Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Multicomponent synthesis of fully substituted thiazoles using glycine-based dithiocarbamates, acetic anhydride and nitroalkenes

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EXPERIMENTAL SECTION

General. Chemicals were purchased from commercial suppliers and used without further purification. Glycine-based dithiocarbamates and nitroalkenes were prepared according to the literatures. Thin layer chromatography (TLC) was performed on aluminum plates coated with silica-gel 60 F254 (Merck). The TLC plates were visualized by UV fluorescence (λmax= 254 nm). ^{1}H and ^{13}C NMR analyses were recorded on a Bruker Avance 300 (^{1}H-NMR: 300 MHz, ^{13}C-NMR: 75 MHz, ^{1}H decoupled). All NMR spectra were reported in parts per million (ppm) and measured relative to residual solvent $CHCl_3$ [δ ($CHCl_3$): 7.27 ppm or δ ($CHCl_3$): 77.16 ppm]. HRMS (High Resolution Mass Spectra) was measured on a THERMO SCIENTIFIC Advantage and a THERMO SCIENTIFIC Exactive instrument equipped with an APCI source in the positive-ion mode.

General Procedure for the synthesis of thiazole derivatives 3a-t: A mixture of dithiocarbamate (0.5 mmol), nitroalkene (0.5 mmol), acetic anhydride (1.5 mmol), and sodium acetate (0.5 mmol) was stirred at 85 °C for 1 h under neat conditions. Progress of the reaction was monitored by TLC (eluent: petroleum ether / ethyl acetate, 8:2). After completion of the reaction, the reaction mixture was purified by flash column chromatography (silica gel, petroleum ether / ethyl acetate; 5/1). The structures of the products were confirmed by ^{1}H and ^{13}C NMR and HRMS analyses.

2-(benzylsulfanyl)-4-(2-nitro-1-phenylethyl)-1,3-thiazol-5-yl acetate (**3a**): Pale yellow oil (70%, 145 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.22 (m, 10H), 5.22 (dd, J = 12.4, 7.7 Hz, 1H), 4.98 (dd, J = 14.5, 6.9 Hz, 1H), 4.91 (dd, J = 12.4, 6.9 Hz, 1H), 4.37 (AB_q, J = 13.3 Hz, 2H), 2.28 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 166.1, 155.8, 141.3, 138.4, 137.6 ,

136.6, 128.9, 128.9, 128.5, 127.9, 127.8, 127.5, 78.2, 42.1, 38.6, 20.3 ppm; HRMS (ESI) calculated for $C_{20}H_{19}N_2O_4S_2$ $[M+H]^+$: 415.0786; Found: 415.0782.

*2-(benzylsulfanyl)-4-[2-nitro-1-(thiophen-2-yl)ethyl]-1,3-thiazol-5-yl acetate (**3b**):* Pale yellow oil (85%, 178 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.21 (m, 6H), 6.99–6.93 (m, 2H), 5.36–5.29 (t, J = 6.9 Hz, 1H), 5.15 (dd, J = 13.3, 8.5 Hz, 1H), 4.94 (dd, J = 13.3, 6.9 Hz, 1H), 4.39 (s, 2H), 2.34 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 156.6, 141.5, 139.5, 137.5, 136.5 , 128.9, 128.6, 127.5, 126.9, 125.9, 125.4, 78.5, 38.6, 37.3, 20.3 ppm; HRMS (ESI) calculated for $C_{18}H_{17}N_2O_4S_3$ $[M+H]^+$: 421.0350; Found: 421.0348.

*2-(benzylsulfanyl)-4-[1-(4-methoxyphenyl)-2-nitroethyl]-1,3-thiazol-5-yl acetate (**3c**):* Pale yellow oil (60%, 133 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.26 (m, 5H), 7.24 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 5.17 (dd, J = 11.5, 6.8 Hz, 1H), 4.98–4.84 (m, 2H), 4.38 (AB_q, J = 13.0 Hz, 2H), 3.79 (s, 3H), 2.29 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 166.1, 158.9, 155.9, 141.0, 138.6, 136.5, 129.5, 128.9, 128.8, 128.5, 127.5, 114.2, 78.3, 55.1, 41.2, 38.5, 20.3 ppm; HRMS (ESI) calculated for $C_{21}H_{21}N_2O_5S_2$ $[M+H]^+$: 445.0892; Found: 445.0889.

*2-(benzylsulfanyl)-4-[1-(naphthalen-1-yl)-2-nitroethyl]-1,3-thiazol-5-yl acetate (**3d**):* Pale yellow oil (51%, 118 mg); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.85-7.76 (m, 1H), 7.67-7.51 (m, 2H), 7.47–7.36 (m, 2H), 7.34–7.25 (m, 5H), 5.93 (dd, J = 9.5, 5.5 Hz, 1H), 5.47 (dd, J = 13.7, 9.6 Hz, 1H), 4.98 (dd, J = 13.7, 5.5 Hz, 1H), 4.40 (AB_q, J = 13 Hz, 2H), 2.12 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 165.9, 155.9, 141.4, 138.4, 136.6, 133.9, 133.3, 130.6, 129.2, 128.8, 128.5, 128.4, 127.4, 126.7, 125.9, 125.8, 125.4, 122.1, 38.5, 37.2, 29.62, 20.1 ppm; HRMS (ESI) calculated for $C_{24}H_{21}N_2O_4S_2$ $[M+H]^+$: 465.0943; Found: 465.0942.

*4-(2-nitro-1-phenylethyl)-2-(prop-2-en-1-ylsulfanyl)-1,3-thiazol-5-yl acetate (**3e**):* Pale yellow oil (72%, 131 mg); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 7.42–7.22 (m, 5H), 5.98-5.85 (m, 1H), 5.28-5.10 (m, 3H), 5.04-4.86 (m, 2H), 3.77 (d, J = 7 Hz, 2H), 2.28 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 166.1, 155.8, 141.3, 138.4, 137.5, 132.5, 128.8, 127.9, 127.8, 118.7, 78.1, 42.1, 37.3, 20.2 ppm; HRMS (ESI) calculated for $C_{16}H_{17}N_2O_4S_2$ $[M+H]^+$: 365.0630; Found: 365.0628.

*4-[2-nitro-1-(thiophen-2-yl)ethyl]-2-(prop-2-en-1-ylsulfanyl)-1,3-thiazol-5-yl acetate (**3f**):* Pale yellow oil (81%, 150 mg); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 7.24 (dd, J = 5.1, 1.2 Hz, 3H), 7.02-6.92 (m, 2H), 6.02-5.85 (m, 1H), 5.32 (dd, J = 8.3, 7.0 Hz, 1H), 5.26 – 5.11 (m, 3H), 4.94 (dd, J = 13.2, 6.8 Hz, 1H), 3.79 (d, J = 7 Hz, 2H), 2.35 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 166.1, 156.4, 141.5, 139.6, 137.5, 132.5, 126.8, 125.9, 125.4, 118.8, 78.5, 37.4, 37.2, 20.3 ppm; HRMS (ESI) calculated for $C_{14}H_{15}N_2O_4S_3$ $[M+H]^+$: 371.0194; Found: 371.0193.

*4-[1-(4-methoxyphenyl)-2-nitroethyl]-2-(prop-2-en-1-ylsulfanyl)-1,3-thiazol-5-yl acetate (**3g**):* Pale yellow oil (54%, 106 mg); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 7.28 (dd, J = 6.8, 2.1 Hz, 2H), 6.85 (dd, J = 6.8, 2.0 Hz, 2H), 5.98-5.82 (m, 1H), 5.23-5.08 (m, 3H), 4.98-4.84 (m, 2H), 3.78 (s, 3H), 3.75 (d, J = 7.1 Hz, 2H), 2.29 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 166.0, 158.9, 155.6, 141.0, 138.7, 132.5, 129.4, 128.9, 118.7, 114.1, 78.2, 55.1, 41.2, 37.2, 20.2 ppm; HRMS (ESI) calculated for $C_{17}H_{19}N_2O_5S_2$ $[M+H]^+$: 395.0735; Found: 395.0731.

*4-[1-(naphthalen-1-yl)-2-nitroethyl]-2-(prop-2-en-1-ylsulfanyl)-1,3-thiazol-5-yl acetate (**3h**)*: Pale yellow oil (46%, 95 mg); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 8.32 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.81 (d, J = 7.7 Hz, 1H), 7.65-7.50 (m, 2H), 7.49–7.39 (m, 2H), 6.02 – 5.83 (m, 2H), 5.48 (dd, J = 13.9, 10.0 Hz, 1H), 5.25-5.10 (m, 2H), 4.97 (dd, J = 13.6, 6.0 Hz,

1H), 3.80 (dd, J = 7.0, 0.7 Hz, 2H), 2.12 (s, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 165.9, 155.7, 141.4, 138.5, 133.9, 133.3, 132.5, 130.7, 129.2, 128.4, 126.7, 126.0, 125.8, 125.4, 122.2, 118.7, 77.4, 37.4, 37.3, 20.1 ppm; HRMS (ESI) calculated for $C_{20}H_{19}N_2O_4S_2$ $[M+H]^+$: 415.0786; Found: 415.0781.

*2-(butylsulfanyl)-4-(2-nitro-1-phenylethyl)-1,3-thiazol-5-yl acetate (**3i**):* Pale yellow oil (70%, 133 mg); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 7.46 – 7.23 (m, 5H), 5.30 – 5.14 (m, 1H), 5.03 – 4.84 (m, 2H), 3.23 – 3.02 (m, 2H), 2.28 (s, 3H), 1.79 – 1.65 (m, 2H), 1.54-1.40 (m, 2H), 0.99-0.90 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 166.1, 157.6, 140.8, 138.2, 137.6, 128.8, 127.9, 127.8, 78.2, 42.1, 33.9, 31.4, 21.8, 20.2, 13.5 ppm; HRMS (ESI) calculated for $C_{17}H_{21}N_2O_4S_2$ $[M+H]^+$: 381.0943; Found: 381.0940.

*2-(butylsulfanyl)-4-[2-nitro-1-(thiophen-2-yl)ethyl]-1,3-thiazol-5-yl acetate (**3j**):* Pale yellow oil (88%, 170 mg); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 7.23 (dd, J = 5.1, 1.1 Hz, 1H), 7.02-6.98 (m, 1H), 6.97-6.92 (m, 1H), 5.34–5.28 (m, 1H), 5.15 (dd, J = 13.1, 8.4 Hz, 1H), 4.93 (dd, J = 13.2, 6.9 Hz, 1H), 3.22-3.12 (m, 2H), 2.35 (s, 3H), 1.79–1.67 (m, 2H), 1.55-1.40 (m, 2H), 0.99-0.91 (m, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 166.2, 158.1, 140.9, 139.6, 137.3, 126.8, 125.9, 125.4, 78.6, 37.4, 33.8, 31.3, 21.8, 20.3, 13.5 ppm; HRMS (ESI) calculated for $C_{15}H_{20}N_2O_4S_3$ $[M+H]^+$: 365.0507; Found: 365.0505.

*2-(butylsulfanyl)-4-[1-(4-chlorophenyl)-2-nitroethyl]-1,3-thiazol-5-yl acetate (**3k**)*: Pale yellow oil (72%, 149 mg); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 7.34-7.28 (m, 4H), 5.14 (dd, J = 10.6, 5.6 Hz, 1H), 4.99 – 4.86 (m, 2H), 3.15 (t, J = 7.3 Hz, 2H), 2.31 (s, 3H), 1.78 - 1.66 (m, 2H), 1.55-1.47 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 166.1,

158.0, 140.8, 137.6, 136.0, 133.7, 129.3, 129.0, 78.0, 41.4, 33.8, 31.3, 21.8, 20.3, 13.5 ppm; HRMS (ESI) calculated for $C_{17}H_{20}ClN_2O_4S_2$ $[M+H]^+$: 415.0553; Found: 415.0549.

*2-(butylsulfanyl)-4-[2-nitro-1-(3-nitrophenyl)ethyl]-1,3-thiazol-5-yl acetate (**3l**):* Brown oil (80%, 170 mg); ^{1}H NMR ($CDCl_3$, 300.1 MHz): δ 8.32 (t, J = 1.9 Hz, 1H), 8.15 (d, J = 9.5 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 5.16 (dd, J = 10.7, 6.2 Hz, 1H), 5.10 (dd, J = 13.1, 6.6 Hz, 1H), 5.02 (dd, J = 10.7, 6.6 Hz, 1H), 3.18 (t, J = 6.5 Hz, 2H), 2.35 (s, 3H), 1.77-1.65 (m, 2H), 1.54-1.38 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 166.0, 158.8, 148.3, 141.2, 139.5, 136.4, 134.1, 129.9, 123.1, 122.9, 77.7, 41.4, 33.7, 31.2, 21.7, 20.3, 13.5 ppm; HRMS (ESI) calculated for $C_{17}H_{20}N_3O_6S_2$ $[M+H]^+$: 426.0794; Found: 426.0789.

*4-[2-nitro-1-(thiophen-2-yl)ethyl]-2-(propan-2-ylsulfanyl)-1,3-thiazol-5-yl acetate (**3m**):* Pale yellow oil (65%, 121 mg); ^{1}H NMR ($CDCl_3$, 300.1 MHz) δ 7.22 (d, J = 5.1 Hz, 1H), 7.00 (d, J = 3.3 Hz, 1H), 6.94 (dd, J = 5.0, 3.7 Hz, 1H), 5.32 (t, J = 7.2 Hz, 1H), 5.18 (dd, J = 13.2, 8.6 Hz, 1H), 4.94 (dd, J = 13.1, 6.9 Hz, 1H), 3.80-3.70 (m, 1H), 2.35 (s, 3H), 1.40 (d, J = 6.8 Hz, 6H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 166.0, 156.2, 141.7, 139.6, 137.7, 126.8, 125.9, 125.4, 78.5, 40.3, 37.2, 23.1, 23.0, 20.3; HRMS (ESI) calculated for $C_{14}H_{17}N_2O_4S_3$ $[M+H]^+$: 373.0350; Found: 373.0346.

*4-[1-(2,4-dichlorophenyl)-2-nitroethyl]-2-(propan-2-ylsulfanyl)-1,3-thiazol-5-yl acetate (**3n**):* Pale yellow oil (58%, 126 mg); ^{1}H NMR ($CDCl_3$, 300.1 MHz) δ 7.43 (d, J = 2.1 Hz, 1H), 7.37 (d, J = 8.5 Hz, 1H), 7.23 (dd, J = 8.5, 2.1 Hz, 1H), 5.57 (dd, J = 9.2, 6.3 Hz, 1H), 5.20 (dd, J = 13.6, 9.2 Hz, 1H), 4.85 (dd, J = 13.6, 6.3 Hz, 1H), 3.79-3.63 (m, 1H), 2.31 (s, 3H), 1.39 (d, J = 6.7 Hz, 6H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 166.0, 156.2, 142.1, 137.3, 134.1, 133.9,

133.6, 130.3, 129.5, 127.7, 77.2, 40.3, 37.2, 23.0, 22.9, 20.2 ppm; HRMS (ESI) calculated for $C_{16}H_{17}Cl_2N_2O_4S_2$ $[M+H]^+$: 435.0007; Found: 435.0004.

*4-[1-(4-chlorophenyl)-2-nitroethyl]-2-(propan-2-ylsulfanyl)-1,3-thiazol-5-yl acetate (**3o**):* Pale yellow oil (60%, 120 mg); ^1H NMR ($CDCl_3$, 300.1 MHz) δ 7.44–7.10 (m, 4H), 5.18 (dd, J = 11.7, 6.9 Hz, 1H), 5.01-4.86 (m, 2H), 3.79-3.64 (m, 1H), 2.30 (s, 3H), 1.42 – 1.37 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 166.0, 156.1, 141.7, 138.0, 136.0, 133.7, 129.2, 129.0, 78.0, 41.4, 40.3, 23.1, 23.0, 20.3 ppm; HRMS (ESI) calculated for $C_{16}H_{18}ClN_2O_4S_2$ $[M+H]^+$: 401.0397; Found: 401.0392.

*2-(hexylsulfanyl)-4-(2-nitro-1-phenylethyl)-1,3-thiazol-5-yl acetate (**3p**):* Pale yellow oil (88%, 179 mg); ^1H NMR ($CDCl_3$, 300.1 MHz) δ 7.40 – 7.22 (m, 5H), 5.22 (dd, J = 12.1, 7.4 Hz, 1H), 5.03-4.86 (m, 2H), 3.16 (t, J = 7.3 Hz, 2H), 2.27 (s, 3H), 1.81-1.66 (m, 2H), 1.51–1.26 (m, 6H), 0.92 (t, J = 6.7 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 166.1, 157.5, 140.7, 138.1, 137.5, 128.8, 127.8, 127.7, 78.1, 42.0, 34.1, 31.2, 29.2, 28.3, 22.4, 20.2, 13.9 ppm; HRMS (ESI) calculated for $C_{19}H_{25}N_2O_4S_2$ $[M+H]^+$: 409.1256; Found: 409.1252.

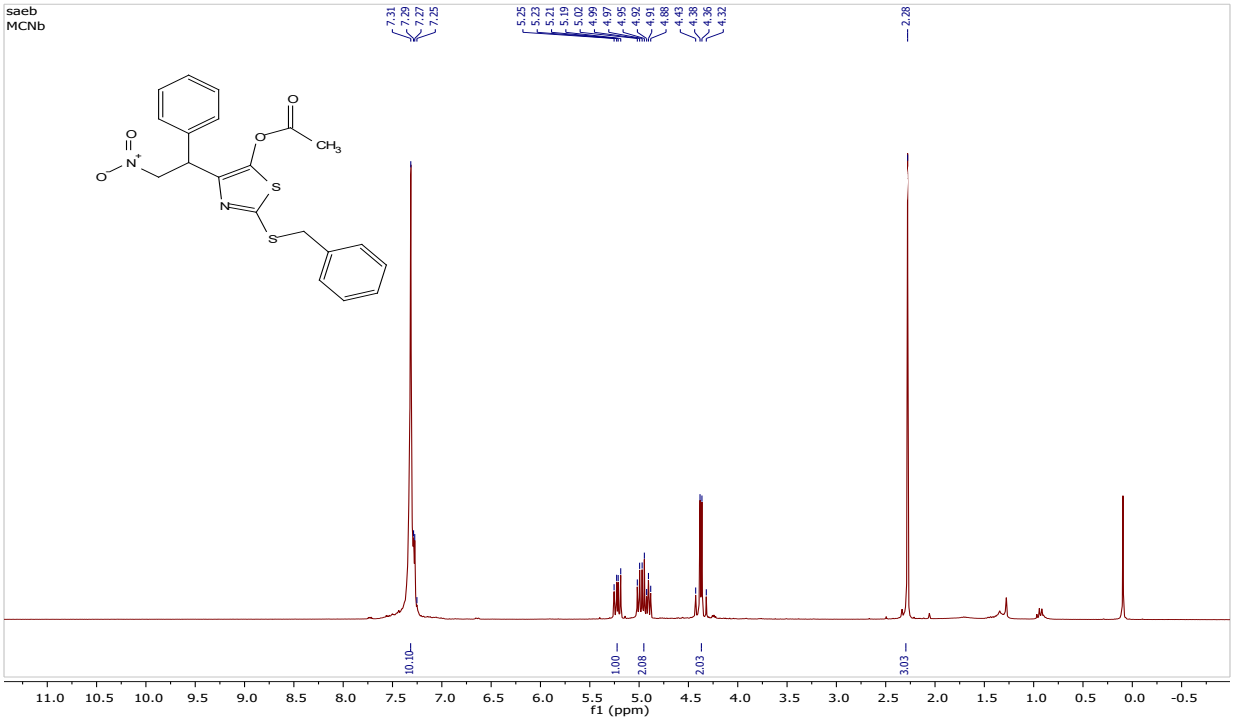
*2-(hexylsulfanyl)-4-[2-nitro-1-(thiophen-2-yl)ethyl]-1,3-thiazol-5-yl acetate (**3q**):* Pale yellow oil (84%, 174 mg); ^1H NMR ($CDCl_3$, 300.1 MHz) δ 7.23 (d, J = 5.0 Hz, 1H), 7.00 (d, J = 3.2 Hz, 1H), 6.95 (dd, J = 5.0, 3.6 Hz, 1H), 5.31 (t, J = 7.4 Hz, 1H), 5.14 (dd, J = 13.2, 8.3 Hz, 1H), 4.93 (dd, J = 13.2, 7.0 Hz, 1H), 3.22-3.11 (m, 2H), 2.34 (s, 3H), 1.80-1.67 (m, 2H), 1.51 – 1.26 (m, 6H), 0.91 (t, J = 6.7 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 166.1, 158.1, 140.9, 139.6, 137.2, 126.8, 125.9, 125.4, 78.5, 37.4, 34.1, 31.2, 29.3, 28.3, 22.4, 20.3, 13.9 ppm; HRMS (ESI) calculated for $C_{17}H_{23}N_2O_4S_3$ $[M+H]^+$: 415.0820; Found: 415.0816.

