# Supporting Information

# Unusual Radical Addition on a Heteroaromatic Nitrogen. A convenient Access to New Pyrimidine Derivatives

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**Contents:**

# General Experimental Methods

Anhydrous THF was obtained by distillation from sodium-benzophenone ketyl under nitrogen. Other solvents were used as supplied by commercial sources. Petroleum ether refers to the fraction of light petroleum ether, boiling between 40-60°C. All liquid reagents were distilled prior to use. Purification procedures were in accordance with the instructions in D. D. Perrin and W. L. F. Armarego, "Purification of Laboratory Chemicals", Fourth Edition, The Bath Press, Bath, 2002. All reactions were carried out under dry, oxygen free nitrogen. Flash chromatography was performed on silica gel (SDS, 60 Å C. C. 40-63 μm) as the stationary phase. Thin Layer Chromatography (TLC) was performed on alumina plates pre-coated with silica gel (Merck silica gel, 60 $F_{254}$), which were visualized by the quenching of UV fluorescence ($\lambda_{max}$ = 254 nm and/or 366 nm) and/or by staining with vanillin in acidic ethanol followed by heating. Melting points were recorded by heating on Reichert plates under a microscope and are uncorrected. Infrared spectra were recorded as solutions in $CCl_4$ using $CaF_2$ cells, on a Perkin-Elmer FT 1600. Absorption maxima ($\nu_{max}$) are reported in wavenumbers ($cm^{-1}$) and only selected peaks are reported. Magnetic resonance spectra were recorded at ambient temperature on either a Bruker AMX 400, or a Bruker Avance DPX 400 instruments. Proton magnetic resonance spectra ($^1$H NMR) were recorded at 400 MHz and coupling constants (*J*) are reported to ± 0.5 Hz. The following abbreviations were utilized to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. Carbon magnetic resonance spectra ($^{13}$C NMR) were recorded at 100.6 MHz. Chemical shifts ($\delta_H$, $\delta_C$) are quoted in parts per million (ppm) and are referenced to the residual solvent peak ($CDCl_3$: $\delta_H$ = 7.26 and $\delta_C$ = 77.0). Low-resolution mass spectra (*m/z*) were recorded by chemical ionization (CI/$NH_3$) on a Hewlett-Packard HP 5989B and only report molecular species ($[M+H]^+$, $[M+NH_4]^+$) and other major fragments. High-resolution mass spectra were recorded by positive electron impact ionization (EI+) at 70 eV on a JEOL JMS-GCmate II mass spectrometer. The quoted masses are accurate to ± 5 ppm.

**General procedure A for the intermolecular addition of xanthate:**

A solution of olefin (n mmol) and xanthate (2-3 n mmol) in ethyl acetate (n mL) was refluxed 10 min under nitrogen and 10 mol % of DLP were added followed by 5 mol % every 90 min until complete consumption of the olefin. The mixture was then cooled down to room temperature and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel to yield the corresponding xanthate.

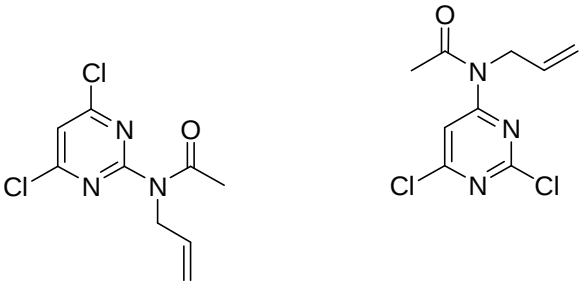
**General procedure B for the radical cyclisation to diazaindolines:**

A solution of xanthate **14a-e** (n mmol) in ethyl acetate (10 n mL) was refluxed 10 min. under nitrogen. Dibenzoyl peroxide (75% in water) (1.2 n mmol) was then added followed by 20 mol % of DLP every 60 min until complete consumption of the xanthate. The mixture was then cooled down to room temperature and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel to yield the corresponding diazaindoline **15a-e**. Residual benzoic acid may contamine the final compound but can be readily eliminated by filtration through a short pad of basic alumina.

**General procedure C for the radical cyclisation to dihydroimidazopyrimidinones:**

A solution of xanthate **9a-g** (n mmol) in ethyl acetate (10-15n mL) was refluxed 10 min. under nitrogen. 20 mol % of DLP were then added followed by 20 mol % every 60 min until complete consumption of the xanthate. The mixture was then cooled down to room temperature and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel to yield the corresponding bicycle **10a-g**.

***N*-allyl-N-(4,6-dichloropyrimidin-2-yl)acetamide (7a) and *N*-allyl-N-(2,6-dichloropyrimidin-4-yl)acetamide (7b)**



Allylamine (34.4 mL, 458 mmol, 2.4 equiv.) in ethanol (35 mL) was slowly added to a solution of trichloropyrimidine (21.94 mL, 190.8 mmol, 1.0 equiv.) in ethanol (200 mL) at 0°C. After the addition was complete, the mixture was stirred 3 hours at room temperature. The solvent was then removed under reduced pressure and the residue was dissolved in dichloromethane and washed with water. The organics were dried ($MgSO_4$), filtered and concentrated. The resulting crude was dissolved in acetic anhydride (100 mL) and heated at reflux temperature for 2 hours. Evaporation under reduced pressure yielded an oil that was dissolved in dichloromethane and then washed with 5% $NaHCO_3$, water and brine. The organics were dried, filtered and the solvent removed under reduced pressure. Purification by flash chromatography on silica gel (petroleum ether-diethyl ether 99:1 to 50:50) gave **7a** (13.09 g 28%**)** and **7b** (26.18 g, 56 %**).**

**7a :**

**$^1$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 7.03 (s, 1H), 5.78-5.85 (m, 1H), 5.11-5.16 (m, 1H), 5.05-5.08 (m, 1H), 4.62-4.66 (d, *J* = 5.6 Hz, 2H), 2.53 (s, 3H).

**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 171.9 (C), 161.7 (2C), 159.8 (C), 132.7 (CH), 117.4 ($CH_2$), 115.3 (CH), 47.8 ($CH_2$), 26.8 ($CH_3$).

**IR ($CCl_4$):** $\nu_{max}$ 3085, 2989, 2957, 1700, 1645.

**MS** (CI, $NH_3$) *m/z* 246 ($MH^+$), 248 ($MH+2^+$), 250 ($MH+4^+$).

**HRMS (EI+):** calculated for $C_9H_9ON_3Cl_2$ 245.0123, found 245.0123.

**7b :**

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 8.06 (s, 1H), 5.91 (m, 1H), 5.24 (m, 1H), 5.13 (m, 1H), 4.64 (d, *J* = 4.8 Hz, 2H), 2.41 (s, 3H).

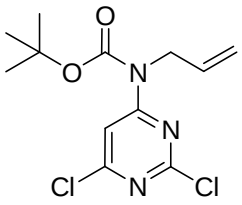
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 172.4 (C), 162.6 (C), 161.6 (C), 159 (C), 132.1 (CH), 117.3 ($CH_2$), 111.4 (CH), 48.9 ($CH_2$), 26.8 ($CH_3$).

**IR ($CCl_4$):** $\nu_{max}$ 3087, 2985, 1707, 1647, 1551, 1529, 1407.

**MS** (CI, $NH_3$) *m/z* 246 ($MH^+$), 248 ($MH+2^+$), 250 ($MH+4^+$).

**HRMS (EI+):** calculated for $C_9H_9ON_3Cl_2$ 245.0123, found 245.0123.

***Tert*-butyl allyl(2,6-dichloropyrimidin-4-yl)carbamate (7c)**




Following the procedure described for **7a** and **7b**, and using standard conditions for Boc protection, **7c** was obtained in 53% yield for two steps (on a 20 mmol scale).

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 8.11 (s, 1H), 5.87 (m, 1H), 5.13-5.21, (m, 2H), 4.61 (d, *J* = 5.6 Hz, 2H), 1.54 (s, 9H).

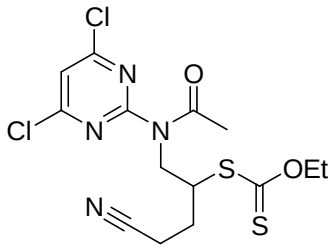
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 162.1 (C), 161.9 (C), 158.9 (C), 152.6 (C), 132.6 (CH), 117.4 ($CH_2$), 110.0 (C), 84.0 (C), 48.1 ($CH_2$), 28.0 ($3CH_3$).

**IR ($CCl_4$):** $\nu_{max}$ 2980, 1730, 1555, 1527

**MS** (CI, $NH_3$) *m/z* 304 ($MH^+$), 306 ($MH+2^+$), 308 ($MH+4^+$).

**HRMS (EI+):** calculated for $C_{12}H_{15}O_2N_3Cl_2$ 303.0541, found 303.0540.

***S*-4-cyano-1-(*N*-(4,6-dichloropyrimidin-2-yl)acetamido)butan-2-yl *O*-ethyl carbonodithioate (9a)**




Following general procedure A for intermolecular radical addition, the reaction was carried out using olefin **7a** (208 mg, 0.84 mmol, 1.0 equiv) and xanthate **8a** (409 mg, 2.53 mmol, 3.0 equiv.) in ethyl acetate (0.8 mL). The reaction needed 15 mol % of DLP to go to completion. Purification by chromatography by silica gel (petroleum ether/ethyl acetate 9/1 to 7/3) gave compound **9a** (337 mg, 98 %).

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 7.71 (s, 1H, H-Ar), 4.63 (q, *J* = 7.1 Hz, 2H), 4.48 (dd, *J* = 14.0, 8.5 Hz, 1H), 4.33 (dd, *J* = 14.0, 6.3 Hz, 1H), 4.19 (m, 1H), 2.60 (m, 2H), 2.53 (s, 3H), 2.15 (m, 1H), 2.00 (m, 1H), 1.41 (t, *J* = 7.1 Hz, 3H).

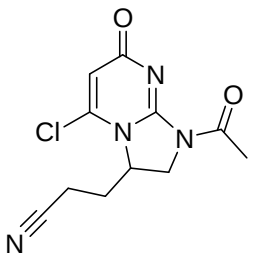
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 211.8 (C), 172.4 (C), 161.9 (2C), 159.7 (C), 118.8 (C), 115.9 (CH), 70.6 ($CH_2$), 48.7 (CH), 47.3 ($CH_2$), 28.1 ($CH_2$), 26.4 ($CH_3$), 15.0 ($CH_2$), 13.7 ($CH_3$).

**IR ($CCl_4$):** $\nu_{max}$ 3155, 2985, 2937, 1816, 1795, 1741, 1701, 1530.

**MS** (CI, $NH_3$) *m/z* 407 ($MH^+$), 409 ($MH+2^+$), 411 ($MH+4^+$).

**HRMS (EI+):** calculated for $C_{14}H_{16}N_4O_2S_2Cl_2$ 406.0092, found 406.0091.

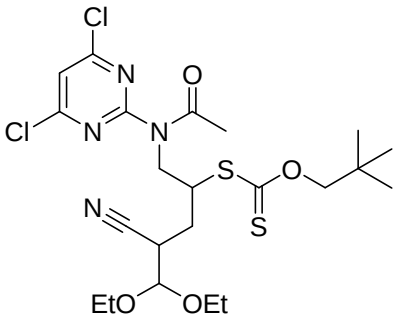
**3-(1-acetyl-5-chloro-7-oxo-1,2,3,7-tetrahydroimidazo[1,2-*a*]pyrimidin-3-yl)propanenitrile (10a)**



Following general procedure C for radical cyclisation, the reaction was carried out using xanthate **9a** (137 mg, 0.34 mmol, 1.0 equiv.) in ethyl acetate (3.5 mL), and needed 80 mol % of DLP to go to completion. Purification by chromatography on silica gel (petroleum ether/ ethyl acetate, 1/1 to 3/7) gave the corresponding bicycle **10a** (60 mg, 80 %).

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 6.14 (s, 1H), 4.67 (m, 1H), 4.14 (dd, *J* = 12.1, 9.6 Hz, 1H), 3.94 (dd, *J* = 12.1, 3.8 Hz, 1H), 2.64 (s, $CH_3$), 2.51 (m, 2H), 2.39 (m, 1H), 2.11 (m, 1H).
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 169.4 (C), 159.5 (C), 158.9 (C), 150.3 (C), 117.9 (C), 106.9 (CH), 51.2 ($CH_2$), 47.4 (CH), 28.3 ($CH_3$), 24.9 ($CH_2$), 13.3 ($CH_2$).
**IR ($CCl_4$):** $\nu_{max}$ 3155, 2928, 1696, 1595, 1538.
**MS** (CI, $NH_3$) *m/z* 267 ($MH^+$), 369 ($MH+2^+$).
**HRMS (EI+):** calculated for $C_{11}H_{11}O_2N_4Cl$ 266.0571, found 266.0570.

***S*-4-cyano-1-(*N*-(4,6-dichloropyrimidin-2-yl)acetamido)-5,5-diethoxypentan-2-yl *O*-neopentyl carbonodithioate (9b)**




Following general procedure A for intermolecular radical addition, the reaction was carried out using olefin **7a** (240 mg, 0.97 mmol, 1.0 equiv) and xanthate **8b** (595 mg, 1.95 mmol, 2.0 equiv.) in ethyl acetate (1.0 mL). The reaction needed 10 mol % of DLP to go to completion. Purification by chromatography by silica gel (petroleum ether/ethyl acetate 9/1 to 8/2) gave compound **9b** (335 mg, 62 %) as a 1:1 mixture of unseparable diastereoisomers.

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 7.09 (s, 1H), 4.60-4.57 (m, 1H), 4.56-4.52 (m, 1H), 4.47-4.34 (m, 1H), 4.29-4.23 (m, 3H), 3.79-3.53 (m, 4H), 3.20-3.09 (m, 1H), 2.51 (s, 3H), 2.25-2.09 (m, 2H), 1.24-1.21 (m, 6H), 0.99 (S, 9H).

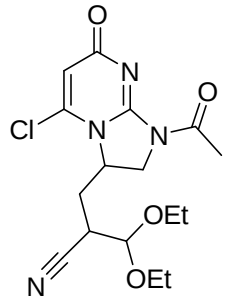
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 212.4 (C), 172.3 (C), 161.8 (2C), 159.7 (C), 118.9 (C), 115.9 (CH), 100.8 (CH), 83.7 ($CH_2$), 64.1 ($2CH_2$), 48.0 ($CH_2$), 47.0 (CH), 35.2 (CH), 31.8 ($CH_2$), 30.2 (C), 26.5 ($3CH_3$), 26.4 ($CH_3$), 15.0 ($2CH_3$).

**IR ($CCl_4$):** $\nu_{max}$ 3155, 2982, 2255, 1817, 1794, 1691, 1641.

**MS** (CI, $NH_3$) *m/z* 551 ($MH^+$), 553 ($MH+2^+$), 555 ($MH+4^+$).

**HRMS (EI+):** calculated for $C_{22}H_{32}O_4N_4Cl_2S_2$ 550.1242 found 550.1240.

**2-((1-acetyl-5-chloro-7-oxo-1,2,3,7-tetrahydroimidazo[1,2-*a*]pyrimidin-3-yl)methyl)-3,3-diethoxypropanenitrile (10b)**




Following general procedure C for radical cyclisation, the reaction was carried out using xanthate **9b** (315 mg, 0.57 mmol, 1.0 equiv.) in ethyl acetate (7.0 mL), and needed 160 mol % of DLP to go to completion. Purification by chromatography on silica gel (petroleum ether/ ethyl acetate, 8/2 to 1/1) gave the corresponding bicycle **10b** (132 mg, 63 %).

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 6.13 (s, 1H), 4.77 (m, 1H), 4.60-4.58 (2d, *J* = 5.1 Hz), 4.15-4.08 (m, 2H), 3.74 (m, 2H), 3.58 (m, 2H), 3.11-2.94 (2m), 2.65 (s, 3H), 2.48 (m, 1H), 2.10 (m, 1H), 1.22 (m, 6H).

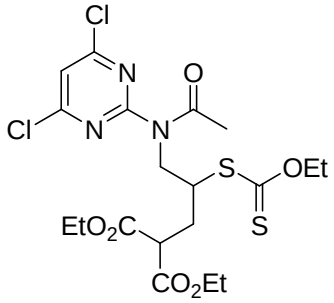
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 169.4 (C), 159.6 (C), 158.8 (C), 150.4 (C), 118.3 (C), 106.9 (CH), 100.9 (CH), 64.4 ($2CH_2$), 50.7 (CH), 48.1 ($CH_2$), 33.9 ($CH_2$), 30.8 ($CH_2$), 24.9 ($CH_3$), 15.0 ($2CH_3$).

**IR ($CCl_4$):** $\nu_{max}$. 2984, 2939, 2254, 1732, 1689, 1594, 1538.

**MS** (CI, $NH_3$) *m/z* 369 ($MH^+$), 371 ($MH+2^+$).

**HRMS (EI+):** calculated for $C_{16}H_{21}O_4N_4Cl$ 368.1251, found 368.1250.

**Diethyl 2-(3-(*N*-(4,6-dichloropyrimidin-2-yl)acetamido)-2-(ethoxycarbonothioylthio)propyl)malonate (9c)**



Following general procedure A for intermolecular radical addition, the reaction was carried out using olefin **7a** (232 mg, 0.94 mmol, 1.0 equiv) and xanthate **8c** (792 mg, 2.83 mmol, 3.0 equiv.) in ethyl acetate (0.9 mL). The reaction needed 35 mol % of DLP to go to completion. Purification by chromatography by silica gel (petroleum ether/ethyl acetate 9/1 to 8/2) gave compound **9c** (436 mg, 87 %).

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 7.06 (s, 1H), 4.59 (q, *J* = 7.1 Hz, 2H), 4.44 (dd, *J* = 14.9, 8.8 Hz, 1H), 4.35 (dd, *J* = 13.9, 6.4 Hz, 1H), 4.17 (m, 5H), 3.61 (m, 1H), 2.51 (s, 3H), 2.38 (m, 1H), 2.13 (m, 1H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.24 (m, 6H).

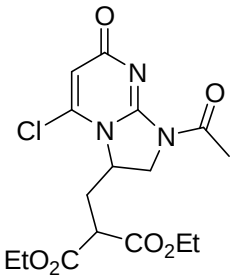
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 212.3 (C), 172.3 (C), 168.8 (C), 168.5 (C), 161.7 (2C), 159.8 (C), 115.6 (CH), 70.3 ($CH_2$), 61.6 ($2CH_2$), 49.6 (CH), 48.2 ($CH_2$), 47.9 (CH), 30.6 ($CH_2$), 26.4 ($CH_3$), 14.00 ($2CH_3$), 13.7 ($CH_3$).

**IR ($CCl_4$):** $\nu_{max}$ 1751, 1735, 1701, 1559, 1530.

**MS** (CI, $NH_3$) *m/z* 526 ($MH^+$), 528 ($MH+2^+$), 530 ($MH+4^+$).

**HRMS (EI+):** calculated for $C_{19}H_{25}O_6N_3Cl_2S_2$ 525.0562, found 525.0562.

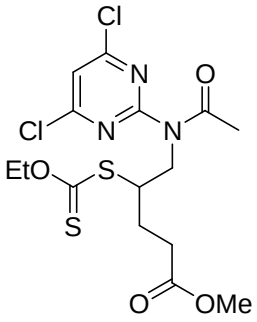
**Diethyl 2-((1-acetyl-5-chloro-7-oxo-1,2,3,7-tetrahydroimidazo[1,2-*a*]pyrimidin-3-yl)methyl)malonate (10c)**



Following general procedure C for radical cyclisation, the reaction was carried out using xanthate **9c** (170 mg, 0.32 mmol, 1.0 equiv.) in ethyl acetate (4.8 mL), and needed 100 mol % of DLP to go to completion. Purification by chromatography on silica gel (petroleum ether/ ethyl acetate, 1/1 to 3/7) gave the corresponding bicycle **10c** (75 mg, 60 %).

**$^1$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 6.11 (s, 1H), 4.73 (m, 1H), 4.18 (m, 4H), 4.04 (m, 2H), 3.52 (t, *J* = 7.4 Hz, 1H), 2.64 (s, $CH_3$), 2.47 (m, 1H), 2.35 (m, 1H), 1.25 (m, 6H).
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 169.4 (C), 168.2 (2C), 159.5 (C), 158.6 (C), 150.4 (C), 106.9 (CH), 62.0 ($2CH_2$), 50.5 (CH), 48.3 ($CH+CH_2$), 32.3 ($CH_2$), 24.9 ($CH_3$), 13.9 ($2CH_3$).
**IR ($CCl_4$):** $\nu_{max}$ 2984, 2939, 1732, 1689, 1594, 1538.
**MS** (CI, $NH_3$) *m/z* 386 ($MH^+$), 388 ($MH+2^+$).
**HRMS (EI+):** calculated for $C_{16}H_{20}O_6N_3Cl$ 385.1041, found 385.1042.

**Methyl 5-(*N*-(4,6-dichloropyrimidin-2-yl)acetamido)-4-(ethoxycarbonothioylthio)pentanoate (9d)**




Following general procedure A for intermolecular radical addition, the reaction was carried out using olefin **7a** (103 mg, 0.42 mmol, 1.0 equiv) and xanthate **8d** (324 mg, 1.67 mmol, 4.0 equiv.) in ethyl acetate (0.5 mL). The reaction needed 35 mol % of DLP to go to completion. Purification by chromatography by silica gel (petroleum ether/ethyl acetate 9/1 to 8/2) gave compound **9d** (153 mg, 83 %).

**$^1$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 7.08 (s, 1H), 4.61 (m, 2H), 4.45 (dd, *J* = 13.9, 9.1 Hz, 1H), 4.31 (dd, *J* = 13.9, 6.0 Hz, 1H), 4.18 (m, 1H), 3.66 (s, 3H), 2.51 (m, 2H), 2.50 (s, 3H), 2.09 (m, 1H), 1.93 (m, 1H), 1.40 (t, *J* = 7.1 Hz, 3H).

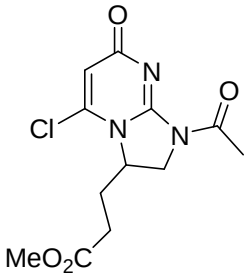
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 212.9 (C), 173.0 (C), 172.4 (C), 161.7 (2C), 159.9 (C), 115.7 (CH), 70.2 ($CH_2$), 51.7 ($CH_3$), 49.4 (CH), 48.1 ($CH_2$), 31.3 ($CH_2$), 27.0 ($CH_2$), 26.4 ($CH_3$), 13.7 ($CH_3$).

**IR ($CCl_4$):** $\nu_{max}$ 2927, 2855, 1741, 1699, 1559, 1529, 1448, 1368.

**MS** (CI, $NH_3$) *m/z* 440 ($MH^+$), 442 ($MH+2^+$), 444 ($MH+4^+$).

**HRMS (EI+):** calculated for $C_{15}H_{19}O_4N_3Cl_2S_2$ 439.0194, found 439.0194.

**Methyl 3-(1-acetyl-5-chloro-7-oxo-1,2,3,7-tetrahydroimidazo[1,2-*a*]pyrimidin-3-yl)propanoate (10d)**




Following general procedure C for radical cyclisation, the reaction was carried out using xanthate **9d** (140 mg, 0.32 mmol, 1.0 equiv.) in ethyl acetate (4.8 mL), and needed 120 mol % of DLP to go to completion. Purification by chromatography on silica gel (petroleum ether/ ethyl acetate, 1/1 to 3/7) gave the corresponding bicycle **10d** (67 mg, 71 %).

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 6.13 (s, 1H), 4.65 (m, 1H), 4.06 (dd, *J* = 11.7, 9.6 Hz, 1H), 3.98 (dd, *J* = 12.0, 3.4 Hz, 1H), 3.66 (s, 3H), 2.65 (s, $CH_3$), 2.39 (m, 2H), 2.32 (m, 1H), 2.08 (m, 1H).

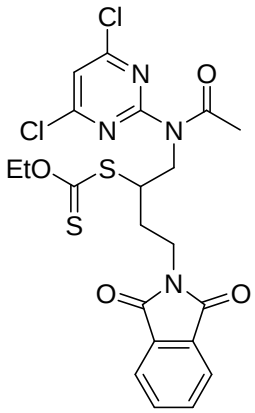
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 172.2 (C), 169.5 (C), 159.5 (C), 158.6 (C), 150.5 (C), 106.9 (CH), 51.9 ($CH_3$), 51.7 (CH), 47.6 ($CH_2$), 29.1 ($CH_2$), 27.7 ($CH_2$), 24.9 ($CH_3$).

**IR ($CCl_4$):** $\nu_{max}$ 3155, 2984, 1816, 1794, 1688, 1594, 1538.

**MS** (CI, NH3) *m/z* 300 ($MH^+$), 302 ($MH+2^+$).

**HRMS (EI+):** calculated for $C_{12}H_{14}O_4N_3Cl$ 299.0673, found 299.0675.

**_S_-1-(_N_-(4,6-dichloropyrimidin-2-yl)acetamido)-4-(1,3-dioxoisoindolin-2-yl)butan-2-yl _O_-ethyl carbonodithioate (9e)**




Following general procedure A for intermolecular radical addition, the reaction was carried out using olefin **7a** (127 mg, 0.52 mmol, 1.0 equiv) and xanthate **8e** (741 mg, 2.58 mmol, 5.0 equiv.) in ethyl acetate (0.5 mL). The reaction needed 45 mol % of DLP to go to completion. Purification by chromatography by silica gel (petroleum ether/ethyl acetate 9/1 to 8/2) gave compound **9e** (227 mg, 82 %).

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 7.81 (m, 2H), 7.71 (m, 2H), 7.04 (s, 1H), 4.60 (m, 2H), 4.49 (dd, *J* = 14.0, 9.0 Hz, 1H), 4.36 (dd, *J* = 14.0, 5.9 Hz, 1H), 4.19 (m, 1H), 3.87 (t, *J* = 7.4 Hz, 2H), 2.51 (s, 3H), 2.13 (m, 1H), 2.03 (m, 1H), 1.39 (t, *J* = 7.1 Hz, 3H).

