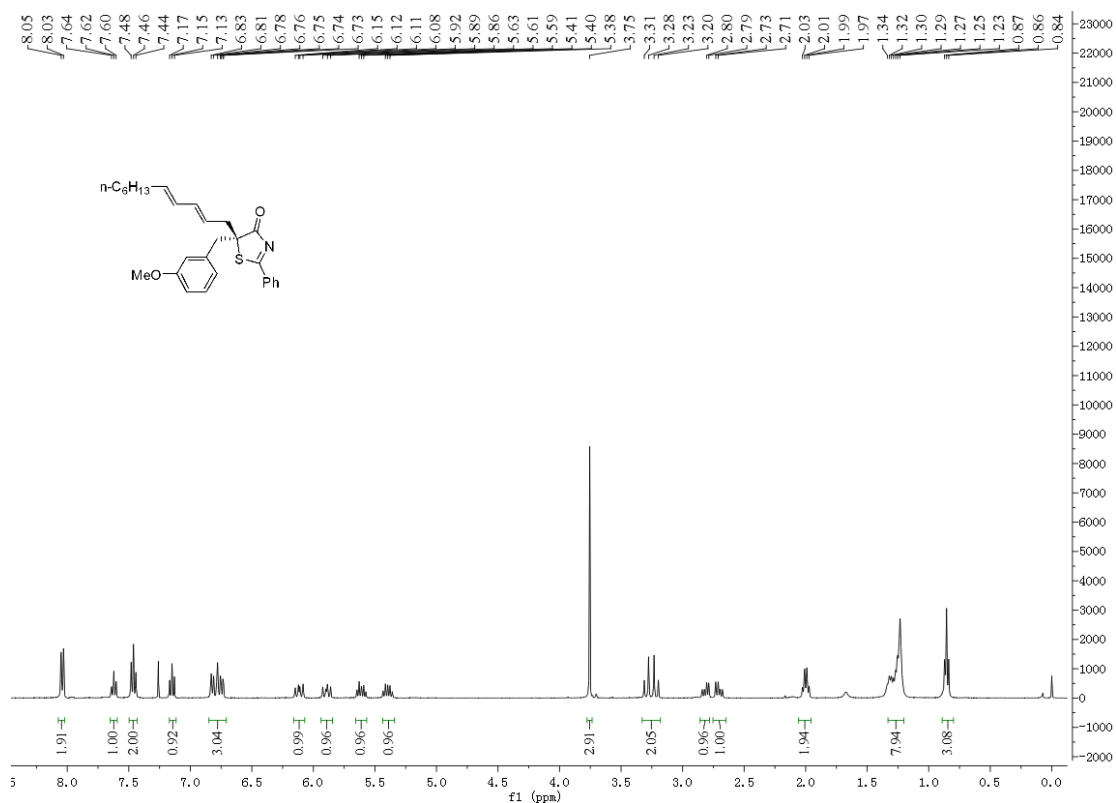
(R)-5-benzyl-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3aa)



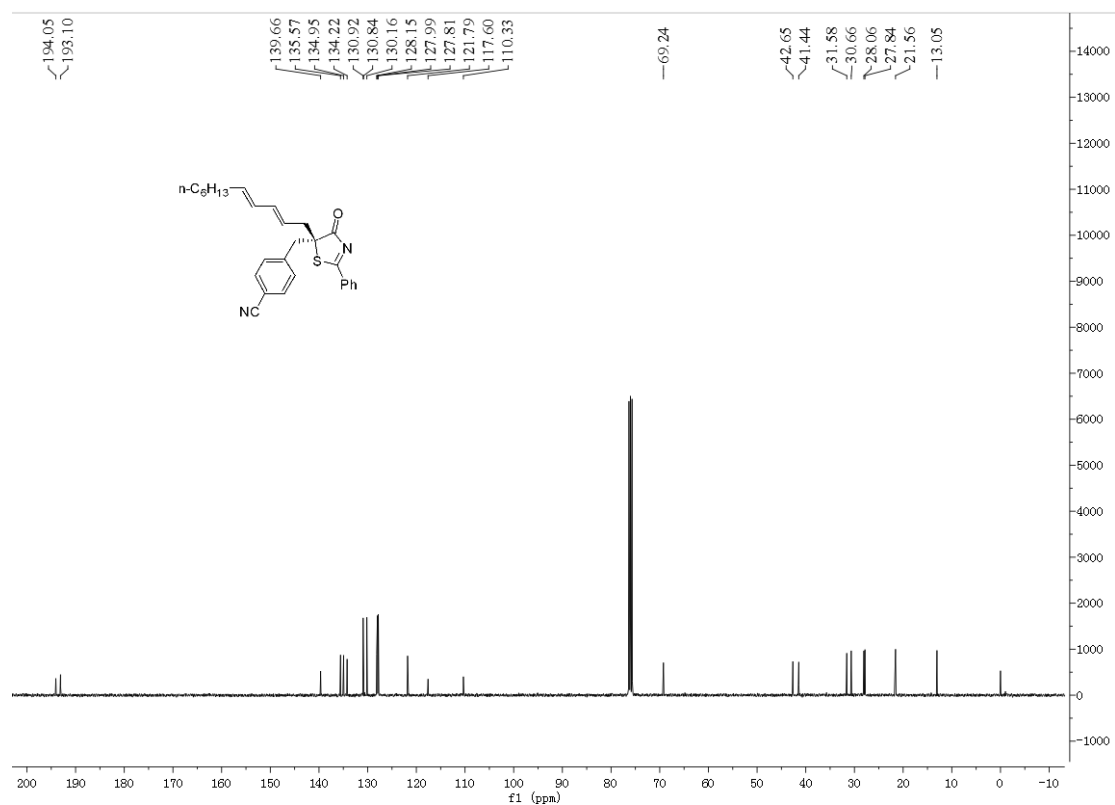
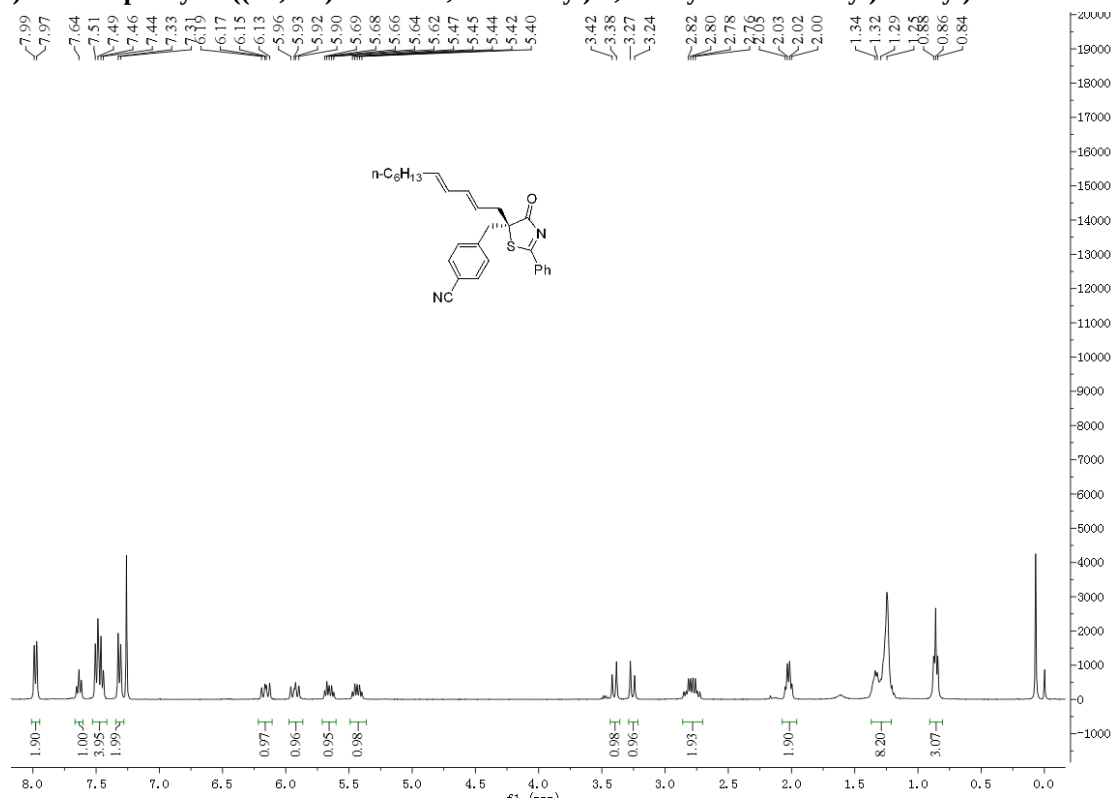
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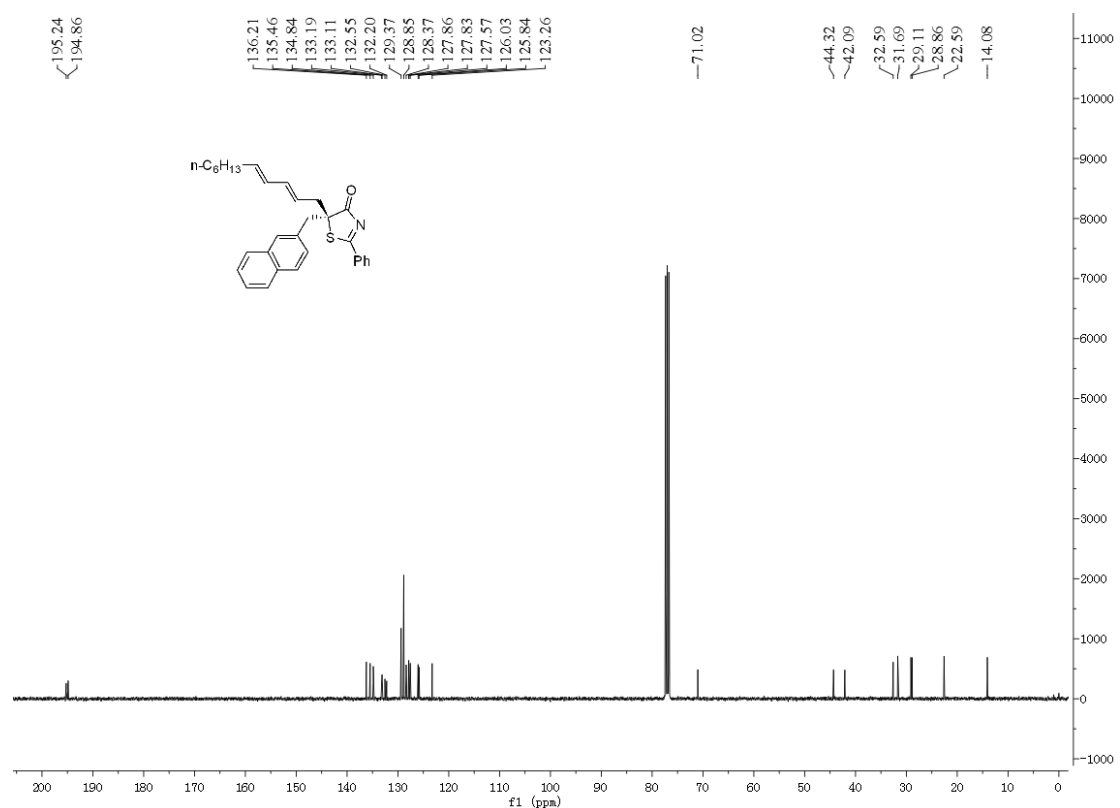
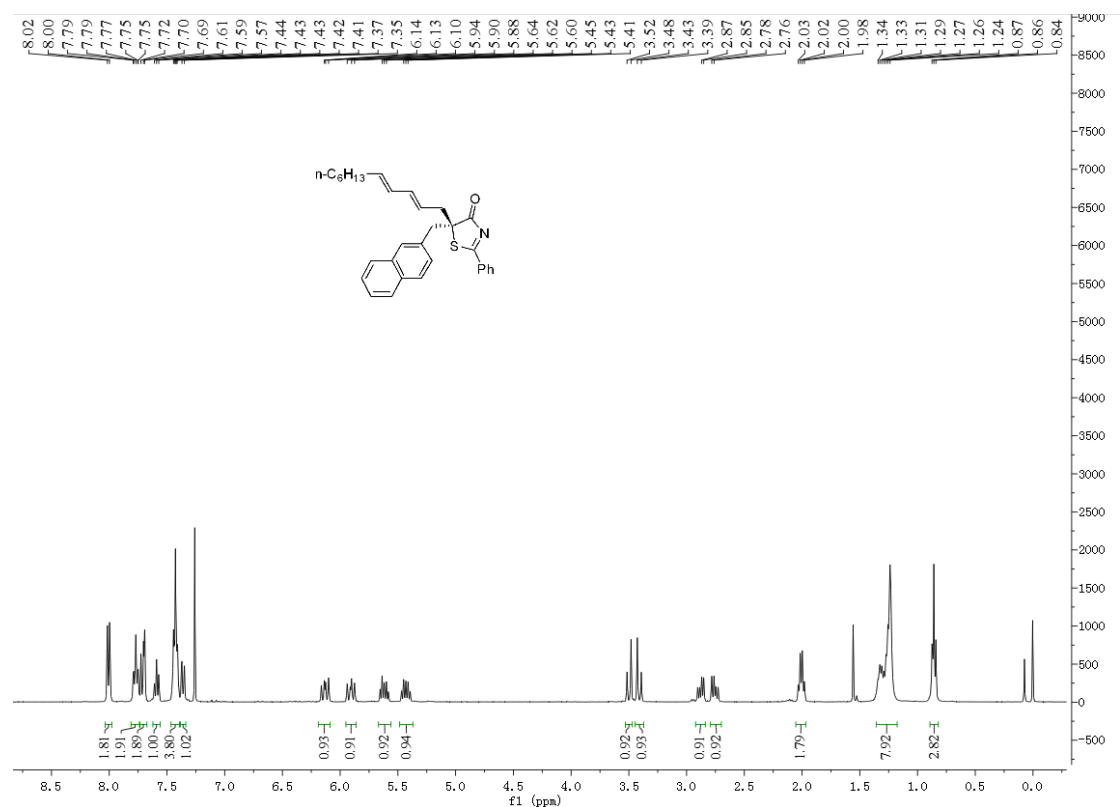
(R)-5-(3-methylbenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ca)



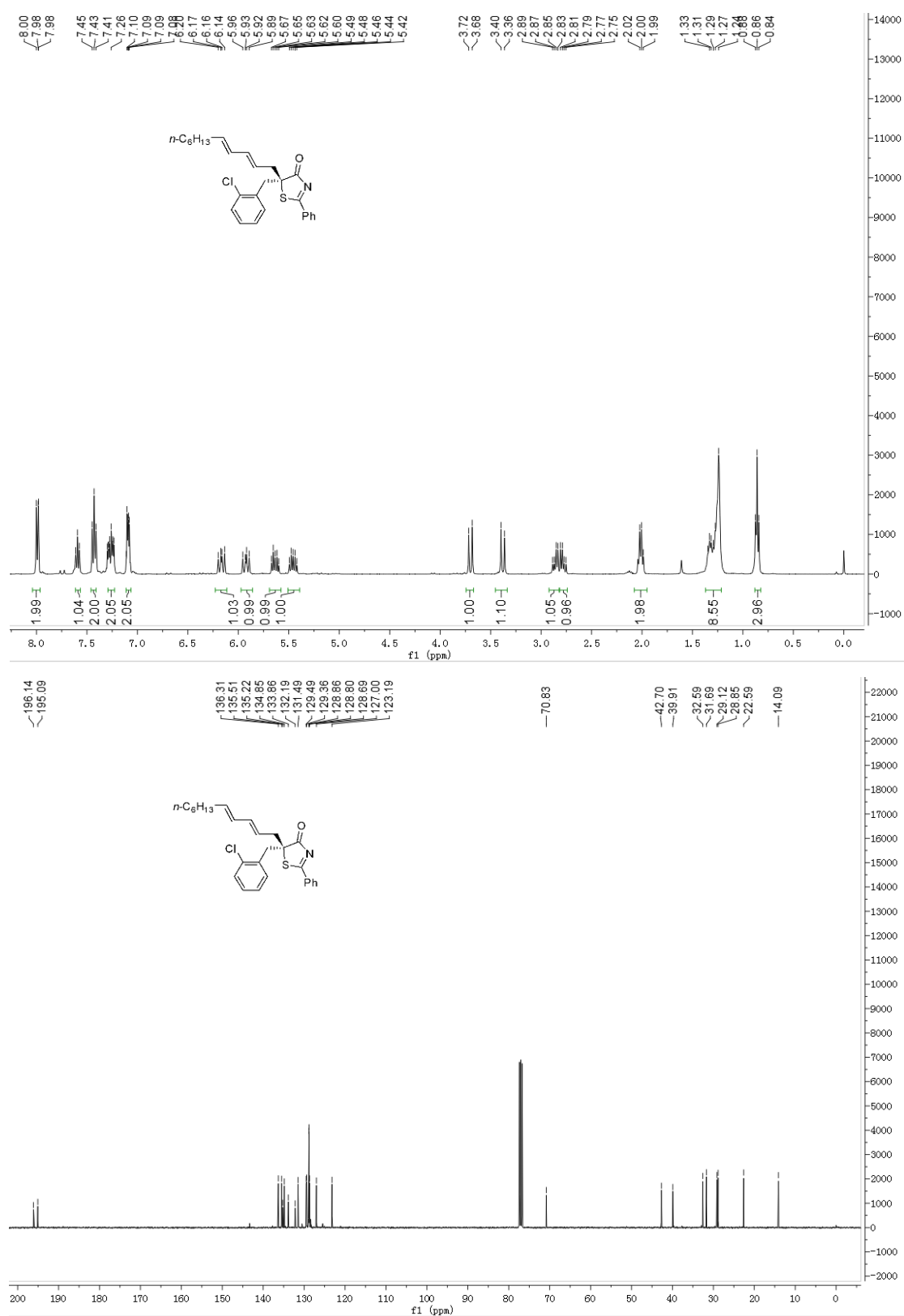
4-(((R)-4-oxo-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl)-4, 5-dihydrothiazol-5-yl) methyl) Benzonitrile (3da)



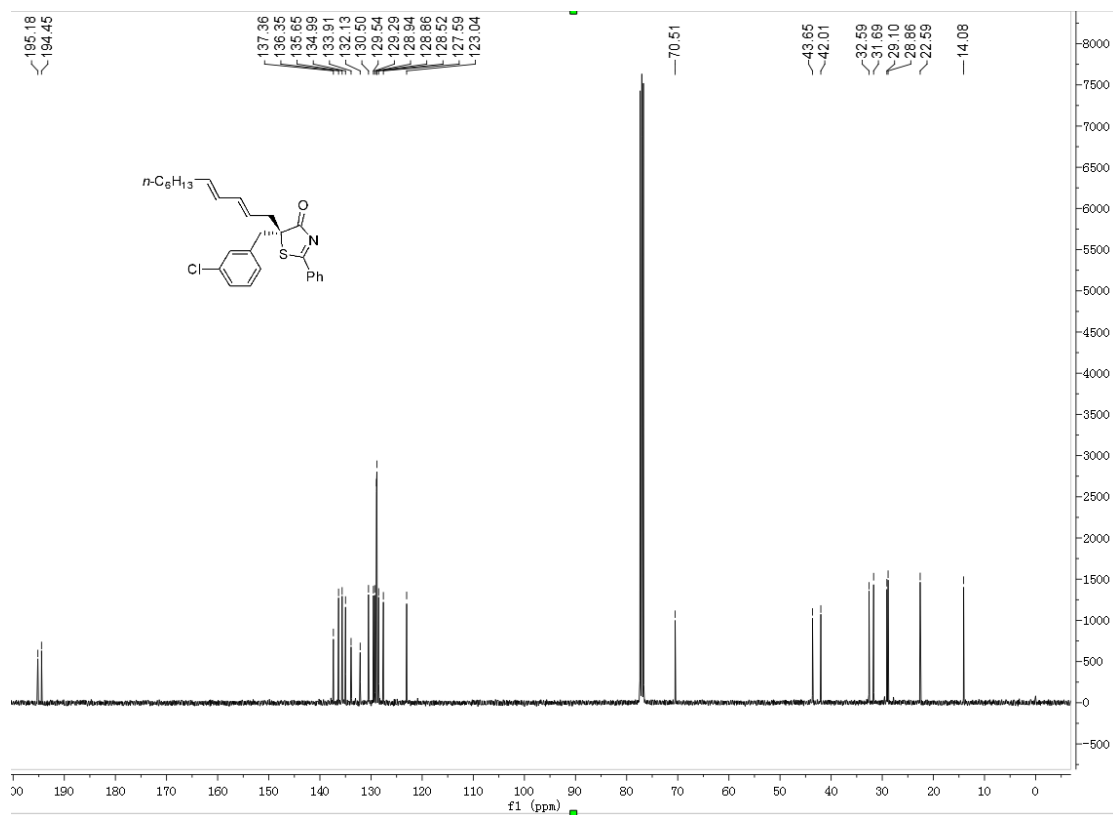
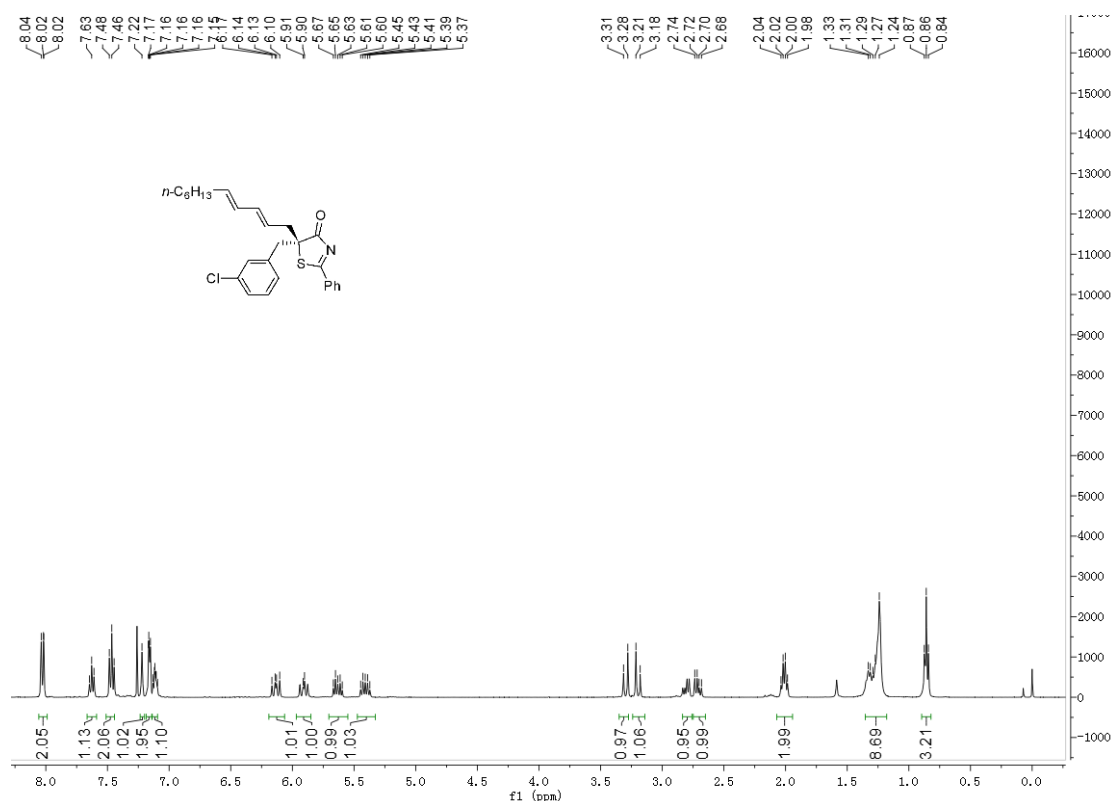
(R)-5-(naphthalen-2-ylmethyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ea)



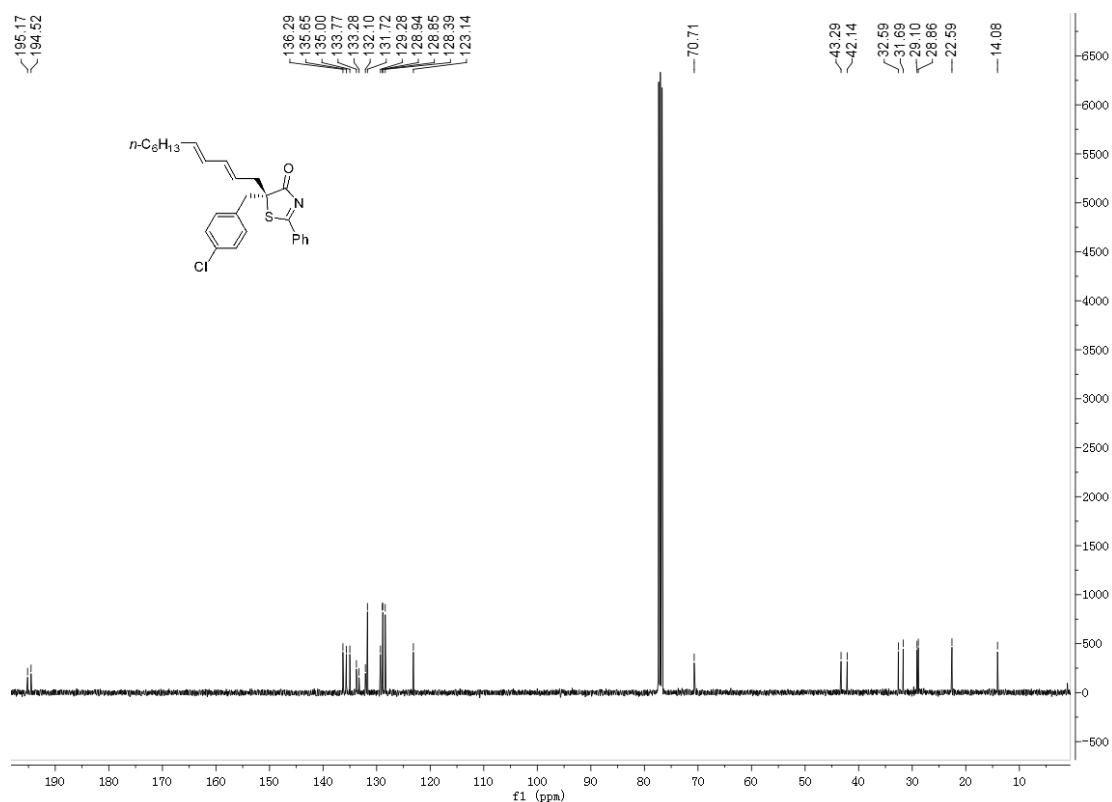
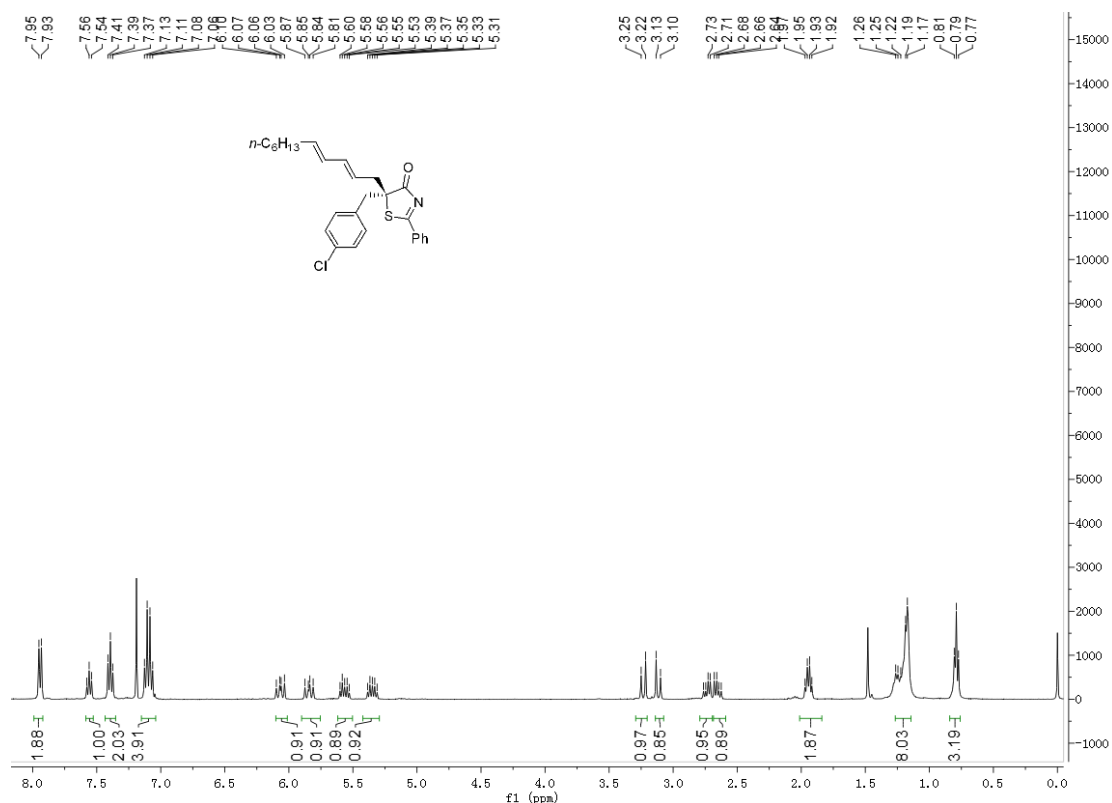
(R)-5-(2-chlorobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3fa)



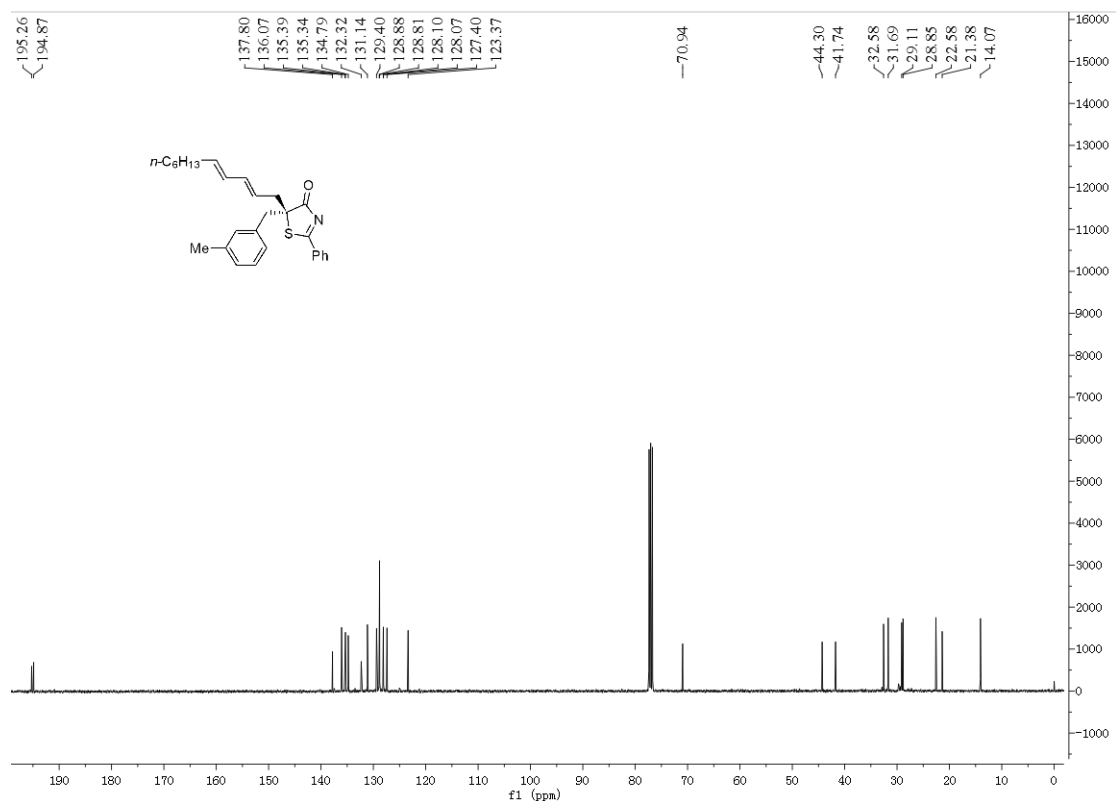
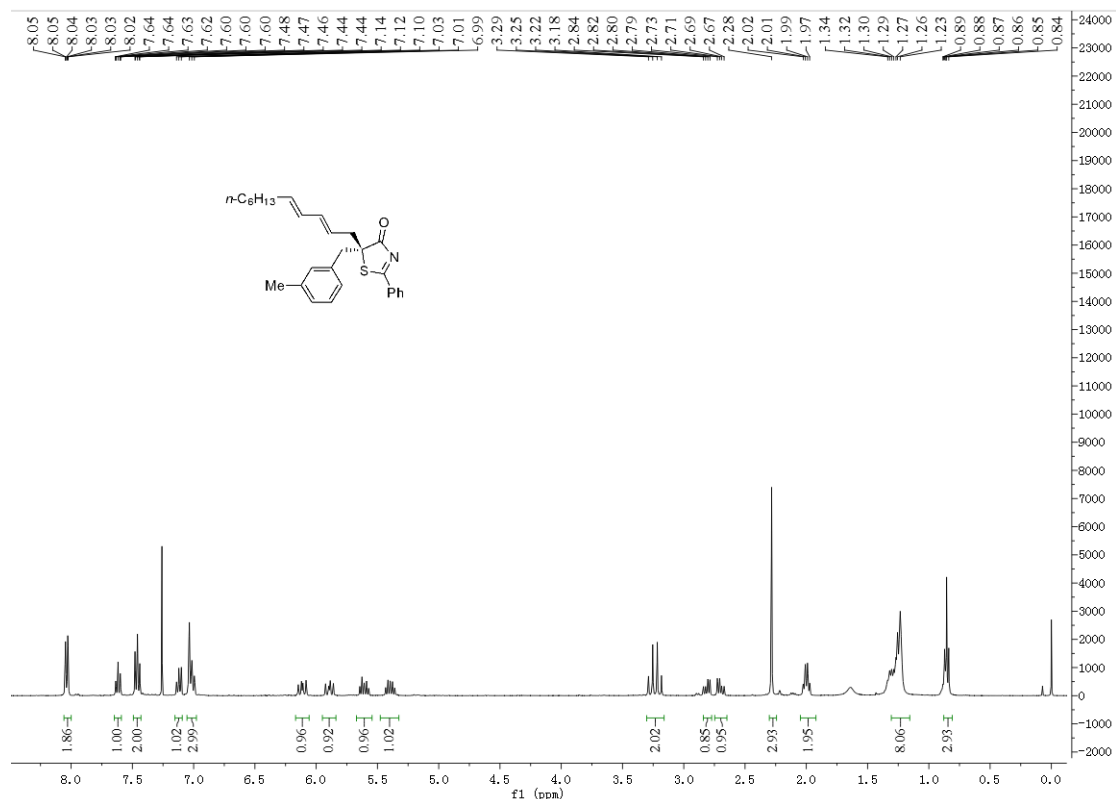
(R)-5-(3-chlorobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ga)



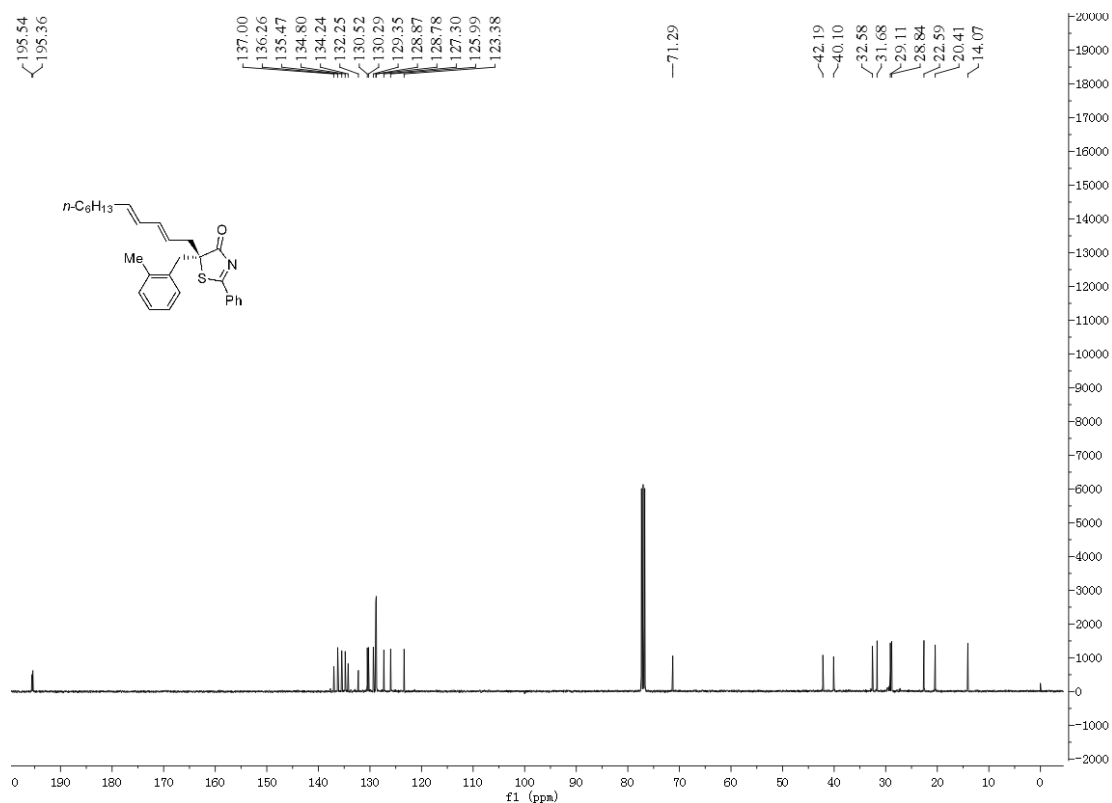
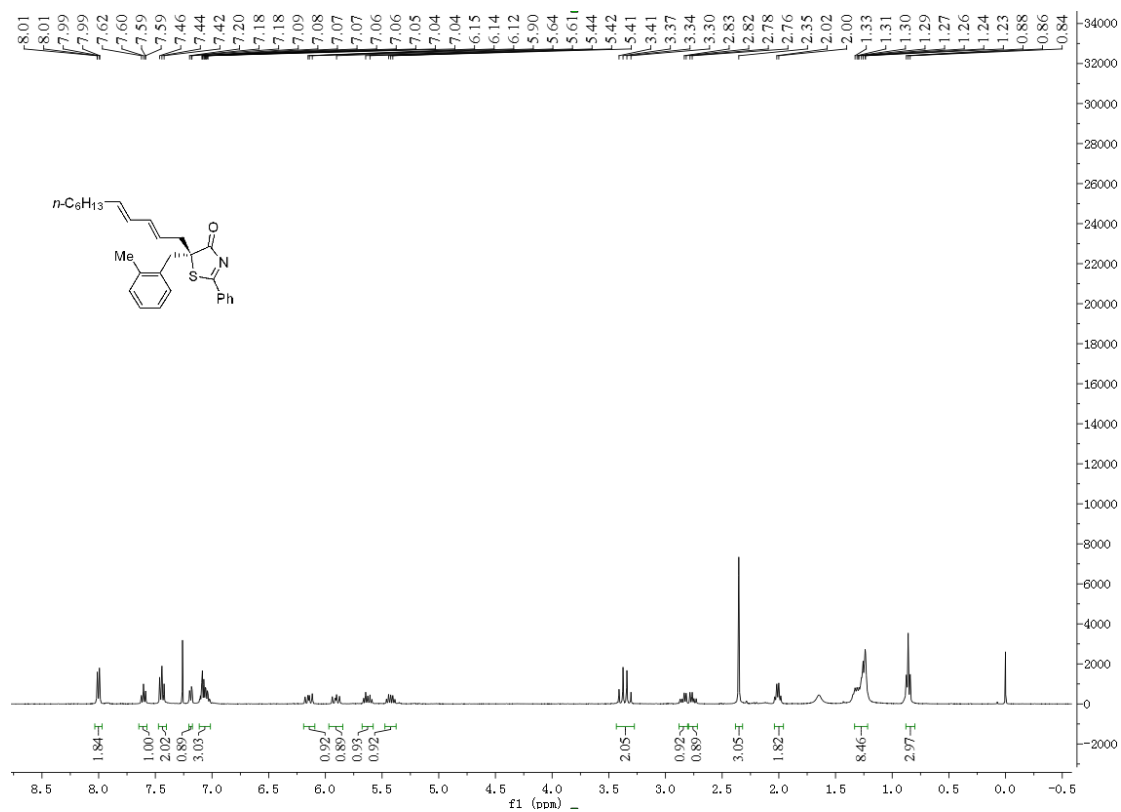
(R)-5-(4-chlorobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ha)



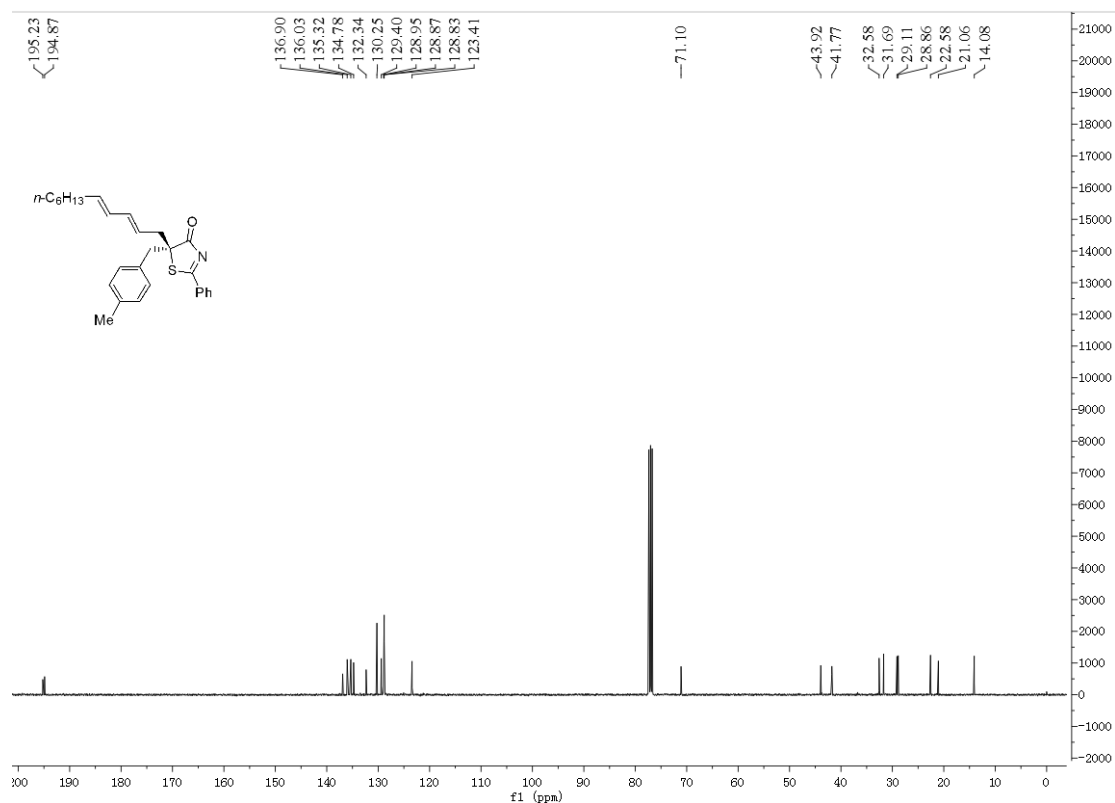
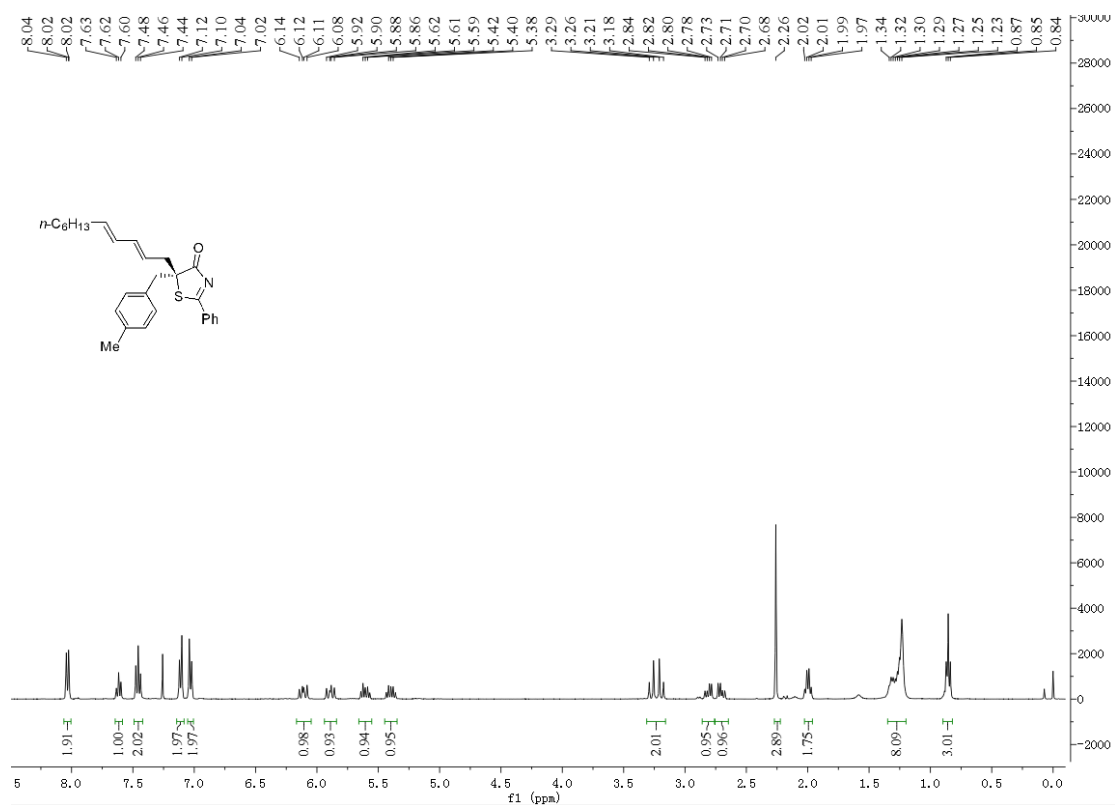
(R)-5-(3-methylbenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ia)



