Electronic Supplementary Information

N-Sulfenyl Phthalimides Enabled Markovnikov Hydrothiolation of Unactivated Alkenes *via* Ligand Promoted Cobalt Catalysis

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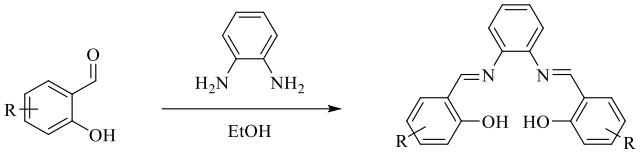
1. General Information.

All chemicals, unless otherwise noted, were purchased from commercial sources and were used without further purification. Unless stated otherwise, all reactions were carried out under argon atmosphere. Ligand **L_1-L_4** were purchased from Bidepharm. Diphenylsilane (Ph_2SiH_2) was purchased from Bidepharm. All other commercial reagents and solvents were purchased from Energy-Chemical Ltd., Bidepharm. and Macklin Biochemical Co. Ltd., respectively, and used as received unless otherwise noted. Starting materials including **a1-a11**, **a13**, **a25**, **a28**, **a34**, **a39, a41** and **a55** were purchased from bidepharm. and Energy-Chemical Ltd. Substrates **a12, a14-a24**, **a26-a27**, **a29-a33**, **a35-38**, **a40** and **b43-b53** are known compounds and were prepared according to previously reported procedures with slight modification. Biologically active molecules **a56-a63** were synthesized according to the literatures with slight modification. The material of the reaction vessel is common glass from Synthware and then put it on magnetic stirring.

The nuclear magnetic resonance spectra were recorded on the Bruker Ascend^{TM} 400 MHz NMR spectrometer or Bruker AVANCE NEO 600 MHz NMR spectrometer with tetramethylsilane (TMS) as an internal standard. All ^{1}H NMR data are reported in δ units, parts per million (ppm), and were measured relative to the residual proton signal in the deuterated solvent at 7.26 ppm ($CDCl_3$) and 3.31 ppm (d_4-CH_3OH). All ^{13}C NMR spectra are ^{1}H decoupled and reported in ppm relative to the solvent signal at 77.16 ppm ($CDCl_3$) and 48.8 ppm (d_4-CH_3OH). High resolution mass spectra were recorded using a Q Exactive mass spectrometer (Thermo Fisher Scientific, USA). Digital melting point apparatus was used to record the Melting Point of the compound in degree centigrade (°C) and are uncorrected.

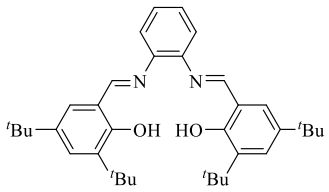
2. Experimental Procedures.

2.1) Synthesis of Ligand [1-4].



1,2-diaminobenzene (1.0 equiv., 0.5 mmol) was added to a solution of salicylaldehyde analogues (2.0 equiv., 1 mmol) in ethanol (2 mL) and stirred overnight at room temperature under argon atmosphere. The product of the reaction was filtered, washed with a small amount of hexane, and the solid residue was drained under vacuum and stored under argon atmosphere protection.

L5



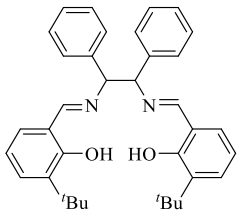
Yellow solid. 232 mg, 90% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 13.58 (s, 2H), 8.69 (s, 2H), 7.47 (s, 2H), 7.34 (dt, *J* = 7.2, 3.6 Hz, 2H), 7.30 – 7.22 (m, 4H), 1.47 (s, 18H), 1.35 (s, 18H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.7, 158.6, 142.8, 140.3, 137.2, 128.2, 127.3, 126.8, 119.8, 118.4, 35.1, 34.2, 31.5, 29.4.

HRMS (ESI) m/z: Calcd for $C_{34}H_{48}N_2O_2Na$ $[M+Na]^+$: 539.3608; found: 539.3610.

L6



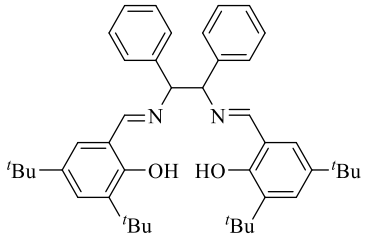
Yellow solid. 188 mg, 71% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 13.81 (s, 2H), 8.39 (s, 2H), 7.30 – 7.17 (m, 12H), 7.02 (d, *J* = 7.2 Hz, 2H), 6.74 (t, *J* = 5.2 Hz, 2H), 4.75 (s, 2H), 1.45 (s, 18H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.9, 160.3, 139.5, 137.1, 130.1, 129.6, 128.3, 128.0, 127.5, 118.6, 117.9, 80.2, 34.8, 29.3.

HRMS (ESI) m/z: Calcd for $C_{36}H_{40}N_2O_2Na$ $[M+Na]^+$: 555.2982; found: 555.2977.

***L*$_7$**



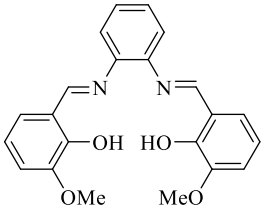
Yellow solid. 273 mg, 85% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 13.62 (s, 2H), 8.42 (s, 2H), 7.33 (d, *J* = 2.5 Hz, 2H), 7.20 (q, *J* = 4.6, 3.9 Hz, 10H), 7.00 (d, *J* = 2.5 Hz, 2H), 4.75 (s, 2H), 1.44 (s, 18H), 1.23 (s, 18H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.2, 158.0, 140.0, 139.8, 136.4, 128.3, 128.0, 127.4, 127.1, 126.3, 117.9, 80.1, 35.0, 34.0, 31.4, 29.4.

HRMS (ESI) m/z: Calcd for $C_{44}H_{56}N_2O_2Na$ $[M+Na]^+$: 667.4234; found: 667.4233.

***L*$_8$**



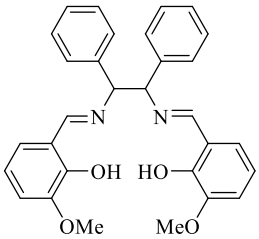
Red solid. 149 mg, 95% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 13.20 (s, 2H), 8.64 (s, 2H), 7.37 – 7.31 (m, 2H), 7.22 – 7.17 (m, 2H), 7.01 (dd, *J* = 14.6, 7.8 Hz, 4H), 6.88 (t, *J* = 8.1 Hz, 2H), 3.91 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.3, 151.6, 148.6, 142.5, 127.6, 123.9, 120.3, 119.2, 118.5, 115.1, 56.2.

HRMS (ESI) m/z: Calcd for $C_{22}H_{20}N_2O_4Na$ $[M+Na]^+$: 399.1315; found: 399.1320.

***L*$_9$**



Yellow solid. 200 mg, 84% yield.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 13.83 (s, 2H), 8.39 (s, 2H), 7.27 – 7.05 (m, 10H), 7.01 – 6.69 (m, 6H), 4.72 (s, 2H), 3.91 (s, 6H).

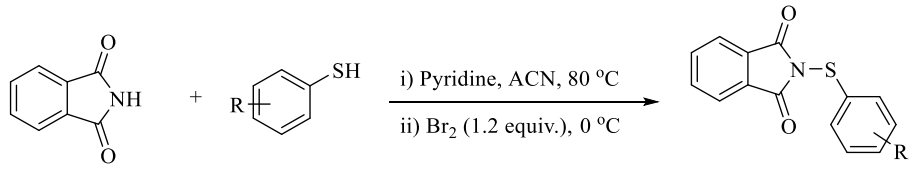
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.1, 151.1, 148.1, 139.1, 128.3, 127.9, 127.6, 123.4, 118.4, 118.2, 114.2, 80.3, 56.0.

HRMS (ESI) m/z: Calcd for $C_{30}H_{28}N_2O_4Na$ $[M+Na]^+$: 503.1941; found: 503.1944.

2.2) Synthesis of starting materials.

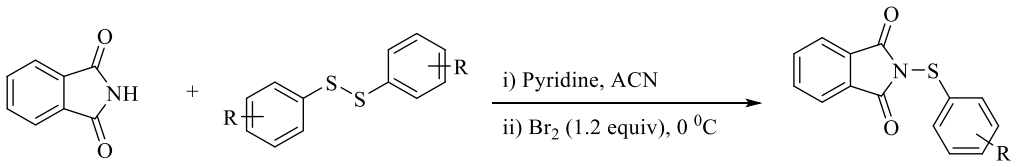
2.2.1 Synthesis of *N*-sulfenyl phthalimides.

Method A for N- sulfenyl phthalimides [5]:



A suspension of phthalimide (1.47 g, 10.0 mmol) and thiophenols (11.0 mmol, 1.1 equiv.) in CH_3CN (5.0 mL) and pyridine (4.0 mL) was heated to 80 ℃ and then cooled to room temperature. The mixture was treated with a solution of Br_2 (615 µL in 5.0 mL CH_3CN, 12.0 mmol, 1.2 equiv.) dropwise over 10 mins. Upon complete addition of Br_2 solution, the mixture was stirred for 2 h at 0 ℃ and was subsequently quenched by dropwise addition of H_2O (15.0 mL). Filtration of the suspension and washing of the precipitate with pre-cooled CH_3OH (0 ℃, 3 × 10.0 mL). Further purification was achieved by recrystallization in ethyl acetate through hot cooling to room temperature. **b44-b45** and **b48-b51** were prepared according to the above procedure.

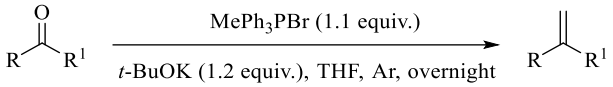
Method B for N-sulfenyl phthalimides [5]:



A suspension of phthalimide (1.47 g, 10.0 mmol) and disufides (11.0 mmol, 1.1 equiv.) in CH_3CN (5.0 mL) and pyridine (4.0 mL) was heated to 80 ℃ and then cooled to room temperature. The mixture was treated with a solution of Br_2 (615 µL in 5.0 mL CH_3CN, 12.0 mmol, 1.2 equiv.) dropwise over 10 mins. Upon complete addition of Br_2 solution, the mixture was stirred for 2 h at 0 ℃ and was subsequently quenched by dropwise addition of H_2O (15.0 mL). Filtration of the suspension and washing of the precipitate with pre-cooled CH_3OH (0 ℃, 3 × 10.0 mL). Further purification was achieved by recrystallization in ethyl acetate through hot cooling to room temperature. **b43, b46-b47**, **b52** and **b53** were prepared according to the above procedure.

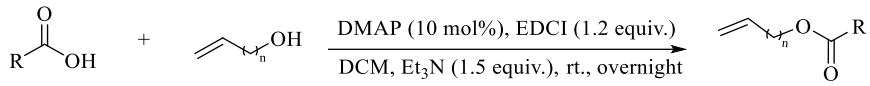
2.2.2 Synthesis of unactivated alkenes.

Method C [6]**:**



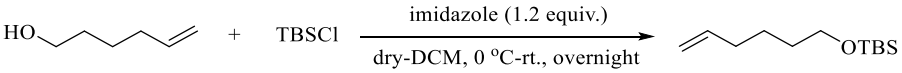
To a solution of methyltriphenylphosphonium bromide (1.13 g, 3.3 mmol) in dry THF (3 mL) was added *t*-BuOK (3.6 mL, 3.6 mmol) under argon and 0 ℃ ice bath and the mixture was stirred for 30 min to 1 hour. Then a solution of ketones (3.0 mmol, 1.0 equiv.) in dry THF (3.0 mL) was added slowly. The mixture was stirred overnight at room temperature. The reaction mixture passed through a silica gel pad (~ 5 g) using *n*-hexane as the eluent and the solvents were removed under reduced pressure. Purification of the crude product by flash column chromatography using *n*-hexane/ethyl acetate as the eluent afforded the substrates. **a35-a38** and **a40** were prepared according to the above procedure.

Method D [7]**:**



A 100 mL flask fitted with a stirring bar was charged with a solution of acids (1.1 equiv., 6.0 mmol), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDCI, 1.15 g, 6.0 mmol), triethylamine (1.04 mL, 7.5 mmol), and 4-dimethylaminopyridine (DMAP, 61.1 mg, 0.5 mmol) in dichloromethane (25.0 mL). Alcohol (1.0 equiv., 5.0 mmol) was then added at 0 °C, and the reaction mixture was stirred overnight at room temperature. The resulting mixture was diluted with DCM (50.0 mL), and washed successively by saturated aqueous $NaHCO_3$, and brine. The organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuo. Purification of the crude product by flash column chromatography using *n*-hexane/ethyl acetate = 10/1 (v/v) as the eluent afforded the desired substrate. **a21-a24**, **a56-a59 and a61-a62** were prepared according to the above procedure.

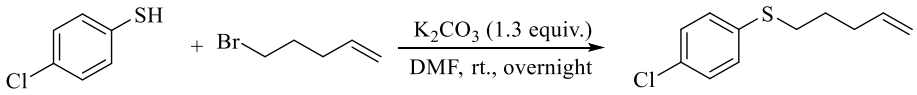
Synthesis of a12 [8]**:**



To a dry round bottom flask containing a magnetic stir bar were added 5-Hexen-1-ol (400 mg, 4 mmol), imidazole (326 mg, 4.8 mmol), and dry DCM (1.0 mL), then TBSCl (720 mg, 4.8 mmol) in dry DCM (0.8 mL) was slowly added at 0 °C. The reaction was warmed to room temperature and stirred overnight, then sat. NH_4Cl aq. was added and extracted with DCM. The combined organic layer was washed with brine, dried with Na_2SO_4, filtered, and concentrated. The crude product was purified by

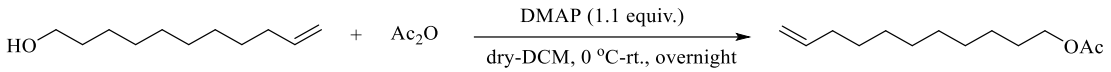
silica gel chromatography using *n*-hexane/ethyl acetate = 20/1 (v/v) as the eluent to give **a12** (700 mg, 82%) as a colorless oil.

***Synthesis of a18 [9]*:**



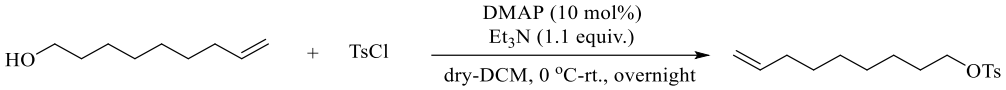
To a solution of 4-chlorothiophenol (432 mg, 3.0 mmol) in DMF (6.5 mL) was added K_2CO_3 (539 mg, 3.9 mmol), followed by the 5-bromo-1-pentene (447 mg, 3 mmol). The reaction was stirred at room temperature overnight and then diluted with water. The combined hexane extracts were dried with Na_2SO_4 and the solvent was removed under reduced pressure. The oily residue was purified by flash chromatography on silica gel (*n*-hexane/ethyl acetate = 100/1 (v/v)). The oily precipitate was dried in vacuo to afford the desired **a18** (564 mg, 89%) as a colorless oil.

***Synthesis of a19 [8]*:**



To a solution of undec-10-en-1-ol (510 mg, 3 mmol) in dry DCM (3 mL) were added DMAP (402 mg, 3.30 mmol) and Ac_2O (314 uL, 3.3 mmol) at 0 ℃, then the reaction was warmed to room temperature. After stirring overnight, sat. NH_4Cl aq. was added and extracted with DCM. The combined organic layer was washed with brine, dried with Na_2SO_4, filtered, and concentrated. The crude product was purified by silica gel chromatography using *n*-hexane/ethyl acetate = 40/1 (v/v) to give **a19** (572 mg, 90%) as a yellow oil.

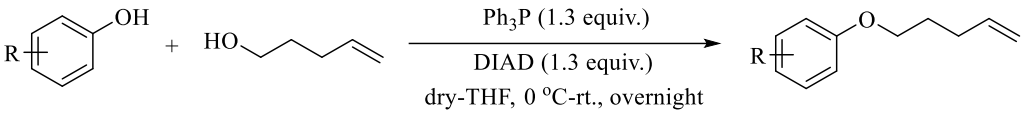
***Synthesis of a20 [10]*:**



An oven-dried 100 mL round-bottom-flask equipped with a Teflon-coated magnetic stir bar was charged with 8-Nonen-1-ol (468 mg, 3.0 mmol) and DMAP (37 mg, 0.3 mmol). The flask was sealed with a rubber septum. The flask was then briefly evacuated and backfilled with nitrogen. Anhydrous DCM (5 mL) and triethylamine (0.45 mL, 3.3 mmol, 1.1 equiv.) were added to the flask via syringe. The solution was cooled to 0 ℃ before a solution of TsCl (627 mg, 3.3 mmol) in 3.0 mL DCM was added. The mixture was stirred at 0 ℃ for 2 h, then quenched with saturated aq. NH_4Cl (30 mL) and extracted with DCM (3 x 20 mL). The combined organic phases were washed with brine, dried over Na_2SO_4 and

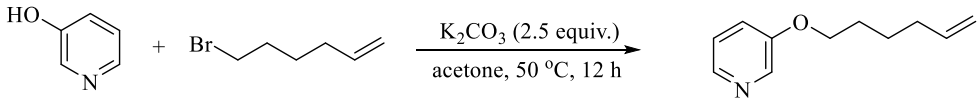
concentrated in vacuo. Purification by column chromatography using *n*-hexane/ethyl acetate = 30/1 (v/v) to afforded **a20** (0.78 g, 86% yield) as a colorless oil.

Method E [11]**:**



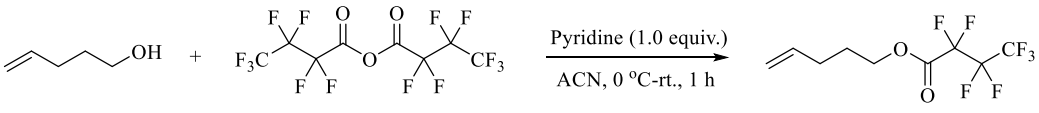
An oven-dried flask was charged with pent-4-en-1-ol (1.0 equiv.), triphenylphosphine (1.3 equiv.), phenol (1.3 equiv.), 15 mL of dry THF, and a magnetic stir bar. The solution was cooled to 0 ℃, and diisopropyl azodicarboxylate (DIAD) (1.3 equiv.) was added dropwise. The resulting mixture was warmed to rt. After stirring for 24 h, the reaction was concentrated in vacuo. The crude material was purified by flash column chromatography or preparative TLC to yield pure ether. **a14-a15, a17 and a63** were prepared according to the above procedure. (Note: **a17** used hex-5-en-1-ol as a start material. **a63** used 3-Buten-1-ol as a start material.)

Synthesis of a16 [12]**:**



A mixture of 3-pyridinol (475 mg, 5.0 mmol), 6-bromo-1-pentene (896 mg, 5.5 mmol), acetone (30 mL), and anhydrous potassium carbonate (1.7 g, 12.5 mmol) was stirred at 50 ℃ for 12 h. After cooled to room temperature, the reaction mixture was poured into water (100 mL), and most portion of acetone (ca. 90%) was carefully removed under reduced pressure. Dichloromethane (20 mL) was added to the residue, and then washed with water and brine, dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by flash chromatography on silica gel with *n*-hexane/ethyl acetate (10:1) as eluent to afford **a16** (354 mg, 40% yield) as brown liquid.

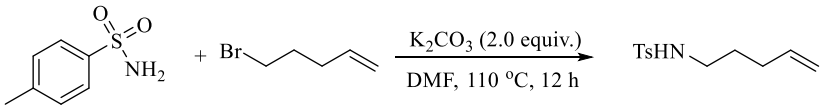
Synthesis of a26 [13]**:**



In an oven-dried round-bottom flask equipped with a PTFE-coated stirring bar, 4-penten-1-ol (430 mg, 5.0 mmol), pyridine (395 mg, 5.0 mmol), and 5 mL of acetonitrile were added, followed by stirring in an ice bath. heptafluorobutyric anhydride (2.05 g, 5.0 mmol) was added dropwise to the obtained solution. The reaction solution obtained by stirring the solution for 1 hour at room temperature was added to 30 mL of saturated aqueous sodium bicarbonate, followed by extraction by using 50 mL of ethyl

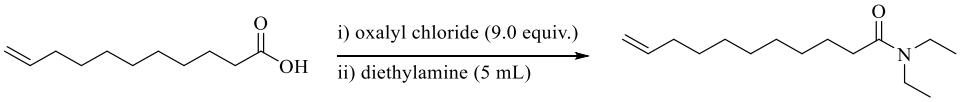
acetate. Then, the organic phase was washed with 30 mL of saturated brine, thereafter dehydrated using magnesium sulfate and filtered. The filtrate was distilled off under reduced pressure and the residue was purified by flash column chromatography on silica with *n*-hexane/ethyl acetate (50:1), affording **a26** (253 mg, 18%) as a yellow oil.

Synthesis of a27 [14]**:**



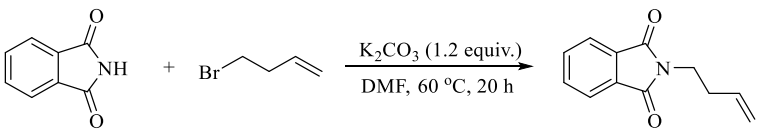
To a round-bottomed flask equipped with a stirring bar was charged with *p*-toluenesulfonamide (1.02 g, 6 mmol), K_2CO_3 (1.38 g, 10 mmol) and dry DMF (15 mL). 5-Bromo-1-pentene (745 mg, 5 mmol) was slowly added and heated to 110 ℃. The reaction was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and added water and extracted with ethyl acetate. The combined organic layers were washed by brine and then dried over anhydrous Na_2SO_4, filtered, concentrated and eventually purified silica gel column chromatography with *n*-hexane/ethyl acetate (10:1) to give the desired compounds **a27** (877 mg, 73%).

Synthesis of a29 [15]**:**



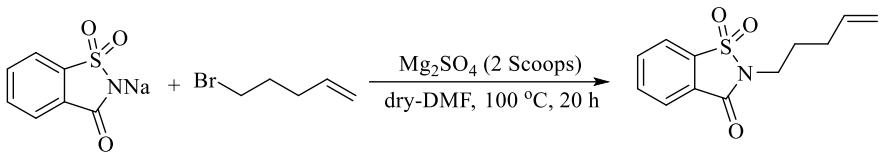
A solution of undec-10-enoic acid (1.84 g, 10 mmol) and oxalyl chloride (11.7 g, 93 mmol) in dry 50 mL THF was stirred at 0 ℃ for 2 h. Removal of the excess oxalyl chloride with evaporation in vacuo to give a residue which was re-dissolved in 10 mL dry THF. The resulting solution was then added in one pot to a solution of 5 mL diethylamine in 25 mL THF at 0 ℃. After stirring for 2 h, to the solution was added with 150 mL water. The mixture was then extracted with 3×50 mL Et_2O. The extracts were combined and washed with 5 % 50 mL HCl and 50 mL water. The organic layer was dried over $MgSO_4$. Removal of the solvent in vacuo afforded a residue which was purified by flash column chromatography with *n*-hexane/ethyl acetate (20:1) to afford **a29** (1.1g, 46%) as white solid.

Synthesis of a30 [16]**:**



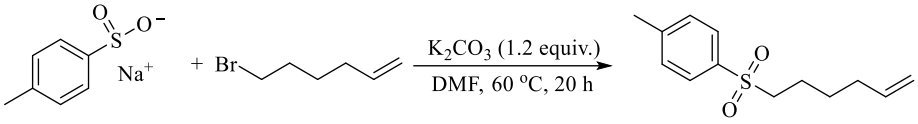
In an oven-dried round-bottom flask equipped with a PTFE-coated stirring bar, phthalimide (1.47 g, 10.0 mmol) and K_2CO_3 (1.66 g, 12.0 mmol) were suspended in DMF (20 mL), then 4-bromobut-1-ene (1.48 g, 11.0 mmol) was added in one portion, then the reaction was stirred at 60 ℃ for 20 h. After cooling down to room temperature, the reaction was diluted with water (50 mL) and extracted twice with EtOAc (50 mL each time). The combined organic extracts were washed twice with water (80 mL each time) and once with brine (80 mL), then were dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was purified by flash column chromatography on silica with *n*-hexane/ethyl acetate (15:1), affording **a30** (1.45 g, 72%) as a white solid.

Synthesis of a31 [16]**:**



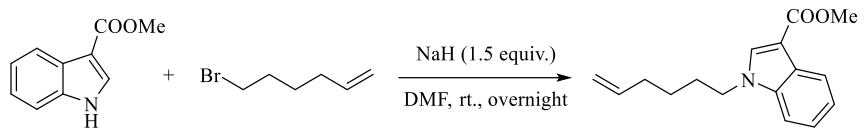
In an oven-dried Schlenk tube equipped with a PTFE-coated stirring bar, sodium saccharin dihydrate (1.2 g, 5.0 mmol), $MgSO_4$ (two scoops), dry DMF (20 mL) and 1-bromopentene (0.9 mL, 7.5 mmol) were charged and stirred at 100 ℃ for 20 h, then the reaction was warmed to room temperature and diluted with water (50 mL). The aqueous layer was extracted twice with EtOAc (30 mL each time), then the combined organic extracts were washed three times with water (30 mL each time), then dried over $MgSO_4$ and the solvent was removed in vacuo. The crude product was purified by flash column chromatography on silica with *n*-hexane/ethyl acetate 9:1 to 7:1, affording **a31** (1.15 g, 92% yield) as a colorless thick gum.

Synthesis of a32 [16]**:**



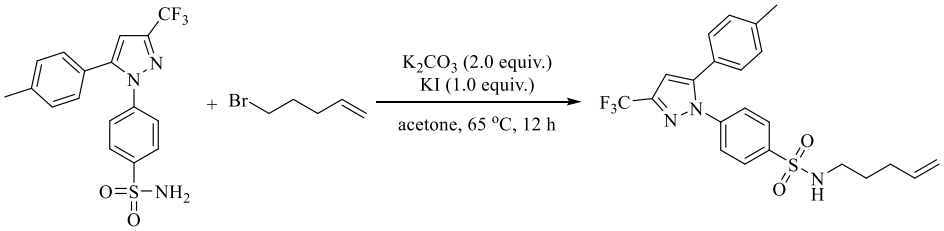
In an oven-dried round-bottom flask equipped with a PTFE-coated stirring bar, sodium *p*-toluenesulfinate (1.78 g, 10.0 mmol) and K_2CO_3 (1.66 g, 12.0 mmol) were suspended in DMF (20 mL), then 6-bromohex-1-ene (1.49 mL, 11.0 mmol) was added in one portion, then the reaction was stirred at 60 ℃ for 20 h. After cooling down to room temperature, the reaction was diluted with water (50 mL) and extracted twice with EtOAc (50 mL each time). The combined organic extracts were washed twice with water (80 mL each time) and once with brine (80 mL), then were dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was purified by flash column chromatography on silica with *n*-hexane/ethyl acetate (15:1), affording **a32** (1.74 g, 73%) as a colorless oil.

***Synthesis of a33 [17]*:**



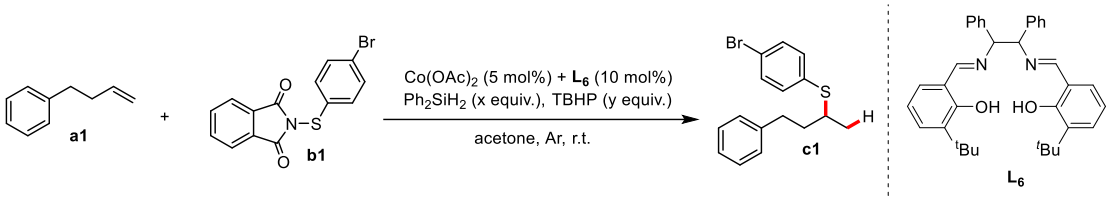
A solution of methyl indole-3-carboxylate (0.53 g, 3.0 mmol) in anhydrous DMF (10.0 mL) was treated with sodium hydride (0.18 g, 4.5 mmol) and 6-bromohex-1-ene (0.45 mL, 3.3 mmol). The reaction mixture was stirred for overnight and quenched with a solution of saturated aq. NH_4Cl (10 mL) and diluted with ethyl acetate (10 mL). The mixture was then extracted with EtOAc (2 x 10 mL), washed with brine, dried over Na_2SO_4, and concentrated to give a crude mixture. Purification by flash chromatography (20% EtOAc in *n*-hexanes) afforded the **a33** (579 mg, 75%) as green oil.

***Synthesis of a60 [11]*:**



An oven-dried 20-mL vial was charged with 5-bromopent-1-ene (0.67 g, 4.5 mmol), Celecoxib (1.0 g, 3.0 mmol), potassium carbonate (0.83 g, 6.0 mmol), potassium iodide (0.50 g, 3.0 mmol), 7.5 mL of dry acetone, and a magnetic stir bar. The reaction was heated at 65 ℃ for 12 h and filtered. The product was purified by flash column chromatography (15% EtOAc in *n*-hexanes) to afford the corresponding compound **a60** (676 mg, 52%) as a white solid.

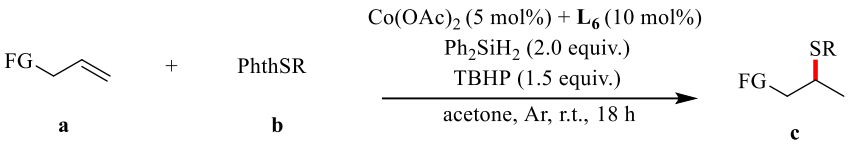
2.3) Optimization of the amount of silane and TBHP. [a]



Entry	Ph_2SiH_2 (x equiv.)	TBHP (y equiv.)	**c1** (%)[b]
1	1.0	1.5	22
2	1.0	2.0	28
3	1.5	1.5	45
4	2.0	1.0	33
5	2.0	1.5	75
6	2.0	2.0	36

[a] **a1** (0.3 mmol, 1.5 equiv.), **b1** (0.2 mmol, 1.0 equiv.), $Co(OAc)_2$ (5 mol %), $\mathbf{L_6}$ (10 mol%), Ph_2SiH_2 (x equiv.) and TBHP (y equiv.) in acetone (3.0 mL). [b]Isolated yield.

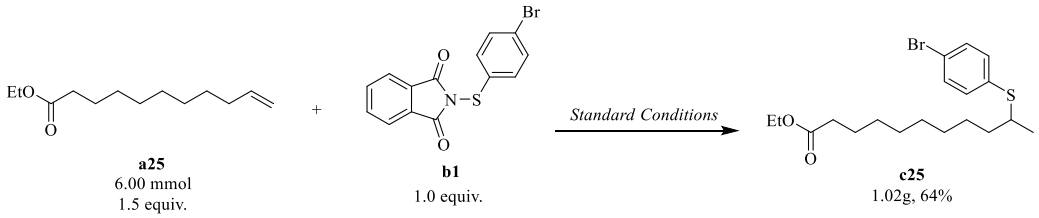
2.4) General procedure for Co-catalyzed Markovnikov hydrothiolation reaction.



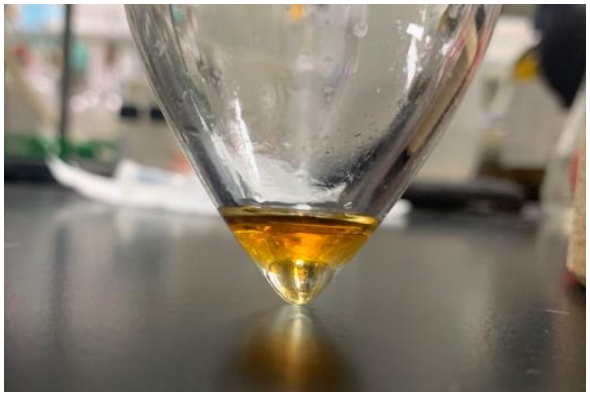
a **b** **c**

To a solution of **a** (0.30 mmol, 1.5 equiv.), **b** (0.20 mmol, 1.0 equiv.), $Co(OAc)_2$ (2 mg, 5.0 mol%) and $\mathbf{L_6}$ (4 mg, 10.0 mol%) in acetone (3.0 mL) was added Ph_2SiH_2 (73 mg, 2.0 equiv.) and *tert*-butyl hydroperoxide (24 mg, 1.5 equiv.) successively under argon atmosphere in a sealed tube. The resulting mixture was stirred at room temperature. After reaction finished, the reaction mixture was concentrated under reduced pressure. The residue was purified on a silica gel column to afford the products.

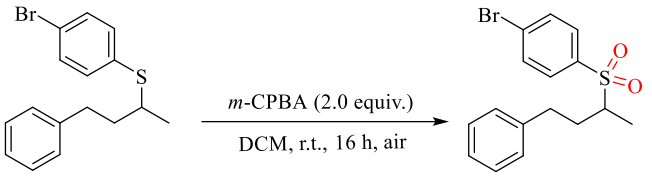
2.5) Gram-scale synthesis.



To a solution of **a25** (1.27 g, 6.00 mmol, 1.5 equiv.), **b1** (1.28 g, 4.00 mmol, 1.0 equiv.), $Co(OAc)_2$ (35 mg, 5.0 mol%) and $\mathbf{L_6}$ (85 mg, 10.0 mol%) in acetone (20.0 mL) was added Ph_2SiH_2 (1.48 mL, 2.0 equiv.) and *tert*-butyl hydroperoxide (0.60 mL, 1.5 equiv.) successively under an argon atmosphere in a sealed tube. The resulting mixture was stirred at room temperature. After reaction finish, the reaction mixture was concentrated under reduced pressure. The residue was purified on a silica gel column (*n*-hexane/ethyl acetate = 50:1, v/v) to afford the products as orange oil (1.02 g, 64%).

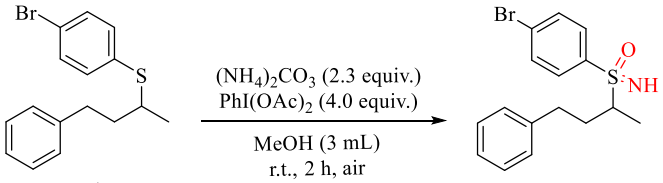


2.6) Synthetic applications.



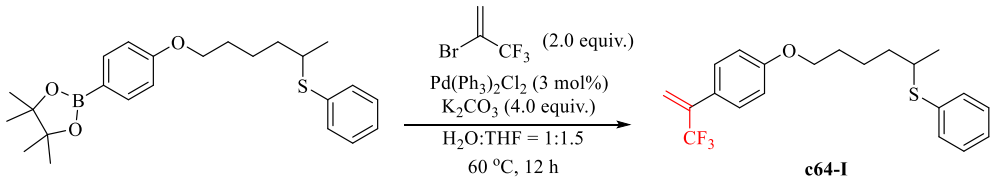
c1 **c1-I** 99%

To a stirred solution of **c1** (64 mg, 0.2 mmol) in DCM (3 mL) was added, dropwise over 15 min, a solution of *m*-CPBA (103 mg, 0.6 mmol) in DCM (1 mL). The reaction mixture was stirred for 16 h, washed with saturated $NaHCO_3$ solution (3 x 30 mL) and water (30 mL), dried with $MgSO_4$ and concentrated under reduced pressure to yield the crude product as a white solid [18]. The residue was purified on a silica gel column (*n*-hexane/ethyl acetate = 10:1, v/v) to afford the **c1-I** as white solid (69 mg, 99%).



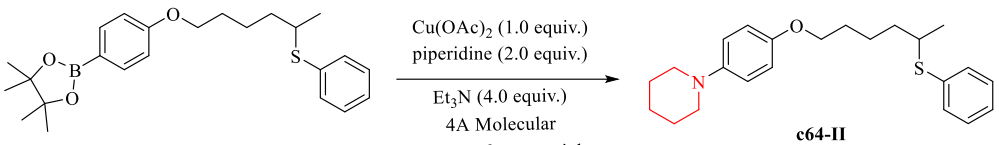
c1 **c1-II** 79%

To a solution of **c1** (64 mg, 0.2 mmol) in MeOH (3 mL) was added $(NH_4)_2CO_3$ (44 mg, 0.46 mmol) and $PhI(OAc)_2$ (257 mg, 0.8 mmol) under air atmosphere in a sealed tube. The resulting mixture was stirred at room temperature. After reaction finished, the reaction mixture was concentrated under reduced pressure [19]. The residue was purified on a silica gel column (*n*-hexane/ethyl acetate = 10:1, v/v) to afford the **c1-II** as white solid (55 mg, 79%).



c64 **c64-I** 78%

Product **c64** (123 mg, 0.3 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.009 mmol), K_2CO_3 (165 mg, 1.2 mmol) were dissolved in THF (0.9 mL) and H_2O (0.6 mL) in a two-neck flask under argon atmosphere. Then, 2-bromo-3,3,3 trifluoroprop-1-ene (65 µL, 0.6 mmol) was added dropwise into the mixture. The mixture was heated to 60 °C in an oil bath for at least 12 h. Then the mixed solution was extracted with ethyl acetate (3 × 15.0 mL). The organic layer was washed with brine (20.0 mL), dried over Na_2SO_4, and then concentrated under reduced pressure [5]. The residue was purified on a silica gel column (*n*-hexane/ethyl acetate = 60:1, v/v) to afford the **c64-I** as yellow oil (87 mg, 78%).



c64 **c64-II** 40%

In a 10 mL dried pyrex screw-top reaction tube (borosilicate glass), product **c64** (123 mg, 0.3 mmol), piperidine (51 mg, 0.6 mmol), $Cu(OAc)_2$ (55 mg, 0.3 mmol), Et_3N (0.17 mL, 1.2 mmol) and 50 mg 4A molecular sieves were added into CH_3CN (3 mL), the reaction mixture was degassed under argon by sparging for 5 min, then put the tube in 80 ℃ oil bath overnight. When the reaction finished, the reaction mixture was allowed to cool to room temperature and filtered through a short pad of celite, washed with EtOAc (2 mL x 3) [20]. The residue was purified on a silica gel column (*n*-hexane/ethyl acetate = 20:1, v/v) to afford the **c64-II** as brown oil (30 mg, 40%).

2.7) Crystal structure determination of c10, c34, c37 and c38.

A suitable crystal of **c10** was mounted with glue at the end of a glass fiber. Data collection for **c10** was performed on a Rigaku OD (Enhance Cu X-ray Source, Kα, λ = 1.54184 Å) with CCD Plate (XtaLAB Pro: Kappa single) under 150 K. Data were processed with the CrysAlisPro 1.171.39.28b (Rigaku Oxford Diffraction, 2015).

Structure was solved by ShelXT[6] in Olex2 1.5[7] and refined on F^2 using full-matrix least-squares (SHELXL-2018 in Olex2 1.5). Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. Crystal data and structure refinement parameters are summarized in **Table S1**. CCDC No. 2281719

Single crystals of **c10** were prepared in acetonitrile solution of **c10**. Colourless block crystals formed.

Table S1. The X-ray crystallography analysis of compound c10

Compound	**c10**
Empirical formula	$C_{29}H_{39}BrS$
Formula weight	499.57
Crystal system	Monoclinic
Space group	*C*2/*c*
a (Å)	22.1141(6)
b (Å)	5.2760(2)
c (Å)	45.0011(15)
α (°)	90
β (°)	95.564(3)
γ (°)	90
V (Å^3)	5225.7(3)
Z	8
Temperature (K)	150(2)
Density (calculated)	1.270 g/cm^3
Absorption coefficient	2.970 mm^{-1}

F(000)	2112
Crystal size	0.20 × 0.05 × 0.02 mm^3
Theta range for data collection	3.948 to 71.356 °
Index ranges	-26<=h<=25, -6<=k<=3, -55<=l<=51
Reflections collected	9862
Independent reflections	4815 [R_{int} = 0.0357]
Completeness	97.7% to theta = 67.684 °
Data / restraints / parameters	4815 / 0 / 291
Goodness-of-fit on F^2	1.054
Final *R* indices [*I*>2sigma(*I*)][a]	R_1 = 0.0757 wR_2 = 0.2051
R indices (all data)[a]	R_1 = 0.0834 wR_2 = 0.2113
Extinction coefficient	N/A
Absolute structure parameter	N/A
Largest diff. peak and hole	1.052 and -0.582 e.$Å^{-3}$

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{[\Sigma w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$ for all data.

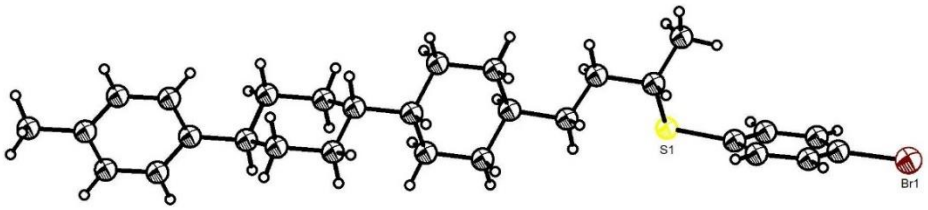


Figure S1. Molecular structure of **c10** with 50% thermal ellipsoid.

CCDC Number: 2281719

A suitable crystal of **c34** was mounted with glue at the end of a glass fiber. Data collection for **c34** was performed on a Rigaku OD (Enhance Cu X-ray Source, Kα, λ = 1.54184 Å) with CCD Plate (XtaLAB Pro: Kappa single) under 298 K. Data were processed with the CrysAlisPro 1.171.39.28b (Rigaku Oxford Diffraction, 2015).

Structure was solved by ShelXT[6] in Olex2 1.5[7] and refined on F^2 using full-matrix least-squares (SHELXL-2018 in Olex2 1.5). Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. Crystal data and structure refinement parameters are summarized in **Table S2**. CCDC No. 2281720

Single crystals of **c34** were prepared in acetonitrile solution of **c34**.

Table S2. The X-ray crystallography analysis of compound c34

Compound	**c34**
Empirical formula	$C_{15}H_{20}BrNO_2S$
Formula weight	358.29
Crystal system	Triclinic
Space group	*P*-1
a (Å)	6.0887(5)
b (Å)	10.8043(10)
c (Å)	13.1121(11)
α (°)	80.047(7)
β (°)	88.378(7)
γ (°)	79.464(7)
V (Å^3)	835.26(13)
Z	2
Temperature (K)	298(2)
Density (calculated)	1.425 g/cm^3
Absorption coefficient	4.529 mm^{-1}
F(000)	368

Crystal size	0.55 × 0.08 × 0.05 mm^3
Theta range for data collection	3.422 to 68.242 °
Index ranges	-7<=h<=6, -13<=k<=12, -15<=l<=15
Reflections collected	6744
Independent reflections	2990 [R_{int} = 0.0400]
Completeness	97.9 % to theta = 67.684 °
Data / restraints / parameters	2990 / 0 / 185
Goodness-of-fit on F^2	1.073
Final R indices [I>2sigma(I)][a]	R_1 = 0.0465 wR_2 = 0.1309
R indices (all data)[a]	R_1 = 0.0524 wR_2 = 0.1357
Extinction coefficient	N/A
Absolute structure parameter	N/A
Largest diff. peak and hole	0.672 and -0.641 e.Å^{-3}

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{[\Sigma w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$ for all data.

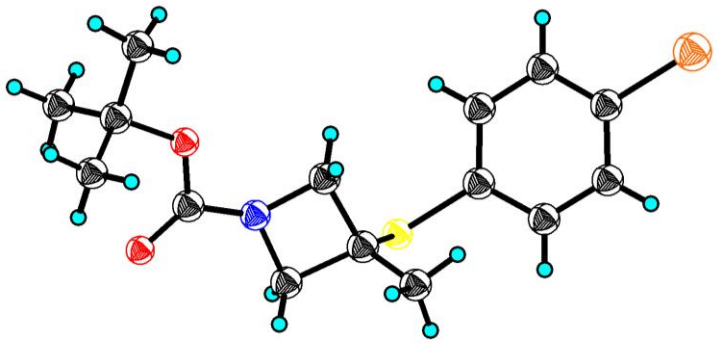


Figure S2. Molecular structure of **c34** with 50% thermal ellipsoid.

CCDC Number: 2281720

A suitable crystal of **c37** was mounted with glue at the end of a glass fiber. Data collection for **c37** was performed on a Rigaku OD (Enhance Cu X-ray Source, Kα, λ = 1.54184 Å) with CCD Plate (XtaLAB Pro: Kappa single) under 150 K. Data were processed with the CrysAlisPro 1.171.39.28b (Rigaku Oxford Diffraction, 2015).

Structure was solved by ShelXT[6] in Olex2 1.5[7] and refined on F^2 using full-matrix least-squares (SHELXL-2018 in Olex2 1.5). Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. Crystal data and structure refinement parameters are summarized in **Table S3**. CCDC No. 2281781

Single crystals of **c37** were prepared in acetonitrile solution of **c37**.

Table S3. The X-ray crystallography analysis of compound c37

Compound	**c37**
Empirical formula	$C_{19}H_{21}BrS$
Formula weight	361.33
Crystal system	Orthorhombic
Space group	*Pna2₁*
a (Å)	9.09912(15)
b (Å)	9.97277(13)
c (Å)	37.5925(4)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	3411.27(8)
Z	8
Temperature (K)	150(2)
Density (calculated)	1.407 g/cm^3
Absorption coefficient	4.337 mm^{-1}
F(000)	1488
Crystal size	0.35 × 0.15 × 0.01 mm^3

Theta range for data collection	4.434 to 71.749 °
Index ranges	-10<=h<=10, -11<=k<=12, -46<=l<=46
Reflections collected	37814
Independent reflections	6516 [Rint = 0.0453]
Completeness	100.0 % to theta = 67.684 °
Data / restraints / parameters	6516 / 1 / 381
Goodness-of-fit on F^2	1.070
Final R indices [I>2sigma(I)][a]	R_1 = 0.0402 wR_2 = 0.0978
R indices (all data)[a]	R_1 = 0.0422 wR_2 = 0.0988
Extinction coefficient	N/A
Absolute structure parameter	-0.024(2)
Largest diff. peak and hole	0.719 and -0.290 e.Å^{-3}

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{[\Sigma w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$ for all data.

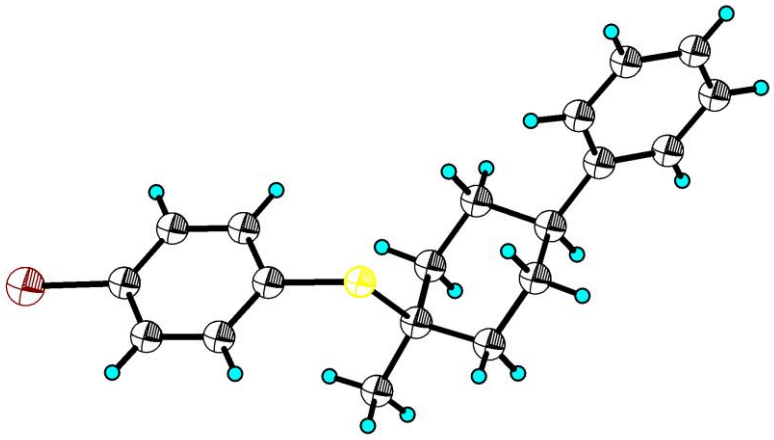


Figure S3. Molecular structure of **c37** with 50% thermal ellipsoid.

CCDC Number: 2281781

A suitable crystal of **c38** was mounted with glue at the end of a glass fiber. Data collection for **c38** was performed on a Rigaku OD (Enhance Cu X-ray Source, Kα, λ = 1.54184 Å) with CCD Plate (XtaLAB Pro: Kappa single) under 150 K. Data were processed with the CrysAlisPro 1.171.39.28b (Rigaku Oxford Diffraction, 2015).

Structure was solved by ShelXT[6] in Olex2 1.5[7] and refined on F^2 using full-matrix least-squares (SHELXL-2018 in Olex2 1.5). Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were generated geometrically. Crystal data and structure refinement parameters are summarized in **Table S4**. CCDC No. 2281721

Single crystals of **c38** were prepared in acetonitrile solution of **c38**.

Table S4. The X-ray crystallography analysis of compound c38

Compound	**c38**
Empirical formula	$C_{17}H_{21}BrS$
Formula weight	337.31
Crystal system	Orthorhombic
Space group	*Pna2₁*
a (Å)	11.19329(7)
b (Å)	19.33429(12)
c (Å)	6.77041(4)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	1465.214(16)
Z	4
Temperature (K)	150(2)
Density (calculated)	1.529 g/cm^3
Absorption coefficient	4.999 mm^{-1}
F(000)	696
Crystal size	0.40 × 0.10 × 0.05 mm^3

Theta range for data collection	4.565 to 71.048 °
Index ranges	-13<=h<=13, -23<=k<=23, -6<=l<=8
Reflections collected	14601
Independent reflections	2250 [R_{int} = 0.0283]
Completeness	99.7 % to theta = 67.684 °
Data / restraints / parameters	2250 / 1 / 174
Goodness-of-fit on F^2	1.068
Final R indices [I>2sigma(I)][a]	R_1 = 0.0202 wR_2 = 0.0549
R indices (all data)[a]	R_1 = 0.0203 wR_2 = 0.0549
Extinction coefficient	N/A
Absolute structure parameter	0.27(2)
Largest diff. peak and hole	0.291 and -0.312 e.Å^{-3}

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{[\Sigma w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$ for all data.

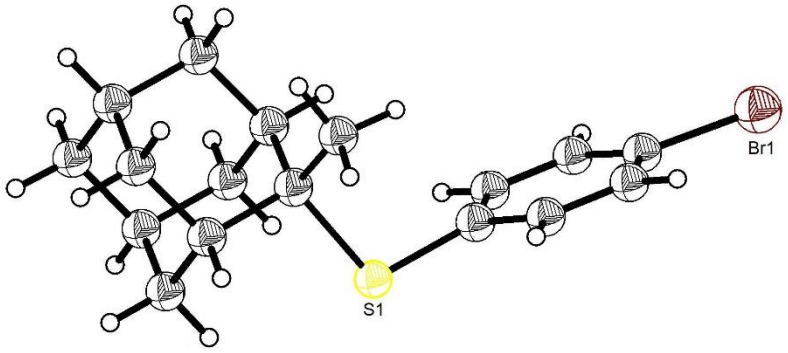
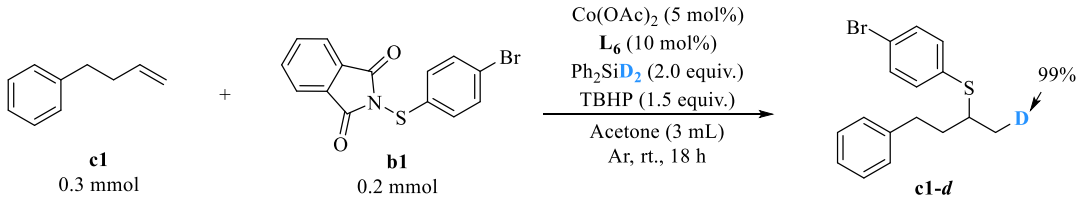


Figure S4. Molecular structure of **c38** with 50% thermal ellipsoid.

CCDC Number: 2281721

2.8) Deuterium labeling experiment.

Preparation of Ph_2SiD_2 [21]: A three-necked flask equipped with a reflux condenser and a magnetic stir bar was flame-dried under reduced pressure, and then cooled under an Ar atmosphere. $LiAlD_4$ (0.42 g, 10.0 mmol.) and dry-Et_2O (40 mL) was added successively under 0 °C, then followed by Ph_2SiCl_2 (1.1 mL, 5.0 mmol.) dropwise over 2 min. The resulting mixture was refluxed for overnight. After the reaction was completed, the resulting suspension was filtered through celite and cooled to 0 °C. The filtrate was quenched by the dropwise addition of chilled H_2O with vigorous stirring and extracted with Et_2O. The combined organic layers were dried over anhydrous $MgSO_4$ and concentrated in vacuo under 0 °C to provide Ph_2SiD_2 as a yellow oil with 83% deuterium incorporation. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.68 – 7.61 (m, 4H), 7.50 – 7.37 (m, 6H), 3.52 (q, J = 7.0 Hz, 0.34H).



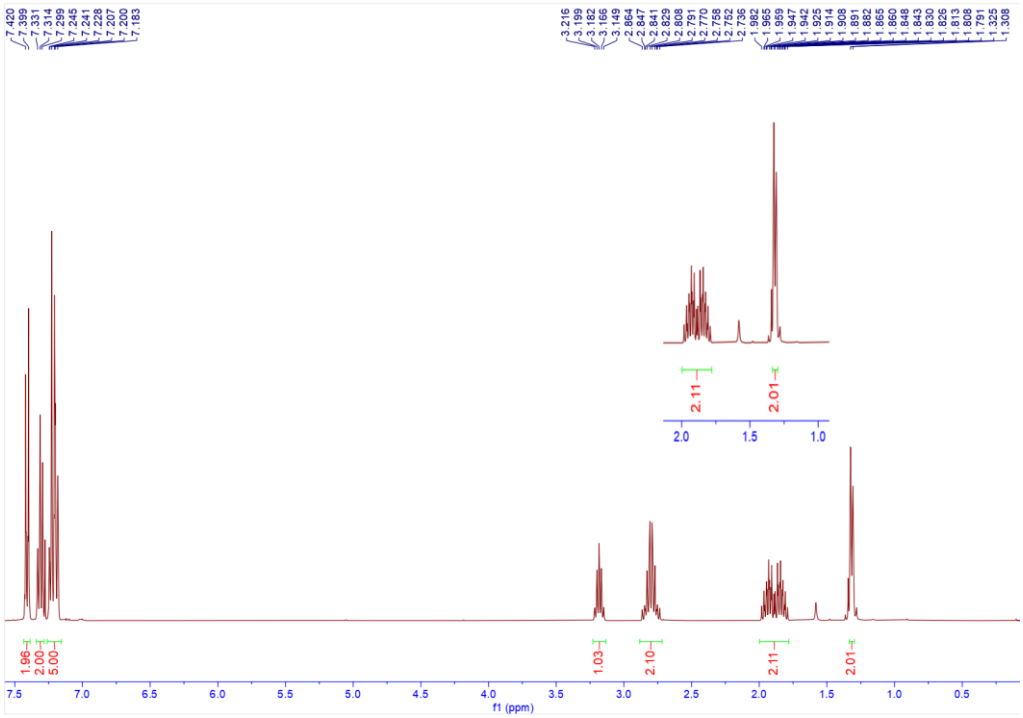
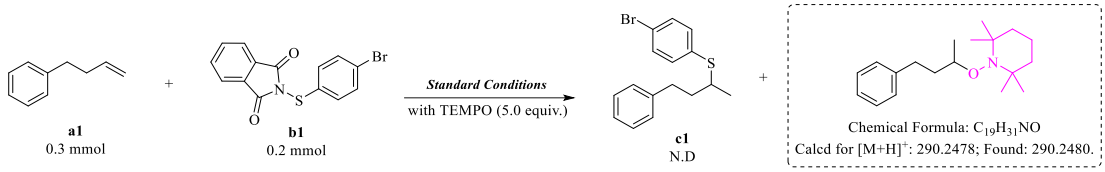


Figure S5. ^{1}H NMR spectra of **c1-*d***

2.9) Radical trapping experiments.



To a solution of alkene **a1** (45 μL, 0.30 mmol.), N-S reagent **b1** (66mg, 0.20 mmol.), $Co(OAc)_2$ (2 mg, 5.0 mol%.) and **L6** (4 mg, 10.0 mol%.) in acetone (3.0 mL) was added Ph_2SiH_2 (73 mg, 0.4 mmol.), *tert*-butyl hydroperoxide (24 mg, 0.3 mmol.) and TEMPO (156 mg, 1.0 mmol.) successively under an argon atmosphere in a sealed tube. The resulting mixture was stirred at room temperature. After reaction finished, the reaction mixture was concentrated under reduced pressure.

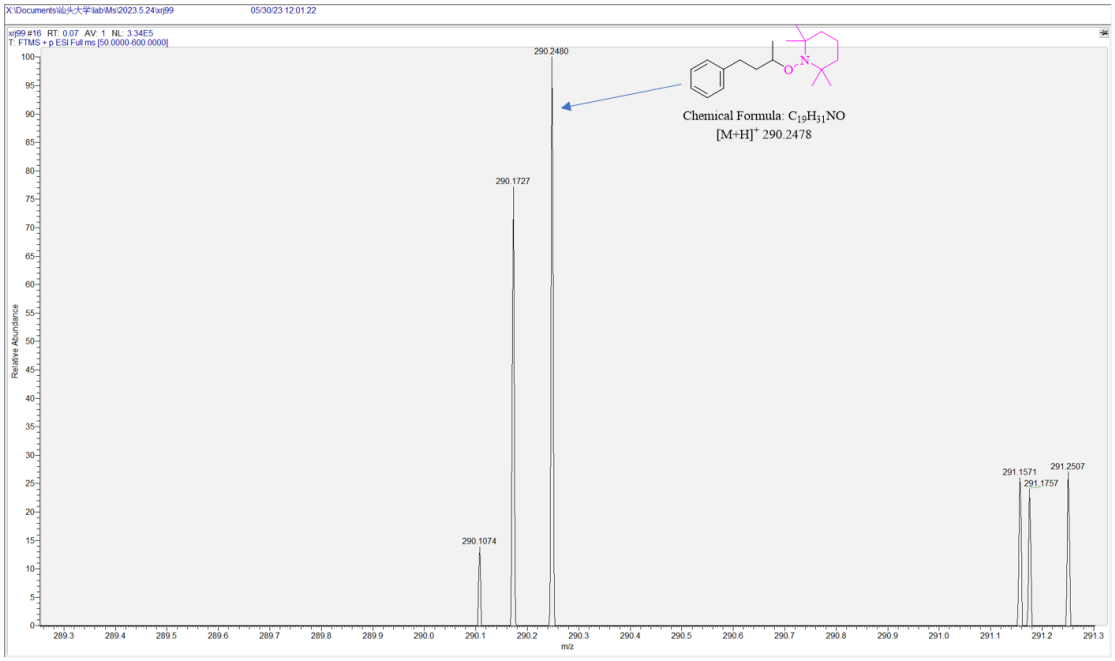
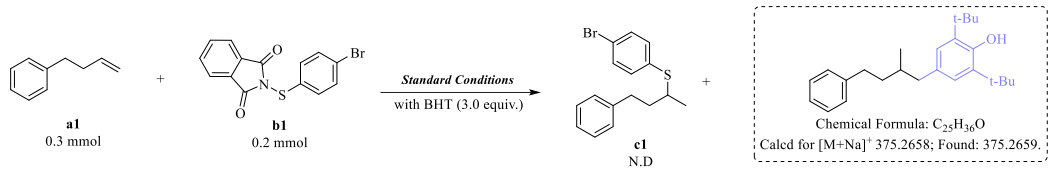


Figure S6. HRMS spectra of TEMPO-mediated reaction.



To a solution of alkene **a1** (45 μL, 0.30 mmol.), N-S reagent **b1** (66mg, 0.20 mmol.), $Co(OAc)_2$ (2 mg, 5.0 mol%.) and **L6** (4 mg, 10.0 mol%.) in acetone (3.0 mL) was added Ph_2SiH_2 (73 mg, 0.4 mmol.), *tert*-butyl hydroperoxide (24 mg, 0.3 mmol.) and BHT (132 mg, 0.6 mmol.) successively under an argon atmosphere in a sealed tube. The resulting mixture was stirred at room temperature. After reaction finished, the reaction mixture was concentrated under reduced pressure.

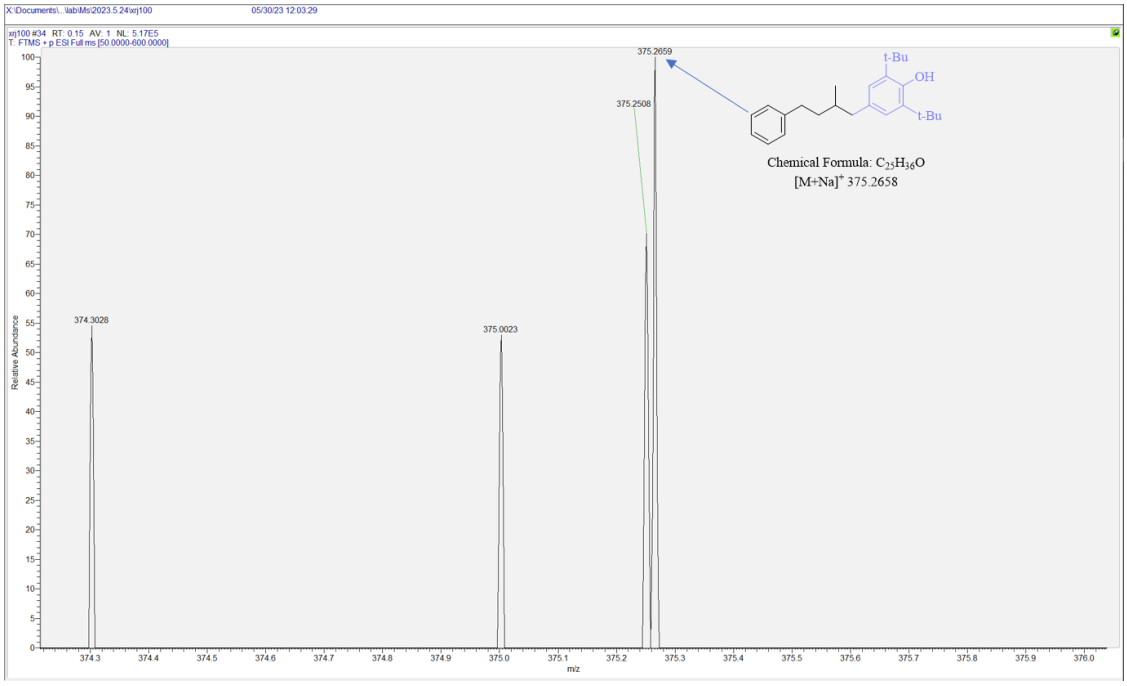
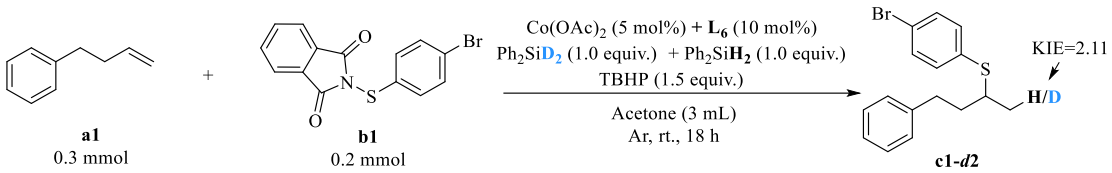


Figure S7. HRMS spectra of BHT-mediated reaction.

2.10) KIE experiment.



To a solution of **a1** (45 μL, 0.30 mmol.), **b1** (66 mg, 0.2 mmol.), $Co(OAc)_2$ (2 mg, 5.0 mol%) and **L6** (4 mg, 10.0 mol%.) in acetone (3.0 mL) was added Ph_2SiH_2 (34 mg, 0.2 mmol.)、Ph_2SiD_2 (34 mg, 0.2 mmol.) and *tert*-Butyl hydroperoxide (30 μL, 0.15 mmol.) successively under an argon atmosphere in a sealed tube. The resulting mixture was stirred at room temperature. After reaction finish, the reaction mixture was concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel. The product **1-*d*2** was analyzed by ^{1}H NMR spectroscopy.

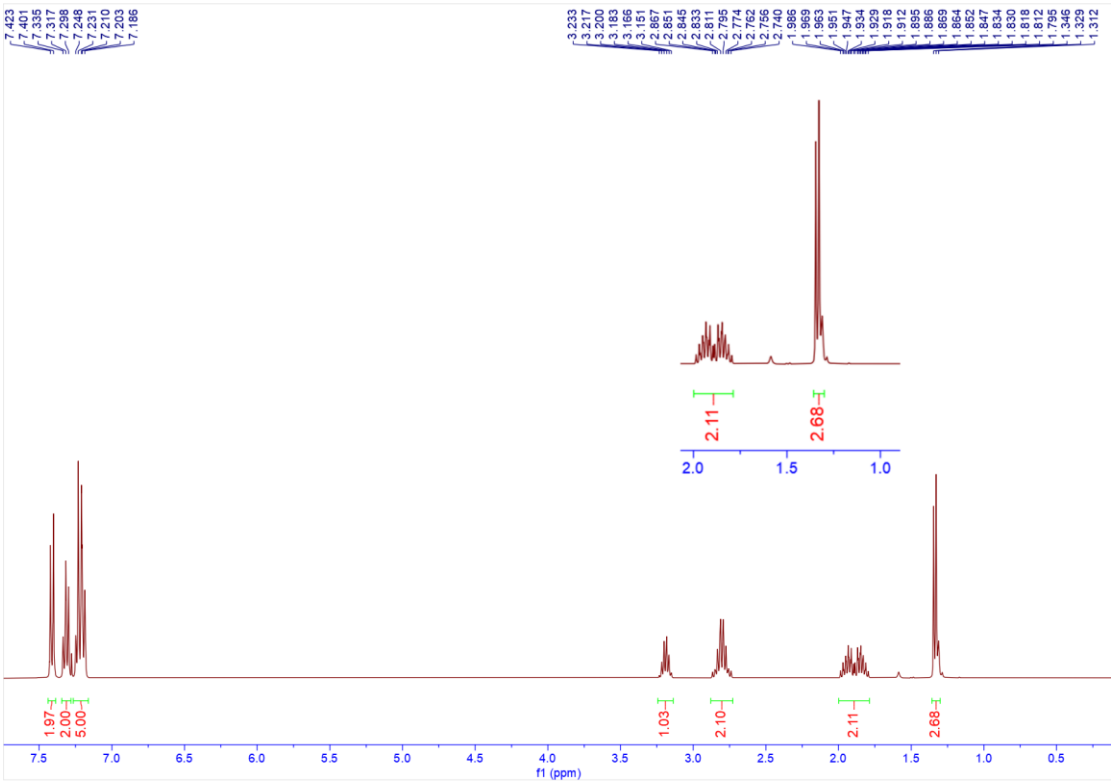
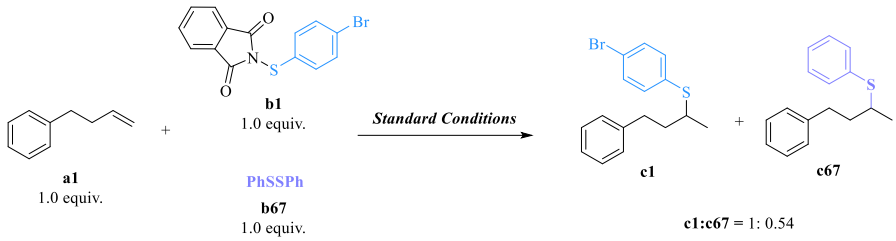


Figure S8. ^{1}H NMR spectra of the **c1-*d*2**.

2.11) Competition experiment.



To a solution of **a1** (30 μL, 0.20 mmol), **b1** (66 mg, 0.2 mmol), **b67** (44 mg, 0.2 mmol), $Co(OAc)_2$ (2 mg, 5.0 mol%) and $\mathbf{L_6}$ (4 mg, 10.0 mol%) in acetone (3.0 mL) was added Ph_2SiH_2 (74 μL, 0.4 mmol) and *tert*-Butyl hydroperoxide (30 μL, 0.15 mmol) successively under an argon atmosphere in a sealed tube. The resulting mixture was stirred at room temperature. After reaction finish, the reaction mixture was concentrated under reduced pressure. The resulting crude product was purified by flash column chromatography on silica gel. Ratio between the two products is determined by ^1H NMR with BHT as an internal standard.

2.12) References.

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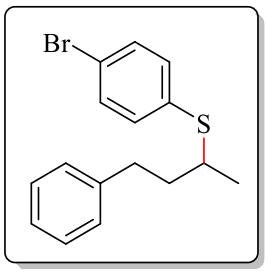
3. Analytical data of target compounds.

(4-bromophenyl)(4-phenylbutan-2-yl)sulfane (c1)



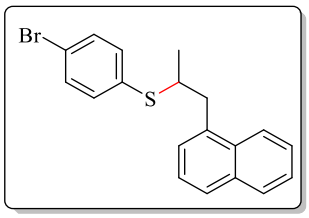
Purification by column chromatography on silica gel (*n*-hexane/ethyl acetate = 100:1, v/v) afforded the title compound as a colorless oil (48 mg, 75% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.26 – 7.17 (m, 4H), 3.20 (h, *J* = 6.7 Hz, 1H), 2.90 – 2.71 (m, 2H), 2.02 – 1.78 (m, 2H), 1.34 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.5, 134.4, 133.4, 128.5, 126.0, 120.8, 42.6, 38.1, 33.1, 21.1.

HRMS (ESI) m/z: Calcd for $C_{16}H_{18}BrS$ $[M+H]^+$, 323.0287.; Found, 323.0284.

(4-bromophenyl)(1-(naphthalen-1-yl)propan-2-yl)sulfane (c2)



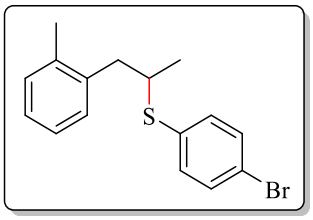
Purification by column chromatography on silica gel (hexane/ethyl acetate = 100:1, v/v) afforded the title compound as a colorless oil (54 mg, 76% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.83 (m, 1H), 7.83 – 7.79 (m, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.42 (dd, *J* = 13.1, 8.4 Hz, 3H), 7.36 – 7.29 (m, 3H), 3.66 – 3.49 (m, 2H), 3.07 (dd, *J* = 13.5, 8.9 Hz, 1H), 1.27 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.1, 134.3, 134.2, 134.0, 131.9, 128.9, 127.6, 127.4, 126.0, 125.5, 125.3, 123.5, 121.3, 44.4, 40.6, 20.7.

HRMS (ESI) m/z: Calcd for $C_{19}H_{18}BrS$ $[M+H]^+$, 359.0288.; Found, 359.0295.

(4-bromophenyl)(1-(*o*-tolyl)propan-2-yl)sulfane (c3)

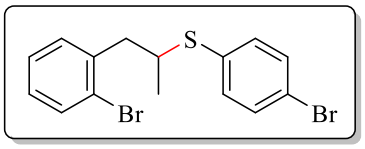


Purification by column chromatography on silica gel (hexane/ethyl acetate = 100:1, v/v) afforded the title compound as a green oil (48 mg, 75% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.22 – 7.08 (m, 4H), 3.48 – 3.35 (m, 1H), 3.03 (dd, *J* = 13.8, 5.4 Hz, 1H), 2.70 (dd, *J* = 13.8, 9.3 Hz, 1H), 2.26 (s, 3H), 1.26 (d, *J* = 6.7 Hz, 3H).

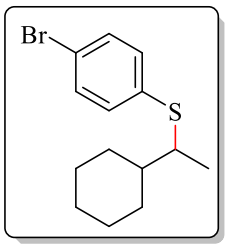
^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.3, 136.2, 134.3, 134.0, 131.9, 130.4, 130.1, 126.6, 125.8, 121.2, 44.1, 40.5, 20.4, 19.5.
HRMS (ESI) m/z: Calcd for $C_{16}H_{18}BrS$ $[M+H]^+$, 323.0287.; Found, 323.0283.

(4-bromophenyl)(1-(2-bromophenyl)propan-2-yl)sulfane (c4)



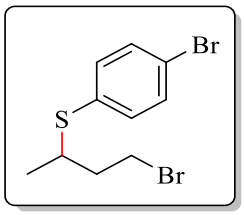
Purification by column chromatography on silica gel (hexane/ethyl acetate = 100:1, v/v) afforded the title compound as a colorless oil (46 mg, 64% yield).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.9 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 13.0 Hz, 2H), 7.26 – 7.19 (m, 2H), 7.09 (td, *J* = 7.4, 2.1 Hz, 1H), 3.59 (dq, *J* = 13.5, 6.8 Hz, 1H), 3.11 (dd, *J* = 13.6, 6.1 Hz, 1H), 2.85 (dd, *J* = 13.6, 8.6 Hz, 1H), 1.26 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.4, 134.0, 133.9, 133.0, 131.9, 128.3, 127.3, 124.7, 121.1, 43.5, 43.1, 20.4.
HRMS (ESI) m/z: Calcd for $C_{15}H_{15}Br_2S$ $[M+H]^+$, 386.9235.; Found, 386.9231.

(4-bromophenyl)(1-cyclohexylethyl)sulfane (c5)



Purification by column chromatography on silica gel (hexane/ethyl acetate = 150:1, v/v) afforded the title compound as a colorless oil (48 mg, 80% yield).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 5.7 Hz, 2H), 3.19 – 3.08 (m, 1H), 1.86 – 1.75 (m, 4H), 1.67 (dd, *J* = 11.5, 3.6 Hz, 1H), 1.61 – 1.46 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 3H), 1.23 – 1.03 (m, 5H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.7, 132.9, 131.8, 120.2, 49.7, 42.8, 30.7, 29.1, 26.5, 26.4, 26.4, 17.9.
HRMS (ESI) m/z: Calcd for $C_{14}H_{20}BrS$ $[M+H]^+$, 301.0443.; Found, 301.0449.

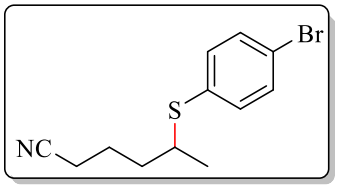
(4-bromobutan-2-yl)(4-bromophenyl)sulfane (c6)



Purification by column chromatography on silica gel (hexane/ethyl acetate = 150:1, v/v) afforded the title compound as a colorless oil (46 mg, 72% yield).

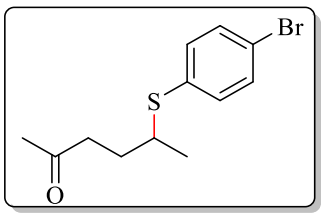
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 3.56 (ddt, *J* = 38.8, 10.1, 6.7 Hz, 2H), 3.38 (h, *J* = 6.8 Hz, 1H), 2.18 – 1.96 (m, 2H), 1.31 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.0, 133.4, 132.0, 121.4, 42.1, 39.2, 30.8, 20.9.
HRMS (ESI) m/z: Calcd for $C_{10}H_{13}Br_2S$ $[M+H]^+$, 324.9079.; Found, 324.9079.

5-((4-bromophenyl)thio)hexanenitrile (c7)



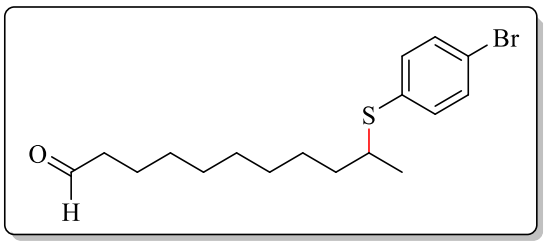
Purification by column chromatography on silica gel (hexane/ethyl acetate = 30:1, v/v) afforded the title compound as a yellow oil (48 mg, 85% yield).
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 4.5 Hz, 2H), 3.18 (h, *J* = 6.5 Hz, 1H), 2.36 (t, *J* = 7.1 Hz, 2H), 1.91 – 1.77 (m, 2H), 1.70 (q, *J* = 8.2, 7.4 Hz, 2H), 1.29 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 134.0, 133.6, 132.1, 121.4, 119.3, 43.0, 35.4, 22.8, 21.2, 17.1.
HRMS (ESI) m/z: Calcd for $C_{12}H_{15}BrNS$ $[M+H]^+$, 286.0082.; Found, 286.0075.

5-((4-bromophenyl)thio)hexan-2-one (c8)



Purification by column chromatography on silica gel (hexane/ethyl acetate = 50:1, v/v) afforded the title compound as a colorless oil (41 mg, 72% yield).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 3.21 (h, *J* = 6.7 Hz, 1H), 2.63 (td, *J* = 7.7, 3.6 Hz, 2H), 2.14 (s, 3H), 1.90 – 1.72 (m, 2H), 1.27 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 207.9, 134.0, 133.6, 131.9, 121.0, 43.0, 40.6, 30.1, 30.0, 21.3.
HRMS (ESI) m/z: Calcd for $C_{12}H_{16}BrOS$ $[M+H]^+$, 289.0079.; Found, 289.0074.

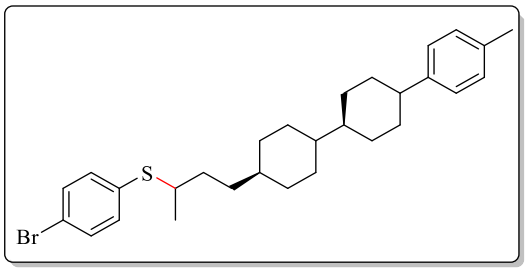
10-((4-bromophenyl)thio)undecanal (c9)



Purification by column chromatography on silica gel (hexane/ethyl acetate = 40:1, v/v) afforded the title compound as a brown oil (44 mg, 62% yield).