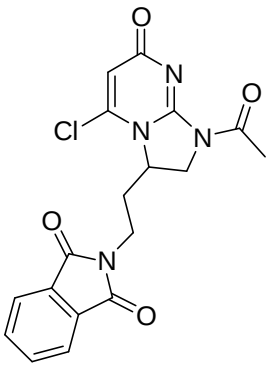
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 212.6 (C), 172.4 (C), 168.0 (2C), 161.7 (2C), 159.9 (C), 133.9 (2CH), 132.0 (2C), 123.2 (2CH), 115.7 (CH), 70.2 ($CH_2$), 48.1 ($CH_2$), 47.2 (CH), 35.7 ($CH_2$), 30.5 ($CH_2$), 26.5 ($CH_3$), 13.6 ($CH_3$).

**IR ($CCl_4$):** $\nu_{max}$ 2927, 2855, 1741, 1699, 1559, 1529, 1448, 1368.

**MS** (CI, $NH_3$) *m/z* 527 ($MH^+$), 529 ($MH+2^+$), 531 ($MH+4^+$).

**HRMS (EI+):** calculated for $C_{21}H_{20}O_4N_4Cl_2S_2$ 526.0303, found 526.0300.

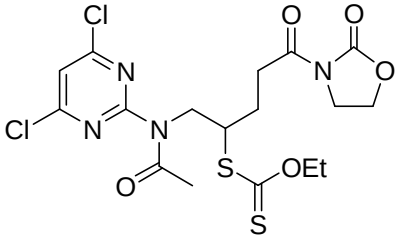
**2-(2-(1-acetyl-5-chloro-7-oxo-1,2,3,7-tetrahydroimidazo[1,2-*a*]pyrimidin-3-yl)ethyl)isoindoline-1,3-dione (10e)**



Following general procedure C for radical cyclisation, the reaction was carried out using xanthate **9e** (200 mg, 0.375 mmol, 1.0 equiv.) in ethyl acetate (5.6 mL), and needed 120 mol % of DLP to go to completion. Purification by chromatography on silica gel (petroleum ether/ ethyl acetate, 1/1) gave the corresponding bicycle **10e** (98 mg, 68 %).

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 7.83 (m, 2H), 7.71 (m, 2H), 5.99 (s, 1H), 4.61 (tt, *J* = 8.9, 3.9 Hz, 1H), 4.17 (m, 2H), 3.77 (m, 2H), 2.65 (s, $CH_3$), 2.47 (m, 1H), 2.10 (m, 1H).
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 169.6 (C), 168.0 (2C), 159.3 (C), 158.6 (C), 150.5 (C), 134.2 (2CH), 131.7 (2C), 123.4 (2CH), 106.8 (CH), 50.7 (CH), 47.4 ($CH_2$), 33.3 ($CH_2$), 30.8 ($CH_2$), 25.0 ($CH_3$).
**IR ($CCl_4$):** $\nu_{max}$ 3155, 2984, 1816, 1794, 1688, 1594, 1538.
**MS** (CI, $NH_3$) *m/z* 387 ($MH^+$), 389 ($MH+2^+$).
**HRMS (EI+):** calculated for $C_{18}H_{15}O_4N_4Cl$ 386.0782, found 386.0778.

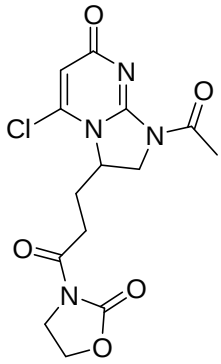
***S*-1-(*N*-(4,6-dichloropyrimidin-2-yl)acetamido)-5-oxo-5-(2-oxooxazolidin-3-yl)pentan-2-yl *O*-ethyl carbonodithioate 9f**



Following general procedure A for intermolecular radical addition, the reaction was carried out using olefin **7a** (404 mg, 1.64 mmol, 1.0 equiv) and xanthate **8f** (410 mg, 1.64 mmol, 1.0 equiv.) in ethyl acetate (2.0 mL). The reaction needed 40 mol % of DLP to go to completion. Purification by chromatography by silica gel (petroleum ether/ethyl acetate 9/1 to 8/2) gave compound **9f** (455 mg, 56 %) along with recovered olefin (18%) and cyclised product (11%).

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 7.07 (s, 1H), 4.60 (m, 2H), 4.47 (dd, *J* = 14.0, 8.9 Hz, 1H), 4.39 (t, *J* = 8.1 Hz, 2H), 4.34 (dd, *J* = 14.1, 6.2 Hz, 1H), 4.18 (m, 1H), 3.99 (t, *J* = 8.1 Hz, 2H), 3.11 (m, 2H), 2.51 (s, 3H), 2.13 (m, 1H), 2.00 (m, 1H), 1.40 (t, *J* = 7.1 Hz, 3H).
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 213.1 (C), 172.4 (2C), 161.7 (2C), 160.0 (C), 153.4 (C), 115.7 (CH), 70.3 ($CH_2$), 62.1 ($CH_2$), 49.3 ($CH_2$), 48.1 (CH), 42.5 ($CH_2$), 32.4 ($CH_2$), 26.4 ($CH_2$), 26.3 ($CH_3$), 13.7 ($CH_3$).
**IR ($CCl_4$):** $\nu_{max}$ 2988, 2922, 1792, 1704, 1556, 1532, 1447, 1422, 1384, 1224, 1108, 1050, 1005.
**MS** (CI, $NH_3$) *m/z* 495 ($MH^+$), 497 ($MH+2^+$), 499 ($MH+4^+$).
**HRMS (EI+):** calculated for $C_{17}H_{20}O_5N_4Cl_2S_2$ 494.0252, found 494.0248.

**3-(3-(1-acetyl-5-chloro-7-oxo-1,2,3,7-tetrahydroimidazo[1,2-*a*]pyrimidin-3-yl)propanoyl)oxazolidin-2-one (10f)**




Following general procedure C for radical cyclisation, the reaction was carried out using xanthate **9f** (440 mg, 0.89 mmol, 1.0 equiv.) in ethyl acetate (13.3 mL), and needed 120 mol % of DLP to go to completion. Purification by chromatography on silica gel (petroleum ether/ ethyl acetate, 6/4 to 4/6) gave the corresponding bicycle **10f** (126 mg, 40 %).

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 6.11 (s, 1H), 4.69 (m, 1H), 4.42 (t, *J* = 8.2 Hz, 2H), 4.03 (m, 2H), 3.98 (t, *J* = 8.1 Hz), 3.00 (m, 2H), 2.65 (s, $CH_3$), 2.33 (m, 1H), 2.12 (m, 1H).

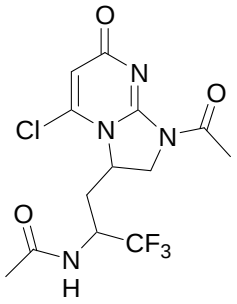
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 171.5 (C), 169.7 (C), 159.7 (C), 158.7 (C), 150.6 (C), 107.0 (CH), 62.3 ($CH_2$), 51.7 (CH), 48.0 ($CH_2$), 42.5 ($CH_2$), 30.6 ($CH_2$), 27.5 ($CH_2$), 25.0 ($CH_3$).

**IR ($CCl_4$):** $\nu_{max}$ 2925, 1790, 1699, 1593, 1540, 1479, 1438, 1380, 1345, 1302, 1228, 1115, 1061.

**MS** (CI, $NH_3$) *m/z* 355 ($MH^+$), 357 ($MH+2^+$).

**HRMS (EI+):** calculated for $C_{14}H_{15}O_5N_4Cl$ 354.0731, found 354.0731.

### *N*-(3-(1-acetyl-5-chloro-7-oxo-1,2,3,7-tetrahydroimidazo[1,2-a]pyrimidin-3-yl)-1,1,1-trifluoropropan-2-yl)acetamide (10g)




Following general procedure A for intermolecular radical addition, the reaction was carried out using olefin **7a** (145 mg, 0.59 mmol, 1.0 equiv) and xanthate **8g** (154 mg, 0.59 mmol, 1.0 equiv.) in ethyl acetate (0.6 mL). The reaction needed 40 mol % of DLP to go to completion. Ethyl acetate (12 mL) was then added and the solution was refluxed 10 min under nitrogen. DLP was then added portionwise until consumption of the xanthate. The reaction needed 120 mol% of DLP to go to completion. Purification by chromatography on silica gel (petroleum ether/ ethyl acetate, 6/4 to 4/6) gave the corresponding bicycle **10g** (110 mg, 51 %).

**$^{1}$H-NMR (400 MHz, $((CD_3)_2SO$):** $\delta_H$ 8.75-8.53 (2d, *J* = 9.5 Hz, 1H, NH), 6.23 (s, 1H), 4.74-4.53 (m, 2H), 4.07-3.92 (m, 2H), 2.47 (s, 3H), 2.21 (m, 2H), 1.77 (s, 3H).

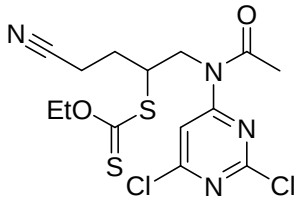
**$^{13}$C-NMR (100 MHz, $((CD_3)_2SO$):** $\delta_c$ 169.9 (C), 169.4 (C), 168.7 (C), 158.9 (C), 157.2 (C), 151.2 (C), 105.8 (CH), 49.8 ($CH_2$), 46.9 (CH), 28.2 ($CH_2$), 24.6 ($2CH_3$), 21.9 ($CH_2$).

**IR ($CCl_4$):** $\nu_{max}$ 2925, 1790, 1699, 1593, 1540, 1479, 1438, 1380, 1345, 1302, 1228, 1115, 1061.

**MS** (CI, NH3) *m/z* 367 ($MH^+$), 369 ($MH+2^+$).

**HRMS (EI+):** calculated for $C_{13}H_{14}O_3N_4ClF_3$ 366.0707, found 366.0708.

***S*-4-cyano-1-(*N*-(2,6-dichloropyrimidin-4-yl)acetamido)butan-2-yl *O*-ethyl carbonodithioate (14a)**




Following general procedure A for intermolecular radical addition, the reaction was carried out using olefin **7b** (321 mg, 1.30 mmol, 1.0 equiv) and xanthate **8a** (421 mg, 2.60 mmol, 2.0 equiv.) in ethyl acetate (1.3 mL). The reaction needed 20 mol % of DLP to go to completion. Purification by chromatography by silica gel (petroleum ether/ethyl acetate 3/2) gave compound **14a** (408 mg, 77 %).

**$^1$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 7.75 (s, 1H), 4.60 (m, 2H), 4.44 (dd, *J* = 13.3, 4.3 Hz, 1H), 4.24-4.13 (m, 2H), 2.66-2.50 (m, 2H), 2.43 (s, 3H), 2.14 (m, 1H), 2.00 (m, 1H), 1.38 (t, *J* = 7.1 Hz, 3H).

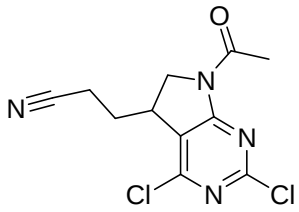
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 211.5 (C), 171.6 (C), 162.7 (C), 162.1 (C), 159.1 (C), 118.5 (C), 112.2 (CH), 71.1 ($CH_2$), 49.2 ($CH_2$), 49.0 (CH), 27.9 ($CH_2$), 25.1 ($CH_3$), 15.0 ($CH_2$), 13.6 ($CH_3$).

**IR ($CCl_4$):** $\nu_{max}$ 2985, 2937, 2250, 1741, 1709, 1555, 1370.

**MS** (CI, $NH_3$) *m/z* 407 ($MH^+$), 409 ($MH+2^+$), 411 ($MH+4^+$).

**HRMS (EI+):** calculated for $C_{14}H_{16}N_4O_2S_2Cl_2$ 406.0092, found 406.0090.

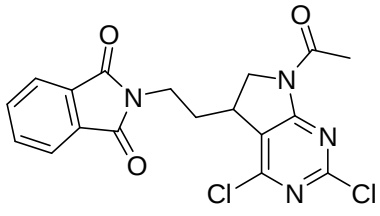
**3-(7-acetyl-2,4-dichloro-6,7-dihydro-5*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl)propanenitrile (15a)**



Following general procedure B for radical cyclisation, the reaction was carried out using xanthate **14a** (104 mg, 0.25 mmol, 1.0 equiv.) in ethyl acetate (3 mL), dibenzoylperoxide (99 mg, 0.30 mmol, 1.2 equiv.) and needed 100 mol % of DLP to go to completion. Purification by chromatography on silica gel (petroleum ether/ ethyl acetate, 7/3 to 6/4) gave the corresponding diazaindoline **15a** (37 mg, 54 %).

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 4.22 (dd, *J* = 12.5, 9.8 Hz, 1H), 3.95 (dd, *J* = 12.5, 4.1 Hz, 1H), 3.53 (tt, *J* = 9.7, 3.8 Hz, 1H), 2.66 (s, 3H), 2.55-2.31 (m, 3H), 1.95-1.86 (m, 1H).
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 169.8 (C), 163.8 (C), 159.5 (C), 155.8 (C), 120.8 (C), 118.0 (C), 51.1 ($CH_2$), 33.6 (CH), 28.1 ($CH_2$), 25.3 ($CH_3$), 14.6 ($CH_2$).
**IR ($CCl_4$):** $\nu_{max}$ 3121, 2986, 2248, 1816, 1795, 1697, 1645, 1559.
**MS** (CI, $NH_3$) *m/z* 285 ($MH^+$), 287 ($MH+2^+$), 289 ($MH+4^+$).
**HRMS (EI+):** calculated for $C_{11}H_{10}ON_4Cl_2$ 284.0232, found 284.0231.

**2-(2-(7-acetyl-2,4-dichloro-6,7-dihydro-5H-pyrrolo[2,3-*d*]pyrimidin-5-yl)ethyl)isoindoline-1,3-dione (15b)**



Following general procedure A for intermolecular radical addition, the reaction was carried out using olefin **7b** (78 mg, 0.32 mmol, 1.0 equiv) and xanthate **8e** (91 mg, 0.32 mmol, 1.0 equiv.) in ethyl acetate (0.3 mL). The reaction needed 15 mol % of DLP to go to completion. The solvent was then removed under reduced pressure and the crude xanthate was rapidly

eluted through a short pad of silica with petroleum ether and ethyl acetate (7/3). Ethyl acetate (5 mL) was added to the residual oil. The solution was refluxed 10 min under nitrogen and dibenzoyl peroxide (123 mg, 0.38 mmol, 1.2 equiv.) was added. The reaction needed 100 mol % of DLP to go to completion. Purification by chromatography by silica gel (petroleum ether/ethyl acetate 3/2) gave compound **15b** (77 mg, 60 %).

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 7.88 (m, 2H), 7.77 (m, 2H), 4.31 (dd, *J* = 12.4, 10.2 Hz, 1H), 4.15 (dd, *J* = 12.6, 4.4 Hz, 1H), 3.84 (t, *J* = 7.4 Hz, 2H), 3.43 (m, 1H), 2.70 (s, 3H), 2.42 (m, 1H), 2.00 (m, 1H).

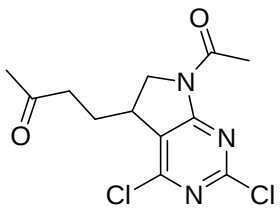
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 169.9 (C), 168.0 (2C), 163.9 (C), 158.9 (C), 155.5 (C), 134.2 (2CH), 131.7 (2C), 123.4 (2CH), 121.7 (C), 51.5 ($CH_2$), 34.6 ($CH_2$), 32.4 (CH), 30.7 ($CH_2$), 25.4 ($CH_3$).

**IR ($CCl_4$):** $\nu_{max}$ 1702, 1560, 1527, 1446, 1230.

**MS** (CI, $NH_3$) *m/z* 405 ($MH^+$), 407 ($MH+2^+$), 409 ($MH+4^+$).

**HRMS (EI+):** calculated for $C_{18}H_{14}O_3N_4Cl_2$ 404.0443, found 404.0441.

**4-(7-acetyl-2,4-dichloro-6,7-dihydro-5*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl)butan-2-one (15c)**




Following general procedure A for intermolecular radical addition, the reaction was carried out using olefin **7b** (114 mg, 0.46 mmol, 1.0 equiv) and xanthate derived from chloroacetone (163 mg, 0.92 mmol, 2.0 equiv.) in ethyl acetate (0.5 mL). The reaction needed 40 mol % of DLP to go to completion. The solvent was then removed under reduced pressure and the crude xanthate was rapidly eluted through a short pad of silica with petroleum ether and ethyl acetate (7/3). Ethyl acetate (5 mL) was added to the residual oil. The solution was refluxed 10 min under nitrogen and dibenzoyl peroxide (178 mg, 0.55 mmol, 1.2 equiv.) was added. The reaction needed 100 mol % of DLP to go to completion. Purification by chromatography by silica gel (petroleum ether/ethyl acetate 3/2) gave compound **15c** (62 mg, 45 %).

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 4.17 (dd, *J* = 12.3, 9.7 Hz, 1H), 3.94 (dd, *J* = 12.3, 4.1 Hz, 1H), 3.44 (tt, *J* = 9.5, 4 Hz, 1H), 2.69 (s, $CH_3$), 2.54 (t, *J* = 7.5, 2H), 2.30 (m, 1H), 2.21 (s, 3H), 1.88-1.78 (m, 1H).

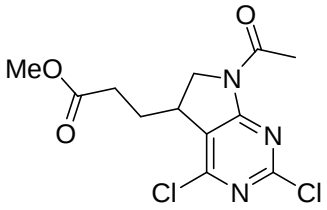
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 206.7 (C), 169.9 (C), 163.8 (C), 158.9 (C), 155.7 (C), 122.3 (C), 51.6 ($CH_2$), 39.5 ($CH_2$), 33.7 (CH), 29.9 ($CH_3$), 26.2 ($CH_2$), 25.4 ($CH_3$).

**IR ($CCl_4$):** $\nu_{max}$ 3155, 2928, 1816, 1794, 1719, 1693, 1590.

**MS** (CI, $NH_3$) *m/z* 302 ($MH^+$), 304 ($MH+2^+$), 306 ($MH+4^+$).

**HRMS (EI+):** calculated for $C_{12}H_{13}O_2N_3Cl_2$ 301.0385, found 301.0382.

**Methyl 3-(7-acetyl-2,4-dichloro-6,7-dihydro-5H-pyrrolo[2,3-*d*]pyrimidin-5-yl)propanoate (15d)**




Following general procedure A for intermolecular radical addition, the reaction was carried out using olefin **7b** (209 mg, 0.85 mmol, 1.0 equiv) and xanthate **8d** (330 mg, 1.70 mmol, 2.0 equiv.) in ethyl acetate (1.0 mL). The reaction was stopped after 35 mol % of DLP. Filtration through a short pad of silica (elution with petroleum ether/ethyl acetate 7/3) yielded 211 mg of a 3/1 mixture of addition xanthate and bicycle (45% and 15% respectively, 22% of the olefin were recovered). This crude mixture was diluted with ethyl acetate (7 mL). The solution was refluxed 10 min under nitrogen and dibenzoyl peroxide (185 mg, 0.575 mmol, 1.2 equiv.) was added. The reaction needed 100 mol % of DLP to go to completion. Purification by chromatography by silica gel (petroleum ether/ethyl acetate 3/2) gave compound **10d** (118 mg, 72 %).

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 4.14 (dd, *J* = 12.3, 9.8 Hz, 1H), 3.94 (dd, *J* = 12.4, 4.1 Hz, 1H), 3.69 (s, 3H), 3.45 (m, 1H), 2.66 (s, 3H), 2.41 (m, 2H), 2.30 (m, 1H), 1.89 (m, 1H).

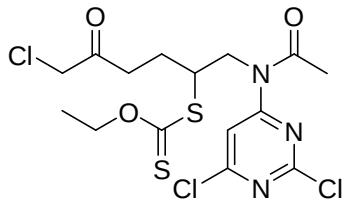
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 172.5 (C), 169.8 (C), 163.8 (C), 158.9 (C), 155.6 (C), 122.0 (C), 51.8 ($CH_3$), 51.4 ($CH_2$), 33.7 (CH), 30.4 ($CH_2$), 27.4 ($CH_2$), 25.3 ($CH_3$).

**IR ($CCl_4$):** $\nu_{max}$ 2954, 1740, 1692, 1591, 1551, 1481, 1439.

**MS** (CI, $NH_3$) *m/z* 318 ($MH^+$), 320 ($MH+2^+$), 322 ($MH+4^+$).

**HRMS (EI+):** calculated for $C_{12}H_{13}O_3N_3Cl_2$ 317.0334, found 317.0333.

**_S_-6-chloro-1-(_N_-(2,6-dichloropyrimidin-4-yl)acetamido)-5-oxohexan-2-yl _O_-ethyl carbonodithioate (14e)**



Following general procedure A for intermolecular radical addition, the reaction was carried out using olefin **7b** (203 mg, 0.82 mmol, 1.0 equiv) and xanthate derived from 1,3-dichlorocetone (351 mg, 1.64 mmol, 2.0 equiv.) in ethyl acetate (0.8 mL). The reaction was stopped after 30 mol % of DLP. Purification by chromatography by silica gel (petroleum ether/ethyl acetate 7/3) gave compound **14e** (116 mg, 31 % NMR yield, contaminated with lauric acid[1]) and unreacted olefin (97 mg, 48%).

**$^1$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 7.84 (s, 1H), 4.64 (q, *J* = 7.1 Hz, 2H), 4.47 (dd, *J* = 14.1, 5.3 Hz, 1H), 4.17 (m, 2H), 4.12 (s, 2H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.50 (s, 3H), 2.20 (m, 1H), 1.92 (m, 1H), 1.43 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 212.7 (C), 201.5 (C), 171.8 ($CH_3$), 162.6 (C), 162.3 (C), 159.0 (C), 112.4 (CH), 70.9 ($CH_2$), 49.8 ($CH_2$), 49.6 (CH), 48.0 ($CH_2$), 36.5 ($CH_2$), 29.4 ($CH_2$), 22.6 ($CH_3$), 14.3 ($CH_3$).

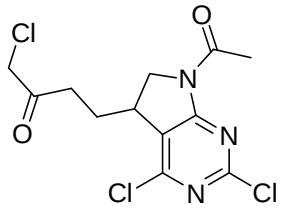
**IR ($CCl_4$):** $\nu_{max}$ 3155, 2985, 1817, 1794, 1706, 1469.

**MS** (CI, $NH_3$) *m/z* 457 ($MH^+$), 459 ($MH+2^+$), 461 ($MH+4^+$).

**HRMS (EI+):** calculated for $C_{15}H_{18}O_3N_3Cl_3S_2$ 456.9855, found 456.9853.

[1] Usually, lauric acid can be removed by filtration through basic alumina but the xanthate moiety is not stable under these conditions.

**4-(7-acetyl-2,4-dichloro-6,7-dihydro-5*H*-pyrrolo[2,3-*d*]pyrimidin-5-yl)-1-chlorobutan-2-one (15e)**



Following general procedure B for radical cyclisation, the reaction was carried out using xanthate **14e** (107 mg, 0.23 mmol, 1.0 equiv.) in ethyl acetate (2.3 mL), dibenzoylperoxide (90 mg, 0.28 mmol, 1.2 equiv.) and needed 80 mol % of DLP to go to completion. Purification by chromatography on silica gel (petroleum ether/ ethyl acetate, 8/2 to 6/4) gave the corresponding bicycle **15e** (41 mg, 52 %).

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 4.13 (dd, *J* = 12.3, 9.8 Hz, 1H), 4.07 (s, 2H), 3.90 (dd, *J* = 12.4, 4.1 Hz, 1H), 3.42 (m, 1H), 2.71 (t, *J* = 7.8, 2H), 2.66 (s, $CH_3$), 2.30 (m, 1H), 1.94 (m, 1H).

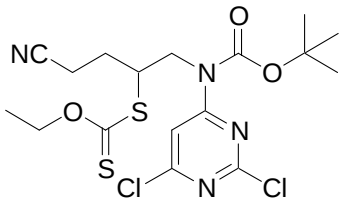
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 201.3 (C, C(O)), 169.9 (C, C(O)), 163.8 (C, C-Ar), 159.1 (C, C-Ar), 155.8 (C, C-Ar), 122.0 (C, C-Ar), 51.6 ($CH_2$, C-1), 47.9 ($CH_2$, C-5), 35.8 ($CH_2$, C-4), 33.7 (CH, C-2), 26.2 ($CH_2$, C-3), 25.4 ($CH_3$, Ac).

**IR ($CCl_4$):** $\nu_{max}$ 3155, 2985, 1817, 1794, 1694, 1644, 1470 .

**MS** (CI, $NH_3$) *m/z* 336 ($MH^+$), 338 ($MH+2^+$), 340 ($MH+4^+$).

**HRMS (EI+):** calculated for $C_{12}H_{12}O_2N_3Cl_3$ 334.9995, found 334.9994.

**Tert-butyl 4-cyano-2-(ethoxycarbonothioylthio)butyl(2,6-dichloropyrimidin-4-yl)carbamate (16a)**



Following general procedure A for intermolecular radical addition, the reaction was carried out using olefin **7c** (1.50 g, 4.93 mmol, 2 equiv.) and xanthate **8a** (397 mg, 2.465 mmol, 1

equiv.) in ethyl acetate (2.5 mL). The reaction needed 15 mol % of DLP to go to completion. Purification (petroleum ether/ethyl acetate 9/1 to 8/2) yielded **16a** (1.11 g, 97%).

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 8.05 (s, 1H), 4.61 (m, 2H), 4.45 (dd, *J* = 13.7, 9.0 Hz, 1H), 4.30-4.22 (m, 2H), 2.61 (m, 2H), 2.14 (m, 1H), 2.04 (m, 1H), 1.58 (s, 9H), 1.38 (t, *J* = 7.1 Hz, 3H, $CH_3$).