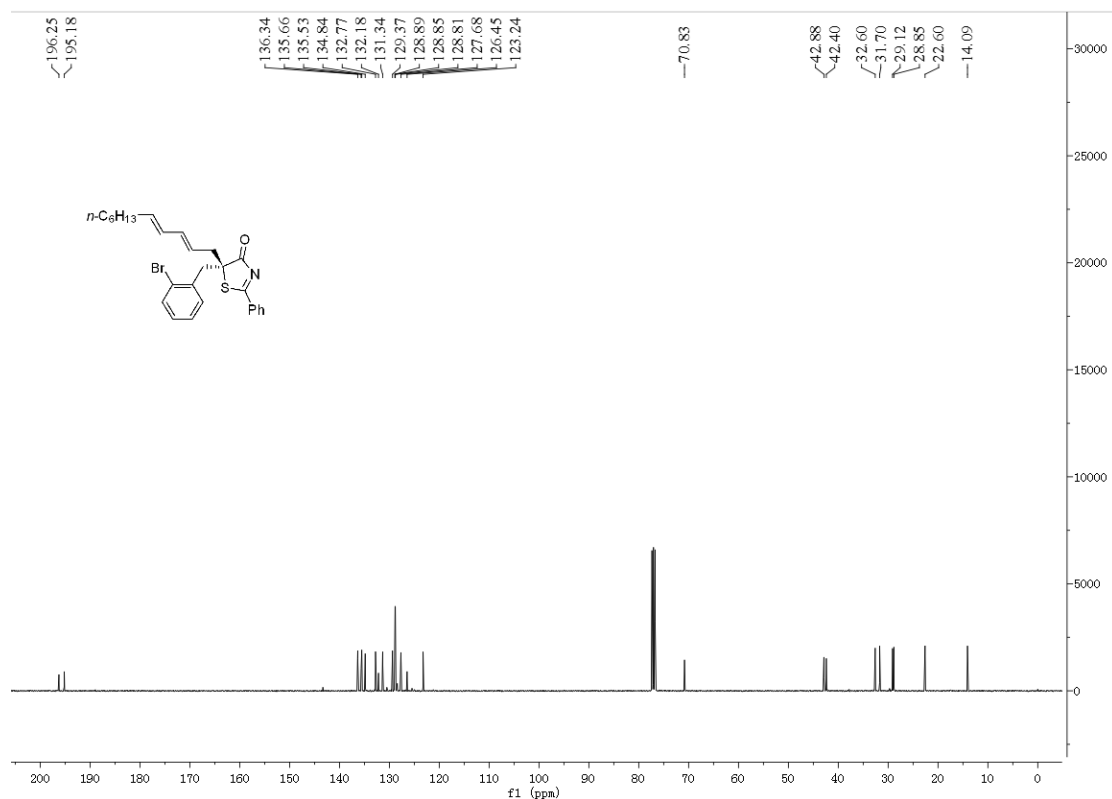
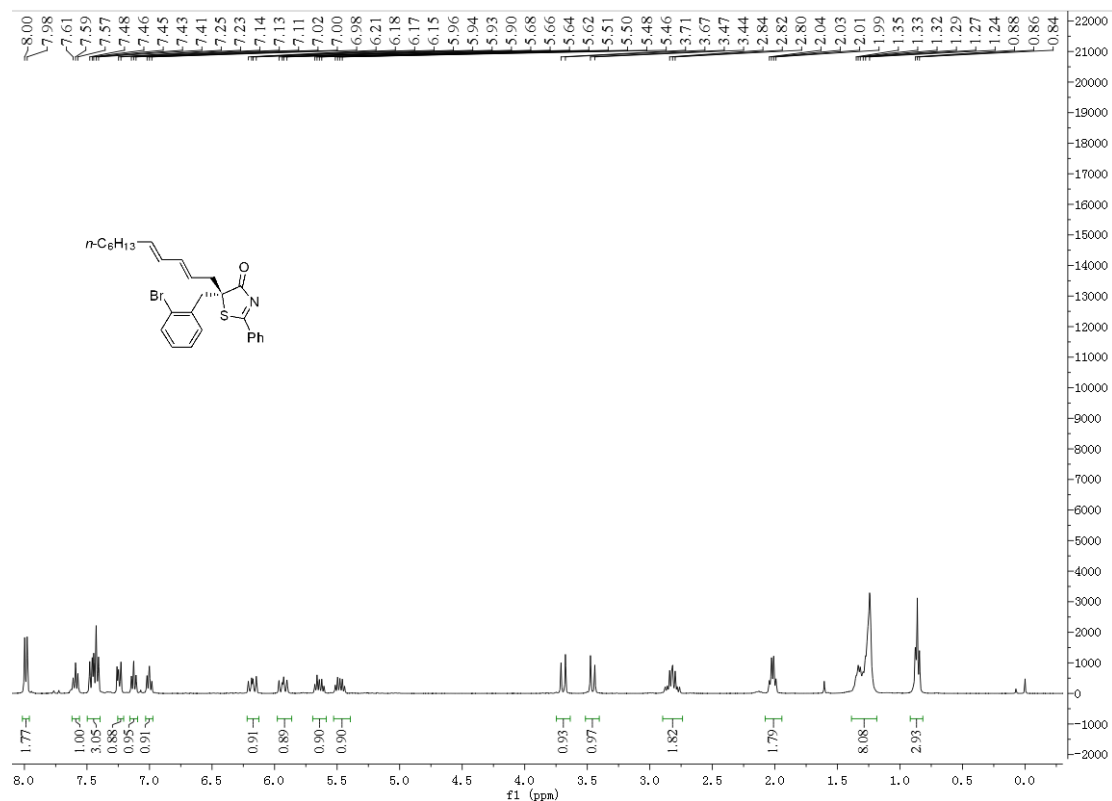
(R)-5-(2-methylbenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ja)



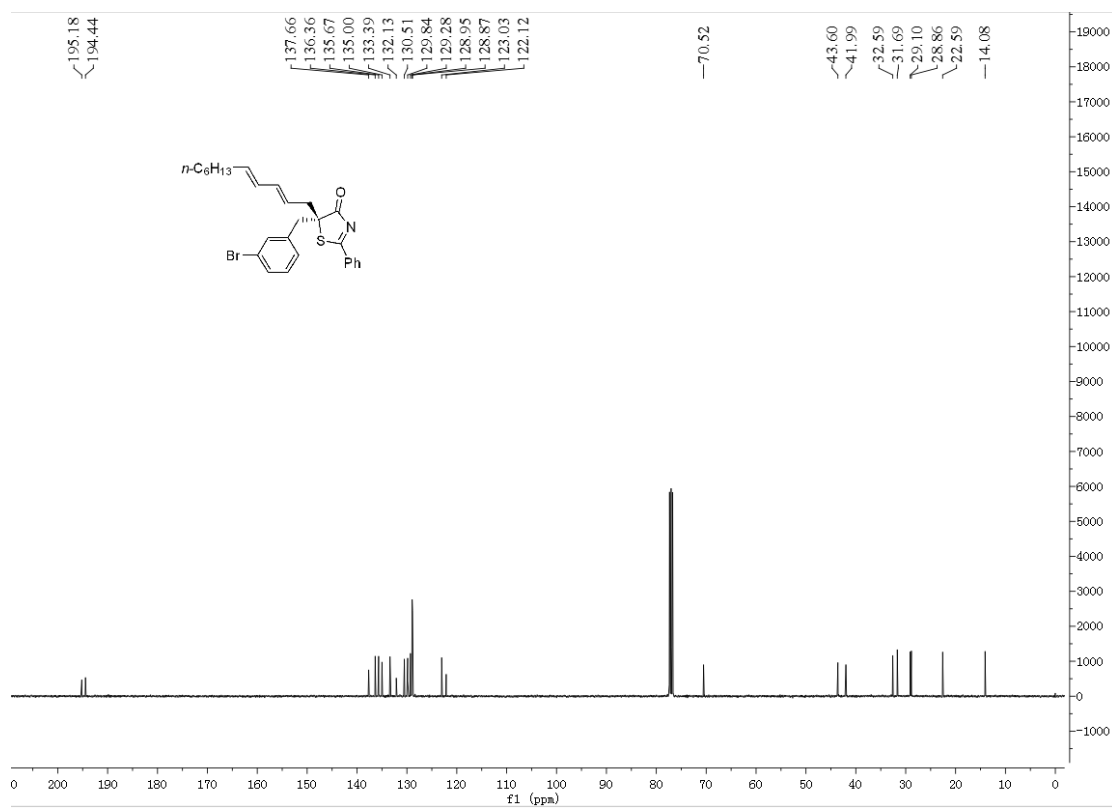
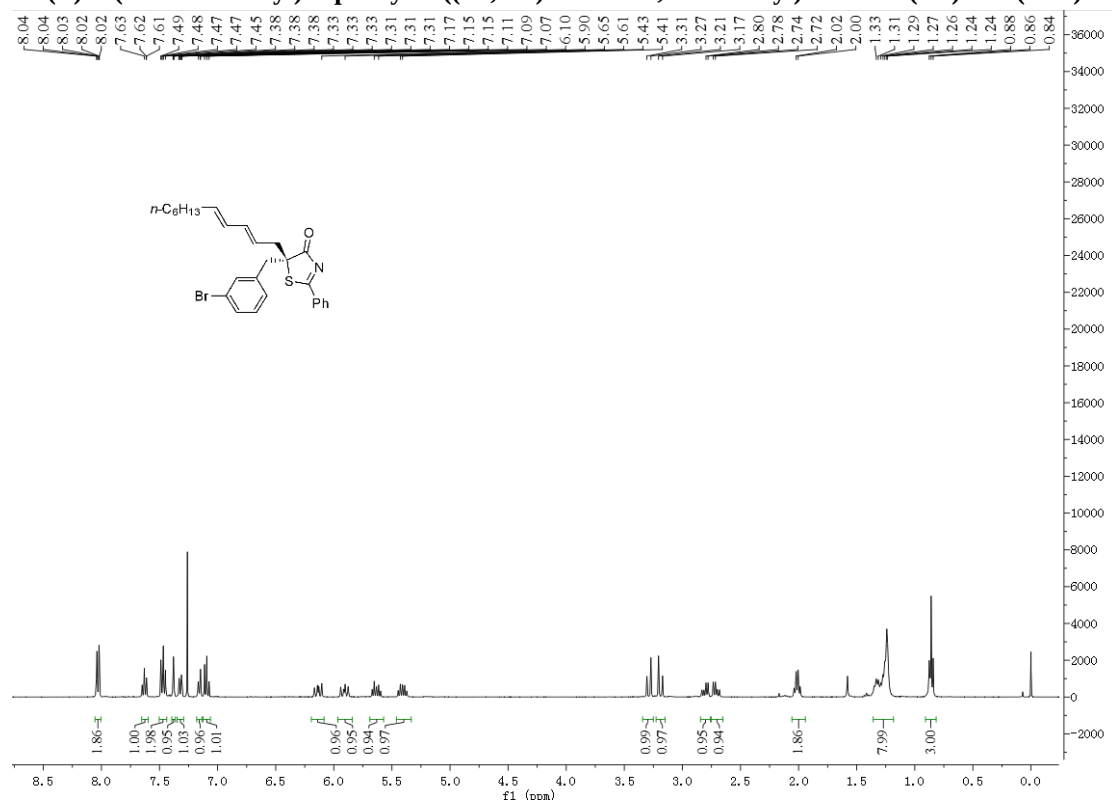
(R)-5-(4-methylbenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ka)



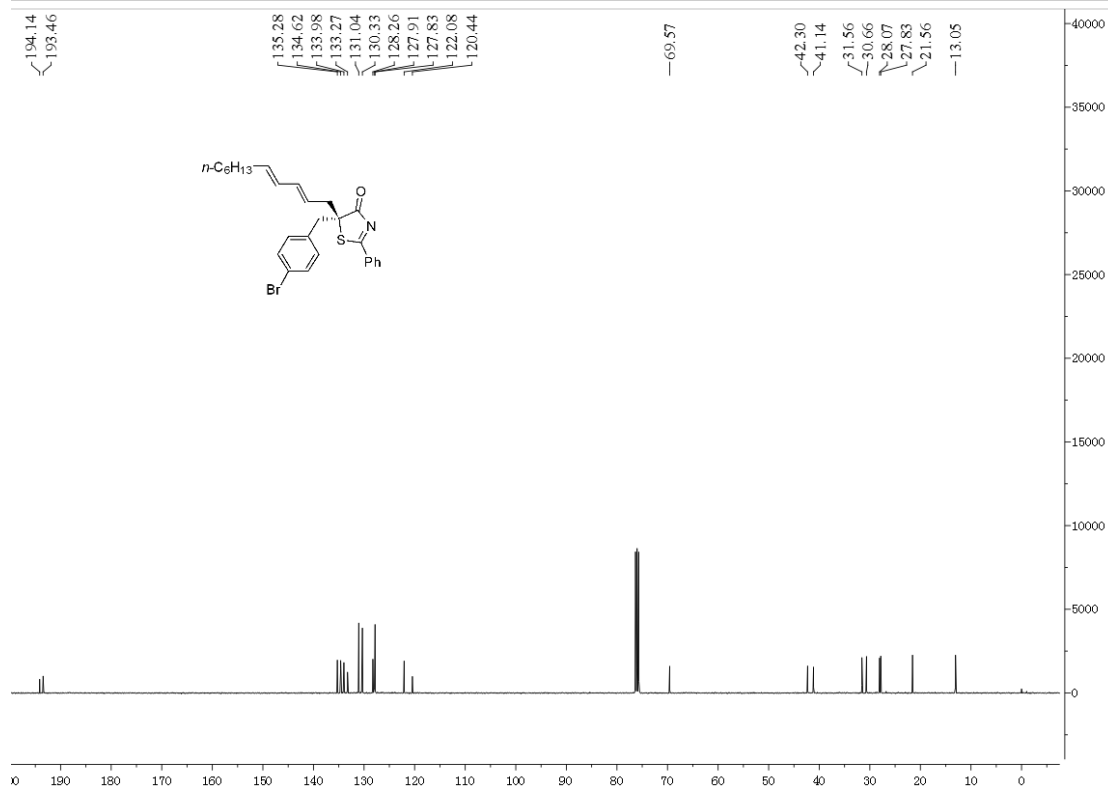
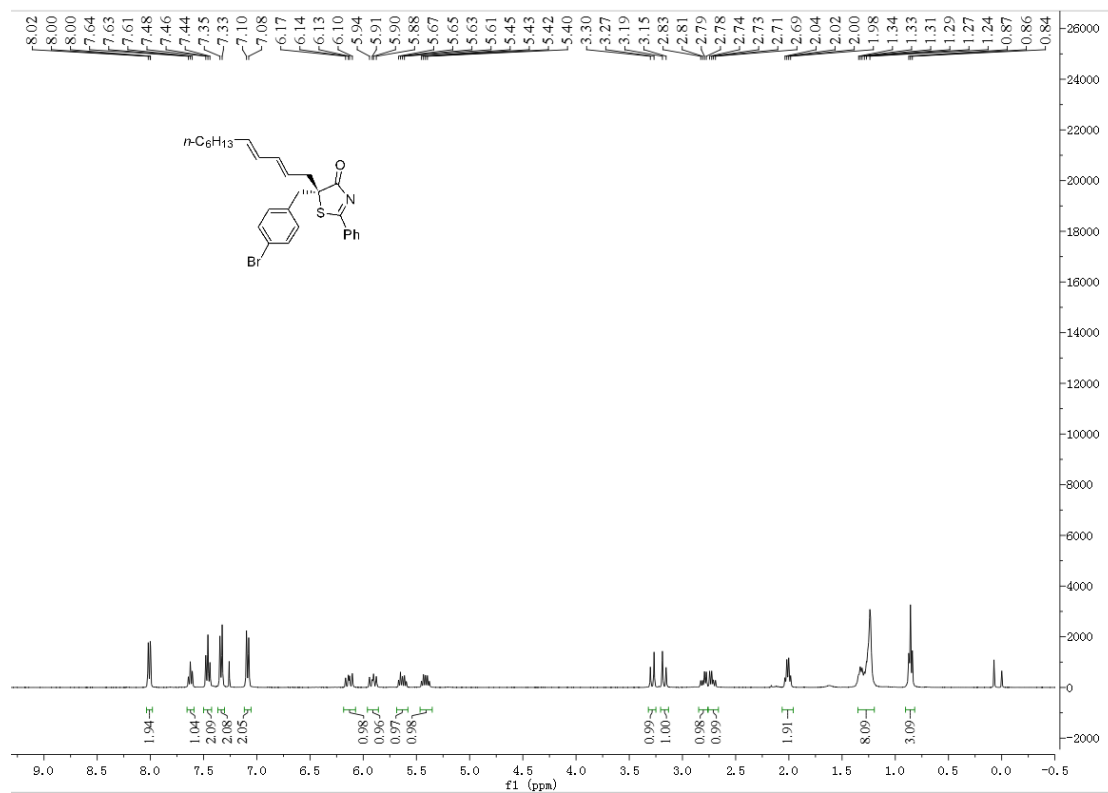
(R)-5-(2-bromobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3la)



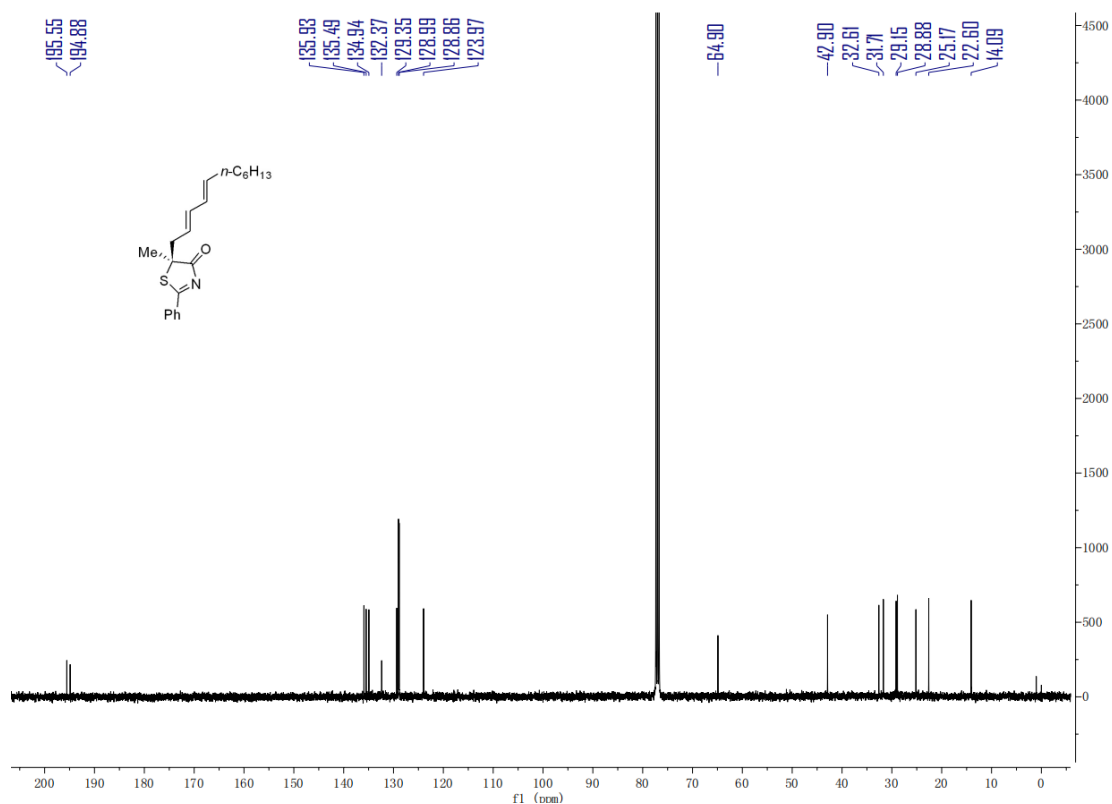
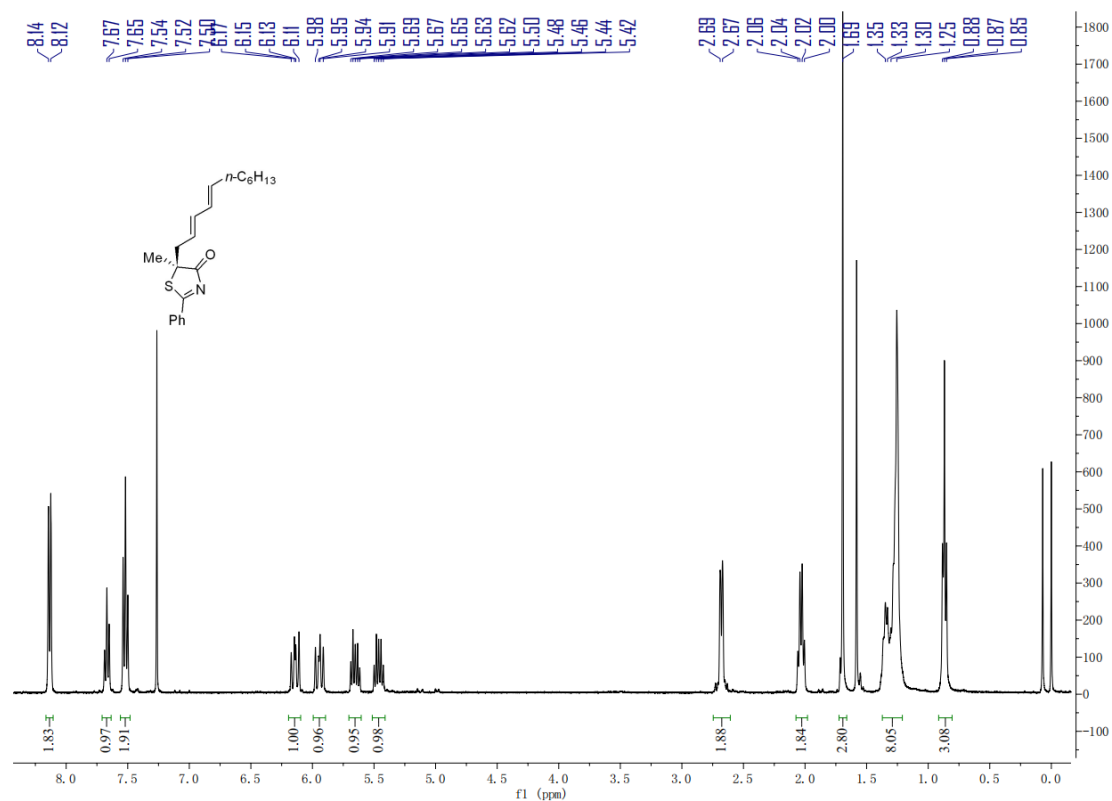
(R)-5-(3-bromobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ma)



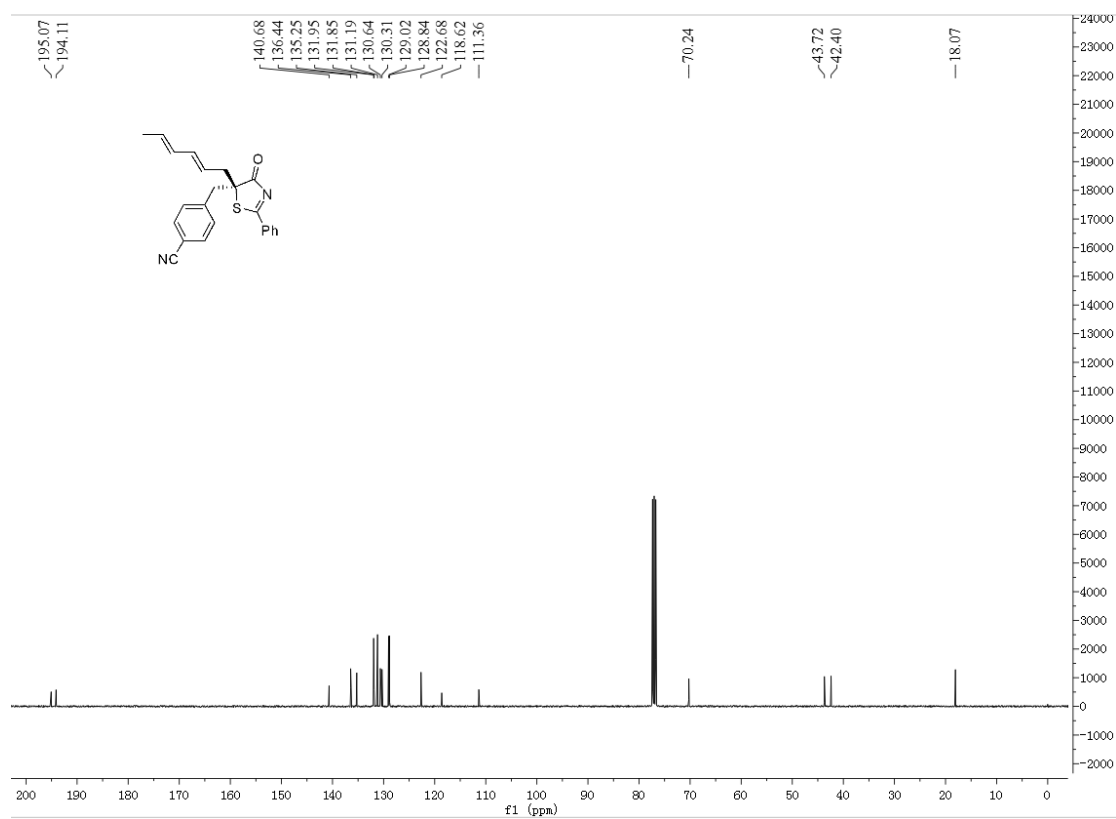
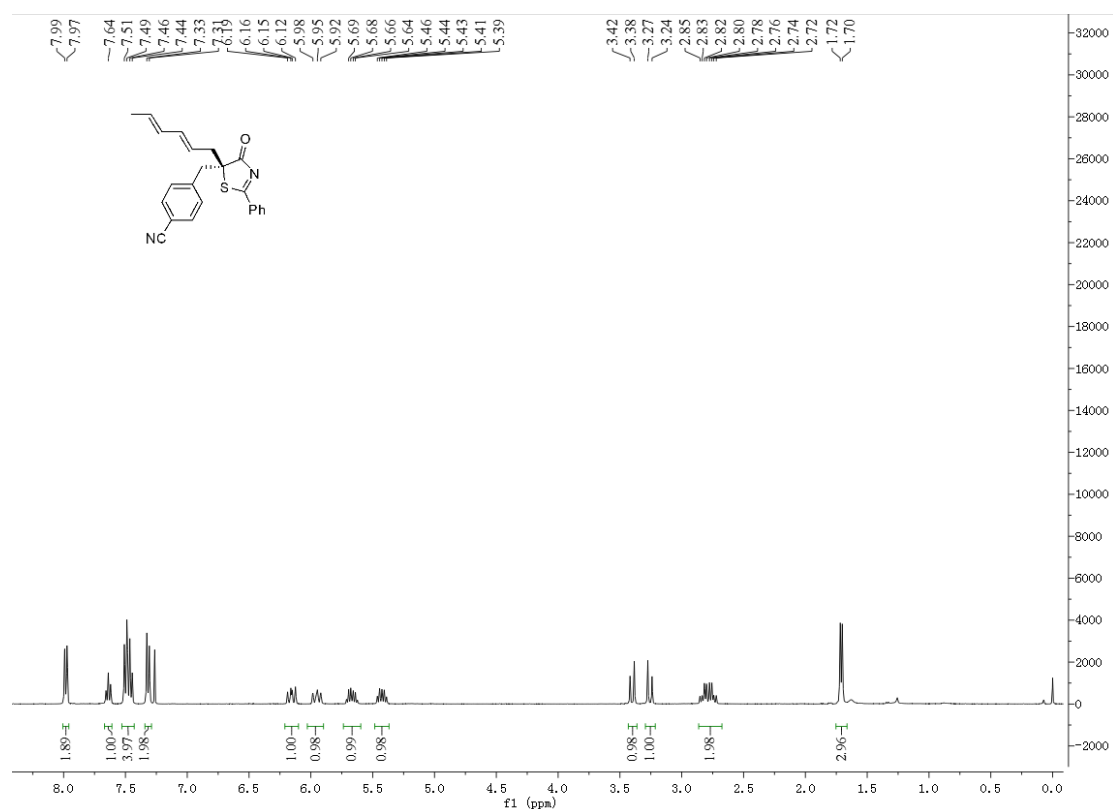
(R)-5-(4-bromobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3na)



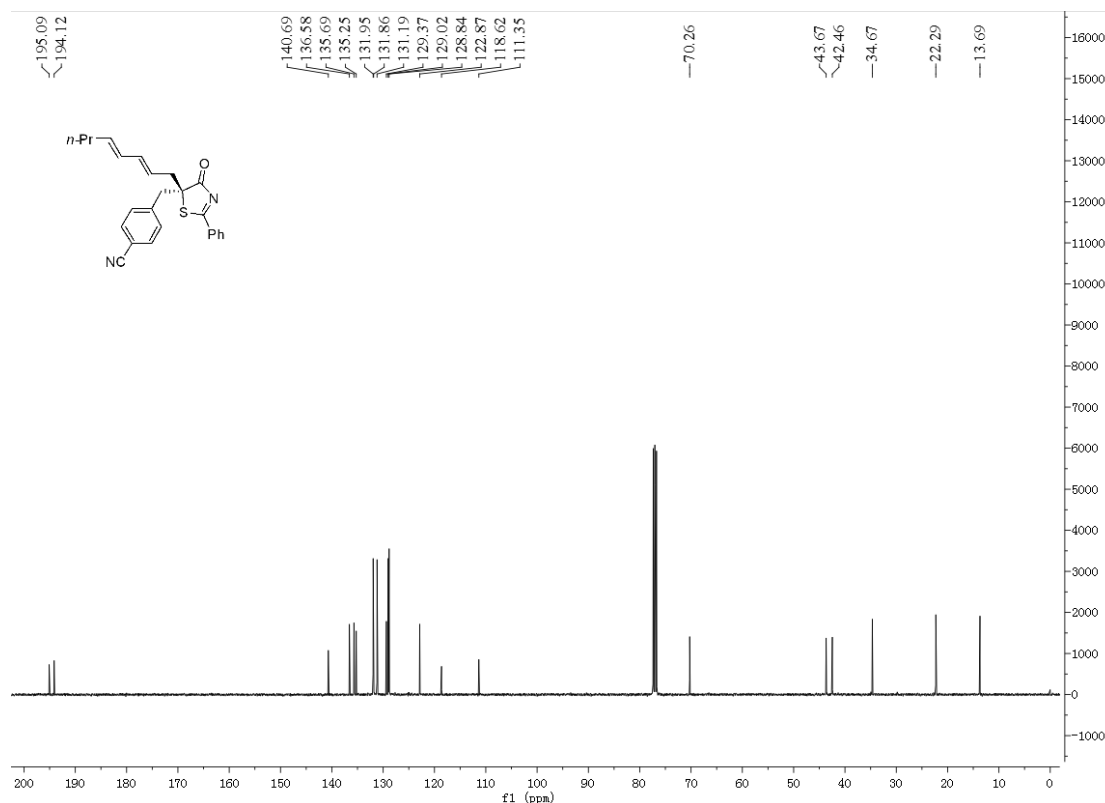
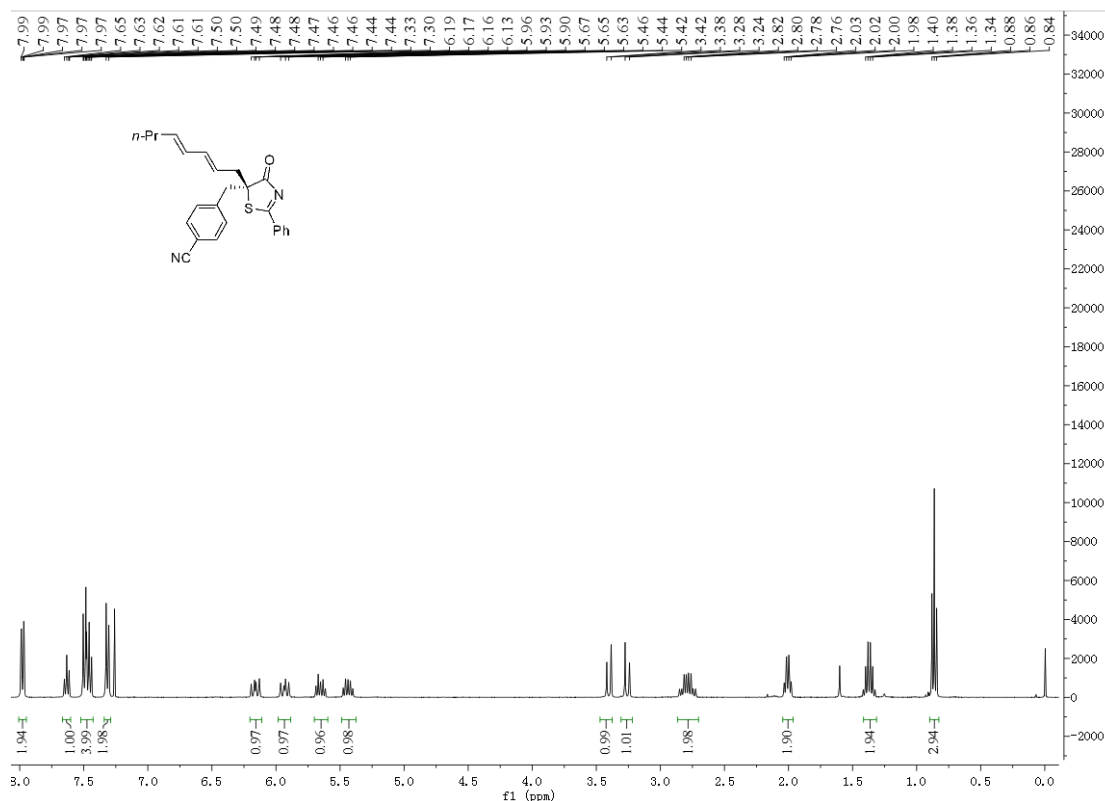
(S)-5-methyl-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one
(30a)



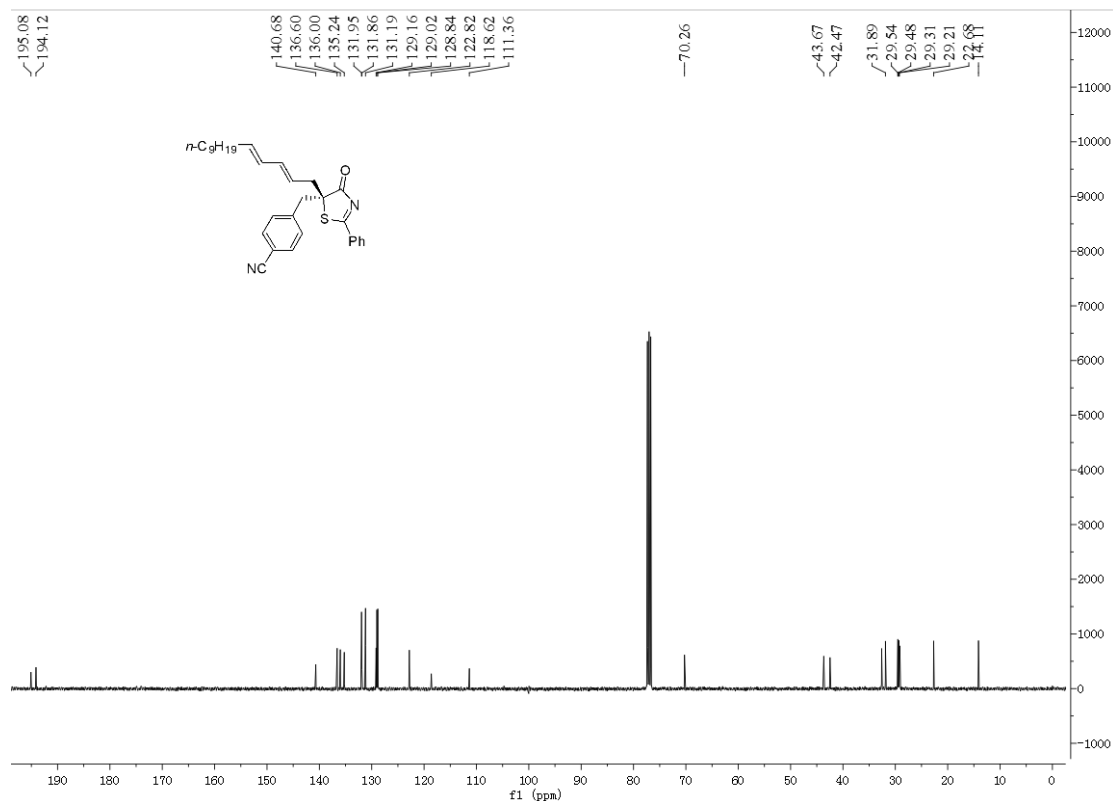
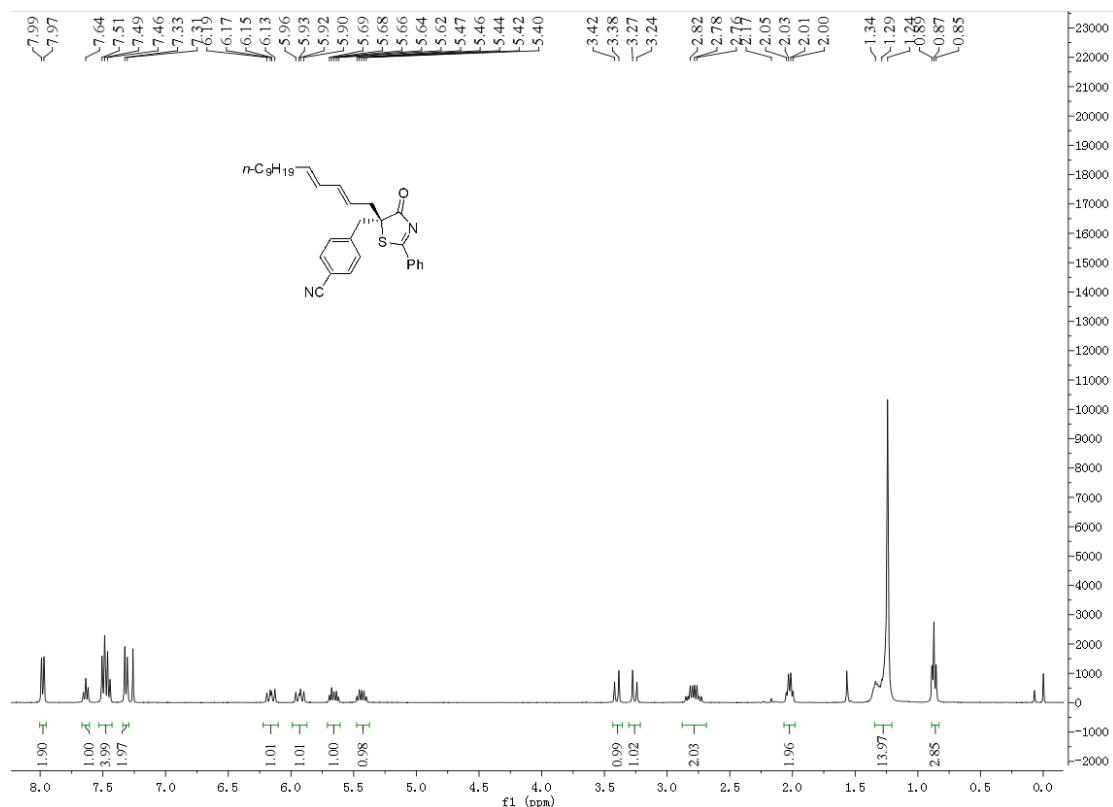
4-(((*R*)-5-((*2E*, *4E*)-hexa-2, 4-dien-1-yl)-4-oxo-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3db)



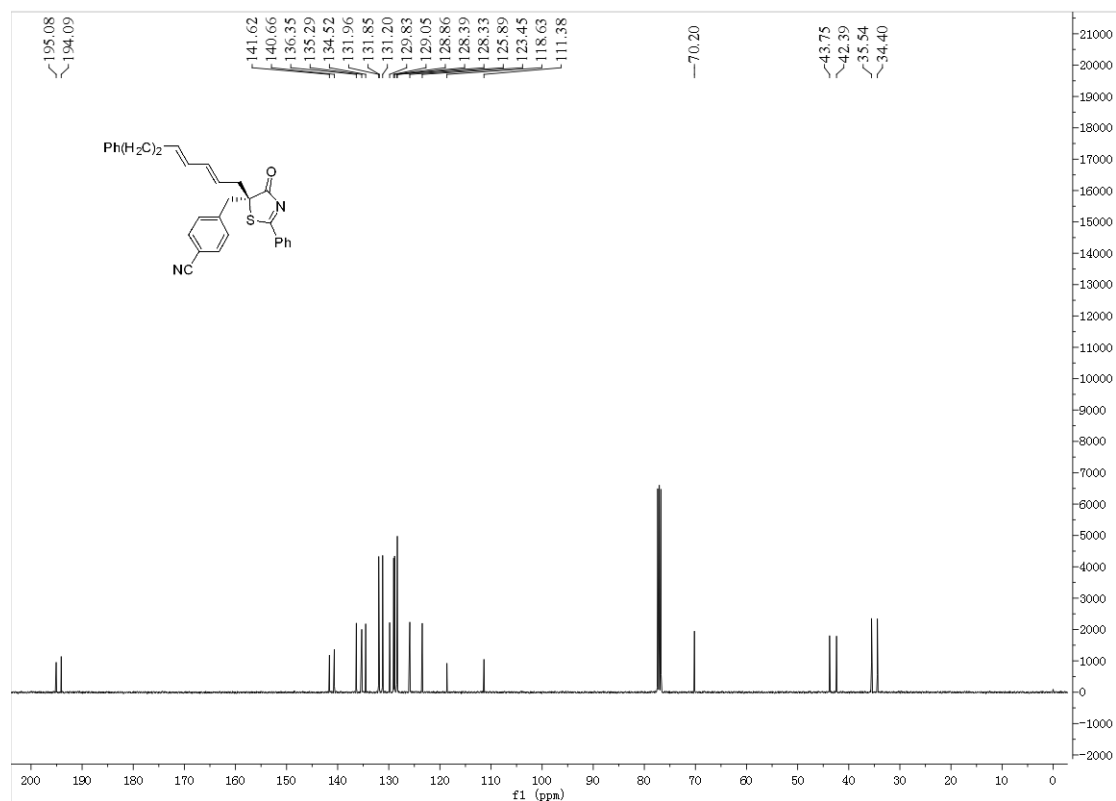
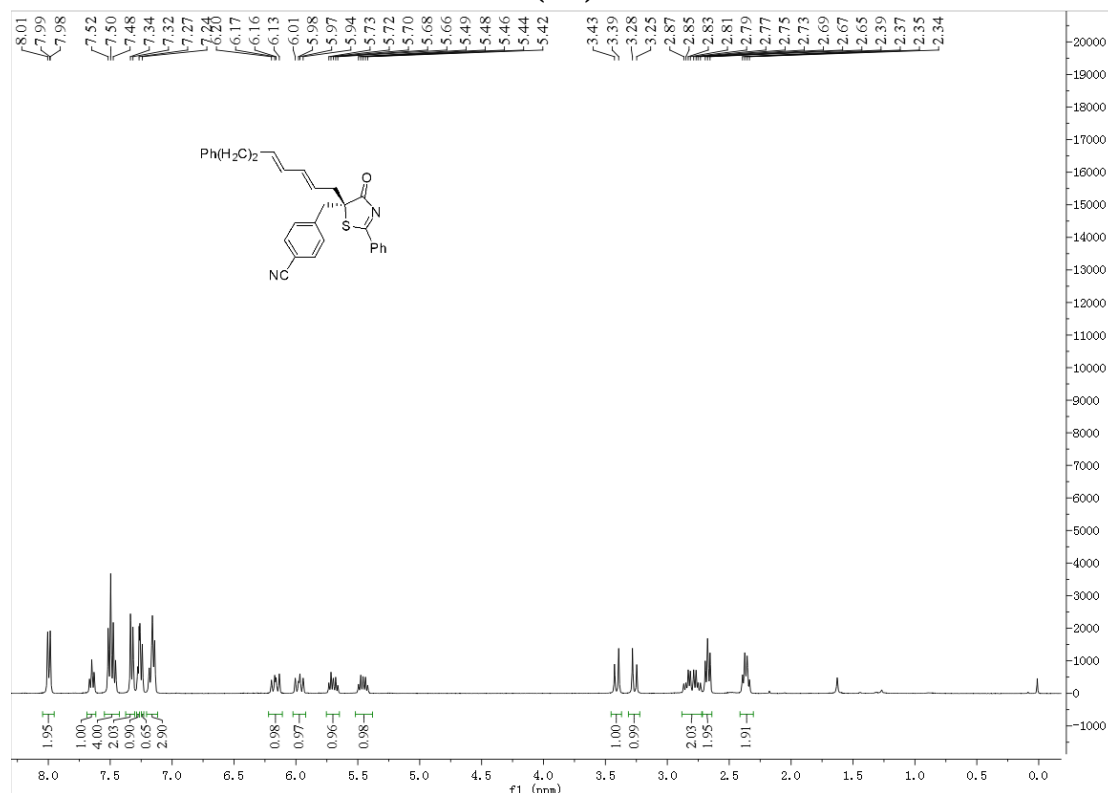
4-(((R)-5-((2E, 4E)-octa-2, 4-dien-1-yl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3dc)



