Convenient one-pot access to 2*H*-3-nitro-thiochromenes from 2-bromobenzaldehydes, sodium sulfide and β-nitrostyrenes

Thi Thu Huong Le, [a] Chitose Youhei,[a,b] Quy Hien Le, [a] Thanh Binh Nguyen, *[c] Dinh Hung Mac,*[a]

[a.] *Medicinal Chemistry Laboratory, Faculty of Chemistry, VNU University of Science, 19 Le Thanh Tong, Ha Noi, Viet Nam, email macdinhhung@hus.edu.vn*
[b.] *Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashihiroshima, Hiroshima 739-8526, Japan*
[c.] *Institut de Chimie des Substances Naturelles, CNRS UPR 2301, Université Paris-Sud, Université Paris-Saclay, 1 avenue de la Terrasse, 91198 Gif-sur-Yvette, France email nguyen@icsn.cnrs-gif.fr*

Supporting information

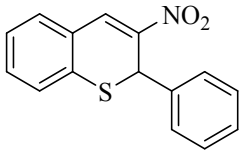
All the reactions were carried out under Nitrogen atmosphere. Unless otherwise noted, all the reagents obtained from commercial sources were used without further purification. All solvents were dried by standard methods. Tetrahydrofuran were dried with sodium and benzophenone and were used immediately after distillation. Dichloromethane was dried with diphosphoruspentoxide (P_2O_5). Pentane was distilled and then dried with sodium. Analytical thin-layer chromatography (TLC) was performed on 0.25 mm Merck precoated silica gel plates (60-F_{254}). Column chromatography was carried out with the same kind of silica gel. The TLC plates were visualized with a UV lamp (254 nm and 366 nm) and/or with TLC visualizing solutions activated with heat, including: *p*-anisaldehyde solution and potassium permanganate solution. ^{1}H-NMR and ^{13}C-NMR were recorded on BRUKER 500 MHz Ascend (Hanoi University of Science, Vietnam National University) instruments using tetramethylsilane (TMS) as the internal standard and $CDCl_3$ as the solvent (^{1}H-NMR: TMS at 0.00 ppm, $CDCl_3$: at 7.26 ppm; ^{13}C-NMR: $CDCl_3$ at 77.0 ppm). Chemical shifts are reported in parts per million (ppm). Data are reported as follows: chemical shift, multiplicity (s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet), coupling constants (Hertz), and integration. X-Ray experiment has been performed with Bruker D8 Quest, Mass spectral analyzes have been performed with a LTQ Orbitrap XL (Hanoi University of Science, Vietnam National University)

General procedure for the synthesis of thiochromene

$Na_2S.9H_2O$ (1 equiv) was dissolved in DMA under nitrogen atmosphere at 90°C over 30 min then 2-bromobenzaldehyde (1.5 equiv) were added to the solution and stirred for another 90 min at 90°C. After cooled to room temperature, nitrostyrene (2.5 equiv) and K_2CO_3 (2.5 equiv) were added to the mixture and the solution was

stirred for 20h at room temperature. After completion of reaction, the reaction was diluted by water extracted by dichloromethane (3x10ml). The organic layer was evaporated by vacuum to obtain crude product. The crude was purified by column chromatography (hexane: EtOAc = 15: 1).

3-nitro-2-phenyl-*2H*-thiochromene (3a)



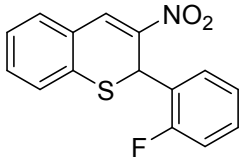
148mg, 55% in 1 mmol scale

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.23 (s, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.29 – 7.14 (m, 8H), 5.55 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.69, 139.97, 132.41, 132.26, 132.23, 132.17, 129.43, 129.16, 128.98, 128.50, 128.25, 127.40, 126.44, 126.22, 39.86.

HRMS m/z calculated for [M+Na]+ C15H11NNaO2S 292.0408 found 292.0413

2-(2-fluorophenyl)-3-nitro-*2H*-thiochromene (3b)



24mg, 42% in 0.2 mmol scale

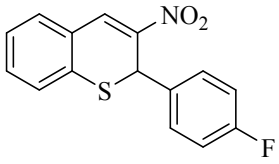
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.41 (d, *J* = 13.7 Hz, 1H), 8.36 (s, 1H), 7.70 – 7.54 (m, *2H*), 7.53 – 7.47 (m, *2H*), 7.47 – 7.39 (m, *2H*), 7.38 – 7.32 (m, 1H), 7.32 – 7.27 (m, 1H), 7.30 – 7.23 (m, *2H*), 7.22 – 7.12 (m, 3H), 7.04 (td, *J* = 7.6, 1.3 Hz, 1H), 6.94 (dd, *J* = 7.8, 1.6 Hz, 1H), 6.04 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.61 (d, J_{C-F} = 249.4 Hz), 142.05, 133.38, 132.53, 132.24, 132.11, 130.10 (d, J_{C-F} = 8.5 Hz), 128.10, 127.56, 127.04 (d, J_{C-F} = 2.7Hz) 126.80, 126.70, 126.54, 124.34 (d, J_{C-F} = 3.8 Hz), 116.16 (d, J_{C-F} = 21.3 Hz), 32.83 (d, *J* = 4.4 Hz).

^{19}F-NMR (471MHz, $CDCl_3$) δ -116.5

HRMS m/z calculated for [M+Na]+ C15H10FNNaO2S 310.0314 found 310.0319

2-(4-fluorophenyl)-3-nitro-*2H*-thiochromene (3c)



30mg, 52% in 0.2mmol scale

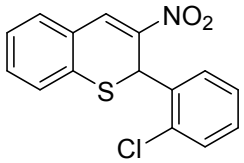
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.16 (dd, *J* = 13.7, 7.8 Hz, 1H), 7.08 (dd, *J* = 8.6, 5.2 Hz, 1H), 6.81 (t, *J* = 8.6 Hz, 1H), 5.43 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.65 (d, J_{C-F} = 247.7 Hz), 143.66, 135.91 (d, J_{C-F} = 3.3 zHz), 132.55, 132.24, 132.21, 131.99, 128.11, 128.06, 128.00, 127.47, 126.59, 115.89 (d, J_{C-F} = 21.9 Hz), 39.19.

^{19}F-NMR (471MHz, $CDCl_3$) δ -113.2

HRMS m/z calculated for [M+Na]+ C15H10FNNaO2S 310.0314 found 310.0319

2-(2-chlorophenyl)-3-nitro-*2H*-thiochromene (3d)



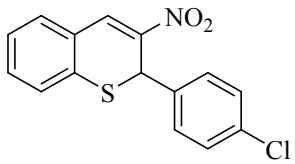
44mg, 72% in 0.2 mmol scale

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.31 (s, 1H), 7.53 – 7.45 (m, *2H*), 7.32 (td, *J* = 7.6, 1.4 Hz, 1H), 7.27 – 7.18 (m, 4H), 7.09 (dd, *J* = 10.2, 8.2 Hz, 1H), 6.99 – 6.85 (m, *2H*), 5.90 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.05, 133.38, 132.53, 132.50, 132.24, 132.11, 130.13, 130.07, 128.10, 127.56, 127.05, 127.03, 126.54, 124.35, 124.32, 116.24, 116.07, 32.84, 32.80.

HRMS m/z calculated for [M+Na]+ C15H10ClNNaO2S 326.0018 found 326.0025

2-(4-chlorophenyl)-3-nitro-*2H*-thiochromene (3e)



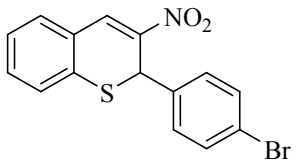
22mg, 36% in 0.2 mmol scale

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 7.38 (d, *J* = 7.5 Hz, *2H*), 7.25 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 8.9 Hz, 4H), 7.10 (d, *J* = 8.5 Hz, *2H*), 7.03 (d, *J* = 8.5 Hz, *2H*), 5.41 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.37, 138.42, 134.40, 132.60, 132.40, 132.26, 131.86, 129.16, 128.12, 127.61, 127.48, 126.65, 39.27.

HRMS m/z calculated for [M+Na]+ C15H10ClNNaO2S 326.0018 found 326.0027

2-(4-bromophenyl)-3-nitro-*2H*-thiochromene (3f)



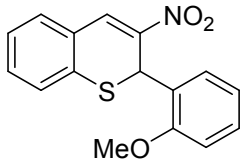
35mg, 51% in 0.2 mmol scale

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.16 (s, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 3H), 7.20 (d, *J* = 7.3 Hz, 3H), 7.01 (d, *J* = 8.4 Hz, *2H*), 5.43 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.29, 138.92, 132.61, 132.43, 132.27, 132.12, 131.83, 128.12, 127.92, 127.49, 126.67, 122.55, 39.34.

HRMS m/z calculated for [M+Na]+ C15H10BrNNaO2S 369.9513 found 369.9521

2-(2-methoxyphenyl)-3-nitro-*2H*-thiochromene (3g)



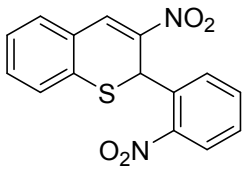
21mg, 35% in 0.2 mmol scale

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.30 (s, 1H), 7.47 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.28 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.24 – 7.13 (m, 3H), 6.91 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.87 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.72 (td, *J* = 7.5, 1.1 Hz, 1H), 6.02 (s, 1H), 3.92 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.19, 142.74, 133.25, 133.18, 132.15, 132.06, 129.51, 128.32, 127.52, 127.18, 126.31, 126.11, 120.50, 111.21, 55.75, 33.35.

HRMS m/z calculated for [M+Na]+ C16H13NNaO3S 322.0514 found 322.0523

3-nitro-2-(2-nitrophenyl)-*2H*-thiochromene (3h)



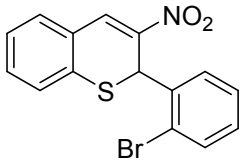
25mg, 40% in 0.2 mmol scale

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.37 (s, 1H), 8.22 – 8.01 (m, 1H), 7.60 – 7.47 (m, 1H), 7.46 – 7.38 (m, 3H), 7.34 (td, *J* = 7.6, 1.5 Hz, 1H), 7.30 – 7.23 (m, *2H*), 7.21 (d, *J* = 7.9 Hz, 1H), 7.16 (dd, *J* = 7.0, 2.3 Hz, 1H), 6.44 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.88, 142.07, 134.49, 134.31, 133.92, 132.89, 132.43, 132.35, 129.15, 127.74, 127.57, 126.73, 126.27, 34.98.

HRMS m/z calculated for [M+Na]+ C15H10N2NaO4S 337.0259 found 337.0267

2-(2-bromophenyl)-3-nitro-*2H*-thiochromene (3i)



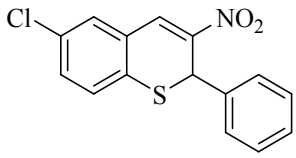
40mg, 58% in 0.2 mmol scale

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 7.69 – 7.58 (m, 1H), 7.50 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.31 (td, *J* = 7.6, 1.5 Hz, 1H), 7.31 – 7.21 (m, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.15 – 7.03 (m, 1H), 7.03 – 6.83 (m, 1H), 6.03 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 142.57, 137.61, 133.88, 133.78, 132.60, 132.26, 132.09, 129.73, 128.18, 127.89, 127.74, 126.88, 126.58, 122.22, 39.36.

HRMS m/z calculated for [M+Na]+ C15H10BrNNaO2S 369.9513 found 369.9521

6-chloro-3-nitro-2-phenyl-*2H*-thiochromene (3j)



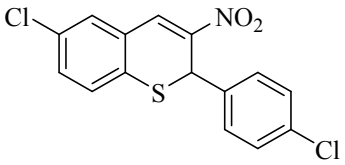
27mg, 45% in 0.2 mmol scale

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.46 (d, *J* = 1.8 Hz, 1H), 7.28 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.24 (dd, *J* = 4.3, 2.2 Hz, 3H), 7.18 (dd, *J* = 11.5, 6.0 Hz, 3H), 5.55 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.66, 139.39, 132.11, 132.07, 131.31, 130.97, 130.51, 129.70, 129.09, 128.72, 128.55, 126.21, 39.85.

HRMS m/z calculated for [M+Na]+ 326.0018 found 326.0026

6-chloro-2-(4-chlorophenyl)-3-nitro-*2H*-thiochromene (3k)



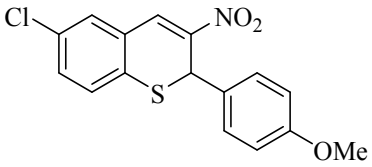
35mg, 52% in 0.2 mmol scale

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.48 (d, *J* = 1.7 Hz, 1H), 7.31 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.21 (dd, *J* = 8.3, 2.9 Hz, 3H), 7.12 (d, *J* = 8.4 Hz, *2H*), 5.52 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.34, 137.84, 134.65, 132.32, 132.29, 131.40, 131.15, 130.10, 129.55, 129.27, 128.62, 127.60, 39.26.

HRMS m/z calculated for [M+Na]+ C15H9Cl2NNaO2S 359.9629 found 359.9633

6-chloro-2-(4-methoxyphenyl)-3-nitro-*2H*-thiochromene (3l)



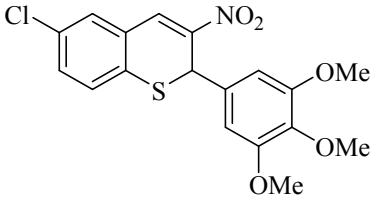
32mg, 48% in 0.2 mmol scale

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.57 – 7.36 (m, *2H*), 7.33 – 7.23 (m, *2H*), 7.19 (d, *J* = 8.4 Hz, 1H), 7.08 (d, *J* = 8.6 Hz, *2H*), 6.74 (d, *J* = 8.6 Hz, *2H*), 5.50 (s, 1H), 3.72 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.88, 144.93, 132.02, 131.96, 131.60, 131.23, 130.60, 129.67, 128.62, 127.48, 114.42, 55.28, 39.40.

HRMS m/z calculated for [M+Na]+ C16H12ClNNaO3S 356.0124 found 356.0131

6-chloro-3-nitro-2-(3,4,5-trimethoxyphenyl)-*2H*-thiochromene (3m)



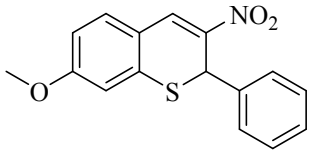
33mg, 42% in 0.2 mmol scale

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.48 (t, *J* = 4.6 Hz, 1H), 7.32 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 3H), 6.39 (s, *2H*), 5.51 (s, 1H), 3.78 (s, 3H), 3.71 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.50, 144.80, 138.49, 134.81, 132.15, 131.03, 130.70, 130.66, 129.66, 128.64, 103.41, 60.79, 56.09, 40.11.

HRMS m/z calculated for [M+Na]+ C18H16ClNNaO5S 416.0335 found 416.0342

7-methoxy-3-nitro-2-phenyl-*2H*-thiochromene (3n)



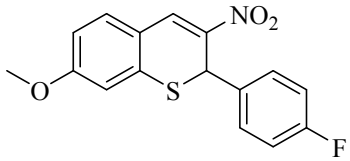
37mg, 62% in 0.2 mmol scale

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.21 (s, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.17 (m, 4H), 6.77 (d, *J* = 7.3 Hz, *2H*), 6.77 (d, *J* = 7.3 Hz, *2H*), 5.54 (s, 1H), 3.81 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.87, 141.19, 140.33, 134.53, 133.96, 132.45, 128.95, 128.40, 126.24, 121.30, 113.16, 112.21, 77.29, 77.04, 76.79, 55.62, 40.11.

HRMS m/z calculated for [M+Na]+ C16H13NNaO3S 322.0514 found 322.0518

2-(4-fluorophenyl)-7-methoxy-3-nitro-*2H*-thiochromene (3o)



36mg, 57% in 0.2 mmol scale

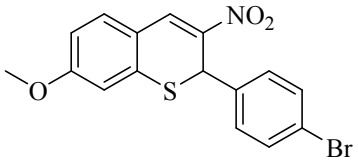
^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.20 (s, 1H), 7.45 – 7.36 (m, 1H), 7.22 – 7.12 (m, *2H*), 6.98 – 6.85 (m, *2H*), 6.85 – 6.67 (m, 3H), 5.52 (s, 1H), 3.79 (d, *J* = 27.1 Hz, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.97, 162.60 (d, $J_{C\text{-}F}$=246Hz), 161.62, 141.15, 136.28, 136.25, 134.27, 134.03, 132.41, 128.06, 128.00, 121.13, 115.85 (*z*=21.7Hz) 113.25, 112.29, 55.64, 39.42.

^{19}F-NMR (471MHz, $CDCl_3$) δ -113.4

HRMS m/z calculated for [M+Na]+ C16H12FNNaO3S 340.0420 found 340.0428

2-(4-bromophenyl)-7-methoxy-3-nitro-*2H*-thiochromene (3p)



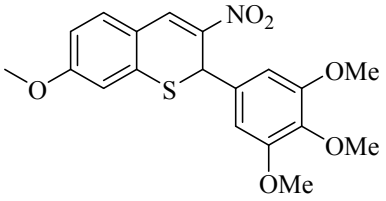
41mg, 55% in 0.2 mmol scale

1H NMR (500 MHz, Chloroform-d) δ 8.20 (s, 1H), 7.43 – 7.38 (m, 1H), 7.37 – 7.33 (m, *2H*), 7.12 – 7.03 (m, *2H*), 6.80 – 6.75 (m, *2H*), 5.48 (s, 1H), 3.82 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 163.01, 140.75, 139.29, 134.11, 134.07, 132.63, 132.07, 127.95, 122.40, 121.13, 113.31, 112.33, 77.29, 77.04, 76.78, 55.65, 39.57

HRMS m/z calculated for [M+Na]+ C16H12BrNNaO3S 399.9619 found 399.9623

7-methoxy-3-nitro-2-(3,4,5-trimethoxyphenyl)-*2H*-thiochromene (3q)



37mg, 48% in 0.2 mmol scale

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.20 (s, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.77 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.42 (s, *2H*), 5.47 (s, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 3.70 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.89, 153.39, 141.35, 138.18, 135.76, 134.62, 133.69, 132.25, 121.27, 113.21, 112.33, 103.30, 77.29, 77.04, 76.79, 60.75, 60.39, 56.00, 55.64, 40.39

HRMS m/z calculated for [M+Na]+ C19H19NNaO6S 412.0831 found 412.0836

2-(3-nitro-2H-thiochromen-2-yl)furan

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 7.47 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.29 – 7.22 (m, 2H), 6.19 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.05 (d, *J* = 3.3 Hz, 1H), 5.68 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.54, 143.18, 141.42, 132.66, 132.30, 132.27, 132.19, 128.21, 127.60, 126.51, 110.68, 107.71, 33.89.

HRMS m/z calculated for [M+Na]+ C13H9NNaO3S 282.0201 found 282.0208

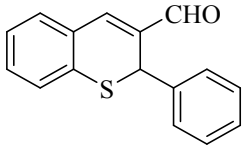
3-nitro-2-(thiophen-2-yl)-2H-thiochromene

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 7.48 (d, *J* = 7.1 Hz, 1H), 7.37 (dd, *J* = 6.3, 1.6 Hz, 2H), 7.31 – 7.24 (m, 1H), 7.10 (dd, *J* = 5.0, 1.3 Hz, 1H), 6.88 (dt, *J* = 3.6, 1.0 Hz, 1H), 6.82 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.84 (s, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.98, 132.43, 132.23, 131.99, 131.55, 128.20, 127.77, 126.67, 125.58, 125.38, 35.57.

HRMS m/z calculated for [M+Na]+ C13H9NNaO2S2 297.9972 found 297.9980f

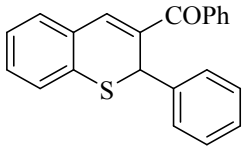
2-phenyl-2*H*-thiochromene-3-carbaldehyde (4)



^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.67 (s, 1H), 7.47 (s, 1H), 7.41 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.18 – 7.21 (m, *m* 5H), 5.21 (s, 1H).

13C NMR (126 MHz, CDCl3) δ 191.1, 145.1, 141.7, 134.8, 134.1, 131.8, 131.0, 129.9, 128.7, 127.8, 127.6, 126.5, 125.9, 38.4.

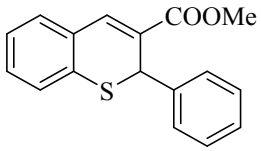
phenyl(2-phenyl-2*H*-thiochromen-3-yl)methanone (5)



^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.69 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.45 (dd, *J* = 8.3, 6.8 Hz, 1H), 7.32 – 7.16 (m, 5H), 7.11 (td, *J* = 7.2, 1.6 Hz, 1H), 5.48 (s, 1H).

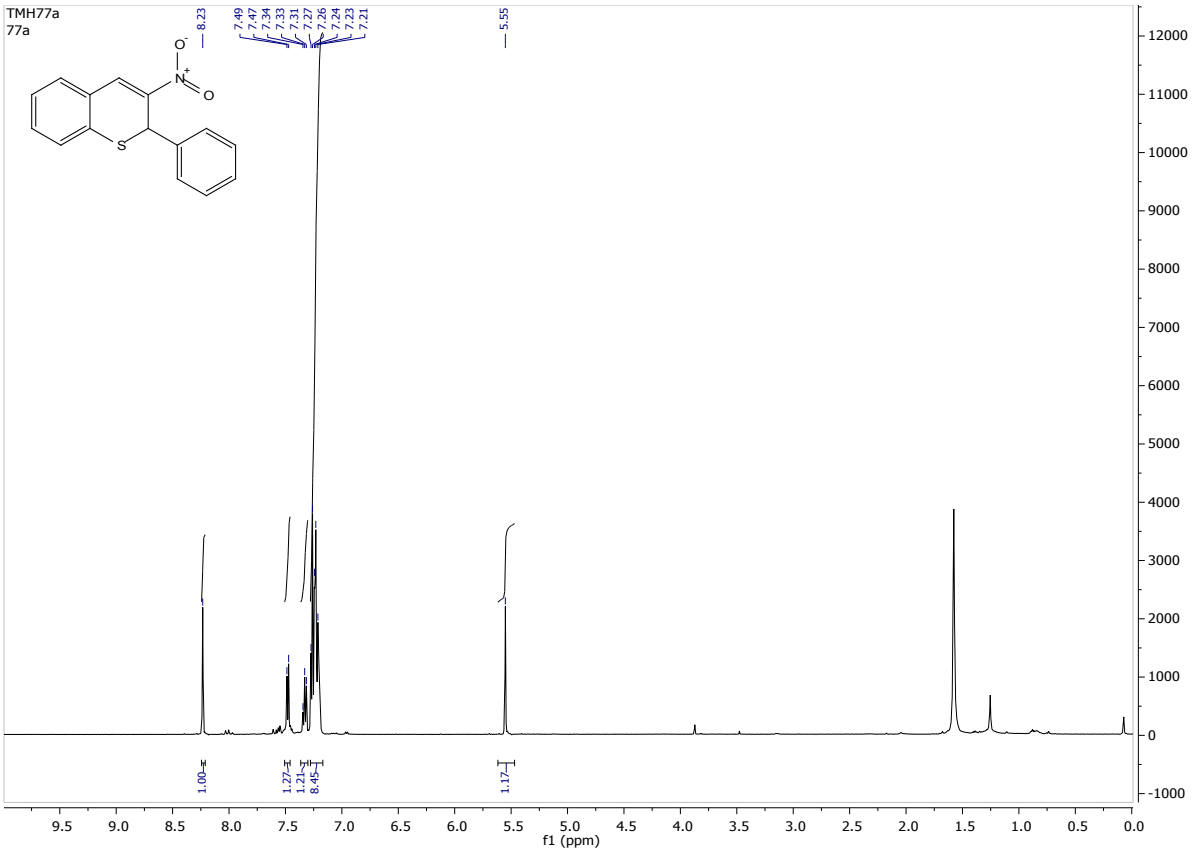
13C NMR (126 MHz, CDCl3) δ 195.7, 141.9, 140.0, 138.1, 133.2, 132.7, 131.9, 131.1, 130.8, 130.4, 129.2, 128.7, 128.4, 127.7, 127.6, 126.6, 125.7, 40.2.