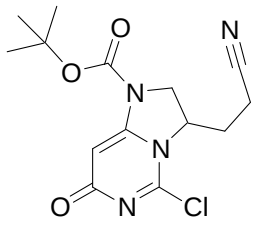
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 212.0 (C), 162.2 (C), 161.9 (C), 158.7 (C), 151.9 (C), 118.3 (C), 110.3 (CH), 85.1 (C), 70.7 ($CH_2$), 49.2 (CH), 47.7 ($CH_2$), 28.8 ($CH_2$), 27.9 ($3CH_3$), 15.0 ($CH_2$), 13.7 ($CH_3$).

**IR ($CCl_4$):** $\nu_{max}$ 2253, 1737, 1557, 1527, 1418.

**MS** (CI, NH3) *m/z* 365 (MH-Boc$^+$), 367 (MH+2-Boc$^+$), 369 (MH+4-Boc$^+$).

**HRMS (EI+):** calculated for $C_{17}H_{22}O_3N_4Cl_2S_2$ 464.0515, found 464.0515.

**Tert-butyl 5-chloro-3-(2-cyanoethyl)-7-oxo-2,3-dihydroimidazo[1,2-f]pyrimidine-1(7H)-carboxylate (19)**




Following general procedure C for radical cyclisation, the reaction was carried out using xanthate **16a** (950 mg, 2.04 mmol, 1 equiv.) in ethyl acetate (31 mL) and needed 140 mol % of DLP to go to completion. Purification (petroleum ether/ethyl acetate 7/3 to 0/1) yielded the corresponding diazaindoline (100 mg, 14%), along with a 6 : 1 mixture of pyrimidinones (350 mg,53%). A fraction of the major compound **19** was separated and characterised.

**$^{1}$H-NMR (400 MHz, $CDCl_3$):** $\delta_H$ 6.73 (s, 1H), 4.71 (m, 1H), 4.21 (dd, *J* = 11.3, 9.8 Hz, 1H), 4.02 (m, 1H), 2.56-2.49 (m, 3H), 2.18 (m, 1H), 1.56 (s, 9H).

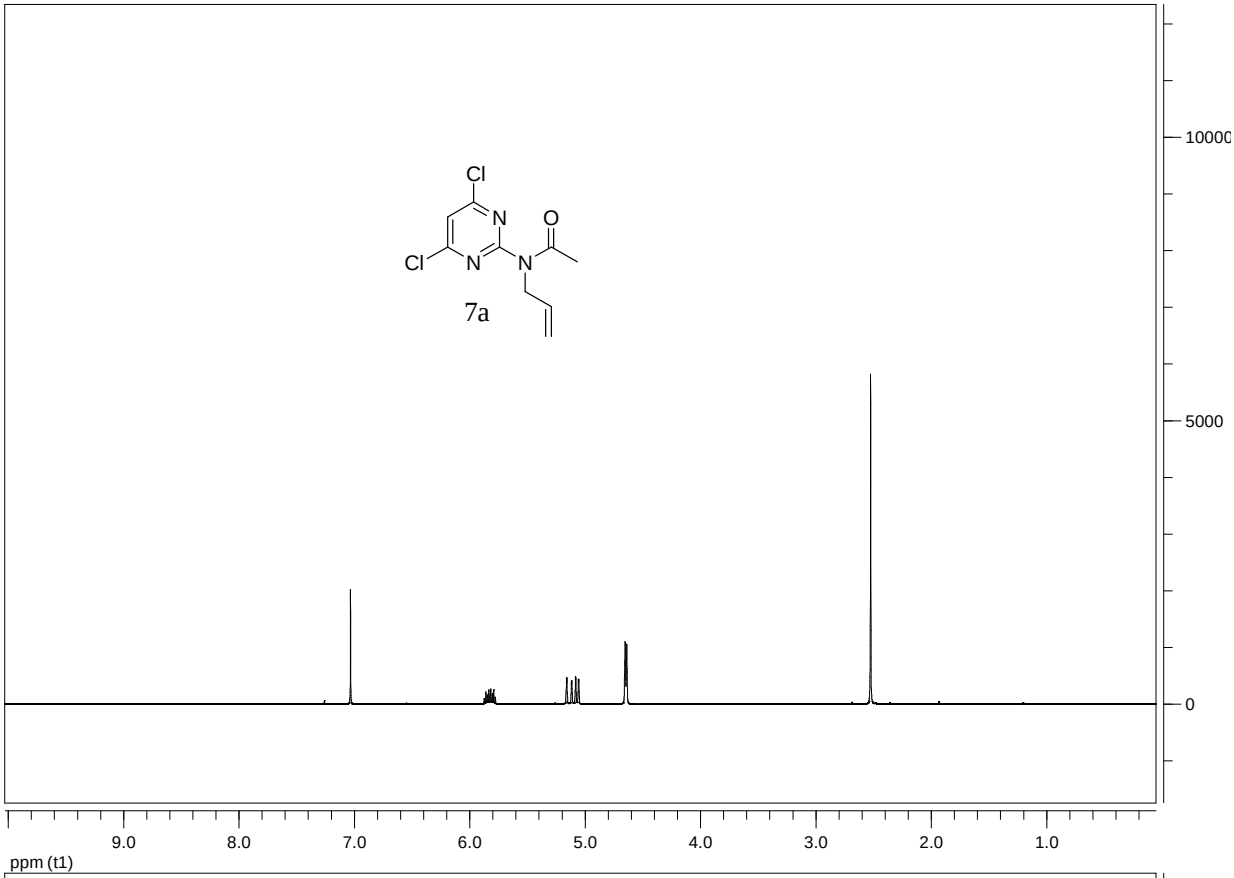
**$^{13}$C-NMR (100 MHz, $CDCl_3$):** $\delta_c$ 167.9 (C), 152.8 (C), 152.1 (C), 148.9 (C), 118.2 (C), 90.5 (CH), 85.9 (C), 54.6 (CH), 50.0 ($CH_2$), 27.9 ($CH_2$+$3CH_3$), 13.4 ($CH_2$).

