Supplementary Information (SI) for Organic Chemistry Frontiers.

Supporting Information

Copper-Catalyzed Remote Asymmetric Yne-Allylic Substitution: Construction of Thiazolidinone Derivatives with Consecutive Chiral Centers

Zi-Han Wang [a], Jia-Run Wang [a], Ying-Ying Wei [a], Bing Liu*[b] and Tao-Yan Lin*[a]

[a]Key Laboratory of Green and Precise Synthetic Chemistry and Applications, Ministry of Education, School of Chemistry and Materials Science, Huaibei Normal University, Huaibei, Anhui 235000, P. R. China
Email: linty@chnu.edu.cn
[b]Research Institute for Doping Analyses, Shanghai University of Sport, Shanghai 200438, P. R. China
Email: liubing2019@sus.edu.cn

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1. General Information

All air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under nitrogen. ^{1}H NMR, ^{13}C NMR spectra were measured at 600 MHz and 151 MHz in $CDCl_3$ using TMS signal (δ 0.00 ppm) and the residual signals from $CHCl_3$: (δ = 7.26 ppm for ^{1}H, δ = 77.00 ppm for ^{13}C) as internal references for ^{1}H and ^{13}C NMR respectively. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, qd = quartet of doublets, ddd = doublet of doublet of doublets, m = multiplet), coupling constant (Hz), and integration. High resolution mass spectra were acquired by Agilent 6545 Accurate-Mass Q-TOF LC/MS System. Melting points were determined on a WRS-1B digital melting point apparatus. The er value was determined by HPLC with a chiral stationary phase. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh). X-ray Crystallography was collected at 173 K a on a CCD area detector (Supernova Dual Source, Cu at Zero equipped with an AtlasS2 diffractometer or XtaLAB AFC12 (RINC): Kappa single diffractometer) using Cu Kα radiation. The substrates **1** and **2** were synthesized according to published procedures. The spectral data of the substrates were consisted with that reported in the literature. All other chemicals and solvents were purchased from commercial company and used as received.

2. General Procedure I: the Synthesis of yne-allylic esters 1

The yne-allylic esters **1** were prepared according to the literatures,[1] and all the spectra data are in agreement with the reports.

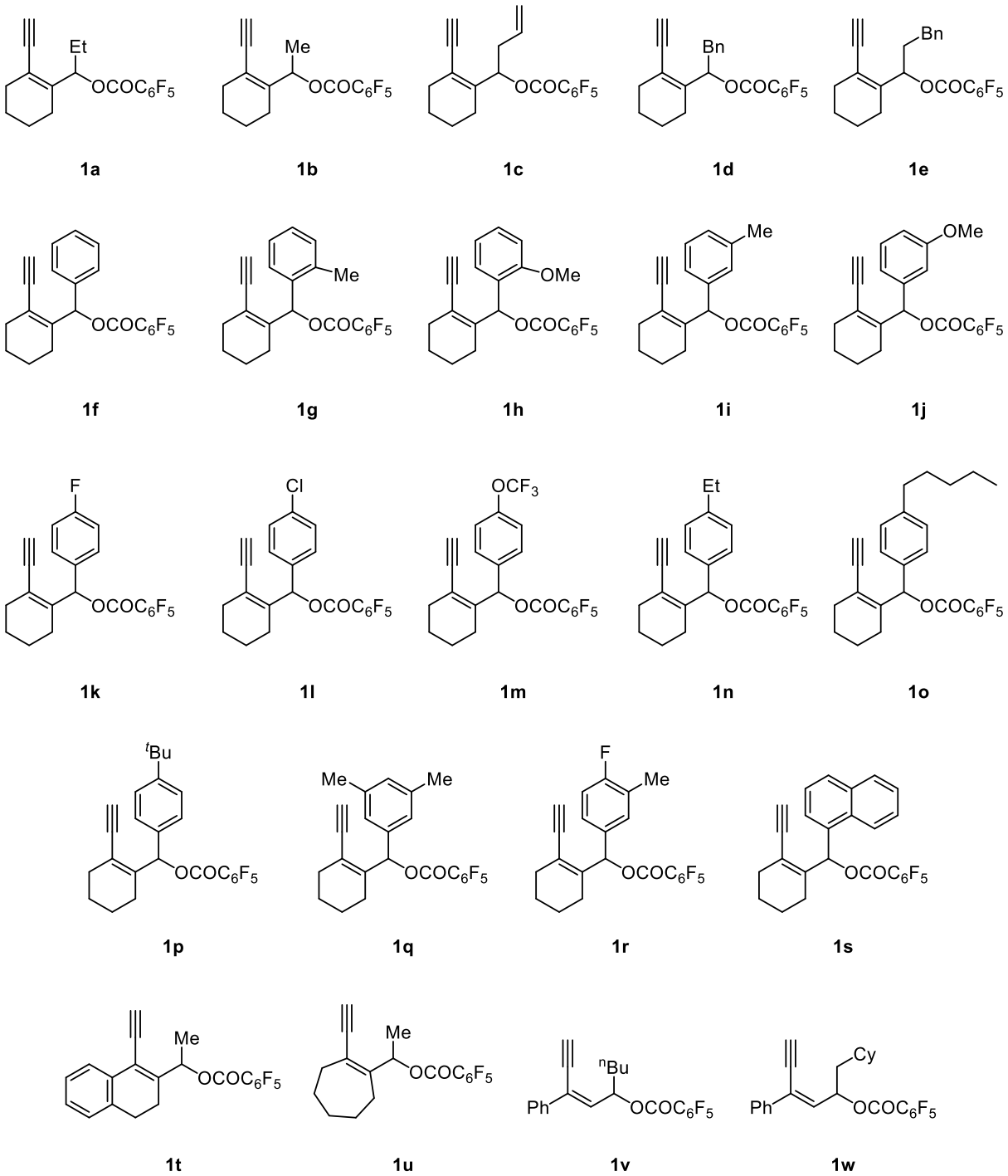
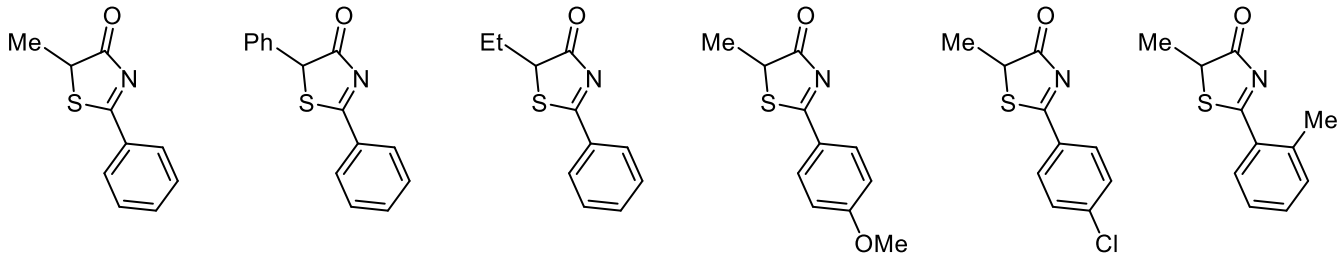


Figure S1. The summary of yne-allylic esters **1**

3. General Procedure II: the Synthesis of thiazolidinones 2

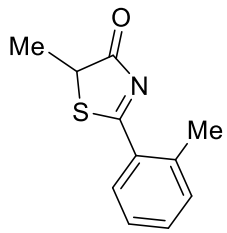
The thiazolidinones **2** were prepared according to the literatures,[2] and all the spectra data are in agreement with the reports. The new compound **2f** was prepared by the literature method and the spectra data is shown in this supporting information.



2a **2b** **2c** **2d** **2e** **2f**

Figure S2. The summary of thiazolidinones **2**.

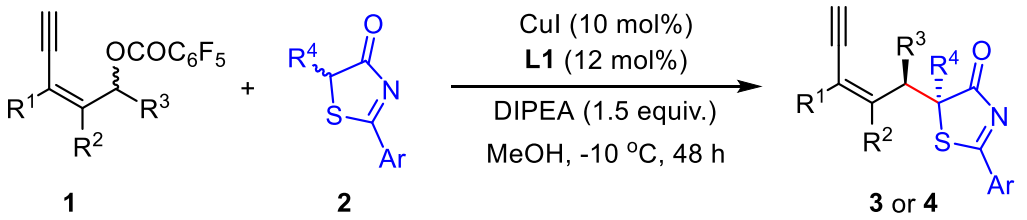
5-methyl-2-(*o*-tolyl)thiazol-4(5H)-one:2f



Light yellow solid.

^{1}H NMR (600 MHz, DMSO-d_6)): δ 10.2 (s, 1H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.32-7.27 (m, 3H), 2.53 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6): δ 158.2, 158.1, 135.2, 132.6, 131.5, 128.9, 128.4, 126.3, 102.9, 21.2, 8.9. HRMS (ESI) calcd for $C_{11}H_{12}NOS$ [$(M+H^+)$]: 206.0634, found: 206.0632.

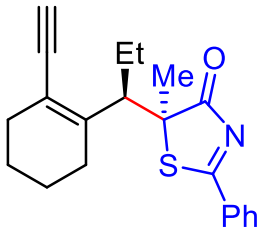
4. General Procedure III: General Procedure for Copper-Catalyzed Remote Asymmetric Yne-allylic Substitution of Yne-Allylic Esters with thiazolidinones



1 **2** **3** or **4**

To a mixture of CuI (1.9 mg, 10 mol%), **L1** (4.4 mg, 12 mol%), Yne-Allylic Esters **1** (0.1 mmol), **2** (0.15 mmol) and DIPEA (0.15 mmol) was added MeOH (1.0 mL) at -10 ^{o}C under nitrogen atmosphere. Upon complete consumption of **1** (TLC monitoring, about 48 h), the solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel column (hexanes/EtOAc = 20:1, v/v) to afford the desired product **3** or **4**.

(*S*)-5-((*R*)-1-(2-ethynylcyclohex-1-en-1-yl)propyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3a



White solid. 30 mg, 89% yield, 10:1 dr, 93.6:6.4 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17 (d, *J* = 7.8 Hz, 2H), 7.67-7.65 (m, 1H), 7.53-7.50 (m, 2H), 3.87 (dd, *J* = 11.4 and 3.0 Hz, 1H), 3.20 (s, 1H), 2.35-2.26 (m, 2H), 2.09-2.06 (m, 1H), 1.92-1.89 (m, 1H), 1.73-1.67 (m, 2H), 1.61-1.59 (m, 2H), 1.57 (s, 3H), 1.53-1.49 (m, 1H), 1.16-1.11 (m, 1H), 0.77 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.6, 195.2, 142.1, 134.9, 132.3, 129.0, 128.8, 121.0, 83.8, 81.2, 67.5, 53.5, 30.5, 25.8, 24.7, 22.4, 22.3, 21.8, 11.3. HRMS (ESI) calcd for $C_{21}H_{24}NOS$ [$(M+H^+)$]: 338.1573, found: 338.1567. HPLC analysis of the product: Daicel Chiralpak ADH column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: 25.06 min (major), 31.22 min (minor).

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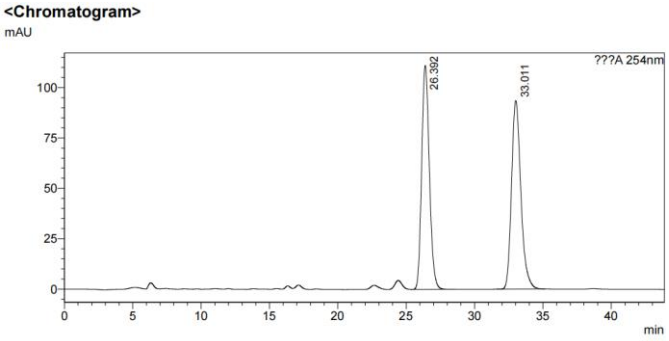

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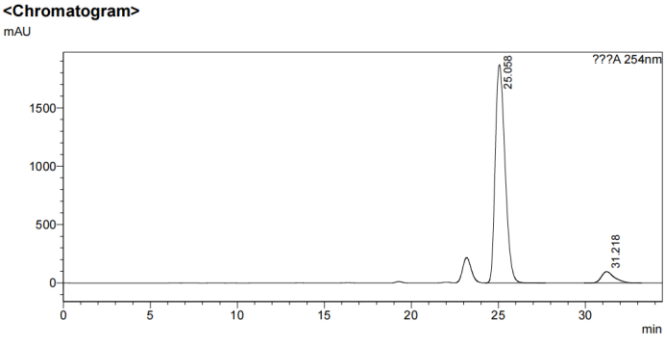

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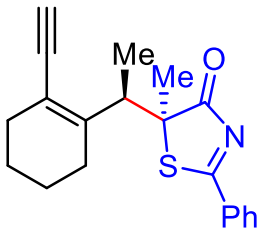
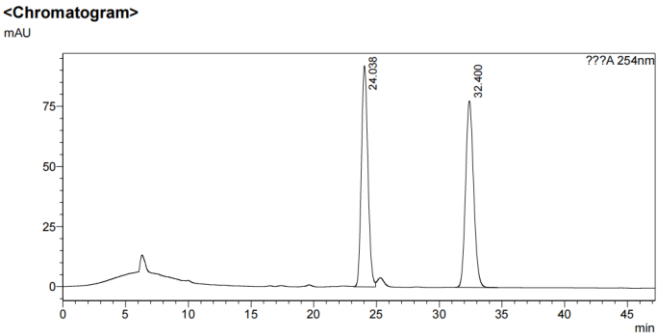
2	31.218	5014504	96889	6.440		M	
Total		77863935	1964822				

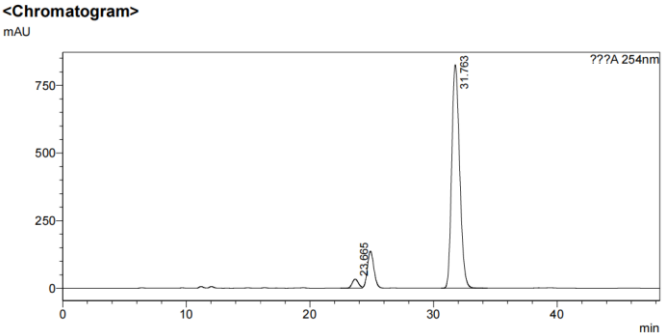
(*S*)-5-((*R*)-1-(2-ethynylcyclohex-1-en-1-yl)ethyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3b



Yellow solid. 25 mg, 77% yield, 7:1 dr, 97:3 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17 (d, *J* = 7.2 Hz, 2.00H, major), 8.12 (d, *J* = 7.2 Hz, 0.28H, minor), 7.68-7.64 (m, 1.14H), 7.53-7.50 (m, 2.28H), 4.04 (q, *J* = 13.8 and 7.2 Hz, 1.00H, major), 3.81 (q, *J* = 14.4 and 7.2 Hz, 0.14H, minor), 3.22 (s, 1.00H, major), 3.13 (s, 0.14H, minor), 2.32-2.22 (m, 2.60H), 2.19-2.12 (m, 1.40H), 1.96-1.92 (m, 1.12H), 1.76 (s, 0.42H, minor), 1.75-1.62 (m, 3.00H), 1.60 (s, 3.00H, major), 1.57-1.49 (m, 1.00H), 1.20 (d, *J* = 7.2 Hz, 0.42H, minor), 0.94 (d, *J* = 7.2 Hz, 3.00H, major). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.4, 195.2, 194.5, 193.9, 146.7, 144.5, 134.9, 134.8, 132.3, 132.2, 129.0, 128.9, 128.8, 128.7, 118.7, 118.0, 84.1, 83.5, 81.3, 81.1, 68.3, 67.9, 46.5, 45.6, 30.44, 30.40, 25.7, 25.2, 25.0, 24.8, 22.4, 22.3, 22.2, 22.1, 14.53, 14.48. HRMS (ESI) calcd for $C_{20}H_{22}NOS$ [$(M+H^+)$]: 324.1417, found: 324.1412. HPLC analysis of the product: Daicel Chiralpak ADH column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: 23.67 min (minor), 31.76 min (major).





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Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	24.038	3328376	91929	49.100			
2	32.400	3450402	77531	50.900			
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???A 254nm

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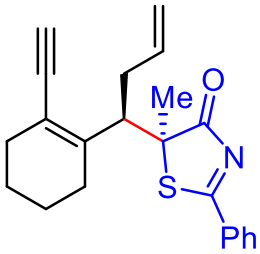
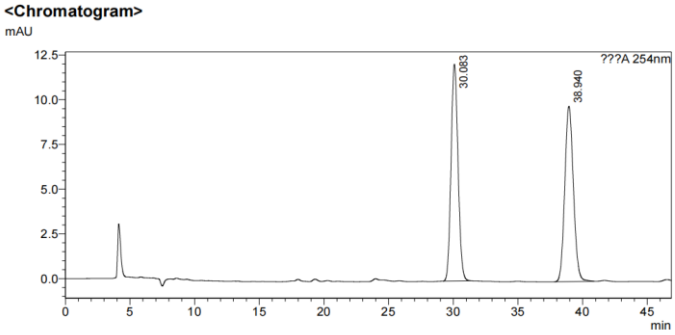
1	23.665	1200873	33803	3.153			
2	31.763	36883568	825431	96.847			
Total		38084441	859234				

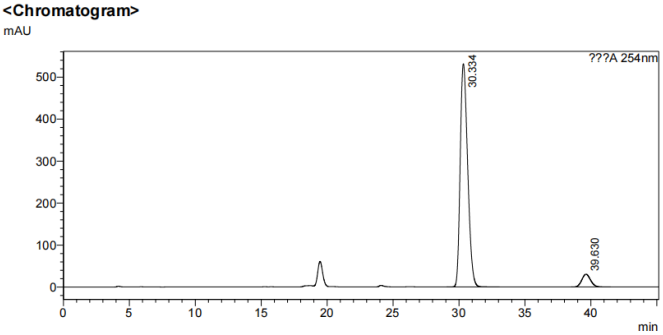
(*S*)-5-((*R*)-1-(2-ethynylcyclohex-1-en-1-yl)but-3-en-1-yl)-5-methyl-2-phenylthiazol-4(5H)-one: 3c



Yellow liquid. 24 mg, 69% yield, 14:1 dr, 94:6 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17 (d, *J* = 7.2 Hz, 2H), 7.68-7.66 (m, 1H), 7.54-7.51 (m, 2H), 5.65-5.58 (m, 1H), 4.91 (dd, *J* = 16.8 and 13.2 Hz, 2H), 4.07 (dd, *J* = 11.4 and 4.8 Hz, 1H), 3.22 (s, 1H), 2.28-2.22 (m, 3H), 2.11-2.08 (m, 1H), 1.95-1.90 (m, 2H), 1.73-1.62 (m, 3H), 1.59 (s, 3H), 1.57-1.54 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.3, 195.0, 142.0, 135.02, 134.94, 132.2, 129.0, 128.8, 120.8, 116.3, 83.6, 81.4, 67.0, 51.3, 33.4, 30.4, 25.8, 25.0, 22.24, 22.20. HRMS (ESI) calcd for $C_{22}H_{24}NOS$ [$(M+H^+)$]: 350.1573, found: 350.1569. HPLC analysis of the product: Daicel Chiralpak IC-3 column; hexane/2-propanol = 95/5, 0.8 mL/min. Retention times: 30.33 min (major), 39.63 min (minor).





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Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
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2	38.940	454121	9809	49.959			
Total		908978	21926				

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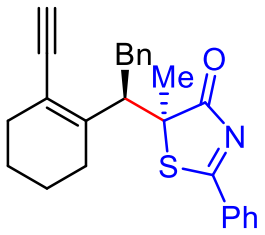
1	30.334	20835771	531096	93.710		M	
2	39.630	1398509	30380	6.290			
Total		22234280	561476				

(*S*)-5-((*R*)-1-(2-ethynylcyclohex-1-en-1-yl)-2-phenylethyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3d



Yellow liquid. 27 mg, 68% yield, 18:1 dr, 92:8 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.22-8.20 (m, 2H), 7.70-7.68 (m, 1H), 7.56-7.53 (m, 2H), 7.20-7.17 (m, 2H), 7.15-7.14 (m, 1H), 7.11-7.10 (m, 2H), 4.35 (dd, *J* = 11.4 and 4.2 Hz, 1H), 3.09 (s, 1H), 2.73-2.69 (m, 1H), 2.53-2.50 (m, 1H), 2.22-2.13 (m, 2H), 2.01-1.93 (m, 2H), 1.71-1.66 (m, 1H), 1.63 (s, 3H), 1.53-1.49 (m, 2H), 1.45-1.39 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.4, 195.1, 140.9, 138.2, 135.0, 132.3, 129.1, 129.0, 128.9, 127.9, 126.1, 121.5, 83.5, 80.9, 67.3, 53.0, 35.2, 30.2, 26.0, 25.1, 22.2, 22.1. HRMS (ESI) calcd for $C_{26}H_{26}NOS$ [$(M+H^+)$]: 400.1730, found: 400.1727. HPLC analysis of the product: Daicel Chiralpak ODH column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: 15.95 min (minor), 19.97 min (major).

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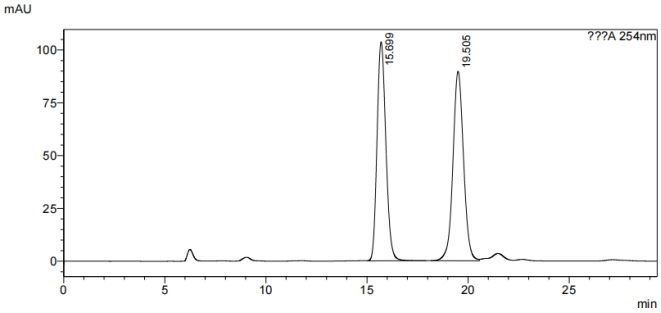

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???A 254nm

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Total		6414556	193259				

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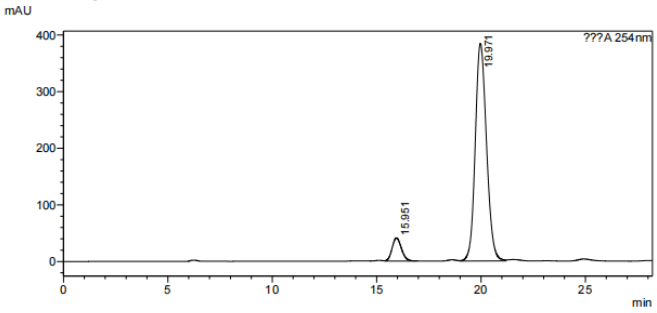

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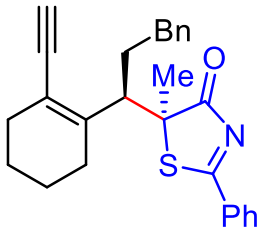
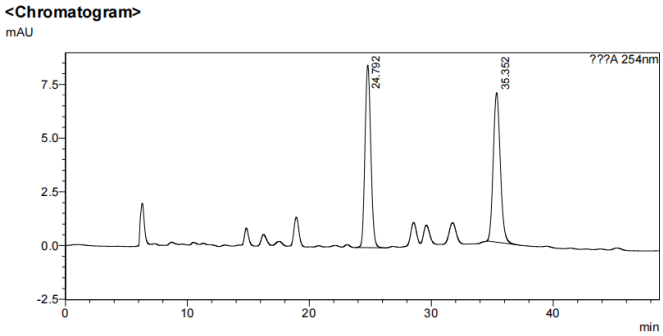
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.951	1270022	40848	8.096		M	
2	19.971	14417125	384305	91.904		M	
Total		15687146	425153				

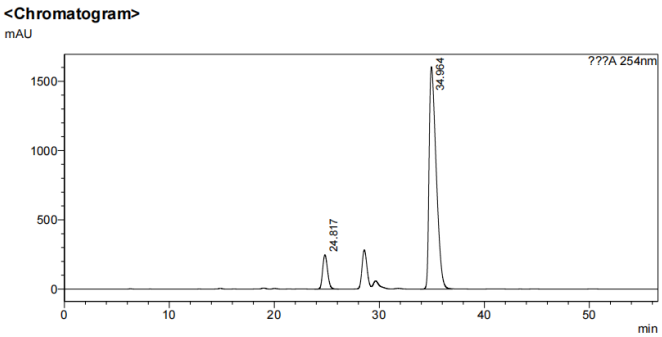
(*S*)-5-((*R*)-1-(2-ethynylcyclohex-1-en-1-yl)-3-phenylpropyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3e



White solid. 21 mg, 51% yield, 8:1 dr, 90.3:9.7 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14 (d, *J* = 7.8 Hz, 2.00H, major), 8.10 (d, *J* = 7.8 Hz, 0.24H, minor), 7.66-7.64 (m, 1.12H), 7.52-7.49 (m, 2.24H), 7.25-7.24 (m, 0.24H), 7.22-7.19 (m, 2.00H), 7.17-7.14 (m, 0.36H), 7.13-7.08 (m, 3.00H), 4.08 (dd, *J* = 12.0 and 3.6 Hz, 1.00H, major), 3.74 (dd, *J* = 9.6 and 5.4 Hz, 0.12H, minor), 3.24 (s, 1.00H, major), 3.14 (s, 0.12H, minor), 2.60-2.54 (m, 1.12H), 2.45-2.40 (m, 1.12H), 2.36-2.28 (m, 2.24H), 2.17-2.11 (m, 1.12H), 1.99-1.94 (m, 1.12H), 1.85-1.77 (m, 1.60H), 1.75 (s, 0.36H, minor), 1.74-1.61 (m, 3.00H), 1.60 (s, 3.00H, major), 1.58-1.52 (m, 1.00H), 1.42-1.37 (m, 1.12H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.4, 195.2, 194.3, 193.1, 144.1, 141.9, 141.8, 141.5, 134.9, 134.8, 133.3, 132.2, 129.1, 128.9, 128.8, 128.7, 128.4, 128.31, 128.27, 128.2, 125.9, 125.8, 121.4, 121.0, 84.3, 83.6, 81.6, 81.3, 67.8, 67.3, 52.0, 50.8, 33.8, 33.5, 30.9, 30.6, 30.5, 30.0, 25.8, 25.3, 25.2, 24.9, 22.4, 22.34, 22.27, 22.2. HRMS (ESI) calcd for $C_{27}H_{28}NOS$ [$(M+H^+)$]: 414.1886, found: 414.1885. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: 24.82 min (minor), 34.96 min (major).





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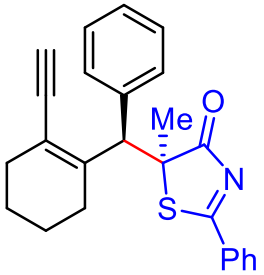
2	34.964	74951943	1604615	90.308		M	
Total		82995492	1851301				

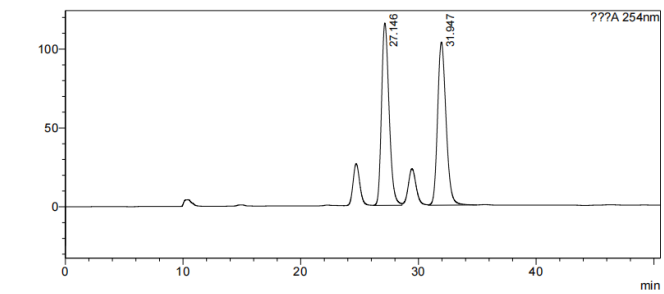
(*S*)-5-((*R*)-(2-ethynylcyclohex-1-en-1-yl)(phenyl)methyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3f



White solid. 35 mg, 91% yield, 4:1 dr, 98:2 er, 86:14 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12 (d, *J* = 7.8 Hz, 0.50H, minor), 8.08 (d, *J* = 7.8 Hz, 2.00H, major), 7.65-7.62 (m, 1.25H), 7.52-7.44 (m, 3.00H), 7.33-7.31 (m, 0.50H), 7.27-7.25 (m, 2.25H), 7.15-7.10 (m, 3.00H), 5.31 (s, 1.00H, major), 5.18 (s, 0.25H, minor), 3.28 (s, 0.25H, minor), 3.26 (s, 1.00H, major), 2.36-2.22 (m, 5.20H), 2.16-2.08 (m, 1.00H), 1.73 (s, 3.00H, major), 1.71 (s, 0.75H, minor), 1.67-1.62 (m, 2.50H), 1.51-1.40 (m, 1.30H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.3, 195.4, 194.6, 194.3, 144.3, 142.8, 139.1, 138.3, 134.8, 132.2, 129.05, 129.01, 129.00, 128.9, 128.74, 128.71, 128.5, 128.4, 128.2, 128.0, 127.3, 127.1, 120.7, 119.1, 84.2, 83.6, 81.7, 81.5, 67.4, 66.4, 57.7, 56.8, 30.7, 30.5, 28.1, 27.4, 26.8, 26.1, 22.5, 22.4, 22.1, 21.8. HRMS (ESI) calcd for $C_{25}H_{24}NOS$ [$(M+H^+)$]: 386.1573, found: 386.1562. HPLC analysis of the product: Daicel Chiralpak ODH column; hexane/2-propanol = 95/5, 0.3 mL/min. Retention times: for major product: 25.58 min (major), 30.22 min (minor); for minor product: 23.40 min (minor), 27.71 min (major).

<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	27.146	5153811	115618	49.939			
2	31.947	5166425	103353	50.061			
Total		10320236	218971				

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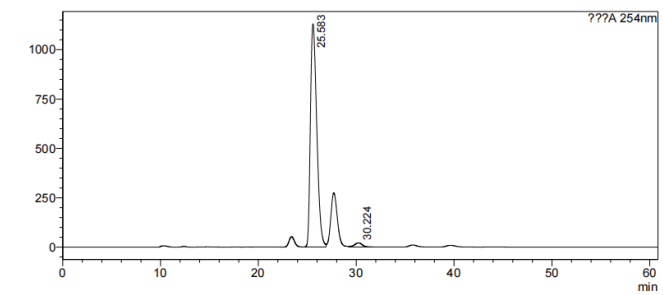

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	25.583	50921267	1129197	97.758		M	
2	30.224	1167852	20751	2.242		M	
Total		52089120	1149948				

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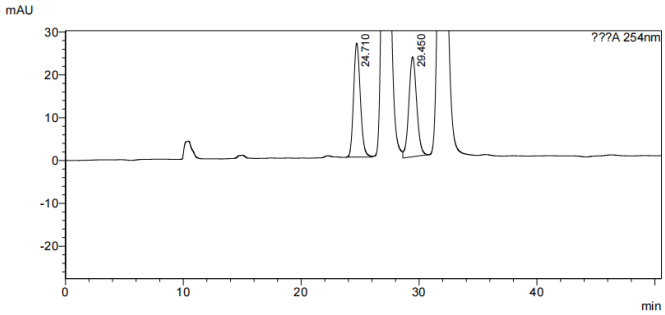

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	24.710	1054734	26589	49.461		M	
2	29.450	1077710	23294	50.539		M	
Total		2132444	49883				

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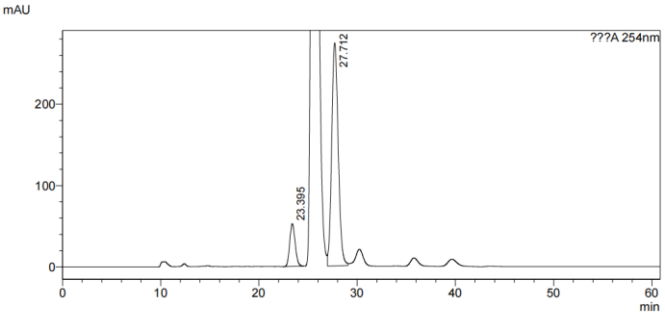
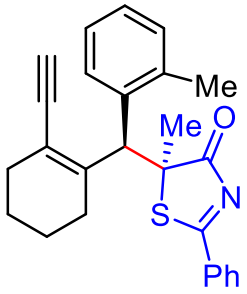


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.395	2030798	52325	13.854		M	
2	27.712	12627404	273955	86.146		M	
Total		14658202	326281				

(*S*)-5-((*S*)-(2-ethynylcyclohex-1-en-1-yl)(o-tolyl)methyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3g



Yellow solid. 31 mg, 78% yield, 4:1 dr, 76.5:23.5 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12 (d, *J* = 7.8 Hz, 2.00H, major), 8.10 (d, *J* = 7.8 Hz, 0.50H, minor), 7.67-7.65 (m, 1.25H), 7.56-7.54 (m, 1.00H), 7.52-7.50 (m, 2.50H), 7.46-7.45 (m, 0.25H), 7.19-7.17 (m, 0.25H), 7.15-7.13 (m, 0.50H), 7.10-7.09 (m, 1.00H), 7.03-7.00 (m, 1.00H), 6.91-6.89 (m, 1.00H), 5.45 (s, 1.00H, major), 5.39 (s, 0.25H, minor), 3.31 (s, 1.00H, major), 3.29 (s, 0.25H, minor), 2.64-2.61 (m, 0.25H), 2.50 (s, 3.00H, major), 2.47 (s, 0.75H, minor), 2.44-2.33 (m, 2.25H), 2.29-2.24 (m, 1.50H), 2.17-2.13 (m, 0.25H), 2.04-2.00 (m, 1.00H), 1.87 (s, 3.00H, major), 1.75 (s, 0.75H, minor), 1.68-1.60 (m, 3.75H), 1.55-1.50 (m, 1.00H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.1, 194.9, 193.7, 193.6, 143.1, 142.2, 138.13, 138.08, 136.8, 136.5, 134.8, 134.7, 132.31, 132.25, 131.04, 131.02, 129.0, 128.8, 128.7, 128.6, 127.8, 127.0, 126.9, 126.7, 125.5, 125.2, 120.7, 119.8, 84.7, 84.6, 81.7, 81.6, 68.6, 68.2, 53.3, 51.5, 31.1, 30.9, 28.5, 27.5, 26.8, 26.7, 22.5, 22.4, 21.99, 21.90, 21.0. HRMS (ESI) calcd for $C_{26}H_{26}NOS$ [$(M+H^+)$]: 400.1730, found: 400.1726. HPLC analysis of the product: Daicel Chiralpak ODH column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: 11.73 min (major), 13.39 min (minor).

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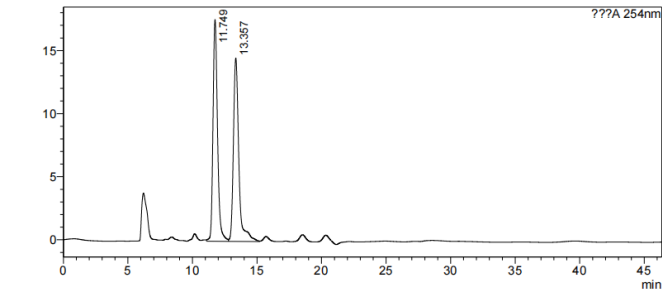

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.749	427970	17566	50.165			
2	13.357	425156	14528	49.835		V M	
Total		853127	32095				

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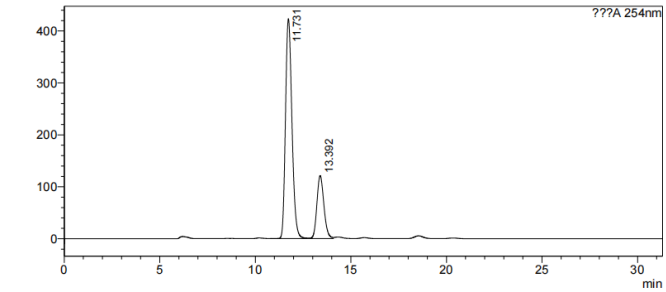
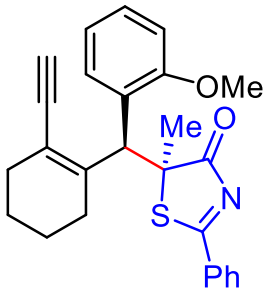


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.731	9960802	423194	76.305			
2	13.392	3093179	121319	23.695		V	
Total		13053982	544513				

(*S*)-5-((*S*)-(2-ethynylcyclohex-1-en-1-yl)(2-methoxyphenyl)methyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3h



White solid. 26 mg, 63% yield, 11:1 dr, 96.7:3.3 er, 95:5 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11 (d, *J* = 7.8 Hz, 2H), 7.67-7.64 (m, 1H), 7.52-7.49 (m, 3H), 7.11-7.08 (m, 1H), 6.81-6.80 (m, 1H), 6.69-6.66 (m, 1H), 5.83 (s, 1H), 3.82 (s, 3H), 3.26 (s, 1H), 2.35-2.27 (m, 3H), 2.10-2.07 (m, 1H), 1.83 (s, 3H), 1.71-1.61 (m, 2H), 1.57-1.52 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 194.9, 193.4, 157.7, 142.4, 134.7, 132.4, 128.9, 128.7, 128.0, 127.7, 127.3, 120.5, 119.9, 111.4, 84.5, 80.8, 67.8, 55.9, 48.1, 30.9, 28.2, 26.8, 22.6, 22.1. HRMS (ESI) calcd for $C_{26}H_{26}NO_2S$ [$(M+H^+)$]: 416.1679, found: 416.1675. HPLC analysis of the product: Daicel Chiralpak ASH column; hexane/2-propanol = 94/6, 0.3 mL/min. Retention times: for major product: 31.52 min (minor), 43.48 min (major); for minor product: 29.46 min (major), 37.09 min (minor).

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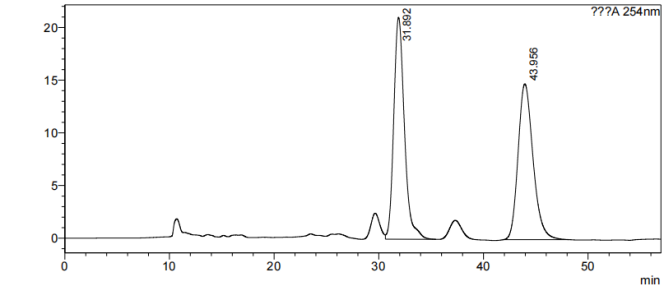

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	31.892	1495618	21060	50.369			
2	43.956	1473694	14795	49.631			
Total		2969313	35856				

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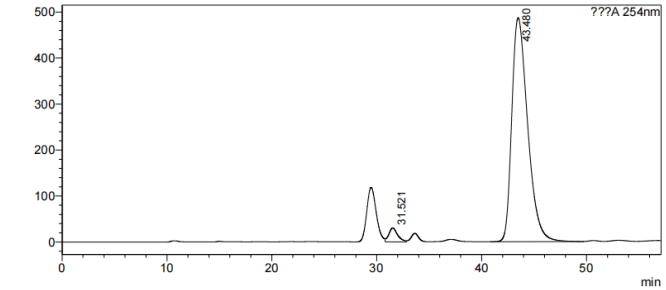

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	31.521	1763352	30260	3.324			
2	43.480	51287191	487199	96.676		M	
Total		53050543	517459				

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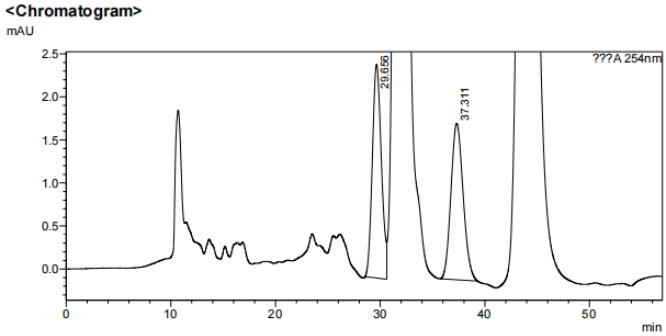

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	29.656	148214	2483	50.155		M	
2	37.311	147297	1819	49.845		M	
Total		295512	4302				

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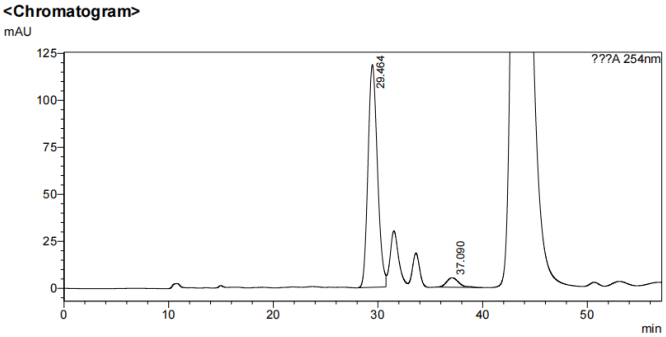
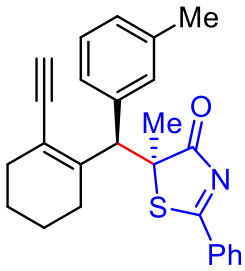


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	29.464	7404521	118396	94.752		M	
2	37.090	410087	5034	5.248		M	
Total		7814608	123430				

(*S*)-5-((*R*)-(2-ethynylcyclohex-1-en-1-yl)(m-tolyl)methyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3i



Light yellow liquid. 37 mg, 93% yield, 2:1 dr, 97.4:2.6 er, 82.6:17.4 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14 (d, *J* = 7.8 Hz, 1.00H, minor), 8.09 (d, *J* = 7.8 Hz, 2.00H, major), 7.67-7.63 (m, 1.50H), 7.53-7.48 (m, 3.00H), 7.27-7.26 (m, 0.50H), 7.23-7.20 (m, 1.00H), 7.11-7.08 (m, 2.50H), 7.03-7.00 (m, 1.00H), 6.93-6.92 (m, 1.00H), 5.27 (s, 1.00H, major), 5.16 (s, 0.50H, minor), 3.29 (s, 0.50H, minor), 3.28 (s, 1.00H, major), 2.36 (s, 1.50H, minor), 2.35-2.22 (m, 5.25H), 2.19 (s, 3.00H, major), 2.16-2.10 (m, 1.00H), 1.74 (s, 3.00H, major), 1.71 (s, 1.50H, minor), 1.69-1.58 (m, 4.25H), 1.50-1.39 (m, 1.50H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.4, 194.6, 194.3, 193.8, 144.4, 142.9, 138.9, 138.15, 138.09, 137.7, 134.81, 134.78, 132.31, 132.26, 130.0, 129.5, 129.0, 128.9, 128.70, 128.67, 128.3, 128.1, 128.0, 127.9, 125.9, 125.1, 120.5, 119.0, 84.2, 83.6, 81.6, 81.4, 67.5, 66.5, 57.7, 56.8, 30.7, 30.5, 28.1, 27.3, 26.8, 26.1, 22.5, 22.4, 22.1, 21.8, 21.6, 21.5. HRMS (ESI) calcd for $C_{26}H_{26}NOS$ [$(M+H^+)$]: 400.1730, found: 400.1726. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: for major product: 28.79 min (major), 35.07 min (minor); for minor product: 24.52 min (minor), 43.12 min (major).

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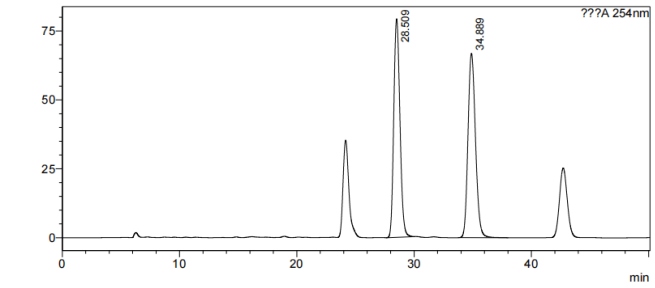

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	28.509	2894067	79253	49.333			
2	34.889	2972377	66907	50.667			
Total		5866443	146160				

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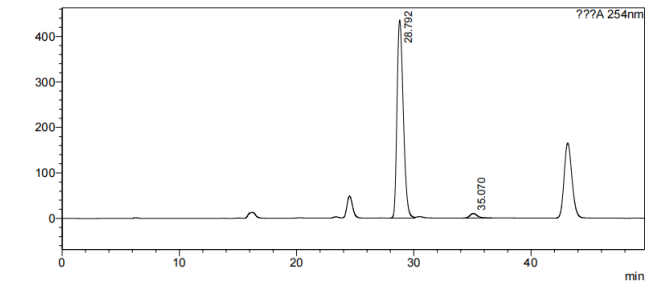

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	28.792	16206334	435458	97.355		M	
2	35.070	440373	9988	2.645			
Total		16646707	445446				

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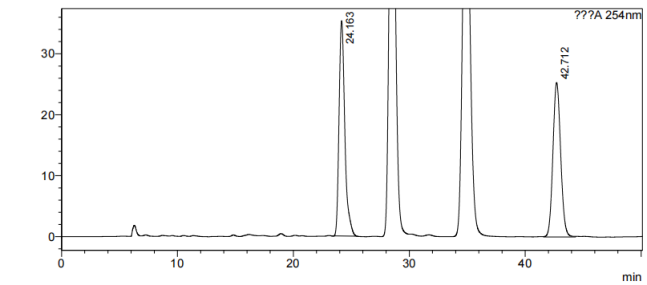

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	24.163	1224082	35305	50.970		M	
2	42.712	1177503	25337	49.030		M	
Total		2401585	60642				

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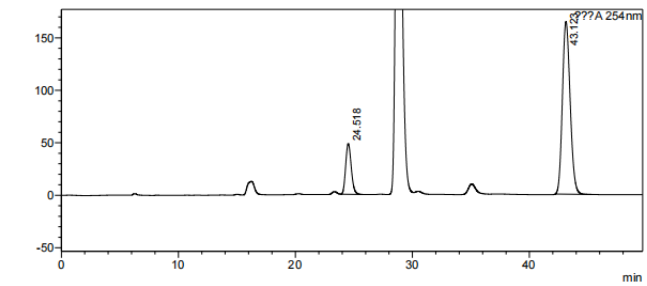
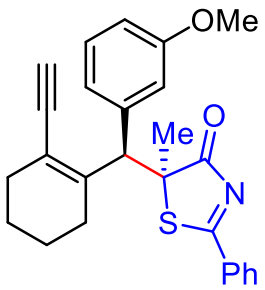


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	24.518	1597281	48242	17.390		M	
2	43.123	7587543	164553	82.610		M	
Total		9184824	212795				

(*S*)-5-((*R*)-(2-ethynylcyclohex-1-en-1-yl)(3-methoxyphenyl)methyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3j



Colorless liquid. 37 mg, 89% yield, 3:1 dr, 97.5:2.5 er, 87:13 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.66-7.64 (m, 1H), 7.51-7.48 (m, 2H), 7.07-7.04 (m, 1H), 6.87-6.84 (m, 2H), 6.68-6.66 (m, 1H), 5.29 (s, 1H), 3.64 (s, 3H), 3.27 (s, 1H), 2.36-2.21 (m, 4H), 1.73 (s, 3H), 1.69-1.61 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.3, 194.4, 159.2, 142.7, 139.8, 134.9, 132.2, 129.1, 129.0, 128.7, 120.71, 120.66, 114.2, 112.6, 83.6, 81.7, 66.3, 56.6, 55.0, 30.5, 27.6, 26.7, 22.5, 22.1. HRMS (ESI) calcd for $C_{26}H_{26}NO_2S$ [$(M+H^+)$]: 416.1679, found: 416.1676. HPLC analysis of the product: Daicel Chiralpak ODH column; hexane/2-propanol = 95/5, 0.3 mL/min. Retention times: for major product: 35.94 min (major), 41.61 min (minor); for minor product: 30.79 min (minor), 38.60 min (major).

