Supplementary Information

Carbonyldiimidazole (CDI) Promoted Direct and Instantaneous Thio-esterification of Carboxylic Acid and Thiol at Ambient Temperature

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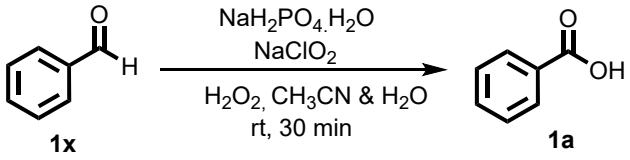
Experimental Section:

1. General methods:

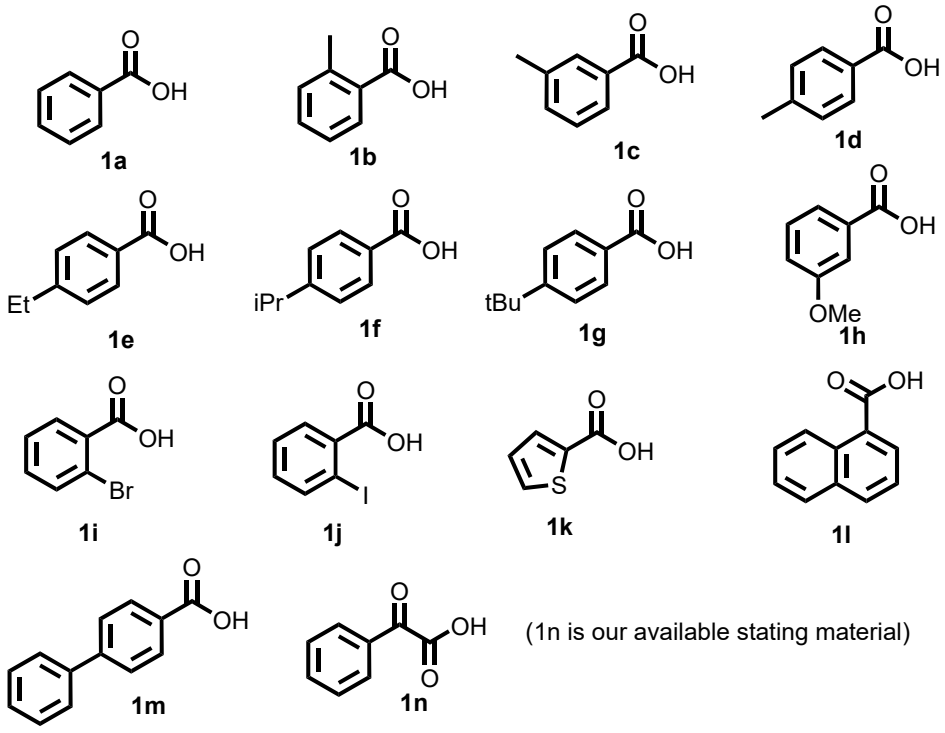
All the reactions were performed under nitrogen atmosphere in oven dried flasks. TLC was performed using 100-200 mesh silica gel plates. The column chromatography was performed using silica gel 100-200 mesh. TLC plates were visualized under UV light at 254 nm and molecular iodine vapour. ^{1}H NMR spectra were recorded on Bruker 400 MHz spectrometer and ^{13}C NMR Spectra were recorded on Bruker 100 MHz spectrometer using $CDCl_3$ as a solvent with TMS as the internal standard. The chemical shift values at 7.28 and 77 ppm are referenced for $CDCl_3$ solvent. The data of HRMS was carried out on a high-resolution mass spectrometer instrument. Melting points were measured with a Lab X India digital melting point apparatus. All the commercial reagents were used from a different commercial source. CH_2Cl_2 and CH_3CN were purified by using the traditional drying procedure.

2. General method for synthesizing carboxylic acids 1a-1m.

a. Typical procedure for the synthesis of carboxylic acid 1a.



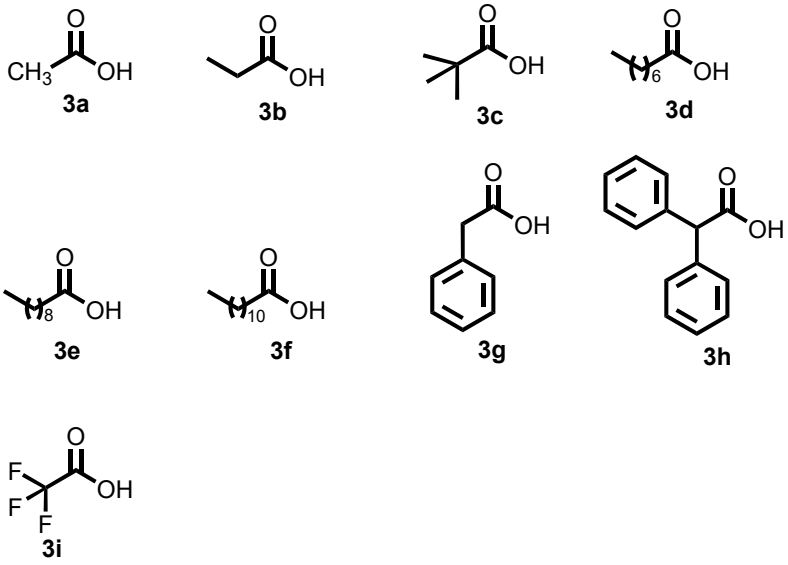
1x → 1a



Into a mixture of Benzaldehyde **1x** (150mg, 3.2 mmol), $NaH_2PO_4.H_2O$ (115mg, 1.90 mmol) and H_2O_2 (0.12 ml) in CH_3CN (1.5 ml) was added dropwise $NaClO_2$ (438 mg, 11 mmol) in H_2O (1.5 ml) at 25^0C for 15 min. After adding Na_2SO_3 (28 mg, 0.50 mmol), the mixture was evaporated under reduced pressure. The mixture was acidified by adding 2N HCl and extracted with ethyl acetate. The extract was washed with H_2O, dried with Na_2SO_4. Solvent was removed under reduced pressure to dryness to produce Benzoic Acid **1a** (152 mg, 88%) as white solid.

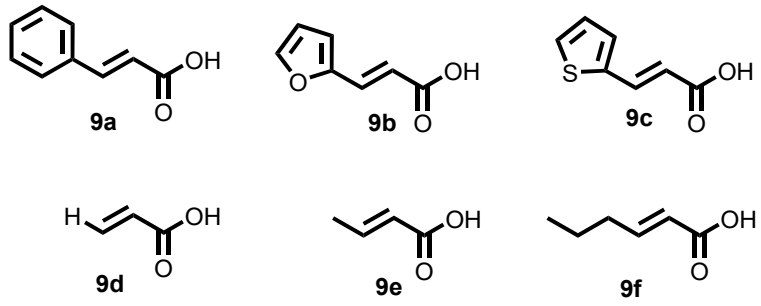
Carboxylic acids **1b- 1m** were synthesized from their corresponding aryl aldehydes as per the procedure mentioned above. **1n** is our available carboxylic acid.

b. Typical procedure for the synthesis of aliphatic acids (3a-3i).



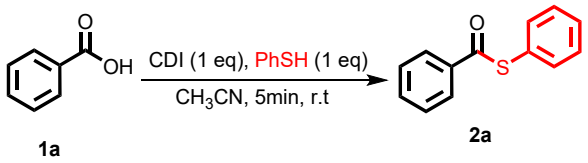
3a- 3i are the available aliphatic acids.

c. Typical procedure for the synthesis of alpha beta unsaturated acids (9a-9f).



9a-9f are the available alpha beta unsaturated acids.

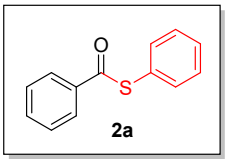
3. General procedure for the synthesis of thioester 2a.



Dry CH_3CN (3ml) solution of Benzoic acid **1a** (0.8 mmol, 100mg) and CDI (0.8 mmol) was taken in a 50 ml dry round bottom flask fitted with magnetic stir bar under N_2 atmosphere. Then PhSH (0.8 mmol) was added into this mixture. The mixture was stirred at room temperature for 5 min. After the total consumption of the starting material **1a** as shown by TLC, the mixture was evaporated under reduced pressure & then the reaction mixture was quenched by ethyl acetate followed by water. The combined organic layer was separated, washed with brine solution (twice) and collected over anhydrous sodium sulphate.

The concentrated organic solution was then loaded on a 100-200 mesh column of silica gel & eluted with hexane: ethyl acetate (98:2) to get purified thioester **2a** (163 mg, 95%) as yellowish solid.

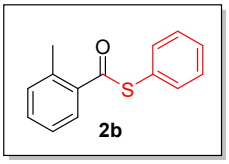
S-phenyl benzothioate(2a)



mp- 99°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 8.14-8.09 (m, 2H), 7.68-7.63 (m, 1H), 7.60 (dd, *J*= 6.6, 3.1Hz,2H), 7.56-7.49 (m, 5H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 190.2, 136.7, 135.2, 133.8, 129.6, 129.3, 128.9, 127.6,127.4; **IR** (neat, cm^{-1}) =1664; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{13}H_{10}NaOS$: 237.0350; found 237.0353.

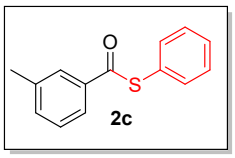
4. Characterization data of thioester 2b-2n, 4a-4h, 6a-6g

S-phenyl 2-methylbenzothioate(2b)



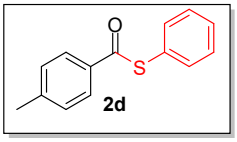
According to the above-mentioned procedure, carboxylic acid **1b** (0.7 mmol, 100 mg) upon reaction with CDI (0.7 mmol) & PhSH (0.7 mmol) to afford thioester **2b** (144 mg, 90%) as orange solid. **mp**-123°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.00 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.59-7.57 (m, 2H), 7.53-7.45 (m, 4H), 7.35-7.30 (m, 2H), 2.55 (s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$) δ =192.2, 137.5, 136.7, 134.9, 132.1, 131.8, 129.5, 129.3, 128.7, 128.2, 125.9, 20.8; **IR** (neat, cm^{-1}) = 1674; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{14}H_{12}NaOS$: 251.0507; found 251.0509.

S-phenyl 3-methylbenzothioate(2c)



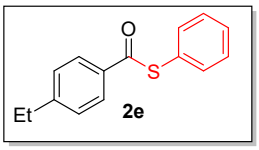
According to the above-mentioned procedure, carboxylic acid **1c** (0.7 mmol,100 mg) upon reaction with CDI (0.7 mmol) & PhSH (0.7 mmol) to afford thioester **2c** (142 mg, 89%) as white solid. **mp**-122°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.91-7.88 (m, 2H), 7.58 (dt, *J*= 5.7, 1.7 Hz, 2H), 7.51 (dd, *J*= 5.0, 1.9 Hz, 3H), 7.47-7.39 (m, 2H), 2.4 (s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$) δ = 190.3, 136.7, 135.1, 134.5, 129.5, 129.3, 128.6, 127.9, 127.5, 124.7, 21.4; **IR** (neat, cm^{-1}) = 1673; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{14}H_{12}NaOS$: 251.0507; found 251.0510.

S-phenyl 4-methylbenzothioate(2d)



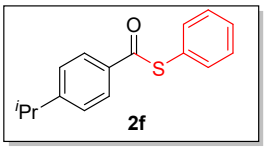
According to the above-mentioned procedure, carboxylic acid **1d** (0.7 mmol, 100 mg) upon reaction with CDI (0.7 mmol) & PhSH (0.7mmol) to afford thioester **2d** (146 mg, 91%) as yellow solid. **mp**-121°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.99 (d, *J*= 8.3 Hz, 2H), 7.57 (dd, *J*=4.7,1.6 Hz, 2H), 7.50 (dt, *J*= 4.6, 2.9 Hz, 3H), 7.32 (d, *J*=8.0 Hz, 2H), 2.47(s, 3H); **^{13}C NMR** (100MHz,$CDCl_3$) δ= 189.7, 144.6, 135.2, 134.1, 130.7, 129.5, 129.2, 127.6, 21.8; **IR** (neat, cm^{-1}) = 1675; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{14}H_{12}NaOS$: 251.0507; found 251.0512.

S-phenyl 4-ethylbenzothioate(2e)



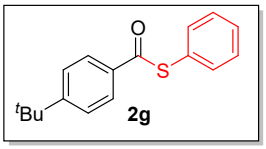
According to the above-mentioned procedure, carboxylic acid **1e** (0.6 mmol, 100 mg) upon reaction with CDI (0.6 mmol) & PhSH (0.6 mmol) to afford thioester **2e** (132 mg, 91%) as white solid **mp**-135°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.99-7.97 (m, 2H), 7.54-7.53 (m, 2H), 7.47 (d, *J*=2.6 Hz, 3H), 7.34 (d, *J*= 8.3 Hz, 2H), 2.75 (q, *J*=7.6 Hz, 2H), 1.30 (t, *J*= 7.6Hz, 2H); **^{13}C NMR** (100MHz,$CDCl_3$) δ= 189.8, 150.8, 135.2, 134.3, 129.5, 129.2, 128.3, 127.7, 127.5, 29.0, 15.2; **IR** (neat, cm^{-1}) = 1678; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{15}H_{14}NaOS$: 265.0663; found 265.0667.

S-phenyl 4-isopropylbenzothioate(2f)



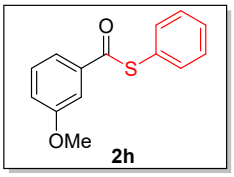
According to the above-mentioned procedure, carboxylic acid **1f** (0.6 mmol, 100 mg) upon reaction with CDI (0.6 mmol) & PhSH (0.6 mmol) to afford thioester **2f** (141 mg, 92%) as orange solid. **mp**-131°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 8.04 (d, *J*= 8.2 Hz, 2H), 7.58 (dd, *J*= 6.6, 3.2Hz, 2H), 7.50 (dd, *J*=5.1, 2.0 Hz, 3H), 7.41-7.37 (m, 2H), 3.03 (hept, *J*= 6.9 Hz, 1H), 1.34 (d, *J*= 6.9 Hz, 6H); **^{13}CNMR**(100MHz,$CDCl_3$) δ= 189.7, 135.2, 134.5, 129.5, 129.3, 127.8, 127.5 ,126.9, 34.4, 23.7; **IR** (neat, cm^{-1}) = 1677; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{16}H_{16}NaOS$: 279.0820; found 279.0824.

S-phenyl 4-(tert-butyl)benzothioate(2g)



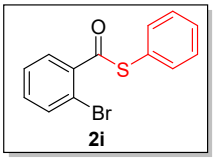
According to the above-mentioned procedure, carboxylic acid **1g** (0.5 mmol, 100 mg) upon reaction with CDI (0.5 mmol) & PhSH (0.5 mmol) to afford thioester **2g** (126 mg, 93%) as yellowish liquid.**^{1}H NMR** (400 MHz, $CDCl_3$) δ= 8.04-8.01 (m, 2H), 7.57-7.53 (m, 4H), 7.50 (dd, *J*= 5.1, 1.9 Hz, 3H), 1.40 (s, 9H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 189.6, 157.6, 135.2, 134.1, 129.5, 129.3,127.5, 127.5, 125.8, 35.3, 31.1; **IR** (neat, cm^{-1}) = 1675; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{17}H_{18}NaOS$: 293.0976; found 293.0979.

S-phenyl 3-methoxybenzothioate(2h)



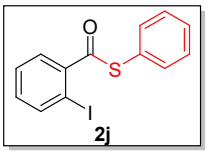
According to the above-mentioned procedure, carboxylic acid **1h** (0.6 mmol, 100 mg) upon reaction with CDI (0.6 mmol) & PhSH (0.6 mmol) to afford thioester **2h** (144 mg, 98%) as yellowish liquid.**^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.74-7.67 (m, 1H), 7.57 (dt, *J*= 4.0, 3.0 Hz, 3H), 7.50 (dd, *J*= 5.0,1.9 Hz, 3H), 7.43 (t, *J*= 8.0Hz, 1H), 7.19 (ddd, *J*= 8.4, 2.7, 1.0 Hz, 1H), 3.88 (s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 190.1, 159.9, 137.9, 135.1, 129.7, 129.5, 129.2, 127.3, 120.1, 111.7, 55.5; **IR** (neat, cm^{-1}) = 1679; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{14}H_{12}NaO_2S$: 267.0456; found 267.0459.

S-phenyl 2-bromobenzothioate(2i)



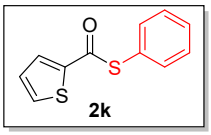
According to the above-mentioned procedure, carboxylic acid **1i** (0.4 mmol, 100 mg) upon reaction with CDI (0.4 mmol) & PhSH (0.4mmol) to afford thioester **2i** (116 mg, 80%) as white solid. **mp**-172°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.75 (dd, *J*= 7.6, 1.8 Hz, 1H), 7.69 (dd, *J*= 7.9, 1.3 Hz, 1H), 7.59-7.54 (m, 2H), 7.49 (dd, *J*= 5.0, 2.0 Hz, 3H), 7.41 (dd, *J*= 24.0, 1.6 Hz, 2H); **^{13}C NMR** (100MHz,$CDCl_3$) δ= 191.2, 139.2, 135.2, 134.5, 134.1, 132.3, 129.8, 129.4, 129.1, 127.2, 119.1; **IR** (neat, cm^{-1}) = 1670; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{13}H_9BrNaOS$: 314.9455; found 314.9458.

S-phenyl 2-iodobenzothioate(2j)



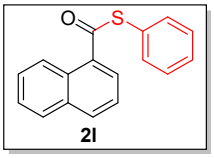
According to the above-mentioned procedure, carboxylic acid **1j** (0.4 mmol, 100 mg) upon reaction with CDI (0.4 mmol) & PhSH (0.4 mmol) to afford thioester **2j** (116 mg, 85%) as white solid. **mp**-170°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.99 (dd, *J*= 7.9, 1.1 Hz,1H), 7.74 (dd, *J*= 7.7, 1.6 Hz, 1H), 7.62-7.56 (m, 2H), 7.53-7.43 (m, 4H), 7.21 (td, *J*= 7.7, 1.6 Hz, 1H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 192.4, 142.4, 140.7, 134.5, 132.5, 129.8, 129.4, 128.5, 128.1, 127.5, 91.5; **IR** (neat, cm^{-1}) = 1671; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{13}H_9INaOS$: 362.9317; found 362.9320.

S-phenyl thiophene-2-carbothioate(2k)



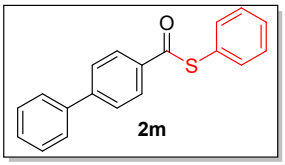
According to the above-mentioned procedure, carboxylic acid **1k** (0.7mmol, 100 mg) upon reaction with CDI (0.7 mmol) & PhSH (0.7 mmol) to afford thioester **2k** (140 mg, 82%) as orange solid. **mp**-163°C;**^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.94 (dd, *J*= 3.9, 1.2Hz,1H), 7.69 (dd, *J*= 5.0, 1.2 Hz, 1H), 7.59-7.54 (m, 2H), 7.48 (dt, *J*= 4.9, 1.8 Hz, 3H), 7.19 (dd, *J*= 5.0 ,3.8 Hz, 1H); **^{13}C NMR** (100MHz,$CDCl_3$) δ= 182.1, 141.4, 135.1, 133.3, 131.6, 129.7, 129.3, 128.1, 126.9; **IR** (neat, cm^{-1}) = 1640; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{11}H_8NaOS_2$: 242.9914; found 242.9918.

S-phenyl naphthalene-1-carbothioate(2l)



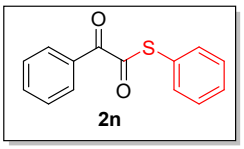
According to the above-mentioned procedure, carboxylic acid **1l** (0.5 mmol, 100 mg) upon reaction with CDI (0.5 mmol) & PhSH (0.5 mmol) to afford thioester **2l** (138 mg, 90%) as brownish solid. **mp**-190°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 8.61-8.59 (m, 1H), 8.27 (dd, *J*= 7.3, 1.2 Hz, 1H), 8.08 (dt, *J*= 8.3, 1.1 Hz, 1H), 7.93 (dd, *J*= 7.8, 1.7 Hz, 1H), 7.66-7.53 (m, 8H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 192.3, 135.2, 134.9, 134.7, 133.8, 133.4, 129.6, 129.4, 128.4, 128.2, 128.1, 126.8, 125.3, 124.5; **IR** (neat, cm^{-1}) = 1672; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{17}H_{12}NaOS$: 287.0507; found 287.0510.

S-phenyl [1,1'-biphenyl]-4-carbothioate(2m)



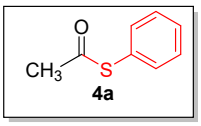
According to the above-mentioned procedure, carboxylic acid **1m** (0.5mmol, 100 mg) upon reaction with CDI (0.5 mmol) & PhSH (0.5 mmol) to afford thioester **2m** (133 mg, 91%) as white solid. **mp**-206°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 8.16-8.13 (m, 2H), 7.76-7.74 (m, 2H), 7.69-7.67 (m, 2H), 7.60-7.58 (m, 2H), 7.54-7.50 (m, 5H), 7.47 (d, *J*= 7.3 Hz, 1H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 189.7, 140.4, 139.7, 135.3, 135.2, 129.5, 129.3, 129.1, 128.4, 128.1, 127.4, 127.3; **IR** (neat, cm^{-1}) = 1673; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{19}H_{14}NaOS$: 313.0663; found 313.0667.

S-phenyl 2-oxo-2-phenylethanethioate(2n)



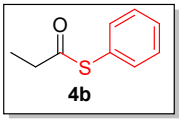
According to the above-mentioned procedure, carboxylic acid **1n** (0.6mmol, 100 mg) upon reaction with CDI (0.6 mmol) & PhSH (0.6 mmol) to afford thioester **2n** (148 mg, 92%) as yellowish liquid.**^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.59-7.53 (m, 4H), 7.45 (dddd, *J*= 7.1, 6.1, 4.9, 1.7 Hz, 6H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 188.4, 135.2, 130.1, 129.4, 127.1; **IR** (neat, cm^{-1}) = 1709, 1650; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{14}H_{10}NaO_2S$: 265.0299; found 265.0303.

S-phenyl ethanethioate(4a)



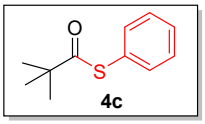
According to the above-mentioned procedure, carboxylic acid **3a** (1.66 mmol, 100 mg) upon reaction with CDI (1.66 mmol) & PhSH (1.66 mmol) to afford thioester **4a** (192 mg, 76%) as white liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.48-7.41 (m, 5H), 2.45 (s, 1H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 194.2, 134.5, 129.5, 129.2, 127.9, 30.2; **IR** (neat, cm^{-1}) = 1703; **HRMS** (ESI) m/z $(M+H)^+$ calculated for C_8H_9OS: 153.0374; found 153.0377.

S-phenyl propanethioate(4b)



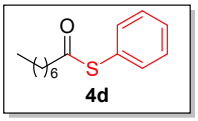
According to the above-mentioned procedure, carboxylic acid **3b** (1.34 mmol, 100 mg) upon reaction with CDI (1.34 mmol) & PhSH (1.34 mmol) to afford thioester **4b** (175mg, 78%) as white liquid.**^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.47-7.42 (m, 5H), 2.72 (q, J= 7.5 Hz, 2H), 1.26 (t, J= 7.5 Hz, 3H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 198.3, 134.6, 129.3, 129.2, 127.8, 37.1, 9.6; **IR** (neat, cm^{-1}) = 1704; **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_9H_{11}OS$: 167.0531; found 167.0534.

S-phenyl 2,2-dimethylpropanethioate(4c)



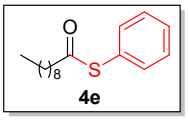
According to the above-mentioned procedure, carboxylic acid **3c** (0.9 mmol, 100 mg) upon reaction with CDI (0.9 mmol) & PhSH (0.9 mmol) to afford thioester **4c** (161mg, 85%) as yellowish liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.46-7.38 (m, 5H), 1.35 (s, 9H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 204.7, 135.0, 129.1, 129.1, 128.1, 46.9, 27.4; **IR** (neat, cm^{-1}) = 1706; **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{11}H_{15}OS$: 195.0844; found 195.0848.

S-phenyl octanethioate(4d)



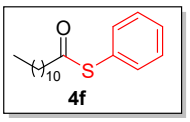
According to the above-mentioned procedure, carboxylic acid **3d** (0.6 mmol, 100 mg) upon reaction with CDI (0.6 mmol) & PhSH (0.6 mmol) to afford thioester **4d** (127mg, 78%) as white liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.46-7.42 (m, 5H), 2.69 (t, J= 7.5 Hz, 2H), 1.75 (p, J= 7.4 Hz, 2H), 1.47-1.27 (m, 8H), .94-.91 (m, 3H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 197.5, 134.5, 129.3, 129.2, 128.0, 43.7, 31.6, 28.9, 25.6, 22.6, 14.1; **IR** (neat, cm^{-1}) = 1709; **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{14}H_{21}OS$: 237.1313; found 237.1317.

S-phenyl decanethioate(4e)



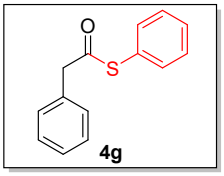
According to the above-mentioned procedure, carboxylic acid **3e** (0.5 mmol, 100 mg) upon reaction with CDI (0.5 mmol) & PhSH (0.5 mmol) to afford thioester **4e** (123mg, 80%) as yellowish liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.46-.7.41 (m, 5H), 2.68 (t, J= 7.5 Hz, 2H), 1.74 (p, J=7.4 Hz, 2H). 1.44-1.26 (m, 12H), .92 (t, J= 6.7 Hz, 3H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 197.6, 134.5, 129.3, 129.2, 127.9, 43.7, 31.8, 29.4, 29.3, 28.9, 25.6, 22.7, 14.2; **IR** (neat, cm^{-1}) = 1707; **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{16}H_{25}OS$: 265.1626; found 265.1630.

S-phenyl dodecanethioate(4f)



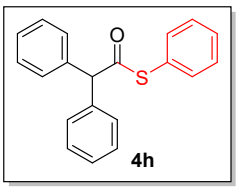
According to the above-mentioned procedure, carboxylic acid **3f** (0.4 mmol, 100 mg) upon reaction with CDI (0.4 mmol) & PhSH (0.4 mmol) to afford thioester **4f** (119mg, 81%) as white liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.47-7.39 (m, 5H), 2.68 (t, J= 7.5 Hz, 2H), 1.74 (p, J= 7.4 Hz, 2H), 1.41-1.29 (m, 16H), .92 (t, J= 6.8 Hz, 3H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 197.6, 134.5, 129.3, 129.2, 128.0, 43.7, 31.9, 29.6, 29.5, 29.4, 29.3, 29.0, 25.6, 22.7, 14.2; **IR** (neat, cm^{-1}) = 1705; **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{18}H_{29}OS$: 293.1939; found 293.1942.

S-phenyl 2-phenylethanethioate(4g)



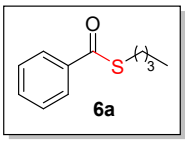
According to the above-mentioned procedure, carboxylic acid **3g** (0.7 mmol, 100 mg) upon reaction with CDI (0.7 mmol) & PhSH (0.7 mmol) to afford thioester **4g** (132 mg, 79%) as white liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.42-7.32 (m, 10H), 3.96 (s, 2H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 195.4, 134.5, 133.3, 129.7, 129.5, 129.21, 128.7, 127.7, 127.6, 50.2; **IR** (neat, cm^{-1}) = 1710; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{14}H_{12}NaOS$: 251.0507; found 251.0510.

S-phenyl 2,2-diphenylethanethioate(4h)



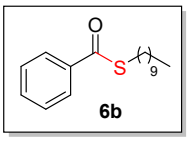
According to the above-mentioned procedure, carboxylic acid **3h** (0.4 mmol, 100 mg) upon reaction with CDI (0.4 mmol) & PhSH (0.4 mmol) to afford thioester **4h** (115mg, 80%) as white solid. **mp**-190°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.51-7.35 (m, 15H), 5.41 (s, 1H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 196.7, 138.1, 134.5, 129.6, 129.3, 128.9, 128.8, 127.9, 127.7, 64.9; **IR** (neat, cm^{-1}) = 1712; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{20}H_{16}NaOS$: 327.0820; found 327.0824.

S-butyl benzothioate(6a)



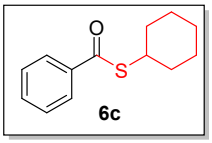
According to the above-mentioned procedure, benzoic acid **1a** (1 equiv, 100 mg) upon reaction with CDI & 1 butane thiol to afford thioester **6a** (138mg, 87%) as white liquid.**^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.88-7.85(m,2H), 7.46-7.41(m,1H), 7.33(dd, J= 8.5, 7.1Hz, 2H), 2.97(t, J= 7.3Hz, 2H). 1.57-1.51(m, 2H), 1.35(h, J= 7.3Hz,2H), .85(t, J= 7.4Hz, 3H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 192.1, 137.2, 133.2, 128.6, 127.2, 31.6, 28.7, 22.1, 13.7; **IR** (neat, cm^{-1}) = 1656; **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{11}H_{15}OS$: 195.0844; found 195.0847.

S-decyl benzothioate(6b)



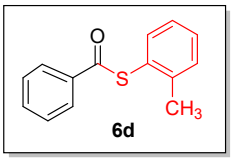
According to the above-mentioned procedure, benzoic acid **1a** (0.8 mmol, 100 mg) upon reaction with CDI (0.8 mmol) & 1 decane thiol (0.8 mmol) to afford thioester **6b** (202mg, 89%) as white liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 8.00-7.98 (m, 2H), 7.59-7.54 (m, 1H), 7.45 (dd, J= 8.4, 7.1 Hz, 1H), 3.09 (t, J= 7.4 Hz, 2H), 1.68 (q, J= 7.5 Hz, 2H), 1.34-1.28 (m, 14H), .90 (t, J= 6.8 Hz, 3H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 192.1, 137.3, 133.2, 128.5, 127.2, 31.9, 29.7, 29.7, 29.6, 29.5, 29.5, 29.3, 29.2, 29.1, 29.0, 22.7, 14.2; **IR** (neat, cm^{-1}) = 1658; **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{17}H_{27}OS$: 279.1783; found 279.1787.

S-cyclohexyl benzothioate(6c)



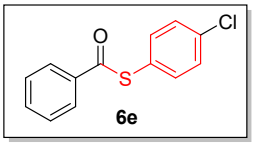
According to the above-mentioned procedure, benzoic acid **1a** (0.8 mmol, 100 mg) upon reaction with CDI (0.8 mmol) & cyclohexane thiol (0.8 mmol) to afford thioester **6c** (154mg, 86%) as white liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.98-7.96 (m, 2H), 7.57-7.53 (m, 1H), 7.44 (dd, *J*= 8.4, 7.0 Hz, 2H), 3.75 (tt, *J*= 10.1, 3.9 Hz, 1H), 2.06-2.02 (m, 2H), 1.79-1.74 (m, 2H), 1.65-1.62 (m, 1H), 1.55-1.45 (m, 4H), 1.38-1.28 (m, 1H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 191.8, 137.4, 133.2, 128.5, 127.2, 42.5, 33.2, 26.1, 25.6; **IR** (neat, cm^{-1}) = 1660; **HRMS** (ESI) m/z $(M+H)^+$ calculated for $C_{13}H_{17}OS$: 221.1000; found 221.1004.

S-(o-tolyl) benzothioate(6d)



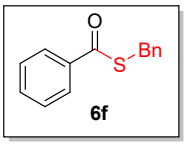
According to the above-mentioned procedure, benzoic acid **1a** (0.8 mmol, 100 mg) upon reaction with CDI (0.8 mmol) & 2-methyl thiol (0.8 mmol) to afford thioester 6d (175mg, 94%) as white liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 8.16-8.14 (m, 2H), 7.69-7.65 (m, 1H), 7.60-7.53 (m, 3H), 7.46-7.43 (m, 2H), 7.37-7.33 (m, 1H), 2.50 (s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 189.7, 142.7, 136.8, 136.5, 133.7, 130.9, 130.4, 128.8, 127.6, 126.8, 126.7, 20.9; **IR** (neat, cm^{-1}) = 1662; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{14}H_{12}NaOS$: 251.0507; found 251.0510.

S-(4-chlorophenyl) benzothioate(6e)



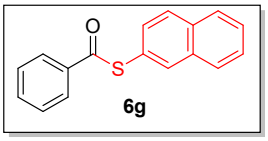
According to the above-mentioned procedure, benzoic acid **1a** (0.8 mmol, 100 mg) upon reaction with CDI (0.8 mmol) & 4-chloro thiol (0.8 mmol) to afford thioester **6e** (194 mg, 96%) as white solid. **mp**-142°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 8.07-8.04 (m, 2H), 7.68-7.60 (m, 1H), 7.53-7.46 (m, 6H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 189.5, 136.4, 136.3, 136.0, 133.9, 129.5, 128.9, 127.6, 125.9; **IR** (neat, cm^{-1})= 1661; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{13}H_9ClNaOS$: 270.9960; found 270.9963.

S-benzyl benzothioate(6f)



According to the above-mentioned procedure, benzoic acid **1a** (0.8 mmol, 100 mg) upon reaction with CDI (0.8 mmol) & benzyl thiol (0.8 mmol) to afford thioester **6f** (175 mg, 92%) as white liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 8.03-8.01 (m, 2H), 7.62-7.58 (m, 1H), 7.50-7.34 (m, 7H), 4.37 (s, 2H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 191.4, 137.5, 136.7, 133.5, 129.0, 128.6, 128.7, 127.4, 127.4, 33.4; **IR** (neat, cm^{-1}) = 1654; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{14}H_{12}NaOS$: 251.0507; found 251.0511.

S-(naphthalen-2-yl) benzothioate(6g)



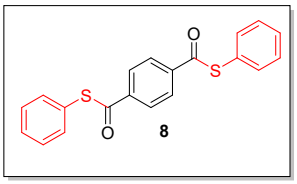
According to the above-mentioned procedure, benzoic acid **1a** (0.8 mmol, 100 mg) upon reaction with CDI (0.8 mmol) & 2-napthiol (0.8 mmol) to afford thioester **6g** (200 mg, 93%) as white solid. **mp**-191°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 8.10 (dt, *J*= 7.1Hz, 1.4 Hz, 3H), 7.96-7.87 (m, 3H), 7.65 (d, *J*= 7.4 Hz, 1H), 7.60-7.51 (m, 5H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 190.4, 136.6, 135.0, 133.7, 133.6, 133.5, 131.4, 128.9, 128.8, 128.0, 127.8, 127.5, 127.2, 126.5, 124.7; **IR** (neat, cm^{-1}) = 1663; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{17}H_{12}NaOS$: 287.0507; found 287.0511.

5. General Procedure for the synthesis of thioester 8:

Dry CH_3CN (3ml) solution of Terephthalic acid **7**(0.6 mmol, 100mg) and CDI (1.2 mmol) was taken in a 50 ml dry round bottom flask fitted with magnetic stir bar under N_2 atmosphere. Then PhSH (1.2 mmol) was added into this mixture. The mixture was stirred at room temperature for 30min. After the total consumption of the starting material **7** as shown by TLC, the mixture was evaporated under reduced pressure & then the reaction mixture was quenched by ethyl acetate followed by water. The combined organic layer was separated, washed with brine solution (twice) and collected over anhydrous sodium sulphate.

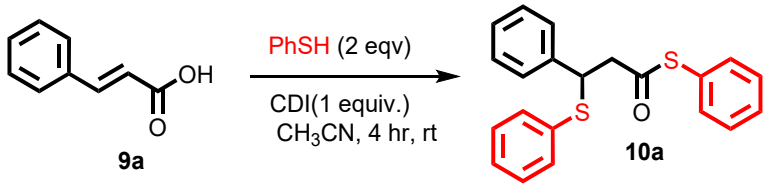
The concentrated organic solution was then loaded on a 100-200 mesh column of silica gel & eluted with hexane: ethyl acetate (95:5) to get purified thioester **8**(183 mg, 87%) as white solid.