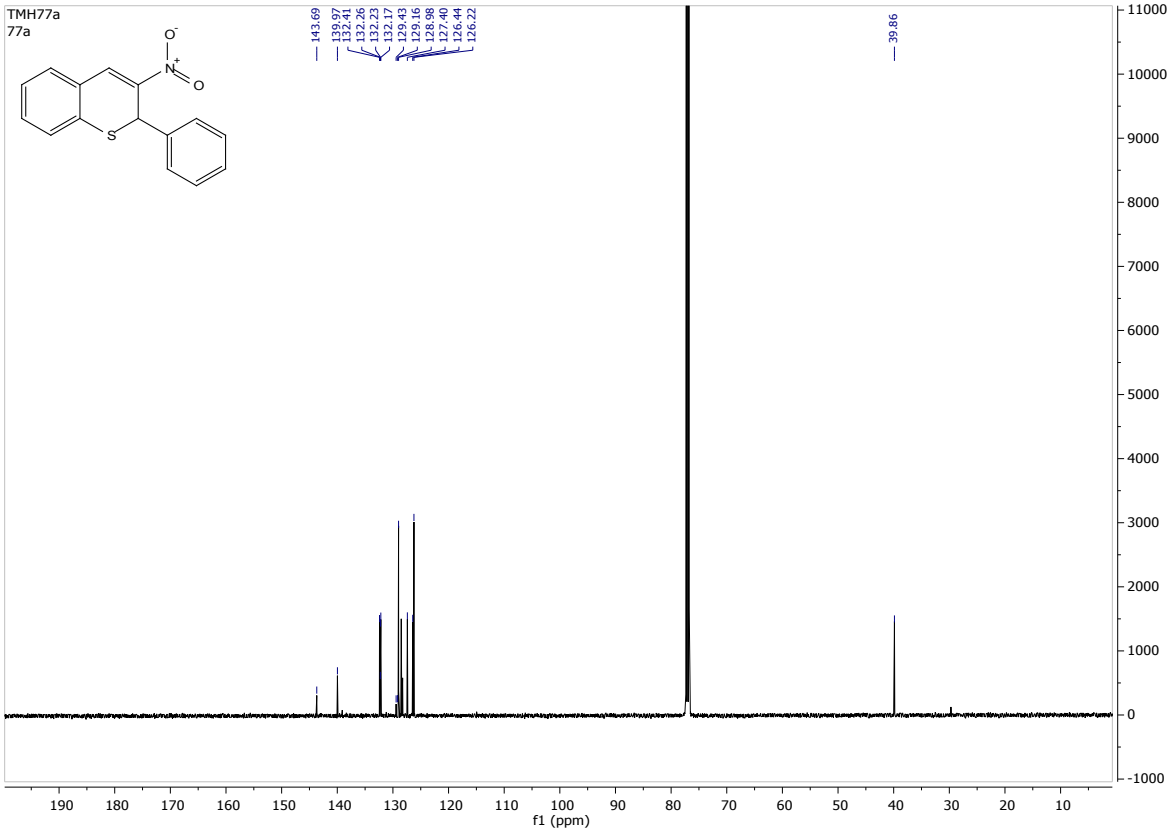
methyl 2-phenyl-2H-thiochromene-3-carboxylate (6)

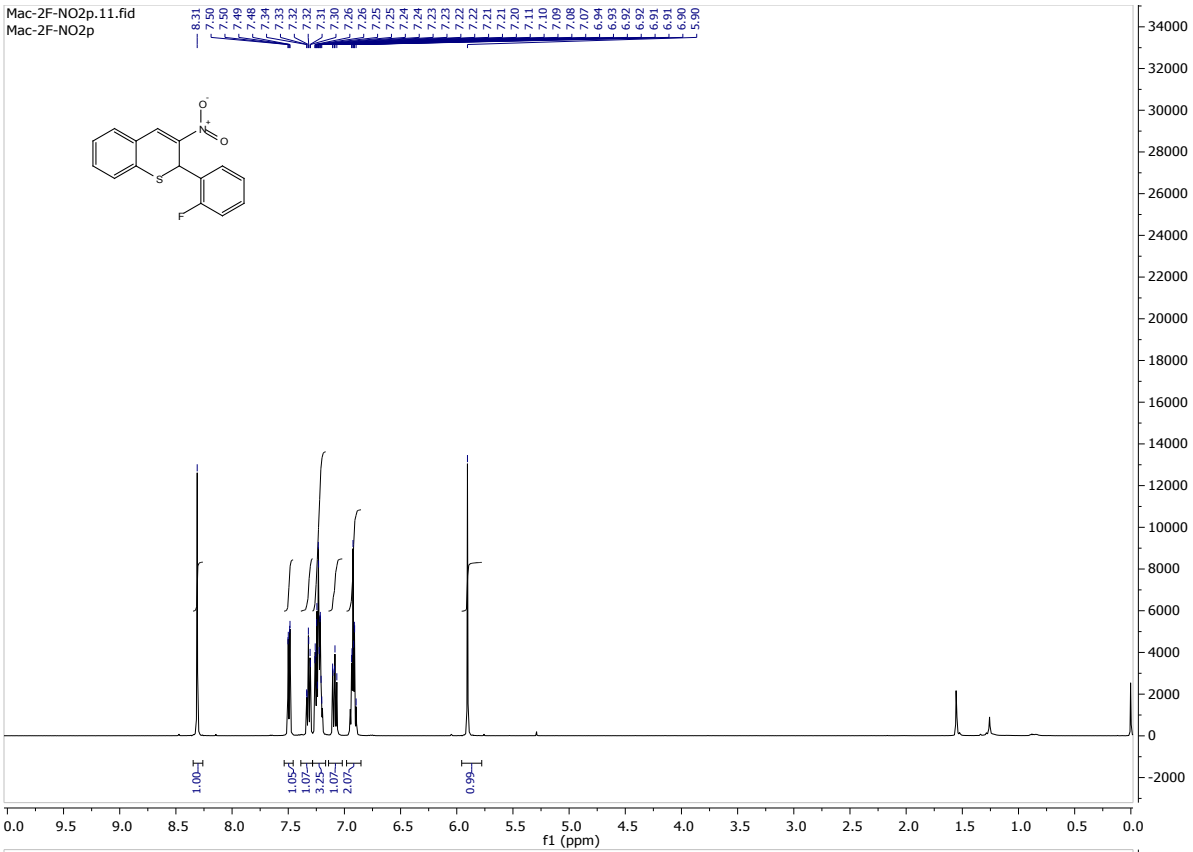


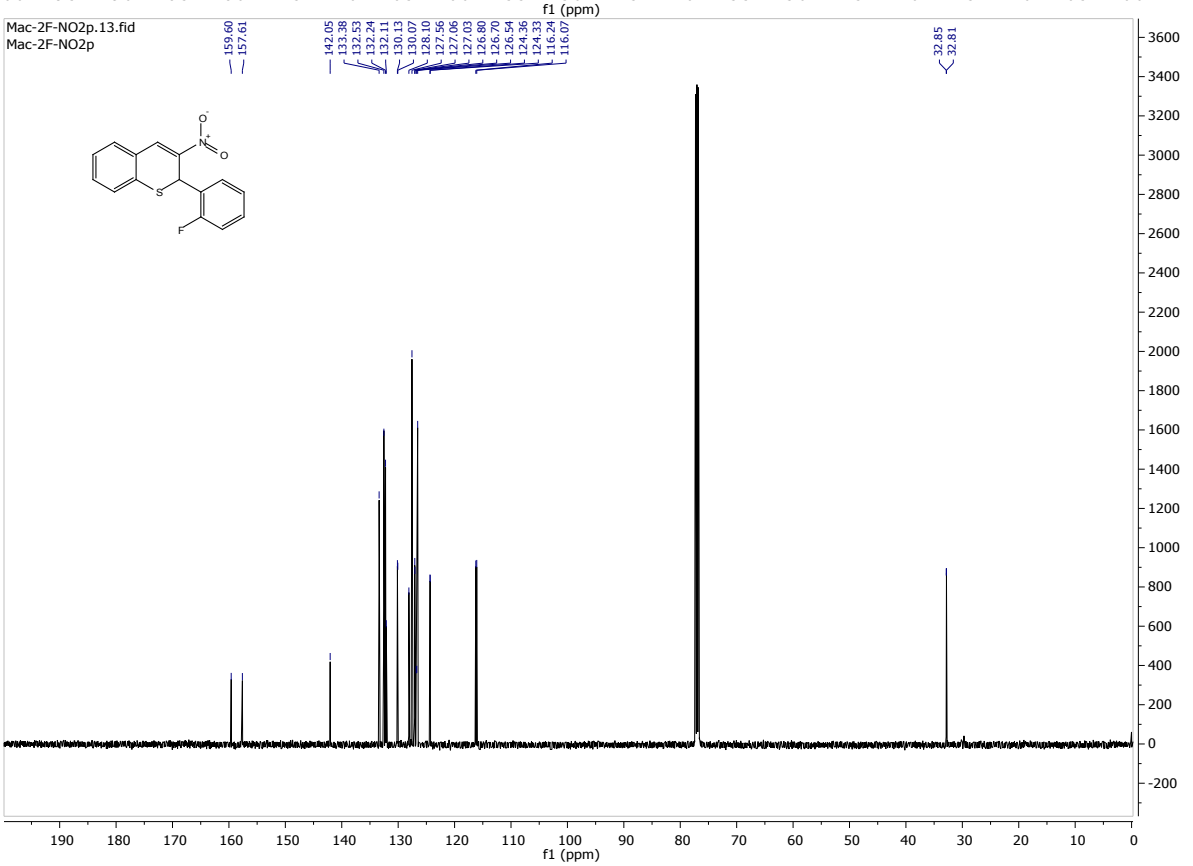
1H NMR (500 MHz, CDCl3) δ 7.84 (s, 1H), 7.25 – 7.15 (m, 5H), 7.08 (t, *J* = 7.9 Hz, 1H), 7.01 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.81 (dd, *J* = 8.1, 0.9 Hz, 1H), 5.23 (s, 1H), 4.10 – 3.91 (m, 2H), 3.78 (s, 3H)

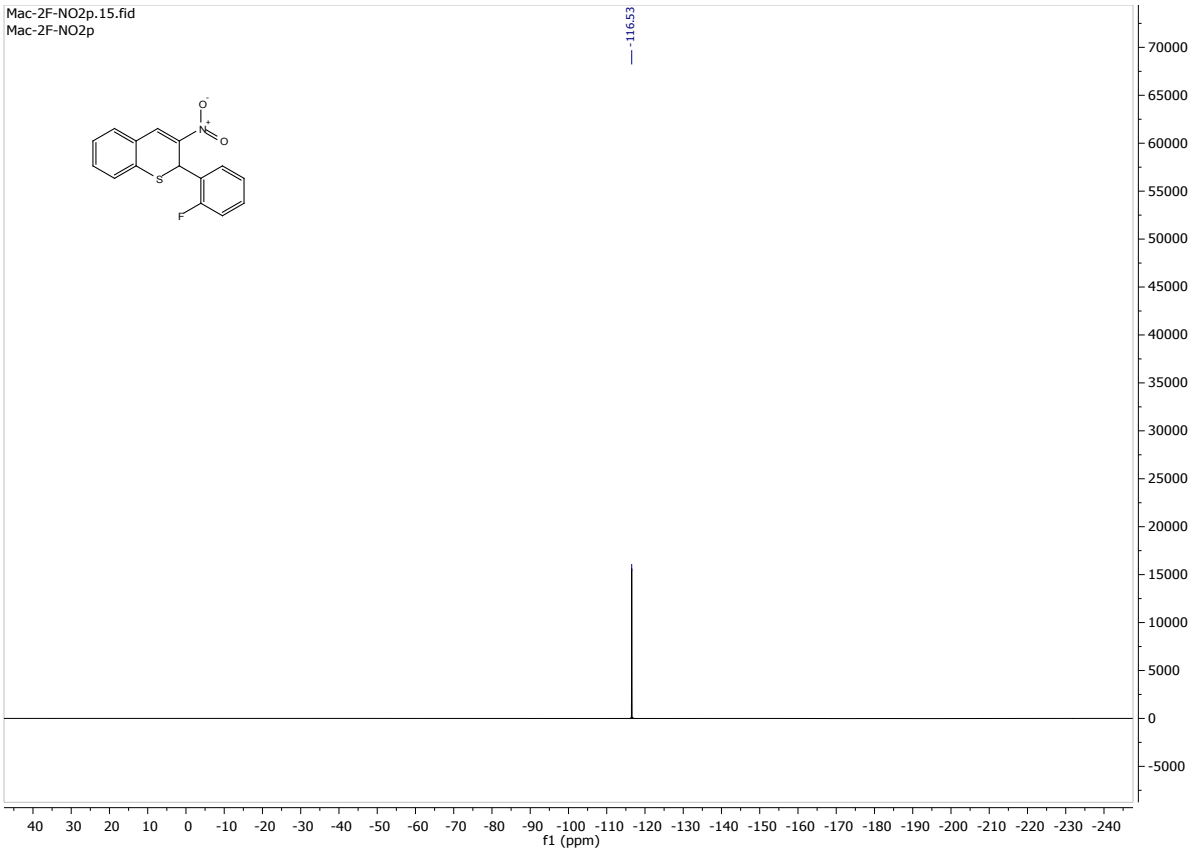
13C NMR (126 MHz, CDCl3) δ 165.38, 153.84, 141.53, 136.03, 129.92, 127.51, 126.51, 125.70, 124.18, 123.72, 122.14, 120.57, 112.61, 63.50, 51.23, 38.56.

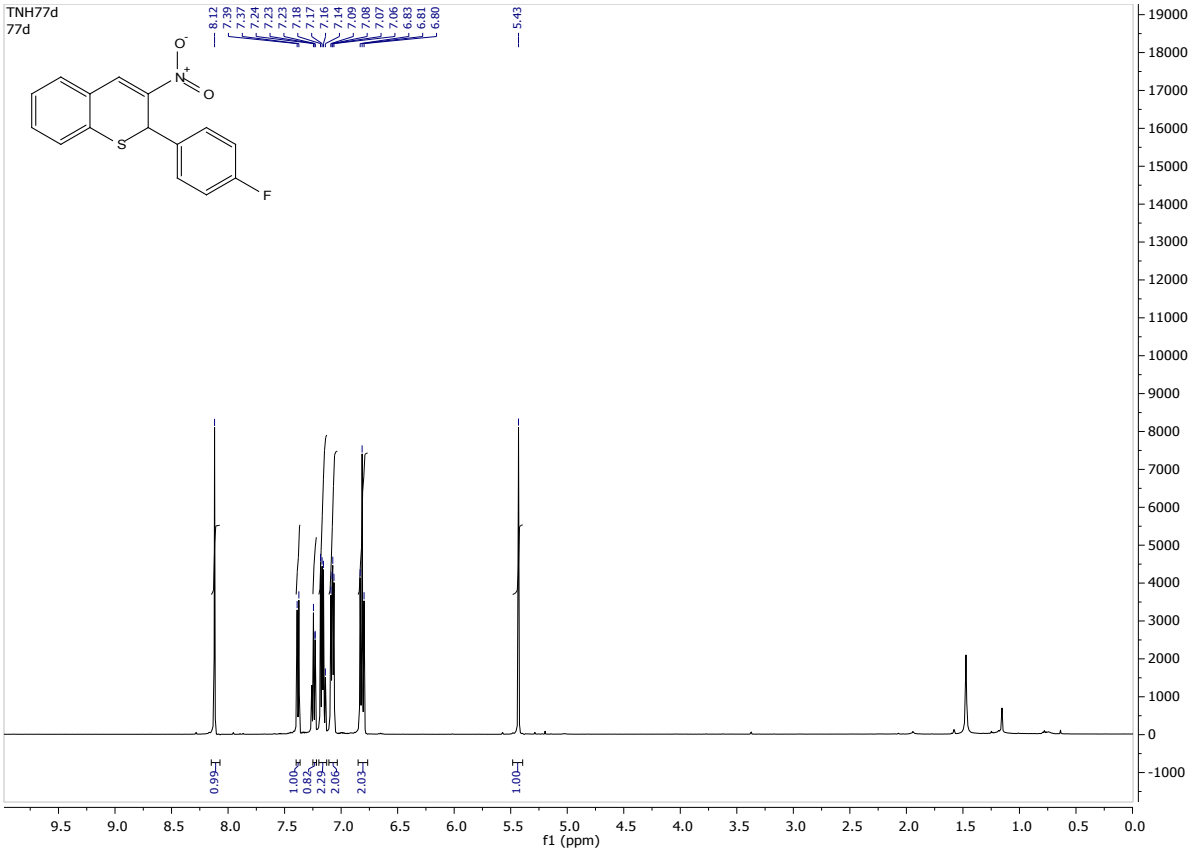

TMH77a
77a
8.23
7.49
7.47
7.34
7.33
7.31
7.27
7.26
7.24
7.23
7.21
5.55
1.00
1.27
1.21
8.45
1.17
f1 (ppm)

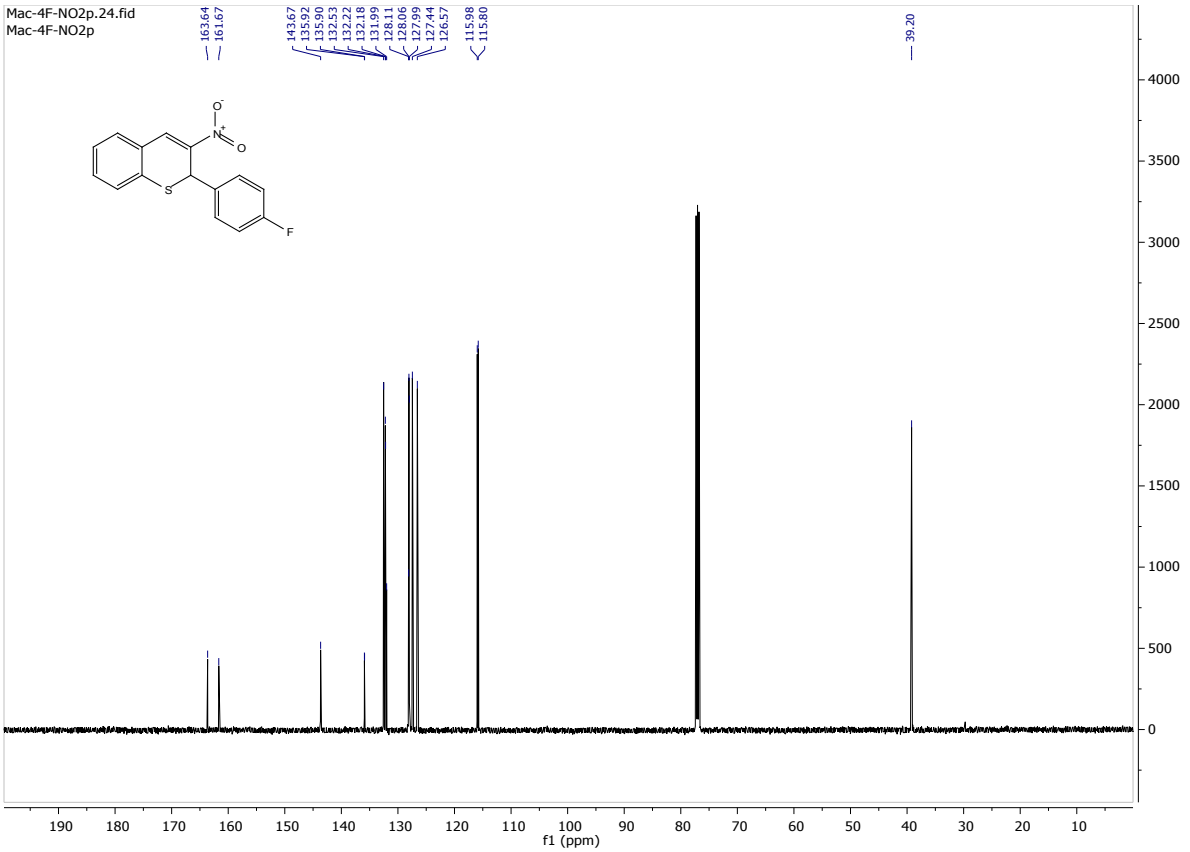

TMH77a
77a
143.69
139.97
132.41
132.26
132.23
132.17
129.43
129.16
128.98
127.40
126.44
126.22
39.86
f1 (ppm)

