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Supplementary Information

Synthesis of New Family of Thiazoline and Thiazole Esters and Investigation of their Thermal Properties

Juliana M. F. M. Schneider, Eric S. Sales, Paolo R. Livotto, Paulo H. Schneider and Aloir A. Merlo*

Instituto de Química, Universidade Federal do Rio Grande do Sul (UFRGS), 90040-060 Porto Alegre-RS, Brazil

General methods

All starting materials were purchased from commercial suppliers (Sigma Aldrich Chemical Co., Acros Organics and ABCR Chemicals) and used without further purification. All reactions were carried out under a nitrogen atmosphere in oven-dried glassware with magnetic stirring. Solvents were dried, purified and degassed under classical methods. Solvents used in extraction and purification were distilled prior to use. Thin layer chromatography (TLC) was performed using silica gel 60 F254 aluminum sheets and the visualization of the spots has been done under UV light (254 nm) or stained with iodine vapor. Products were purified by flash chromatography on silica gel 60 M, 230-400 mesh. Melting and mesophase transition temperatures and textures of the samples points were measured using an Olympus BX43 microscope equipped with a Mettler Toledo FP82HT Hot Stage FP90. ^{1}H (^{13}C) NMR spectra were recorded at 300 (75) MHz on a Varian Inova and 400 (100) MHz Bruker spectrometer using $CDCl_3$ as solvent. The ^{1}H and ^{13}C chemical shifts were reported in parts *per* million (δ) referenced to residual solvent signals at $\delta_{H/C}$ 7.26/77.00 ($CDCl_3$) relative to tetramethylsilane (TMS) as internal standard. Coupling constants *J* [Hz] were directly taken from the spectra and are not averaged. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). ATR/FTIR spectra were recorded on a Varian FT-IR-640 spectrometer. Low-resolution mass spectra were obtained with a Shimadzu GC-MS-QP5050 mass spectrometer interfaced with a Shimadzu GC-17A gas chromatograph equipped with a DB-17 MS capillary column. HRMS spectra were obtained from a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer equipped with an Infinity™ cell, a 7.0 Tesla superconducting magnet, an RF-only hexapole ion guide and an external electrospray ion source (off axis spray) and with ESI(+)-MS and tandem ESI(+)-MS/MS using a hybrid high-resolution and high accuracy MicroTOF-Q II mass spectrometer (Bruker Daltonics), or on a Micromass Q-TOFmicro instrument.

*e-mail: aloir.merlo@ufrgs.br

General procedure for the synthesis of Thiazolines **4a-c**

A solution of *L*-cysteine hidrochloride (60 mmol; 10.8 g), $NaHCO_3$ (60 mmol; 5.3 g), the appropriate nitrile (20 mmol) in 85 mL of ethanol was refluxed for 30 min. After, the pH was adjusted to 8.0 by adding a few drops of morpholine, and the reflux was continued for additional 12 h. The ethanol was removed; the residue dissolved in distilled water and acidified to pH 1.5 by adding concentrated HCl. The product was extracted with CH_2Cl_2 (3 × 50 mL), the organic layers where combined, dried over $MgSO_4$ and the solvent removed under vacuum. The products were obtained with satisfactory purity and were used in the next step without further purification.

(*R*)-2-[4-(Octyloxy)phenyl]-4,5-dihydrothiazole-4-carboxylic acid (**4a**)

Beige solid; mp 103 °C; yield: 88%; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 0.84 (t, 3H, *J* 6.4 Hz, CH_3), 1.38-1.24 (m, 10H, $(CH_2)_5$), 1.72-1.65 (m, 2H, CH_2), 3.63-3.60 (m, 2H, SCH_2), 3.99 (t, 2H, *J* 6.5 Hz, OCH_2), 5.23 (t, 1H, *J* 8.3 Hz, NCH), 6.99 (d, 2H, *J* 8.9 Hz, Ar-H), 7.71 (d, 2H, *J* 8.9 Hz, Ar-H); ^{13}C NMR (DMSO-d_6, 75.5 MHz) δ 171.96, 167.45, 161.38, 129.91, 124.82, 114.48, 78.25, 67.77, 34.94, 31.25, 28.74, 28.67, 28.57, 25.47, 22.09, 13.93.

(*R*)-2-[4'-(Octyloxy)biphenyl-4-yl]-4,5-dihydrothiazole-4-carboxylic acid (**4b**)

Beige solid; mp 186 °C; yield 53%; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 0.90-0.88 (m, 3H, CH_3), 1.79-1.30 (m, 10H, $(CH_2)_5$), 2.60-2.48 (m, 2H, CH_2), 4.00-3.73 (m, 2H, SCH_2), 5.29 (t, 1H, *J* 8.8 Hz, NCH), 6.99 (d, 2H, *J* 8.3 Hz, ArH),

7.57 (d, 2H, *J* 8.3 Hz, ArH), 7.60 (d, 2H, *J* 8.3 Hz, ArH), 7.89 (d, 2H, *J* 8.1 Hz, ArH), 7.99 (bs, 1H, OH).

(*R*)-2-(4-Bromophenyl)-4,5-dihydrothiazole-4-carboxylic acid (**4c**)

Pale pink solid; mp 183 °C; yield 86%; ^{1}H NMR (DMSO-d_6, 300 MHz) δ 3.68-3.71 (m, 2H, SCH_2), 5.31 (t, 1H, *J* 8.4 Hz, NCH), 7.85-7.68 (m, 4H, Ar-H); ^{13}C NMR (DMSO-d_6, 75.5 MHz) δ 172.12, 167.86, 132.39, 131.90, 130.48, 125.88, 78.83, 35.73.

General procedure for esterification of thiazolines **6a-k**

To a stirred solution of the corresponding thiazoline (**4a**-**c**) (2.0 mmol) in dry CH_2Cl_2 (8 mL) under N_2 atmosphere at room temperature, were added subsequently the chosen alcohol or phenol (2.0 mmol) EDCI (2.0 mmol) and catalytic amount of DMAP. After 16 h the organic phase was transferred to an extraction funnel, washed with saturated $NaHCO_3$ (2 × 10 mL), water (2 × 10 mL) and the organic layer was dried with Na_2SO_4. The solvent was evaporated and the remaining product was purified by chromatography (hexanes/AcOEt = 80:20).

(*R*)-Decyl 2-(4-bromophenyl)-4,5-dihydrothiazole-4-carboxylate (**6a**)

Yield 71%; yellow oil; IR (KBr) ν/cm^{-1} 2923, 2856, 1737, 1604, 1508, 1232, 1174, 1141, 836, 700; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75 (d, 2H, *J* 8.6 Hz, ArH), 7.56 (d, 2H, *J* 8.6 Hz, ArH), 5.28 (t, 1H, *J* 9.0 Hz, NCH), 4.24 (t, 2H, *J* 6.7 Hz, OCH_2), 3.80-3.62 (m, 2H, SCH_2), 1.76-1.64 (m, 2H, CH_2), 1.41-1.20 (m, 14H, $(CH_2)_7$), 0.89 (t, 3H, *J* 6.9 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 170.55, 170.02, 131.69, 131.42, 130.05, 126.35, 78.36, 65.97, 35.67, 31.83, 29.50, 29.46, 29.26, 29.16, 28.47, 25.77, 22.64, 14.08.

(*R*)-3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl 2-(4-bromophenyl)-4,5-dihydrothiazole-4-carboxylate (**6b**)

Yield 70%; white solid; mp 56 °C; IR (KBr) ν/cm^{-1} 2917, 2848, 1760, 1592, 1504, 1197, 1172, 1012, 937, 829; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.73 (d, 2H, *J* 8.6 Hz, ArH), 7.56 (d, 2H, *J* 8.6 Hz, ArH), 5.28 (t, 1H, *J* 9.1 Hz, NCH), 4.63-4.46 (m, 2H, OCH_2), 3.75-3.60 (m, 2H, SCH_2), 2.67-2.44 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.39, 170.23, 131.75, 131.40, 130.03, 126.44, 120.00-107.00 (4C), 78.17, 57.55 (t, *J* 4.6 Hz, CH_2), 35.51, 30.38, (t, *J* 21.8 Hz, CH_2).

(*R*)-4-(Nonyloxy)phenyl 2-(4-bromophenyl)-4,5-dihydrothiazole-4-carboxylate (**6c**)

Yield 62%; white solid; mp 107 °C; IR (KBr) ν/cm^{-1} 2929, 2854, 1737, 1587, 1232, 1182, 1141, 700, 649; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.77 (d, 2H, *J* 8.5 Hz, ArH), 7.56 (d, 2H, *J* 8.5 Hz, ArH), 7.06 (d, 2H, *J* 9.0 Hz, ArH), 6.88 (d, 2H, *J* 9.1 Hz, ArH), 5.49 (t, 1H, *J* 9.1 Hz, NCH), 3.93 (t, 2H, *J* 6.5 Hz, OCH_2), 3.89-3.72 (m, 2H, SCH_2), 1.89-1.70 (m, 2H, CH_2), 1.54-1.19 (m, 12H, $(CH_2)_6$), 0.88 (t, 3H, *J* 6.7 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.32, 169.56, 157.03, 143.80, 131.75, 131.48, 130.08, 126.41, 121.99, 114.98, 78.48, 68.35, 35.69, 31.84, 29.50, 29.36, 29.23, 29.21, 25.99, 22.65, 14.10.

(*R*)-Decyl 4,5-dihydro-2-[4-(octyloxy)phenyl]thiazole-4-carboxylate (**6d**)

Yield 43%; white solid; mp 43 °C; IR (KBr) ν/cm^{-1} 2921, 2854, 2364, 1654, 1511, 1238, 823; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (d, 2H, *J* 8.8 Hz, ArH), 6.92 (d, 2H, *J* 8.9 Hz, ArH), 5.28 (dd, 1H, *J* 9.1, 8.2 Hz, NCH), 4.24 (d, 2H, *J* 6.7 Hz, OCH_2), 4.01 (t, 2H, *J* 6.6 Hz, OCH_2), 3.79-3.56 (m, 2H, SCH_2), 1.90-1.76 (m, 2H, CH_2), 1.76-1.65 (m, 2H, CH_2), 1.56-1.19 (m, 26H, $(CH_2)_6$ and $(CH_2)_7$), 0.96-0.84 (m, 6H, 2 CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 170.83, 162.48, 131.40, 130.78 126.44, 114.34, 68.24, 65.97, 35.38, 31.86, 31.77, 29.49, 29.30, 29.28, 29.20, 29.19, 29.09, 28.29, 28.49, 28.31, 25.95, 25.79, 22.66, 22.63, 14.10, 14.08.

(*R*)-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl 4,5-dihydro-2-[4-(octyloxy)phenyl]thiazole-4-carboxylate (**6e**)

Yield 60%; white solid; mp 97 °C; IR (KBr) ν/cm^{-1} 2921, 2852, 1737, 1604, 1174, 1141, 1018, 836, 700, 651; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.82 (d, 2H, *J* 8.9 Hz, ArH), 6.92 (d, 2H, *J* 8.9 Hz, ArH), 5.38 (t, 1H, *J* 8.8 Hz, NCH), 4.89-4.60 (m, 2H, OCH_2CF_2), 4.01 (t, 2H, *J* 6.6 Hz, OCH_2), 3.73-3.63 (m, 2H, SCH_2), 1.90-1.70 (m, 2H, CH_2), 1.59-1.19 (m, 10H, $(CH_2)_5$), 0.90 (t, 3H, *J* 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 171.55, 169.58, 162.22, 130.44, 124.80, 114.31, 60.40 (t, *J* 4.6 Hz, CH_2), 59.86, 35.32, 31.88, 29.54, 29.53, 29.35, 29.30, 29.10, 25.96, 22.66, 14.09.

(*R*)-3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl 4,5-dihydro-2-[4-(octyloxy)phenyl]thiazole-4-carboxylate (**6f**)

Yield 58%; white solid; mp 62 °C; IR (KBr) ν/cm^{-1} 2919, 2854, 1762, 1594, 1506, 1473, 1255, 1203, 1178, 1018, 836; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, 2H, *J* 8.8 Hz, ArH), 6.89 (d, 2H, *J* 8.9 Hz, ArH), 5.26 (t, 1H, *J* 8.9 Hz, NCH), 4.57-4.47 (m, 2H, OCH_2), 3.98 (t, 2H, *J* 6.6 Hz, OCH_2), 3.72-3.53 (m, 2H, SCH_2), 2.68-2.45 (m, 2H, CH_2), 1.85-1.71 (m, 2H, CH_2), 1.55-1.16 (m, 10H, $(CH_2)_5$), 0.88 (t, 3H, *J* 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 170.72, 170.59, 162.09, 130.35, 124.99,120.00-107.00 (6C), 114.23, 77.93, 68.14, 57.36, 35.20, 31.84, 30.38 (t, *J* 21.7 Hz, CH_2), 29.51, 29.50, 29.32, 29.27, 29.07, 25.93, 22.62, 13.99.

(*R*)-4-(Nonyloxy)phenyl 4,5-dihydro-2-[4-(octyloxy)phenyl] thiazole-4-carboxylate (**6g**)

Yield 83%; white solid; mp 104 °C; IR (KBr) ν/cm^{-1} 2919, 2852, 1648, 1546, 1249, 1025, 831, 671; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.84 (d, 2H, *J* 8.9 Hz, ArH), 7.06 (d, 2H, *J* 9.1 Hz, ArH), 6.99-6.82 (m, 4H, ArH), 5.52-5.38 (m, 1H, NCH), 4.11-3.87 (m, 4H, OCH_2), 3.87-3.65 (m, 2H, SCH_2), 1.93-1.69 (m, 4H, 2 CH_2), 1.55-1.17 (m, 22H, $(CH_2)_5$ and $(CH_2)_6$), 1.02-0.81 (m, 6H, 2 CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.60, 169.97, 162.03, 156.98, 143.93, 130.39, 125.13, 122.06, 115.50, 114.97, 114.26, 78.33, 68.36, 68.18, 35.49, 31.85, 31.78, 29.51, 29.37, 29.31, 29.23, 29.20, 29.10, 26.00, 25.96, 22.65, 22.63, 14.09.

(*R*)-Decyl 4,5-dihydro-2-[4-(octyloxy)biphenyl]thiazole-4-carboxylate (**6h**)

Yield 56%; white solid; mp 108 °C; IR (KBr) ν/cm^{-1} 2929, 2852, 1704, 1666, 1598, 1536, 1496, 1390, 1236, 1191, 819; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.91 (d, 2H, *J* 8.5 Hz, ArH), 7.67-7.47 (m, 4H, ArH), 6.97 (d, 2H, *J* 8.9 Hz, ArH), 5.29 (t, 1H, *J* 8.9 Hz, NCH), 4.23 (t, 2H, *J* 6.8 Hz, OCH_2), 4.00 (t, 2H, *J* 6.6 Hz, OCH_2), 3.68 (dd, 2H, *J* 11.2, 9.0 Hz, SCH_2), 1.89-1.57 (m, 4H, 2 CH_2), 1.57-1.10 (m, 24H, $(CH_2)_5$ and $(CH_2)_7$), 0.88 (t, 6H, *J* 6.8 Hz, 2 CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.79, 159.32, 153.66, 144.12, 131.93, 130.42, 128.84, 128.10, 126.47, 114.85, 78.57, 68.06, 55.74, 34.07, 32.78, 32.74, 32.00, 31.83, 31.76, 31.34, 29.57, 29.39, 29.30, 26.06, 25.40, 25.35, 24.59, 22.60, 14.05.

(*R*)-2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl 4,5-dihydro-2-(4-(octyloxy)biphenyl)thiazole-4-carboxylate (**6i**)

Yield 76%; white solid; mp 168 °C; IR (KBr) ν/cm^{-1} 2925, 2850, 1737, 1600, 1494, 1232, 1184, 1141, 829, 700, 655; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.84 (d, 2H, *J* 8.4 Hz, ArH), 7.61-7.40 (m, 4H, ArH), 6.91 (d, 2H, *J* 8.8 Hz, ArH), 5.34 (t, 1H, *J* 8.9 Hz, NCH), 4.85-4.49 (m, 2H, OCH_2), 3.93 (t, 2H, *J* 6.6 Hz, OCH_2), 3.63 (dd, 2H, *J* 8.9, 1.5 Hz, SCH_2), 1.85-1.60 (m, 2H, CH_2), 1.26 (m, 8H, $(CH_2)_5$), 0.82 (t, 3H, *J* 6.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 172.07, 169.37, 159.38, 144.46, 132.04, 130.35, 129.20, 128.19, 126.57, 120.00-107.00 (8C), 114.90, 68.12, 60.18 (t, *J* 21.7 Hz, CH_2), 35.30, 31.80, 29.68, 29.34, 29.22, 26.02, 22.64, 14.08.

(*R*)-3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl 4,5-dihydro-2-(4-(octyloxy)biphenyl)thiazole-4-carboxylate (**6j**)

Yield 72%; white solid; mp 108 °C; IR (KBr) ν/cm^{-1} 2919, 2856, 1752, 1592, 1508, 1475, 1255, 1203, 1018, 939, 829; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.94 (d, 2H, *J* 8.5 Hz, ArH), 7.72-7.52 (m, 4H, ArH), 7.00 (d, 2H, *J* 8.5 Hz, ArH), 5.34 (t, 1H, *J* 8.9 Hz, NCH), 4.64-4.51 (m, 2H, OCH_2), 4.03 (t, 2H, *J* 6.6 Hz, OCH_2), 3.80-3.61 (m, 2H, SCH_2), 2.75-2.48 (m, 2H, CH_2), 1.92-1.75 (m, 2H, CH_2), 1.60-1.21 (m, 10H, $(CH_2)_5$), 0.92 (t, 3H, *J* 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 171.46, 170.41, 159.35, 144.32, 132.07, 130.50, 129.16, 128.18, 126.54, 120.00-107.00 (5C), 114.89, 77.90, 68.12, 57.51, 35.25, 31.80, 30.43 (t, *J* 21.7 Hz, CH_2), 29.35, 29.30, 29.23, 26.03, 22.65, 14.09.

(*R*)-4-(Nonyloxy)phenyl 4,5-dihydro-2-[4-(octyloxy)biphenyl] thiazole-4-carboxylate (**6k**)

Yield 80%; white solid; mp 108 °C; IR (KBr) ν/cm^{-1} 2919, 2852, 1648, 1598, 1508, 1469, 1245, 1184, 1027, 933, 829, 719; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.96 (d, 2H, *J* 8.4 Hz, ArH), 7.62 (d, 2H, *J* 8.5 Hz, ArH), 7.56 (d, 2H, *J* 8.8, Hz ArH), 7.08 (d, 2H, *J* 9.1 Hz, ArH), 6.98 (d, 2H, *J* 8.8 Hz, ArH), 6.88 (d, 2H, *J* 9.1 Hz, ArH), 5.53 (dd, 1H, *J* 9.2, 8.6 Hz, NCH), 4.00 (t, 2H, *J* 6.6 Hz, OCH_2), 3.93 (t, 2H, *J* 6.5 Hz, OCH_2), 3.82 (dd, 2H, *J* 11.3, 8.9 Hz, SCH_2), 1.89-1.70 (m, 4H, 2 CH_2), 1.36 -1.10 (m, 22H, $(CH_2)_5$ and $(CH_2)_6$), 0.96-0.81 (m, 6H, 2 CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 171.32, 169.78, 159.32, 157.02, 144.26, 143.90, 132.11, 130.65, 129.19, 128.19, 126.55, 122.05, 115.06, 114.99, 114.89, 78.29, 68.38, 68.12, 35.47, 33.85, 31.85, 31.80, 31.79, 29.50, 29.36, 29.34, 29.22, 26.02, 26.00, 25.56, 24.89, 22.64, 14.09.