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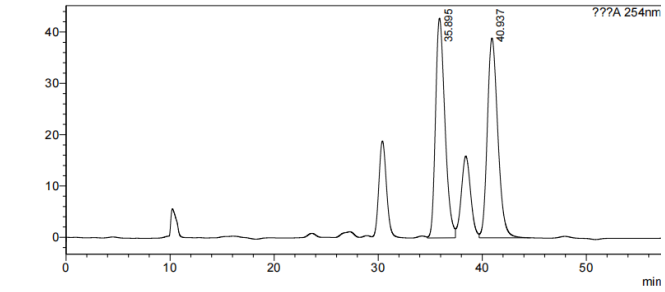

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	35.895	2688937	42826	49.631			
2	40.937	2728946	38923	50.369			
Total		5417883	81750				

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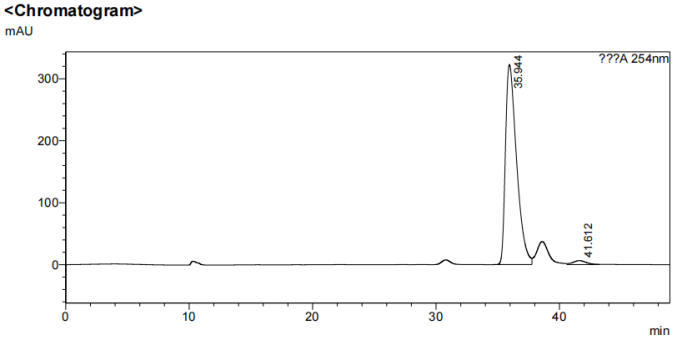

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	35.944	20225661	322915	97.557			
2	41.612	506478	6471	2.443		M	
Total		20732139	329386				

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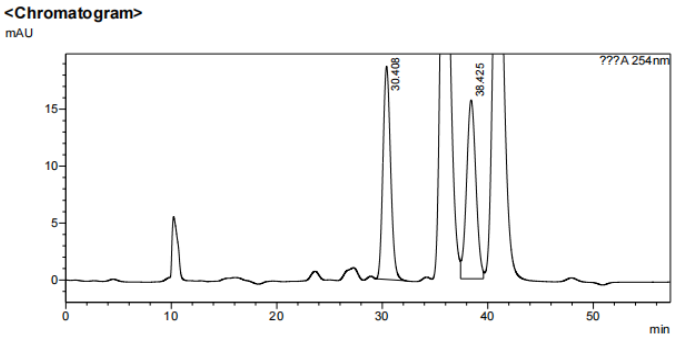

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	30.408	941465	18724	49.332		M	
2	38.425	966968	15703	50.668		M	
Total		1908433	34426				

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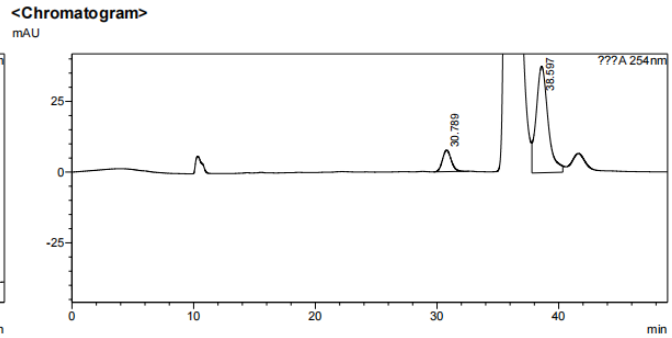
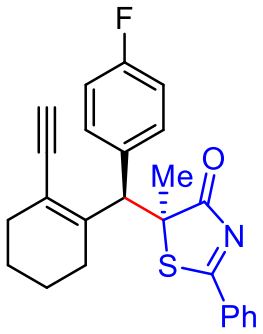


<Peak Table>

???A 254nm

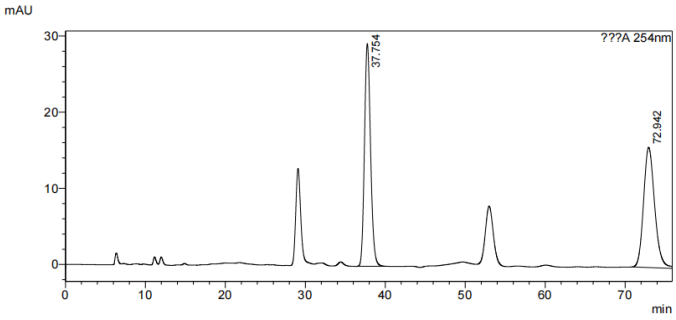
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	30.789	378597	7588	12.919		M	
2	38.597	2551901	37628	87.081		M	
Total		2930498	45215				

(*S*)-5-((*R*)-(2-ethynylcyclohex-1-en-1-yl)(4-fluorophenyl)methyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3k



Light yellow solid. 27 mg, 67% yield, 4:1 dr, 98:2 er, 88.3:11.7 er. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11 (d, *J* = 8.4 Hz, 0.50H, minor), 8.08 (d, *J* = 7.8 Hz, 2.00H, major), 7.68-7.65 (m, 1.00H), 7.53-7.49 (m, 3.00H), 7.43-7.41 (m, 0.50H), 7.29-7.27 (m, 1.75H), 7.03-7.00 (m, 0.50H), 6.85-6.82 (m, 2.00H), 5.28 (s, 1.00H, major), 5.16 (s, 0.25H, minor), 3.29 (s, 1.25H), 2.36-2.24 (m, 5.00H), 2.14-1.98 (m, 1.00H), 1.73 (s, 3.00H, major), 1.72 (s, 0.75H, minor), 1.65-1.62 (m, 3.00H), 1.52-1.45 (m, 1.00H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.3, 195.0, 194.4, 193.8, 162.8, 162.7, 161.2, 161.1, 144.2, 142.5, 135.00, 134.97, 134.8 (d, *J* = 3.3 Hz, minor), 134.1 (d, *J* = 3.2 Hz, major), 132.2, 132.1, 130.6 (d, *J* = 8.2 Hz, minor), 130.2 (d, *J* = 7.4 Hz, major), 128.89 (d, *J* = 36.1 Hz, major), 128.88 (d, *J* = 45.5 Hz, minor), 120.8, 119.3, 115.4 (d, *J* = 22.0 Hz, minor), 115.1 (d, *J* = 21.6 Hz, major), 84.1, 83.4, 82.0, 81.7, 67.5, 66.5, 57.0, 56.2, 30.6, 30.5, 27.9, 27.2, 26.8, 26.0, 22.5, 22.4, 22.0, 21.8. ^{19}F NMR (566 MHz, $CDCl_3$): δ -115.0 (minor), -115.4 (major). HRMS (ESI) calcd for $C_{25}H_{23}FNOS$ [$(M+H^+)$]: 404.1479, found: 404.1475. HPLC analysis of the product: Daicel Chiralpak ADH column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: for major product: 37.66 min (major), 72.93 min (minor); for minor product: 29.08 min (minor), 52.94 min (major).

<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	37.754	1546066	29238	50.459			
2	72.942	1517926	15778	49.541		M	
Total		3063992	45015				

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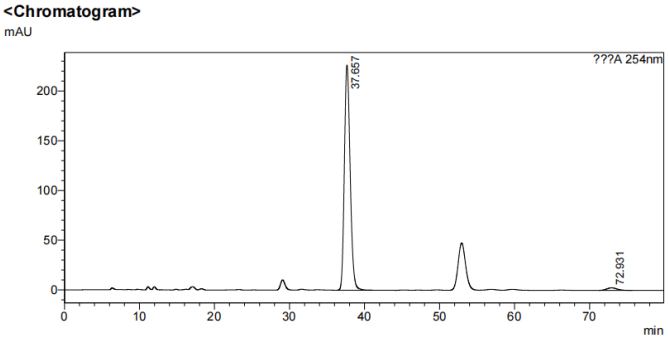

<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	37.657	12108547	226244	98.071			
2	72.931	238180	2552	1.929			
Total		12346728	228796				

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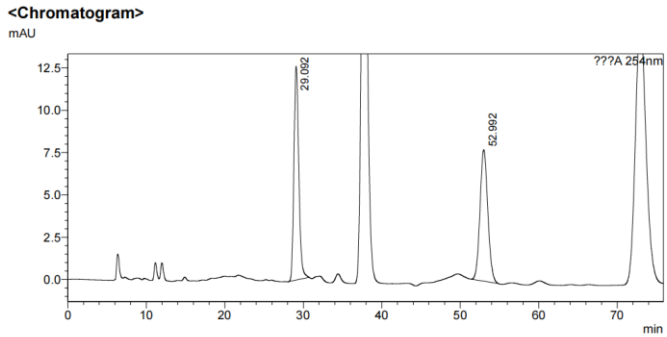

<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	29.092	543199	12629	50.245		M	
2	52.992	537911	7764	49.755		M	
Total		1081110	20392				

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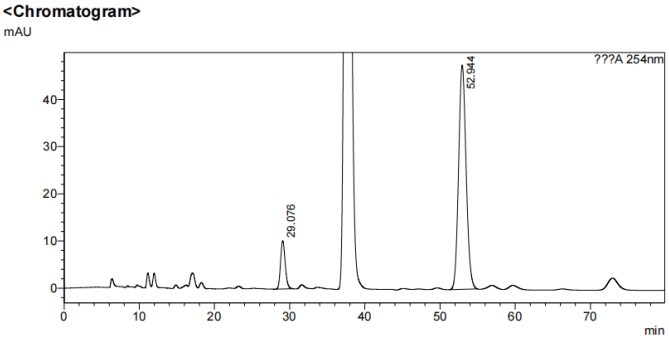
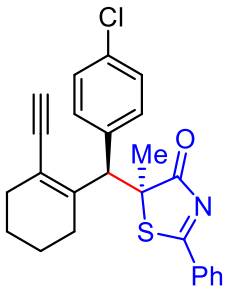


<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	29.076	436184	10204	11.675		M	
2	52.944	3299738	47513	88.325		M	
Total		3735922	57717				

(*S*)-5-((*R*)-(4-chlorophenyl)(2-ethynylcyclohex-1-en-1-yl)methyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3l



White solid. 37 mg, 79% yield, 3.3:1 dr, 98:2 er, 88:12 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11 (d, *J* = 7.2 Hz, 0.60H, minor), 8.09 (d, *J* = 7.2 Hz, 2.00H, major), 7.67-7.64 (m, 1.00H), 7.53-7.49 (m, 2.90H), 7.38 (d, *J* =8.4 Hz, 0.60H, minor), 7.29 (d, *J* = 8.4 Hz, 0.60H, minor), 7.23 (d, *J* = 8.4 Hz, 2.00H, major), 7.12 (d, *J* = 8.4 Hz, 2.00H, major), 5.27 (s, 1.00H, major), 5.15 (s, 0.30H, minor), 3.28 (s, 1.30H), 2.35-2.22 (m, 5.50H), 2.13-2.09 (m, 0.90H), 1.73 (s, 3.00H, major), 1.72 (s, 0.90H, minor), 1.68-1.57 (m, 4.00H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.2, 194.4, 194.3, 193.6, 143.9, 142.2, 137.6, 136.8, 135.03, 134.99, 133.2, 133.0, 132.1, 132.0, 130.3, 129.9, 129.02, 129.00, 128.8, 128.7, 128.6, 128.4, 121.1, 119.5, 84.0, 83.3, 82.0, 81.8, 67.2, 66.3, 57.0, 56.2, 30.6, 30.5, 28.0, 27.3, 26.8, 26.0, 22.5, 22.4, 22.0, 21.7. HRMS (ESI) calcd for $C_{25}H_{23}ClNOS$ [$(M+H^+)$]: 420.1183, found: 420.1180. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 92/8, 1.0 mL/min. Retention times: for major product: 14.60 min (major), 17.11 min (minor); for minor product: 11.18 min (minor), 15.70 min (major).

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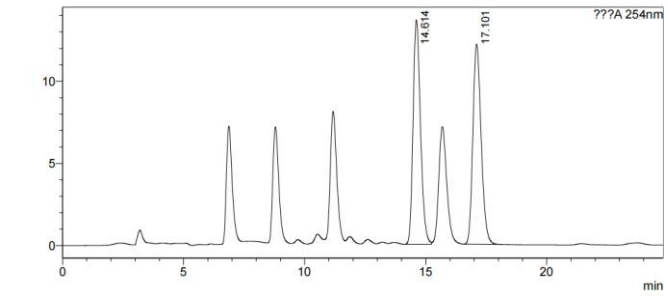

<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.614	290717	13660	50.089			
2	17.101	289683	12167	49.911		M	
Total		580401	25828				

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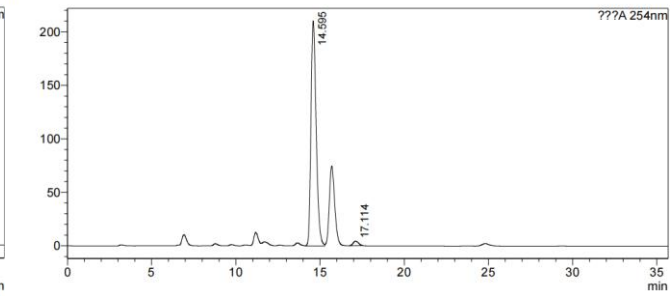

<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.595	4518034	210163	97.963			
2	17.114	93932	4227	2.037		M	
Total		4611966	214389				

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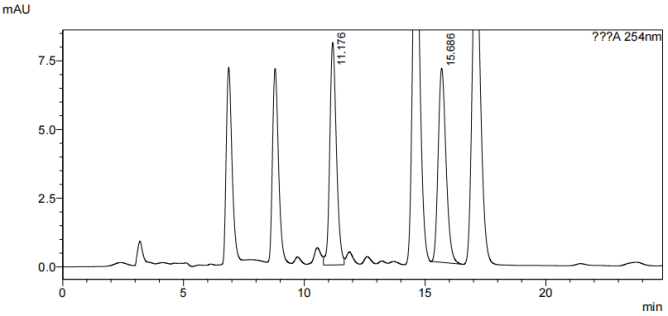
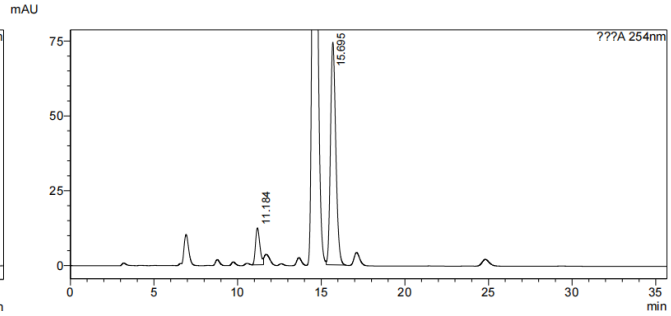


<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.176	154895	8090	49.181		M	
2	15.686	160053	7067	50.819		M	
Total		314948	15157				

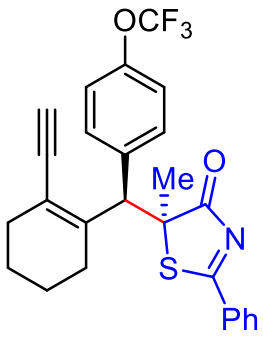
<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.184	226643	12300	12.081		M	
2	15.695	1649377	74275	87.919		M	
Total		1876020	86576				

(*S*)-5-((*R*)-(2-ethynylcyclohex-1-en-1-yl)(4-(trifluoromethoxy)phenyl)methyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3m



Yellow liquid. 38 mg, 81% yield, 1.4:1 dr, 98.2:1.8 er, 91.6:8.4 er. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11 (d, *J* = 7.8 Hz, 1.40H, minor), 8.08 (d, *J* = 7.2 Hz, 2.00H, major), 7.68-7.65 (m, 1.60H), 7.53-7.50 (m, 4.90H), 7.31 (d, *J* = 7.8 Hz, 2.00H, major), 7.17 (d, *J* = 8.4 Hz, 1.40H, minor), 6.99 (d, *J* = 8.4 Hz, 2.00H, major), 5.31 (s, 1.00H, major), 5.19 (s, 0.70H, minor), 3.29 (s, 1.70H), 2.37-2.26 (m, 6.20H), 2.14-2.05 (m, 2.00H), 1.74 (s, 3.00H, major), 1.72 (s, 2.10H, minor), 1.69-1.64 (m, 2.40H), 1.52-1.42 (m, 3.00H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.2, 194.4, 194.3, 193.6, 148.4, 148.2, 143.8, 142.2, 137.7, 136.9, 135.1, 135.0, 132.1, 132.0, 130.4, 129.9, 129.1, 129.0, 128.8, 128.7, 121.2, 120.8, 120.5, 119.7, 84.0, 83.3, 82.1, 81.8, 67.2, 66.3, 57.0, 56.2, 30.6, 30.5, 30.1, 29.7, 27.9, 27.3, 26.7, 26.0, 22.5, 22.4, 22.0, 21.7. ^{19}F NMR (566 MHz, $CDCl_3$): δ -57.8. HRMS (ESI) calcd for $C_{26}H_{23}F_3NO_2S$ [$(M+H^+)$]: 470.1396, found: 470.1395. HPLC analysis of the product: Daicel Chiralpak IC-3 column; hexane/2-propanol = 95/5, 0.3 mL/min. Retention times: for major product: 44.85 min (major), 61.80 min (minor); for minor product: 40.57 min (minor), 58.11 min (major).

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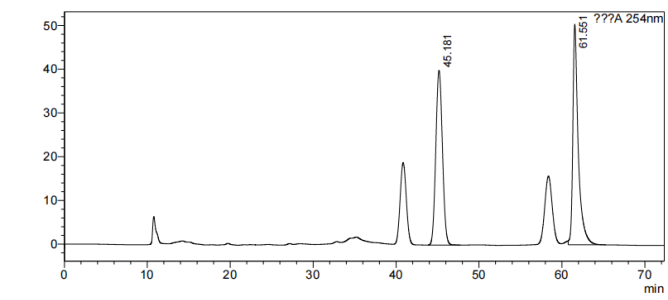

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	45.181	2221704	39928	49.273			
2	61.551	2287255	50371	50.727		M	
Total		4508959	90300				

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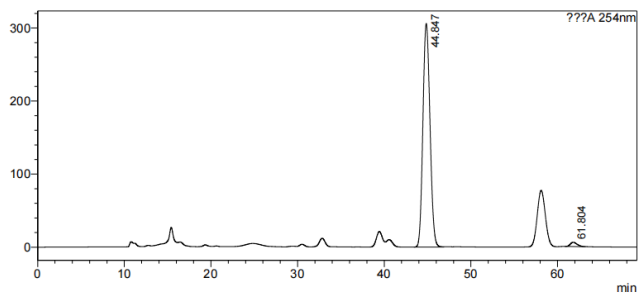
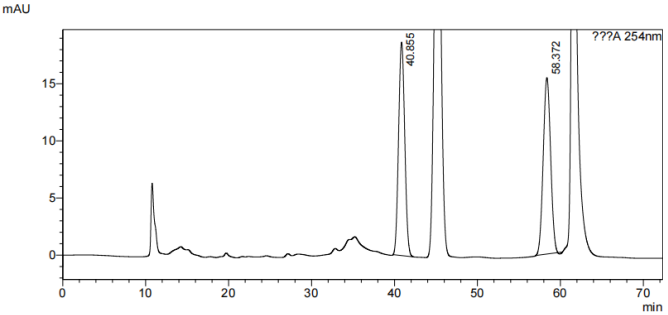


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	44.847	17351346	306040	98.122		M	
2	61.804	332089	5996	1.878		M	
Total		17683435	312036				

<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	40.855	966423	18690	50.341		M	
2	58.372	953329	15432	49.659		M	
Total		1919753	34122				

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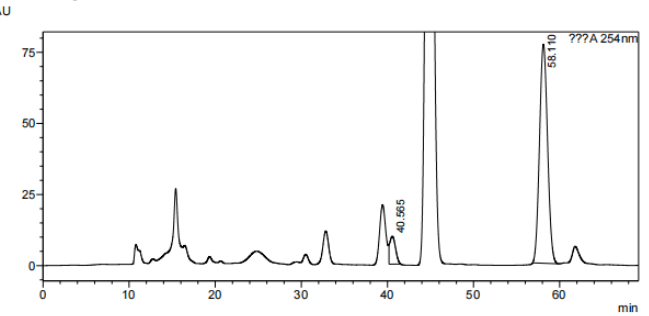
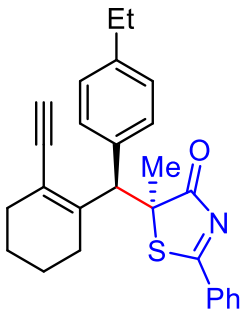


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	40.565	454738	9784	8.354		M	
2	58.110	4988752	76951	91.646		M	
Total		5443490	86735				

(*S*)-5-((*R*)-(4-ethylphenyl)(2-ethynylcyclohex-1-en-1-yl)methyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3n



Light yellow liquid. 38 mg, 92% yield, 3.2:1 dr, 98:2 er, 84.6:15.4 er. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14 (d, *J* = 7.2 Hz, 0.60H, minor), 8.10 (d, *J* = 7.8 Hz, 2.00H, major), 7.67-7.63 (m, 1.30H), 7.53-7.48 (m, 2.60H), 7.37 (d, *J* = 7.8 Hz, 0.60H, minor), 7.19 (d, *J* = 7.8 Hz, 2.00H, major), 7.16 (d, *J* = 7.8 Hz, 0.60H, minor), 6.97 (d, *J* = 8.4 Hz, 2.00H, major), 5.29 (s, 1.00H, major), 5.16 (s, 0.30H, minor), 3.28 (s, 0.30H, minor), 3.27 (s, 1.00H, major), 2.63 (q, *J* = 15.0 and 7.2 Hz, 0.60H, minor), 2.50 (q, *J* = 15.6 and 7.8 Hz, 2.00H, major), 2.36-2.32 (m, 2.00H), 2.29-2.19 (m, 3.00H), 2.16-2.09 (m, 0.50H), 1.73 (s, 3.00H, major), 1.71 (s, 0.90H, minor), 1.68-1.60 (m, 3.90H), 1.50-1.39 (m, 1.00H), 1.23 (t, *J* = 7.8 Hz, 0.90H, minor), 1.12 (t, *J* = 7.2Hz, 3.00H, major). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.4, 194.6, 194.3, 193.8, 144.5, 143.2, 143.0, 142.9, 136.2, 135.4, 134.80, 134.78, 132.31, 132.26, 129.0, 128.9, 128.73, 128.70, 128.3, 127.9, 127.7, 120.4, 118.8, 115.1, 84.2, 83.6, 81.6, 81.4, 67.6, 66.5, 57.3, 56.5, 30.6, 30.5, 28.3, 28.2, 28.1, 27.4, 26.7, 26.0, 22.5, 22.4, 22.1, 21.8, 15.2, 15.1. HRMS (ESI) calcd for $C_{27}H_{28}NOS$ [$(M+H^+)$]: 414.1886, found: 414.1881. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: for major product: 45.24 min (major), 54.97 min (minor); for minor product: 25.44 min (minor), 40.18 min (major).

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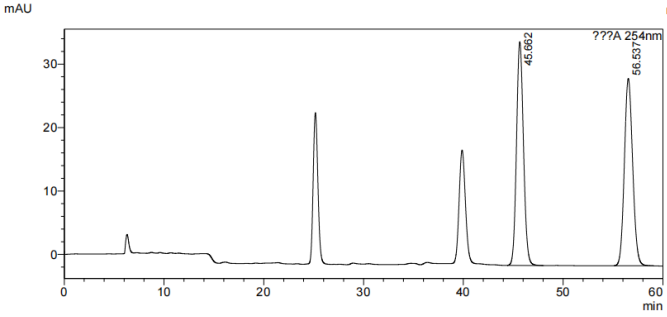

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	45.662	1709436	35264	50.064			
2	56.537	1705046	29523	49.936			
Total		3414482	64788				

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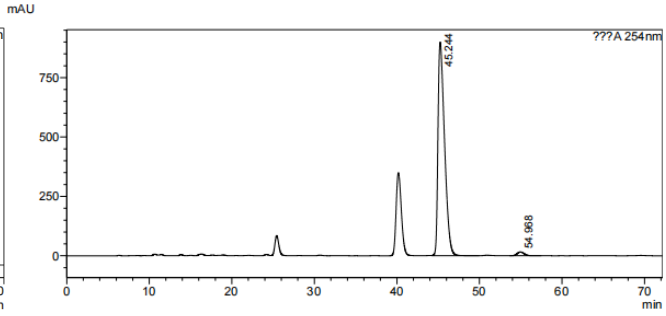

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	45.244	49802495	899017	98.141			
2	54.968	943227	15990	1.859			
Total		50745722	915006				

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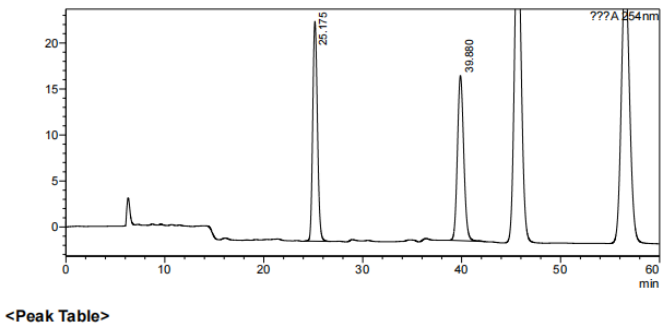

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	25.175	786487	23863	49.694		M	
2	39.880	796157	17928	50.306		M	
Total		1582644	41791				

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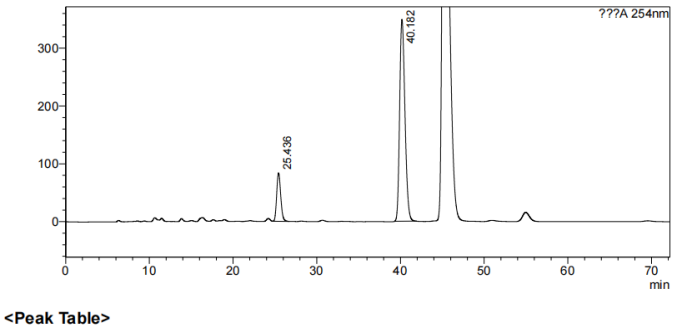
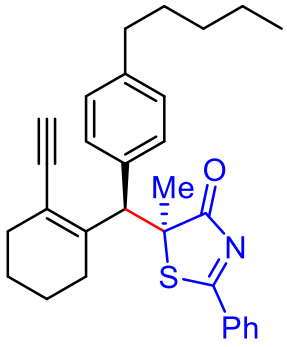


<Peak Table>

???A 254nm

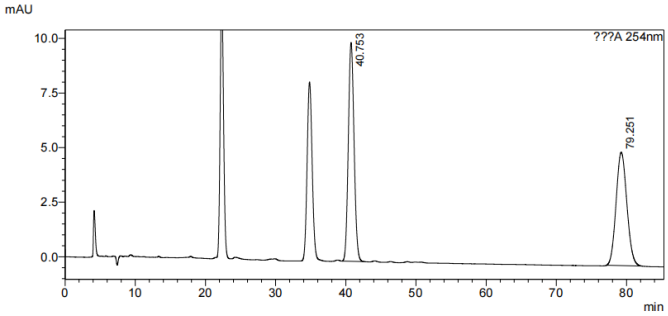
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	25.436	2797969	83772	15.356		M	
2	40.182	15422237	349115	84.644		M	
Total		18220206	432887				

(*S*)-5-((*R*)-(2-ethynylcyclohex-1-en-1-yl)(4-pentylphenyl)methyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3o



Yellow liquid. 29 mg, 64% yield, 3:1 dr, 97.7:2.3 er, 85.3:14.7 er. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.8 Hz, 0.66H, minor), 8.09 (d, *J* = 7.8 Hz, 2.00H, major), 7.67-7.63 (m, 1.33H), 7.53-7.48 (m, 2.66H), 7.35 (d, *J* = 7.2 Hz, 0.66H, minor), 7.16 (d, *J* = 7.8 Hz, 2.00H, major), 7.13 (d, *J* = 7.8 Hz, 0.66H, minor), 6.94 (d, *J* = 7.2 Hz, 2.00H, major), 5.28 (s, 1.00H, major), 5.15 (s, 0.33 H, minor), 3.28 (s, 0.33H, minor), 3.26 (s, 1.00H, major), 2.57 (t, *J* = 7.2 Hz, 0.66H, minor), 2.44 (t, *J* = 7.8 Hz, 2.00H, major), 2.36-2.10 (m, 6.00H), 1.73 (s, 3.00H, major), 1.71 (s, 0.99H, minor), 1.68-1.60 (m, 4.00H), 1.51-1.46 (m, 2.62H), 1.32-1.19 (m, 6.00H), 0.89 (t, *J* = 6.0 Hz, 0.99H, minor), 0.83 (t, *J* = 7.2 Hz, 3.00H, major). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.5, 194.7, 194.4, 193.8, 144.6, 143.0, 142.0, 141.7, 136.1, 135.3, 134.80, 134.77, 132.33, 132.29, 129.4, 129.0, 128.92, 128.87, 128.7, 128.5, 128.23, 128.22, 120.4, 118.9, 84.3, 83.6, 81.6, 81.3, 67.7, 66.6, 57.4, 56.6, 35.5, 35.3, 31.6, 31.4, 30.9, 30.8, 30.7, 30.5, 28.1, 27.3, 26.8, 26.1, 22.6, 22.53, 22.51, 22.4, 22.1, 21.8, 14.01, 13.95. HRMS (ESI) calcd for $C_{30}H_{34}NOS$ [$(M+H^+)$]: 456.2356, found: 456.2355. HPLC analysis of the product: Daicel Chiralpak IC-3 column; hexane/2-propanol = 95/5, 0.8 mL/min. Retention times: for major product: 40.26 min (major), 78.86 min (minor); for minor product: 22.16 min (minor), 34.55 min (major).

<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	40.753	568626	10021	50.630			
2	79.251	554481	5194	49.370			
Total		1123107	15215				

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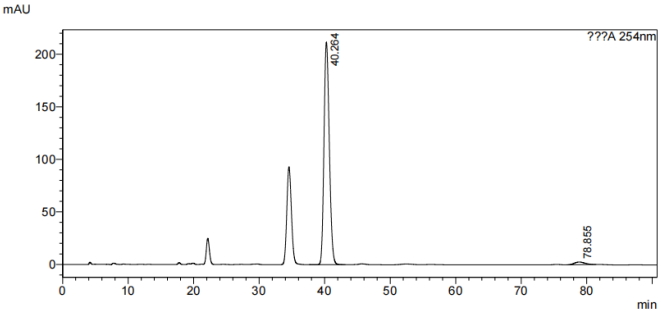

<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	40.264	11935913	211643	97.653		M	
2	78.855	286899	2620	2.347			
Total		12222812	214263				

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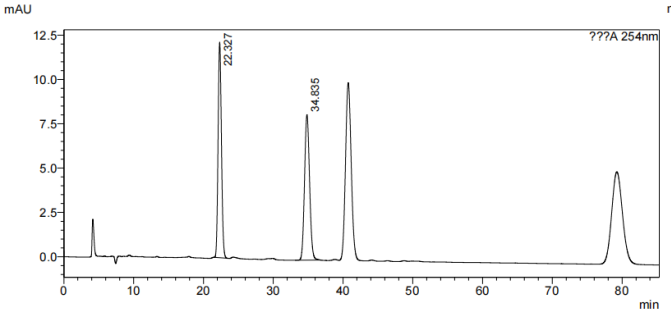
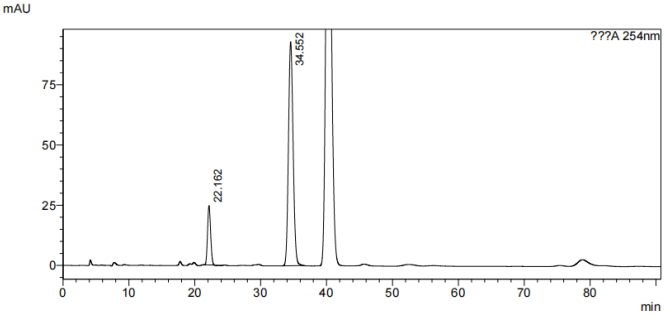


<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.327	406291	12153	49.705		M	
2	34.835	411109	8198	50.295		M	
Total		817401	20351				

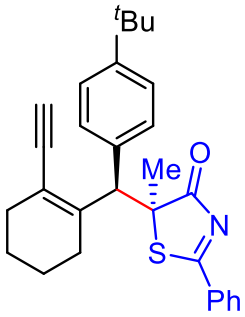
<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.162	786988	24555	14.714		M	
2	34.552	4561745	92957	85.286		M	
Total		5348733	117512				

(*S*)-5-((*R*)-(4-(tert-butyl)phenyl)(2-ethynylcyclohex-1-en-1-yl)methyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3p



Yellow liquid. 28 mg, 63% yield, 3.2:1 dr, 98.5:1.5 er, 88:12 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.13 (d, *J* = 7.8 Hz, 0.62H, minor), 8.10 (d, *J* = 7.8 Hz, 2.00H, major), 7.67-7.63 (m, 1.31H), 7.53-7.48 (m, 2.62H), 7.39-7.37 (m, 0.62H), 7.34-7.32 (m, 0.62H), 7.18-7.14 (m, 4.00H), 5.30 (s, 1.00H, major), 5.17 (s, 0.31H, minor), 3.28 (s, 0.31H, minor), 3.26 (s, 1.00H, major), 2.36-2.20 (m, 5.48H), 1.73 (s, 3.00H, major), 1.71 (s, 0.93H, minor), 1.69-1.61 (m, 4.00H), 1.49-1.41 (m, 1.00H), 1.31 (s, 2.79H, minor), 1.19 (s, 9.00H, major). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.5, 194.6, 194.3, 193.8, 150.0, 149.6, 144.5, 143.0, 135.8, 135.1, 134.78, 134.76, 132.33, 132.29, 129.0, 128.9, 128.7, 128.6, 127.9, 125.4, 125.1, 120.4, 118.8, 114.8, 84.2, 83.6, 81.5, 81.3, 67.7, 66.4, 57.2, 56.3, 34.4, 34.2, 31.3, 31.2, 30.6, 30.5, 28.2, 27.4, 26.7, 26.0, 22.5, 22.4, 22.1, 21.8. HRMS (ESI) calcd for $C_{29}H_{32}NOS$ [$(M+H^+)$]: 442.2199, found: 442.2196. HPLC analysis of the product: Daicel Chiralpak ADH column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: for major product: 30.31 min (major), 33.78 min (minor); for minor product: 18.12 min (minor), 27.46 min (major).

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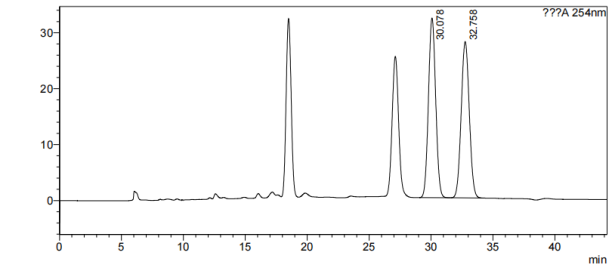

<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	30.078	1306408	32127	50.710			
2	32.758	1269844	27947	49.290			
Total		2576252	60074				

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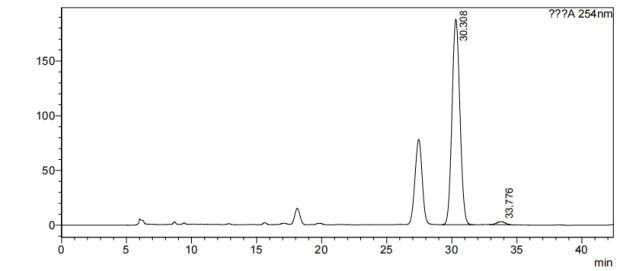
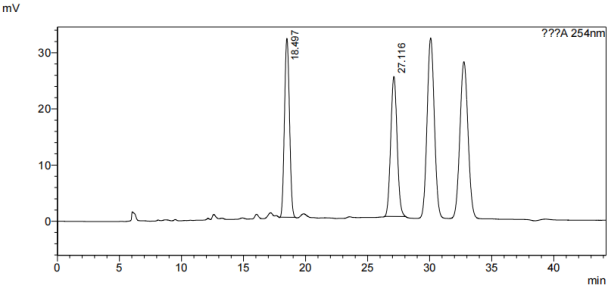


<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	30.308	7953685	187839	98.408			
2	33.776	128682	2812	1.592			
Total		8082366	190652				

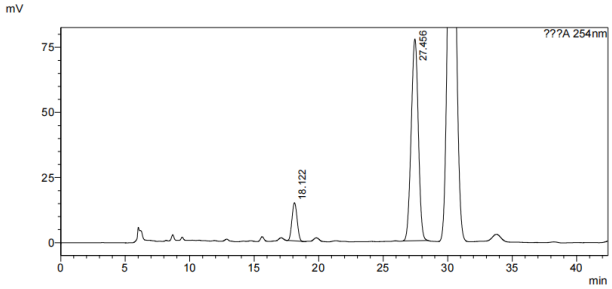
<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.497	895062	31822	50.021		M	
2	27.116	894302	24930	49.979		M	
Total		1789364	56752				

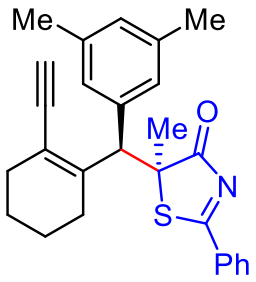
<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.122	404908	14626	12.006		M	
2	27.456	2967627	77470	87.994		M	
Total		3372536	92096				

(*S*)-5-((*R*)-(3,5-dimethylphenyl)(2-ethynylcyclohex-1-en-1-yl)methyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3q



Colorless liquid. 33 mg, 80% yield, 1.2:1 dr, 96.5:3.5 er, 80.2:19.8 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.15 (d, *J* = 7.8 Hz, 1.70H, minor), 8.09 (d, *J* = 7.8 Hz, 2.00H, major), 7.68-7.63 (m, 1.85H), 7.53-7.48 (m, 3.70H), 7.04 (s, 1.70H, minor), 6.91 (s, 0.85H, minor), 6.90 (s, 2.00H, major), 6.75 (s, 1.00H, major), 5.23 (s, 1.00H, major), 5.12 (s, 0.85H, minor), 3.29 (s, 0.85H, minor), 3.28 (s, 1.00H, major), 2.36-2.35 (m, 1.00H), 2.32 (s, 5.10H, minor), 2.29-2.18 (m, 4.90H), 2.18-2.16 (m, 1.00H), 2.13 (s, 6.00H, major), 1.73 (s, 3.00H, major), 1.71 (s, 2.55H, minor), 1.69-1.53 (m, 4.30H), 1.50-1.38 (m, 2.60H), 1.32-1.27 (m, 1.00H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.4, 194.7, 194.4, 193.8, 144.4, 143.0, 138.9, 138.1, 137.9, 137.4, 134.8, 134.7, 132.3, 132.2, 129.01, 128.97, 128.93, 128.88, 128.7, 128.6, 126.8, 126.2, 120.4, 118.8, 84.3, 83.7, 81.6, 81.3, 67.5, 66.6, 57.6, 56.8, 30.7, 30.6, 28.1, 27.2, 26.8, 26.2, 22.6, 22.4, 22.1, 21.8, 21.5, 21.4. HRMS (ESI) calcd for $C_{27}H_{28}NOS$ [$(M+H^+)$]: 414.1886, found: 414.1885. HPLC analysis of the product: Daicel Chiralpak IC-3 column; hexane/2-propanol = 92/8, 1.0 mL/min. Retention times: for major product: 30.93 min (minor), 44.28 min (major); for minor product: 14.67 min (minor), 19.95 min (major).

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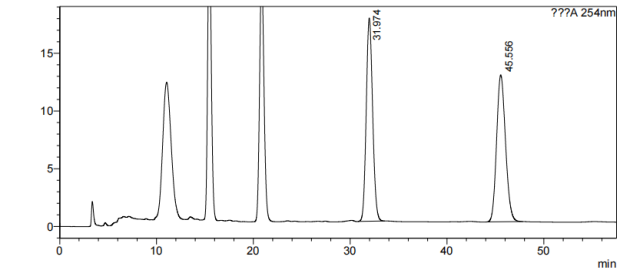

<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	31.974	807574	17596	49.817			
2	45.556	813502	12711	50.183			
Total		1621076	30307				

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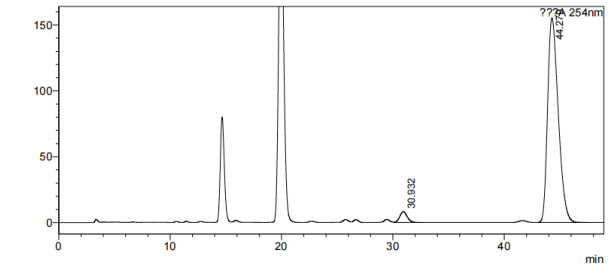

<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	30.932	387878	8213	3.624			
2	44.279	10313716	155276	96.376			
Total		10701594	163489				

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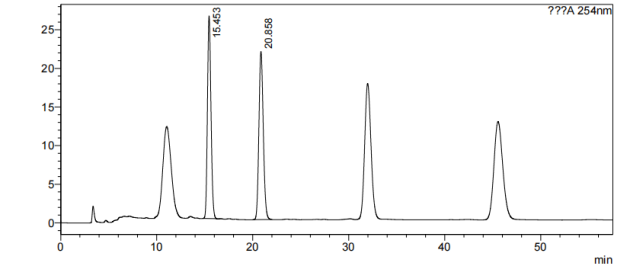
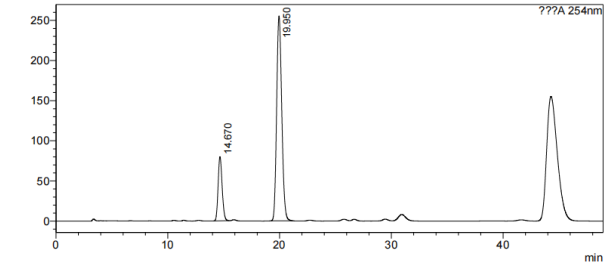


<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.453	671413	26227	49.366		M	
2	20.858	688662	21749	50.634		M	
Total		1360075	47977				

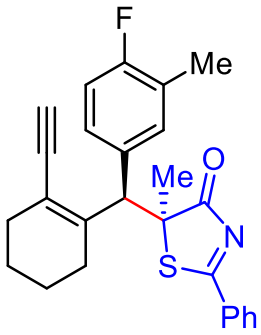
<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.670	2003658	79793	19.840		M	
2	19.950	8095183	254957	80.160		M	
Total		10098841	334750				

(*S*)-5-((*R*)-(2-ethynylcyclohex-1-en-1-yl)(4-fluoro-3-methylphenyl)methyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3r



Yellow liquid. 37 mg, 85% yield, 2:1 dr, 97.7:2.3 er, 86:14 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12 (d, *J* = 7.2 Hz, 1.12H, minor), 8.08 (d, *J* = 7.8 Hz, 2.00H, major), 7.68-7.65 (m, 1.56H), 7.53-7.48 (m, 3.12H), 7.23-7.22 (m, 1.12H), 7.11-7.09 (m, 2.00H), 6.96-6.93 (m, 0.56H), 6.76-6.73 (m, 1.00H), 5.23 (s, 1.00H, major), 5.11 (s, 0.56H, minor), 3.29 (s, 1.56H), 2.35-2.31 (m, 3.12H), 2.27 (s, 1.68H, minor), 2.23-2.13 (m, 3.12H), 2.11 (s, 3.00H, major), 1.72 (s, 3.00H, major), 1.71 (s, 1.68H, minor), 1.64-1.58 (m, 4.00H), 1.51-1.39 (m, 2.24H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.3, 194.5, 194.4, 193.7, 161.4, 161.3, 159.73, 159.65, 144.3, 142.7, 134.92, 134.91, 134.5 (d, *J* = 4.3 Hz, minor), 133.7 (d, *J* = 3.8 Hz, major), 132.21, 132.18, 132.11, 132.08, 128.9 (d, *J* = 47.0 Hz, minor), 128.8 (d, *J* = 44.1 Hz, major), 127.6 (d, *J* = 8.0 Hz, minor), 126.9 (d, *J* = 8.2 Hz, major), 124.8 (d, *J* = 17.7 Hz, minor), 124.4 (d, *J* = 17.8 Hz, major), 120.6, 119.1, 114.9 (d, *J* = 22.8 Hz, minor), 114.5 (d, *J* = 21.7 Hz, major), 84.1, 83.5, 81.9, 81.6, 67.6, 66.6, 57.0, 56.3, 30.6, 30.5, 27.9, 27.2, 26.7, 26.0, 22.5, 22.4, 22.0, 21.8, 14.8 (d, *J* = 3.0 Hz, minor), 14.6 (d, *J* = 3.2 Hz, major). ^{19}F NMR (566 MHz, $CDCl_3$): δ -119.4 (minor), -119.7 (major). HRMS (ESI) calcd for $C_{26}H_{25}FNOS$ [$(M+H^+)$]: 418.1635, found: 418.1634. HPLC analysis of the product: Daicel Chiralpak IC-3 column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: for major product: 34.90 min (major), 47.44 min (minor); for minor product: 29.58 min (minor), 40.70 min (major).