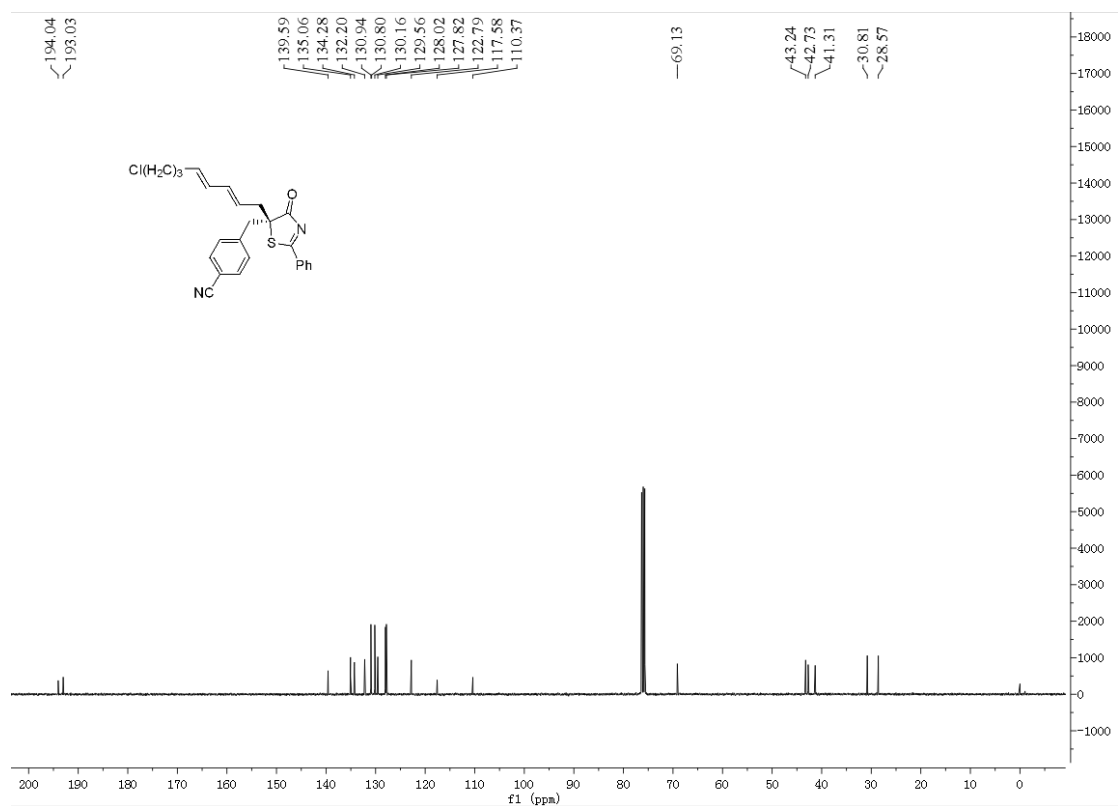
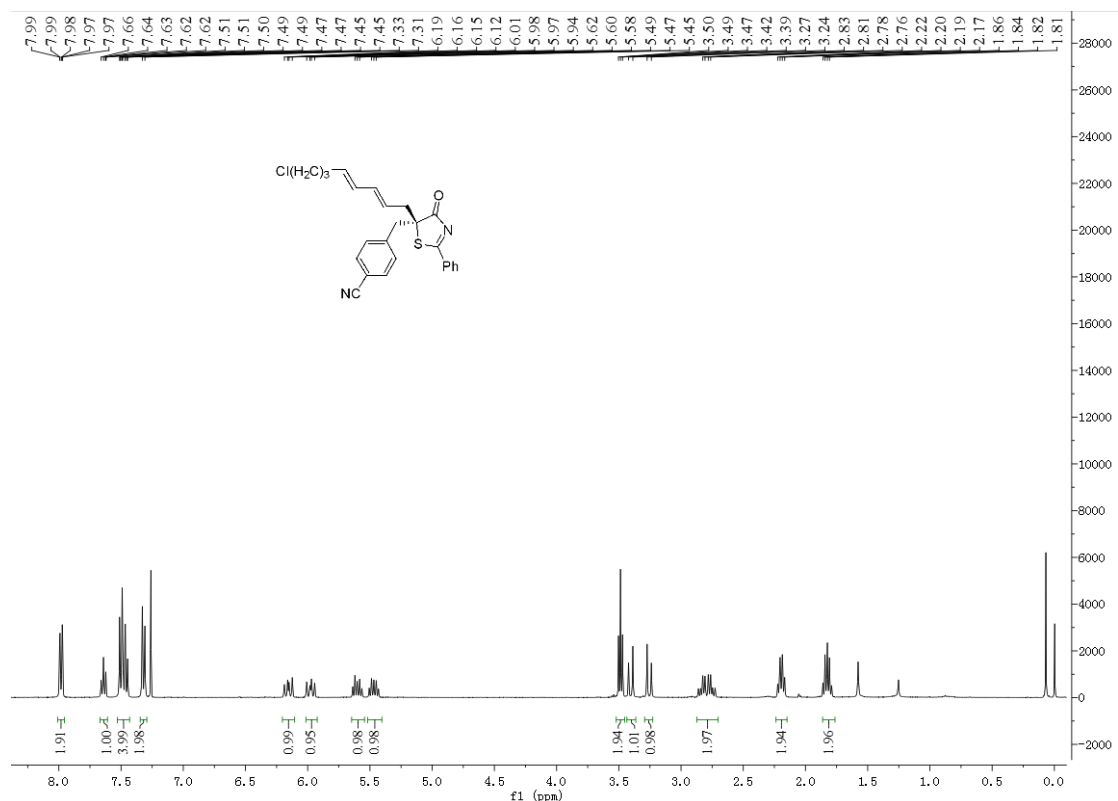
4-(((R)-4-oxo-2-phenyl-5-((2E, 4E)-tetradeca-2, 4-dien-1-yl)-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3dd)



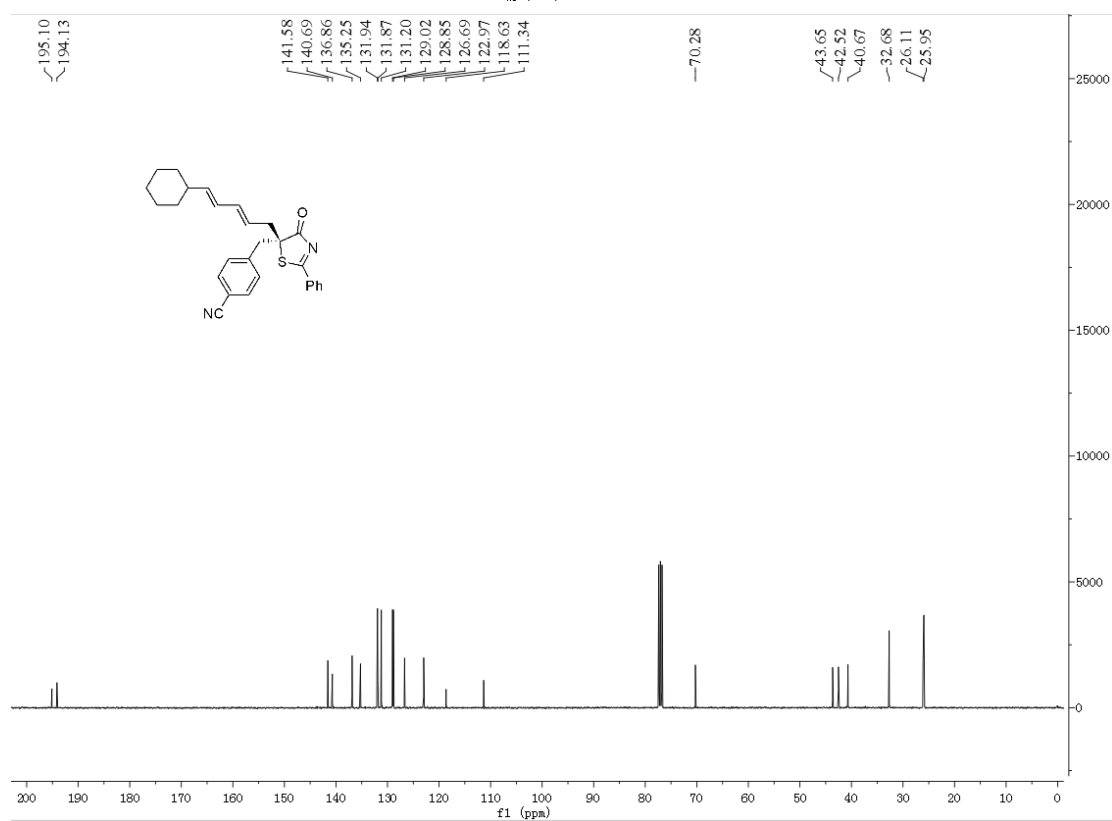
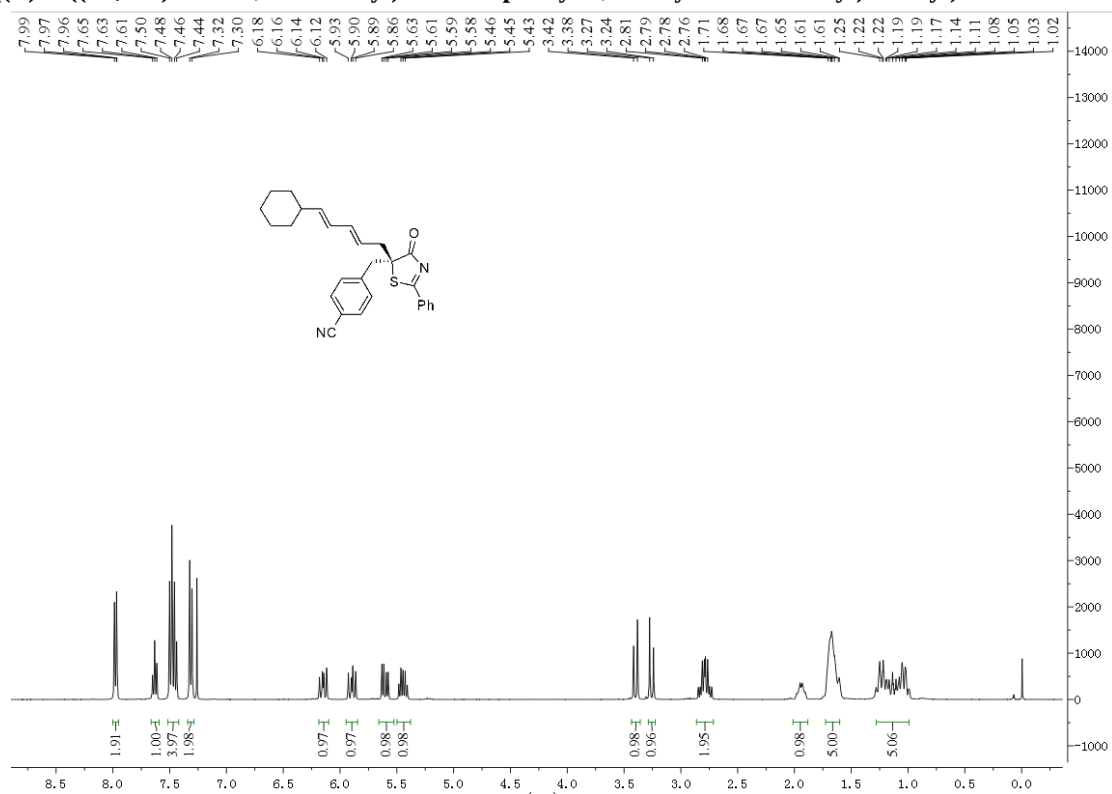
4-(((*R*)-4-oxo-2-phenyl-5-((2*E*, 4*E*)-5-(*p*-tolyl) penta-2, 4-dien-1-yl)-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3de)



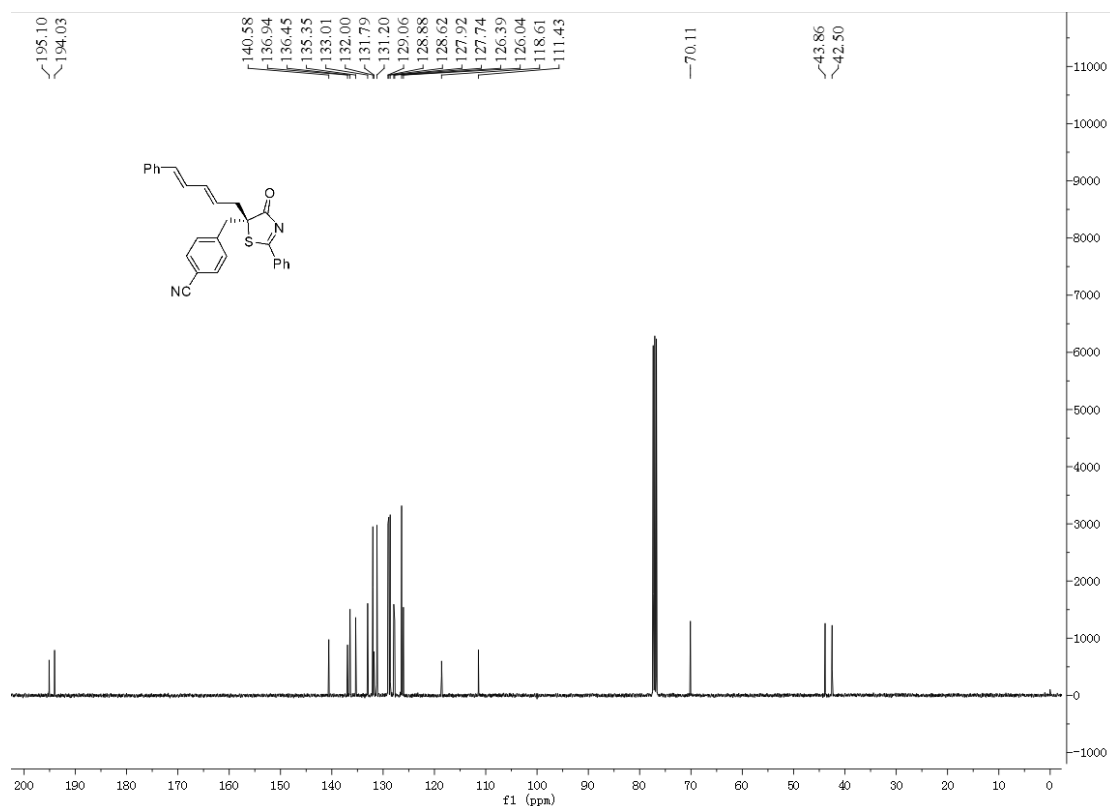
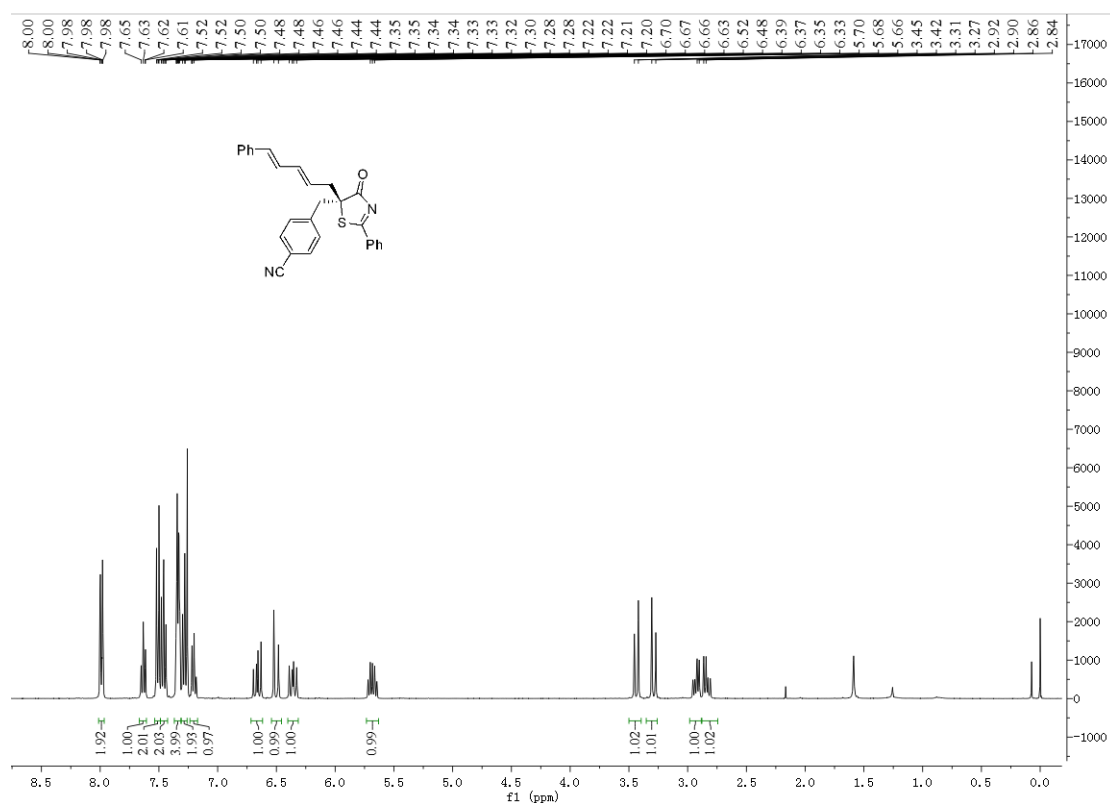
4-(((*R*)-5-((*2E*, *4E*)-8-chloroocta-2, 4-dien-1-yl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3df)



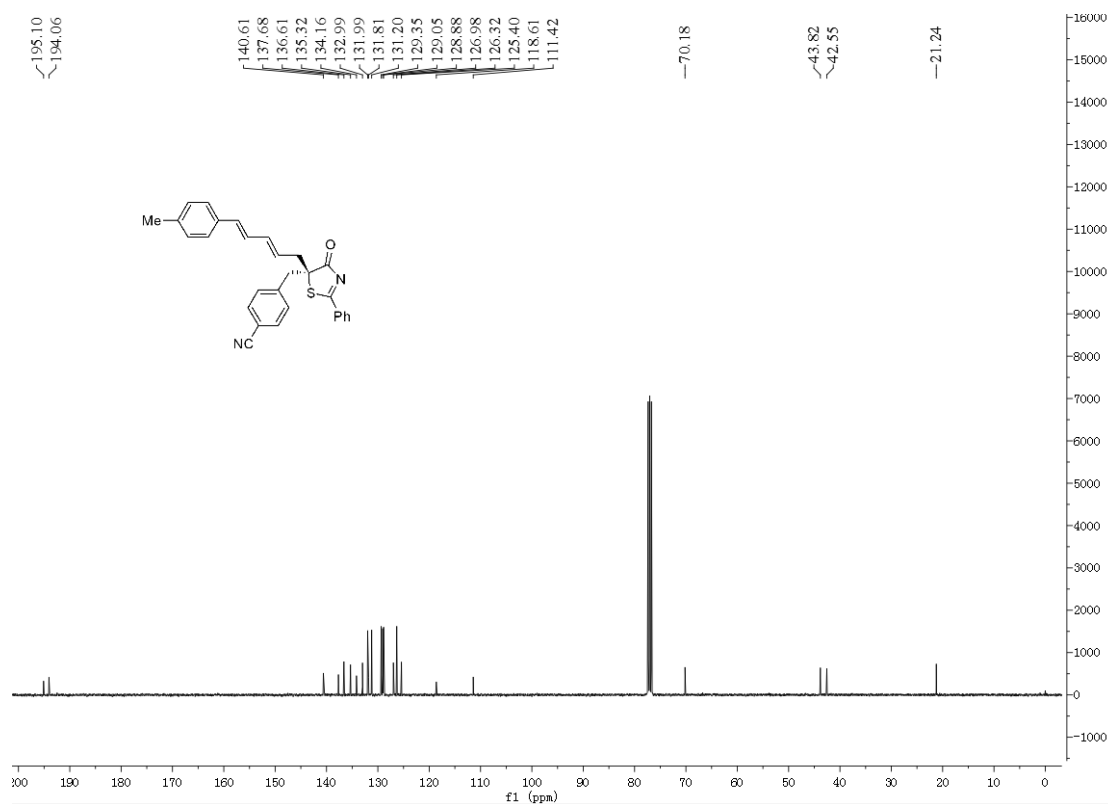
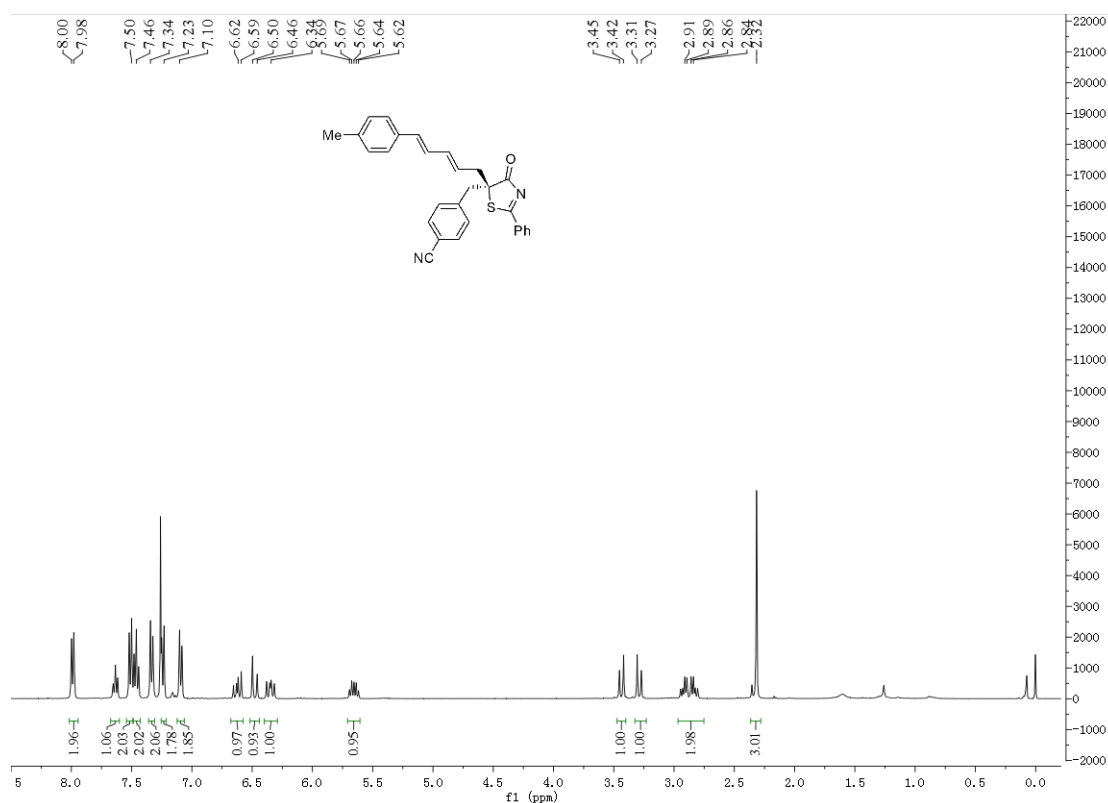
4-(((R)-5-((2E, 4E)-hexa-2, 4-dien-1-yl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3dg)



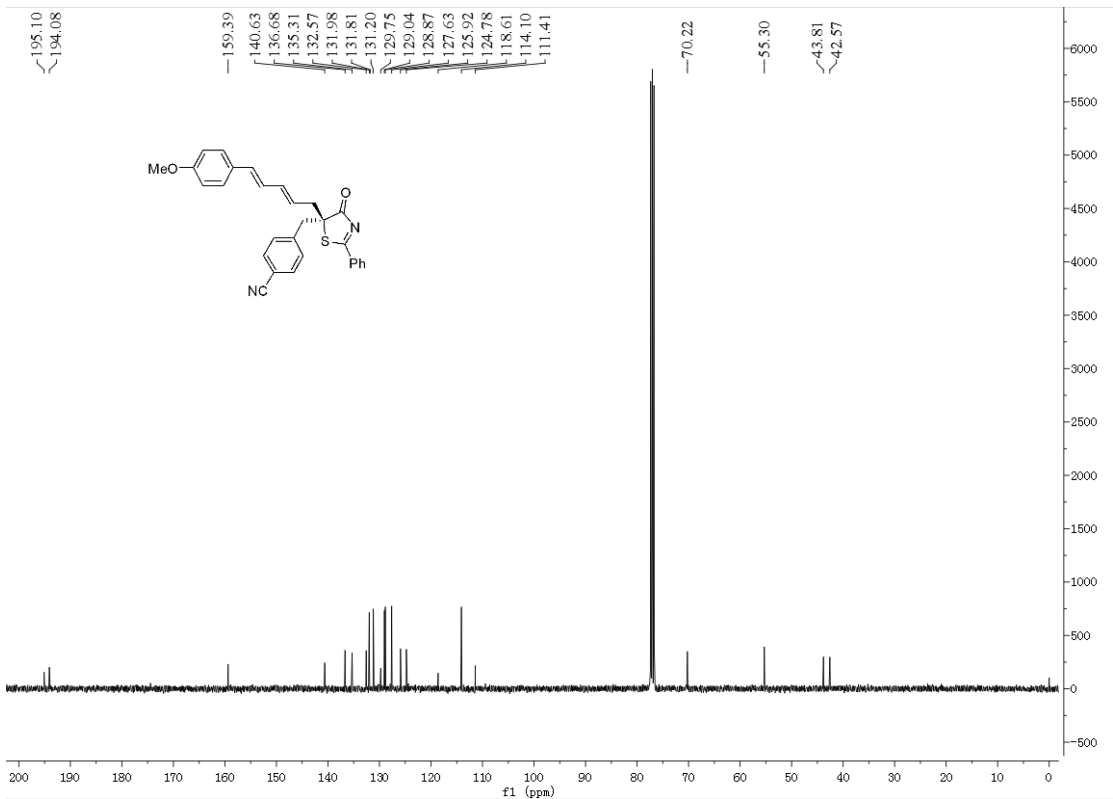
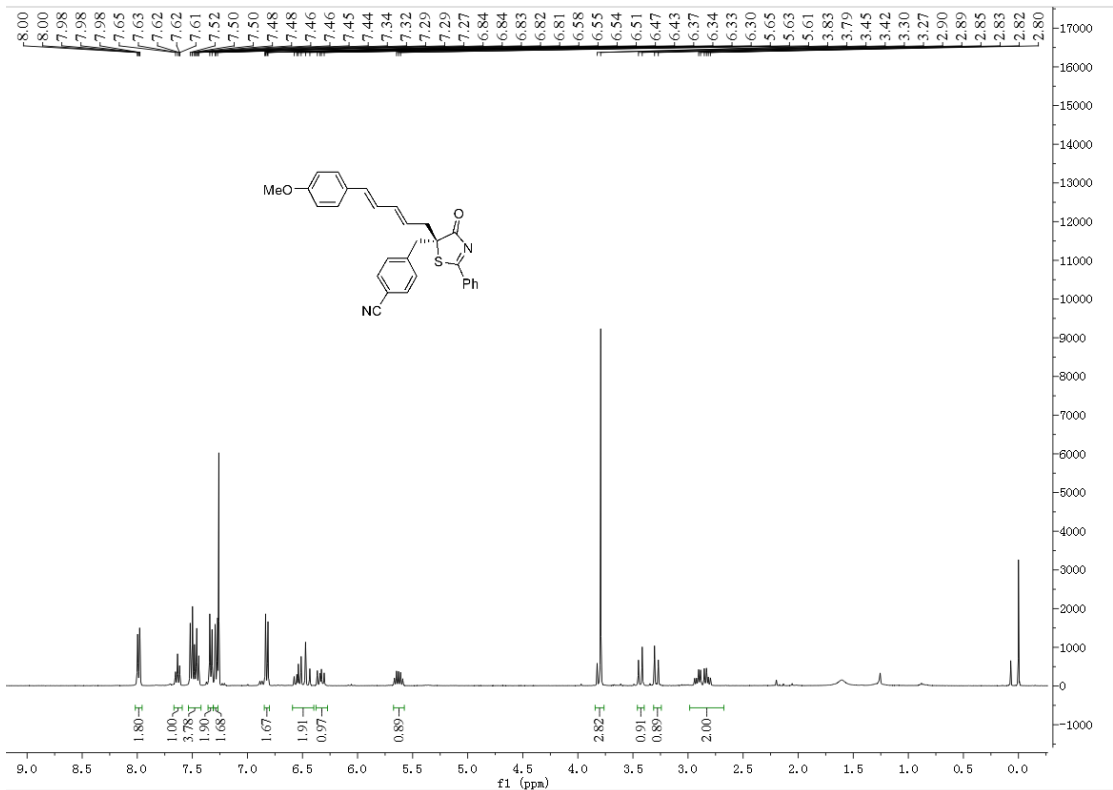
4-(((*R*)-4-oxo-2-phenyl-5-((*2E*, *4E*)-5-phenylpenta-2, 4-dien-1-yl)-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3dh)



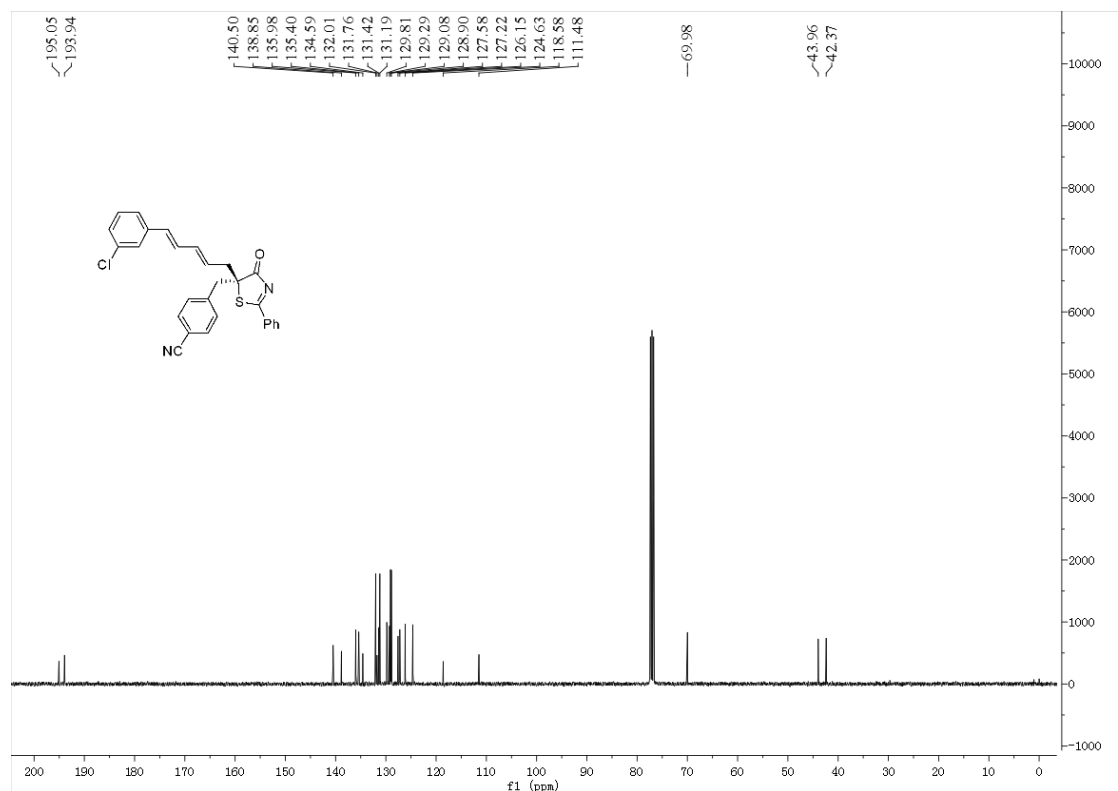
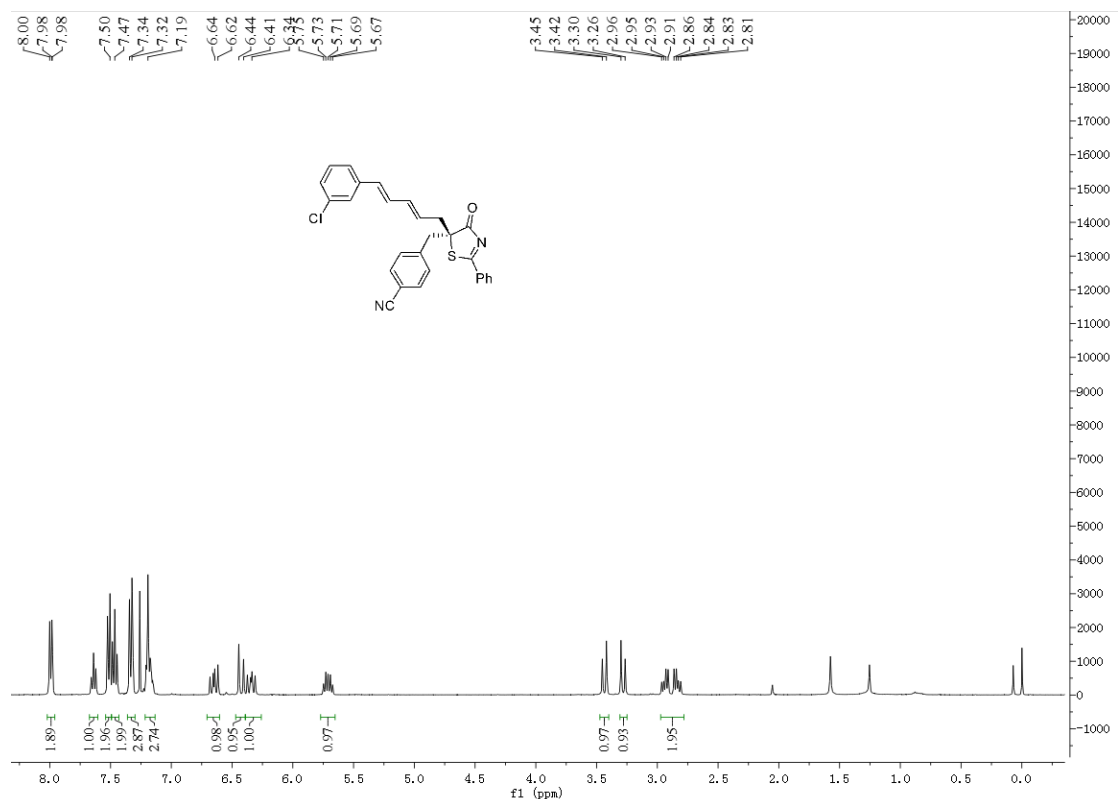
4-(((R)-4-oxo-2-phenyl-5-((2E, 4E)-5-(p-tolyl) penta-2, 4-dien-1-yl)-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3di)



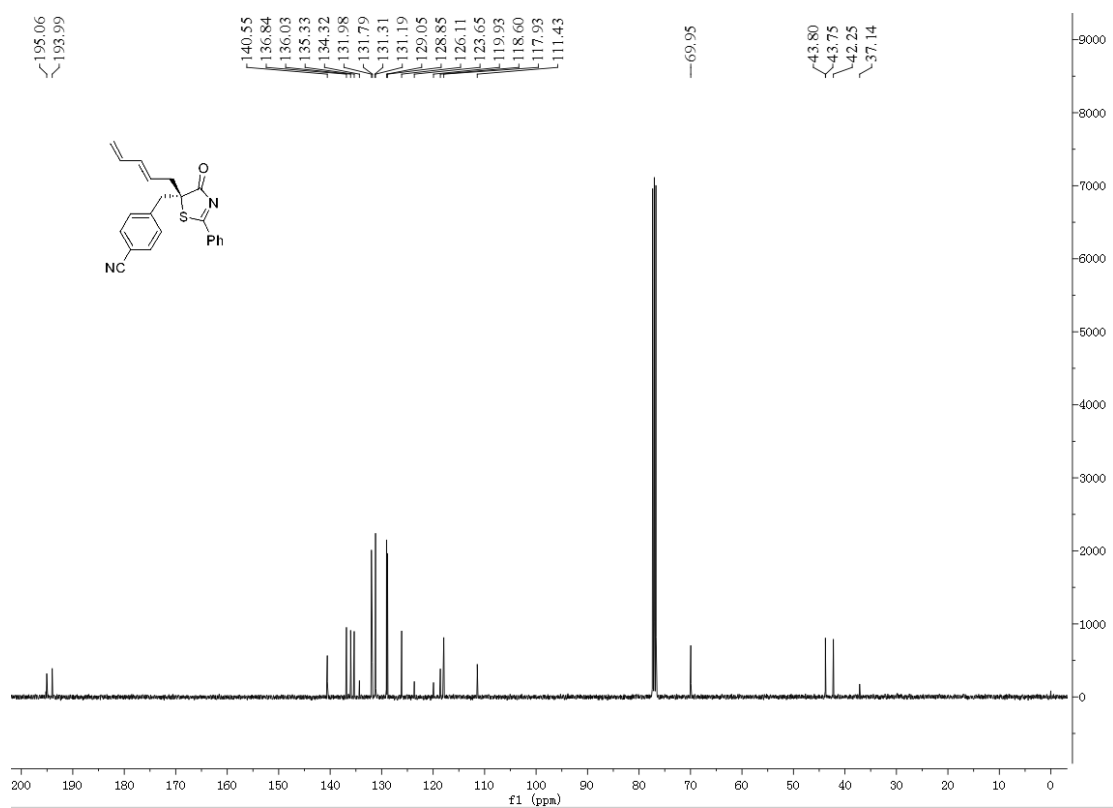
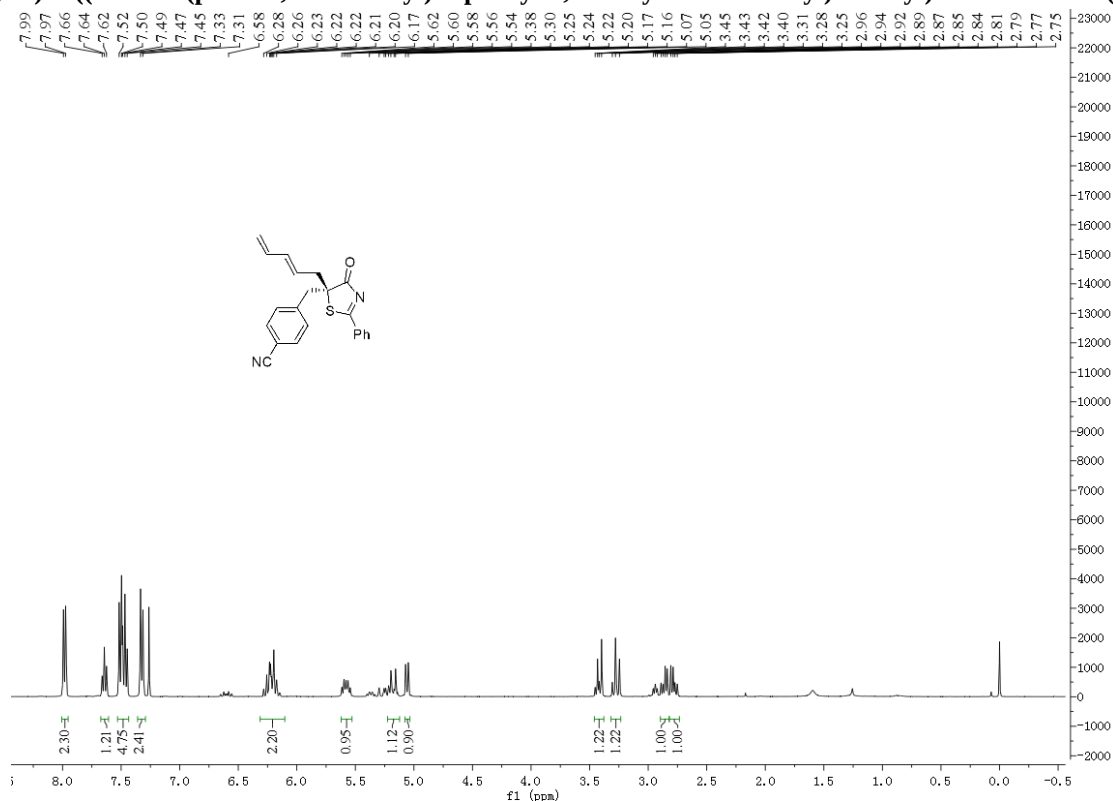
4-(((R)-5-((2E, 4E)-5-(4-methoxyphenyl) penta-2, 4-dien-1-yl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3dj)



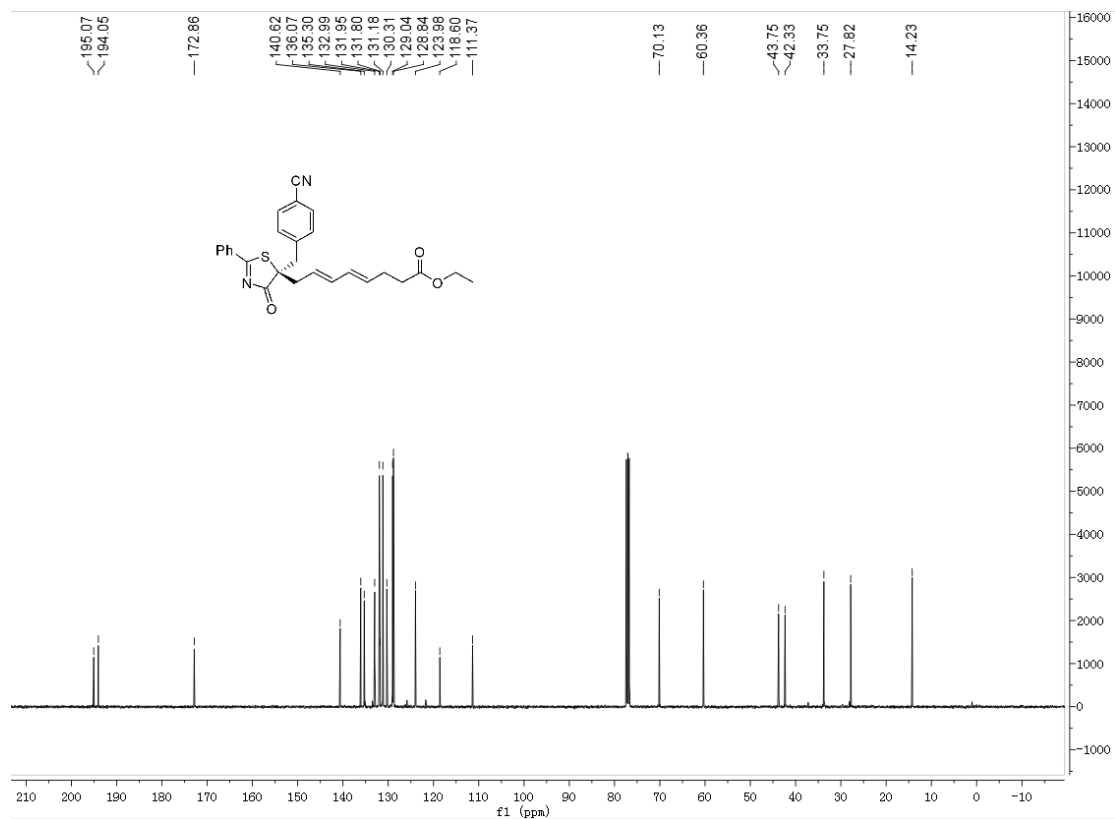
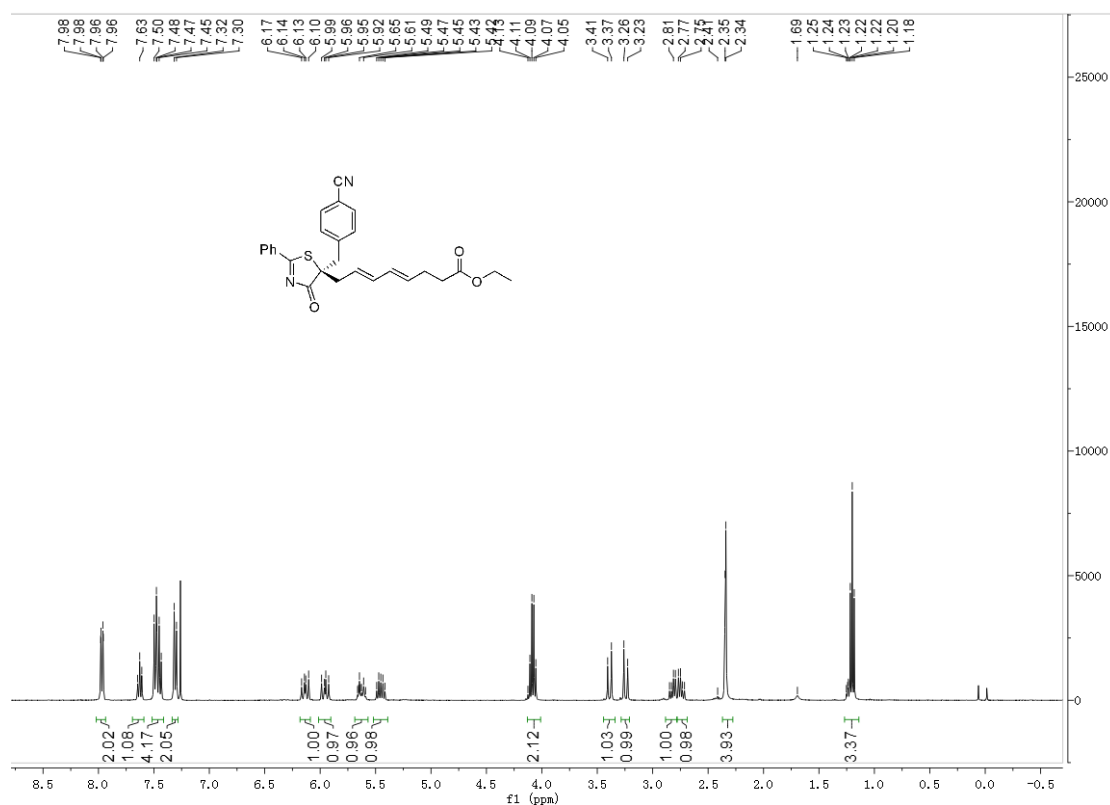
4-(((R)-5-((2E, 4E)-5-(3-chlorophenyl) penta-2, 4-dien-1-yl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3dk)



