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Supporting Information

Versatile One-Pot Synthesis of Benzo-fused Thiacycles by Copper Catalysis

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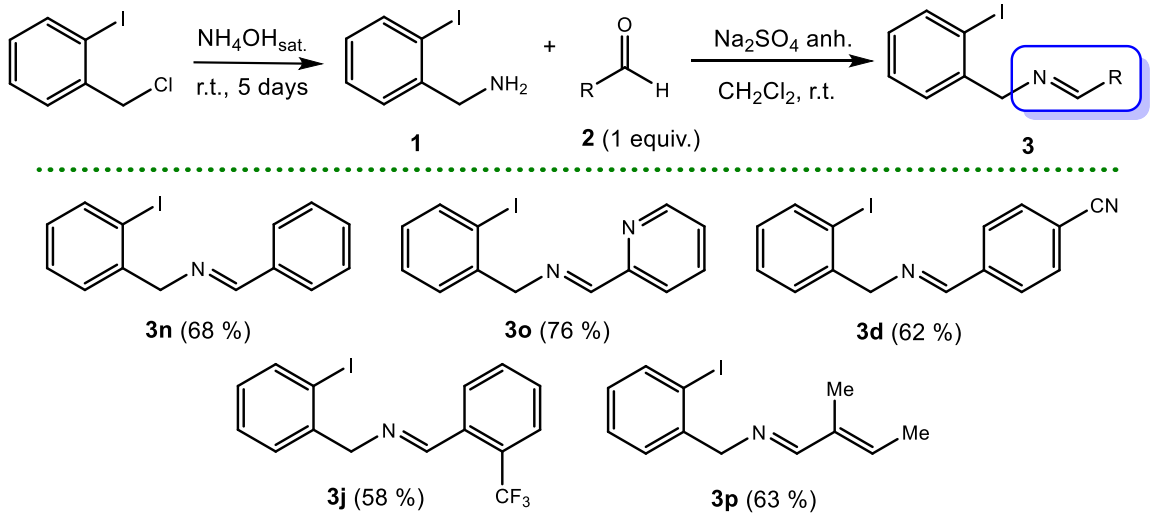
1. General Information

KSCOMe, HSCOPh, aldehydes and standard reagents of the highest grade available, were all purchased from commercial sources and used without further purification. 2-iodophenyl)methanamines (**1a-d**)[1] and *N*-(2-iodobenzyl)-imines (**3**)[2] were synthesized according to established methodologies. Azides **7a-d**[3] and nitriles **12a-e**[4] were prepared by standard substitution procedures with NaN_3 and KCN, respectively.

Toluene was distilled by standard procedures and stored over molecular sieves (4 Å). All the reaction products were isolated by column chromatography (silica gel, pentane/dichloromethane/ethylacetate) from the reaction mixture and characterized by ^{1}H, and ^{13}C NMR and mass spectrometry. ^{1}H and ^{13}C NMR spectra were recorded at 400.16 and 100.62 MHz respectively on a Bruker 400 spectrometer, and all spectra were reported in δ (ppm) relative to Me_4Si, with $CDCl_3$ or $(CD_3)_2CO$ as a solvent. Gas chromatographic analyses were performed on Agilent 5890 with a flame-ionization detector, on 30 m capillary column of a 0.32 mm x 0.25 μm film thickness, with a 5% phenylpolysiloxane phase. GC-MS analyses were conducted on a Shimadzu apparatus by electronic impact (70 eV) positive mode employing a 30 m x 0.25 mm x 0.25 μm with a 5% phenylpolysiloxane phase column. HRMS spectra were recorded on a micrOTOFII LC mass spectrometer. Ionization was achieved by ESI and detection setup on positive mode.

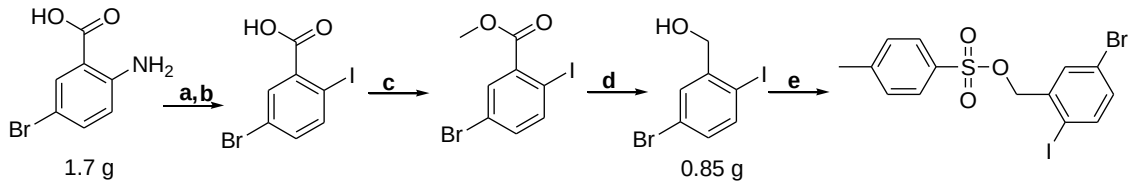
2. General Experimental Procedures

General procedure for the synthesis of imines 3d, j, n-p. In a first step, the precursor (2-iodophenyl)methanamine (**1**) was obtained by reaction of 1-(chloromethyl)-2-iodobenzene and NH_4OH saturated solution, with stirring for 5 days at room temperature. Then, *N*-(2-iodobenzyl)-imines (**3**) derivatives were synthesized by condensation reactions of **1** with a variety of aldehydes, isolated and purified according to established methodologies (Scheme S1).



Scheme S1. Synthesis of imines **3d**, **j, n-p.**

Synthesis of 5-bromo-2-iodobenzyl tosylate:



Conditions: **a**) *i*. 1.1 Equiv. $NaNO_2$, H_2SO_4, 0º C-RT, 30 mL DMSO 1 h; *ii*. 4 Equiv. KI in H_2O (in two portions in 2 h), RT, 6 h; **b**) 150 mL Na_2SO_3 (aqueous sat. soln.), 100 mL EtOAc, 20 min.; **c**) 3 Equiv. Me_2SO_4, 3 Equiv. K_2CO_3, 20 mL MeCN, RT, 8 h; **d**) 2.5 Equiv. $LiAlH_4$, Et_2O, 0º C-RT, 8 h. *Overall yield (after 4 steps) 38 %*; e) 1.5 Equiv. TsCl, 10 Equiv. KOH (finely powdered), 25 mL Et_2O, 0º C-RT, 2 h, *96 %*.

5-Bromo-2-iodobenzyl tosylate was prepared based on traditional procedures starting from commercially available 5-bromo-anthranilic acid, as depicted above. Briefly, the 5-bromo-anthranilic acid (1.7 g, 7.82 mmol) was dissolved in DMSO (30 mL), then H_2SO_4 (50 mL, 30 %) was added and the solution was cooled to 0 °C (ice/NaCl bath). Under stirring, $NaNO_2$ (595 mg, 1.1 equiv.) was added and the ice/NaCl bath was removed. After 1 h at room temperature, KI (2.63 g dissolved in 15 mL of water, 2 equiv.) was added and the stirring continued for 1 h. Then, another portion of KI (2.63 g dissolved in 15 mL of water, 2 equiv.) was added and the stirring continued for 5 h. To this solution, Na_2SO_3 (aqueous sat. soln. 100 mL) and EtOAc (100 mL) were added and stirred for 20 min. Exhaustive extraction of the aqueous phase with EtOAc (3x75 mL) and washing of the combined EtOAc layers with water (3x75 mL), after solvent evaporation, afforded a yellow solid that was subjected to methylation using Me_2SO_4 (3 Equiv.) and K_2CO_3 (3 Equiv.) in MeCN (20 mL) at room temperature and stirred for 8 h. Then MeOH (10 mL) was added and stirred for 20

min. at room temperature in order to consume the remaining Me_2SO_4. The crude was concentrated under vacuum to yield a yellowish oil. This product was submitted to reduction with $LiAlH_4$ (2.5 equiv, 750 mg) in dry Et_2O (20 mL) at 0 °C. Stirring was continued 30 min. at 0 °C and then the temperature evolved until room temperature while stirring for 7 h. After that, the reaction was cooled down to 0 °C, quenched with EtOAc (5 mL) and stirred for 15 min. Then, in order to destroy the greyish suspension, potassium sodium tartrate (La Rochelle' salt) aqueous sat. soln. (30 mL) was added and stirred for additional 15 min. Then, the crude was partitioned with Et_2O (3x75 mL) and water (3x75 mL), the organic layers combined, dried over Na_2SO_4 (anh.) and concentrated to afford the corresponding 5-bromo-4-iodo-benzyl alcohol (0.85 g), as white crystals in 38 % overall yield (4 steps). The identity of this compound was confirmed by comparison with reported NMR data.[5] This compound (0.6 g) was subjected to tosylation by dissolving TsCl (440 mg 1.5 equiv.) in Et_2O (20 mL) containing 5-bromo-4-iodo-benzyl alcohol and further addition of finely powdered KOH (1.07 g, 10 equiv.) at 0 °C. The stirring was continued for 2 h at room temperature.

General experimental procedures for the reactions of amines 1a-d and aldehydes 2 (Table 1).

The reactions were carried out in a 10 mL two-necked Schlenk tube, equipped with a nitrogen gas inlet and a magnetic stirrer. The tube was dried under vacuum, filled with nitrogen and then loaded with dried toluene (4.0 mL). Amine **1** (0.5 mmol) and aldehyde **2** (0.5 mmol) were added to the degassed solvent under nitrogen and stirred at 50 °C for 1 h. Then, **4** (1.5 equiv., 0.75 mmol), CuI (10 mol%, 0.05 mmol) and 1,10-phenanthroline (20 mol%, 0.1 mmol) were added and the reaction was stirred at 100 °C for 24 h. The reaction mixture was cooled to room temperature. Diethyl ether (20 mL) and brine (20 mL) were added and the mixture was stirred. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic extract was dried over Na_2SO_4, and the products were isolated by column chromatography from the crude reaction mixture. The identity of all the products was confirmed by ^{1}H and ^{13}C NMR, GC-MS and HRMS spectrometry.

General experimental procedures for the reactions of imines 3 with KSCOMe (4) (Table 3).

The reactions were carried out in a 10 mL two-necked Schlenk tube, equipped with a nitrogen gas inlet and a magnetic stirrer. The tube was dried under vacuum, filled with nitrogen and then loaded with dried toluene (4.0 mL). Imine **3** (0.5 mmol), CuI (10 mol %), 1,10-phenanthroline (20 mol %) and finally potassium thioacetate (**4**, 0.75 mmol) were added to the degassed solvent under nitrogen

and stirred at 100 °C for 24 h. The reaction mixture was cooled to room temperature. Diethylether (20 mL) and brine (20 mL) were added and the mixture was stirred. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic extract was dried over Na_2SO_4, and the products were isolated by column chromatography from the crude reaction mixture. The identity of all the products was confirmed by ^{1}H and ^{13}C NMR, GC-MS and HRMS spectrometry.

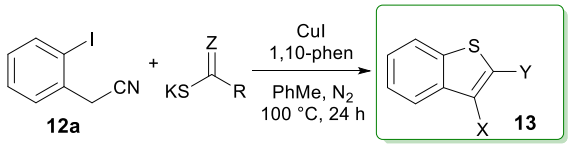
General experimental procedures for the reactions of azido derivatives (7a-c) and commercially available sulfur nucleophiles (Table 4).

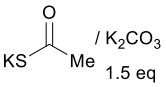
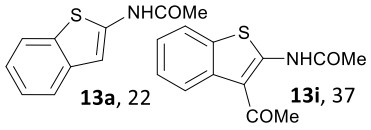
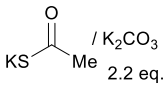
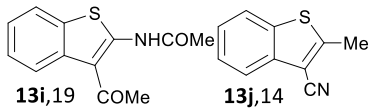
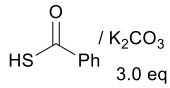
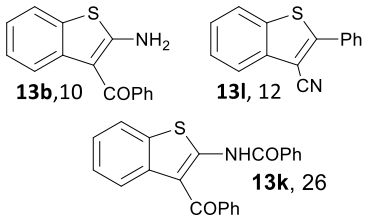
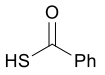
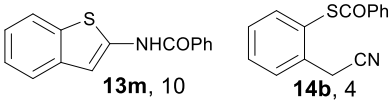
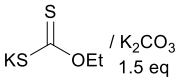
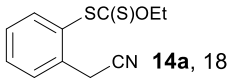
The reactions were carried out in a 10 mL two-necked Schlenk tube, equipped with a nitrogen gas inlet and a magnetic stirrer. The tube was dried under vacuum, filled with nitrogen and then loaded with dried toluene (2.0 mL). Azide **7** (0.25 mmol), CuI (10 mol %), 1,10-phenanthroline (20 mol %) and finally sulfur nucleophile (0.375 mmol) were added to the degassed solvent under nitrogen and stirred at 100 °C for 24 h. The reaction mixture was cooled to room temperature. Diethyl ether (10 mL) and brine (10 mL) were added and the mixture was stirred. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 × 10 mL). The combined organic extract was dried over Na_2SO_4 and the products were isolated by column chromatography from the crude reaction mixture. The identity of all the products was confirmed by ^{1}H and ^{13}C NMR, GC-MS and HRMS spectrometry.

General experimental procedures for the reactions of nitrile derivatives (12a-e) and commercially available sulfur nucleophiles (Table 5).

The reactions were carried out in a 10 mL two-necked Schlenk tube, equipped with a nitrogen gas inlet and a magnetic stirrer. The tube was dried under vacuum, filled with nitrogen and then loaded with dried toluene (2.0 mL). Nitrile **12** (0.25 mmol), CuI (10 mol %), 1,10-phenanthroline (20 mol %) and finally sulfur nucleophile (0.375 mmol) were added to the degassed solvent under nitrogen and stirred at 100 °C for 24 h. The reaction mixture was cooled to room temperature. Diethyl ether (10 mL) and brine (10 mL) were added and the mixture was stirred. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2 × 10 mL). The combined organic extract was dried over Na_2SO_4, and the products were isolated by column chromatography from the crude reaction mixture. The identity of all the products was confirmed by ^{1}H and ^{13}C NMR, GC-MS and HRMS spectrometry.

3. Table S1. Effect of the amount of base on the formation of benzo[*b*]thiophenes **13** from **12a** and thiocarboxylic nucleophiles.[a]



Entry	Nucleophile/base	**13**, isolated yield (%)
1		
2[b]		
3[c]		
4		
5[c]		

[a]Reaction Conditions: **12a** (0.25 mmol), sulfur nucleophile (1.5 equiv., 0.375 mmol), CuI (10 mol%, 0.025 mmol), 1,10-phenanthroline (20 mol%, 0.05 mmol) in toluene (2 mL) at 100 °C for 24 h. Base = eq. of K_2CO_3 added. [b]Together with 40% of the corresponding di-(aryl) sulfide. [c]Together with 20% of the corresponding di-(aryl) sulfide.

4. Characterization Data of Compounds

5-Bromo-2-iodobenzyl tosylate: Upon concentration, the resulting white solid was recrystalised from acetone to render the expected tosylate in 96% isolated yield. ^{1}H-NMR (400MHz, $CDCl_3$): δ = 7.81 (d, J = 8.3 Hz, 2H); 7.60 (d, J = 8.4 Hz, 1H); 7.40 (d, J = 2.2 Hz, 1H); 7.33 (d, J = 8.3 Hz, 2H); 7.11 (dd, J = 8.4; 2.2 Hz, 2H); 5.02 (s, 2H); 2.44 (s, 3H). ^{13}C-NMR (100.62 MHz, $CDCl_3$): δ = 145.2, 140.6, 139.0, 133.4, 132.8, 132.4, 129.9 (2C), 128.0 (2C), 122.7, 95.4, 74.2, 21.6. This compound was used as substrate for the preparation of **1c**, **7c** and **12c**. ESI-HRMS m/z [M + Na]$^+$ calcd for $C_{14}H_{12}BrINaO_3S$ 488.8627, found 488.8652.

(*E*)-*N*-(2-Iodobenzyl)-1-phenylmethanimine (3n): the imine **3n** was isolated by vacuum micro-distillation to afford the pure compound as a light-yellow oil. ^{1}H-NMR (400MHz, $CDCl_3$): δ = 8.44 (s, 1H), 7.87 (dd, *J* = 7.9; 1.0 Hz, 1H), 7.84 – 7.81 (m, 2H), 7.47 – 7.40 (m, 4H), 7.35 (td, *J* = 7.6; 1.1 Hz, 1H), 7.00 – 6.96 (m, 1H), 4.84 (s, 2H). ^{13}C-NMR (100.62 MHz, $CDCl_3$): δ = 163.0, 141.8, 139.2, 136.1, 131.0, 129.3, 128.7, 128.7, 128.4, 128.3, 99.3, 68.9. MS (EI) *m/z* (relative intensity) 322 (M^+ +1, 10), 321 (M^+, 74), 320 (69), 218 (11), 217 (100), 194 (26), 165 (14), 117 (20), 91 (57), 90 (74), 89 (54), 65 (13), 63 (19), 51 (13). ESI-HRMS m/z $[M + H]^+$ calcd for $C_{14}H_{13}IN$ 322.00872, found 322.00923.

(*E*)-*N*-(2-iodobenzyl)-1-(pyridin-2-yl)methanimine (3o): the imine **3o** was isolated by vacuum micro-distillation to afford the pure compound as a brown oil. ^{1}H-NMR (400MHz, $CDCl_3$): δ = 8.66 (ddd, *J* = 4.9; 1.7; 0.9 Hz, 1H), 8.51 (t, *J* = 1.5 Hz, 1H), 8.10 (dt, *J* = 7.9; 1.0 Hz, 1H), 7.87 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.78 – 7.74 (m, 1H), 7.40 – 7.32 (m, 3H), 7.00 – 6.96 (m, 1H), 4.91 (d, *J* = 1.4 Hz, 2H). ^{13}C-NMR (100.62 MHz, $CDCl_3$): δ= 163.7; 154.5; 149.5; 141.2; 139.4; 136.6; 129.6; 128.9; 128.4; 124.9; 121.4; 99.5; 68.6. MS (EI) *m/z* (relative intensity) 322 (M^+, 3), 321 (8), 320 (100), 193 (43), 192 (80), 166 (18), 165 (10), 103 (11), 83 (15), 76 (11), 64 (13), 63 (16), 50 (9). ESI-HRMS m/z $[M + H]^+$calcd for $C_{13}H_{12}IN_2$323.00397, found 323.00525.

(*E*)-4-(((2-Iodobenzyl)imino)methyl)benzonitrile (3d): the imine **3d** was isolated by vacuum micro-distillation to afford the pure compound as a yellow solid. ^{1}H-NMR (400MHz, $CDCl_3$): δ = 8.45 (t, *J* = 1.4 Hz, 1H), 7.91 – 7.86 (m, 3H), 7.72 (dt, *J* = 6.6; 1.8 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.02 – 6.97 (m, 1H), 4.88 (d, *J* = 1.4 Hz, 2H). ^{13}C-NMR (100.62 MHz, $CDCl_3$): δ = 160.8; 141.0; 139.9; 139.4; 132.5; 129.4; 129.0; 128.7; 128.5; 118.5; 114.2; 99.3; 68.9. MS (EI) *m/z* (relative intensity) 346 (M^+, 38), 345 (16), 218 (16), 217 (100), 142 (9), 91 (29), 90 (56), 89 (34), 63 (14), 51 (8). ESI-HRMS m/z $[M + H]^+$alcd for $C_{15}H_{12}IN_2$347.00397, found 347.00360.

(*E*)-*N*-(2-Iodobenzyl)-1-(2-(trifluoromethyl)phenyl)methanimine (3j): the imine **3j** was isolated by vacuum micro-distillation to afford the pure compound as a yellow solid. ^{1}H-NMR (400MHz, $CDCl_3$):δ = 8.82 (d, *J* = 1.6 Hz, 1H), 8.33 (d, *J* = 7.8 Hz, 1H), 7.88 (dd, *J* = 7.9; 1.0 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.40 – 7.33 (m, 2H), 6.99 (td, *J* = 7.8; 2.1 Hz, 1H), 4.90 (d, *J* = 1.1 Hz, 2H). ^{13}C-NMR (100.62 MHz, $CDCl_3$): δ= 159.2; 141.3; 139.4; 134.2; 132.0; 130.3; 129.4; 128.9; 128.5; 128.4; 125.5; 125.6; 122.8; 99.3; 69.2. MS (EI) *m/z*(relative intensity) 389 (M^+, 32), 387 (13), 218 (17), 217 (100), 185 (6), 91 (58), 90 (59), 89 (40), 63 (11), 51 (5). ESI-HRMS m/z $[M + H]^+$calcd for $C_{15}H_{12}F_3IN$ 389.99610, found 389.99601.

(1*E*,2*E*)-*N*-(2-Iodobenzyl)-2-methylbut-2-en-1-imine (3p): the imine **3p** was isolated by vacuum micro-distillation to afford the pure compound asa yellow oil.^{1}H-NMR (400MHz, $CDCl_3$): δ = 7.94 (s, 1H), 7.83 (d, *J* = 7.7 Hz), 7.32 (dd, *J* = 4.9; 0.8 Hz, 2H), 6.95 (qd, *J* = 8.0; 4.0 Hz, 1H), 6.04 – 5.99 (m, 1H), 4.66 (s, 2H), 1.92 (dd, *J* = 1.08; 1.12 Hz, 3H), 1.87 (d, *J* = 7.2 Hz, 3H).^{13}C-NMR (100.62 MHz, $CDCl_3$): δ = 167.6; 142.4; 139.2; 137.3; 137.1; 129.2; 128.6; 128.4; 99.3; 68.6; 14.4; 11.4. MS (EI) *m/z* (relative intensity) 300 (M^+ +1, 13), 299 (M^+, 93), 284 (75), 218 (11), 217 (100), 157 (18), 156 (14), 144 (10), 117 (10), 116 (10), 96 (13), 91 (40), 90 (76), 89 (64), 82 (60), 65 (14), 63 (21), 41 (23). ESI-HRMS m/z $[M + H]^+$calcd for $C_{12}H_{15}IN$ 300.02437, found 300.02315.

1-(2-(Pyridin-4-yl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5a): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with dichloromethane/ethylacetate) to afford pure **5a** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): mixture of interconverting rotational isomers with respect to *N*-formyl bond, at a 1:0.4 ratio (major : minor isomers), δ = 8.53 (d, *J* = 4.6 Hz, 2H, H-3' and H-5'), 8.52 (d, *J* = 4.6 Hz, 2H, H-3' and H-5'), 7.29 – 7.10 (m, 10H, H-2' H-6' and H-5 to H-8), 7.02 (s, 1H, H-2, major isomer), 6.14 (s, 1H, H-2, minor isomer), 4.96 (d, *J* = 15.8 Hz, 1H, H_2-4a, minor isomer), 4.62 (d, *J* = 15.8 Hz, 1H, H_2-4a, major isomer), 4.48 (d, *J* = 15.8 Hz, 1H, H_2-4b, minor isomer), 4.35 (d, *J* = 15.8 Hz, 1H, H_2-4b, major isomer), 2.29 (s, 3H, H_3-12, major isomer), 2.16 (s, 3H, H_3-12, minor isomer). ^{13}C NMR (100.62 MHz, $CDCl_3$): mixture of interconverting rotational isomers: δ = 169.9 (C, CO-11, major isomer); 169.9 (C, CO-11, minor isomer); 150.2 (CH, C-3' and C-5', minor isomer); 150.0 (CH, C-3' and C-5', major isomer); 148.4 (C, C-1', minor isomer); 148.3 (C, C-1', major isomer); 134.1 (C, C-10); 131.8 (C, C-9, major isomer); 131.4 (C, C-9, minor isomer); 129.9 (C, C-10); 128.8; 128.7; 128.4; 128.1; 127.2; 127.0; 126.1; 125.8; 122.1 (CH, C-2' and C-6', major isomer); 121.2 (CH, C-2' and C-6', minor isomer); 60.2 (CH, C-2, minor isomer); 55.5 (CH, C-2, major isomer); 46.5 (CH_2, C-4, major isomer); 44.0 (CH_2, C-4, minor isomer); 22.2 (CH_3, C-12, minor isomer); 22.1 (CH_3, C-12, major isomer). MS (EI) *m/z* (relative intensity) 270 (M^+, 27), 227 (100), 212 (33), 211 (29), 196 (18), 195 (26), 175 (16), 168 (15), 149 (16), 148 (20), 147 (19), 136 (21), 124 (40), 123 (53), 122 (35), 117 (26), 93 (65), 82 (20), 78 (38), 77 (36), 73 (30), 51 (25), 45 (41), 43 (71). ESI-HRMS m/z $[M + H]^+$ calcd for $C_{15}H_{15}N_2OS$ 271.08996, found 271.08897.

1-(2-(4-Bromophenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5b): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with dichloromethane/ethylacetate) to afford pure **5b** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$):

mixture of interconverting rotational isomers with respect to *N*-formyl bond, at a 1:0.5 ratio (major : minor isomers), δ =7.42 (bd, *J* = 8.4 Hz, 4H, H-3' and H-5'), 7.31 – 7.06 (m, 12H, H-2' H-6' and H-5 to H-8),7.05 (s, 1H, H-2, major isomer), 6.13 (s, 1H, H-2, minor isomer), 5.07 (d, *J* = 15.7 Hz, H_2-4a, 2H, minor isomer), 4.56 (d, *J* = 16.0 Hz, H_2-4a, 2H, major isomer), 4.29 (d, *J* = 15.7 Hz, H_2-4b, 2H, minor isomer), 4.29 (d, *J* = 16.0 Hz, H_2-4b, 2H, major isomer), 2.23 (s, 3H, H_3-12, major isomer), 2.15 (s, 3H, H_3-12, minor isomer). ^{13}C NMR (100.62 MHz, $CDCl_3$): mixture of interconverting rotational isomers: δ = 169.8 (C, CO-11, minor isomer), 169.6 (C, CO-11, major isomer), 138.3, 138.1, 134.2, 132.1, 131.9, 131.7, 131.4, 130.6, 129.2, 128.5, 128.3, 128.2, 127.9, 127.9, 127.0, 126.6, 125.6, 122.3, 122.1, 60.7 (CH, C-2, minor isomer), 55.7 (CH, C-2, major isomer), 45.9 (CH_2, C-4, major isomer), 43.5 (CH_2, C-4, minor isomer), 22.2 (CH_3, C-12, minor isomer), 22.1 (CH_3, C-12, major isomer). ESI-HRMS m/z $[M + H]^+$ calcd for $C_{16}H_{15}BrNOS$ 348.00522, found 348.00650.

1-(2-(4-Chlorophenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5c): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with dichloromethane/ethylacetate) to afford pure **5c** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): mixture of interconverting rotational isomers with respect to *N*-formyl bond, at a 1:0.5 ratio (major : minor isomers), δ = 7.38-7.36 (bd, *J* = 8.4 Hz, 4H, H-3' and H-5'), 7.27-7.01 (m, 12H, H-2' H-6' and H-5 to H-8), 7.07 (s, 1H, H-2, major isomer), 6.15 (s, 1H, H-2, minor isomer), 5.08 (d, *J* = 15.6 Hz, 2H, H_2-4a, minor isomer), 4.56 (d, *J* = 16.0 Hz, 2H, H_2-4a, major isomer), 4.32 (d, *J* = 15.6 Hz, 2H, H_2-4b, minor isomer), 4.28 (d, *J* = 16.0 Hz, 2H, H_2-4b, major isomer), 2.23 (s, 3H, H_3-12, major isomer), 2.15 (s, 3H, H_3-12, minor isomer). ^{13}C NMR (100.62 MHz, $CDCl_3$): mixture of interconverting rotational isomers: δ = 169.8 (C, CO-11, minor isomer), 169.6 (C, CO-11, major isomer), 137.8, 137.5, 134.2, 134.2, 133.9, 132.1, 131.4, 130.7, 130.7, 128.9, 128.7, 128.5, 128.3, 128.2, 127.9, 127.9, 127.0, 126.6, 125.6, 60.6 (CH, C-2, minor isomer), 55.6 (CH, C-2, major isomer), 45.8 (CH_2, C-4, major isomer), 43.4 (CH_2, C-4, minor isomer), 22.2 (CH_3, C-12, minor isomer), 22.1 (CH_3, C-12, major isomer). ESI-HRMS m/z $[M + H]^+$ calcd for $C_{16}H_{15}ClNOS$ 304.05574, found 304.05480.

4-(3-Acetyl-3,4-dihydro-2*H*-benzo[*e*][1,3]thiazin-2-yl)benzonitrile (5d): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether/diethyl ether) to afford pure **5d** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): mixture of interconvertingrotational isomers with respect to *N*-formyl bond, at a 1:0.4 ratio (major :minor isomers), δ = 7.49 (d, *J* = 8.2 Hz, 2H, H-2' and H-6', major isomer, overlapping); 7.49 (d, *J* = 8.2

Hz, 2H, H-3' and H-5', minor isomer, overlapping), 7.41 (d, *J* = 8.2 Hz, 2H, H-3' and H-5', major isomer), 7.33 (d, *J* = 8.2 Hz, 2H, H-2' and H-6', minor isomer), 7.20 – 7.05 (m, 8H, H-5 to H-8), 6.96 (s, 1H, H-2, major isomer), 6.13 (s, 1H, H-2, minor isomer), 4.89 (d, *J* = 15.7 Hz, 1H, H_2-4a, minor isomer), 4.55 (d, *J* = 15,8 Hz, 1H, H_2-4a, major isomer), 4.39 (d, *J* = 15,7 Hz, 1H, H_2-4b, minor isomer), 4.28 (d, *J* = 15,8 Hz, 1H, H_2-4b, major isomer), 2.20 (s, 3H, H_3-12, major isomer), 2.07 (s, 3H,H_3-12, minor isomer). ^{13}C NMR (100.62 MHz, $CDCl_3$): mixture of interconverting rotational isomers: δ = 170.4 (C, CO-11, minor isomer); 169.9 (C, CO-11, major isomer); 144.7 (C, C-1', minor isomer); 144.6 (C, C-1', major isomer); 132.9; 132.5; 132.4 (CH, C-2' and C-6', major isomer); 132.1; 131.6; 129.9; 128.8; 128.7 (CH); 128.5 (CH); 128.1; 128.1 (CH, C-3' and C-5', minor isomer); 128.0 (CH, C-3' and C-5', major isomer); 127.2 (CH, C-5, major isomer); 127.1 (CH, C-2' and C-6', minor isomer); 126.2 (CH); 118.5 (C, CN-7'); 112.2 (C, C-4', minor isomer); 111.9 (C, C-4', major isomer); 60.8 (CH, C-2, minor isomer); 56.3 (CH, C-2, major isomer); 46.6 (CH_2, C-4, major isomer); 44.0 (CH_2, C-4, minor isomer); 22.2 (CH_3, C-12, minor isomer); 22.1 (CH_3, C-12, major isomer). MS (EI) *m/z* (relative intensity) 294 (M^+, 30), 265 (9), 217 (19), 128 (100), 189 (13), 91 (42), 65 (7). ESI-HRMS m/z $[M + H]^+$ calcd for $C_{17}H_{15}N_2OS$ 295.08996, found 295.08858.

1-(2-(4-Nitrophenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5e): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with dichloromethane/ethylacetate) to afford pure **5e** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): mixture of interconverting rotational isomers with respect to *N*-formyl bond, at a 1:0.4 ratio (major : minor isomers), δ = 8.12 (d, *J* = 8.4 Hz, 4H, major and minor isomers), 7.53 (d, *J* = 8.4 Hz, 2H, major isomer), 7.45 (d, *J* = 8.4 Hz, 2H, minor isomer), 7.28-7.16 (m, 8H, H-5 to H-8), 7.05 (s, 1H, H-2, major isomer), 6.23 (s, 1H, H-2, minor isomer), 4.95 (d, *J* = 15.6 Hz, 2H, H_2-4a, minor isomer), 4.64 (d, *J* = 15.6 Hz, 2H, H_2-4a, major isomer), 4.53 (d, *J* = 15.6 Hz, 2H, H_2-4b, minor isomer), 4.39 (d, *J* = 15.6 Hz, 2H, H_2-4b, major isomer), 2.29 (s, 3H, H_3-12, major isomer), 2.14 (s, 3H, H_3-12, minor isomer). ^{13}C NMR (100.62 MHz, $CDCl_3$): mixture of interconverting rotational isomers: δ = 169.9(C, CO-11, major isomer), 169.9(C, CO-11, minor isomer), 147.5, 146.6, 134.4, 132.3, 131.5, 130.0, 129.1, 128.9, 128.8, 128.5, 128.2, 128.1, 127.3, 127.2, 126.4, 123.9, 123.7, 123.0, 60.6 (CH, C-2, minor isomer), 56.3 (CH, C-2, major isomer), 46.8 (CH_2, C-4, major isomer), 44.2 (CH_2, C-4, minor isomer), 22.3 (CH_3, C-12, minor isomer), 22.1 (CH_3, C-12, major isomer). ESI-HRMS m/z $[M + H]^+$ calcd for $C_{16}H_{15}N_2O_3S$ 315.07979, found 315.08071.

1-(2-(4-Methoxyphenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5f): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with dichloromethane/ethylacetate) to afford pure **5f** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): mixture of interconverting rotational isomers with respect to *N*-formyl bond, at a 1:0.7 ratio (major :minor isomers), δ = 7.38 (d, *J* = 8.6 Hz, 2H, H-2' and H-6', major isomer), 7.32 – 7.03 (m, 9H, H-5 to H-8, H-2' and H-6'), 7.11 (s, 1H, H-2, major isomer); 6.84 – 6.81 (m, 4H, H-5´and H-3'), 6.15 (s, 1H, H-2, minor isomer), 5.19 (d, *J* = 15.7 Hz, 1H, H_2-4a, minor isomer), 4.51 (d, *J* = 16.3 Hz, 1H, H_2-4a, major isomer), 4.27 (d, *J* = 16.3 Hz, 1H, H_2-4b, major isomer), 4.22 (d, *J* = 15.7 Hz, 1H, H_2-4b, minor isomer), 3.77 (s, 6H, H_3-7'), 2.20 (s, 3H, H_3-12, major isomer), 2.16 (s, 3H, H_3-12, minor isomer). ^{13}C NMR (100.62 MHz, $CDCl_3$): mixture of interconverting rotational isomers: δ = 169.8 (C, CO-11, minor isomer); 169.4 (C, CO-11, major isomer); 159.5 (C, C-4', minor isomer); 159.4 (C, C-4', major isomer); 134.2; 132.7; 131.4; 131.2; 131.0; 130.9; 128.9 (CH, C-2' and C-6'); 128.2; 128.1; 128.0; 127.8; 127.7; 126.9; 126.2; 125.1; 114.3; 114.1 (CH, C-3' and C-5', minor isomer); 113.9 (CH, C-3' and C-5', major isomer); 60.8 (CH, C-2, minor isomer); 55.5 (CH, C-2, major isomer); 55.3 (CH_3, C-7'); 45.4 (CH_2, C-4, major isomer); 43.1 (CH_2, C-4, minor isomer); 22.2 (CH_3, C-12, minor isomer); 22.1 (CH_3, C-12, major isomer). MS (EI) *m/z* (relative intensity) 299 (M^+, 29), 256 (30), 241 (15), 240 (67), 225 (10), 166 (15), 148 (23), 136 (31), 134 (33), 124 (11), 123 (23), 122 (31), 121 (100), 91 (11), 78 (18), 77 (24), 51 (8), 45 (16), 43 (40). ESI-HRMS m/z $[M + H]^+$ calcd for $C_{17}H_{18}NO_2S$ 300.10528, found 300.10599.

1-(2-(4-(trifluoromethyl)phenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5g): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with dichloromethane/ethylacetate) to afford pure **5g** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): mixture of interconverting rotational isomers with respect to *N*-formyl bond, at a 1:0.5 ratio (major : minor isomers), δ = 7.54 (m, 6H, H aromatics), 7.43 (d, *J* = 8.0 Hz, 2H, H aromatics), 7.28 – 7.12 (m, 8H, H aromatics), 7.10 (s, 1H, H-2 of major isomer, overlapping), 6.21 (s, 1H, H-2 of minor isomer), 5.06 (d, *J* = 15.8 Hz, 1H, H_2-4a, minor isomer), 4.60 (d, *J* = 16.0 Hz, 1H, H_2-4a, major isomer), 4.39 (d, *J* = 15.7 Hz, 1H, H_2-4b, minor isomer), 4.32 (d, *J* = 16.0 Hz, 1H, H_2-4b, major isomer), 2.26 (s, 3H, H_3-12, major isomer), 2.15 (s, 3H, H_3-12, minor isomer). ^{13}C NMR (100.62 MHz, $CDCl_3$): mixture of interconverting rotational isomers: δ = 170.1, 169.9, 143.5, 143.3, 132.0, 131.9, 130.6, 128.8, 128.6, 128.5, 128.2, 128.2, 128.0, 127.3, 127.0, 126.1, 126.0, 126.0, 125.8, 125.8, 125.8, 125.7, 60.9, 56.2, 46.4, 43.9, 22.5, 22.3. ESI-HRMS m/z $[M + H]^+$ calcd for $C_{17}H_{15}F_3NOS$ 338.08210, found 338.08272.

1-(2-(2-Chlorophenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5h): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with dichloromethane/ethylacetate) to afford pure **5h** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): mixture of interconverting rotational isomers with respect to *N*-formyl bond, at a 1:0.7 ratio (major : minor isomers), δ = 7.38 – 7.05 (m, 16H), 6.38 (s, 1H, H-2, major isomer), 4.96 (d, J = 15.2 Hz, 1H, H_2-4a, major isomer), 4.57 (bd, J = 15.0 Hz, 2H, H_2-4a of minor isomer and H_2-4b of major isomer, overlapping), 4.34 (d, J = 15.9 Hz, 1H, H_2-4b, minor isomer), 2.21 (s, 3H, H_3-12, minor isomer), 2.08 (s, 3H, H_3-12, major isomer).^{13}C NMR (100.62 MHz, $CDCl_3$): mixture of interconverting rotational isomers: δ = 170.3(C, CO-11, major isomer), 169.2(C, CO-11, minor isomer), 137.2, 136.7, 135.4, 133.0, 132.6, 132.2, 131.8, 131.2, 130.1, 130.0, 129.7, 129.4, 129.3, 128.9, 128.6, 128.5, 128.3, 128.1, 128.0, 127.9, 127.0, 126.9, 126.5, 125.7, 58.6(CH, C-2, major isomer), 55.3(CH, C-2, minor isomer), 46.6(CH_2, C-4, minor isomer), 44.2(CH_2, C-4, major isomer), 22.1(CH_3, C-12). ESI-HRMS m/z $[M + H]^+$ calcd for $C_{16}H_{15}ClNOS$ 304.05574, found 304.05682.

1-(2-(2-Methoxyphenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5i): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with dichloromethane/ethylacetate) to afford pure **5i** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): mixture of interconverting rotational isomers with respect to *N*-formyl bond, at a 1:0.4 ratio (major : minor isomers), δ = 7.29-7.12 (m, 13H, H aromatics and H-2 of minor isomer), 6.89 (bd, J = 8.2 Hz, 2H), 6.82 (bt, J = 7.5 Hz, 2H), 6.49 (s, 1H, H-2 of major isomer), 5.18 (d, J = 15.7 Hz, 1H, H_2-4a, major isomer), 4.56 (d, J = 15.8 Hz, 1H, H_2-4a, minor isomer), 4.37 (d, J = 15.8 Hz, 1H, H_2-4b, minor isomer), 4.13 (d, J = 15.7 Hz, 1H, H_2-4b, major isomer), 3.90 (s, 3H, H_3-7', major isomer), 3.88 (s, 3H, H_3-7', minor isomer), 2.19 (s, 6H, H_3-12). ^{13}C NMR (100.62 MHz, $CDCl_3$): mixture of interconverting rotational isomers: δ = 169.9 (C, CO-11, major isomer), 169.1 (C, CO-11, minor isomer), 156.7, 155.9, 133.9, 133.5, 132.6, 131.8, 129.8, 129.5, 128.2, 128.1, 127.9, 127.7, 127.4, 126.7, 125.8, 125.2, 120.5, 120.1, 110.9, 110.6, 56.0 (CH, C-2, major isomer), 55.6 (CH_3, C-7´), 52.8 (CH, C-2, minor isomer), 46.8 (CH_2, C-4, minor isomer), 42.2 (CH_2, C-4, major isomer), 21.7 (CH_3, C-12). ESI-HRMS m/z $[M + H]^+$ calcd for $C_{17}H_{18}NO_2S$ 300.10528, found 300.10630.

1-(2-(2-(Trifluoromethyl)phenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5j): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether/diethyl ether) to afford pure **5j** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): mixture of interconverting rotational isomers with respect to *N*-formyl bond, at a 1:0.8 ratio (major :minor isomers), δ = 7.69 – 7.66 (m, 2H, H-3'), 7.38 – 7.19 (m, 14H, aromatics H), 7.09 (s, 1H, H-

2, minor isomer), 6.39 (s, 1H, H-2, major isomer), 4.96 (d, J = 15.0 Hz, 1H, H_2-4a, major isomer), 4.77 (d, J = 15.0 Hz, 1H, H_2-4b, major isomer), 4.62 (d, J = 15.7 Hz, 1H, H_2-4a, minor isomer), 4.47 (d, J = 15.6 Hz, 1H, H_2-4b, minor isomer), 2.20 (s, 3H, H_3-12, minor isomer), 1.98 (s, 3H, H_3-12, major isomer). ^{19}F-RMN (376 MHz, $CDCl_3$): δ = -58,3 (major isomer), -59,2 (minor isomer). ^{13}C NMR (100.62 MHz, $CDCl_3$): mixture of interconverting rotational isomers, δ = 170.7 (C, CO-11, major isomer); 169.6 (C, CO-11, minor isomer); 139.1 (C, C-1', major isomer); 138.4 (C, C-1', minor isomer); 136.7; 133.4; 132.7; 132.2; 131.7; 131.5; 129.3; 128.9; 128.8; 128.6; 128.5; 128.4; 128.3; 127.7; 127.7; 127.6; 127.4; 127.0; 127.0; 126.9; 126.8; 126.7; 126.2; 124.2; 57.6 (CH, C-2, major isomer); 55.1 (CH, C-2, minor isomer); 47.3 (CH_2, C-4, minor isomer); 45.3 (CH_2, C-4, major isomer); 22.5 (CH_3, C-12, major isomer); 22.3 (CH_3, C-12, minor isomer). MS (EI) *m/z* (relative intensity) 338 (M^+ +1, 17), 337 (M^+, 15), 295 (11), 294 (69), 280 (11), 279 (12), 278 (23), 166 (18), 159 (12), 145 (11), 136 (55), 134 (19), 124 (21), 123 (47), 122 (79), 121 (100), 78 (37), 77 (27), 45 (33). ESI-HRMS m/z $[M + H]^+$ calcd for $C_{17}H_{15}F_3NOS$ 338.08210, found 338.08300.

1-(2-(4-Chlorophenyl)-6-fluoro-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5k): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with pentane/ethylacetate) to afford pure **5k** as a brown oil. ^{1}H NMR (400MHz, $CDCl_3$): mixture of interconverting rotational isomers with respect to *N*-formyl bond, at a 1:0.6 ratio (major :minor isomers), δ = 7.36 – 6.94 (m, 12H), 7.1 (s, 1H), 6.82 (t, J = 8.4 Hz, 2H), 6.18 (s, 1H), 5.07 (d, J = 15.8 Hz, 1H), 4.53 (d, J = 16.1 Hz, 1H), 4.22 (d, J = 16.0 Hz, 2H), 2.22 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (100.62 MHz, $CDCl_3$): mixture of interconverting rotational isomers, δ = 169.9, 169.6, 163.2, 160.7, 137.4, 137.2, 134.5, 134.2, 129.7, 129.4, 129.3, 129.1, 129.0, 128.9, 128.5, 128.4, 128.0, 126.9, 126.9, 115.5, 115.3, 115.2, 114.9, 113.9, 113.7, 112.9, 112.7, 60.6, 60.5, 55.5, 45.2, 42.7, 22.2, 22.1. ESI-HRMS m/z $[M + Na]^+$ calcd for $C_{16}H_{13}ClFNNaOS$ 344.0283, found 344.0291.

1-(6-Bromo-2-(4-chlorophenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5l): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with dichloromethane/ethylacetate) to afford pure **5l** as a brown oil. ^{1}H NMR (400MHz, $CDCl_3$): mixture of interconverting rotational isomers with respect to *N*-formyl bond, at a 1:0.6 ratio (major :minor isomers), δ = 7.37 – 7.24 (m, 12H), 7.15 – 7.08 (m, 2H), 7.11 (s, 1H), 6.18 (s, 1H), 5.13 (d, J = 16.0 Hz, 1H), 4.53 (d, J = 16.4 Hz, 1H), 4.23 (d, J = 16.4 Hz, 1H), 4.17 (d, J = 16.0 Hz, 1H), 2.24 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (100.62 MHz, $CDCl_3$): mixture of interconverting rotational isomers, δ = 170.0, 169.6, 137.3, 137.1, 135.7, 134.6, 134.3, 132.9, 132.8, 132.5, 131.4, 131.3, 131.0, 130.9,

130.0, 129.8, 129.7, 129.3, 129.1, 129.0, 128.1, 120.1, 118.8, 60.7, 55.6, 45.3, 42.8, 22.2. ESI-HRMS m/z $[M + Na]^+$ calcd for $C_{16}H_{13}BrClNNaOS$ 403.9482, found 403.9475.

1-(2-(4-Chlorophenyl)-8-methyl-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5m): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with pentane/ethylacetate) to afford pure **5m** as a brown oil. ^{1}H NMR (400MHz, $CDCl_3$): mixture of interconverting rotational isomers with respect to *N*-formyl bond, at a 1:0.5 ratio (major :minor isomers), δ = 7.35 (d, *J* = 8.3 Hz, 4H), 7.25 (dd, *J* = 8.3, 2.8 Hz, 4H), 7.11 – 7.01 (m, 4H), 6.94 (d, *J* = 7.5 Hz, 2H), 7.06 (s, 1H), 6.14 (s, 1H), 5.01 (d, *J* = 15.6 Hz, 1H), 4.53 (d, *J* = 15.9 Hz, 1H), 4.37 (d, *J* = 15.6 Hz, 1H), 4.29 (d, *J* = 15.9 Hz, 1H), 2.32 (s, 3H), 2.26 (s, 3H), 2.22 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100.62 MHz, $CDCl_3$): mixture of interconverting rotational isomers, δ = 169.9, 169.8, 138.3, 138.0, 136.8, 136.6, 134.7, 134.1, 131.9, 131.8, 129.6, 129.2, 129.0, 128.8, 127.9, 126.2, 125.7, 125.1, 124.7, 60.9, 56.1, 46.5, 44.3, 22.3, 22.1, 19.9. ESI-HRMS m/z $[M + Na]^+$ calcd for $C_{17}H_{16}ClNNaOS$ 340.0533, found 340.0543.

1-(2-Phenyl-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5n): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether/diethyl ether) to afford pure **5n** as a yellow oil. ^{1}H NMR (400MHz, $CDCl_3$): mixture of interconverting rotational isomers with respect to *N*-formyl bond, at a 1:0.7 ratio (major :minor isomers), δ = 7.46 – 7.04 (m, 19H, aromatic H and H-2majorisomer), 6.19 (s, 1H, H-2, minor isomer), 5.18 (d, *J* = 16.0 Hz, 1H, H_2-4a, minor isomer), 4.54 (d, *J* = 16.0 Hz, 1H, H_2-4a, major isomer), 4.29 (d, *J* = 10.2 Hz, 1H, H_2-4b, major isomer), 4.25 (d, *J* = 10.2 Hz, 1H, H_2-4b, minor isomer), 2.22 (s, 3H, H_3-12, major isomer), 2.15 (s, 3H, H_3-12, minor isomer). ^{13}C NMR (100.62 MHz, $CDCl_3$): mixture of interconverting rotational isomers: δ = 169.9 (C, CO-11, minor isomer); 169.5 (C, CO-11, major isomer); 139.1 (C, C-1', minor isomer); 138.8 (C, C-1', major isomer); 134.3 (C, C-10, minor isomer); 132.5 (C, C-10, major isomer); 131.2 (C, C-9); 128.8 (CH, C-5); 128.6; 128.3; 128.3; 128.1; 128.0; 127.9; 127.8; 127.6 (CH, C-6 and C-7); 127.0; 126.5 (CH, C-2' and C-6', major isomer); 126.4; 125.2 (CH, C-2' and C-6', minor isomer); 61.1 (CH, C-2, minor isomer); 56.0 (CH, C-2, major isomer); 45.6 (CH_2, C-4, major isomer); 43.3 (CH_2, C-4, minor isomer); 22.3 (CH_3, C-12, minor isomer); 22.1 (CH_3, C-12, major isomer). MS (EI) *m/z* (relative intensity) 270 (M^+ +1, 8), 269 (M^+, 44), 226 (58), 211 (30), 210 (71), 294 (22), 166 (18), 136 (49), 124 (17), 123 (33), 122 (48), 121 (100), 104 (28), 91 (53), 78 (35), 77 (41), 51 (20), 45 (33), 43 (79). GC-MS HRMS EI[M^+] calcd for $C_{16}H_{15}NOS$ 270.0947, found 270.0966.

1-(2-(Pyridin-2-yl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5o): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether/diethyl ether) to afford pure **5o** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): mixture of interconverting rotational isomers with respect to *N*-formyl bond, at a rate of 1:0.8 (major :minor isomers), δ = 8.57 (t, *J* = 3.9 Hz, 2H, H-3', major and minor isomers), 7.58 (dtd, *J* = 9.3; 7.8; 1.7 Hz, 2H, H-5', major and minor isomers), 7.37 (d, *J* = 7.9 Hz, 1H, H-6', major isomer), 7.28 – 7.12 (m, 11H, H-5 to H-8), 7.06 (s, 1H, H-2, major isomer), 6.26 (s, 1H, H-2, minor isomer), 5.03 (d, *J* = 15.5 Hz, 1H, H_2-4a, minor isomer), 4.65 (d, *J* = 15.6 Hz, 1H, H_2-4a, major isomer), 4.57 (d, *J* = 15.6 Hz, 1H, H_2-4b, major isomer), 4.43 (d, *J* = 15.5 Hz, 1H, H_2-4b, minor isomer), 2.26 (s, 3H, H_3-12, major isomer), 2.13 (s, 3H, H_3-12, minor isomer). ^{13}C NMR (100.62 MHz, $CDCl_3$): mixture of interconverting rotational isomers: δ = 170.2 (C, CO-11, minor isomer); 170.1 (C, CO-11, major isomer); 158.4 (C, C-1', minor isomer); 158.0 (C, C-1', major isomer); 149.8 (CH, C-3', minor isomer); 149.5 (CH, C-3', major isomer); 136.9 (CH, C-5', minor isomer); 136.7 (CH, C-5', major isomer); 134.9 (C, C-10, minor isomer); 133.3 (C, C-10, major isomer); 132.6 (C, C-9, major isomer); 131.1 (C, C-9, minor isomer); 128.5; 128.5; 128.1; 127.9; 127.8; 126.8; 126.6; 125.7; 123.0 (CH, C-4', minor isomer); 122.7 (CH, C-4', major isomer); 121.3 (CH, C-6', major isomer); 120.3 (CH, C-6', minor isomer); 62.3 (CH, C-2, minor isomer); 57.7 (CH, C-2, major isomer); 47.4 (CH_2, C-4, major isomer); 44.0 (CH_2, C-4, minor isomer); 22.3 (CH_3, C-12, minor isomer); 22.2 (CH_3, C-12, major isomer). MS (EI) *m/z* (relative intensity) 270 (M^+, 4), 237 (6), 227 (33), 212 (28), 211 (100), 210 (13), 195 (10), 167 (8), 150 (12), 123 (30), 122 (14), 121 (39), 93 (37), 92 (21), 79 (12), 78 (21), 77 (18), 65 (15), 63 (10), 45 (11). ESI-HRMS m/z $[M + H]^+$ calcd for $C_{15}H_{15}N_2OS$ 271.08996, found 271.09126.

(*E*)-1-(2-(But-2-en-2-yl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5p): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether/diethyl ether) to afford pure **5p** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): mixture of interconverting rotational isomers with respect to *N*-formyl bond, at a 1:1 ratio (major :minor isomers), δ = 7.25 – 7.08 (m, 8H, H aromatics H-5 to H-8), 6.34 (s, 1H, H-2), 5.75 – 5.68 (m, 1H, H-2'), 5.50 – 5.45 (m, 1H, H-2'), 5.39 (s, 1H, H-2), 4.97 (d, *J* = 15.3 Hz, 1H, H-4a), 4.48 (d, *J* = 15.8 Hz, 1H, H-4a), 4.32 (d, *J* = 15.8 Hz, 1H, H-4b), 4.26 (d, *J* = 15.3 Hz, 1H, H-4b), 2.18 (s, 3H, H_3-12), 2.13 (s, 3H, H_3-12), 1.69 (s, 3H, H_3-3'), 1.66 (s, 3H, H_3-3'), 1.59 (d, *J* = 6.7 Hz, 3H, H_3-4'), 1.54 (d, *J* = 6.7 Hz, 3H, H_3-4'). ^{13}C NMR (100.62 MHz, $CDCl_3$): mixture of interconverting rotational isomers: δ = 170.0 (C, CO-12); 169.7 (C, CO-12); 134.9 (C, C-10); 133.2 (C, C-10); 131.9 (C, C-9); 131.8 (C, C-9); 131.6 (C, C-1'); 131.5 (C, C-1'); 128.4; 128.1; 127.9; 127.7; 127.7;

126.7; 126.1; 124.9; 124.8 (CH, C-2'); 124.4 (CH, C-2'); 64.3 (CH, C-2); 59.2 (CH, C-2); 46.0 (CH_2, C-4); 43.7 (CH_2, C-4); 22.1 (CH_3, C-12); 22.0 (CH_3, C-12); 13.7 (CH_3, C-3'); 13.5 (CH_3, C-3' and C-4'); 13.5 (CH_3, C-4'). MS (EI) *m/z* (relative intensity) 248 (M^+ +1, 29), 247 (M^+, 45), 232 (33), 218 (88), 214 (21), 205 (20), 204 (65), 190 (50), 188 (23), 173 (29), 172 (25), 150 (19), 149 (20), 148 (21), 123 (42), 122 (43), 121 (70), 96 (15), 82 (32), 78 (25), 55 (19), 54 (23), 53 (31), 51 (30), 45 (25), 43 (100), 41 (27). ESI-HRMS m/z $[M + H]^+$ calcd for $C_{14}H_{18}NOS$ 248.11036, found 248.11030.