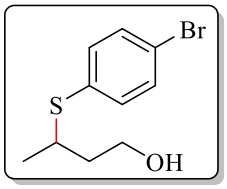
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.77 (t, *J* = 1.8 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 3.18 (h, *J* = 6.6 Hz, 1H), 2.42 (td, *J* = 7.4, 1.8 Hz, 2H), 1.67 – 1.49 (m, 4H), 1.49 – 1.35 (m, 3H), 1.34 – 1.28 (m, 7H), 1.26 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 202.8, 134.8, 133.3, 131.8, 120.6, 43.9, 43.5, 36.5, 29.3, 29.3, 29.1, 26.9, 22.0, 21.0.
HRMS (ESI) m/z: Calcd for $C_{17}H_{26}BrOS$ $[M+H]^+$, 359.0862.; Found, 359.0868.

(4-bromophenyl)(4-(4'-(*p*-tolyl)-[1,1'-bi(cyclohexan)]-4-yl)butan-2-yl)sulfane (c10)



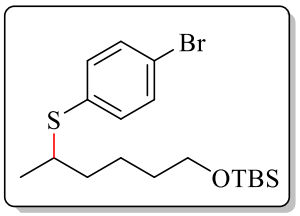
Purification by column chromatography on silica gel (hexane/ethyl acetate = 100:1, v/v) afforded the title compound as a white solid (68 mg, 68% yield). Mp. 99.3 - 103.2 ℃.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.5 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.14 (s, 4H), 3.19 (q, *J* = 6.7 Hz, 1H), 2.51 – 2.39 (m, 1H), 2.36 (s, 3H), 1.99 – 1.91 (m, 2H), 1.90 – 1.83 (m, 2H), 1.79 (d, *J* = 9.9 Hz, 4H), 1.66 (dt, *J* = 16.0, 6.3 Hz, 1H), 1.59 – 1.52 (m, 1H), 1.50 – 1.32 (m, 5H), 1.30 (d, *J* = 6.5 Hz, 3H), 1.28 – 1.14 (m, 4H), 1.08 – 0.88 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.9, 135.2, 134.9, 133.3, 131.9, 129.0, 126.7, 120.6, 44.3, 43.9, 43.4, 42.9, 37.9, 34.7, 34.0, 33.6, 33.5, 30.4, 30.1, 21.1, 21.0.
HRMS (ESI) m/z: Calcd for $C_{29}H_{40}BrS$ $[M+H]^+$, 501.2011.; Found, 501.2013.

3-((4-bromophenyl)thio)butan-1-ol (c11)



Purification by column chromatography on silica gel (hexane/ethyl acetate = 10:1, v/v) afforded the title compound as a brown oil (38 mg, 73% yield).
^{1}H NMR (400 MHz, Methanol-d_4) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 4.61 (s, 1H), 3.79 – 3.63 (m, 2H), 3.42 (h, *J* = 6.8 Hz, 1H), 1.77 (ddt, *J* = 35.8, 14.0, 7.0 Hz, 2H), 1.30 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, Methanol-d_4) δ 134.7, 133.0, 131.6, 120.2, 58.9, 39.5, 39.0, 20.2.
HRMS (ESI) m/z: Calcd for $C_{10}H_{14}BrOS$ $[M+H]^+$, 262.9922.; Found, 262.9926.

((5-((4-bromophenyl)thio)hexyl)oxy)(*tert*-butyl)dimethylsilane (c12)



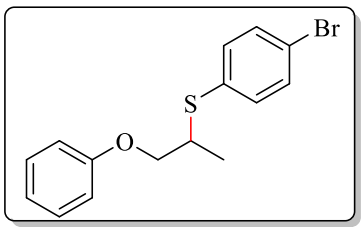
Purification by column chromatography on silica gel (hexane/ethyl acetate = 100:1, v/v) afforded the title compound as a colorless oil (68 mg, 84% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 3.61 (t, *J* = 6.0 Hz, 2H), 3.19 (q, *J* = 6.4 Hz, 1H), 1.74 – 1.57 (m, 1H), 1.52 (m, 5H), 1.28 (d, *J* = 6.7 Hz, 3H), 0.91 (s, 9H), 0.06 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.7, 133.4, 131.8, 120.7, 62.9, 43.5, 36.3, 32.6, 26.0, 23.3, 21.0, 18.3, -5.3.

HRMS (ESI) m/z: Calcd for $C_{18}H_{32}BrOSSi$ $[M+H]^+$, 405.1102.; Found, 405.1105.

(4-bromophenyl)(1-phenoxypropan-2-yl)sulfane (c13)



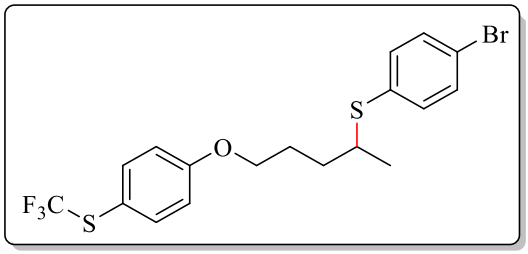
Purification by column chromatography on silica gel (hexane/ethyl acetate = 100:1, v/v) afforded the title compound as a colorless oil (27 mg, 42% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.28 – 7.18 (m, 2H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 7.7 Hz, 2H), 4.03 (dd, *J* = 9.5, 5.0 Hz, 1H), 3.92 – 3.83 (m, 1H), 3.59 – 3.46 (m, 1H), 1.42 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.5, 133.8, 133.4, 132.1, 129.5, 121.4, 121.1, 114.6, 71.5, 42.3, 18.0.

HRMS (ESI) m/z: Calcd for $C_{15}H_{16}BrOS$ $[M+H]^+$, 325.0080.; Found, 325.0082.

(4-bromophenyl)(5-(4-((trifluoromethyl)thio)phenoxy)pentan-2-yl)sulfane (c14)



Purification by column chromatography on silica gel (hexane/ethyl acetate = 100:1, v/v) afforded the title compound as a yellow oil (78 mg, 86% yield).

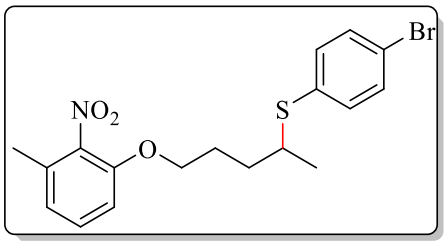
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.98 (t, *J* = 6.2 Hz, 2H), 3.25 (h, *J* = 6.7 Hz, 1H), 1.97 (p, *J* = 6.9 Hz, 2H), 1.83 – 1.66 (m, 2H), 1.32 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.2, 138.3, 134.2, 133.7, 131.9, 129.6 (d, *J* = 309.3 Hz), 121.0, 115.5 (d, *J* = 4.3 Hz), 67.7, 43.3, 32.9, 26.5, 21.1.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -43.90.

HRMS (ESI) m/z: Calcd for $C_{18}H_{19}BrF_3OS_2$ $[M+H]^+$, 452.9987.; Found, 452..9984

(4-bromophenyl)(5-(3-methyl-2-nitrophenoxy)pentan-2-yl)sulfane (c15)



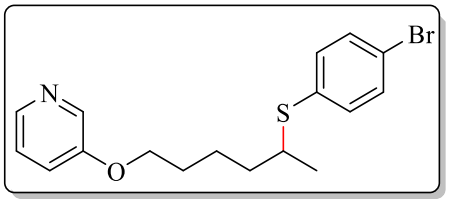
Purification by column chromatography on silica gel (hexane/ethyl acetate = 100:1, v/v) afforded the title compound as a colorless oil (52 mg, 63% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.29 – 7.20 (m, 3H), 6.85 (dd, *J* = 8.0, 5.1 Hz, 2H), 4.05 (t, *J* = 6.1 Hz, 2H), 3.22 (h, *J* = 6.7 Hz, 1H), 2.32 (s, 3H), 2.00 – 1.81 (m, 2H), 1.80 – 1.59 (m, 2H), 1.30 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.1, 134.1, 133.7, 131.9, 131.0, 130.6, 122.6, 121.0, 110.9, 69.0, 43.2, 32.7, 26.3, 21.1, 17.0.

HRMS (ESI) m/z: Calcd for $C_{18}H_{21}BrNO_3S$ $[M+H]^+$, 412.0401.; Found, 412.0410.

3-((5-((4-bromophenyl)thio)hexyl)oxy)pyridine (c16)



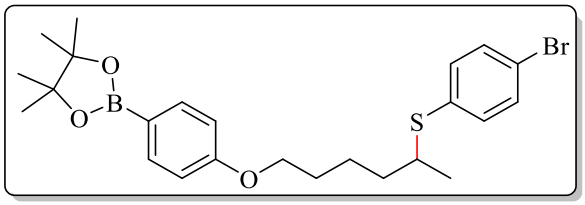
Purification by column chromatography on silica gel (hexane/ethyl acetate = 10:1, v/v) afforded the title compound as a white oil (44 mg, 60% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.31 (d, *J* = 2.8 Hz, 1H), 8.22 (d, *J* = 4.5 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 4.6 Hz, 2H), 7.25 – 7.12 (m, 2H), 3.99 (t, *J* = 6.3 Hz, 2H), 3.21 (h, *J* = 6.4 Hz, 1H), 1.80 (p, *J* = 6.6 Hz, 2H), 1.76 – 1.51 (m, 4H), 1.29 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.2, 141.9, 137.9, 134.4, 133.6, 131.9, 123.9, 121.2, 120.8, 68.0, 43.4, 36.1, 28.9, 23.4, 21.0.

HRMS (ESI) m/z: Calcd for $C_{17}H_{21}BrNOS$ $[M+H]^+$, 368.0502.; Found, 368.0508.

2-(4-((5-((4-bromophenyl)thio)hexyl)oxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (c17)



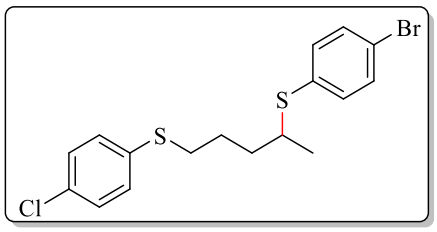
Purification by column chromatography on silica gel (hexane/ethyl acetate = 50:1, v/v) afforded the title compound as a yellow oil (63 mg, 64% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 3.8 Hz, 2H), 6.89 (d, *J* = 8.1 Hz, 2H), 3.99 (t, *J* = 6.3 Hz, 2H), 3.22 (h, *J* = 6.5 Hz, 1H), 1.84 – 1.76 (m, 2H), 1.71 – 1.57 (m, 4H), 1.35 (s, 12H), 1.30 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.6, 136.5, 134.5, 133.6, 131.9, 120.8, 113.9, 83.5, 67.4, 43.5, 36.2, 29.0, 24.9, 23.5, 21.1.

HRMS (ESI) m/z: Calcd for $C_{24}H_{33}BBrO_3S$ $[M+H]^+$, 493.1407.; Found, 493.1407.

(4-bromophenyl)(5-((4-chlorophenyl)thio)pentan-2-yl)sulfane (c18)



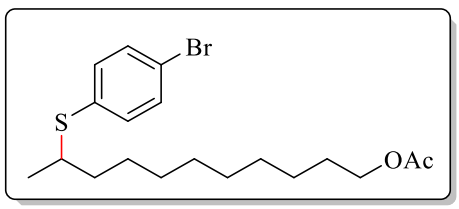
Purification by column chromatography on silica gel (hexane/ethyl acetate = 100:1, v/v) afforded the title compound as a colorless oil (52 mg, 65% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 6.9 Hz, 2H), 7.28 – 7.21 (m, 6H), 3.18 (h, *J* = 6.6 Hz, 1H), 2.90 (t, *J* = 7.0 Hz, 2H), 1.79 (dd, *J* = 15.2, 6.4 Hz, 2H), 1.68 (dt, *J* = 14.4, 7.1 Hz, 2H), 1.27 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.0, 134.2, 133.7, 131.9, 130.6, 129.0, 121.0, 43.2, 35.4, 33.8, 26.3, 21.1.

HRMS (ESI) m/z: Calcd for $C_{17}H_{19}BrClS_2$ $[M+H]^+$, 402.9772.; Found, 402.9773.

10-((4-bromophenyl)thio)undecyl acetate (c19)



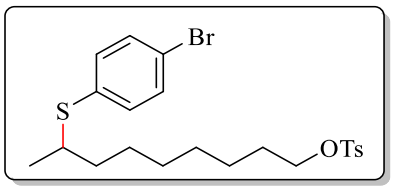
Purification by column chromatography on silica gel (hexane/ethyl acetate = 40:1, v/v) afforded the title compound as a colorless oil (77 mg, 96% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 4.06 (t, *J* = 6.8 Hz, 2H), 3.18 (h, *J* = 6.6 Hz, 1H), 2.06 (s, 3H), 1.68 – 1.43 (m, 6H), 1.43 – 1.28 (m, 10H), 1.27 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.2, 134.8, 133.3, 131.8, 120.6, 64.6, 43.5, 36.5, 29.4, 29.2, 28.6, 27.0, 25.9, 21.0, 21.0.

HRMS (ESI) m/z: Calcd for $C_{19}H_{30}BrO_2S$ $[M+H]^+$, 403.1125.; Found, 403.1121.

8-((4-bromophenyl)thio)nonyl 4-methylbenzenesulfonate (c20)



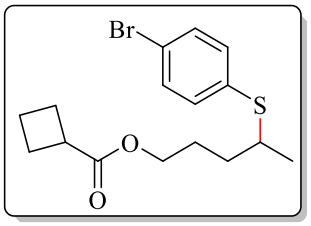
Purification by column chromatography on silica gel (hexane/ethyl acetate = 40:1, v/v) afforded the title compound as a yellow oil (64 mg, 66% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 4.01 (t, *J* = 6.5 Hz, 2H), 3.17 (h, *J* = 6.6 Hz, 1H), 2.44 (s, 3H), 1.67 – 1.33 (m, 7H), 1.25 (d, *J* = 6.7 Hz, 3H), 1.24 – 1.17 (m, 5H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.6, 134.8, 133.3, 131.8, 129.8, 127.9, 120.6, 70.7, 43.4, 36.5, 29.2, 28.8, 28.8, 26.9, 25.3, 21.6, 21.0.

HRMS (ESI) m/z: Calcd for $C_{22}H_{30}BrO_3S_2$ $[M+H]^+$, 487.0795.; Found, 487.0794.

4-((4-bromophenyl)thio)pentyl cyclobutanecarboxylate (c21)



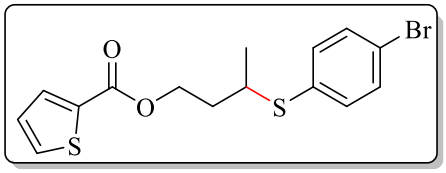
Purification by column chromatography on silica gel (hexane/ethyl acetate = 30:1, v/v) afforded the title compound as a colorless oil (43 mg, 61% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 4.08 (t, *J* = 6.5 Hz, 2H), 3.20 (h, *J* = 6.7 Hz, 1H), 3.10 (q, *J* = 9.4, 8.5 Hz, 1H), 2.26 (dd, *J* = 11.8, 8.9 Hz, 2H), 2.23 – 2.14 (m, 2H), 2.05 – 1.88 (m, 2H), 1.84 – 1.75 (m, 2H), 1.71 – 1.52 (m, 2H), 1.29 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.5, 134.2, 133.7, 131.9, 121.0, 63.8, 43.2, 38.1, 32.8, 26.1, 25.3, 21.0, 18.4.

HRMS (ESI) m/z: Calcd for $C_{16}H_{22}BrO_2S$ $[M+H]^+$, 359.0499.; Found, 359.0491.

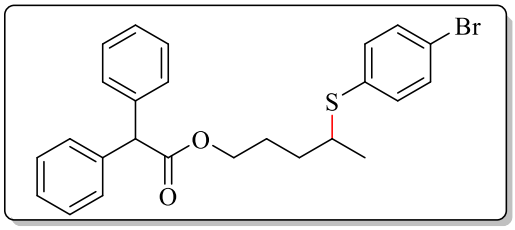
3-((4-bromophenyl)thio)butyl thiophene-2-carboxylate (c22)



Purification by column chromatography on silica gel (hexane/ethyl acetate = 30:1, v/v) afforded the title compound as a colorless oil (46 mg, 62% yield).

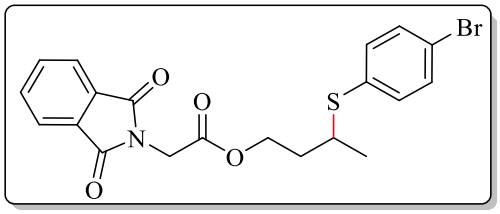
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 4.0 Hz, 1H), 7.56 (d, *J* = 4.9 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.11 (t, *J* = 4.4 Hz, 1H), 4.44 (t, *J* = 6.3 Hz, 2H), 3.35 (h, *J* = 6.8 Hz, 1H), 1.99 (ddq, *J* = 52.0, 13.4, 6.5 Hz, 2H), 1.36 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (151 MHz, Chloroform-*d*) δ 162.0, 133.9, 133.7, 133.6, 133.5, 132.5, 132.0, 127.8, 121.2, 62.6, 40.5, 35.6, 21.2.
HRMS (ESI) m/z: Calcd for $C_{15}H_{16}BrO_2S_2$ $[M+H]^+$, 372.9749.; Found, 372.9752.

4-((4-bromophenyl)thio)pentyl 2,2-diphenylacetate (c23)



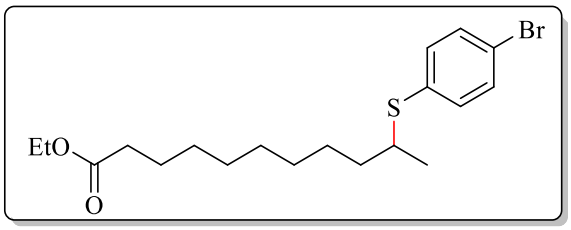
Purification by column chromatography on silica gel (hexane/ethyl acetate = 30:1, v/v) afforded the title compound as a yellow oil (81 mg, 86% yield).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.35 (m, 8H), 7.34 – 7.29 (m, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 5.07 (s, 1H), 4.21 (t, *J* = 7.3 Hz, 2H), 3.17 (h, *J* = 6.7 Hz, 1H), 1.87 – 1.76 (m, 2H), 1.68 – 1.46 (m, 2H), 1.26 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 138.7, 134.2, 133.7, 132.0, 128.7, 127.3, 121.0, 64.8, 57.2, 43.1, 32.8, 26.0, 21.1.
HRMS (ESI) m/z: Calcd for $C_{25}H_{26}BrO_2S$ $[M+H]^+$, 471.0813.; Found, 471.0811.

3-((4-bromophenyl)thio)butyl 2-(1,3-dioxoisoindolin-2-yl)acetate (c24)



Purification by column chromatography on silica gel (hexane/ethyl acetate = 20:1, v/v) afforded the title compound as a colorless oil (75 mg, 83% yield).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.44 (s, 2H), 4.32 (t, *J* = 7.3 Hz, 1H), 3.22 (h, *J* = 6.8 Hz, 1H), 1.87 (dddd, *J* = 27.5, 20.9, 13.4, 6.5 Hz, 2H), 1.28 (d, *J* = 6.7 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.4, 167.1, 134.3, 133.9, 133.6, 132.7, 132.0, 132.0, 123.6, 123.6, 121.3, 63.4, 40.3, 38.9, 35.2, 21.1.
HRMS (ESI) m/z: Calcd for $C_{20}H_{19}BrNO_4S$ $[M+H]^+$, 450.0194.; Found, 450.0192.

ethyl 10-((4-bromophenyl)thio)undecanoate (c25)



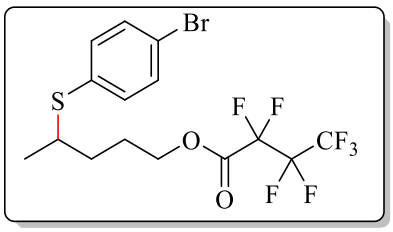
Purification by column chromatography on silica gel (hexane/ethyl acetate = 50:1, v/v) afforded the title compound as a brown oil (69 mg, 86% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.17 (h, *J* = 6.6 Hz, 1H), 2.28 (t, *J* = 7.5 Hz, 2H), 1.65 – 1.54 (m, 4 H), 1.49 – 1.37 (m, 2H), 1.30 – 1.27 (m, 5H), 1.26 (d, *J* = 3.3 Hz, 3H), 1.26 – 1.23 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.8, 134.8, 133.3, 131.8, 120.6, 60.1, 43.5, 36.5, 34.3, 29.3, 29.3, 29.2, 29.1, 26.9, 24.9, 21.0, 14.2.

HRMS (ESI) m/z: Calcd for $C_{19}H_{30}BrO_2S$ $[M+H]^+$, 403.1125.; Found, 403.1125.

4-((4-bromophenyl)thio)pentyl 2,2,3,3,4,4,4-heptafluorobutanoate (c26)



Purification by column chromatography on silica gel (hexane/ethyl acetate = 100:1, v/v) afforded the title compound as a yellow oil (50 mg, 53% yield).

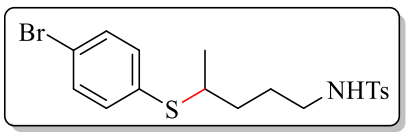
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 4.38 (t, *J* = 6.5 Hz, 2H), 3.19 (h, *J* = 6.7 Hz, 1H), 1.92 (tt, *J* = 8.8, 6.5 Hz, 2H), 1.70 – 1.55 (m, 2H), 1.29 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 158.3 (t, *J* = 29.4 Hz), 134.4, 133.9, 133.7, 132.0, 130.2 (d, *J* = 48.2 Hz), 128.6 (d, *J* = 12.1 Hz), 127.7 (d, *J* = 9.3 Hz), 121.3, 117.4 (dt, *J* = 287.6, 33.4 Hz), 109.4 (d, *J* = 32.9 Hz), 106.7 (dt, *J* = 266.1, 32.4 Hz), 68.2, 43.1, 32.3, 25.5, 21.0.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -80.75 (t, *J* = 8.5 Hz), -119.37 (q, *J* = 8.6 Hz), -126.99.

HRMS (ESI) m/z: Calcd for $C_{15}H_{15}BrF_7O_2S$ $[M+H]^+$, 472.9839.; Found, 472.9833.

***N*-(4-((4-bromophenyl)thio)pentyl)-4-methylbenzenesulfonamide (c27)**



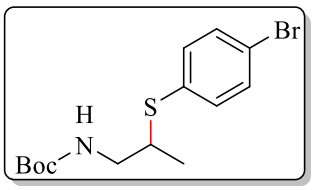
Purification by column chromatography on silica gel (hexane/ethyl acetate = 10:1, v/v) afforded the title compound as a colorless oil (61 mg, 71% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 4.64 (s, 1H), 3.12 (h, *J* = 6.6 Hz, 1H), 2.94 (q, *J* = 6.6 Hz, 2H), 2.44 (s, 3H), 1.69 – 1.55 (m, 2H), 1.58 – 1.42 (m, 2H), 1.22 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.5, 134.1, 133.6, 131.9, 129.7, 127.1, 121.0, 43.1, 42.9, 33.3, 27.0, 21.5, 21.1.

HRMS (ESI) m/z: Calcd for $C_{18}H_{23}BrNO_2S_2$ $[M+H]^+$, 430.0328.; Found, 430.0325.

tert-butyl (2-((4-bromophenyl)thio)propyl)carbamate (c28)



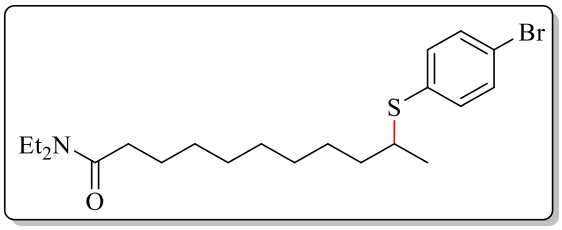
Purification by column chromatography on silica gel (hexane/ethyl acetate = 10:1, v/v) afforded the title compound as a colorless oil (49 mg, 70% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 4.94 (s, 1H), 3.36 – 3.27 (m, 1H), 3.26 – 3.15 (m, 2H), 1.44 (s, 9H), 1.28 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.8, 133.8, 133.2, 132.1, 121.4, 45.5, 43.9, 29.9, 28.4, 18.6.

HRMS (ESI) m/z: Calcd for $C_{14}H_{21}BrNO_2S$ $[M+H]^+$, 348.0451.; Found, 348.0456.

10-((4-bromophenyl)thio)-*N*,*N*-diethylundecanamide (c29)



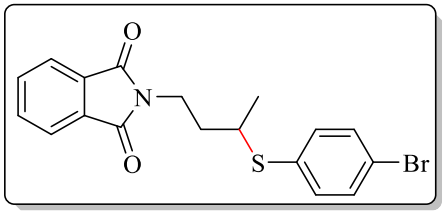
Purification by column chromatography on silica gel (hexane/ethyl acetate = 20:1, v/v) afforded the title compound as a colorless oil (63 mg, 73% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 3.36 (q, *J* = 7.1 Hz, 2H), 3.29 (q, *J* = 7.1 Hz, 2H), 3.16 (h, *J* = 6.6 Hz, 1H), 2.32 – 2.23 (t, *J* = 7.6 Hz, 2H), 1.69 – 1.45 (m, 4H), 1.45 – 1.36 (m, 2H), 1.32 – 1.26 (m, 8H), 1.24 (d, *J* = 6.6 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.3, 134.8, 133.3, 131.8, 120.5, 43.5, 42.0, 40.0, 36.5, 33.1, 29.5, 29.4, 26.9, 25.5, 21.0, 14.4, 13.1.

HRMS (ESI) m/z: Calcd for $C_{21}H_{35}BrNOS$ $[M+H]^+$, 430.1598.; Found, 430.1596.

2-(3-((4-bromophenyl)thio)butyl)isoindoline-1,3-dione (c30)



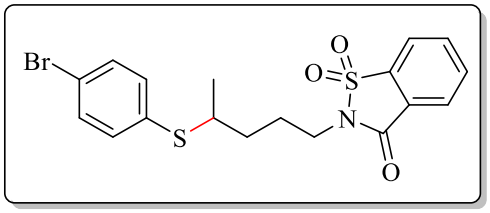
Purification by column chromatography on silica gel (hexane/ethyl acetate = 10:1, v/v) afforded the title compound as a colorless oil (75 mg, 96% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.75 (m, 2H), 7.74 – 7.68 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.86 (dp, *J* = 21.4, 7.3 Hz, 2H), 3.15 (h, *J* = 6.7 Hz, 1H), 1.88 (dh, *J* = 28.7, 7.3 Hz, 2H), 1.32 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.3, 134.6, 134.0, 132.1, 131.9, 123.3, 121.5, 41.5, 35.9, 35.0, 21.2.

HRMS (ESI) m/z: Calcd for $C_{18}H_{17}BrNO_2S$ $[M+H]^+$, 392.0138.; Found, 392.0131.

2-(4-((4-bromophenyl)thio)pentyl)benzo[d]isothiazol-3(2*H*)-one 1,1-dioxide (c31)



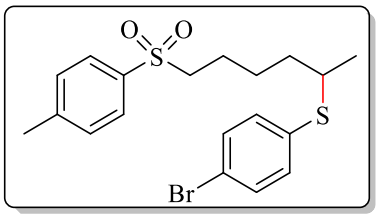
Purification by column chromatography on silica gel (hexane/ethyl acetate = 30:1, v/v) afforded the title compound as a colorless oil (65 mg, 74% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.02 (m, 1H), 7.97 – 7.79 (m, 3H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 3.79 (t, *J* = 7.2 Hz, 2H), 3.23 (h, *J* = 6.7 Hz, 1H), 2.03 (p, *J* = 7.2 Hz, 2H), 1.78 – 1.58 (m, 2H), 1.29 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.0, 137.6, 134.8, 134.4, 134.0, 133.9, 131.9, 127.3, 125.2, 121.1, 120.9, 43.1, 39.0, 33.3, 25.8, 21.0.

HRMS (ESI) m/z: Calcd for $C_{18}H_{19}BrNO_3S_2$ $[M+H]^+$, 441.9964.; Found, 441.9956.

(4-bromophenyl)(6-tosylhexan-2-yl)sulfane (c32)



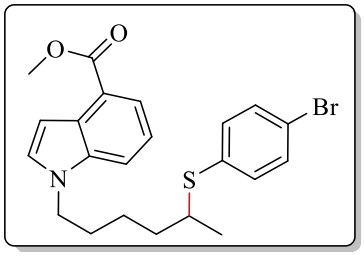
Purification by column chromatography on silica gel (hexane/ethyl acetate = 30:1, v/v) afforded the title compound as a yellow oil (61 mg, 71% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.37 (dd, *J* = 13.4, 8.0 Hz, 4H), 7.21 (d, *J* = 8.3 Hz, 2H), 3.11 (h, *J* = 6.4 Hz, 1H), 3.08 – 3.01 (m, 2H), 2.45 (s, 3H), 1.70 (p, *J* = 7.1 Hz, 2H), 1.51 (p, *J* = 6.6 Hz, 4H), 1.22 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.7, 136.2, 134.2, 133.5, 131.9, 129.9, 128.1, 120.9, 56.2, 43.1, 35.9, 25.6, 22.6, 21.7, 21.0.

HRMS (ESI) m/z: Calcd for $C_{19}H_{24}BrO_2S_2$ $[M+H]^+$, 429.0375.; Found, 429.0370.

methyl 1-(5-((4-bromophenyl)thio)hexyl)-1*H*-indole-4-carboxylate (c33)



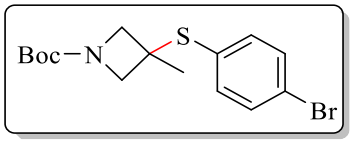
Purification by column chromatography on silica gel (hexane/ethyl acetate = 30:1, v/v) afforded the title compound as a yellow oil (96 mg, 99% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.22 – 7.17 (m, 3H), 7.12 (d, *J* = 3.1 Hz, 1H), 4.14 (t, *J* = 7.0 Hz, 2H), 3.98 (s, 3H), 3.10 (h, *J* = 6.7 Hz, 1H), 1.82 (p, *J* = 7.3 Hz, 2H), 1.67 – 1.37 (m, 4H), 1.21 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.1, 136.7, 134.3, 133.6, 131.9, 129.9, 128.1, 123.0, 121.7, 120.9, 120.6, 114.1, 102.4, 51.8, 46.4, 43.4, 36.1, 30.1, 24.4, 21.1.

HRMS (ESI) m/z: Calcd for $C_{22}H_{25}BrNO_2S$ $[M+H]^+$, 448.0765.; Found, 448.0762.

***tert*-butyl 3-((4-bromophenyl)thio)-3-methylazetidine-1-carboxylate (c34)**



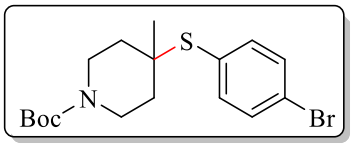
Purification by column chromatography on silica gel (hexane/ethyl acetate = 50:1, v/v) afforded the title compound as a white solid (48 mg, 68% yield). Mp. 80.6 – 83.7 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 4.03 (d, *J* = 8.9 Hz, 2H), 3.82 (d, *J* = 8.9 Hz, 2H), 1.57 (s, 3H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.1, 136.1, 132.2, 131.4, 123.2, 79.9, 62.1, 43.2, 28.3, 26.7.

HRMS (ESI) m/z: Calcd for $C_{15}H_{21}BrNO_2S$ $[M+H]^+$, 360.0451.; Found, 360.0445.

***tert*-butyl 4-((4-bromophenyl)thio)-4-methylpiperidine-1-carboxylate (c35)**



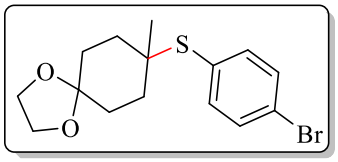
Purification by column chromatography on silica gel (hexane/ethyl acetate = 50:1, v/v) afforded the title compound as a colorless oil (35 mg, 45% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 3.66 – 3.58 (m, 2H), 3.54 – 3.43 (m, 2H), 1.70 – 1.59 (m, 2H), 1.57 – 1.49 (m, 2H), 1.46 (s, 9H), 1.27 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.8, 139.1, 131.9, 123.8, 79.5, 48.3, 37.0, 28.8, 28.4.

HRMS (ESI) m/z: Calcd for $C_{17}H_{25}BrNO_2S$ $[M+H]^+$, 388.0764.; Found, 388.0761.

8-((4-bromophenyl)thio)-8-methyl-1,4-dioxaspiro[4.5]decane (c36)



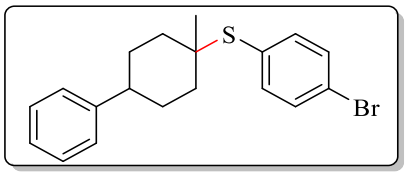
Purification by column chromatography on silica gel (hexane/ethyl acetate = 50:1, v/v) afforded the title compound as a colorless oil (40 mg, 54% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 4.01 – 3.89 (m, 4H), 2.02 (ddd, *J* = 13.8, 11.2, 4.3 Hz, 2H), 1.72 – 1.56 (m, 6H), 1.26 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.9, 131.7, 131.0, 123.5, 108.5, 64.3, 64.2, 49.4, 35.5, 31.2.

HRMS (ESI) m/z: Calcd for $C_{17}H_{25}BrO_2S$ $[M+H]^+$, 374.0733.; Found, 345.0344.

(4-bromophenyl)(1-methyl-4-phenylcyclohexyl)sulfane (c37)



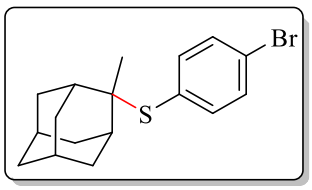
Purification by column chromatography on silica gel (hexane/ethyl acetate = 100:1, v/v) afforded the title compound as a white solid (38 mg, 52% yield). Mp. 64.9 – 66.8 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 6.7 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.41 – 7.33 (m, 4H), 7.30 – 7.21 (m, 1H), 2.54 (tt, *J* = 12.3, 3.6 Hz, 1H), 2.18 (qd, *J* = 13.1, 3.2 Hz, 2H), 1.86 (d, *J* = 14.4 Hz, 2H), 1.77 (dd, *J* = 13.5, 3.3 Hz, 2H), 1.62 – 1.49 (m, 2H), 1.28 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.1, 139.1, 131.7, 131.4, 128.4, 127.0, 126.1, 123.4, 50.4, 44.2, 38.2, 32.0, 29.9.

HRMS (ESI) m/z: Calcd for $C_{19}H_{22}BrS$ $[M+H]^+$, 363.0601.; Found, 363.0598.

(4-bromophenyl)((1*r*,3*r*,5*r*,7*r*)-2-methyladamantan-2-yl)sulfane (c38)



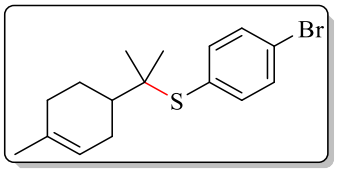
Purification by column chromatography on silica gel (hexane/ethyl acetate = 50:1, v/v) afforded the title compound as a white solid (45 mg, 67% yield). Mp. 131.0 - 132.2 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 2.73 (d, *J* = 15.9 Hz, 2H), 2.17 – 1.60 (m, 12H), 1.35 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.7, 132.3, 131.5, 123.0, 58.4, 39.3, 37.1, 33.8, 27.7, 27.5, 26.4.

HRMS (ESI) m/z: Calcd for $C_{17}H_{22}BrS$ $[M+H]^+$, 339.0600.; Found, 339.0602.

(4-bromophenyl)(2-(4-methylcyclohex-3-en-1-yl)propan-2-yl)sulfane (c39)



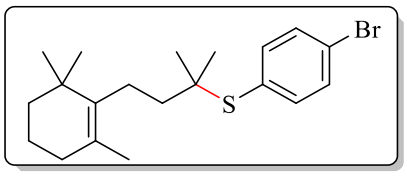
Purification by column chromatography on silica gel (hexane/ethyl acetate = 100:1, v/v) afforded the title compound as a colorless oil (36 mg, 55% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 5.41 – 5.36 (m, 1H), 2.24 – 2.16 (m, 1H), 2.15 – 2.06 (m, 1H), 2.05 – 1.98 (m, 2H), 1.99 – 1.88 (m, 1H), 1.67 (s, 3H), 1.62 – 1.51 (m, 1H), 1.44 – 1.32 (m, 1H), 1.23 (s, 3H), 1.19 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.2, 134.1, 131.6, 131.5, 123.4, 120.7, 53.1, 42.8, 31.2, 27.2, 27.2, 25.1, 24.8, 23.3.

HRMS (ESI) m/z: Calcd for $C_{16}H_{22}BrS$ $[M+H]^+$, 327.0600.; Found, 327.0591.

(4-bromophenyl)(2-methyl-4-(2,6,6-trimethylcyclohex-1-en-1-yl)butan-2-yl)sulfane (c40)



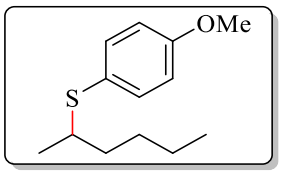
Purification by column chromatography on silica gel (hexane/ethyl acetate = 100:1, v/v) afforded the title compound as a white solid (44 mg, 57% yield). Mp. 68.3-70.3 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 2.19 – 2.10 (m, 2H), 1.92 (t, *J* = 6.3 Hz, 2H), 1.70 – 1.60 (m, 2H), 1.60 – 1.53 (m, 5H), 1.47 – 1.39 (m, 2H), 1.27 (s, 6H), 1.00 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.9, 136.5, 133.0, 131.6, 127.3, 123.3, 50.0, 42.8, 39.9, 35.1, 32.8, 28.7, 28.5, 23.6, 19.9, 19.5.

HRMS (ESI) m/z: Calcd for $C_{20}H_{30}BrS$ $[M+H]^+$, 383.1227.; Found, 383.1232.

hexan-2-yl(4-methoxyphenyl)sulfane (c41)



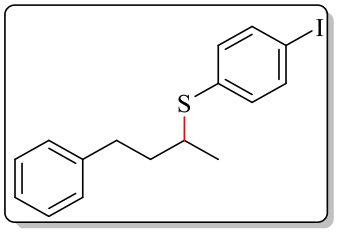
Purification by column chromatography on silica gel (hexane/ethyl acetate = 100:1, v/v) afforded the title compound as a colorless oil (30 mg, 65% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 3.82 (s, 3H), 3.02 (h, *J* = 6.4 Hz, 1H), 1.59 – 1.41 (m, 4H), 1.37 – 1.27 (m, 2H), 1.23 (d, *J* = 6.7 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.3, 135.6, 114.3, 55.3, 44.6, 36.3, 29.3, 22.6, 21.1, 14.0.

HRMS (ESI) m/z: Calcd for $C_{13}H_{21}OS$ $[M+H]^+$, 225.1308.; Found, 225.1310.

(4-iodophenyl)(4-phenylbutan-2-yl)sulfane (c43)



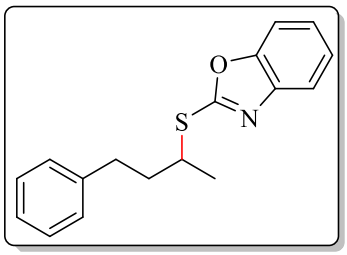
Purification by column chromatography on silica gel (hexane/ethyl acetate = 40:1, v/v) afforded the title compound as a colorless oil (64 mg, 87% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.26 – 7.15 (m, 3H), 7.07 (d, *J* = 8.4 Hz, 2H), 3.19 (h, *J* = 6.7 Hz, 1H), 2.89 – 2.69 (m, 2H), 2.00 – 1.77 (m, 2H), 1.33 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.4, 137.8, 135.4, 133.3, 128.4, 126.0, 91.7, 42.4, 38.1, 33.1, 21.1.

HRMS (ESI) m/z: Calcd for $C_{16}H_{18}IS$ $[M+H]^+$, 369.0168.; Found, 369.0169.

2-((4-phenylbutan-2-yl)thio)benzo[*d*]oxazole (c44)



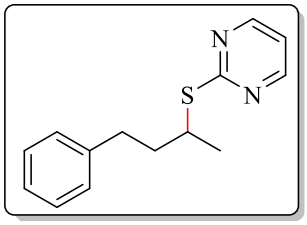
Purification by column chromatography on silica gel (hexane/ethyl acetate = 10:1, v/v) afforded the title compound as a white solid (53 mg, 94% yield). Mp. 141.2 - 143.4 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.33 – 7.15 (m, 5H), 7.10 (d, *J* = 6.7 Hz, 2H), 3.99 (h, *J* = 6.8 Hz, 1H), 2.75 (t, *J* = 8.1 Hz, 2H), 2.03 (ddt, *J* = 30.4, 15.2, 7.5 Hz, 2H), 1.49 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.7, 141.3, 139.4, 128.5, 128.4, 126.0, 122.5, 114.4, 43.4, 38.7, 33.2, 22.0.

HRMS (ESI) m/z: Calcd for $C_{17}H_{18}NOS$ $[M+H]^+$, 284.1104.; Found, 284.1106.

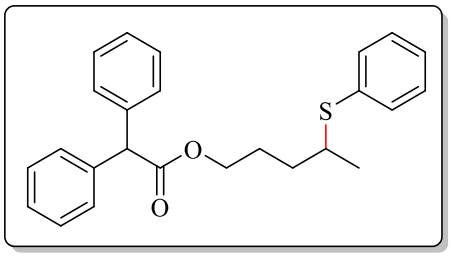
2-((4-phenylbutan-2-yl)thio)pyrimidine (c45)



Purification by column chromatography on silica gel (hexane/ethyl acetate = 10:1, v/v) afforded the title compound as a yellow oil (30 mg, 62% yield).

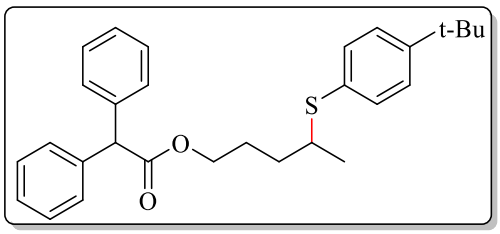
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.51 (d, *J* = 4.8 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.24 – 7.17 (m, 3H), 6.95 (t, *J* = 4.9 Hz, 1H), 3.93 (h, *J* = 6.8 Hz, 1H), 2.82 (t, *J* = 7.0 Hz, 2H), 2.16 – 1.92 (m, 2H), 1.50 (d, *J* = 6.8 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.8, 157.2, 141.8, 134.4, 128.4, 128.3, 125.9, 116.3, 40.2, 38.1, 33.3, 21.2.
HRMS (ESI) m/z: Calcd for $C_{14}H_{17}N_2S$ $[M+H]^+$, 245.1107.; Found, 245.1098.

4-(phenylthio)pentyl 2,2-diphenylacetate (c46)



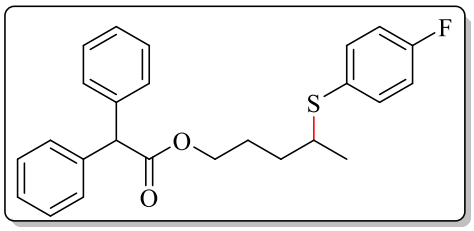
Purification by column chromatography on silica gel (hexane/ethyl acetate = 40:1, v/v) afforded the title compound as a yellow oil (40 mg, 51% yield).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 7.4 Hz, 2H), 7.36 – 7.31 (m, 8H), 7.31 – 7.23 (m, 5H), 5.04 (s, 1H), 4.18 (t, *J* = 7.7 Hz, 2H), 3.18 (h, *J* = 6.6 Hz, 1H), 1.82 (p, *J* = 7.1 Hz, 2H), 1.57 (ddd, *J* = 31.1, 14.2, 6.8 Hz, 2H), 1.25 (d, *J* = 6.4 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 138.7, 134.9, 132.2, 128.9, 128.6, 127.3, 126.9, 64.9, 57.2, 42.9, 32.8, 26.0, 21.2.
HRMS (ESI) m/z: Calcd for $C_{25}H_{27}O_2S$ $[M+H]^+$, 391.1726.; Found, 391.1733.

4-((4-(*tert*-butyl)phenyl)thio)pentyl 2,2-diphenylacetate (c47)



Purification by column chromatography on silica gel (hexane/ethyl acetate = 40:1, v/v) afforded the title compound as a yellow oil (57 mg, 64% yield).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (dd, *J* = 2.6, 1.6 Hz, 4H), 7.34 – 7.32 (m, 8H), 7.31 – 7.28 (m, 2H), 5.04 (s, 1H), 4.19 (td, *J* = 6.5, 3.0 Hz, 2H), 3.12 (h, *J* = 6.7 Hz, 1H), 1.89 – 1.67 (m, 2H), 1.67 – 1.41 (m, 2H), 1.34 (s, 9H), 1.24 (d, *J* = 5.3 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 150.3, 138.7, 132.4, 131.1, 128.6, 127.3, 125.9, 65.0, 57.2, 43.2, 34.5, 32.8, 31.3, 26.0, 21.3.
HRMS (ESI) m/z: Calcd for $C_{29}H_{35}O_2S$ $[M+H]^+$, 447.2352.; Found, 447.2353.

4-((4-fluorophenyl)thio)pentyl 2,2-diphenylacetate (c48)



Purification by column chromatography on silica gel (hexane/ethyl acetate = 50:1, v/v) afforded the title compound as a colorless oil (61 mg, 75% yield).

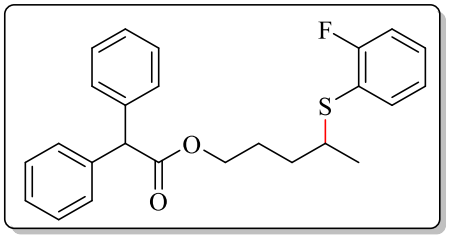
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.37 – 7.32 (m, 8H), 7.32 – 7.27 (m, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 5.04 (s, 1H), 4.19 (t, *J* = 6.5 Hz, 2H), 3.06 (h, *J* = 6.7 Hz, 1H), 1.82 (p, *J* = 6.7 Hz, 2H), 1.54 (dtd, *J* = 28.4, 14.9, 14.5, 7.7 Hz, 2H), 1.22 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 162.4 (d, *J* = 243.4 Hz), 138.7, 135.3 (d, *J* = 8.1 Hz), 129.6, 128.6, 127.3, 115.9 (d, *J* = 21.6 Hz), 64.9, 57.2, 43.9, 32.7, 26.0, 21.1.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.26.

HRMS (ESI) m/z: Calcd for $C_{25}H_{26}FO_2S$ $[M+H]^+$, 409.1632.; Found, 409.1638.

4-((2-fluorophenyl)thio)pentyl 2,2-diphenylacetate (c49)



Purification by column chromatography on silica gel (hexane/ethyl acetate = 40:1, v/v) afforded the title compound as a colorless oil (44 mg, 54% yield).

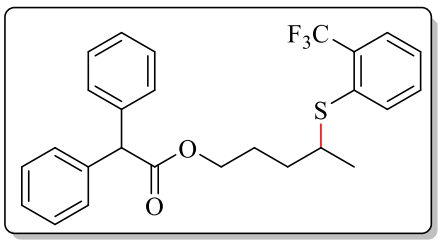
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (t, *J* = 7.7 Hz, 1H), 7.38 – 7.31 (m, 8H), 7.31 – 7.24 (m, 3H), 7.09 (t, *J* = 9.2 Hz, 2H), 5.04 (s, 1H), 4.18 (t, *J* = 7.8 Hz, 2H), 3.24 (h, *J* = 6.7 Hz, 1H), 1.83 (p, *J* = 7.0 Hz, 2H), 1.67 – 1.44 (m, 2H), 1.23 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 162.5 (d, *J* = 245.5 Hz), 138.7, 135.2, 129.5 (d, *J* = 8.0 Hz), 128.6, 127.3, 124.4 (d, *J* = 3.8 Hz), 121.6 (d, *J* = 18.4 Hz), 115.8 (d, *J* = 23.2 Hz), 64.9, 57.2, 42.6 (d, *J* = 2.2 Hz), 32.9, 25.9, 21.1.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -107.6.

HRMS (ESI) m/z: Calcd for $C_{25}H_{26}FO_2S$ $[M+H]^+$, 409.1632.; Found, 409.1624.

4-((2-(trifluoromethyl)phenyl)thio)pentyl 2,2-diphenylacetate (c50)



Purification by column chromatography on silica gel (hexane/ethyl acetate = 40:1, v/v) afforded the title compound as a colorless oil (38 mg, 42% yield).

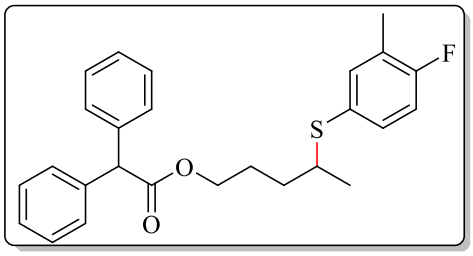
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.9 Hz, 1H), 7.51 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.36 – 7.28 (m, 10H), 7.28 – 7.24 (m, 1H), 5.02 (s, 1H), 4.17 (t, *J* = 7.4 Hz, 2H), 3.30 (h, *J* = 6.6 Hz, 1H), 1.86 – 1.76 (m, 2H), 1.68 – 1.54 (m, 2H), 1.24 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 138.6, 135.3, 133.4, 131.7, 129.9 (d, *J* = 251.1 Hz), 127.3, 126.8 (q, *J* = 6.4 Hz), 126.4, 64.7, 57.1, 43.6, 32.8, 25.9, 20.8.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -60.33.

HRMS (ESI) m/z: Calcd for $C_{26}H_{26}F_3O_2S$ $[M+H]^+$, 459.1600.; Found, 459.1596.

4-((4-fluoro-3-methylphenyl)thio)pentyl 2,2-diphenylacetate (c51)



Purification by column chromatography on silica gel (hexane/ethyl acetate = 40:1, v/v) afforded the title compound as a colorless oil (59 mg, 66% yield).

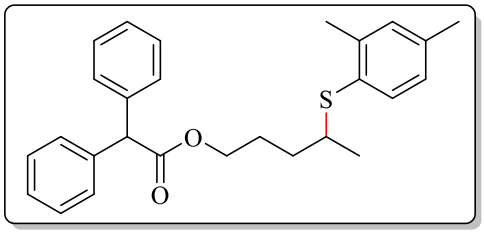
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.34 – 7.28 (m, 9H), 7.27 – 7.23 (m, 2H), 6.92 (dd, *J* = 9.6, 2.9 Hz, 1H), 6.81 (td, *J* = 8.4, 2.9 Hz, 1H), 5.00 (s, 1H), 4.20 – 4.09 (m, 2H), 3.01 (h, *J* = 6.7 Hz, 1H), 2.39 (s, 3H), 1.83 – 1.75 (m, 2H), 1.61 – 1.41 (m, 2H), 1.16 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 172.5, 162.1 (d, *J* = 246.8 Hz), 143.2 (d, *J* = 7.8 Hz), 138.7, 135.4 (d, *J* = 8.2 Hz), 129.2 (d, *J* = 3.2 Hz), 128.6, 127.3, 117.1 (d, *J* = 21.3 Hz), 113.3 (d, *J* = 21.3 Hz), 64.9, 57.2, 43.3, 32.9, 26.0, 21.2, 20.9.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -114.97.

HRMS (ESI) m/z: Calcd for $C_{26}H_{28}FO_2S$ $[M+H]^+$, 423.1789.; Found, 423.1792.

4-((2,4-dimethylphenyl)thio)pentyl 2,2-diphenylacetate (c52)



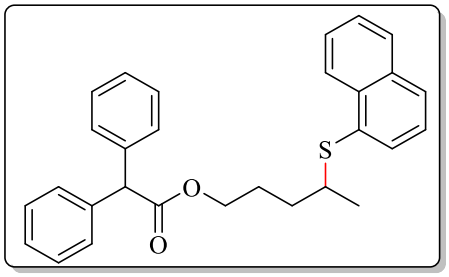
Purification by column chromatography on silica gel (hexane/ethyl acetate = 40:1, v/v) afforded the title compound as a yellow oil (38 mg, 46% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.32 (m, 8H), 7.30 – 7.26 (m, 3H), 7.05 (s, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 5.03 (s, 1H), 4.17 (t, *J* = 5.4 Hz, 2H), 3.10 (h, *J* = 6.6 Hz, 1H), 2.40 (s, 3H), 2.31 (s, 3H), 1.81 (dt, *J* = 14.9, 7.2 Hz, 2H), 1.68 – 1.44 (m, 2H), 1.22 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 140.1, 138.7, 137.0, 133.0, 131.2, 130.7, 128.6, 128.6, 127.3, 127.1, 65.0, 57.2, 42.8, 33.0, 26.0, 21.0, 20.9.

HRMS (ESI) m/z: Calcd for $C_{27}H_{31}O_2S$ $[M+H]^+$, 419.2039.; Found, 419.2043.

4-(naphthalen-1-ylthio)pentyl 2,2-diphenylacetate (c53)



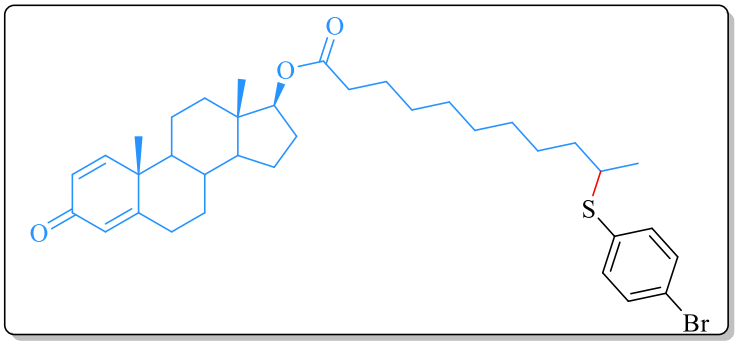
Purification by column chromatography on silica gel (hexane/ethyl acetate = 40:1, v/v) afforded the title compound as a yellow oil (48 mg, 54% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.80 (m, 2H), 7.77 (dd, *J* = 7.8, 3.7 Hz, 2H), 7.54 – 7.42 (m, 3H), 7.35 – 7.27 (m, 9H), 7.27 – 7.23 (m, 1H), 5.00 (s, 1H), 4.18 (t, *J* = 6.5 Hz, 2H), 3.31 (h, *J* = 6.7 Hz, 1H), 1.85 (p, *J* = 7.1 Hz, 2H), 1.70 – 1.44 (m, 2H), 1.29 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 138.7, 133.7, 132.5, 132.2, 130.5, 129.6, 128.6, 128.3, 127.7, 127.3, 127.3, 126.5, 126.0, 64.9, 57.1, 42.9, 32.9, 26.0, 21.2.

HRMS (ESI) m/z: Calcd for $C_{29}H_{29}O_2S$ $[M+H]^+$, 441.1883.; Found, 441.1884.

(10*R*,13*S*,17*S*)-10,13-dimethyl-3-oxo-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-3*H*-cyclopenta[*a*]phenanthren-17-yl 10-((4-bromophenyl)thio)undecanoate (c55)



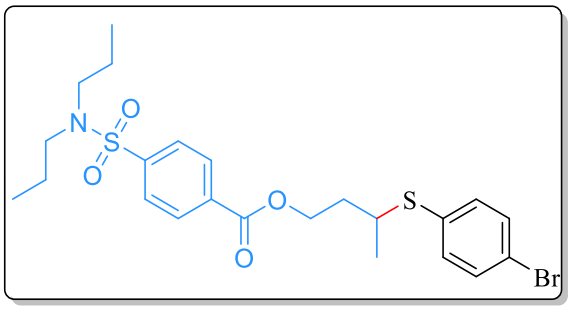
Purification by column chromatography on silica gel (hexane/ethyl acetate = 30:1, v/v) afforded the title compound as a white oil (79 mg, 62% yield).

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.30 (d, J = 6.6 Hz, 2H), 7.28 (dd, J = 7.8, 1.3 Hz, 1H), 6.22 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.08 (t, *J* = 1.6 Hz, 1H), 4.61 (dd, J = 9.2, 7.5 Hz, 1H), 3.27 (h, *J* = 6.6 Hz, 1H), 2.59 (td, *J* = 13.5, 5.2 Hz, 1H), 2.46 – 2.37 (m, 1H), 2.32 (t, *J* = 7.9 Hz, 2H), 2.23 – 2.10 (m, 1H), 2.07 – 1.99 (m, 1H), 1.77 (dt, *J* = 13.4, 10.5 Hz, 4H), 1.74 – 1.56 (m, 5H), 1.56 – 1.39 (m, 5H), 1.35 – 1.30 (m, 8H), 1.29 (s, 3H), 1.27 (d, *J* = 6.7 Hz, 3H), 1.15 – 1.00 (m, 3H), 0.92 (s, 3H).

^{13}C NMR (101 MHz, Methanol-d_4) δ 187.2, 174.1, 171.9, 157.9, 133.9, 133.0, 131.6, 126.2, 122.7, 119.9, 82.3, 52.7, 49.7, 43.9, 42.9, 42.6, 36.5, 36.3, 35.1, 33.9, 33.1, 32.4, 28.9, 28.7, 28.6, 27.1, 26.5, 24.8, 23.2, 22.2, 20.2, 17.7, 11.2.

HRMS (ESI) m/z: Calcd for $C_{36}H_{50}BrO_3S$ $[M+H]^+$, 643.2644.; Found, 643.2636.

3-((4-bromophenyl)thio)butyl 4-(*N*,*N*-dipropylsulfamoyl)benzoate (c56)



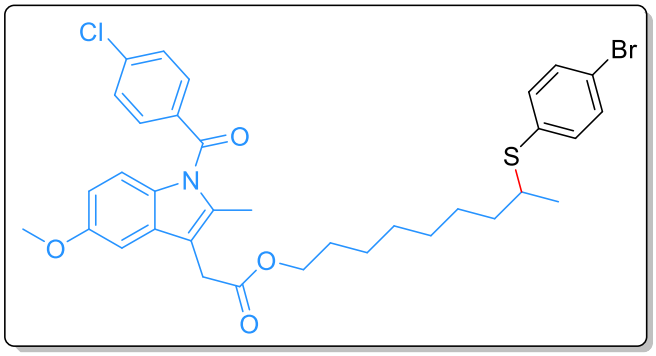
Purification by column chromatography on silica gel (hexane/ethyl acetate = 30:1, v/v) afforded the title compound as a yellow solid (74 mg, 70% yield). Mp. 78.3 - 80.1 ℃.

^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 4.50 (td, *J* = 6.4, 2.1 Hz, 2H), 3.35 (h, *J* = 6.8 Hz, 1H), 3.14 – 3.08 (m, 4H), 2.03 (qd, *J* = 14.5, 7.3 Hz, 2H), 1.56 (h, *J* = 7.4 Hz, 4H), 1.38 (d, *J* = 6.8 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 165.1, 144.4, 134.1, 133.6, 133.4, 132.0, 130.2, 127.0, 121.4, 63.2, 50.0, 40.8, 35.5, 22.0, 21.3, 11.2.

HRMS (ESI) m/z: Calcd for $C_{23}H_{31}BrNO_4S_2$ $[M+H]^+$, 530.0853.; Found, 530.0859.

8-((4-bromophenyl)thio)nonyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (c57)



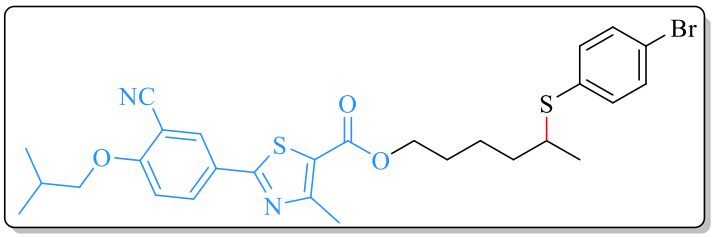
Purification by column chromatography on silica gel (hexane/ethyl acetate = 30:1, v/v) afforded the title compound as a green oil (85 mg, 63% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 2.3 Hz, 1H), 6.87 (d, *J* = 9.0 Hz, 1H), 6.66 (dd, *J* = 9.0, 2.3 Hz, 1H), 4.09 (t, *J* = 6.7 Hz, 2H), 3.83 (s, 3H), 3.65 (s, 2H), 3.16 (h, *J* = 6.7 Hz, 1H), 2.39 (s, 3H), 1.59 (dt, *J* = 19.2, 6.8 Hz, 3H), 1.47 (td, *J* = 14.4, 13.2, 5.9 Hz, 1H), 1.42 – 1.37 (m, 2H), 1.31 – 1.26 (m, 2H), 1.25 (d, *J* = 6.6 Hz, 3H), 1.24 – 1.20 (m, 4H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 171.0, 168.3, 156.0, 139.2, 135.9, 134.8, 133.9, 133.3, 131.8, 131.2, 130.8, 130.7, 129.1, 120.6, 114.9, 112.7, 111.6, 101.3, 65.1, 55.7, 43.5, 36.5, 30.4, 29.4, 29.3, 29.1, 28.6, 27.0, 25.8, 21.0, 13.4.

HRMS (ESI) m/z: Calcd for $C_{34}H_{38}BrClNO_4S$ $[M+H]^+$, 672.1369.; Found, 672.1363.

5-((4-bromophenyl)thio)hexyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (c58)



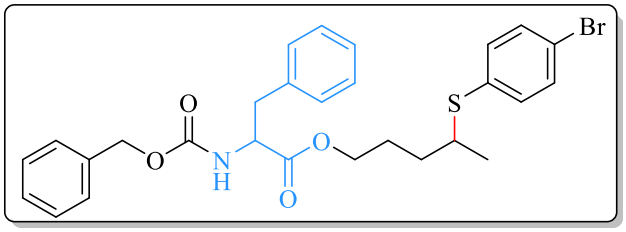
Purification by column chromatography on silica gel (hexane/ethyl acetate = 20:1, v/v) afforded the title compound as a brown solid (77 mg, 66% yield). Mp. 48.7 – 49.9 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (d, *J* = 2.3 Hz, 1H), 8.05 (dd, *J* = 8.9, 2.3 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 1H), 4.28 (t, *J* = 6.5 Hz, 2H), 3.89 (d, *J* = 6.5 Hz, 2H), 3.20 (h, *J* = 6.4, 6.0 Hz, 1H), 2.75 (s, 3H), 2.19 (dp, *J* = 13.3, 6.7 Hz, 1H), 1.77 – 1.55 (m, 6H), 1.28 (d, *J* = 6.7 Hz, 3H), 1.08 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.2, 162.5, 162.0, 161.1, 134.4, 133.5, 132.5, 132.0, 131.9, 126.0, 121.8, 120.8, 115.4, 112.6, 102.9, 75.7, 65.1, 43.3, 36.0, 28.5, 28.1, 23.4, 21.1, 19.0, 17.5.

HRMS (ESI) m/z: Calcd for $C_{28}H_{32}BrN_2O_3S_2$ $[M+H]^+$, 589.1014.; Found, 589.1011.

4-((4-bromophenyl)thio)pentyl ((benzyloxy)carbonyl)phenylalaninate (c59)



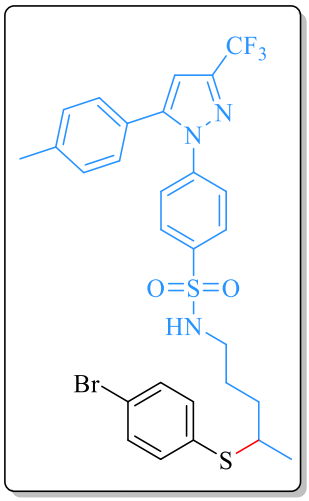
Purification by column chromatography on silica gel (hexane/ethyl acetate = 20:1, v/v) afforded the title compound as a colorless oil (79 mg, 71% yield).

^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.6 Hz, 2H), 7.33 (h, *J* = 7.6, 7.1 Hz, 5H), 7.24 (dd, *J* = 13.0, 8.0 Hz, 5H), 7.09 (d, *J* = 6.7 Hz, 2H), 5.24 (d, *J* = 8.3 Hz, 1H), 5.09 (d, *J* = 4.9 Hz, 2H), 4.63 (q, *J* = 6.2 Hz, 1H), 4.09 (ddt, *J* = 28.9, 16.8, 8.2 Hz, 2H), 3.10 (dtd, *J* = 33.8, 15.5, 14.4, 7.0 Hz, 3H), 1.74 (p, *J* = 7.2 Hz, 2H), 1.56 – 1.46 (m, 2H), 1.25 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.6, 155.7, 136.3, 135.8, 134.1, 133.7, 132.0, 129.3, 128.6, 128.6, 128.2, 128.1, 127.2, 121.1, 67.0, 65.1, 54.9, 43.2, 38.4, 32.7, 25.9, 21.1.

HRMS (ESI) m/z: Calcd for $C_{28}H_{31}BrNO_4S$ $[M+H]^+$, 558.1135.; Found, 558.1137.

_N_-(4-((4-bromophenyl)thio)pentyl)-4-(5-(_p_-tolyl)-3-(trifluoromethyl)-1_H_-pyrazol-1-yl)benzenesulfonamide (c60)



Purification by column chromatography on silica gel (hexane/ethyl acetate = 20:1, v/v) afforded the title compound as a brown solid (82 mg, 64% yield).

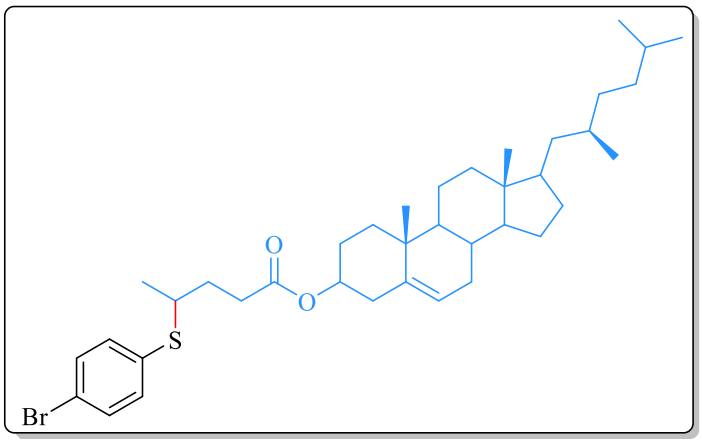
^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 8.7 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 6.4 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.75 (s, 1H), 4.61 (t, *J* = 6.3 Hz, 1H), 3.13 (h, *J* = 6.7 Hz, 1H), 3.00 – 2.93 (m, 2H), 2.38 (s, 3H), 1.72 – 1.61 (m, 2H), 1.53 (dddd, *J* = 14.1, 12.3, 10.0, 6.3 Hz, 2H), 1.23 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.1, 145.3, 144.1 (q, *J* = 38.4 Hz), 142.5, 139.8, 139.4, 134.4, 134.0, 133.6, 132.6, 132.0, 129.8, 128.7, 128.1, 125.7, 125.6, 123.6, 121.1 (q, *J* = 269.2 Hz), 121.1, 106.3, 43.0, 43.0, 33.3, 27.0, 21.3, 21.1.

^{19}F NMR (565 MHz, Chloroform-*d*) δ -62.42.

HRMS (ESI) m/z: Calcd for $C_{28}H_{28}BrF_3N_3O_2S_2$ $[M+H]^+$, 640.0735.; Found, 640.0728.

(10_R_,13_R_)-17-((_R_)-2,5-dimethylhexyl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1_H_-cyclopenta[_a_]phenanthren-3-yl 4-((4-bromophenyl)thio)pentanoate (c61)



Purification by column chromatography on silica gel (hexane/ethyl acetate = 40:1, v/v) afforded the title compound as a brown oil (97 mg, 74% yield).

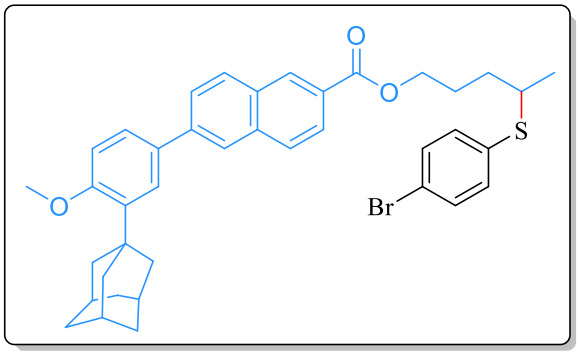
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 2H), 5.38 (d, *J* = 5.9 Hz, 1H), 4.62 (qd, *J* = 10.9, 8.3, 4.1 Hz, 1H), 3.22 (h, *J* = 6.7 Hz, 1H), 2.47 (t, *J* = 7.4 Hz, 2H), 2.32

(t, *J* = 4.6 Hz, 3H), 2.06 – 1.93 (m, 3H), 1.93 – 1.77 (m, 6H), 1.65 – 1.43 (m, 9H), 1.38 – 1.33 (m, 3H), 1.29 (d, *J* = 6.8 Hz, 3H), 1.20 – 1.07 (m, 6H), 1.03 (s, 3H), 0.93 (d, *J* = 6.4 Hz, 3H), 0.89 (d, *J* = 1.8 Hz, 3H), 0.87 (d, *J* = 1.8 Hz, 3H), 0.69 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.4, 139.6, 136.7, 133.7, 131.9, 122.7, 121.1, 74.1, 56.7, 56.2, 50.1, 43.0, 42.3, 39.8, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 31.9, 31.9, 31.6, 28.2, 28.0, 27.8, 26.5, 24.3, 23.9, 22.8, 22.6, 21.1, 19.3, 18.8, 11.9.

HRMS (ESI) m/z: Calcd for $C_{38}H_{58}BrO_2S$ $[M+H]^+$, 659.3321.; Found, 659.3329.

4-((4-bromophenyl)thio)pentyl 6-(3-(adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate (c62)



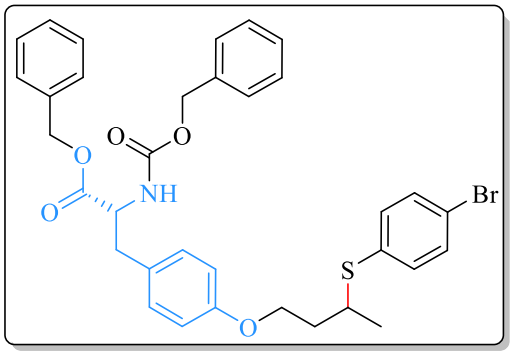
Purification by column chromatography on silica gel (hexane/ethyl acetate = 30:1, v/v) afforded the title compound as a white solid (90 mg, 67% yield). Mp. 112.0 - 114.7 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 (s, 1H), 8.09 – 8.04 (m, 2H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 8.7 Hz, 1H), 7.85 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.67 (d, *J* = 2.4 Hz, 1H), 7.58 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 1H), 4.43 (t, *J* = 6.4 Hz, 2H), 3.93 (s, 3H), 3.31 (h, *J* = 6.6 Hz, 1H), 2.27 – 2.22 (m, 6H), 2.16 (td, *J* = 5.1, 2.4 Hz, 3H), 2.03 (p, *J* = 7.1 Hz, 2H), 1.89 – 1.70 (m, 8H), 1.37 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.8, 159.0, 141.4, 139.0, 136.0, 134.2, 133.7, 132.6, 132.0, 131.3, 130.8, 129.8, 128.3, 127.1, 126.6, 126.0, 125.8, 125.6, 124.8, 121.0, 112.2, 64.7, 55.2, 43.2, 40.7, 37.3, 37.2, 33.0, 29.2, 26.3, 21.1.

HRMS (ESI) m/z: Calcd for $C_{39}H_{42}BrO_3S$ $[M+H]^+$, 671.2019.; Found, 671.2026.

benzyl (2*R*)-2-(((benzyloxy)carbonyl)amino)-3-(4-(3-((4 bromophenyl)thio)butoxy)phenyl)propanoate (c63)



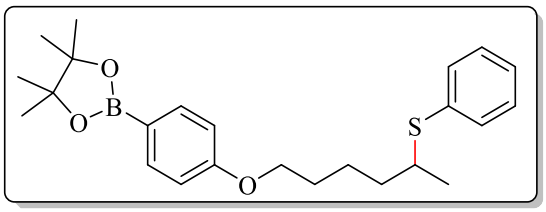
Purification by column chromatography on silica gel (hexane/ethyl acetate = 20:1, v/v) afforded the title compound as a yellow oil (94 mg, 72% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 8.5 Hz, 2H), 7.39 – 7.31 (m, 10H), 7.29 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 2H), 5.30 (d, *J* = 8.3 Hz, 1H), 5.23 – 5.13 (m, 4H), 4.75 – 4.66 (m, 1H), 4.15 – 3.99 (m, 2H), 3.49 (h, *J* = 6.8 Hz, 1H), 3.15 – 3.02 (m, 2H), 2.04 (qd, *J* = 14.2, 7.7 Hz, 2H), 1.38 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.5, 157.9, 155.7, 136.3, 135.2, 134.1, 133.5, 132.0, 130.4, 128.6, 128.6, 128.5, 128.2, 128.1, 127.7, 123.6, 121.0, 114.6, 67.2, 67.0, 65.1, 55.0, 40.4, 37.3, 36.3, 21.4.

HRMS (ESI) m/z: Calcd for $C_{34}H_{35}BrNO_5S$ $[M+H]^+$, 650.1399.; Found, 650.1393.

4,4,5,5-tetramethyl-2-(4-((5-(phenylthio)hexyl)oxy)phenyl)-1,3,2-dioxaborolane (c64)



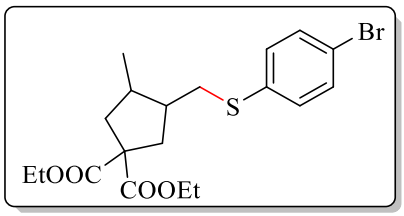
Purification by column chromatography on silica gel (hexane/ethyl acetate = 50:1, v/v) afforded the title compound as a yellow oil (50 mg, 60% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.31 – 7.17 (m, 3H), 6.87 (d, *J* = 8.6 Hz, 2H), 3.97 (t, *J* = 6.4 Hz, 2H), 3.23 (h, *J* = 6.5 Hz, 1H), 1.87 – 1.73 (m, 2H), 1.64 – 1.38 (m, 4H), 1.33 (s, 12H), 1.29 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.6, 136.5, 135.2, 132.1, 128.8, 126.7, 115.2, 113.8, 83.5, 67.4, 43.3, 36.3, 29.0, 24.8, 23.5, 21.1.

HRMS (ESI) m/z: Calcd for $C_{24}H_{34}BO_3S$ $[M+H]^+$, 413.2321.; Found, 413.2316.

diethyl 3-(((4-bromophenyl)thio)methyl)-4-methylcyclopentane-1,1-dicarboxylate (c65)



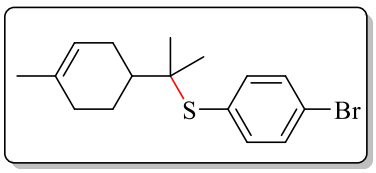
Purification by column chromatography on silica gel (hexane/ethyl acetate = 100:1, v/v) afforded the title compound as a brown oil (55 mg, 64% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 4.17 (qd, *J* = 7.1, 5.3 Hz, 4H), 2.94 (dd, *J* = 12.3, 6.2 Hz, 1H), 2.78 (dd, *J* = 12.2, 7.9 Hz, 1H), 2.45 (dt, *J* = 13.5, 6.3 Hz, 2H), 2.35 – 2.10 (m, 3H), 2.03 (dd, *J* = 13.8, 5.4 Hz, 1H), 1.23 (td, *J* = 7.1, 5.0 Hz, 6H), 0.93 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.6, 136.0, 131.9, 130.8, 119.7, 67.9, 61.5, 58.8, 41.7, 41.2, 38.1, 35.8, 34.7, 25.6, 14.7, 14.0.

HRMS (ESI) m/z: Calcd for $C_{19}H_{26}BrO_4S$ $[M+H]^+$, 431.0711.; Found, 431.0716.

(4-bromophenyl)((2,2,4-trimethylcyclohex-3-en-1-yl)methyl)sulfane (c66)



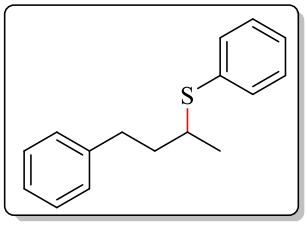
Purification by column chromatography on silica gel (hexane) afforded the title compound as a colorless oil (23 mg, 35% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 5.38 (s, 1H), 2.22 – 2.06 (m, 2H), 2.00 (d, *J* = 7.7 Hz, 2H), 1.98 – 1.86 (m, 1H), 1.66 (s, 3H), 1.57 – 1.50 (m, 1H), 1.43 – 1.28 (m, 1H), 1.23 (s, 3H), 1.18 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.2, 134.1, 131.6, 131.5, 123.4, 120.7, 53.1, 42.8, 31.2, 27.2, 27.2, 25.1, 24.8, 23.3.