S,S-diphenyl benzene-1,4-bis(carbothioate)(8)



mp-302°C; 1H NMR (400 MHz, $CDCl_3$) δ= 8.16 (s, 4H), 7.57-7.53 (m, 4H), 7.52-7.50 (m, 6H); 13C NMR (100MHz, $CDCl_3$) δ= 189.5, 140.4, 135.0, 129.8, 129.4, 127.8, 126.6; IR (neat, cm^{-1}) = 1665; HRMS (ESI) m/z $(M+Na)^+$ calculated for $C_{20}H_{14}NaO_2S_2$: 373.0333; found 373.0336.

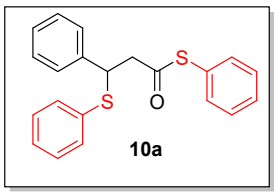
6. General Procedure for the synthesis of thioester 10a:



Dry CH_3CN (3ml) solution of Cinnamic acid **9a** (0.6 mmol, 100mg) and CDI (0.6 mmol) was taken in a 50 ml dry round bottom flask fitted with magnetic stir bar under N_2 atmosphere. Then PhSH (1.34 mmol) was added into this mixture. The mixture was stirred at room temperature for 4 hr. After the total consumption of the starting material **9a** as shown by TLC, the mixture was evaporated under reduced pressure & then the reaction mixture was quenched by ethyl acetate followed by water. The combined organic layer was separated, washed with brine solution (twice) and collected over anhydrous sodium sulphate.

The concentrated organic solution was then loaded on a 100-200 mesh column of silica gel & eluted with hexane: ethyl acetate (98:2) to get purified thioester **10a** (204 mg, 86%) as white solid.

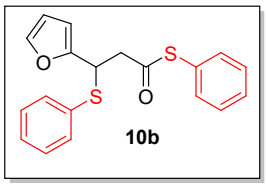
S-phenyl 3-phenyl-3-(phenylthio)propanethioate(10a)



mp-235°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.42-7.36 (m, 5H), 7.34-7.25 (m, 10H), 4.79 (t, *J*= 7.6 Hz, 1H), 3.30 (d, *J*= 7.6 Hz, 2H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 194.7, 139.9, 134.4, 133.6, 133.2, 129.5,129.2, 128.9, 128.6, 127.8, 127.8, 127.7, 127.3, 49.4, 49.2; **IR** (neat, cm^{-1}) = 1710; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{21}H_{18}NaOS_2$: 373.0697; found 373.0699.

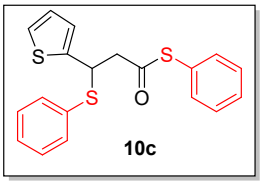
7. Characterization data of thioester 10b-10f

S-phenyl 3-(furan-2-yl)-3-(phenylthio)propanethioate(10b)



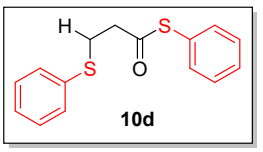
According to the above-mentioned procedure, alpha beta unsaturated acid **9b** (0.7 mmol, 100 mg) upon reaction with CDI (0.7 mmol) & thiophenol (1.44 mmol) to afford thioester **10b** (201 mg, 82%) as yellowish liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.42 (tt, *J*= 5.2, 2.6 Hz, 6H), 7.38-7.35(m,2H), 7.31(dd, *J*=5.3,1.9 Hz, 3H), 6.29(dd, *J*= 3.3, 1.9 Hz, 1H), 6.06 (d, *J*= 3.3 Hz, 1H), 4.81 (t, *J*= 7.5 Hz, 1H), 3.36-3.20 (m, 2H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 194.3, 152.3, 142.3, 134.4, 134.2, 132.5, 129.6, 129.3, 128.9, 128.3, 127.2, 110.3, 107.7, 46.8, 42.5; **IR** (neat, cm^{-1}) = 1701; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{19}H_{16}NaO_2S_2$: 363.0489; found 363.0493.

S-phenyl 3-(phenylthio)-3-(thiophen-2-yl)propanethioate(10c)



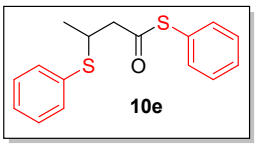
According to the above-mentioned procedure, alpha beta unsaturated acid **9c** (0.6 mmol, 100 mg) upon reaction with CDI (0.6 mmol) & thiophenol (1.29 mmol) to afford thioester **10c** (195 mg, 84%) as brownish liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.44 (ddt, *J*= 8.2, 5.4, 2.7 Hz, 7H), 7.35-7.32 (m, 3H), 7.26 (dd, *J*= 5.0, 1.3 Hz, 1H), 6.93-6.89 (m, 2H), 5.12 (t, *J*= 7.4 Hz, 1H), 3.36 (d, *J*= 7.4 Hz, 2H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 194.3, 144.1, 134.5, 133.5, 133.3, 129.7, 129.3, 129.1, 128.3, 127.3, 126.7, 125.8, 125.1, 50.4, 44.6; **IR** (neat, cm^{-1}) = 1700; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{19}H_{16}NaOS_3$: 379.0261; found 379.0265.

S-phenyl 3-(phenylthio)propanethioate(10d)



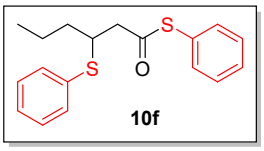
According to the above-mentioned procedure, alpha beta unsaturated acid **9d** (1.38 mmol, 100 mg) upon reaction with CDI (1.38 mmol) & thiophenol (2.77 mmol) to afford thioester **10d** (295 mg, 78%) as white liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.45-7.39 (m, 7H), 7.34 (t, *J*= 7.5 Hz, 2H), 7.26 (td, *J*= 6.5, 2.9 Hz, 1H), 3.25 (dd, *J*= 8.1, 6.8 Hz, 2H), 2.98 (dd, *J*= 8.1, 6.8 Hz, 2H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 195.8, 134.9, 134.5, 130.2, 129.5, 129.2, 129.1, 127.2, 126.7, 43.2, 29.2; **IR** (neat, cm^{-1}) = 1701; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{15}H_{14}NaOS_2$: 297.0384; found 297.0388.

S-phenyl 3-(phenylthio)butanethioate(10e)



According to the above-mentioned procedure, alpha beta unsaturated acid **9e** (1.16 mmol, 100 mg) upon reaction with CDI (1.16 mmol) & thiophenol (2.32 mmol) to afford thioester **10e** (267 mg, 80%) as white liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.50-7.47 (m, 2H), 7.46-7.40 (m, 5H), 7.38-7.31 (m, 3H), 3.76 (ddd, *J*= 8.8, 6.8, 5.3 Hz, 1H), 3.03-2.76 (m, 2H), 1.41 (d, *J*= 6.8 Hz, 3H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 195.5, 134.5, 133.6, 132.7, 129.5, 129.3, 129.1, 127.5, 127.4, 50.3, 39.7, 20.6; **IR** (neat, cm^{-1}) = 1703; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{16}H_{16}NaOS_2$: 311.0540; found 311.0544.

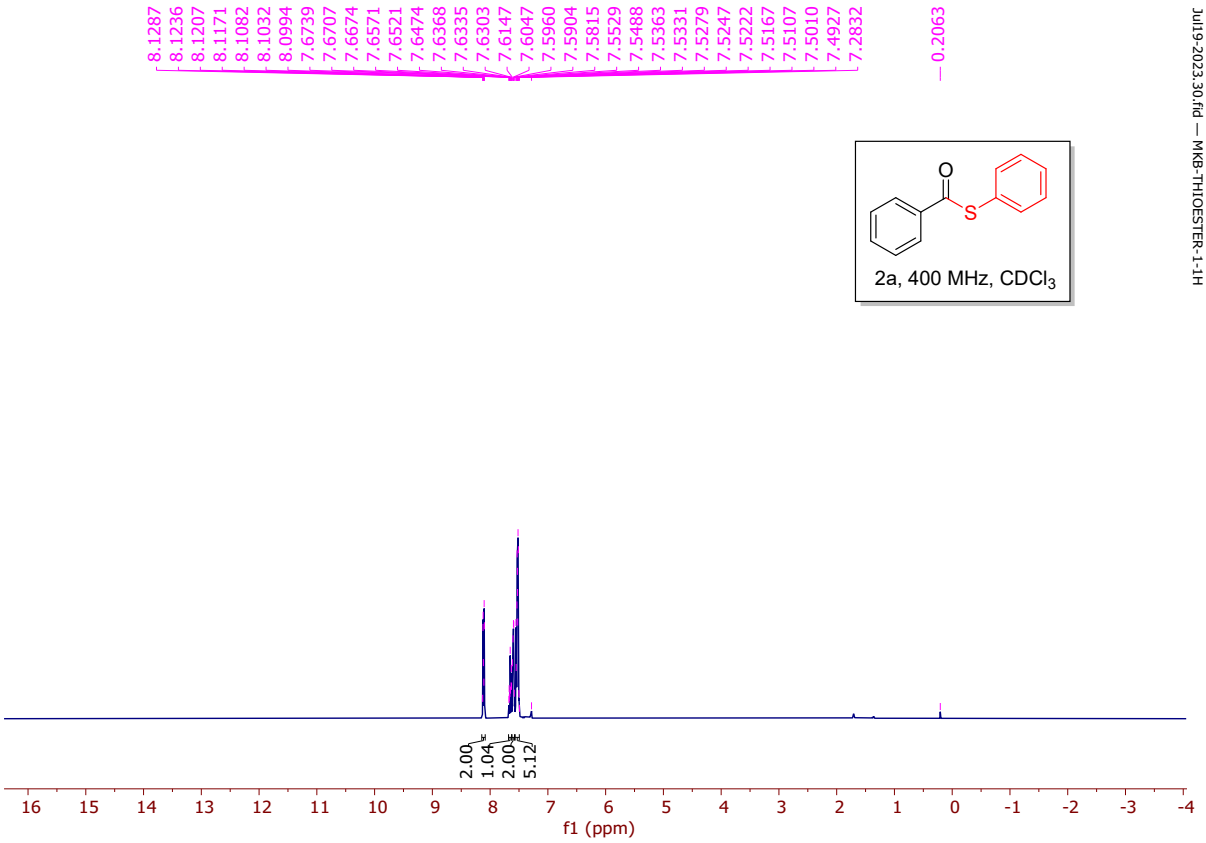
S-phenyl 3-(phenylthio)hexanethioate(10f)

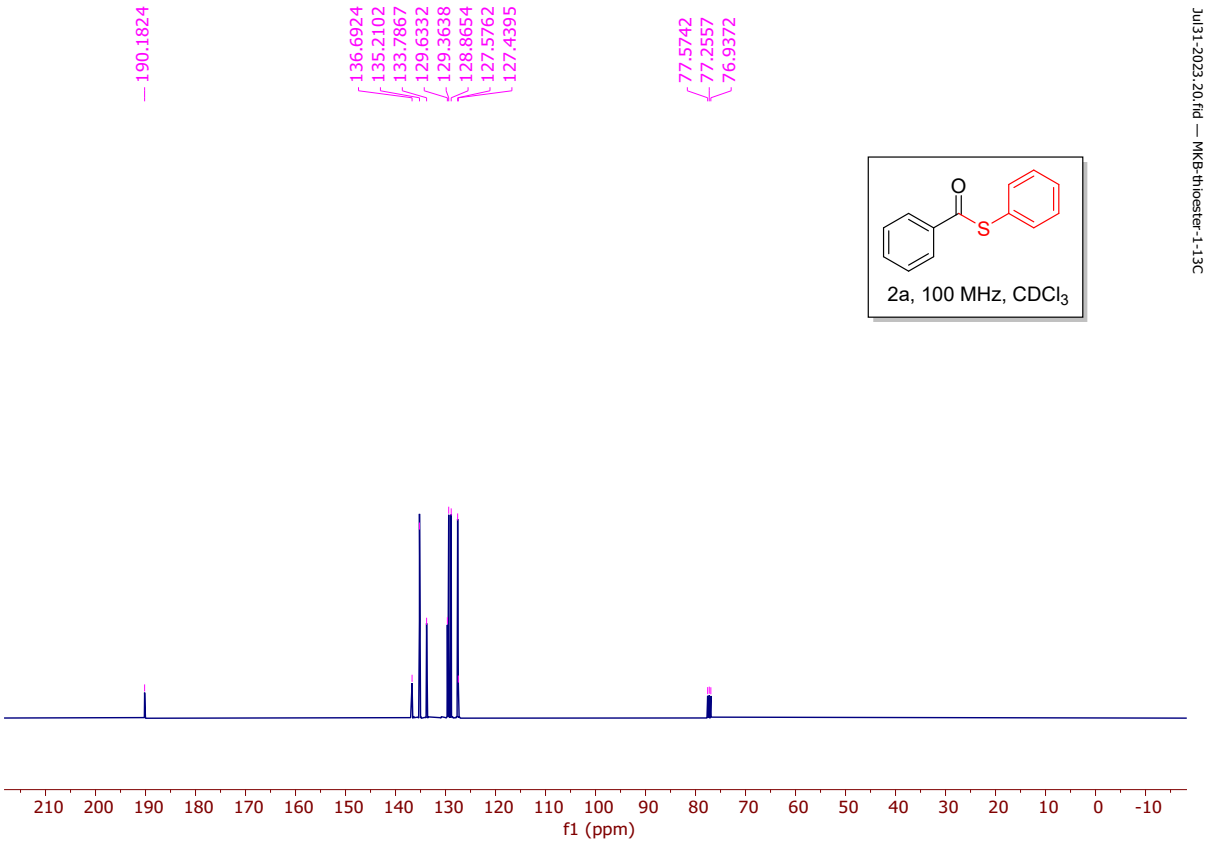


According to the above-mentioned procedure, alpha beta unsaturated acid **9f** (0.8 mmol, 100 mg) upon reaction with CDI (0.8 mmol) & thiophenol (1.75 mmol) to afford thioester **10f** (224 mg, 81%) as white liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ= 7.47 (dt, *J*= 7.3, 1.4 Hz, 2H), 7.44-7.39 (m, 5H), 7.39-7.28 (m, 3H), 2.99-2.84 (m, 2H), 1.69-1.50 (m, 5H), .95 (t, *J*= 7.0 Hz, 3H); **^{13}C NMR** (100MHz, $CDCl_3$) δ= 195.6, 135.1, 134.4, 133.9, 132.6, 129.5, 129.3, 129.0, 127.4, 49.1, 44.8, 36.5, 20.1, 13.7; **IR** (neat, cm^{-1}) = 1705; **HRMS** (ESI) m/z $(M+Na)^+$ calculated for $C_{18}H_{20}NaOS_2$: 339.0853; found 339.0857.

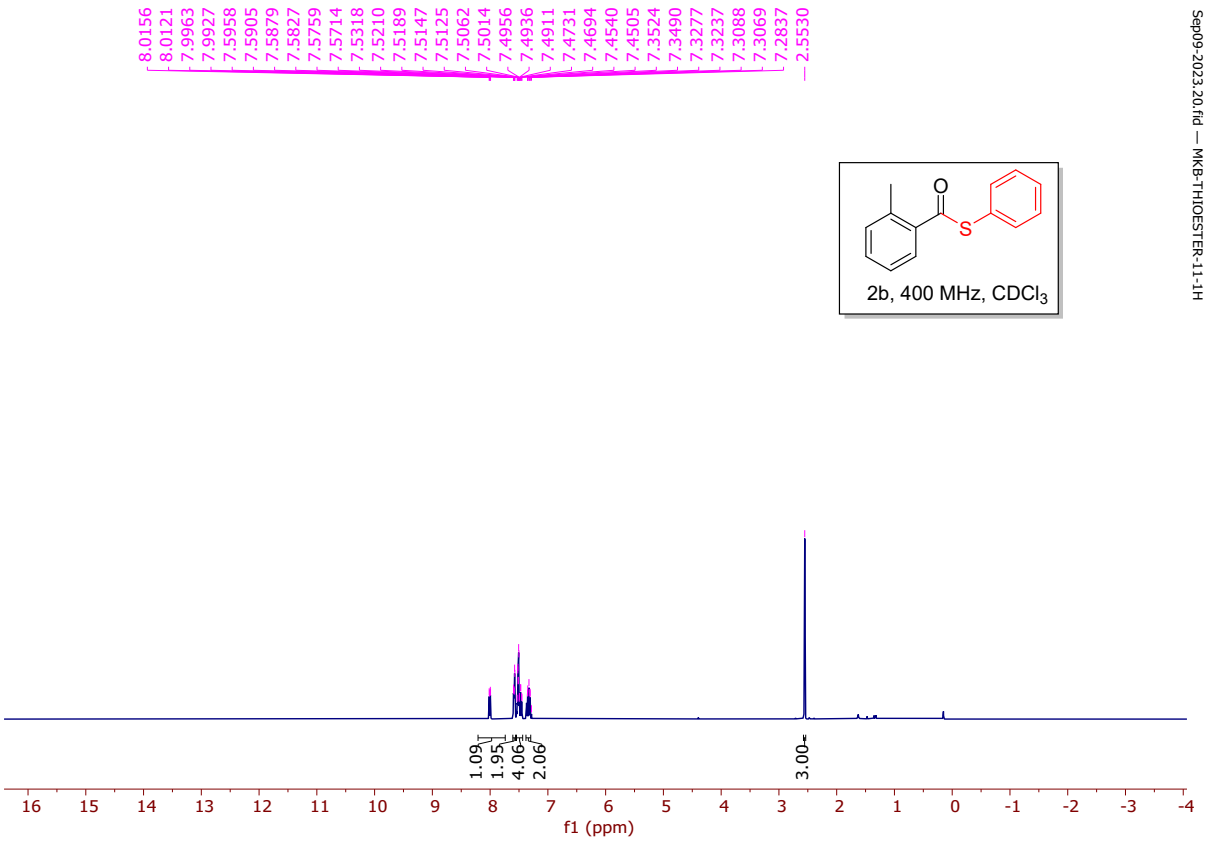
8. Copies of ^{1}H & ^{13}C NMR:

2a - ^{1}H & ^{13}C NMR





2b - ^{1}H & ^{13}C NMR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7.9963
7.9927
7.5958
7.5905
7.5879
7.5827
7.5759
7.5714
7.5318
7.5210
7.5189
7.5147
7.5125
7.5062
7.5014
7.4956
7.4936
7.4911
7.4731
7.4694
7.4540
7.4505
7.3524
7.3490
7.3277
7.3237
7.3088
7.3069
7.2837
2.5530
Sep09-2023.20.fid — MKB-THIOESTER-11-1H
2b, 400 MHz, CDCl3
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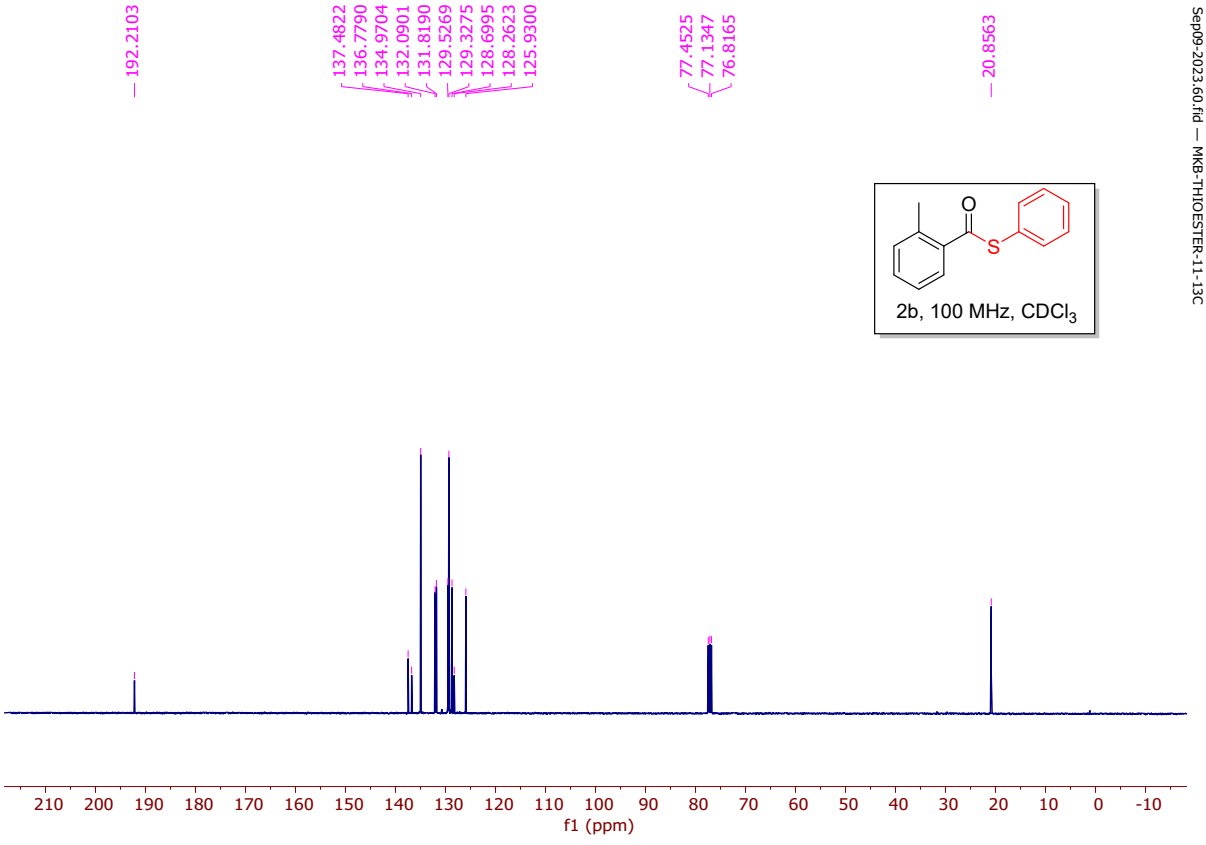
1.95
4.06
2.06
3.00
f1 (ppm)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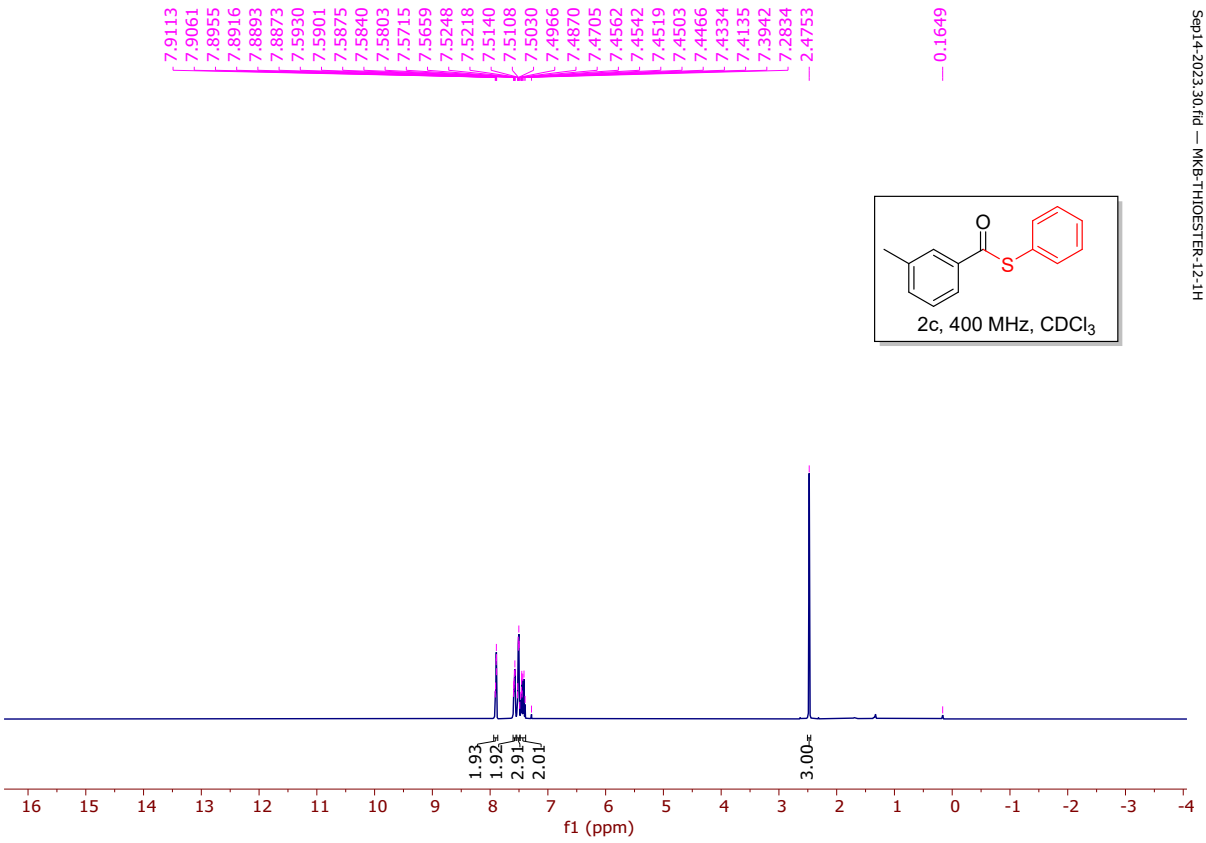
137.4822
136.7790
134.9704
132.0901
131.8190
129.5269
129.3275
128.6995
128.2623
125.9300
77.4525
77.1347
76.8165
20.8563
Sep09-2023.60.fid — MKB-THIOESTER-11-13C
2b, 100 MHz, CDCl3
f1 (ppm)

2c - ^{1}H & ^{13}C NMR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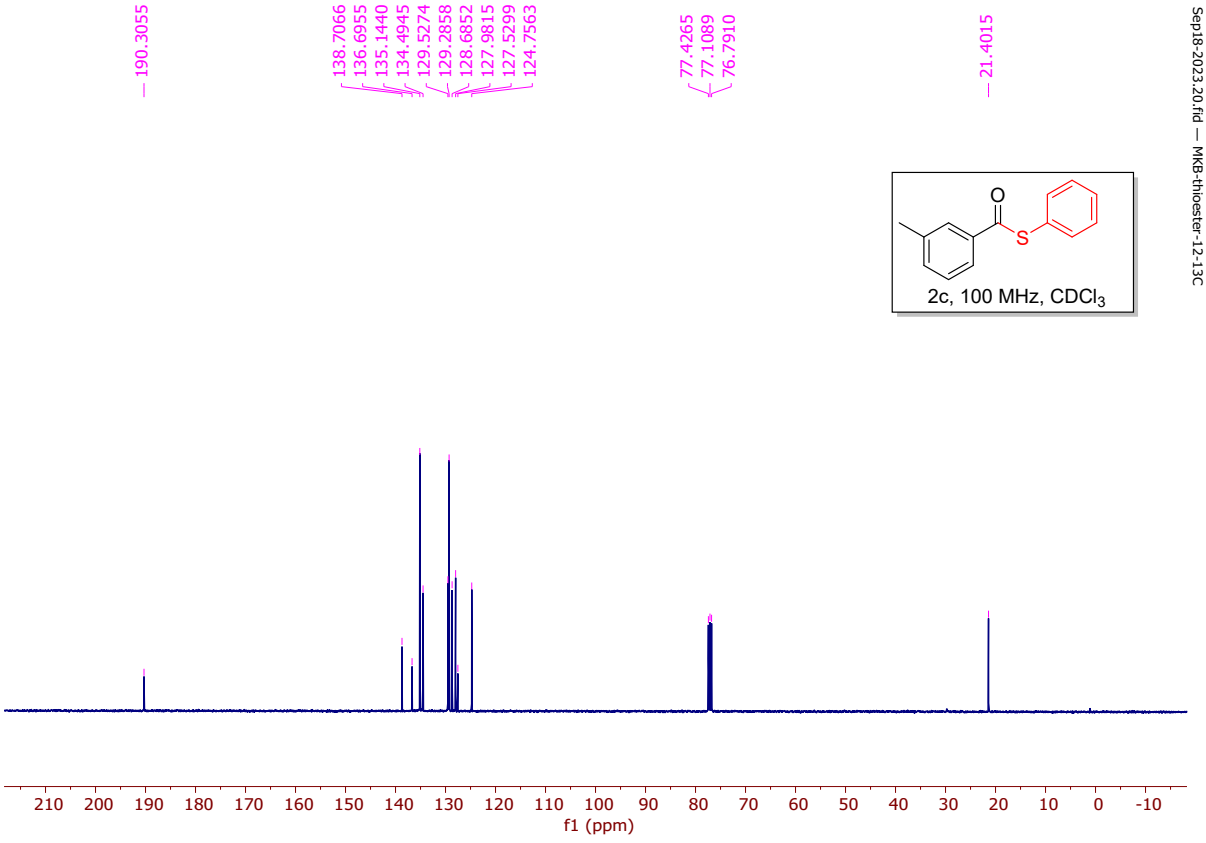
7.9061
7.8955
7.8916
7.8893
7.8873
7.5930
7.5901
7.5875
7.5840
7.5803
7.5715
7.5659
7.5248
7.5218
7.5140
7.5108
7.5030
7.4966
7.4870
7.4705
7.4562
7.4542
7.4519
7.4503
7.4466
7.4334
7.4135
7.3942
7.2834
2.4753
0.1649
Sep14-2023.30.fid — MKB-THIOESTER-12-1H
O
S
2c, 400 MHz, CDCl3
1.93
1.92
2.91
2.01
3.00
f1 (ppm)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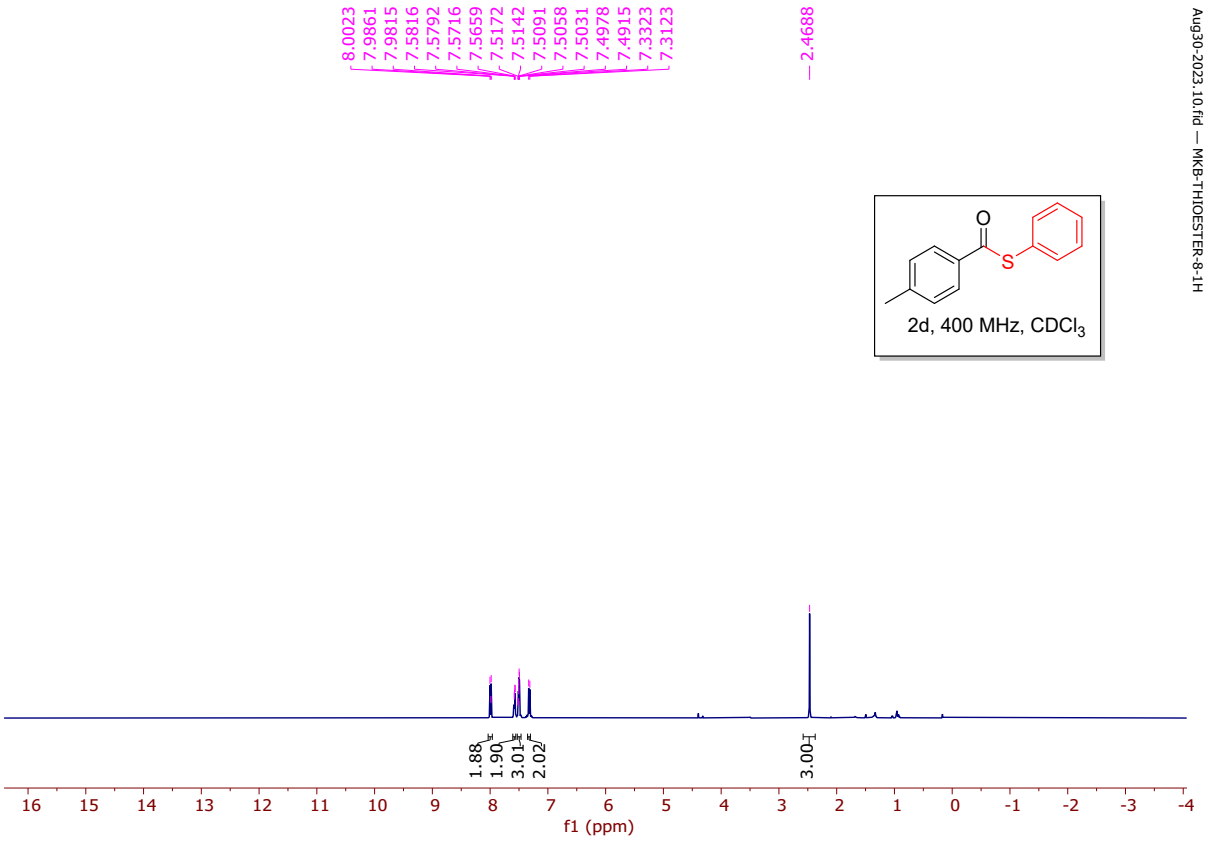
138.7066
136.6955
135.1440
134.4945
129.5274
129.2858
128.6852
127.9815
127.5299
124.7563
77.4265
77.1089
76.7910
21.4015
Sep18-2023.20.fid — MKB-thioester-12-13C
O
S
2c, 100 MHz, CDCl3
f1 (ppm)