3-Methyl-2-iodobenzyl azide (7c): after extraction and solvent remotion, the pure **7c** was obtained as a yellowish oil. ^{1}H-NMR (400MHz, $CDCl_3$): δ = 7.24 – 7.15 (m, 3H), 4.49 (s, 2H), 2.49 (s, 3H). ^{13}C-NMR (100.62 MHz, $CDCl_3$): δ = 143.1, 138.8, 129.7, 128.2, 126.8, 106.3, 60.3, 29.6.

2-Methyl-4*H*-benzo[*e*][1,3]thiazine (8a):[6] after extraction, the crude residue was purified by column chromatography on silica gel (eluting with pentane/diethyl ether) to afford pure **8a** as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 – 7.44 (m, 3H), 7.42 – 7.36 (m, 1H), 4.43 (s, 2H), 2.46 (s, 3H). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ = 193.2; 138.9; 136.8; 130.6; 129.8; 129.1; 127.3; 53.0; 30.3. MS (EI) *m/z* (relative intensity) 163 (M+, 37), 123 (10), 122 (88), 121 (100), 78 (30), 77 (12), 69 (10), 51 (5), 45 (6). ESI-HRMS m/z $[M + H]^+$ calcd for C_9H_8NS 162.03720, found 162.03692.

2-Phenyl-4*H*-benzo[*e*][1,3]thiazine (8b):[7] after extraction, the crude residue was purified by column chromatography on silica gel (eluting with pentane/diethyl ether) to afford pure **8b** as a yellow solid, mp = 40.8 – 42.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.08 – 8.05 (m, 2H), 7.66 – 7.62 (m, 1H), 7.60 – 7.50 (m, 5H), 7.44 (td, *J* = 7.4, 1.9 Hz, 1H), 4.50 (s, 2H).^{13}C NMR (100.62 MHz, $CDCl_3$) δ = 189.3, 139.7, 137.3, 136.3, 134.0, 130.7, 129.8, 129.2, 128.9, 127.7, 126.7, 53.0.

2-Ethoxy-4*H*-benzo[*e*][1,3]thiazine (8c): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with pentane/dichloromethane) to afford pure **8c** as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 – 7.21 (m, 4H), 4.55 (s, 2H), 4.28 (q, *J* = 7,1 Hz, 2H), 1.33 (t, *J* = 7,1 Hz, 3H). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ = 159.5; 131.8; 130.9; 127.4; 127.0; 126.8; 126.7; 64.6; 53.0; 14.4. ESI-HRMS m/z $[M + H]^+$ calcd for $C_{10}H_{12}NOS$ 194.06341, found 194.06399.

6-Fluoro-2-methyl-4*H*-benzo[*e*][1,3]thiazine (8d): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with dichloromethane/ethylacetate) to afford pure **8d** as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22 – 7.18 (m, 1H), 6.98 - 6.94 (m, 2H), 4.53 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ = 163.2, 159.1, 128.2, 128.1, 125.7, 114.5, 114.3, 113.3, 113.1, 55.2, 26.8. ESI-HRMS m/z $[M + H]^+$ calcd for C_9H_9FNS 182.0434, found 182.0427.

***S*-(2-((*N*-acetylacetamido)methyl)phenyl) ethanethioate (10):** after extraction, the crude residue was purified by column chromatography on silica gel (eluting with petroleum ether/diethyl ether) to afford pure **10** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 – 7.40 (m, 2H), 7.33 – 7.28 (m, 1H), 7.06 – 7.04 (m, 1H), 4.98 (s, 2H), 2.46 (s, 3H), 2.39 (s, 6H). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ = 193.3, 173.6, 140.2, 136.6, 130.9, 128.0, 125.7, 125.5, 46.2, 30.3, 26.3. ESI-HRMS m/z $[M + H]^+$ calcd for $C_{13}H_{15}NO_3S$ 266.0845, found 266.0850.

***N*-(2-mercapto-3-methylbenzyl)acetamide (11):** after extraction, the crude residue was purified by column chromatography on silica gel (eluting with petane/ethylacetate) to afford pure **11** as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) mixture of interconverting rotational isomers with respect to *N*-formyl bond, at a 1:0.8 ratio (major : minor isomers), δ = 7.24 – 7.14 (m, 2H), 7.09 – 7.05 (m, 1H), 5.91 (s, 1H), 5.80 (s, 1H), 4.52 (d, *J* = 5.7 Hz, 2H), 4.29 (d, *J* = 5.7 Hz, 2H), 3.52 (s, 1H), 2.38 (s, 3H), 2.33 (s, 3H), 2.01 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ = 170.0, 170.0, 144.3, 143.2, 137.8, 136.4, 133.9, 130.9, 130.3, 130.2, 130.0, 127.9, 127.4, 125.8, 43.7, 42.4, 23.4, 23.3, 22.2, 21.5. ESI-HRMS m/z $[M + H]^+$ calcd for $C_{10}H_{14}NOS$ 196.0791, found 196.0774.

2-(2-Iodo-3-methylphenyl)acetonitrile (12d): after extraction and solvent remotion, the pure **12d** was obtained as a white solid. ^{1}H-NMR (400MHz, $CDCl_3$): δ = 7.34 – 7.20 (m, 3H), 3.87 (s, 2H), 2.50 (s, 3H). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ = 143.5, 134.0, 129.6, 128.6, 126.5, 117.5, 106.4, 31.5, 29.8. ESI-HRMS m/z $[M + Na]^+$ calcd for C_9H_8INNa 279.9594, found 279.9568.

***N*-(Benzo[*b*]thiophen-2-yl)acetamide (13a):[8]** after extraction, the crude residue was purified by column chromatography on silica gel (eluting with dichloromethane/ethylacetate) to afford pure **13a** as a yellow solid, mp = 220 – 222 °C. ^{1}H NMR (400 MHz, acetone-d6) δ = 10.73 (s, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.21 – 7.17 (m, 1H), 6.92 (s, 1H), 2.15 (s, 3H). ^{13}C NMR (100.62 MHz, acetone-d6) δ = 168.1, 141.4, 138.4, 136.0, 125.1, 123.4, 122.6, 122.5, 106.5, 22.9. ESI-HRMS m/z $[M + Na]^+$ calcd for $C_{10}H_9NNaOS$ 214.02971, found 214.02937.

(2-Aminobenzo[*b*]thiophen-3-yl)(phenyl)methanone (13b):[9] after extraction, the crude residue was purified by column chromatography on silica gel (eluting with dichloromethane/ethylacetate) to afford pure **13b** as a yellow solid. ^{1}H NMR (400 MHz, acetone-d6) δ = 8.37 (s, 2H), 7.59 – 7.48 (m, 6H), 7.04 – 7.00 (m, 1H), 6.94 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 6.57 (bd, *J* = 8.0, 1H).^{13}C NMR (100.62 MHz, acetone-d6) δ = 191.1, 167.4, 142.1, 137.7, 130.4, 129.0, 128.4, 127.3, 124.5, 121.9, 121.6, 121.2, 107.9. ESI-HRMS m/z $[M + H]^+$ calcd for $C_{15}H_{12}NOS$ 254.06341, found 254.06336.

2-Ethoxybenzo[*b*]thiophene-3-carbonitrile (13c): after extraction, the crude residue was purified by column chromatography on silica gel (eluting with pentane/dichloromethane) to afford pure **13c** as a yellow solid, decomposes before m. p. ^{1}H NMR (400 MHz, acetone-d6) δ = 7.89 (ddd, *J* = 8.1, 1.0, 0.6 Hz, 1H), 7.66 (ddd, *J* = 8.0, 1.1, 0.6 Hz, 1H), 7.51 (ddd, *J* = 8.0, 7.3, 1.0 Hz, 1H), 7.39 (ddd, *J* = 8.1, 7.3, 1.1 Hz, 1H), 4.52 (q, *J* = 7.0 Hz, 2H), 1.54 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100.62 MHz, acetone-d6) δ = 175.1, 136.3, 130.1, 127.3, 125.4, 123.8, 121.2, 113.7, 104.1, 73.2, 15.0. ESI-HRMS m/z $[M + Na]^+$ calcd for $C_{11}H_9NNaOS$ 226.02971, found 226.02985.

***N*-(5-fluorobenzo[*b*]thiophen-2-yl)acetamide (13d):** after extraction, the crude residue was purified by column chromatography on silica gel (eluting with pentane/ethylacetate) to afford pure **13d** as a white solid. ^{1}H NMR (400 MHz, acetone-d6) δ = 10.58 (s, 1H), 7.61 – 7.56 (m, 2 H), 7.08 (td, *J* = 9.2, 2.4 Hz, 1H), 6.90 (s, 1H), 2.16 (s, 3H). ^{13}C NMR (100.62 MHz, acetone-d6) δ = 171.1, 168.1, 168.0, 161.4, 159.0, 141.2, 141.1, 141.0, 141.0, 137.2, 137.2, 137.1, 137.1, 134.9, 123.8, 123.7, 113.7, 113.4, 108.7, 108.4, 105.8, 105.8, 22.9, 22.9. ESI-HRMS m/z $[M + Na]^+$ calcd for $C_{10}H_8FNNaOS$ 232.0203, found 232.0211.

***N*-(5-bromobenzo[*b*]thiophen-2-yl)acetamide (13e):** after extraction, the crude residue was purified by column chromatography on silica gel (eluting with pentane/ethylacetate) to afford pure **13e** as a light yellow solid. ^{1}H NMR (400 MHz, acetone-d6) δ = 10.52 (s, 1H), 7.79 (d, *J* = 1.8 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.33 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.89 (s, 1H), 2.17 (s, 3H). ^{13}C NMR (100.62 MHz, acetone-d6) δ = 168.1, 143.3, 140.3, 134.9, 126.1, 125.0, 124.4, 118.7, 105.5, 23.0. ESI-HRMS m/z $[M + Na]^+$ calcd for $C_{10}H_8BrNNaOS$ 291.9402, found 291.9400.

***N*-(7-methylbenzo[*b*]thiophen-2-yl)acetamide (13f):** after extraction, the crude residue was purified by column chromatography on silica gel (eluting with pentane/ethylacetate) to afford pure **13f** as a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.15 (s, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.90 (s, 1H), 2.53 (s, 3H), 2.25 (s, 3H). ^{13}C NMR

(100.62 MHz, $CDCl_3$) δ = 167.2, 138.9, 137.1, 135.4, 131.8, 125.0, 123.9, 120.0, 108.2, 23.7, 20.1. ESI-HRMS m/z $[M + Na]^+$ calcd for $C_{11}H_{11}NNaOS$ 228.0454, found 228.0423.

***N*-(3,3-dimethylbenzo[*b*]thiophen-2(3*H*)-ylidene)acetamide (13g):** after extraction, the crude residue was purified by column chromatography on silica gel (eluting with pentane/dichloromethane) to afford pure **13g** as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 – 7.39 (m, 1H), 7.32 – 7.26 (m, 3H), 2.44 (s, 3H), 1.54 (s, 6H). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ = 191.8, 184.5, 143.8, 136.3, 128.3, 126.9, 123.4, 122.9, 56.0, 28.9, 27.5. ESI-HRMS m/z $[M + H]^+$ calcd for $C_{12}H_{14}NOS$ 220.07906, found 220.07876.

***N*-(3,3-dimethylbenzo[*b*]thiophen-2(3*H*)-ylidene)benzamide (13h):** after extraction, the crude residue was purified by column chromatography on silica gel (eluting with pentane/dichloromethane/ethylacetate) to afford pure **13h** as a yellow oil. ^{1}H NMR (400 MHz, acetone-d6) δ = 8.39 – 8.36 (m, 2H), 7.70 - 7.66 (m, 1H), 7.60 – 7.56 (m, 4H), 7.41 – 7.36 (m, 2H), 1.67 (s, 6H). ^{13}C NMR (100.62 MHz, acetone-d6) δ = 195.3, 177.4, 144.7, 137.0, 135.9, 134.3, 131.0, 129.6, 129.3, 128.0, 124.5, 123.8, 57.4, 29.2. ESI-HRMS m/z $[M + H]^+$ calcd for $C_{17}H_{16}NOS$ 282.09471, found 282.09460.

***N*-(3-acetylbenzo[*b*]thiophen-2-yl)acetamide (13i):** after extraction, the crude residue was purified by column chromatography on silica gel (eluting with dichloromethane/ethylacetate) to afford pure **13i** as a yellow solid, mp = 138 – 140 °C. ^{1}H NMR (400 MHz, acetone-d6) δ = 12.78 (s, 1H), 8.10 (bd, *J* = 8.3 Hz, 1H), 7.90 (ddd, *J* = 7.9, 1.1, 0.7 Hz, 1H), 7.48 (ddd, *J* = 8.4, 7.2, 1.2 Hz, 1H), 7.35 (ddd, *J* = 8.1, 7.2, 1.0 Hz, 1H), 2.79 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100.62 MHz, acetone-d6) δ = 196.7, 169.6, 154.0, 134.9, 134.9, 126.6, 124.5, 123.3, 123.1, 115.8, 32.1, 23.8. ESI-HRMS m/z $[M + H]^+$ calcd for $C_{12}H_{12}NO_2S$ 234.05833, found 234.05915.

2-Methylbenzo[*b*]thiophene-3-carbonitrile (13j):[10] after extraction, the crude residue was purified by column chromatography on silica gel (eluting with pentane/dichloromethane/ethylacetate) to afford pure **13j** as a yellow solid, mp = 138 – 140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 (d, *J* = 7.9 Hz, 1H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 2.79 (s, 3H). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ = 154.1, 138.1, 137.6, 126.0, 125.7, 122.4, 122.1, 114.4, 105.6, 15.9.

***N*-(3-benzoylbenzo[*b*]thiophen-2-yl)benzamide (13k):** after extraction, the crude residue was purified by column chromatography on silica gel (eluting with dichloromethane/ethylacetate) to afford pure **13k** as a light brown solid, mp = 201 – 203.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ =13.27 (s, 1H), 8.12 (bd, *J* = 7.2 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.69 (bd, *J* = 8.0 Hz, 2H), 7.64-7.59 (m, 2H), 7.55 (t, *J* = 7.3 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.25 (bt, *J* = 7.5 Hz, 1H), 7.12 (td, *J* = 7.3, 0.8 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ = 194.5, 165.1, 154.4, 140.4, 134.6, 134.4, 133.3, 132.2, 131.9, 129.2, 128.7, 128.5, 128.0, 125.0, 124.0, 123.1, 122.3, 115.4. ESI-HRMS m/z $[M + H]^+$ calcd for $C_{22}H_{16}NO_2S$ 358.08963, found 358.08832.

2-Phenylbenzo[*b*]thiophene-3-carbonitrile (13l):[11] after extraction, the crude residue was purified by column chromatography on silica gel (eluting with dichloromethane/ethylacetate) to afford pure **13l** as a yellow solid, m.p = 172-173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 8.0 Hz, 1H), 7.90 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.45 (m, 5H). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ = 155.2, 139.4, 137.6, 131.7, 130.6, 129.5, 128.4, 126.3, 122.8, 122.5, 115.3, 102.3.

***N*-(Benzo[*b*]thiophen-2-yl)benzamide (13m):**[12] after extraction, the crude residue was purified by column chromatography on silica gel (eluting with pentane/dichloromethane) to afford pure **13m** as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.63 (s, 1H), 7.93 (dd, *J* = 7.1, 1.4 Hz, 2H), 7.79 (bd, *J* = 7.7 Hz, 1H), 7.64 (bd, *J* = 8.0 Hz, 1H), 7.58 (bd, *J* = 7.2 Hz, 1H), 7.52 (bt, *J* = 7.4 Hz, 2H), 7.34 (td, *J* = 7.4, 0.8 Hz, 1H), 7.27 (m, 1H), 7.05 (s, 1H). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ = 164.4, 139.6, 137.2, 135.7, 133.2, 132.6, 129.1, 127.4, 124.7, 123.5, 122.3, 122.1, 107.9.

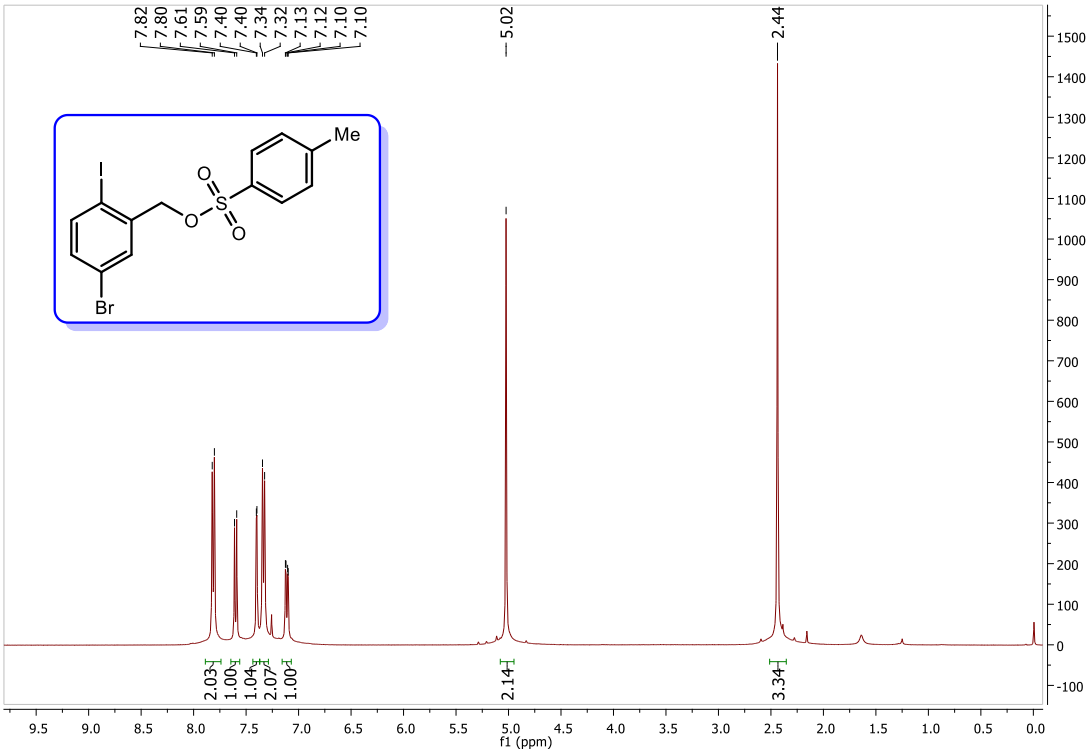
***S*-(2-(Cyanomethyl)phenyl) *O*-ethyl carbonodithioate (14a):** after extraction, the crude residue was purified by column chromatography on silica gel (eluting with pentane/dichloromethane) to afford pure **14a** as a yellow oil. ^{1}H NMR (400 MHz, acetone-d6) δ = 7.72 – 7.69 (m, 1H), 7.65 - 7.61 (m, 2H), 7.53 – 7.49 (m, 1H), 4.61 (q, *J* = 7.2 Hz, 2H), 4.07 (s, 2H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100.62 MHz, acetone-d6) δ = 212.1, 138.2, 136.8, 132.8, 130.9, 130.3, 118.5, 71.9, 23.0, 13.9. ESI-HRMS m/z $[M + H]^+$ calcd for $C_{11}H_{12}NOS_2$ 238.03548, found 238.03585.

***S*-(2-(Cyanomethyl)phenyl)benzothioate (14b):** after extraction, the crude residue was purified by column chromatography on silica gel (eluting with pentane/dichloromethane) to afford pure **14b** as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 7.4 Hz, 2H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.58 - 7.50 (m, 4H), 7.46 – 7.42 (m, 1H), 3.88 (s, 2H). ^{13}C NMR

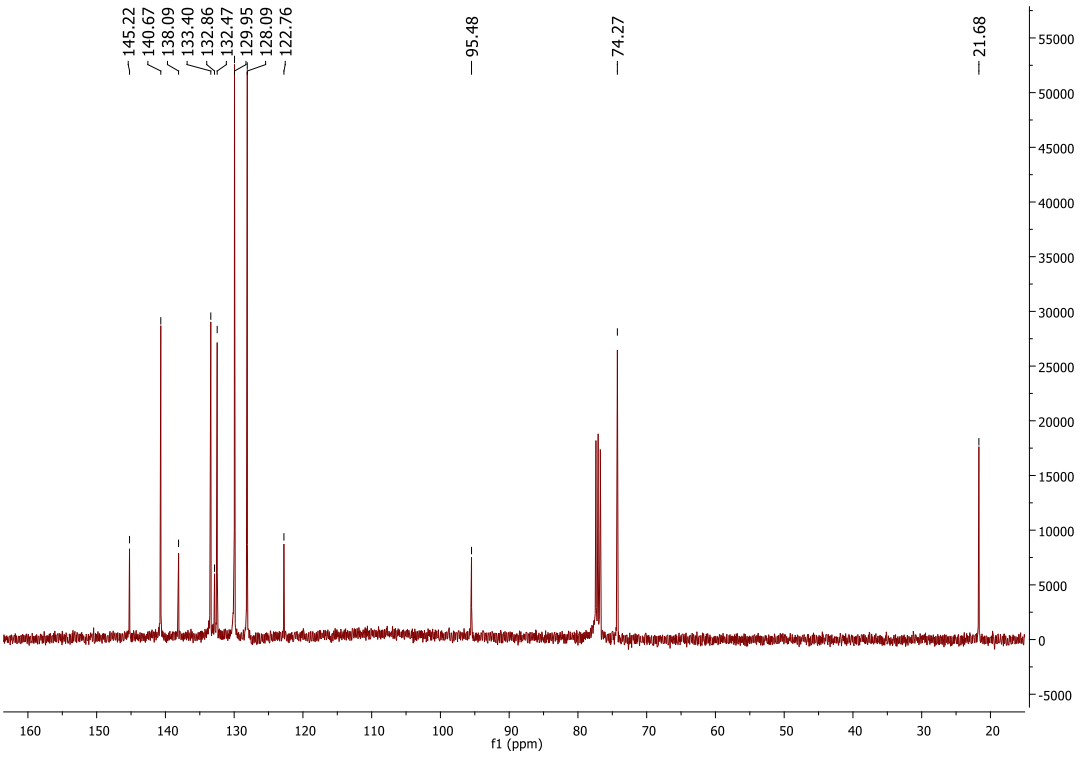
(100.62 MHz, $CDCl_3$) δ = 188.9, 137.3, 136.2, 135.1, 134.3, 131.3, 129.6, 129.3, 129.2, 129.1, 127.9, 117.6, 22.8. ESI-HRMS m/z $[M + Na]^+$ calcd for $C_{15}H_{11}NNaOS$ 276.0440, found 276.0454.

5. ^{1}H and ^{13}C NMR Spectra

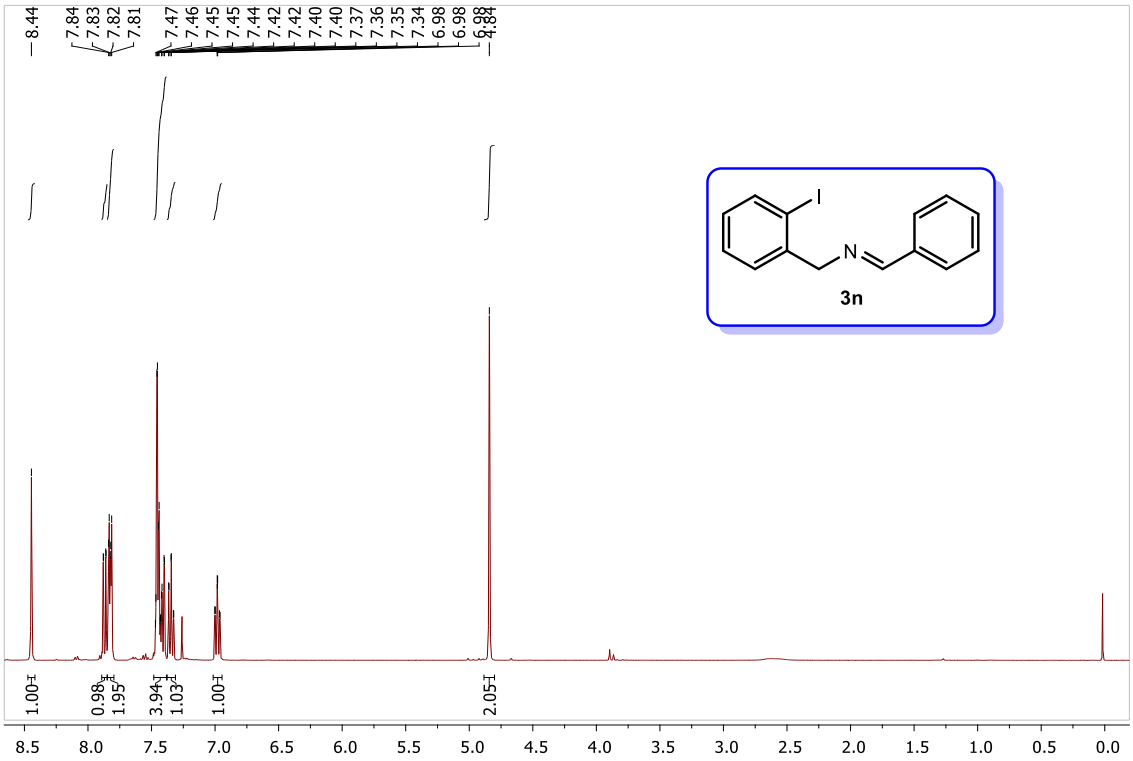
^{1}H NMR ($CDCl_3$) 5-bromo-2-iodobenzyl tosylate

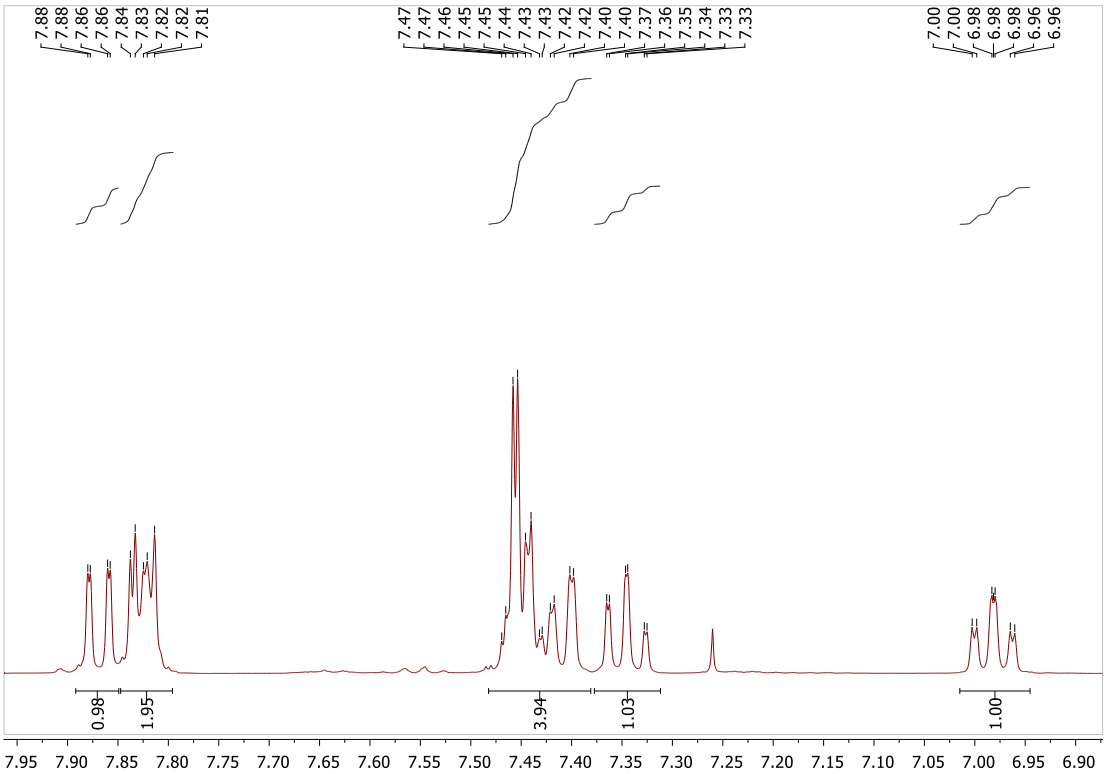


^{13}C NMR ($CDCl_3$) 5-bromo-2-iodobenzyl tosylate

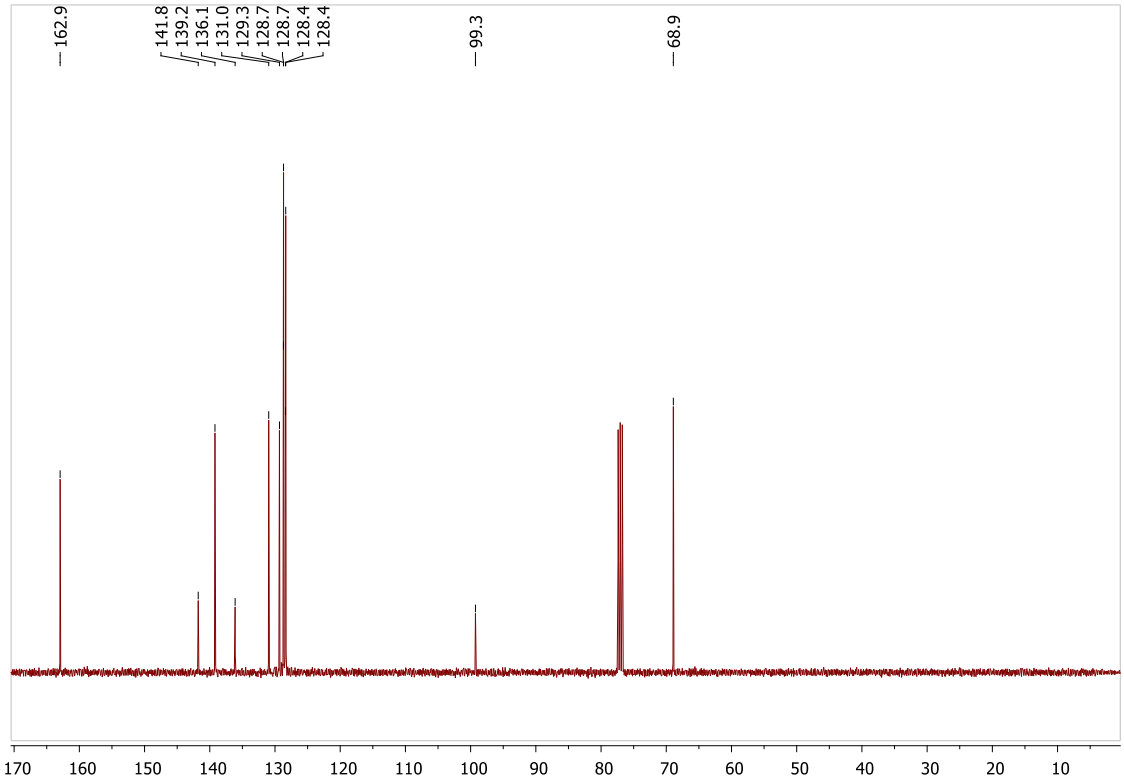


^{1}H NMR ($CDCl_3$) (*E*)-*N*-(2-iodobenzyl)-1-phenylmethanimine (3n)

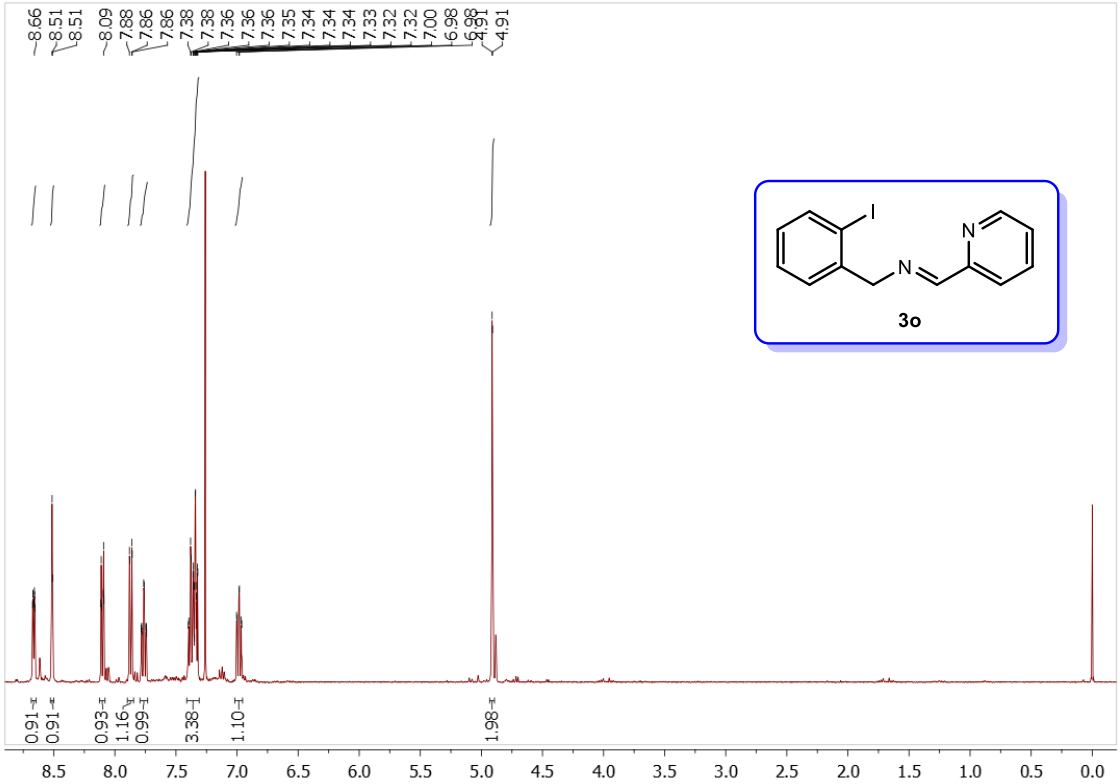


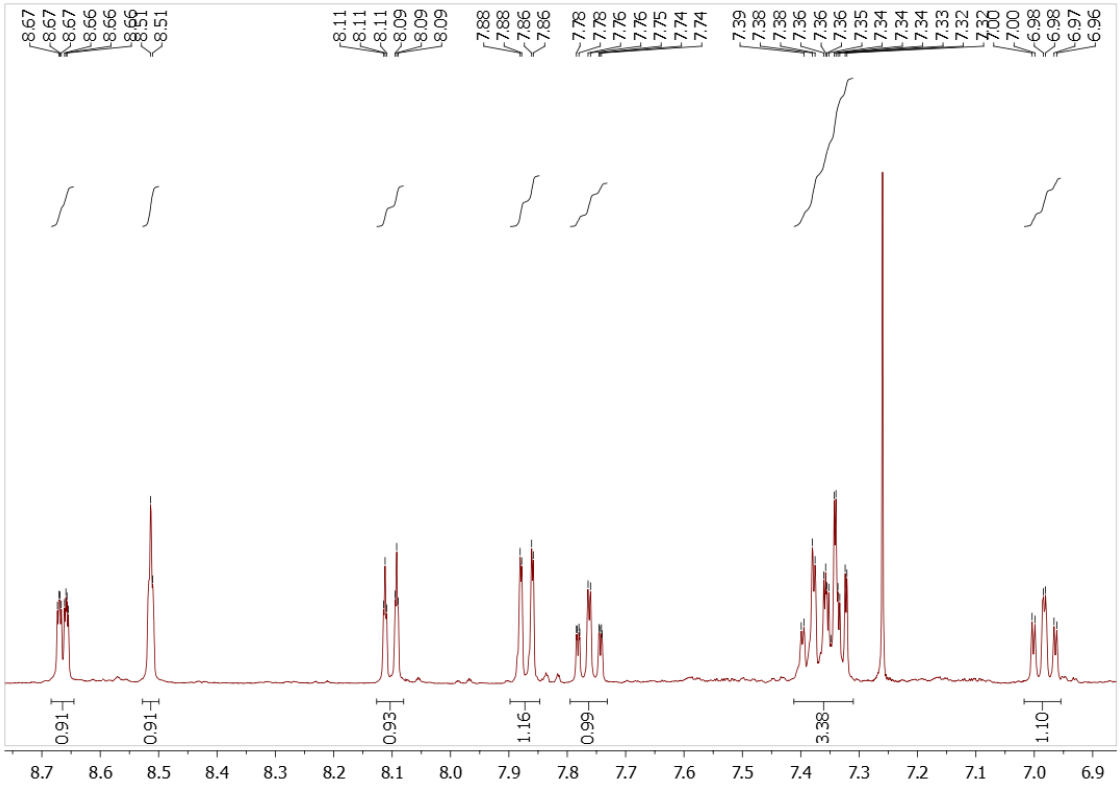


^{13}C NMR ($CDCl_3$) (*E*)-*N*-(2-iodobenzyl)-1-phenylmethanimine (3n)

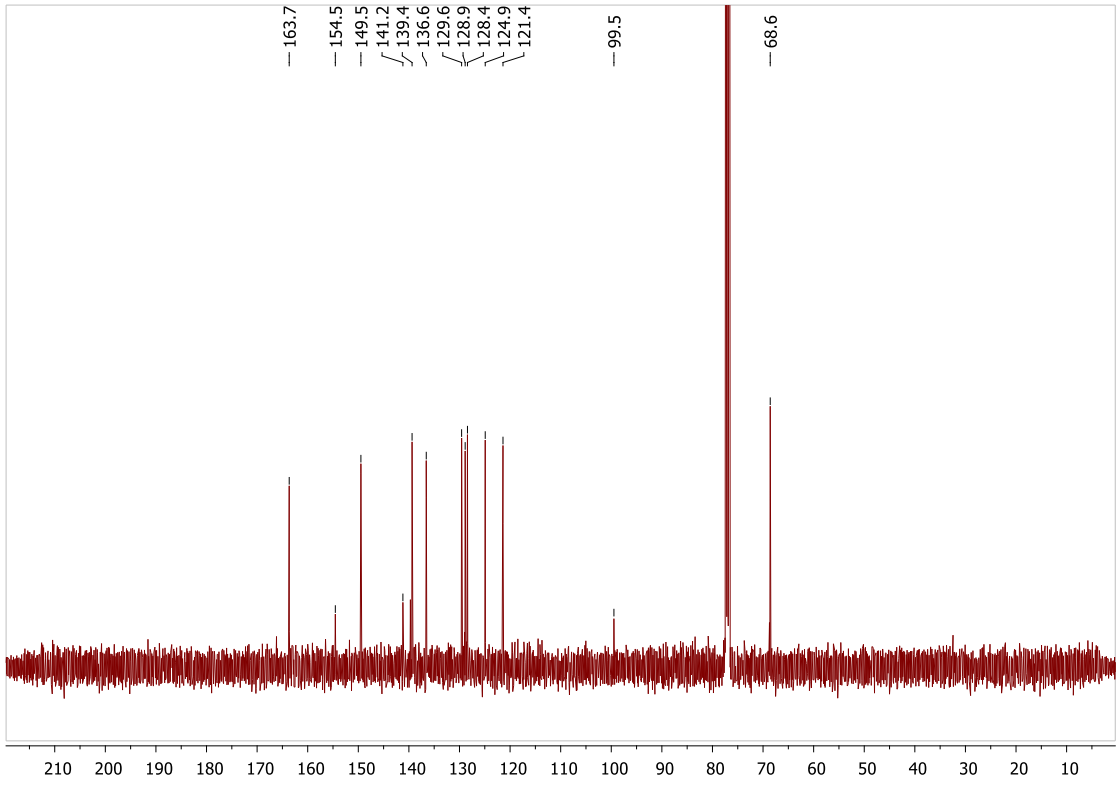


^{1}H NMR ($CDCl_3$) (*E*)-*N*-(2-iodobenzyl)-1-(pyridin-2-yl)methanimine (3o)

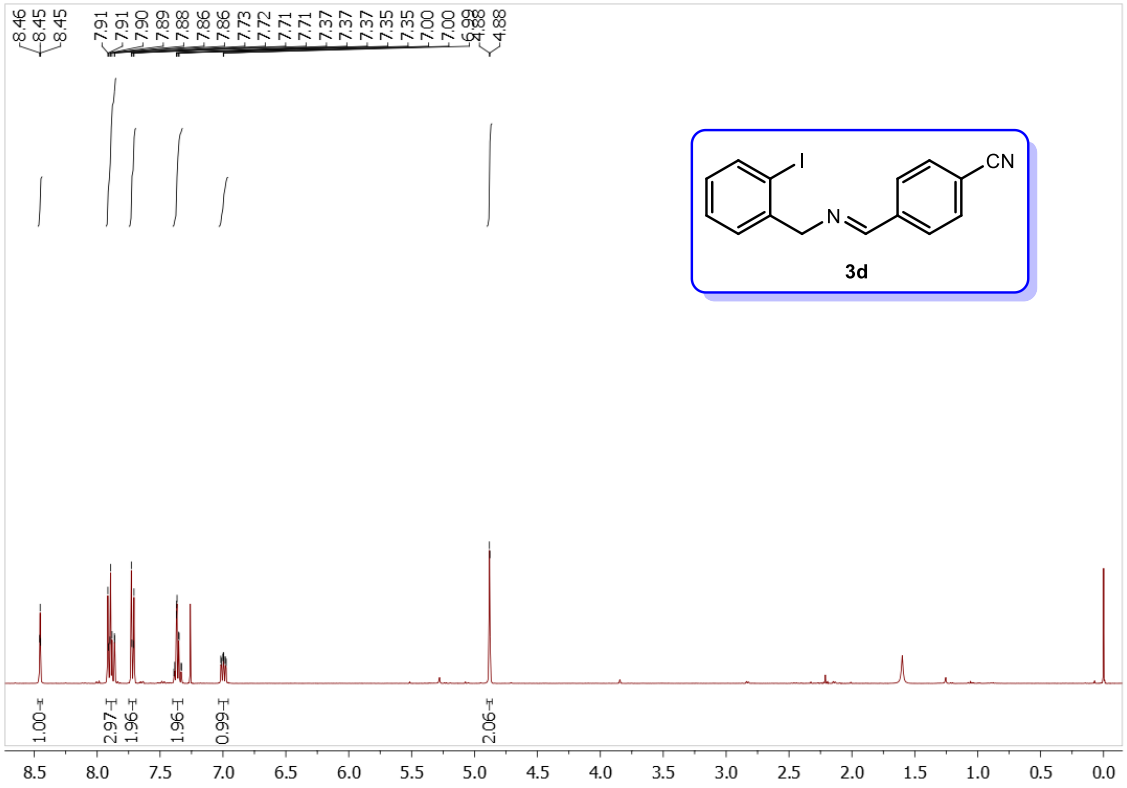


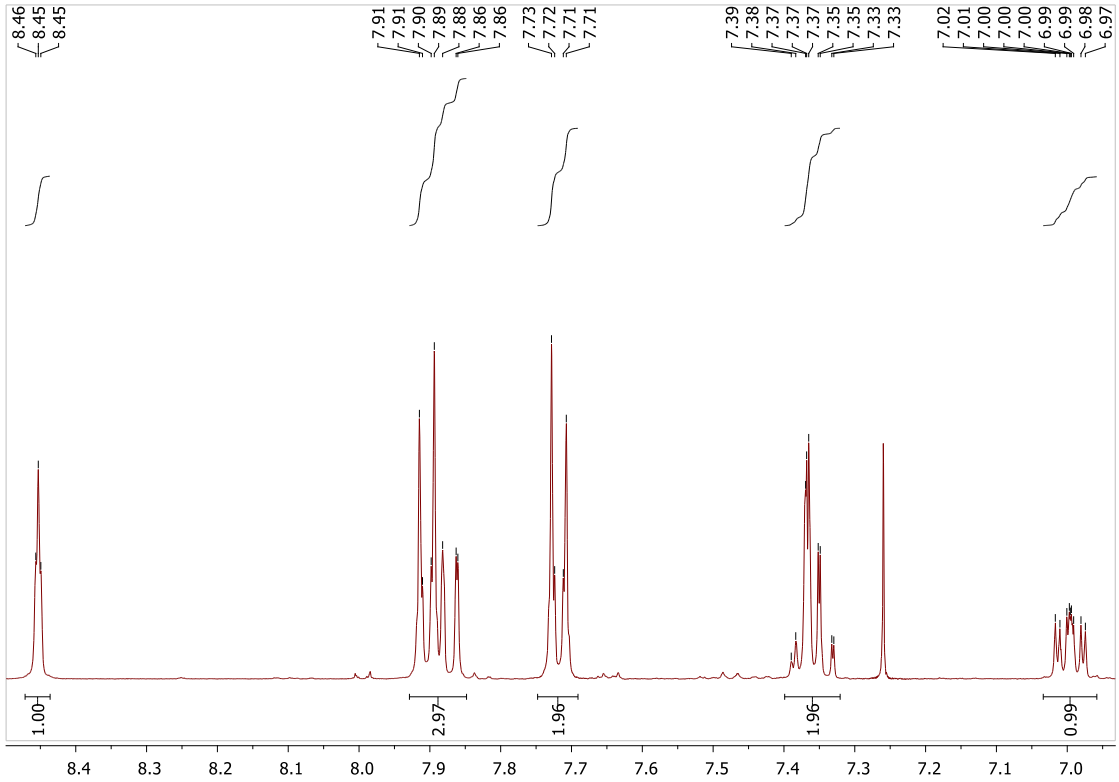


^{13}C NMR ($CDCl_3$) (*E*)-*N*-(2-iodobenzyl)-1-(pyridin-2-yl)methanimine (3o)

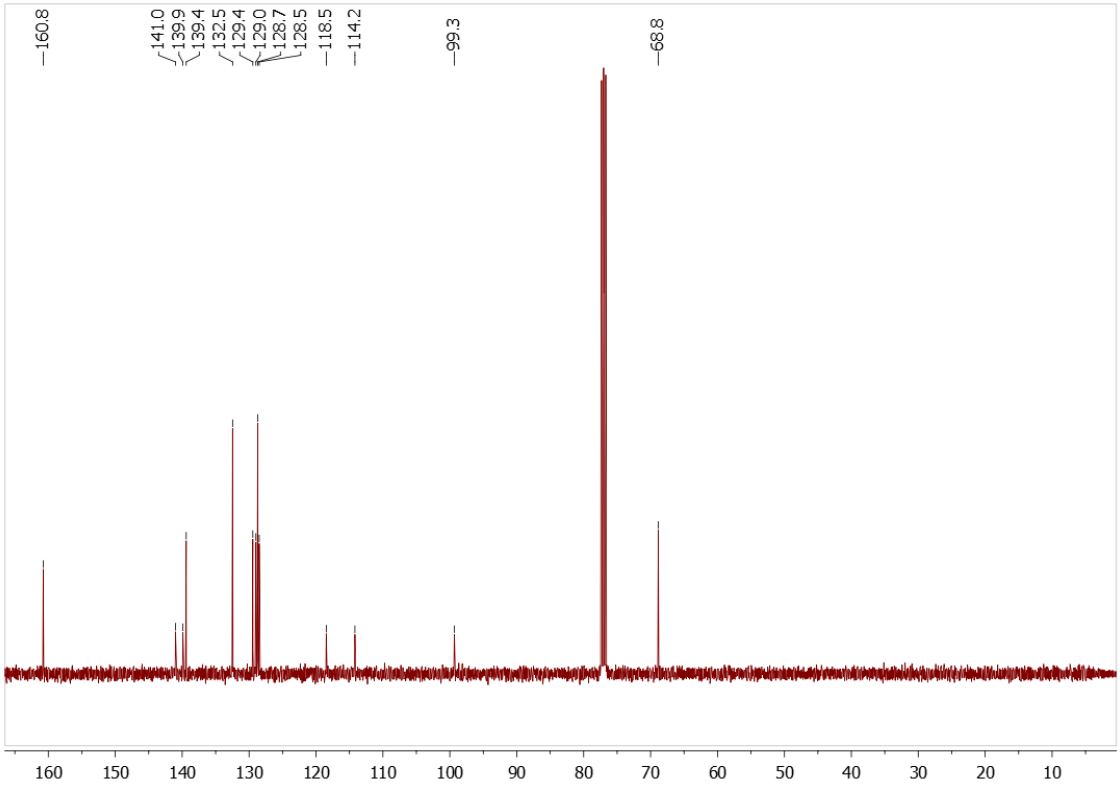


^{1}H NMR ($CDCl_3$) (*E*)-4-(((2-iodobenzyl)imino)methyl)benzonitrile(3d)

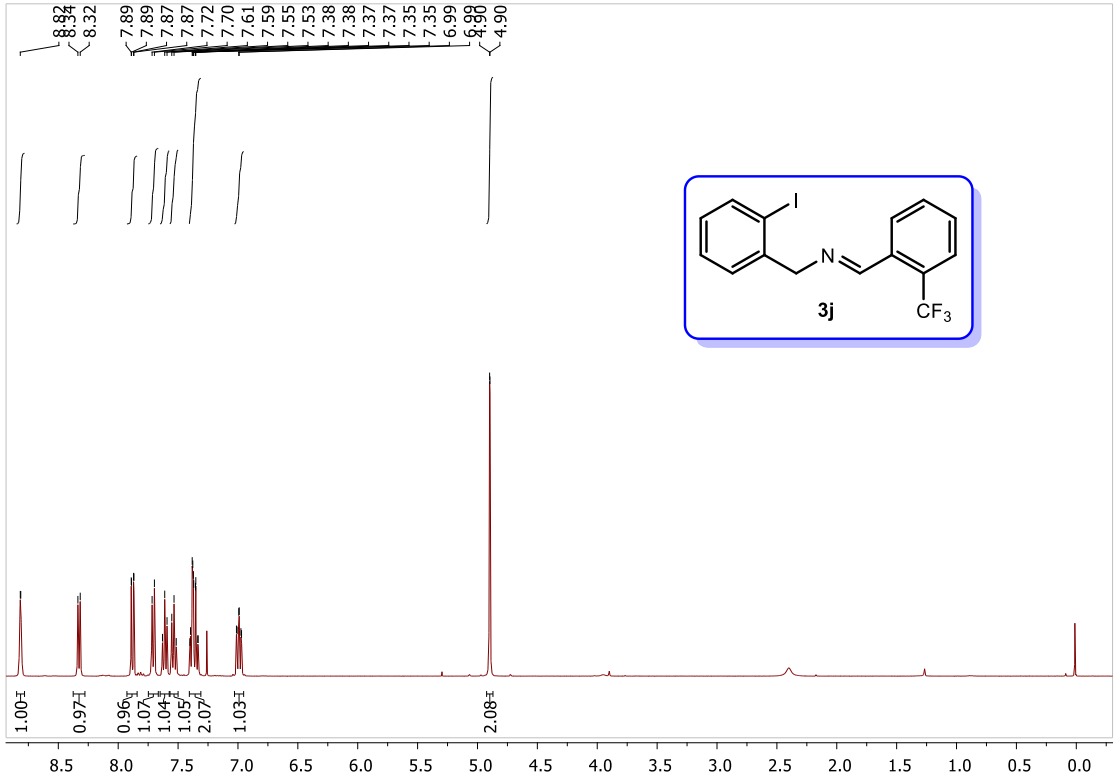


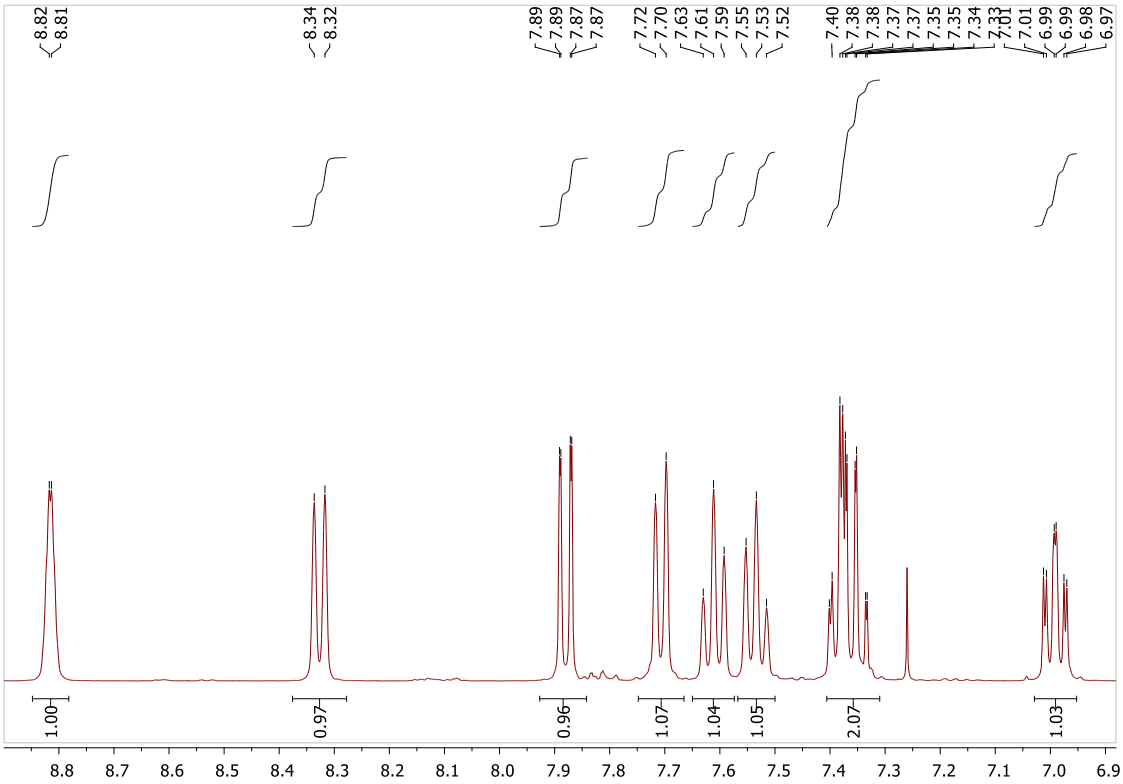


^{13}C NMR ($CDCl_3$) (*E*)-4-(((2-iodobenzyl)imino)methyl)benzonitrile(3d)

