Supporting Information

Anionic 5-Endo-Dig Cyclizations: An Experimental Investigation of In-Plane Aromaticity Involving a Non-Enolate Carbanion Nucleophile

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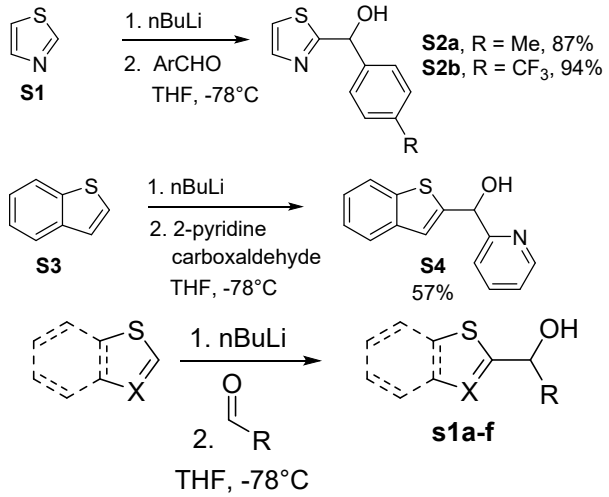
General Remarks

Reagents and solvents were purchased from commercial suppliers. Flash columns (with either 1" or 1.5" diameter and 12" elution length) were packed with silica gel (40-63 μm, 230-400 mesh particle size). In all procedures, "silica plug" refers to a fritted Buchner funnel (350 mL, 3.25" diameter) filled with approximately 60 g of dry silica gel. TLC plates polyester backed, UV-254, 200μm thickness, 5 cm width. Relevant solvent peaks of $CHCl_3$/$CDCl_3$ and TMS are marked on all spectra where they appear.

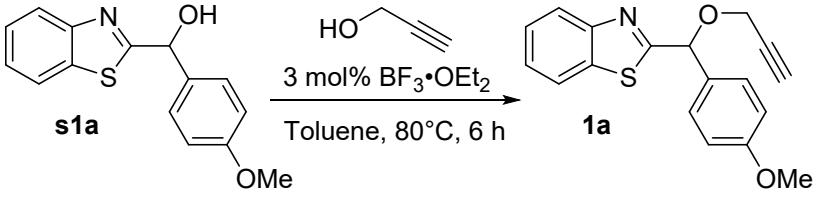
Experimental Procedures

A. Preparation of Secondary Alcohols for substrates 1f, 1h, and 1k:

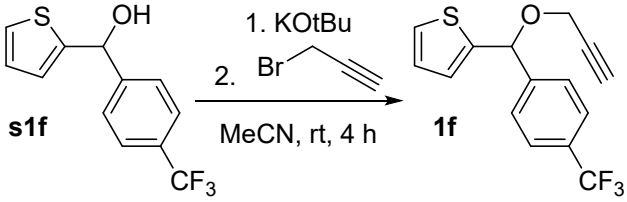


To a dry, argon-filled round-bottom flask at -78°C, THF (20 mL) was added, followed by an aromatic heterocycle (10.0 mmol, 1.0 eq). Then nBuLi (6.88 mL of 1.6 M in hexanes, 11.0 mmol, 1.1 eq) were added dropwise, and the reaction was allowed to stir at -78°C for 1 hour. After this, aromatic aldehyde (11.0 mmol, 1.1 eq) was added and the reaction was allowed to warm to room temperature and left to stir overnight. The reaction was quenched with saturated ammonium chloride and extracted EtOAc (3 times). The organic layers were combined and dried over anhydrous Na_2SO_4. Most of the solvent was evaporated, and the pure product was crystallized from the crude mixture upon addition of excess hexane.

B. Synthesis of Propargyl ethers:



B1: Example used is for the synthesis of 2-[(4-methoxyphenyl)(prop-2-yn-1-yloxy)methyl]-1,3-benzothiazole (**1a**). To a round-bottom flask, toluene (20 mL) and BF_3OEt_2 (0.792 mL, 0.300 mmol, 3 mol%) were added. Then propargyl alcohol (0.896 mL, 12.0 mmol, 1.2 eq) and 1,3-benzothiazol-2-yl(4-methoxyphenyl)methanol (2.71 g, 10.0 mmol, 1.0 eq) were added. The reaction vessel was sealed, heated to 80°C, and left to stir overnight. The reaction mixture was poured directly through a silica plug and flushed with 20% EtOAc in hexanes (500 mL). The solvent was evaporated, and the crude oil was purified by silica gel chromatography with an elution gradient of 1-10% EtOAc/hexanes. Concentration of the desired fractions yielded the propargylated product as a light yellow solid in 67% yield (2.48g).



B2: Example used is for the synthesis of 2-[(prop-2-yn-1-yloxy)[4-(trifluoromethyl)phenyl]methyl]thiophene (**1f**). To a dry, argon-filled round-bottom flask was added ((thiophen-2-yl)[4-(trifluoromethyl)phenyl]methanol (258 mg, 1.0 mmol, 1.0 eq) along with potassium *tert*-butoxide (1.2mL (1M in THF) , 1.2 mmol, 1.2 eq) and acetonitrile (0.5 mL). The reaction mixture

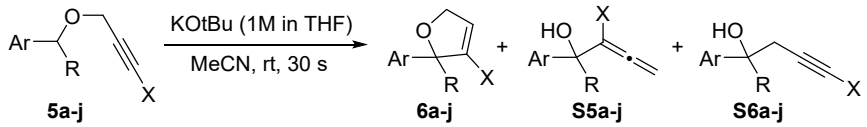
was allowed to stir for 20 minutes at room temperature, then propargyl bromide (0.115 mL, 1.2 mmol, 1.2 eq) was added and the reaction was left to stir at room temperature overnight. The reaction mixture was passed through a silica plug and flushed with 20% EtOAc in hexanes. The solvent was evaporated, and the crude oil was purified by silica gel chromatography with an elution gradient of 1-10% EtOAc/hexanes. Concentration of the desired fractions yielded the propargylated product as a light yellow oil obtained in 46% yield (0.136 g).

C. Synthesis of 2,5-dihydrofurans:

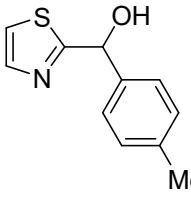
C1: Example used is for the synthesis of 2-[2-(4-methoxyphenyl)-2,5-dihydrofuran-2-yl]-1,3-benzothiazole (**2a**). To a dry, argon-filled round bottom flask containing compound **1a** (309 mg, 1.00 mmol, 1.0eq) was added MeCN (10 mL). Then potassium *tert*-butoxide (0.500 mL of 0.500 mmol, 50 mol%, 1.0 M solution in THF) was added and the reaction was allowed to stir for 30 seconds. The reaction mixture was passed through a silica plug and flushed with 20% EtOAc in hexanes. The solvent was evaporated, and the crude oil was purified by silica gel chromatography with an elution gradient of 0-4% EtOAc/hexanes. Concentration of the desired fractions yielded the cyclic product as a light yellow oil obtained in 49% yield (151 mg).

C2: Example used is for the synthesis of 2-[2-methyl-1-(prop-2-yn-1-yloxy)propyl]-1,3-benzothiazole (**1c**). To a dry, argon-filled round bottom flask, 245mg (1.00 mmol, 1.0 eq) of 2-[2-methyl-1-(prop-2-yn-1-yloxy)propyl]-1,3-benzothiazole (propargyl ether) were added with 10 mL of MeCN. Then 1.20 mL of potassium *tert*-butoxide (1.20 mmol, 1.2 eq, 1.0 M solution in THF) were added and the reaction was allowed to stir for 30 seconds. The reaction mixture was put through a silica plug and flushed with 20% EtOAc in hexanes. The solvent was evaporated, and the crude oil was purified by silica gel chromatography with an elution gradient of 0-4% EtOAc/hexanes. Concentration of the desired fractions yielded the cyclic product as a light yellow oil obtained in 45% yield (123 mg).

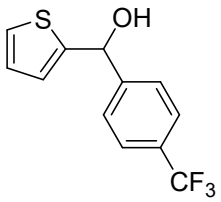
Cyclization of Internal alkynes 5a-e:
While not directly referenced in the publication, internal alkyne substrates in some cases formed the expected allene (**S5**) and quaternary alkyne (**S6**) products. If isolated, these products are reported here.



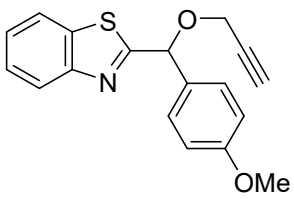
(4-methylphenyl)(1,3-thiazol-2-yl)methanol (s1e): Prepared according to general procedure A. Light yellow solid obtained in 78 % yield (3.20 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 3.3 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 3.3 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.01 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.31, 142.21, 138.66, 138.19, 129.40, 126.57, 119.46, 73.49, 21.26. HRMS (ESI): Calculated for $C_{11}H_{11}NOS$ $[M+H]^+$: 206.0634. Found: 206.0638.



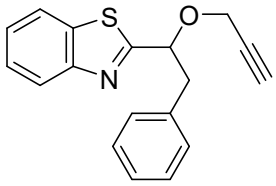
(thiophen-2-yl)[4-(trifluoromethyl)phenyl]methanol (s1f): Prepared according to general procedure A. Light yellow solid obtained in 94 % yield (3.65 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.32 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.98 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.92 (d, *J* = 3.5 Hz, 1H), 6.08 (s, 1H), 2.99 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.13, 146.80, 126.85, 126.55, 126.02, 126.01 – 125.26 (m), 71.64. HRMS (ESI): Calculated for $C_{12}H_9F_3OS$ $[M+H]^+$: 259.0399. Found: 259.0392.



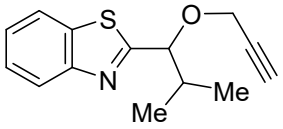
2-[(4-methoxyphenyl)(prop-2-yn-1-yloxy)methyl]-1,3-benzothiazole (1a): Prepared according to general procedure B1. Light yellow solid obtained in 67% yield (2.3 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 1H), 7.89 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.42 – 7.35 (m, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.09 (s, 1H), 4.39 (dd, *J* = 15.9, 2.4 Hz, 1H), 4.25 (dd, *J* = 15.9, 2.4 Hz, 1H), 3.82 (s, 3H), 2.53 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 160.0, 153.1, 135.1, 130.2, 128.9, 126.0, 125.1, 123.3, 121.75, 114.2, 79.6, 78.8, 75.6, 56.2, 55.3. HRMS (ESI): Calculated for $C_{18}H_{15}NO_2S$ $[M+H]^+$: 310.0896. Found: 310.0896.



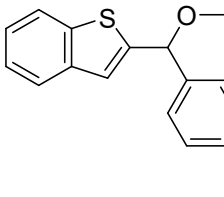
2-[2-phenyl-1-(prop-2-yn-1-yloxy)ethyl]-1,3-benzothiazole (1b): Prepared according to general procedure B2 Light yellow oil obtained in 26% yield (133 mg);). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.46 – 7.40 (m, 1H), 7.32 – 7.23 (m, 5H), 5.24 (dd, *J* = 8.2, 4.9 Hz, 1H), 4.23 (dd, *J* = 15.8, 2.4 Hz, 1H), 4.16 (dd, *J* = 15.8, 2.4 Hz, 1H), 3.35 (dd, *J* = 14.1, 4.9 Hz, 1H), 3.27 (dd, *J* = 14.1, 8.2 Hz, 1H), 2.39 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 153.2, 136.8, 135.0, 129.6, 128.4, 126.8, 126.1, 125.2, 123.2, 121.9, 79.8, 78.8, 75.2, 57.7, 43.1. HRMS (ESI): Calculated for $C_{18}H_{15}NOS$ $[M+H]^+$: 294.0947. Found: 294.0947. Calculated for $[M+Na]^+$: 316.0767. Found: 316.0766.



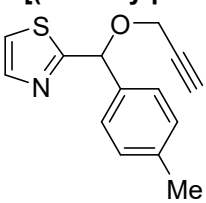
2-[2-methyl-1-(prop-2-yn-1-yloxy)propyl]-1,3-benzothiazole (1c): Prepared according to general procedure B2. Light yellow oil obtained in 45% yield (531mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, J = 8.2, 0.6 Hz, 1H), 7.95 – 7.89 (m, 1H), 7.50 (ddd, J = 8.3, 4.7, 1.1 Hz, 1H), 7.46 – 7.37 (m, 1H), 4.71 (d, J = 6.8 Hz, 1H), 4.38 – 4.29 (m, 1H), 4.19 – 4.11 (m, 1H), 2.46 (td, J = 2.3, 1.0 Hz, 1H), 2.22 (dq, J = 13.5, 6.8 Hz, 1H), 1.11 (d, J = 6.7 Hz, 3H), 0.98 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 153.0, 135.0 , 126.0, 125.2, 123.1, 121.9, 84.0, 79.2, 74.9, 57.6, 34.7, 18.7, 18.3. HRMS (ESI): Calculated for $C_{14}H_{15}NOS$ $[M+H]^+$: 246.0947. Found: 246.0948. Calculated for $[M+Na]^+$: 268.0767. Found: 268.0768.



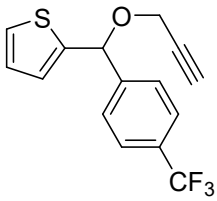
1-benzothiophen-2-yl[4-(trifluoromethyl)phenyl]methyl prop-2-yn-1-yl ether (1d): Prepared according to general procedure B1. Light yellow oil in 92% yield (1.54g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.84 (m, 1H), 7.81 (dd, *J* = 7.0, 1.5 Hz, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.44 – 7.36 (m, 2H), 7.31 (s, 1H), 6.14 (s, 1H), 4.35 (d, *J* = 2.4 Hz, 2H), 2.61 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 144.3 (d, *J* = 1.0 Hz), 140.4, 139.2, 130.4 (q, *J* = 32.4 Hz), 127.4, 125.6 (q, *J* = 3.8 Hz), 124.7, 124.6, 124.2 (q, *J* = 272.1 Hz), 123.9, 123.4, 122.6, 79.0, 77.3, 75.6, 56.1. HRMS (ESI): Calculated for $C_{19}H_{13}F_3OS$ $[M+NH_4]^+$: 364.0977. Found: 364.0982.



2-[(4-methylphenyl)(prop-2-yn-1-yloxy)methyl]-1,3-thiazole (1e): Prepared according to general procedure B2. Light yellow oil obtained in 23% yield (195mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 3.2 Hz, 1H), 7.40 – 7.35 (m, 2H), 7.33 (d, *J* = 3.2 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 2H), 5.99 (s, 1H), 4.34 (dd, *J* = 15.9, 2.4 Hz, 1H), 4.20 (dd, *J* = 15.9, 2.4 Hz, 1H), 2.51 (t, *J* = 2.4 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 142.7, 138.6, 135.5, 129.5, 127.4, 119.5, 79.5, 78.9, 75.4, 56.1, 21.3. HRMS (ESI): Calculated for $C_{14}H_{13}NOS$ $[M+H]^+$: 244.0791. Found: 244.0792. Calculated for $[M+Na]^+$: 266.0610. Found: 266.0613.

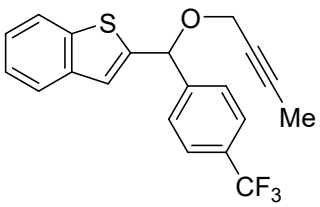


2-{(prop-2-yn-1-yloxy)[4-(trifluoromethyl)phenyl]methyl}thiophene (1f): Prepared according to general procedure B2.



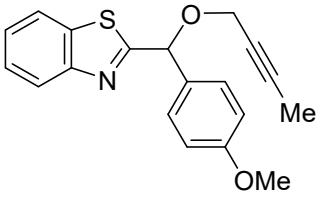
Light yellow oil obtained in 7.5% yield (67mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.37 – 7.33 (m, 1H), 6.99 (dd, *J* = 4.4, 3.1 Hz, 2H), 6.00 (s, 1H), 4.23 (d, *J* = 2.4 Hz, 2H), 2.52 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 144.0, 130.2 (q, *J* = 32.4 Hz), 127.3, 126.7, 126.6, 126.6, 125.5 (q, *J* = 3.7 Hz), 128.4 – 119.8 (m), 79.0, 76.7, 75.3, 55.8. HRMS (ESI): Calculated for $C_{15}H_{11}F_3OS$ $[M+NH_4]^+$: 314.0821. Found: 314.0831.

1-benzothiophen-2-yl[4-(trifluoromethyl)phenyl]methyl but-2-yn-1-yl ether (1g): Prepared according to general procedure B1.



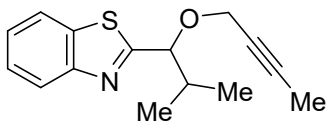
Light yellow oil obtained in 89% yield (1.57g); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 1H), 7.76 – 7.72 (m, 1H), 7.68 – 7.61 (m, 4H), 7.34 (pd, *J* = 7.2, 1.4 Hz, 2H), 7.23 (s, 1H), 6.05 (s, 1H), 4.25 (q, *J* = 2.2 Hz, 2H), 1.92 (t, *J* = 2.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.5, 144.7, 140.4, 139.3, 130.3 (q, *J* = 32.4 Hz), 127.5, 125.6 (q, *J* = 3.7 Hz), 124.7, 124.5, 124.3 (q, *J* = 272.2 Hz), 123.8, 123.1, 122.6, 83.7, 77.2, 74.6, 56.9, 3.7. HRMS (ESI): Calculated for $C_{20}H_{15}F_3OS$ $[M+NH_4]^+$: 378.1134. Found. 378.1141.

2-[(but-2-yn-1-yloxy)(4-methoxyphenyl)methyl]-1,3-benzothiazole (1h): Light yellow oil obtained in 56% yield (709mg);



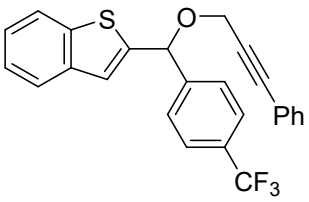
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.1, 0.5 Hz, 1H), 7.93 – 7.87 (m, 1H), 7.51 – 7.44 (m, 3H), 7.42 – 7.36 (m, 1H), 6.96 – 6.89 (m, 2H), 6.08 (s, 1H), 4.38 (dd, *J* = 15.9, 2.4 Hz, 1H), 4.25 (dd, *J* = 15.9, 2.4 Hz, 1H), 3.82 (s, 3H), 2.52 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.96, 159.97, 153.14, 135.09, 130.19, 128.92, 125.98, 125.11, 123.30, 121.75, 114.23, 79.57, 78.77, 77.39, 77.07, 76.76, 75.56, 56.24, 55.31. HRMS (ESI): Calculated for $C_{19}H_{17}NO_2S$ $[M+H]^+$: 324.1053. Found: 324.1061.

2-[1-(but-2-yn-1-yloxy)-2-methylpropyl]-1,3-benzothiazole (1i): Prepared according to general procedure B2.



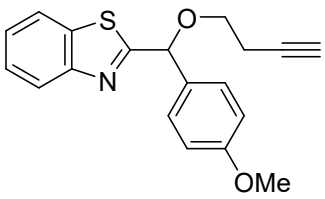
Light yellow oil obtained in 58% yield (733mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (ddd, *J* = 8.2, 1.1, 0.6 Hz, 1H), 7.92 (ddd, *J* = 7.9, 1.2, 0.6 Hz, 1H), 7.50 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.41 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 4.67 (d, *J* = 6.8 Hz, 1H), 4.28 (dq, *J* = 15.3, 2.3 Hz, 1H), 4.12 (dq, *J* = 15.3, 2.3 Hz, 1H), 2.28 – 2.15 (m, 1H), 1.84 (t, *J* = 2.3 Hz, 3H), 1.11 (d, *J* = 6.7 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 153.1, 135.0, 125.9, 125.0, 123.0, 121.8, 83.8, 83.0, 74.6, 58.3, 34.7, 18.7, 18.3, 3.6. HRMS (ESI): Calculated for $C_{15}H_{17}NOS$ $[M+H]^+$: 260.1104. Found: 260.1101.

1-benzothiophen-2-yl[4-(trifluoromethyl)phenyl]methyl 3-phenylprop-2-yn-1-yl ether (1j): Prepared according to general procedure B1.



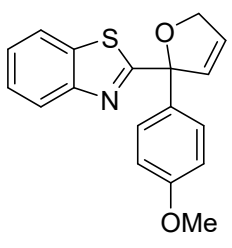
Light yellow oil obtained in 95% yield (402mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.82 (m, 1H), 7.78 – 7.75 (m, 1H), 7.69 (s, 4H), 7.50 – 7.47 (m, 2H), 7.40 – 7.33 (m, 5H), 7.28 (s, *J* = 3.2 Hz, 1H), 6.16 (s, 1H), 4.54 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 144.5, 140.4, 139.2, 131.9, 130.4 (q, *J* = 32.4 Hz), 128.8, 128.5, 127.5, 125.6 (dd, *J* = 7.6, 3.8 Hz), 124.7, 124.5, 128.3 – 120.0 (m), 123.8, 123.3, 122.6, 122.5, 87.4, 84.4, 77.6, 57.1. HRMS (ESI): Calculated for $C_{25}H_{17}F_3OS$ $[M+H]^+$: 423.1025. Found: 423.1011. Calculated for $[M+NH_4]^+$: 440.1290. Found: 440.1285.

2-[(but-3-yn-1-yloxy)(4-methoxyphenyl)methyl]-1,3-benzothiazole (7): Prepared according to general procedure B1.



Light yellow oil obtained in 25% yield (308mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.98 (m, 1H), 7.91 – 7.86 (m, 1H), 7.49 – 7.44 (m, 3H), 7.38 (td, *J* = 7.7, 1.2 Hz, 1H), 6.94 – 6.90 (m, 2H), 5.81 (s, 1H), 3.82 (d, *J* = 5.7 Hz, 3H), 3.79 – 3.73 (m, 2H), 2.61 (tdd, *J* = 7.1, 2.7, 0.7 Hz, 2H), 2.02 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.89 (s), 159.78 (s), 153.11 (s), 135.17 (s), 131.10 (s), 128.37 (s), 125.94 (s), 125.08 (s), 123.23 (s), 121.79 (s), 114.14 (s), 81.64 (s), 80.84 (s), 69.70 (s), 67.63 (s), 55.30 (s), 19.97 (s). HRMS (ESI): Calculated for $C_{19}H_{17}NO_2S$ $[M+H]^+$: 324.1053. Found: 324.1056

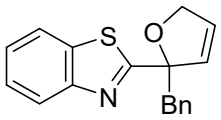
2-[2-(4-methoxyphenyl)-2,5-dihydrofuran-2-yl]-1,3-benzothiazole (2a): Light yellow oil obtained in 49% yield (152mg);



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (ddd, *J* = 8.2, 1.0, 0.6 Hz, 1H), 7.91 (ddd, *J* = 7.9, 1.2, 0.6 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.48 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1H), 7.38 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 6.95 – 6.89 (m, 2H), 6.53 (dt, *J* = 6.0, 2.5 Hz, 1H), 6.13 (dt, *J* = 6.0, 1.6 Hz, 1H), 5.05 – 4.94 (m, 2H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 159.4, 154.1, 135.1, 134.6, 131.3, 127.34, 127.25, 125.9,

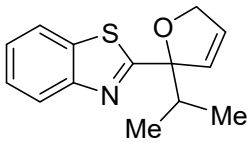
124.9, 123.2, 121.7, 113.9, 94.1, 76.0, 55.3. HRMS (ESI): Calculated for $C_{18}H_{15}NO_2S$ [M+H]$^+$: 310.0896. Found: 310.0896.

2-(2-Benzyl-2,5-dihydro-2-furyl)-1,3-benzothiazole (2b): Prepared according to general procedure B2 (42% yield, amber oil).

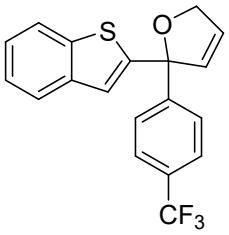


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.38 (d, *J* = 7.1 Hz, 1H), 7.32 – 7.20 (m, 5H), 6.11 (dt, *J* = 5.9, 2.4 Hz, 1H), 5.82 (dt, *J* = 6.0, 1.5 Hz, 1H), 4.85 – 4.79 (m, 1H), 4.54 – 4.49 (m, 1H), 3.56 (d, *J* = 13.9 Hz, 1H), 3.51 (d, *J* = 13.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1 (s), 154.1 (s), 136.2 (s), 135.1 (s), 130.8 (s), 130.5 (s), 127.7 (s), 127.8, 126.5 (s), 125.9 (s), 124.8 (s), 122.9 (s), 121.9 (s), 94.5 (s), 76.4 (s), 45.6 (s). HRMS (ESI): Calculated for $C_{18}H_{15}NOS$ [M+H]$^+$: 294.0947. Found: 294.0948. Calculated for [M+Na]$^+$: 316.0767. Found: 316.0771.

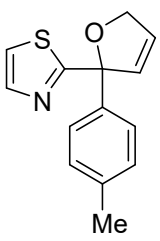
2-[2-(propan-2-yl)-2,5-dihydrofuran-2-yl]-1,3-benzothiazole (2c): Light yellow oil obtained in 24% yield (59 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (ddd, *J* = 8.2, 1.1, 0.6 Hz, 1H), 7.89 (ddd, *J* = 7.9, 1.2, 0.6 Hz, 1H), 7.47 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.42 – 7.34 (m, 1H), 6.07 (dt, *J* = 6.1, 2.4 Hz, 1H), 5.99 (dt, *J* = 6.1, 1.6 Hz, 1H), 4.93 (ddd, *J* = 13.1, 2.4, 1.6 Hz, 1H), 4.83 (ddd, *J* = 13.1, 2.4, 1.6 Hz, 1H), 2.64 (hept, *J* = 6.8 Hz, 1H), 1.03 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.7 , 154.2 , 134.8 , 130.7 , 126.9, 125.8, 124.6, 122.8, 121.7, 97.3, 36.4, 17.2, 16.8. HRMS (ESI): Calculated for $C_{14}H_{15}NOS$ [M+H]$^+$: 246.0947. Found. Calculated for [M+H]$^+$: 246.0958



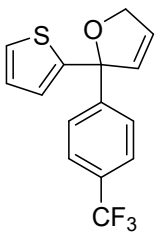
2-(1-benzothiophen-2-yl)-2-[4-(trifluoromethyl)phenyl]-2,5-dihydrofuran (2d): Light yellow oil obtained in 49% yield (93 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.79 (m, 1H), 7.72 – 7.69 (m, 1H), 7.66 (s, 4H), 7.37 – 7.29 (m, 2H), 7.01 (d, *J* = 0.6 Hz, 1H), 6.35 (dt, *J* = 6.0, 2.4 Hz, 1H), 6.19 (dt, *J* = 6.0, 1.6 Hz, 1H), 5.00 (ddd, *J* = 13.3, 2.4, 1.7 Hz, 1H), 4.89 (ddd, *J* = 13.3, 2.4, 1.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1 , 147.8 , 140.1 , 139.5, 131.5, 129.9 (q, *J* = 32.4 Hz), 127.9, 126.4, 125.4 (q, *J* = 3.7 Hz), 124.5, 124.4, 124.2 (q, *J* = 272.2 Hz), 123.8, 122.4, 121.5, 92.1, 75.5. HRMS (ESI): Calculated for $C_{19}H_{13}F_3OS$ [M+H]$^+$: 347.07. Found. 347.0701



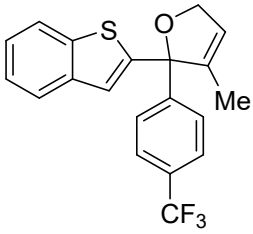
2-[2-(4-methylphenyl)-2,5-dihydrofuran-2-yl]-1,3-Thiazol 2e: Light yellow oil obtained in 35% yield (86 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 3.3 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 3.3 Hz, 1H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.48 – 6.42 (m, 1H), 6.08 (dt, *J* = 6.0, 1.6 Hz, 1H), 4.99 (ddd, *J* = 13.1, 2.4, 1.7 Hz, 1H), 4.94 (ddd, *J* = 13.1, 2.4, 1.7 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 143.2, 140.0, 137.6, 131.7, 129.1, 126.7, 125.7, 119.0, 93.9, 75.8, 21.1. HRMS (ESI): Calculated for $C_{14}H_{13}NOS$ [M+H]$^+$: 244.08. Found. 244.0802



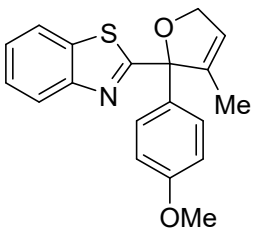
2-(thiophen-2-yl)-2-[4-(trifluoromethyl)phenyl]-2,5-dihydrofuran (2f): Light yellow oil obtained in 39% yield (47 mg); ^{1}H NMR (400 MHz, CDCl3) δ 7.65 – 7.59 (m, 4H), 7.30 (dt, *J* = 4.0, 2.0 Hz, 1H), 6.96 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.76 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.29 (dt, *J* = 6.0, 2.5 Hz, 1H), 6.14 (dt, *J* = 6.0, 1.6 Hz, 1H), 4.95 (ddd, *J* = 13.3, 2.4, 1.7 Hz, 1H), 4.84 (ddd, *J* = 13.3, 2.4, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 148.3, 131.9, 129.7 (q, *J* = 32.4 Hz), 127.4, 126.8, 126.2, 125.8, 125.2 (q, *J* = 3.8 Hz), 125.0, 124.5 (dd, *J* = 620.0, 311.3 Hz), 91.7, 75.1. HRMS (ESI): Calculated for $C_{15}H_{11}F_3OS$ [M+NH^4]$^+$: 314.08. Found. 314.0831



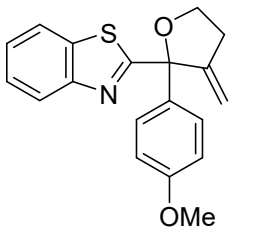
2-(1-benzothiophen-2-yl)-3-methyl-2-[4-(trifluoromethyl)phenyl]-2,5-dihydrofuran (2g): Prepared according to general procedure C1. Light yellow oil obtained in 46% yield (460 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.83 (m, 1H), 7.76 – 7.72 (m, 1H), 7.68 (s, 4H), 7.41 – 7.32 (m, 2H), 7.09 (d, *J* = 0.6 Hz, 1H), 5.88 (dd, *J* = 3.2, 1.6 Hz, 1H), 4.91 – 4.79 (m, 2H), 1.88 (dd, *J* = 3.8, 2.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 146.1, 140.0, 139.7, 139.3, 130.1 (q, *J* = 32.3 Hz), 127.5, 125.1 (d, *J* = 3.6 Hz), 124.5, 124.3, 124.2 (dd, *J* = 545.1, 272.9 Hz), 123.9, 123.8, 122.4, 122.2, 93.4, 73.8, 13.5. HRMS (ESI): Calculated for $C_{20}H_{15}F_3OS$ [M+H]$^+$: 361.0868. Found: 361.0859.



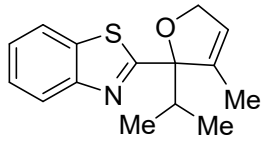
2-[2-(4-methoxyphenyl)-3-methyl-2,5-dihydrofuran-2-yl]-1,3-benzothiazole (2h): Light yellow oil obtained in 46% yield (82 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.05 (m, 1H), 7.94 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.46 – 7.37 (m, 3H), 6.93 – 6.87 (m, 2H), 5.77 (d, *J* = 1.6 Hz, 1H), 4.92 (d, *J* = 1.6 Hz, 2H), 3.82 (d, *J* = 5.6 Hz, 3H), 2.00 – 1.95 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.94 (s), 159.49 (s), 154.30 (s), 139.72 (s), 135.13 (s), 133.05 (s), 128.35 (s), 125.75 (s), 124.79 (s), 123.35 (s), 122.34 (s), 121.67 (s), 113.77 (s), 94.92 (s), 77.40 (s), 77.08 (s), 76.76 (s), 74.50 (s), 55.33 (s), 12.93 (s). HRMS (ESI): Calculated for $C_{19}H_{17}NO_2S$ $[M+H]^+$: 324.1053. Found: 324.1061.



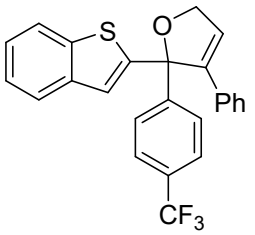
2-[2-(4-methoxyphenyl)-3-methylideneoxolan-2-yl]-1,3-benzothiazole (iso-2h): Prepared according to general procedure C2. Light yellow oil obtained in 23% yield (72 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 5.8, 2.4 Hz, 1H), 7.90 (dd, *J* = 7.9, 0.6 Hz, 1H), 7.59 – 7.53 (m, 2H), 7.46 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1H), 7.40 – 7.35 (m, 1H), 6.93 – 6.88 (m, 2H), 5.48 (t, *J* = 2.3 Hz, 1H), 5.41 (t, *J* = 2.1 Hz, 1H), 4.28 – 4.20 (m, 1H), 4.16 (td, *J* = 8.1, 6.5 Hz, 1H), 3.82 (s, 3H), 2.90 – 2.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.27 (s), 159.36 (s), 154.05 (s), 149.86 (s), 135.38 (s), 133.68 (s), 128.11 (s), 125.72 (s), 124.87 (s), 123.48 (s), 121.62 (s), 113.61 (s), 111.14 (s), 88.14 (s), 66.51 (s), 55.28 (s), 33.12 (s). HRMS (ESI): Calculated for $C_{19}H_{17}NO_2S$ $[M+H]^+$: 324.1053. Found: 324.1060. Calculated for $[M+Na]^+$: 346.0872. Found: 346.0876.