2d - ^{1}H & ^{13}C NMR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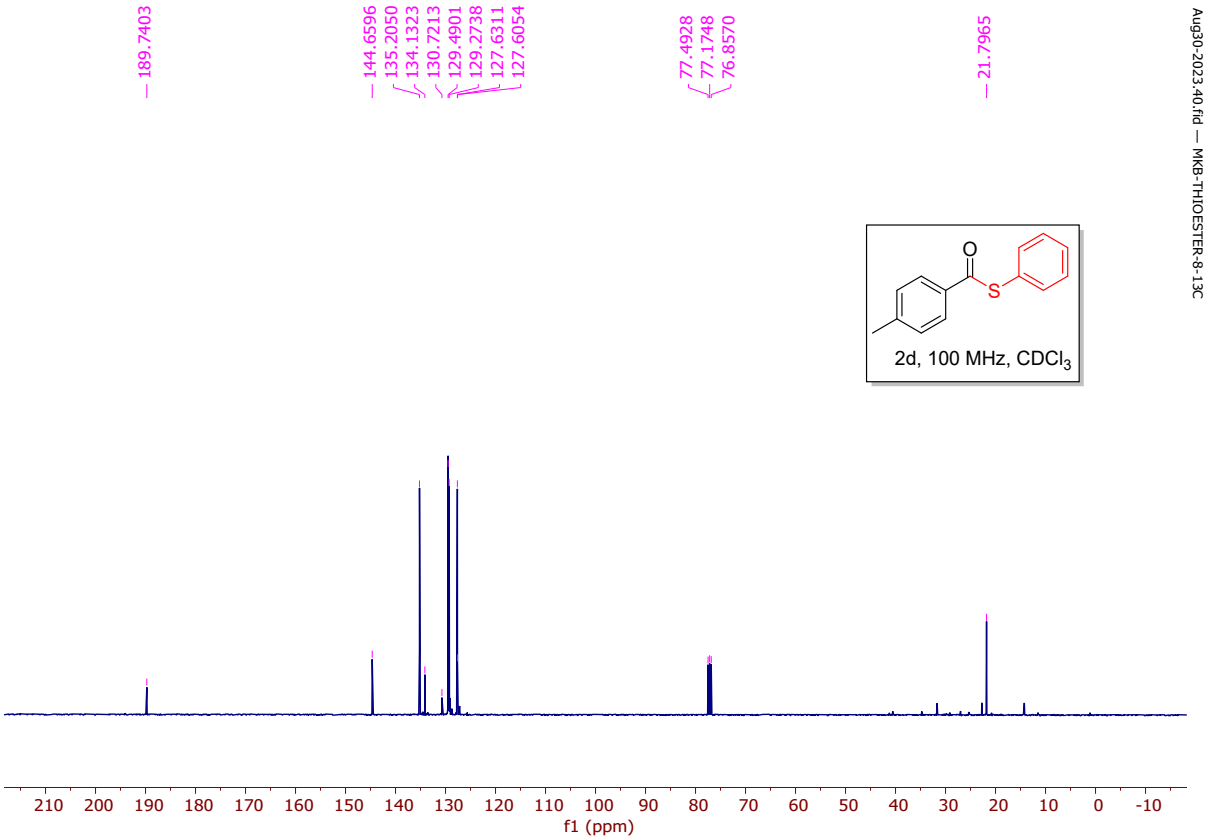
7.9815
7.5816
7.5792
7.5716
7.5659
7.5172
7.5142
7.5091
7.5058
7.5031
7.4978
7.4915
7.3323
7.3123
2.4688
Aug30-2023.10.fid — MKB-THIOESTER-8-1H
O
S
2d, 400 MHz, CDCl3
1.88
1.90
3.01
2.02
3.00
f1 (ppm)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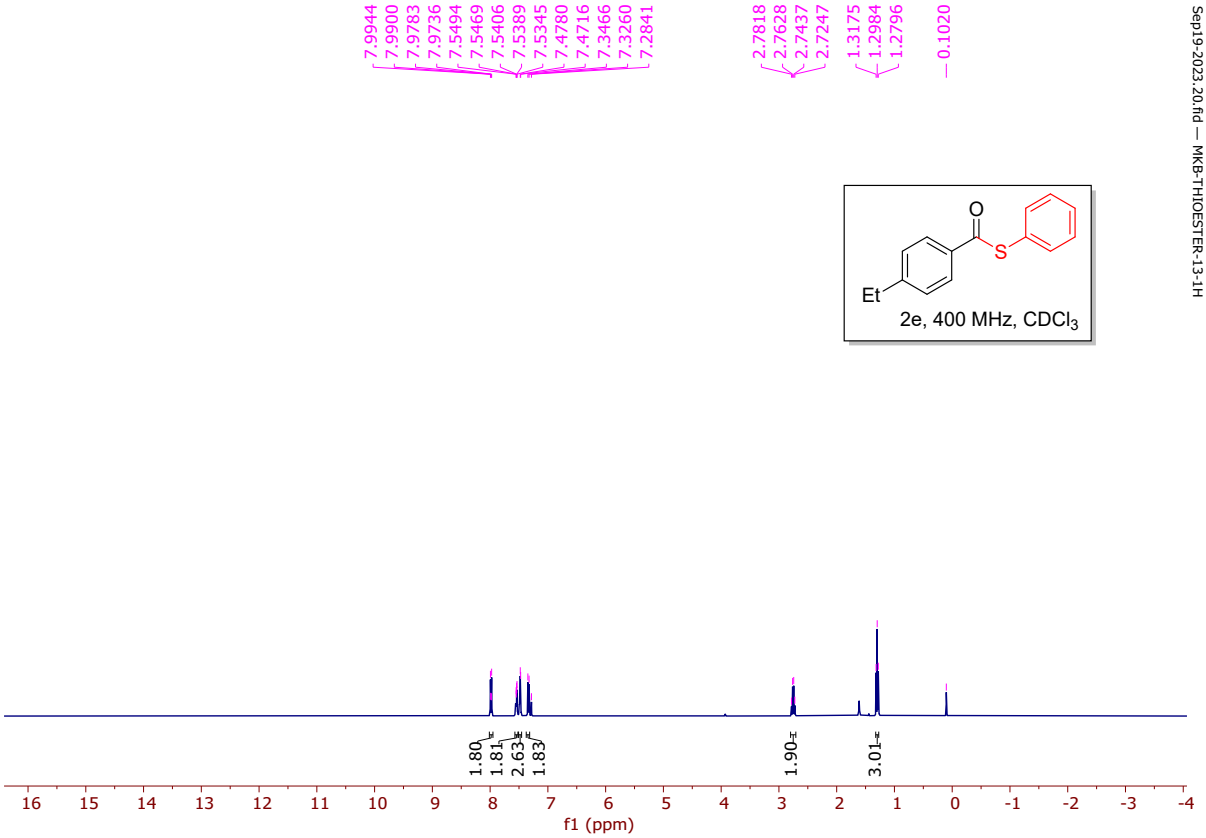
144.6596
135.2050
134.1323
130.7213
129.4901
129.2738
127.6311
127.6054
77.4928
77.1748
76.8570
21.7965
Aug30-2023.40.fid — MKB-THIOESTER-8-13C
O
S
2d, 100 MHz, CDCl3
f1 (ppm)

2e - ^{1}H & ^{13}C NMR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7.9783
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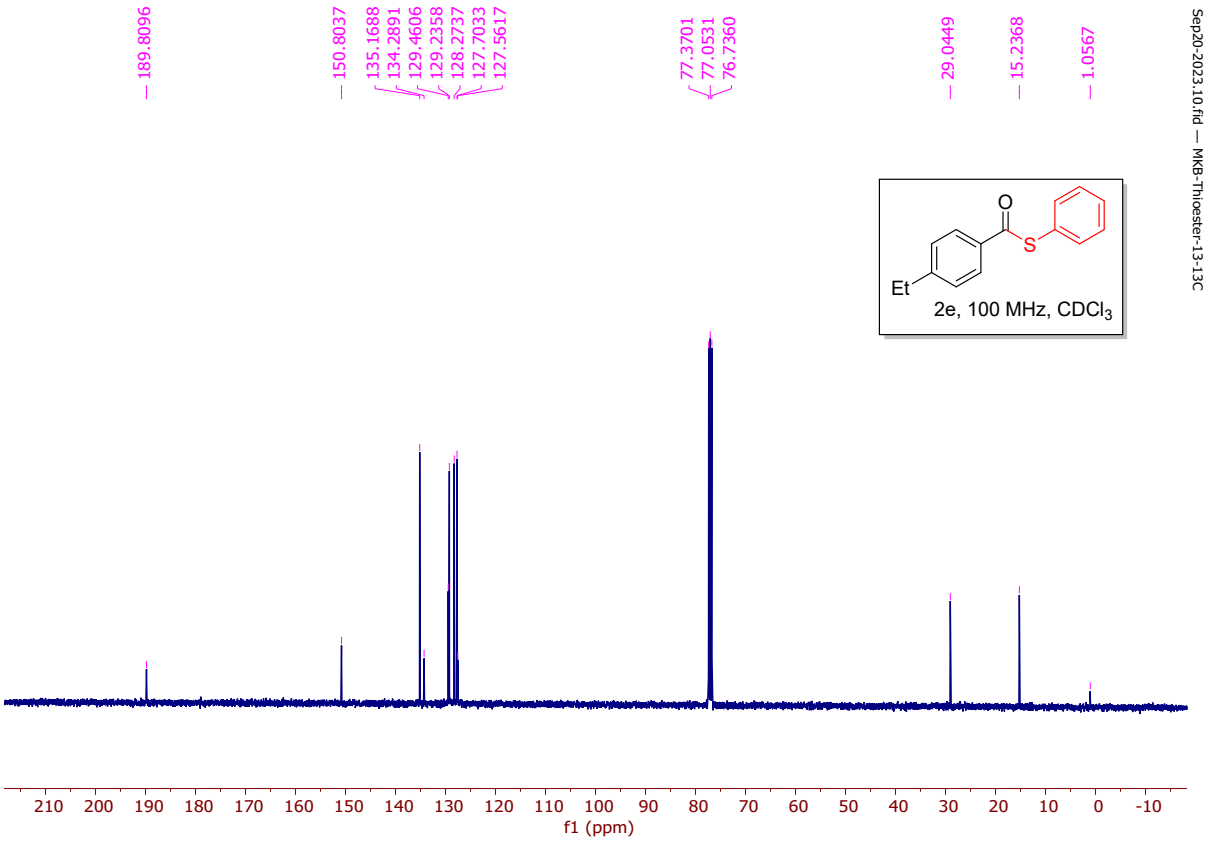
7.5494
7.5469
7.5406
7.5389
7.5345
7.4780
7.4716
7.3466
7.3260
7.2841
2.7818
2.7628
2.7437
2.7247
1.3175
1.2984
1.2796
0.1020
Sep19-2023.20.fid — MKB-THIOESTER-13-1H
O
S
Et
2e, 400 MHz, CDCl3
1.80
1.81
2.63
1.83
1.90
3.01
f1 (ppm)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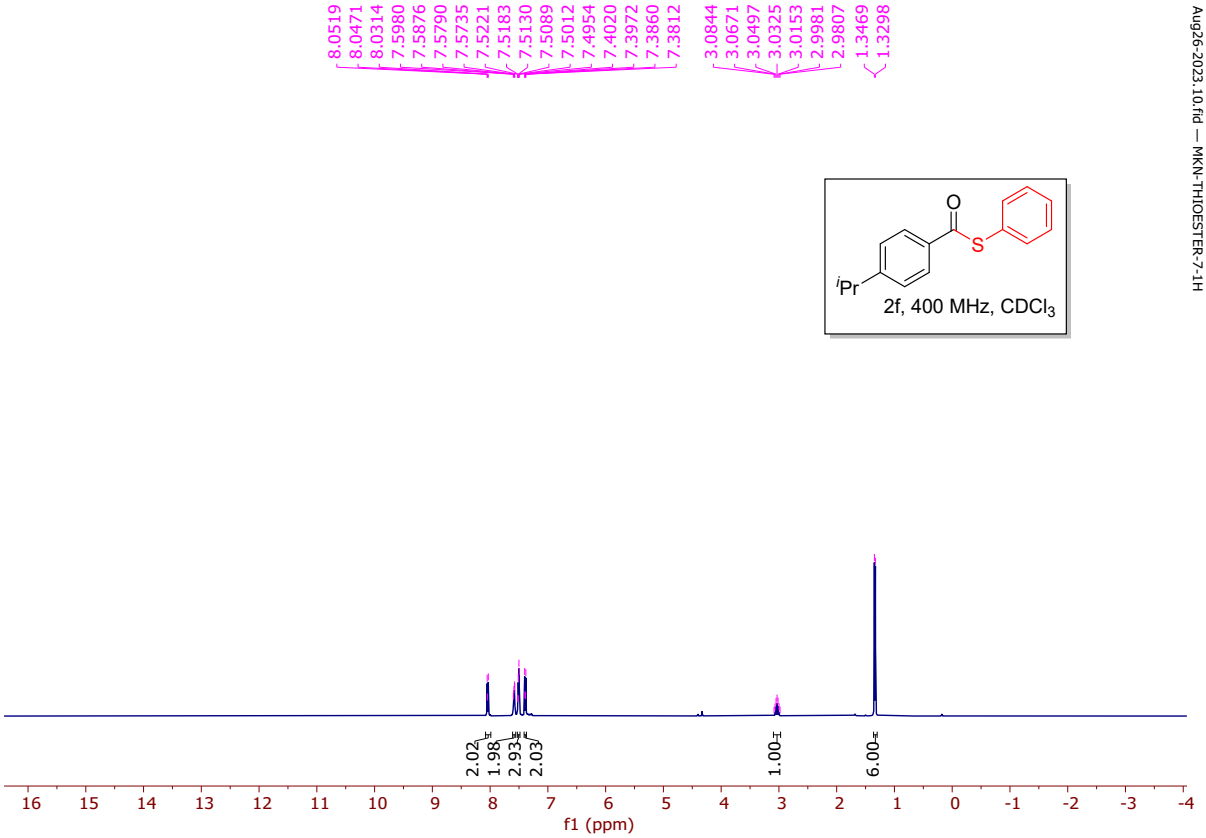
150.8037
135.1688
134.2891
129.4606
129.2358
128.2737
127.7033
127.5617
77.3701
77.0531
76.7360
29.0449
15.2368
1.0567
Sep20-2023.10.fid — MKB-Thioester-13-13C
O
S
Et
2e, 100 MHz, CDCl3
f1 (ppm)

2f - ^{1}H & ^{13}C NMR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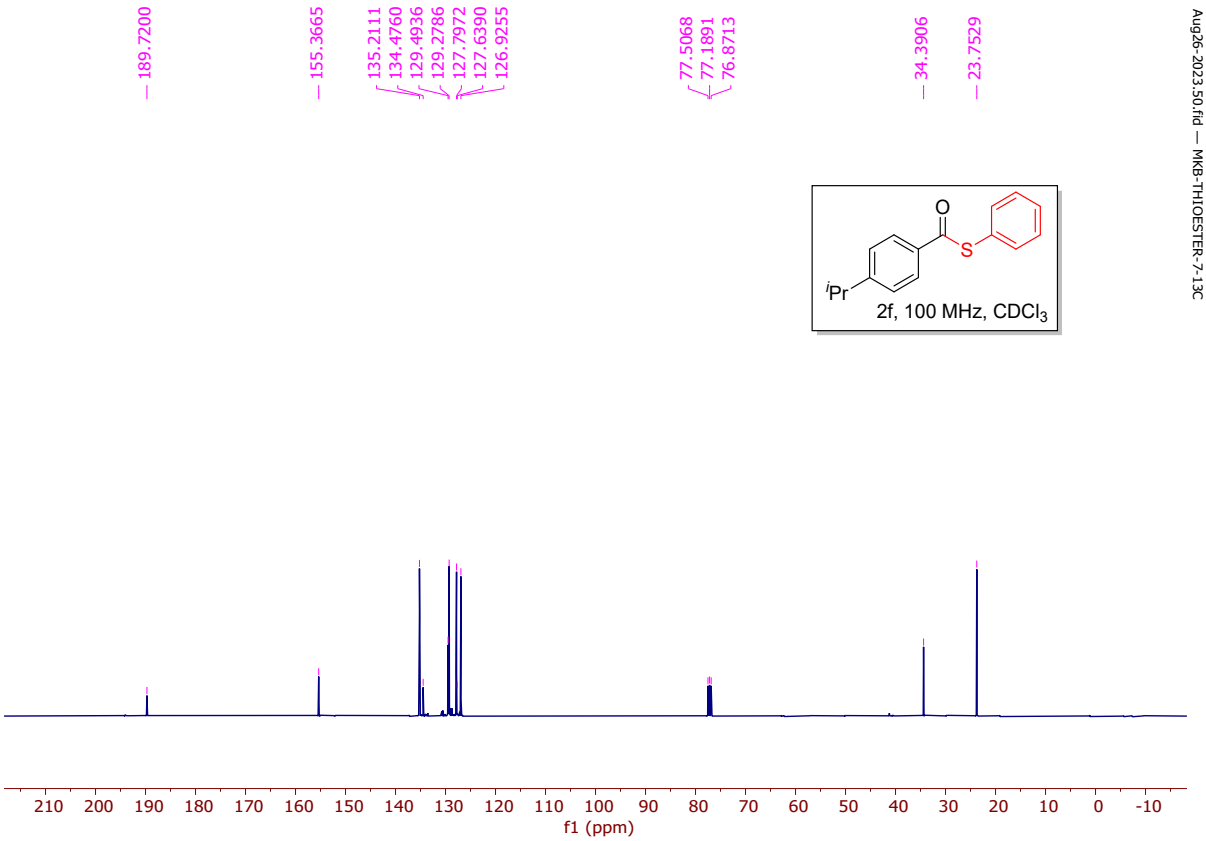
8.0314
7.5980
7.5876
7.5790
7.5735
7.5221
7.5183
7.5130
7.5089
7.5012
7.4954
7.4020
7.3972
7.3860
7.3812
3.0844
3.0671
3.0497
3.0325
3.0153
2.9981
2.9807
1.3469
1.3298
Aug26-2023.10.fid — MKN-THIOESTER-7-1H
O
S
iPr
2f, 400 MHz, CDCl3
2.02
1.98
2.93
2.03
1.00
6.00
f1 (ppm)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135.2111
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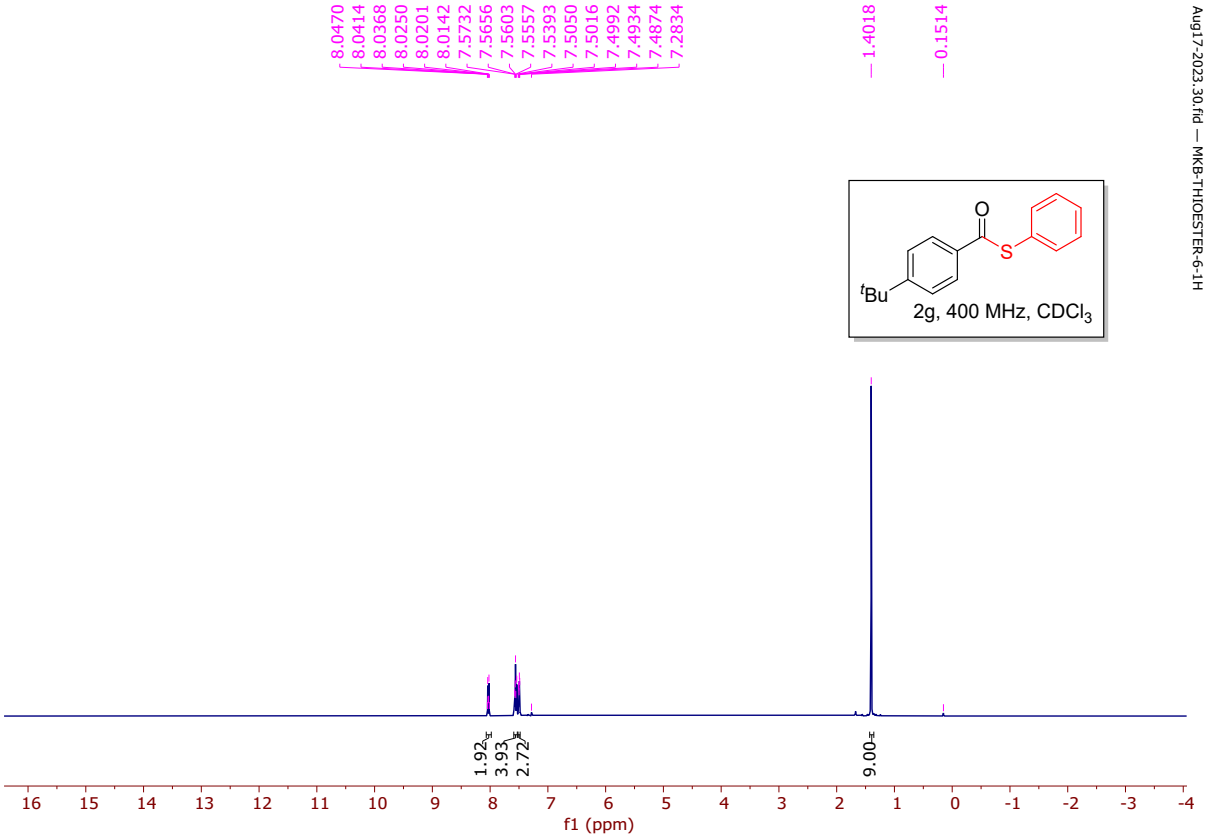
127.7972
127.6390
126.9255
77.5068
77.1891
76.8713
34.3906
23.7529
Aug26-2023.50.fid — MKB-THIOESTER-7-13C
O
S
iPr
2f, 100 MHz, CDCl3
f1 (ppm)

2g - ^{1}H & ^{13}C NMR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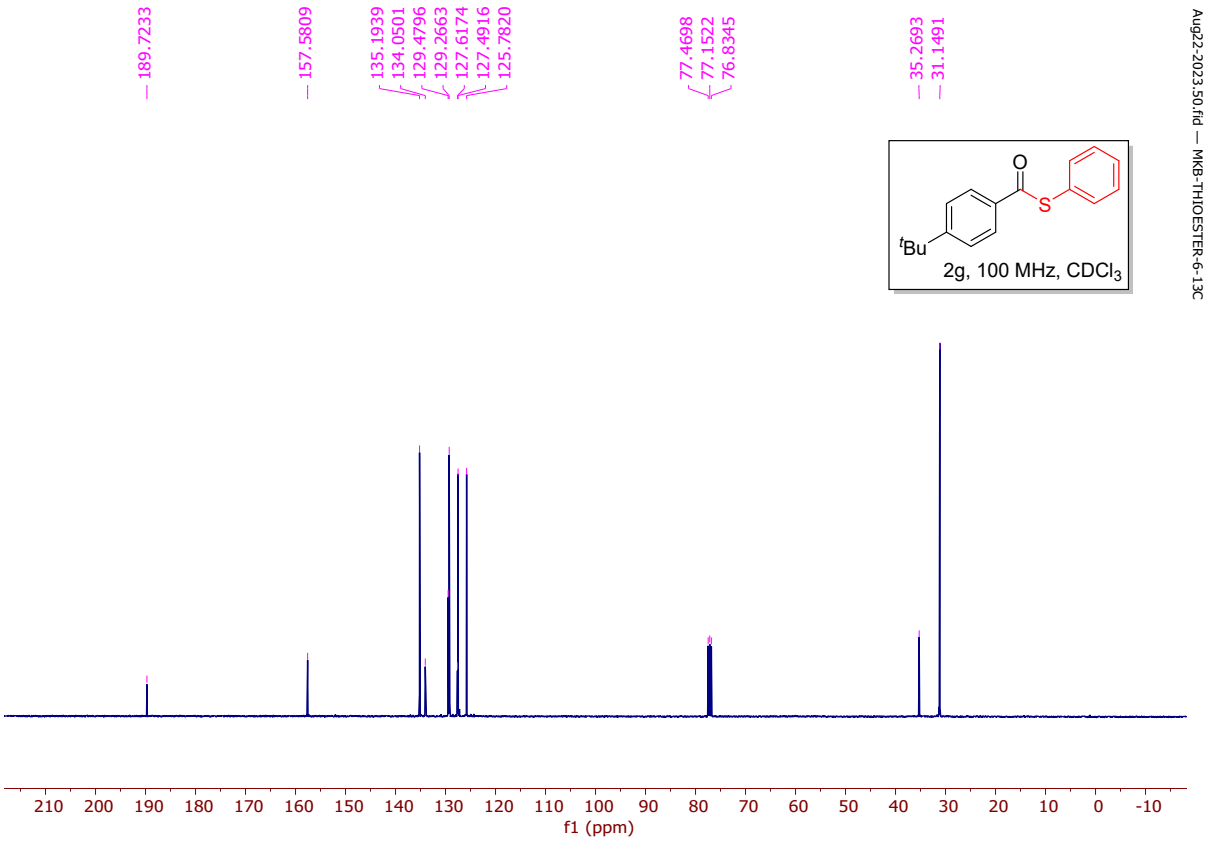
8.0414
8.0368
8.0250
8.0201
8.0142
7.5732
7.5656
7.5603
7.5557
7.5393
7.5050
7.5016
7.4992
7.4934
7.4874
7.2834
1.4018
0.1514
Aug17-2023.30.fid — MKB-THIOESTER-6-1H
2g, 400 MHz, CDCl3
1.92
3.93
2.72
9.00
f1 (ppm)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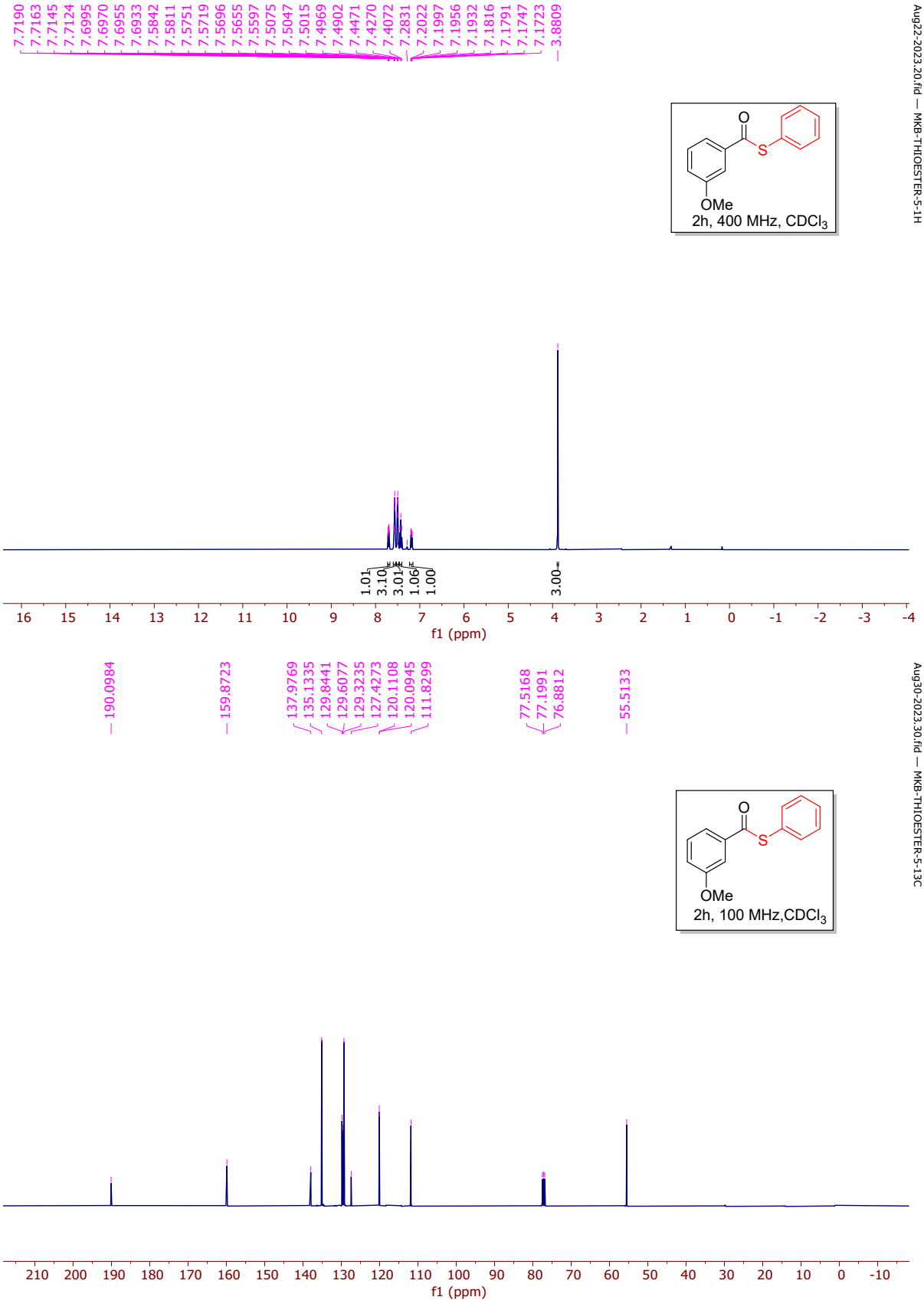
135.1939
134.0501
129.4796
129.2663
127.6174
127.4916
125.7820
77.4698
77.1522
76.8345
35.2693
31.1491
Aug22-2023.50.fid — MKB-THIOESTER-6-13C
2g, 100 MHz, CDCl3
f1 (ppm)

2h - ^{1}H & ^{13}C NMR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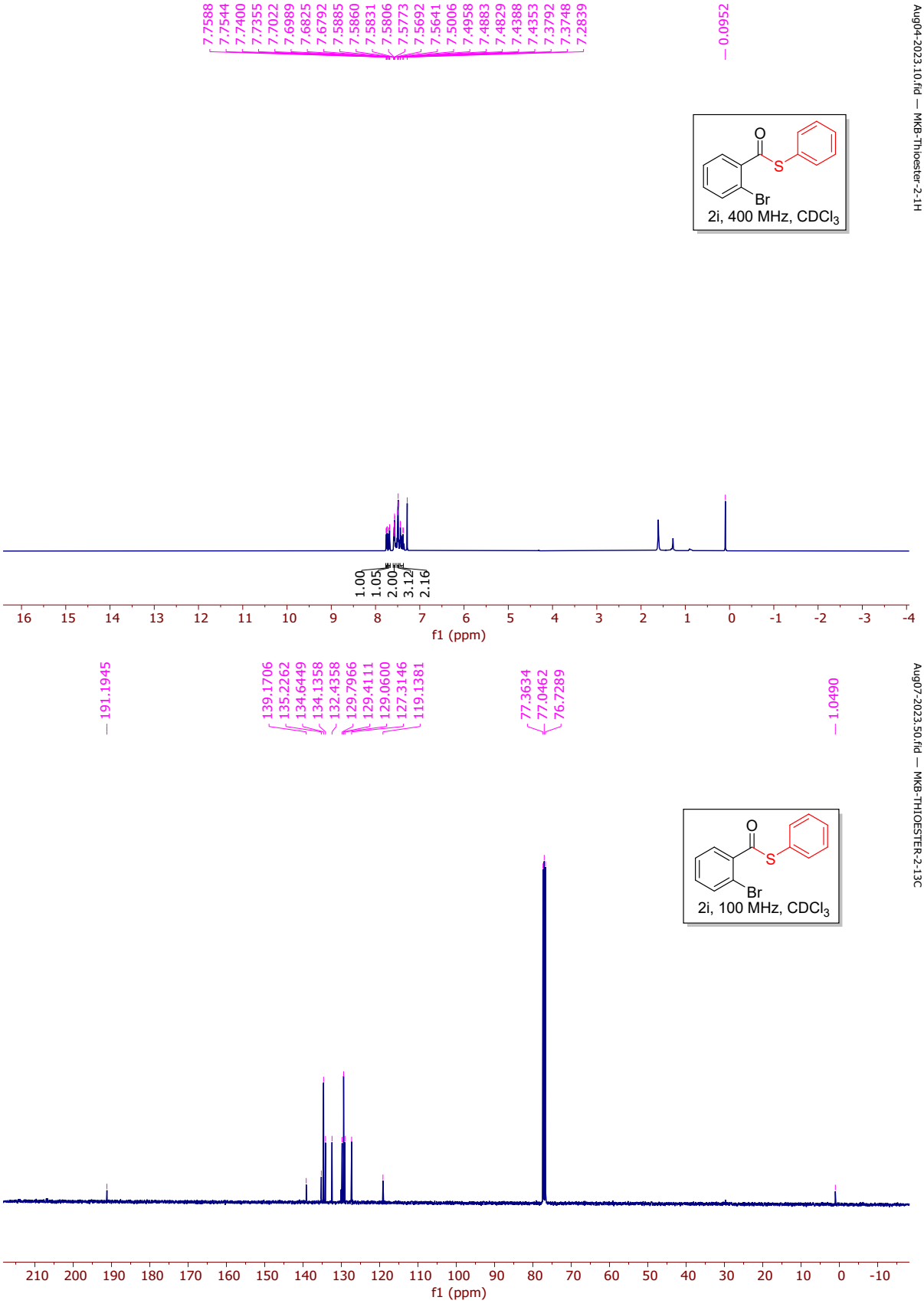
7.7145
7.7124
7.6995
7.6970
7.6955
7.6933
7.5842
7.5811
7.5751
7.5719
7.5696
7.5655
7.5597
7.5075
7.5047
7.5015
7.4969
7.4902
7.4471
7.4270
7.4072
7.2831
7.2022
7.1997
7.1956
7.1932
7.1816
7.1791
7.1747
7.1723
3.8809
Aug22-2023.20.fid — MKB-THIOESTER-5-1H
OMe
2h, 400 MHz, CDCl3
1.01
3.10
3.01
1.06
1.00
3.00
f1 (ppm)
190.0984
159.8723
137.9769
135.1335
129.8441
129.6077
129.3235
127.4273
120.1108
120.0945
111.8299
77.5168
77.1991
76.8812
55.5133
Aug30-2023.30.fid — MKB-THIOESTER-5-13C
OMe
2h, 100 MHz,CDCl3
f1 (ppm)

2i - ^{1}H & ^{13}C NMR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7.7400
7.7355
7.7022
7.6989
7.6825
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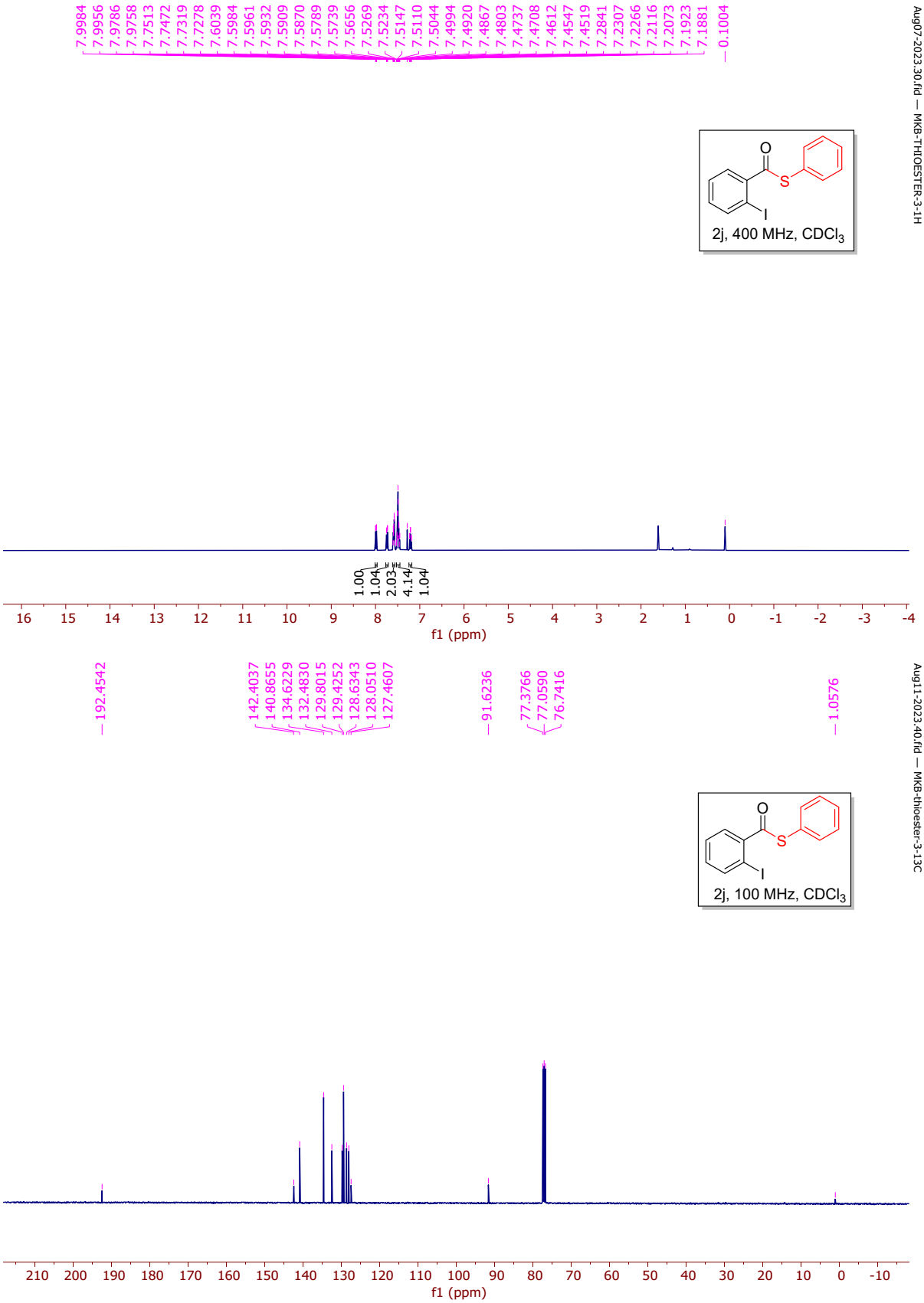
7.5831
7.5806
7.5773
7.5692
7.5641
7.5006
7.4958
7.4883
7.4829
7.4388
7.4353
7.3792
7.3748
7.2839
0.0952
Aug04-2023.10.fid — MKB-Thioester-2-1H
O
S
Br
2i, 400 MHz, CDCl3
1.00
1.05
2.00
3.12
2.16
f1 (ppm)
191.1945
139.1706
135.2262
134.6449
134.1358
132.4358
129.7966
129.4111
129.0600
127.3146
119.1381
77.3634
77.0462
76.7289
1.0490
Aug07-2023.50.fid — MKB-THIOESTER-2-13C
O
S
Br
2i, 100 MHz, CDCl3
f1 (ppm)