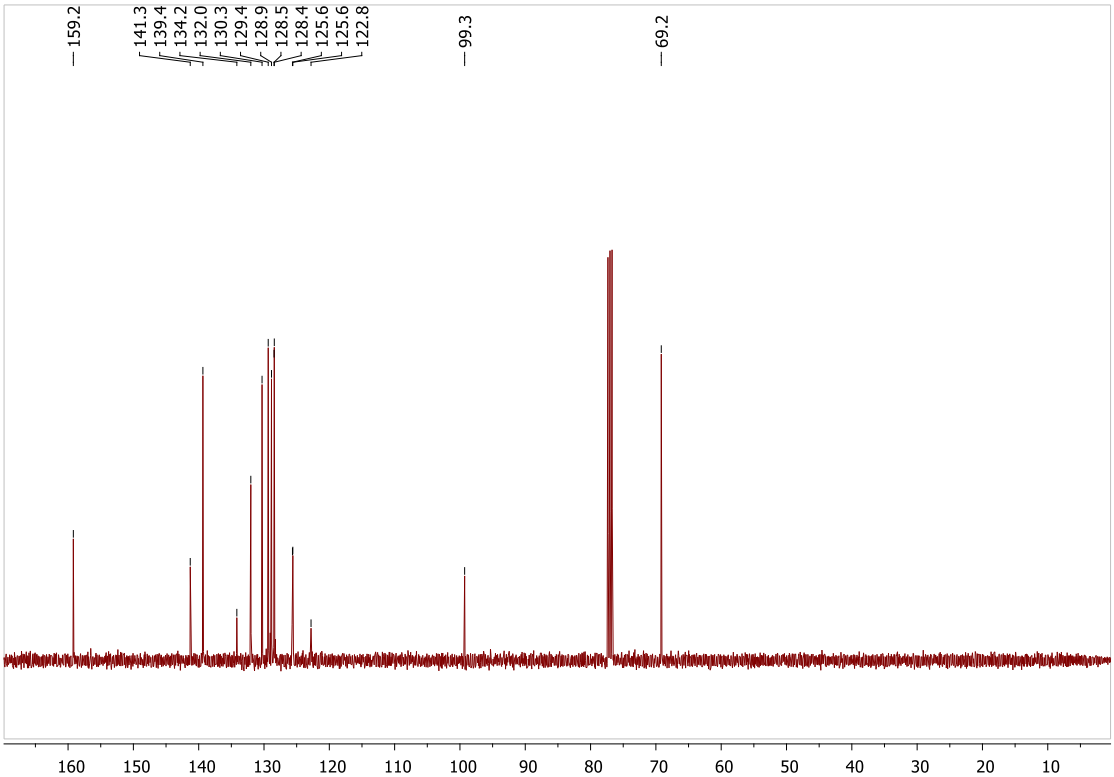


^{1}H NMR (*E*)-*N*-(2-iodobenzyl)-1-(2-(trifluoromethyl)phenyl)methanimine (3j)

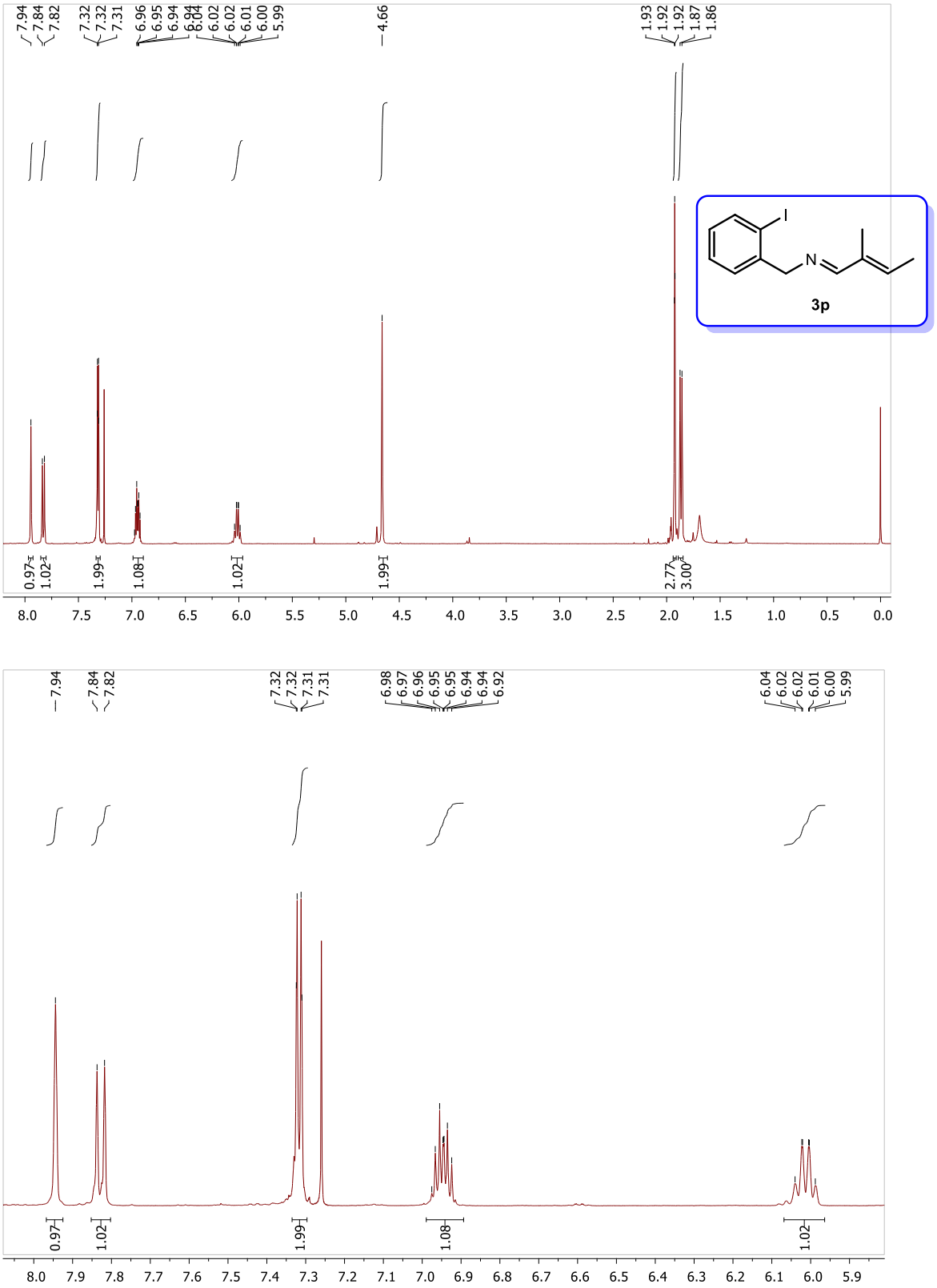




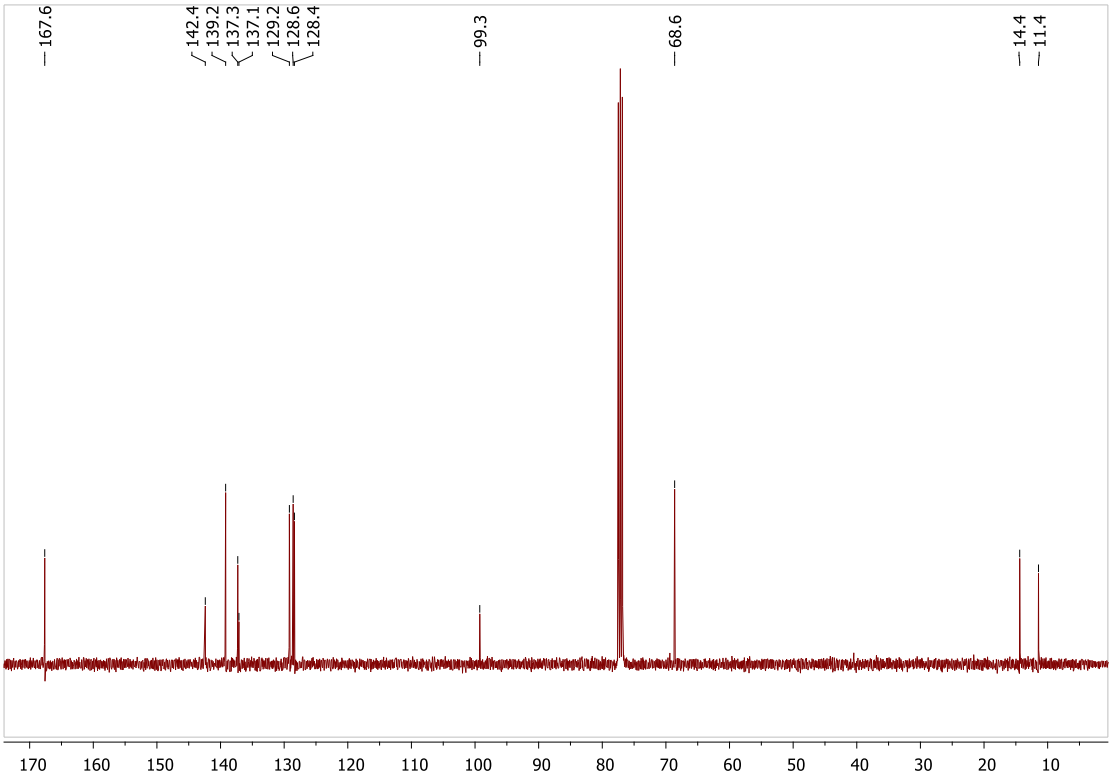
^{13}C NMR (*E*)-*N*-(2-iodobenzyl)-1-(2-(trifluoromethyl)phenyl)methanimine (3j)



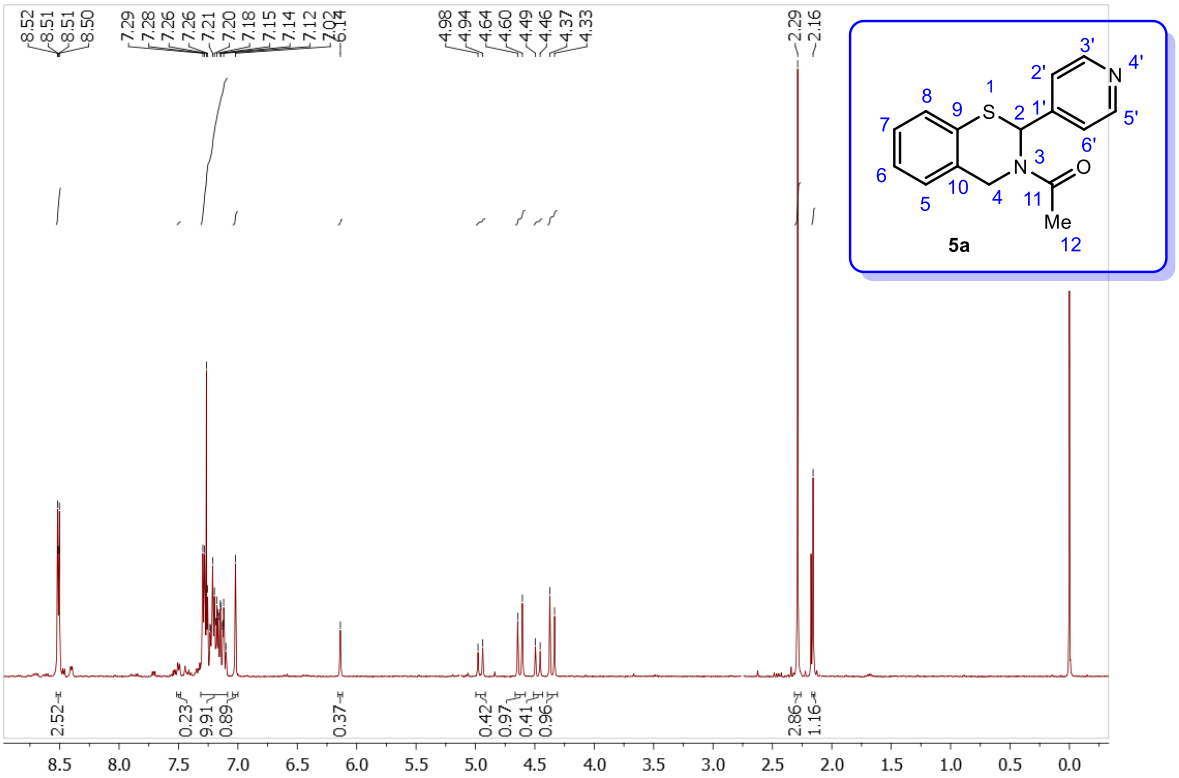
^{1}H NMR (1*E*,2*E*)-*N*-(2-iodobenzyl)-2-methylbut-2-en-1-imine(3p)



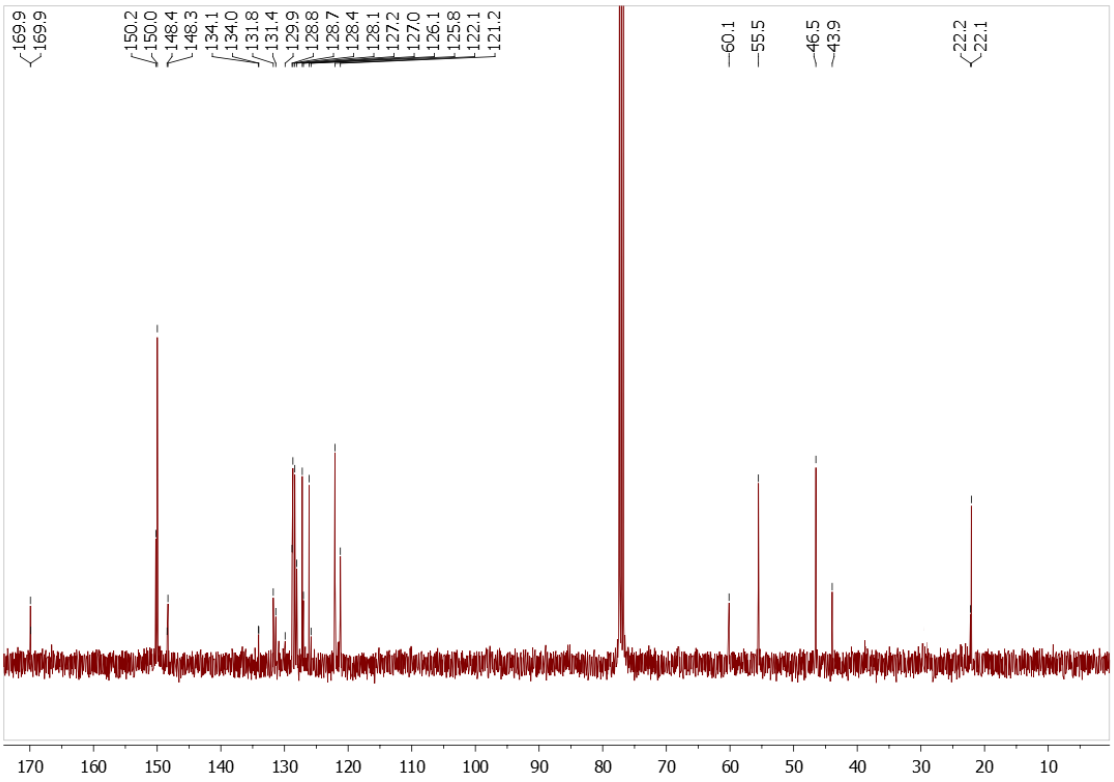
^{13}C NMR (1*E*,2*E*)-*N*-(2-iodobenzyl)-2-methylbut-2-en-1-imine(3p)



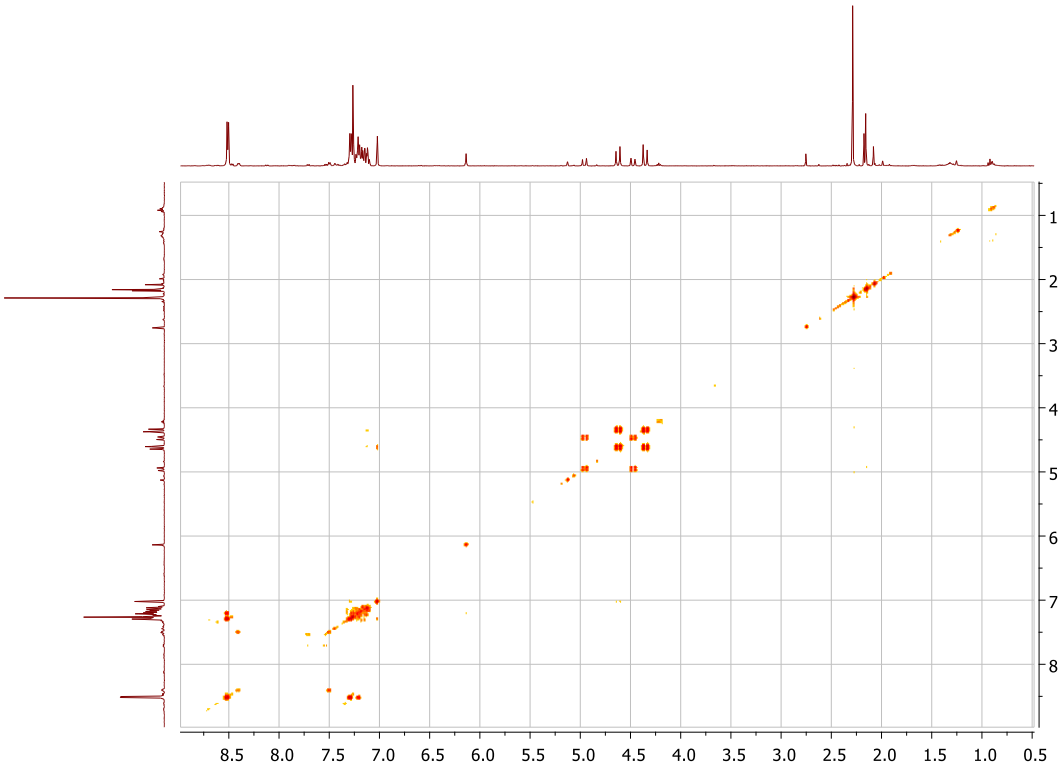
^{1}H NMR ($CDCl_3$)1-(2-(pyridin-4-yl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5a)



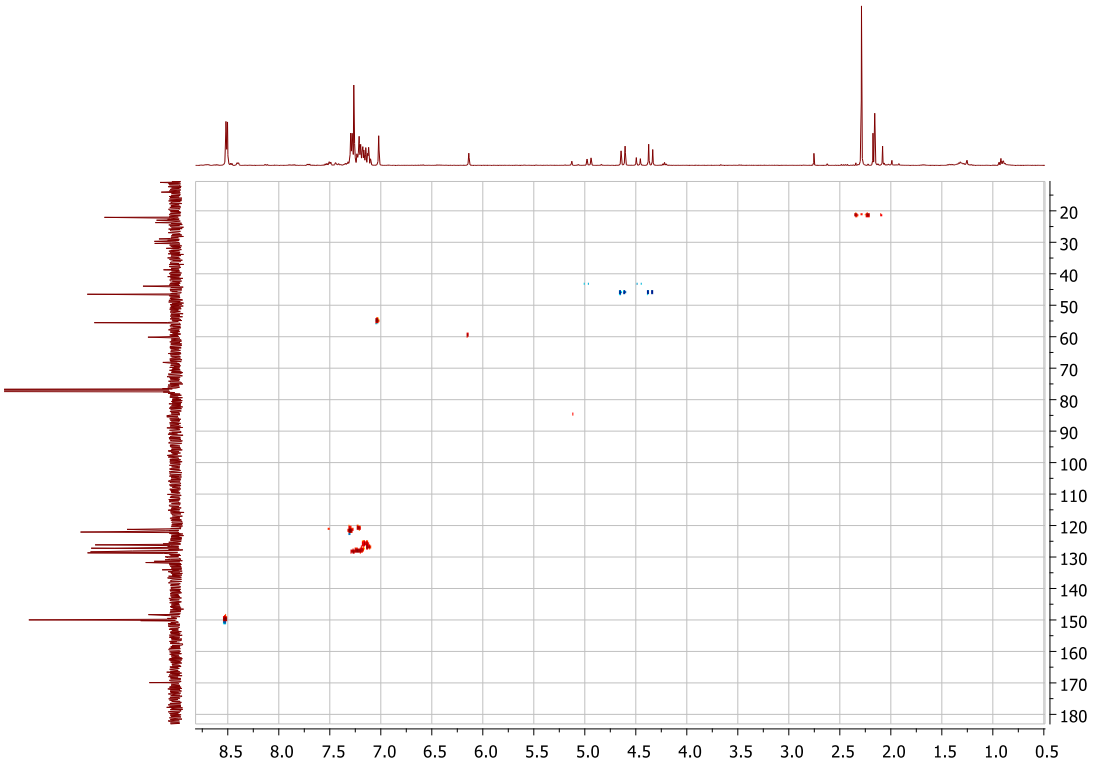
^{13}C NMR($CDCl_3$)1-(2-(pyridin-4-yl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5a)



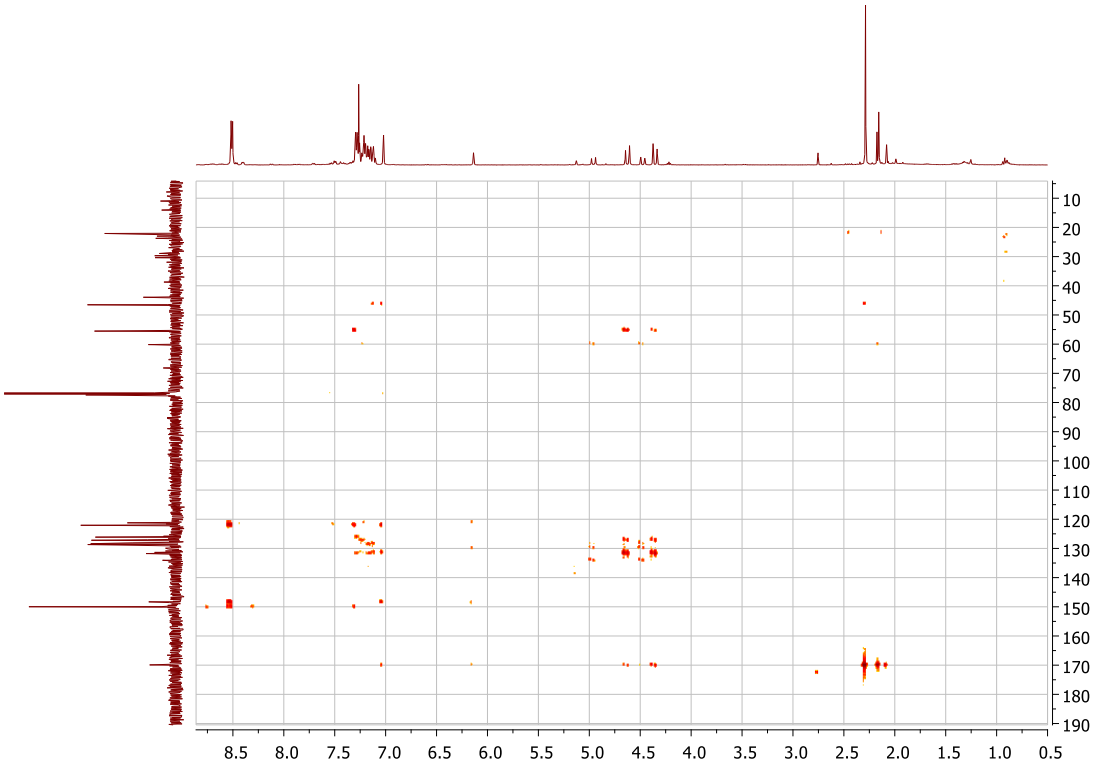
COSY ($CDCl_3$)1-(2-(pyridin-4-yl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5a)



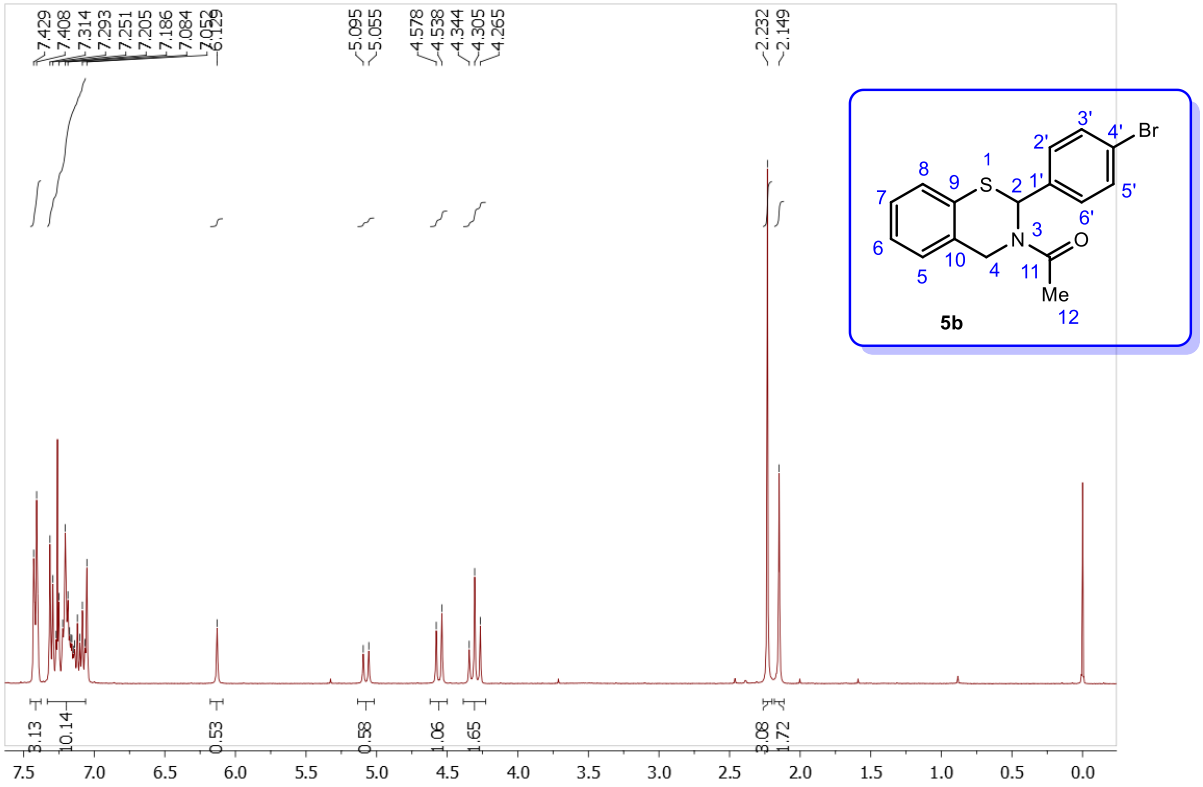
HSQC ($CDCl_3$)1-(2-(pyridin-4-yl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5a)



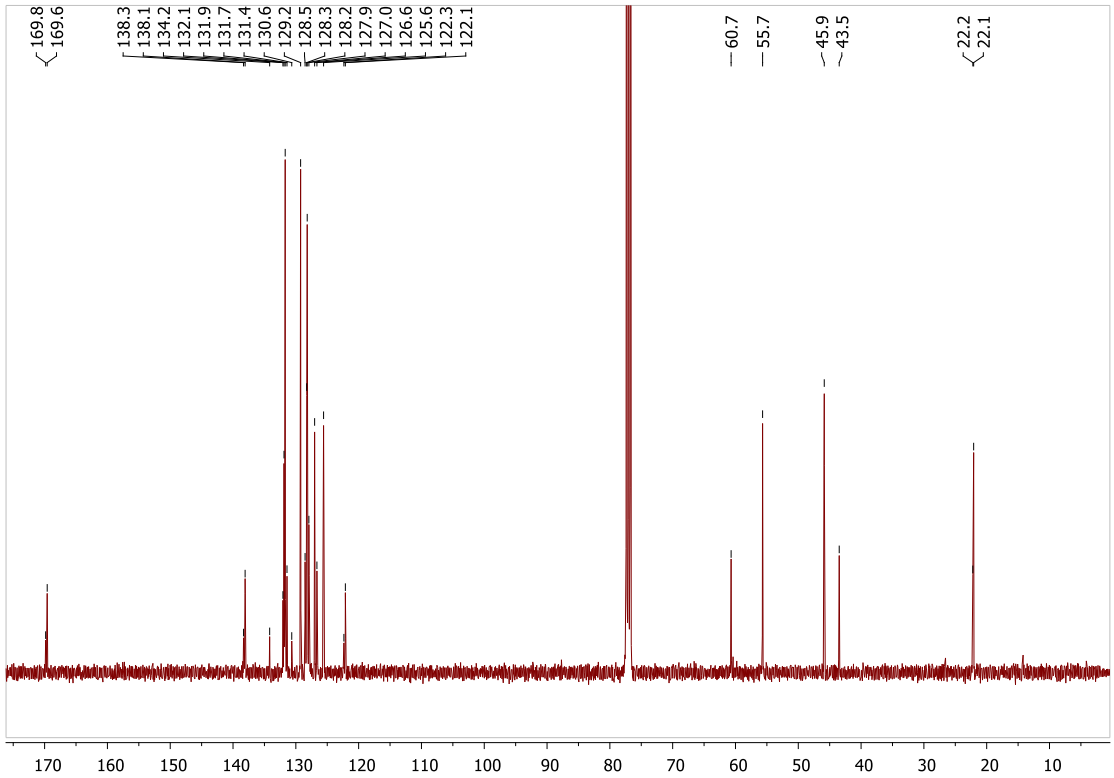
HMBC ($CDCl_3$)1-(2-(pyridin-4-yl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5a)



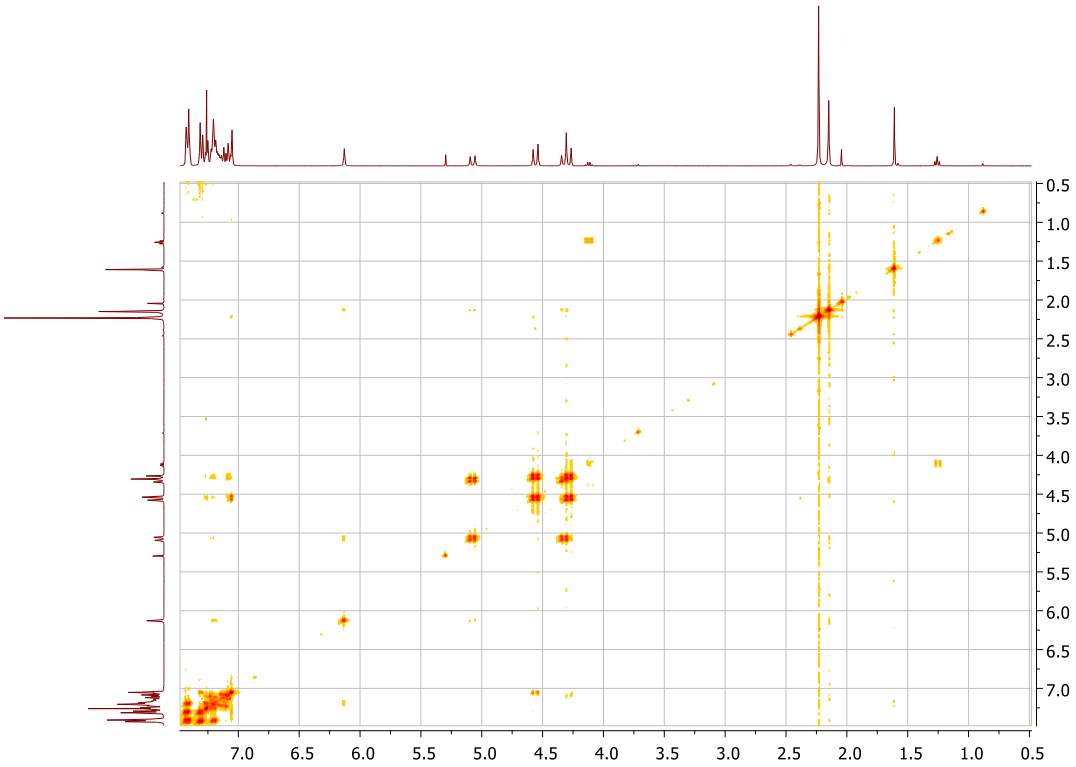
^{1}H NMR ($CDCl_3$)1-(2-(4-bromophenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5b)



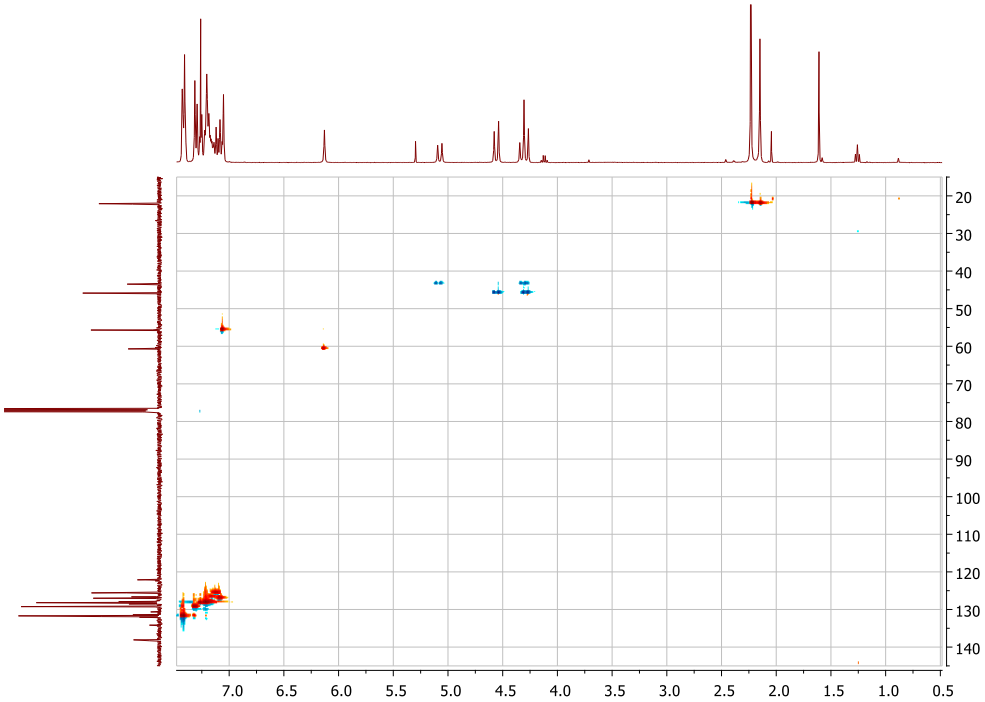
^{13}C NMR ($CDCl_3$)1-(2-(4-bromophenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5b)



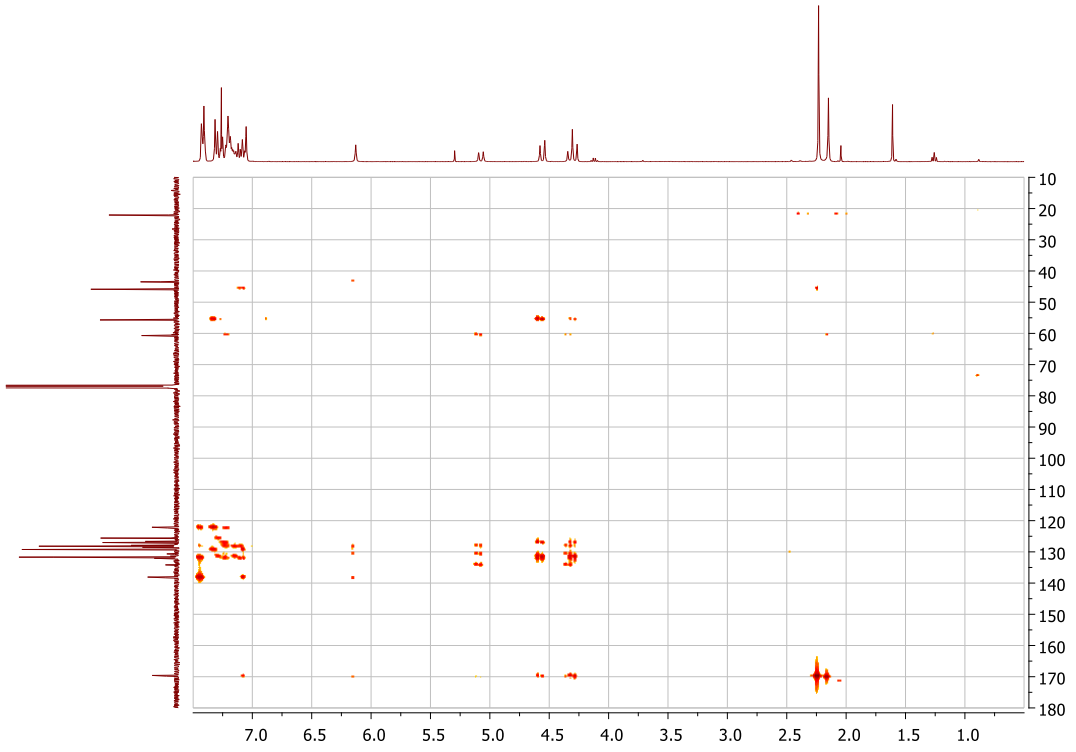
COSY NMR ($CDCl_3$)1-(2-(4-bromophenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5b)



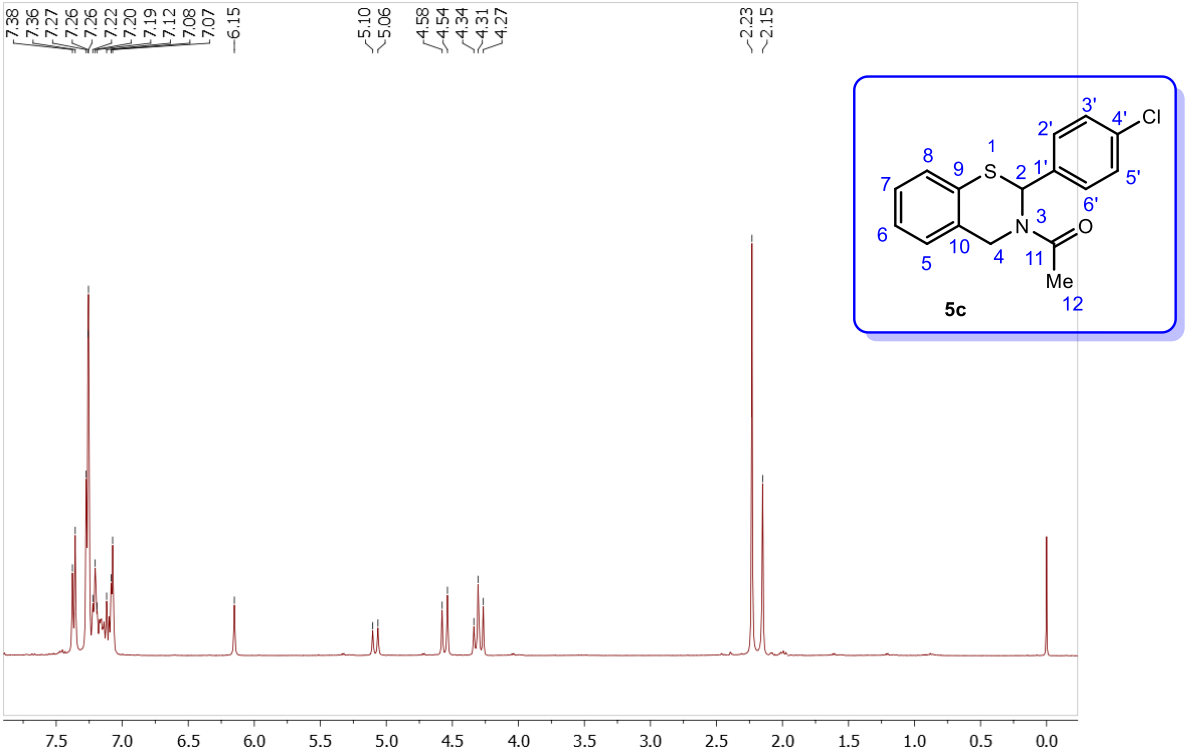
HSQC NMR ($CDCl_3$)1-(2-(4-bromophenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5b)



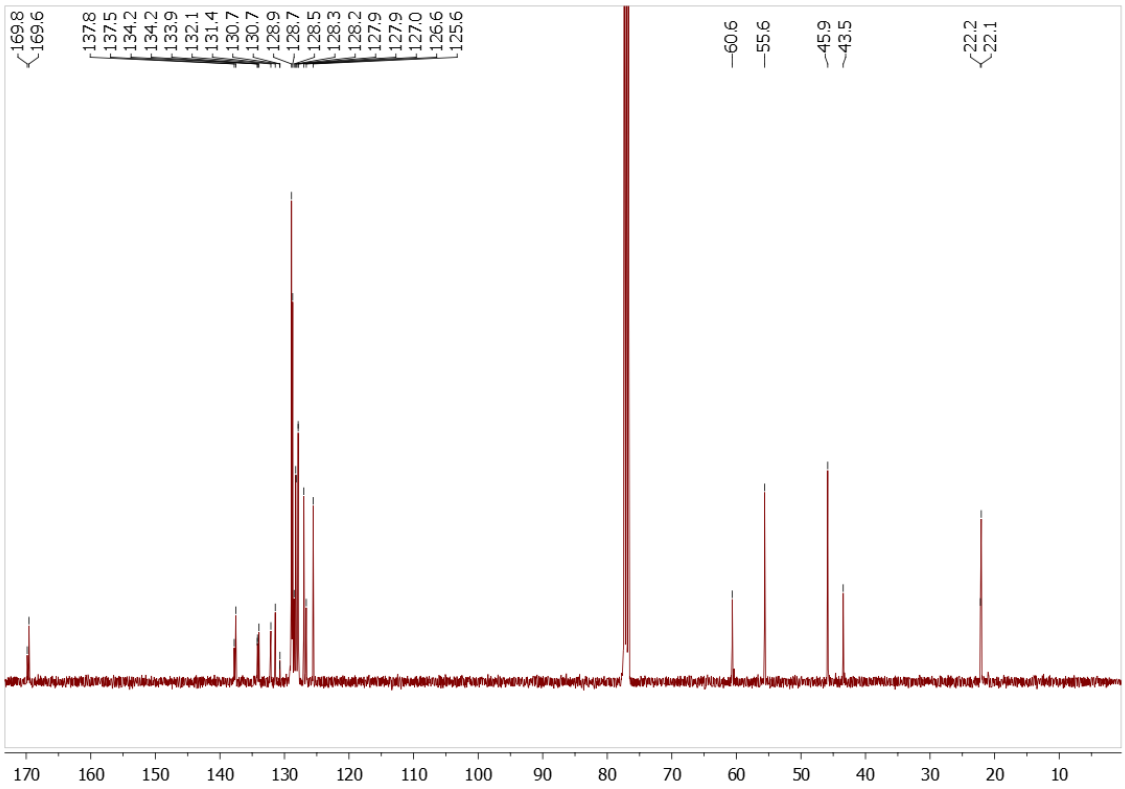
HMBC NMR($CDCl_3$)1-(2-(4-bromophenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5b)



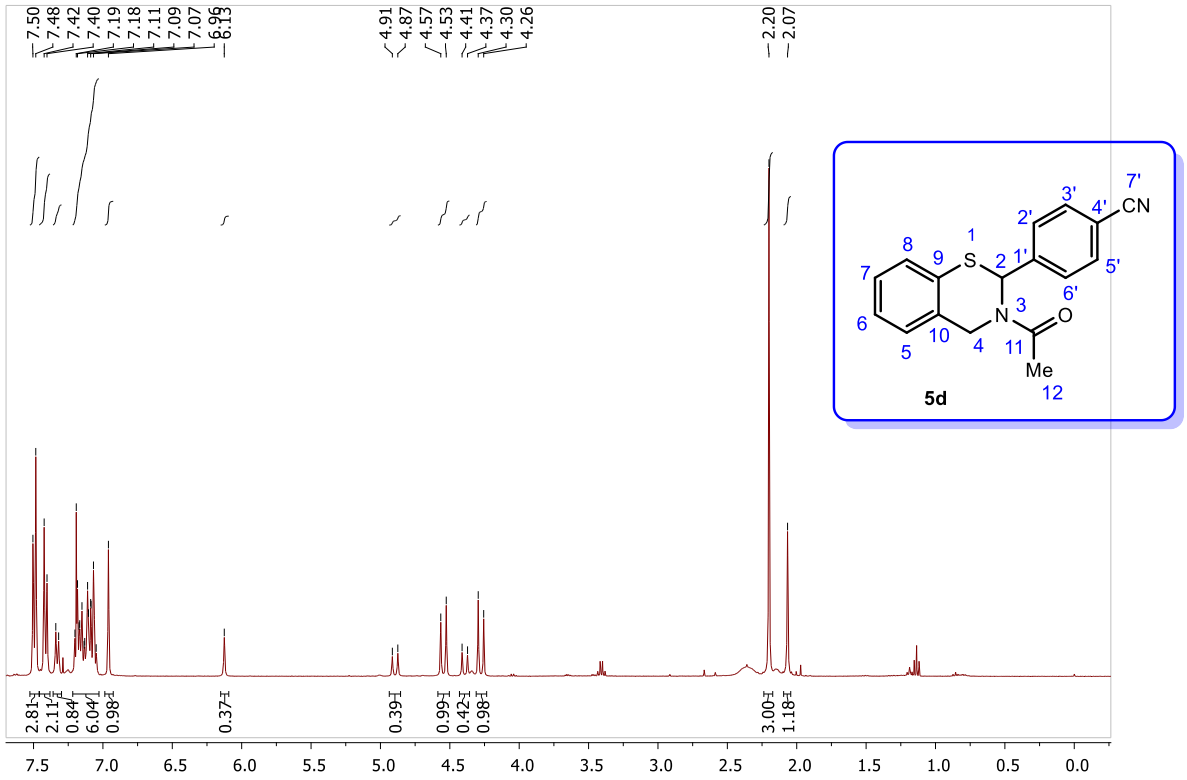
^{1}H NMR ($CDCl_3$)1-(2-(4-chlorophenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5c)



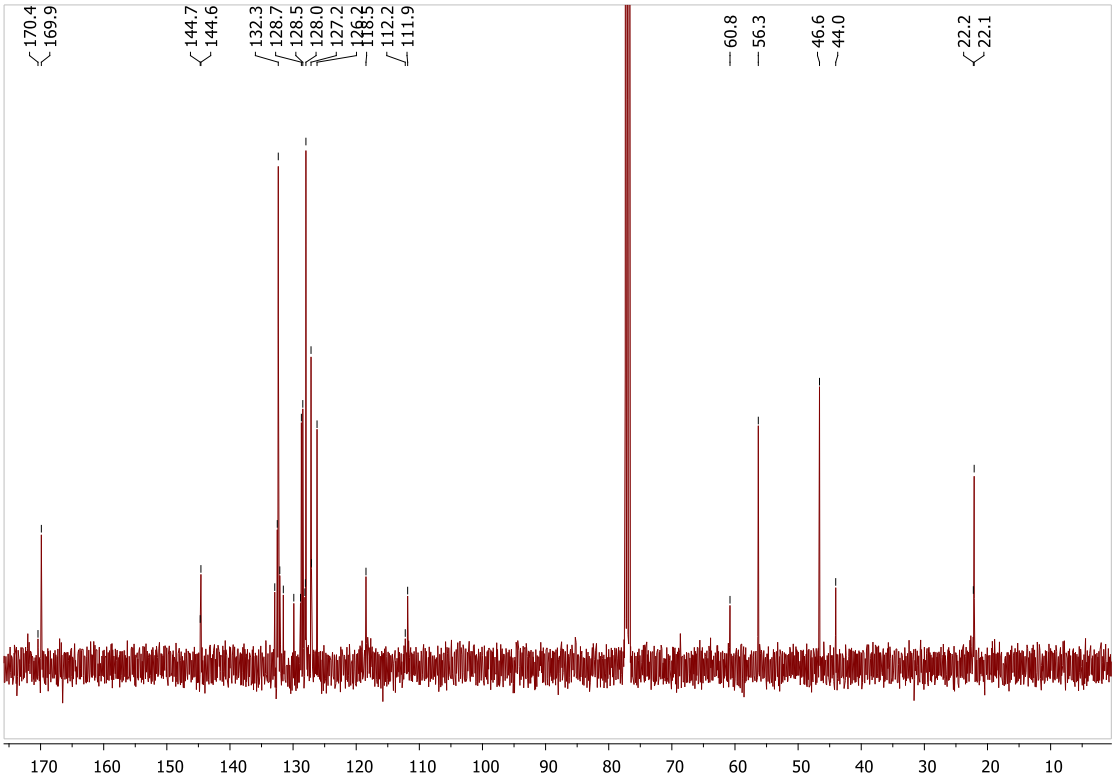
^{13}C NMR ($CDCl_3$)1-(2-(4-chlorophenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5c)



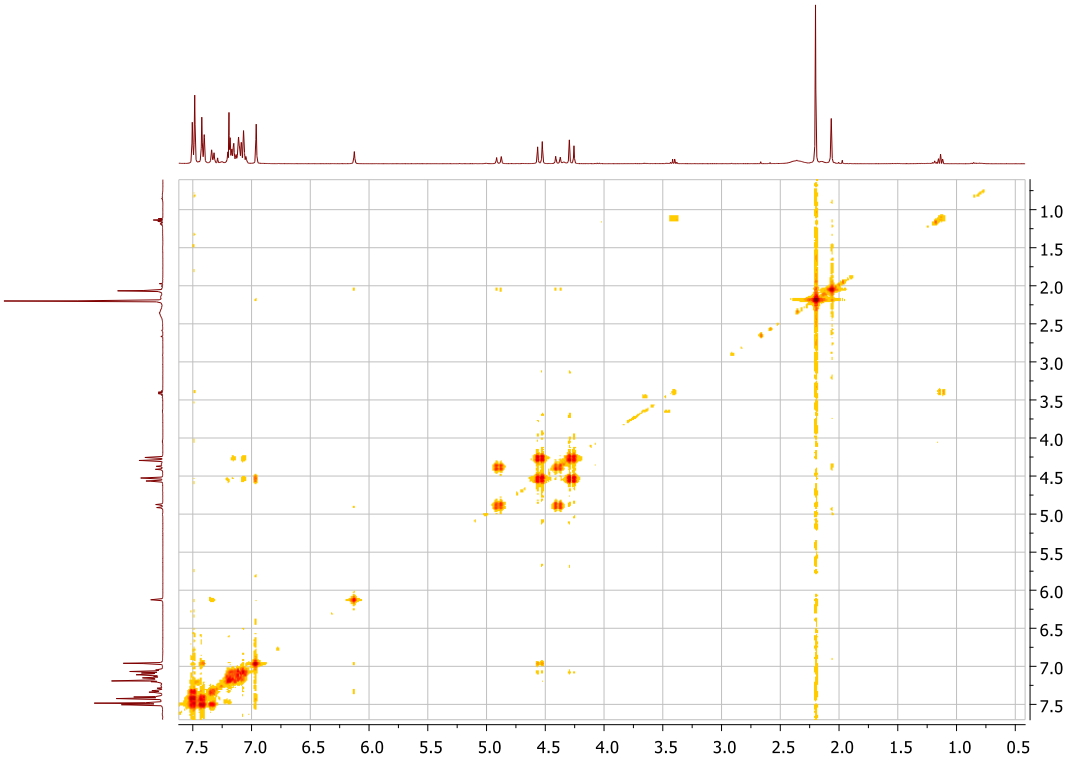
^{1}H NMR ($CDCl_3$) 4-(3-acetyl-3,4-dihydro-2*H*-benzo[*e*][1,3]thiazin-2-yl)benzonitrile (5d)