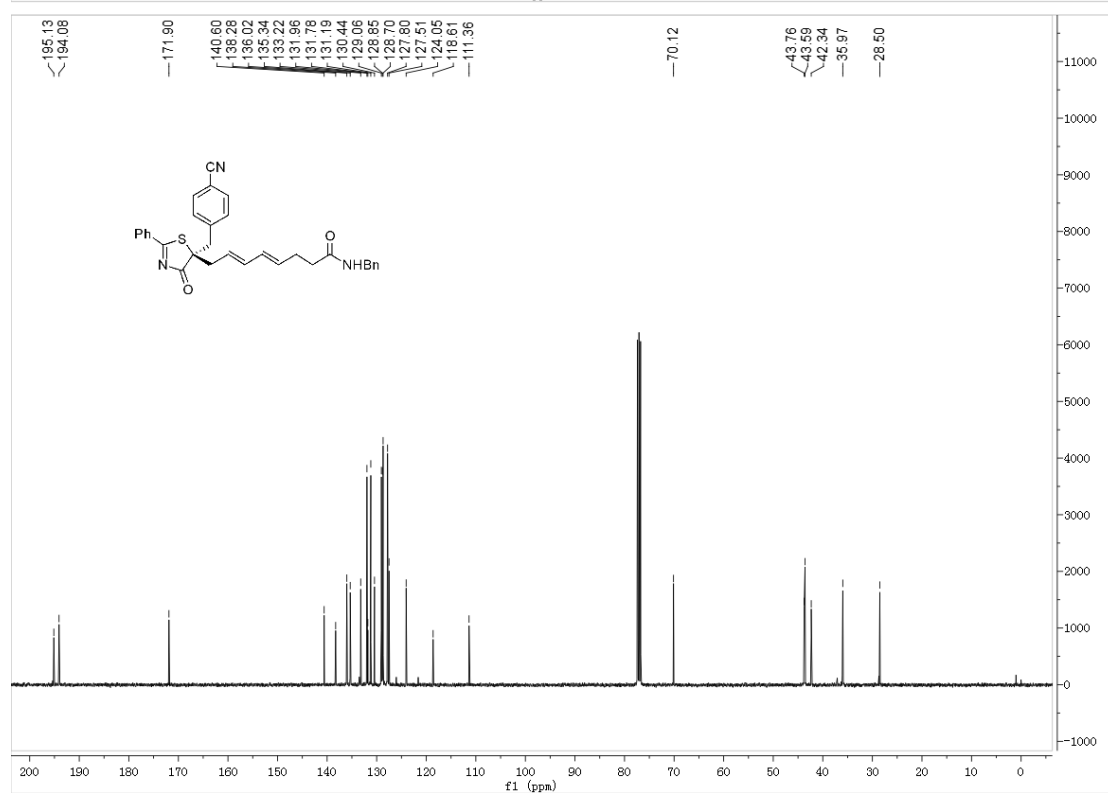
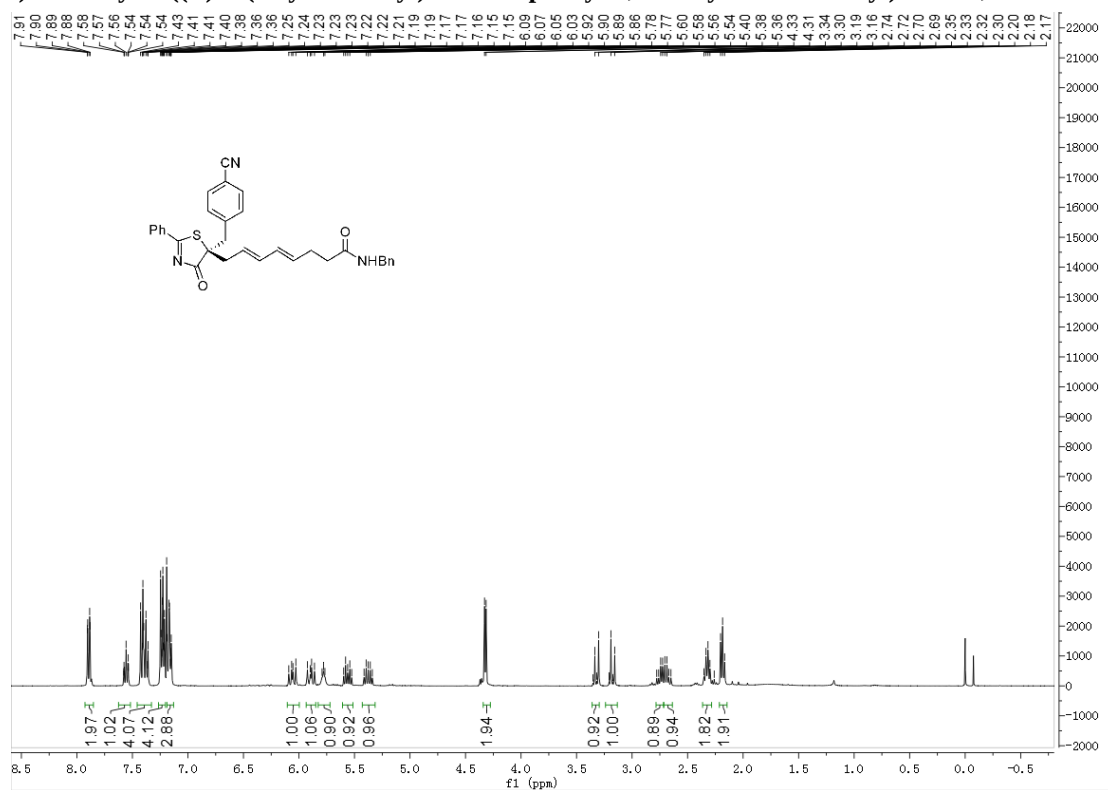
(R, E)-4-((4-oxo-5-(penta-2, 4-dien-1-yl)-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzo-nitrile (3dl)



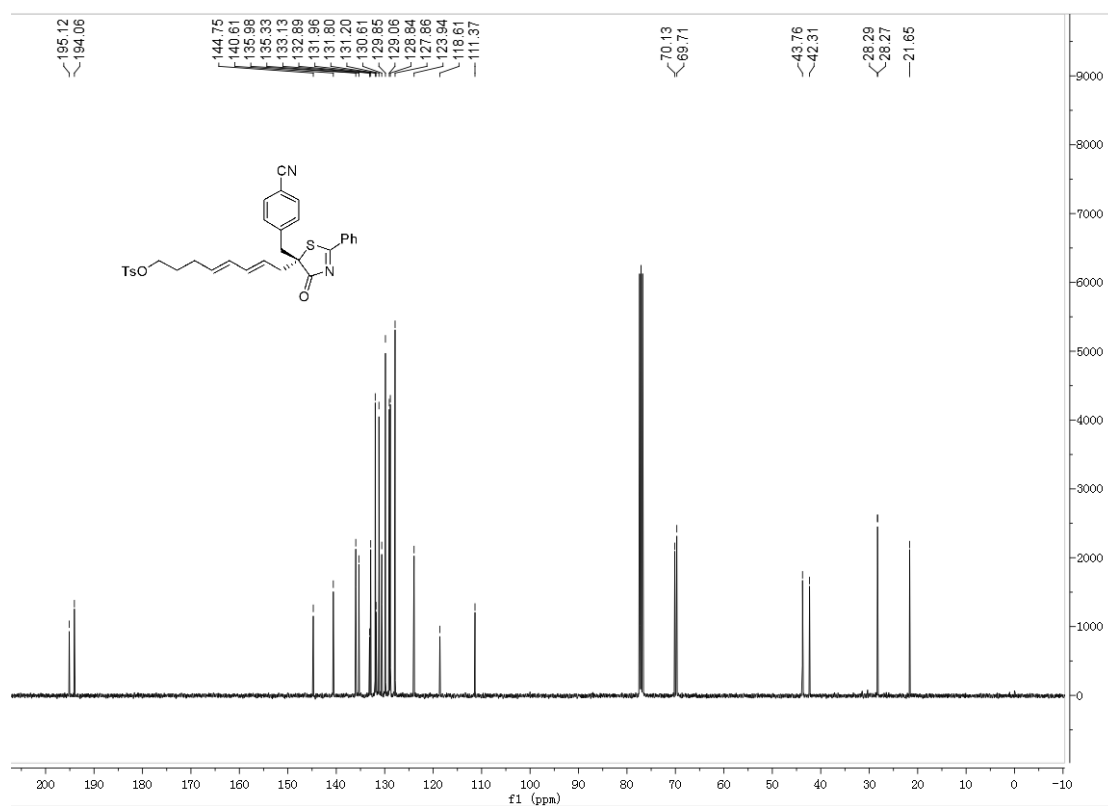
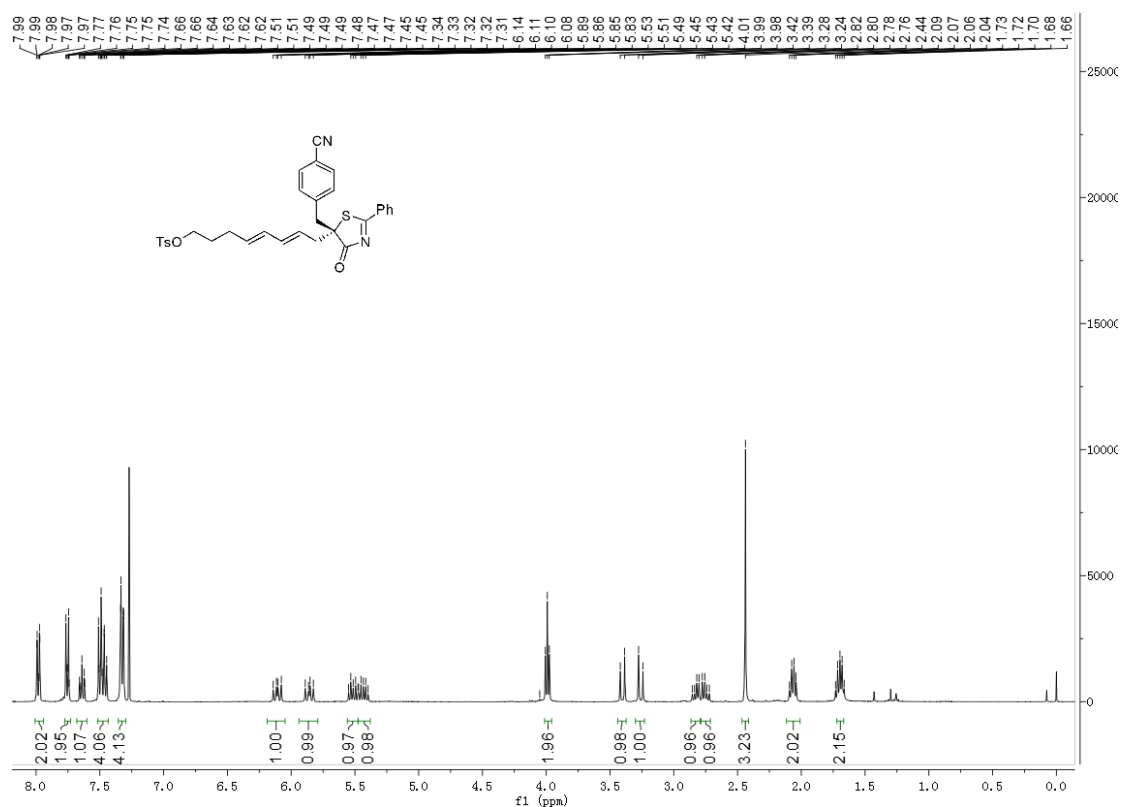
Ethyl (4*E*, 6*E*)-8-((*R*)-5-(4-cyanobenzyl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl)octa-4,6-dienoate (3dm)



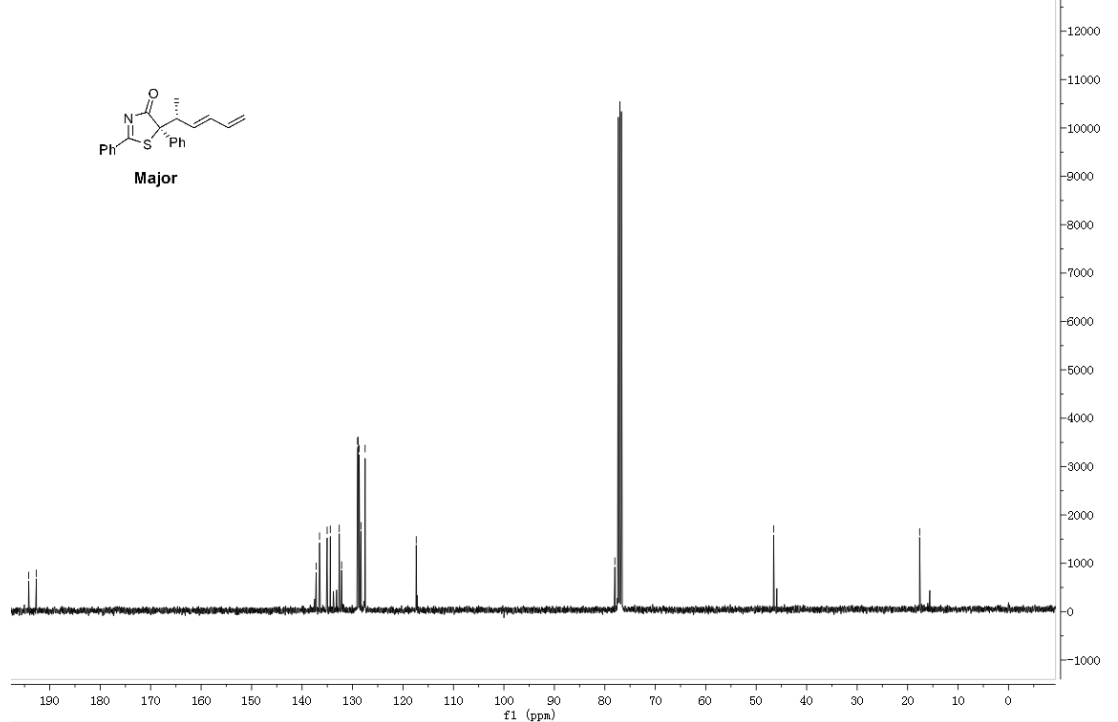
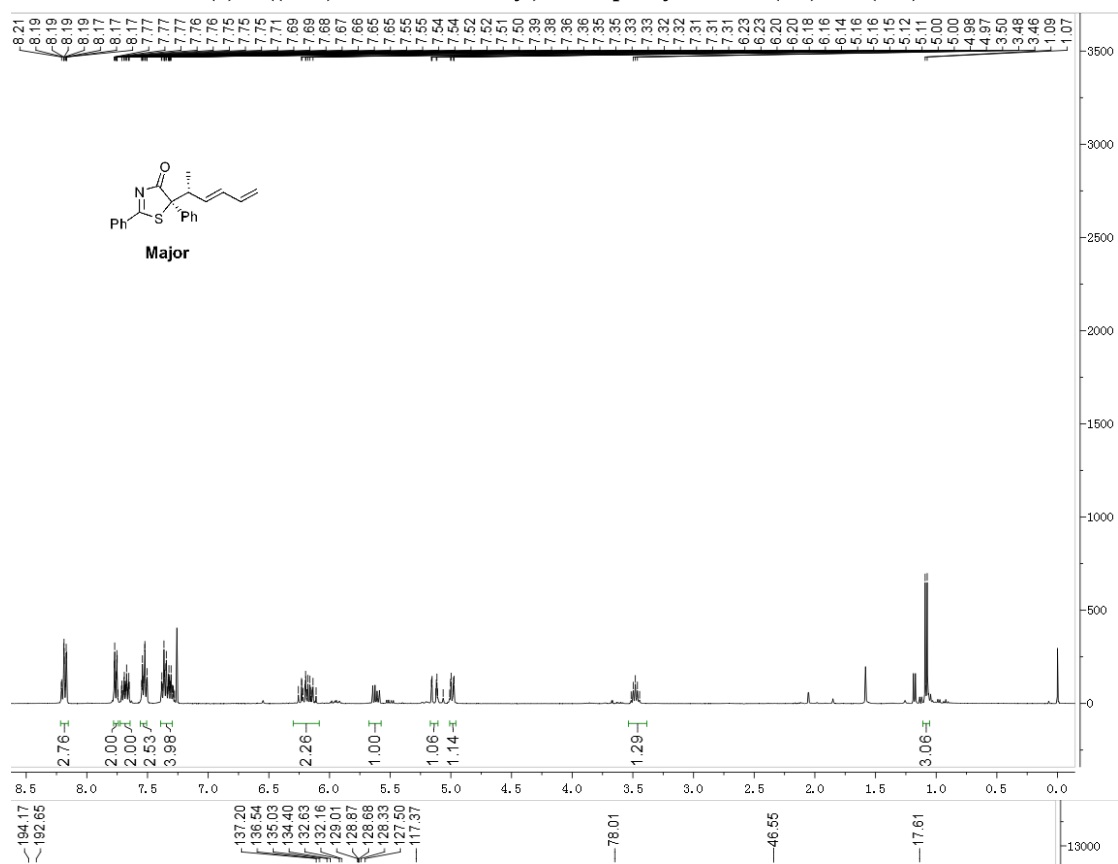
(4*E*, 6*E*)-*N*-benzyl-8-((*R*)-5-(4-cyanobenzyl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) octa-4,6-dienamide (3dn)



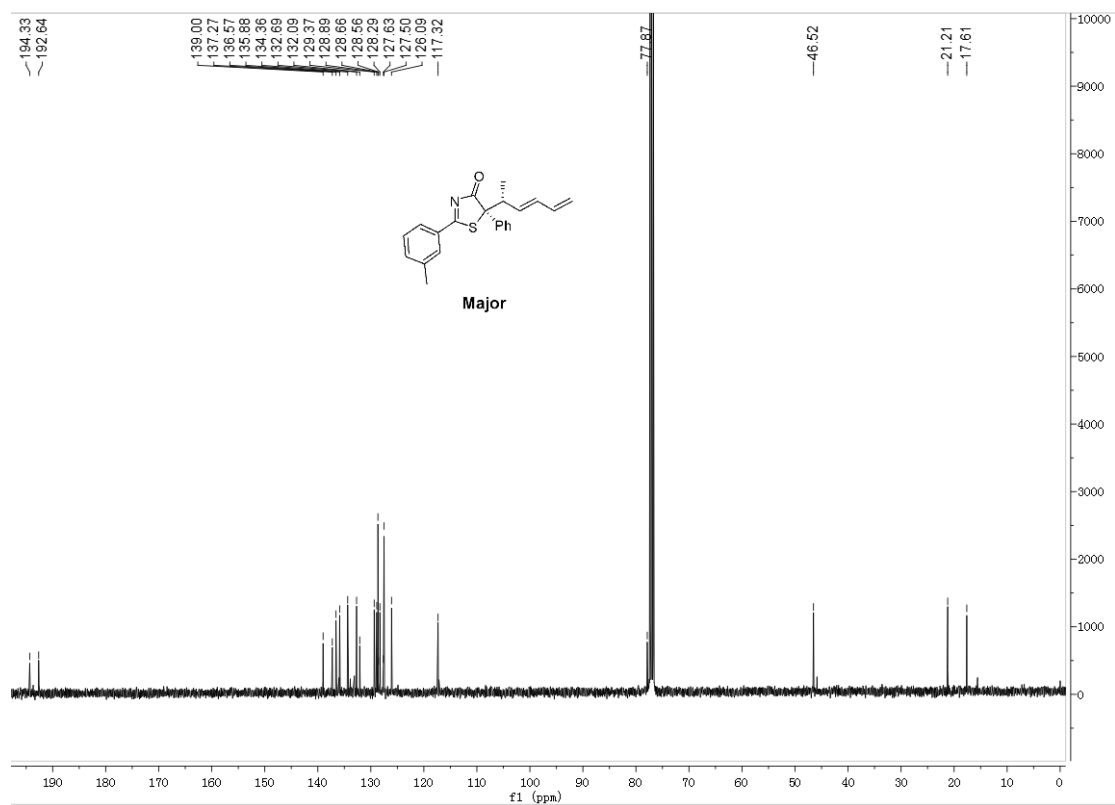
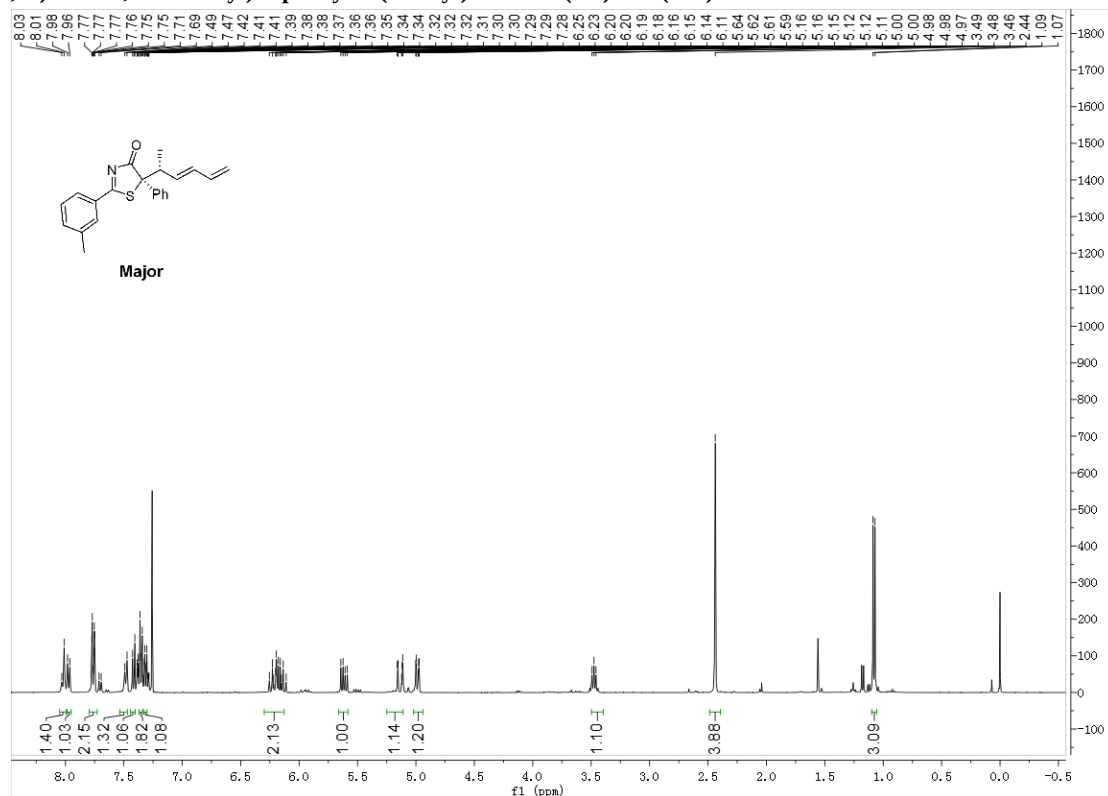
(4E, 6E)-8-((R)-5-(4-cyanobenzyl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) octa-4,6-dien-1-yl 4-methylbenzene sulfonate (3do)



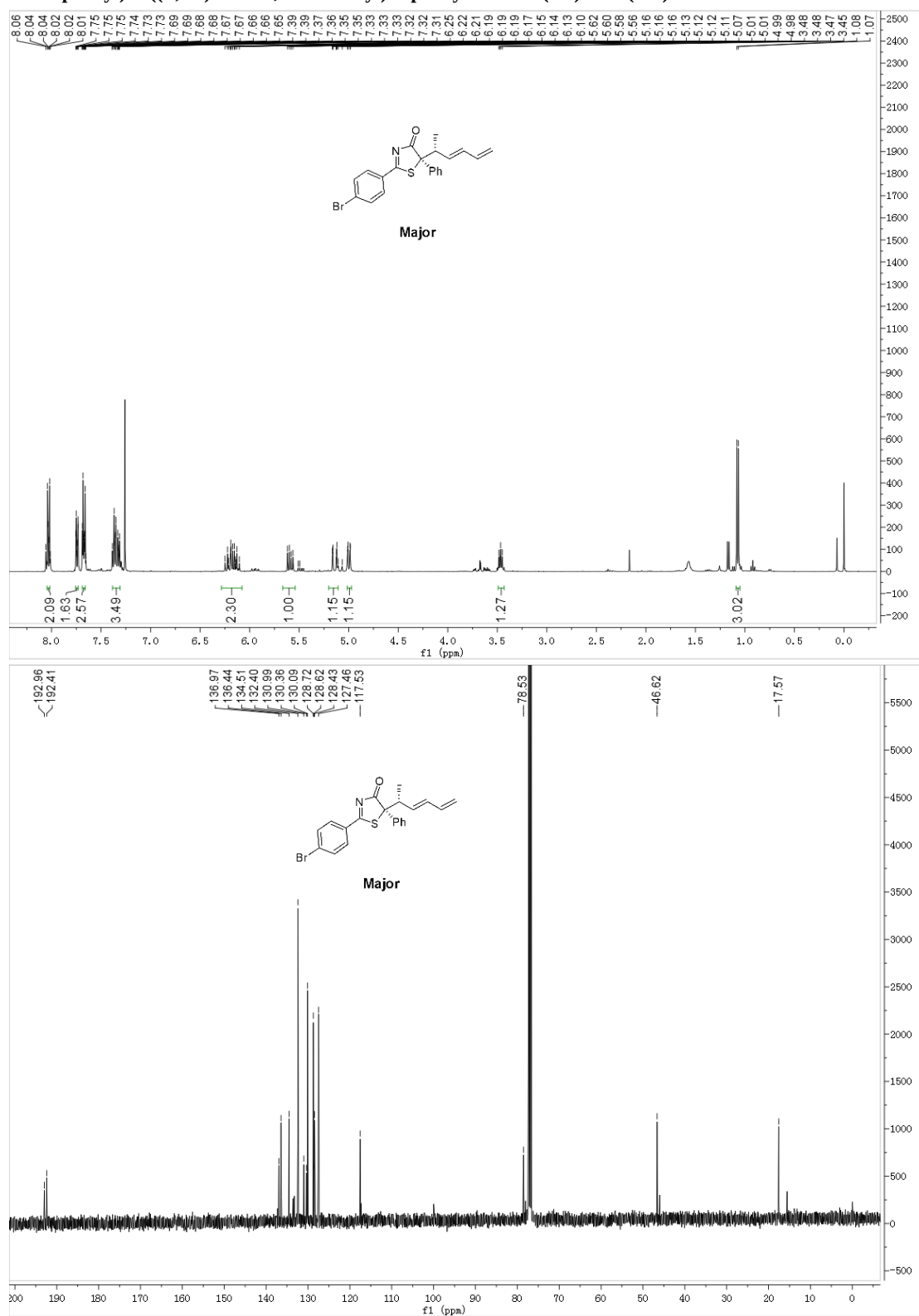
(S)-5-((R, E)-hexa-3, 5-dien-2-yl)-2, 5-diphenylthiazol-4(5H)-one (6aa)



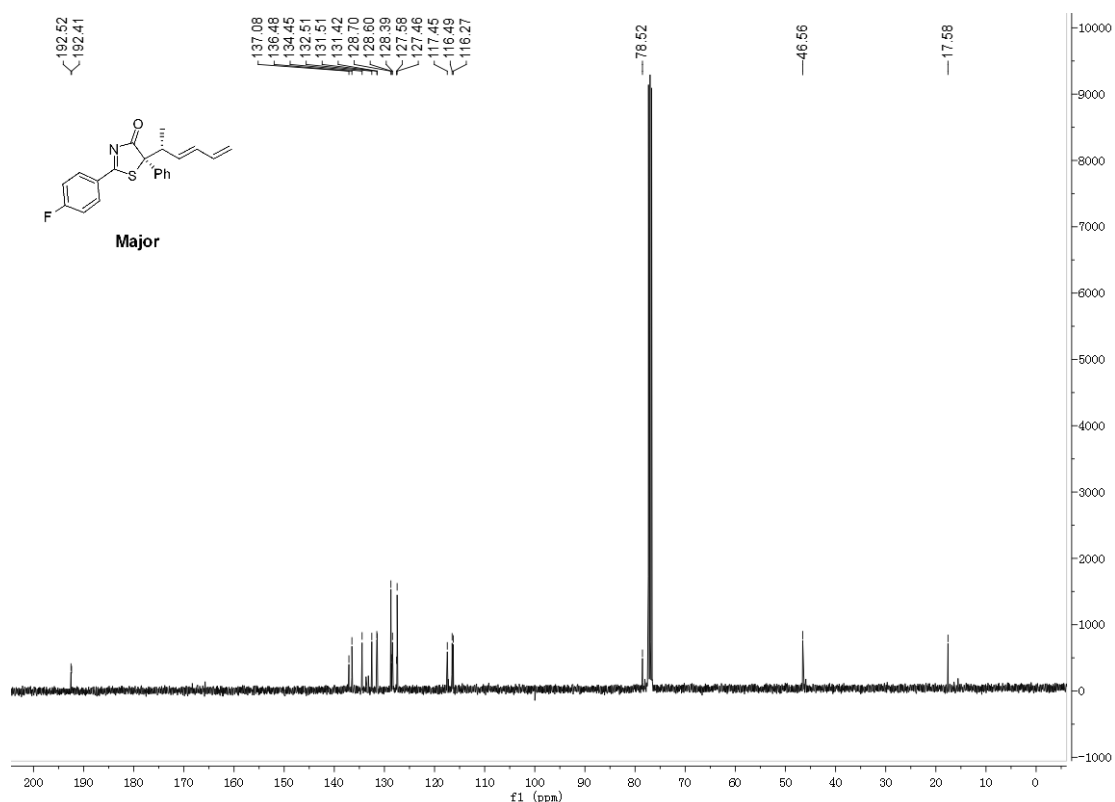
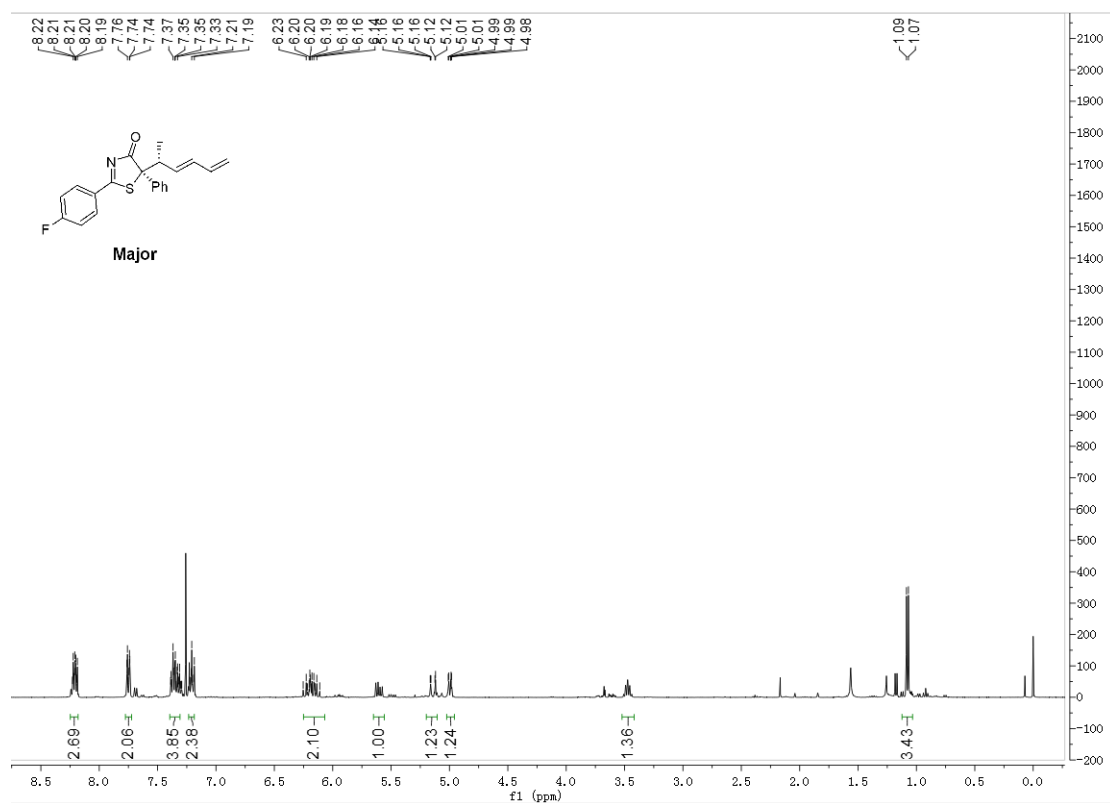
(S)-5-((R, E)-hexa-3, 5-dien-2-yl)-5-phenyl-2-(m-tolyl) thiazol-4(5H)-one (6ba)



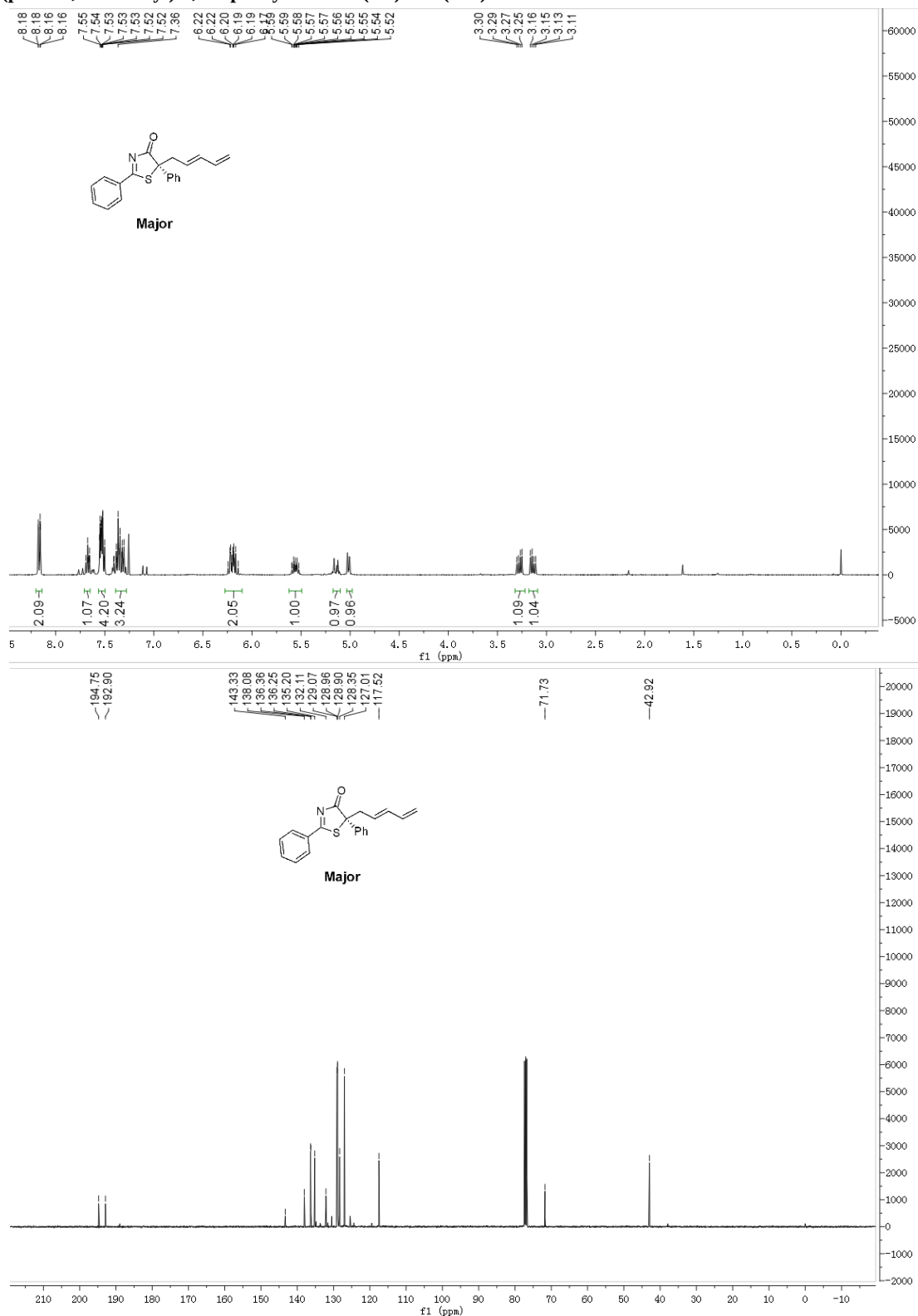
(S)-2-(4-bromophenyl)-5-((R, E)-hexa-3, 5-dien-2-yl)-5-phenylthiazol-4(5H)-one (6ca)



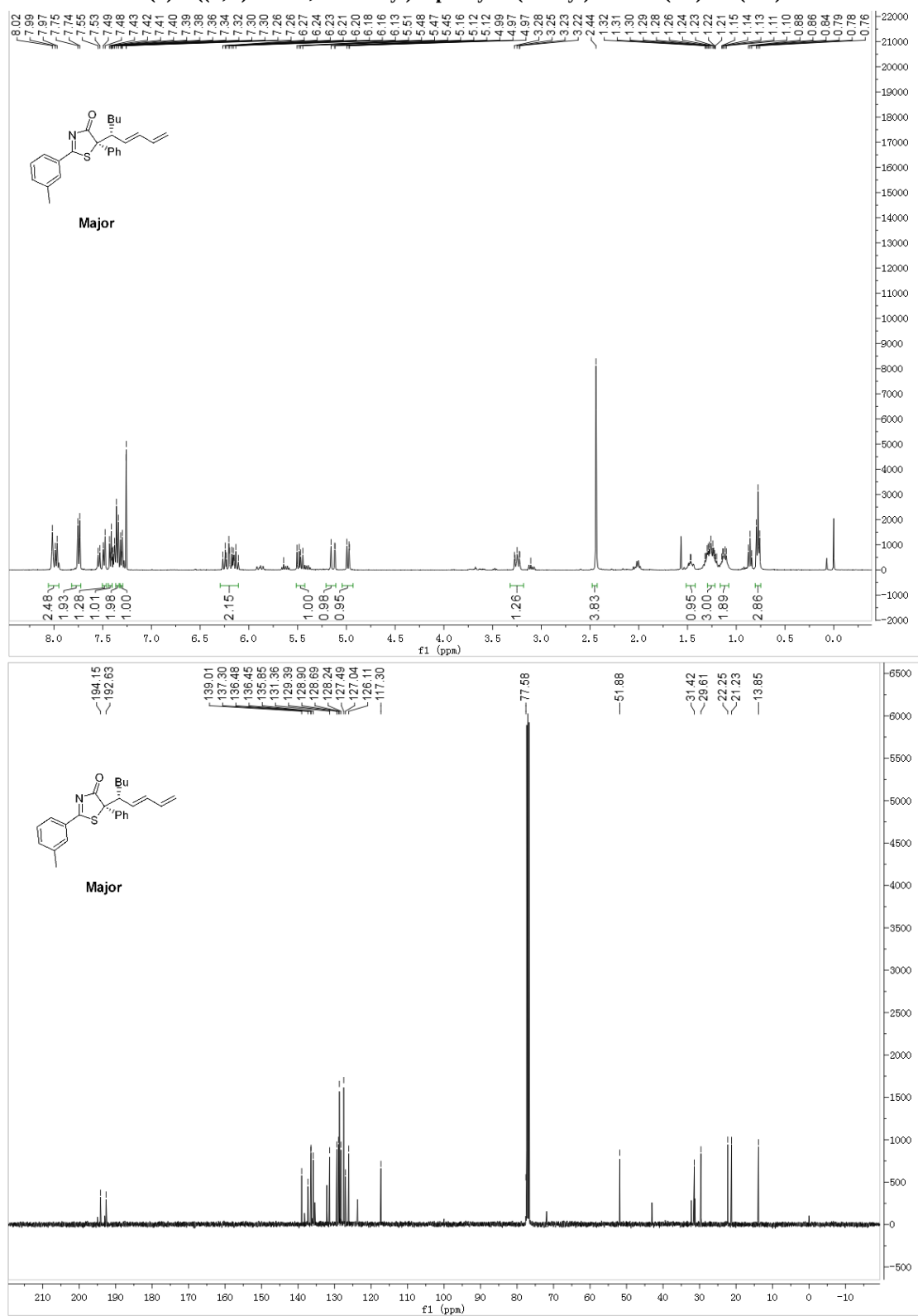
(S)-2-(4-fluorophenyl)-5-((R, E)-hexa-3, 5-dien-2-yl)-5-phenylthiazol-4(5H)-one (6da)



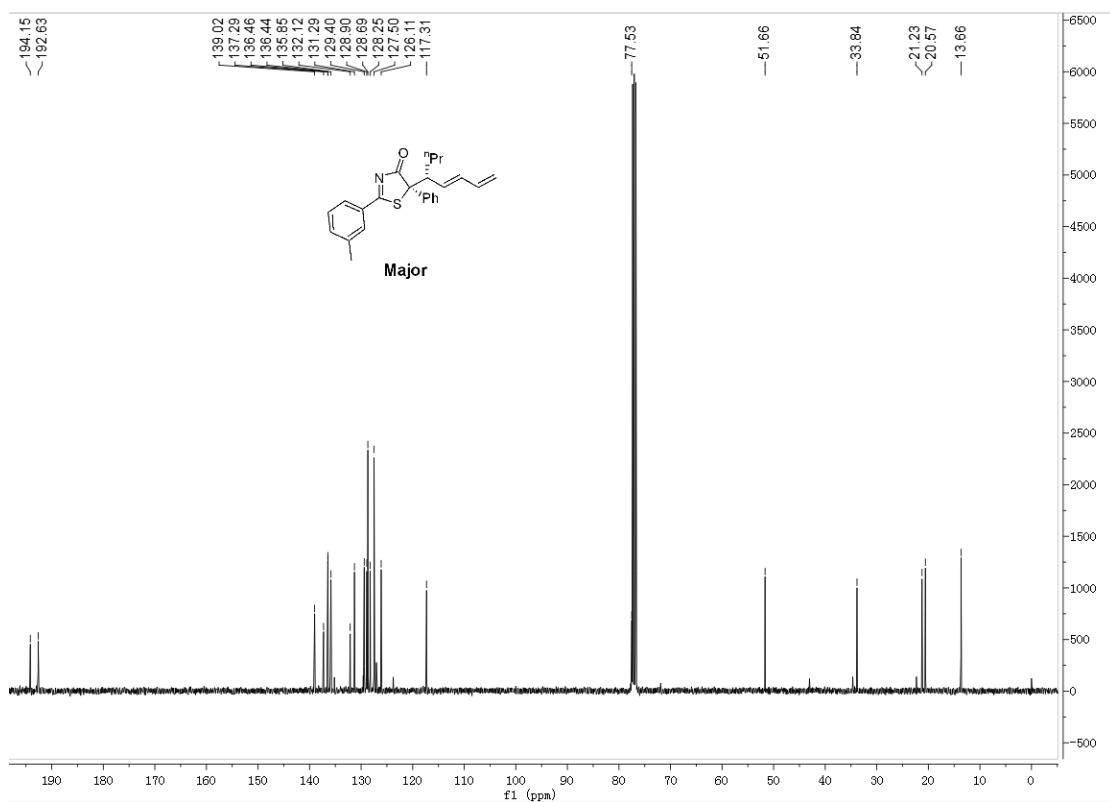
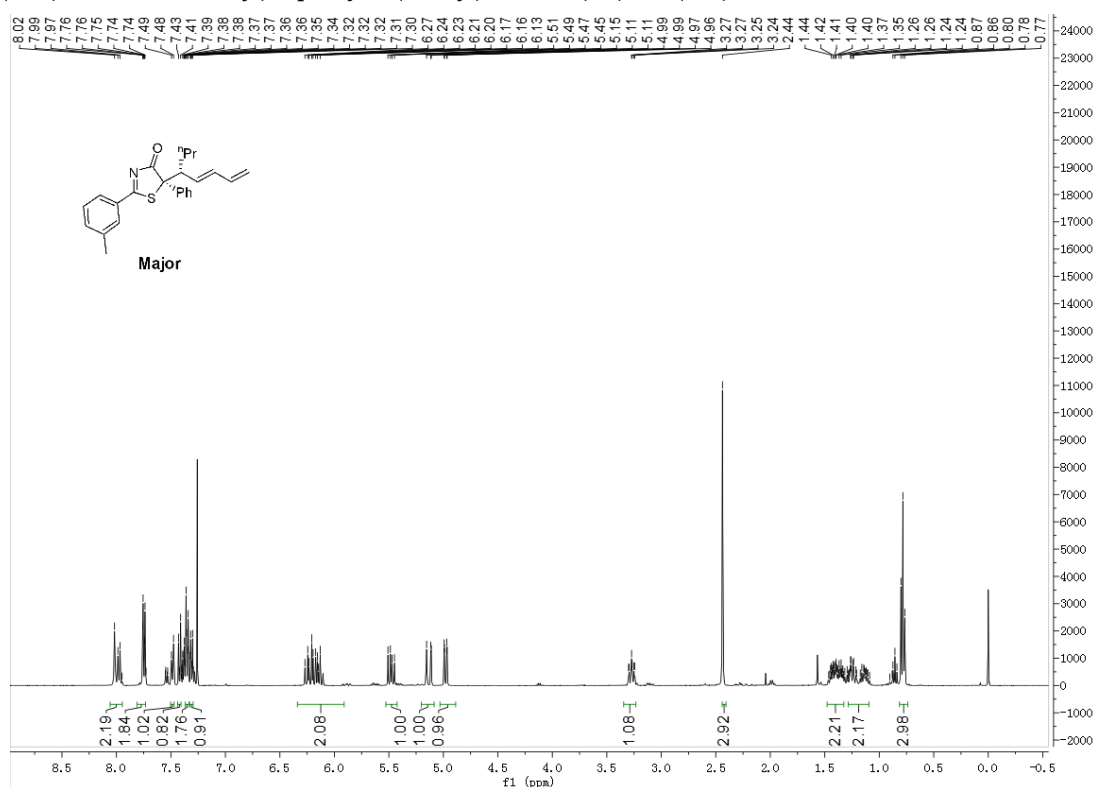
(S,E)-5-(penta-2,4-dien-1-yl)-2,5-diphenylthiazol-4(5H)-one (6ab)