General procedure for the synthesis of tiazoles **7a-k**

The appropriate thiazoline ester (1 mmol) (**6a-k**) and dry CH_2Cl_2 (5 mL) were added to a round bottomed flask under N_2 atmosphere. The system was cooled to 0 °C, and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) (2 mmol) was added and the reaction mixture was stirred for 20 min. Bromotrichloromethane ($BrCCl_3$) (2 mmol) was then added and stirred for additional 16 hours at room temperature. The reaction was quenched with saturated NH_4Cl and the organic layer washed with water (2 × 10 mL), saturated NaCl (2 × 10 mL) and dried over Na_2SO_4. The solvent was finally evaporated and the remaining product was purified by chromatography (hexanes/AcOEt = 80:20).

Decyl 2-(4-Bromophenyl)thiazole-4-carboxylate (**7a**)

Yield: 82%; IR (KBr) ν/cm^{-1} 2919, 2850, 1718, 1454, 1338, 1249, 1218, 1105, 1070, 998, 840, 796, 767; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.07 (s, 1H, SCH), 7.80 (d, 2H, *J* 8.6 Hz, ArH), 7.51 (d, 2H, *J* 8.6 Hz, ArH), 4.30 (t, 2H, *J* 6.8 Hz, OCH_2), 1.88-1.56 (m, 2H, CH_2), 1.43-1.07 (m, 16H, $(CH_2)_8$), 0.80 (t, 3H, *J* 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.51, 161.33, 148.30, 132.18, 131.74, 128.36, 127.11, 125.10, 65.71, 31.89, 29.53,

29.52, 29.30, 29.27, 28.69, 25.94, 22.67, 14.11; HRMS (FTMS + pESI) *m/z,* calcd. for $C_{20}H_{27}BrNO_2S$ [M + H$^+$]: 424.0940, found: 424.0901.

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl 2-(4-bromophenyl)thiazole-4-carboxylate (**7b**)

Yield 66%; IR (KBr) ν/cm^{-1} 2919, 2850, 2364, 1745, 1509, 1454, 1344, 1245, 1211, 1072, 1014, 827, 634; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.11 (s, 1H, SCH), 7.81 (d, 2H, *J* 8.4 Hz, ArH), 7.52 (d, 2H, *J* 8.4 Hz, ArH), 4.62 (t, 2H, *J* 6.5 Hz, OCH_2), 2.80-2.34 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.86, 160.62, 147.14, 132.23, 131.48, 128.33, 128.04, 125.28, 122-106 (6C), 57.24, 30.55 (t, *J* 21.7 Hz, CH_2); HRMS (FTMS + pESI) *m/z,* calcd. for $C_{18}H_{10}BrF_{13}NO_2S$ [M + H$^+$]: 629.9408, found: 629.9404.

4-(Nonyloxy)phenyl 2-(4-bromophenyl)thiazole-4-carboxylate (**7c**)

Yield 51%; IR (KBr) ν/cm^{-1} 2927, 2850, 1729, 1623, 1569, 1311, 1243, 1207, 1141, 1087, 646; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.32 (s, 1H, SCH), 7.89 (d, 2H, *J* 8.6 Hz, ArH), 7.58 (d, 2H, *J* 8.6 Hz, ArH), 7.12 (d, 2H, *J* 9.0 Hz, ArH), 6.90 (d, 2H, *J* 9.1 Hz, ArH), 3.93 (t, 2H, *J* 6.6 Hz, CH_2), 1.82-1.66 (m, 2H, CH_2), 1.38-1.19 (m, 12H, $(CH_2)_6$), 0.86 (t, 3H, *J* 6.9 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.84, 159.98, 157.10, 147.51, 143.91, 132.26, 131.64, 128.54, 128.41, 125.28, 122.29, 115.14, , 68.46, 31.85, 29.51, 29.37, 29.27, 29.23, 26.03, 22.64, 14.06; HRMS (FTMS + pESI) *m/z*, calcd. for $C_{25}H_{29}BrNO_3S$ [M + H$^+$]: 502.1052, found: 502.0942.

Decyl 2-[4-(octyloxy)phenyl]thiazole-4-carboxylate (**7d**)

Yield 74%; IR (KBr) ν/cm^{-1} 2915, 2850, 1722, 1606, 1459, 1297, 1253, 1209, 1172, 1105, 838, 763, 721, 632; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 (s, 1H, SCH), 7.86 (d, 2H, *J* 8.9 Hz, ArH), 6.86 (d, 2H, *J* 8.9 Hz, ArH), 4.28 (t, 2H, *J* 6.9 Hz, OCH_2), 3.92 (t, 2H, *J* 6.6 Hz, OCH_2), 1.79-1.63 (m, 4H, 2 CH_2), 1.43-1.31 (m, 4H, 2 CH_2), 1.31-1.12 (m, 20H, $(CH_2)_4$ and $(CH_2)_6$), 0.87-0.75 (m, 6H, 2 CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 168.77, 161.53, 161.22, 147.77, 128.45, 126.00, 125.45, 114.71, 68.16, 65.50, 31.84, 31.76, 29.50, 29.49, 29.48, 29.37, 29.30, 29.26, 29.24, 29.18, 29.13, 28.66, 25.96, 25.90, 22.63, 22.61, 14.06, 14.05; HRMS (FTMS + pESI) *m/z*, calcd. for $C_{28}H_{44}NO_3S$ [M+H$^+$]: 474.3042, found: 474.3089.

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl 2-[4-(octyloxy)phenyl]thiazole-4-carboxylate (**7e**)

Yield 74%; IR (KBr) ν/cm^{-1} 2917, 2850, 2362, 1724, 1467, 1249, 1209, 1141, 1101, 827, 765, 707; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.07 (s, 1H, SCH), 7.86 (d, 2H, *J* 8.7 Hz, ArH), 6.87 (d, 2H, *J* 8.7 Hz, ArH), 4.79 (t, 2H, *J* 13.4 Hz, OCH_2CF_2), 3.93 (t,2H, *J* 6.5 Hz, OCH_2), 1.85-1.57 (m, 2H, CH_2), 1.49-0.97 (m, 10H, $(CH_2)_5$), 0.80 (t, 3H, *J* 5.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.38, 161.50, 159.39, 145.48, 128.53, 127.99, 125.15, 114.83, 120-107 (3C), 77.42, 68.24, 60.04 (t, *J* 21.6 Hz, CH_2), 31.89, 29.70, 29.56, 29.54, 29.37, 29.31, 29.15, 26.00, 22.67, 14.07; ^{19}F NMR (282 MHz, $CDCl_3$/CF_3CO_2H) δ –80.85 (t, *J* 9.9 Hz), –119.28, –121.93 (3 CF_2), –122.75, –123.21, –126.18.

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl 2-(4-(octyloxy) phenyl)thiazole-4-carboxylate (**7f**)

Yield 76%; IR (KBr) ν/cm^{-1} 2917, 2850, 1747, 1509, 1461, 1214, 1083, 1018, 835, 640; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (s, 1H, SCH), 7.85 (d, 2H, *J* 8.8 Hz, ArH), 6.87 (d, 2H, *J* 8.8 Hz, ArH), 4.59 (t, 2H, *J* 6.6 Hz, OCH_2), 3.92 (t, 2H, *J* 6.6 Hz, OCH_2), 2.71-2.44 (m, 2H, CH_2), 1.80-1.64 (m, 2H, CH_2), 1.45-1.33 (m, 2H, CH_2), 1.33-1.11 (m, 8H $(CH_2)_4$), 0.80 (t, 3H, *J* 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 169.16, 161.41, 160.89, 146.74, 128.51, 127.01, 125.30, 120-107 (5C) 114.81, 68.24, 57.11, 31.89, 30.63 (t, *J* 21.6 Hz, CH_2), 29.55, 29.38, 29.31, 29.16, 26.00, 22.67, 14.08.

4-(Nonyloxy)phenyl 2-[4-(octyloxy)phenyl]thiazole-4-carboxylate (**7g**)

Yield 50%; IR (KBr) ν/cm^{-1} 2927, 2850, 1623, 1571, 1311, 1243, 1087, 829, 644; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.19 (s, 1H, SCH), 7.89 (d, 2H, *J* 8.8 Hz, Ar-H), 7.07 (d, 2H, *J* 9.0 Hz, Ar-H), 6.93-6.80 (m, 4H, Ar-H), 3.93 (t, 2H, *J* 6.6 Hz, OCH_2), 3.88 (t, 2H, *J* 6.6 Hz, OCH_2), 1.78-1.62 (m, 4H, 2 CH_2), 1.45-1.33 (m, 4H, 2 CH_2), 1.33-1.12 (m, 18H, $(CH_2)_4$ and $(CH_2)_5$), 0.87-0.76 (m, 6H, 2 CH_3); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 169.16, 161.39, 160.27, 157.00, 146.98, 143.96, 128.56, 127.61, 125.37, 122.38, 115.08, 114.83, 68.42, 68.25, 31.90, 31.89, 29.57, 29.55, 29.41, 29.39, 29.32, 29.29, 29.27, 29.18, 26.05, 26.01, 22.68, 14.12; HRMS (FTMS+pESI) *m/z* calcd. for $C_{29}H_{36}NNaO_4S$ [M–C_4H_9]Na$^+$: 517.2263, found: 517.2285.

Decyl 2-[4-(octyloxy)biphenyl]thiazole-4-carboxylate (**7h**)

Yield 70%; IR (KBr) ν/cm^{-1} 2921, 2852, 1722, 1459, 1247, 1199, 1097, 823; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.13 (s, 1H, SCH), 8.05 (d, 2H, *J* 8.3 Hz, Ar-H), 7.64 (d, 2H, *J* 8.4 Hz, Ar-H), 7.57 (d, 2H, *J* 8.7 Hz, Ar-H), 6.98 (d, 2H, *J* 8.7 Hz, Ar-H), 4.38 (t, 2H, *J* 6.8 Hz, OCH_2), 4.00 (t, 2H, *J* 6.6 Hz, OCH_2), 1.91-1.72 (m, 4H, 2 CH_2), 1.60-1.18 (m, 24H, $(CH_2)_5$ and $(CH_2)_7$), 0.99-0.80 (m, 6H, 2 CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.63, 161.50, 159.22, 148.08, 143.06, 132.14, 130.99, 128.05, 127.35, 126.93, 126.71, 114.87, 68.10, 65.61, 31.88, 31.80, 29,52; 29.51,

29,38; 29.35, 29.30, 29,28, 29.27, 29,25, 29,24, 29.23, 28.68, 26.03, 25.93, 22.66, 22.65, 14.10.

2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Heptadecafluorononyl 2-[4-(octyloxy)biphenyl]thiazole-4-carboxylate (**7i**)

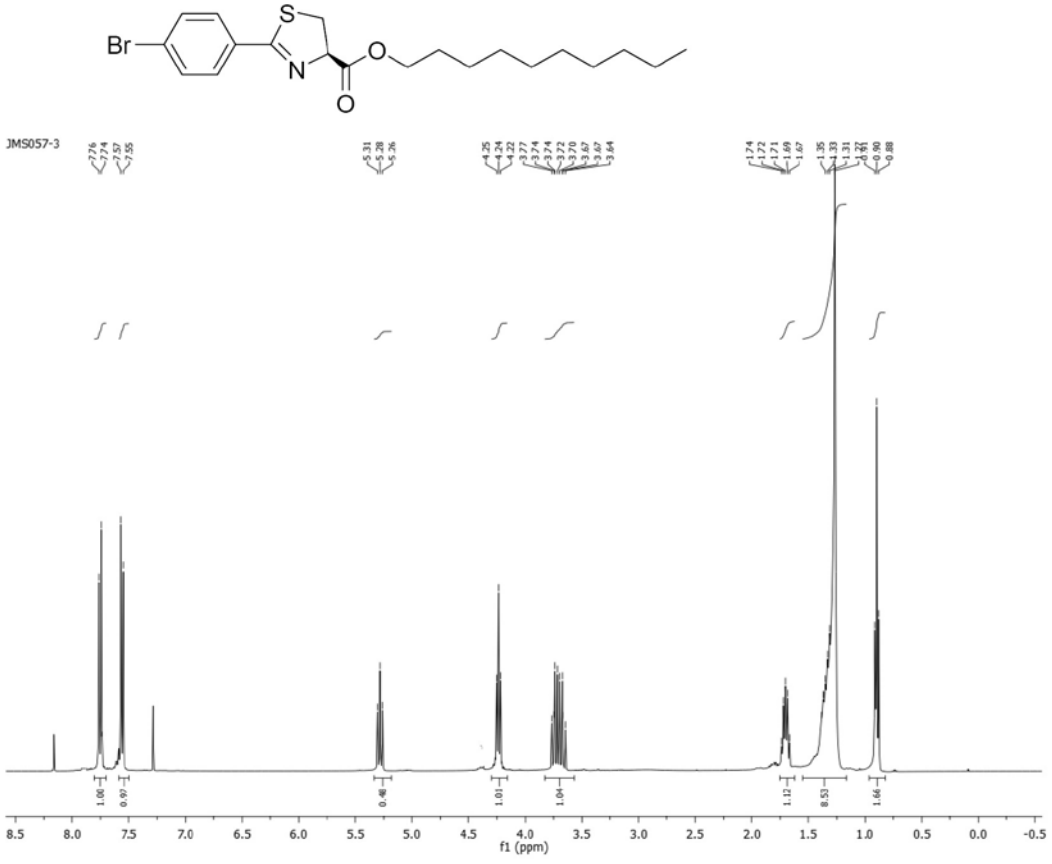
Yield 73%; IR (KBr) ν/cm^{-1} 2921, 2852, 1727, 1600, 1463, 1241, 1199, 1141, 1101, 823, 698, 647; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.22 (s, 1H, SCH), 8.05 (d, 2H, *J* 8.4 Hz, Ar-H), 7.65 (d, 2H, *J* 8.4 Hz, Ar-H), 7.52 (d, 2H, *J* 8.6 Hz, Ar-H), 6.99 (d, 2H, *J* 8.8 Hz, Ar-H), 4.88 (t, 2H, *J* 13.4 Hz, OCH_2), 4.01 (t, 2H, *J* 6.6 Hz, OCH_2), 1.92-1.73 (m, 2H, CH_2), 1.55-1.23 (m, 10H $(CH_2)_5$), 0.90 (t, 3H, *J* 6.5 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.28, 159.42, 159.37, 145.85, 143.50, 132.16, 130.76, 128.57, 128.11, 127.44, 127.08, 120-107 (7C)115.03, 68.23, 60.14 (t, *J* 27.5 Hz, CH_2), 59.78, 31.82, 29.36, 29.29; 29.23, 26.07, 22.65, 14.05.

3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl 2-[4-(octyloxy) biphenyl]thiazole-4-carboxylate (**7j**)

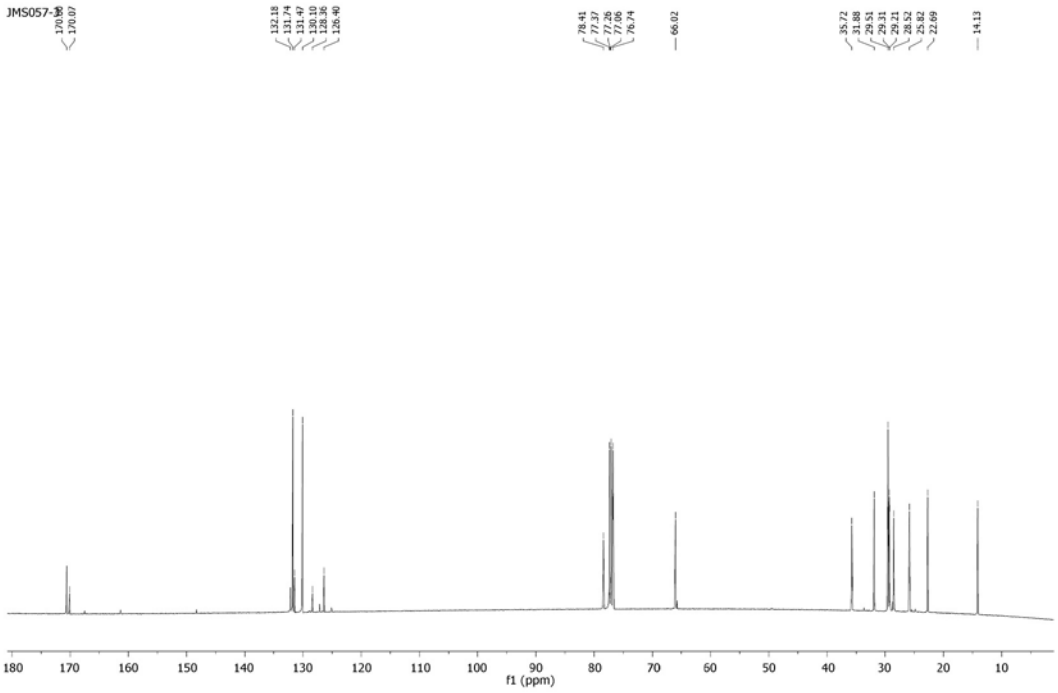
Yield 75%; IR (KBr) ν/cm^{-1} 2919, 2850, 1747, 1602, 1508, 1459, 1344, 1216, 1083, 1020, 831, 746; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.17 (s, 1H, SCH), 8.05 (d, 2H, *J* 8.6 Hz, Ar-H), 7.65 (d, 2H, *J* 8.6 Hz, Ar-H), 7.57 (d, 2H, *J* 8.8 Hz, Ar-H), 6.99 (d, 2H, *J* 8.8 Hz, Ar-H), 4.70 (t, 2H, *J* 6.6 Hz, OCH_2), 4.01 (t, 2H, *J* 6.6 Hz, OCH_2), 2.78-2.53 (m, 2H, CH_2), 1.91-1.71 (m, 2H, CH_2), 1.52-1.23 (m, 10H, $(CH_2)_5$), 0.89 (t, 3H, *J* 6.5 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169.00, 160.82, 159.28, 146.98, 143.26, 132.07, 130.79, 128.08, 127.68, 127.37, 127.00, 120-107 (5C), 114.89, 68.12, 57.18, 31.81, 30.58 (t, *J* 21.7 Hz, CH_2), 29.69, 29.36, 29.25, 29.24, 26.04, 22.66, 14.10.