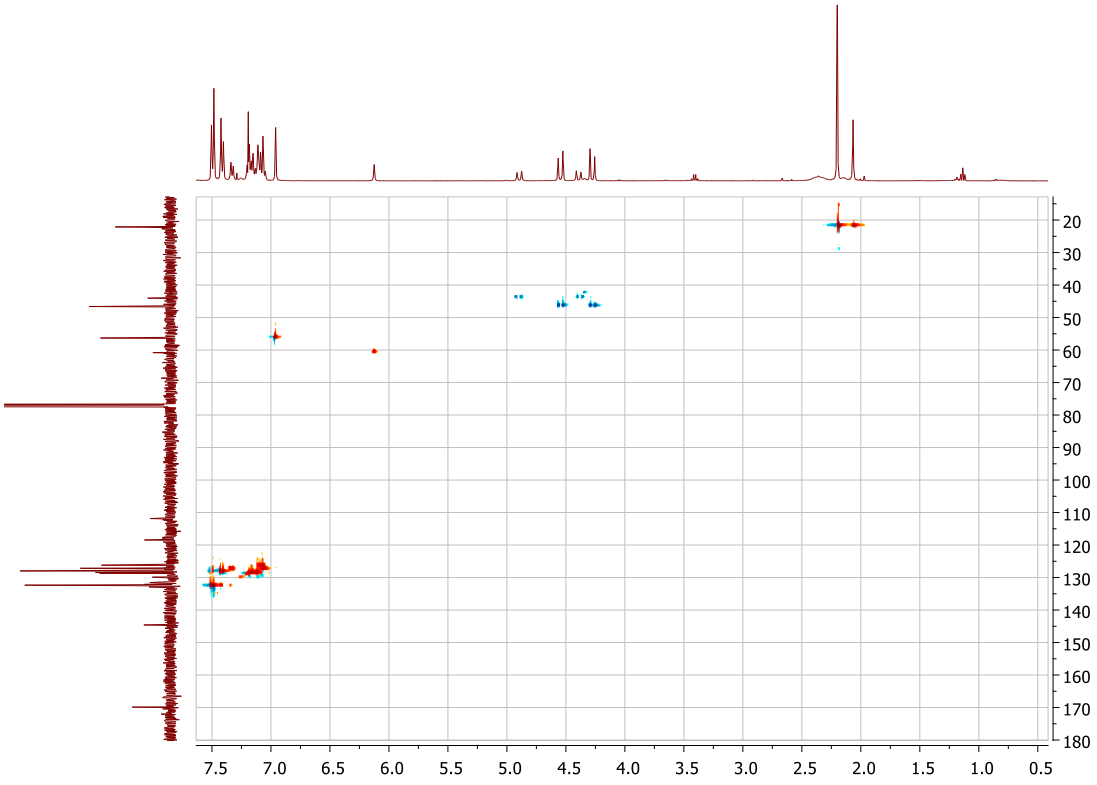
^{13}C NMR($CDCl_3$) 4-(3-acetyl-3,4-dihydro-2*H*-benzo[*e*][1,3]thiazin-2-yl)benzonitrile (5d)



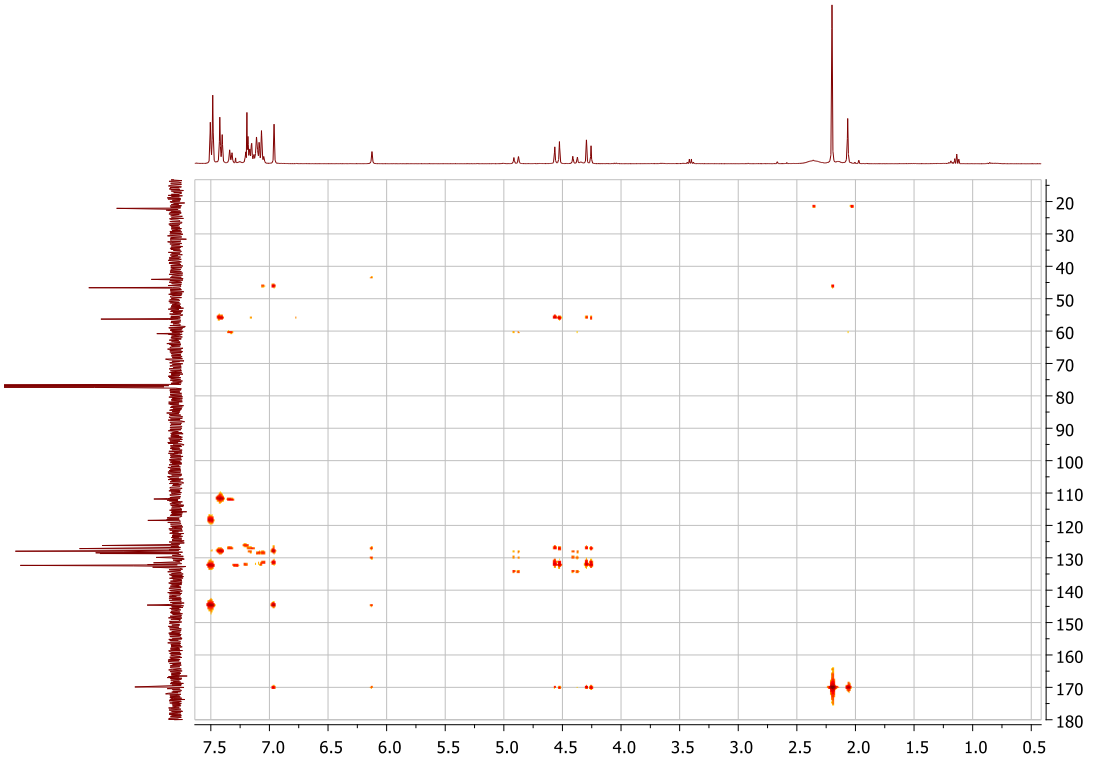
COSY ($CDCl_3$) 4-(3-acetyl-3,4-dihydro-2*H*-benzo[*e*][1,3]thiazin-2-yl)benzonitrile (5d)



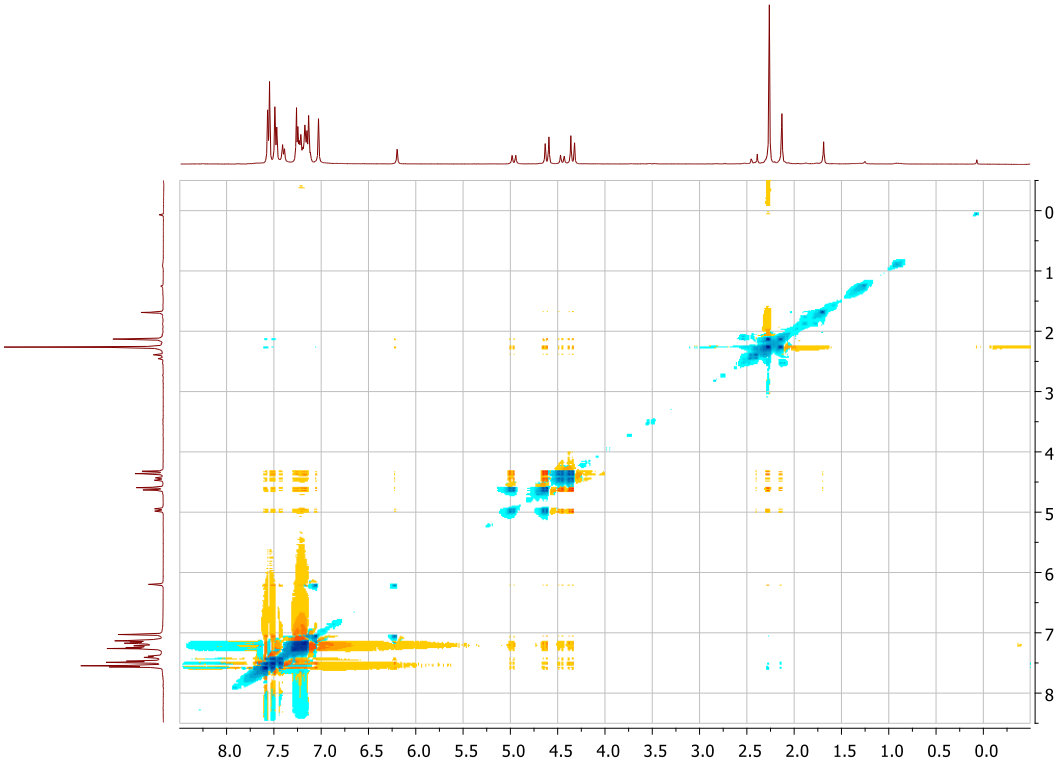
HSQC ($CDCl_3$) 4-(3-acetyl-3,4-dihydro-2*H*-benzo[*e*][1,3]thiazin-2-yl)benzonitrile (5d)



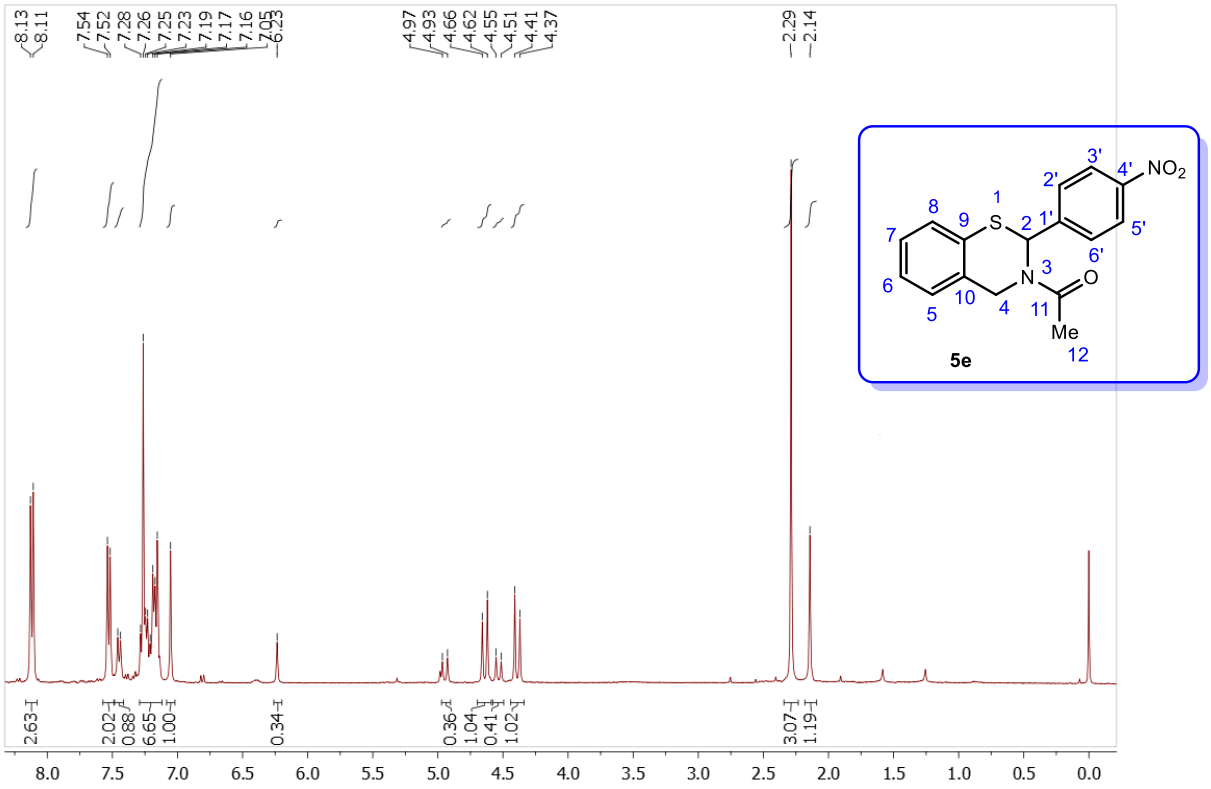
HMBC ($CDCl_3$) 4-(3-acetyl-3,4-dihydro-2*H*-benzo[*e*][1,3]thiazin-2-yl)benzonitrile (5d)



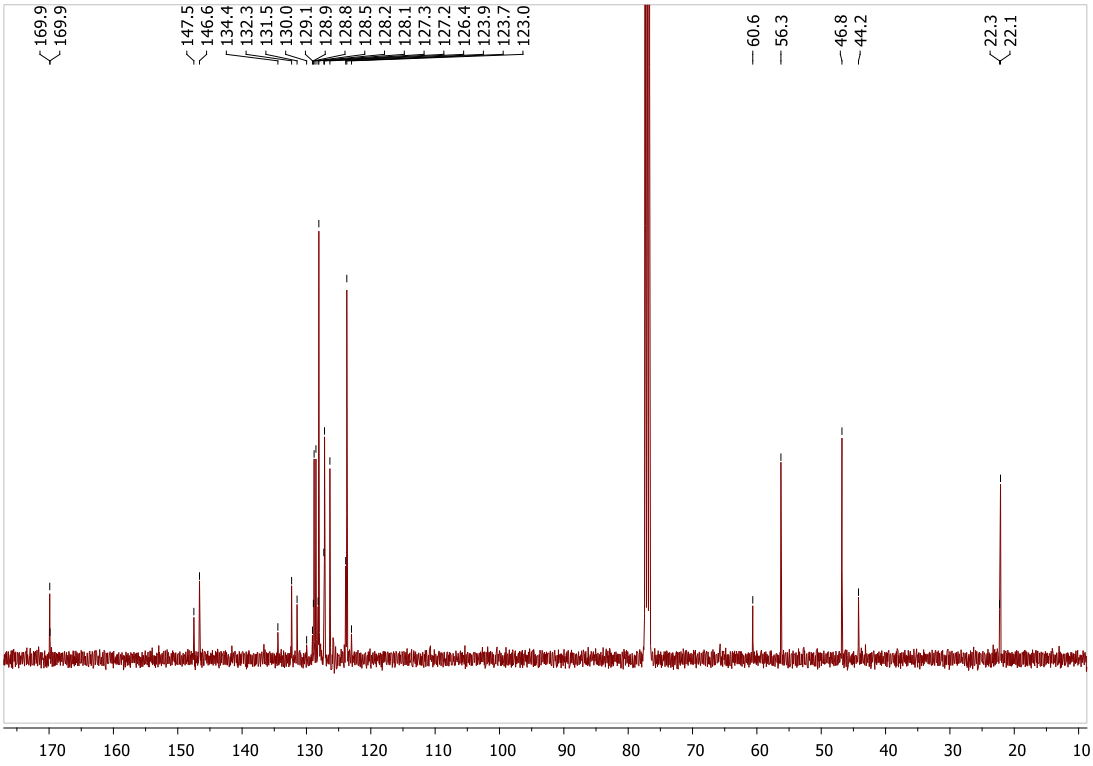
NOE 2D ($CDCl_3$) 4-(3-acetyl-3,4-dihydro-2*H*-benzo[*e*][1,3]thiazin-2-yl)benzonitrile (5d)



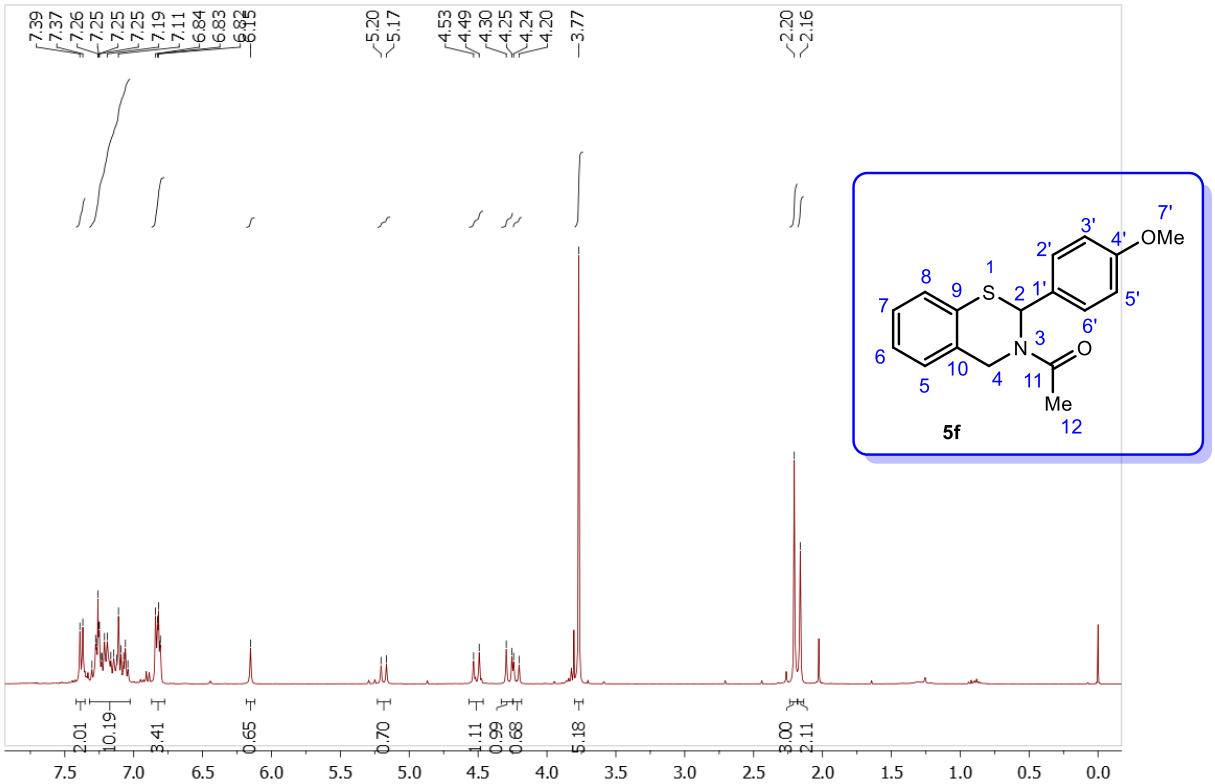
^{1}H NMR ($CDCl_3$)1-(2-(4-Nitrophenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5e)



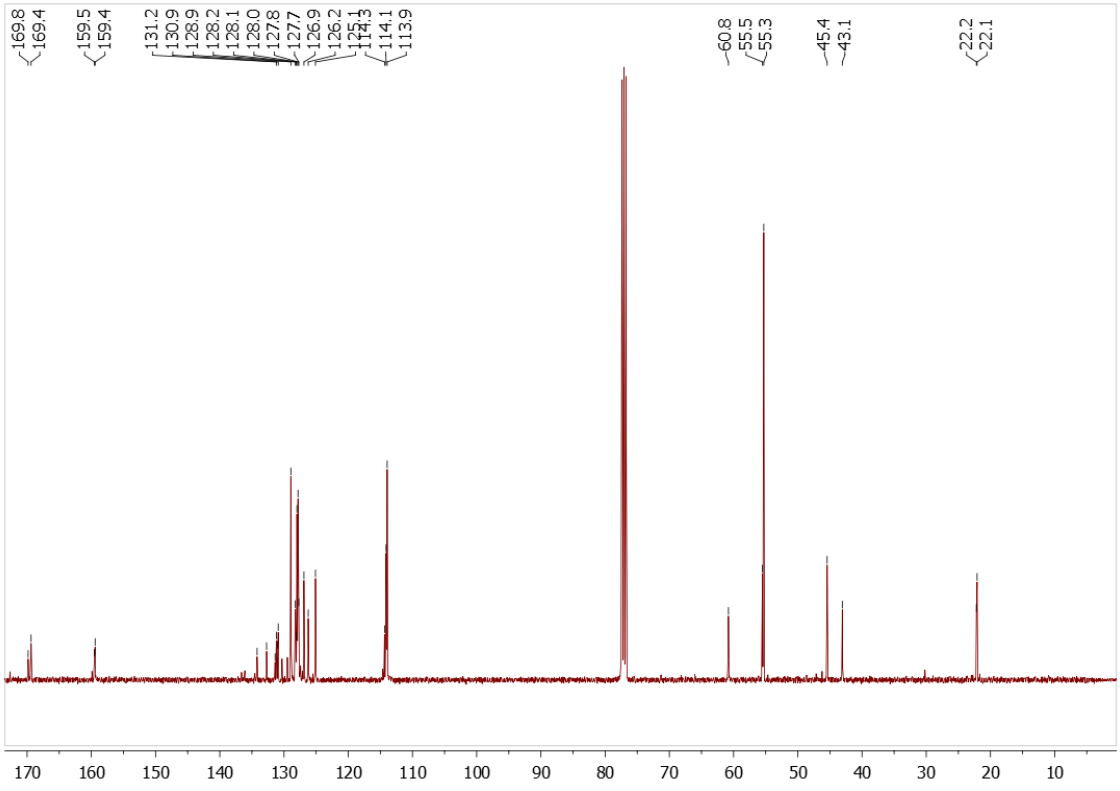
^{13}C NMR ($CDCl_3$)1-(2-(4-Nitrophenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5e)



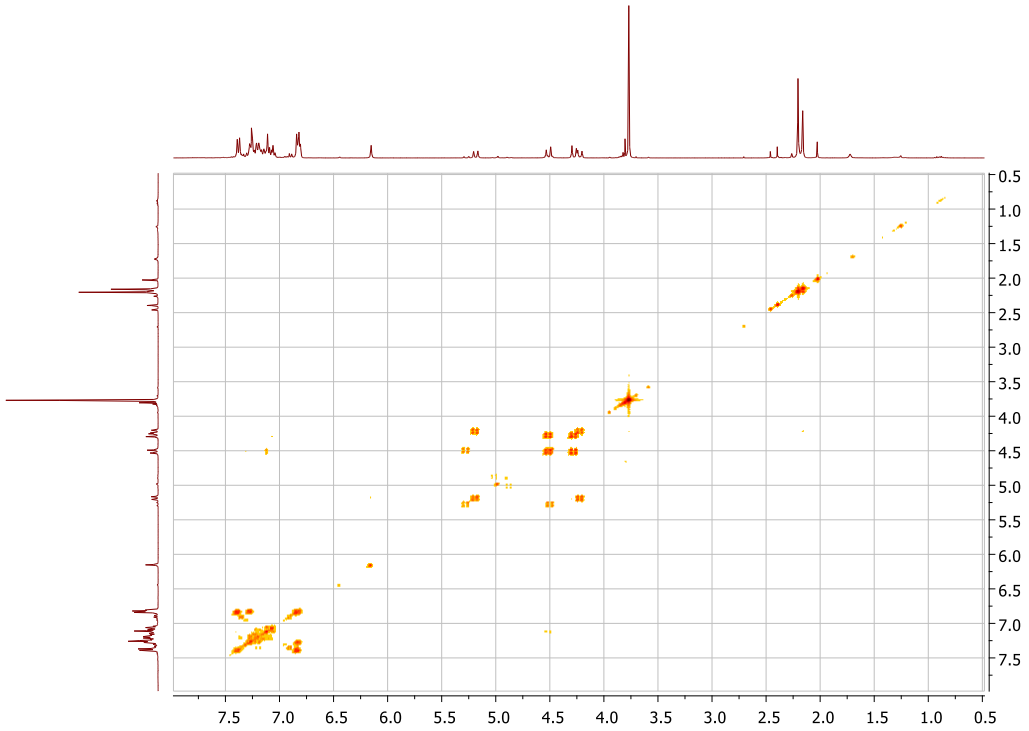
^{1}H NMR ($CDCl_3$)1-(2-(4-methoxyphenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5f)



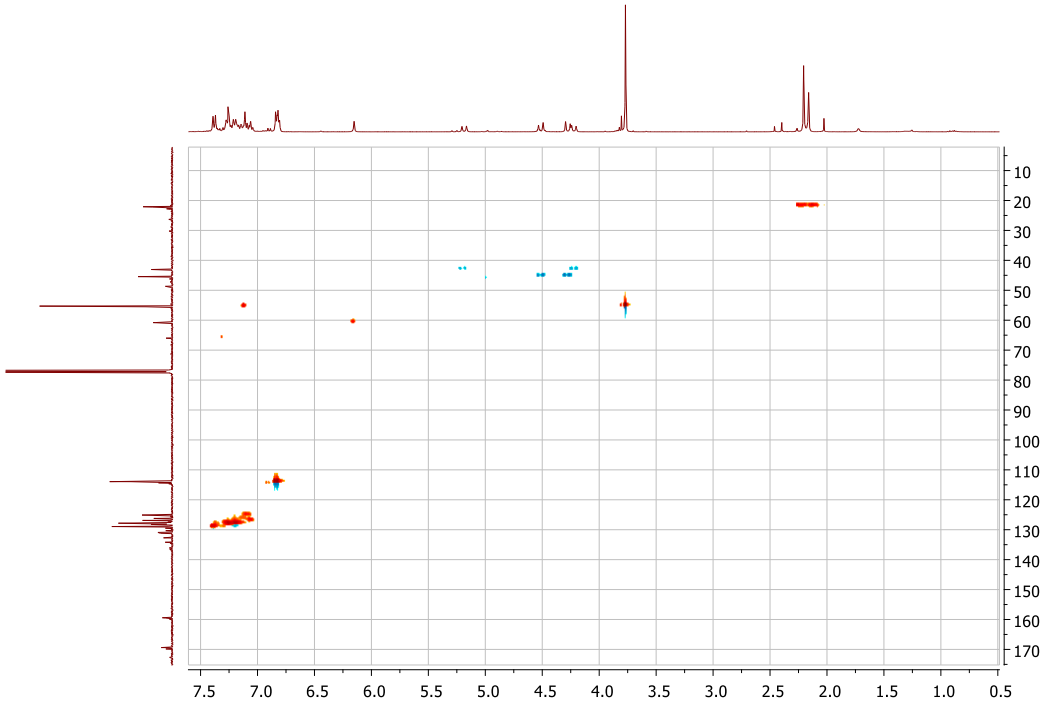
^{13}C NMR ($CDCl_3$)1-(2-(4-methoxyphenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5f)



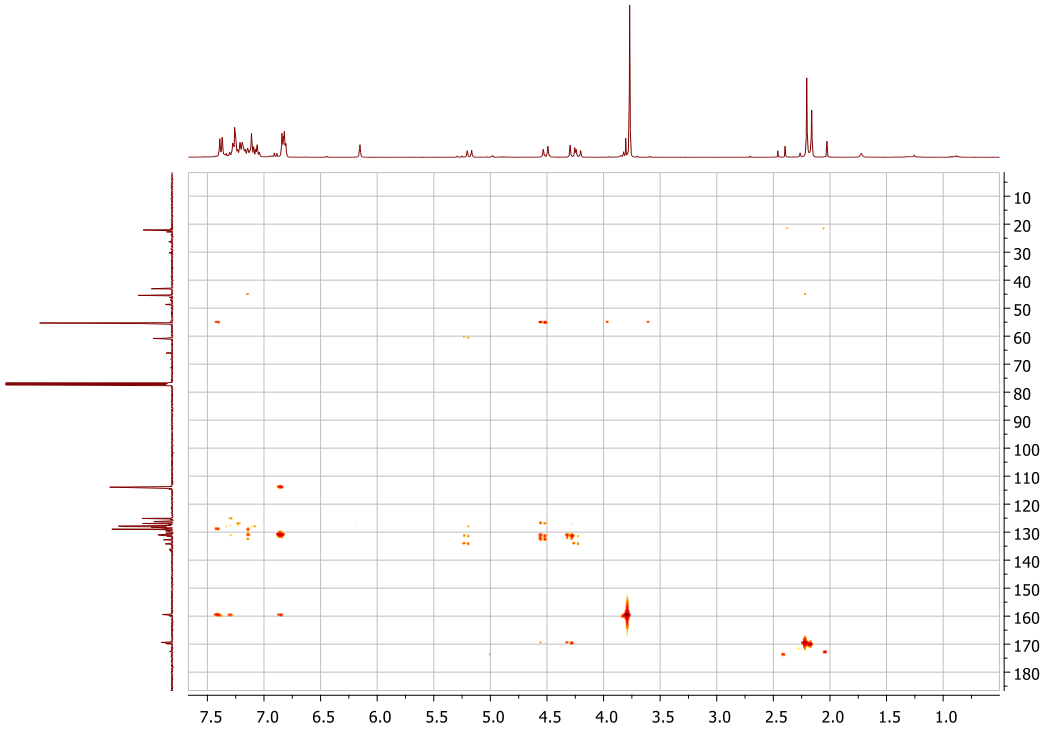
COSY NMR($CDCl_3$)1-(2-(4-methoxyphenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5f)



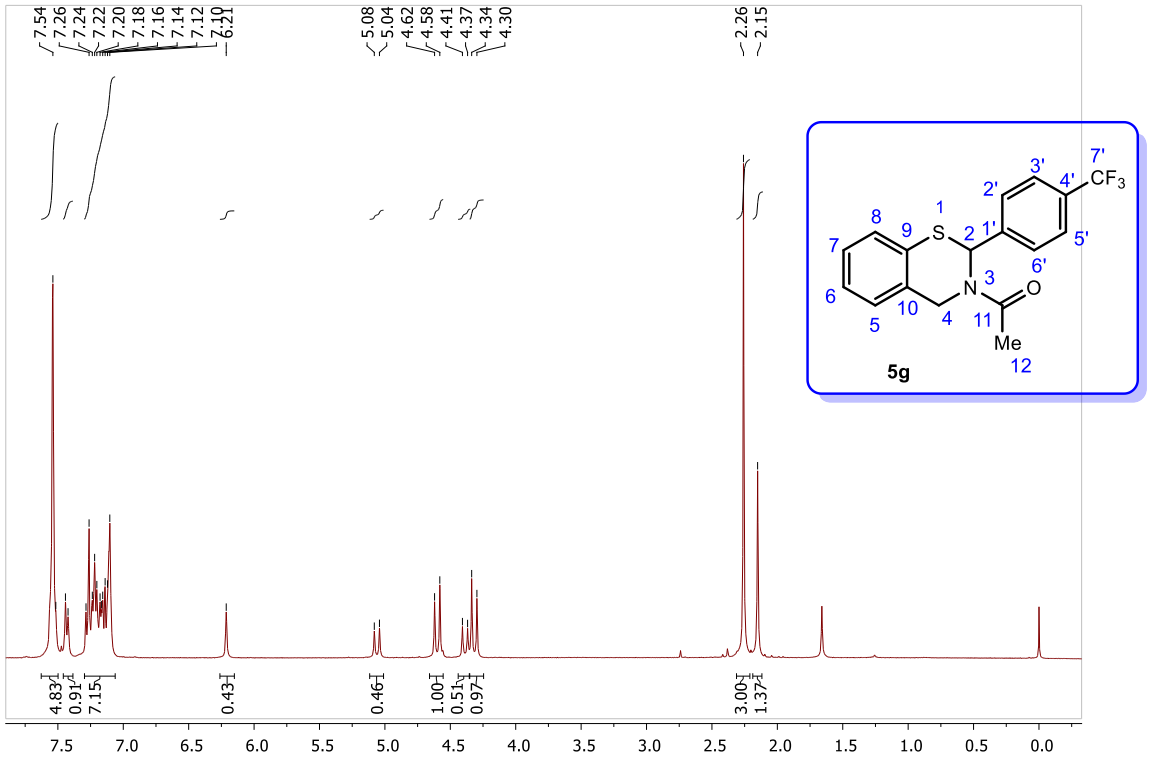
HSQC NMR ($CDCl_3$)1-(2-(4-methoxyphenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5f)



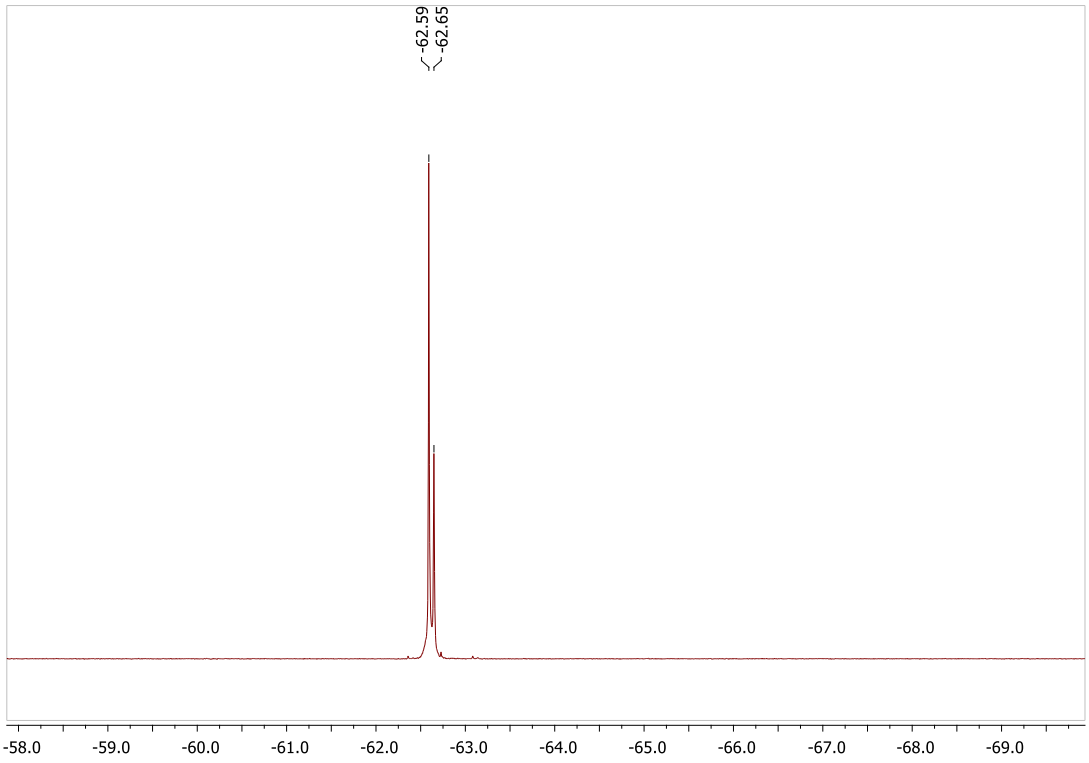
HMBC NMR($CDCl_3$)1-(2-(4-methoxyphenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5f)



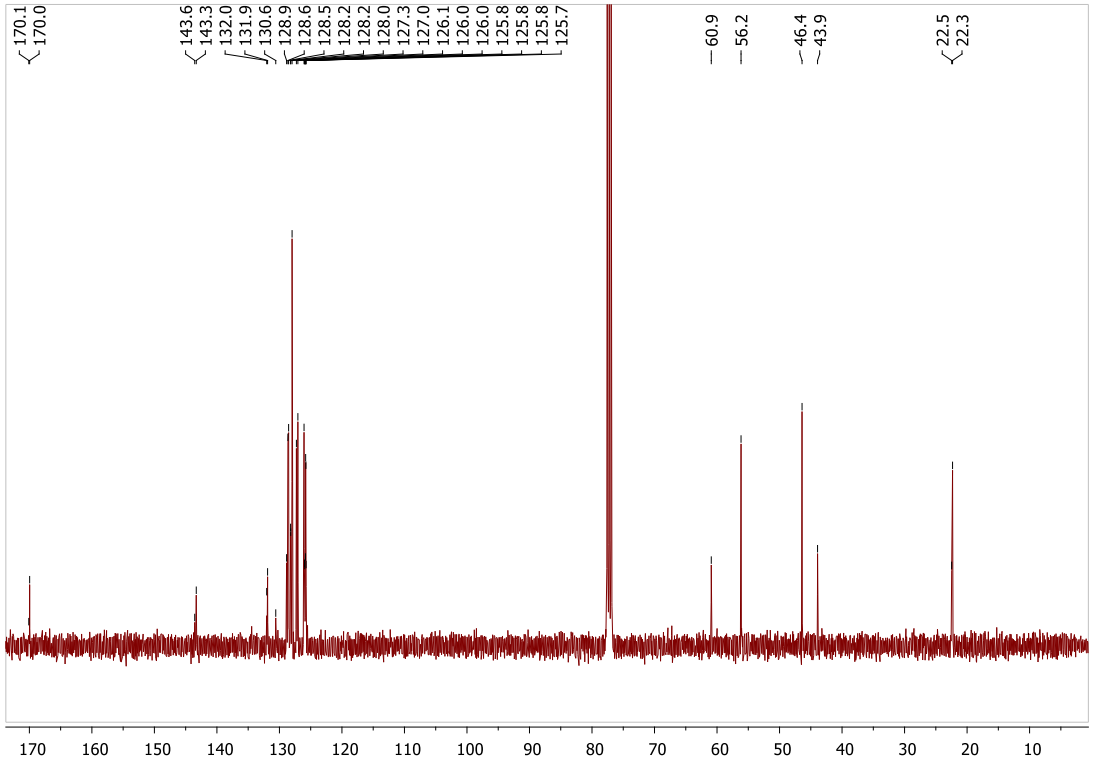
^{1}H NMR ($CDCl_3$)1-(2-(4-(trifluoromethyl)phenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5g)



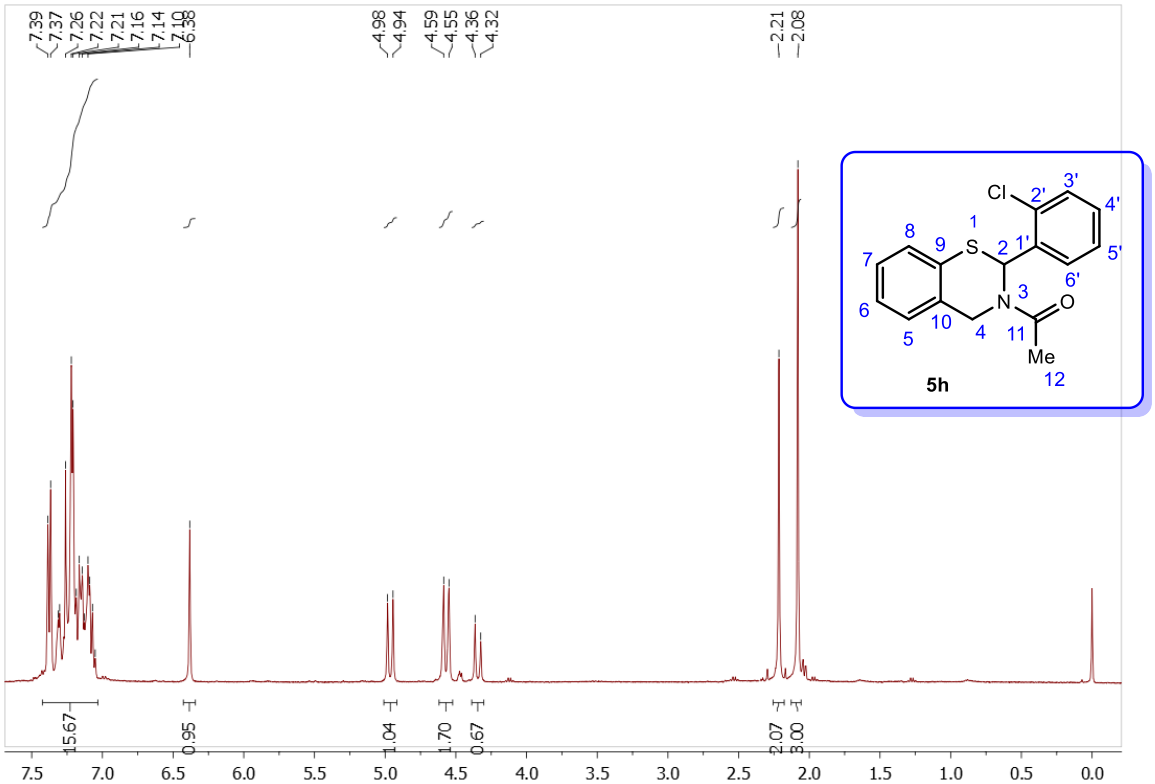
^{19}F NMR ($CDCl_3$)1-(2-(4-(trifluoromethyl)phenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5g)



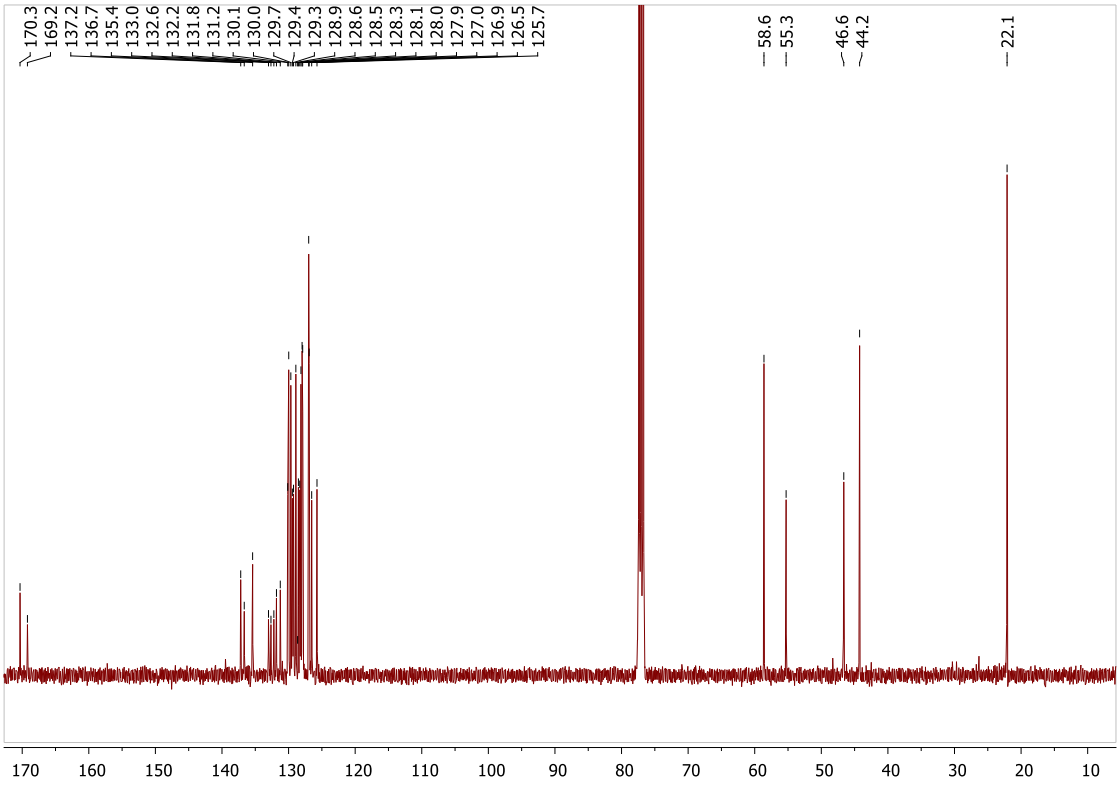
^{13}C NMR ($CDCl_3$)1-(2-(4-(trifluoromethyl)phenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5g)



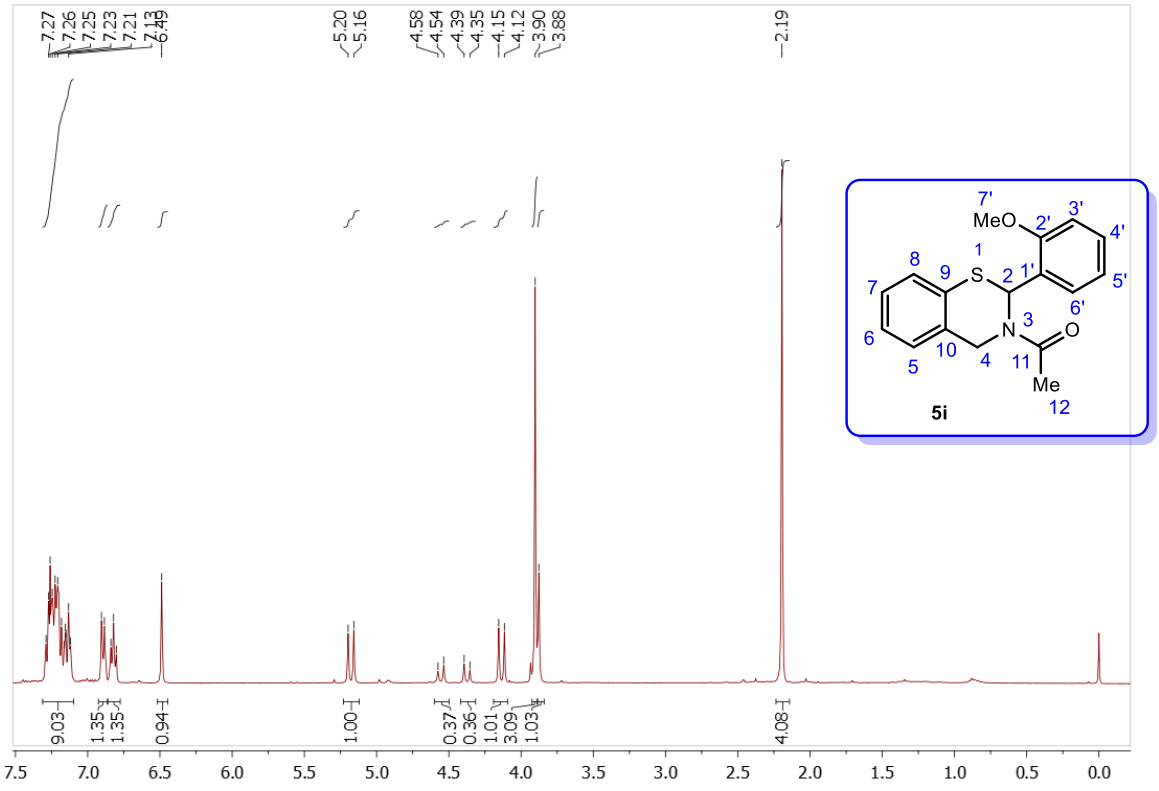
^{1}H NMR ($CDCl_3$)1-(2-(2-Chlorophenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5h)



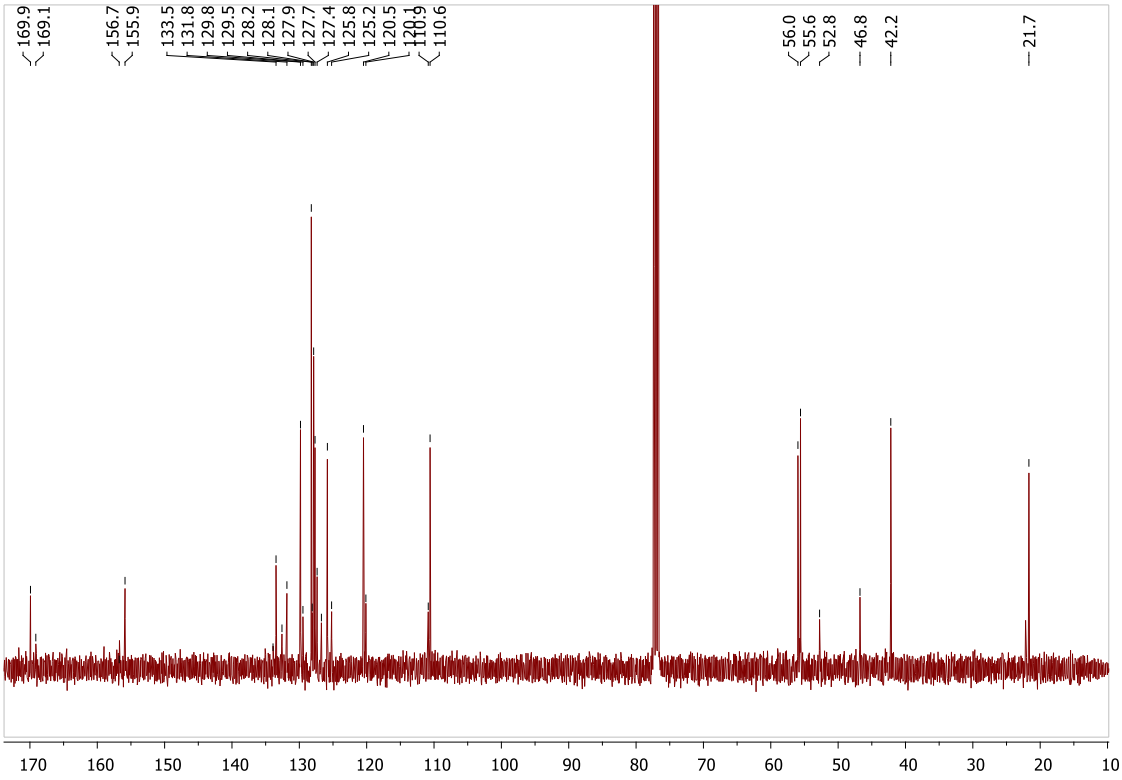
^{13}C NMR ($CDCl_3$)1-(2-(2-Chlorophenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5h)



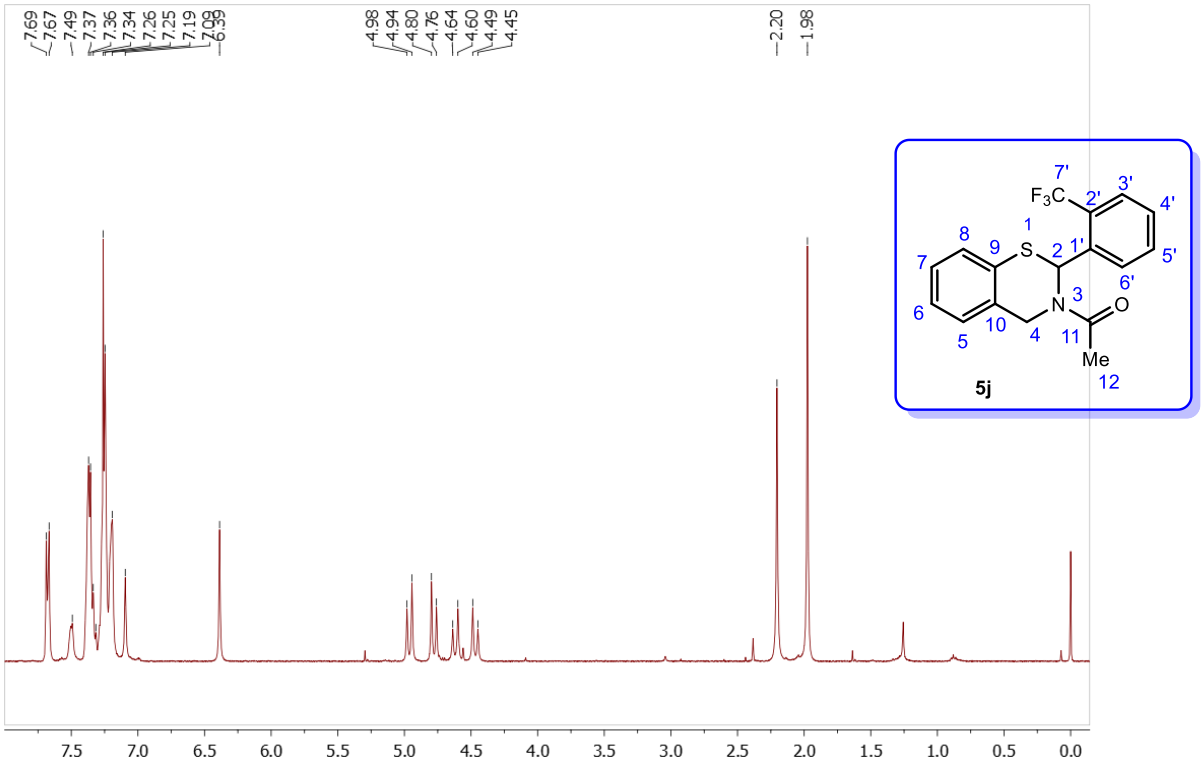
^{1}H NMR ($CDCl_3$)1-(2-(2-Methoxyphenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5i)



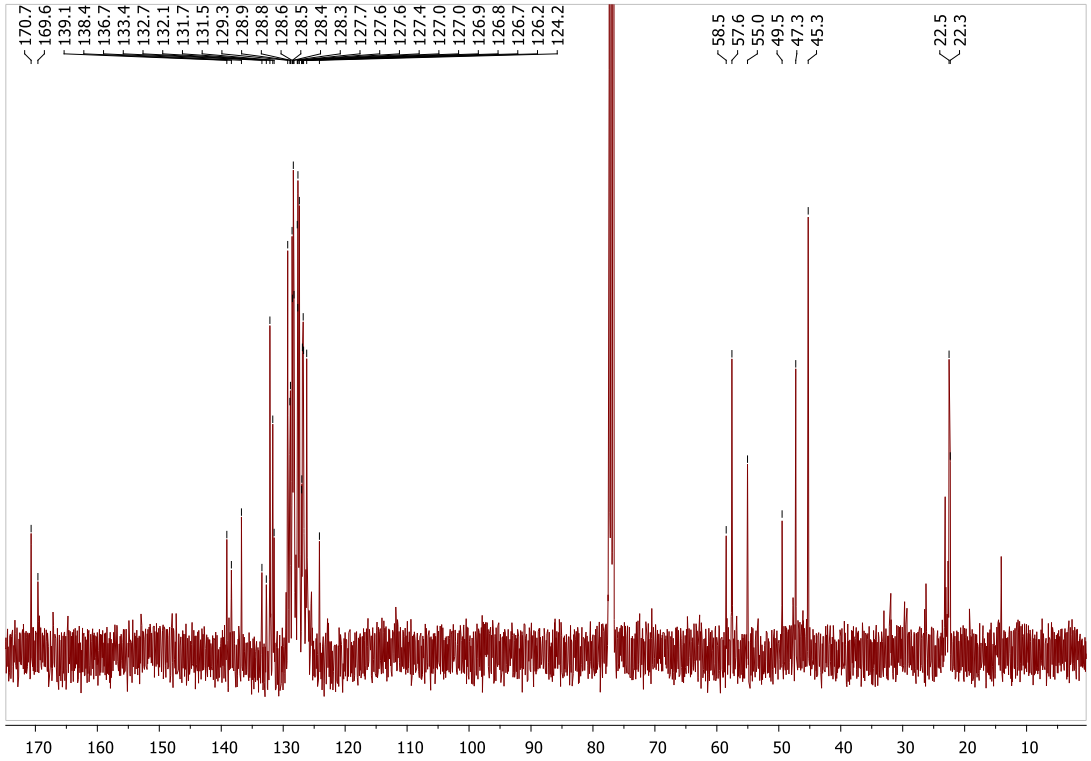
^{13}C NMR ($CDCl_3$)1-(2-(2-Methoxyphenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5i)