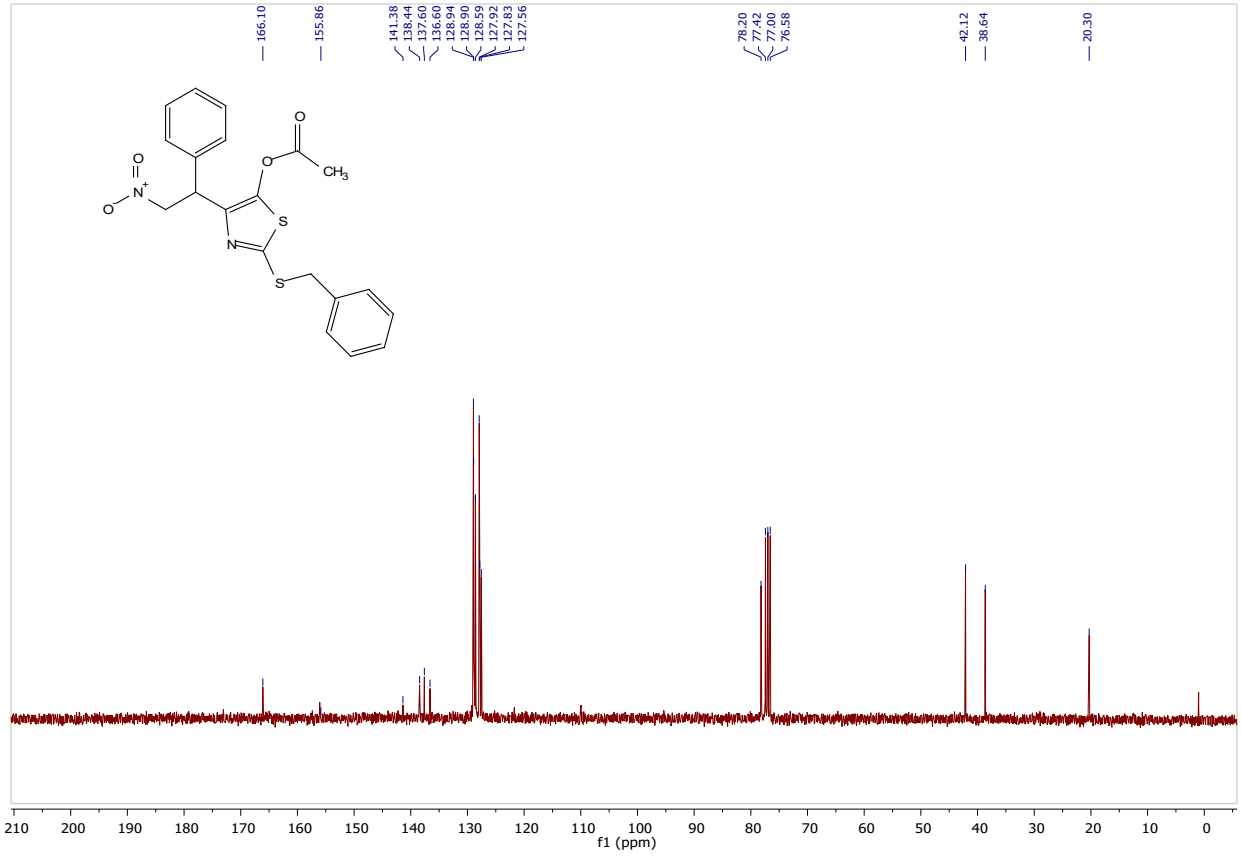
*4-[1-(4-chlorophenyl)-2-nitroethyl] -2-(hexylsulfanyl) -1,3-thiazol-5-yl acetate (**3r**):* Pale yellow oil (45%, 99 mg); ^{1}H NMR ($CDCl_3$, 300.1 MHz) δ 7.41–7.23 (m, 4H), 5.15 (dd, J = 13.5, 8.5 Hz, 1H), 4.99 – 4.87 (m, 2H), 3.14 (t, J = 7.3 Hz, 2H), 2.29 (s, 3H), 1.82-1.63 (m, 2H), 1.53-1.23 (m, 6H), 0.91 (t, J = 6.6 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 166.1, 158.0, 140.8, 137.5, 136.0, 133.7, 129.2, 129.0, 78.0, 41.3, 34.1, 31.2, 29.2, 28.3, 22.4, 20.2, 13.9 ppm; HRMS (ESI) calculated for $C_{19}H_{24}ClN_2O_4S_2$ $[M+H]^+$: 443.0866; Found: 443.0861.

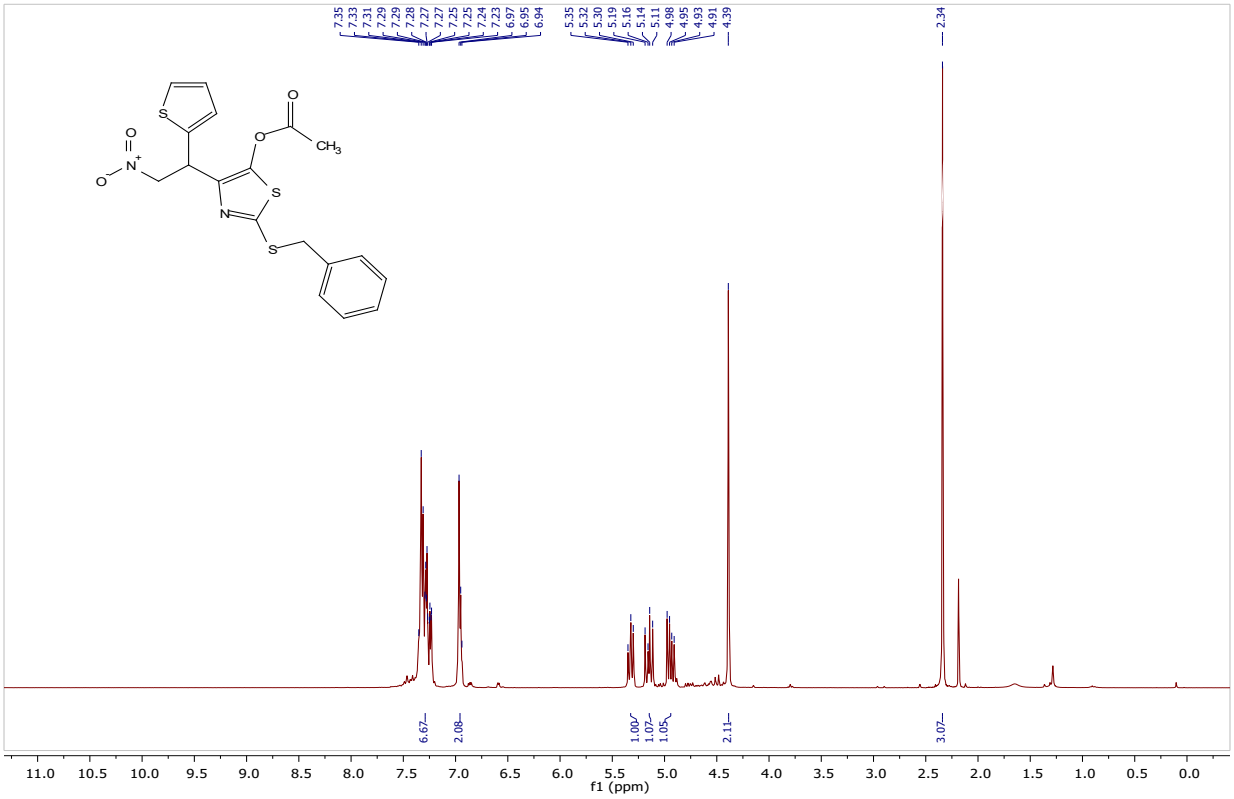
*2-(hexylsulfanyl)-4-[2-nitro-1-(3-nitrophenyl)ethyl]-1,3-thiazol-5-yl acetate (**3s**):* Pale yellow oil (86%, 195 mg); ^{1}H NMR ($CDCl_3$, 300.1 MHz) δ 8.32 (s, 1H), 8.15 (d, J = 7.3 Hz, 1H), 7.75 (d, J = 7.7 Hz, 1H), 7.52 (t, J = 8.0 Hz, 1H), 5.20–5.01 (m, 3H), 3.17 (t, J = 7.3 Hz, 2H), 2.35 (s, 3H), 1.82-1.65 (m, 2H), 1.52–1.38 (m, 2H), 1.38-1.20 (m, 4H), 0.90 (t, J = 6.5 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 166.0, 158.9, 148.3, 141.2, 139.5, 136.4, 134.0, 129.9, 123.2, 122.9, 77.7, 41.4, 34.1, 31.2, 29.2, 28.3, 22.4, 20.3, 13.9 ppm; HRMS (ESI) calculated for $C_{19}H_{24}N_3O_6S_2$ $[M+H]^+$: 454.1107; Found: 454.1105.

*2-(hexylsulfanyl)-4-[2-nitro-1-(4-nitrophenyl)ethyl]-1,3-thiazol-5-yl acetate (**3t**):* Pale yellow oil (65%, 147 mg); ^{1}H NMR ($CDCl_3$, 300.1 MHz) δ 8.18 (d, J = 8.7 Hz, 2H), 7.58 (d, J = 8.7 Hz, 2H), 5.17 (dd, J = 11.4, 6.7 Hz, 1H), 5.10 (dd, J = 14.2, 7.3 Hz, 1H), 5.00 (dd, J = 11.5, 6.8 Hz, 1H), 3.15 (t, J = 7.3 Hz, 2H), 2.33 (s, 3H), 1.79–1.66 (m, 2H), 1.51–1.39 (m, 2H), 1.36–1.25 (m, 4H), 0.90 (t, J = 6.6 Hz, 3H) ppm; ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 166.0, 158.8, 147.3, 144.7, 141.2, 136.3, 128.9, 124.0, 77.5, 41.5, 34.1, 31.2, 29.1, 28.3, 22.4, 20.3, 13.9 ppm; HRMS (ESI) calculated for $C_{19}H_{24}N_3O_6S_2$ $[M+H]^+$: 454.1107; Found: 454.1103.

Copies of ^{1}H and ^{13}C NMR spectra for all products



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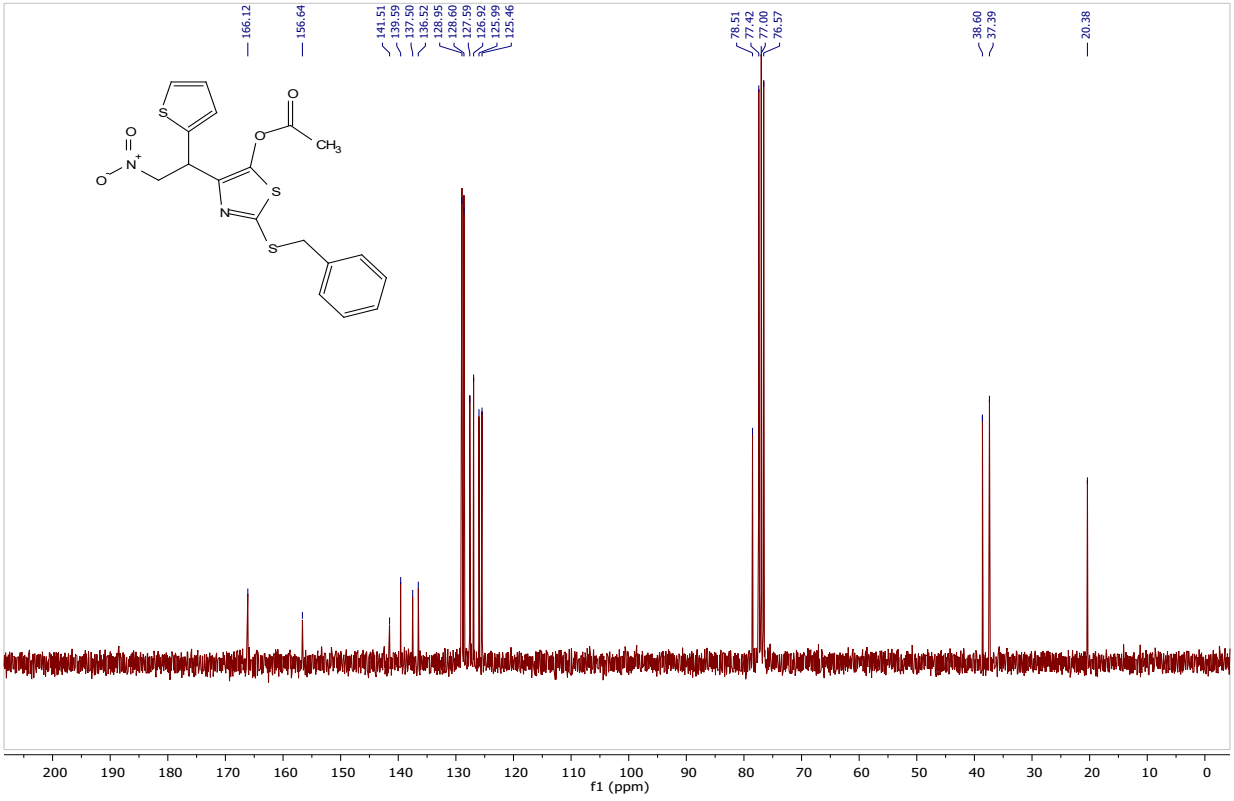
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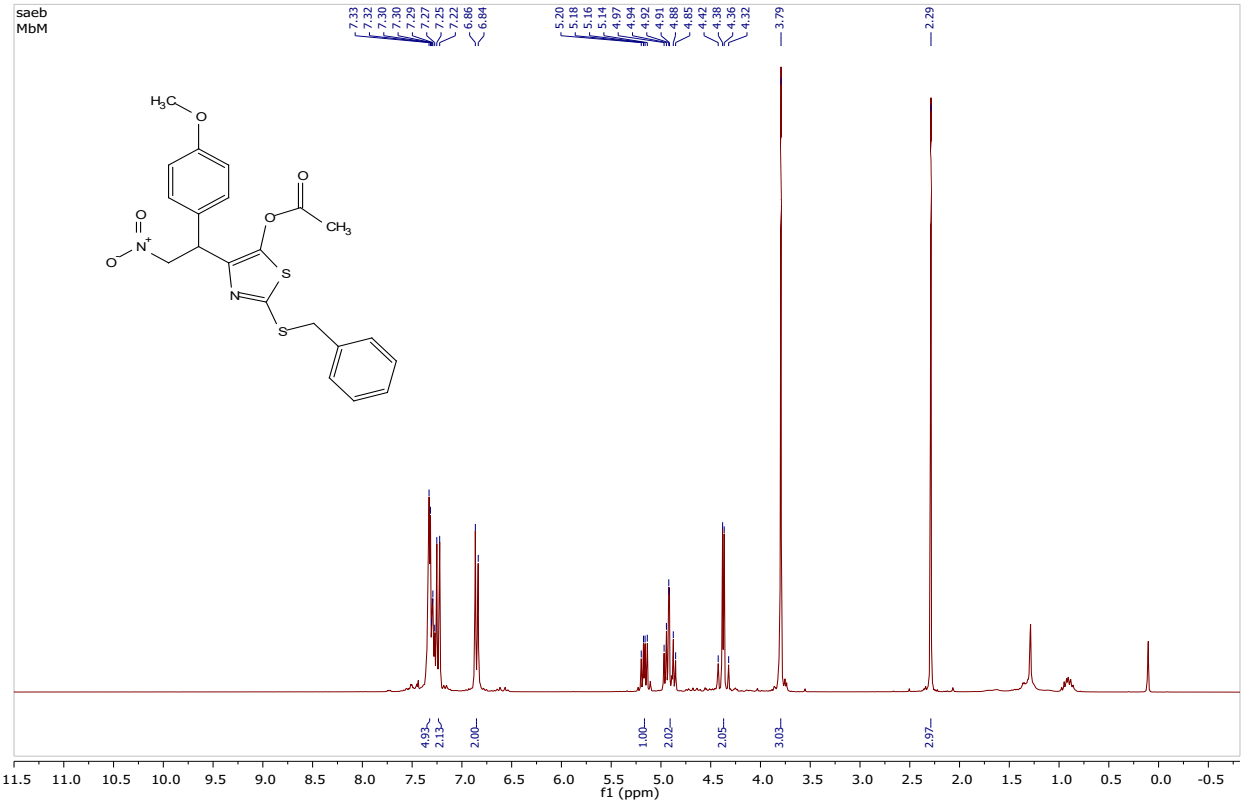
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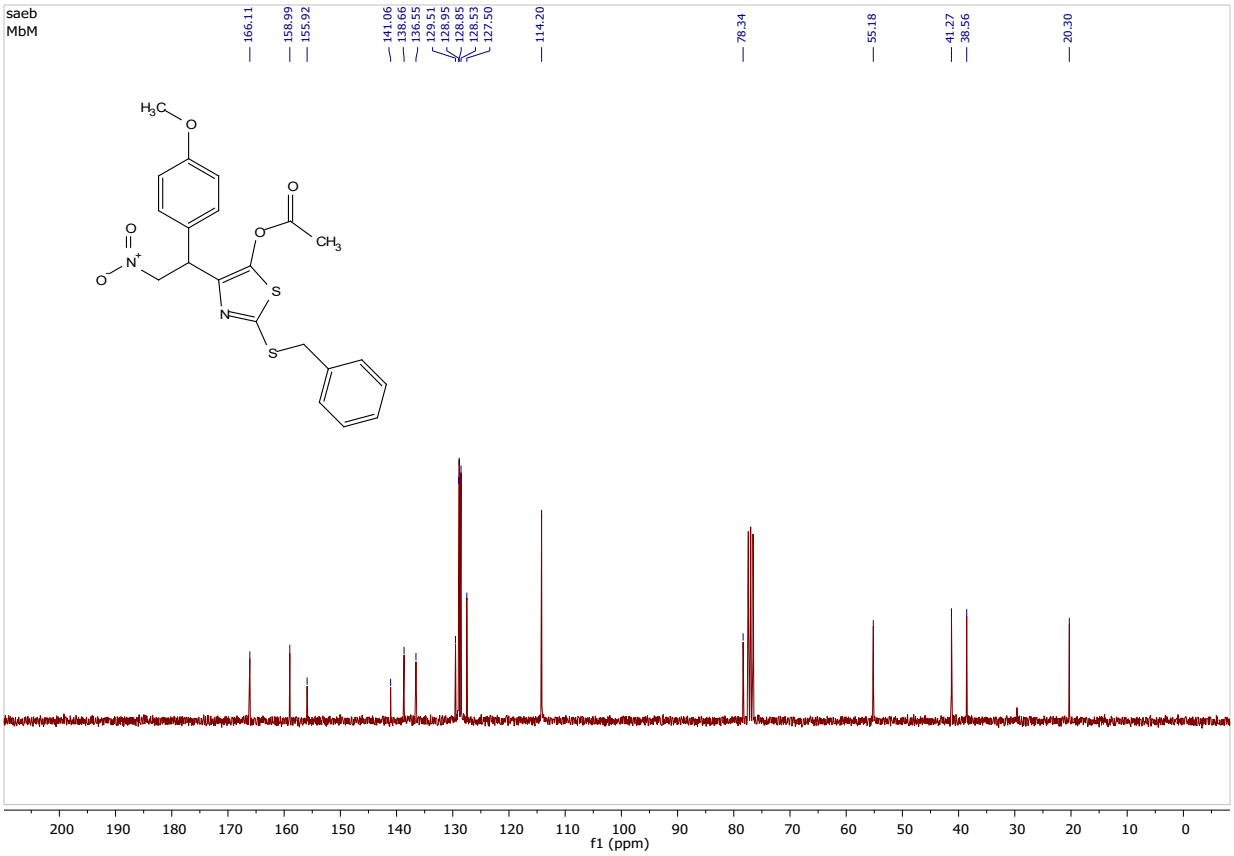
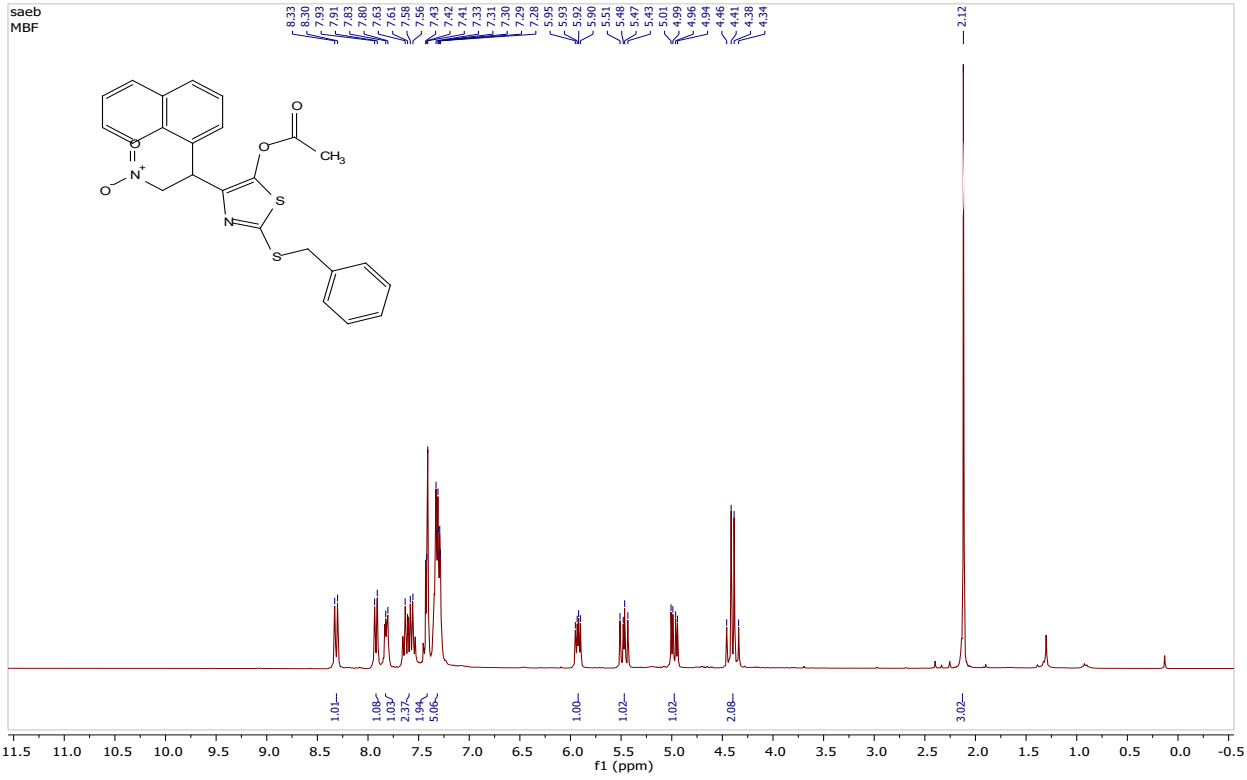
7.32
7.30
7.30
7.29
7.27
7.25
7.22
6.86
6.84
5.20
5.18
5.16
5.14
4.97
4.94
4.92
4.91
4.88
4.85
4.42
4.38
4.36
4.32
3.79
2.29
4.93
2.13
2.00
1.00
2.02
2.05
3.03
2.97
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