**IR ($CCl_4$):** $\nu_{max}$ 3156, 2984, 2250, 1748, 1685, 1611, 1524.

**MS** (CI, NH3) *m/z* 225 (MH-Boc$^+$), 227 (MH+2-Boc$^+$).

**HRMS (EI+):** calculated for $C_{14}H_{17}O_3N_4Cl$ 324.0989, found 324.0992.

# Copies of $^{1}H$ and $^{13}C$ Spectra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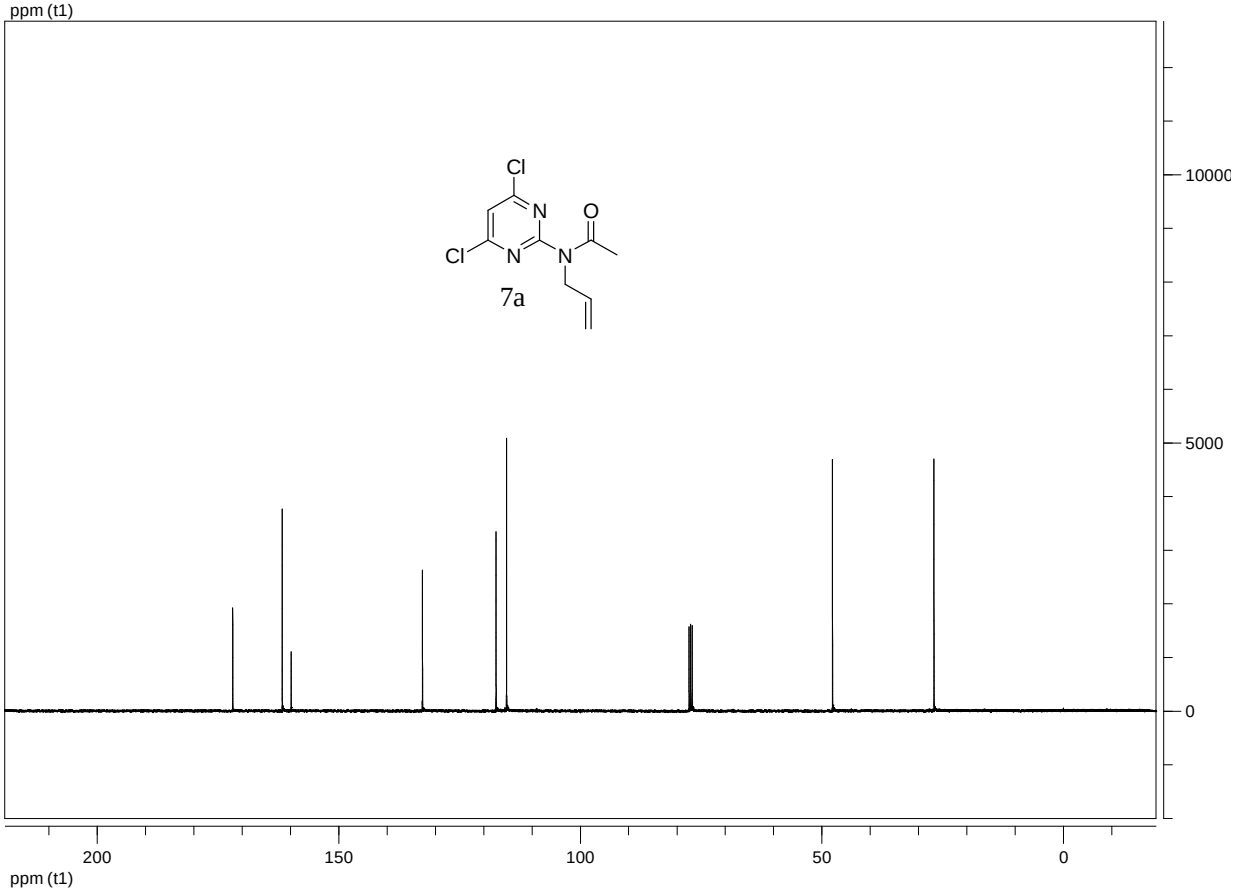
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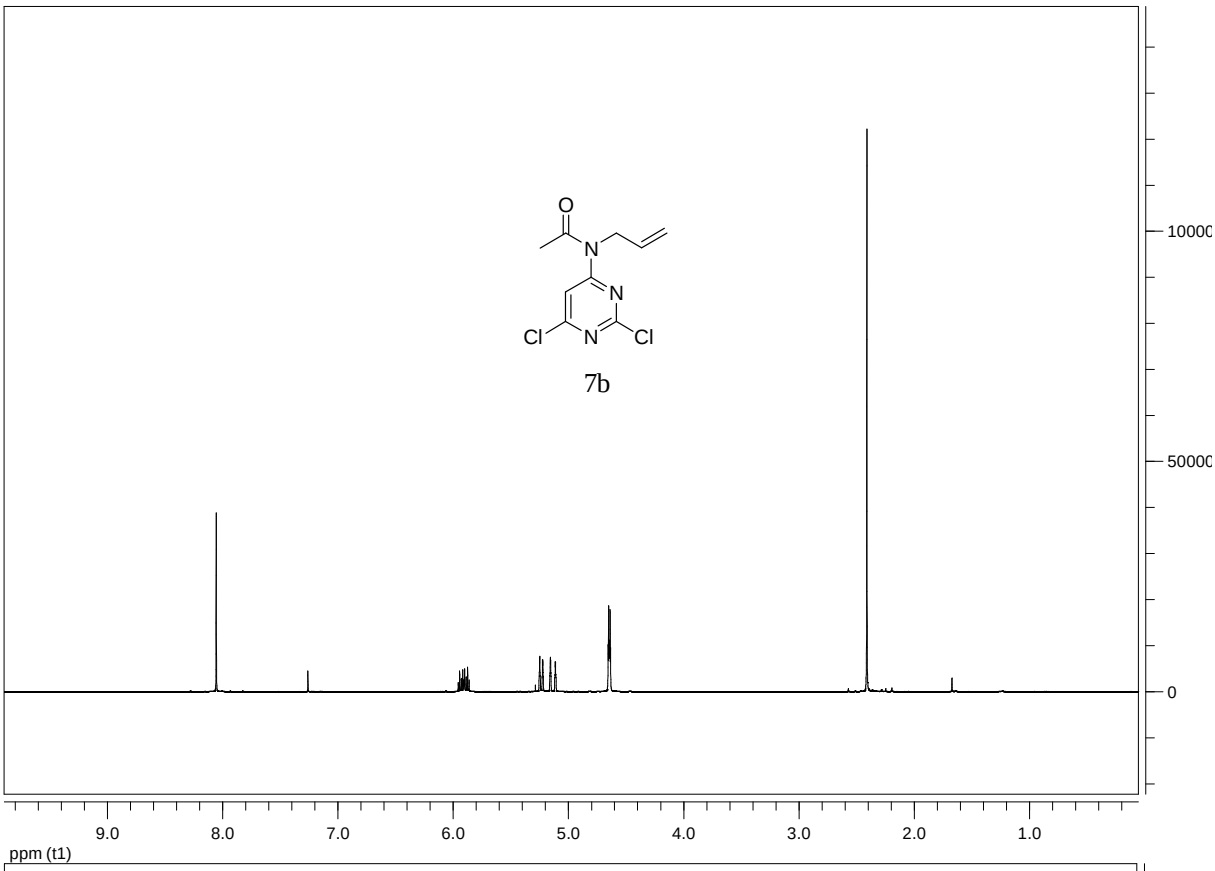
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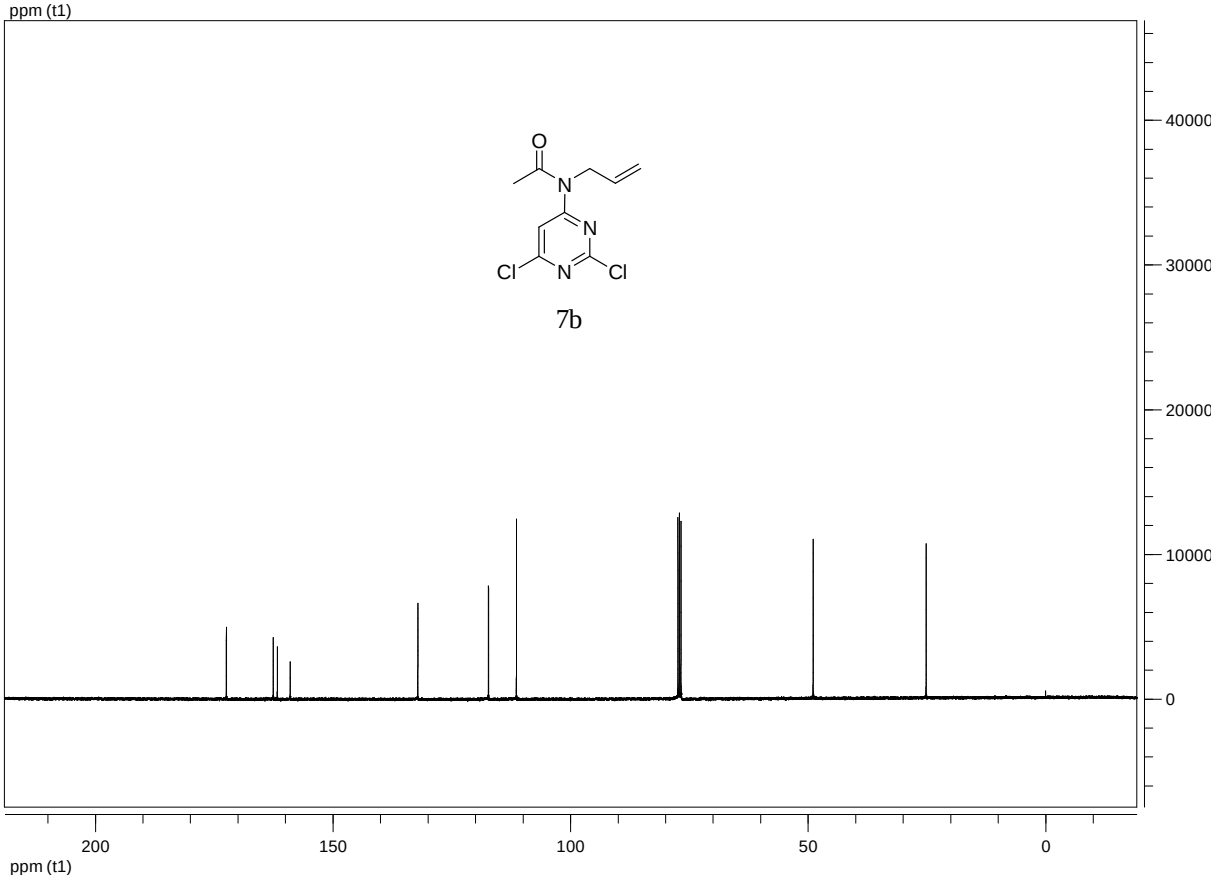
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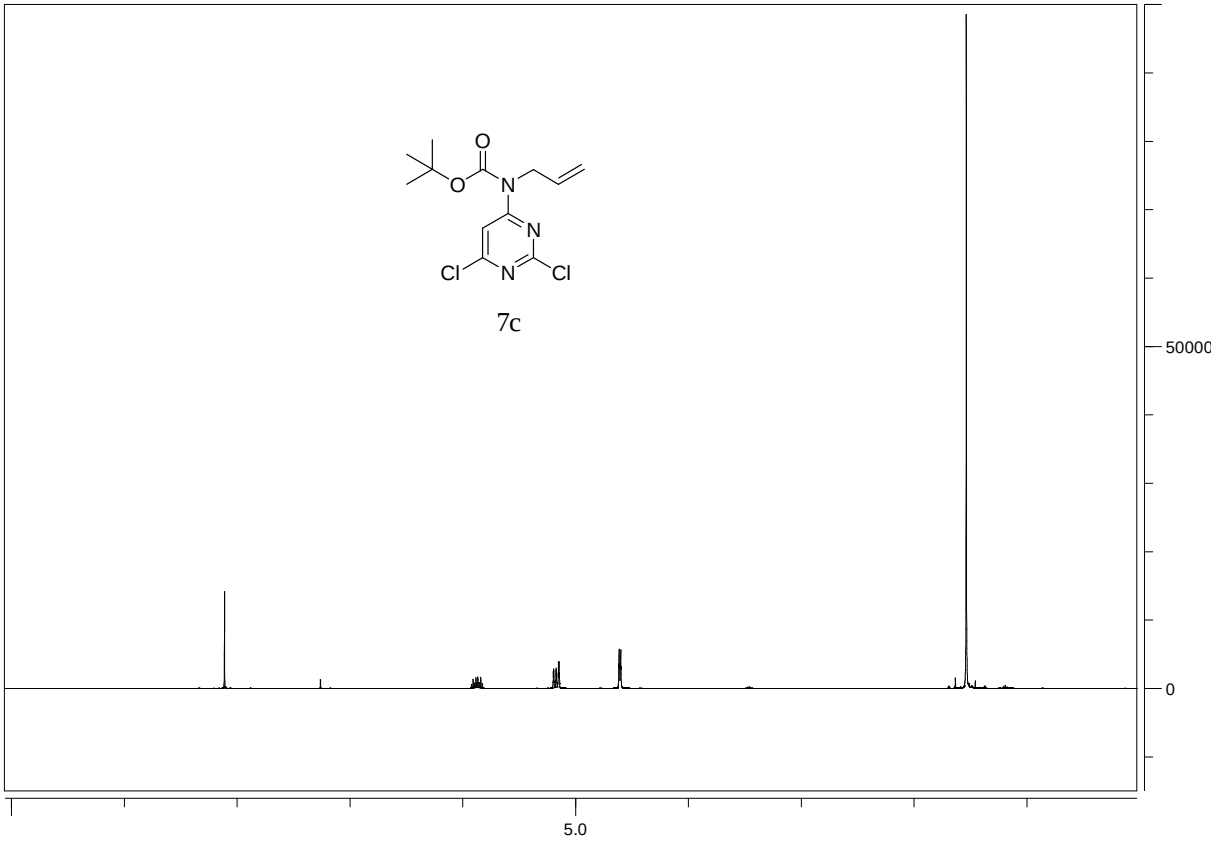
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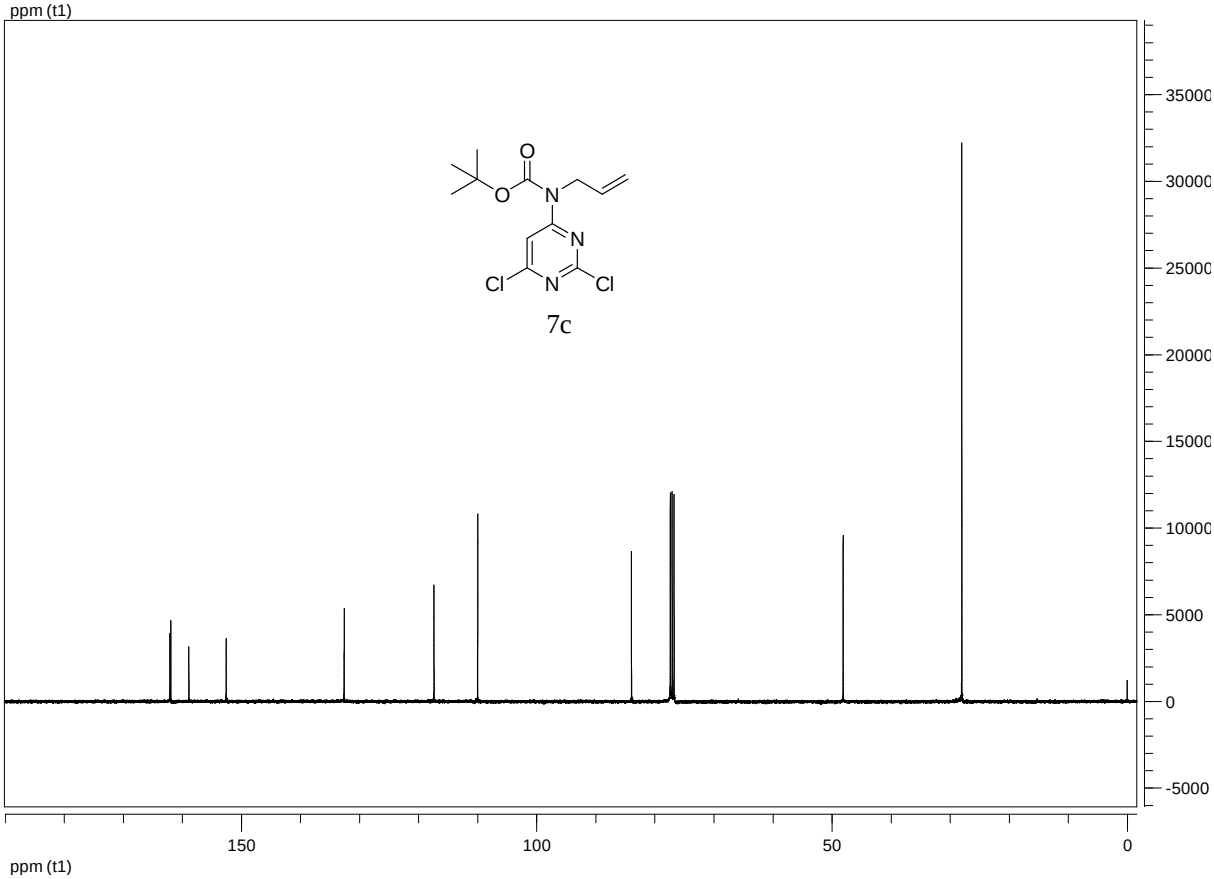
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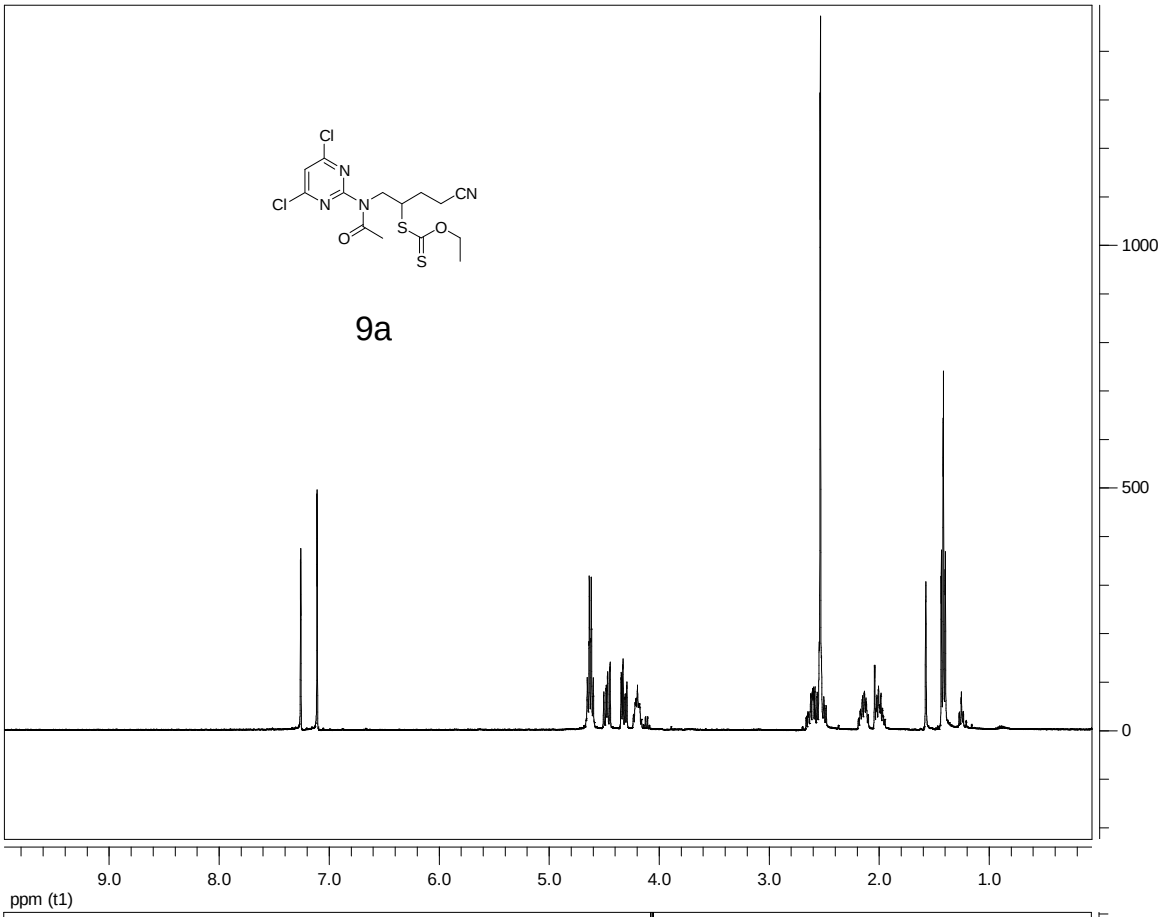
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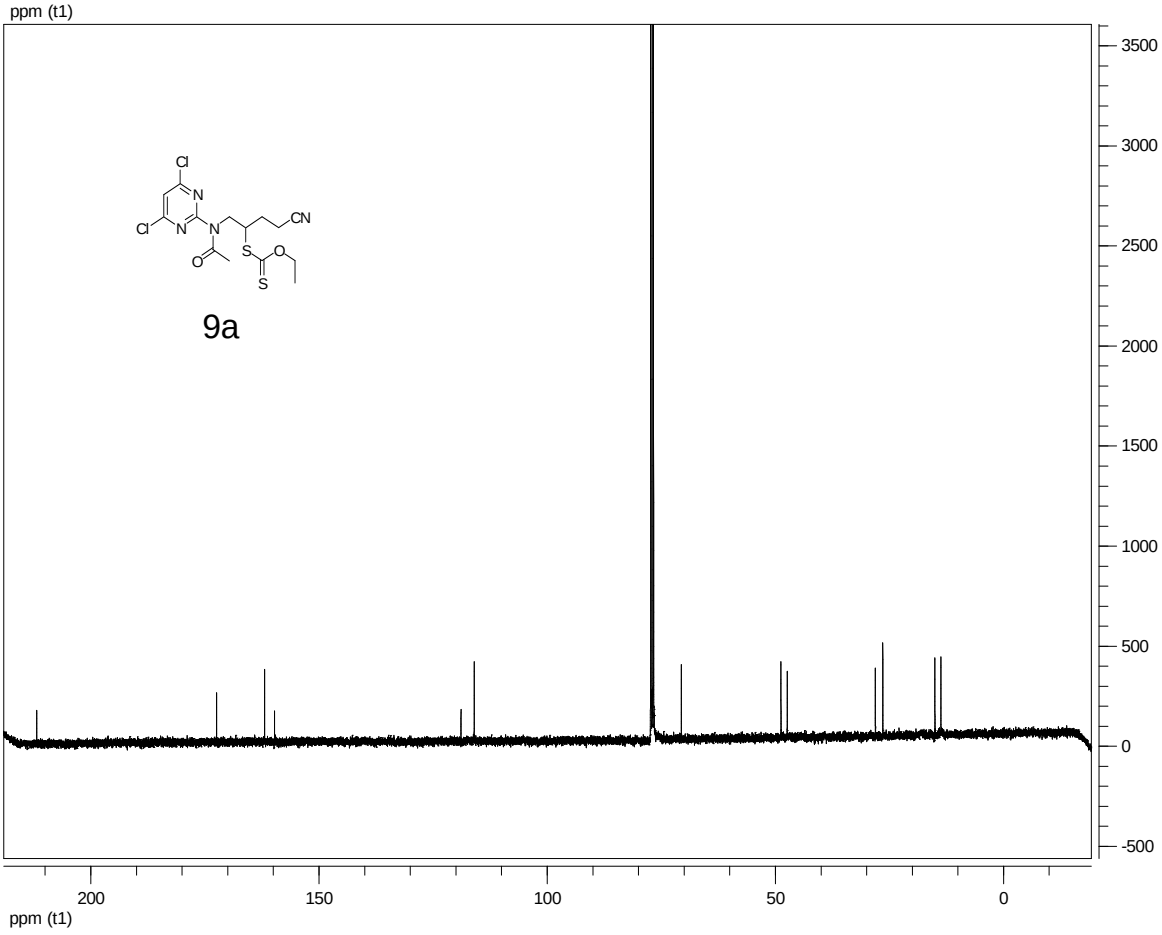
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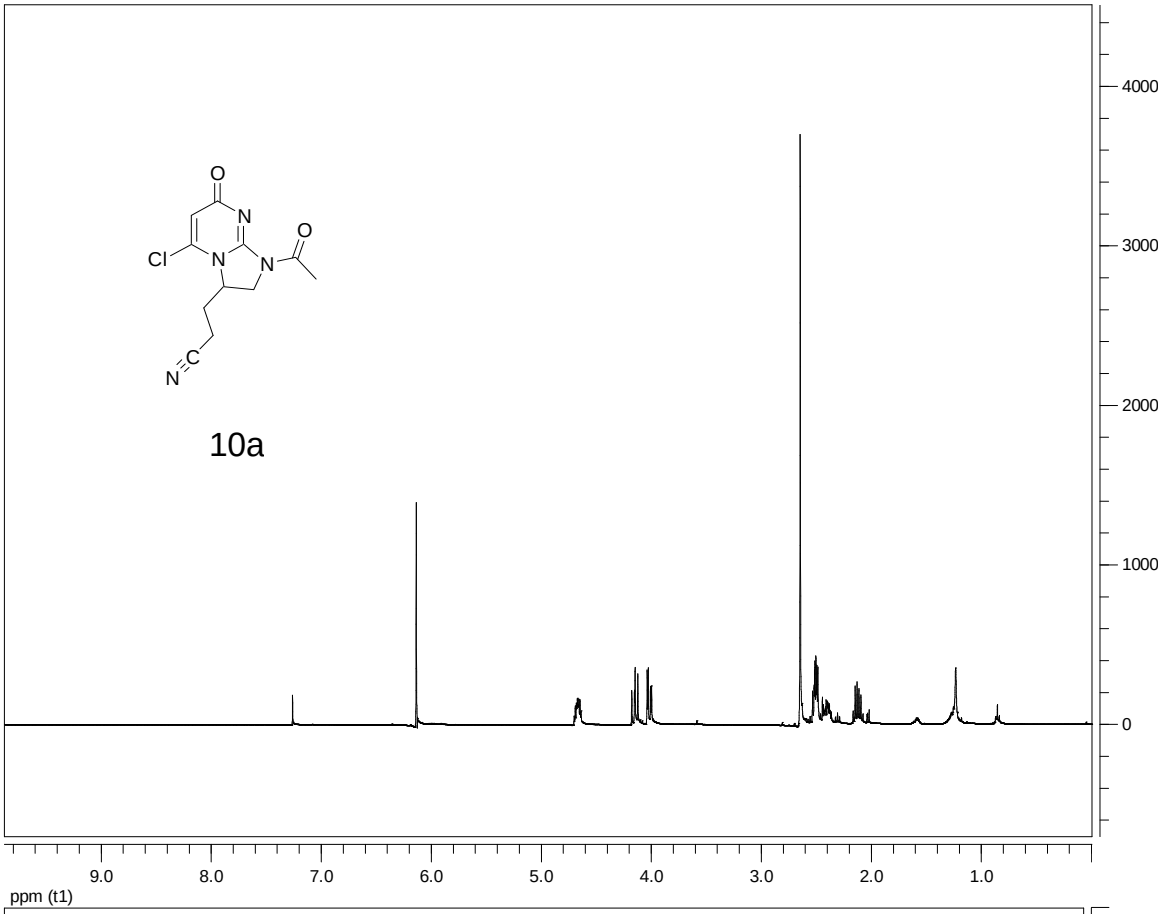
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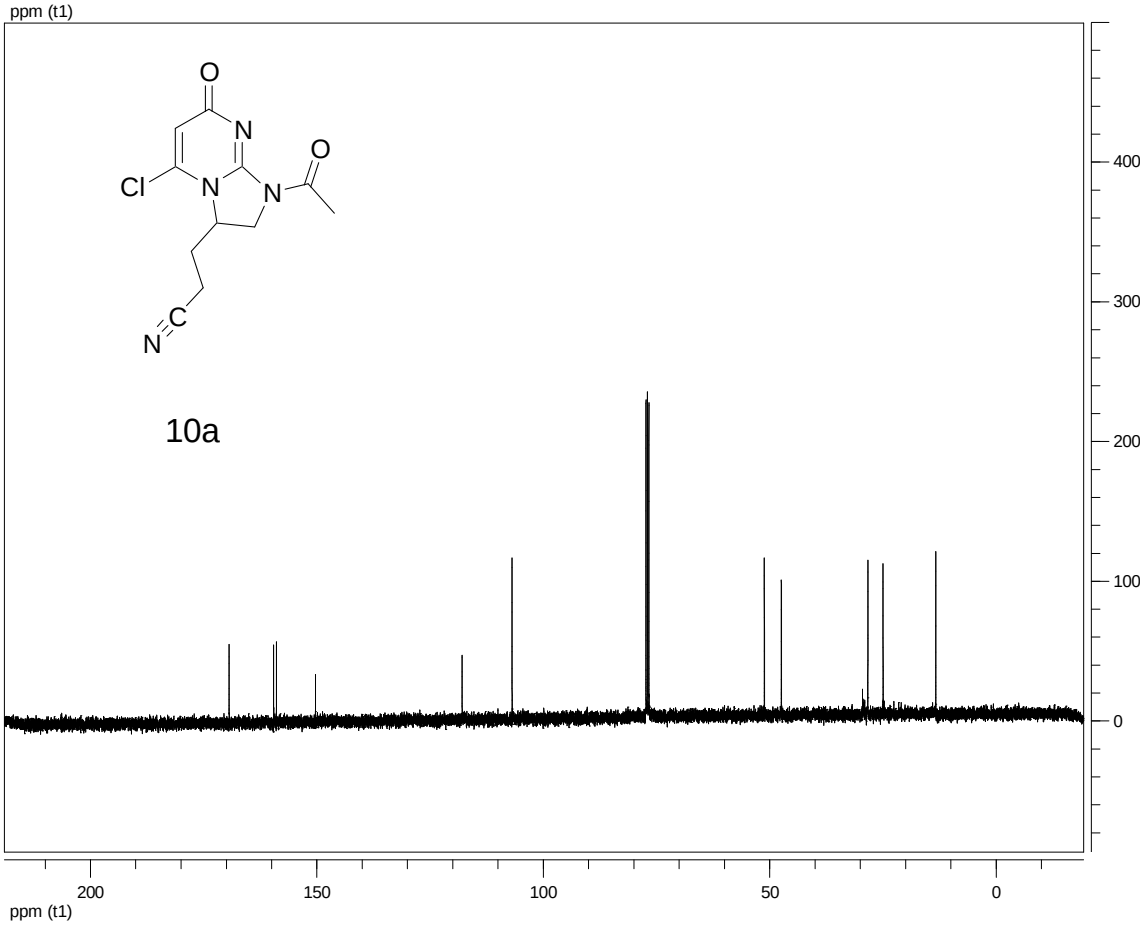