HRMS (ESI) m/z: Calcd for $C_{16}H_{22}BrS$ $[M+H]^+$, 327.0600.; Found, 327.0591.

phenyl(4-phenylbutan-2-yl)sulfane (c67)



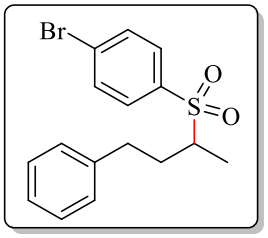
Purification by column chromatography on silica gel (hexane/ethyl acetate = 100:1, v/v) afforded the title compound as a colorless oil (32 mg, 67% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 7.0 Hz, 2H), 7.34 – 7.23 (m, 5H), 7.20 (d, *J* = 6.7 Hz, 2H), 3.23 (h, *J* = 6.7 Hz, 1H), 2.90 – 2.74 (m, 2H), 2.03 – 1.78 (m, 2H), 1.35 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.7, 135.1, 132.0, 128.8, 128.5, 128.4, 126.7, 125.9, 42.6, 38.2, 33.2, 21.2.

HRMS (ESI) m/z: Calcd for $C_{16}H_{19}S$ $[M+H]^+$, 243.1202.; Found, 243.1209.

1-bromo-4-((4-phenylbutan-2-yl)sulfonyl)benzene (c1-I)



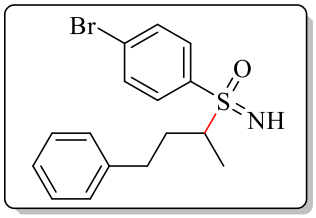
Purification by column chromatography on silica gel (hexane/ethyl acetate = 10:1, v/v) afforded the title compound as a colorless oil (70 mg, 99% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.63 (m, 4H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.1 Hz, 2H), 3.02 (ddp, *J* = 10.4, 6.9, 3.5 Hz, 1H), 2.84 (ddd, *J* = 14.2, 9.2, 5.3 Hz, 1H), 2.66 – 2.54 (m, 1H), 2.36 – 2.23 (m, 1H), 1.80 – 1.66 (m, 1H), 1.33 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.0, 136.2, 132.4, 130.5, 129.0, 128.6, 128.3, 126.4, 59.2, 32.4, 30.7, 13.2.

HRMS (ESI) m/z: Calcd for $C_{16}H_{18}BrO_2S$ $[M+H]^+$, 355.0186.; Found, 355.0190.

(4-bromophenyl)(imino)(4-phenylbutan-2-yl)-λ^6-sulfanone (c1-II)



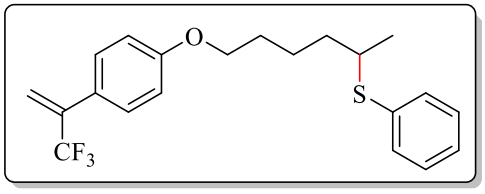
Purification by column chromatography on silica gel (hexane/ethyl acetate = 10:1, v/v) afforded the title compound as a colorless oil (56 mg, 79% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.70 (m, 2H), 7.65 (dd, *J* = 8.6, 2.3 Hz, 2H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.09 (t, *J* = 6.5 Hz, 2H), 3.10 – 2.99 (m, 1H), 2.80 (ddt, *J* = 13.7, 9.0, 3.9 Hz, 2H), 2.64 – 2.21 (m, 2H), 1.76 – 1.61 (m, 1H), 1.33 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.1 (d, *J* = 3.8 Hz), 139.1, 132.2, 130.9 (d, *J* = 2.9 Hz), 128.6, 128.3, 126.3, 60.2, 32.6 (d, *J* = 7.2 Hz), 31.1 (d, *J* = 30.9 Hz), 13.4 (d, *J* = 18.9 Hz).

HRMS (ESI) m/z: Calcd for $C_{16}H_{19}BrNOS$ $[M+H]^+$, 354.0345.; Found, 354.0336.

phenyl(6-(4-(3,3,3-trifluoroprop-1-en-2-yl)phenoxy)hexan-2-yl)sulfane (c64-I)



Purification by column chromatography on silica gel (hexane/ethyl acetate = 100:1, v/v) afforded the title compound as a yellow oil (58 mg, 78% yield).

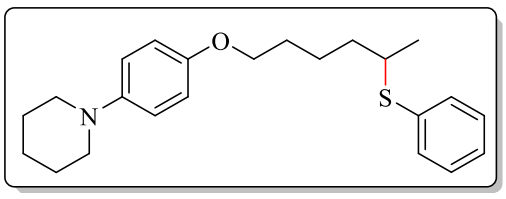
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (dd, *J* = 8.2, 5.0 Hz, 4H), 7.34 – 7.21 (m, 3H), 6.90 (d, *J* = 8.5 Hz, 2H), 5.88 (s, 1H), 5.71 (s, 1H), 3.98 (t, *J* = 6.5 Hz, 2H), 3.25 (h, *J* = 6.5 Hz, 1H), 1.82 (h, *J* = 7.0, 6.5 Hz, 2H), 1.73 – 1.52 (m, 4H), 1.31 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.6, 135.2, 133.8, 132.1, 128.8, 128.6, 128.5 (d, *J* = 6.8 Hz), 126.8, 125.9, 123.5 (d, *J* = 273.9 Hz), 118.7 (q, *J* = 5.7 Hz), 114.5, 67.7, 43.3, 36.2, 29.0, 23.5, 21.1.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -64.77.

HRMS (ESI) m/z: Calcd for $C_{21}H_{24}F_3OS$ $[M+H]^+$, 381.1494.; Found, 381.1487.

1-(4-((5-(phenylthio)hexyl)oxy)phenyl)piperidine (c64-II)



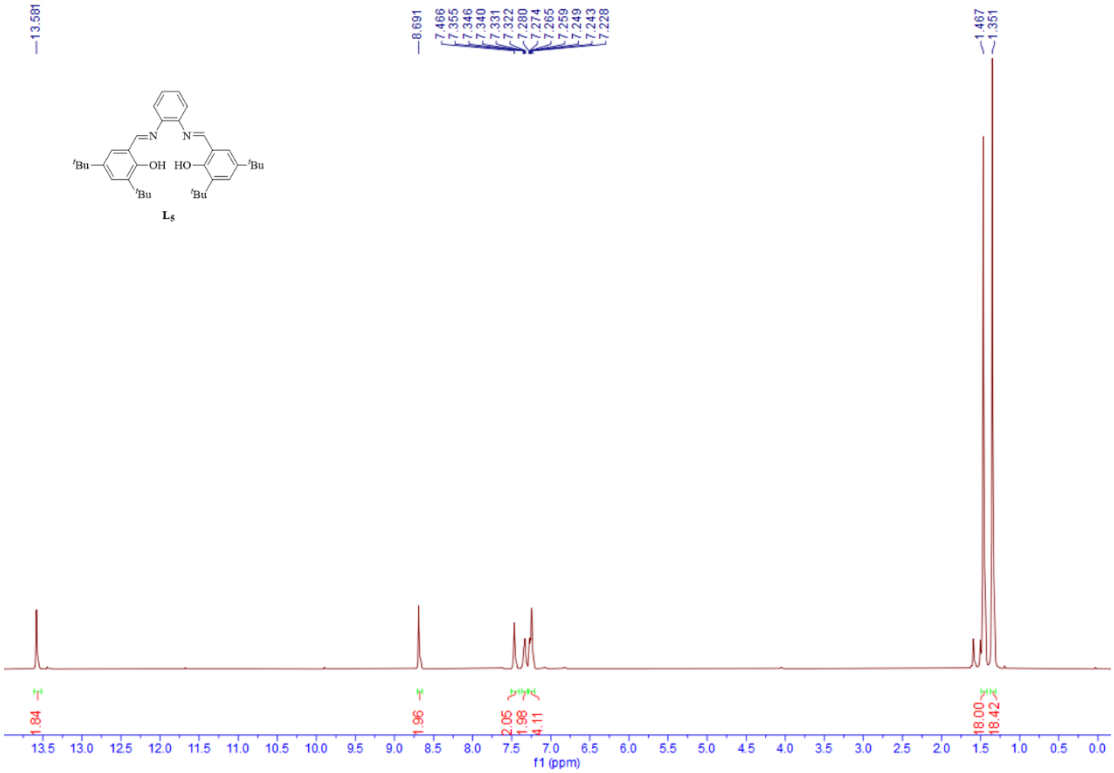
Purification by column chromatography on silica gel (hexane/ethyl acetate = 20:1, v/v) afforded the title compound as a brown oil (30 mg, 40% yield).

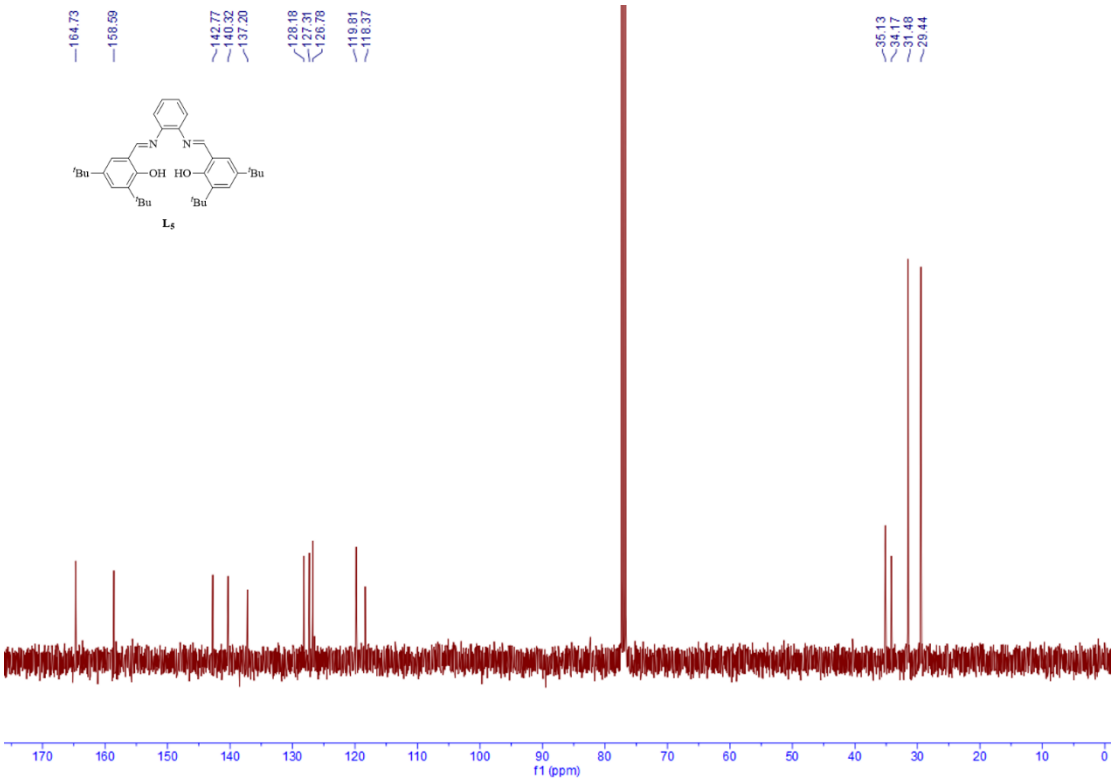
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.32 – 7.21 (m, 3H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.91 (t, *J* = 6.4 Hz, 2H), 3.24 (h, *J* = 6.4 Hz, 1H), 3.03 (t, *J* = 5.3 Hz, 4H), 1.80 – 1.70 (m, 6H), 1.69 – 1.51 (m, 6H), 1.30 (d, *J* = 6.7 Hz, 3H).

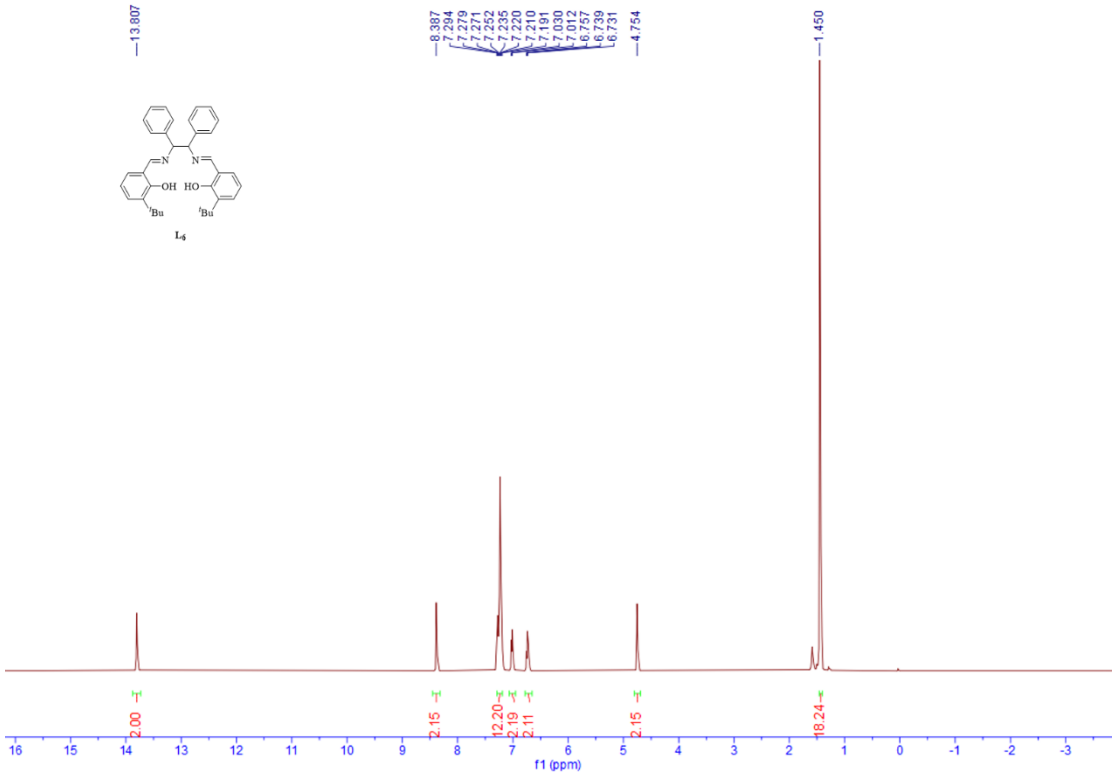
^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.3, 132.1, 128.8, 126.7, 118.8, 115.1, 68.1, 52.4, 43.3, 36.3, 29.2, 26.1, 24.1, 23.6, 21.1.

HRMS (ESI) m/z: Calcd for $C_{23}H_{32}NOS$ $[M+H]^+$, 370.2199.; Found, 370.2195.

4. ^{1}H, ^{13}C, ^{19}F spectra of target compounds.



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7.012
6.757
6.739
6.731
4.754
1.450
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HO
tBu
tBu
L4
2.00
2.15
12.20
2.19
2.11
2.15
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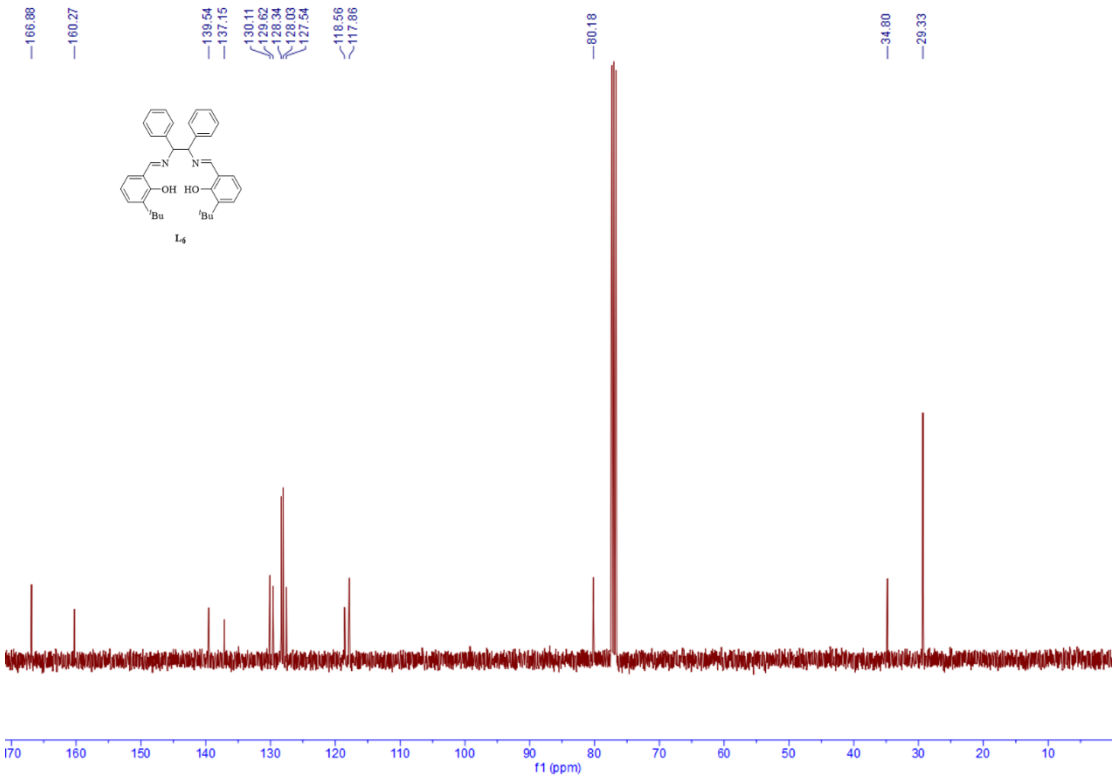
f1 (ppm)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29.33
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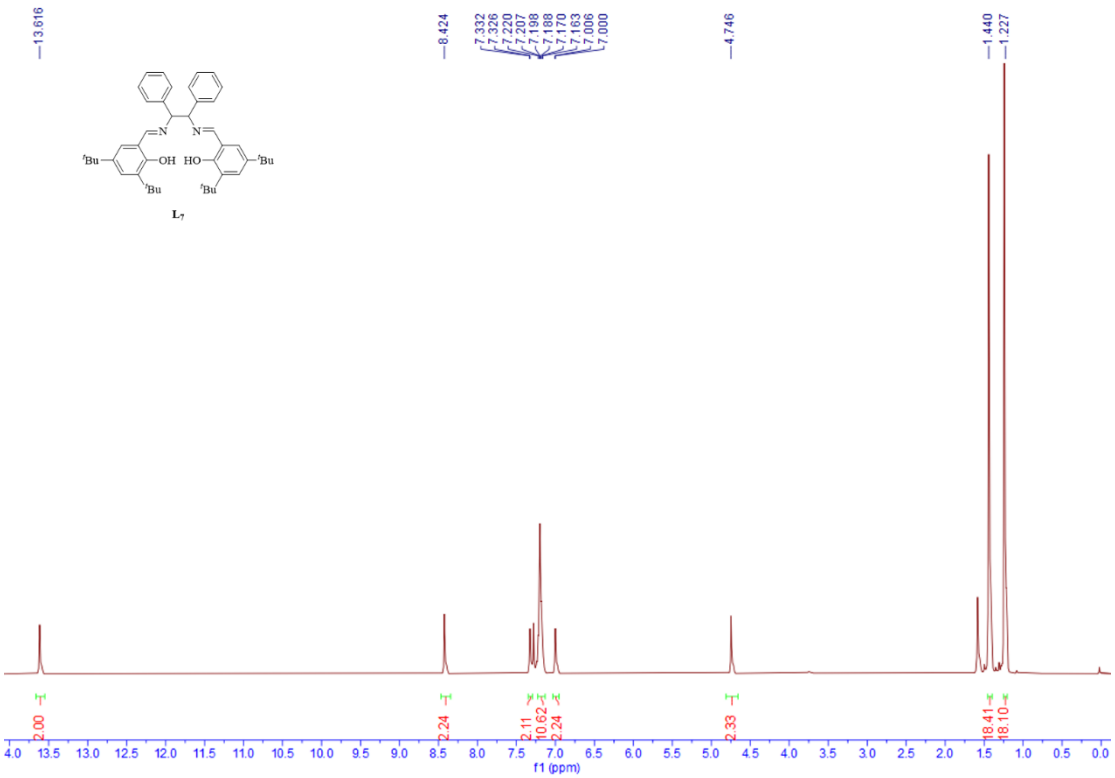
HO
tBu
tBu
L4
f1 (ppm)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HO
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L7
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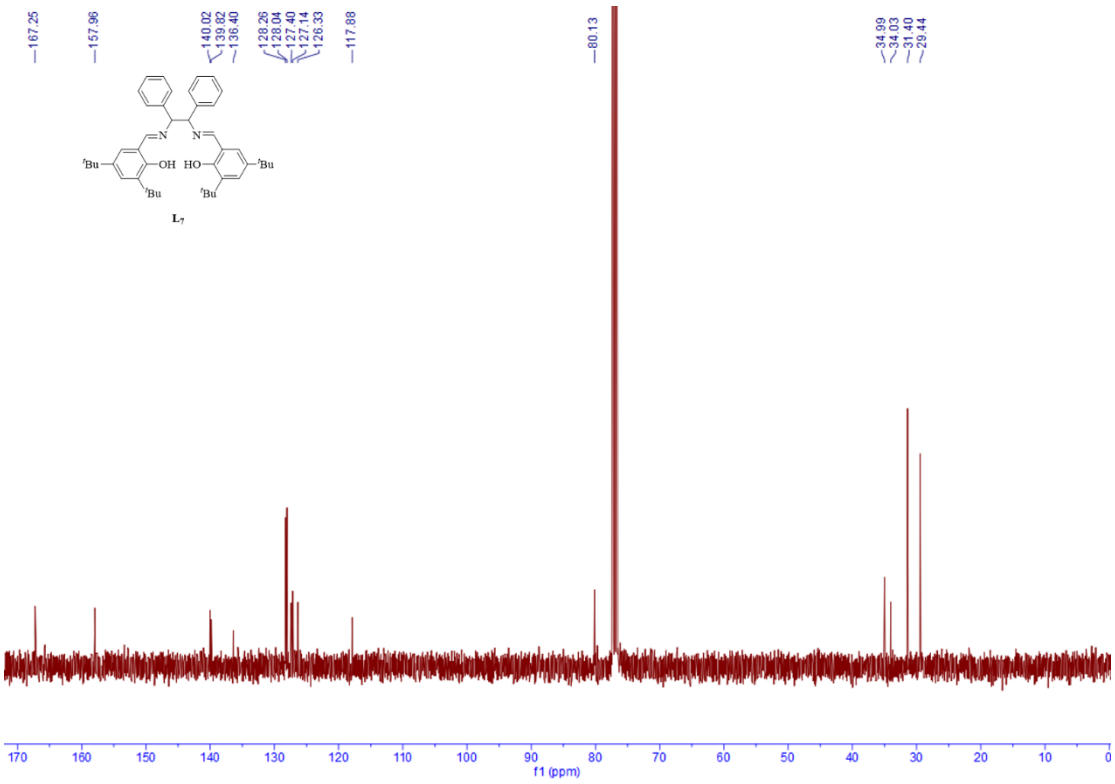
18.10
f1 (ppm)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31.40
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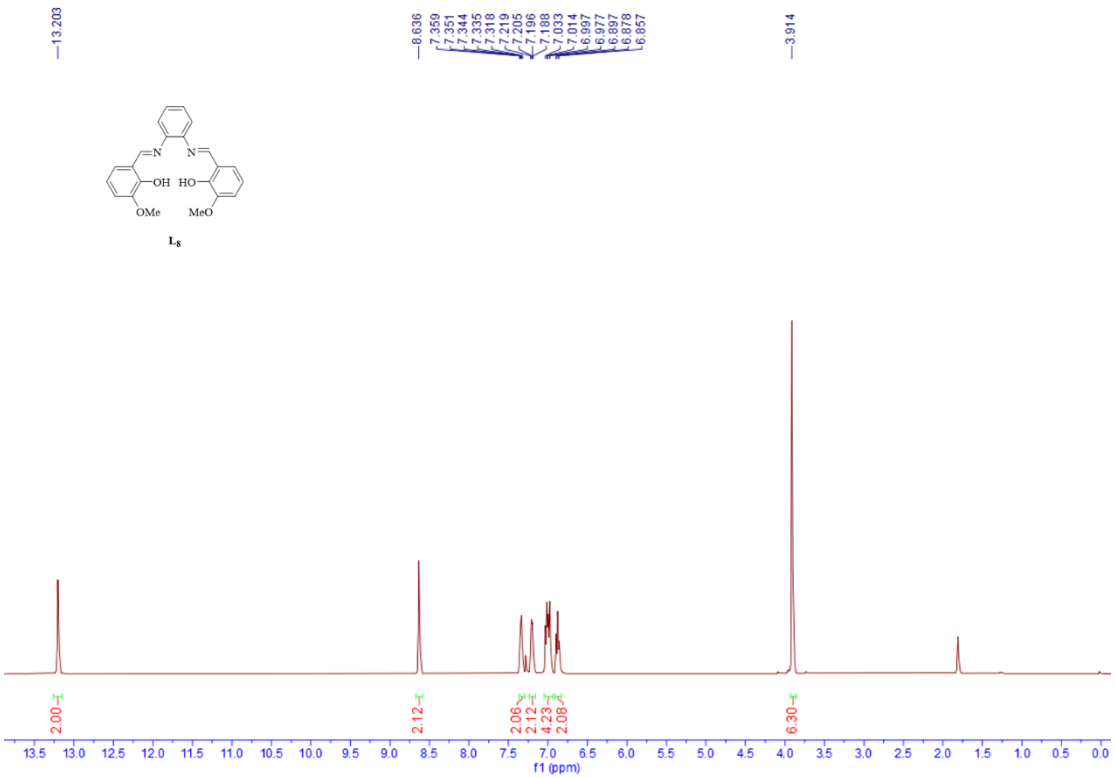
HO
tBu
L7
f1 (ppm)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6.977
6.897
6.878
6.857
3.914
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HO
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MeO
L8
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2.06
2.12
4.23
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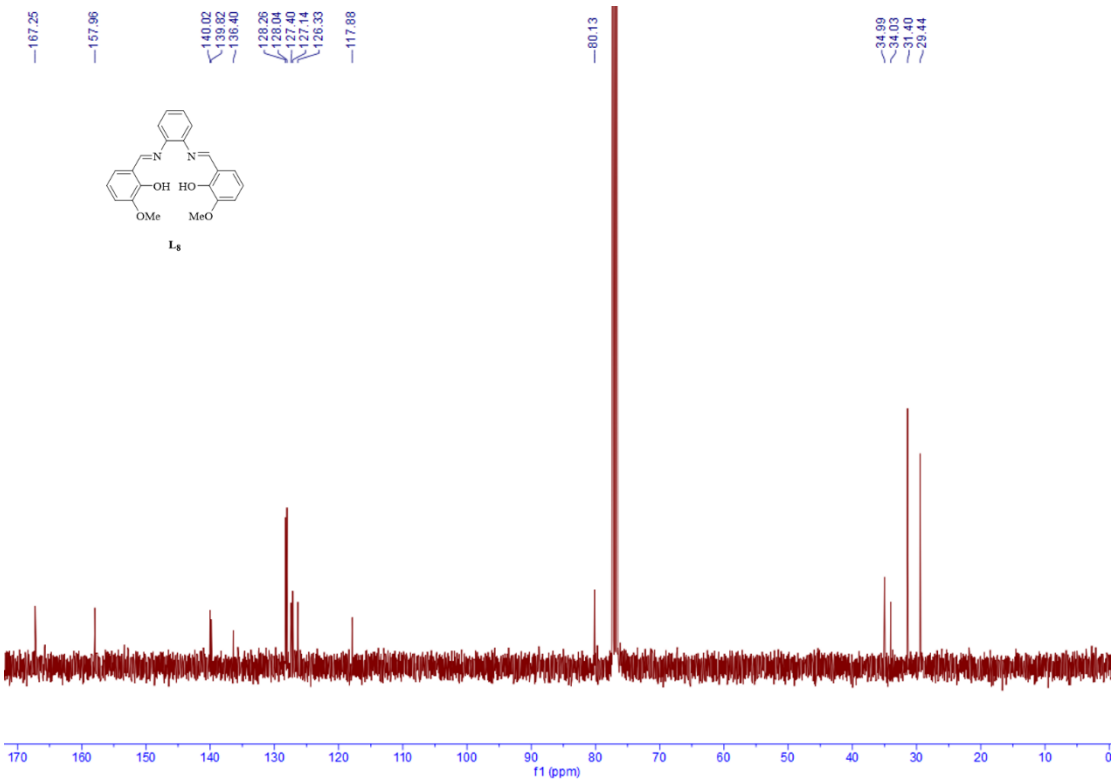
6.30
f1 (ppm)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HO
OMe
MeO
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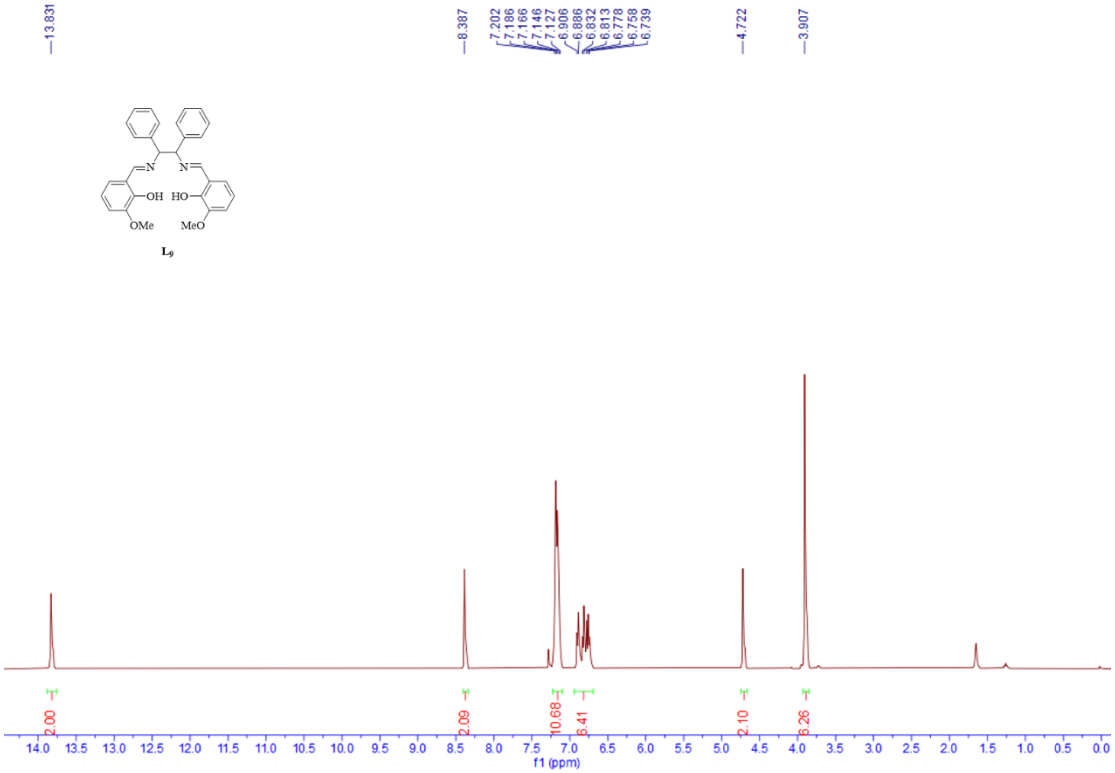
f1 (ppm)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6.739
4.722
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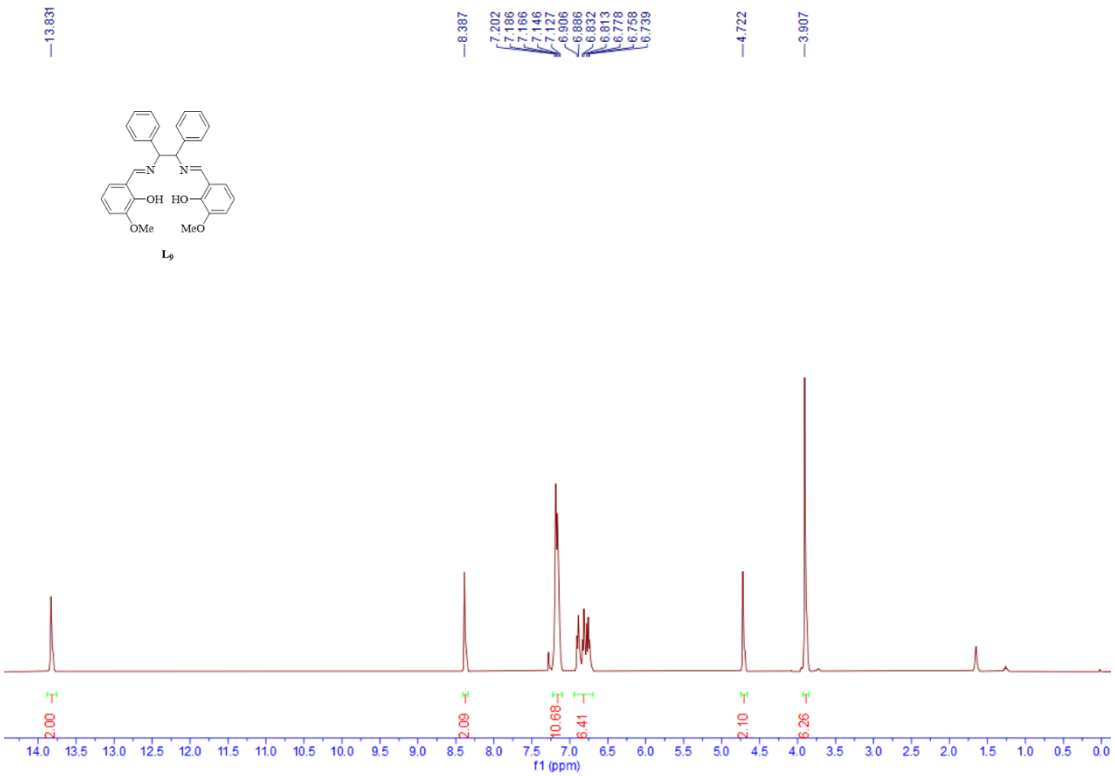
6.26
f1 (ppm)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6.739
4.722
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OMe
MeO
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2.00
2.09
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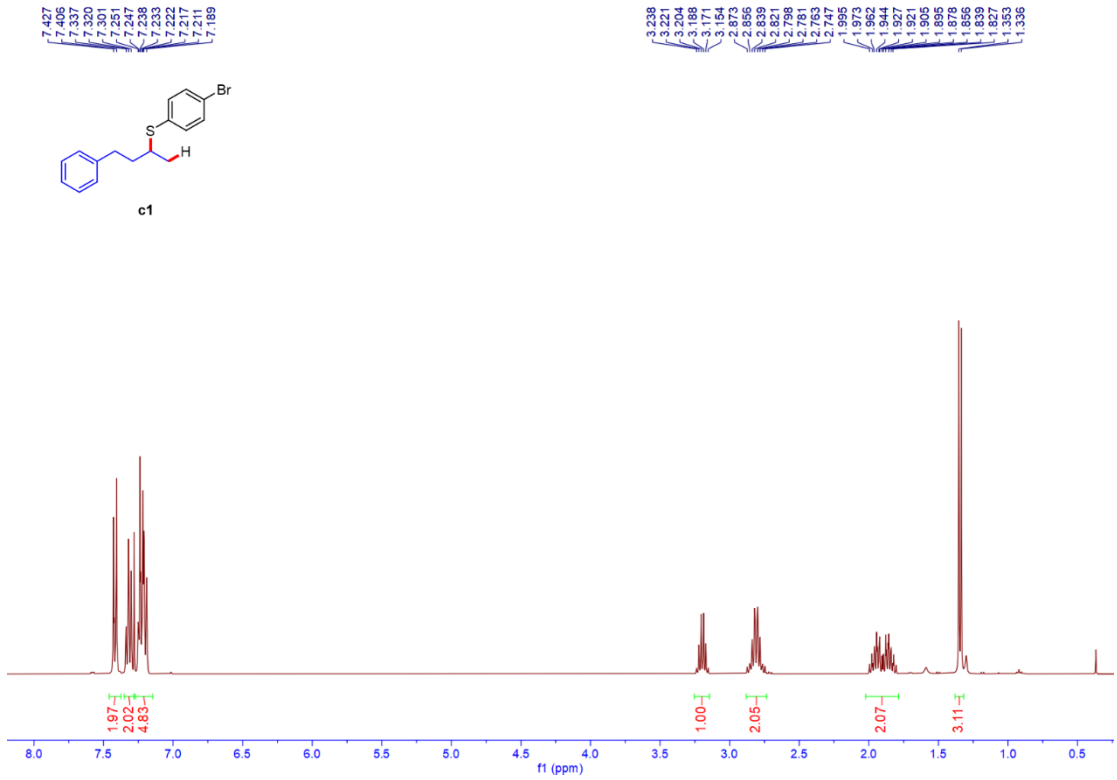
2.10
6.26
f1 (ppm)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3.238
3.221
3.204
3.188
3.171
3.154
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2.839
2.821
2.798
2.781
2.763
2.747
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1.973
1.962
1.944
1.927
1.921
1.905
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S
H
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2.07
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7.0
6.5
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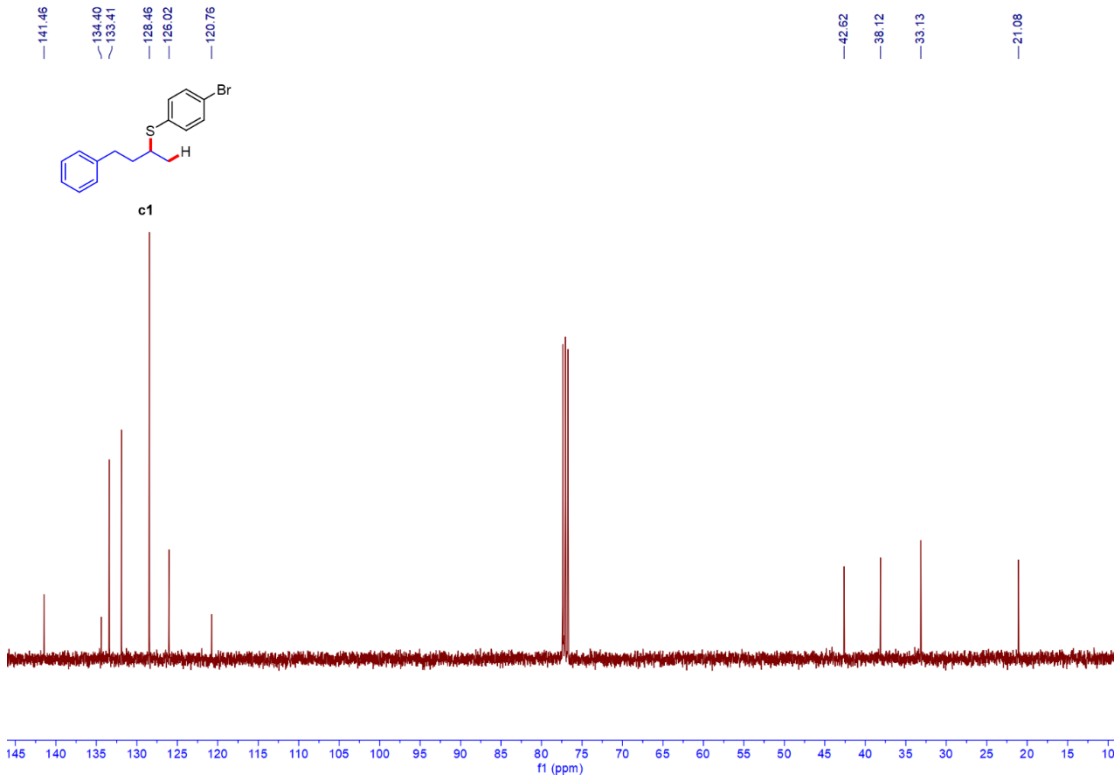
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H
c1
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140
135
130
125
120
115
110
105
100
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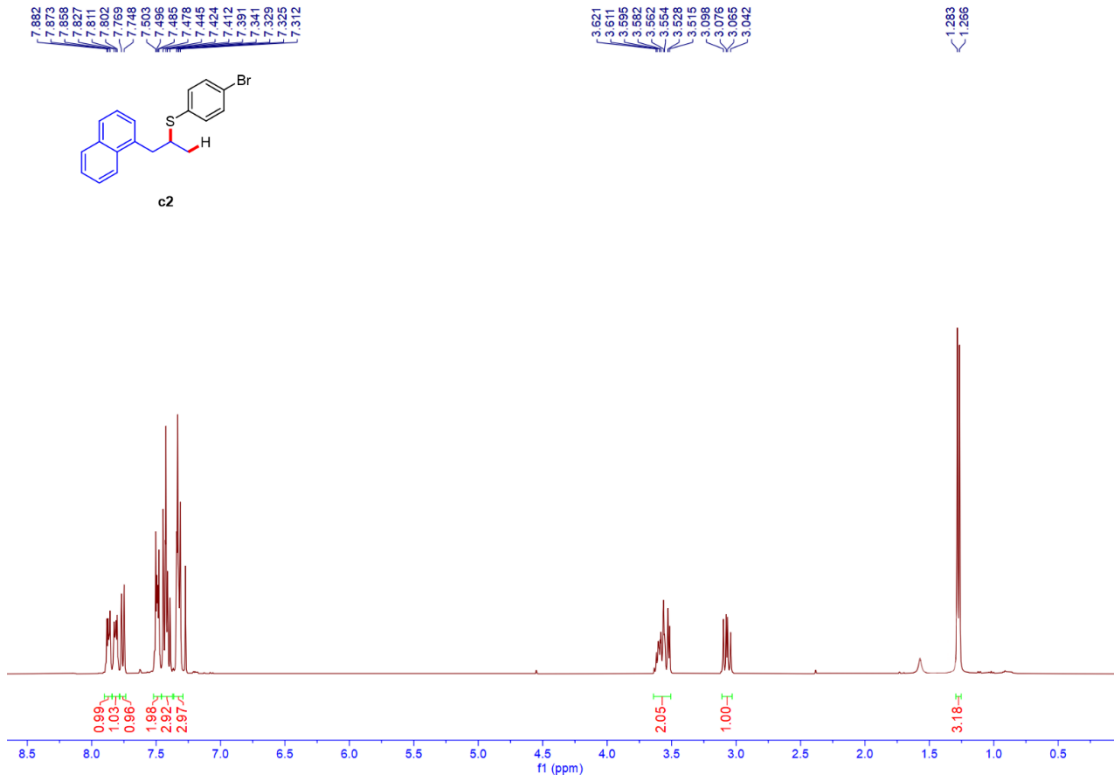
f1 (ppm)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3.611
3.595
3.582
3.562
3.554
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3.076
3.065
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1.266
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S
H
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1.98
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2.97
2.05
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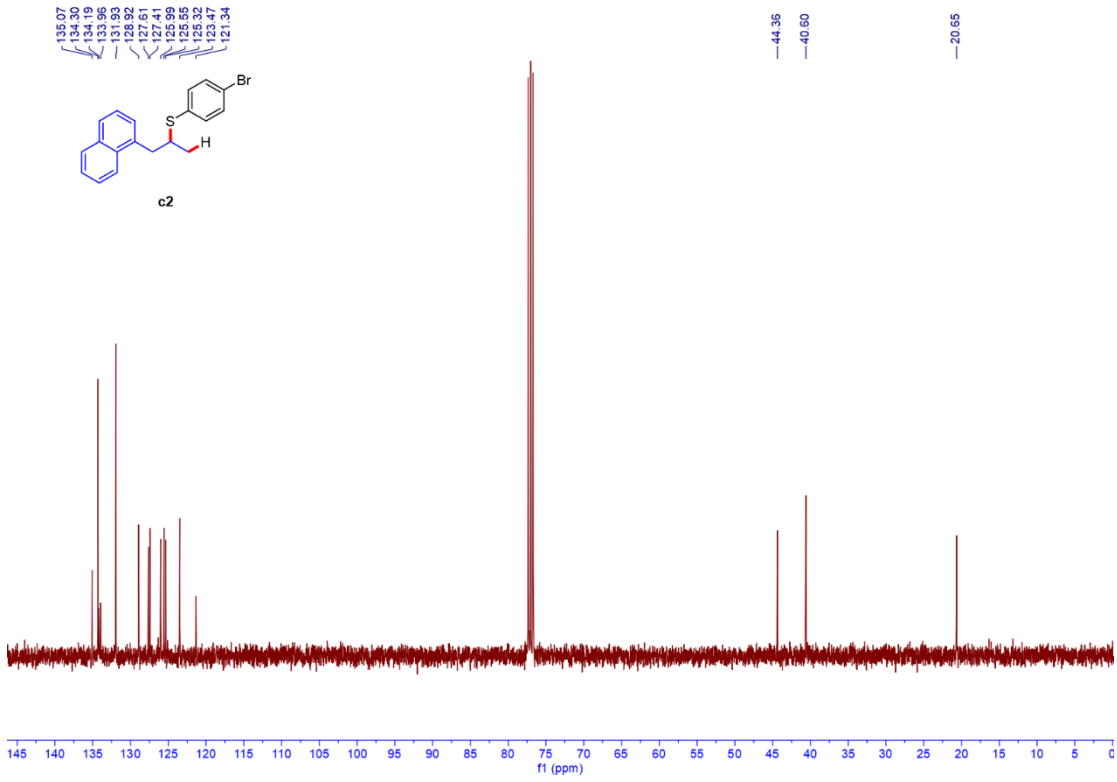
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44.36
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20.65
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S
H
c2
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140
135
130
125
120
115
110
105
100
95
90
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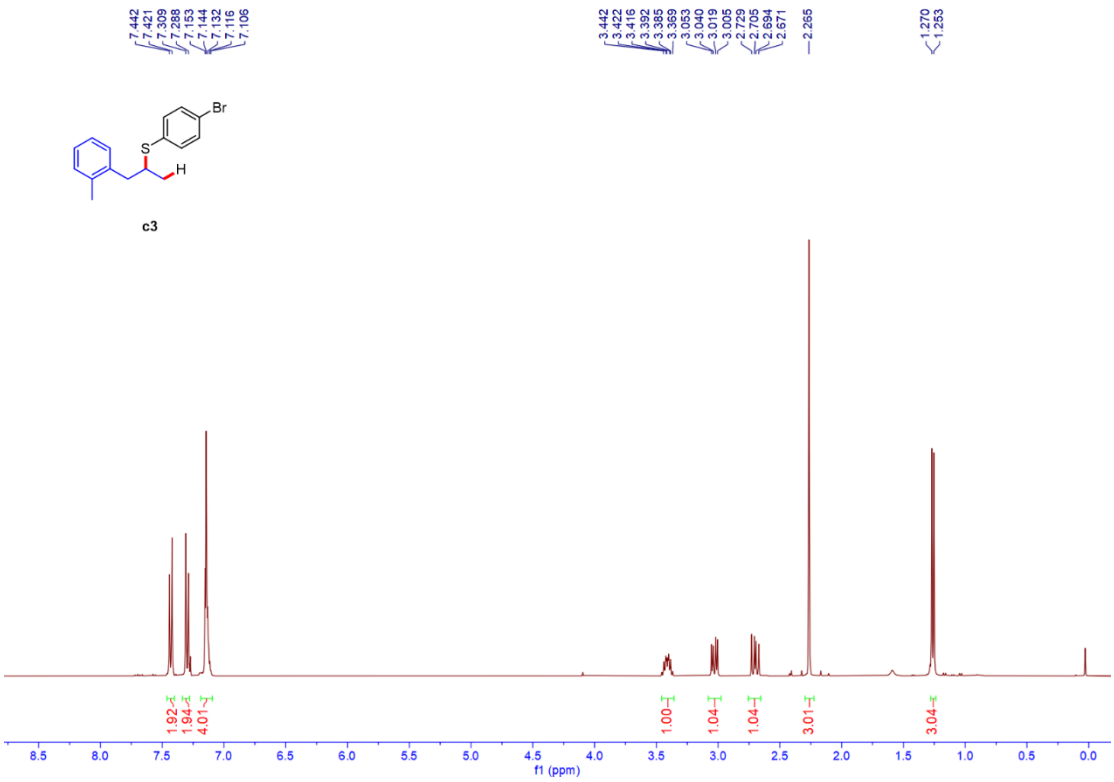
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2.671
2.265
1.270
1.253
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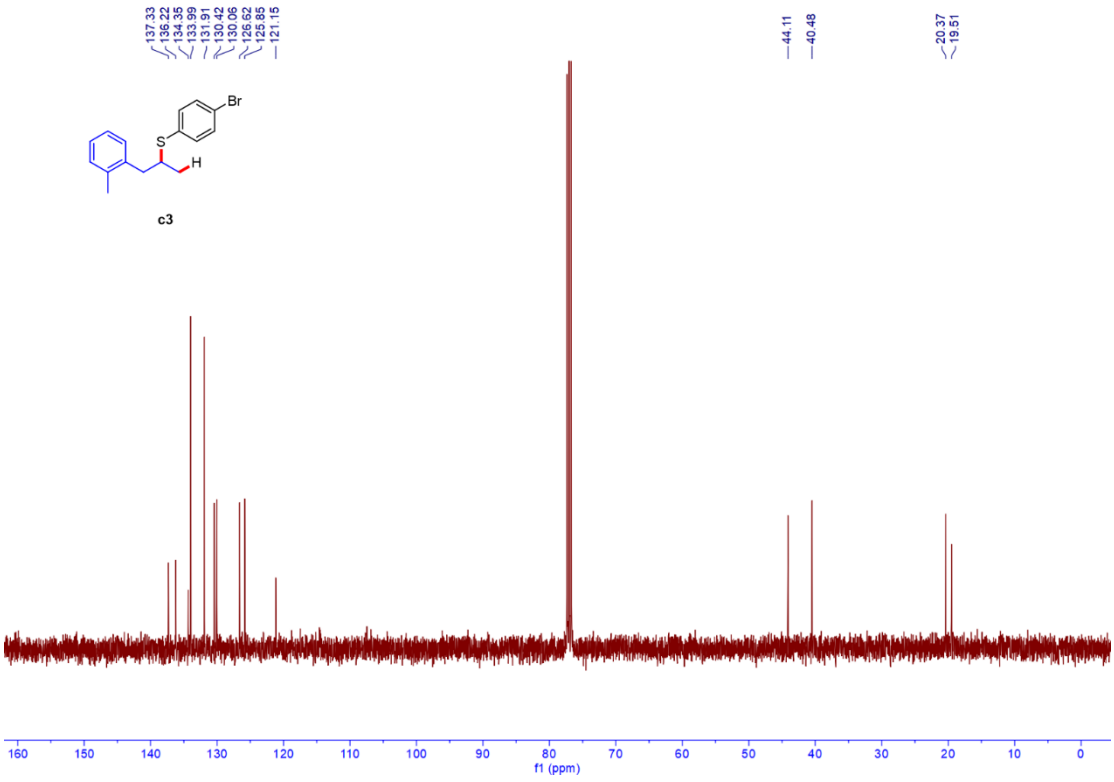
f1 (ppm)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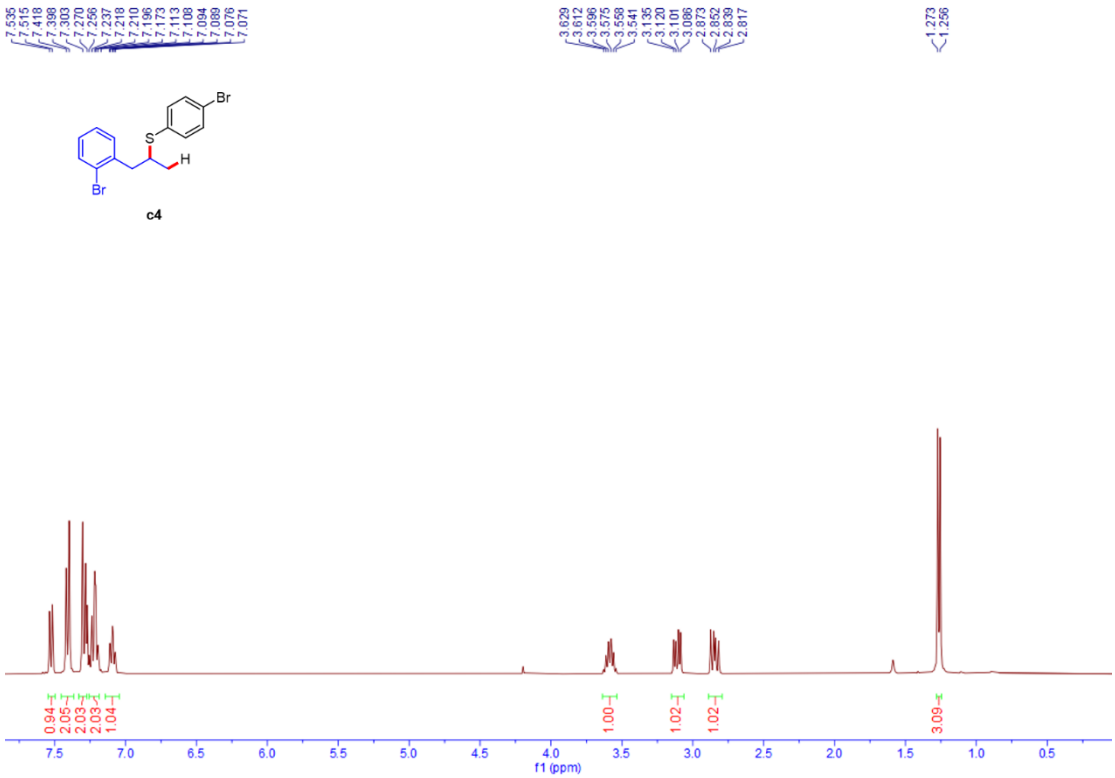
c3
f1 (ppm)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3.558
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1.256
Br
S
H
Br
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1.02
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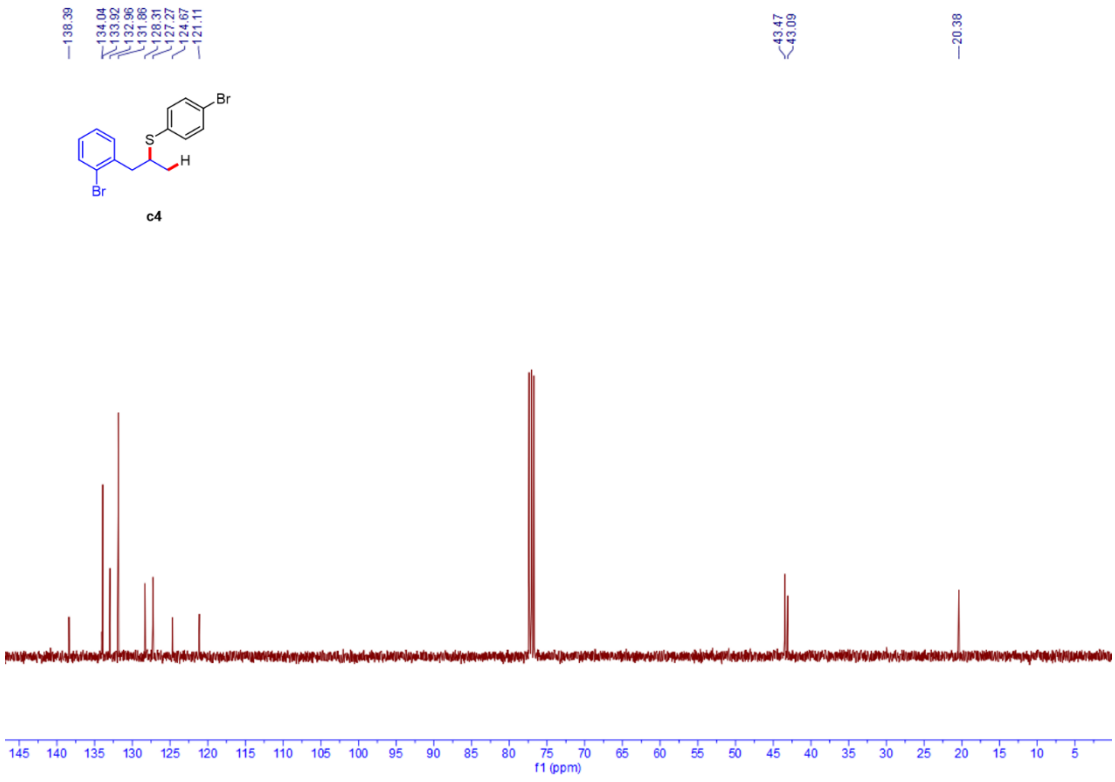
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S
H
Br
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140
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130
125
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115
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95
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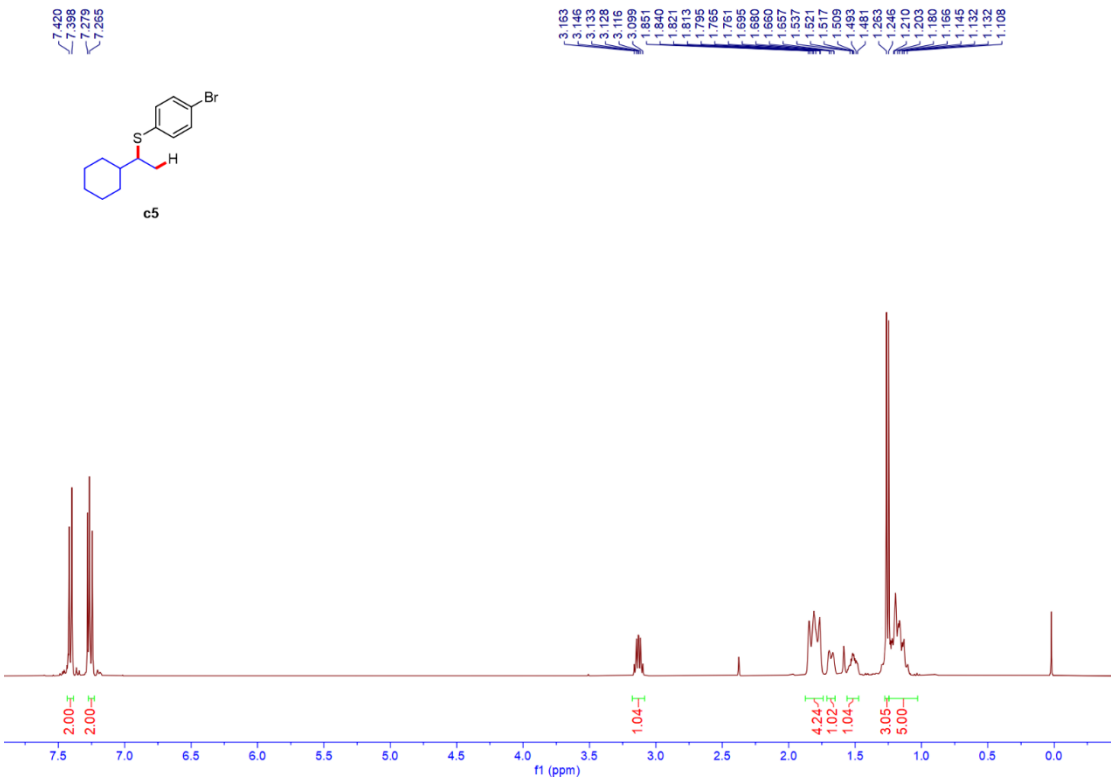
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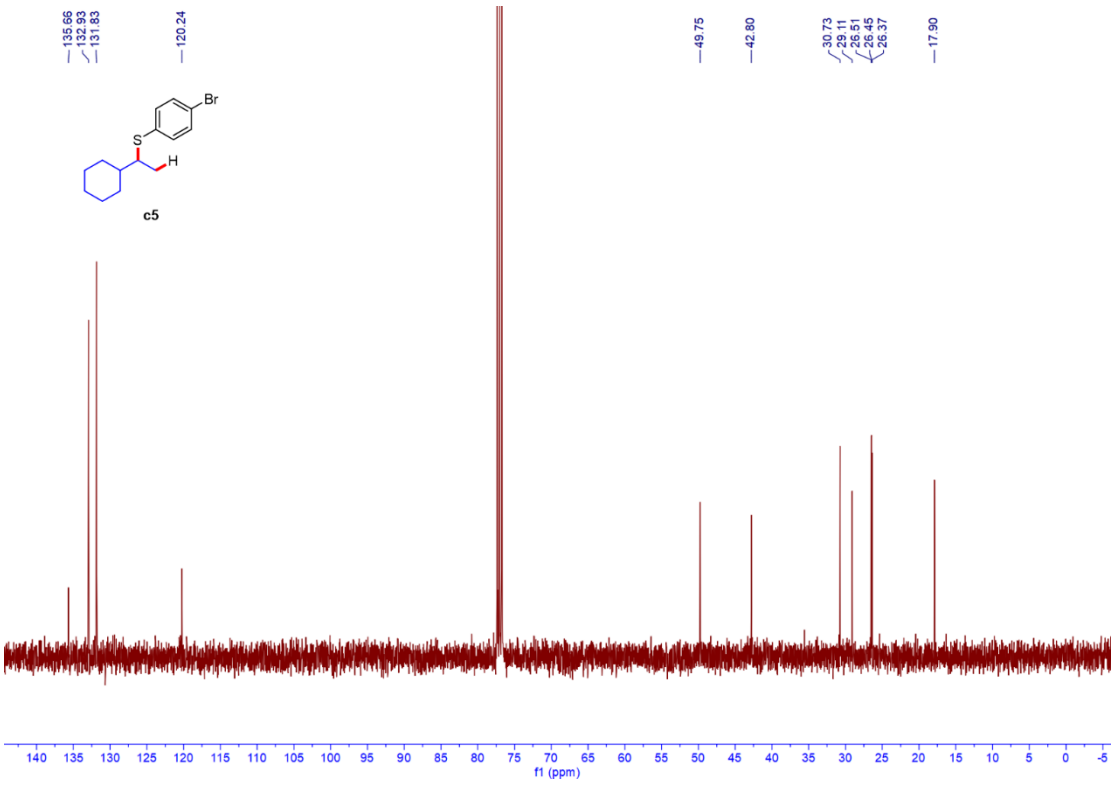
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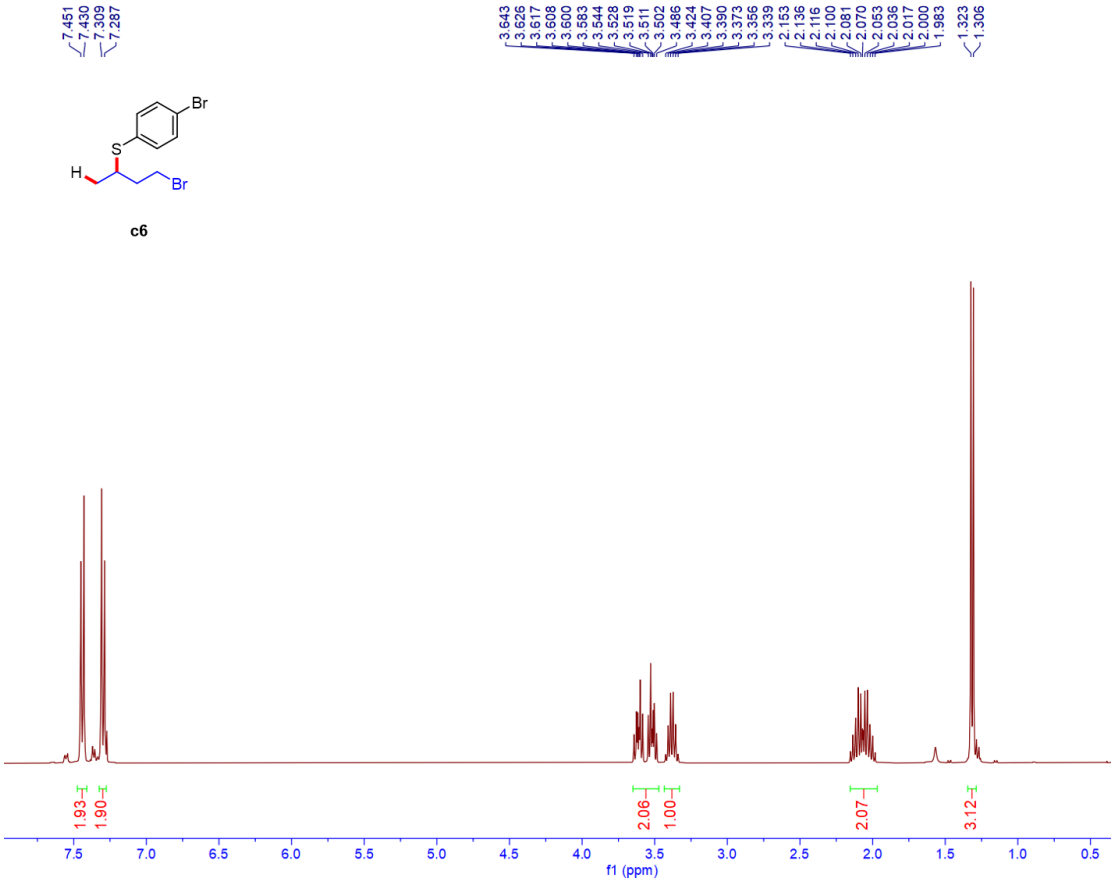
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3.486
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3.407
3.390
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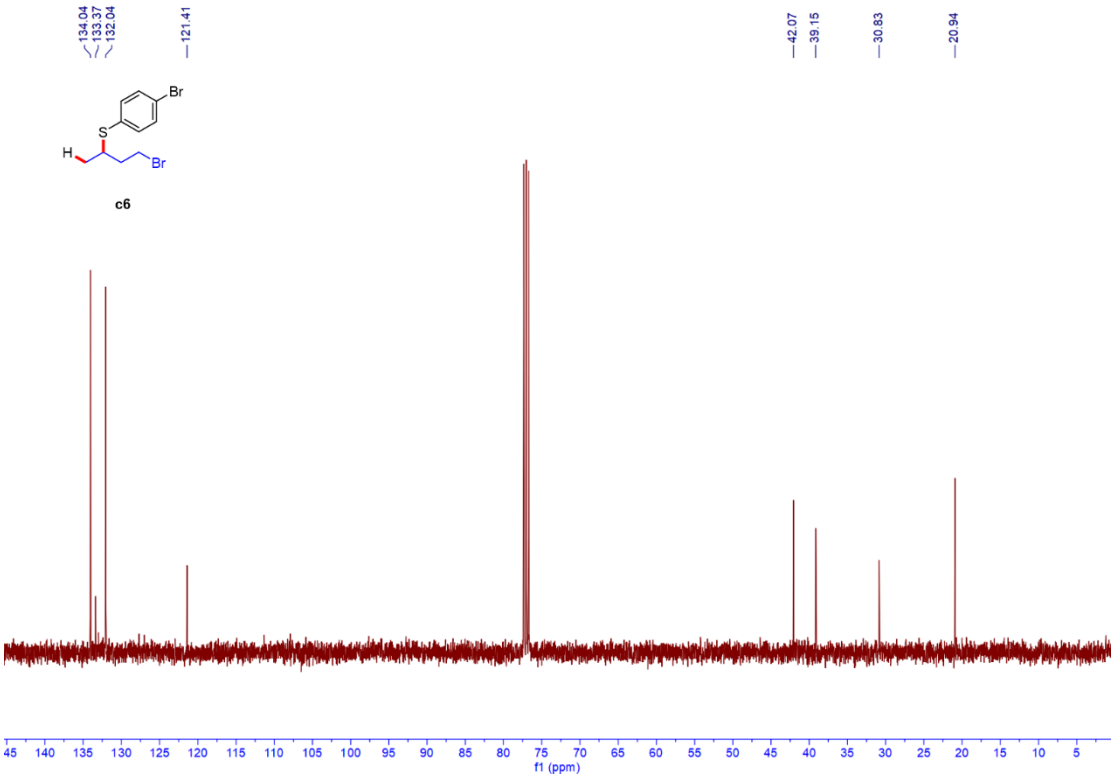
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S
H
Br
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135
130
125
120
115
110
105
100
95
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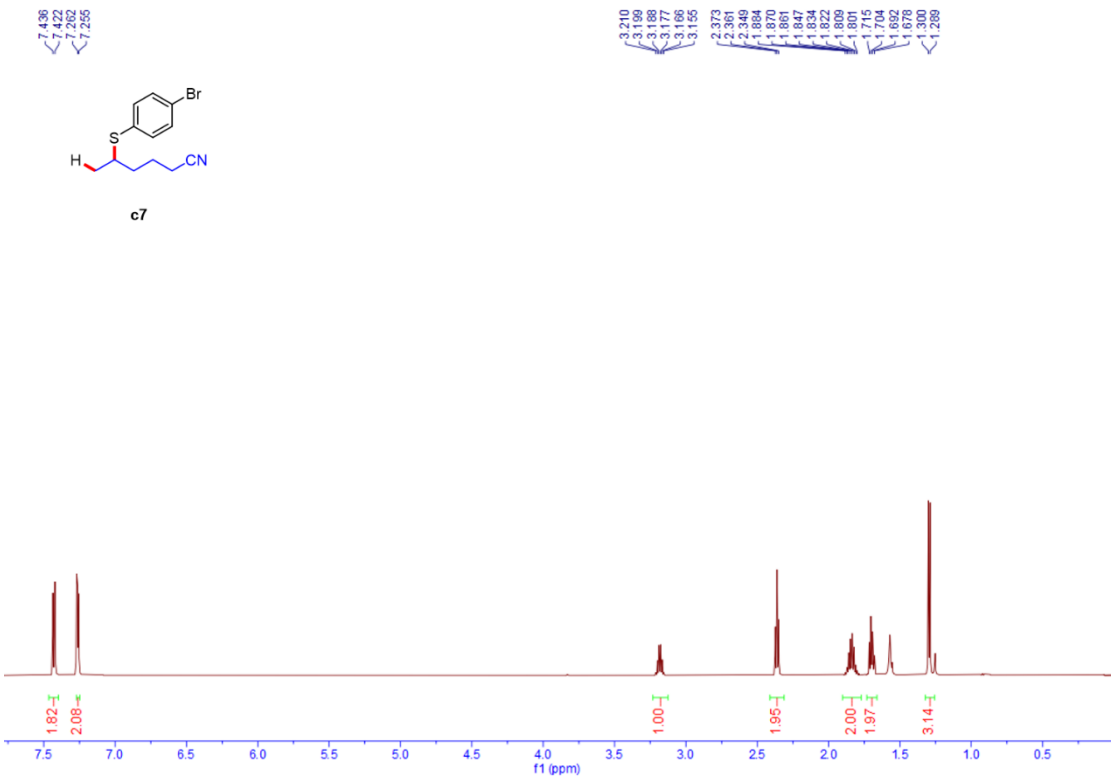
f1 (ppm)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1.692
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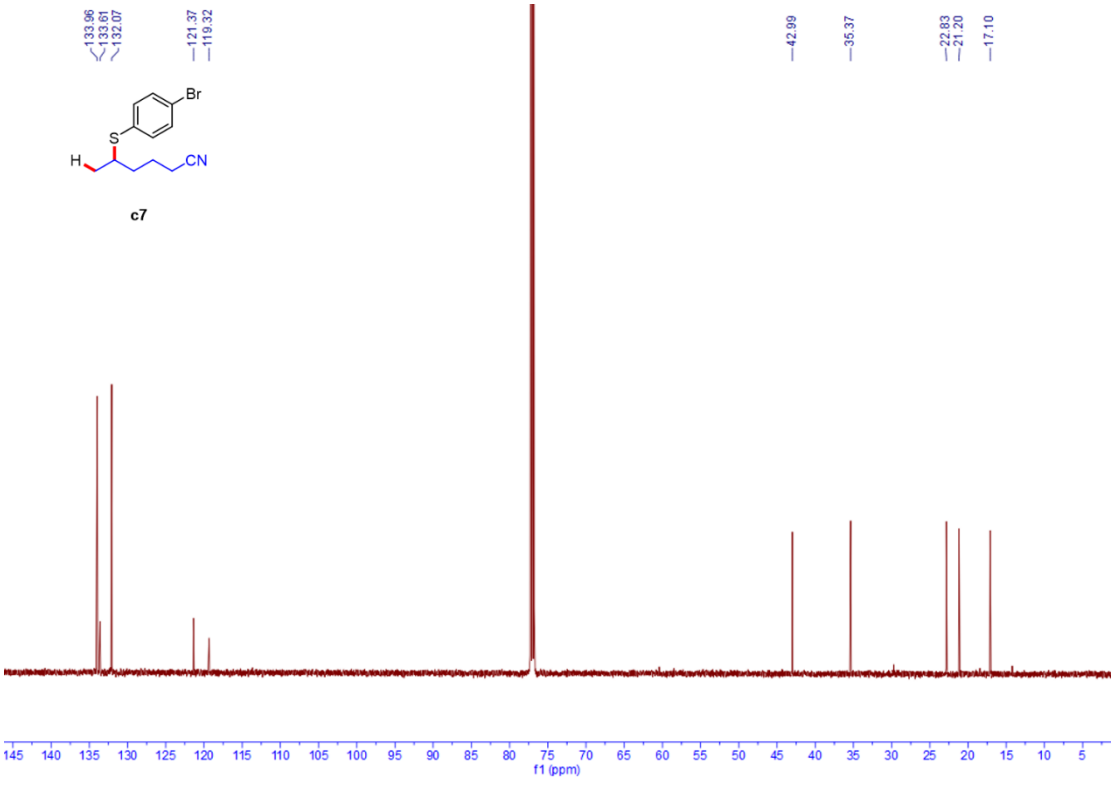
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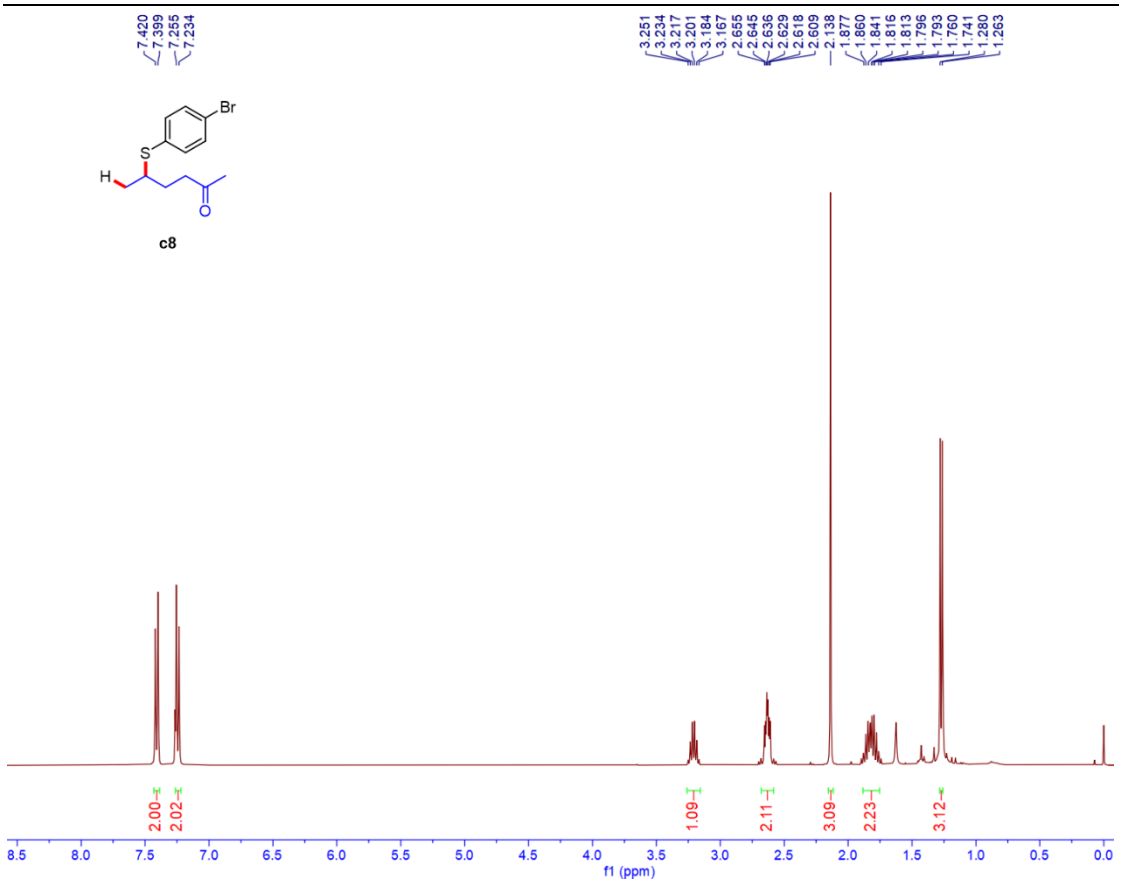
c7
f1 (ppm)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2.138
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1.816
1.813
1.796
1.793
1.760
1.741
1.280
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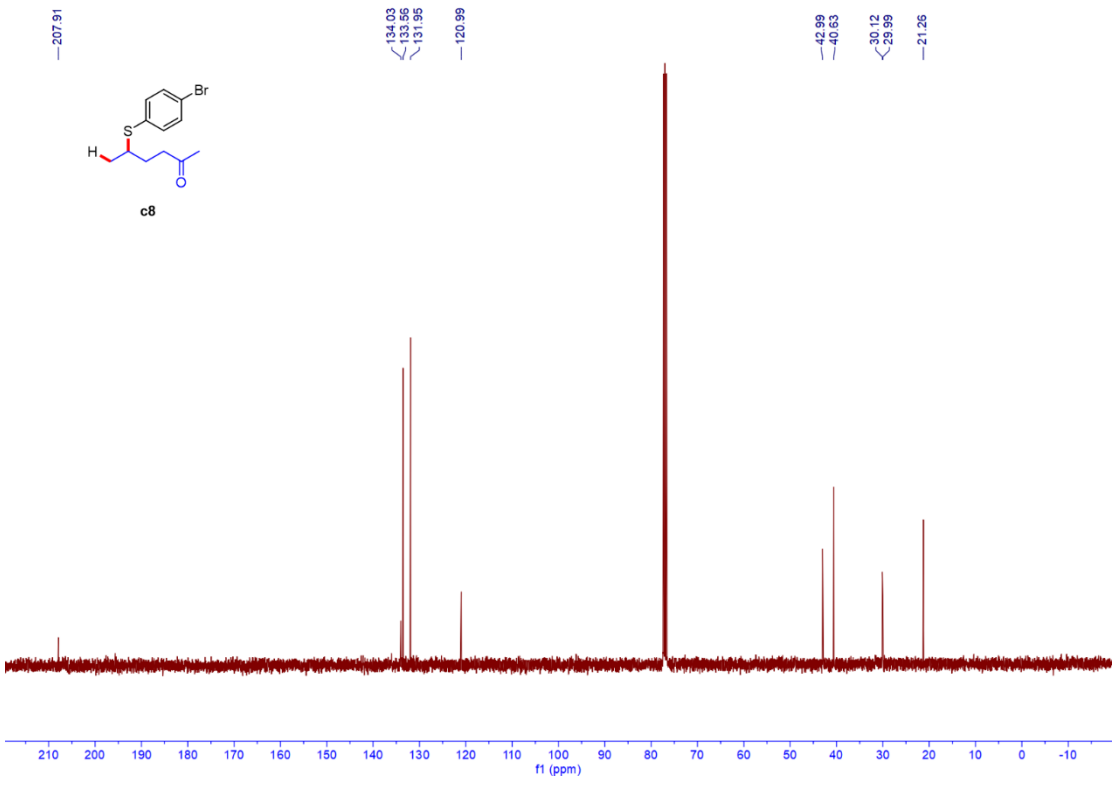
3.12
f1 (ppm)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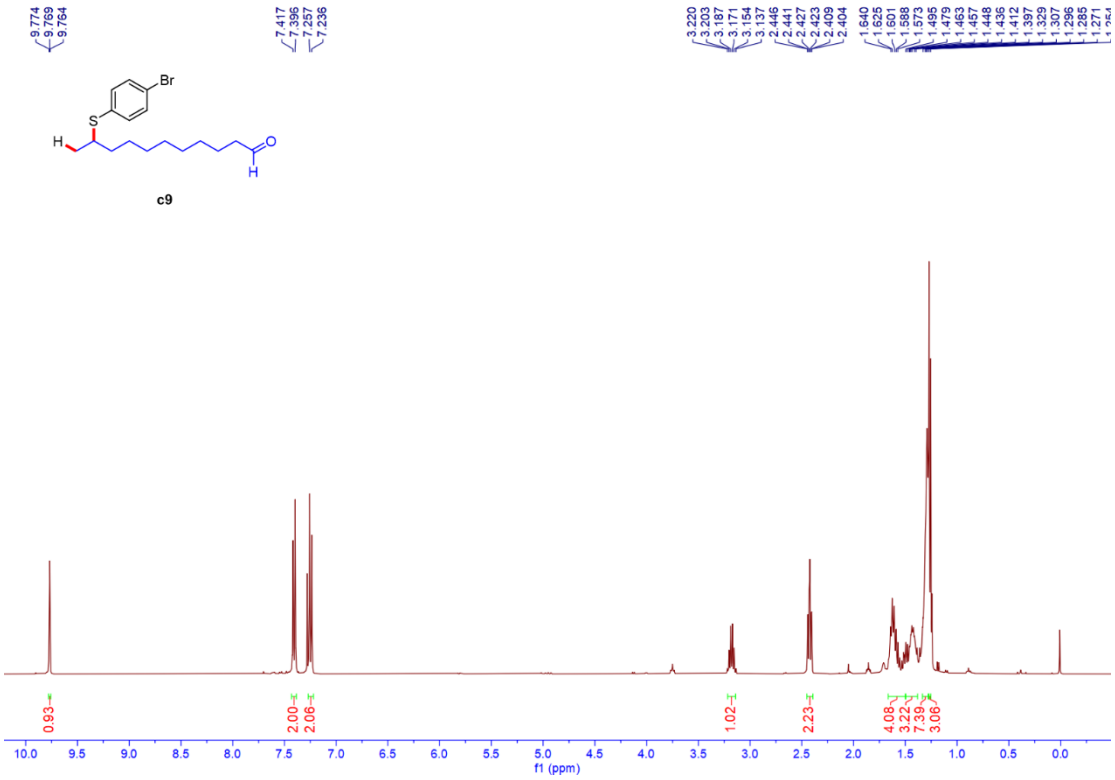
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1.495
1.479
1.463
1.457
1.448
1.436
1.412
1.397
1.329
1.307
1.296
1.285
1.271
Br
S
H
O
H
c9
0.93
2.00
2.06
1.02
2.23
4.08
3.22
7.39
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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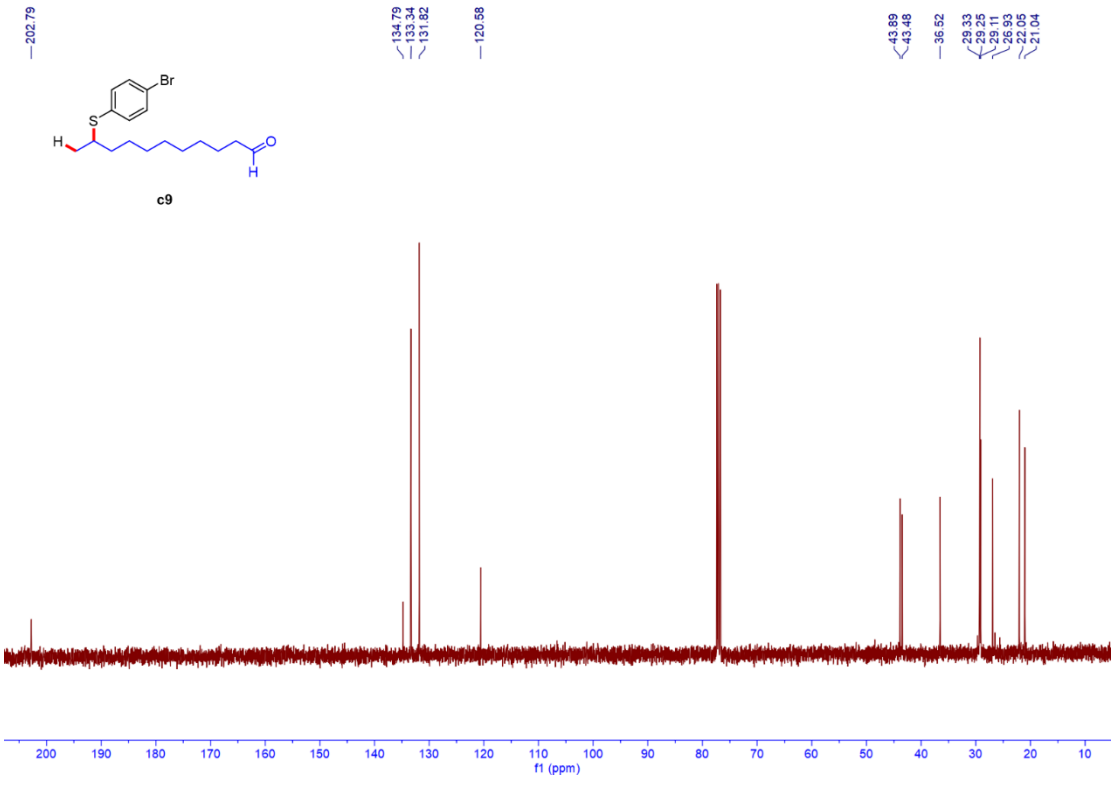
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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134.79
133.34
131.82
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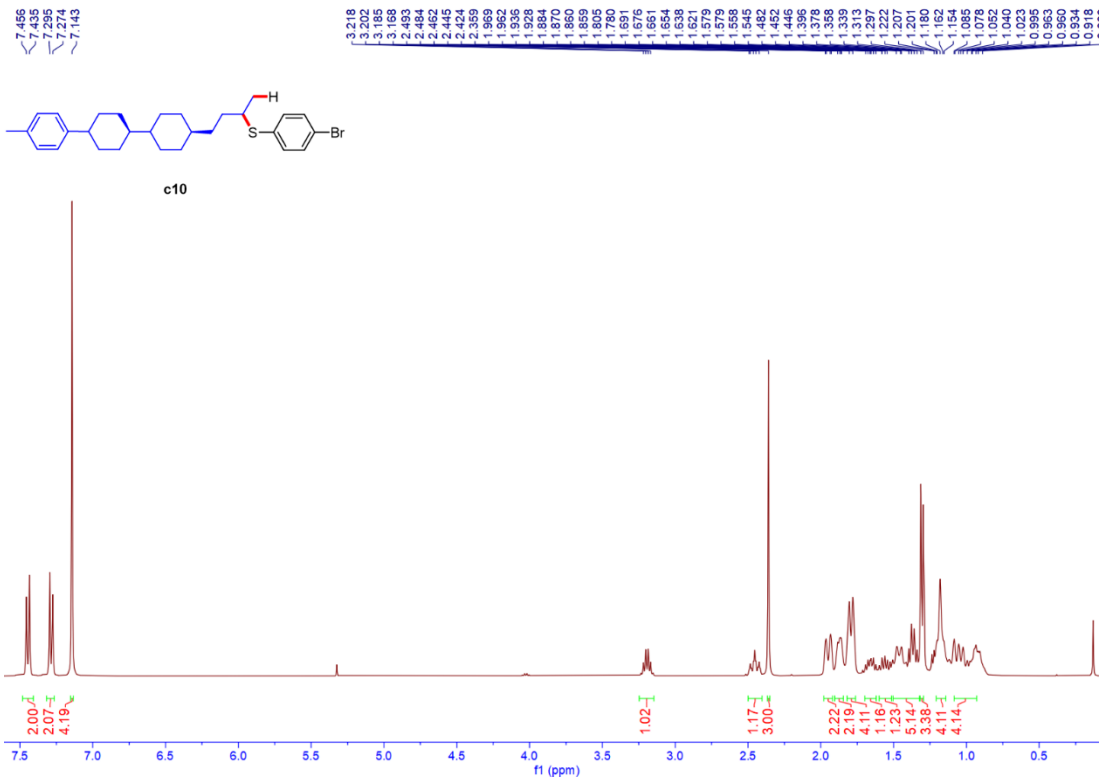
43.89
43.48
36.52
29.33
29.25
29.11
26.93
22.05
21.04
Br
S
H
O
H
c9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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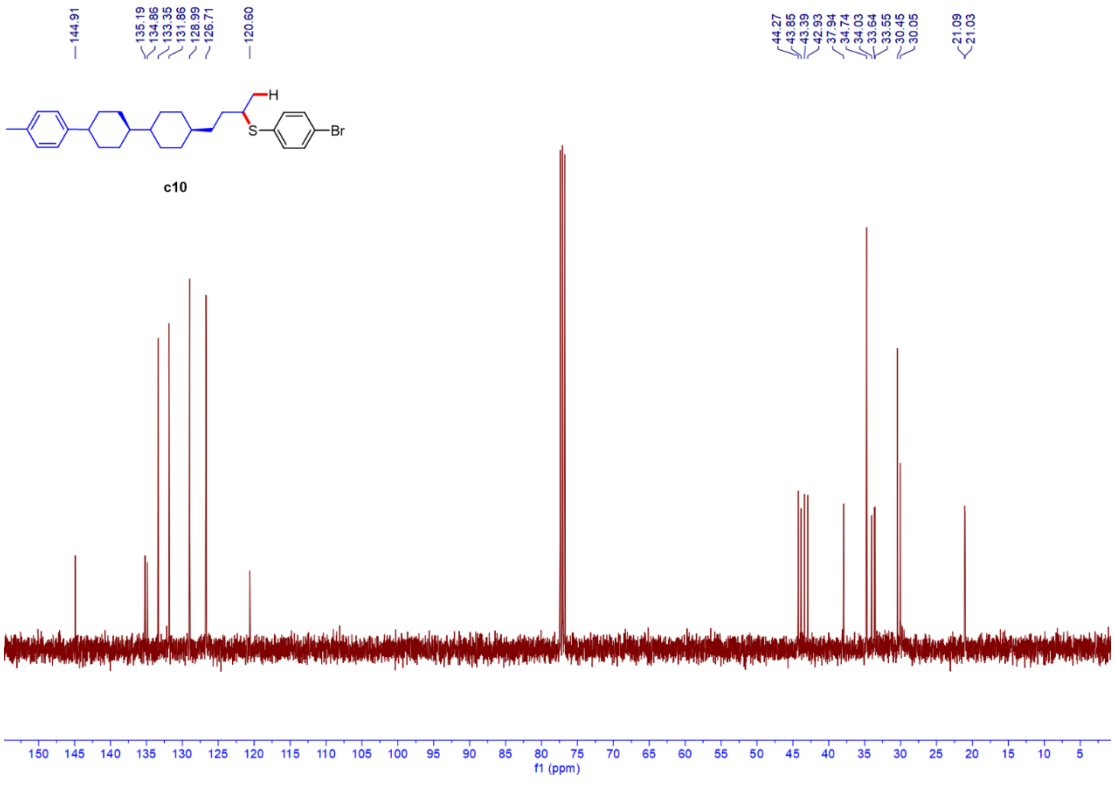
2.462
2.445
2.424
2.359
1.969
1.962
1.936
1.928
1.884
1.870
1.860
1.859
1.805
1.780
1.691
1.676
1.661
1.654
1.638
1.621
1.579
1.579
1.558
1.545
1.482
1.452
1.446
1.396
1.378
1.358
1.339
1.313
1.297
1.222
1.207
1.201
1.180
1.162
1.154
1.085
1.078
1.052
1.040
1.023
0.995
0.963
0.960
0.934
0.918
H
S
Br
c10
2.00
2.07
4.19
1.02
1.17
3.00
2.22
2.19
4.11
1.16
1.23
5.14
3.38
4.11
4.14
f1 (ppm)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135.19
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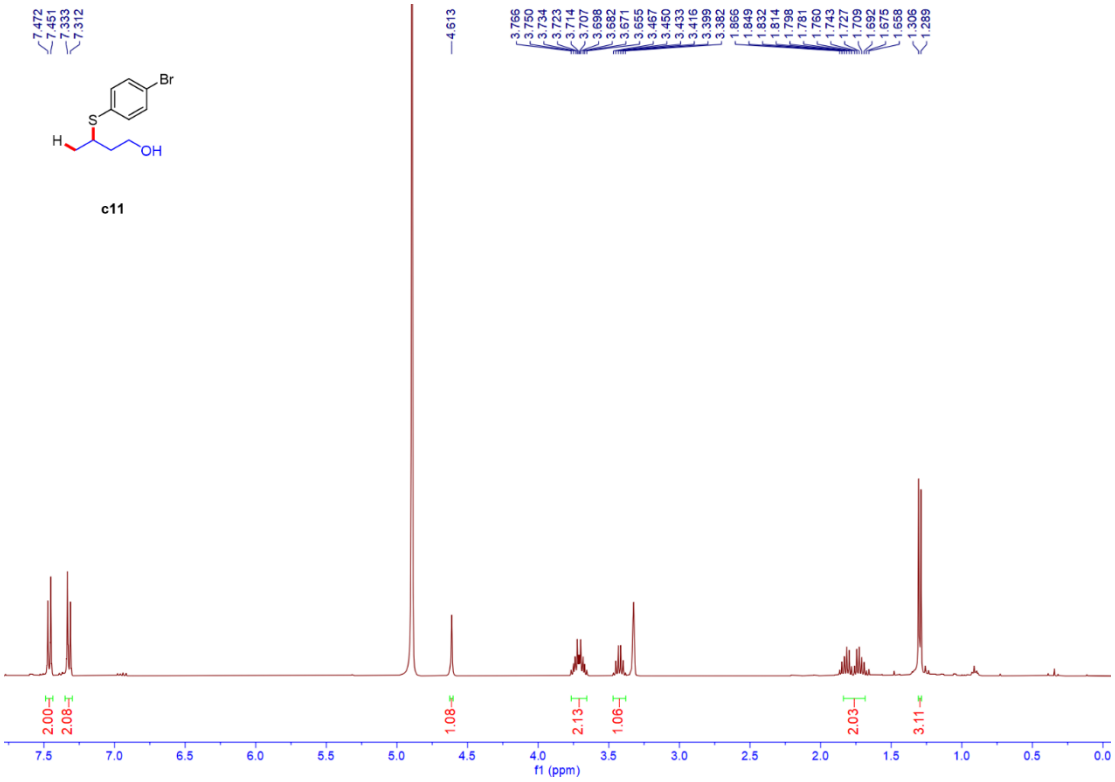
126.71
120.60
44.27
43.85
43.39
42.93
37.94
34.74
34.03
33.64
33.55
30.45
30.05
21.09
21.03
H
S
Br
c10
f1 (ppm)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7.312
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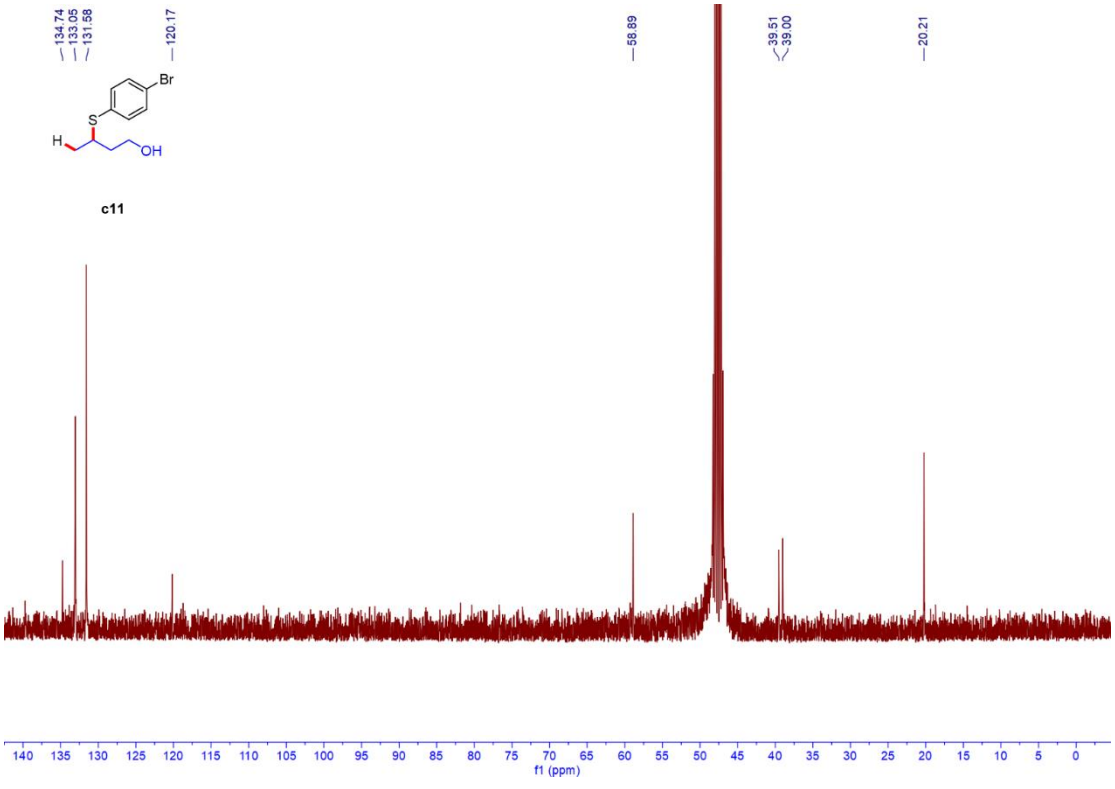
3.766
3.750
3.734
3.723
3.714
3.707
3.698
3.682
3.671
3.655
3.467
3.450
3.433
3.416
3.399
3.382
1.866
1.849
1.832
1.814
1.798
1.781
1.760
1.743
1.727
1.709
1.692
1.675
1.658
1.306
1.289
Br
S
H
OH
c11
2.00
2.08
1.08
2.13
1.06
2.03
3.11
f1 (ppm)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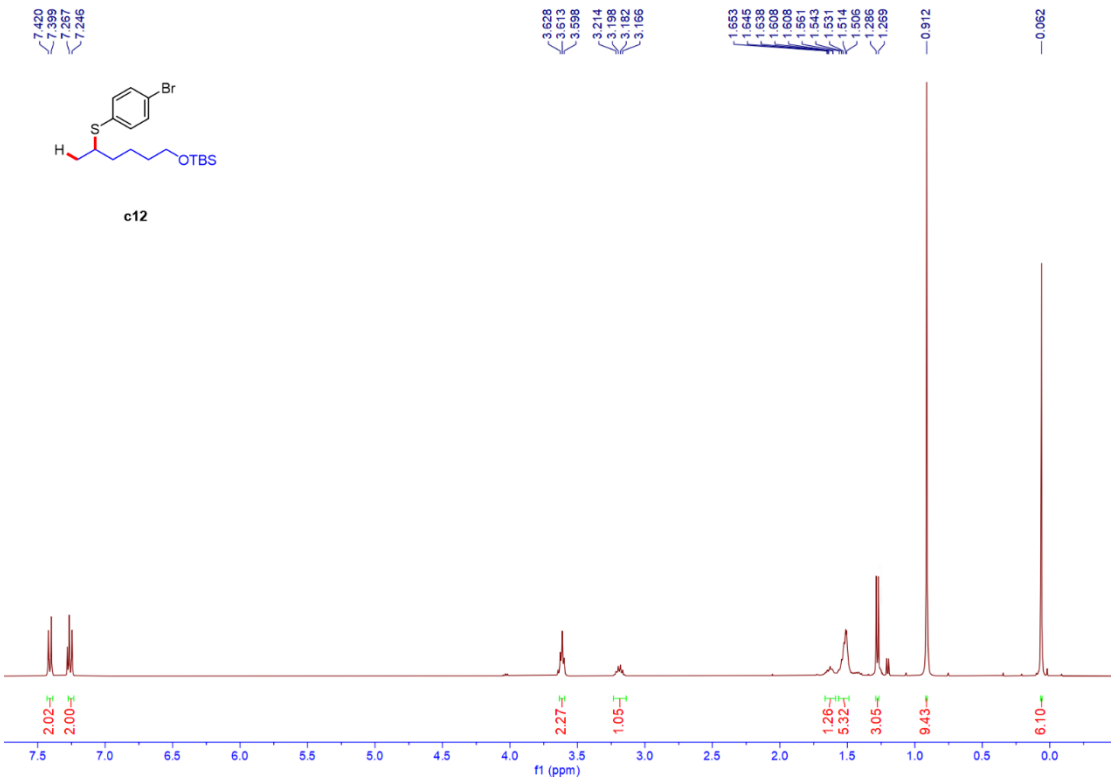
133.05
131.58
120.17
58.89
39.51
39.00
20.21
Br
S
H
OH
c11
f1 (ppm)