4-(Nonyloxy)phenyl 2-[4-(octyloxy)biphenyl]thiazole-4-carboxylate (**7k**)

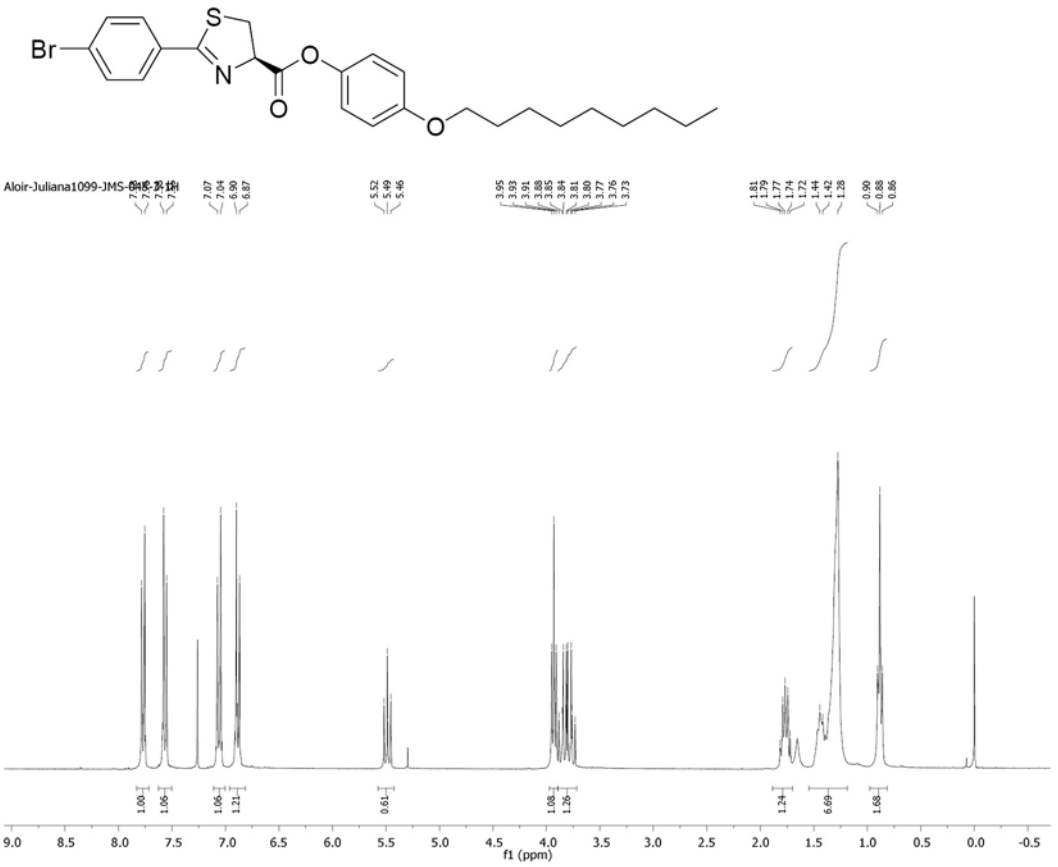
Yield 58%; IR (KBr) ν/cm^{-1} 2933, 2852, 1745, 1602, 1463, 1199, 1145, 825, 655; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.35 (s, 1H, SCH), 8.11 (d, 2H, *J* 8.4 Hz, ArH), 7.68 (d, 2H, *J* 8.4 Hz, ArH), 7.60 (d, 2H, *J* 8.8 Hz, ArH), 7.20 (d, 2H, *J* 9.0 Hz, ArH), 7.08-6.90 (m, 4H, ArH), 4.12-3.95 (m, 4H, 2 OCH_2), 1.95-1.73 (m, 4H, 2 CH_2), 1.63-1.21 (m, 22H, $(CH_2)_5$ and $(CH_2)_6$), 1.03-0.85 (m, 6H, 2 CH_3); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 168.99, 160.15, 159.42, 157.12, 147.47, 144.14, 143.38, 132.28, 131.06, 128.11, 128.06, 127.48, 127.07, 122.35, 115.22, 115.08, 68.57, 68.28, 31.88, 31.82, 29.53, 29.40, 29.36 (2C), 29.33 (2C), 29.32 (2C), 29.24 (2C), 29.23 (2C), 26.08, 22.65, 22.64, 14.03; HRMS (FTMS + pESI) *m/z* calcd. for $C_{34}H_{39}NNaO_4S$ $[M–C_4H_9]Na^+$: 580.2497, found: 580.2495.



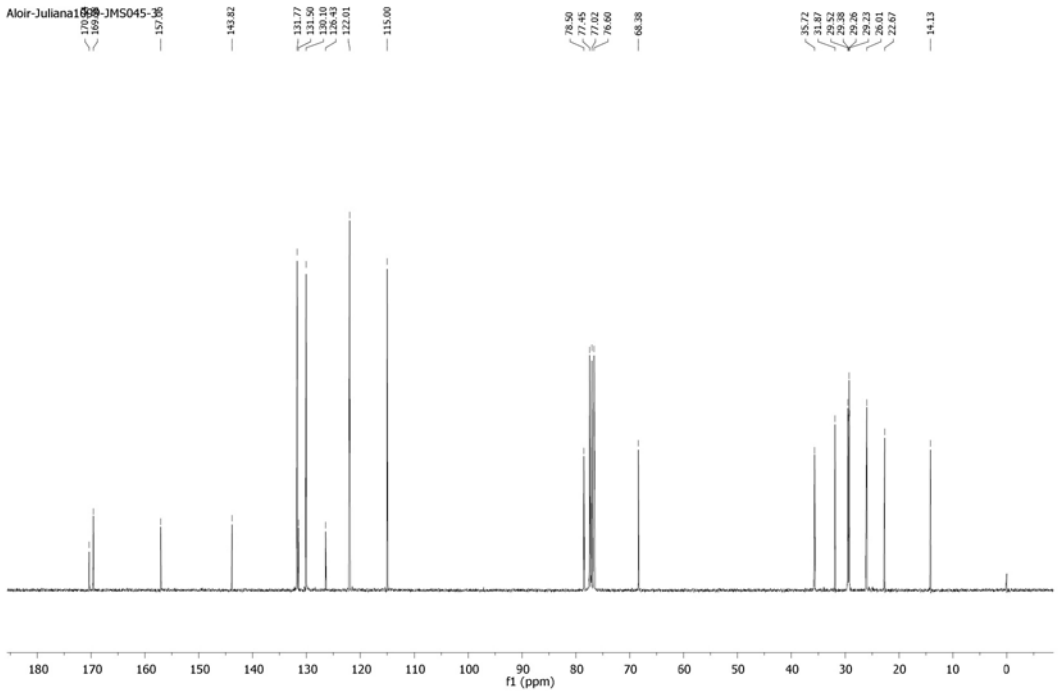
S1. ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of **6a**.



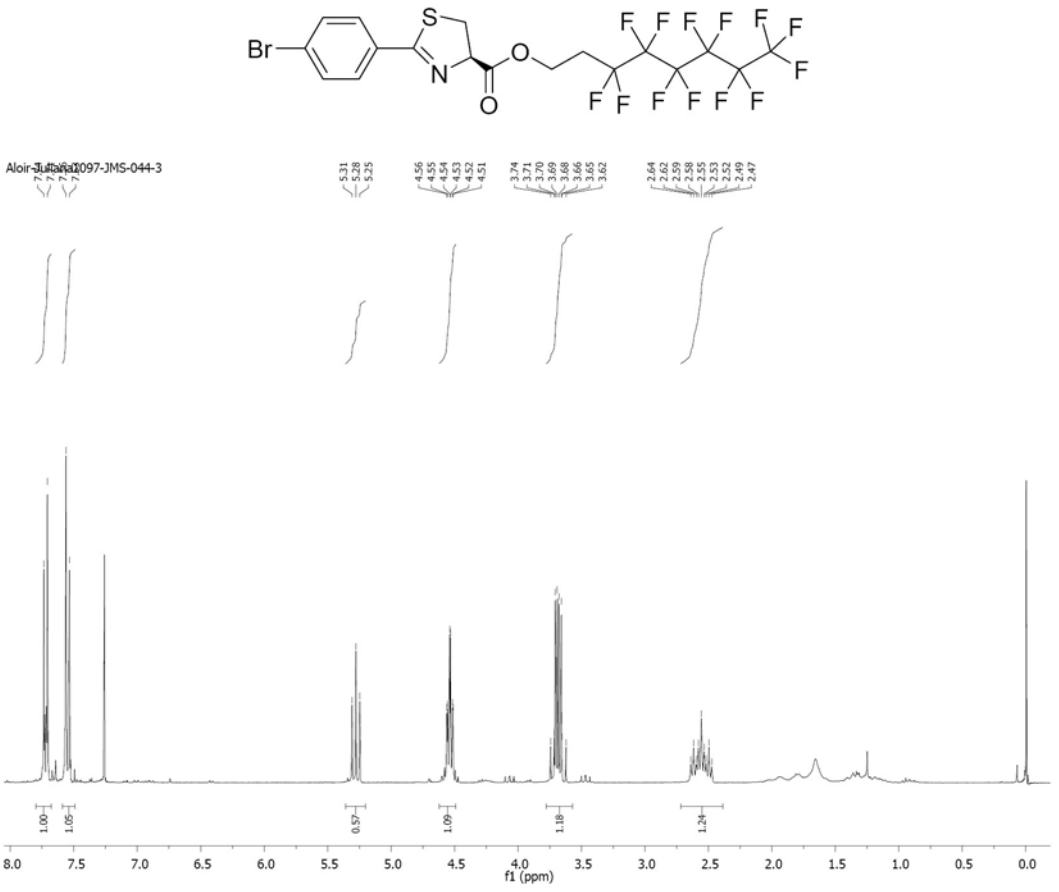
S2. ^{13}C NMR spectra ($CDCl_3$, 100 MHz) of **6a**.



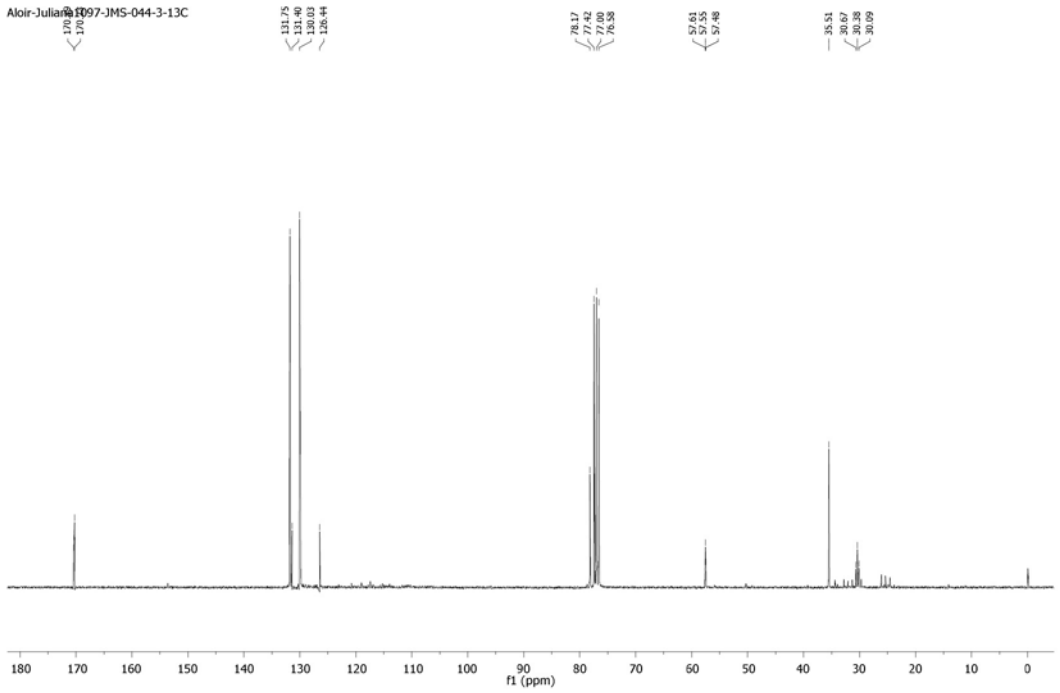
S3. ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of **6c**.



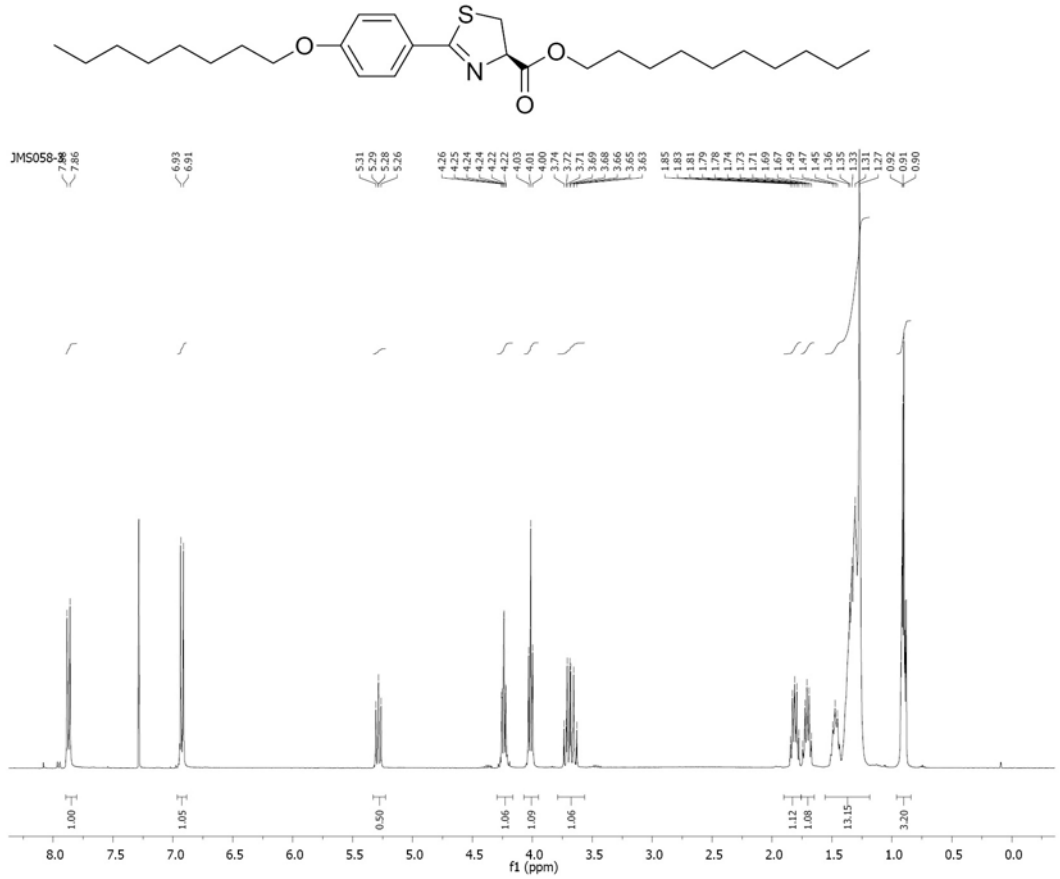
S4. ^{13}C NMR spectra ($CDCl_3$, 75 MHz) of **6c**.



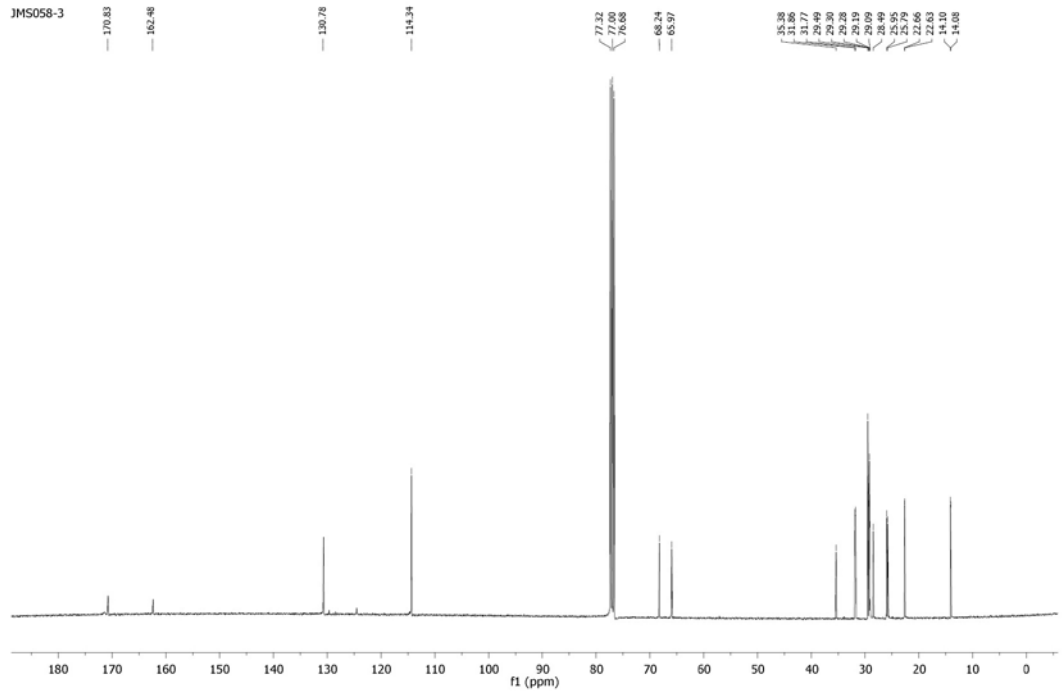
S5. ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of **6b**.



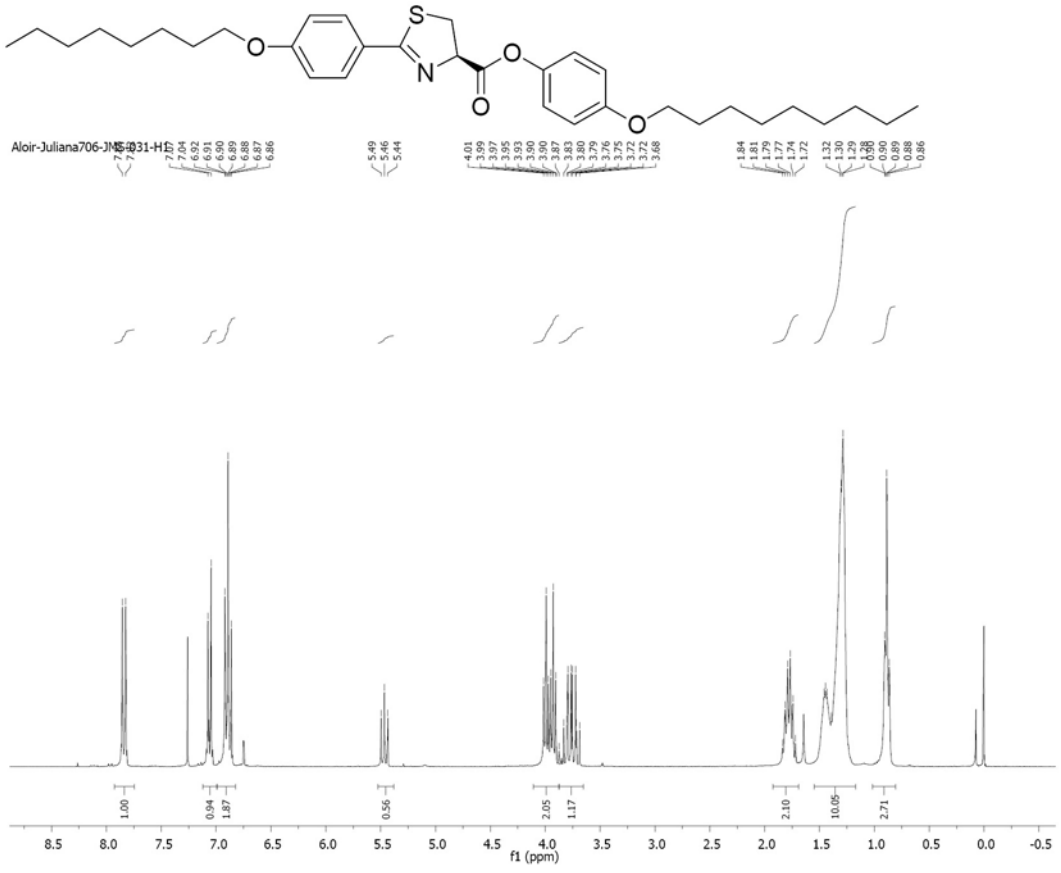
S6. ^{13}C NMR spectra ($CDCl_3$, 75 MHz) of **6b**.