saeb
MbM
166.11
158.99
155.92
141.06
138.66
136.55
129.51
128.95
128.85
128.53
127.50
114.20
78.34
55.18
41.27
38.56
20.30
f1 (ppm)


saeb
MBF
8.33
8.30
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7.91
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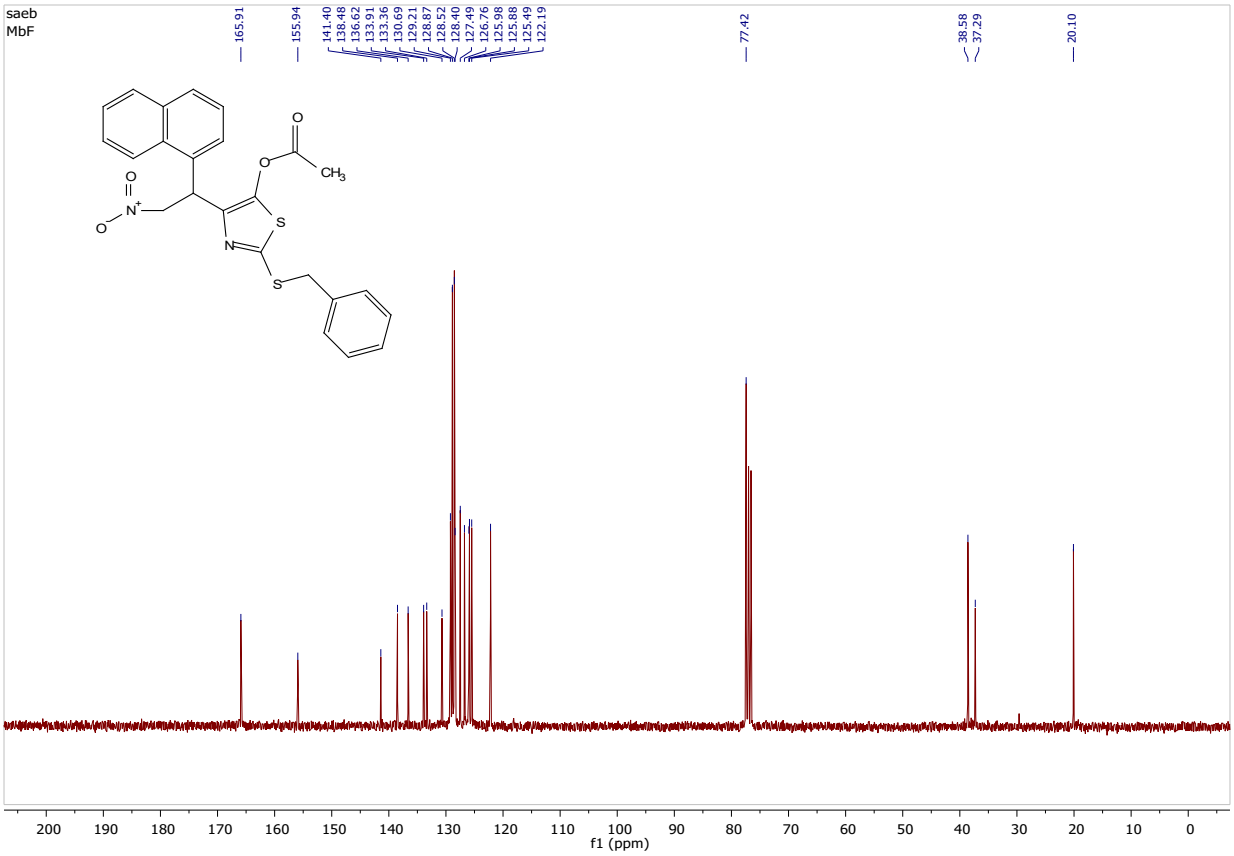
7.80
7.63
7.61
7.58
7.56
7.43
7.42
7.41
7.33
7.31
7.30
7.29
7.28
5.95
5.93
5.92
5.90
5.51
5.48
5.47
5.43
5.01
4.99
4.96
4.94
4.46
4.41
4.38
4.34
2.12
1.01
1.08
1.03
2.37
1.94
5.06
1.00
1.02
1.02
2.08
3.02
f1 (ppm)


saeb
MbF
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133.91
133.36
130.69
129.21
128.87
128.52
128.40
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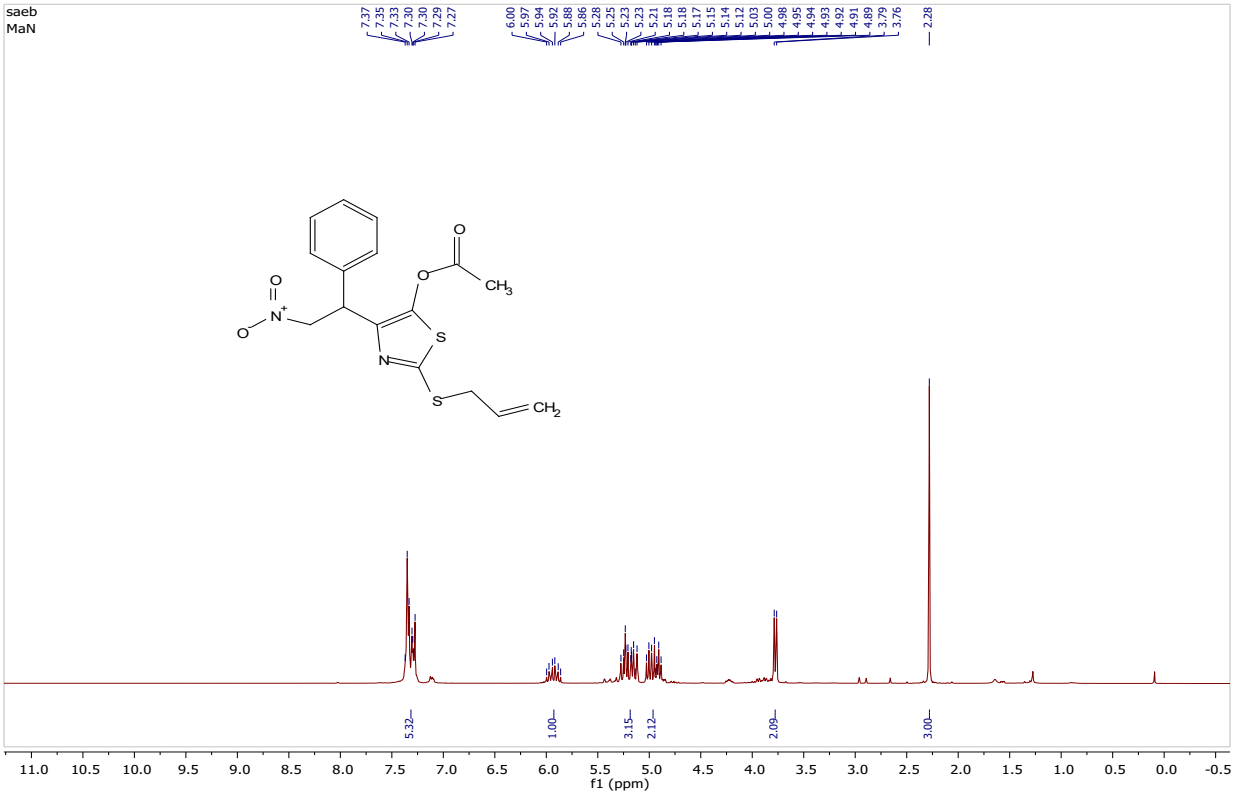
125.98
125.88
125.49
122.19
77.42
38.58
37.29
20.10
f1 (ppm)


saeb
MaN
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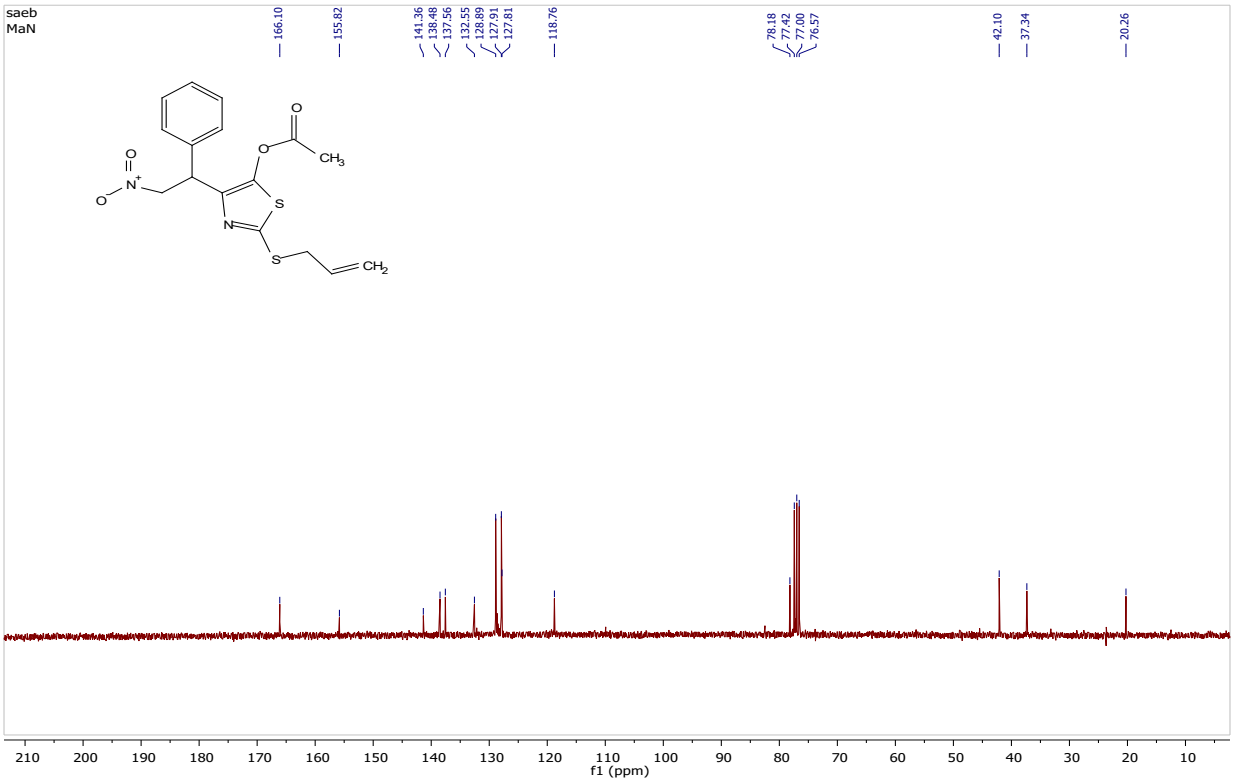
7.35
7.33
7.30
7.30
7.29
7.27
6.00
5.97
5.94
5.92
5.88
5.86
5.28
5.25
5.23
5.23
5.21
5.18
5.18
5.17
5.15
5.14
5.12
5.03
5.00
4.98
4.95
4.94
4.93
4.92
4.91
4.89
3.79
3.76
2.28
5.32
1.00
3.15
2.12
2.09
3.00
f1 (ppm)


saeb
MaN
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155.82
141.36
138.48
137.56
132.55
128.89
127.91
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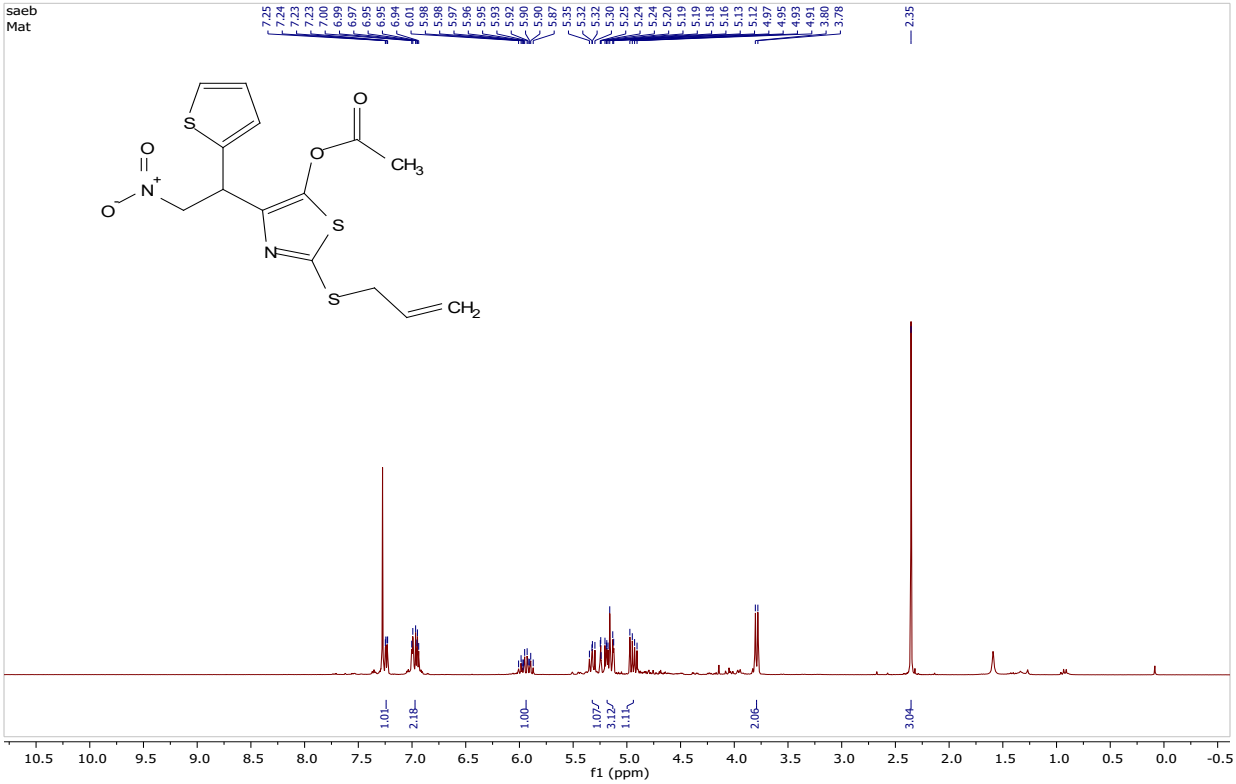
118.76
78.18
77.42
77.00
76.57
42.10
37.34
20.26
f1 (ppm)


saeb
Mat
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7.24
7.23
7.23
7.00
6.99
6.97
6.95
6.95
6.94
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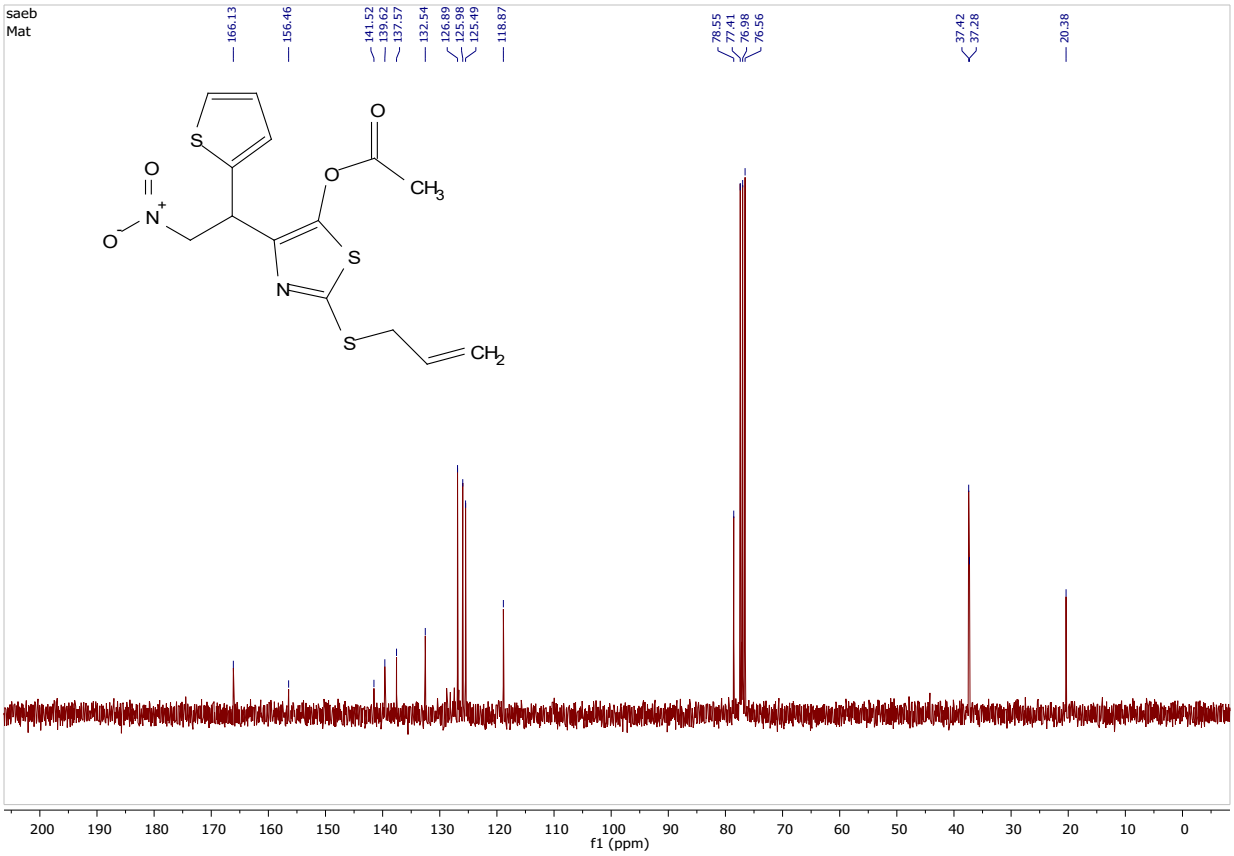
5.98
5.98
5.97
5.96
5.95
5.93
5.92
5.90
5.90
5.87
5.35
5.32
5.32
5.30
5.25
5.24
5.24
5.20
5.19
5.19
5.18
5.16
5.13
5.12
4.97
4.95
4.93
4.91
3.80
3.78
2.35
1.01
2.18
1.00
1.07
3.12
1.11
2.06
3.04
f1 (ppm)


