Supporting Information

Asymmetric Alkynylation/Hydrothiolation Cascade: Enantioselective Synthesis of Thiazolidine-2-imines from Imine, Acetylene and Isothiocyanate

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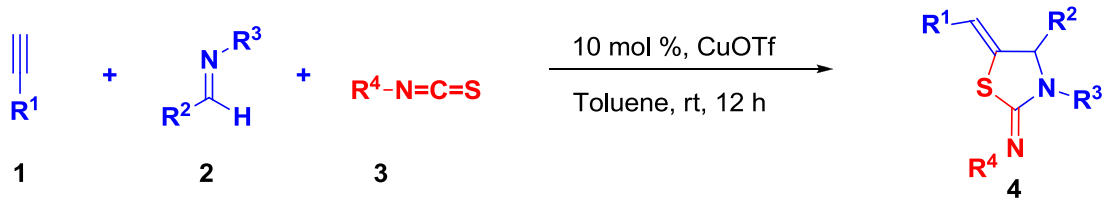
1. General Information

General Aspects: All reactions were carried out under nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise mentioned. All the chemicals were purchased commercially, and used without further purification. Yields refer to chromatographically pure compounds, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel plates (60F-254) using UV light as a visualizing agent and p-anisaldehyde or ninhydrine stain, and heat as developing agents. Silica gel (particle size 100-200 and 230-400 mesh) was used for flash column chromatography. Isothiocyanates was purchased commercially from sigma-Aldrich, Alfa Aesar and Avra chemical and were used without further purification. To avoid the other metal impurities in reaction new glassware, unused stir bars and new syringe were used. All reactions were performed under an argon atmosphere. Neat compounds were used for record IR (Perkin Elmer FT-IR Spectrum-2) spectra. NMR spectra were recorded on either a JEOL DELTA (ECX) 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) or JEOL DELTA (ECX) 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz) in $CDCl_3$ using TMS as an internal standard. Chemical shifts (δ) are given in ppm relative to TMS (δ = 0 ppm) or solvent residual peaks ($CDCl_3$, δ = 7.25 ppm) as internal standard. Coupling constants *J* are reported in Hz. Mass spectrometric data were obtained using WATERS-Q-Tof-Premier-ESI-MS instruments. Melting points measurements were made using a hot stage apparatus of chromatographically pure compound (recrystallized in methanol), unless otherwise stated.

The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of a doublet of a doublet, dt = doublet of a triplet, td = triplet of a doublet, m = multiplet, br = broad.

Experimental Section

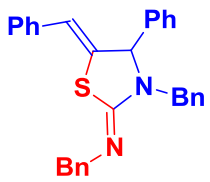
General procedure for the synthesis of thiazolidine-2-imine



1 2 3 4

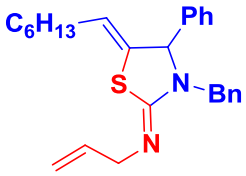
To a magnetically stirred solution of imine **2** (0.50 mmol), phenylacetylene **1** (0.65 mmol) in anhydrous toluene were added isothiocyanate **3** (0.55 mmol) and CuOTf toluene complex (10 mol %) under argon atmosphere. The reaction mixture was stirred at room temperature (35 °C) till completion of starting material (monitored by TLC). The resulted reaction mixture was extracted with EtOAc; organic layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue on silica gel column using EtOAc-petroleum ether (1:19) as eluent furnished thiazolidine-2-imine **4**, 75-95% isolated yield, *Rf* = 0.40 (EtOAc – petroleum ether, 1:19).

(*E*)-*N*-((*Z*)-3-benzyl-5-benzylidene-4-phenylthiazolidin-2-ylidene)-1-phenylmethanamine (4a): The title compound was prepared according to General Procedure using

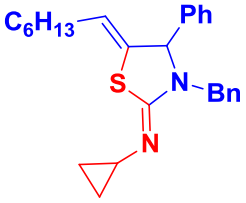


(*E*)-*N*-benzylidene-1-phenylmethanamine (100 mg, 0.51 mmol), phenyl acetylene (67 mg, 0.66 mmol), benzyl isothiocyanate (83 mg, 0.56 mmol), and Cu(OTf) toluene complex (0.051, 10 mol %) in toluene. After 12 h at room temperature (35 °C), White solid; Yield 200 mg (90%); **mp** 100 - 110 °C (recrystallized in methanol); **IR** (neat): ν_{max}/cm^{-1} 3059, 3026, 2921, 1647, 1619, 1582, 1492, 1452, 1390, 1345, 1270, 1192, 1076, 1027, 817, 729, 695; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 - 7.24 (m, 20 H), 6.29 (s, 1 H), 5.52 (d, *J* = 15.1 Hz, 1 H), 5.32 (s, 1 H), 4.82 - 4.67 (m, 2 H), 3.75 (d, *J* = 15.1 Hz, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 155.9, 141.1, 140.3, 137.0, 136.0, 133.8, 131.8, 129.1 (2C), 128.6 (2C), 128.5, 128.3, 128.1, 127.6, 127.4, 127.1, 126.6, 122.4, 70.2, 58.2, 47.4; **HRMS (ESI)** *m/z* calcd. for $C_{30}H_{26}N_2S$ $[M + H]^+$ 447.1895, found 447.1893.

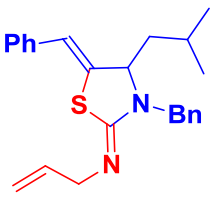
(*Z*)-*N*-((*Z*)-3-benzyl-5-heptylidene-4-phenylthiazolidin-2-ylidene)prop-2-en-1-amine (4b): Viscous oil; Yield 177 mg (88%); **IR** (neat): ν_{max}/cm^{-1} 3063, 3029, 2955, 2926, 2855, 1631, 1494, 1455, 1325, 1195, 1077, 914, 776, 699; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 - 7.12 (m, 11 H), 6.12 - 5.97 (m, 1 H), 5.39 - 5.26 (m, 2 H), 5.20 - 5.09 (m, 2 H), 5.00 (s, 1 H), 4.11 - 3.93 (m, 2 H), 3.59 (d, *J* = 15.1 Hz, 1 H), 1.96 (dquin, *J* = 13.8, 7.1, 7.1, 7.1, 7.1 Hz, 2 H), 1.29 - 1.15 (m, 8 H), 0.84 (t, *J* = 6.8 Hz, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.7, 140.6, 137.1, 136.9, 133.3, 128.9, 128.5, 128.5, 128.4, 127.6, 127.3, 123.3, 114.7, 68.3, 57.1, 47.4, 31.6, 31.4, 28.8, 28.7, 22.6, 14.1; **HRMS (ESI)** *m/z* calcd. for $C_{26}H_{32}N_2S$ $[M + H]^+$ 405.2365, found 405.2365.



(*Z*)-*N*-((*Z*)-3-benzyl-5-heptylidene-4-phenylthiazolidin-2-ylidene)cyclopropanamine (4c): Viscous oil; Yield 153 mg (78%); **IR** (neat): ν_{max}/cm^{-1} 3085, 3063, 3028, 3005, 2955, 2926, 2855, 1697, 16331494, 1454, 1385, 1265, 1192, 1076, 974, 700; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 - 7.19 (m, 8 H), 7.12 - 7.01 (m, 2 H), 5.24 (d, *J* = 15.1 Hz, 1 H), 5.14 (td, *J* = 7.1, 1.7 Hz, 1 H) 4.98 (d, *J* = 1.7 Hz, 1 H), 3.53 (d, *J* = 15.1 Hz, 1 H), 2.72 – 2.68 (m, Hz, 1 H), 2.05 - 1.92 (m, 2 H), 1.30 - 1.18 (m, 8 H), 0.85 (t, *J* = 7.0 Hz, 3 H), 0.78 – 0.73 (m, 2 H), 0.72 - 0.63 (m, 2 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.9, 140.5, 137.1, 133.7, 128.9, 128.6, 128.5, 128.3, 127.6, 127.3, 123.0, 68.2, 47.2, 35.6, 31.7, 31.4, 28.9, 28.7, 22.6, 14.1, 7.6, 7.5; **HRMS (ESI)** *m/z* calcd. for $C_{26}H_{33}N_2S$ $[M + H]^+$ 405.2364, found 405.2361.

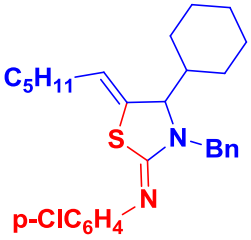


(*Z*)-*N*-((*Z*)-3-benzyl-5-benzylidene-4-isobutylthiazolidin-2-ylidene)prop-2-en-1-an ine (4d): Viscous oil; Yield 156 mg (83%); **IR** (neat): ν_{max}/cm^{-1} 3062, 3028, 2955, 2925, 2868, 1603, 1643, 1495, 1454, 1408, 1235, 1029, 755, 697; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 - 7.19 (m, 8 H), 7.17 - 7.10 (m, 2 H), 5.84 (d, *J* = 15.3 Hz, 1 H), 5.53 (s, 1 H), 5.47 - 5.34 (m, 1 H), 4.95 - 4.88 (m, 1 H), 4.60 - 4.50 (m, 2 H), 4.42 - 4.34 (m, 1 H), 4.29 (ddd, *J* = 5.5, 3.7, 2.3 Hz, 1 H), 4.23 (d, *J* = 15.3 Hz, 1 H), 1.89 (quind, *J* = 13.2, 6.6 Hz, 1 H), 1.81 - 1.73 (m, 1 H), 1.64 (ddd, *J* = 14.6, 7.0, 4.0, Hz 1 H), 0.93 (d, *J* = 2.1 Hz, 3 H), 0.92 (d, *J* = 2.1 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.0, 139.2,

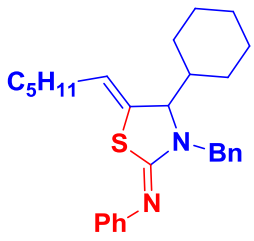


135.8, 135.5, 131.9, 129.6, 128.7, 128.0, 127.8, 127.6, 126.7, 116.7, 100.2, 60.5, 48.8, 47.8, 42.2, 23.6, 23.4, 23.3; **HRMS (ESI)** *m/z* calcd. for $C_{24}H_{28}N_2S$ $[M+H]^+$ 377.2051; found 377.2051.

(*Z*)-*N*-((*Z*)-3-benzyl-4-cyclohexyl-5-hexylidenethiazolidin-2-ylidene)-4-chloroaniline (4e): Viscous oil; Yield 176 mg (80%); **IR** (neat): ν_{max}/cm^{-1} 3029, 2926, 2853, 1619, 1584, 1486, 1452, 1409, 1355, 1292, 1230, 1149, 1089, 1029, 1010, 833, 699; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 - 7.18 (m, 7 H), 6.95 - 6.84 (m, 2 H), 5.44 - 5.33 (m, 2 H), 4.25 (d, *J* = 15.4 Hz, 1 H), 4.02 (s, 1 H), 2.09 - 1.86 (m, 2 H), 1.84 - 1.72 (m, 4 H), 1.68 (d, *J* = 10.8 Hz, 1 H), 1.48 - 1.21 (m, 9 H), 1.18 - 1.01 (m, 3 H), 0.88 (t, *J* = 7.0 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 150.40, 137.2, 130.0, 128.9, 128.7, 128.2, 127.9, 127.5, 123.8, 123.7, 69.5, 47.9, 41.7, 31.5, 31.25, 29.0, 28.7, 26.7, 26.6, 26.5, 26.4, 22.5, 14.2; **HRMS (ESI)** *m/z* calcd. for $C_{28}H_{35}{}^{35}ClN_2S$ $[M + H]^+$ 467.2288, found 467.2283, *m/z* calcd. for $C_{28}H_{35}{}^{37}ClN_2S$ $[M + H]^+$ 469.2258, found 467.2274.

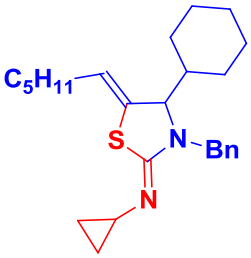


(*Z*)-*N*-((*Z*)-3-benzyl-4-cyclohexyl-5-hexylidenethiazolidin-2-ylidene)aniline (4f): Viscous oil; Yield 177 mg (82%); **IR** (neat): ν_{max}/cm^{-1} 3355, 3028, 2927, 2853, 1629, 1530, 1495, 1452, 1389, 1261, 1028, 964, 696; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 - 7.27 (m, 7 H), 7.08 -7.05 (m, 1 H), 7.02 – 7.68 (m, 2 H), 5.47 (d, *J* = 15.4 Hz, 1 H), 5.37 (t, *J* = 6.8 Hz, 1 H), 4.29 (d, *J* = 16.0 Hz, 1 H), 4.05 (br. s., 1 H), 2.05 (dq, *J* = 14.3, 7.2 Hz, 1 H), 1.96 (dq, *J* = 14.4, 7.4 Hz, 1 H), 1.81 (br. s., 4 H), 1.71 (d, *J* = 11.4 Hz, 1 H), 1.48 (d, *J* = 6.3 Hz, 1 H), 1.43 - 1.35 (m, 2 H), 1.34 - 1.22 (m, 6 H), 1.18 - 1.06 (m, 3 H), 0.90 (t, *J* = 6.8 Hz, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.36, 151.84, 137.44, 130.39, 128.90, 128.67, 127.89, 127.37, 123.32, 123.05, 122.43, 69.39, 47.92, 41.77, 31.45, 31.19, 28.98, 28.73, 26.68, 26.61, 26.55, 26.44, 22.53, 14.14; **HRMS (ESI)** *m/z* calcd. for $C_{28}H_{36}N_2S$ $[M + H]^+$ 433.2677, found 431.2657.

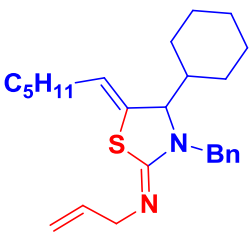


(*Z*)-*N*-((*Z*)-3-benzyl-4-cyclohexyl-5-hexylidenethiazolidin-2-ylidene)cyclopropanamine (4g): Viscous oil; Yield 172 mg (87%); **IR** (neat): ν_{max}/cm^{-1} 3085, 3004, 2926,

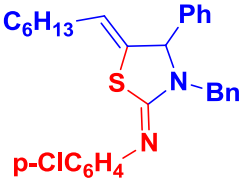
2853, 1698, 1631, 1494, 1451, 1402, 1354, 1290, 1233, 1192, 1030, 721, 699; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 - 7.26 (m, 2 H), 7.25 - 7.19 (m, 3 H), 5.32 (t, *J* = 7.1 Hz, 1 H), 5.22 (d, *J* = 15.2 Hz, 1 H), 4.06 (d, *J* = 15.5 Hz, 1 H), 3.89 (br. s., 1 H), 2.63 - 2.58 (m, 1 H), 2.17 - 2.00 (m, 2 H), 1.74 (br. s., 2 H) 1.67 (d, *J* = 11.6 Hz, 3 H), 1.42 (dd, *J* = 11.3, 6.7 Hz, 3 H), 1.35 - 1.28 (m, 4 H), 1.20 (t, *J* = 9.4 Hz, 2 H), 1.12 - 1.03 (m, 3 H), 0.91 (t, *J* = 6.8 Hz, 3 H), 0.72 - 0.65 (m, 2 H), 0.59 - 0.54 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.2, 137.6, 130.9, 128.4, 127.7, 127.1, 122.7, 68.9, 47.7, 41.6, 35.2, 31.4, 31.2, 28.8, 28.7, 26.6, 26.6, 26.5, 26.3, 22.5, 14.1, 7.4, 7.3; **HRMS (ESI)** *m/z* calcd. for $C_{25}H_{36}N_2S$ $[M + H]^+$ 397.2677, found 397.2672.



(*Z*)-*N*-((*Z*)-3-benzyl-4-cyclohexyl-5-hexylidenethiazolidin-2-ylidene)prop-2-en-1-amine (4h): Viscous oil; Yield 173 mg (86%); **IR** (neat): ν_{max}/cm^{-1} 3027, 2926, 2854, 1629, 1494, 1452, 1400, 1324, 1231, 1077, 1029, 993, 699; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 - 7.15 (m, 5 H), 6.02 - 5.88 (m, 1 H), 5.39 - 5.28 (m, 2 H), 5.21 (d, *J* = 17.1 Hz, 1 H), 5.05 (d, *J* = 10.3 Hz, 1 H), 4.15 (d, *J* = 16.0 Hz, 1 H), 3.97 - 3.83 (m, 3 H), 2.17 - 1.95 (m, 3 H), 1.82 -1.59 (m, 6 H), 1.43 (br. s., 3 H), 1.33 (br. s., 5 H), 1.21 (t, *J* = 9.1 Hz, 2 H) 1.14 – 0.98 (m, 3 H) 0.91 (t, *J* = 6.3 Hz, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 157.3, 137.7, 136.9, 130.5, 128.40, 127.6, 127.0, 122.8, 114.2, 68.9, 56.7, 47.7, 41.6, 31.4, 31.15, 28.9, 28.6, 26.56, 26.4, 26.3, 22.4, 14.1; **HRMS (ESI)** *m/z* calcd. for $C_{25}H_{36}N_2S$ $[M + H]^+$ 397.2677, found 397.2670.

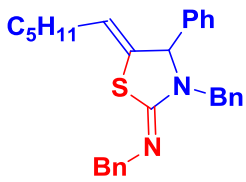


(*Z*)-*N*-((*Z*)-3-benzyl-5-heptylidene-4-phenylthiazolidin-2-ylidene)-4-chloroaniline (4i): Viscous oil; Yield 177 mg (75%); **IR** (neat): ν_{max}/cm^{-1} 3029, 2926, 2854, 1620, 1585, 1486, 1455, 1395, 1355, 1270, 1148, 1089, 1010, 834, 698; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.06 - 6.96 (m, 2 H), 5.43 (d, *J* = 15.1 Hz, 1 H), 5.16 (td, *J* = 7.3, 1.7 Hz, 1 H), 5.10 (d, *J* = 1.7 Hz, 1 H), 3.68 (d, *J* = 14.8 Hz, 1 H), 1.94 - 1.81 (m, 2 H), 1.25 - 1.18 (m, 4 H), 1.17 - 1.09 (m, 4 H), 0.82 (t, *J* = 7.1 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9, 150.4, 140.2, 136.6, 132.9, 129.1, 128.7, 128.6, 128.5, 127.7, 127.6, 123.8,

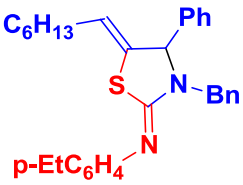


123.7, 68.5, 47.5, 31.6, 31.4, 28.8, 28.7, 22.6, 14.1; **HRMS (ESI)** *m/z* calcd. for $C_{29}H_{31}N_2SCl$ $[M + H]^+$ 475.1975; found 475.1973.

(*Z*)-*N*-((*Z*)-3-benzyl-5-hexylidene-4-phenylthiazolidin-2-ylidene)-1-phenylmethanamine (4j): Viscous oil; Yield 177 mg (76%); **IR** (neat): ν_{max}/cm^{-1} 3064, 3020, 2924, 2845, 1749, 1639, 1643, 1534, 1325, 1356, 1314, 1288, 1175, 1104, 1068, 877, 750, 716, 699; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 - 7.40 (m, 2 H), 7.39 - 7.31 (m, 4 H), 7.29 - 7.22 (m, 5 H), 7.21 - 7.16 (m, 2 H), 5.42 (d, *J* = 15.1 Hz, 1 H), 5.19 (dt, *J* = 7.2, 1.8 Hz, 1 H), 5.08 (d, *J* = 1.8, 1 H), 4.72 - 4.42 (m, 2 H), 3.64 (d, *J* = 15.1 Hz, 1 H), 2.05 - 1.90 (m, 2 H), 1.36 - 1.11 (m, 6 H), 0.84 (t, *J* = 7.1 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.0, 140.3, 136.9, 133.0, 128.8, 128.5, 128.4, 128.3, 128.2, 127.5, 127.4, 127.2, 126.4, 123.3, 68.2, 58.1, 47.3, 31.3, 28.3, 22.3, 14.0; **HRMS (ESI)** *m/z* calcd. for $C_{29}H_{32}N_2S$ $[M+H]^+$ 441.2364, found 441.2375.

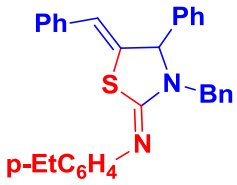


(*Z*)-*N*-((*Z*)-3-benzyl-5-heptylidene-4-phenylthiazolidin-2-ylidene)-4-ethylaniline (4k): Viscous oil; Yield 187 mg (80%); **IR** (neat): ν_{max}/cm^{-1} 3028, 2958, 2927, 2855, 1626, 1601, 1506, 1494, 1454, 1355, 1270, 1194, 1147, 1028, 837, 699; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 - 7.26 (m, 10 H), 7.21 (d, *J* = 8.2 Hz, 2 H), 7.10 – 7.02 (m, 2 H), 5.50 (d, *J* = 15.2 Hz, 1 H), 5.16 (td, *J* = 7.1, 1.5 Hz, 1 H), 5.12 (d, *J* = 1.5 Hz, 1 H), 3.71 (d, *J* = 14.9 Hz, 1 H), 2.69 (q, *J* = 7.6 Hz, 2 H), 1.97 - 1.84 (m, 2 H), 1.29 (t, *J* = 7.6 Hz, 3 H), 1.24 (dt, *J* = 13.2, 6.8 Hz, 4 H), 1.20 -1.11 (m, 4 H), 0.85 (t, *J* = 7.1 Hz, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 156.3, 149.4, 140.4, 139.1, 136.9, 133.5, 129.0, 128.7, 128.6, 128.5, 128.4, 127.7, 127.5, 123.3, 122.1, 68.4, 47.5, 31.6, 31.3, 28.8, 28.7, 28.5, 22.6, 15.8, 14.2; **HRMS (ESI)** *m/z* calcd. for $C_{31}H_{36}N_2S$ $[M + H]^+$ 469.2677, found 469.2676.

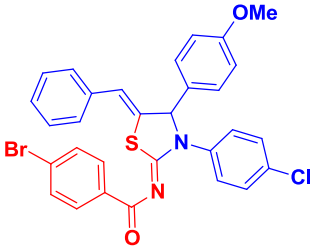


(*Z*)-*N*-((*Z*)-3-benzyl-5-benzylidene-4-phenylthiazolidin-2-ylidene)-4-ethylaniline (4l): White solid; Yield 195 mg (95%); **mp** 110 - 130 °C (recrystallized in methanol); **IR** (neat): ν_{max}/cm^{-1} 3453, 3027, 2963, 2929, 1641, 1454, 1398, 1273, 1147, 774, 699; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49 - 7.42 (m, 3 H), 7.41 - 7.30 (m, 7 H), 7.30 - 7.22 (m, 4 H), 7.21 - 7.14 (m, 3 H), 7.08 (d, *J* = 8.3 Hz, 2 H) 6.23 (s, 1 H), 5.57 (d, *J* = 14.8

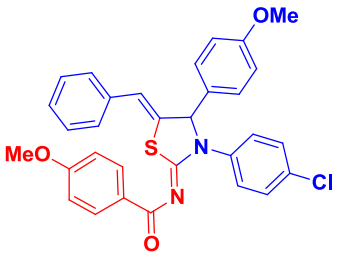
Hz, 1 H), 5.33 (s, 1 H), 3.77 (d, *J* = 14.8 Hz, 1 H), 2.72 (q, *J* = 7.6 Hz, 2 H), 1.32 (t, *J* = 7.5 Hz, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 155.7, 148.8, 140.1, 139.2, 136.7, 135.8, 134.0, 129.2, 128.8, 128.7, 128.5, 128.0, 127.7, 127.6, 127.1, 122.5, 122.1, 70.3, 47.5, 28.5, 15.7; **HRMS (ESI)** *m/z* calcd. for $C_{31}H_{28}N_2S$ $[M + H]^+$ 461.2051, found 461.2057.

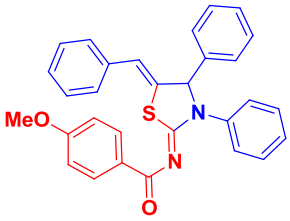


(*Z*)-*N*-((*Z*)-5-benzylidene-3-(4-chlorophenyl)-4-(4-methoxyphenyl)thiazolidin-2-ylidene)-4-bromobenzamide (4m): Viscous oil; Yield 179 mg (85%); **mp** 215 - 230 °C (recrystallized in methanol); **IR** (neat): ν_{max}/cm^{-1} 3270, 2923, 1610, 1589, 1509, 1492, 1461, 1406, 1303, 1165, 1110, 1010, 762; **^{1}H NMR** (500 MHz, $CDCl_3$) *δ* 7.98 - 7.80 (m, *J* = 8.5 Hz, 2 H), 7.53 - 7.45 (m, 2 H), 7.40 - 7.28 (m, 6 H), 7.27 - 7.12 (m, 5 H), 6.83 (d, *J* = 8.7 Hz, 2 H), 6.37 (d, *J* = 2.1 Hz, 1 H), 5.85 (d, *J* = 2.1 Hz, 1 H), 3.77 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 175.2, 168.7, 160.0, 137.4, 135.2, 134.9, 134.7, 133.2, 131.4, 131.3, 131.0, 129.1, 128.9, 128.7, 128.4, 128.4, 127.6, 127.4, 124.6, 114.5, 72.0, 55.2; **HRMS (ESI)** *m/z* calcd. for $C_{30}H_{22}{}^{79}BrClN_2O_2S$ $[M + H]^+$ 589.0352, found 589.0361, *m/z* calcd. for $C_{29}H_{21}{}^{81}BrClN_2O_2S$ $[M + H]^+$ 591.0332, found 591.0354.



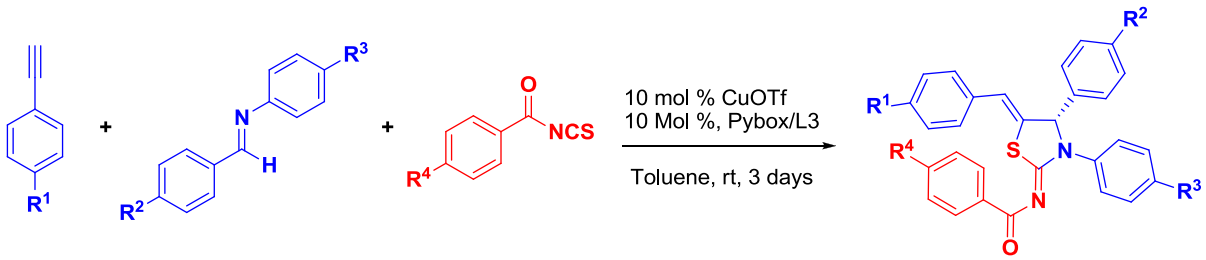
(*Z*)-*N*-((*Z*)-5-benzylidene-3-(4-chlorophenyl)-4-(4-methoxyphenyl)thiazolidin-2-ylidene)-4-methoxybenzamide (4n): White solide; Yield 190 mg (80%); **mp** 210 - 220 °C (recrystallized in methanol); **IR** (neat): ν_{max}/cm^{-1} 3060, 1600, 1513, 1491, 1407, 1382, 1303, 1252, 1159, 1029, 894; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.07 - 8.00 (m, 2 H), 7.41 - 7.28 (m, 6 H), 7.26 - 7.16 (m, 6 H), 6.88 - 6.80 (m, 4 H), 6.36 (d, *J* = 2.1 Hz, 1 H), 5.84 (d, *J* = 2.1 Hz, 1 H), 3.81 (s, 3 H), 3.76 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) *δ* 175.5, 167.6, 163.0, 159.9, 137.6, 135.3, 135.1, 132.8, 131.9, 131.2, 129.0, 128.8, 128.7, 128.6, 128.4, 127.4, 124.1, 114.4, 113.3, 71.6, 55.3, 55.2; **HRMS (ESI)** *m/z* calcd. for $C_{31}H_{25}{}^{35}ClN_2O_3S$ $[M + H]^+$ 541.1353, found 541.1354, *m/z* calcd. for $C_{31}H_{25}{}^{37}ClN_2O_3S$ $[M + H]^+$ 543.1342, found 543.1342.



(*Z*)-*N*-((*Z*)-5-benzylidene-3,4-diphenylthiazolidin-2-ylidene)-4-methoxybenzamide (4o): White solid; Yield 197 mg (83%); **mp** 200 - 215 °C (recrystallized in methanol); 

IR (neat): ν_{max}/cm^{-1} 3062, 3029, 2927, 1719, 1632, 1603, 1524, 1384, 1356, 1314, 1288, 1175, 1102, 1068, 877, 780, 716, 699; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 - 8.00 (m, 2 H), 7.45 - 7.18 (m, 16 H), 6.87 - 6.76 (m, 2 H), 6.41 (d, *J* = 1.8 Hz, 1 H), 5.93 (d, *J* = 2.1 Hz, 1 H), 3.80 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.5, 162.9, 139.5, 139.1, 135.4, 135.3, 131.9, 129.0, 128.9, 128.8, 128.6, 128.4, 127.4, 127.3, 126.9 , 124.0, 113.2, 72.3, 55.3; **HRMS (ESI)** *m/z* calcd. for $C_{30}H_{24}N_2O_2S$ $[M+H]^+$ 477.1637, found 477.1639.

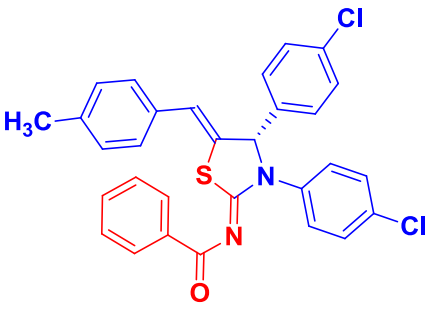
General Procedure for the enantioselective three component synthesis of thiazolidin-2-ylideneamine catalyzed by Cu (I) Complex:



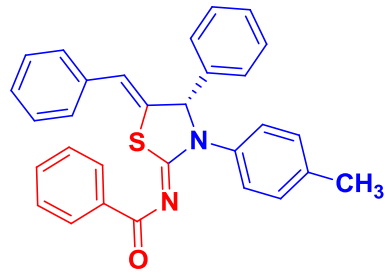
13 14 15 16

A solution of a ligand pybox/**L3** (10 mol %) and copper(I)OTf toluene complex (10 mmol %) in dry toluene (3 mL) was stirred at room temperature (30 °C) for 30 minutes. An imine **14** (0.50 mmol) and alkyne **13** (0.65 mmol) were added and the whole mixture was stirred for additional few hours at same temperature. At that temperature (30 °C) benzoyl isothiocyanate **15** (0.55 mmol) was added, the reaction mixture was stirred at room temperature for 3 days. After completion of the reaction (monitoring by TLC), the mixture was concentrated in vacuo and purified over silica gel column chromatography (2-10% EtOAc in petroleum ether) yielded pure thiazolidin-2-ylideneamine **16,** 75-95%. The enantiomeric excess was determined by HPLC with a Chiralcel OD-H column using hexane:isopropanol (19:1) as eluent.

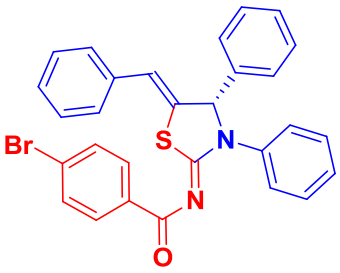
(*Z*)-*N*-((*Z*)-5-benzylidene-3-(4-chlorophenyl)-4-(4-methoxyphenyl)thiazolidin-2-ylidene) benzamide (16a): White solid; Yield 237 mg (90%); **mp** 210 - 220 °C (recrystallized in methanol); 99% *ee*; *Rf* = 0.58 (EtOAc:petroleum ether = 1:19); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ = 254 nm, TR(major) = 18.77 min and TR(minor) = 40.6 min; Optical Rotation: $[\alpha]_D^{25}$ = +17.0 (c 2.0, $CHCl_3$).; **IR** (neat): ν_{max}/cm^{-1} 3021, 2914, 1599, 1509, 1491, 1408, 1315, 1292, 1091, 1015, 894, 717; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.15 - 8.03 (m, 2 H), 7.51 - 7.42 (m, 1 H), 7.39 - 7.19 (m, 12 H), 7.14 (m, 2 H), 6.30 (d, *J* = 1.8 Hz, 1 H), 5.88 (d, *J* = 2.0 Hz, 1 H), 2.33 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) *δ* 176.1, 168.5, 137.8, 137.8, 137.3, 135.8, 134.9, 133.1, 132.9, 132.5, 132.2, 129.8, 129.4, 129.4, 129.2, 128.8, 128.3, 128.2, 128.1, 124.7, 71.4, 21.3; **HRMS (ESI)** *m/z* calcd. for $C_{30}H_{22}{}^{35}Cl_2N_2OS$ $[M + H]^+$ 529.0908, found 529.0908, *m/z* calcd. for $C_{30}H_{22}{}^{37}Cl_2N_2OS$ $[M + H]^+$ 531.0879, found 531.0900.



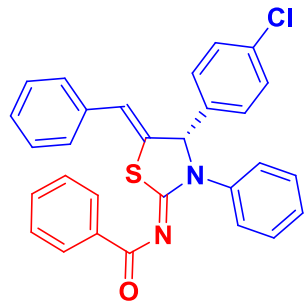
(*Z*)-*N*-((*Z*)-5-benzylidene-4-phenyl-3-p-tolylthiazolidin-2-ylidene)benzamide (16b): White solid; Yield 202 mg (88%); **mp** 180 - 200 °C (recrystallized in methanol); 98% *ee*; *Rf* = 0.50 (EtOAc: petroleum ether = 1:19); HPLC conditions: Diacel chiralcel AD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ = 254 nm, TR(major) = 39.93 min and TR(minor) = 21.94 min; Optical Rotation: $[\alpha]_D^{25}$ = +8.5 (c 01.6, $CHCl_3$). **IR** (neat): ν_{max}/cm^{-1} 3229, 3062, 3030, 2922, 1598, 1553, 1511, 1468, 1346, 1295, 1216, 1107, 1063, 825, 718; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.15 (d, *J* = 8.2 Hz, 2 H), 7.49 - 7.20 (m, 13 H), 7.19 - 7.10 (m, 4 H), 6.42 (s, 1 H), 5.92 (s, 1 H), 2.32 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) *δ* 176.1, 168.3, 139.5, 137.2, 136.2, 136.1, 135.3, 135.1, 132.1, 129.8, 129.4, 128.9, 128.7, 128.5, 128.3, 128.0, 127.4, 126.6, 124.0, 72.6, 21.1; **HRMS (ESI)** *m/z* calcd. for $C_{30}H_{24}N_2OS$ $[M + H]^+$ 461.1688, found 461.1670.



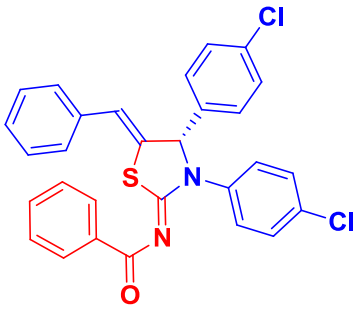
(*Z*)-*N*-((*Z*)-5-benzylidene-3,4-diphenylthiazolidin-2-ylidene)-4-bromobenzamide (16c): Vicious oil; Yield 224 mg (85%); 95.4% *ee*; *Rf* = 0.58 (EtOAc: petroleum ether = 1:19); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ = 254 nm, TR(major) = 26.52 min and TR(minor) = 11.46 min; Optical Rotation: $[\alpha]_D^{25}$ = +10.7 (c 0.8, CHCl3). **IR** (neat): ν_{max}/cm^{-1} 3061, 2924, 2852, 1724, 1620, 1598, 1587, 1511, 1452, 1397, 1313, 1298, 1164, 1067, 1010, 890, 762, 694; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 - 7.80 (m, 2 H), 7.50 - 7.44 (m, 2 H), 7.42 - 7.20 (m, 15 H), 6.43 (s, 1 H), 5.94 (s, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.2, 168.8, 139.3, 138.8, 135.2, 135.1, 134.8, 131.4, 131.3, 129.1, 128.9, 128.6, 128.4, 127.6, 127.5, 127.5, 127.2, 126.9, 124.4, 72.6; **HRMS (ESI)** *m/z* calcd. for $C_{29}H_{21}{}^{79}BrN_2OS$ $[M + H]^+$ 525.0636, found 525.0639, *m/z* calcd. for $C_{29}H_{21}{}^{81}BrN_2OS$ $[M + H]^+$ 527.0616, found 527.0618.



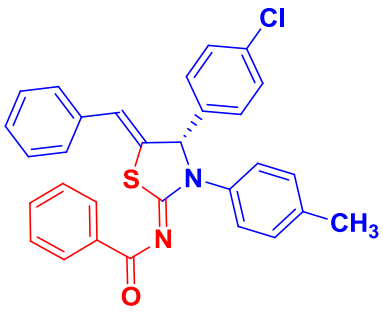
(*Z*)-*N*-((*Z*)-5-benzylidene-3-(4-chlorophenyl)-4-(4-methoxyphenyl)thiazolidin-2-ylidene)benzamide (16d): White solid; Yield 212 mg (88%); **mp** 215 - 230 °C (recrystallized in methanol); 80% *ee*; *Rf* = 0.50 (EtOAc: petroleum ether = 1:19); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ = 254 nm, TR(major) = 13.51 min and TR(minor) = 31.00 min; Optical Rotation: $[\alpha]_D^{25}$ = +20.2 (c 0.8, CHCl3). **IR** (neat): ν_{max}/cm^{-1} 3051, 2951, 2924, 1614, 1575, 1512, 1486, 1451, 1389, 1314, 1291, 1079, 892, 716; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.1 Hz, 2 H), 7.48 - 7.31 (m, 9 H), 7.30 - 7.23 (m, 7 H), 6.39 (d, *J* = 1.8 Hz, 1 H), 5.93 (d, *J* = 2.1 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.1, 168.3, 138.7, 138.0, 135.9, 135.1, 134.8, 134.6, 132.3, 129.8, 129.3, 129.0, 128.8, 128.7, 128.4, 128.1, 127.6, 127.6, 126.9, 124.5, 71.6; **HRMS (ESI)** *m/z* calcd. for $C_{29}H_{21}{}^{35}ClN_2OS$ $[M + H]^+$ 481.1141, found 481.1141, *m/z* calcd. for $C_{29}H_{21}{}^{37}ClN_2OS$ $[M + H]^+$ 483.1112, found 483.1128.



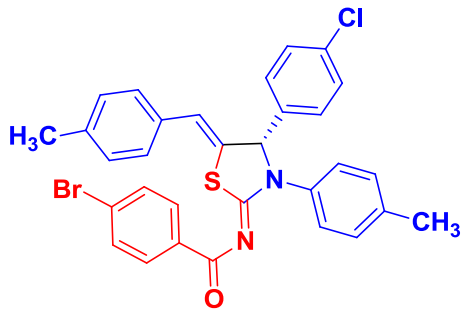
(*Z*)-*N*-((*Z*)-5-benzylidene-3,4-bis(4-chlorophenyl)thiazolidin-2-ylidene)benzamide (16e): White solid; Yield 237 mg (87%); **mp** 200 - 215 °C (recrystallized in methanol); 94.6% *ee*; *Rf* = 0.50 (EtOAc: petroleum ether = 1:19); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ = 254 nm, TR(major) = 47.02 min and TR(minor) = 16.38 min; Optical Rotation: $[\alpha]_D^{25}$ = -9.5 (c 0.8, $CHCl_3$). **IR** (neat): ν_{max}/cm^{-1} 3061, 1630, 1614, 1597, 1575, 1512, 1490, 1410, 1385, 1315, 1293, 1262, 1203, 1168, 1014, 893, 716; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 - 7.99 (m, 2 H), 7.52 - 7.43 (m, 1 H), 7.42 - 7.18 (m, 15 H), 6.34 (s, 1 H), 5.90 (s, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.1, 168.3, 137.7, 137.2, 135.7, 135.0, 134.2, 133.1, 132.5, 129.8, 129.4, 129.2, 128.8, 128.7, 128.4, 128.2, 128.1, 127.7, 124.7, 71.3; **HRMS (ESI)** *m/z* calcd. for $C_{29}H_{20}{}^{35}Cl_2N_2OS$ $[M + Cl]^-$ 549.0362, found 549.0354, *m/z* calcd. for $C_{29}H_{20}{}^{37}Cl_2N_2OS$ $[M + Cl]^-$ 551.0332, found 551.0302.



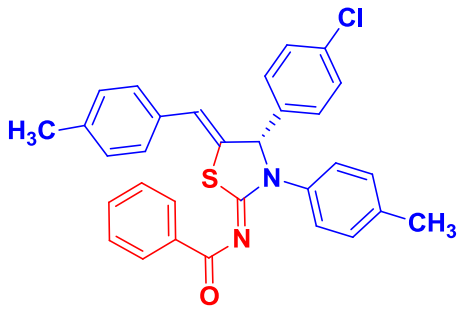
(*Z*)-*N*-((*Z*)-5-benzylidene-4-(4-chlorophenyl)-3-p-tolylthiazolidin-2-ylidene)benzamide (16f): White solid; Yield 212 mg (86%); **mp** 200 - 215 °C (recrystallized in methanol); 99% *ee*; *Rf* = 0.50 (EtOAc:petroleum ether = 1:19); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ = 254 nm, TR(major) = 10.22 min and TR(minor) = 27.14 min; Optical Rotation: $[\alpha]_D^{25}$ = +12.0 (c 1.8, $CHCl_3$). **IR** (neat): ν_{max}/cm^{-1} 3465, 3028, 2951, 1613, 1574, 1510, 1489, 1462, 1389, 1305, 1285, 1168, 1059, 1015, 826, 717; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 - 8.09 (m, 2 H), 7.48 - 7.43 (m, 1 H), 7.42 - 7.32 (m, 6 H), 7.28 - 7.22 (m, 5 H), 7.18 - 7.12 (m, 4 H), 6.36 (s, 1 H), 5.91 (s, 1 H), 2.33 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.0, 168.1, 138.0, 137.3, 135.9, 135.1, 134.5, 132.2, 129.7, 129.5, 129.1, 128.8, 128.5, 128.3, 128.0, 127.5, 126.5, 124.3, 71.5, 21.0; **HRMS (ESI)** *m/z* calcd. for $C_{30}H_{23}{}^{35}ClN_2OS$ $[M + H]^+$ 495.1298, found 495.1281, *m/z* calcd. for $C_{30}H_{23}{}^{37}ClN_2OS$ $[M + H]^+$ 496.1331, found 496.1335.



(*Z*)-4-bromo-*N*-((*S*,*Z*)-4-(4-chlorophenyl)-5-(4-methylbenzylidene)-3-p-tolylthiazolidin-2-ylidene)benzamide (16g): White solid; Yield 246 mg (84%); **mp** 140 - 155 °C (recrystallized in methanol); 99% *ee*; *Rf* = 0.50 (EtOAc:petroleum ether = 1:19); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ= 254 nm, TR(major) = 10.60 min and TR(minor) = 24.01 min; Optical Rotation: $[\alpha]_D^{25}$ = +13.0 (c 1.4, $CHCl_3$). **IR** (neat): ν_{max}/cm^{-1} 3027, 2920, 1622, 1563, 1508, 1410, 1396, 1289, 1164, 1069, 1010, 893, 762; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.3 Hz, 2 H), 7.46 (d, *J* = 8.5 Hz, 2 H), 7.30 - 7.22 (m, 6 H), 7.17 - 7.09 (m, 6 H), 6.31 (s, 1 H), 5.90 (s, 1 H), 2.39 (s, 3H), 2.24 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.1, 168.5, 137.9, 137.5, 137.4, 135.9, 135.0, 134.6, 132.9, 132.2, 131.3, 131.2, 129.5, 129.3, 129.1, 128.8, 128.2, 127.1, 126.5, 124.5, 71.6, 21.2, 21.0; **HRMS (ESI)** *m/z* calcd. for $C_{31}H_{24}{}^{79}BrClN_2OS$ $[M + H]^+$ 587.0559, found 587.0551, *m/z* calcd. for $C_{31}H_{24}{}^{81}BrClN_2OS$ $[M + H]^+$ 589.0539, found 589.0526.

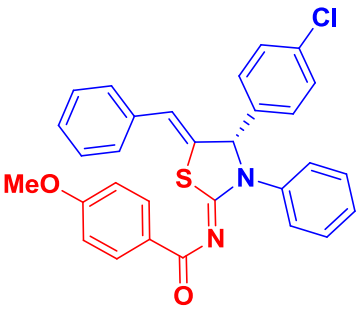


(*Z*)-*N*-((*Z*)-5-benzylidene-3-(4-chlorophenyl)-4-(4-methoxyphenyl)thiazolidin-2-ylidene)benzamide (16h): White solid; Yield 242 mg (95%); **mp** 220 - 230 °C (recrystallized in methanol); 90% *ee*; *Rf* = 0.50 (EtOAc:petroleum ether = 1:19); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ = 254 nm, TR(major) = 11.40 min and TR(minor) = 21.82 min; Optical Rotation: $[\alpha]_D^{25}$ = +10.5 (c 1.1, $CHCl_3$). **IR** (neat): ν_{max}/cm^{-1} 3026, 2920, 1630, 1614, 1575, 1508, 1485, 1388, 1315, 1294, 1089, 1062, 893, 716; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 - 8.00 (m, 2 H), 7.45 (t, *J* = 7.5 Hz, 1 H), 7.35 (t, *J* = 7.5 Hz, 2 H), 7.31 - 7.26 (m, 6 H), 7.18 - 7.11 (m, 6 H), 6.34 (s, 1 H), 5.89 (s, 1 H), 2.33 (s, 6 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.1, 168.3, 138.2, 137.6, 137.4, 136.1, 136.1, 134.6, 133.4, 132.3, 132.2, 129.8, 129.6, 129.3, 129.2, 128.8, 128.3, 128.0, 126.6, 124.3, 71.7, 21.2, 21.1; **HRMS (ESI)** *m/z*

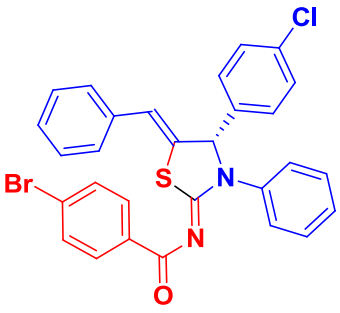


calcd. for $C_{31}H_{25}{}^{35}ClN_2OS$ [M + H]$^+$ 509.1454, found 509.1452, *m/z* calcd. for $C_{31}H_{25}{}^{37}ClN_2OS$ [M + H]$^+$ 511.1425, found 511.1437.

(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-4-(4-chlorophenyl)-3-phenylthiazolidin-2-ylidene)-4-methoxybenzamide (16i): Viscous oil; Yield 204 mg (80%); 86.6% *ee*; *Rf* = 0.40 (EtOAc:petroleum ether = 2:18); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ = 254 nm, TR(major) = 35.12 min and TR(minor) = 42.33 min; Optical Rotation: $[\alpha]_D^{25}$ +20.5 (c 0.8, $CHCl_3$). **IR** (neat): ν_{max}/cm^{-1} 3062, 2931, 2836, 1599, 1516, 1492, 1468, 1452, 1317, 1302, 1253, 1160, 1066, 1015, 776, 693; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 - 7.97 (m, 2 H), 7.41 - 7.31 (m, 6 H), 7.29 - 7.21 (m, 8 H), 6.91 - 6.72 (m, 2 H), 6.35 (d, *J* = 1.8 Hz, 1 H), 5.92 (d, *J* = 2.4 Hz, 1 H), 3.78 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.5, 167.5, 162.9, 138.8, 138.0, 135.1, 134.7, 134.6, 131.9, 129.2, 128.9, 128.8, 128.7, 128.6, 128.3, 127.5, 127.4, 126.8, 124.2, 113.2, 71.3, 55.2; **HRMS (ESI)** *m/z* calcd. for $C_{30}H_{23}{}^{35}ClN_2O_2S$ [M + H]$^+$ 511.1247, found 511.1245; *m/z* calcd. for $C_{30}H_{23}{}^{37}ClN_2O_2S$ [M + H]$^+$ 513.1218, found 513.1230.

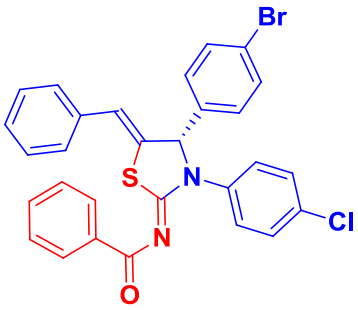


(*Z*)-*N*-((*Z*)-5-benzylidene-4-(4-chlorophenyl)-3-phenylthiazolidin-2-ylidene)-4-bromobenzamide (16j): White solid; Yield 212 mg (76%); **mp** 185 - 220 °C (recrystallized in methanol); 71% *ee*; *Rf* = 0.50 (EtOAc: petroleum ether = 1:19); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ = 254 nm, TR(major) = 10.21 min and TR(minor) = 32.45 min; Optical Rotation: $[\alpha]_D^{25}$ = +18.5 (c 0.6, $CHCl_3$). **IR** (neat): ν_{max}/cm^{-1} 3063, 2921, 1587, 1509, 1491, 1466, 1451, 1396, 1372, 1289, 1165, 1068, 1010, 762, 693; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 - 7.85 (m, 2 H), 7.47 - 7.43 (m, 2 H), 7.39 - 7.31 (m, 6 H), 7.30 - 7.23 (m, 8 H), 6.35 (d, *J* = 1.7 Hz, 1 H), 5.95 (d, *J* = 1.7 Hz, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.1, 168.5, 138.5, 137.7, 134.9, 134.8, 134.7, 134.2, 131.3, 131.2, 129.2, 128.9, 128.8, 128.6, 128.3, 127.7, 127.6, 127.2, 126.8, 124.6, 71.6; **HRMS**



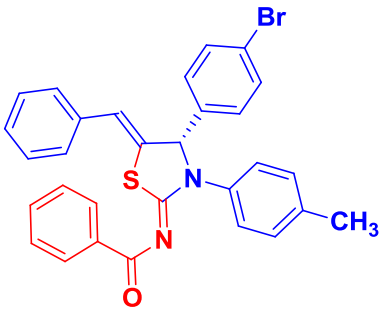
(ESI) *m/z* calcd. for $C_{29}H_{20}{}^{79}BrClN_2OS$ $[M + H]^+$ 559.0246, found 559.0244, *m/z* calcd. for $C_{29}H_{20}{}^{81}BrClN_2OS$ $[M + H]^+$ 561.0226, found 561.0244.