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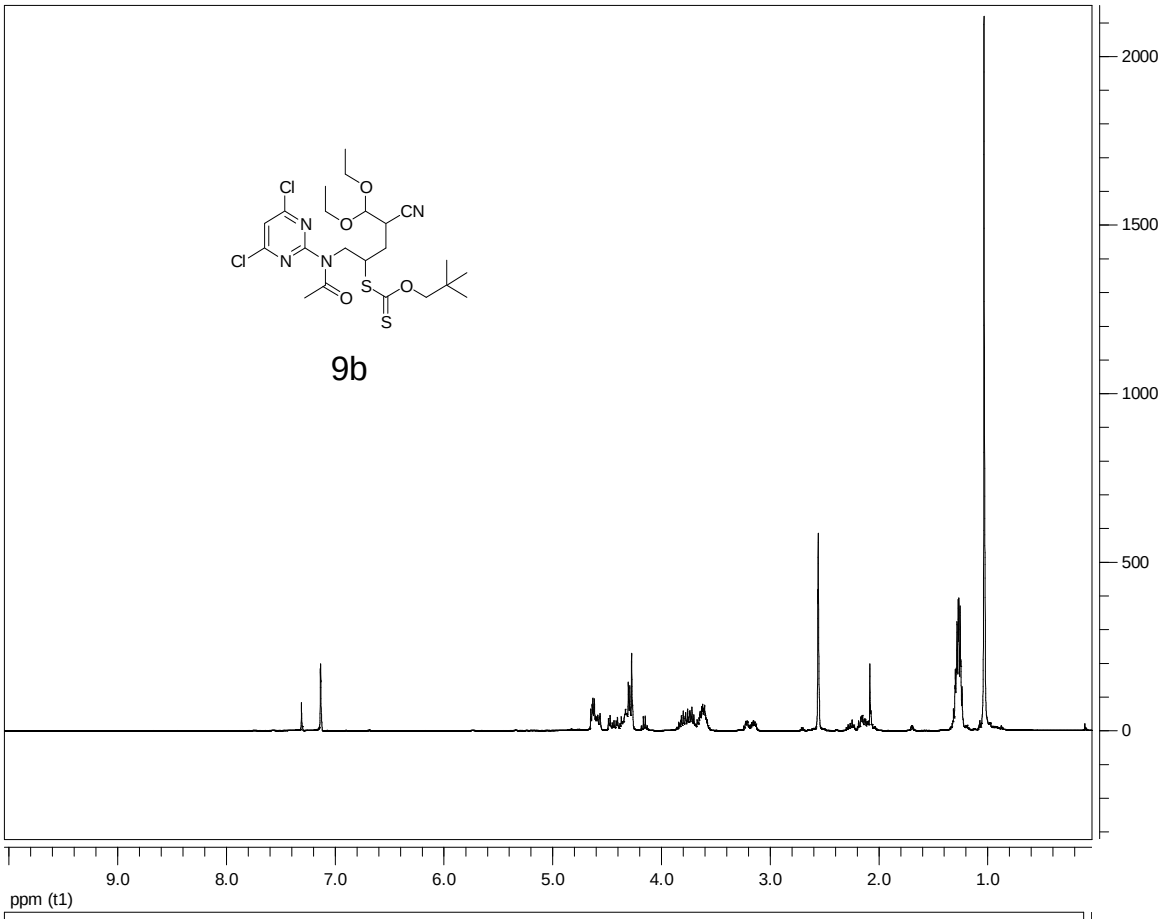
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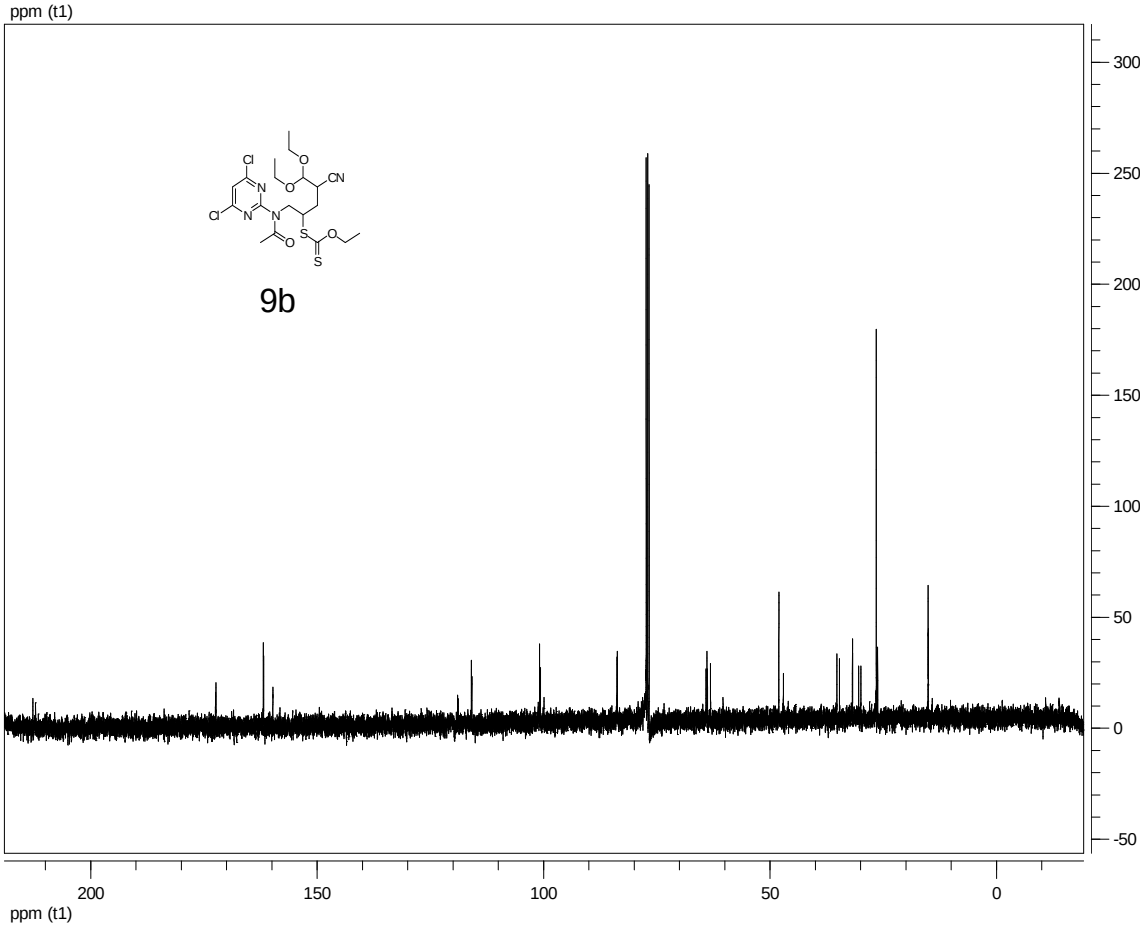
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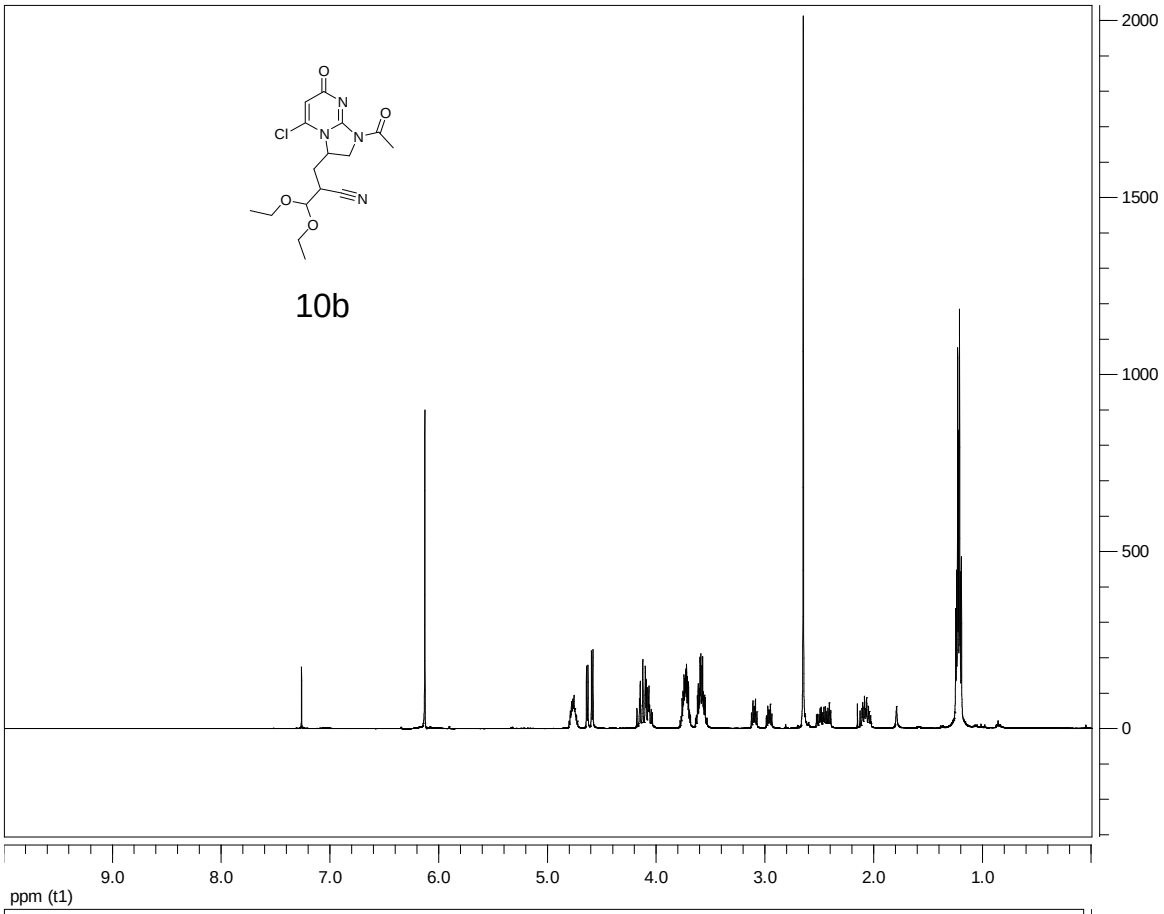
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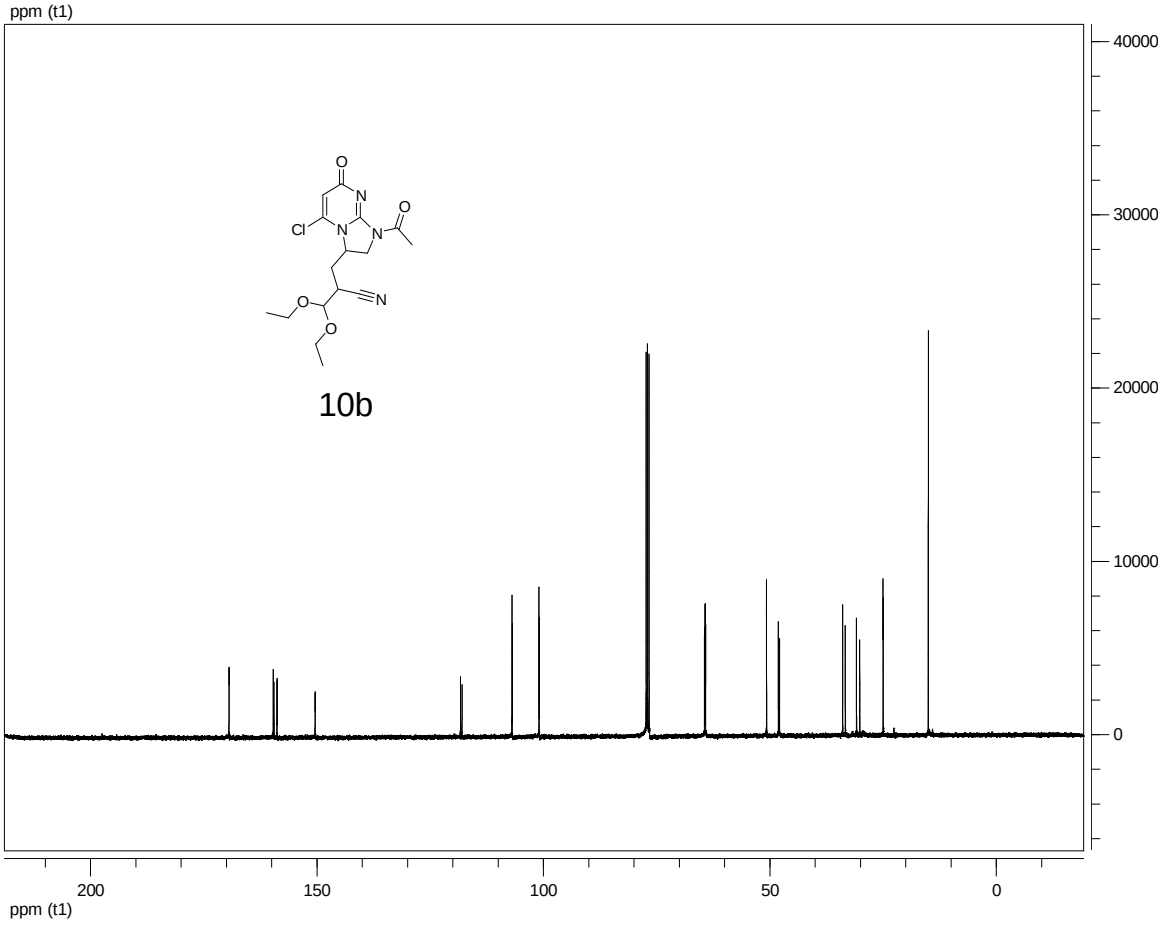
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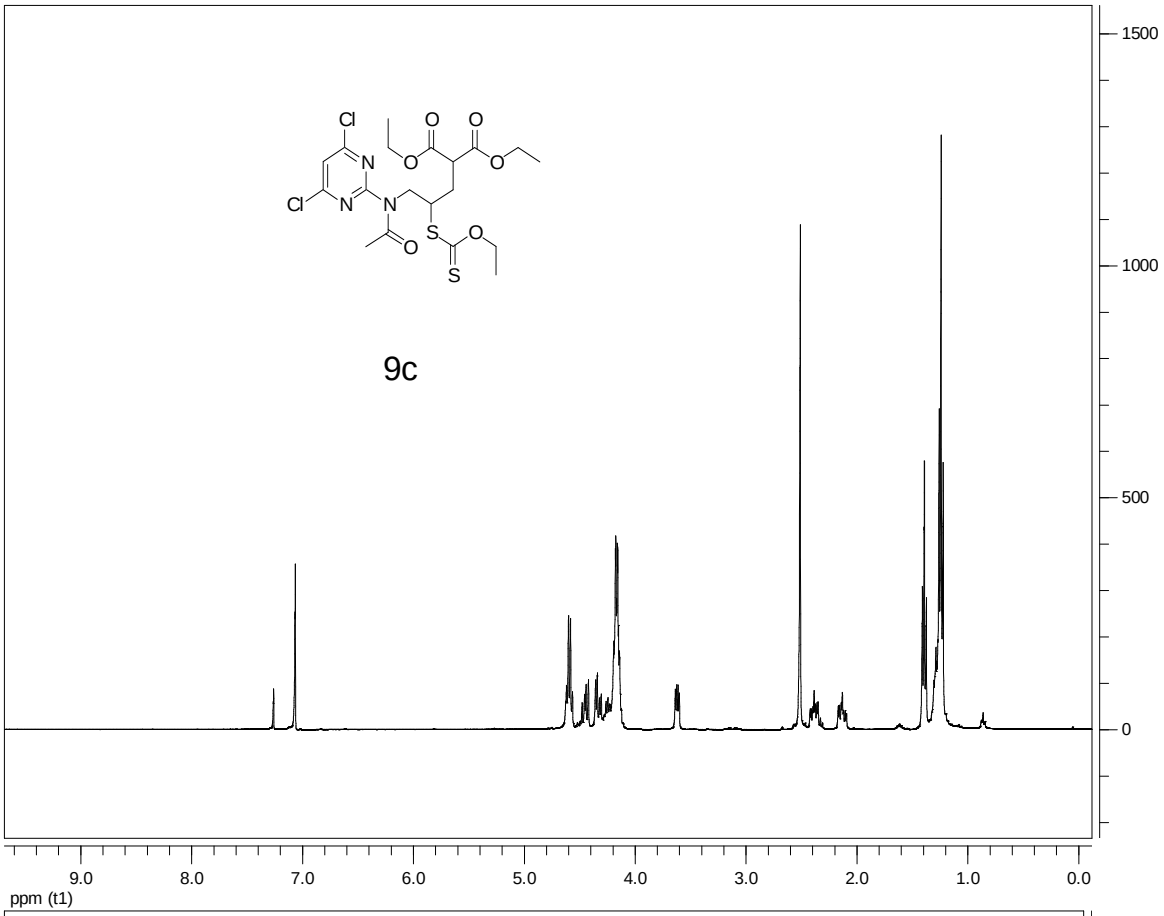
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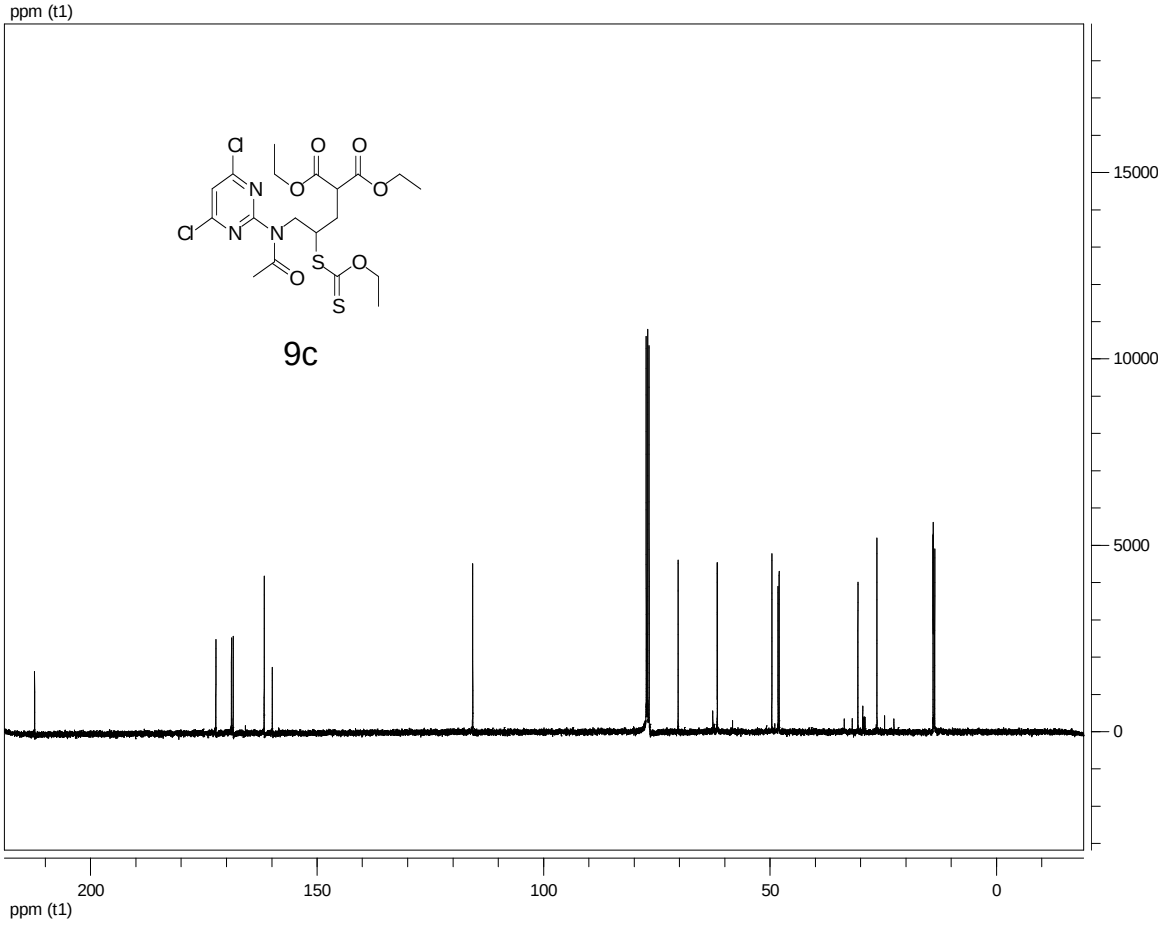
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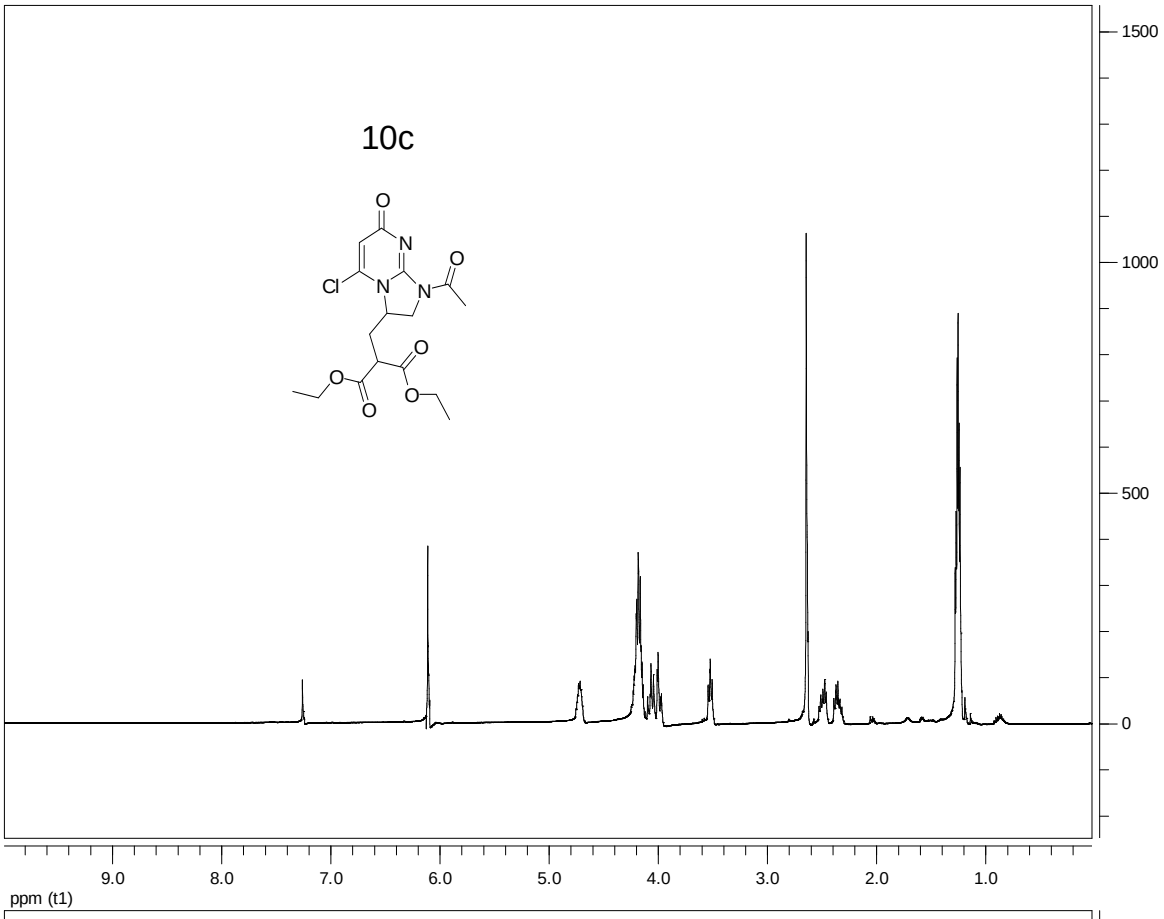
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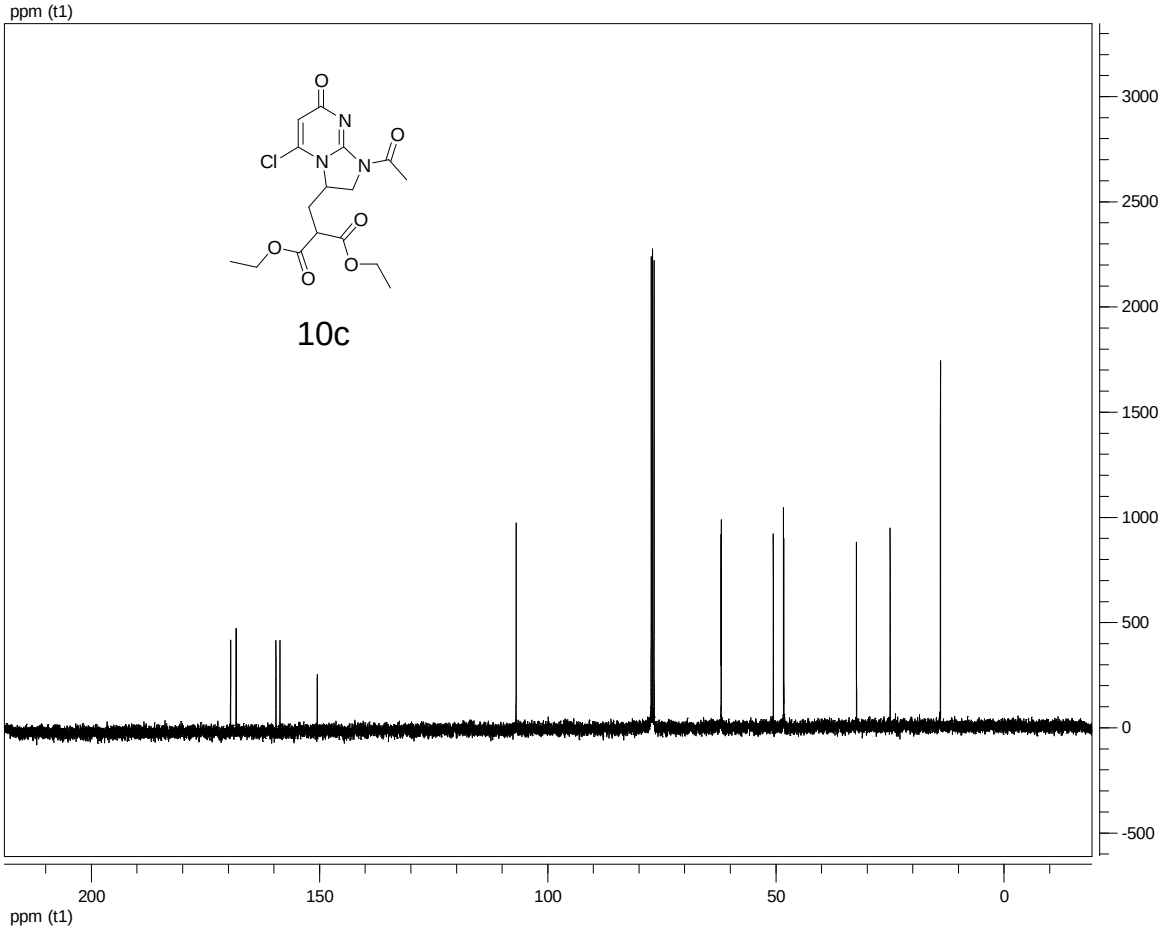
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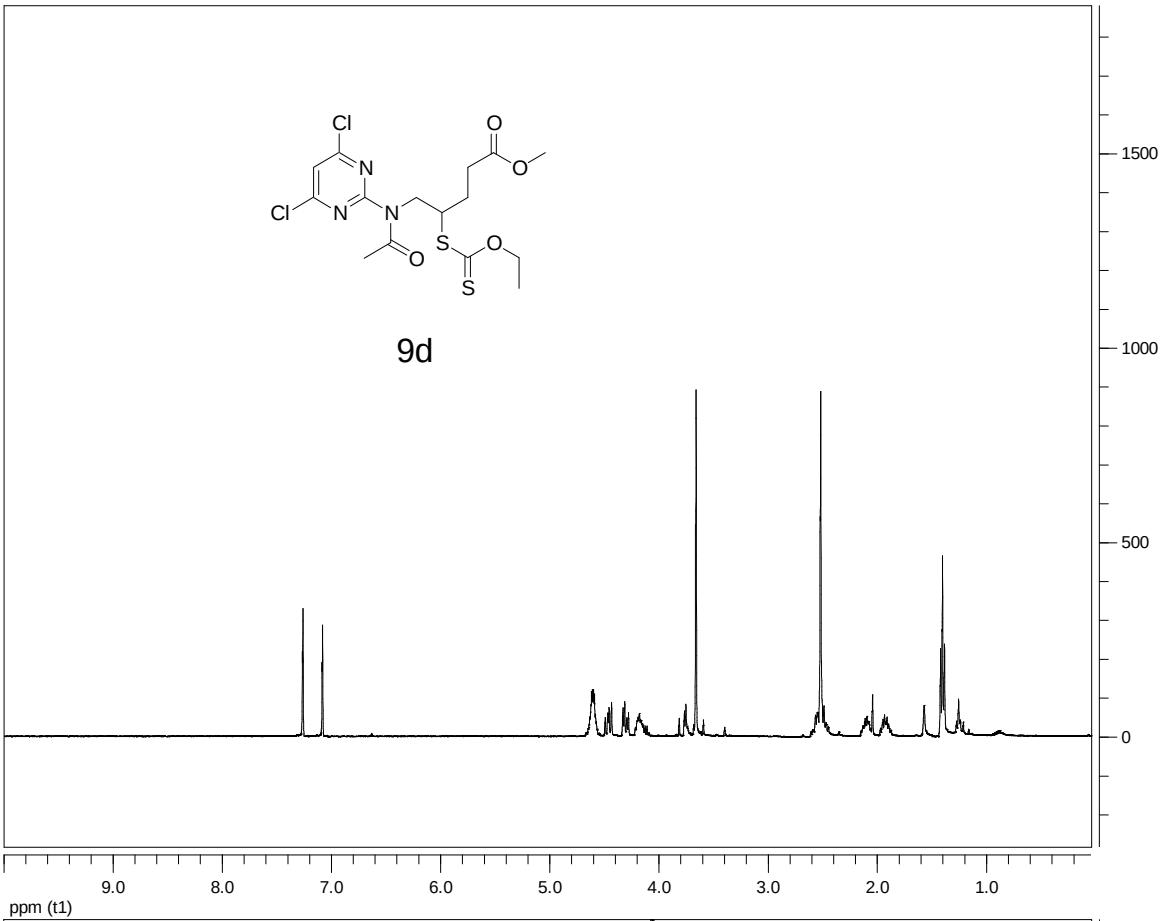
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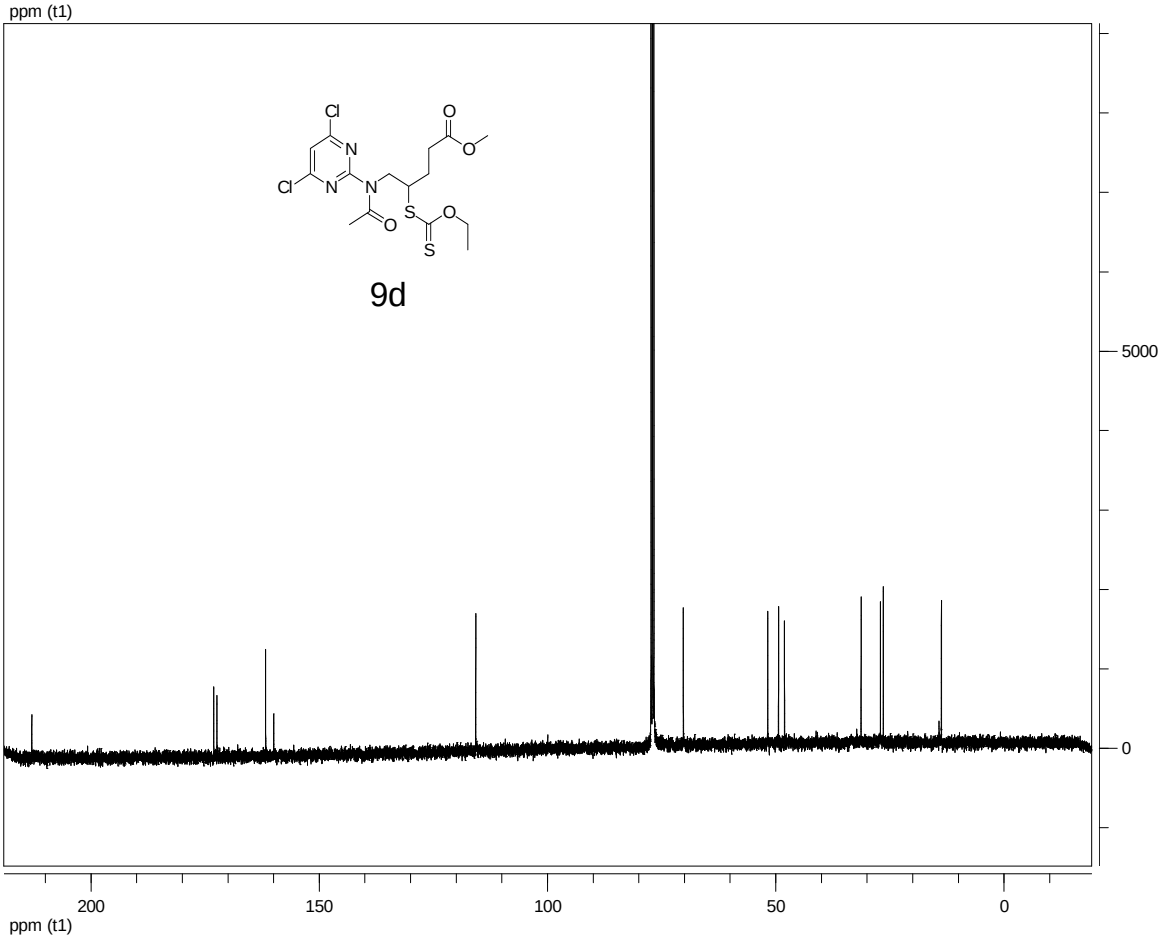
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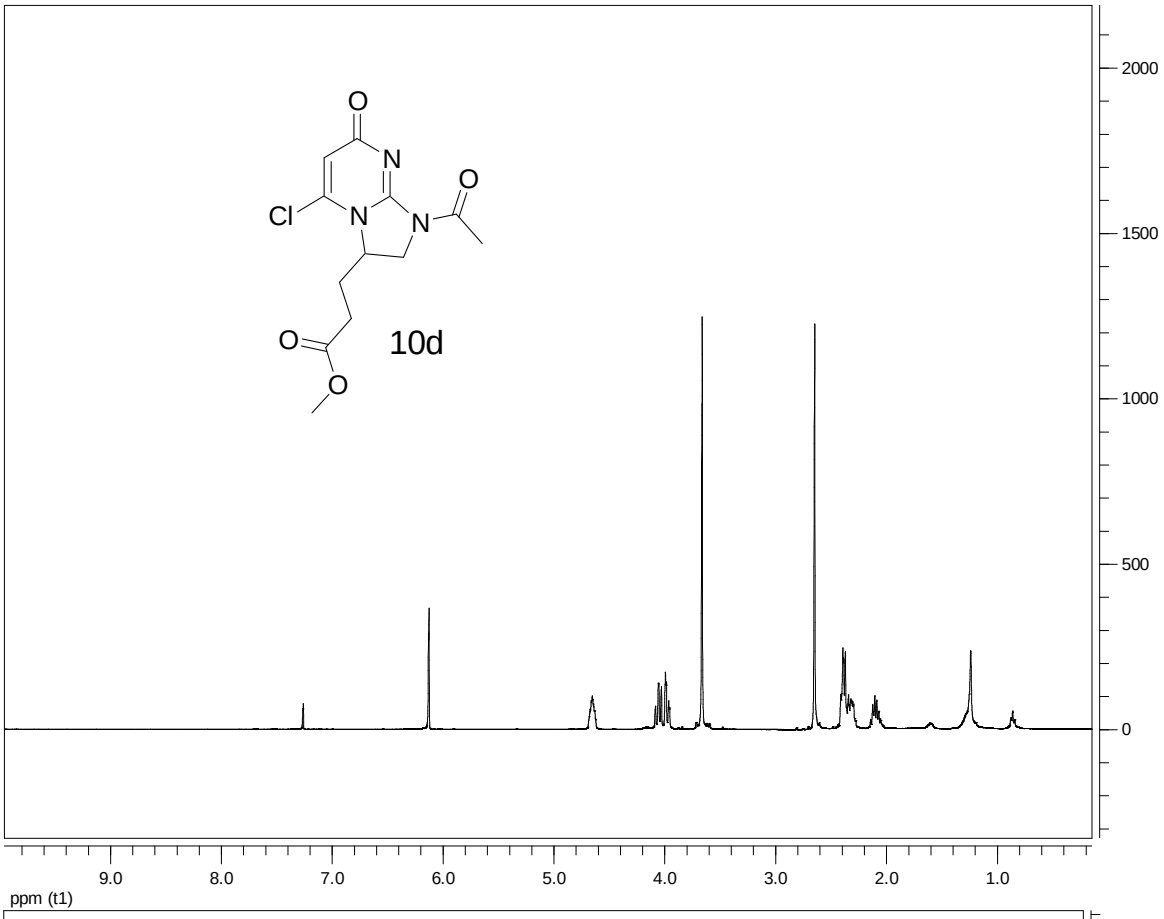