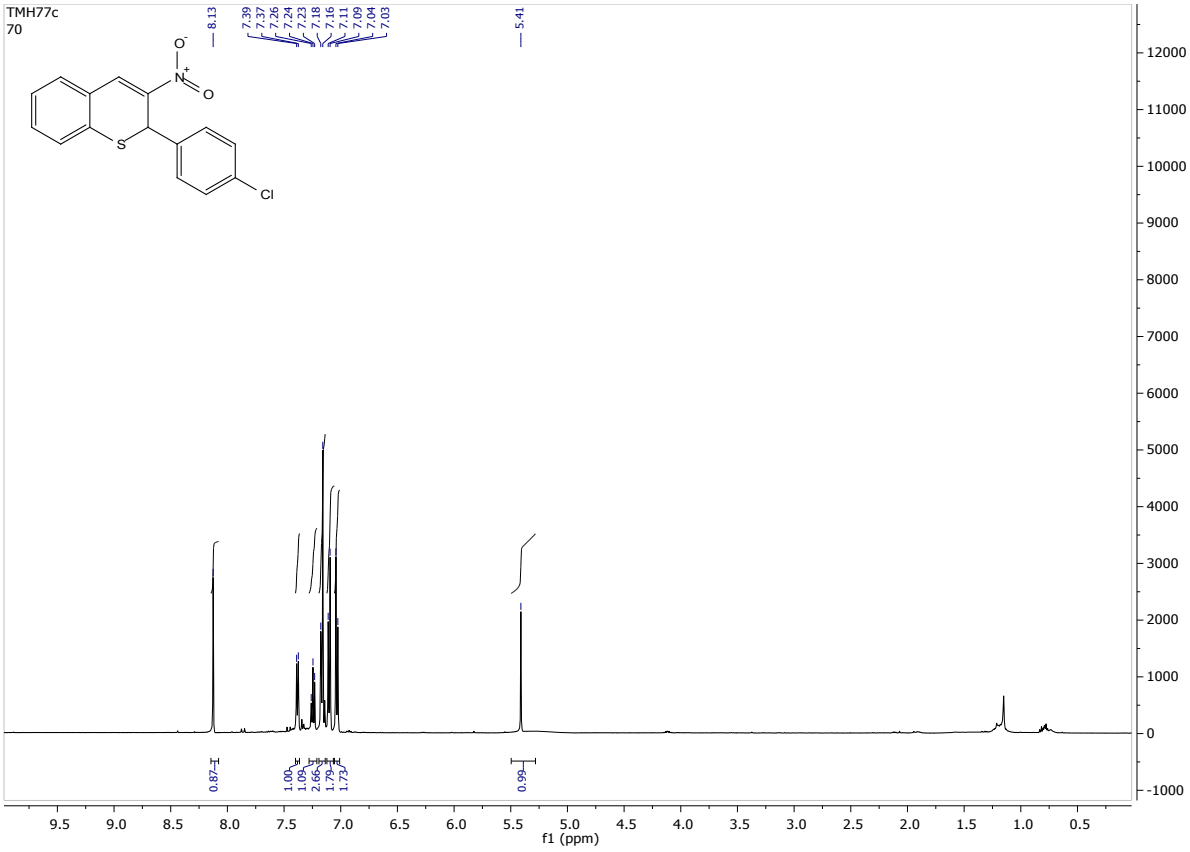

Mac-2F-NO2p.11.fid
Mac-2F-NO2p
8.31
7.50
7.50
7.49
7.48
7.34
7.33
7.32
7.32
7.31
7.30
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.11
7.10
7.09
7.08
7.07
6.94
6.93
6.92
6.92
6.91
6.91
6.90
5.90
1.00
1.05
1.07
3.25
1.07
2.07
0.99
f1 (ppm)

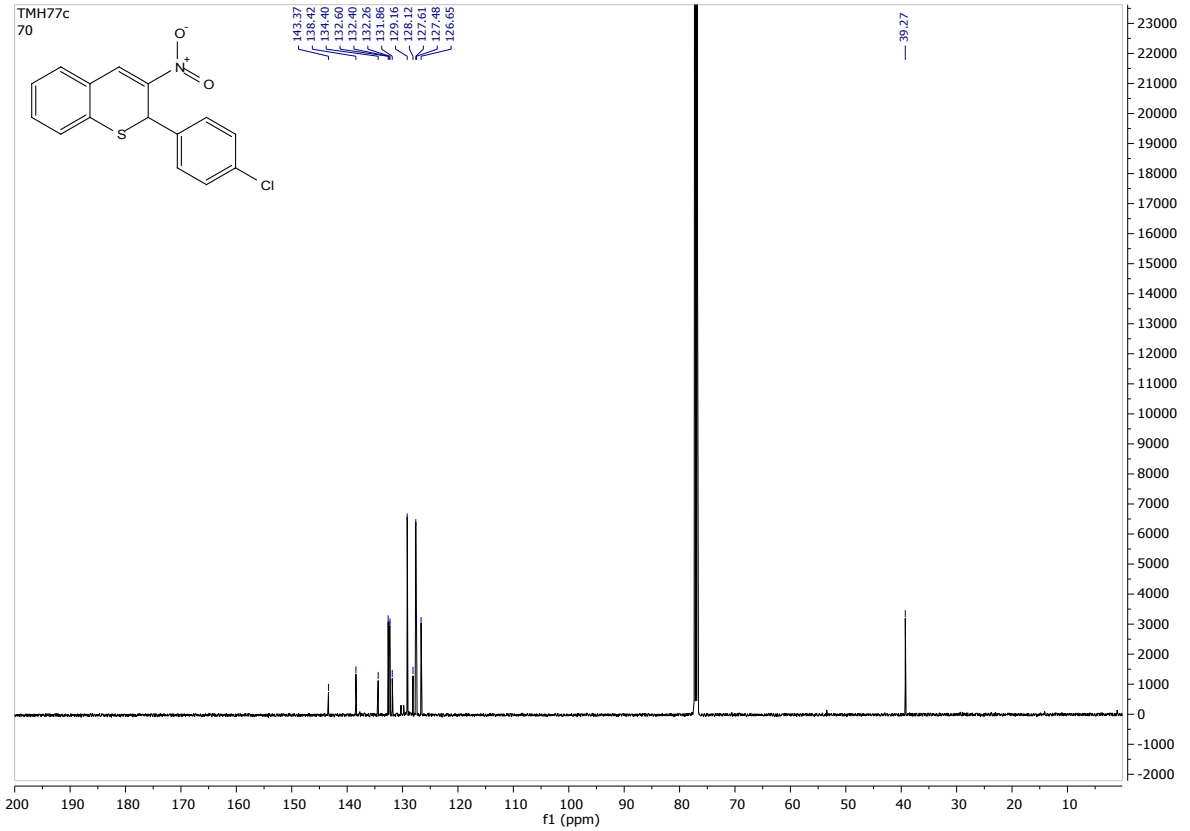

Mac-2F-NO2p.13.fid
Mac-2F-NO2p
159.60
157.61
142.05
133.38
132.53
132.24
132.11
130.13
130.07
128.10
127.56
127.06
127.03
126.80
126.70
126.54
124.36
124.33
116.24
116.07
32.85
32.81
f1 (ppm)

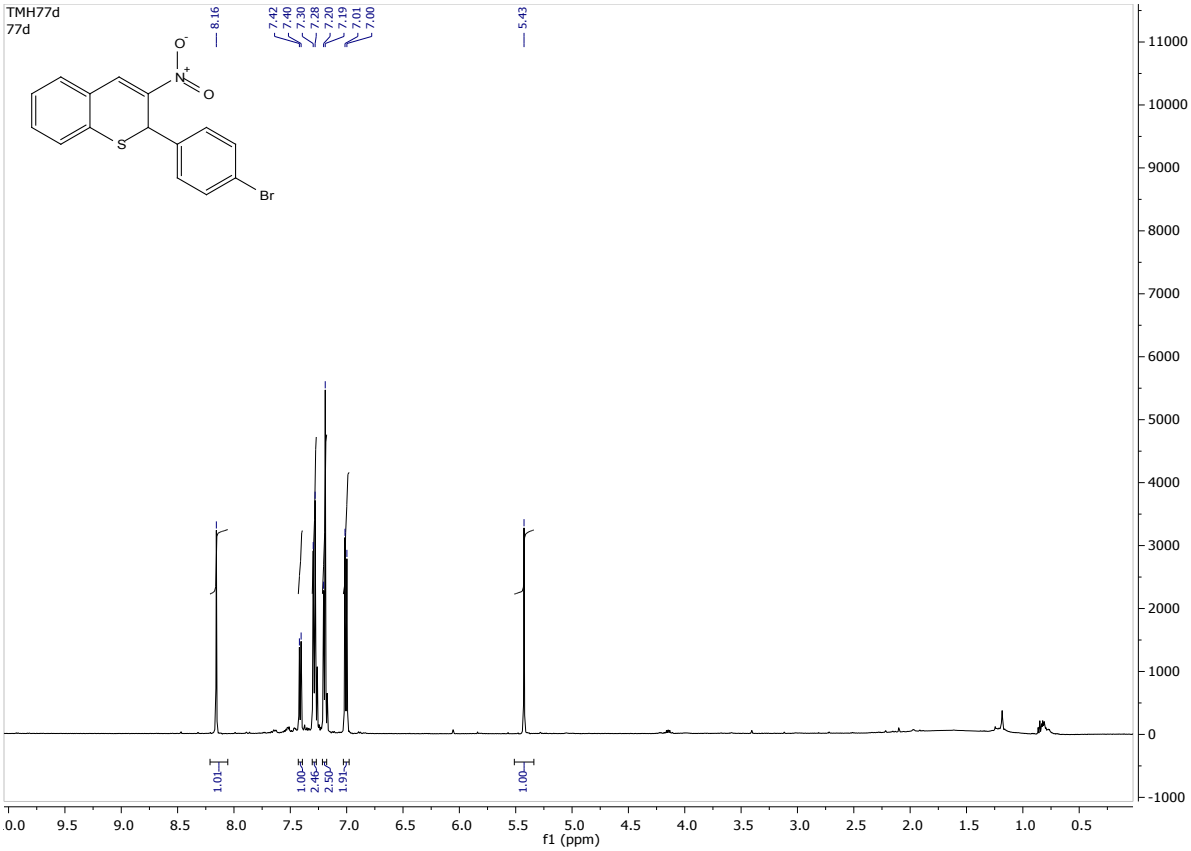

Mac-2F-NO2p.15.fid
Mac-2F-NO2p
-116.53
f1 (ppm)

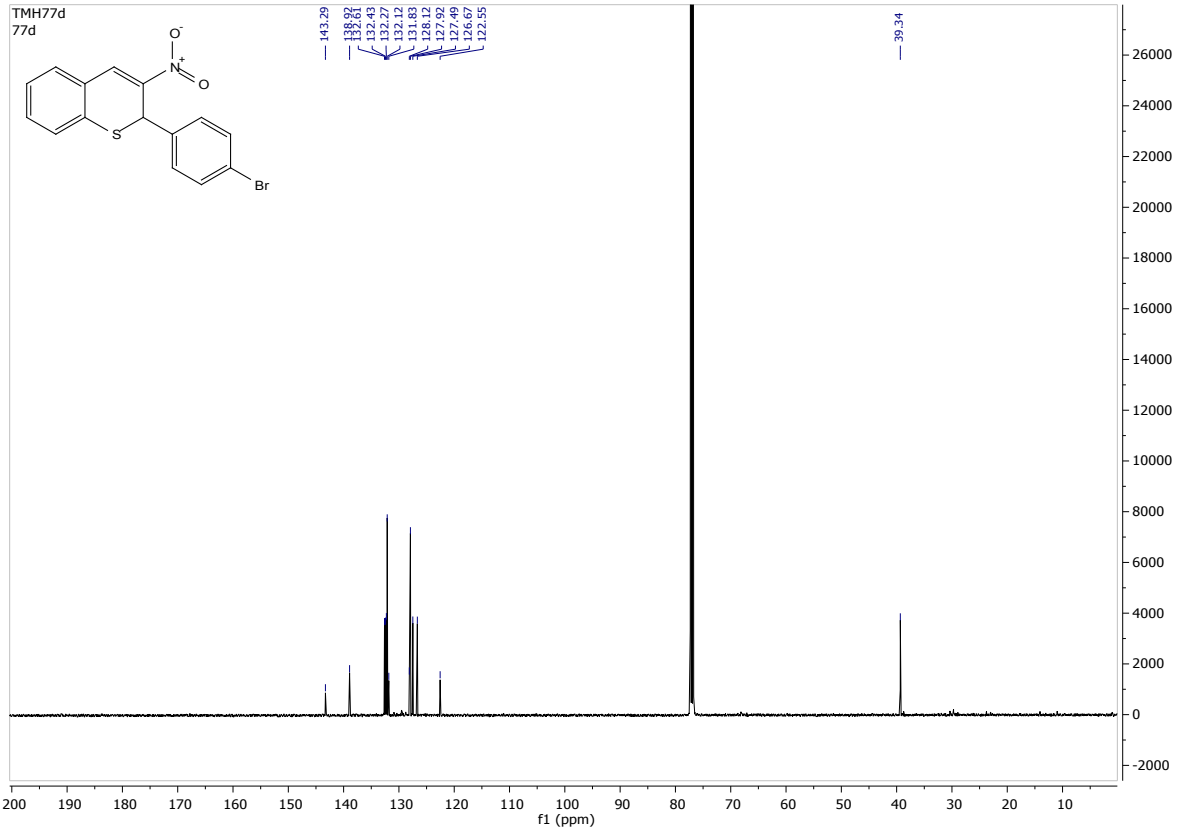

TNH77d
77d
8.12
7.39
7.37
7.24
7.23
7.23
7.18
7.17
7.16
7.14
7.09
7.08
7.07
7.06
6.83
6.81
6.80
5.43
0.99
1.00
0.82
2.29
2.06
2.03
1.00
f1 (ppm)

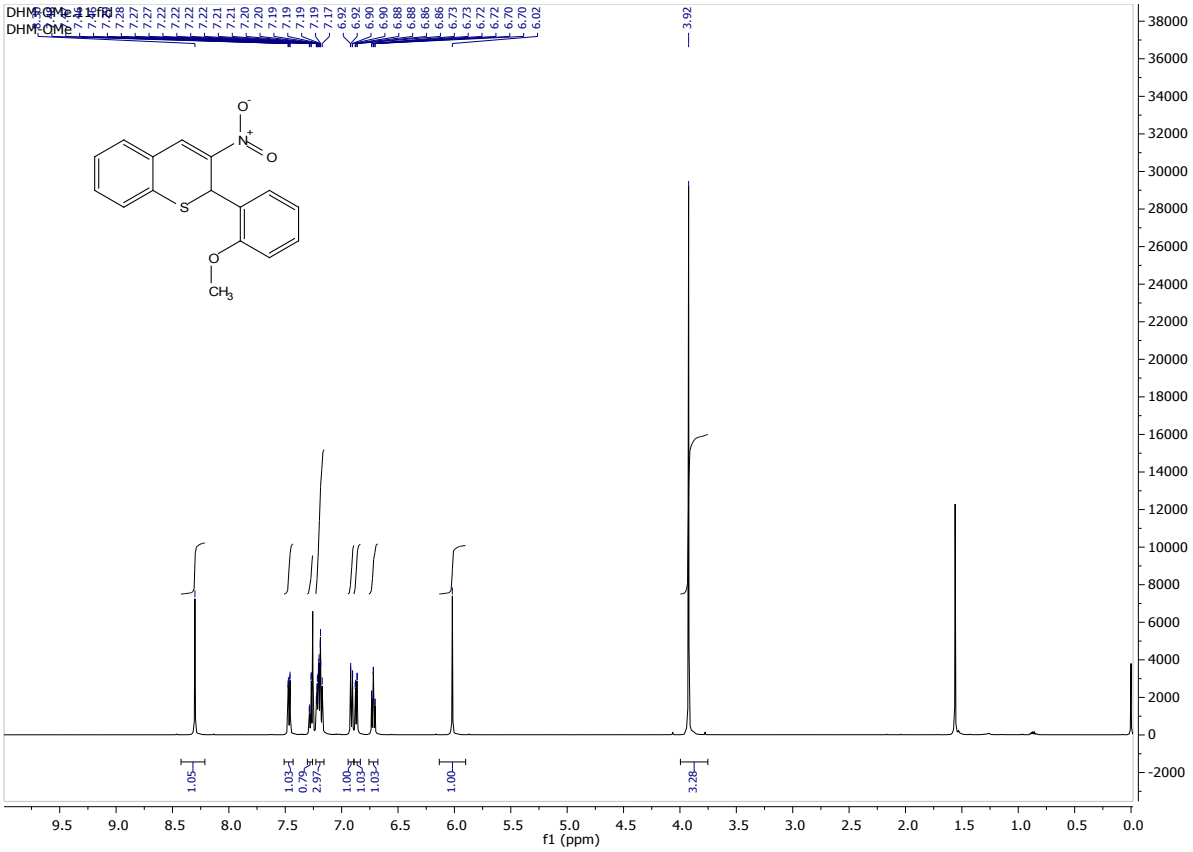

Mac-4F-NO2p.24.fid
Mac-4F-NO2p
163.64
161.67
143.67
135.92
133.90
132.53
132.22
132.18
131.99
128.11
128.06
127.99
127.44
126.57
115.98
115.80
39.20
f1 (ppm)

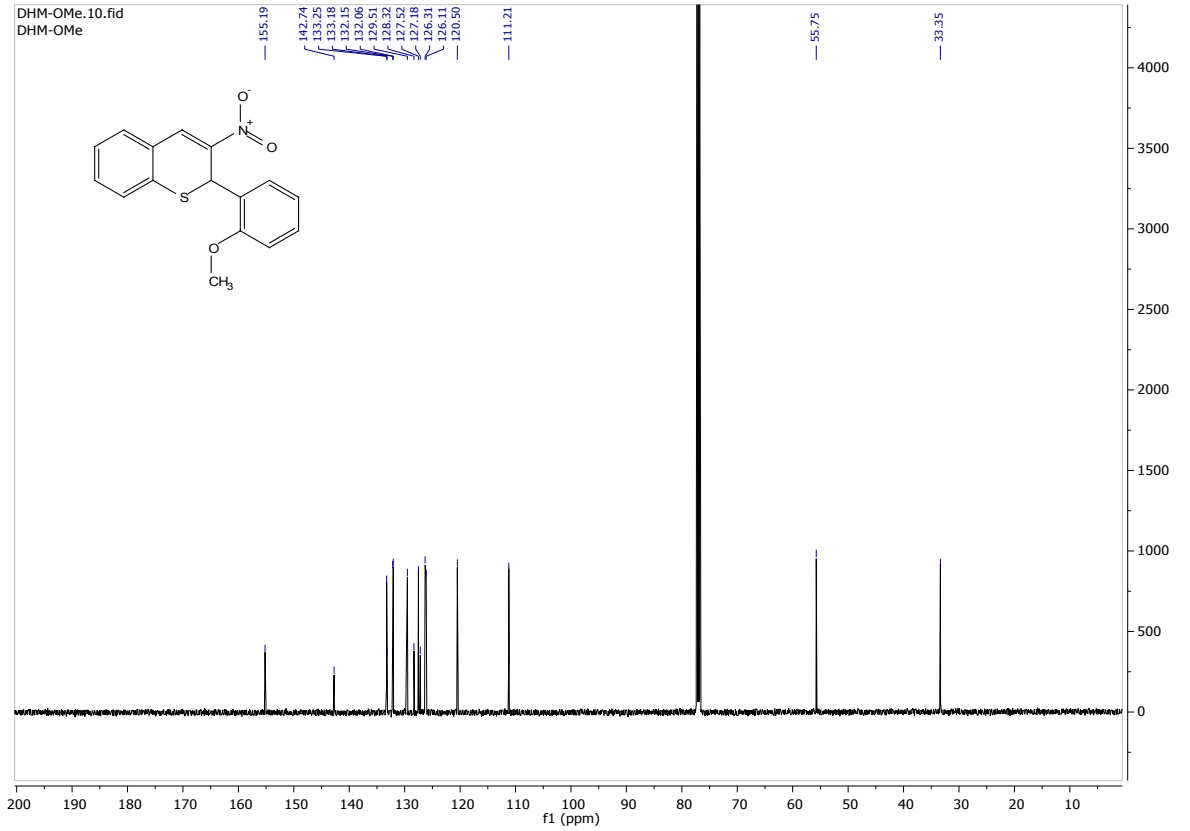

TMH77c
70
8.13
7.39
7.37
7.26
7.24
7.23
7.18
7.16
7.11
7.09
7.04
7.03
5.41
0.87
1.00
1.09
2.66
1.79
1.73
0.99
f1 (ppm)

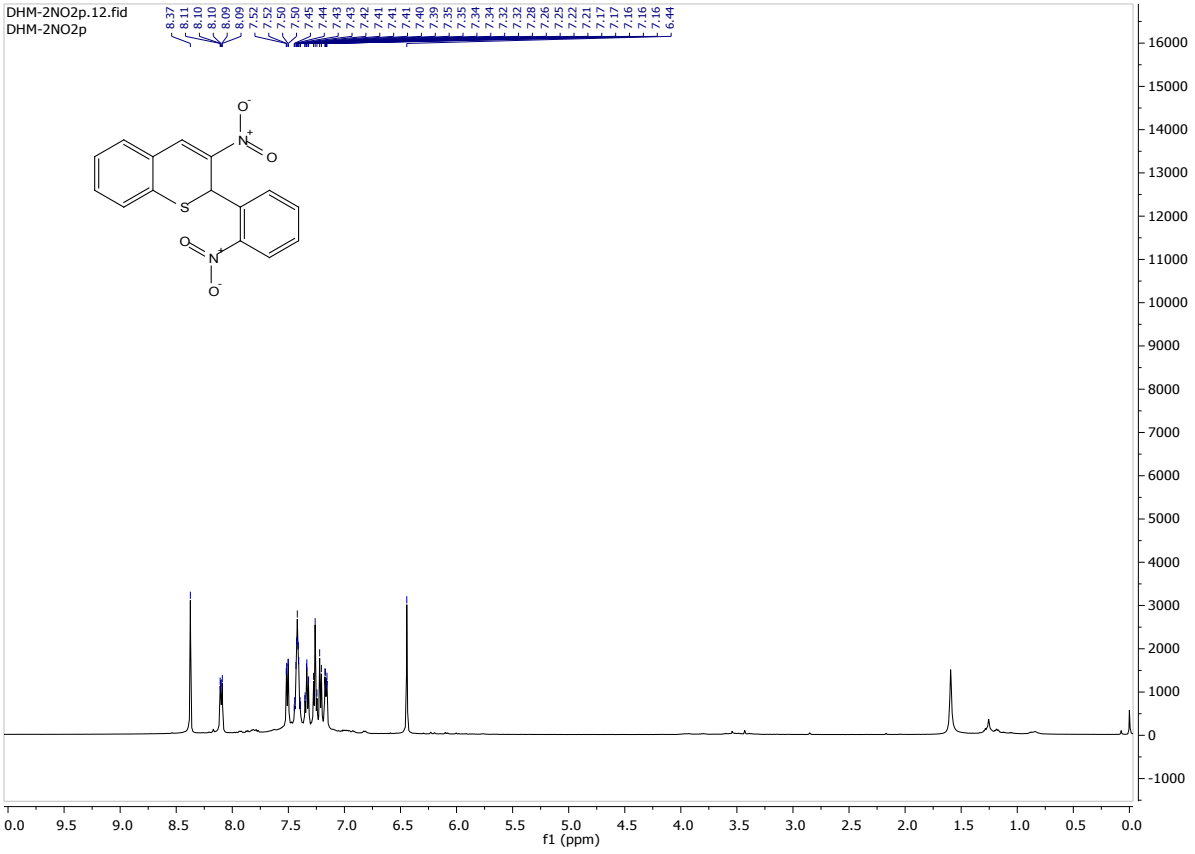

TMH77c
70
143.37
138.42
134.40
132.60
132.40
132.26
131.86
129.16
128.12
127.61
127.48
126.65
39.27
f1 (ppm)