((*Z*)-*N*-((*Z*)-5-benzylidene-4-(4-bromophenyl)-3-(4-chlorophenyl)thiazolidin-2-ylidene)benzamide (16k): White solid; Yield 210 mg (75%); **mp** 195 - 220 °C



(recrystallized in methanol); 91% *ee*; *Rf* = 0.58 (EtOAc:petroleum ether = 1:19); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ = 254 nm, TR(major) = 30.20 min and TR(minor) = 10.85 min; Optical Rotation: $[\alpha]_D^{25}$ = -29.0 (c 0.53, $CHCl_3$). **IR** (neat): ν_{max}/cm^{-1} 3429, 3061, 2924, 1631, 1614, 1574, 1512, 1485, 1408, 1315, 1293, 1168, 1091, 1062, 1011, 893, 716; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 - 7.91 (m, 2 H), 7.50 - 7.42 (m, 3 H), 7.39 - 7.30 (m, 8 H), 7.24 - 7.17 (m, 4 H), 6.35 (d, *J* = 2.1 Hz, 1 H), 5.88 (d, *J* = 2.1 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.1, 168.4, 138.2, 137.2, 135.7, 135.0, 134.1, 133.1, 132.4, 131.9, 129.8, 129.5, 129.2, 129.1, 128.7, 128.4, 128.2, 127.7, 126.8, 124.8, 71.4; **HRMS (ESI)** *m/z* calcd. for $C_{29}H_{20}{}^{79}BrClN_2OS$ $[M + H]^+$ 559.0246, found 559.0244, *m/z* calcd. for $C_{29}H_{20}{}^{81}BrClN_2OS$ $[M + H]^+$ 561.0226, found 561.0233.

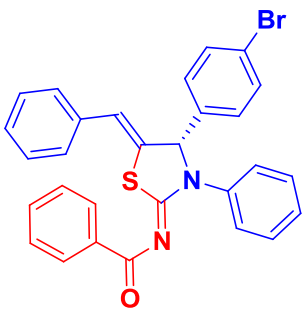
(*Z*)-*N*-((*Z*)-5-benzylidene-3-(4-chlorophenyl)-4-(4-methoxyphenyl)thiazolidin-2-ylidene)benzamide (16l): White solid; Yield 205 mg (80%); **mp** 190 - 205 °C



(recrystallized in methanol); 91% *ee*; *Rf* = 0.42 (EtOAc: petroleum ether = 1:19); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ = 254 nm, TR(major) = 10.22 min and TR(minor) = 28.45 min; Optical Rotation: $[\alpha]_D^{25}$ = +31.2 (c 0.23, $CHCl_3$). **IR** (neat): ν_{max}/cm^{-1} 3027, 2923, 1613, 1574, 1510, 1485, 1462, 1316, 1295, 1217, 1123, 1011, 895, 717; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.9 Hz, 2 H), 7.48 - 7.32 (m, 10 H), 7.27 - 7.18 (m, 3 H), 7.15 (s, 4 H), 6.37 (s, 1 H), 5.89 (s, 1 H), 2.34 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.1, 168.2, 138.6, 137.4, 136.0, 136.0, 135.1, 134.5,

132.2, 132.2, 129.8, 129.6, 129.1, 128.6, 128.3, 128.0, 127.6, 126.5, 124.4, 122.8, 71.7, 21.1; **HRMS (ESI)** *m/z* calcd. for $C_{30}H_{23}{}^{79}BrN_2OS$ $[M + H]^+$ 539.0793, found 539.0796, *m/z* calcd. for $C_{30}H_{23}{}^{81}BrN_2OS$ $[M + H]^+$ 541.0772, found 541.0774.

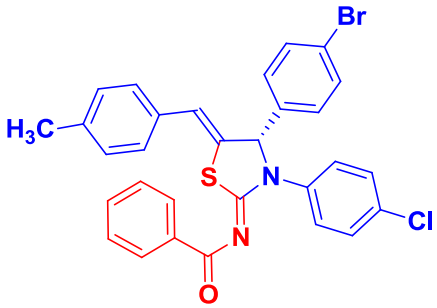
(*E*)-*N*-((*Z*)-5-benzylidene-4-(4-bromophenyl)-3-phenylthiazolidin-2-ylidene)ben



zamide (16m): White solid; Yield 199 mg (76%); **mp** 210 - 230 °C (recrystallized in methanol); 99% *ee*; *Rf* = 0.50 (EtOAc:petroleum ether = 1:19); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ = 254 nm, TR(major) = 13.70 min and TR(minor) = 32.49 min; Optical Rotation: $[\alpha]_D^{25}$ = +13.0 (c 0.15, $CHCl_3$). **IR** (neat): ν_{max}/cm^{-1} 3062, 1579, 1597, 1614, 1512, 1485, 1294, 1168, 1122, 1062, 716; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.9 Hz, 2 H), 7.49 - 7.32 (m, 11 H), 7.30 - 7.19 (m, 6 H), 6.38 (s, 1 H), 5.93 (s, 1 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.1, 168.2, 138.7, 138.5, 135.9, 135.1, 134.5, 132.3, 132.2, 129.8, 129.1, 129.0, 128.6, 128.4, 128.0, 127.6, 127.6, 126.8, 124.5, 122.9, 71.6; **HRMS (ESI)** *m/z* calcd. for $C_{29}H_{21}{}^{79}BrN_2S$ $[M + H]^+$ 525.0636, found 525.0632, *m/z* calcd. for $C_{27}H_{27}{}^{81}BrN_2S$ $[M + H]^+$ 527.0616, found 527.0617.

(*Z*)-*N*-((*Z*)-4-(4-bromophenyl)-3-(4-chlorophenyl)-5-(4-methylbenzylidene)thiazo

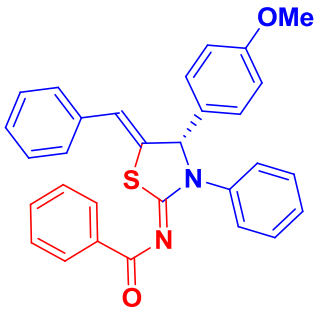
lidin-2-ylidene)benzamide (16n): White solid; Yield 240 mg (84%); **mp** 230 - 250 °C (recrystallized in methanol); 88.5% *ee*; *Rf* = 0.50 (EtOAc:petroleum ether = 1:19); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ = 254 nm, TR(major) = 34.22 min and TR(minor) = 17.50 min; Optical Rotation: $[\alpha]_D^{25}$ = 18.2 (c 0.7, $CHCl_3$). **IR**



(neat): ν_{max}/cm^{-1} 3011, 2923, 2901, 1630, 1574, 1510, 1485, 1407, 1380, 1314, 1292, 1201, 1160, 1090, 1060, 1011, 893, 829, 716; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 1.1, 8.4 Hz, 2 H), 7.48 - 7.42 (m, 3 H), 7.39 - 7.30 (m, 4 H), 7.27 (d, *J* = 8.2 Hz, 2 H), 7.23 - 7.13 (m, 6 H), 6.34 (d, *J* = 1.8 Hz, 1 H), 5.86 (s, 1 H), 2.33 (s, 3 H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.1, 168.5, 138.3, 137.8, 137.3, 135.8, 133.1, 132.8,

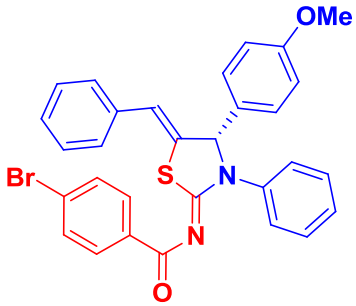
132.5, 132.4, 132.2, 131.9, 129.8, 129.4, 129.2, 129.1, 128.4, 128.2, 124.8, 123.1, 71.5, 21.3; **HRMS (ESI)** *m/z* calcd. for $C_{30}H_{22}{}^{79}BrClN_2OS$ $[M + H]^+$ 573.0403, found 573.0401, *m/z* calcd. for $C_{30}H_{22}{}^{81}BrClN_2OS$ $[M + H]^+$ 575.0383, found 575.0381.

(*Z*)-*N*-((*Z*)-5-benzylidene-4-(4-methoxyphenyl)-3-phenylthiazolidin-2-ylidene)ben



zamide (16o): White solid; Yield 188 mg (79%); **mp** 140 - 195 °C (recrystallized in methanol); 98.7% *ee*; *Rf* = 0.25 (EtOAc:petroleum ether = 1:19); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ = 254 nm, TR(major) = 21.25 min and TR(minor) = 36.74 min; Optical Rotation: $[\alpha]_D^{25}$ = +8.0 (c 0.7, $CHCl_3$). **IR** (neat): ν_{max}/cm^{-1} 3011, 2925, 2853, 1609, 1597, 1572, 1521, 1494, 1453, 1296, 1268, 1253, 1203, 1175, 1062, 1023, 890, 716, 692, 562; **^{1}H NMR** (500 MHz, $CDCl_3$) *δ* 8.08 (d, *J* = 7.3 Hz, 2 H), 7.48 - 7.39 (m, 3 H), 7.38 - 7.31 (m, 6 H), 7.29 - 7.21 (m, 6 H), 6.82 (d, *J* = 8.6 Hz, 2 H), 6.41 (s, 1 H), 5.90 (s, 1 H), 3.76 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) *δ* 176.1, 168.2, 159.9, 139.1, 136.2, 135.4, 132.2, 131.5, 129.8, 128.9, 128.9, 128.6, 128.4, 128.0, 127.4, 127.1, 124.1, 114.4, 72.1, 55.2; **HRMS (ESI)** *m/z* calcd. for $C_{30}H_{24}N_2O_2S$ $[M + H]^+$ 477.1637, found 477.1638.

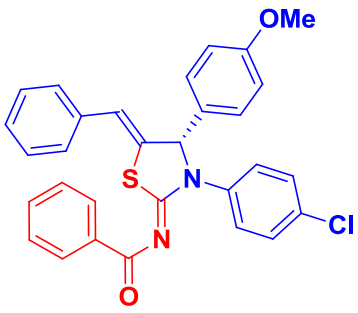
(*Z*)-*N*-((*Z*)-5-benzylidene-4-(4-methoxyphenyl)-3-phenylthiazolidin-2-ylidene)-4-bromo benzamide (16p): White solid; Yield 120 mg (87%); **mp** 195 - 220 °C



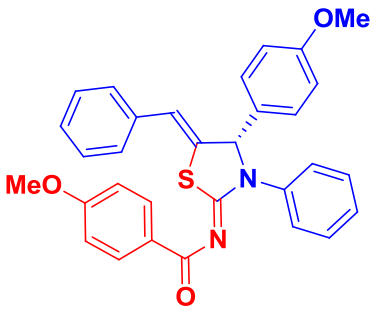
(recrystallized in methanol); 82.6% *ee*; *Rf* = 0.58 (EtOAc:petroleum ether = 1:19); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ= 254 nm, TR(major) = 31.18 min and TR(minor) = 13.98 min; Optical Rotation: $[\alpha]_D^{25}$ = +8.5 (c 0.4, $CHCl_3$). **IR** (neat): ν_{max}/cm^{-1} 3336, 3015, 2926, 1726, 1310, 1587, 1510, 1452, 1396, 1306, 1251, 1166, 1067, 1029, 1009, 891, 762; **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.96 - 7.83 (m, 2 H), 7.49 - 7.43 (m, 2 H), 7.42 - 7.31 (m, 6 H), 7.29 - 7.17 (m, 7 H), 6.88 - 6.70 (m, 2 H), 6.40 (d, *J* = 2.1 Hz, 1 H), 5.89 (d, *J* = 2.1 Hz, 1 H), 3.76 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) *δ* 175.2, 168.6, 159.9, 138.9, 135.3, 135.1, 135.0, 131.3, 131.3, 131.3, 128.9, 128.6, 128.3, 127.6, 127.5,

127.1, 127.1, 124.3, 114.4, 72.2, 55.2; **HRMS (ESI)** *m/z* calcd. for $C_{30}H_{23}{}^{79}BrN_2O_2S$ $[M + H]^+$ 555.0743, found 555.0731, *m/z* calcd. for $C_{30}H_{23}{}^{81}BrN_2O_2S$ $[M + H]^+$ 557.0721, found 557.0731.

(*Z*)-*N*-((*Z*)-5-benzylidene-3-(4-chlorophenyl)-4-(4-methoxyphenyl)thiazolidin-2-ylidene) benzamide (16q): White solid; Yield 204 mg (80%); **mp** 185 - 200 °C (recrystallized in methanol); 95% *ee*; *Rf* = 0.58 (EtOAc:petroleum ether = 1:19); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ= 254 nm, TR(major) = 17.82 min and TR(minor) = 48.46 min; Optical Rotation: $[\alpha]_D^{25}$ = +8.5 (c 0.8, $CHCl_3$). **IR** (neat): ν_{max}/cm^{-1} 3061, 2931, 2835, 1611, 1574, 1510, 1490, 1448, 1407, 1315, 1250, 1091, 1024, 716; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.3 Hz, 2 H), 7.50 - 7.45 (m, 1 H), 7.41 - 7.30 (m, 8 H), 7.26 - 7.18 (m, 5 H), 6.86 - 6.81 (m, 2 H), 6.39 (d, *J* = 1.8 Hz, 1 H), 5.87 (d, *J* = 1.8 Hz, 1 H), 3.77 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.1, 168.3, 159.9, 137.5, 135.9, 135.3, 134.9, 132.9, 132.4, 131.1, 129.8, 129.1, 128.9, 128.7, 128.4, 128.1, 127.5, 124.4, 114.5, 71.8, 55.2; **HRMS (ESI)** *m/z* calcd. for $C_{30}H_{24}{}^{35}ClN_2O_2S$ $[M + H]^+$ 511.1247, found 511.1221, *m/z* calcd. for $C_{30}H_{24}{}^{37}ClN_2O_2S$ $[M + H]^+$ 513.1247, found 513.1211.

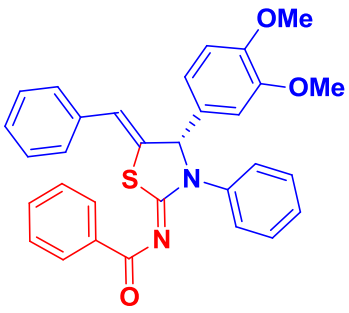


(*Z*)-*N*-((*S,Z*)-5-benzylidene-4-(4-methoxyphenyl)-3-phenylthiazolidin-2-ylidene)-4-meth oxybenzamide (**16r):** White solid; Yield 202 mg (80%); **mp** 190 - 230 °C (recrystallized in methanol); 86% *ee*; *Rf* = 0.40 (EtOAc: petroleum ether = 2:18); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ = 254 nm, TR(major) = 27.45 min and TR(minor) = 32.81 min; Optical Rotation: $[\alpha]_D^{25}$ = +12.5 (c 0.4, CHCl3). **IR** (neat): ν_{max}/cm^{-1} 3003, 2928, 2837, 1599, 1572, 1515, 1453, 1388, 1318, 1252, 1159, 1064, 1029, 892, 777, 696; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.6 Hz, 2 H), 7.43 - 7.38 (m, 2 H), 7.37 - 7.30 (m, 4 H), 7.28 - 7.21 (m, 6 H), 6.82 (dd, *J* = 8.7, 6.2 Hz, 4 H), 6.38 (d, *J* =



1.8 Hz, 1 H), 5.88 (d, *J* = 1.8 Hz, 1 H), 3.80 (s, 3 H), 3.75 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 175.5, 167.6, 162.9, 159.8, 139.2, 135.6, 135.4, 131.9, 131.6, 128.9, 128.8, 128.8, 128.6, 128.4, 127.3, 127.3, 127.1, 123.9, 114.3, 113.3, 72.0, 55.3, 55.2.; **HRMS (ESI)** *m/z* calcd. for $C_{31}H_{26}N_2O_3S$ $[M + H]^+$ 507.1742, found 507.1745.

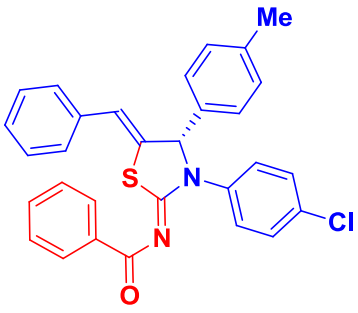
(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-4-(3,4-dimethoxyphenyl)-3-phenylthiazolidin-2-ylide



ne)benzamide (16s): Viscous oil; Yield 204 mg (81%); 60% *ee*; *Rf* = 0.40 (EtOAc: petroleum ether = 2:18); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ = 254 nm, TR (major) = 56.10 min and TR (minor) = 30.50 min; Optical Rotation: $[\alpha]_D^{25}$ = +8.5 (c 0.2, $CHCl_3$). **IR** (neat): ν_{max}/cm^{-1} 3021, 2926, 1614, 1573, 1486, 1451, 1390, 1293, 1260, 1024, 891, 689; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 - 7.99 (m, 2 H), 7.47 - 7.40 (m, 3 H), 7.38 - 7.31 (m, 6 H), 7.29 - 7.22 (m, 4 H), 6.86 (dd, *J* = 7.9, 1.8 Hz, 1 H), 6.81 (d, *J* = 1.8 Hz, 1 H), 6.75 (d, *J* = 8.6 Hz, 1 H), 6.41 (d, *J* = 1.8 Hz, 1 H), 5.90 (d, *J* = 1.8 Hz, 1 H), 3.83 (s, 3 H), 3.80 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.1, 168.2, 149.4, 149.4, 139.0, 136.1, 135.3, 135.0, 132.2, 131.6, 129.8, 128.8, 128.6, 128.4, 128.0, 127.4, 127.0, 124.2, 120.7, 110.9, 109.9, 72.3, 56.0, 55.7; **HRMS (ESI)** *m/z* calcd. for $C_{31}H_{26}N_2O_3S$ $[M + H]^+$ 507.1742, found 507.1741.

(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-3-(4-chlorophenyl)-4-p-tolylthiazolidin-2-ylidene)ben

zamide (**16t):** White solid; Yield 220 mg (89%); **mp** 175 - 200 °C (recrystallized in



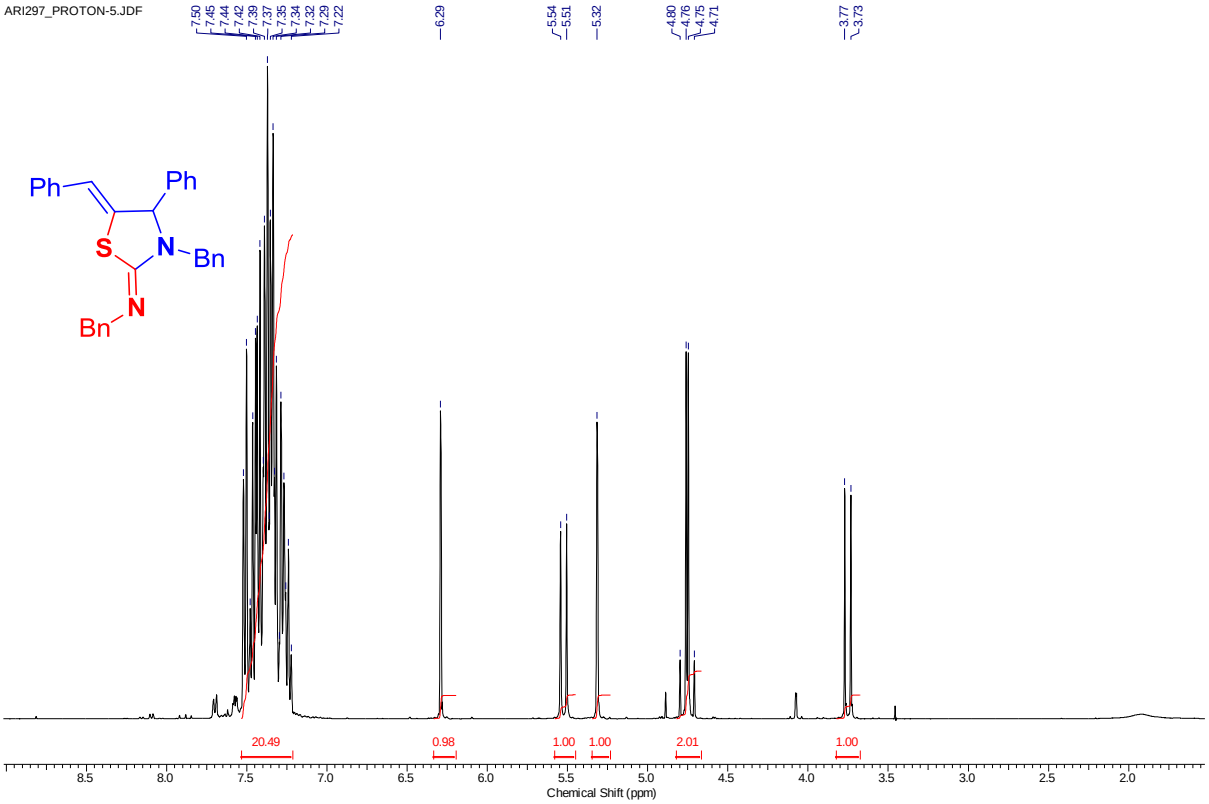
methanol); 84% *ee*; Rf = 0.50 (EtOAc: petroleum ether = 1:19); HPLC conditions: Diacel chiralcel OD-H (150 mm x 4.6 mm I.D.), 95:5 hexane:i-PrOH, 1 mL/min flow rate, λ = 254 nm, TR(major) = 22.72 min and TR(minor) = 10.37 min; Optical Rotation: $[\alpha]_D^{25}$ +15.0 (c 0.6, $CHCl_3$). **IR** (neat): ν_{max}/cm^{-1} 3020, 2914, 1637, 1589, 1500, 1480, 1340, 1247, 1128, 1088, 1019, 849, 688; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (m, 2 H), 7.41 - 7.29 (m, 9 H), 7.26 - 7.20 (m, 5 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 6.40 (d, *J* = 1.7 Hz, 1 H), 5.88 (d, *J* = 2.3 Hz, 1 H), 2.31 (s, 3 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ

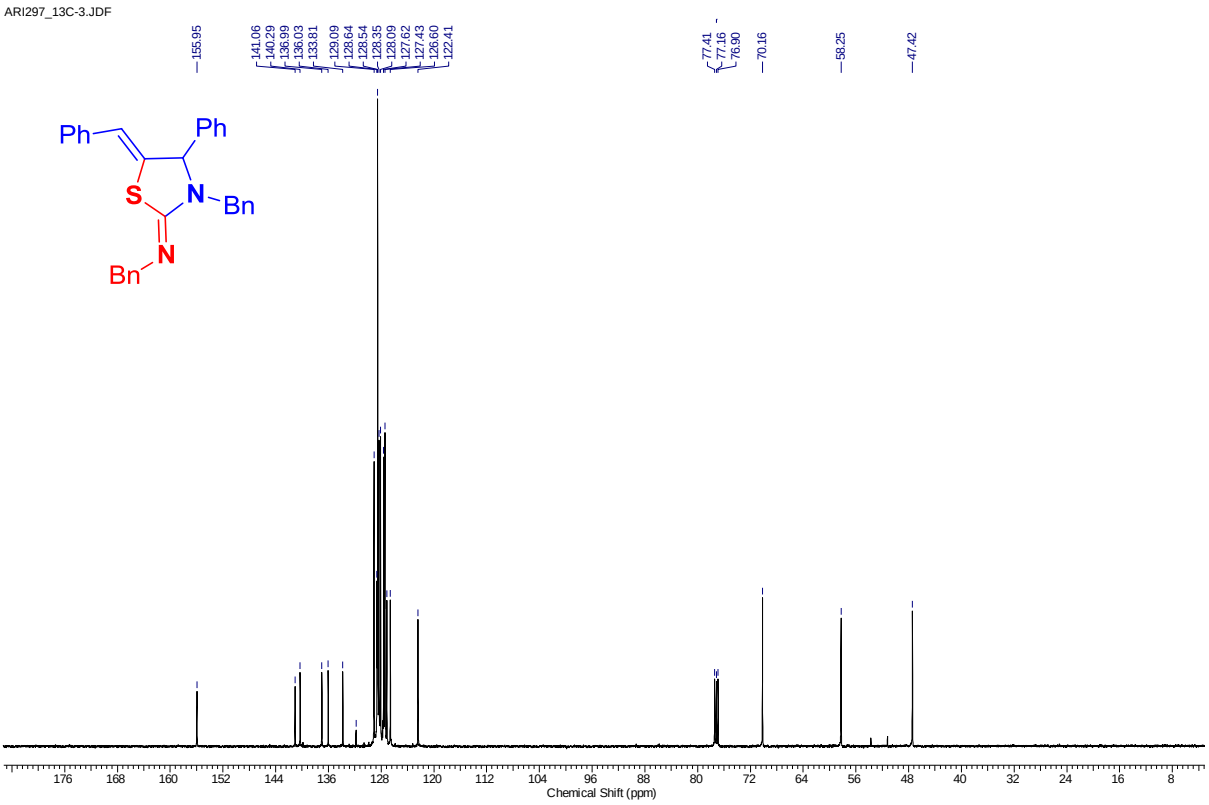
176.0, 168.4, 138.9, 137.5, 136.1, 135.3, 134.8, 132.9, 132.3, 129.8, 129.8, 129.0, 128.6, 128.4, 128.2, 128.1, 127.5, 127.3, 125.3, 124.3, 72.0, 21.2; **HRMS (ESI)** *m*/*z* calcd. for $C_{30}H_{23}{}^{35}ClN_2OS$ $[M + H]^+$ 495.1298, found 495.1297.

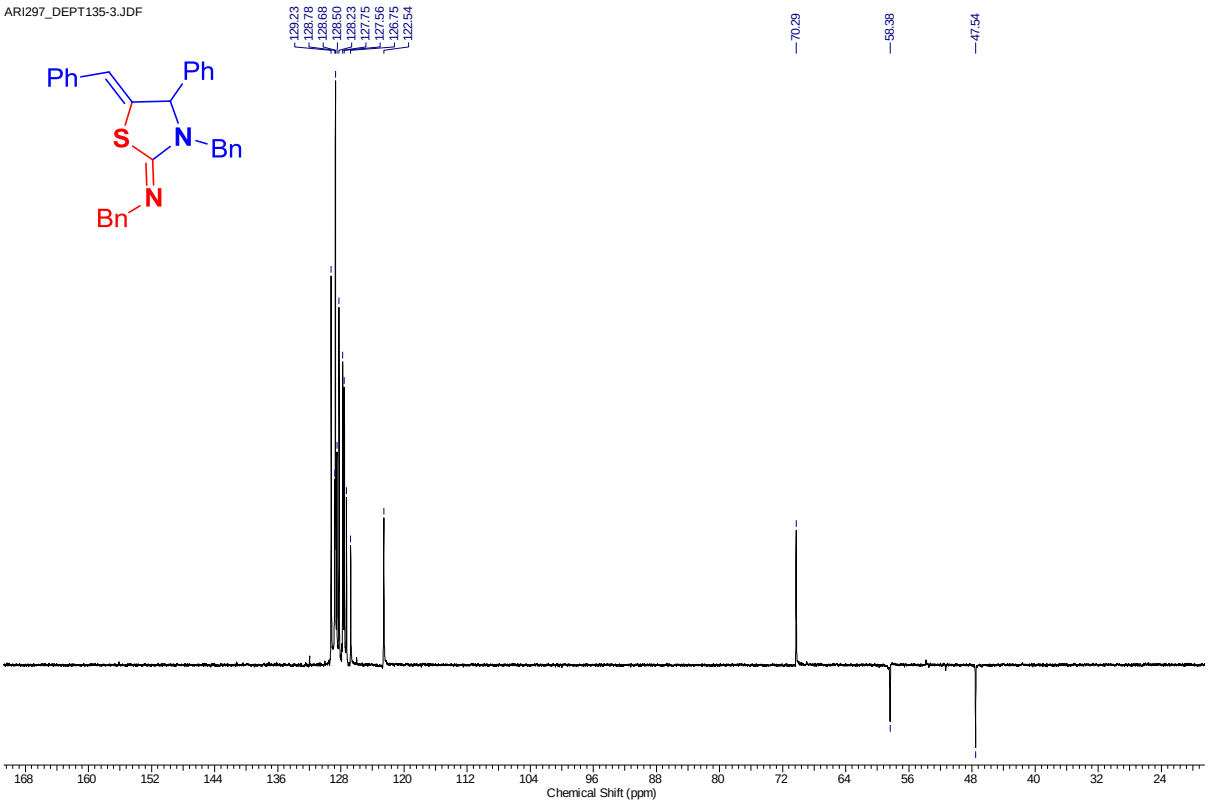
PyBOX - 2,6-bis((R)-5,5-dibutyl-4-phenyl-4,5-dihydrooxazol-2-yl)pyridine (L3): Prepared acoording to the reference **1**

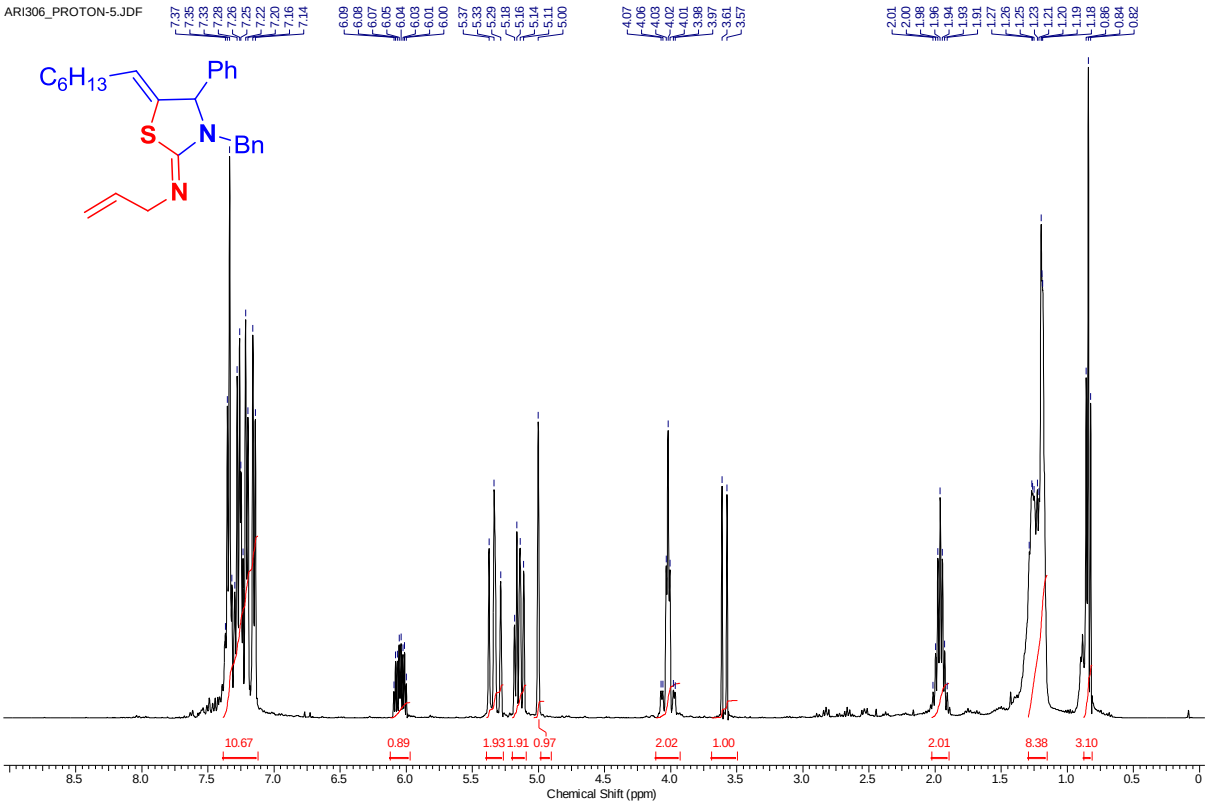
(1) Lee, J. Y.; You, Y. S.; Kang, S. H. *J. Am. Chem. Soc.* **2011**, *133*, 1772

NMR SPECTRA of COMPOUND (4a-4o)

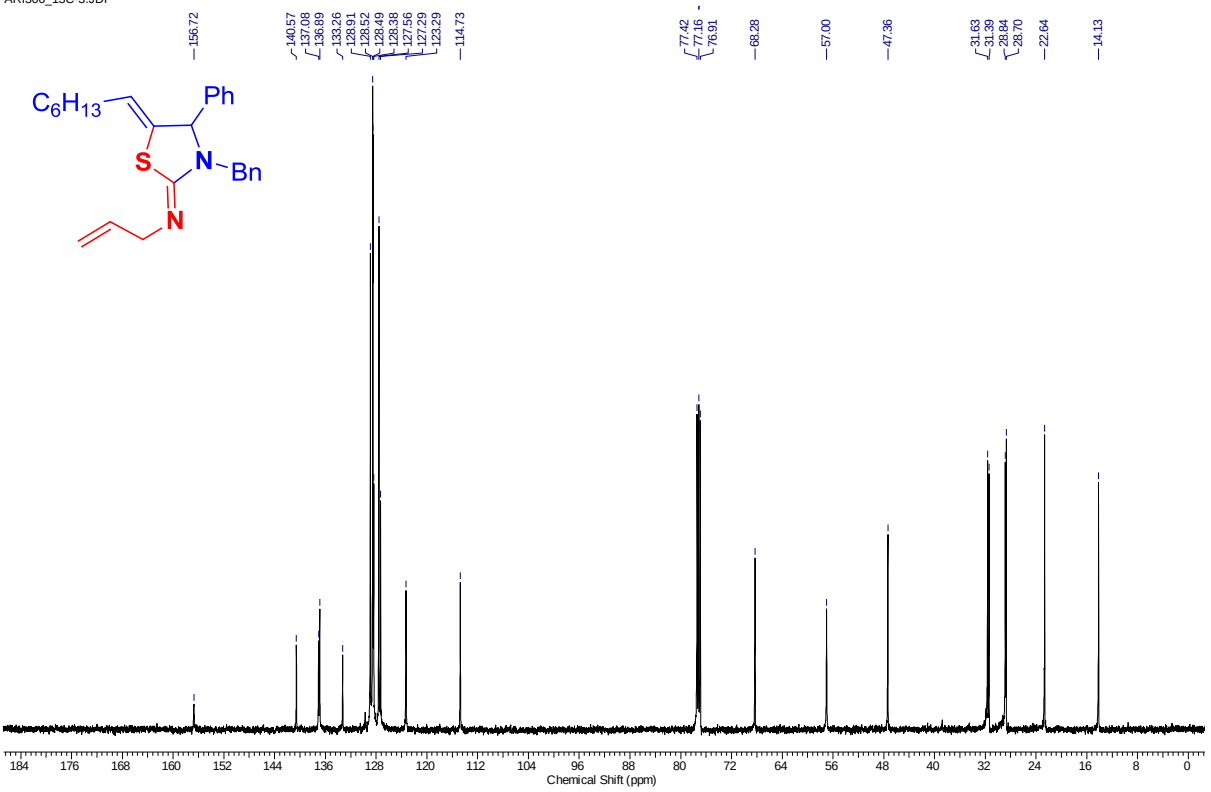




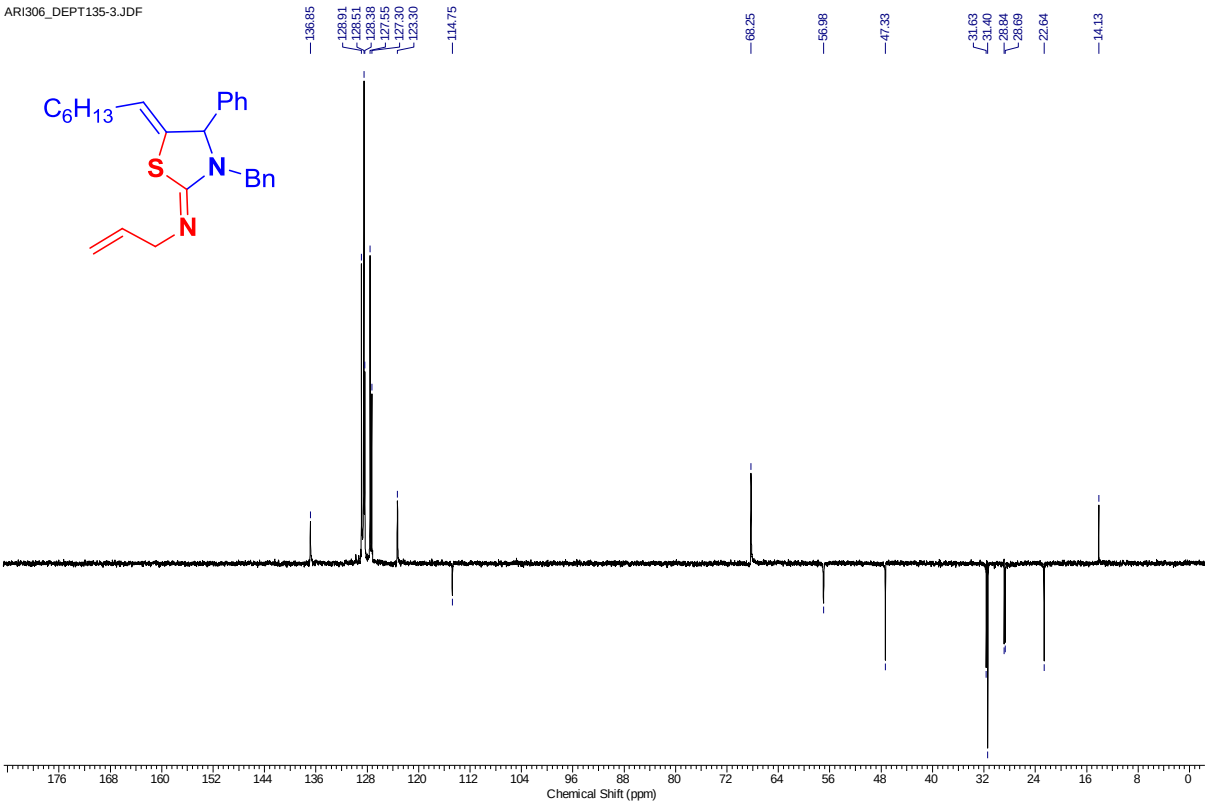

ARI297_DEPT135-3.JDF
129.23
128.78
128.68
128.50
128.23
127.75
127.56
126.75
122.54
70.29
58.38
47.54
Ph
Ph
S
N
Bn
N
Bn
Chemical Shift (ppm)

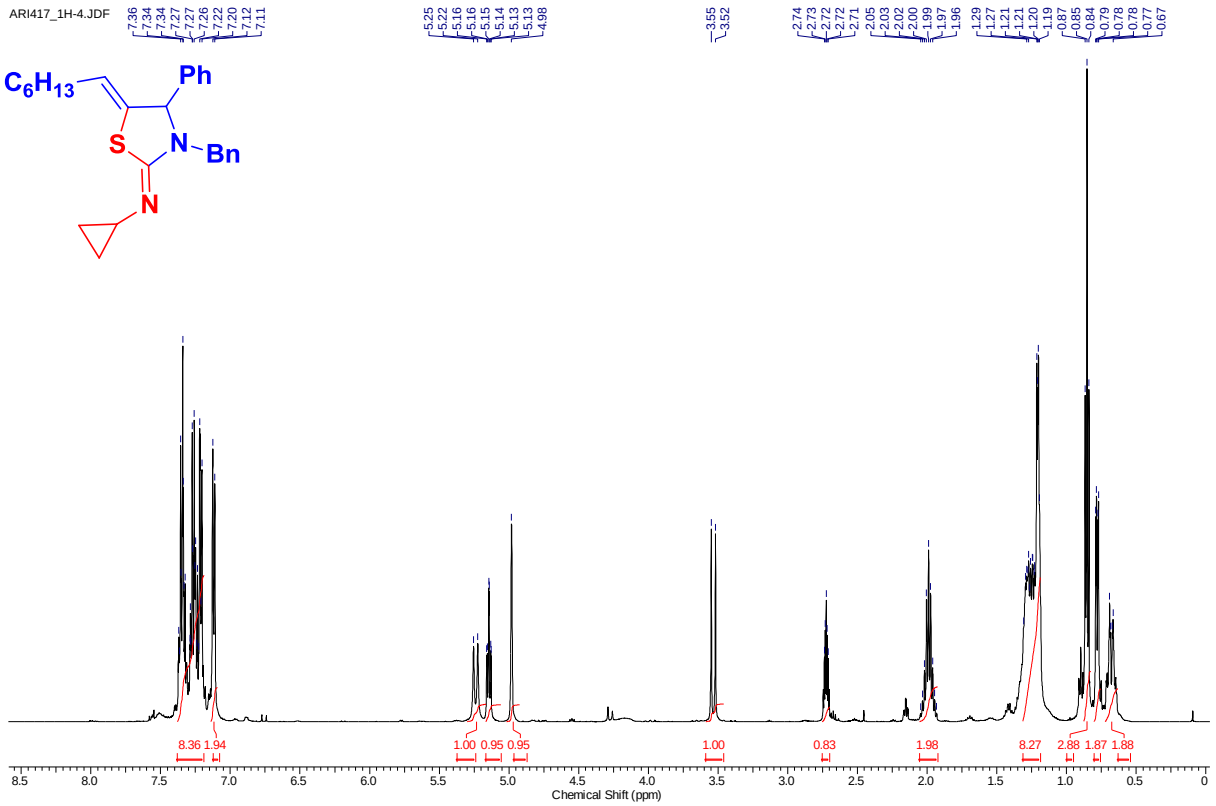

ARI306_PROTON-5.JDF
7.37
7.35
7.33
7.28
7.26
7.25
7.22
7.20
7.16
7.14
6.09
6.08
6.07
6.05
6.04
6.03
6.01
6.00
5.37
5.33
5.29
5.18
5.16
5.14
5.11
5.00
4.07
4.06
4.03
4.02
4.01
3.98
3.97
3.61
3.57
2.01
2.00
1.98
1.96
1.94
1.93
1.91
1.27
1.26
1.25
1.23
1.21
1.20
1.19
1.18
0.86
0.84
0.82
C6H13
Ph
S
N
Bn
N
10.67
0.89
1.93
1.91
0.97
2.02
1.00
2.01
8.38
3.10
Chemical Shift (ppm)

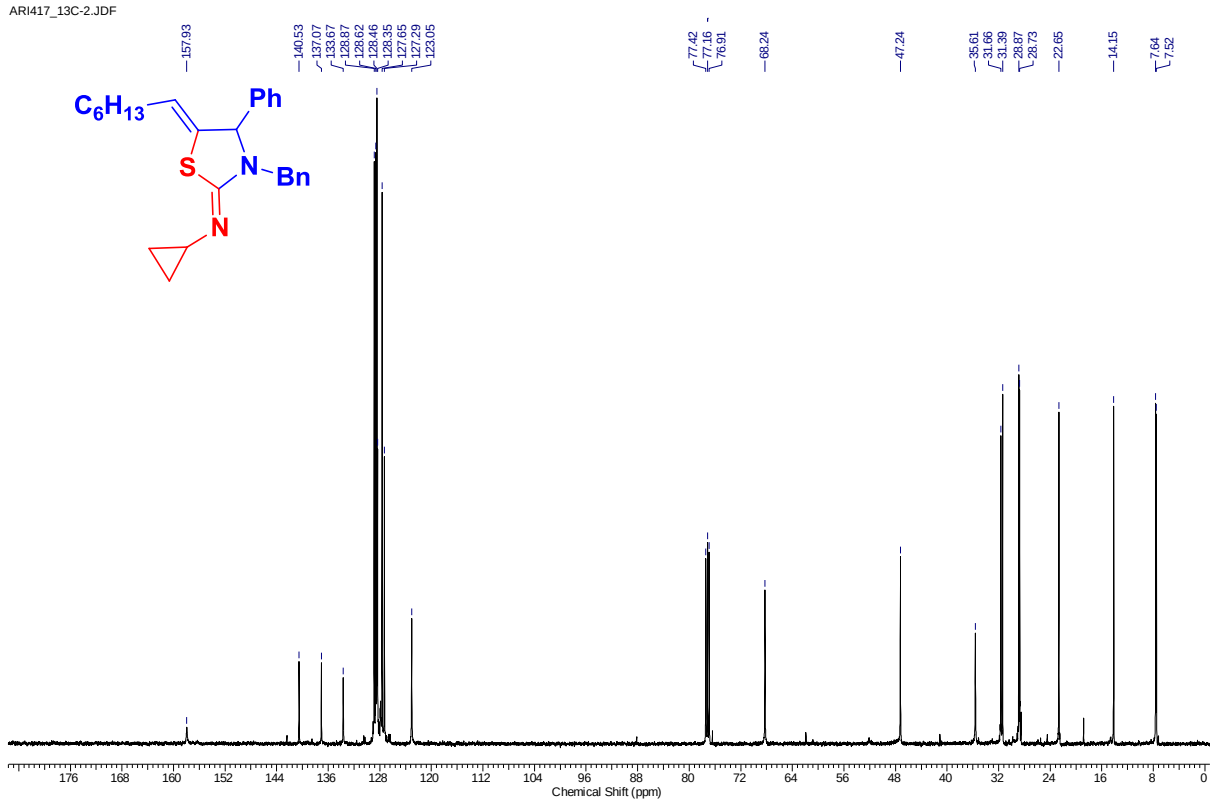
ARI306_13C-3.JDF

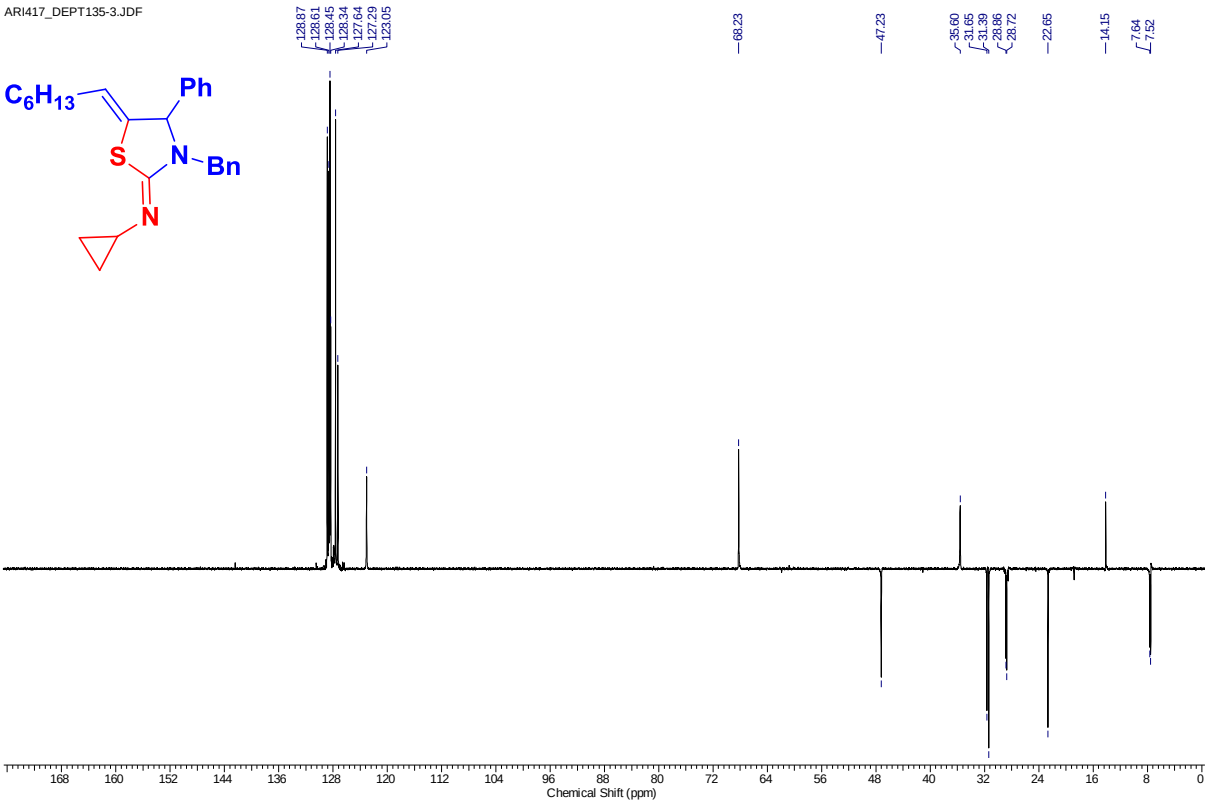


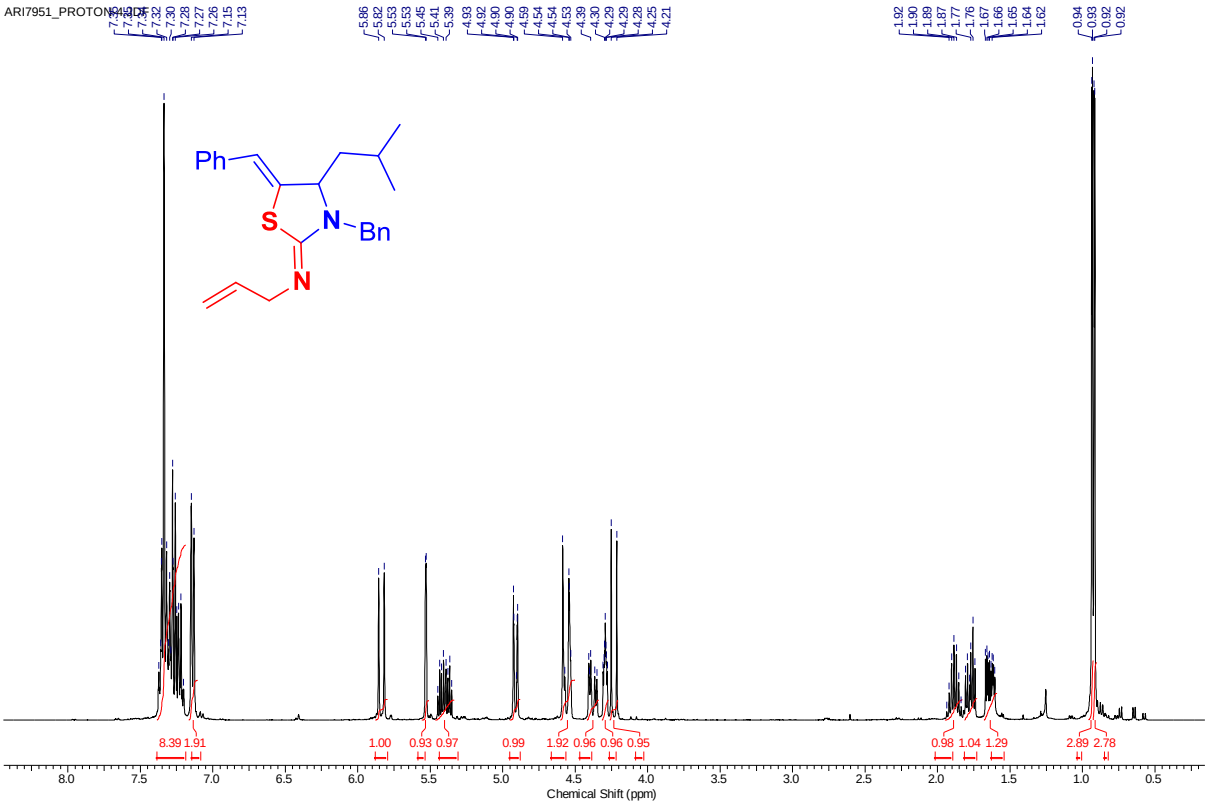
ARI306_DEPT135-3.JDF

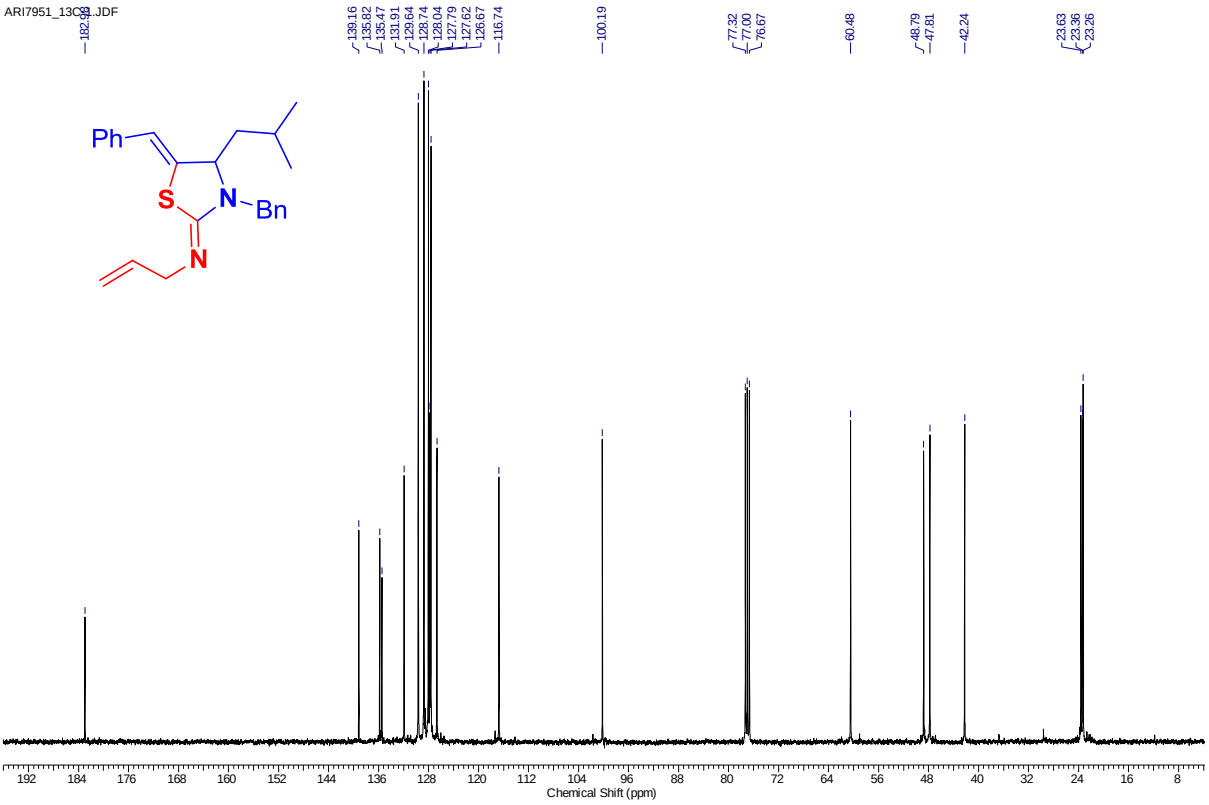


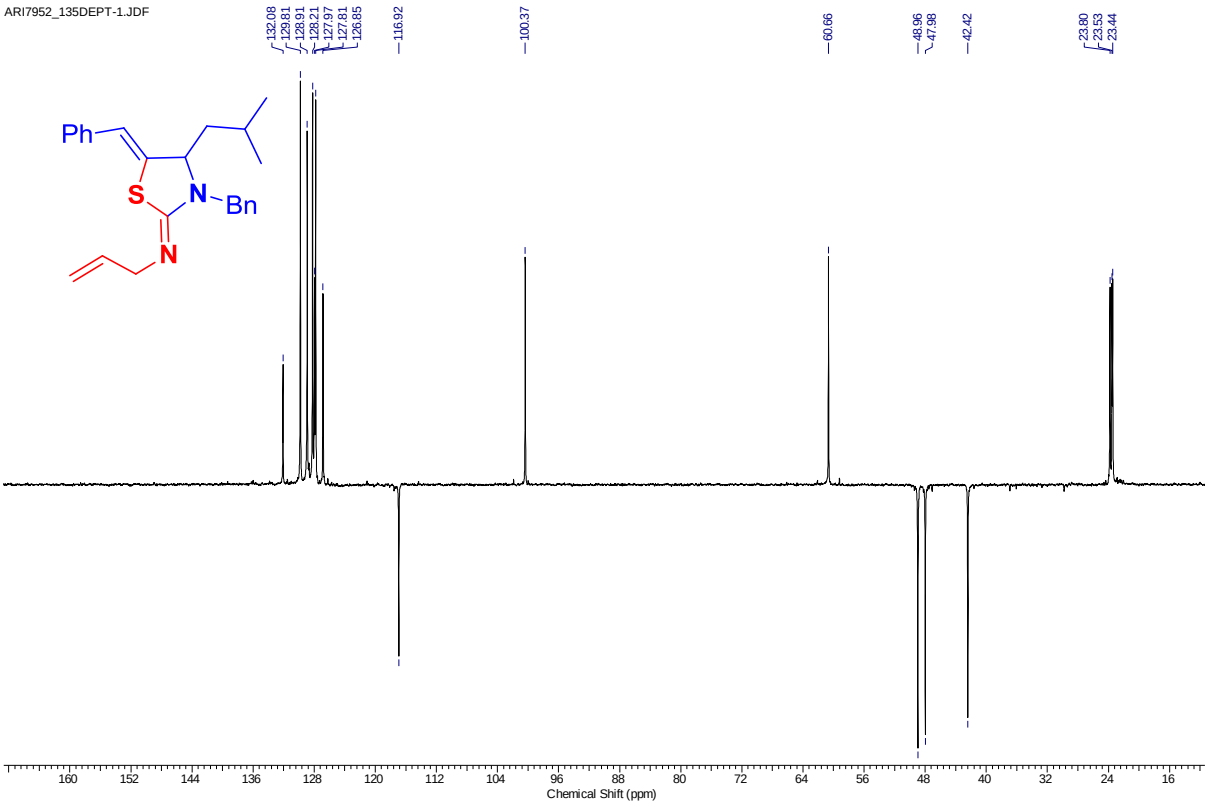

ARI417_1H-4.JDF
7.36 7.34 7.34 7.27 7.27 7.26 7.22 7.20 7.12 7.11
5.25 5.22 5.16 5.16 5.15 5.14 5.13 5.13 4.98
3.55 3.52
2.74 2.73 2.72 2.72 2.71 2.05 2.03 2.02 2.00 1.99 1.97 1.96
1.29 1.27 1.21 1.21 1.20 1.19 0.87 0.85 0.84 0.79 0.78 0.78 0.77 0.67
C6H13
Ph
S
N
Bn
N
8.36 1.94
1.00 0.95 0.95
1.00
0.83
1.98
8.27
2.88 1.87 1.88
Chemical Shift (ppm)