7.420
7.399
7.267
7.246
3.628
3.613
3.598
3.214
3.198
3.182
3.166
1.653
1.645
1.638
1.608
1.608
1.561
1.543
1.531
1.514
1.506
1.286
1.269
0.912
0.062
Br
S
H
OTBS
c12
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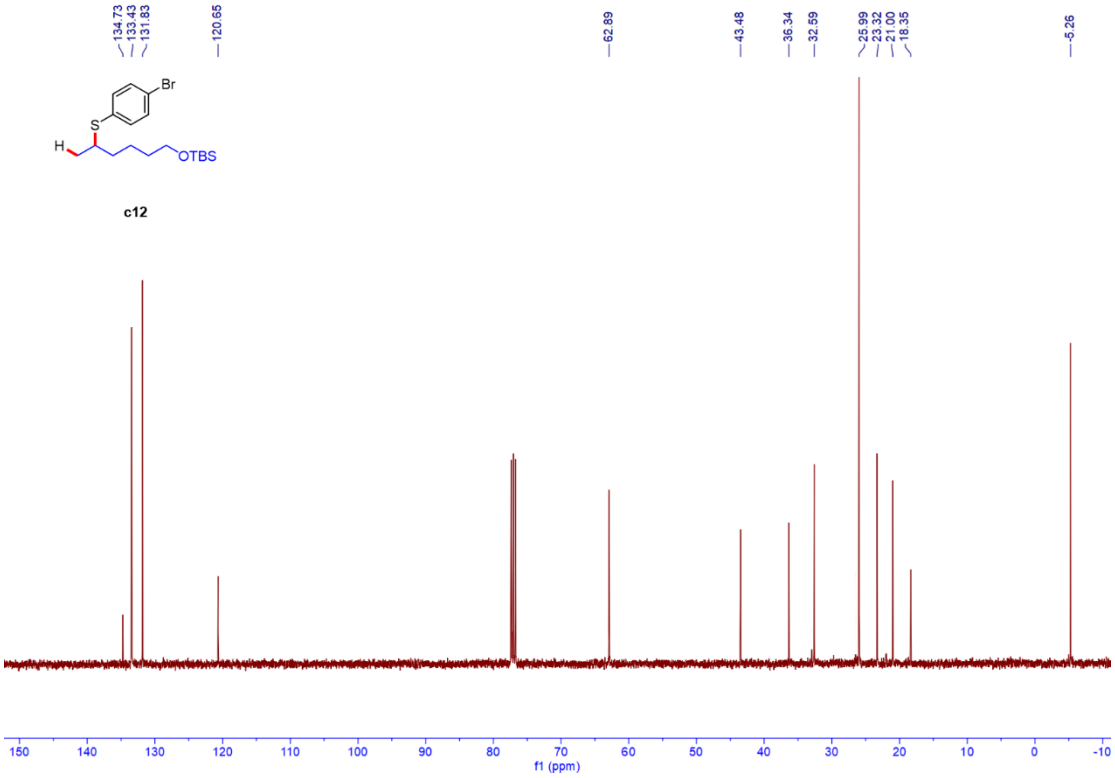
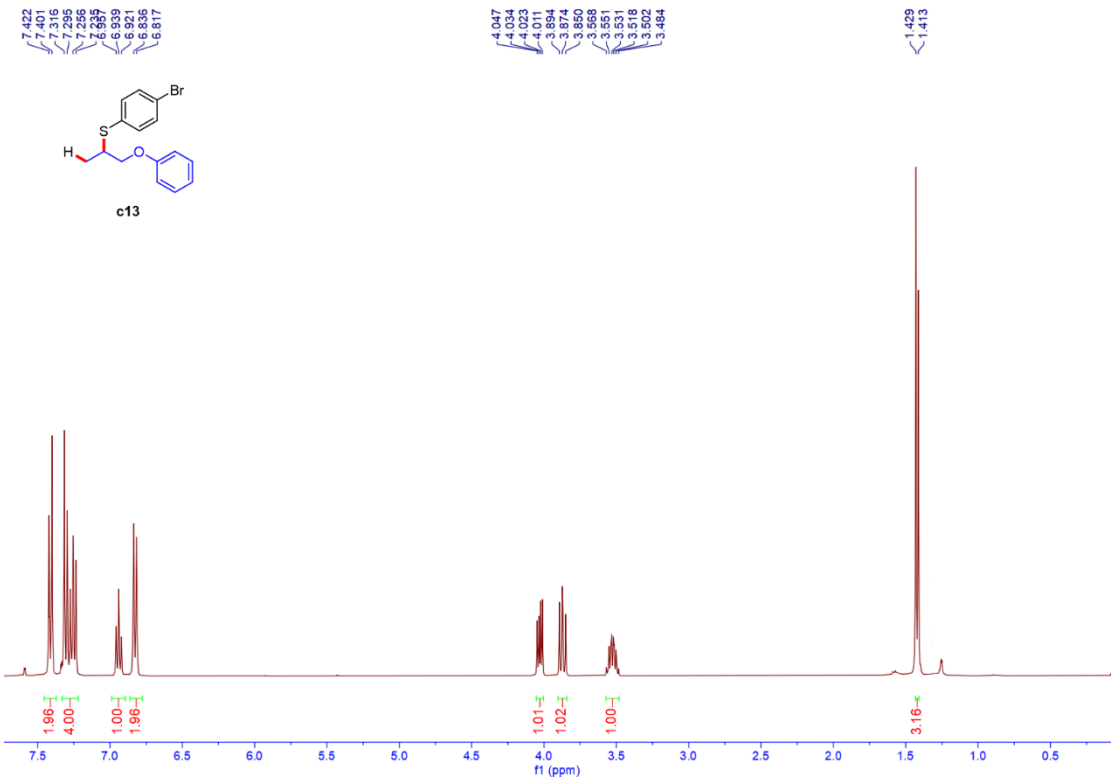
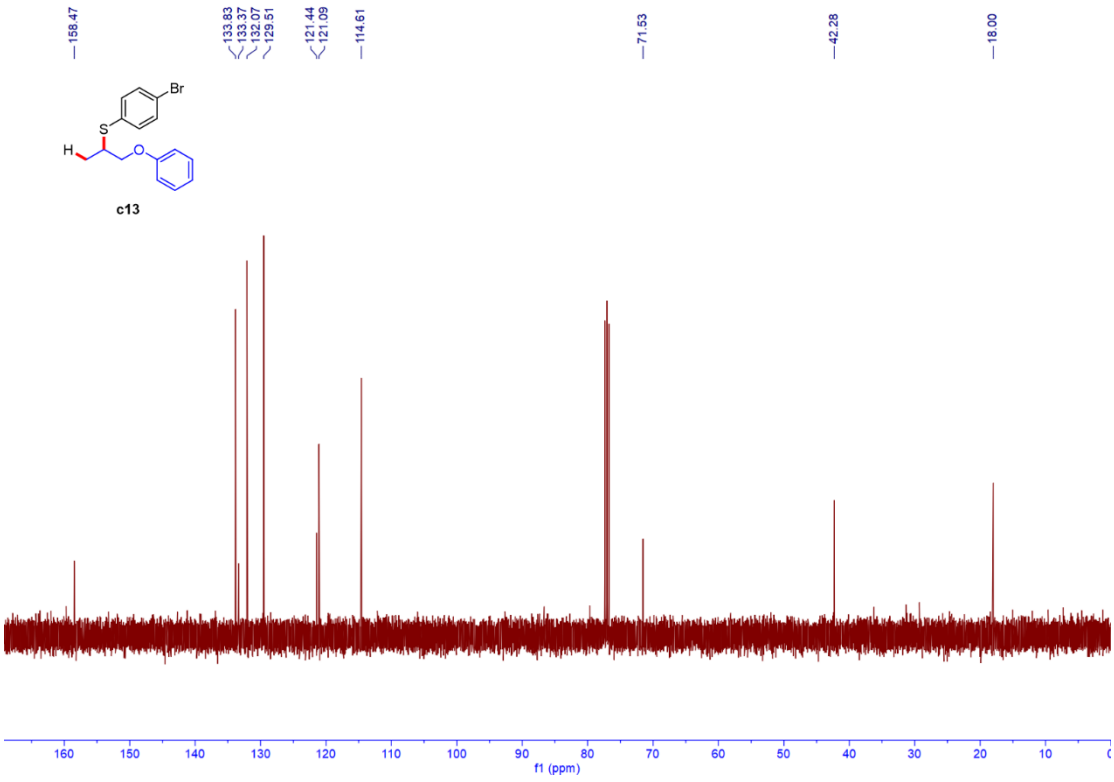
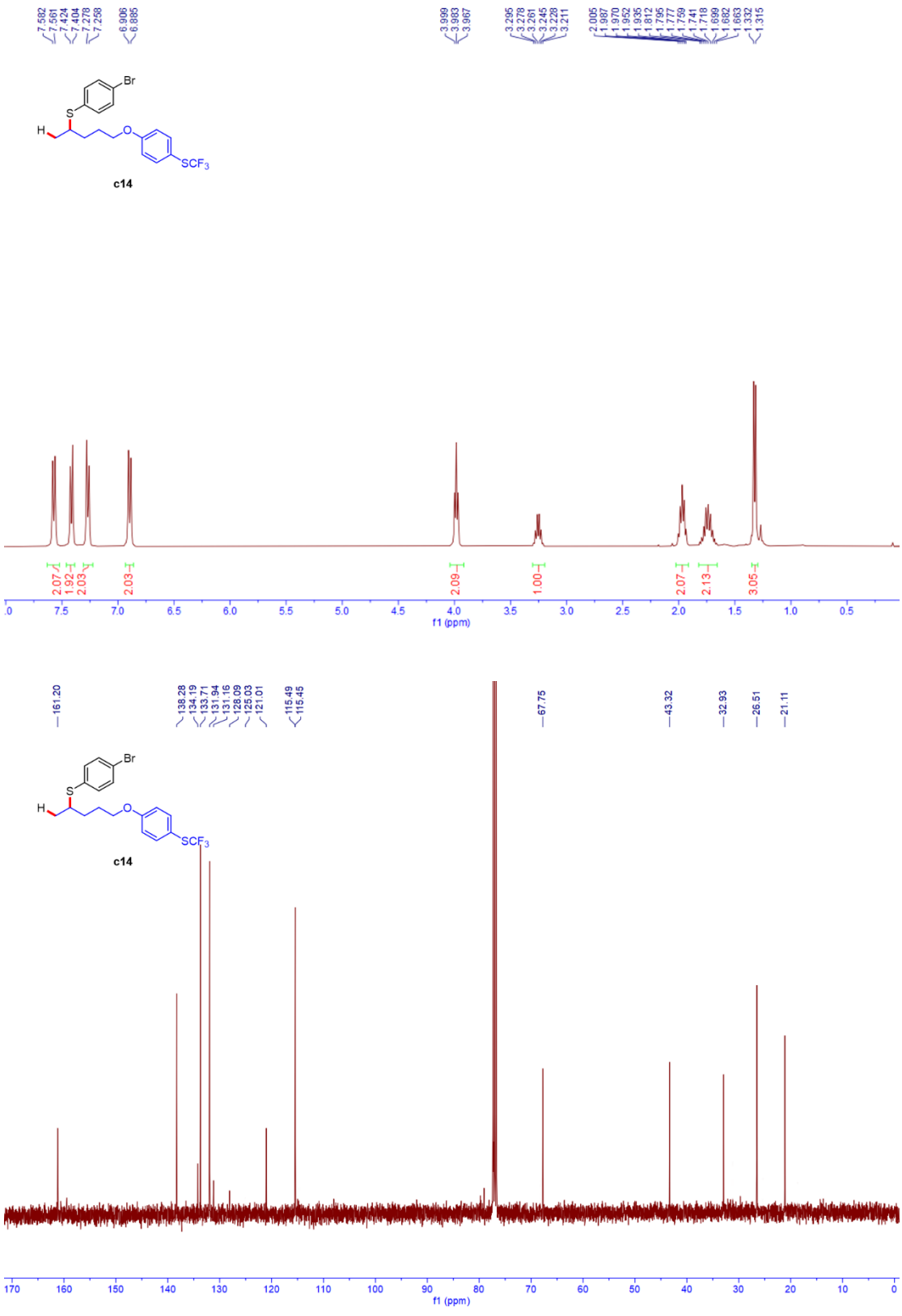
2.00
2.27
1.05
1.26
5.32
3.05
9.43
6.10
f1 (ppm)


134.73
133.43
131.83
120.65
62.89
43.48
36.34
32.59
25.99
23.32
21.00
18.35
-5.26
Br
S
H
OTBS
c12
f1 (ppm)


7.422
7.401
7.316
7.295
7.256
6.939
6.921
6.836
6.817
4.047
4.034
4.023
4.011
3.894
3.874
3.850
3.568
3.551
3.531
3.518
3.502
3.484
1.429
1.413
Br
S
H
O
c13
1.96
4.00
1.00
1.96
1.01
1.02
1.00
3.16
f1 (ppm)


158.47
133.83
133.37
132.07
129.51
121.44
121.09
114.61
71.53
42.28
18.00
Br
S
H
O
c13
f1 (ppm)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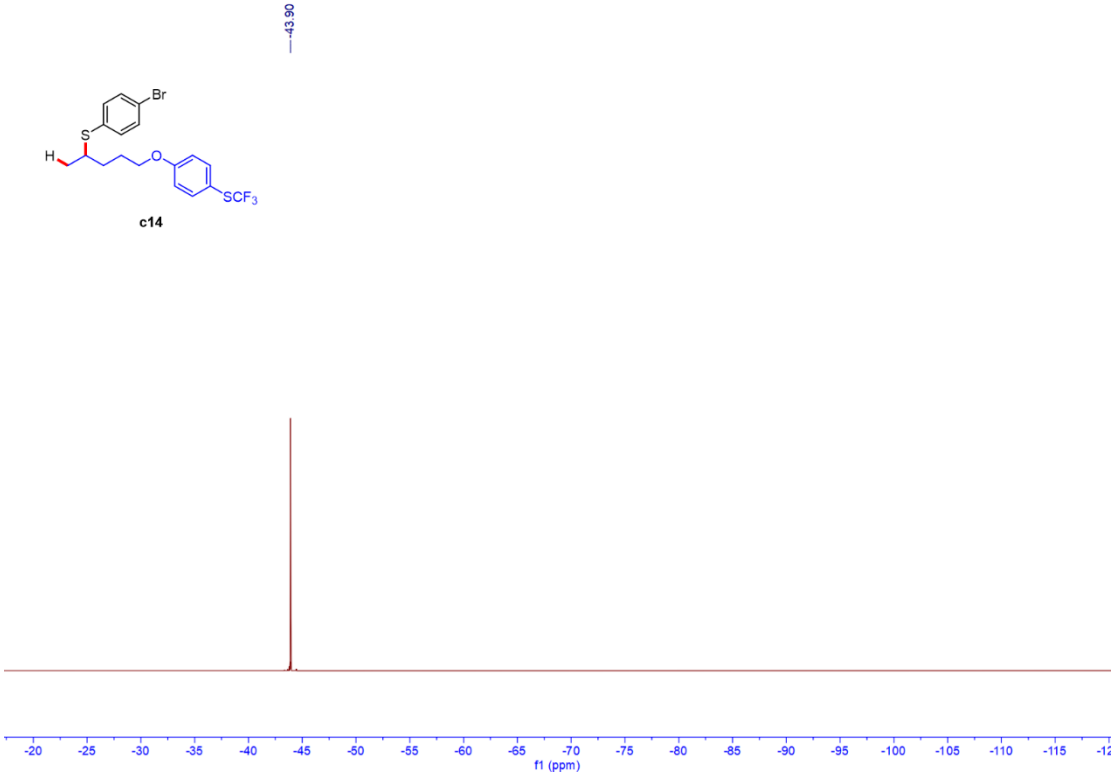
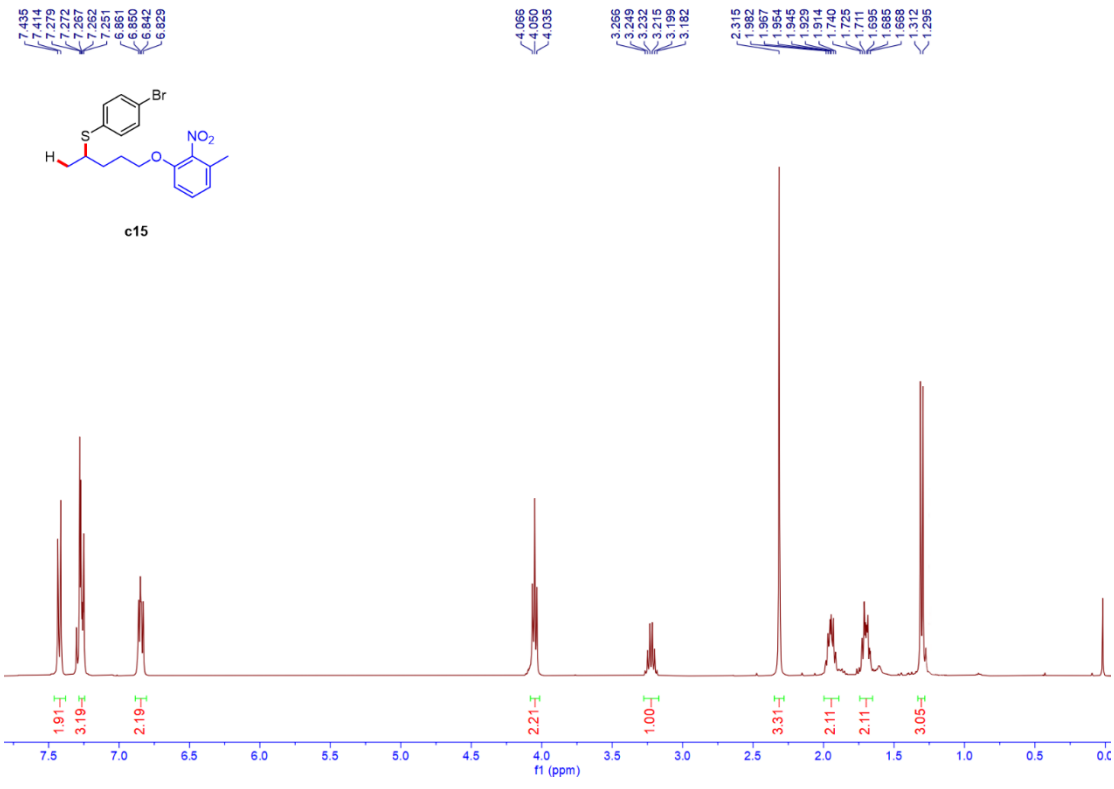
7.561
7.424
7.404
7.278
7.258
6.906
6.885
3.999
3.983
3.967
3.295
3.278
3.261
3.245
3.228
3.211
2.005
1.987
1.970
1.952
1.935
1.912
1.795
1.777
1.759
1.741
1.718
1.699
1.682
1.663
1.332
1.315
Br
S
H
O
SCF3
c14
2.07
1.92
2.03
2.03
2.09
1.00
2.07
2.13
3.05
f1 (ppm)
161.20
138.28
134.19
133.71
131.94
131.16
128.09
125.03
121.01
115.49
115.45
67.75
43.32
32.93
26.51
21.11
f1 (ppm)


-43.90
Br
S
H
O
SCF3
c14
-20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115
f1 (ppm)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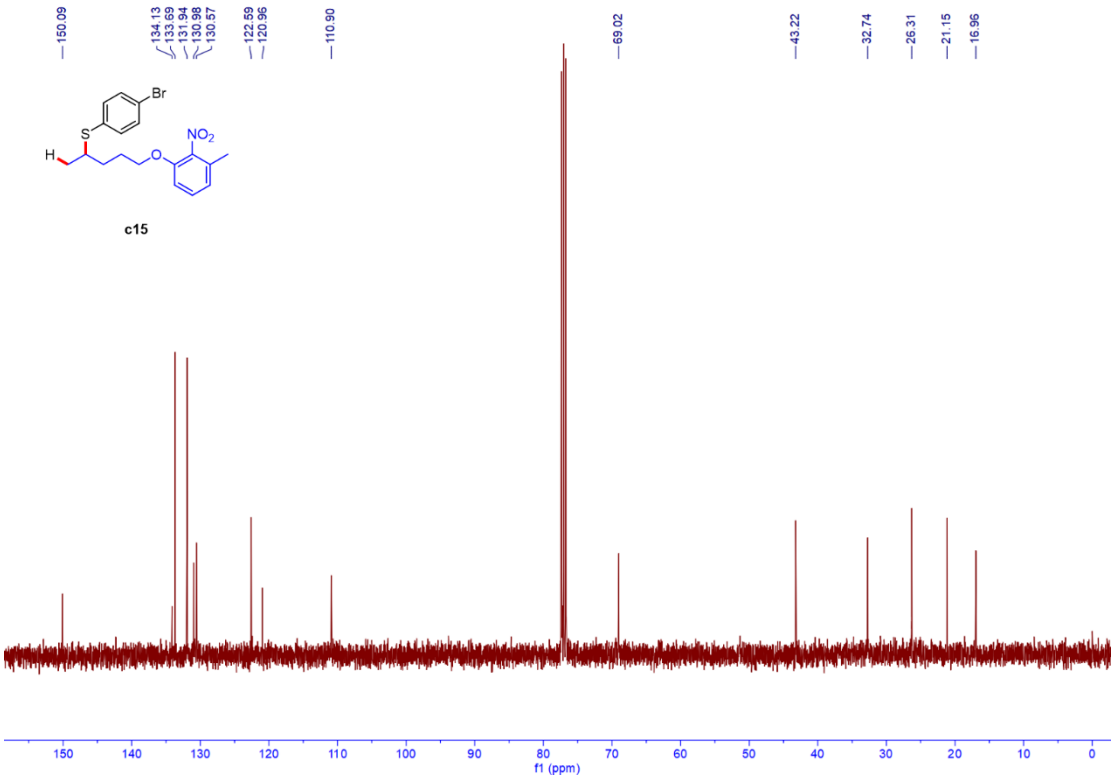
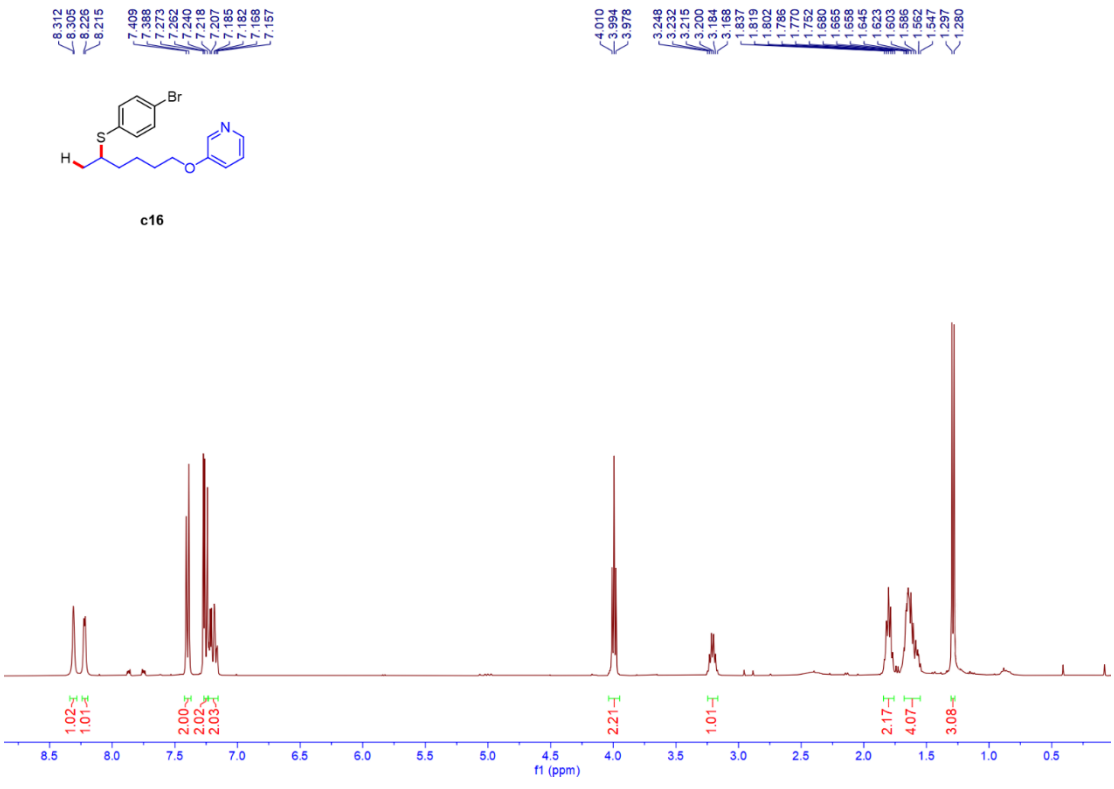
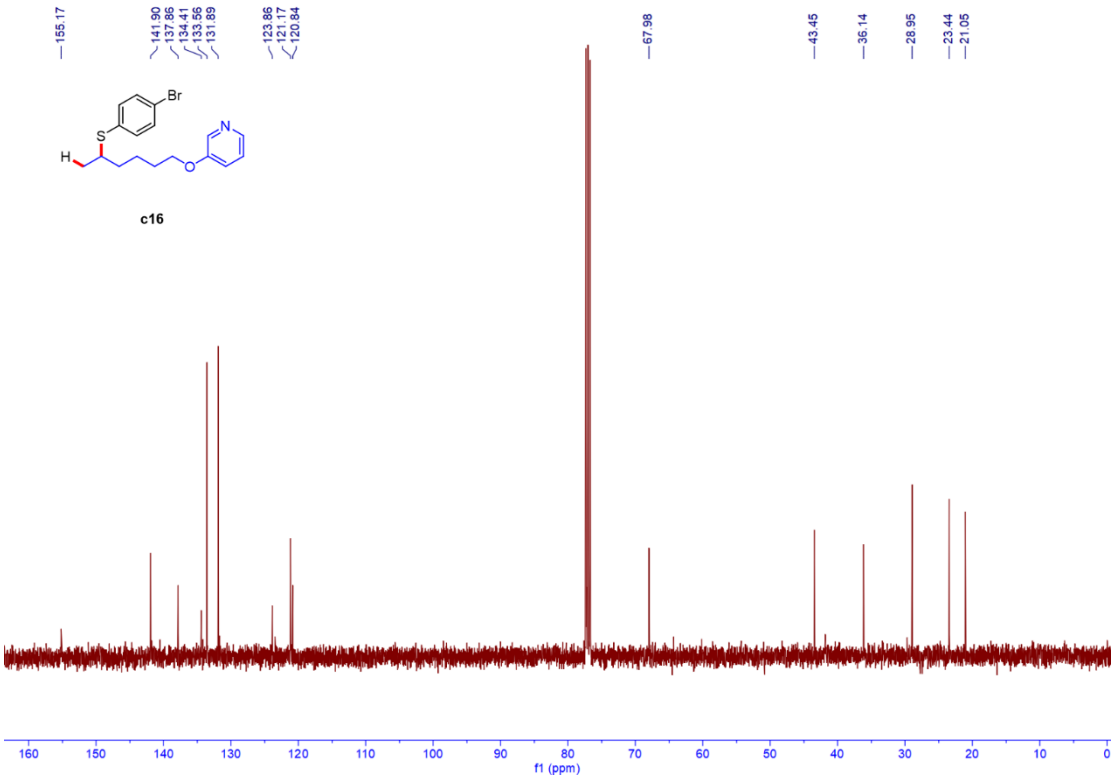
4.066 4.050 4.035
3.266 3.249 3.232 3.215 3.199 3.182
2.315 1.982 1.967 1.954 1.945 1.929 1.914 1.740 1.725 1.711 1.695 1.685 1.668 1.312 1.295
Br
S
H
O
NO2
c15
1.91 3.19 2.19 2.21 1.00 3.31 2.11 2.11 3.05
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


150.09
134.13
133.69
131.94
130.98
130.57
122.59
120.96
110.90
69.02
43.22
32.74
26.31
21.15
16.96
Br
S
H
O
NO2
c15
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.312
8.305
8.226
8.215
7.409
7.388
7.273
7.262
7.240
7.218
7.207
7.185
7.182
7.168
7.157
4.010
3.994
3.978
3.248
3.232
3.215
3.200
3.184
3.168
1.837
1.819
1.802
1.786
1.770
1.752
1.680
1.665
1.658
1.645
1.623
1.603
1.586
1.562
1.547
1.297
1.280
Br
S
H
N
O
c16
1.02
1.01
2.00
2.02
2.03
2.21
1.01
2.17
4.07
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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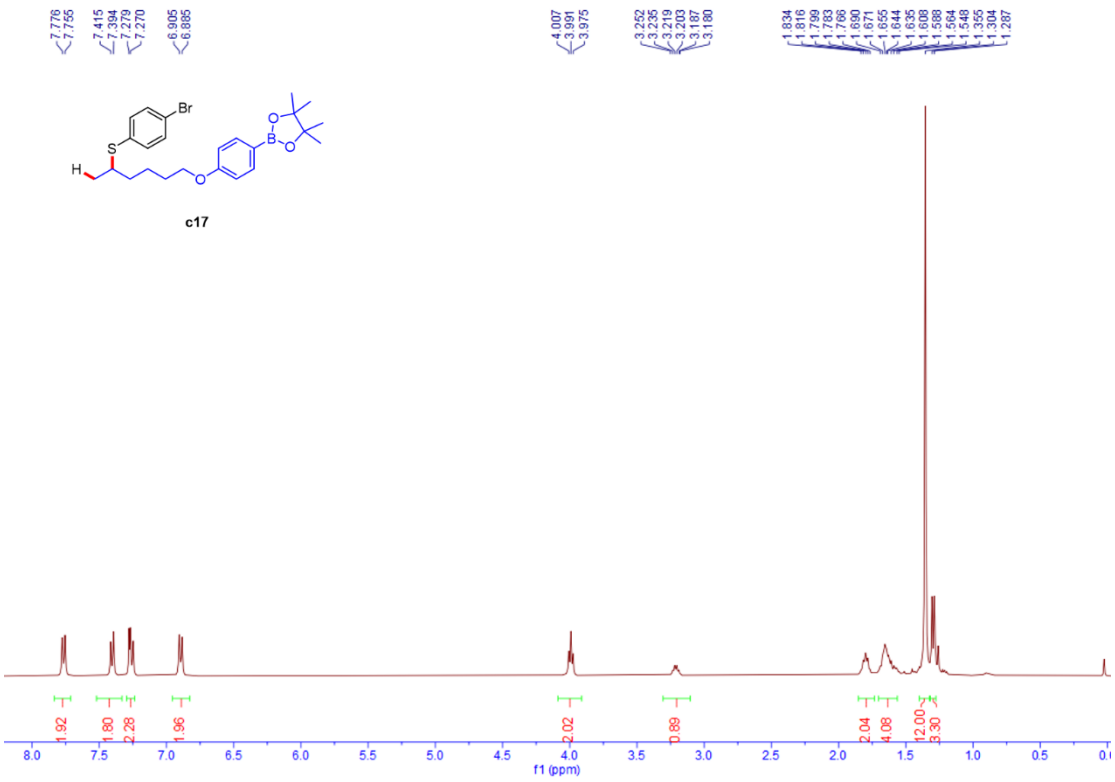
137.86
134.41
134.56
131.89
123.86
121.17
120.84
67.98
43.45
36.14
28.95
23.44
21.05
Br
S
H
N
O
c16
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.279
7.270
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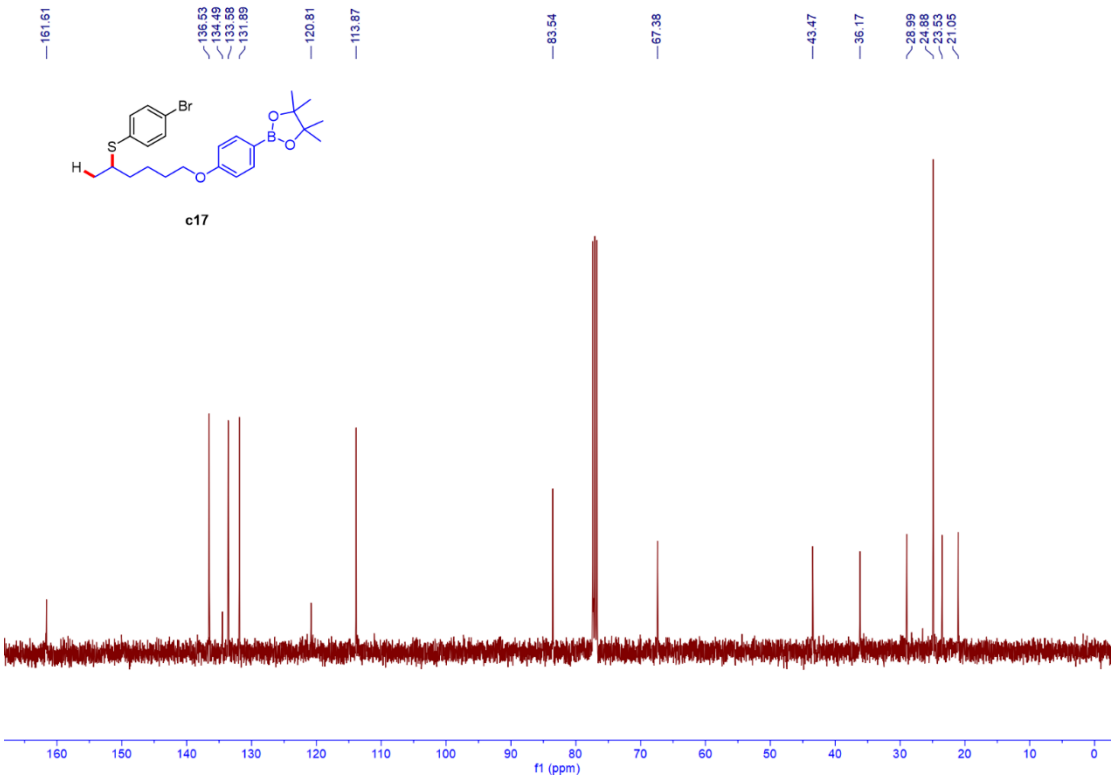
6.885
4.007
3.991
3.975
3.252
3.235
3.219
3.203
3.187
3.180
1.834
1.816
1.799
1.783
1.766
1.690
1.671
1.655
1.644
1.635
1.608
1.588
1.564
1.548
1.355
1.304
1.287
Br
S
H
O
B
O
O
c17
1.92
1.80
2.28
1.96
2.02
0.89
2.04
4.08
12.00
3.30
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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136.53
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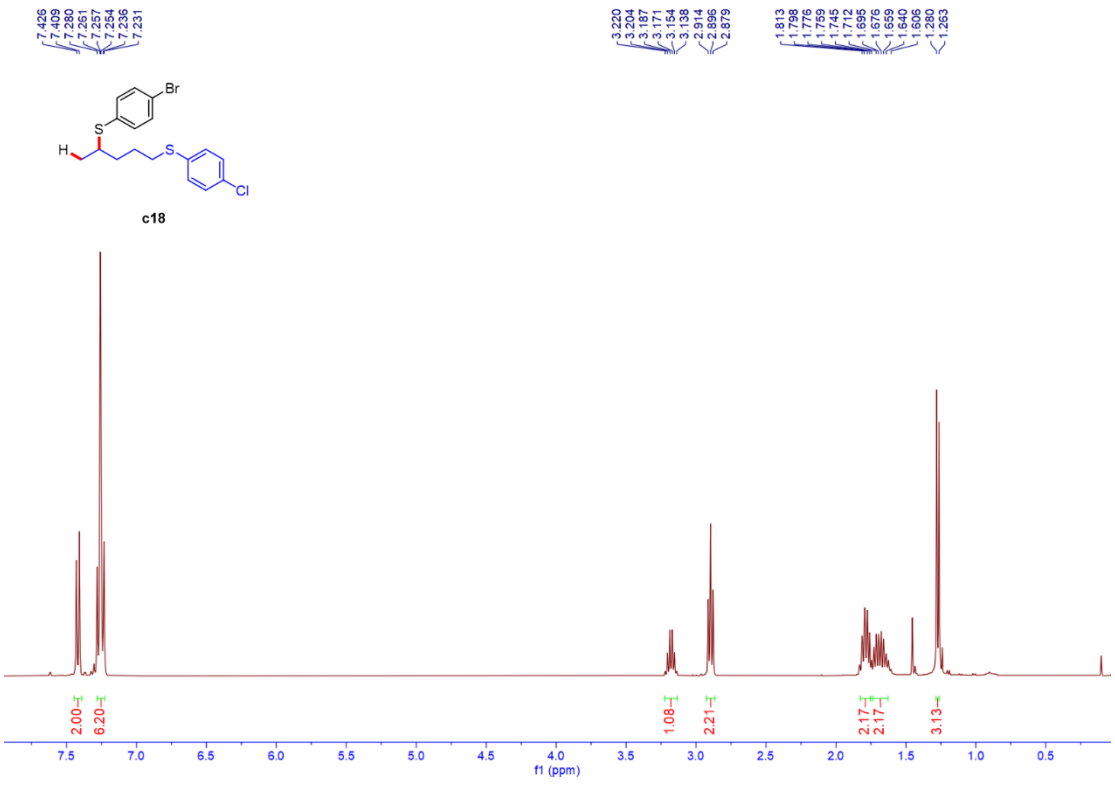
131.89
120.81
113.87
83.54
67.38
43.47
36.17
28.99
24.88
23.53
21.05
Br
S
H
O
B
O
O
c17
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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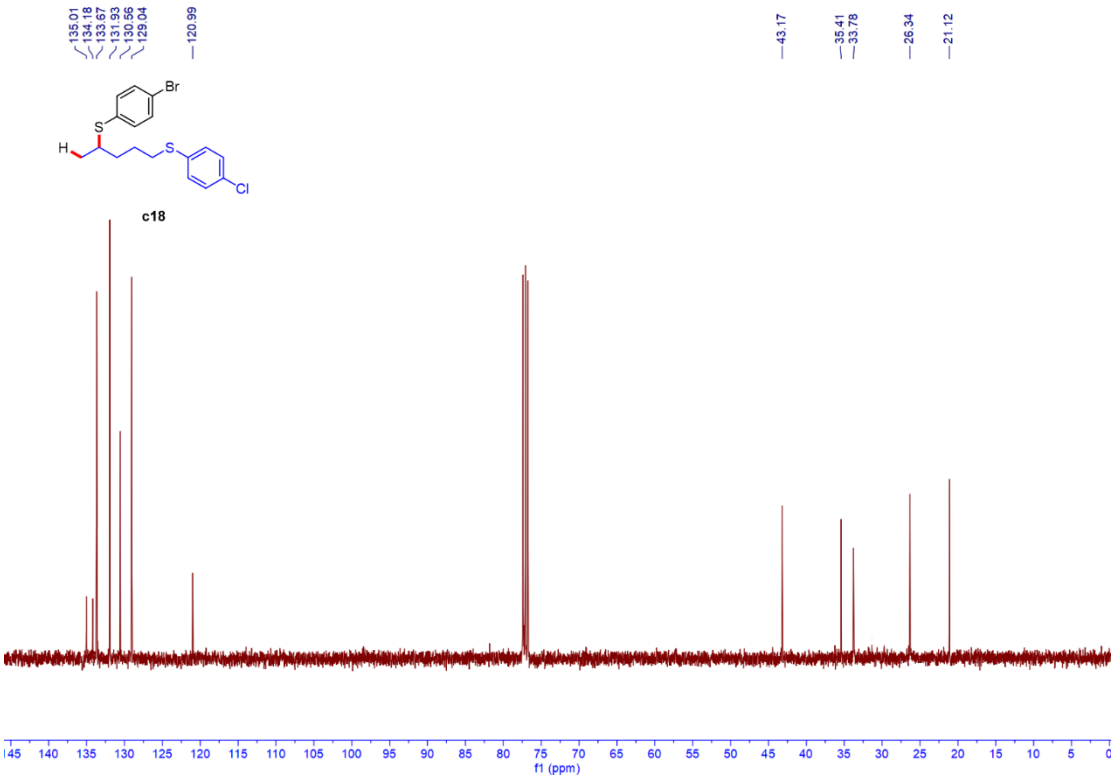
7.261
7.257
7.254
7.236
7.231
3.220
3.204
3.187
3.171
3.154
3.138
2.914
2.896
2.879
1.813
1.798
1.776
1.759
1.745
1.712
1.695
1.676
1.659
1.640
1.606
1.280
1.263
Br
S
H
S
Cl
c18
2.00
6.20
1.08
2.21
2.17
2.17
3.13
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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134.18
133.67
131.93
130.56
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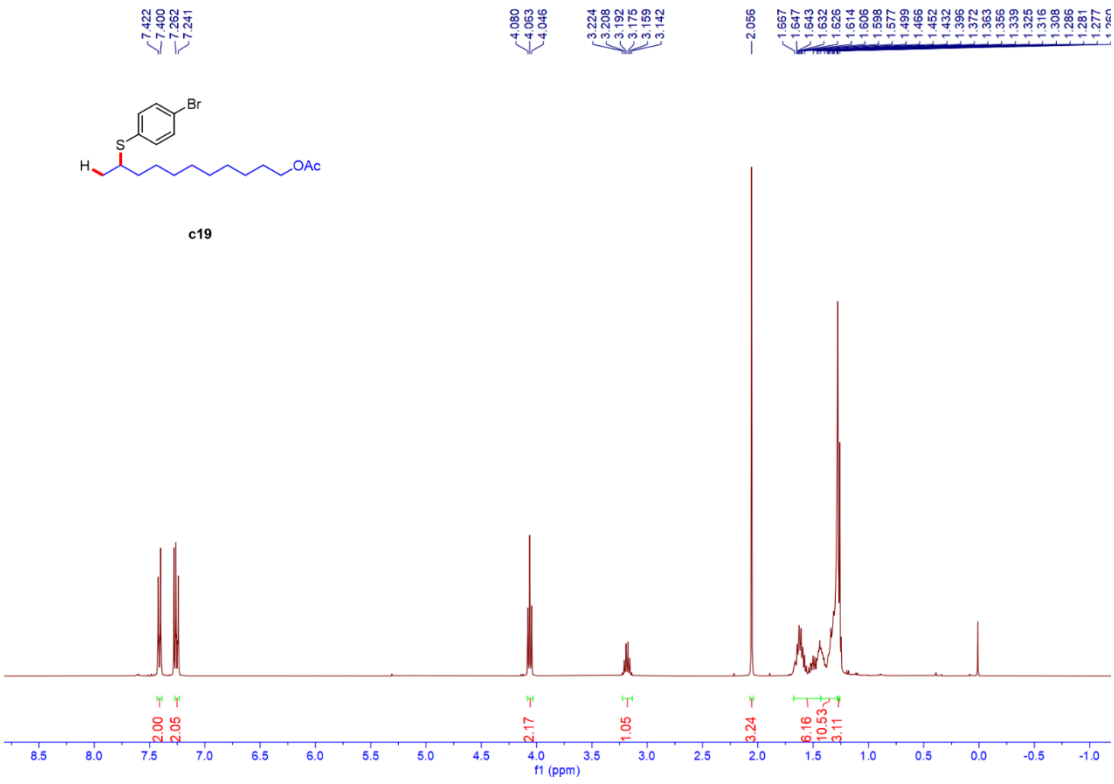
120.99
43.17
35.41
33.78
26.34
21.12
Br
S
H
S
Cl
c18
f1 (ppm)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7.262
7.241
4.080
4.063
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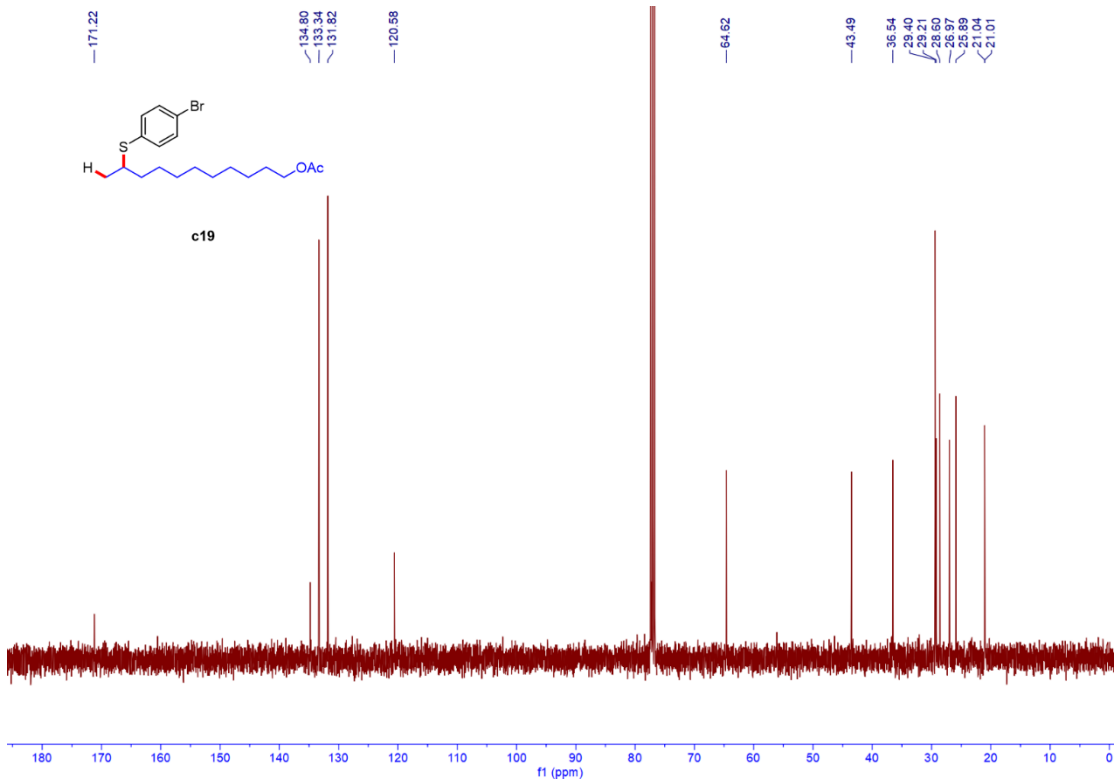
3.224
3.208
3.192
3.175
3.159
3.142
2.056
1.667
1.647
1.643
1.632
1.626
1.614
1.606
1.598
1.577
1.499
1.466
1.452
1.432
1.396
1.372
1.363
1.356
1.339
1.325
1.316
1.308
1.286
1.281
1.277
Br
S
H
OAc
c19
2.00
2.05
2.17
1.05
3.24
6.16
10.53
3.11
f1 (ppm)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131.82
120.58
64.62
43.49
36.54
29.40
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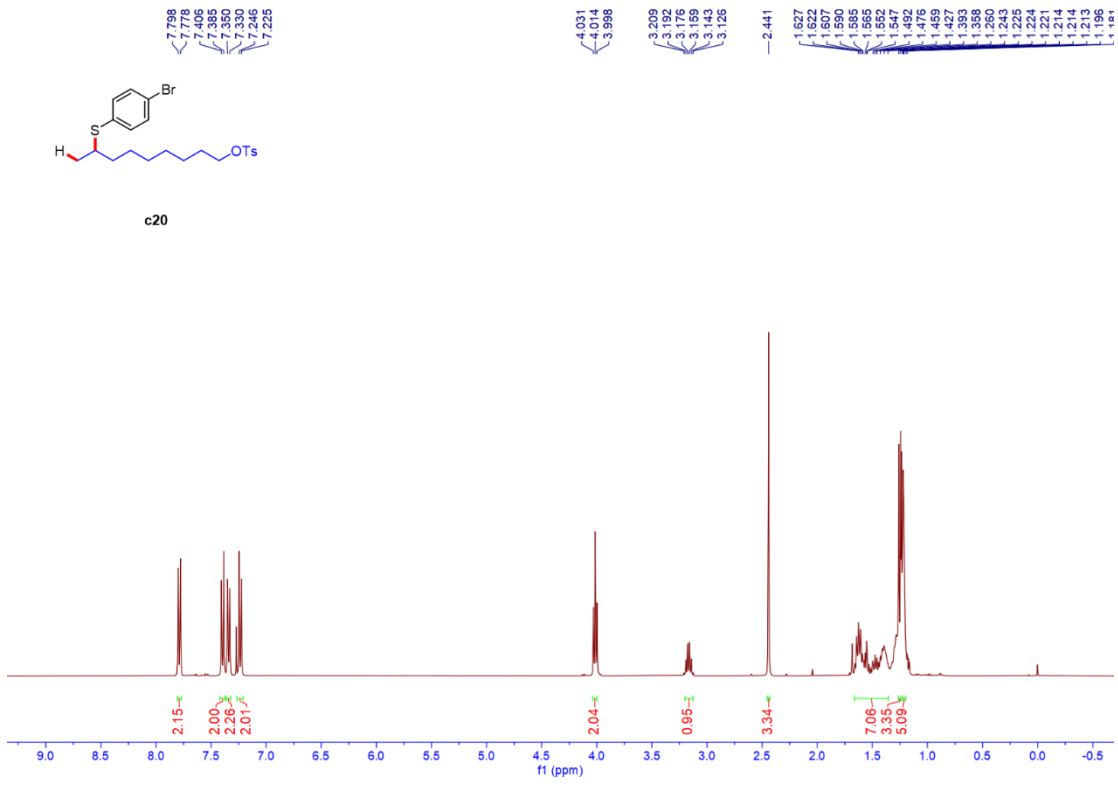
28.60
26.97
25.89
21.04
21.01
Br
S
H
OAc
c19
f1 (ppm)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4.014
3.998
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3.192
3.176
3.159
3.143
3.126
2.441
1.627
1.622
1.607
1.590
1.585
1.565
1.552
1.547
1.492
1.476
1.459
1.427
1.393
1.358
1.260
1.243
1.225
1.224
1.221
1.214
1.214
1.213
1.196
Br
S
H
OTs
c20
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2.00
2.28
2.01
2.04
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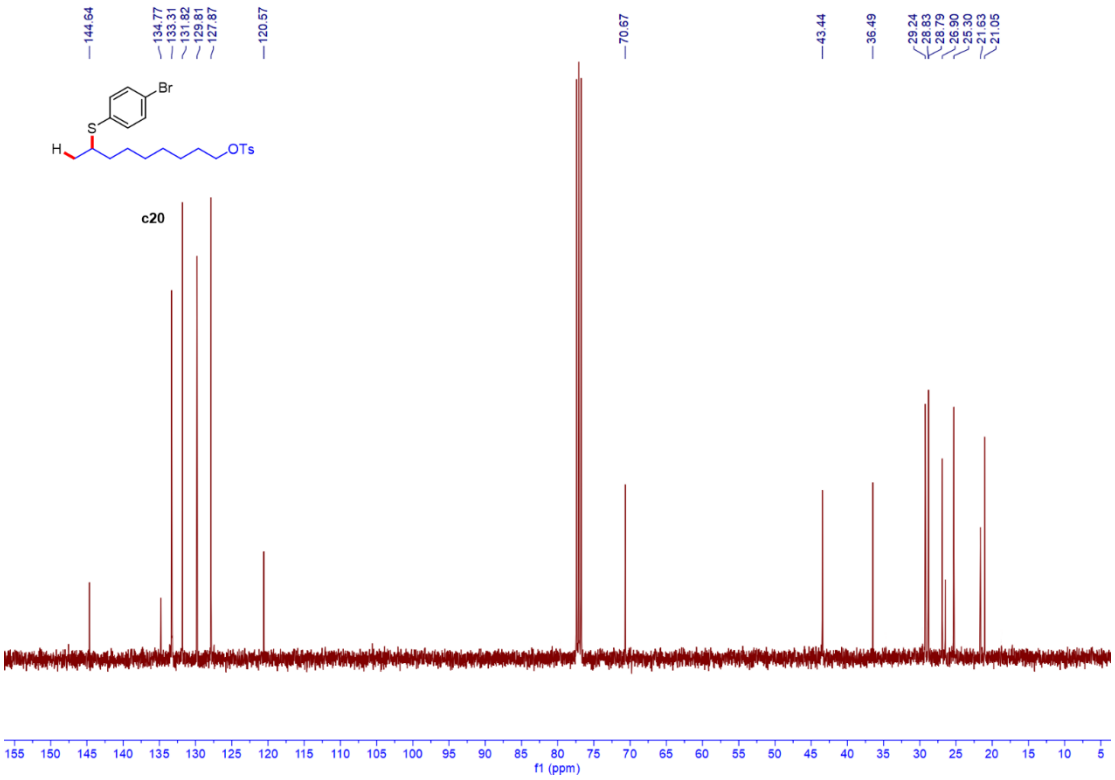
3.34
7.06
3.35
5.09
f1 (ppm)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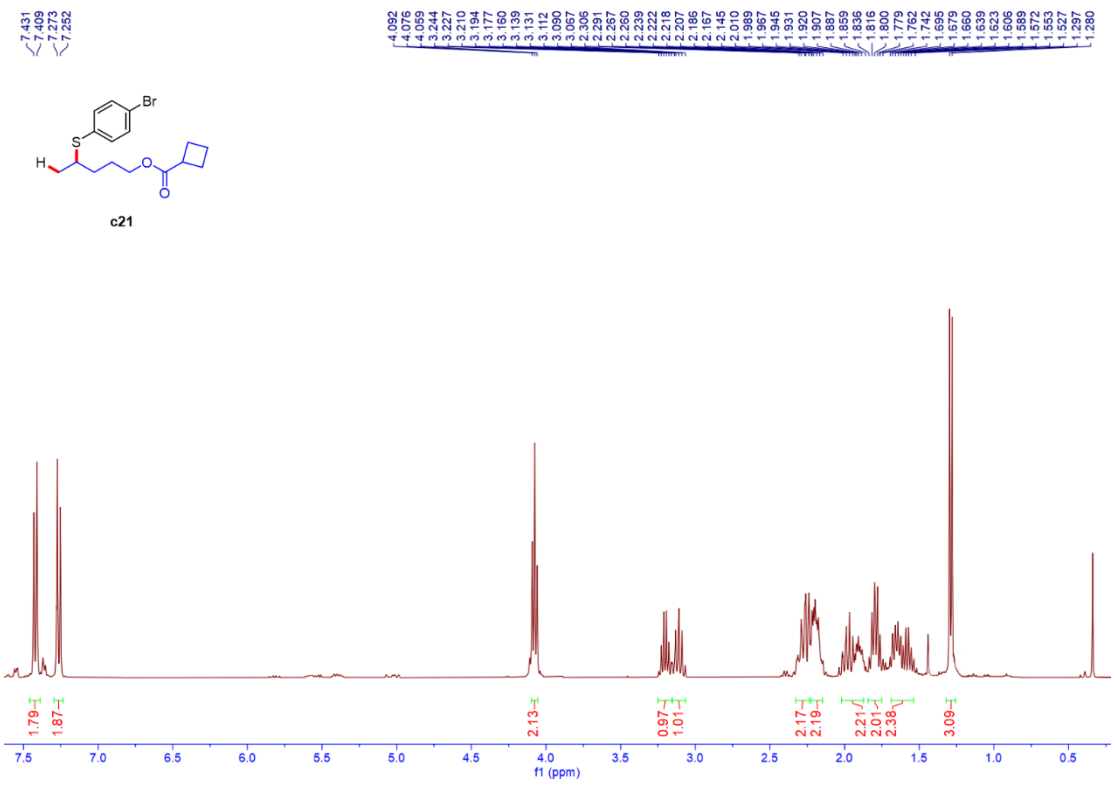
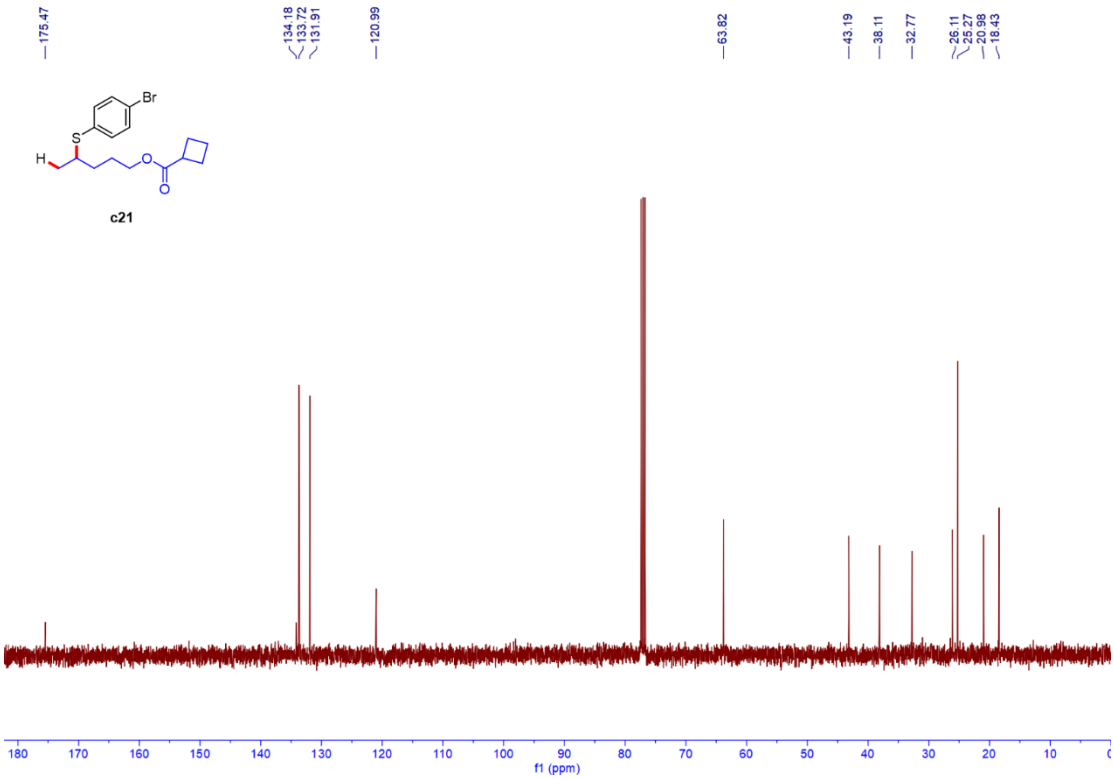
129.81
127.87
120.57
70.67
43.44
36.49
29.24
28.83
28.79
26.90
25.50
21.63
21.05
Br
S
H
OTs
c20
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)