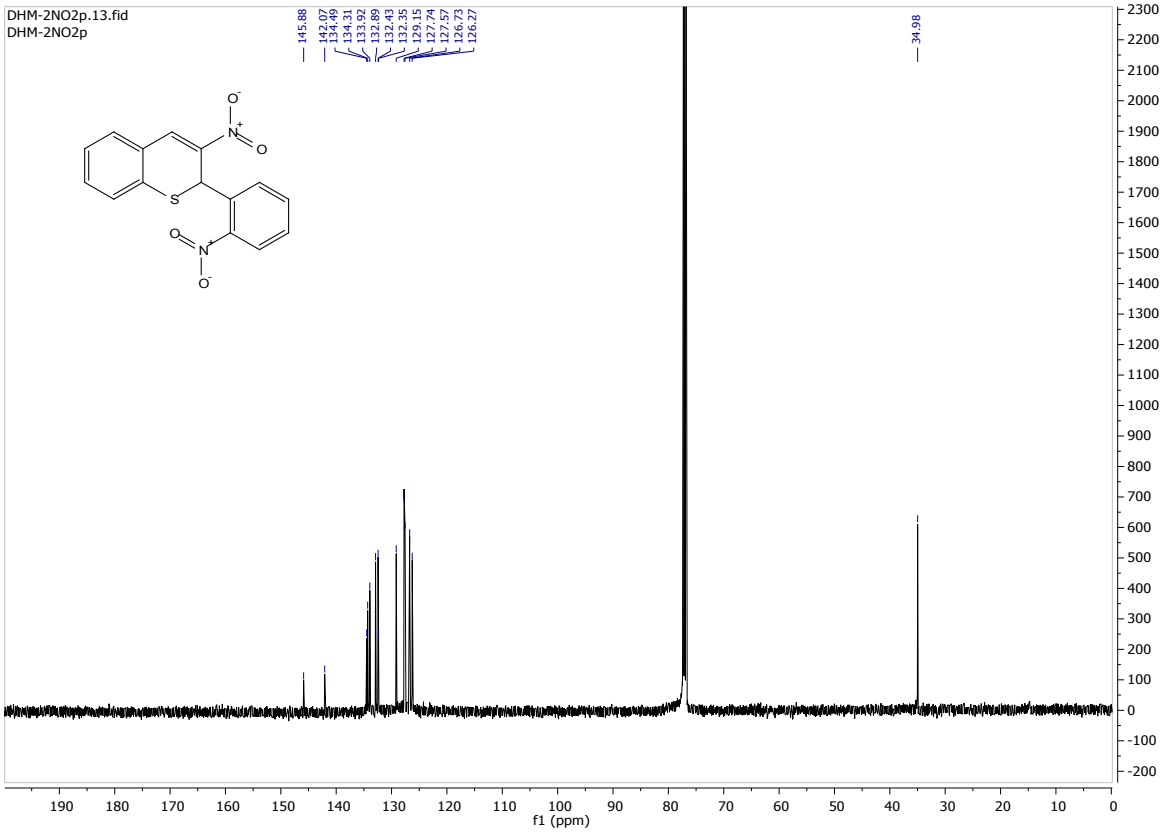

TMH77d
77d
8.16
7.42
7.40
7.30
7.28
7.20
7.19
7.01
7.00
5.43
1.01
1.00
2.46
2.50
1.91
1.00
f1 (ppm)

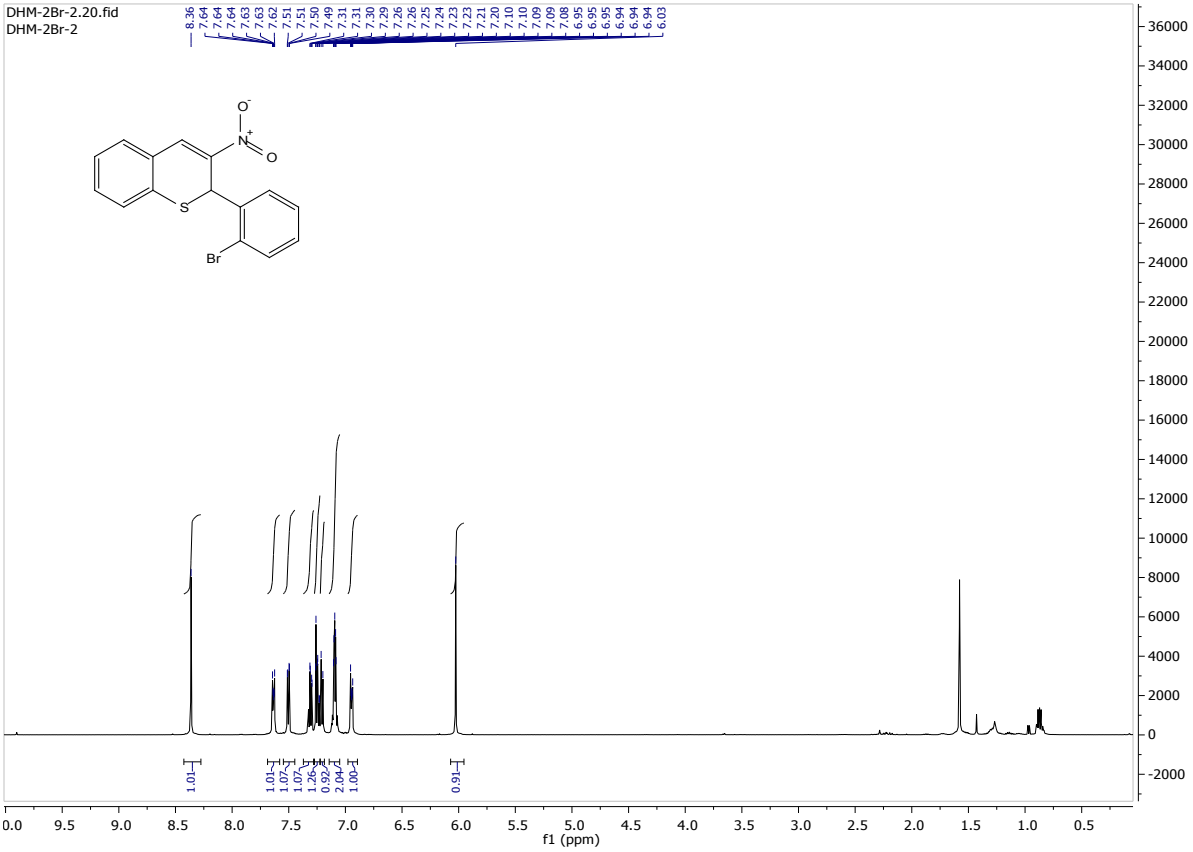

TMH77d
77d
143.29
138.97
132.61
132.43
132.27
132.12
131.83
128.12
127.92
127.49
126.67
122.55
39.34
Br
f1 (ppm)

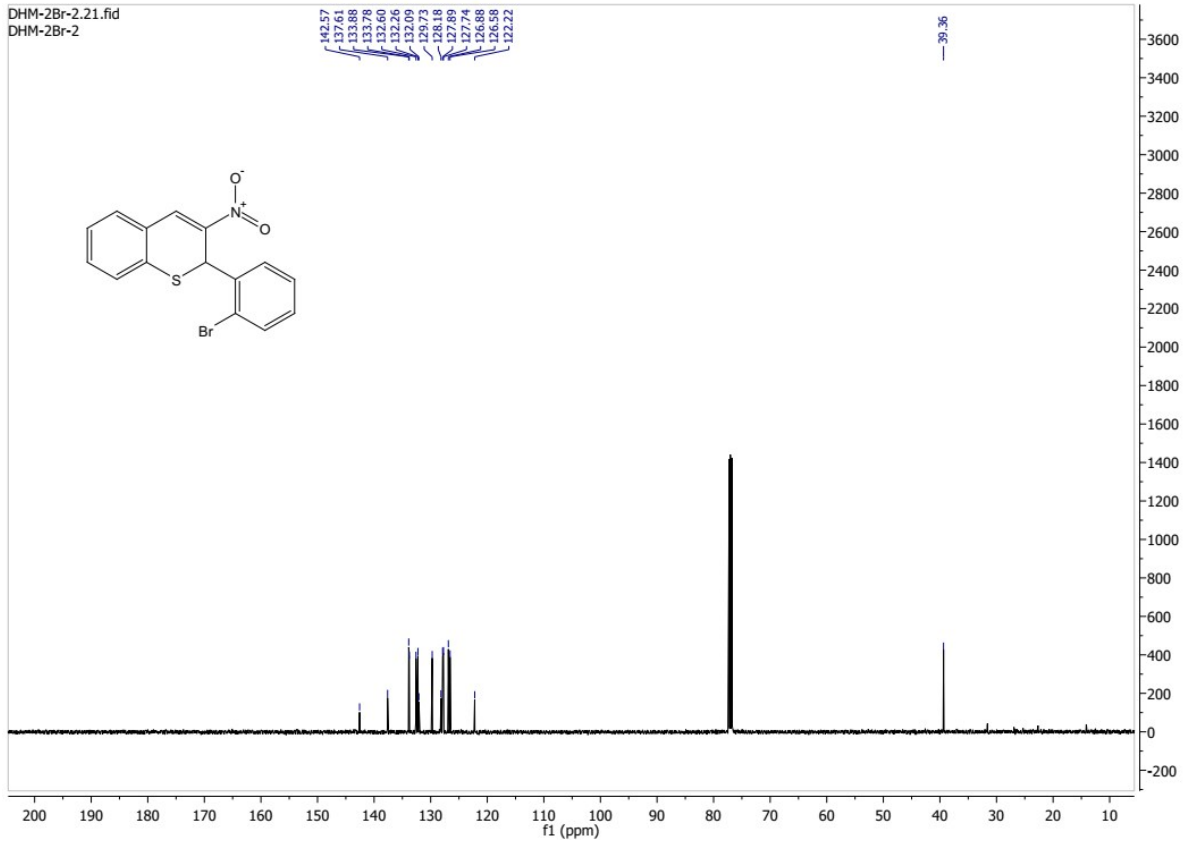

DHM-OMe
3.92
CH3
1.05
1.03
0.75
2.97
1.00
1.03
1.03
1.00
3.28
f1 (ppm)

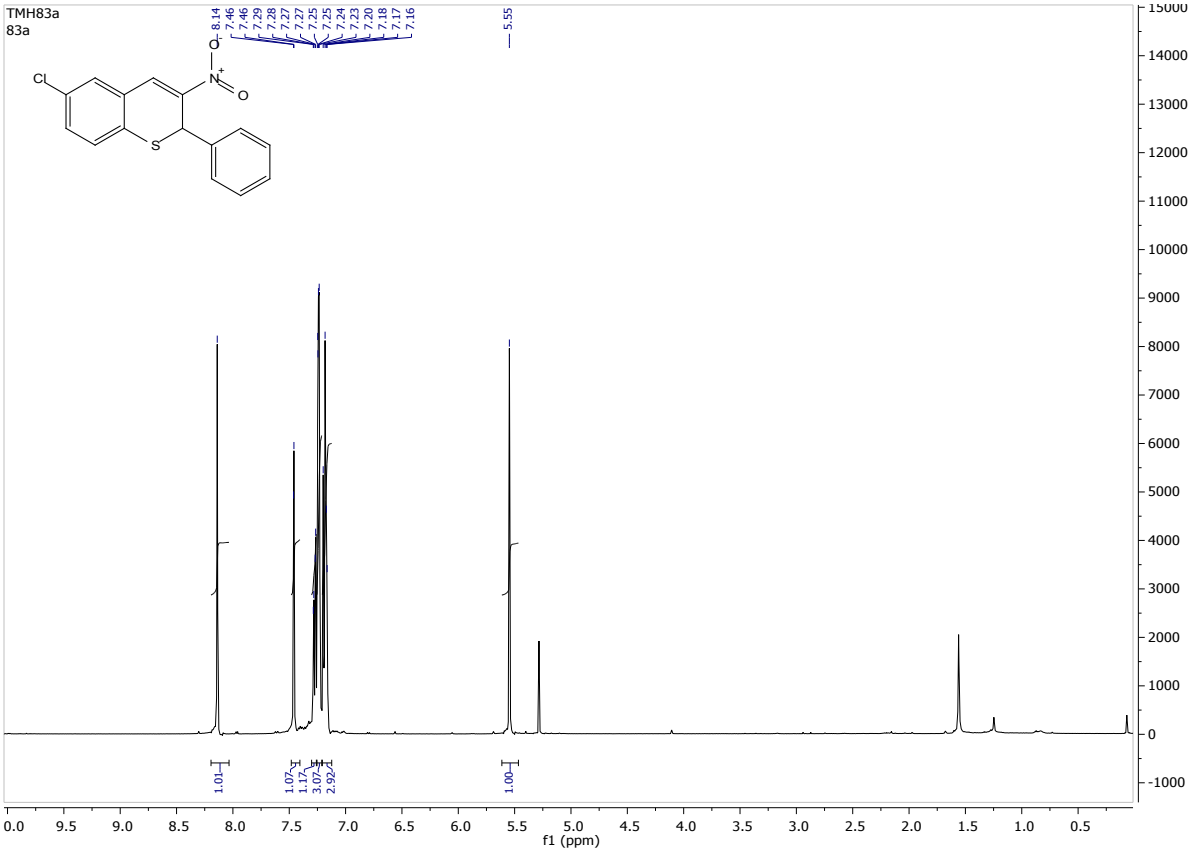

DHM-OMe.10.fid
DHM-OMe
155.19
142.74
133.25
133.18
132.15
132.06
129.51
128.32
127.52
127.18
126.31
126.11
120.50
111.21
55.75
33.35
f1 (ppm)

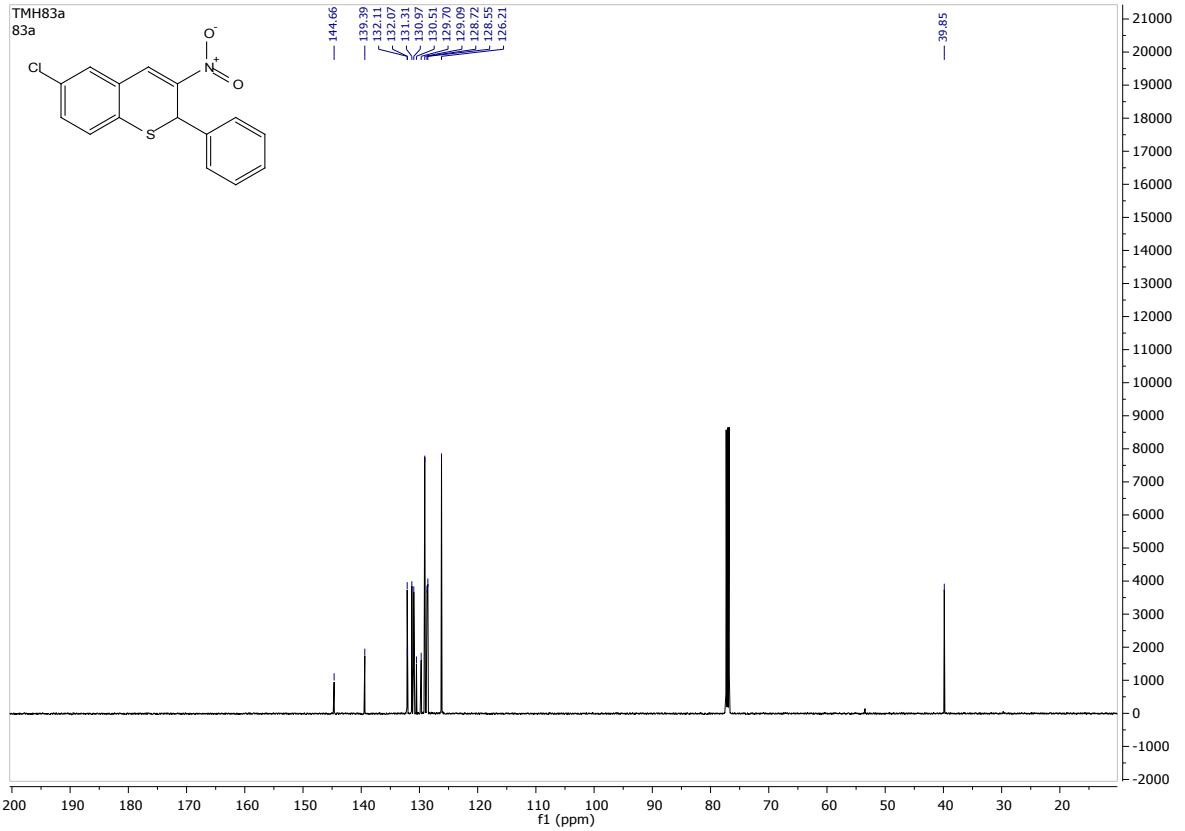

DHM-2NO2p.12.fid
DHM-2NO2p
f1 (ppm)

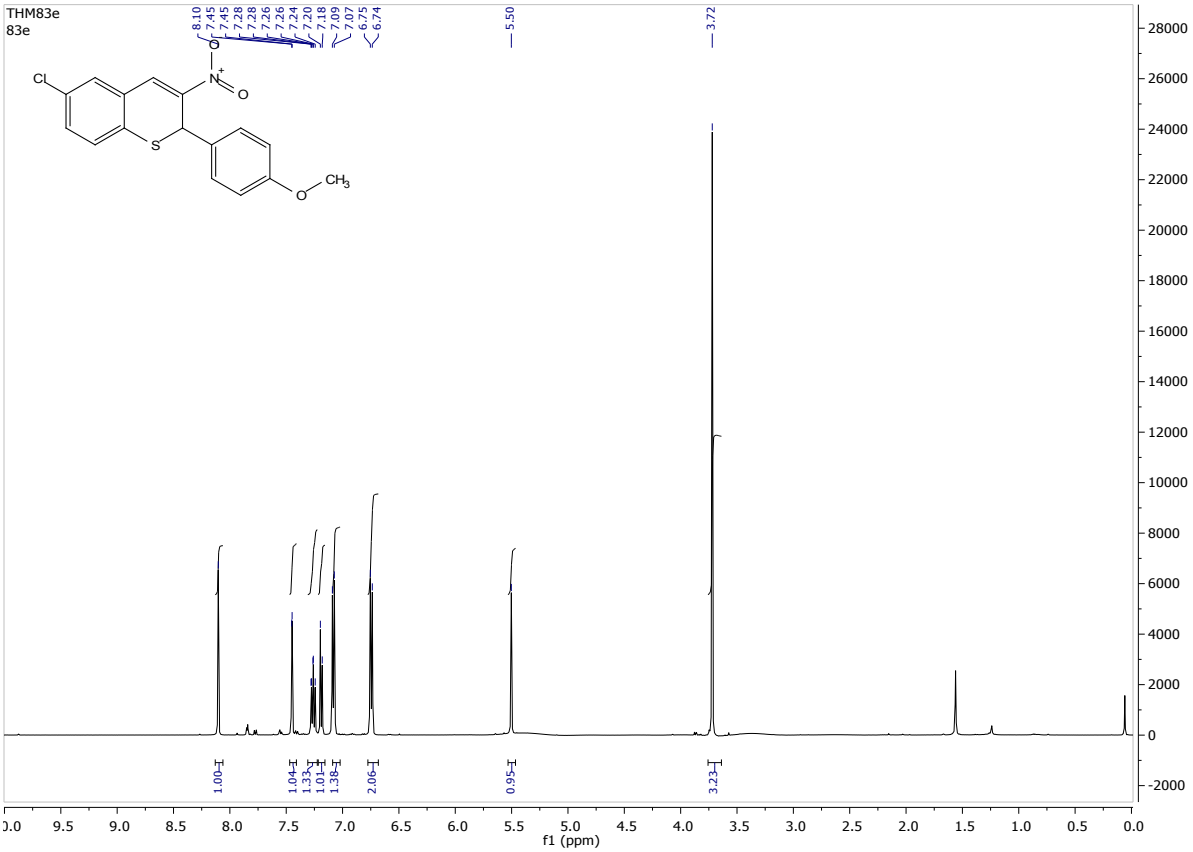

DHM-2NO2p.13.fid
DHM-2NO2p
145.88
142.07
134.49
134.31
133.92
132.89
132.43
132.35
129.15
127.74
127.57
126.73
126.27
34.98
O
N
O
S
O
N
O
f1 (ppm)

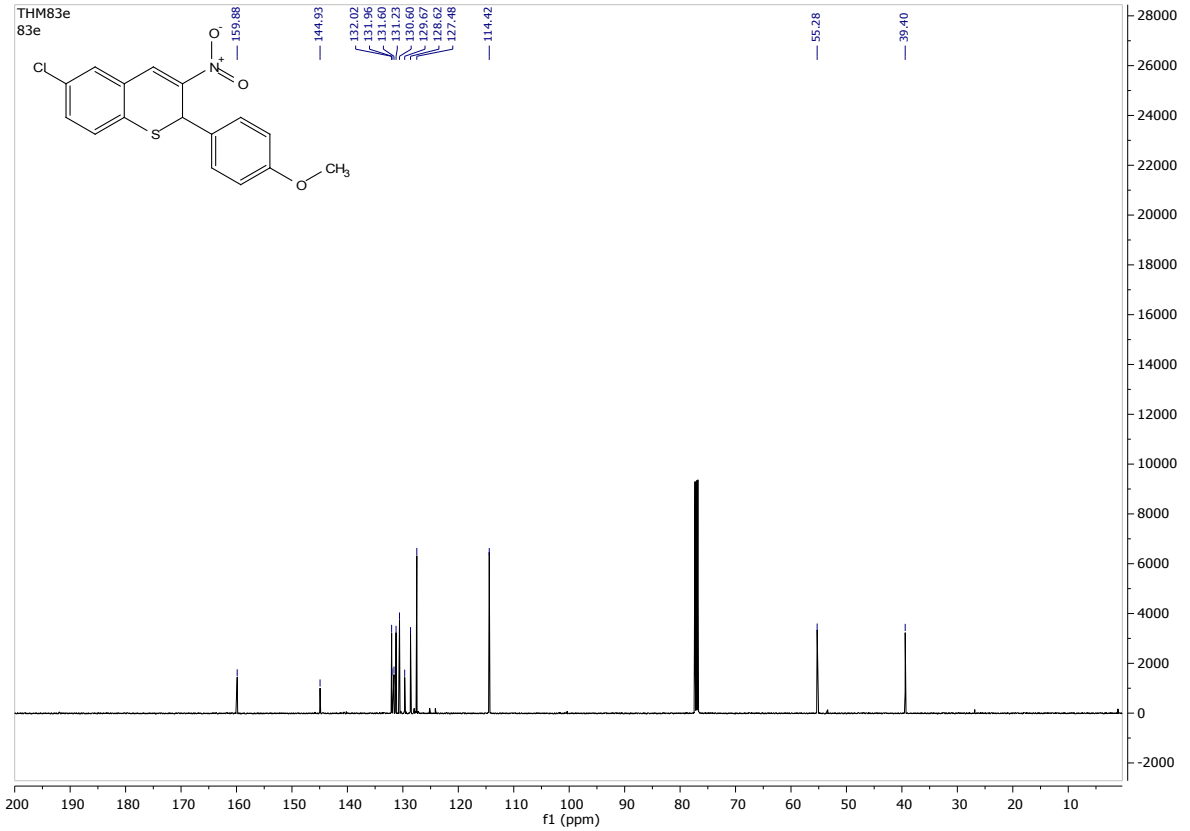

DHM-2Br-2.20.fid
DHM-2Br-2
8.36
7.64
7.64
7.64
7.63
7.63
7.62
7.51
7.51
7.50
7.49
7.31
7.31
7.30
7.29
7.26
7.26
7.25
7.24
7.23
7.23
7.21
7.20
7.10
7.10
7.09
7.09
7.08
6.95
6.95
6.95
6.94
6.94
6.94
6.03
O
N
O
S
Br
1.01
1.01
1.07
1.07
1.26
0.92
2.04
1.00
0.91
f1 (ppm)