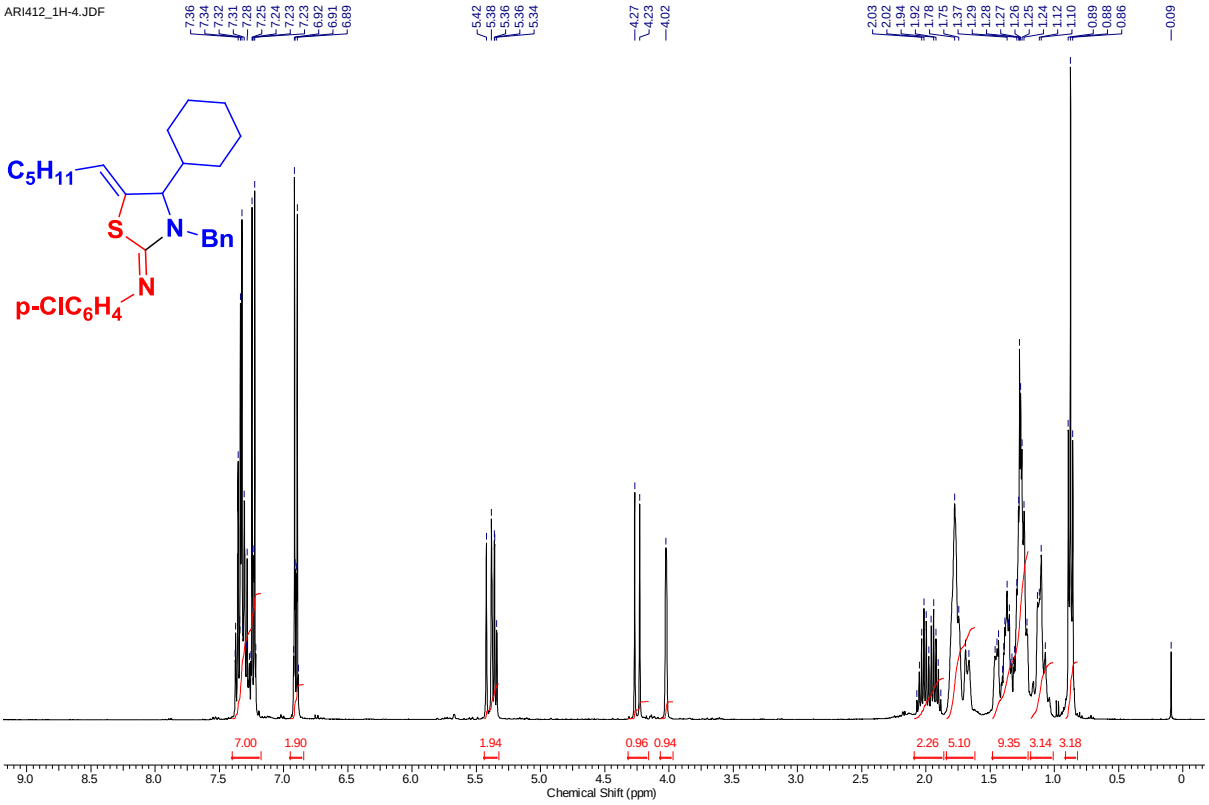

ARI417_13C-2.JDF
157.93
140.53 137.07 133.67 128.87 128.62 128.46 128.35 127.65 127.29 123.05
77.42 77.16 76.91
68.24
47.24
35.61 31.66 31.39 28.97 28.73
22.65
14.15
7.64 7.52
C6H13
Ph
S
N
Bn
N
Chemical Shift (ppm)

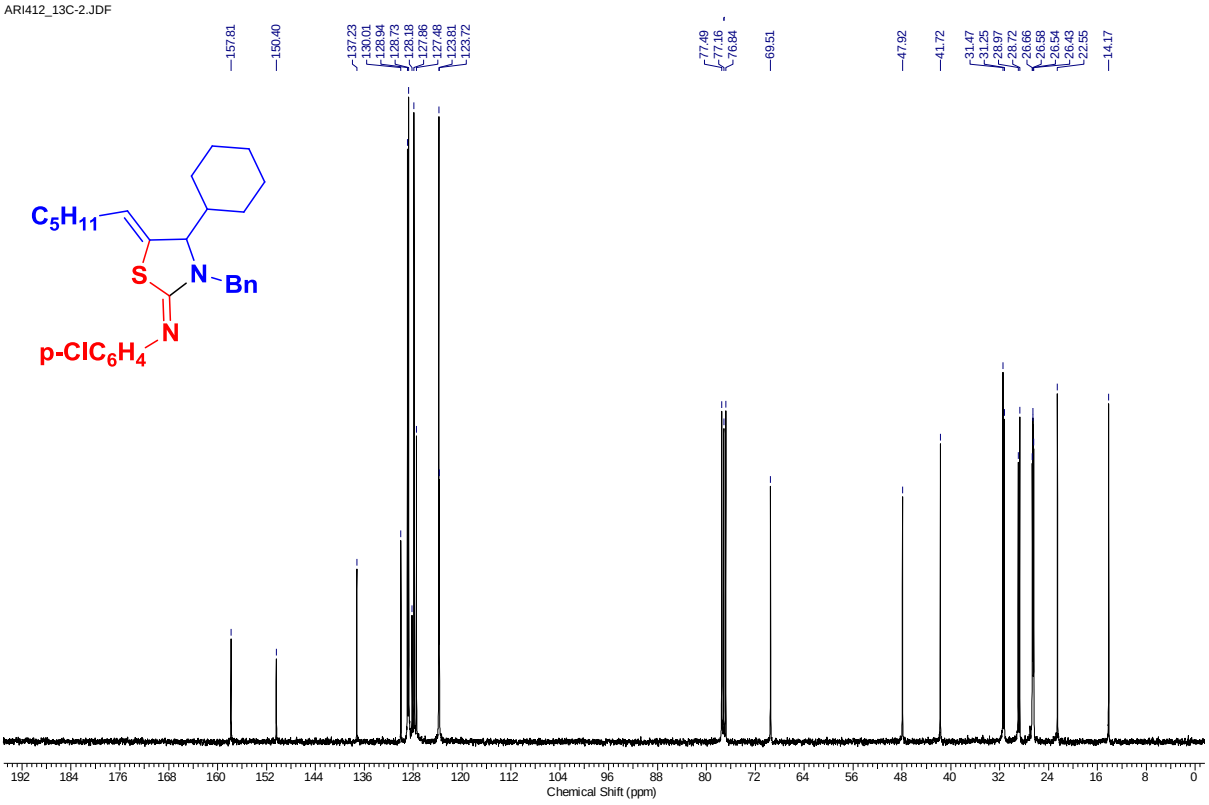

ARI417_DEPT135-3.JDF
128.87
128.61
128.45
128.34
127.64
127.29
123.05
68.23
47.23
35.60
31.65
31.39
28.86
28.72
22.65
14.15
7.64
7.52
C6H13
Ph
S
N
Bn
N
168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

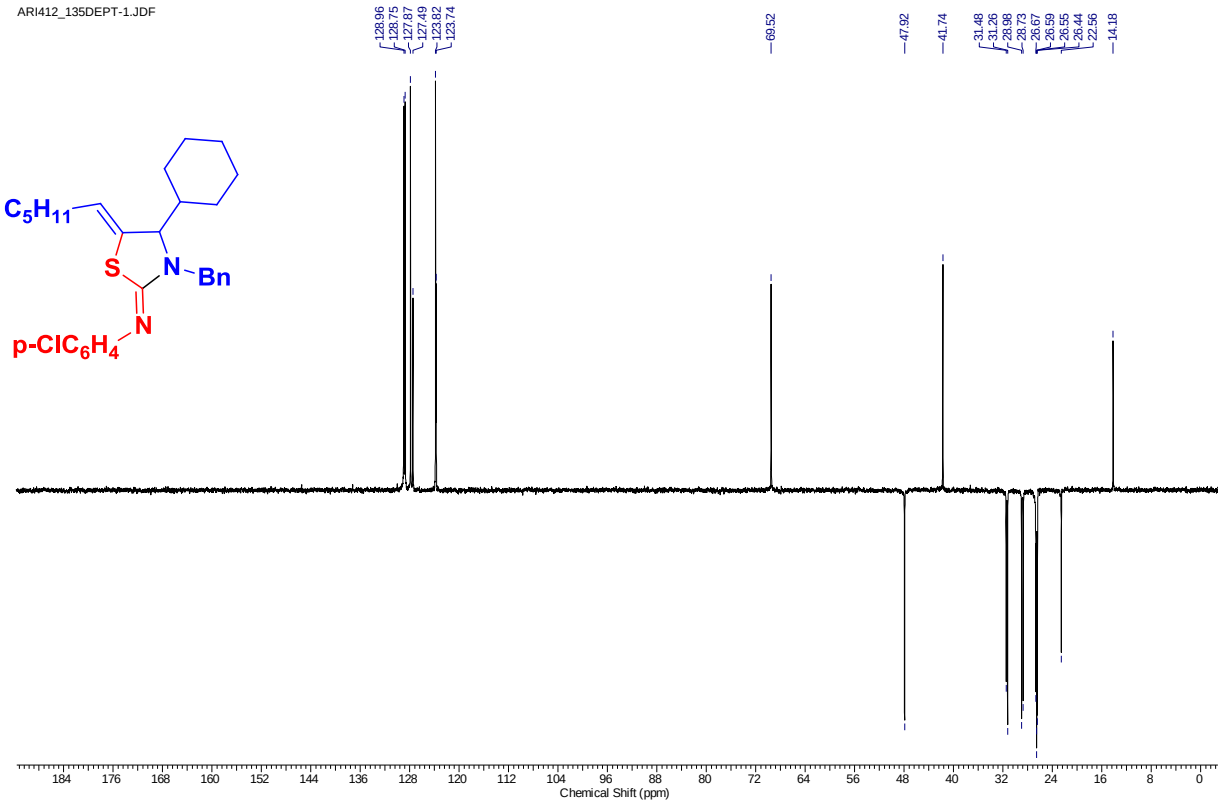

ARI7951_PROTON_4.JDF
7.39
7.34
7.32
7.30
7.28
7.27
7.26
7.15
7.13
5.86
5.82
5.53
5.53
5.45
5.41
5.39
4.93
4.92
4.90
4.90
4.59
4.54
4.54
4.53
4.39
4.30
4.29
4.29
4.28
4.25
4.21
1.92
1.90
1.89
1.87
1.77
1.76
1.67
1.66
1.65
1.64
1.62
0.94
0.93
0.92
0.92
Ph
S
N
Bn
N
8.39 1.91
1.00 0.93 0.97
0.99
1.92 0.96 0.96 0.95
0.98 1.04 1.29
2.89 2.78
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
Chemical Shift (ppm)

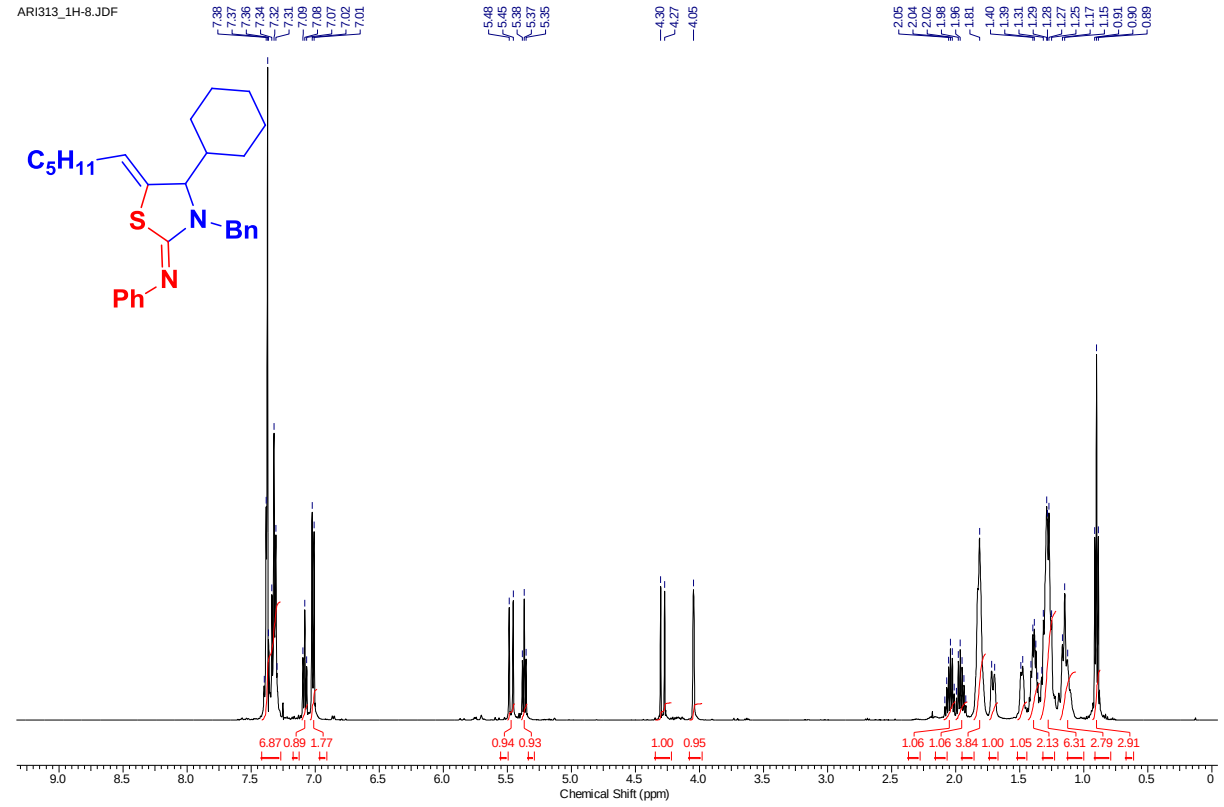

ARI7951_13C1.JDF
182.39
139.16
135.82
135.47
131.91
129.64
128.74
128.04
127.79
127.62
126.67
116.74
100.19
77.32
77.00
76.67
60.48
48.79
47.81
42.24
23.63
23.36
23.26
Ph
S
N
Bn
N
Chemical Shift (ppm)


ARI7952_135DEPT-1.JDF
132.08
129.81
128.91
128.21
127.97
127.81
126.85
116.92
100.37
60.66
48.96
47.98
42.42
23.80
23.53
23.44
Ph
S
N
Bn
N
Chemical Shift (ppm)

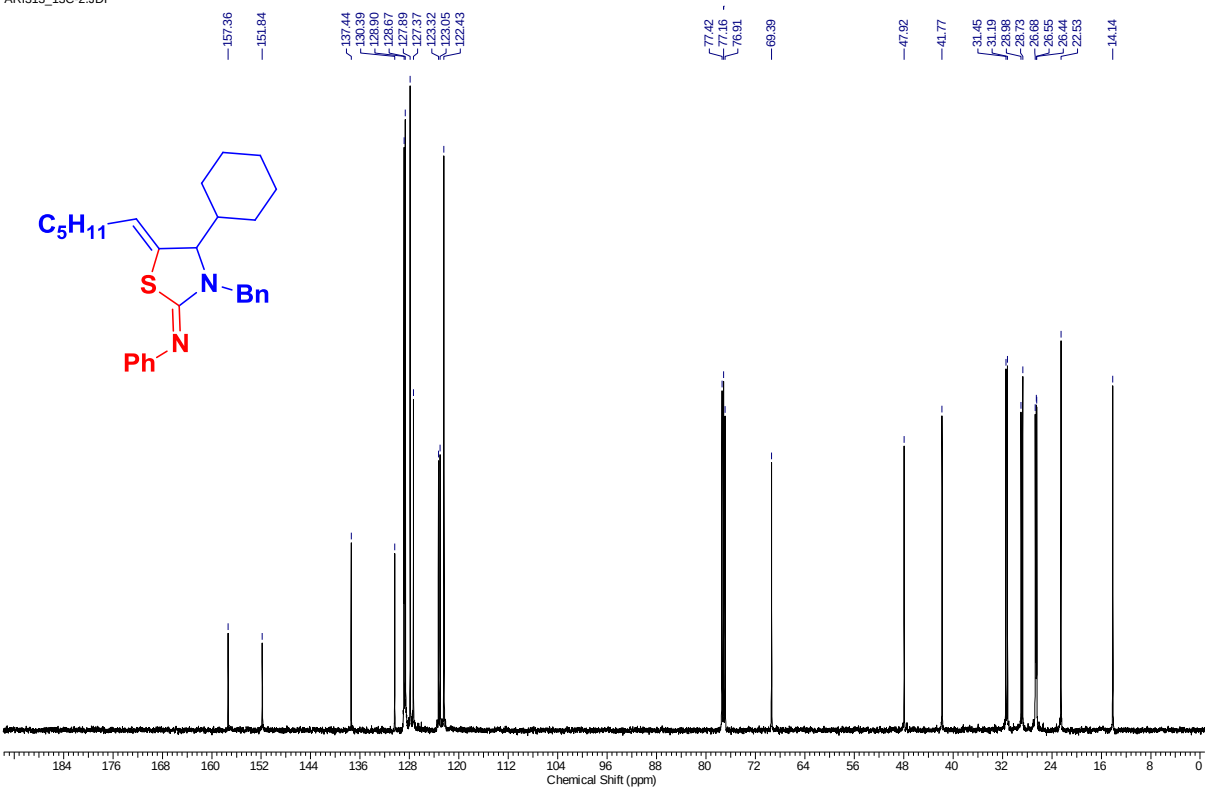

ARI412_1H-4.JDF
7.36
7.34
7.32
7.31
7.28
7.25
7.24
7.23
7.23
6.92
6.91
6.89
5.42
5.38
5.36
5.36
5.34
4.27
4.23
4.02
2.03
2.02
1.94
1.92
1.78
1.75
1.37
1.29
1.28
1.27
1.26
1.25
1.24
1.12
1.10
0.89
0.88
0.86
0.09
C5H11
S
N
Bn
N
p-ClC6H4
7.00
1.90
1.94
0.96
0.94
2.26
5.10
9.35
3.14
3.18
Chemical Shift (ppm)


ARI412_13C-2.JDF
157.81
150.40
137.23
130.01
128.94
128.73
128.18
127.86
127.48
123.81
123.72
77.49
77.16
76.84
69.51
47.92
41.72
31.47
31.25
28.97
28.72
26.66
26.58
26.54
26.43
22.55
14.17
C5H11
S
N
Bn
N
p-ClC6H4
Chemical Shift (ppm)

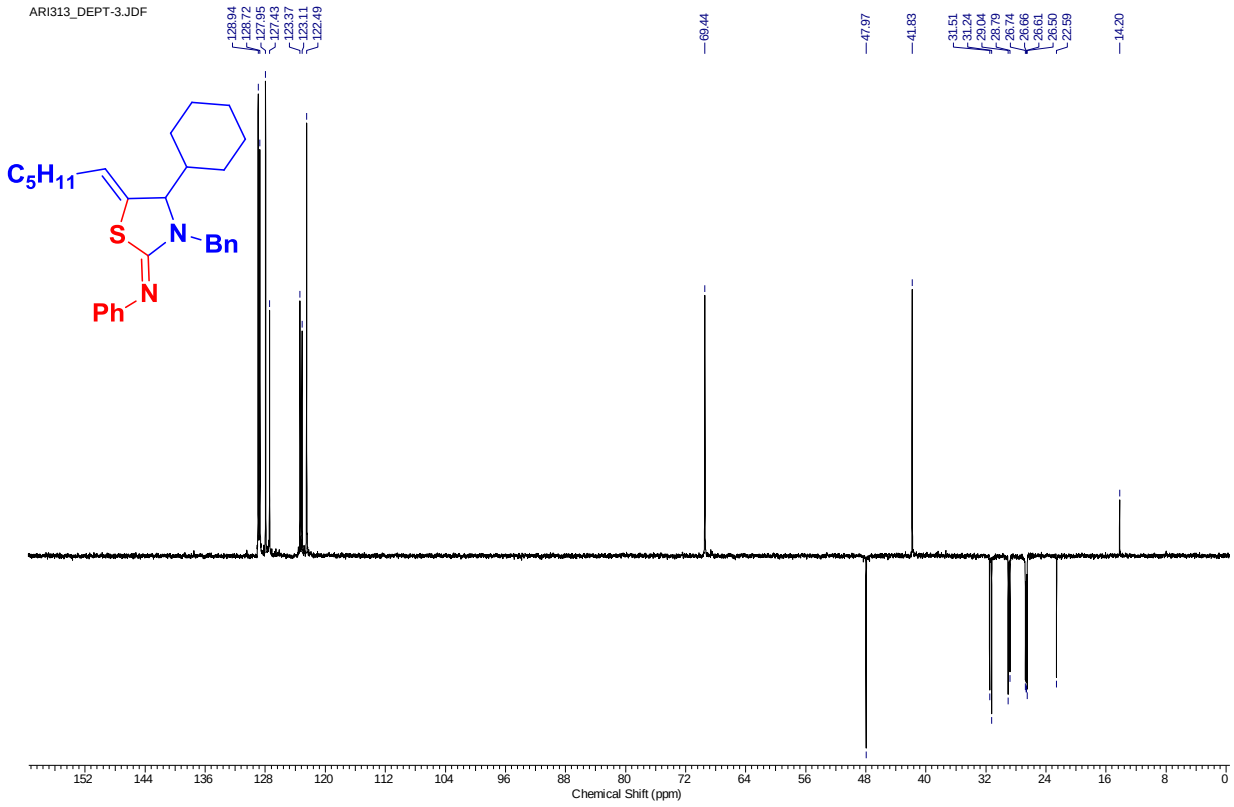

ARI412_135DEPT-1.JDF
128.96
128.75
127.87
127.49
123.82
123.74
69.52
47.92
41.74
31.48
31.26
28.98
28.73
26.67
26.59
26.55
26.44
22.56
14.18
C5H11
S
N
Bn
N
p-ClC6H4
184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

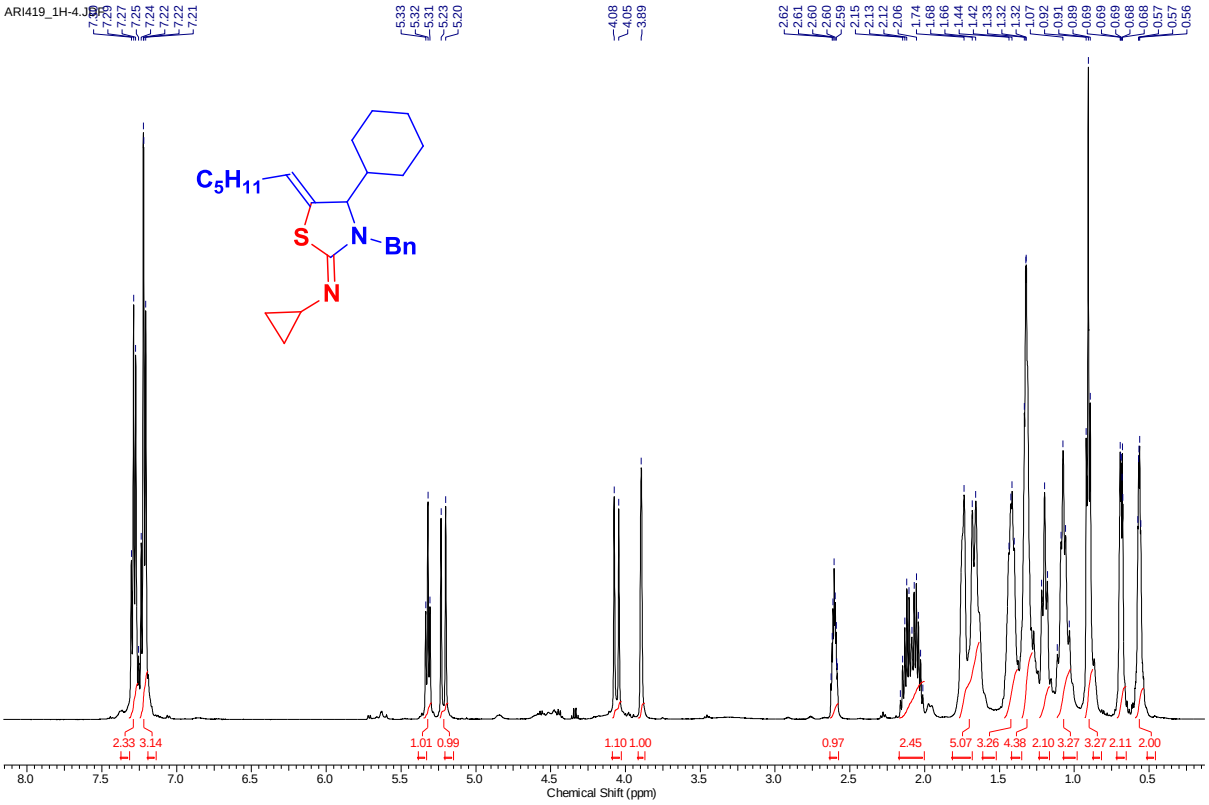

ARI313_1H-8.JDF
7.38
7.37
7.36
7.34
7.32
7.31
7.09
7.08
7.07
7.02
7.01
5.48
5.45
5.38
5.37
5.35
4.30
4.27
4.05
2.05
2.04
2.02
1.98
1.96
1.81
1.40
1.39
1.31
1.29
1.28
1.27
1.25
1.17
1.15
0.91
0.90
0.89
C5H11
S
N
Bn
N
Ph
6.87 0.89 1.77
0.94 0.93
1.00 0.95
1.06 1.06 3.84 1.00 1.05 2.13 6.31 2.79 2.91
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

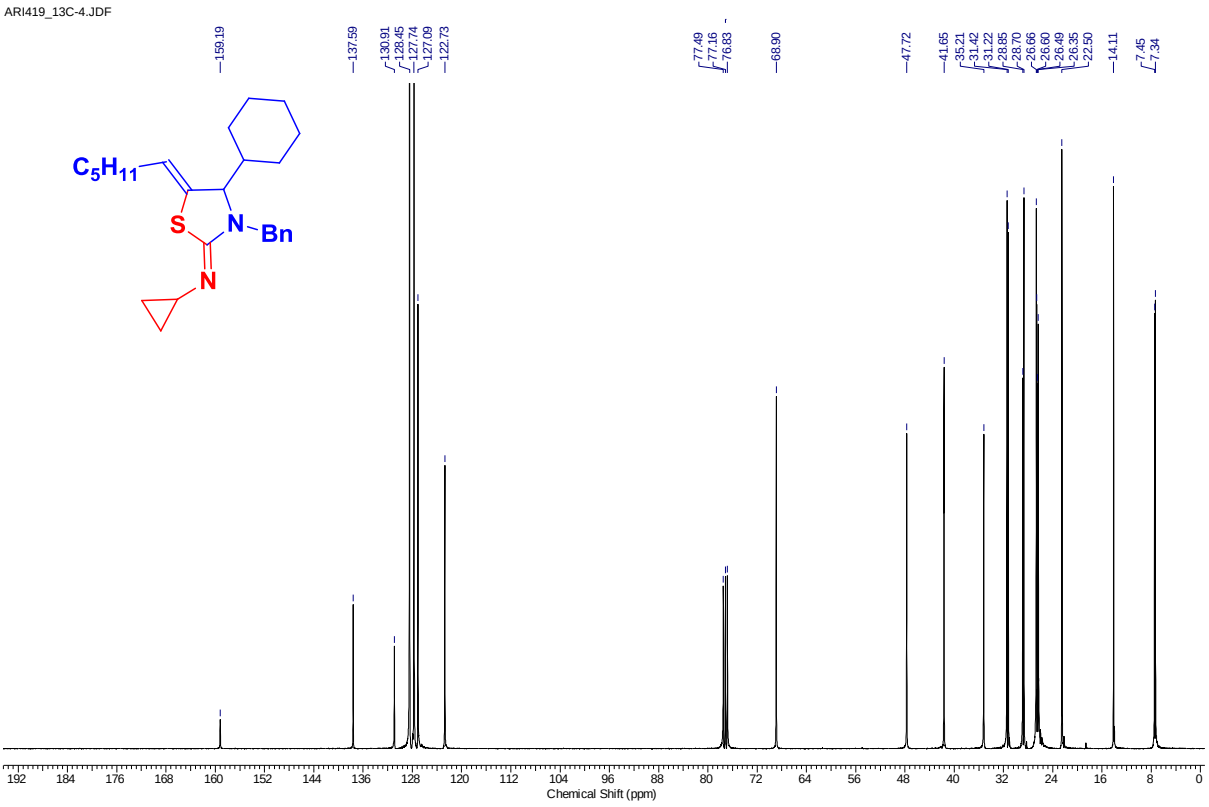
ARI313_13C-2.JDF

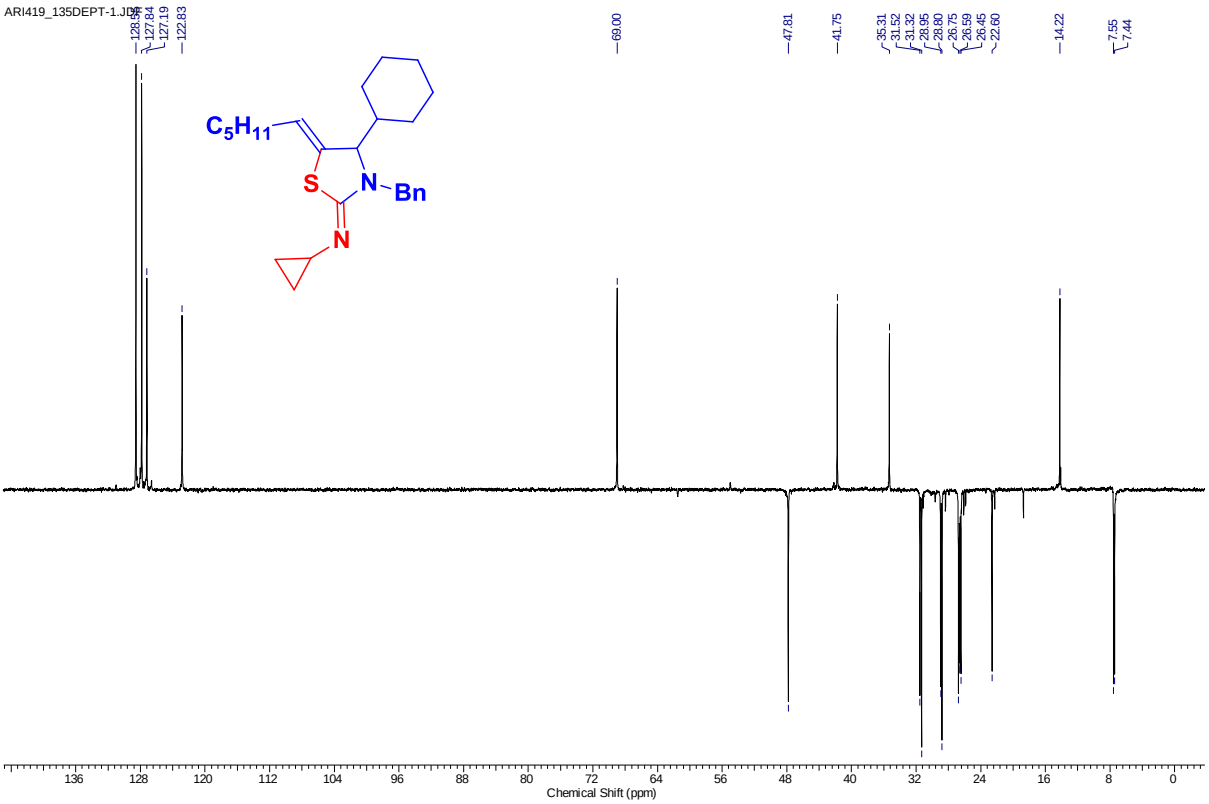


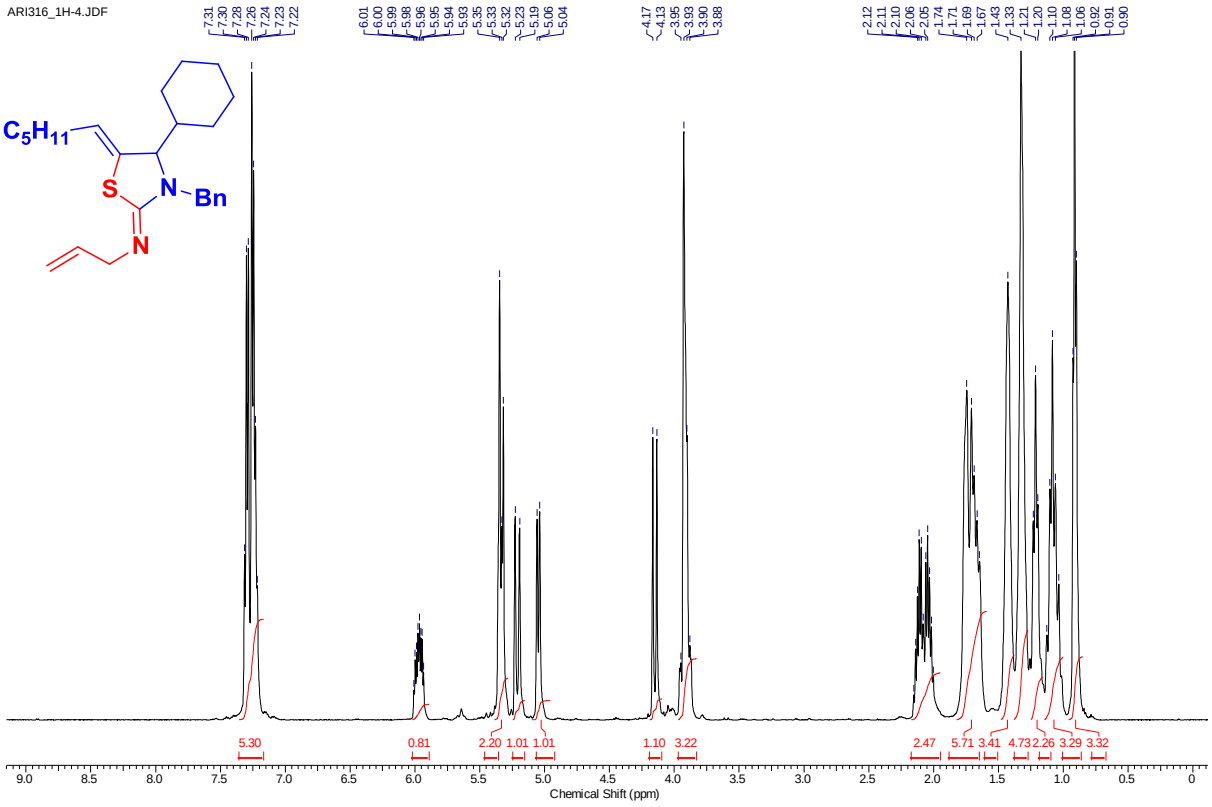
ARI313_DEPT-3.JDF



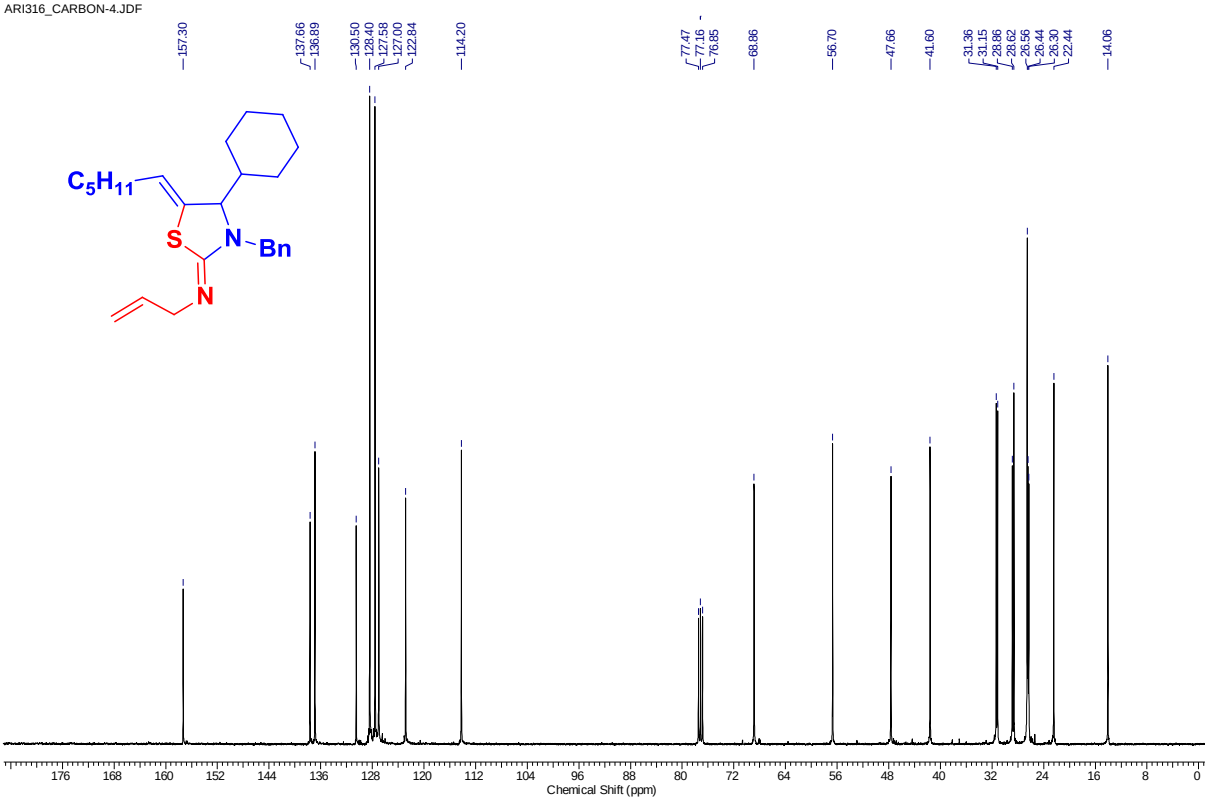

ARI419_1H-4.JDF
7.29
7.27
7.25
7.24
7.22
7.22
7.21
5.33
5.32
5.31
5.23
5.20
4.08
4.05
3.89
2.62
2.61
2.60
2.60
2.59
2.15
2.13
2.12
2.06
1.74
1.68
1.66
1.44
1.42
1.33
1.32
1.32
1.07
0.92
0.91
0.89
0.69
0.69
0.69
0.68
0.68
0.57
0.57
0.56
C5H11
S
N
Bn
N
2.33 3.14
1.01 0.99
1.10 1.00
0.97
2.45
5.07 3.26 4.38 2.10 3.27 3.27 2.11 2.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
Chemical Shift (ppm)


ARI419_13C-4.JDF
159.19
137.59
130.91
128.45
127.74
127.09
122.73
77.49
77.16
76.83
68.90
47.72
41.65
35.21
31.42
31.22
28.85
28.70
26.66
26.60
26.49
26.35
22.50
14.11
7.45
7.34
C5H11
S
N
Bn
N
192 184 176 168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

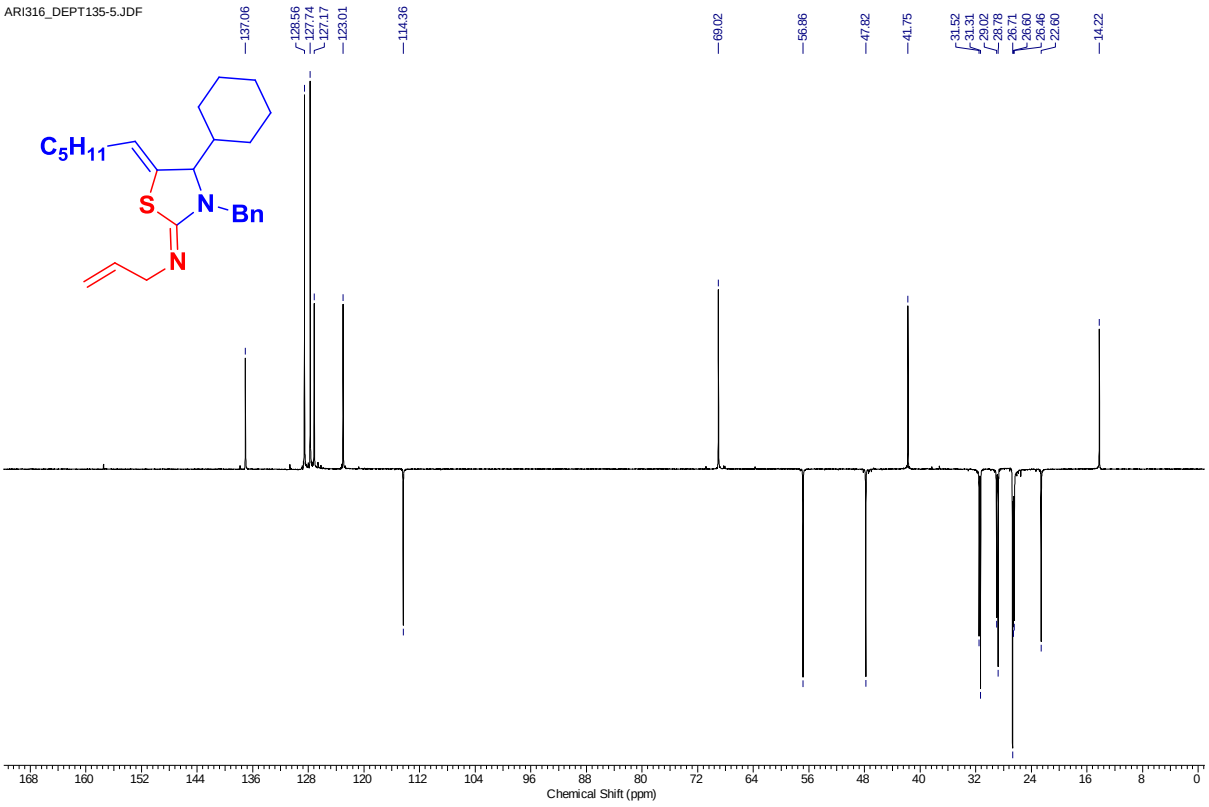

ARI419_135DEPT-1.JDF
128.59
127.84
127.19
122.83
69.00
47.81
41.75
35.31
31.52
31.32
28.95
28.80
26.75
26.59
26.45
22.60
14.22
7.55
7.44
C5H11
S
N
Bn
N
Chemical Shift (ppm)

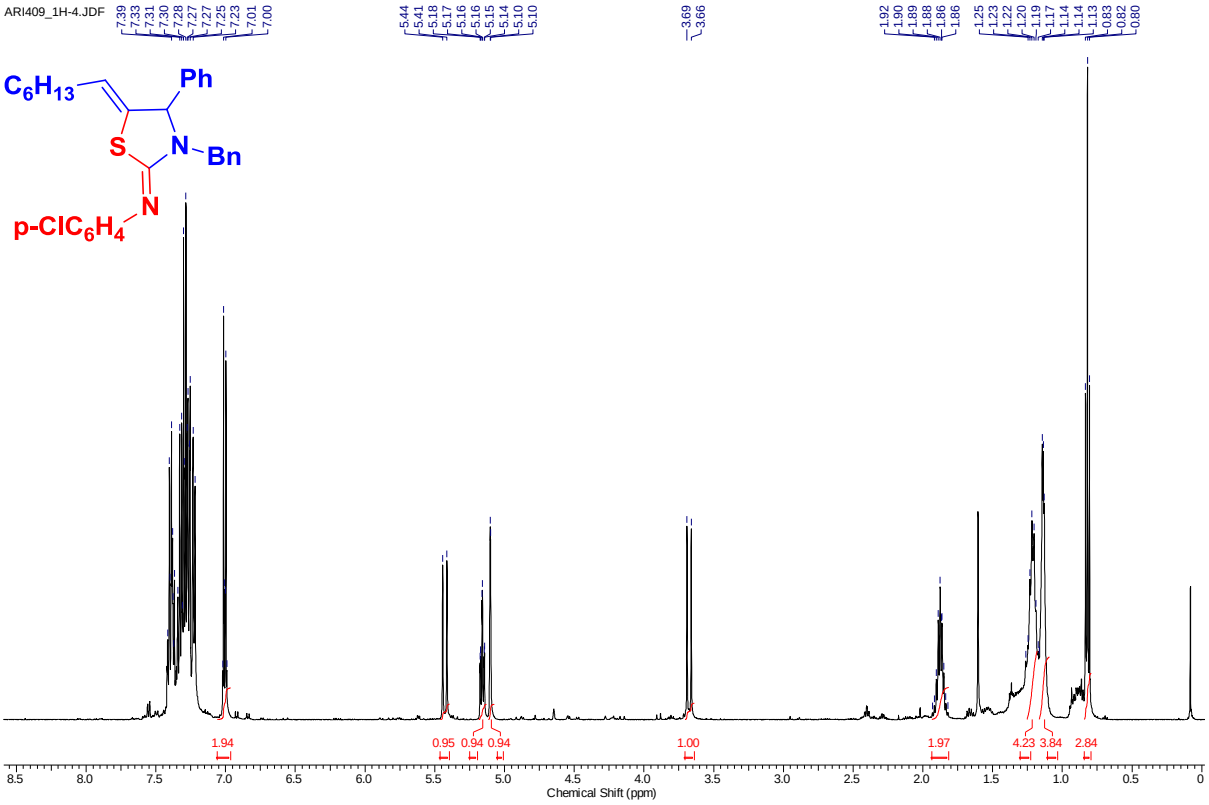

ARI316_1H-4.JDF
7.31
7.30
7.28
7.26
7.24
7.23
7.22
6.01
6.00
5.99
5.98
5.96
5.95
5.94
5.93
5.35
5.33
5.32
5.23
5.19
5.06
5.04
4.17
4.13
3.95
3.93
3.90
3.88
2.12
2.11
2.10
2.06
2.05
1.74
1.71
1.69
1.67
1.43
1.33
1.21
1.20
1.10
1.08
1.06
0.92
0.91
0.90
C5H11
S
N
Bn
N
5.30
0.81
2.20
1.01
1.01
1.10
3.22
2.47
5.71
3.41
4.73
2.26
3.29
3.32
Chemical Shift (ppm)