2j - ^{1}H & ^{13}C NMR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7.5909
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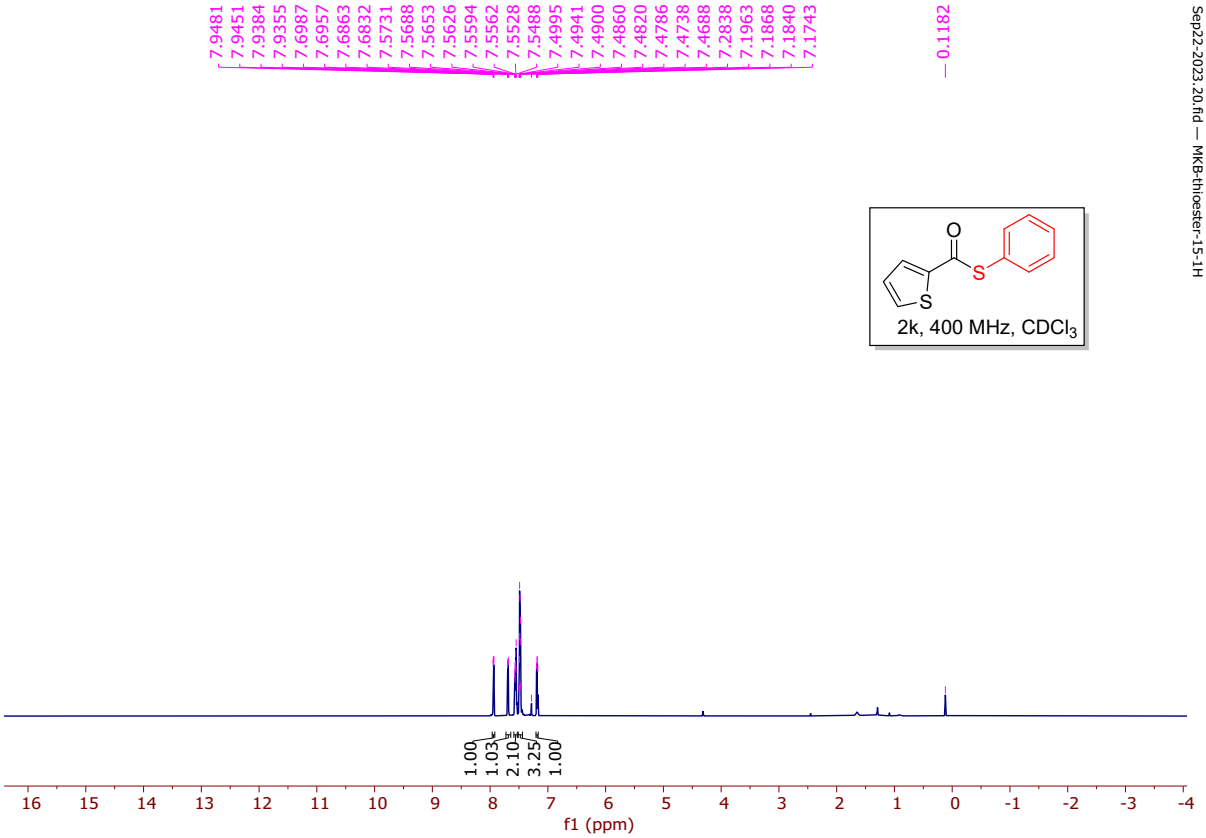
7.5789
7.5739
7.5656
7.5269
7.5234
7.5147
7.5110
7.5044
7.4994
7.4920
7.4867
7.4803
7.4737
7.4708
7.4612
7.4547
7.4519
7.2841
7.2307
7.2266
7.2116
7.2073
7.1923
7.1881
0.1004
Aug07-2023.30.fid — MKB-THIOESTER-3-1H
O
S
I
2j, 400 MHz, CDCl3
1.00
1.04
2.03
4.14
1.04
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)
192.4542
142.4037
140.8655
134.6229
132.4830
129.8015
129.4252
128.6343
128.0510
127.4607
91.6236
77.3766
77.0590
76.7416
1.0576
Aug11-2023.40.fid — MKB-thioester-3-13C
O
S
I
2j, 100 MHz, CDCl3
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)

2k - ^{1}H & ^{13}C NMR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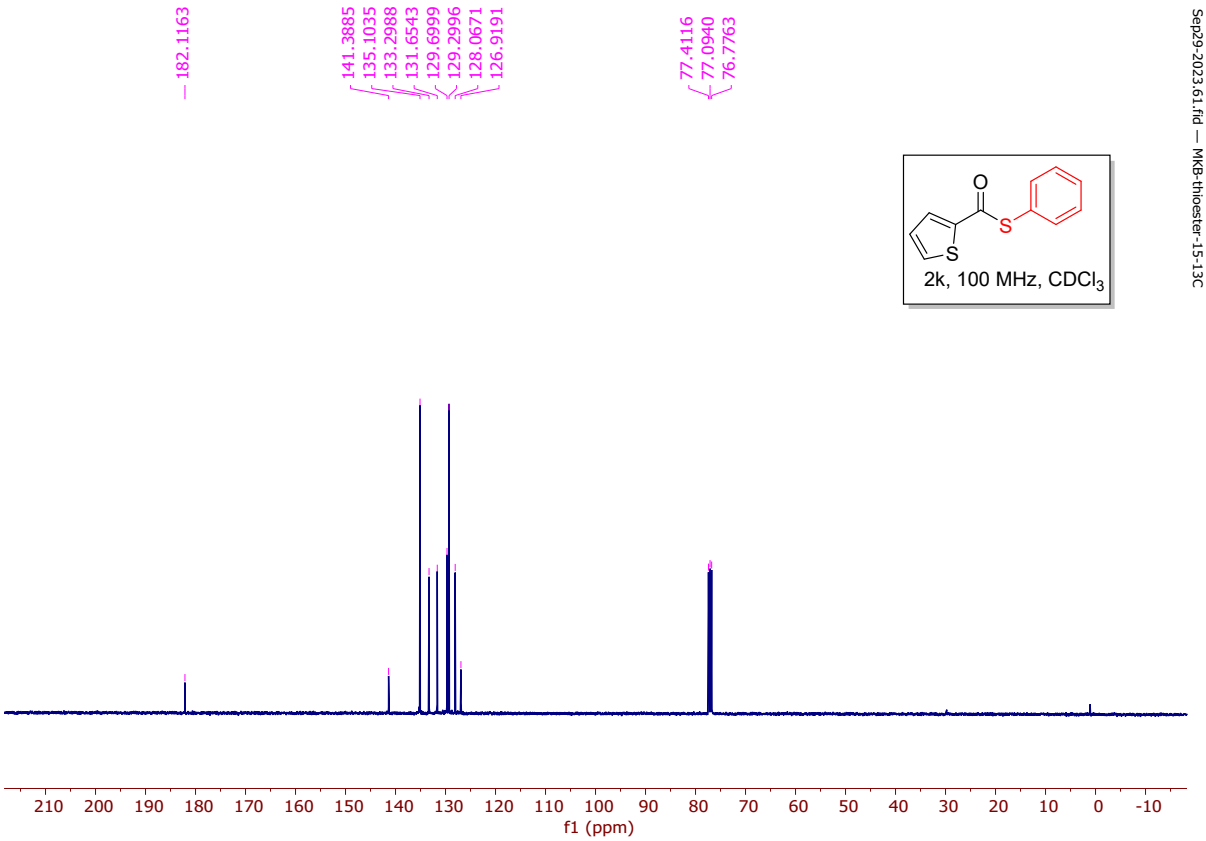
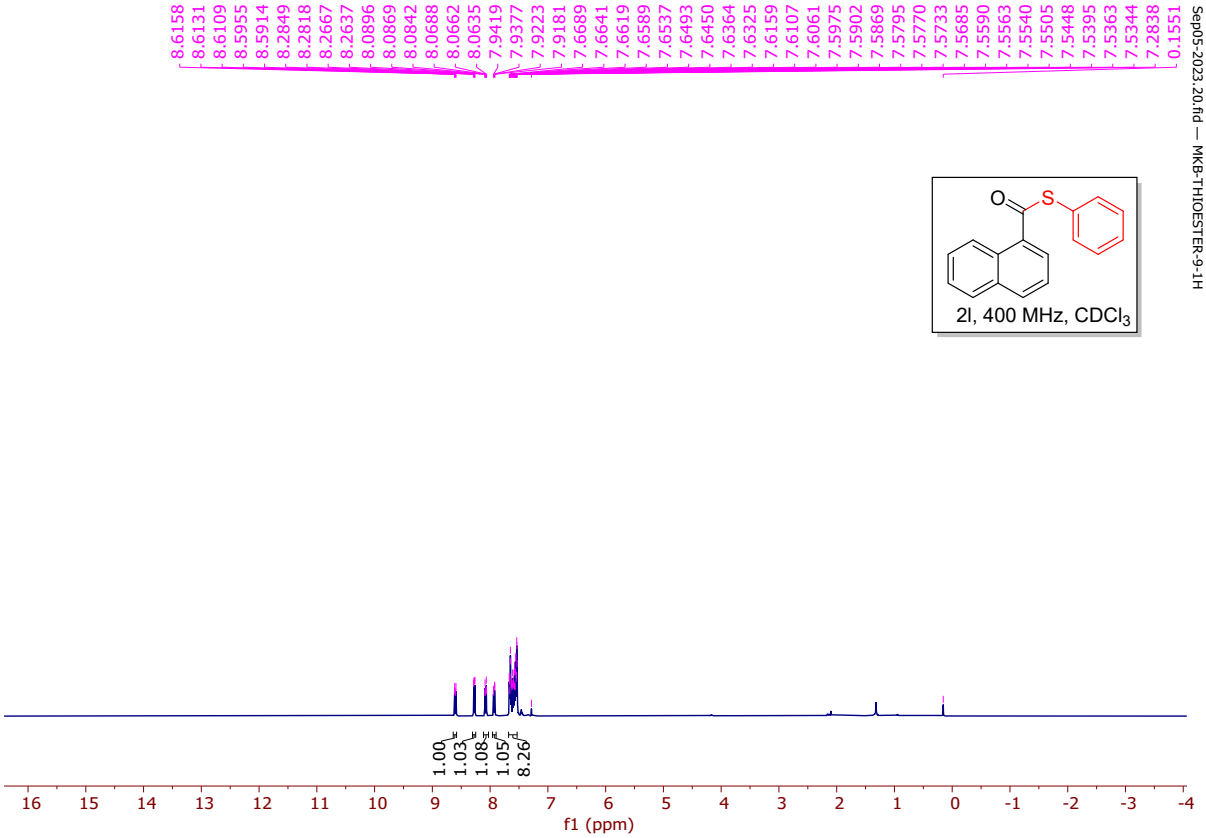
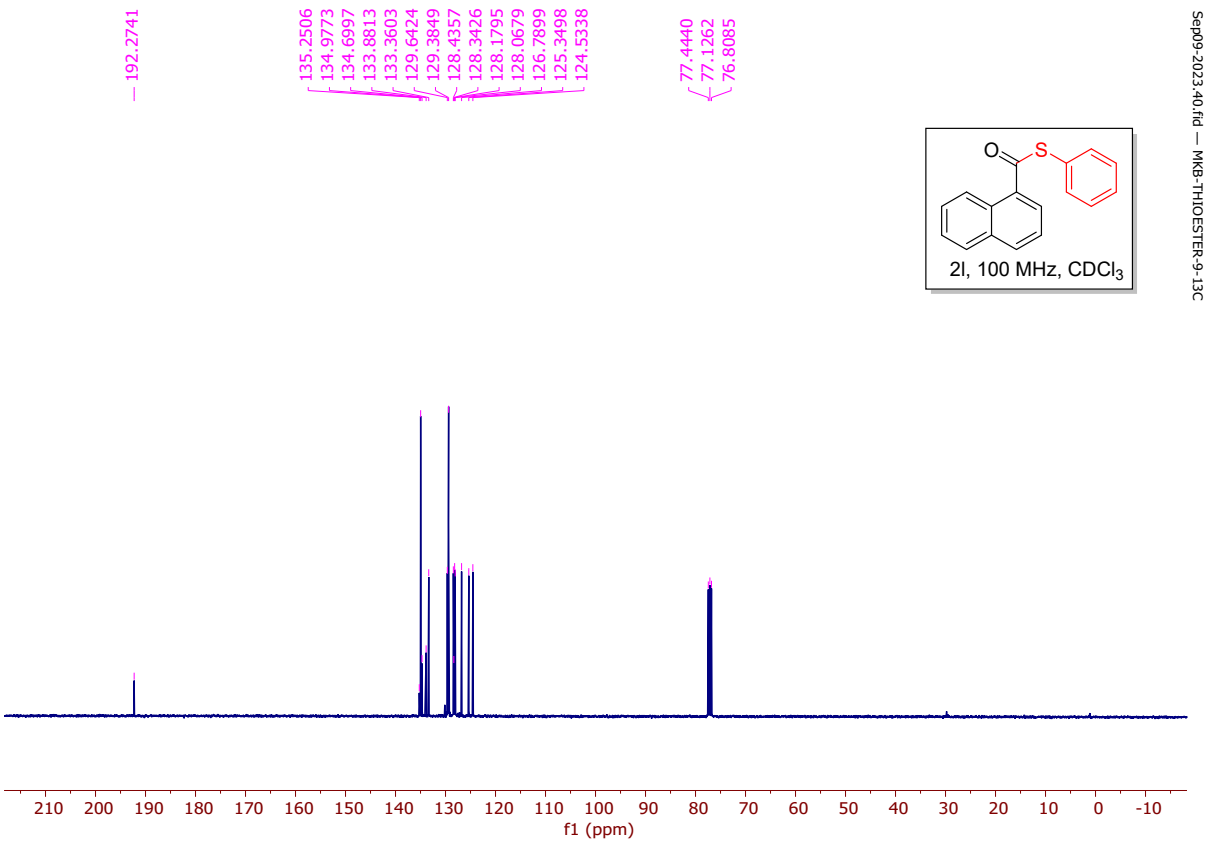
7.4786
7.4738
7.4688
7.2838
7.1963
7.1868
7.1840
7.1743
0.1182
Sep22-2023.20.fid — MKB-thioester-15-1H
O
S
S
2k, 400 MHz, CDCl3
1.00
1.03
2.10
3.25
1.00
f1 (ppm)

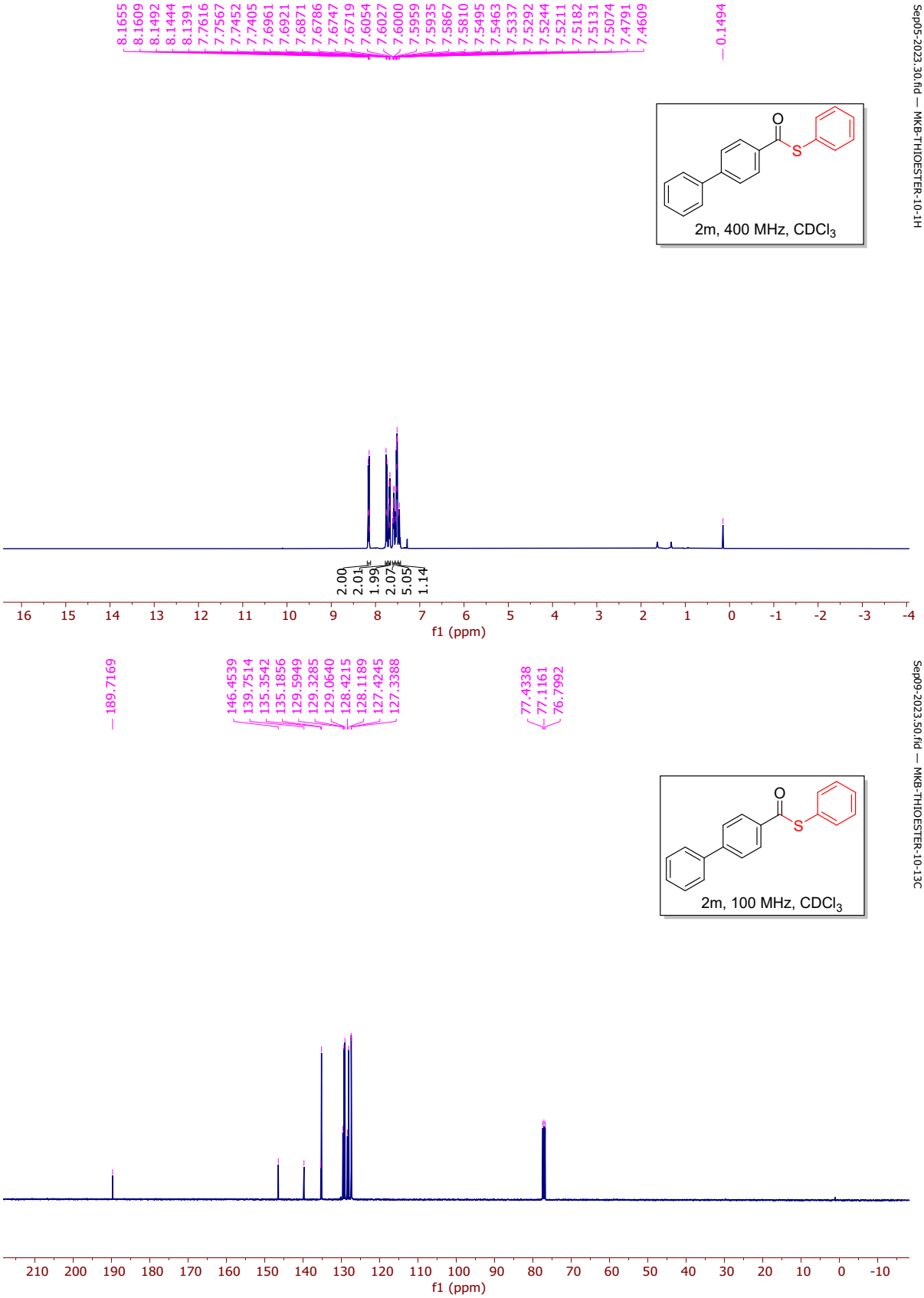

182.1163
141.3885
135.1035
133.2988
131.6543
129.6999
129.2996
128.0671
126.9191
77.4116
77.0940
76.7763
Sep29-2023.61.fid — MKB-thioester-15-13C
O
S
S
2k, 100 MHz, CDCl3
f1 (ppm)

2l - ^{1}H & ^{13}C NMR

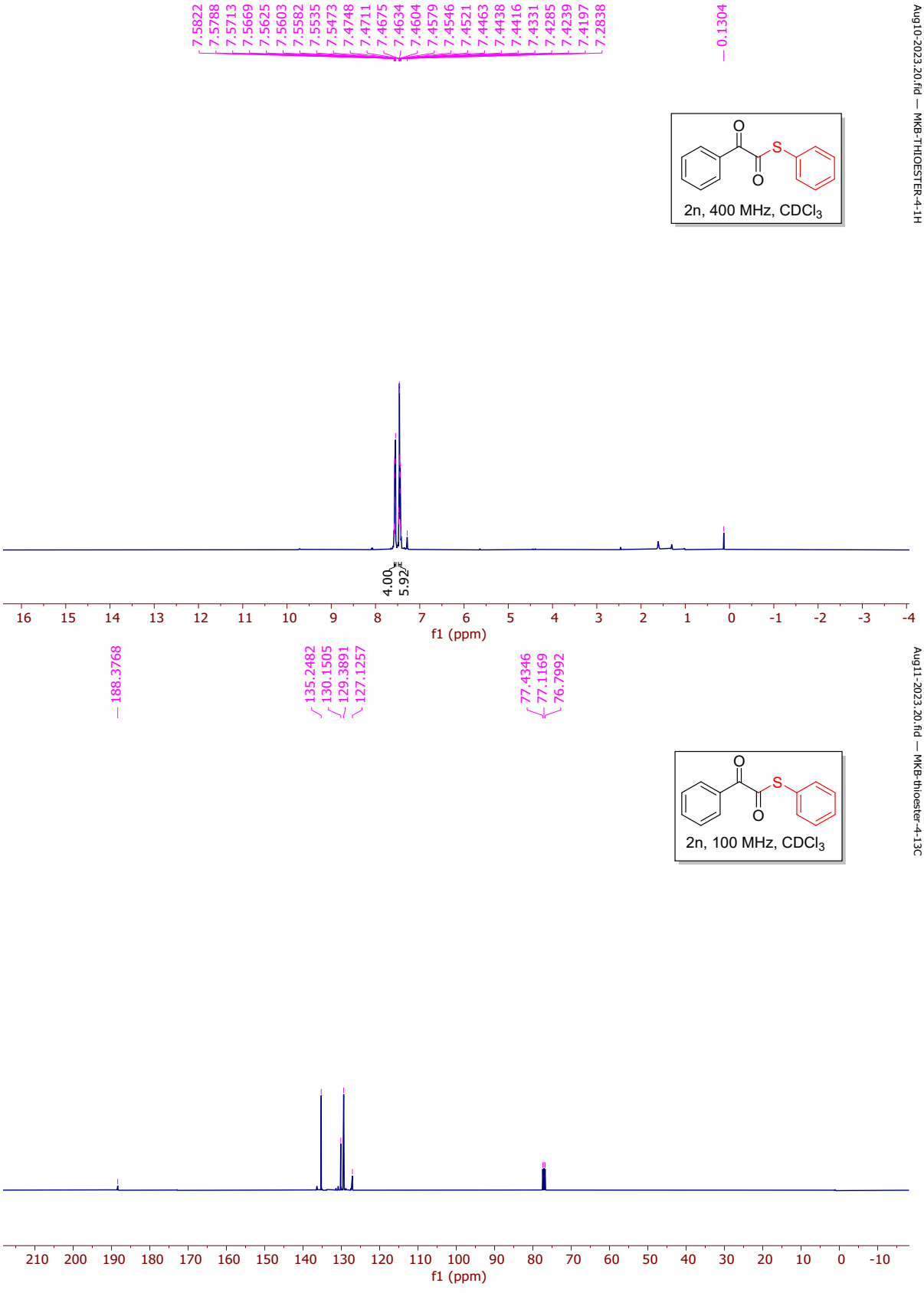

8.6158
8.6131
8.6109
8.5955
8.5914
8.2849
8.2818
8.2667
8.2637
8.0896
8.0869
8.0842
8.0688
8.0662
8.0635
7.9419
7.9377
7.9223
7.9181
7.6689
7.6641
7.6619
7.6589
7.6537
7.6493
7.6450
7.6364
7.6325
7.6159
7.6107
7.6061
7.5975
7.5902
7.5869
7.5795
7.5770
7.5733
7.5685
7.5590
7.5563
7.5540
7.5505
7.5448
7.5395
7.5363
7.5344
7.2838
0.1551
Sep05-2023.20.fid — MKB-THIOESTER-9-1H
2l, 400 MHz, CDCl3
1.00
1.03
1.08
1.05
8.26
f1 (ppm)


192.2741
135.2506
134.9773
134.6997
133.8813
133.3603
129.6424
129.3849
128.4357
128.3426
128.1795
128.0679
126.7899
125.3498
124.5338
77.4440
77.1262
76.8085
Sep09-2023.40.fid — MKB-THIOESTER-9-13C
2l, 100 MHz, CDCl3
f1 (ppm)

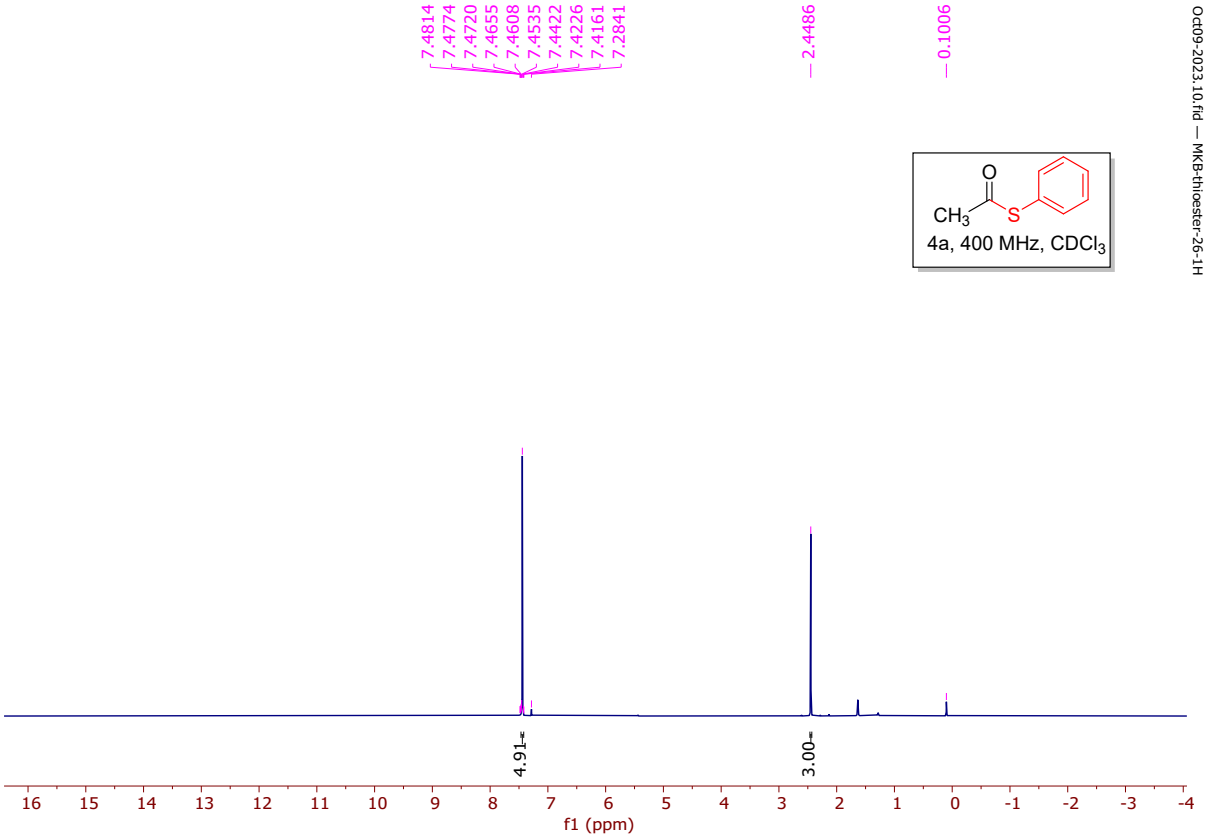
2m - ^{1}H & ^{13}C NMR

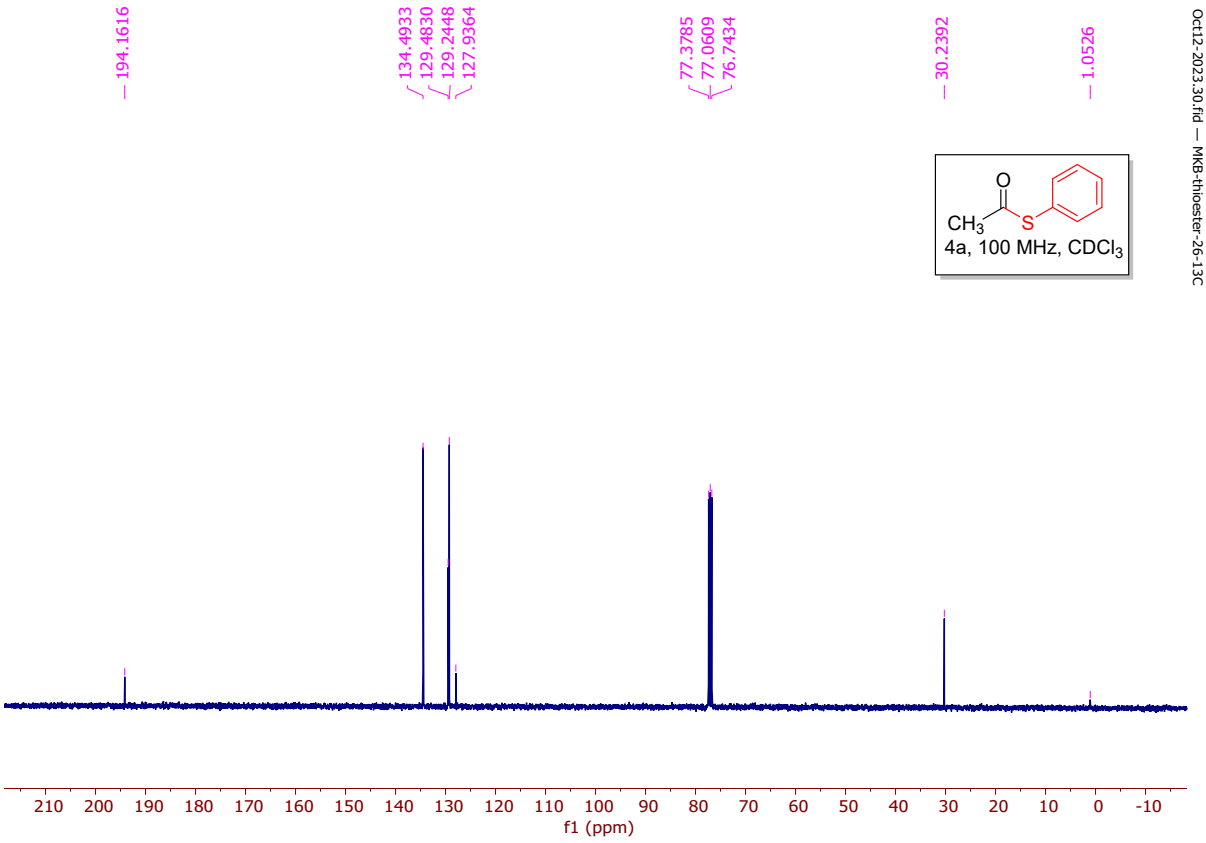

8.1655
8.1609
8.1492
8.1444
8.1391
7.7616
7.7567
7.7452
7.7405
7.6961
7.6921
7.6871
7.6786
7.6747
7.6719
7.6054
7.6027
7.6000
7.5959
7.5935
7.5867
7.5810
7.5495
7.5463
7.5337
7.5292
7.5244
7.5211
7.5182
7.5131
7.5074
7.4791
7.4609
0.1494
Sep05-2023.30.fid — MKB-THIOESTER-10-1H
2m, 400 MHz, CDCl3
2.00
2.01
1.99
2.07
5.05
1.14
f1 (ppm)
189.7169
146.4539
139.7514
135.3542
135.1856
129.5949
129.3285
129.0640
128.4215
128.1189
127.4245
127.3388
77.4338
77.1161
76.7992
Sep09-2023.50.fid — MKB-THIOESTER-10-13C
2m, 100 MHz, CDCl3
f1 (ppm)

2n - ^{1}H & ^{13}C NMR

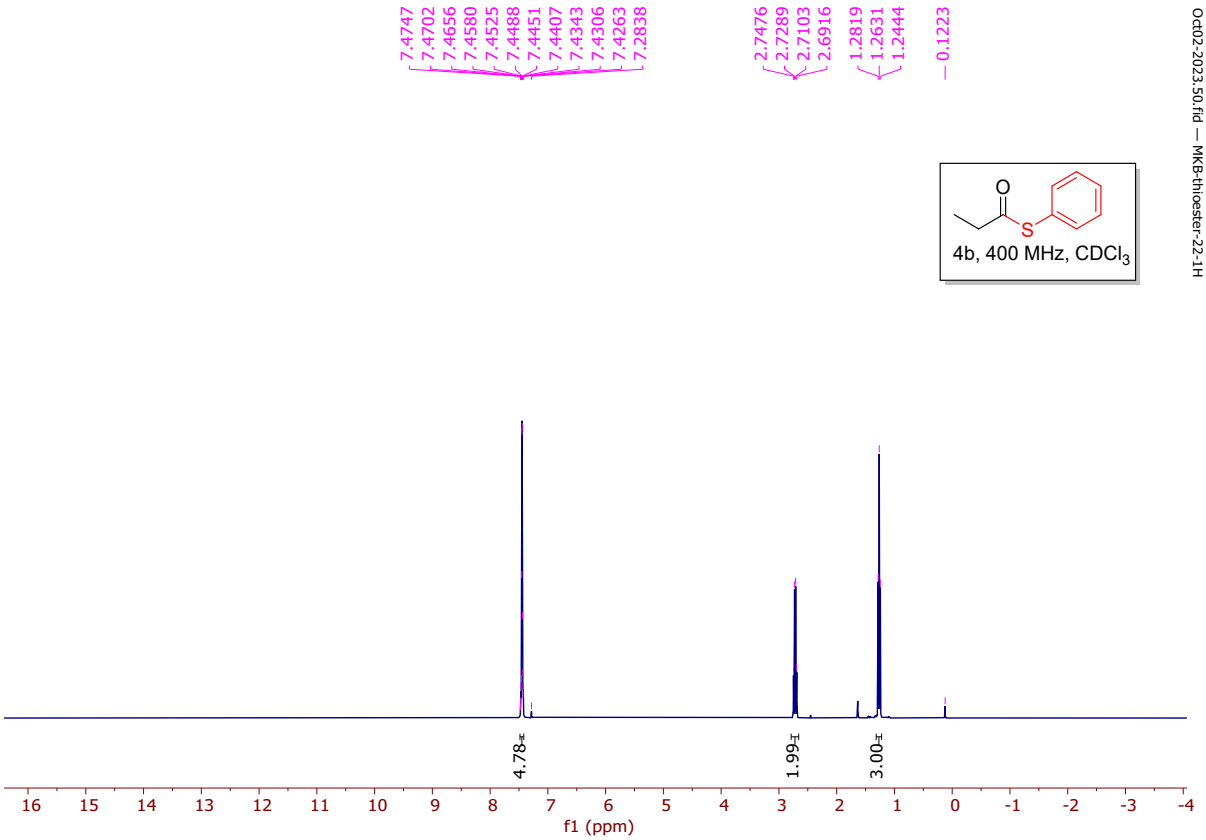

7.5822
7.5788
7.5713
7.5669
7.5625
7.5603
7.5582
7.5535
7.5473
7.4748
7.4711
7.4675
7.4634
7.4604
7.4579
7.4546
7.4521
7.4463
7.4438
7.4416
7.4331
7.4285
7.4239
7.4197
7.2838
0.1304
Aug10-2023.20.fid — MKB-THIOESTER-4-1H
2n, 400 MHz, CDCl3
4.00
5.92
f1 (ppm)
188.3768
135.2482
130.1505
129.3891
127.1257
77.4346
77.1169
76.7992
Aug11-2023.20.fid — MKB-thioester-4-13C
2n, 100 MHz, CDCl3
f1 (ppm)

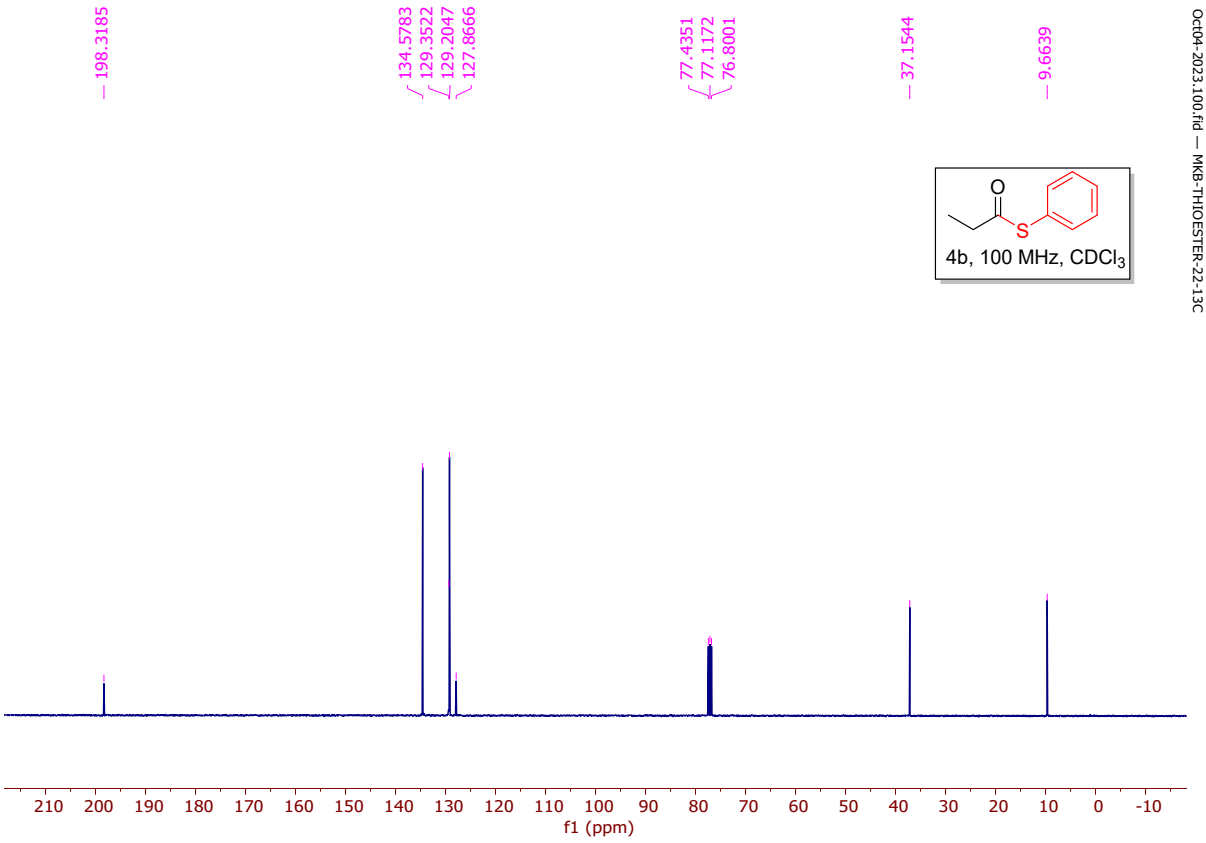
4a - ^{1}H & ^{13}C NMR


7.4814
7.4774
7.4720
7.4655
7.4608
7.4535
7.4422
7.4226
7.4161
7.2841
2.4486
0.1006
Oct09-2023.10.fid — MKB-thioester-26-1H
CH3
O
S
4a, 400 MHz, CDCl3
4.91
3.00
f1 (ppm)