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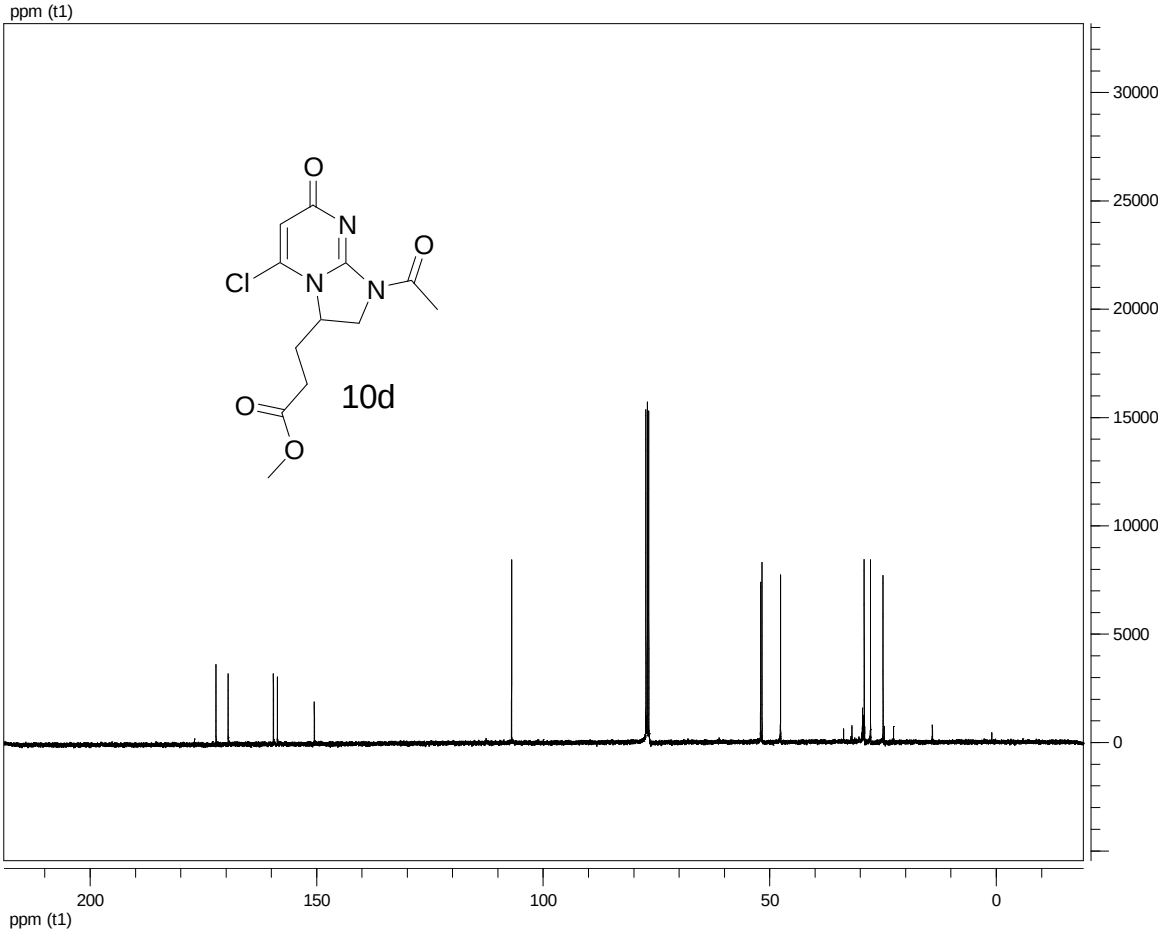
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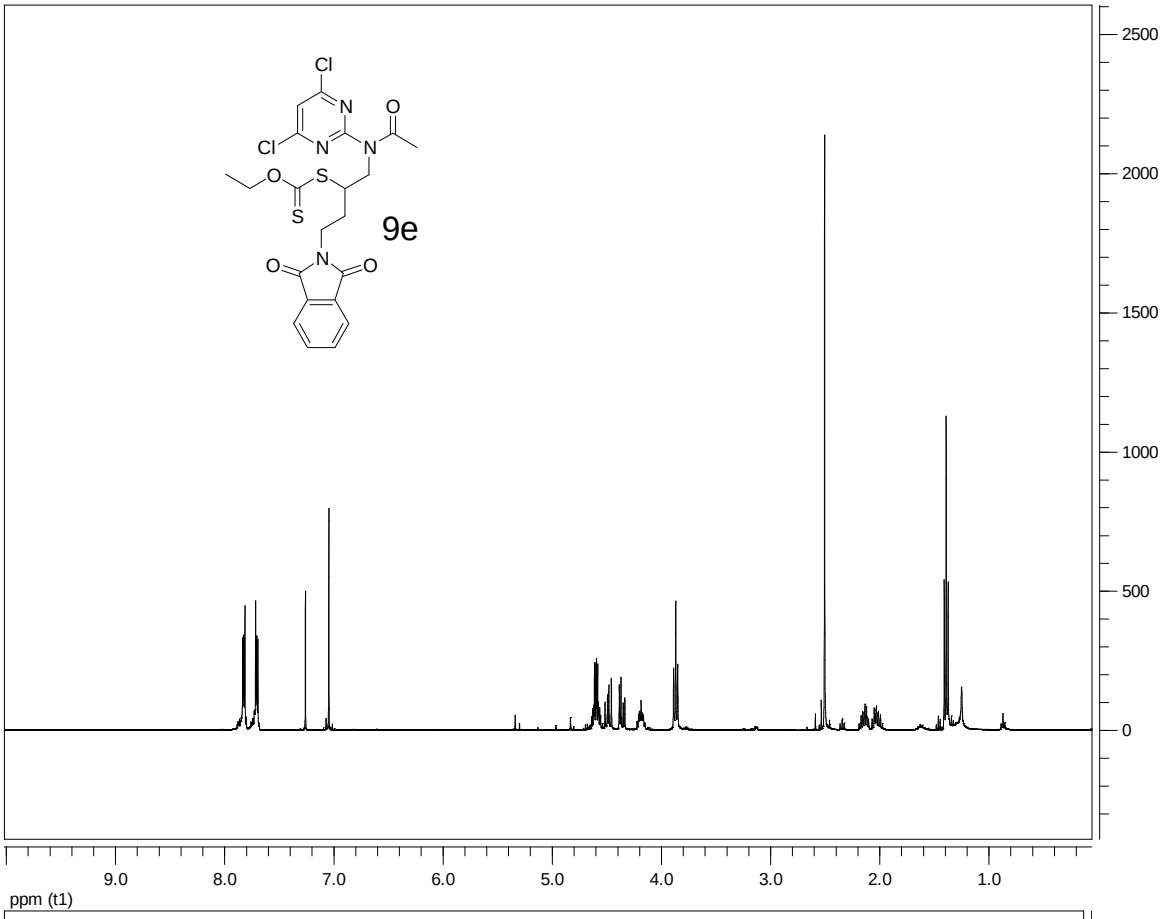
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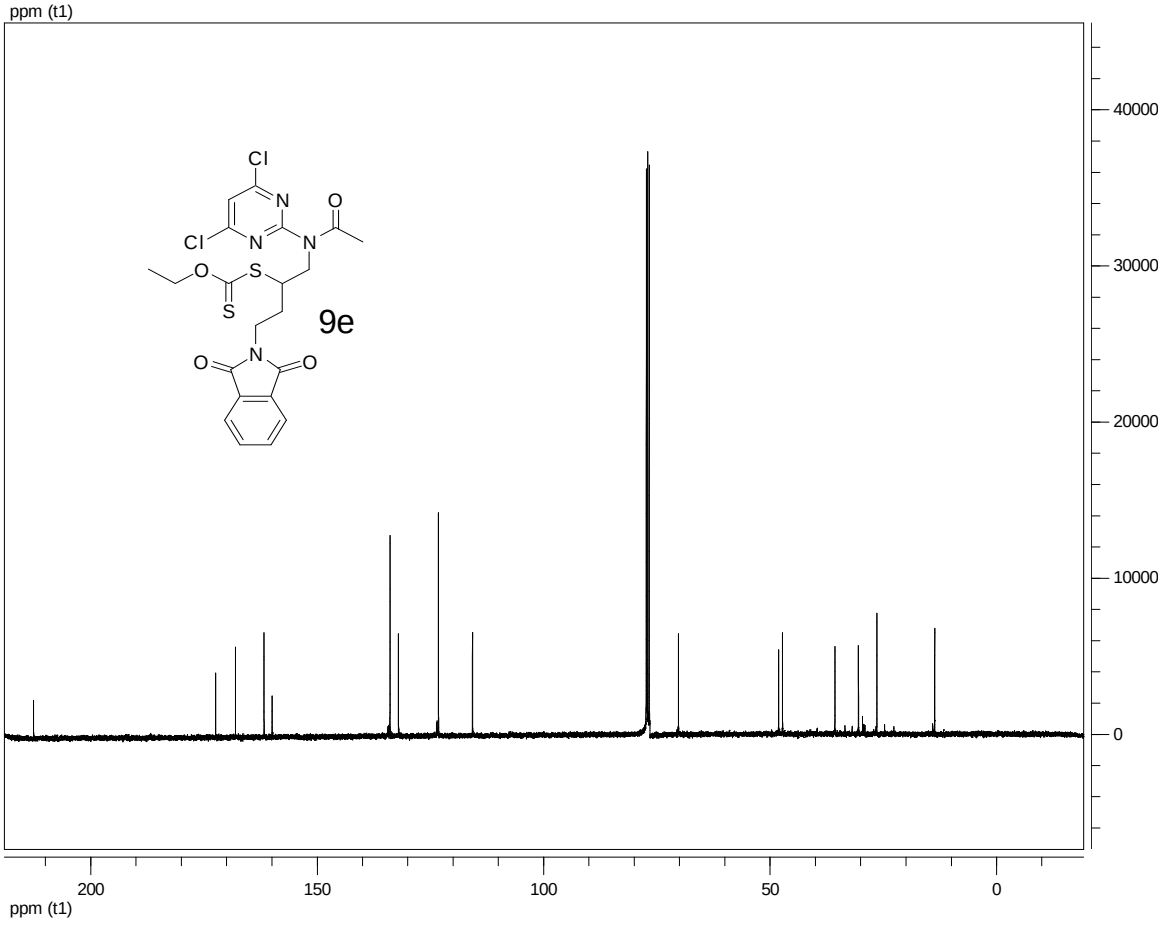
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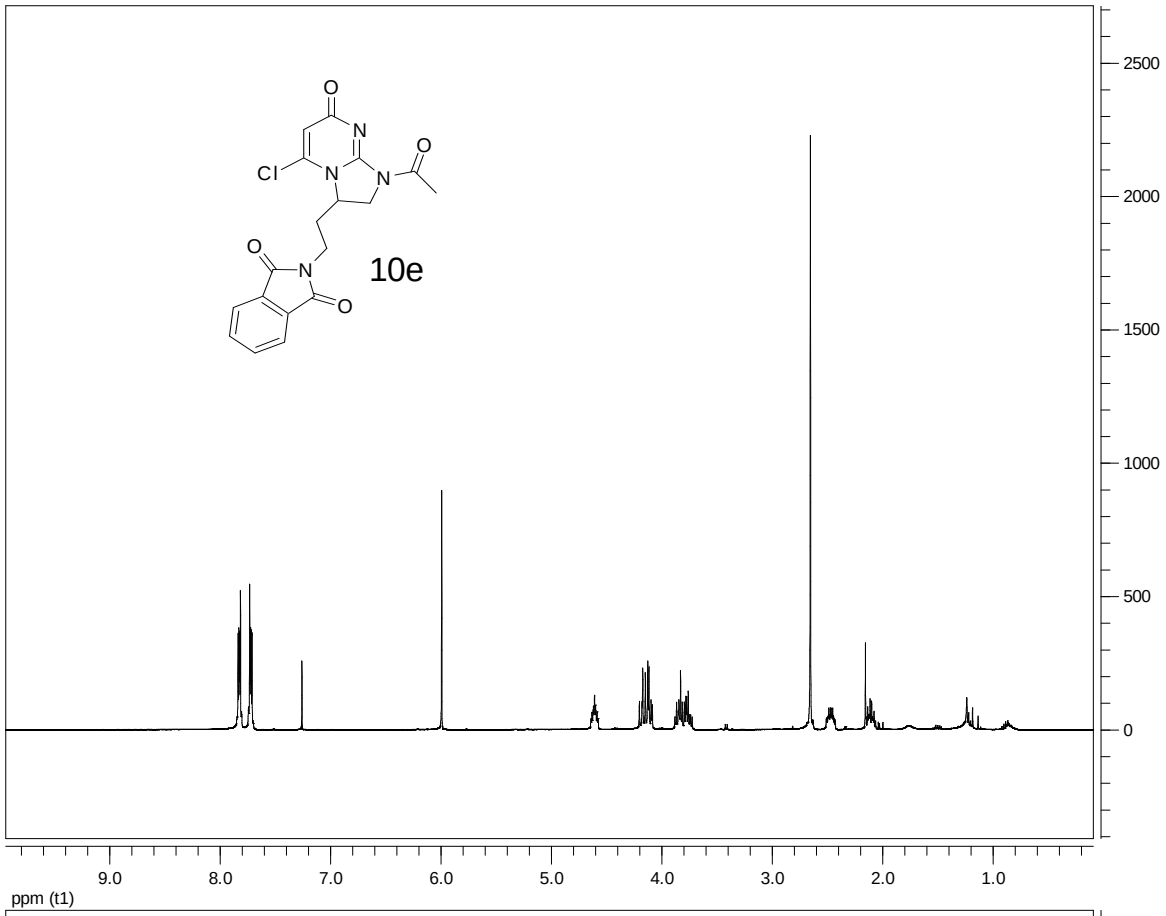
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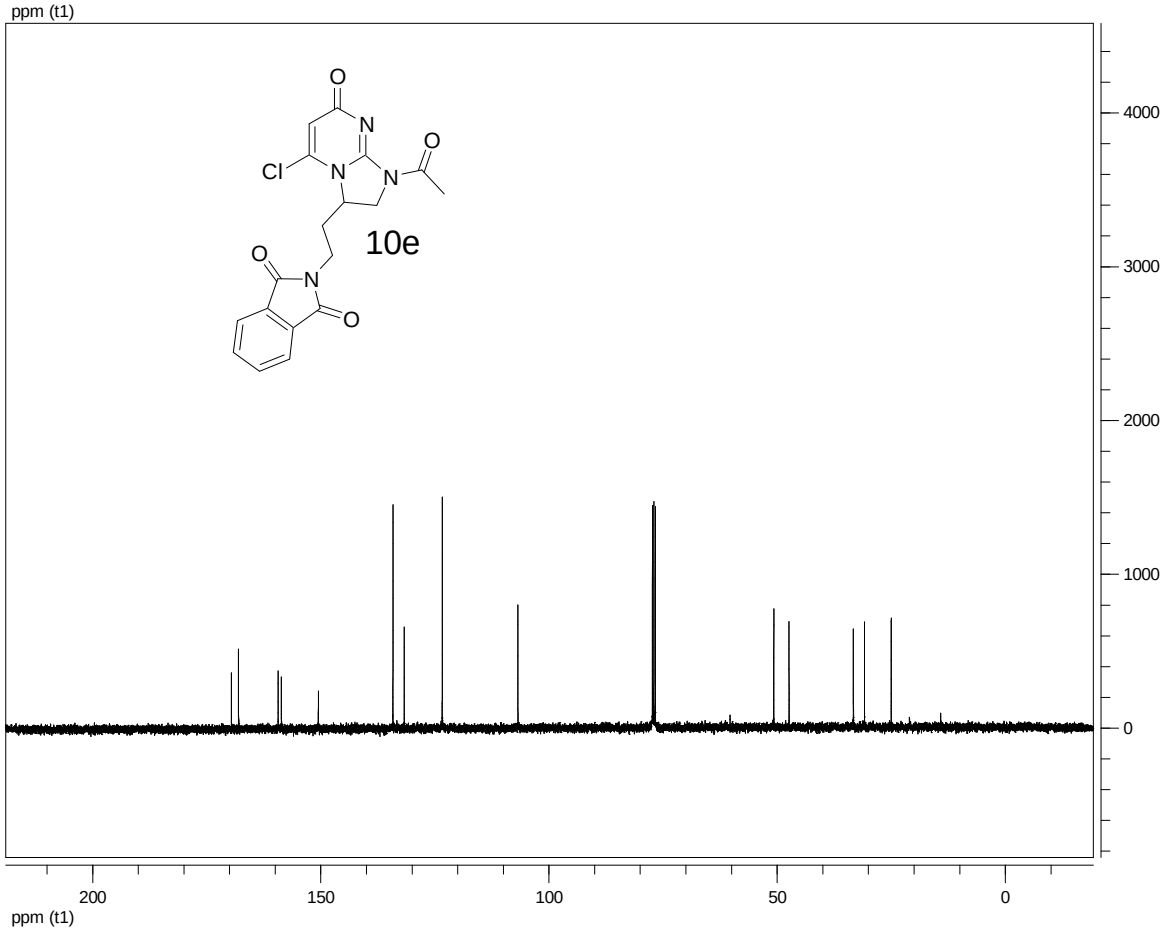
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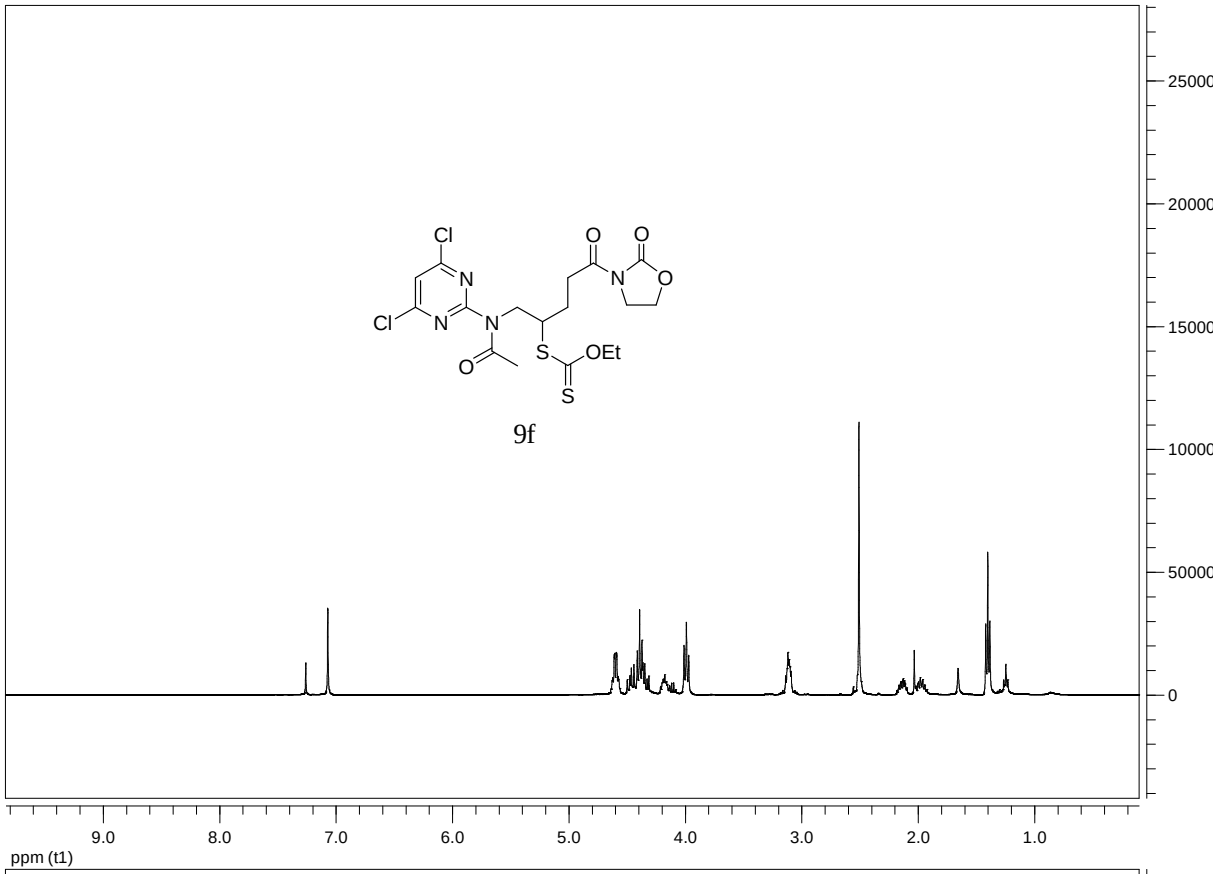
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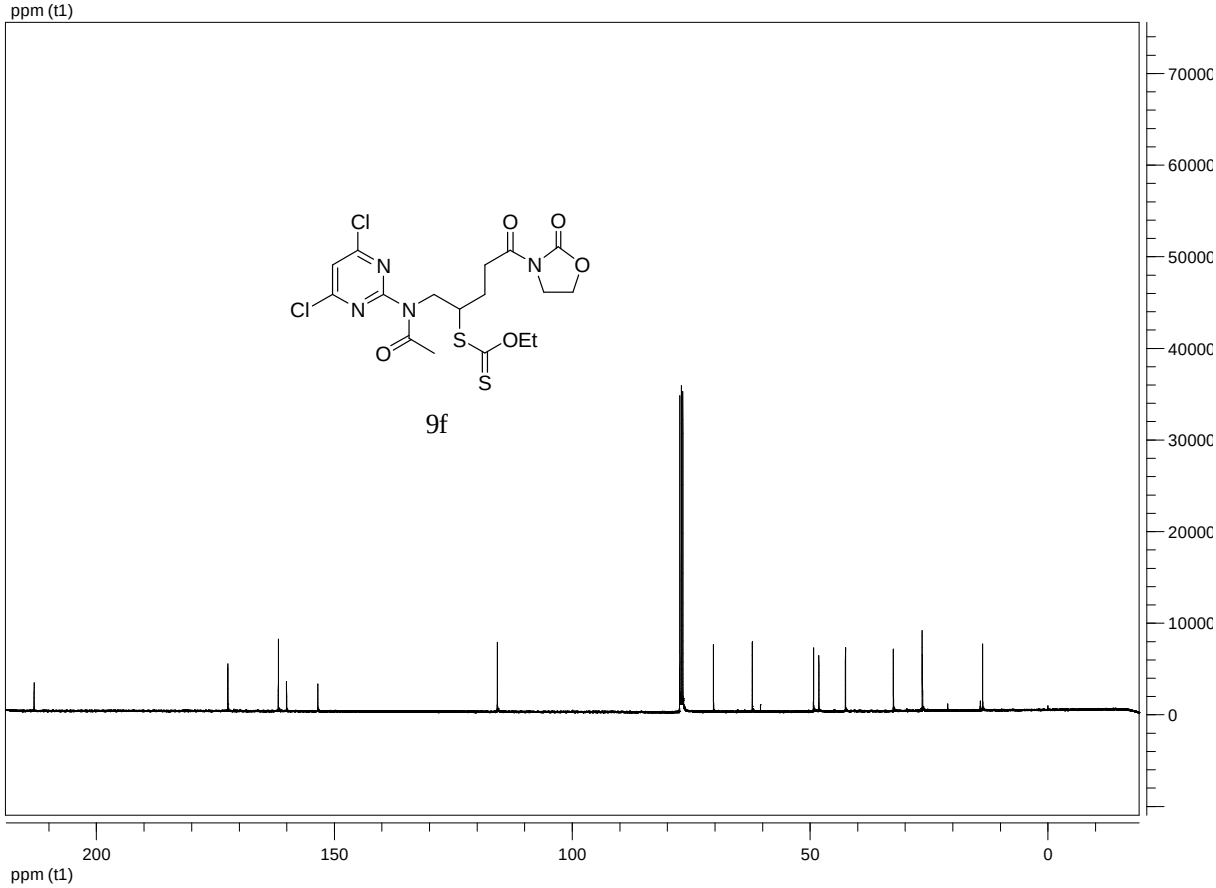
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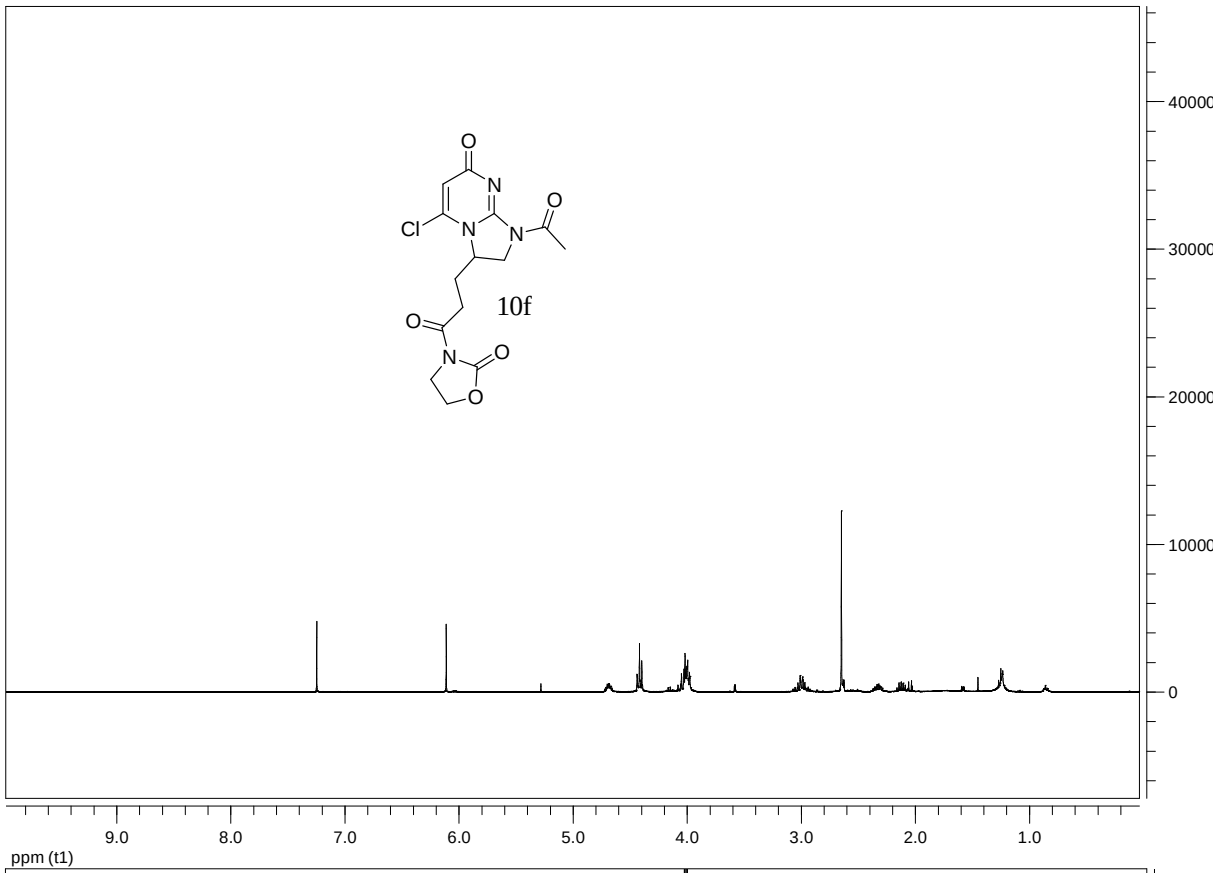
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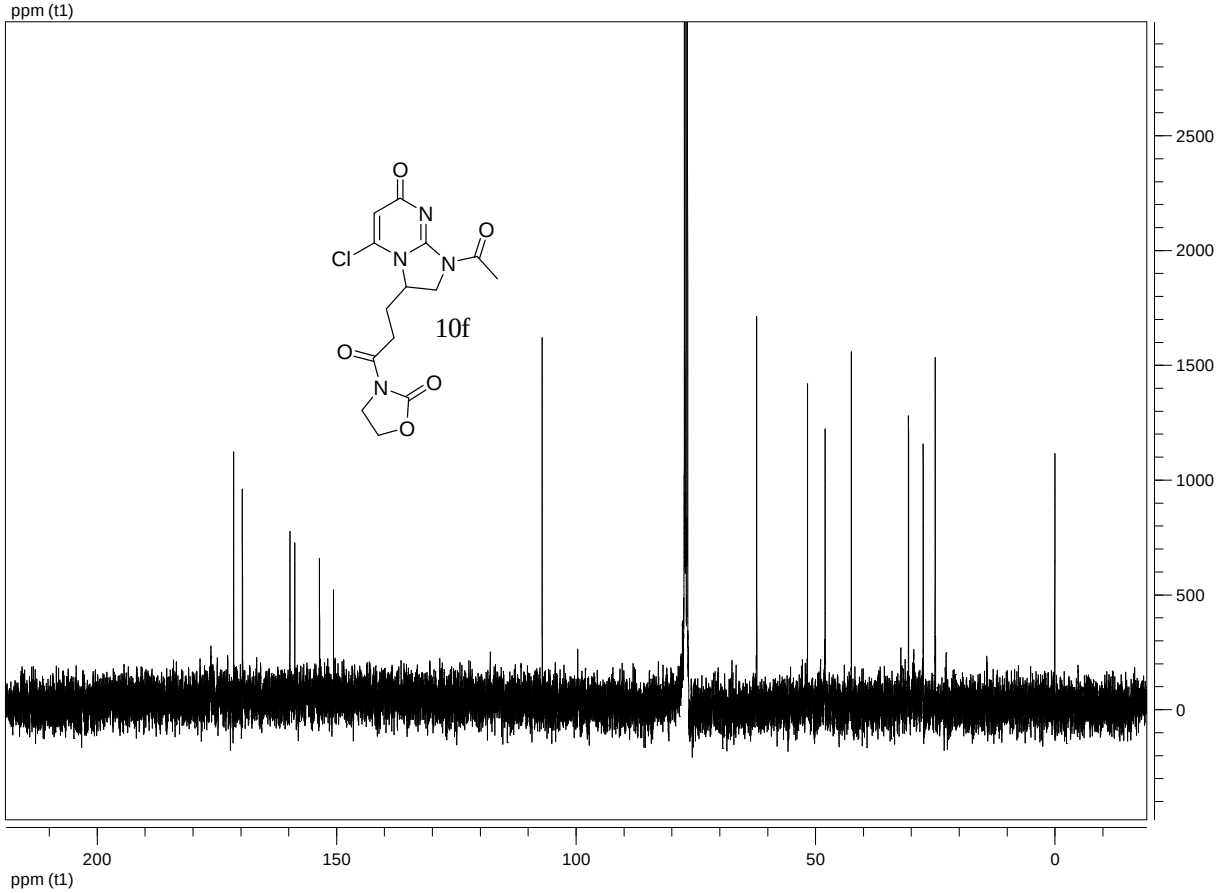
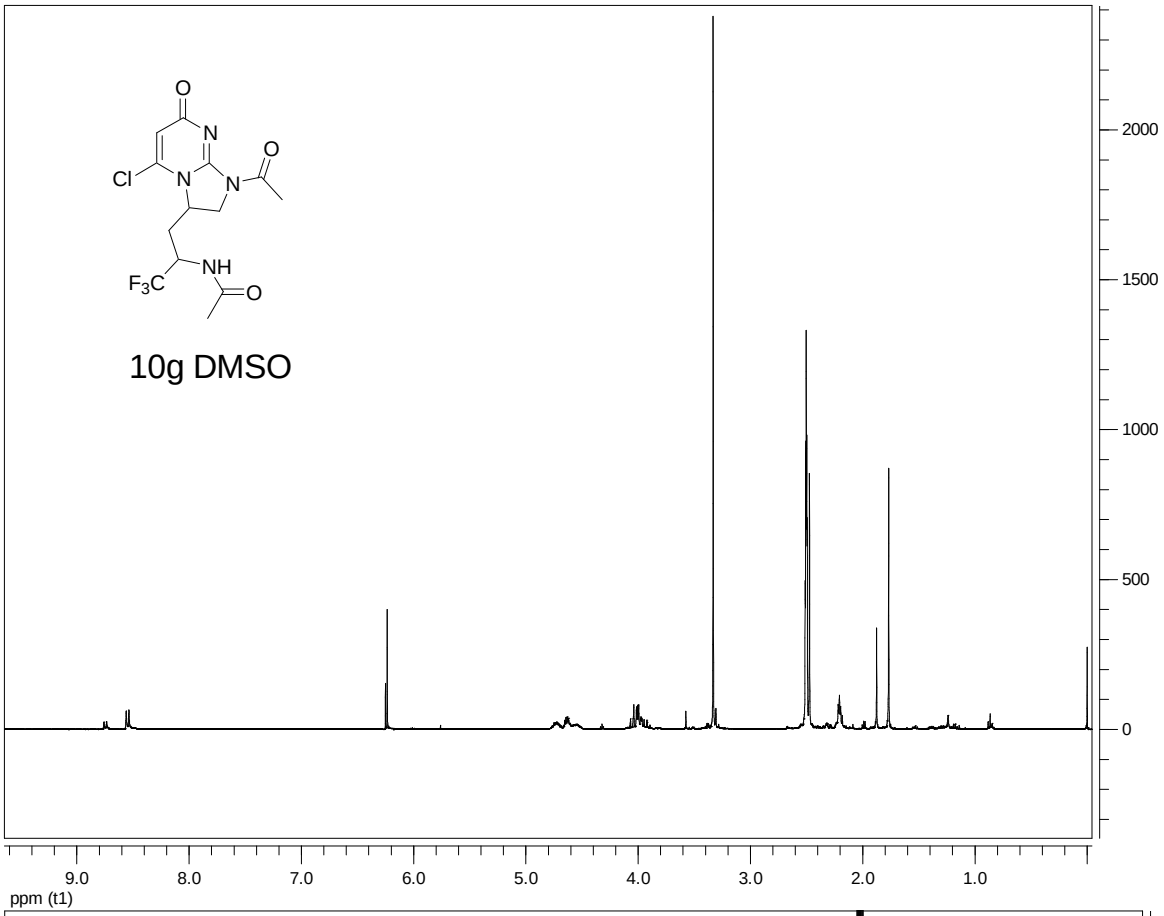
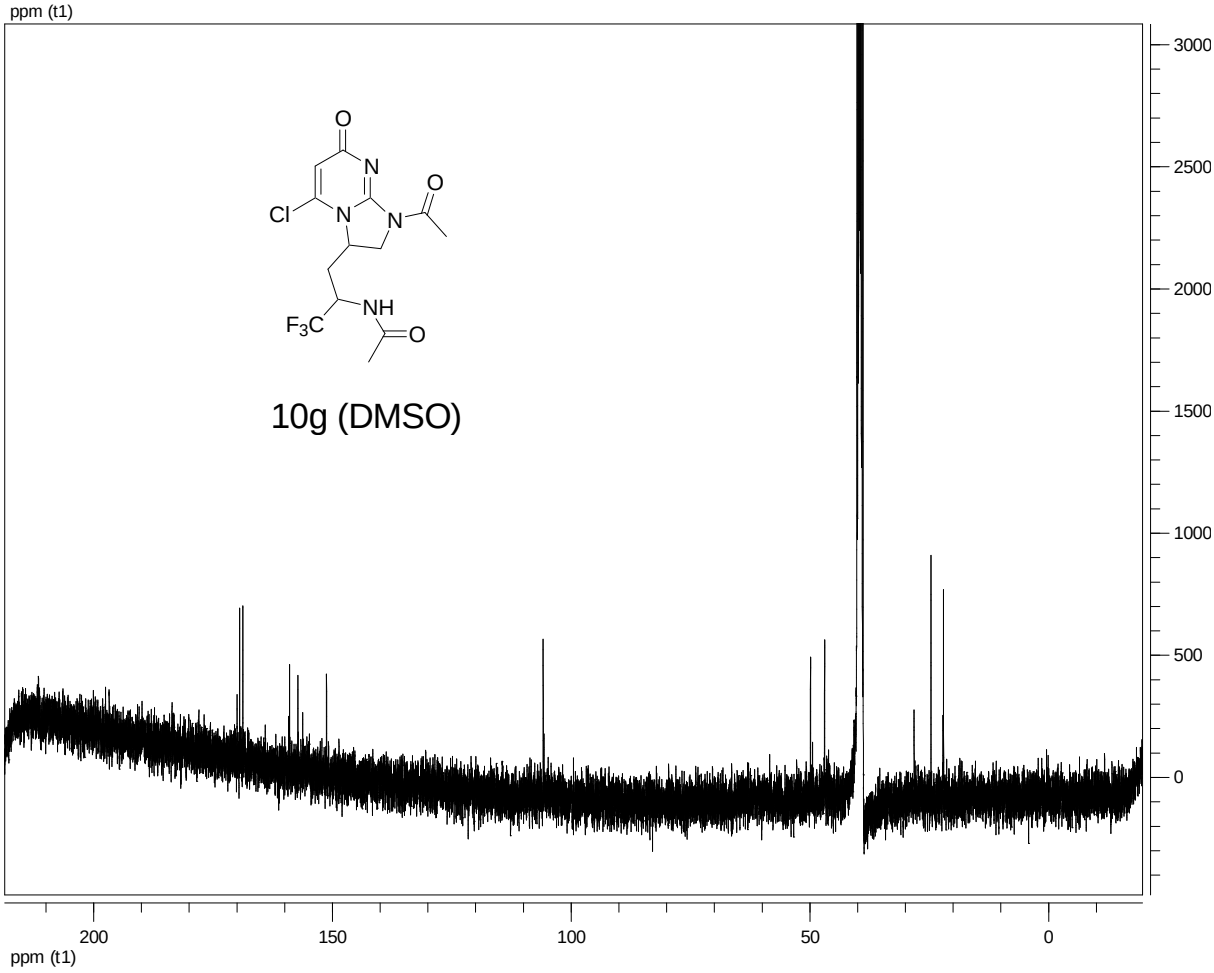
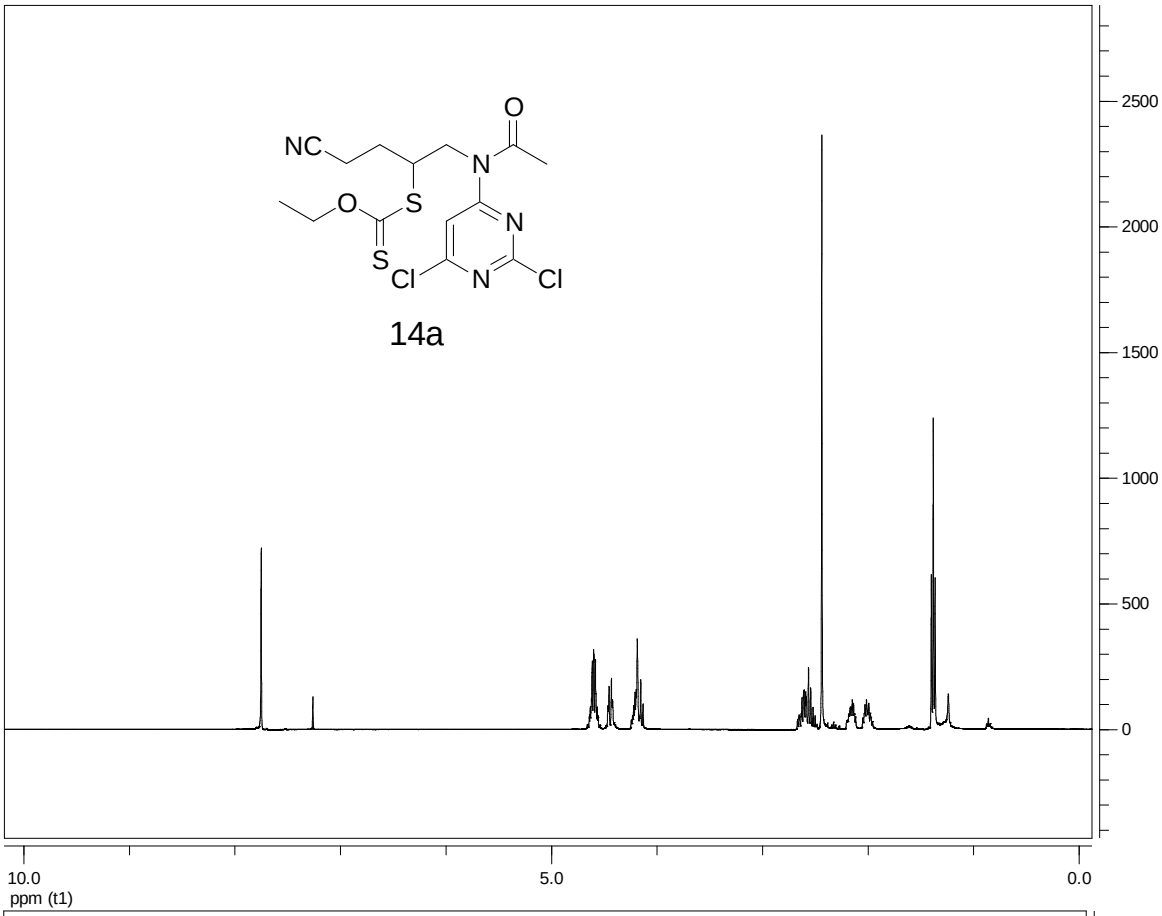
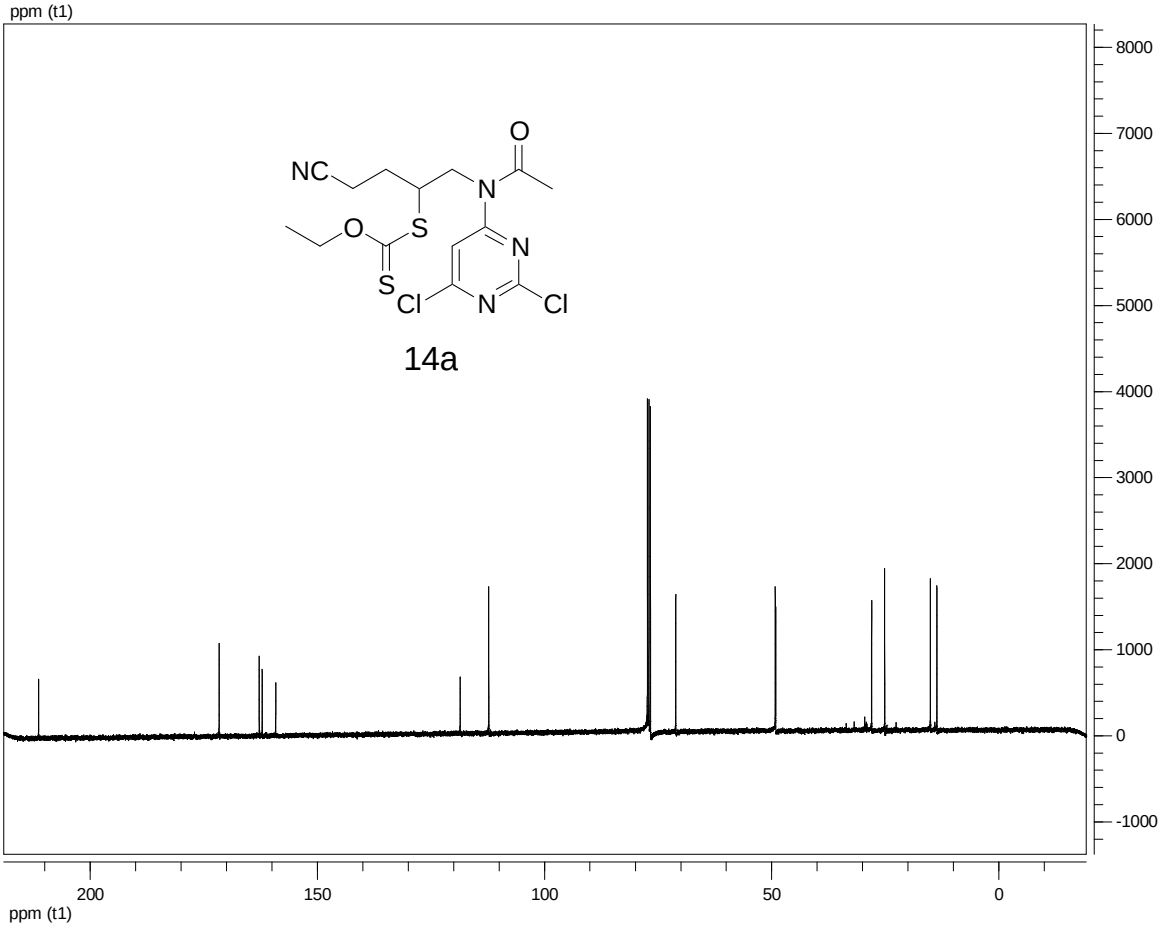
30000
20000
10000
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