saeb
Mat
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156.46
141.52
139.62
137.57
132.54
126.89
125.98
125.49
118.87
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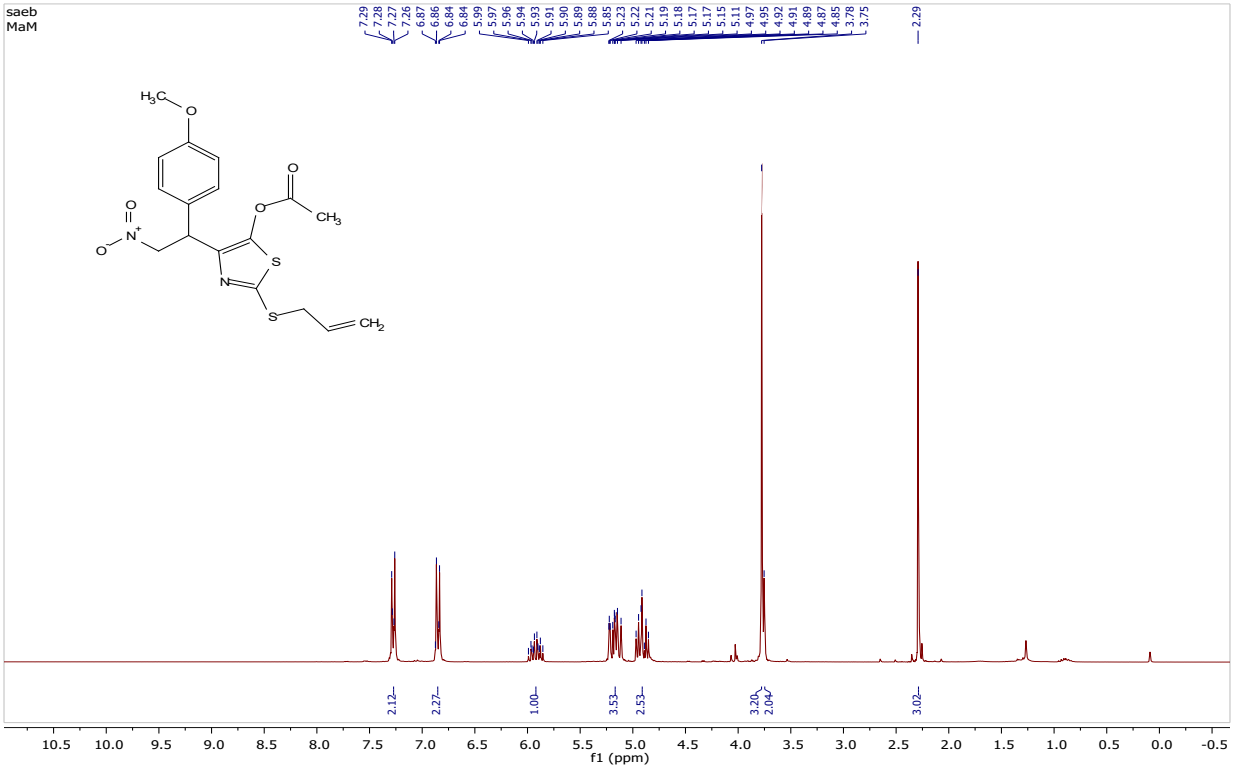
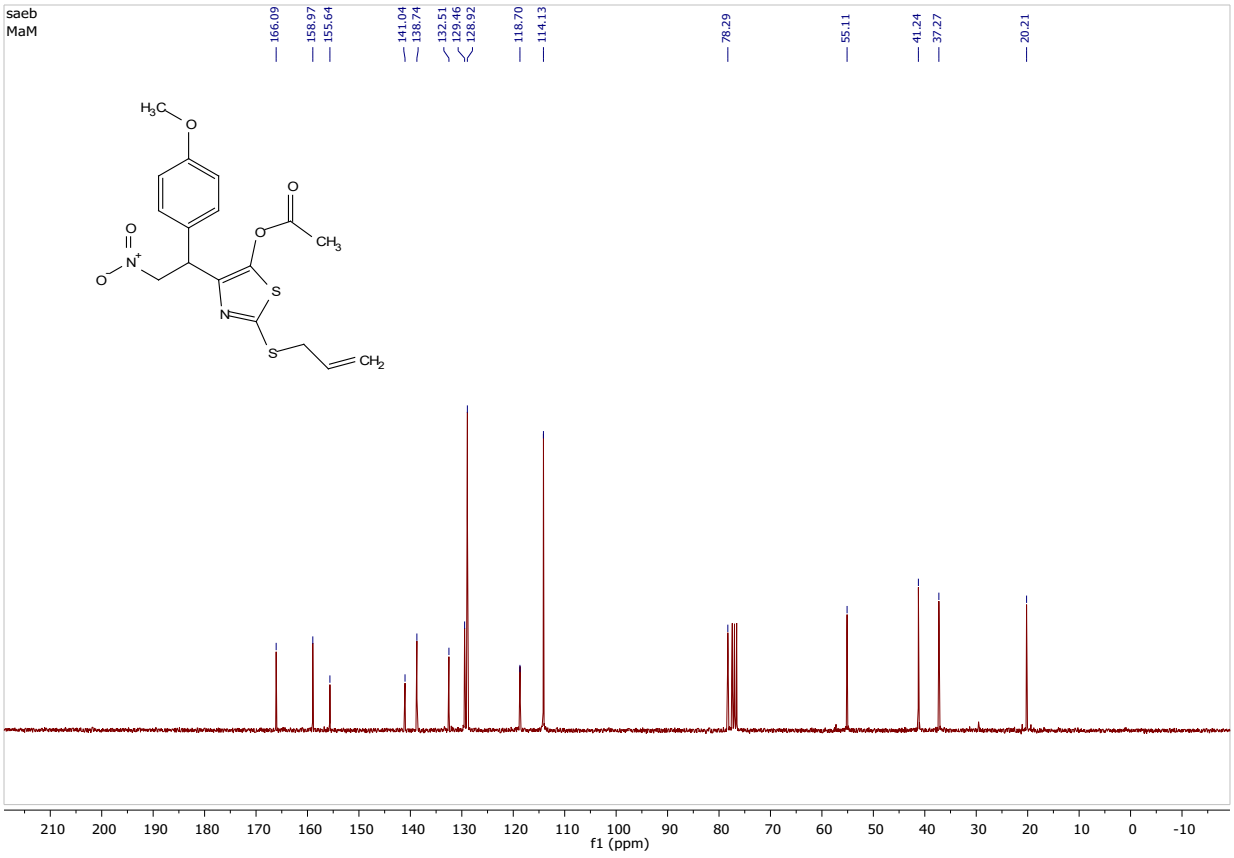
77.41
76.98
76.56
37.42
37.28
20.38
f1 (ppm)


saeb
MaM
f1 (ppm)


saeb
MaM
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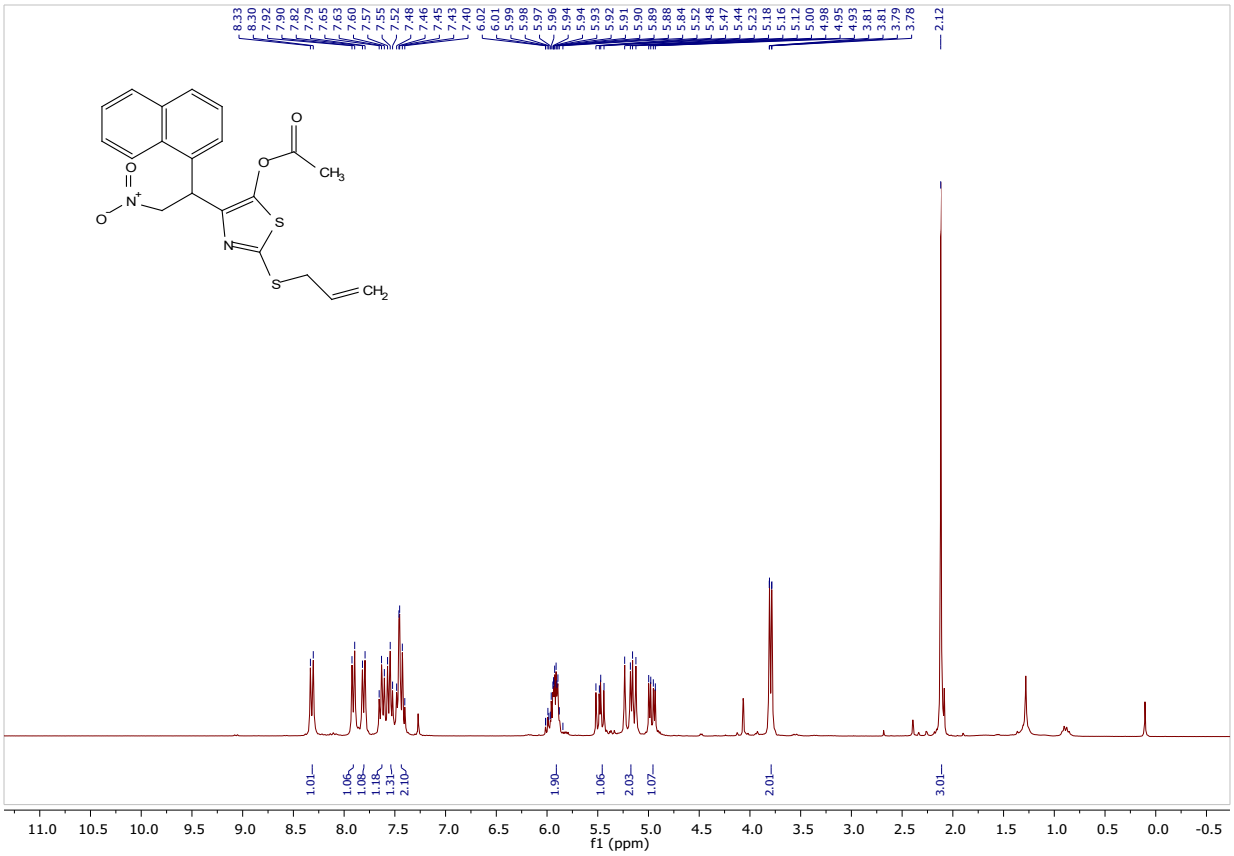
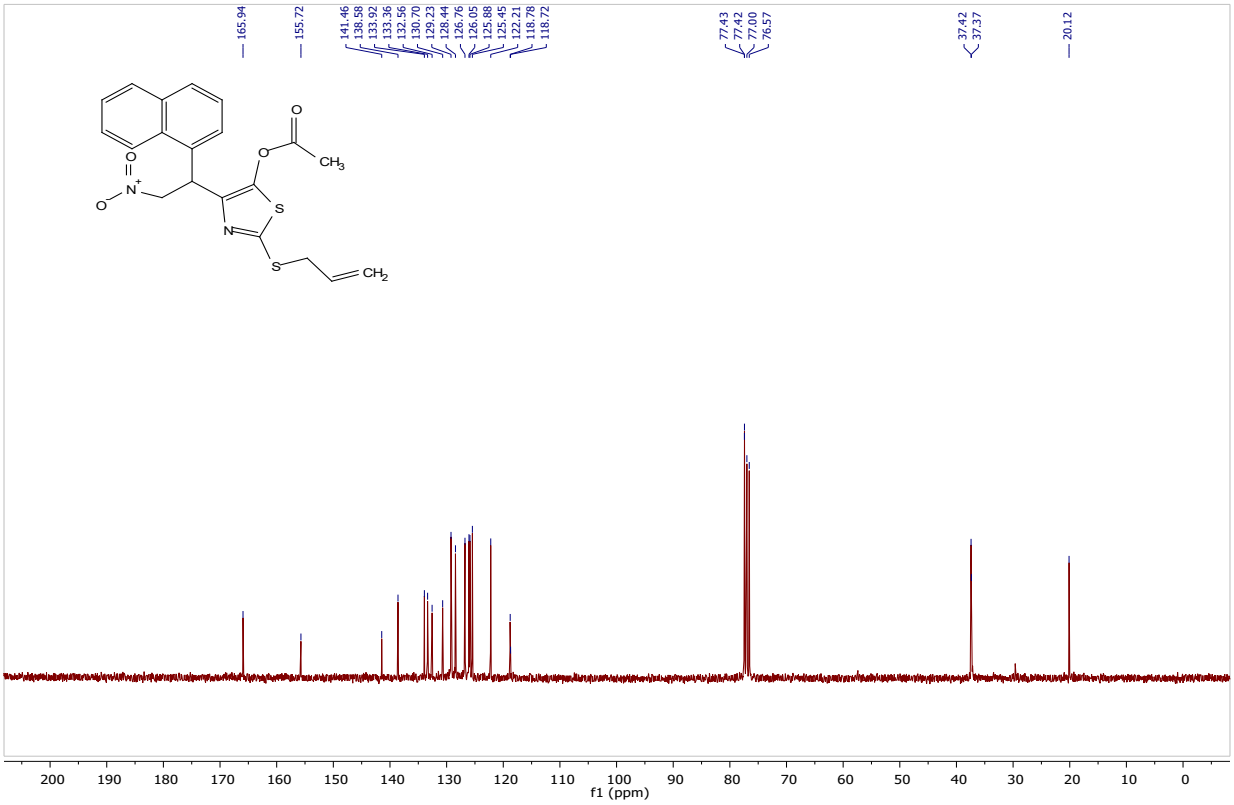
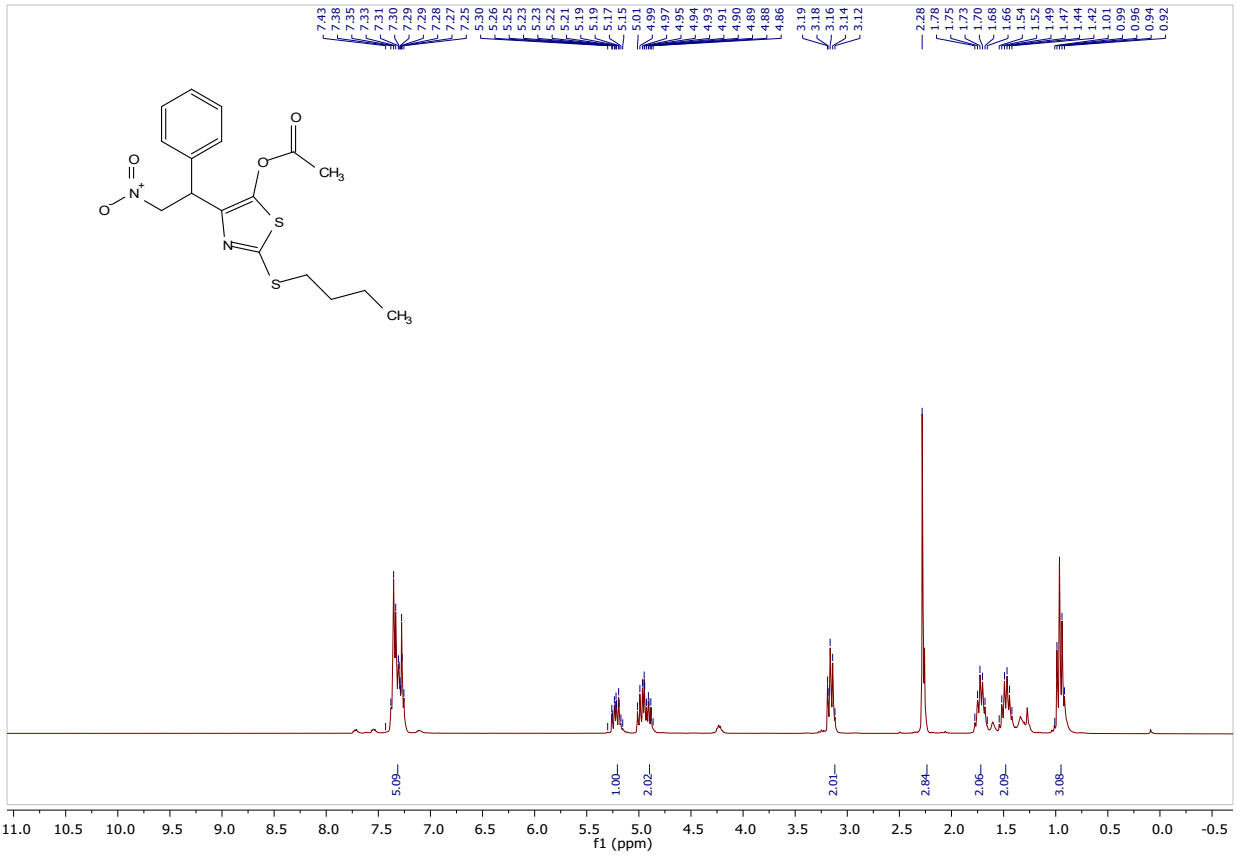
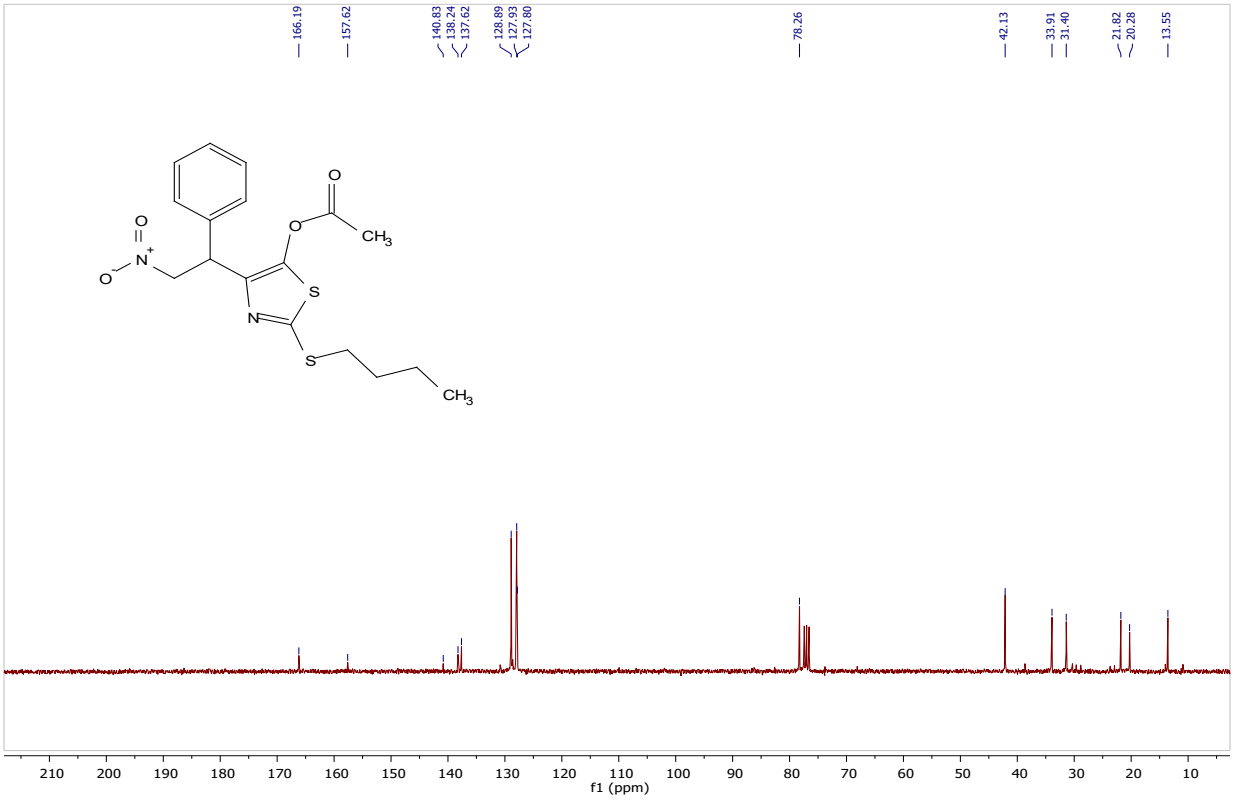
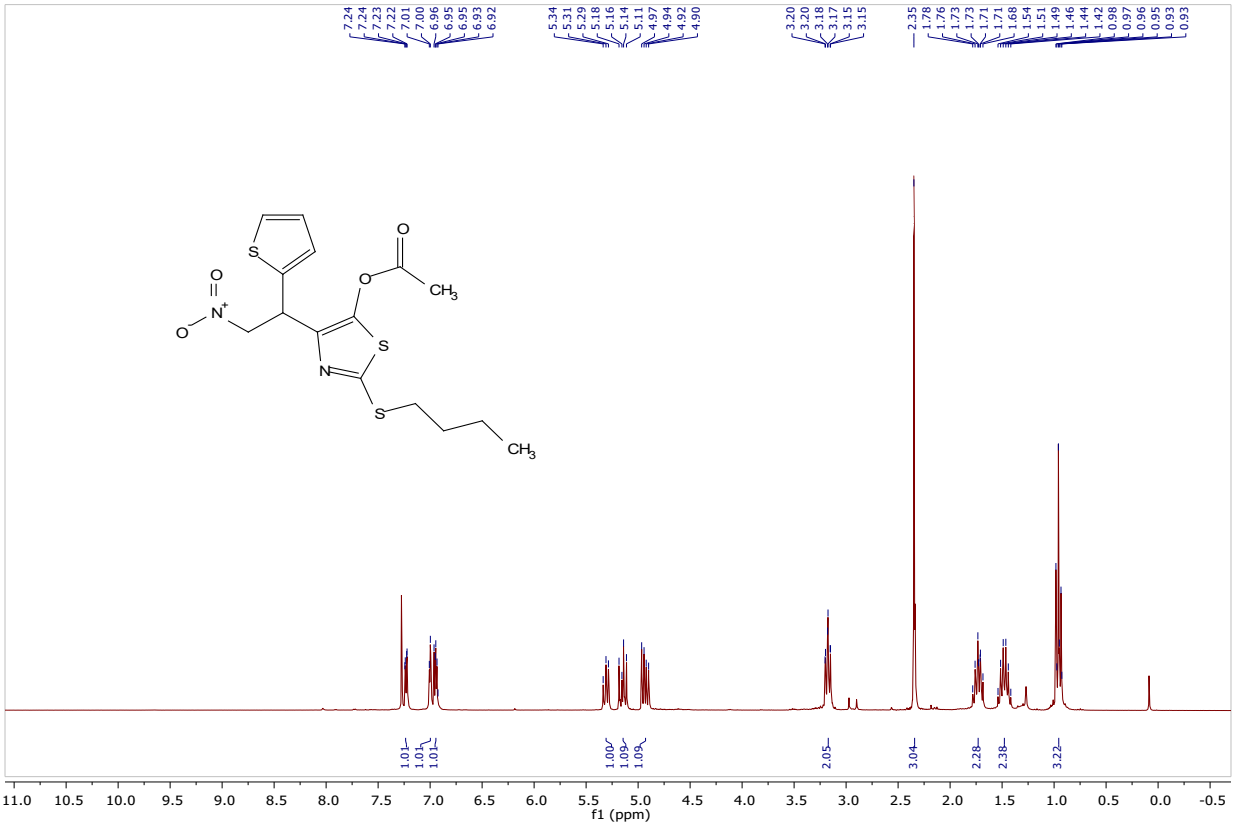
158.97
155.64
141.04
138.74
132.51
129.46
128.92
118.70
114.13
78.29
55.11
41.24
37.27
20.21
f1 (ppm)