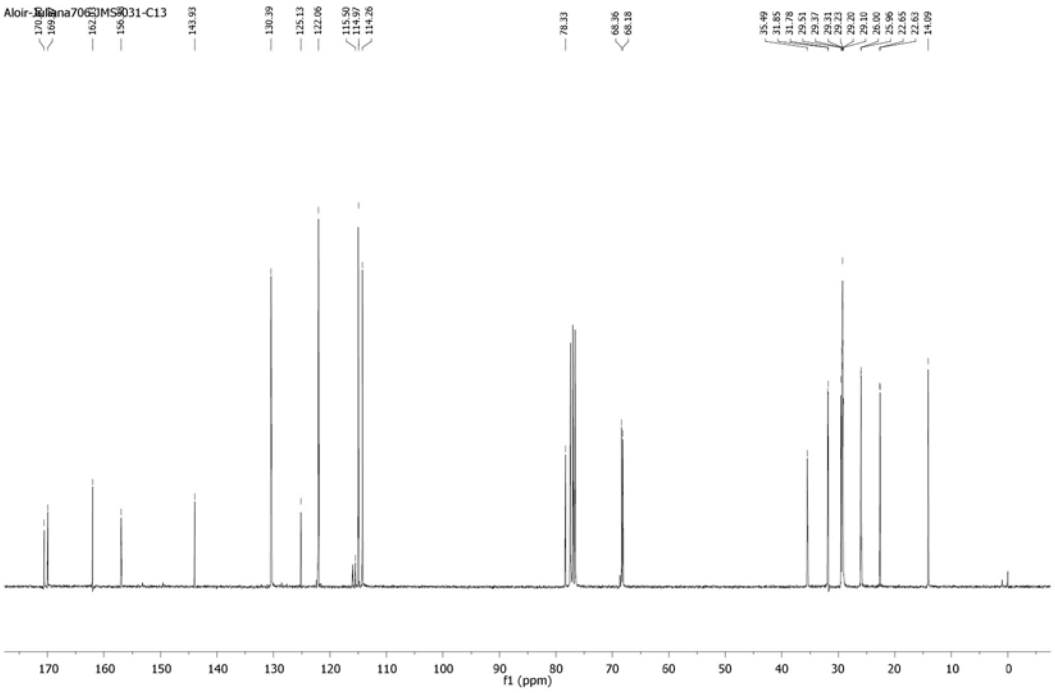
S7. ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of **6d**.



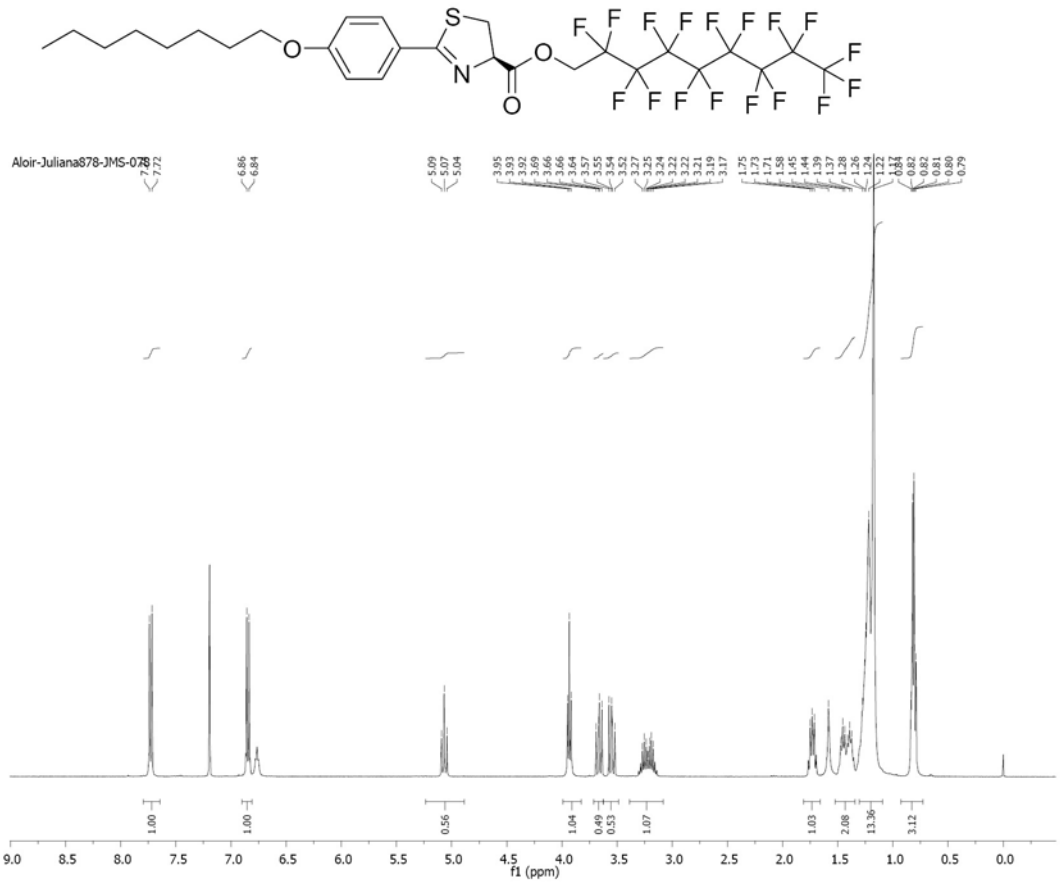
S8. ^{13}C NMR spectra ($CDCl_3$, 100 MHz) of **6d**.



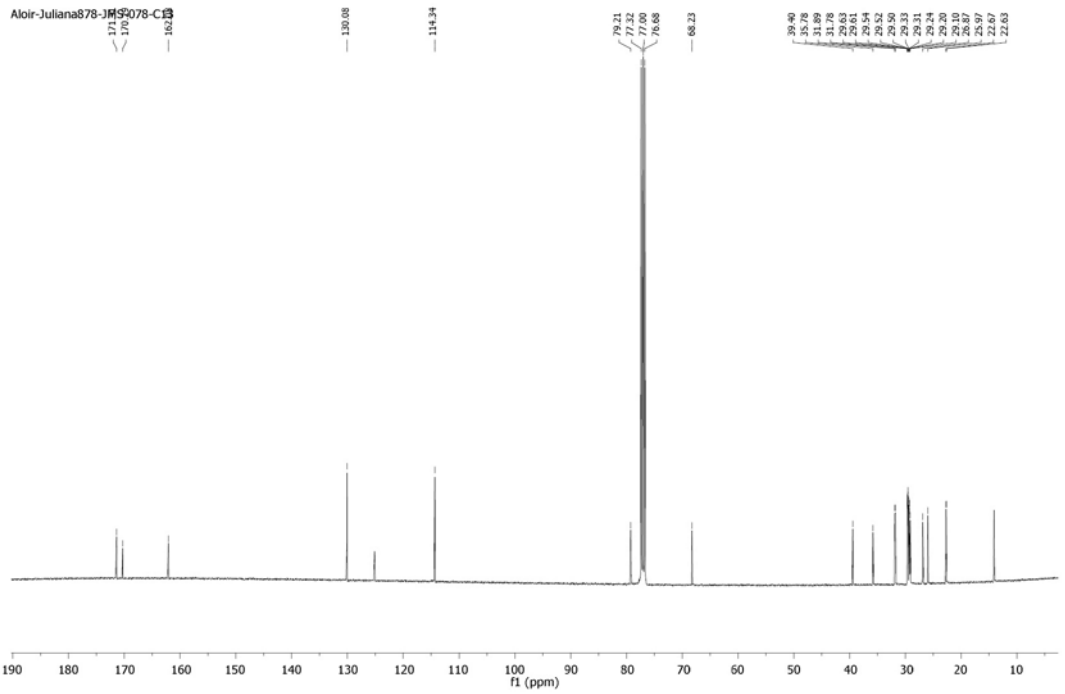
S9. ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of **6g**.



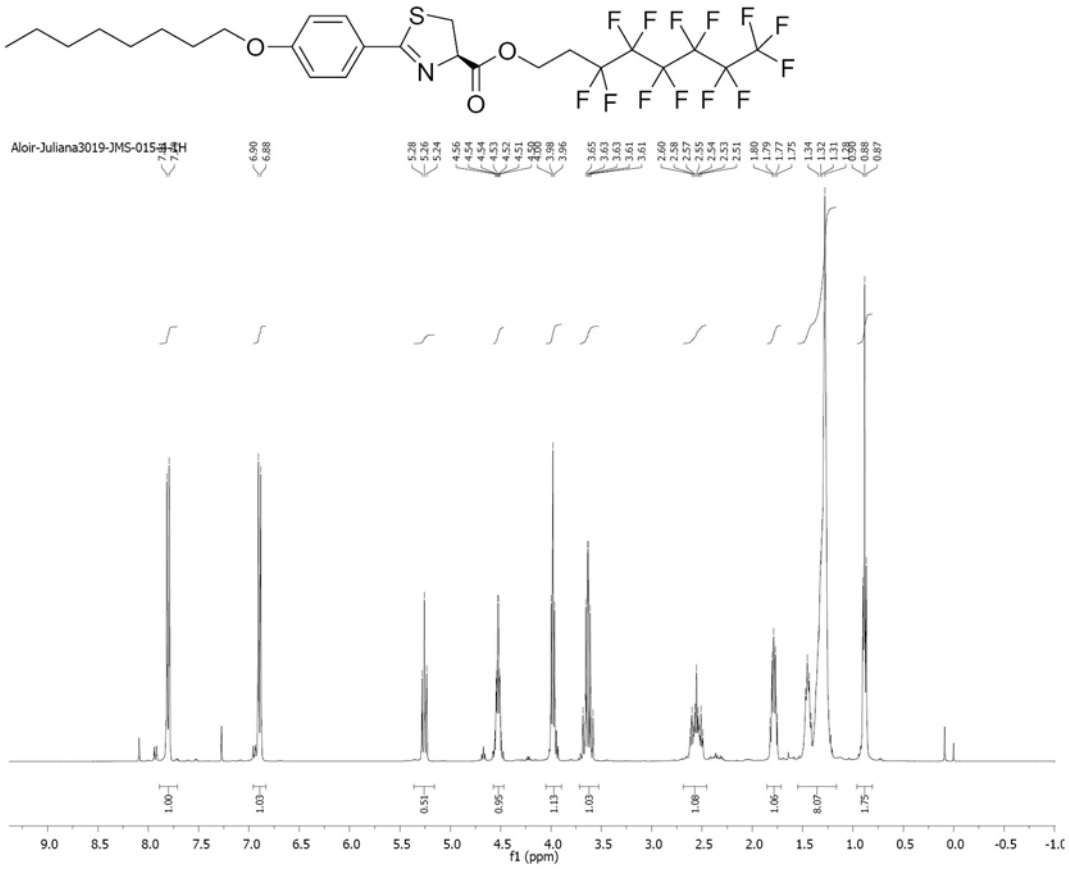
S10. ^{13}C NMR spectra ($CDCl_3$, 75 MHz) of **6g**.



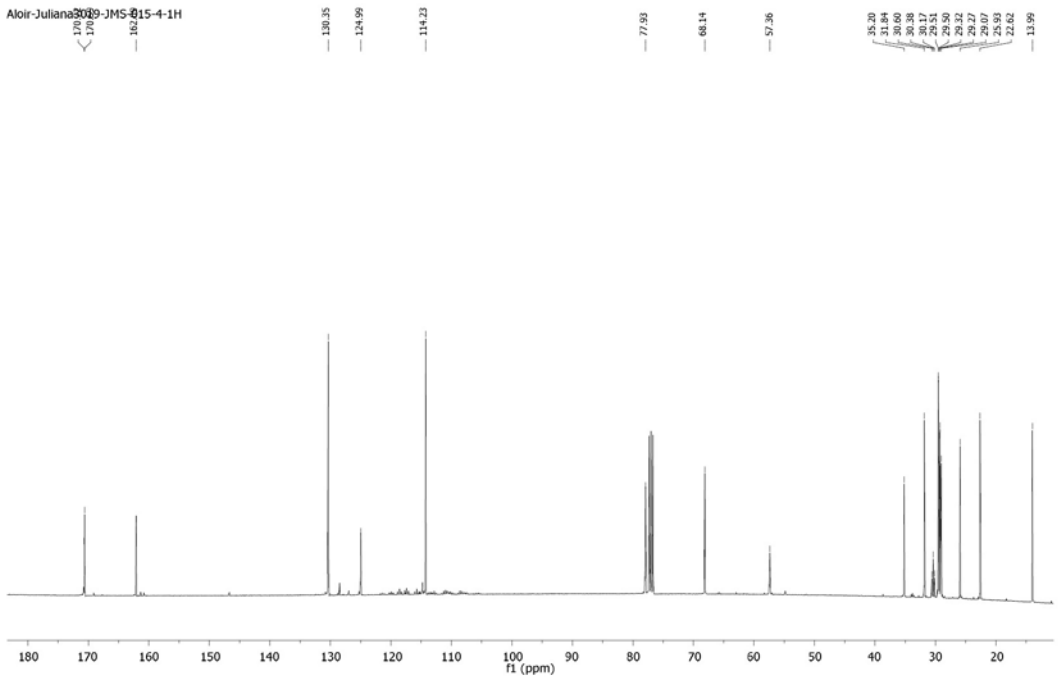
S11. ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of **6e**.



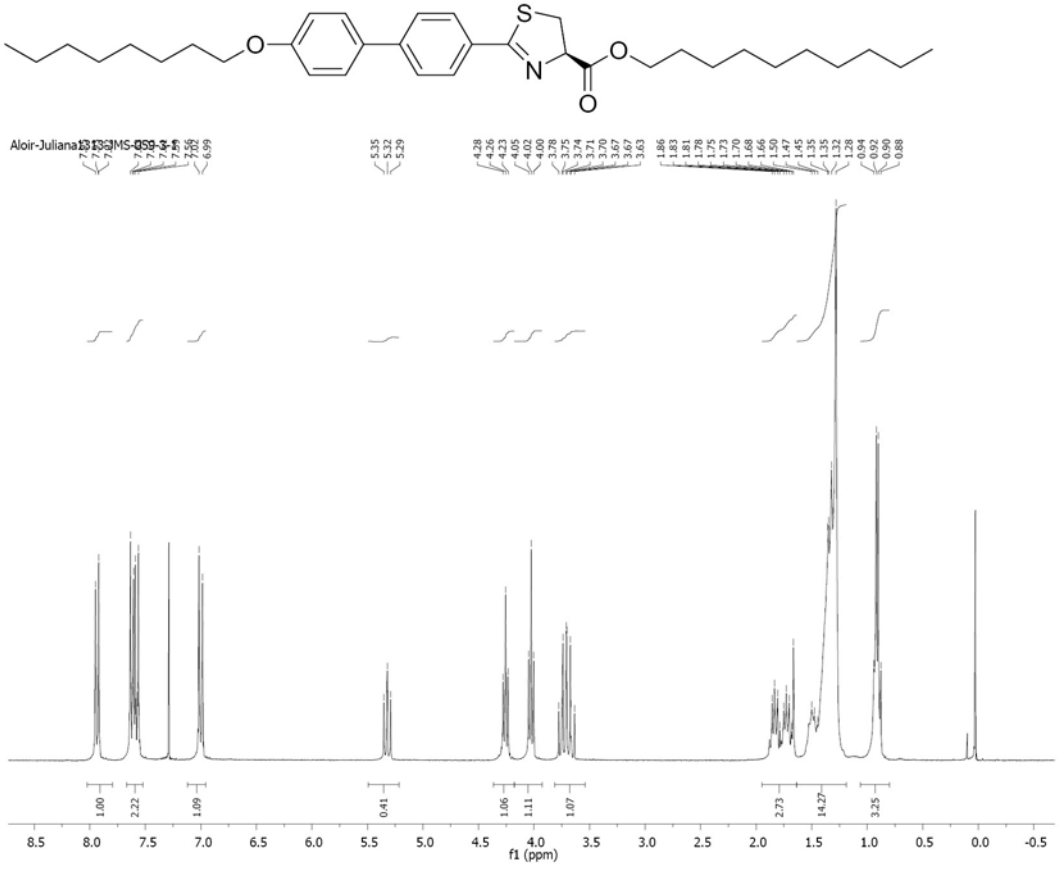
S12. ^{13}C NMR spectra ($CDCl_3$, 100 MHz) of **6e**.



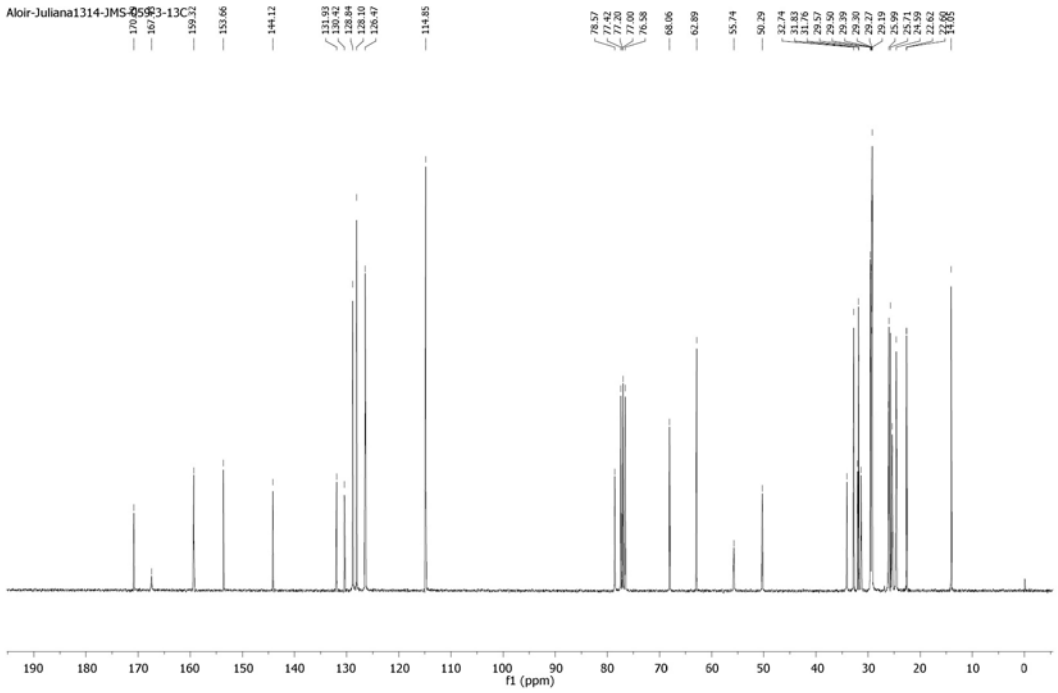
S13. ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of **6f**.