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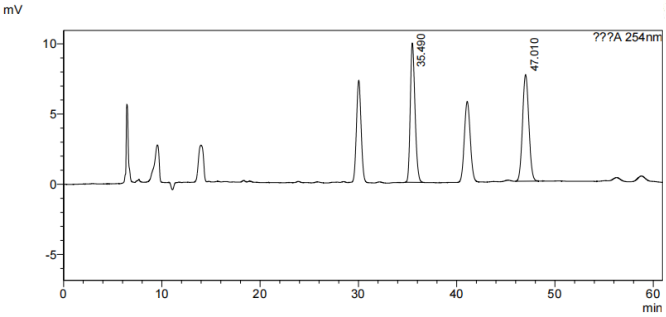

<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	35.490	332177	9930	49.572			
2	47.010	337912	7591	50.428			
Total		670090	17521				

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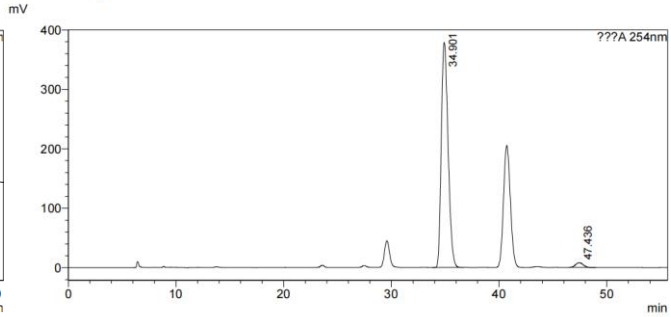
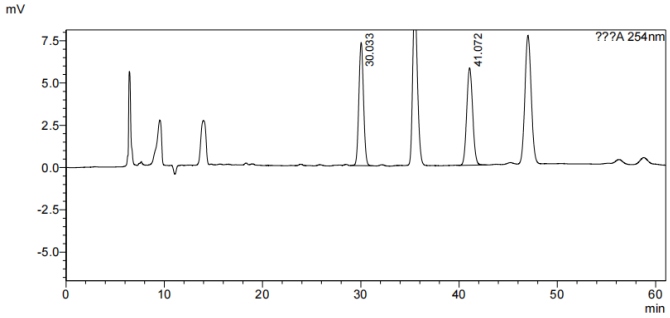


<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	34.901	16608001	378665	97.663			
2	47.436	397399	8003	2.337		M	
Total		17005399	386668				

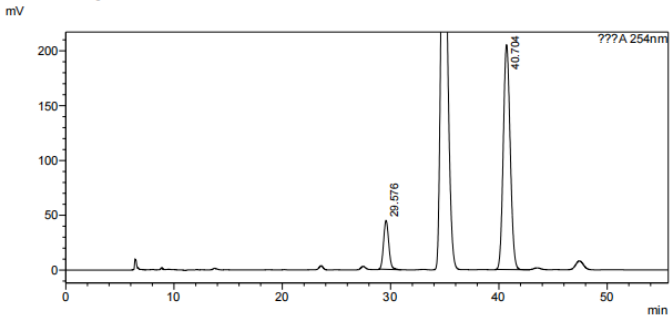
<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	30.033	240782	7278	49.902		M	
2	41.072	241724	5750	50.098		M	
Total		482506	13028				

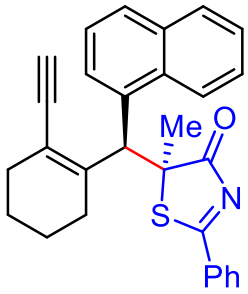
<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	29.576	1488774	44688	14.077		M	
2	40.704	9087167	205141	85.923		M	
Total		10575941	249829				

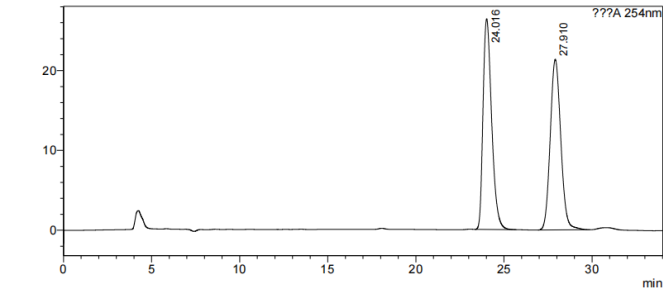
(*S*)-5-((*S*)-(2-ethynylcyclohex-1-en-1-yl)(naphthalen-1-yl)methyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3s



White solid. 29 mg, 67% yield, 2.6:1 dr, 97.5:2.5 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.54 (d, *J* = 9.0 Hz, 1H), 8.16 d, *J* = 7.2 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.70-7.67 (m, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.62 d, *J* = 7.2 Hz, 1H), 7.56-7.52 (m, 3H), 7.46-7.44 (m, 1H), 7.20-7.18 (m, 1H), 6.02 (s, 1H), 3.48 (s, 1H), 2.44-2.36 (m, 2H), 2.30-2.26 (m, 1H), 1.98 (s, 3H), 1.85-1.82 (m, 1H), 1.66-1.59 (m, 2H), 1.52-1.44 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 194.6, 193.5, 143.1, 135.1, 134.9, 134.0, 132.5, 132.4, 129.0, 128.8, 128.6, 128.0, 126.2, 125.5, 124.5, 124.4, 124.0, 120.7, 84.8, 82.5, 68.3, 50.4, 30.8, 29.5, 26.8, 22.4, 22.0. HRMS (ESI) calcd for $C_{29}H_{26}NOS$ [$(M+H^+)$]: 436.1730, found: 436.1726. HPLC analysis of the product: Daicel Chiralpak IC-3 column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: 24.41 min (major), 28.20 min (minor).

<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	24.016	897549	26385	50.257			
2	27.910	888352	21361	49.743			
Total		1785902	47746				

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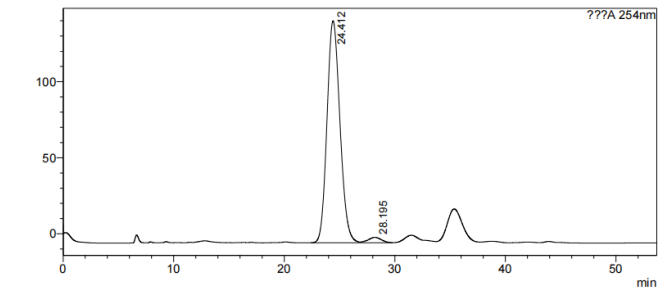
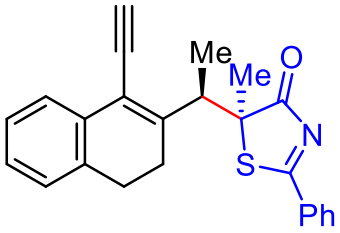


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	24.412	11888942	145915	97.543			
2	28.195	299448	3550	2.457		V	
Total		12188390	149465				

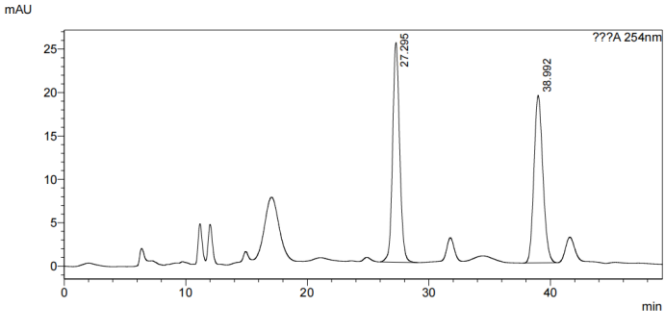
(*S*)-5-((*R*)-1-(1-ethynyl-3,4-dihydronaphthalen-2-yl)ethyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3t



Yellow solid. 36 mg, 97% yield, 8.2:1 dr, 87:13 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17 (d, *J* = 7.8 Hz, 2.00H, major), 8.11 (d, *J* = 7.8 Hz, 0.24H, minor), 7.87-7.80 (m, 0.24H), 7.68-7.65 (m, 2.00H), 7.63-7.59 (m, 0.24H), 7.53-7.50 (m, 2.24H), 7.26-7.24 (m, 1.12H), 7.19-7.17 (m, 1.00H), 7.14-7.11 (m, 1.00H), 4.22 (q, *J* = 13.2 and 6.6 Hz, 1.00H, major), 4.01 (q, *J* = 13.2 and 6.6 Hz, 0.12H, minor), 3.49 (s, 1.00H, major), 3.40 (s, 0.12H, minor), 2.81-2.75 (m, 2.00H), 2.72-2.60 (m, 0.48H), 2.44-2.38 (m, 1.00H), 2.36-2.29 (m, 1.00H), 1.82 (s, 0.36H, minor), 1.67 (s, 3.00H, major), 1.28 (d, *J* = 7.2 Hz, 0.36H, minor), 1.06 (d, *J* = 6.6 Hz, 3.00H, major). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.9, 195.1, 194.2, 193.9, 149.1, 147.3, 135.04, 135.00, 134.9, 134.4, 132.7, 132.6, 132.2, 130.3, 129.01, 128.97, 128.8, 128.7, 127.6, 127.5, 126.9, 126.83, 126.77, 126.5, 125.8, 125.7, 119.9, 119.5, 84.6, 84.5, 80.3, 79.7, 68.4, 68.2, 46.5, 45.7, 27.55, 27.51, 25.8, 24.7, 24.4, 23.8, 14.4, 14.2. HRMS (ESI) calcd for $C_{24}H_{22}NOS$ [$(M+H^+)$]: 372.1417, found: 372.1410. HPLC analysis of the product: Daicel Chiralpak ADH column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: 27.14 min (minor), 38.51 min (major).

<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	27.295	1015383	25283	50.680			
2	38.992	988138	19290	49.320			
Total		2003521	44573				

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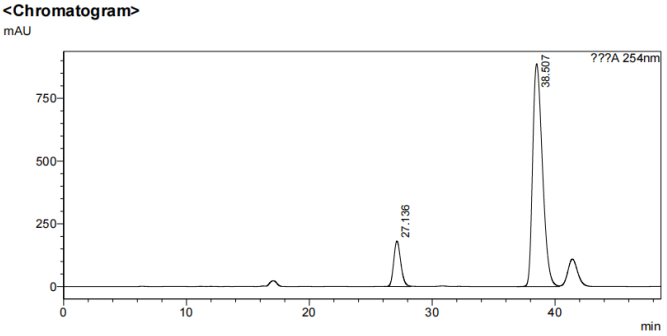
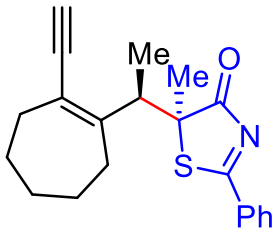


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	27.136	7232185	181489	12.850		M	
2	38.507	49047528	887577	87.150			
Total		56279714	1069066				

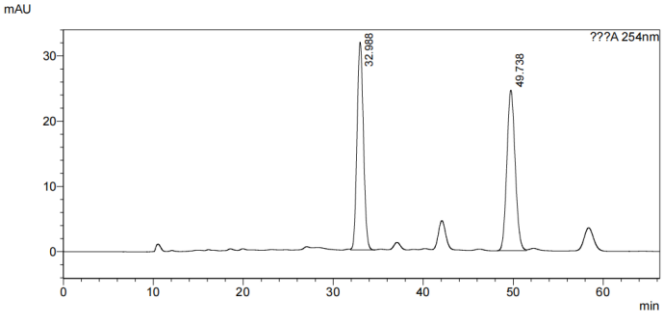
(*S*)-5-((*R*)-1-(2-ethynylcyclohept-1-en-1-yl)ethyl)-5-methyl-2-phenylthiazol-4(5H)-one: 3u



Light yellow solid. 30 mg, 89% yield, 7.5:1 dr, 89:11 er, 88.5:11.5 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17 (d, *J* = 7.8 Hz, 2.00H, major), 8.11 (d, *J* = 7.8 Hz, 0.26H, minor), 7.68-7.65 (m, 1.13H), 7.53-7.51 (m, 2.26H), 3.99 (q, *J* = 13.2 and 6.0 Hz, 1.00H, major), 3.77 (q, *J* = 13.8 and 7.2 Hz, 0.13H, minor), 3.32 (s, 1.00H, major), 3.21 (s, 0.13H, minor), 2.49-2.33 (m, 3.00H), 2.31-2.29 (m, 2.10H), 1.81-1.77 (m, 2.35H), 1.75 (s, 0.39H, minor), 1.66 (s, 3.00H, major), 1.60-1.57 (m, 1.00H), 1.53-1.43 (m, 2.85H), 1.22 (d, *J* = 6.6 Hz, 0.39H, minor), 0.93 (d, *J* =6.6 Hz, 3.00H, major). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.4, 195.2, 194.2, 193.9, 152.9, 150.9, 134.9, 134.7, 132.3, 132.2, 129.0, 128.9, 128.8, 128.7, 124.9, 124.3, 85.5, 85.0, 82.1, 81.9, 68.7, 68.5, 47.1, 46.4, 34.80, 34.76, 32.5, 32.4, 29.0, 28.5, 26.7, 26.6, 26.1, 25.9, 25.8, 24.3, 14.0, 13.9. HRMS (ESI) calcd for $C_{21}H_{24}NOS$ [$(M+H^+)$]: 338.1537, found: 338.1569. HPLC analysis of the product: Daicel Chiralpak ADH column; hexane/2-propanol = 95/5, 0.3 mL/min. Retention times: for major product: 33.93 min (minor), 50.64 min (major); for minor product: 43.07 min (major), 59.39 min (minor).

<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	32.988	1571347	31831	49.857			
2	49.738	1580368	24587	50.143			
Total		3151715	56418				

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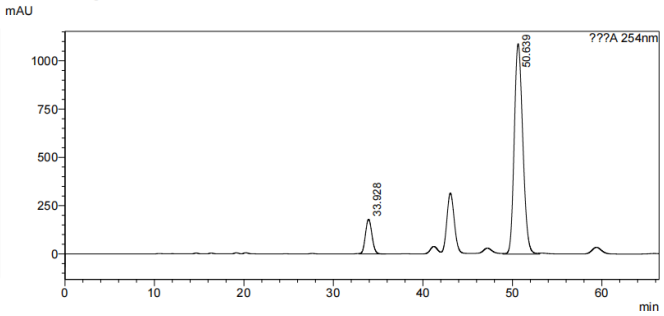
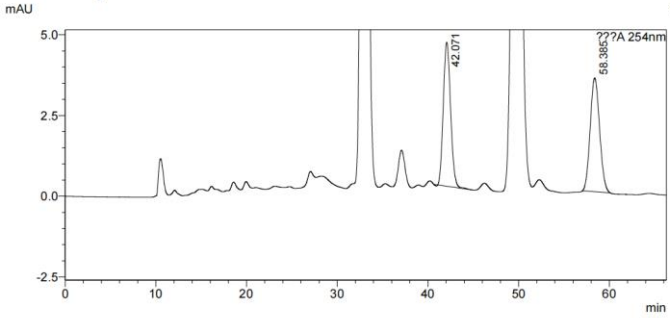


<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	33.928	9113956	179681	11.197		M	
2	50.639	72279076	1089103	88.803		M	
Total		81393033	1268784				

<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	42.071	249487	4456	49.520		M	
2	58.385	254321	3527	50.480		M	
Total		503809	7984				

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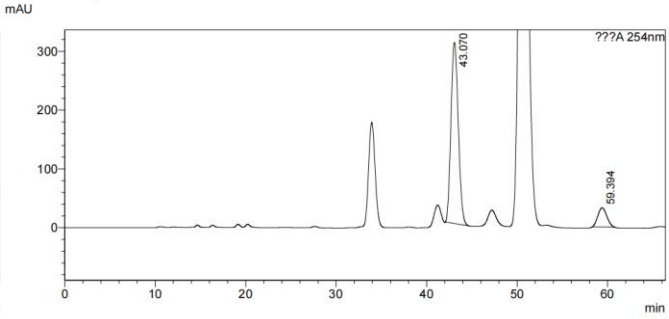
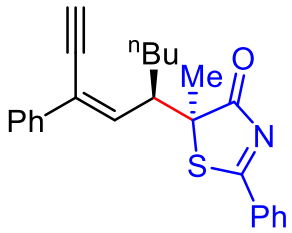


<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	43.070	17324866	308091	88.430		M	
2	59.394	2266823	32755	11.570		M	
Total		19591689	340846				

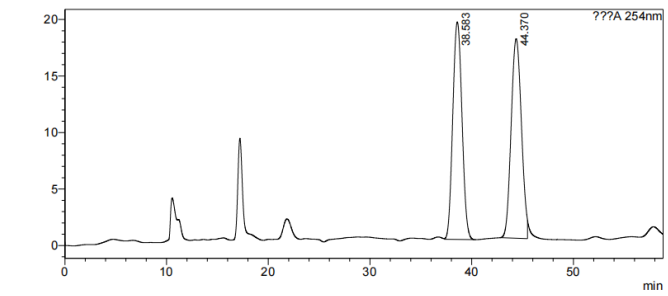
(*S*)-5-methyl-2-phenyl-5-((*R*,*E*)-3-phenylnon-3-en-1-yn-5-yl)thiazol-4(5H)-one: 3v



Yellow liquid. 29 mg, 75% yield, 7:1 dr, 78.5:21.5 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.18 (d, *J* = 7.8 Hz, 2.00H, major), 8.15 (d, *J* = 7.8 Hz, 0.28H, minor), 7.70-7.67 (m, 1.14H), 7.65 (d, *J* = 7.8 Hz, 2.00H, major), 7.59 (d, *J* = 7.8 Hz, 0.28H, minor), 7.55-7.53 (m, 2.28H), 7.41-7.38 (m, 2.28H), 7.35-7.31 (m, 1.14H), 6.52 (d, *J* = 10.2 Hz, 0.14H, minor), 6.13 (d, *J* = 10.2 Hz, 1.00H, major), 3.62-3.58 (m, 1.00H), 3.47-3.43 (m, 0.14H), 3.41 (s, 1.00H, major), 3.37 (s, 0.14H, minor), 1.80 (s, 0.42H, minor), 1.73 (s, 3.00H, major), 1.70-1.61 (m, 0.56H), 1.45-1.35 (m, 2.28H), 1.31-1.22 (m, 4.00H), 0.85 (t, *J* = 6.6Hz, 0.42H, minor), 0.81 (t, *J* = 6.6 Hz, 3.00H, major). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.6, 195.3, 194.8, 194.6, 138.4, 137.7, 137.2, 137.0, 135.1, 135.0, 132.3, 132.2, 129.04, 129.02, 128.9, 128.8, 128.5, 128.3, 128.1, 127.9, 127.6, 127.3, 126.3, 126.2, 84.2, 83.7, 80.9, 80.5, 69.5, 68.2, 49.3, 48.6, 30.5, 30.3, 29.4, 29.2, 25.7, 24.8, 22.6, 22.5, 13.9. HRMS (ESI) calcd for $C_{25}H_{26}NOS$ [$(M+H^+)$]: 388.1730, found: 388.1725. HPLC analysis of the product: Daicel Chiralpak ADH column; hexane/2-propanol = 97/3, 0.3 mL/min. Retention times: 38.25 min (major), 43.99 min (minor).

<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	38.583	1215148	19248	49.536			
2	44.370	1237928	17654	50.464		M	
Total		2453076	36903				

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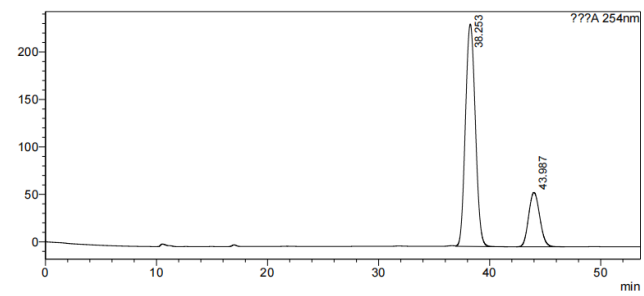
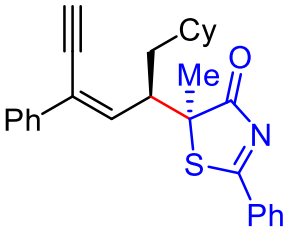


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	38.253	14513517	234340	78.524			
2	43.987	3969403	57208	21.476			
Total		18482920	291548				

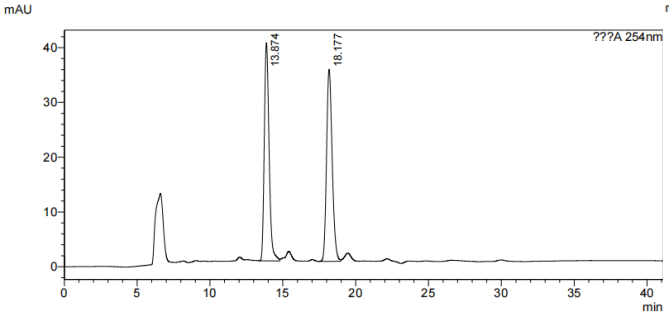
(*S*)-5-((*R*,*E*)-1-cyclohexyl-4-phenylhex-3-en-5-yn-2-yl)-5-methyl-2-phenylthiazol-4(5H)-one: 3w



Yellow liquid. 27 mg, 75% yield, 11:1 dr, 83.5:16.5 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17 (d, *J* = 7.2 Hz, 2H), 7.70-7.65 (m, 3H), 7.55-7.53 (m, 2H), 7.41-7.39 (m, 2H), 7.36-7.32 (m, 1H), 6.13 (d, *J* = 10.2 Hz, 1H), 3.74-3.70 (m, 1H), 3.41 (s, 1H), 1.99-1.97 (m, 1H), 1.74 (s, 3H), 1.67-1.65 (m, 1H), 1.59-1.57 (m, 2H), 1.48-1.46 (m, 1H), 1.39-1.35 (m, 1H), 1.20-1.06 (m, 5H), 0.88-0.81 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.5, 195.2, 138.7, 137.0, 135.1, 132.3, 129.0, 128.9, 128.5, 128.3, 127.3, 126.2, 84.1, 80.5, 69.7, 46.7, 38.4, 35.2, 34.5, 32.4, 26.4, 26.2, 26.0, 25.8. HRMS (ESI) calcd for $C_{28}H_{30}NOS$ [$(M+H^+)$]: 428.2043, found: 428.2039. HPLC analysis of the product: Daicel Chiralpak IC-3 column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: 13.88 min (major), 18.17 min (minor).

<Chromatogram>

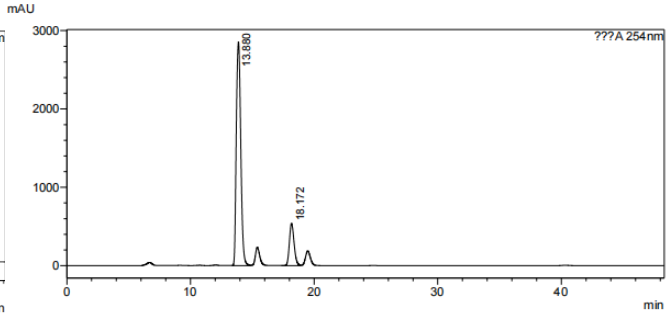


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.874	910352	39813	49.071		M	
2	18.177	944809	35015	50.929			
Total		1855160	74829				

<Chromatogram>

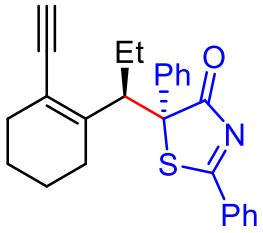


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.880	71837879	2852902	83.504			
2	18.172	14191585	537813	16.496			
Total		86029465	3390715				

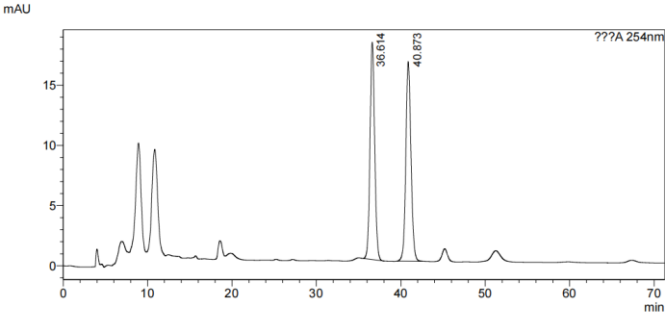
(*R*)-5-((*R*)-1-(2-ethynylcyclohex-1-en-1-yl)propyl)-2,5-diphenylthiazol-4(5H)-one: 4a



Colorless liquid. 24 mg, 60% yield, 16:1 dr, 93:7 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.21 (d, *J* = 7.8 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.69-7.66 (m, 1H), 7.54-7.52 (m, 2H), 7.30-7.23 (m, 3H), 4.45 (d, *J* = 10.2 Hz, 1H), 3.18 (s, 1H), 2.13-2.04 (m, 2H), 1.92-1.89 (m, 1H), 1.75-1.72 (m, 2H), 1.50-1.45 (m, 3H), 1.35-1.31 (m, 1H), 1.23-1.18 (m, 1H), 0.86 (t, *J* = 7.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 194.5, 193.5, 142.1, 137.2, 135.0, 132.1, 129.0, 128.8, 128.1, 128.0, 127.5, 120.7, 84.3, 80.8, 75.6, 55.5, 30.3, 25.1, 22.7, 22.3, 22.0, 11.8. HRMS (ESI) calcd for $C_{26}H_{26}NOS$ [$(M+H^+)$]: 400.1730, found: 400.1727. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 90/10, 0.8 mL/min. Retention times: 35.43 min (major), 39.95 min (minor).

<Chromatogram>

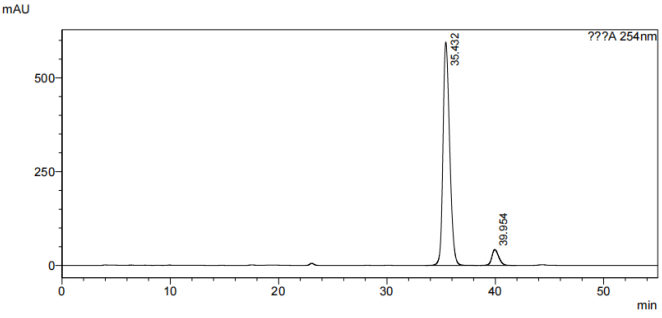


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	36.614	694026	18050	49.620			
2	40.873	704667	16567	50.380			
Total		1398694	34617				

<Chromatogram>

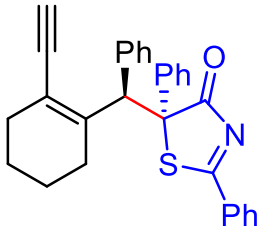


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	35.432	25536675	595134	93.106		M	
2	39.954	1890861	42199	6.894		M	
Total		27427536	637332				

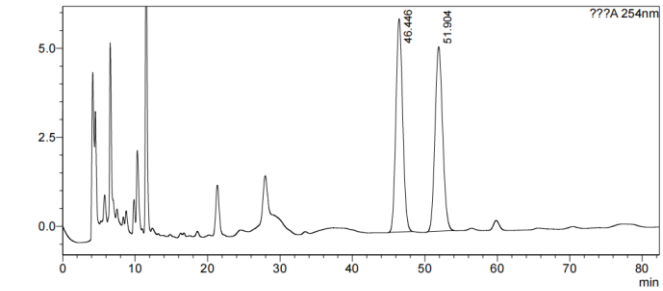
(*R*)-5-((*R*)-(2-ethynylcyclohex-1-en-1-yl)(phenyl)methyl)-2,5-diphenylthiazol-4(5H)-one: 4b



White solid. 34 mg, 76% yield, 4.4:1 dr, 94:6 er,

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.18 (d, *J* = 7.2 Hz, 0.46H, minor), 8.06 (d, *J* = 7.8 Hz, 2.00H, major), 7.93-7.91 (m, 0.23H), 7.82 (d, *J* = 7.2 Hz, 0.23H, minor), 7.79 (d, *J* = 7.8 Hz, 2.00H, major), 7.68-7.66 (m, 0.23H), 7.64-7.61 (m, 1.00H), 7.54-7.51 (m, 0.46H), 7.48-7.45 (m, 2.00H), 7.42-7.40 (m, 0.46H), 7.37-7.33 (m, 4.00H), 7.30-7.28 (m, 0.92H), 7.24-7.22 (m, 0.46H), 7.19-7.15 (m, 3.00H), 7.12-7.10 (m, 1.00H), 5.95 (s, 1.00H, major), 5.87 (s, 0.23H, minor), 3.29 (s, 0.23H, minor), 3.25 (s, 1.00H, major), 2.47-2.44 (m, 1.00H), 2.29-2.26 (m, 0.60H), 2.22-2.13 (m, 0.84H), 2.11-2.05 (m, 2.00H), 1.95-1.92 (m, 1.00H), 1.58-1.47 (m, 3.00H), 1.41-1.36 (m, 1.40H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 194.4, 193.3, 193.0, 191.4, 144.4, 143.4, 139.1, 138.5, 138.3, 137.2, 135.0, 134.9, 132.1, 131.9, 129.6, 129.04, 129.02, 128.9, 128.8, 128.7, 128.43, 128.39, 128.2, 128.14, 128.05, 127.9, 127.7, 127.5, 127.2, 126.9, 120.7, 120.5, 84.1, 83.4, 82.4, 81.6, 75.0, 74.9, 58.1, 57.5, 30.6, 30.2, 29.7, 28.4, 22.6, 22.4, 21.8, 21.7. HRMS (ESI) calcd for $C_{30}H_{26}NOS$ [$(M+H^+)$]: 448.1730, found: 448.1726. HPLC analysis of the product: Daicel Chiralpak IC-3 column; hexane/2-propanol = 90/10, 0.8 mL/min. Retention times: 46.17 min (minor), 51.33 min (major).

<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	46.446	389406	5983	50.670			
2	51.904	379111	5173	49.330			
Total		768517	11156				

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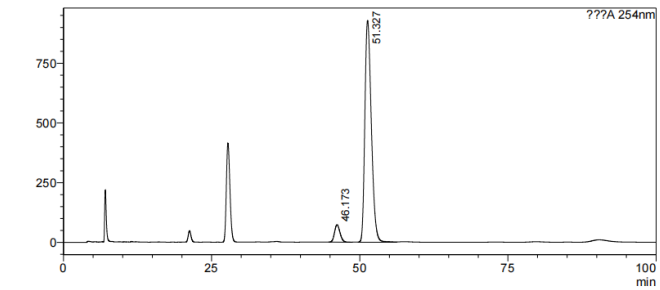
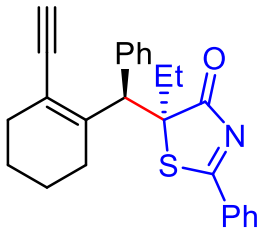


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	46.173	4685350	72916	6.217			
2	51.327	70679620	928104	93.783		M	
Total		75364970	1001019				

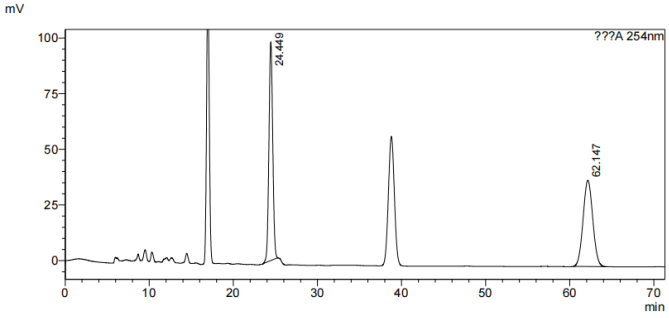
(*S*)-5-ethyl-5-((*R*)-(2-ethynylcyclohex-1-en-1-yl)(phenyl)methyl)-2-phenylthiazol-4(5H)-one: 4c



Light yellow solid. 29 mg, 73% yield, 4.5:1 dr, 94.5:5.5 er, 90:10 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.15 (d, *J* = 7.8 Hz, 0.44H, minor), 8.09 (d, *J* = 7.8 Hz, 2.00H, major), 7.68-7.63 (m, 1.22H), 7.53-7.52 (m, 0.44H), 7.50-7.45 (m, 2.44H), 7.36-7.35 (m, 2.00H), 7.33-7.30 (m, 0.44H), 7.25-7.21 (m, 0.22H), 7.15-7.10 (m, 3.00H), 5.31 (s, 1.00H, major), 5.25 (s, 0.22H, minor), 3.29 (s, 0.22H, minor), 3.28 (s, 1.00H, major), 2.42-2.39 (m, 1.00H), 2.34-2.31 (m, 1.00H), 2.27-2.25 (m, 2.00H), 2.19-2.10 (m, 0.88H), 2.00-1.92 (m, 1.22H), 1.73-1.70 (m, 1.22H), 1.66-1.62 (m, 4.00H), 1.57-1.45 (m, 0.88H), 0.86 (t, *J* = 7.2 Hz, 3.00H, major), 0.82 (t, *J* = 7.2 Hz, 0.66H, minor). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.2, 194.9, 194.6, 193.9, 144.4, 143.0, 139.2, 138.2, 134.81, 134.77, 132.3, 132.2, 129.1, 129.03, 128.99, 128.9, 128.8, 128.7, 128.5, 128.1, 127.3, 127.2, 120.3, 119.0, 84.3, 83.6, 81.7, 81.3, 73.4, 72.6, 58.4, 58.0, 32.5, 32.0, 30.7, 30.6, 26.9, 26.5, 22.6, 22.5, 22.0, 21.8, 8.5, 8.4. HRMS (ESI) calcd for $C_{26}H_{26}NOS$ [$(M+H^+)$]: 400.1730, found: 400.1727. HPLC analysis of the product: Daicel Chiralpak ADH column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: for major product: 24.13 min (major), 61.59 min (minor); for minor product: 16.81 min (minor), 38.35 min (major).

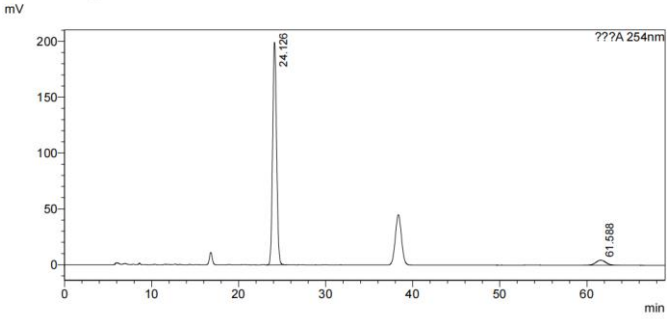
<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	24.449	3084521	98141	49.946		M	
2	62.147	3091233	38700	50.054		M	
Total		6175754	136841				

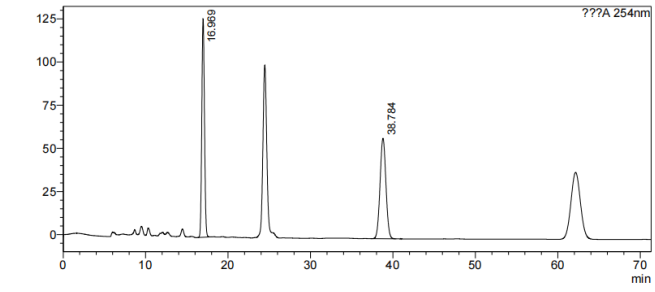
<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	24.126	6246668	199223	94.502		M	
2	61.588	363402	4569	5.498		M	
Total		6610070	203792				

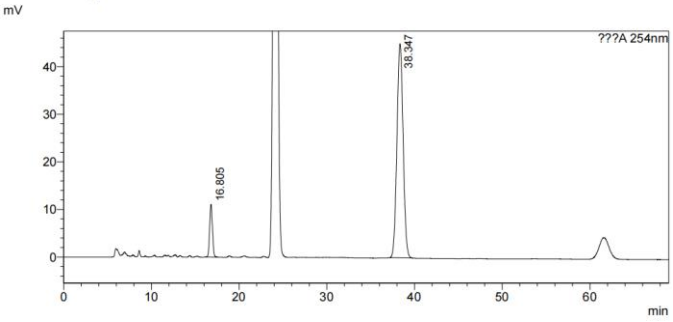
<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.969	2857487	126633	49.750		M	
2	38.784	2886260	58195	50.250		M	
Total		5743747	184828				

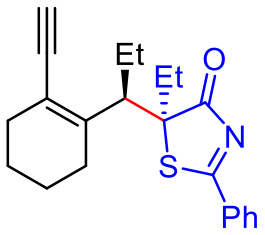
<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.805	248205	11089	10.102		M	
2	38.347	2208753	44981	89.898		M	
Total		2456957	56070				

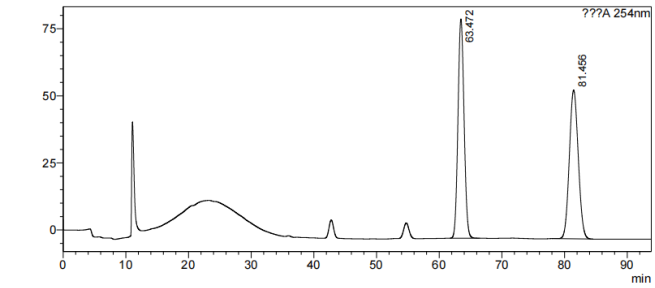
(*S*)-5-ethyl-5-((*R*)-1-(2-ethynylcyclohex-1-en-1-yl)propyl)-2-phenylthiazol-4(5H)-one: 4d



Yellow solid. 23 mg, 66% yield, 11:1 dr, 81:19 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.19 (d, *J* = 7.8 Hz, 2H), 7.68-7.66 (m, 1H), 7.54-7.51 (m, 2H), 3.88 (dd, *J* = 11.4 and 3.6 Hz, 1H), 3.21 (s, 1H), 2.33-2.26 (m, 2H), 2.18-2.12 (m, 1H), 2.10-2.07 (m, 1H), 1.90-1.87 (m, 1H), 1.77-1.66 (m, 3H), 1.58-1.54 (m, 3H), 1.19-1.12 (m, 1H), 0.81-0.75 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.2, 196.1, 142.4, 134.9, 132.3, 129.0, 128.8, 120.7, 83.9, 81.1, 73.7, 54.3, 30.8, 30.5, 24.8, 22.4, 22.3, 21.6, 11.2, 8.5. HRMS (ESI) calcd for $C_{22}H_{26}NOS$ [$(M+H^+)$]: 352.1370, found: 352.1368. HPLC analysis of the product: Daicel Chiralpak IC-3 column; hexane/2-propanol = 96/4, 0.3 mL/min. Retention times: 62.58 min (major), 81.16 min (minor).

<Chromatogram>

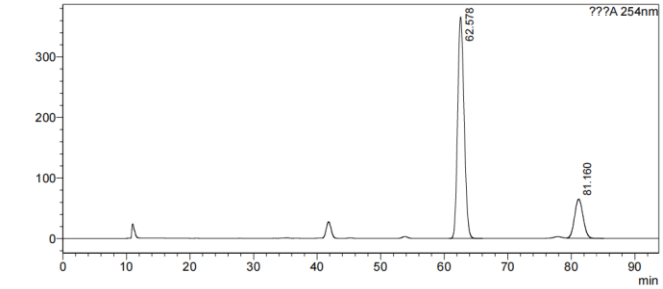


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	63.472	5509413	81707	50.149			
2	81.456	5476641	55469	49.851		M	
Total		10986054	137176				

<Chromatogram>

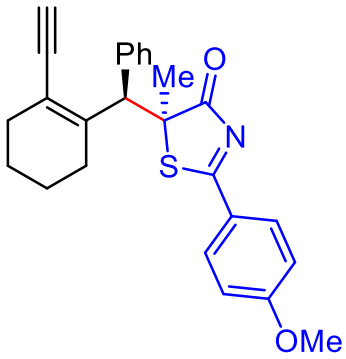


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	62.578	25936872	365823	81.046			
2	81.160	6065832	64808	18.954			
Total		32002704	430630				

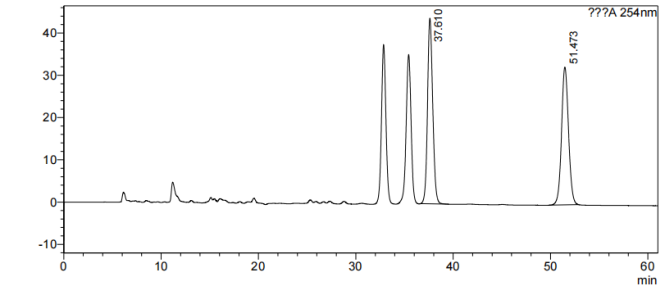
(*S*)-5-((*R*)-(2-ethynylcyclohex-1-en-1-yl)(phenyl)methyl)-2-(4-methoxyphenyl)-5-methylthiazol-4(5H)-one: 4e



White solid. 36 mg, 87% yield, 4.4:1 dr, 98:2 er, 88:12 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10 (d, *J* = 9.0 Hz, 0.46H, minor), 8.07 (d, *J* = 8.4 Hz, 2.00H, major), 7.46-7.45 (m, 0.46H), 7.33-7.31 (m, 0.46H), 7.29-7.26 (m, 2.00H), 7.15-7.09 (m, 3.14H), 6.99-6.95 (m, 2.55H), 5.30 (s, 1.00H, major), 5.18 (s, 0.23H, minor), 3.89 (s, 0.69H, minor), 3.88 (s, 3.00H, major), 3.28 (s, 0.23H, minor), 3.26 (s, 1.00H, major), 2.36-2.22 (m, 4.85H), 2.16-2.09 (m, 0.50H), 1.73 (s, 3.00H, major), 1.70 (s, 0.69H, minor), 1.68-1.57 (m, 4.00H), 1.47-1.42 (m, 0.49H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.3, 194.5, 193.0, 192.4, 165.2, 164.0, 144.5, 143.0, 139.2, 138.4, 131.1, 129.8, 129.0, 128.4, 128.2, 128.0, 127.2, 127.0, 124.9, 124.8, 120.5, 118.9, 114.35, 114.29, 84.2, 83.6, 81.6, 81.3, 67.3, 66.2, 57.7, 56.7, 55.7, 30.6, 30.5, 28.1, 27.6, 26.8, 26.0, 22.5, 22.4, 22.1, 21.8. HRMS (ESI) calcd for $C_{26}H_{26}NO_2S$ [$(M+H^+)$]: 416.1679, found: 416.1675. HPLC analysis of the product: Daicel Chiralpak IA-3 column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: for major product: 37.60 min (major), 51.67 min (minor); for minor product: 32.86 min (minor), 35.42 min (major).

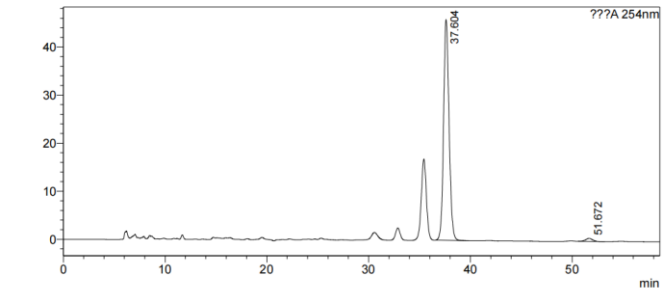
<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	37.610	1632772	43893	50.168		M	
2	51.473	1621814	32596	49.832		M	
Total		3254586	76488				

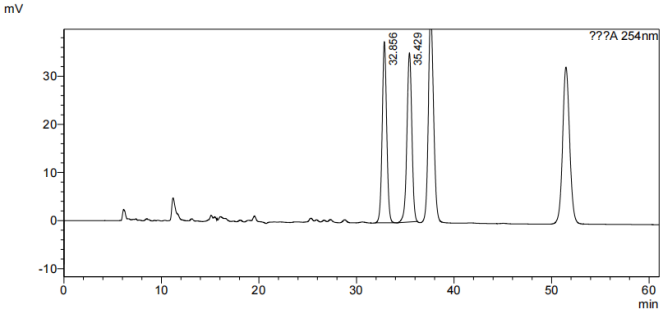
<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	37.604	1724818	45942	98.334		M	
2	51.672	29230	622	1.666		M	
Total		1754048	46565				

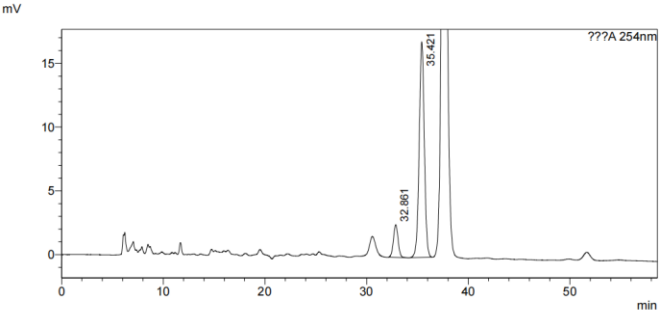
<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	32.856	1209879	37666	49.583		M	
2	35.429	1230219	35159	50.417		M	
Total		2440097	72825				

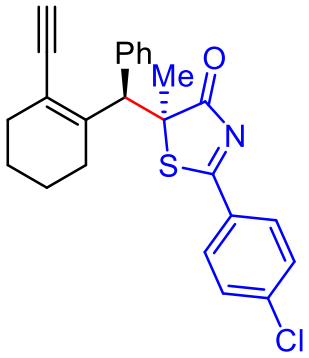
<Chromatogram>



<Peak Table>
???A 254nm

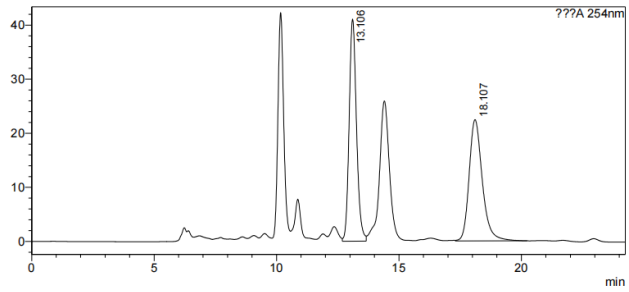
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	32.861	81676	2563	12.119		M	
2	35.421	592265	16896	87.881		M	
Total		673941	19459				

(*S*)-2-(4-chlorophenyl)-5-((*R*)-(2-ethynylcyclohex-1-en-1-yl)(phenyl)methyl)-5-methylthiazol-4(5H)-one: 4f



Yellow liquid. 30 mg, 72% yield, 3.4:1 dr, 98:2 er, 87.5:12.5 er.
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.4 Hz, 0.58H, minor), 8.02 (d, *J* = 9.0 Hz, 2.00H, major), 7.49 (d, *J* = 8.4 Hz, 0.58H, minor), 7.47 (d, *J* = 8.4 Hz, 2.00H, major), 7.44-7.43 (m, 0.70H), 7.34-7.31 (m, 0.65H), 7.27-7.26 (m, 2.30H), 7.16-7.11 (m, 2.80H), 5.30 (s, 1.00H, major), 5.19 (s, 0.29H, minor), 3.29 (s, 0.29H, minor), 3.28 (s, 1.00H, major), 2.37-2.22 (m, 5.32H), 2.15-2.09 (m, 0.70H), 1.74 (s, 3.00H, major), 1.72 (s, 0.87H, minor), 1.69-1.62 (m, 4.30H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 195.2, 194.4, 193.0, 192.4, 144.2, 142.6, 141.41, 141.39, 138.9, 138.2, 130.7, 130.6, 129.9, 129.4, 129.3, 129.0, 128.5, 128.4, 128.2, 128.1, 127.4, 127.2, 120.8, 119.3, 84.1, 83.5, 81.8, 81.5, 67.9, 66.9, 57.8, 57.0, 30.6, 30.5, 27.9, 27.3, 26.9, 26.1, 22.5, 22.4, 22.0, 21.8. HRMS (ESI) calcd for $C_{25}H_{23}ClNOS$ [$(M+H^+)$]: 420.1183, found: 420.1180. HPLC analysis of the product: Daicel Chiralpak ASH column; hexane/2-propanol = 90/10, 0.5 mL/min. Retention times: for major product: 13.15 min (minor), 18.20 min (major); for minor product: 10.16 min (major), 14.44 min (minor).