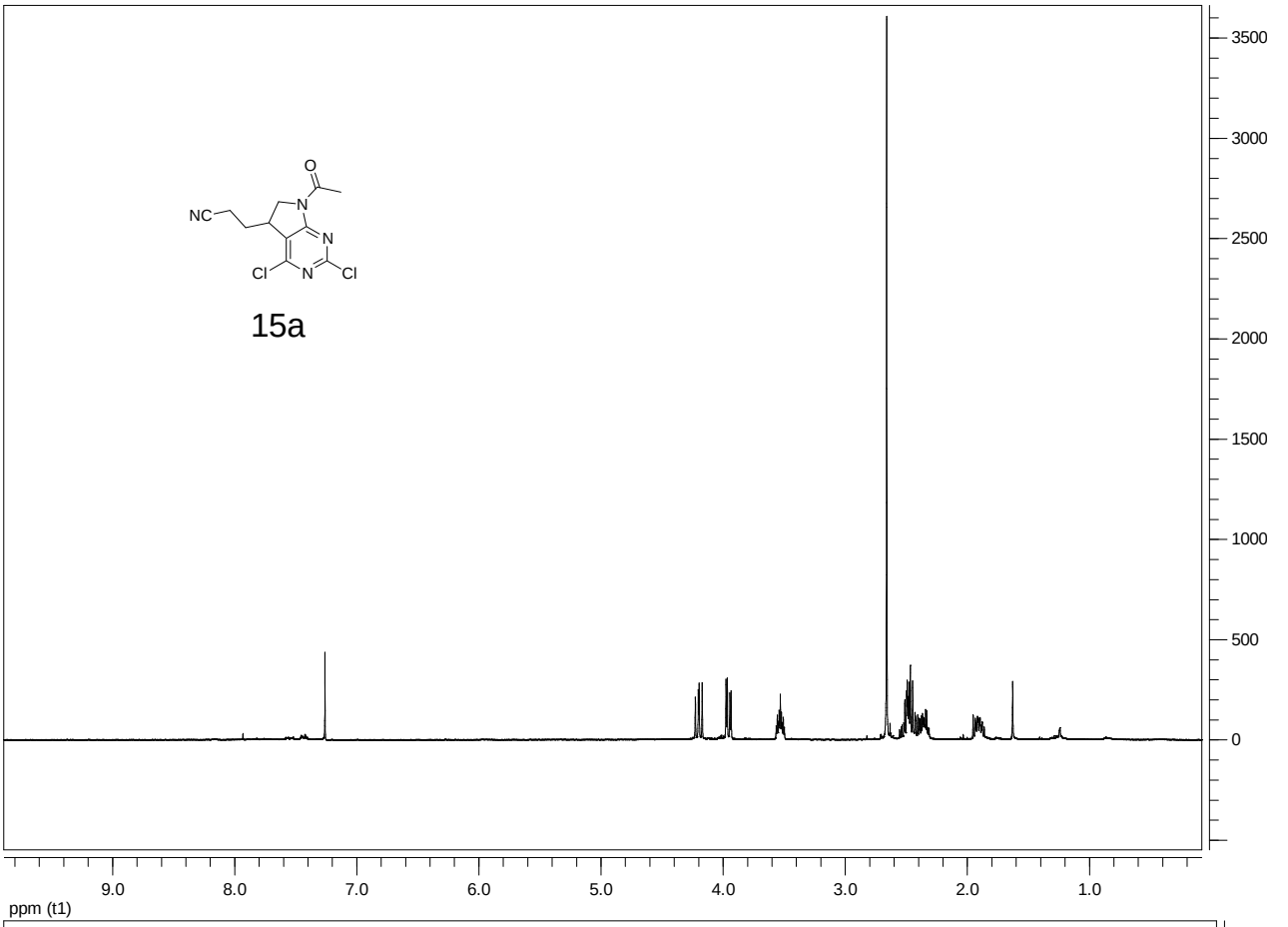

10f
2500
2000
1500
1000
500
0
200
150
100
50
0
ppm (t1)

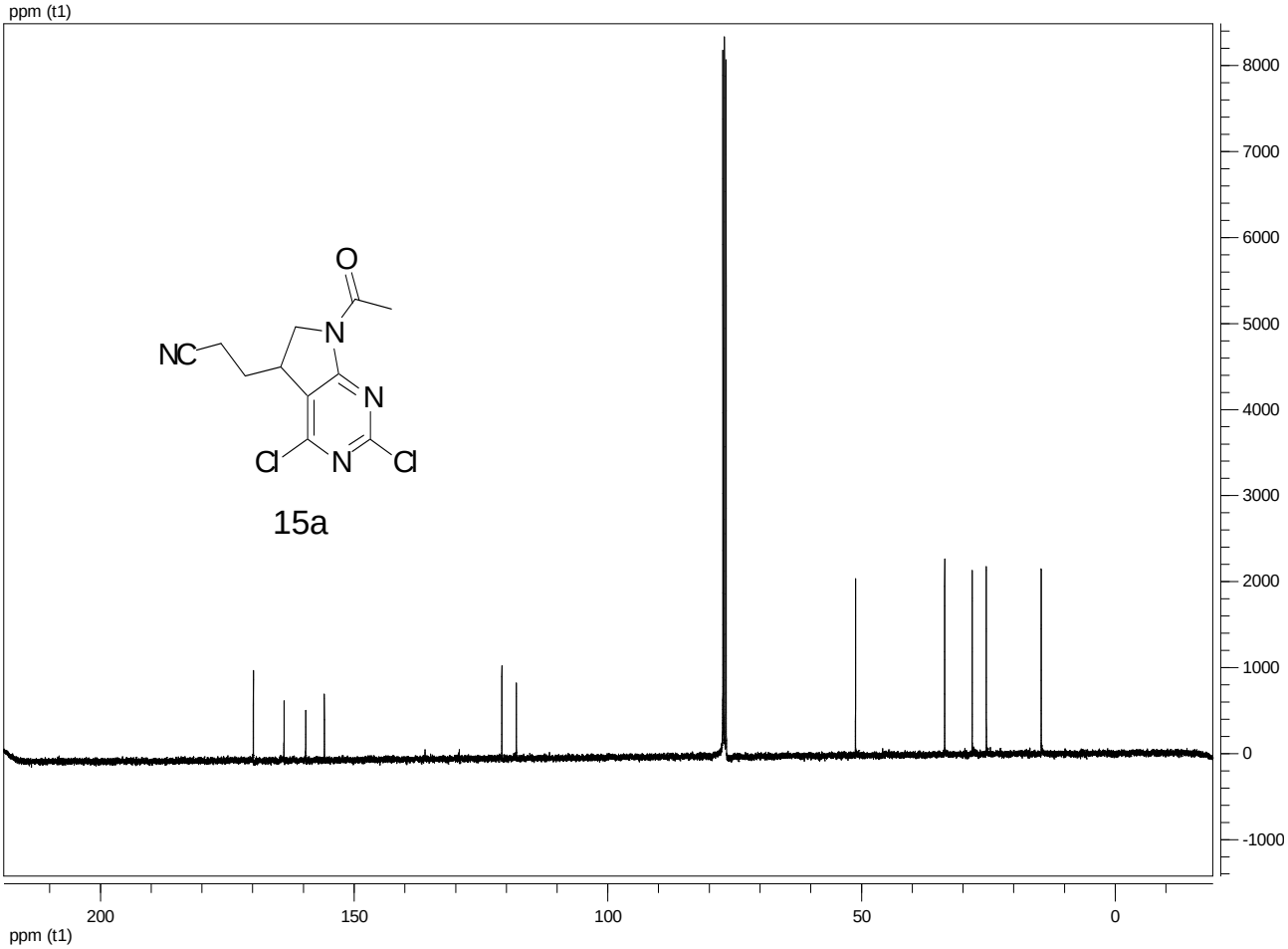

O
N
O
Cl
N
N
NH
F3C
O
10g DMSO
2000
1500
1000
500
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

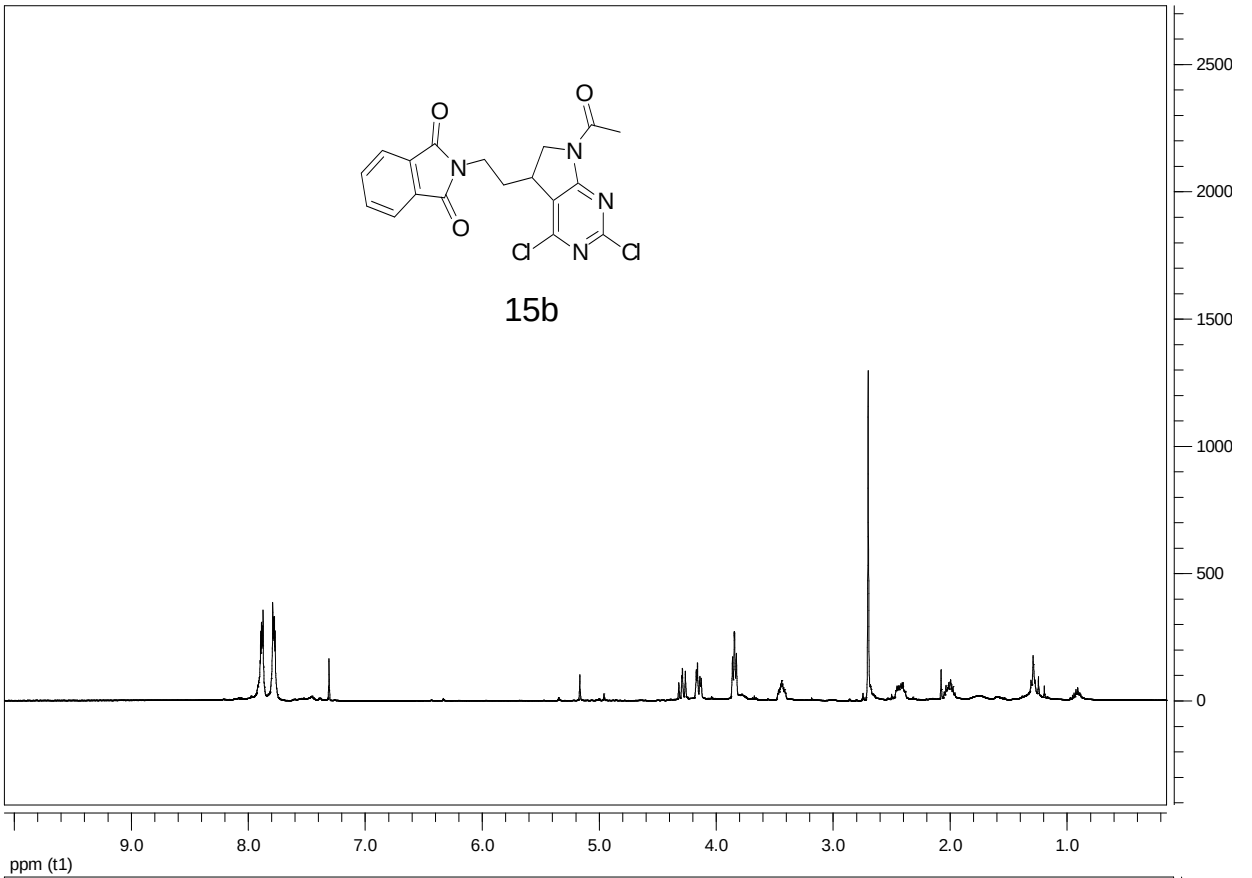

O
N
O
Cl
N
N
NH
F3C
O
10g (DMSO)
3000
2500
2000
1500
1000
500
0
200
150
100
50
0
ppm (t1)