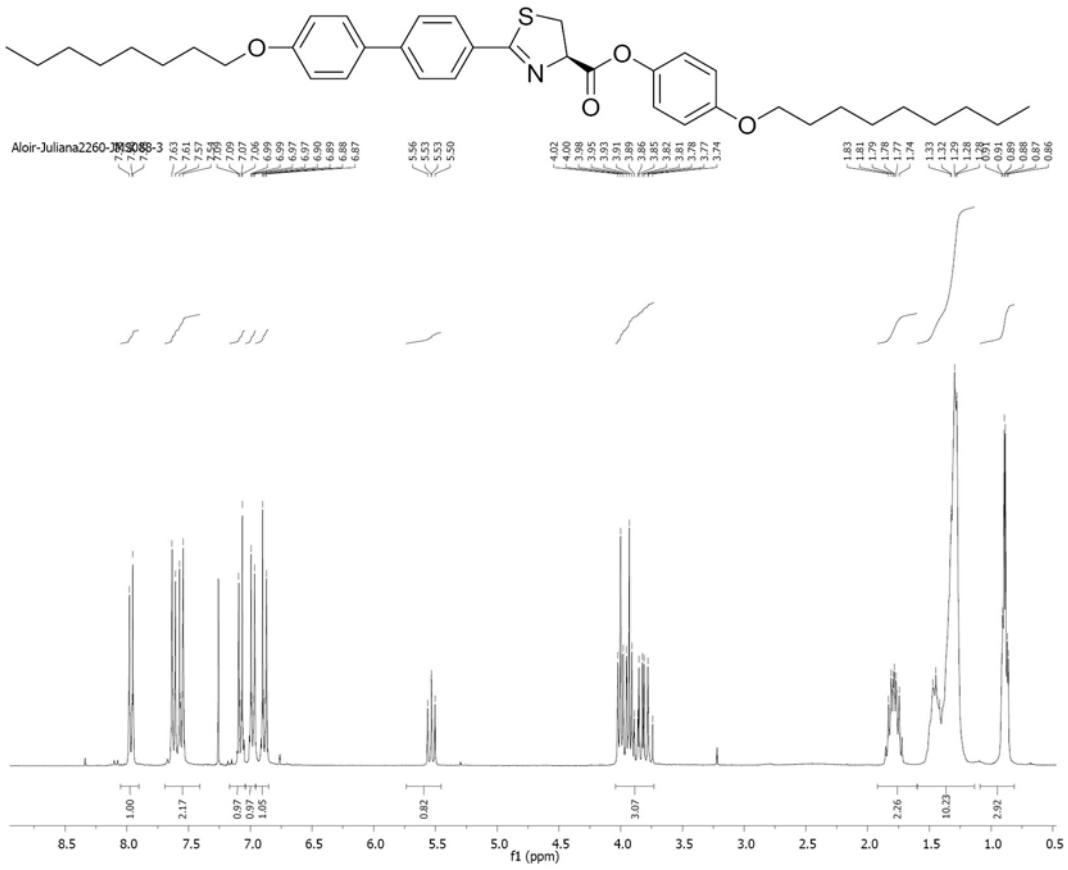
S14. ^{13}C NMR spectra ($CDCl_3$, 100 MHz) of **6f**.



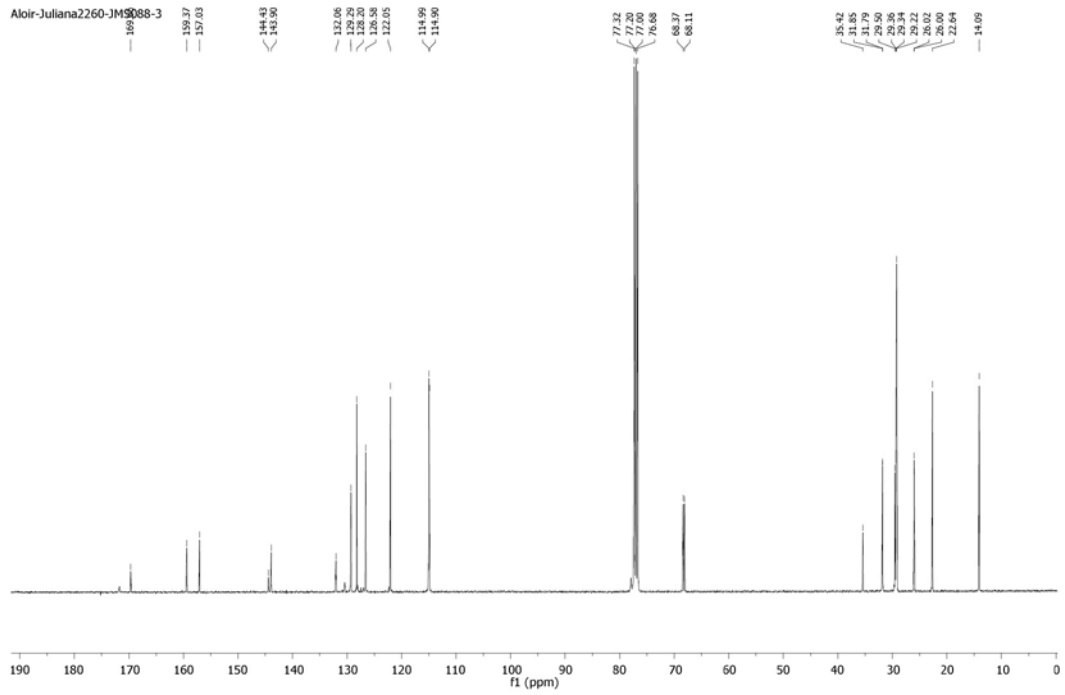
S15. ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of **6h**.



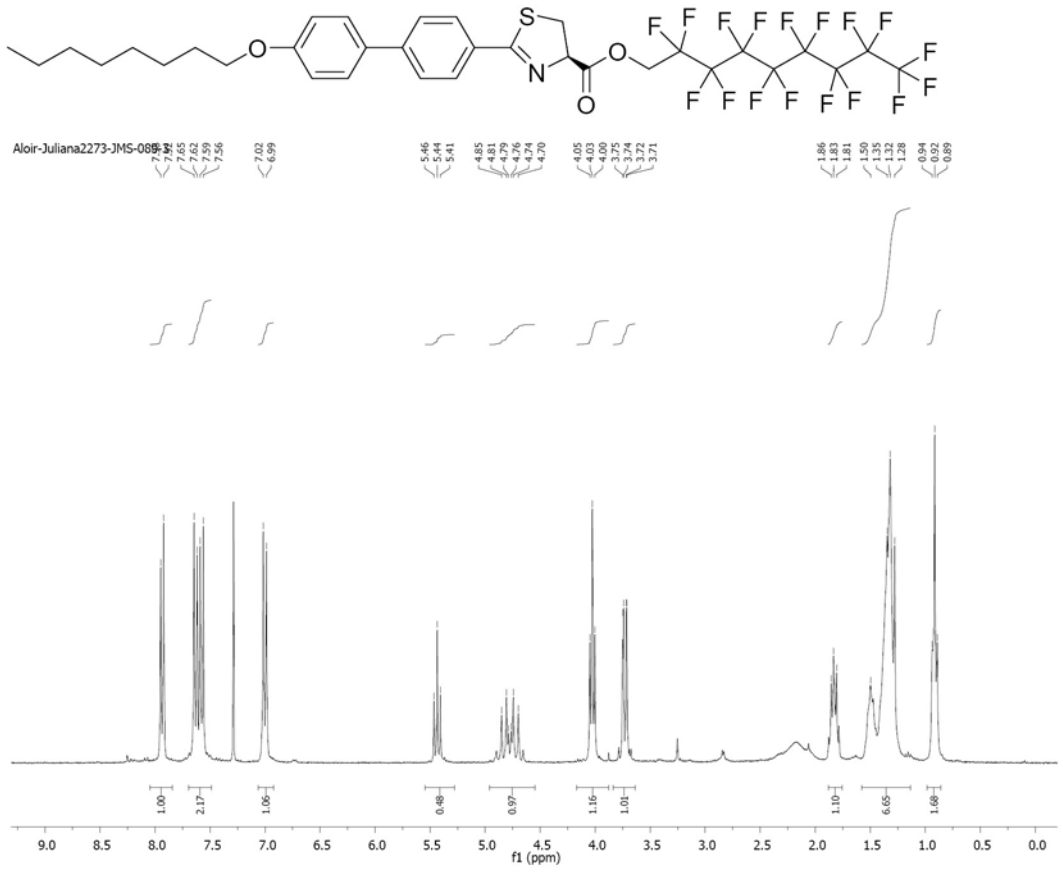
S16. ^{13}C NMR spectra ($CDCl_3$, 75 MHz) of **6h**.



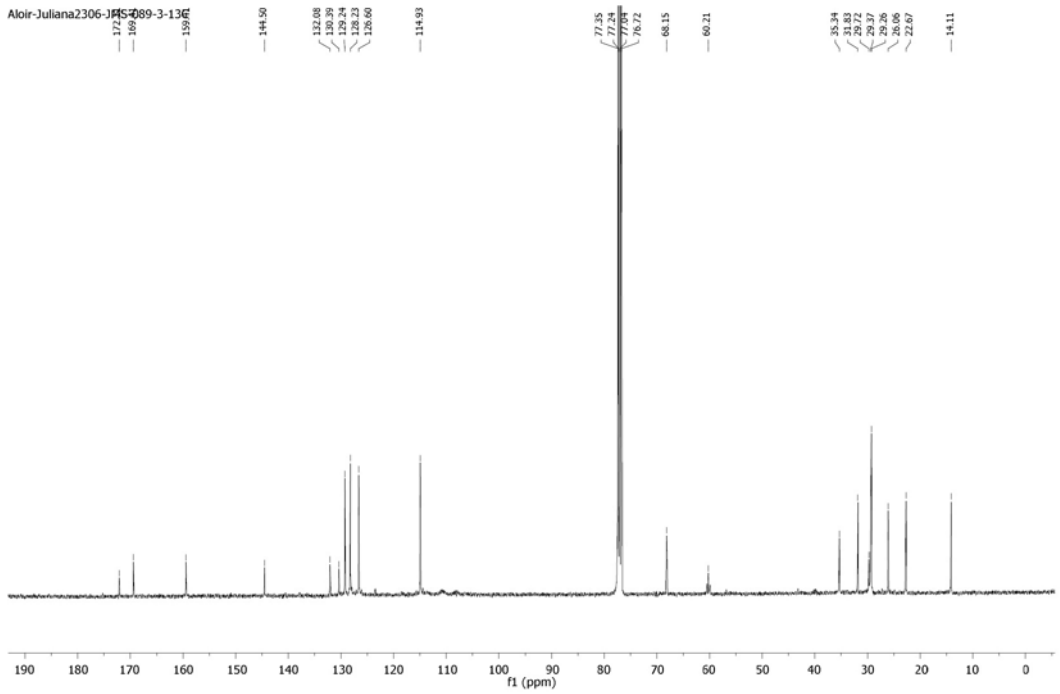
S17. ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of **6k**.



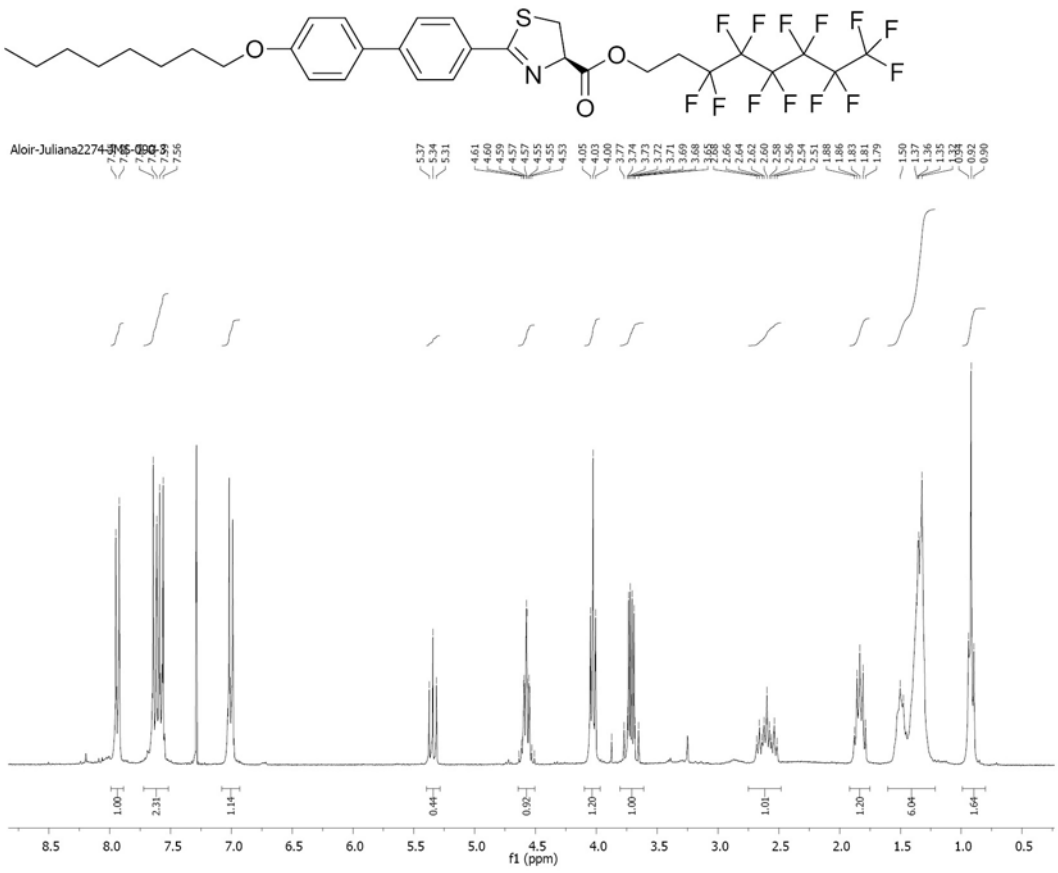
S18. ^{13}C NMR spectra ($CDCl_3$, 75 MHz) of **6k**.



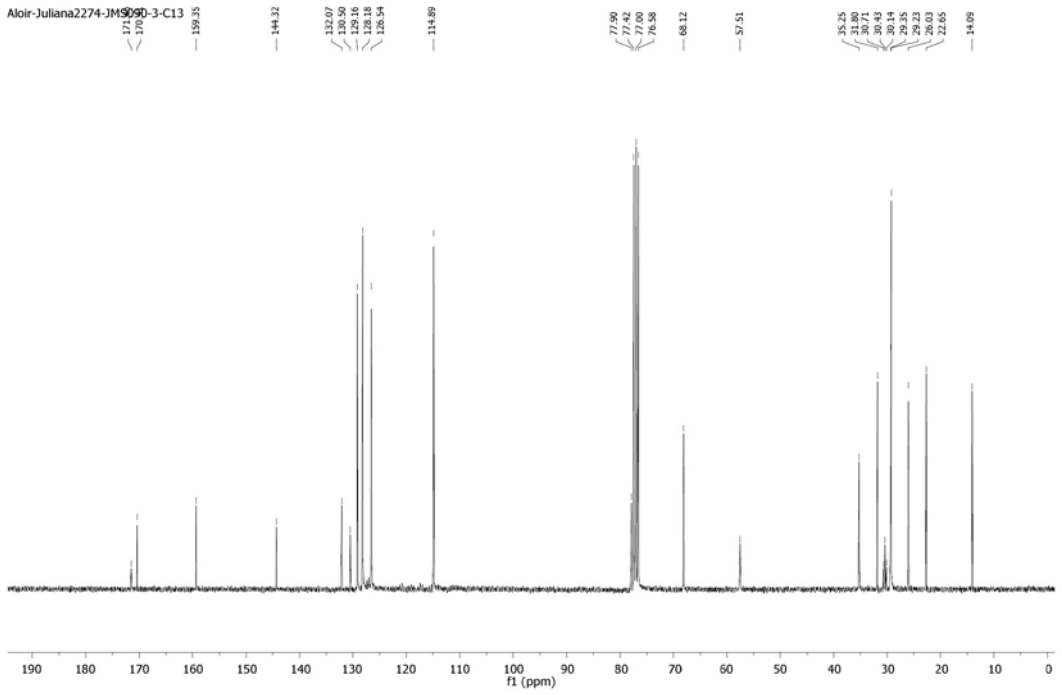
S19. ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of **6i**.



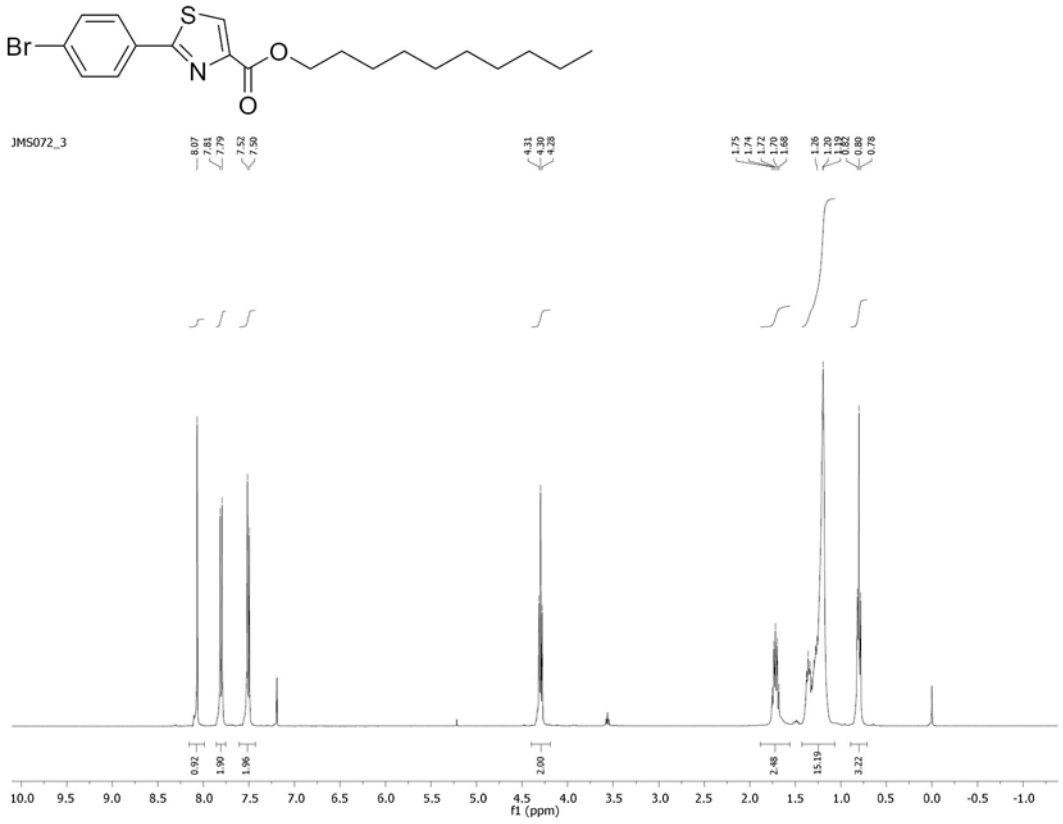
S20. ^{13}C NMR spectra ($CDCl_3$, 75 MHz) of **6i**.