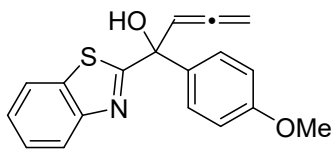
2-[3-methyl-2-(propan-2-yl)-2,5-dihydrofuran-2-yl]-1,3-benzothiazole (2i): Prepared according to general procedure C2. Light yellow oil obtained in 24% yield (59mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.89 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.47 (ddd, *J* = 8.3, 7.3, 1.3 Hz, 1H), 7.36 (ddd, *J* = 8.3, 7.3, 1.1 Hz, 1H), 5.57 (dd, *J* = 3.1, 1.6 Hz, 1H), 4.95 – 4.88 (m, 1H), 4.79 – 4.72 (m, 1H), 2.83 – 2.71 (m, 1H), 1.91 (dd, *J* = 3.8, 2.1 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 154.4, 138.6, 135.0, 125.6, 124.4, 122.9, 121.7, 121.2, 97.5, 75.4, 33.6, 17.0, 16.1, 12.0. HRMS (ESI): Calculated for $C_{15}H_{17}NOS$ $[M+H]^+$: 260.1104. Found: 260.1101.



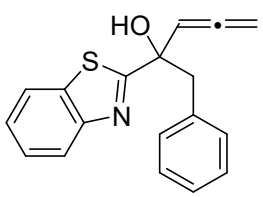
2-(1-benzothiophen-2-yl)-3-phenyl-2-[4-(trifluoromethyl)phenyl]-2,5-dihydrofuran (2j): Prepared according to general procedure C1. Light yellow oil obtained in 27.5% yield (96.1mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 1H), 7.70 – 7.60 (m, 5H), 7.38 – 7.32 (m, 2H), 7.30 – 7.23 (m, 3H), 7.19 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.01 (s, *J* = 6.9 Hz, 1H), 6.45 (t, *J* = 1.8 Hz, 1H), 5.04 (dd, *J* = 13.9, 1.9 Hz, 1H), 4.95 (dd, *J* = 13.9, 1.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 146.3, 143.9, 140.2, 139.4, 133.3, 130.2 (q, *J* = 32.4 Hz), 128.5, 128.3, 128.0, 127.9, 126.2 (dd, *J* = 410.7, 228.4 Hz), 126.1, 125.1 (q, *J* = 3.7 Hz), 124.6, 124.3, 123.9, 123.1, 122.4, 92.7, 73.6. HRMS (ESI): Calculated for $C_{25}H_{17}F_3OS$ $[M+H]^+$: 423.1025. Found: 423.1007.



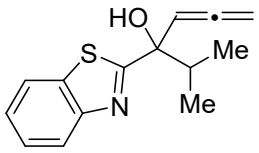
1-(1,3-benzothiazol-2-yl)-1-(4-methoxyphenyl)buta-2,3-dien-1-ol (3a): Light yellow oil obtained in 35% yield (109 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.02 (m, 1H), 7.87 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.48 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 1H), 7.42 – 7.35 (m, 1H), 6.94 – 6.88 (m, 2H), 6.23 (t, *J* = 6.6 Hz, 1H), 5.04 (d, *J* = 6.6 Hz, 2H), 4.19 – 4.13 (m, 1H), 3.84 – 3.80 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.9, 177.5, 159.4, 153.0, 135.64, 135.62, 127.7, 126.0, 125.1, 123.3, 121.7, 113.7, 98.8, 81.0, 76.76, 55.0. HRMS (ESI): Calculated for $C_{18}H_{15}NO_2S$ $[M+H]^+$: 310.0896. Found: 310.0900. Calculated for $[M+Na]^+$: 332.0716. Found: 332.0721.



3-(1,3-benzothiazol-2-yl)-2-methylhexa-4,5-dien-3-ol (3b): Prepared according to general procedure C2. Light yellow oil obtained in 22% yield (mg); δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.92 – 7.88 (m, 1H), 7.54 – 7.48 (m, 1H), 7.44 – 7.37 (m, 1H), 7.27 – 7.19 (m, 5H), 5.87 (t, *J* = 6.6 Hz, 1H), 5.02 (dd, *J* = 11.1, 6.6 Hz, 1H), 4.93 (dd, *J* = 11.1, 6.6 Hz, 1H), 3.52 (d, *J* = 13.6 Hz, 1H), 3.42 (d, *J* = 13.6 Hz, 1H), 3.12 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.5 (s), 177.4 (s), 153.3 (s), 135.3 (s), 135.2 (s), 130.9 (s), 128.1 (s), 127.0 (s), 126.0 (s), 124.9 (s), 123.0 (s), 121.8 (s), 97.8 (s), 81.0 (s), 75.7 (s), 47.9 (s). HRMS (ESI): Calculated for $C_{18}H_{15}NOS$ $[M+H]^+$: 294.0947. Found: 294.0958.

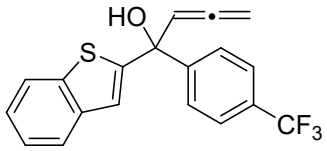


3-(1,3-benzothiazol-2-yl)-2-methylhexa-4,5-dien-3-ol (3c):



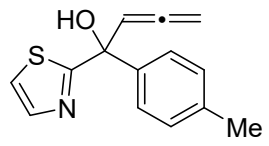
Prepared according to general procedure C2. Light Yellow oil obtained in 25% yield (69mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.2, 0.5 Hz, 1H), 7.91 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.49 (ddd, *J* = 8.4, 2.0, 1.0 Hz, 1H), 7.40 (dt, *J* = 14.1, 4.1 Hz, 1H), 5.82 (t, *J* = 6.6 Hz, 1H), 5.11 (qdd, *J* = 11.0, 6.6, 0.8 Hz, 2H), 3.19 (s, 1H), 2.45 (dt, *J* = 13.6, 6.8 Hz, 1H), 1.11 (d, *J* = 6.8 Hz, 3H), 0.93 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.80, 178.39, 153.23, 135.19, 125.92, 124.83, 122.92, 121.73, 98.01, 38.32, 16.75 (d, *J* = 5.0 Hz). HRMS (ESI): Calculated for $C_{14}H_{15}NOS$ $[M+H]^+$: 246.0947. Found: 246.0958.

1-(1-benzothiophen-2-yl)-1-[4-(trifluoromethyl)phenyl]buta-2,3-dien-1-ol (3d): Prepared according to general procedure



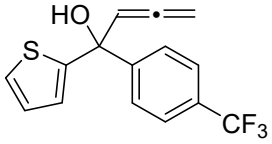
C1. Light yellow oil obtained in 36% yield (93mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.78 (m, 1H), 7.73 (dd, *J* = 12.3, 5.0 Hz, 3H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.36 (pd, *J* = 7.1, 1.4 Hz, 2H), 7.22 (s, 1H), 6.04 (t, *J* = 6.6 Hz, 1H), 5.11 (d, *J* = 6.6 Hz, 2H), 3.04 (s, *J* = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.8 , 151.1, 148.4, 140.0, 139.2, 129.9 (q, *J* = 32.5 Hz), 126.6, 125.2 (q, *J* = 3.7 Hz), 124.7, 124.5, 124.1 (q, *J* = 272.2 Hz), 123.9, 122.4, 122.1, 99.4, 81.5, 75.3. HRMS (ESI): Calculated for $C_{19}H_{13}F_3OS$ $[M+NH_4]^+$: 364.0977. Found:364.0990.

1-(4-methylphenyl)-1-(1,3-thiazol-2-yl)buta-2,3-dien-1-ol (3e): Prepared according to general procedure C1. Light yellow



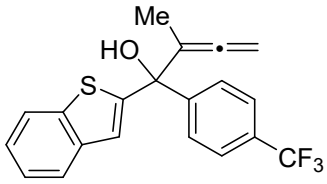
oil obtained in 37% yield (94mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 3.2 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.29 (d, *J* = 3.3 Hz, 1H), 7.19 (dd, *J* = 8.5, 0.6 Hz, 2H), 6.14 (t, *J* = 6.6 Hz, 1H), 5.04 (dd, *J* = 8.5, 4.0 Hz, 1H), 5.00 (dd, *J* = 8.5, 3.9 Hz, 1H), 3.85 (s, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.6, 176.5, 142.4, 141.0, 137.8, 129.0, 126.0, 119.6, 99.1, 80.9, 76.5, 21.1. HRMS (ESI): HRMS (ESI): Calculated for $C_{14}H_{13}NOS$ $[M+H]^+$: 224.1070. Found: 246.0956.

1-(thiophen-2-yl)-1-[4-(trifluoromethyl)phenyl]buta-2,3-dien-1-ol (3f): Prepared according to general procedure C1.



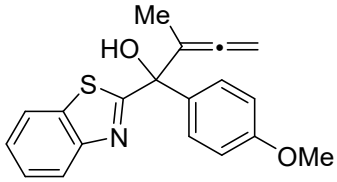
Light yellow oil obtained in 32% yield (39mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.31 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.01 – 6.94 (m, 2H), 5.98 (t, *J* = 6.6 Hz, 1H), 5.07 (d, *J* = 6.6 Hz, 2H), 2.92 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.7, 150.7, 149.1, 129.7 (q, *J* = 32.4 Hz), 126.7, 126.5, 125.9, 125.6, 125.1 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.1 Hz), 99.9, 81.3, 74.9. HRMS (ESI): Calculated for $C_{15}H_{11}F_3OS$ $[M+H]^+$: 297.06. Found. 297.0564

1-(1-benzothiophen-2-yl)-2-methyl-1-[4-(trifluoromethyl)phenyl]buta-2,3-dien-1-ol (3g): Light yellow oil obtained in



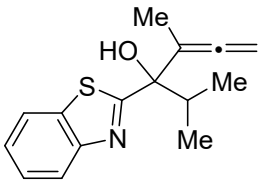
50% yield (500mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.78 (m, 1H), 7.73 (dd, *J* = 12.3, 5.0 Hz, 3H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.36 (pd, *J* = 7.1, 1.4 Hz, 2H), 7.22 (s, 1H), 6.04 (t, *J* = 6.6 Hz, 1H), 5.11 (d, *J* = 6.6 Hz, 2H), 3.04 (s, *J* = 2.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.8 , 151.1, 148.4, 140.0, 139.2, 129.9 (q, *J* = 32.5 Hz), 126.6, 125.2 (q, *J* = 3.7 Hz), 124.7, 124.5, 124.1 (q, *J* = 272.2 Hz), 123.9, 122.4, 122.1, 99.4, 81.5, 75.3. HRMS (ESI): Calculated for $C_{20}H_{15}F_3OS$ $[M+NH_4]^+$: 378.1134. Found. 378.1134

1-(1,3-benzothiazol-2-yl)-1-(4-methoxyphenyl)-2-methylbuta-2,3-dien-1-ol (3h): Light yellow solid obtained in 36% yield

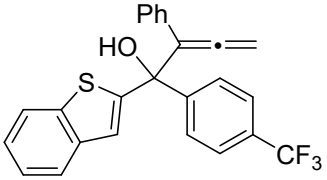


(87mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 1H), 7.83 (ddd, *J* = 8.0, 1.1, 0.6 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.49 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1H), 7.40 – 7.34 (m, 1H), 6.98 – 6.91 (m, 2H), 4.70 (dd, *J* = 6.3, 3.1 Hz, 2H), 4.48 (s, 1H), 3.84 (s, 3H), 1.87 (t, *J* = 3.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.94 (s), 159.49 (s), 154.30 (s), 139.72 (s), 135.13 (s), 133.05 (s), 128.35 (s), 125.75 (s), 124.79 (s), 123.35 (s), 122.34 (s), 121.67 (s), 113.77 (s), 94.92 (s), 77.40 (s), 77.08 (s), 76.76 (s), 74.50 (s), 55.33 (s), 12.93 (s). HRMS (ESI): Calculated for $C_{19}H_{17}NO_2S$ $[M+H]^+$: 324.1053. Found: 324.1061.

2-(2,3,4-trimethylhexa-4,5-dien-3-yl)-1,3-benzothiazole (3i): Prepared according to general procedure C2. Light yellow

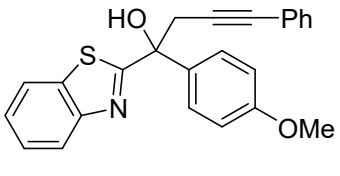


oil obtained in 16% yield (39mg);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.99 (m, 2H), 7.92 – 7.87 (m, 2H), 7.51 – 7.44 (m, 2H), 7.41 – 7.34 (m, 2H), 5.10 – 4.99 (m, 2H), 3.52 (s, 1H), 2.73 – 2.64 (m, 1H), 1.87 (t, *J* = 3.1 Hz, 3H), 1.09 (d, *J* = 6.7 Hz, 3H), 0.87 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.9, 178.1, 152.9, 135.6, 125.8, 124.8, 122.9, 121.7, 105.3, 80.0, 79.3, 34.8, 16.7, 16.5, 14.5. HRMS (ESI): Calculated for $C_{15}H_{17}NOS$ $[M+H]^+$: 260.1104. Found: 260.1101.

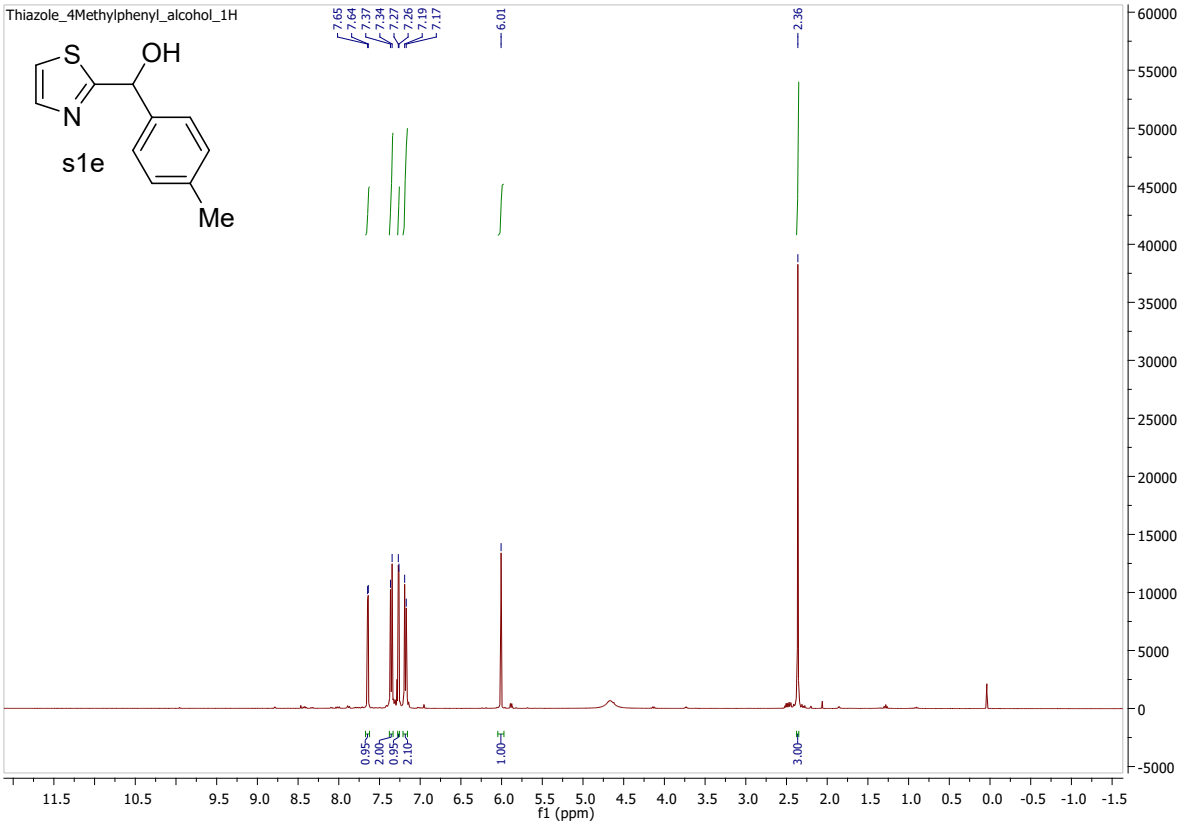


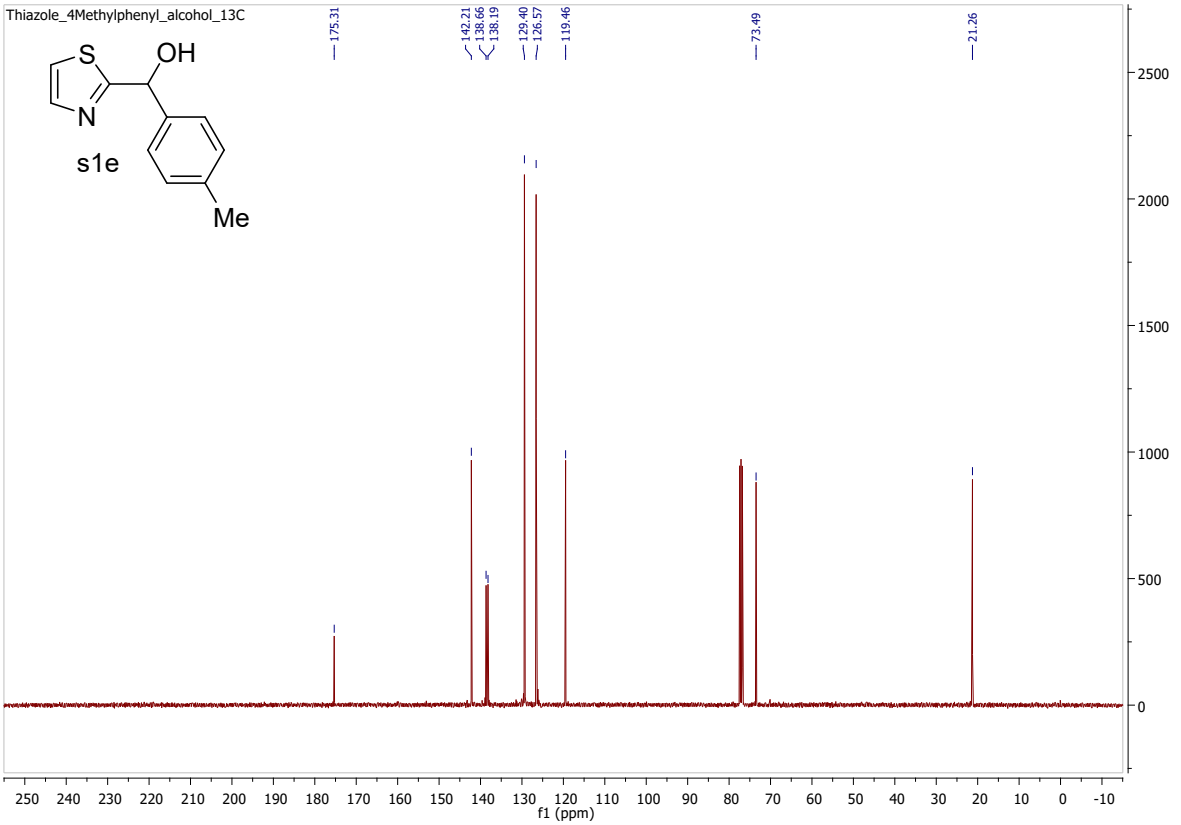
1-(1-benzothiophen-2-yl)-2-phenyl-1-[4-(trifluoromethyl)phenyl]buta-2,3-dien-1-ol (3j): Prepared according to general procedure C1. Light yellow oil obtained in 8% yield (27 mg);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (t, *J* = 8.1 Hz, 1H), 7.80 – 7.74 (m, 2H), 7.74 – 7.71 (m, 1H),

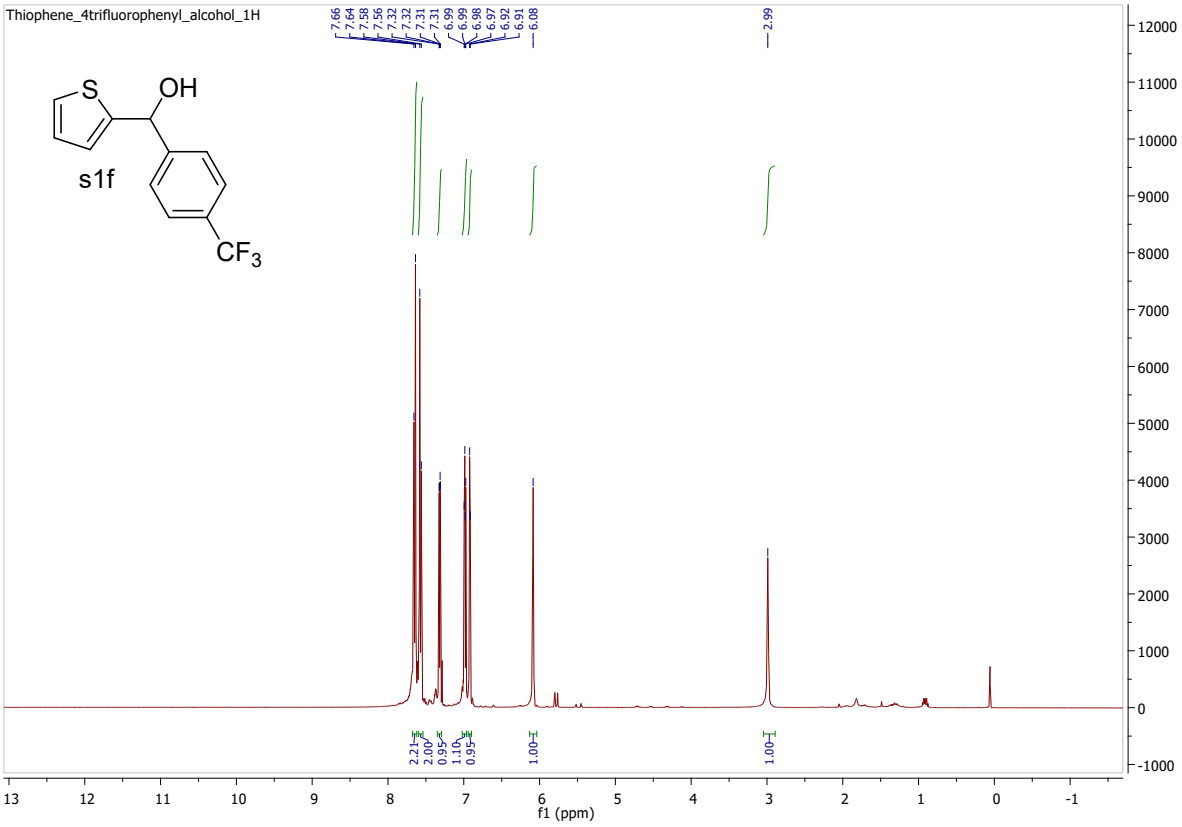
7.67 (d, *J* = 8.5 Hz, 2H), 7.41 – 7.25 (m, 7H), 7.13 (s, 1H), 5.03 (d, *J* = 12.5 Hz, 1H), 4.98 (d, *J* = 12.5 Hz, 1H), 3.30 (br s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.2, 151.2, 148.4, 140.2, 139.3, 133.3, 130.0 (q, *J* = 32.4 Hz), 128.5, 128.4, 127.7, 126.3, 125.1 (dd, *J* = 7.4, 3.7 Hz), 124.6, 124.4, 124.1 (q, *J* = 272.2 Hz), 123.9 (s, *J* = 1.3 Hz), 122.6, 122.4, 112.4, 85.5, 79.3. HRMS (ESI): Calculated for $C_{25}H_{17}F_3OS$ $[M+NH_4]^+$: 440.1290. Found: 440.1305.

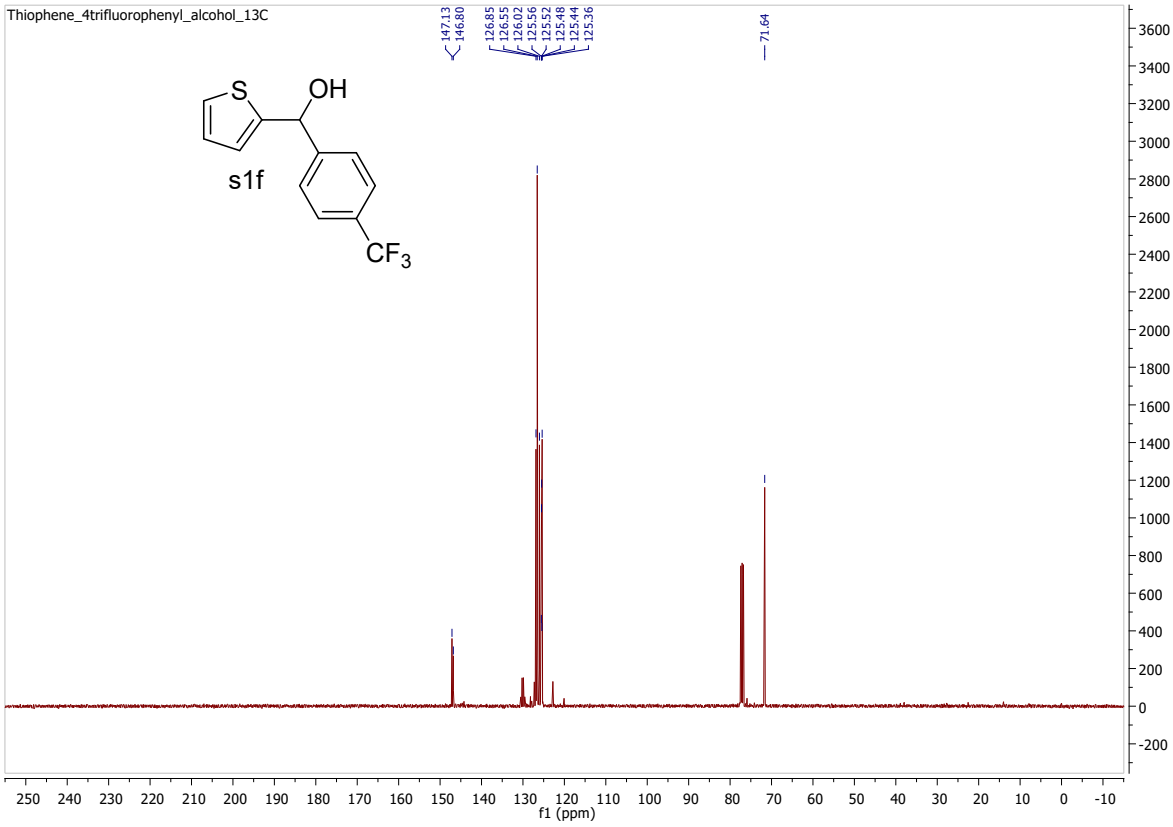
1-(1-benzothiophen-2-yl)-4-phenyl-1-[4-(trifluoromethyl)phenyl]but-3-yn-1-ol (4j): Light yellow oil obtained in 11.6% yield (40.5 mg). 

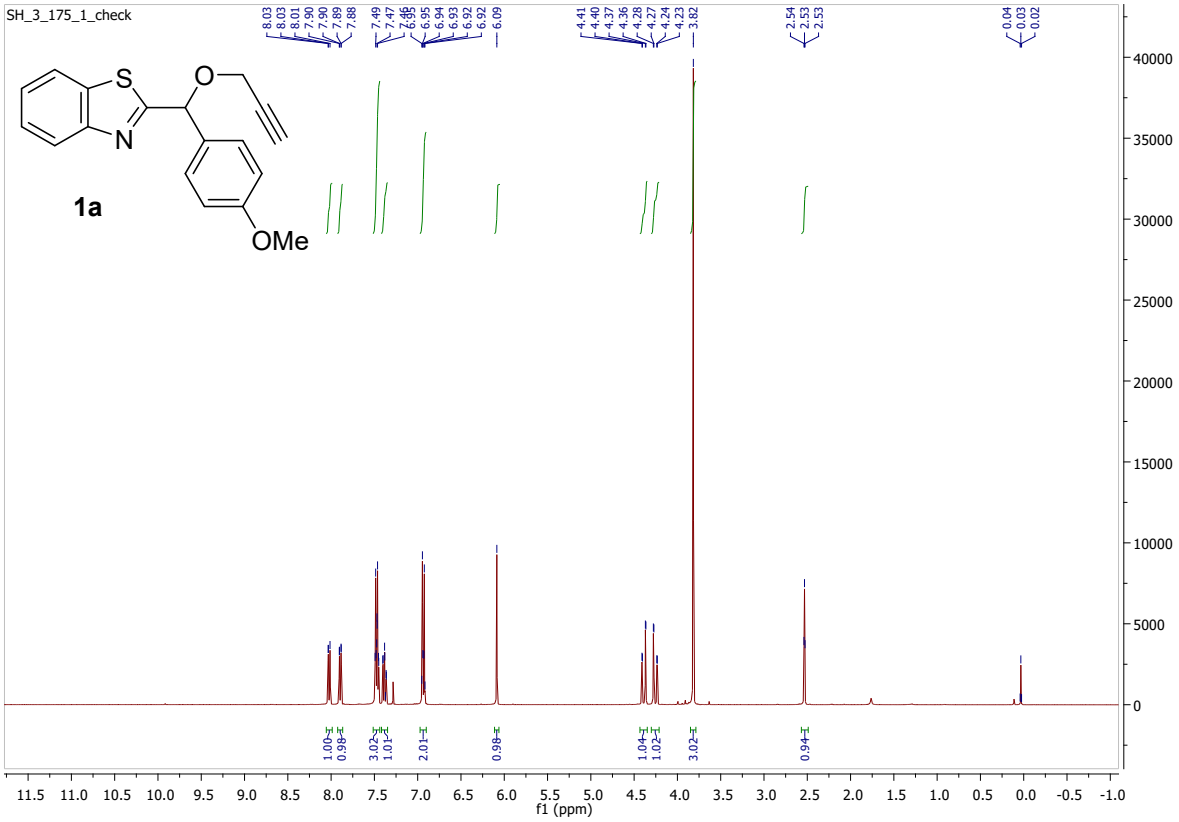
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (t, *J* = 8.1 Hz, 1H), 7.80 – 7.74 (m, 3H), 7.66 (t, *J* = 8.4 Hz, 2H), 7.41 – 7.25 (m, 8H), 3.57 (d, *J* = 16.9 Hz, 1H), 3.46 (d, *J* = 16.9 Hz, 1H), 3.44 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2 (s), 148.2 (s), 139.9 (s), 139.3 (s), 131.8 (s), 130.0 (q, *J* = 32.4 Hz), 128.8 (s), 128.6 (s), 127.4 (s), 126.3 (s), 125.3 (dd, *J* = 7.4, 3.7 Hz), 124.7 (s), 124.5 (s), 124.1 (q, *J* = 272.2 Hz), 123.9 (s, *J* = 1.3 Hz), 122.4 (s), 121.6 (s), 84.1 (s), 80.2 (s), 76.3 (s), 35.5 (s). HRMS (ESI): Calculated for $C_{25}H_{17}F_3OS$ $[M+NH_4]^+$: 440.1290. Found: 440.1305.