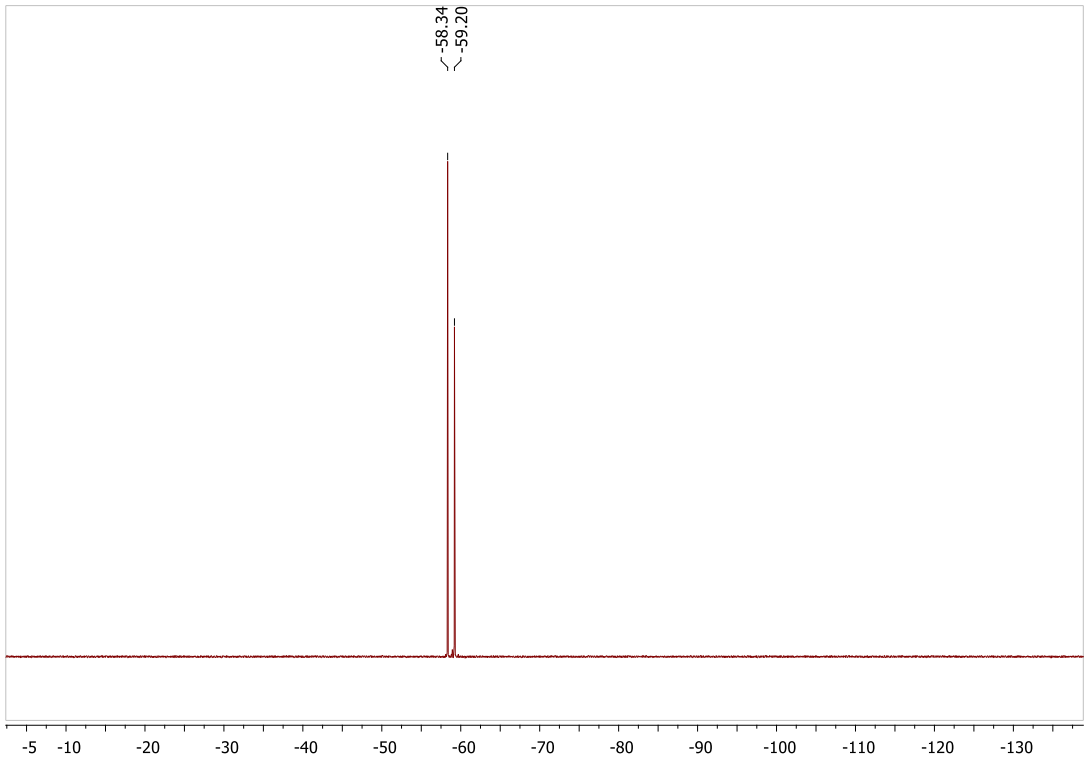
^{1}H NMR ($CDCl_3$)1-(2-(2-(trifluoromethyl)phenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5j)



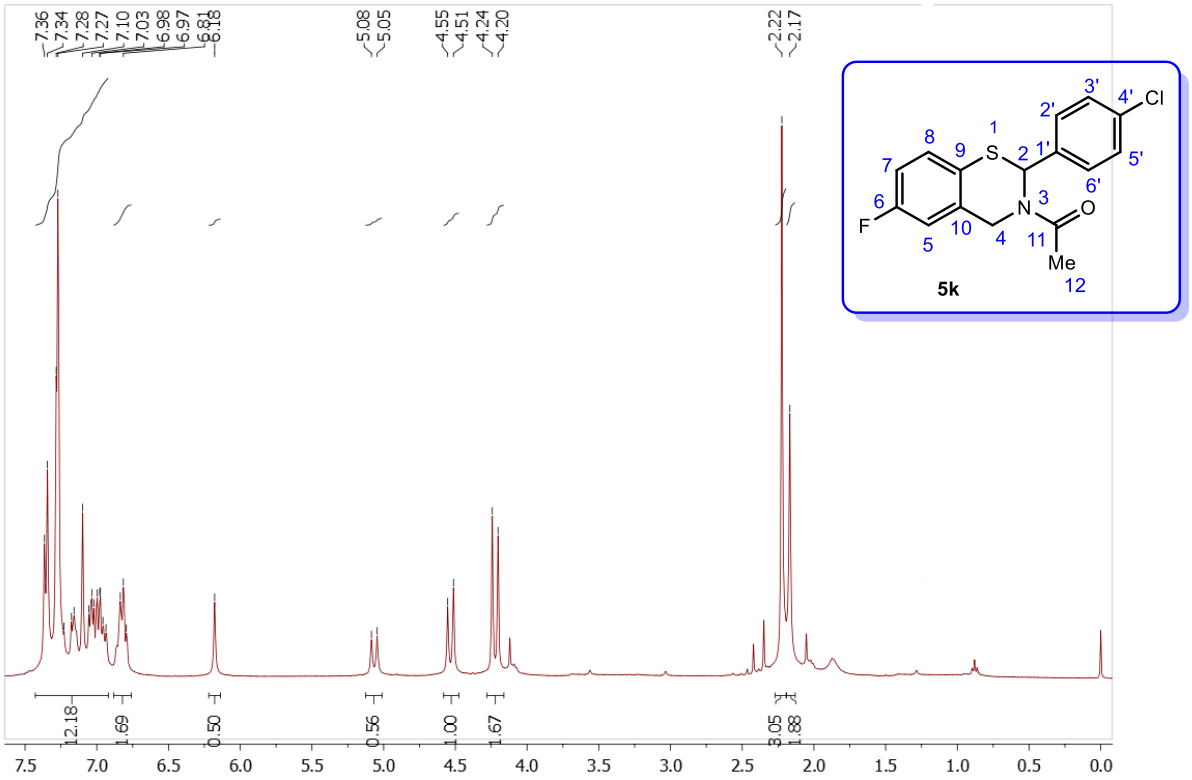
^{13}C NMR($CDCl_3$)1-(2-(2-(trifluoromethyl)phenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5j)



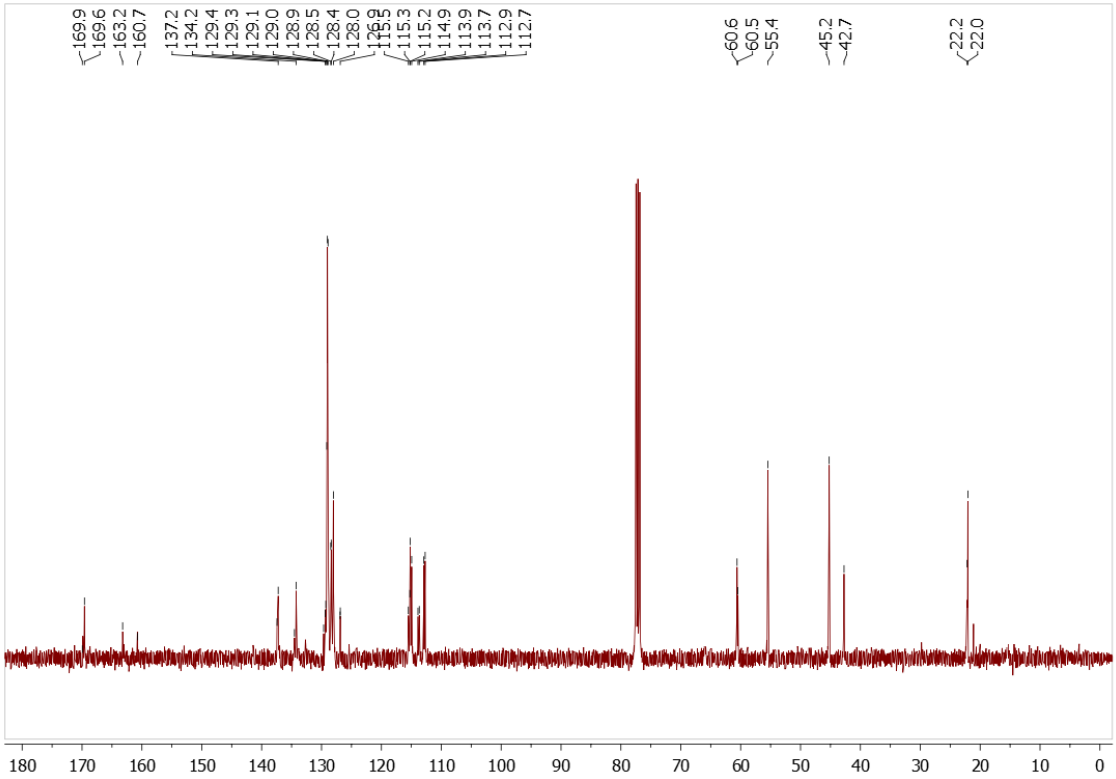
^{19}F NMR (376 MHz, $CDCl_3$)1-(2-(2-(trifluoromethyl)phenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5j)



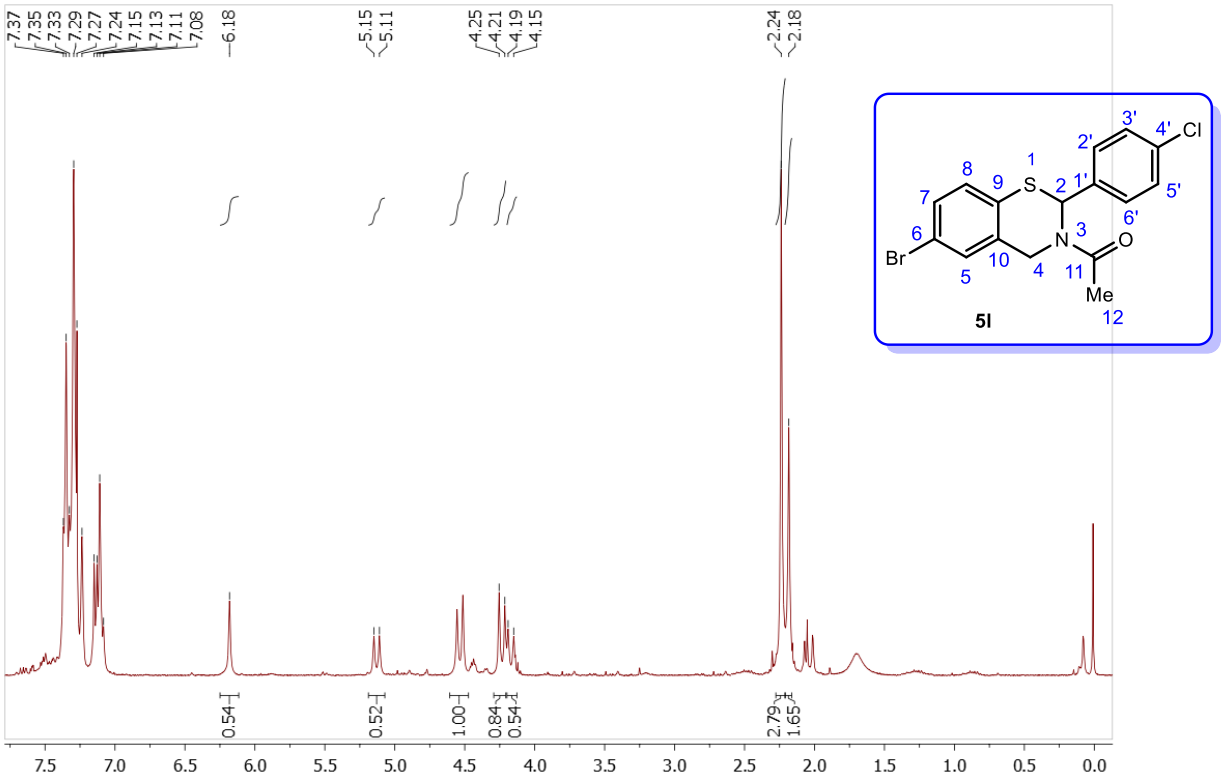
^{1}H NMR ($CDCl_3$) 1-(2-(4-Chlorophenyl)-6-fluoro-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5k)



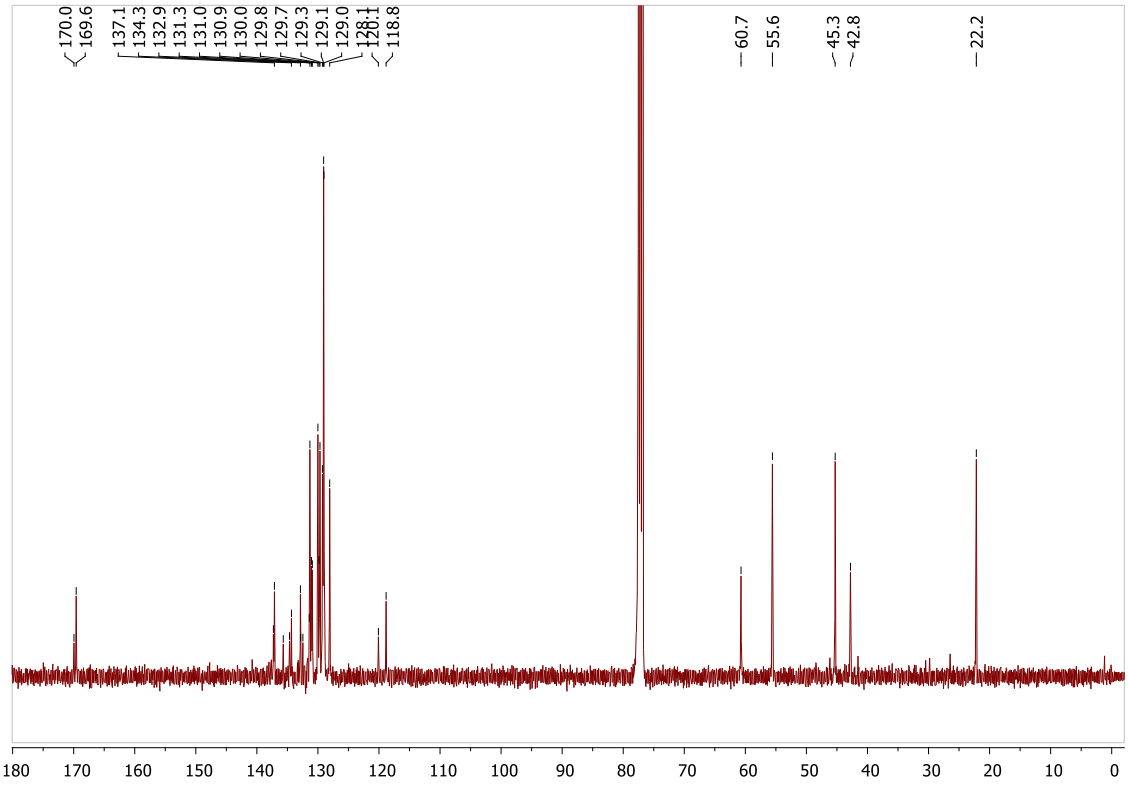
^{13}C NMR ($CDCl_3$) 1-(2-(4-Chlorophenyl)-6-fluoro-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5k)



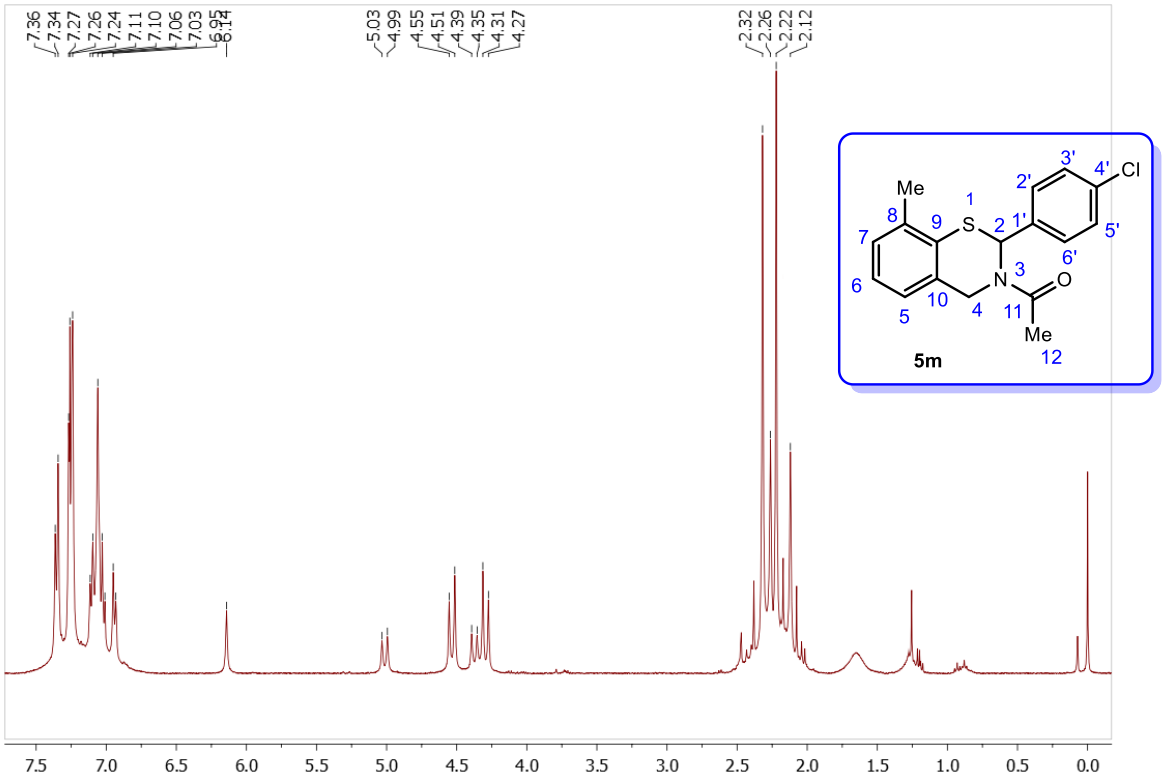
^{1}H NMR ($CDCl_3$) 1-(6-Bromo-2-(4-chlorophenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5l)



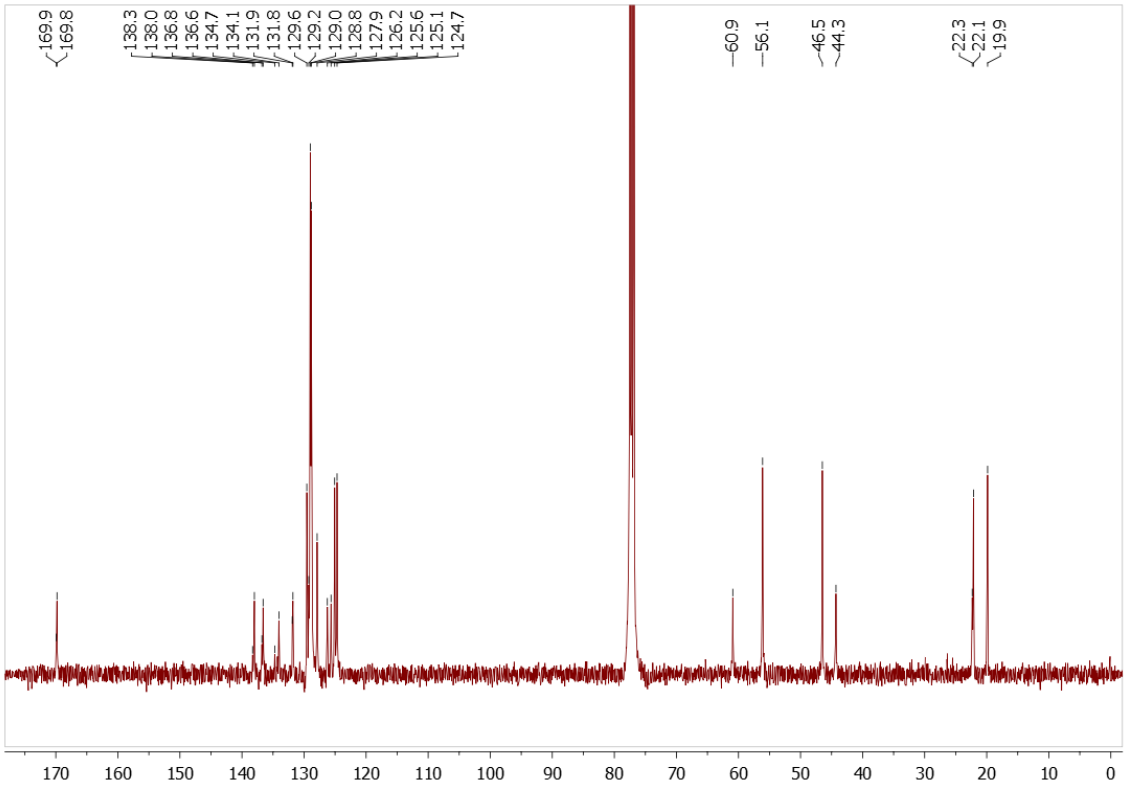
^{13}C NMR ($CDCl_3$) 1-(6-Bromo-2-(4-chlorophenyl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5l)



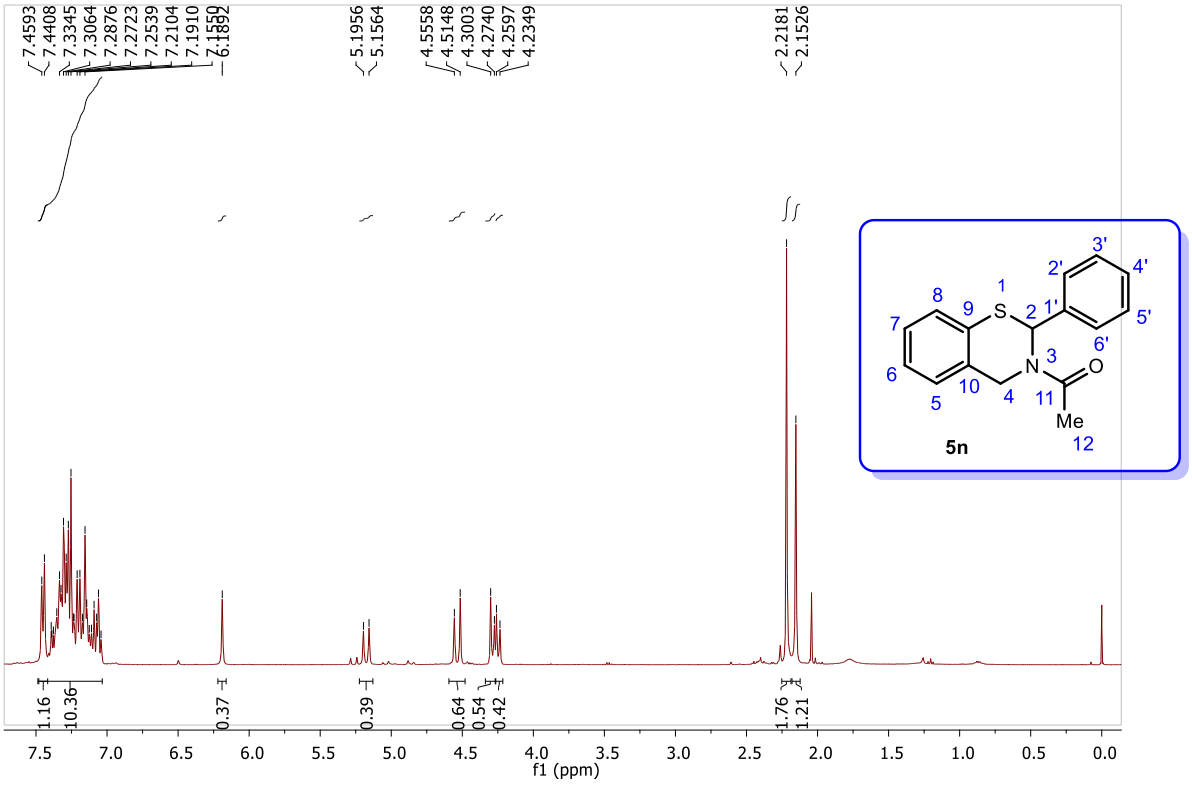
^{1}H NMR ($CDCl_3$) 1-(2-(4-Chlorophenyl)-8-methyl-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5m)



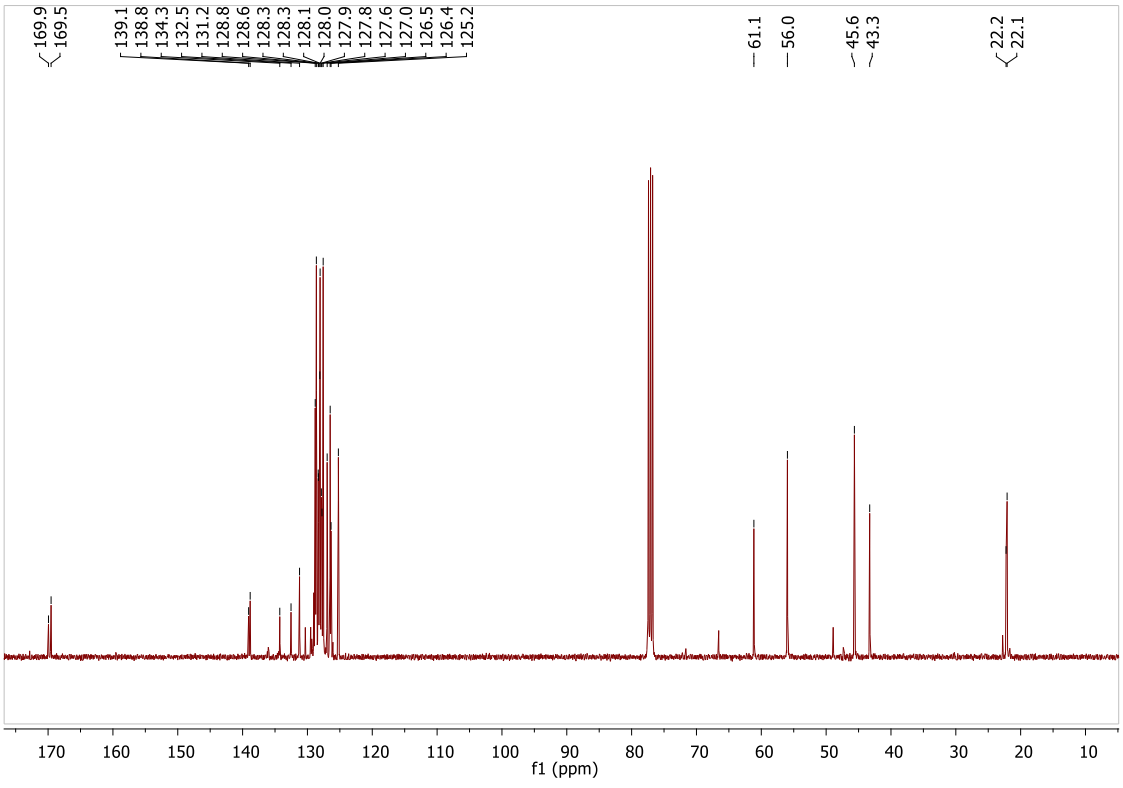
^{13}C NMR ($CDCl_3$) 1-(2-(4-Chlorophenyl)-8-methyl-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5m)



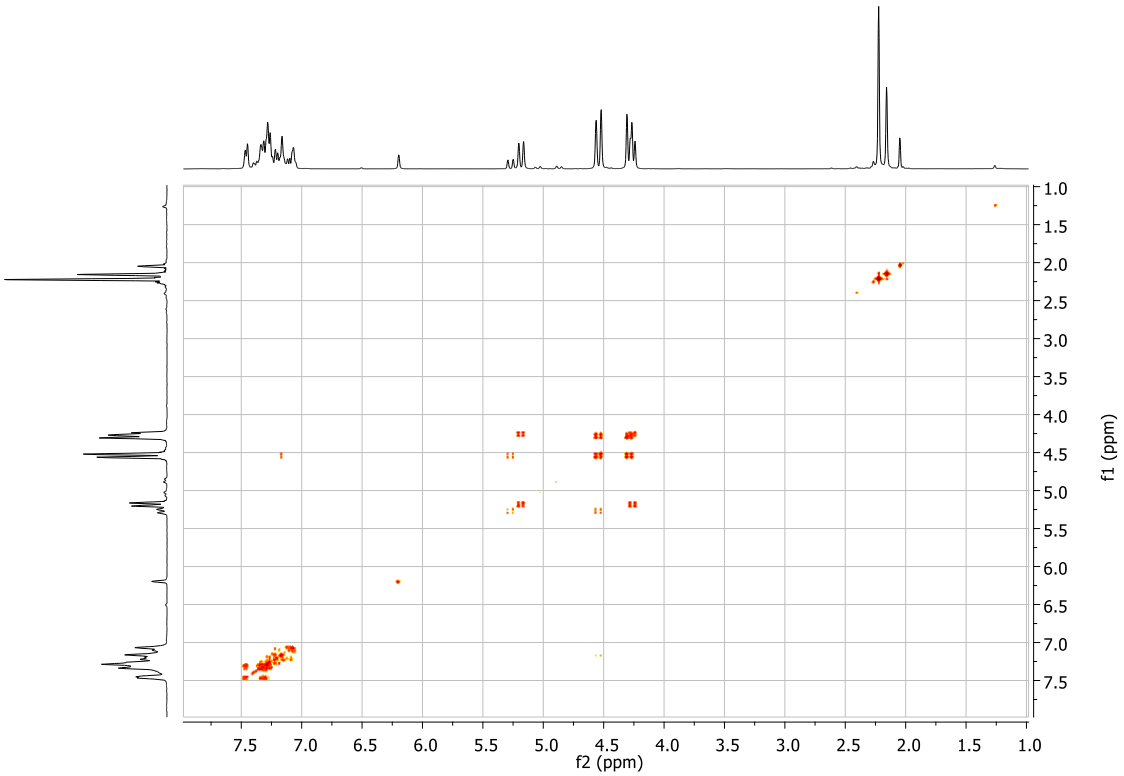
^{1}H NMR ($CDCl_3$) 1-(2-phenyl-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5n)



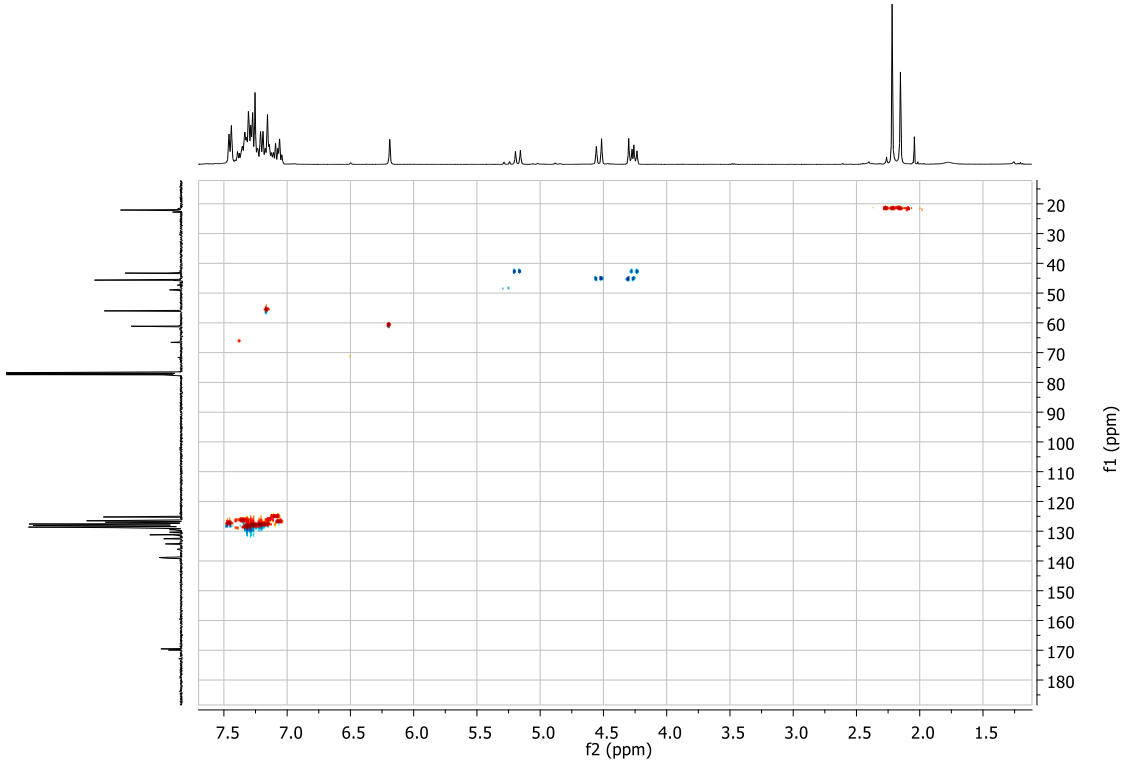
^{13}C NMR ($CDCl_3$) 1-(2-phenyl-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5n)



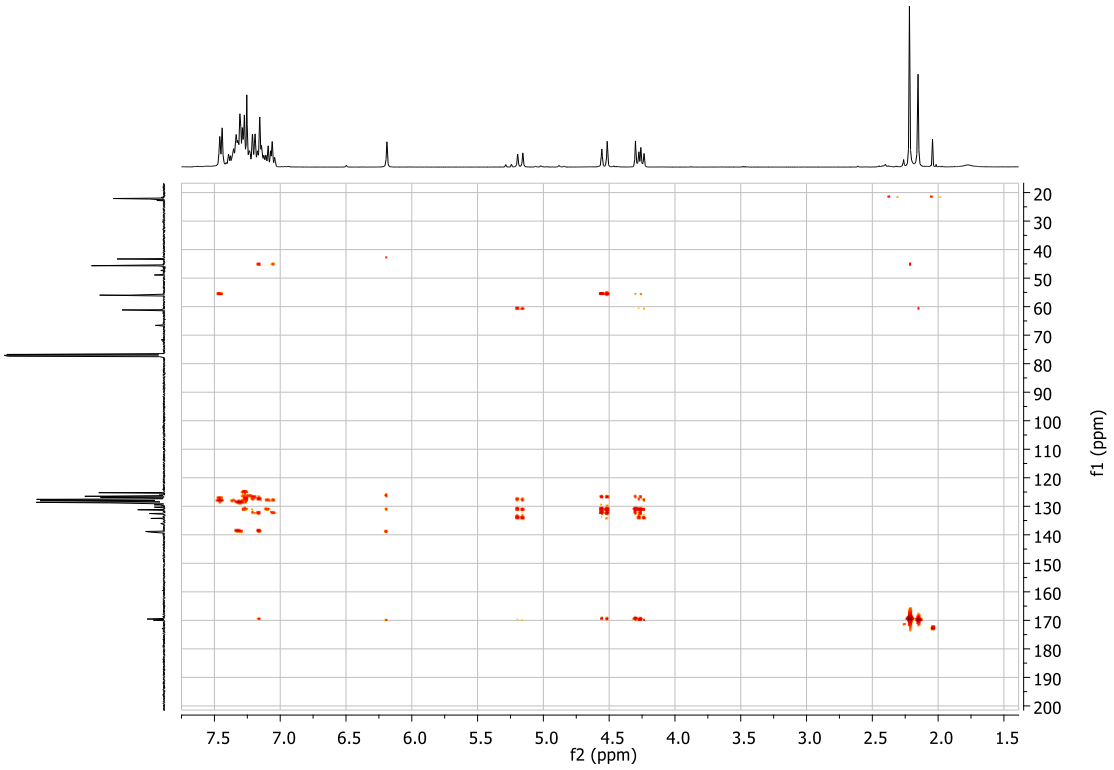
COSY ($CDCl_3$) 1-(2-phenyl-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5n)



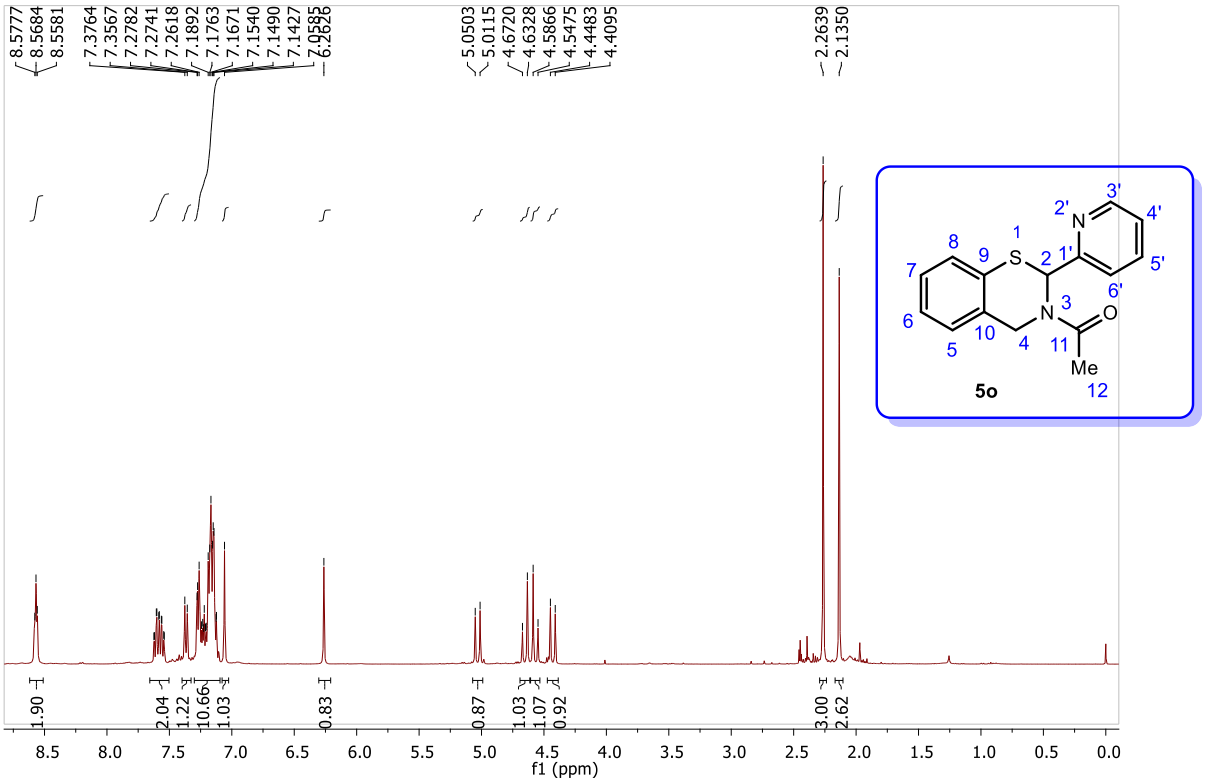
HSQC ($CDCl_3$) 1-(2-phenyl-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5n)



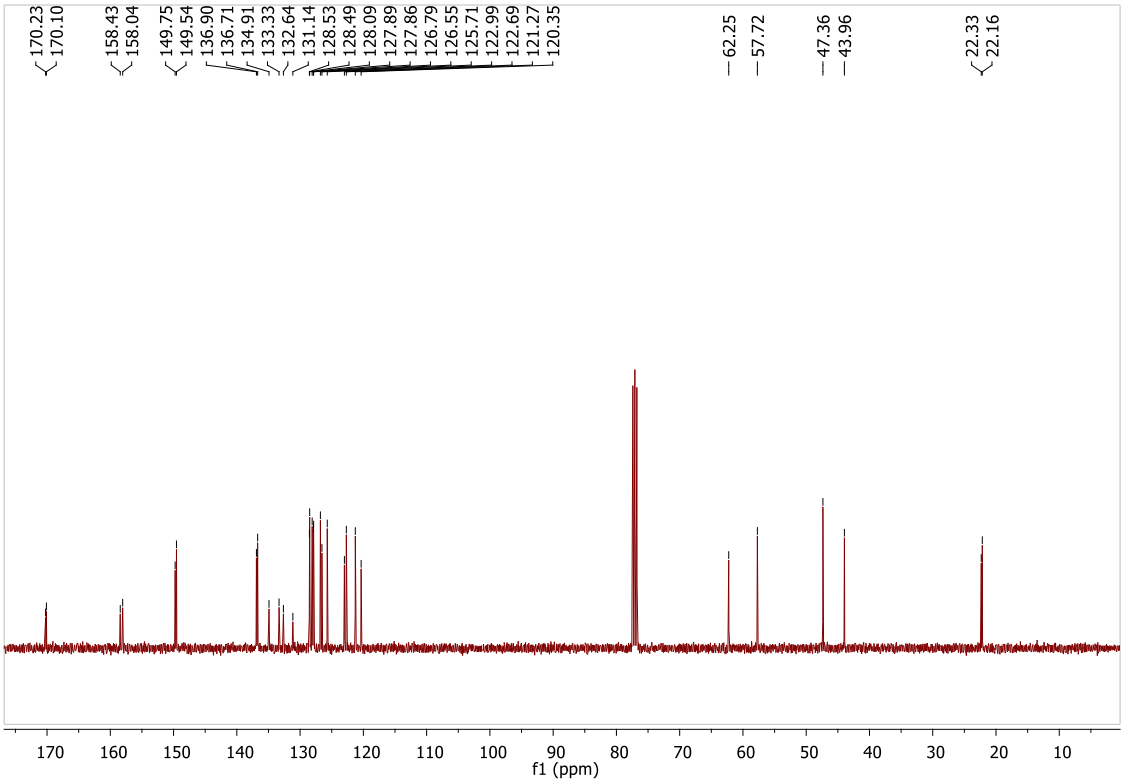
HMBC ($CDCl_3$) 1-(2-phenyl-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5n)



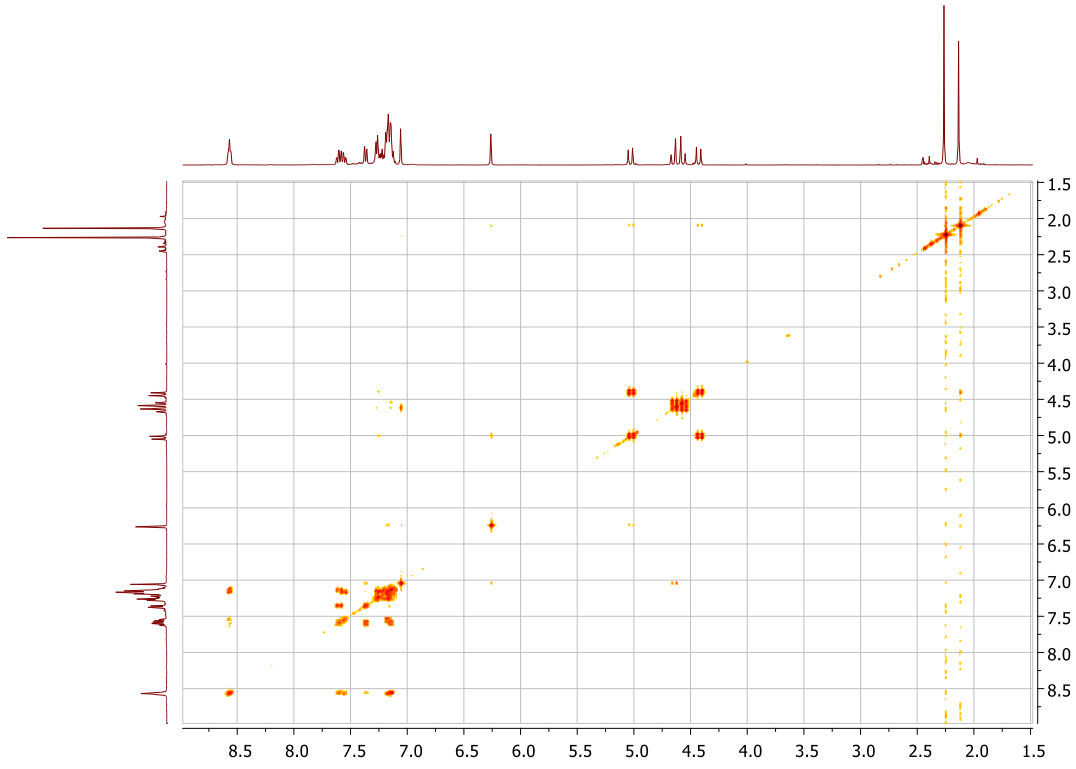
^{1}H NMR ($CDCl_3$)1-(2-(pyridin-2-yl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5o)



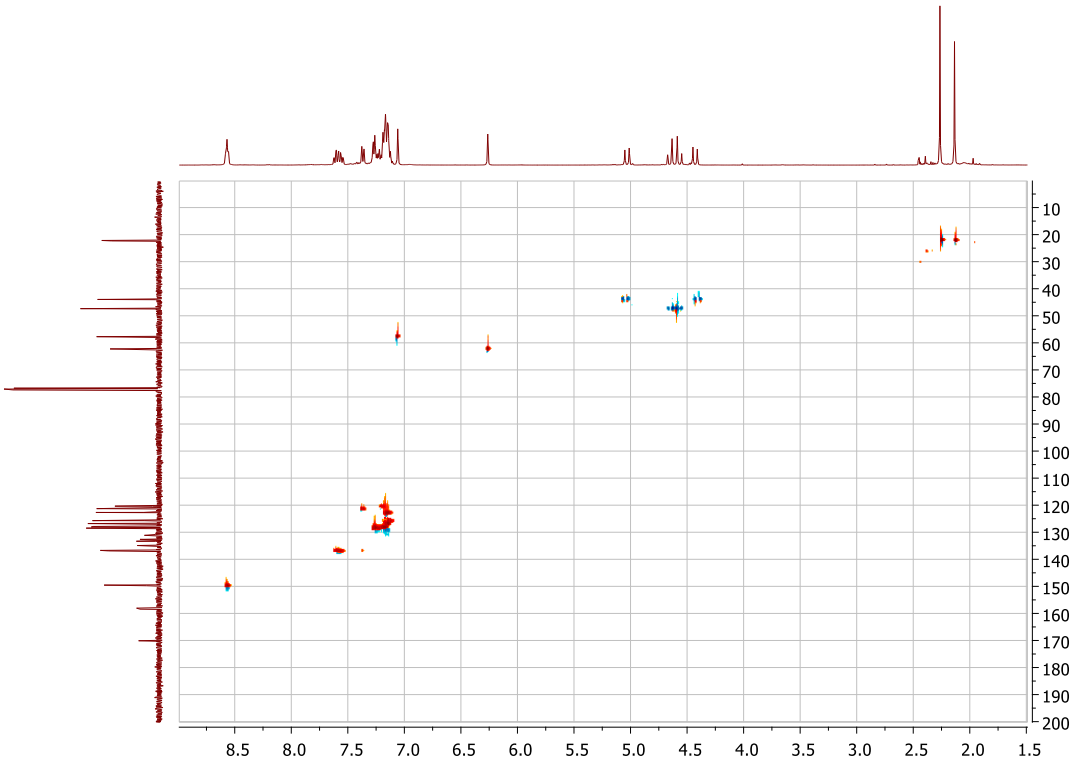
^{13}C NMR($CDCl_3$)1-(2-(pyridin-2-yl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5o)



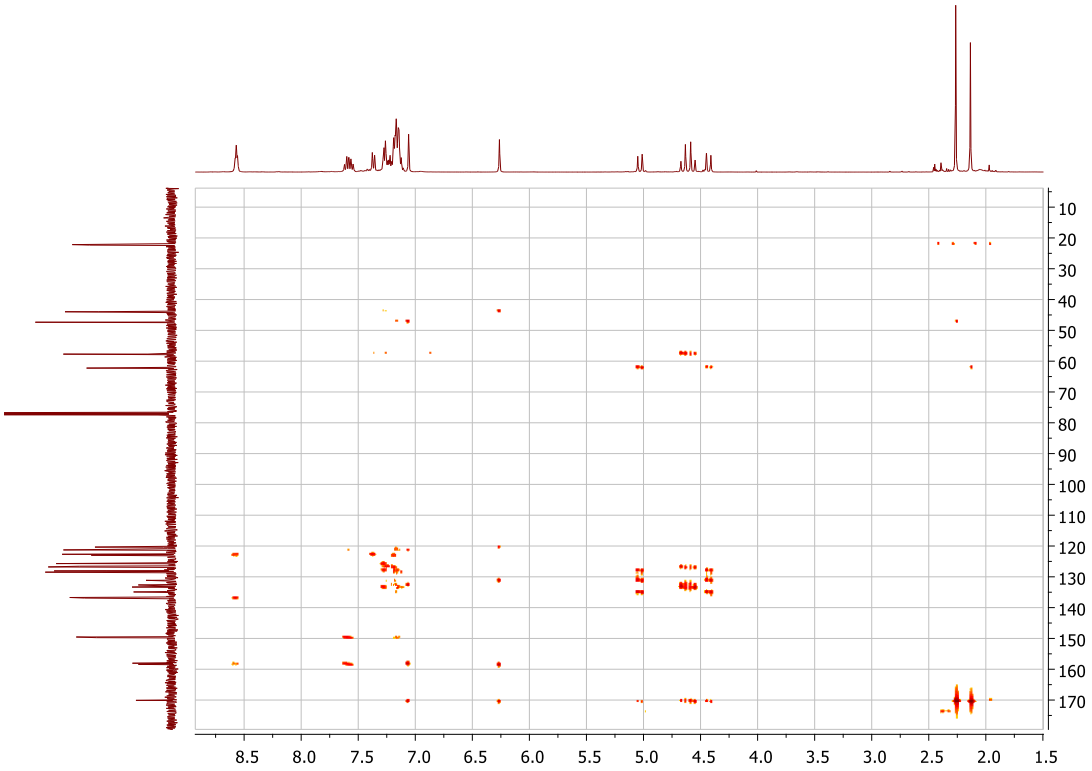
COSY ($CDCl_3$)1-(2-(pyridin-2-yl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5o)



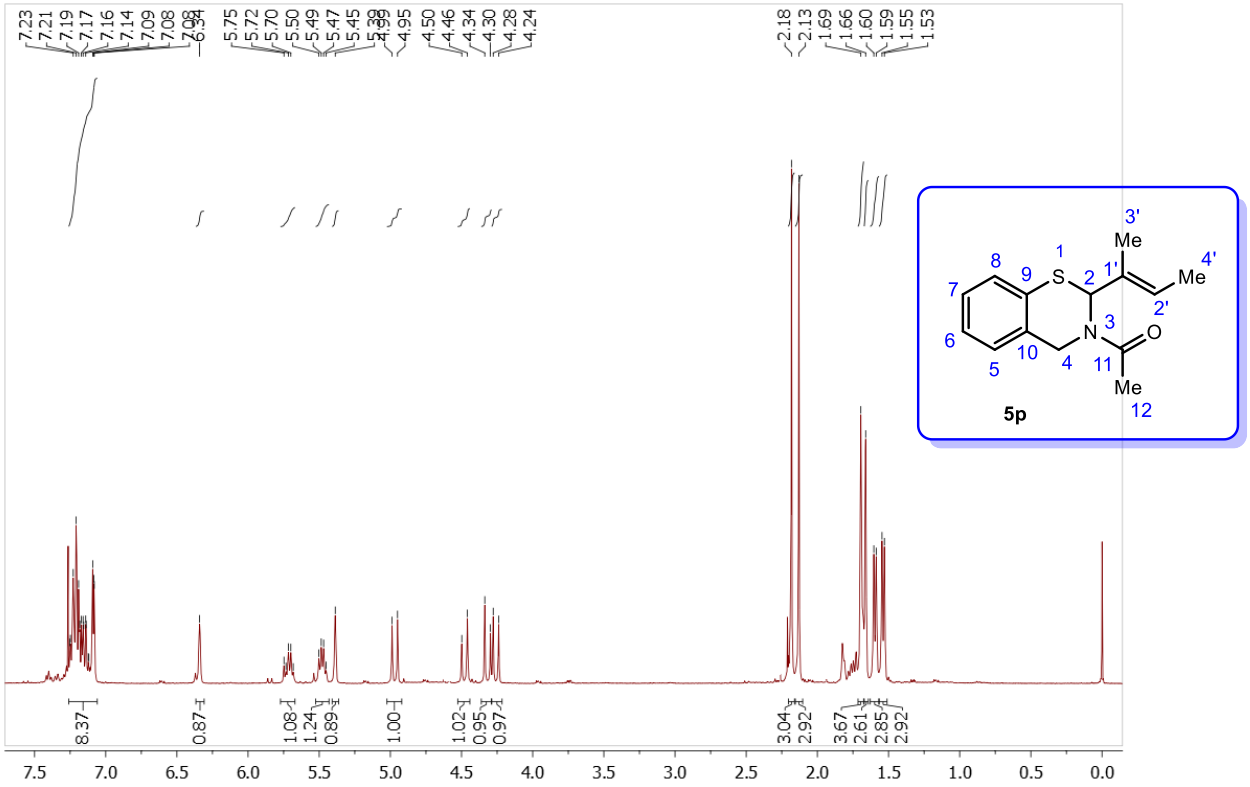
HSQC ($CDCl_3$)1-(2-(pyridin-2-yl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5o)



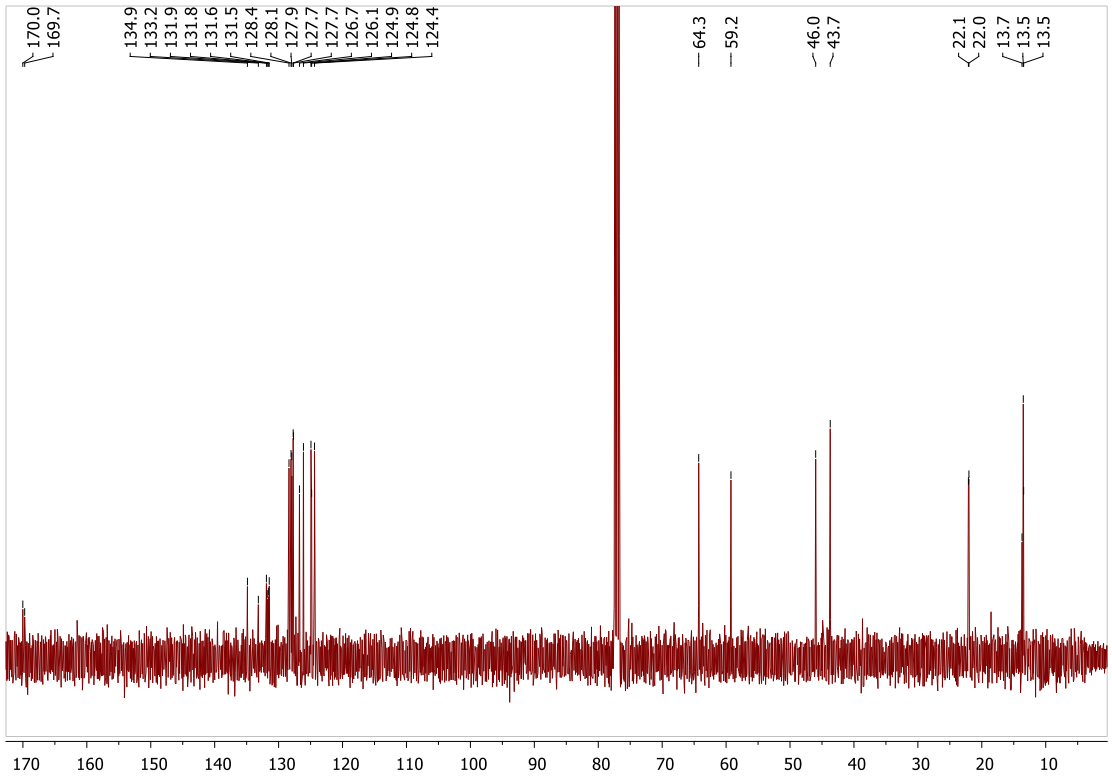
HMBC ($CDCl_3$)1-(2-(pyridin-2-yl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5o)