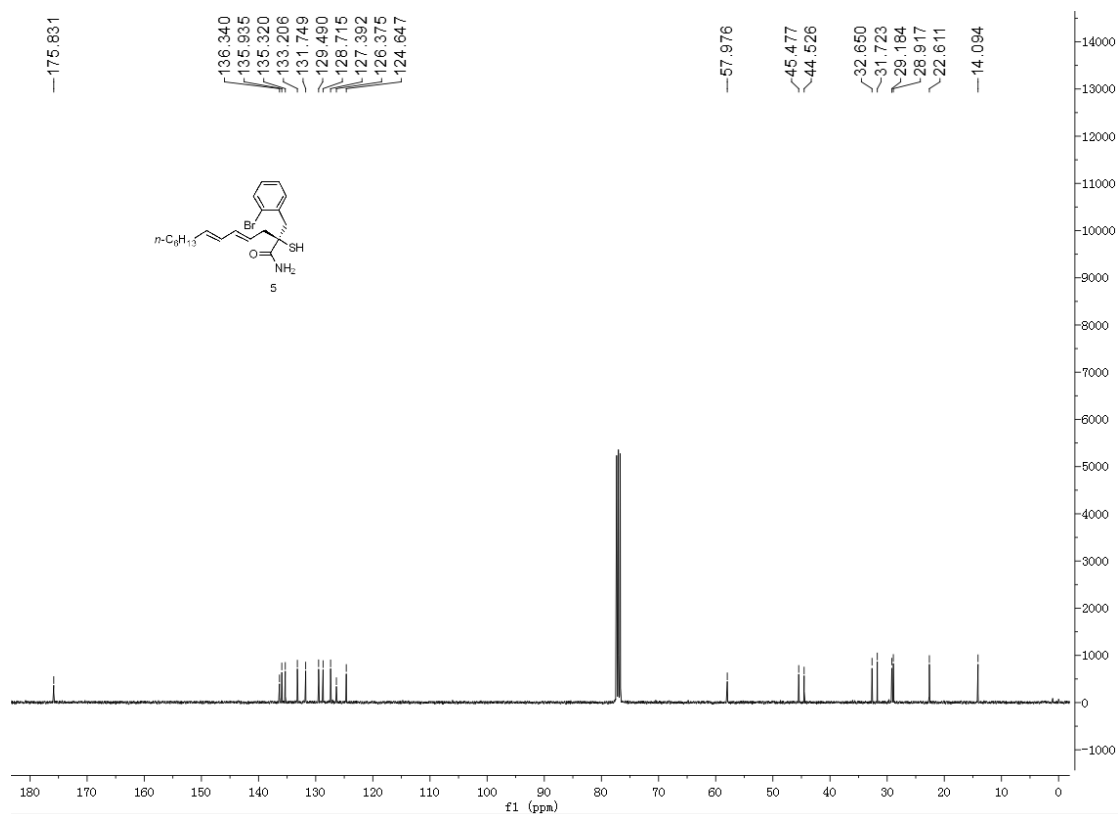
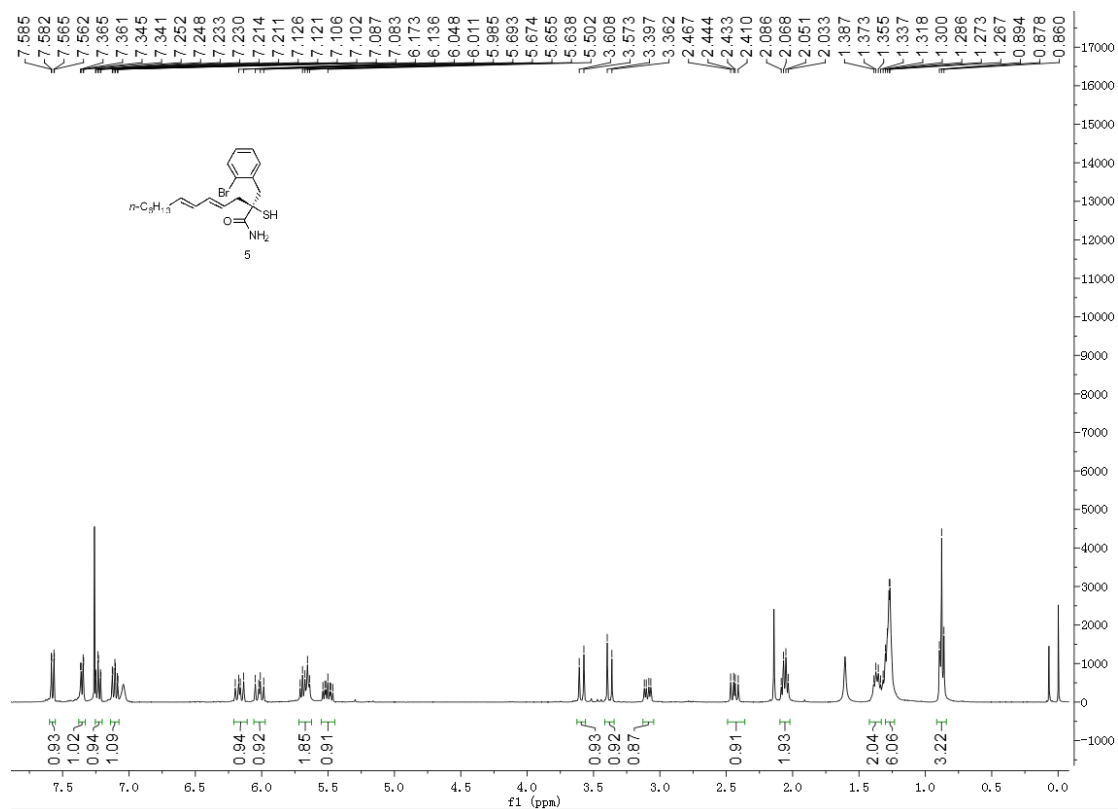
(S)-5-((R,E)-deca-1,3-dien-5-yl)-5-phenyl-2-(m-tolyl)thiazol-4(5H)-one(6bc)



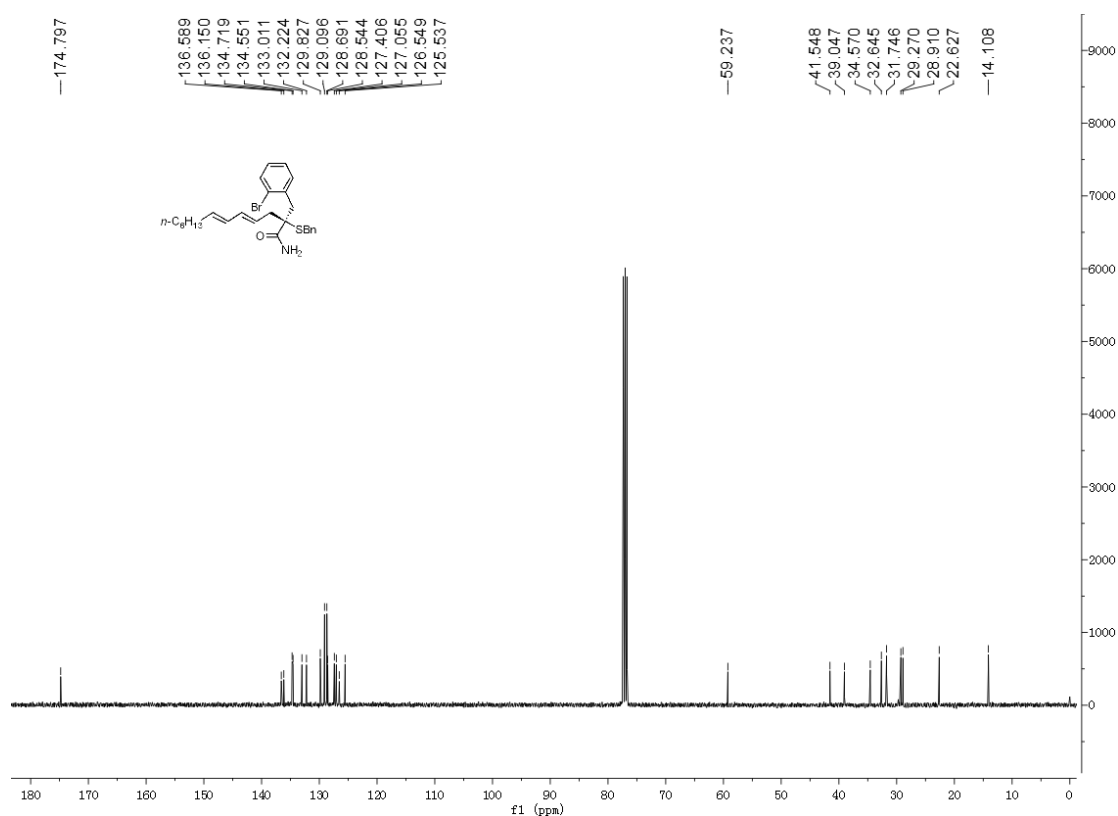
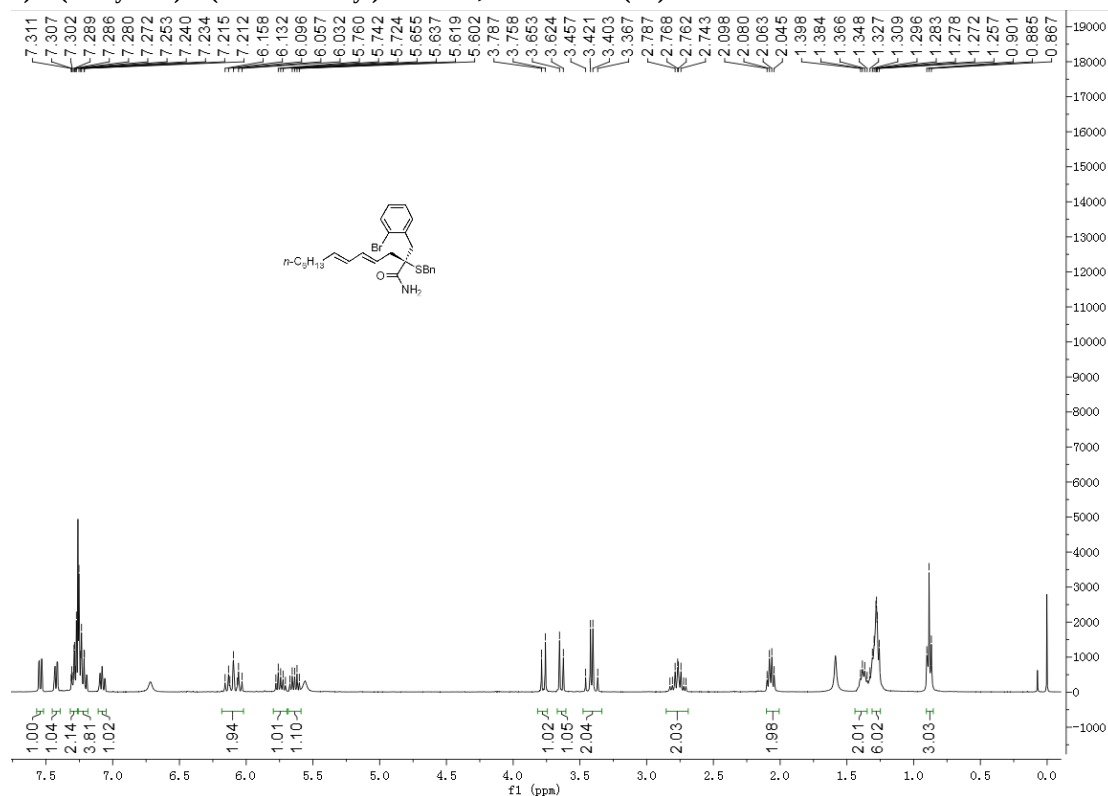
(S)-5-((R, E)-nona-1, 3-dien-5-yl)-5-phenyl-2-(m-tolyl) thiazol-4(5H)-one (6bd)



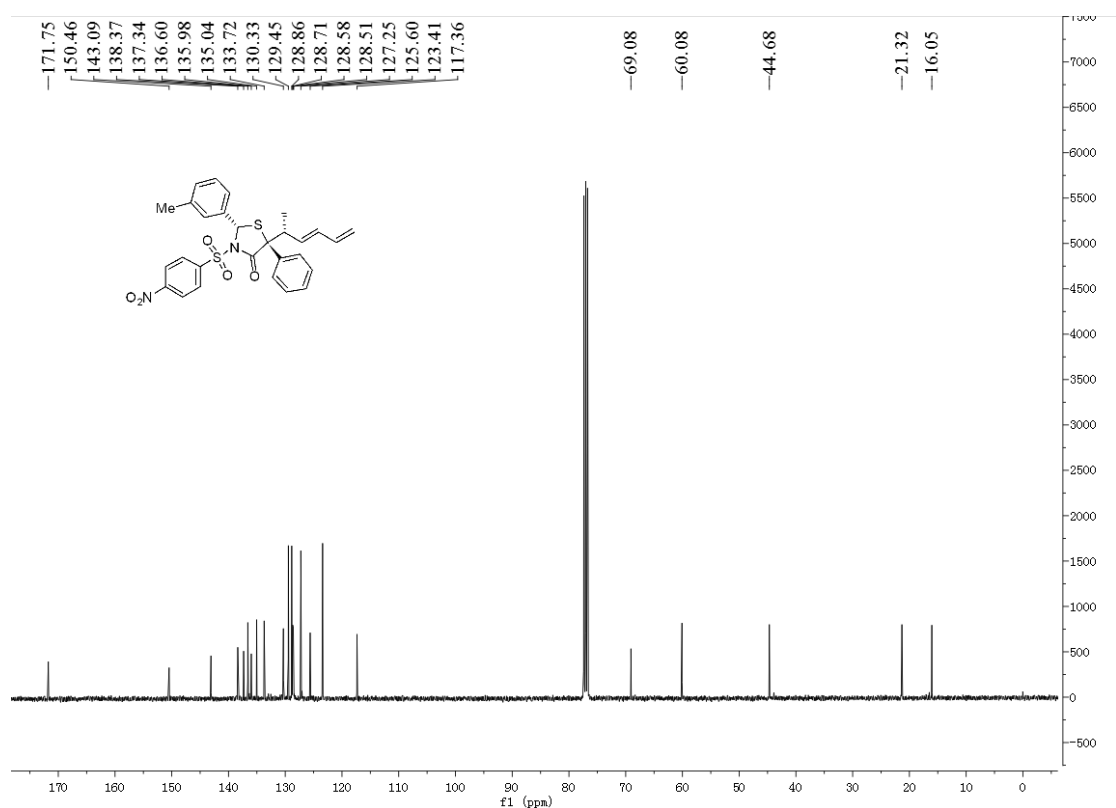
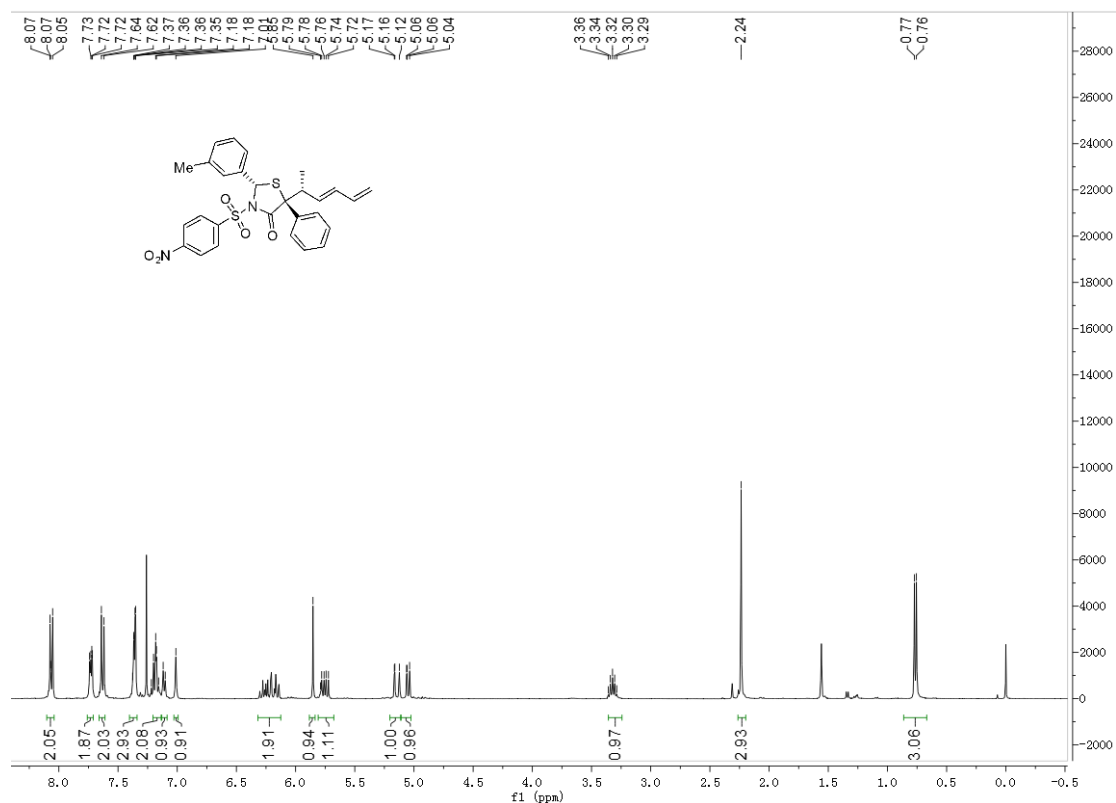
(S, 4E, 6E)-2-(2-bromobenzyl)-2-mercaptotrideca-4, 6-dienamide (P1)



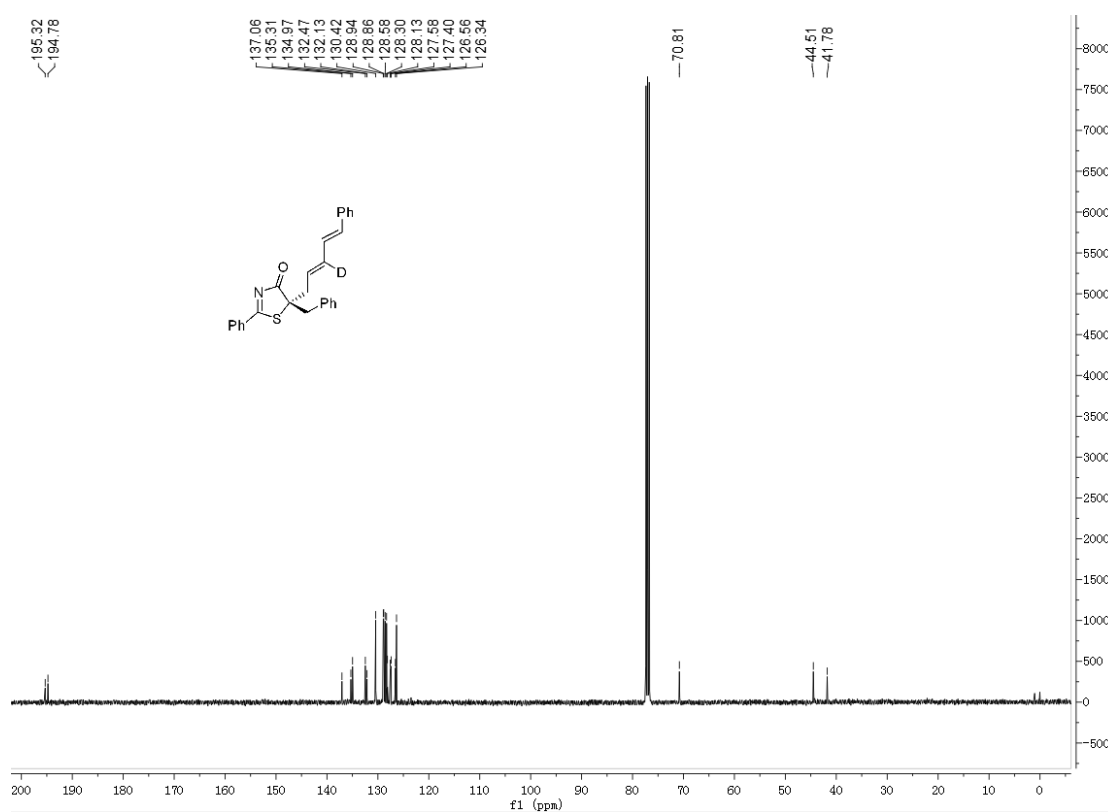
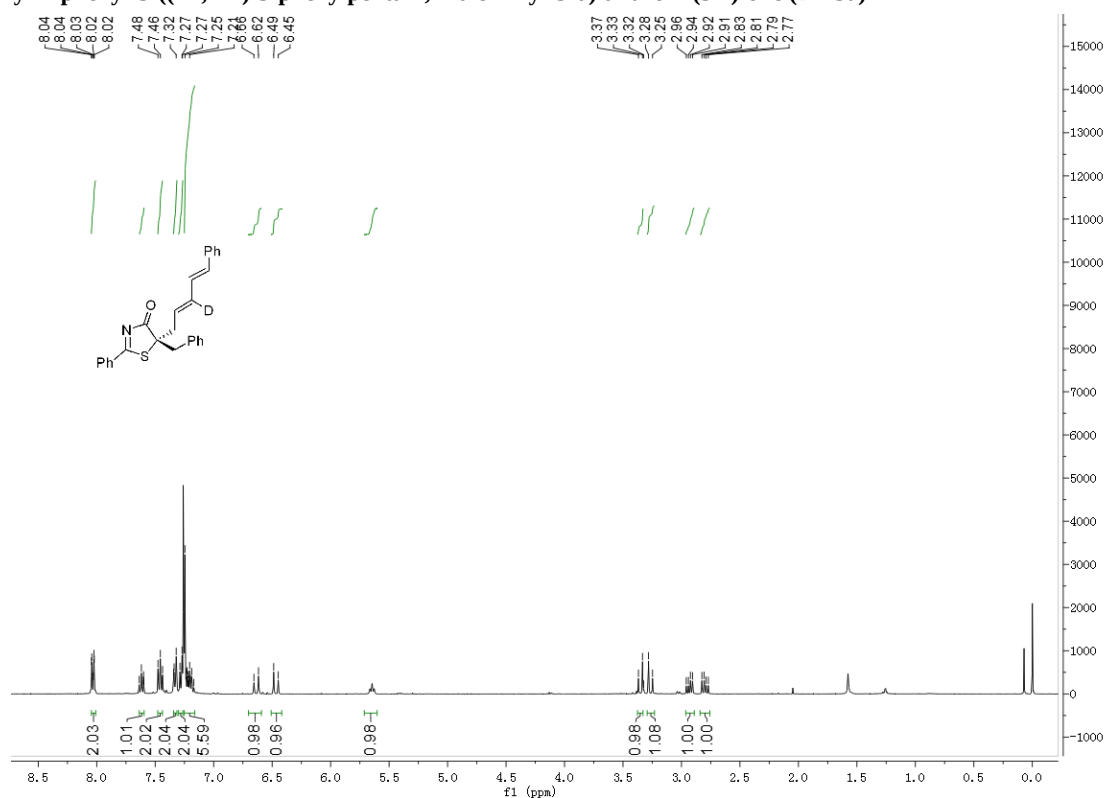
(S, 4E, 6E)-2-(benzylthio)-2-(2-bromobenzyl) trideca-4, 6-dienamide (P2)



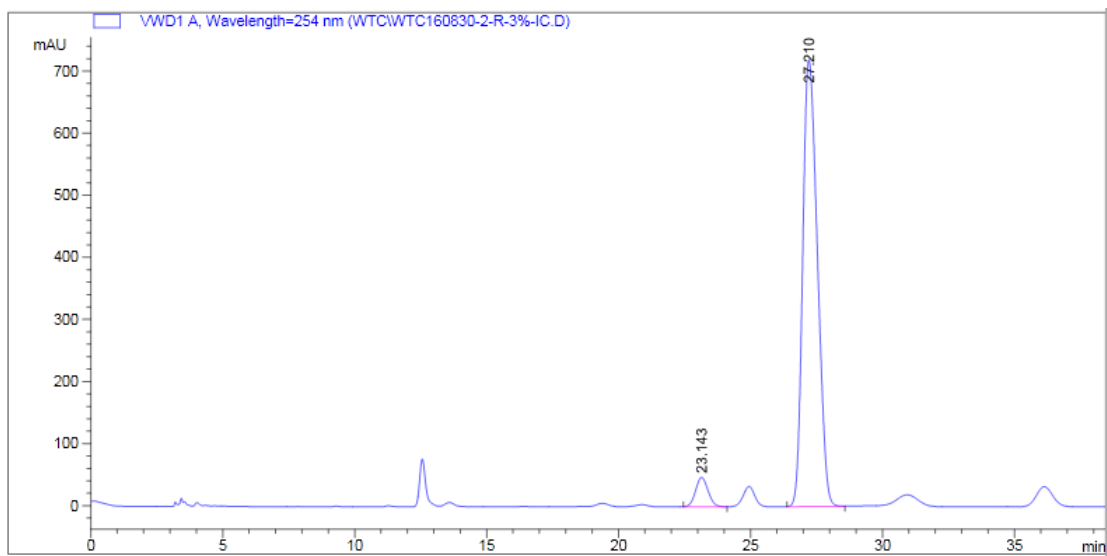
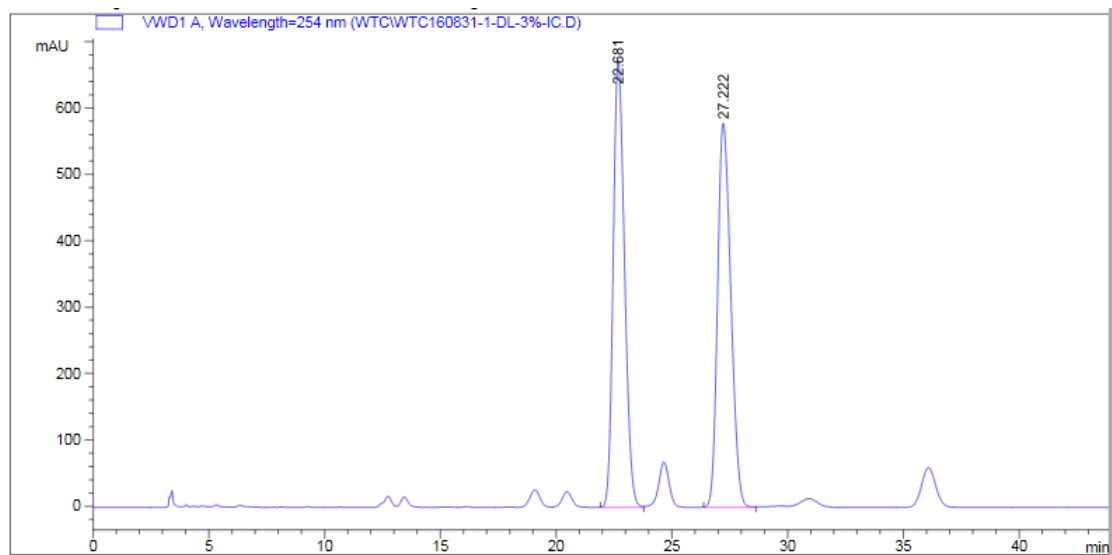
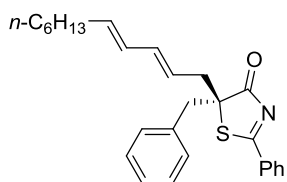
(2*S*, 5*S*)-5-((*R*,*E*)-hexa-3,5-dien-2-yl)-3-((4-nitrophenyl)sulfonyl)-2,5-diphenylthiazolidin-4-one (P3)



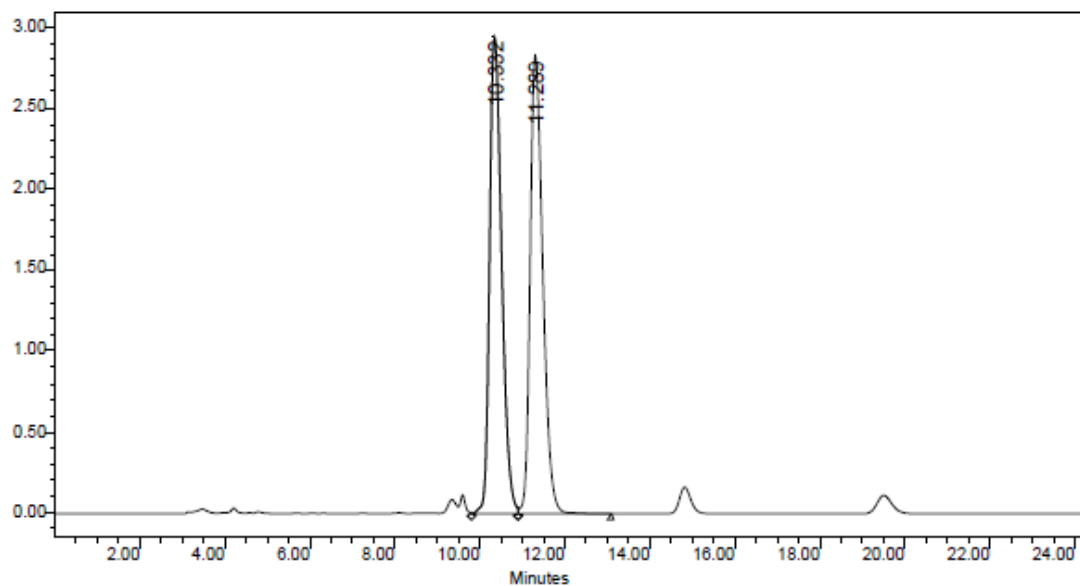
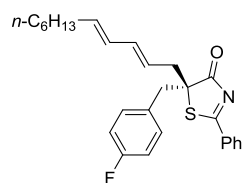
R-5-benzyl-2-phenyl-5-((2*E*, 4*E*)-5-phenylpenta-2, 4-dien-1-yl-3-d) thiazol-4(5*H*)-one (D2-3a)



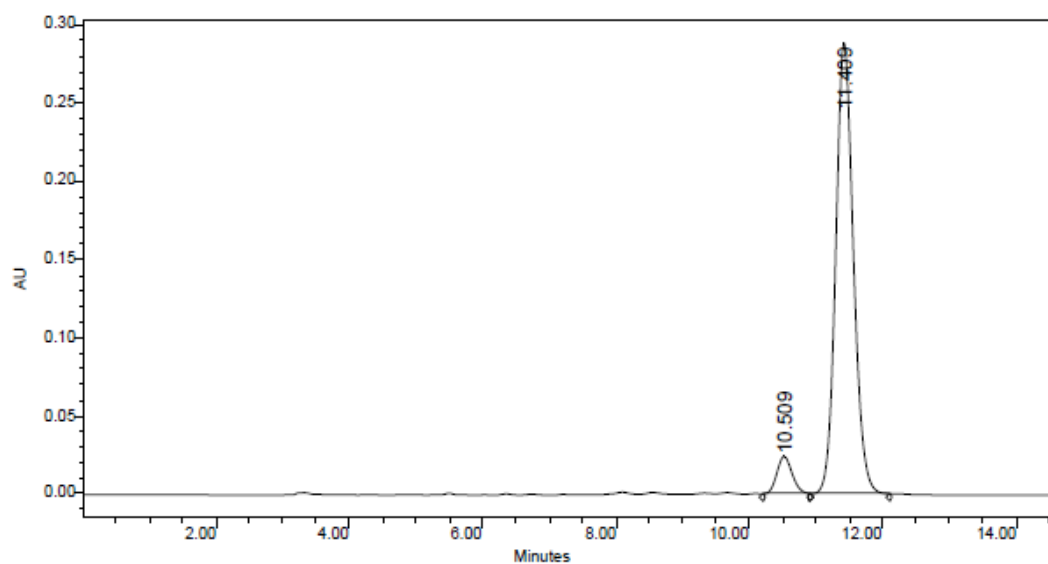
(R) -5-benzyl-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3aa)



(R)-5-(4-fluorobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ba)

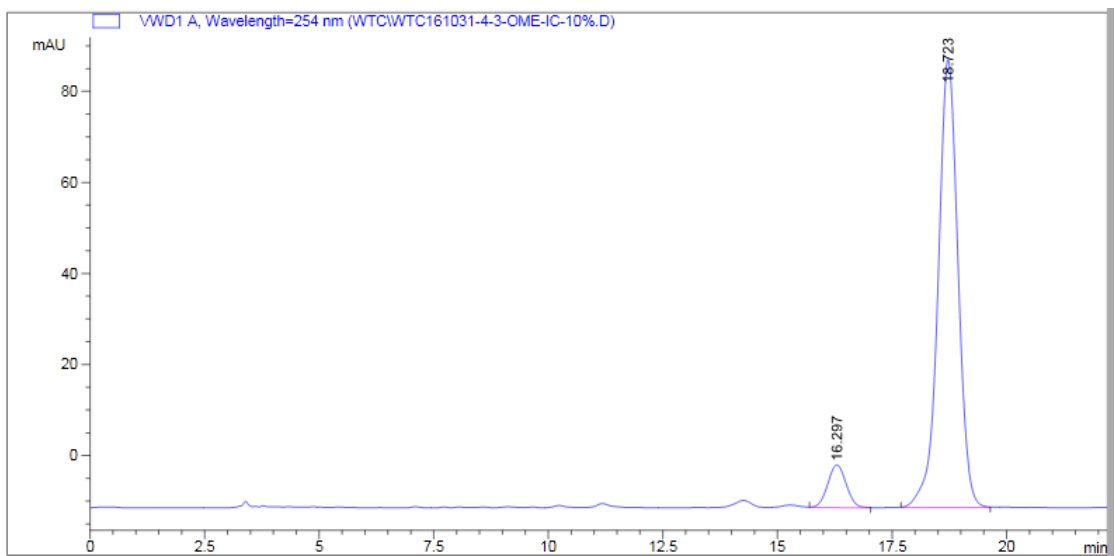
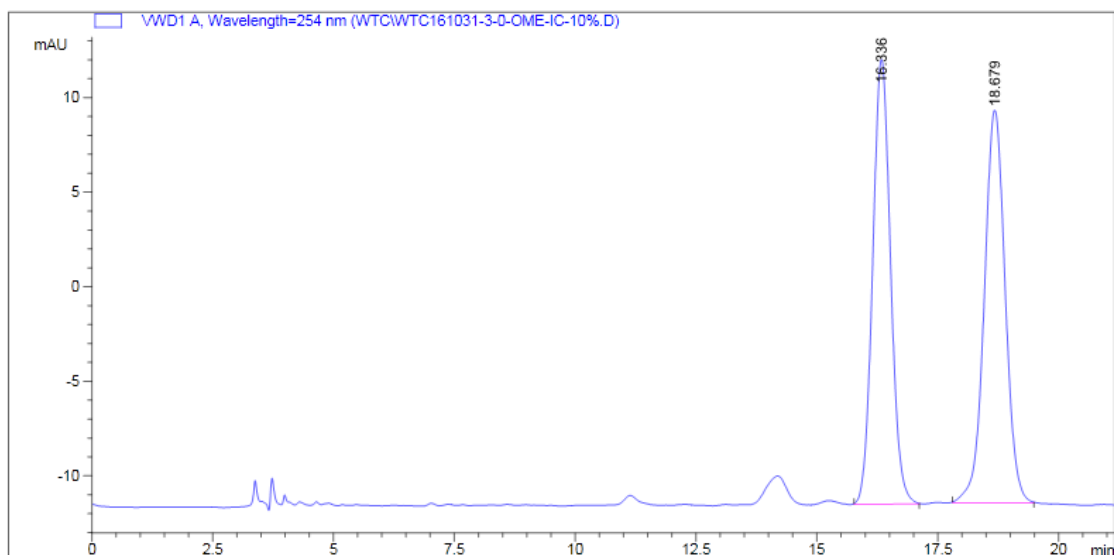
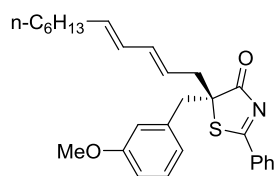


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
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2	11.289	58417133	50.16	2830351	49.02

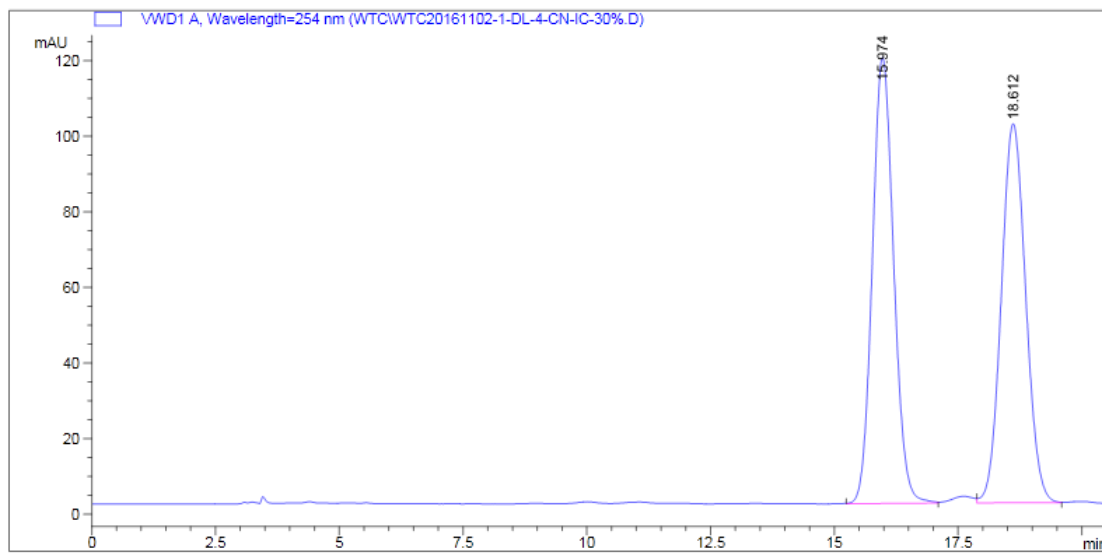
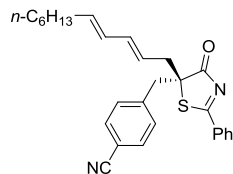


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.509	408232	7.08	24544	7.82
2	11.409	5358564	92.92	289296	92.18

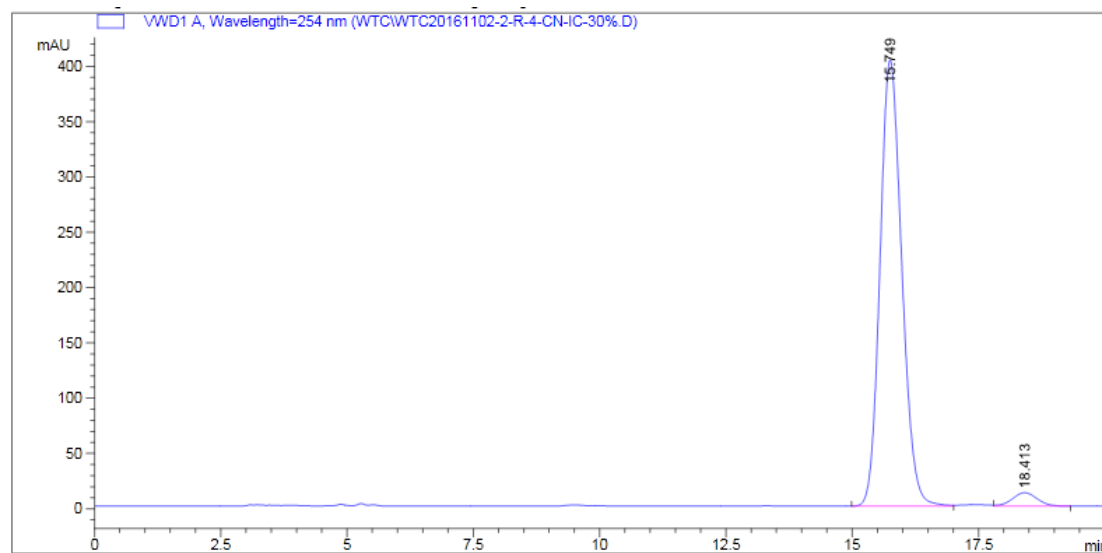
(R)-5-(3-methoxybenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ca)



4-(((R)-4-oxo-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl)-4, 5-dihydrothiazol-5-yl) methyl) Benzonitrile (3da)

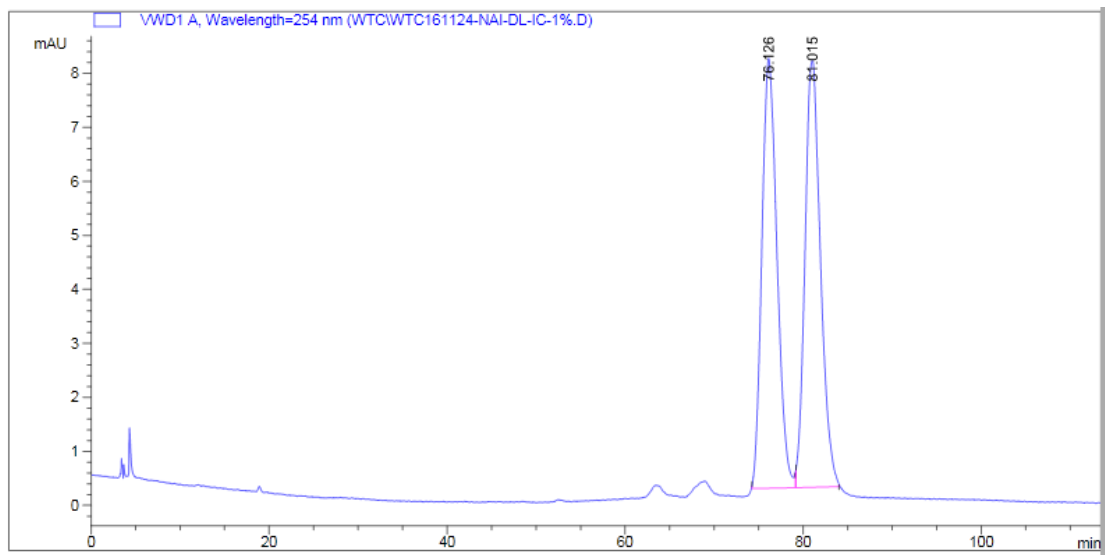
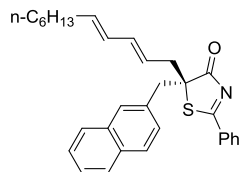


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	15.974	BB	0.4656	3529.66943	117.95927	50.7021
2	18.612	VB	0.5319	3431.91309	100.24349	49.2979

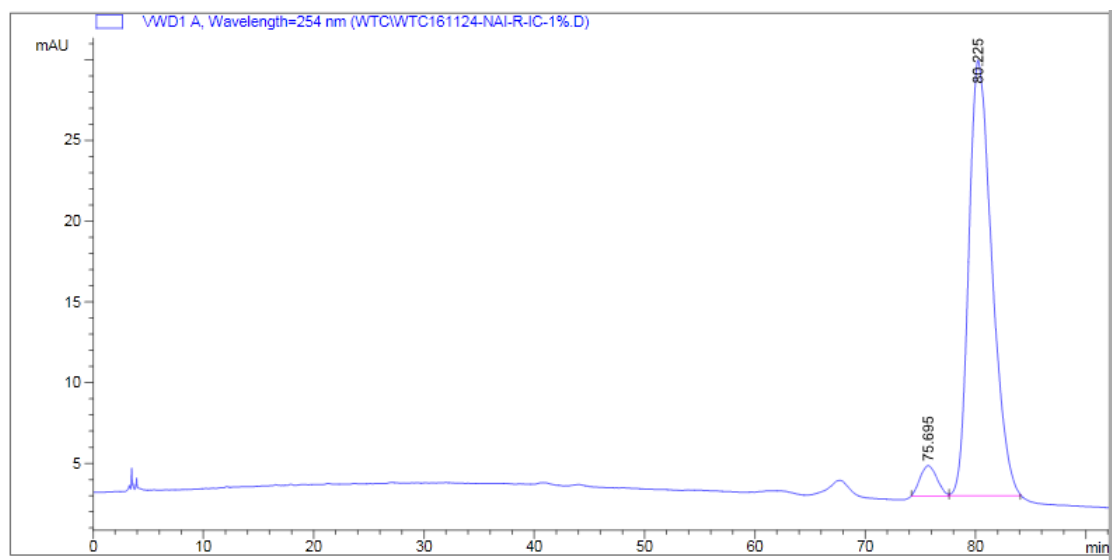


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.749	BB	0.4642	1.20747e4	403.38535	96.6750
2	18.413	VB	0.5338	415.29031	12.16227	3.3250

(R)-5-(naphthalen-2-ylmethyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ea)

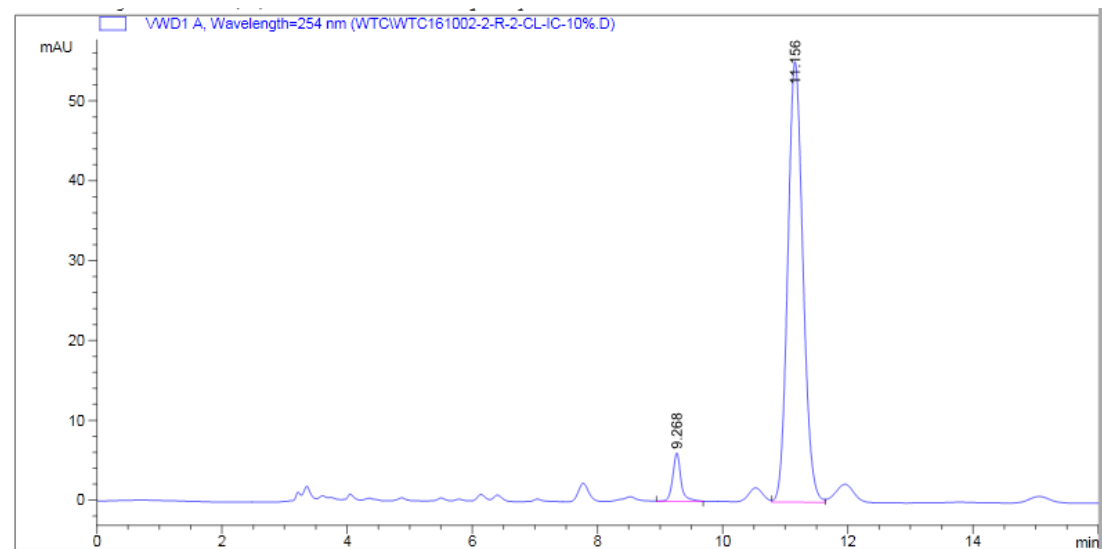
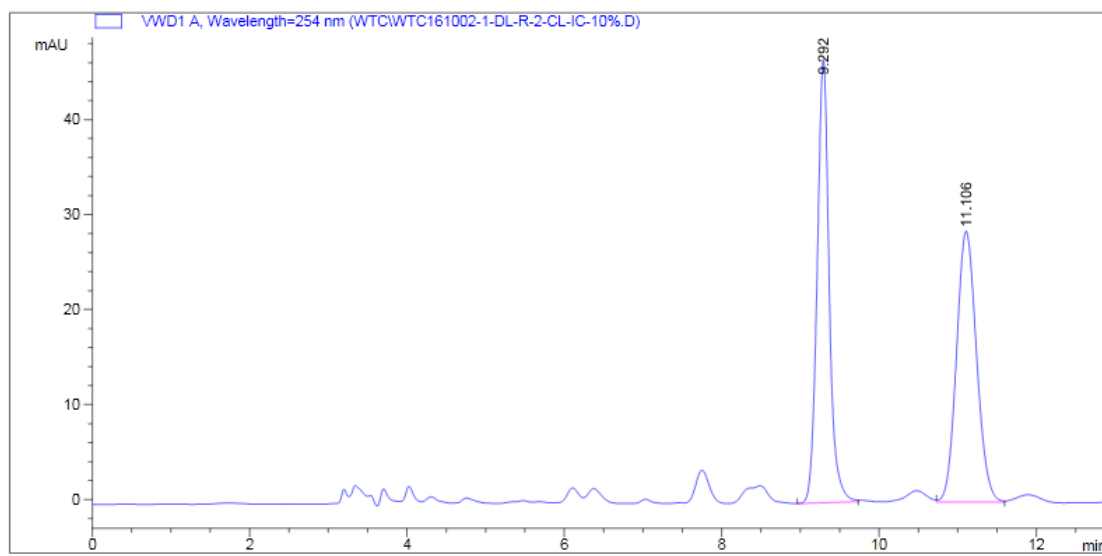
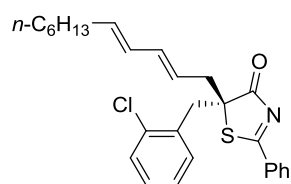


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	76.126	BB	1.4912	938.59900	49.5329	7.95692
2	81.015	BB	1.4328	956.29938	50.4671	7.89911