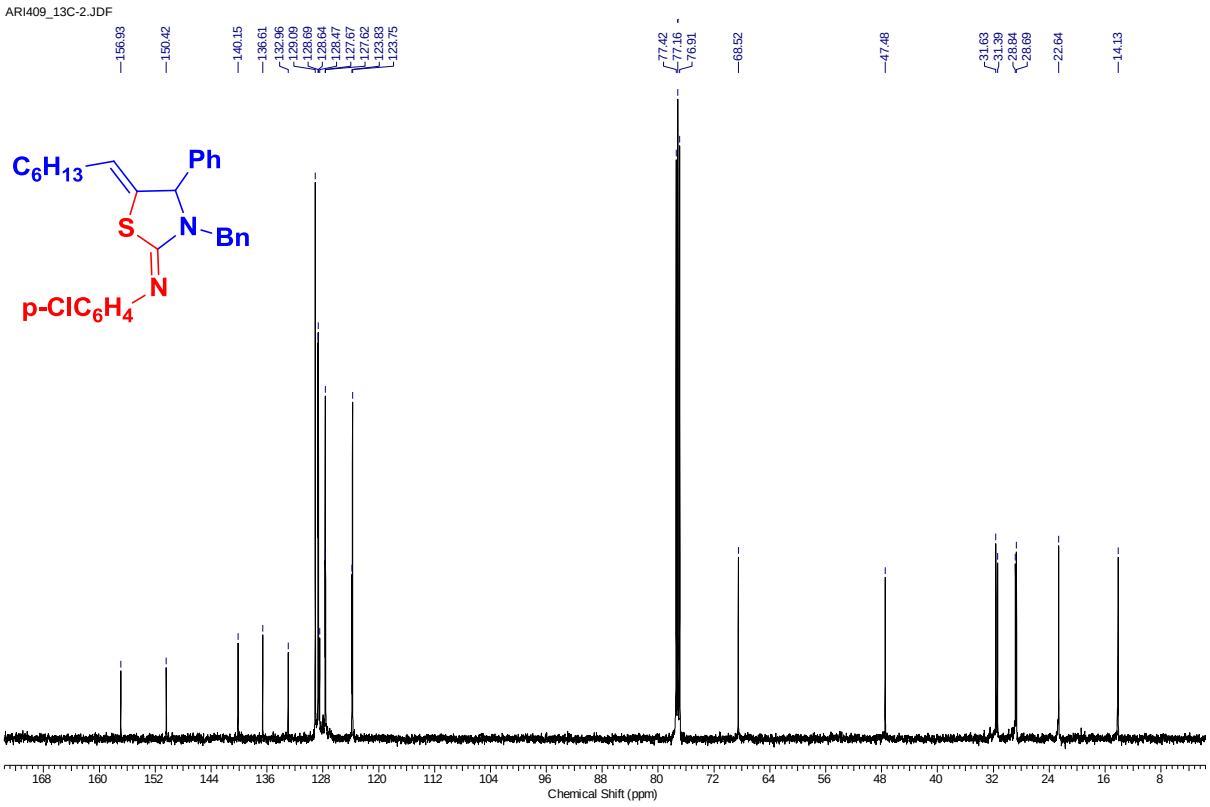
ARI316_CARBON-4.JDF

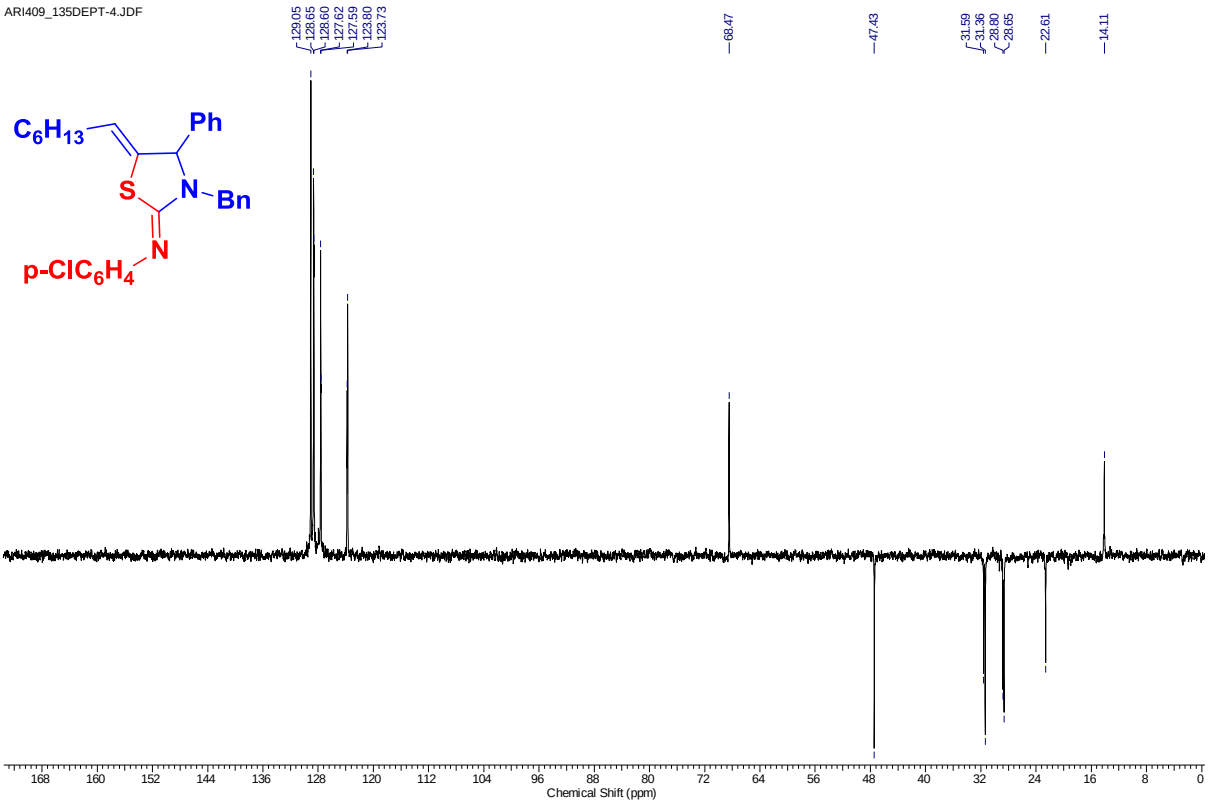


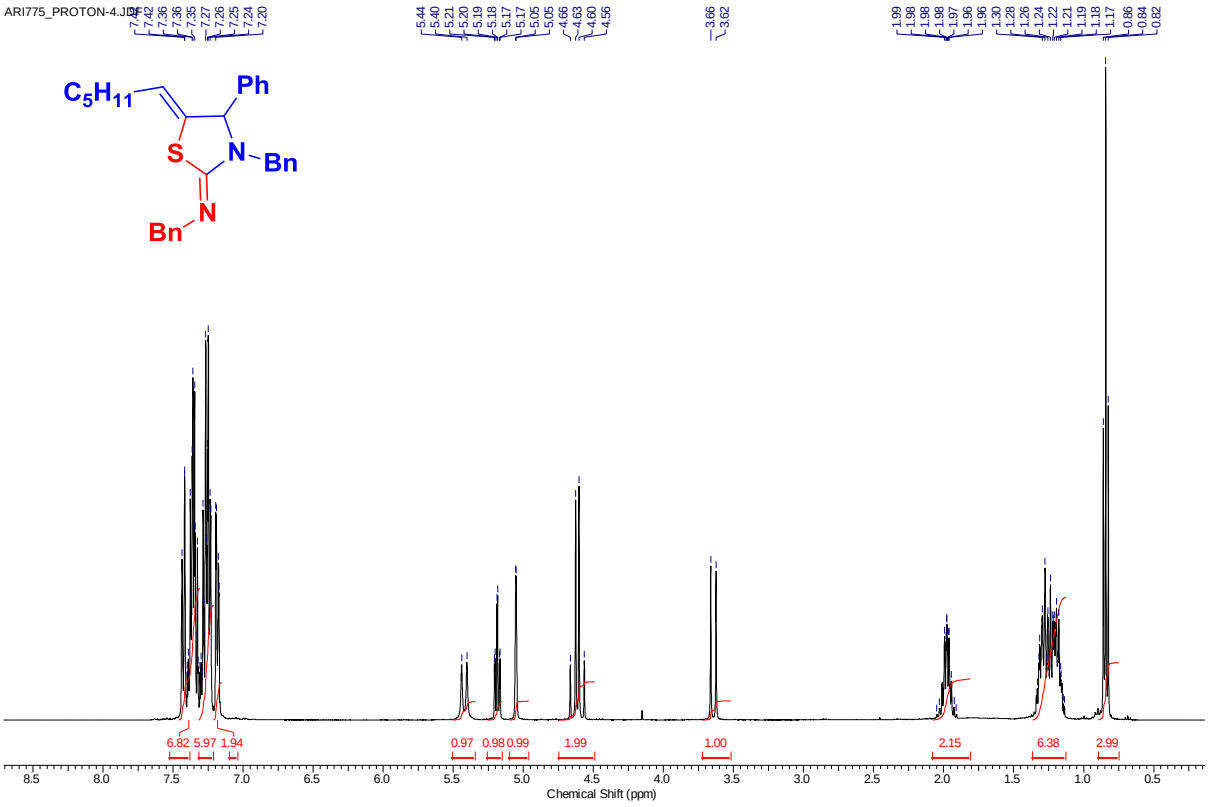
ARI316_DEPT135-5.JDF

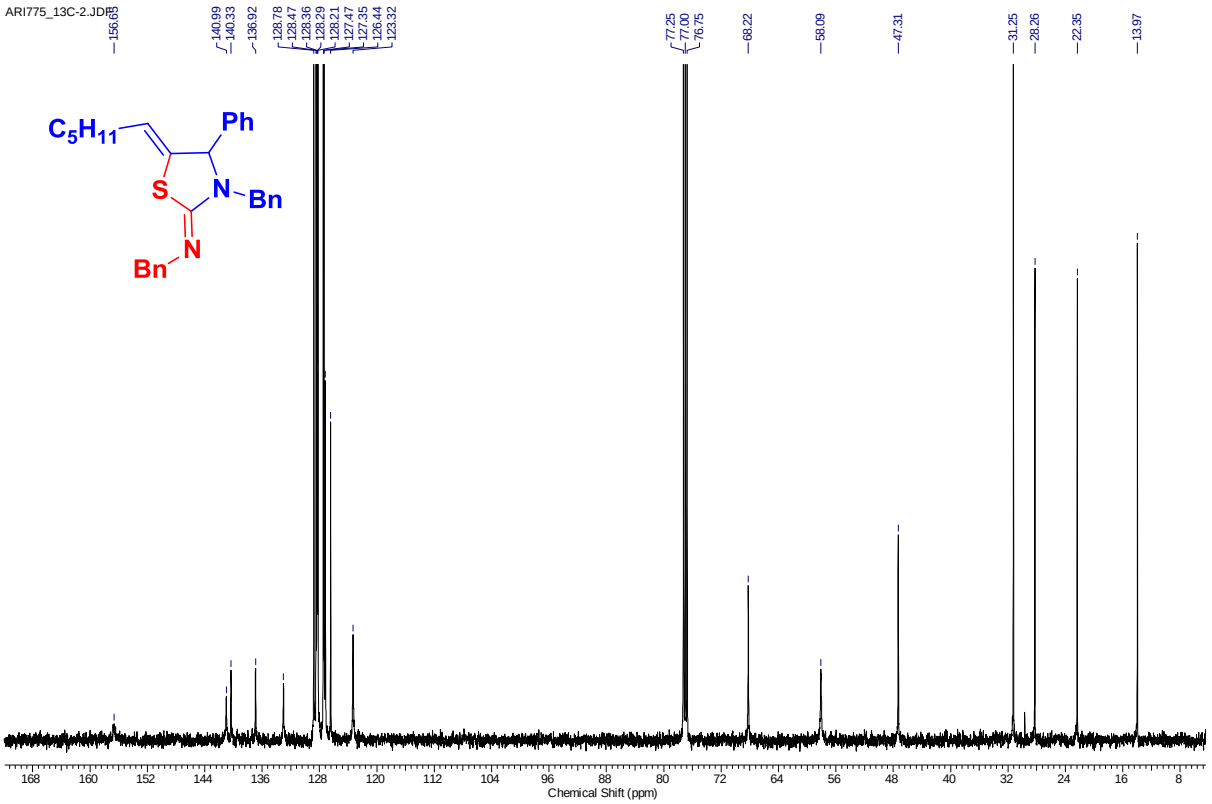


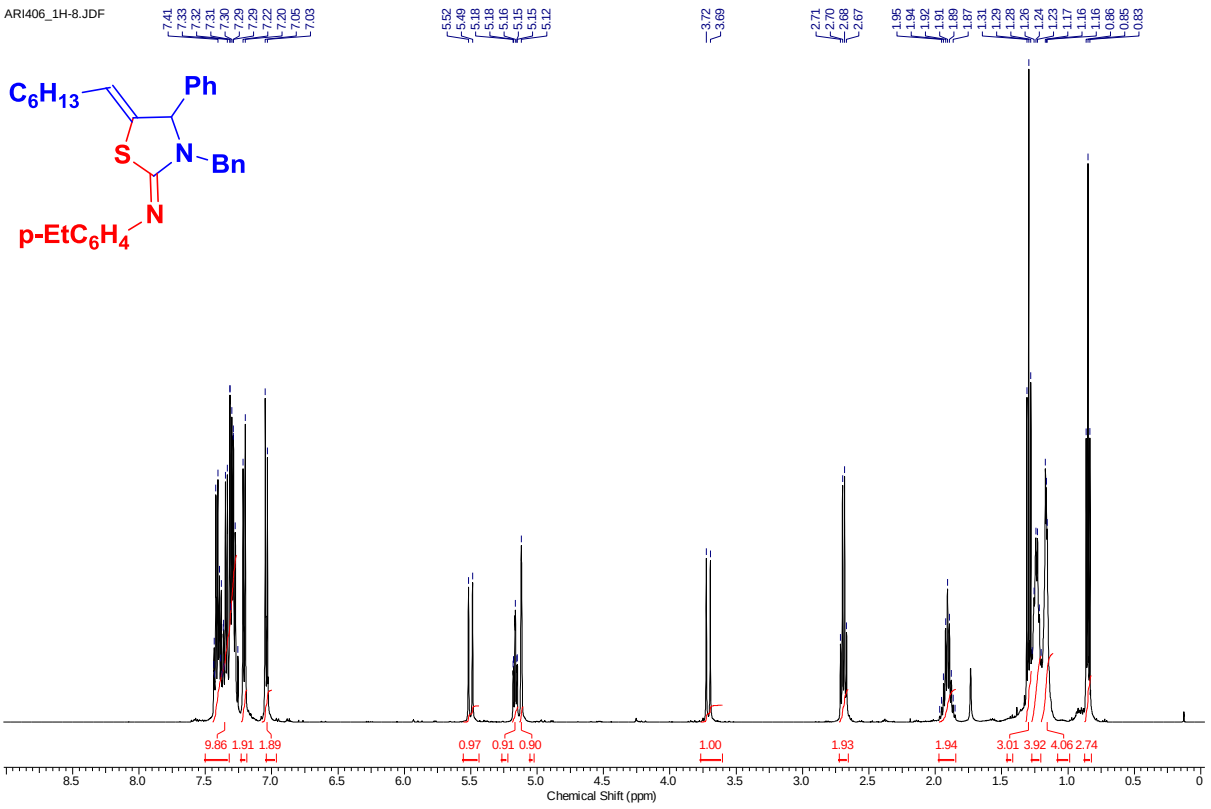

ARI409_1H-4.JDF
7.39 7.33 7.31 7.30 7.28 7.27 7.27 7.25 7.23 7.01 7.00
5.44 5.41 5.18 5.17 5.16 5.16 5.15 5.14 5.10 5.10
3.69 3.66
1.92 1.90 1.89 1.88 1.86 1.86
1.25 1.23 1.22 1.20 1.19 1.17 1.14 1.14 1.13 0.83 0.82 0.80
C6H13
Ph
S
N
Bn
N
p-ClC6H4
1.94
0.95 0.94 0.94
1.00
1.97
4.23 3.84 2.84
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


ARI409_13C-2.JDF
156.93 150.42 140.15 136.61 132.96 129.09 128.69 128.64 128.47 127.67 127.62 123.83 123.75
77.42 77.16 76.91
68.52
47.48
31.63 31.39 28.84 28.69
22.64
14.13
C6H13
Ph
S
N
Bn
N
p-ClC6H4
168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8
Chemical Shift (ppm)

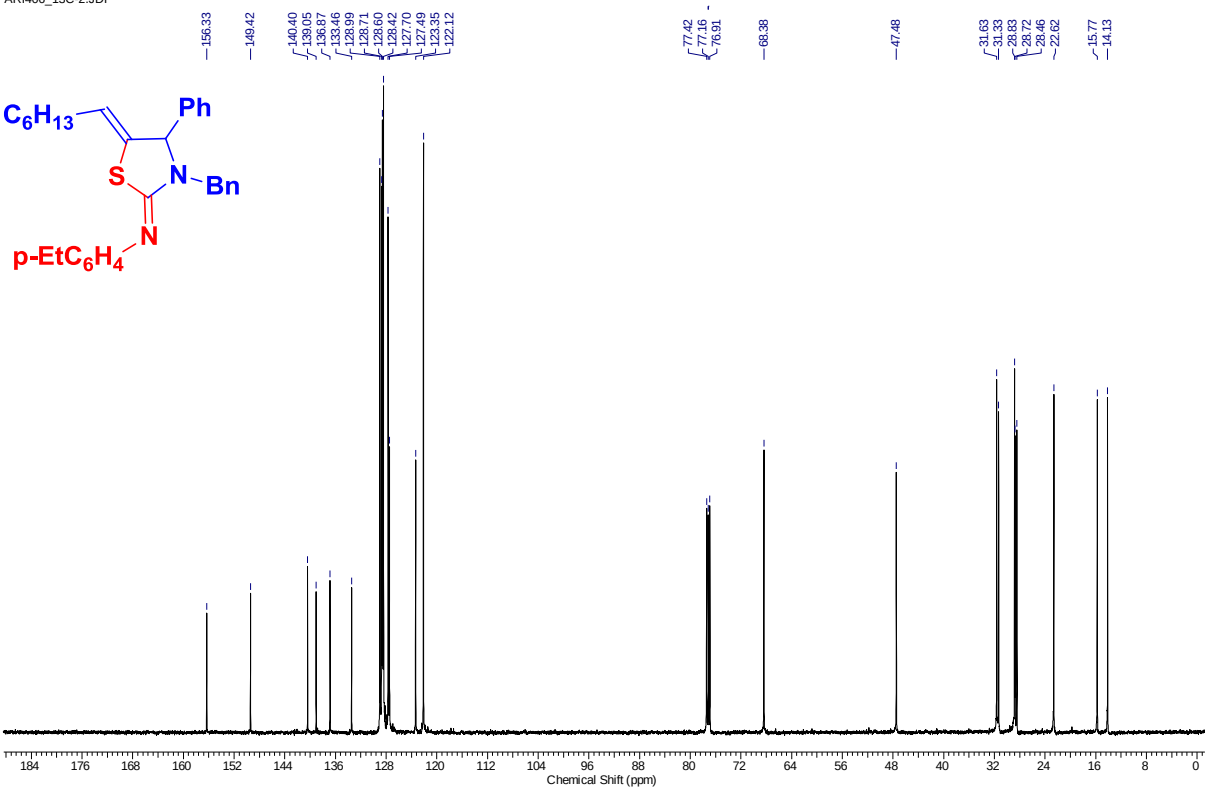

ARI409_135DEPT-4.JDF
129.05
128.65
128.60
127.62
127.59
123.80
123.73
68.47
47.43
31.59
31.36
28.80
28.65
22.61
14.11
C6H13
Ph
S
N
Bn
N
p-ClC6H4
168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)


ARI775_PROTON-4.JDF
7.44
7.42
7.36
7.36
7.35
7.27
7.26
7.25
7.24
7.20
5.44
5.40
5.21
5.20
5.19
5.18
5.17
5.17
5.05
5.05
4.66
4.63
4.60
4.56
3.66
3.62
1.99
1.98
1.98
1.98
1.97
1.96
1.96
1.30
1.28
1.26
1.24
1.22
1.21
1.19
1.18
1.17
0.86
0.84
0.82
C5H11
Ph
S
N
Bn
Bn
N
6.82 5.97 1.94
0.97 0.98 0.99
1.99
1.00
2.15
6.38
2.99
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
Chemical Shift (ppm)

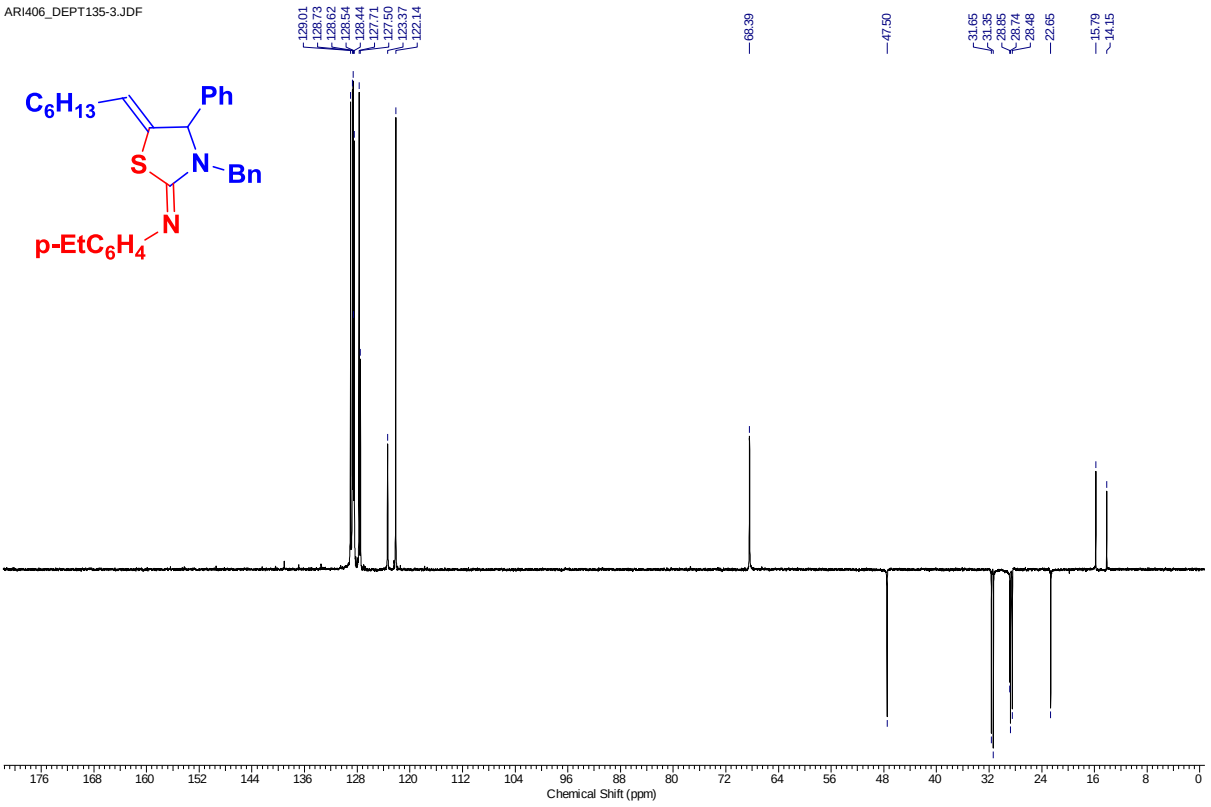

ARI775_13C-2.JDF
156.65
140.99
140.33
136.92
128.78
128.47
128.36
128.29
128.21
127.47
127.35
126.44
123.32
77.25
77.00
76.75
68.22
58.09
47.31
31.25
28.26
22.35
13.97
C5H11
Ph
S
N
Bn
N
Bn
Chemical Shift (ppm)

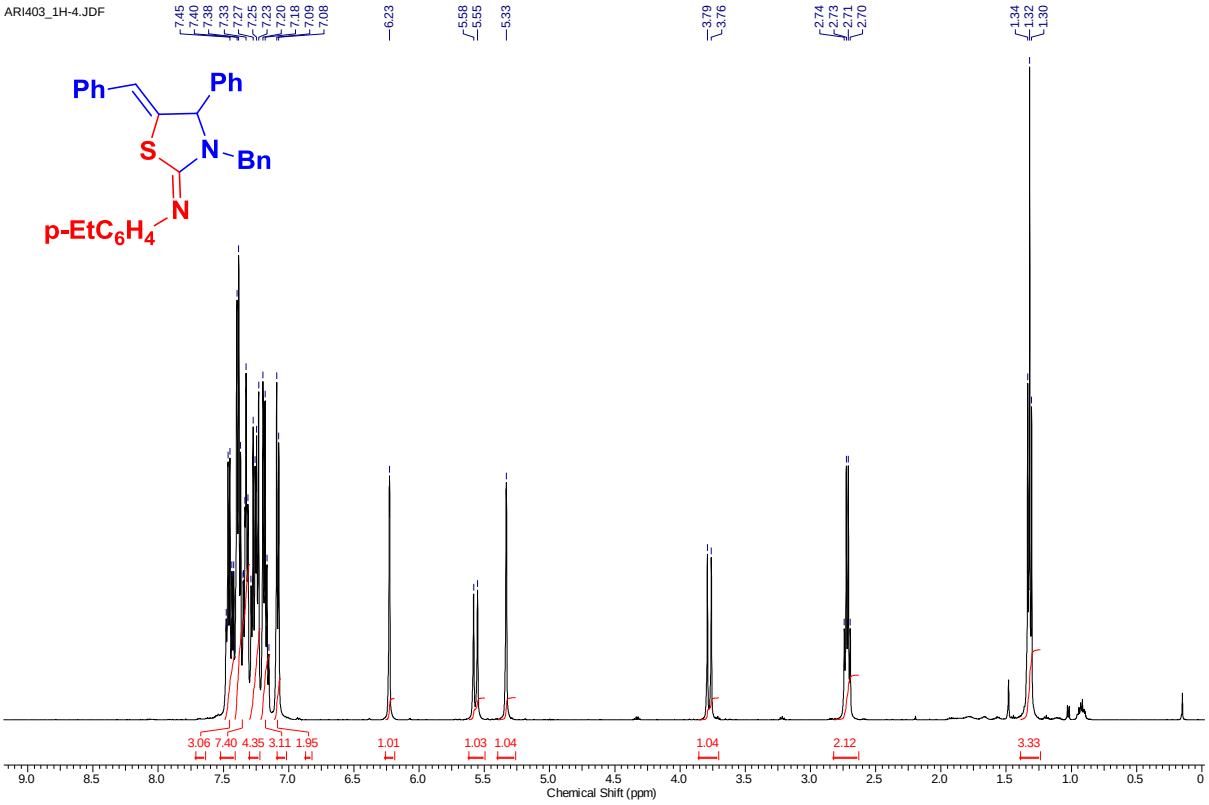

ARI406_1H-8.JDF
7.41
7.33
7.32
7.31
7.30
7.29
7.29
7.22
7.20
7.05
7.03
5.52
5.49
5.18
5.18
5.16
5.15
5.15
5.12
3.72
3.69
2.71
2.70
2.68
2.67
1.95
1.94
1.92
1.91
1.89
1.87
1.31
1.29
1.28
1.26
1.24
1.23
1.17
1.16
1.16
0.86
0.85
0.83
C6H13
Ph
S
N
Bn
N
p-EtC6H4
9.86
1.91
1.89
0.97
0.91
0.90
1.00
1.93
1.94
3.01
3.92
4.06
2.74
Chemical Shift (ppm)

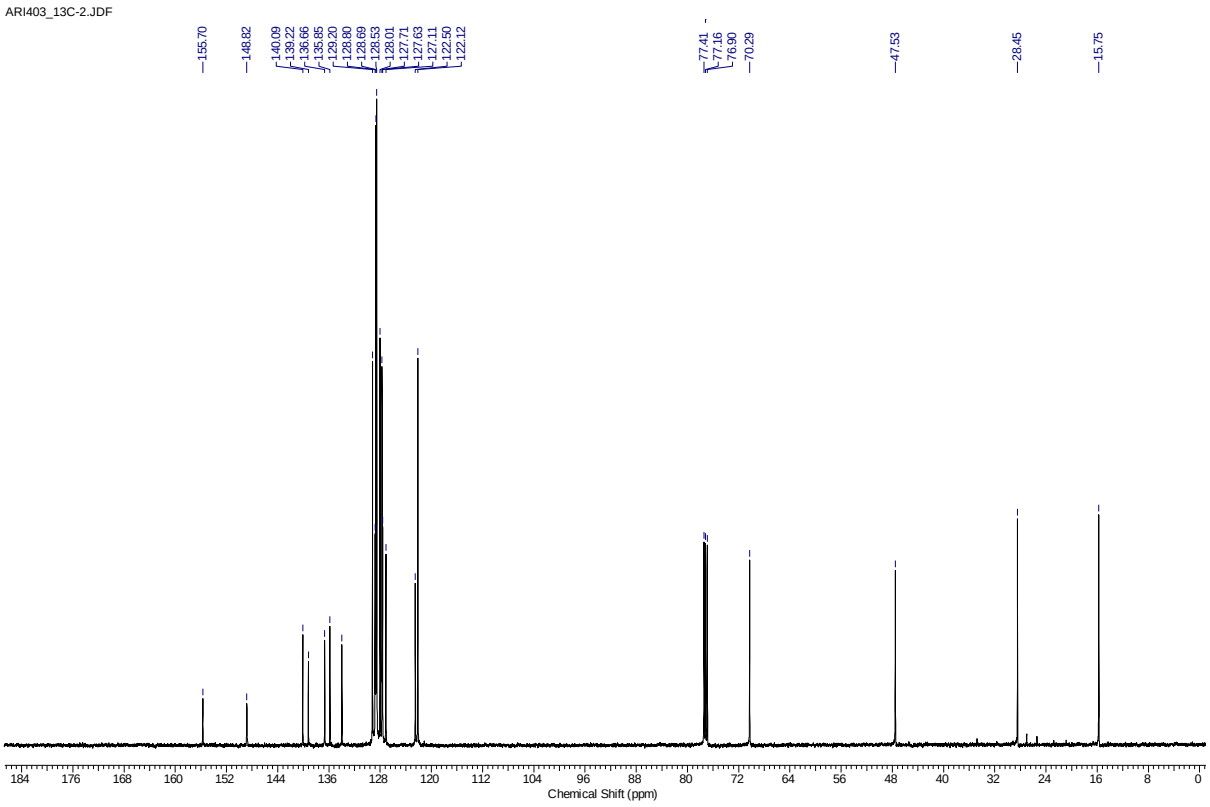
ARI406_13C-2.JDF

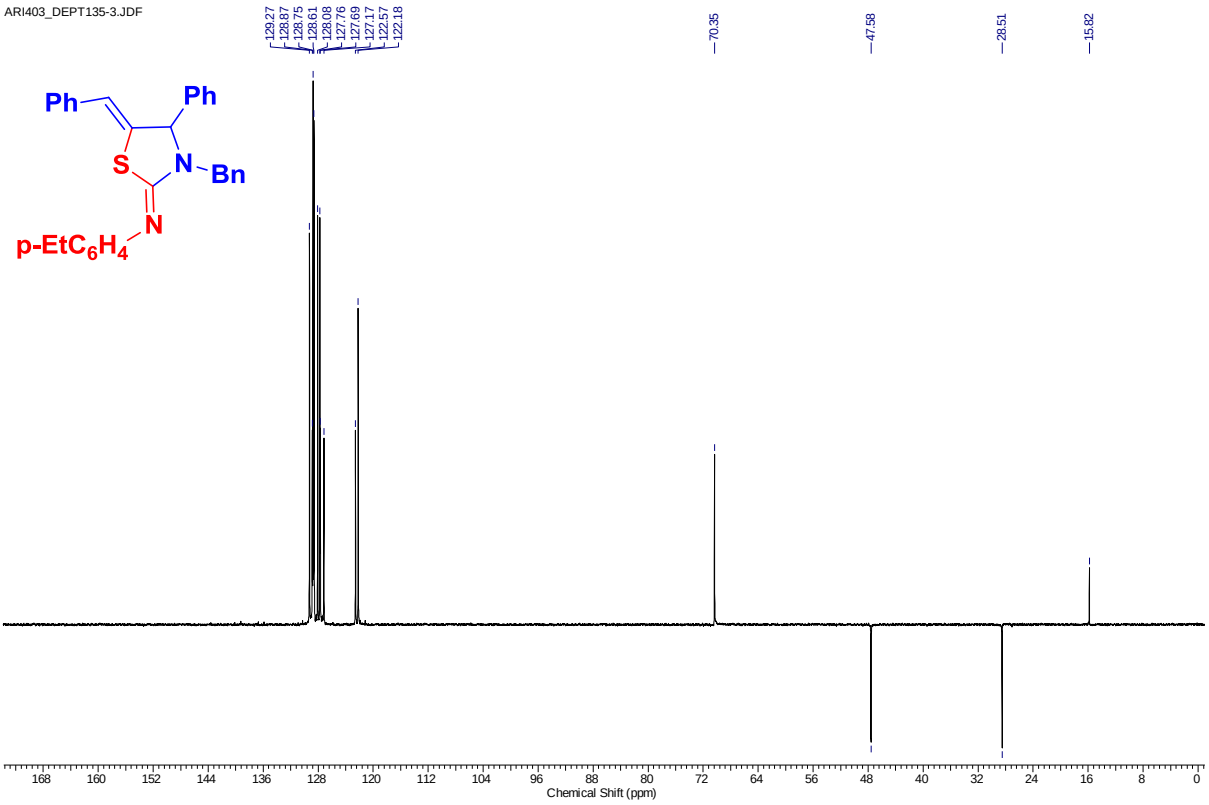


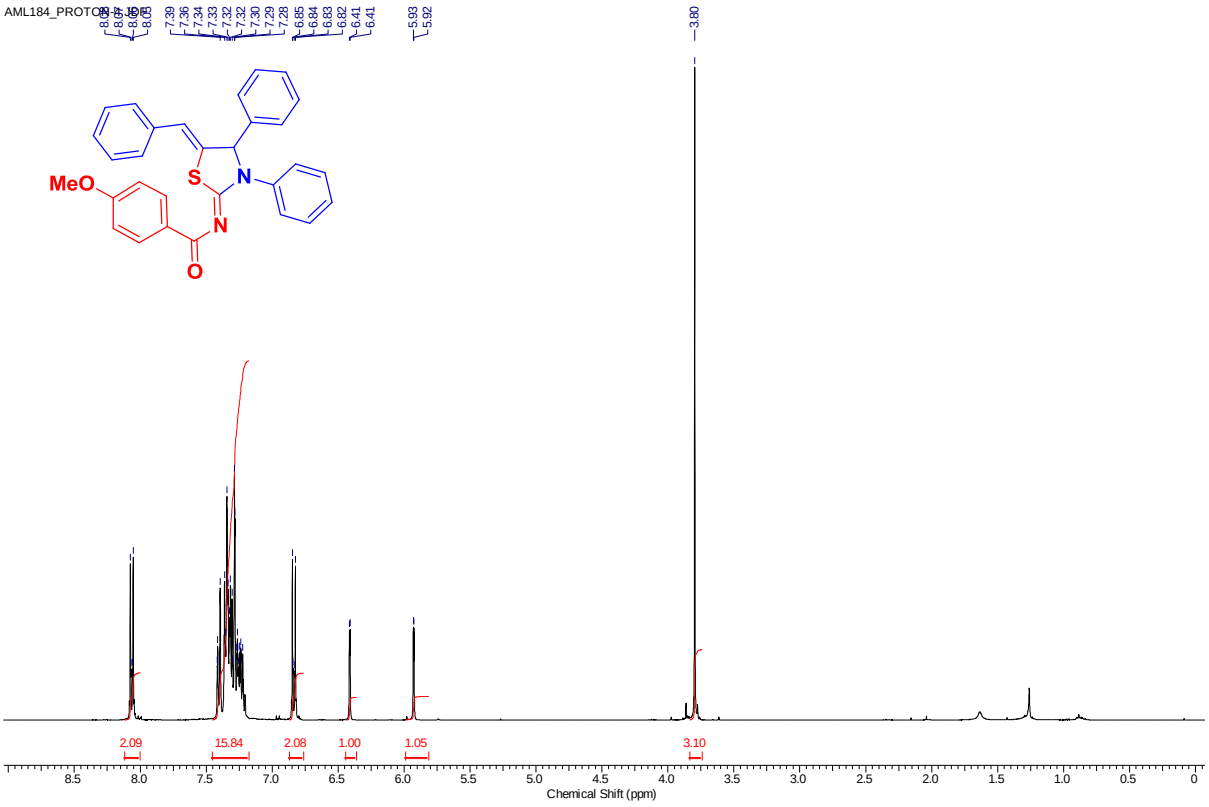
ARI406_DEPT135-3.JDF

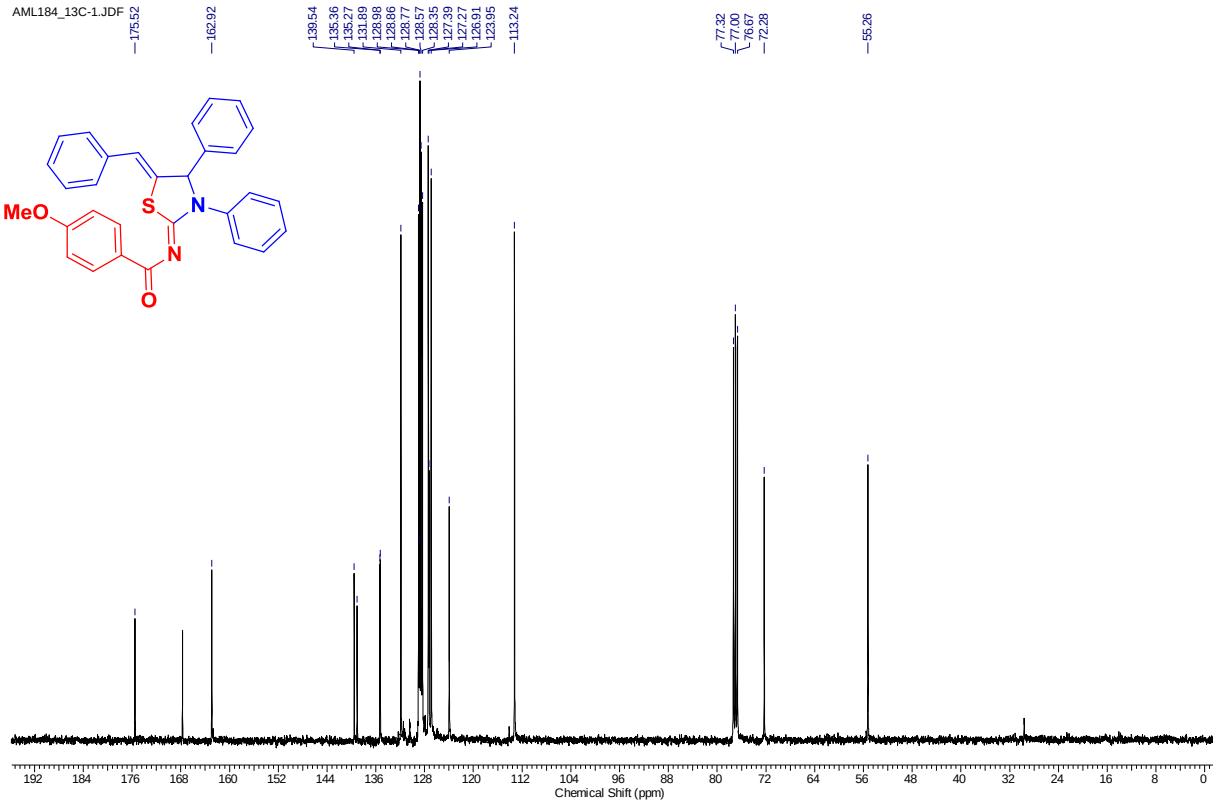


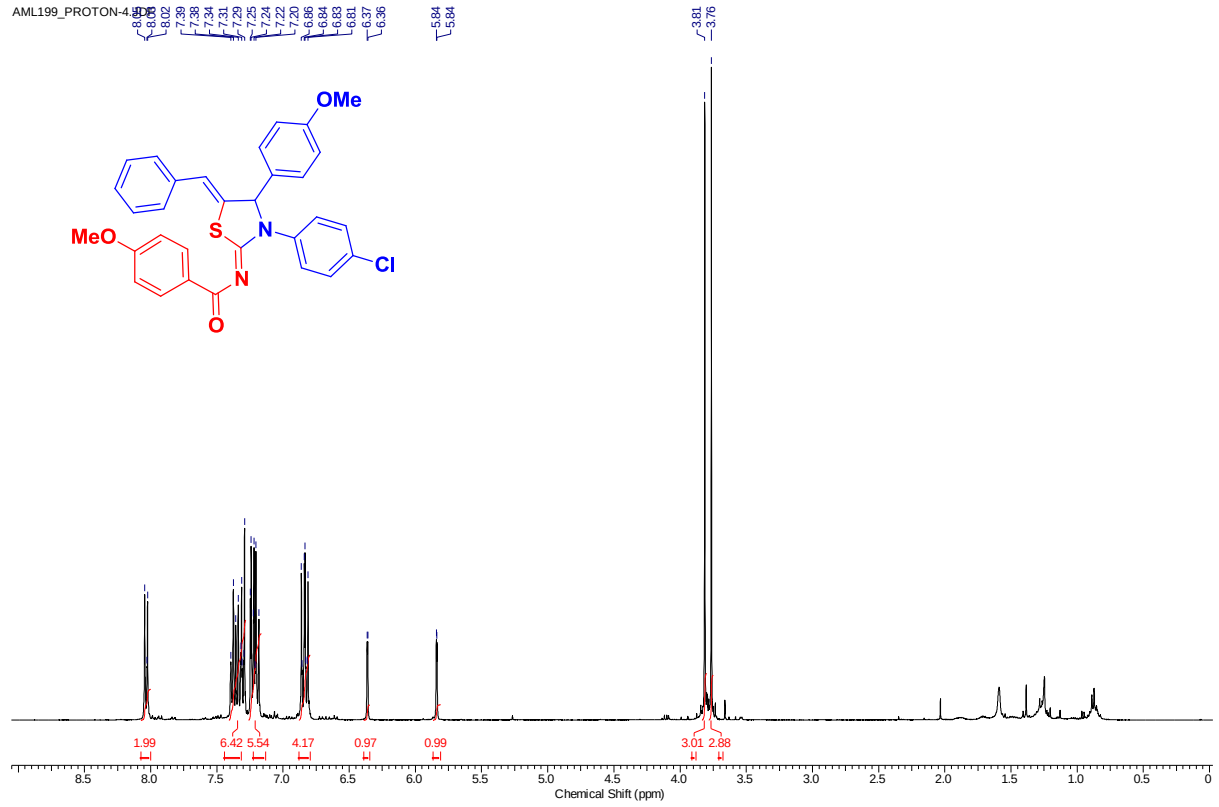

ARI403_1H-4.JDF
Ph
Ph
S
N
Bn
N
p-EtC6H4
Chemical Shift (ppm)

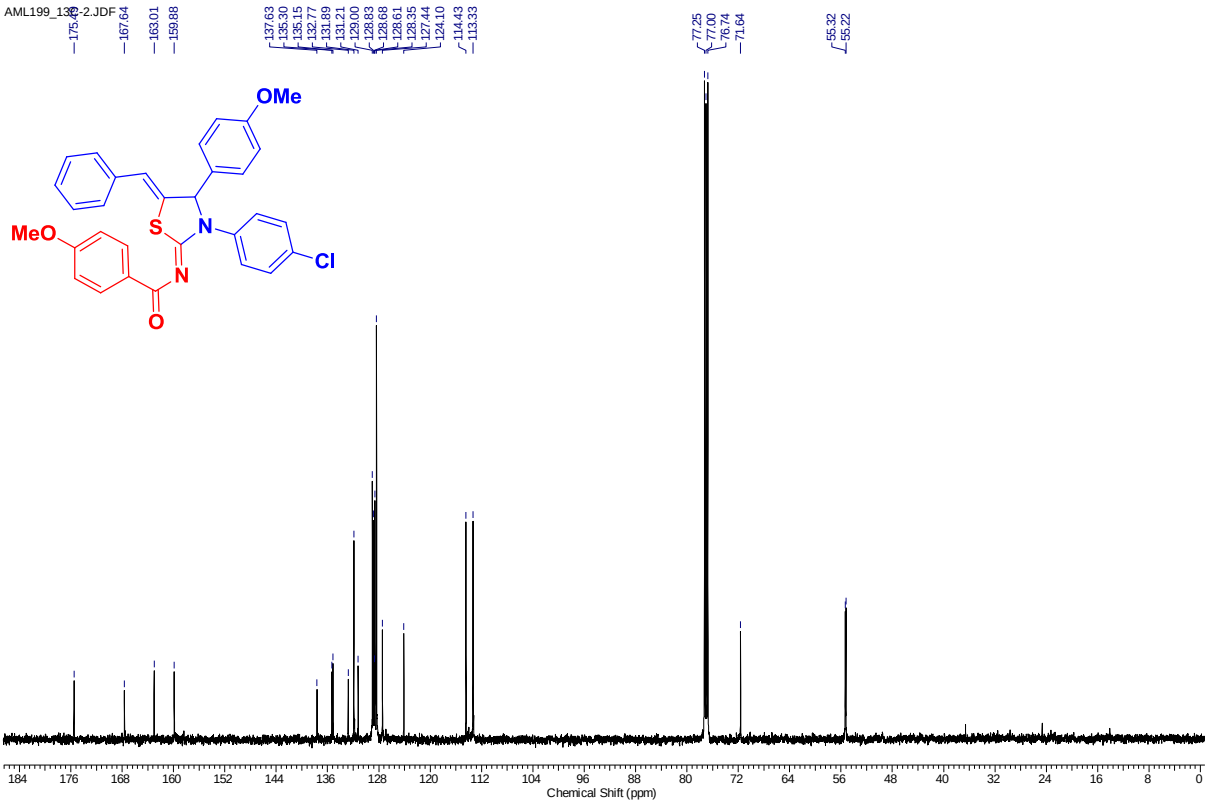

ARI403_13C-2.JDF
Chemical Shift (ppm)

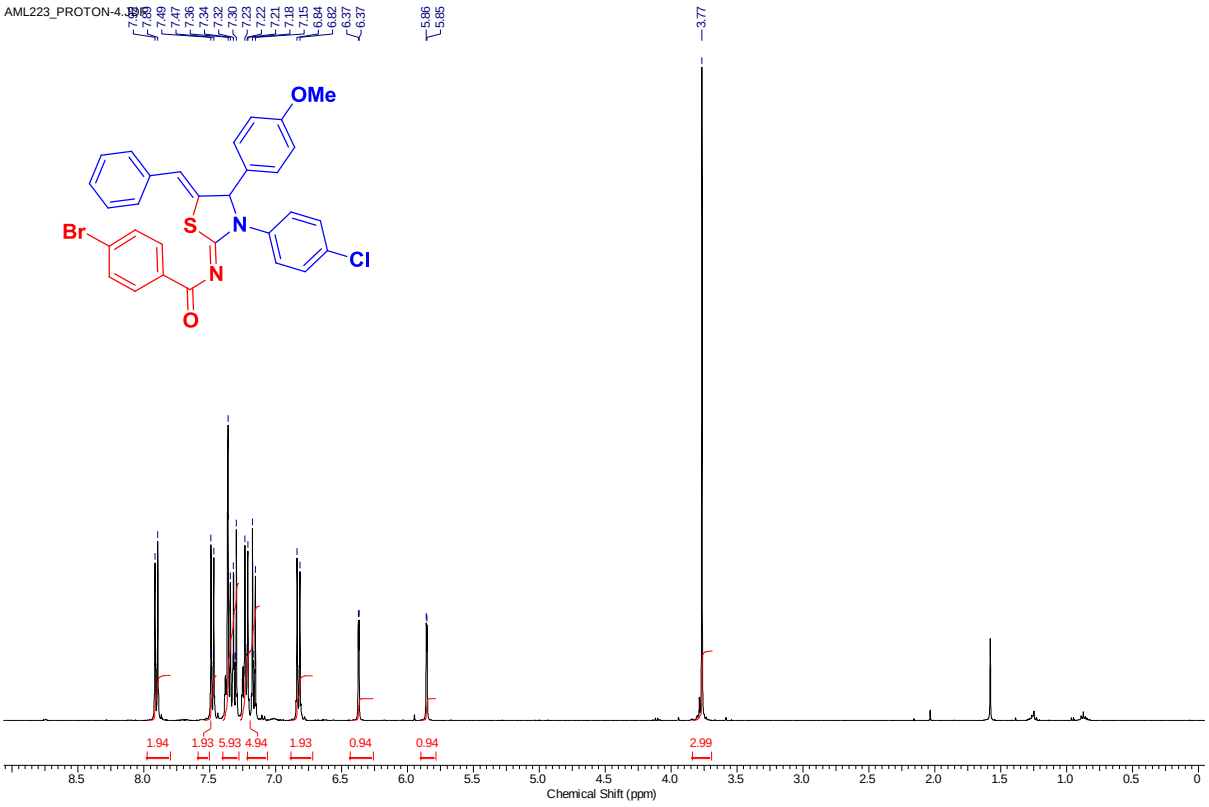

ARI403_DEPT135-3.JDF
129.27
128.87
128.75
128.61
128.08
127.76
127.69
127.17
122.57
122.18
70.35
47.58
28.51
15.82
Ph
Ph
S
N
Bn
N
p-EtC6H4
168 160 152 144 136 128 120 112 104 96 88 80 72 64 56 48 40 32 24 16 8 0
Chemical Shift (ppm)