<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.106	854967	41027	50.486			
2	18.107	838497	22423	49.514			
Total		1693463	63450				

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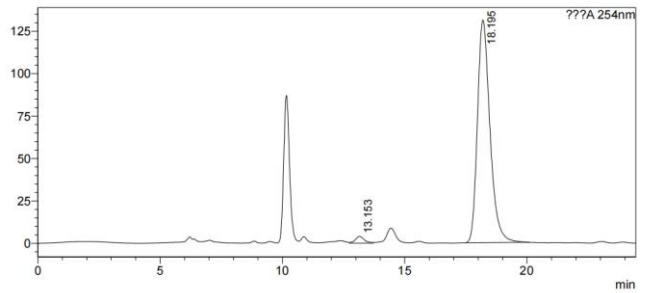
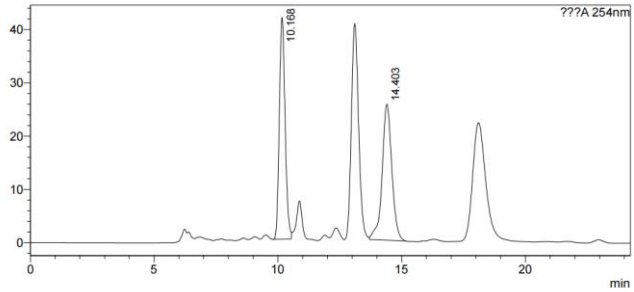


<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.153	102600	4017	2.147			
2	18.195	4676363	131230	97.853		M	
Total		4778963	135247				

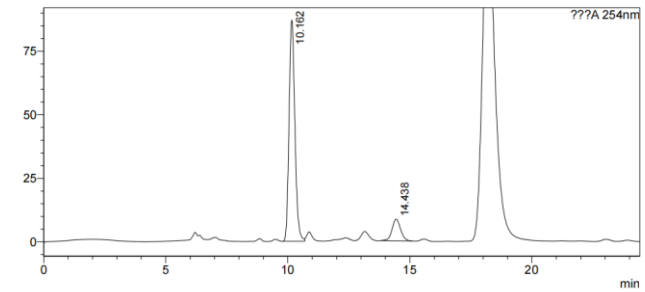
<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.168	677496	41574	49.246		M	
2	14.403	698233	25529	50.754		M	
Total		1375729	67103				

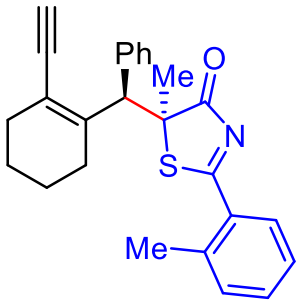
<Chromatogram>



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.162	1445052	86935	87.490		M	
2	14.438	206624	8526	12.510		M	
Total		1651676	95461				

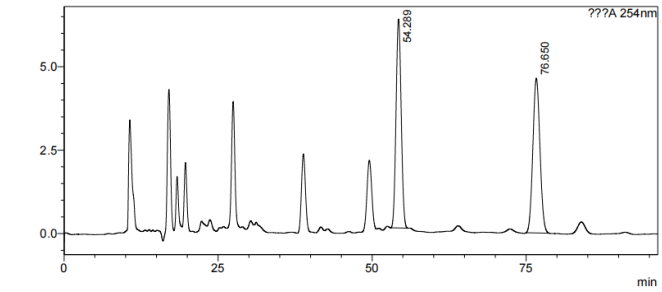
(*S*)-5-((*R*)-(2-ethynylcyclohex-1-en-1-yl)(phenyl)methyl)-5-methyl-2-(o-tolyl)thiazol-4(5H)-one: 4g



Colorless liquid. 39 mg, 98% yield, 3:1 dr, 98:2 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.8 Hz, 0.33H, minor), 7.73 (d, *J* = 7.8 Hz, 1.00H, major), 7.47-7.42 (m, 2.00H), 7.33-7.31 (m, 3.00H), 7.30-7.27 (m, 2.64H), 7.19-7.15 (m, 3.00H), 5.27 (s, 1.00H, major), 5.20 (s, 0.33H, minor), 3.29 (s, 0.33H, minor), 3.28 (s, 1.00H, major), 2.61 (s, 0.99H, minor), 2.39 (s, 3.00H, major), 2.37-2.37 (m, 4.00H), 2.25-2.24 (m, 0.66H), 2.17-2.13 (m, 0.66H), 1.744 (s, 3.00H, major), 1.739 (s, 0.99H, minor), 1.67-1.60 (m, 4.00H), 1.57-1.43 (m, 1.32H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.1, 195.8, 195.3, 194.9, 144.4, 142.7, 138.95, 138.91, 138.7, 138.3, 132.9, 132.7, 132.3, 132.2, 132.1, 131.9, 130.0, 129.3, 129.1, 128.7, 128.4, 128.1, 127.3, 127.2, 126.1, 126.0, 120.7, 119.1, 84.2, 83.5, 81.9, 81.5, 67.0, 66.3, 58.0, 57.5, 30.7, 30.6, 27.5, 27.1, 26.6, 26.3, 22.6, 22.5, 22.03, 21.91, 21.87, 21.5. HRMS (ESI) calcd for $C_{26}H_{26}NOS$ [$(M+H^+)$]: 400.1730, found: 400.1726. HPLC analysis of the product: Daicel Chiralpak IC-3 column; hexane/2-propanol = 90/10, 0.3 mL/min. Retention times: 76.54 min (minor), 54.04 min (major).

<Chromatogram>

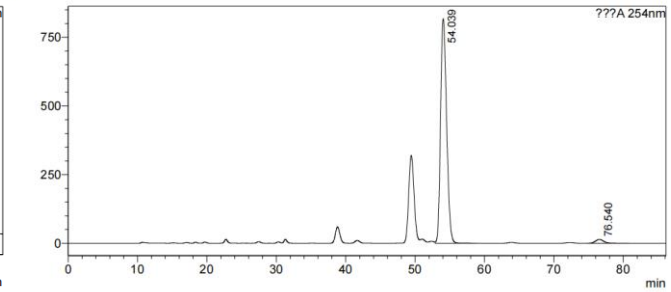


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	54.289	363827	6262	49.523			
2	76.650	370830	4637	50.477			
Total		734657	10900				

<Chromatogram>



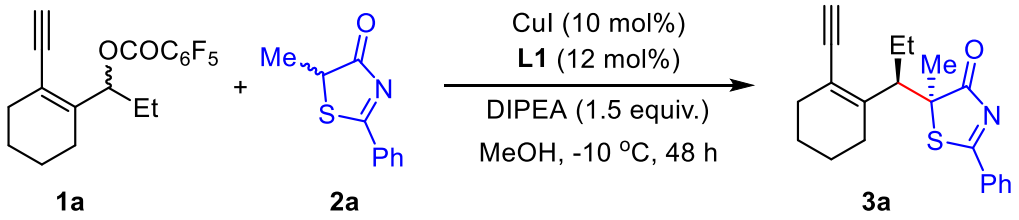
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	54.039	49380798	817437	97.763			
2	76.540	1129693	13693	2.237			
Total		50510491	831131				

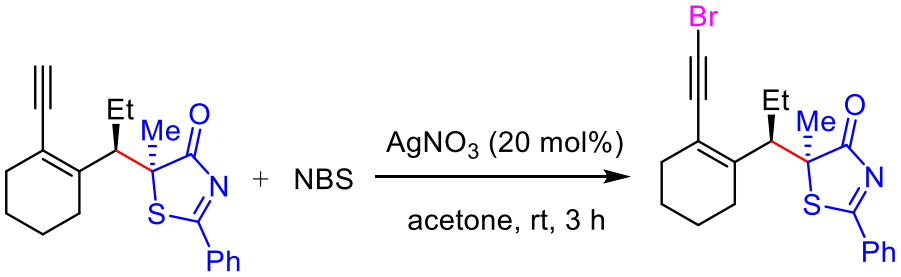
5. General Procedure IV: General Procedure for

Gram-scale reaction



1a **2a** **3a**

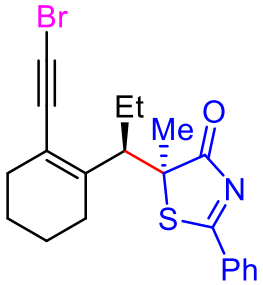
To a mixture of CuI (10 mol%), **L12** (12 mol%), Yne-Allylic Esters **1a** (2 mmol), thiazolidinone **2a** (3 mmol) and DIPEA (3 mmol) was added CH_3OH (15 mL) at -10 ^oC under nitrogen atmosphere. Upon complete consumption of Yne-Allylic Esters **1a** (TLC monitoring, about 48 h), the solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel column (hexanes/EtOAc = 20:1, v/v) to afford the desired product **3a** (0.531 g, 79% yield, 93:7 er, 10:1 dr; 98.5:1.5 er, >20:1 dr after recrystallization).



3a **5a**

Procedure: According to general procedure **3a** (34 mg, 0.1 mmol), $AgNO_3$ (3.4 mg, 20 mol%) and NBS (21.4 mg, 0.12 mmol) are dissolved in acetone (1 mL) and stirred for 3 hours at room temperature. Removal of the solvent under reduced pressure and purification by chromatography on silica gel (petroleum ether/ethyl acetate, v: v = 20:1) to afford the product **5a**.

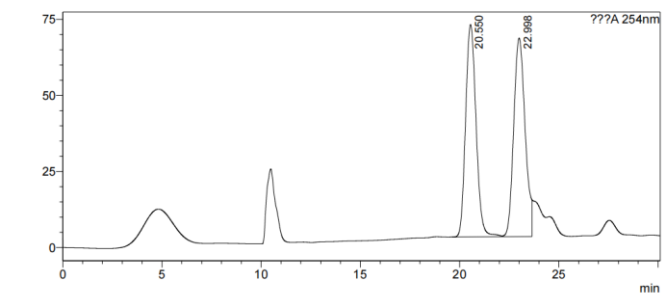
(*S*)-5-((*R*)-1-(2-(bromoethynyl)cyclohex-1-en-1-yl)propyl)-5-methyl-2-phenylthiazol-4(5H)-one: 5a



Colorless liquid. 33 mg, 80% yield, 98.4:1.6 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.16 (d, *J* = 7.8 Hz, 2H), 7.67-7.65 (m, 1H), 7.53-7.50 (m, 2H), 3.73 (dd, *J* = 11.4 and 3.0 Hz, 1H), 2.34-2.24 (m, 2H), 2.07-2.04 (m, 1H), 1.91-1.88 (m, 1H), 1.74-1.68 (m, 2H), 1.62-1.58 (m, 1H), 1.56 (s, 3H), 1.53-1.48 (m, 1H), 1.16-1.11 (m, 1H), 0.86-0.83 (m, 1H), 0.76 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.4, 195.1, 142.1, 134.8, 132.3, 129.0, 128.8, 121.6, 80.2, 67.4, 53.7, 52.7, 30.5, 25.9, 24.8, 22.4, 21.7, 11.4. HRMS (ESI) calcd for $C_{21}H_{23}BrNOS$ [$(M+H^+)$]: 416.0678, found: 416.0676. HPLC analysis of the product: Daicel Chiralpak ODH column; hexane/2-propanol = 95/5, 0.3 mL/min. Retention times: 22.82 min (minor), 20.32 min (major).

<Chromatogram>

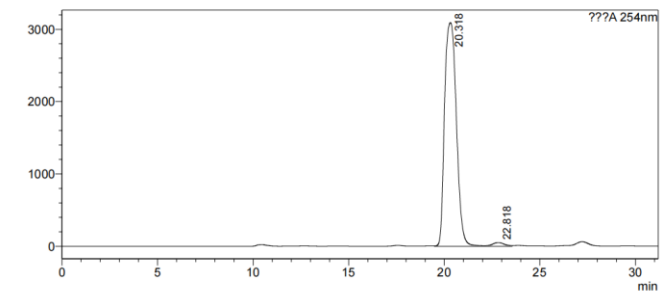


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.550	2563648	69811	49.582			
2	22.998	2606878	65244	50.418		V M	
Total		5170527	135055				

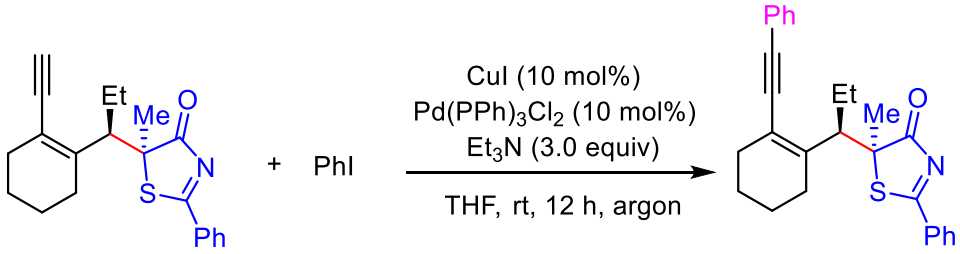
<Chromatogram>



<Peak Table>

???A 254nm

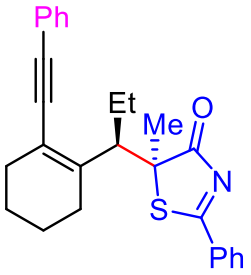
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.318	132601887	3091941	98.360			
2	22.818	2210554	49965	1.640		V	
Total		134812441	3141906				



3a **5b**

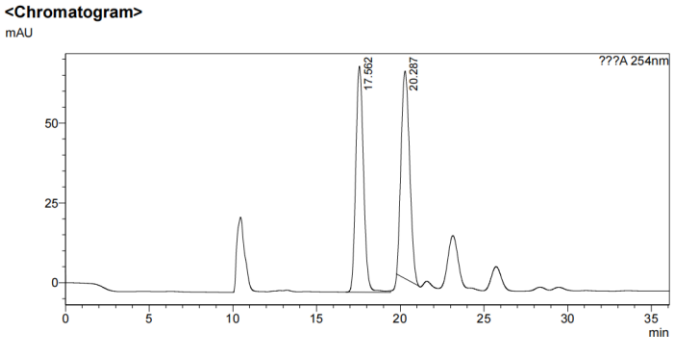
Procedure: Iodobenzene (30.6 mg, 0.15 mmol) and **3a** (34 mg, 0.1 mmol) were dissolved in THF, and Et_3N (30.4 mg, 0.3 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol) and CuI (1.9 mg, 0.01 mmol) were added. The mixture was stirred at room temperature under argon atmosphere for 12 h. When the reaction was completed as monitored by TLC, the solution was quenched carefully with saturated NH_4Cl solution and then warmed to room temperature. The product was extracted with ethyl acetate (5 mL × 3), and dried over anhydrous Na_2SO_4. After filtration and evaporation in vacuo, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v: v = 20:1) to afford the product **5b**.

(*S*)-5-methyl-2-phenyl-5-((*R*)-1-(2-(phenylethynyl)cyclohex-1-en-1-yl)propyl)thiazol-4(5H)-one: 5b



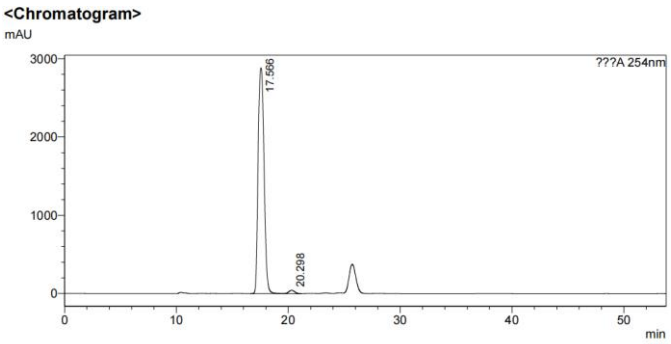
Yellow liquid. 32 mg, 77% yield, 98.4:1.6 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.18 (d, *J* = 7.8 Hz, 2H), 7.68-7.65 (m, 1H), 7.60-7.59 (m, 2H), 7.54-7.51 (m, 2H), 7.35-7.33 (m, 2H), 7.31-7.28 (m, 1H), 4.04 (dd, *J* = 11.4 and 3.6 Hz, 1H), 2.44-2.36 (m, 2H), 2.14-2.11 (m, 1H), 1.98-1.96 (m, 1H), 1.80-1.66 (m, 4H), 1.63 (s, 3H), 1.60-1.52 (m, 1H), 1.18-1.13 (m, 1H), 0.81 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.7, 195.1, 140.8, 134.8, 132.4, 131.6, 129.0, 128.8, 128.3, 127.9, 123.7, 121.9, 93.2, 89.8, 67.6, 53.7, 30.4, 25.9, 24.9, 22.5, 22.4, 21.8, 11.6. HRMS (ESI) calcd for $C_{27}H_{28}NOS$ [$(M+H^+)$]: 414.1886, found: 414.1884. HPLC analysis of the product: Daicel Chiralpak ODH column; hexane/2-propanol = 95/5, 0.3 mL/min. Retention times: 20.30 min (minor), 17.57 min (major).



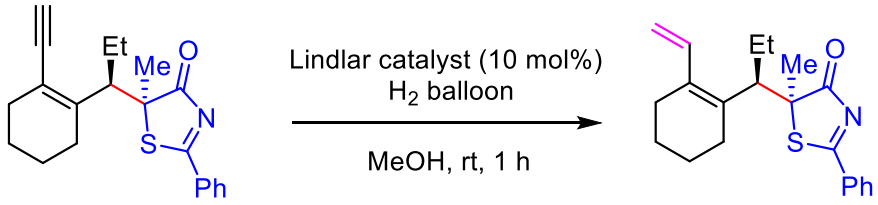
<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.562	2281674	70766	49.628		S M	
2	20.287	2315846	65018	50.372		M	
Total		4597520	135783				



<Peak Table>
???A 254nm

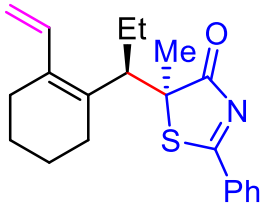
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.566	106516256	2887108	98.394			
2	20.298	1738912	44804	1.606		V	
Total		108255168	2931913				



3a **5c**

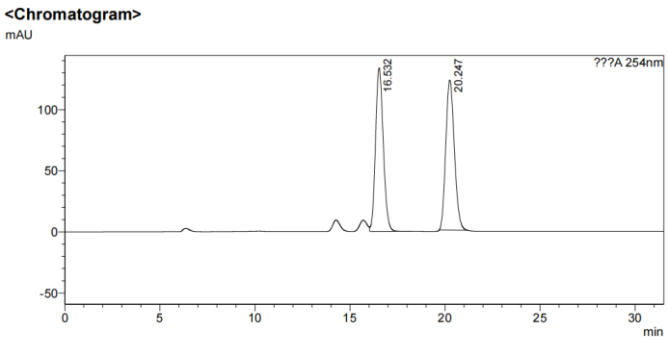
Procedure: In a flask were placed **3a** (34 mg, 0.1 mmol), 10 mol% Lindlar catalyst (2 mg) and 1 mL MeOH, and the mixture was stirred using a magnetic stirrer at room temperature under a hydrogen atmosphere for 1 h. When the reaction was completed as monitored by TLC, the EA was added, and then the mixture was passed through a membrane filter. After filtration and evaporation in vacuo, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v: v = 20:1) to afford the product **5c**.

(*S*)-5-methyl-2-phenyl-5-((*R*)-1-(2-vinylcyclohex-1-en-1-yl)propyl)thiazol-4(5H)-one: 5c



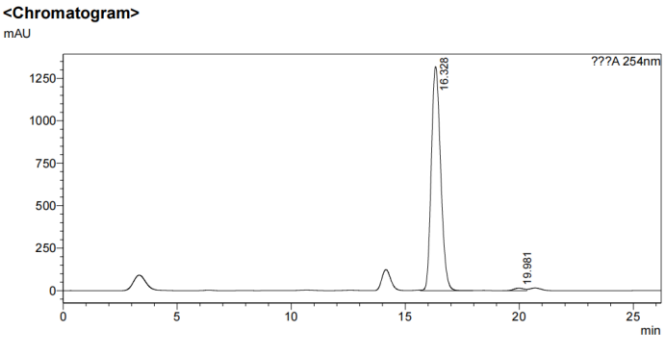
Colorless liquid. 33 mg, 97% yield, 98.8:1.2 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17 (d, *J* = 7.8 Hz, 2H), 7.68-7.66 (m, 1H), 7.53-7.51 (m, 2H), 7.11 (dd, *J* = 16.8 and 10.8 Hz, 1H), 5.25 (d, *J* = 16.8 Hz, 1H), 5.08 (d, *J* = 10.8 Hz, 1H), 3.70 (dd, *J* = 10.8 and 3.6 Hz, 1H), 2.36-2.27 (m, 2H), 2.14-2.11 (m, 1H), 1.92-1.89 (m, 1H), 1.74-1.72 (m, 2H), 1.65-1.63 (m, 1H), 1.60-1.56 (m, 2H), 1.47 (s, 3H), 1.12-1.07 (m, 1H), 0.71 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 197.8, 195.9, 139.3, 134.8, 132.4, 128.9, 128.8, 124.9, 67.8, 49.5, 29.5, 26.3, 26.2, 24.5, 23.3, 23.1, 21.7, 13.1, 11.8. HRMS (ESI) calcd for $C_{21}H_{26}NOS$ [$(M+H^+)$]: 340.1730, found: 340.1727. HPLC analysis of the product: Daicel Chiralpak ADH column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: 19.98 min (minor), 16.33 min (major).



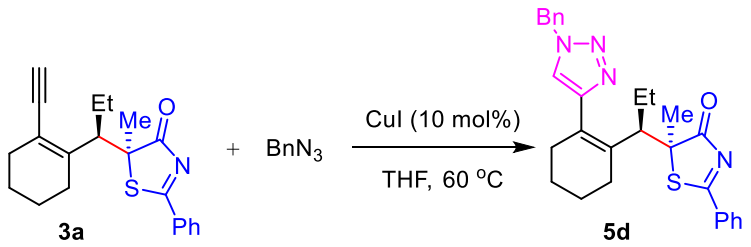
<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.532	3784688	133607	49.584			
2	20.247	3848191	122638	50.416		M	
Total		7632879	256246				



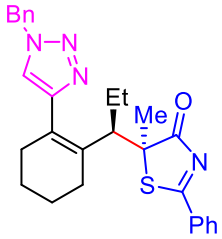
<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.328	37603776	1318609	98.775		M	
2	19.981	466372	15375	1.225			
Total		38070149	1333983				



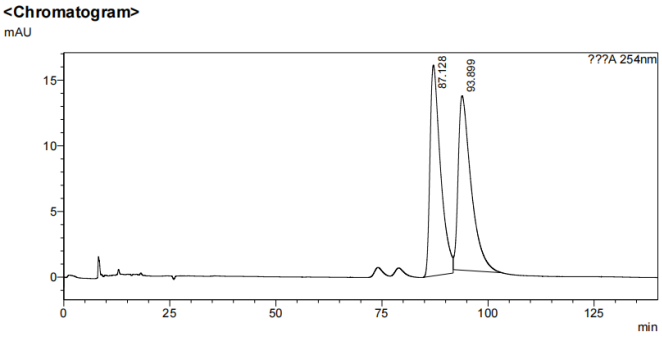
Procedure: BnN_3 (40 mg, 0.3 mmol) and **3a** (34 mg, 0.1 mmol) were dissolved in THF, and CuI (1.9 mg, 0.01 mmol) were added. The mixture was stirred at 60 ℃ (oil bath temperature) under argon atmosphere for 12 h. When the reaction was completed as monitored by TLC. After filtration and evaporation in vacuo, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v: v = 20:1) to afford the product **5d.**

(*S*)-5-((*R*)-1-(2-(1-benzyl-1H-1,2,3-triazol-5-yl)cyclohex-1-en-1-yl)propyl)-5-methyl-2-phenylthiazol-4(5H)-one: 5d



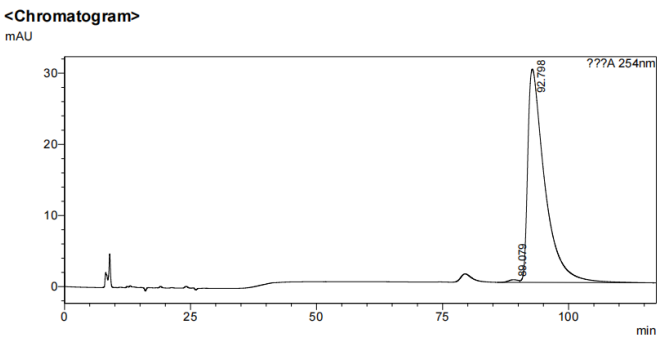
White solid. 33 mg, 70% yield, 99.3:0.7 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.15 (d, *J* = 7.8 Hz, 2H), 7.66-7.64 (m, 1H), 7.52-7.49 (m, 2H), 7.46 (s, 1H), 7.42-7.40 (m, 2H), 7.35-7.30 (m, 3H), 5.63-5.57 (m, 2H), 3.46 (dd, *J* = 10.8 and 3.0 Hz, 1H), 2.54-2.46 (m, 2H), 2.16-2.13 (m, 1H), 1.93-1.91 (m, 1H), 1.79-1.77 (m, 2H), 1.73-1.62 (m, 2H), 1.60-1.52 (m, 1H), 1.48 (s, 3H), 1.05-1.00 (m, 1H), 0.67 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 197.0, 195.5, 148.3, 134.9, 134.8, 133.2, 132.3, 129.4, 129.1, 128.9, 128.7, 128.5, 127.7, 121.4, 67.4, 54.0, 50.7, 31.4, 26.2, 24.8, 22.8, 22.6, 21.9, 11.7. HRMS (ESI) calcd for $C_{28}H_{31}N_4OS$ [$(M+H^+)$]: 471.2213, found: 471.2211. HPLC analysis of the product: Daicel Chiralpak IB-3 column; hexane/2-propanol = 94/6, 0.4 mL/min. Retention times: 89.08 min (minor), 92.80 min (major).



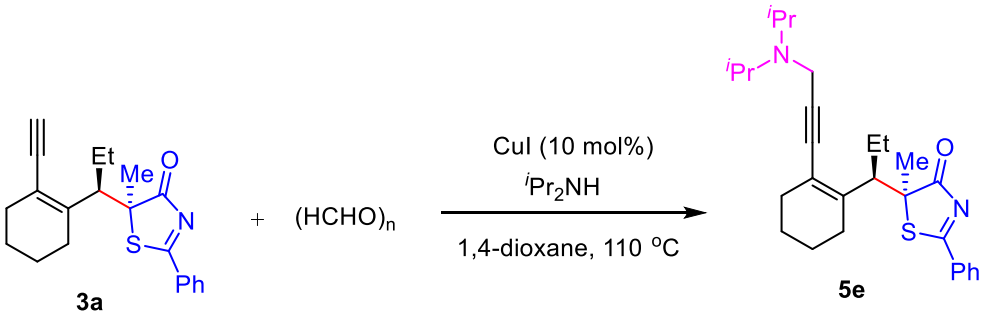
<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	87.128	2770969	16039	49.463		M	
2	93.899	2831087	13285	50.537		M	
Total		5602056	29324				



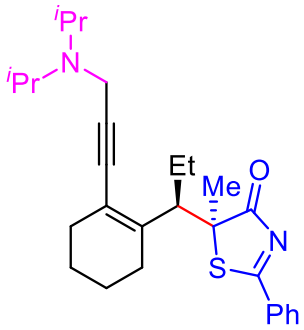
<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	89.079	48505	370	0.683		M	
2	92.798	7058205	30002	99.317		V M	
Total		7106710	30372				



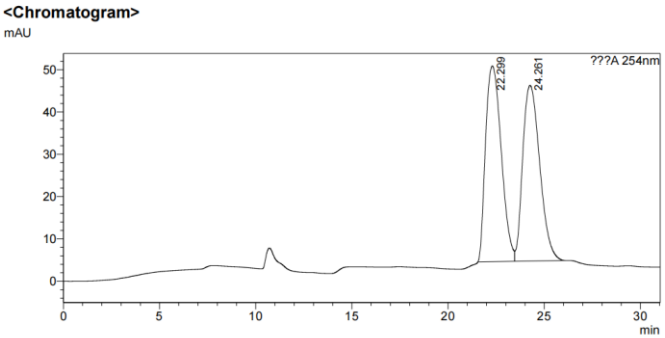
Procedure: $(HCHO)_n$ (5.1 mg, 0.16 mmol), $^{i}Pr_2NH$ (14.2 mg, 0.14 mmol) and **3a** (34 mg, 0.1 mmol) were dissolved in 1,4-dioxane, and CuI (1.9 mg, 0.01 mmol) were added. The mixture was stirred at 110 ℃ (oil bath temperature) under air atmosphere for 12 h. When the reaction was completed as monitored by TLC. After filtration and evaporation in vacuo, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v: v = 20:1) to afford the product **5e.**

(*S*)-5-((*R*)-1-(2-(3-(diisopropylamino)prop-1-yn-1-yl)cyclohex-1-en-1-yl)propyl)-5-methyl-2-phenylthiazol-4(5H)-one: 5e



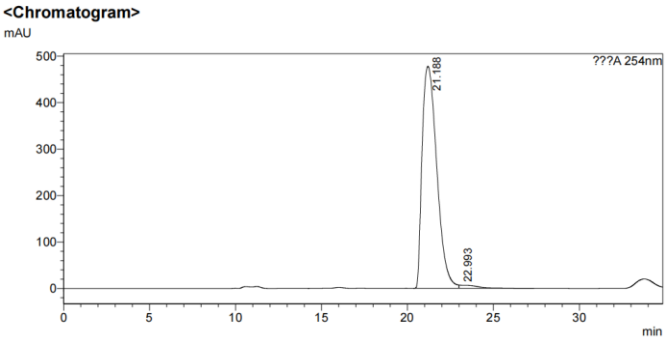
Yellow liquid. 36 mg, 80% yield, 98.2:1.8 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.16 (d, *J* = 7.8 Hz, 2H), 7.67-7.64 (m, 1H), 7.52-7.50 (m, 2H), 3.83 (dd, *J* = 11.4 and 3.6 Hz, 1H), 3.69 (s, 2H), 3.38-3.32 (m, 2H), 2.29-2.23 (m, 2H), 2.06-2.03 (m, 1H), 1.88-1.85 (m, 1H), 1.75-1.66 (m, 2H), 1.61-1.57 (m, 2H), 1.55 (s, 3H), 1.52-1.47 (m, 1H), 1.17 (d, *J* = 6.0 Hz, 12H), 1.14-1.06 (m, 1H), 0.75 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 196.6, 195.0, 138.7, 134.8, 132.4, 128.9, 128.8, 122.1, 92.2, 83.9, 67.5, 53.6, 48.3, 34.7, 31.5, 30.8, 30.1, 29.7, 25.8, 24.6, 22.55, 22.50, 21.7, 20.65, 20.57, 11.4. HRMS (ESI) calcd for $C_{28}H_{39}N_2OS$ [$(M+H^+)$]: 451.2778, found: 451.2775. HPLC analysis of the product: Daicel Chiralpak ADH column; hexane/2-propanol = 97/3, 0.3 mL/min. Retention times: 22.99 min (minor), 21.19 min (major).



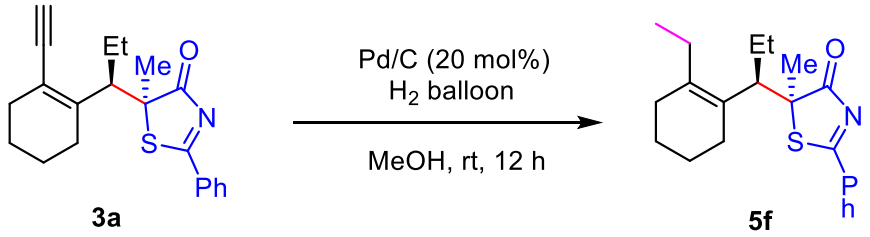
<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.299	2622342	46260	50.593		M	
2	24.261	2560825	41546	49.407		V M	
Total		5183167	87806				



<Peak Table>
???A 254nm

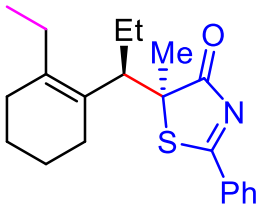
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.188	28381110	477860	98.143		M	
2	22.993	537057	7001	1.857		V M	
Total		28918166	484861				



3a **5f**

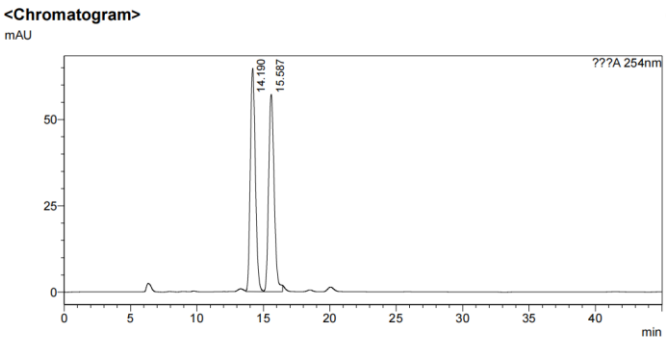
Procedure: In a flask were placed **3a** (34 mg, 0.1 mmol), 20 mol% Pd/C (2 mg) and 1 mL MeOH, and the mixture was stirred using a magnetic stirrer at room temperature under a hydrogen atmosphere for 12 h. When the reaction was completed as monitored by TLC, the EA was added, and then the mixture was passed through a membrane filter. After filtration and evaporation in vacuo, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v: v = 20:1) to afford the product **5f**.

(*S*)-5-((*R*)-1-(2-ethylcyclohex-1-en-1-yl)propyl)-5-methyl-2-phenylthiazol-4(5H)-one: 5f



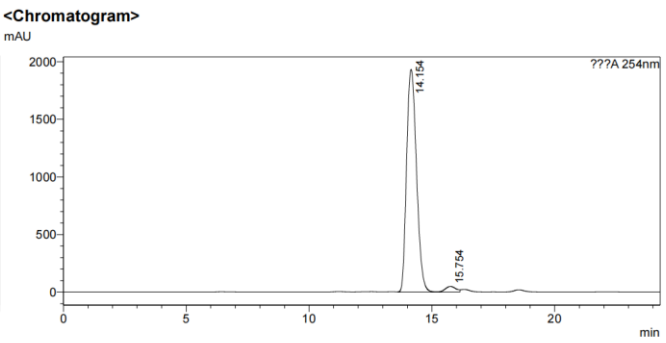
Colorless liquid. 25 mg, 73% yield, 97.3:2.7 er.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17 (d, *J* = 7.8 Hz, 2H), 7.67-7.64 (m, 1H), 7.52-7.50 (m, 2H), 3.39 (dd, *J* = 10.8 and 3.0 Hz, 1H), 2.32-2.26 (m, 1H), 2.13-2.05 (m, 3H), 1.97-1.95 (m, 1H), 1.76-1.73 (m, 1H), 1.69-1.54 (m, 5H), 1.50 (s, 3H), 1.01 (t, *J* = 7.8 Hz, 3H), 0.96-0.83 (m, 1H), 0.72 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 197.8, 195.9, 139.3, 134.8, 132.4, 128.9, 128.8, 124.9, 67.8, 49.5, 29.5, 26.3, 26.2, 24.5, 23.3, 23.1, 21.7, 13.1, 11.8. HRMS (ESI) calcd for $C_{21}H_{28}NOS$ [$(M+H^+)$]: 342.1886, found: 342.1881. HPLC analysis of the product: Daicel Chiralpak ADH column; hexane/2-propanol = 95/5, 0.5 mL/min. Retention times: 15.75 min (minor), 14.15 min (major).



<Peak Table>
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.190	1723485	64651	50.965			
2	15.587	1658231	57072	49.035		V M	
Total		3381716	121723				



<Peak Table>
???A 254nm

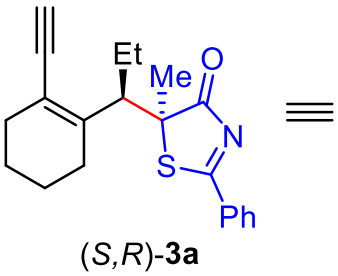
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.154	54141181	1932381	97.273			
2	15.754	1518051	49797	2.727		V	
Total		55659232	1982178				

6. References.

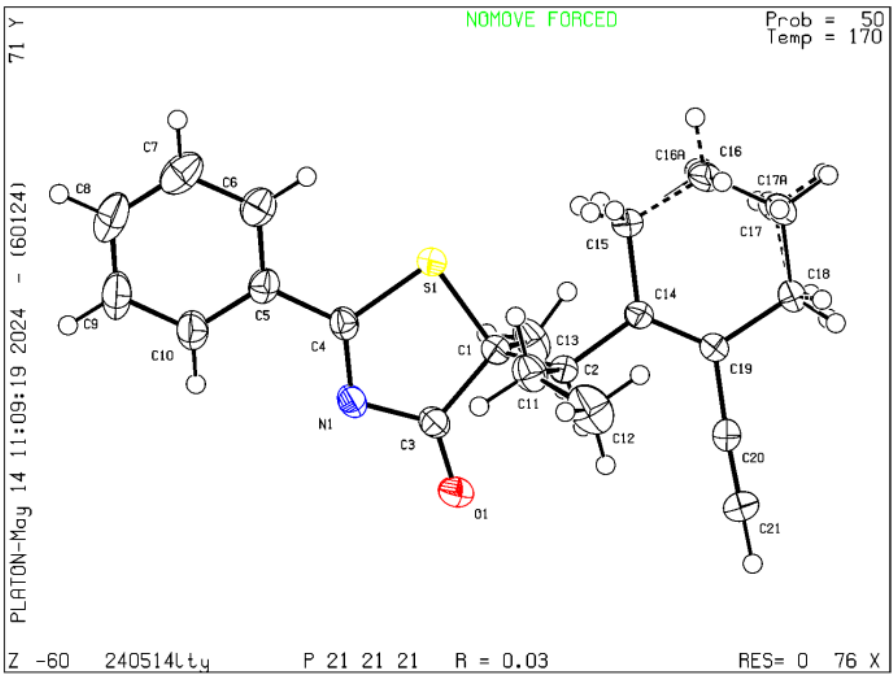
[1] a) H.-H. Kong, C. Zhu, S. Deng, G. Xu, R. Zhao, C. Yao, H.-M. Xiang, C. Zhao, X. Qi, H. Xu, *J. Am. Chem. Soc.* **2022**, *144*, 21347−21355; b) M.-D. Li, Z.-H. Wang, H. Zhu, X.-R. Wang, J.-R. Wang, T.-Y. Lin, *Angew. Chem. Int. Ed.* **2023**, e202313911.

[2] a) T.-C. Wang, Z.-Y. Han, P.-S. Wang, H.-C. Lin, S.-W. Luo, L.-Z. Gong, *Org. Lett.* **2018**, *20*, 4740−4744; b) F. A. J. Kerdesky, J. H. Holms, J. L. Moore, R. L. Bell, R. D. Dyer, G. W. Carter, D. W. Brooks. *J. Med. Chem.* **1991**, *34*, 2158−2165.

7. Crystal Structure of (*S,R*)-3a



(*S,R*)-**3a**



Method for single crystals cultivation: **3a** (50.0 mg) was dissolved in *n*-hexane/ dichloromethane (v/v =80:20, 2.0 mL) in a vial at room temperature. The vial was properly sealed with parafilm and kept at 25 ^{o}C to allow the slow evaporation of the solvents until a single crystal was obtained. The absolute configuration of compound **(*S,R*)-3a** is determined by anomalous dispersion with Ga Kα radiation (λ =1.34139 Å) as X-ray source for X-ray diffraction experiment, and a Flack parameter of -0.01(2) is obtained as result. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 2372766.

Table 1 Crystal data and structure refinement for 240514lty.

Identification code	240514lty
Empirical formula	C21H23NOS
Formula weight	337.46
Temperature/K	170.00
Crystal system	orthorhombic
Space group	P212121
a/Å	10.7747(2)
b/Å	11.7976(2)
c/Å	14.5095(3)
α / °	90
β / °	90
γ / °	90
Volume/Å3	1844.38(6)
Z	4
ρ calcg/cm3	1.215
μ /mm-1	1.044
F(000)	720.0
Crystal size/mm3	0.17 × 0.17 × 0.05
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	8.404 to 109.782
Index ranges	-12 ⩽ h ⩽ 13, -14 ⩽ k ⩽ 14, -17 ⩽ l ⩽ 17
Reflections collected	16049
Independent reflections	3491 [Rint = 0.0515, Rsigma = 0.0387]
Data/restraints/parameters	3491/65/238
Goodness-of-fit on F2	1.032
Final R indexes [I>=2σ (I)]	R1 = 0.0277, wR2 = 0.0724
Final R indexes [all data]	R1 = 0.0288, wR2 = 0.0733
Largest diff. peak/hole / e Å-3	0.30/-0.20
Flack parameter	0.026(8)

Table 2 Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for 240514lty. Ueq is defined as 1/3 of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
S1	3202.3(5)	3425.3(4)	3233.6(3)	36.58(15)
O1	1687.1(16)	784.7(12)	2199.3(10)	39.7(4)
N1	2214.9(15)	1452.0(14)	3629.5(11)	28.8(4)
C14	3939.4(17)	3324.6(16)	873.2(12)	22.7(4)
C2	3614.0(18)	2348.8(15)	1509.1(12)	25.4(4)
C19	3852.9(17)	3212.5(16)	-47.6(13)	23.8(4)
C5	2965.9(19)	2459.6(16)	4974.8(14)	28.6(4)
C18	4196.1(19)	4149.1(17)	-723.0(14)	29.5(4)
C3	2123.4(18)	1529.0(17)	2666.9(13)	28.1(4)
C1	2613.1(19)	2646.6(16)	2239.1(13)	27.0(4)
C20	3473(2)	2159.6(17)	-464.9(13)	31.5(4)
C11	4772(2)	1802.0(18)	1940.2(15)	35.6(5)
C15	4432(2)	4405.6(16)	1297.5(14)	31.3(5)
C6	3766(2)	3287(2)	5320.0(15)	36.6(5)
C13	1508(2)	3271.5(19)	1810.0(17)	40.9(5)
C10	2360(2)	1729.6(19)	5583.2(14)	36.8(5)
C4	2746.6(18)	2338.3(17)	3978.4(13)	26.6(4)
C21	3221(3)	1301.7(18)	-847.5(15)	43.0(6)
C7	3954(2)	3382(2)	6266.6(16)	45.8(6)
C9	2549(3)	1840(2)	6522.9(15)	48.6(6)
C8	3340(3)	2662(2)	6860.3(16)	51.0(6)
C12	5629(2)	1284(2)	1230(2)	54.5(7)
C16	4469(5)	5411(4)	638(3)	31.5(11)
C17	4982(5)	5072(3)	-297(2)	32.3(11)
C17A	4268(8)	5294(5)	-254(4)	29.8(16)
C16A	5010(9)	5201(8)	628(6)	35.8(18)

Table 3 Anisotropic Displacement Parameters (Å2×103) for 240514lty. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	U11	U22	U33	U23	U13	U12
S1	60.3(3)	24.0(2)	25.4(2)	-2.70(19)	9.3(2)	-10.8(2)
O1	53.6(9)	30.8(8)	34.7(8)	1.6(6)	-5.3(7)	-14.8(7)
N1	32.2(8)	27.2(8)	26.9(8)	5.8(7)	1.1(7)	-2.7(7)
C14	24.6(9)	20.1(9)	23.5(9)	0.4(8)	-0.3(7)	0.1(8)
C2	34.3(10)	20.0(9)	22.0(9)	-0.1(7)	0.5(7)	-0.2(8)
C19	25.6(9)	21.7(9)	24.0(9)	1.4(7)	0.5(7)	-2.1(7)
C5	31.3(10)	29.3(10)	25.3(9)	-0.8(8)	2.7(8)	9.0(8)
C18	37.0(11)	27.9(10)	23.8(9)	4.3(8)	0.6(8)	-5.7(8)
C3	30.0(9)	25.3(9)	29.1(9)	3.4(8)	0.5(8)	-2.5(8)
C1	34.5(10)	21.5(9)	24.9(9)	1.6(7)	1.2(8)	-1.3(8)
C20	41.0(12)	31.3(11)	22.3(9)	1.2(8)	1.5(8)	-7.2(9)
C11	38.0(11)	30.9(10)	37.7(11)	8.4(9)	-1.0(9)	6.3(9)
C15	42.7(12)	25.3(10)	25.8(10)	-1.4(8)	-1.9(9)	-7.9(9)
C6	34.6(11)	41.4(12)	33.9(11)	-2.7(10)	0.3(9)	4.7(10)
C13	37.0(11)	37.0(11)	48.6(12)	15.3(10)	7.9(10)	7.0(9)
C10	45.3(12)	36.2(12)	29.0(10)	3.5(9)	7.3(9)	6.2(10)
C4	28.5(10)	26.2(9)	24.9(10)	2.8(8)	5.2(8)	2.9(8)
C21	63.5(15)	33.3(11)	32.0(11)	-6.8(9)	0.8(11)	-14.6(11)
C7	44.0(12)	53.5(14)	39.9(12)	-12.4(12)	-11.5(10)	12.4(12)
C9	66.7(16)	53.1(15)	26.1(11)	7.9(10)	9.8(11)	13.1(13)
C8	64.5(16)	61.9(15)	26.4(11)	-3.9(11)	-4.3(12)	22.2(14)
C12	48.3(14)	44.5(15)	70.7(18)	13.9(13)	13.1(14)	21.6(11)
C16	37(3)	23.6(19)	33.9(19)	0.4(15)	0(2)	-6.7(18)
C17	38(3)	28.3(18)	30.4(18)	5.2(13)	2.7(17)	-10.5(17)
C17A	37(4)	22(3)	30(3)	5(2)	2(3)	-4(3)
C16A	43(4)	32(4)	33(3)	3(3)	-6(4)	-18(3)

Table 4 Bond Lengths for 240514lty.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C1	1.825(2)	C18	C17	1.511(4)
S1	C4	1.7475(19)	C18	C17A	1.514(6)
O1	C3	1.205(2)	C3	C1	1.550(3)
N1	C3	1.403(2)	C1	C13	1.533(3)
N1	C4	1.295(3)	C20	C21	1.186(3)
C14	C2	1.516(2)	C11	C12	1.513(3)
C14	C19	1.346(3)	C15	C16	1.524(5)
C14	C15	1.512(3)	C15	C16A	1.488(8)
C2	C1	1.552(3)	C6	C7	1.393(3)
C2	C11	1.538(3)	C10	C9	1.385(3)
C19	C18	1.522(3)	C7	C8	1.379(4)
C19	C20	1.441(3)	C9	C8	1.381(4)
C5	C6	1.395(3)	C16	C17	1.519(6)
C5	C10	1.395(3)	C17A	C16A	1.513(10)
C5	C4	1.472(3)			

Table 5 Bond Angles for 240514lty.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	S1	C1	91.25(9)	C3	C1	C2	108.50(15)
C4	N1	C3	111.58(17)	C13	C1	S1	110.45(15)
C19	C14	C2	120.89(16)	C13	C1	C2	111.81(16)
C19	C14	C15	120.75(17)	C13	C1	C3	107.91(16)
C15	C14	C2	118.27(15)	C21	C20	C19	175.8(2)
C14	C2	C1	113.83(15)	C12	C11	C2	112.79(19)
C14	C2	C11	112.23(16)	C14	C15	C16	114.2(2)
C11	C2	C1	112.41(16)	C16A	C15	C14	114.4(4)
C14	C19	C18	123.42(17)	C7	C6	C5	120.0(2)
C14	C19	C20	121.42(17)	C9	C10	C5	119.8(2)
C20	C19	C18	115.10(16)	N1	C4	S1	118.36(14)
C6	C5	C4	121.31(18)	N1	C4	C5	122.23(18)
C10	C5	C6	119.58(19)	C5	C4	S1	119.41(15)
C10	C5	C4	119.10(19)	C8	C7	C6	119.7(2)
C17	C18	C19	113.30(19)	C8	C9	C10	120.4(2)
C17A	C18	C19	111.8(3)	C7	C8	C9	120.5(2)
O1	C3	N1	122.73(18)	C17	C16	C15	111.4(4)
O1	C3	C1	121.81(17)	C18	C17	C16	110.5(4)
N1	C3	C1	115.46(17)	C16A	C17A	C18	110.0(6)
C2	C1	S1	114.33(14)	C15	C16A	C17A	112.1(6)
C3	C1	S1	103.30(12)				

Table 6 Torsion Angles for 240514lty.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C3	C1	S1	-178.15(17)	C1	S1	C4	N1	0.21(17)
O1	C3	C1	C2	-56.4(3)	C1	S1	C4	C5	-179.26(16)
O1	C3	C1	C13	64.9(3)	C1	C2	C11	C12	167.77(18)
N1	C3	C1	S1	2.4(2)	C20	C19	C18	C17	-160.5(3)
N1	C3	C1	C2	124.06(18)	C20	C19	C18	C17A	165.6(4)
N1	C3	C1	C13	-114.62(19)	C11	C2	C1	S1	49.2(2)
C14	C2	C1	S1	-79.77(18)	C11	C2	C1	C3	-65.4(2)
C14	C2	C1	C3	165.55(15)	C11	C2	C1	C13	175.68(17)
C14	C2	C1	C13	46.7(2)	C15	C14	C2	C1	58.9(2)
C14	C2	C11	C12	-62.4(2)	C15	C14	C2	C11	-70.2(2)
C14	C19	C18	C17	16.9(4)	C15	C14	C19	C18	-1.9(3)
C14	C19	C18	C17A	-17.0(4)	C15	C14	C19	C20	175.33(18)
C14	C15	C16	C17	-44.3(5)	C15	C16	C17	C18	59.2(6)
C14	C15	C16A	C17A	42.3(10)	C6	C5	C10	C9	0.6(3)
C2	C14	C19	C18	-178.43(18)	C6	C5	C4	S1	-14.6(3)
C2	C14	C19	C20	-1.2(3)	C6	C5	C4	N1	165.96(19)
C2	C14	C15	C16	-167.6(3)	C6	C7	C8	C9	0.6(4)
C2	C14	C15	C16A	165.8(5)	C10	C5	C6	C7	-0.1(3)
C19	C14	C2	C1	-124.47(19)	C10	C5	C4	S1	165.48(16)
C19	C14	C2	C11	106.4(2)	C10	C5	C4	N1	-14.0(3)
C19	C14	C15	C16	15.8(4)	C10	C9	C8	C7	-0.1(4)
C19	C14	C15	C16A	-10.8(5)	C4	S1	C1	C2	-119.04(14)
C19	C18	C17	C16	-44.7(5)	C4	S1	C1	C3	-1.35(13)
C19	C18	C17A	C16A	47.0(8)	C4	S1	C1	C13	113.82(15)
C5	C6	C7	C8	-0.5(3)	C4	N1	C3	O1	178.1(2)
C5	C10	C9	C8	-0.5(3)	C4	N1	C3	C1	-2.4(2)
C18	C17A	C16A	C15	-61.2(11)	C4	C5	C6	C7	179.94(19)
C3	N1	C4	S1	1.2(2)	C4	C5	C10	C9	-179.4(2)
C3	N1	C4	C5	-179.33(17)					

Table 7 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for 240514lty.