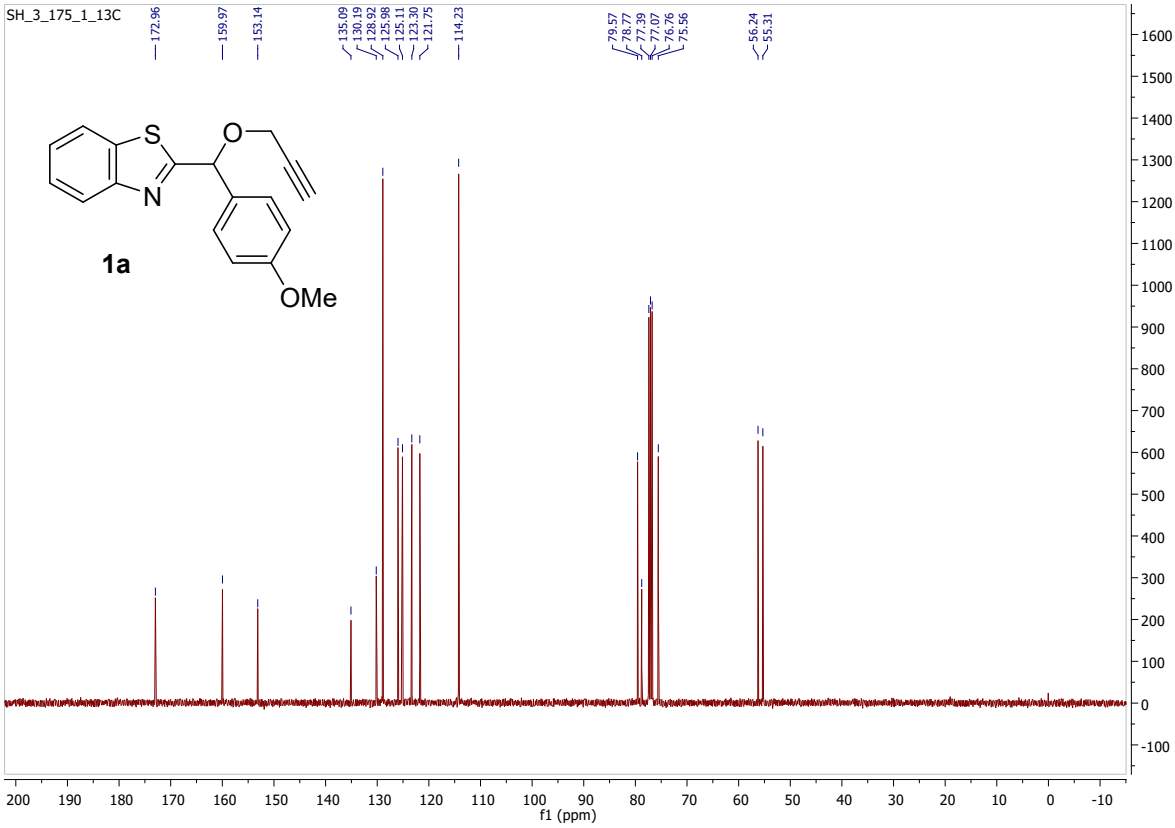

Thiazole_4Methylphenyl_alcohol_1H
S
OH
N
s1e
Me
7.65
7.64
7.37
7.34
7.27
7.26
7.19
7.17
6.01
2.36
0.95
2.00
0.95
2.10
1.00
3.00
f1 (ppm)


Thiazole_4Methylphenyl_alcohol_13C
S
OH
N
s1e
Me
175.31
142.21
138.66
138.19
129.40
126.57
119.46
73.49
21.26
f1 (ppm)


Thiophene_4trifluorophenyl_alcohol_1H
7.66
7.64
7.58
7.56
7.32
7.32
7.31
7.31
6.99
6.99
6.98
6.97
6.92
6.91
6.08
2.99
S
OH
s1f
CF3
2.21
2.00
0.95
1.10
0.95
1.00
1.00
f1 (ppm)


Thiophene_4trifluorophenyl_alcohol_13C
147.13
146.80
126.85
126.55
126.02
125.56
125.52
125.48
125.44
125.36
71.64
S
OH
s1f
CF3
f1 (ppm)


SH_3_175_1_check
1a
OMe
f1 (ppm)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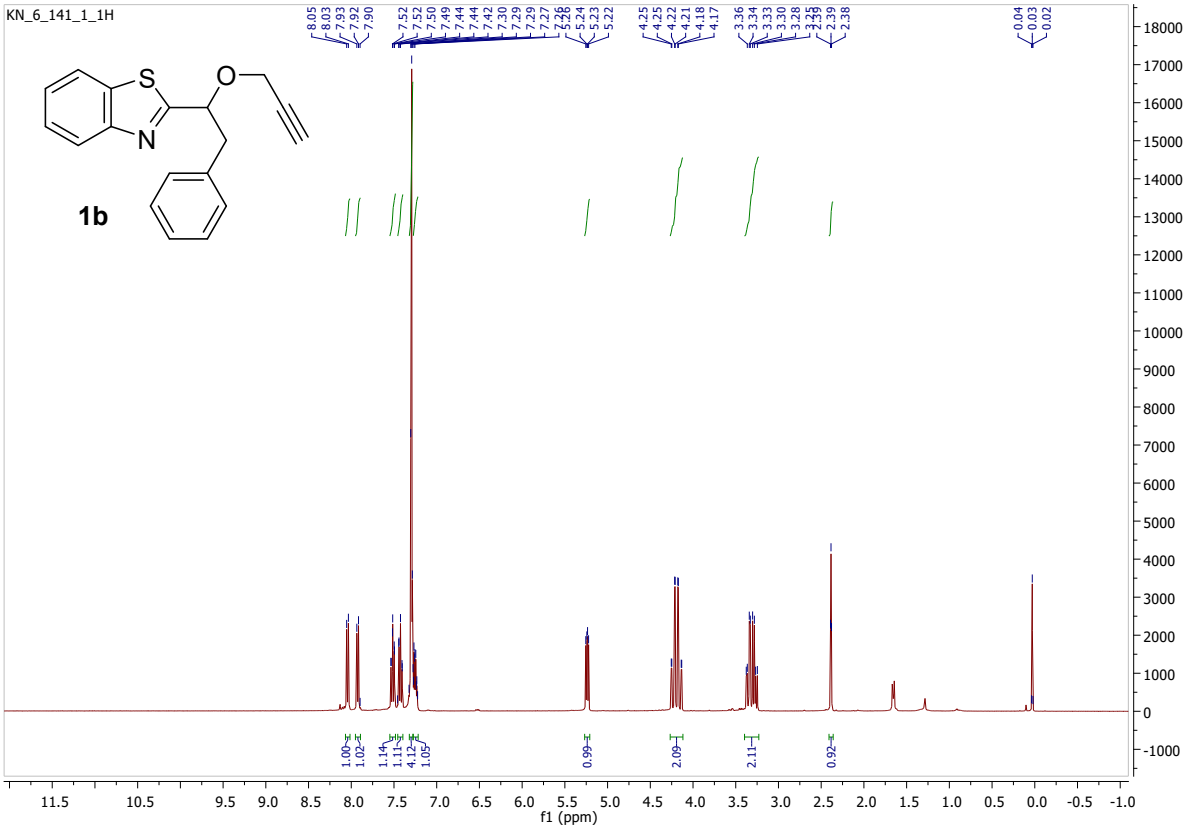
1a
OMe
f1 (ppm)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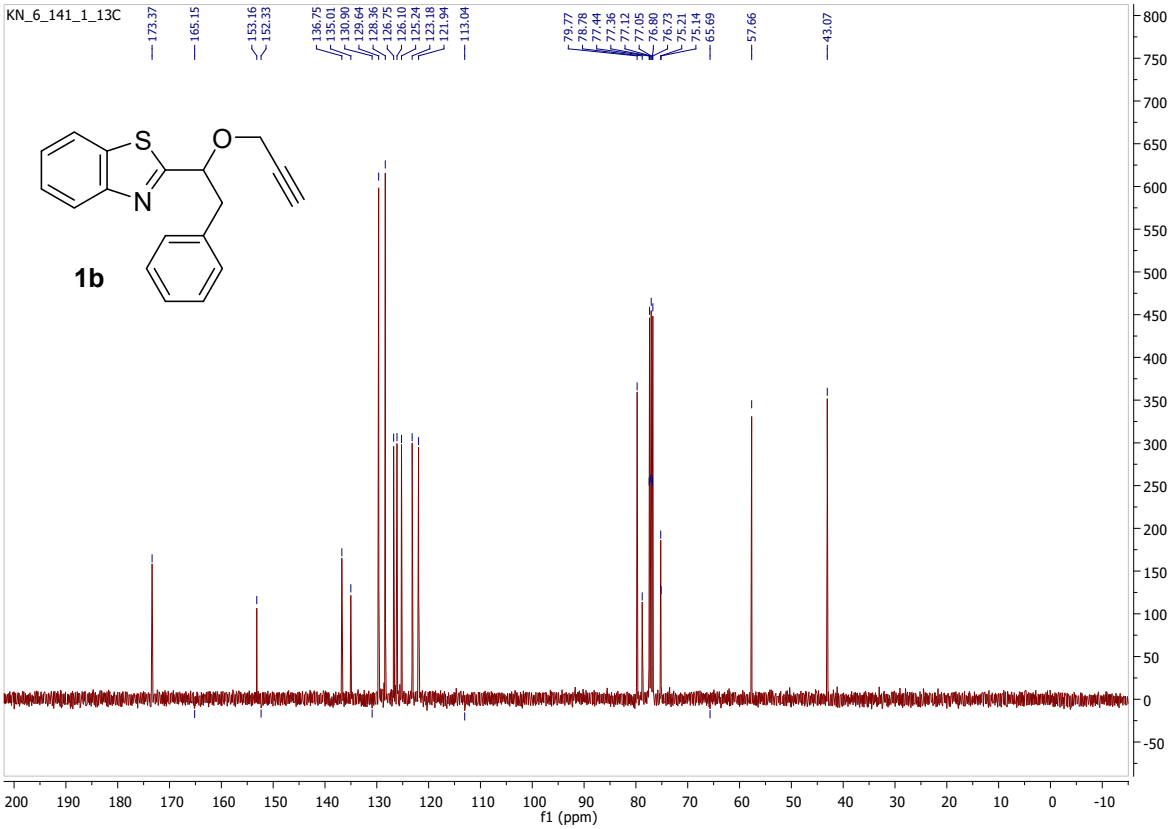
1b
f1 (ppm)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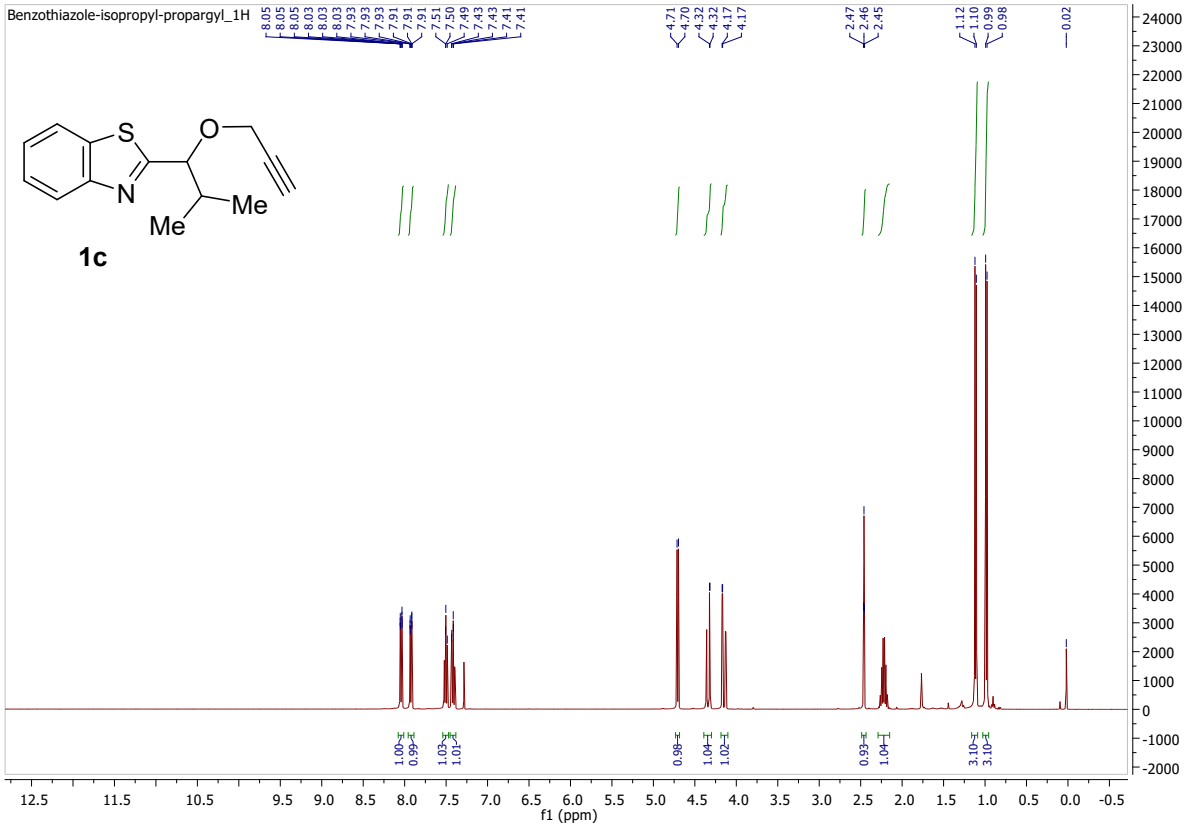
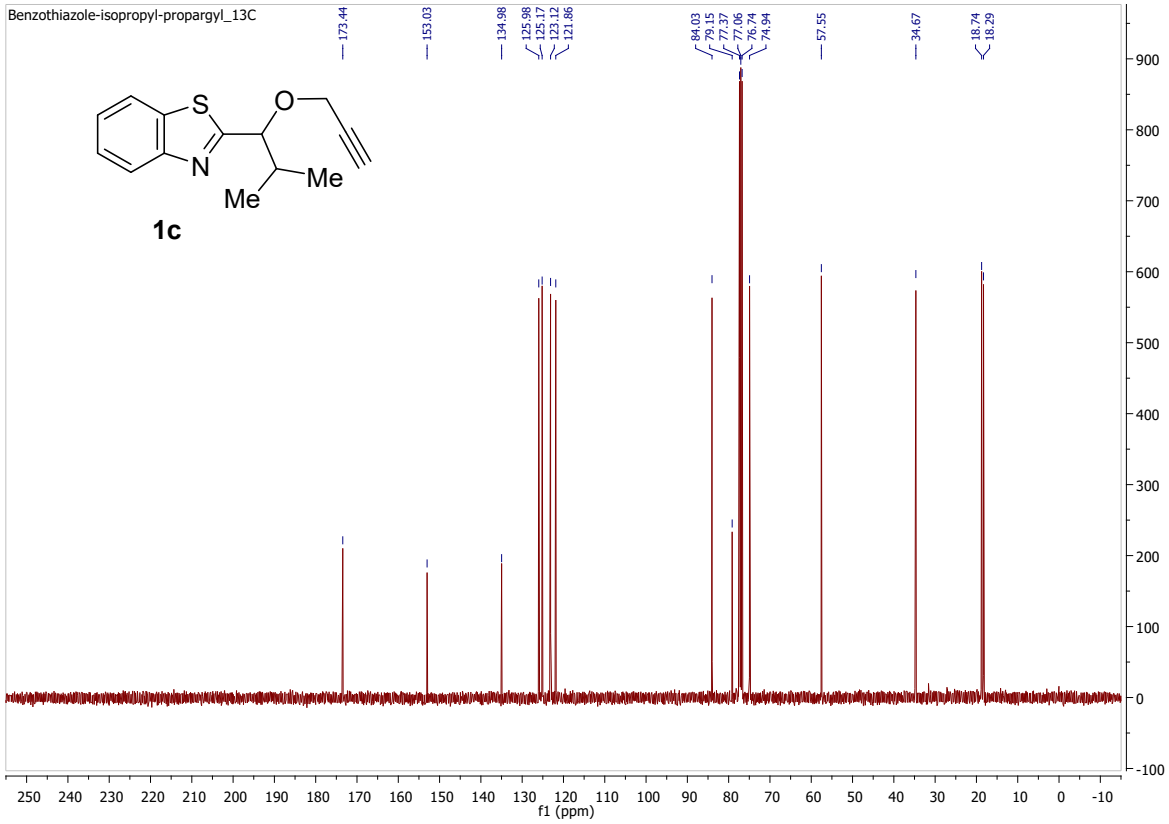
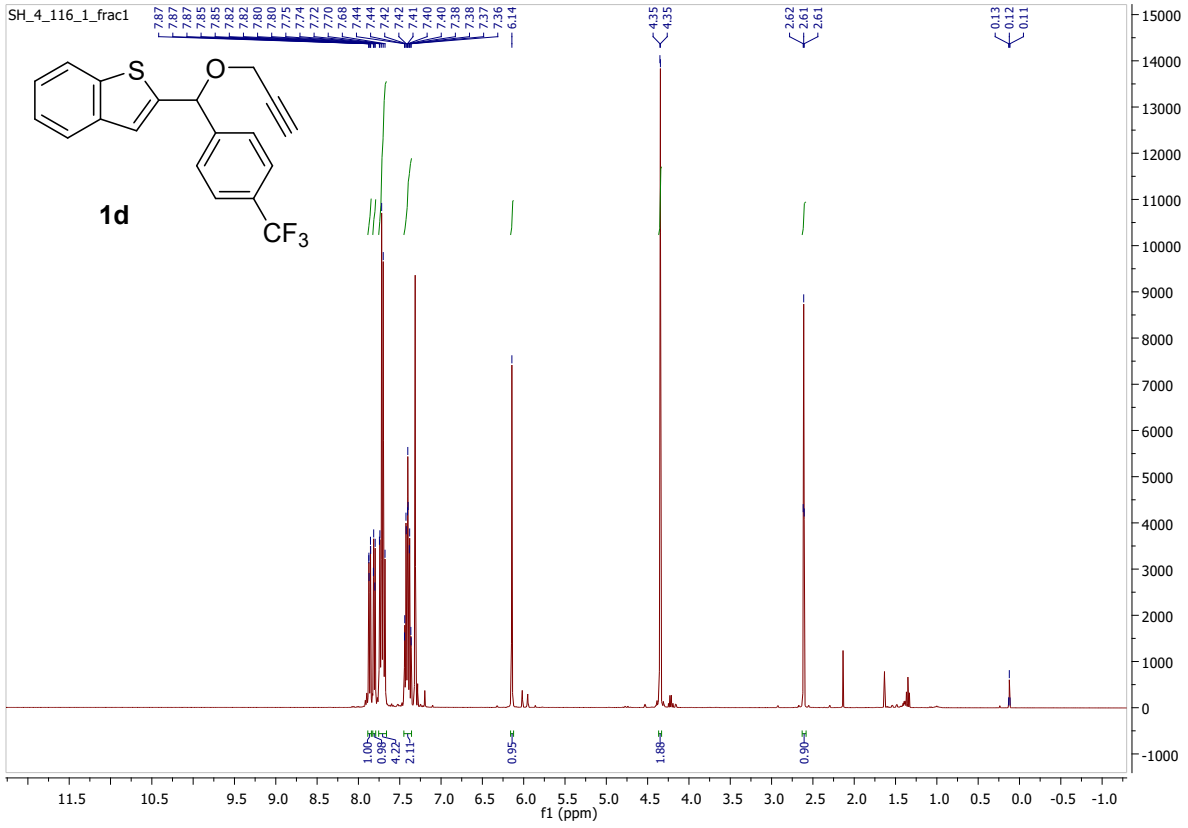
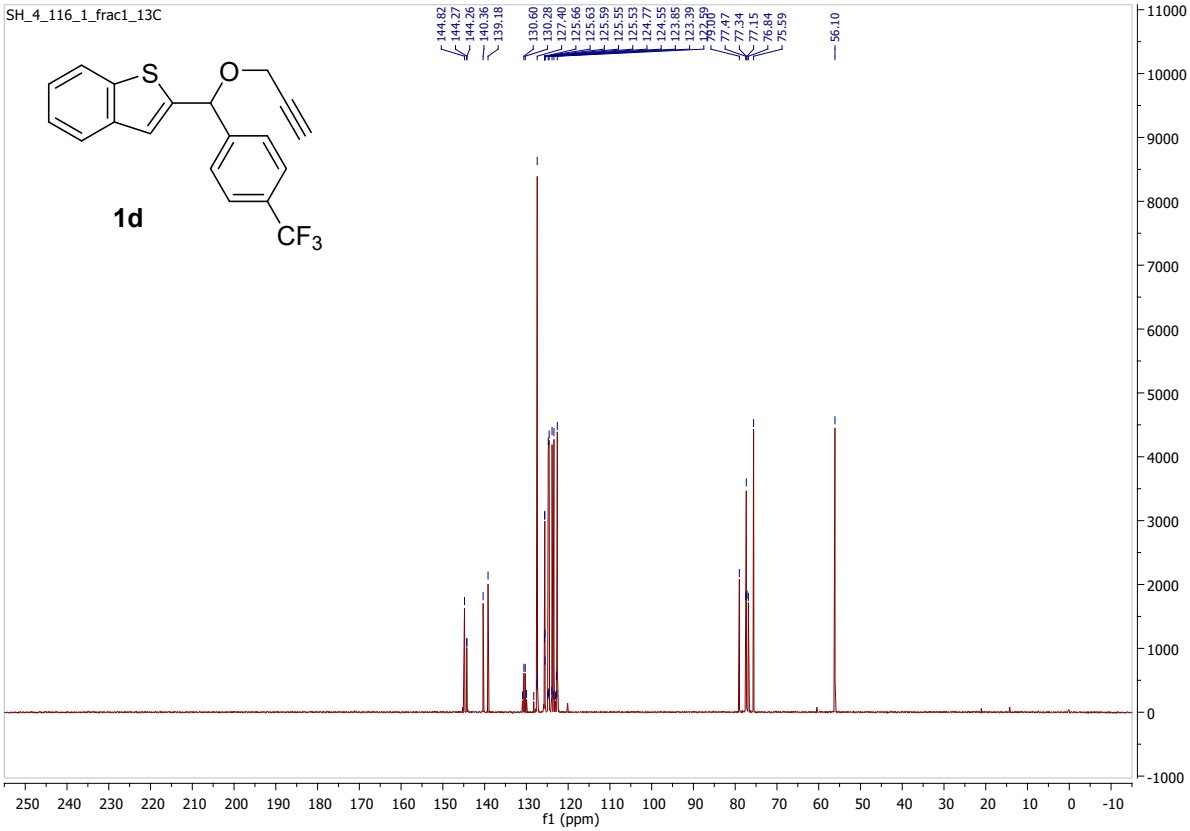
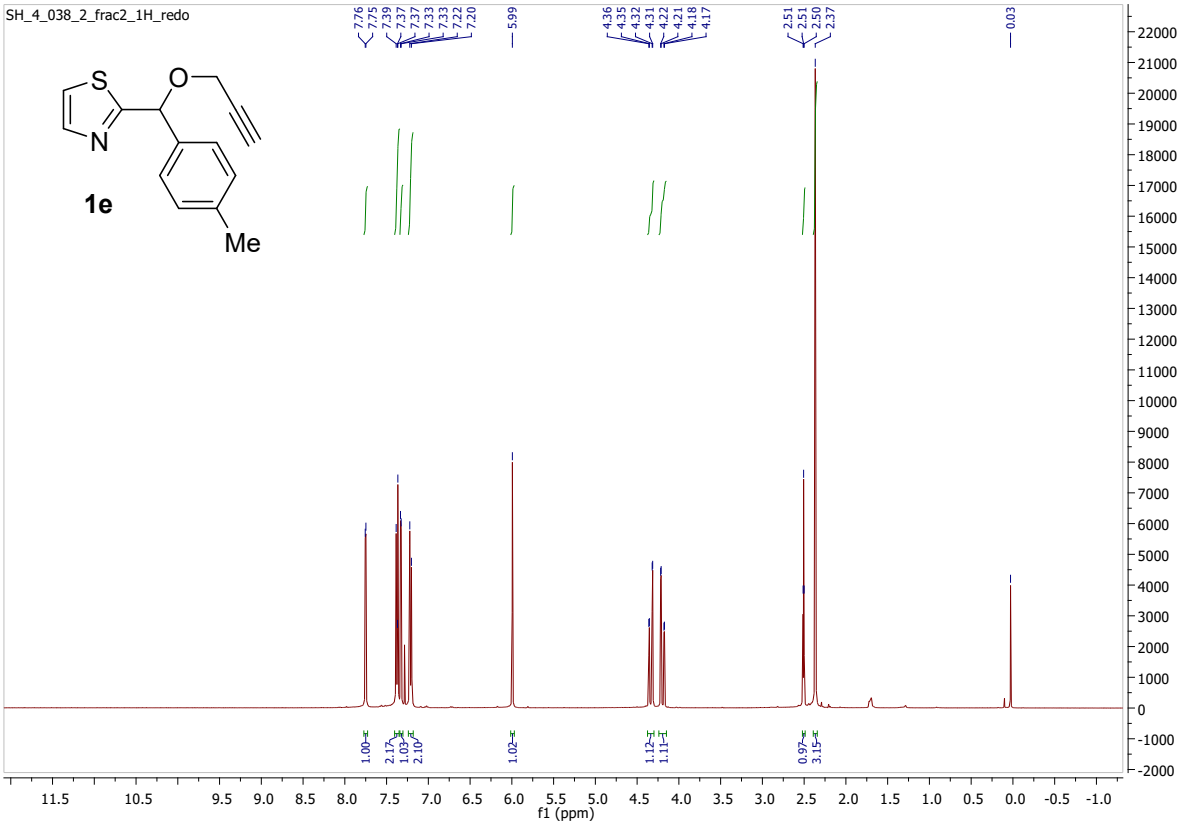
1b
f1 (ppm)

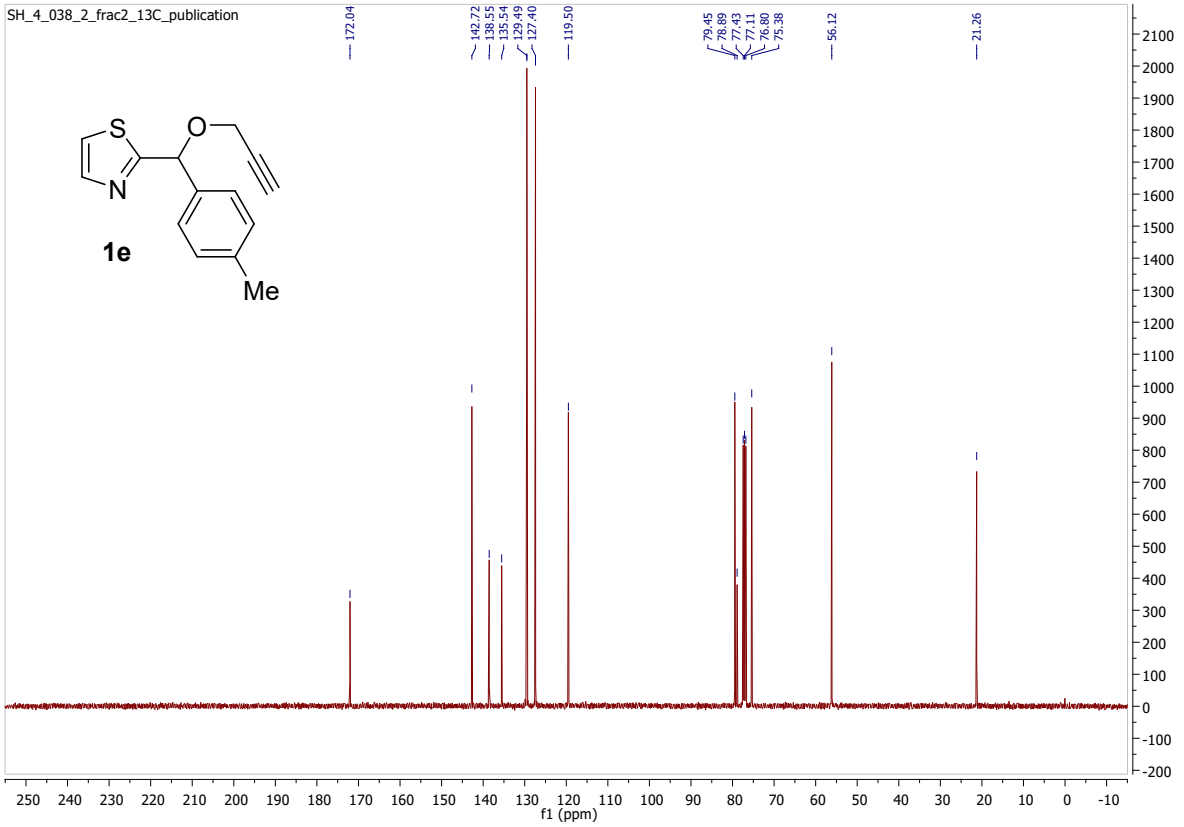

Benzothiazole-isopropyl-propargyl_1H
1c
f1 (ppm)

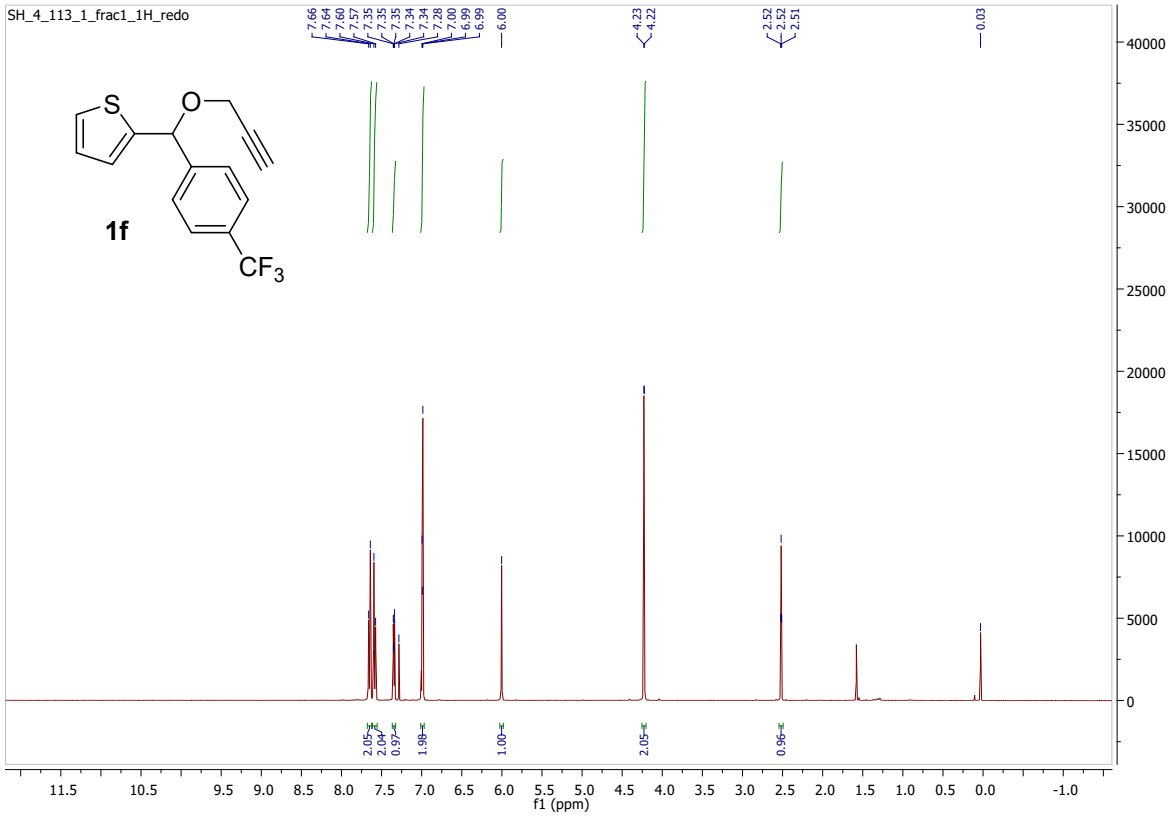

Benzothiazole-isopropyl-propargyl_13C
1c
f1 (ppm)


SH_4_116_1_frac1
1d
f1 (ppm)


SH_4_116_1_frac1_13C
1d
f1 (ppm)


SH_4_038_2_frac2_1H_redo
1e
Me
f1 (ppm)


SH_4_038_2_frac2_13C_publication
1e
Me
f1 (ppm)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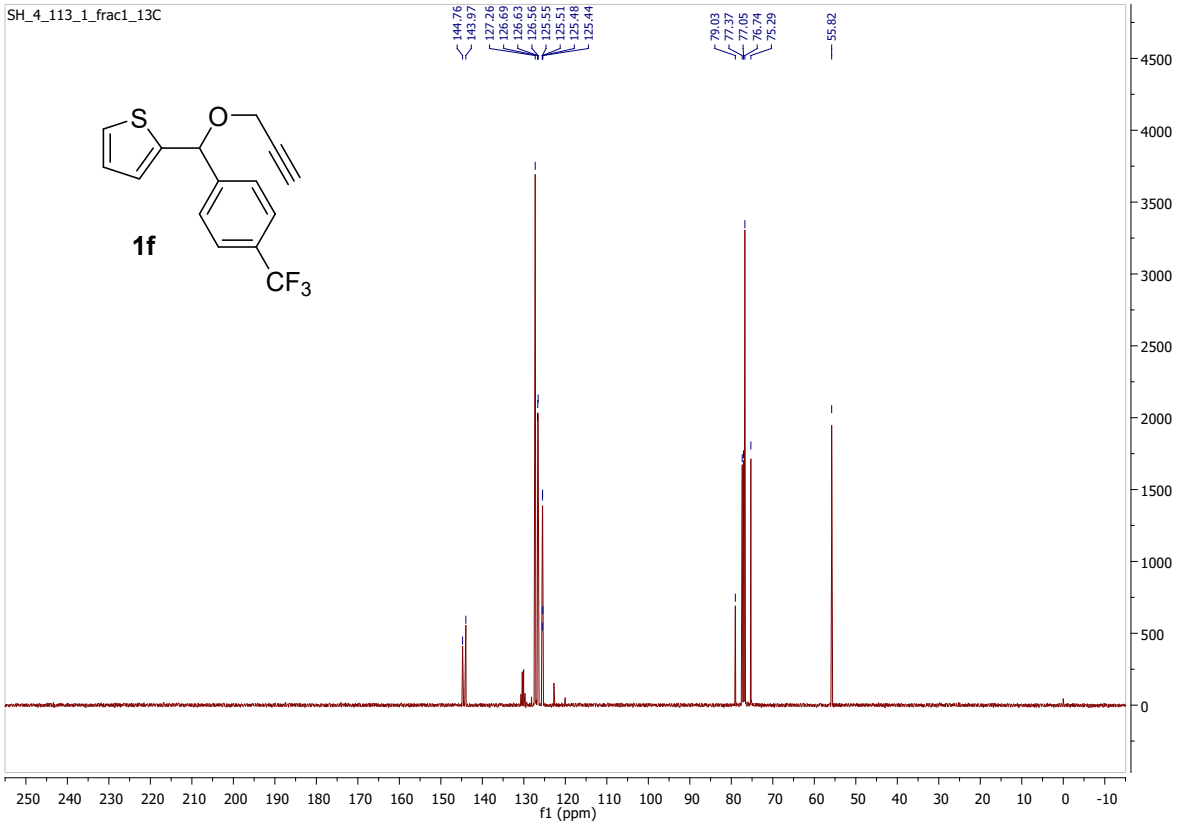
7.35
7.35
7.34
7.34
7.28
7.00
6.99
6.99
6.00
4.23
4.22
2.52
2.52
2.51
0.03
S
O
1f
CF3
2.05
2.04
0.97
1.98
1.00
2.05
0.96
f1 (ppm)