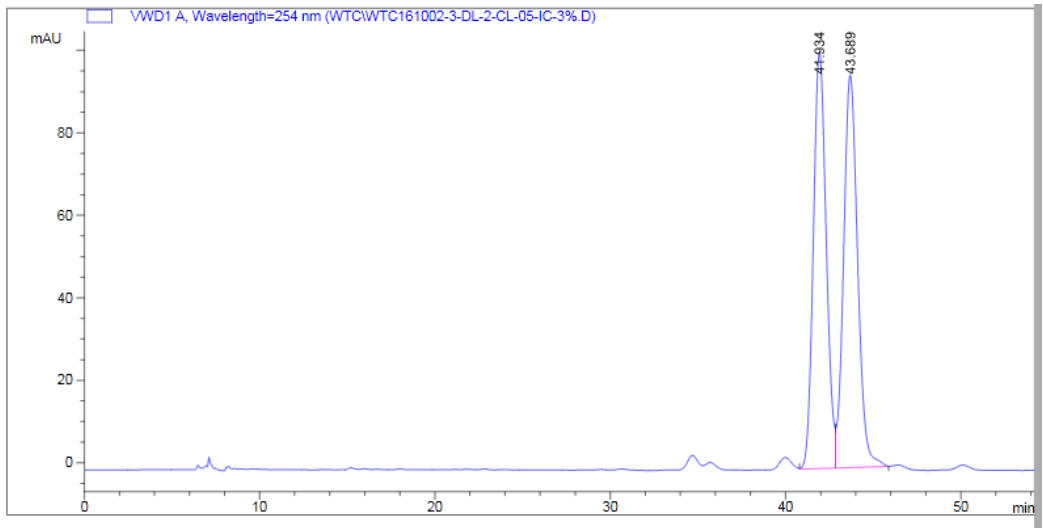
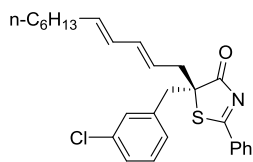


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area %	Height [mAU]
1	75.695	BV	1.2533	201.56993	4.8818	1.89618
2	80.225	VB	2.0140	3927.42578	95.1182	26.98469

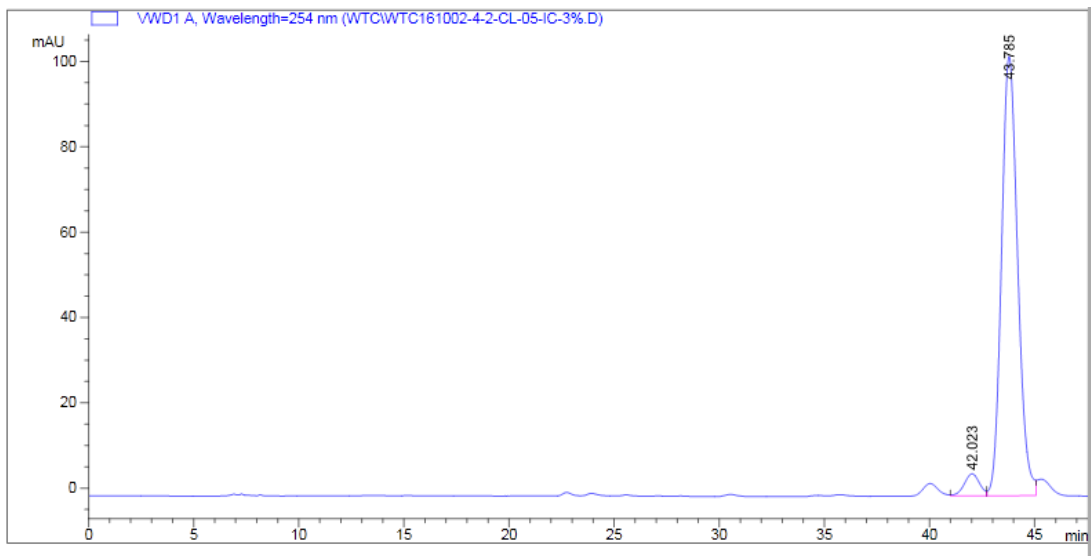
(R)-5-(2-chlorobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3fa)



(R)-5-(3-chlorobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ga)

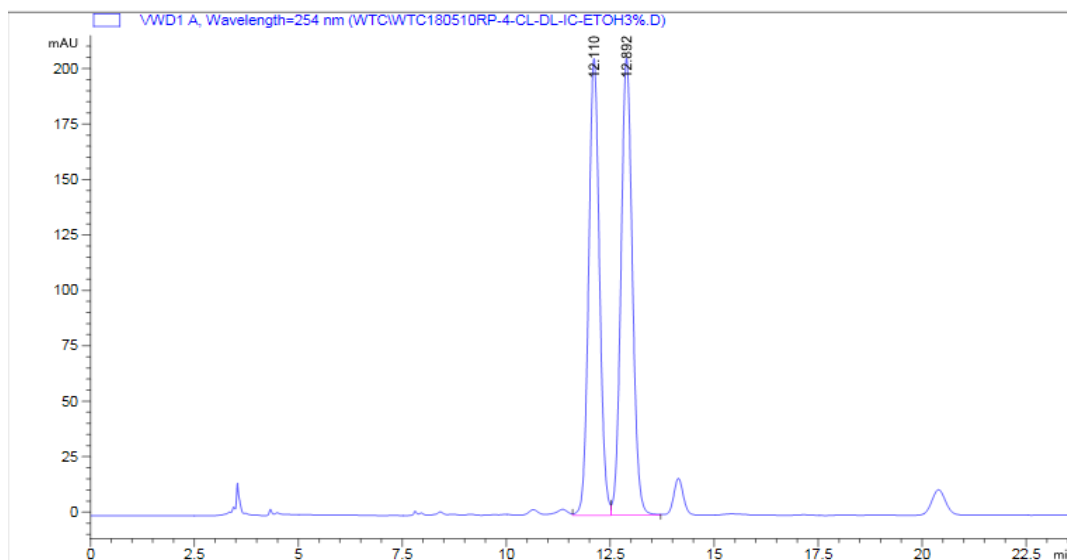
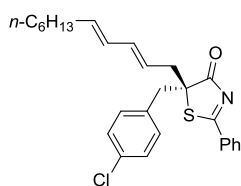


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	41.934	VV	0.7804	5151.51025	100.93130	49.3594
2	43.689	VB	0.8344	5285.22168	95.15025	50.6406

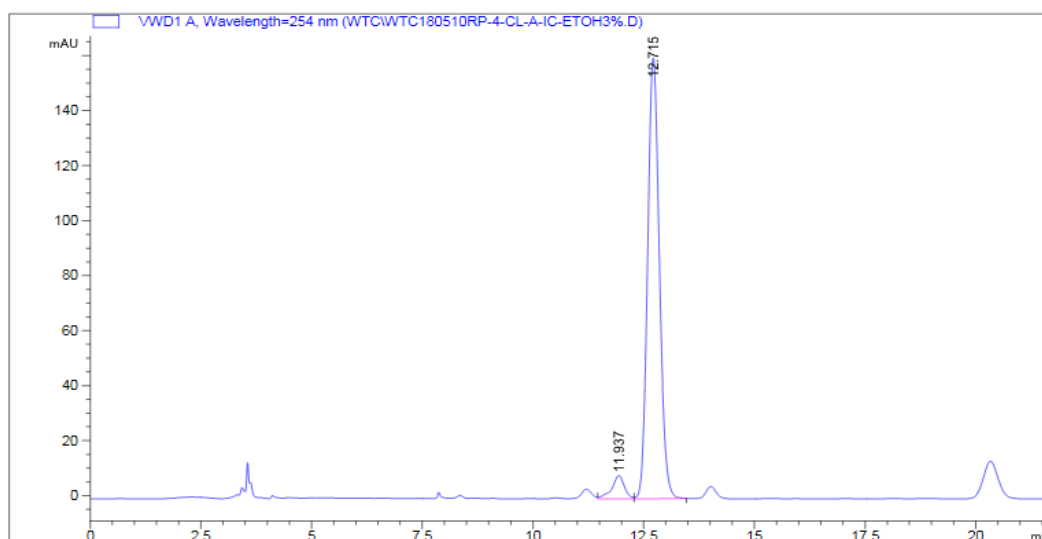


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	42.023	VV	0.7373	263.40503	5.16804	4.5708
2	43.785	VV	0.7922	5499.38037	102.93120	95.4292

(R)-5-(4-chlorobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ha)

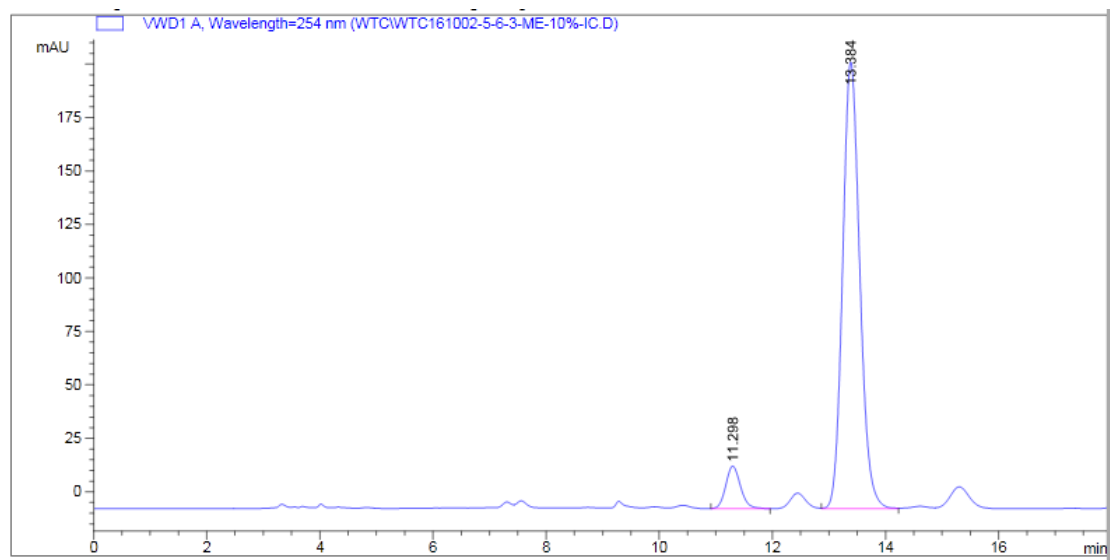
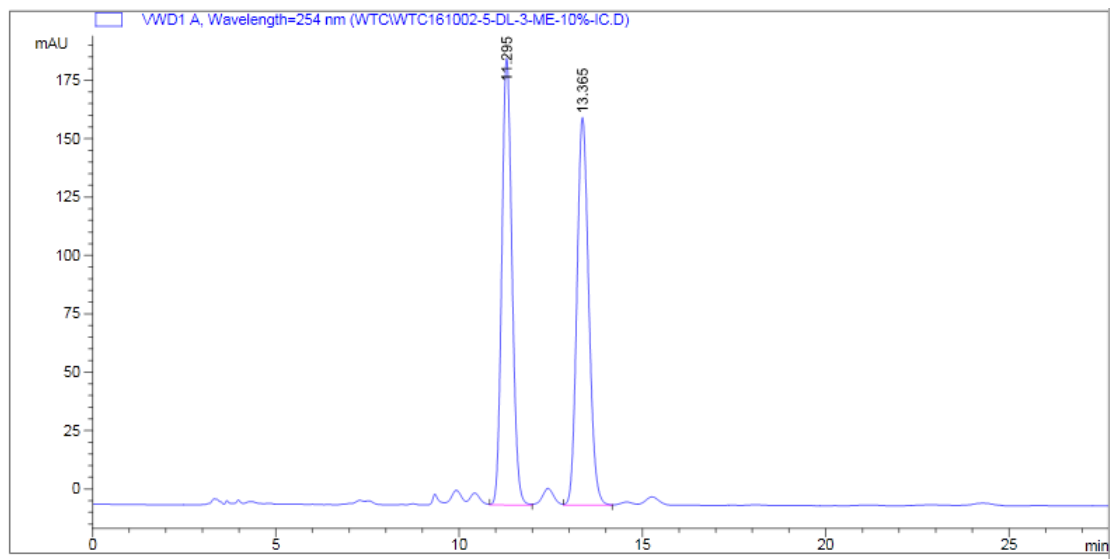
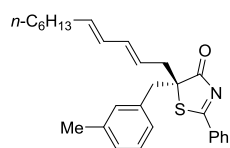


Peak #	RetTime [min]	Type	Width [min]	Area mAU * s	Height [mAU]	Area %
1	12.110	VV	0.2795	3713.27173	205.93370	48.6040
2	12.892	VB	0.2944	3926.57056	206.00824	51.3960

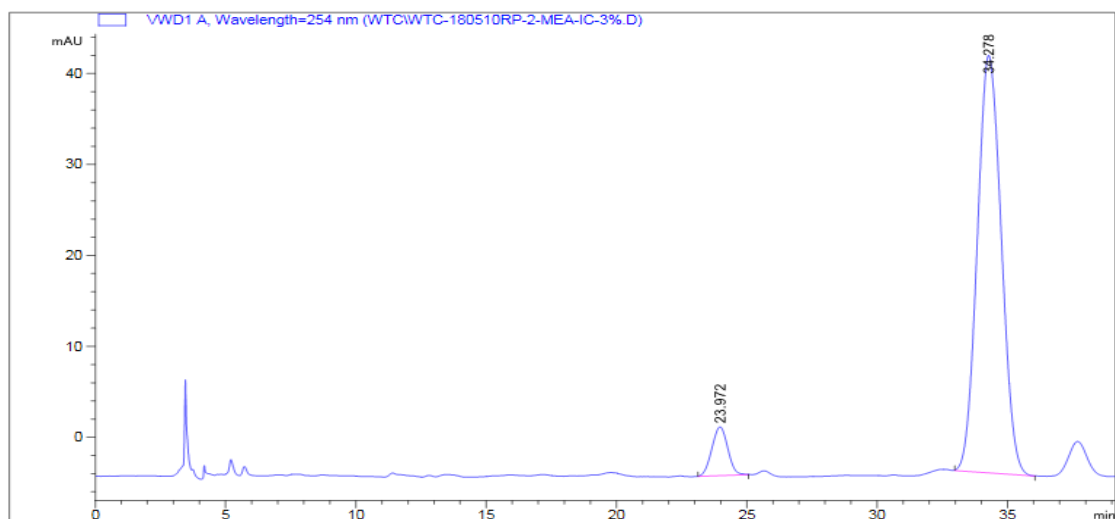
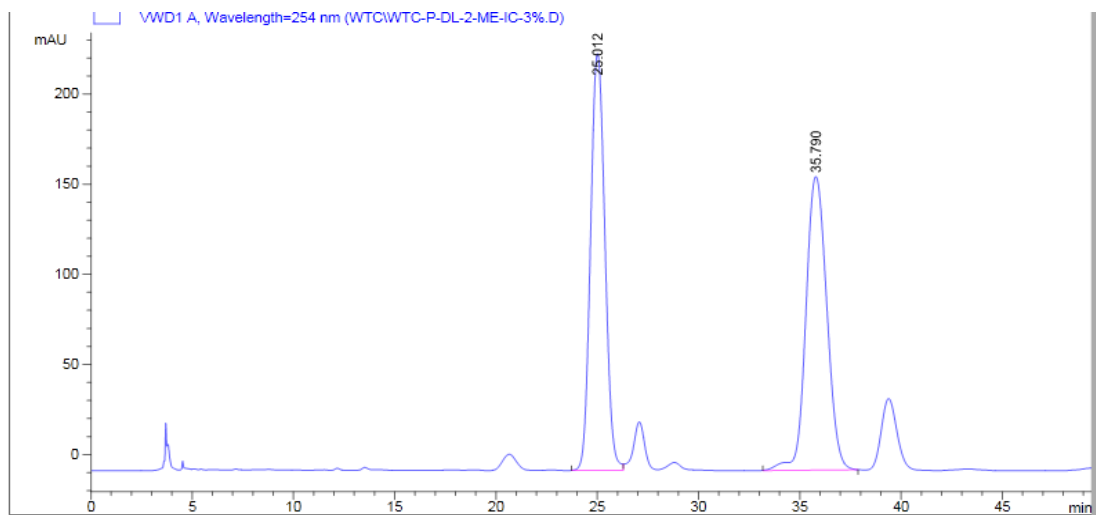
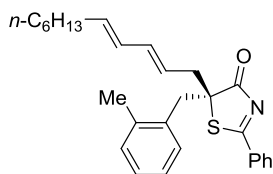


Peak #	RetTime [min]	Type	Width [min]	Area mAU * s	Height [mAU]	Area %
1	11.937	VV	0.2917	165.37163	8.39105	5.3465
2	12.715	VB	0.2825	2927.71924	160.10959	94.6535

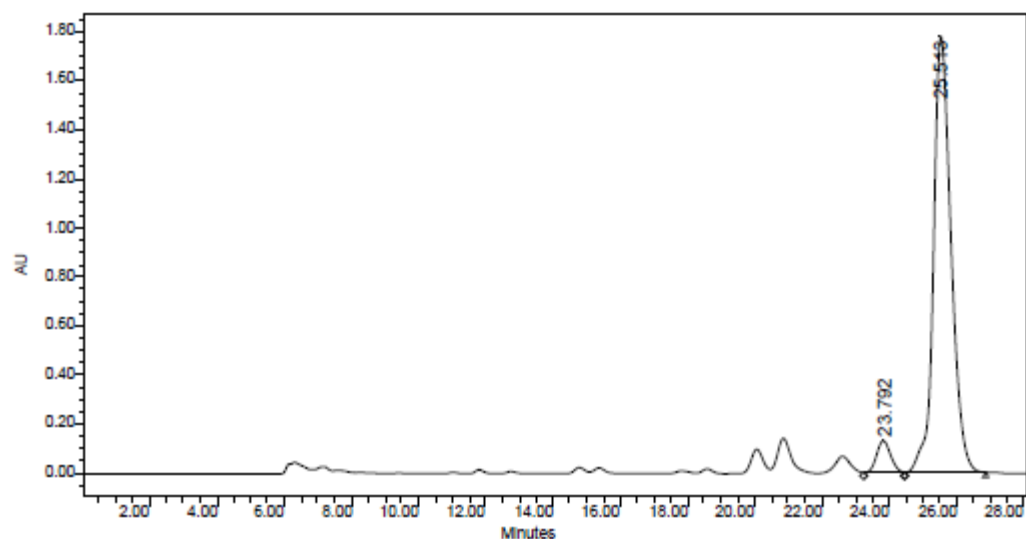
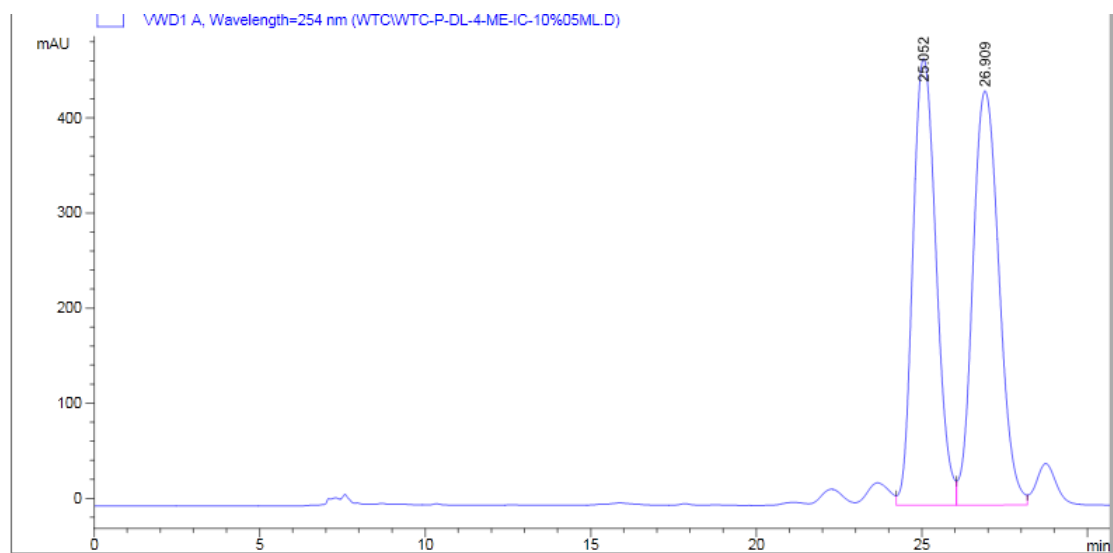
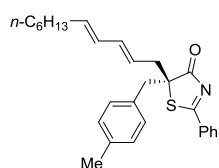
(R)-5-(3-methylbenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ia)



(R)-5-(2-methylbenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ja)

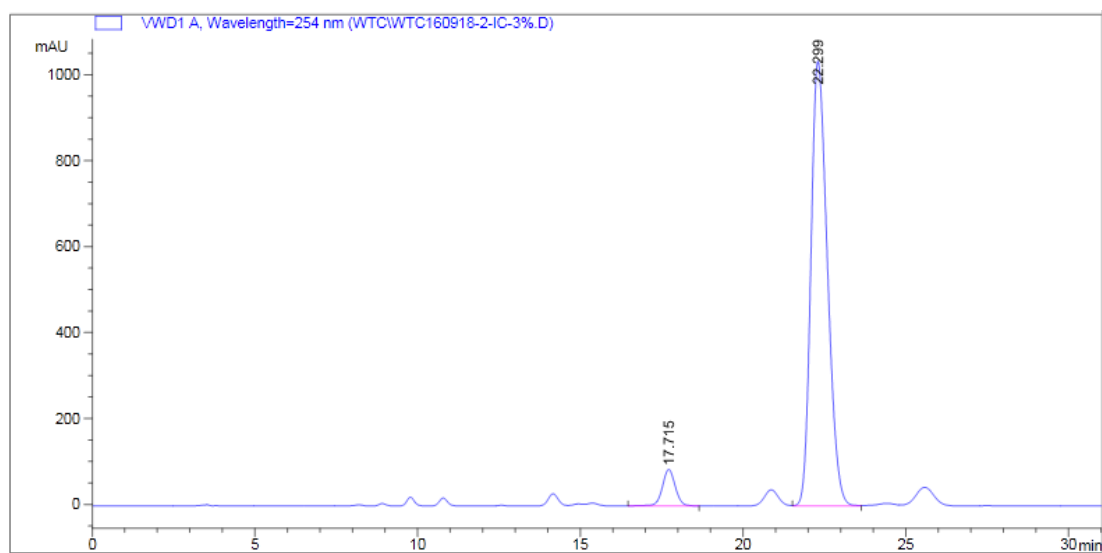
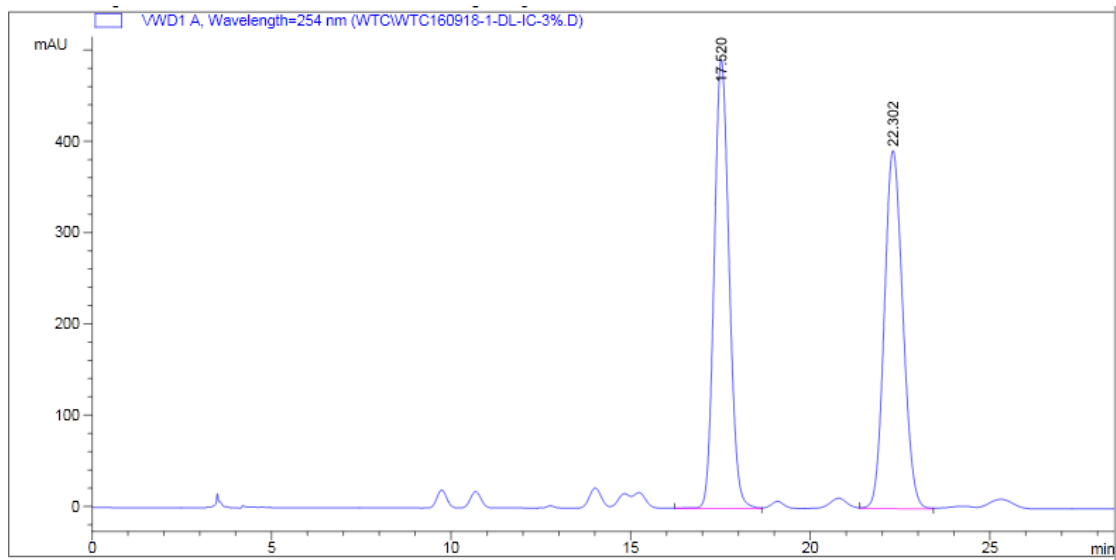
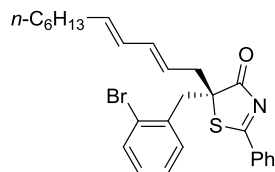


(R)-5-(4-methylbenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ka)

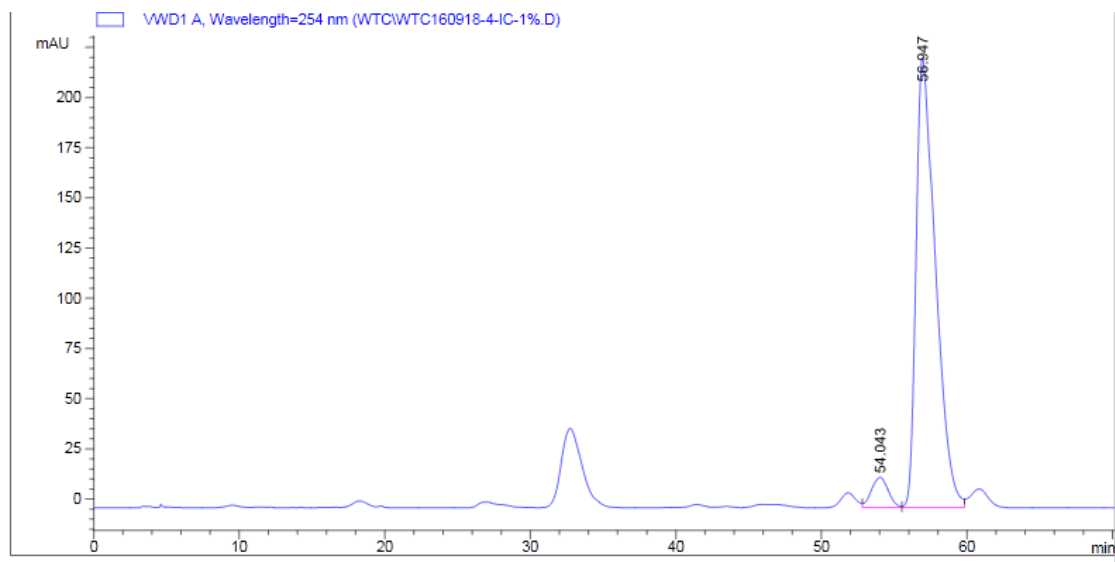
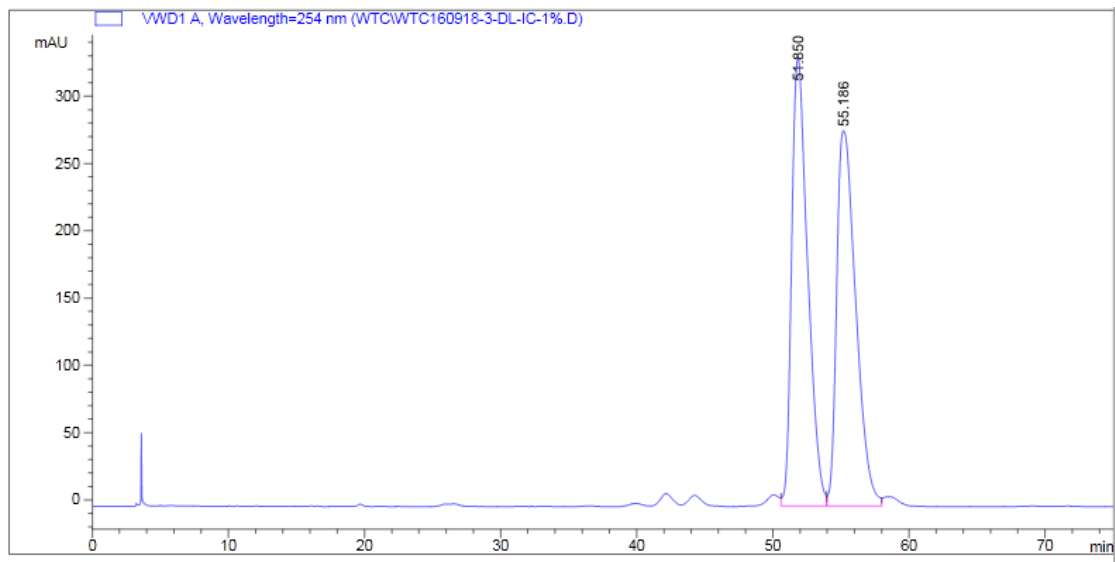
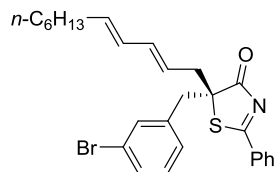


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	23.792	3865785	5.64	131686	6.90
2	25.513	64627226	94.36	1777987	93.10

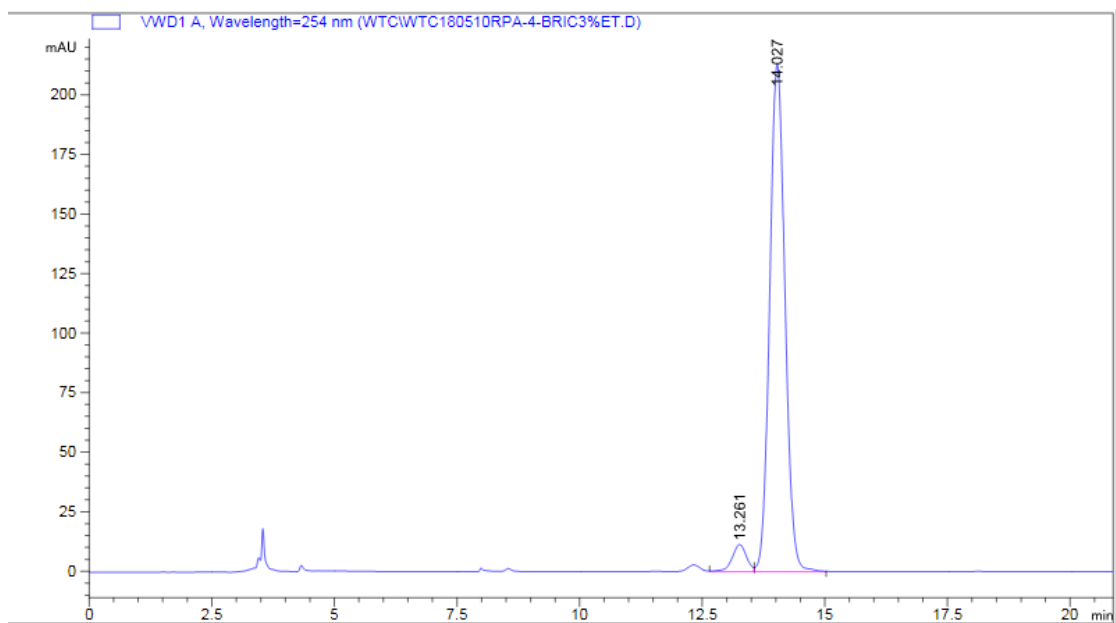
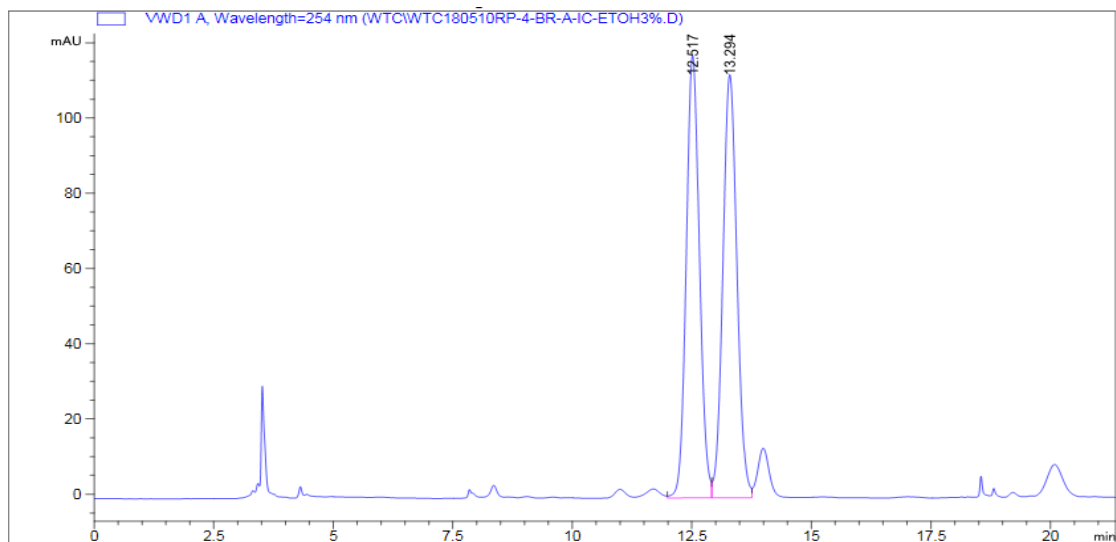
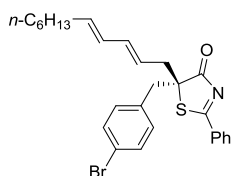
(R)-5-(2-bromobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3la)



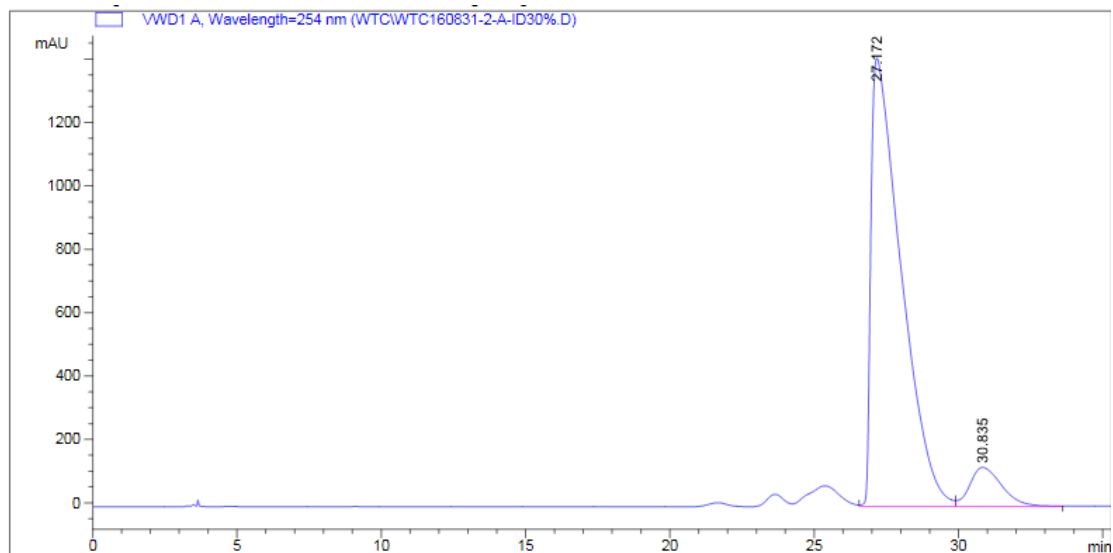
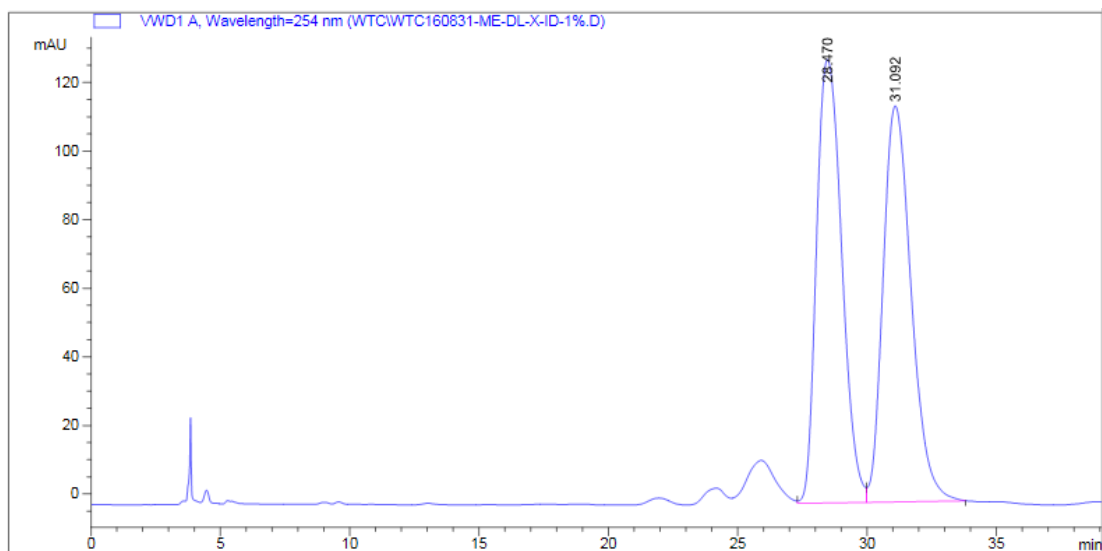
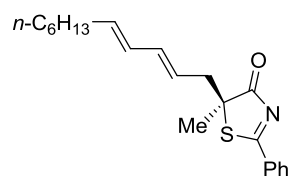
(R)-5-(3-bromobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3ma)



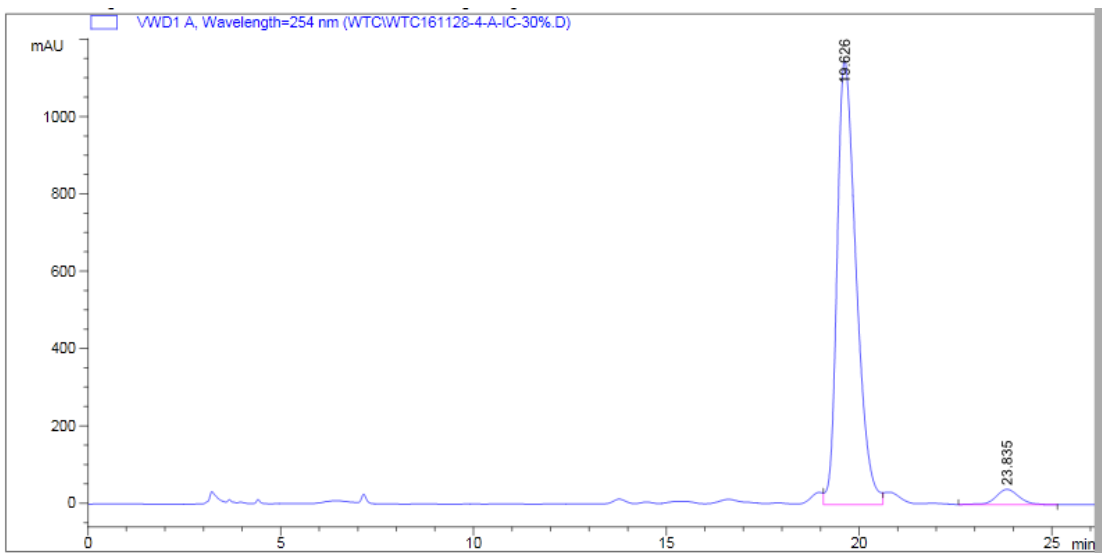
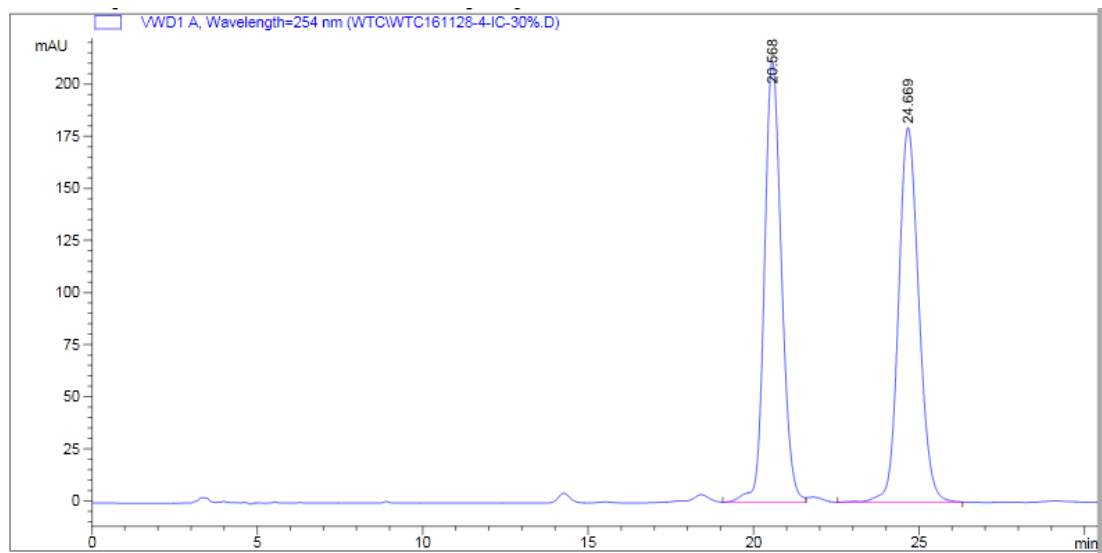
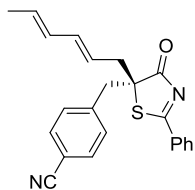
(R)-5-(4-bromobenzyl)-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (3na)



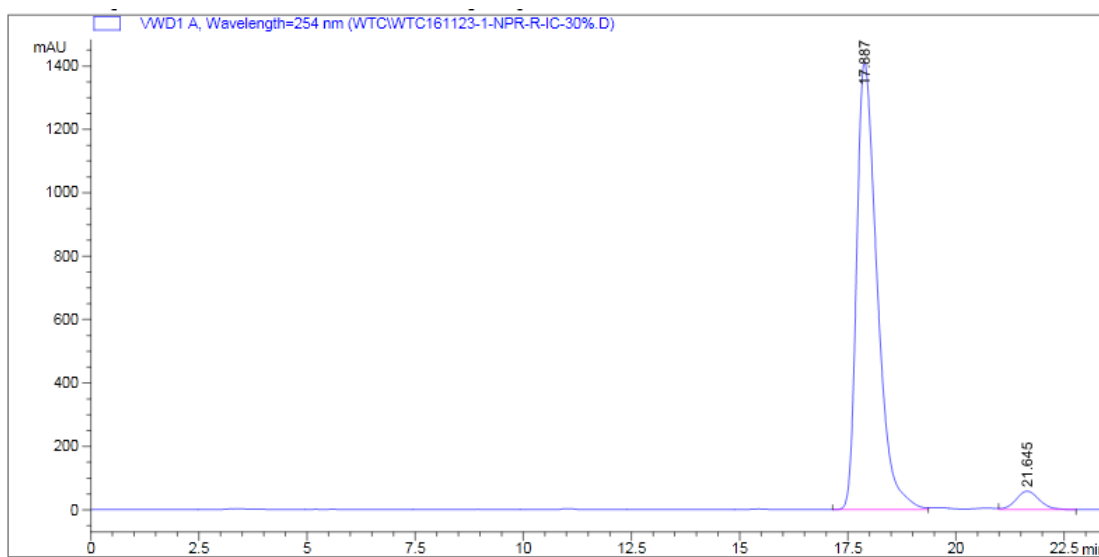
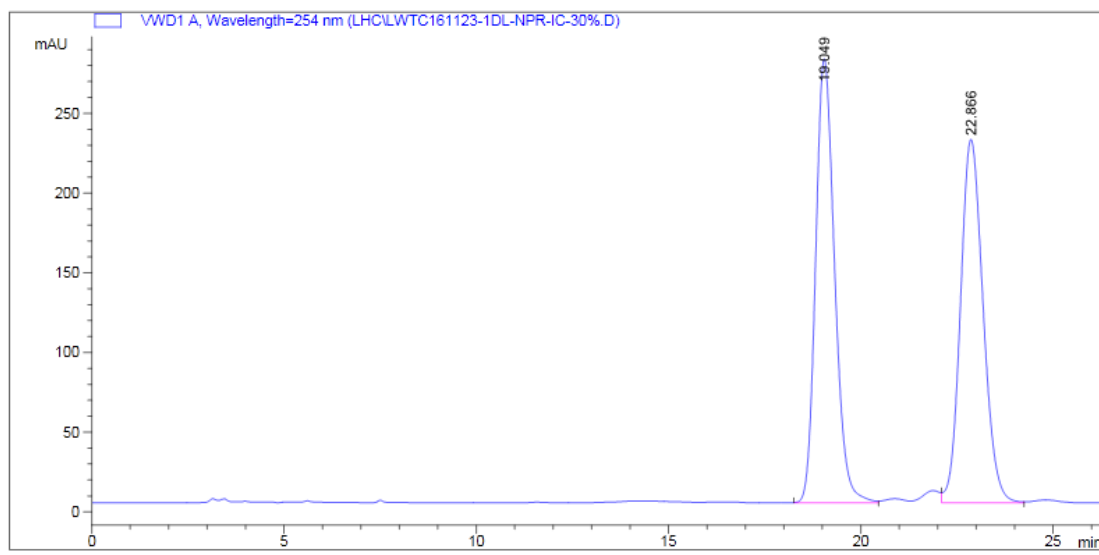
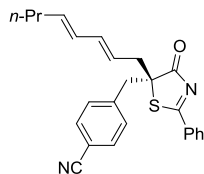
(S)-5-methyl-2-phenyl-5-((2E, 4E)-undeca-2, 4-dien-1-yl) thiazol-4(5H)-one (30a)