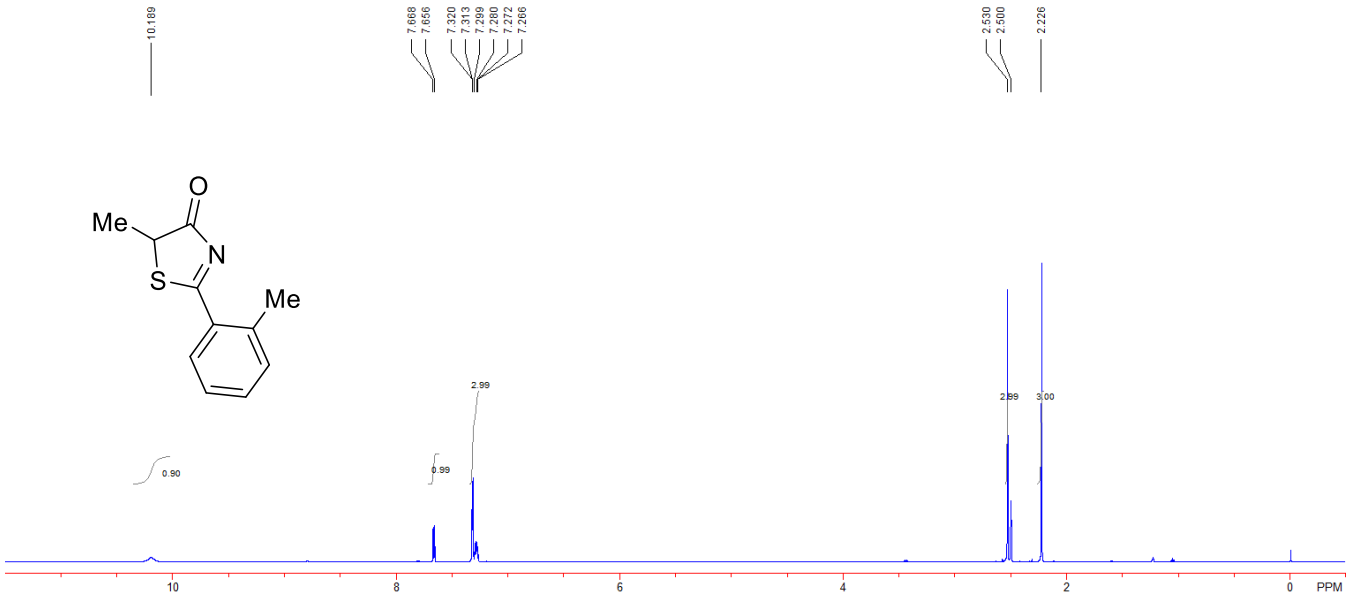
Atom	x	y	z	U(eq)
H2	3235.36	1753.04	1107.43	31
H18A	4653.78	3812.12	-1247.37	35
H18B	3425.26	4491.28	-968.93	35
H18C	5008.69	3972.35	-1007.2	35
H18D	3568.46	4179.67	-1220.69	35
H11A	5233.08	2384.42	2292.48	43
H11B	4507.97	1205.77	2378.39	43
H15A	5282.15	4263.89	1529.58	38
H15B	3906.65	4606.96	1832.68	38
H15C	3740.81	4800.04	1612.3	38
H15D	5055.87	4205.57	1771.37	38
H6	4182.43	3785.57	4909.17	44
H13A	859.72	3375.34	2276.29	61
H13B	1177.05	2825.32	1295.99	61
H13C	1780.18	4013.47	1583.41	61
H10	1820.63	1158.92	5353.68	44
H21	3019.46	614.43	-1154.09	52
H7	4503.79	3941.53	6502.36	55
H9	2131.91	1347.43	6937.88	58
H8	3462.44	2731.71	7506.29	61
H12A	5930.71	1877.82	813.96	82
H12B	5175.79	711.95	873.9	82
H12C	6334.89	926.93	1541.03	82
H16A	3620.13	5716.93	560.48	38
H16B	4993.97	6016.33	904.56	38
H17A	4994.86	5740.26	-709.21	39
H17B	5845.62	4797.65	-225.72	39
H17C	4666.21	5848.58	-672.1	36
H17D	3420	5567.25	-112.98	36
H16C	5858.99	4935.83	480.05	43
H16D	5079.37	5960.44	913.46	43

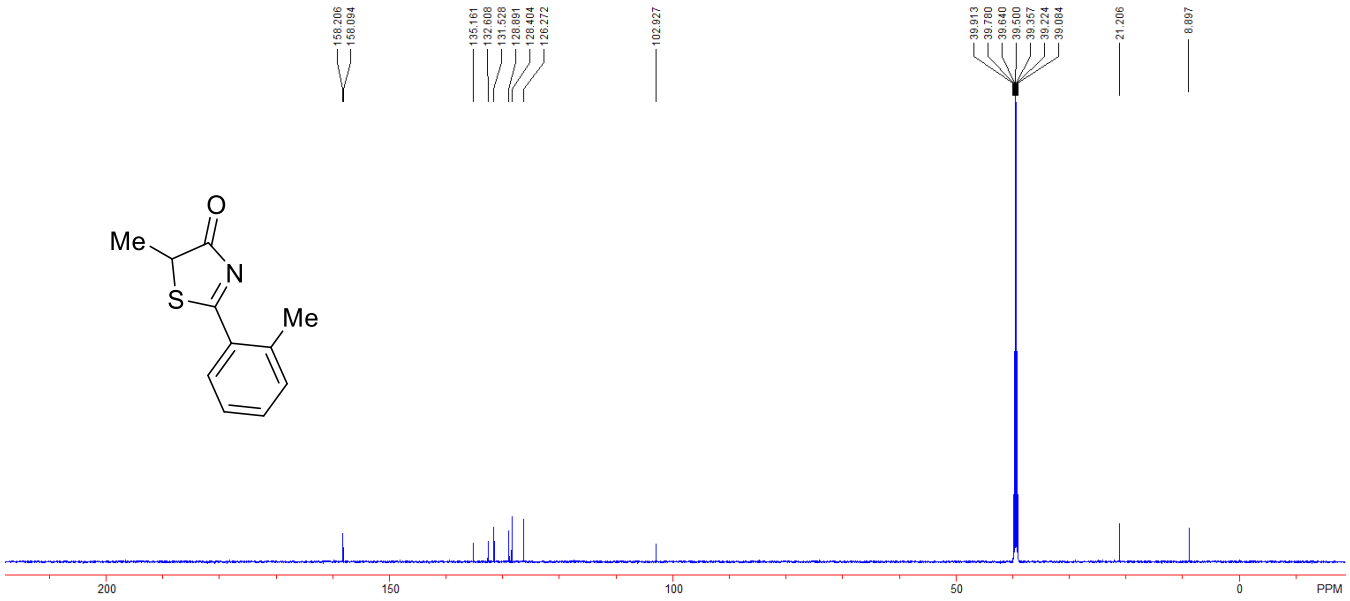
Table 8 Atomic Occupancy for 240514lty.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
H18A	0.625(8)	H18B	0.625(8)	H18C	0.375(8)
H18D	0.375(8)	H15A	0.625(8)	H15B	0.625(8)
H15C	0.375(8)	H15D	0.375(8)	C16	0.625(8)
H16A	0.625(8)	H16B	0.625(8)	C17	0.625(8)
H17A	0.625(8)	H17B	0.625(8)	C17A	0.375(8)
H17C	0.375(8)	H17D	0.375(8)	C16A	0.375(8)
H16C	0.375(8)	H16D	0.375(8)		

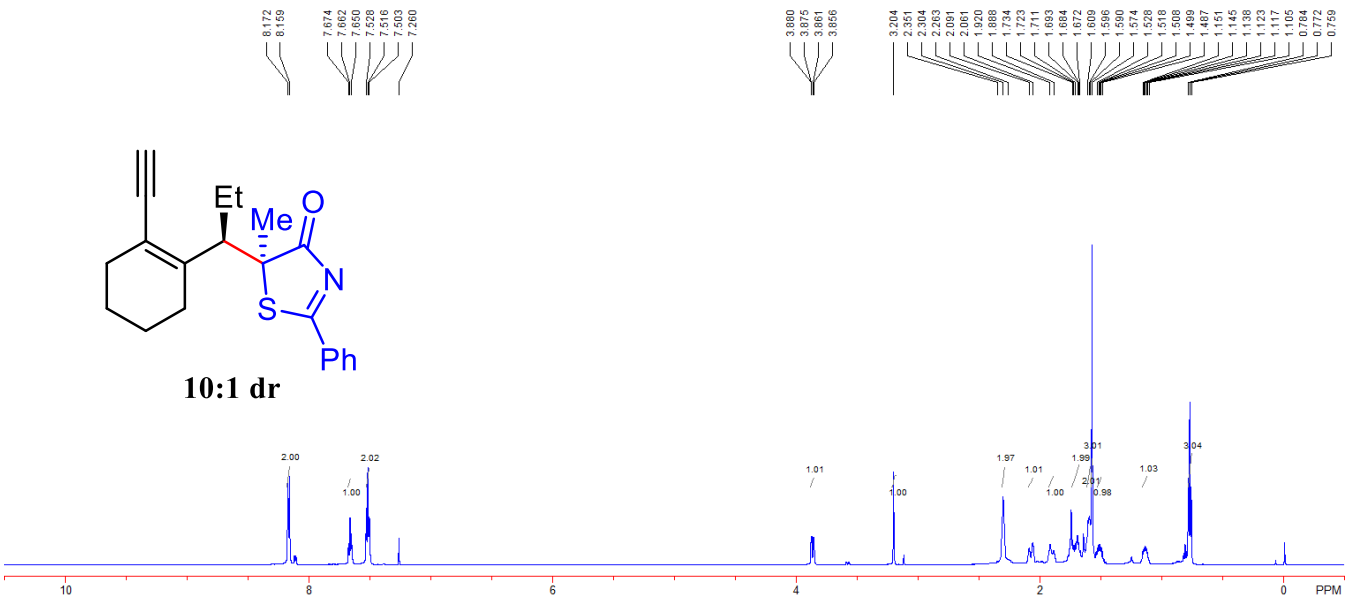
8. ^{1}H, ^{13}C and ^{19}F NMR Spectra for New Compounds

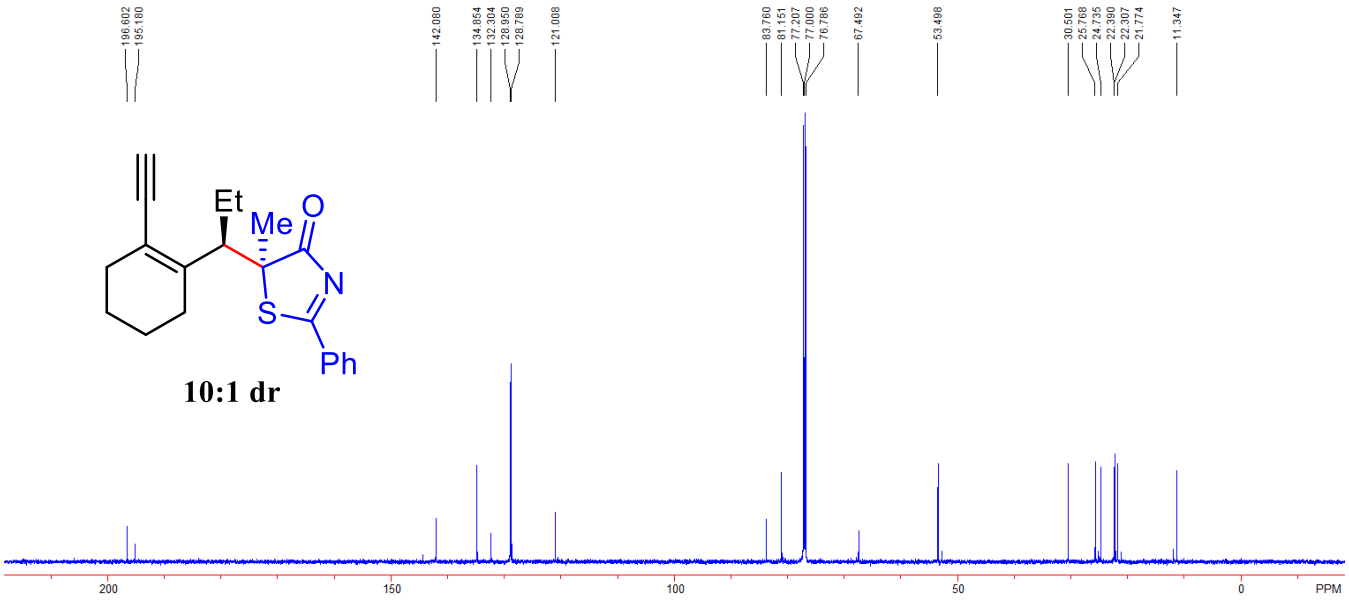
^{1}H and ^{13}C NMR (DMSO-d_6) Spectra for Compound **2f**



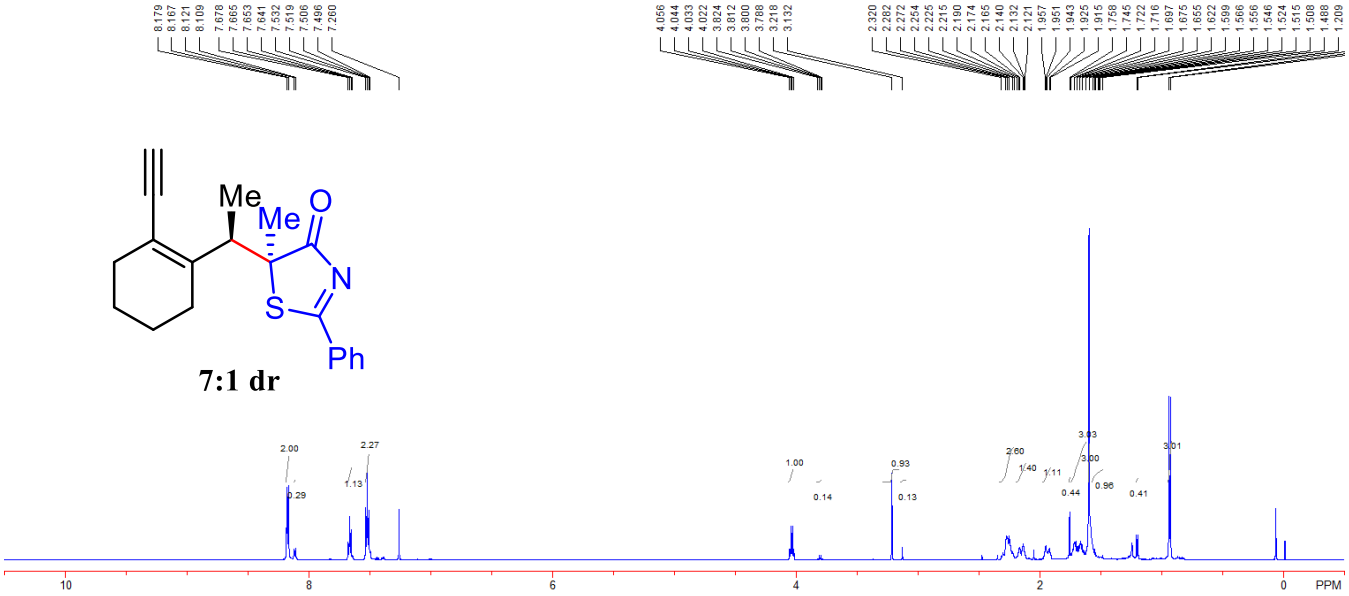


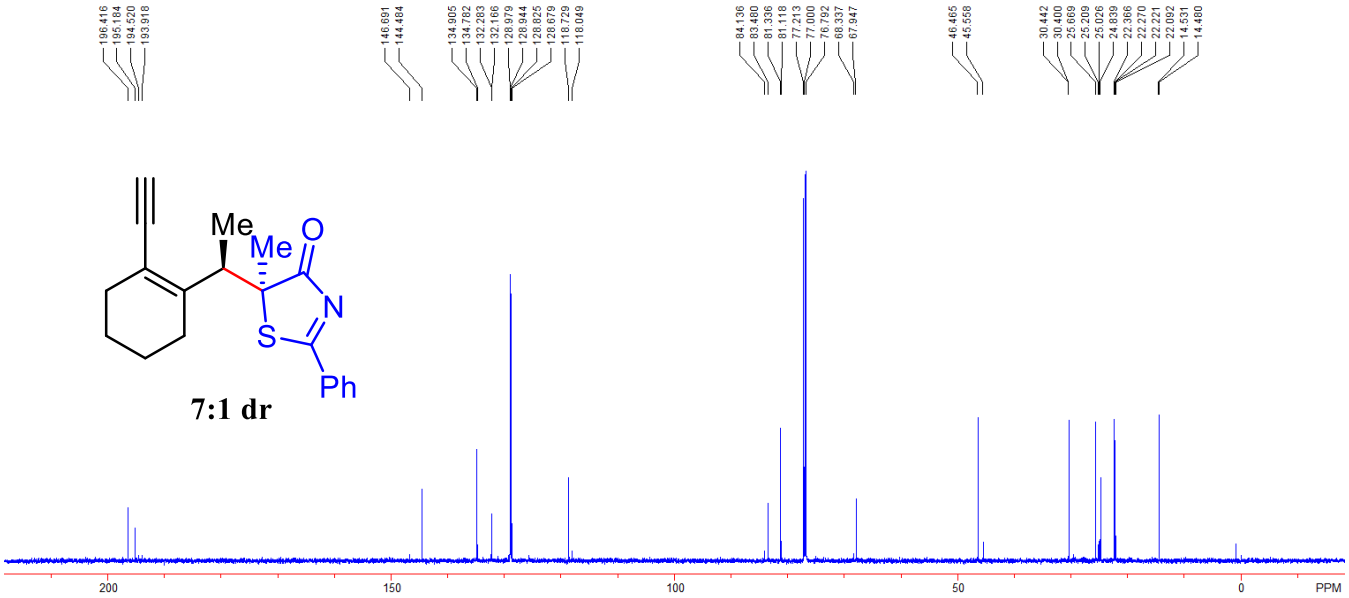
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3a**



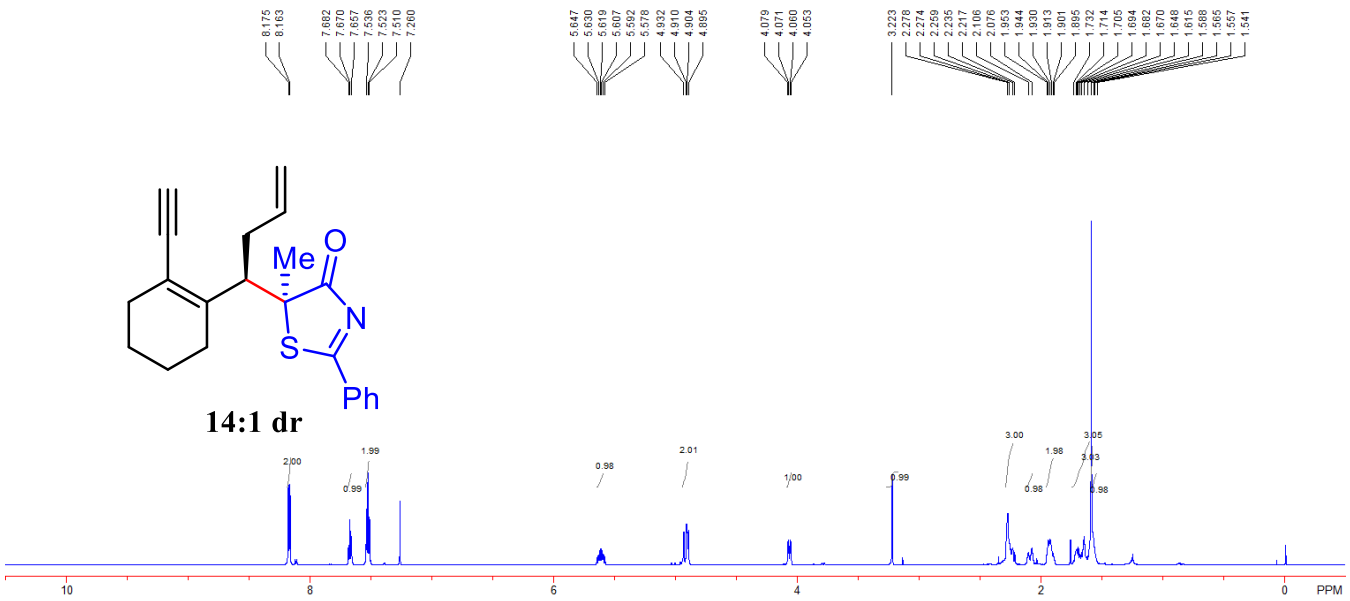


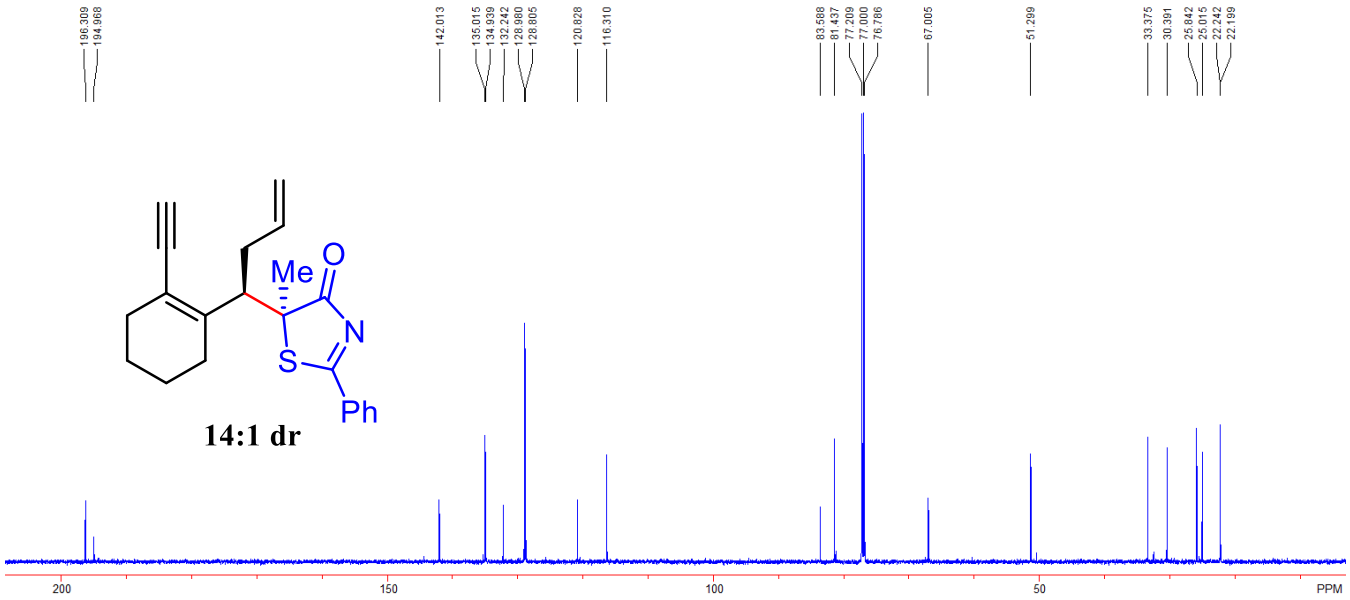
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3b**



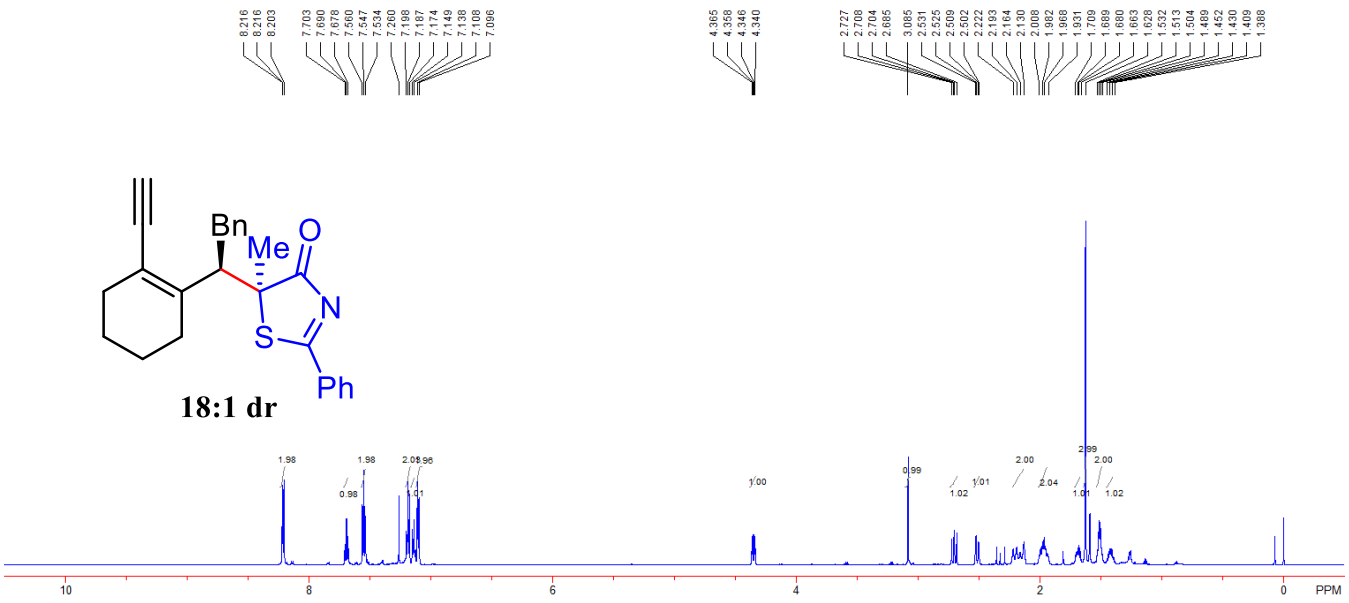


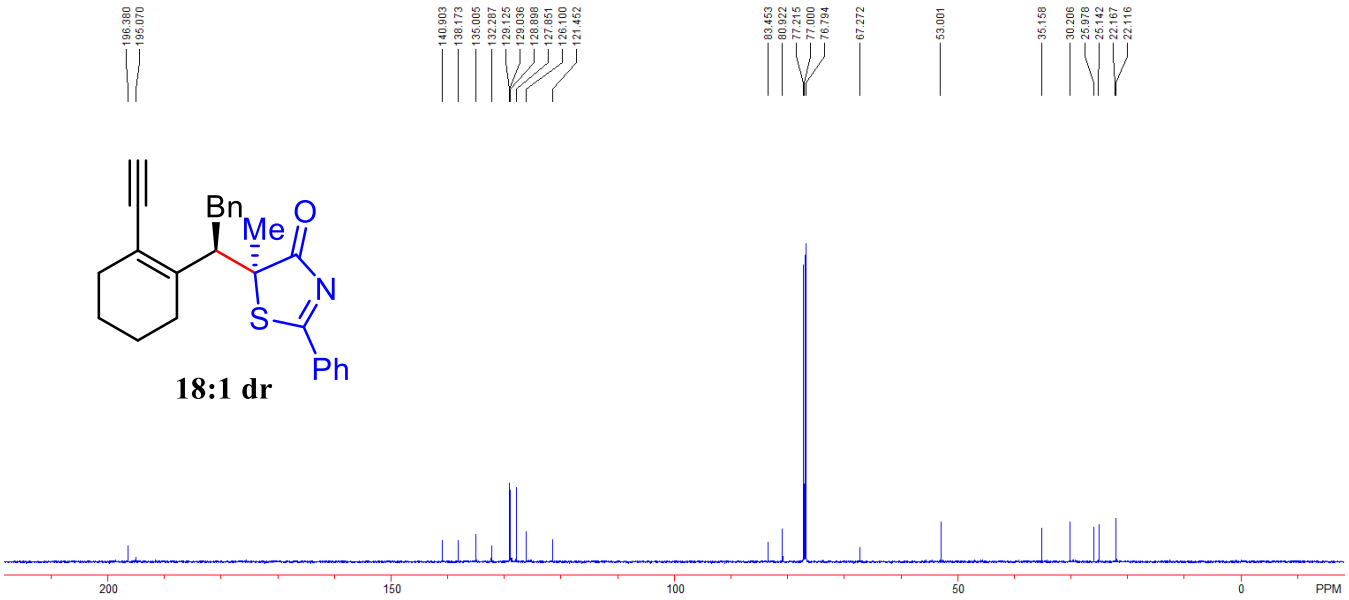
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3c**



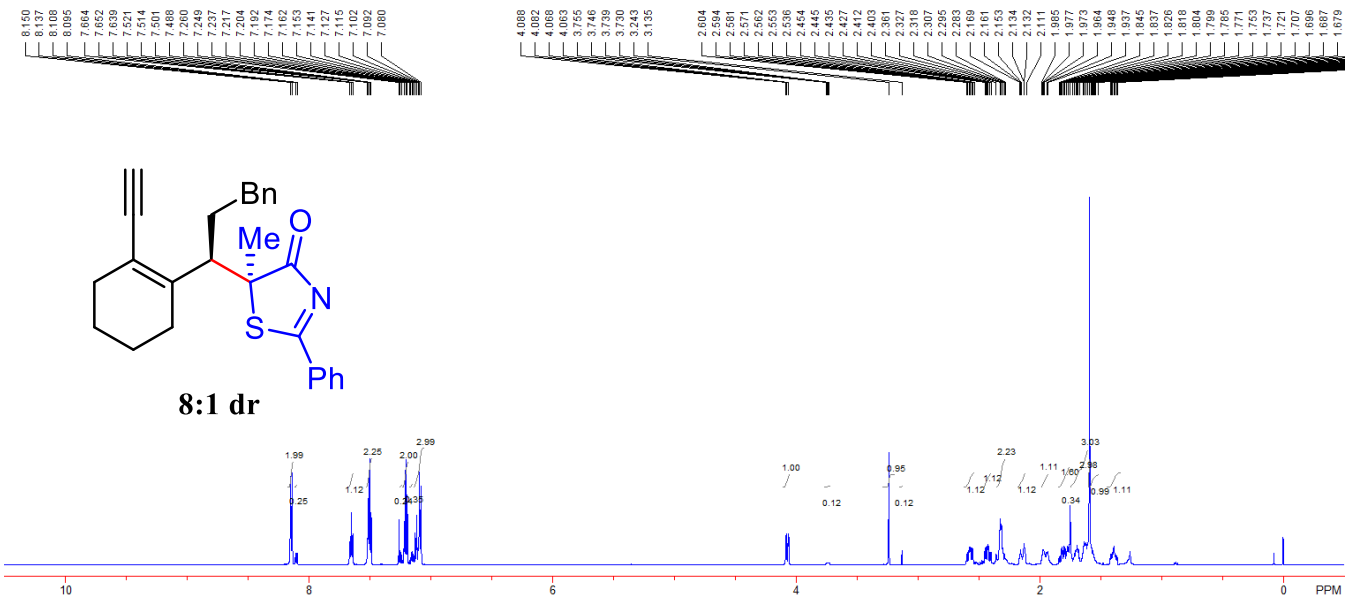


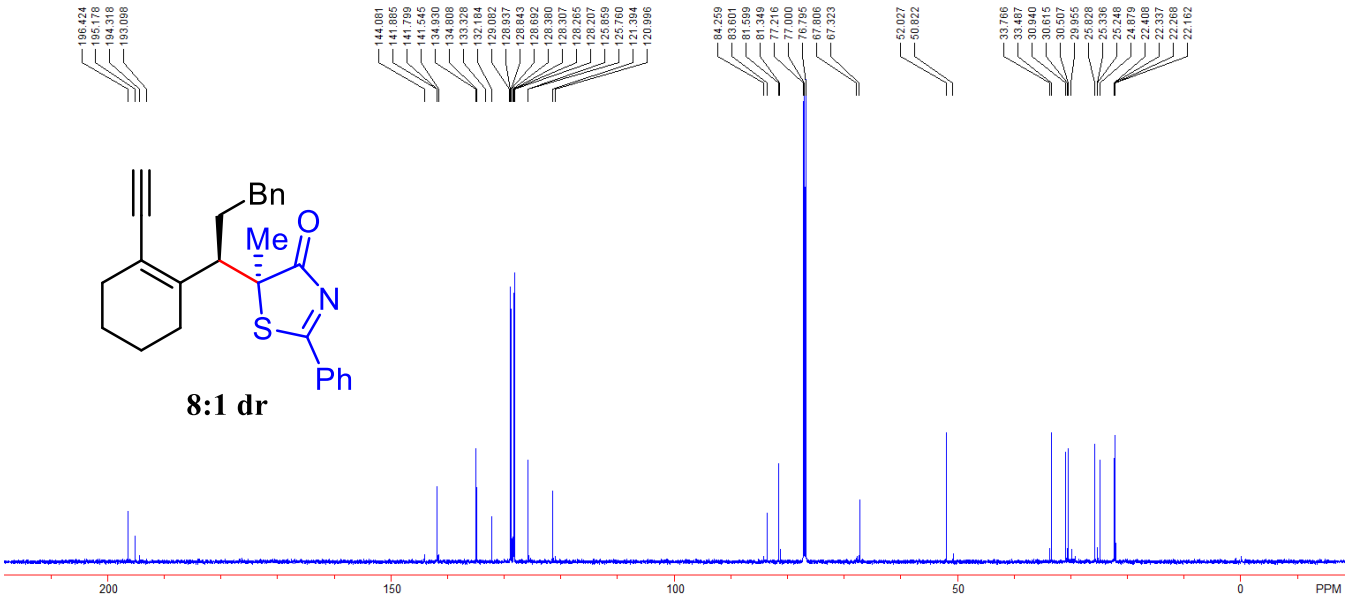
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3d**



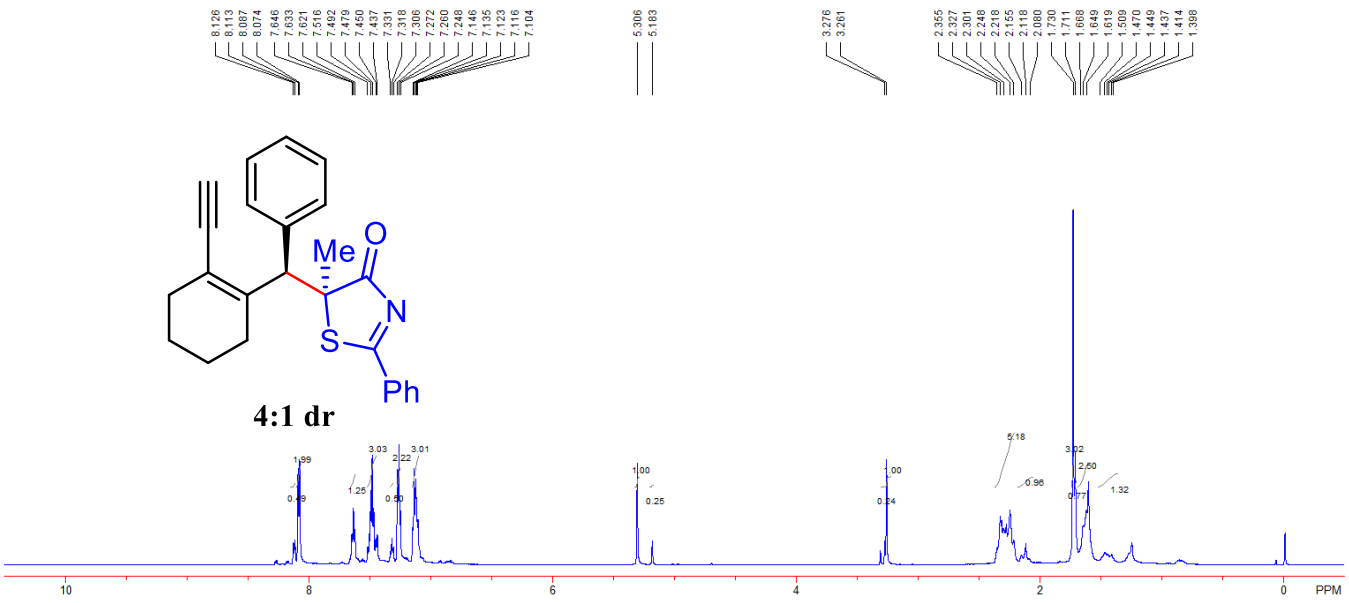


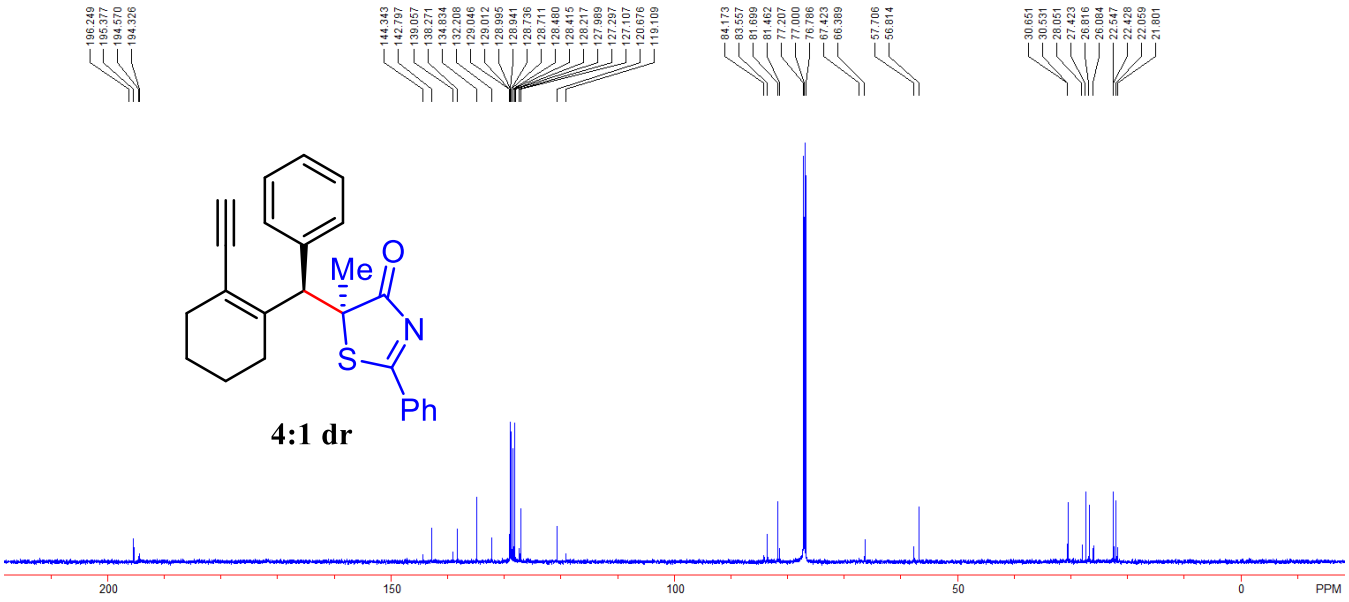
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3e**



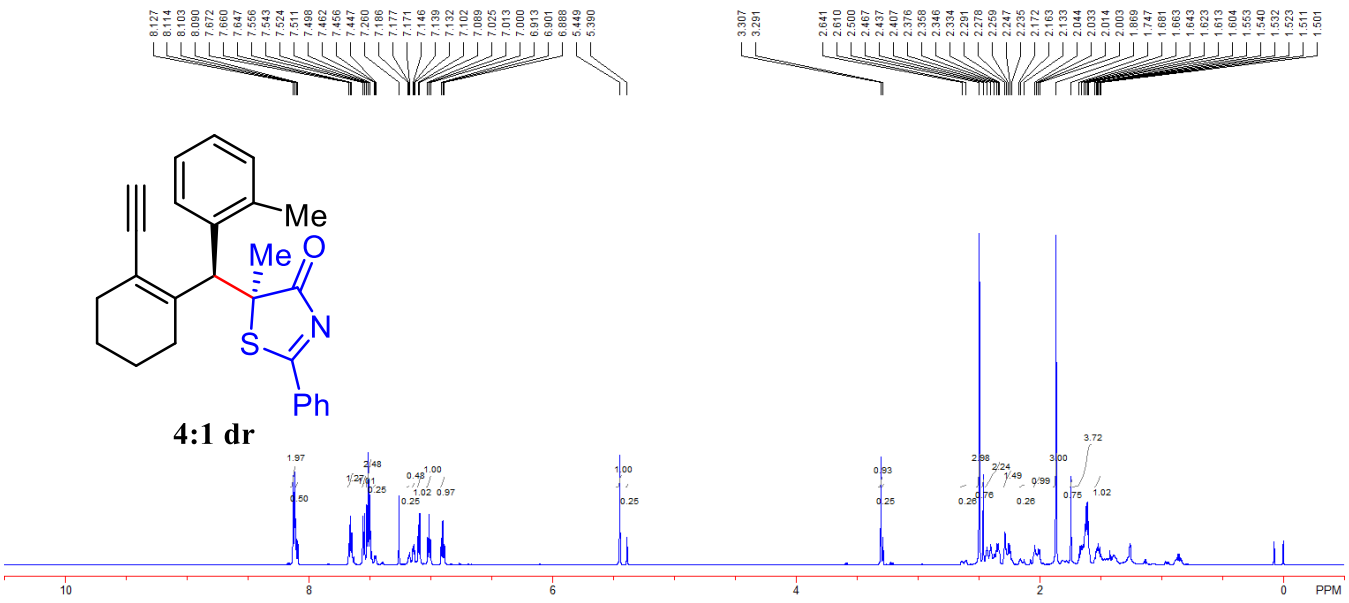


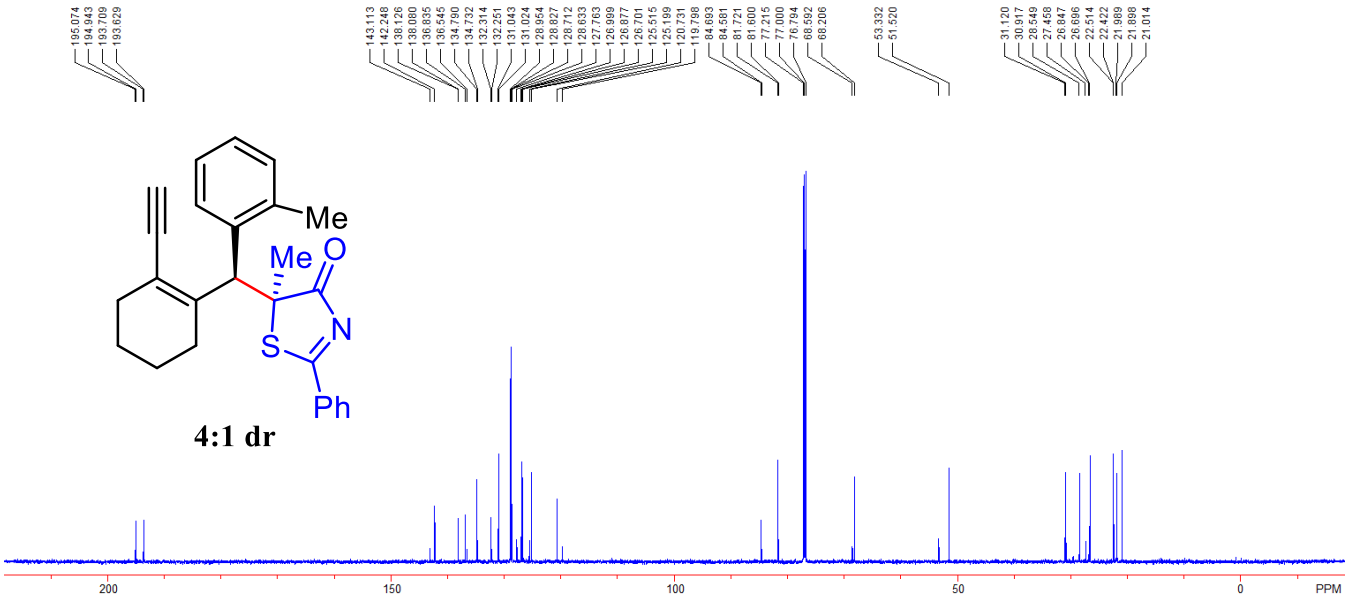
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3f**