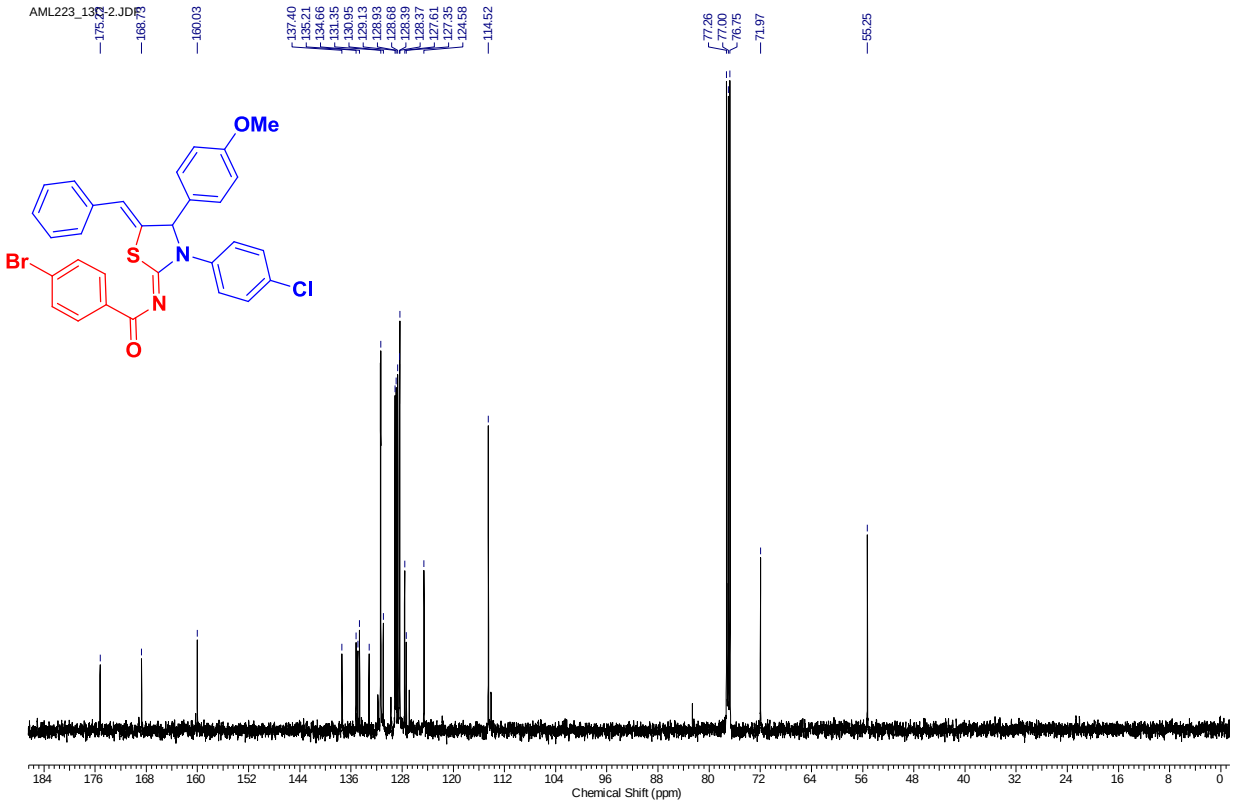

AML184_PROTON-4.JDF
8.04
8.03
8.02
8.01
7.39
7.36
7.34
7.33
7.32
7.32
7.30
7.29
7.28
6.65
6.64
6.63
6.62
6.41
6.41
5.93
5.92
3.80
MeO
S
N
N
O
2.09
15.84
2.08
1.00
1.05
3.10
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


AML184_13C-1.JDF
175.52
162.92
139.54
135.36
135.27
131.89
128.98
128.86
128.77
128.57
128.35
127.39
127.27
126.91
123.95
113.24
77.32
77.00
76.67
72.28
55.26
MeO
S
N
N
O
Chemical Shift (ppm)

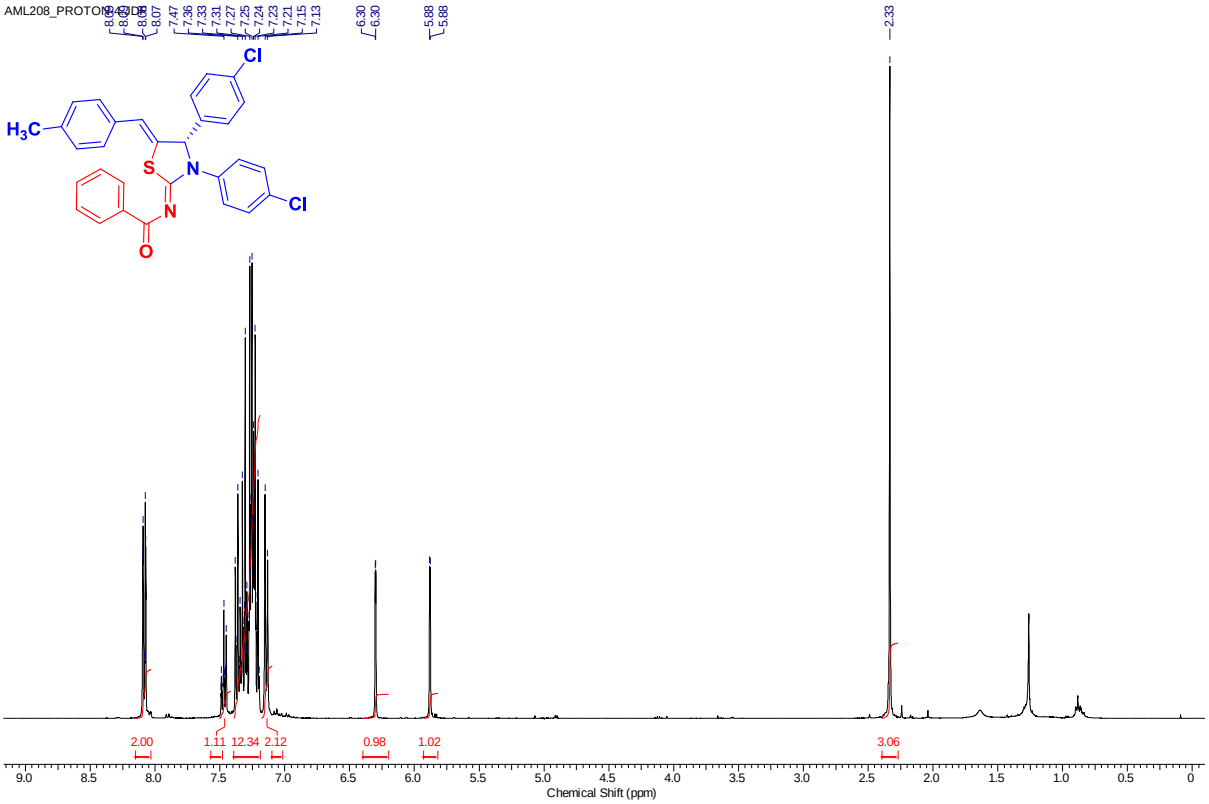

AML199_PROTON-4.JDF
8.04
8.02
7.39
7.38
7.34
7.31
7.29
7.25
7.24
7.22
7.20
6.66
6.64
6.63
6.61
6.37
6.36
5.84
5.84
3.81
3.76
OMe
MeO
S
N
N
Cl
O
1.99
6.42
5.54
4.17
0.97
0.99
3.01
2.88
Chemical Shift (ppm)

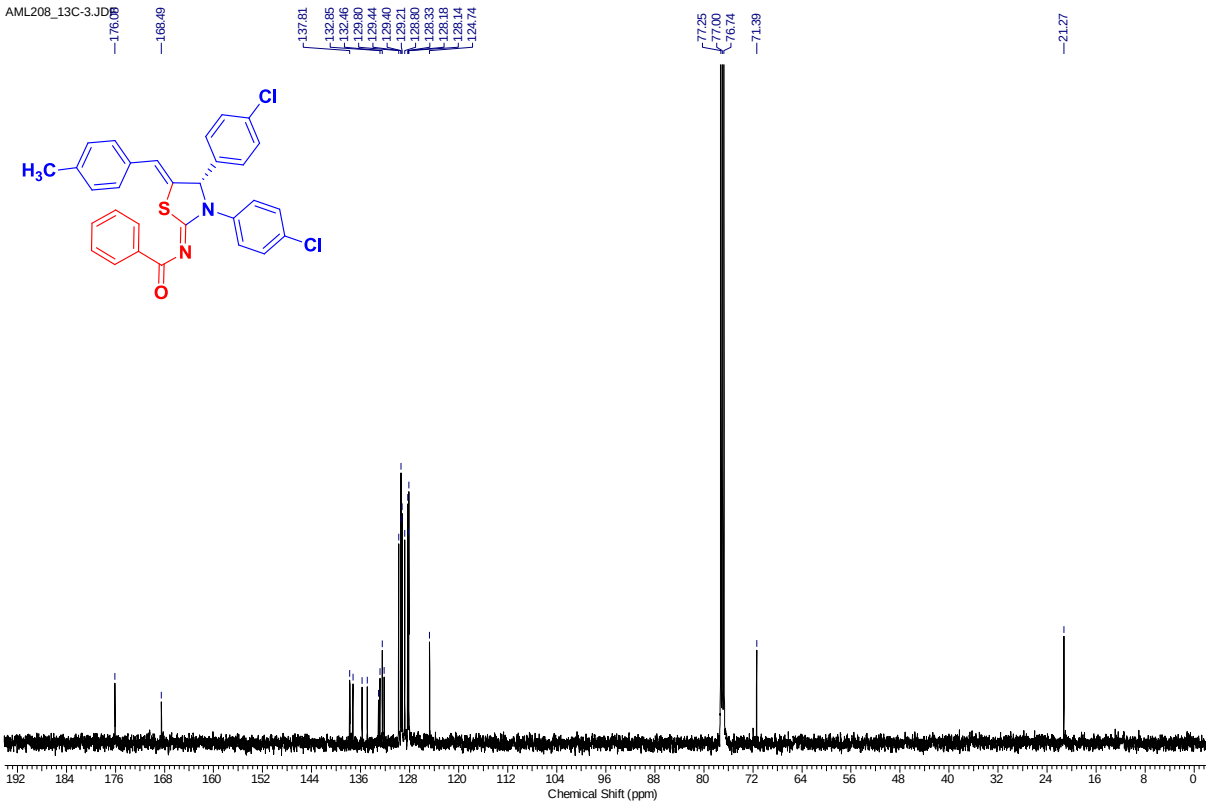

AML199_132-2.JDF
175.42
167.64
163.01
159.98
137.63
135.30
135.15
132.77
131.89
131.21
129.00
128.83
128.68
128.61
128.35
127.44
124.10
114.43
113.33
77.25
77.00
76.74
71.64
55.32
55.22
OMe
MeO
S
N
N
Cl
O
Chemical Shift (ppm)

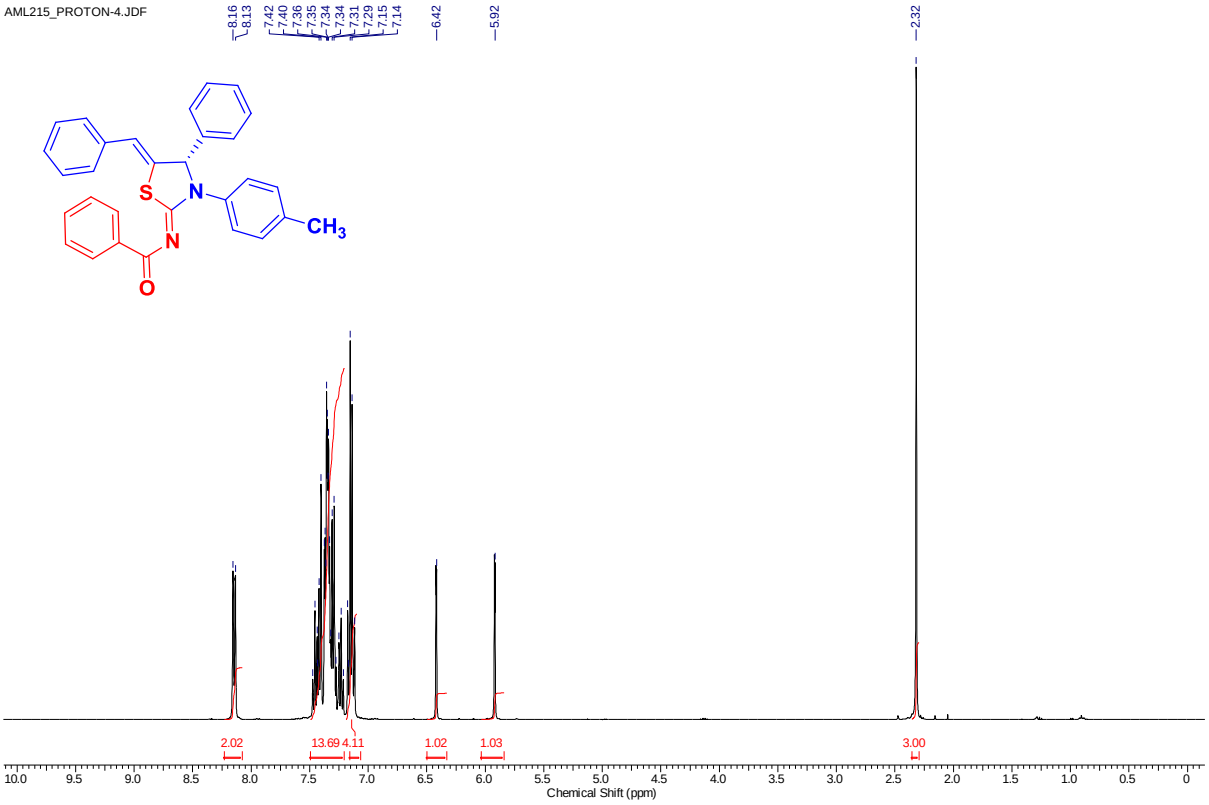

AML223_PROTON-4.JDF
7.96
7.95
7.89
7.49
7.47
7.36
7.34
7.32
7.30
7.23
7.22
7.21
7.18
7.15
6.84
6.82
6.37
6.37
5.96
5.85
3.77
OMe
Br
S
N
N
Cl
O
1.94
1.93
5.93
4.94
1.93
0.94
0.94
2.99
Chemical Shift (ppm)

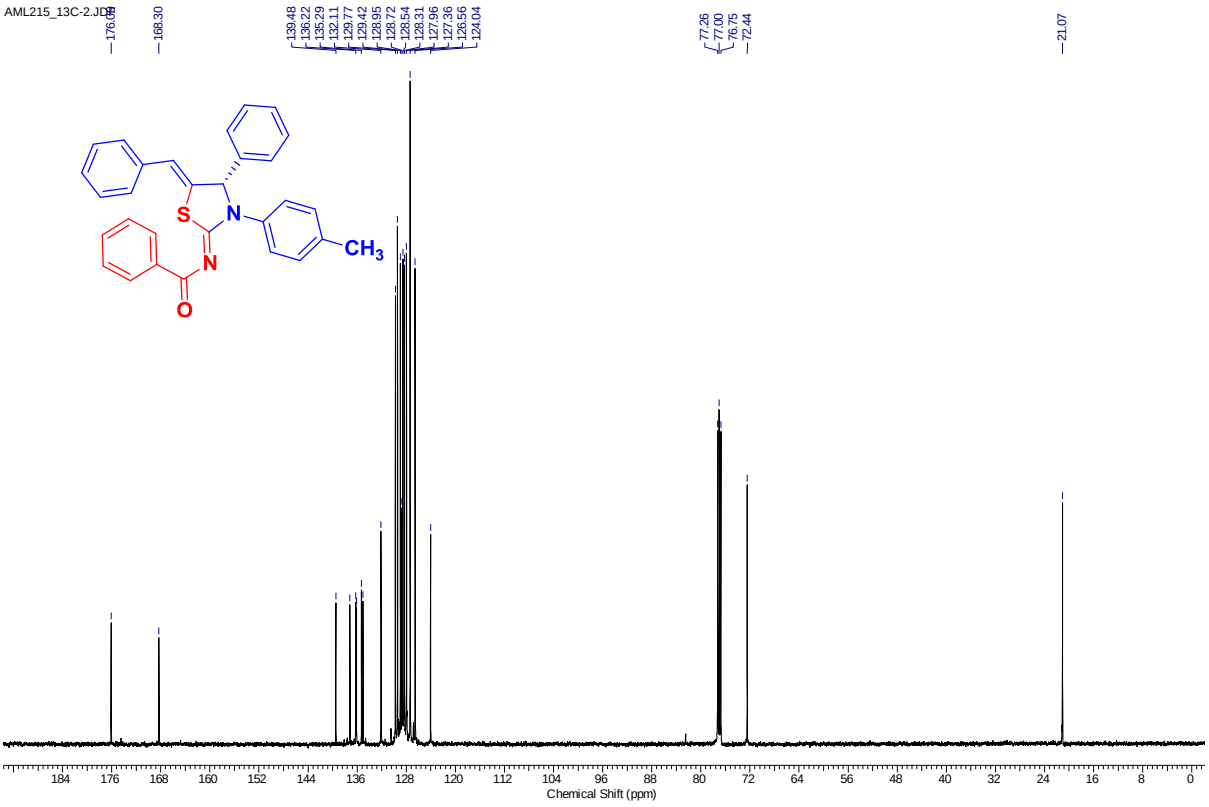

AML223_13C-2.JDF
175.34
168.73
160.03
137.40
135.21
134.66
131.35
130.95
129.13
128.93
128.68
128.39
128.37
127.61
127.35
124.58
114.52
77.26
77.00
76.75
71.97
55.25
OMe
Br
S
N
N
Cl
O
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

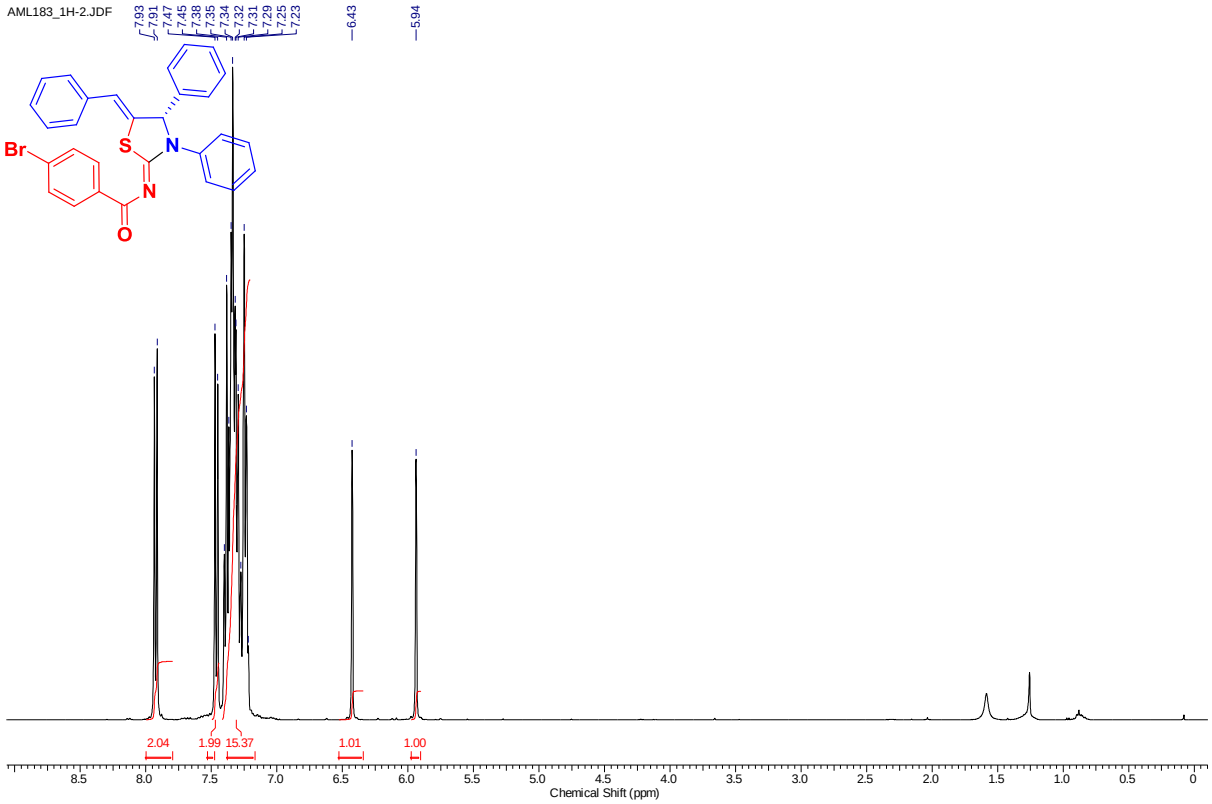
NMR Of Chiral Thiazolidine-2-imine (16a-16t)

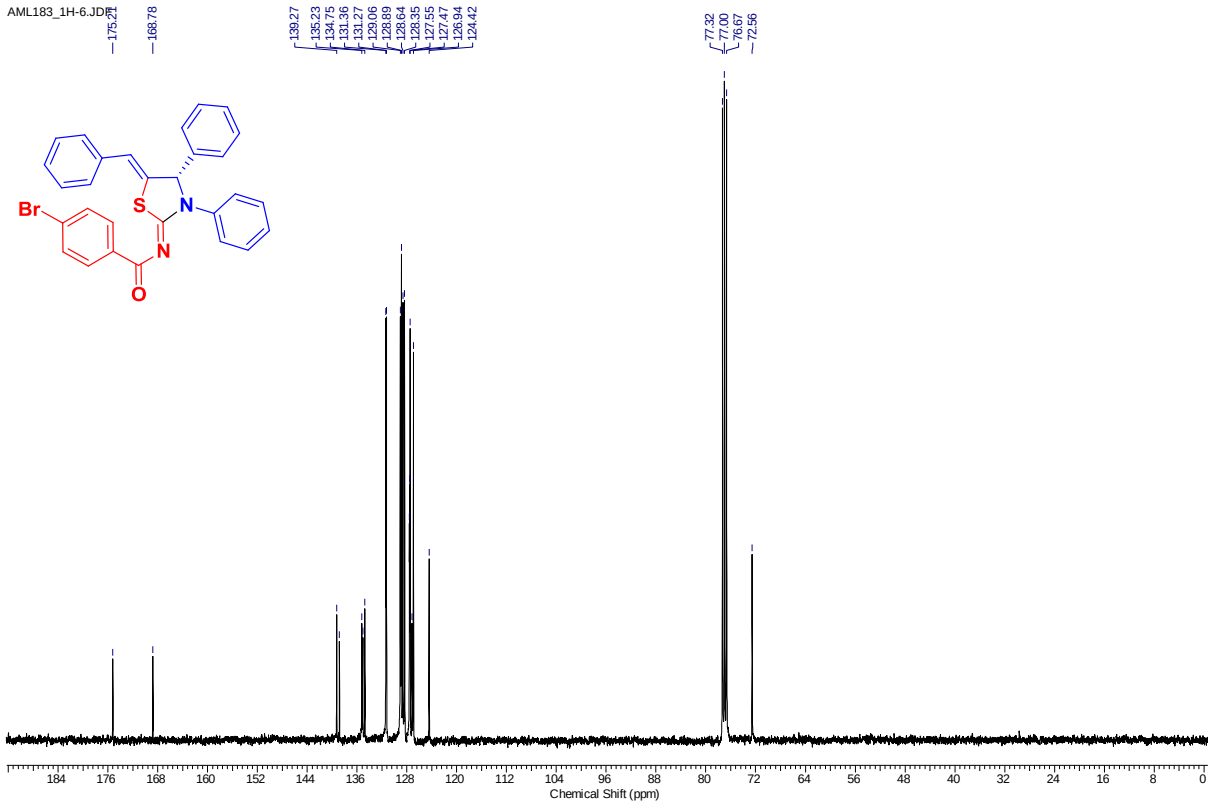


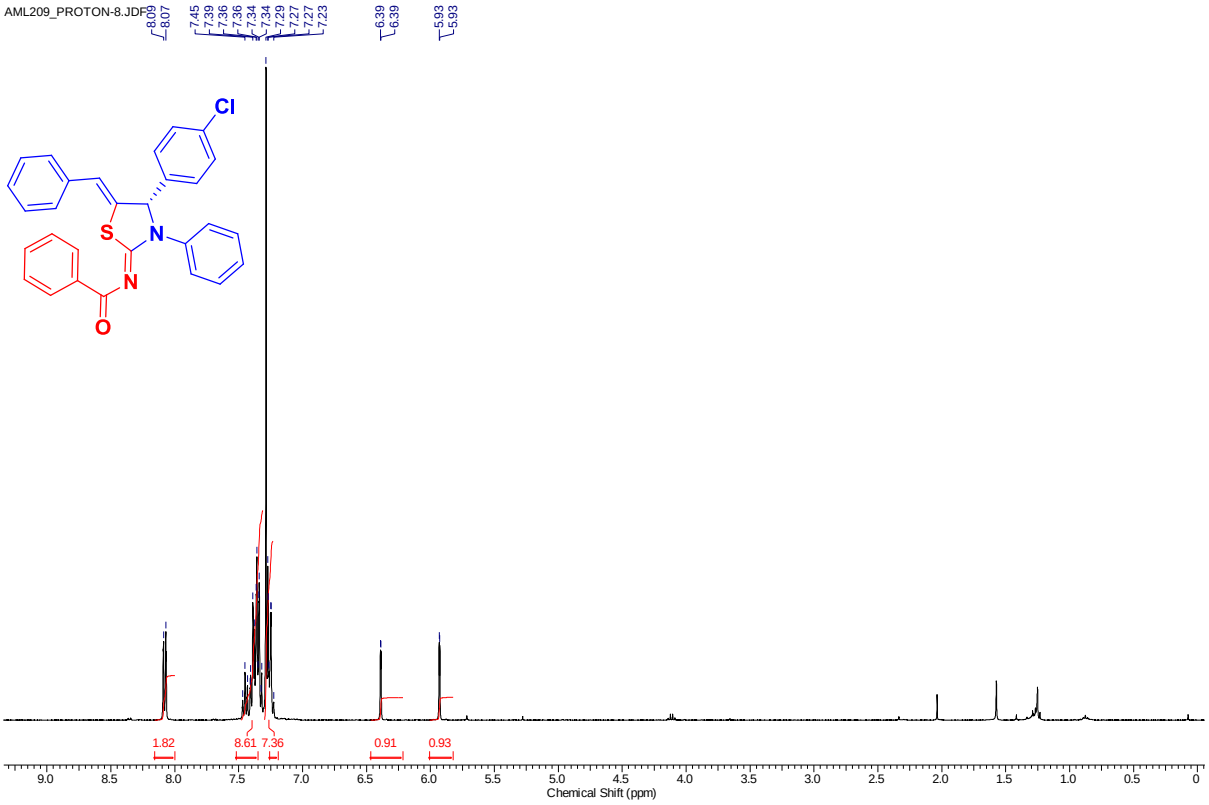


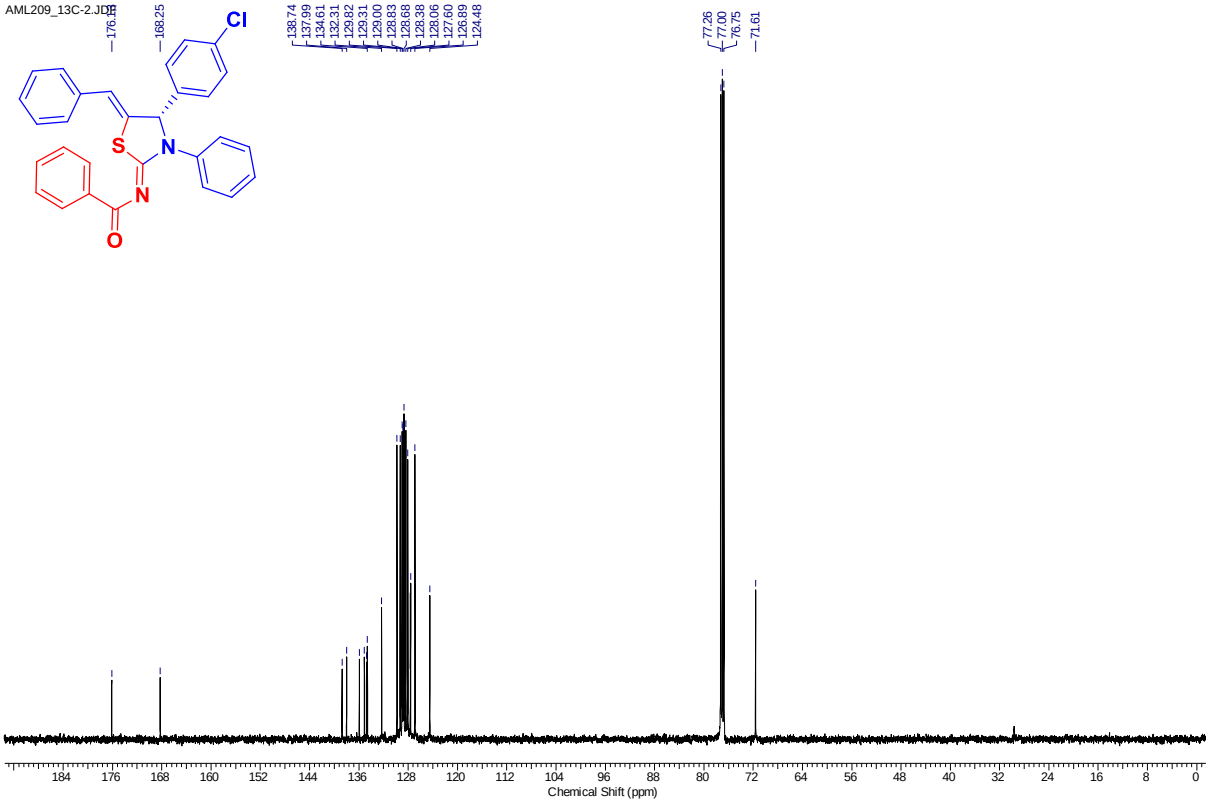

AML215_PROTON-4.JDF
8.16
8.13
7.42
7.40
7.36
7.35
7.34
7.34
7.31
7.29
7.15
7.14
6.42
5.92
2.32
S
N
N
O
CH3
2.02
13.69
4.11
1.02
1.03
3.00
Chemical Shift (ppm)

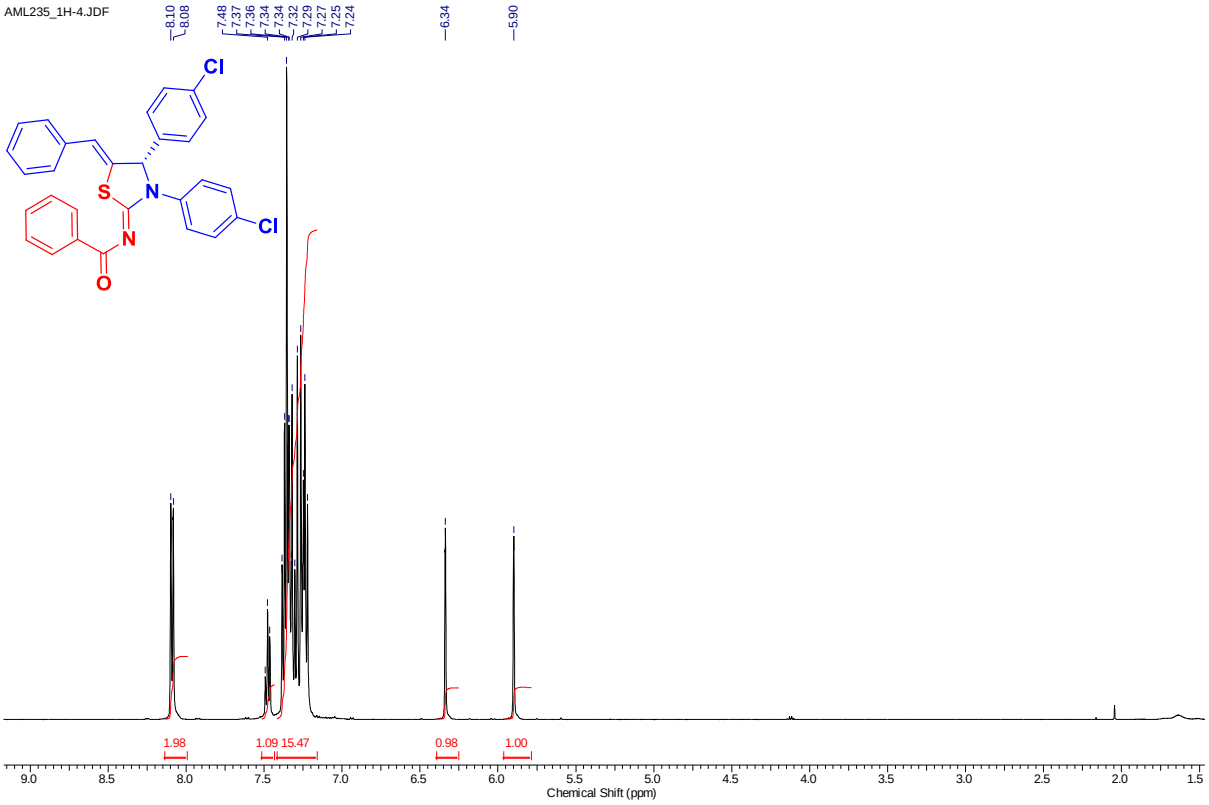

AML215_13C-2.JDF
176.04
168.30
139.48
136.22
135.29
132.11
129.77
129.42
128.95
128.72
128.54
128.31
127.96
127.36
126.56
124.04
77.26
77.00
76.75
72.44
21.07
S
N
N
O
CH3
Chemical Shift (ppm)

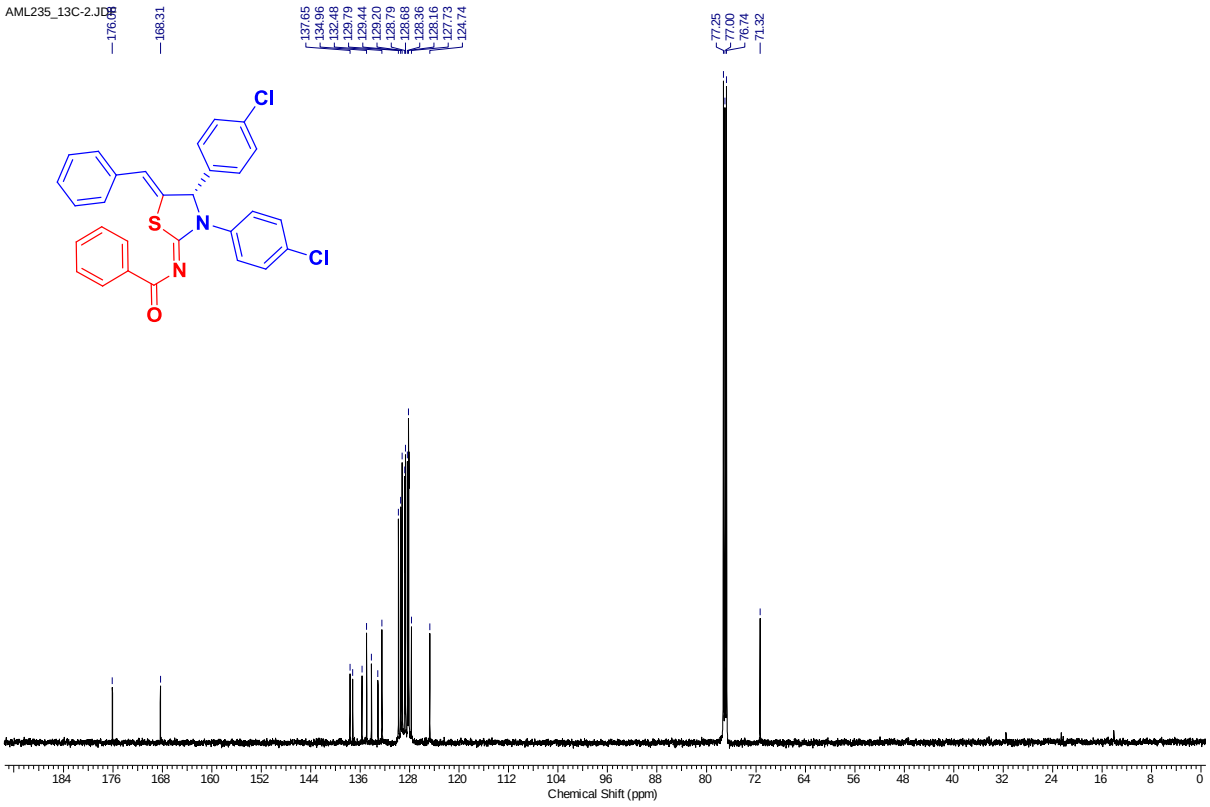

AML183_1H-2.JDF
7.93
7.91
7.47
7.45
7.38
7.35
7.34
7.32
7.31
7.29
7.25
7.23
6.43
5.94
Br
S
N
N
O
2.04
1.99
15.37
1.01
1.00
Chemical Shift (ppm)

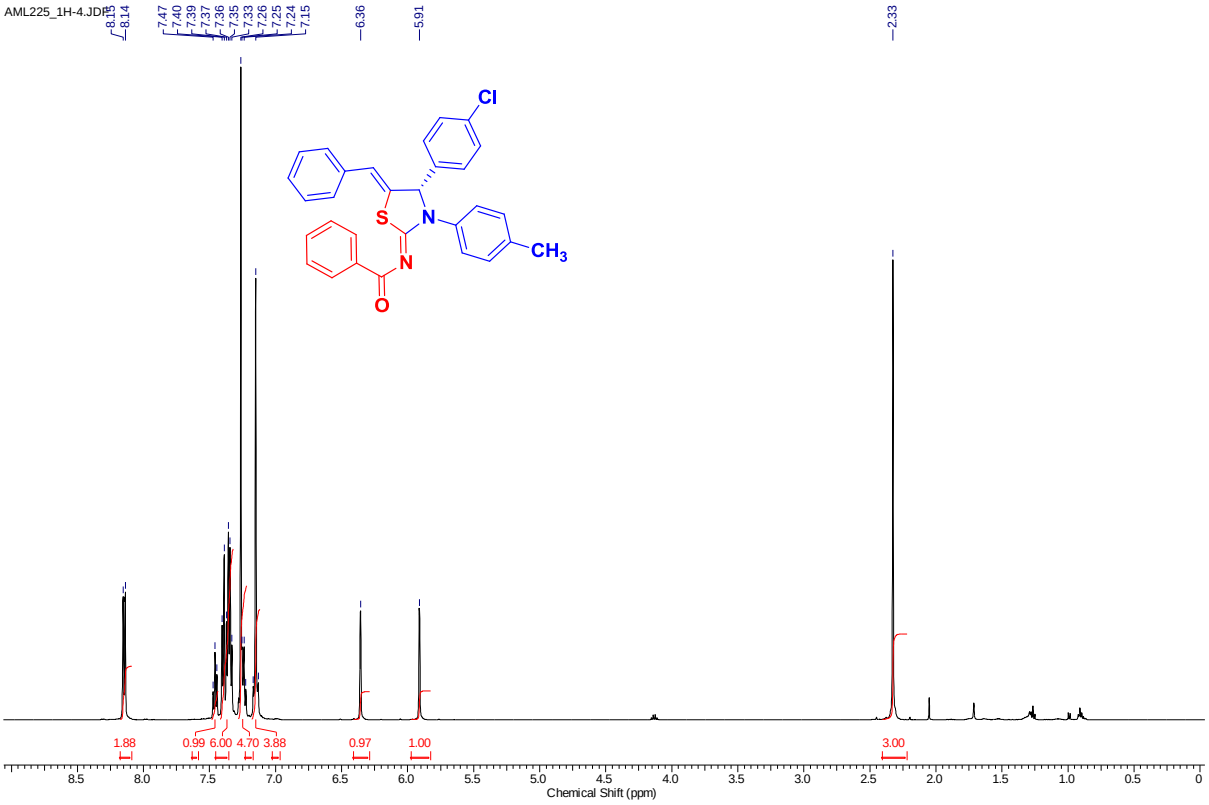

AML183_1H-6.JDF
175.21
168.78
139.27
135.23
134.75
131.36
131.27
129.06
128.89
128.64
128.35
127.55
127.47
126.94
124.42
77.32
77.00
76.67
72.56
Br
S
N
N
O
Chemical Shift (ppm)

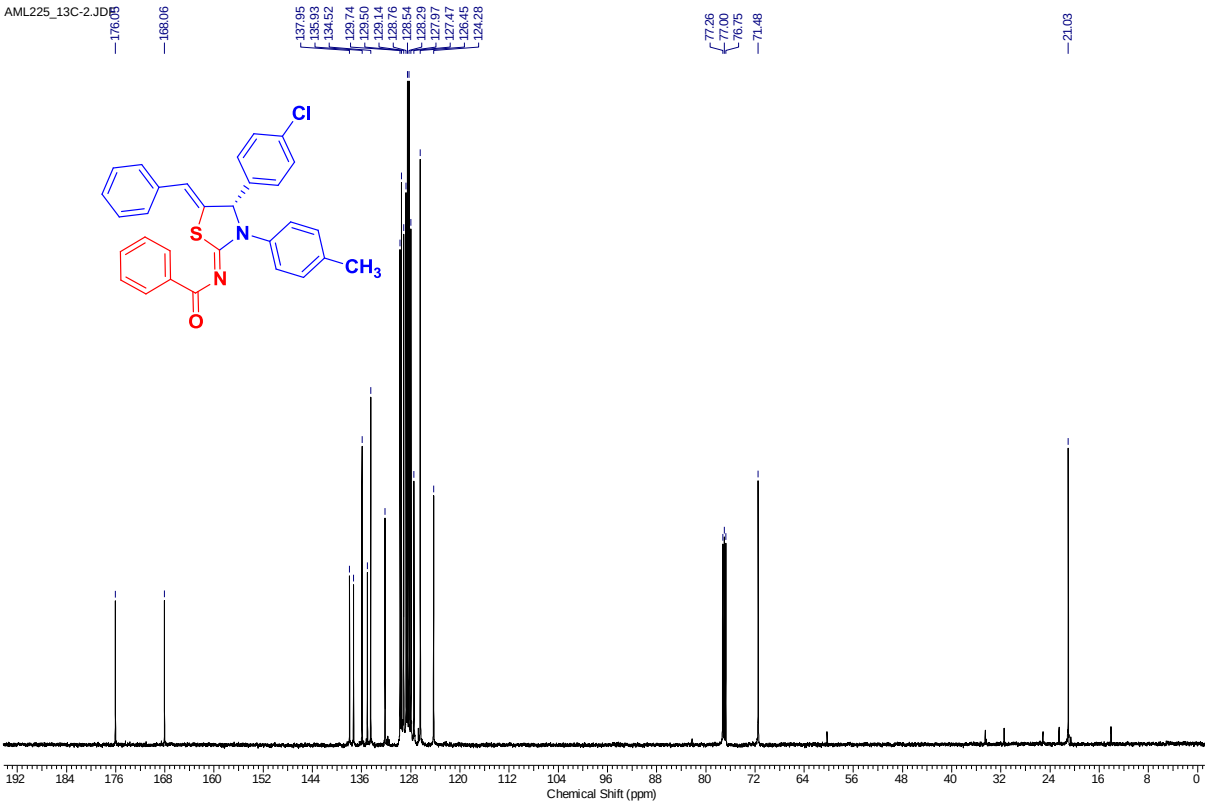

AML209_PROTON-8.JDF
8.09
8.07
7.45
7.39
7.36
7.36
7.34
7.34
7.29
7.27
7.27
7.23
6.39
6.39
5.93
5.93
Cl
S
N
N
O
1.82
8.61
7.36
0.91
0.93
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

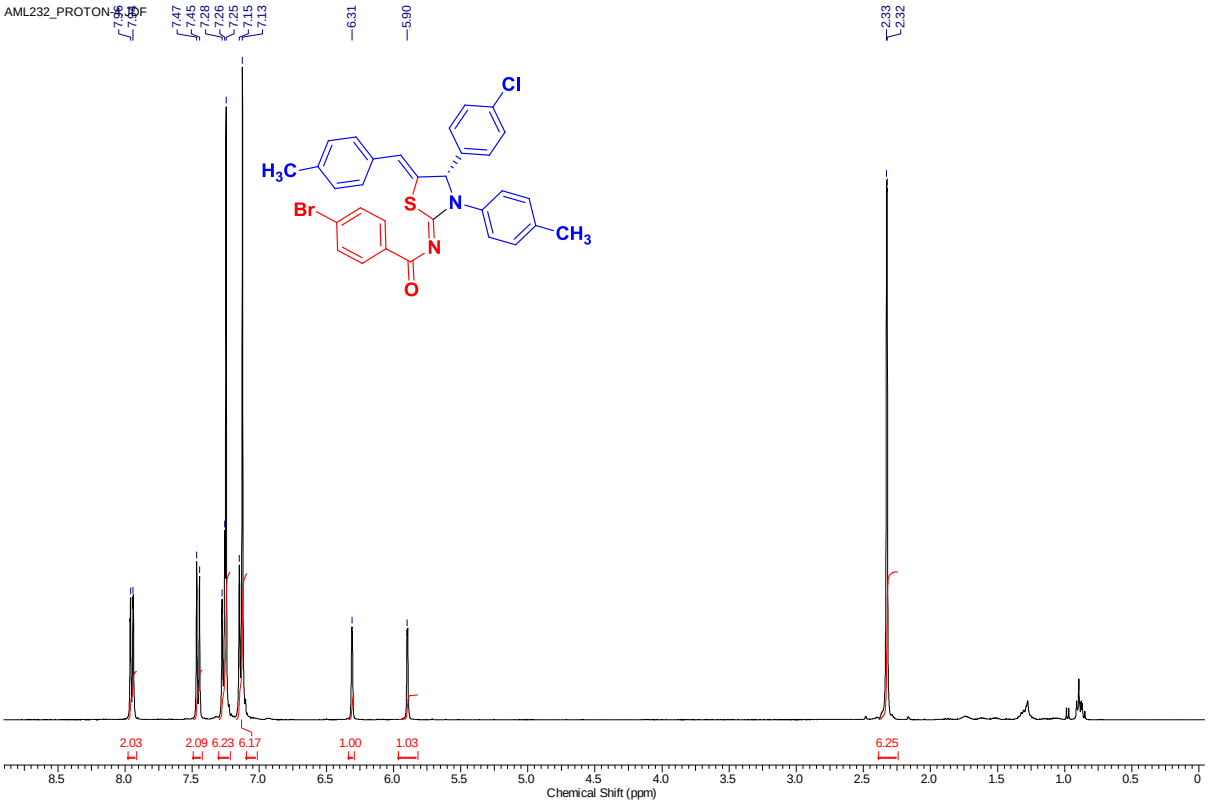

AML209_13C-2.JDF
176.18
168.25
138.74
137.99
134.61
132.31
129.82
129.31
129.00
128.83
128.68
128.38
128.06
127.60
126.89
124.48
77.26
77.00
76.75
71.61
Cl
S
N
N
O
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

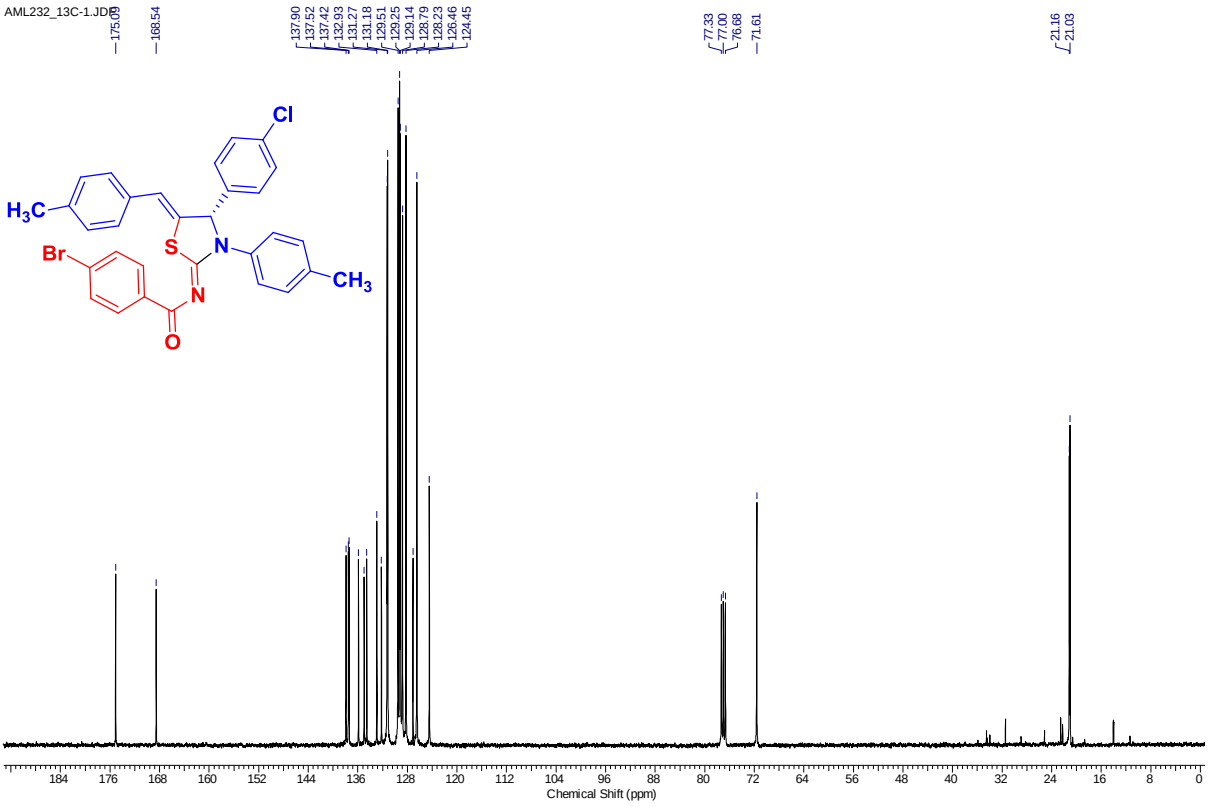

AML235_1H-4.JDF
8.10
8.08
7.48
7.37
7.36
7.34
7.34
7.32
7.29
7.27
7.25
7.24
6.34
5.90
Cl
S
N
Cl
N
O
1.98
1.09
15.47
0.98
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
Chemical Shift (ppm)