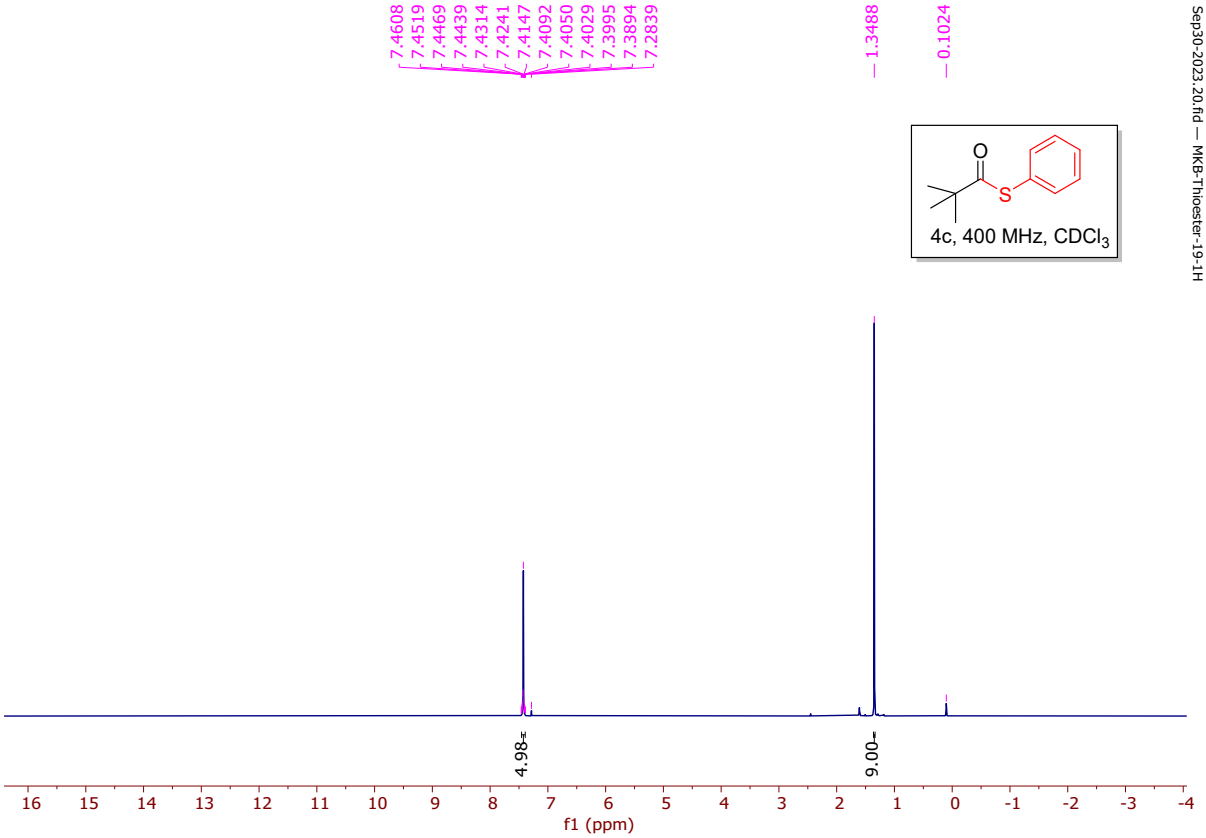

194.1616
134.4933
129.4830
129.2448
127.9364
77.3785
77.0609
76.7434
30.2392
1.0526
Oct12-2023.30.fid — MKB-thioester-26-13C
CH3
O
S
4a, 100 MHz, CDCl3
f1 (ppm)

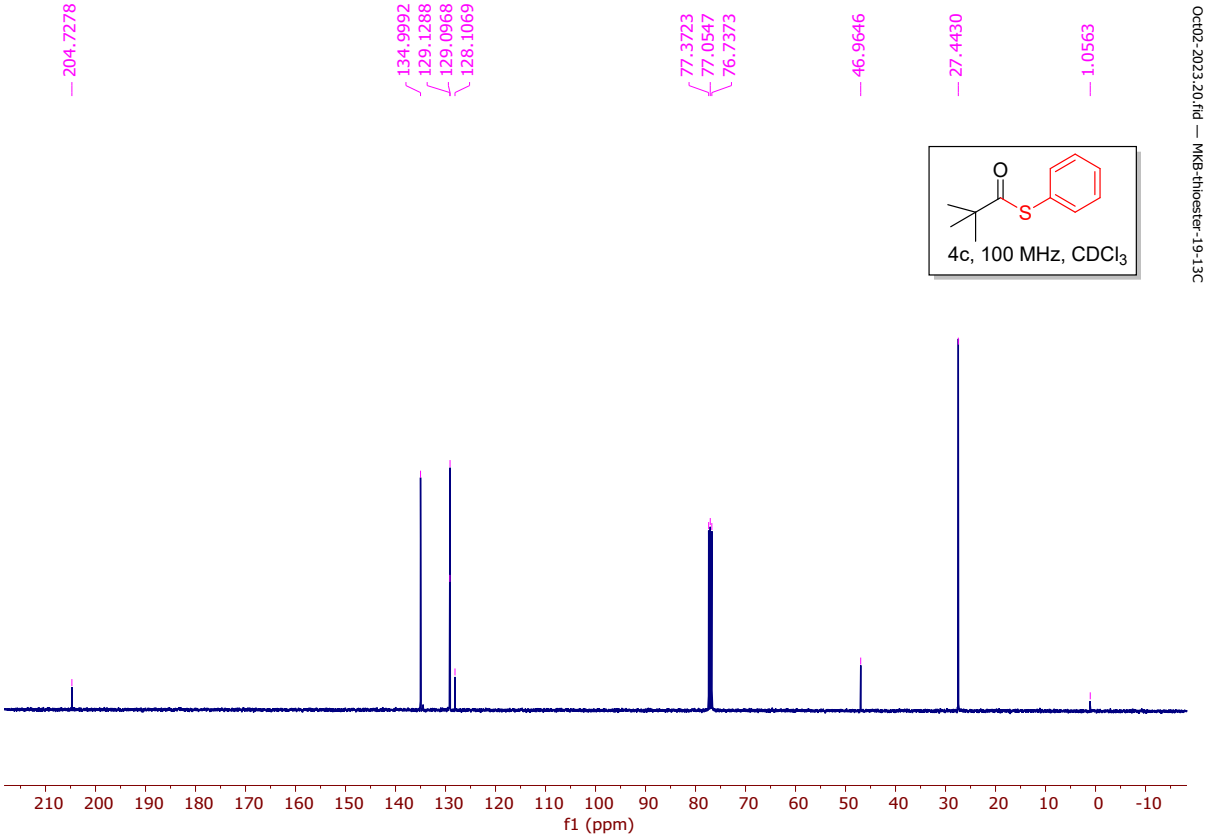
4b - ^{1}H & ^{13}C NMR


7.4747
7.4702
7.4656
7.4580
7.4525
7.4488
7.4451
7.4407
7.4343
7.4306
7.4263
7.2838
2.7476
2.7289
2.7103
2.6916
1.2819
1.2631
1.2444
0.1223
Oct02-2023.50.fid — MKB-thioester-22-1H
4b, 400 MHz, CDCl3
4.78
1.99
3.00
f1 (ppm)

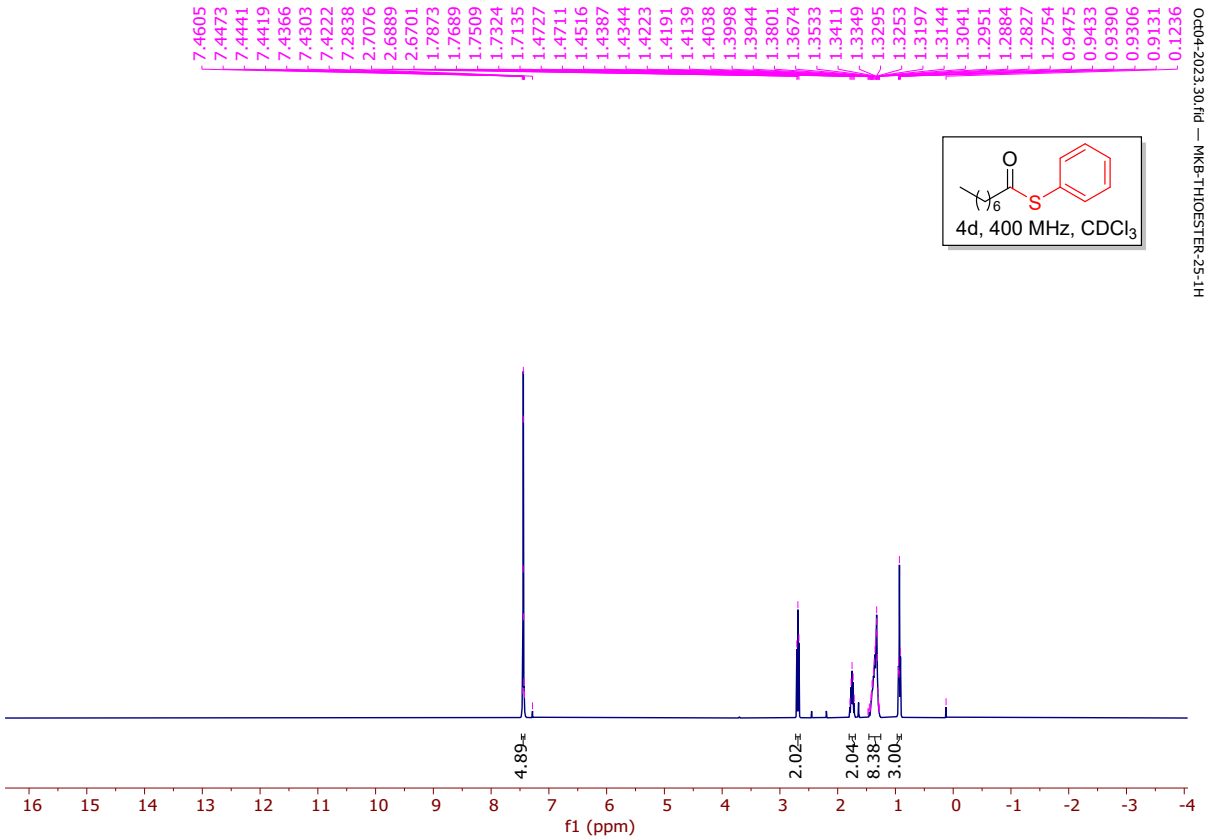

198.3185
134.5783
129.3522
129.2047
127.8666
77.4351
77.1172
76.8001
37.1544
9.6639
Oct04-2023.100.fid — MKB-THIOESTER-22-13C
4b, 100 MHz, CDCl3
f1 (ppm)

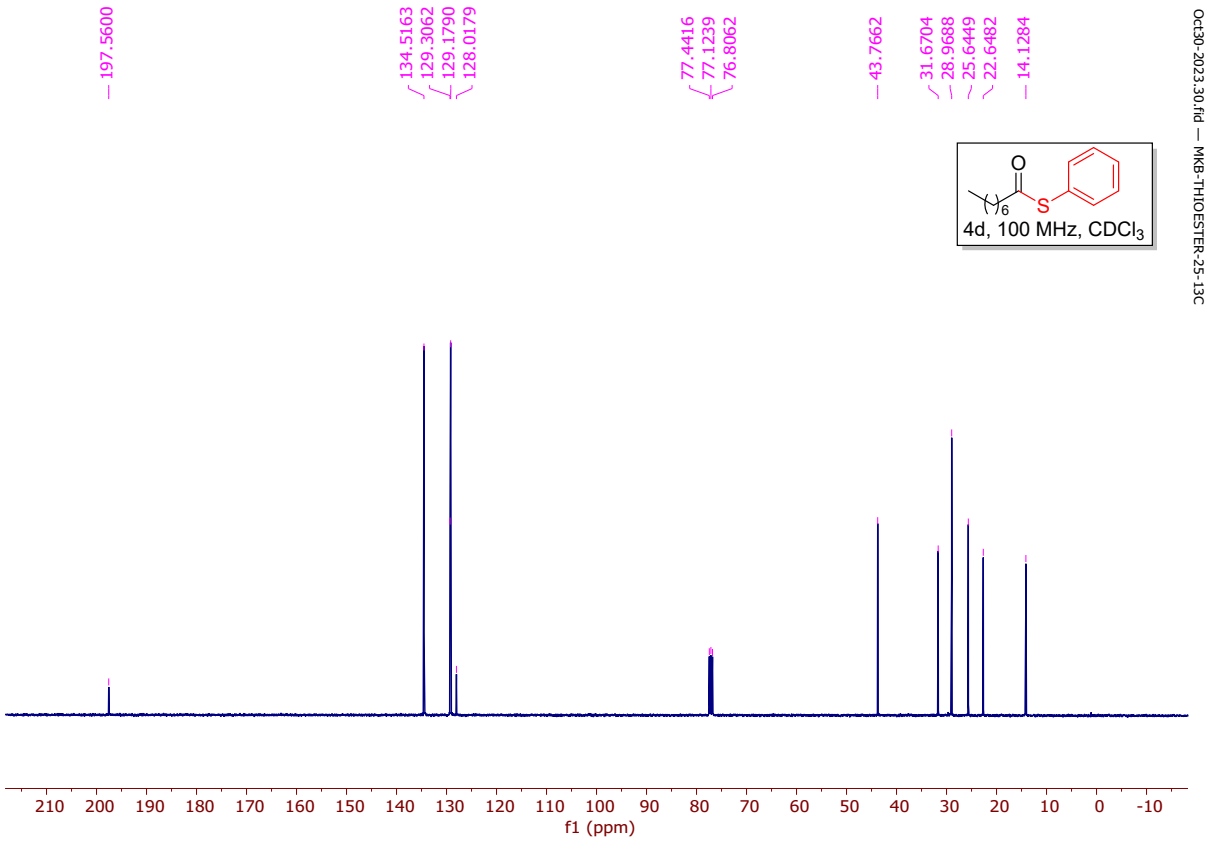
4c - ^{1}H & ^{13}C NMR


7.4608
7.4519
7.4469
7.4439
7.4314
7.4241
7.4147
7.4092
7.4050
7.4029
7.3995
7.3894
7.2839
1.3488
0.1024
4c, 400 MHz, CDCl3
4.98
9.00
f1 (ppm)
Sep30-2023.20.fid — MKB-Thioester-19-1H

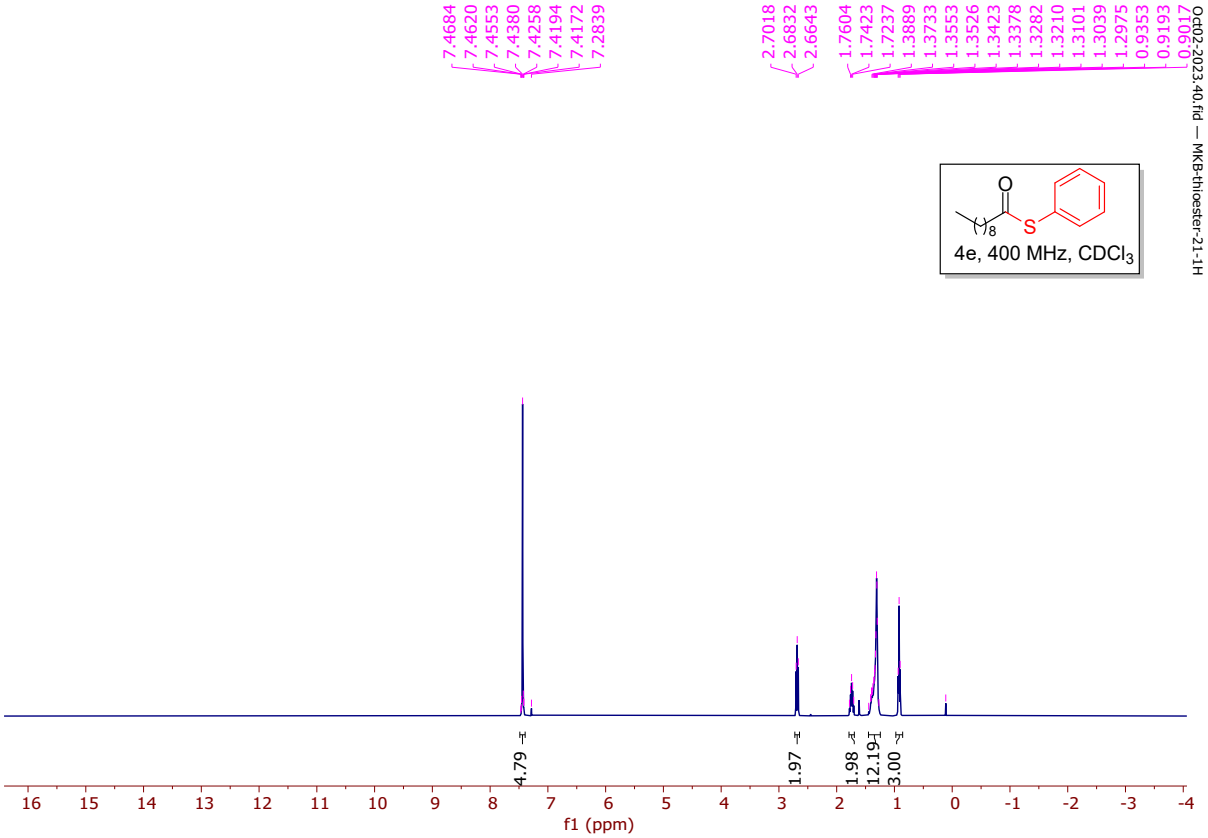

204.7278
134.9992
129.1288
129.0968
128.1069
77.3723
77.0547
76.7373
46.9646
27.4430
1.0563
4c, 100 MHz, CDCl3
f1 (ppm)
Oct02-2023.20.fid — MKB-thioester-19-13C

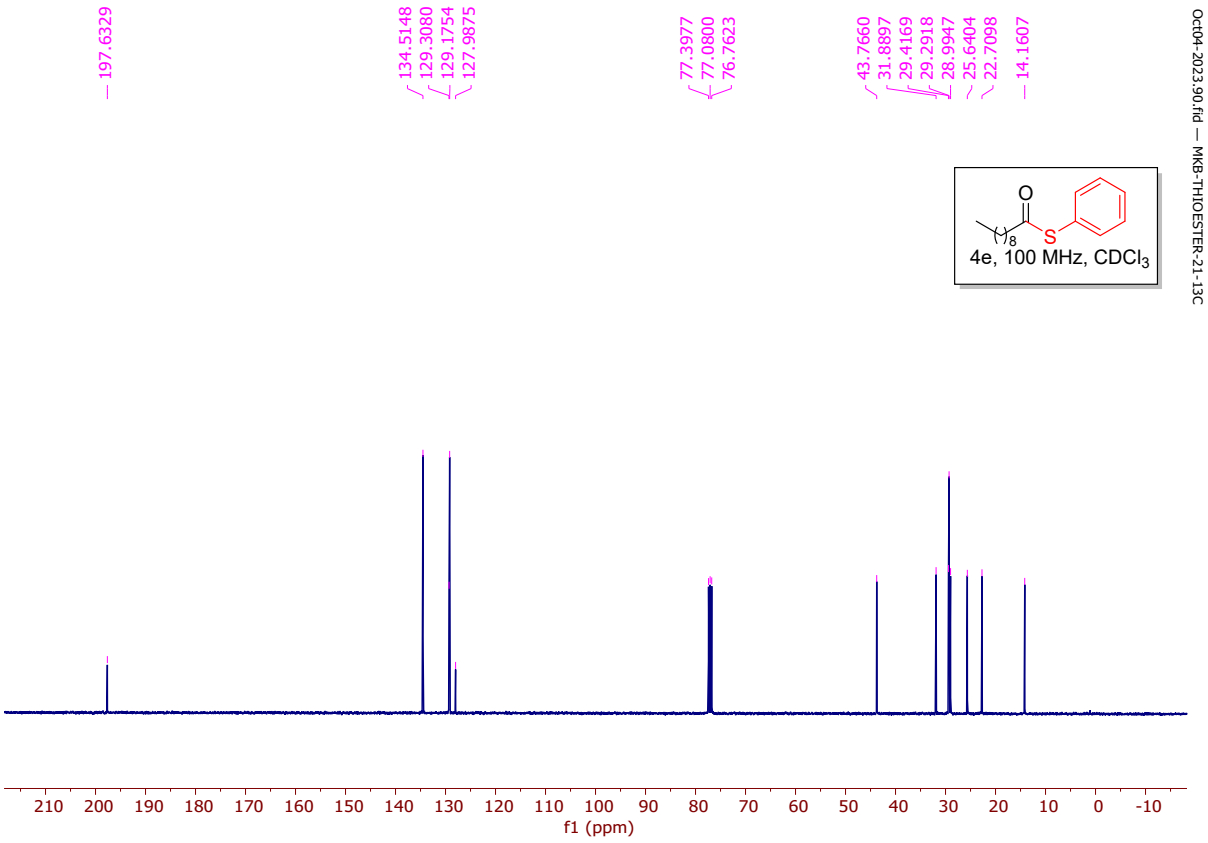
4d - ^{1}H & ^{13}C NMR


7.4605
7.4473
7.4441
7.4419
7.4366
7.4303
7.4222
7.2838
2.7076
2.6889
2.6701
1.7873
1.7689
1.7509
1.7324
1.7135
1.4727
1.4711
1.4516
1.4387
1.4344
1.4223
1.4191
1.4139
1.4038
1.3998
1.3944
1.3801
1.3674
1.3533
1.3411
1.3349
1.3295
1.3253
1.3197
1.3144
1.3041
1.2951
1.2884
1.2827
1.2754
0.9475
0.9433
0.9390
0.9306
0.9131
0.1236
Oct04-2023.30.fid — MKB-THIOESTER-25-1H
4d, 400 MHz, CDCl3
4.89
2.02
2.04
8.38
3.00
f1 (ppm)

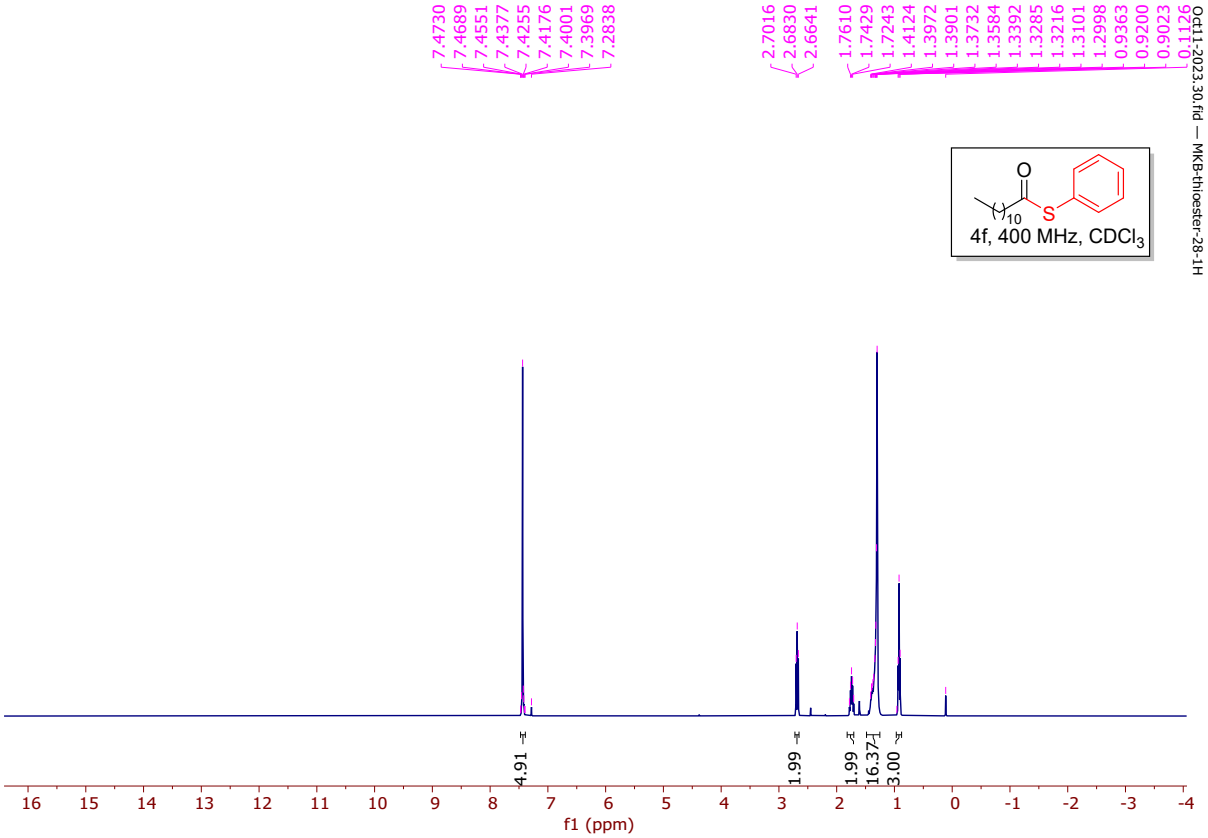

197.5600
134.5163
129.3062
129.1790
128.0179
77.4416
77.1239
76.8062
43.7662
31.6704
28.9688
25.6449
22.6482
14.1284
Oct30-2023.30.fid — MKB-THIOESTER-25-13C
4d, 100 MHz, CDCl3
f1 (ppm)

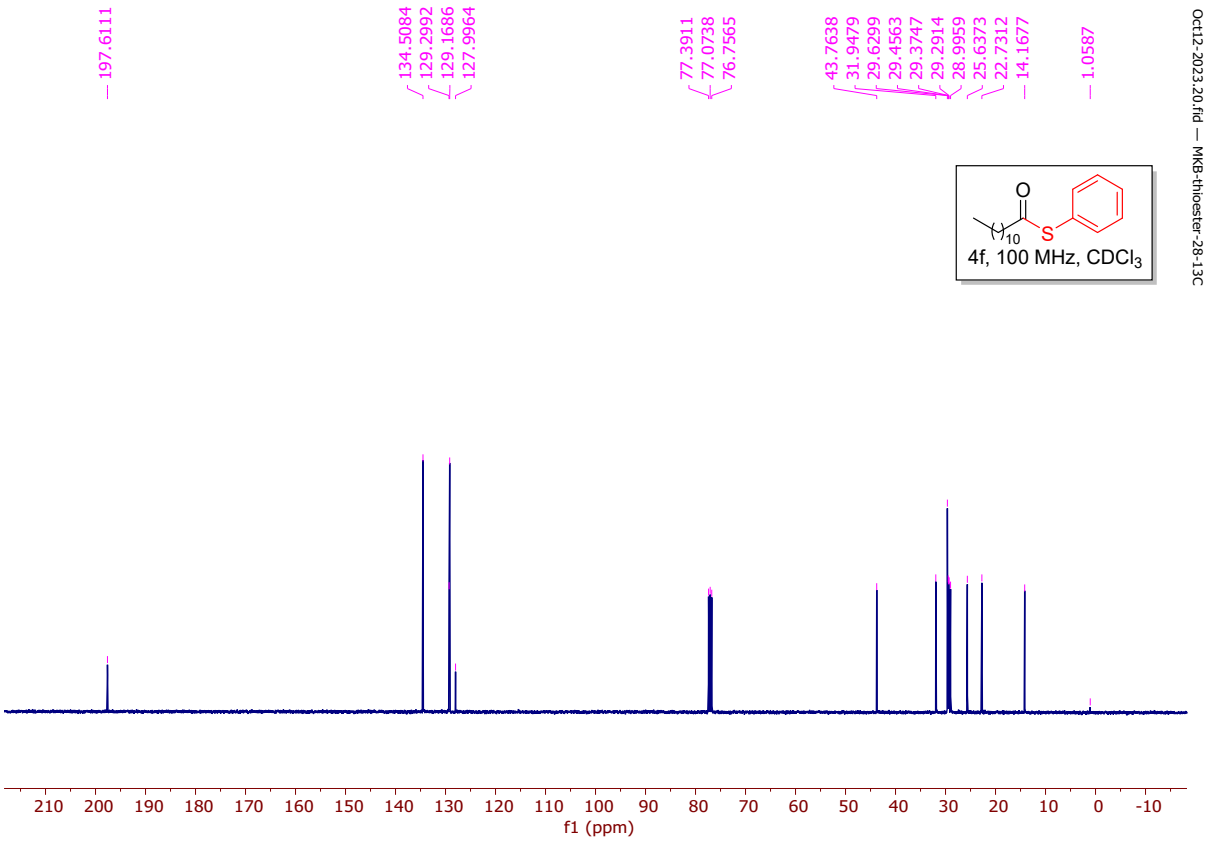
4e - ^{1}H & ^{13}C NMR


7.4684
7.4620
7.4553
7.4380
7.4258
7.4194
7.4172
7.2839
2.7018
2.6832
2.6643
1.7604
1.7423
1.7237
1.3889
1.3733
1.3553
1.3526
1.3423
1.3378
1.3282
1.3210
1.3101
1.3039
1.2975
0.9353
0.9193
0.9017
Oct02-2023-40.fid — MKB-thioester-21-1H
4e, 400 MHz, CDCl3
4.79
1.97
1.98
12.19
3.00
f1 (ppm)

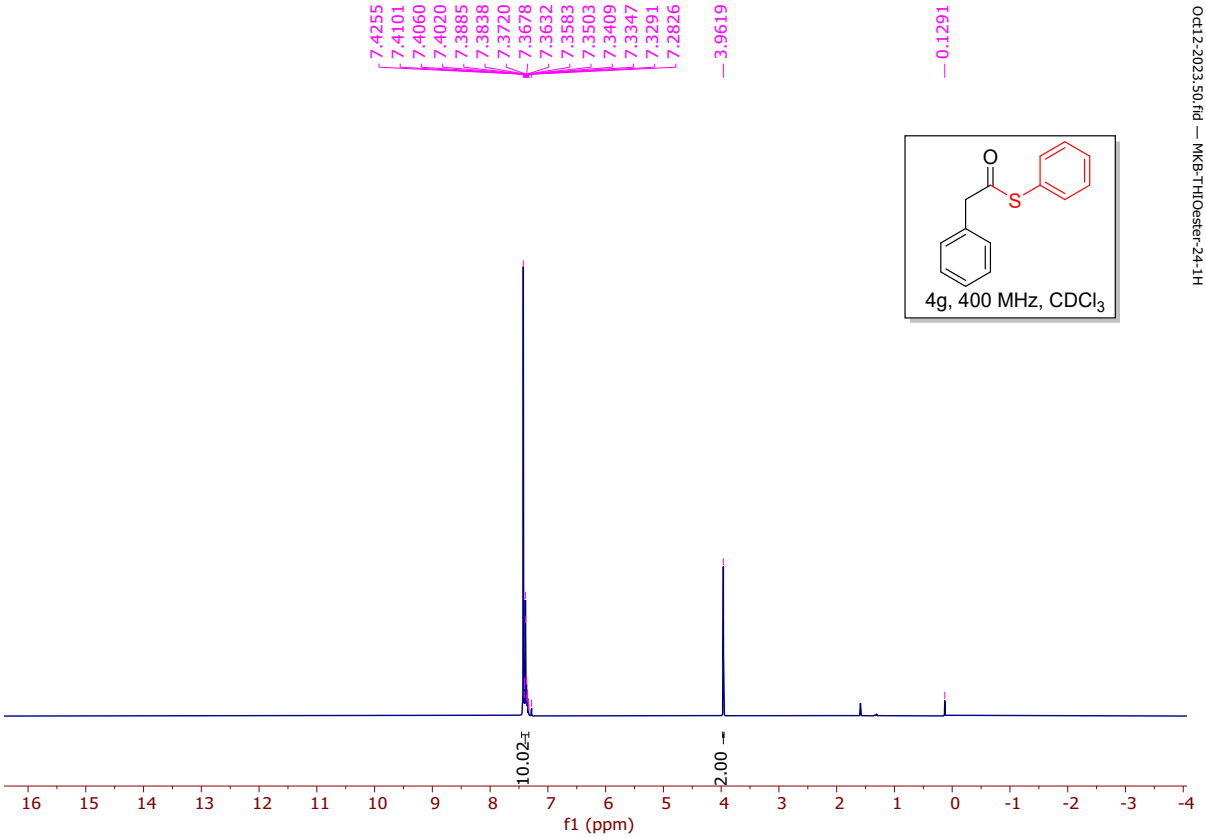

197.6329
134.5148
129.3080
129.1754
127.9875
77.3977
77.0800
76.7623
43.7660
31.8897
29.4169
29.2918
28.9947
25.6404
22.7098
14.1607
Oct04-2023-90.fid — MKB-THIOESTER-21-13C
4e, 100 MHz, CDCl3
f1 (ppm)

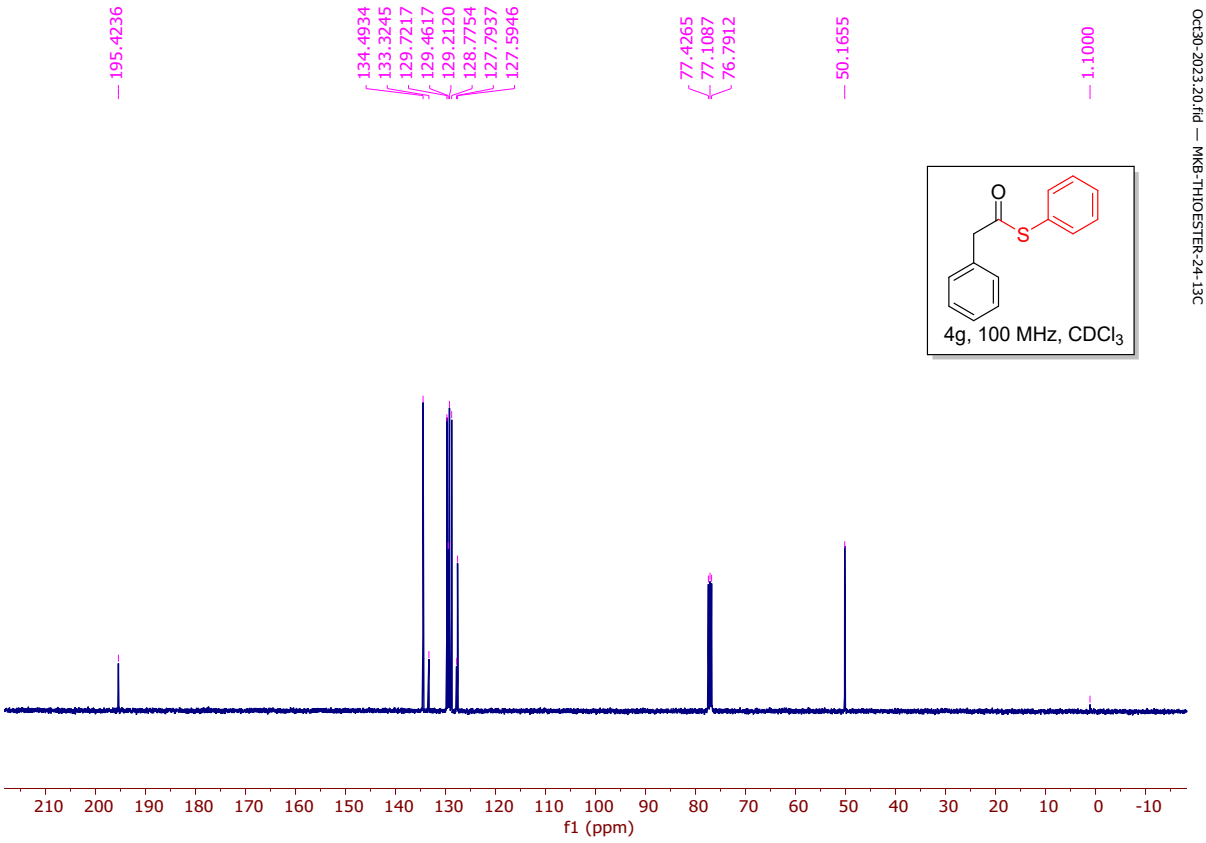
4f - ^{1}H & ^{13}C NMR


7.4730
7.4689
7.4551
7.4377
7.4255
7.4176
7.4001
7.3969
7.2838
2.7016
2.6830
2.6641
1.7610
1.7429
1.7243
1.4124
1.3972
1.3901
1.3732
1.3584
1.3392
1.3285
1.3216
1.3101
1.2998
0.9363
0.9200
0.9023
0.1126
Oct11-2023.30.fid — MKB-thioester-28-1H
4f, 400 MHz, CDCl3
4.91
1.99
1.99
16.37
3.00
f1 (ppm)