8.33
8.30
7.92
7.90
7.82
7.79
7.65
7.63
7.60
7.57
7.55
7.52
7.48
7.46
7.45
7.43
7.40
6.02
6.01
5.99
5.98
5.97
5.96
5.94
5.94
5.93
5.92
5.91
5.90
5.89
5.88
5.84
5.52
5.48
5.47
5.44
5.23
5.18
5.16
5.12
5.00
4.98
4.95
4.93
3.81
3.81
3.79
3.78
2.12
1.01
1.06
1.08
1.18
1.31
2.10
1.90
1.06
2.03
1.07
2.01
3.01
f1 (ppm)


165.94
155.72
141.46
138.58
133.92
133.36
132.56
130.70
129.23
128.44
126.76
126.05
125.88
125.45
122.21
118.78
118.72
77.43
77.42
77.00
76.57
37.42
37.37
20.12
f1 (ppm)


7.43 7.38 7.35 7.33 7.31 7.30 7.29 7.29 7.28 7.27 7.25 5.30 5.26 5.25 5.23 5.23 5.22 5.21 5.19 5.19 5.17 5.15 5.01 4.99 4.97 4.95 4.94 4.93 4.91 4.90 4.89 4.88 4.86 3.19 3.18 3.16 3.14 3.12 2.28 1.78 1.75 1.73 1.70 1.68 1.66 1.54 1.52 1.49 1.47 1.44 1.42 1.01 0.99 0.96 0.94 0.92
O
O
O
CH3
N+
O-
S
N
S
CH3
5.09 1.00 2.02 2.01 2.84 2.06 2.09 3.08
11.0 10.5 10.0 9.5 9.0 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 0.0 -0.5
f1 (ppm)