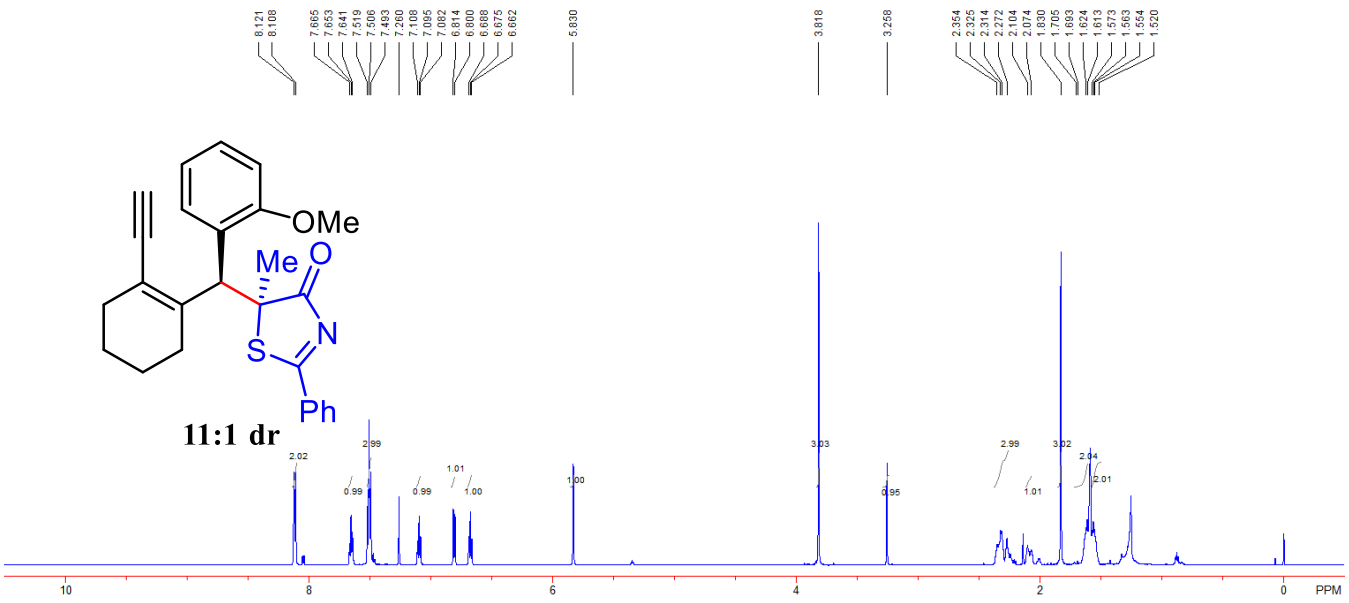


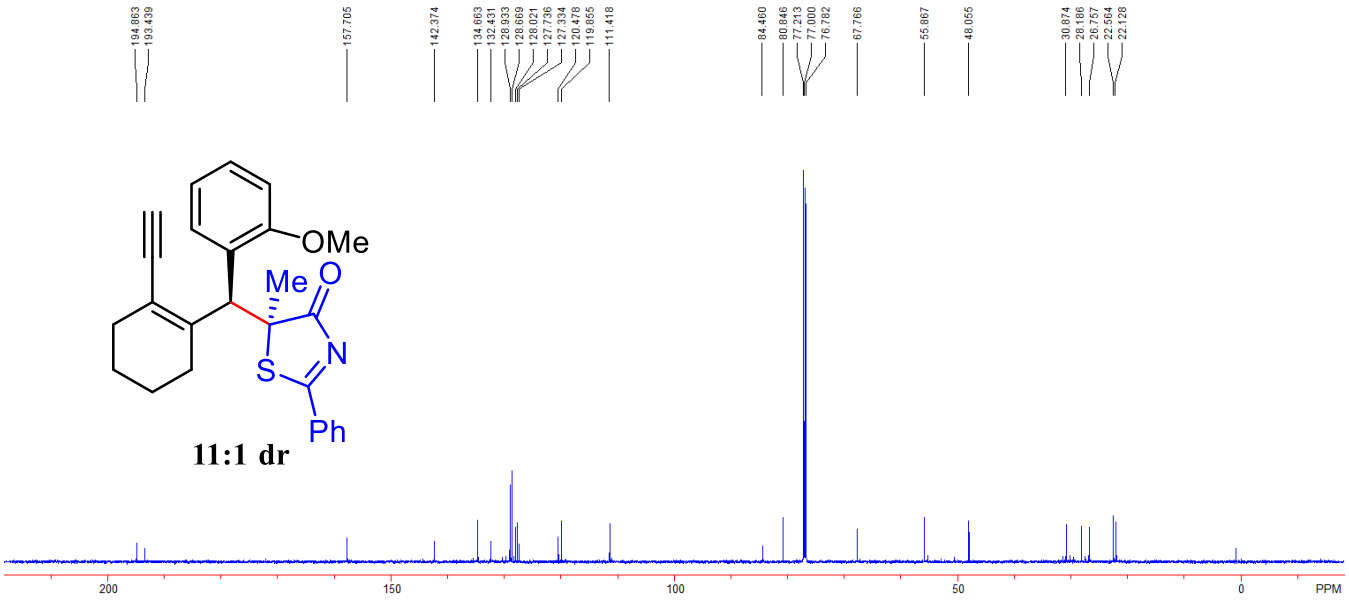
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3g**



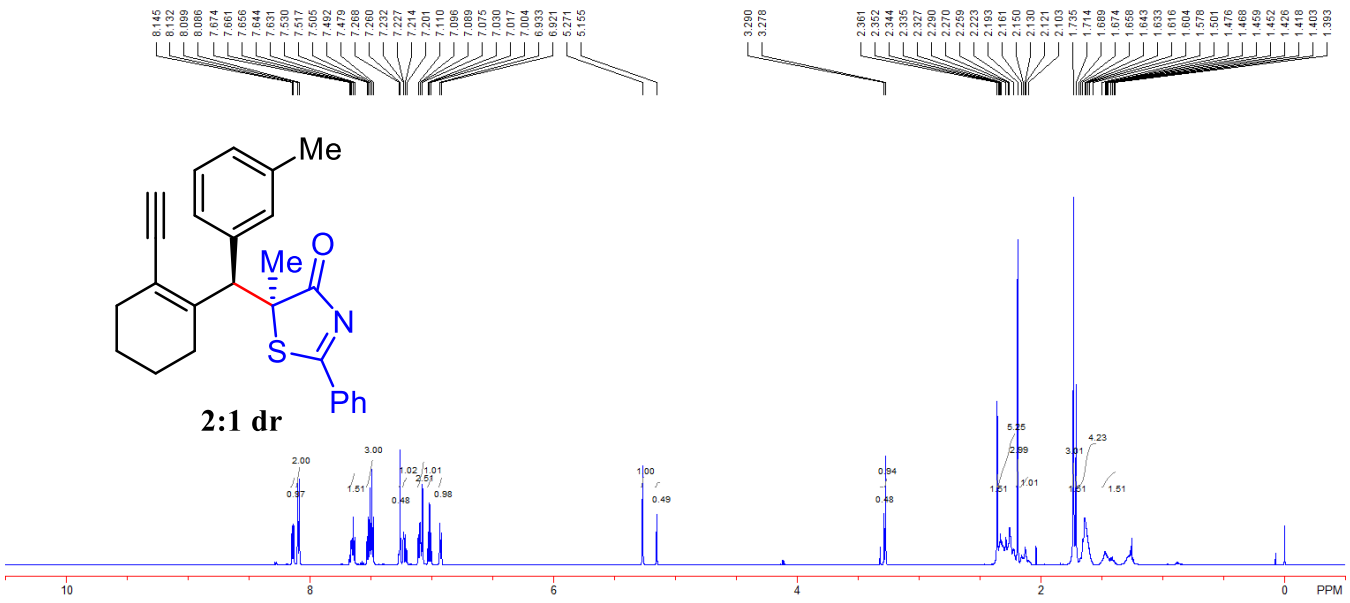


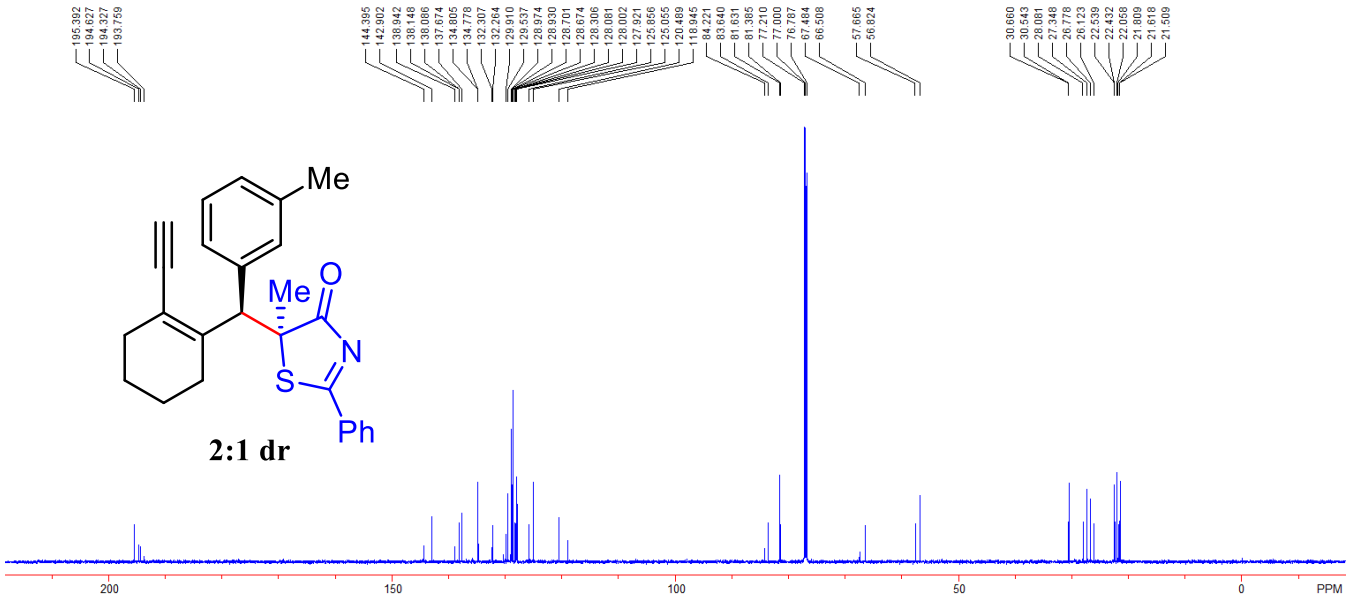
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3h**



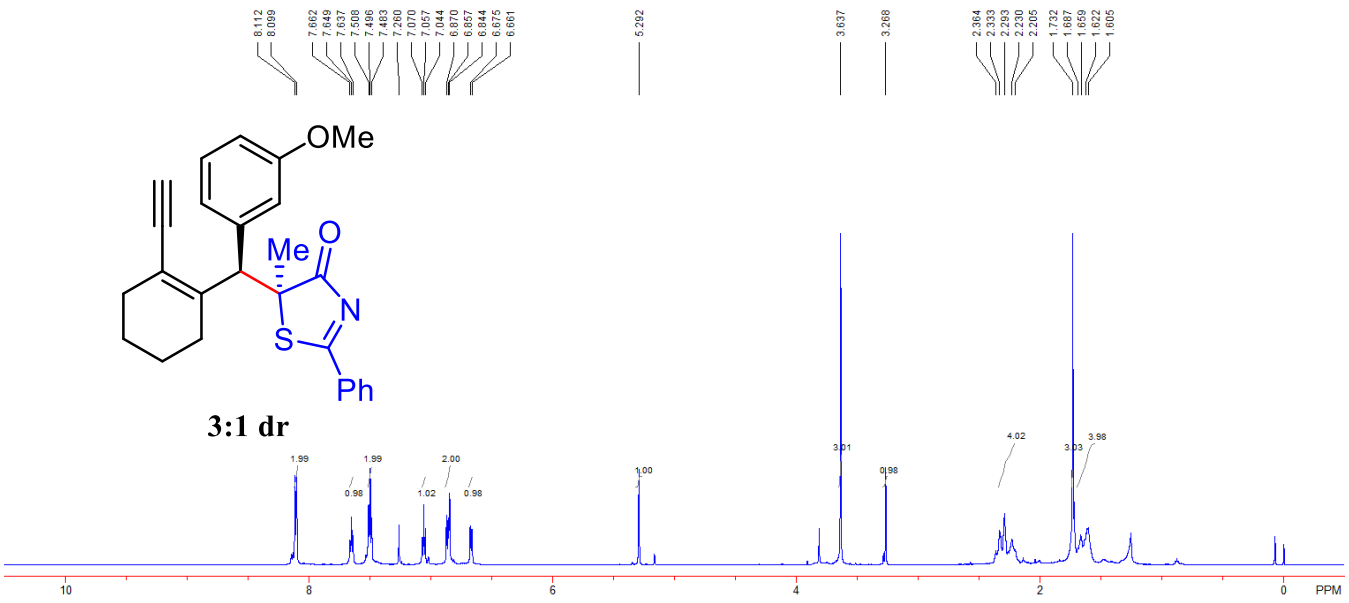


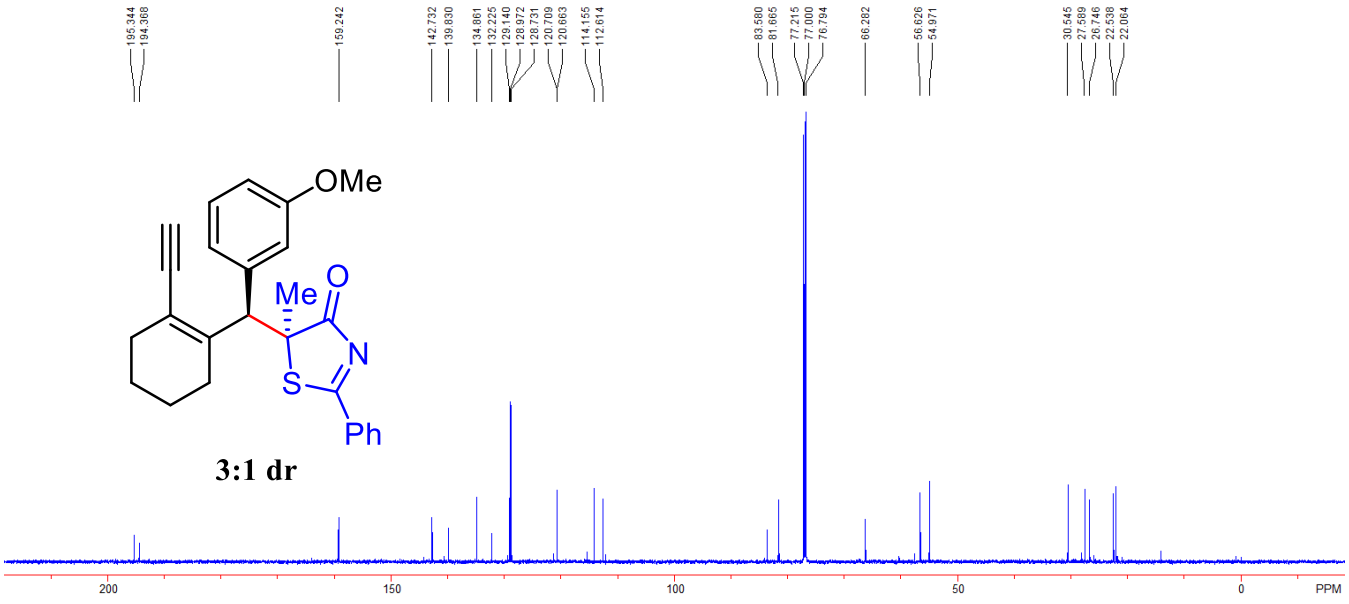
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3i**



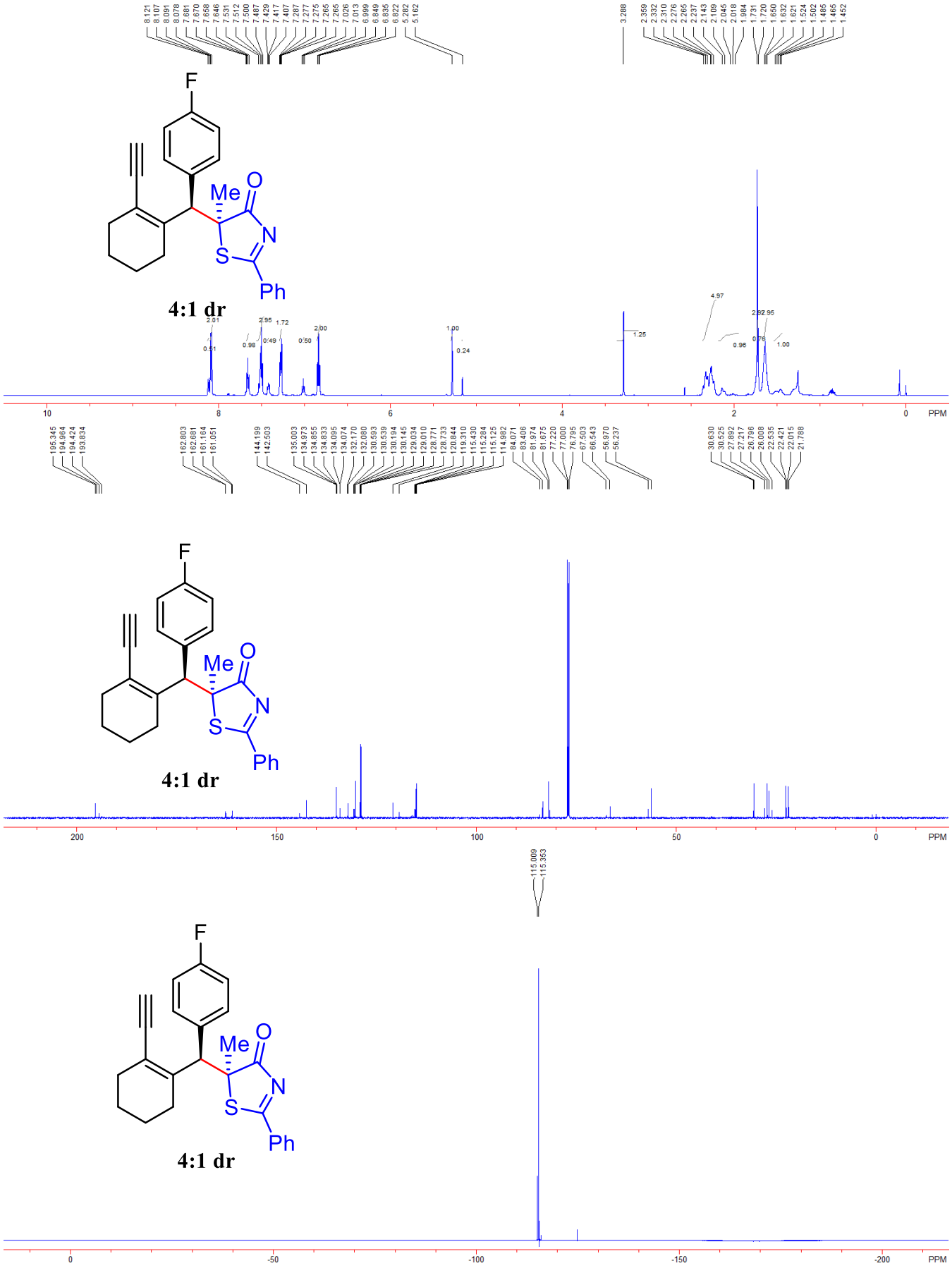


^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3j**

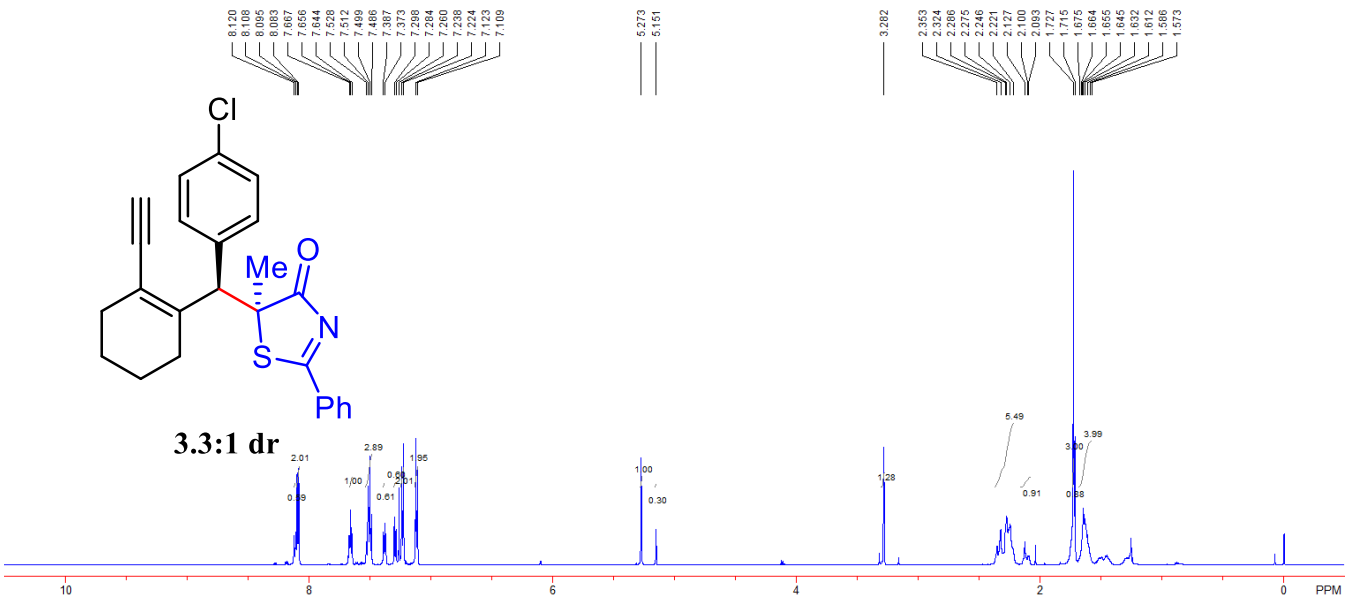


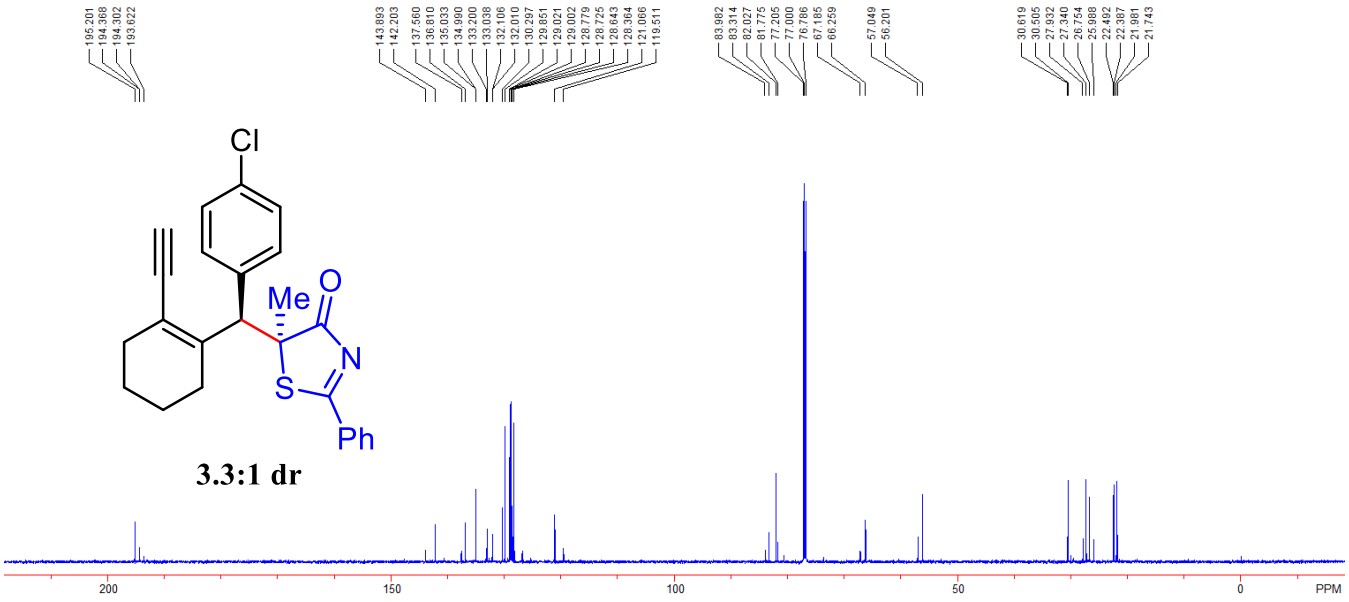


^{1}H, ^{13}C and ^{19}F NMR ($CDCl_3$) Spectra for Compound **3k**

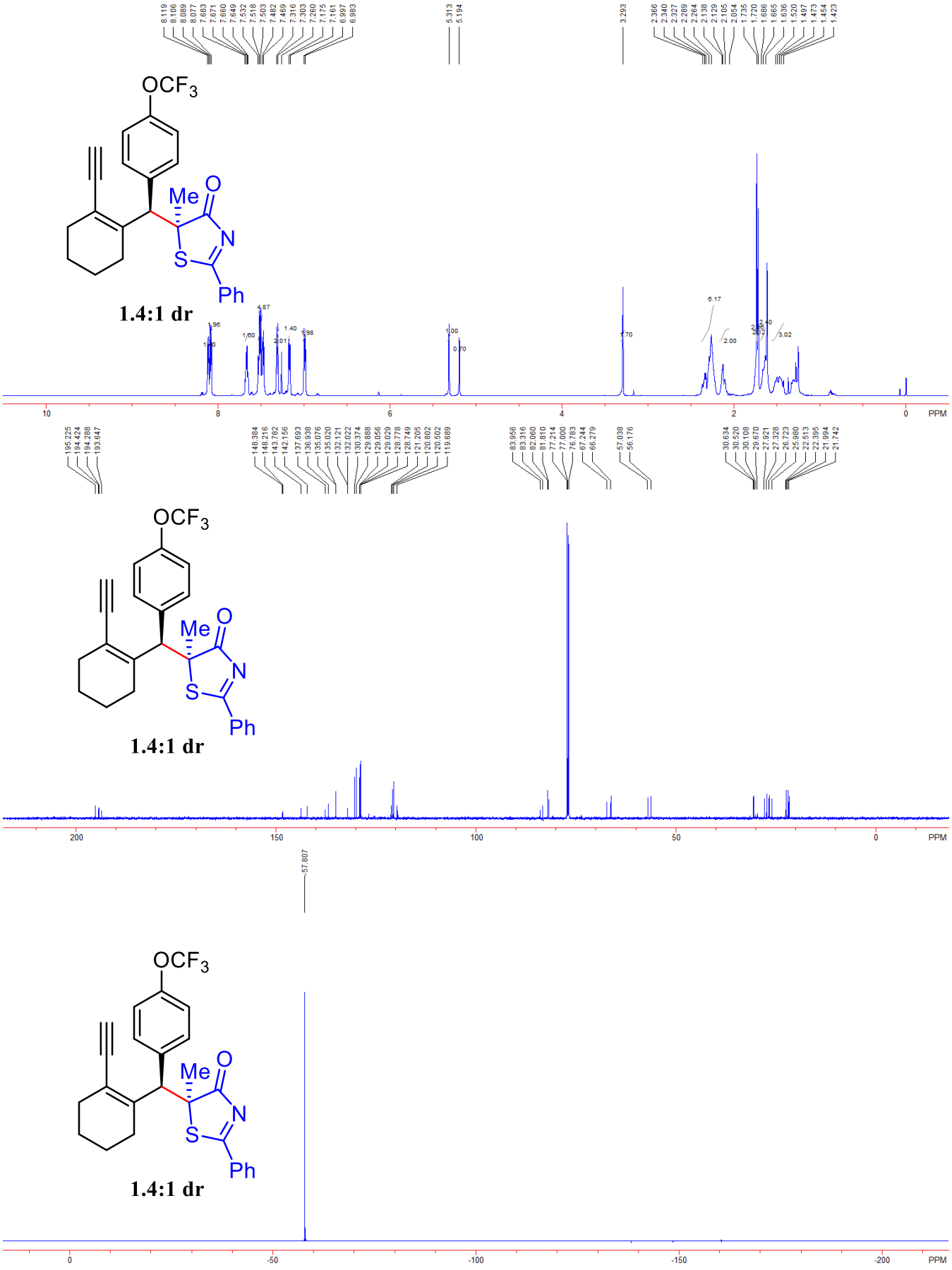


^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3l**

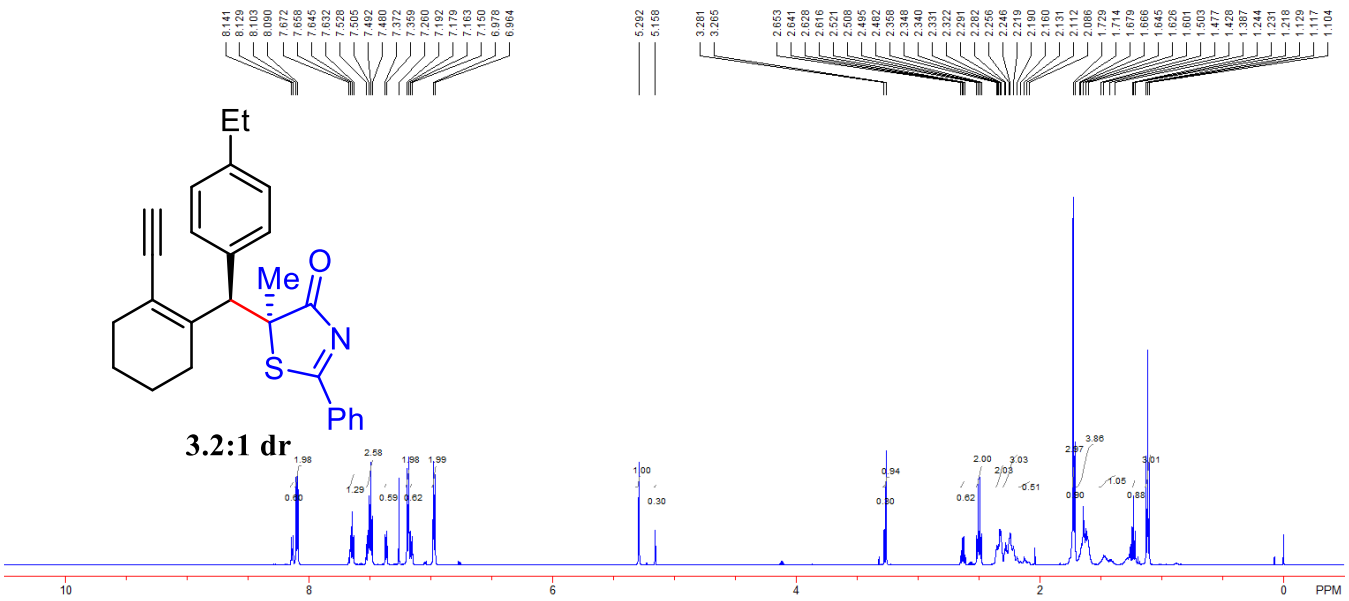


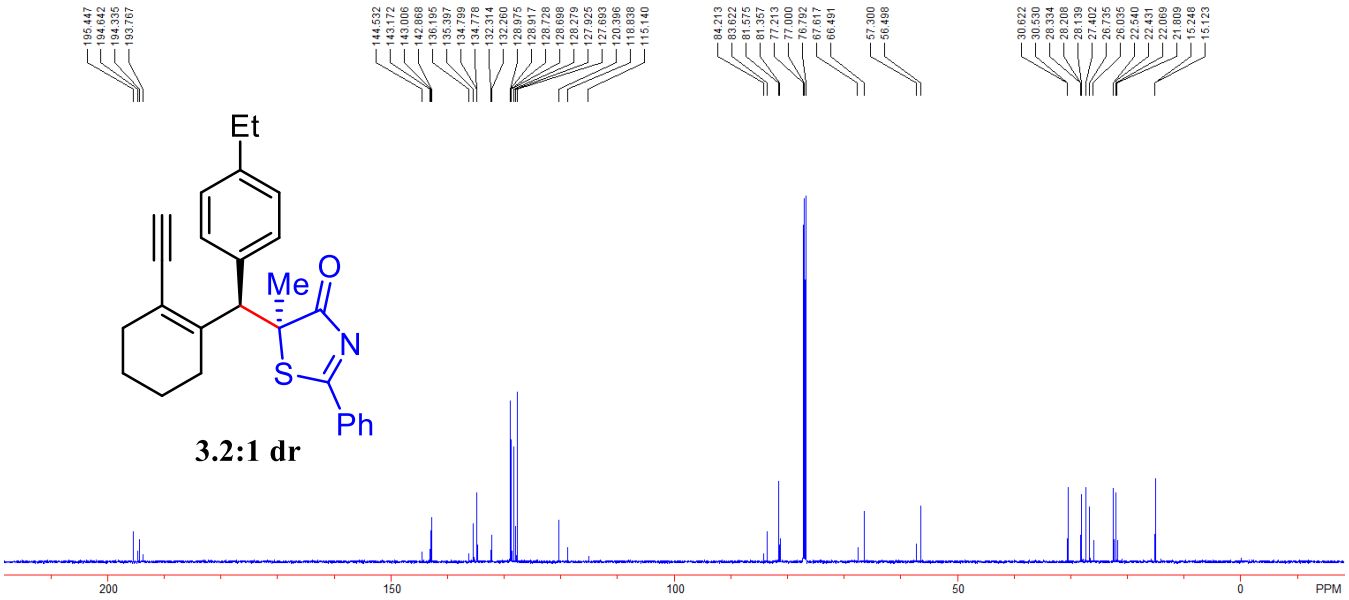


^{1}H, ^{13}C and ^{19}F NMR ($CDCl_3$) Spectra for Compound **3m**

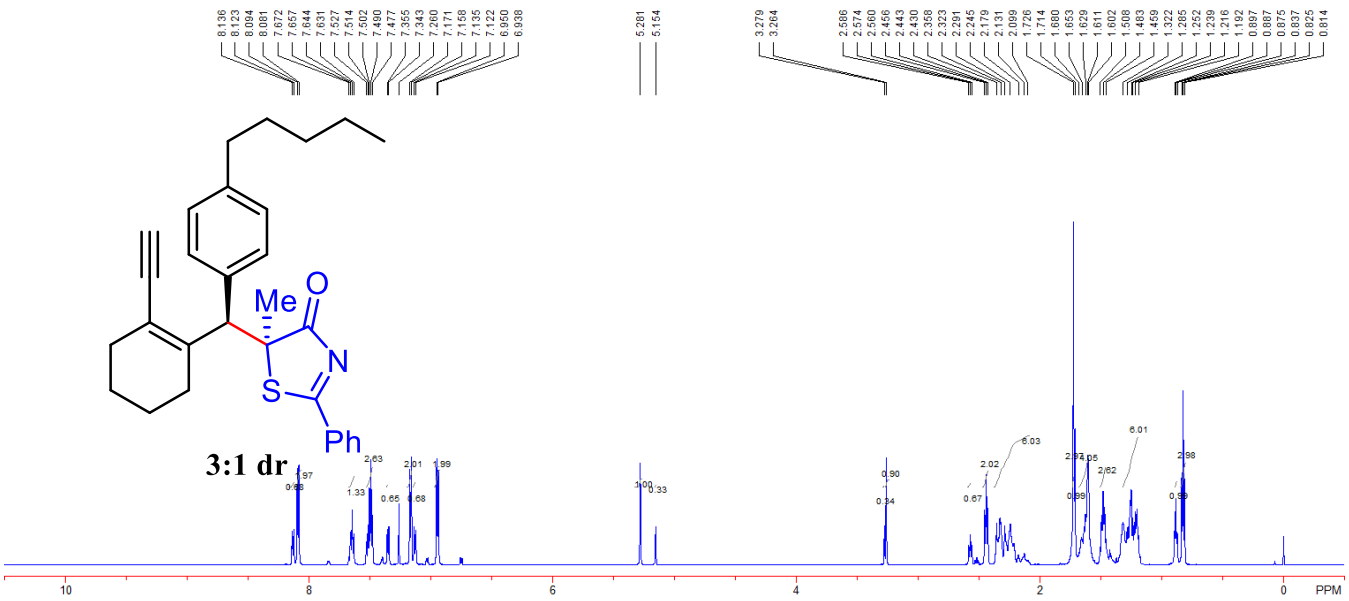


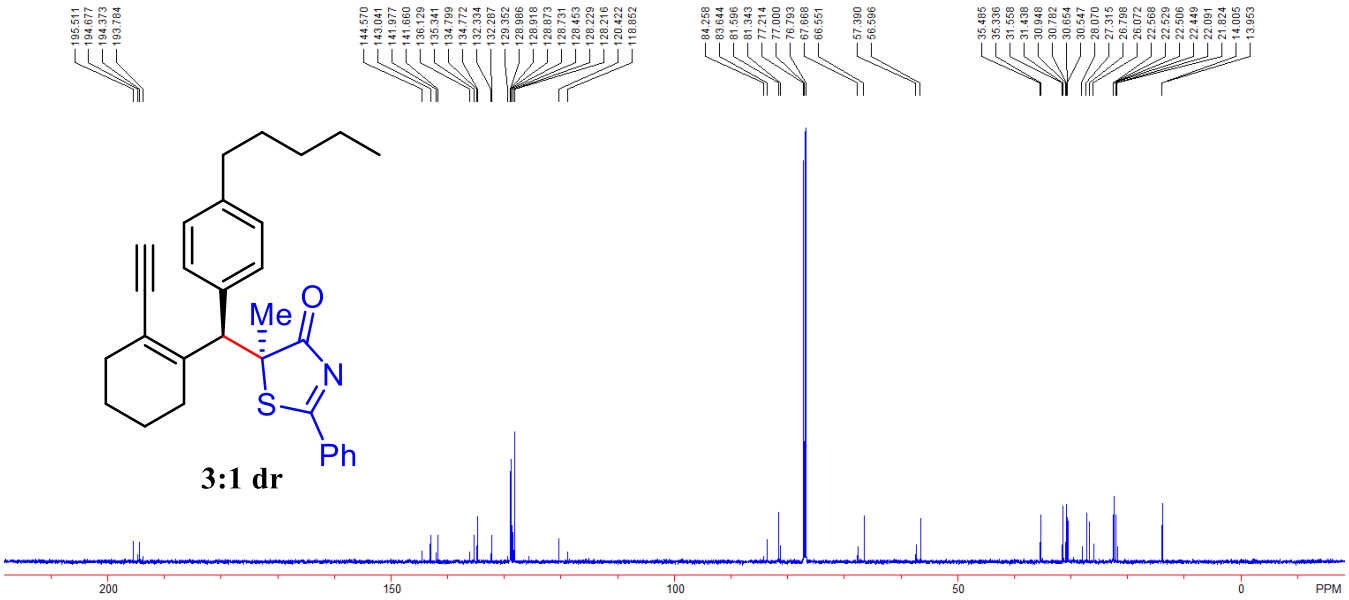
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3n**



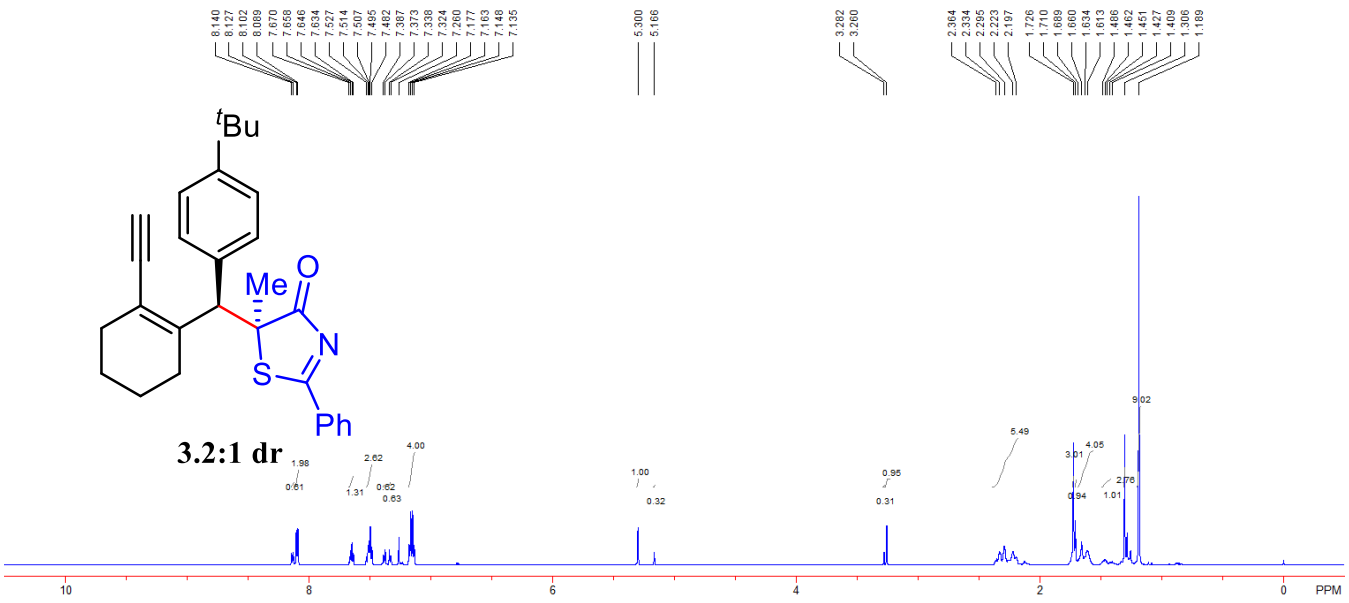


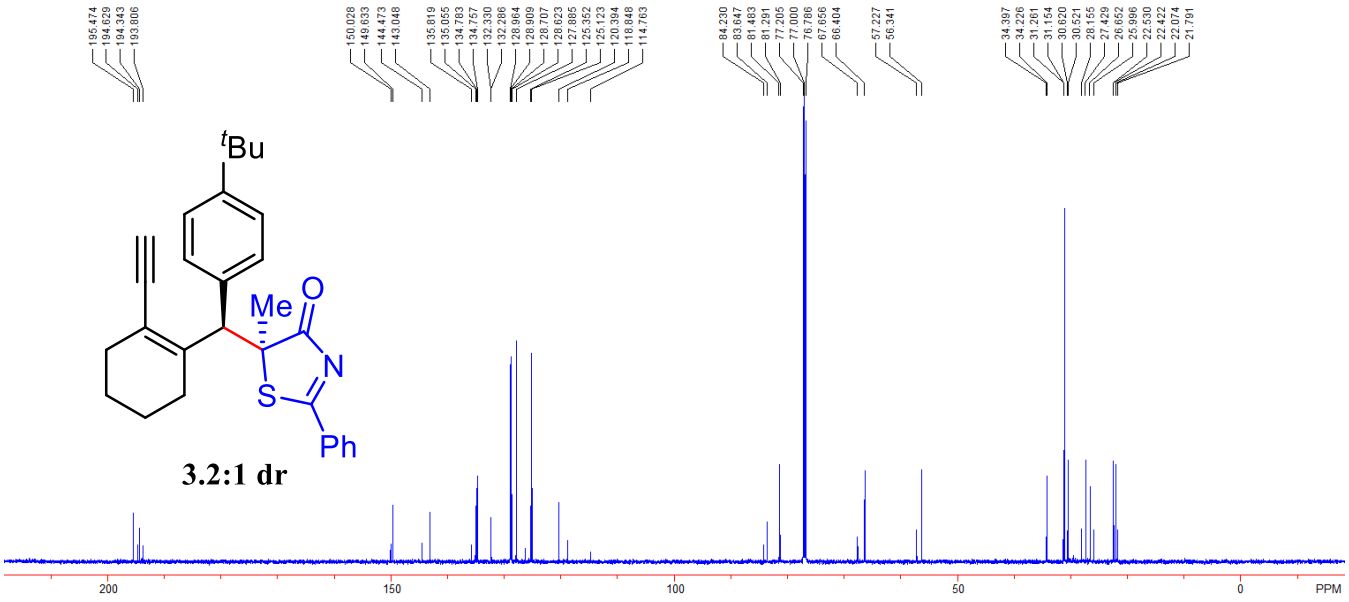
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3o**