7.431
7.409
7.273
7.252
Br
S
H
O
O
c21
1.79
1.87
2.13
0.97
1.01
2.17
2.19
2.21
2.01
2.38
3.09
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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131.91
120.99
63.82
43.19
38.11
32.77
26.11
25.27
20.58
18.43
Br
S
H
O
O
c21
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140
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120
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80
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50
40
30
20
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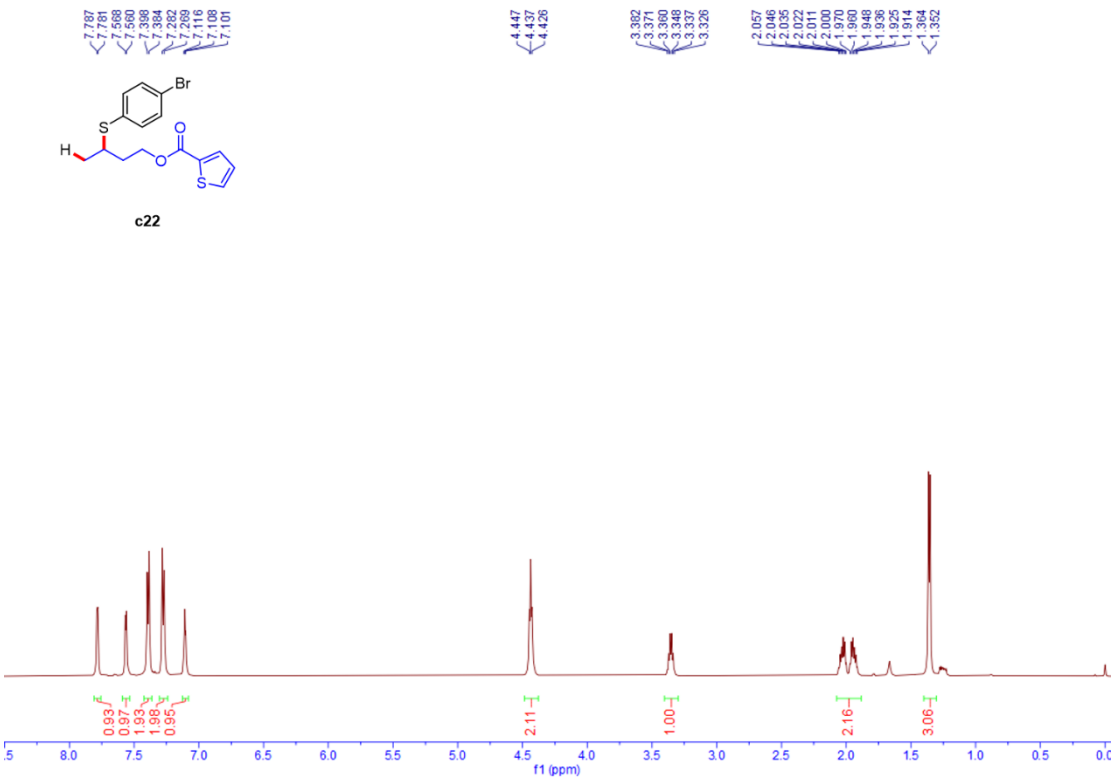
f1 (ppm)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7.269
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7.108
7.101
4.447
4.437
4.426
3.382
3.371
3.360
3.348
3.337
3.326
2.057
2.046
2.035
2.022
2.011
2.000
1.970
1.960
1.948
1.936
1.925
1.914
1.364
1.352
Br
S
H
O
O
S
c22
0.93
0.97
1.93
1.98
0.95
2.11
1.00
2.16
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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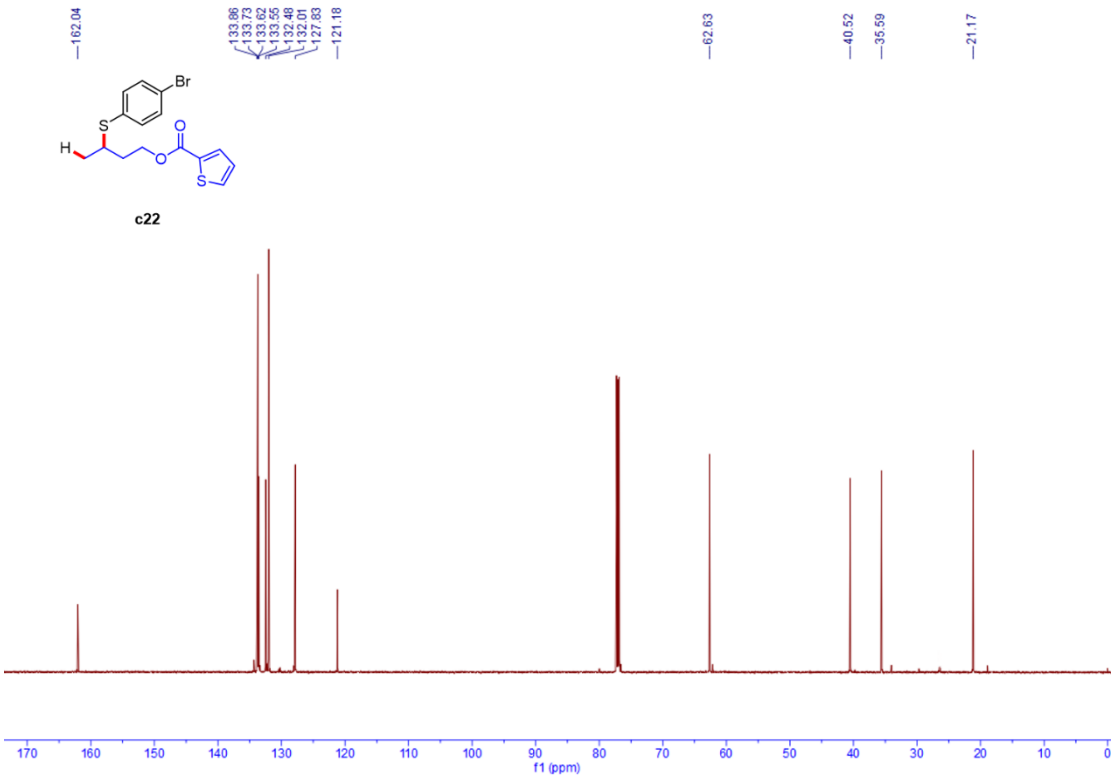
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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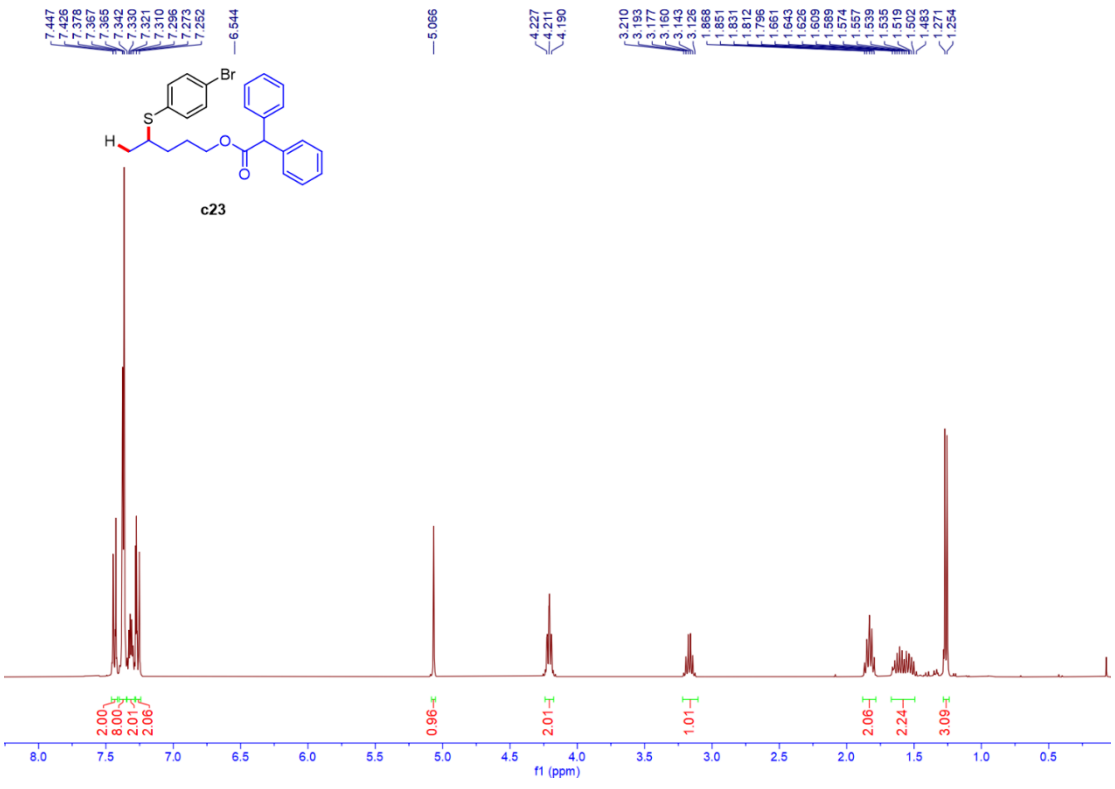
133.86
133.73
133.62
133.55
132.48
132.01
127.83
121.18
62.63
40.52
35.59
21.17
Br
S
H
O
O
S
c22
f1 (ppm)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7.378
7.367
7.365
7.342
7.330
7.321
7.310
7.296
7.273
7.252
6.544
5.066
4.227
4.211
4.190
3.210
3.193
3.177
3.160
3.143
3.126
1.868
1.851
1.831
1.812
1.796
1.661
1.643
1.626
1.609
1.589
1.574
1.557
1.539
1.535
1.519
1.503
1.483
1.271
1.254
Br
S
H
O
O
c23
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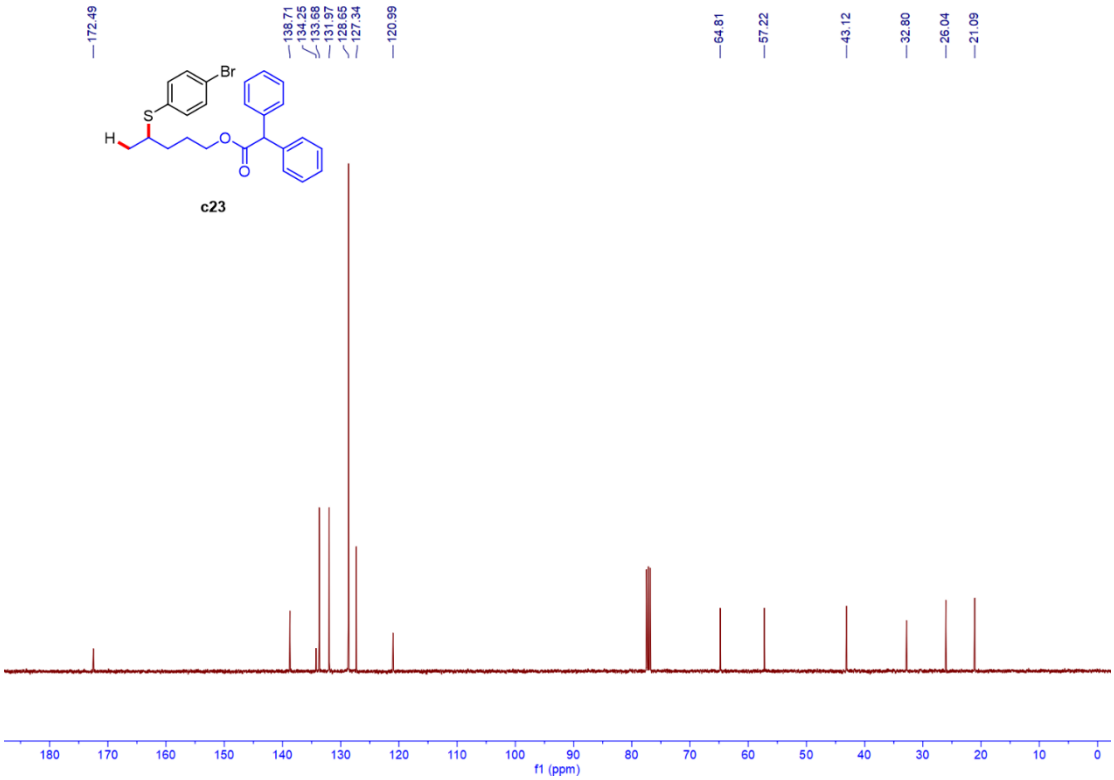
2.01
2.06
0.96
2.01
1.01
2.06
2.24
3.09
f1 (ppm)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138.71
134.25
133.68
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128.65
127.34
120.99
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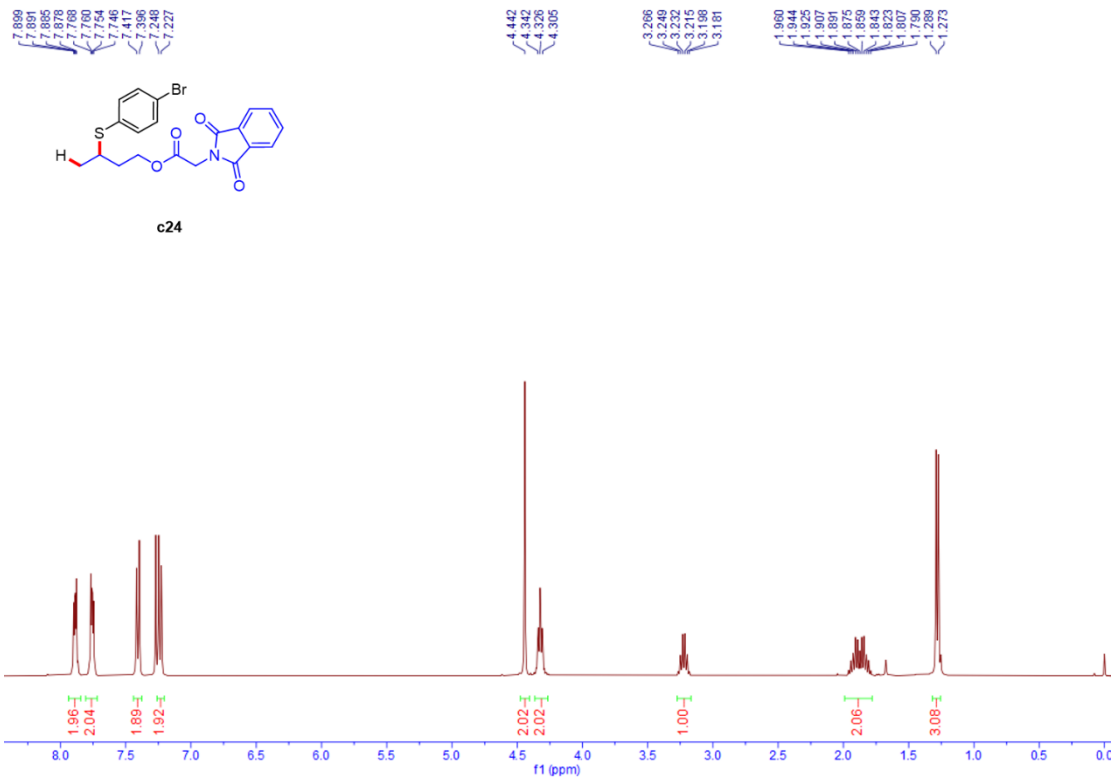
43.12
32.80
26.04
21.09
Br
S
H
O
O
c23
f1 (ppm)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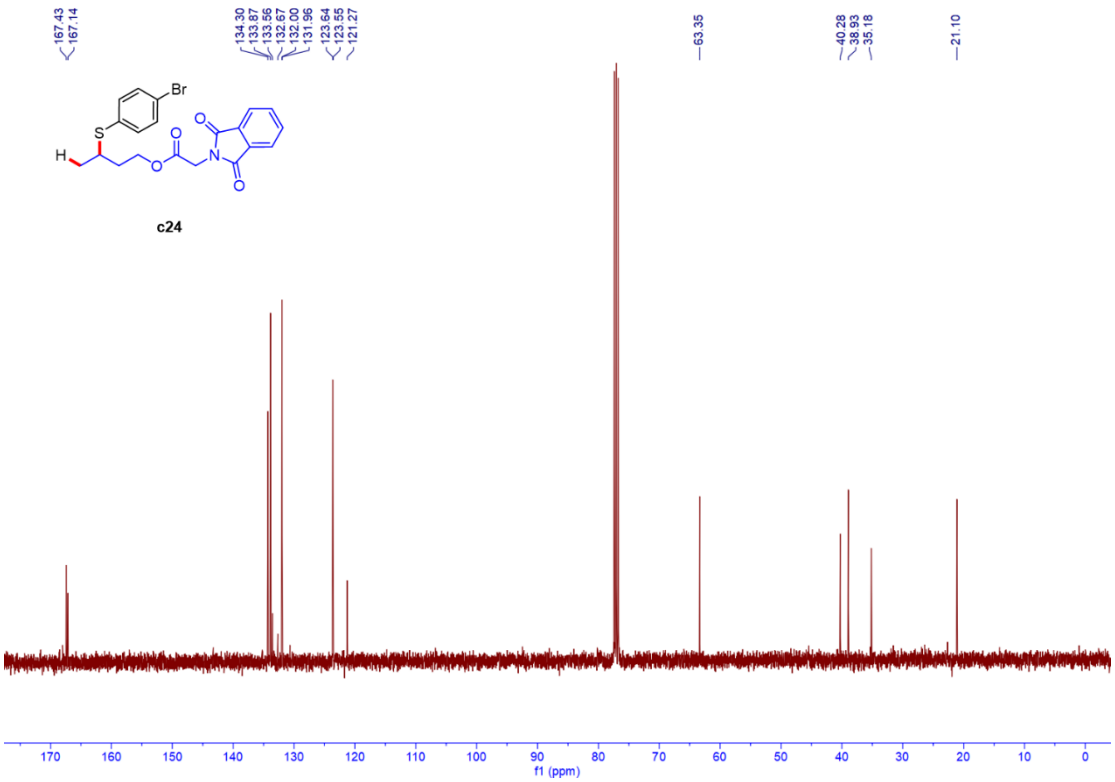
7.768
7.760
7.754
7.746
7.417
7.396
7.248
7.227
4.442
4.342
4.326
4.305
3.266
3.249
3.232
3.215
3.198
3.181
1.960
1.944
1.925
1.907
1.891
1.875
1.859
1.843
1.823
1.807
1.790
1.289
1.273
Br
S
H
O
O
N
O
c24
1.96
2.04
1.89
1.92
2.02
2.02
1.00
2.06
3.08
f1 (ppm)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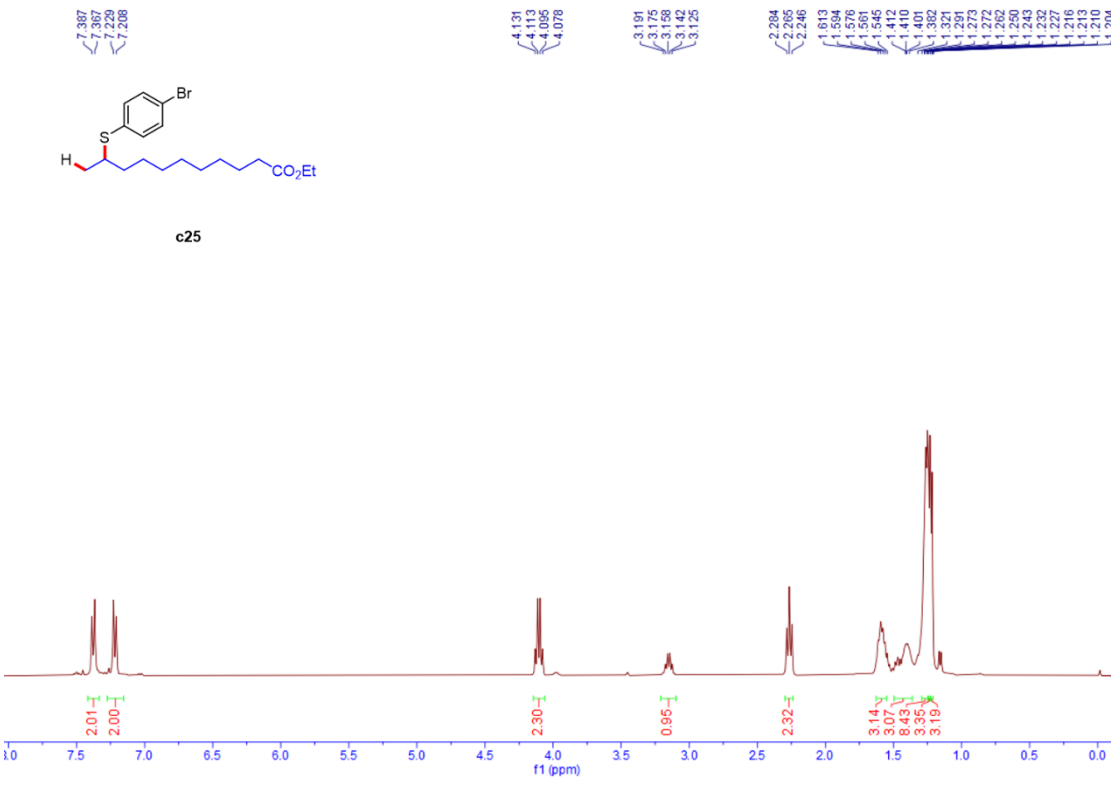
167.14
134.30
133.87
133.56
132.67
132.00
131.96
123.64
123.55
121.27
63.35
40.28
38.93
35.18
21.10
Br
S
H
O
O
O
N
O
f1 (ppm)

c24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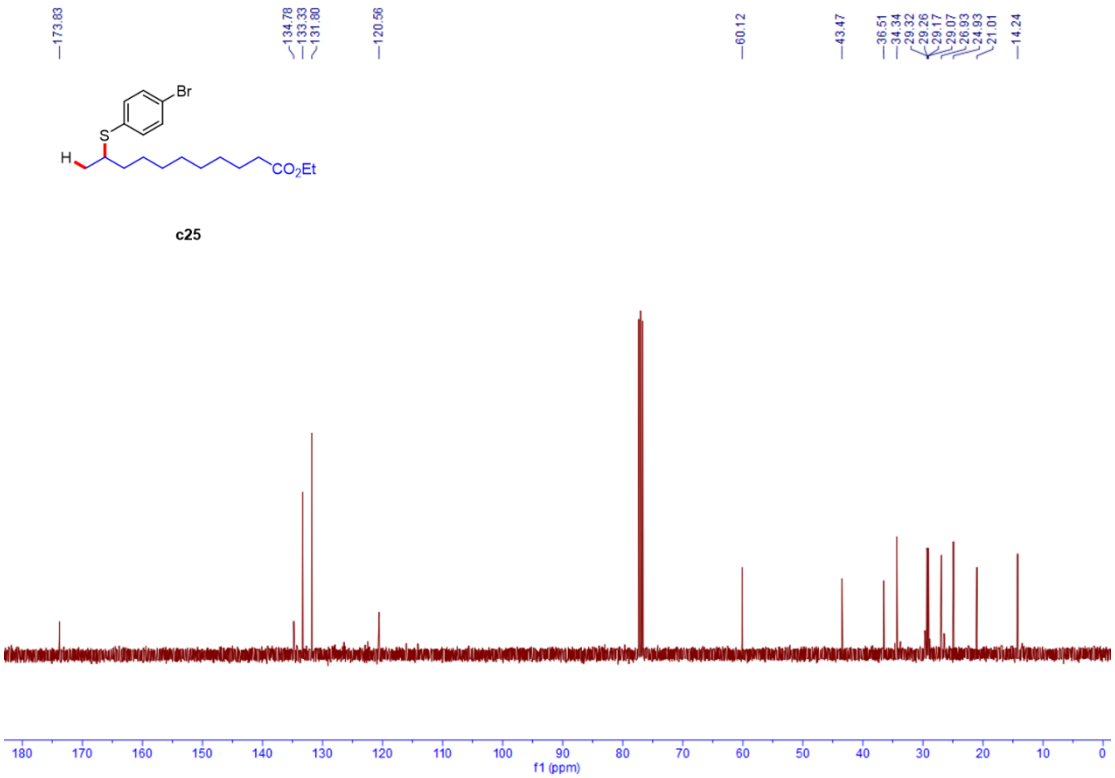
7.229
7.208
4.131
4.113
4.095
4.078
3.191
3.175
3.158
3.142
3.125
2.284
2.265
2.246
1.613
1.594
1.576
1.561
1.545
1.412
1.410
1.401
1.382
1.321
1.291
1.273
1.272
1.262
1.250
1.243
1.232
1.227
1.216
1.213
1.210
Br
S
H
CO2Et
2.01
2.00
2.30
0.95
2.32
3.14
3.07
8.43
3.35
3.19
f1 (ppm)

c25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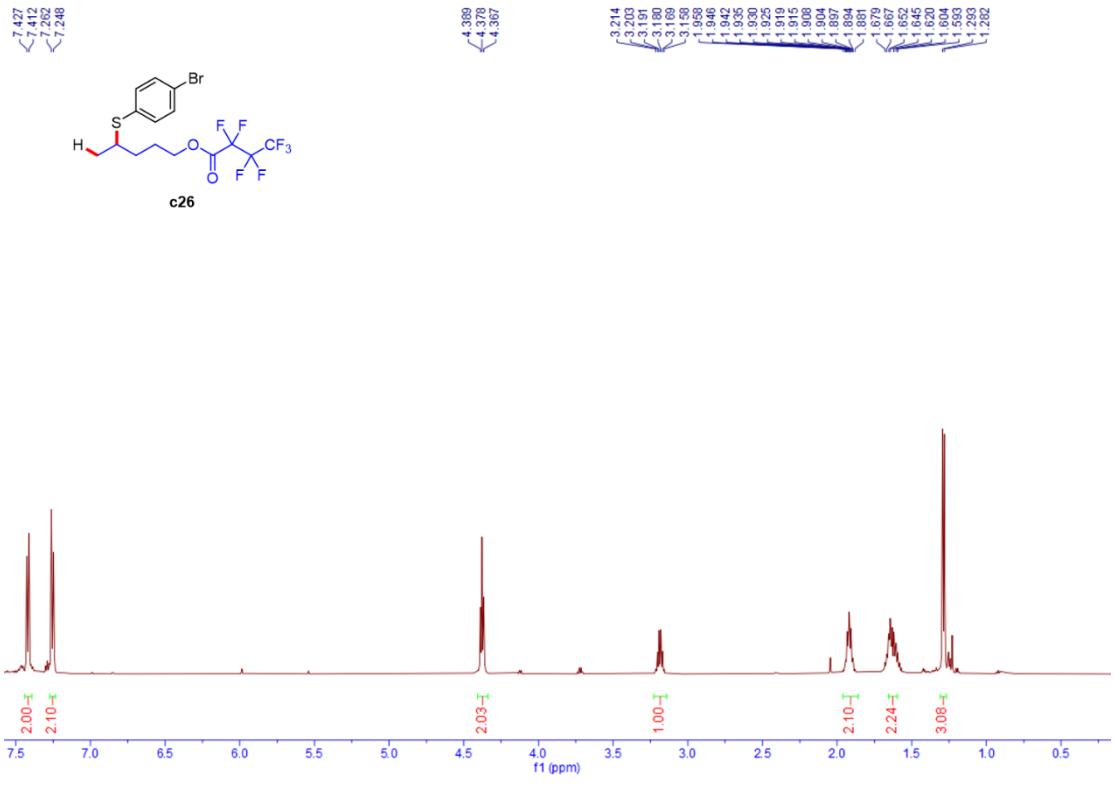
134.78
133.33
131.80
120.56
60.12
43.47
36.51
34.34
29.32
29.26
29.17
29.07
26.93
24.93
21.01
14.24
Br
S
H
CO2Et
c25
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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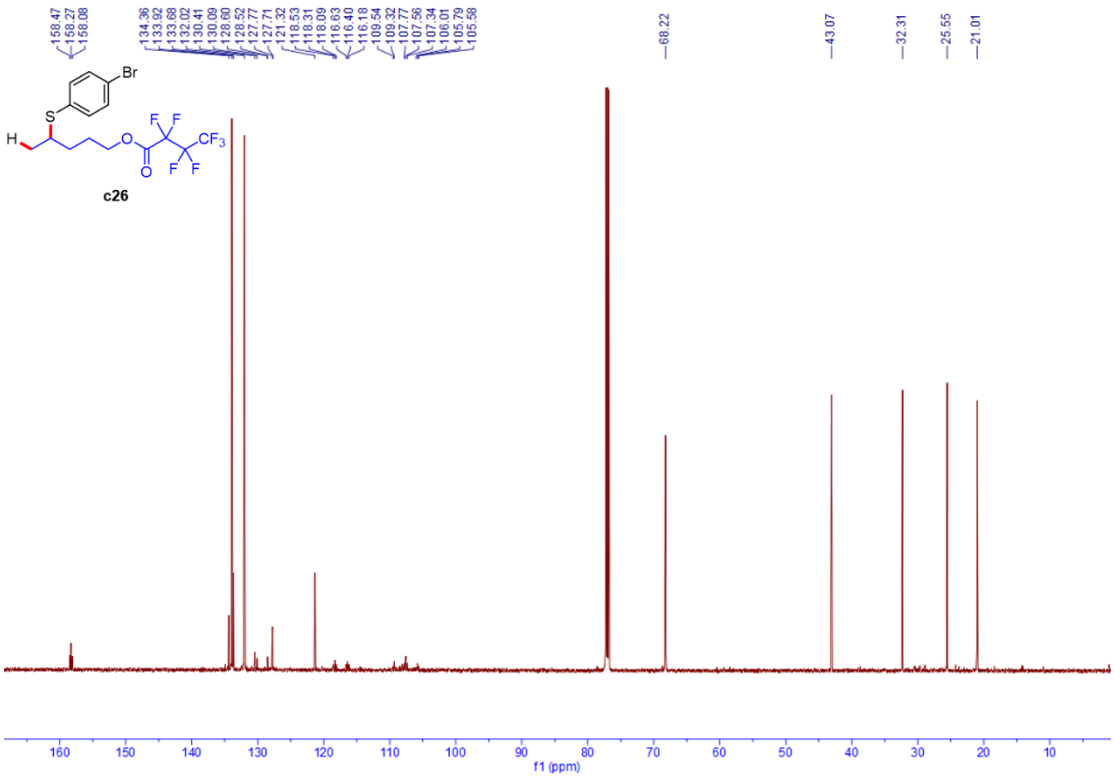
4.378
4.367
3.214
3.203
3.191
3.180
3.169
3.158
1.958
1.946
1.942
1.935
1.930
1.925
1.919
1.915
1.908
1.904
1.897
1.894
1.881
1.679
1.667
1.652
1.645
1.620
1.604
1.593
1.293
1.262
Br
S
H
O
F
F
CF3
F
F
c26
2.00
2.10
2.03
1.00
2.10
2.24
3.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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158.27
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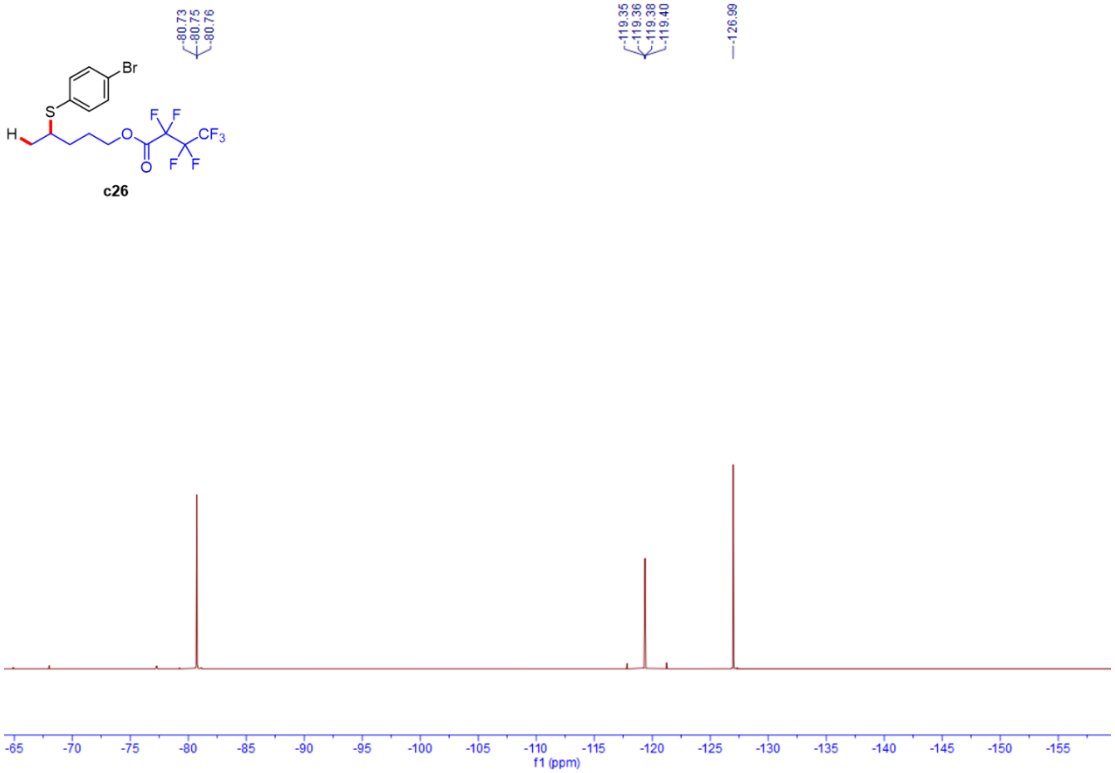
133.68
132.02
130.41
130.09
130.00
128.62
127.77
127.71
121.32
118.53
118.31
118.09
116.63
116.40
116.18
109.54
109.32
107.77
107.56
107.34
106.01
105.79
105.58
68.22
43.07
32.31
25.55
21.01
Br
S
H
O
F F
CF3
F F
O
c26
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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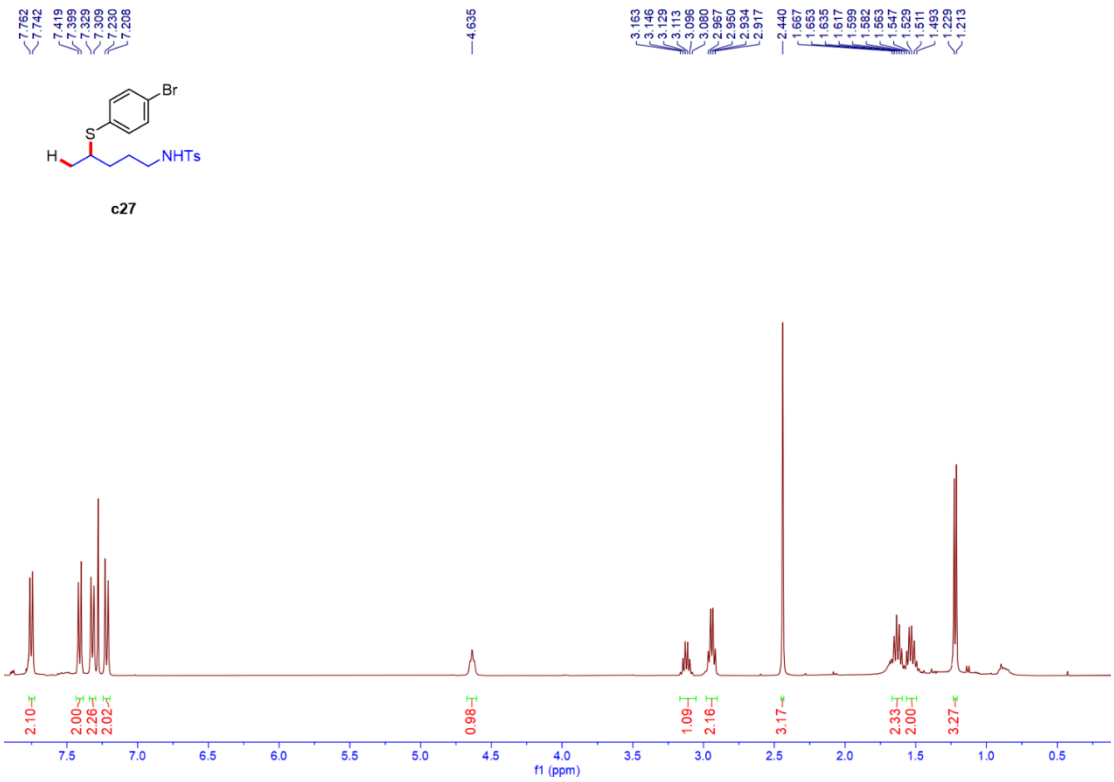
80.75
80.76
119.35
119.36
119.38
119.40
126.99
Br
S
H
O
F F
CF3
F F
O
c26
-65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155
f1 (ppm)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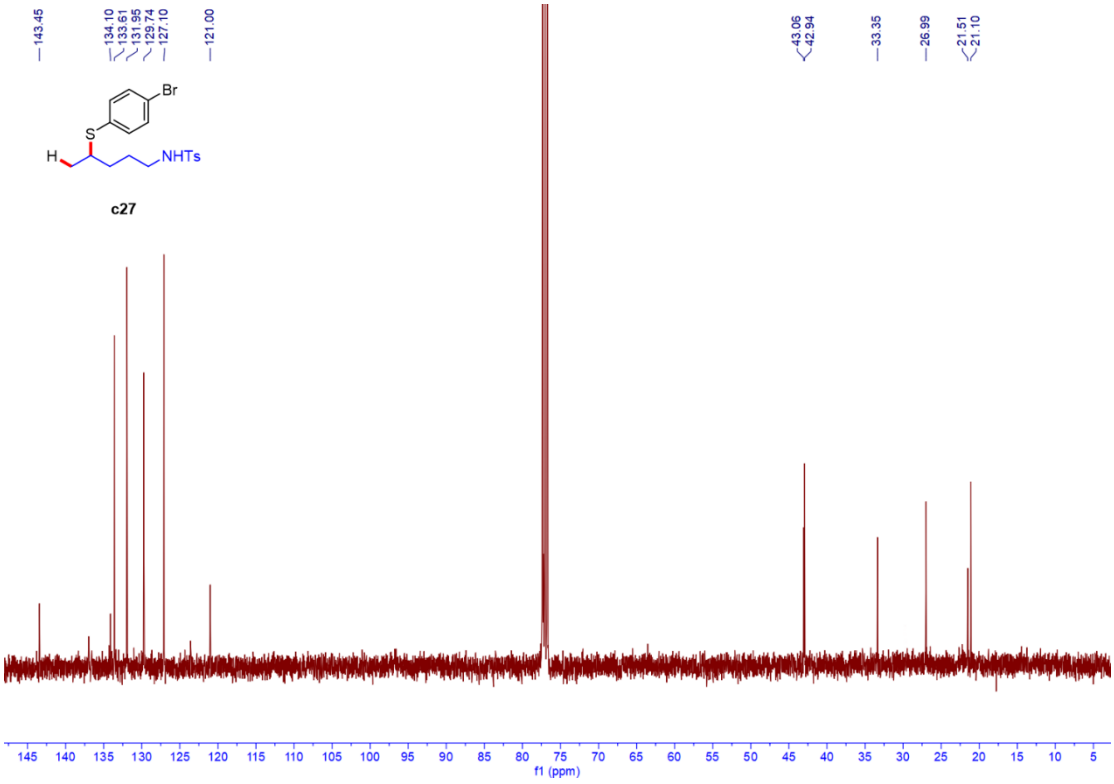
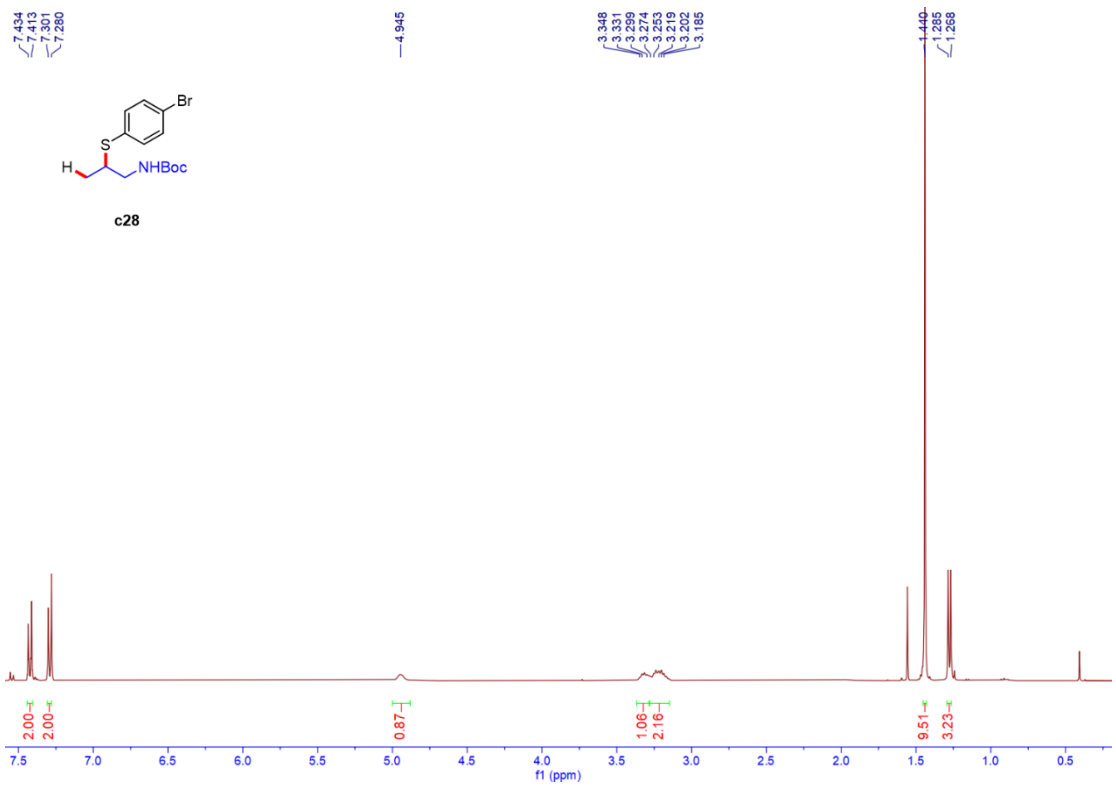
7.309
7.230
7.208
4.635
3.163
3.146
3.129
3.113
3.096
3.080
2.967
2.950
2.934
2.917
2.440
1.667
1.653
1.635
1.617
1.599
1.582
1.563
1.547
1.529
1.511
1.493
1.229
1.213
Br
S
H
NHTs
c27
2.10
2.00
2.26
2.02
0.98
1.09
2.16
3.17
2.33
2.00
3.27
f1 (ppm)


143.45
134.10
133.61
131.95
129.74
127.10
121.00
43.06
42.94
33.35
26.99
21.51
21.10
Br
S
H
NHTs
c27
f1 (ppm)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7.301
7.280
4.945
3.348
3.331
3.299
3.274
3.253
3.219
3.202
3.185
1.440
1.285
1.268
Br
S
H
NHBoc
c28
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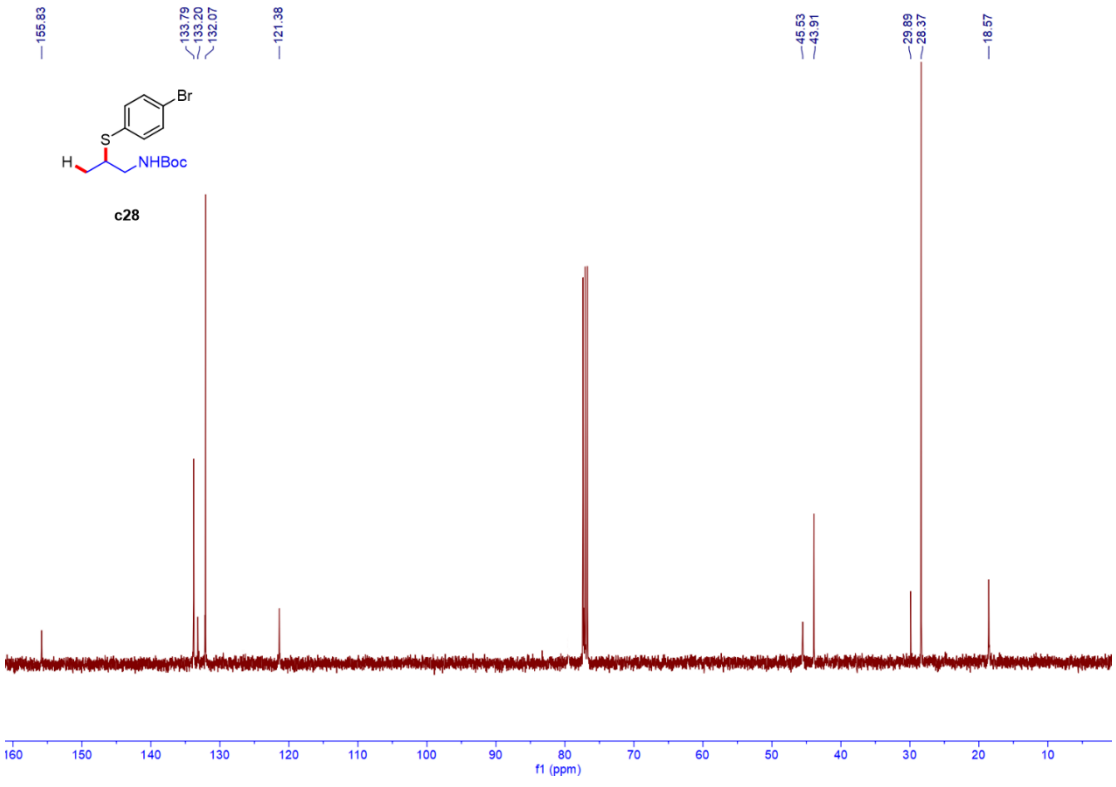
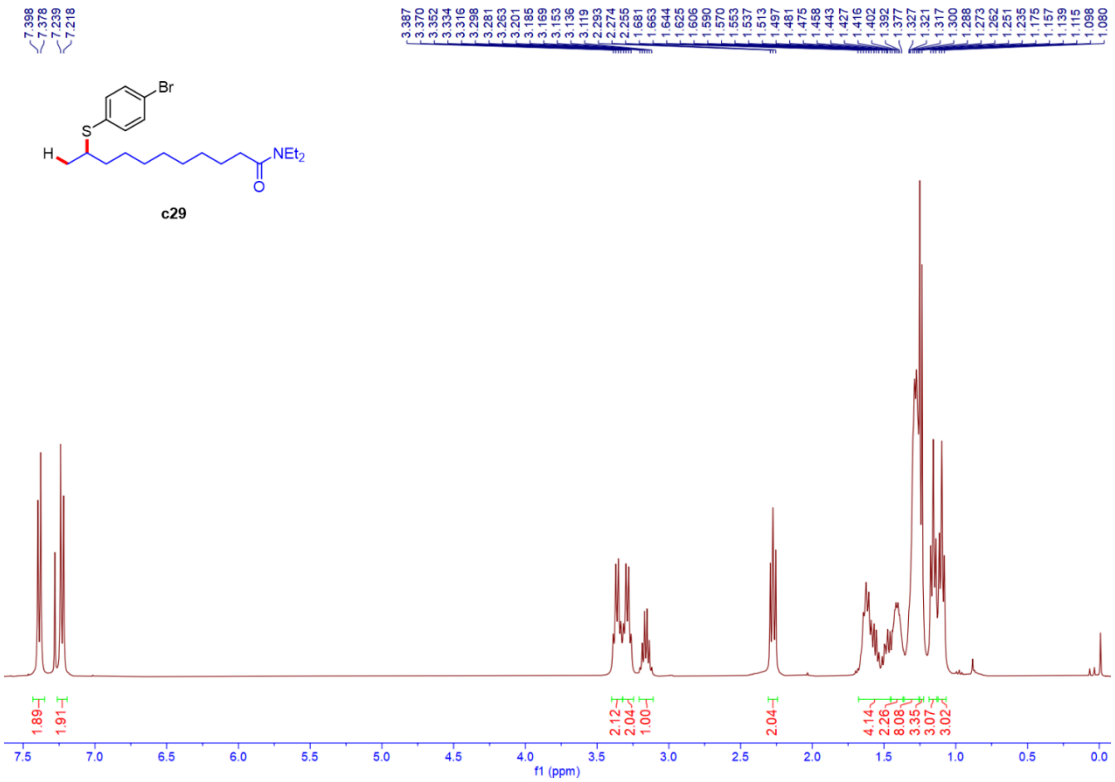
2.00
0.87
1.06
2.16
9.51
3.23
f1 (ppm)


155.83
133.79
133.20
132.07
121.38
45.53
43.91
29.89
28.37
18.57
Br
S
H
NHBoc
c28
f1 (ppm)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3.298
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3.263
3.201
3.185
3.169
3.153
3.136
3.119
2.293
2.274
2.255
1.681
1.663
1.644
1.625
1.606
1.590
1.570
1.553
1.537
1.513
1.497
1.481
1.475
1.458
1.443
1.427
1.416
1.402
1.392
1.377
1.327
1.311
1.300
1.288
1.273
1.262
1.251
1.235
1.175
1.157
1.139
1.115
1.098
1.080
Br
S
H
NEt2
O
c29
1.89
1.91
2.12
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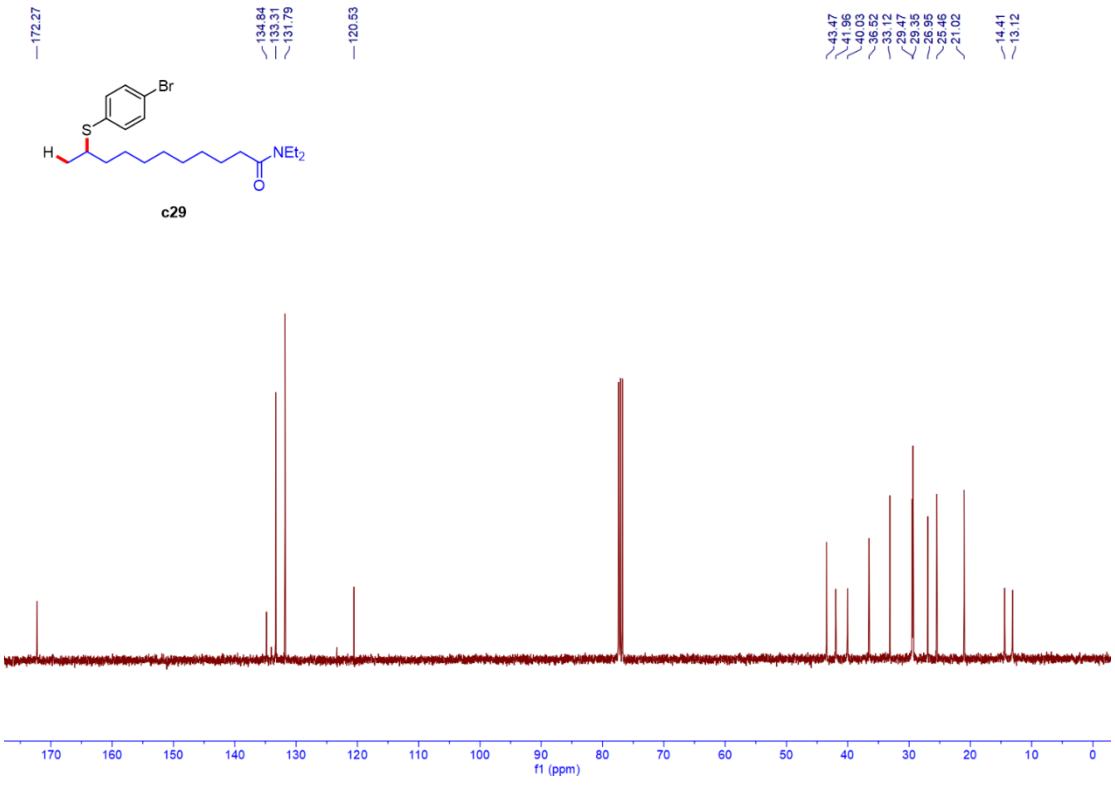
1.00
2.04
4.14
2.26
8.08
3.35
3.07
3.02
f1 (ppm)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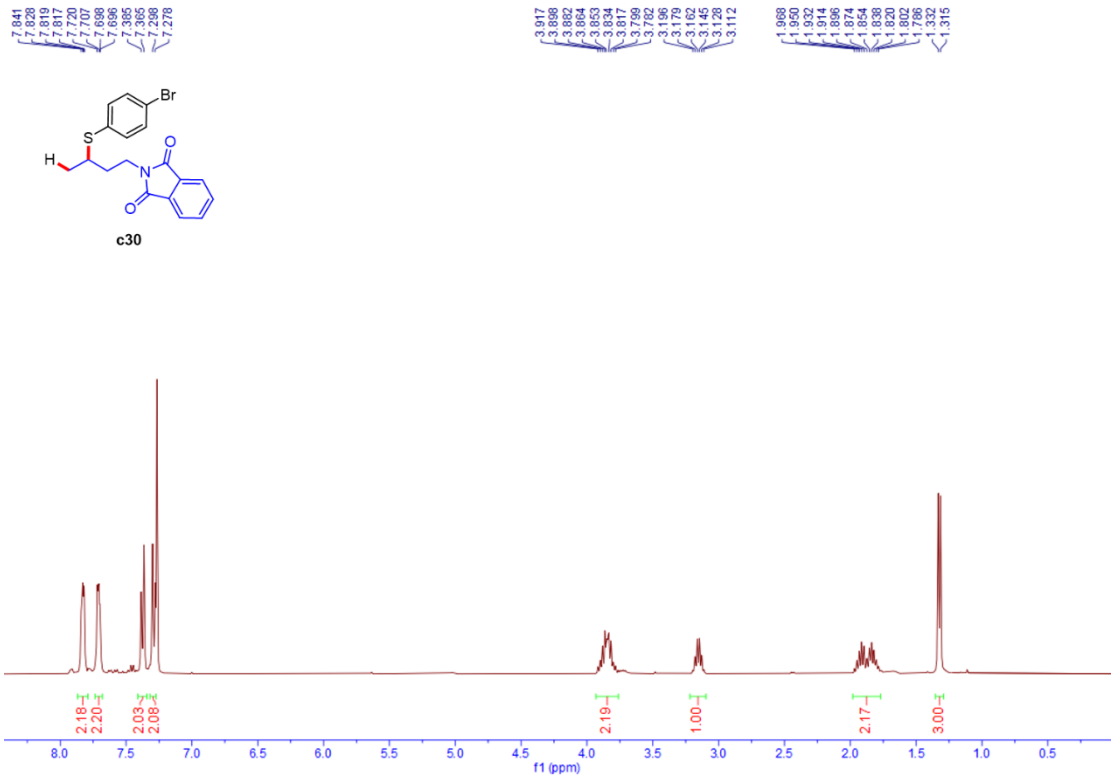
40.03
36.52
33.12
29.47
29.35
26.95
25.46
21.02
14.41
13.12
Br
S
H
NEt2
O
c29
f1 (ppm)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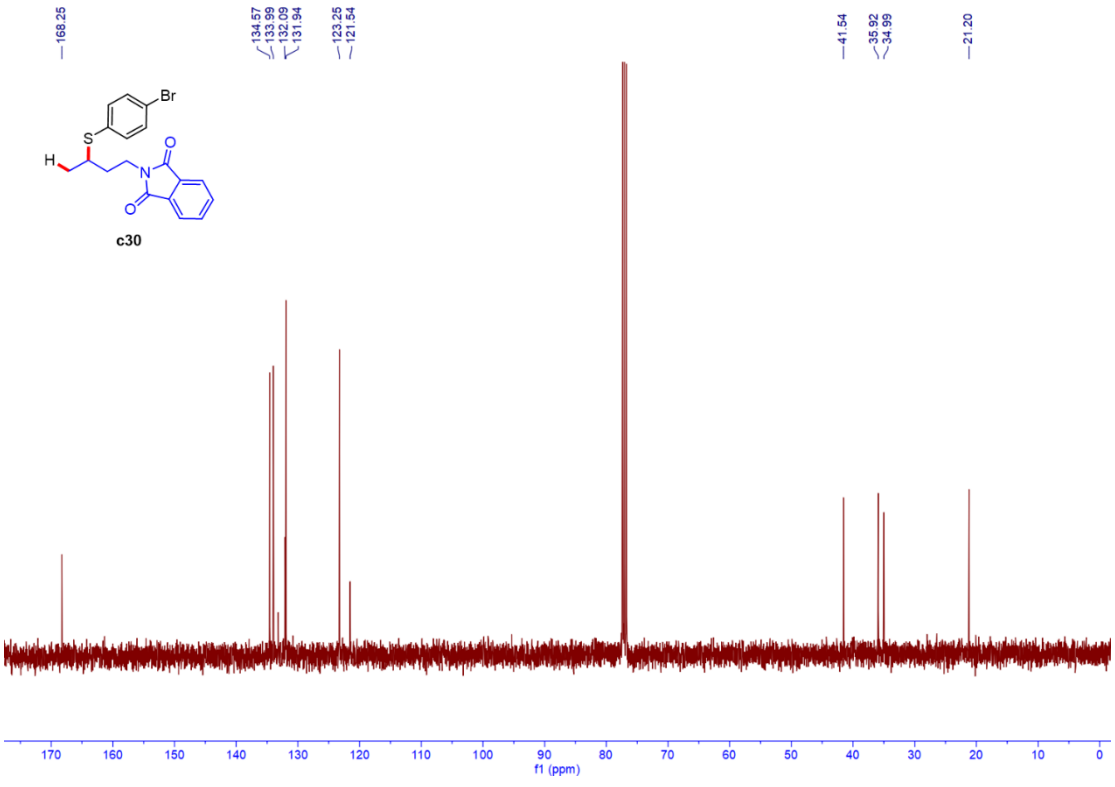
7.819
7.817
7.720
7.707
7.698
7.696
7.385
7.365
7.298
7.278
3.917
3.898
3.882
3.864
3.853
3.834
3.817
3.799
3.782
3.196
3.179
3.162
3.145
3.128
3.112
1.968
1.950
1.932
1.914
1.896
1.874
1.854
1.838
1.820
1.802
1.786
1.332
1.315
Br
S
H
N
O
O
c30
2.18
2.20
2.03
2.08
2.19
1.00
2.17
3.00
f1 (ppm)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41.54
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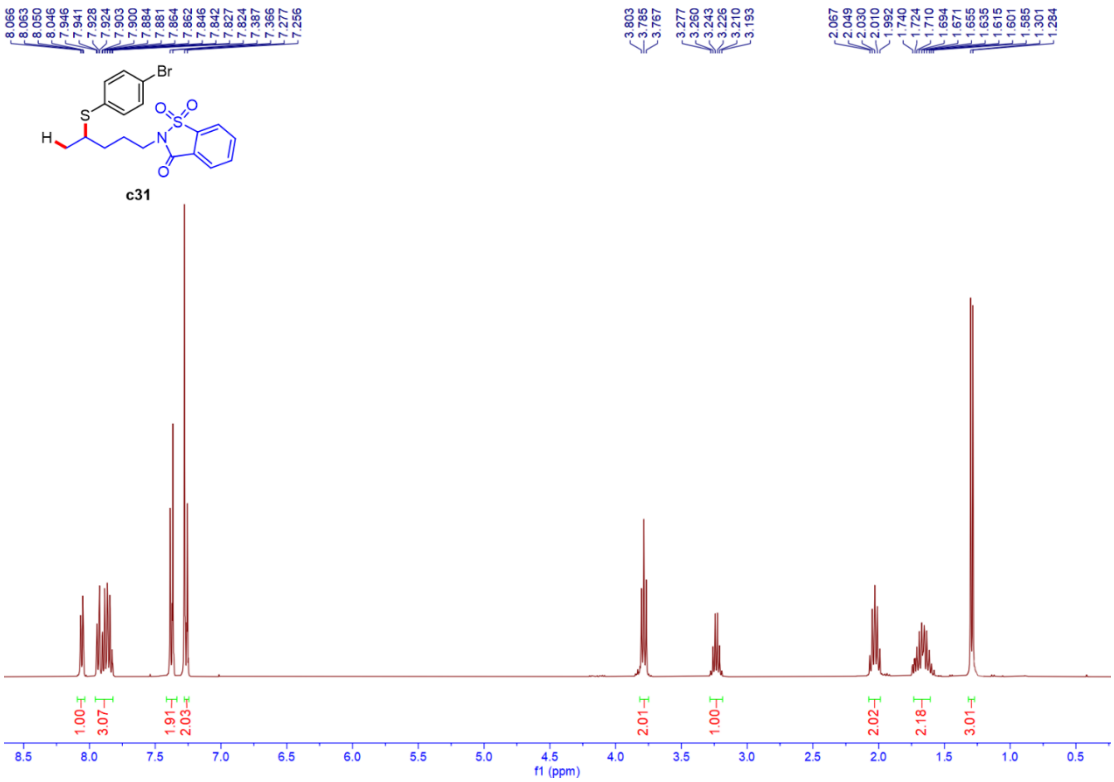
34.99
21.20
Br
S
H
N
O
O
c30
f1 (ppm)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7.924
7.903
7.900
7.884
7.881
7.864
7.862
7.846
7.842
7.827
7.824
7.387
7.366
7.277
7.256
3.803
3.785
3.767
3.277
3.260
3.243
3.226
3.210
3.193
2.067
2.049
2.030
2.010
1.992
1.740
1.724
1.710
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1.671
1.655
1.635
1.615
1.601
1.585
1.301
1.284
Br
S
H
O
O
S
N
O
c31
1.00
3.07
1.91
2.03
2.01
1.00
2.02
2.18
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
2.5
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1.5
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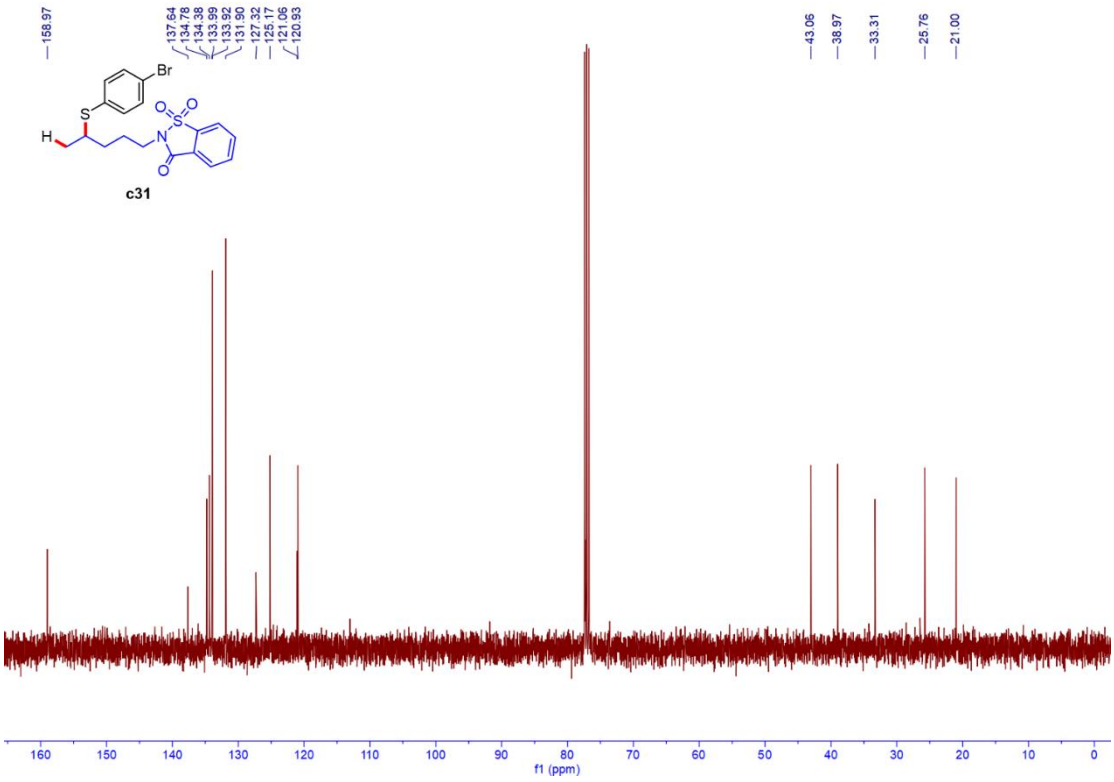
0.5
f1 (ppm)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131.90
127.32
125.17
121.06
120.93
43.06
38.97
33.31
25.76
21.00
Br
S
H
O
O
S
N
O
c31
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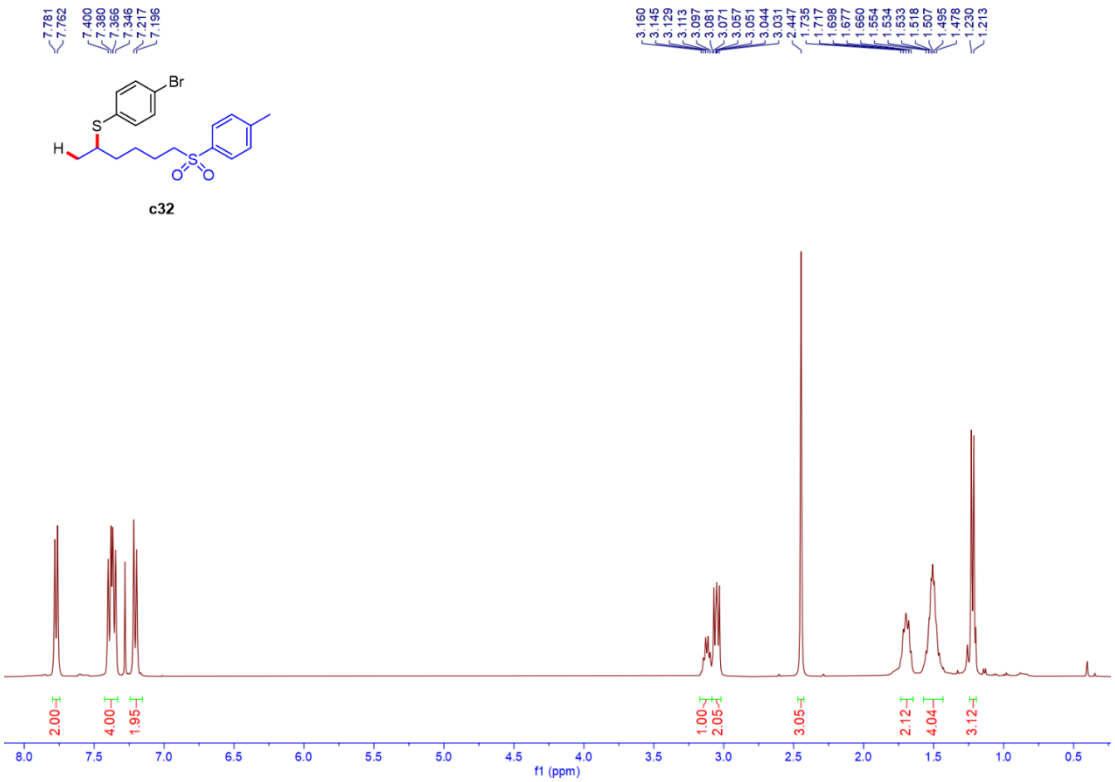
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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3.113
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3.081
3.071
3.057
3.051
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3.031
2.447
1.735
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1.554
1.534
1.533
1.518
1.507
1.495
1.478
1.230
1.213
Br
S
H
O
O
c32
2.00
4.00
1.95
1.00
2.05
3.05
2.12
4.04
3.12
8.0
7.5
7.0
6.5
6.0
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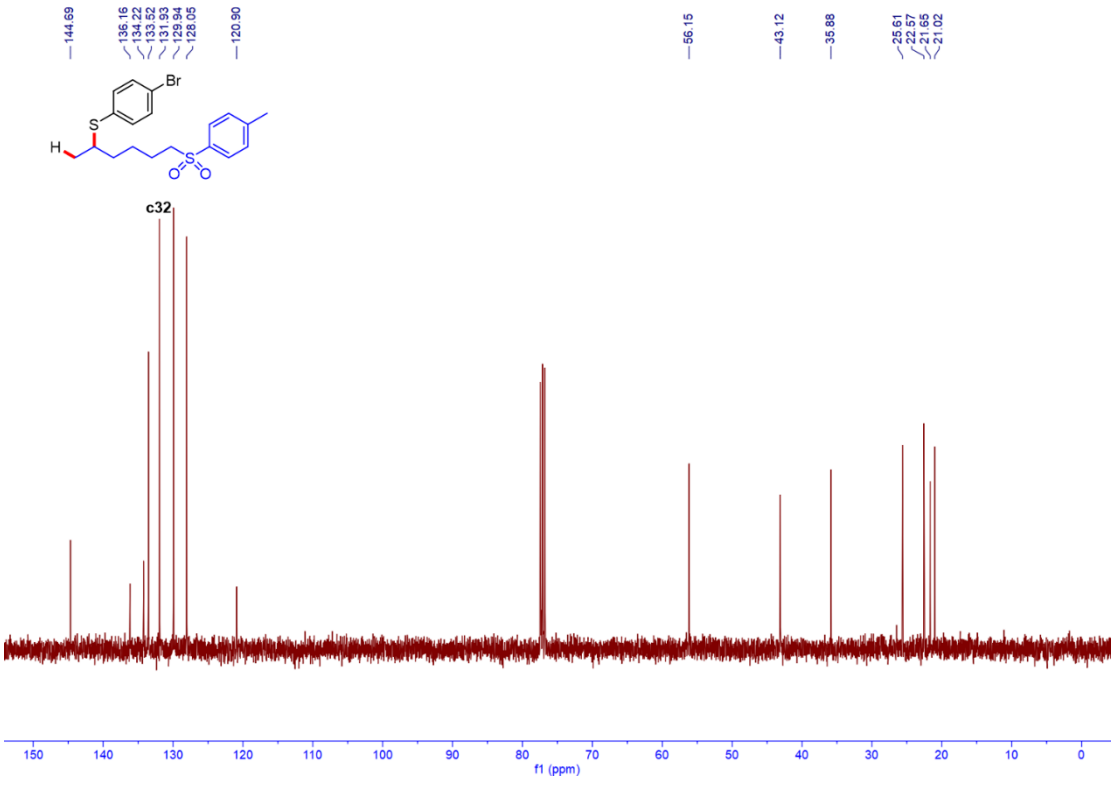
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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131.93
129.94
128.05
120.90
56.15
43.12
35.88
25.61
22.57
21.65
21.02
Br
S
H
O
O
c32
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130
120
110
100
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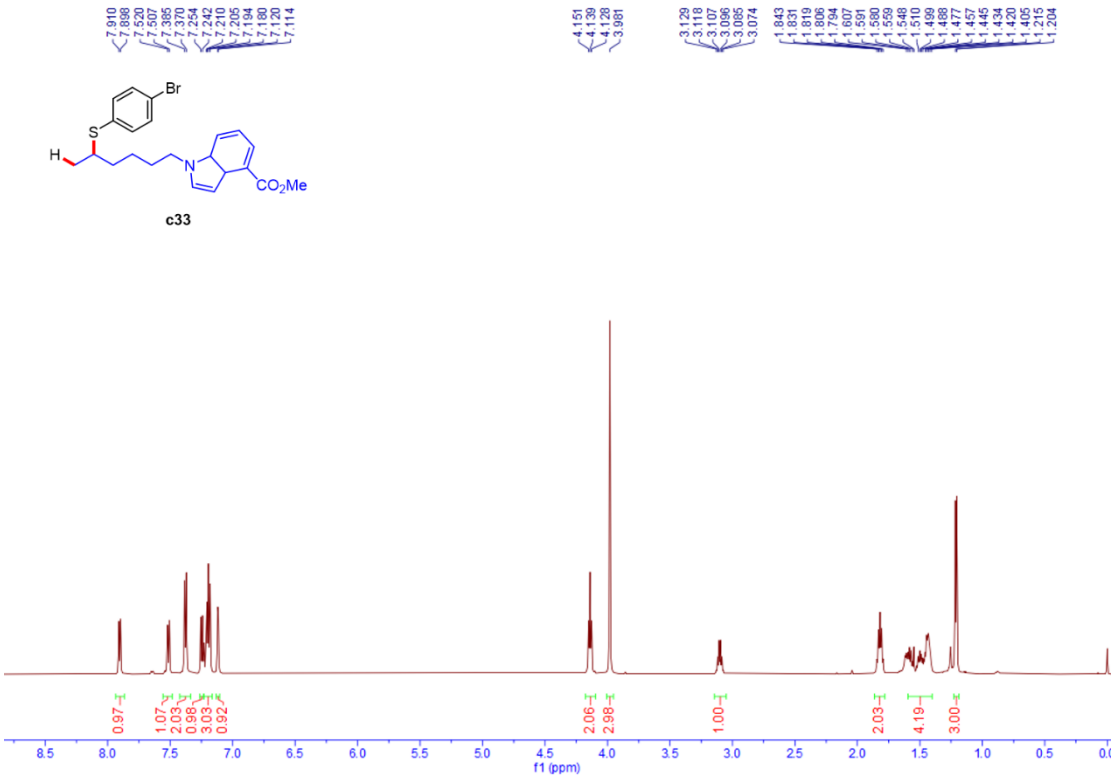
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.114
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4.139
4.128
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3.129
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3.107
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3.085
3.074
1.843
1.831
1.819
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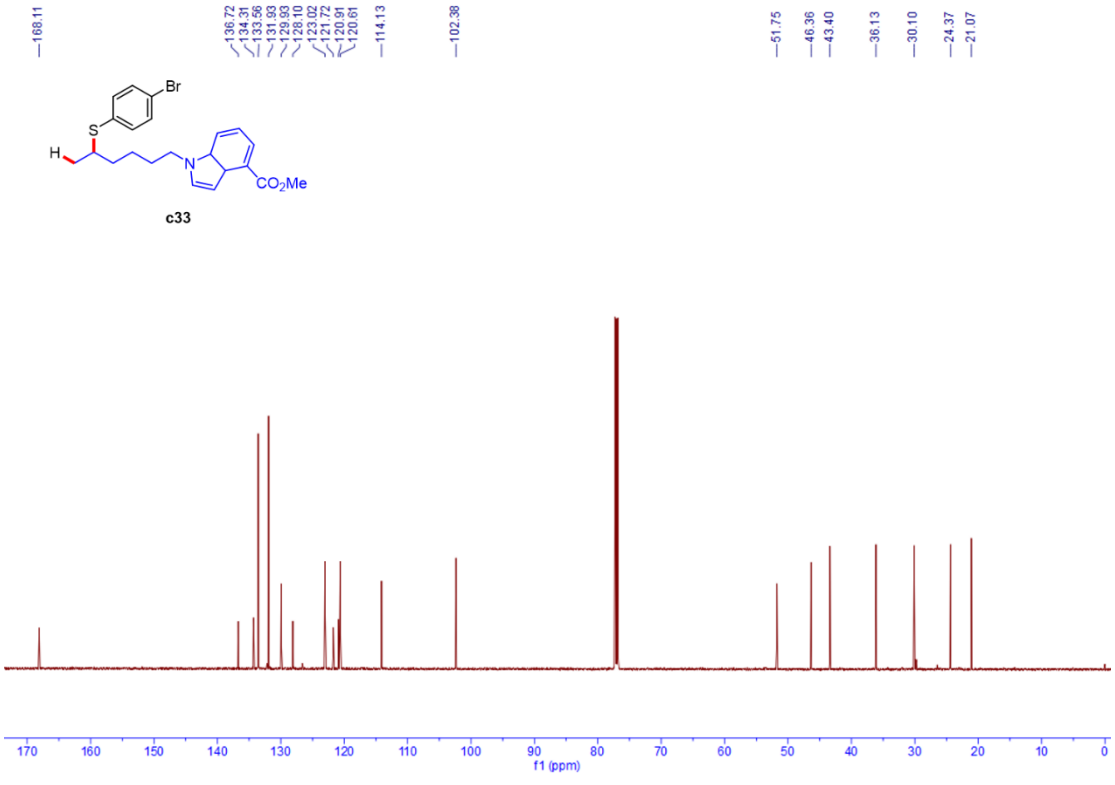
1.580
1.559
1.548
1.510
1.499
1.488
1.477
1.457
1.445
1.434
1.420
1.405
1.215
1.204
Br
S
H
N
CO2Me
c33
0.97
1.07
2.03
0.98
3.03
0.92
2.06
2.98
1.00
2.03
4.19
3.00
f1 (ppm)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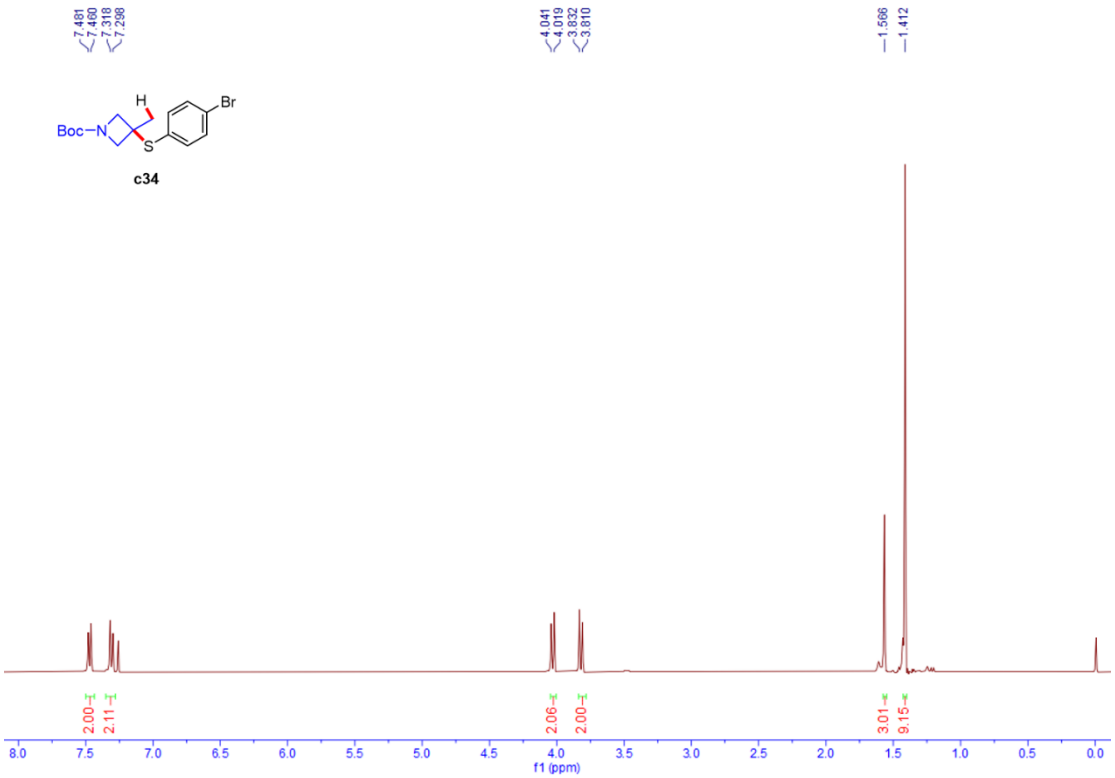
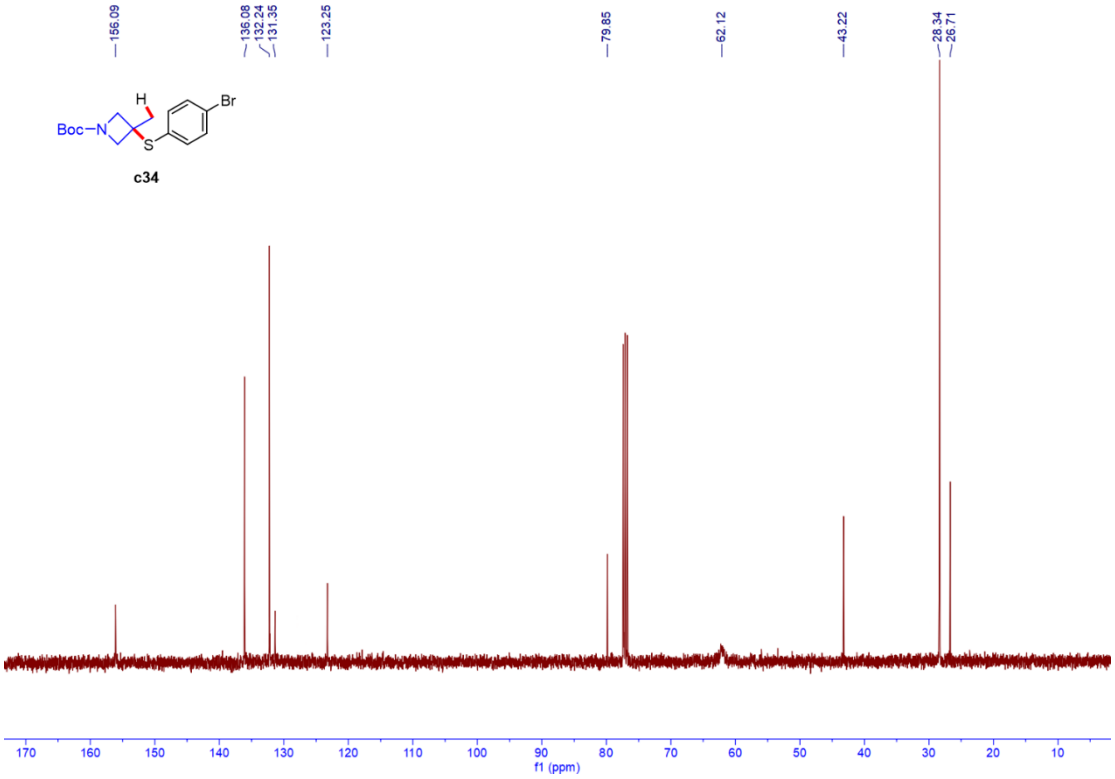
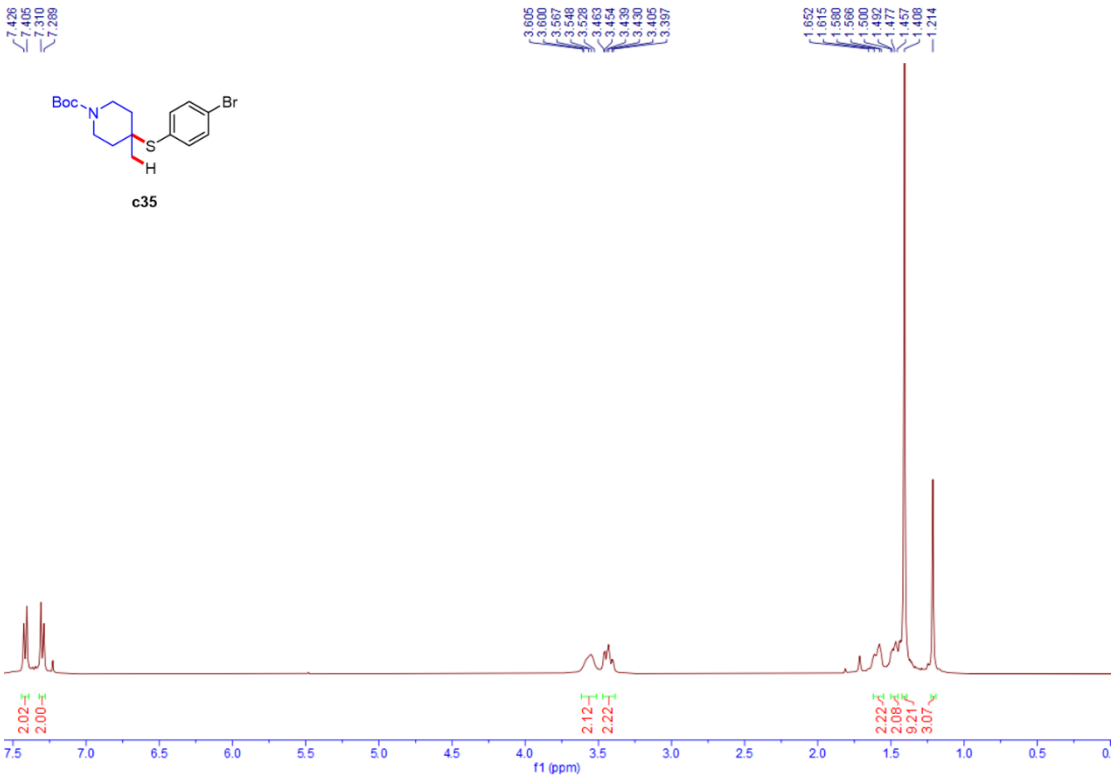
134.31
133.56
131.93
129.93
128.10
123.02
121.72
120.91
120.61
114.13
102.38
51.75
46.36
43.40
36.13
30.10
24.37
21.07
Br
S
H
N
CO2Me
c33
f1 (ppm)