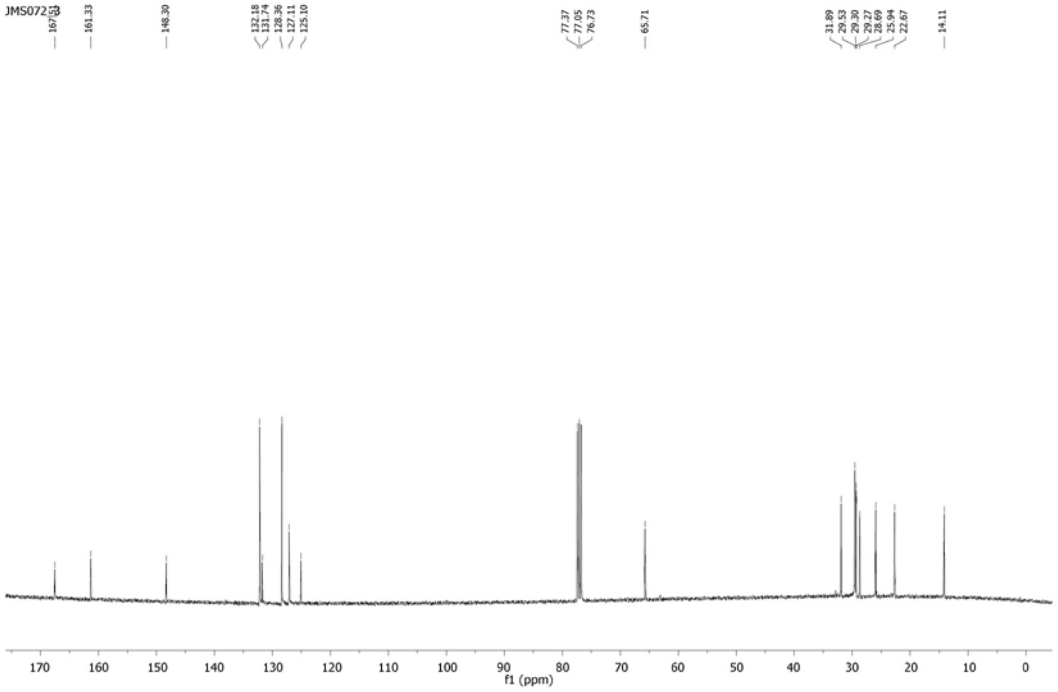
S21. ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of **6j**.



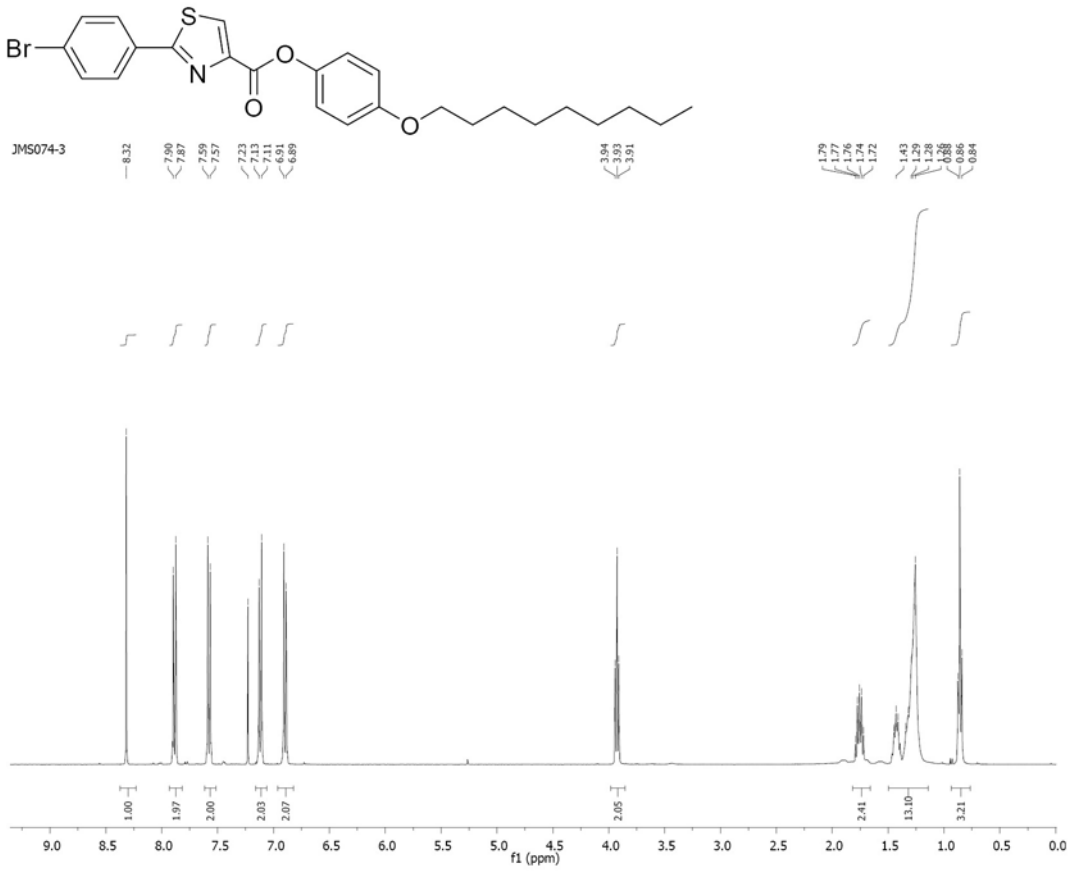
S22. ^{13}C NMR spectra ($CDCl_3$, 75 MHz) of **6j**.



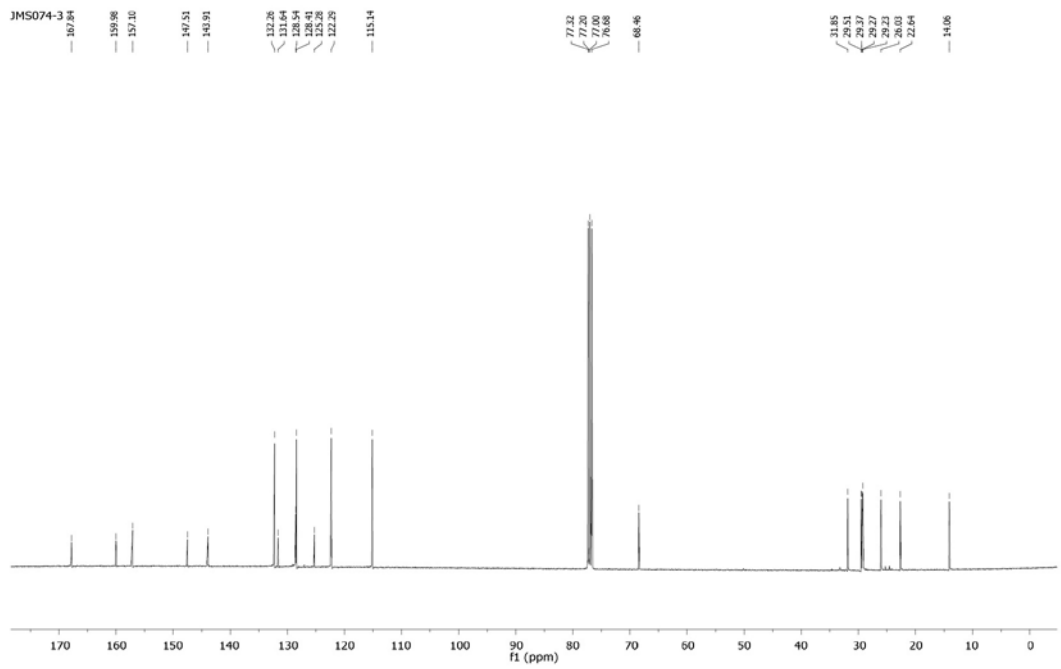
S23. ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of **7a**.



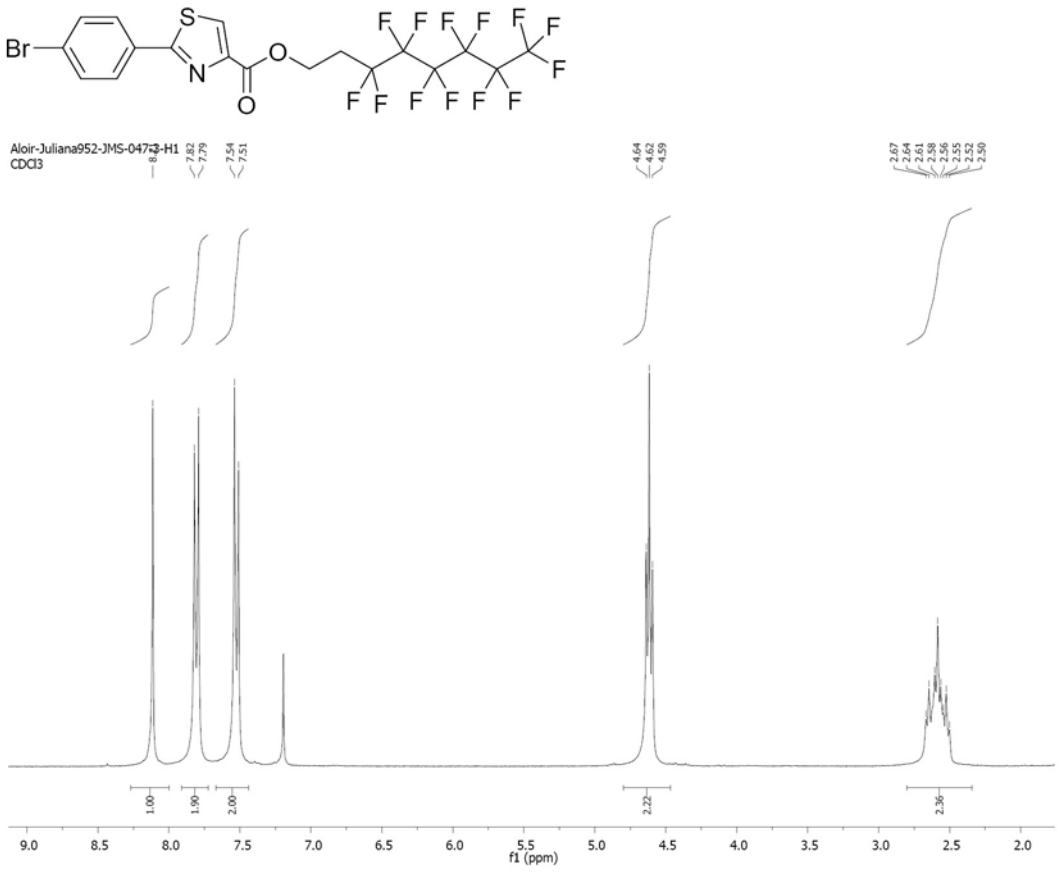
S24. ^{13}C NMR spectra ($CDCl_3$, 100 MHz) of **7a**.



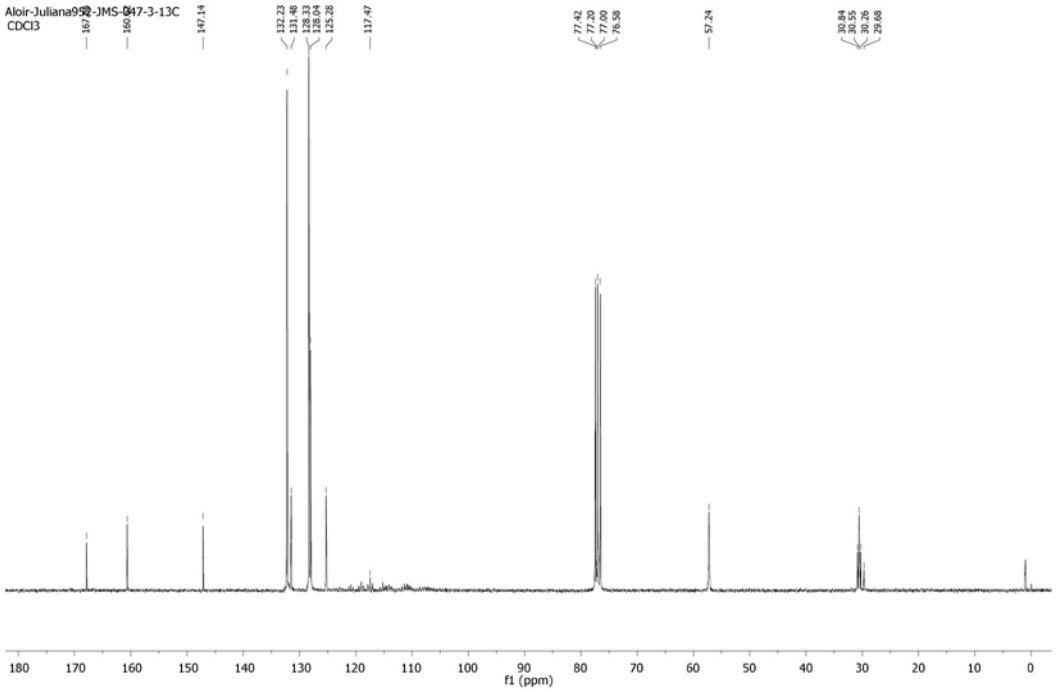
S25. ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of **7c**.



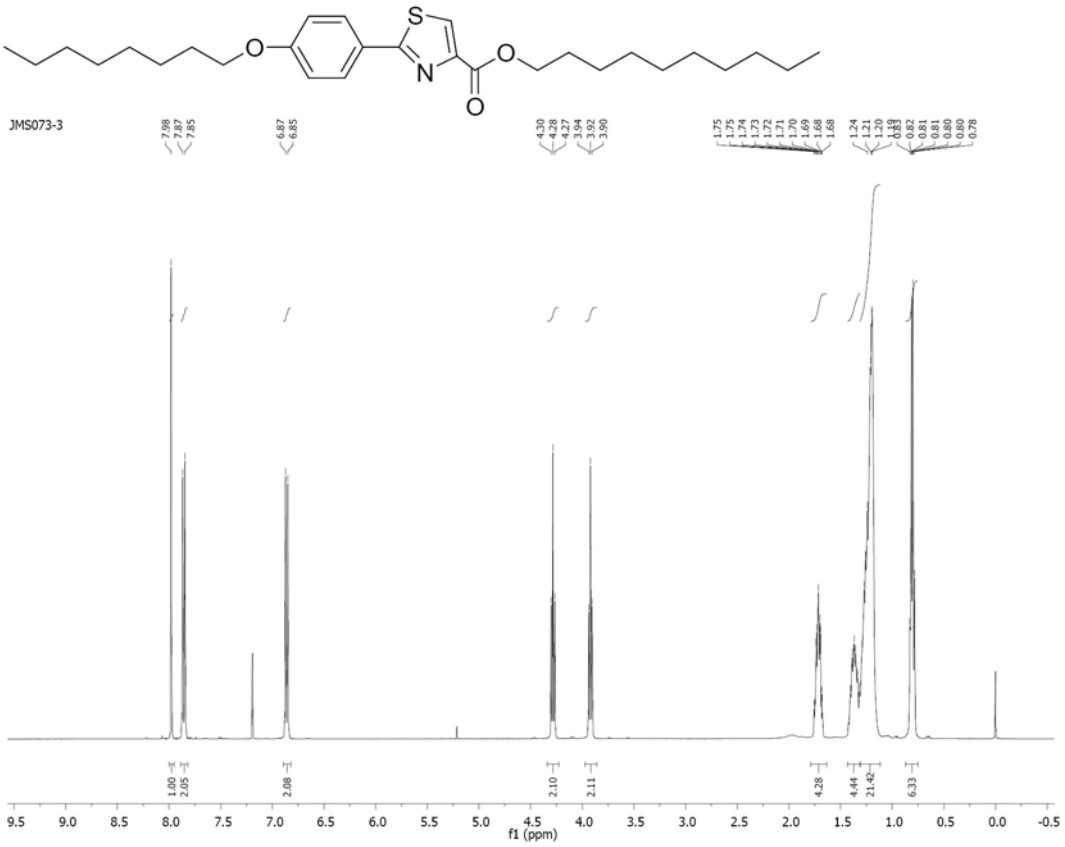
S26. ^{13}C NMR spectra ($CDCl_3$, 100 MHz) of **7c**.



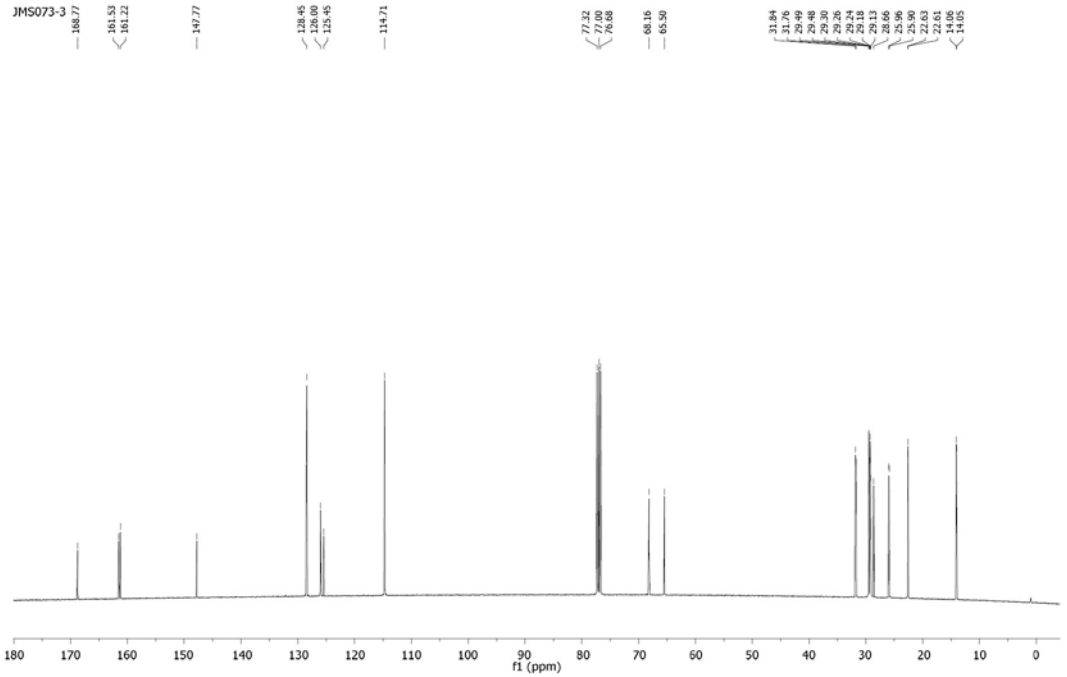
S27. ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of **7b**.



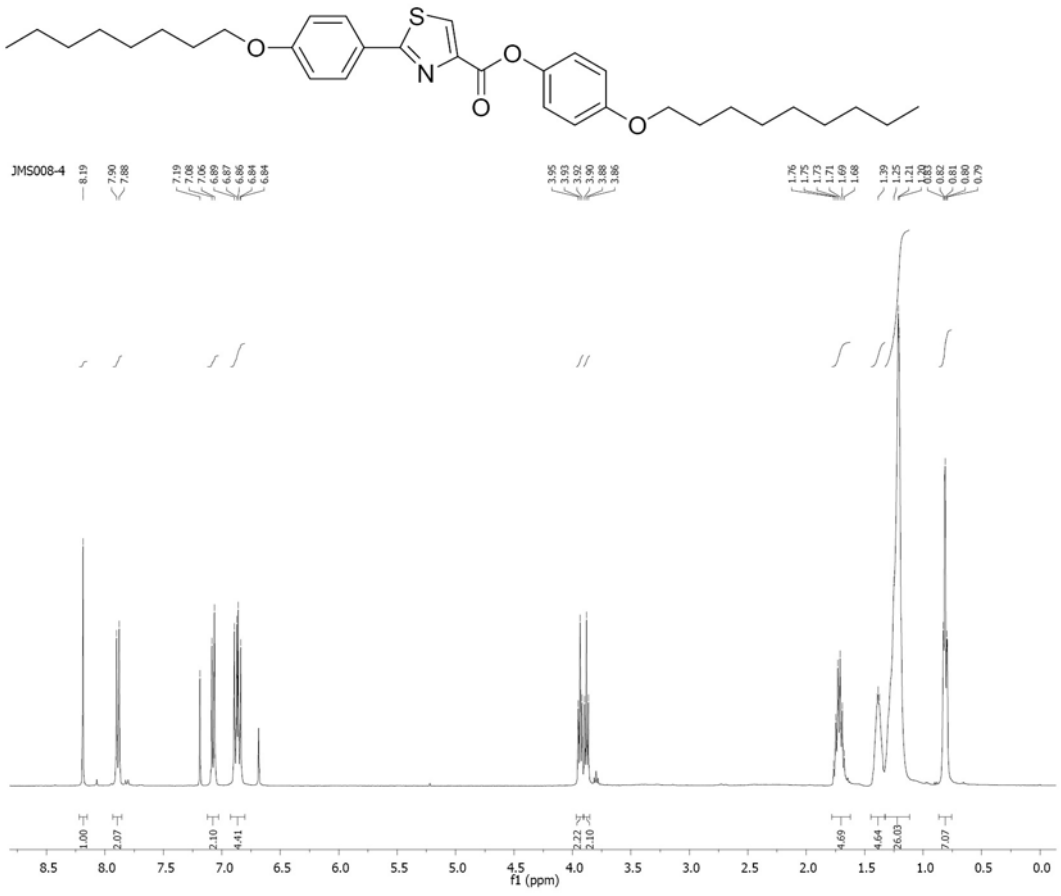
S28. ^{13}C NMR spectra ($CDCl_3$, 75 MHz) of **7b**.