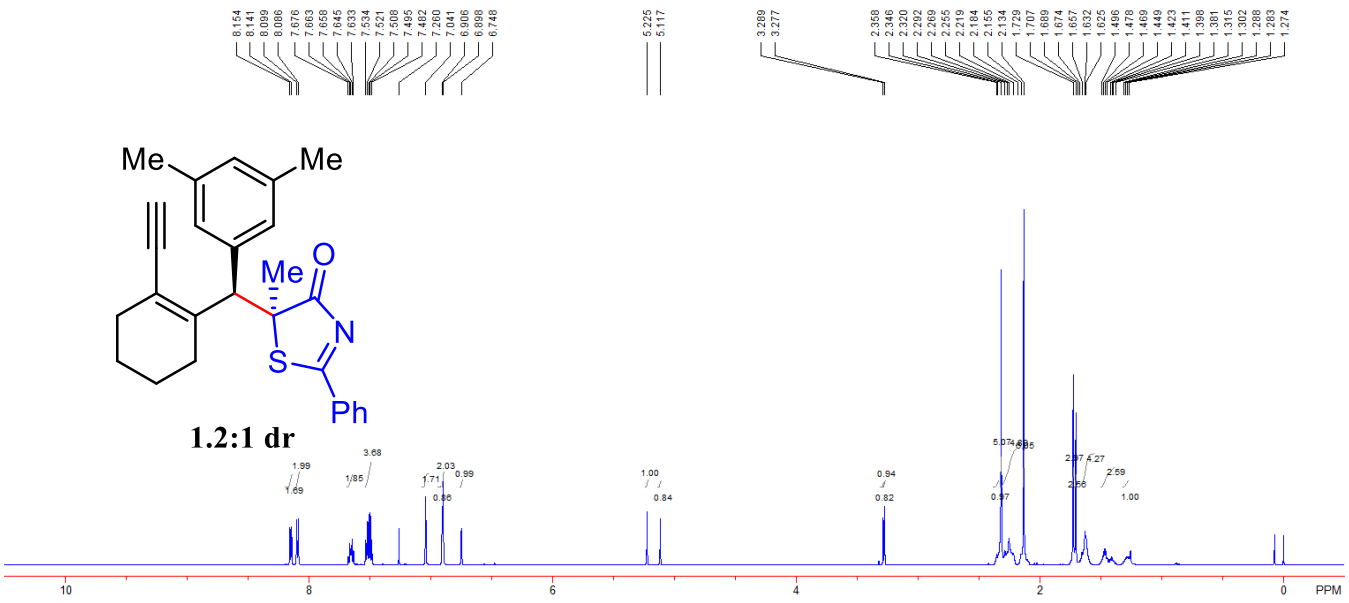


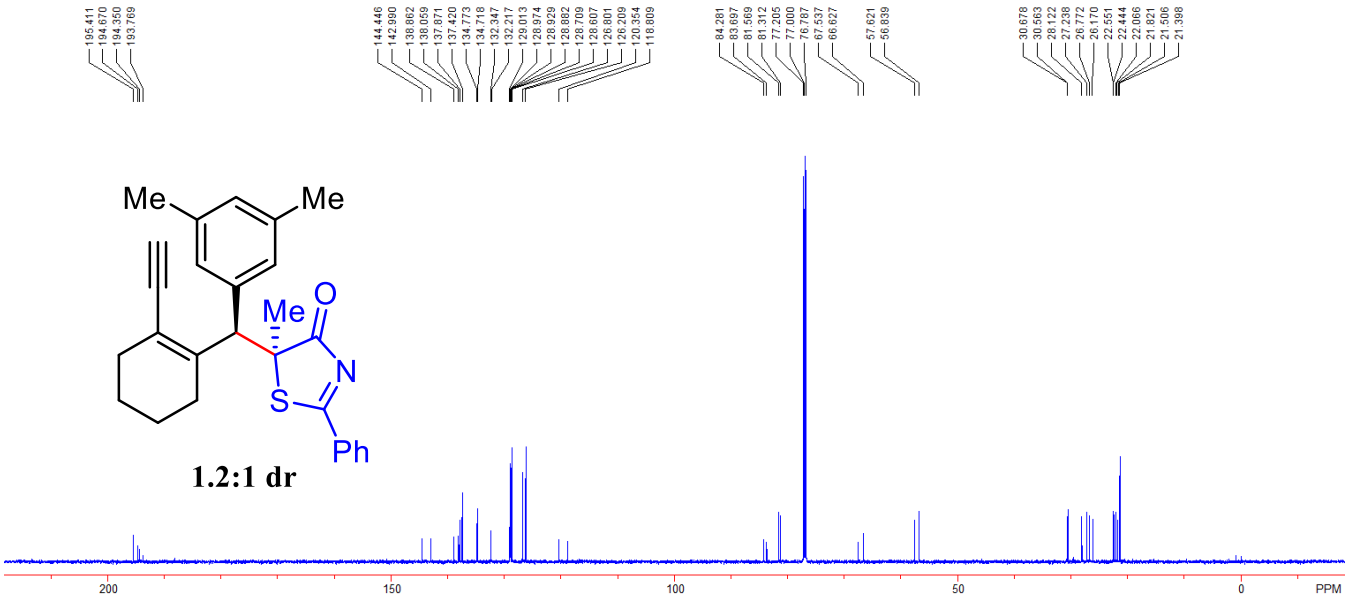
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3p**



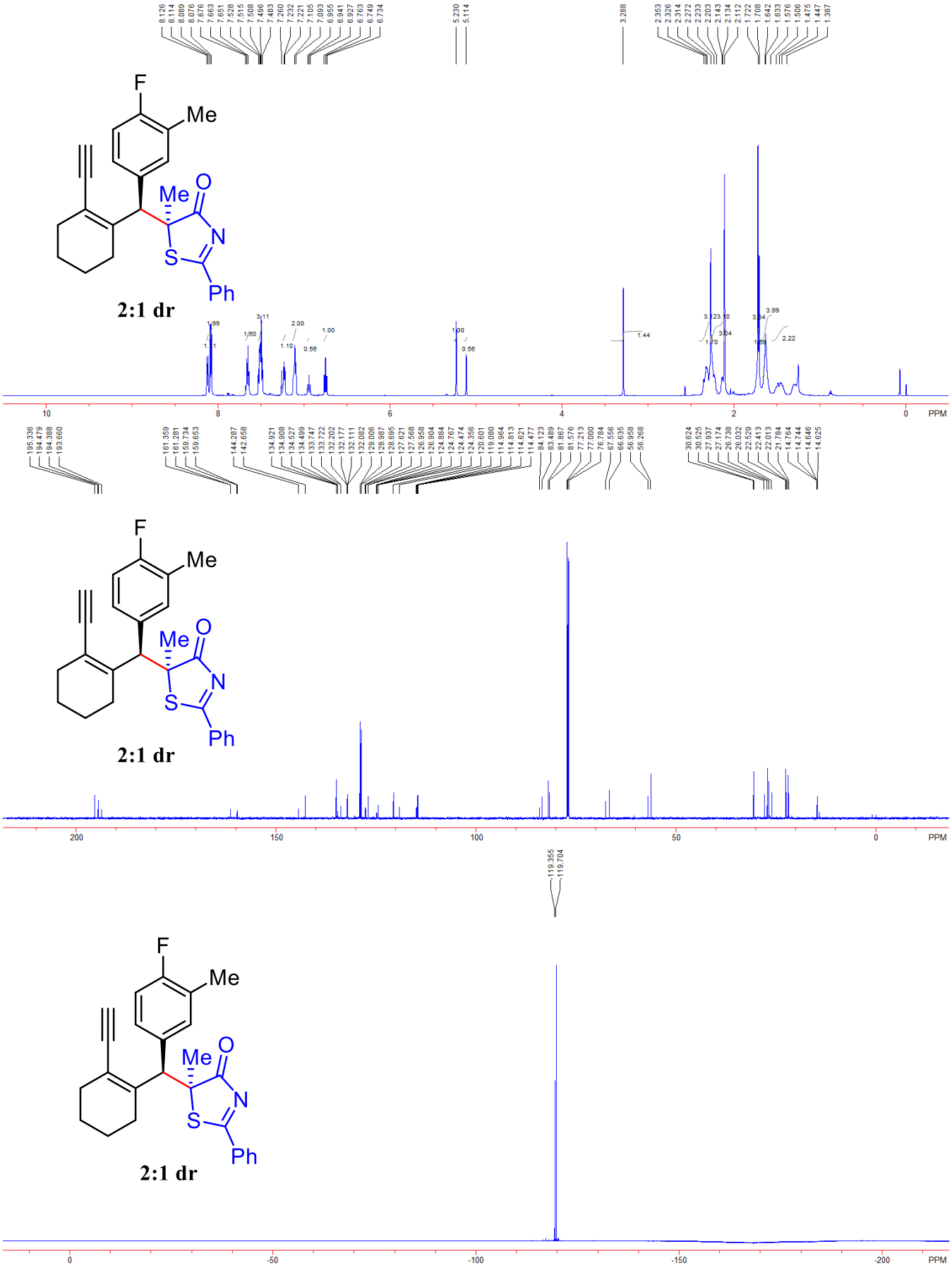


^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3q**

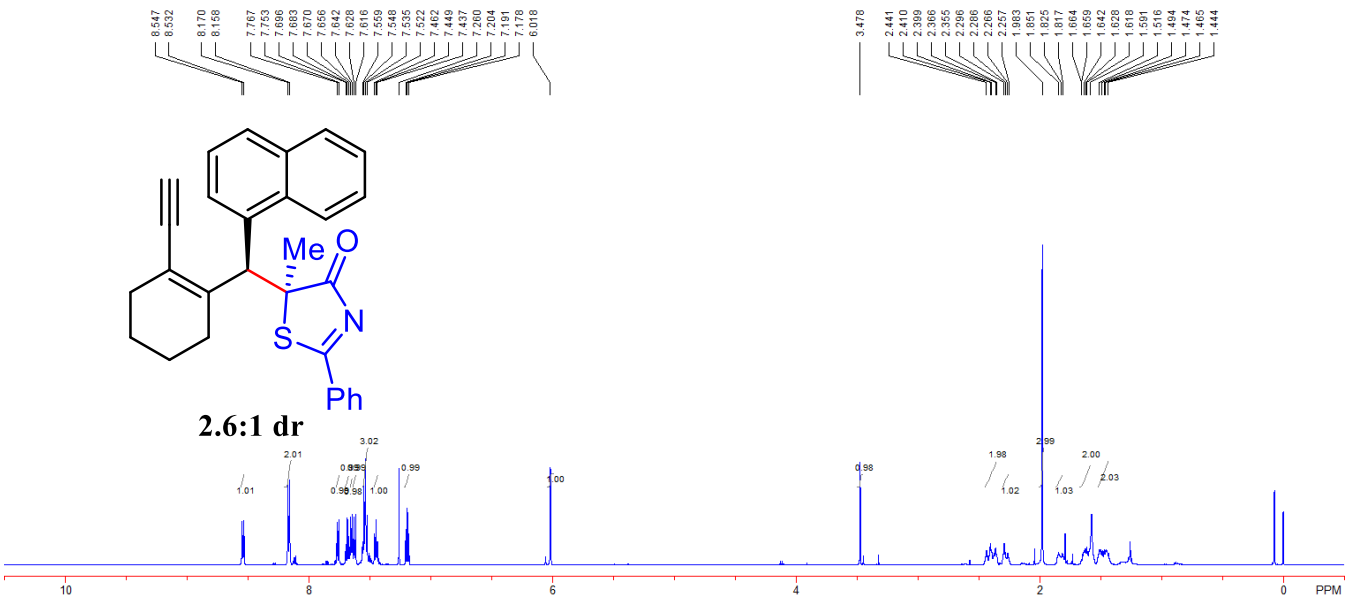


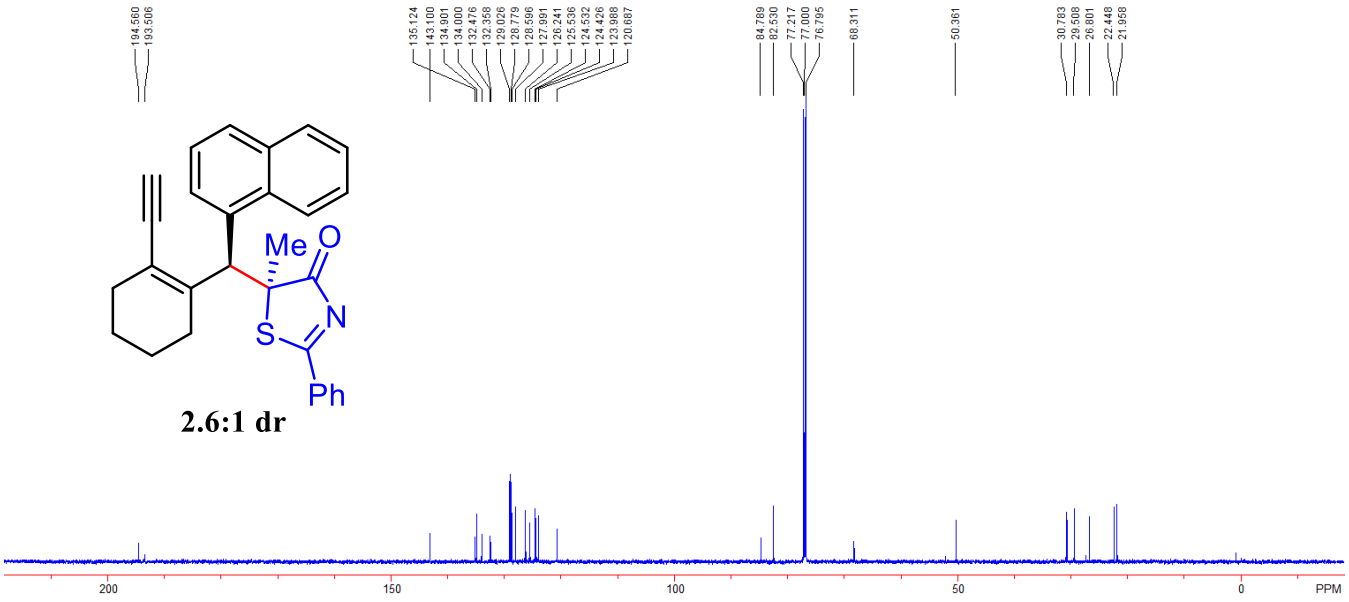


^{1}H, ^{13}C and ^{19}F NMR ($CDCl_3$) Spectra for Compound **3r**

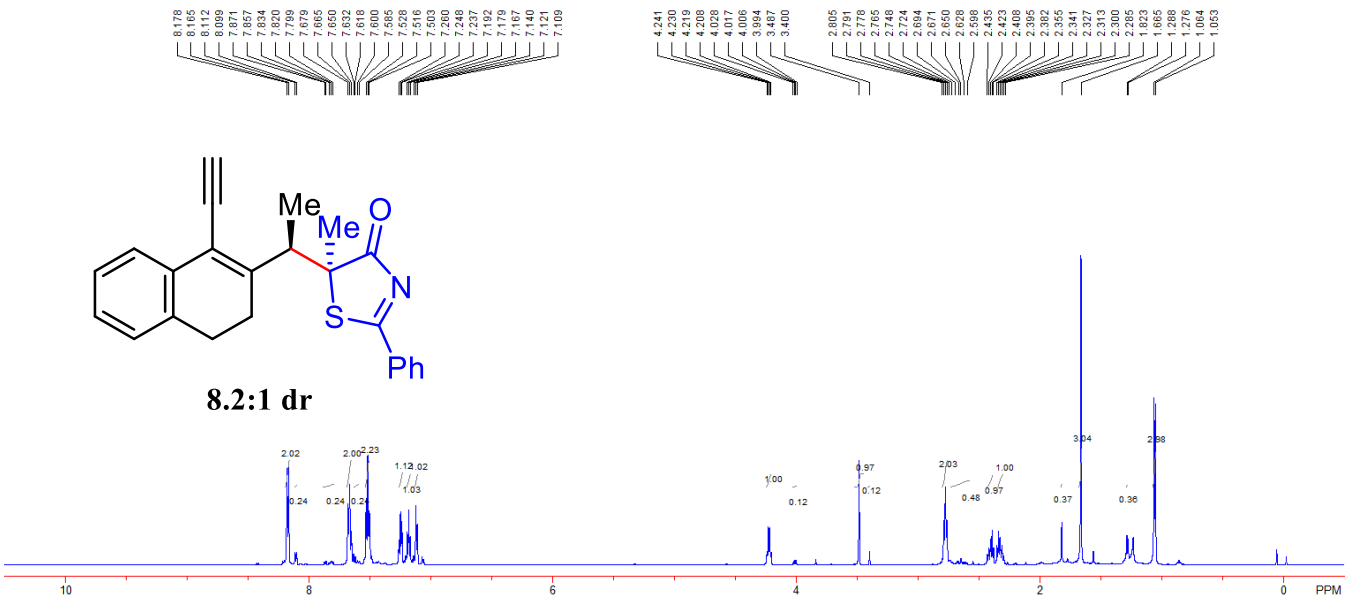


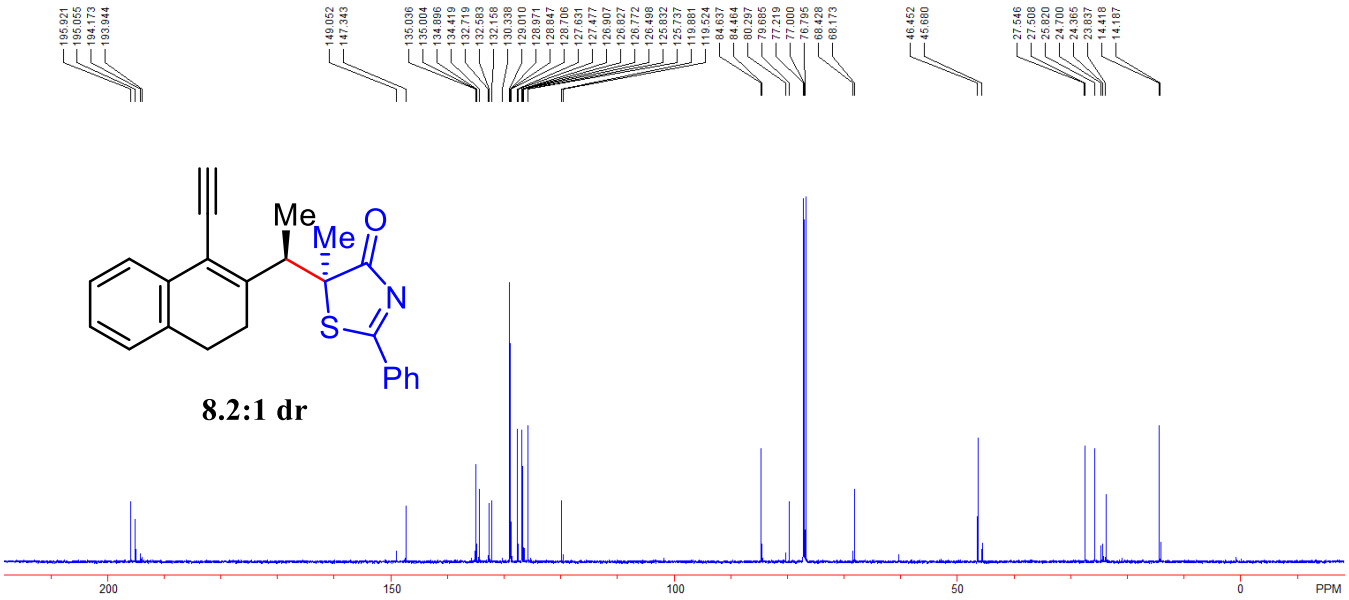
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3s**



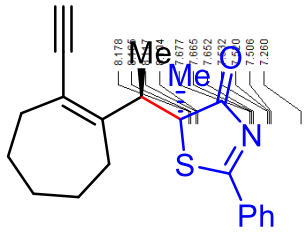


^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3t**





^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3u**



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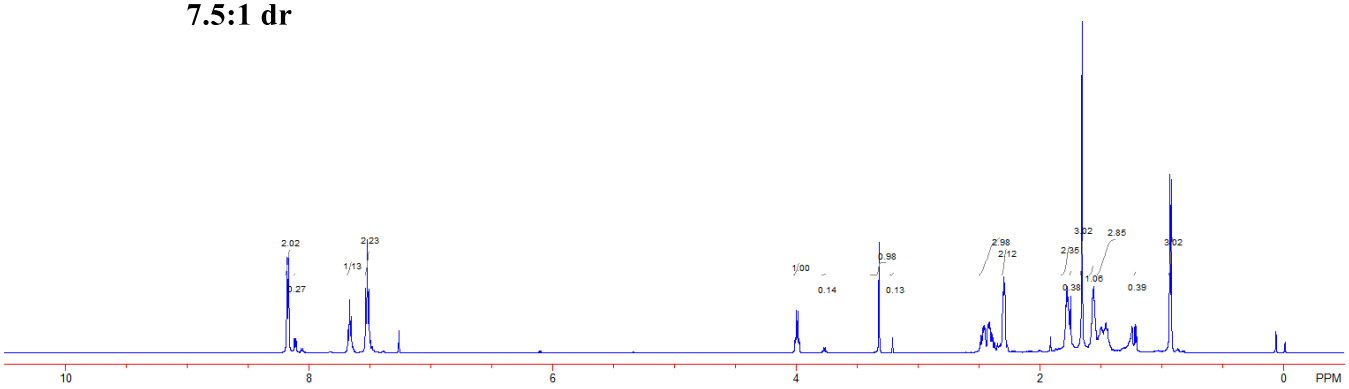

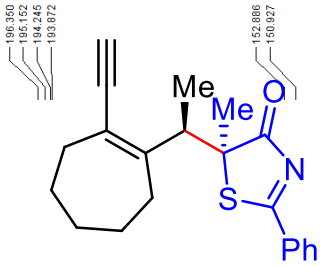

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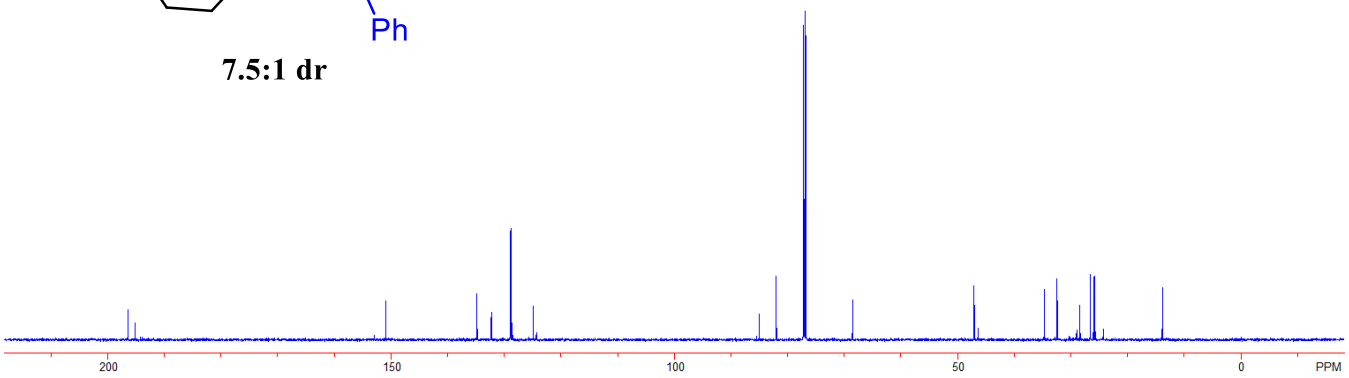
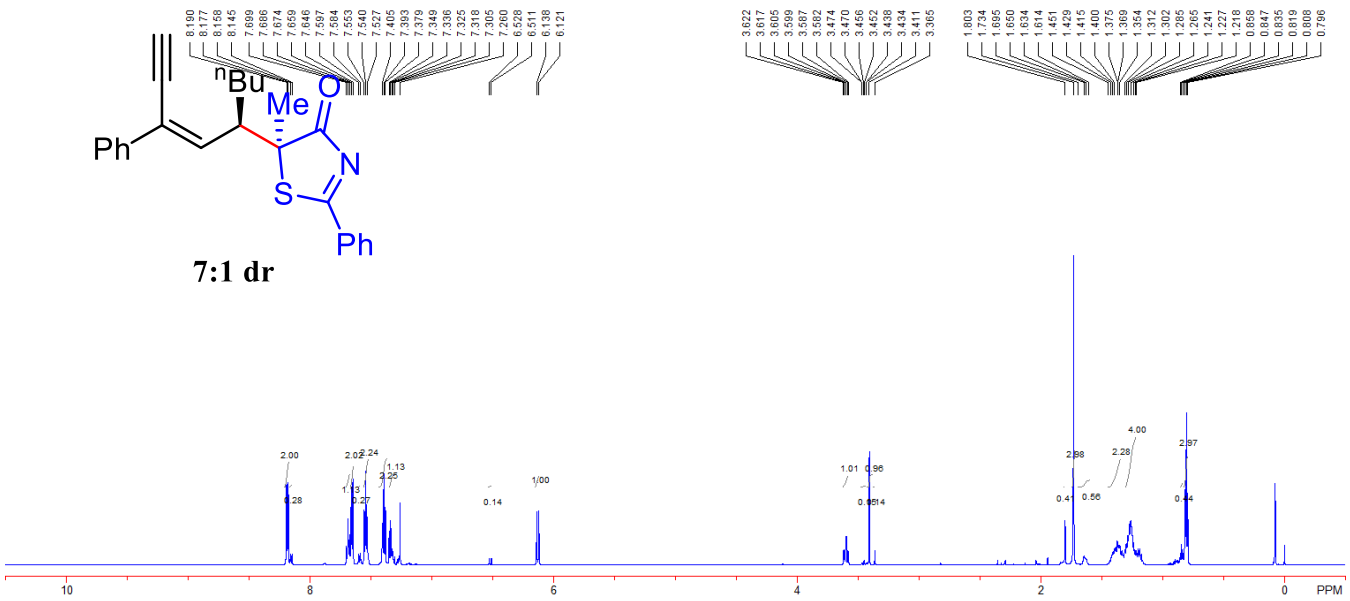
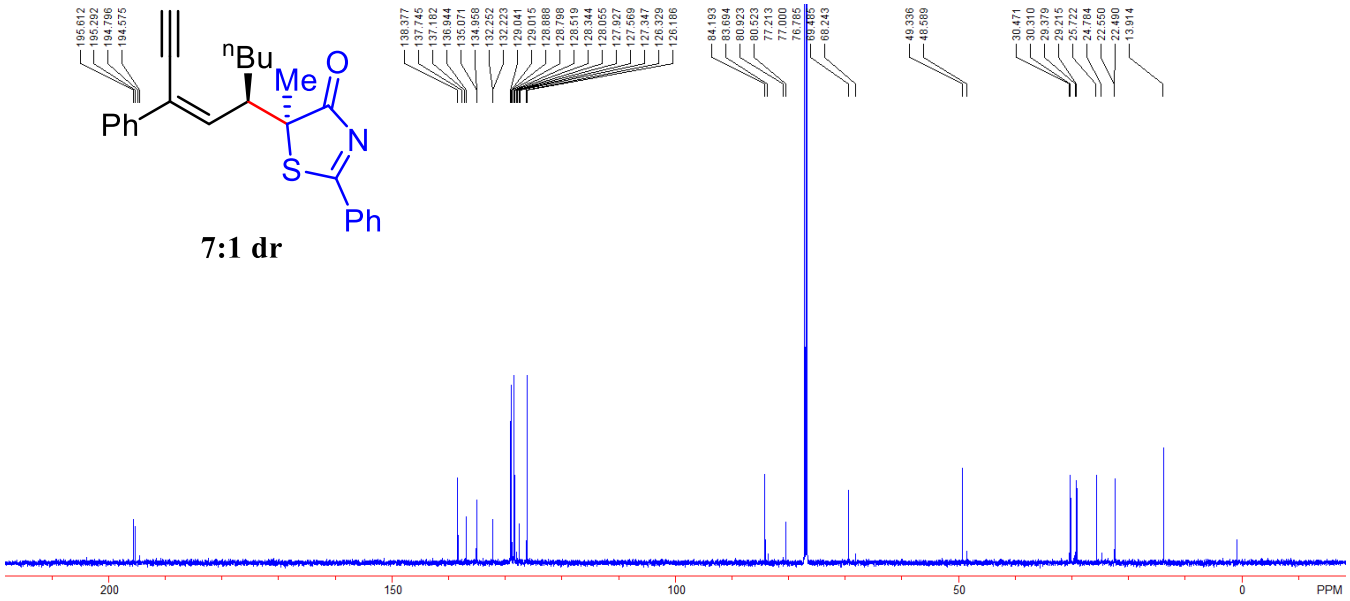
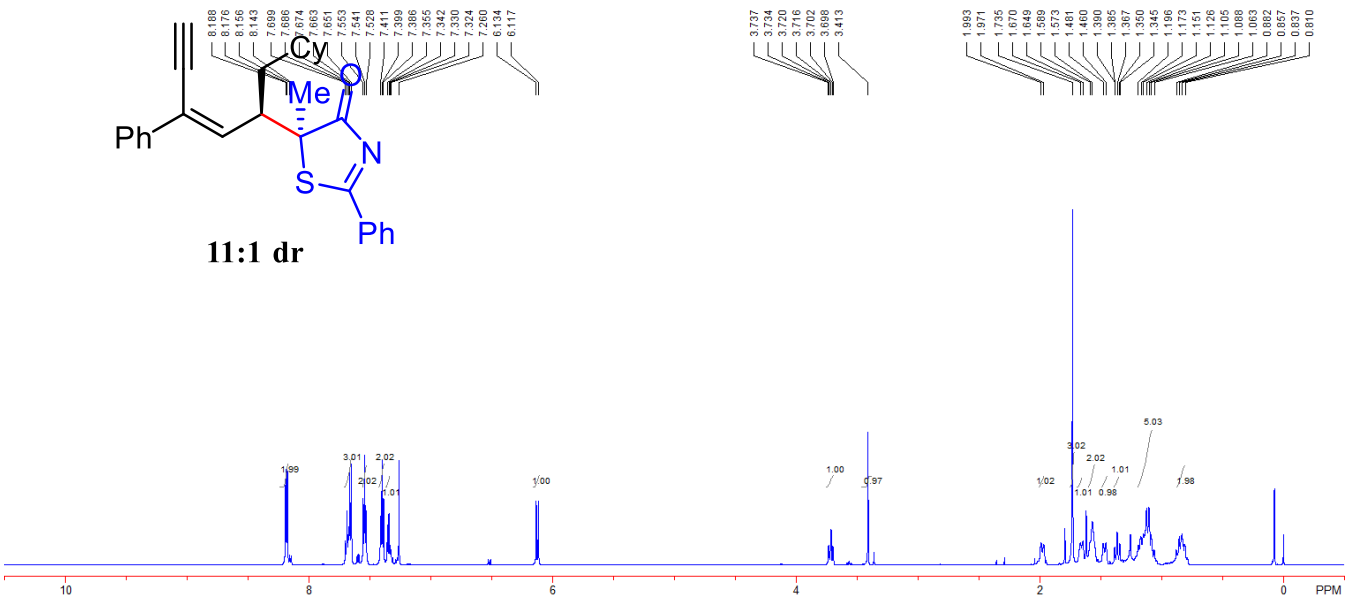


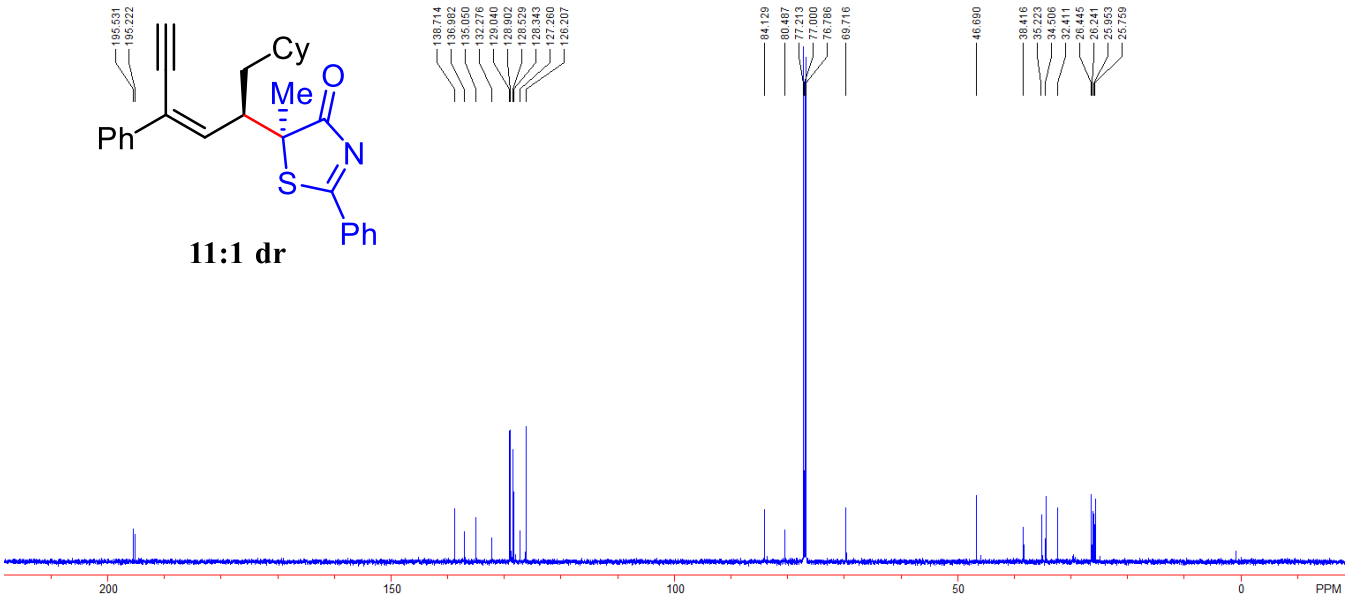
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3v**



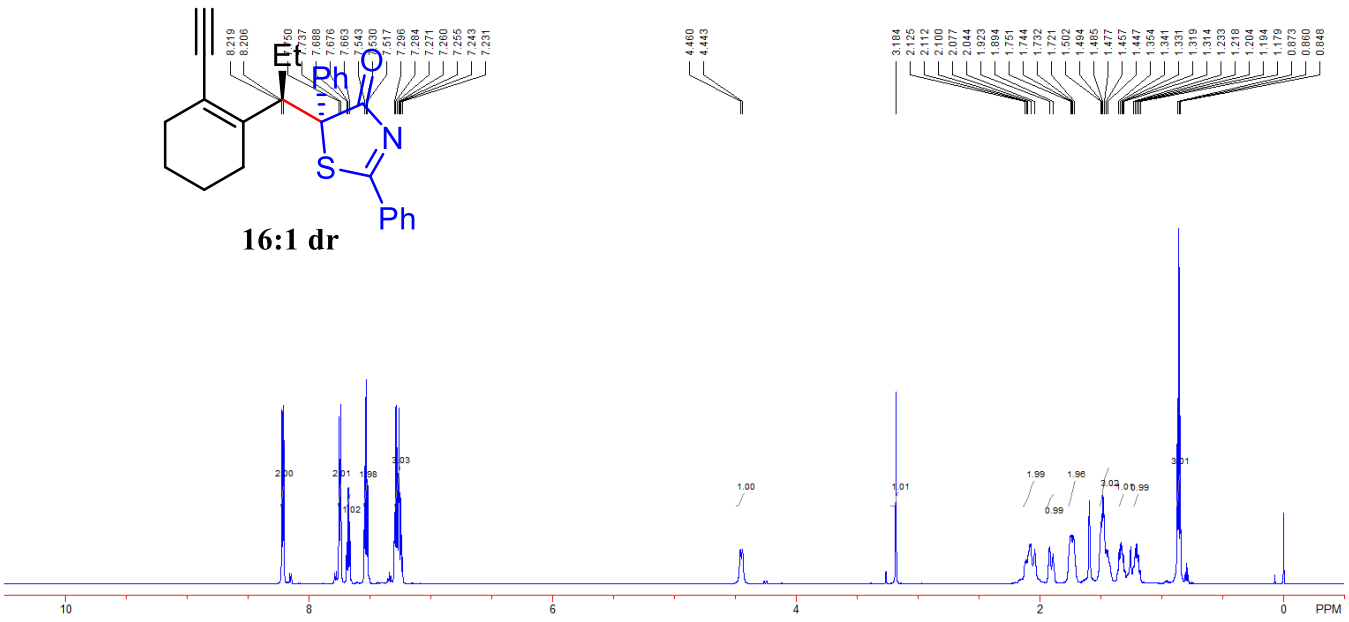


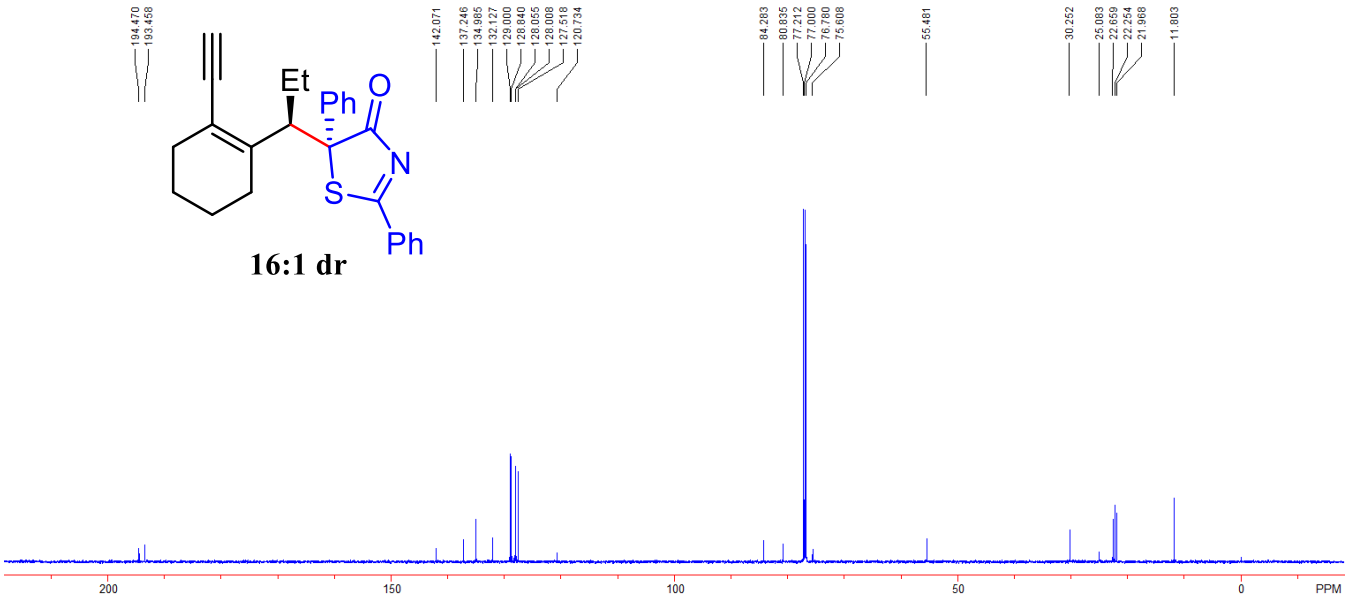
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **3w**



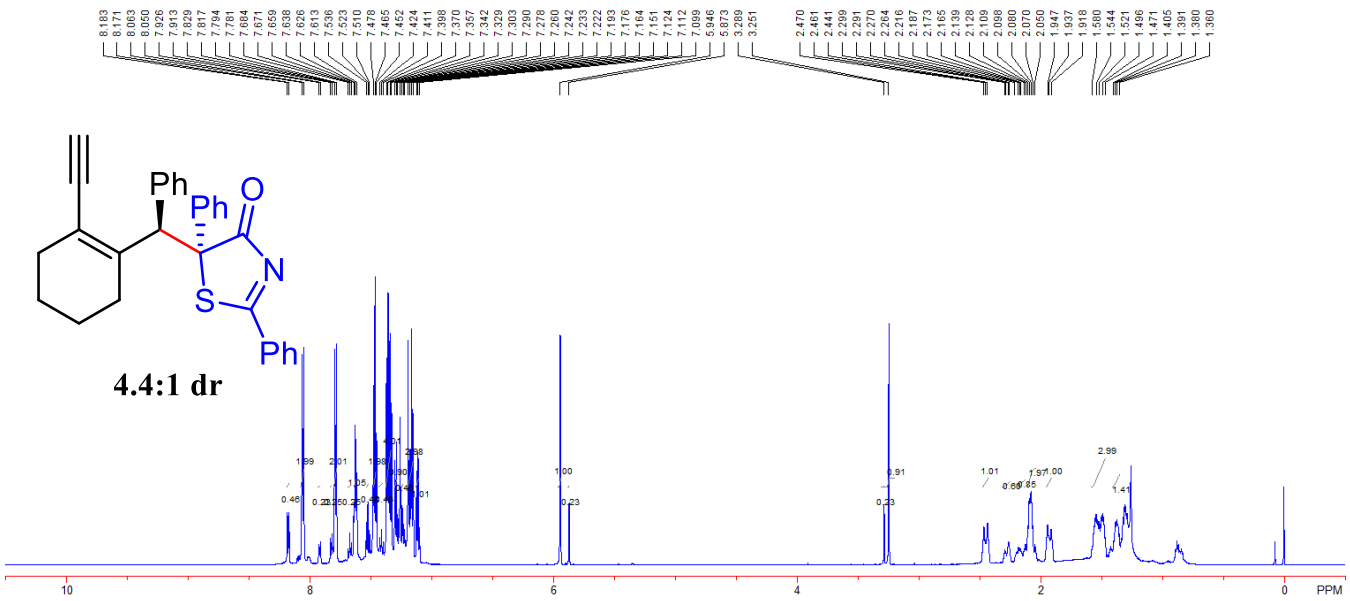


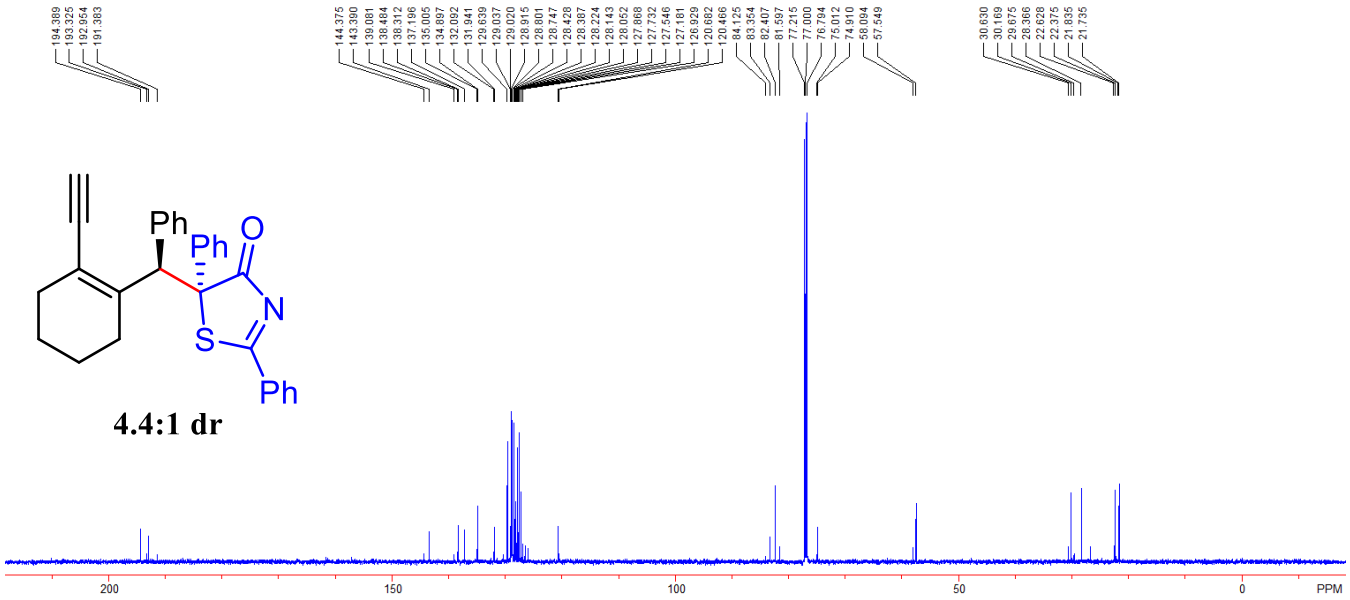
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **4a**



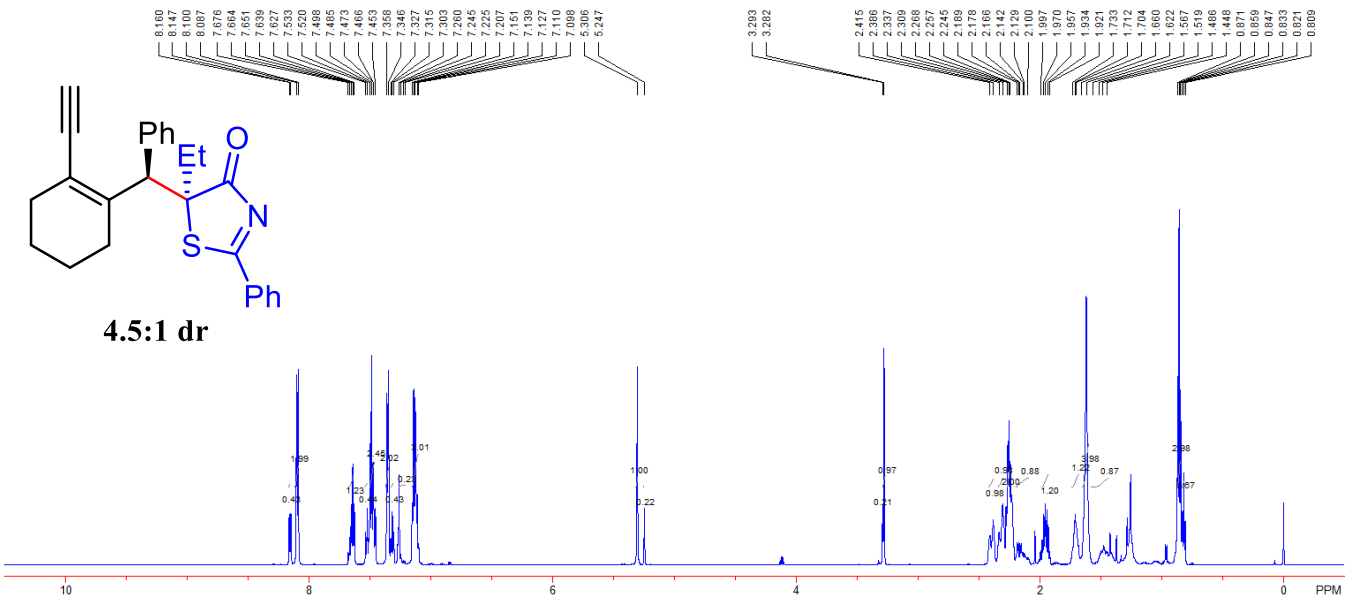


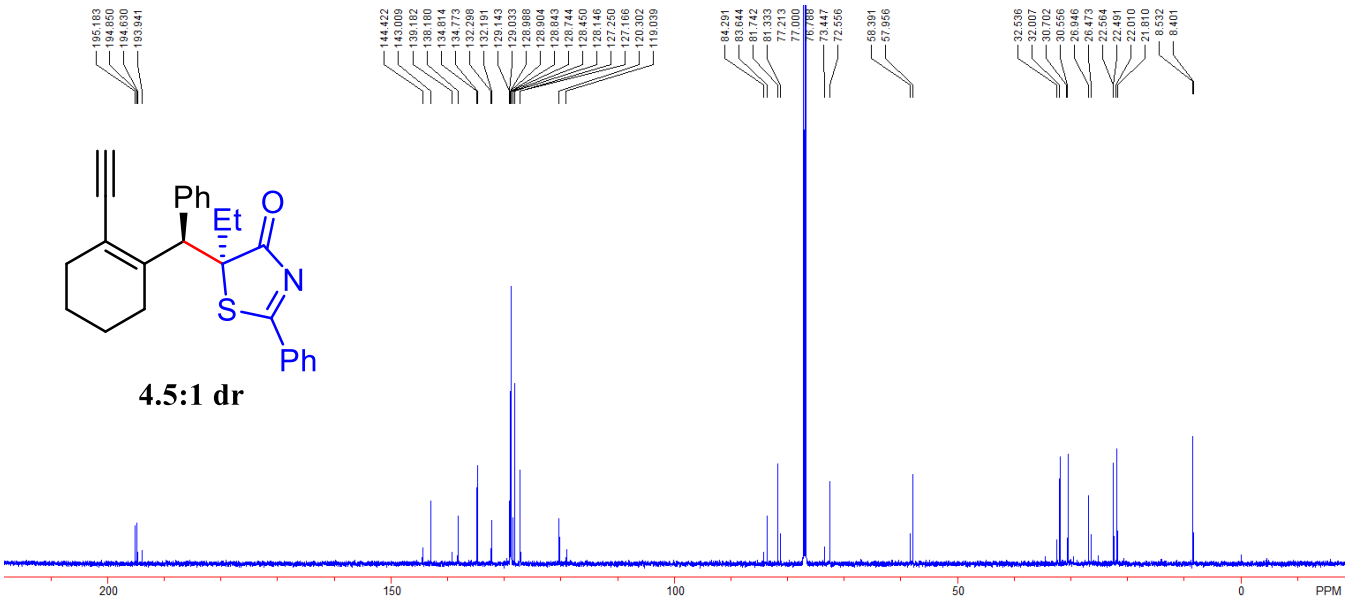
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **4b**