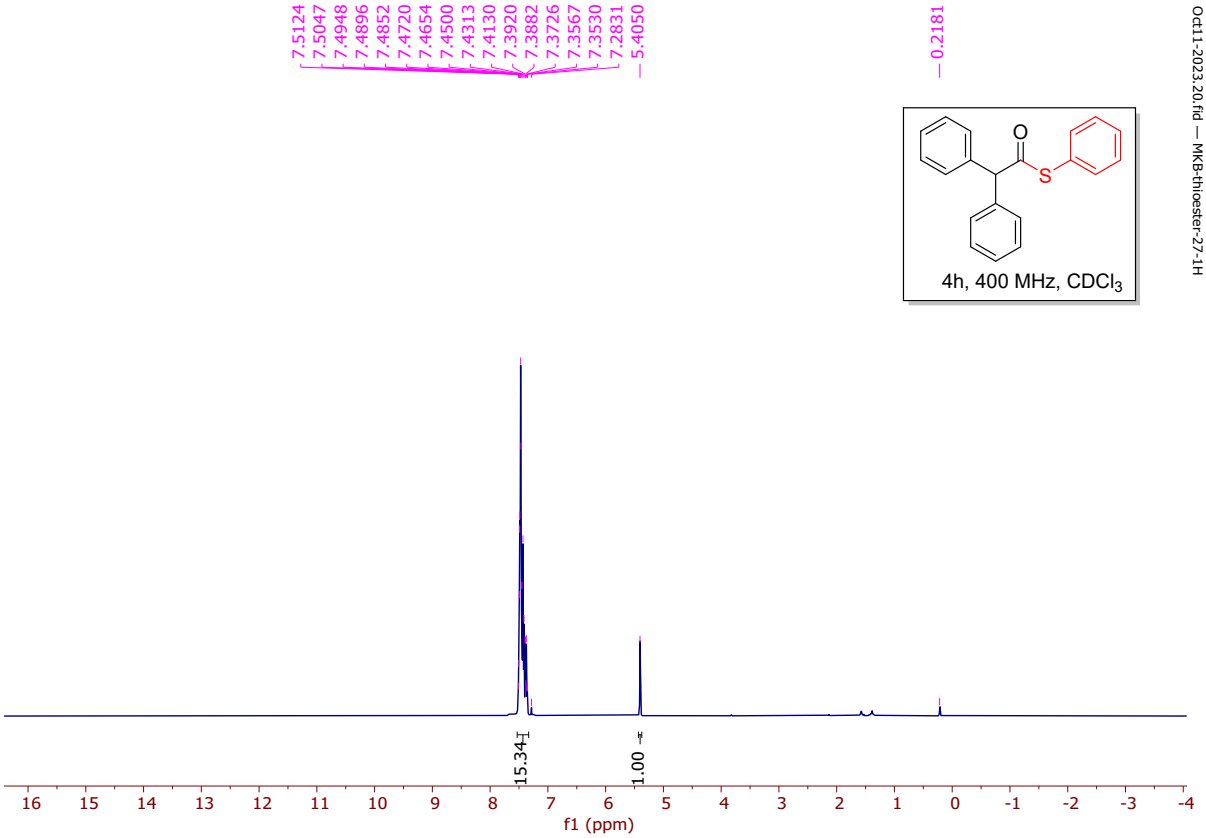

197.6111
134.5084
129.2992
129.1686
127.9964
77.3911
77.0738
76.7565
43.7638
31.9479
29.6299
29.4563
29.3747
29.2914
28.9959
25.6373
22.7312
14.1677
1.0587
Oct12-2023.20.fid — MKB-thioester-28-13C
4f, 100 MHz, CDCl3
f1 (ppm)

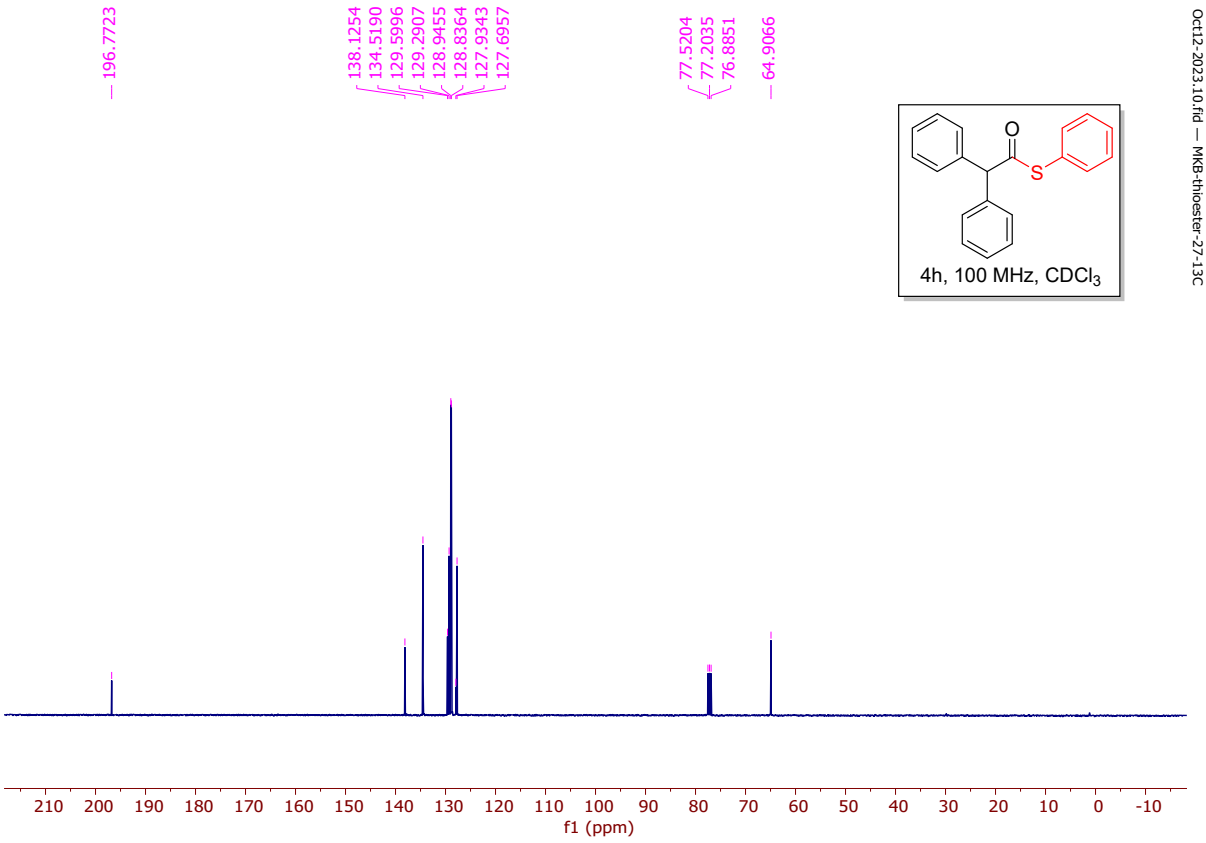
4g - ^{1}H & ^{13}C NMR


7.4255
7.4101
7.4060
7.4020
7.3885
7.3838
7.3720
7.3678
7.3632
7.3583
7.3503
7.3409
7.3347
7.3291
7.2826
3.9619
0.1291
Oct12-2023.50.fid — MKB-THIOester-24-1H
4g, 400 MHz, CDCl3
10.02
2.00
f1 (ppm)

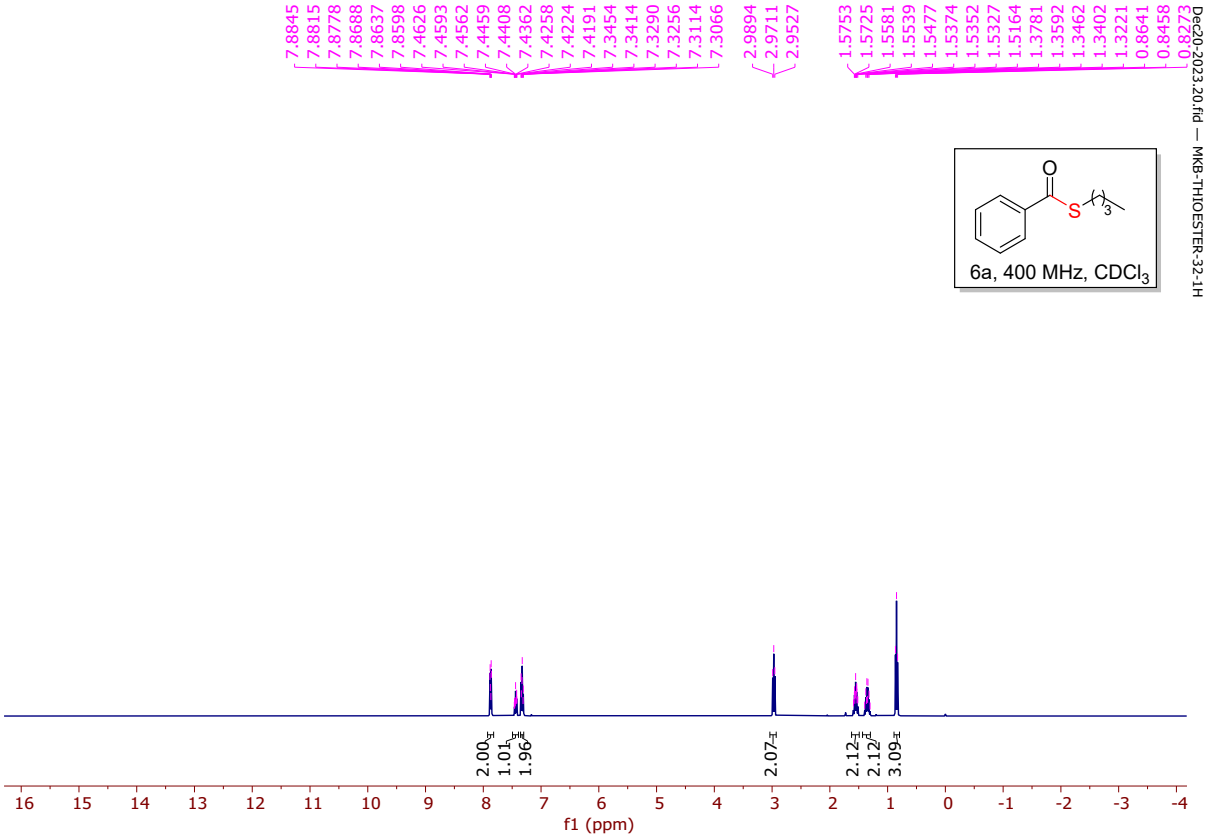

195.4236
134.4934
133.3245
129.7217
129.4617
129.2120
128.7754
127.7937
127.5946
77.4265
77.1087
76.7912
50.1655
1.1000
Oct30-2023.20.fid — MKB-THIOESTER-24-13C
4g, 100 MHz, CDCl3
f1 (ppm)

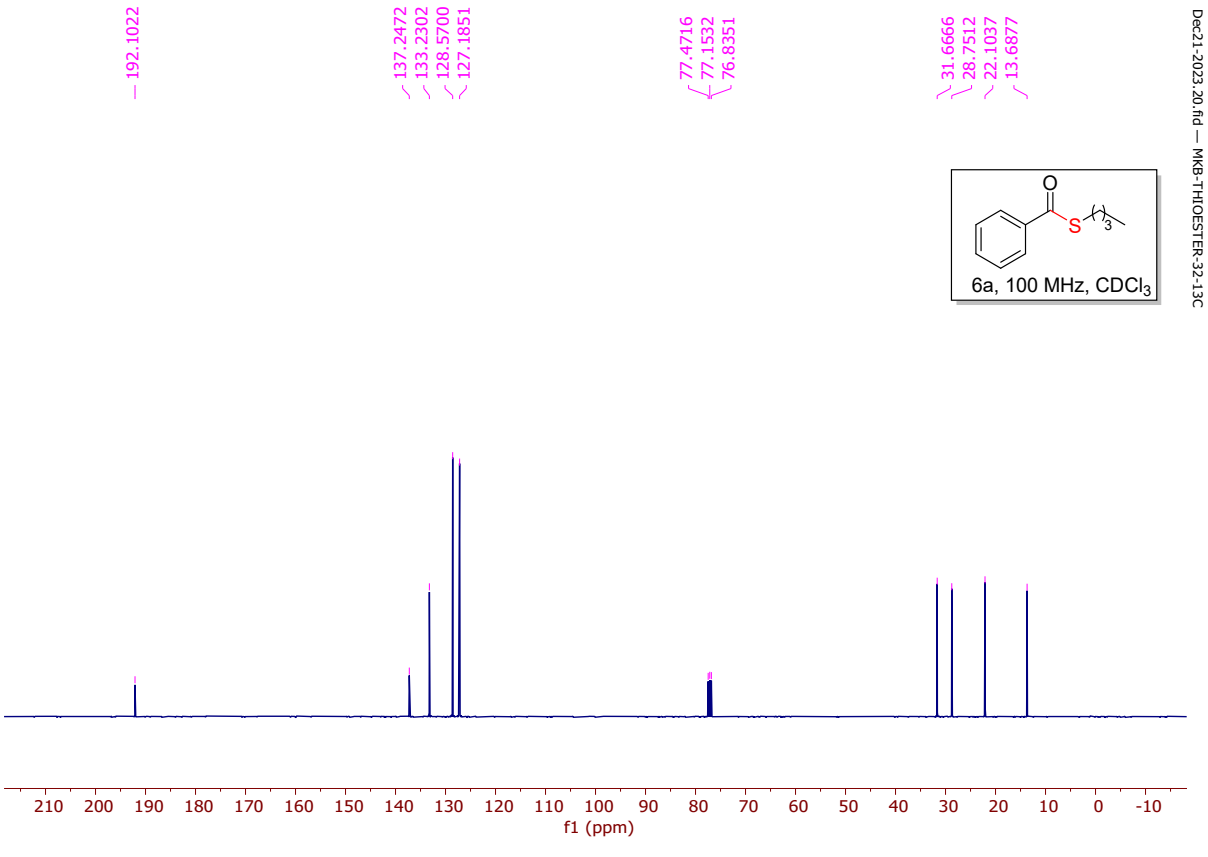
4h - ^{1}H & ^{13}C NMR


7.5124
7.5047
7.4948
7.4896
7.4852
7.4720
7.4654
7.4500
7.4313
7.4130
7.3920
7.3882
7.3726
7.3567
7.3530
7.2831
5.4050
0.2181
4h, 400 MHz, CDCl3
Oct11-2023.20.fid — MKB-thioester-27-1H
15.34
1.00
f1 (ppm)

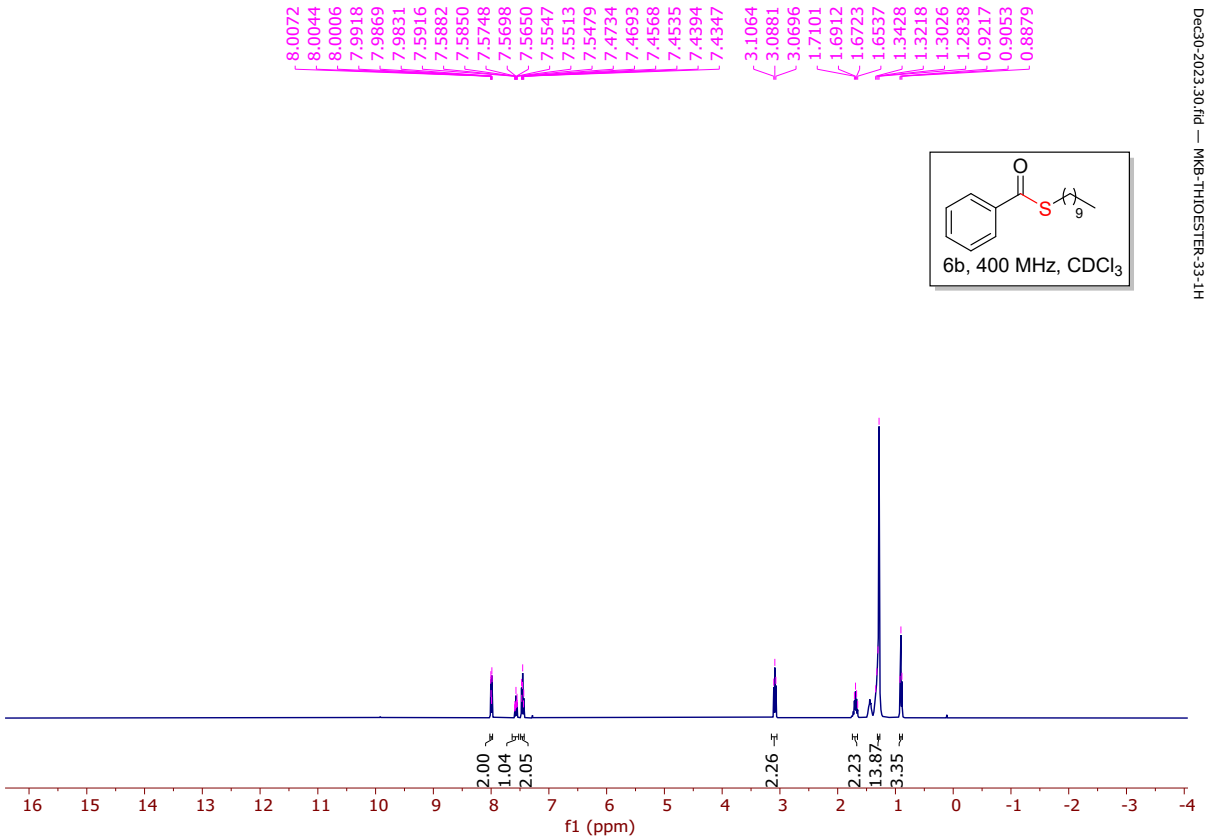

196.7723
138.1254
134.5190
129.5996
129.2907
128.9455
128.8364
127.9343
127.6957
77.5204
77.2035
76.8851
64.9066
4h, 100 MHz, CDCl3
Oct12-2023.10.fid — MKB-thioester-27-13C
f1 (ppm)

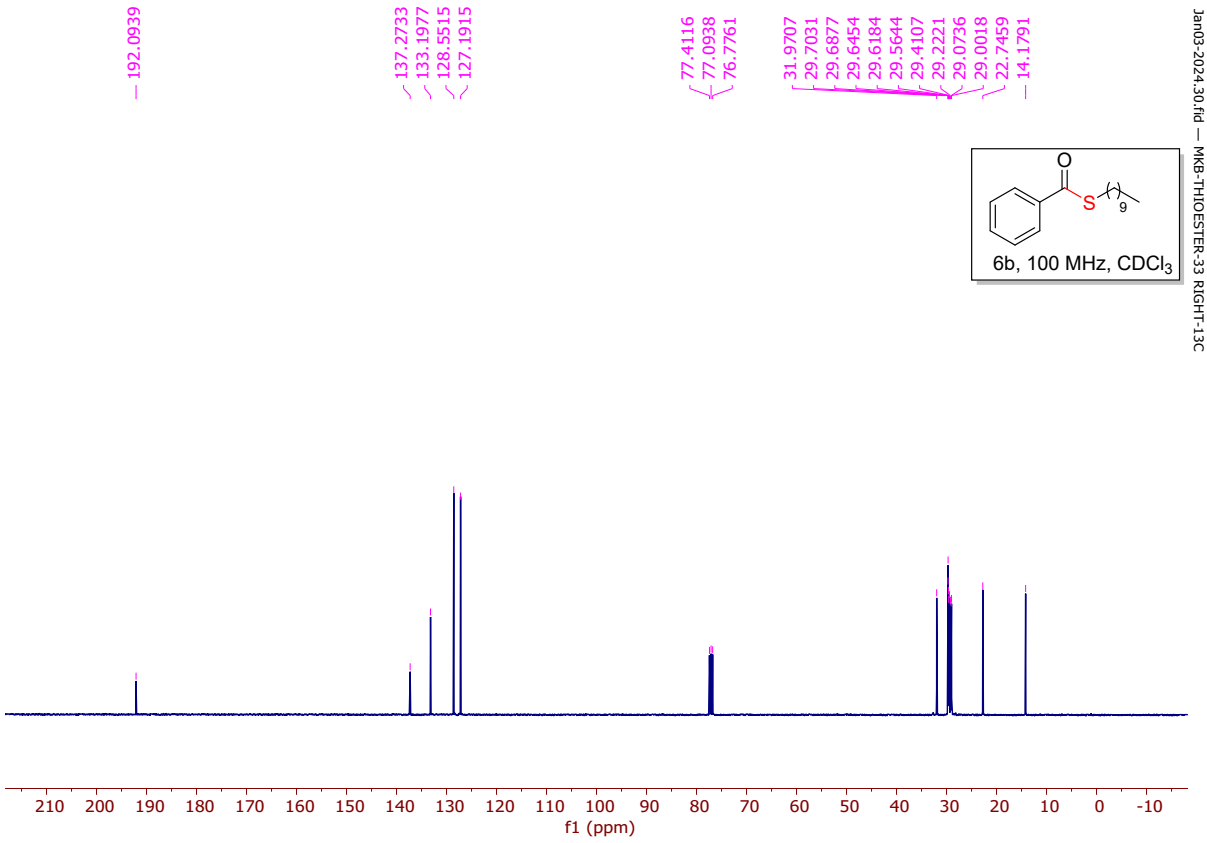
6a - ^{1}H & ^{13}C NMR


7.8845
7.8815
7.8778
7.8688
7.8637
7.8598
7.4626
7.4593
7.4562
7.4459
7.4408
7.4362
7.4258
7.4224
7.4191
7.3454
7.3414
7.3290
7.3256
7.3114
7.3066
2.9894
2.9711
2.9527
1.5753
1.5725
1.5581
1.5539
1.5477
1.5374
1.5352
1.5327
1.5164
1.3781
1.3592
1.3462
1.3402
1.3221
0.8641
0.8458
0.8273
Dec20-2023.20.fid — MKB-THIOESTER-32-1H
6a, 400 MHz, CDCl3
2.00
1.01
1.96
2.07
2.12
2.12
3.09
f1 (ppm)

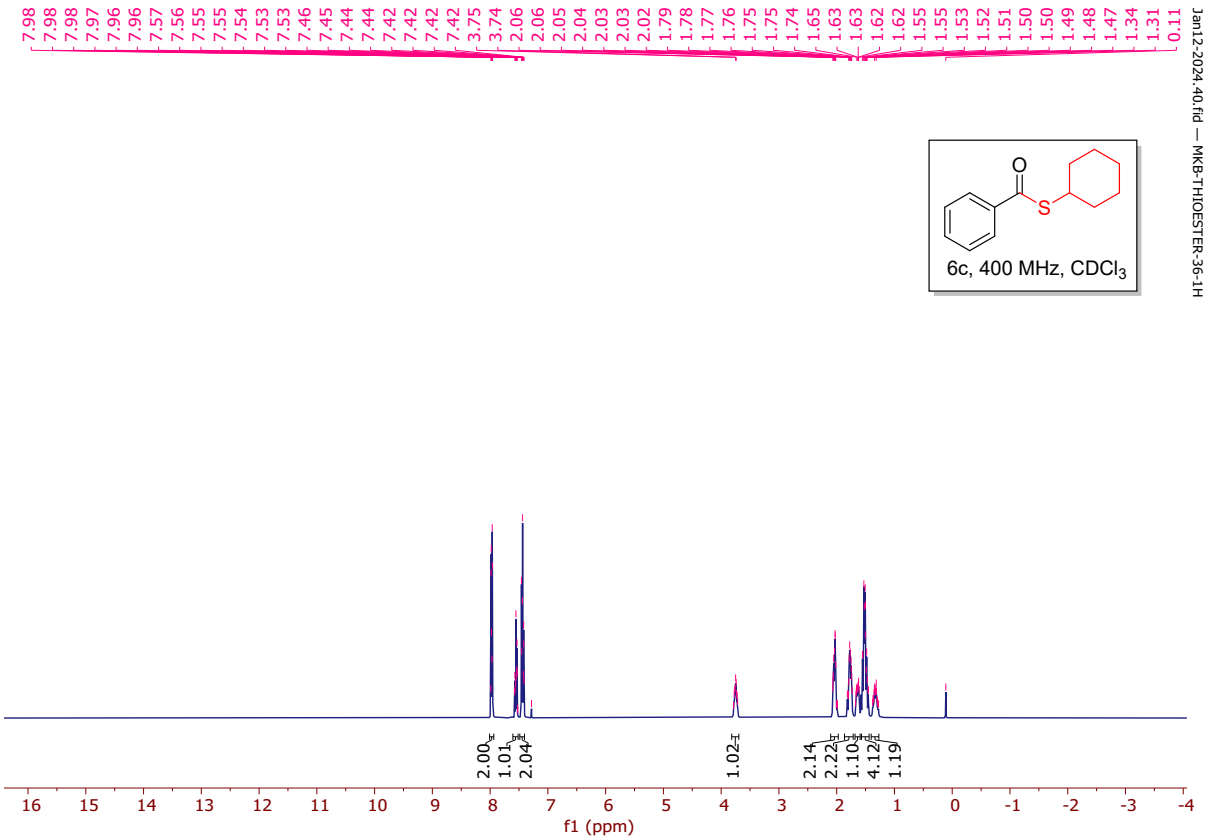

192.1022
137.2472
133.2302
128.5700
127.1851
77.4716
77.1532
76.8351
31.6666
28.7512
22.1037
13.6877
Dec21-2023.20.fid — MKB-THIOESTER-32-13C
6a, 100 MHz, CDCl3
f1 (ppm)

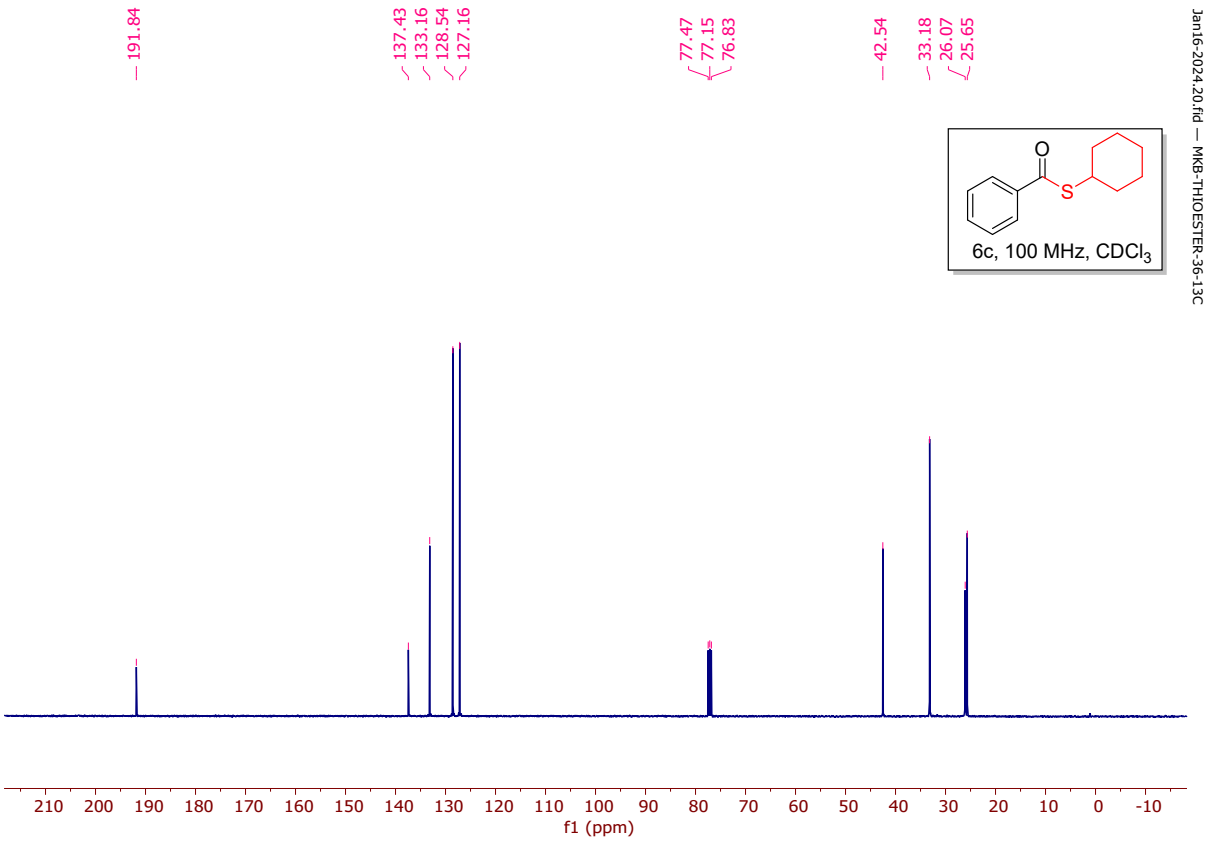
6b - ^{1}H & ^{13}C NMR


8.0072
8.0044
8.0006
7.9918
7.9869
7.9831
7.5916
7.5882
7.5850
7.5748
7.5698
7.5650
7.5547
7.5513
7.5479
7.4734
7.4693
7.4568
7.4535
7.4394
7.4347
3.1064
3.0881
3.0696
1.7101
1.6912
1.6723
1.6537
1.3428
1.3218
1.3026
1.2838
0.9217
0.9053
0.8879
Dec30-2023.30.fid — MKB-THIOESTER-33-1H
6b, 400 MHz, CDCl3
2.00
1.04
2.05
2.26
2.23
13.87
3.35
f1 (ppm)

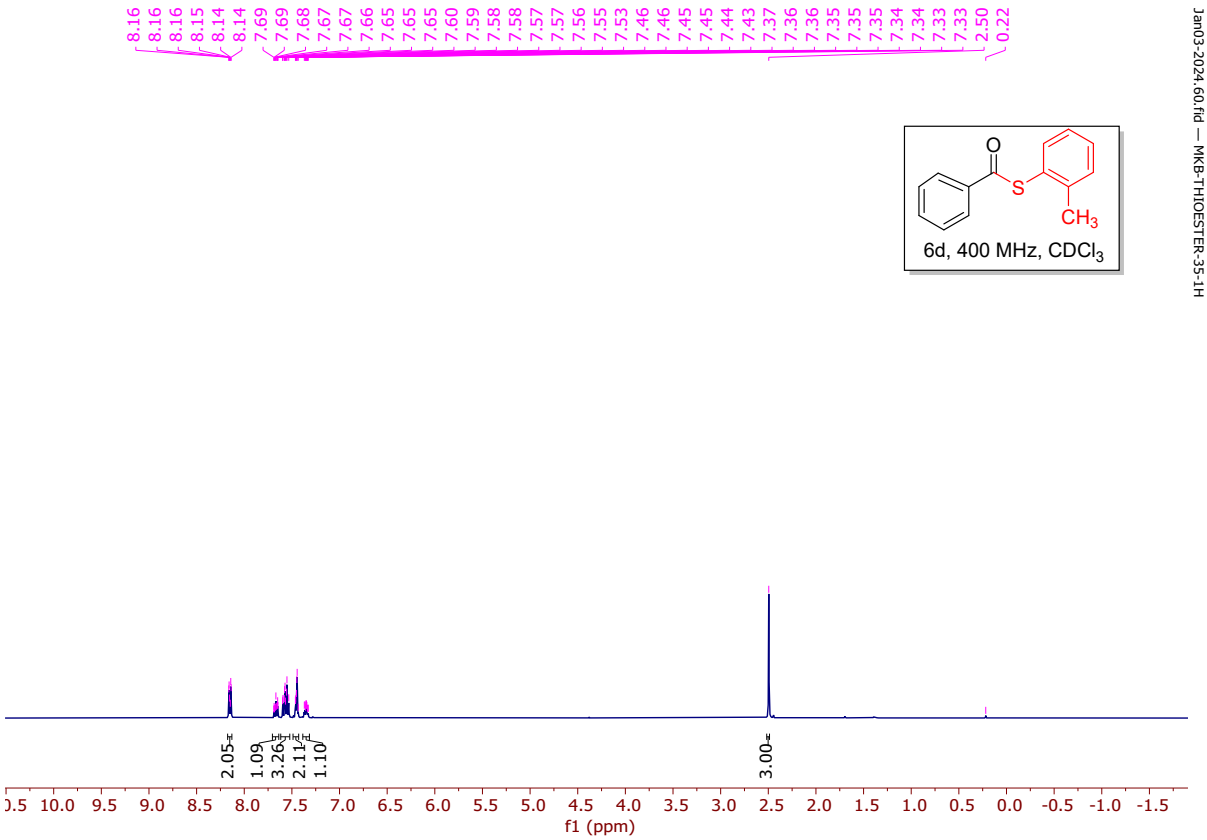

192.0939
137.2733
133.1977
128.5515
127.1915
77.4116
77.0938
76.7761
31.9707
29.7031
29.6877
29.6454
29.6184
29.5644
29.4107
29.2221
29.0736
29.0018
22.7459
14.1791
Jan03-2024.30.fid — MKB-THIOESTER-33 RIGHT-13C
6b, 100 MHz, CDCl3
f1 (ppm)