7.481
7.460
7.318
7.298
4.041
4.019
3.832
3.810
1.566
1.412
Boc–N
H
Br
S
c34
2.00
2.11
2.06
2.00
3.01
9.15
f1 (ppm)


156.09
136.08
132.24
131.35
123.25
79.85
62.12
43.22
28.34
26.71
Boc–N
H
Br
S
c34
f1 (ppm)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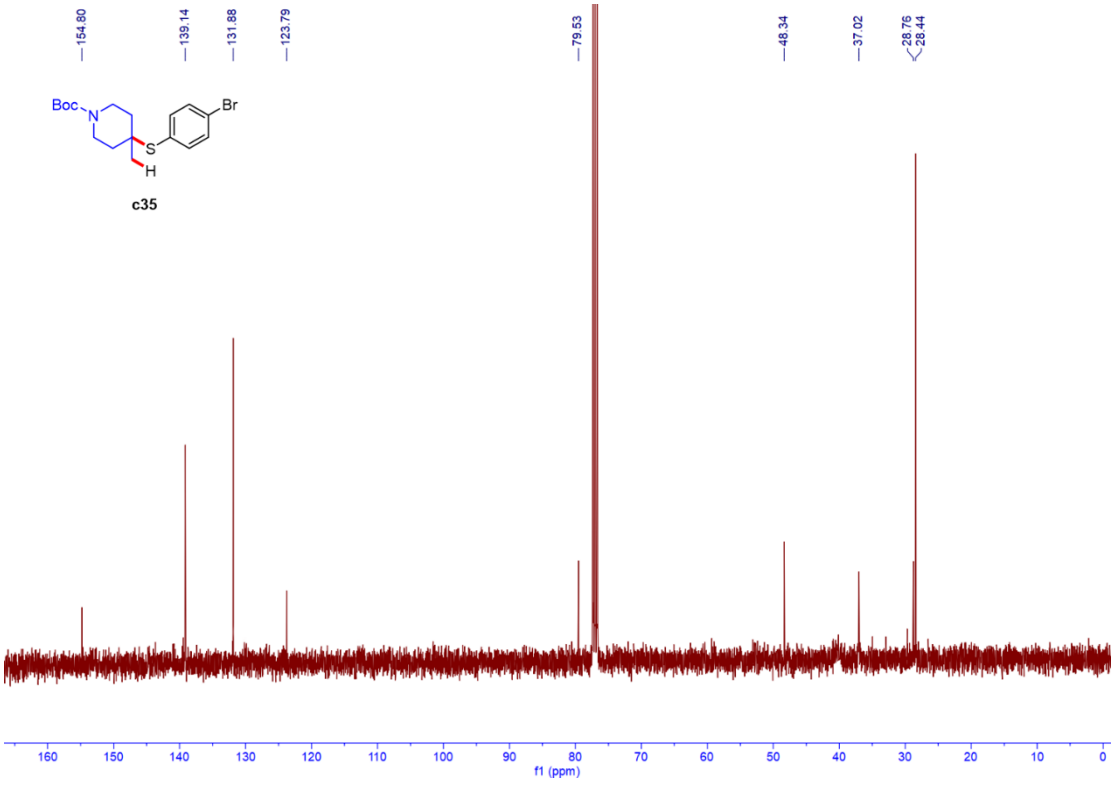
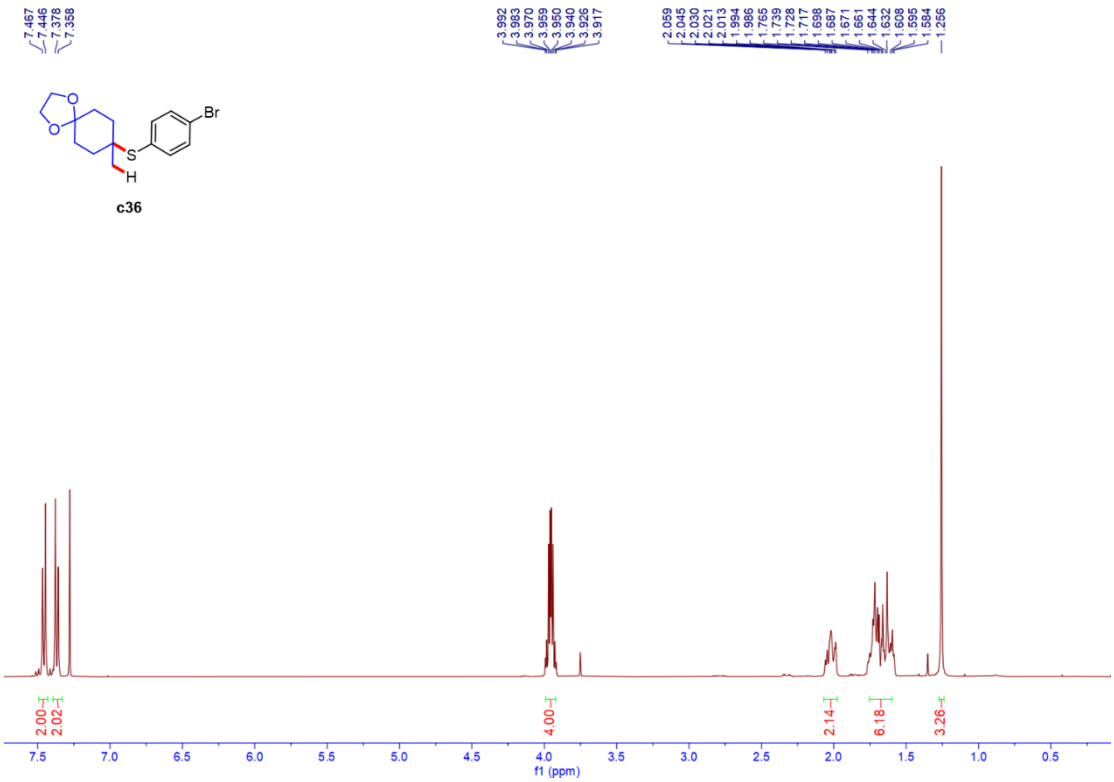
7.405
7.310
7.289
3.605
3.600
3.567
3.548
3.528
3.463
3.454
3.439
3.430
3.405
3.397
1.652
1.615
1.580
1.566
1.500
1.492
1.477
1.457
1.408
1.214
Boc
N
S
H
Br
c35
2.02
2.00
2.12
2.22
2.22
2.08
9.21
3.07
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


154.80
139.14
131.88
123.79
79.53
48.34
37.02
28.76
28.44
Boc
N
S
H
Br
c35
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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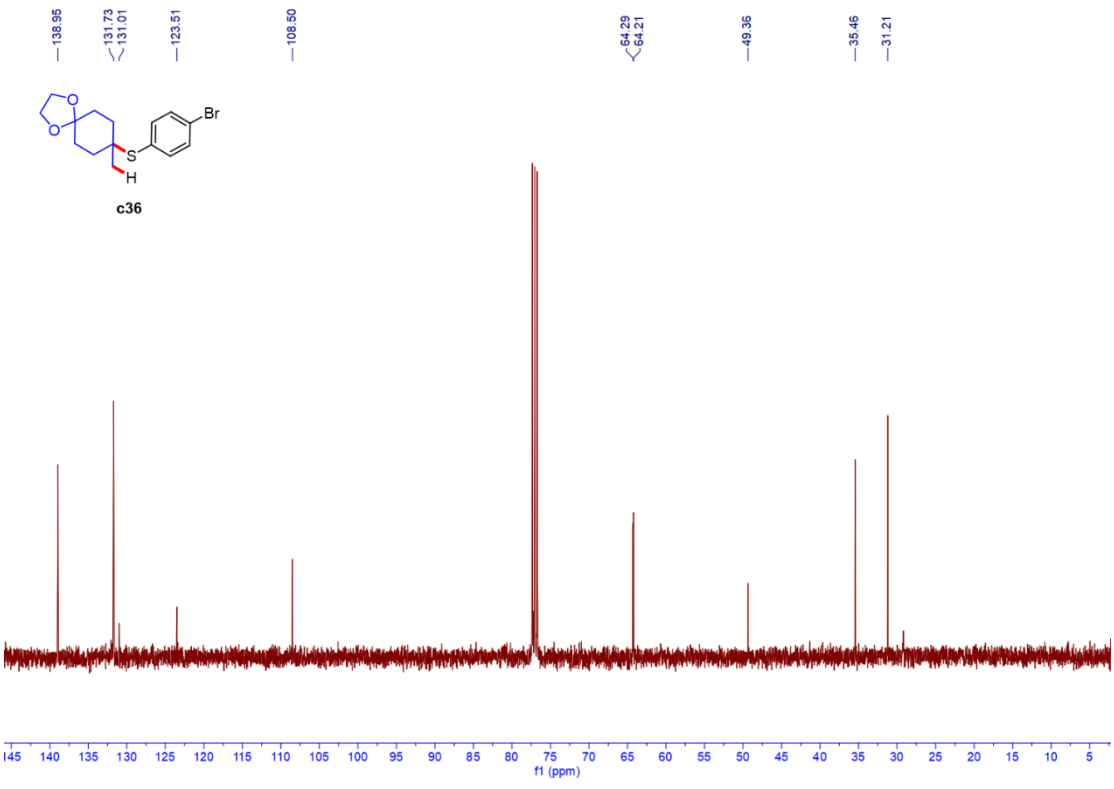
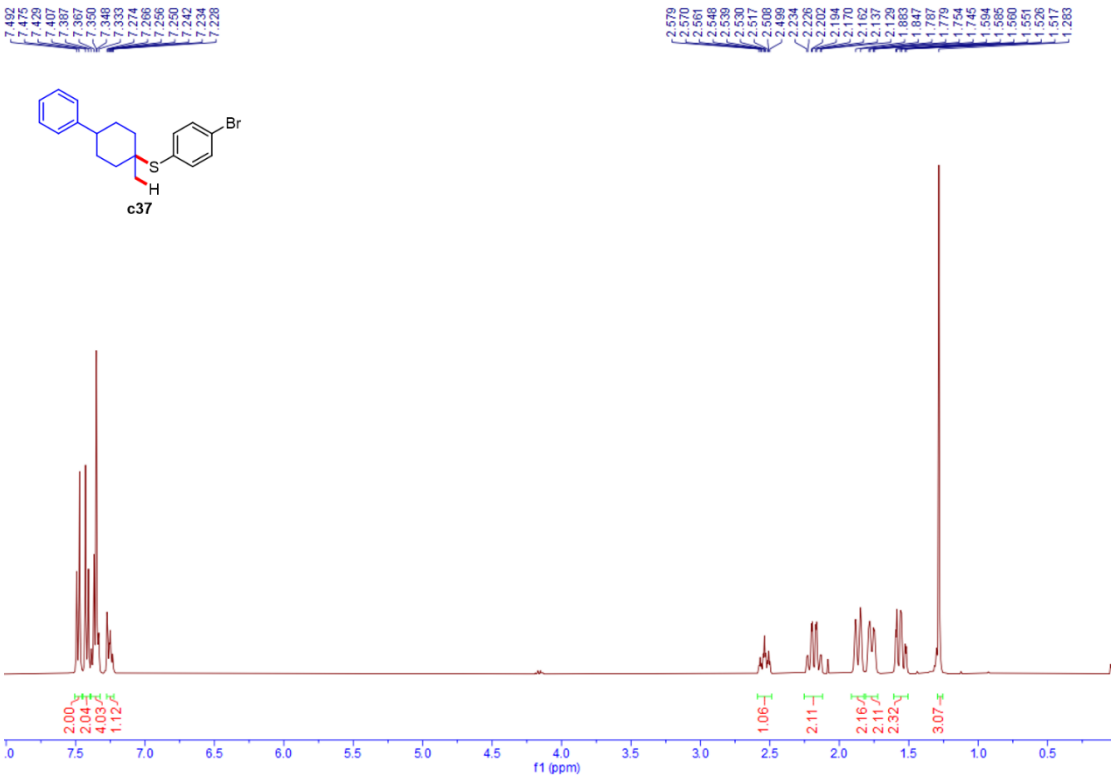
7.446
7.378
7.358
3.992
3.983
3.970
3.959
3.950
3.940
3.926
3.917
2.059
2.045
2.030
2.021
2.013
1.994
1.986
1.765
1.739
1.728
1.717
1.698
1.687
1.671
1.661
1.644
1.632
1.608
1.595
1.584
1.256
Br
S
H
c36
2.00
2.02
4.00
2.14
6.18
3.26
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


138.95
131.73
131.01
123.51
108.50
64.29
64.21
49.36
35.46
31.21
Br
S
H
c36
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)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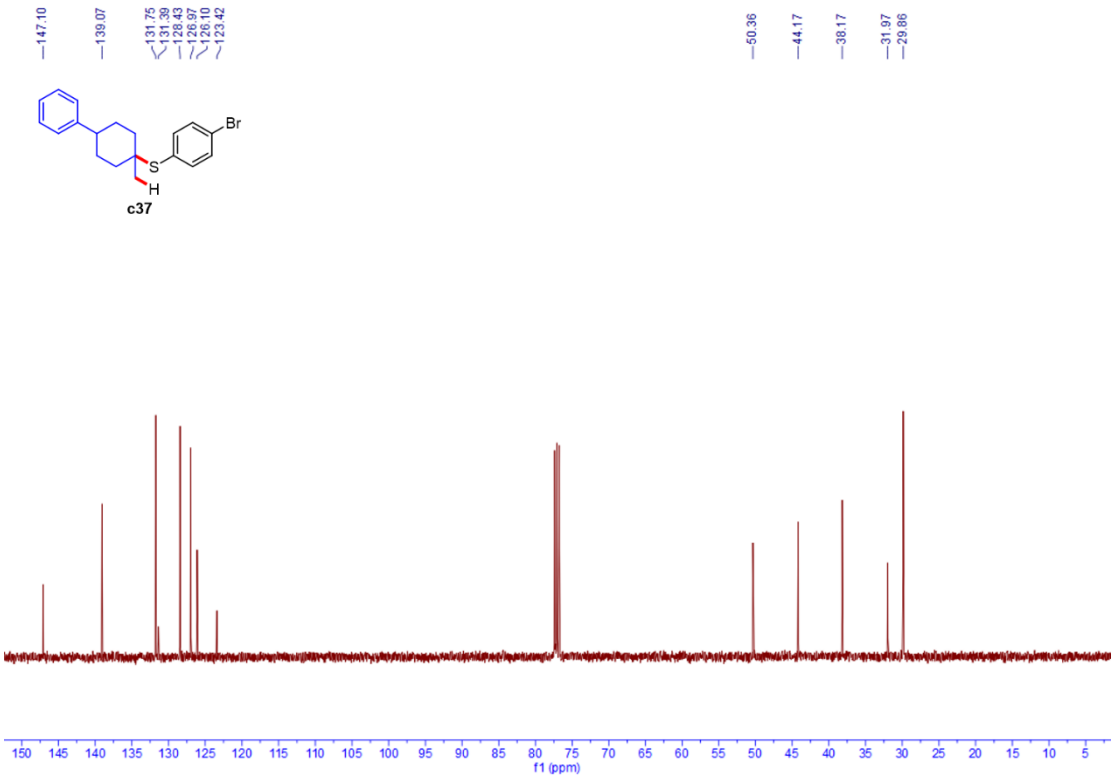
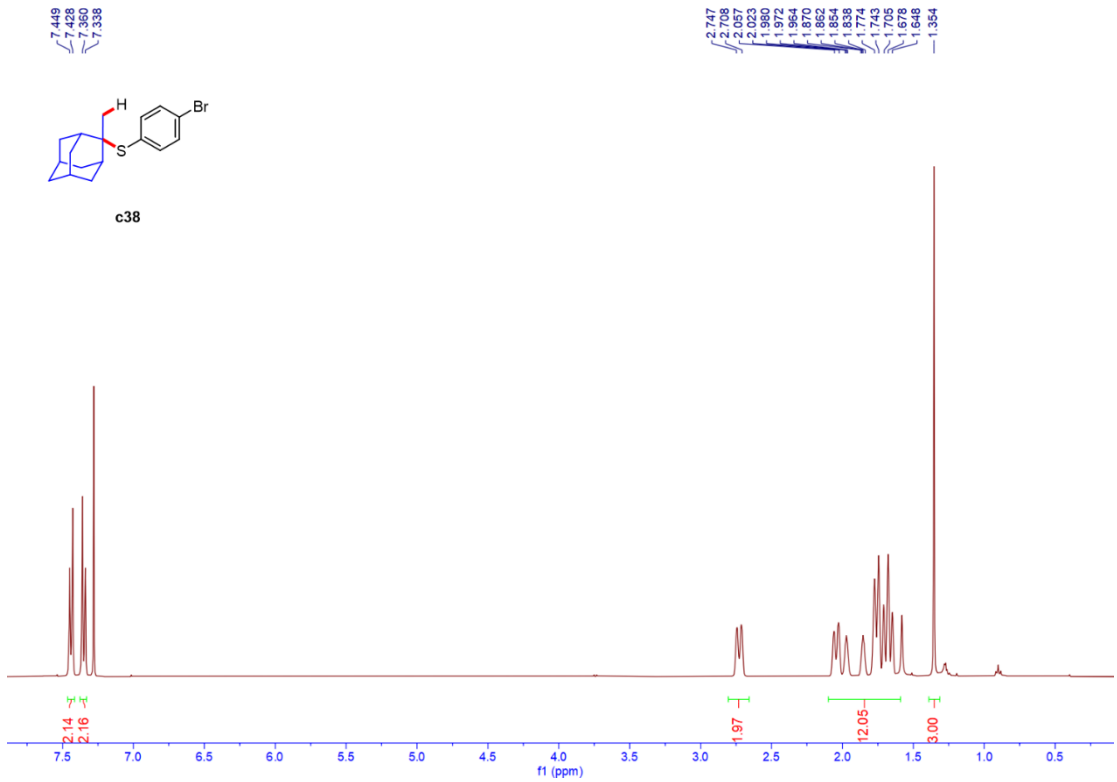
7.475
7.429
7.407
7.387
7.367
7.350
7.348
7.333
7.274
7.266
7.256
7.250
7.242
7.234
7.228
2.579
2.570
2.561
2.548
2.539
2.530
2.517
2.508
2.499
2.234
2.226
2.202
2.194
2.170
2.162
2.137
2.129
1.883
1.847
1.787
1.779
1.754
1.745
1.594
1.585
1.560
1.551
1.526
1.517
1.283
Br
S
H
c37
2.00
2.04
4.03
1.12
1.06
2.11
2.16
2.11
2.32
3.07
f1 (ppm)


147.10
139.07
131.75
131.39
128.43
126.97
126.10
123.42
50.36
44.17
38.17
31.97
29.86
Br
S
H
c37
f1 (ppm)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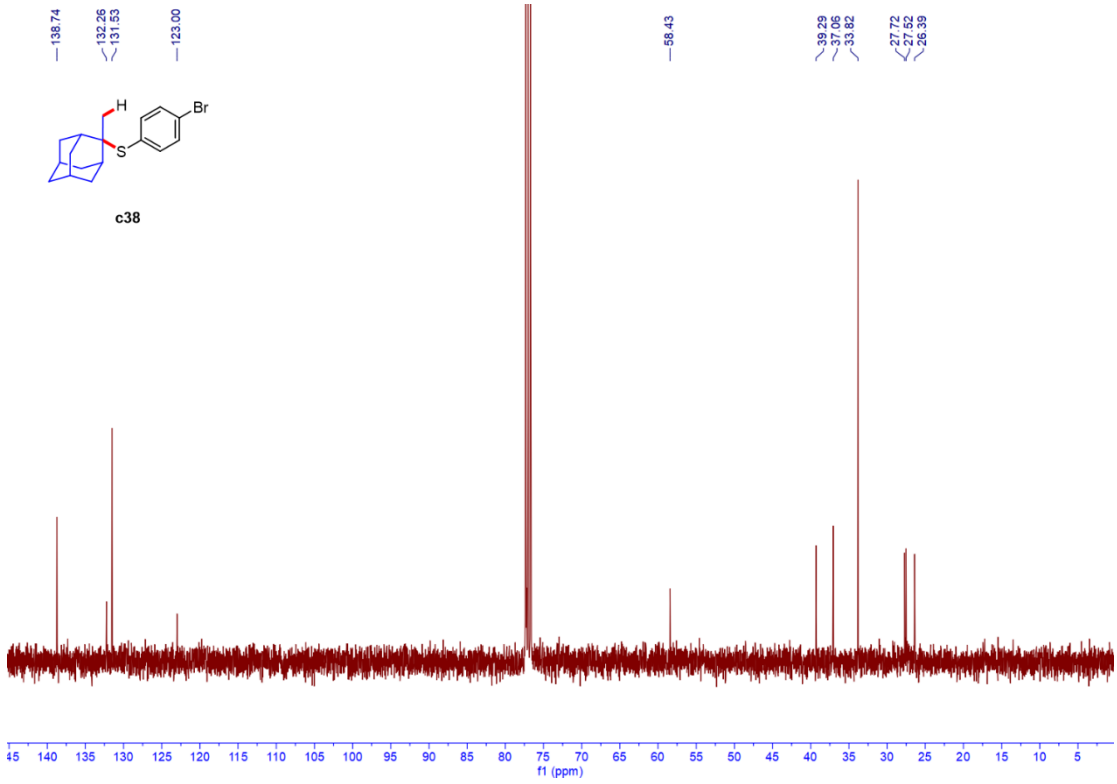
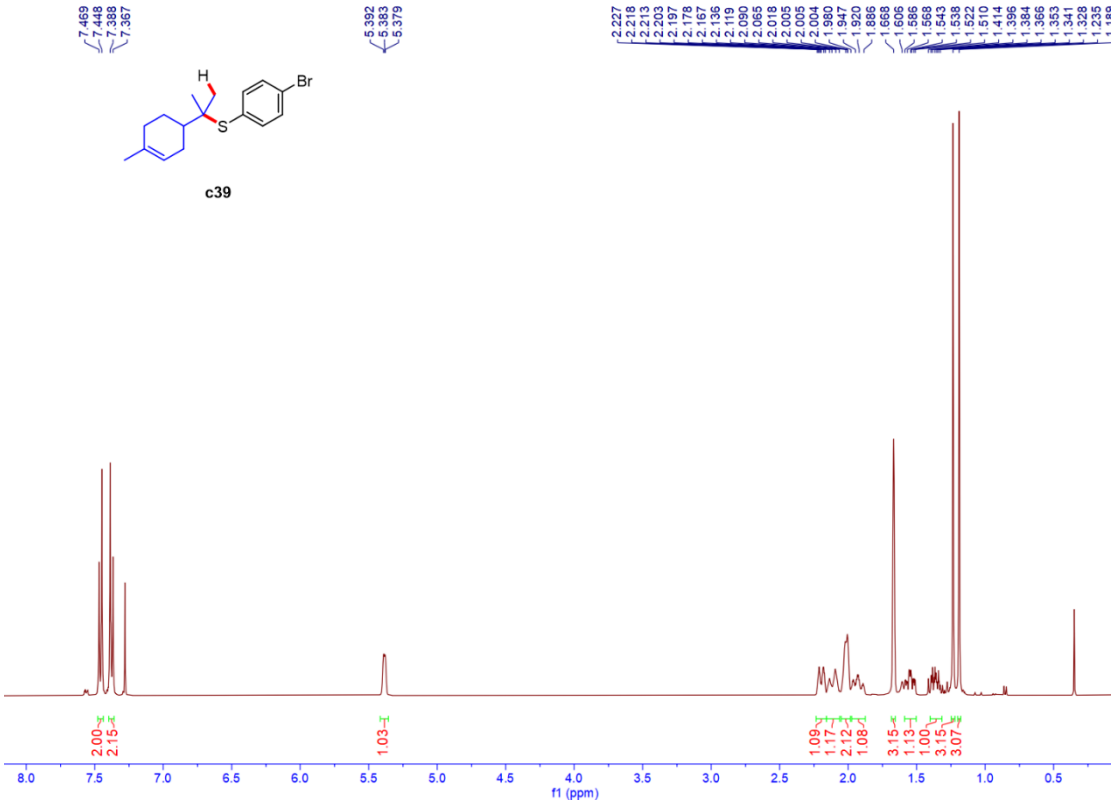
7.428
7.360
7.338
2.747
2.708
2.057
2.023
1.980
1.972
1.964
1.870
1.862
1.854
1.838
1.774
1.743
1.705
1.678
1.648
1.354
H
Br
S
c38
2.14
2.16
1.97
12.05
3.00
f1 (ppm)


138.74
132.26
131.53
123.00
58.43
39.29
37.06
33.82
27.72
27.52
26.39
H
Br
S
c38
f1 (ppm)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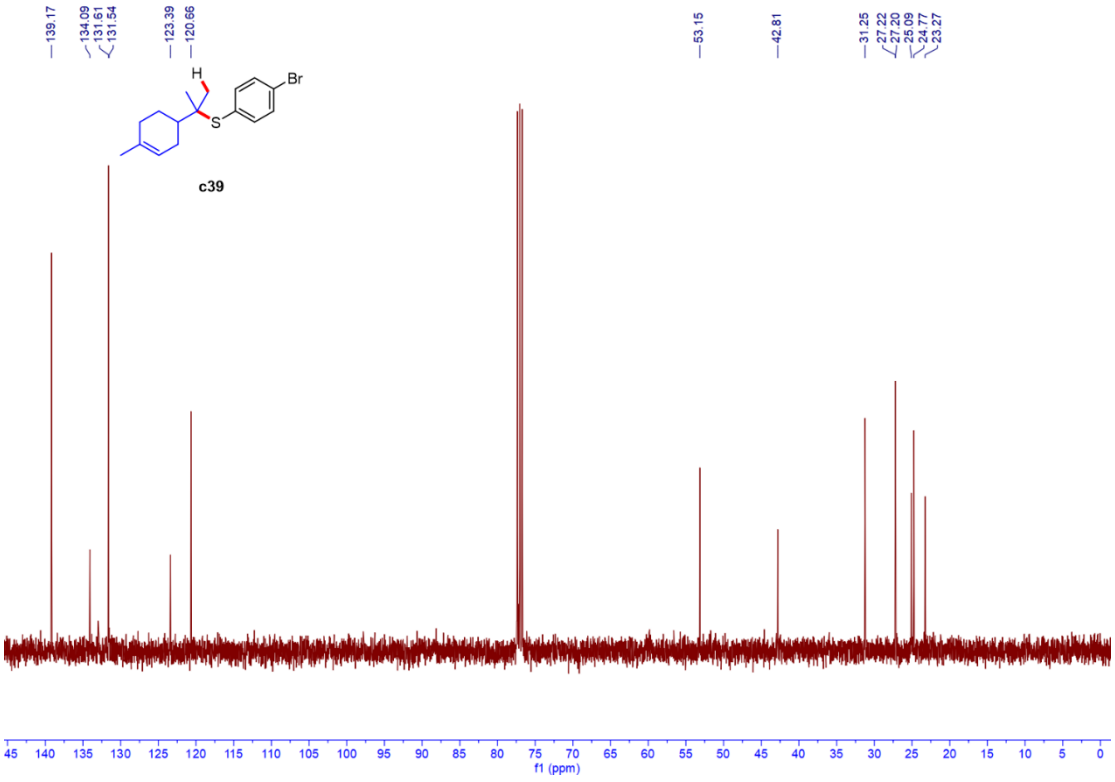
7.367
5.392
5.383
5.379
2.227
2.218
2.213
2.203
2.197
2.178
2.167
2.135
2.119
2.090
2.065
2.018
2.005
2.004
1.980
1.947
1.920
1.886
1.668
1.606
1.586
1.568
1.543
1.538
1.522
1.510
1.414
1.395
1.384
1.366
1.353
1.341
1.328
1.235
H
Br
S
c39
2.00
2.15
1.03
1.09
1.17
2.12
1.08
3.15
1.13
1.00
3.15
3.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


139.17
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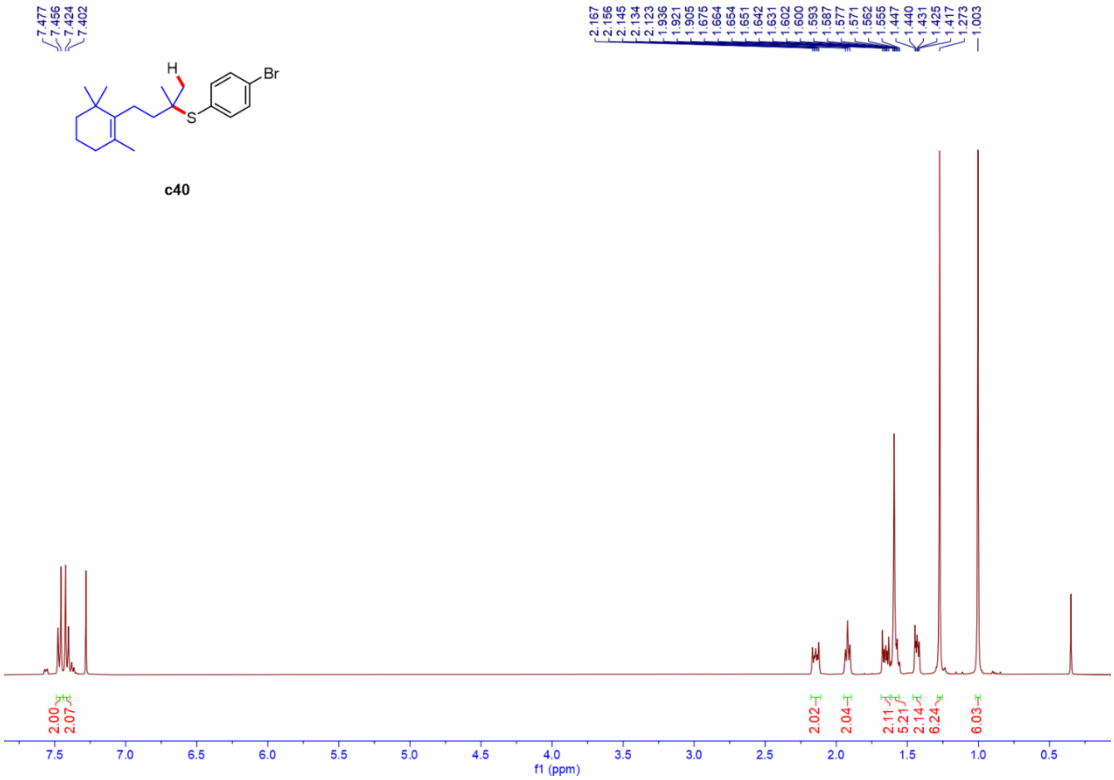
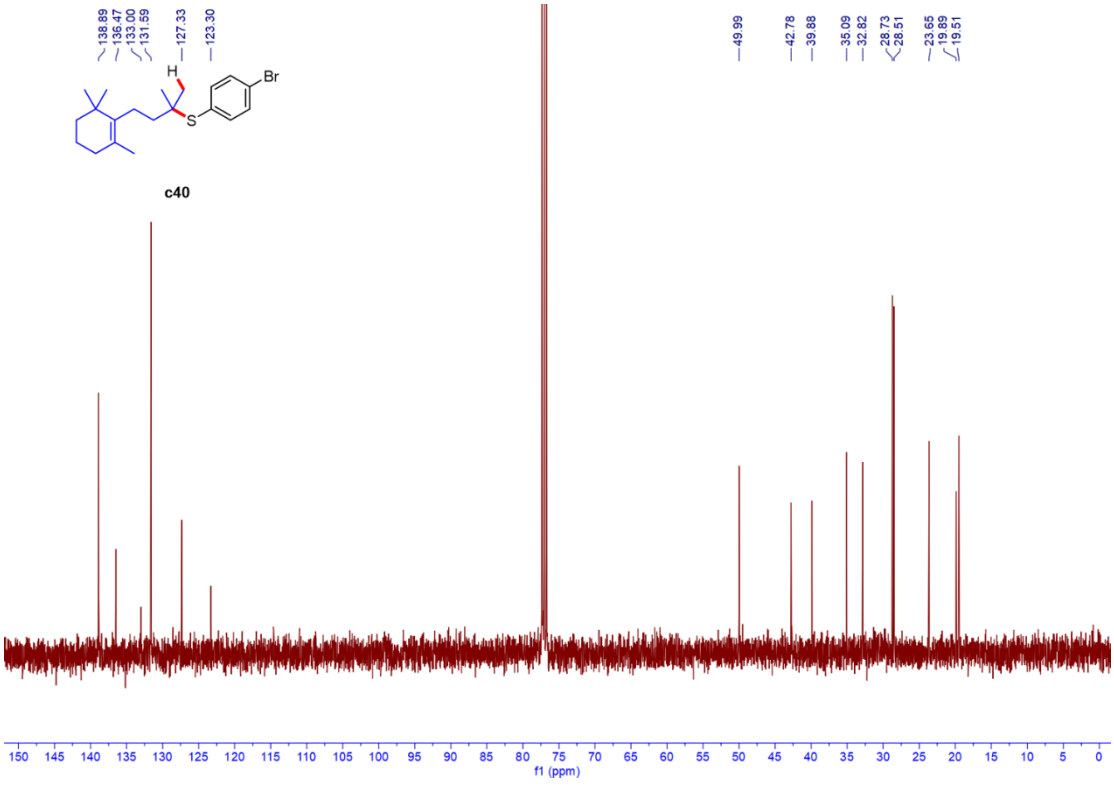
131.61
131.54
123.39
120.66
53.15
42.81
31.25
27.22
27.20
25.09
24.77
23.27
H
Br
S
c39
45
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)


7.477
7.456
7.424
7.402
H
Br
S
c40
2.167
2.156
2.145
2.134
2.123
1.936
1.921
1.905
1.675
1.664
1.654
1.651
1.642
1.631
1.602
1.600
1.593
1.587
1.577
1.571
1.562
1.555
1.447
1.440
1.431
1.425
1.417
1.273
1.003
2.00
2.07
2.02
2.04
2.11
5.21
2.14
6.24
6.03
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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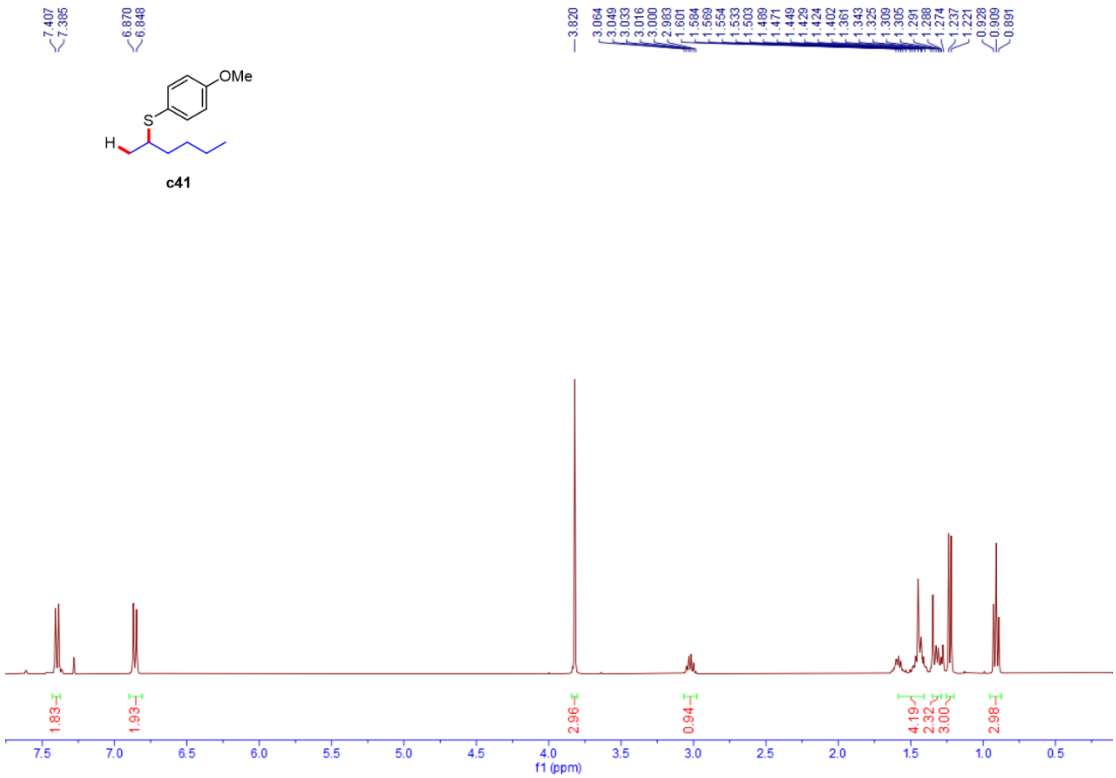
H
Br
S
c40
49.99
42.78
39.88
35.09
32.82
28.73
28.51
23.65
19.89
19.51
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
f1 (ppm)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3.064
3.049
3.033
3.016
3.000
2.983
1.601
1.584
1.569
1.554
1.533
1.503
1.489
1.471
1.449
1.429
1.424
1.402
1.361
1.343
1.325
1.309
1.305
1.291
1.288
1.274
1.237
1.221
0.928
0.909
0.891
OMe
S
H
c41
1.83
1.93
2.96
0.94
4.19
2.32
3.00
2.98
7.5
7.0
6.5
6.0
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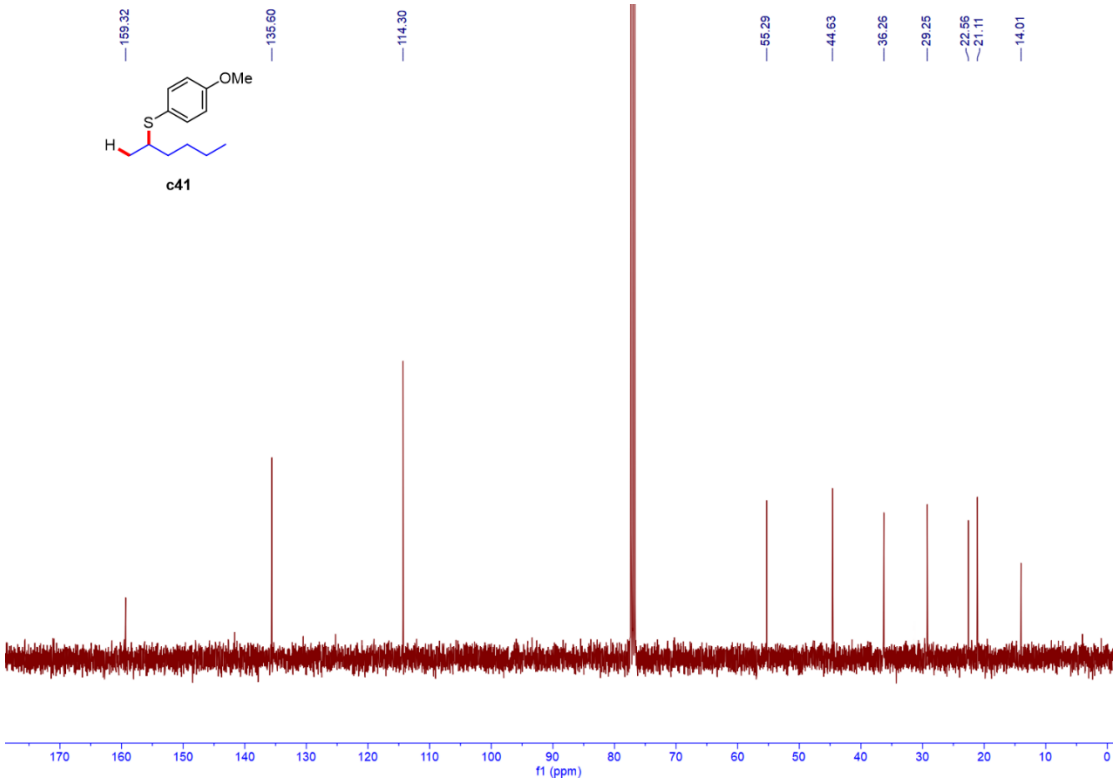
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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55.29
44.63
36.26
29.25
22.56
21.11
14.01
OMe
S
H
c41
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160
150
140
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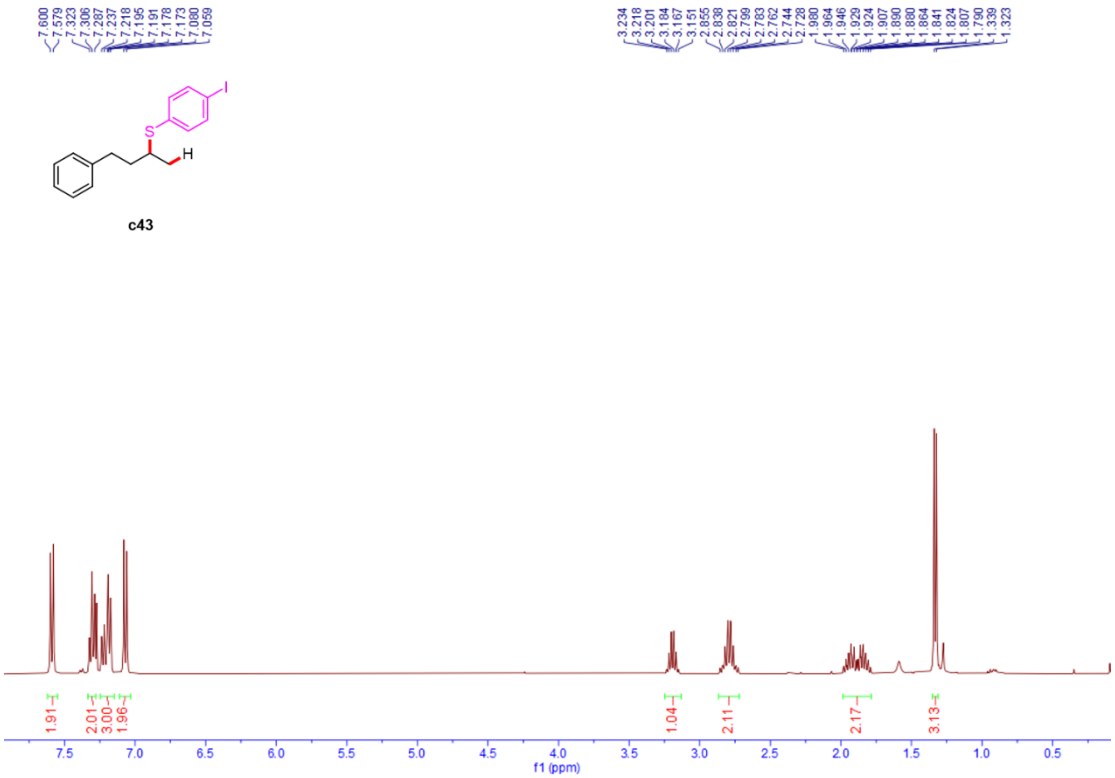
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.600
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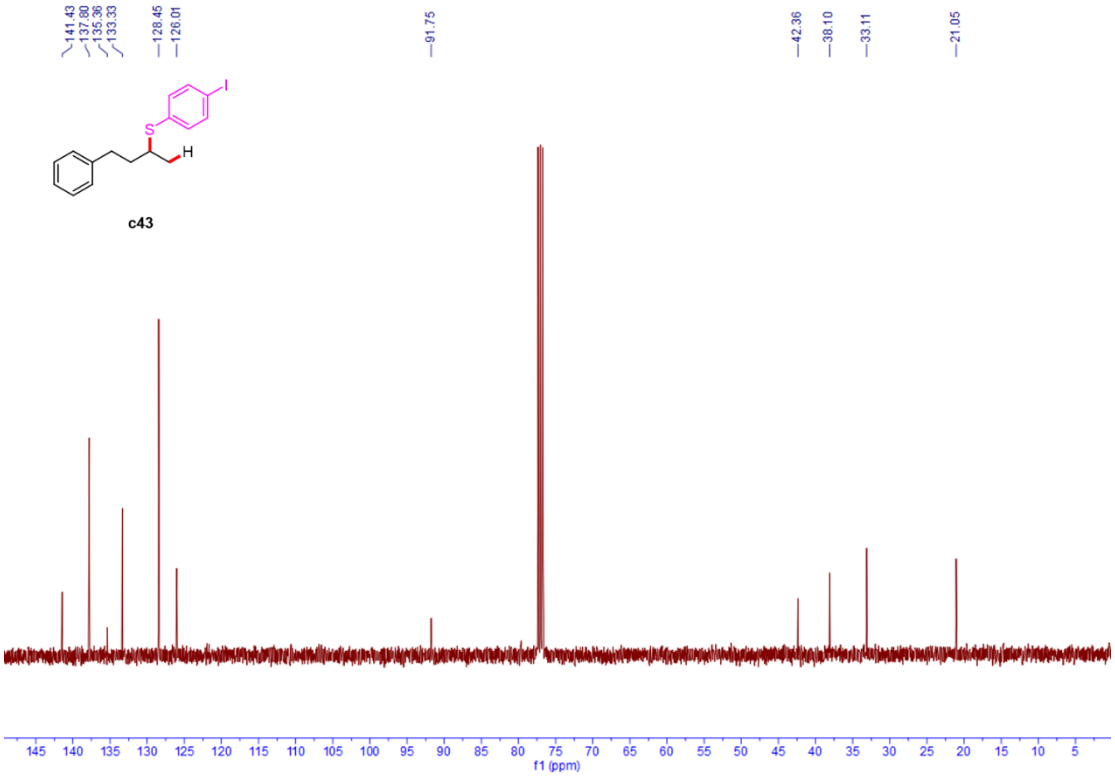
7.287
7.237
7.218
7.195
7.191
7.178
7.173
7.080
7.059
3.234
3.218
3.201
3.184
3.167
3.151
2.855
2.838
2.821
2.799
2.783
2.762
2.744
2.728
1.980
1.964
1.946
1.929
1.924
1.907
1.890
1.880
1.864
1.841
1.824
1.807
1.790
1.339
1.323
I
S
H
c43
1.91
2.01
3.00
1.96
1.04
2.11
2.17
3.13
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


141.43
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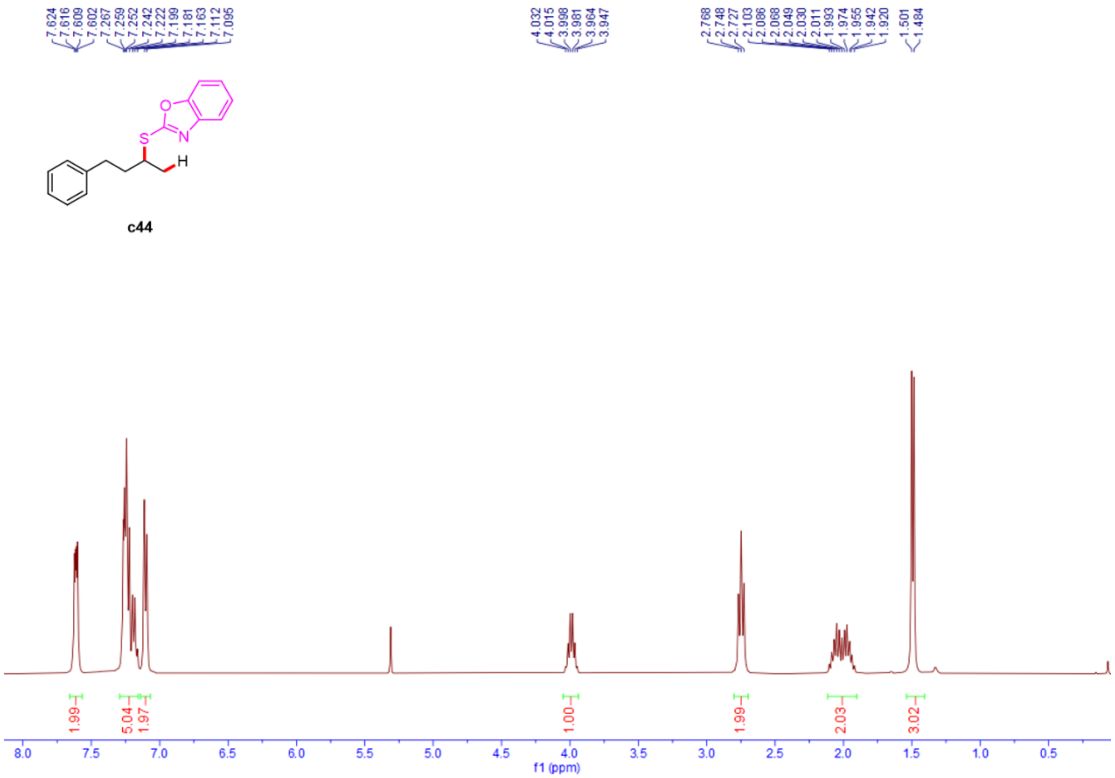
133.33
128.45
126.01
91.75
42.36
38.10
33.11
21.05
I
S
H
c43
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
f1 (ppm)


7.624
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7.602
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7.259
7.252
7.242
7.222
7.199
7.181
7.163
7.112
7.095
4.032
4.015
3.998
3.981
3.964
3.947
2.768
2.748
2.727
2.103
2.086
2.068
2.049
2.030
2.011
1.993
1.974
1.955
1.942
1.920
1.501
1.484
O
S
N
H
c44
1.99
5.04
1.97
1.00
1.99
2.03
3.02
8.0
7.5
7.0
6.5
6.0
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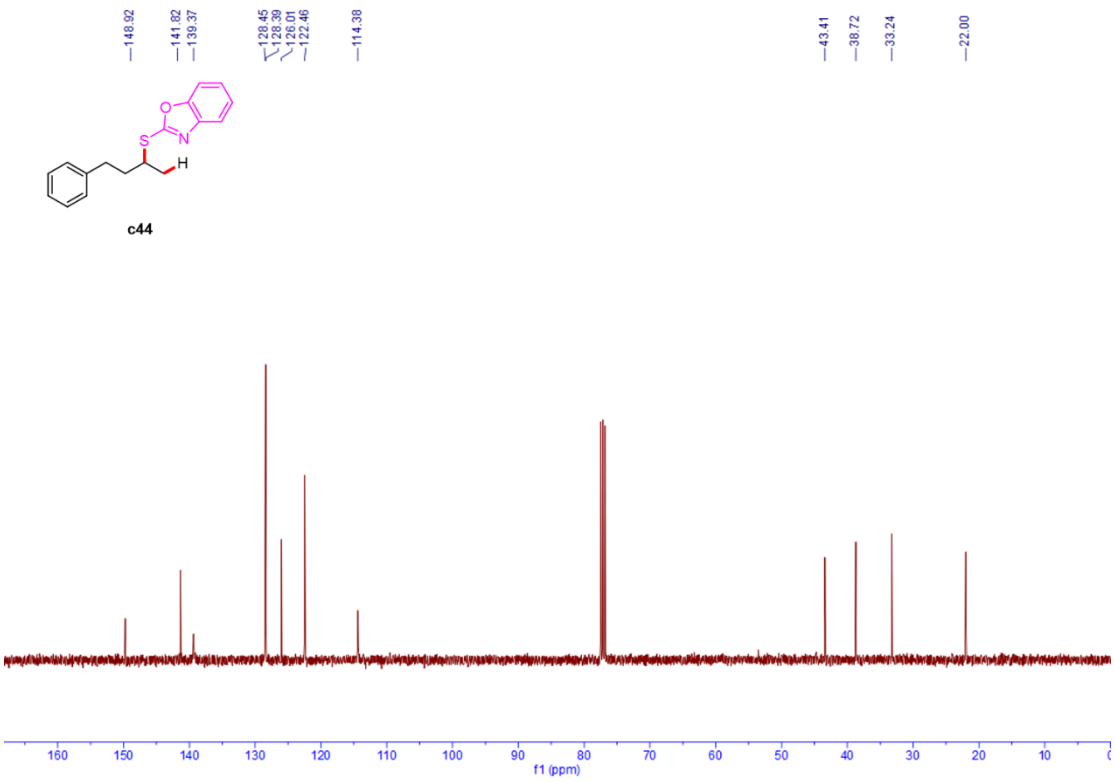
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


148.92
141.82
139.37
128.45
128.39
126.01
122.46
114.38
43.41
38.72
33.24
22.00
O
S
N
H
c44
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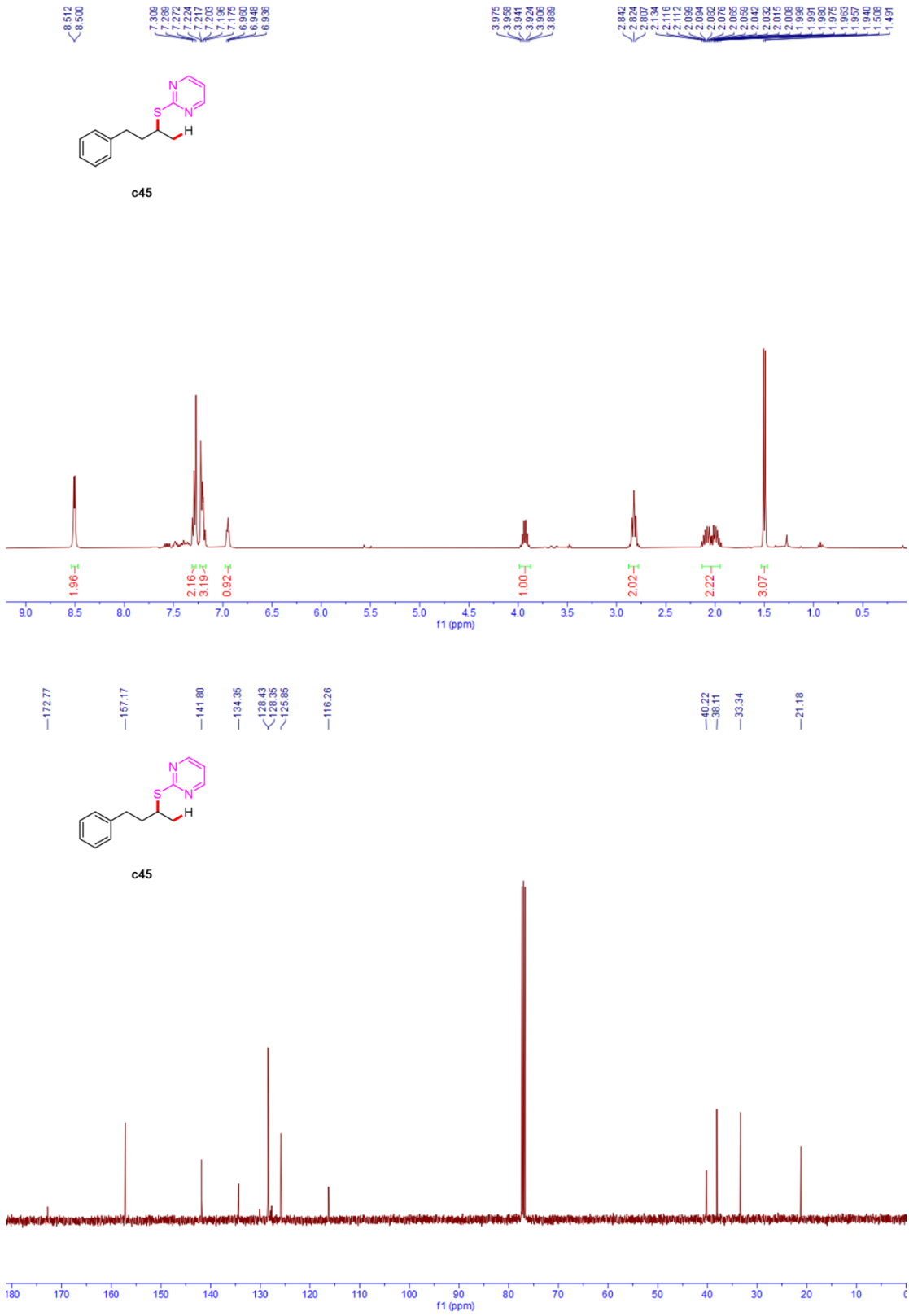
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.289
7.272
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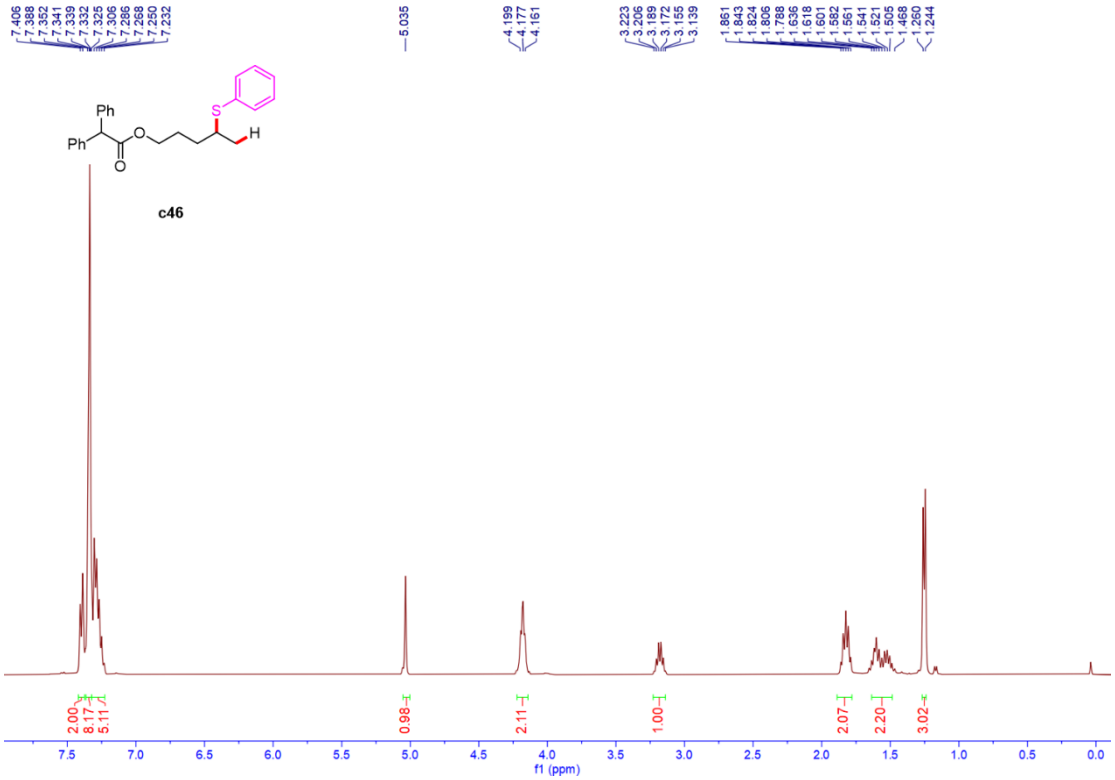
7.203
7.196
7.175
6.960
6.948
6.936
3.975
3.958
3.941
3.924
3.906
3.889
2.842
2.824
2.807
2.134
2.116
2.112
2.099
2.094
2.082
2.076
2.065
2.059
2.042
2.032
2.015
2.008
1.998
1.991
1.980
1.975
1.963
1.957
1.940
1.508
1.491
N
S
N
H
c45
1.96
2.16
3.19
0.92
1.00
2.02
2.22
3.07
f1 (ppm)
172.77
157.17
141.80
134.35
128.43
128.35
125.85
116.26
40.22
38.11
33.34
21.18
N
S
N
H
c45
f1 (ppm)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7.268
7.250
7.232
5.035
4.199
4.177
4.161
3.223
3.206
3.189
3.172
3.155
3.139
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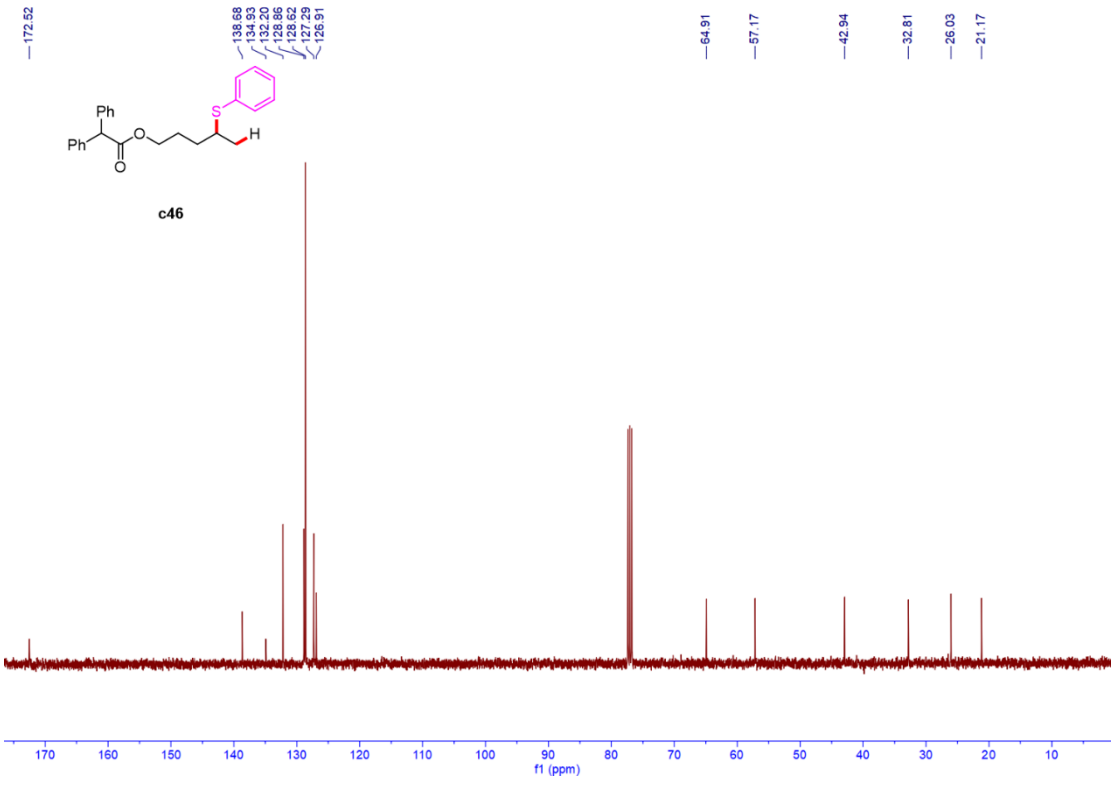
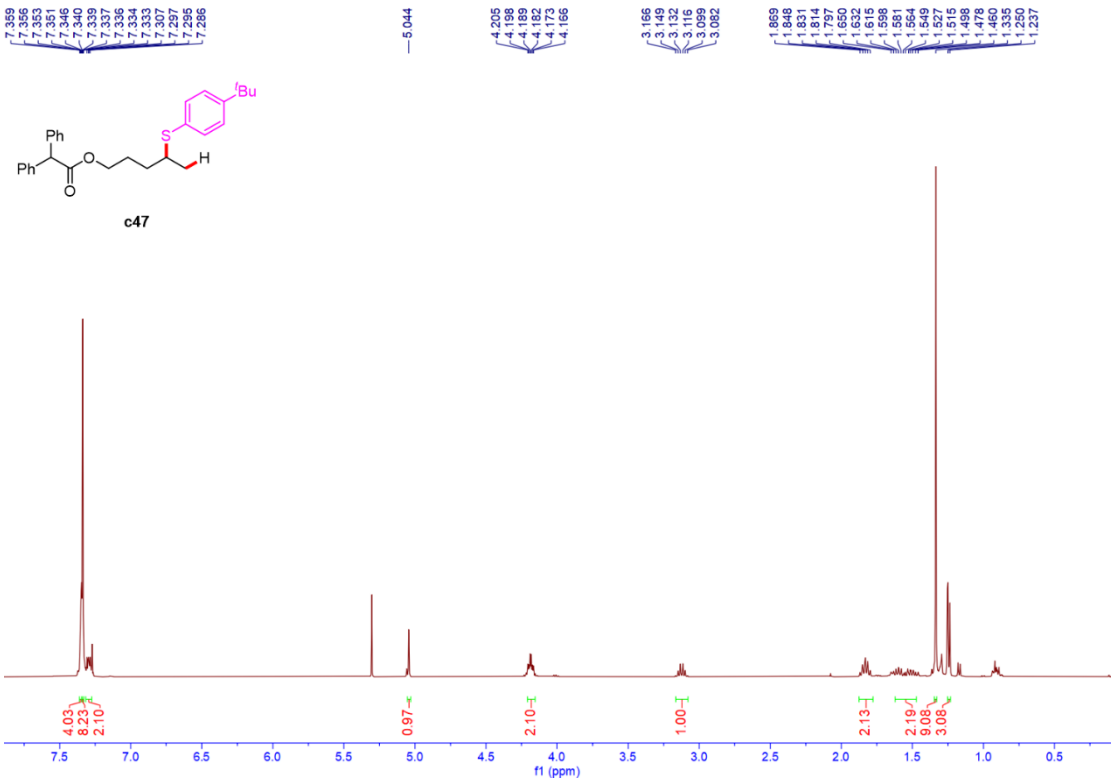
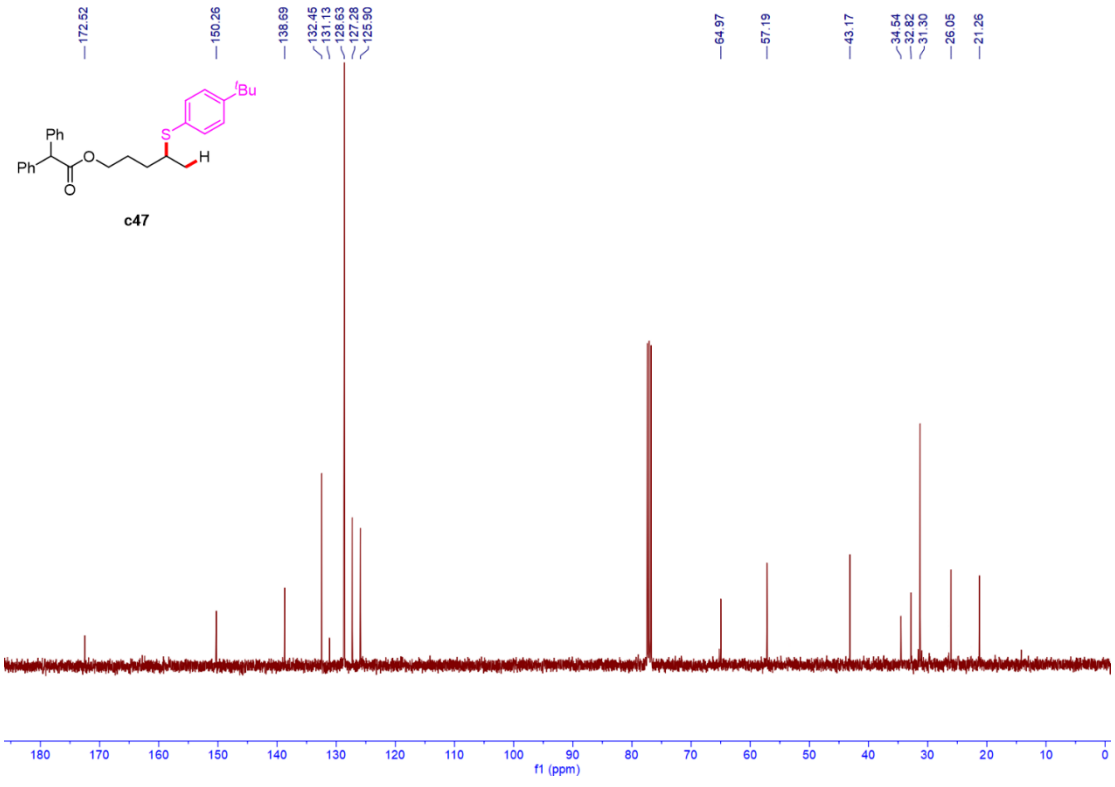
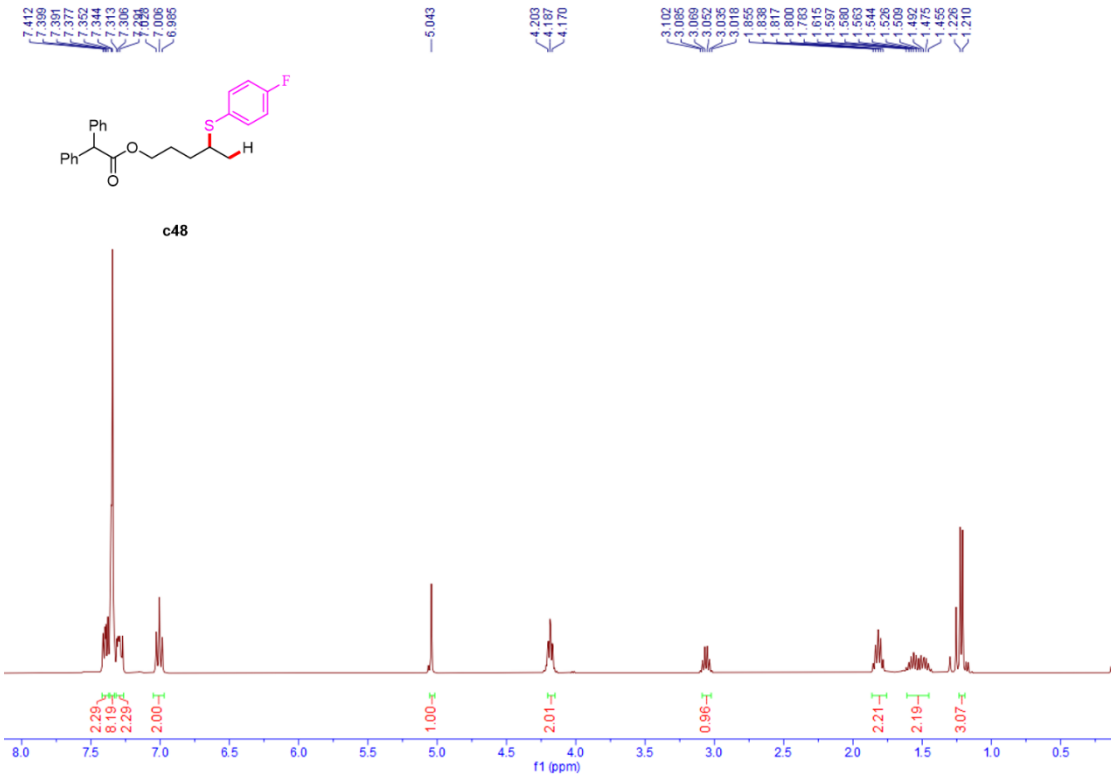
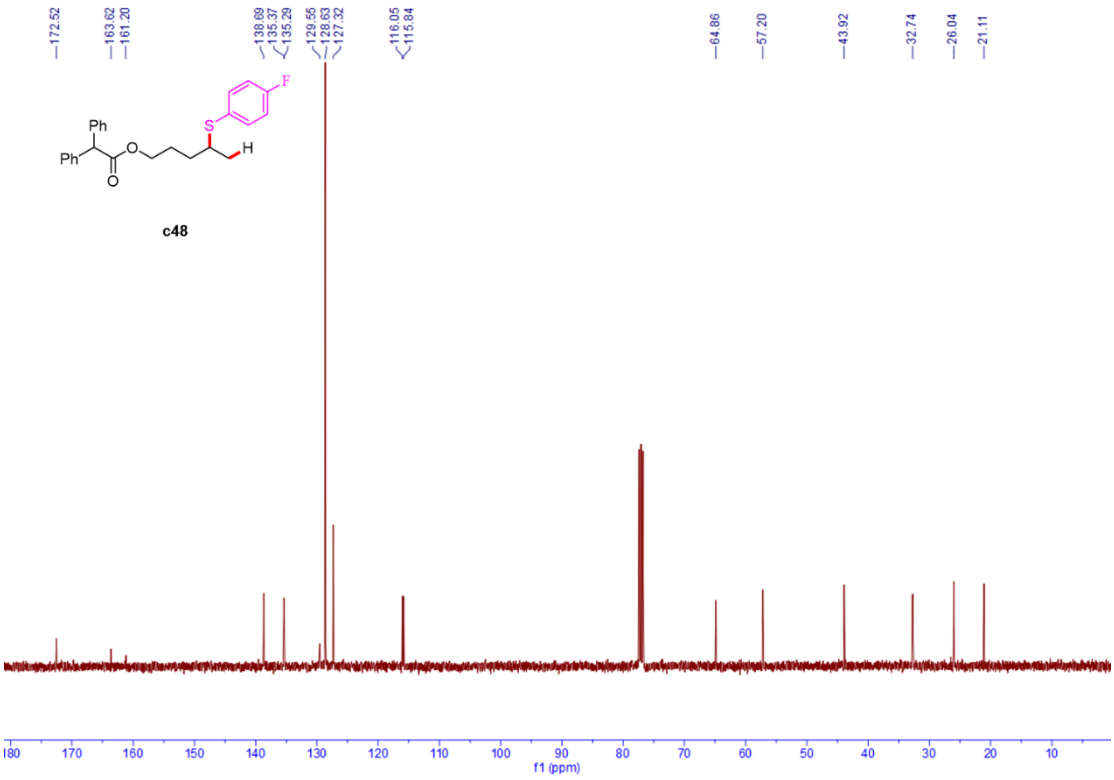
1.843
1.824
1.806
1.788
1.636
1.618
1.601
1.582
1.561
1.541
1.521
1.505
1.468
1.260
1.244
Ph
Ph
O
O
S
H
c46
2.00
8.17
5.11
0.98
2.11
1.00
2.07
2.20
3.02
f1 (ppm)