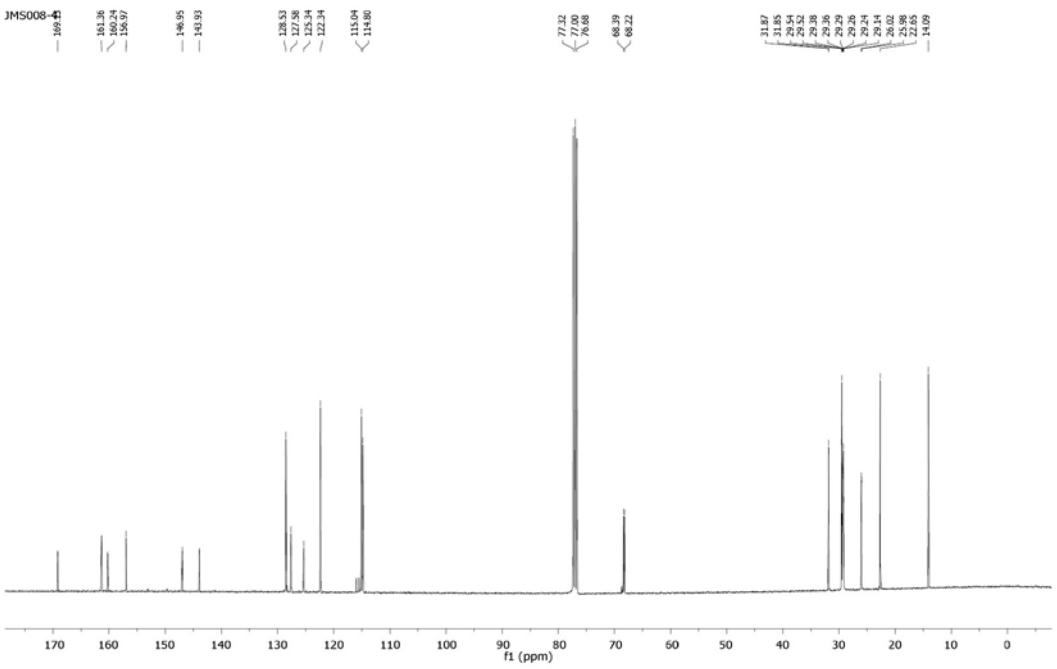
S29. ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of **7d**.



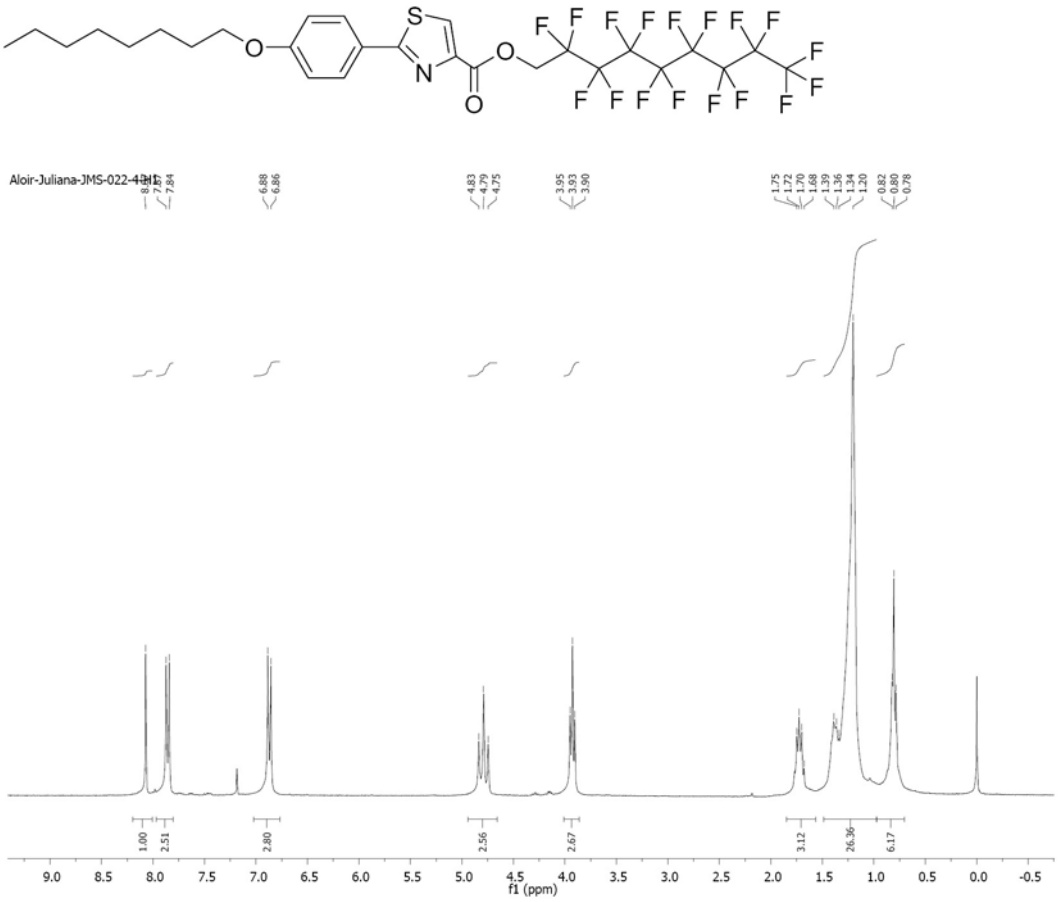
S30. ^{13}C NMR spectra ($CDCl_3$, 100 MHz) of **7d**.



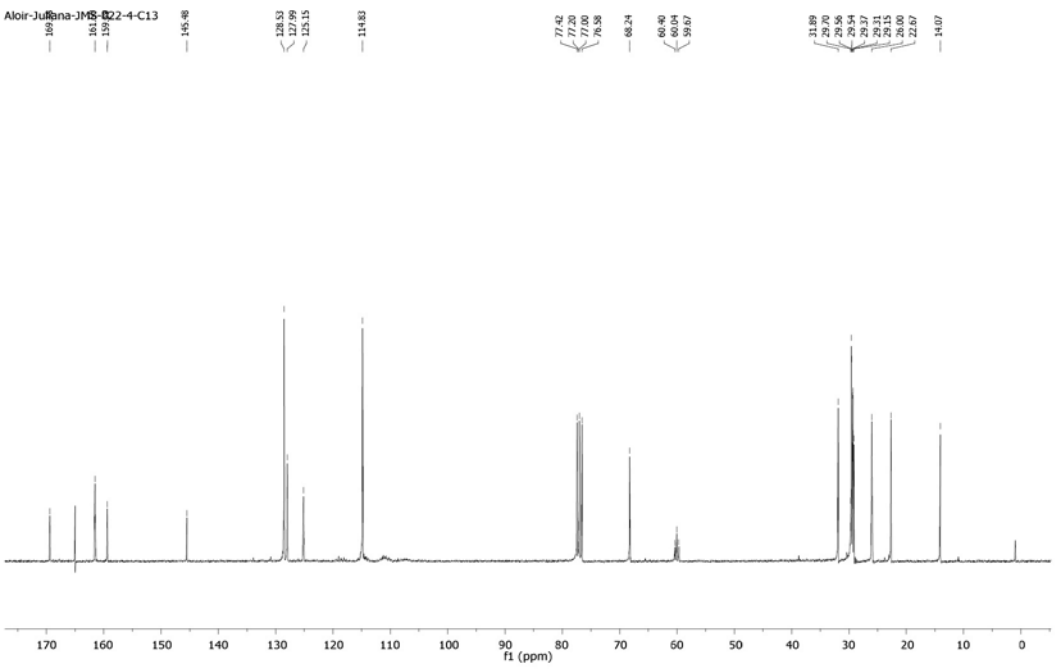
S31. ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of **7g**.



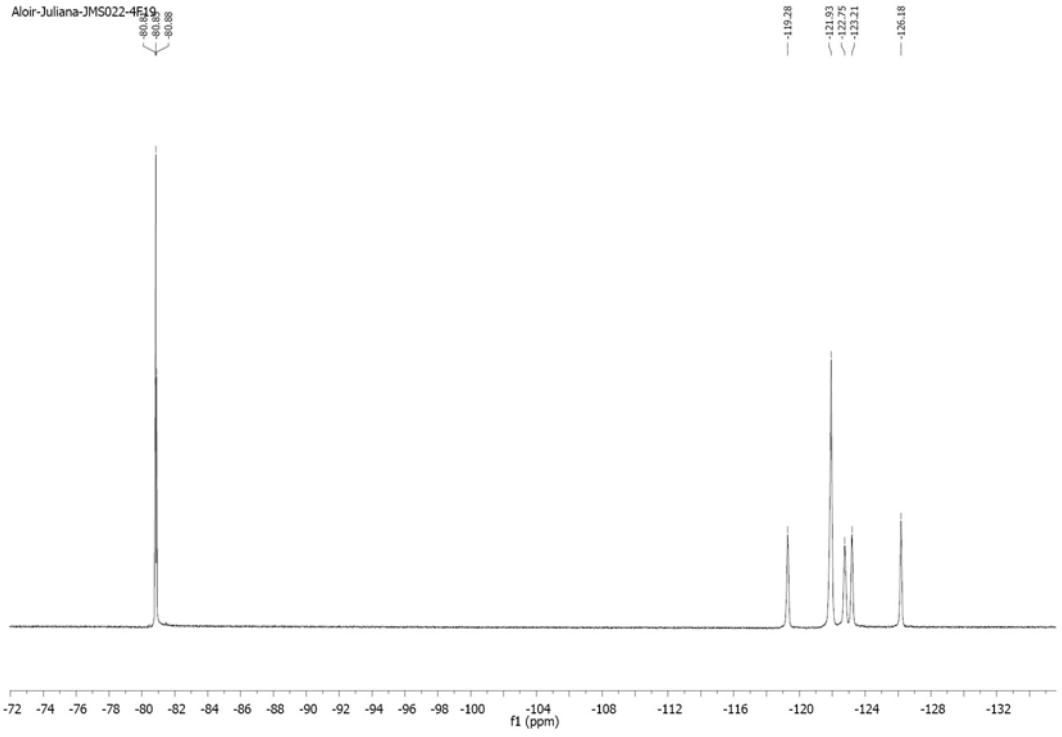
S32. ^{13}C NMR spectra ($CDCl_3$, 100 MHz) of **7g**.



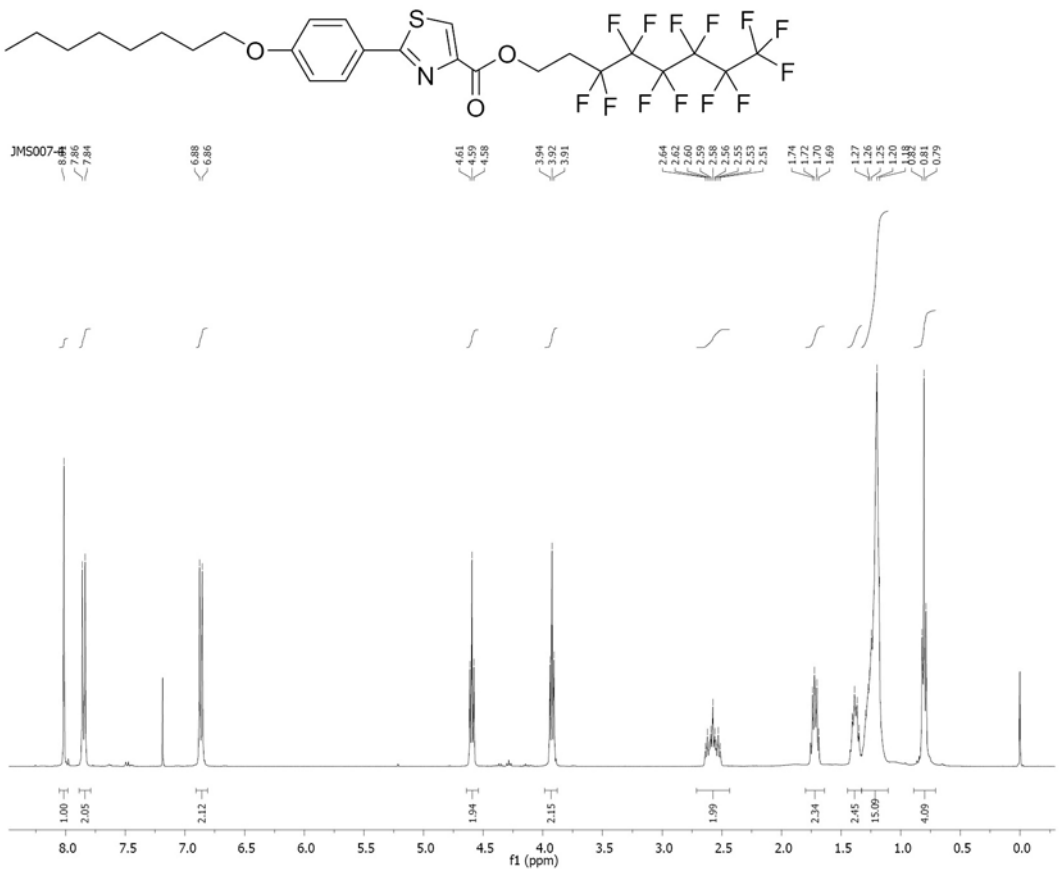
S33. ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of **7e**.



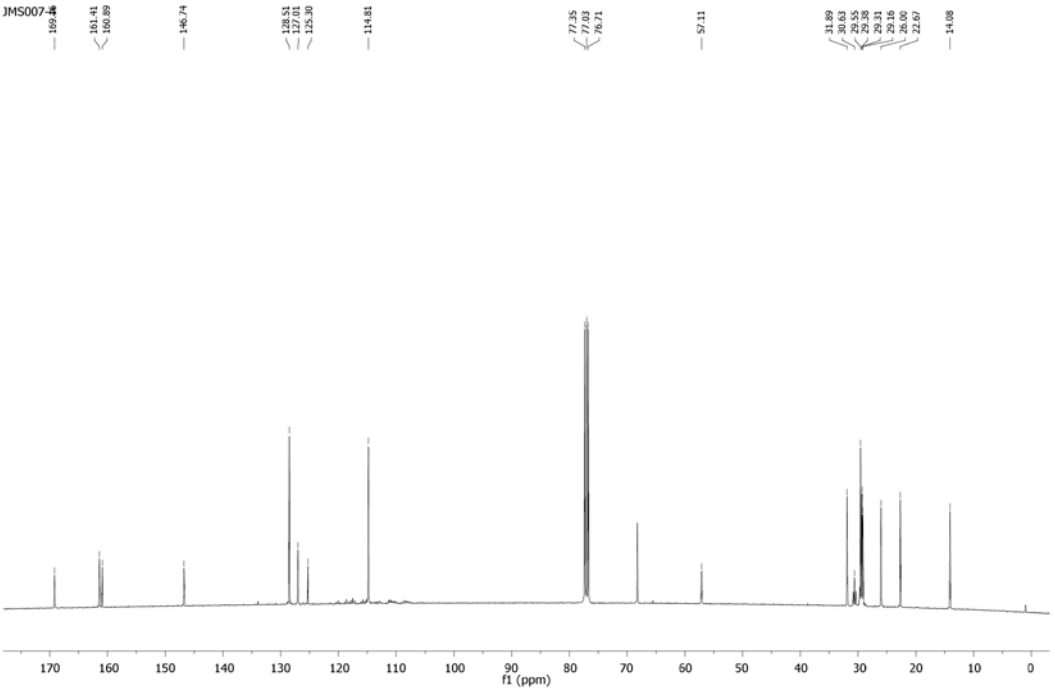
S34. ^{13}C NMR spectra ($CDCl_3$, 75 MHz) of **7e**.



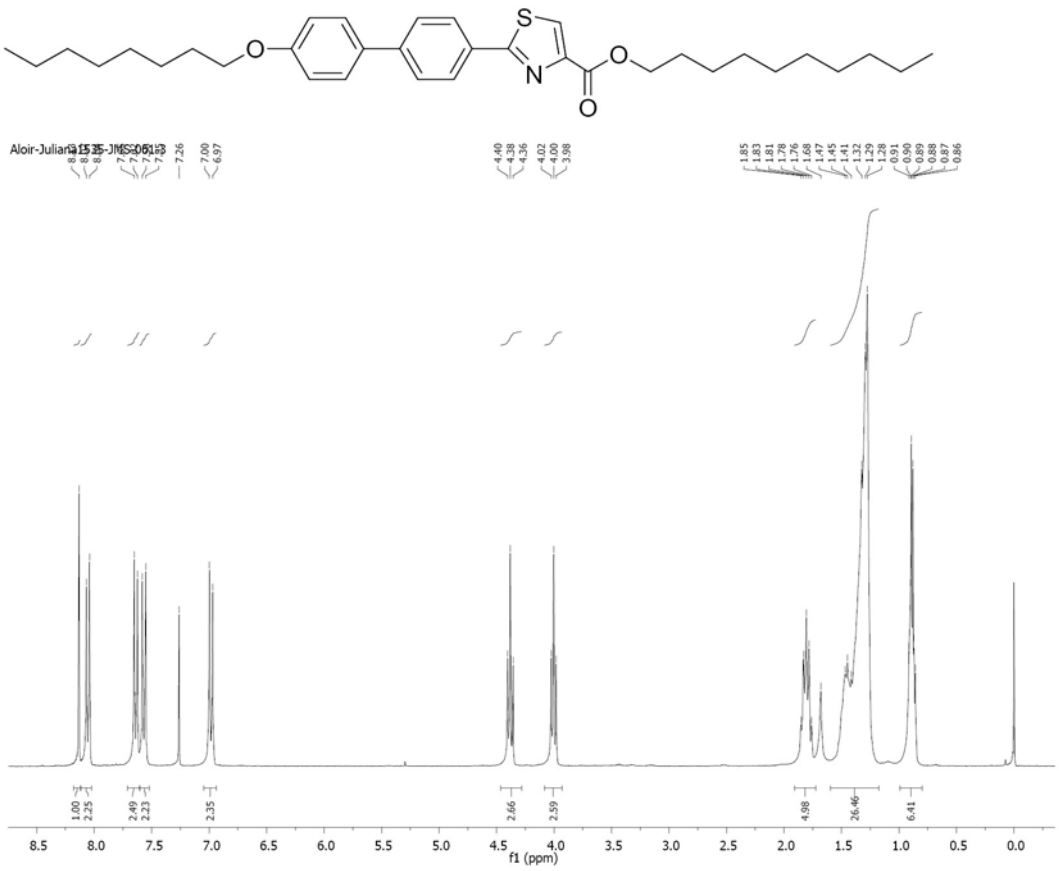
S35. ^{19}F NMR spectra ($CDCl_3/CF_3CO_2H$, 282 MHz) of **7e**.