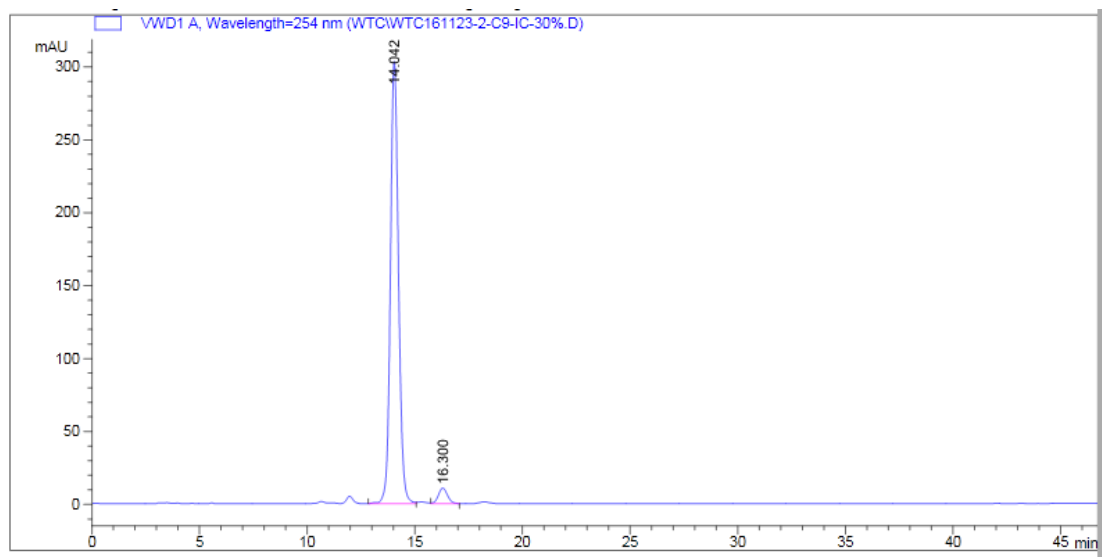
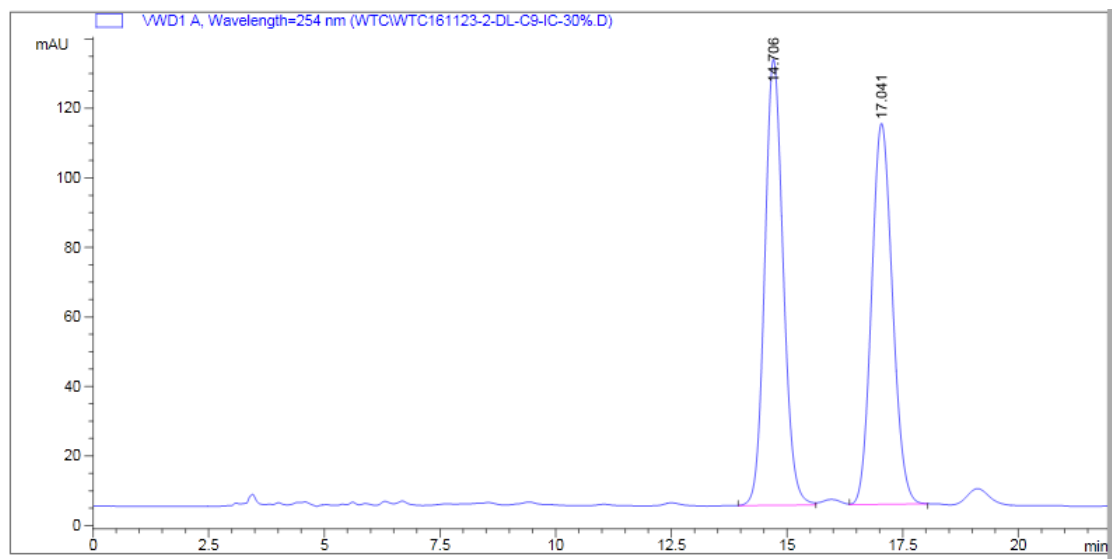
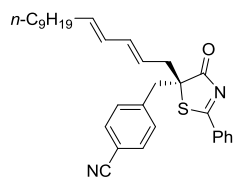
4-(((R)-5-((2E, 4E)-hexa-2, 4-dien-1-yl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3db)



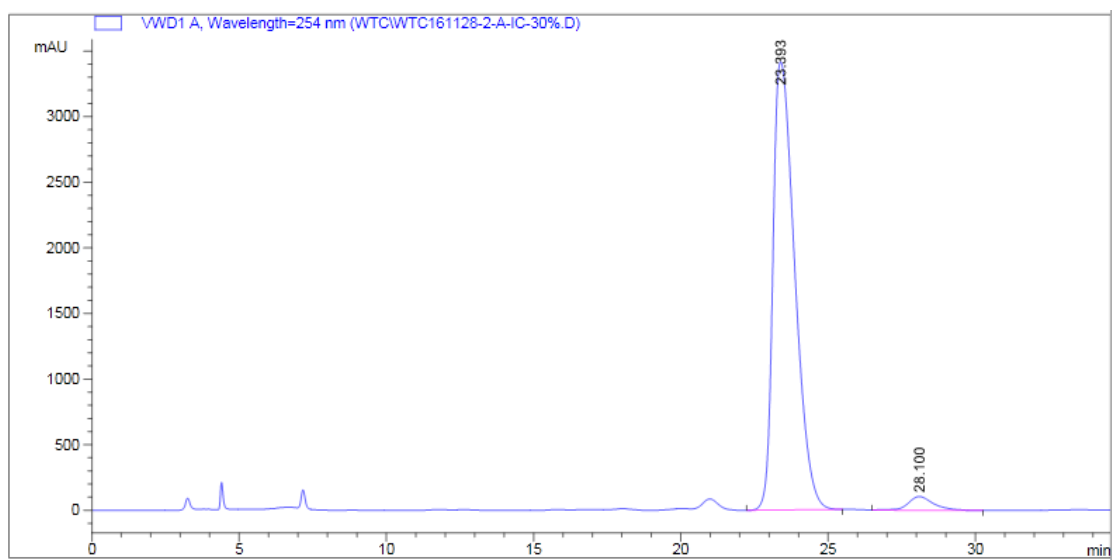
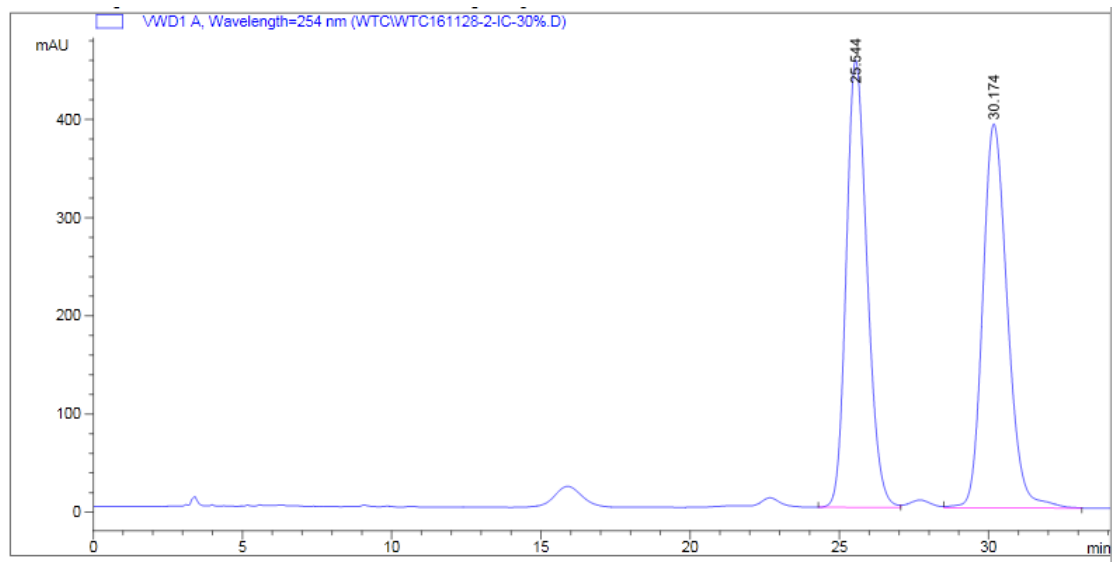
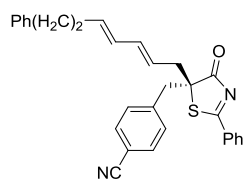
4-(((R)-5-((2E, 4E)-octa-2, 4-dien-1-yl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3dc)



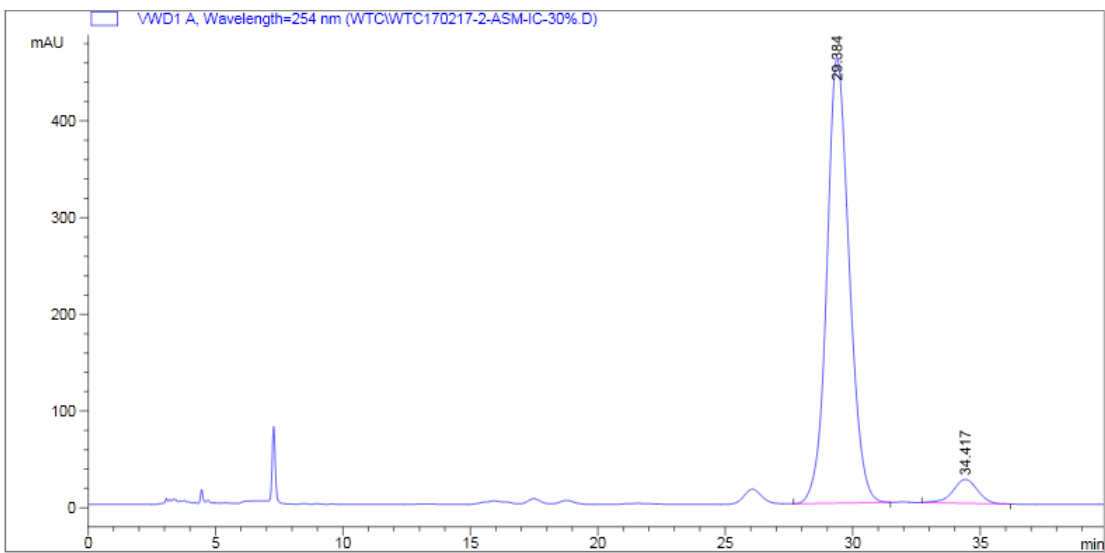
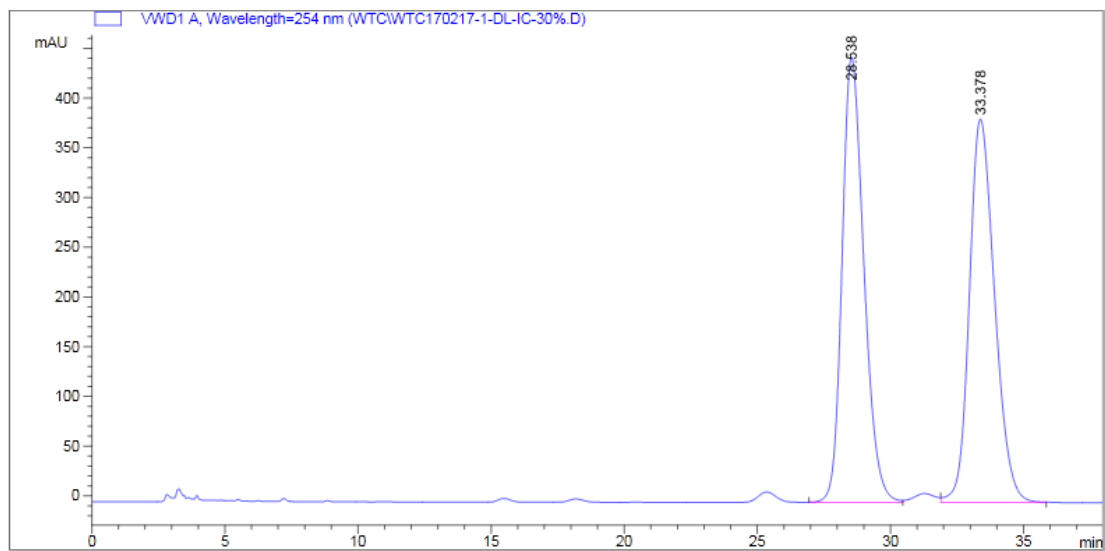
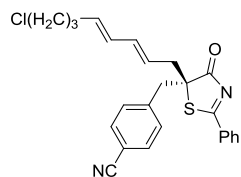
4-(((*R*)-4-oxo-2-phenyl-5-((2*E*, 4*E*)-tetradeca-2, 4-dien-1-yl)-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3dd)



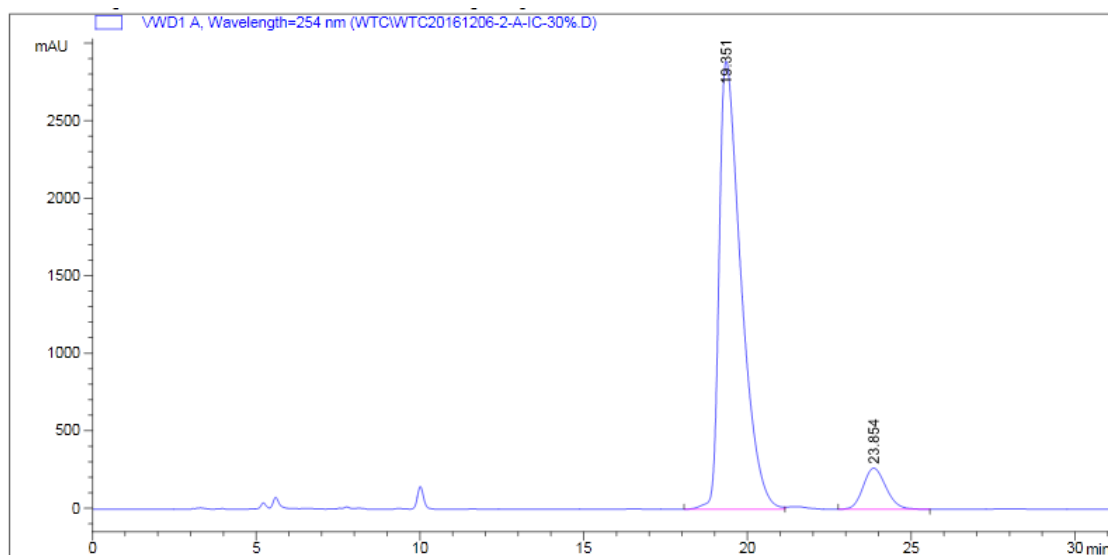
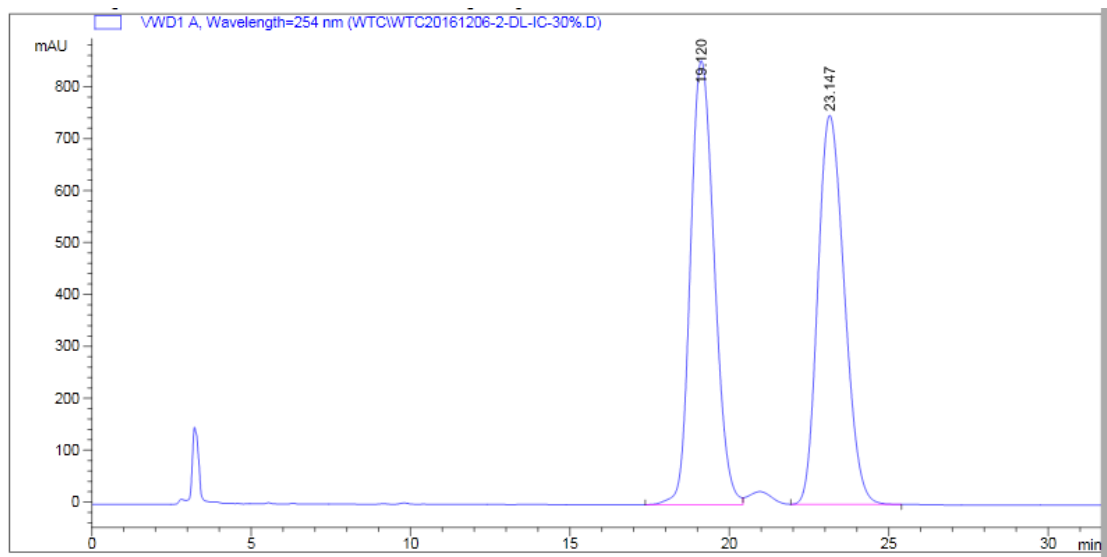
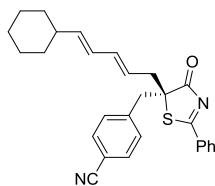
4-(((*R*)-4-oxo-2-phenyl-5-((2*E*, 4*E*)-5-(*p*-tolyl) penta-2, 4-dien-1-yl)-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3de)



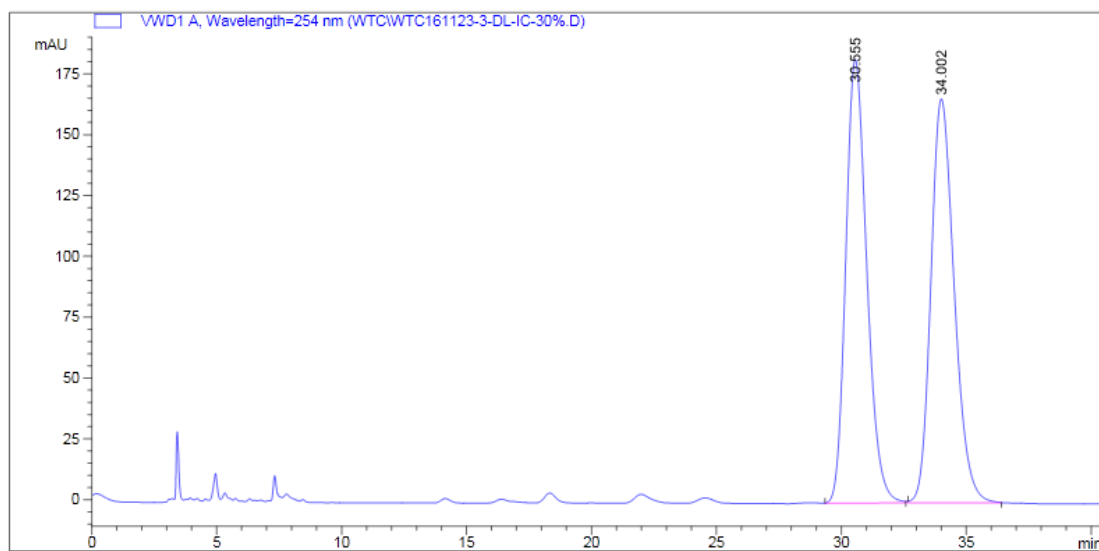
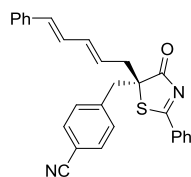
4-(((*R*)-5-((2*E*, 4*E*)-8-chloroocta-2, 4-dien-1-yl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3df)



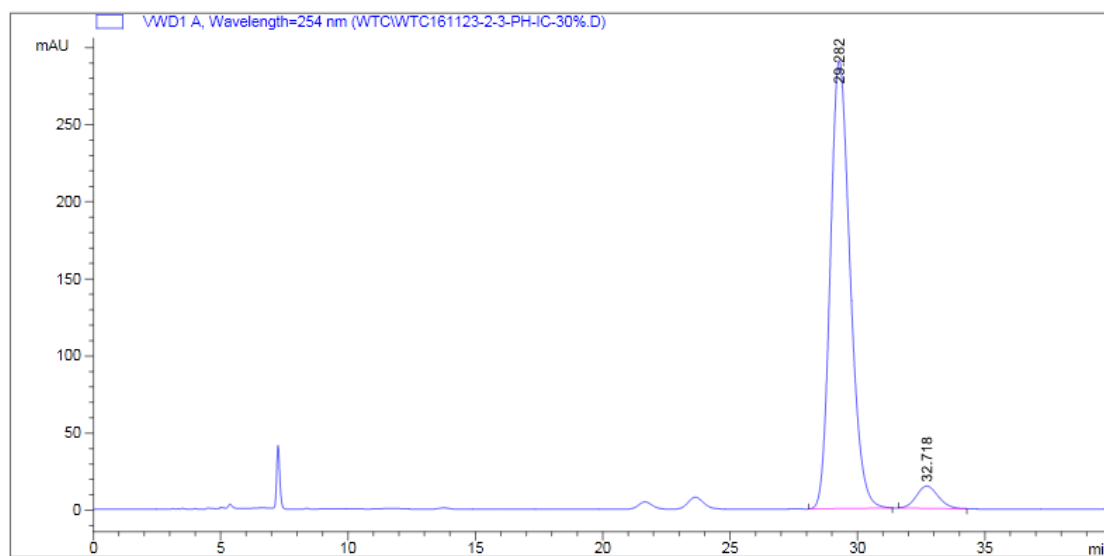
4-(((*R*)-5-((2*E*, 4*E*)-hexa-2, 4-dien-1-yl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3dg)



4-(((*R*)-4-oxo-2-phenyl-5-((*2E*, *4E*)-5-phenylpenta-2, 4-dien-1-yl)-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3dh)

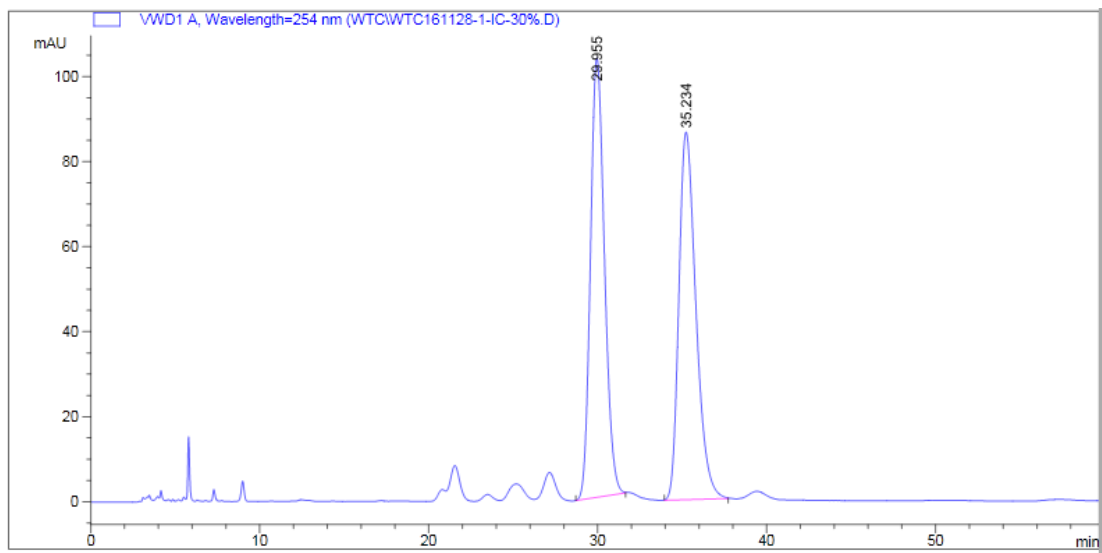
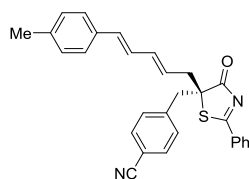


Peak #	RetTime [min]	Type	Width [min]	Area mAU * s	Height [mAU]	Area %
1	30.555	BB	0.8986	1.06310e4	182.34328	49.7063
2	34.002	BB	0.9962	1.07566e4	166.00945	50.2937

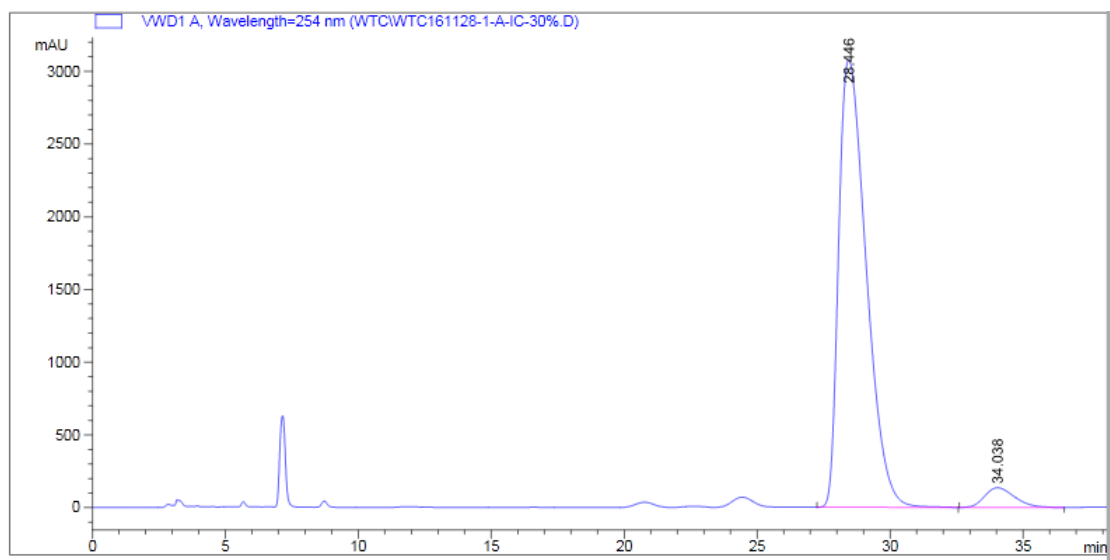


Peak #	RetTime [min]	Type	Width [min]	Area mAU * s	Height [mAU]	Area %
1	29.282	BB	0.8349	1.56472e4	290.59613	94.8104
2	32.718	BB	0.9230	856.47491	14.36026	5.1896

4-(((*R*)-4-oxo-2-phenyl-5-((2*E*, 4*E*)-5-(*p*-tolyl) penta-2, 4-dien-1-yl)-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3di)

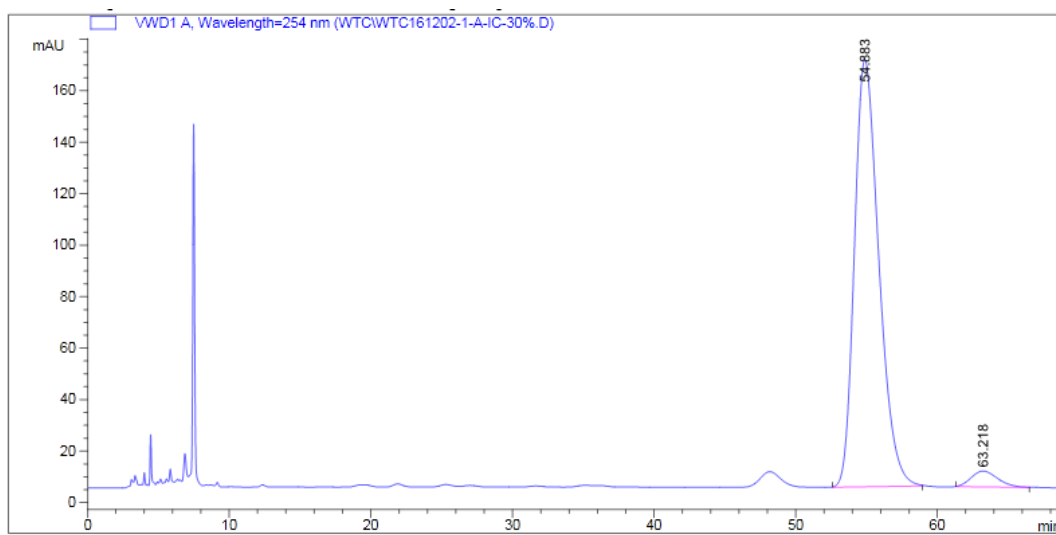
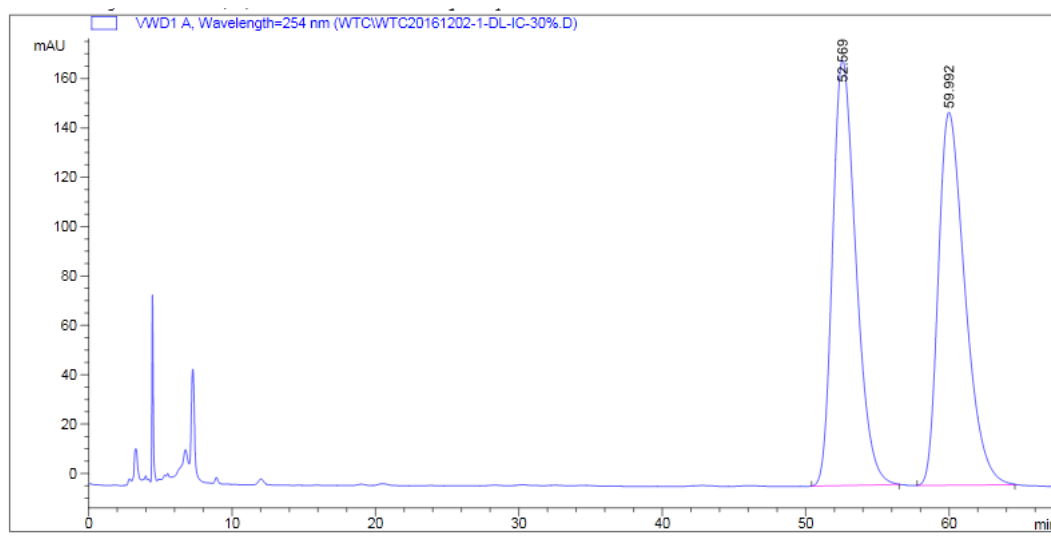
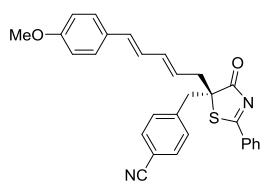


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	29.955	BB	0.8943	5960.58984	103.32975	49.6284
2	35.234	BB	1.0726	6049.84766	86.45821	50.3716

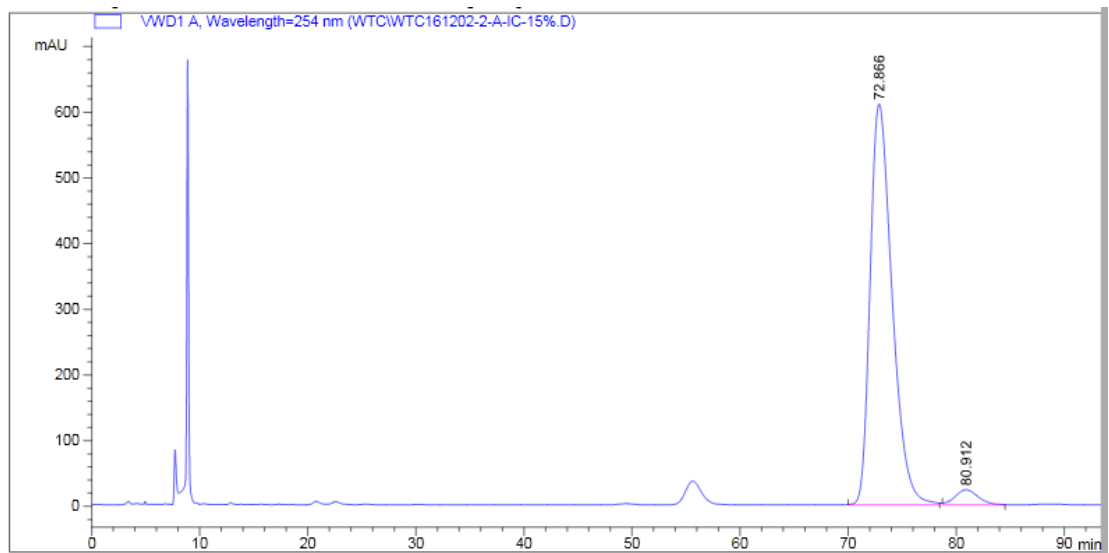
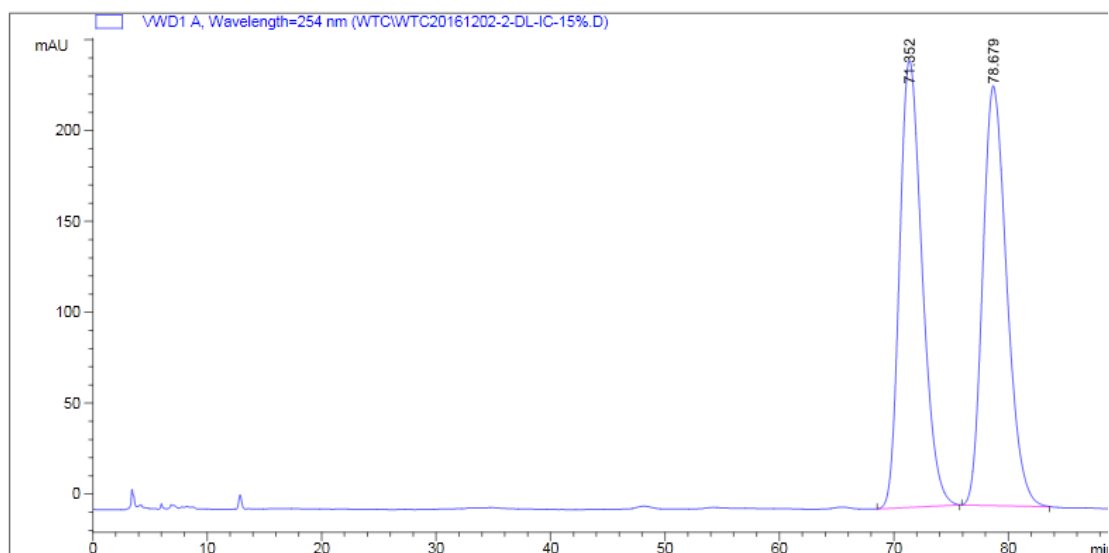
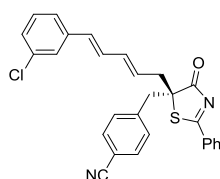


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	28.446	BB	1.1163	2.21006e5	3076.11890	95.4130
2	34.038	BB	1.2177	1.06250e4	135.27673	4.5870

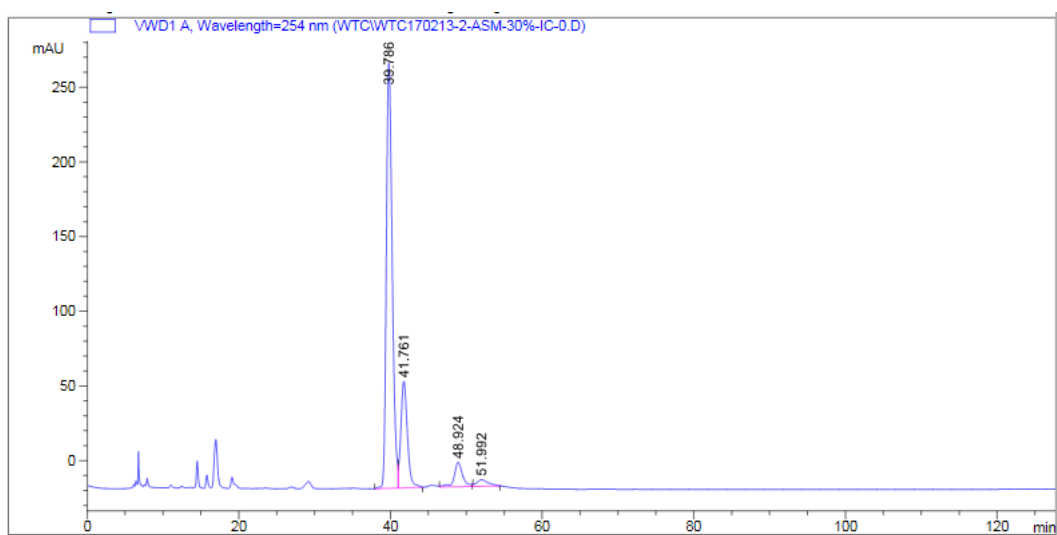
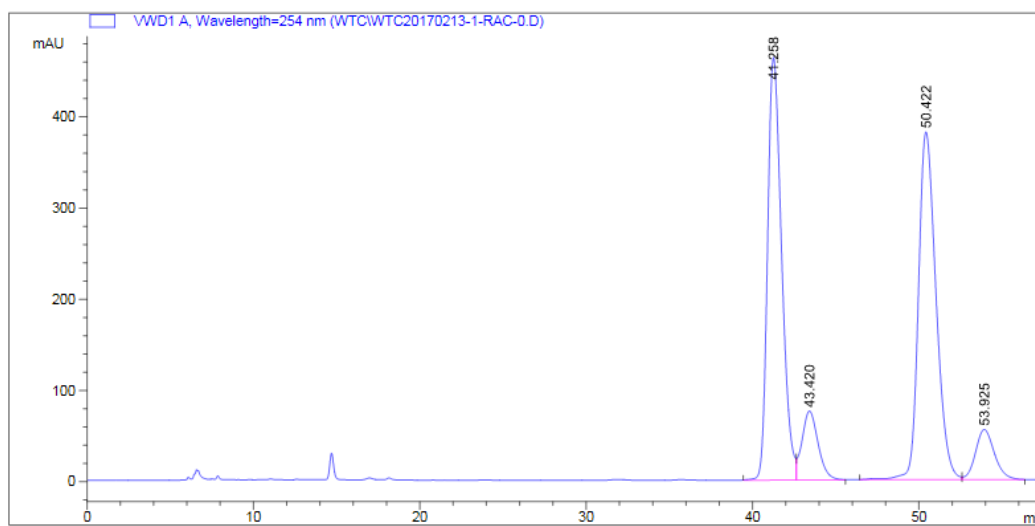
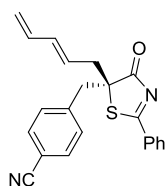
4-(((R)-5-((2E, 4E)-5-(4-methoxyphenyl) penta-2, 4-dien-1-yl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile (3dj)



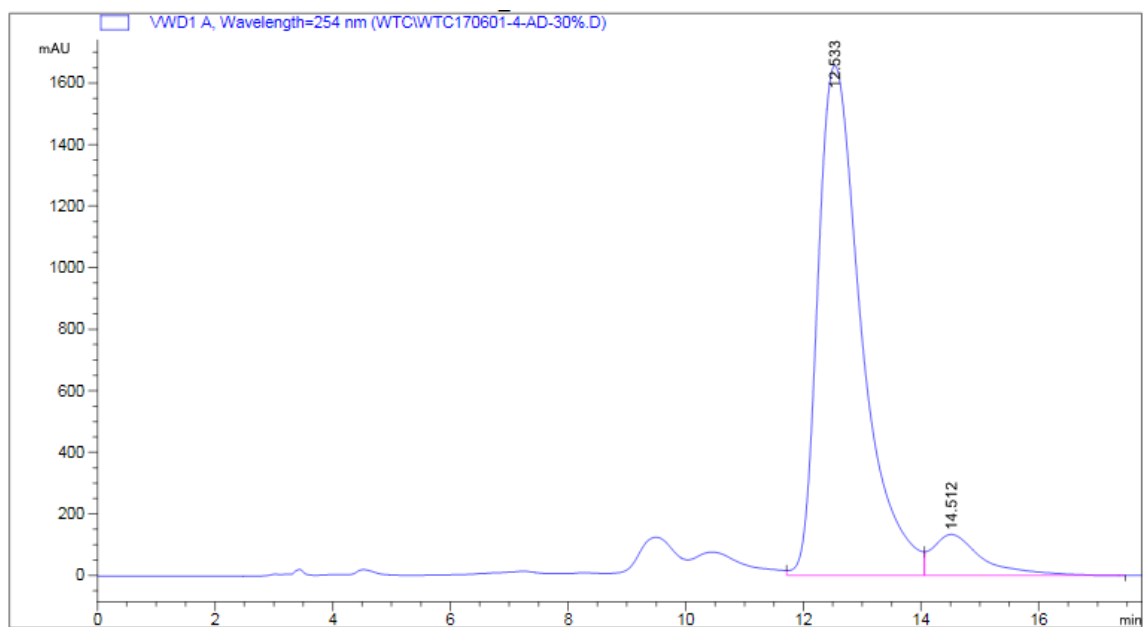
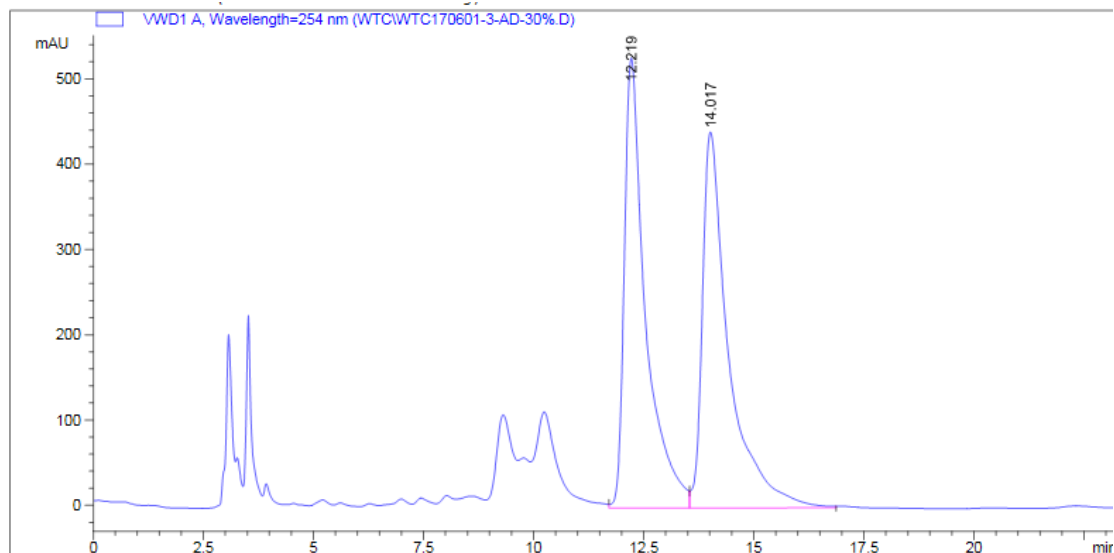
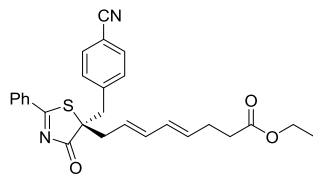
4-(((*R*)-5-((2*E*, 4*E*)-5-(3-chlorophenyl) penta-2, 4-dien-1-yl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzonitrile
(3dk)



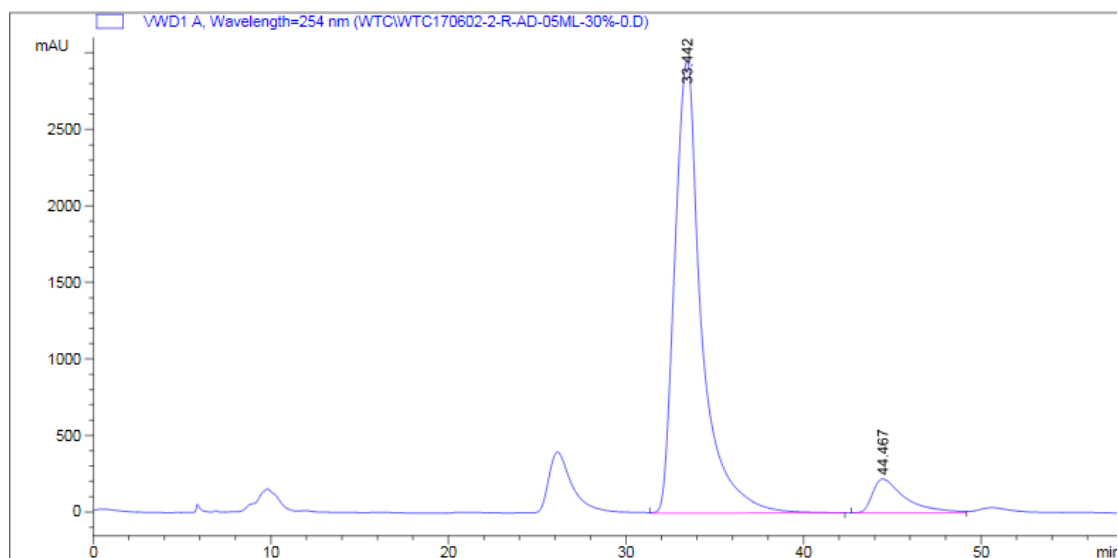
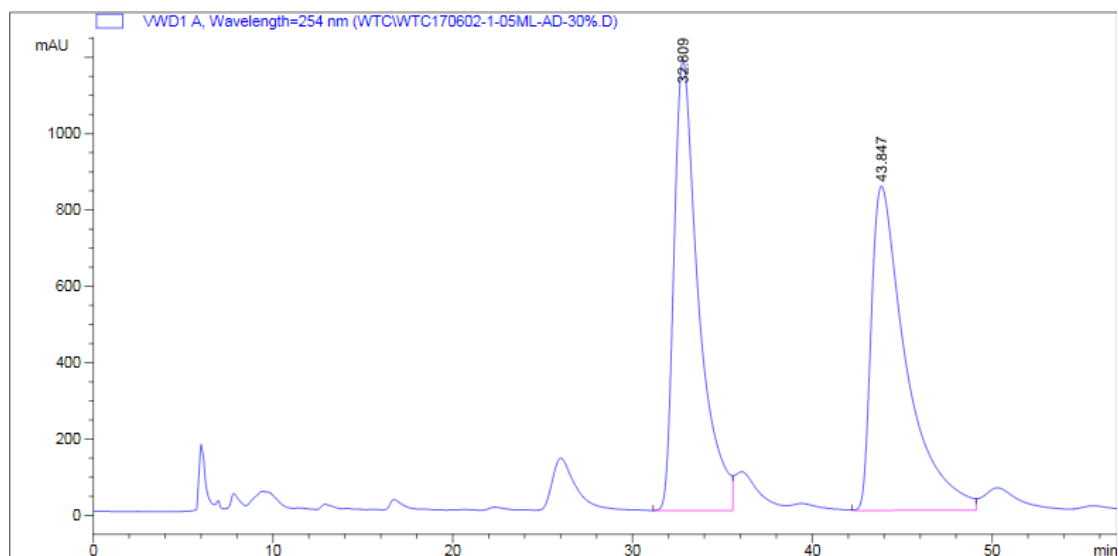
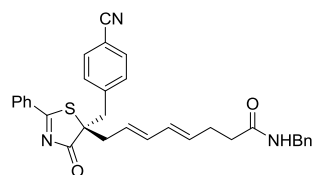
(*R, E*)-4-((4-oxo-5-(penta-2, 4-dien-1-yl)-2-phenyl-4, 5-dihydrothiazol-5-yl) methyl) benzo-nitrile (3dl)