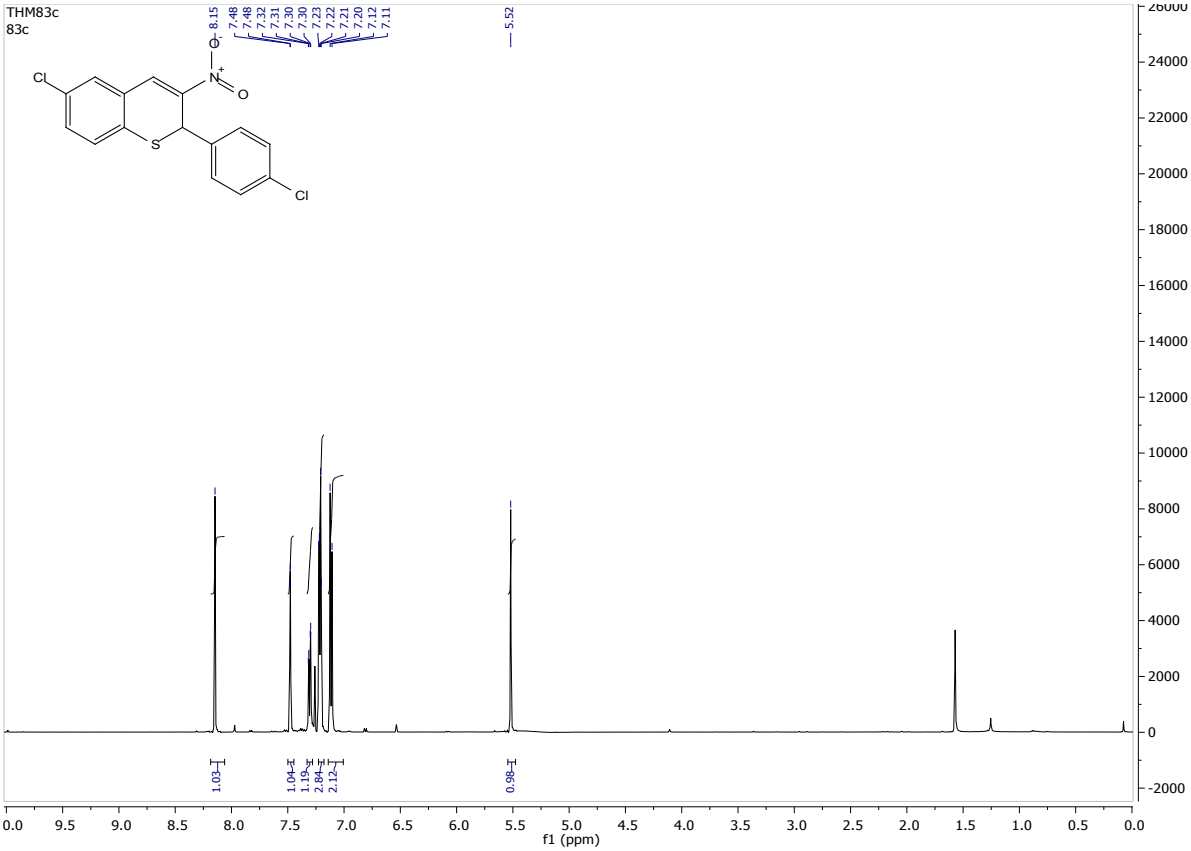

DHM-2Br-2.21.fid
DHM-2Br-2
142.57
137.61
133.88
133.78
132.60
132.26
132.09
129.73
128.18
127.89
127.74
126.88
126.58
122.22
39.36
O
N
O
S
Br
f1 (ppm)

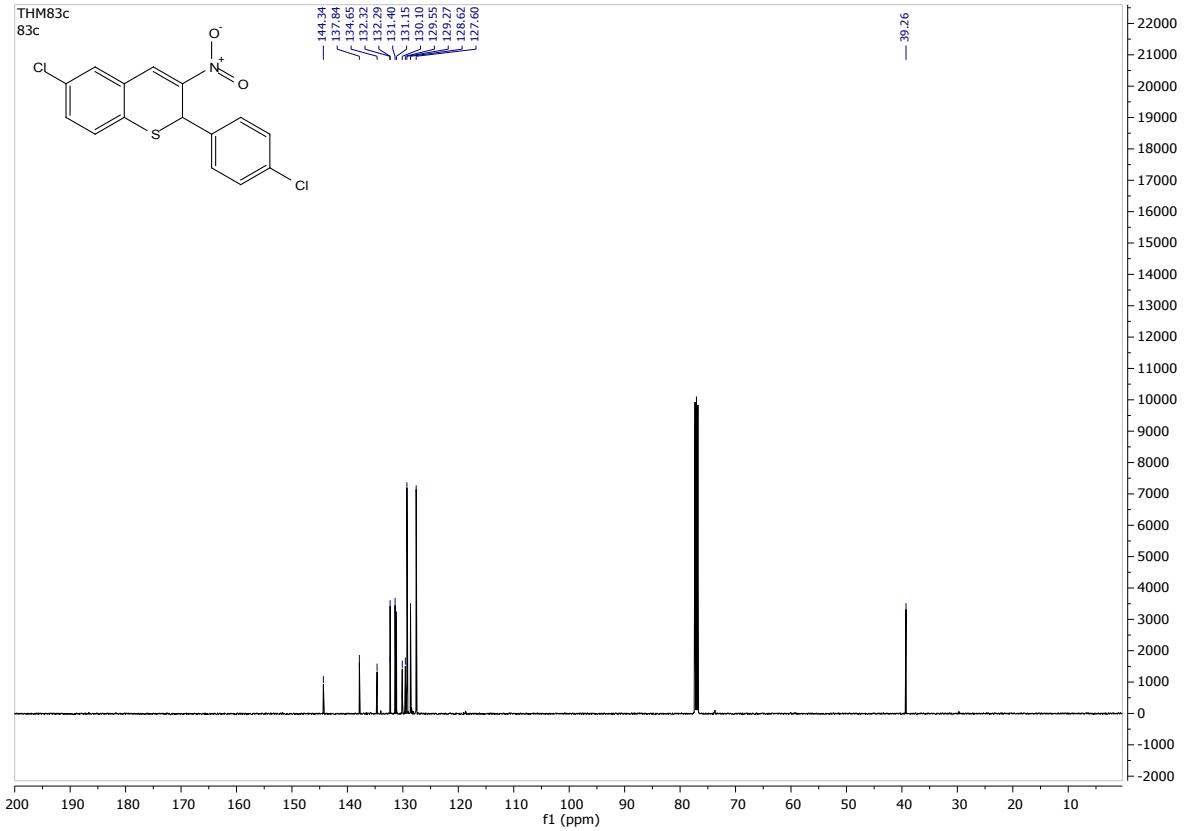

TMH83a
83a
8.14
7.46
7.46
7.29
7.28
7.27
7.27
7.25
7.25
7.24
7.23
7.20
7.18
7.17
7.16
5.55
O
N
O
Cl
S
1.01
1.07
1.12
3.07
2.92
1.00
f1 (ppm)

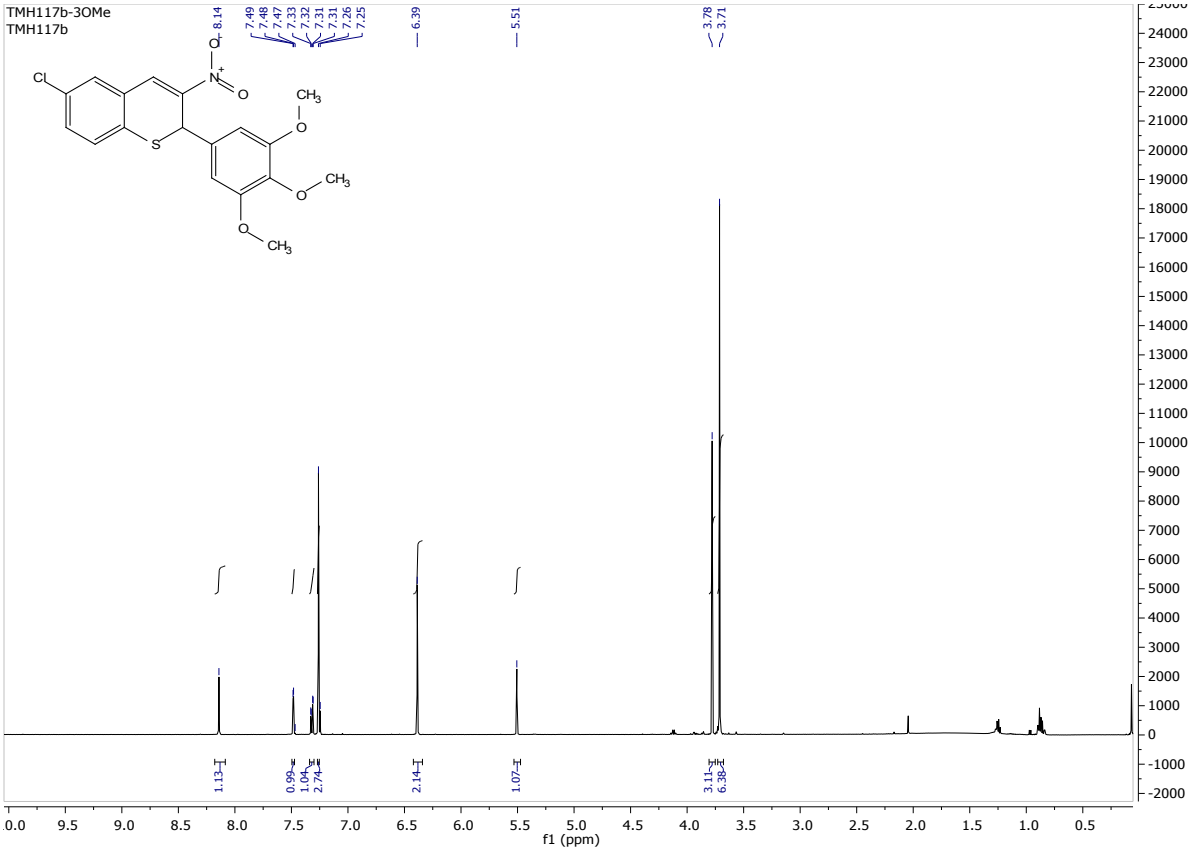

TMH83a
83a
144.66
139.39
132.11
132.07
131.31
130.97
130.51
129.70
129.09
128.72
128.55
126.21
39.85
f1 (ppm)

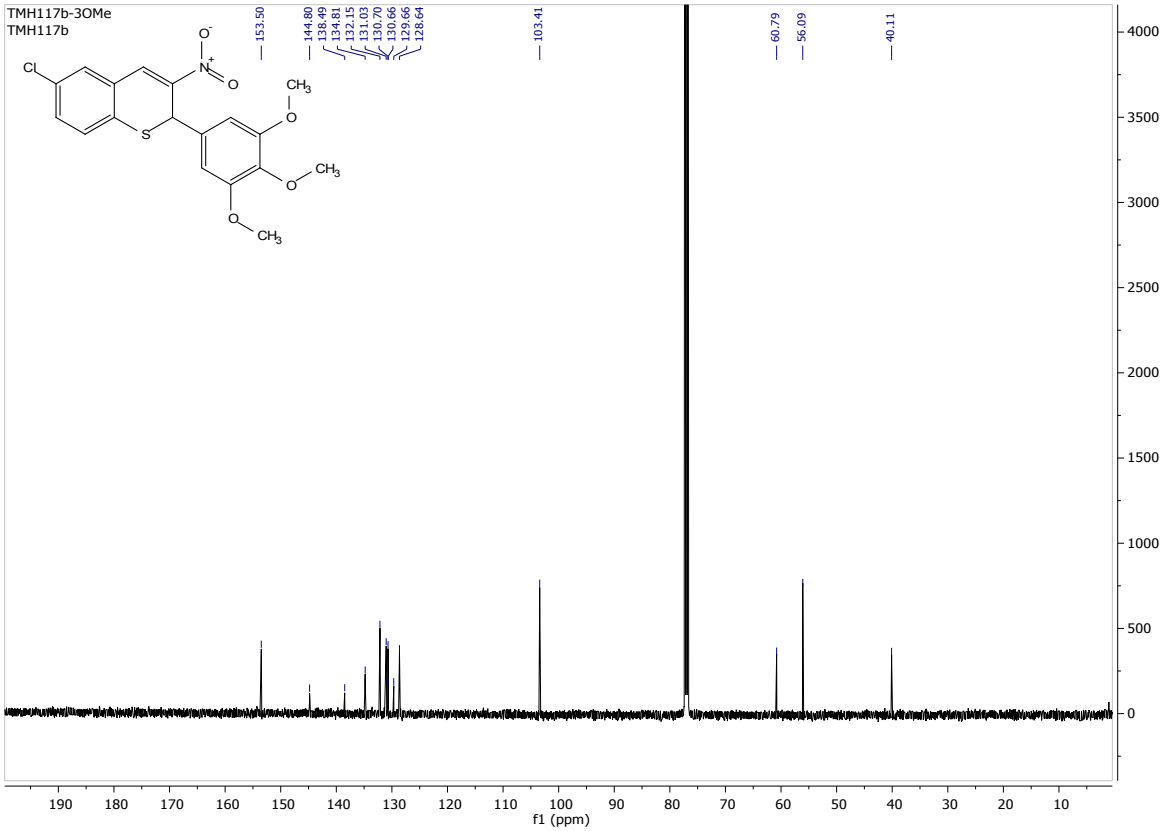

THM83e
83e
8.10
7.45
7.45
7.28
7.28
7.26
7.26
7.24
7.20
7.18
7.09
7.07
6.75
6.74
5.50
3.72
1.00
1.04
1.33
1.01
1.38
2.06
0.95
3.23
f1 (ppm)

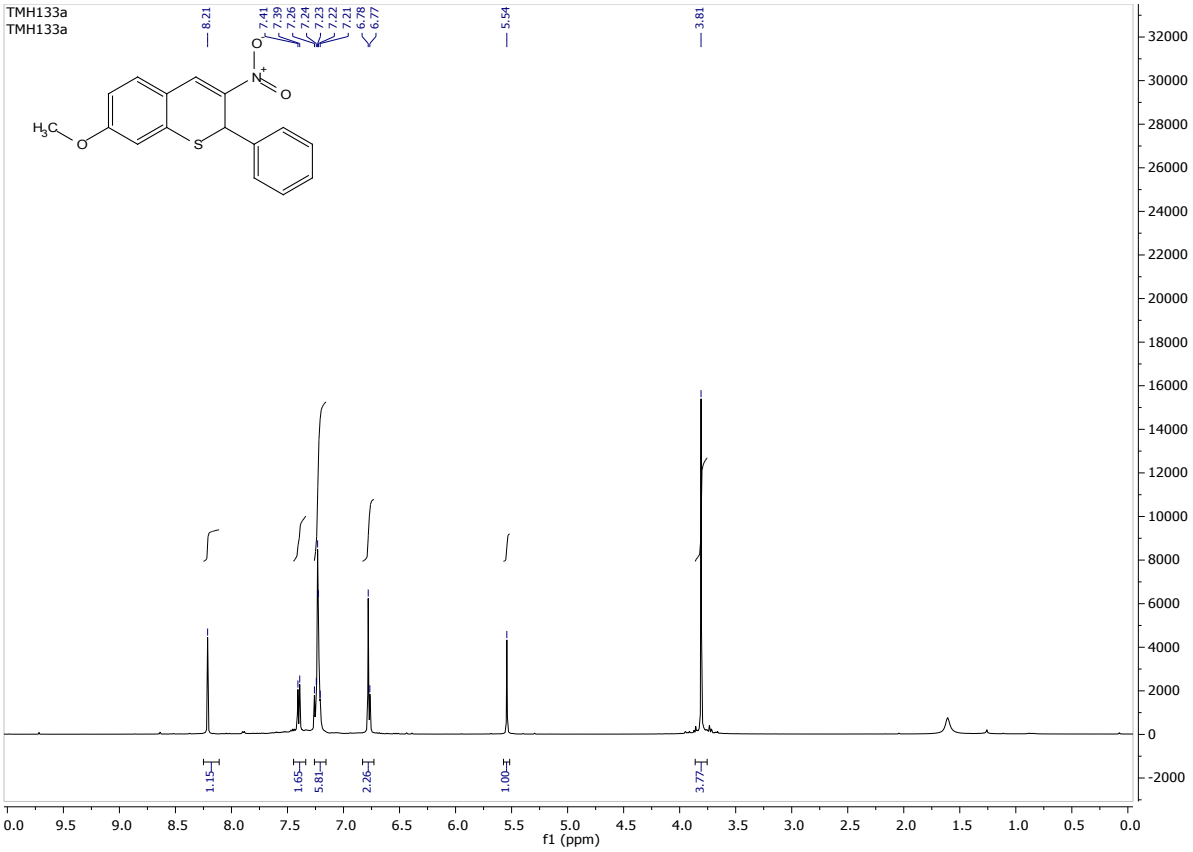

THM83e
83e
159.88
144.93
132.02
131.96
131.60
131.23
130.60
129.67
128.62
127.48
114.42
55.28
39.40
f1 (ppm)

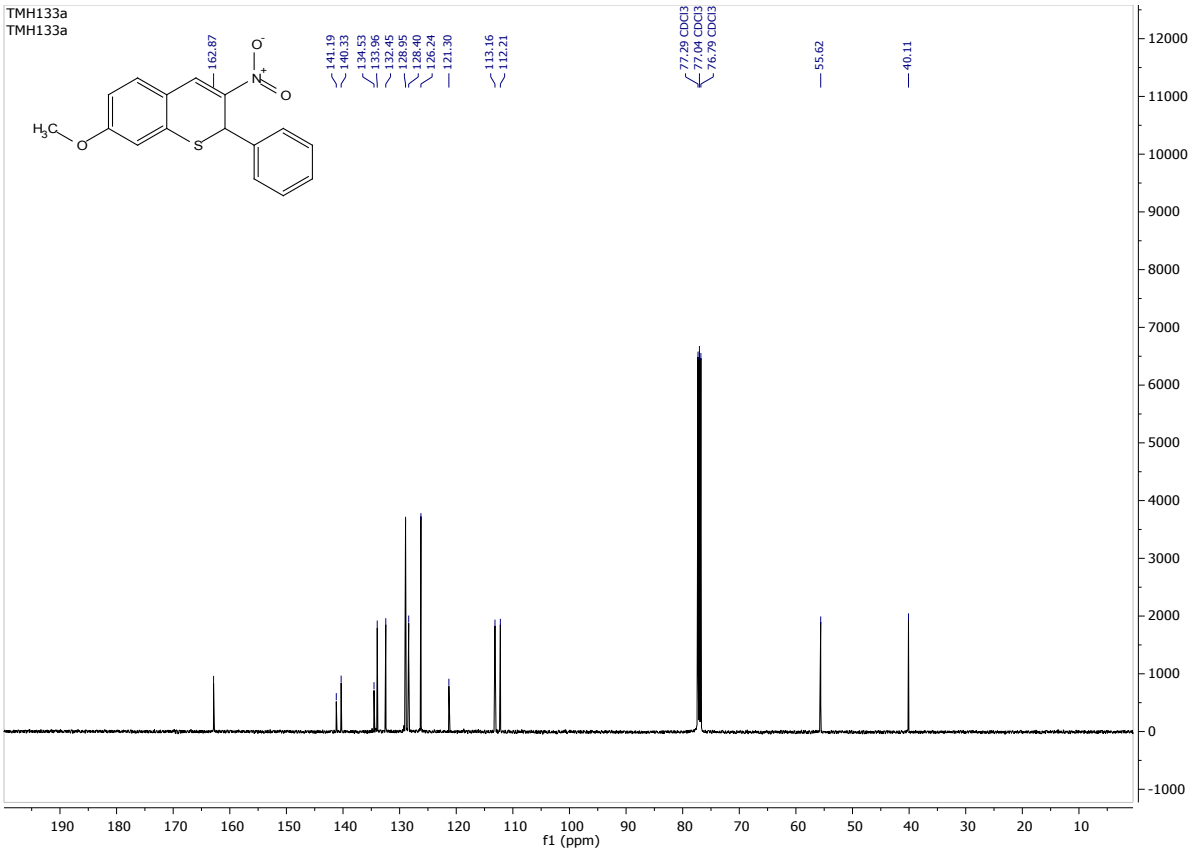

THM83c
83c
8.15
7.48
7.48
7.32
7.31
7.30
7.30
7.23
7.22
7.21
7.20
7.12
7.11
5.52
1.03
1.04
1.19
2.84
2.12
0.98
f1 (ppm)