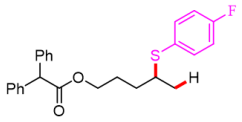

172.52
138.68
134.93
132.20
128.86
128.62
127.29
126.91
64.91
57.17
42.94
32.81
26.03
21.17
Ph
Ph
O
O
S
H
c46
f1 (ppm)


7.359
7.356
7.353
7.351
7.346
7.340
7.339
7.337
7.336
7.334
7.333
7.307
7.297
7.295
7.286
5.044
4.205
4.198
4.189
4.182
4.173
4.166
3.166
3.149
3.132
3.116
3.099
3.082
1.869
1.848
1.831
1.814
1.797
1.650
1.632
1.615
1.598
1.581
1.564
1.549
1.527
1.515
1.498
1.478
1.460
1.335
1.250
1.237
Ph
Ph
O
O
S
tBu
H
c47
4.03
8.23
2.10
0.97
2.10
1.00
2.13
2.19
9.08
3.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


172.52
150.26
138.69
132.45
131.13
128.63
127.28
125.90
64.97
57.19
43.17
34.54
32.82
31.30
26.05
21.26
Ph
Ph
O
O
S
tBu
H
c47
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

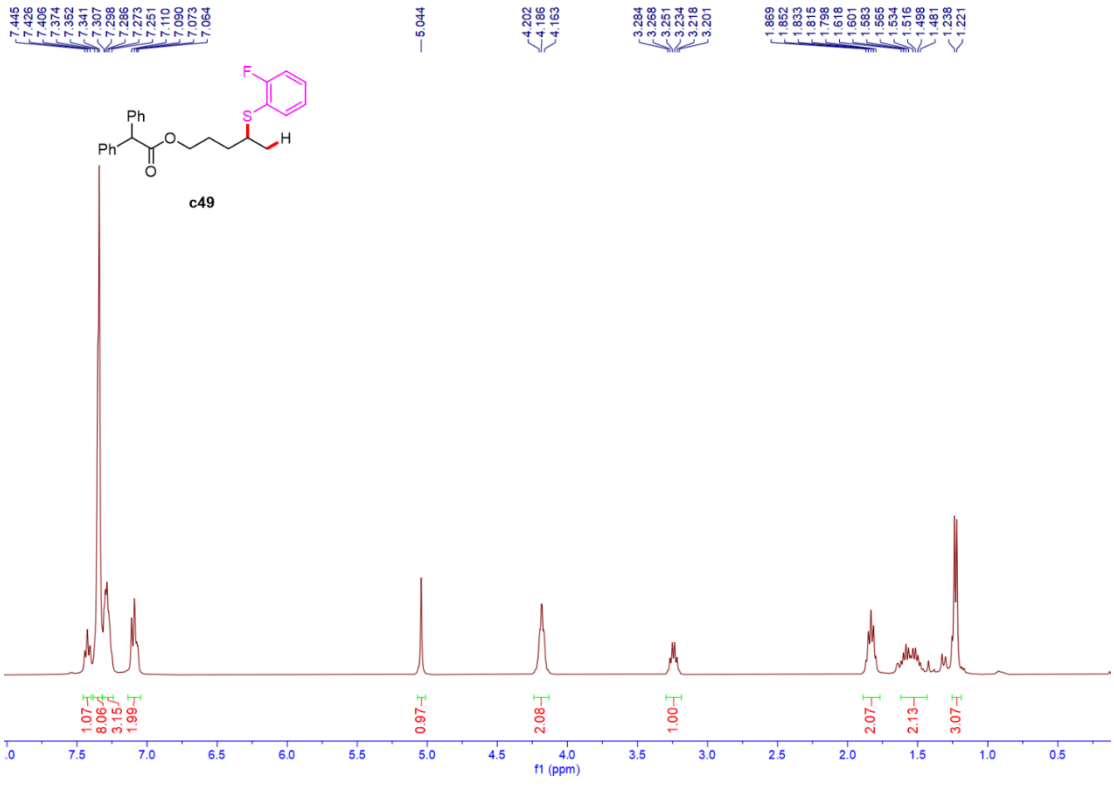

7.412
7.396
7.391
7.377
7.352
7.344
7.313
7.306
7.291
7.028
7.006
6.985
5.043
4.203
4.187
4.170
3.102
3.085
3.069
3.052
3.035
3.018
1.855
1.838
1.817
1.800
1.783
1.615
1.597
1.580
1.563
1.544
1.526
1.509
1.492
1.475
1.455
1.226
1.210
F
S
H
Ph
Ph
O
O
c48
2.29
8.19
2.29
2.00
1.00
2.01
0.96
2.21
2.19
3.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


172.52
163.62
161.20
138.69
135.37
135.29
129.55
129.63
127.32
116.05
115.84
64.86
57.20
43.92
32.74
26.04
21.11
F
S
H
Ph
Ph
O
O
c48
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Ph
Ph
O
O
S
F
H

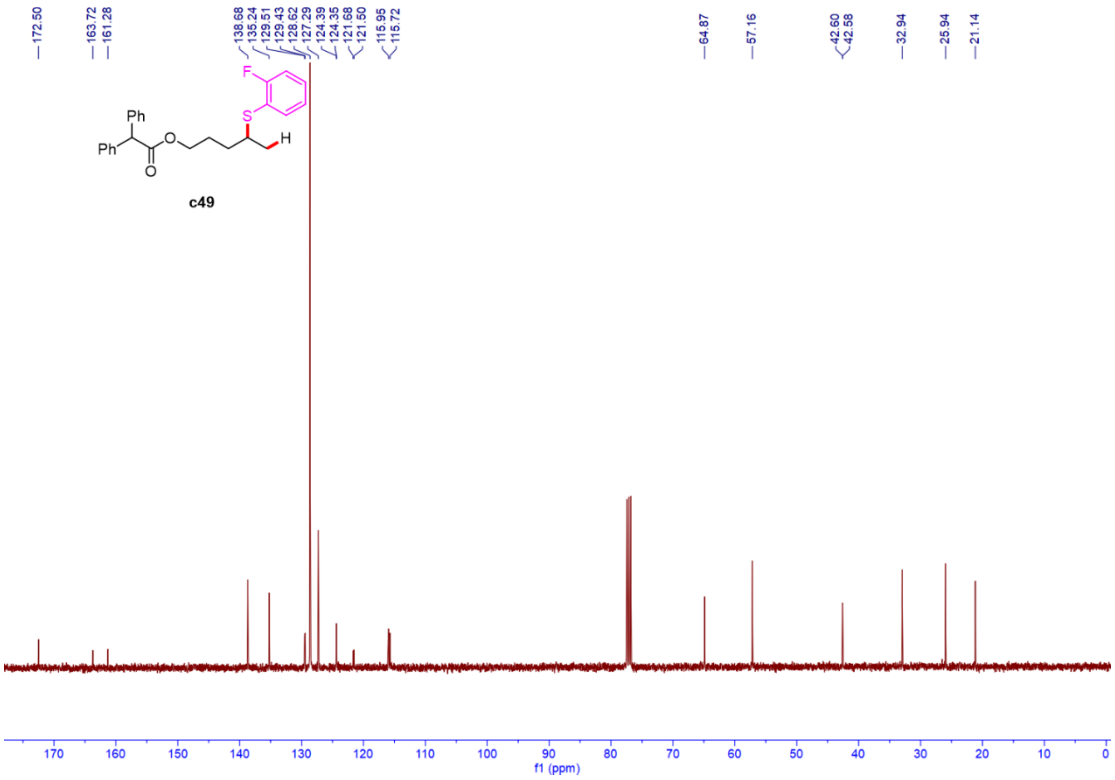
c48

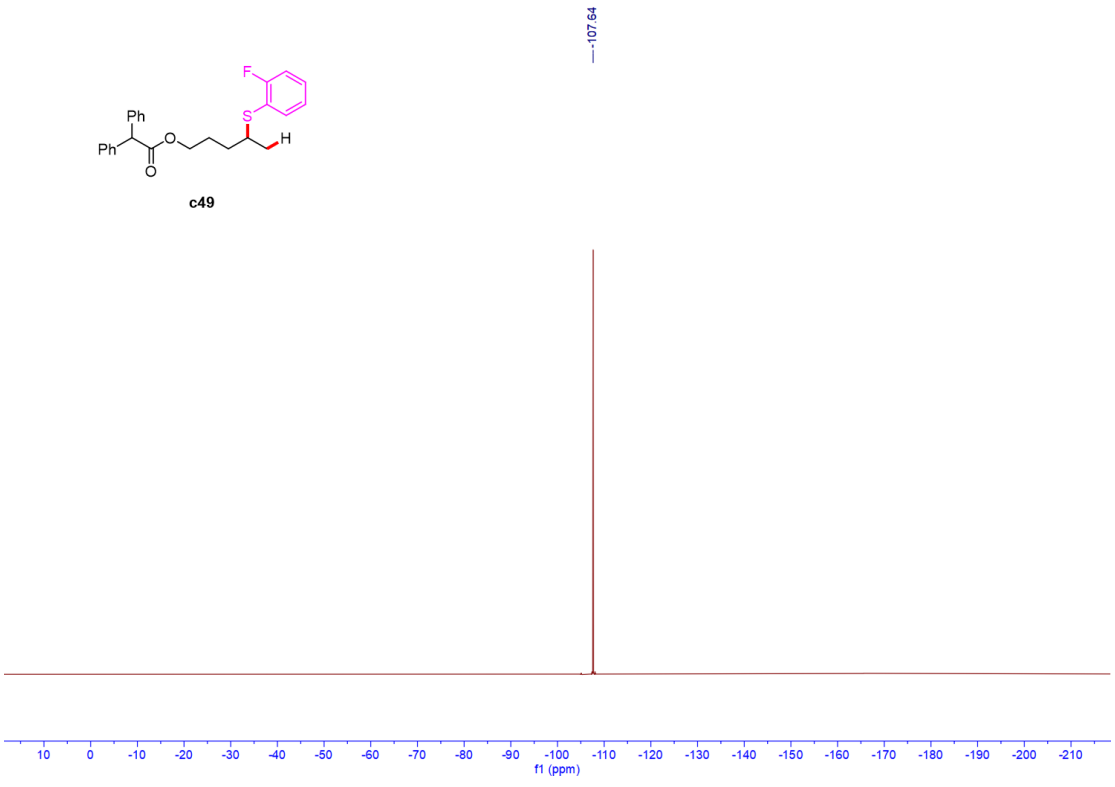
-114.25
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

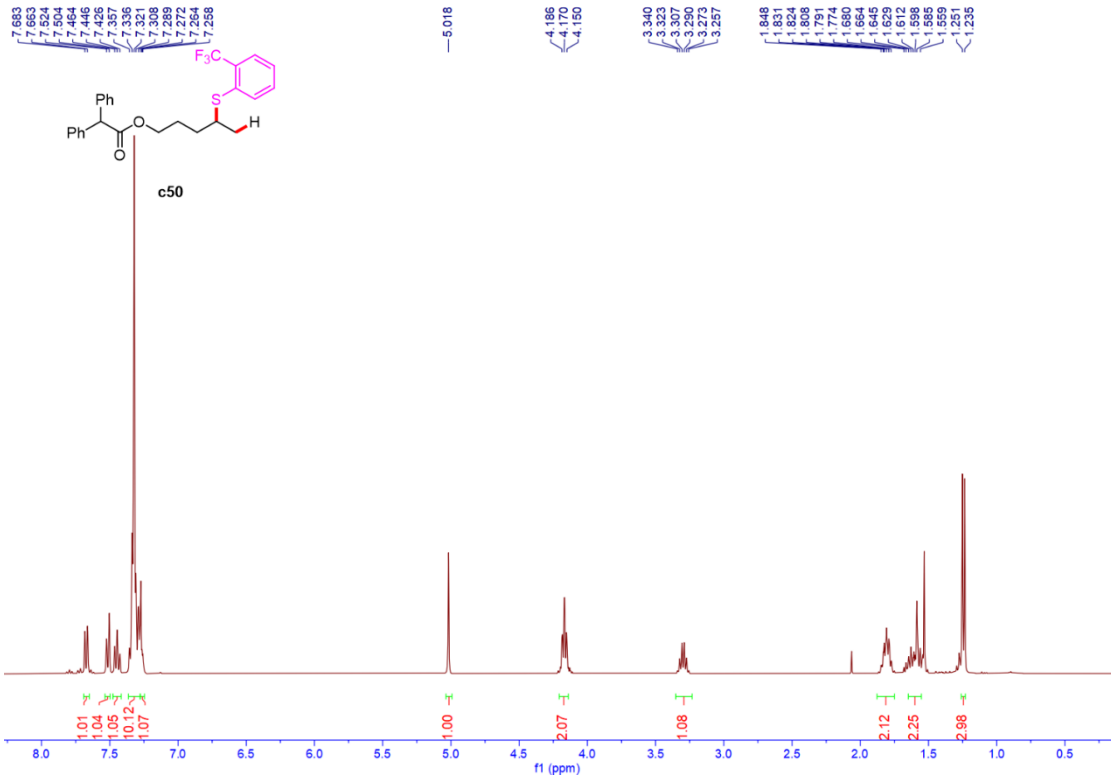

7.445
7.426
7.406
7.374
7.352
7.341
7.307
7.298
7.286
7.273
7.251
7.110
7.090
7.073
7.064
5.044
4.202
4.186
4.163
3.284
3.268
3.251
3.234
3.218
3.201
1.869
1.852
1.833
1.815
1.798
1.618
1.601
1.583
1.565
1.534
1.516
1.498
1.481
1.238
1.221
1.07
8.08
3.15
1.99
0.97
2.08
1.00
2.07
2.13
3.07
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

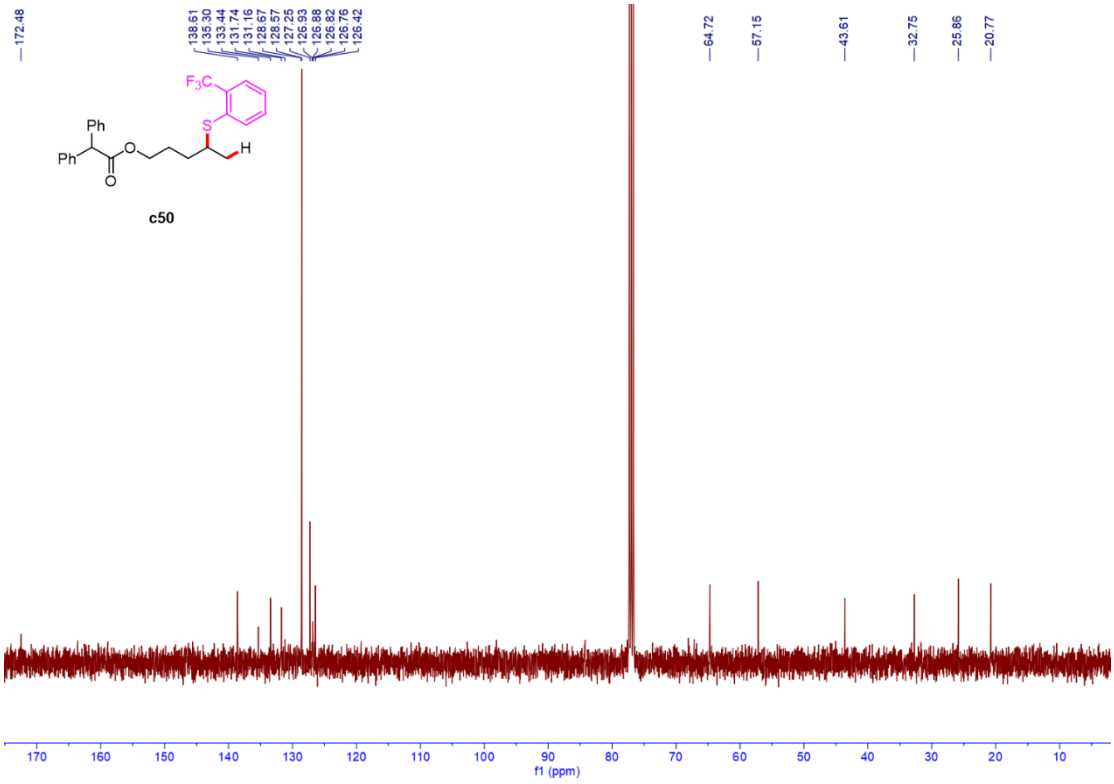
Ph
Ph
O
O
S
F
H

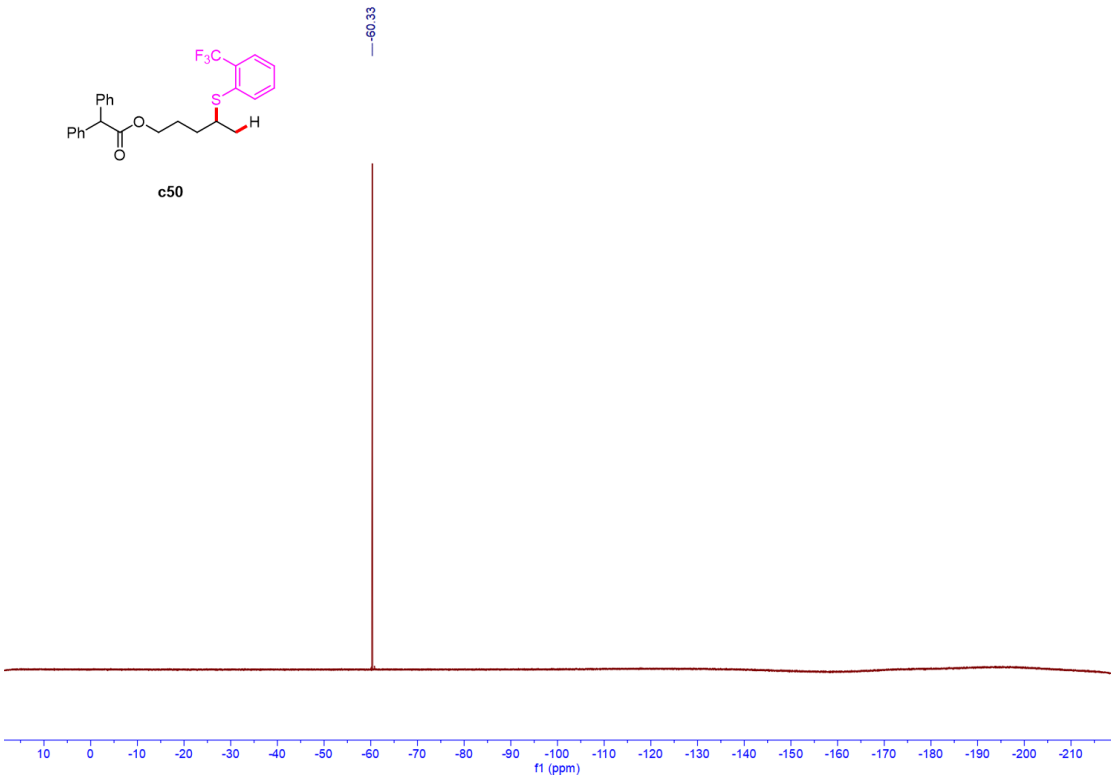
c49

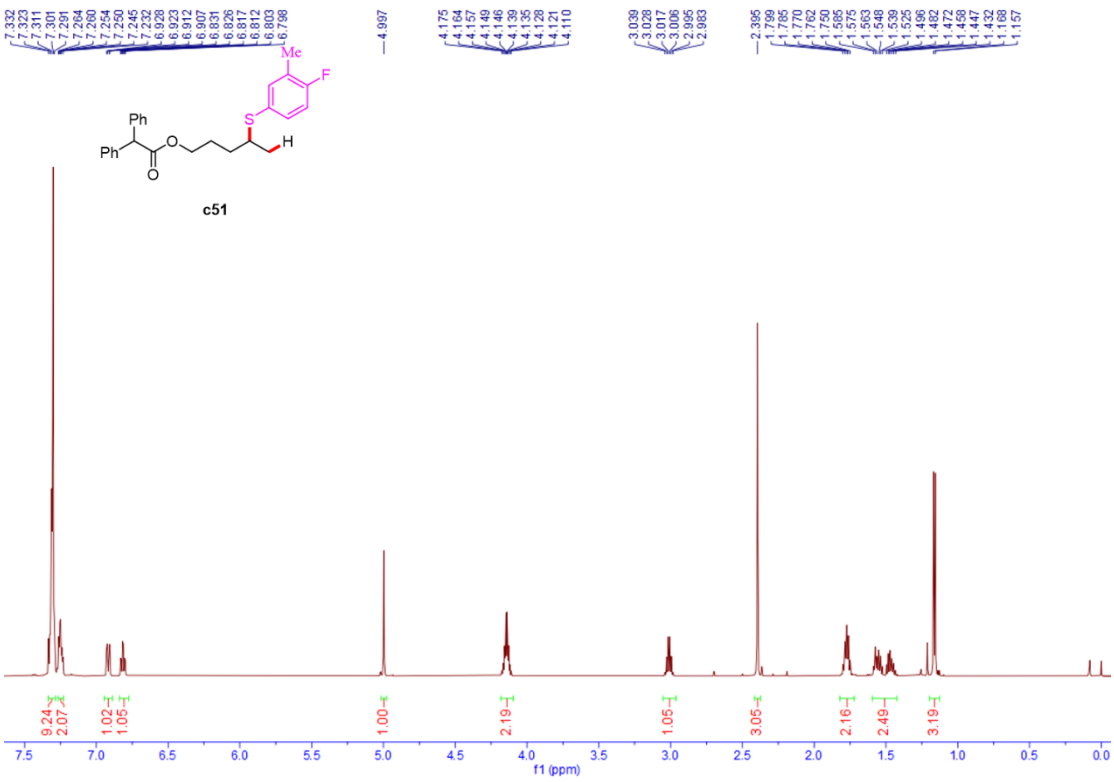

172.50
163.72
161.28
138.68
135.24
129.51
129.43
128.62
127.29
124.39
124.35
121.68
121.50
115.95
115.72
64.87
57.16
42.60
42.58
32.94
25.94
21.14
F
S
Ph
Ph
O
O
H
c49
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

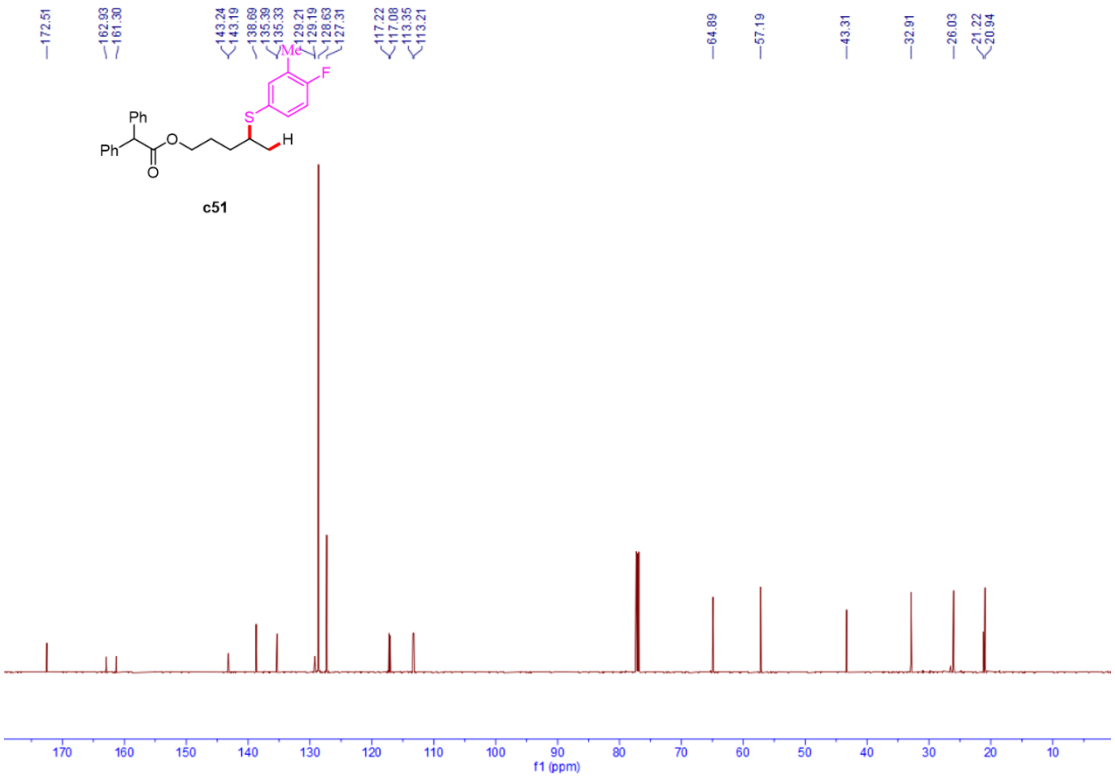

-107.64
F
S
Ph
Ph
O
O
H
c49
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

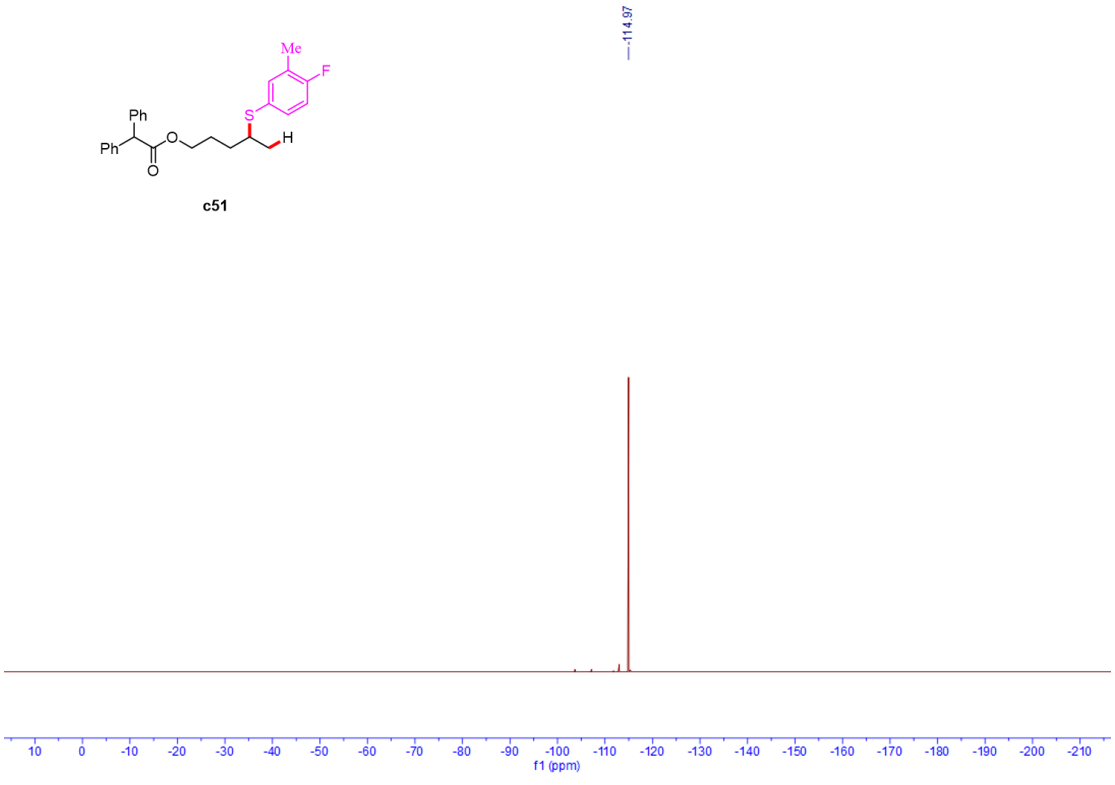

7.683
7.663
7.524
7.504
7.444
7.426
7.357
7.336
7.321
7.308
7.289
7.272
7.264
7.258
5.018
4.186
4.170
4.150
3.340
3.323
3.307
3.290
3.273
3.257
1.848
1.831
1.824
1.808
1.791
1.774
1.680
1.664
1.645
1.629
1.612
1.598
1.585
1.559
1.251
1.235
F3C
S
Ph
Ph
O
O
H
c50
1.01
1.04
1.05
10.12
1.07
1.00
2.07
1.08
2.12
2.25
2.98
f1 (ppm)

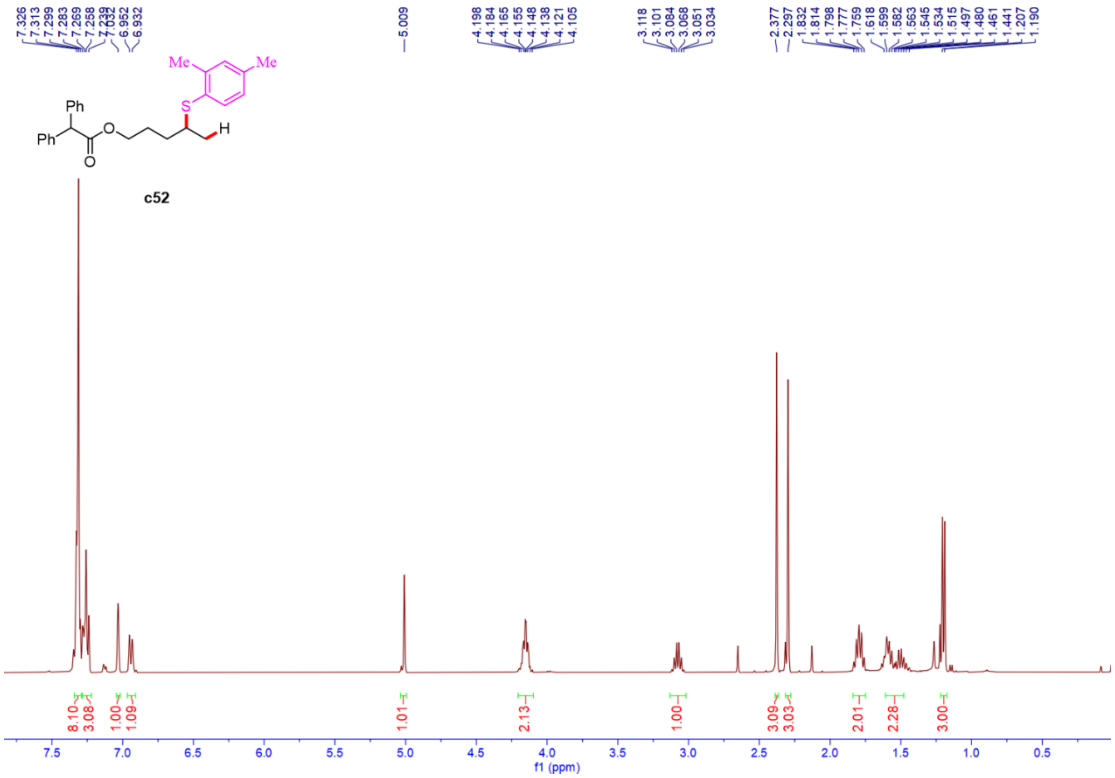

172.48
138.61
135.30
133.44
131.74
131.16
128.67
128.57
127.25
126.93
126.88
126.82
126.76
126.42
64.72
57.15
43.61
32.75
25.86
20.77
F3C
S
Ph
Ph
O
O
H
c50
f1 (ppm)

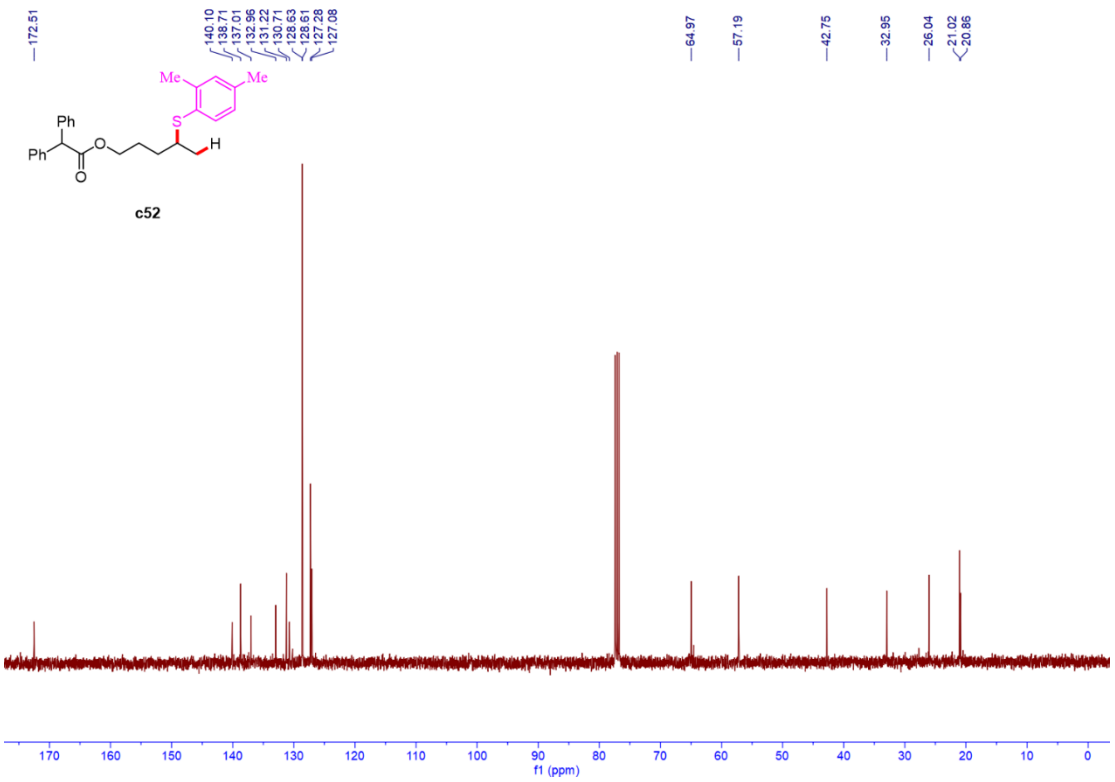

F3C
S
Ph
Ph
O
O
H
c50
-60.33
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

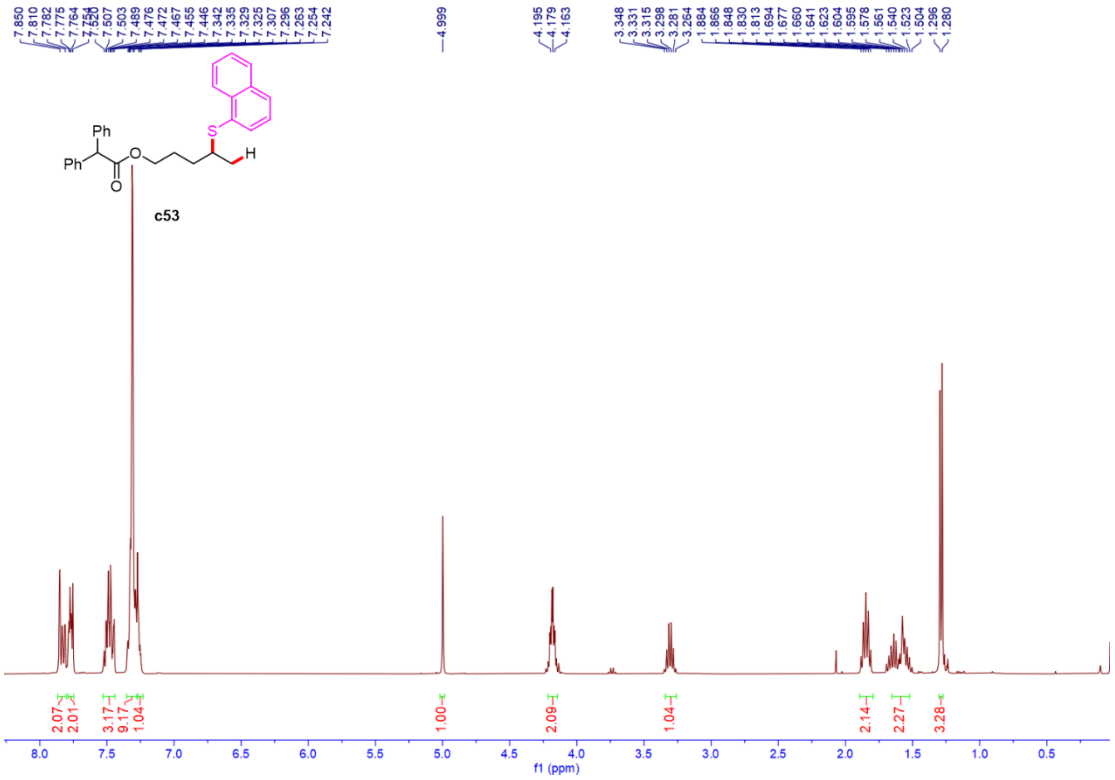

7.332 7.323 7.311 7.301 7.291 7.264 7.260 7.254 7.250 7.245 7.232 6.928 6.923 6.912 6.907 6.831 6.826 6.817 6.812 6.803 6.798
4.997
4.175 4.164 4.157 4.149 4.146 4.139 4.135 4.128 4.121 4.110
3.039 3.028 3.017 3.006 2.995 2.983
2.395 1.799 1.785 1.770 1.762 1.750 1.585 1.575 1.563 1.548 1.539 1.525 1.496 1.482 1.472 1.458 1.447 1.432 1.168 1.157
Me
F
S
Ph
Ph
O
O
H
c51
9.24 2.07 1.02 1.05 1.00 2.19 1.05 3.05 2.16 2.49 3.19
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

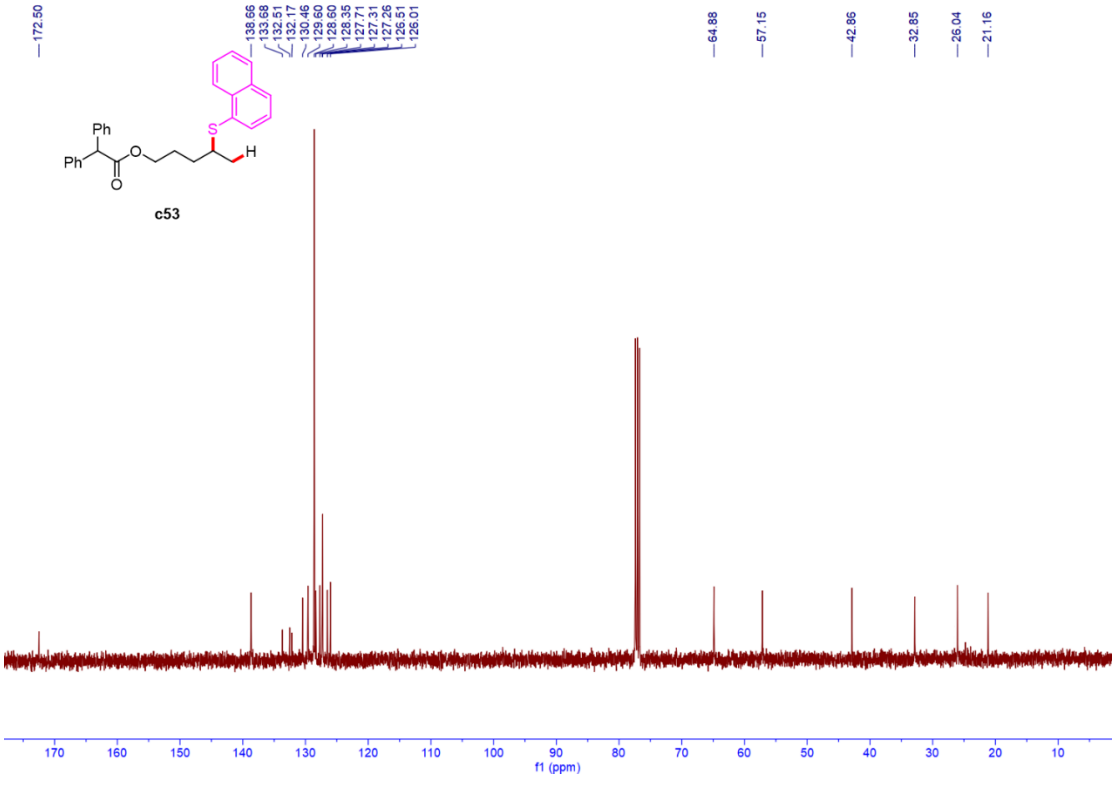

172.51
162.93
161.30
143.24
143.19
138.69
135.39
135.33
129.21
129.19
128.63
127.31
117.22
117.08
113.35
113.21
64.89
57.19
43.31
32.91
26.03
21.22
20.94
Me
F
S
H
Ph
Ph
O
O
c51
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

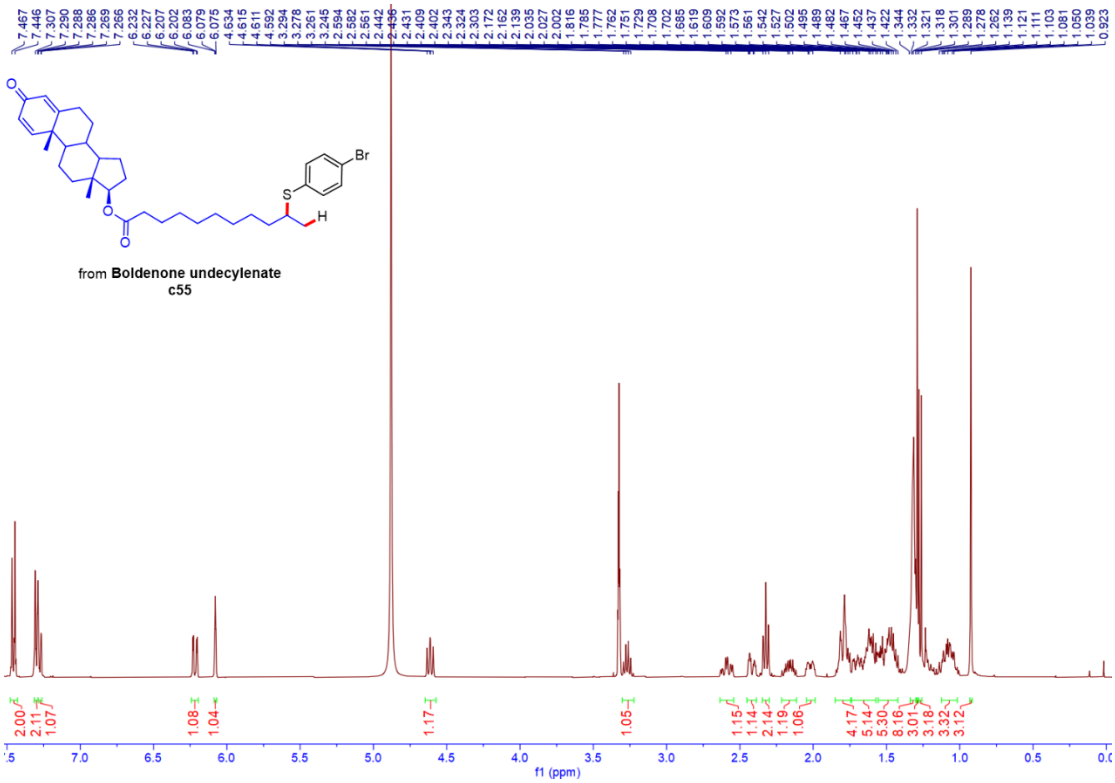

114.97
Me
F
S
H
Ph
Ph
O
O
c51
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

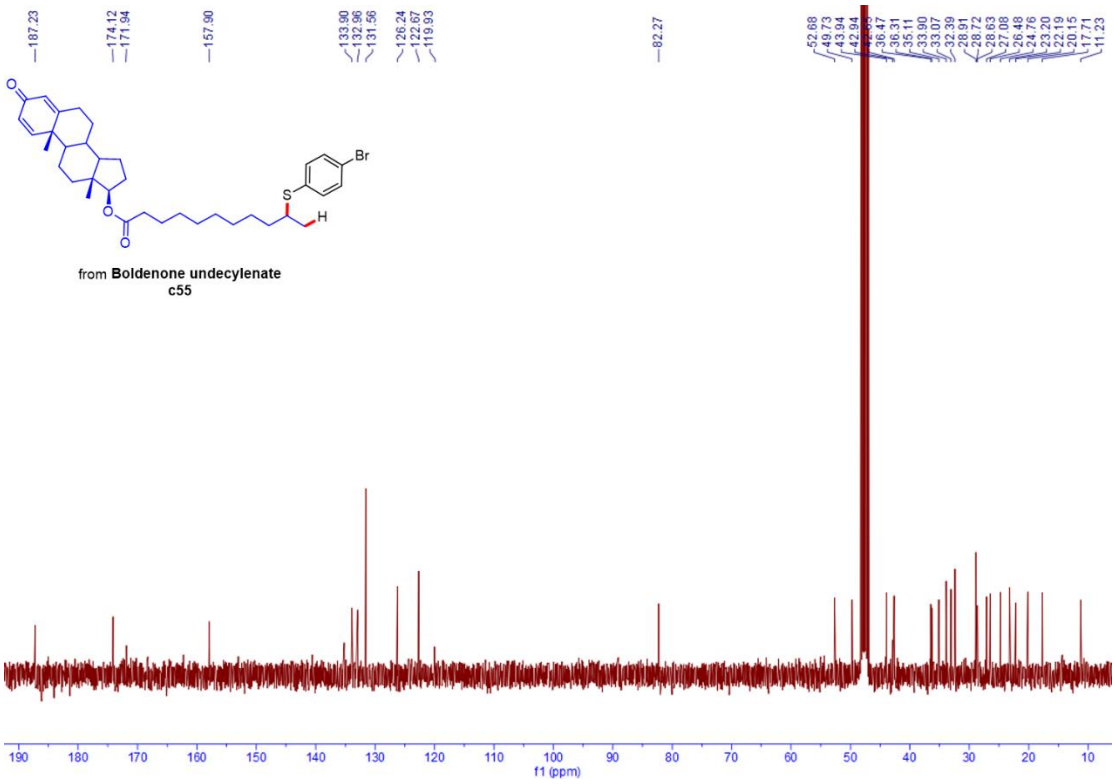

7.326
7.313
7.299
7.283
7.269
7.258
7.039
6.952
6.932
5.009
4.198
4.184
4.165
4.155
4.148
4.138
4.121
4.105
3.118
3.101
3.084
3.068
3.051
3.034
2.377
2.297
1.832
1.814
1.798
1.777
1.759
1.618
1.599
1.582
1.563
1.545
1.534
1.515
1.497
1.480
1.461
1.441
1.207
1.190
Me
Me
S
H
Ph
Ph
O
O
c52
8.10
3.08
1.00
1.09
1.01
2.13
1.00
3.09
3.03
2.01
2.28
3.00
f1 (ppm)

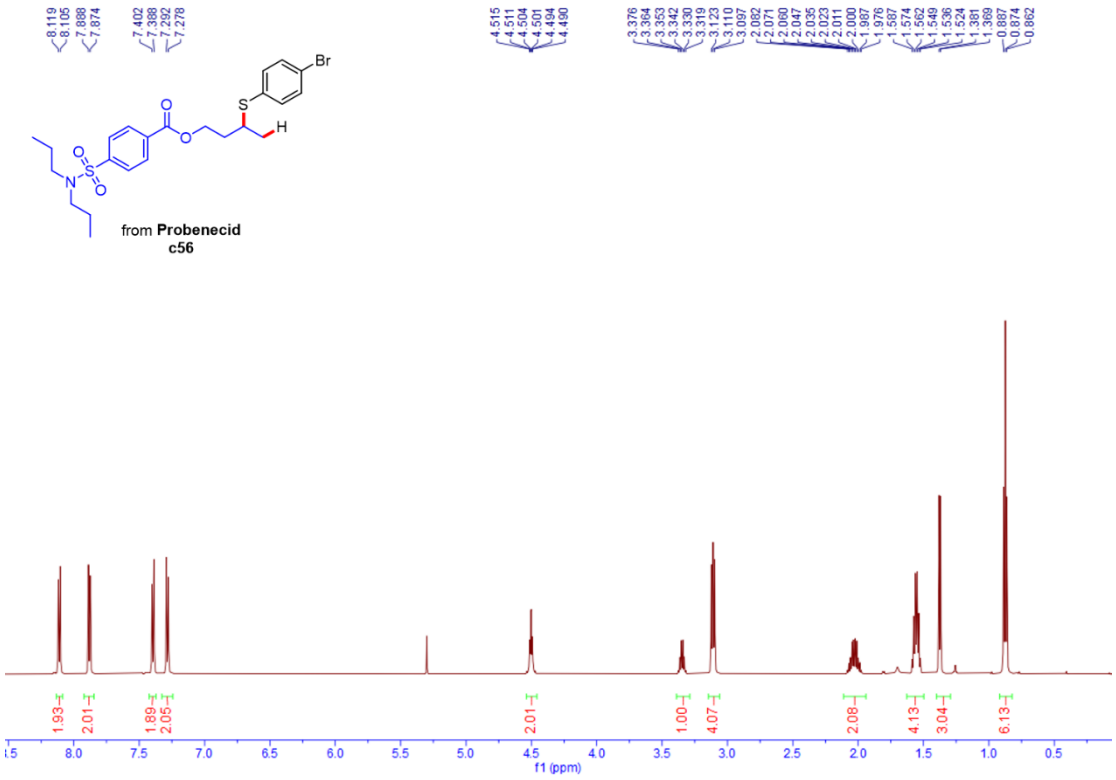

172.51
140.10
138.71
137.01
132.96
131.22
130.71
128.63
128.61
127.28
127.08
64.97
57.19
42.75
32.95
26.04
21.02
20.86
Me
Me
S
H
Ph
Ph
O
O
c52
f1 (ppm)

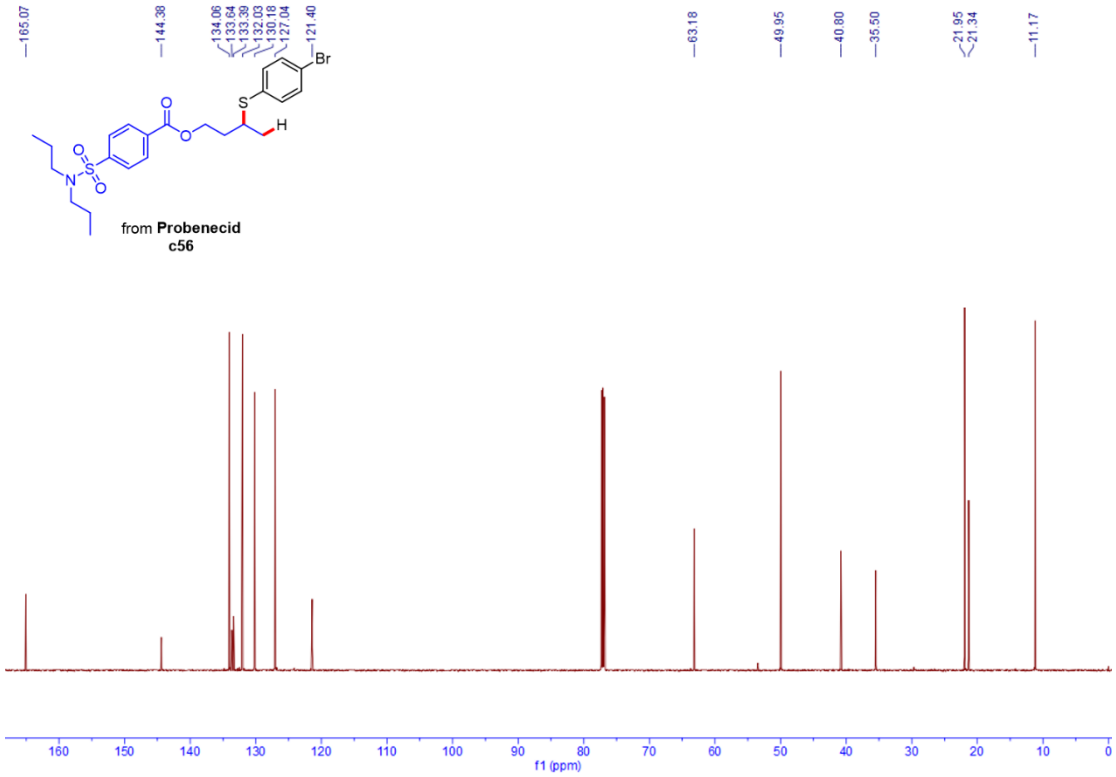

7.850
7.810
7.782
7.775
7.764
7.524
7.507
7.503
7.489
7.476
7.472
7.467
7.455
7.446
7.342
7.335
7.329
7.325
7.307
7.296
7.263
7.254
7.242
4.999
4.195
4.179
4.163
3.348
3.331
3.315
3.298
3.281
3.264
1.884
1.865
1.848
1.830
1.813
1.694
1.677
1.660
1.641
1.623
1.604
1.595
1.578
1.561
1.540
1.523
1.504
1.296
1.280
Ph
Ph
O
O
S
H
c53
2.07
2.01
3.17
9.17
1.04
1.00
2.09
1.04
2.14
2.27
3.28
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

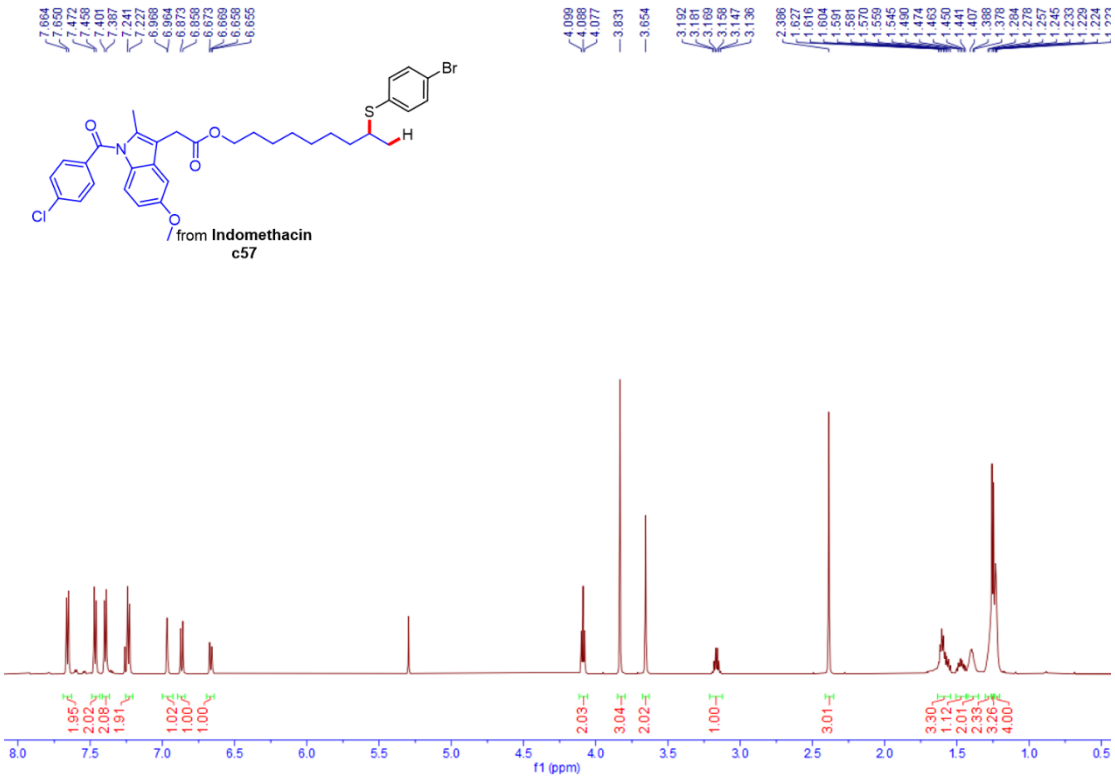

172.50
138.66
133.68
132.51
132.17
130.46
129.60
128.60
128.35
127.71
127.31
127.26
126.51
126.01
64.88
57.15
42.86
32.85
26.04
21.16
Ph
Ph
O
O
S
H
c53
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

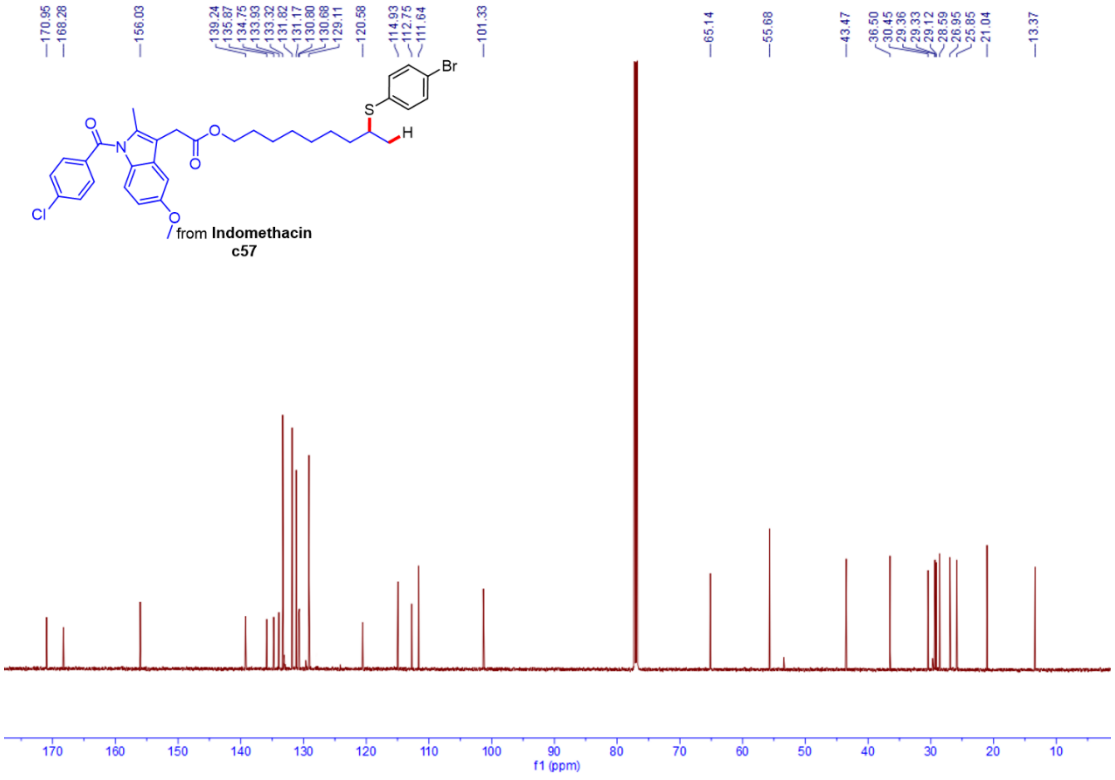

Br
S
H
O
O
from Boldenone undecylenate
c55
f1 (ppm)

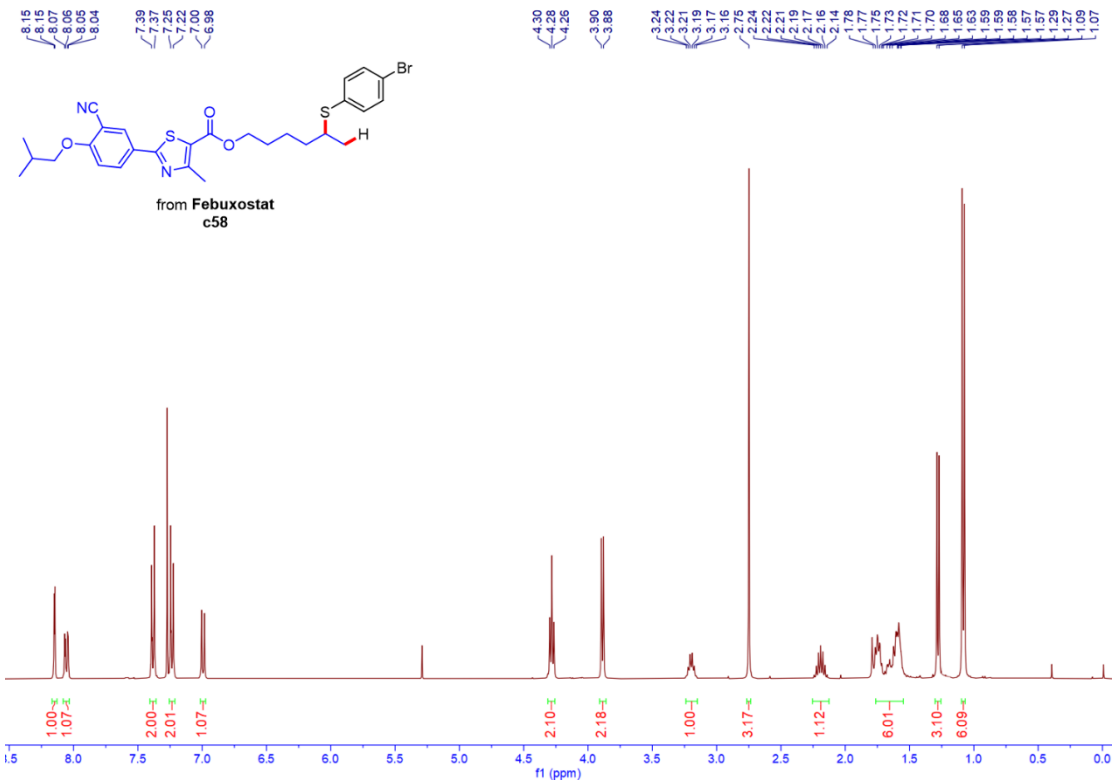

Br
S
H
O
O
from Boldenone undecylenate
c55
f1 (ppm)

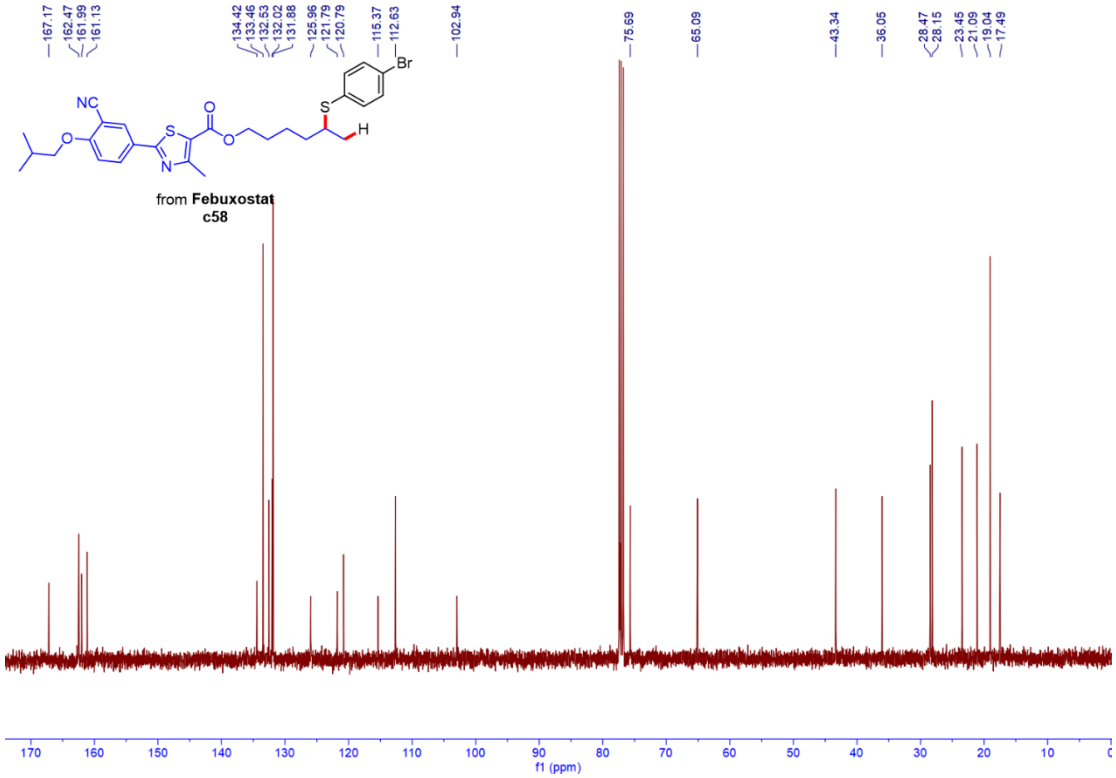

8.119
8.105
7.888
7.874
7.402
7.388
7.292
7.278
4.515
4.511
4.504
4.501
4.494
4.490
3.376
3.364
3.353
3.342
3.330
3.319
3.123
3.110
3.097
2.082
2.071
2.060
2.047
2.035
2.023
2.011
2.000
1.987
1.976
1.587
1.574
1.562
1.549
1.536
1.524
1.381
1.369
0.887
0.874
0.862
Br
S
H
O
O
O
N
O
S
O
from Probenecid
c56
1.93
2.01
1.89
2.05
2.01
1.00
4.07
2.08
4.13
3.04
6.13
f1 (ppm)