SH_4_113_1_frac1_13C
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126.56
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125.51
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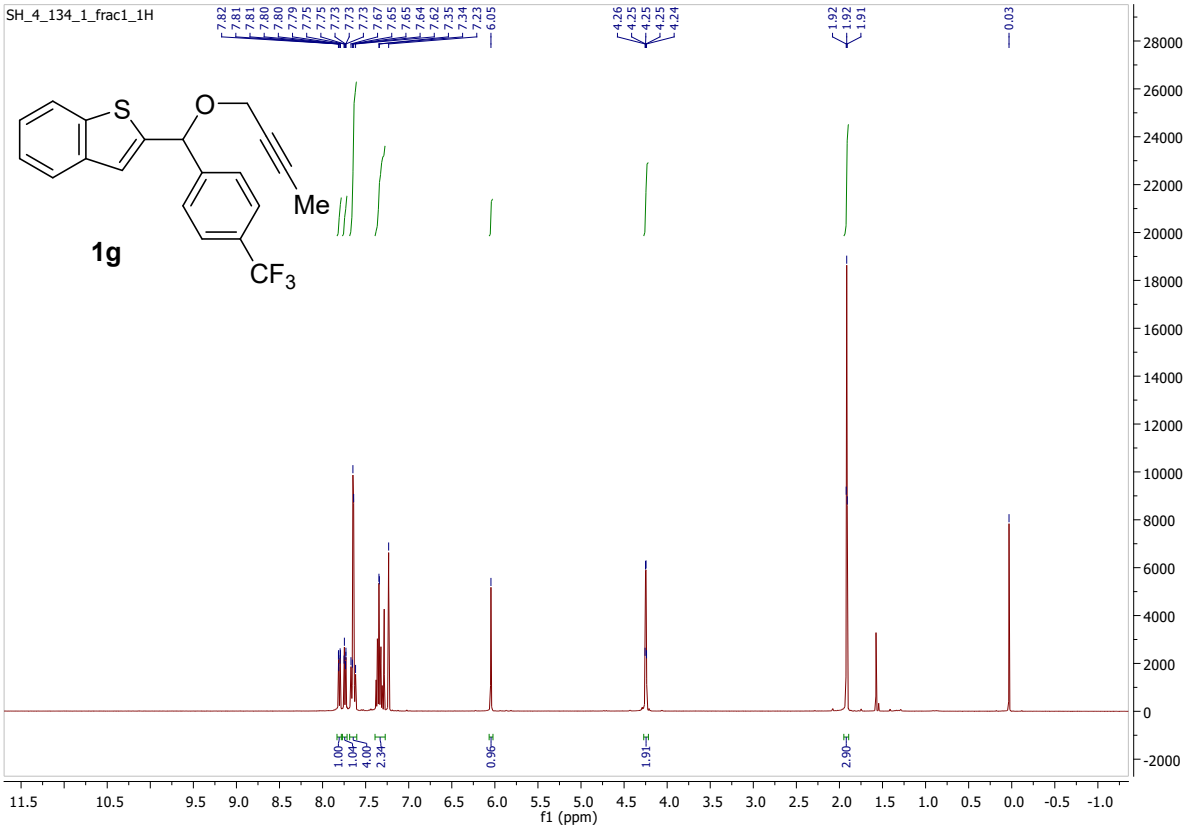
55.82
S
O
1f
CF3
f1 (ppm)


SH_4_134_1_frac1_1H
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7.81
7.81
7.80
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7.67
7.65
7.65
7.64
7.62
7.35
7.34
7.23
6.05
4.26
4.25
4.25
4.25
4.24
1.92
1.92
1.91
0.03
S
O
Me
1g
CF3
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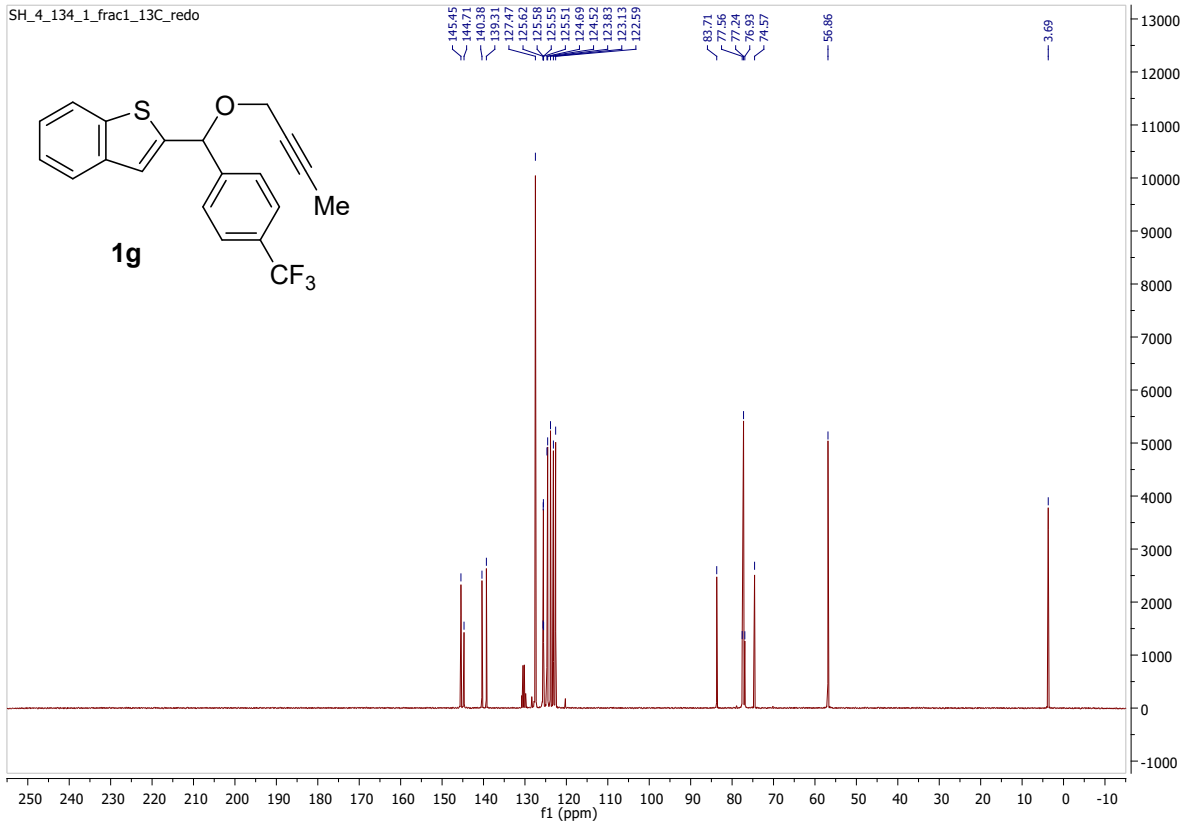
1.04
4.00
2.34
0.96
1.91
2.90
f1 (ppm)


SH_4_134_1_frac1_13C_redo
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139.31
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125.58
125.55
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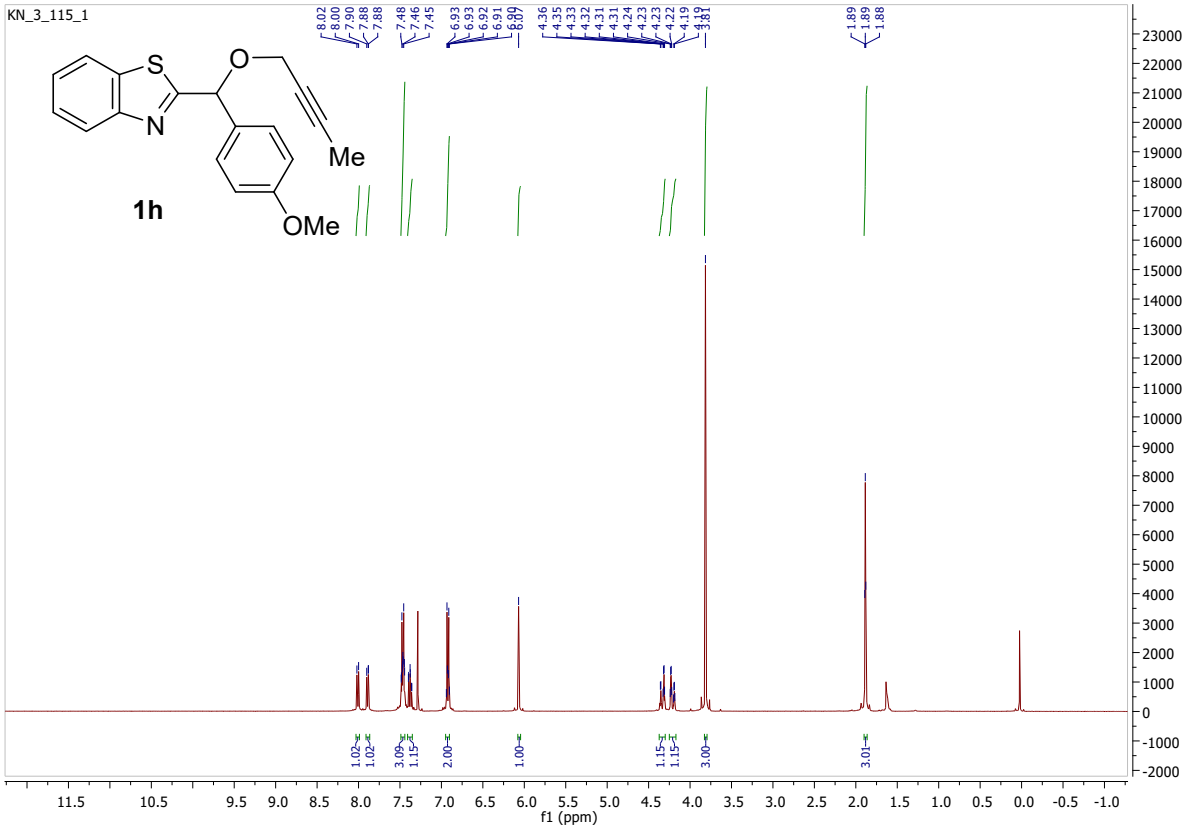
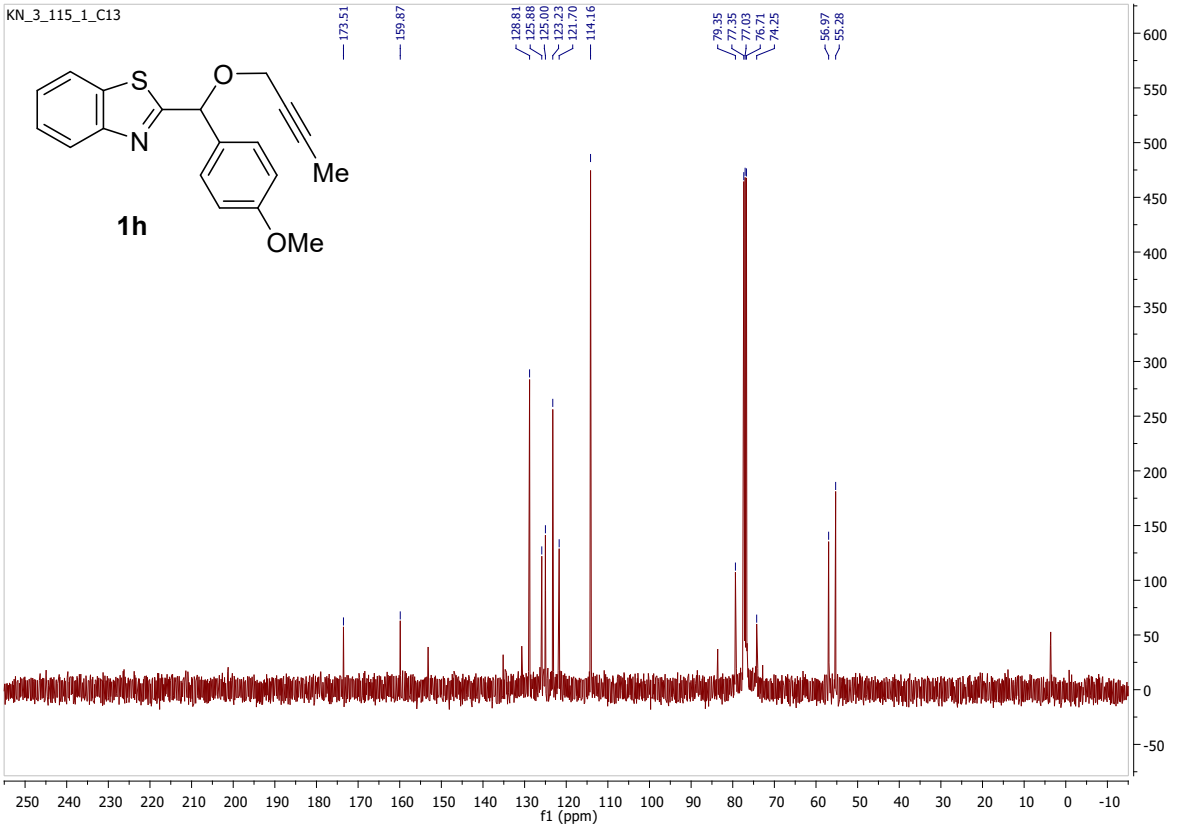
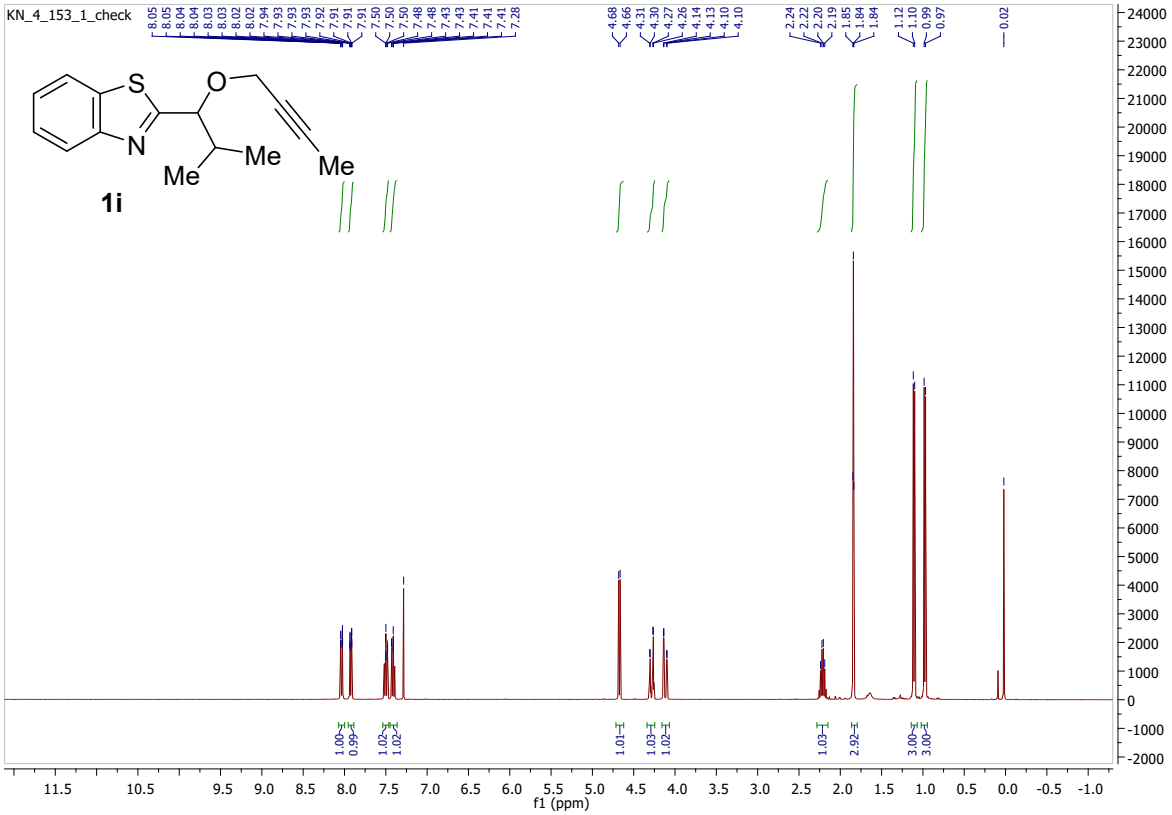
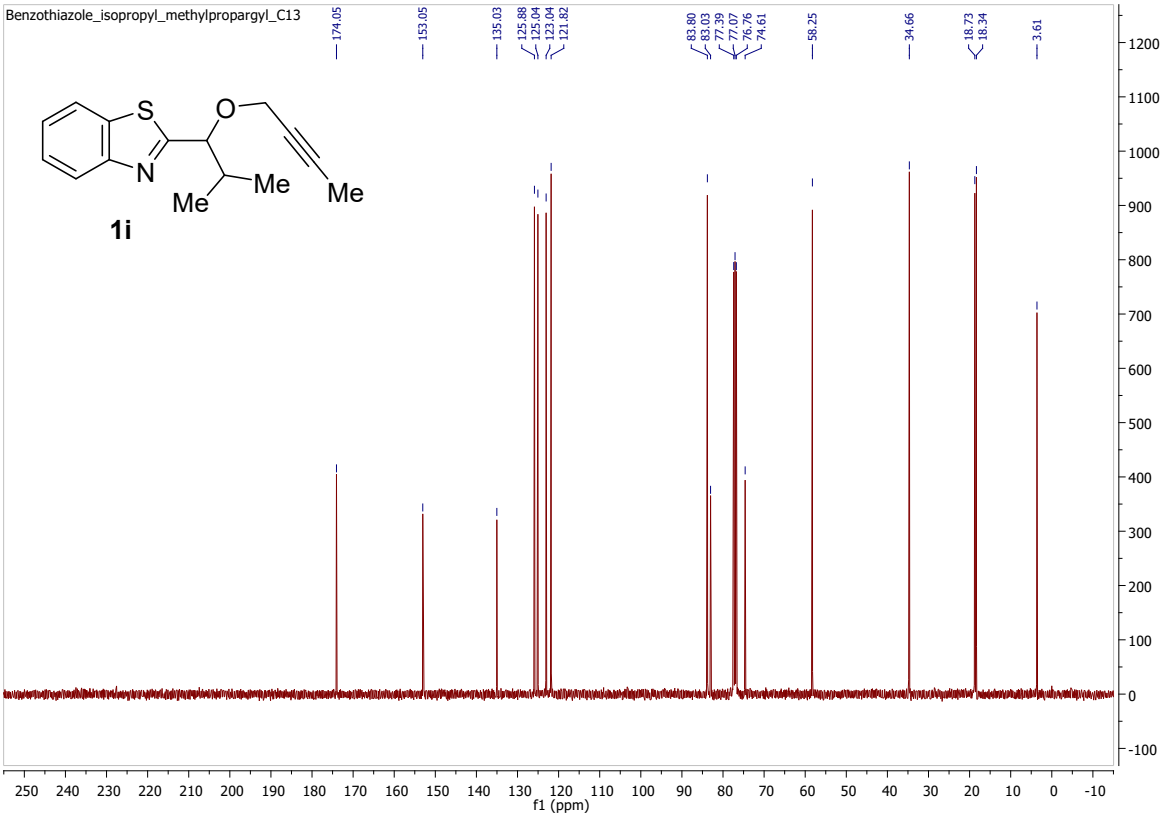
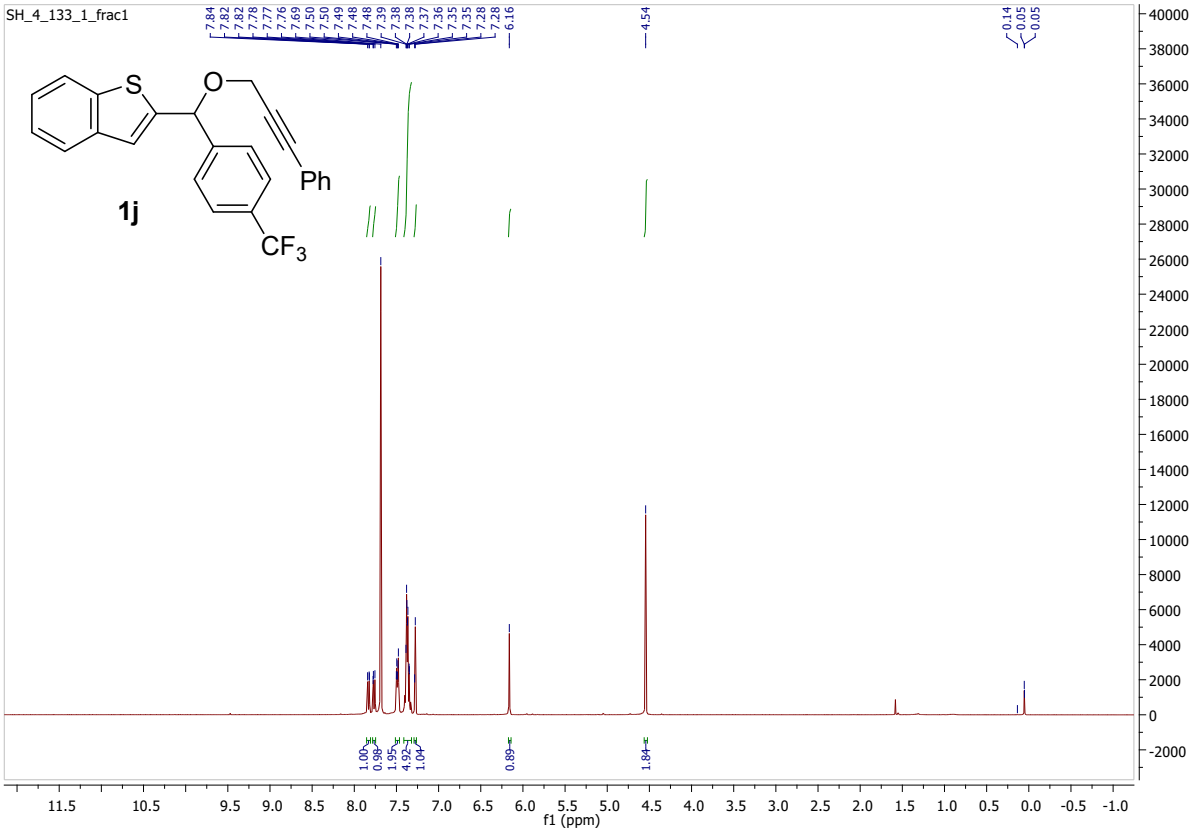
124.69
124.52
123.83
123.13
122.59
83.71
77.56
77.24
76.93
74.57
56.86
3.69
S
O
Me
1g
CF3
f1 (ppm)

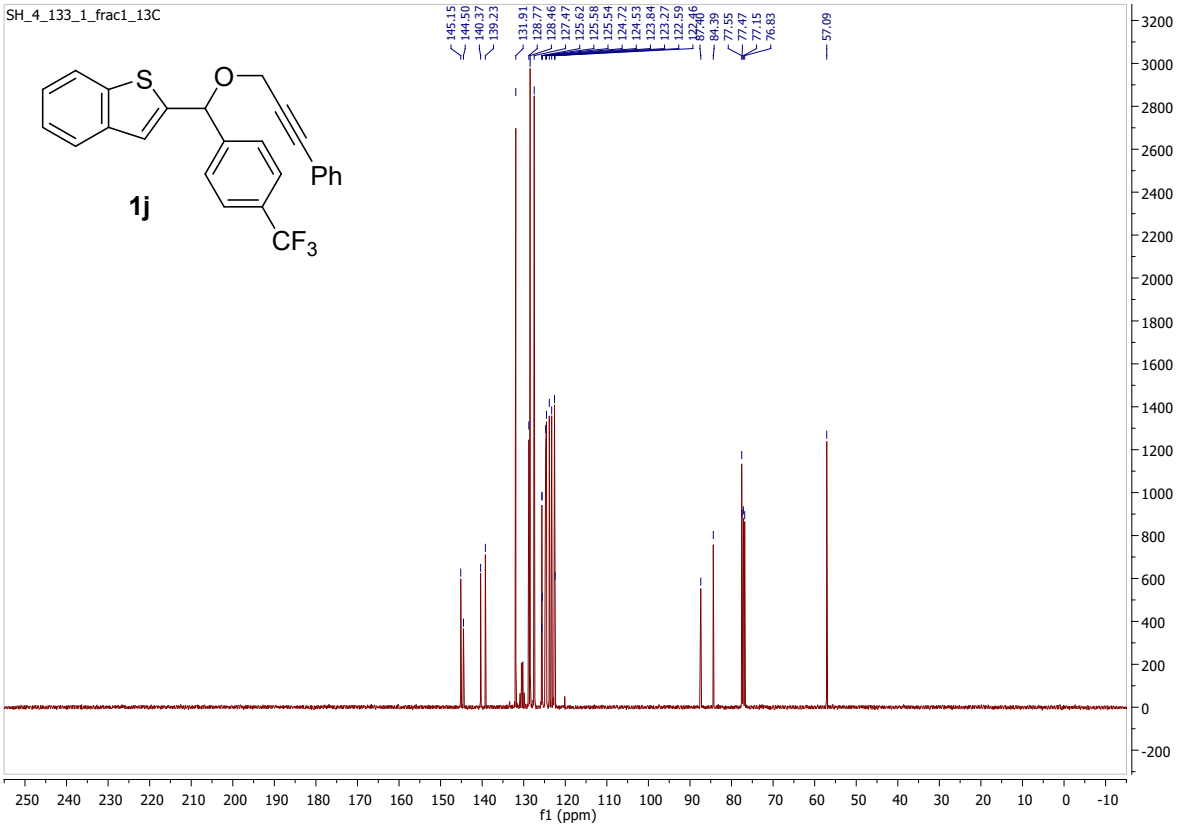

KN_3_115_1
1h
f1 (ppm)

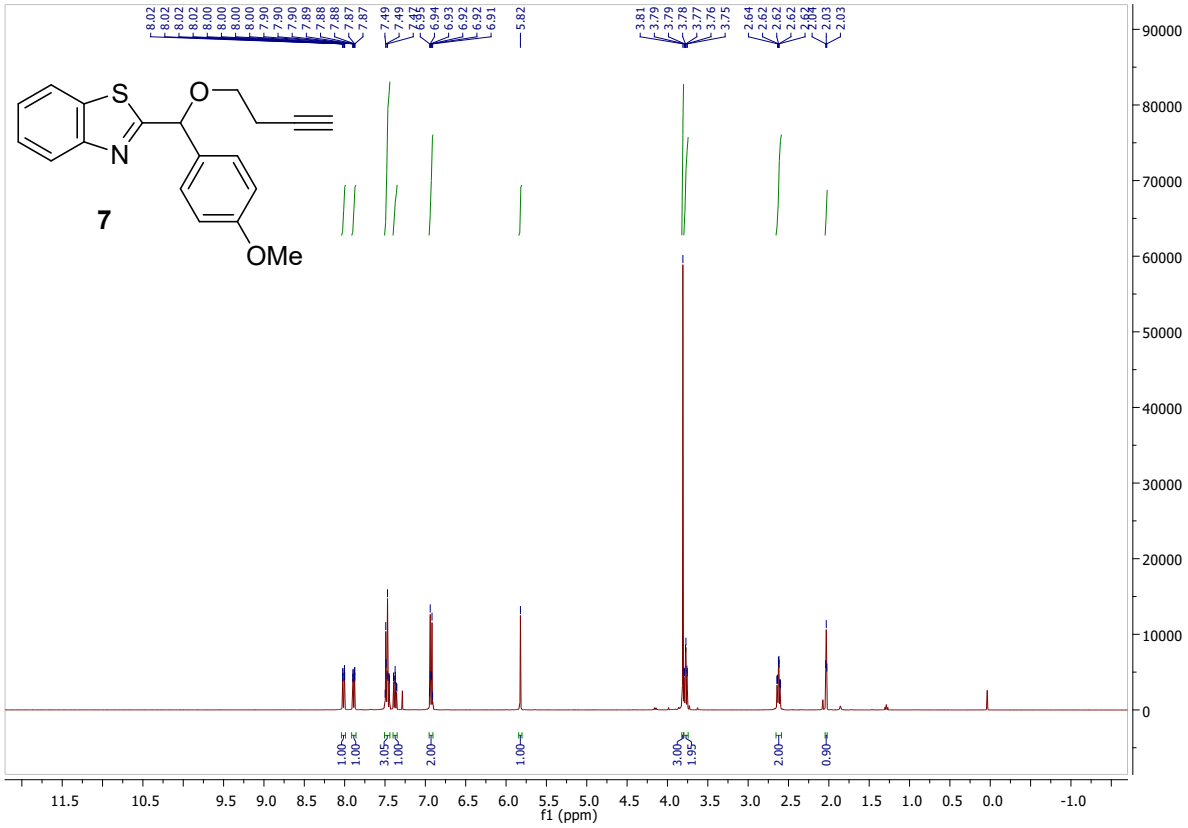

KN_3_115_1_C13
1h
f1 (ppm)

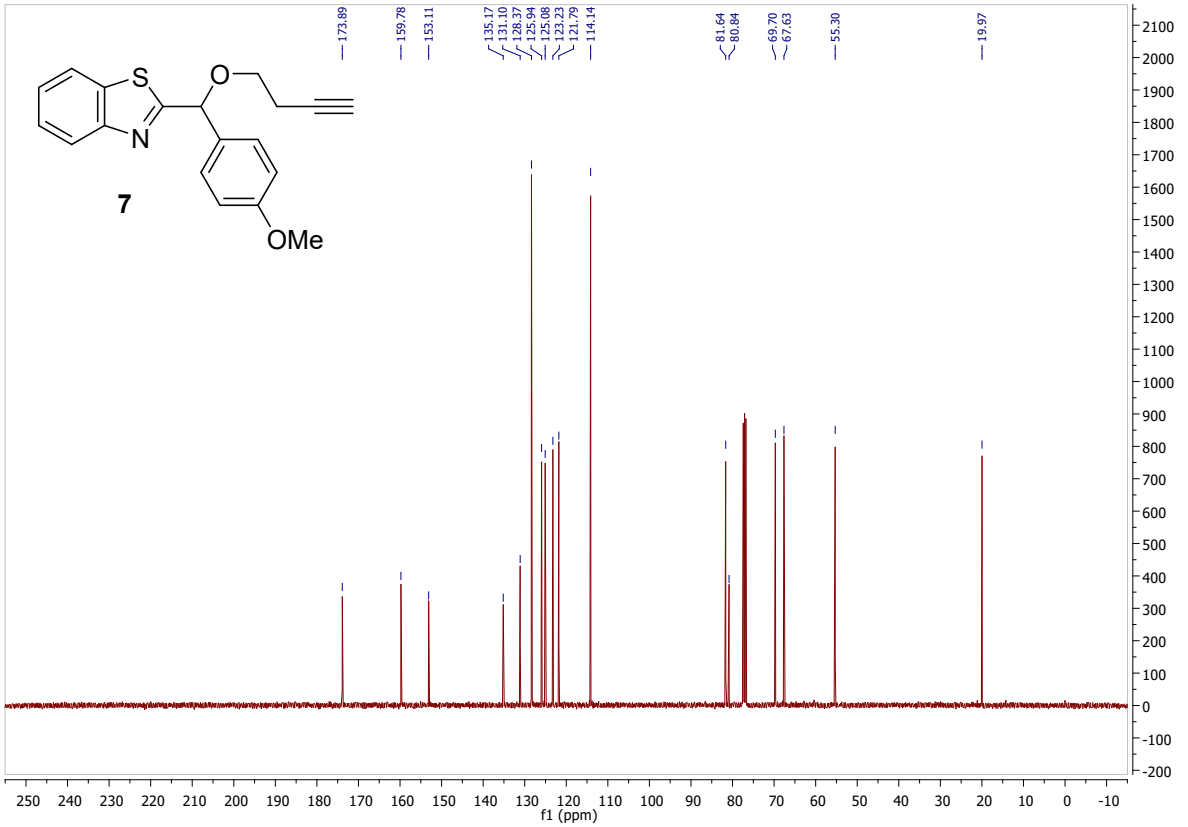

KN_4_153_1_check
1i
f1 (ppm)