166.19 157.62 140.83 138.24 137.62 128.89 127.93 127.80 78.26 42.13 33.91 31.40 21.82 20.28 13.55
O
O
O
CH3
N+
O-
S
N
S
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.24
7.24
7.23
7.22
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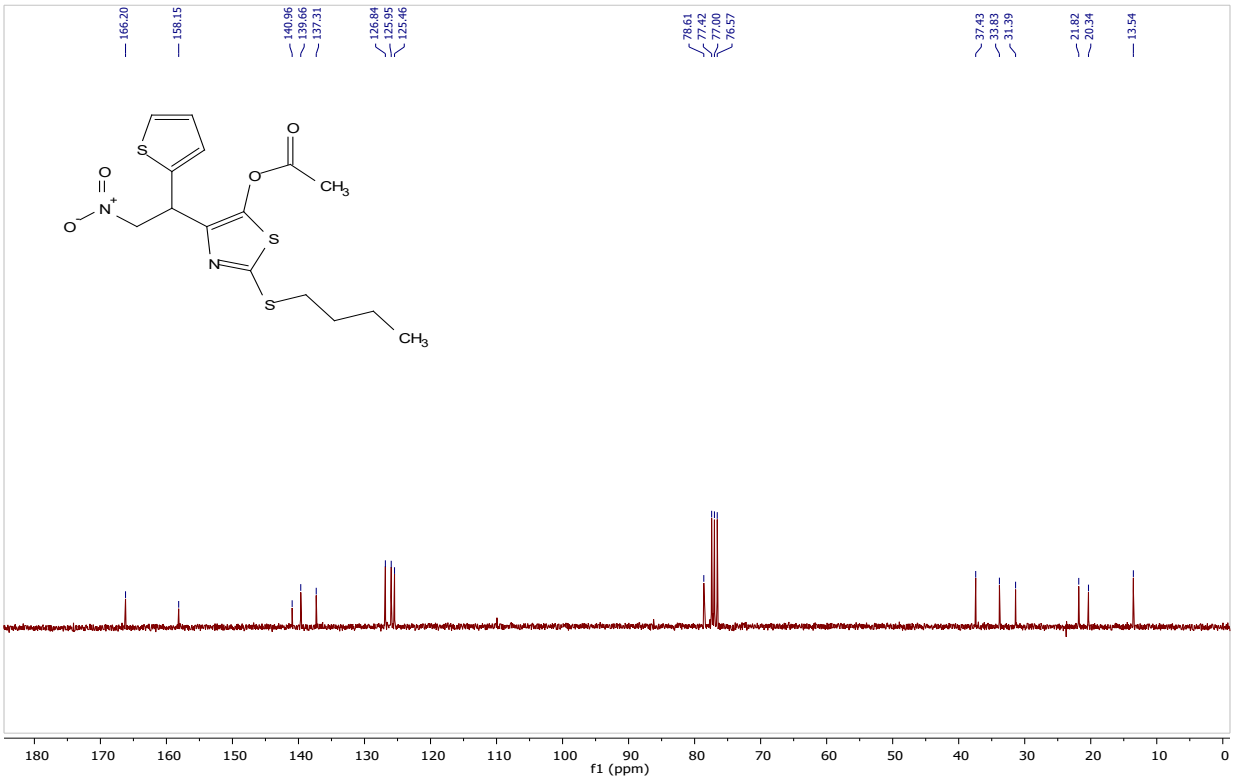
7.00
6.96
6.95
6.95
6.93
6.92
5.34
5.31
5.29
5.18
5.16
5.14
5.11
4.97
4.94
4.92
4.90
3.20
3.20
3.18
3.17
3.15
3.15
2.35
1.78
1.76
1.73
1.73
1.71
1.71
1.68
1.54
1.51
1.49
1.46
1.44
1.42
0.98
0.97
0.96
0.95
0.93
0.93
1.01
1.01
1.01
1.00
1.09
1.09
2.05
3.04
2.28
2.38
3.22
11.0 10.5 10.0 9.5 9.0 8.5 8.0 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 0.0 -0.5
f1 (ppm)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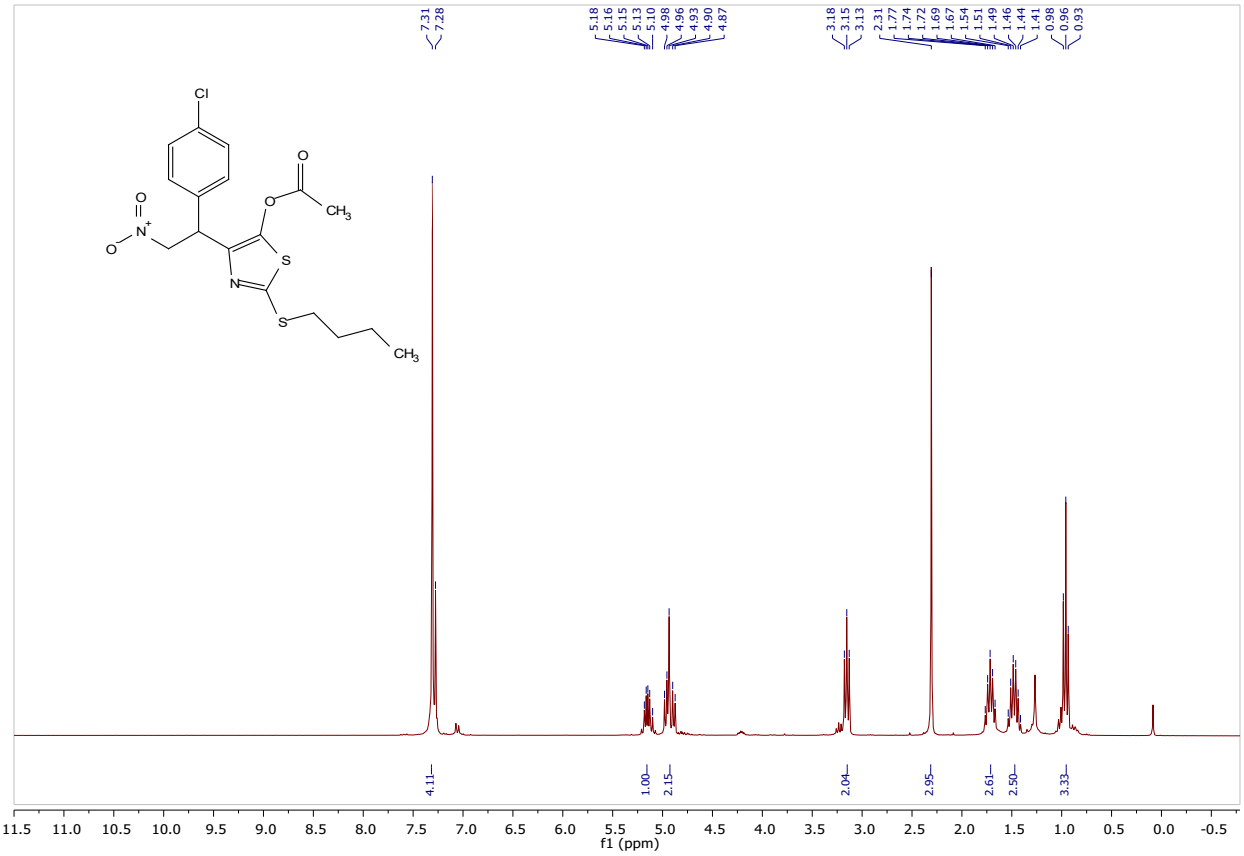
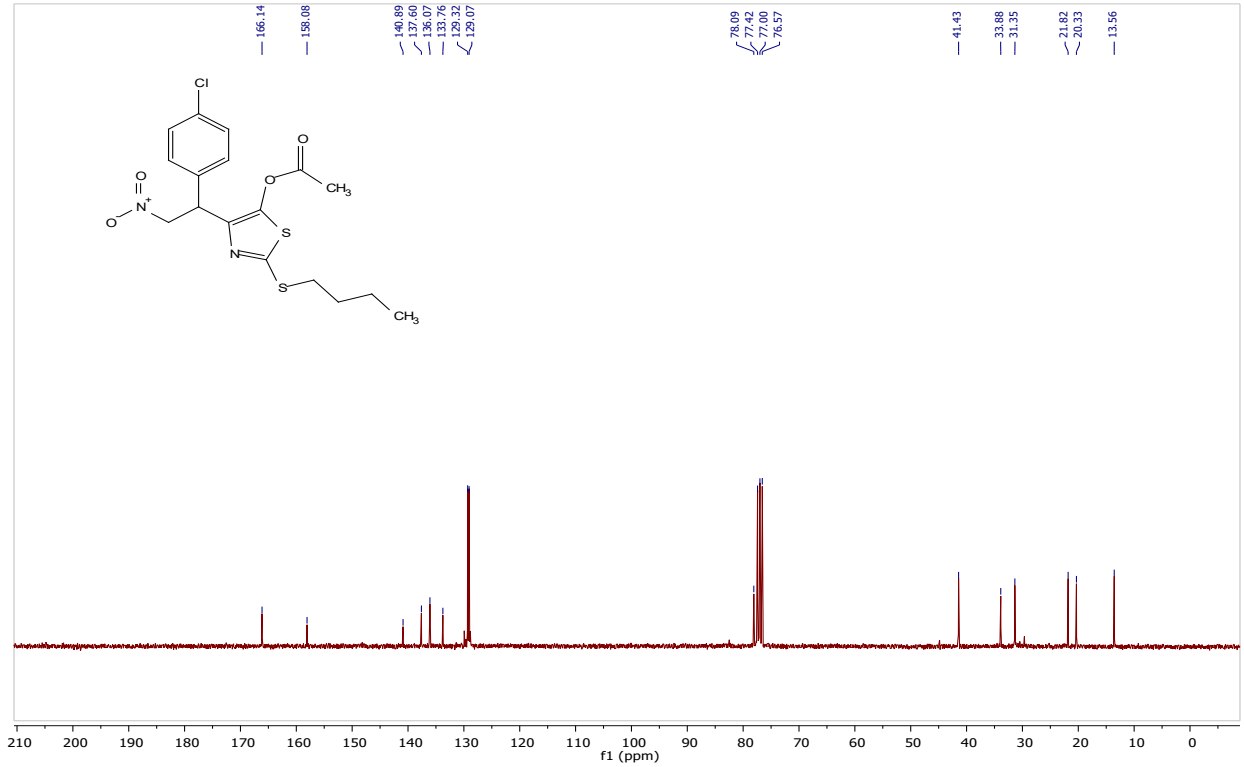
158.15
140.96
139.66
137.31
126.84
125.95
125.46
78.61
77.42
77.00
76.57
37.43
33.83
31.39
21.82
20.34
13.54
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.31
7.28
5.18
5.16
5.15
5.13
5.10
4.98
4.96
4.93
4.90
4.87
3.18
3.15
3.13
2.31
1.77
1.74
1.72
1.69
1.67
1.54
1.51
1.49
1.46
1.44
1.41
0.98
0.96
0.93
Cl
O
O
CH3
O
N+
O-
S
N
S
CH3
4.11
1.00
2.15
2.04
2.95
2.61
2.50
3.33
11.5 11.0 10.5 10.0 9.5 9.0 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 0.0 -0.5
f1 (ppm)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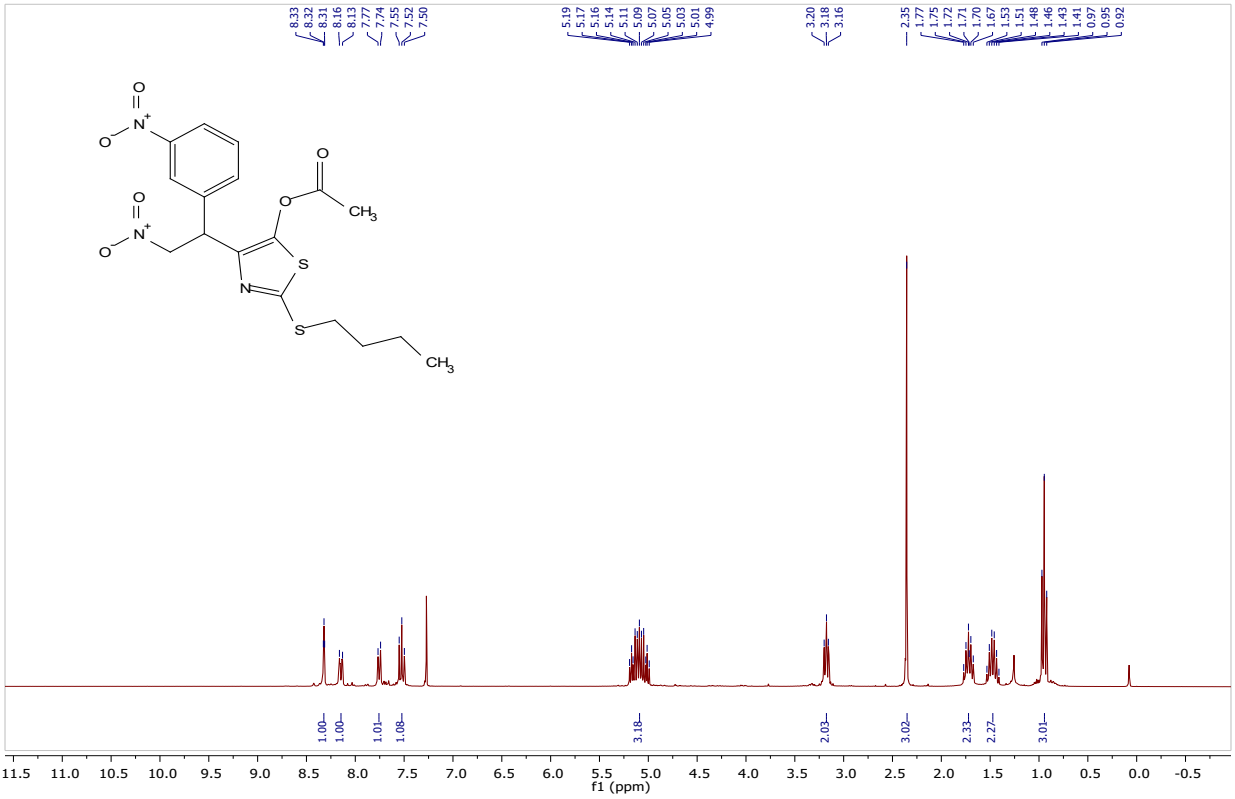
136.07
133.76
129.32
129.07
78.09
77.42
77.00
76.57
41.43
33.88
31.35
21.82
20.33
13.56
Cl
O
O
CH3
O
N+
O-
S
N
S
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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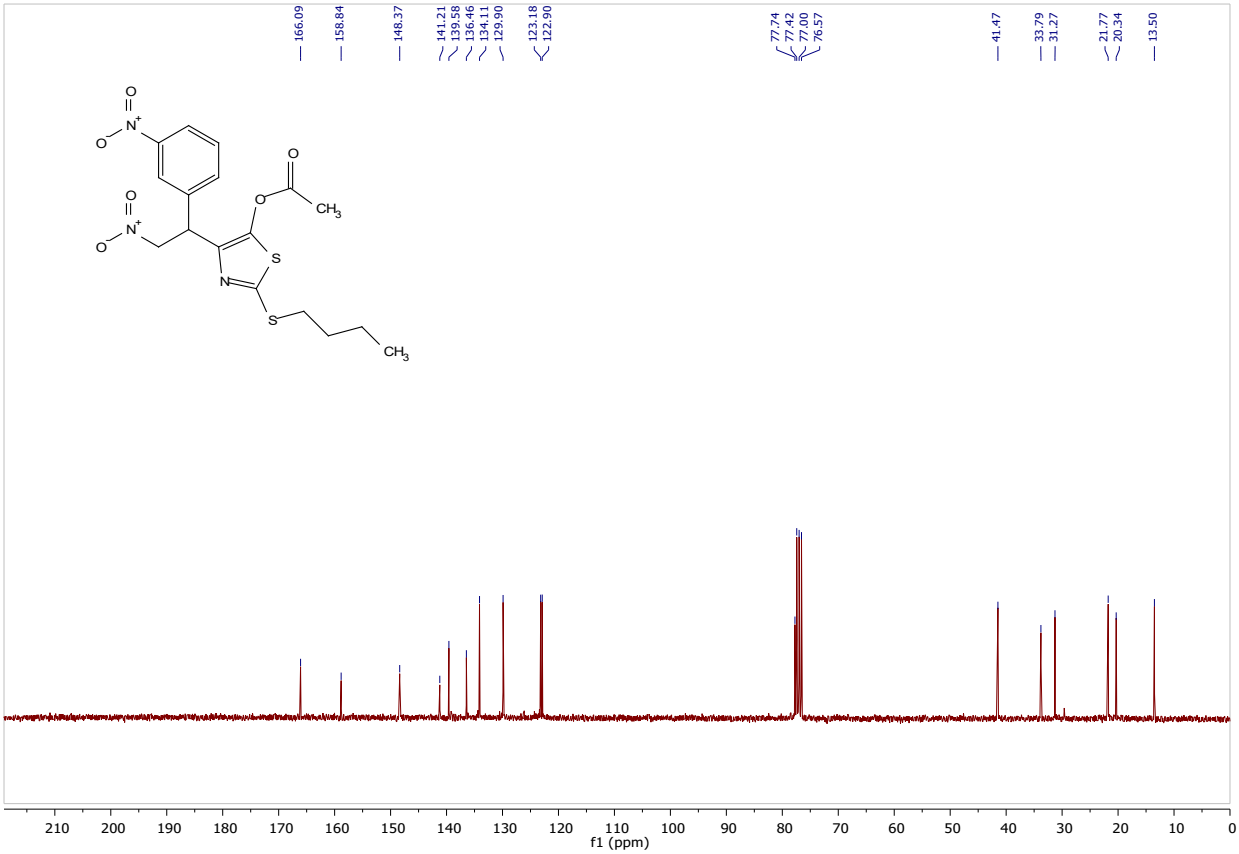
8.32
8.31
8.16
8.13
7.77
7.74
7.55
7.52
7.50
5.19
5.17
5.16
5.14
5.11
5.09
5.07
5.05
5.03
5.01
4.99
3.20
3.18
3.16
2.35
1.77
1.75
1.72
1.71
1.70
1.67
1.53
1.51
1.48
1.46
1.43
1.41
0.97
0.95
0.92
1.00
1.00
1.01
1.08
3.18
2.03
3.02
2.33
2.27
3.01
f1 (ppm)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158.84
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141.21
139.58
136.46
134.11
129.90
123.18
122.90
77.74
77.42
77.00
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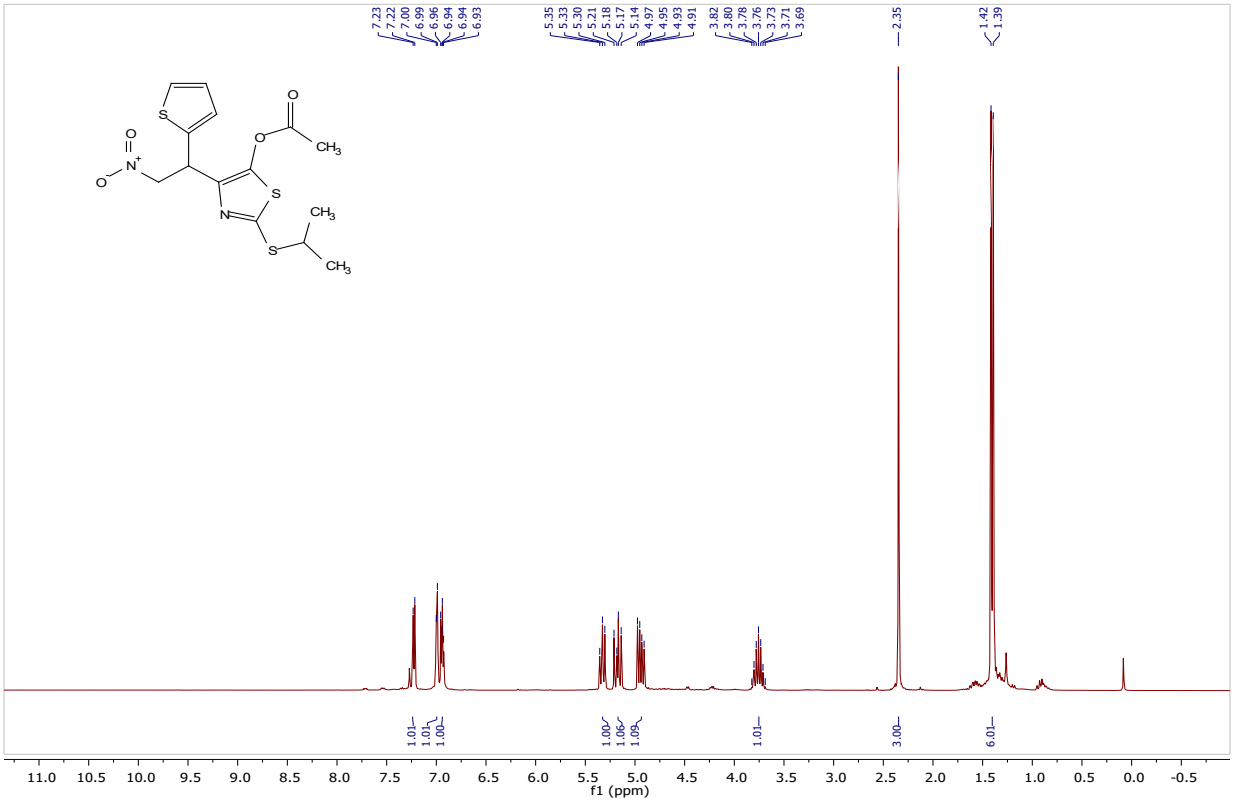
31.27
21.77
20.34
13.50
f1 (ppm)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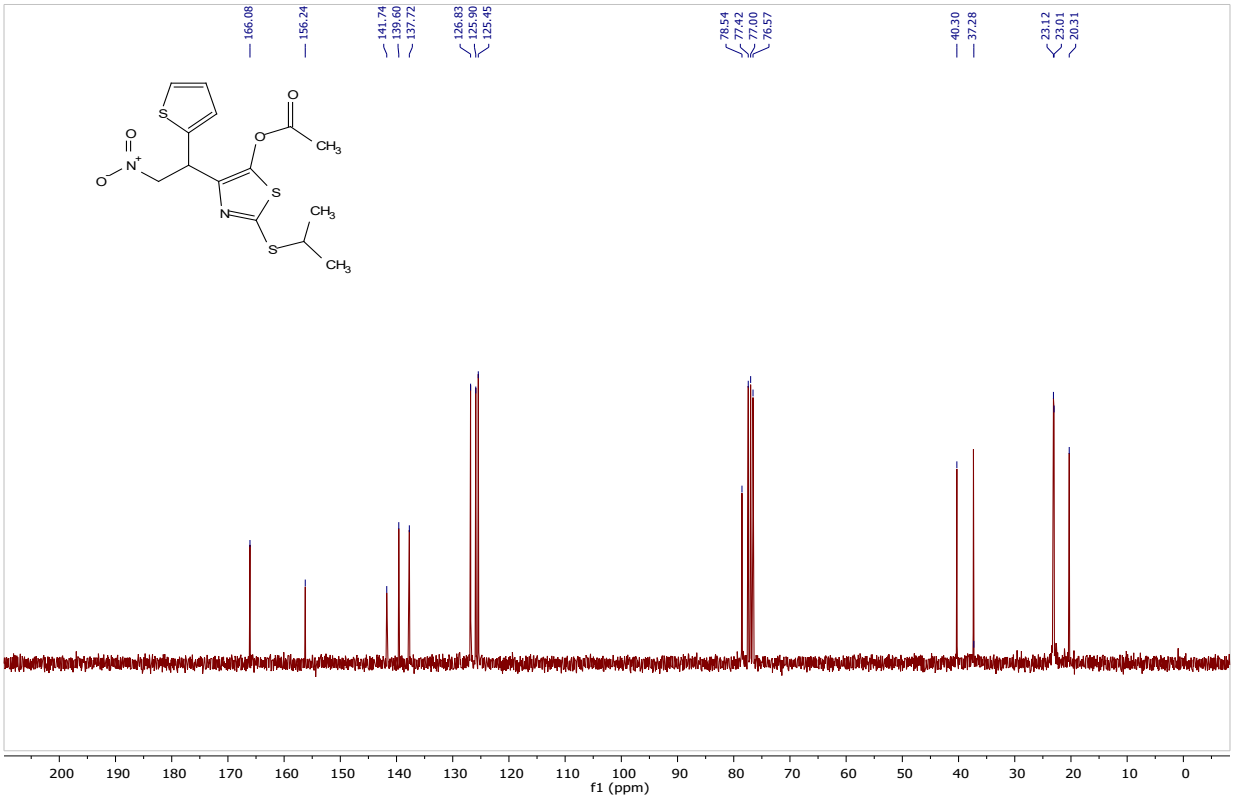
6.99
6.96
6.94
6.94
6.93
5.35
5.33
5.30
5.21
5.18
5.17
5.14
4.97
4.95
4.93
4.91
3.82
3.80
3.78
3.76
3.73
3.71
3.69
2.35
1.42
1.39
1.01
1.01
1.00
1.00
1.06
1.09
1.01
3.00
6.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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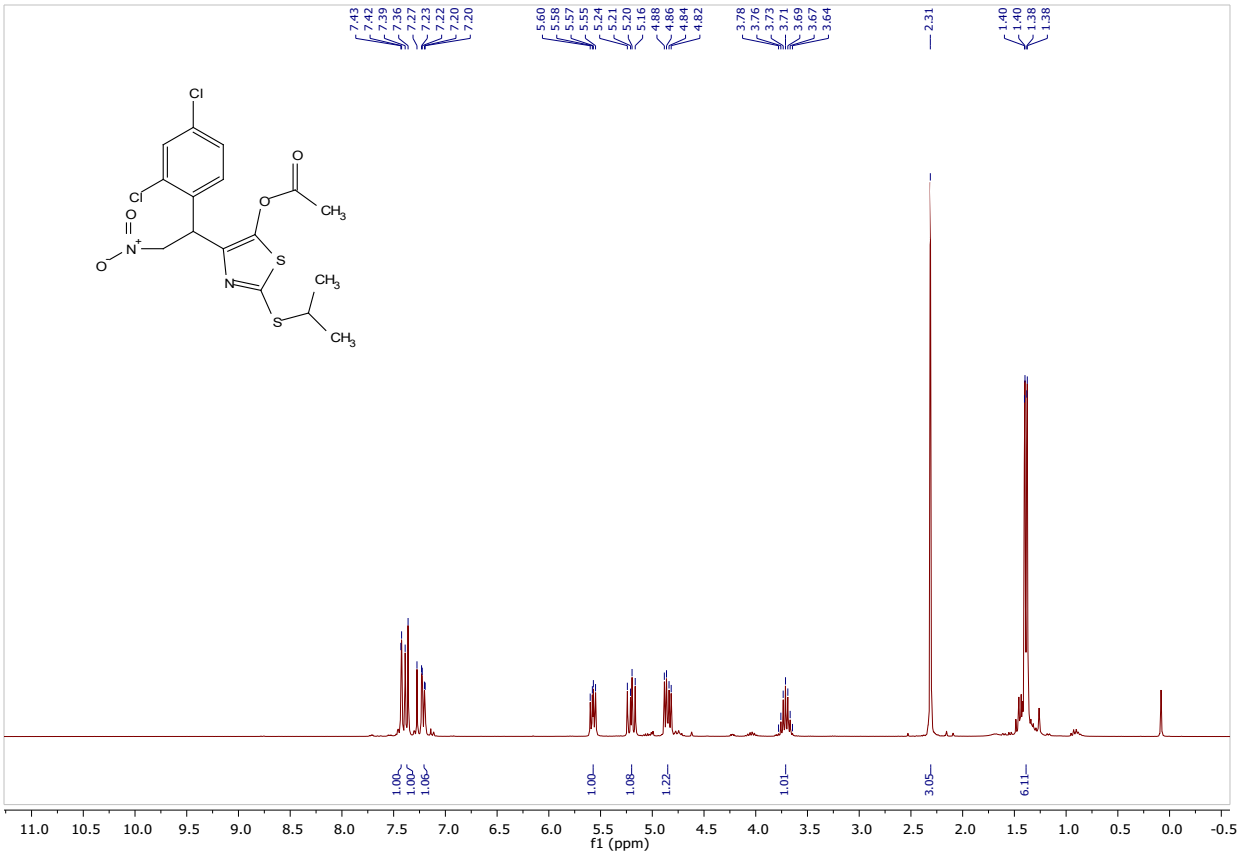