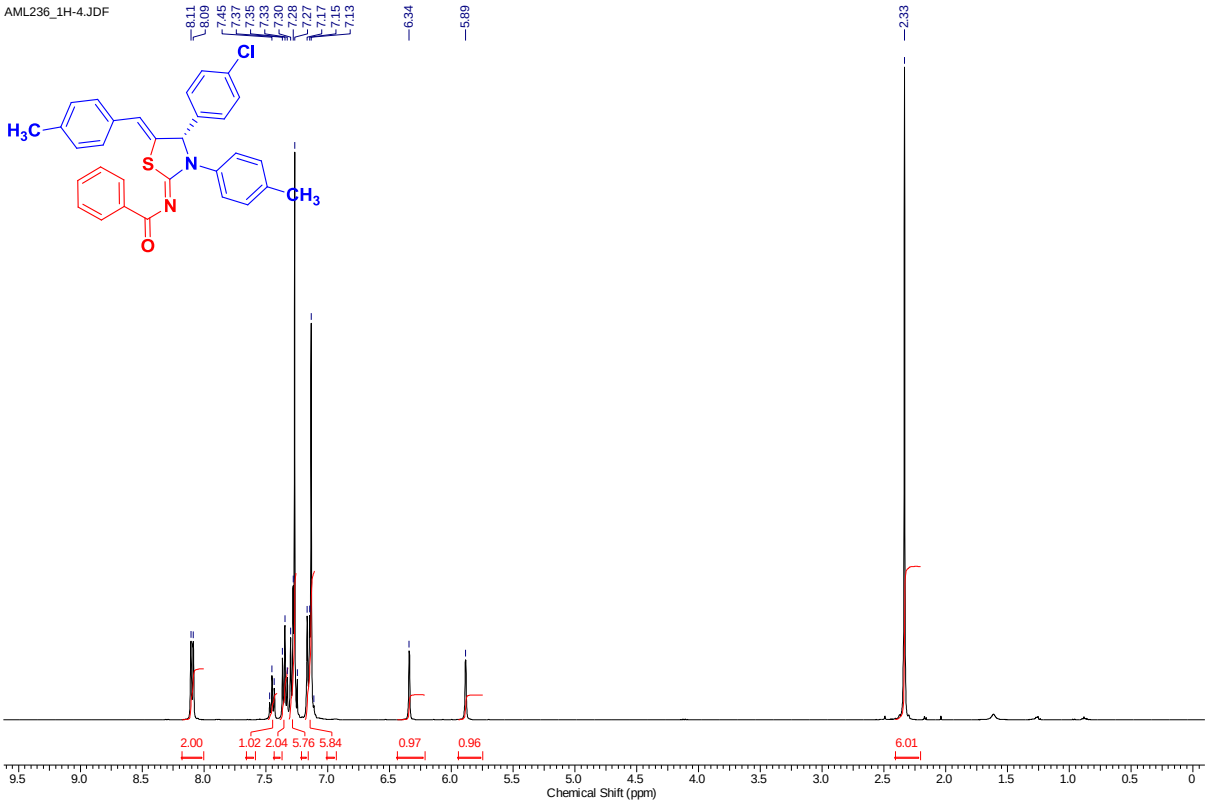

AML235_13C-2.JDF
176.08
168.31
137.65
134.96
132.48
129.79
129.44
129.20
128.79
128.68
128.36
128.16
127.73
124.74
77.25
77.00
76.74
71.32
Cl
S
N
Cl
N
O
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

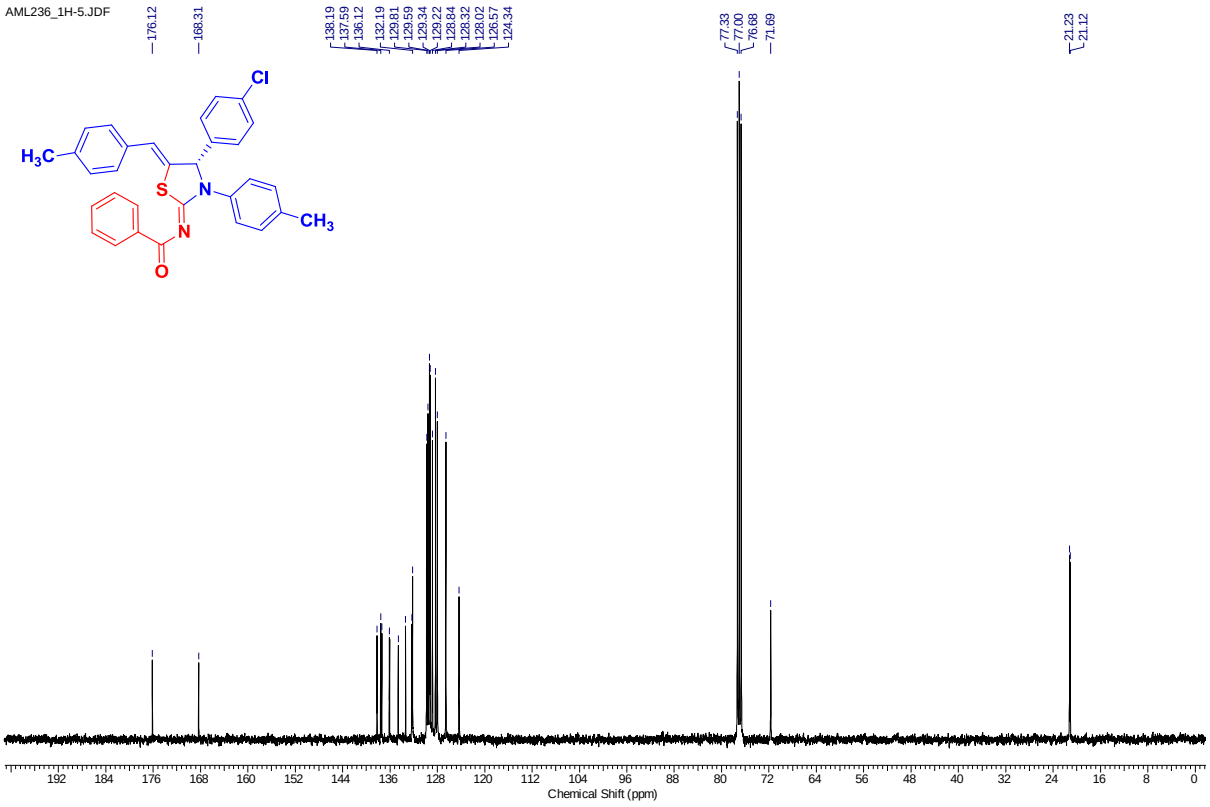

AML225_1H-4.JDF
8.15
8.14
7.47
7.40
7.39
7.37
7.36
7.35
7.33
7.26
7.25
7.24
7.15
6.36
5.91
2.33
Cl
S
N
N
O
CH3
1.88
0.99
6.00
4.70
3.88
0.97
1.00
3.00
Chemical Shift (ppm)

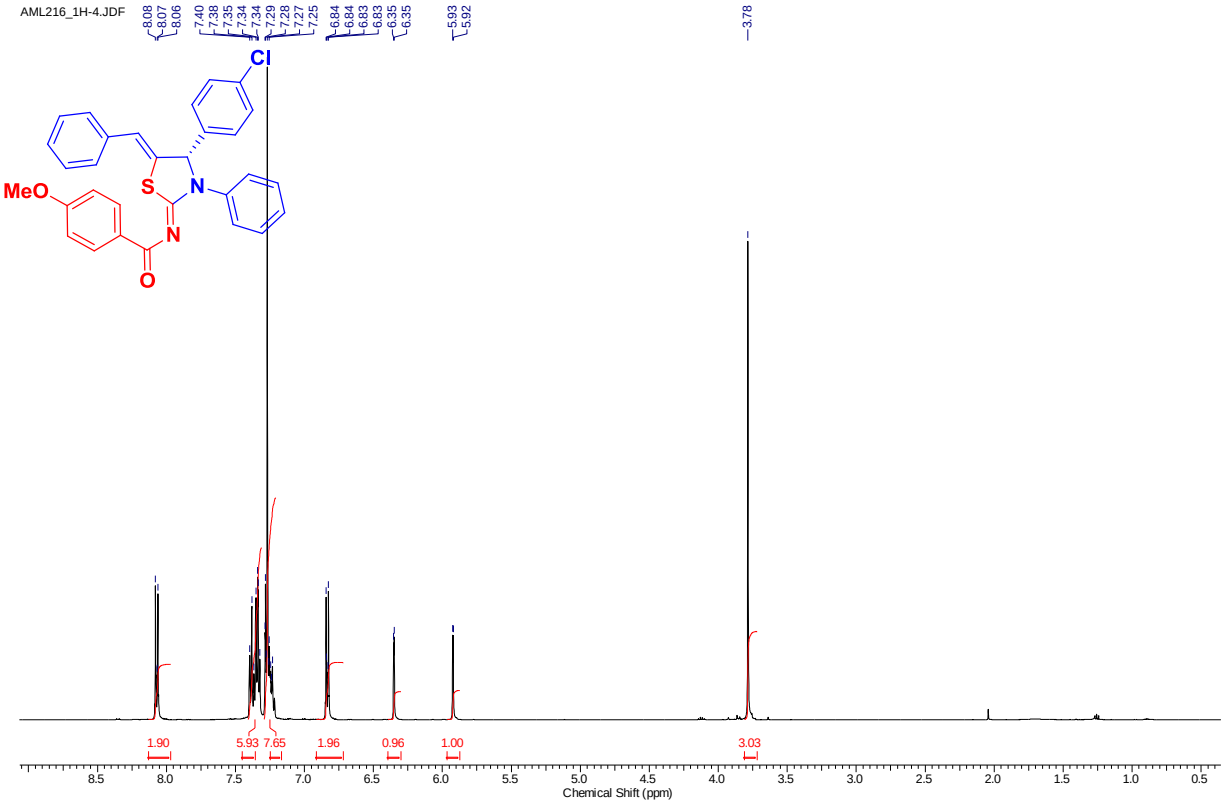

AML225_13C-2.JDF
176.05
168.06
137.95
135.93
134.52
129.74
129.50
129.14
128.76
128.54
128.29
127.97
127.47
126.45
124.28
77.26
77.00
76.75
71.48
21.03
Cl
S
N
N
O
CH3
Chemical Shift (ppm)

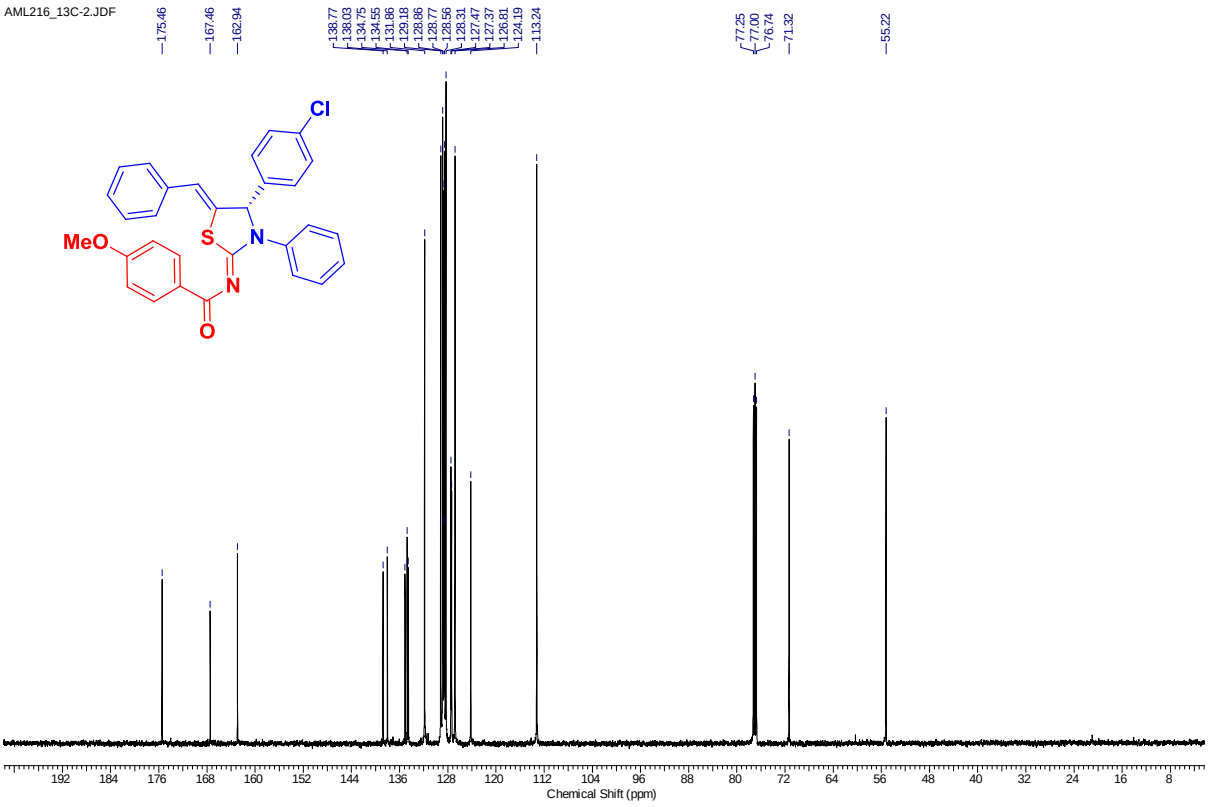

AML232_PROTON-6.1.DF
7.96
7.94
7.47
7.45
7.28
7.26
7.25
7.15
7.13
6.31
5.90
2.33
2.32
Cl
H3C
Br
S
N
CH3
N
O
2.03
2.09
6.23
6.17
1.00
1.03
6.25
Chemical Shift (ppm)

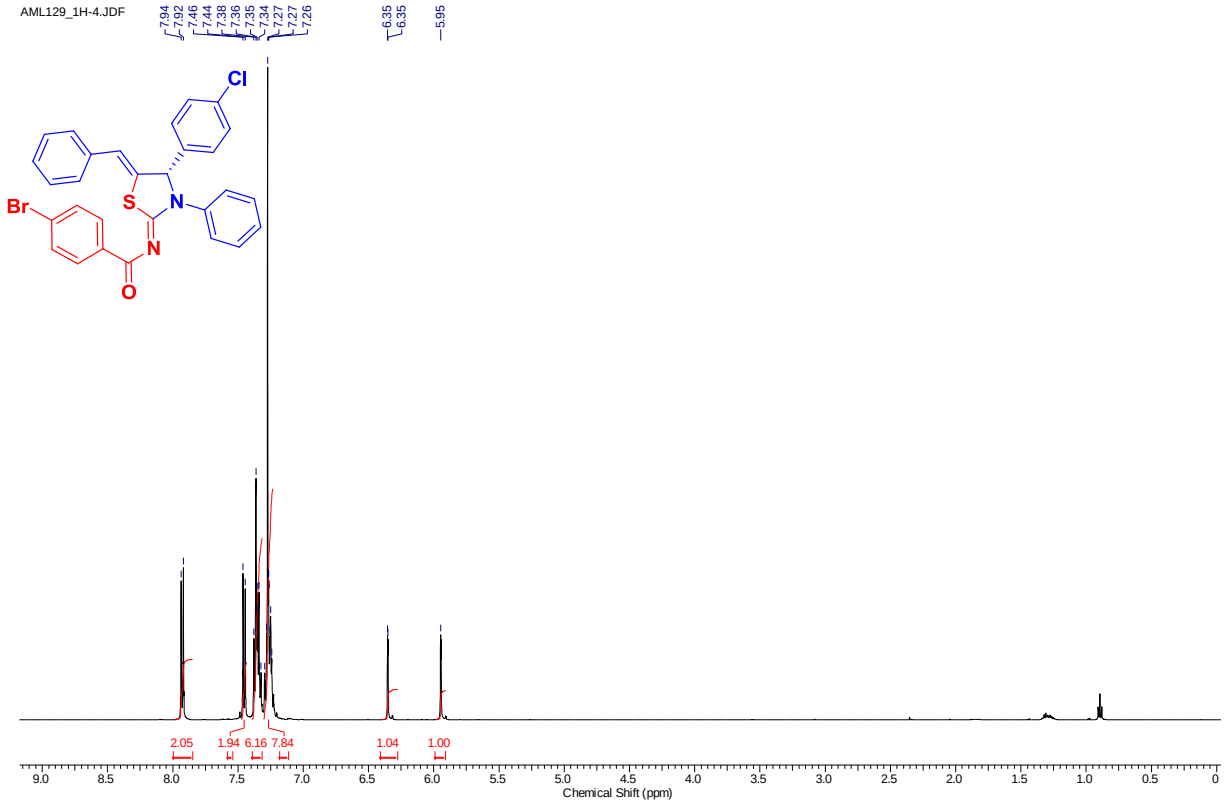

AML232_13C-1.JDF
175.03
168.54
137.90
137.52
137.42
132.93
131.27
131.18
129.51
129.25
129.14
128.79
128.23
126.46
124.45
77.33
77.00
76.68
71.61
21.16
21.03
Cl
H3C
Br
S
N
CH3
N
O
Chemical Shift (ppm)

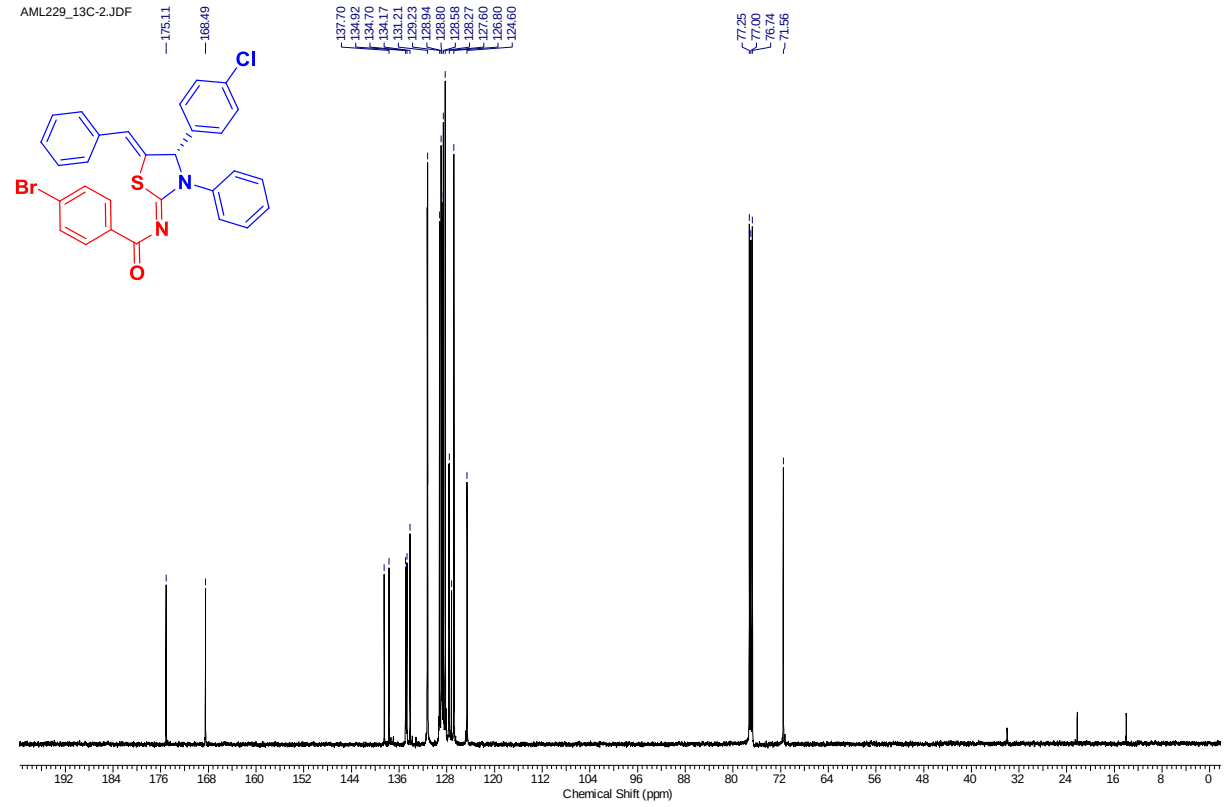

AML236_1H-4.JDF
8.11
8.09
7.45
7.37
7.35
7.33
7.30
7.28
7.27
7.17
7.15
7.13
6.34
5.89
2.33
Cl
H3C
S
N
N
CH3
O
2.00
1.02
2.04
5.76
5.84
0.97
0.96
6.01
Chemical Shift (ppm)

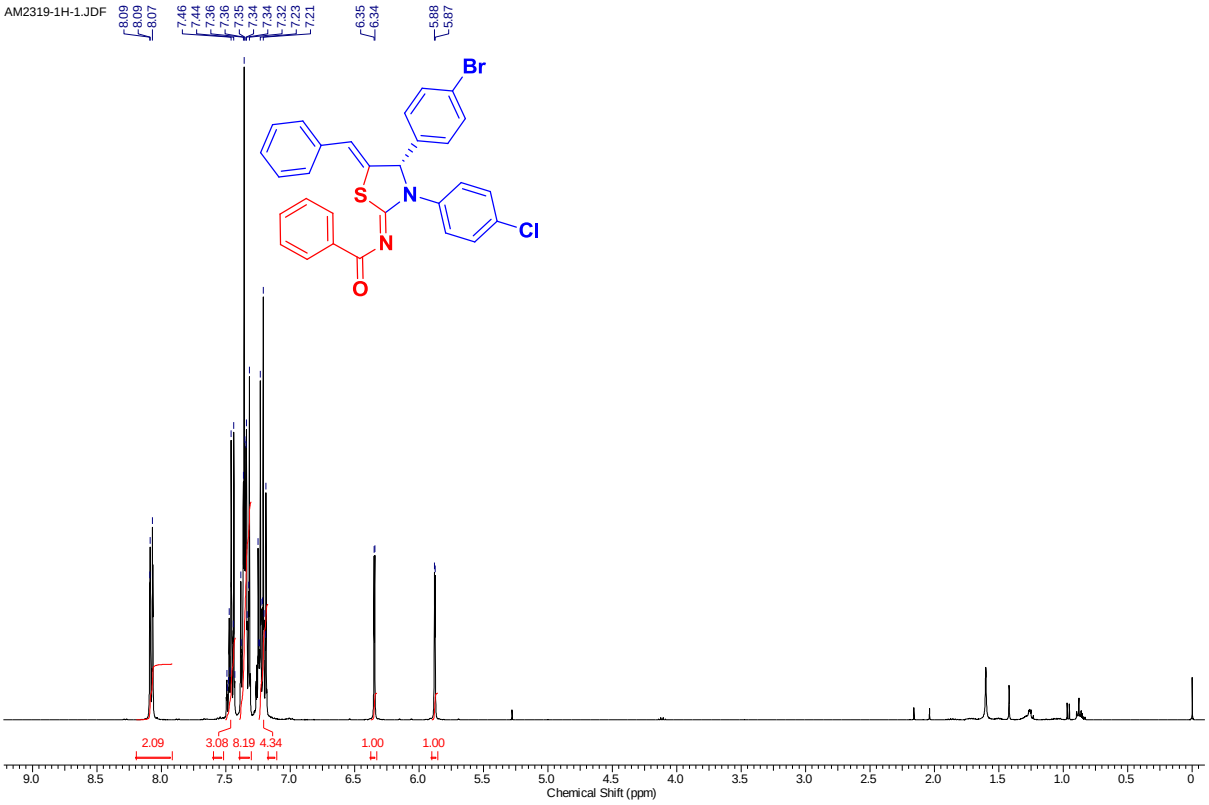

AML236_1H-5.JDF
176.12
168.31
138.19
137.59
136.12
132.19
129.81
129.59
129.34
129.22
128.84
128.32
128.02
126.57
124.34
77.33
77.00
76.68
71.69
21.23
21.12
Cl
H3C
S
N
N
CH3
O
Chemical Shift (ppm)

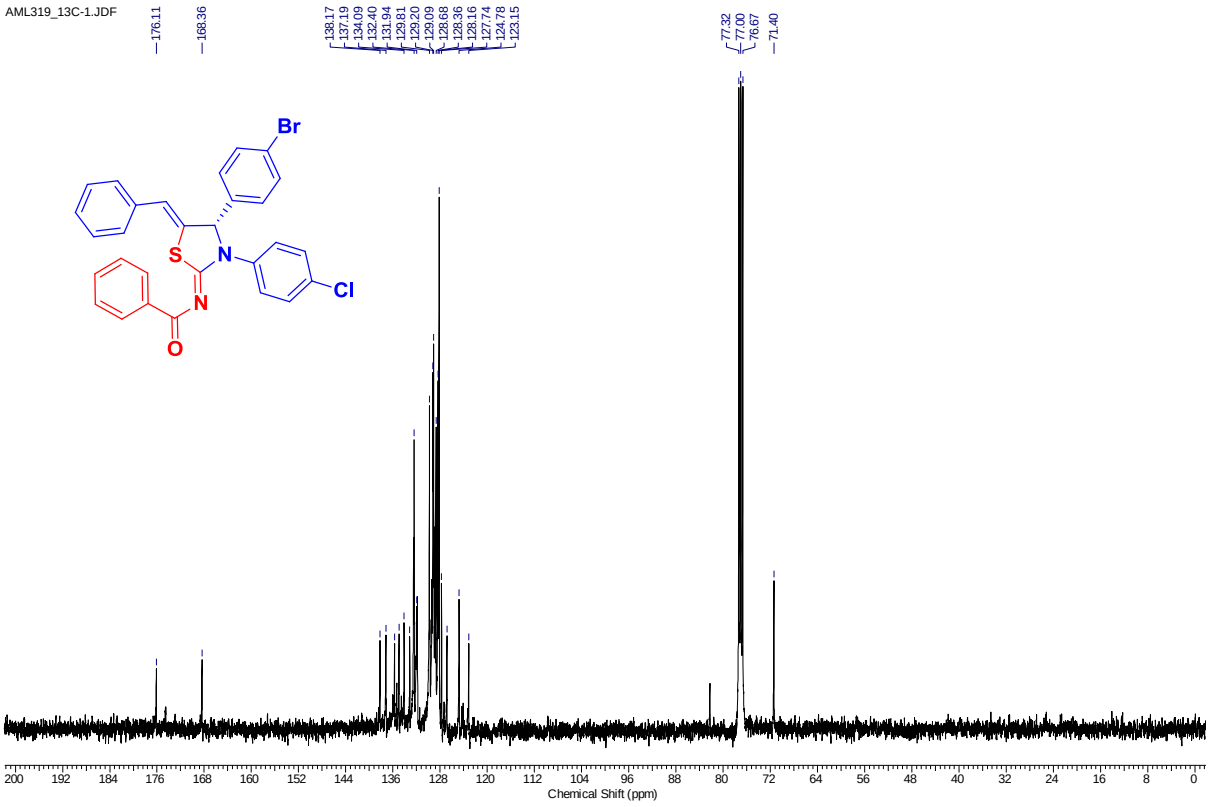

AML216_1H-4.JDF
8.08
8.07
8.06
7.40
7.38
7.35
7.34
7.34
7.29
7.28
7.27
7.25
6.84
6.84
6.83
6.83
6.35
6.35
5.93
5.92
3.78
Cl
MeO
S
N
N
O
1.90
5.93
7.65
1.96
0.96
1.00
3.03
Chemical Shift (ppm)

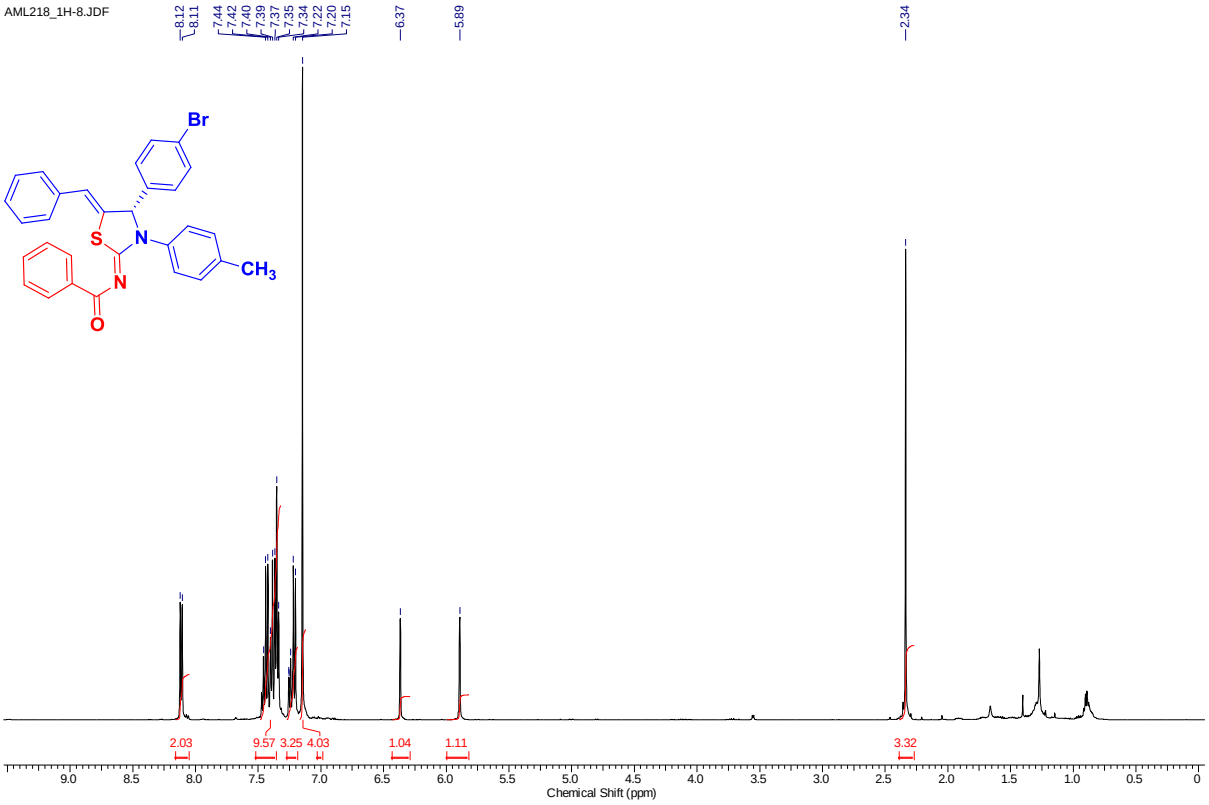

AML216_13C-2.JDF
175.46
167.46
162.94
138.77
138.03
134.75
134.55
131.86
129.18
128.86
128.77
128.56
128.31
127.47
127.37
126.81
124.19
113.24
77.25
77.00
76.74
71.32
55.22
Cl
MeO
S
N
N
O
Chemical Shift (ppm)

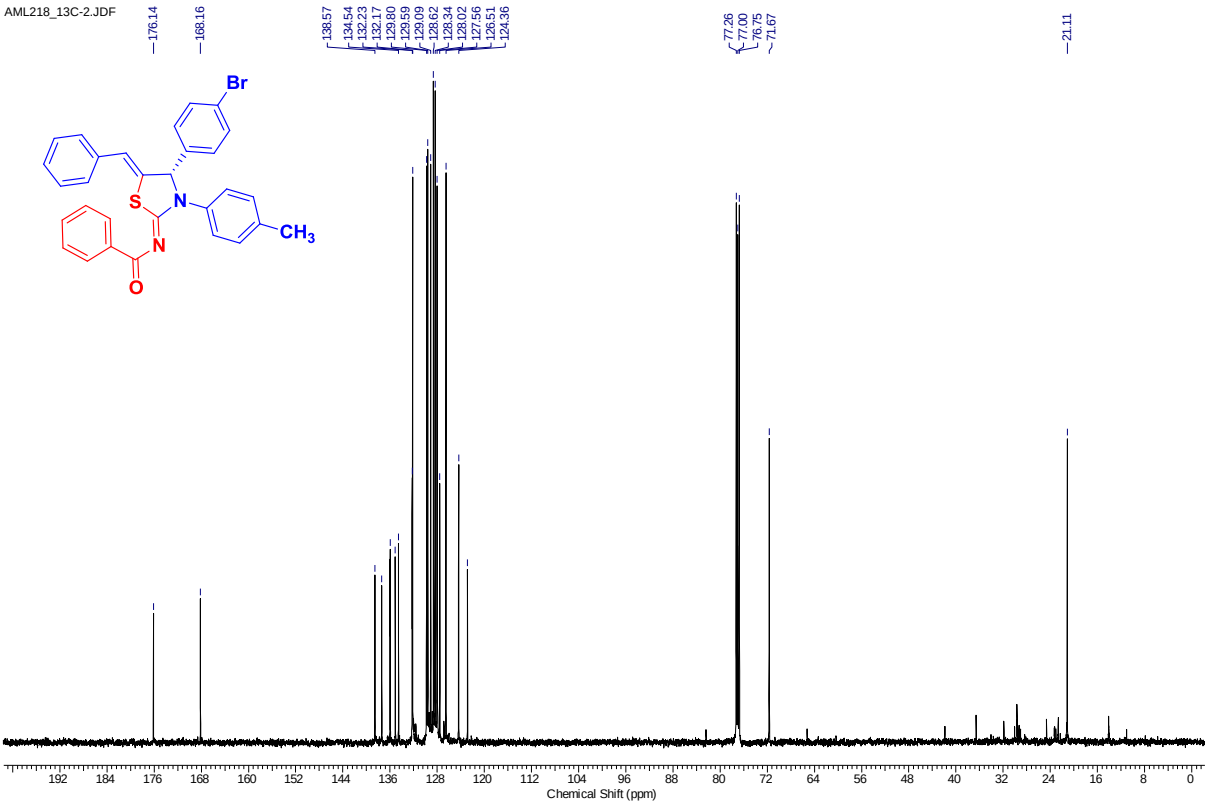

AML129_1H-4.JDF
7.94
7.92
7.46
7.44
7.38
7.36
7.35
7.34
7.27
7.27
7.26
6.35
6.35
5.95
Cl
Br
S
N
N
O
2.05
1.94
6.16
7.84
1.04
1.00
Chemical Shift (ppm)

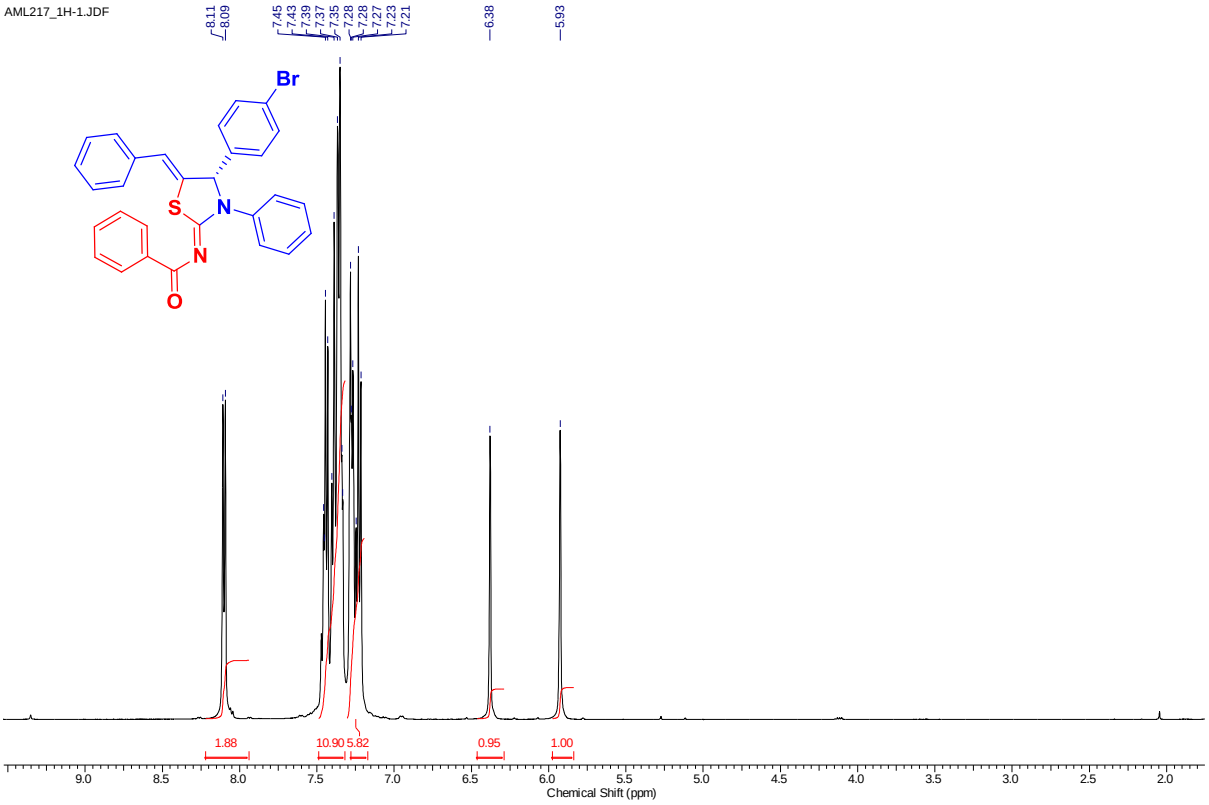

AML229_13C-2.JDF
175.11
168.49
137.70
134.92
134.70
134.17
131.21
129.23
128.94
128.80
128.58
128.27
127.60
126.90
124.60
77.25
77.00
76.74
71.56
Cl
Br
S
N
N
O
Chemical Shift (ppm)

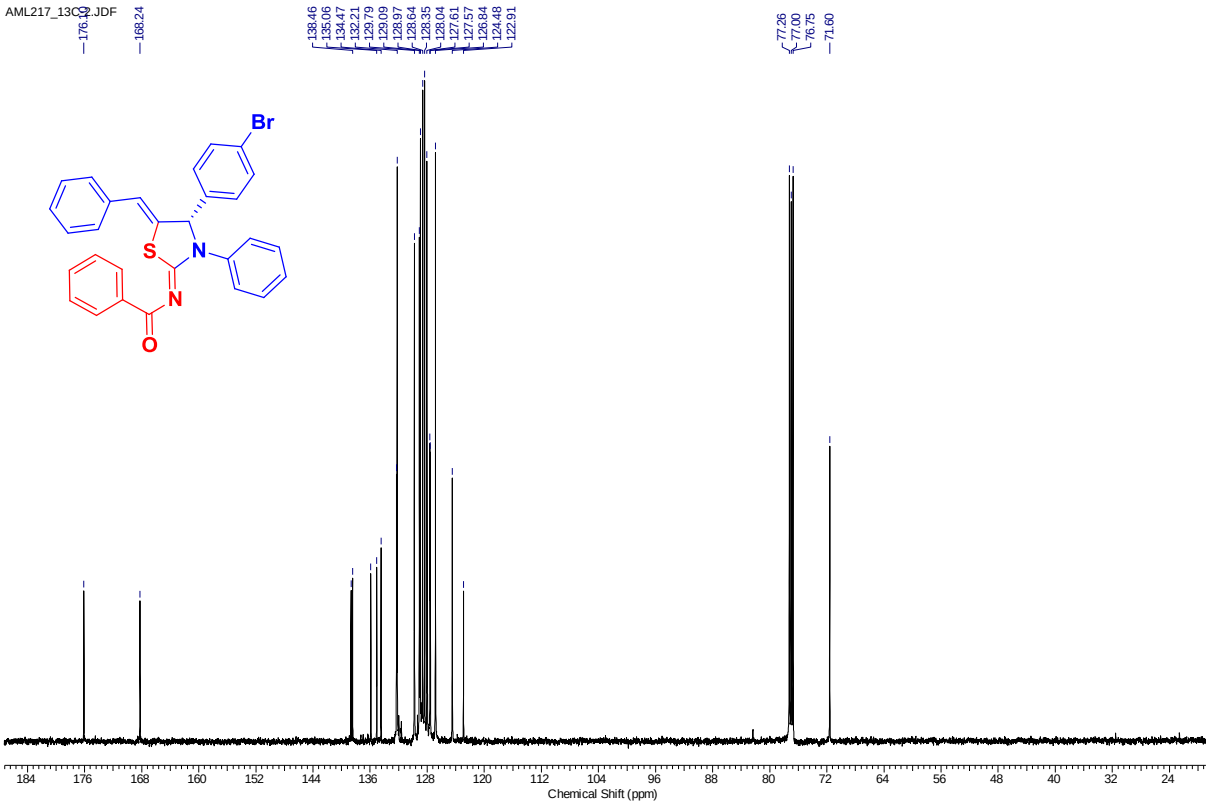

AM2319-1H-1.JDF
8.09
8.09
8.07
7.46
7.44
7.36
7.36
7.35
7.34
7.34
7.32
7.23
7.21
6.35
6.34
5.88
5.87
Br
S
N
N
Cl
O
2.09
3.08
8.19
4.34
1.00
1.00
Chemical Shift (ppm)

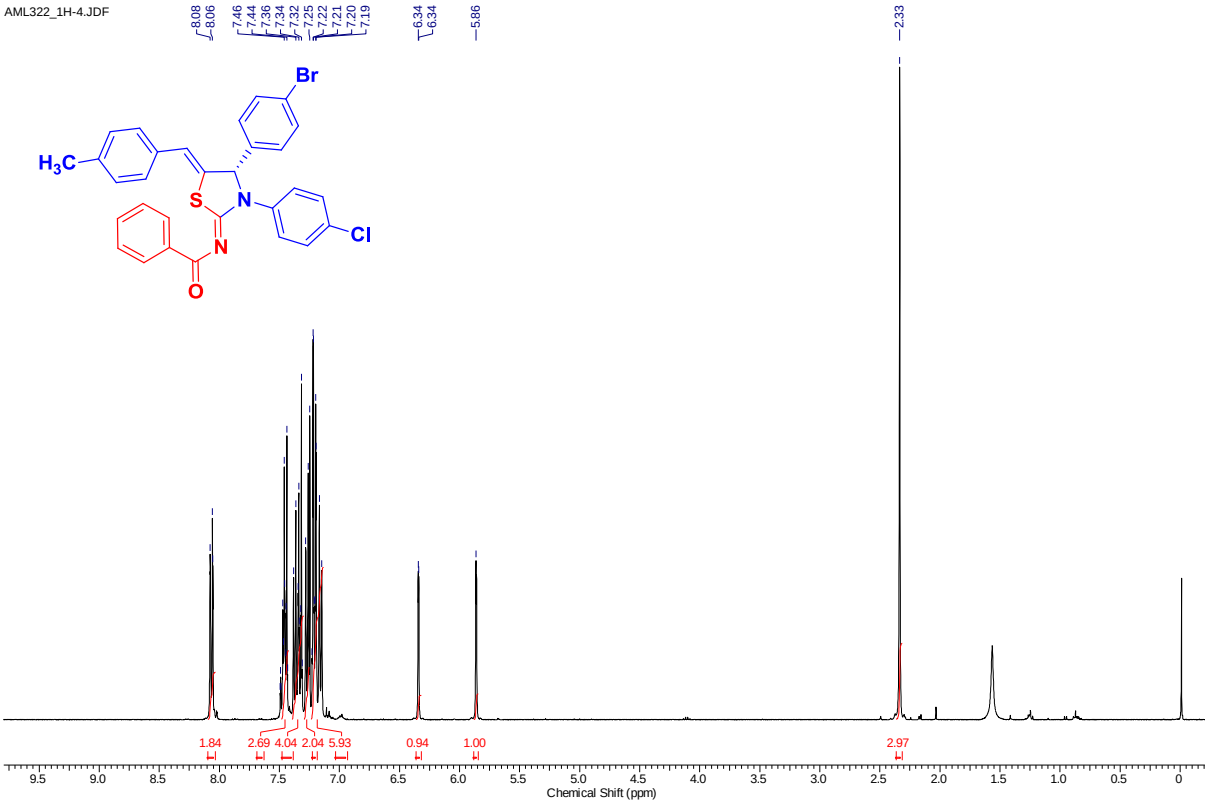

AML319_13C-1.JDF
176.11
168.36
138.17
137.19
134.09
132.40
131.94
129.81
129.20
129.09
128.68
128.36
128.16
127.74
124.78
123.15
77.32
77.00
76.67
71.40
Br
S
N
N
Cl
O
Chemical Shift (ppm)

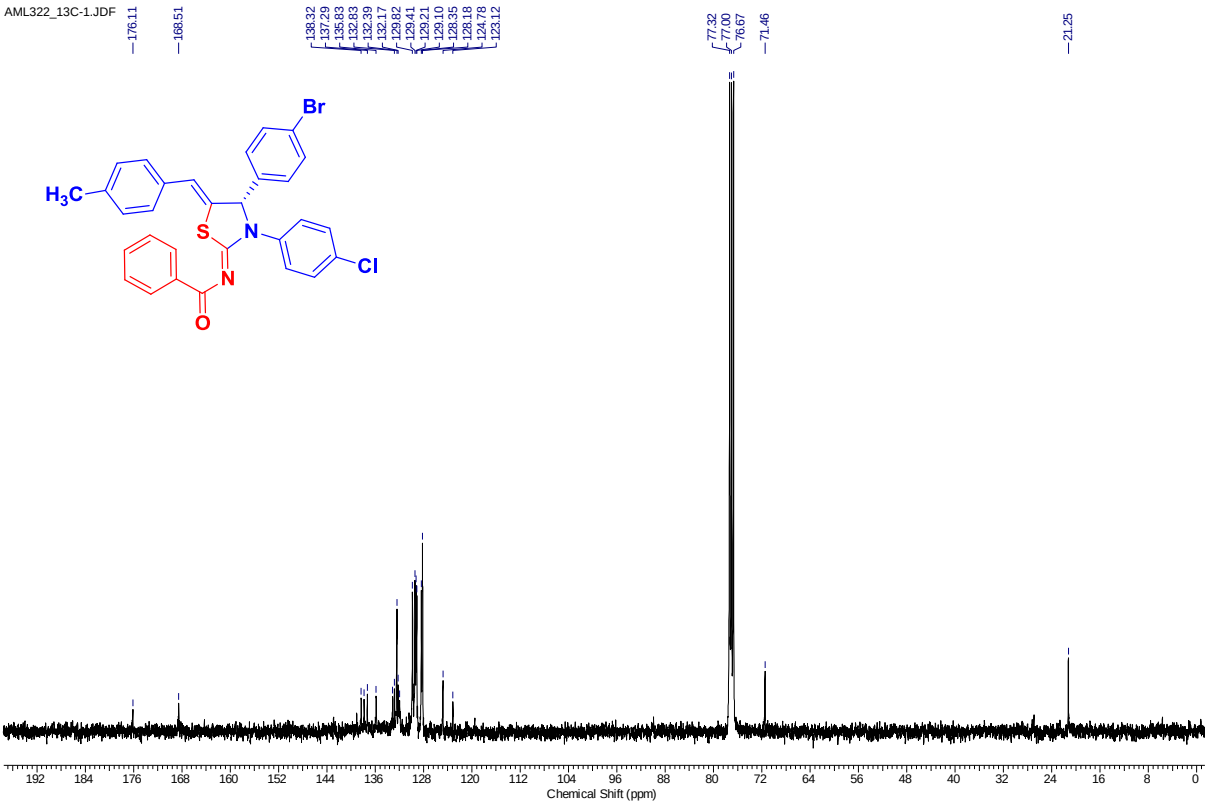

AML218_1H-8.JDF
8.12
8.11
7.44
7.42
7.40
7.39
7.37
7.35
7.34
7.22
7.20
7.15
6.37
5.89
2.34
Br
S
N
N
O
CH3
2.03
9.57
3.25
4.03
1.04
1.11
3.32
Chemical Shift (ppm)

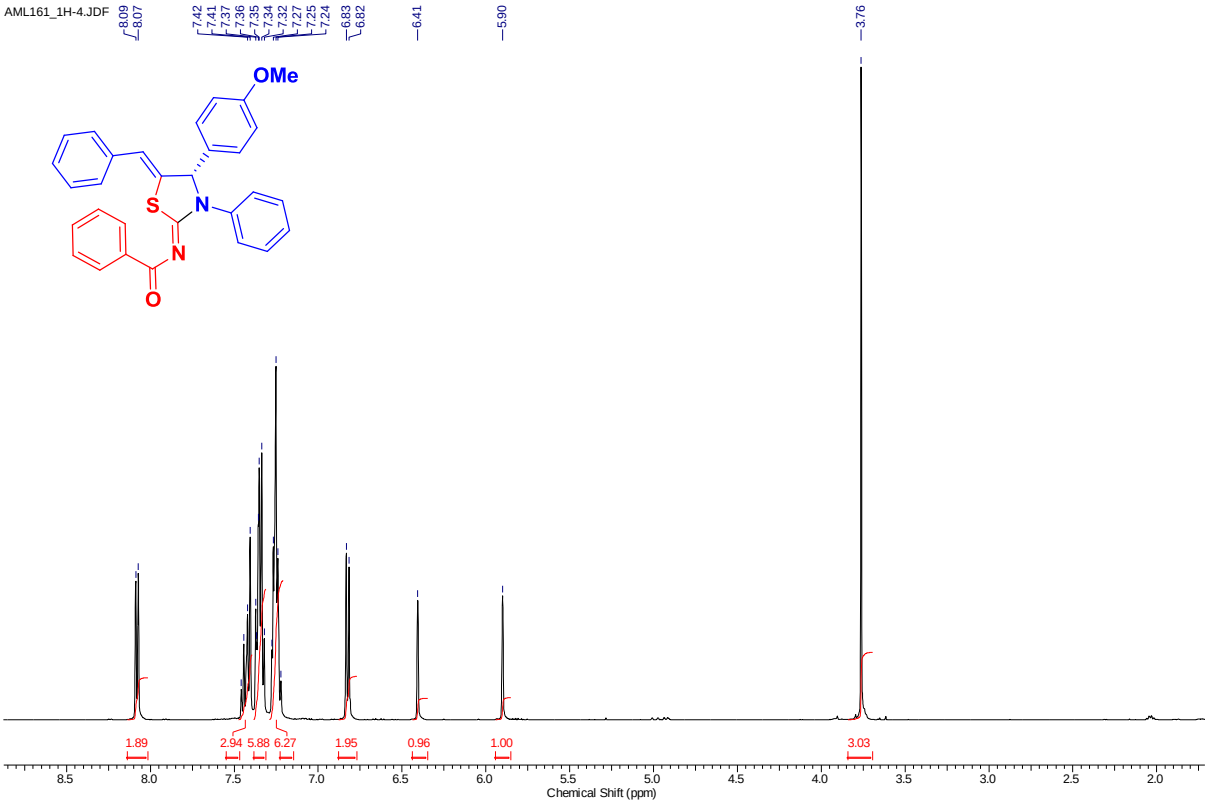

AML218_13C-2.JDF
176.14
168.16
138.57
134.54
132.23
132.17
129.80
129.59
129.09
128.62
128.34
128.02
127.56
126.51
124.36
77.26
77.00
76.75
71.67
21.11
Br
S
N
N
O
CH3
Chemical Shift (ppm)