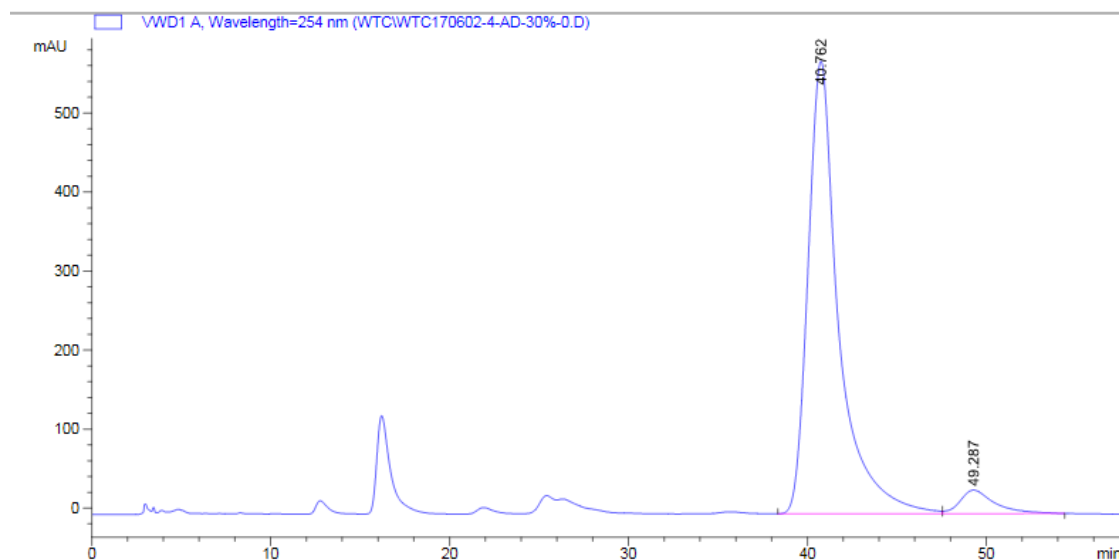
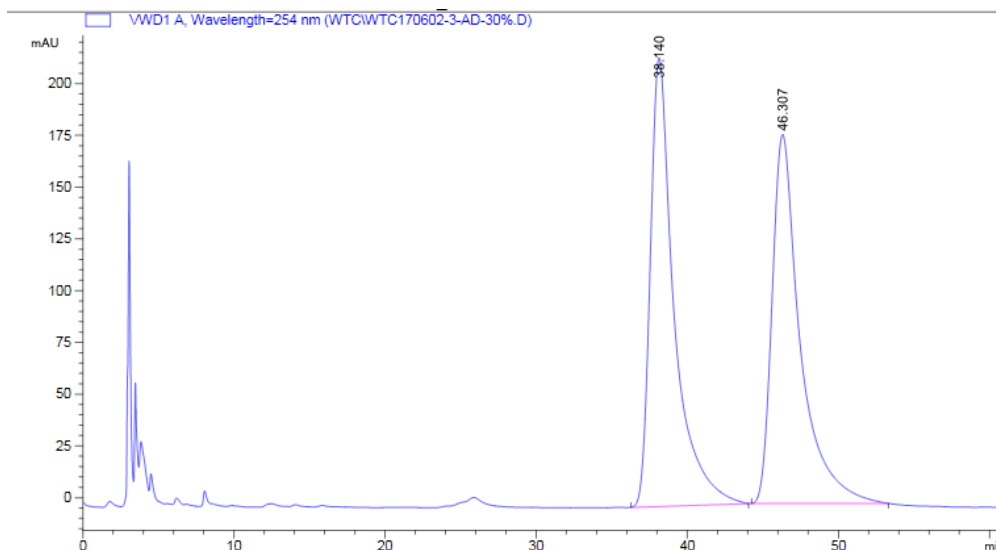
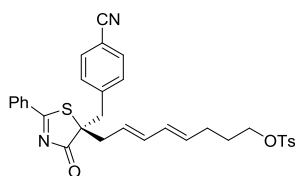
Ethyl (4E, 6E)-8-((R)-5-(4-cyanobenzyl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl)octa-4,6-dienoate (3dm)



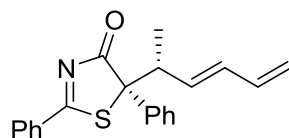
(4E, 6E)-N-benzyl-8-((R)-5-(4-cyanobenzyl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) octa-4,6-dienamide (3dn)



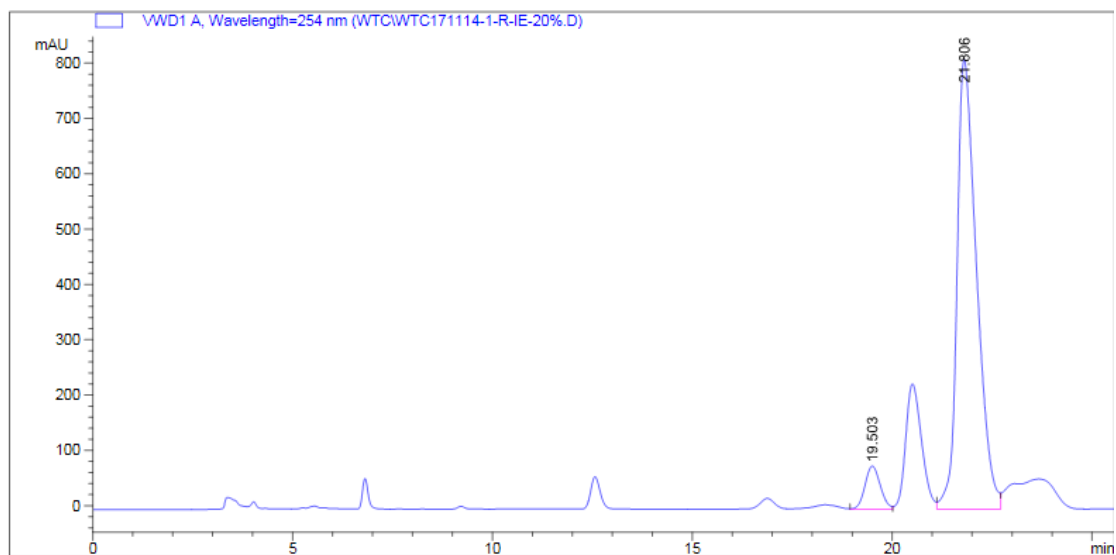
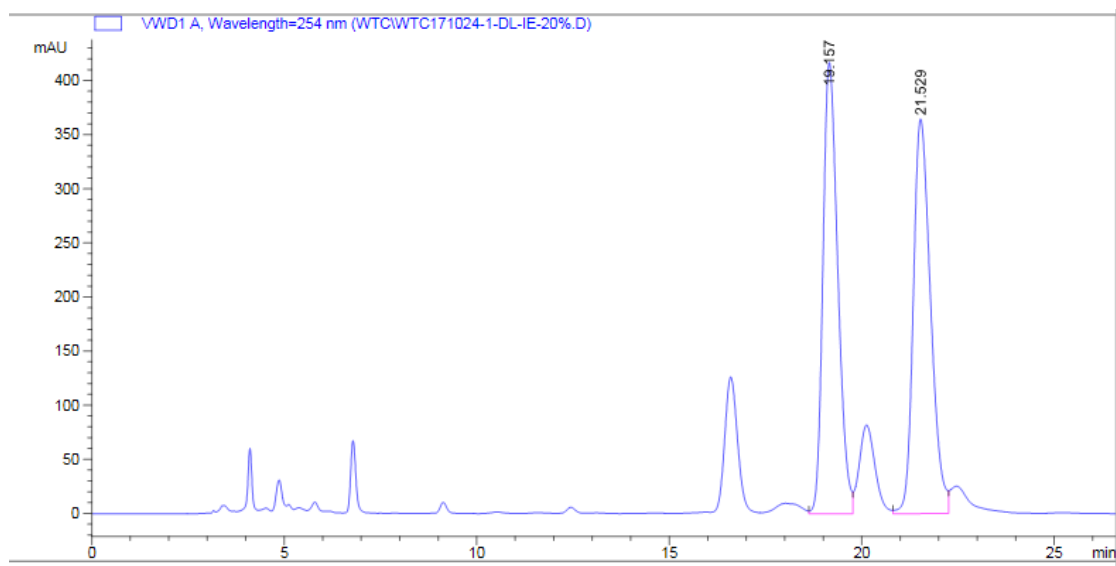
(4E, 6E)-8-((R)-5-(4-cyanobenzyl)-4-oxo-2-phenyl-4, 5-dihydrothiazol-5-yl) octa-4,6-dien-1-yl 4-methylbenzenesulfonate (3 do)



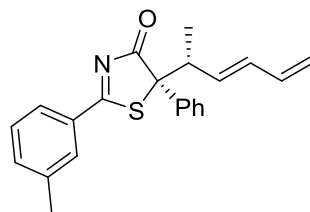
(S)-5-((R, E)-hexa-3, 5-dien-2-yl)-2, 5-diphenylthiazol-4(5H)-one (6aa)



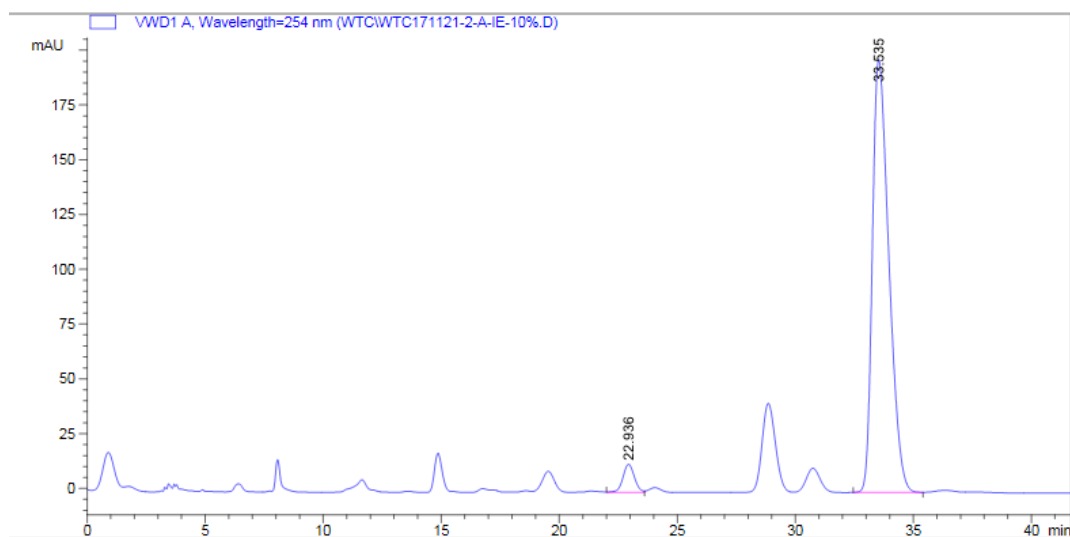
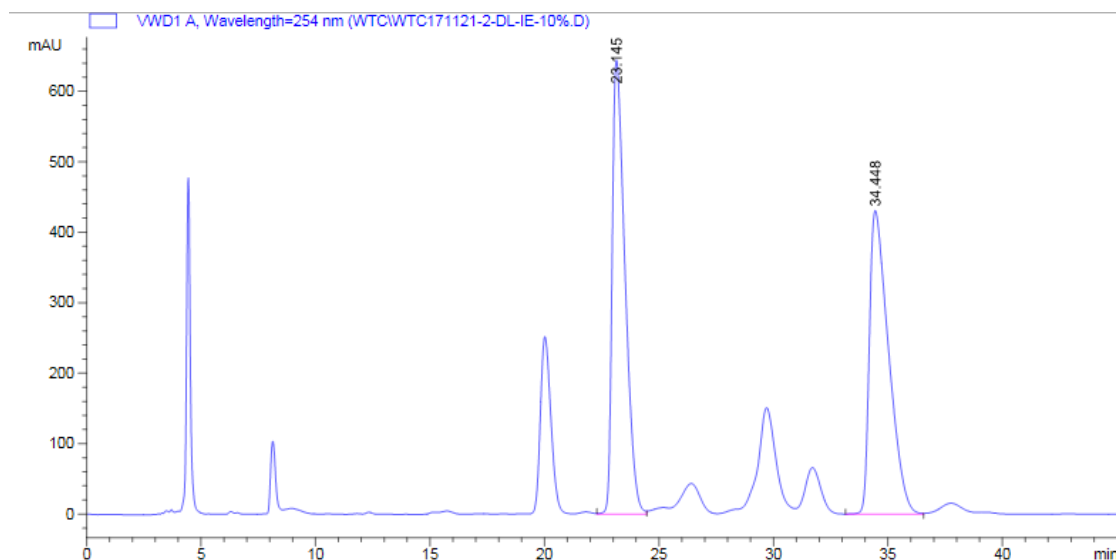
Major



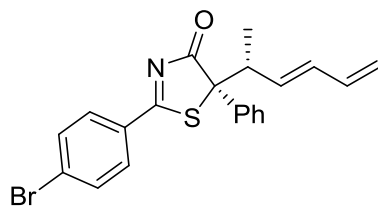
(S)-5-((R, E)-hexa-3, 5-dien-2-yl)-5-phenyl-2-(m-tolyl) thiazol-4(5H)-one (6ba)



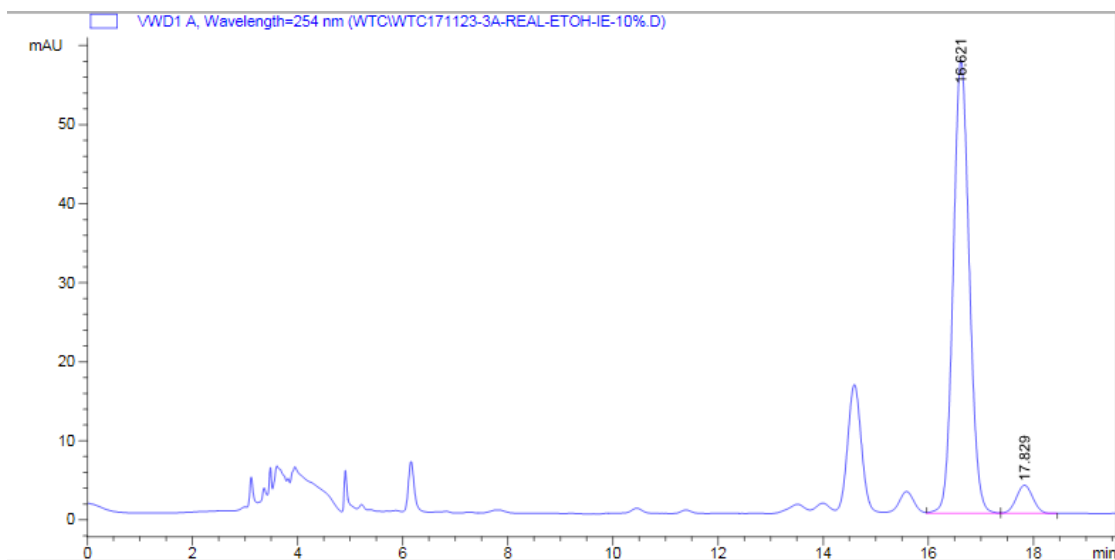
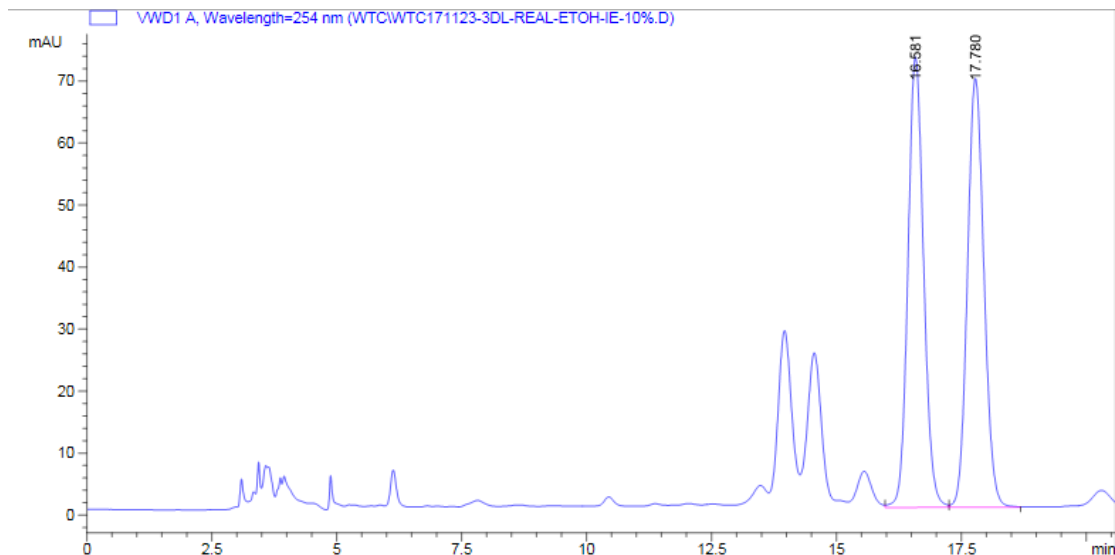
Major



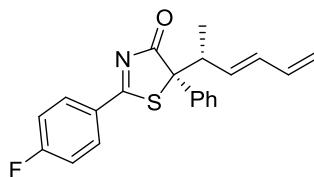
(S)-2-(4-bromophenyl)-5-((R, E)-hexa-3, 5-dien-2-yl)-5-phenylthiazol-4(5H)-one (6ca)



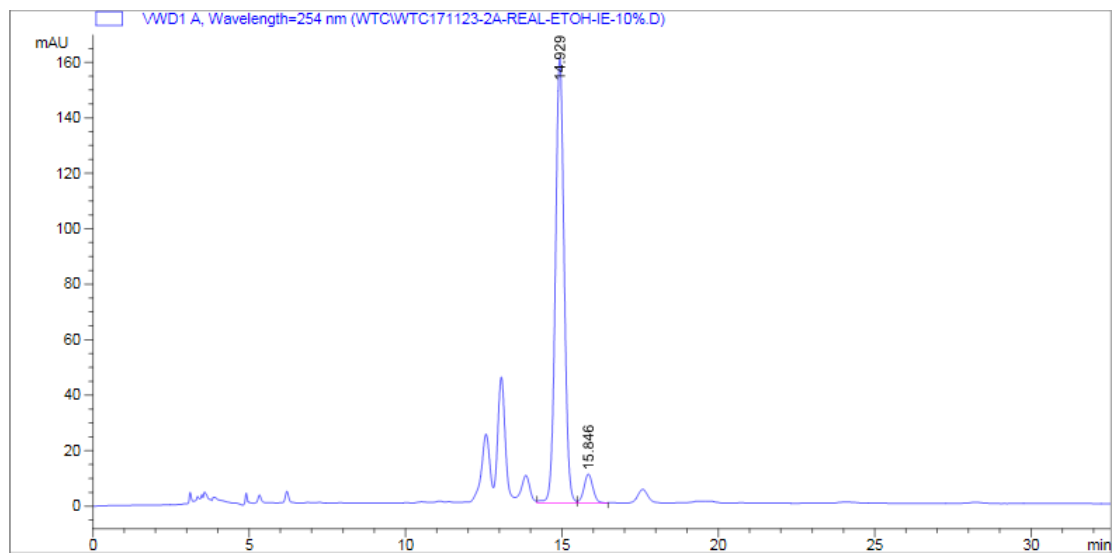
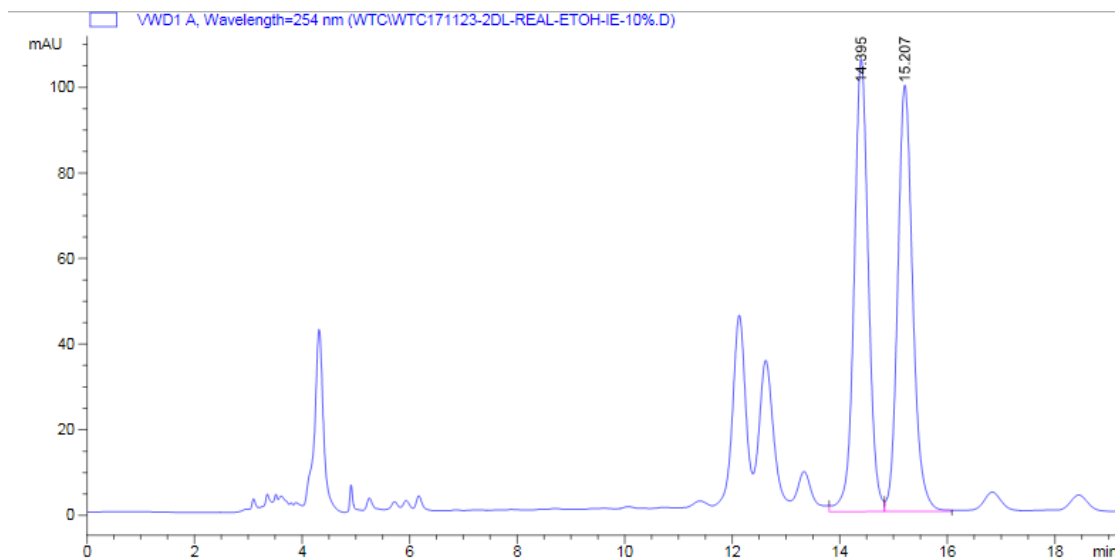
Major



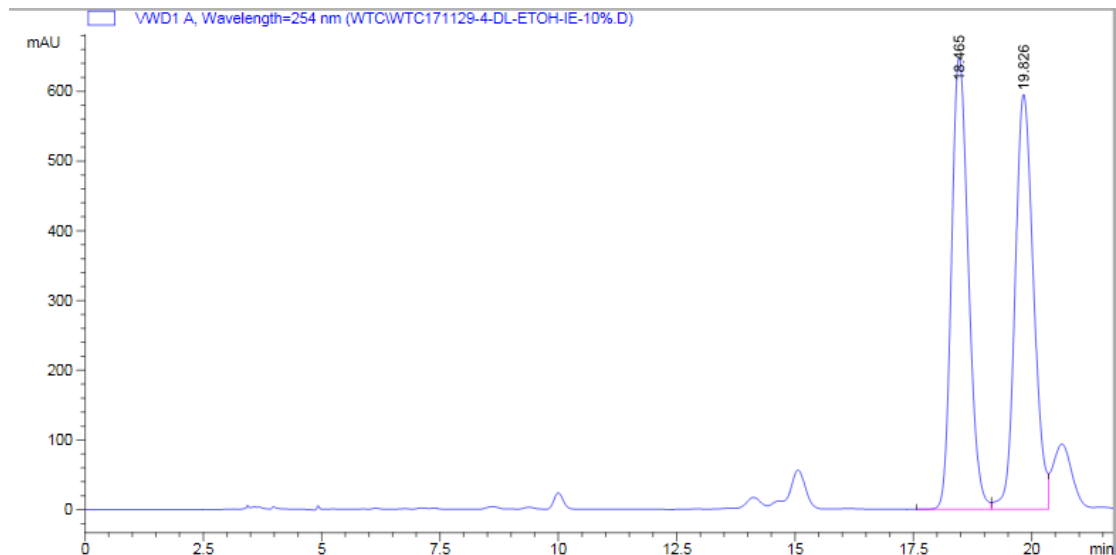
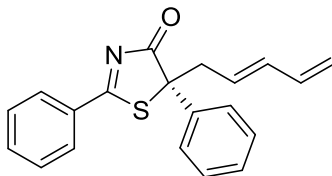
(S)-2-(4-fluorophenyl)-5-((R, E)-hexa-3, 5-dien-2-yl)-5-phenylthiazol-4(5H)-one (6da)



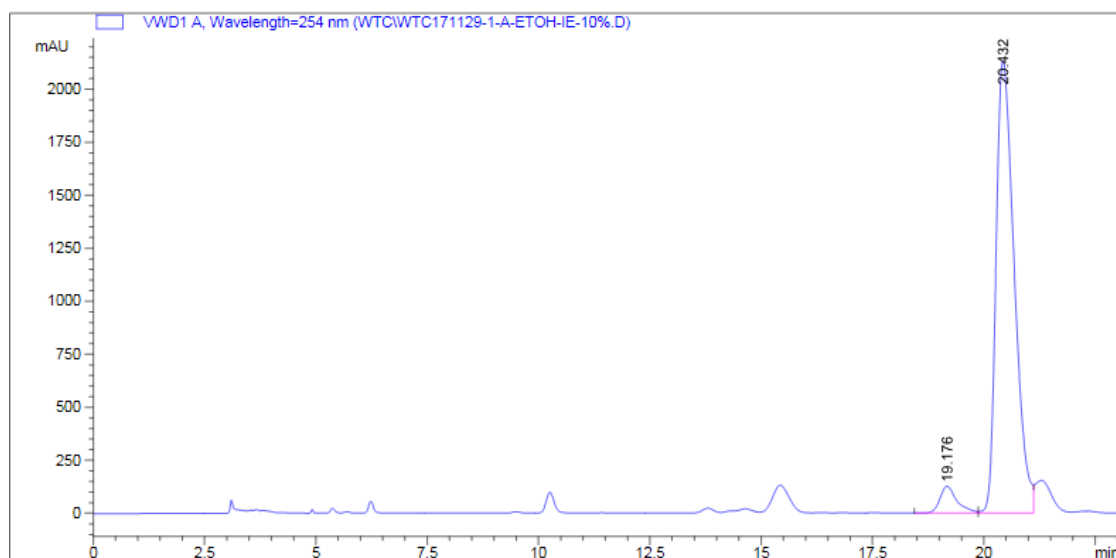
Major



(S, E)-5-(penta-2, 4-dien-1-yl)-2, 5-diphenylthiazol-4(5H)-one (6ab)

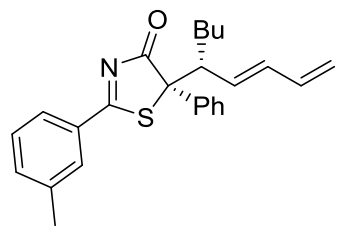


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.465	VV	0.3817	1.60382e4	648.51019	49.8331
2	19.826	VV	0.4214	1.61456e4	595.05988	50.1669

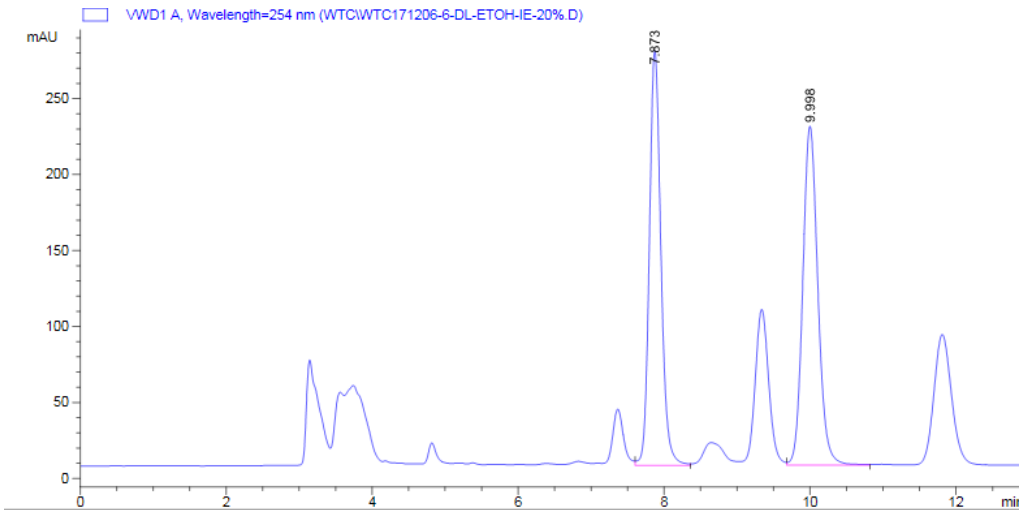


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.176	VV	0.3959	3421.10962	126.97567	5.3362
2	20.432	VV	0.4429	6.06906e4	2131.24463	94.6638

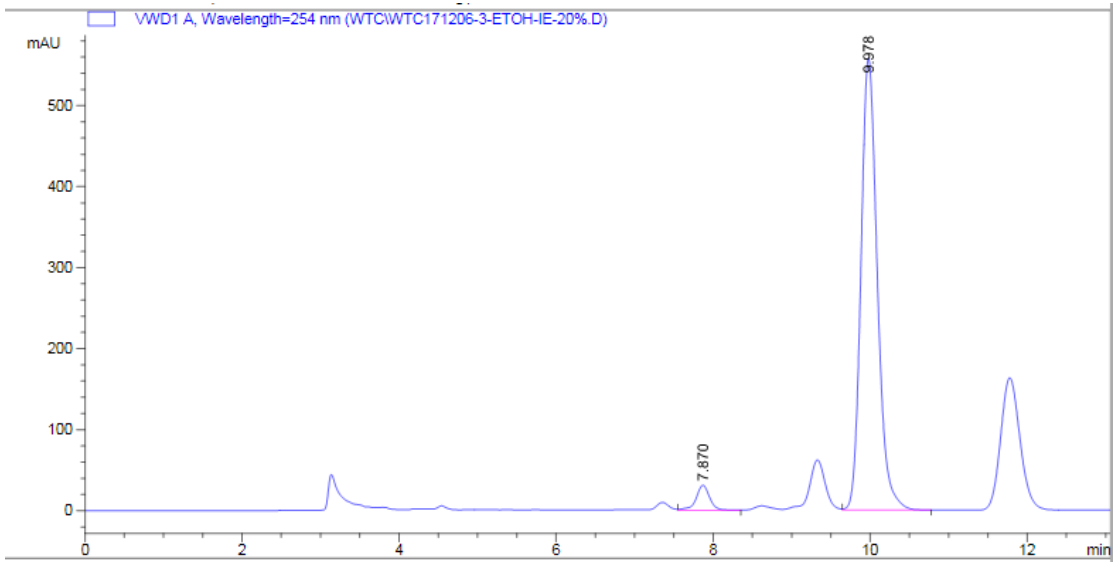
(S)-5-((R,E)-deca-1,3-dien-5-yl)-5-phenyl-2-(m-tolyl)thiazol-4(5H)-one (6bc)



Major

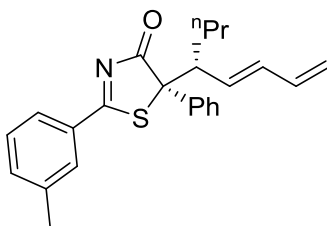


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	7.873	VV	0.1689	2997.06763	272.86258	48.3287
2	9.998	VV	0.2200	3204.36206	223.08243	51.6713

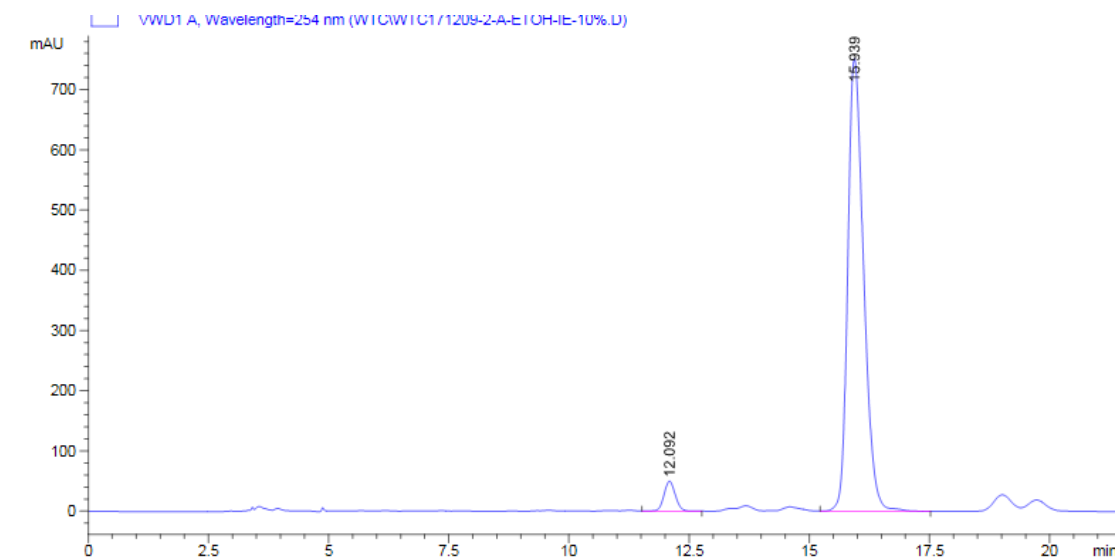
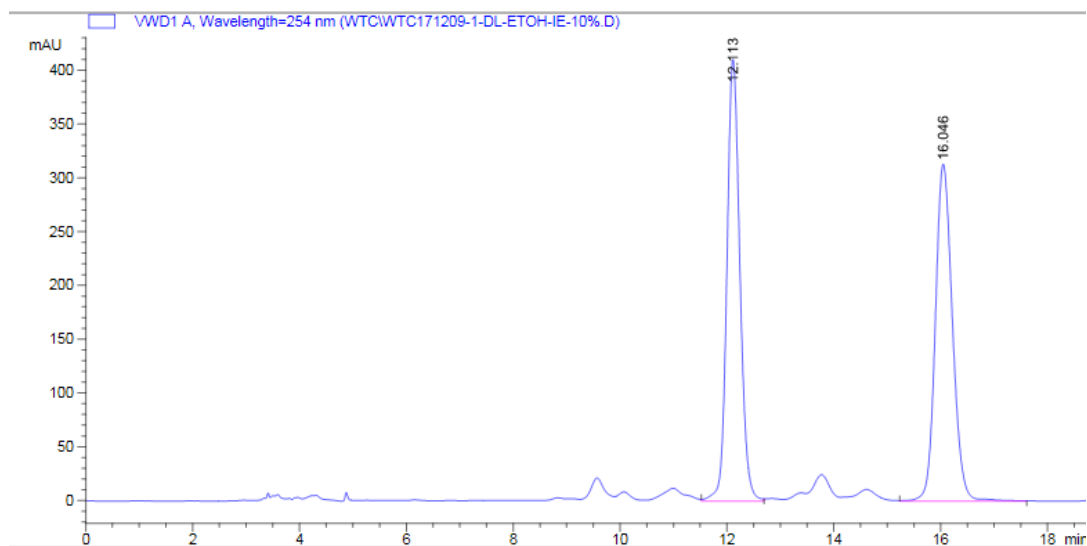


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	7.870	VV	0.1819	373.96054	30.91031	4.4256
2	9.978	VB	0.2241	8075.94141	558.10651	95.5744

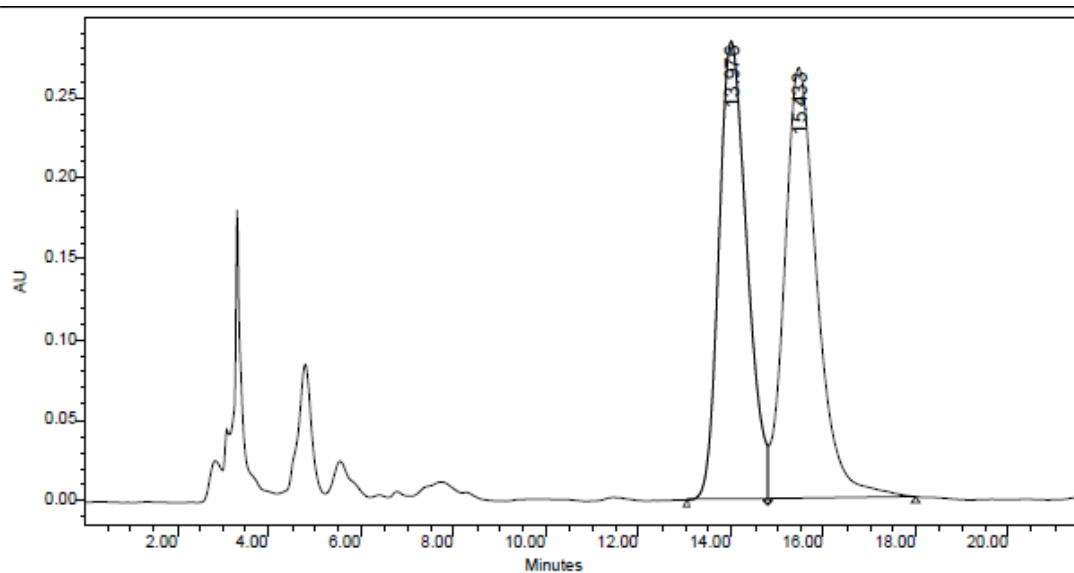
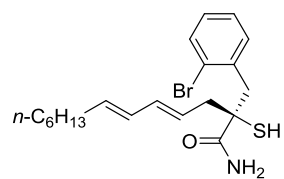
(S)-5-((R, E)-nona-1, 3-dien-5-yl)-5-phenyl-2-(m-tolyl) thiazol-4(5H)-one (6bd)



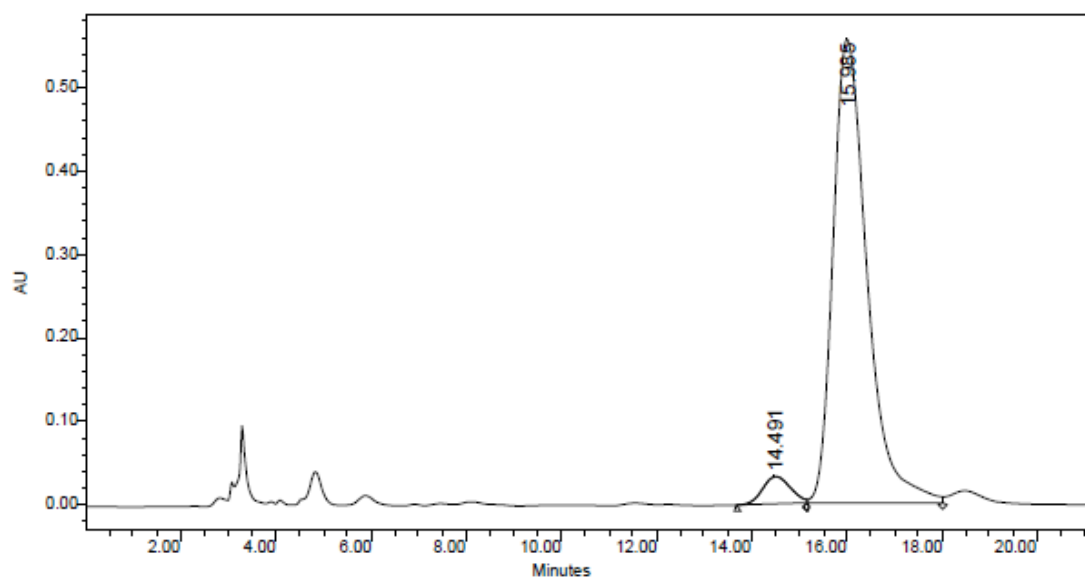
Major



(S, 4E, 6E)-2-(2-bromobenzyl)-2-mercaptotrideca-4, 6-dienamide (P1)

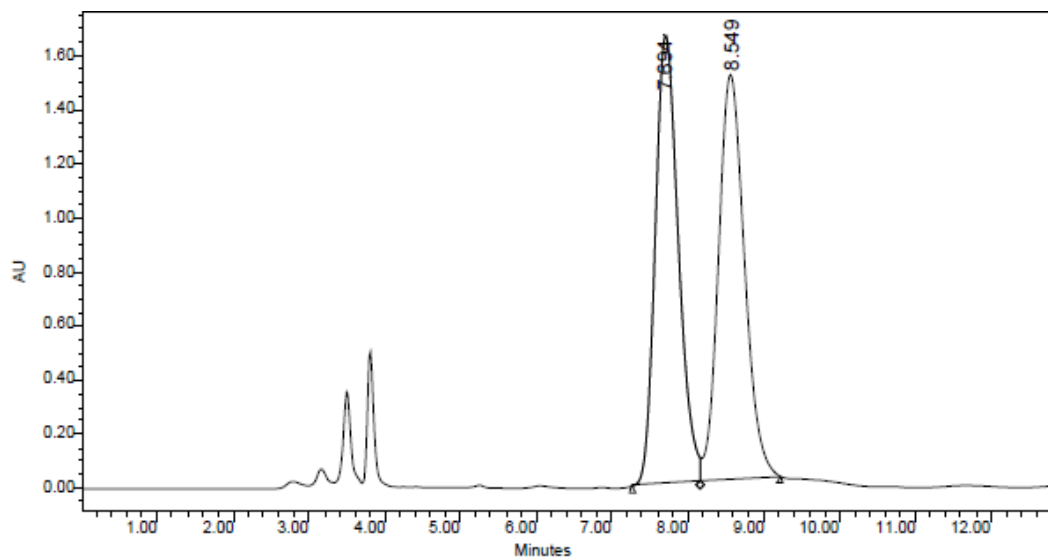
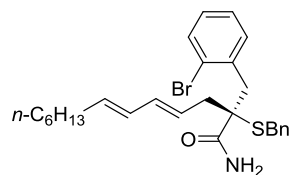


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	13.976	11996006	47.82	283611	51.52
2	15.433	13091085	52.18	266886	48.48

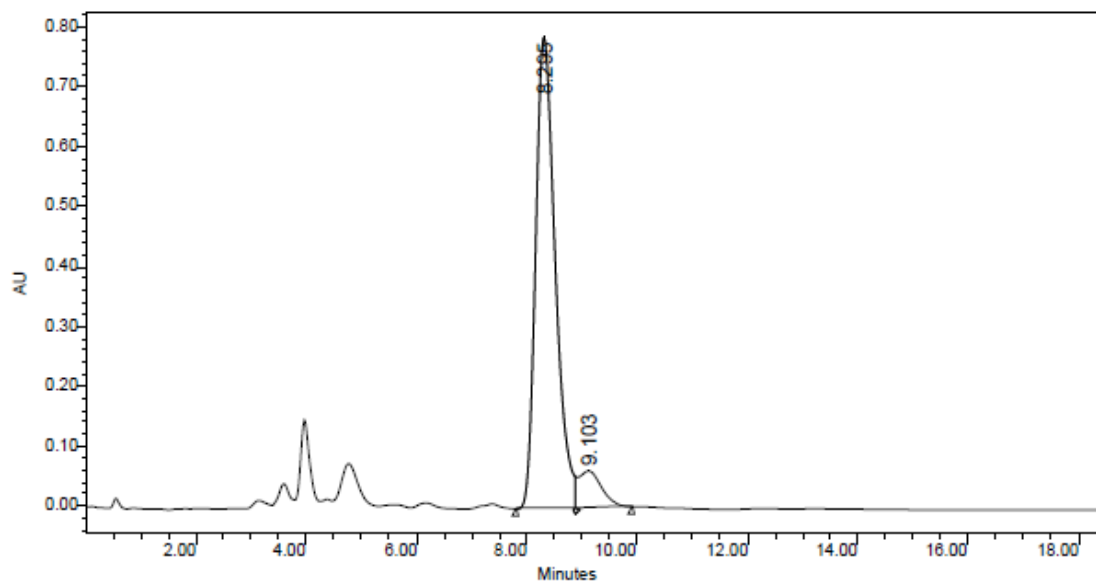


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	14.491	1399413	4.80	33481	5.67
2	15.985	27752708	95.20	556649	94.33

(S, 4E, 6E)-2-(benzylthio)-2-(2-bromobenzyl) trideca-4, 6-dienamide (P2)

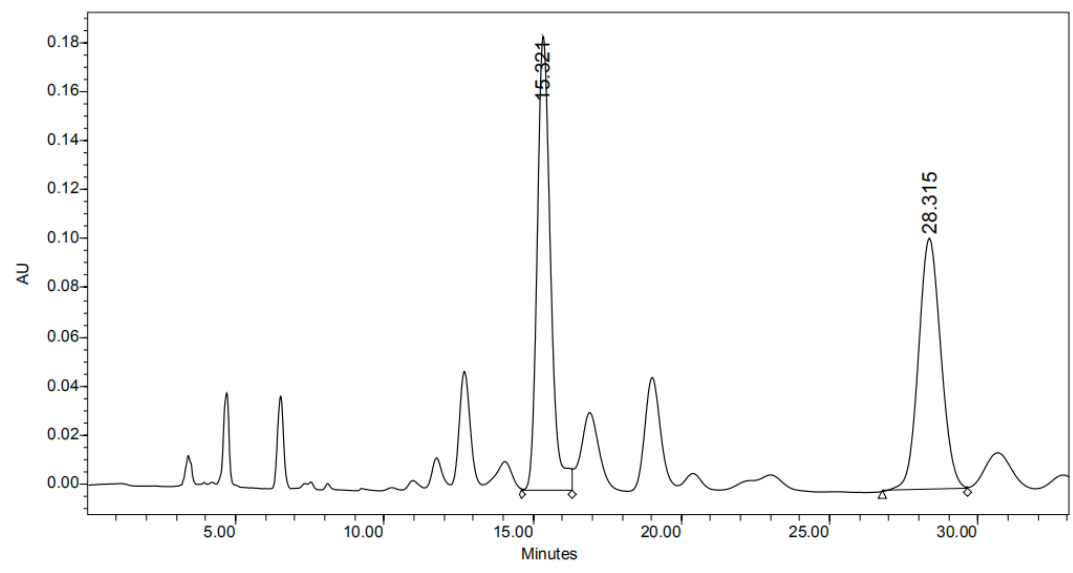
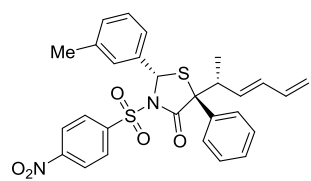


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.694	35279328	49.62	1661220	52.54
2	8.549	35818056	50.38	1500424	47.46

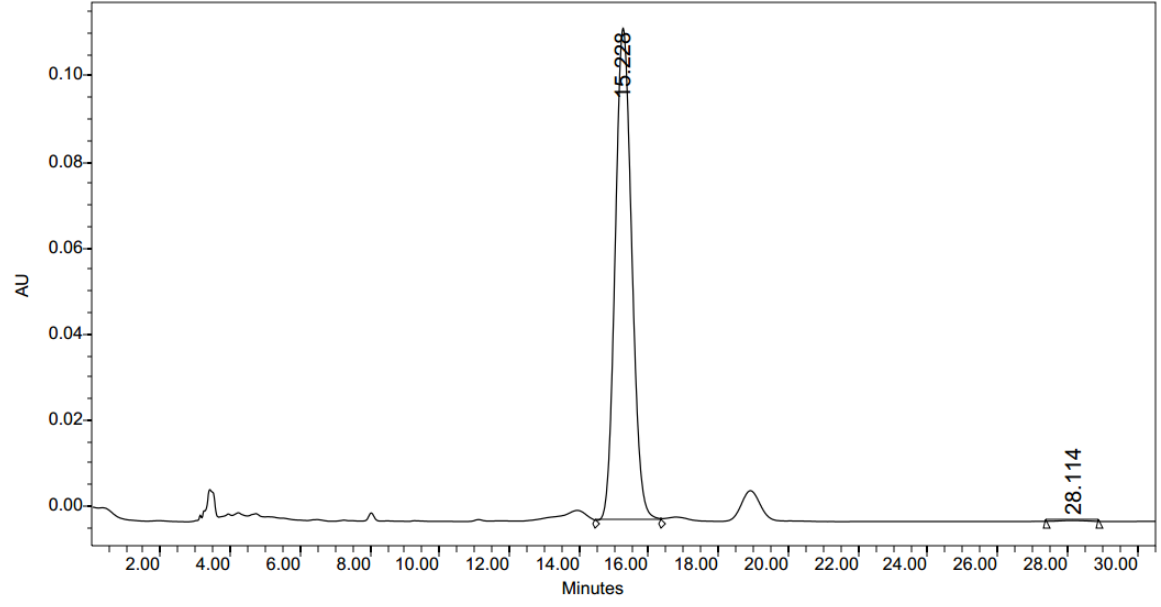


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.295	19505474	91.88	788190	92.76
2	9.103	1723058	8.12	61528	7.24

(2*S*, 5*S*)-5-((*R,E*)-hexa-3,5-dien-2-yl)-3-((4-nitrophenyl)sulfonyl)-2,5-diphenylthiazolidin-4-one (P3)



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	15.321	5815763	51.71	185402	64.34
2	28.315	5431897	48.29	102777	35.66



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	15.228	3813179	99.75	114660	99.83
2	28.114	9644	0.25	196	0.17