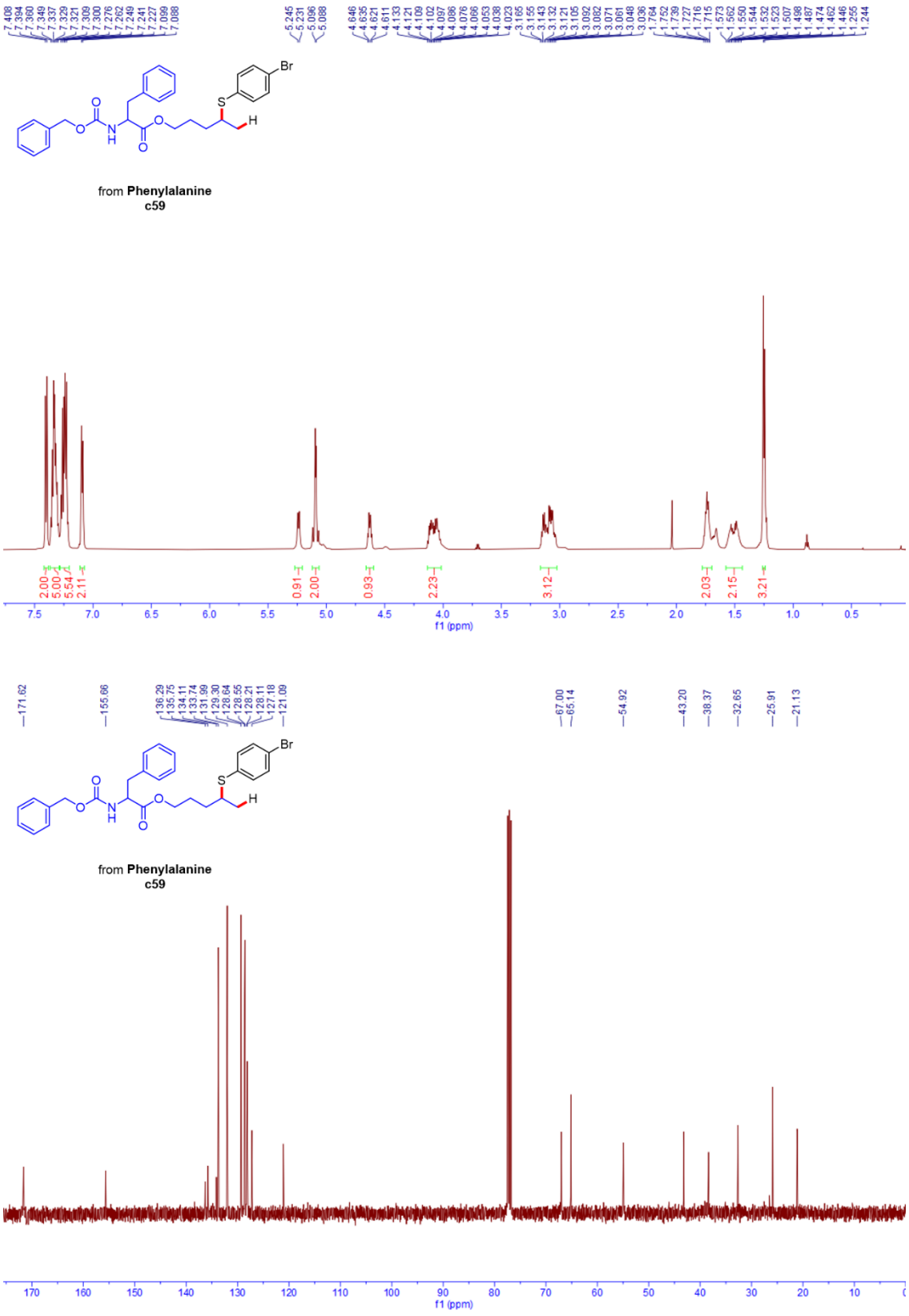

165.07
144.38
134.06
133.84
133.39
132.03
130.18
127.04
121.40
63.18
49.95
40.80
35.50
21.95
21.34
11.17
Br
S
H
O
O
O
N
O
S
O
from Probenecid
c56
f1 (ppm)

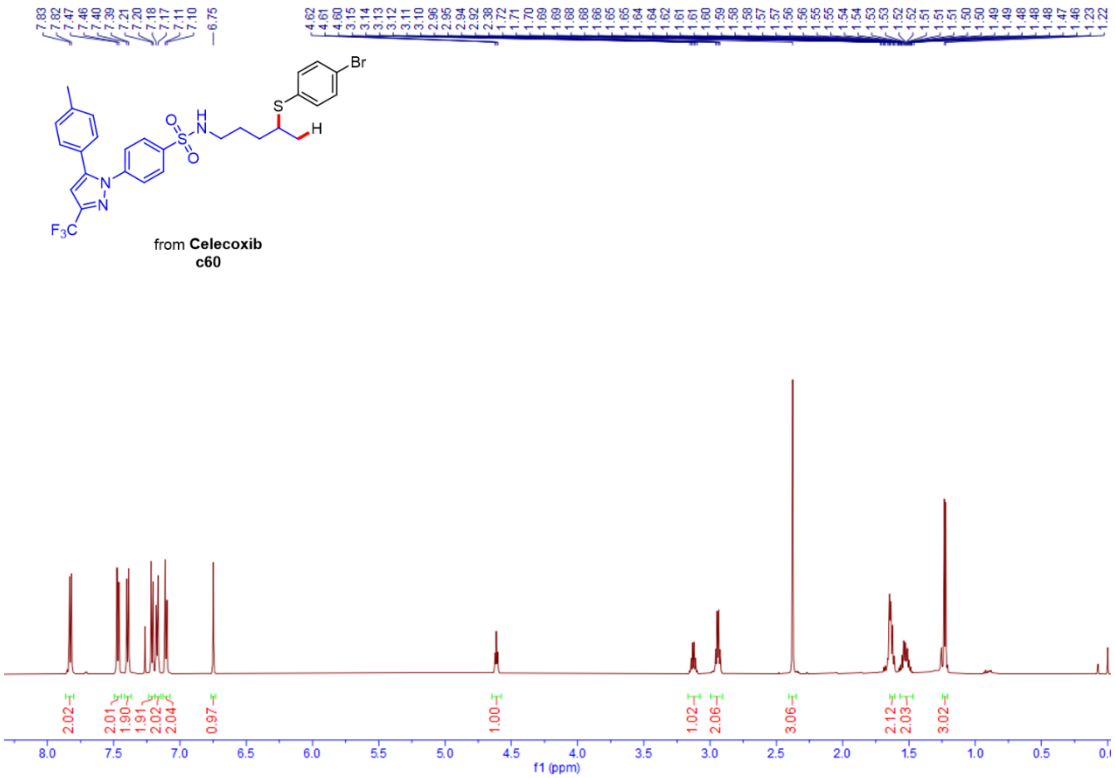

from Indomethacin
c57
f1 (ppm)

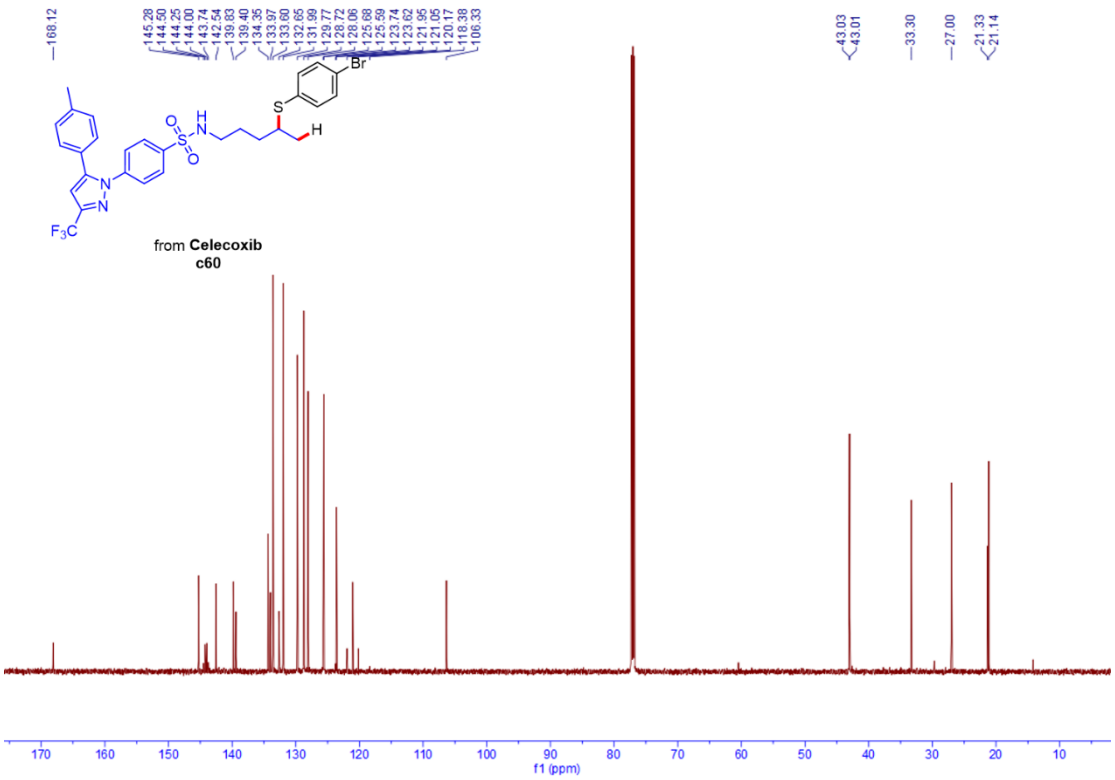

from Indomethacin
c57
f1 (ppm)

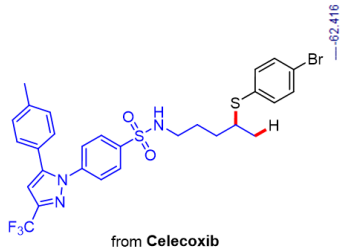

from Febuxostat
c58
f1 (ppm)


from Febuxostat
c58
f1 (ppm)

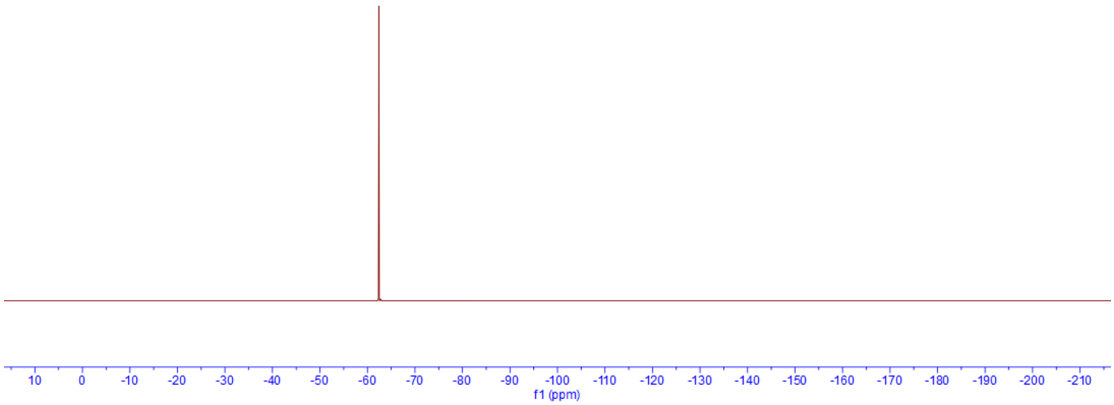

7.408
7.394
7.360
7.349
7.337
7.329
7.321
7.309
7.300
7.276
7.262
7.249
7.241
7.227
7.099
7.088
5.245
5.231
5.096
5.088
4.646
4.635
4.621
4.611
4.133
4.121
4.109
4.102
4.097
4.086
4.076
4.066
4.053
4.038
4.023
3.165
3.155
3.143
3.132
3.121
3.105
3.092
3.082
3.071
3.061
3.048
3.036
1.764
1.752
1.739
1.727
1.716
1.715
1.573
1.562
1.550
1.544
1.532
1.522
1.507
1.498
1.487
1.474
1.462
1.446
1.255
1.244
Br
S
H
O
N
H
O
O
O
from Phenylalanine
c59
2.00
5.00
5.54
2.11
0.91
2.00
0.93
2.23
3.12
2.03
2.15
3.21
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
171.62
155.66
136.29
135.75
134.11
133.74
131.99
129.30
128.64
128.55
128.21
128.11
127.18
121.09
67.00
65.14
54.92
43.20
38.37
32.65
25.91
21.13
Br
S
H
O
N
H
O
O
O
from Phenylalanine
c59
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

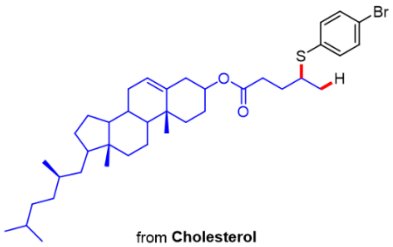

from Celecoxib
c60
f1 (ppm)


from Celecoxib
c60
f1 (ppm)

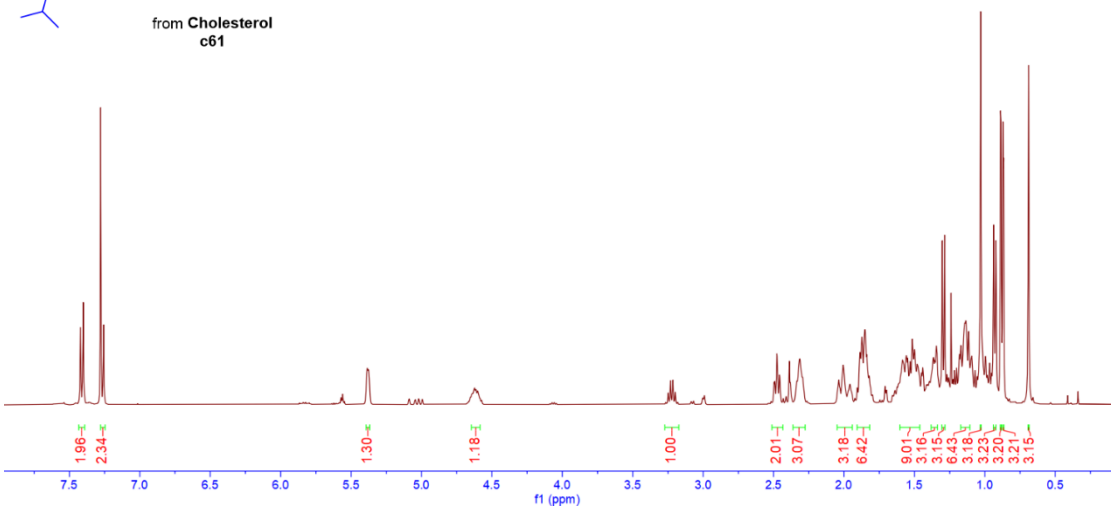


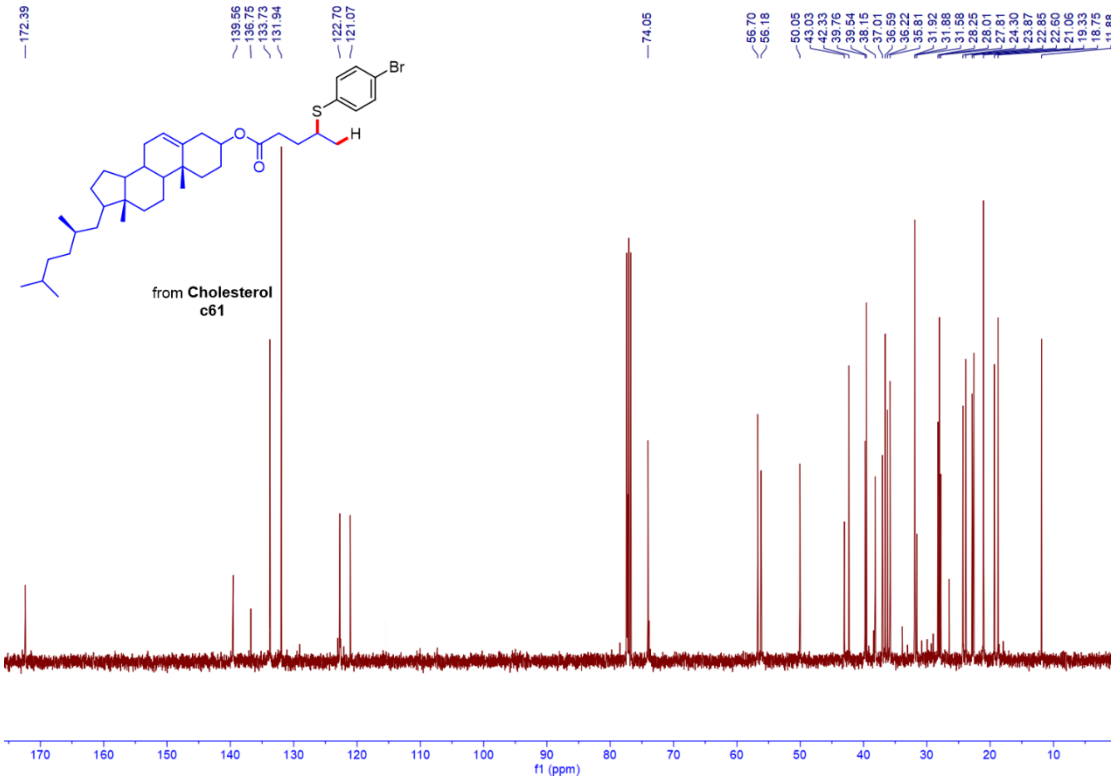
from **Celecoxib**
c60

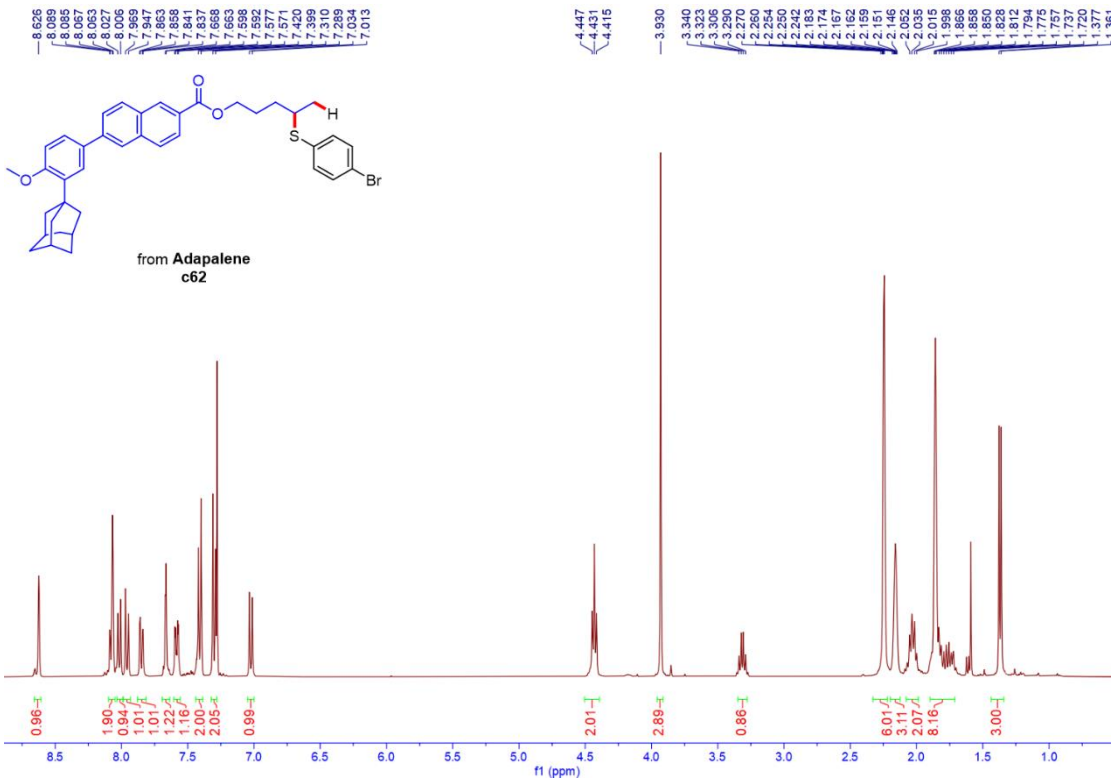


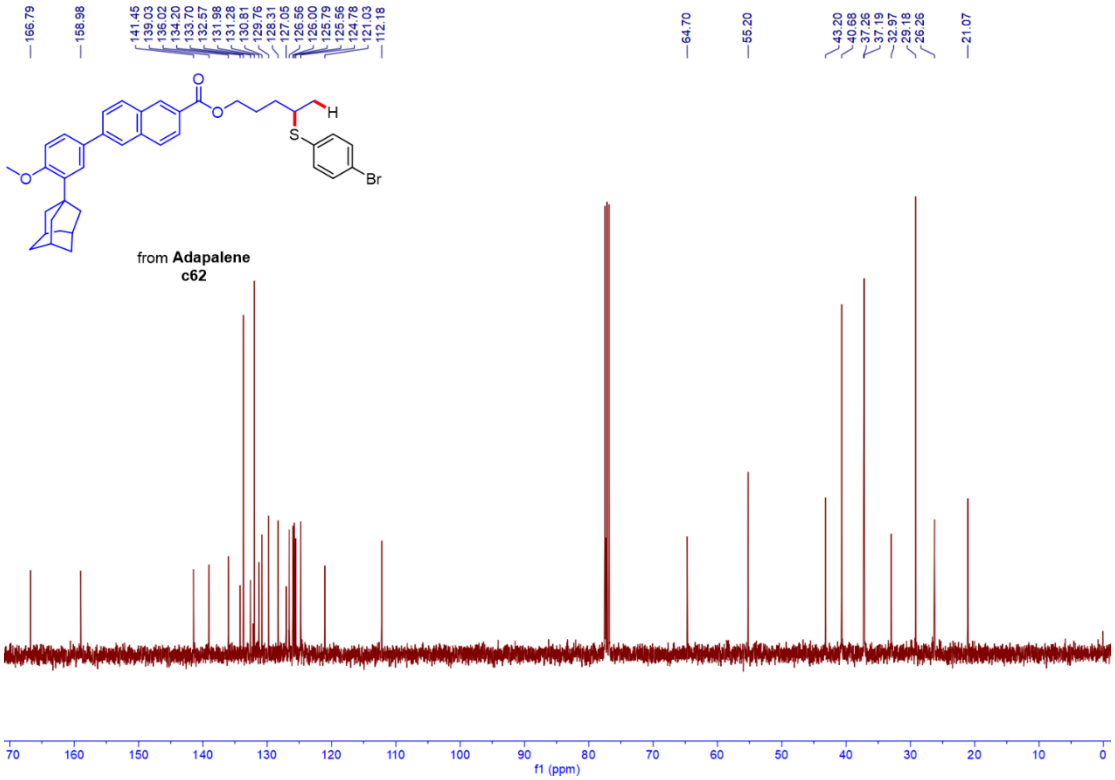


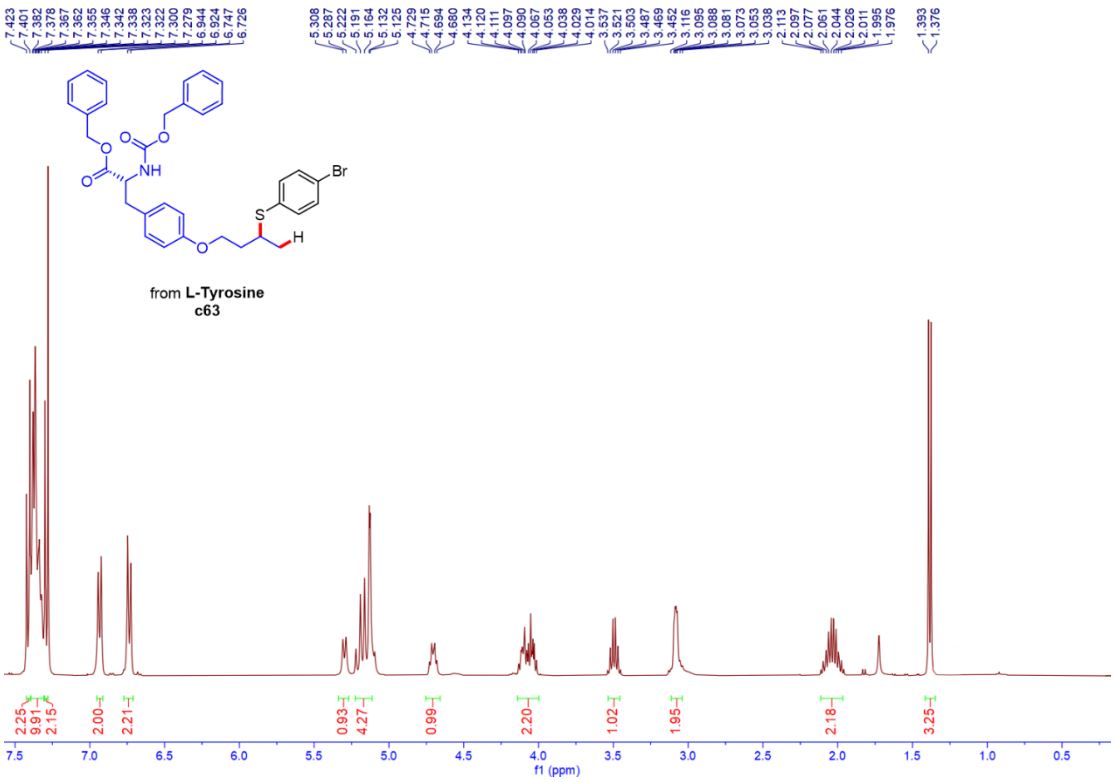
from **Cholesterol**
c61

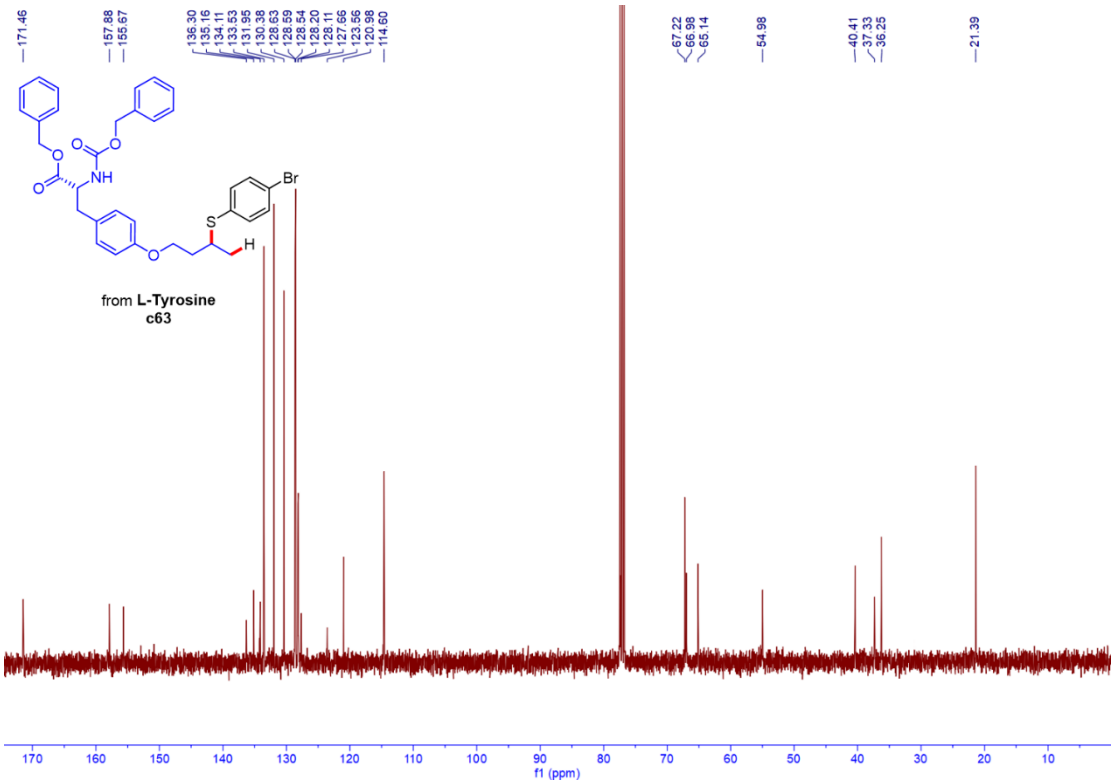


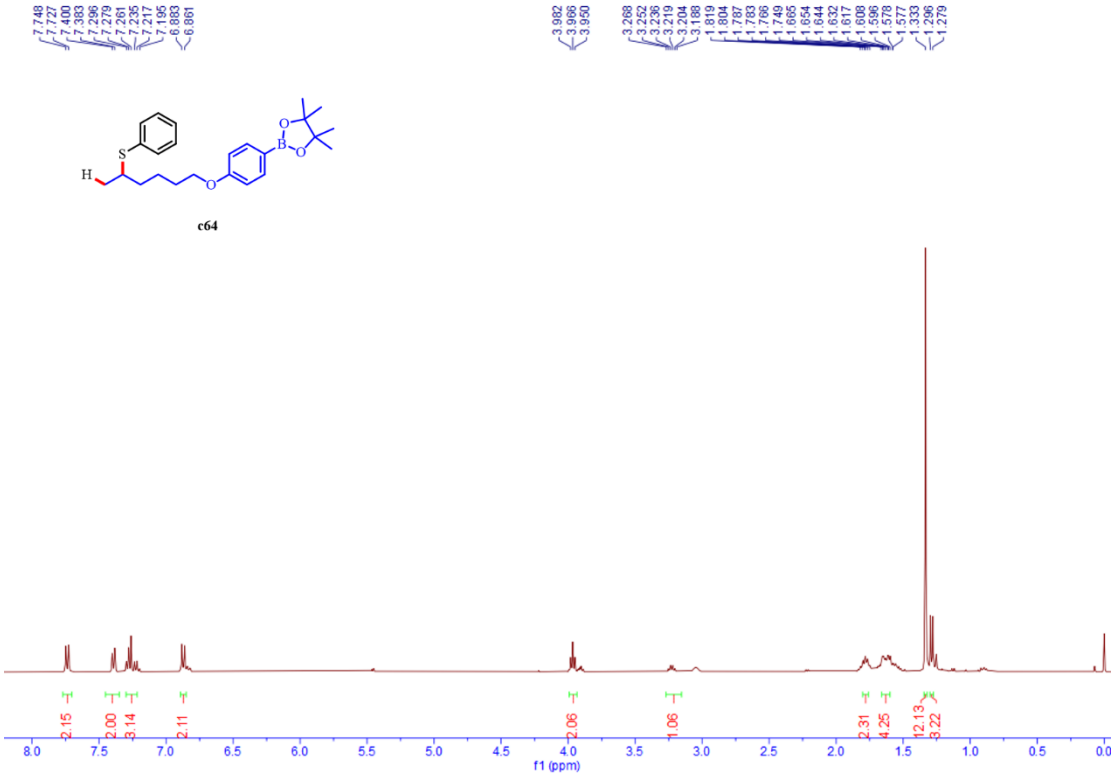

from Cholesterol
c61
f1 (ppm)

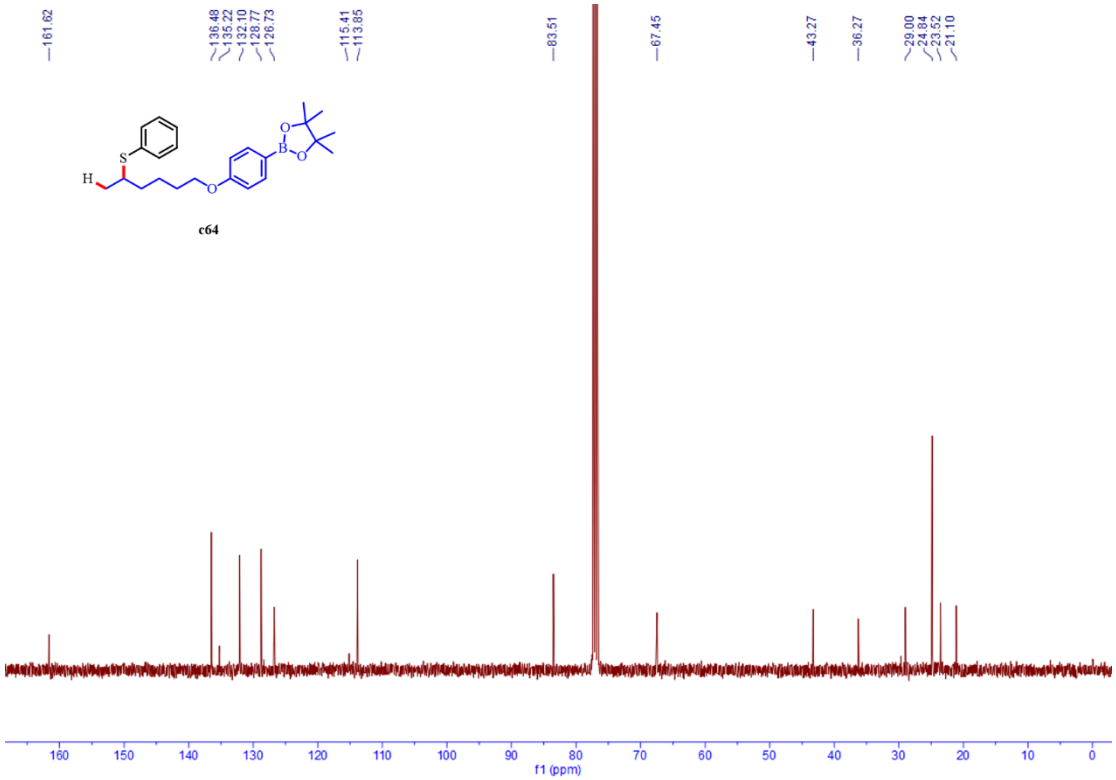

from Adapalene
c62
f1 (ppm)


166.79
158.98
141.45
139.03
136.02
134.20
133.70
132.57
131.98
131.28
130.81
129.76
128.31
127.05
126.56
126.00
125.79
125.56
124.78
121.03
112.18
64.70
55.20
43.20
40.68
37.26
37.19
32.97
29.18
26.26
21.07
O
O
H
S
Br
O
from Adapalene
c62
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

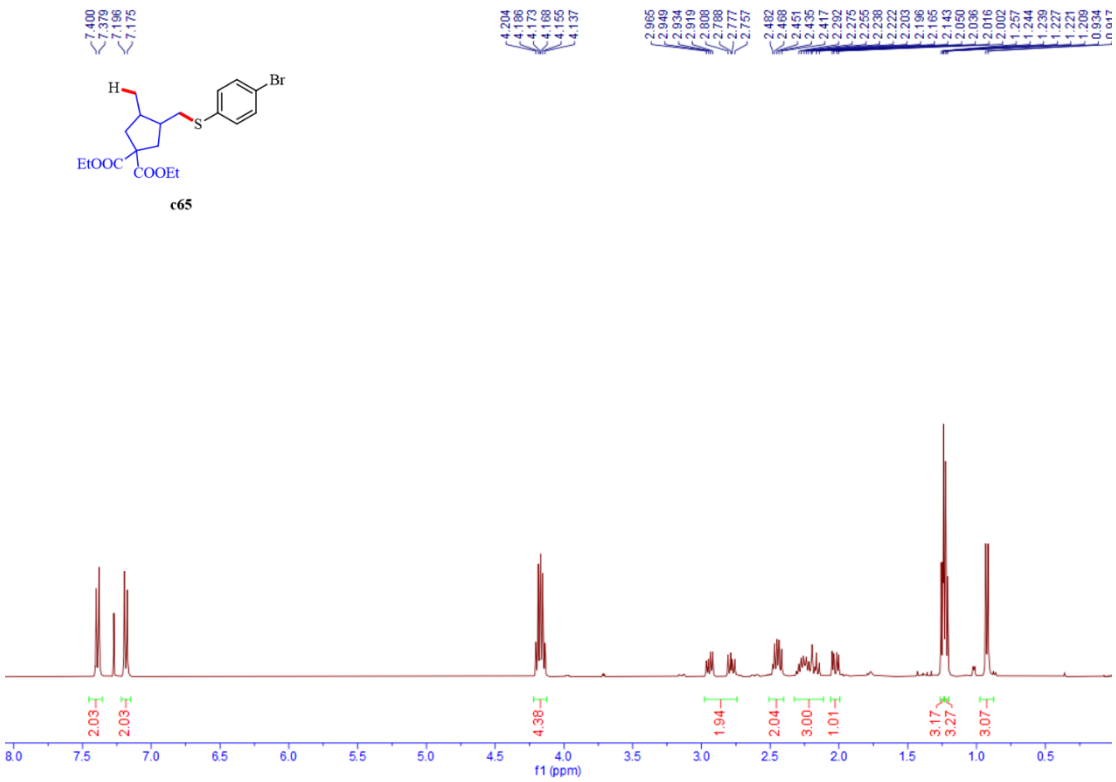

7.423
7.401
7.382
7.378
7.367
7.362
7.355
7.346
7.342
7.338
7.323
7.322
7.300
7.279
6.944
6.924
6.747
6.726
5.308
5.287
5.222
5.191
5.164
5.132
5.125
4.729
4.715
4.694
4.680
4.134
4.120
4.111
4.097
4.090
4.067
4.053
4.038
4.029
4.014
4.007
3.521
3.503
3.487
3.469
3.452
3.116
3.095
3.088
3.081
3.073
3.053
3.038
2.113
2.097
2.077
2.061
2.044
2.026
2.011
1.995
1.976
1.393
1.376
O
O
O
O
NH
Br
S
H
from L-Tyrosine
c63
2.25
9.91
2.15
2.00
2.21
0.93
4.27
0.99
2.20
1.02
1.95
2.18
3.25
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


171.46
157.88
155.67
136.30
135.16
134.11
133.53
131.95
130.38
128.63
128.59
128.54
128.20
128.11
127.66
123.56
120.98
114.60
67.22
66.98
65.14
54.98
40.41
37.33
36.25
21.39
Br
S
H
NH
O
from L-Tyrosine
c63
f1 (ppm)

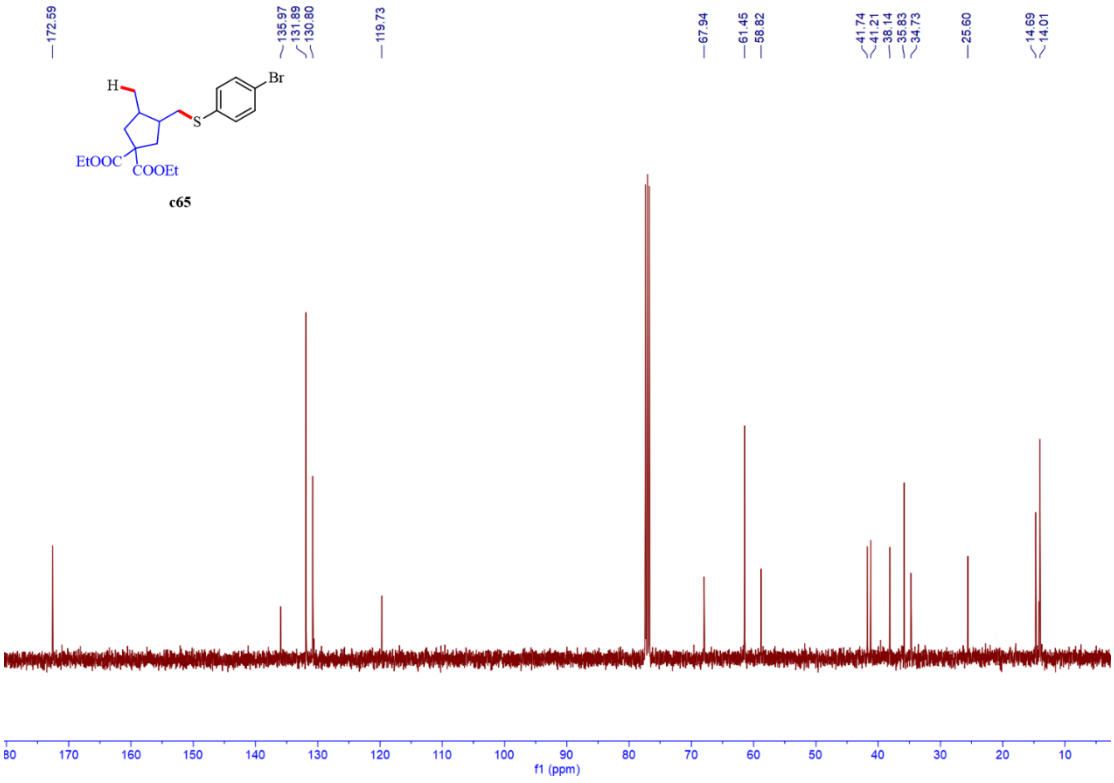

7.748
7.727
7.400
7.383
7.296
7.279
7.261
7.235
7.217
7.195
6.883
6.861
3.982
3.966
3.950
3.268
3.252
3.236
3.219
3.204
3.188
1.819
1.804
1.787
1.783
1.766
1.749
1.665
1.654
1.644
1.632
1.617
1.608
1.596
1.578
1.577
1.333
1.296
1.279
S
H
O
B
c64
2.15
2.00
3.14
2.11
2.06
1.06
2.31
4.25
12.13
3.22
f1 (ppm)


161.62
136.48
135.22
132.10
128.77
126.73
115.41
113.85
83.51
67.45
43.27
36.27
29.00
24.84
23.52
21.10
f1 (ppm)

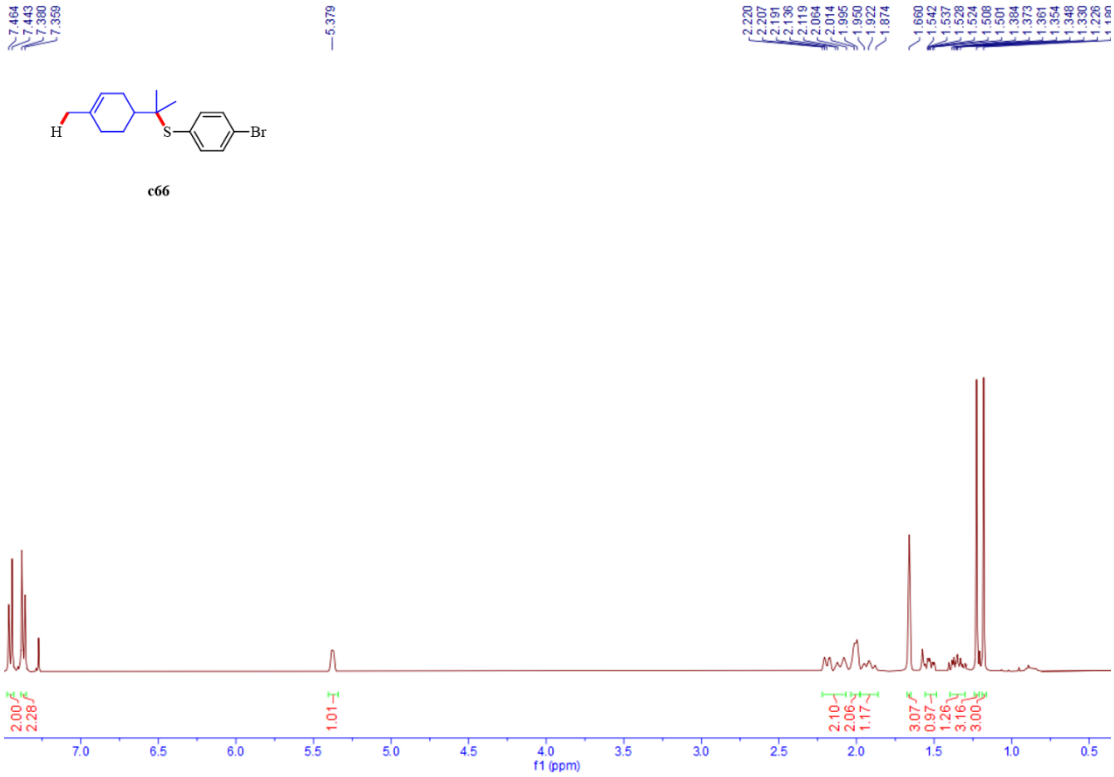
c64


7.400
7.379
7.196
7.175
4.204
4.186
4.173
4.168
4.155
4.137
2.965
2.949
2.934
2.919
2.808
2.788
2.777
2.757
2.482
2.468
2.451
2.435
2.417
2.292
2.275
2.255
2.238
2.222
2.203
2.196
2.165
2.143
2.050
2.036
2.016
2.002
1.257
1.244
1.239
1.227
1.221
1.209
0.934
2.03
2.03
4.38
1.94
2.04
3.00
1.01
3.17
3.27
3.07
f1 (ppm)

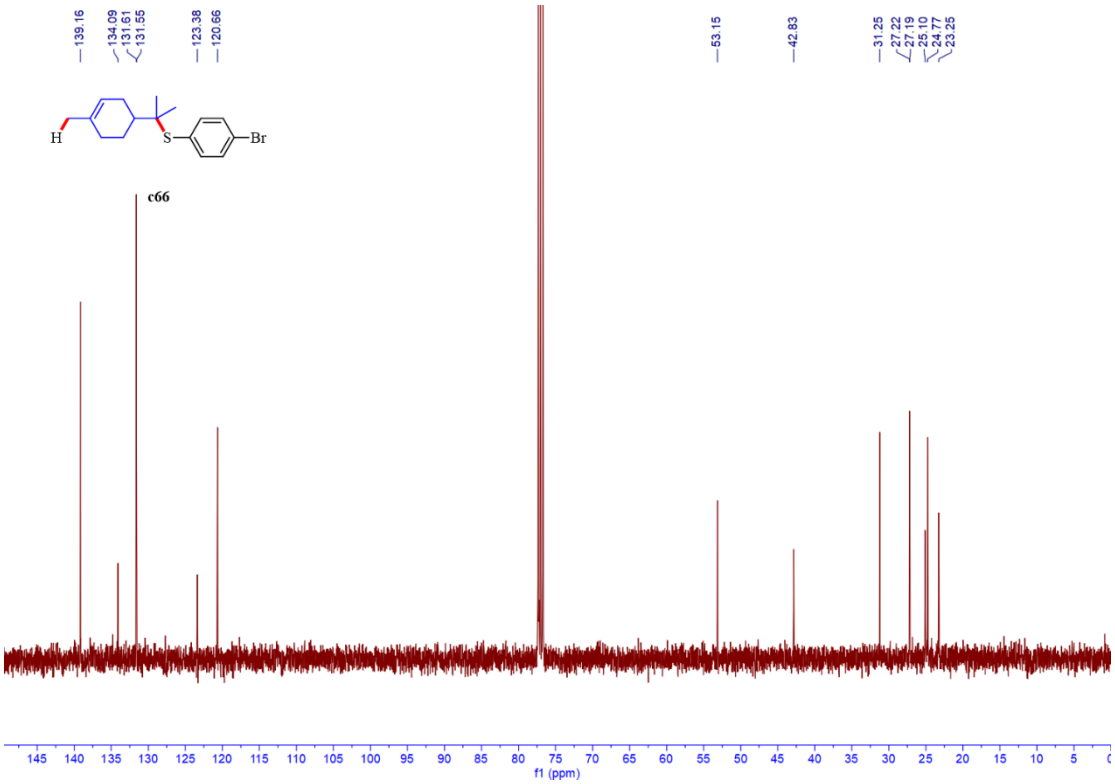
c65


172.59
135.97
131.89
130.80
119.73
67.94
61.45
58.82
41.74
41.21
38.14
35.83
34.73
25.60
14.69
14.01
H
Br
S
EtOOC
COOEt
f1 (ppm)

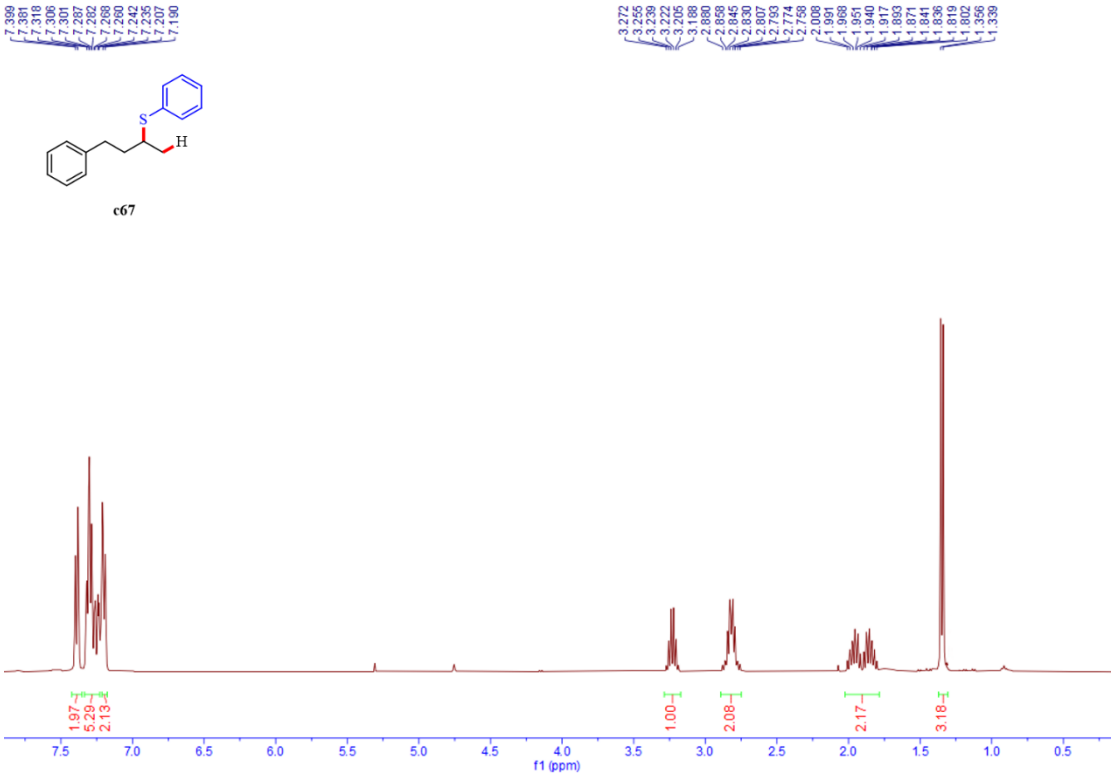
c65


7.464
7.443
7.380
7.359
5.379
2.220
2.207
2.191
2.136
2.119
2.064
2.014
1.995
1.950
1.922
1.874
1.660
1.542
1.537
1.528
1.524
1.508
1.501
1.384
1.373
1.361
1.354
1.348
1.330
1.226
H
S
Br
2.00
2.28
1.01
2.10
2.06
1.17
3.07
0.97
1.26
3.16
3.00
f1 (ppm)

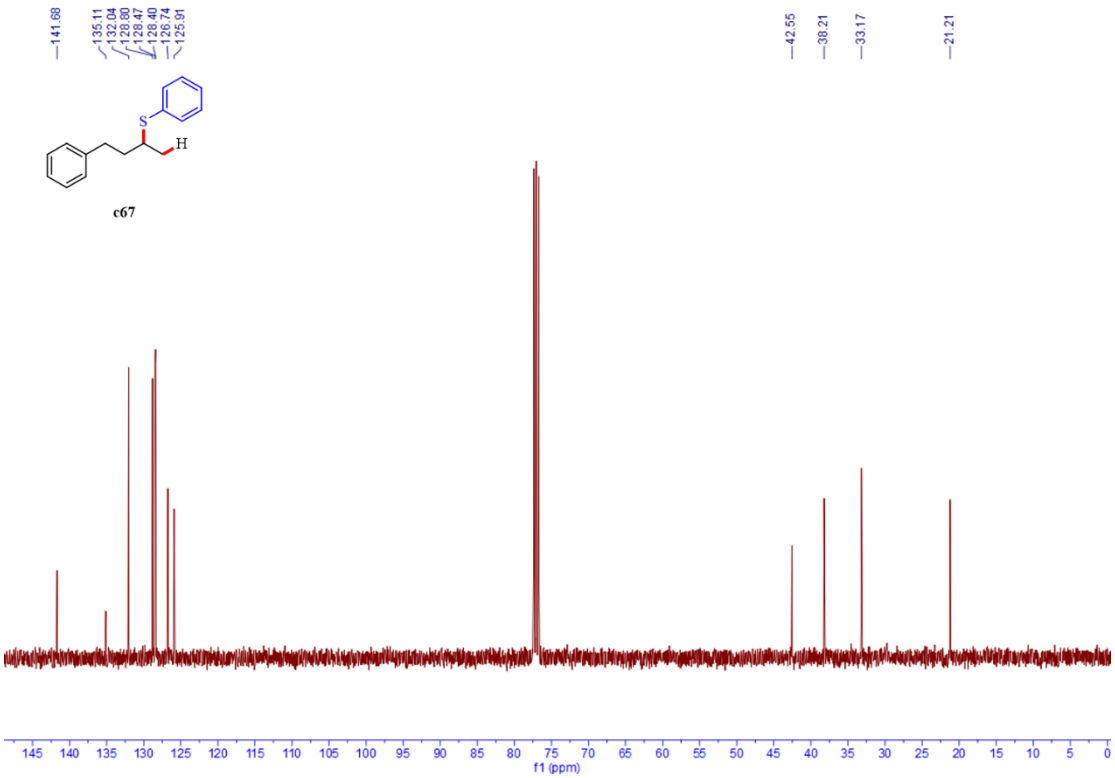
c66

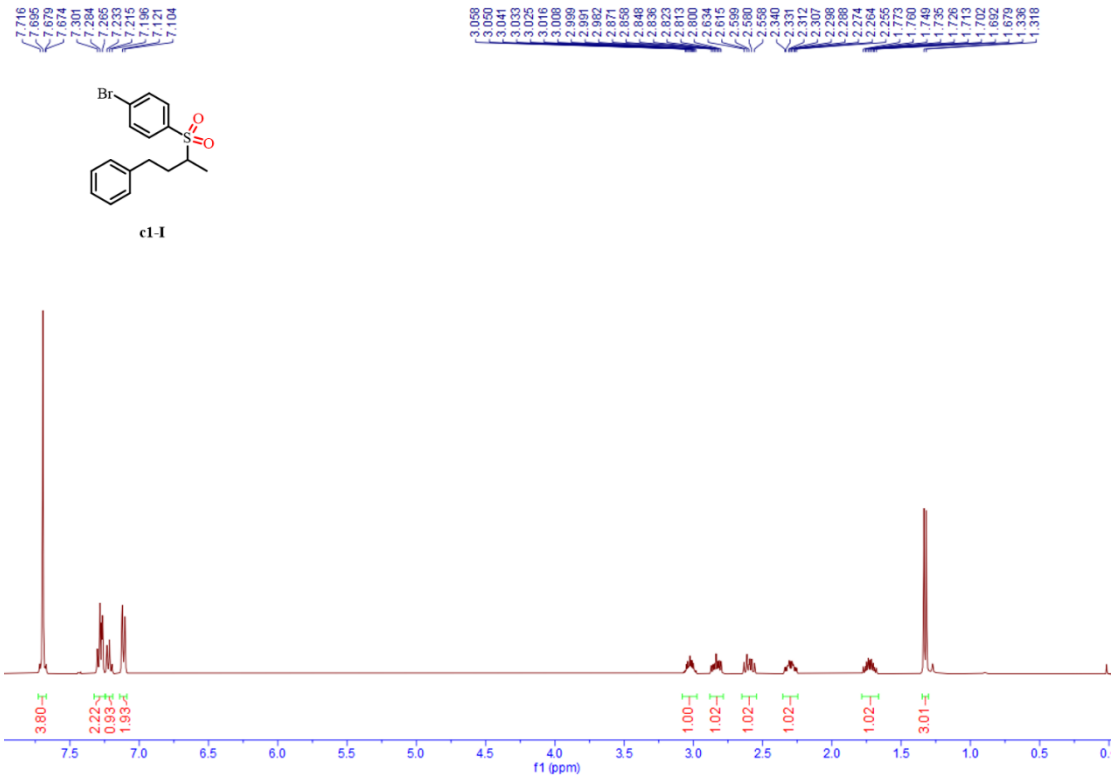

139.16
134.09
131.61
131.55
123.38
120.66
53.15
42.83
31.25
27.22
27.19
25.10
24.77
23.25
H
S
Br
f1 (ppm)

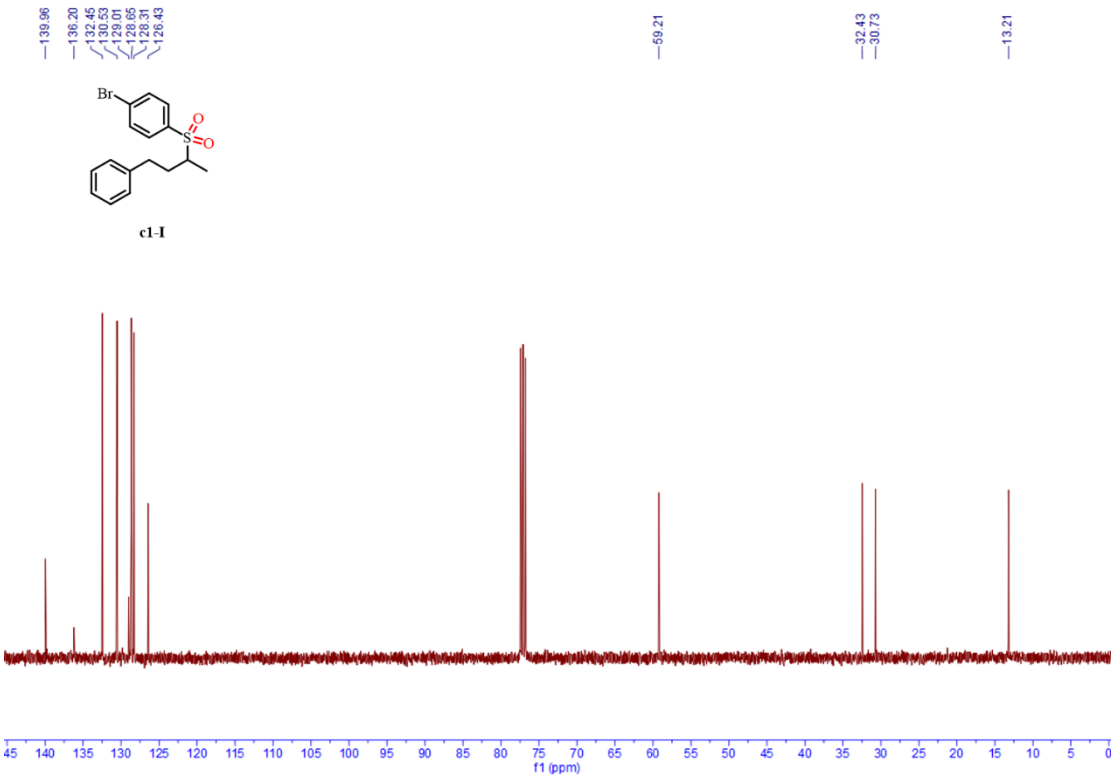
c66


7.399
7.381
7.318
7.306
7.301
7.287
7.282
7.268
7.260
7.242
7.235
7.207
7.190
3.272
3.255
3.239
3.222
3.205
3.188
2.880
2.858
2.845
2.830
2.807
2.793
2.774
2.758
2.008
1.991
1.968
1.951
1.940
1.917
1.893
1.871
1.841
1.836
1.819
1.802
1.356
1.339
S
H
1.97
5.29
2.13
1.00
2.08
2.17
3.18
f1 (ppm)

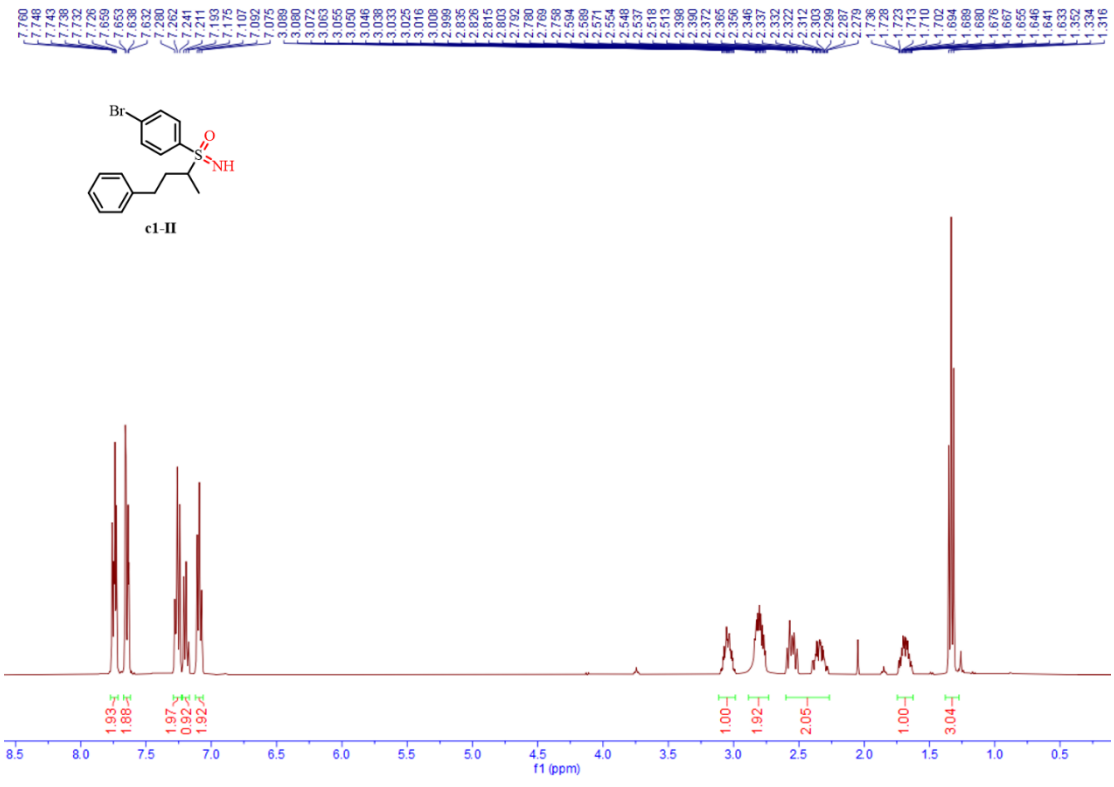
c67


141.68
135.11
132.04
128.80
128.47
128.40
126.74
125.91
42.55
38.21
33.17
21.21
S
H
c67
f1 (ppm)

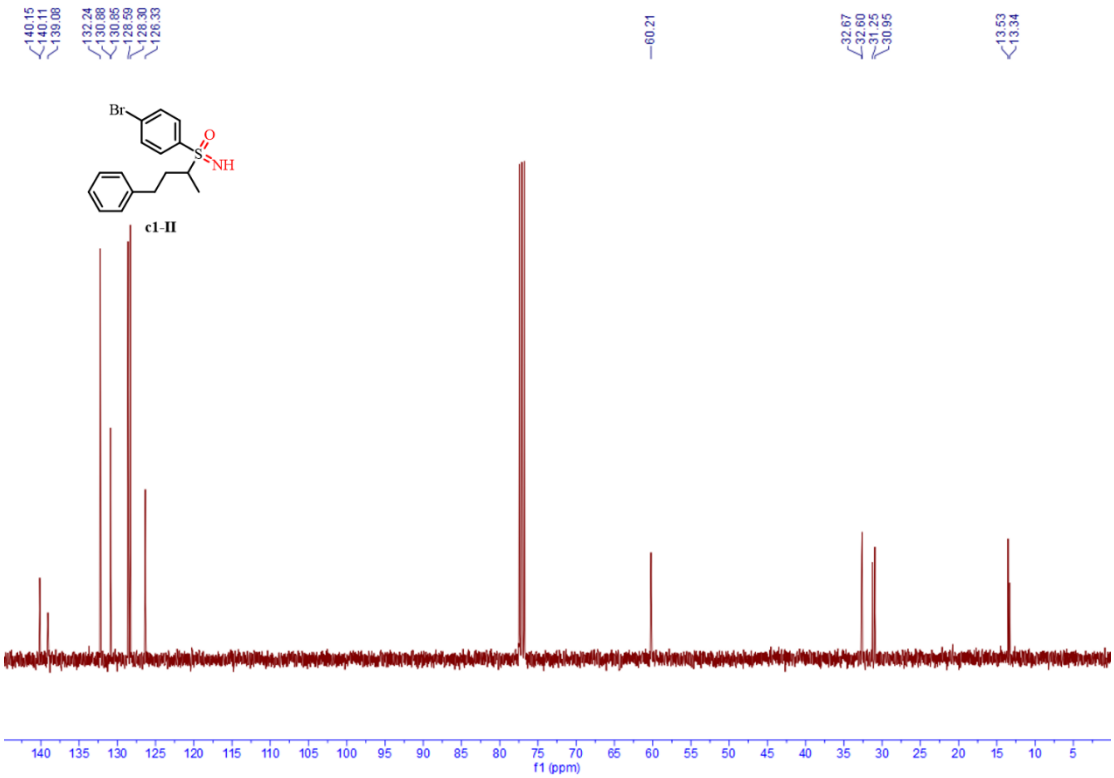

7.716
7.695
7.679
7.674
7.301
7.284
7.265
7.233
7.215
7.196
7.121
7.104
3.058
3.050
3.041
3.033
3.025
3.016
3.008
2.999
2.991
2.982
2.871
2.858
2.848
2.836
2.823
2.813
2.800
2.634
2.615
2.599
2.580
2.558
2.340
2.331
2.312
2.307
2.288
2.288
2.274
2.264
2.255
1.773
1.760
1.749
1.726
1.713
1.702
1.692
1.679
1.336
1.318
Br
O
S
O
c1-I
3.80
2.22
0.93
1.93
1.00
1.02
1.02
1.02
1.02
3.01
f1 (ppm)


139.96
136.20
132.45
130.53
129.01
128.65
128.31
126.43
59.21
32.43
30.73
13.21
Br
O
S
O
f1 (ppm)

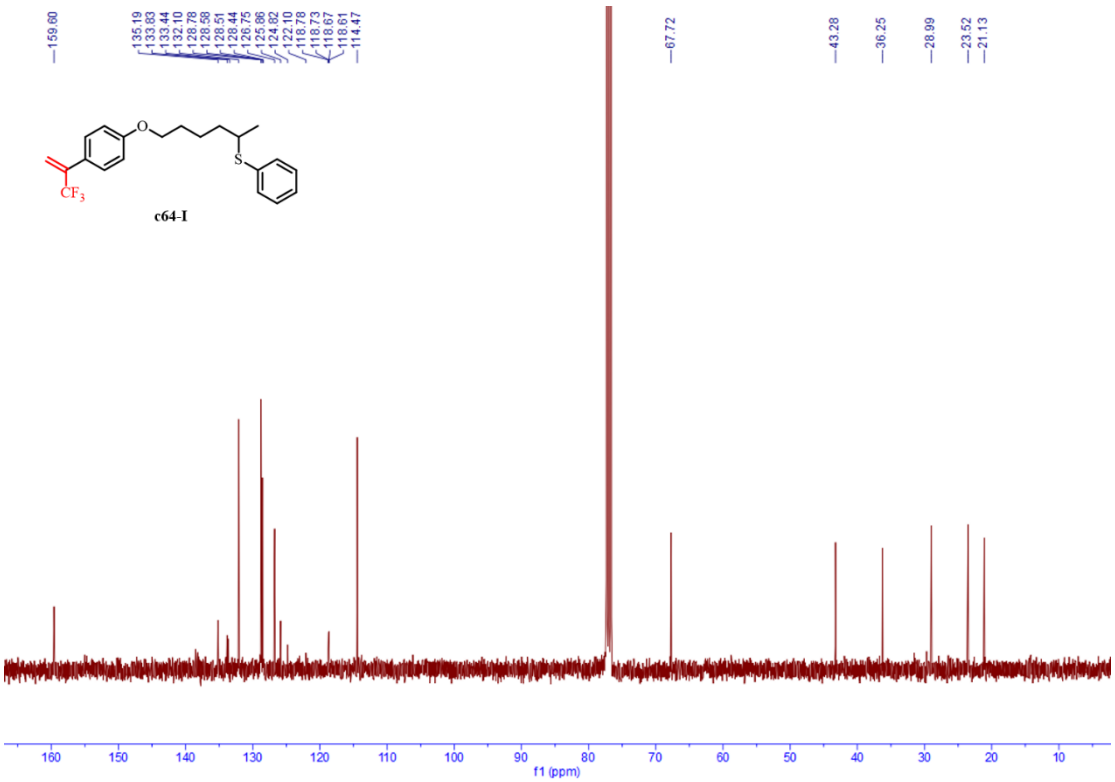
c1-I


Br
O
S
NH
1.93
1.88
1.97
0.92
1.92
1.00
1.92
2.05
1.00
3.04
f1 (ppm)

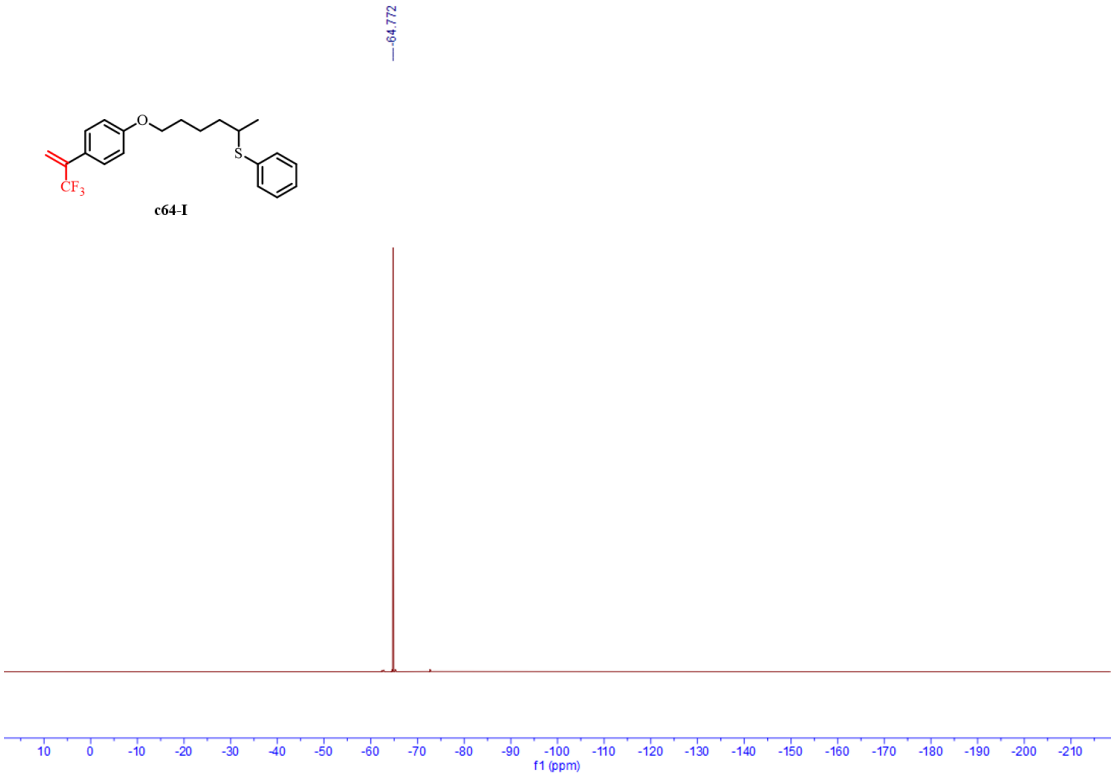
c1-II


140.15
140.11
139.08
132.24
130.88
130.85
128.59
128.30
126.33
60.21
32.67
32.60
31.25
30.95
13.53
13.34
Br
O
S
NH
c1-II
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

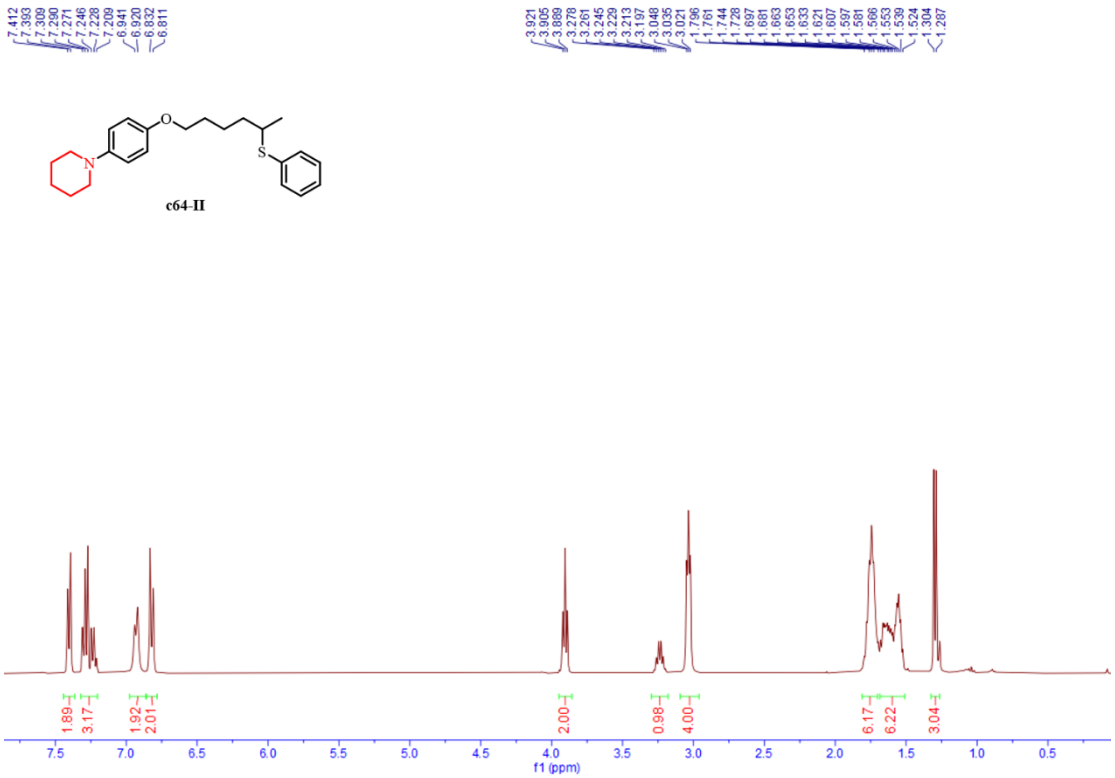

7.407
7.396
7.388
7.375
7.341
7.300
7.281
7.240
6.892
6.871
5.863
5.698
3.980
3.964
3.948
3.277
3.260
3.244
3.228
3.212
3.196
1.828
1.811
1.794
1.777
1.761
1.707
1.644
1.305
1.288
O
S
CF3
c64-I
4.00
1.09
1.13
1.03
2.05
1.05
1.05
2.03
1.00
2.14
4.05
3.12
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


159.60
135.19
133.83
133.44
132.10
128.78
128.58
128.51
128.44
126.75
125.86
124.82
122.10
118.78
118.73
118.67
118.61
114.47
67.72
43.28
36.25
28.99
23.52
21.13
O
S
CF3
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

c64-I


-64.772
O
S
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

c64-I


7.412
7.393
7.309
7.290
7.271
7.246
7.228
7.209
6.941
6.920
6.832
6.811
3.921
3.905
3.889
3.278
3.261
3.245
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3.035
3.021
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1.653
1.633
1.621
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1.597
1.581
1.566
1.553
1.539
1.524
1.304
1.287
O
N
S
c64-II
1.89
3.17
1.92
2.01
2.00
0.98
4.00
6.17
6.22
3.04
7.5
7.0
6.5
6.0
5.5
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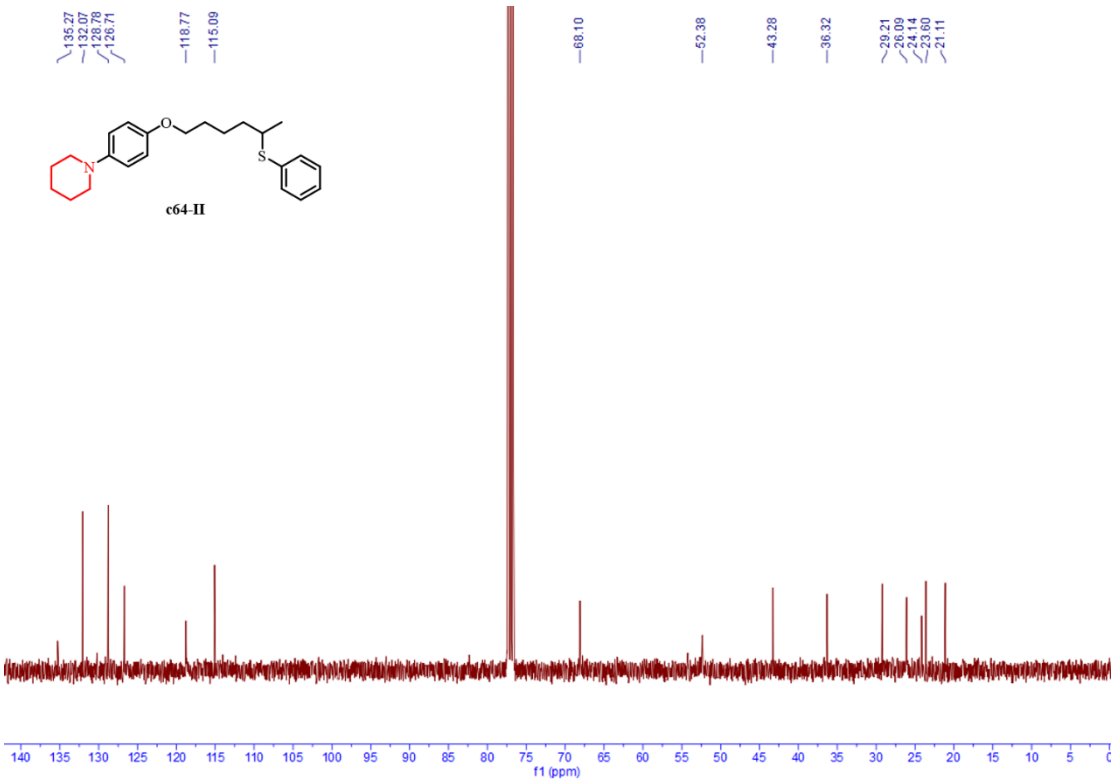
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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126.71
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68.10
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43.28
36.32
29.21
26.09
24.14
23.60
21.11
O
N
S
c64-II
140
135
130
125
120
115
110
105
100
95
90
85
80
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50
45
40
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30
25
20
15
10
5
f1 (ppm)