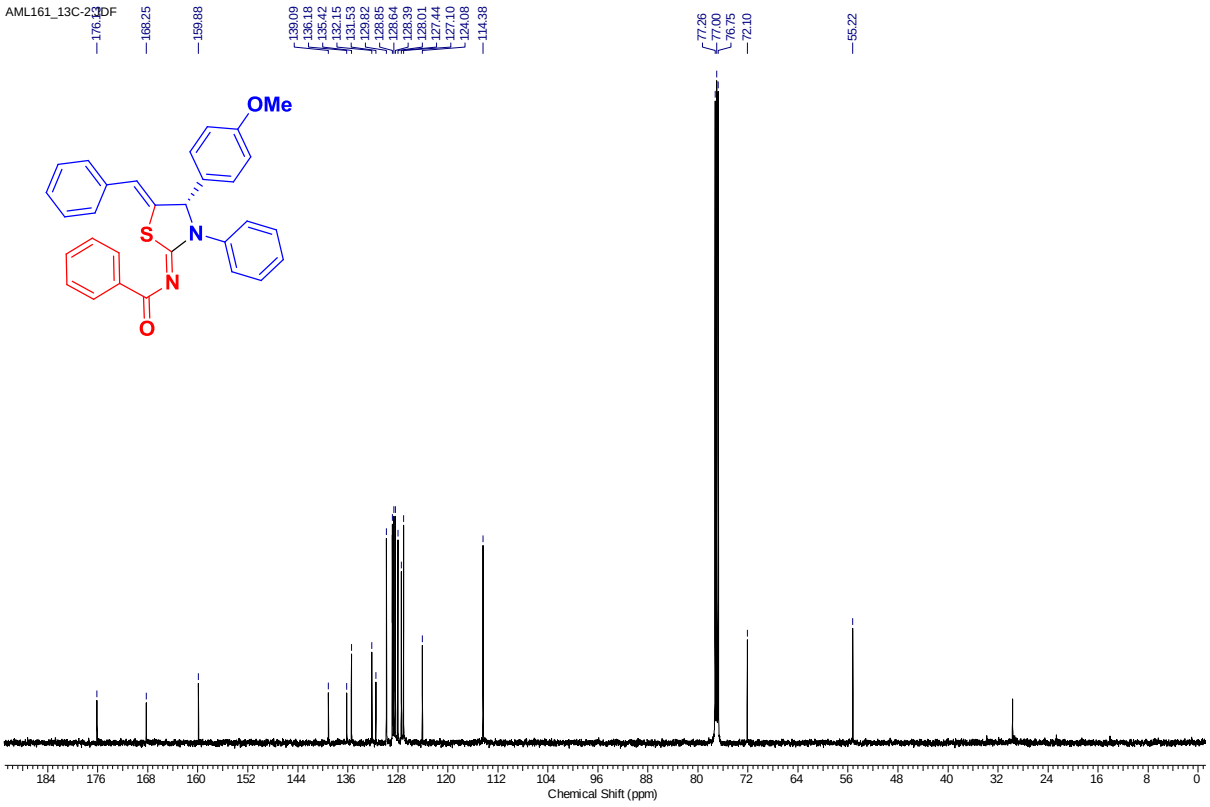

AML217_1H-1.JDF
8.11
8.09
7.45
7.43
7.39
7.37
7.35
7.28
7.28
7.27
7.23
7.21
6.38
5.93
Br
S
N
N
O
1.88
10.90
5.82
0.95
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical Shift (ppm)

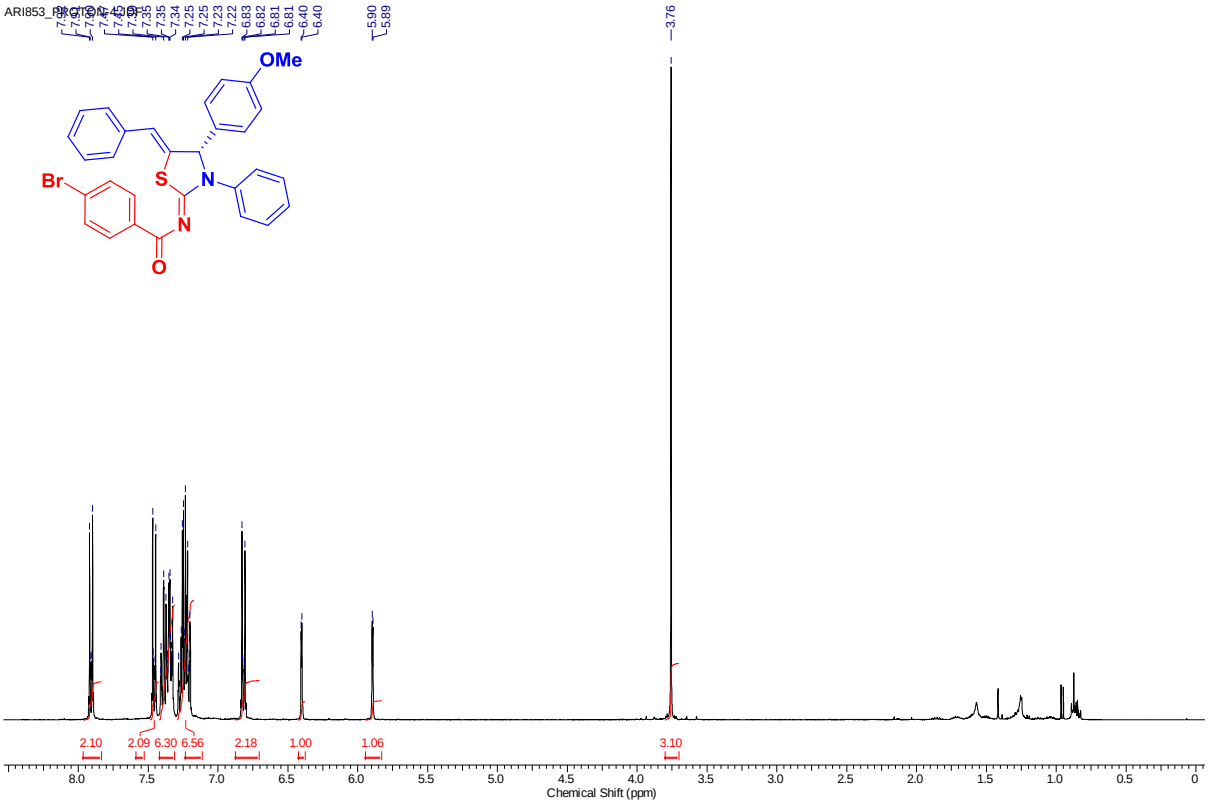

AML217_13C-2.JDF
176.10
168.24
138.46
135.06
134.47
132.21
129.79
129.09
128.97
128.64
128.35
128.04
127.61
127.57
126.84
124.48
122.91
77.26
77.00
76.75
71.60
Br
S
N
N
O
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
Chemical Shift (ppm)

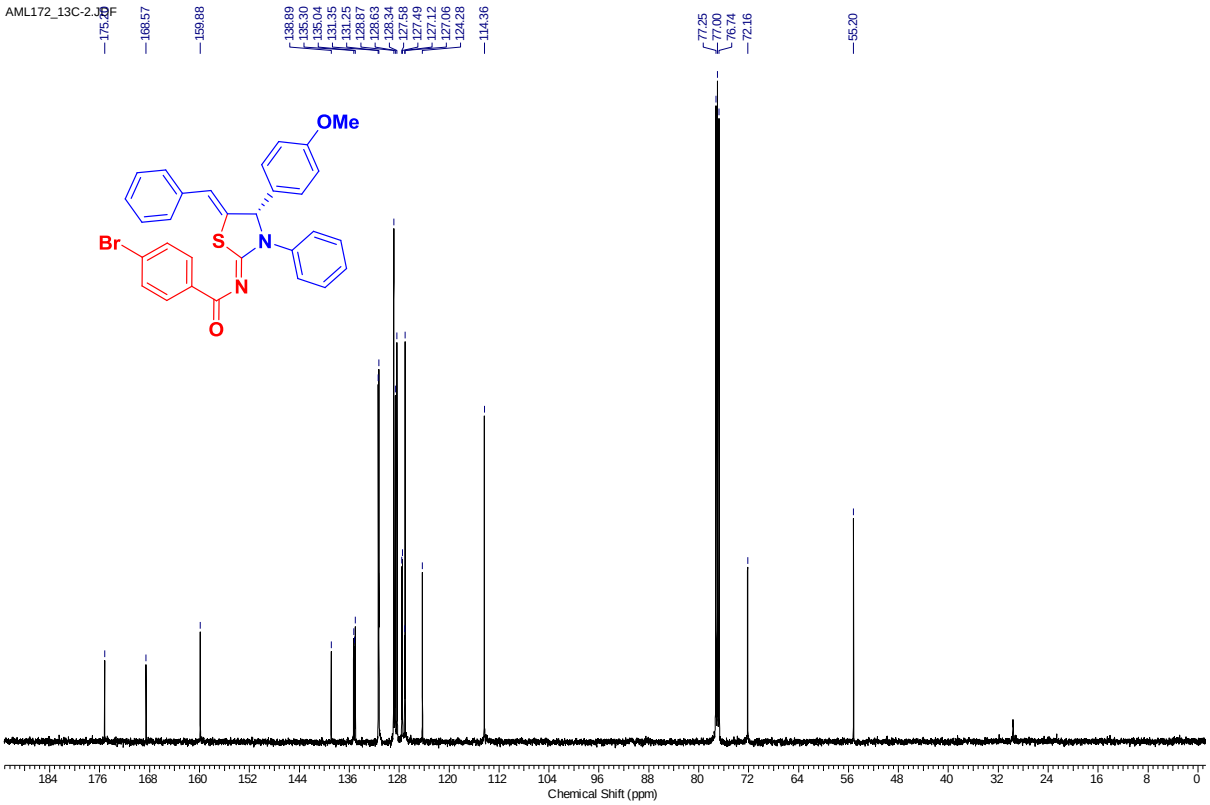

AML322_1H-4.JDF
8.08
8.06
7.46
7.44
7.36
7.34
7.32
7.25
7.22
7.21
7.20
7.19
6.34
6.34
5.86
2.33
Br
H3C
S
N
Cl
N
O
1.84
2.69
4.04
2.04
5.93
0.94
1.00
2.97
Chemical Shift (ppm)

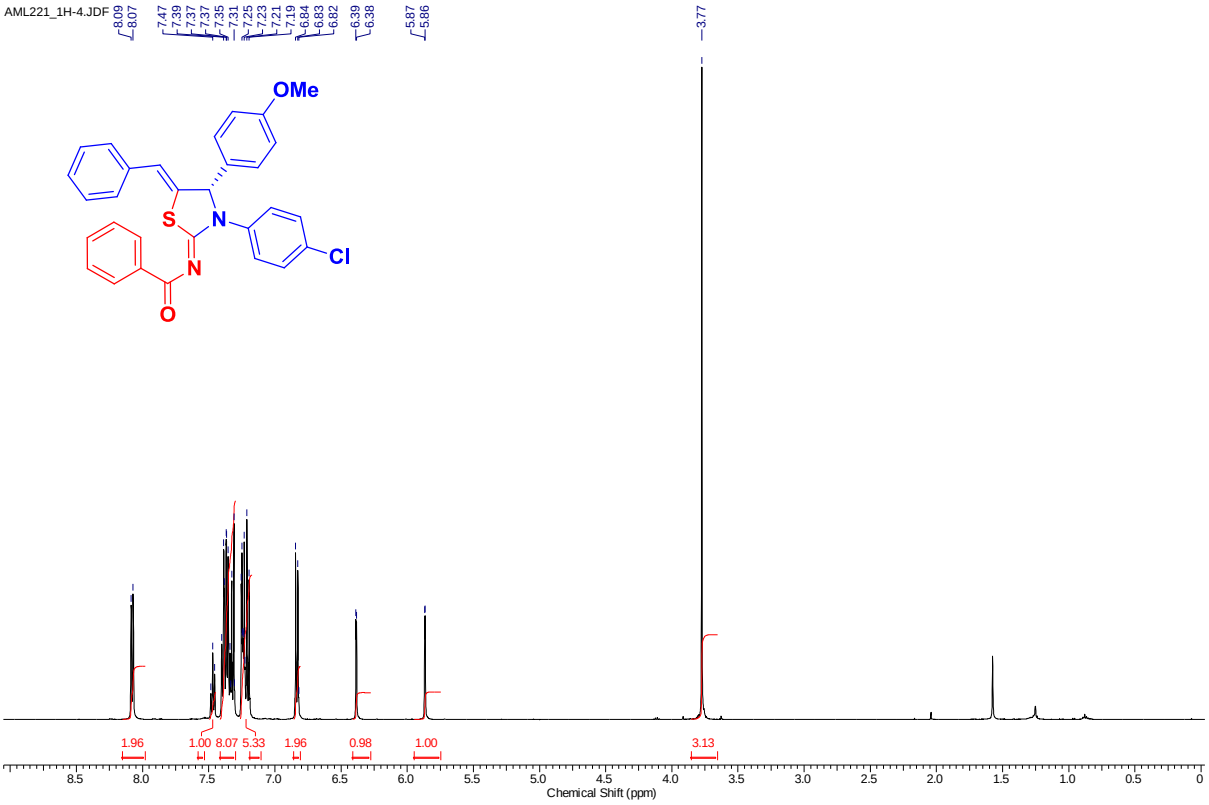

AML322_13C-1.JDF
176.11
168.51
138.32
137.29
135.83
132.83
132.39
132.17
129.82
129.41
129.21
129.10
128.35
128.18
124.78
123.12
77.32
77.00
76.67
71.46
21.25
Br
H3C
S
N
Cl
N
O
Chemical Shift (ppm)

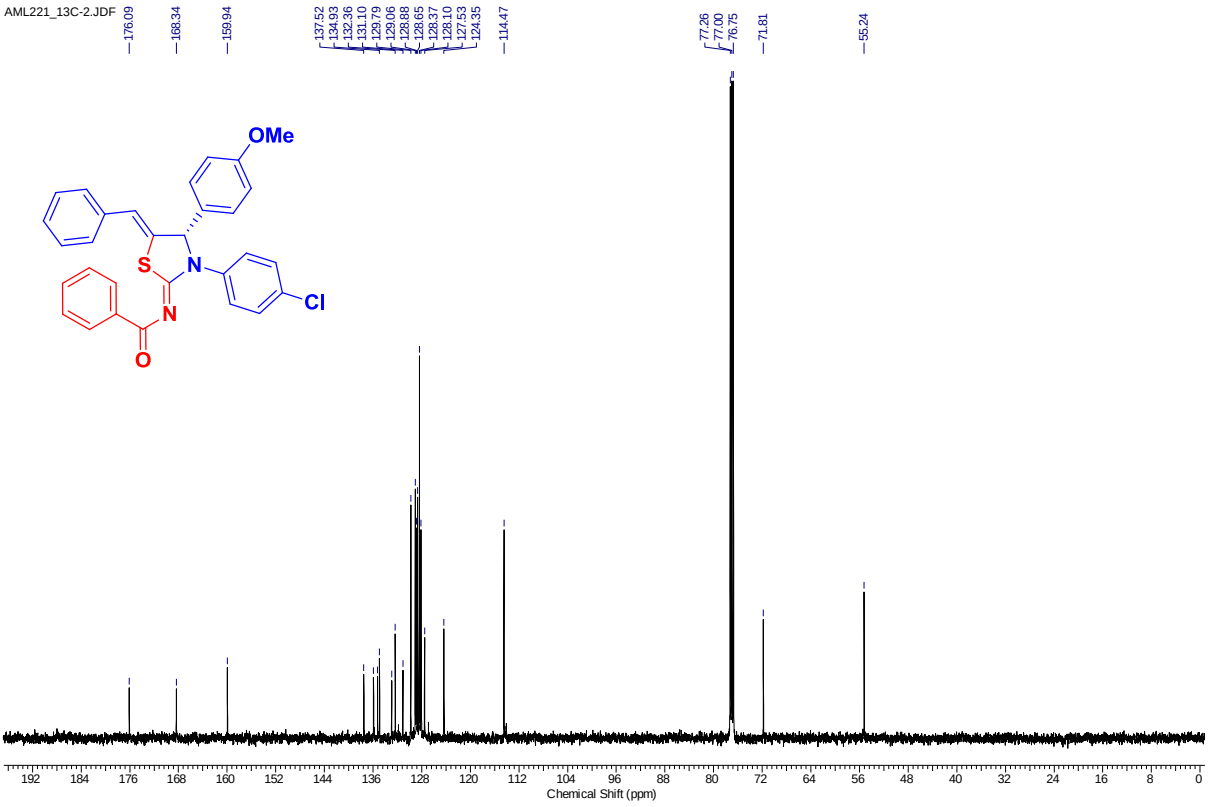

AML161_1H-4.JDF
8.09
8.07
7.42
7.41
7.37
7.36
7.35
7.34
7.32
7.27
7.25
7.24
6.83
6.82
6.41
5.90
3.76
OMe
S
N
N
O
1.89
2.94
5.88
6.27
1.95
0.96
1.00
3.03
Chemical Shift (ppm)

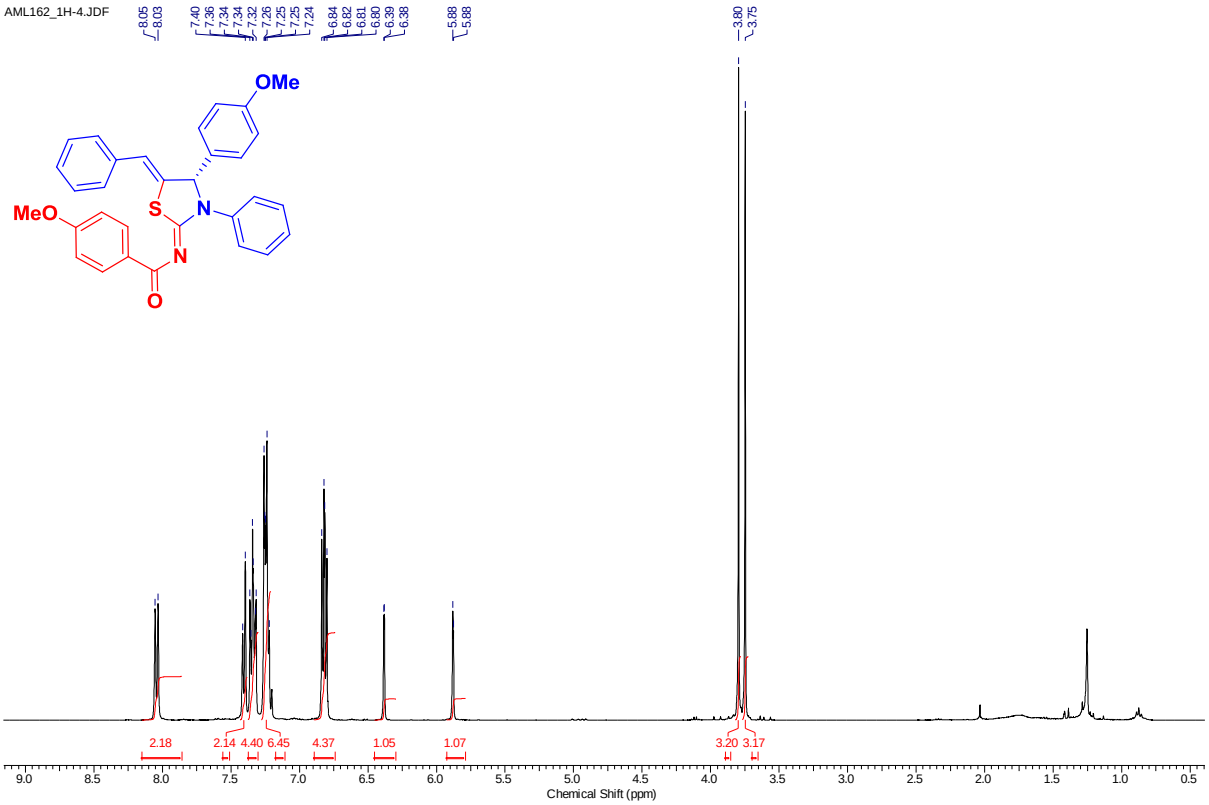

AML161_13C-2.JDF
176.21
168.25
159.88
139.09
136.18
135.42
132.15
131.53
129.82
128.85
128.64
128.39
128.01
127.44
127.10
124.08
114.38
77.26
77.00
76.75
72.10
55.22
OMe
S
N
N
O
Chemical Shift (ppm)

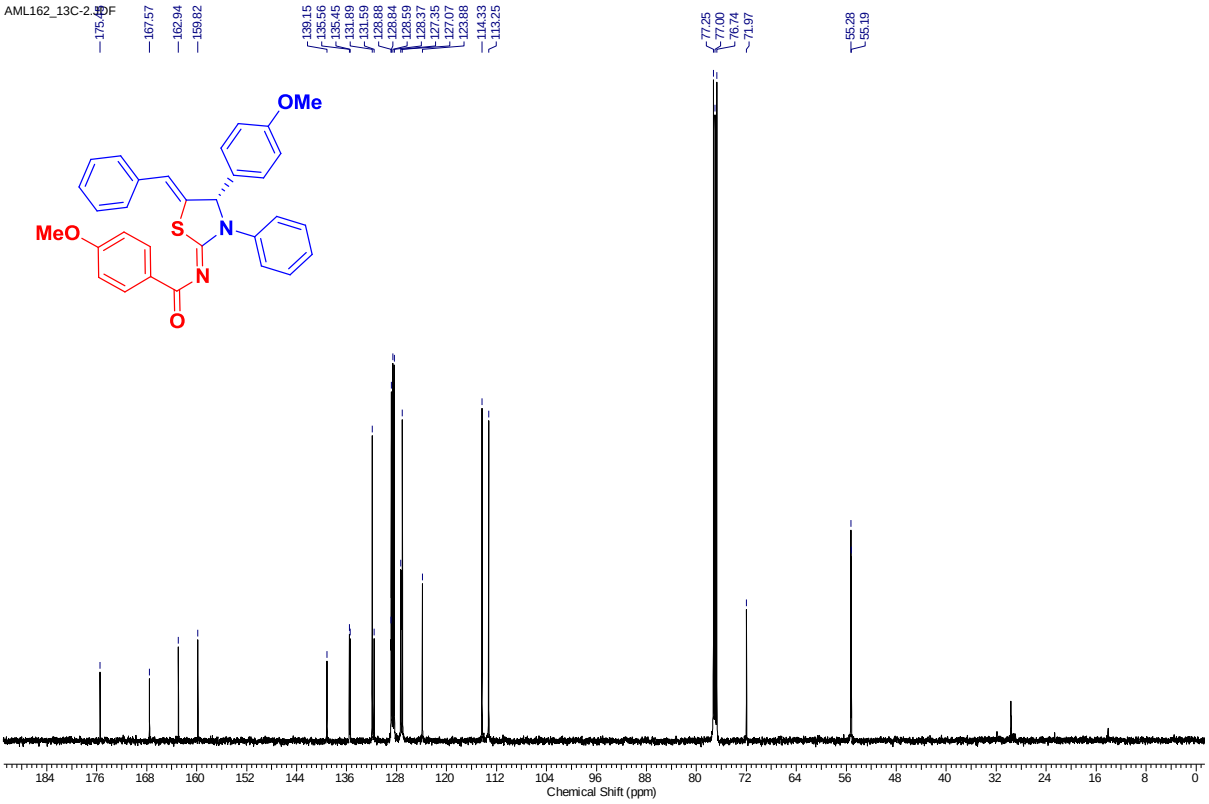

OMe
Br
S
N
N
O
3.76
5.90
5.89
2.10
2.09
6.30
6.56
2.18
1.00
1.06
3.10
Chemical Shift (ppm)

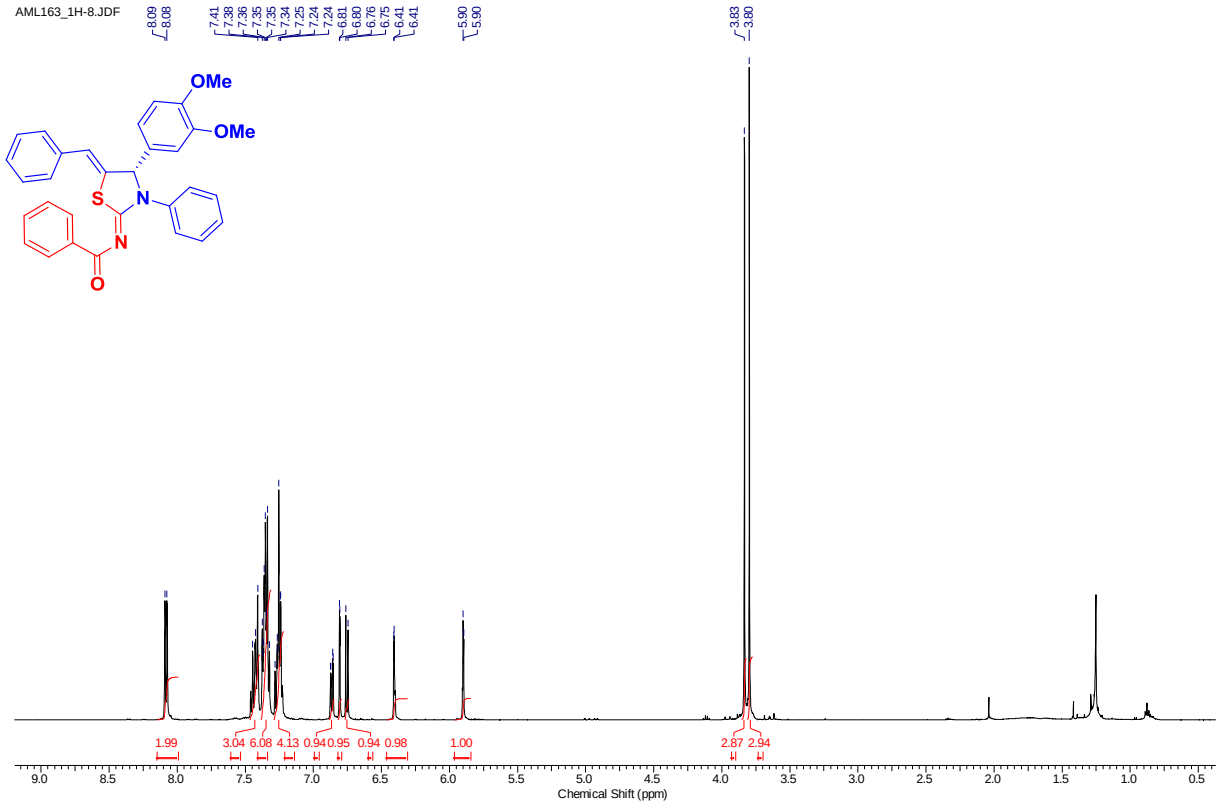

OMe
Br
S
N
N
O
175.32
168.57
159.88
138.89
135.30
135.04
131.35
131.25
128.87
128.63
128.34
127.58
127.49
127.12
127.06
124.28
114.36
77.25
77.00
76.74
72.16
55.20
Chemical Shift (ppm)

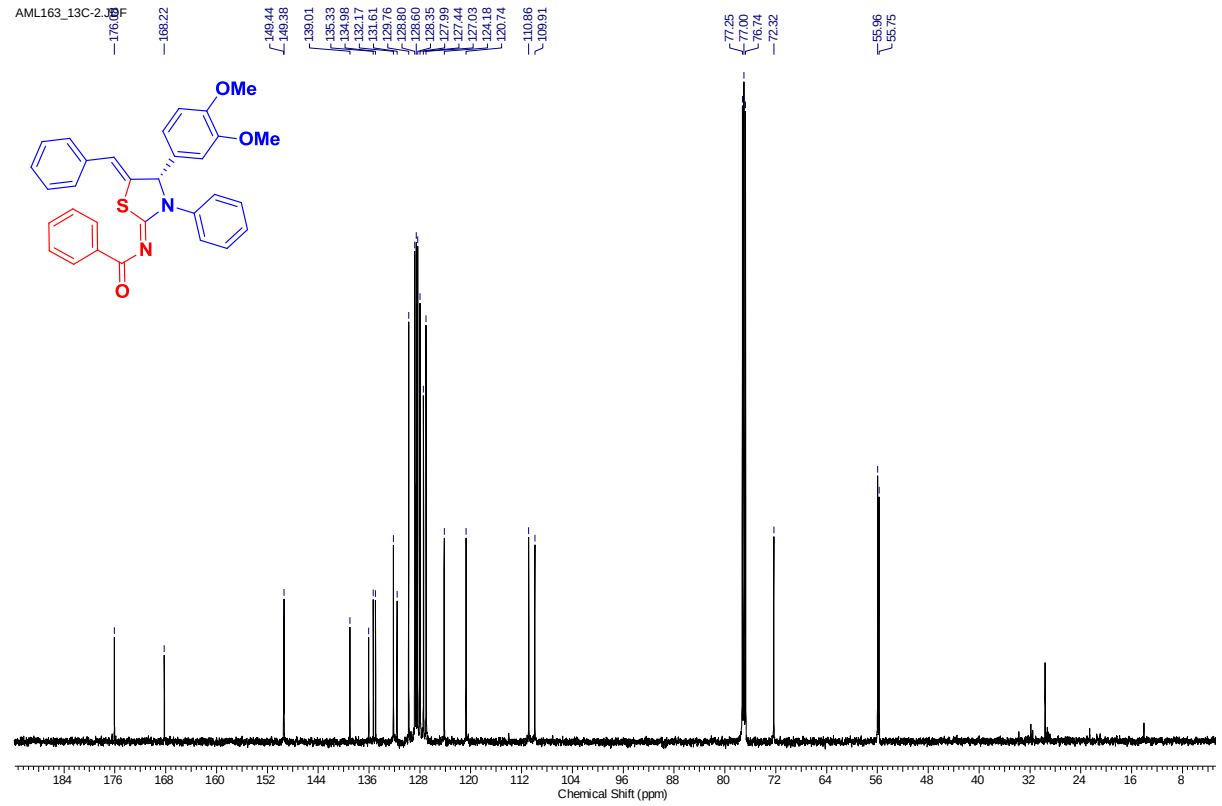

AML221_1H-4.JDF
8.09
8.07
7.47
7.39
7.37
7.37
7.35
7.31
7.25
7.23
7.21
7.19
6.84
6.83
6.82
6.39
6.38
5.87
5.86
3.77
OMe
S
N
N
Cl
O
1.96
1.00
8.07
5.33
1.96
0.98
1.00
3.13
Chemical Shift (ppm)

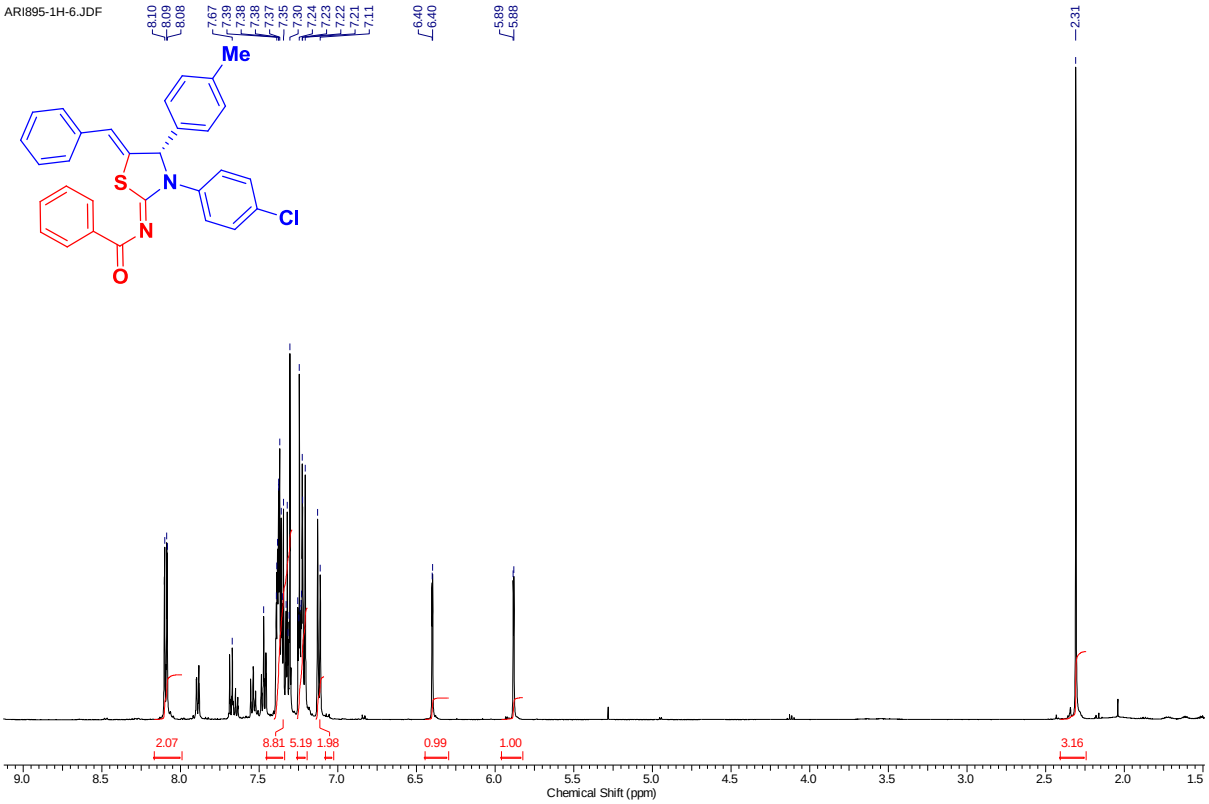

AML221_13C-2.JDF
176.09
168.34
159.94
137.52
134.93
132.36
131.10
129.79
129.06
128.88
128.65
128.37
128.10
127.53
124.35
114.47
77.26
77.00
76.75
71.81
55.24
OMe
S
N
N
Cl
O
Chemical Shift (ppm)

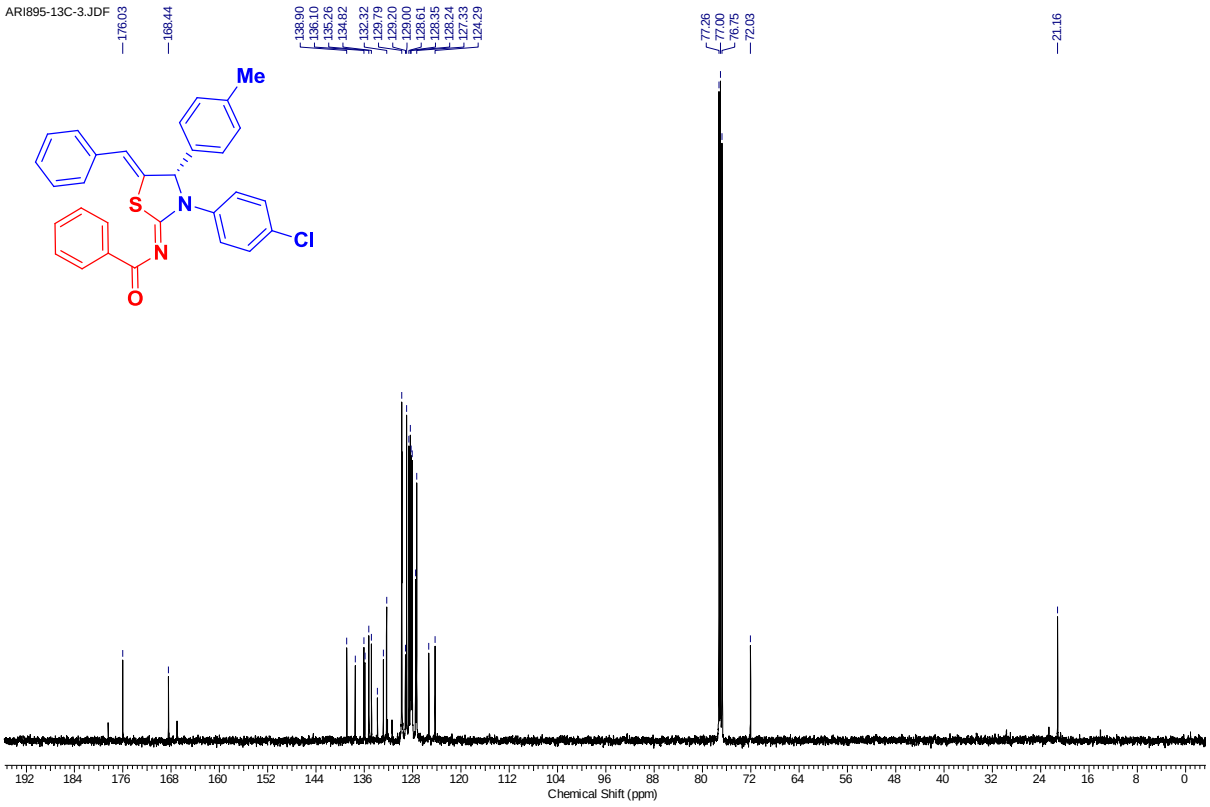

AML162_1H-4.JDF
8.05
8.03
7.40
7.36
7.34
7.34
7.32
7.26
7.25
7.25
7.24
6.84
6.82
6.81
6.80
6.39
6.38
5.88
5.88
3.80
3.75
OMe
MeO
S
N
N
O
2.18
2.14
4.40
6.45
4.37
1.05
1.07
3.20
3.17
Chemical Shift (ppm)


AML162_13C-2.JDF
175.48
167.57
162.94
159.82
139.15
135.56
135.45
131.89
131.59
128.88
128.84
128.59
128.37
127.35
127.07
123.88
114.33
113.25
77.25
77.00
76.74
71.97
55.28
55.19
OMe
MeO
S
N
N
O
Chemical Shift (ppm)


AML163_1H-8.JDF
OMe
OMe
S
N
N
O
Chemical Shift (ppm)


OMe
OMe
S
N
N
O
Chemical Shift (ppm)


ARI895-1H-6.JDF
8.10
8.09
8.08
7.67
7.39
7.38
7.38
7.37
7.35
7.30
7.24
7.23
7.22
7.21
7.11
6.40
6.40
5.89
5.88
2.31
Me
S
N
Cl
N
O
2.07
8.81
5.19
1.98
0.99
1.00
3.16
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
Chemical Shift (ppm)


ARI895-13C-3.JDF
176.03
168.44
138.90
136.10
135.26
134.62
132.32
129.79
129.20
129.00
128.61
128.35
128.24
127.33
124.29
77.26
77.00
76.75
72.03
21.16
Me
S
N
Cl
N
O
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
8
0
Chemical Shift (ppm)

Compound 4a

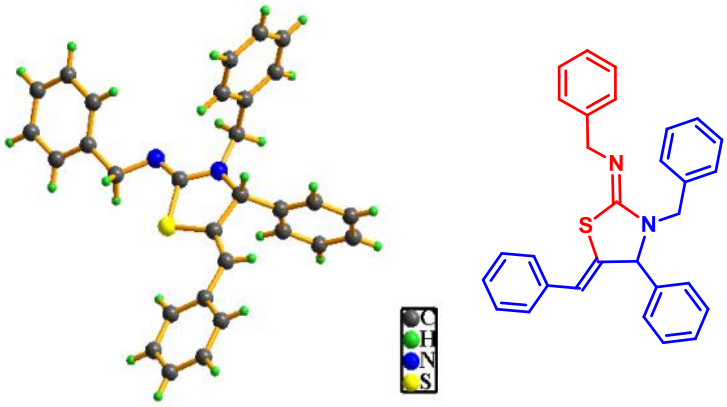


Table 1 Crystal data and structure refinement for **4a**

Identification code	10nova	
Empirical formula	$C_{30}H_{25}N_2S$	
Formula weight	445.58	
Temperature	293(2) K	
Wavelength	0.71073 A	
Unit cell dimensions	a = 19.059(5) A	α = 90°.
	b = 5.6470(14) A	β = 93.669(8)°.
	c = 42.733(11) A	γ = 90°.
Volume	4590(2) A^3	
Z, Calculated density	8, 1.290 Mg/m^3	
Absorption coefficient	0.162 mm^-1	
F(000)	1880	
Theta range for data collection	0.95 to 28.36 deg.	
Limiting indices	-18<=h<=24, -7<=k<=7, -54<=l<=48	
Reflections collected / unique	13660 / 5329 [R(int) = 0.0458]	
Completeness to theta = 28.36	92.6 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5329 / 0 / 298	
Goodness-of-fit on F^2	1.107	
Final R indices [I>2sigma(I)]	R1 = 0.0657, wR2 = 0.1690	
R indices (all data)	R1 = 0.0999, wR2 = 0.2344	
Largest diff. peak and hole	0.931 and -0.456 e.A^-3	

Compound 16l

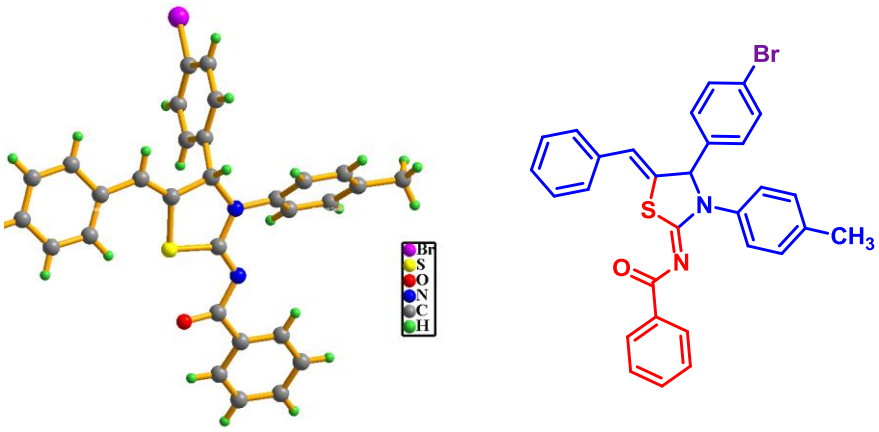
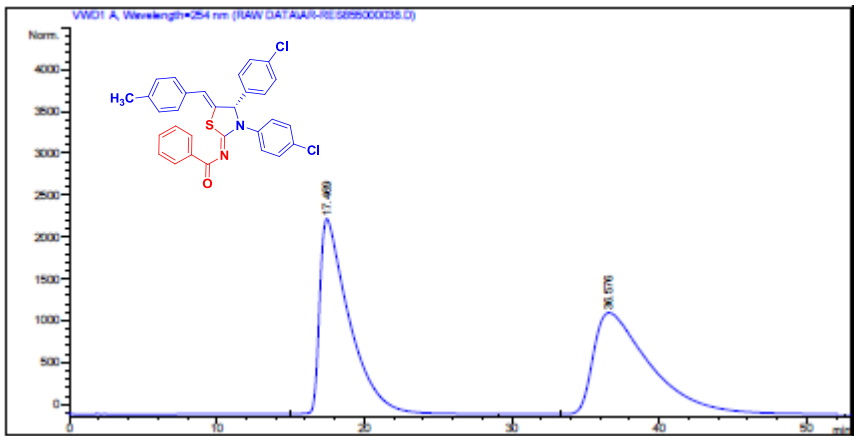


Table 2 Crystal data and structure refinement for **16l**

Empirical formula	$C_{30}H_{23}BrN_2OS$
Formula weight	539.47
Temperature/K	173(2)
Crystal system	triclinic
Space group	P1
a/Å	9.724(5)
b/Å	11.581(5)
c/Å	11.774(5)
α/°	75.443(5)
β/°	87.986(5)
γ/°	89.040(5)
Volume/Å^3	1282.5(10)
Z	2
ρ_{calc}mg/mm^3	1.397
m/mm^{-1}	1.710
F(000)	552.0
Crystal size/mm^3	0.21 × 0.18 × 0.16
2Θ range for data collection	4.192 to 50.998°
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -14 ≤ l ≤ 14
Reflections collected	13366
Independent reflections	9327[R(int) = 0.0578]
Data/restraints/parameters	9327/9/611
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0884, wR_2 = 0.1450
Final R indexes [all data]	R_1 = 0.1707, wR_2 = 0.1736
Largest diff. peak/hole / e Å^{-3}	0.85/-0.54
Flack parameter	0.108(9)

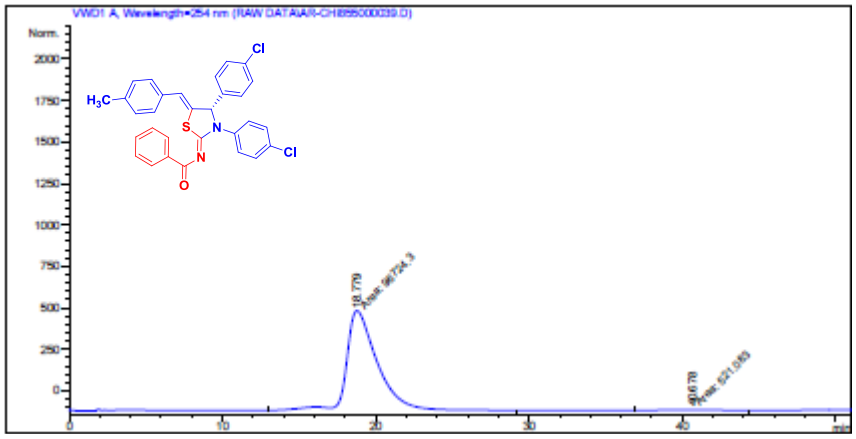
HPLC DATA of CHIRAL COMPOUNDS

(*Z*)-*N*-((*S*,*Z*)-3,4-bis(4-chlorophenyl)-5-(4-methylbenzylidene)thiazolidin-2-ylidene) benzamide (16a):



Signal 1: VWD1 A, Wavelength=254 nm

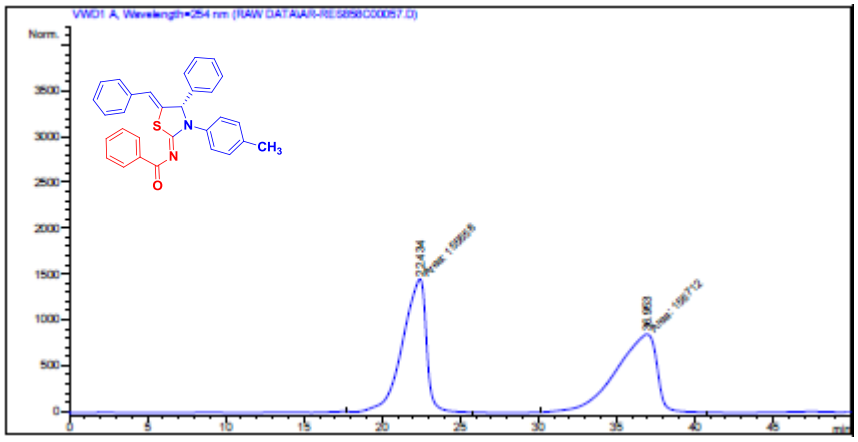
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.469	VB	1.9354	3.23857e5	2335.19214	50.1056
2	36.576	BB	3.4756	3.22492e5	1211.42871	49.8944



Signal 1: VWD1 A, Wavelength=254 nm

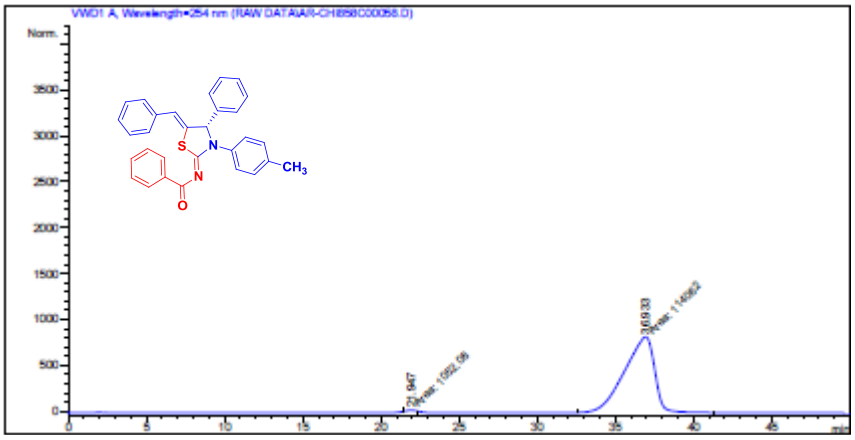
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.779	MM	2.6320	9.67243e4	612.48083	99.4642
2	40.678	MM	0.0000	521.08337	4.96181	0.5358

(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-4-phenyl-3-p-tolylthiazolidin-2-ylidene)benzamide (16b):



Signal 1: VWD1 A, Wavelength=254 nm

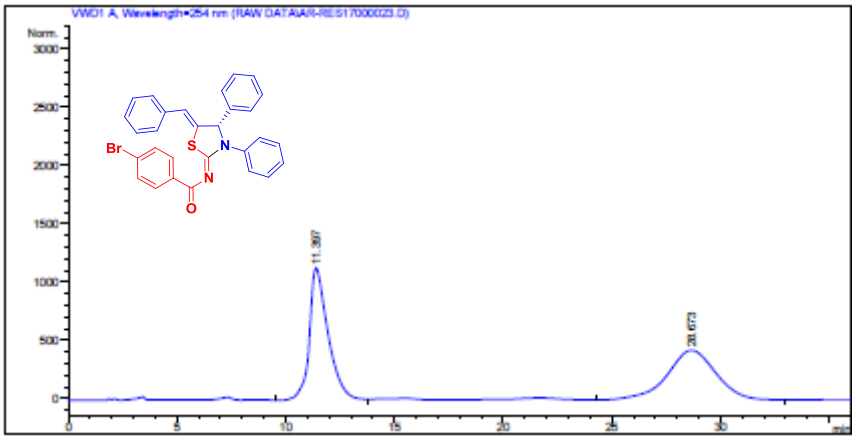
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.434	MM	1.7765	1.55658e5	1460.32056	49.8312
2	36.953	MM	3.0446	1.56712e5	857.85571	50.1688



Signal 1: VWD1 A, Wavelength=254 nm

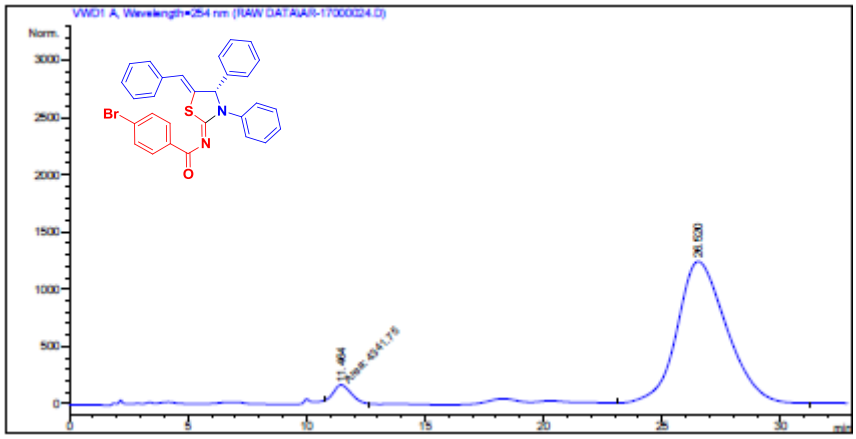
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.947	MM	0.7350	1052.08057	23.85522	0.9139
2	36.933	MM	2.2871	1.14062e5	831.21075	99.0861