137.72
126.83
125.90
125.45
78.54
77.42
77.00
76.57
40.30
37.28
23.12
23.01
20.31
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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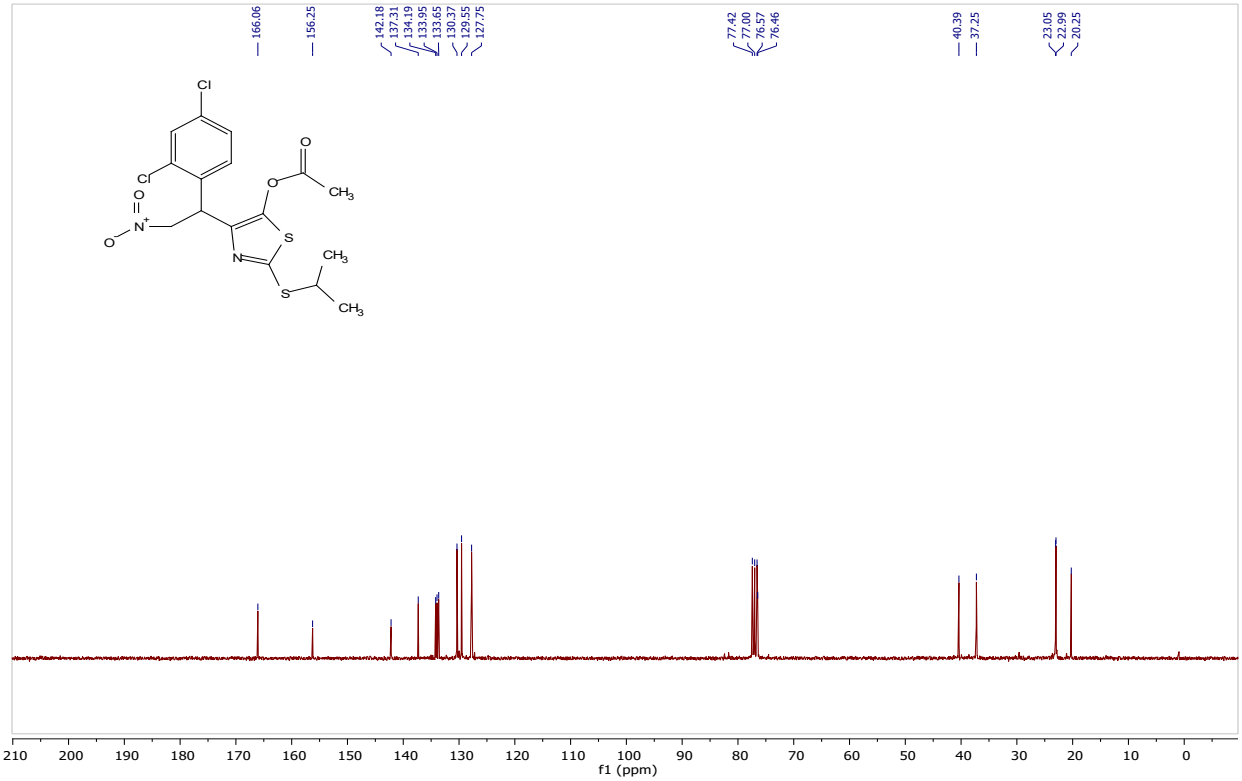
7.20
7.20
5.60
5.58
5.57
5.55
5.24
5.21
5.20
5.16
4.88
4.86
4.84
4.82
3.78
3.76
3.73
3.71
3.69
3.67
3.64
2.31
1.40
1.40
1.38
1.38
Cl
Cl
O
O
CH3
O
N+
O-
S
N
S
CH3
CH3
1.00
1.00
1.06
1.00
1.08
1.22
1.01
3.05
6.11
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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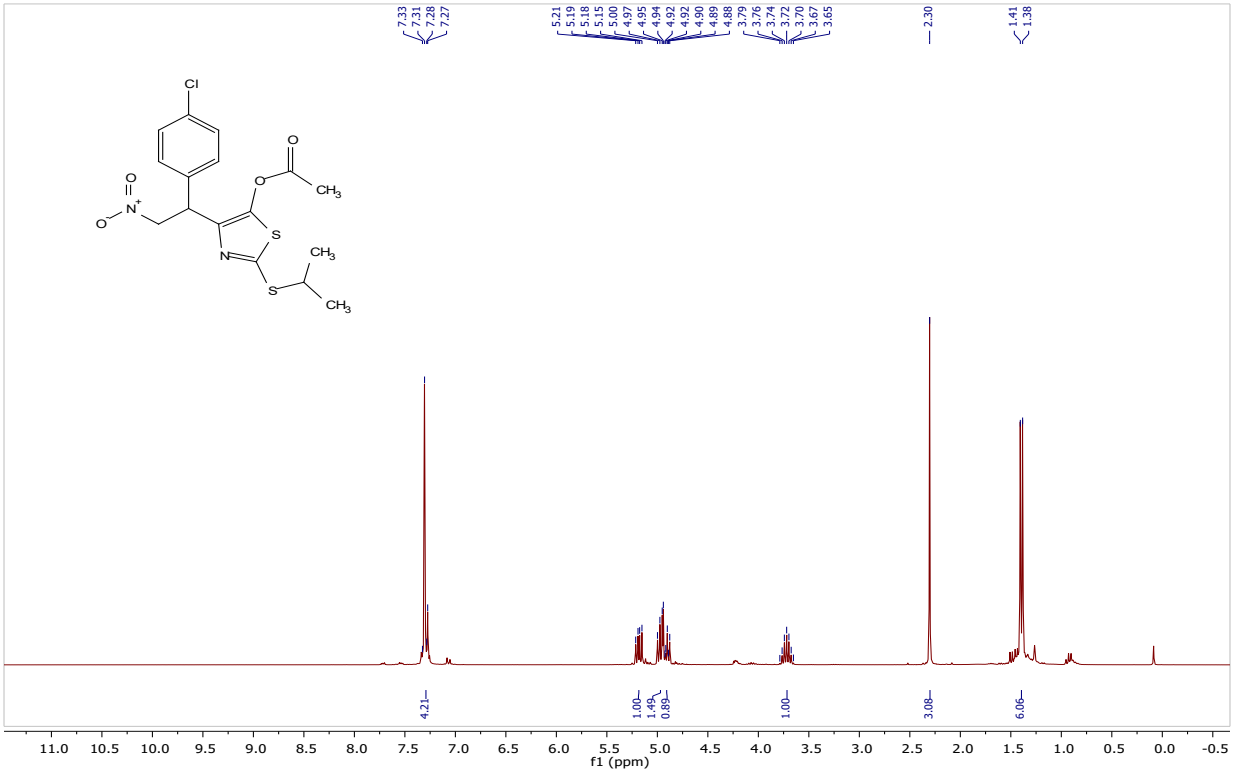
134.19
133.95
133.65
130.37
129.55
127.75
77.42
77.00
76.57
76.46
40.39
37.25
23.05
22.99
20.25
Cl
Cl
O
O
CH3
O
N+
O-
S
N
S
CH3
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.33
7.31
7.28
7.27
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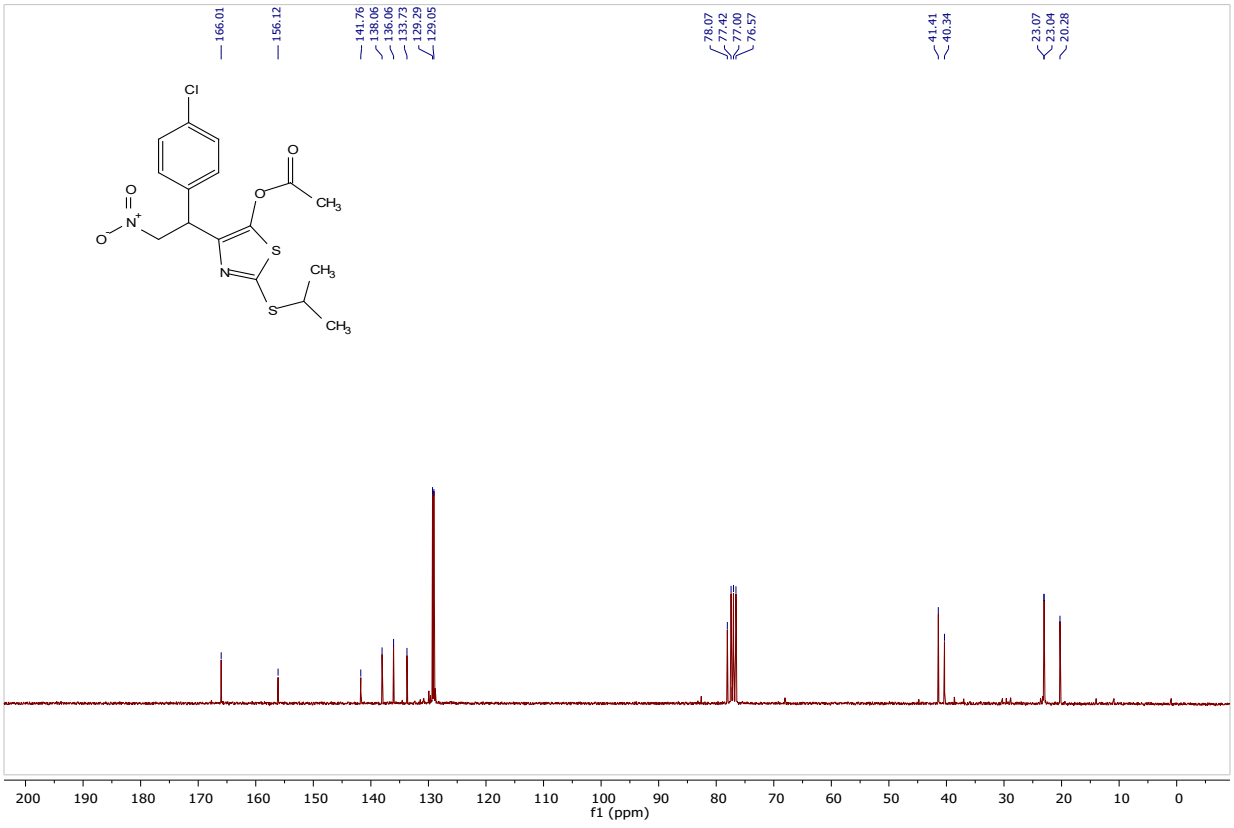
5.19
5.18
5.15
5.00
4.97
4.95
4.94
4.92
4.92
4.90
4.89
4.88
3.79
3.76
3.74
3.72
3.70
3.67
3.65
2.30
1.41
1.38
Cl
O
O
CH3
O
N+
O-
S
N
CH3
S
CH3
4.21
1.00
1.49
0.89
1.00
3.08
6.06
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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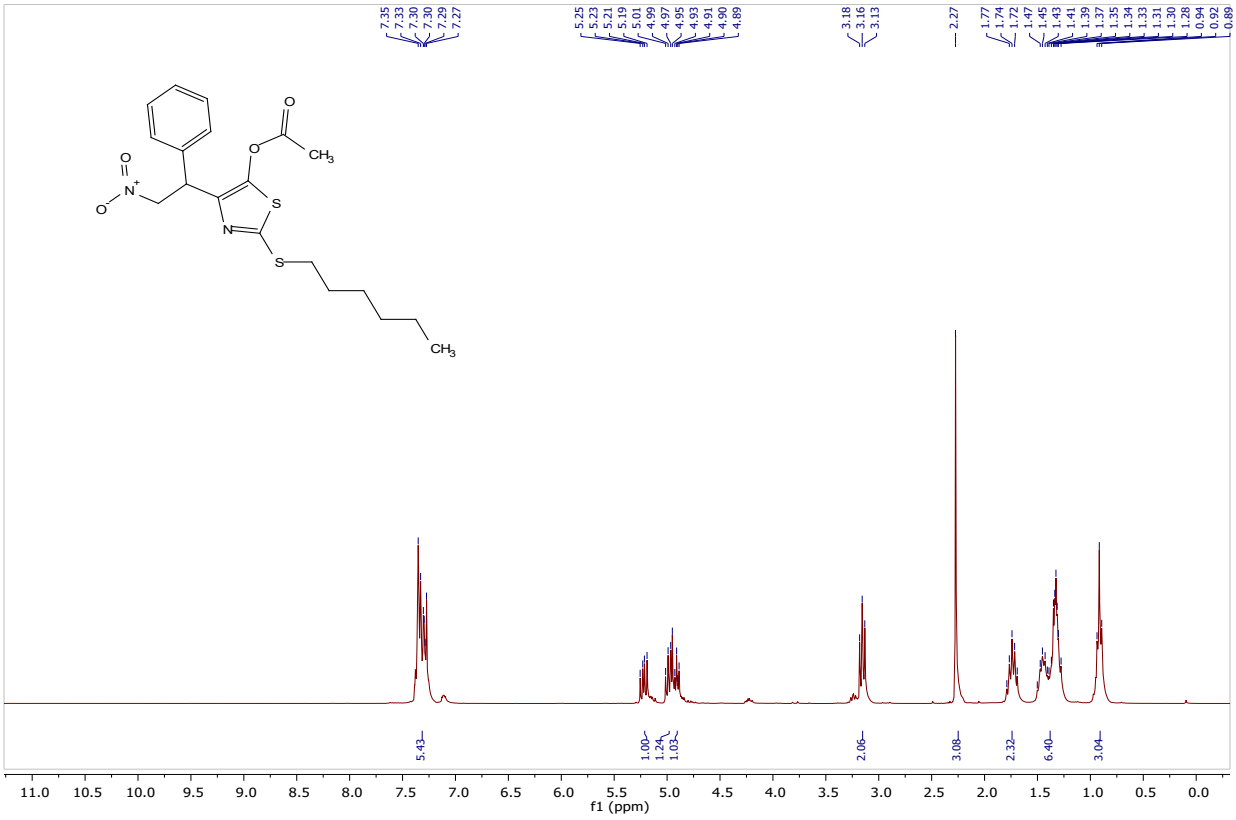
136.06
133.73
129.29
129.05
78.07
77.42
77.00
76.57
41.41
40.34
23.07
23.04
20.28
Cl
O
O
CH3
O
N+
O-
S
N
CH3
S
CH3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.35
7.33
7.30
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7.27
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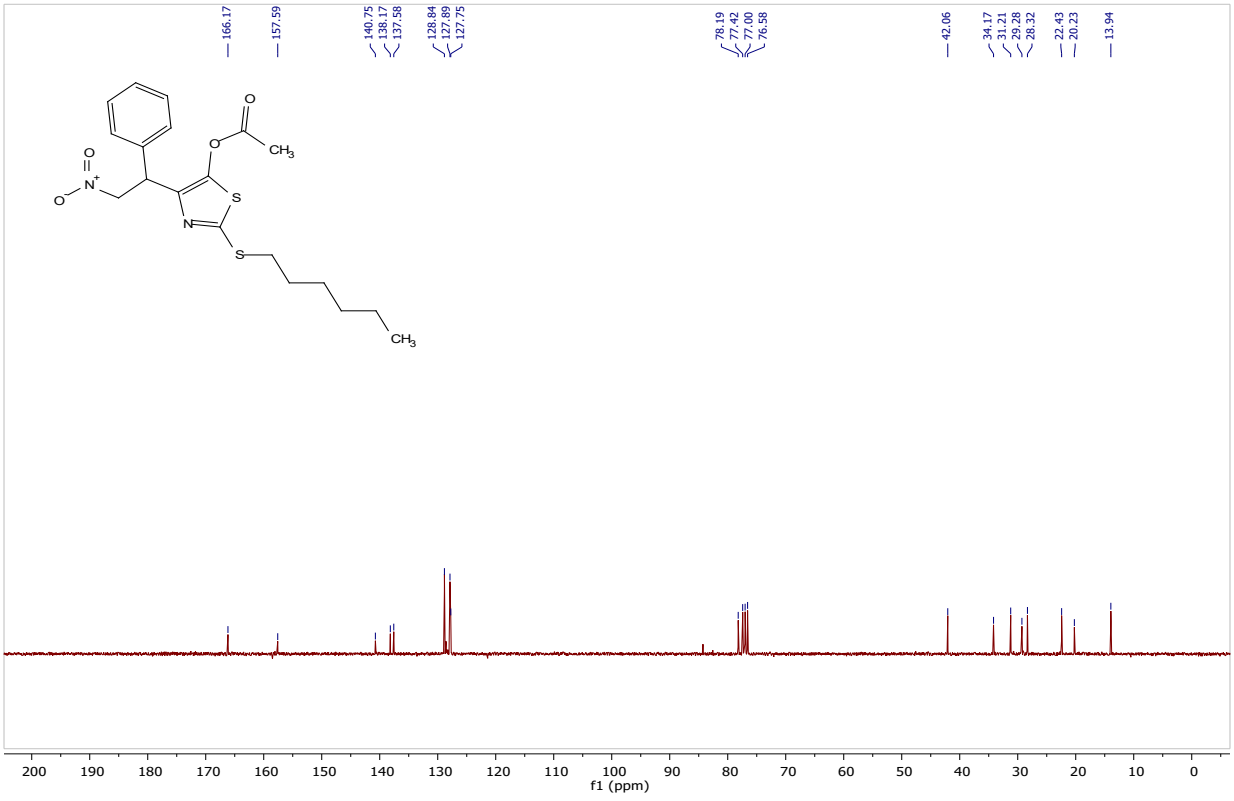
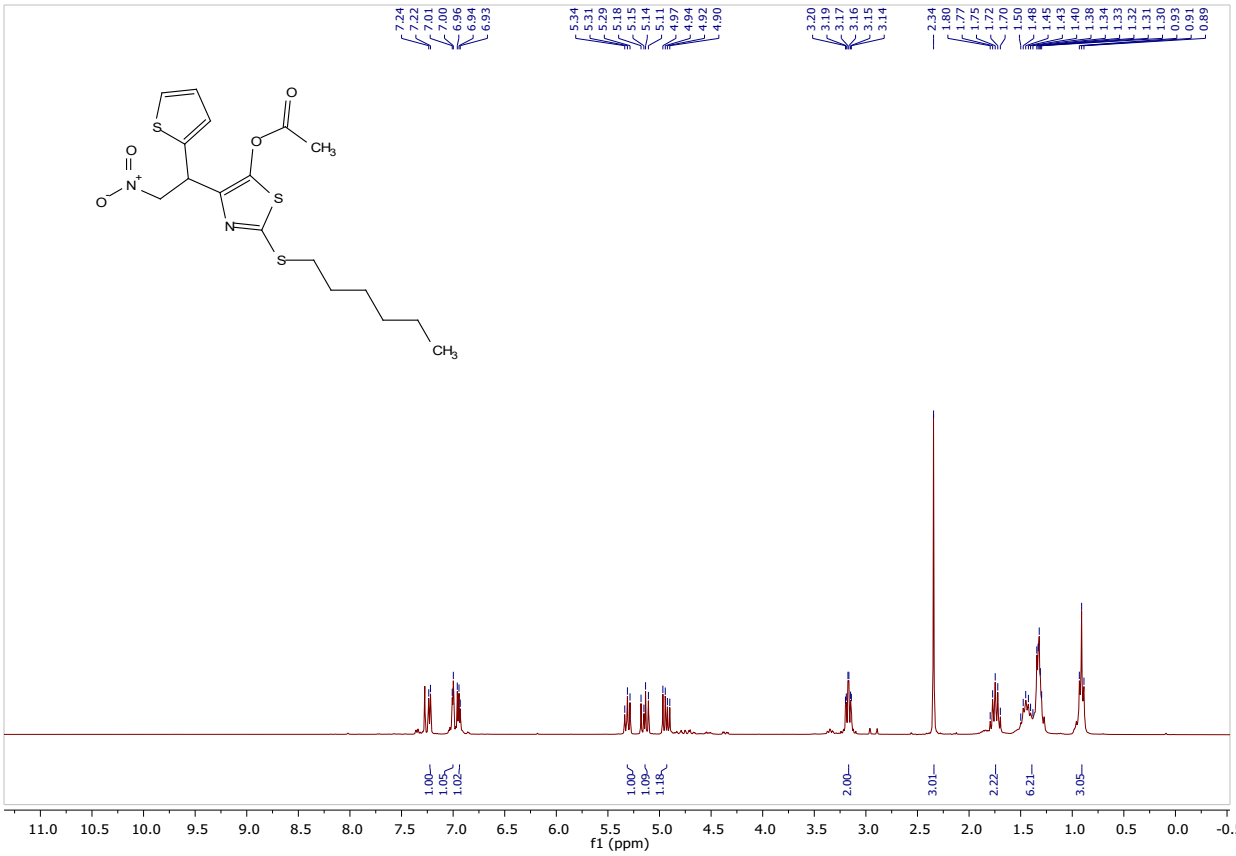
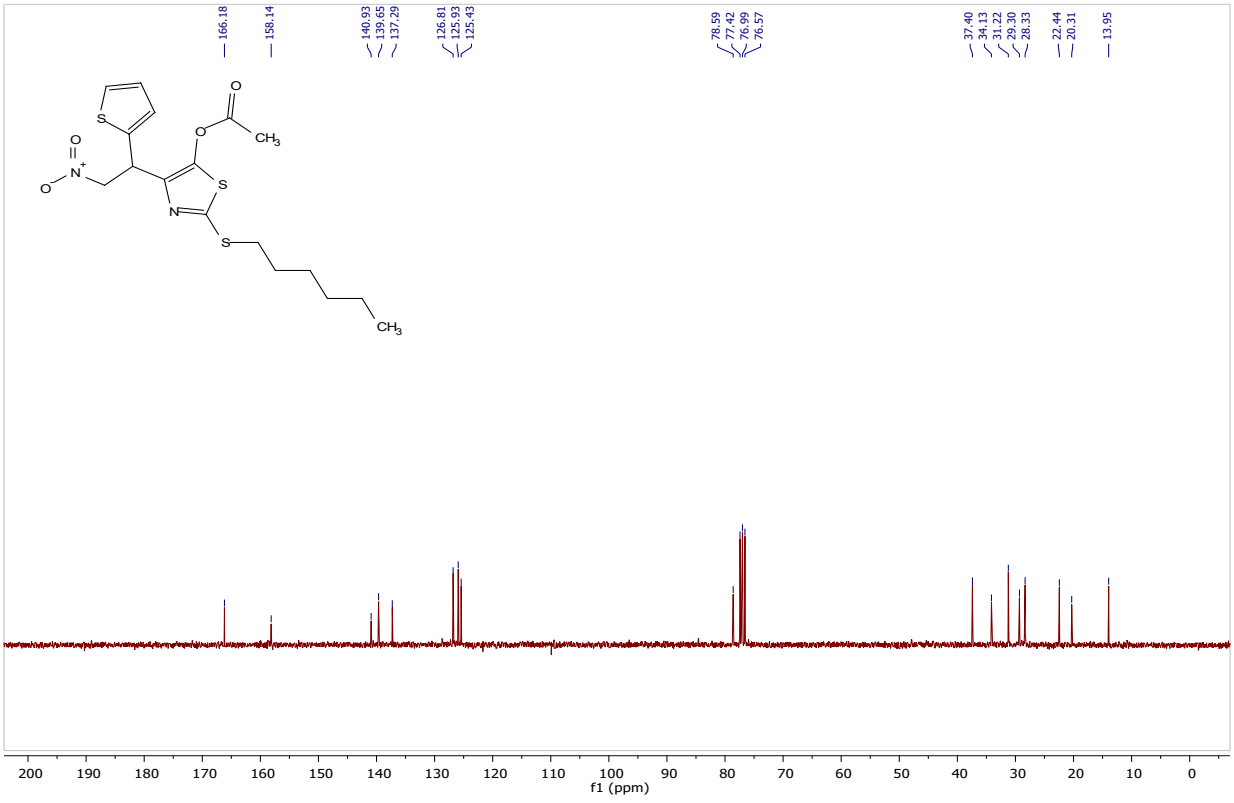
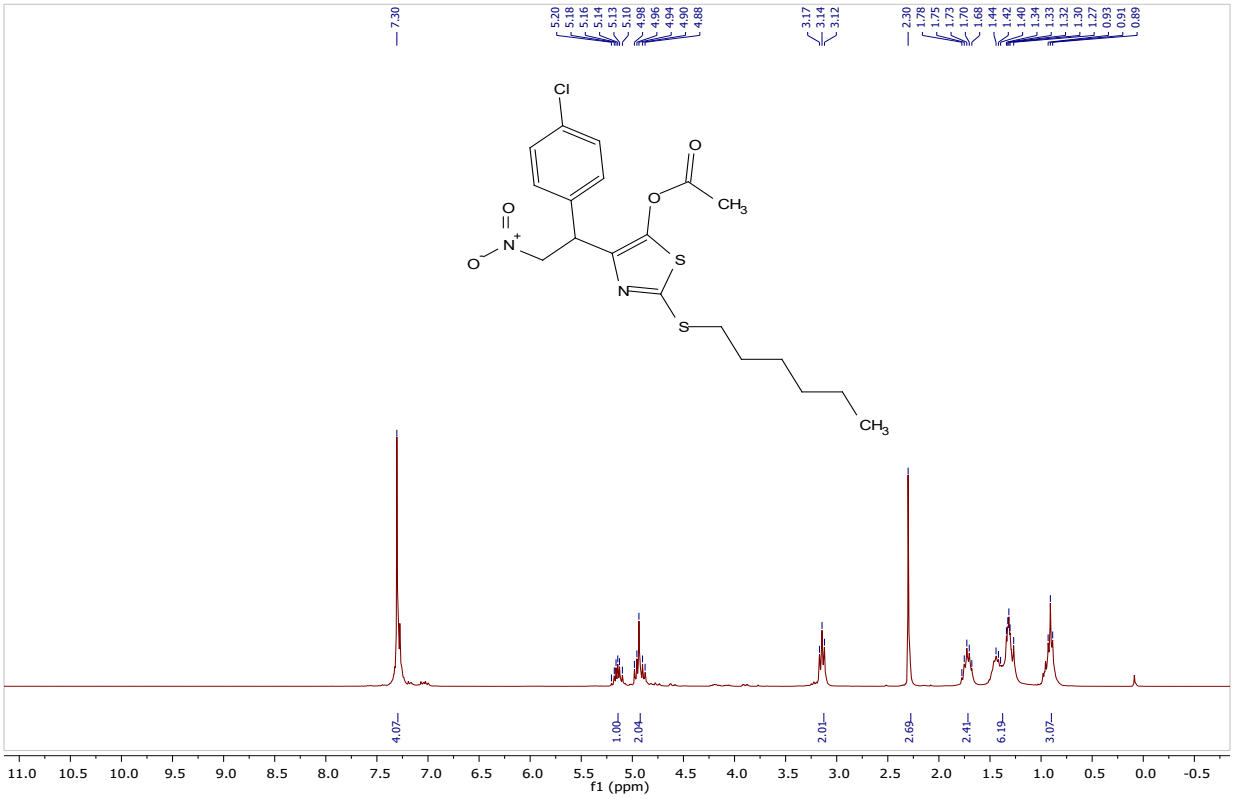
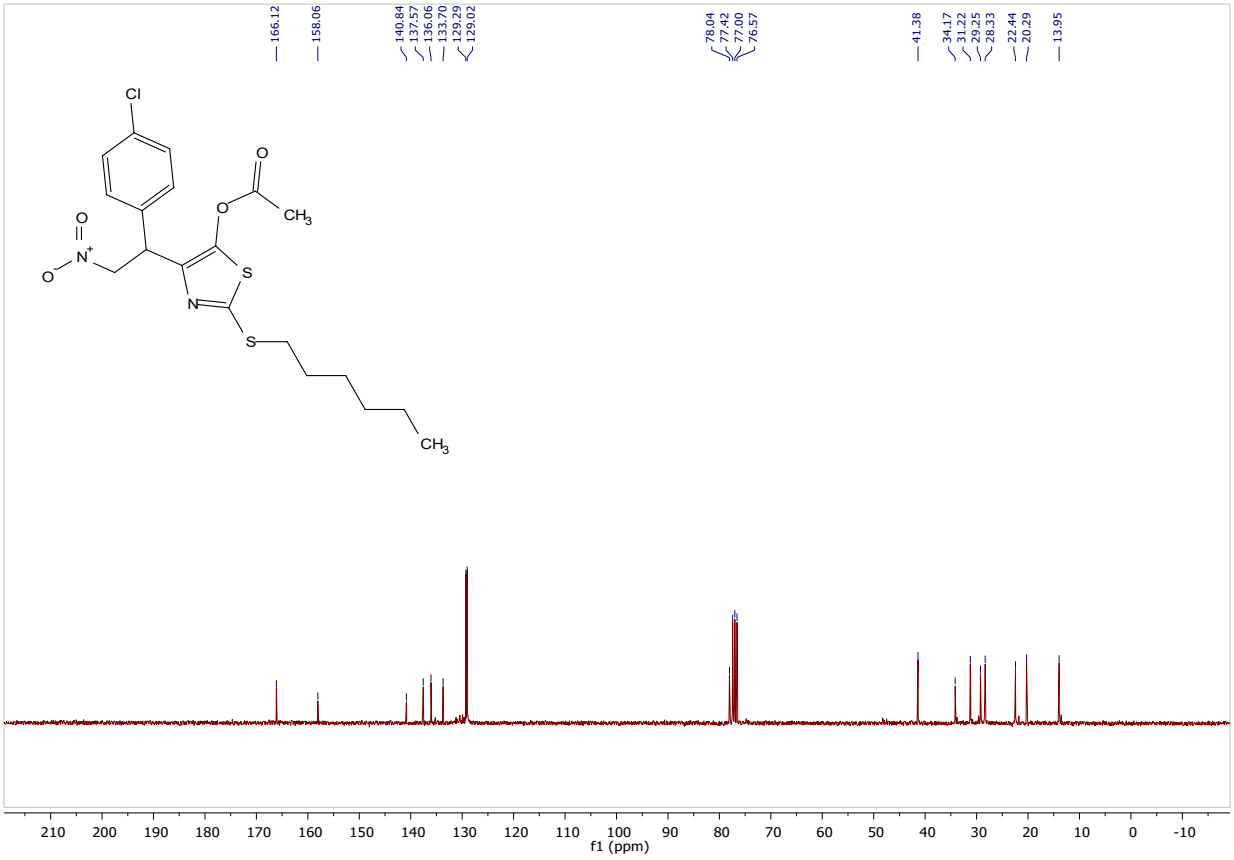
5.23
5.21
5.19
5.01
4.99
4.97
4.95
4.93
4.91
4.90
4.89
3.18
3.16
3.13
2.27
1.77
1.74
1.72
1.47
1.45
1.43
1.41
1.39
1.37
1.35
1.34
1.33
1.31
1.30
1.28
0.94
0.92
0.89
O
O
CH3
O
N+
O-
S
N
S
CH3
5.43
1.00
1.24
1.03
2.06
3.08
2.32
6.40
3.04
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.17
157.59
140.75
138.17
137.58
128.84
127.89
127.75
78.19
77.42
77.00
76.58
42.06
34.17
31.21
29.28
28.32
22.43
20.23
13.94
O
O
CH3
O
N+
O-
S
N
S
CH3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.24
7.22
7.01
7.00
6.96
6.94
6.93
5.34
5.31
5.29
5.18
5.15
5.14
5.11
4.97
4.94
4.92
4.90
3.20
3.19
3.17
3.16
3.15
3.14
2.34
1.80
1.77
1.75
1.72
1.70
1.50
1.48
1.45
1.43
1.40
1.38
1.34
1.33
1.32
1.31
1.30
0.93
0.91
0.89
1.00
1.05
1.02
1.00
1.09
1.18
2.00
3.01
2.22
6.21
3.05
11.0 10.5 10.0 9.5 9.0 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 0.0 -0.5
f1 (ppm)