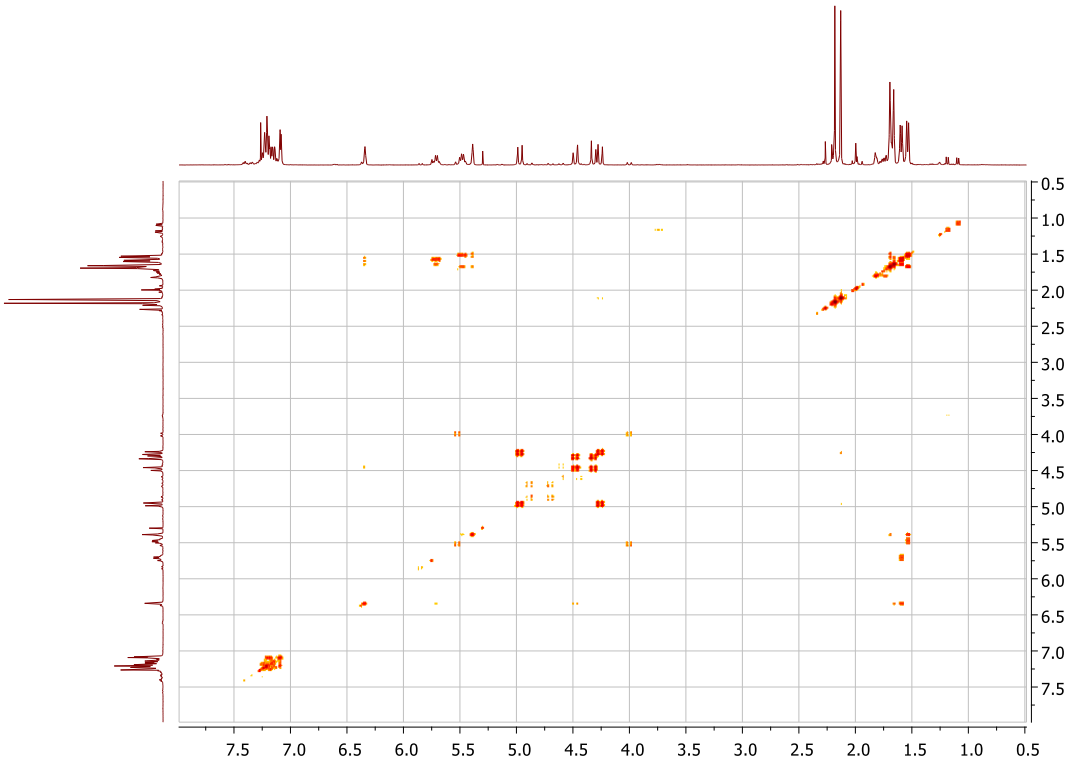
^{1}H NMR ($CDCl_3$)(*E*)-1-(2-(but-2-en-2-yl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5p)



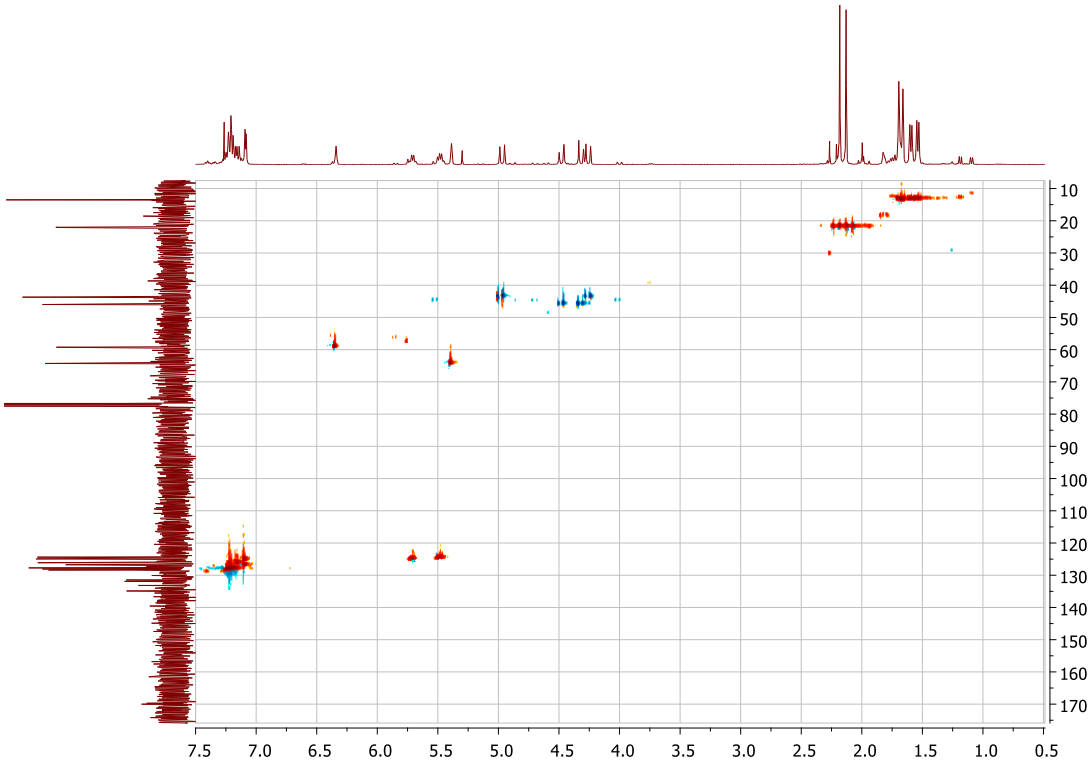
^{13}C NMR($CDCl_3$)(*E*)-1-(2-(but-2-en-2-yl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5p)



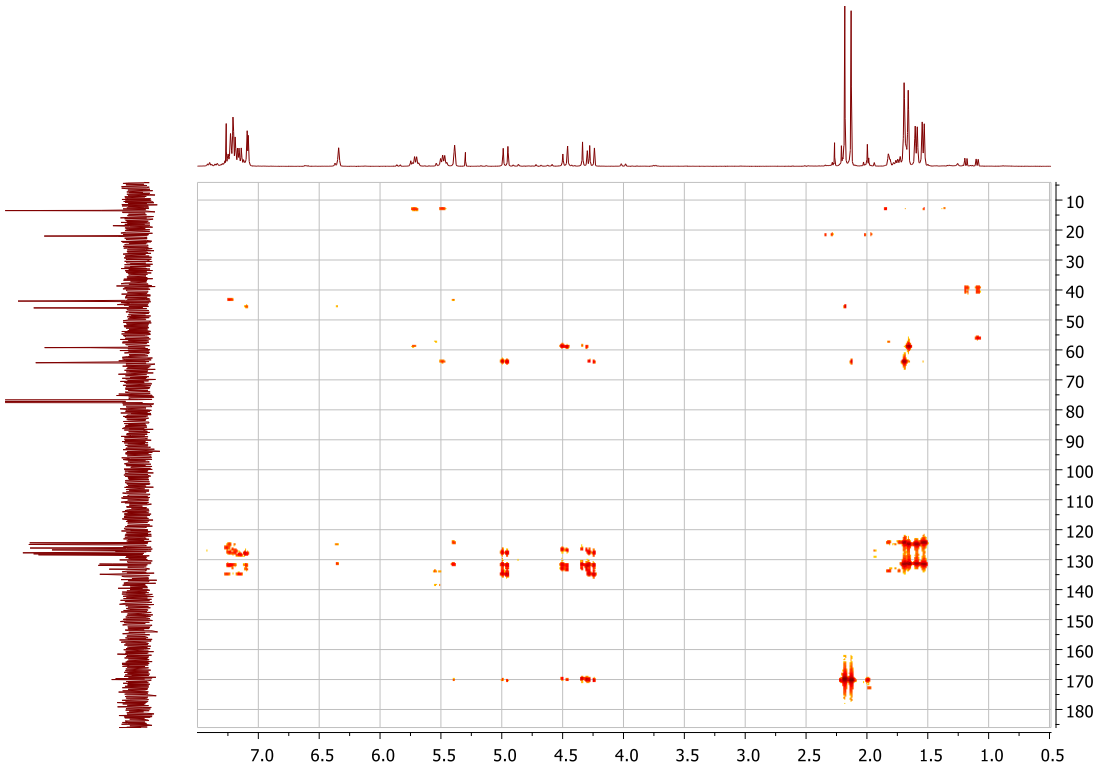
COSY ($CDCl_3$) (*E*)-1-(2-(but-2-en-2-yl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5p)



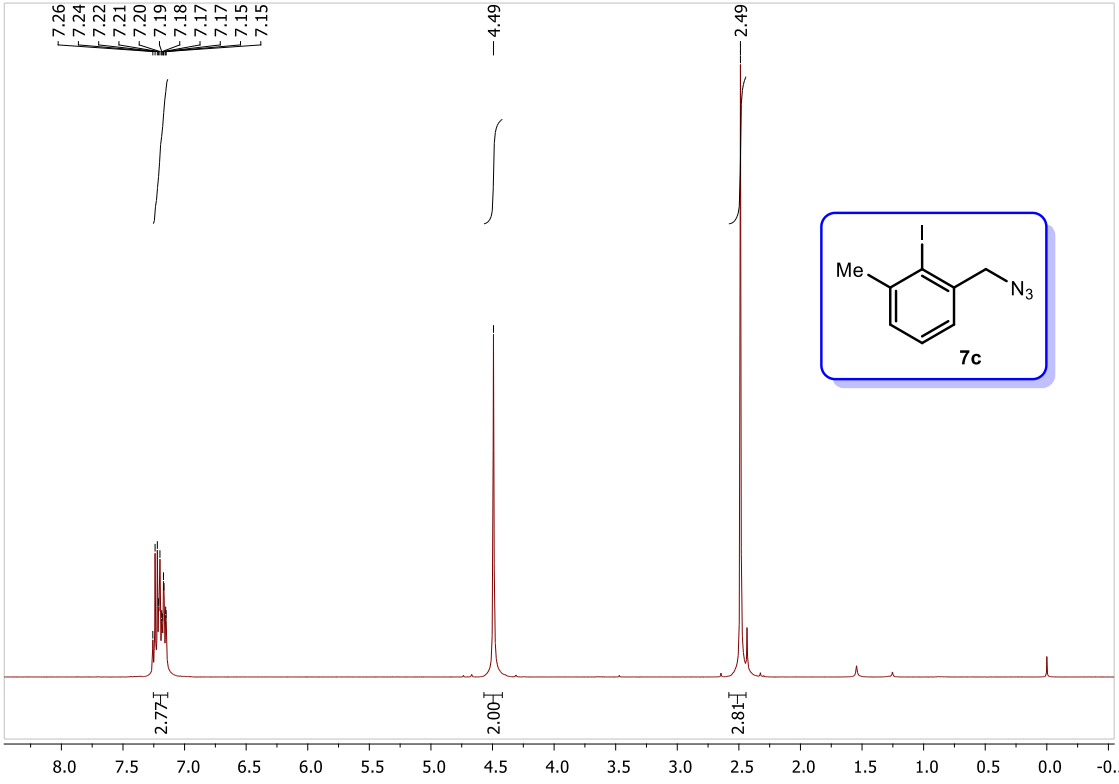
HSQC ($CDCl_3$) (*E*)-1-(2-(but-2-en-2-yl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5p)



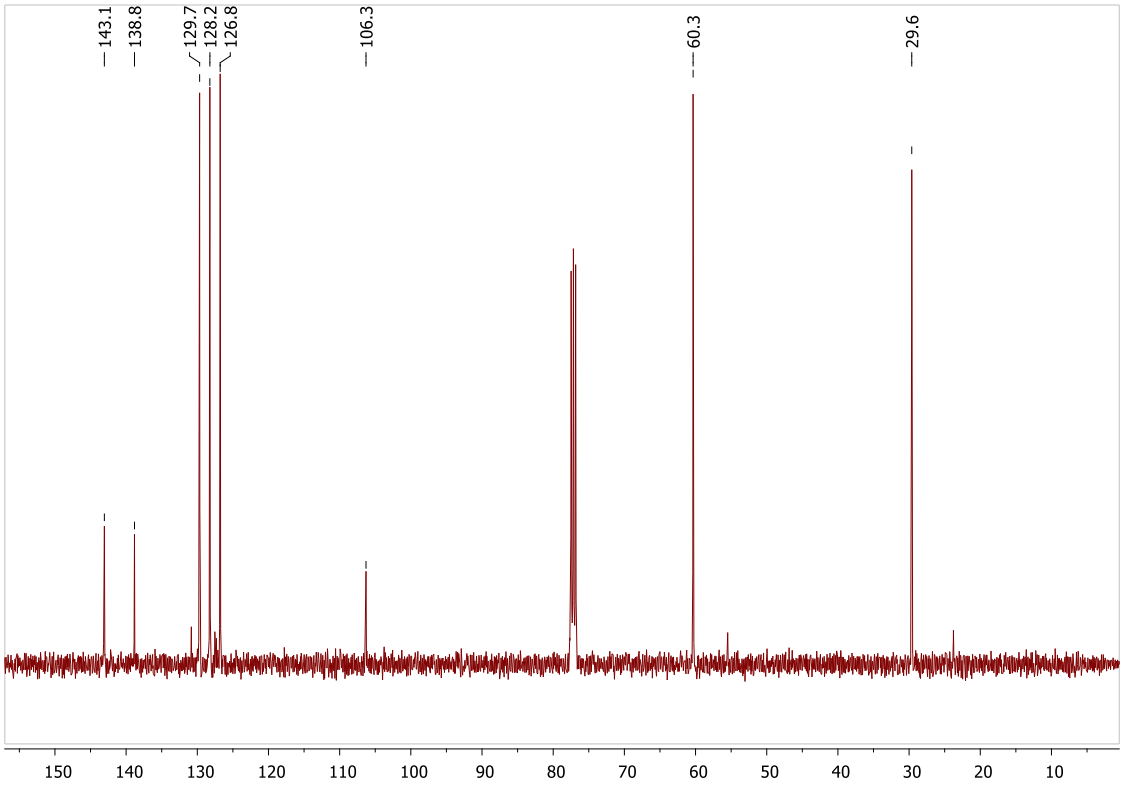
HMBC ($CDCl_3$) (*E*)-1-(2-(but-2-en-2-yl)-2*H*-benzo[*e*][1,3]thiazin-3(4*H*)-yl)ethan-1-one (5p)



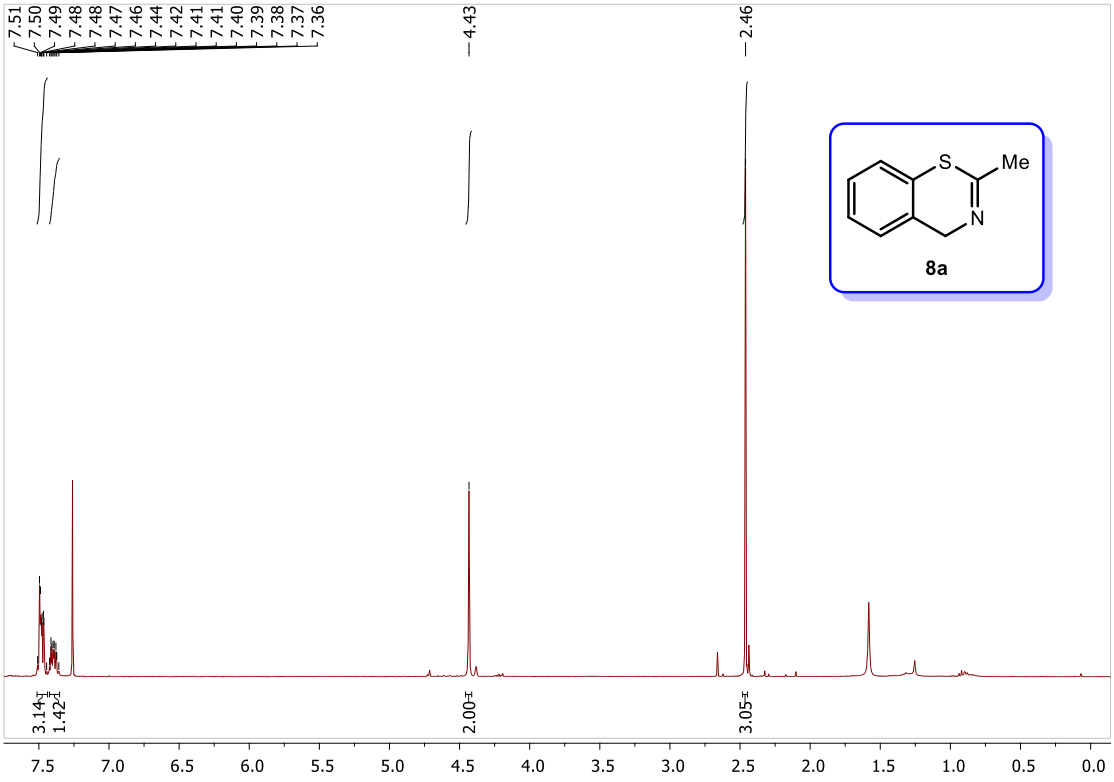
^{1}H NMR ($CDCl_3$) 3-methyl-2-iodobenzyl azide (7c)



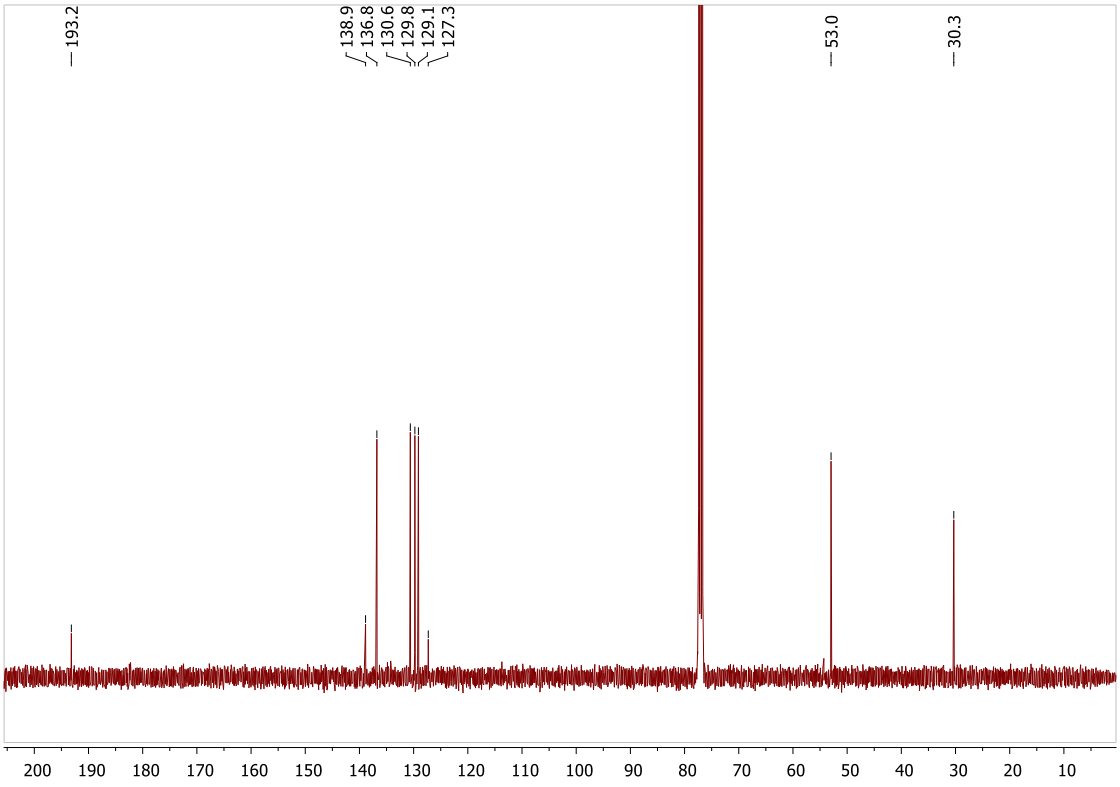
^{13}C NMR ($CDCl_3$) 3-methyl-2-iodobenzyl azide (7c)



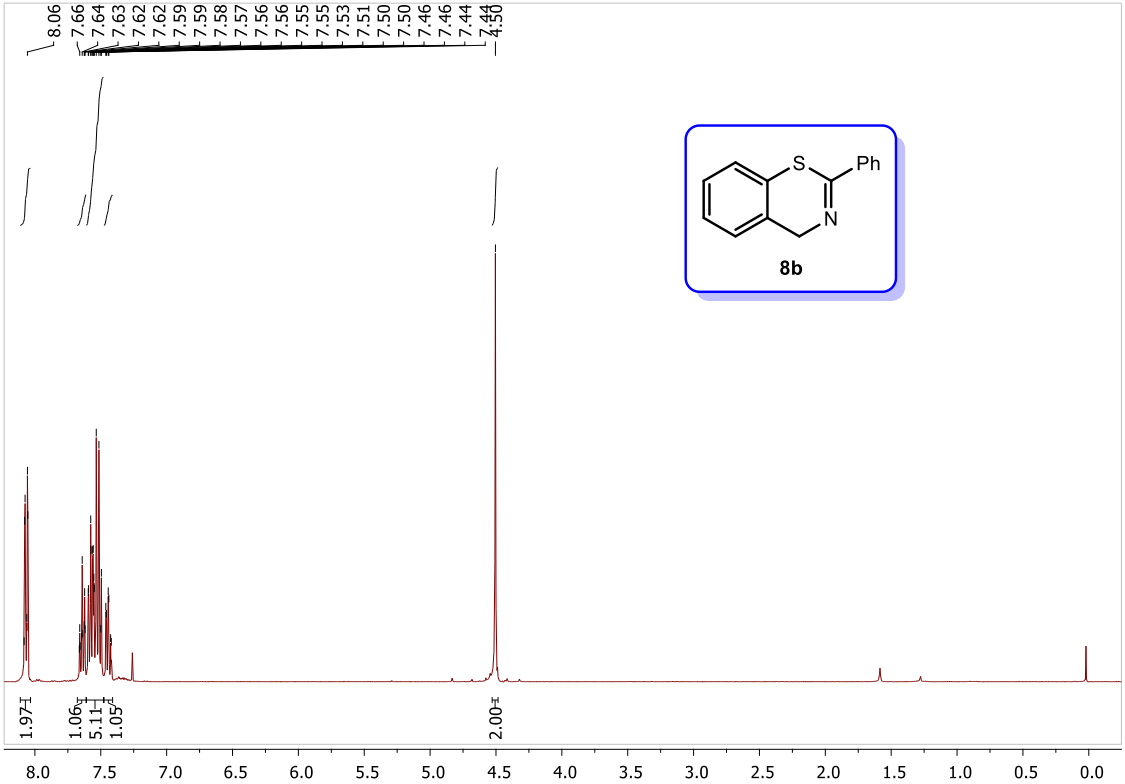
^{1}H NMR ($CDCl_3$) 2-methyl-4*H*-benzo[*e*][1,3]thiazine (8a)

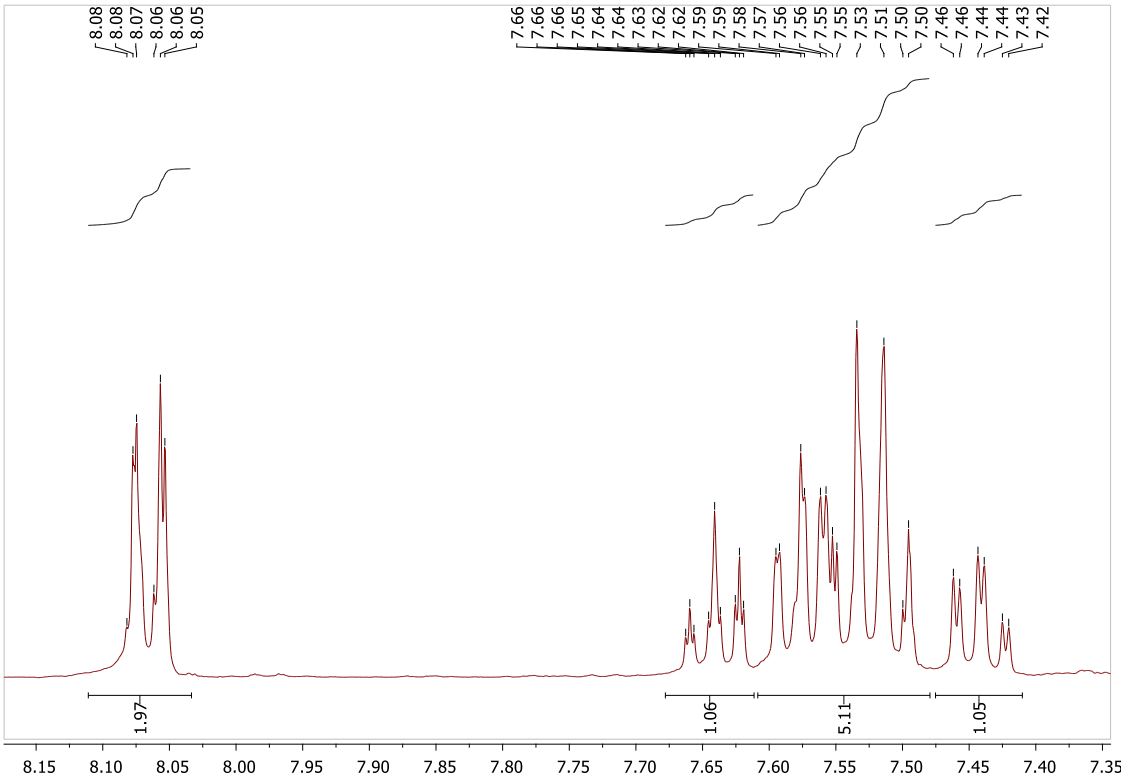


^{13}C NMR ($CDCl_3$) 2-methyl-4*H*-benzo[*e*][1,3]thiazine (8a)

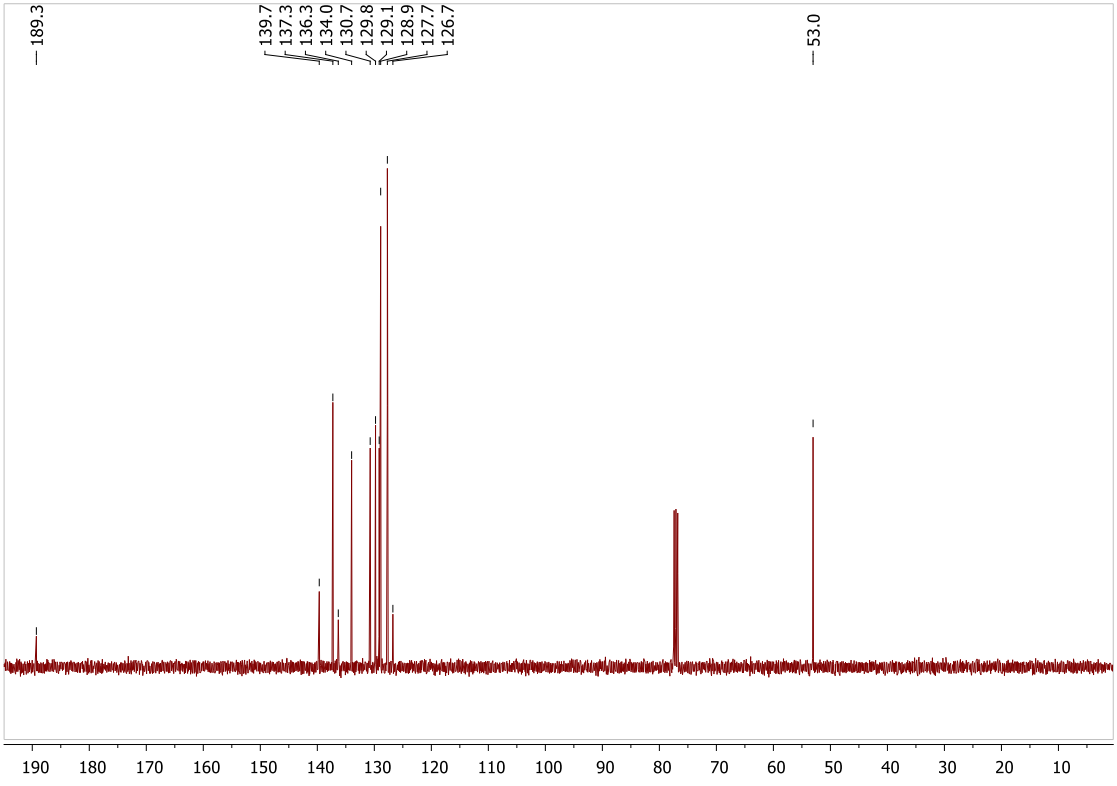


^{1}H NMR ($CDCl_3$) 2-phenyl-4*H*-benzo[*e*][1,3]thiazine (8b)

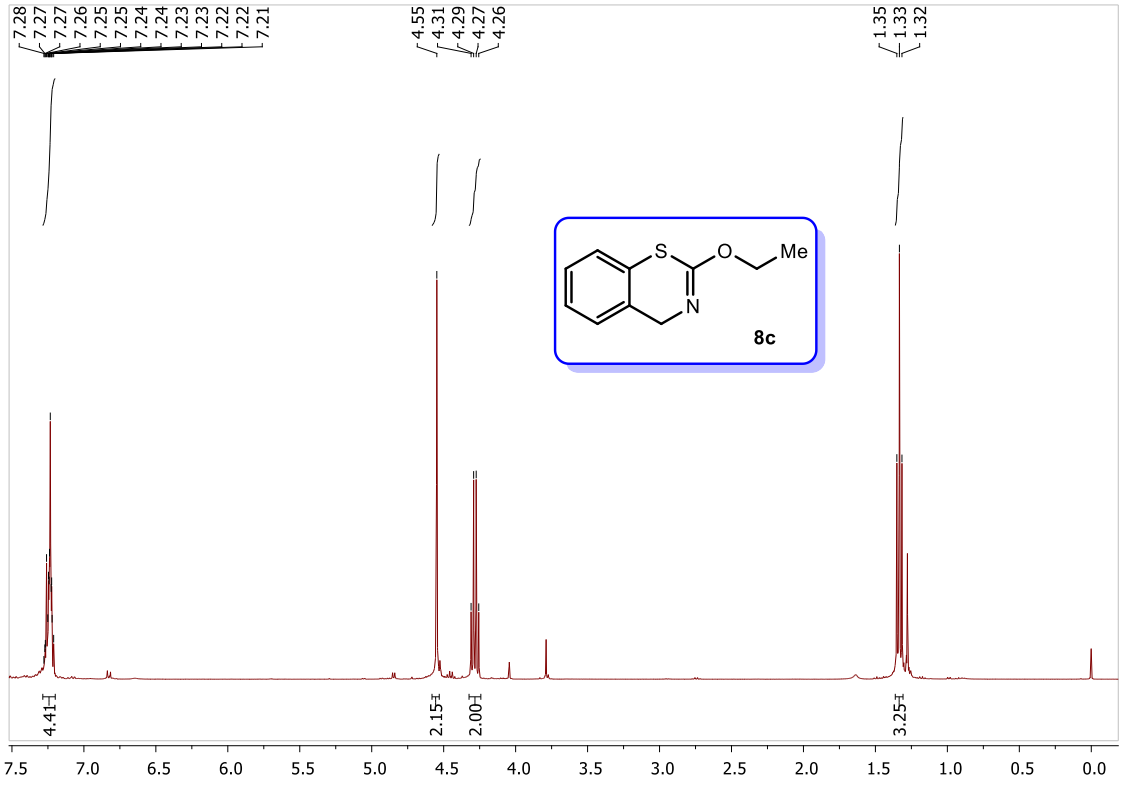




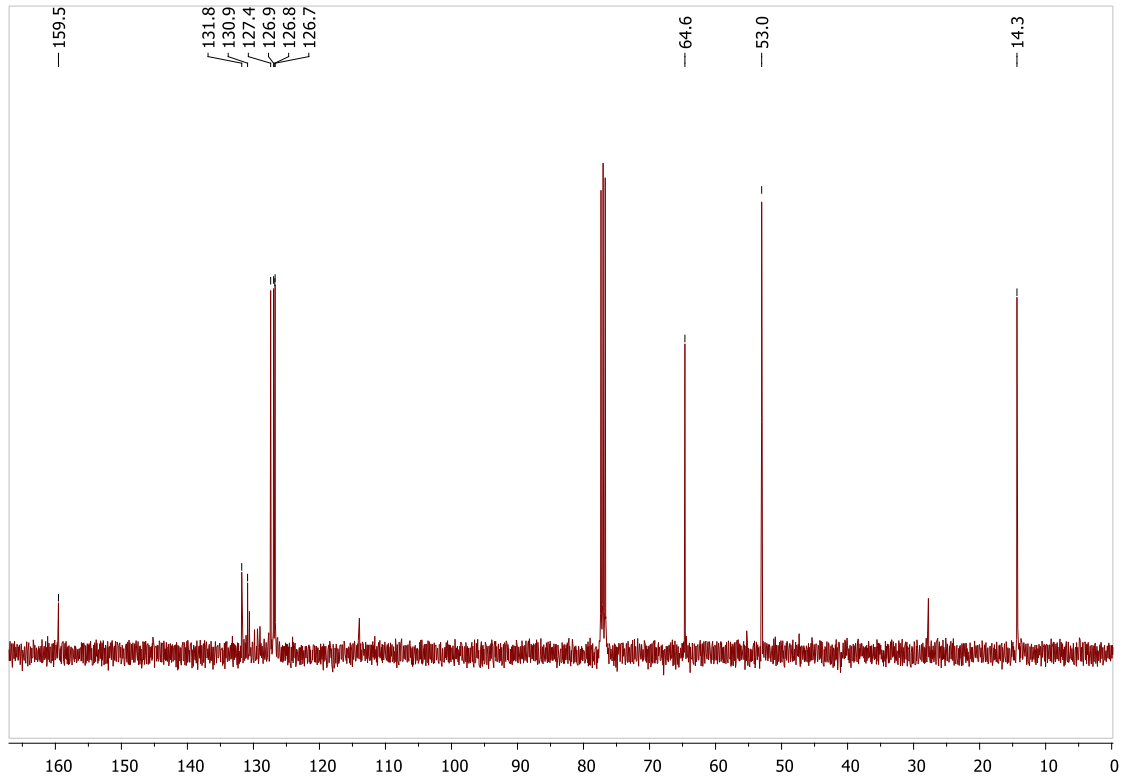
^{13}C NMR ($CDCl_3$) 2-phenyl-4*H*-benzo[*e*][1,3]thiazine (8b)



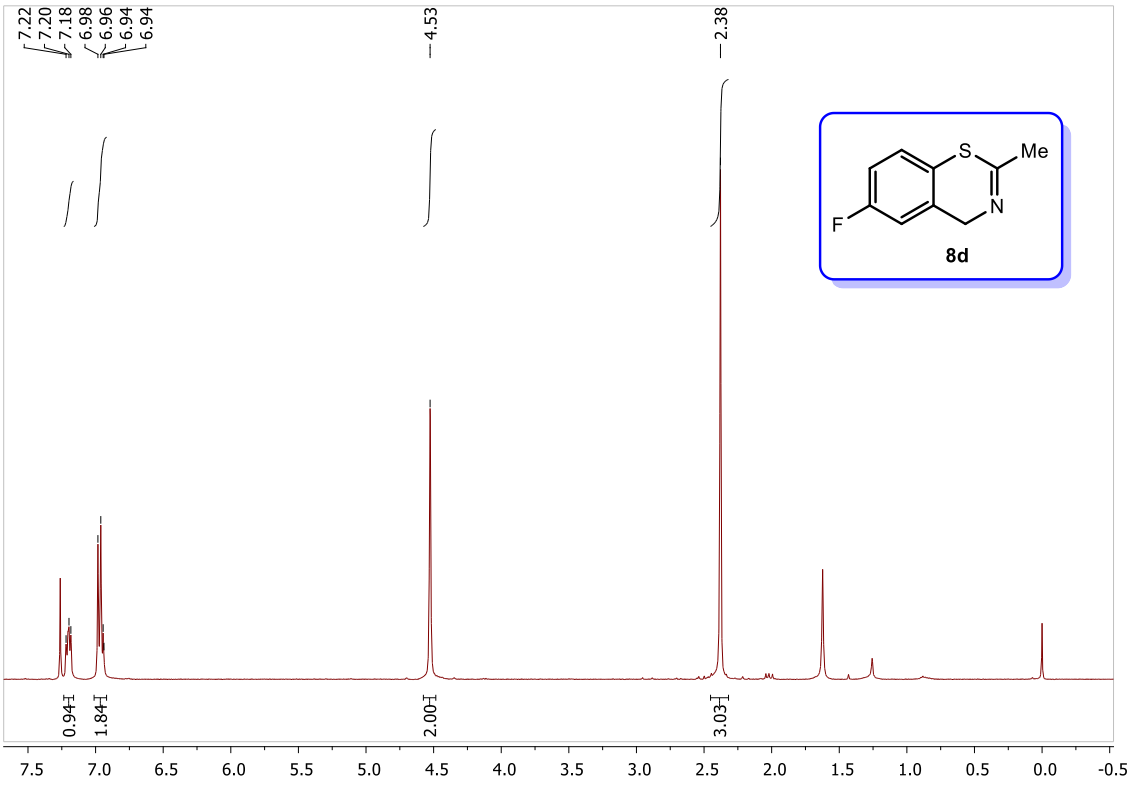
^{1}H NMR ($CDCl_3$) 2-ethoxy-4*H*-benzo[*e*][1,3]thiazine (8c)



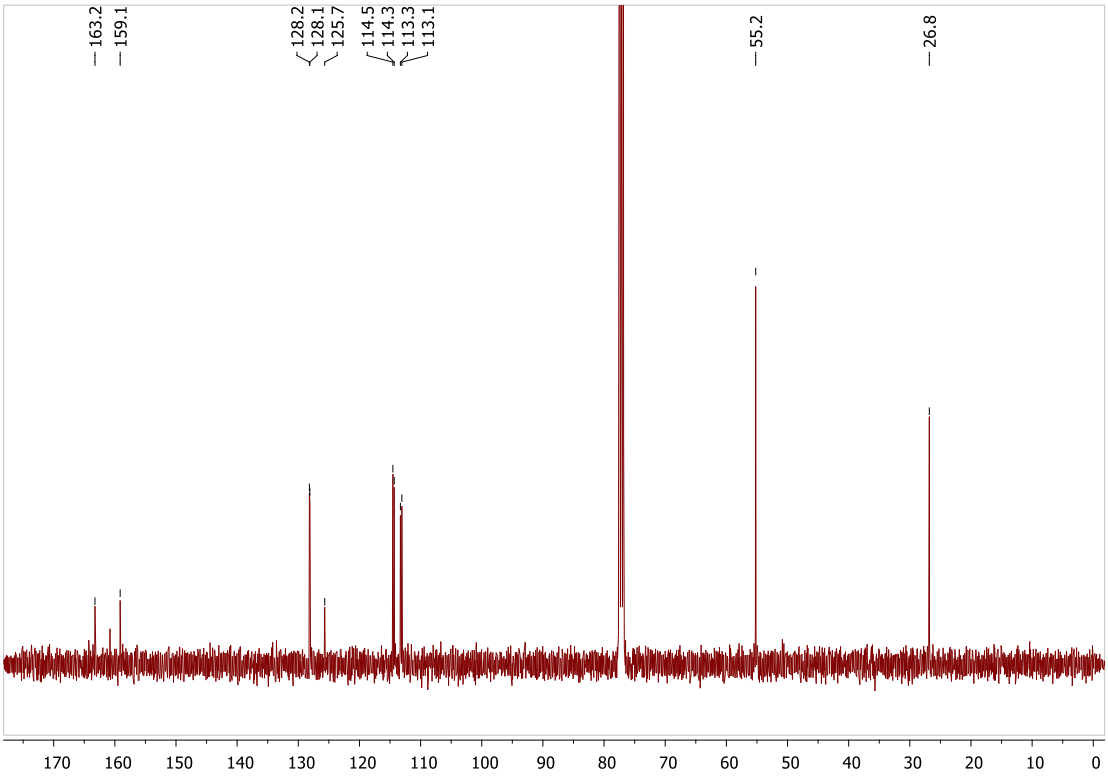
^{13}C NMR ($CDCl_3$) 2-ethoxy-4*H*-benzo[*e*][1,3]thiazine (8c)



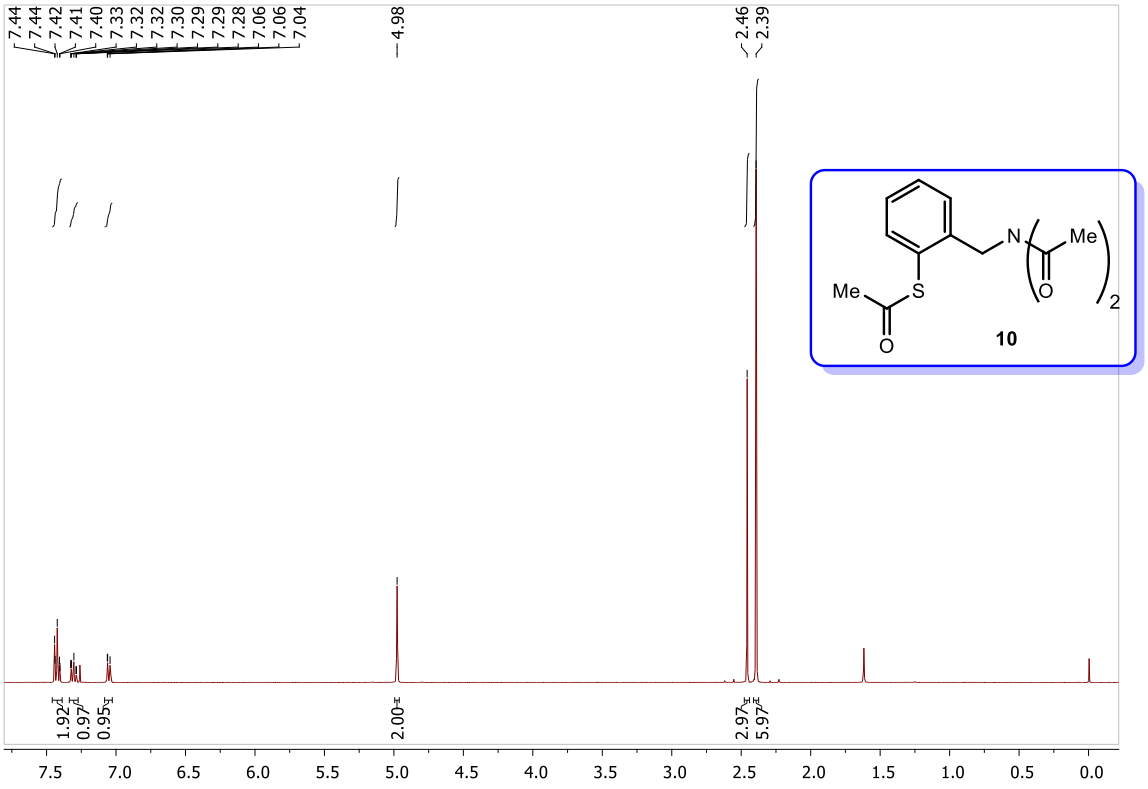
^{1}H NMR ($CDCl_3$) 6-Fluoro-2-methyl-4*H*-benzo[*e*][1,3]thiazine (8d)

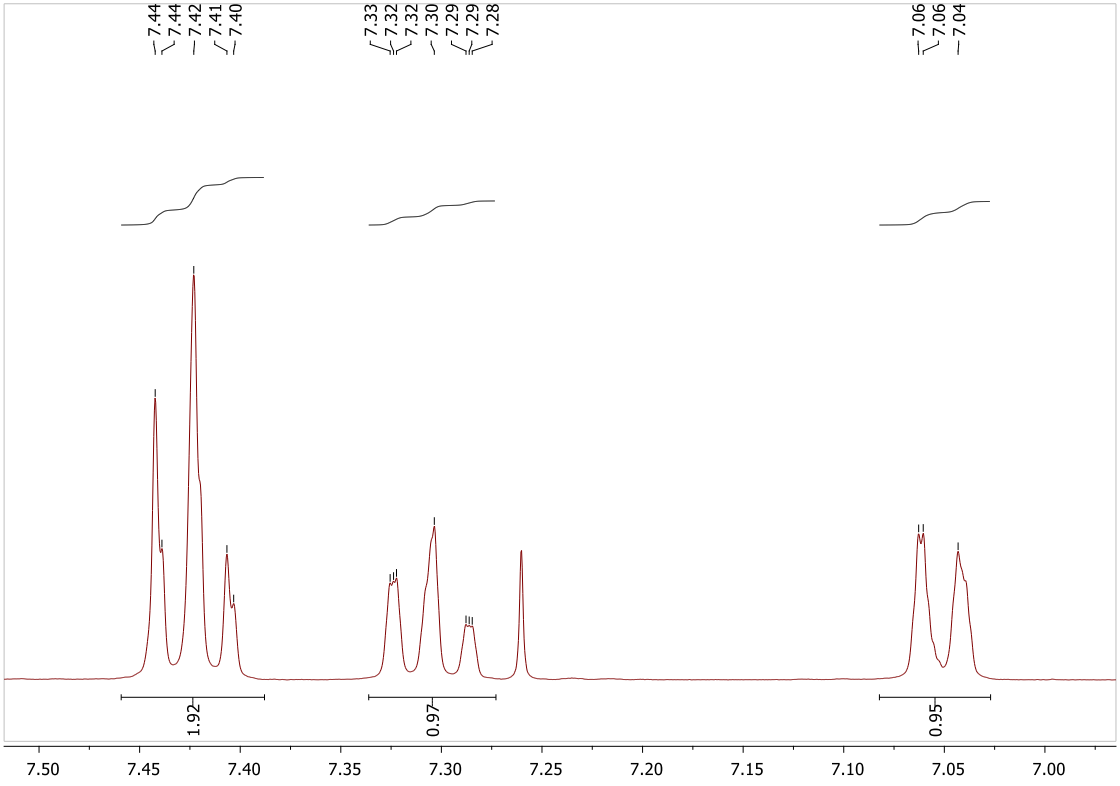


^{13}C NMR ($CDCl_3$) 6-Fluoro-2-methyl-4*H*-benzo[*e*][1,3]thiazine (8d)

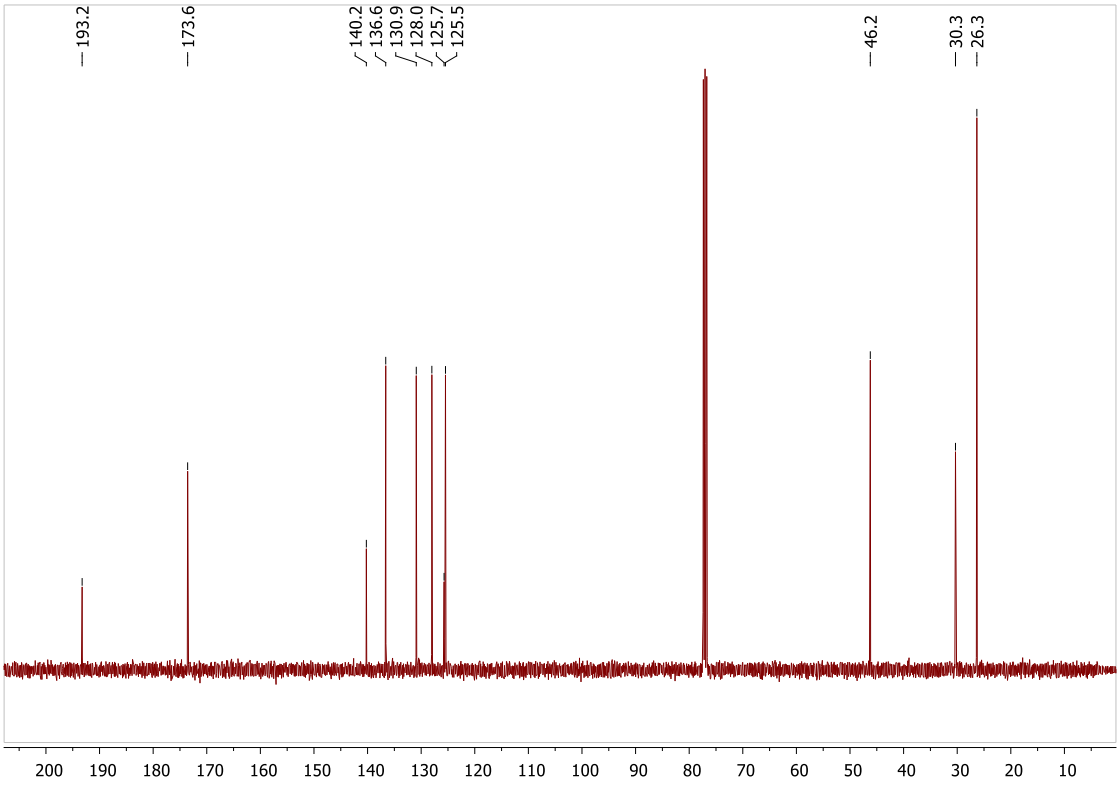


^{1}H NMR ($CDCl_3$) *S*-(2-((*N*-acetylacetamido)methyl)phenyl) ethanethioate (10)

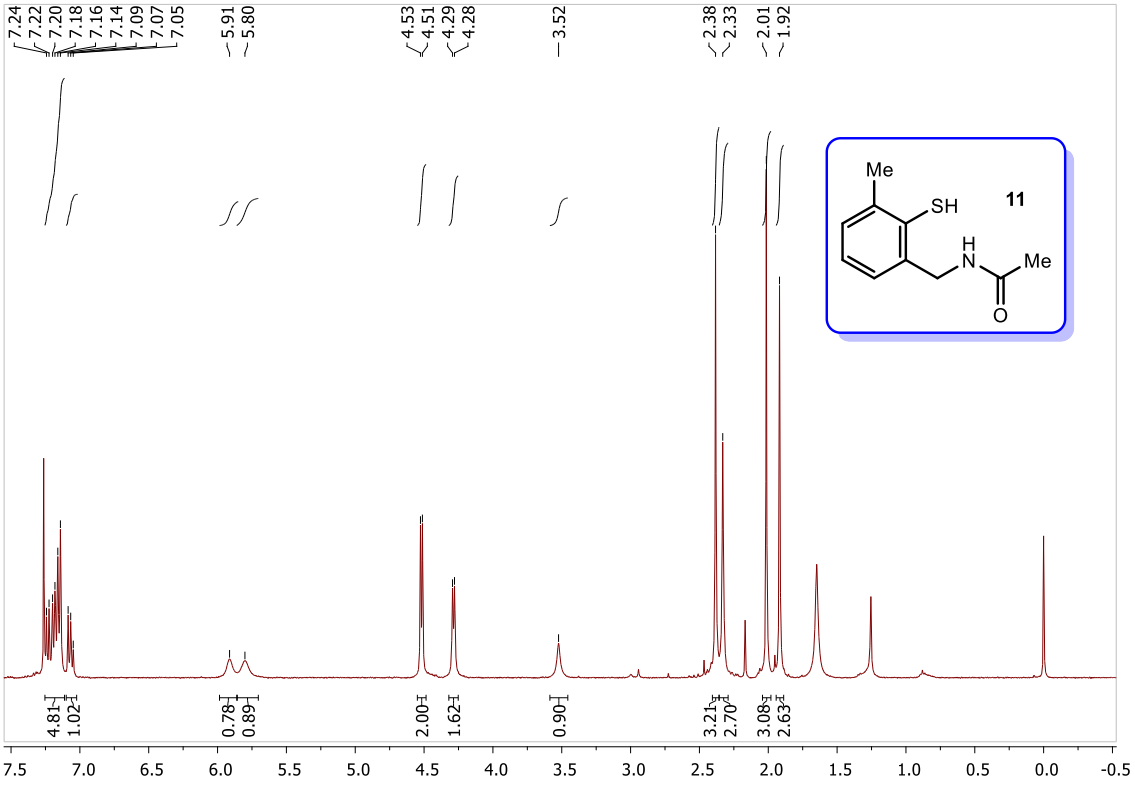




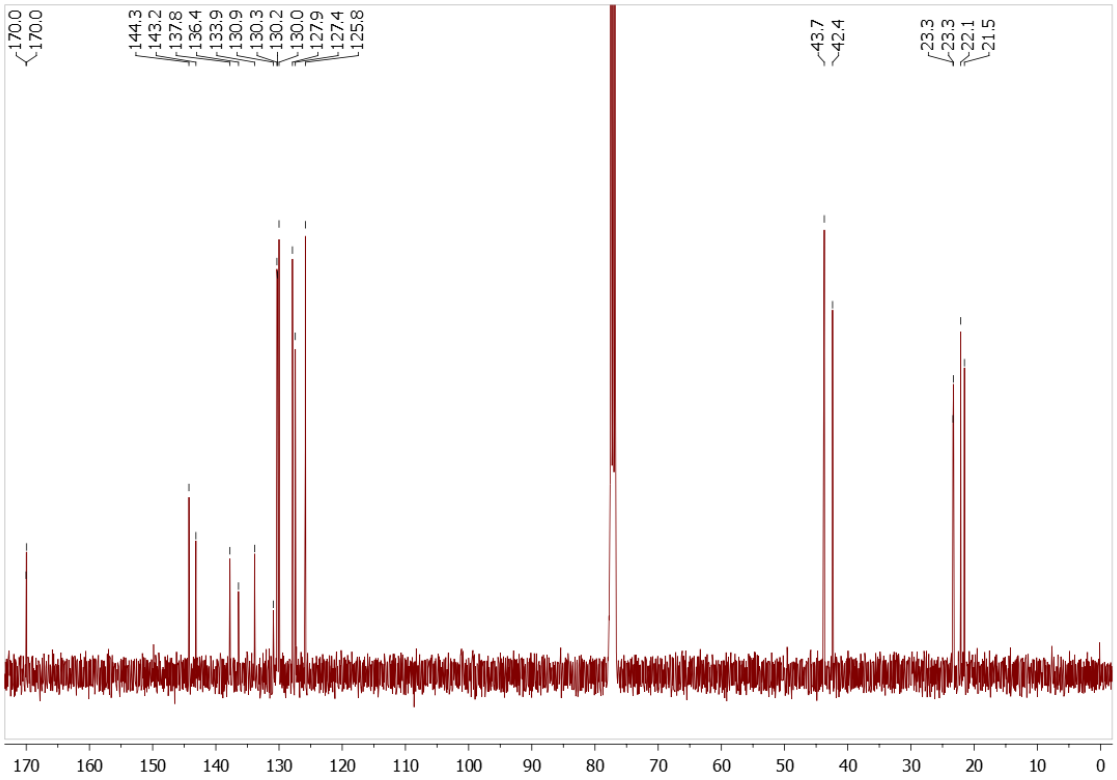
^{13}C NMR ($CDCl_3$) *S*-(2-((*N*-acetylacetamido)methyl)phenyl) ethanethioate (10)