(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-3,4-diphenylthiazolidin-2-ylidene)-4-bromobenzamide (16c)



Signal 1: VWD1 A, Wavelength=254 nm

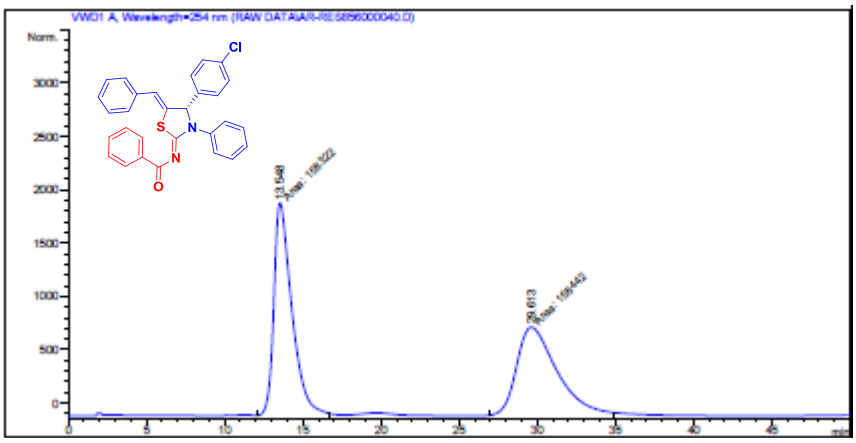
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.397	VV	0.8721	6.83999e4	1137.22961	50.0482
2	28.673	VB	2.3881	6.82681e4	428.97061	49.9518



Signal 1: VWD1 A, Wavelength=254 nm

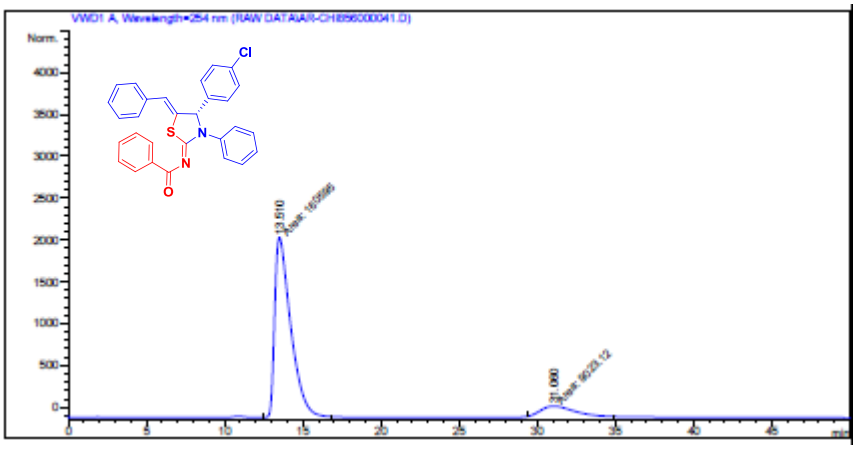
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.464	MM	0.6377	4341.75244	113.48058	2.2543
2	26.520	VB	2.1815	1.88253e5	1256.71179	97.7457

(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-4-(4-chlorophenyl)-3-phenylthiazolidin-2-ylidene)benzami de (16d):



Signal 1: VWD1 A, Wavelength=254 nm

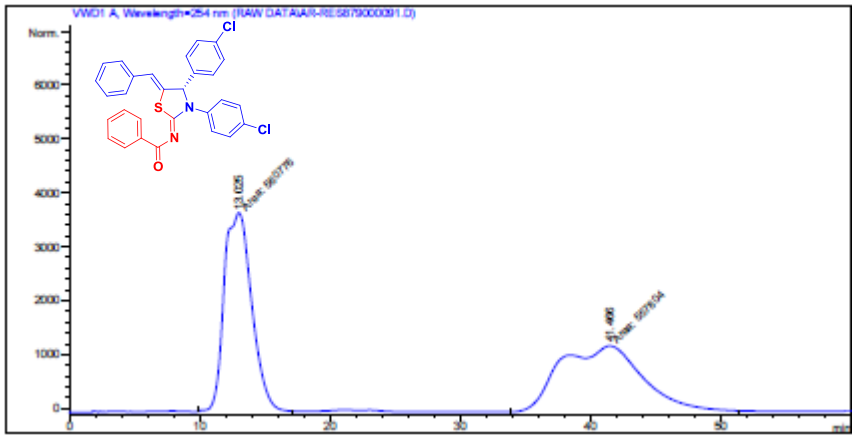
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.548	MM	1.3307	1.58322e5	1982.98108	49.9810
2	29.613	MM	3.1032	1.58442e5	850.94617	50.0190



Signal 1: VWD1 A, Wavelength=254 nm

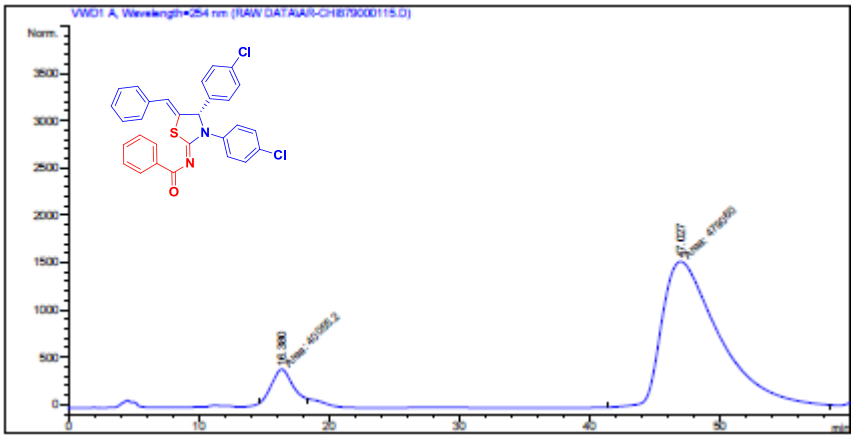
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.510	MM	1.2281	1.60595e5	2179.44482	94.6803
2	31.060	MM	1.7002	9023.11621	88.45177	5.3197

(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-3,4-bis(4-chlorophenyl)thiazolidin-2-ylidene)benzamide (16e):



Signal 1: VWD1 A, Wavelength=254 nm

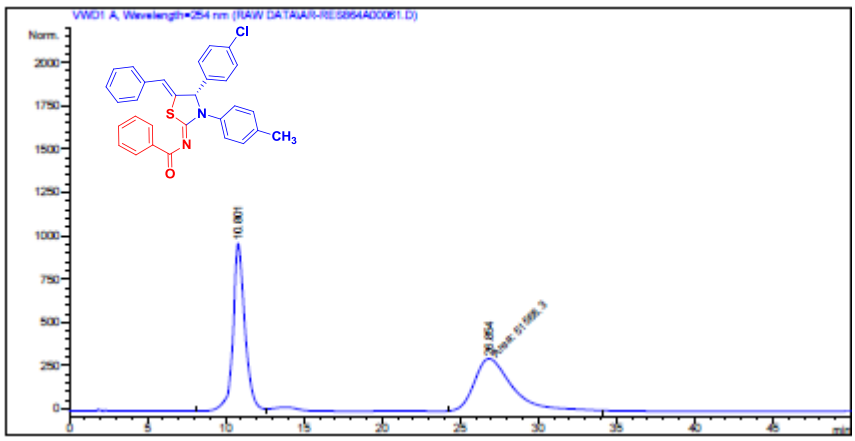
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.025	MM	2.5029	5.60776e5	3734.19775	50.1329
2	41.466	MM	7.5111	5.57804e5	1237.73401	49.8671



Signal 1: VWD1 A, Wavelength=254 nm

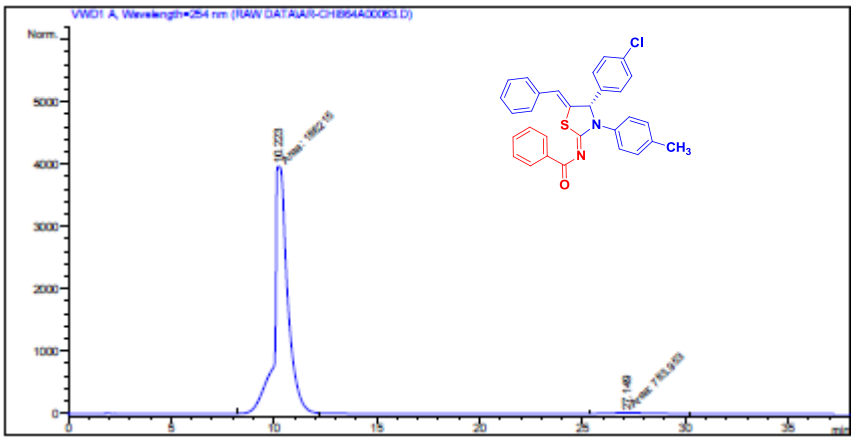
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.380	MM	1.8373	4.00552e4	363.35306	7.7161
2	47.027	MM	5.1593	4.79060e5	1547.54822	92.2839

(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-4-(4-chlorophenyl)-3-p-tolylthiazolidin-2-ylidene)benzamide (16f):



Signal 1: VWD1 A, Wavelength=254 nm

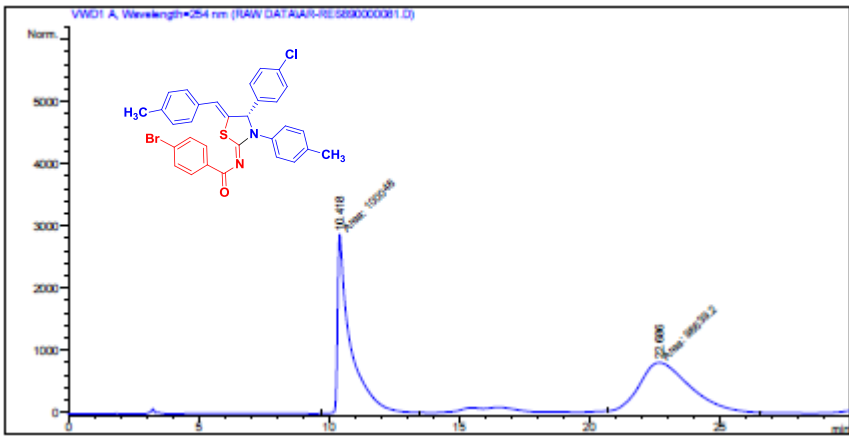
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.801	BB	0.7765	5.13874e4	965.92957	49.9122
2	26.854	MM	2.8228	5.15683e4	304.47430	50.0878



Signal 1: VWD1 A, Wavelength=254 nm

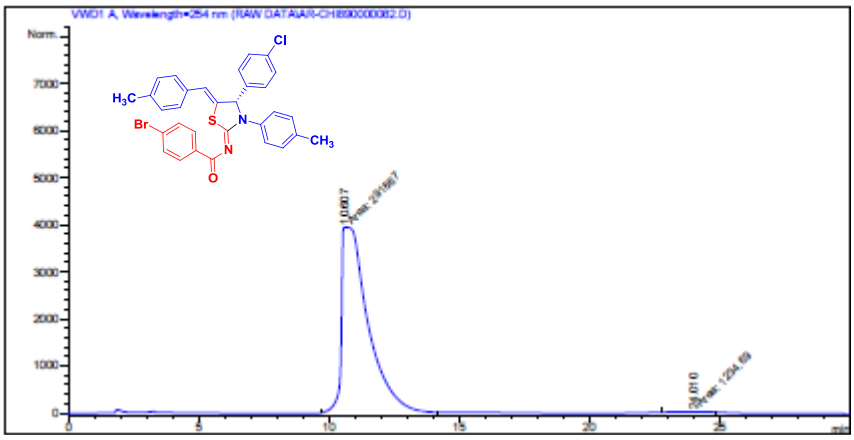
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.223	MM	0.7780	1.86215e5	3989.42676	99.5808
2	27.149	MM	1.9154	783.95264	5.06550	0.4192

(*Z*)-4-bromo-*N*-((*S*,*Z*)-4-(4-chlorophenyl)-5-(4-methylbenzylidene)-3-p-tolylthiazolidin-2-ylidene)benzamide (16g):



Signal 1: VWD1 A, Wavelength=254 nm

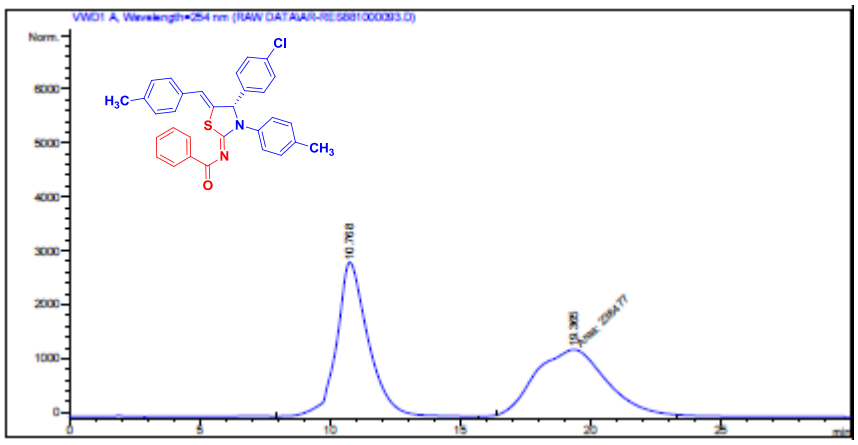
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.418	MM	0.5742	1.00048e5	2903.94824	50.3544
2	22.686	MM	2.1211	9.86392e4	775.06665	49.6456



Signal 1: VWD1 A, Wavelength=254 nm

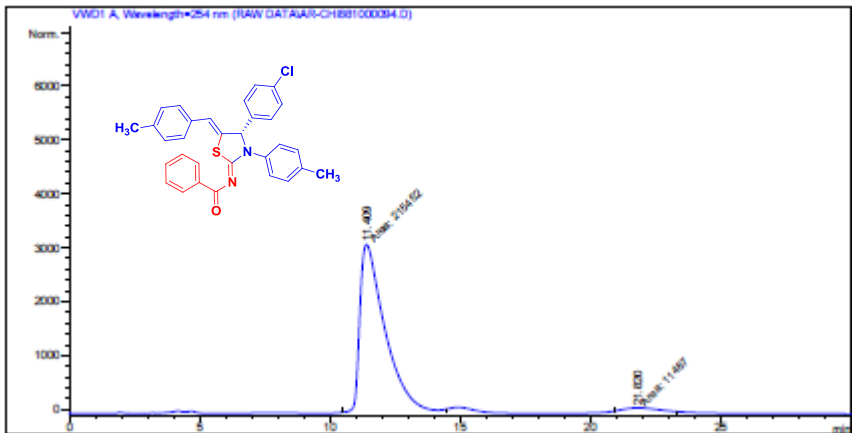
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.607	MM	1.2193	2.91867e5	3989.53418	99.5788
2	24.010	MM	1.7776	1234.68530	8.93791	0.4212

(*Z*)-*N*-((*S*,*Z*)-4-(4-chlorophenyl)-5-(4-methylbenzylidene)-3-p-tolylthiazolidin-2-ylidene) benzamide (16h):



Signal 1: VWD1 A, Wavelength=254 nm

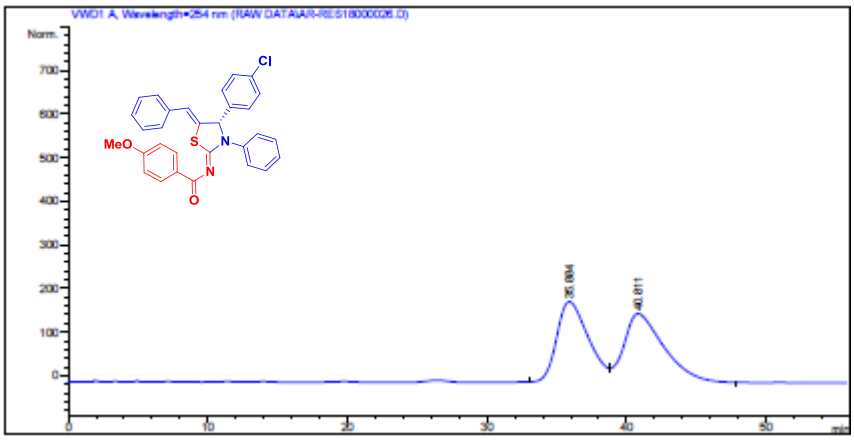
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.768	VB	1.2013	2.42816e5	2865.14746	50.4507
2	19.365	MM	3.1994	2.38477e5	1242.30542	49.5493



Signal 1: VWD1 A, Wavelength=254 nm

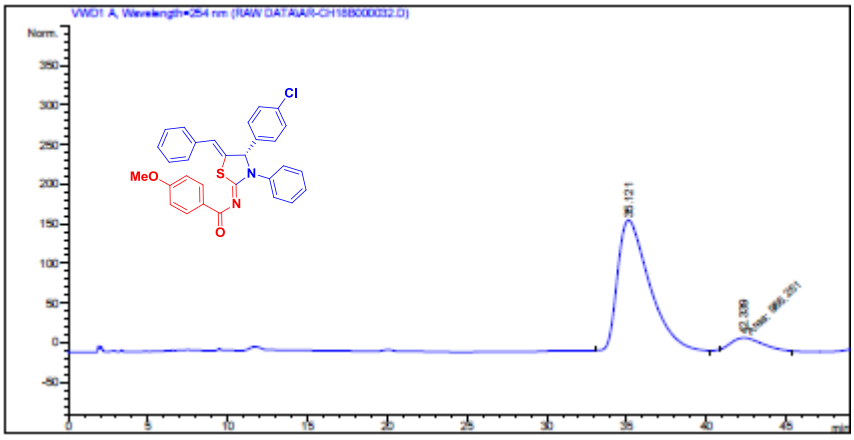
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.409	MM	1.1480	2.15452e5	3127.91357	94.9383
2	21.820	MM	1.6982	1.14870e4	112.73946	5.0617

(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-4-(4-chlorophenyl)-3-phenylthiazolidin-2-ylidene)-4-methoxy benzamide (16i):



Signal 1: VWD1 A, Wavelength=254 nm

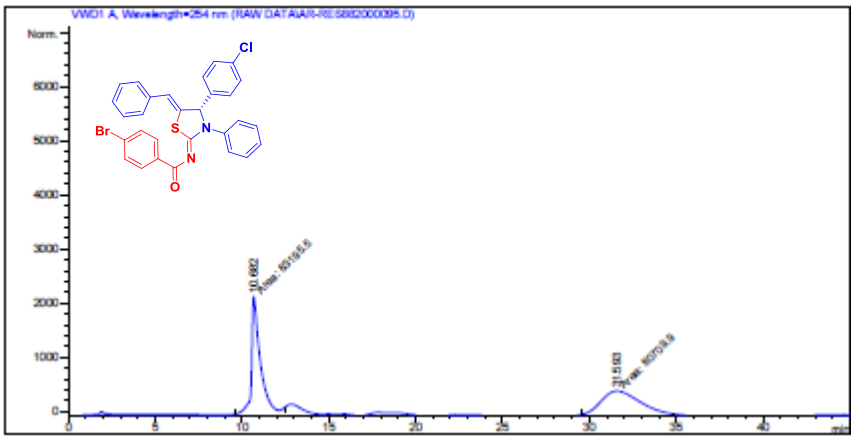
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	35.884	BV	2.2712	2.93010e4	184.88571	48.2745
2	40.811	VB	2.7671	3.13955e4	157.77046	51.7255



Signal 1: VWD1 A, Wavelength=254 nm

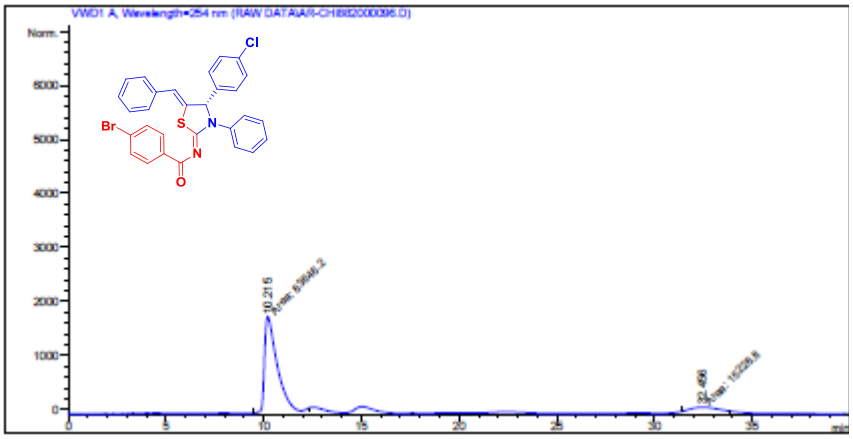
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	35.121	BB	1.9822	2.33974e4	166.29004	95.9553
2	42.339	MM	1.5933	986.25116	10.31657	4.0447

(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-4-(4-chlorophenyl)-3-phenylthiazolidin-2-ylidene)-4-bromobenzamide (16j):



Signal 1: VWD1 A, Wavelength=254 nm

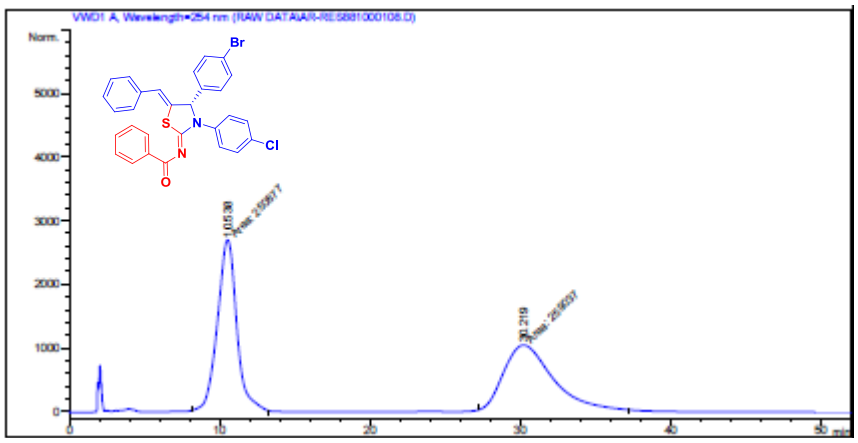
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.682	MM	0.6279	8.31955e4	2208.14551	50.7582
2	31.593	MM	2.8039	8.07099e4	479.74597	49.2418



Signal 1: VWD1 A, Wavelength=254 nm

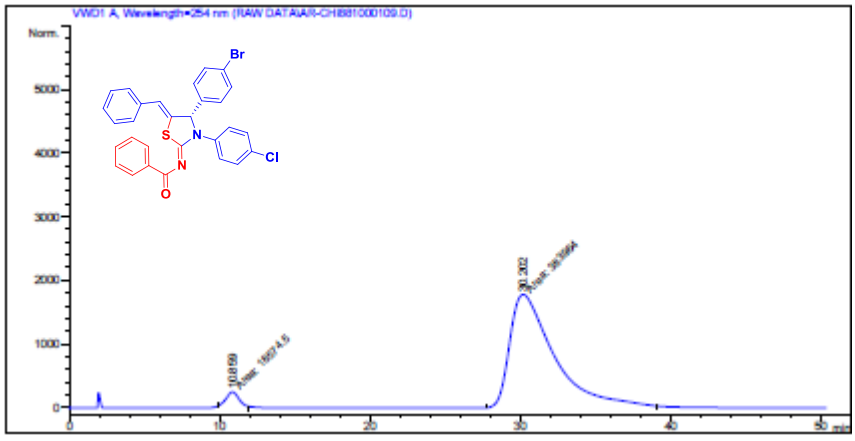
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.215	MM	0.7646	8.36462e4	1823.37805	84.5979
2	32.456	MM	1.7894	1.52288e4	141.84351	15.4021

(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-4-(4-bromophenyl)-3-(4-chlorophenyl)thiazolidin-2-ylidene)benzamide (16k):



Signal 1: VWD1 A, Wavelength=254 nm

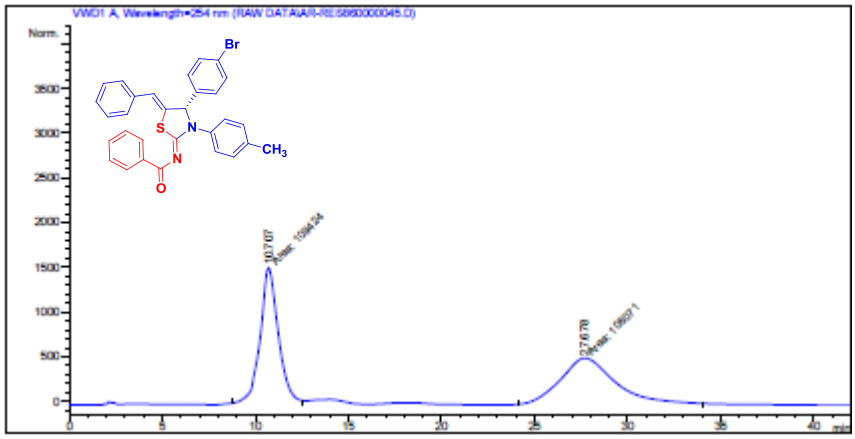
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.538	MM	1.5354	2.50877e5	2723.31909	49.1999
2	30.219	MM	4.0335	2.59037e5	1070.34619	50.8001



Signal 1: VWD1 A, Wavelength=254 nm

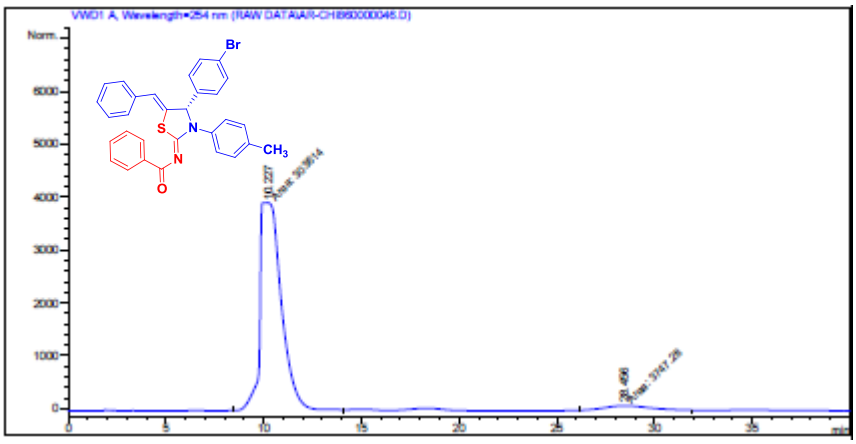
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.859	MM	1.1443	1.85745e4	270.53302	4.6143
2	30.202	MM	3.5506	3.83964e5	1802.34985	95.3857

(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-4-(4-bromophenyl)-3-p-tolylthiazolidin-2-ylidene)benzami de (16l):



Signal 1: VWD1 A, Wavelength=254 nm

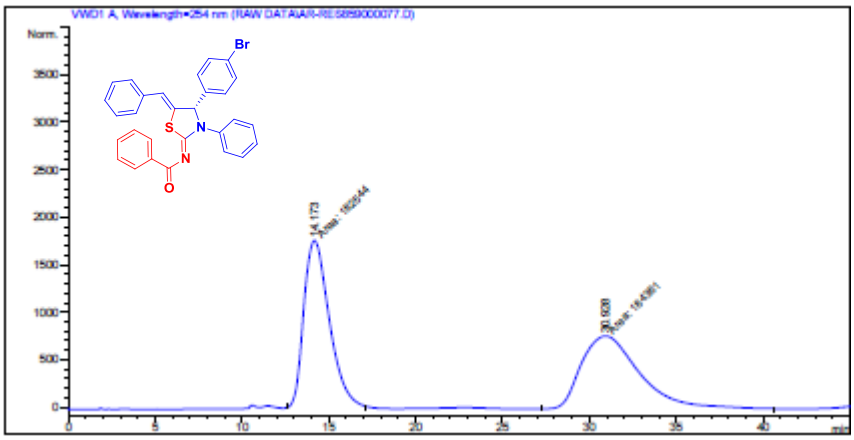
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.707	MM	1.1817	1.09424e5	1543.25000	50.3109
2	27.678	MM	3.4301	1.08071e5	525.11884	49.6891



Signal 1: VWD1 A, Wavelength=254 nm

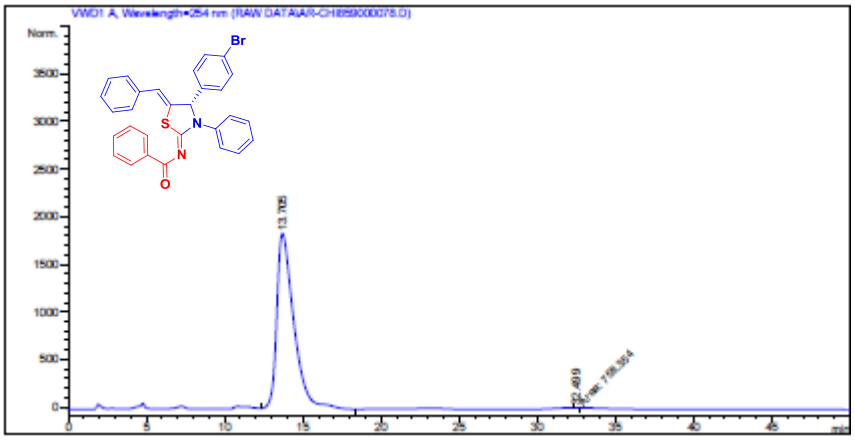
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.227	MM	1.2822	3.03614e5	3946.53027	98.7808
2	28.456	MM	1.4696	3747.28345	42.49862	1.2192

(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-4-(4-bromophenyl)-3-phenylthiazolidin-2-ylidene)benzamide (16m):



Signal 1: VWD1 A, Wavelength=254 nm

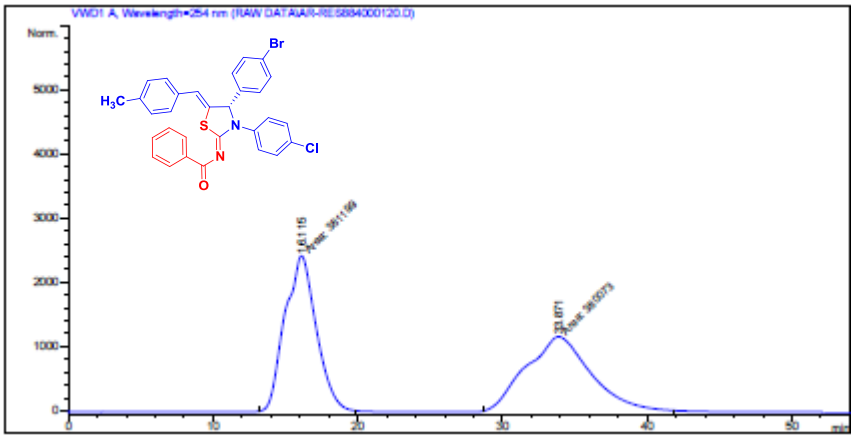
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.173	MM	1.7125	1.82544e5	1776.53760	49.7523
2	30.928	MM	3.9574	1.84361e5	776.44305	50.2477



Signal 1: VWD1 A, Wavelength=254 nm

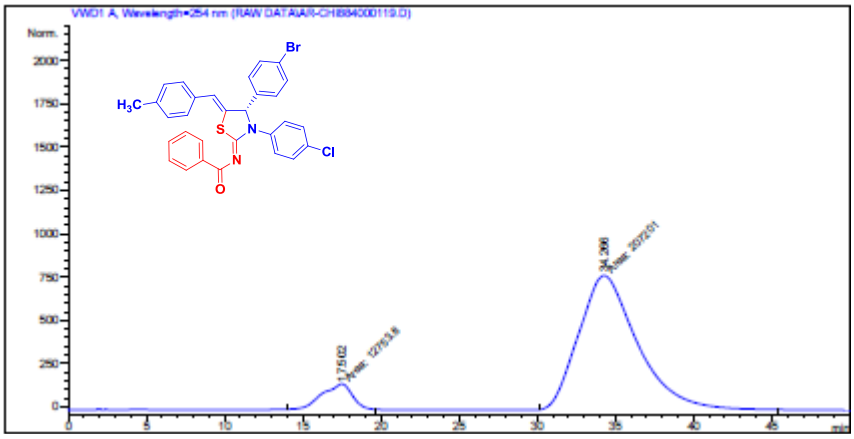
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.705	VB	1.1154	1.39881e5	1843.19946	99.4608
2	32.499	MM	0.4748	758.35431	26.61832	0.5392

(*Z*)-*N*-((*S*,*Z*)-4-(4-bromophenyl)-3-(4-chlorophenyl)-5-(4-methylbenzylidene) thiazolidin-2-ylidene)benzamide (16n):



Signal 1: VWD1 A, Wavelength=254 nm

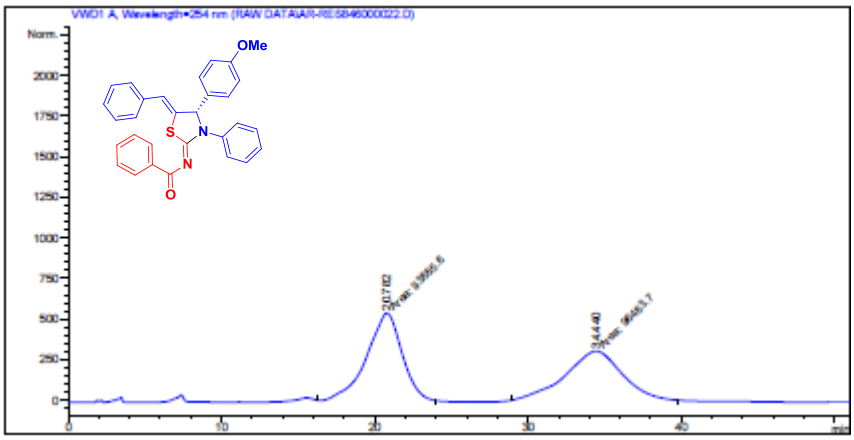
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.115	MM	2.5780	3.81199e5	2464.39111	50.0740
2	33.871	MM	5.3640	3.80073e5	1180.93384	49.9260



Signal 1: VWD1 A, Wavelength=254 nm

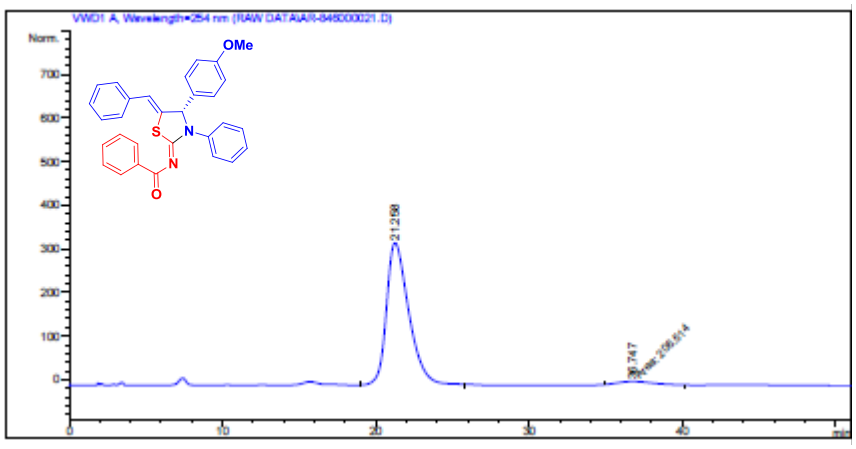
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.502	MM	1.8438	1.27538e4	115.28410	5.7984
2	34.266	MM	4.4326	2.07201e5	779.07678	94.2016

(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-4-(4-methoxyphenyl)-3-phenylthiazolidin-2-ylidene)benzamide (16o):



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.782	MM	2.8101	9.38856e4	556.84326	49.3176
2	34.440	MM	4.8456	9.64837e4	331.86261	50.6824

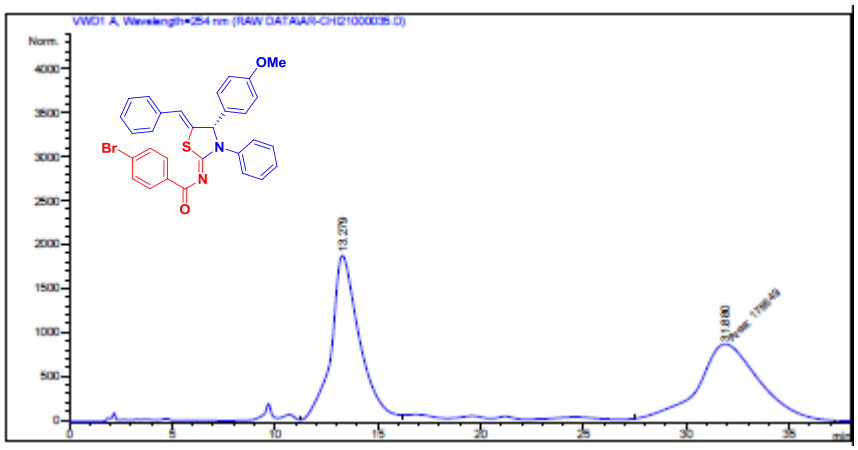


Signal 1: VWD1 A, Wavelength=254 nm

Signal 1: VWD1 A, Wavelength=254 nm

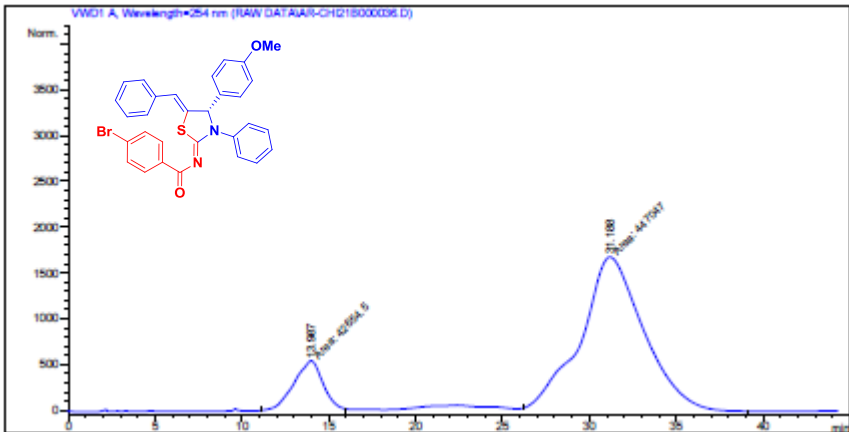
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.258	BB	1.5397	3.28166e4	325.63815	99.3746
2	36.747	MM	0.8941	206.51445	2.75907	0.6254

(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-4-(4-methoxyphenyl)-3-phenylthiazolidin-2-ylidene)-4-bromobenzamide (16p):



Signal 1: VWD1 A, Wavelength=254 nm

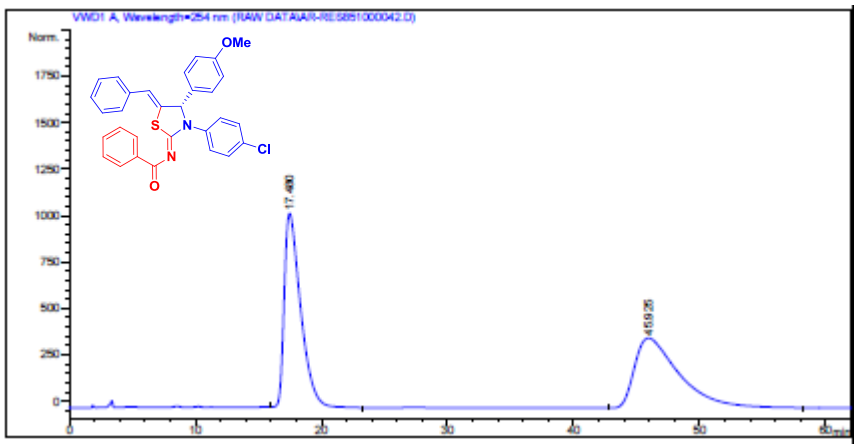
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.279	VV	1.3715	1.84238e5	1892.71411	50.7701
2	31.880	MM	3.4252	1.78649e5	869.29755	49.2299



Signal 1: VWD1 A, Wavelength=254 nm

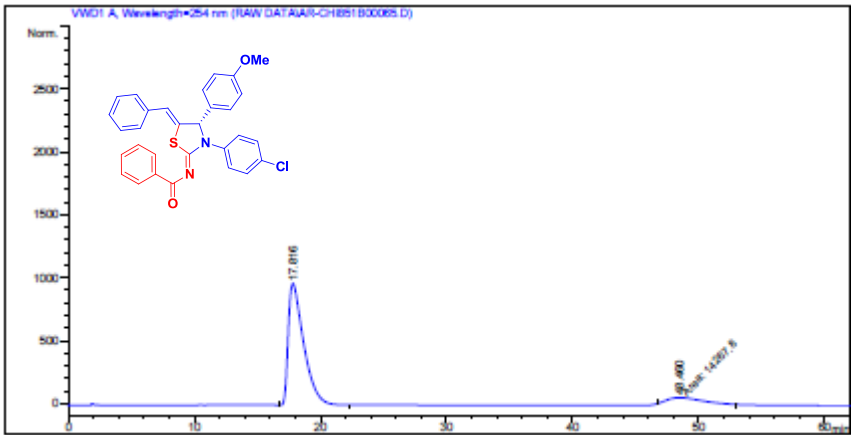
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.987	MM	1.5889	4.26545e4	447.41437	8.7103
2	31.188	MM	4.3794	4.47047e5	1701.31604	91.2897

(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-3-(4-chlorophenyl)-4-(4-methoxyphenyl)thiazolidin-2-ylidene)benzamide (16q):



Signal 1: VWD1 A, Wavelength=254 nm

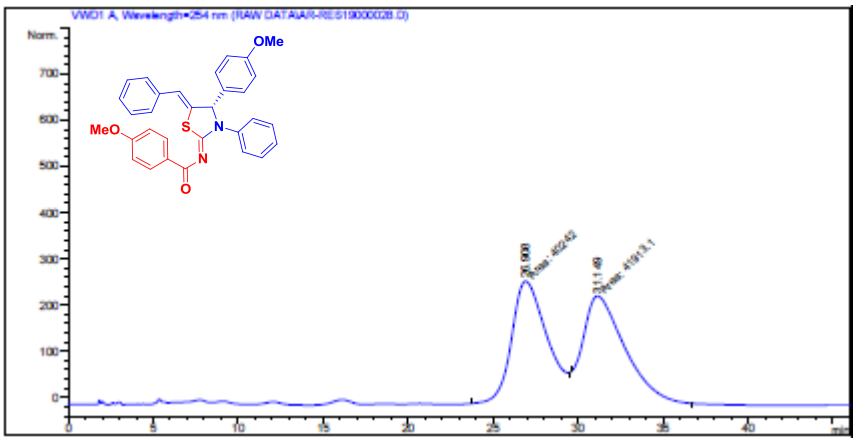
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.480	VB	1.3520	9.45749e4	1045.84363	50.5560
2	45.925	BB	3.4008	9.24948e4	376.64822	49.4440



Signal 1: VWD1 A, Wavelength=254 nm

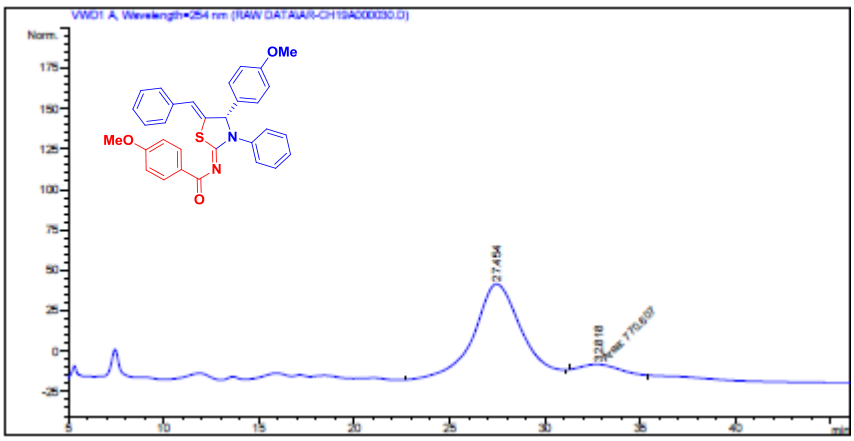
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.816	VB	1.2359	8.21527e4	966.84283	85.2025
2	48.460	MM	3.2279	1.42678e4	73.66892	14.7975

(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-4-(4-methoxyphenyl)-3-phenylthiazolidin-2-ylidene)-4-methoxybenzamide (16r):



Signal 1: VWD1 A, Wavelength=254 nm

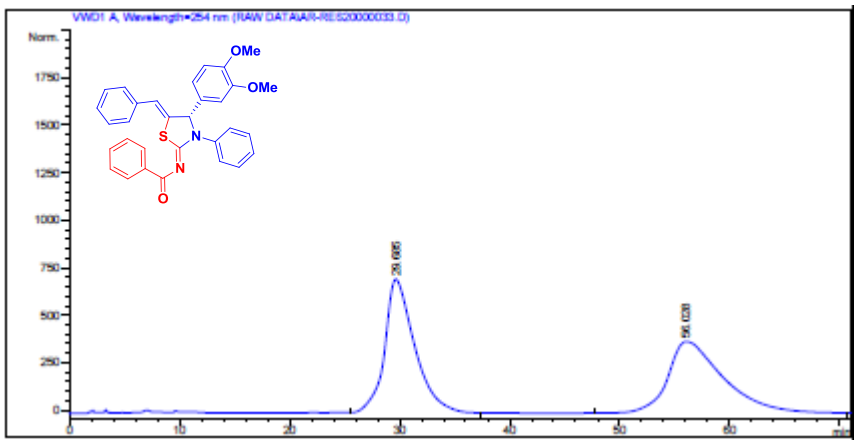
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.908	MM	2.4975	4.02420e4	268.54755	48.9829
2	31.149	MM	2.9301	4.19131e4	238.40834	51.0171



Signal 1: VWD1 A, Wavelength=254 nm

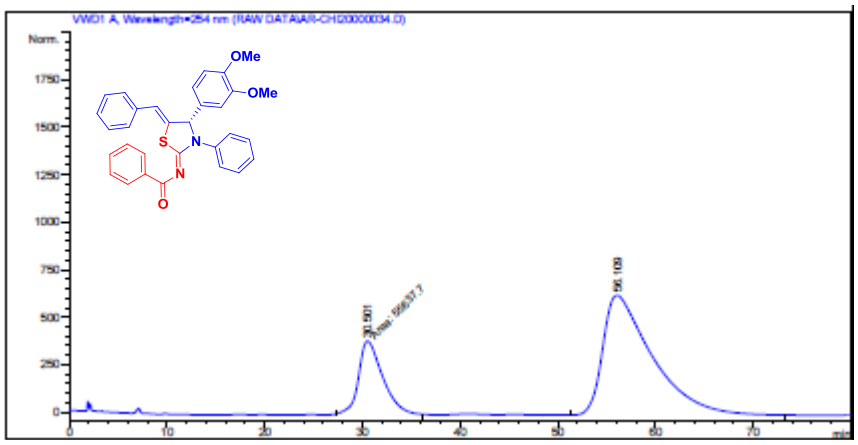
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.454	BV	2.5048	1.02219e4	58.65755	92.9897
2	32.818	MM	2.3294	770.60687	5.51362	7.0103

(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-4-(3,4-dimethoxyphenyl)-3-phenylthiazolidin-2-ylidene)benzamide (16s):



Signal 1: VWD1 A, Wavelength=254 nm

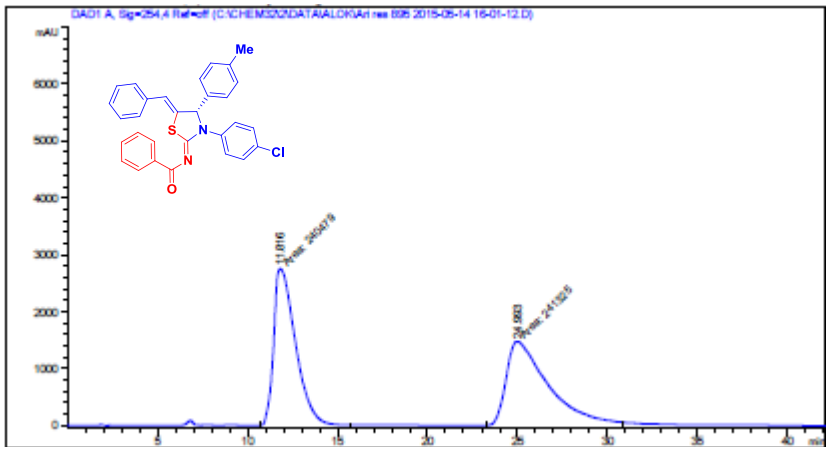
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	29.685	VB	2.6011	1.32971e5	702.60950	50.2889
2	56.028	BB	4.3276	1.31443e5	375.85074	49.7111



Signal 1: VWD1 A, Wavelength=254 nm

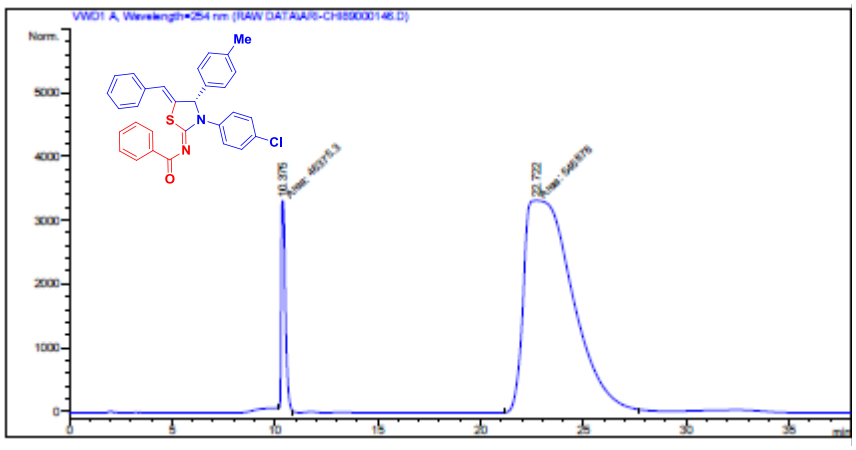
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	30.501	MM	2.5512	5.56377e4	363.46753	20.1473
2	56.109	BB	4.2324	2.20518e5	626.83087	79.8527

(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-3-(4-chlorophenyl)-4-p-tolylthiazolidin-2-ylidene)benzamide (16t):



Peak RetTime Type Width Area Height Area

#	[min]		[min]	[mAU*s]	[mAU]	%
1	11.816	MM	1.4506	2.40479e5	2762.95215	49.9122
2	24.993	MM	2.6962	2.41325e5	1491.74109	50.0878



Signal 1: VWD1 A, Wavelength=254 nm

Peak RetTime Type Width Area Height Area

#	[min]		[min]	mAU *s	[mAU]	%
1	10.375	MM	0.2347	4.63753e4	3292.56030	7.8171
2	22.722	MM	2.7401	5.46877e5	3326.35767	92.1829