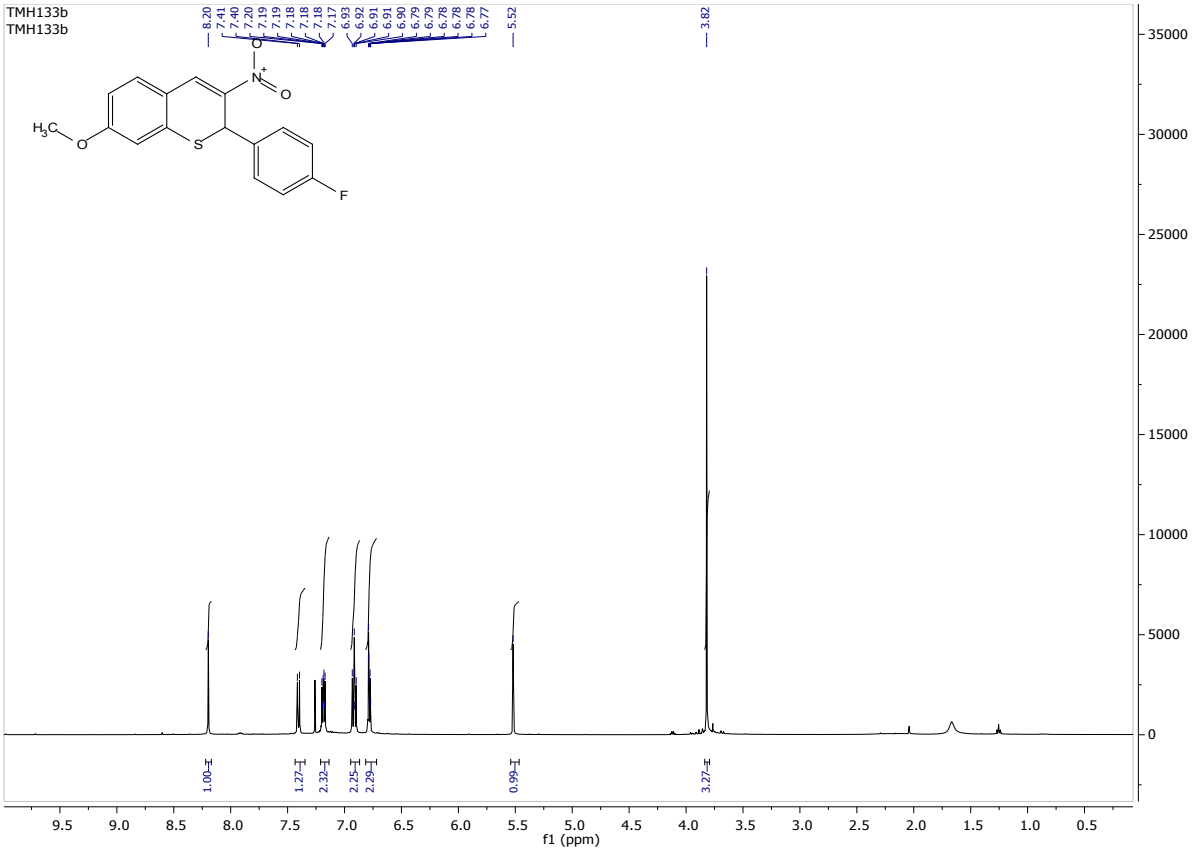

THM83c
83c
144.34
137.84
134.65
132.32
132.29
131.40
131.15
130.10
129.55
129.27
128.62
127.60
39.26
f1 (ppm)


TMH117b-3OMe
TMH117b
8.14
7.49
7.48
7.47
7.33
7.32
7.31
7.31
7.26
7.25
6.39
5.51
3.78
3.71
1.13
0.99
1.04
2.74
2.14
1.07
3.11
6.38
f1 (ppm)


TMH117b-3OMe
TMH117b
153.50
144.80
138.49
134.81
132.15
131.03
130.70
130.66
129.66
128.64
103.41
60.79
56.09
40.11
f1 (ppm)


TMH133a
TMH133a
8.21
7.41
7.39
7.26
7.24
7.23
7.22
7.21
6.78
6.77
5.54
3.81
1.15
1.65
5.81
2.26
1.00
3.77
f1 (ppm)


TMH133a
TMH133a
162.87
141.19
140.33
134.53
133.96
132.45
128.95
128.40
126.24
121.30
113.16
112.21
77.29 CDCl3
77.04 CDCl3
76.79 CDCl3
55.62
40.11
f1 (ppm)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TMH133b
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7.41
7.40
7.20
7.19
7.18
7.18
7.17
6.93
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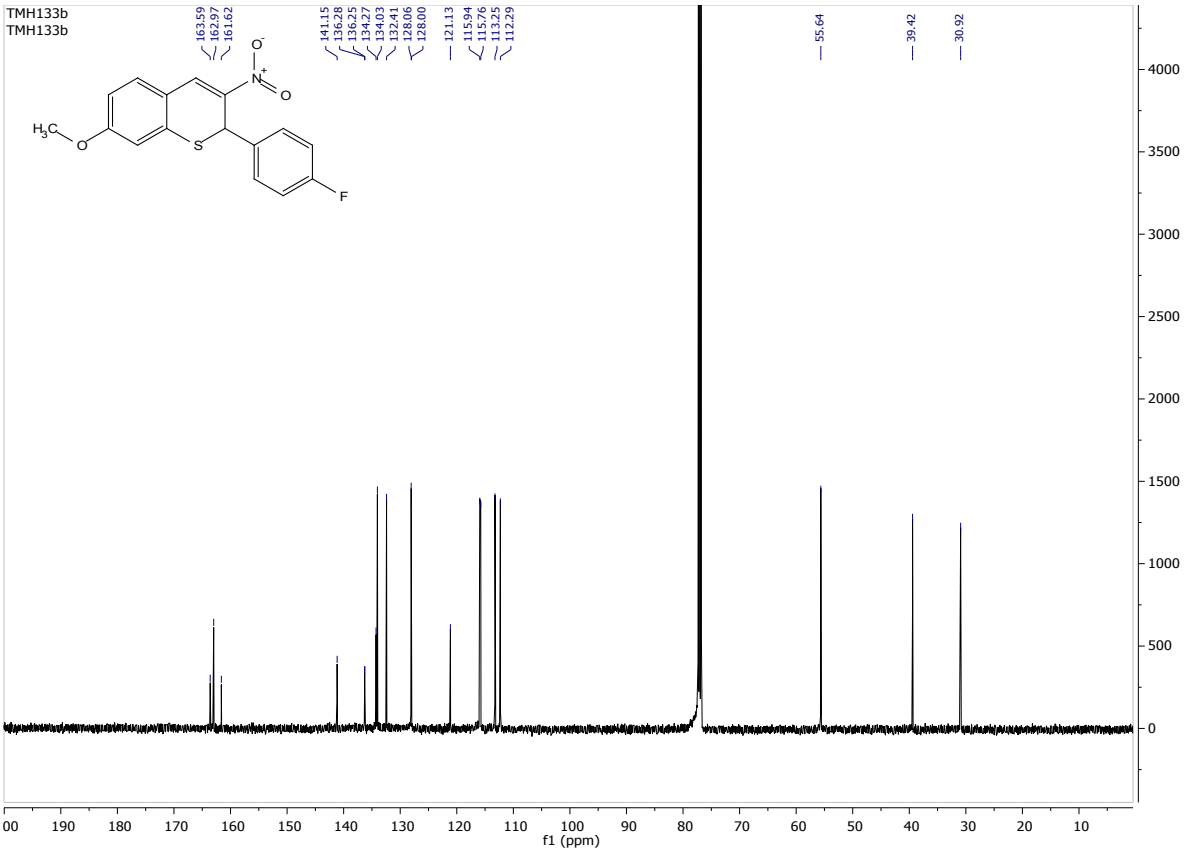
6.91
6.91
6.90
6.79
6.79
6.78
6.78
6.78
6.77
5.52
3.82
1.00
1.27
2.32
2.25
2.29
0.99
3.27
f1 (ppm)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TMH133b
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141.15
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136.25
134.27
134.03
132.41
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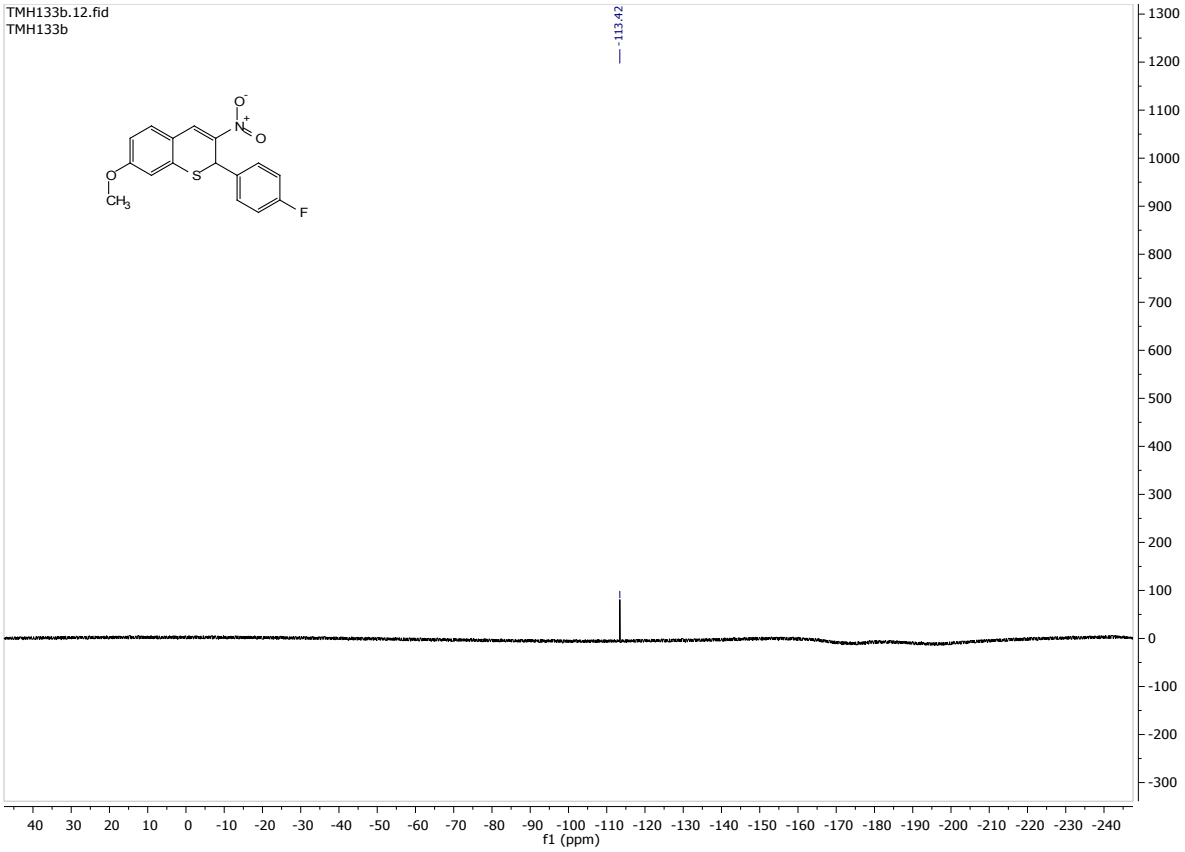
128.00
121.13
115.94
115.76
113.25
112.29
55.64
39.42
30.92
f1 (ppm)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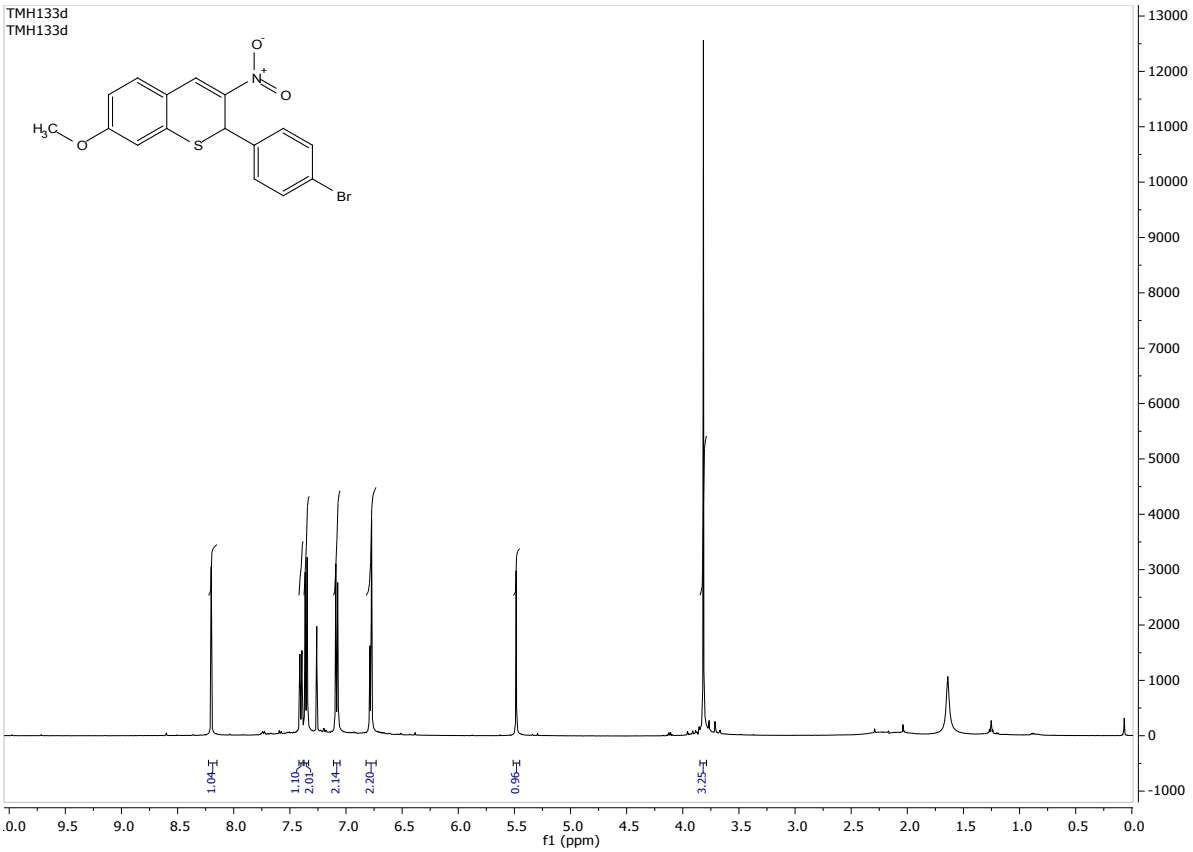
TMH133b
-113.42
f1 (ppm)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TMH133d
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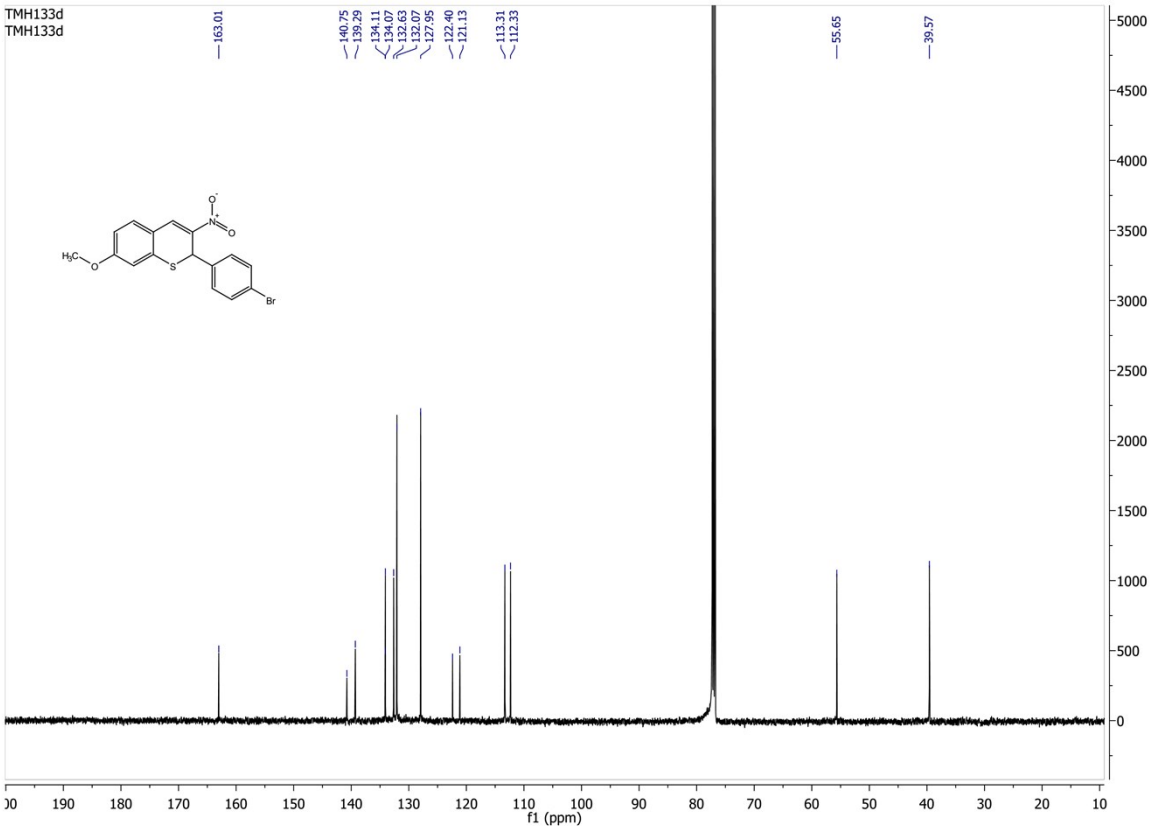
2.01
2.14
2.20
0.96
3.25
f1 (ppm)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TMH133d
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122.40
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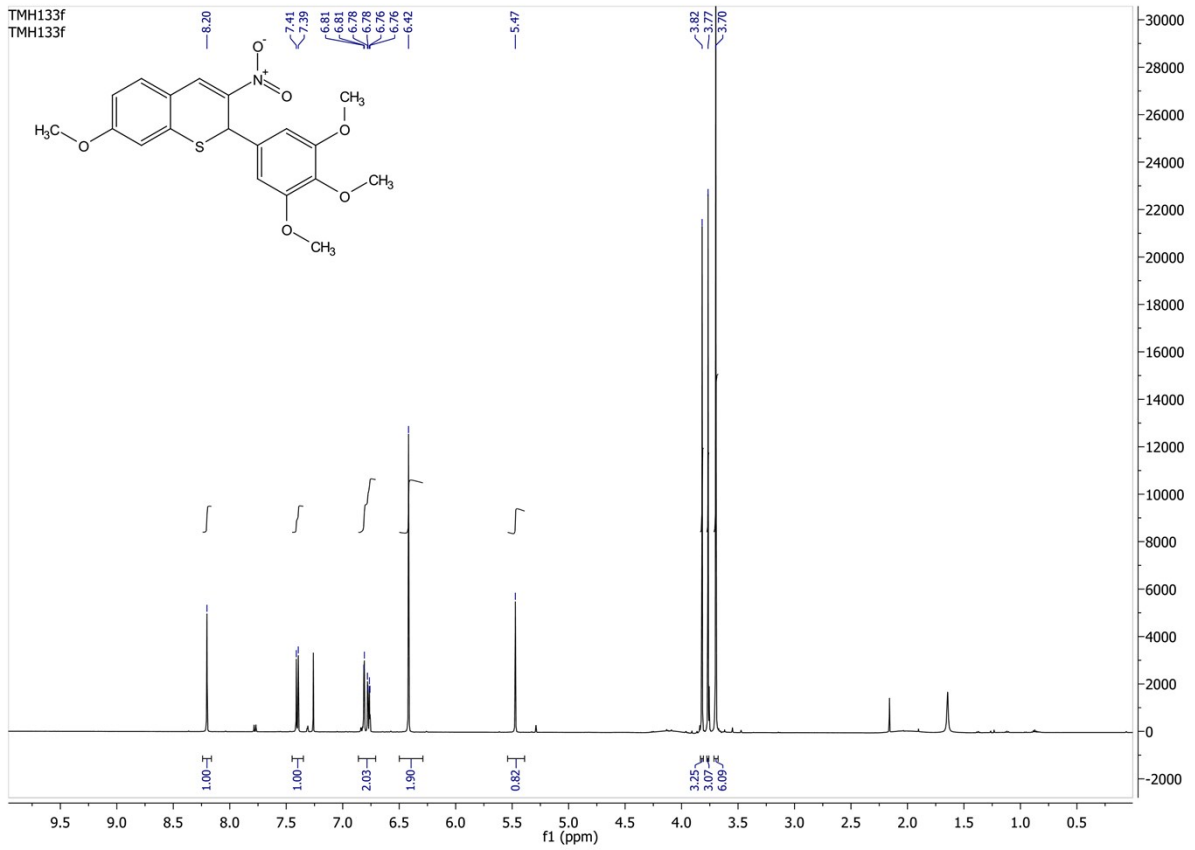
113.31
112.33
55.65
39.57
f1 (ppm)