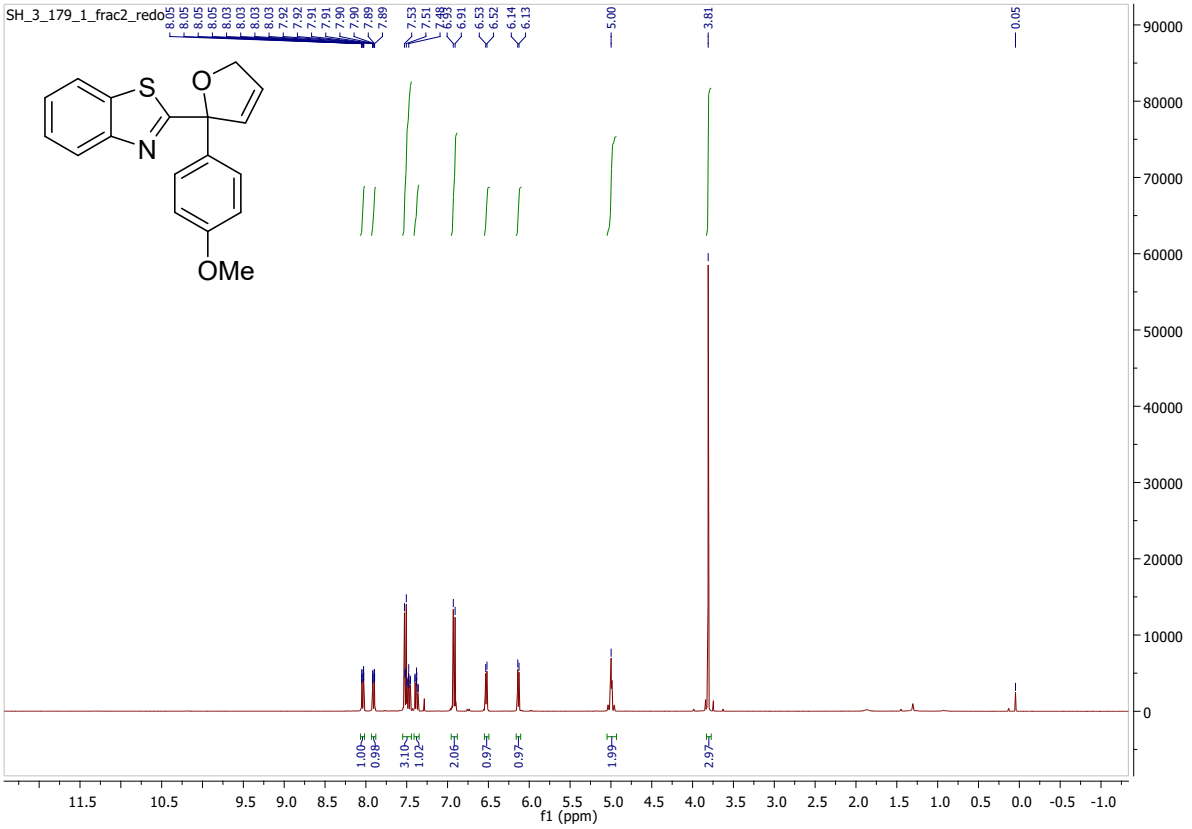

Benzothiazole_isopropyl_methylpropargyl_C13
1i
f1 (ppm)

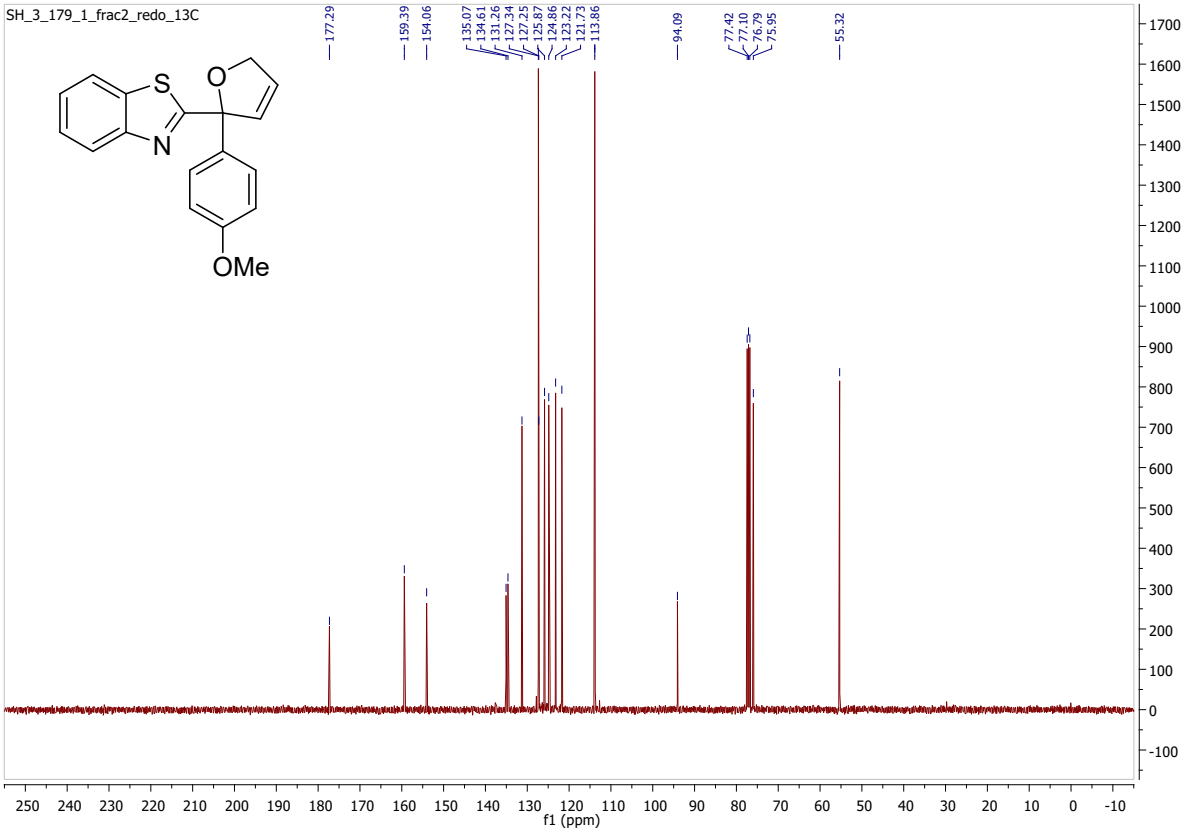

SH_4_133_1_frac1
1j
Ph
CF3
f1 (ppm)

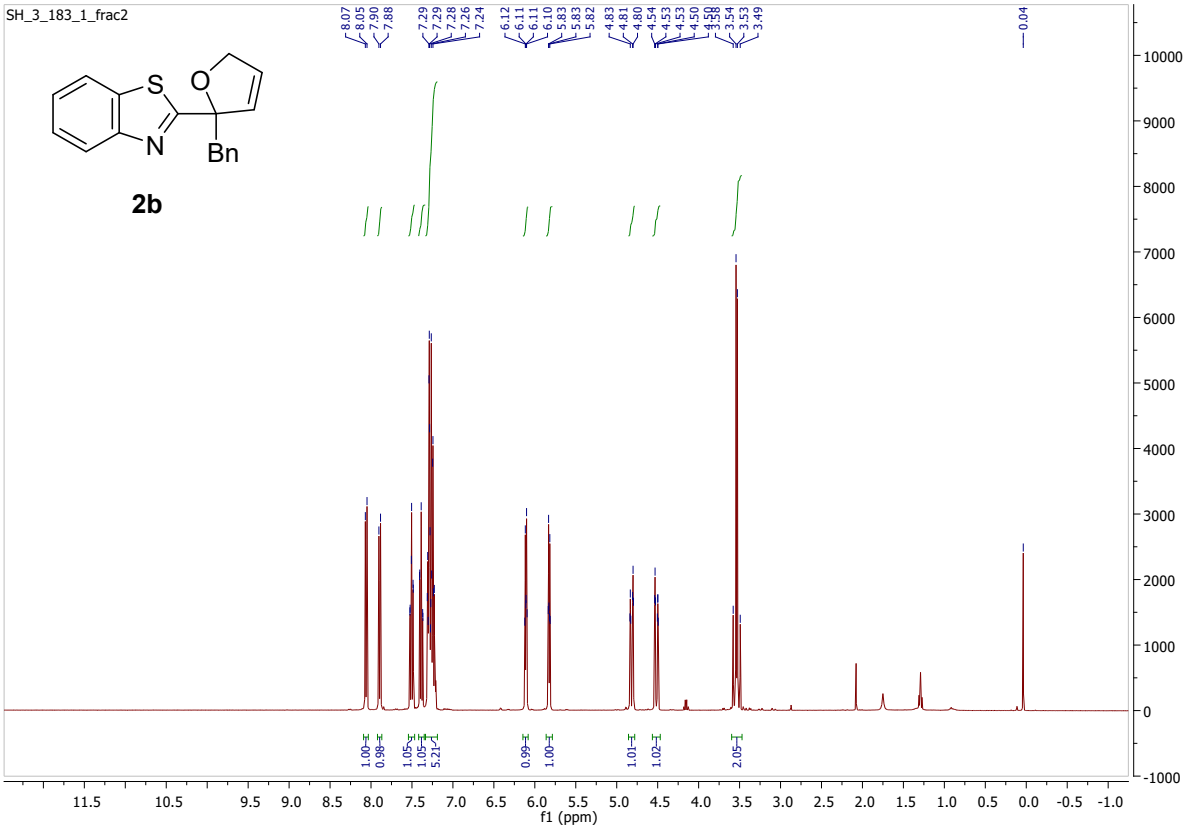

SH_4_133_1_frac1_13C
1j
Ph
CF3
f1 (ppm)

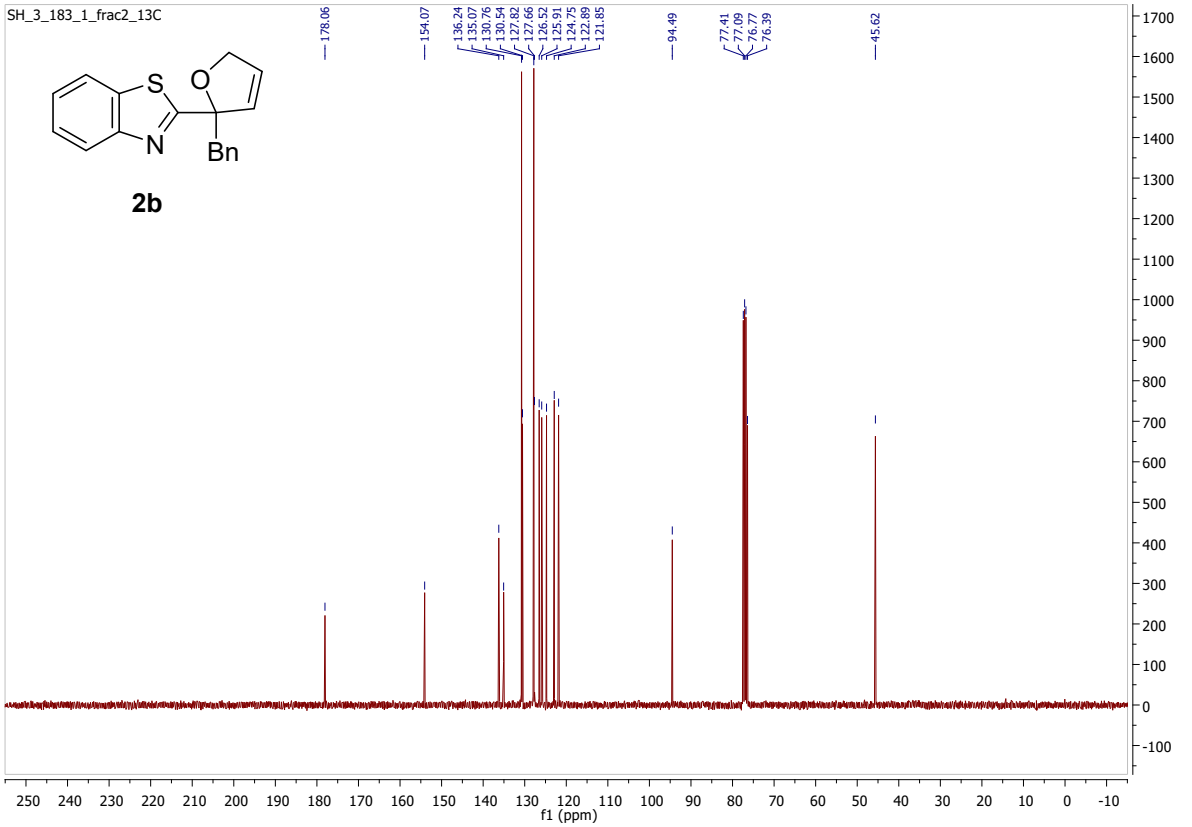

S
O
N
7
OMe
f1 (ppm)

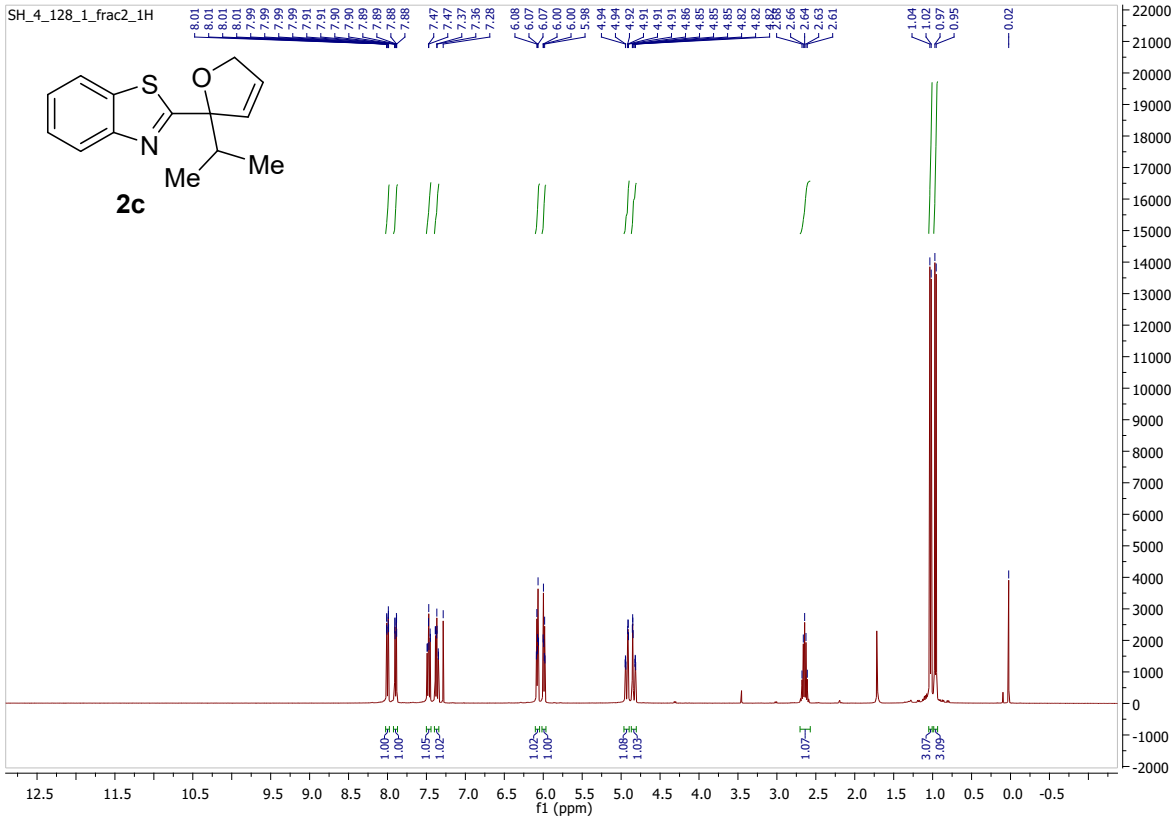

S
O
N
7
OMe
f1 (ppm)

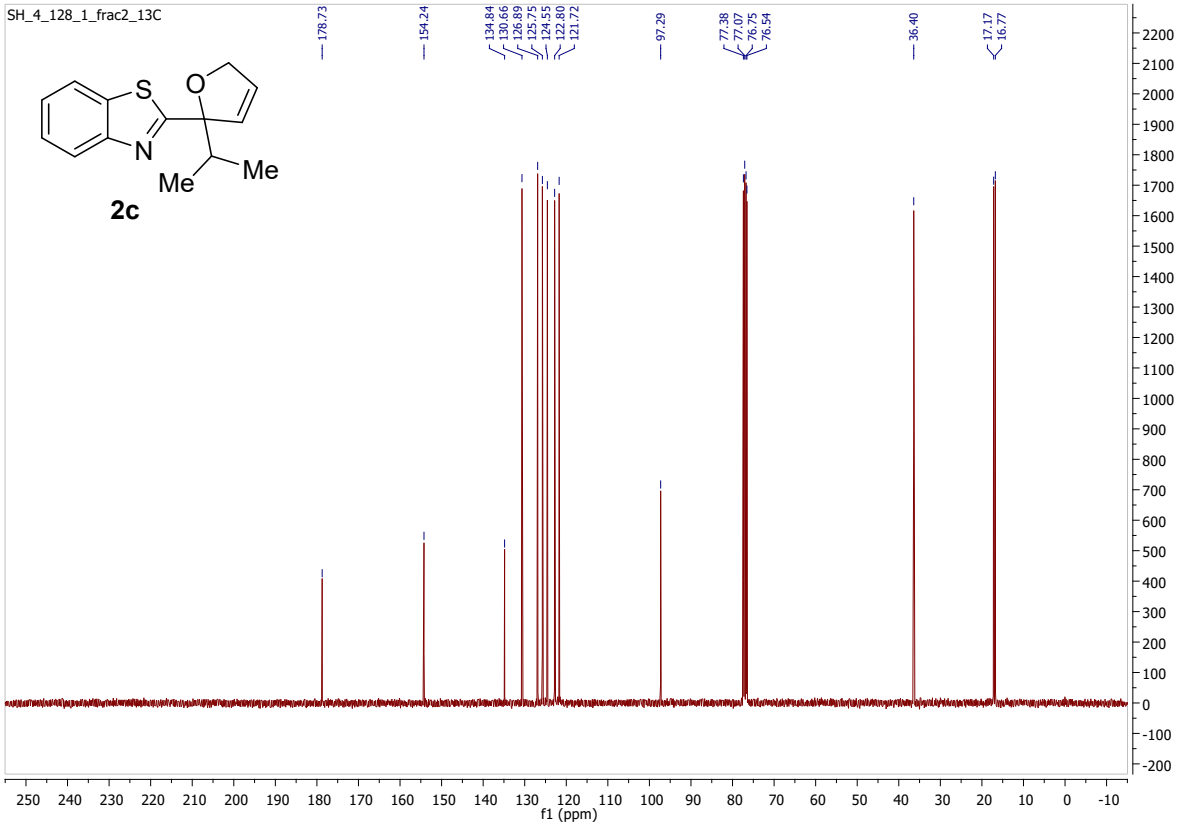

SH_3_179_1_frac2_redo
S
O
N
OMe
8.05
8.05
8.05
8.05
8.03
8.03
8.03
8.03
7.92
7.91
7.91
7.90
7.90
7.89
7.89
7.53
7.51
6.91
6.53
6.52
6.14
6.13
5.00
3.81
0.05
1.00
0.98
3.10
1.02
2.06
0.97
0.97
1.99
2.97
f1 (ppm)

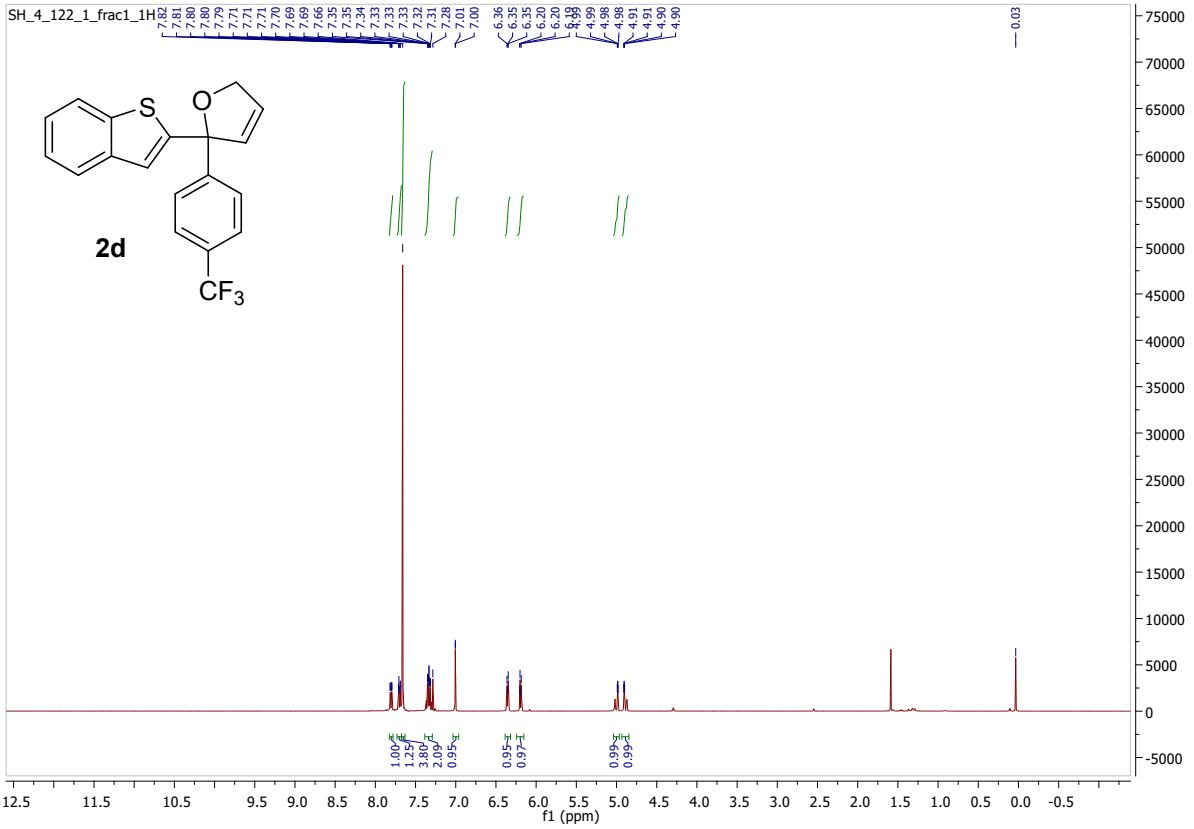

SH_3_179_1_frac2_redo_13C
S
O
N
OMe
177.29
159.39
154.06
135.07
134.61
131.26
127.34
127.25
125.87
124.86
123.22
121.73
113.86
94.09
77.42
77.10
76.79
75.95
55.32
f1 (ppm)

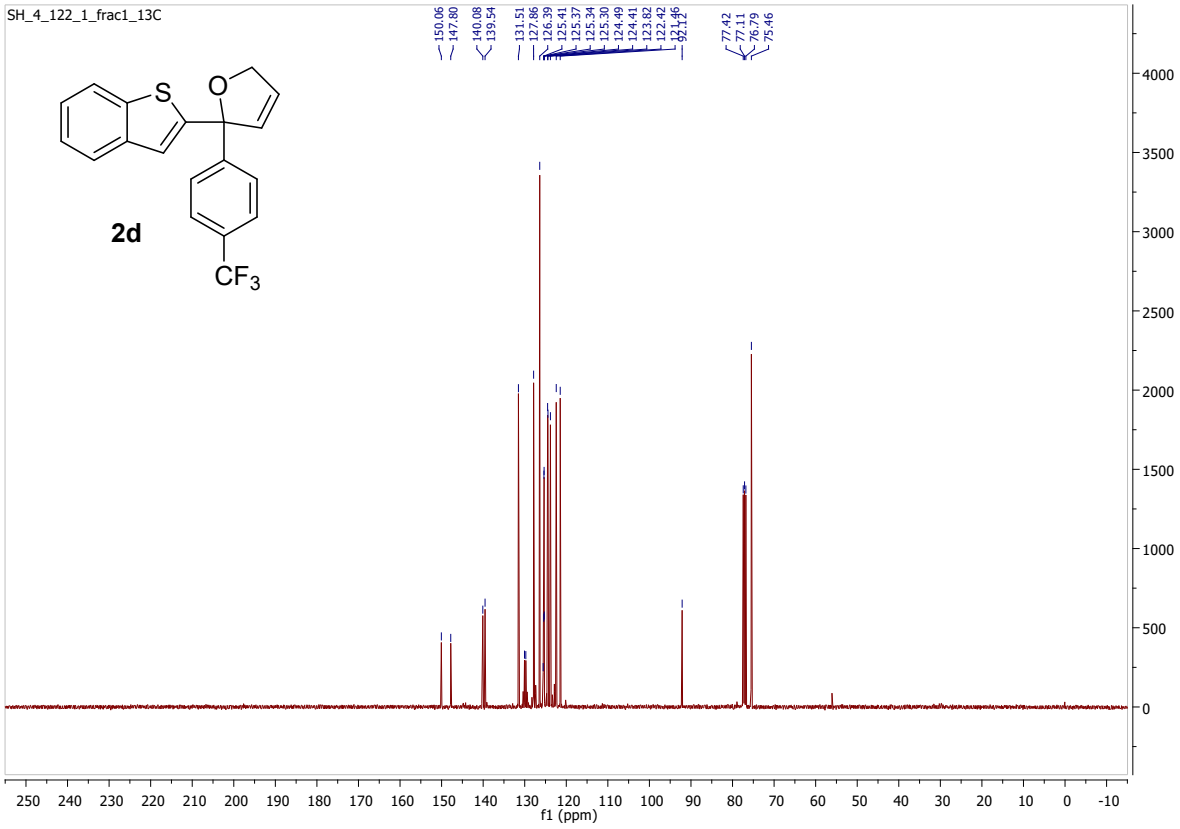

SH_3_183_1_frac2
8.07
8.05
7.90
7.88
7.29
7.29
7.28
7.26
7.24
6.12
6.11
6.11
6.10
5.83
5.83
5.82
4.83
4.81
4.80
4.54
4.53
4.53
4.50
3.54
3.53
3.49
0.04
S
O
N
Bn
2b
1.00
0.98
1.05
1.05
5.21
0.99
1.00
1.01
1.02
2.05
f1 (ppm)

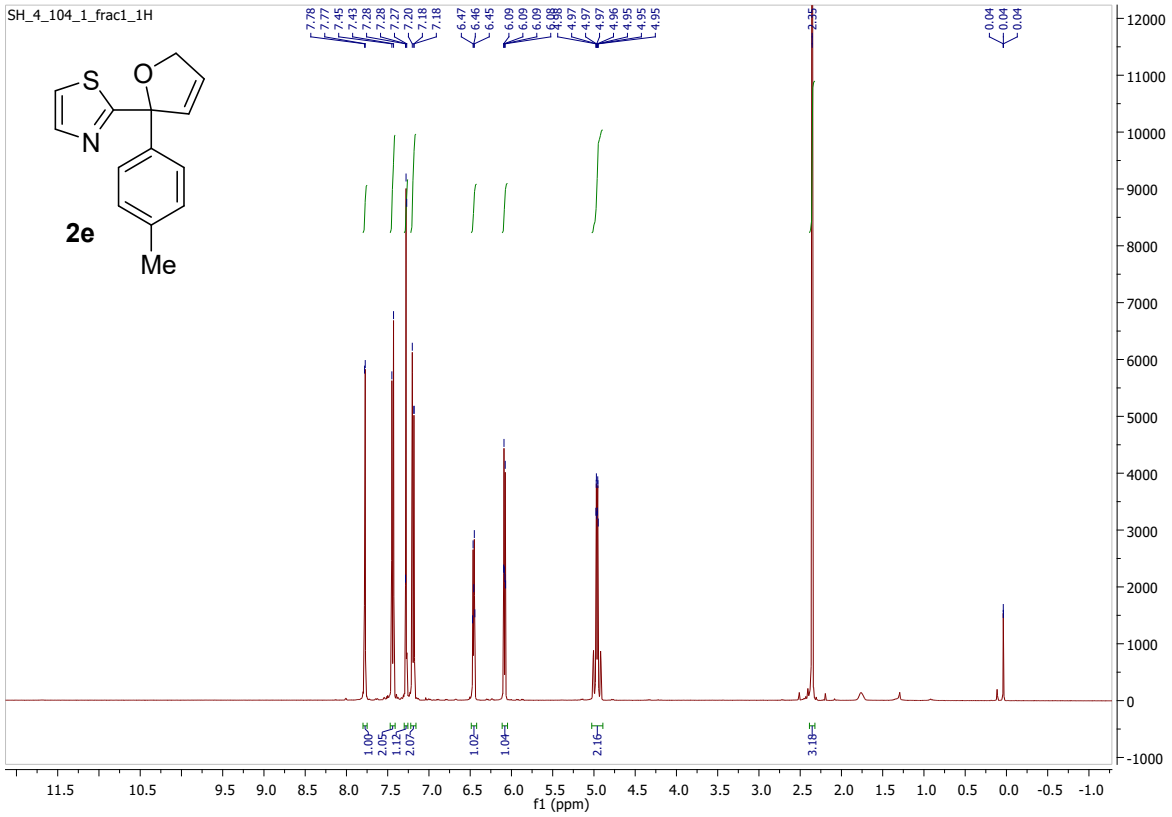

SH_3_183_1_frac2_13C
178.06
154.07
136.24
135.07
130.76
130.54
127.82
127.66
126.52
125.91
124.75
122.89
121.85
94.49
77.41
77.09
76.77
76.39
45.62
S
O
N
Bn
2b
f1 (ppm)

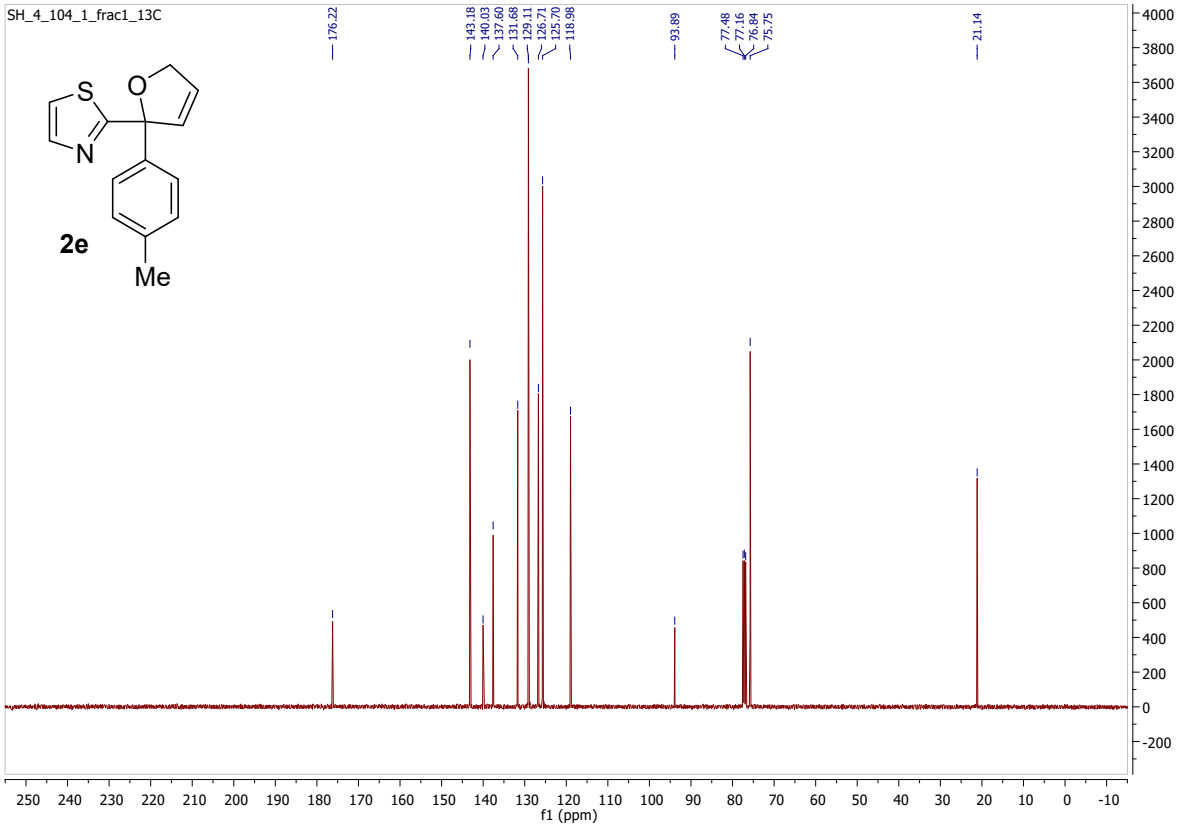

SH_4_128_1_frac2_1H
S
O
N
Me
Me
2c
f1 (ppm)