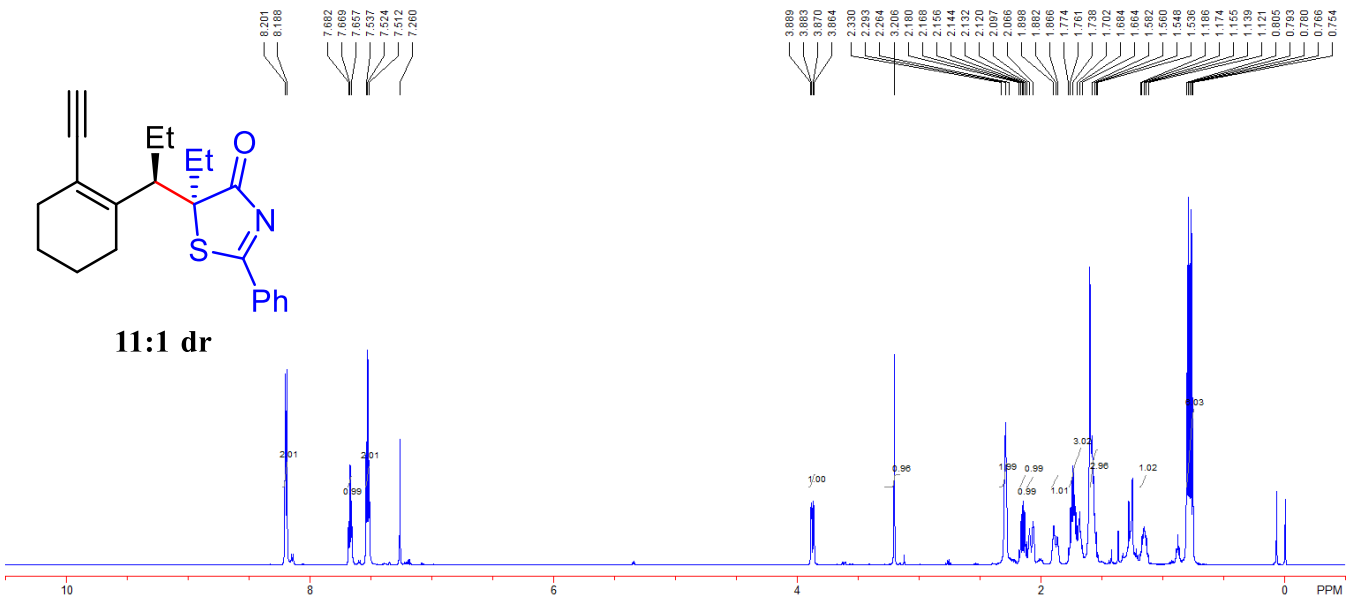


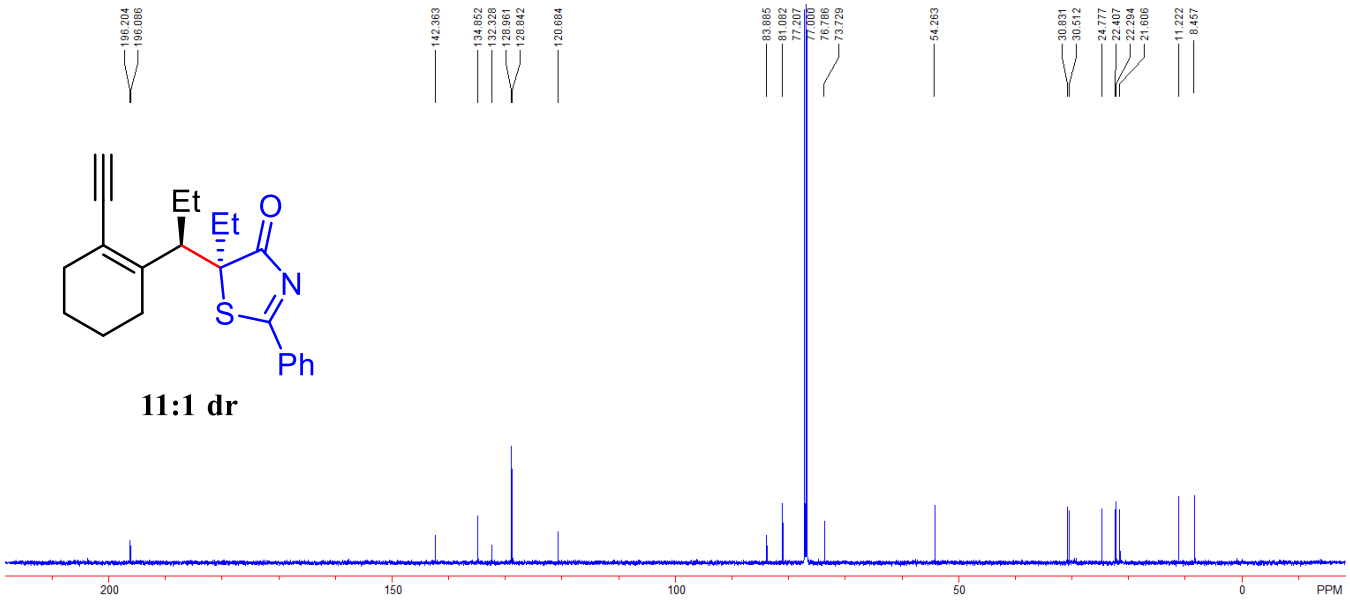
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **4c**



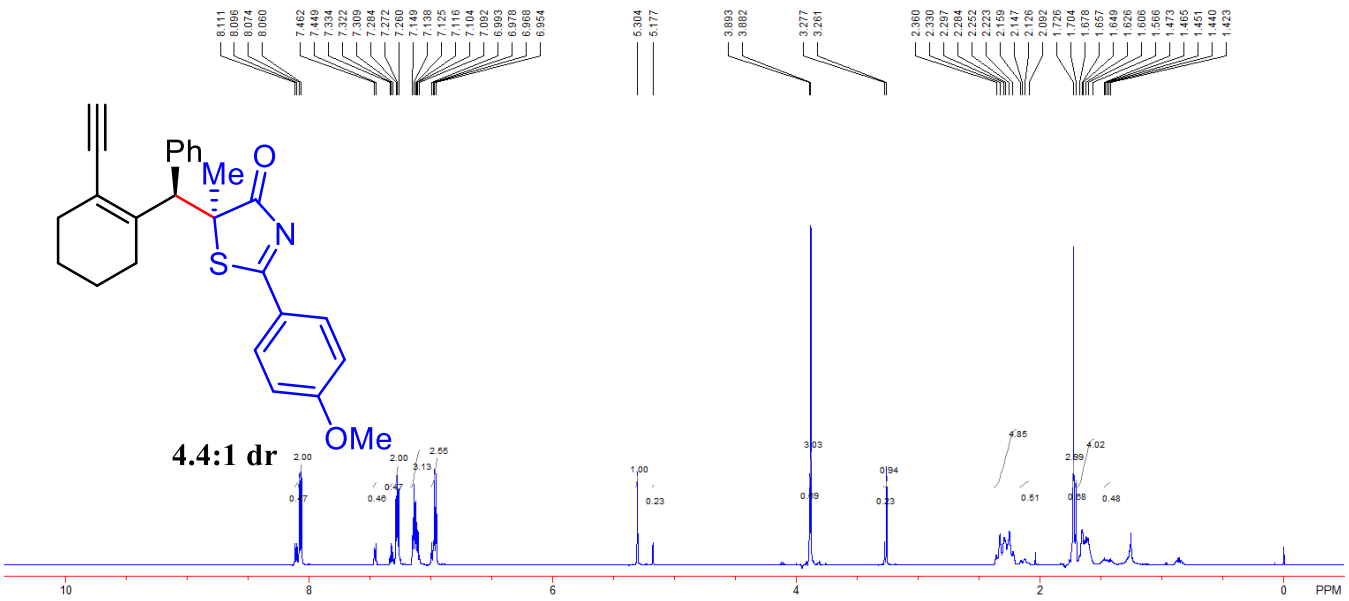


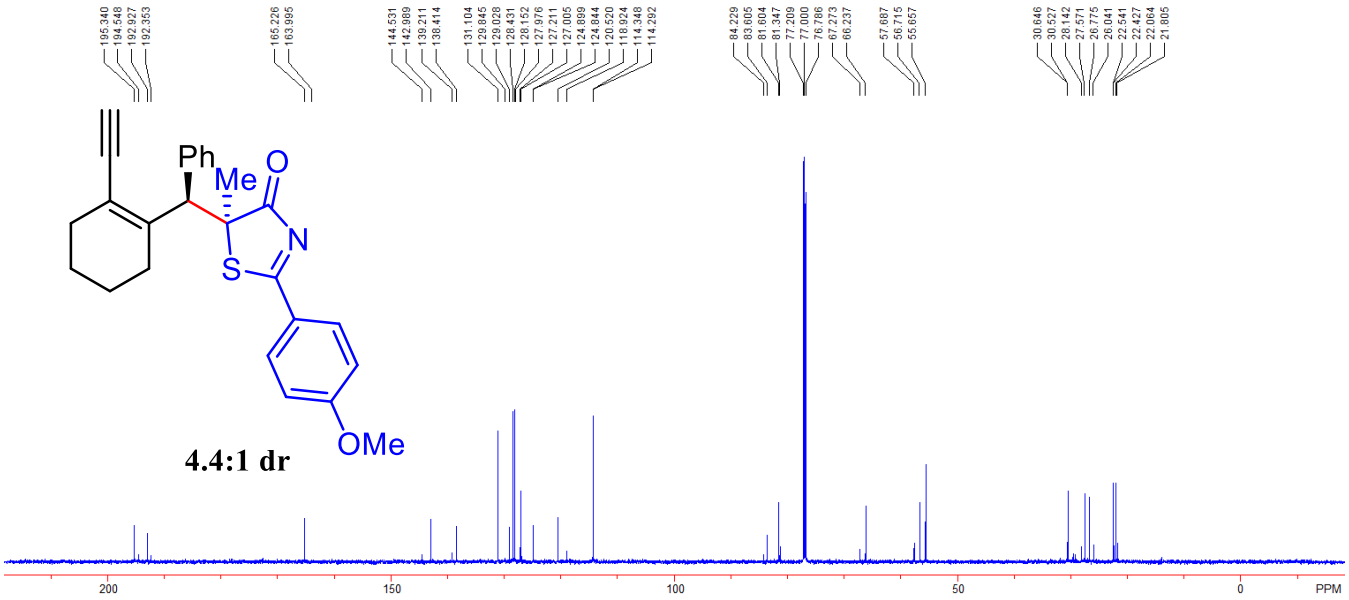
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **4d**



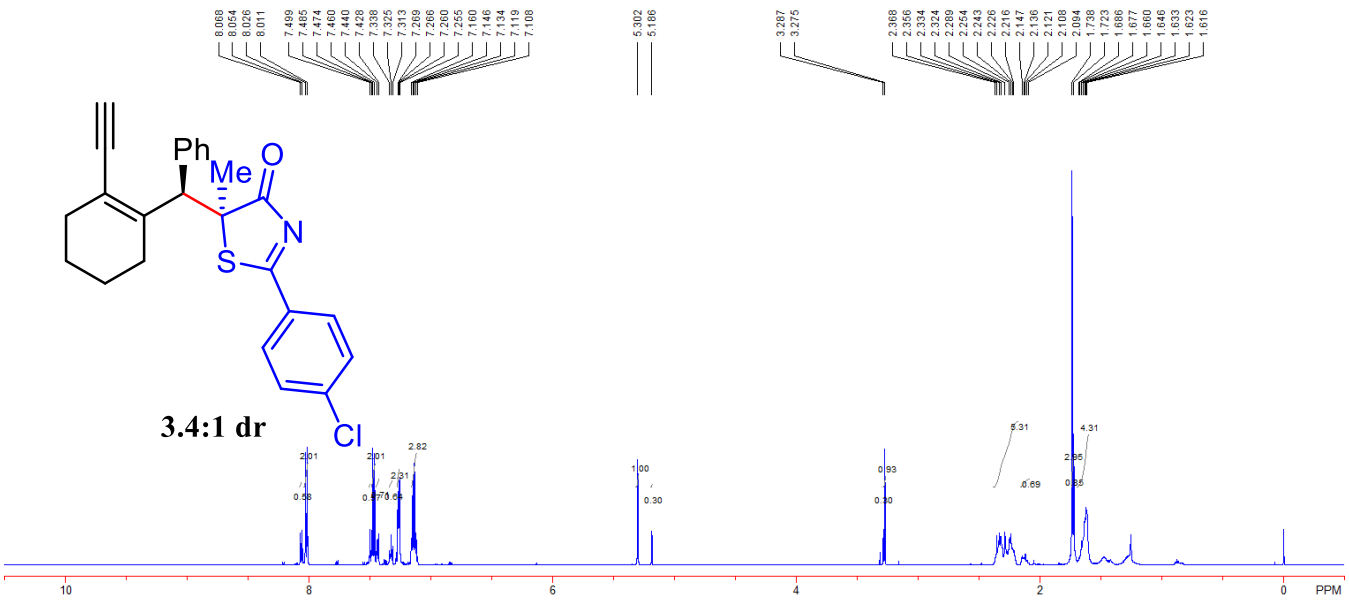


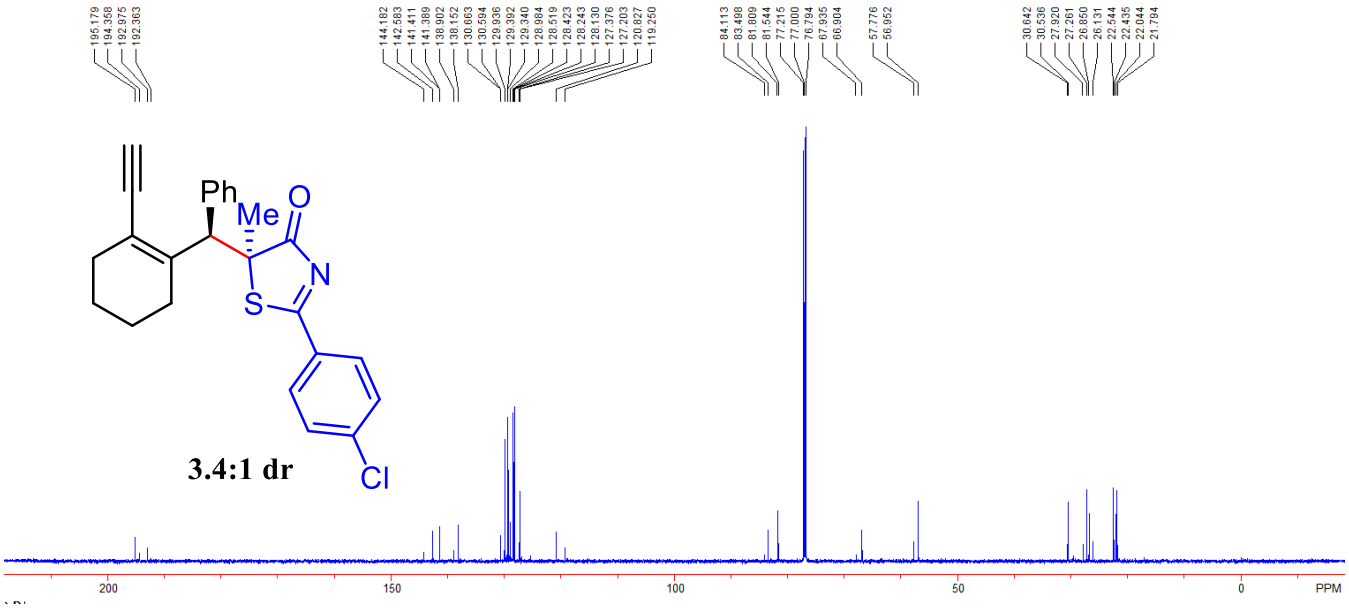
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **4e**



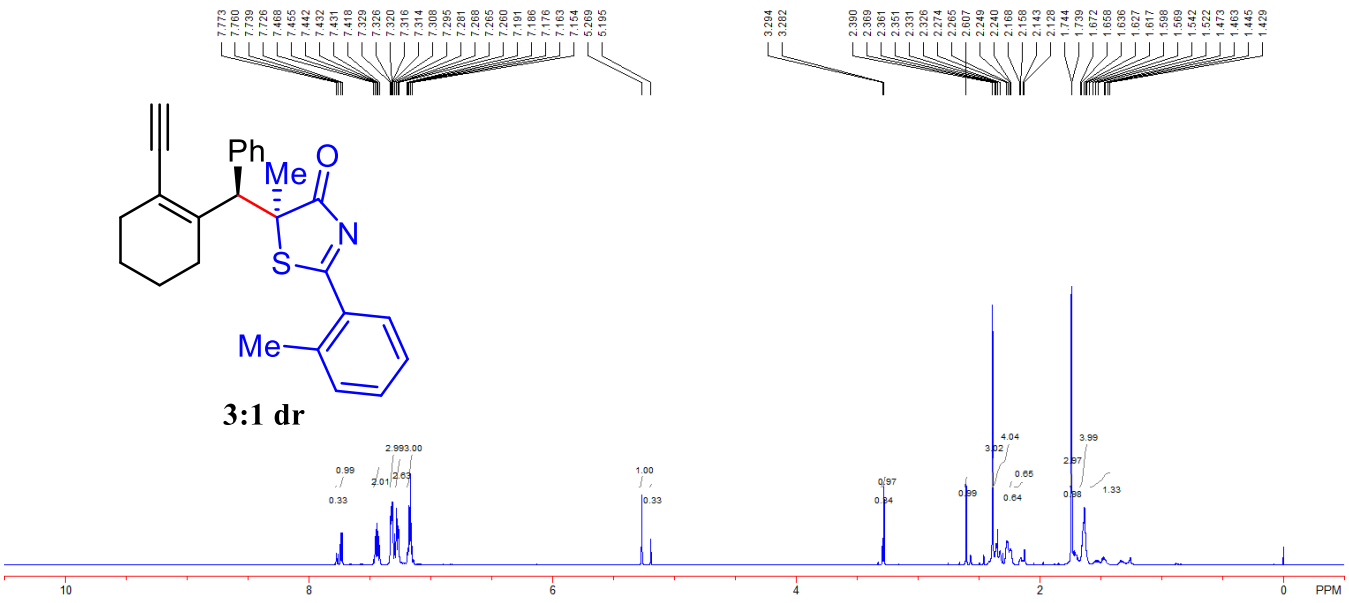


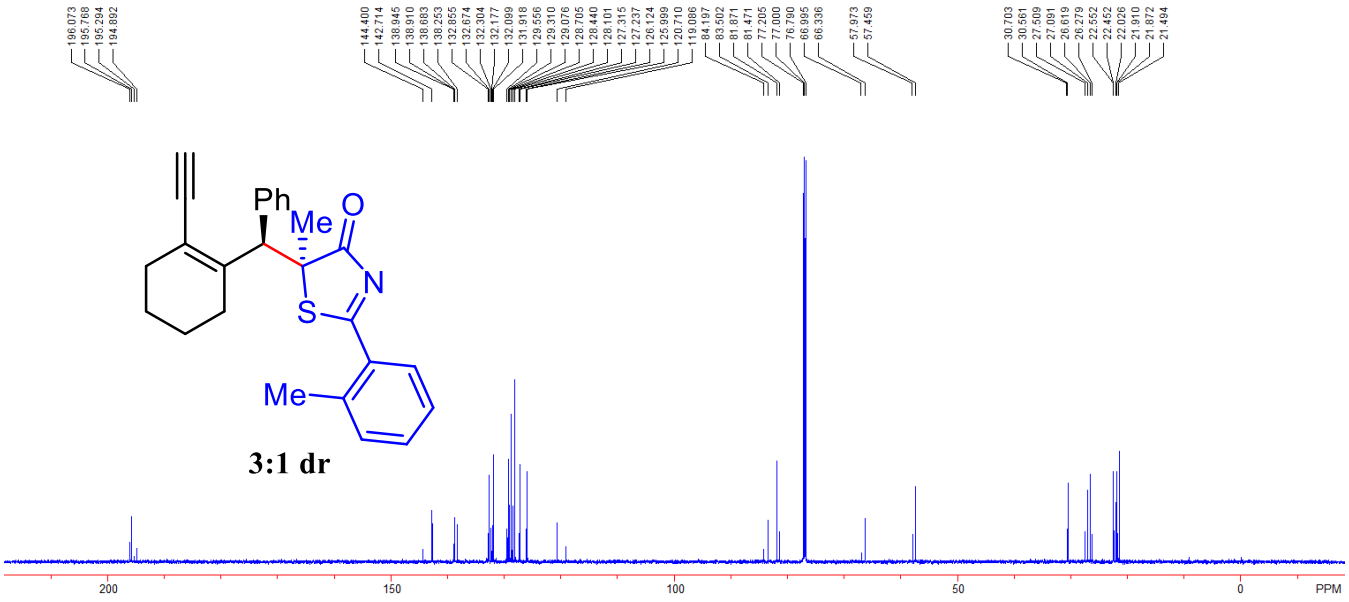
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **4f**



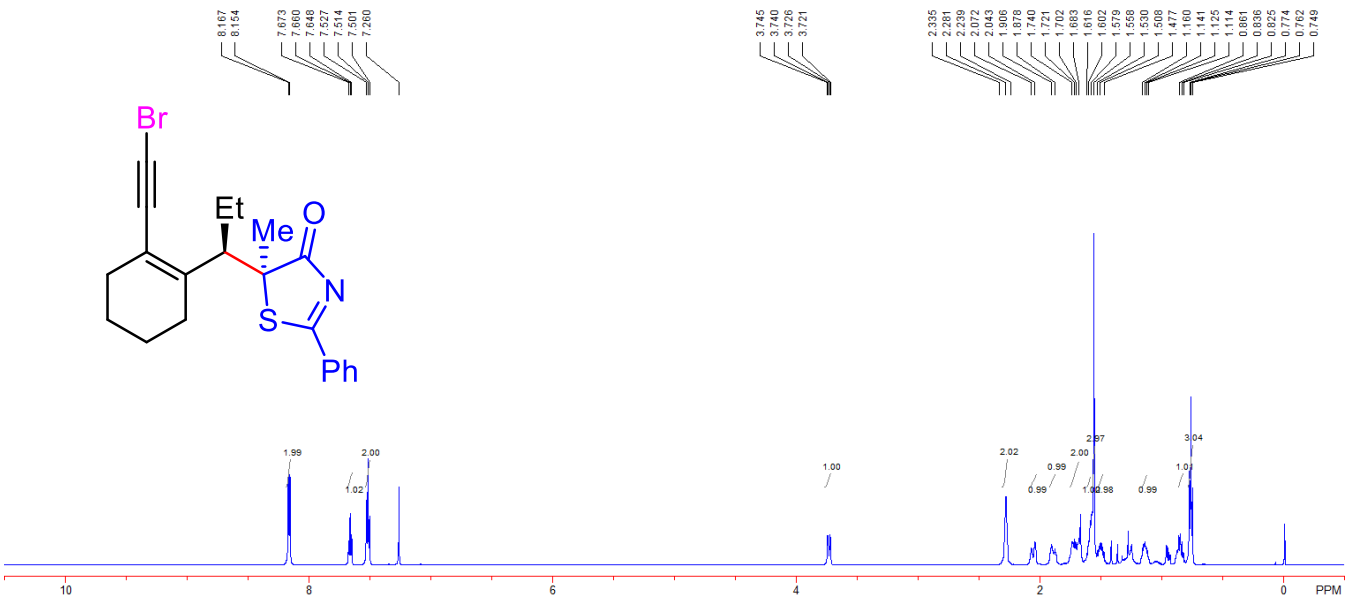


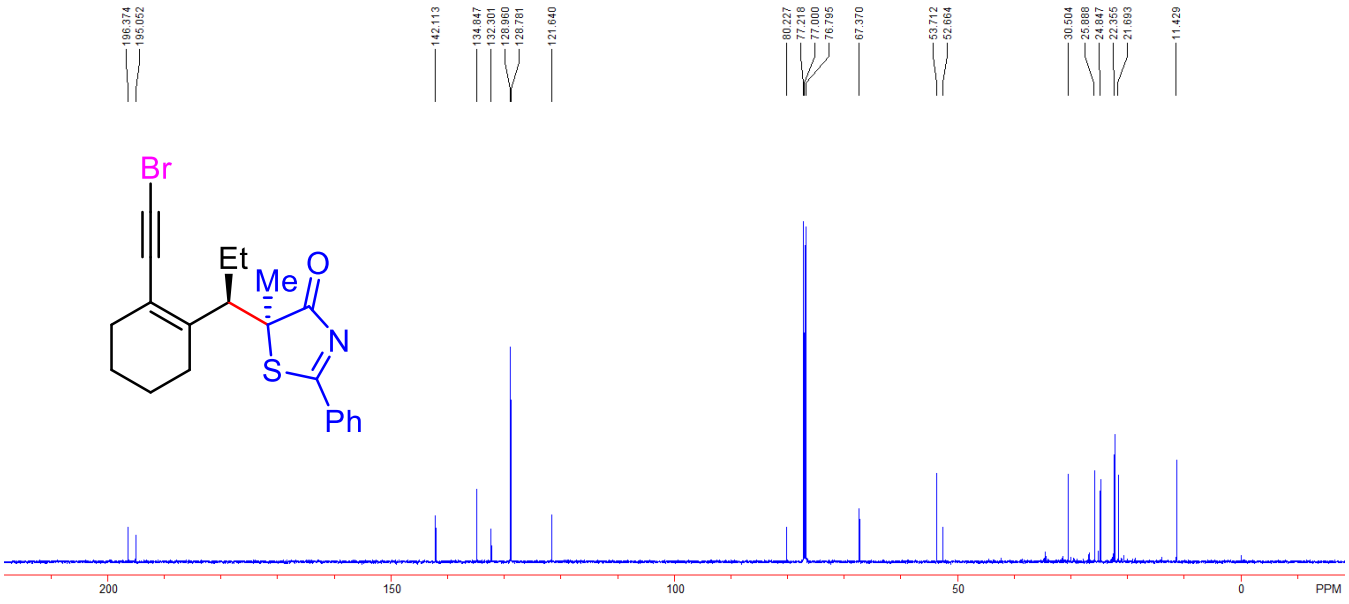
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **4g**



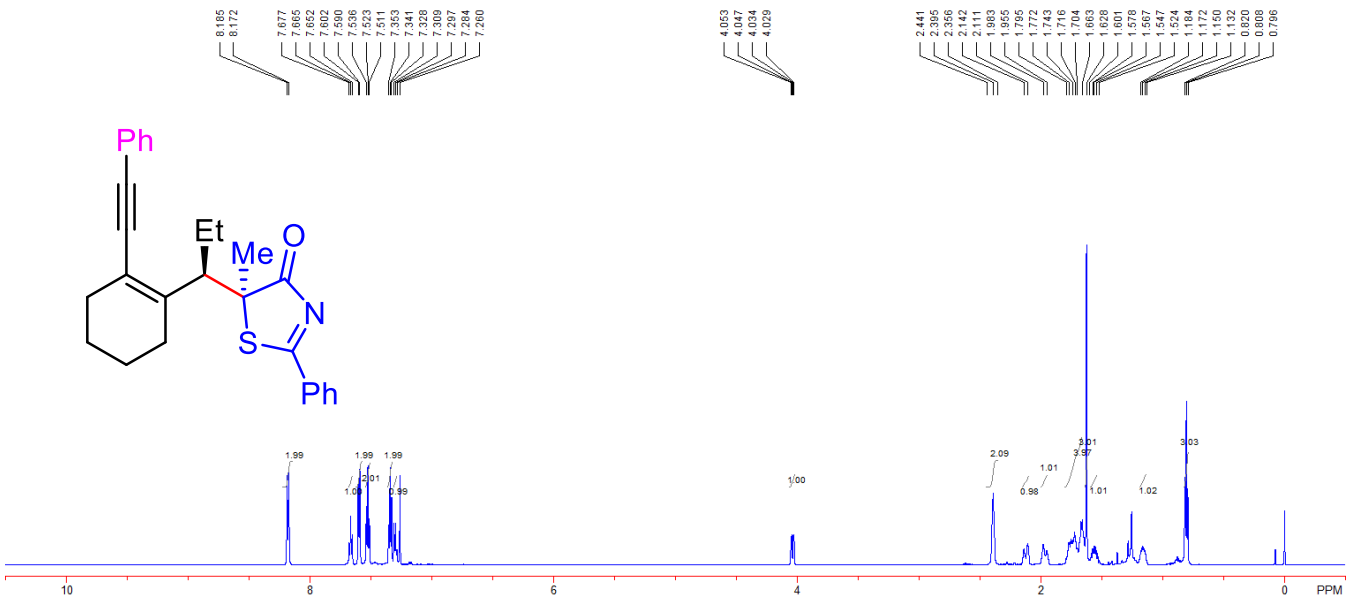


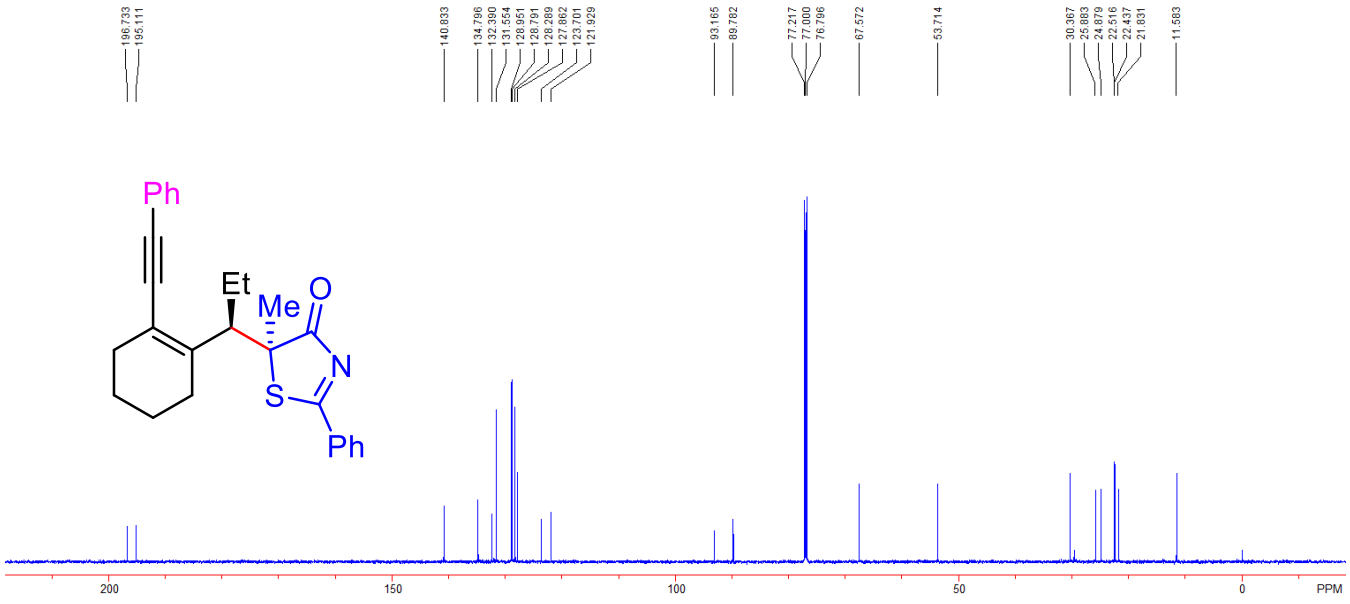
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **5a**



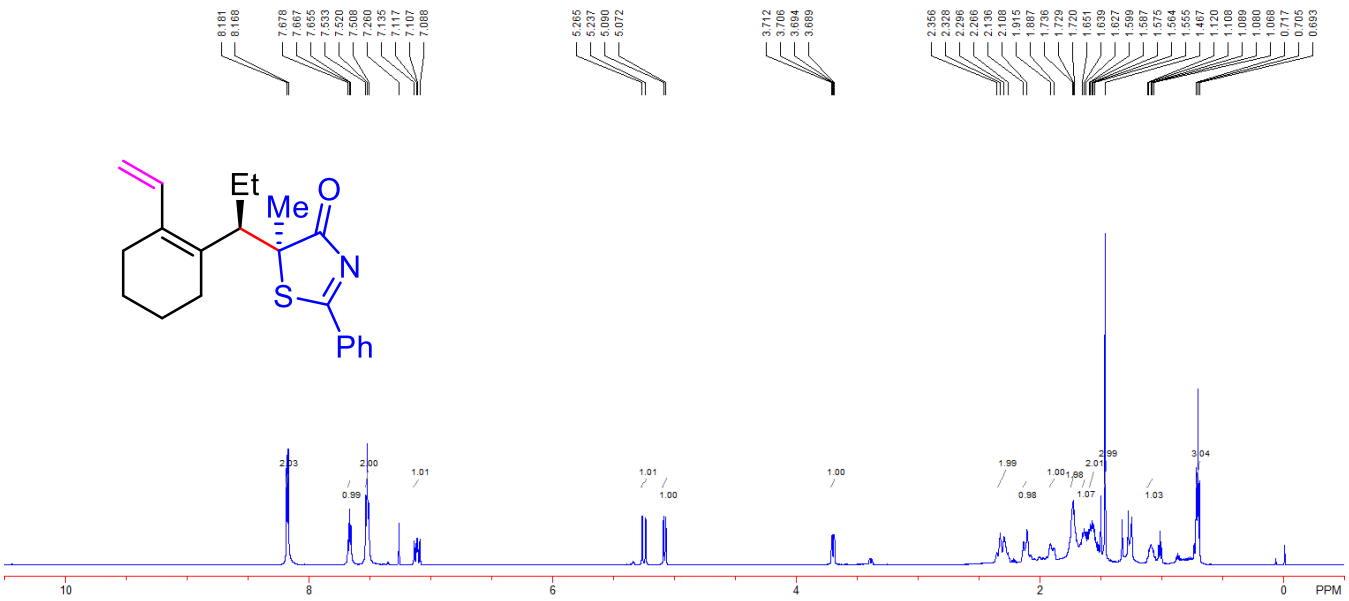


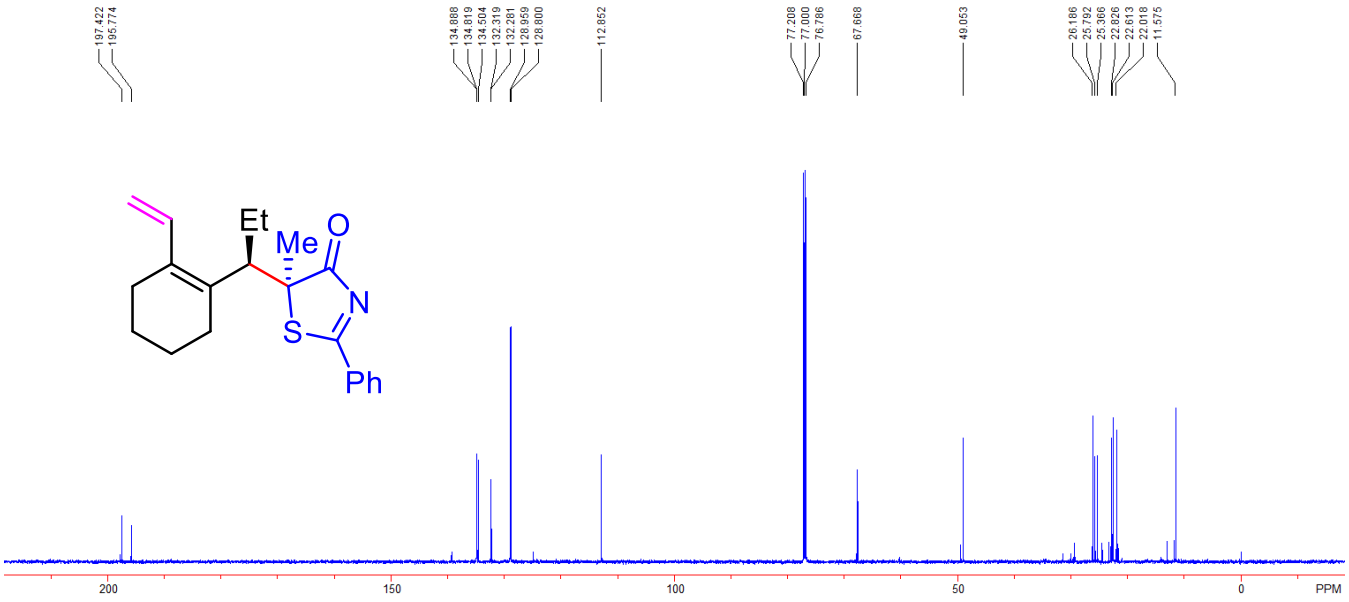
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **5b**



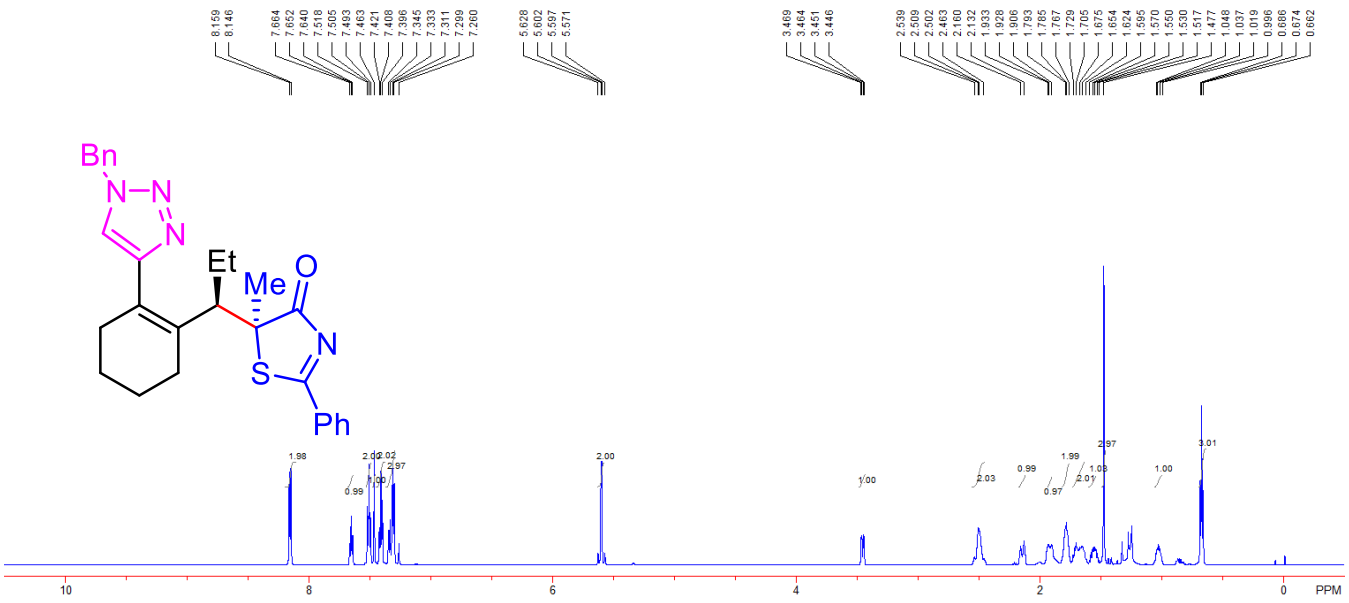


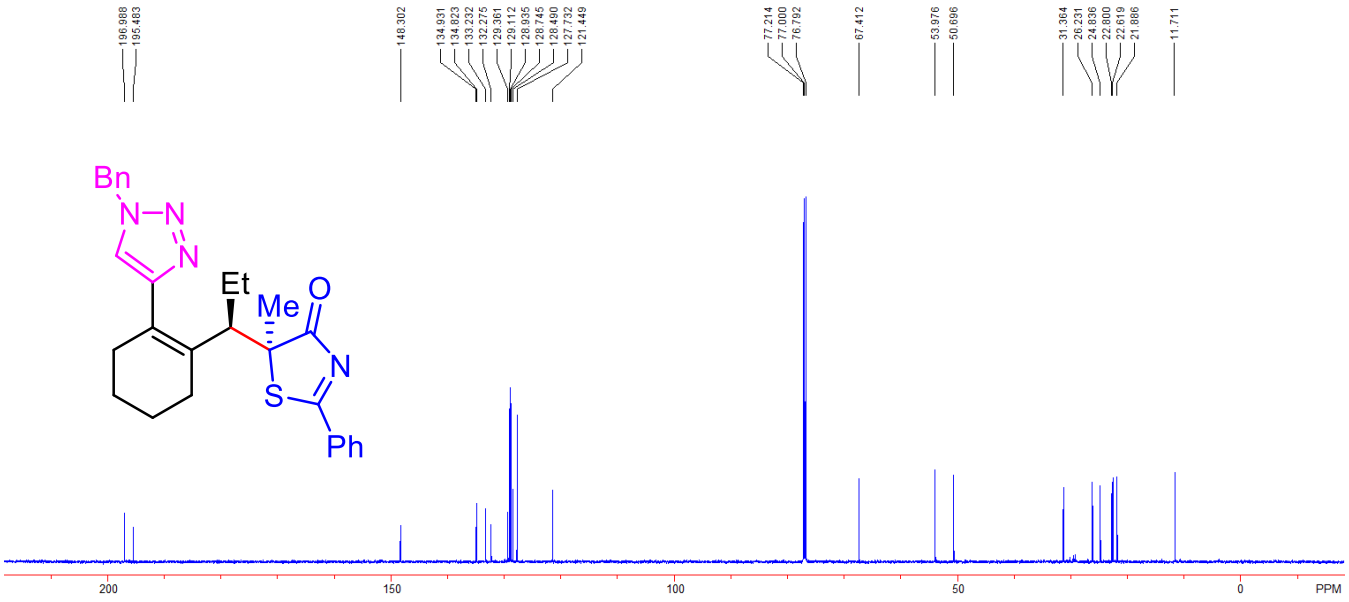
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **5c**



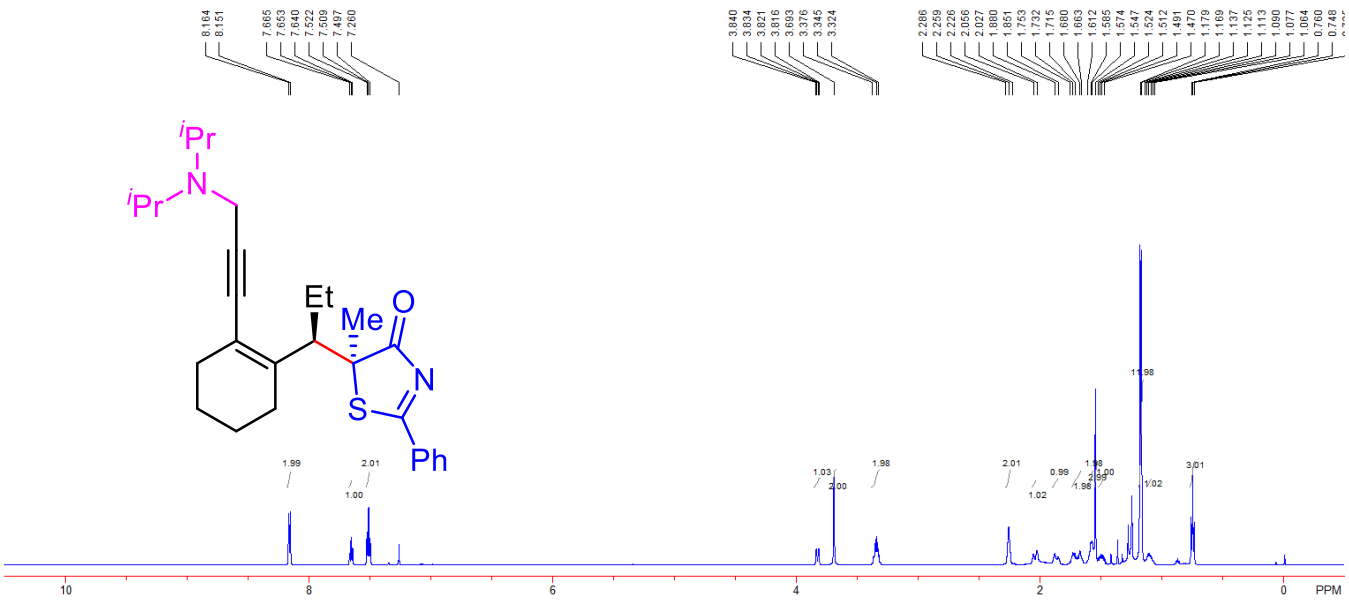


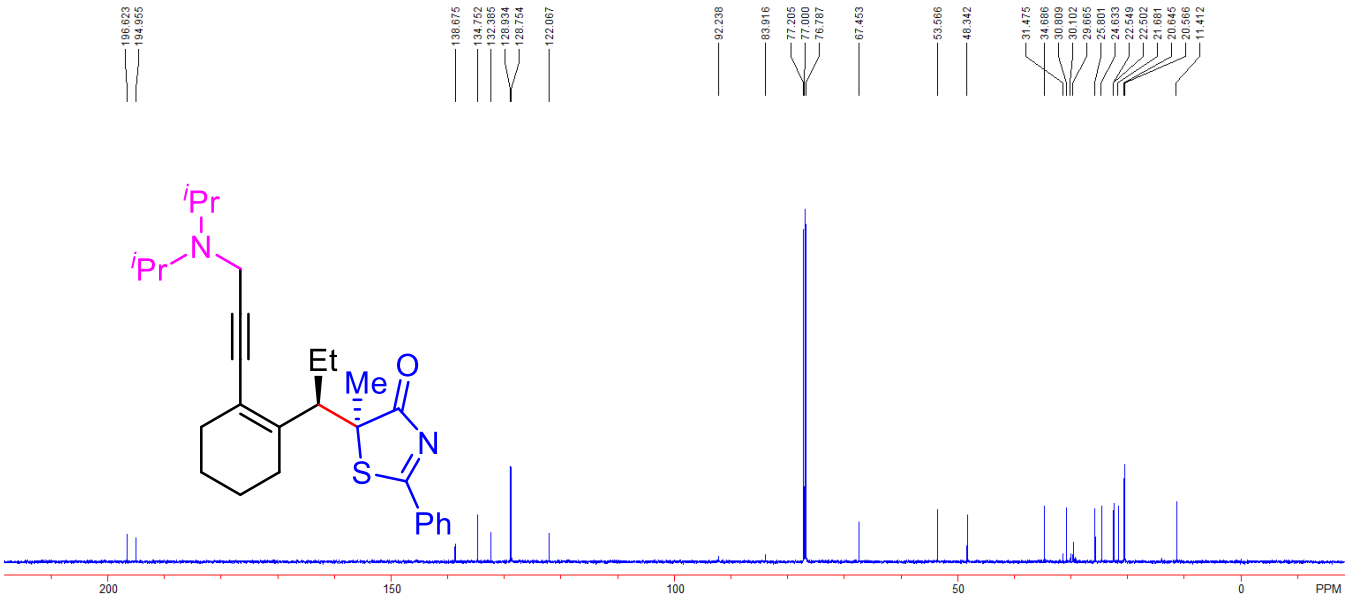
^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **5d**





^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **5e**





^{1}H and ^{13}C NMR ($CDCl_3$) Spectra for Compound **5f**