TMH133f
TMH133f
8.20
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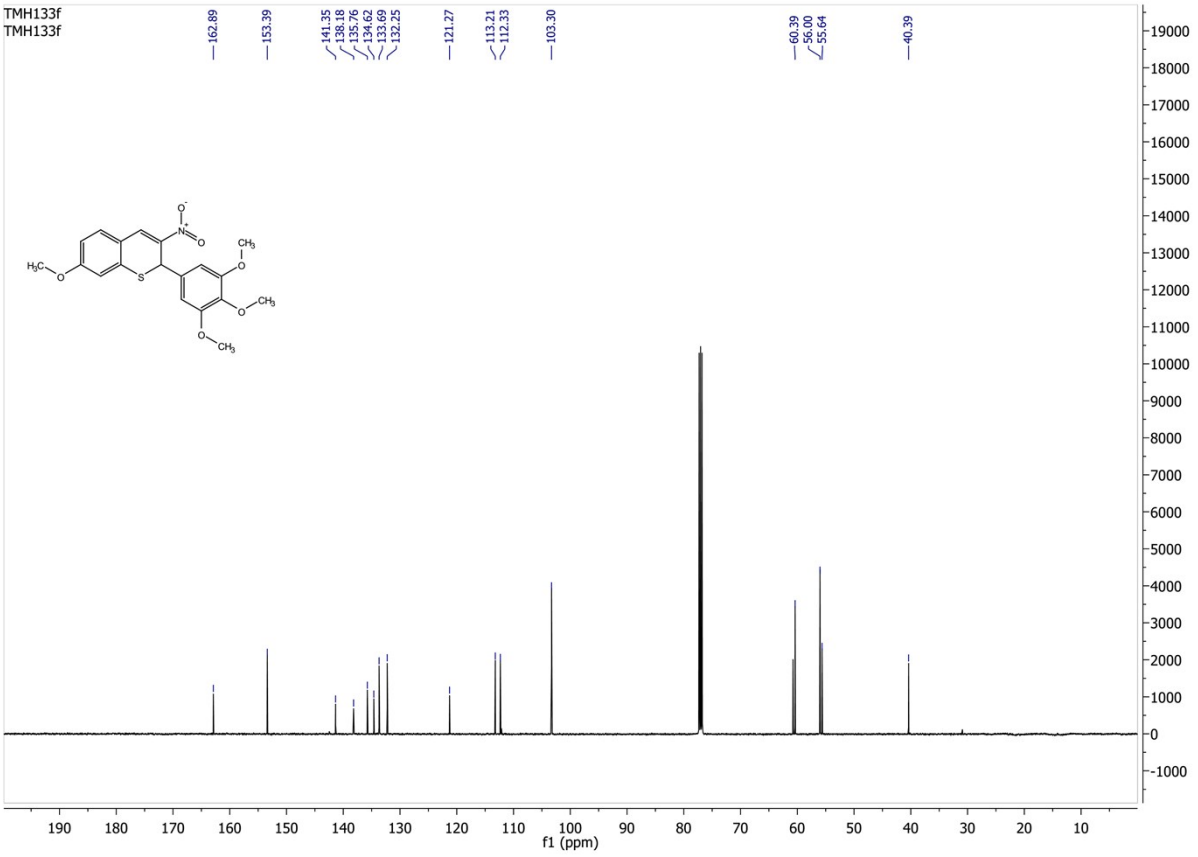
7.39
6.81
6.81
6.78
6.78
6.76
6.76
6.42
5.47
3.82
3.77
3.70
1.00
1.00
2.03
1.90
0.82
3.25
3.07
6.09
f1 (ppm)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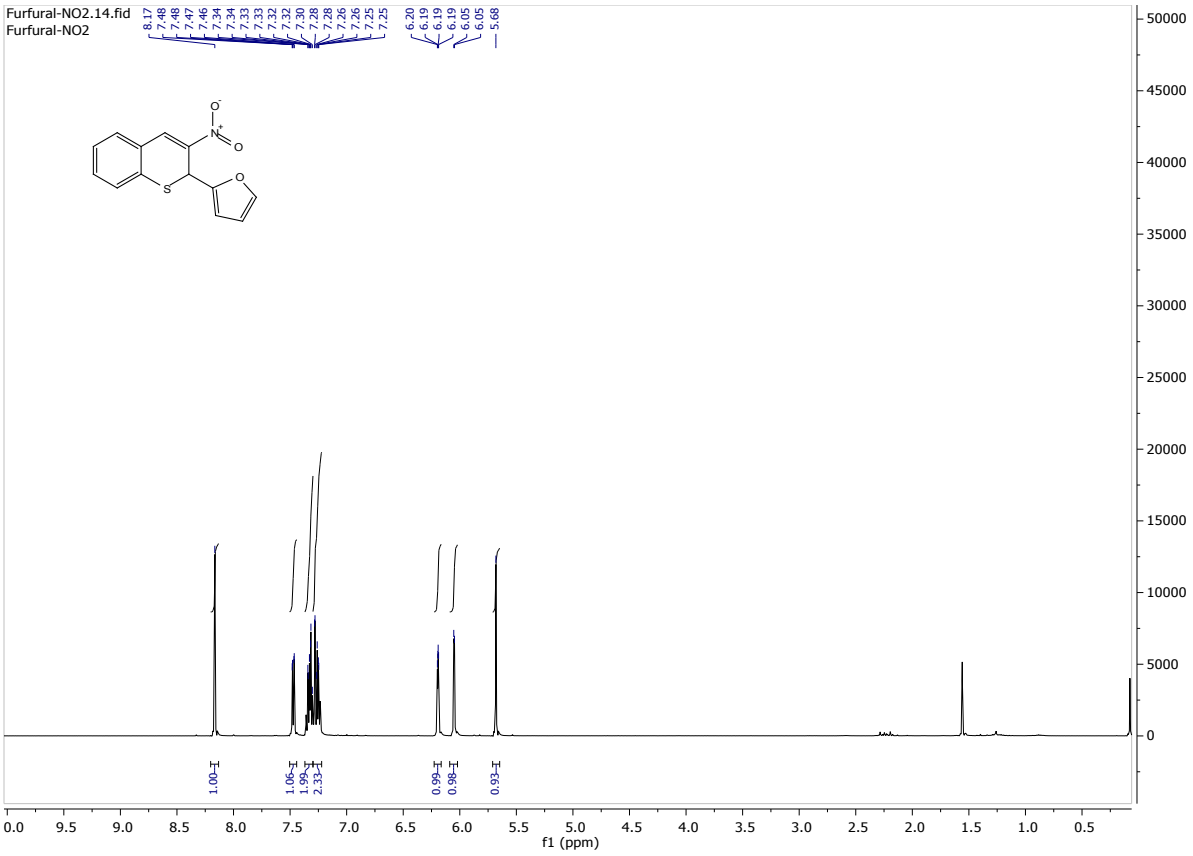
TMH133f
162.89
153.39
141.35
138.18
135.76
134.62
133.69
132.25
121.27
113.21
112.33
103.30
60.39
56.00
55.64
40.39
f1 (ppm)


Furfural-NO2.14.fid
Furfural-NO2
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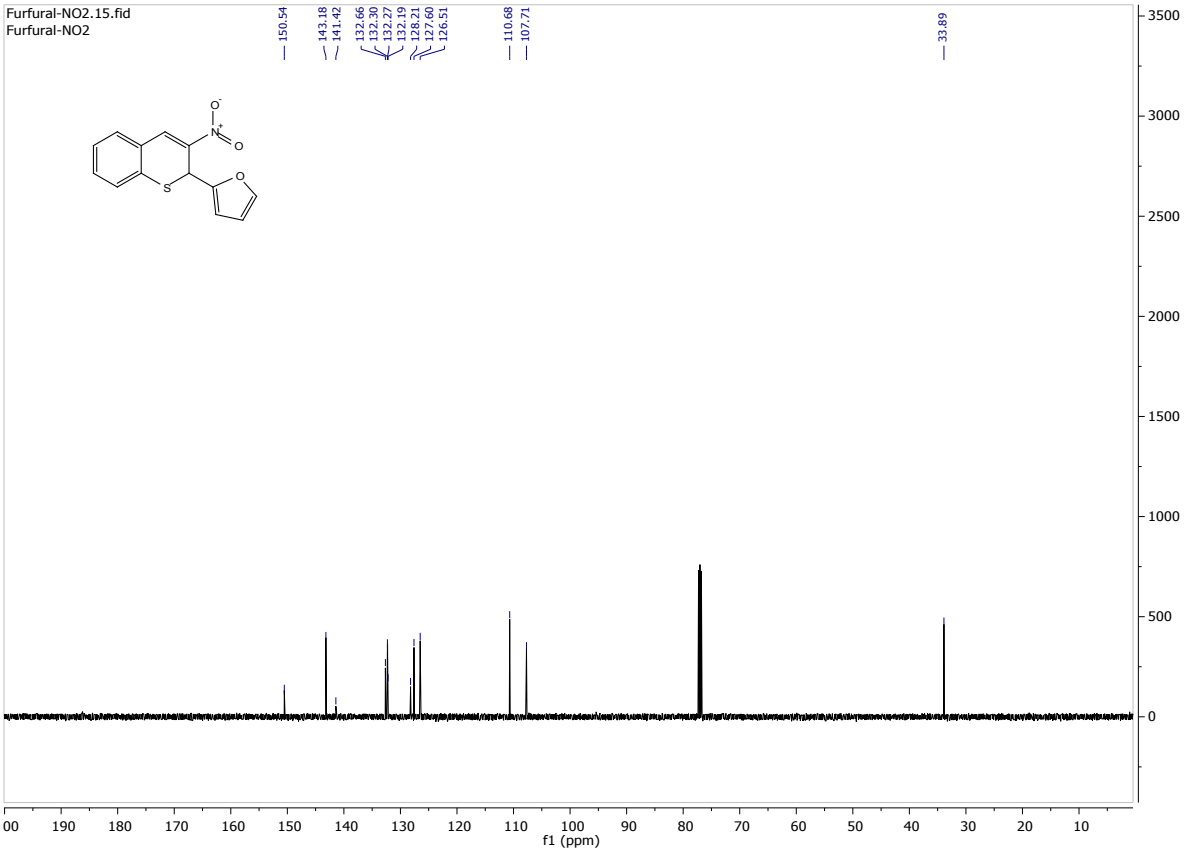
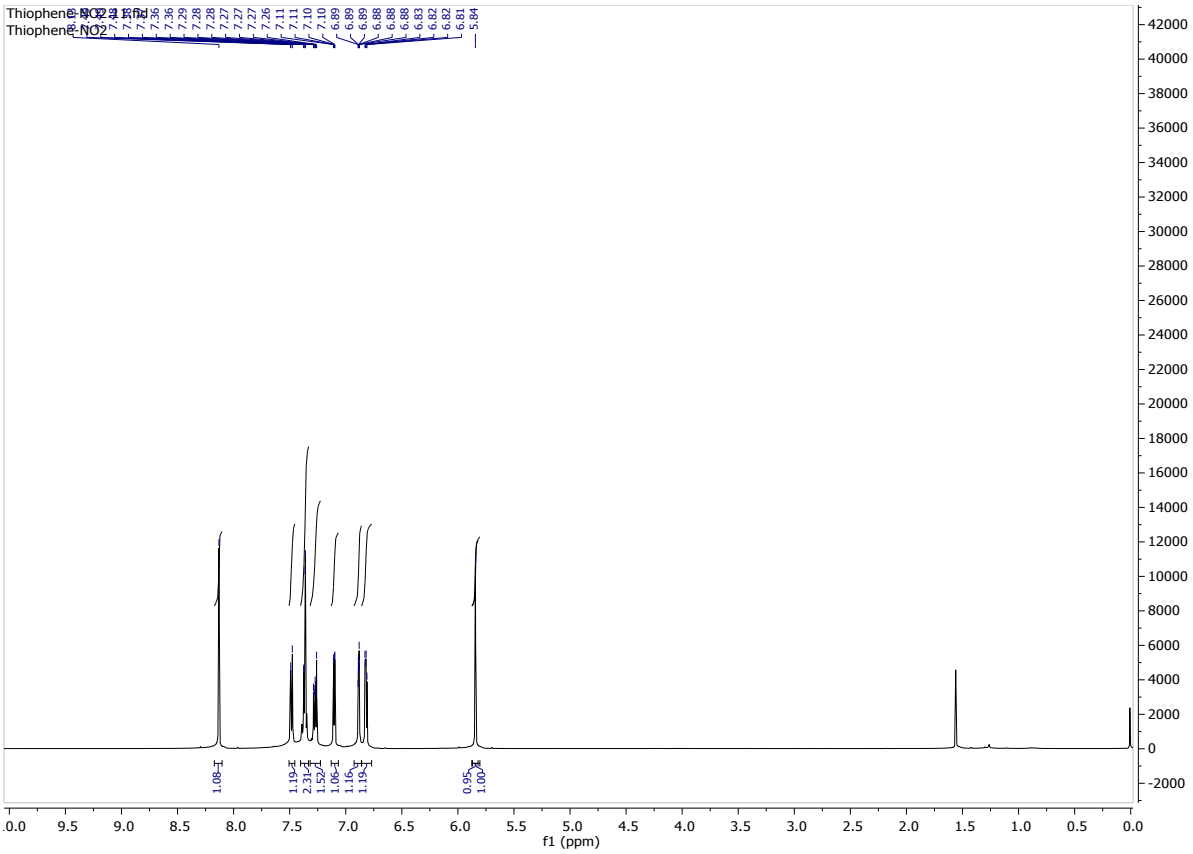
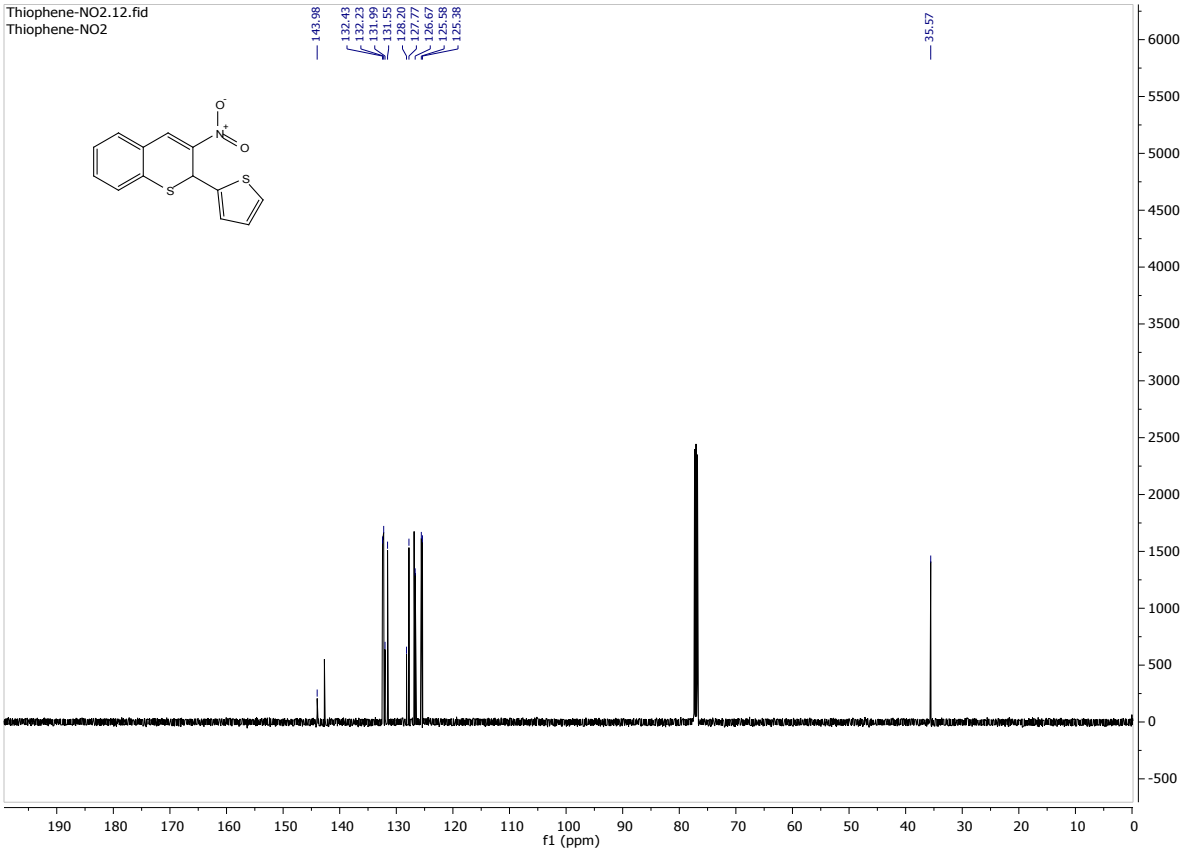
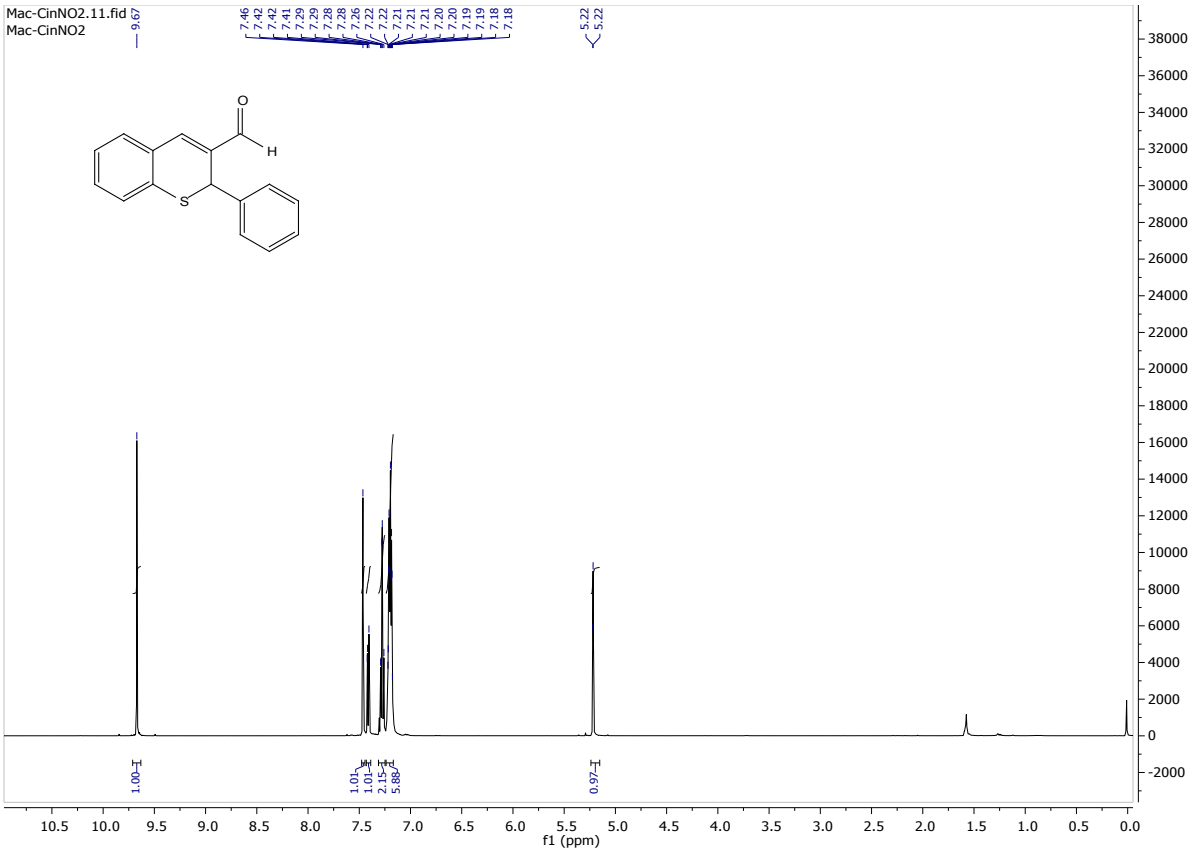
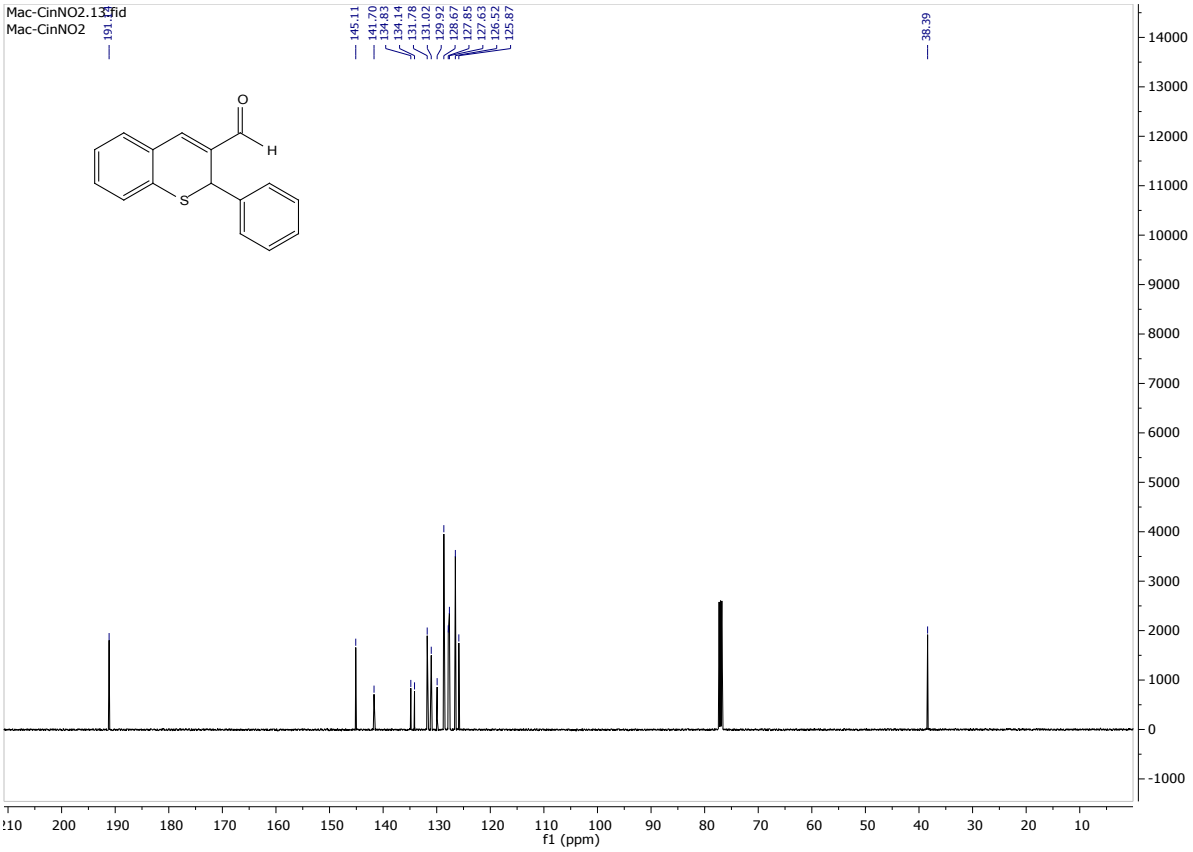
7.48
7.48
7.47
7.46
7.34
7.34
7.33
7.33
7.32
7.32
7.30
7.28
7.28
7.26
7.26
7.25
7.25
6.20
6.19
6.19
6.19
6.05
6.05
5.68
1.00
1.06
1.99
2.33
0.99
0.98
0.93
f1 (ppm)


Furfural-NO2.15.fid
Furfural-NO2
150.54
143.18
141.42
132.66
132.30
132.27
132.19
128.21
127.60
126.51
110.68
107.71
33.89
f1 (ppm)


Thiophene-NO2.11.fid
Thiophene-NO2
7.36
7.29
7.28
7.27
7.27
7.26
7.11
7.10
6.89
6.89
6.88
6.88
6.83
6.82
6.82
6.81
5.84
1.08
1.19
2.31
1.52
1.06
1.16
1.19
0.95
1.00
f1 (ppm)


Thiophene-NO2.12.fid
Thiophene-NO2
143.98
132.43
132.23
131.99
131.55
128.20
127.77
126.67
125.58
125.38
35.57
O
N
O
S
S
f1 (ppm)


Mac-CinNO2.11.fid
Mac-CinNO2
9.67
7.46
7.42
7.42
7.41
7.29
7.29
7.28
7.28
7.26
7.22
7.22
7.21
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.18
5.22
5.22
O
H
S
1.00
1.01
1.01
2.15
5.88
0.97
f1 (ppm)