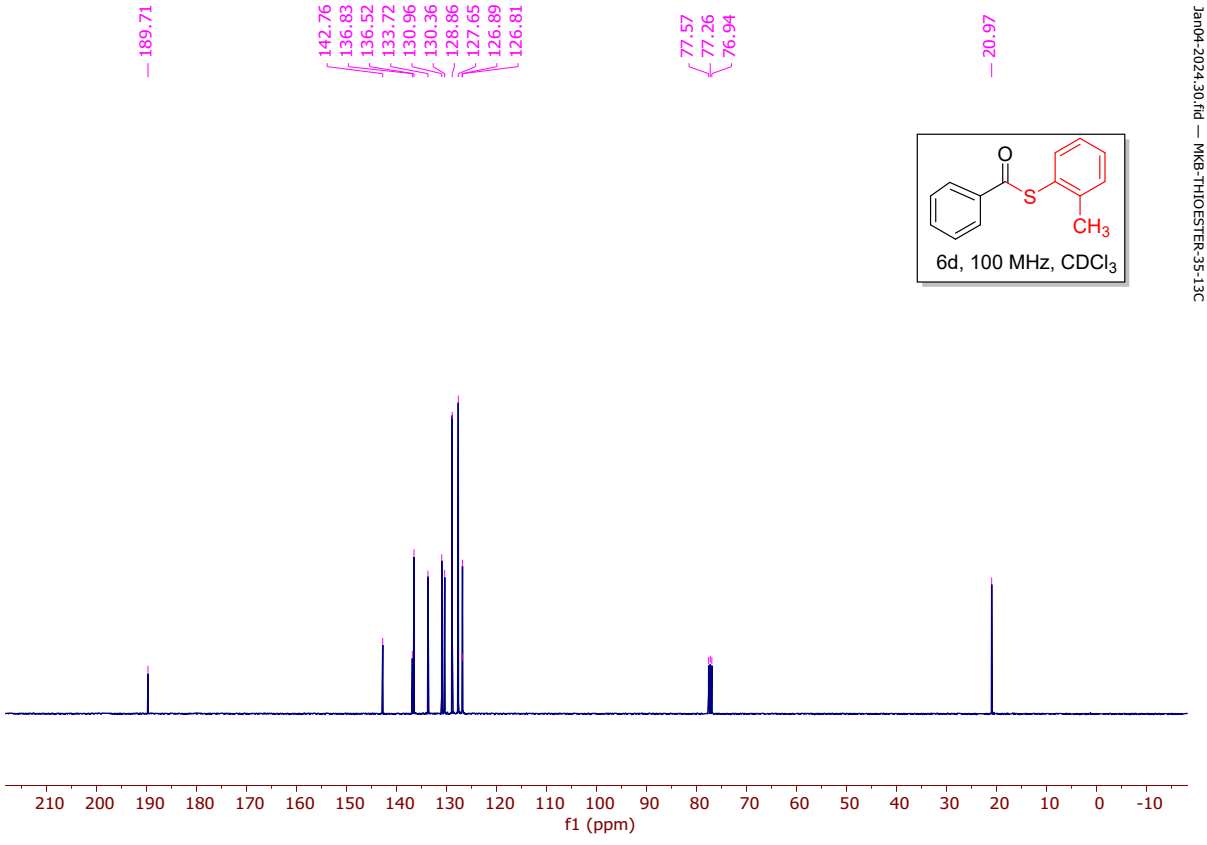
6c - ^{1}H & ^{13}C NMR


7.98 7.98 7.98 7.97 7.96 7.96 7.57 7.56 7.55 7.55 7.54 7.53 7.53 7.46 7.45 7.44 7.44 7.42 7.42 7.42 7.42 3.75 3.74 2.06 2.06 2.05 2.04 2.03 2.03 2.02 1.79 1.78 1.77 1.76 1.75 1.75 1.74 1.65 1.63 1.63 1.62 1.62 1.55 1.55 1.53 1.52 1.51 1.50 1.50 1.49 1.48 1.47 1.34 1.31 0.11
Jan12-2024.40.fid — MKB-THIOESTER-36-1H
6c, 400 MHz, CDCl3
2.00 1.01 2.04 1.02 2.14 2.22 1.10 4.12 1.19
f1 (ppm)

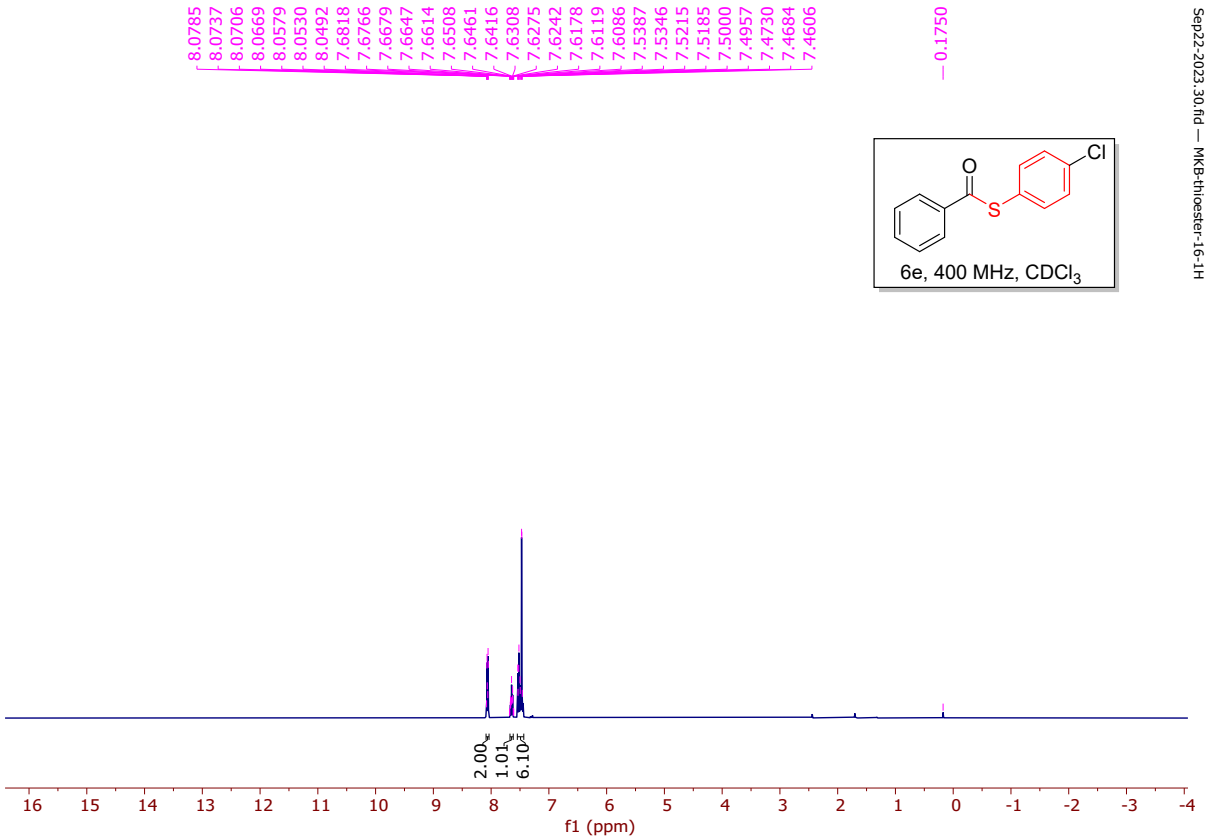

191.84
137.43 133.16 128.54 127.16
77.47 77.15 76.83
42.54
33.18 26.07 25.65
Jan16-2024.20.fid — MKB-THIOESTER-36-13C
6c, 100 MHz, CDCl3
f1 (ppm)

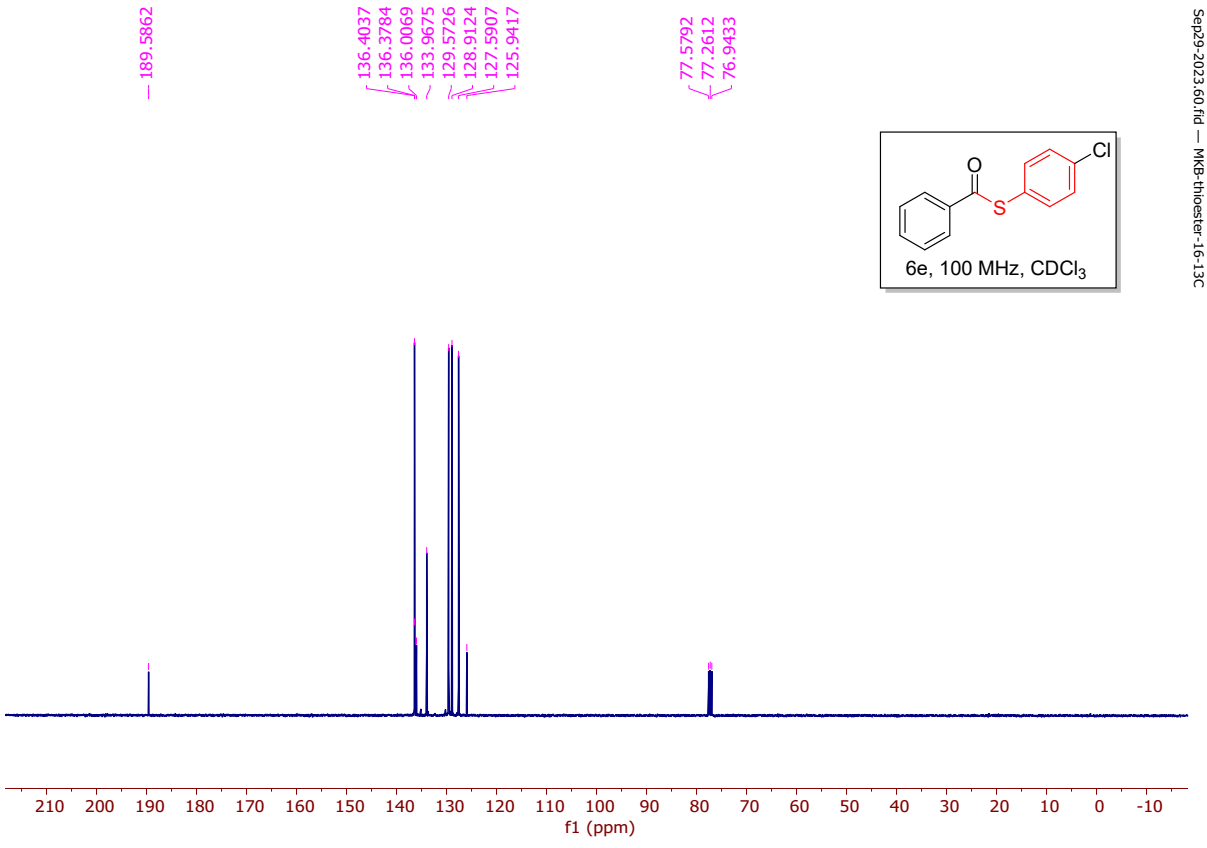
6d - ^{1}H & ^{13}C NMR


8.16 8.16 8.16 8.15 8.14 8.14 7.69 7.69 7.68 7.67 7.67 7.66 7.65 7.65 7.65 7.60 7.59 7.58 7.58 7.57 7.57 7.56 7.55 7.53 7.46 7.46 7.45 7.45 7.44 7.43 7.37 7.36 7.36 7.35 7.35 7.35 7.34 7.34 7.33 7.33 2.50 0.22
Jan03-2024.60.fid — MKB-THIOESTER-35-1H
O
S
CH3
6d, 400 MHz, CDCl3
2.05 1.09 3.26 2.11 1.10 3.00
f1 (ppm)

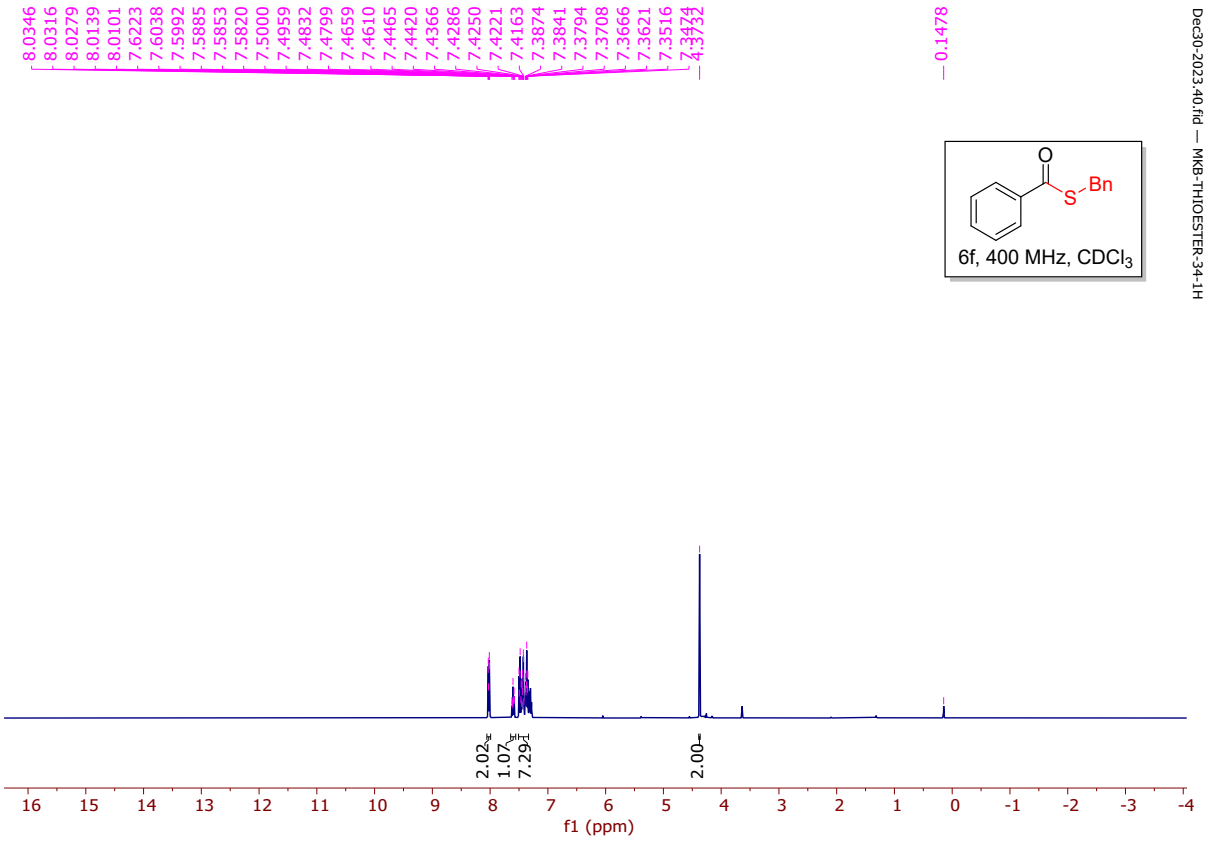

189.71
142.76 136.83 136.52 133.72 130.96 130.36 128.86 127.65 126.89 126.81
77.57 77.26 76.94
20.97
Jan04-2024.30.fid — MKB-THIOESTER-35-13C
O
S
CH3
6d, 100 MHz, CDCl3
f1 (ppm)

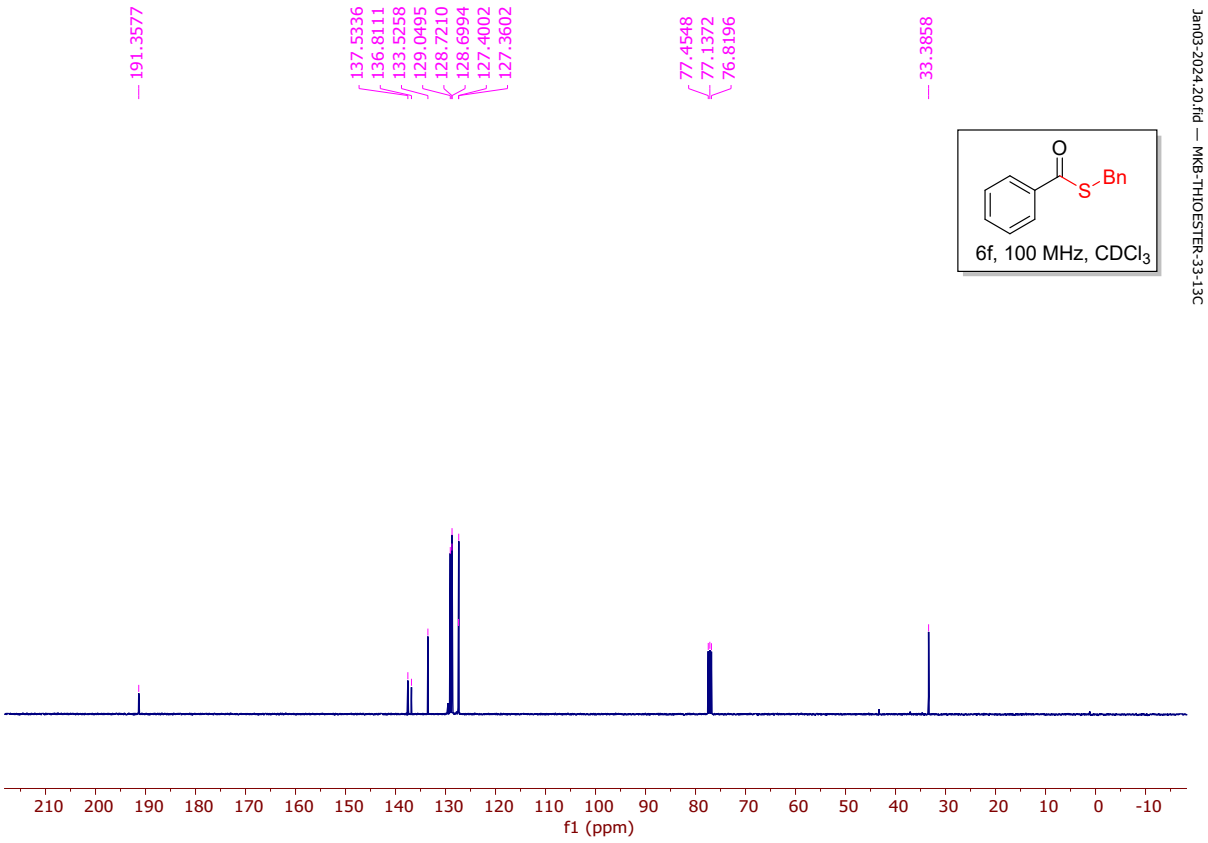
6e - ^{1}H & ^{13}C NMR


8.0785
8.0737
8.0706
8.0669
8.0579
8.0530
8.0492
7.6818
7.6766
7.6679
7.6647
7.6614
7.6508
7.6461
7.6416
7.6308
7.6275
7.6242
7.6178
7.6119
7.6086
7.5387
7.5346
7.5215
7.5185
7.5000
7.4957
7.4730
7.4684
7.4606
0.1750
Sep22-2023.30.fid — MKB-thioester-16-1H
Cl
O
S
6e, 400 MHz, CDCl3
2.00
1.01
6.10
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

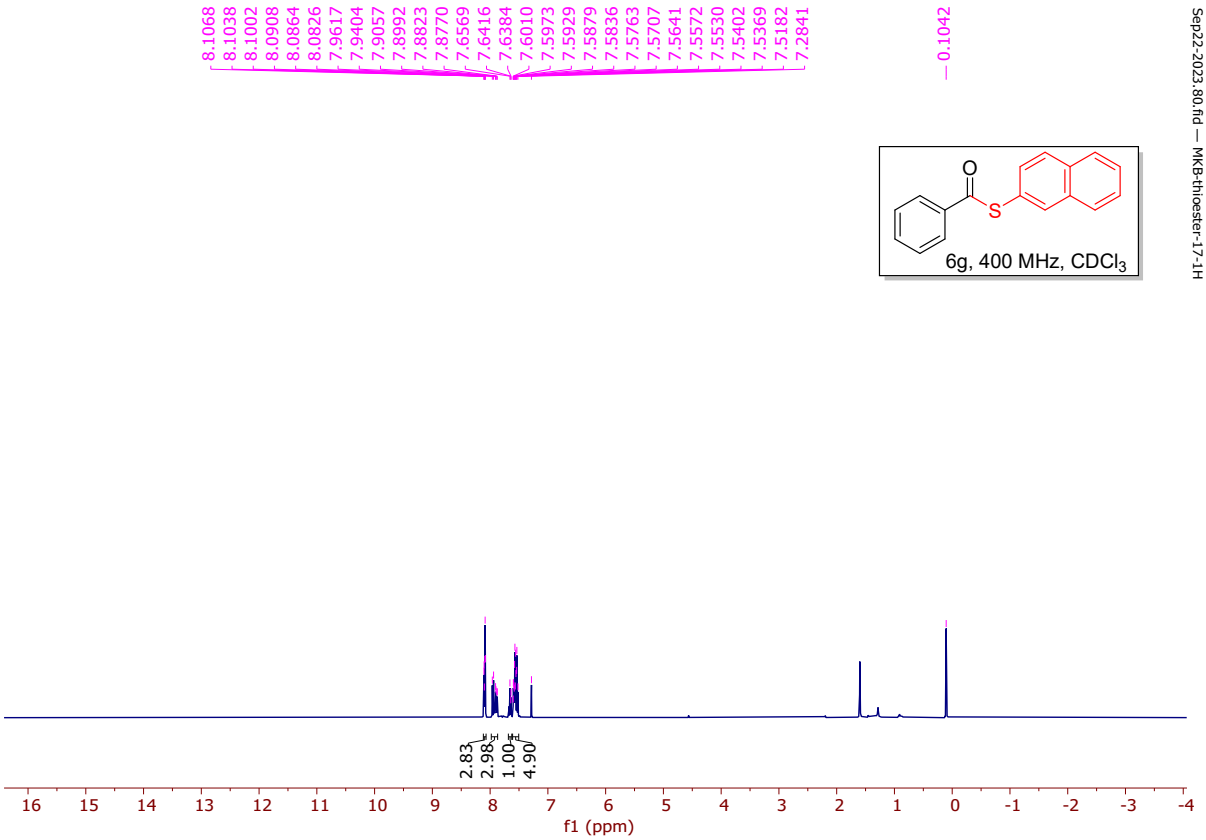

189.5862
136.4037
136.3784
136.0069
133.9675
129.5726
128.9124
127.5907
125.9417
77.5792
77.2612
76.9433
Sep29-2023.60.fid — MKB-thioester-16-13C
Cl
O
S
6e, 100 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

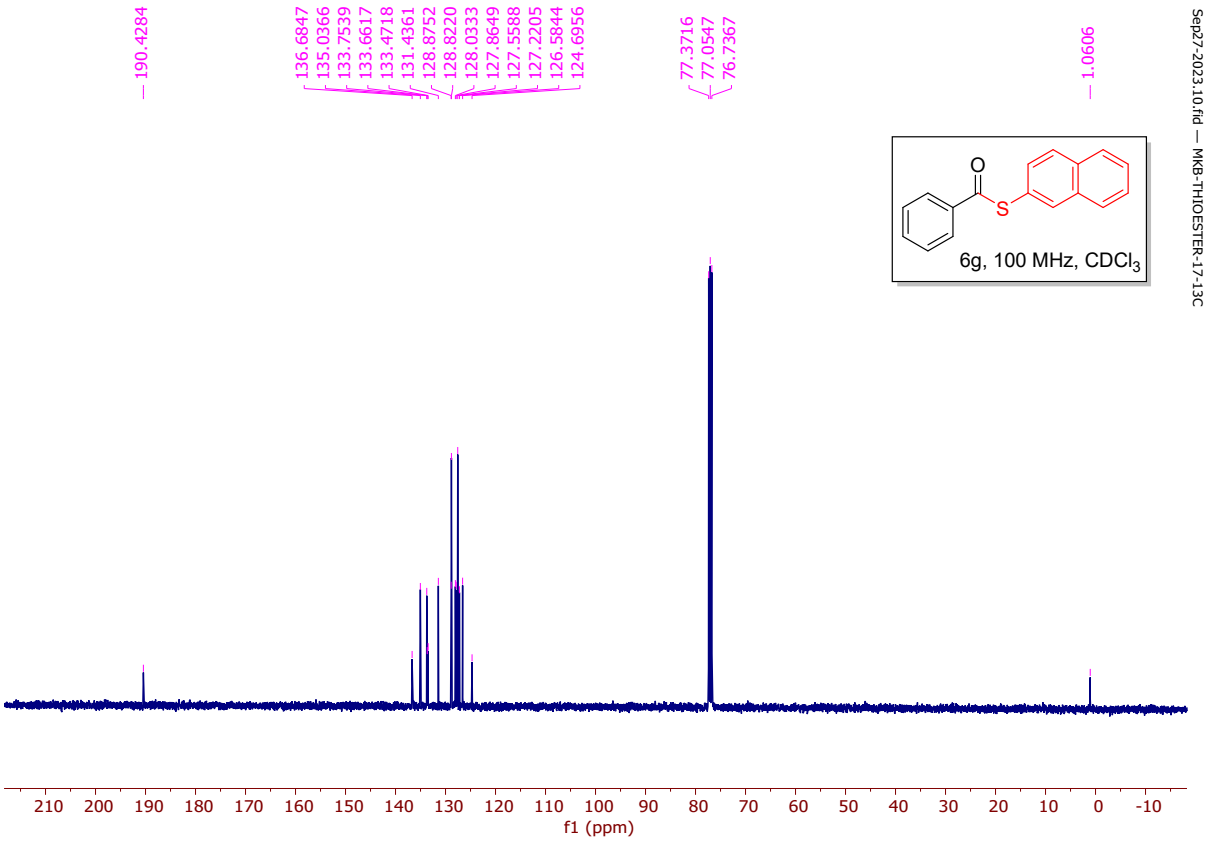
6f - ^{1}H & ^{13}C NMR


8.0346
8.0316
8.0279
8.0139
8.0101
7.6223
7.6038
7.5992
7.5885
7.5853
7.5820
7.5000
7.4959
7.4832
7.4799
7.4659
7.4610
7.4465
7.4420
7.4366
7.4286
7.4250
7.4221
7.4163
7.3874
7.3841
7.3794
7.3708
7.3666
7.3621
7.3516
7.3424
7.3732
0.1478
Dec30-2023-40.fid — MKB-THIOESTER-34-1H
O
S
Bn
6f, 400 MHz, CDCl3
2.02
1.07
7.29
2.00
f1 (ppm)

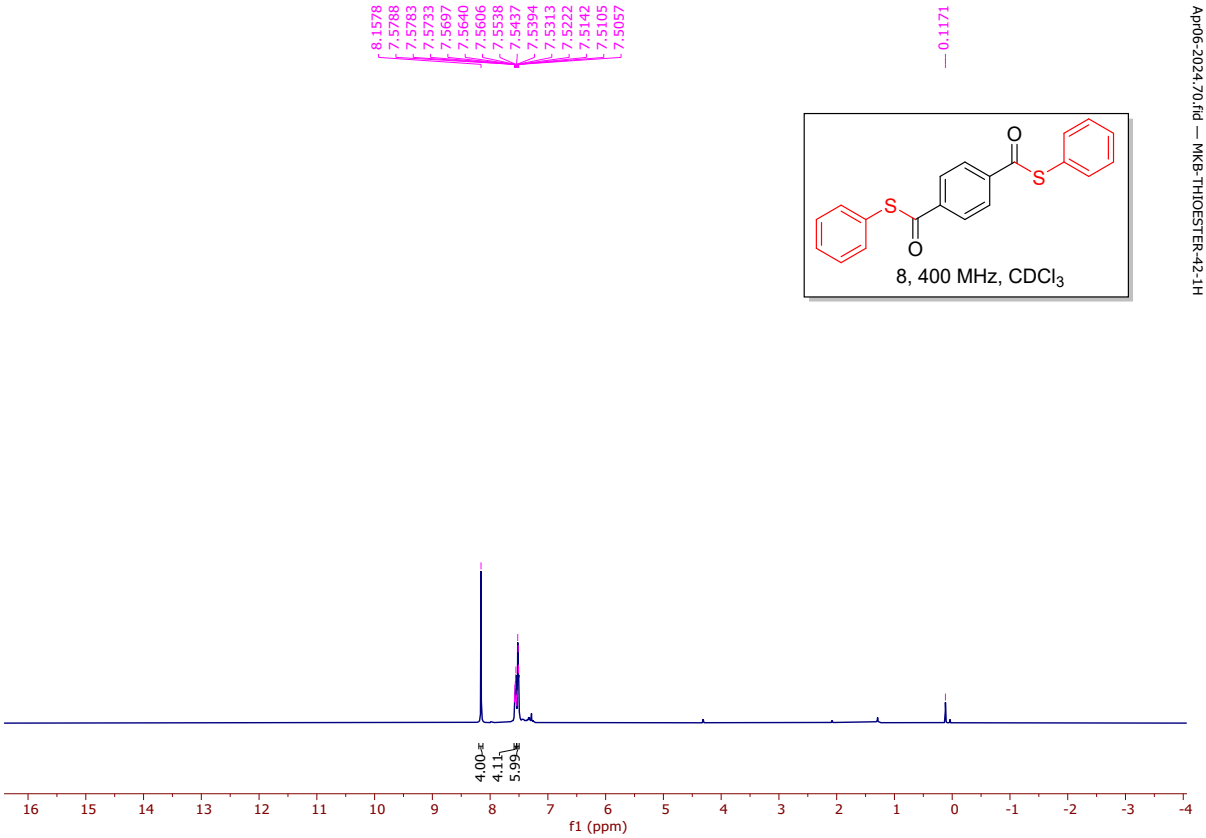

191.3577
137.5336
136.8111
133.5258
129.0495
128.7210
128.6994
127.4002
127.3602
77.4548
77.1372
76.8196
33.3858
Jan03-2024-20.fid — MKB-THIOESTER-33-13C
O
S
Bn
6f, 100 MHz, CDCl3
f1 (ppm)

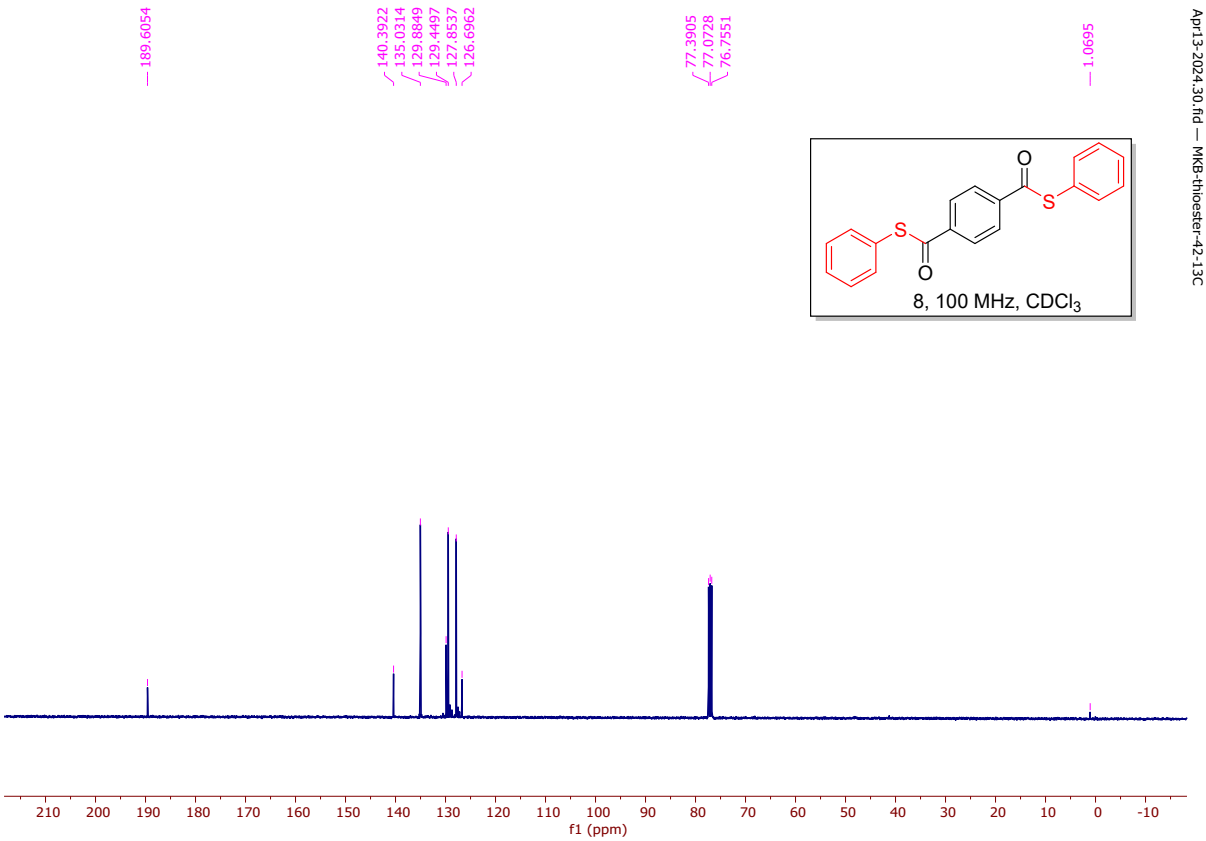
6g - ^{1}H & ^{13}C NMR


8.1068
8.1038
8.1002
8.0908
8.0864
8.0826
7.9617
7.9404
7.9057
7.8992
7.8823
7.8770
7.6569
7.6416
7.6384
7.6010
7.5973
7.5929
7.5879
7.5836
7.5763
7.5707
7.5641
7.5572
7.5530
7.5402
7.5369
7.5182
7.2841
0.1042
O
S
6g, 400 MHz, CDCl3
Sep22-2023.80.fid — MKB-thioester-17-1H
2.83
2.98
1.00
4.90
f1 (ppm)

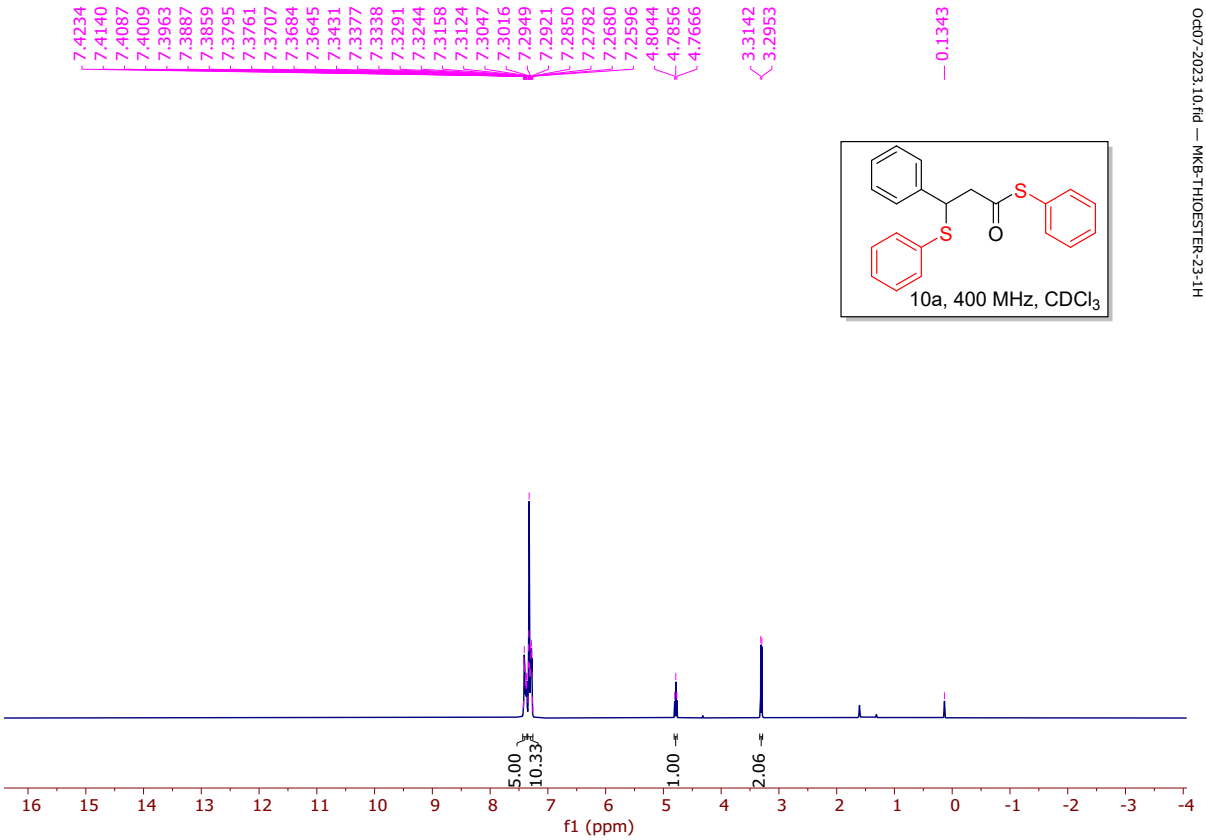

190.4284
136.6847
135.0366
133.7539
133.6617
133.4718
131.4361
128.8752
128.8220
128.0333
127.8649
127.5588
127.2205
126.5844
124.6956
77.3716
77.0547
76.7367
1.0606
O
S
6g, 100 MHz, CDCl3
Sep27-2023.10.fid — MKB-THIOESTER-17-13C
f1 (ppm)