166.18
158.14
140.93
139.65
137.29
126.81
125.93
125.43
78.59
77.42
76.99
76.57
37.40
34.13
31.22
29.30
28.33
22.44
20.31
13.95
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.30
5.20
5.18
5.16
5.14
5.13
5.10
4.98
4.96
4.94
4.90
4.88
3.17
3.14
3.12
2.30
1.78
1.75
1.73
1.70
1.68
1.44
1.42
1.40
1.34
1.33
1.32
1.30
1.27
0.93
0.91
0.89
Cl
O
O
CH3
O
N+
O-
S
N
S
CH3
4.07
1.00
2.04
2.01
2.69
2.41
6.19
3.07
11.0 10.5 10.0 9.5 9.0 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 0.0 -0.5
f1 (ppm)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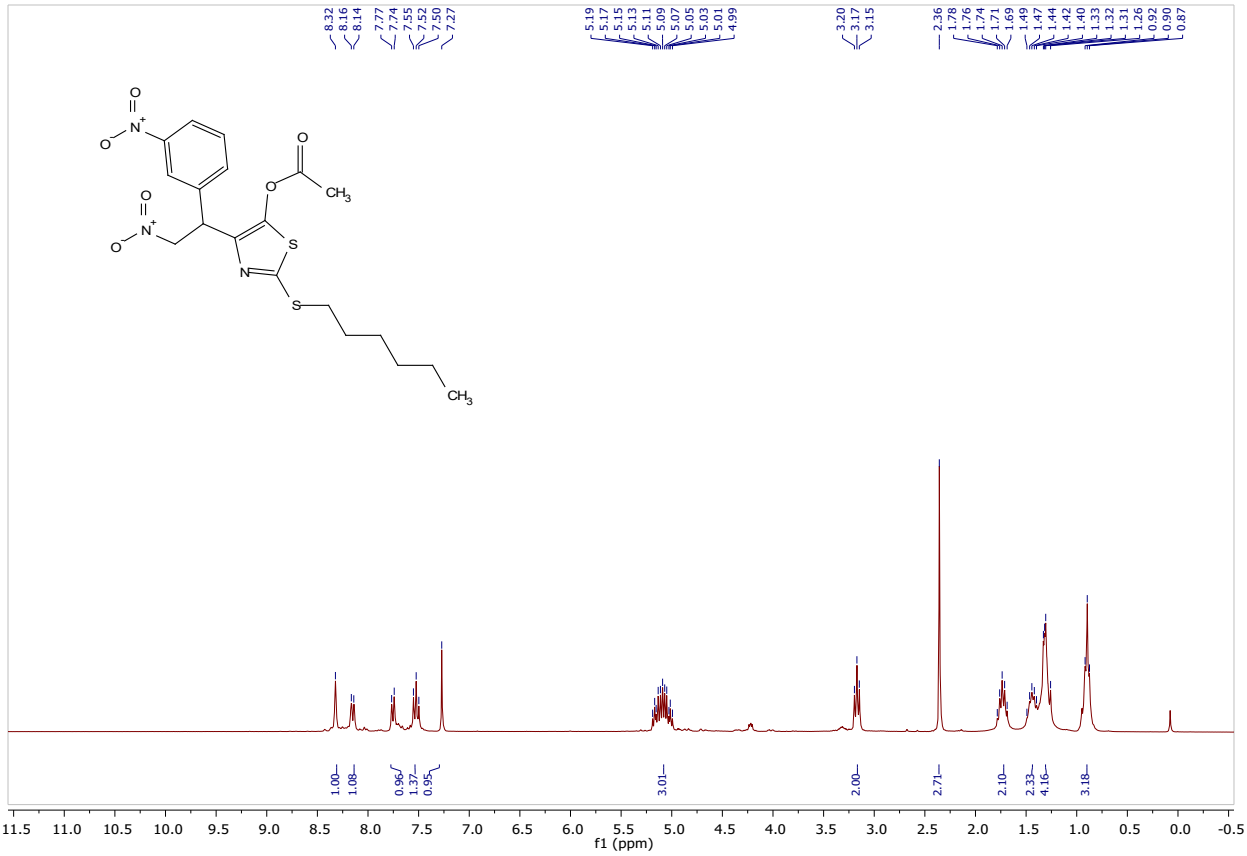
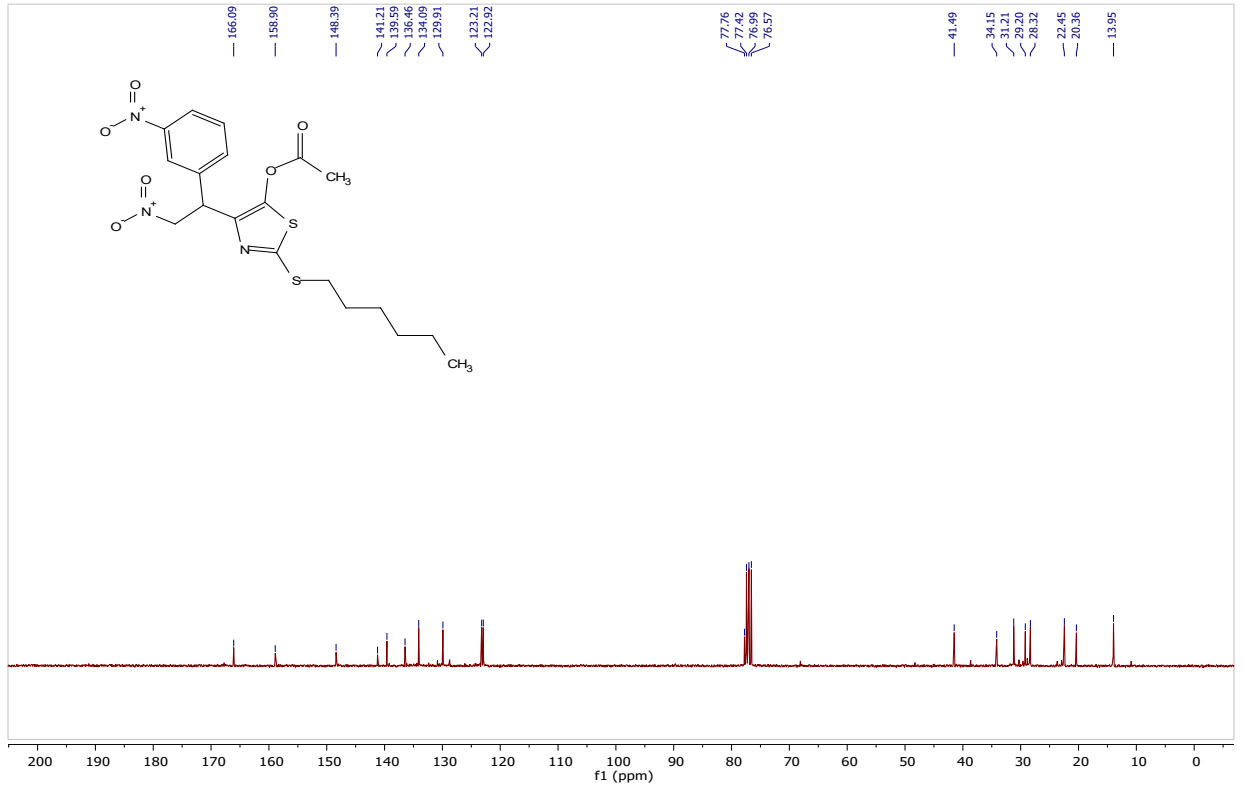
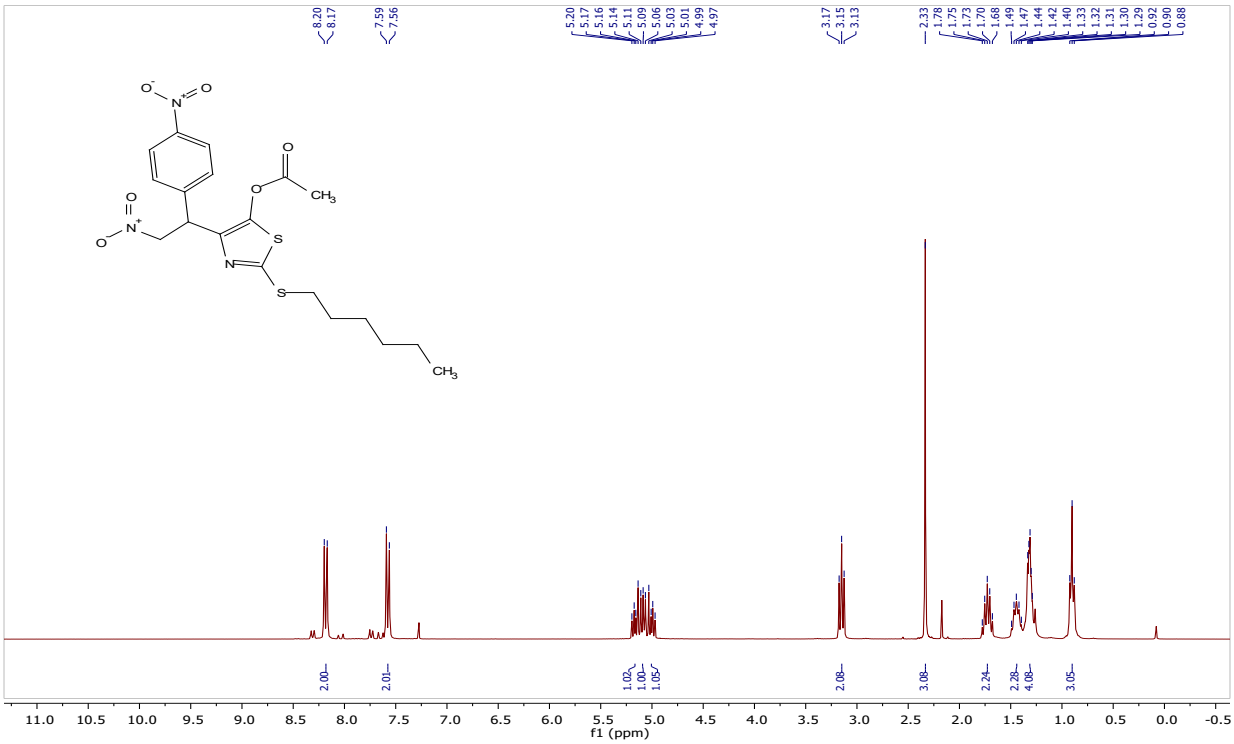
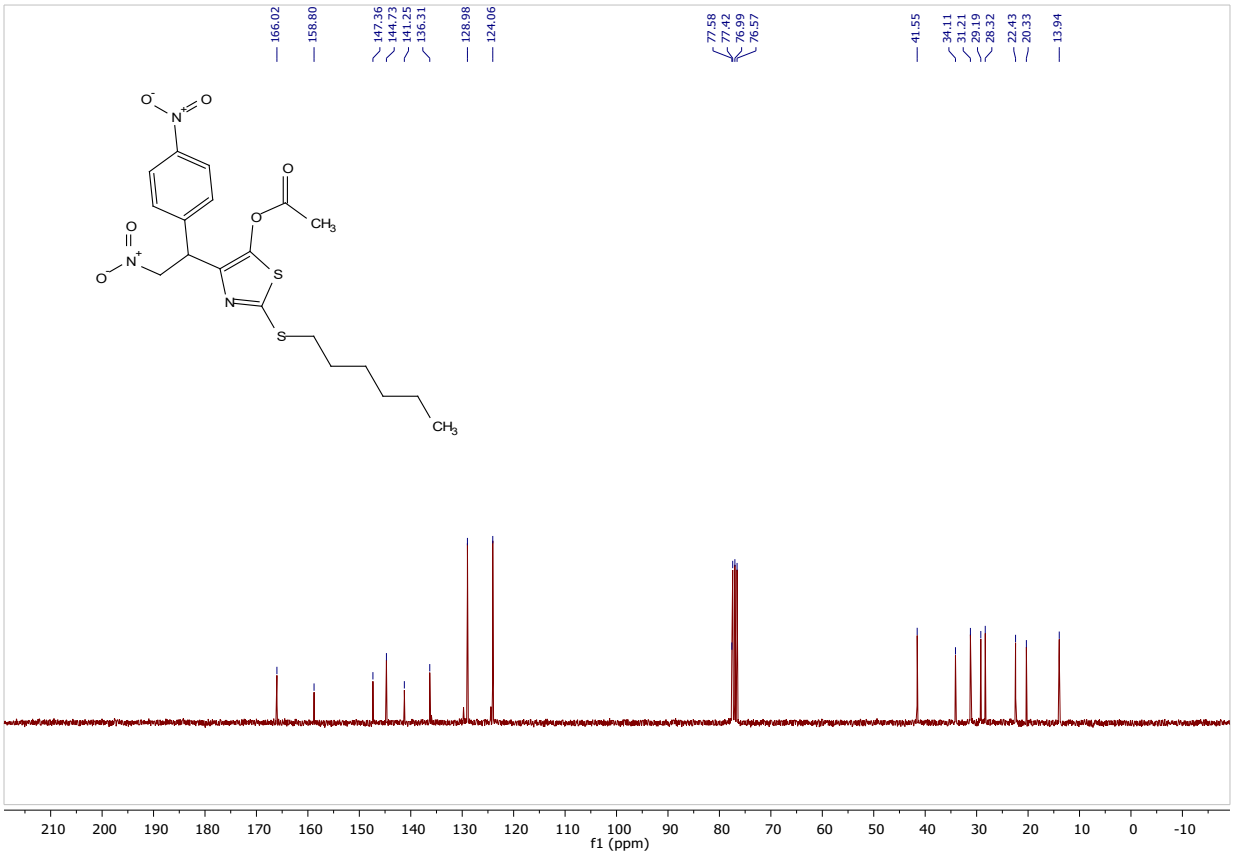
137.57
136.06
133.70
129.29
129.02
78.04
77.42
77.00
76.57
41.38
34.17
31.22
29.25
28.33
22.44
20.29
13.95
Cl
O
O
CH3
O
N+
O-
S
N
S
CH3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.32
8.16
8.14
7.77
7.74
7.55
7.52
7.50
7.27
5.19
5.17
5.15
5.13
5.11
5.09
5.07
5.05
5.03
5.01
4.99
3.20
3.17
3.15
2.36
1.78
1.76
1.74
1.71
1.69
1.49
1.47
1.44
1.42
1.40
1.33
1.32
1.31
1.26
0.92
0.90
0.87
1.00
1.08
0.96
1.37
0.95
3.01
2.00
2.71
2.10
2.33
4.16
3.18
f1 (ppm)


166.09
158.90
148.39
141.21
139.59
136.46
134.09
129.91
123.21
122.92
77.76
77.42
76.99
76.57
41.49
34.15
31.21
29.20
28.32
22.45
20.36
13.95
f1 (ppm)


8.20
8.17
7.59
7.56
5.20
5.17
5.16
5.14
5.11
5.09
5.06
5.03
5.01
4.99
4.97
3.17
3.15
3.13
2.33
1.78
1.75
1.73
1.70
1.68
1.49
1.47
1.44
1.42
1.40
1.33
1.32
1.31
1.30
1.29
0.92
0.90
0.88
2.00
2.01
1.02
1.00
1.05
2.08
3.08
2.24
2.28
4.08
3.05
f1 (ppm)


166.02
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141.25
136.31
128.98
124.06
77.58
77.42
76.99
76.57
41.55
34.11
31.21
29.19
28.32
22.43
20.33
13.94
f1 (ppm)