Mac-CinNO2.13.fid
Mac-CinNO2
191.15
145.11
141.70
134.83
134.14
131.78
131.02
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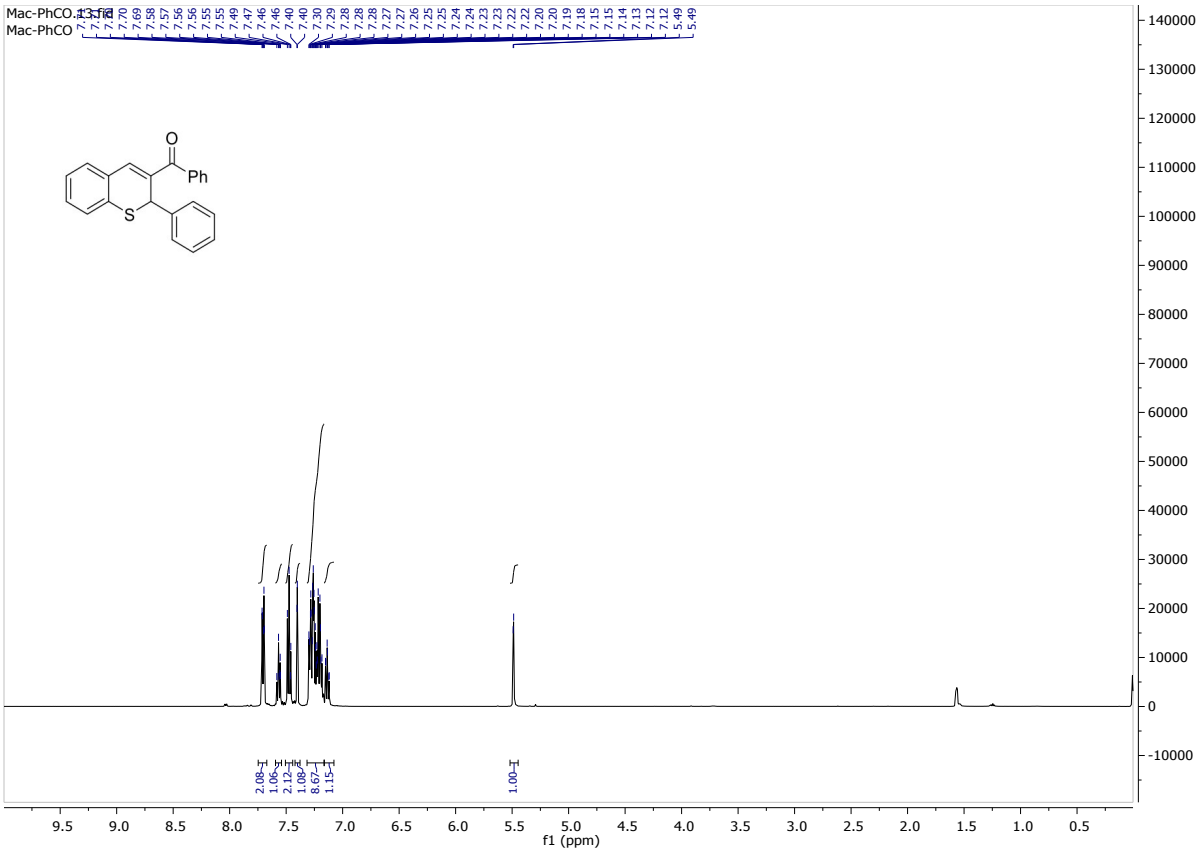
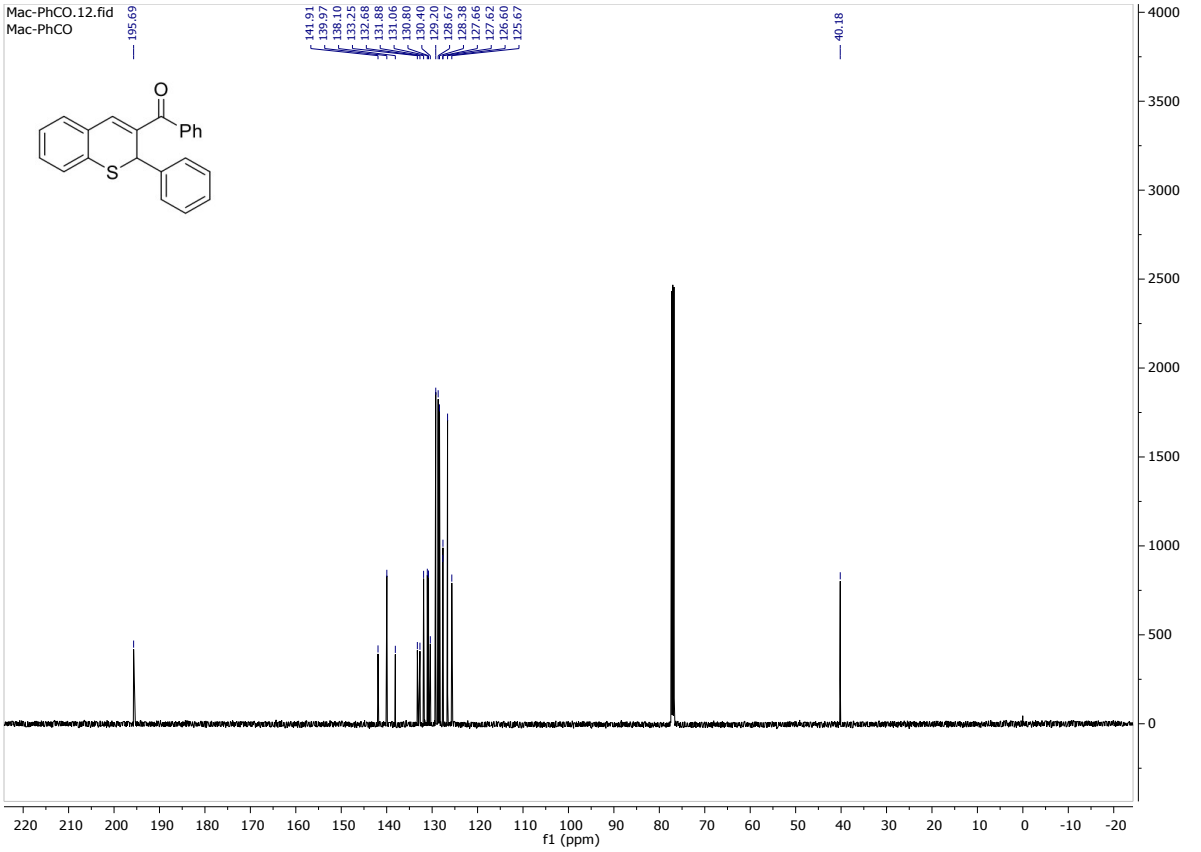
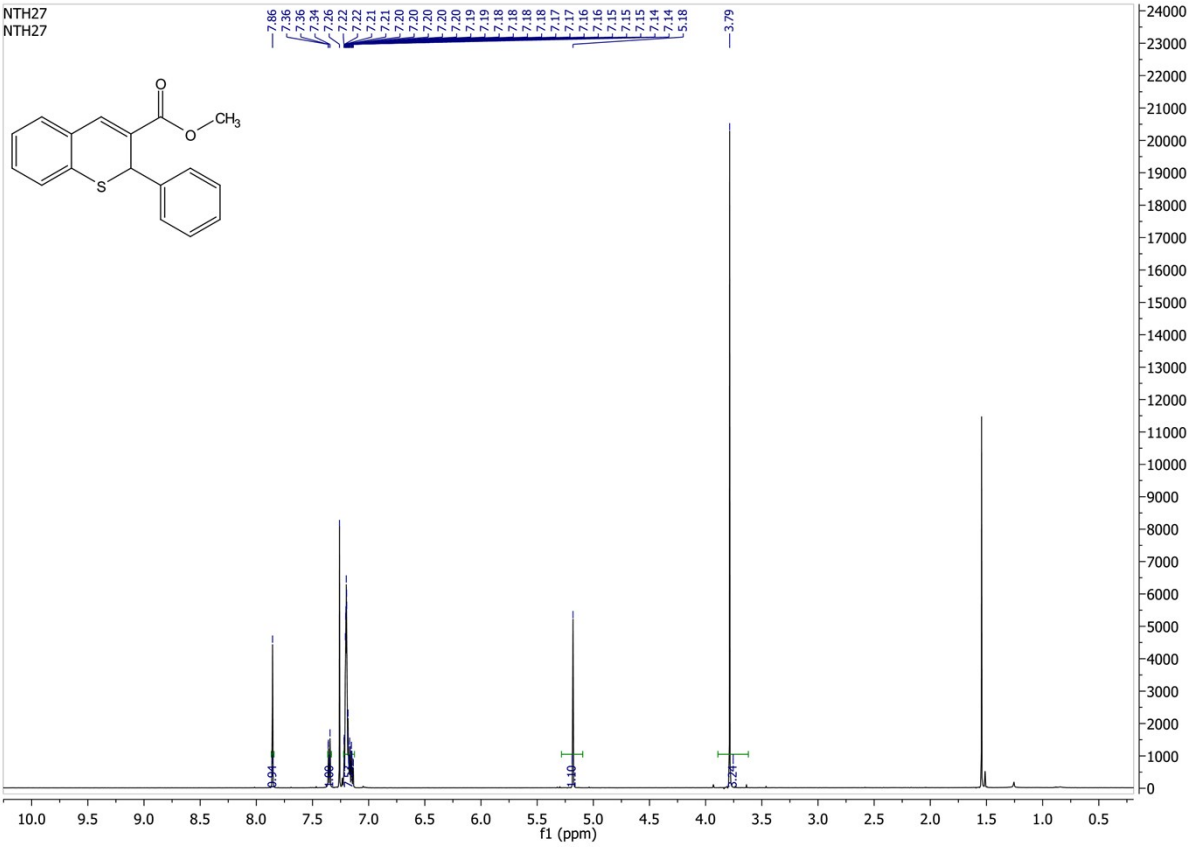
127.85
127.63
126.52
125.87
38.39
O
H
S
f1 (ppm)


Mac-PhCO.13.fid
Mac-PhCO
O
Ph
S
2.08
1.06
2.12
1.08
8.67
1.15
1.00
f1 (ppm)


Mac-PhCO.12.fid
Mac-PhCO
195.69
141.91
139.97
138.10
133.25
132.68
131.88
131.06
130.80
130.40
129.20
128.67
128.38
127.66
127.62
126.60
125.67
40.18
O
Ph
S
f1 (ppm)



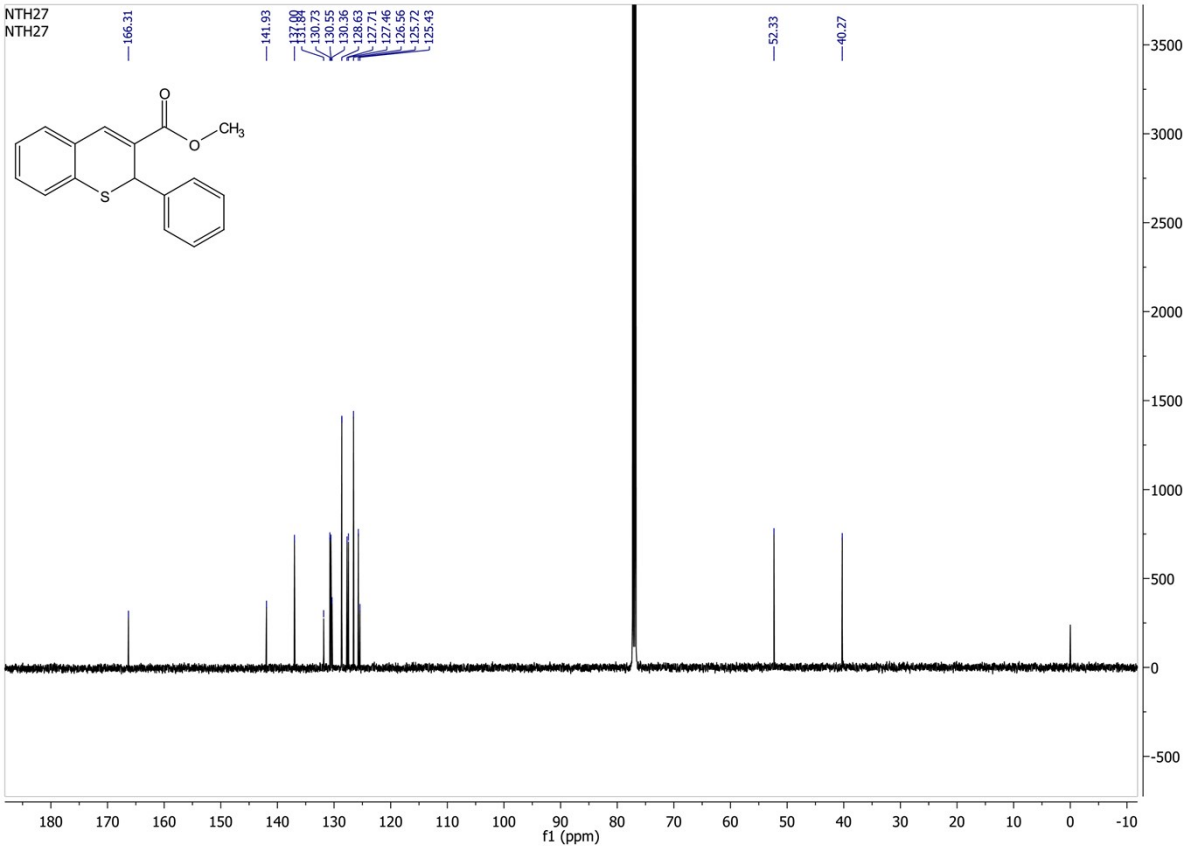


Table 1 Crystal data and structure refinement for thiochrom.

Identification code	thiochrom

Empirical formula	$C_{15}H_{11}NO_2S$
Formula weight	269.31
Temperature/K	100.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.9636(3)
b/Å	10.3969(4)
c/Å	13.4271(5)
α/°	90
β/°	94.8620(10)
γ/°	90
Volume/Å^3	1246.82(8)
Z	4
ρ_{calc}g/cm^3	1.435
μ/mm^{-1}	0.255
F(000)	560.0
Crystal size/mm^3	0.17 × 0.17 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.014 to 56.664
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -17 ≤ l ≤ 17
Reflections collected	31745
Independent reflections	3105 [R_{int} = 0.0290, R_{sigma} = 0.0140]
Data/restraints/parameters	3105/0/172
Goodness-of-fit on F^2	1.059
Final R indexes [I>=2σ (I)]	R_1 = 0.0296, wR_2 = 0.0721
Final R indexes [all data]	R_1 = 0.0344, wR_2 = 0.0746
Largest diff. peak/hole / e Å^{-3}	0.38/-0.24

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for thiochrom. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	6056.6(10)	4152.9(9)	2182.4(7)	20.86(19)
N1	5140.1(11)	5018.6(10)	2267.2(7)	15.0(2)
C1	3063.6(12)	6064.5(11)	3099.4(8)	12.4(2)
C2	4199.5(12)	5000.4(11)	3114.0(8)	12.3(2)
O2	4941.9(11)	5909.6(9)	1665.8(7)	26.4(2)
C3	4377.5(12)	4016.8(11)	3755.4(8)	12.9(2)
C4	3511.8(12)	3858.2(11)	4613.8(8)	12.5(2)
C5	3639.8(13)	2712.7(11)	5167.8(9)	15.2(2)
C6	2851.5(13)	2547.6(12)	6004.2(9)	17.8(2)
C7	1908.7(13)	3518.2(12)	6293.7(9)	17.5(2)

C8	1756.0(13)	4656.4(12)	5750.5(9)	15.6(2)
C9	2570.1(12)	4842.2(11)	4918.3(8)	12.9(2)
S10	2511.3(3)	6372.5(3)	4362.5(2)	13.95(8)
C11	1708.6(12)	5834.7(11)	2360.1(8)	12.4(2)
C12	885.3(13)	4696.0(11)	2370.2(8)	14.3(2)
C13	-387.3(13)	4533.3(12)	1712.4(9)	17.5(2)
C14	-846.8(14)	5504.6(13)	1041.5(9)	19.7(2)
C15	-23.3(14)	6631.9(12)	1019.7(9)	20.0(3)
C16	1255.5(13)	6793.9(12)	1674.9(9)	16.9(2)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for thiochrom. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	19.5(4)	18.7(4)	25.9(5)	0.3(4)	10.5(3)	4.3(3)
N1	13.7(5)	15.3(5)	16.5(5)	-0.1(4)	3.7(4)	-1.4(4)
C1	12.9(5)	11.4(5)	13.0(5)	0.2(4)	2.1(4)	0.1(4)
C2	10.0(5)	13.9(5)	13.1(5)	-1.7(4)	2.1(4)	-0.6(4)
O2	31.3(5)	25.1(5)	24.7(5)	11.2(4)	12.8(4)	6.6(4)
C3	10.3(5)	13.8(5)	14.5(5)	-1.7(4)	0.9(4)	0.4(4)
C4	10.5(5)	14.4(5)	12.2(5)	-0.7(4)	-0.7(4)	-0.8(4)
C5	13.2(5)	16.1(5)	16.2(5)	0.4(4)	0.3(4)	1.4(4)
C6	17.6(6)	19.0(6)	16.7(5)	4.3(4)	0.1(4)	-0.9(5)
C7	16.0(5)	23.6(6)	13.3(5)	0.4(4)	2.9(4)	-2.4(5)
C8	13.4(5)	18.4(6)	15.2(5)	-3.8(4)	1.8(4)	0.1(4)
C9	11.6(5)	14.1(5)	12.5(5)	-1.0(4)	-1.6(4)	-0.4(4)
S10	15.66(14)	12.12(14)	14.05(14)	-1.90(10)	1.18(10)	2.11(10)
C11	11.4(5)	14.0(5)	12.1(5)	-1.4(4)	2.6(4)	1.9(4)
C12	14.8(5)	13.9(5)	14.3(5)	0.1(4)	2.4(4)	1.5(4)
C13	16.0(5)	17.4(6)	19.2(6)	-3.0(4)	2.3(4)	-2.0(4)
C14	16.3(6)	25.5(6)	16.7(6)	-2.7(5)	-2.3(4)	1.6(5)
C15	21.3(6)	21.6(6)	16.7(6)	3.9(5)	-1.8(5)	3.4(5)
C16	17.9(6)	15.4(5)	17.3(5)	1.7(4)	1.7(4)	0.3(4)

Table 4 Bond Lengths for thiochrom.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N1	1.2304(13)	C6	C7	1.3926(17)
N1	C2	1.4719(14)	C7	C8	1.3907(17)
N1	O2	1.2318(13)	C8	C9	1.3988(16)
C1	C2	1.5025(15)	C9	S10	1.7562(12)
C1	S10	1.8348(11)	C11	C12	1.3958(16)
C1	C11	1.5210(15)	C11	C16	1.3938(16)
C2	C3	1.3377(16)	C12	C13	1.3925(16)

C3	C4	1.4525(15)	C13	C14	1.3921(17)
C4	C5	1.4037(16)	C14	C15	1.3868(18)
C4	C9	1.4089(15)	C15	C16	1.3947(17)
C5	C6	1.3872(16)			

Table 5 Bond Angles for thiochrom.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	N1	C2	119.52(9)	C8	C7	C6	120.35(11)
O1	N1	O2	123.36(10)	C7	C8	C9	120.11(11)
O2	N1	C2	117.12(9)	C4	C9	S10	122.12(9)
C2	C1	S10	110.62(8)	C8	C9	C4	119.83(10)
C2	C1	C11	113.30(9)	C8	C9	S10	117.76(9)
C11	C1	S10	111.57(7)	C9	S10	C1	103.53(5)
N1	C2	C1	114.35(9)	C12	C11	C1	121.37(10)
C3	C2	N1	117.53(10)	C16	C11	C1	119.36(10)
C3	C2	C1	127.95(10)	C16	C11	C12	119.25(10)
C2	C3	C4	123.72(10)	C13	C12	C11	120.15(11)
C5	C4	C3	119.45(10)	C14	C13	C12	120.26(11)
C5	C4	C9	119.11(10)	C15	C14	C13	119.86(11)
C9	C4	C3	121.42(10)	C14	C15	C16	119.95(11)
C6	C5	C4	120.63(11)	C11	C16	C15	120.52(11)
C5	C6	C7	119.94(11)				

Table 6 Torsion Angles for thiochrom.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	N1	C2	C1	−176.50(10)	C5	C6	C7	C8	-0.23(18)
O1	N1	C2	C3	-0.80(15)	C6	C7	C8	C9	-1.10(17)
N1	C2	C3	C4	−178.86(10)	C7	C8	C9	C4	1.88(17)
C1	C2	C3	C4	-3.83(18)	C7	C8	C9	S10	-172.03(9)
C1	C11	C12	C13	177.29(10)	C8	C9	S10	C1	-159.38(9)
C1	C11	C16	C15	−177.03(10)	C9	C4	C5	C6	0.01(17)
C2	C1	S10	C9	-34.40(9)	S10	C1	C2	N1	-156.79(8)
C2	C1	C11	C12	52.96(14)	S10	C1	C2	C3	28.04(15)
C2	C1	C11	C16	−128.72(11)	S10	C1	C11	C12	-72.66(12)
C2	C3	C4	C5	171.70(11)	S10	C1	C11	C16	105.65(10)
C2	C3	C4	C9	-9.81(17)	C11	C1	C2	N1	77.07(12)
O2	N1	C2	C1	2.46(14)	C11	C1	C2	C3	-98.09(13)
O2	N1	C2	C3	178.16(11)	C11	C1	S10	C9	92.70(8)
C3	C4	C5	C6	178.54(10)	C11	C12	C13	C14	-0.03(17)

C3	C4	C9	C8	179.83(10)	C12	C11	C16	C15	1.33(17)
C3	C4	C9	S10	-6.19(15)	C12	C13	C14	C15	0.81(18)
C4	C5	C6	C7	0.77(18)	C13	C14	C15	C16	-0.51(19)
C4	C9	S10	C1	26.86(10)	C14	C15	C16	C11	-0.57(18)
C5	C4	C9	C8	-1.33(16)	C16	C11	C12	C13	-1.03(16)
C5	C4	C9	S10	172.31(8)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for thiochrom.

Atom	*x*	*y*	*z*	U(eq)
H1	3566	6862	2879	15
H3	5112	3386	3643	15
H5	4272	2044	4968	18
H6	2955	1773	6379	21
H7	1367	3402	6865	21
H8	1098	5309	5945	19
H12	1194	4030	2827	17
H13	-944	3757	1722	21
H14	-1723	5395	600	24
H15	-330	7293	559	24
H16	1822	7564	1654	20

Experimental

Single crystals of $C_{15}H_{11}NO_2S$ **[thiochrom]** were **[]**. A suitable crystal was selected and **[]** on a **Bruker D8 Quest** diffractometer. The crystal was kept at 100.0 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the olex2.refine [3] refinement package using Gauss-Newton minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2.
3.

Crystal structure determination of [thiochrom]

Crystal Data for $C_{15}H_{11}NO_2S$ (M =269.31 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 8.9636(3) Å, b = 10.3969(4) Å, c = 13.4271(5) Å, β = 94.8620(10)°, V = 1246.82(8) Å^3, Z = 4, T = 100.0 K, μ(MoKα) = 0.255 mm^{-1}, *Dcalc* = 1.435 g/cm^3, 31745 reflections measured (6.014° ≤ 2Θ ≤ 56.664°), 3105 unique (R_{int} = 0.0290, R_{sigma} = 0.0140) which were used in all calculations. The final R_1 was 0.0296 (I > 2σ(I)) and wR_2 was 0.0746 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

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1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
2.a Ternary CH refined with riding coordinates:
 C1(H1)
2.b Aromatic/amide H refined with riding coordinates:
 C3(H3), C5(H5), C6(H6), C7(H7), C8(H8), C12(H12), C13(H13), C14(H14),
 C15(H15), C16(H16)
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