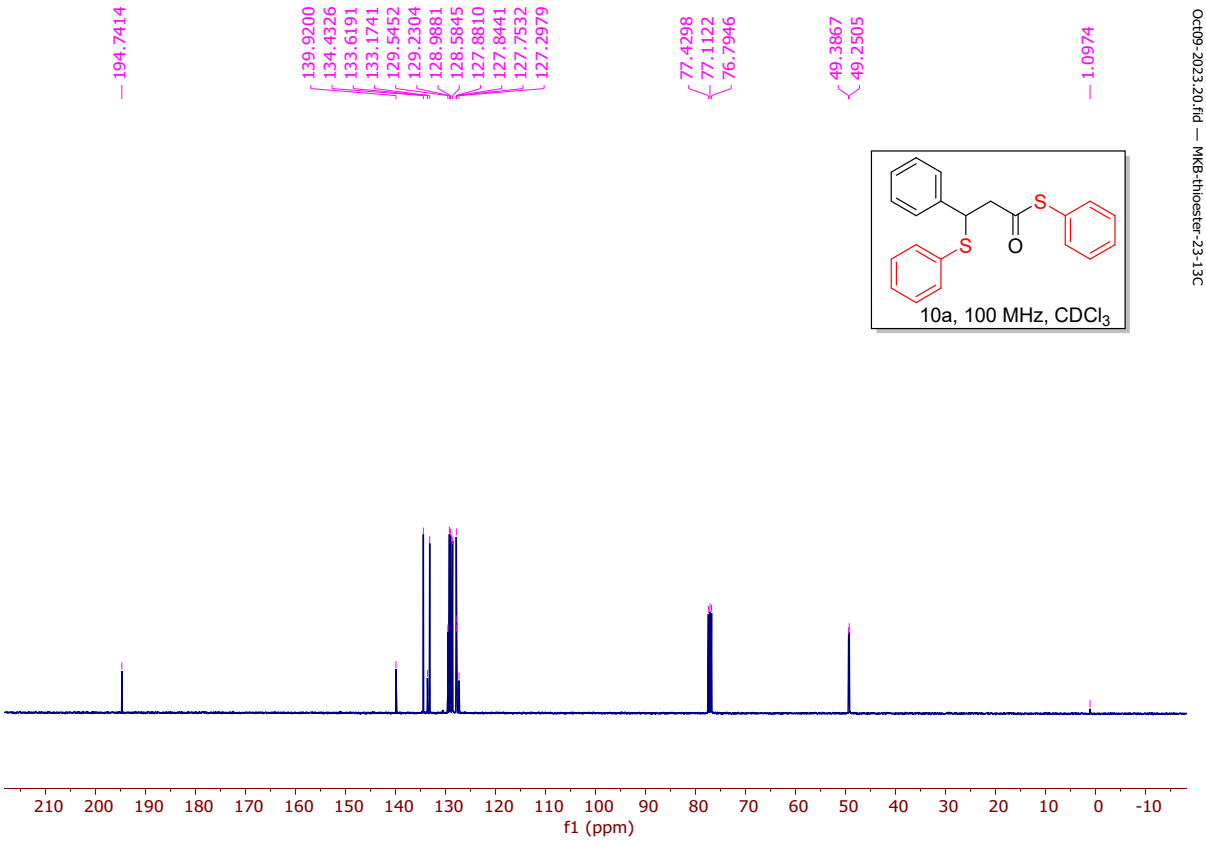
8- 1H & 13C NMR


8.1578
7.5788
7.5783
7.5733
7.5697
7.5640
7.5606
7.5538
7.5437
7.5394
7.5313
7.5222
7.5142
7.5105
7.5057
0.1171
Apr06-2024.70.fid — MKB-THIOESTER-42-1H
8, 400 MHz, CDCl3
4.00
4.11
5.99
f1 (ppm)

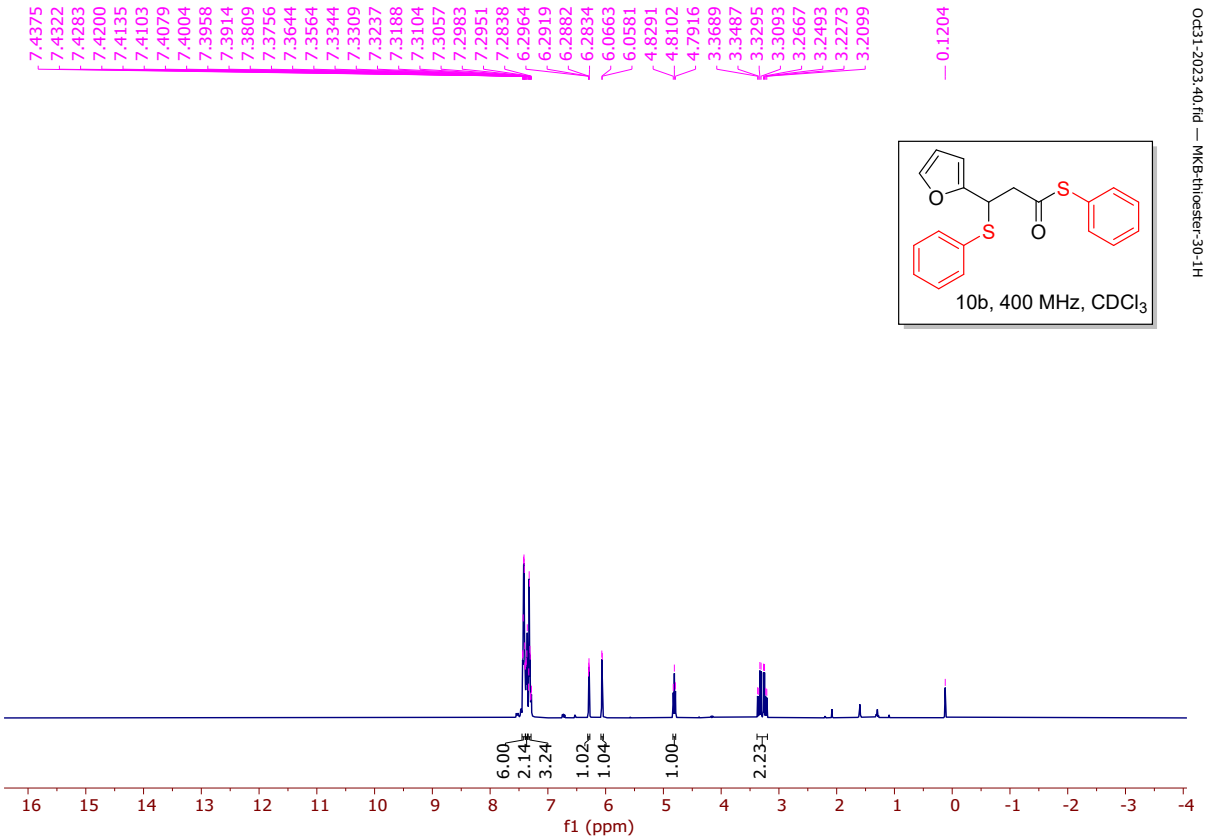

189.6054
140.3922
135.0314
129.8849
129.4497
127.8537
126.6962
77.3905
77.0728
76.7551
1.0695
Apr13-2024.30.fid — MKB-thioester-42-13C
8, 100 MHz, CDCl3
f1 (ppm)

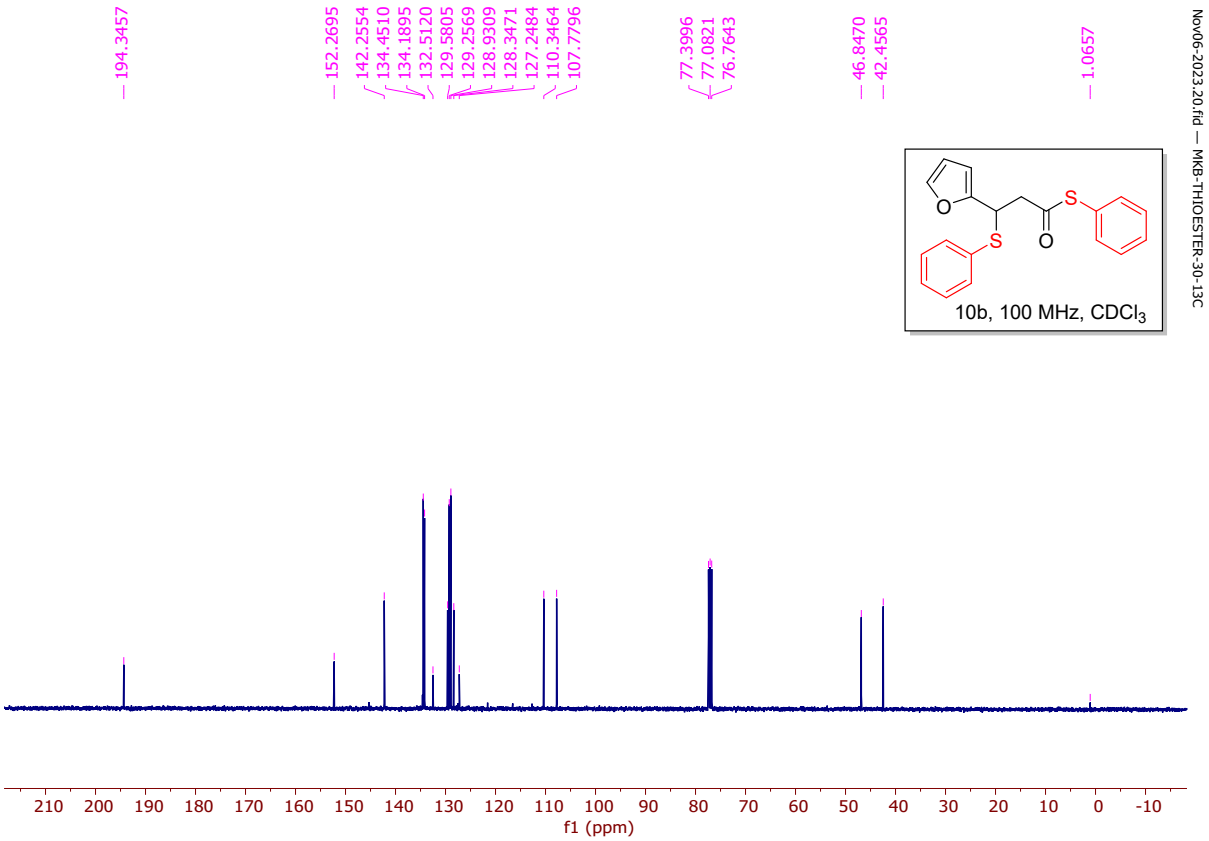
10a - ^{1}H & ^{13}C NMR



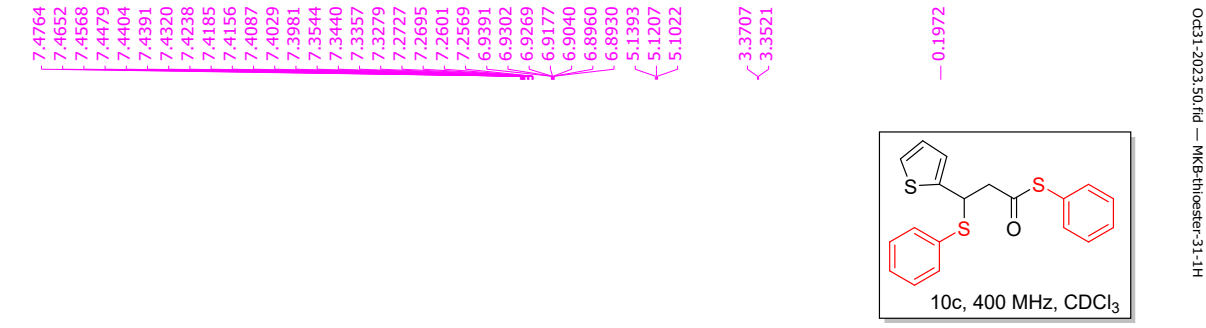


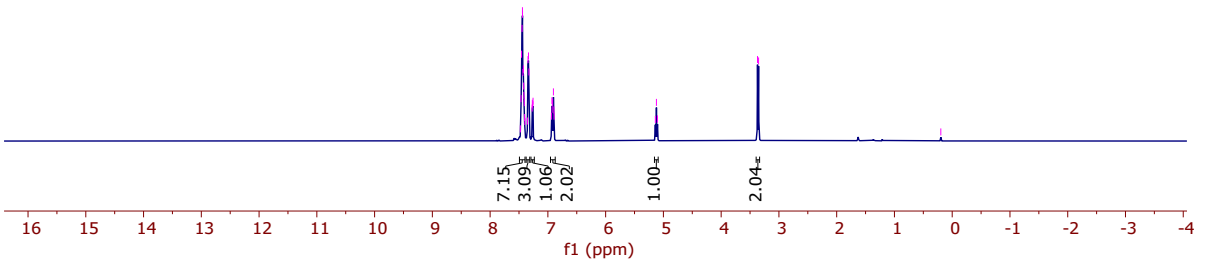
10b - ^{1}H & ^{13}C NMR

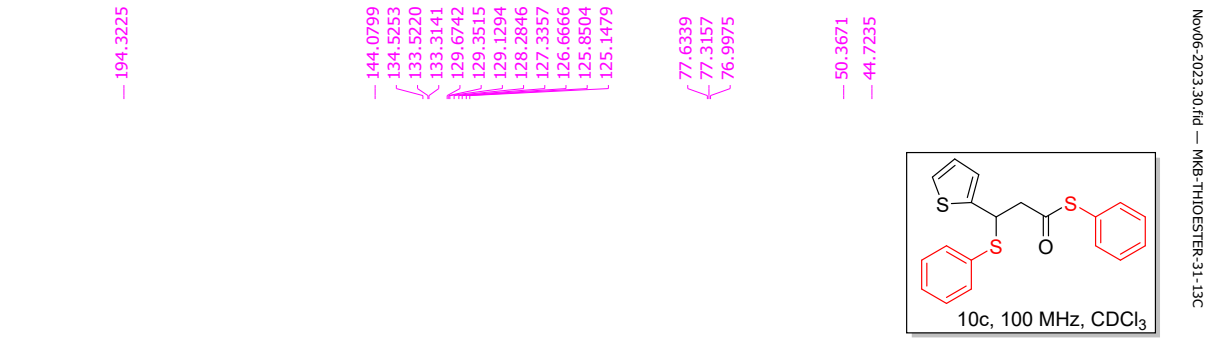


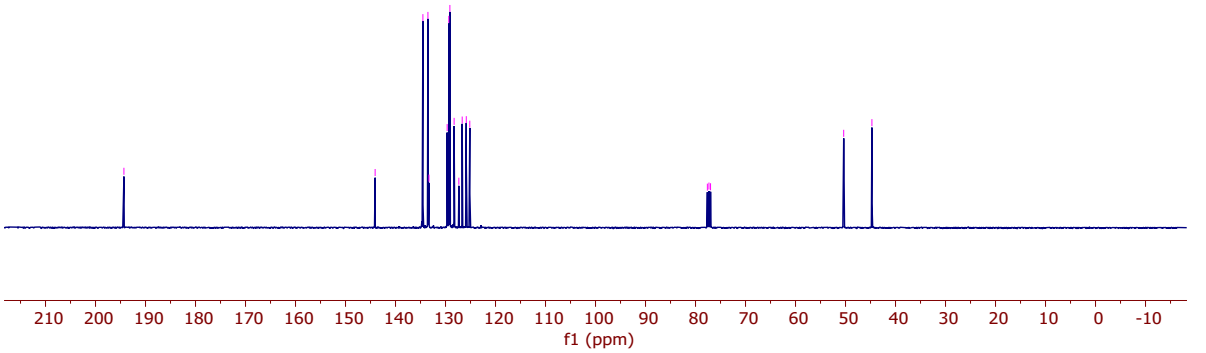


10c - ^{1}H & ^{13}C NMR

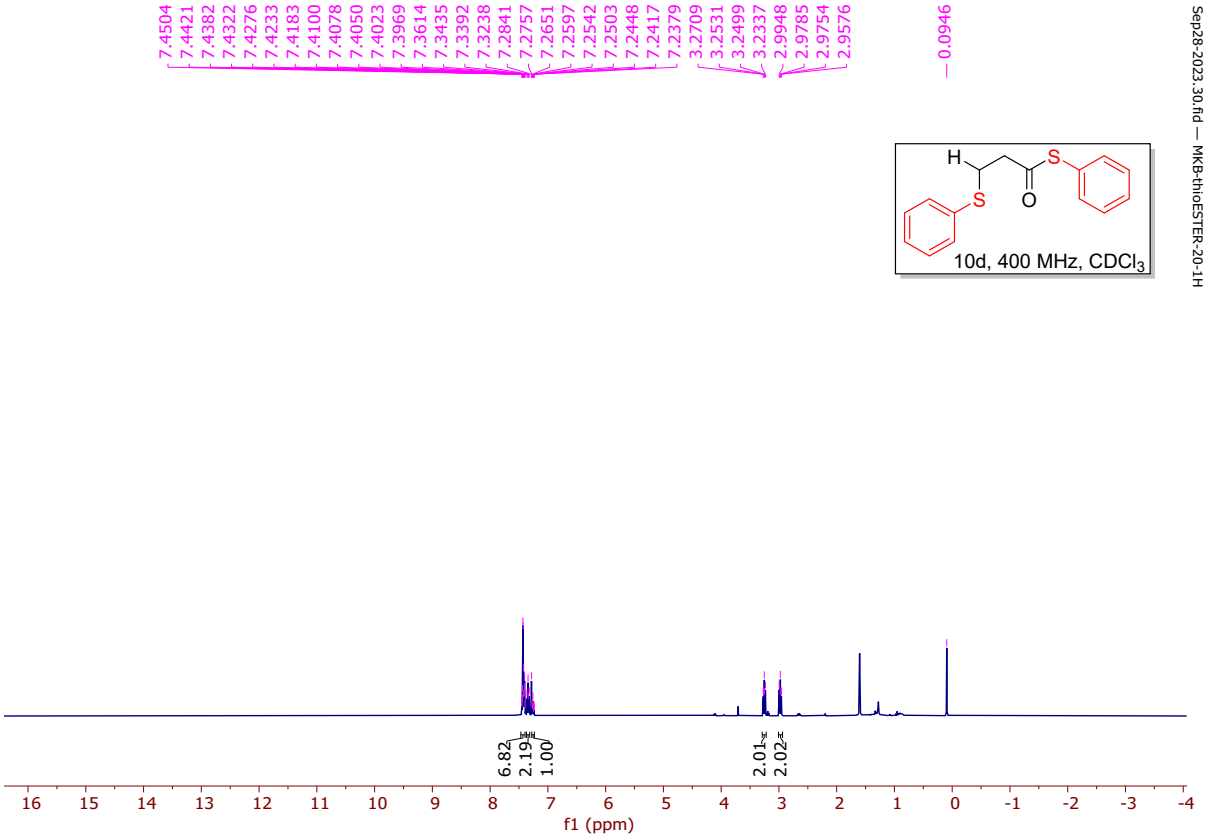


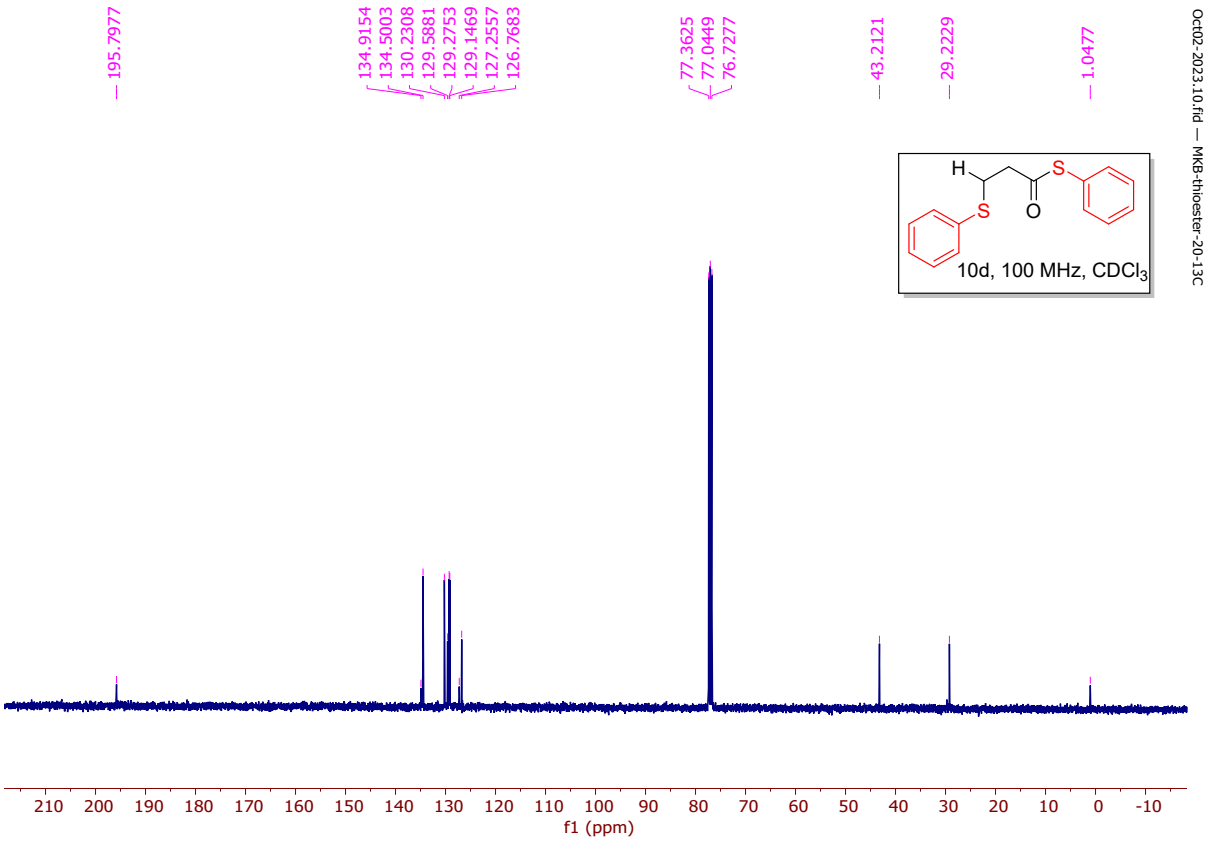




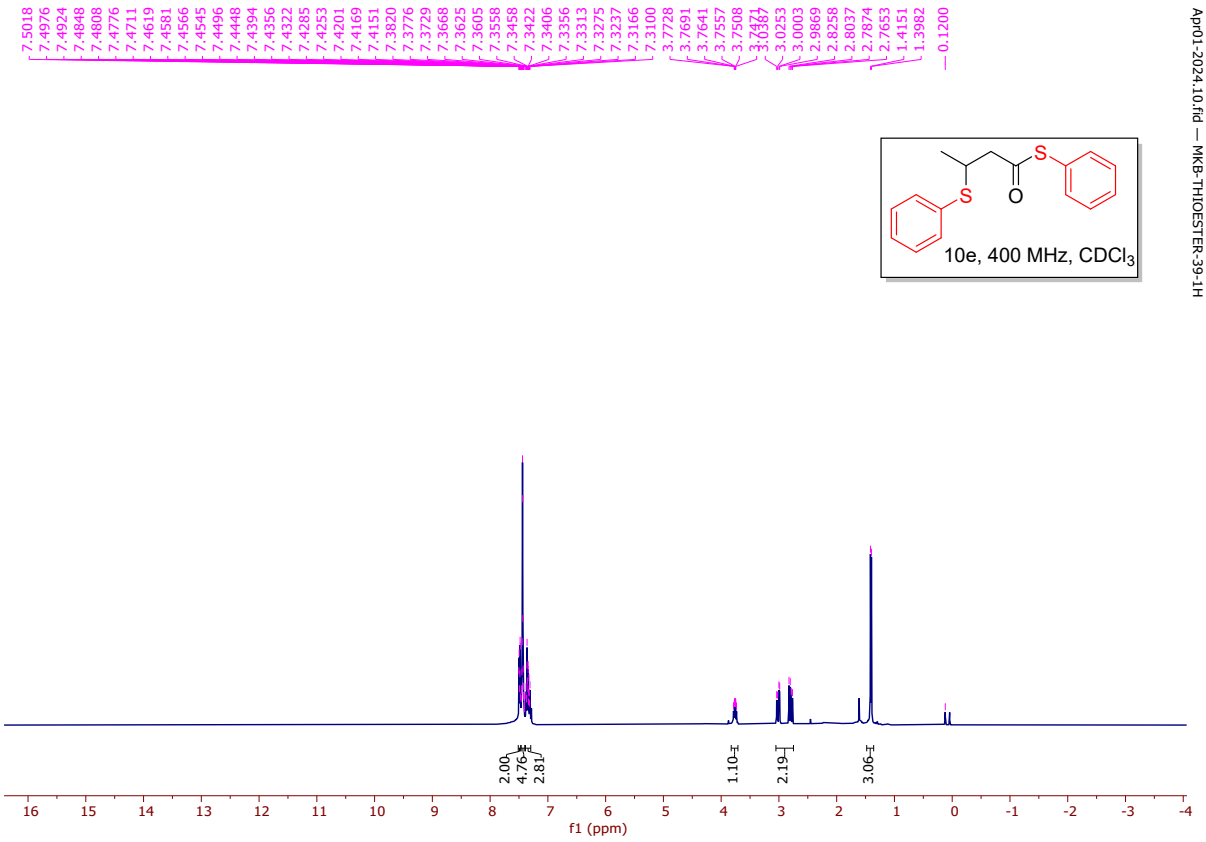


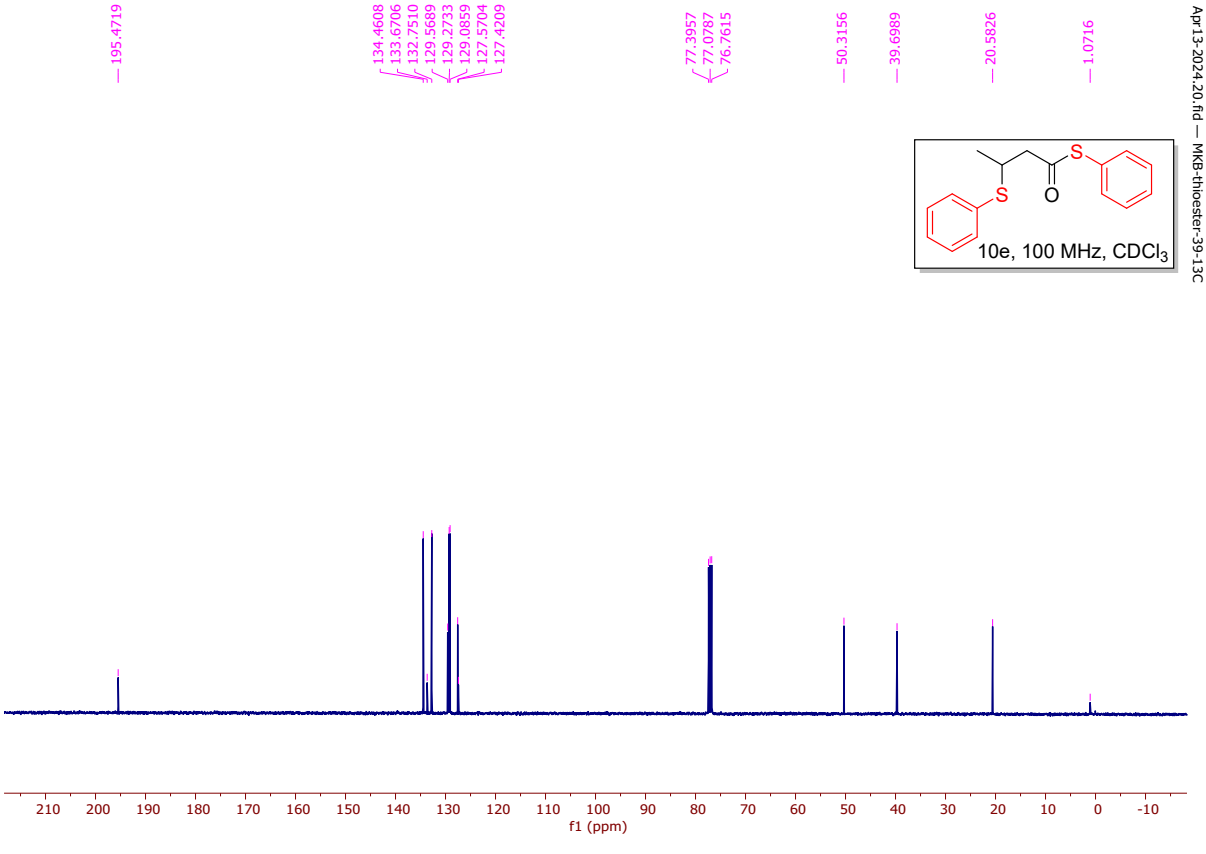
10d - ^{1}H & ^{13}C NMR



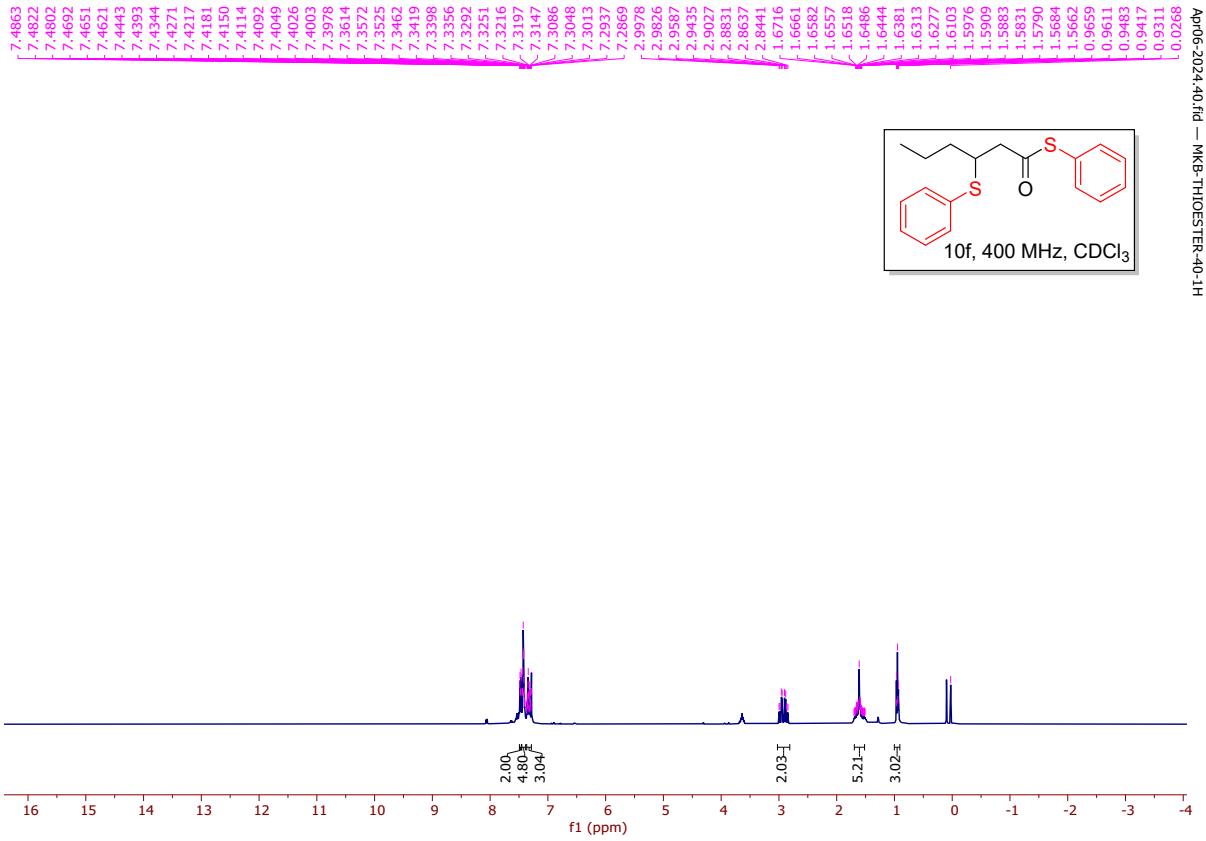


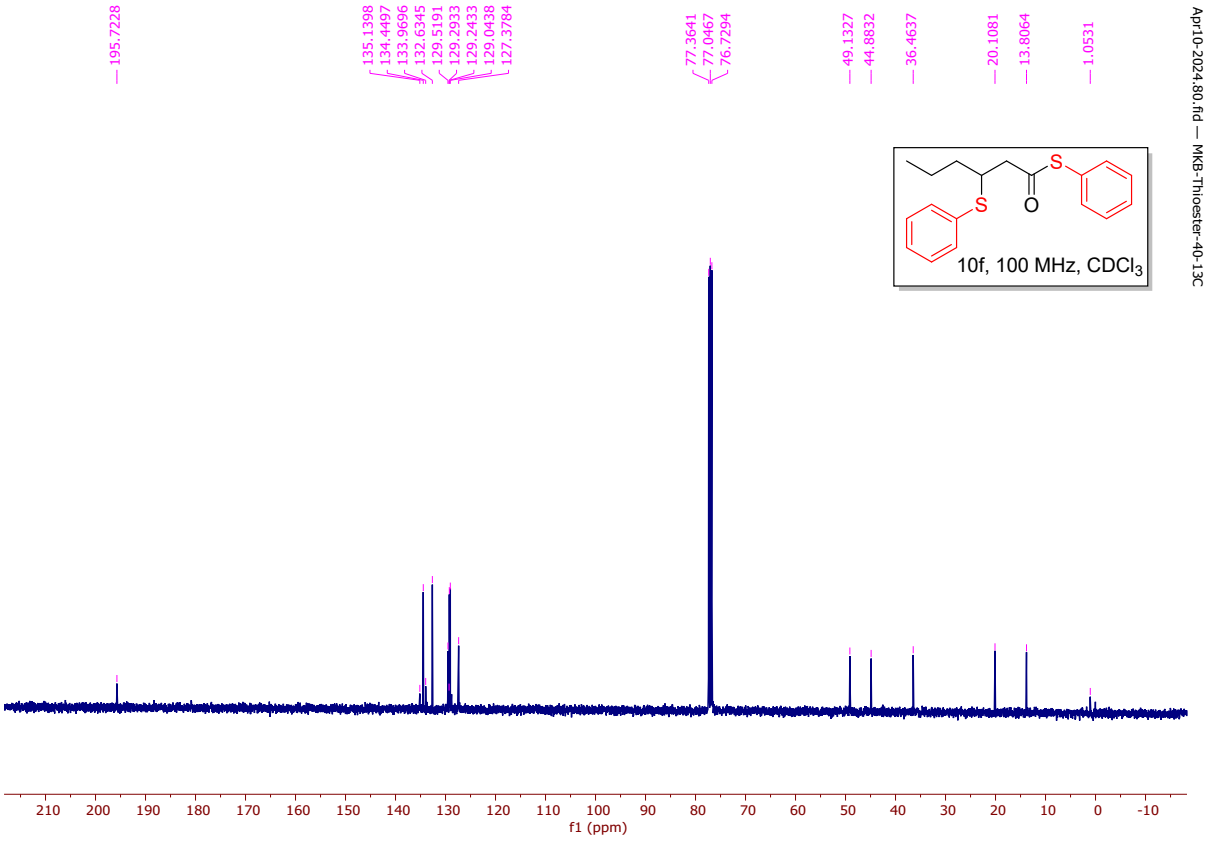
10e - ^{1}H & ^{13}C NMR





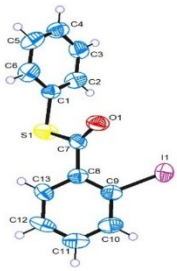
10f - ^{1}H & ^{13}C NMR





9. Single crystal XRD study of thioester 2j

ORTEP diagram of 2j drawn with 50% contour space probability for all non-H atoms.



Refined crystal data of 2j (CCDC no – 2339403)	
Empirical formula	$C_{13}H_9IOS$
Formula weight	340.1785
Temperature/K	298
Crystal system	Monoclinic
Space group	P 21/C
a/Å	18.834(3)
b/Å	7.9364(13)
c/Å	17.557(3)
α/°	90
β/°	103.605(6)
γ/°	90
Volume/Å^3	2550.7(7)
Z	27
ρ/g.cm^{-3}	1.772
μ/mm^{-1}	2.650
F (000)	1312
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.225 to 24.854
Index ranges	$-22 \leq h \leq 22, -9 \leq k \leq 9, -20 \leq l \leq 20$
Reflections collected	57729
Independent reflections	4423
Goodness-of-fit on F^2	1.160
Final R indexes [I >= 2σ (I)]	$R_1 = 0.0494$, $wR_2 = 0.1512$
Final R indexes (all data)	$R_1 = 0.0723$, $wR_2 = 0.1699$