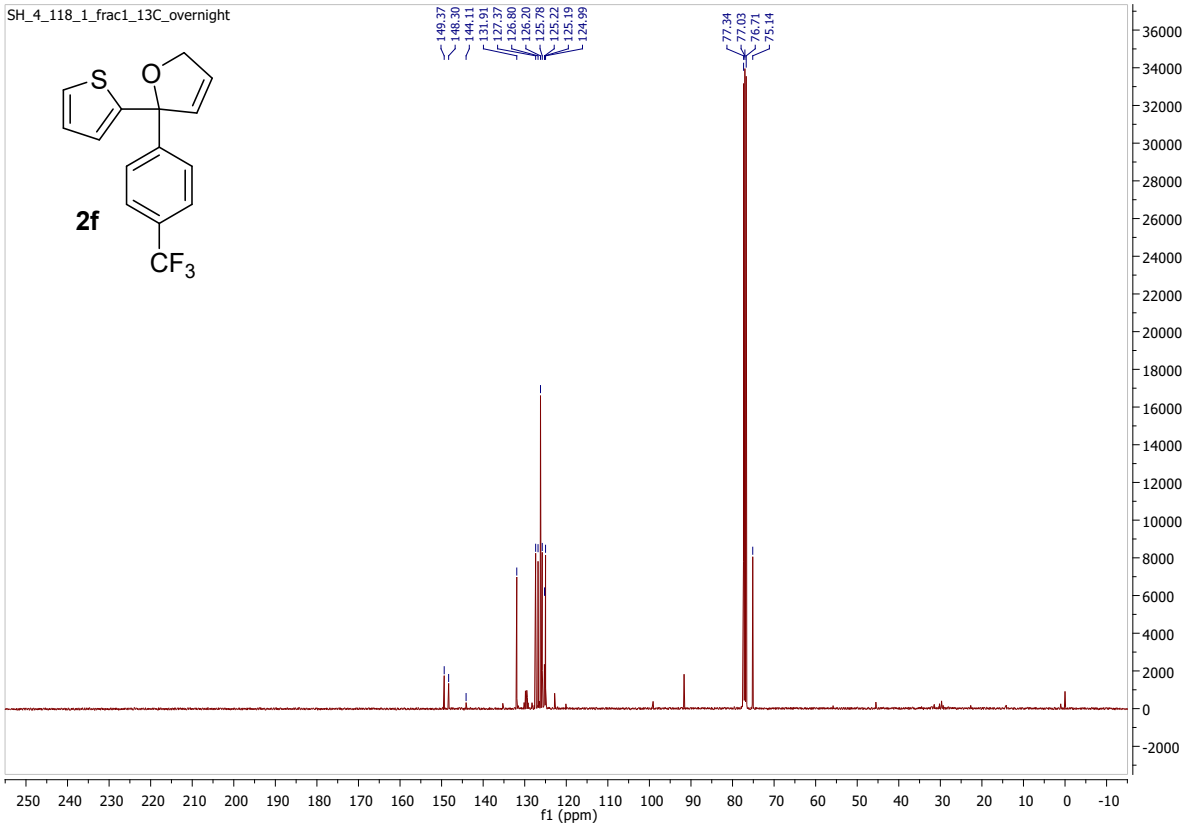

SH_4_128_1_frac2_13C
S
O
N
Me
Me
2c
f1 (ppm)

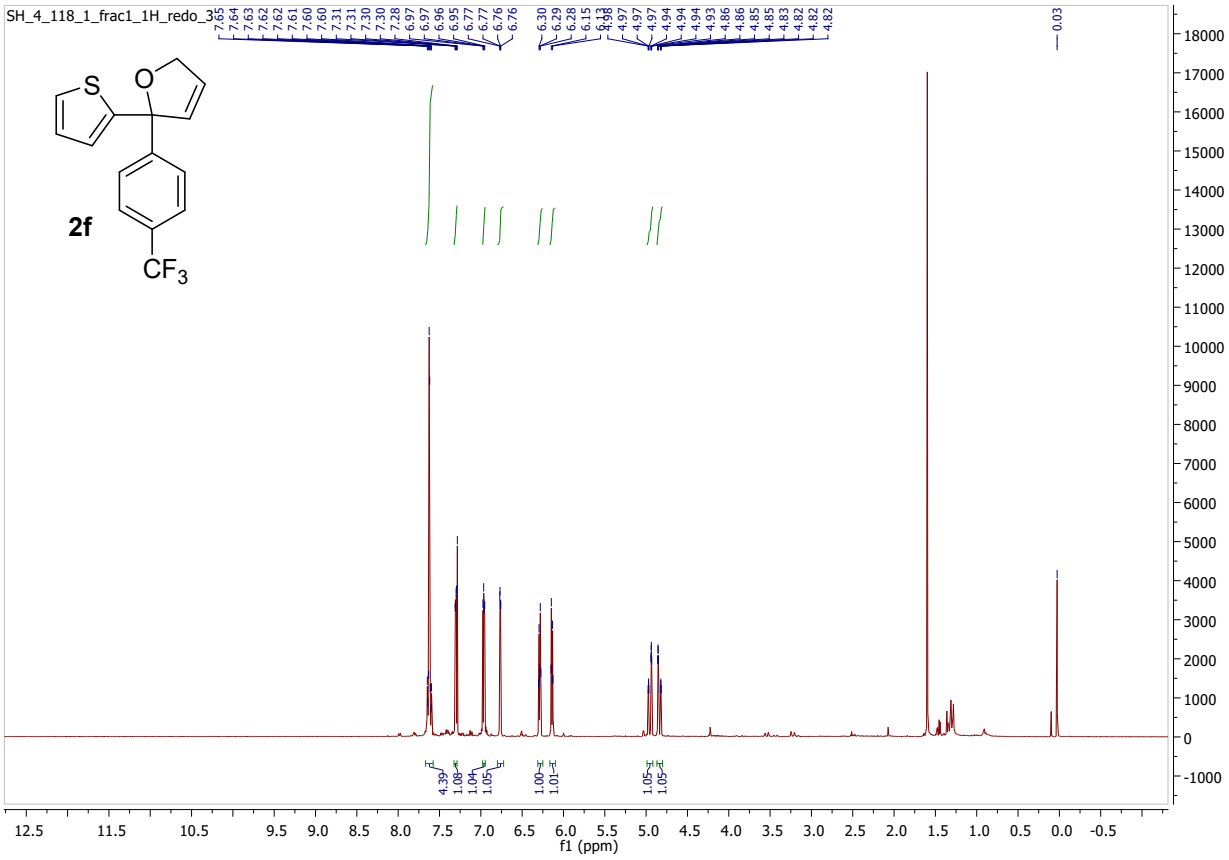

SH_4_122_1_frac1_1H
2d
S
O
CF3
f1 (ppm)

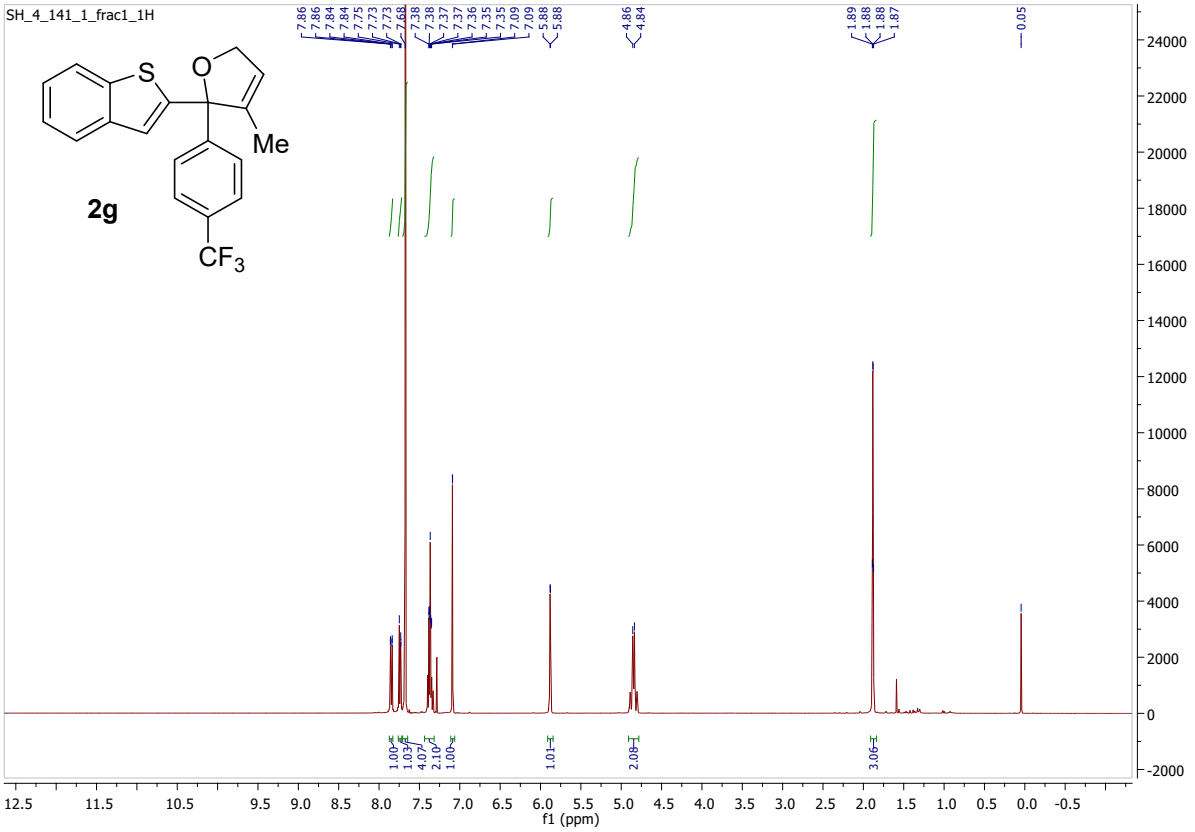

SH_4_122_1_frac1_13C
2d
S
O
CF3
f1 (ppm)

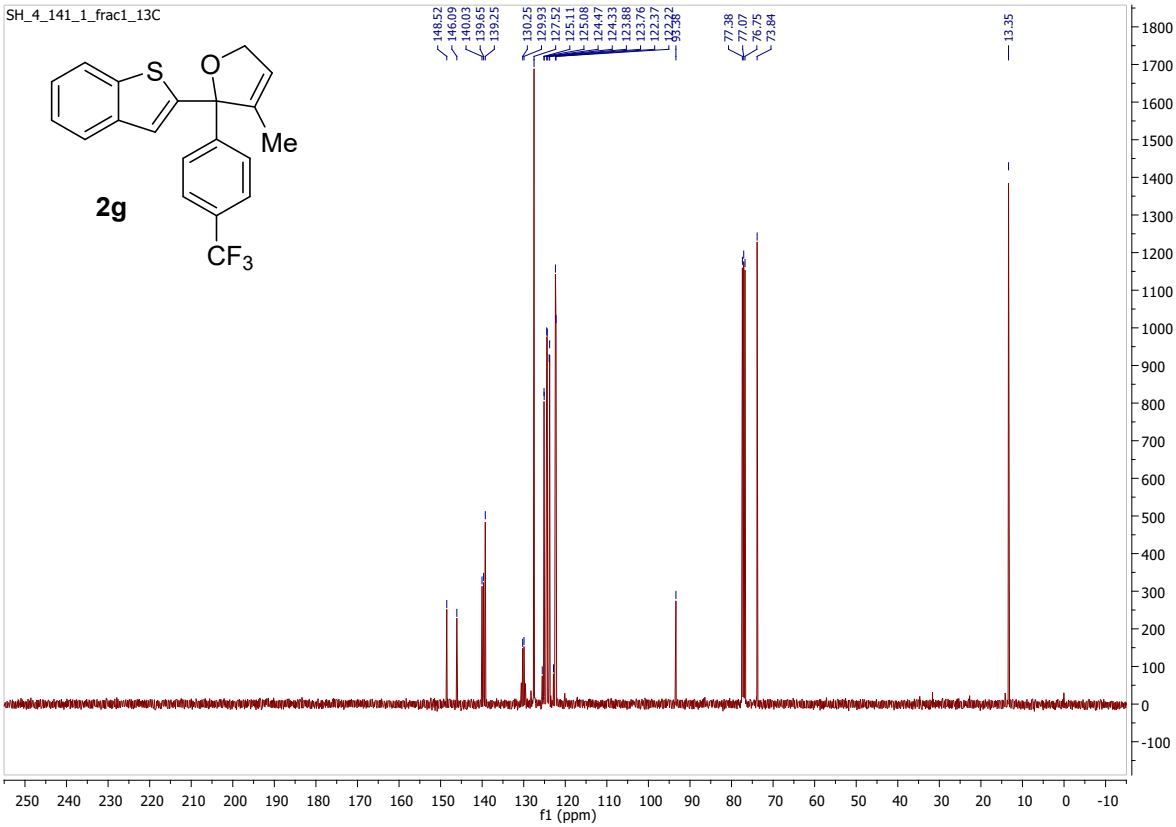

SH_4_104_1_frac1_1H
2e
Me
f1 (ppm)

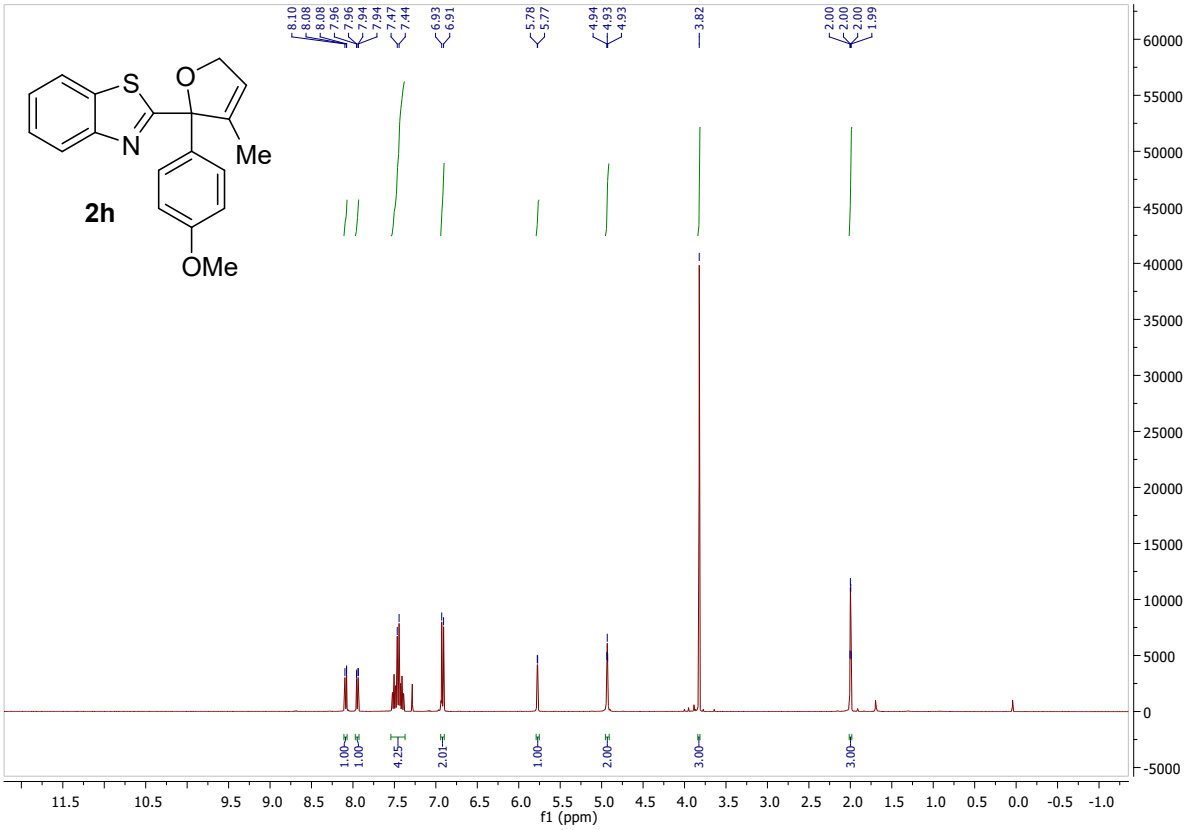

SH_4_104_1_frac1_13C
2e
Me
f1 (ppm)

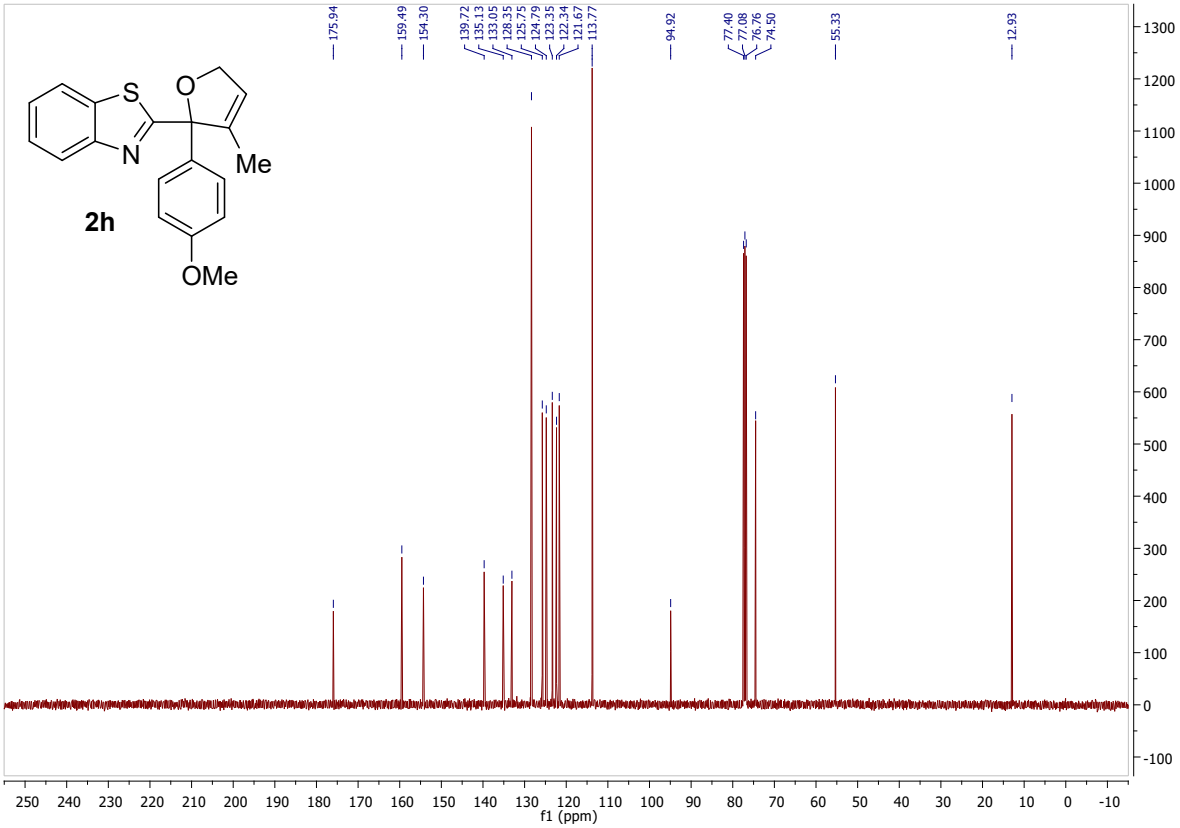

SH_4_118_1_frac1_13C_overnight
149.37
148.30
144.11
131.91
127.37
126.80
126.20
125.78
125.22
125.19
124.99
77.34
77.03
76.71
75.14
S
O
2f
CF3
f1 (ppm)

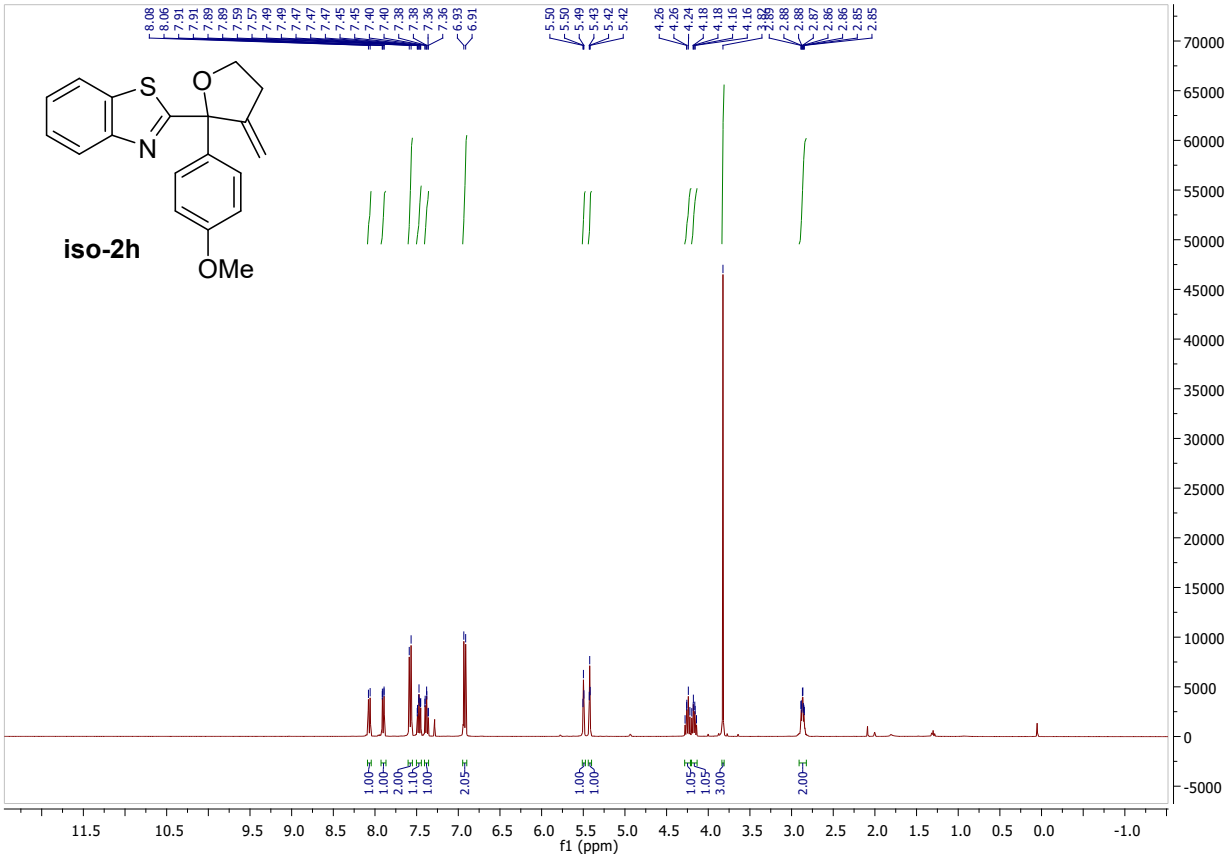

SH_4_118_1_frac1_1H_redo_3
7.65
7.64
7.63
7.62
7.61
7.60
7.60
7.31
7.31
7.30
7.30
7.28
6.97
6.97
6.96
6.95
6.77
6.76
6.76
6.30
6.29
6.28
6.15
4.97
4.97
4.97
4.94
4.94
4.94
4.93
4.86
4.86
4.85
4.85
4.83
4.82
4.82
4.82
0.03
4.39
1.08
1.04
1.05
1.00
1.01
1.05
1.05
S
O
2f
CF3
f1 (ppm)

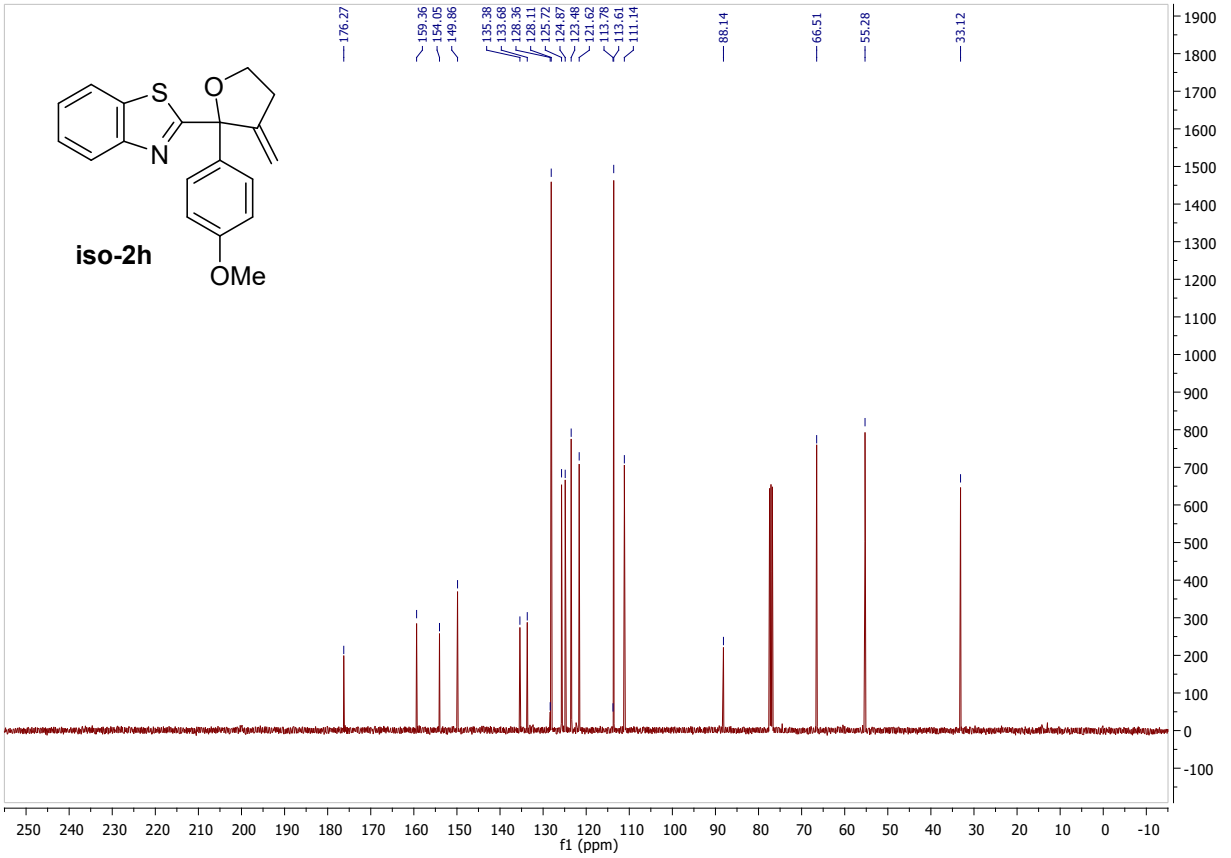

SH_4_141_1_frac1_1H
2g
Me
CF3
f1 (ppm)

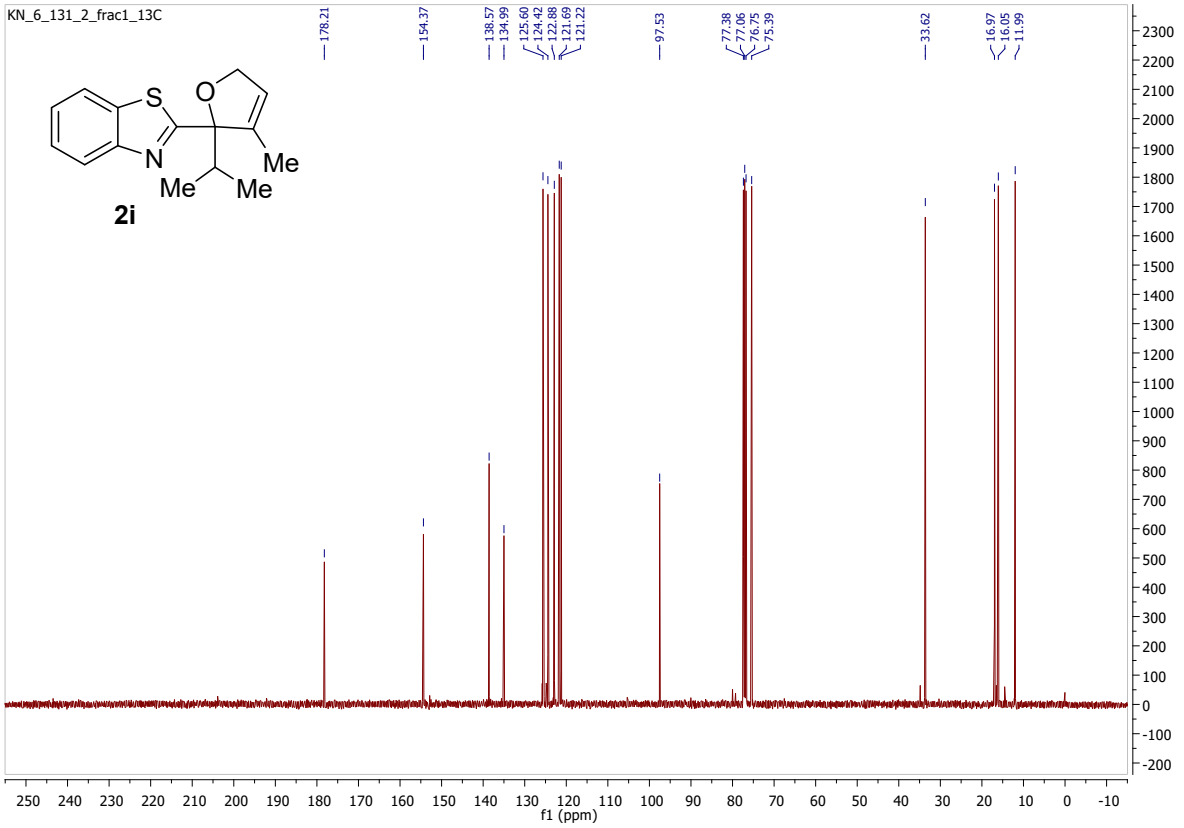

SH_4_141_1_frac1_13C
2g
Me
CF3
f1 (ppm)

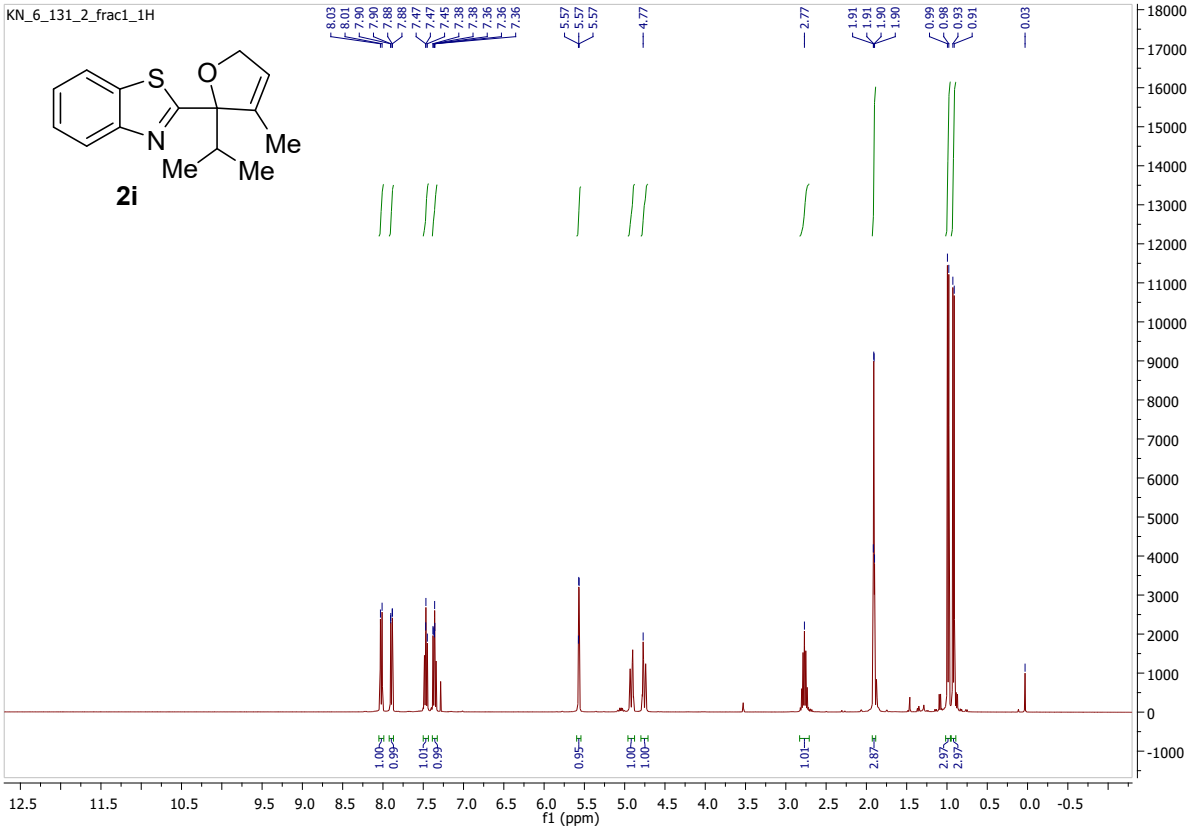

8.10
8.08
8.08
7.96
7.96
7.94
7.94
7.47
7.44
6.93
6.91
5.78
5.77
4.94
4.93
4.93
3.82
2.00
2.00
2.00
1.99
S
O
N
Me
2h
OMe
1.00
1.00
4.25
2.01
1.00
2.00
3.00
3.00
f1 (ppm)