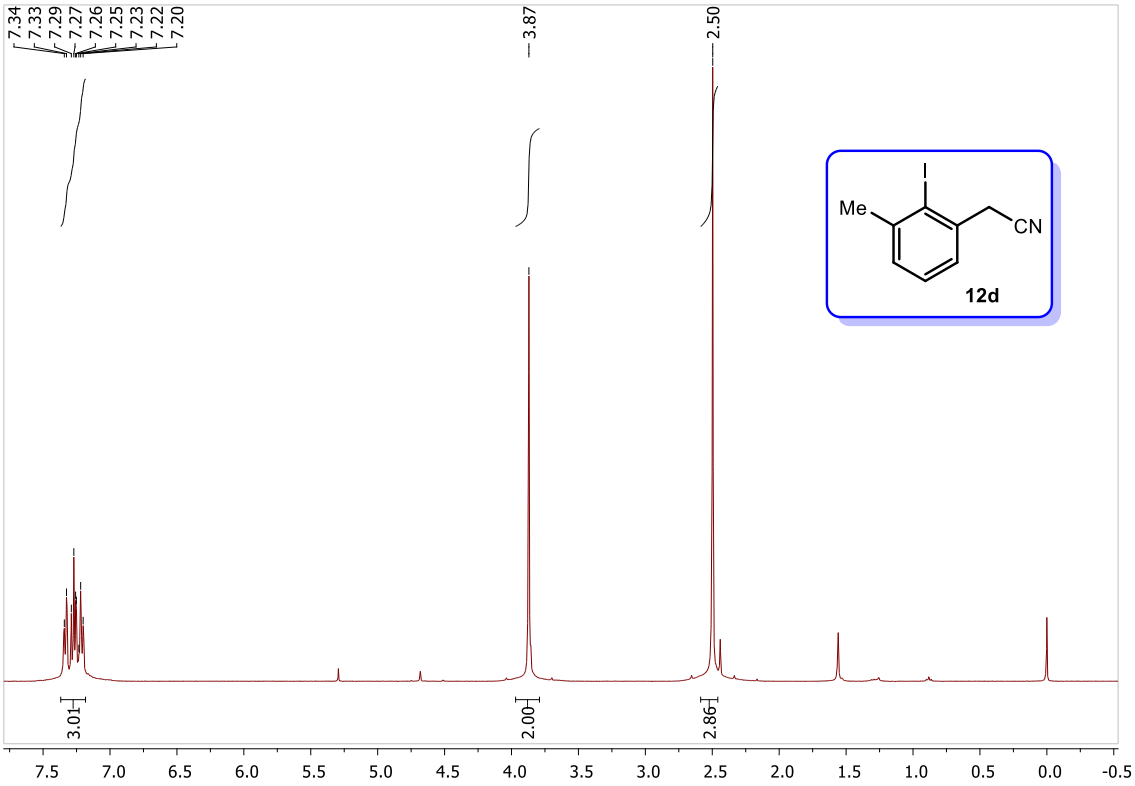
^{1}H NMR ($CDCl_3$) *N*-(2-mercapto-3-methylbenzyl)acetamide (11)



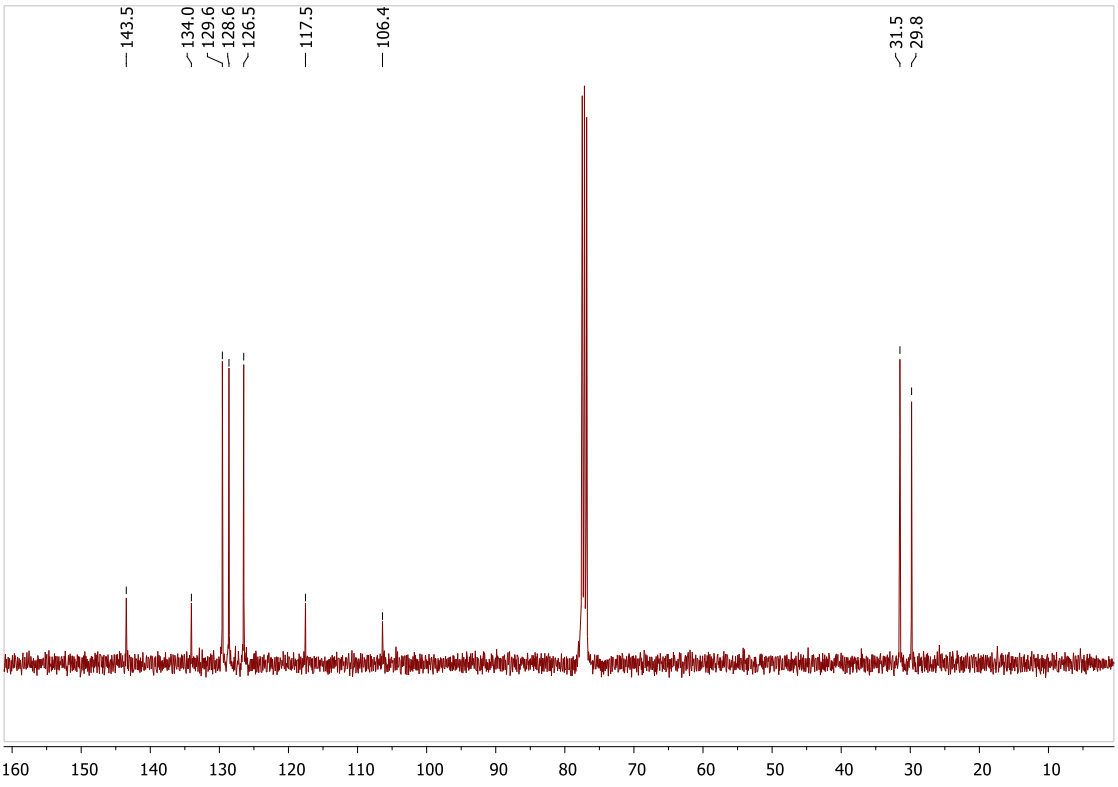
^{13}C NMR ($CDCl_3$) *N*-(2-mercapto-3-methylbenzyl)acetamide (11)



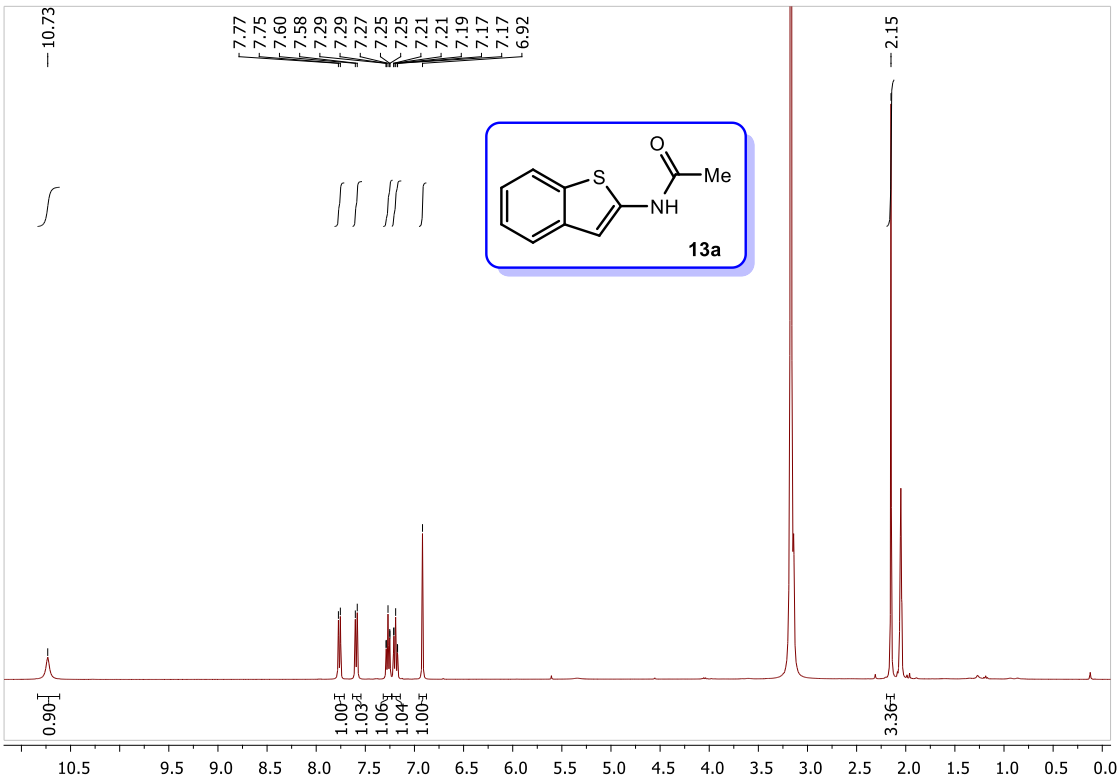
^{1}H NMR ($CDCl_3$) 2-(2-iodo-3-methylphenyl)acetonitrile (12d)



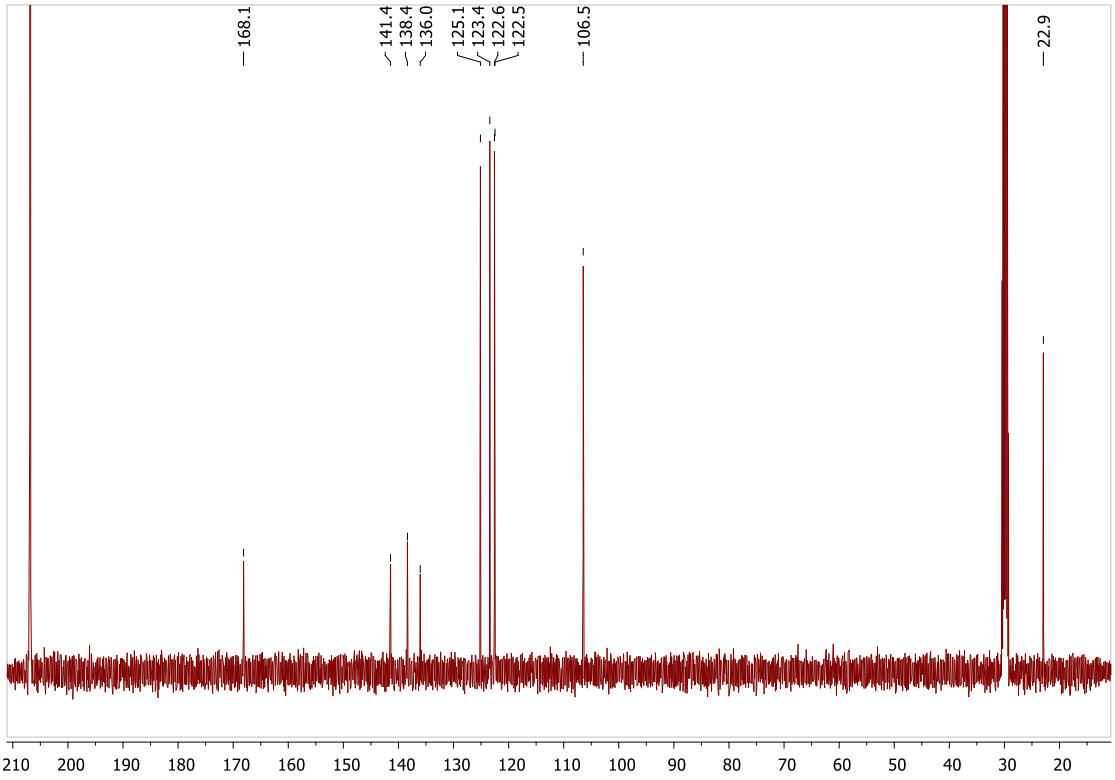
^{13}C NMR ($CDCl_3$) 2-(2-iodo-3-methylphenyl)acetonitrile (12d)



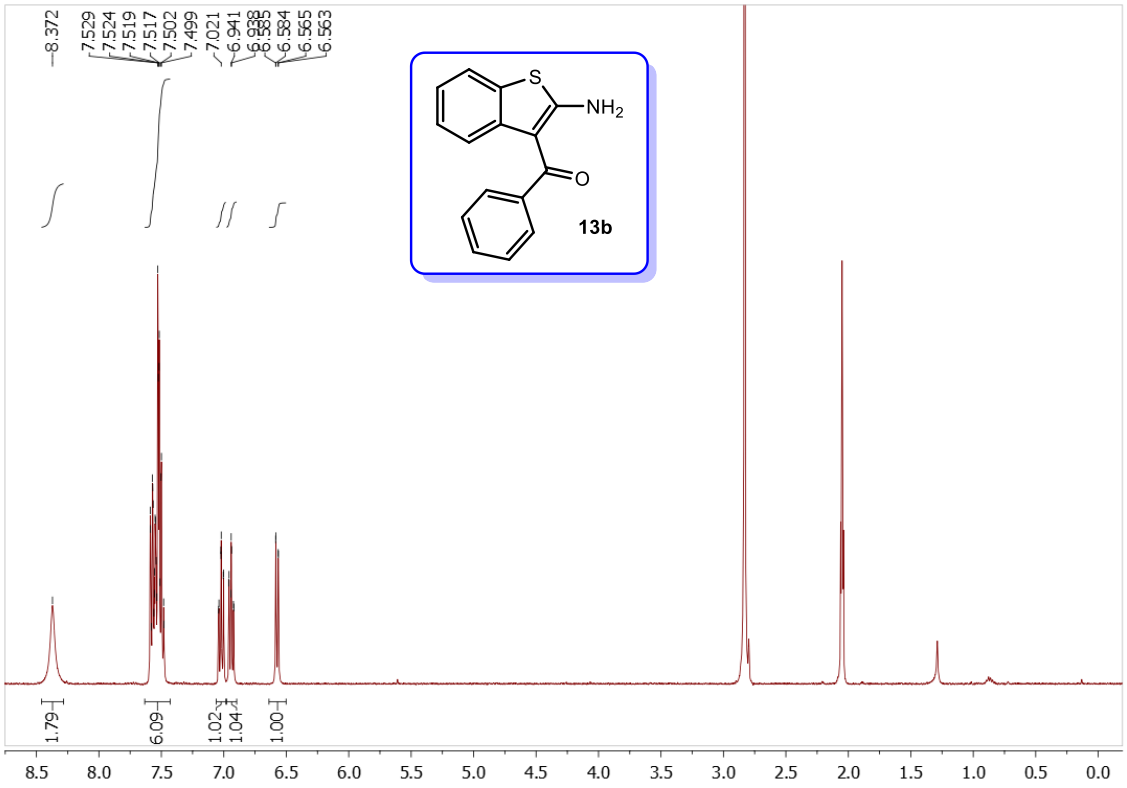
^{1}H NMR (acetone-d6) *N*-(benzo[*b*]thiophen-2-yl)acetamide (13a)



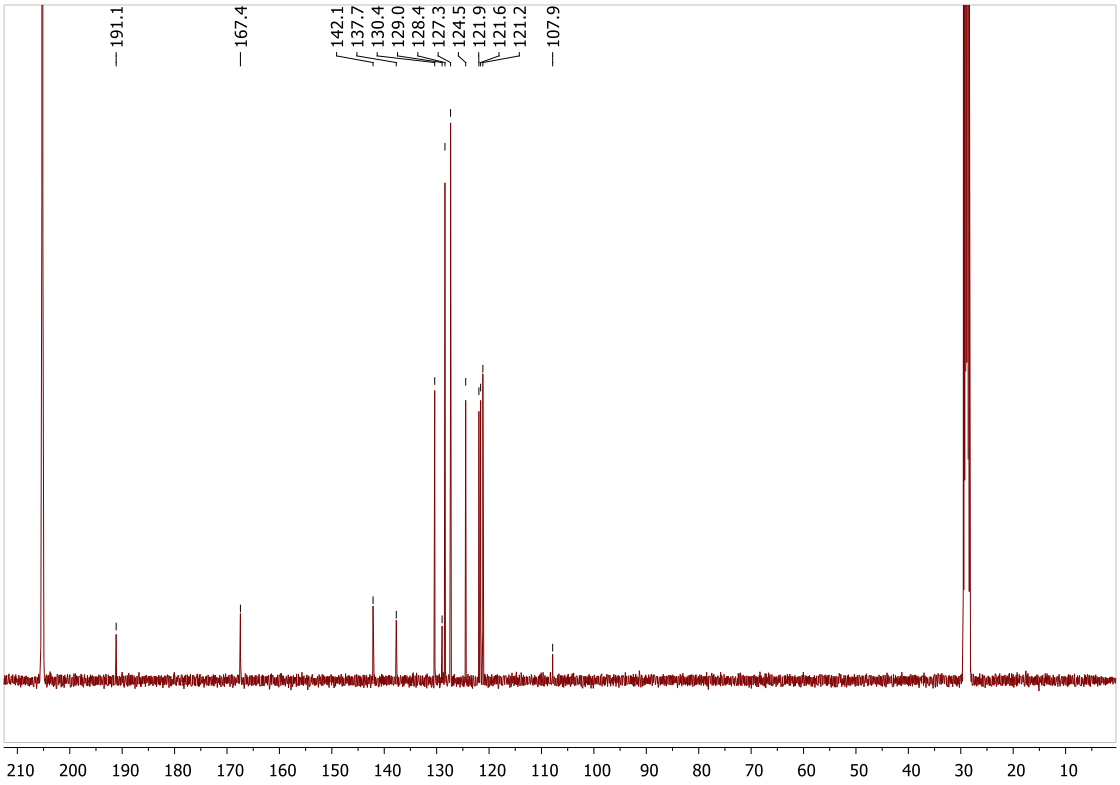
^{13}C NMR (acetone-d6)*N*-(benzo[*b*]thiophen-2-yl)acetamide (13a)



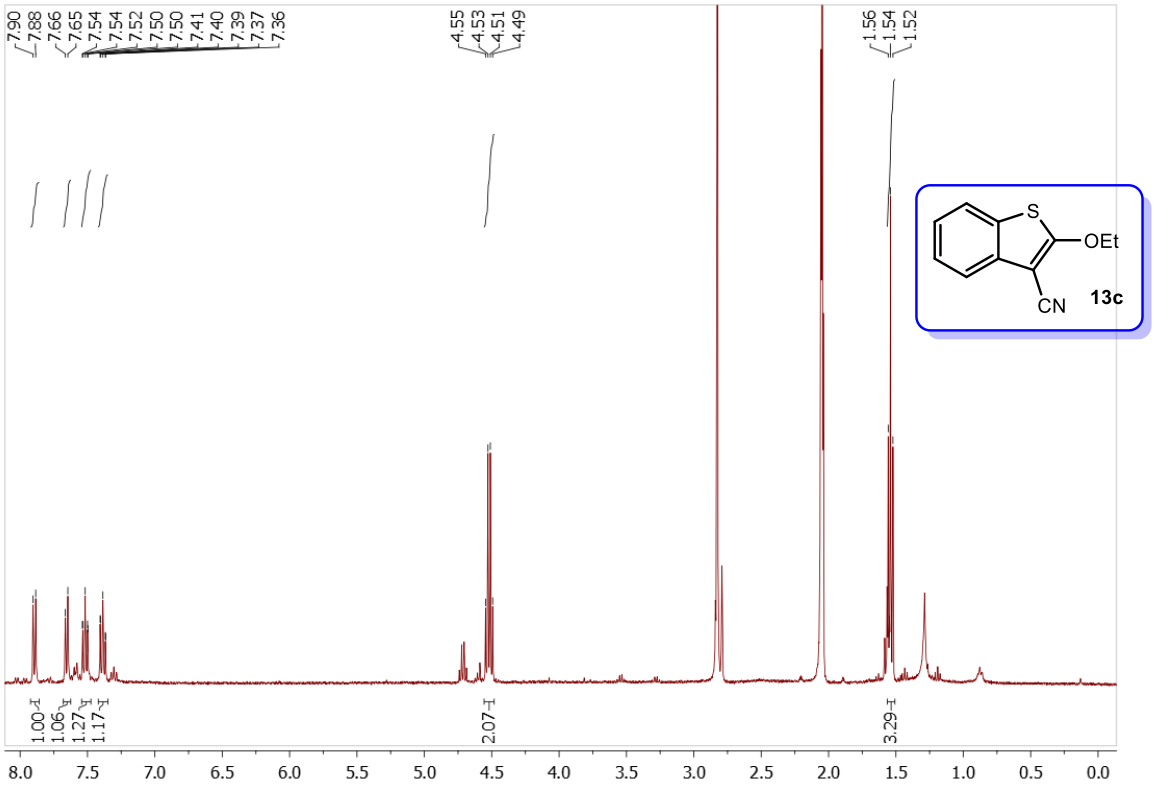
^{1}H NMR (acetone-d6) (2-Aminobenzo[*b*]thiophen-3-yl)(phenyl)methanone(13b)

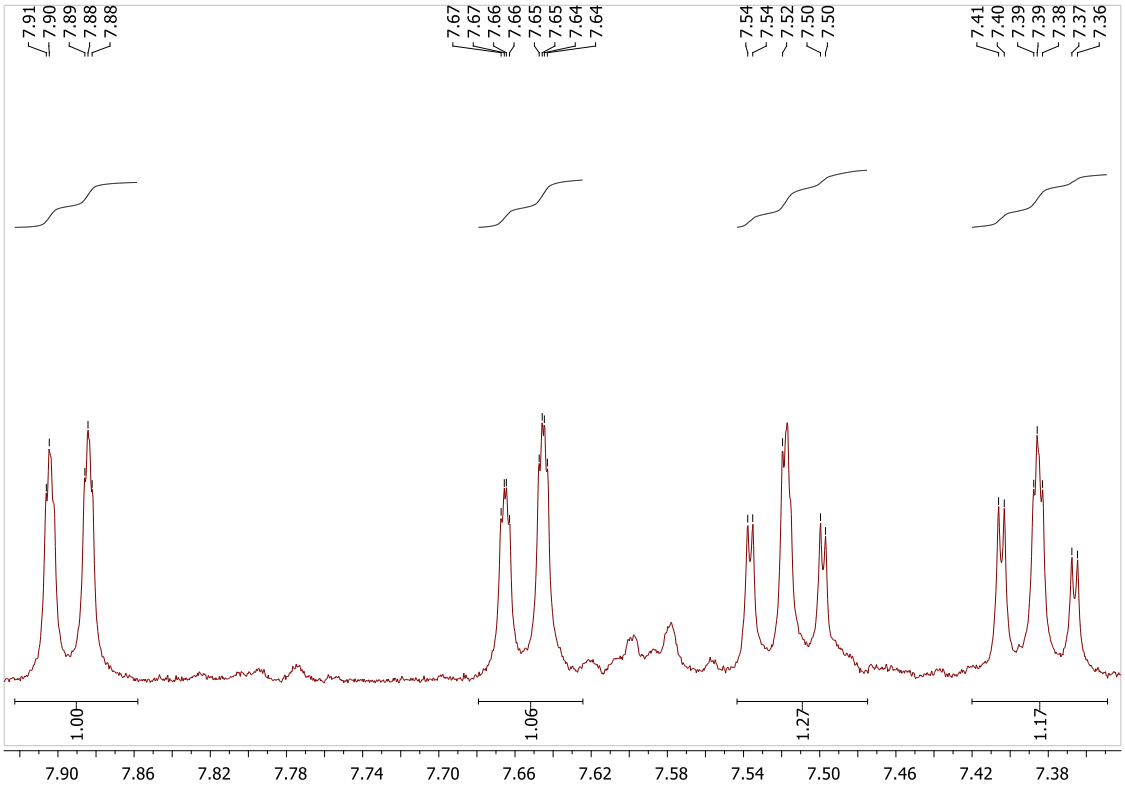


^{13}C NMR (acetone-d6) (2-Aminobenzo[*b*]thiophen-3-yl)(phenyl)methanone(13b)

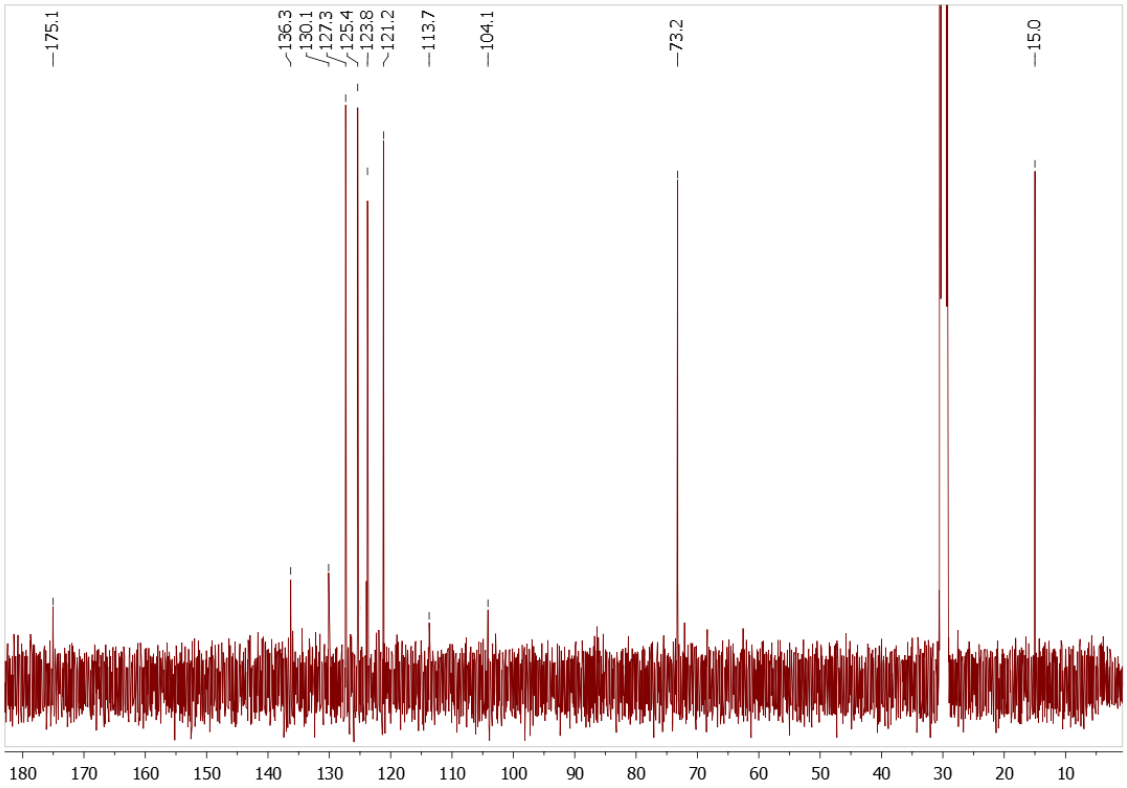


^{1}H NMR (acetone-d6) 2-ethoxybenzo[*b*]thiophene-3-carbonitrile (13c)

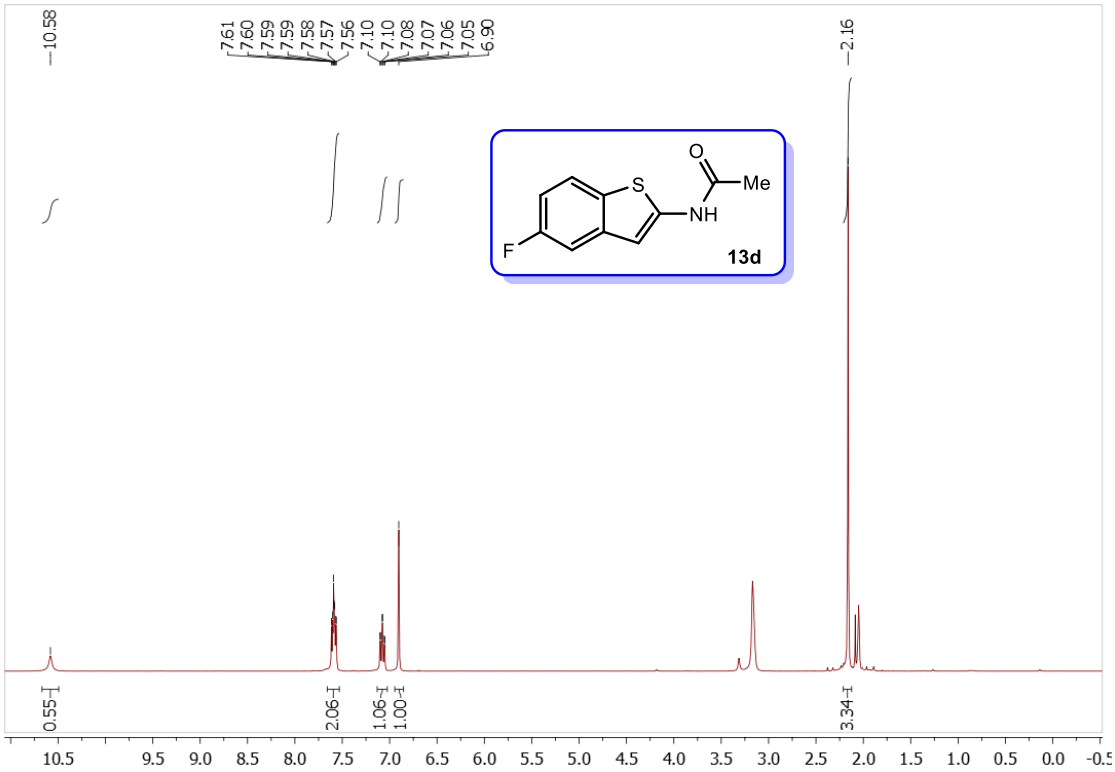




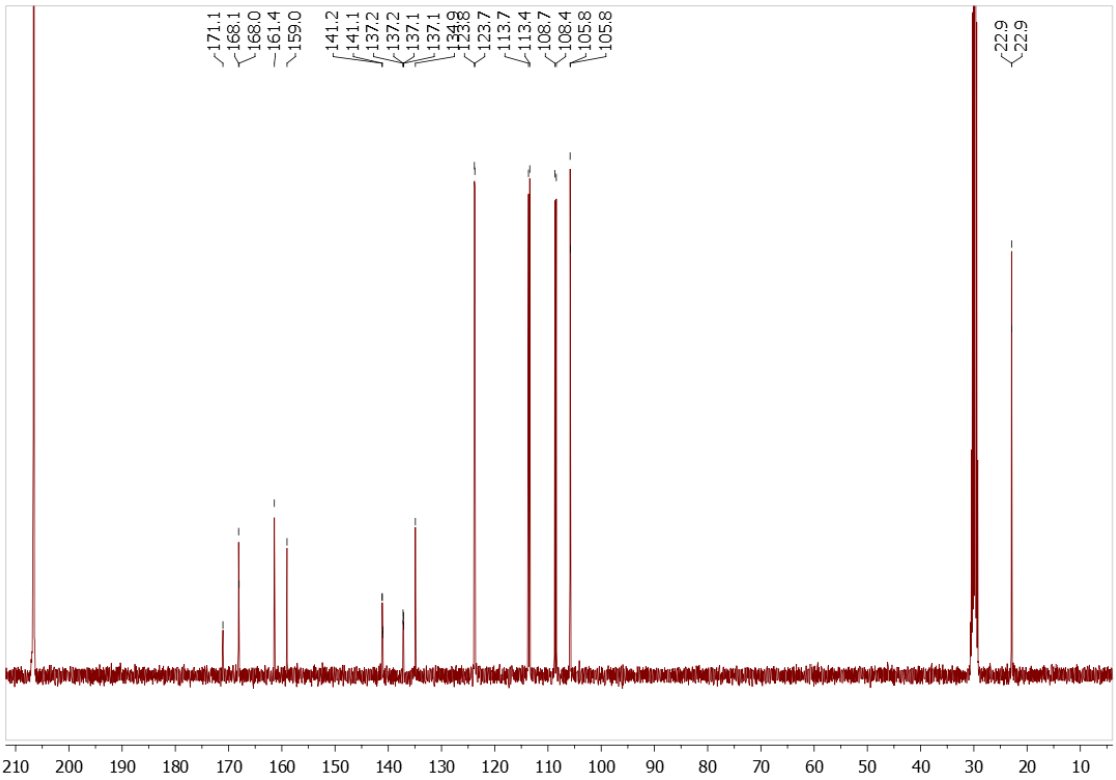
^{13}C NMR (acetone-d6) 2-ethoxybenzo[*b*]thiophene-3-carbonitrile (13c)



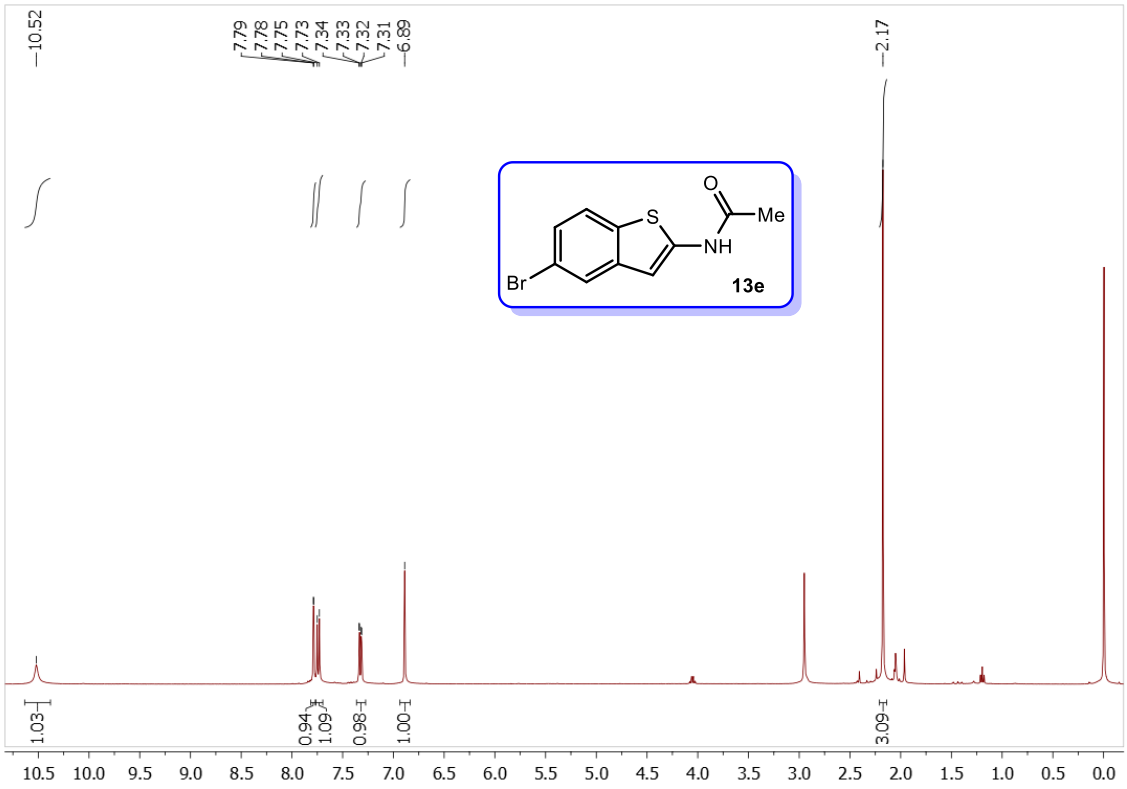
^{1}H NMR (acetone-d6) *N*-(5-fluorobenzo[*b*]thiophen-2-yl)acetamide (13d)



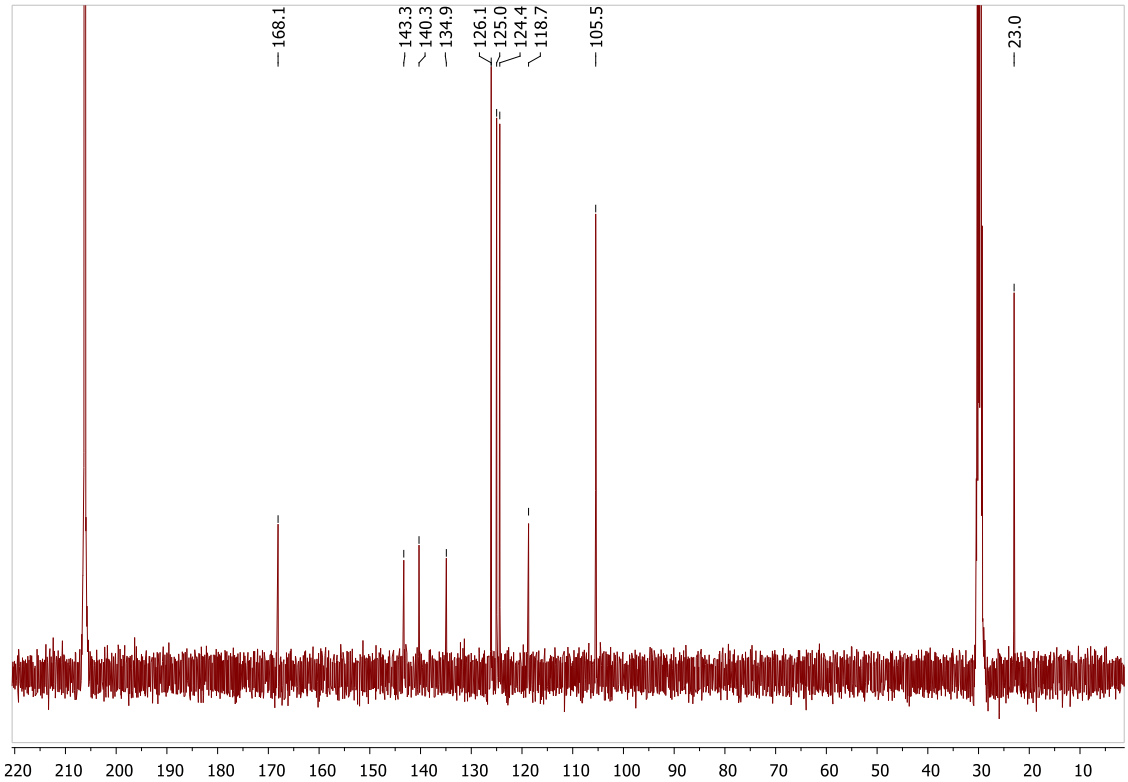
^{13}C NMR (acetone-d6) *N*-(5-fluorobenzo[*b*]thiophen-2-yl)acetamide (13d)



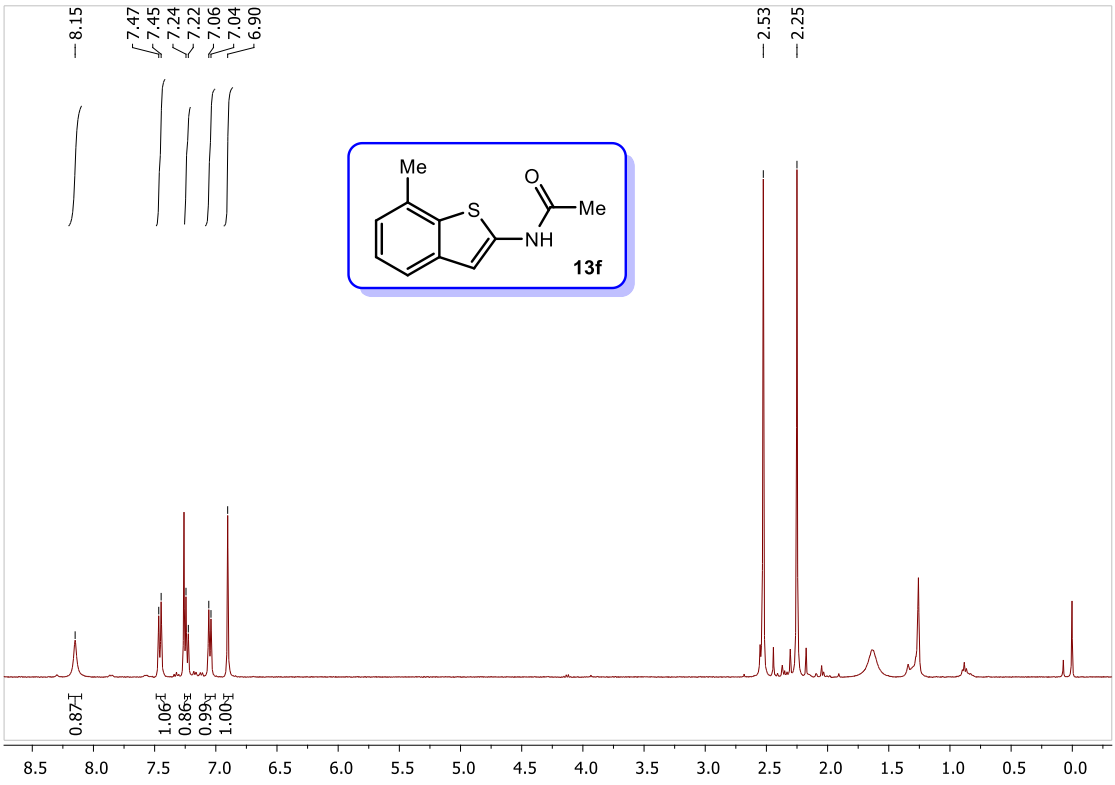
^{1}H NMR (acetone-d6) *N*-(5-bromobenzo[*b*]thiophen-2-yl)acetamide (13e)



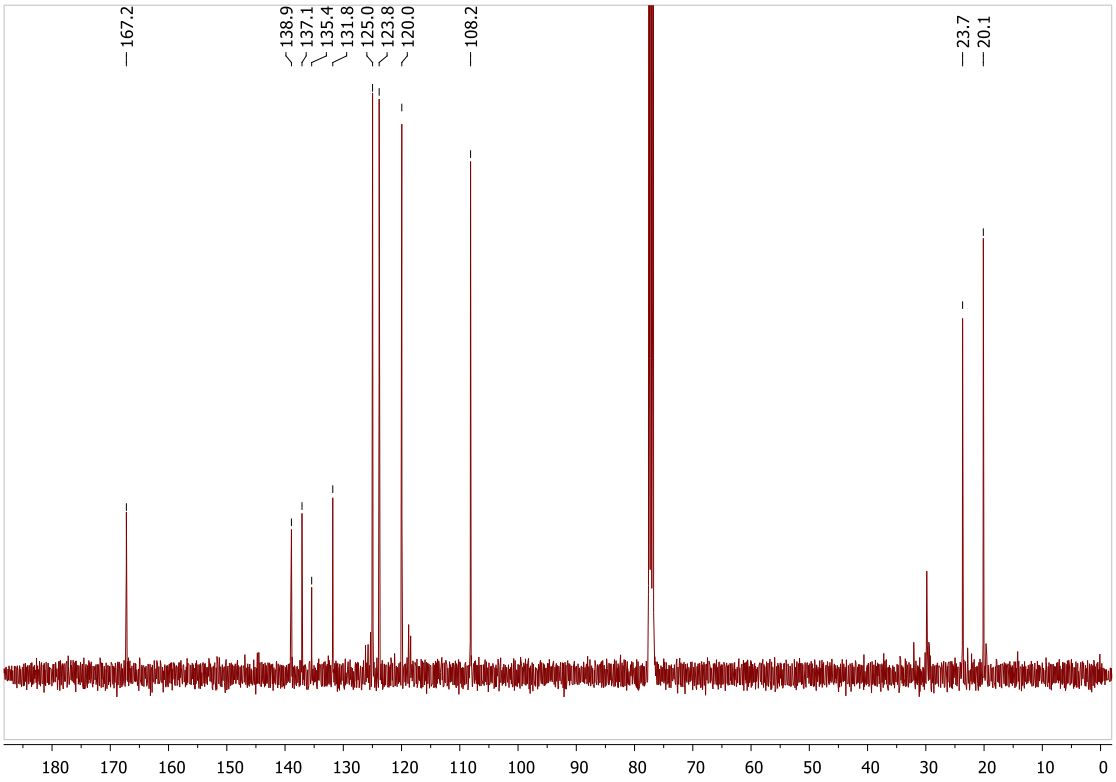
^{13}C NMR (acetone-d6) *N*-(5-bromobenzo[*b*]thiophen-2-yl)acetamide (13e)



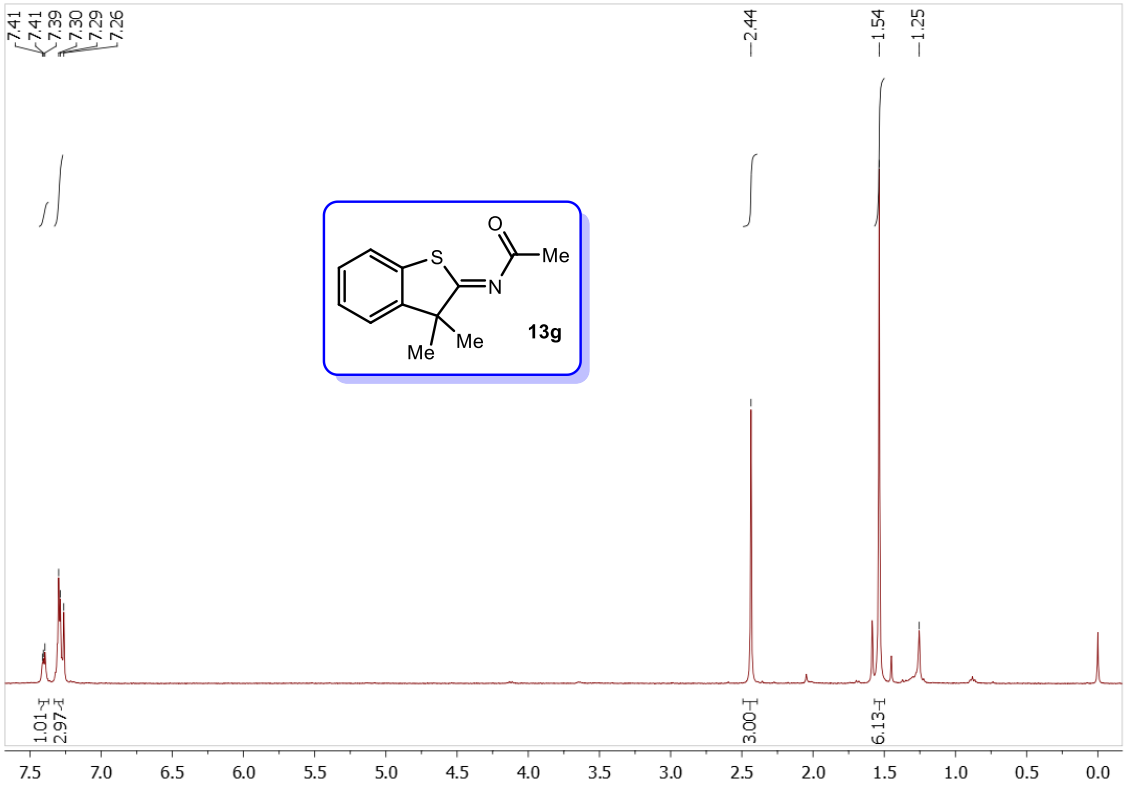
^{1}H NMR ($CDCl_3$) *N*-(7-methylbenzo[*b*]thiophen-2-yl)acetamide (13f)



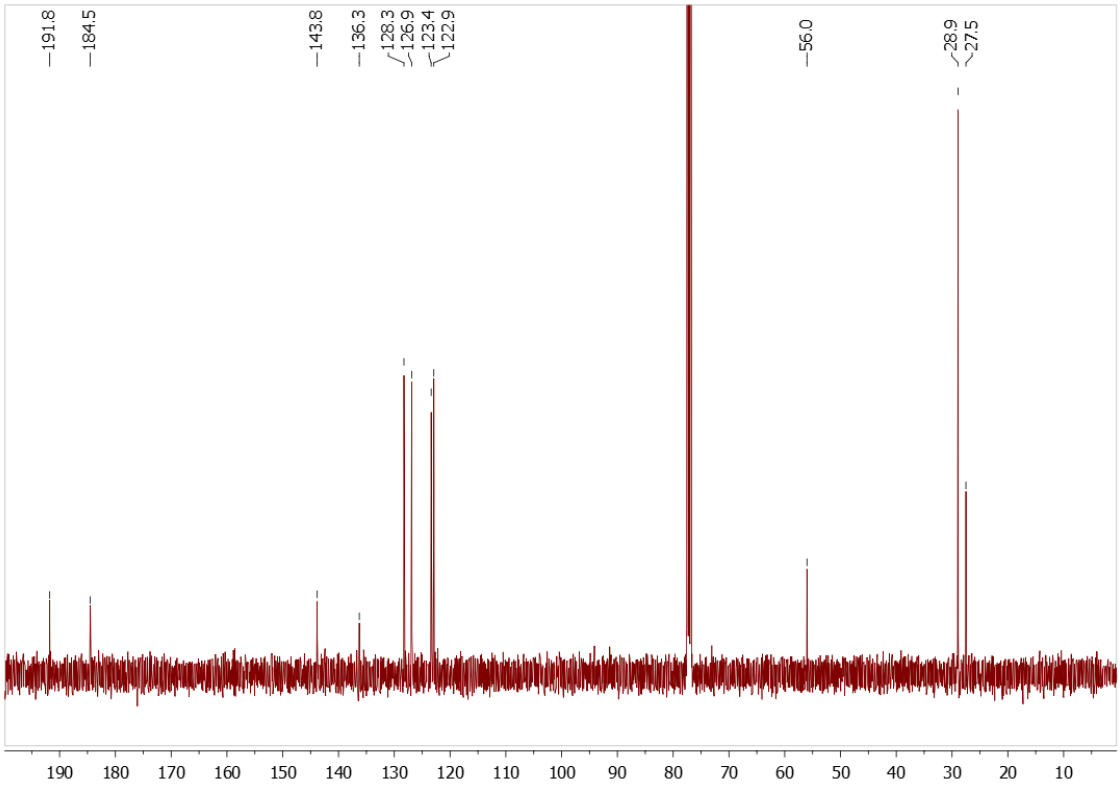
^{13}C NMR ($CDCl_3$) *N*-(7-methylbenzo[*b*]thiophen-2-yl)acetamide (13f)



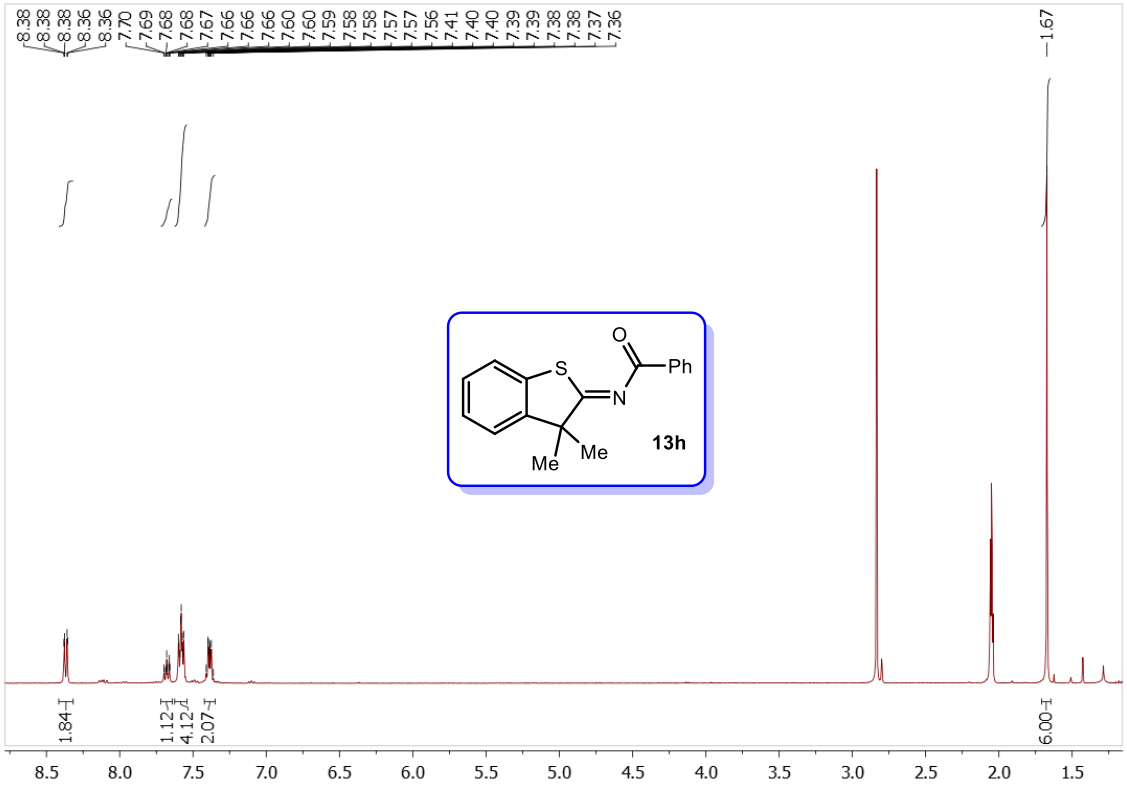
^{1}H NMR ($CDCl_3$) *N*-(3,3-dimethylbenzo[*b*]thiophen-2(3*H*)-ylidene)acetamide(13g)