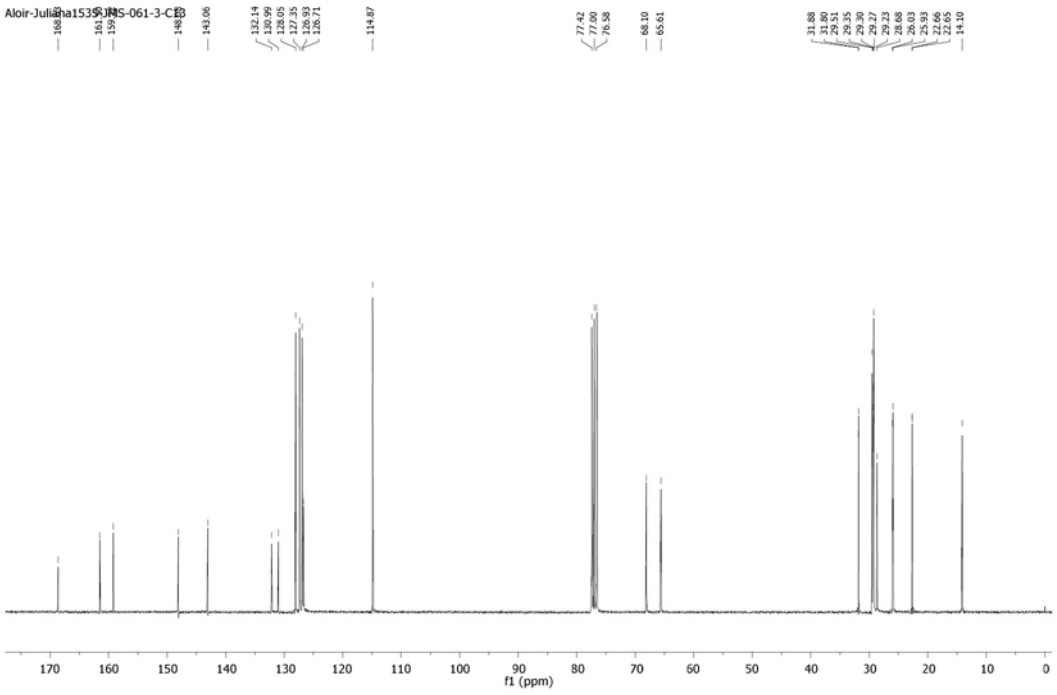
S36. ^{1}H NMR spectra ($CDCl_3$, 400 MHz) of **7f**.



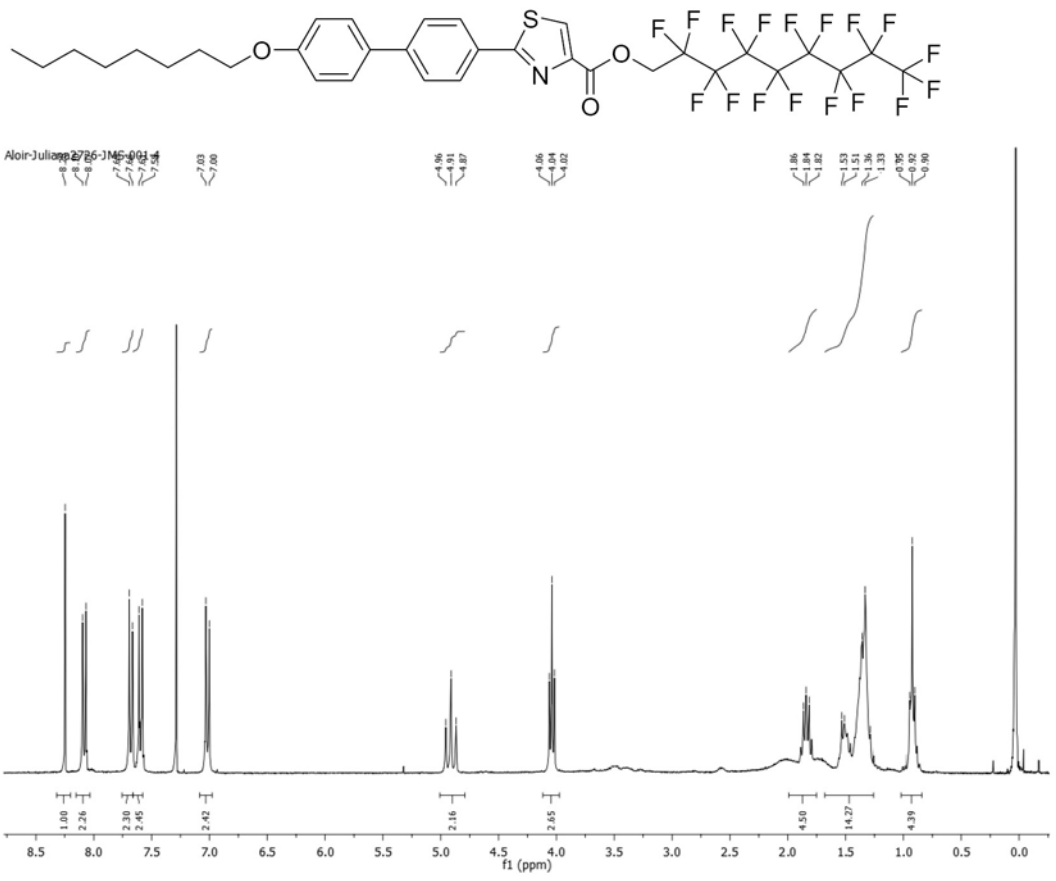
S37. ^{13}C NMR spectra ($CDCl_3$, 100 MHz) of **7f**.



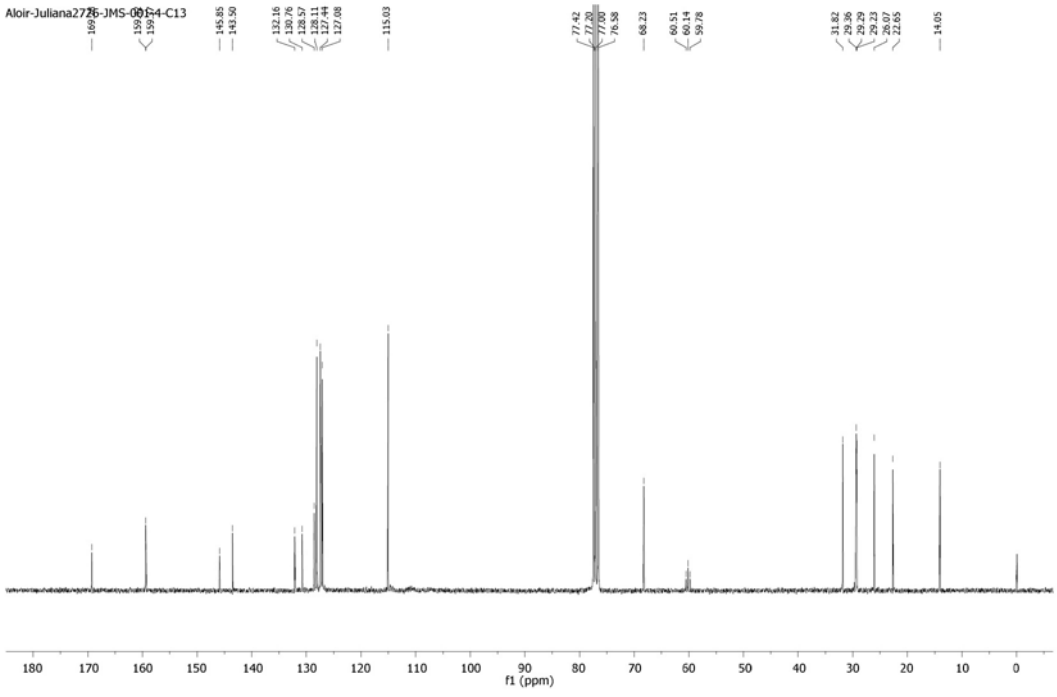
S38. ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of **7h**.



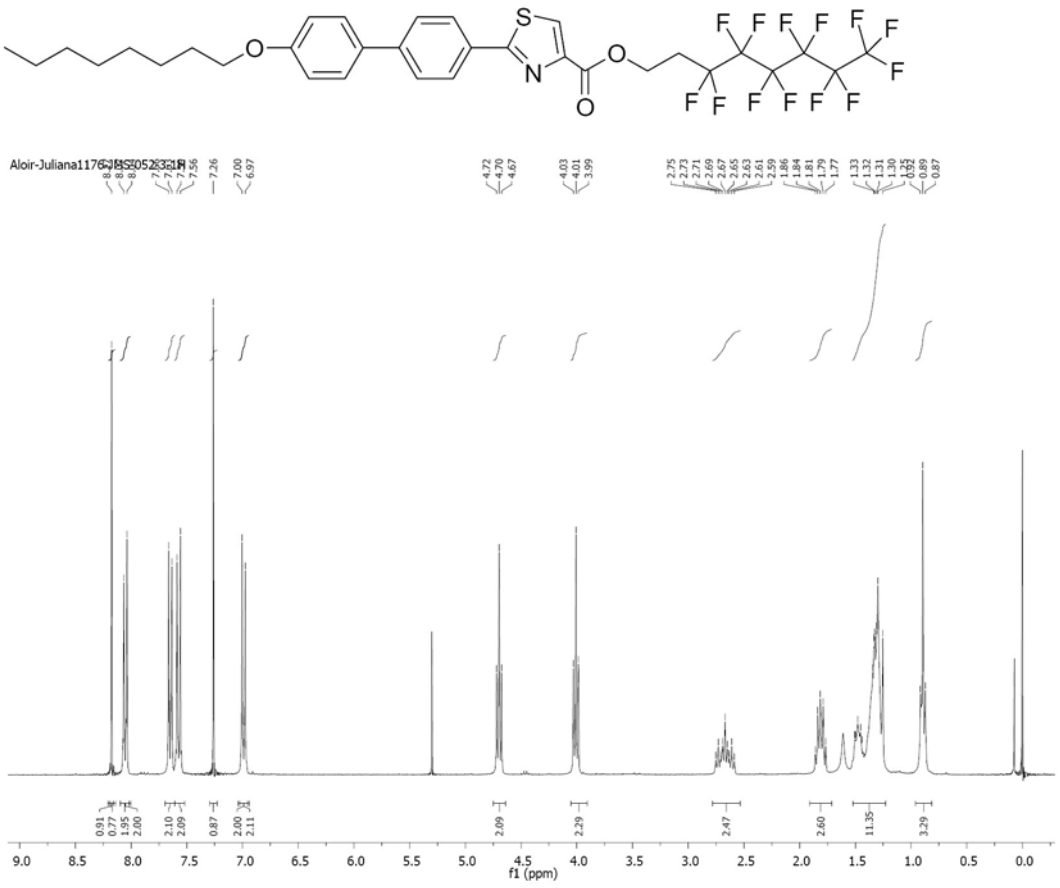
S39. ^{13}C NMR spectra ($CDCl_3$, 75 MHz) of **7h**.



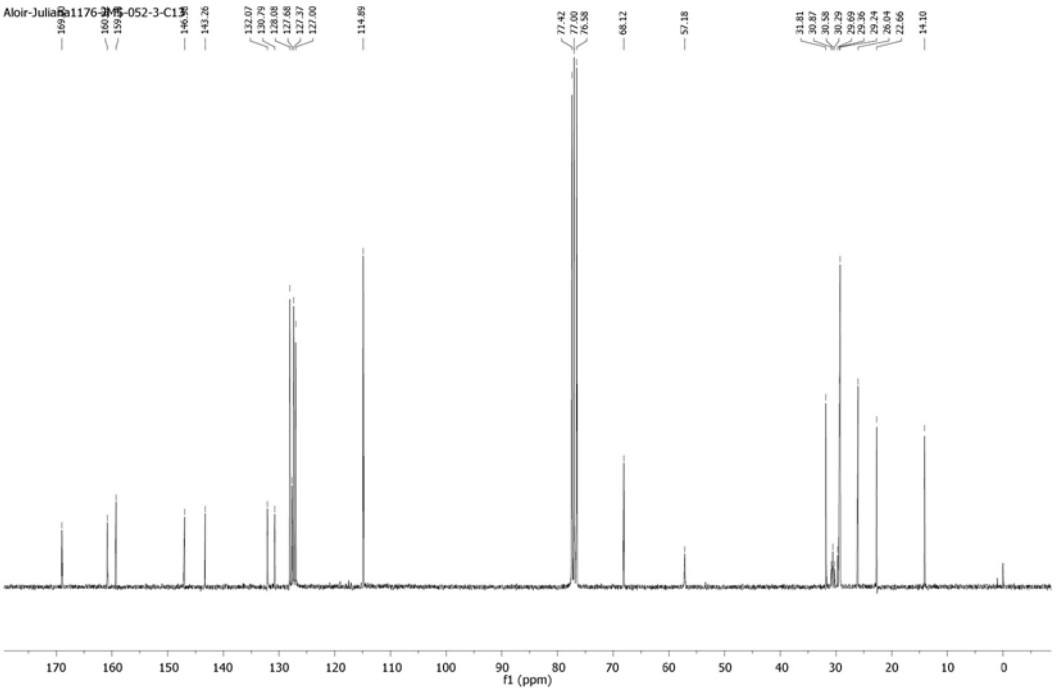
S40. [1]H NMR spectra ($CDCl_3$, 300 MHz) of **7i**.



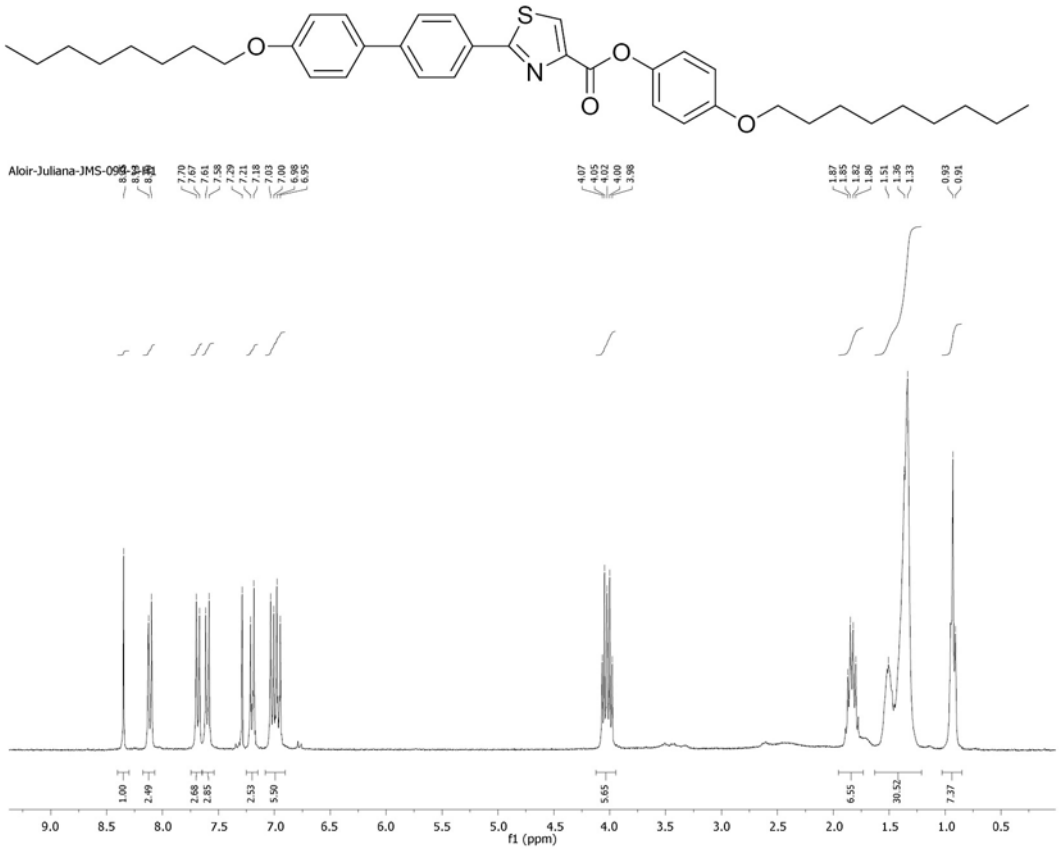
S41. [13]C NMR spectra ($CDCl_3$, 75 MHz) of **7i**.



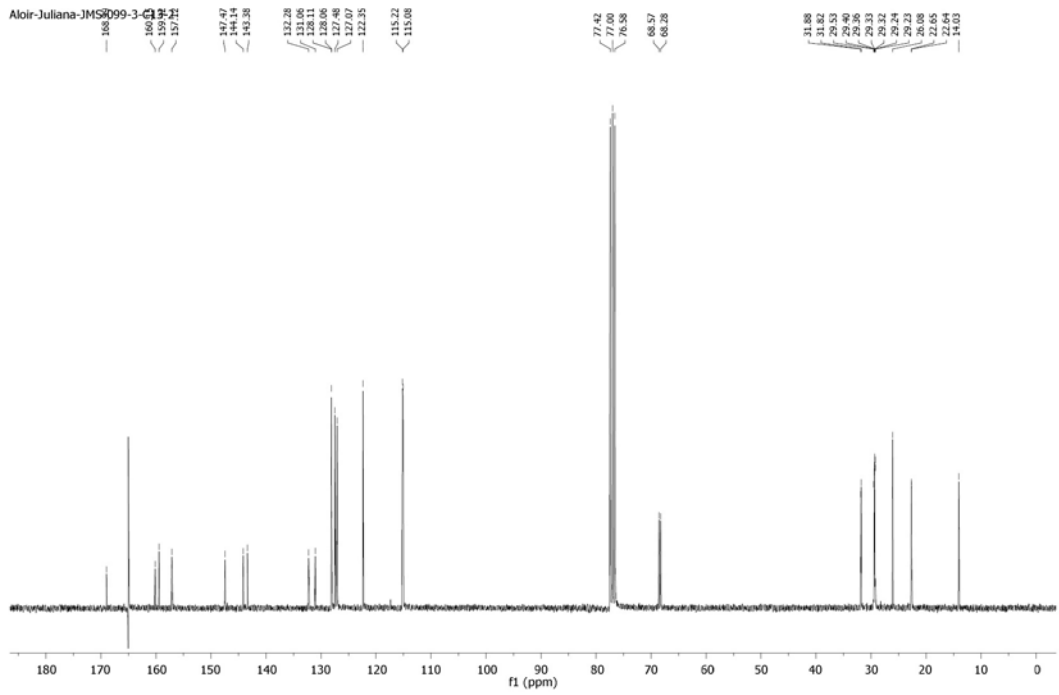
S42. ^{1}H NMR spectra ($CDCl_3$, 300 MHz) of **7j**.



S43. ^{13}C NMR spectra ($CDCl_3$, 75 MHz) of **7j**.



S44. [1]H NMR spectra ($CDCl_3$, 300 MHz) of **7k**.



S45. [13]C NMR spectra ($CDCl_3$, 75 MHz) of **7k**.