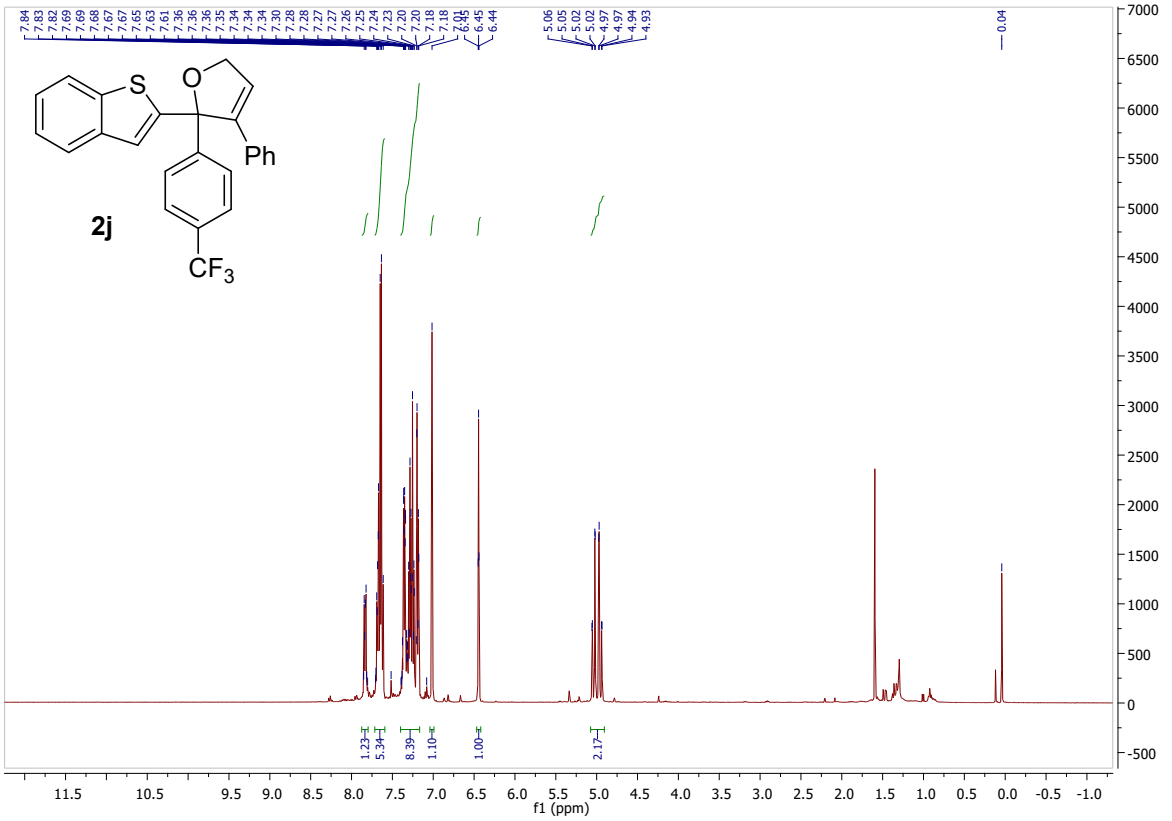

175.94
159.49
154.30
139.72
135.13
133.05
128.35
125.75
124.79
123.35
122.34
121.67
113.77
94.92
77.40
77.08
76.76
74.50
55.33
12.93
S
O
N
Me
2h
OMe
f1 (ppm)

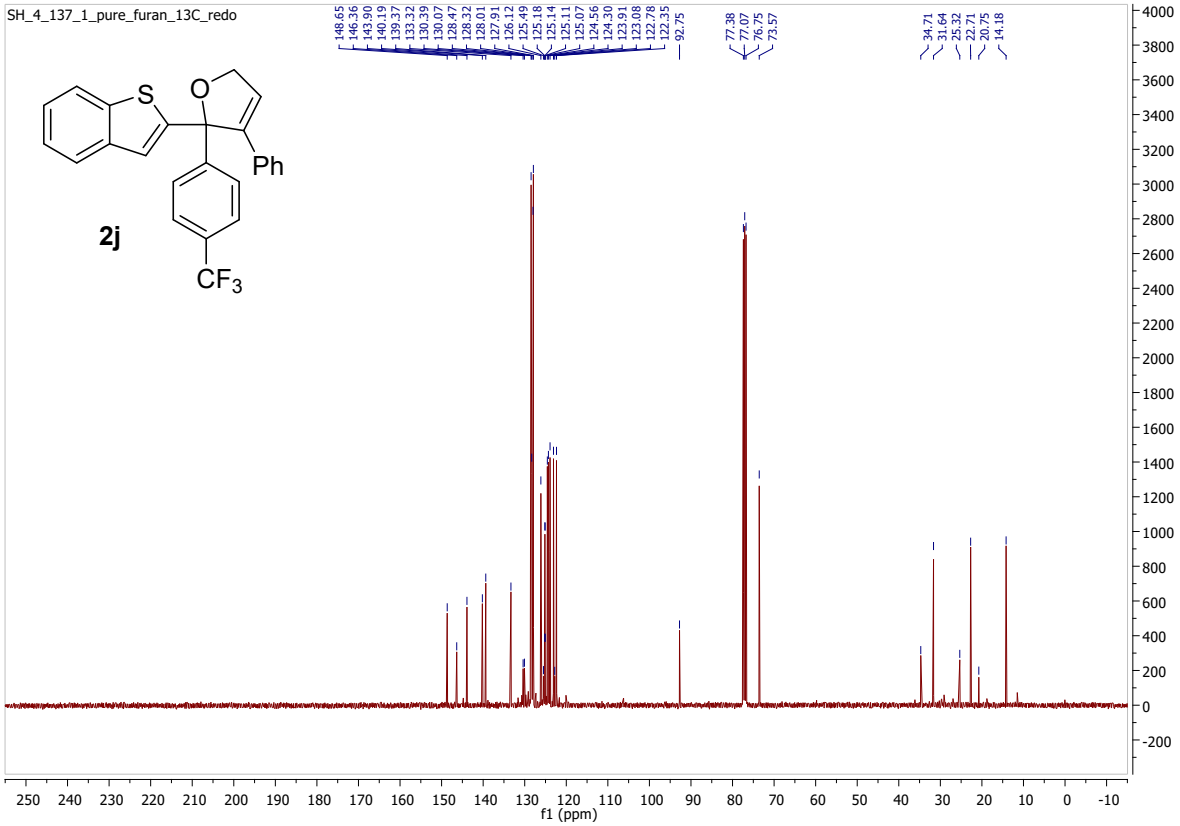

iso-2h
OMe
f1 (ppm)

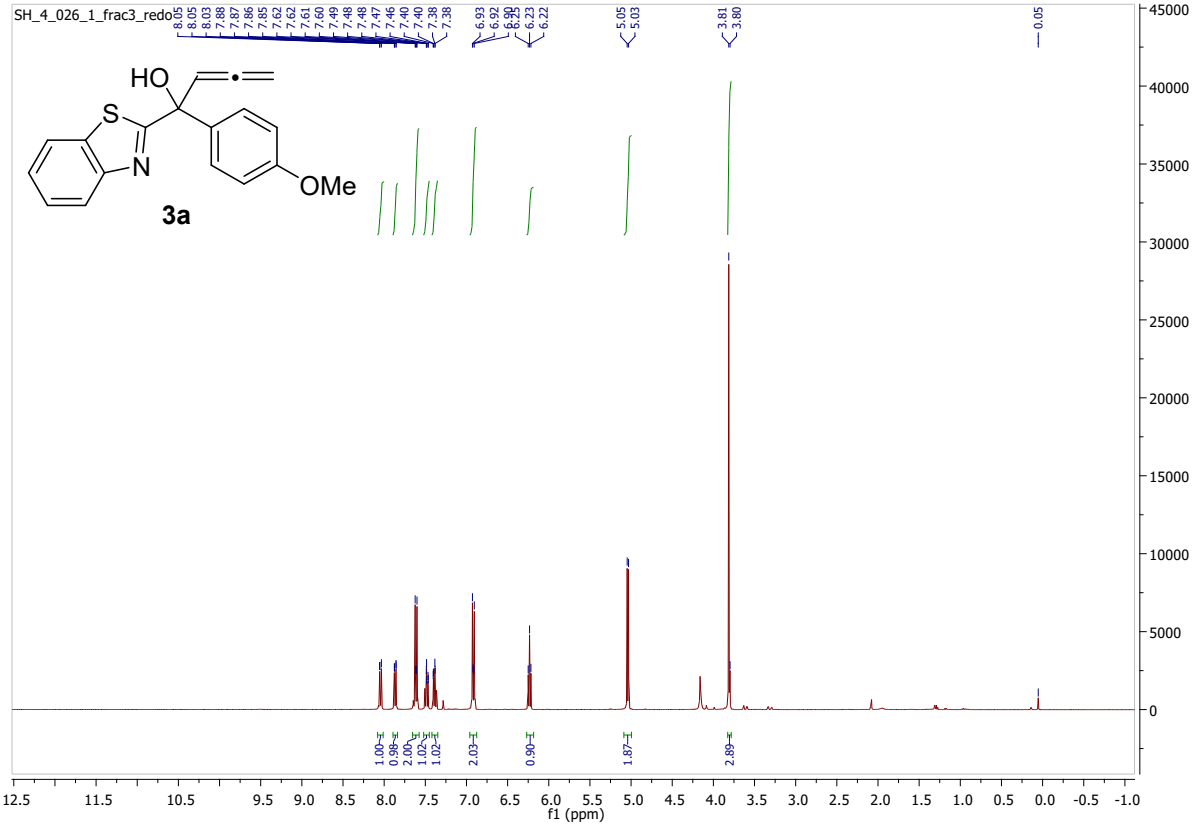

iso-2h
OMe
f1 (ppm)

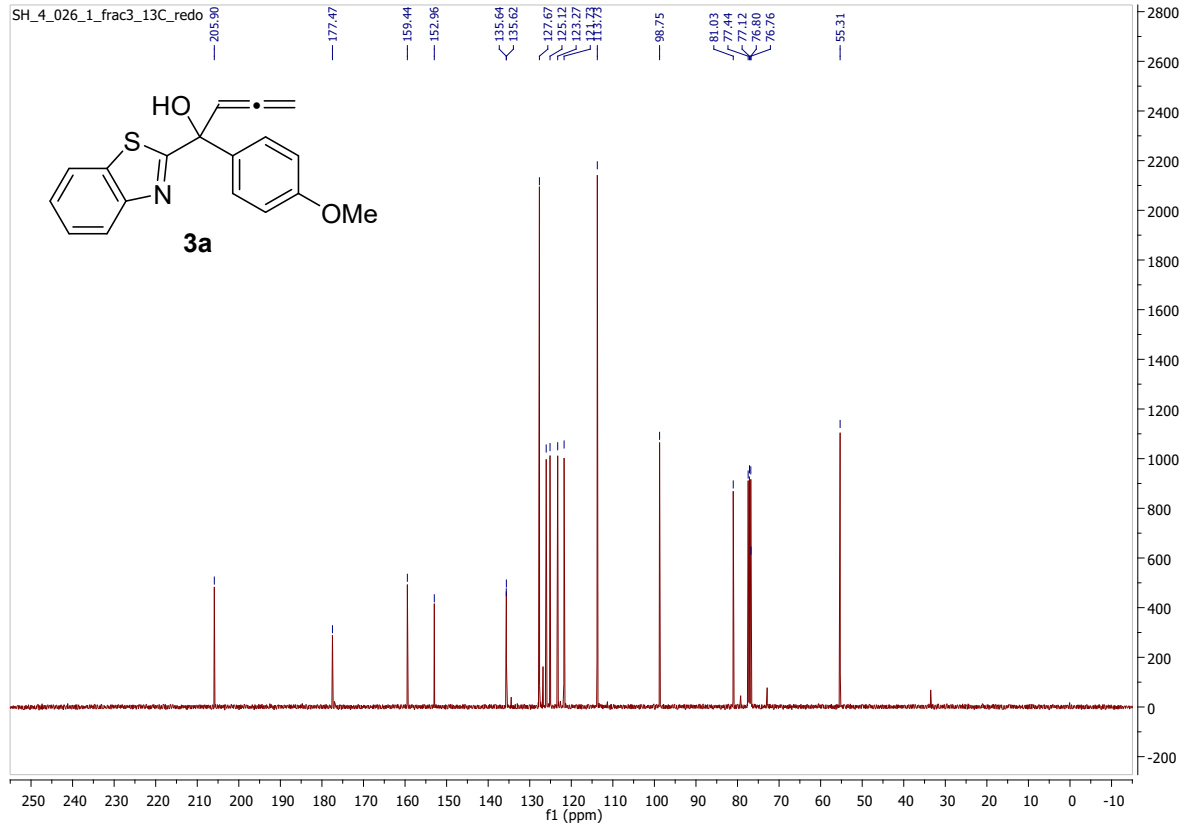

KN_6_131_2_frac1_13C
178.21
154.37
138.57
134.99
125.60
124.42
122.88
121.69
121.22
97.53
77.38
77.06
76.75
75.39
33.62
16.97
16.05
11.99
S
O
N
Me
Me
Me
2i
f1 (ppm)

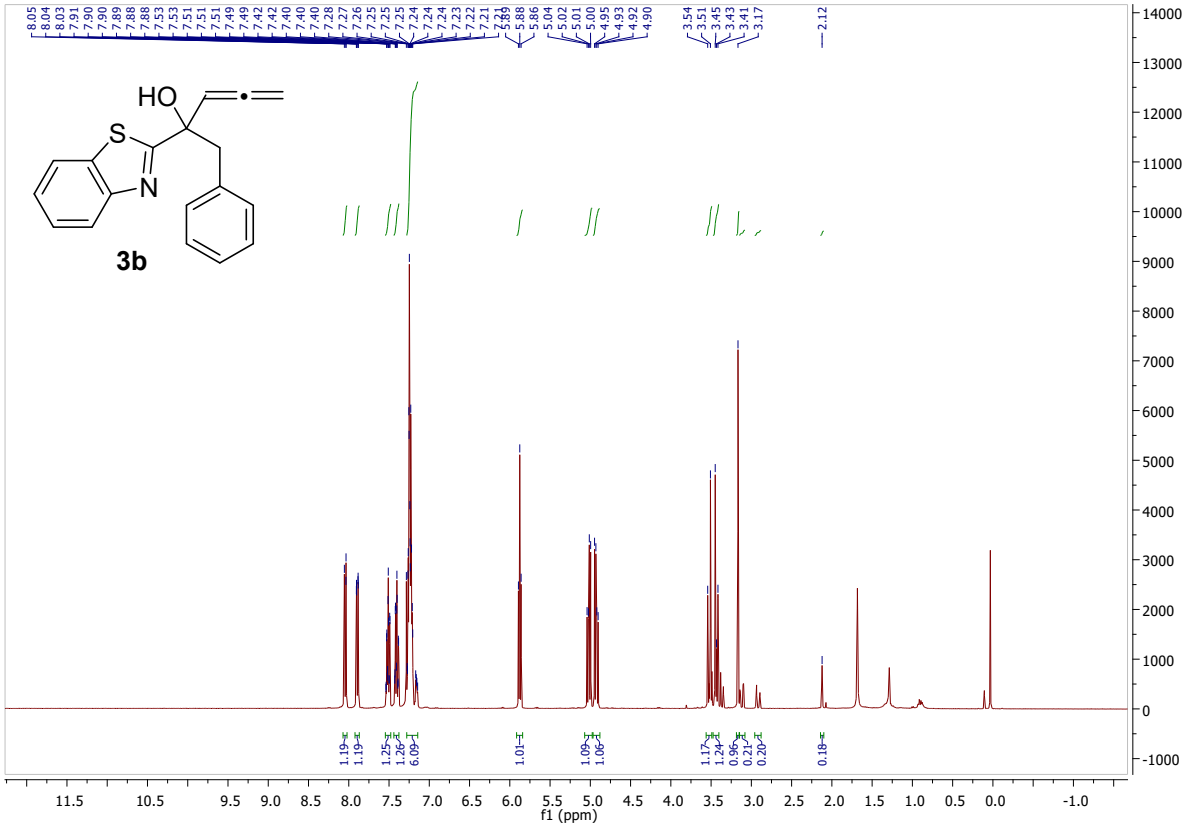

KN_6_131_2_frac1_1H
8.03
8.01
7.90
7.90
7.88
7.88
7.47
7.47
7.45
7.38
7.38
7.36
7.36
7.36
5.57
5.57
5.57
4.77
2.77
1.91
1.91
1.90
1.90
0.99
0.98
0.93
0.91
0.03
1.00
0.99
1.01
0.99
0.95
1.00
1.00
1.01
2.87
2.97
2.97
S
O
N
Me
Me
Me
2i
f1 (ppm)

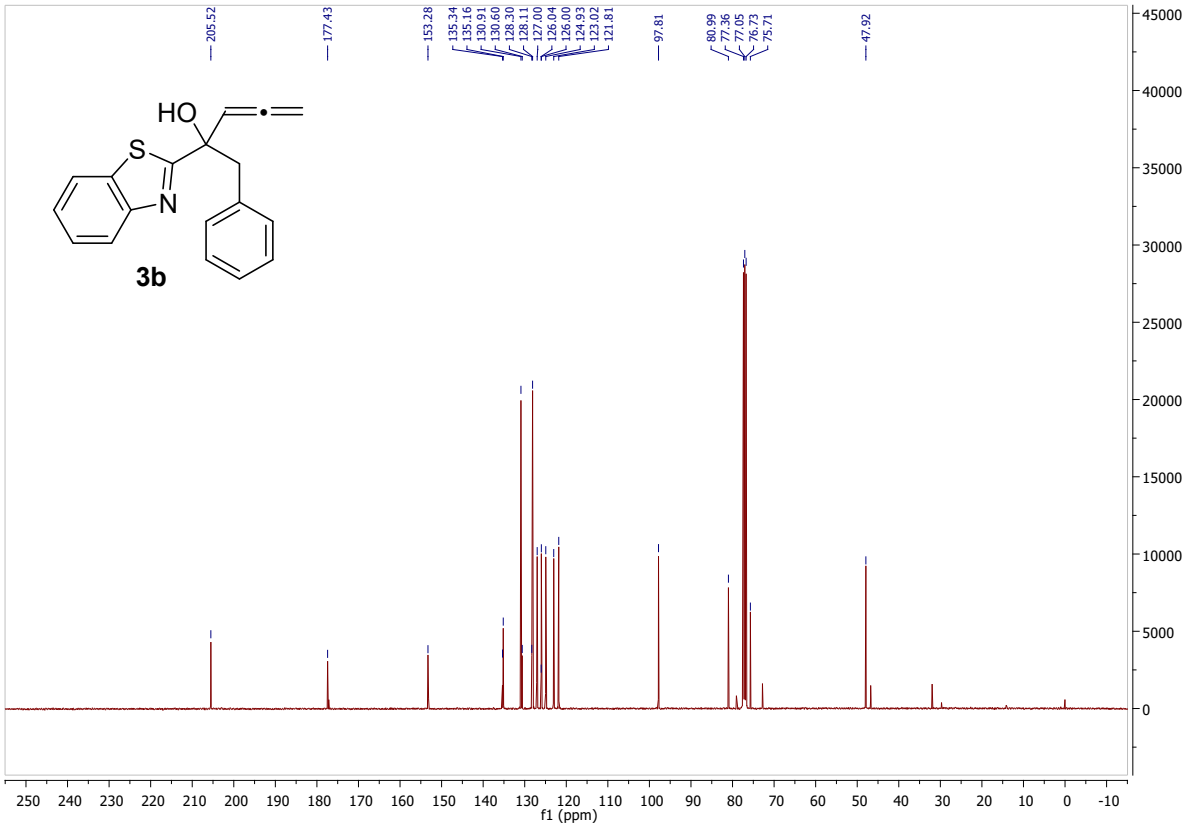

2j
S
O
Ph
CF3
f1 (ppm)

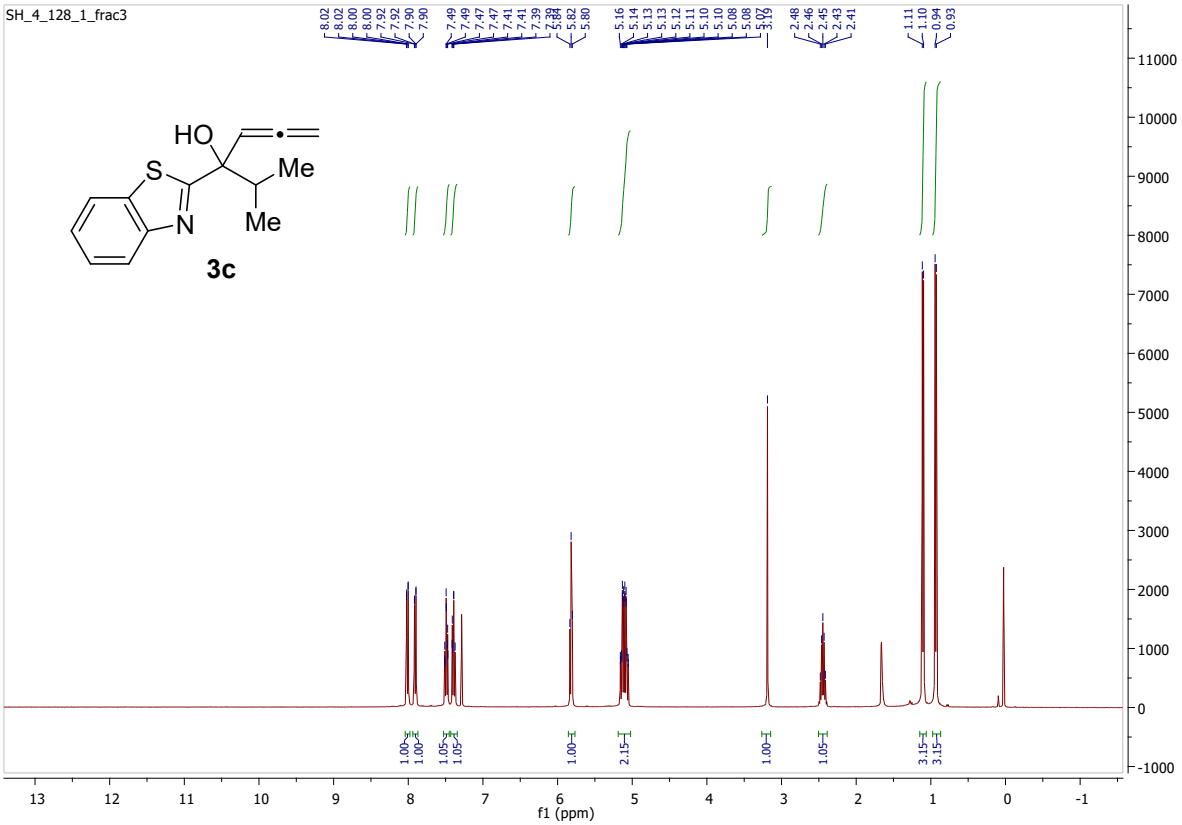

SH_4_137_1_pure_furan_13C_redo
2j
S
O
Ph
CF3
f1 (ppm)

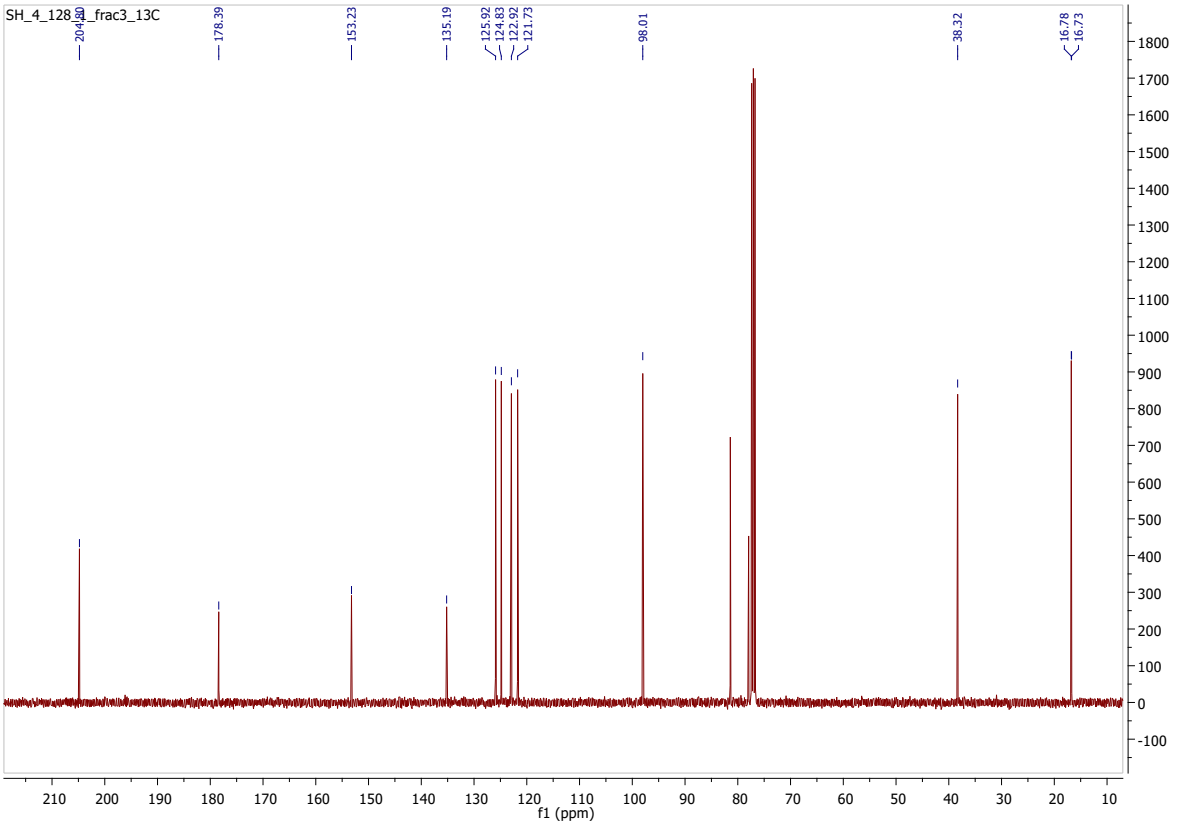

SH_4_026_1_frac3_redo
HO
S
N
OMe
3a
f1 (ppm)

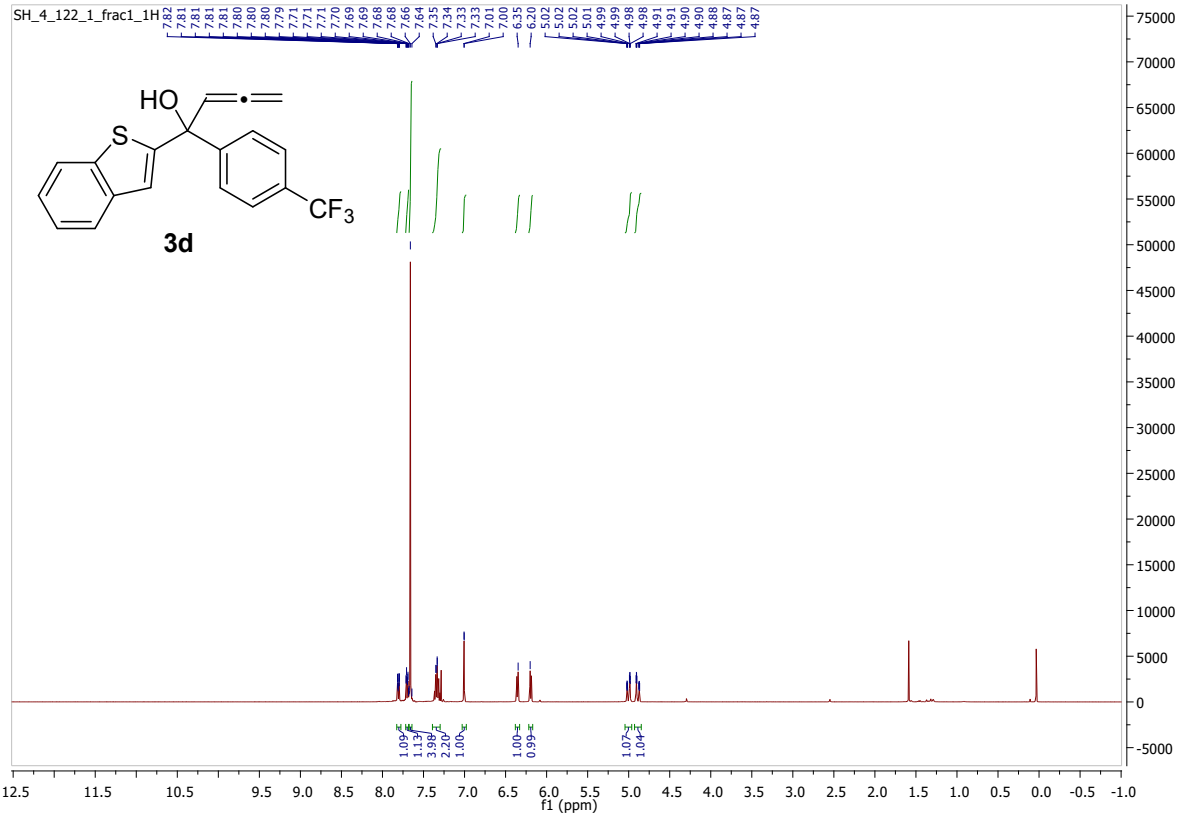

SH_4_026_1_frac3_13C_redo
HO
S
N
OMe
3a
f1 (ppm)

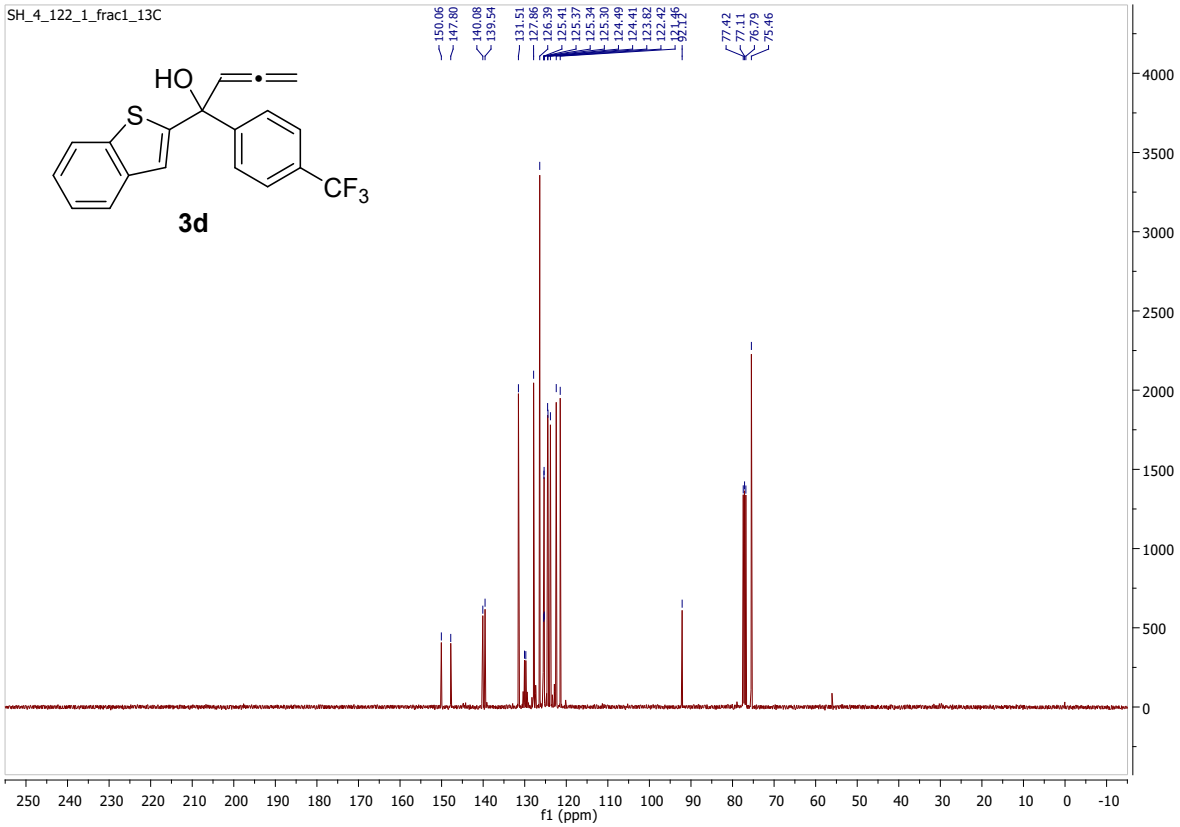

HO
S
N
3b
f1 (ppm)