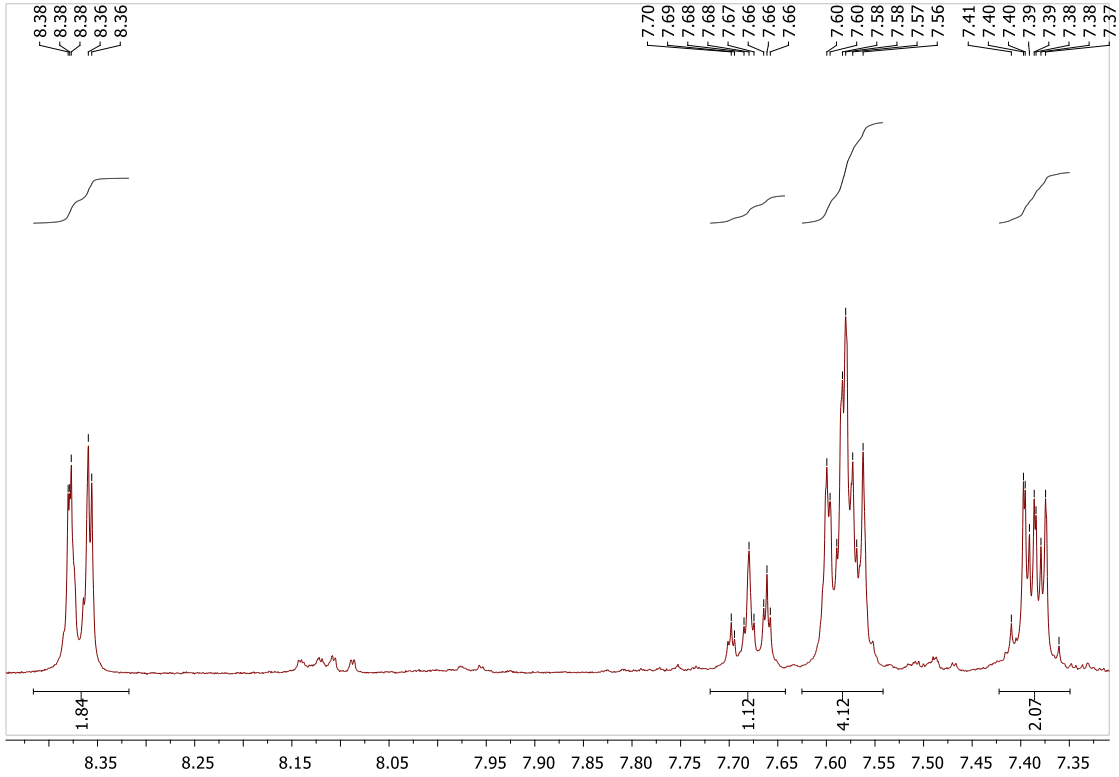


^{13}C NMR ($CDCl_3$)*N*-(3,3-dimethylbenzo[*b*]thiophen-2(3*H*)-ylidene)acetamide(13g)

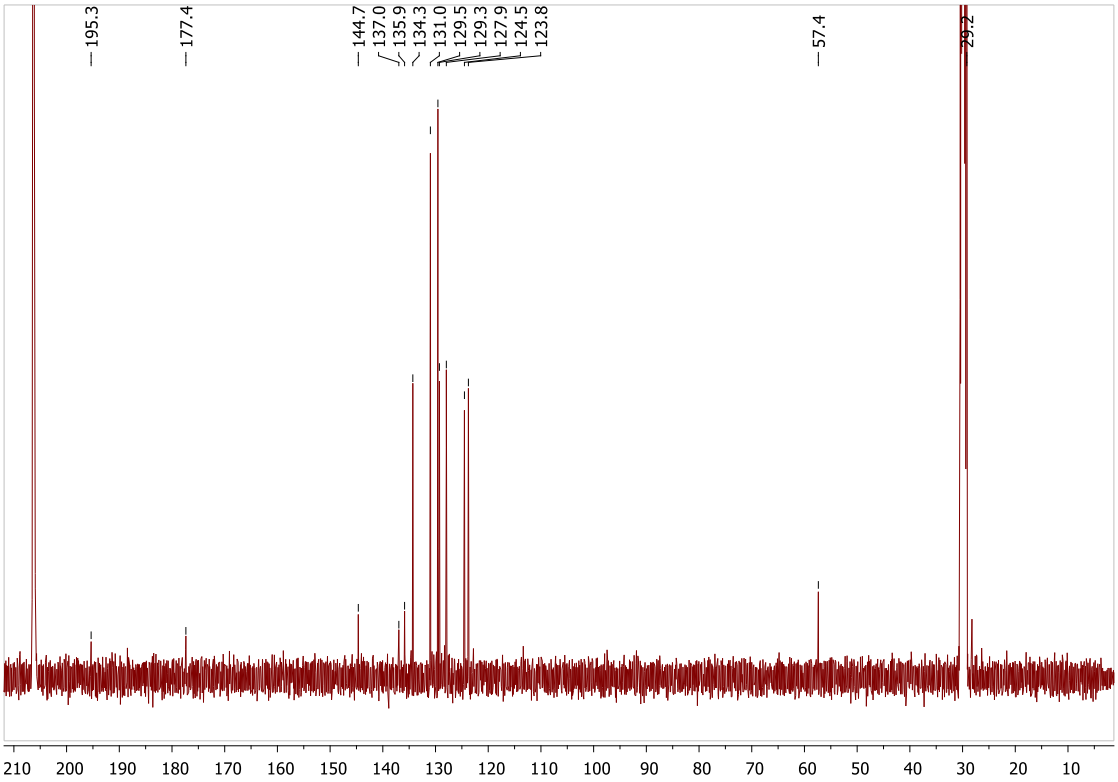


^{1}H NMR (acetone-d6)*N*-(3,3-dimethylbenzo[*b*]thiophen-2(3*H*)-ylidene)benzamide (13h)

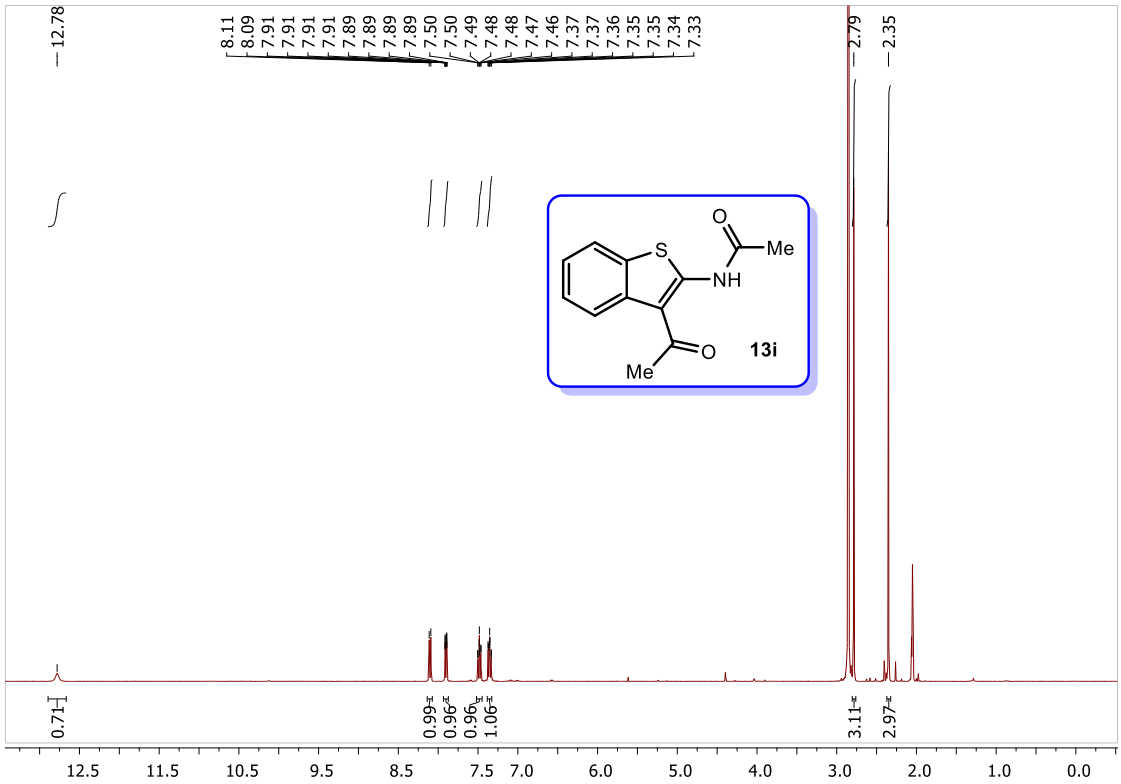




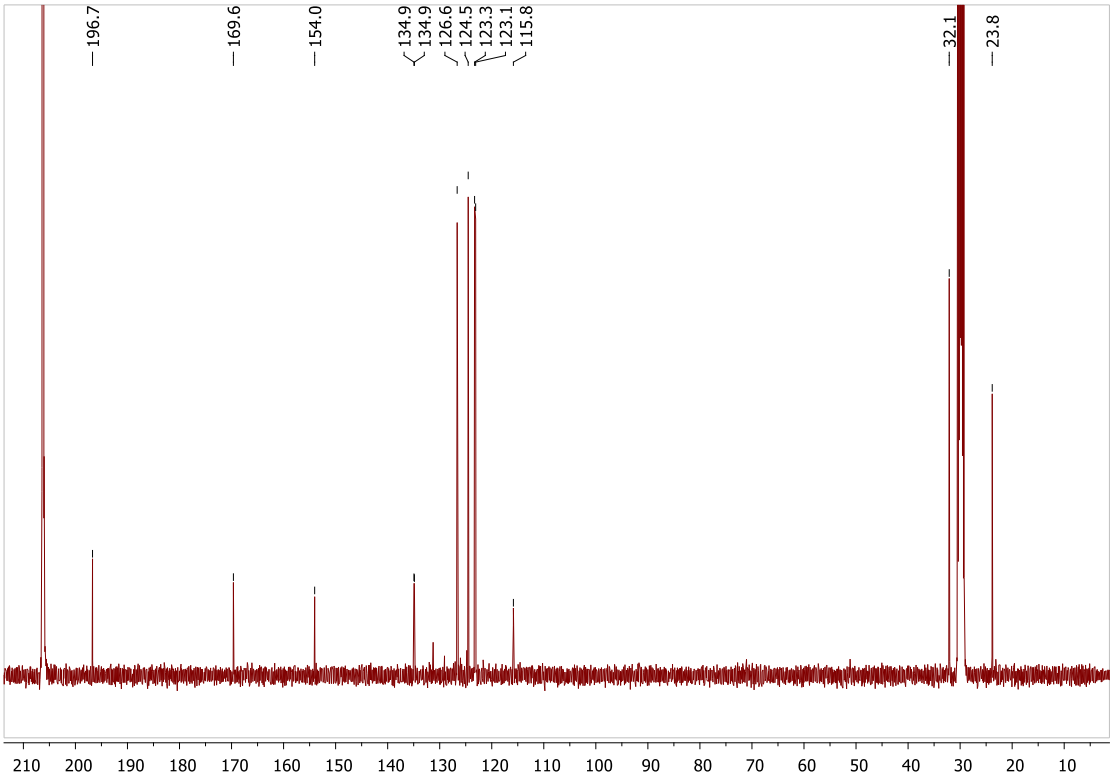
^{13}C NMR (acetone-d6)*N*-(3,3-dimethylbenzo[*b*]thiophen-2(3*H*)-ylidene)benzamide (13h)



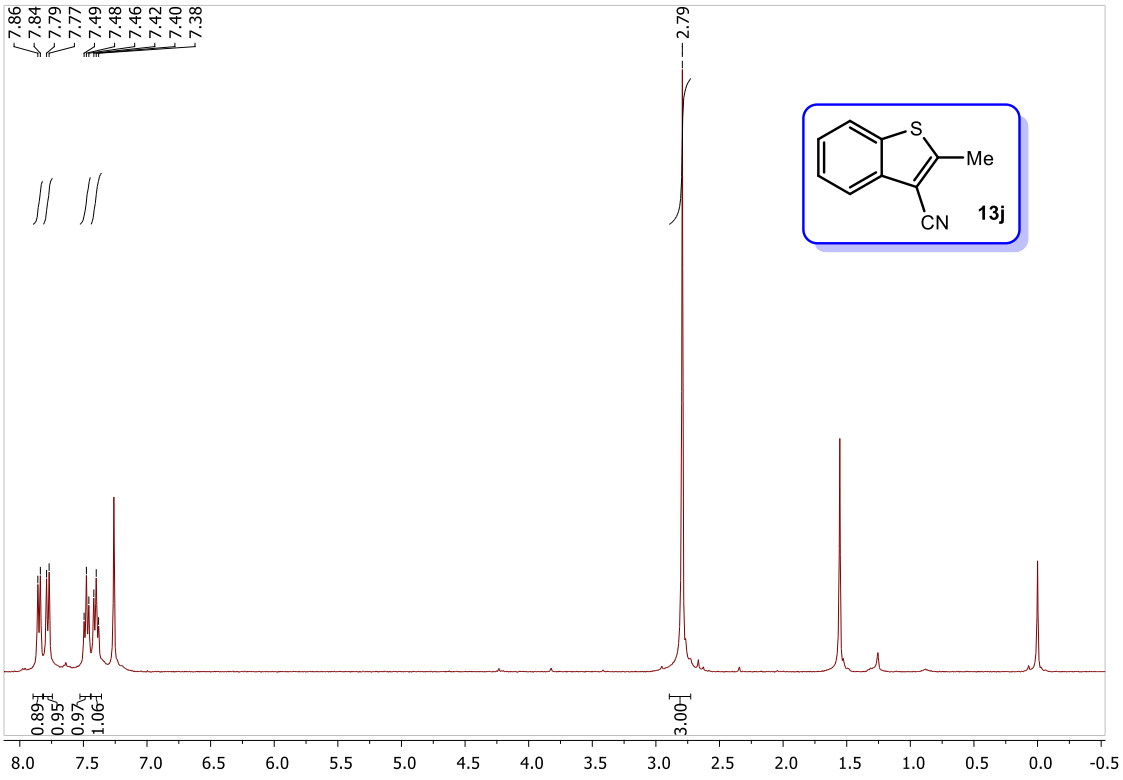
^{1}H NMR (acetone-d6) *N*-(3-acetylbenzo[*b*]thiophen-2-yl)acetamide (13i)



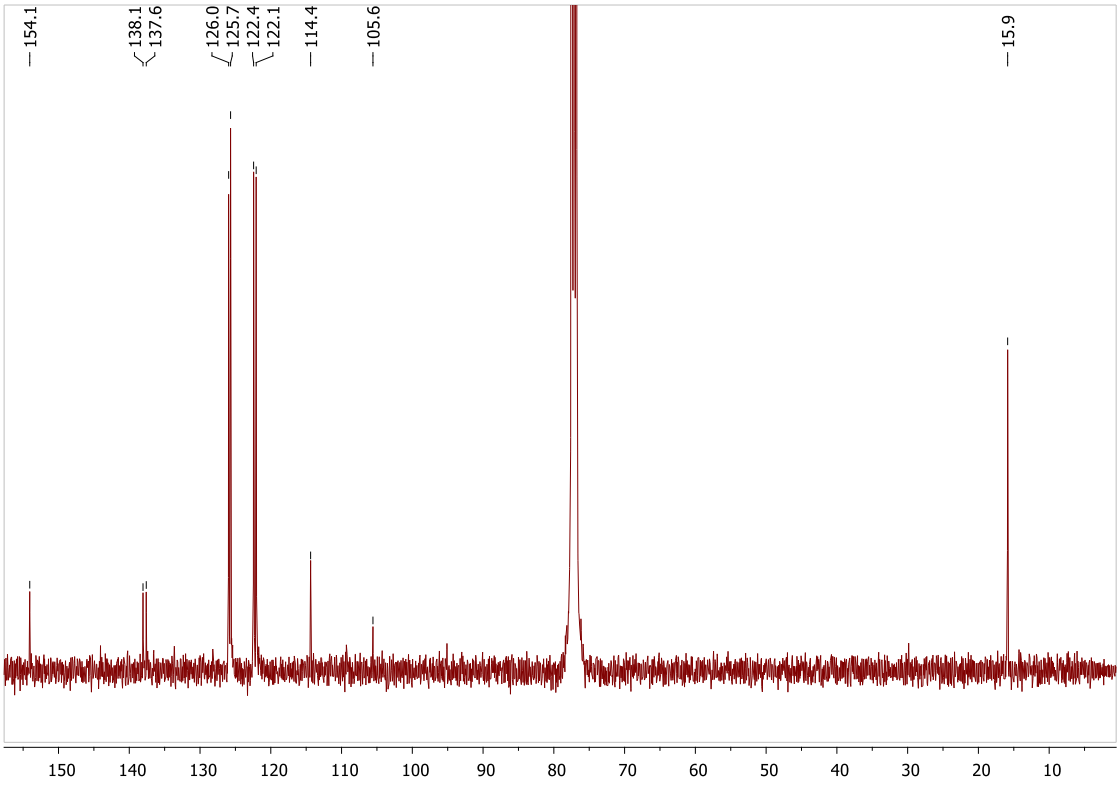
^{13}C NMR (acetone-d6) *N*-(3-acetylbenzo[*b*]thiophen-2-yl)acetamide (13i)



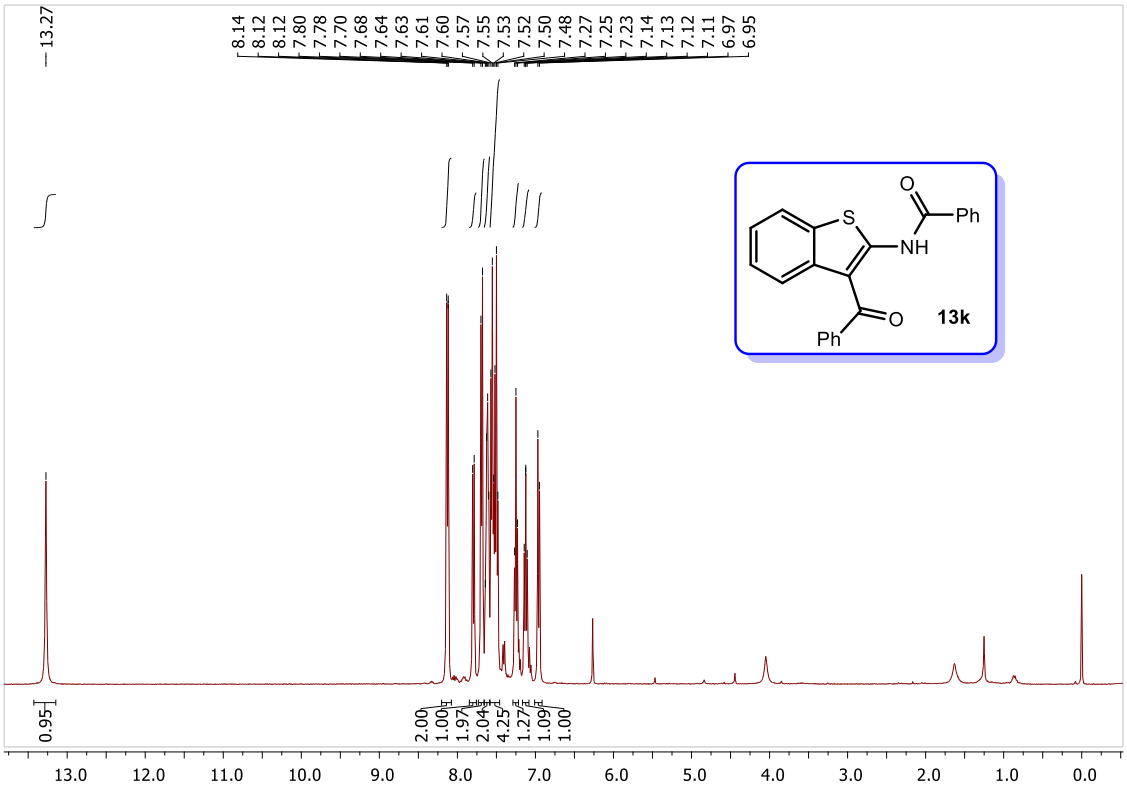
^{1}H NMR ($CDCl_3$)2-methylbenzo[*b*]thiophene-3-carbonitrile (13j)

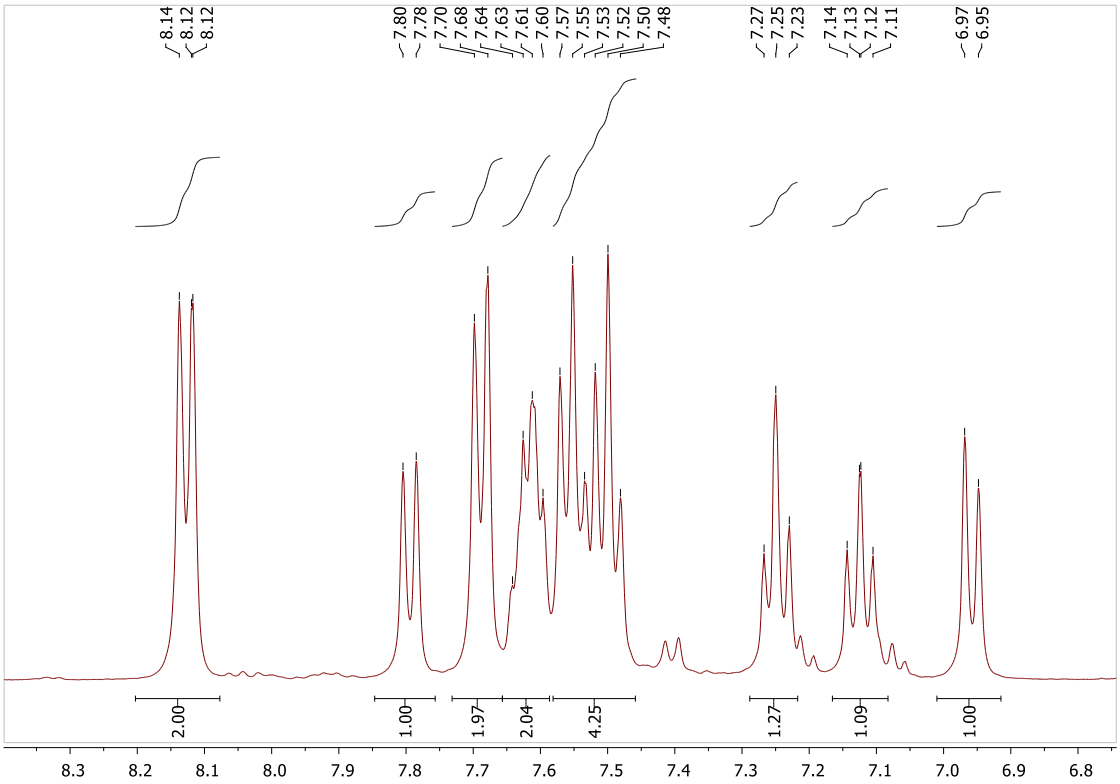


^{13}C NMR ($CDCl_3$)2-methylbenzo[*b*]thiophene-3-carbonitrile (13j)

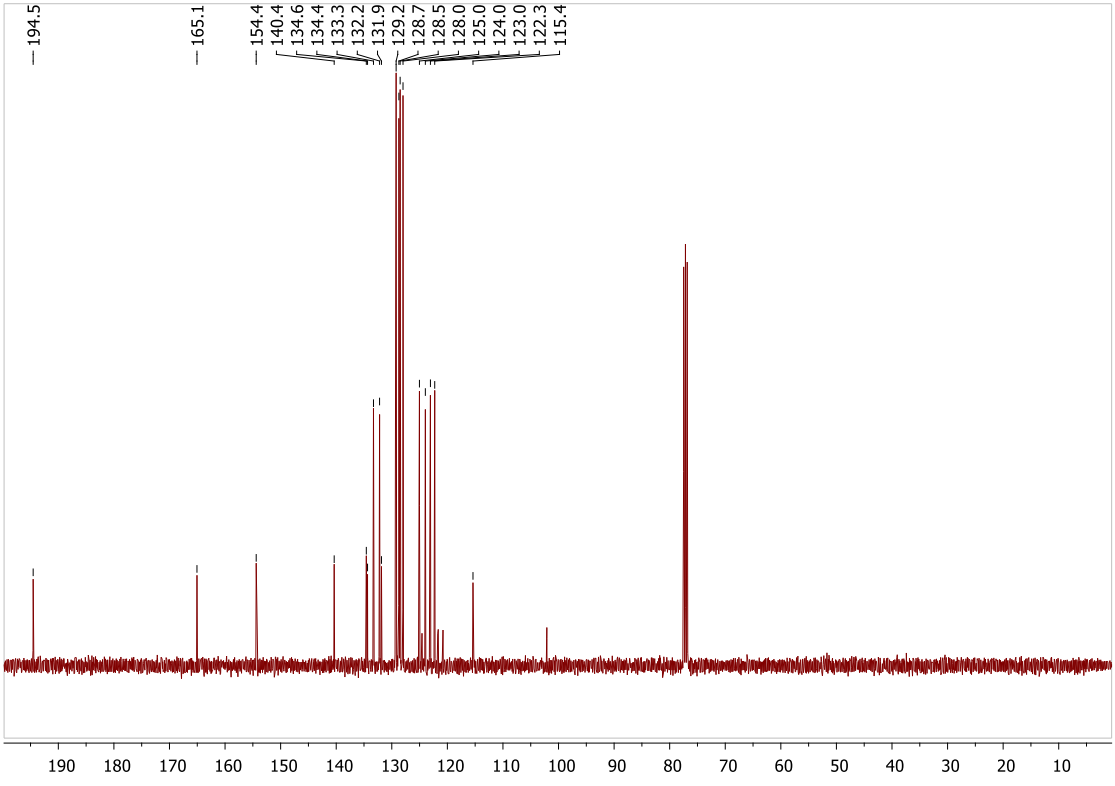


^{1}H NMR ($CDCl_3$) *N*-(3-benzoylbenzo[*b*]thiophen-2-yl)benzamide (13k)

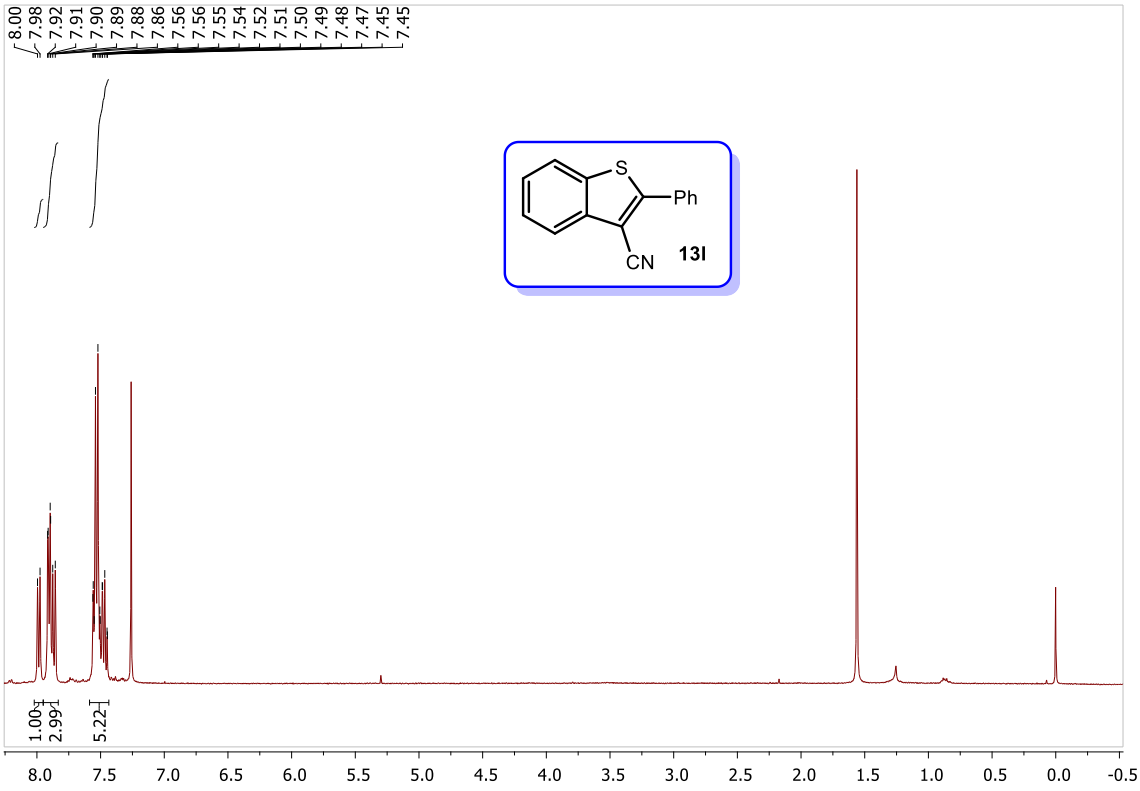


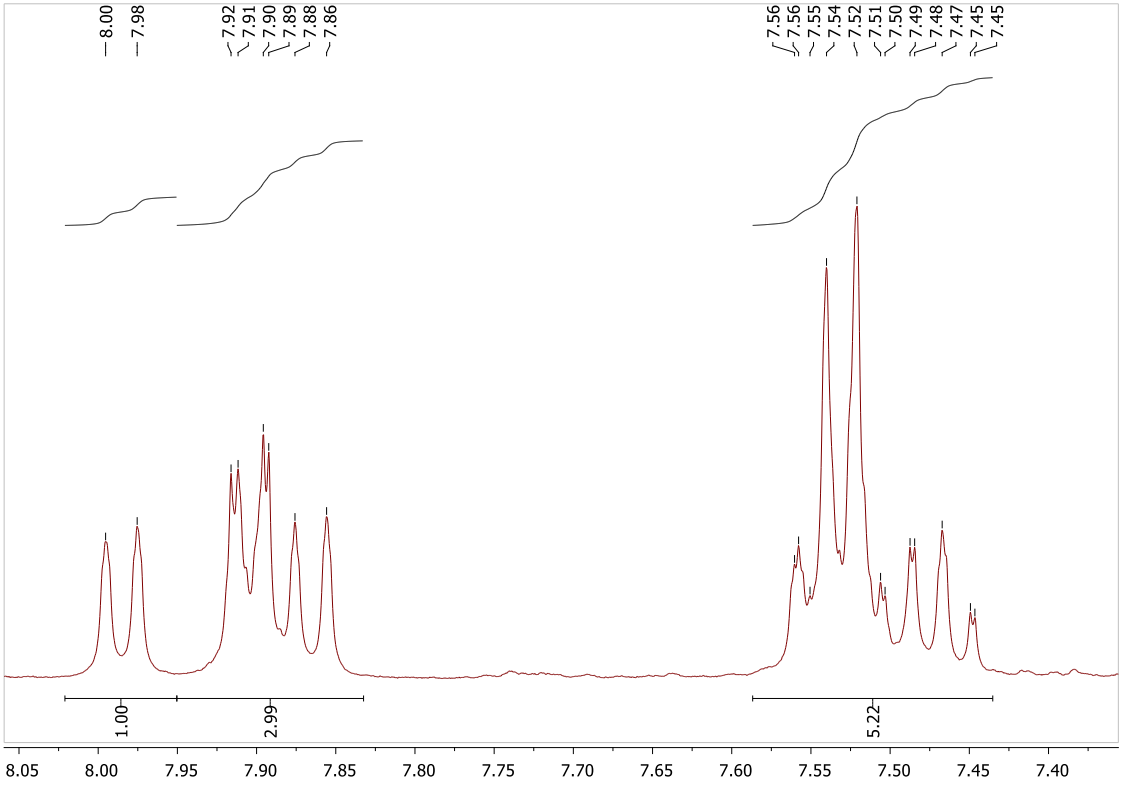


^{13}C NMR ($CDCl_3$) *N*-(3-benzoylbenzo[*b*]thiophen-2-yl)benzamide (13k)

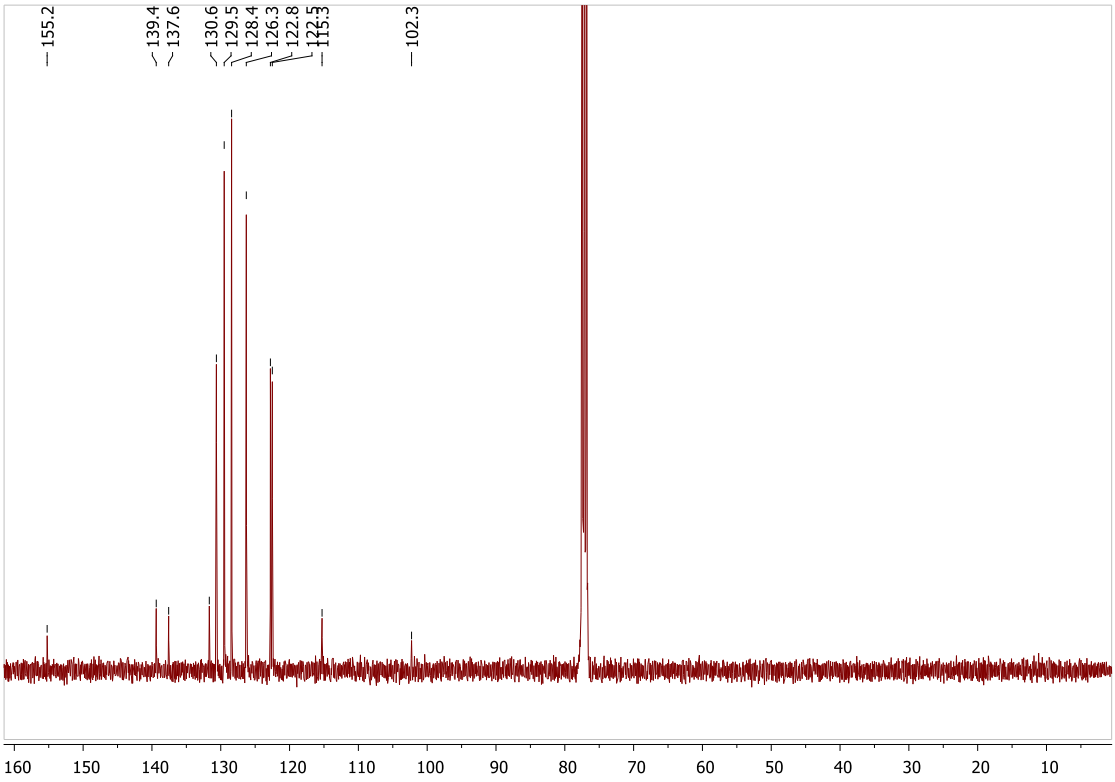


^{1}H NMR ($CDCl_3$) 2-phenylbenzo[*b*]thiophene-3-carbonitrile (13l)

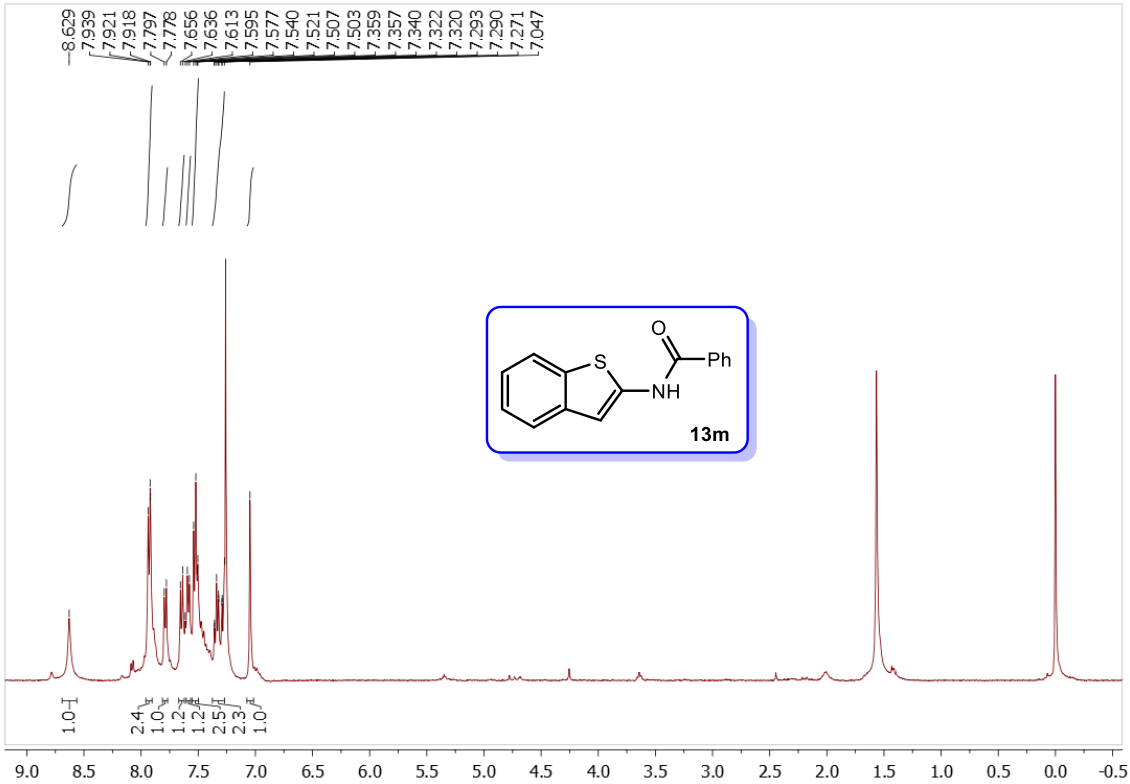




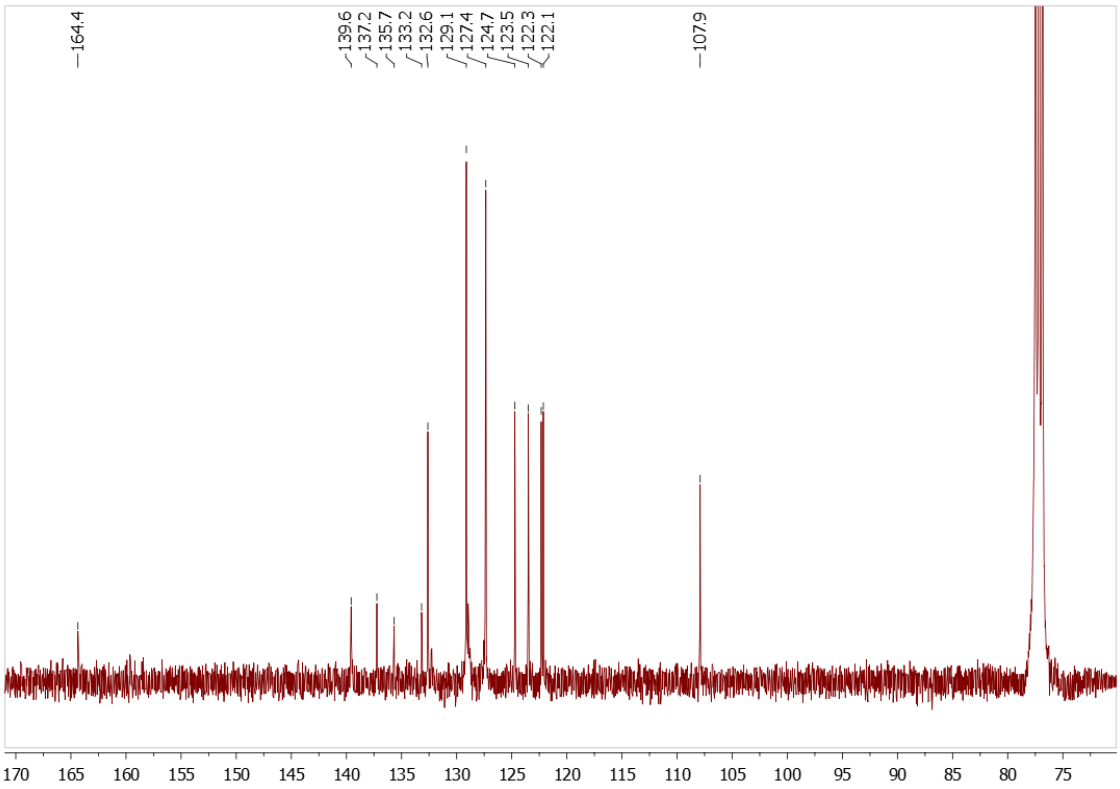
^{13}C NMR ($CDCl_3$) 2-phenylbenzo[*b*]thiophene-3-carbonitrile (13l)



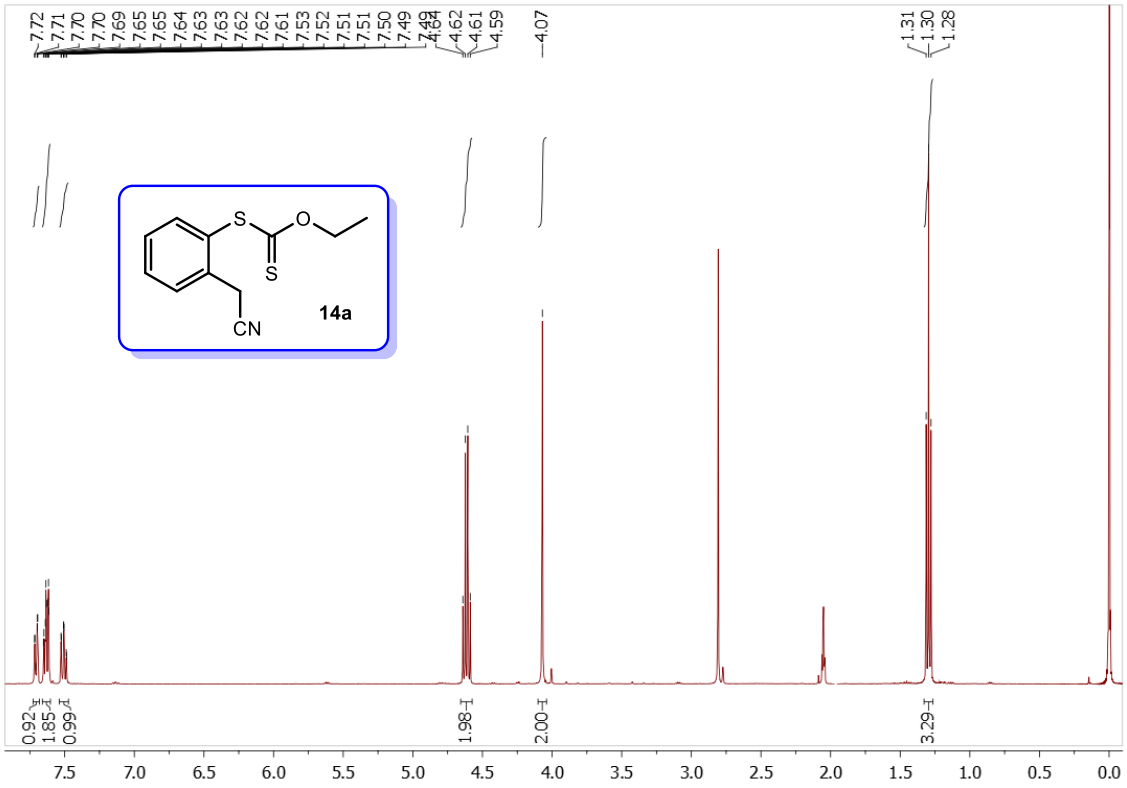
^{1}H NMR ($CDCl_3$)*N*-(benzo[*b*]thiophen-2-yl)benzamide (13m)



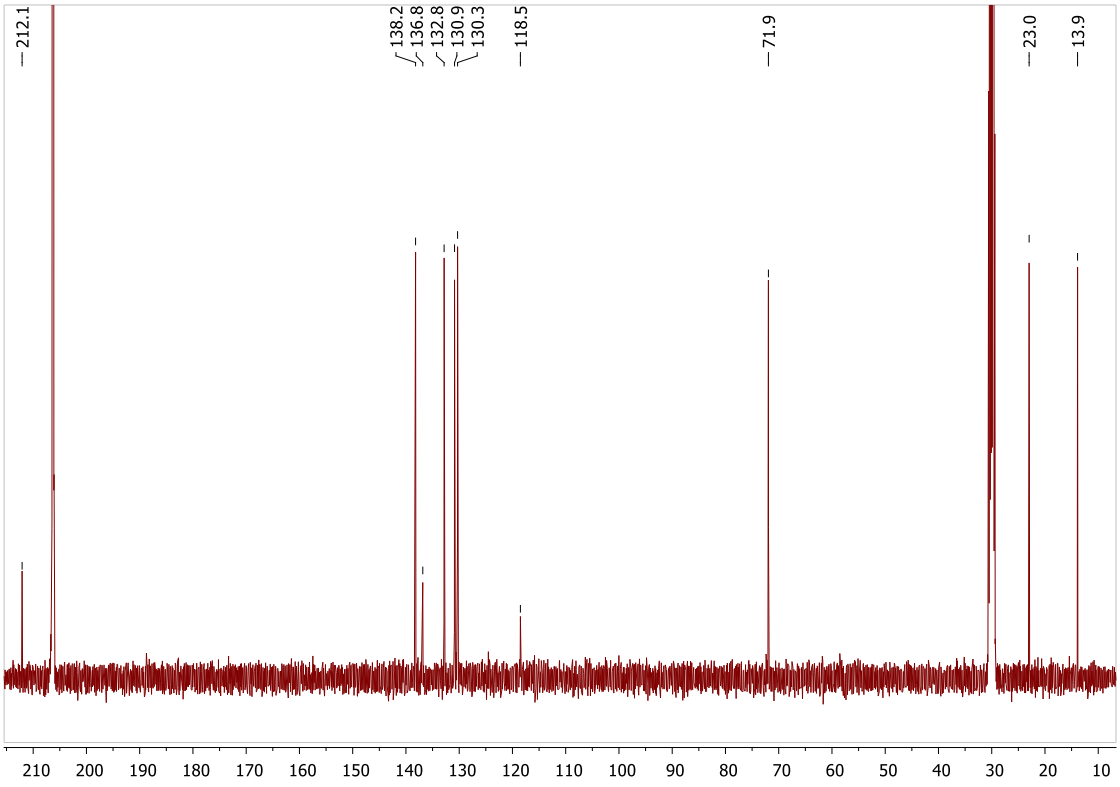
^{13}C NMR ($CDCl_3$)*N*-(benzo[*b*]thiophen-2-yl)benzamide (13m)



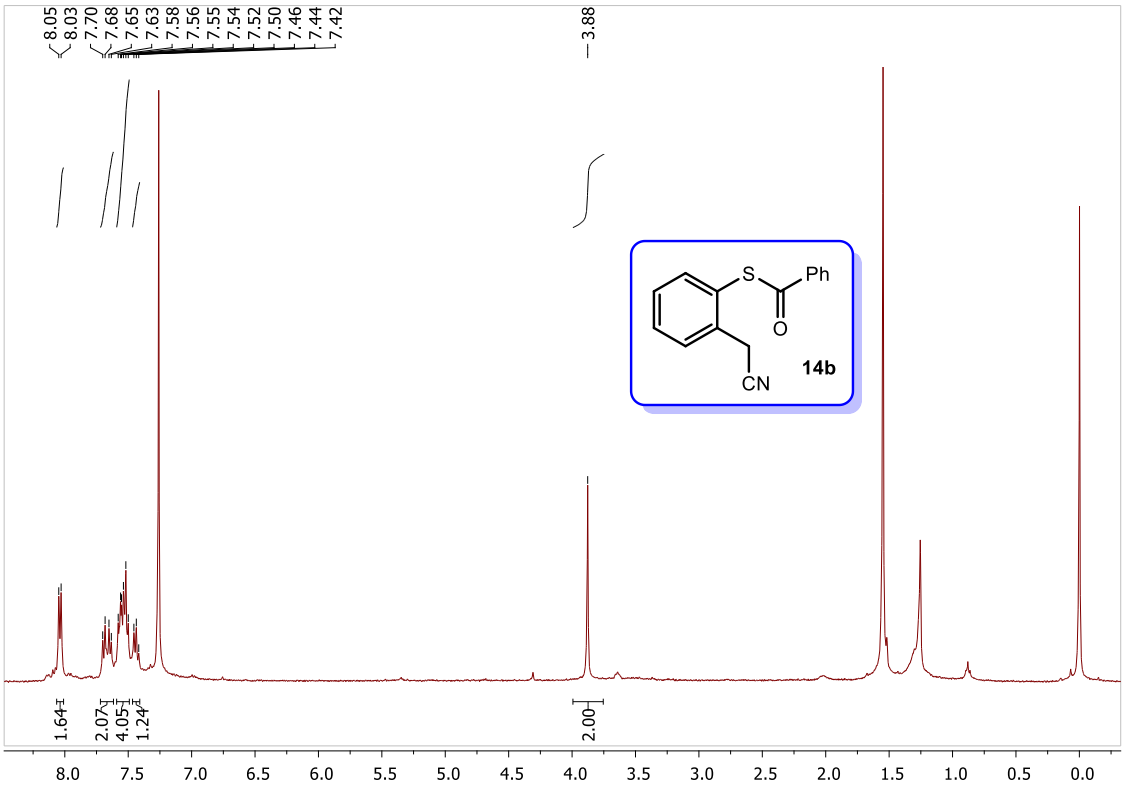
^{1}H NMR (acetone-d6) *S*-(2-(cyanomethyl)phenyl) *O*-ethyl carbonodithioate (14a)



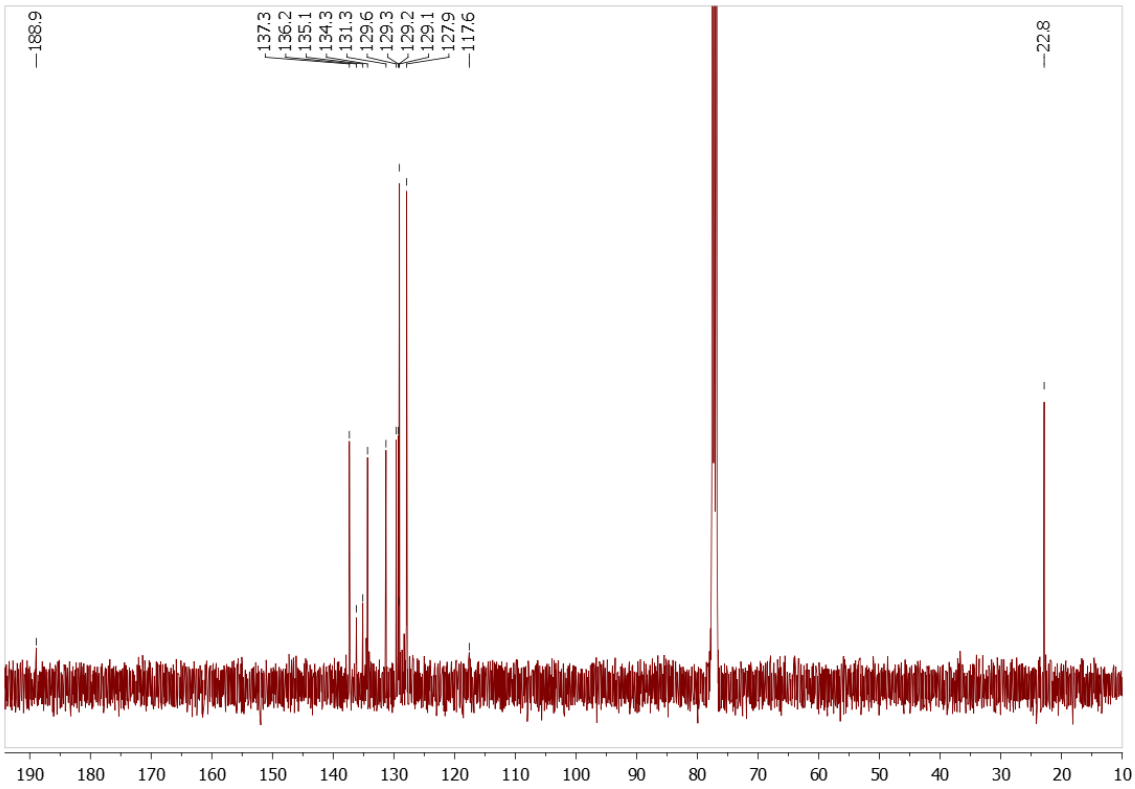
^{13}C NMR (acetone-d6) *S*-(2-(cyanomethyl)phenyl) *O*-ethyl carbonodithioate (14a)



^{1}H NMR ($CDCl_3$) *S*-(2-(cyanomethyl)phenyl) benzothioate(14b)



^{13}C NMR ($CDCl_3$) *S*-(2-(cyanomethyl)phenyl) benzothioate(14b)



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