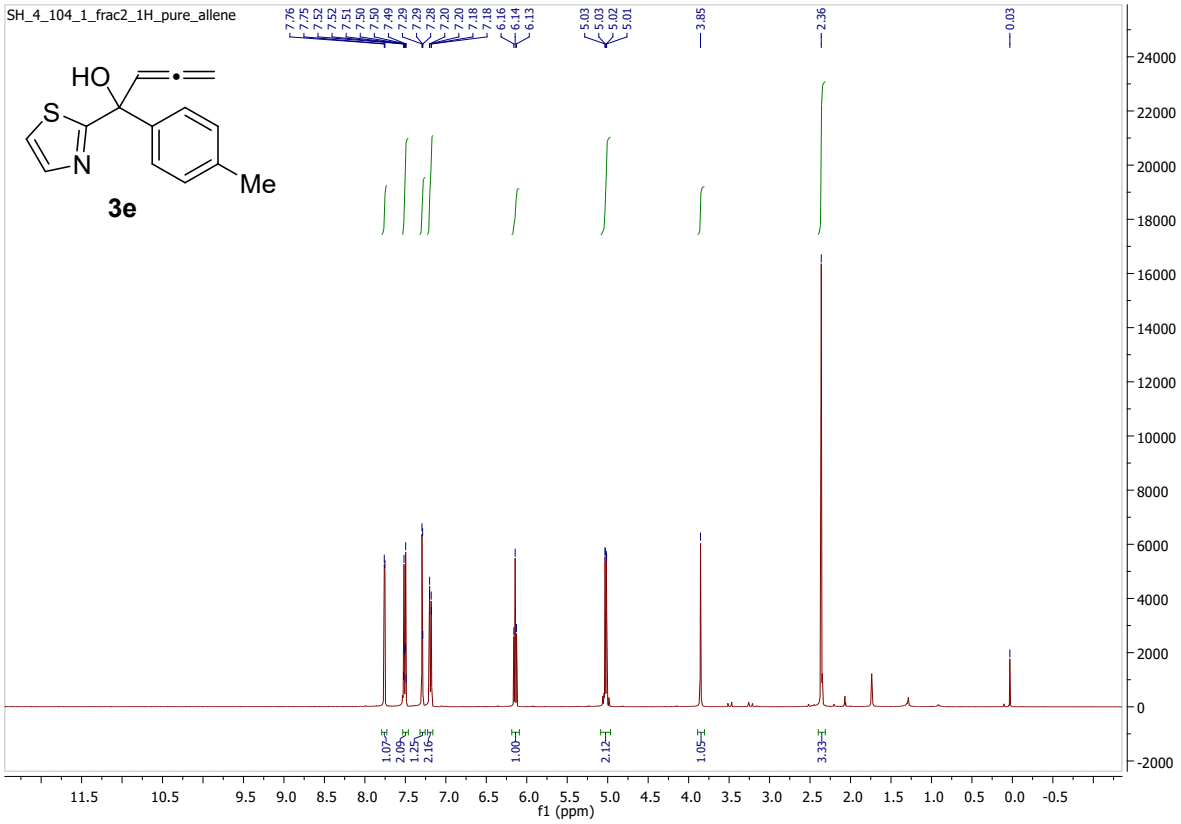

HO
S
N
3b
f1 (ppm)

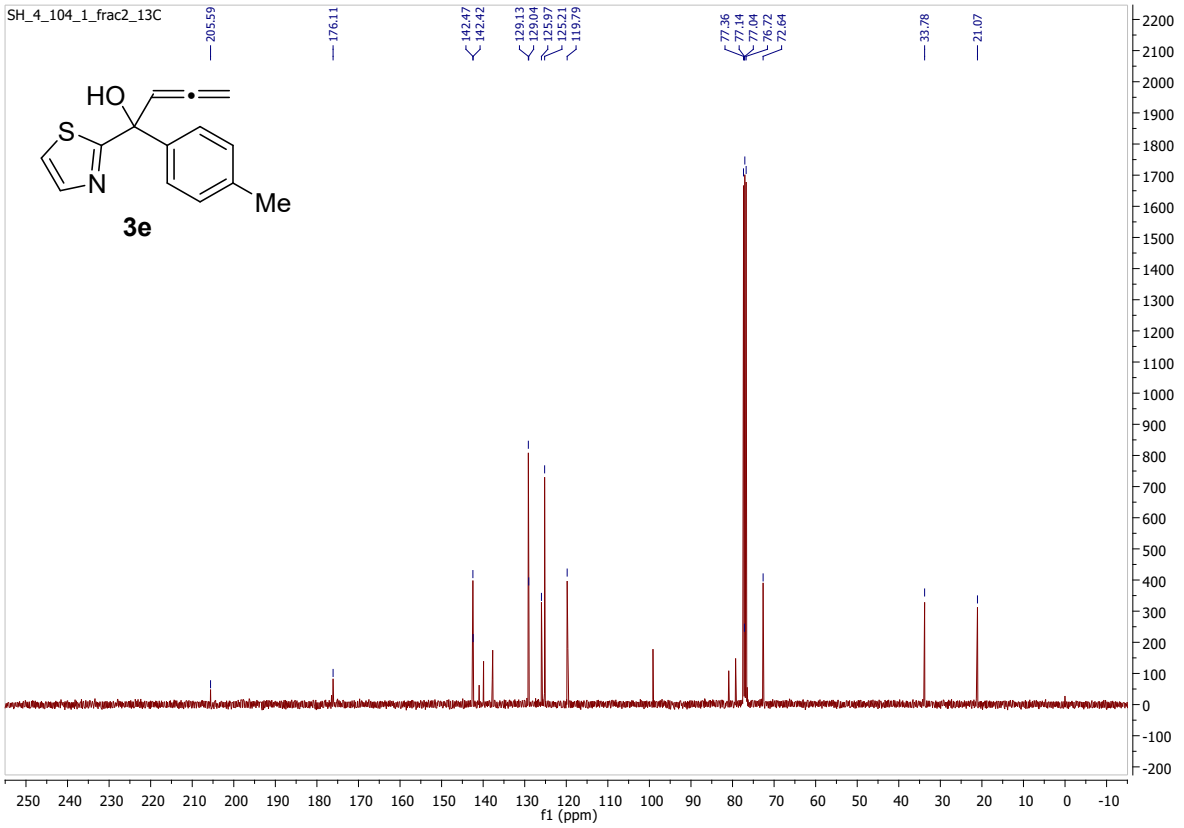

SH_4_128_1_frac3
HO
S
N
Me
Me
3c
f1 (ppm)

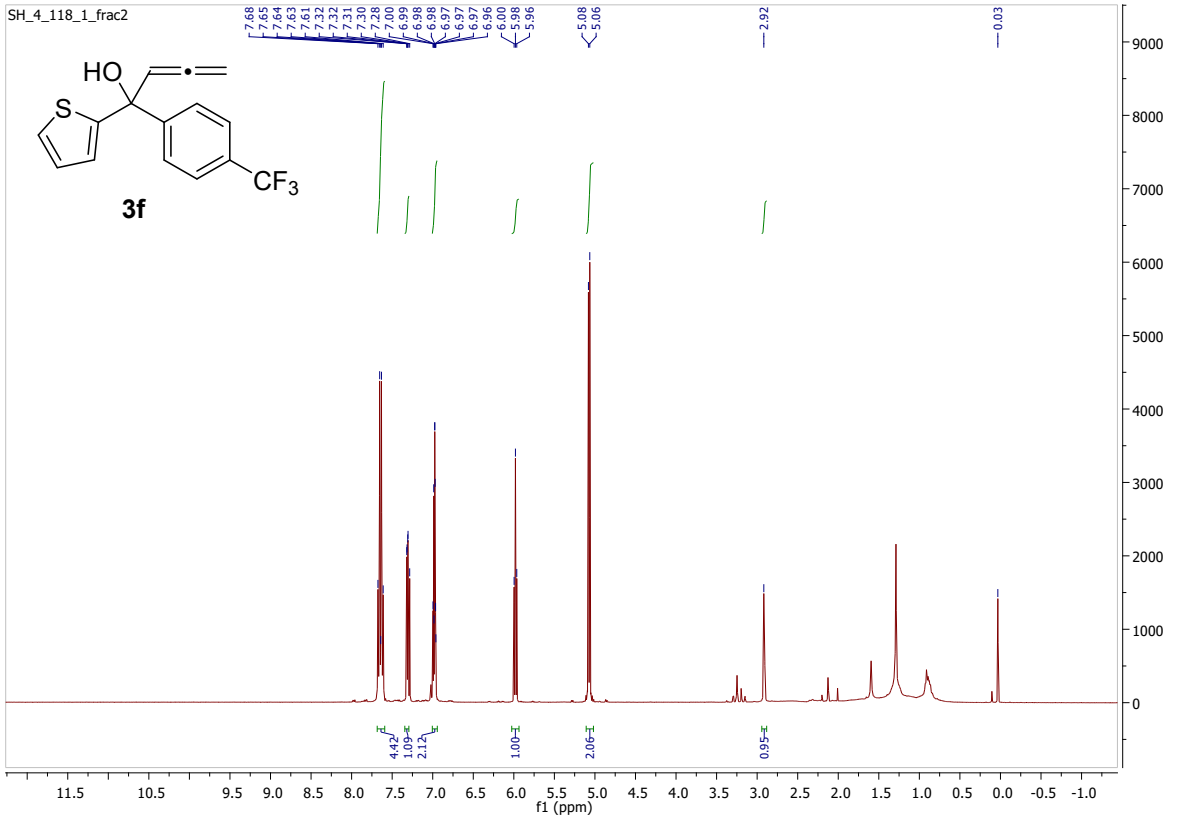

SH_4_128_1_frac3_13C
204.40
178.39
153.23
135.19
125.92
124.83
122.92
121.73
98.01
38.32
16.78
16.73
f1 (ppm)

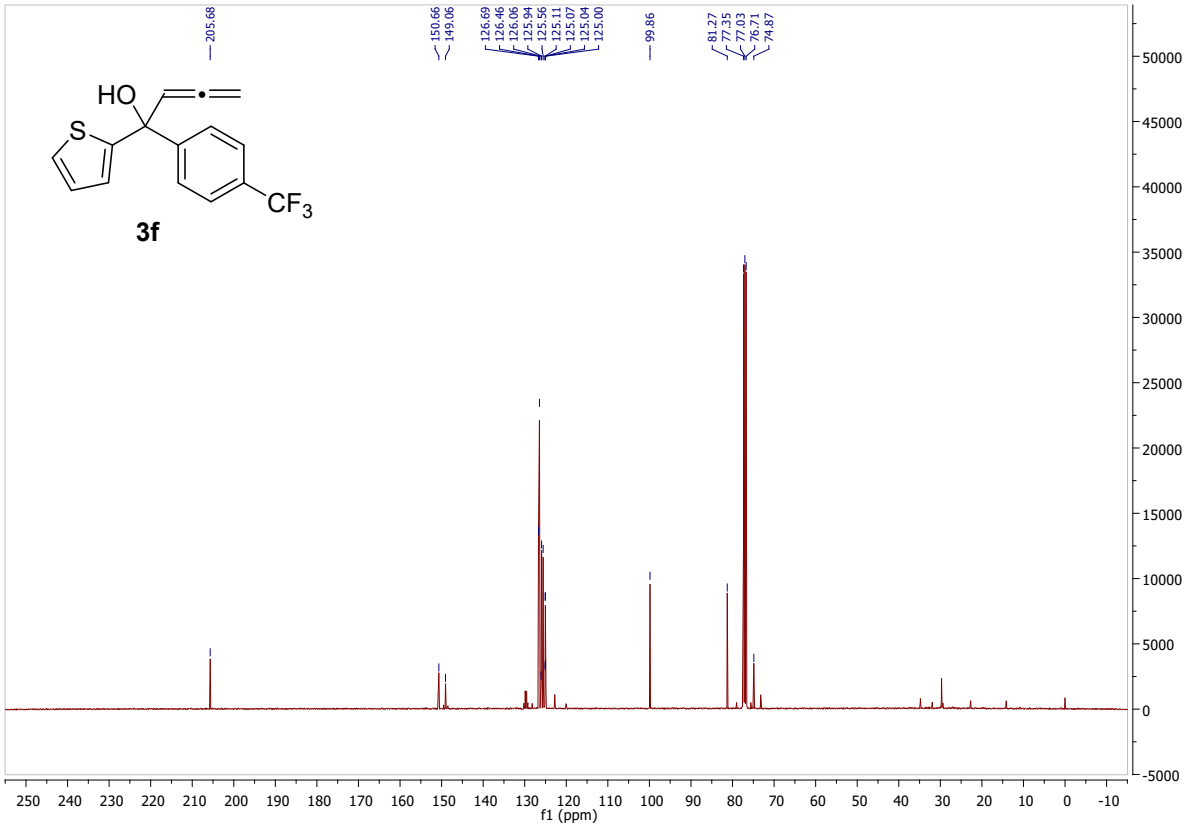

SH_4_122_1_frac1_1H
HO
S
CF3
3d
f1 (ppm)

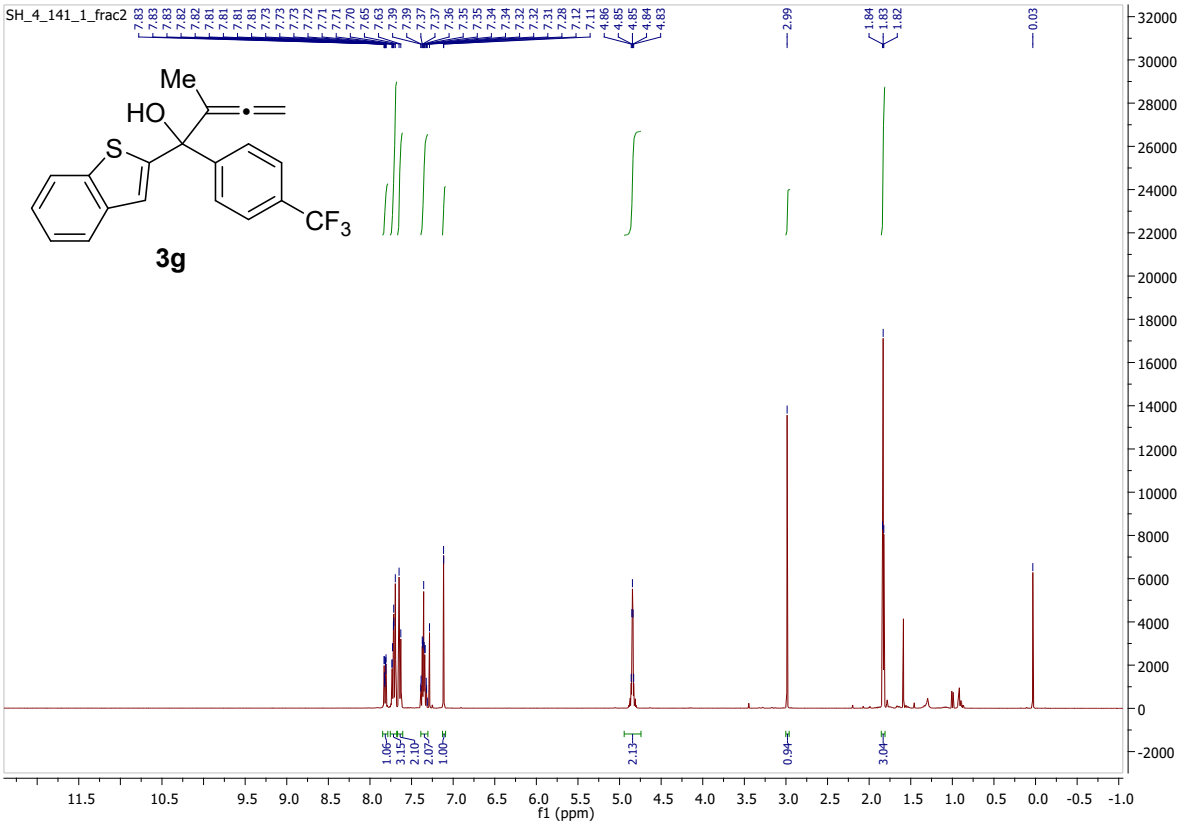

SH_4_122_1_frac1_13C
HO
S
CF3
3d
f1 (ppm)

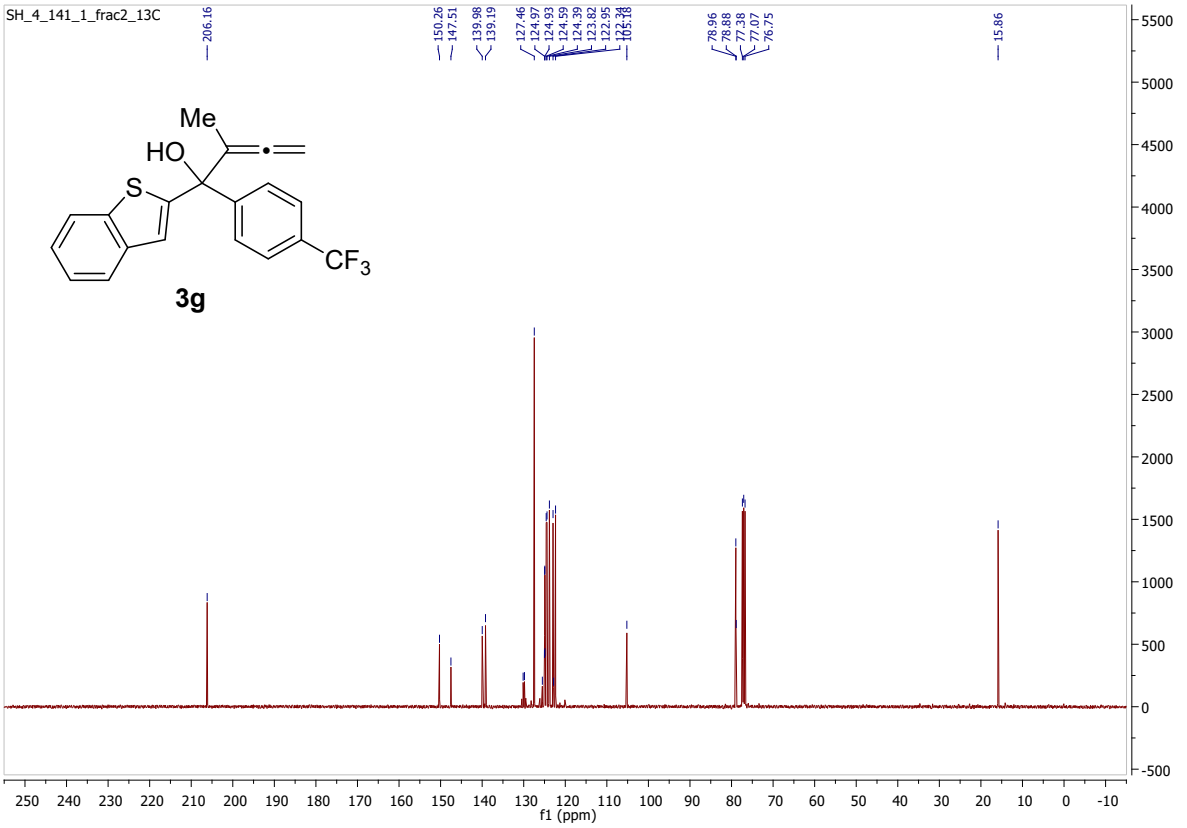

SH_4_104_1_frac2_1H_pure_allene
HO
S
N
Me
3e
7.76
7.75
7.52
7.52
7.51
7.50
7.50
7.49
7.29
7.29
7.28
7.20
7.20
7.18
7.18
6.16
6.14
6.13
5.03
5.03
5.02
5.01
3.85
2.36
0.03
1.07
2.09
1.25
2.16
1.00
2.12
1.05
3.33
f1 (ppm)

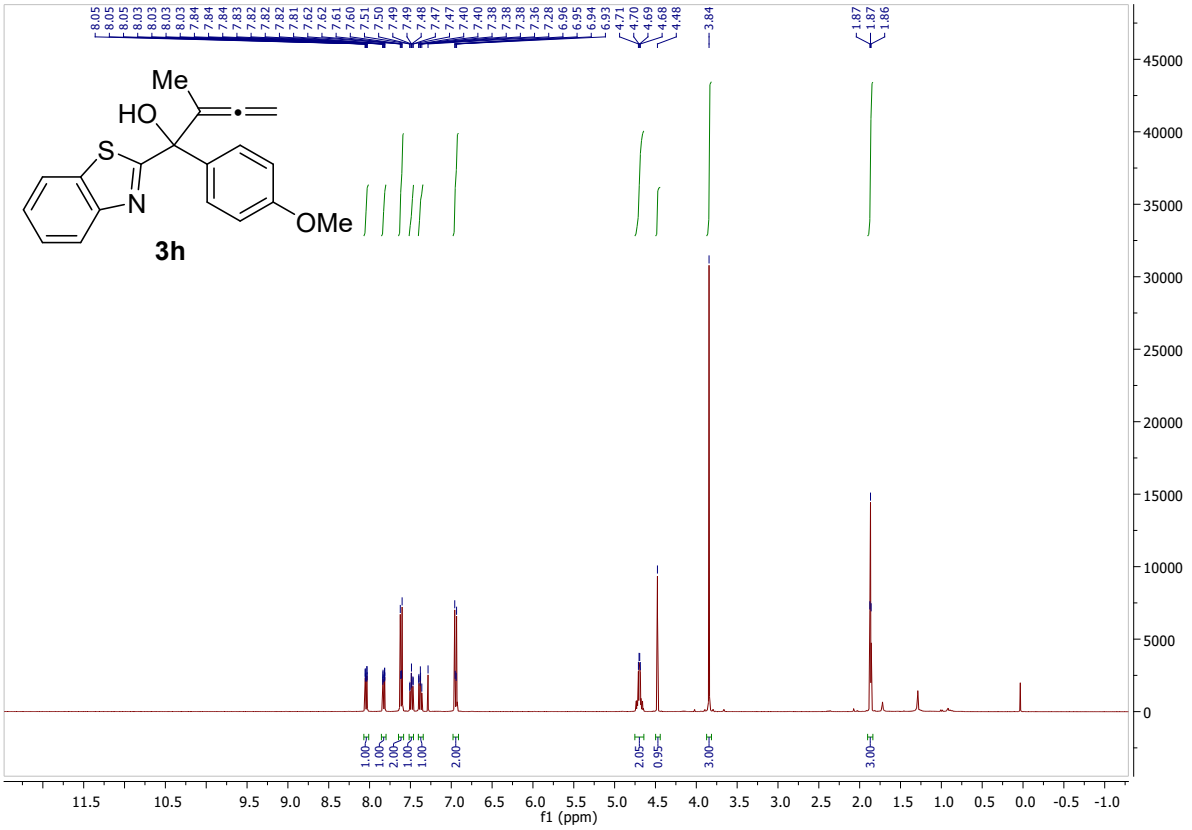

SH_4_104_1_frac2_13C
HO
S
N
Me
3e
205.59
176.11
142.47
142.42
129.13
129.04
125.97
125.21
119.79
77.36
77.14
77.04
76.72
72.64
33.78
21.07
f1 (ppm)

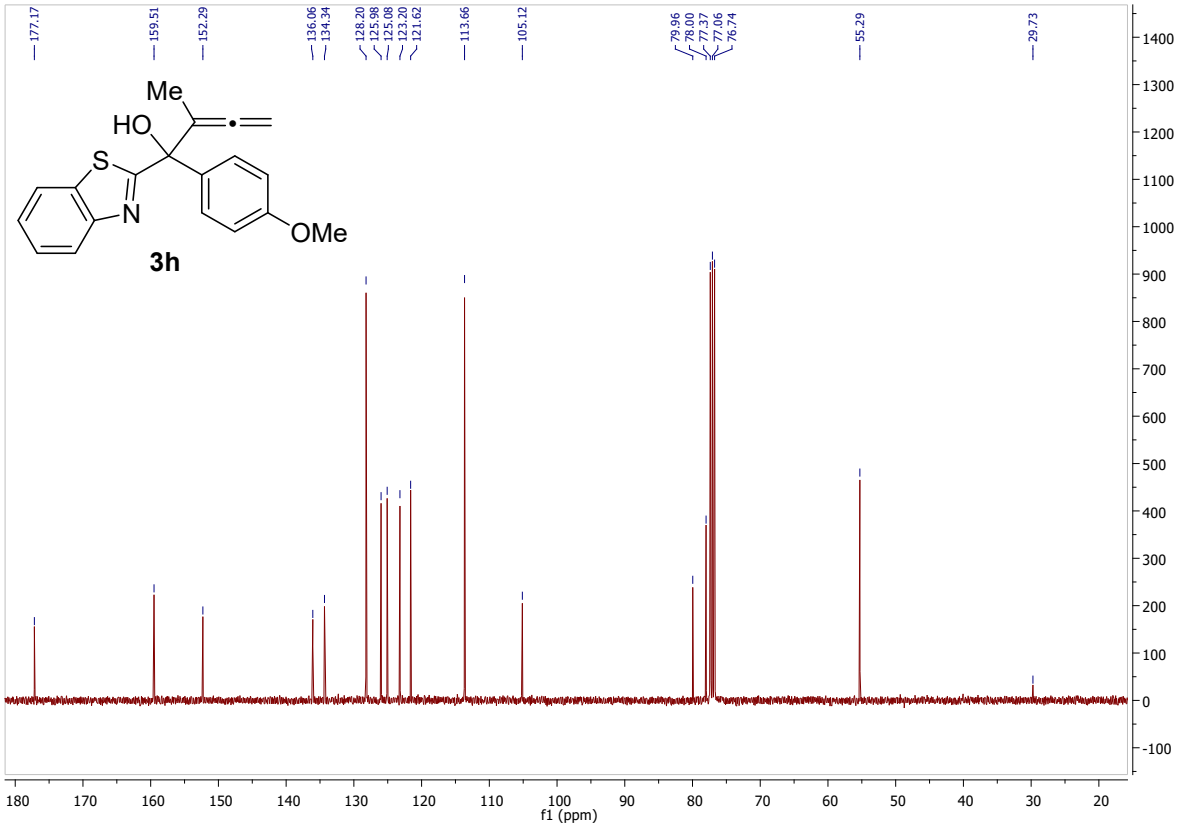

SH_4_118_1_frac2
HO
S
CF3
3f
7.68
7.65
7.64
7.63
7.61
7.32
7.32
7.31
7.30
7.28
7.00
6.99
6.98
6.98
6.97
6.97
6.97
6.96
6.00
5.98
5.96
5.08
5.06
2.92
0.03
4.42
1.09
2.12
1.00
2.06
0.95
f1 (ppm)

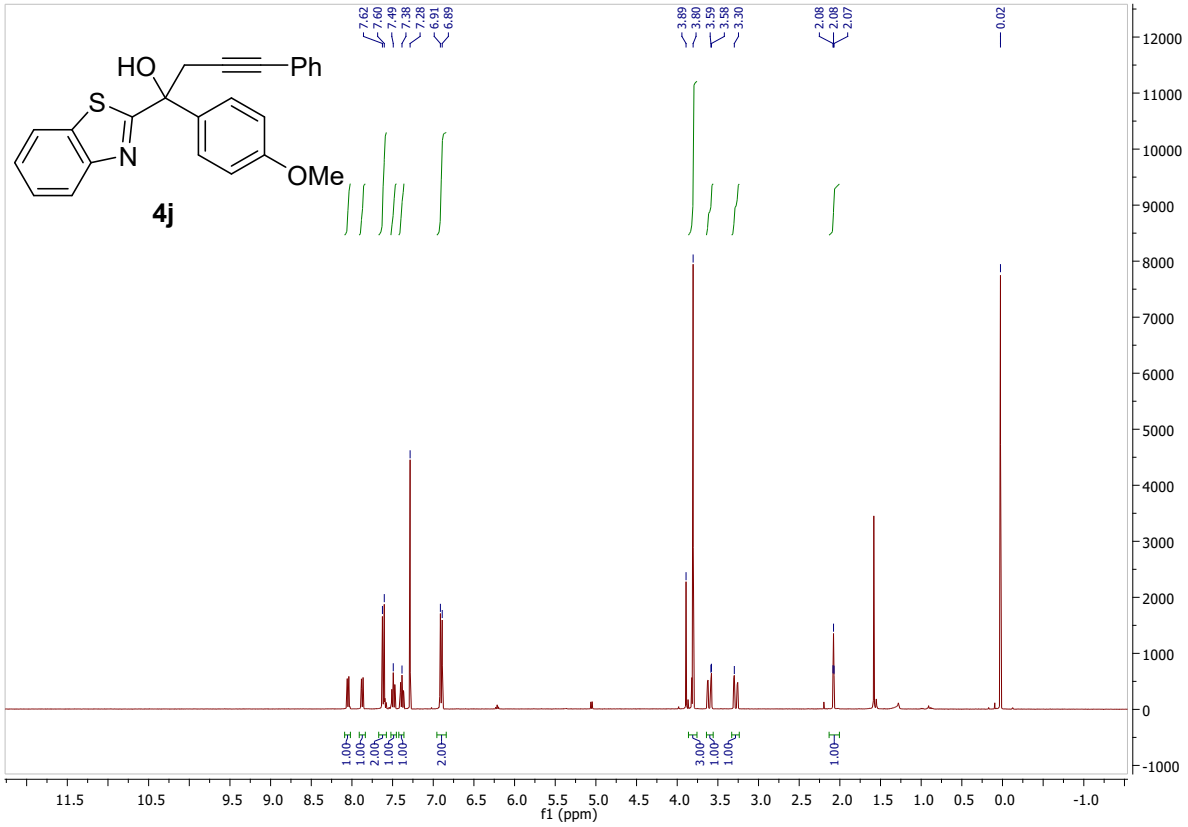

HO
S
CF3
3f
205.68
150.66
149.06
126.69
126.46
126.06
125.94
125.56
125.11
125.07
125.04
125.00
99.86
81.27
77.35
77.03
76.71
74.87
f1 (ppm)

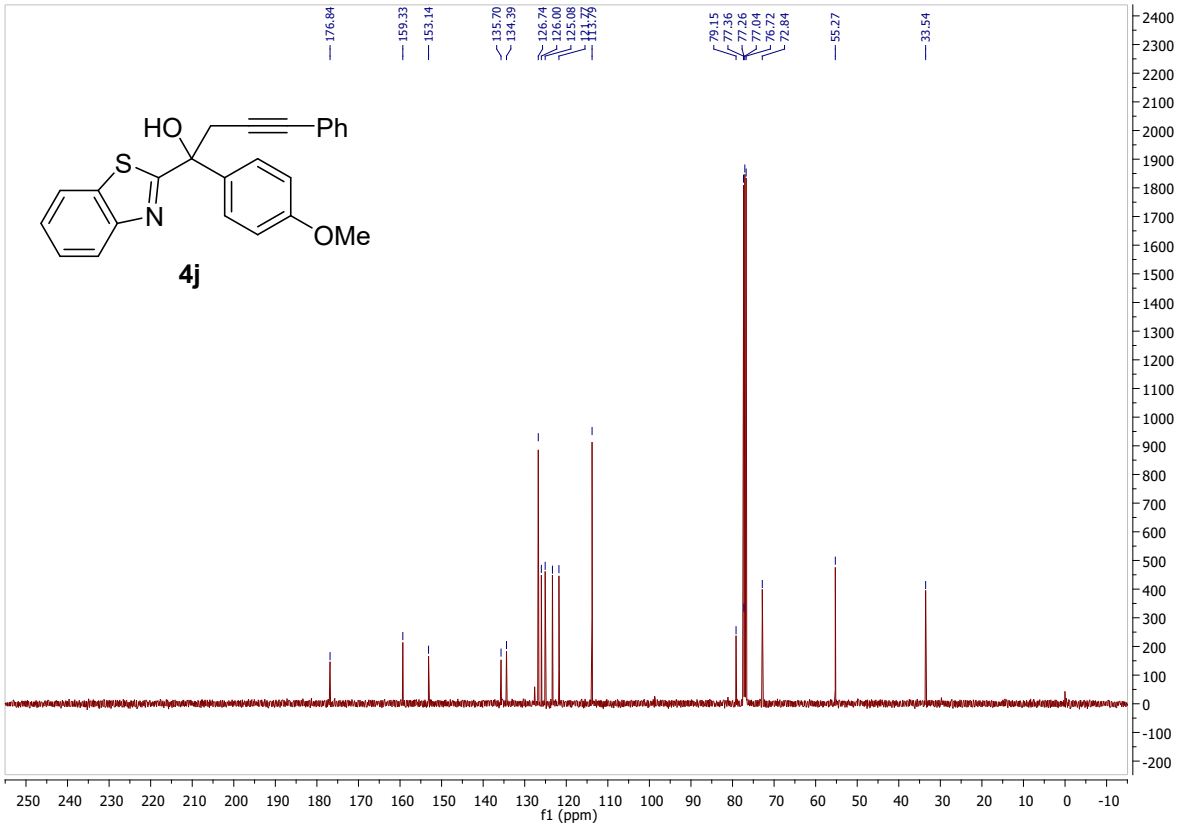

SH_4_141_1_frac2
Me
HO
S
CF3
3g
f1 (ppm)


SH_4_141_1_frac2_13C
Me
HO
S
CF3
3g
f1 (ppm)


Me
HO
S
N
OMe
3h
f1 (ppm)


Me
HO
S
N
OMe
3h
f1 (ppm)


HO
Ph
S
N
OMe
4j
7.62
7.60
7.49
7.38
7.28
6.91
6.89
3.89
3.80
3.59
3.58
3.30
2.08
2.08
2.07
0.02
f1 (ppm)


HO
Ph
S
N
OMe
4j
176.84
159.33
153.14
135.70
134.39
126.74
126.00
125.08
79.15
77.36
77.26
77.04
76.72
72.84
55.27
33.54
f1 (ppm)