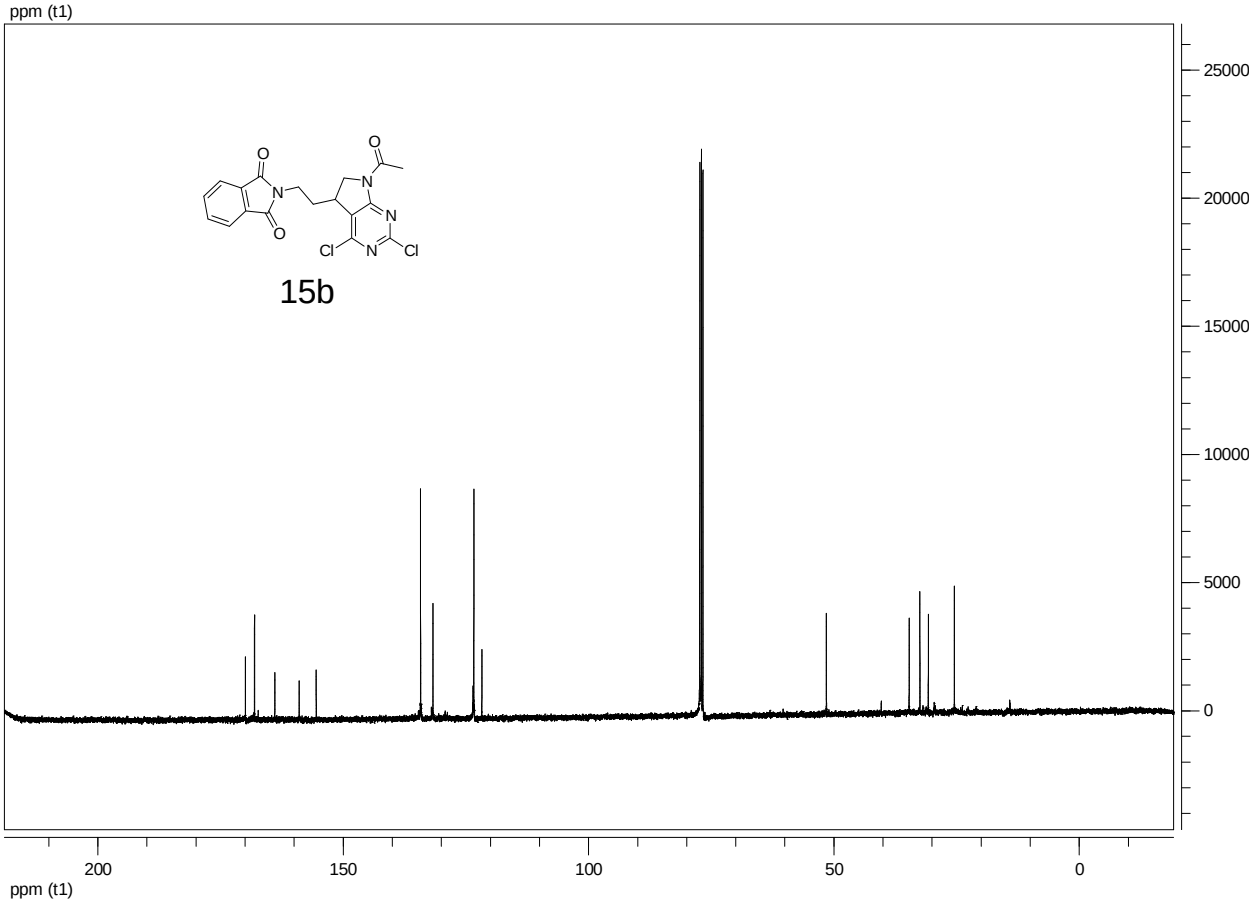

NC
O
N
O
S
N
S
Cl
N
Cl
14a
2500
2000
1500
1000
500
0
10.0
5.0
0.0
ppm (t1)

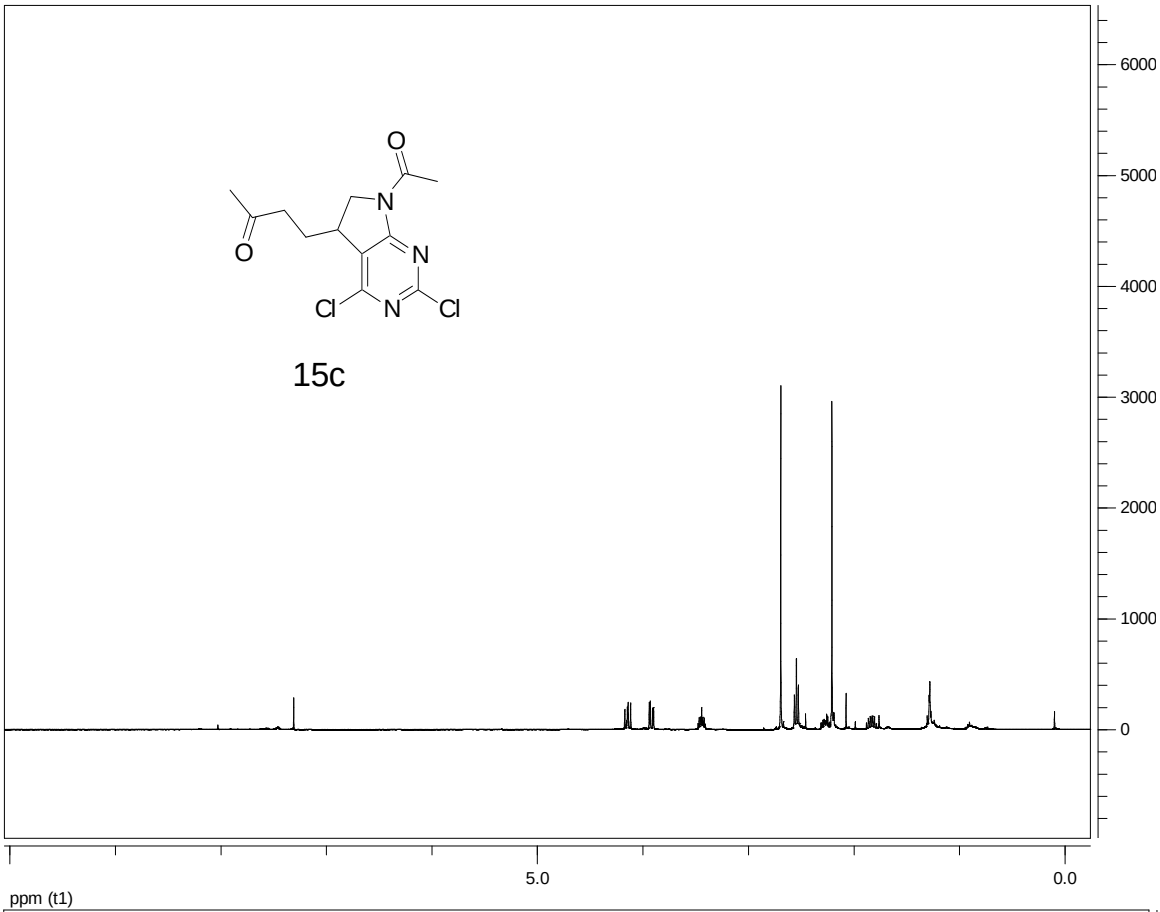

NC
O
N
O
S
N
S
Cl
N
Cl
14a
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
150
100
50
0
ppm (t1)

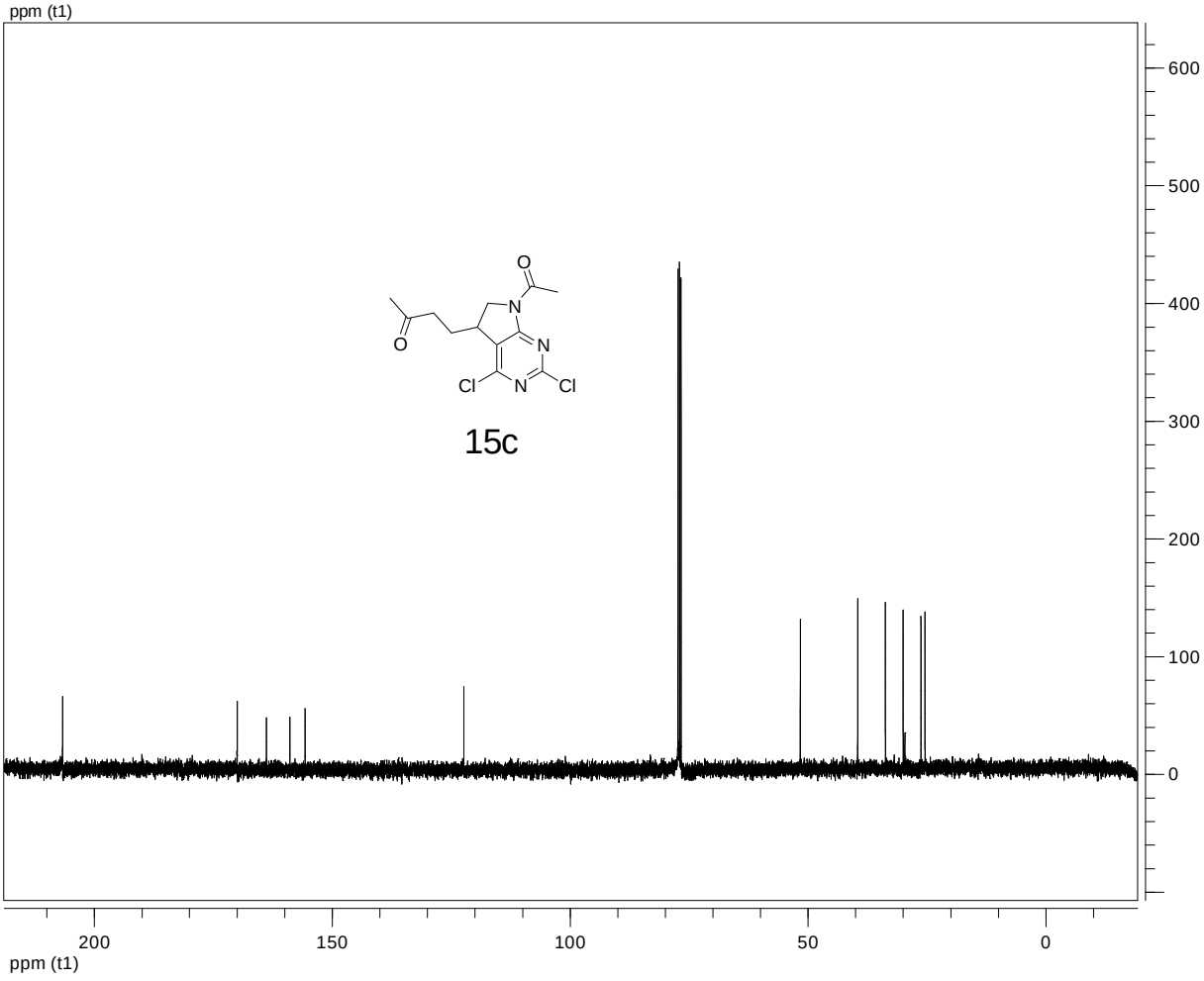

O
N
NC
N
Cl
N
Cl
15a
3500
3000
2500
2000
1500
1000
500
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

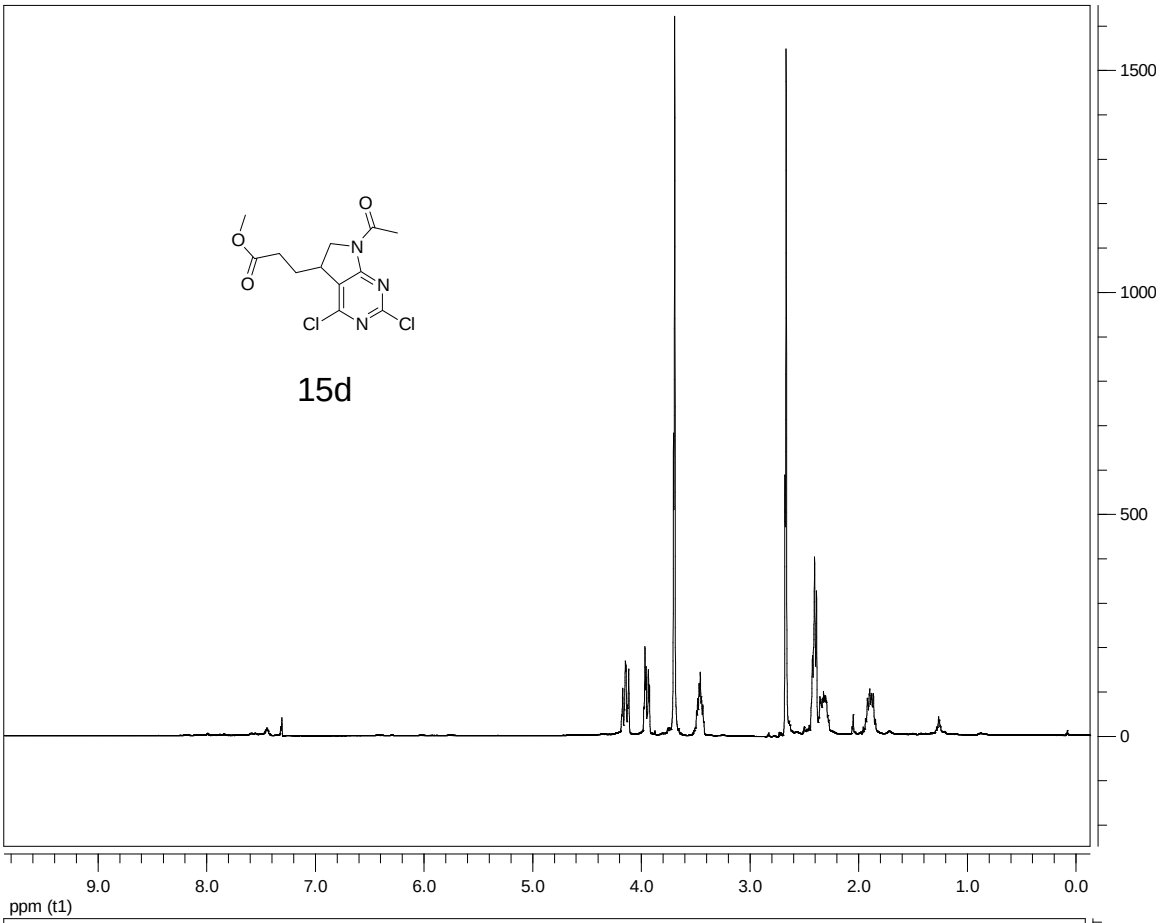

O
N
NC
N
Cl
N
Cl
15a
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
200
150
100
50
0
ppm (t1)

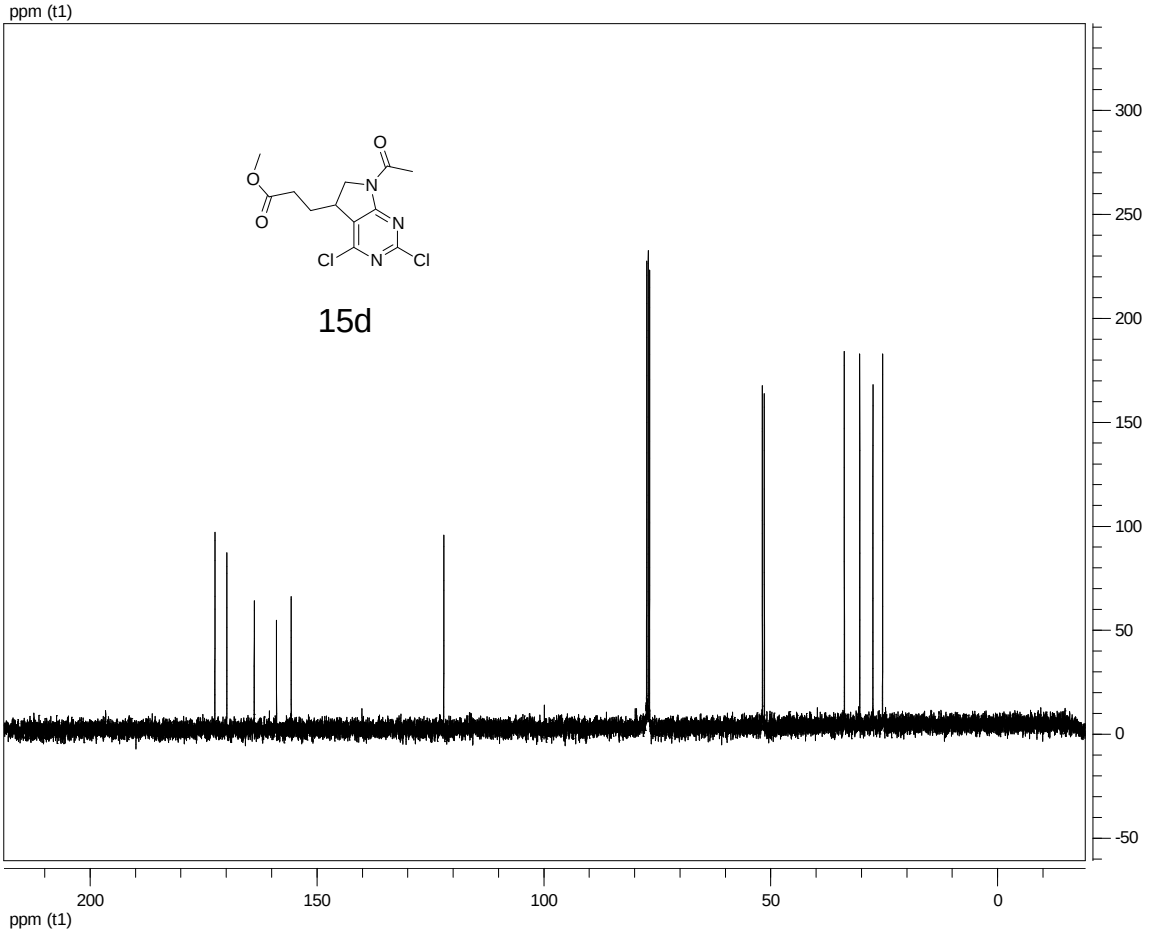

15b
2500
2000
1500
1000
500
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

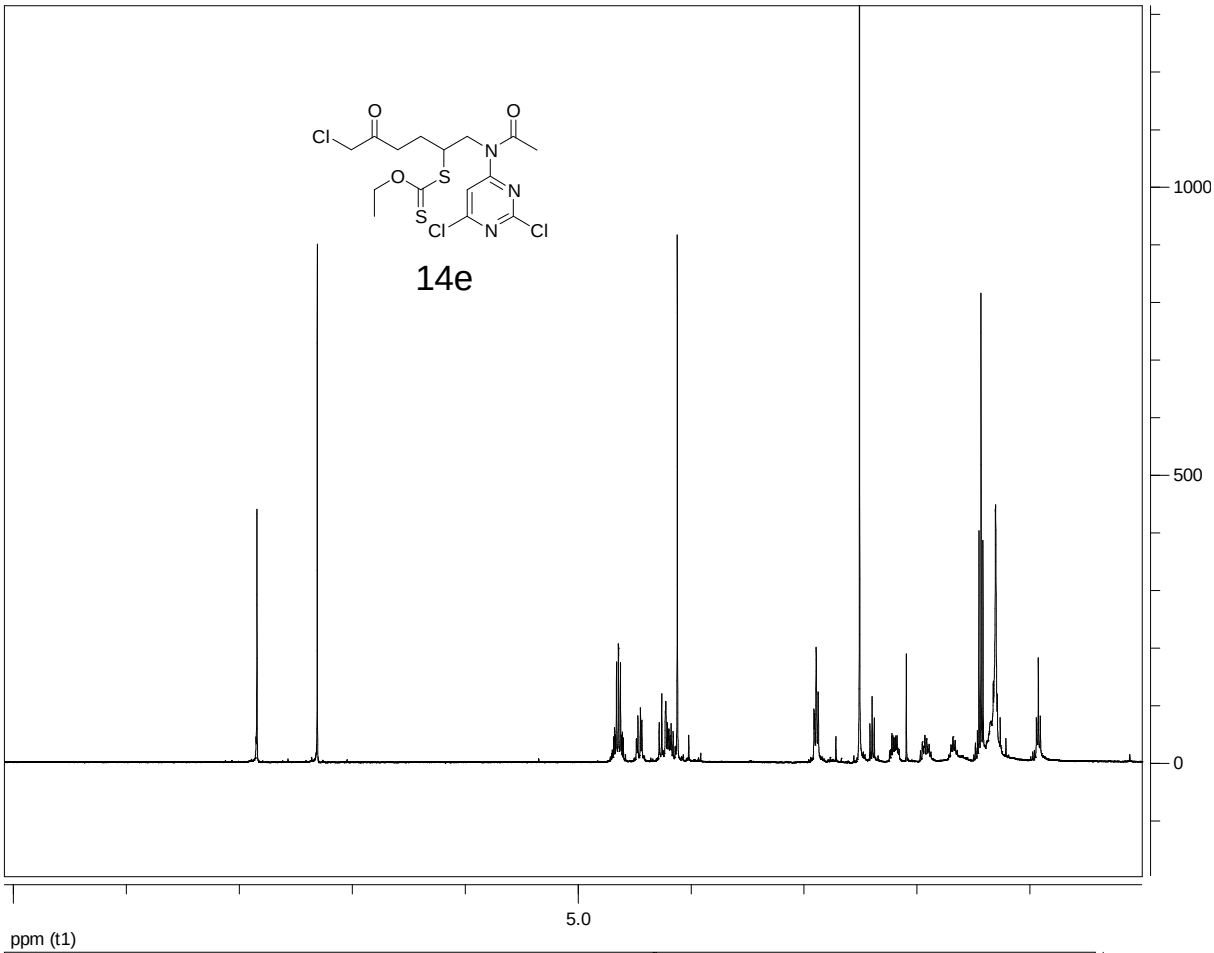

15b
25000
20000
15000
10000
5000
0
200
150
100
50
0
ppm (t1)

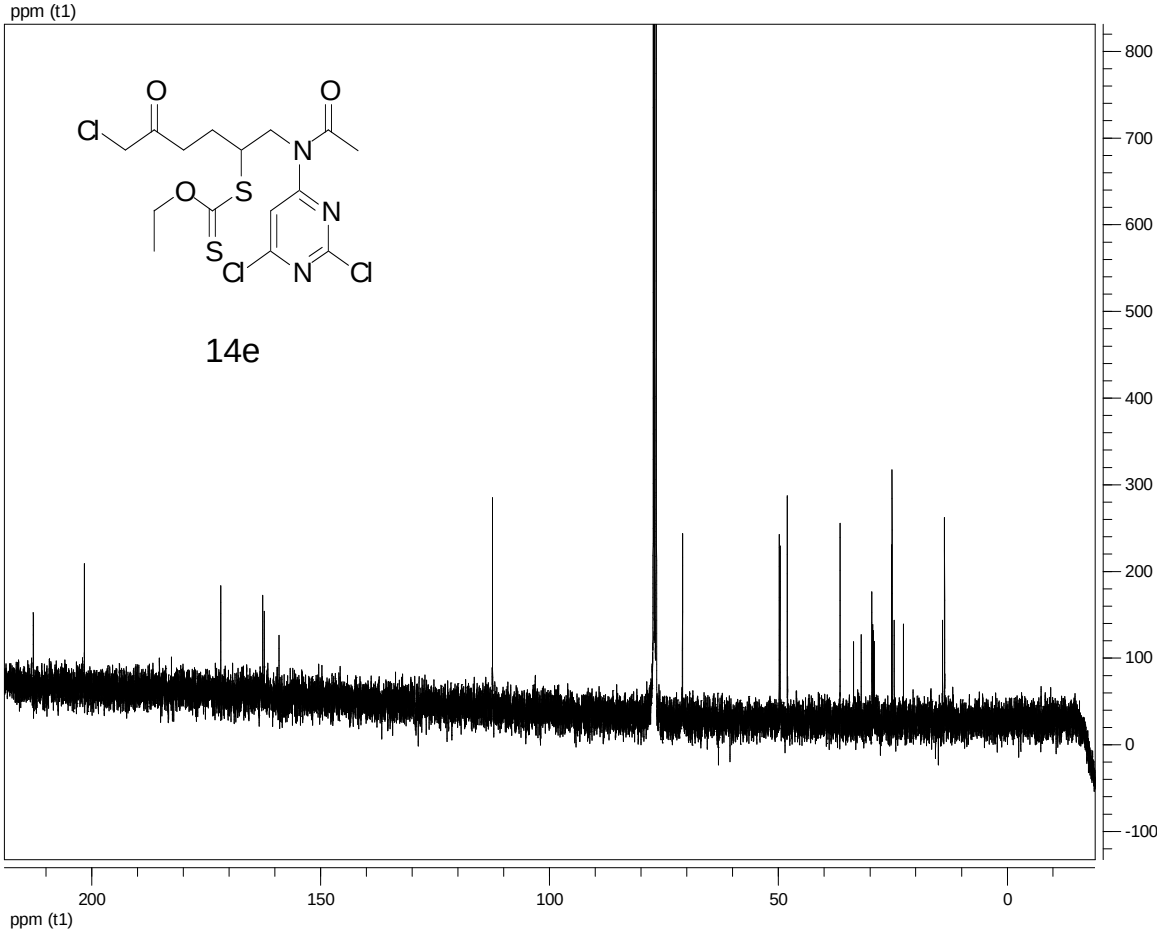

O
N
O
N
Cl
N
Cl
15c
6000
5000
4000
3000
2000
1000
0
5.0
0.0
ppm (t1)

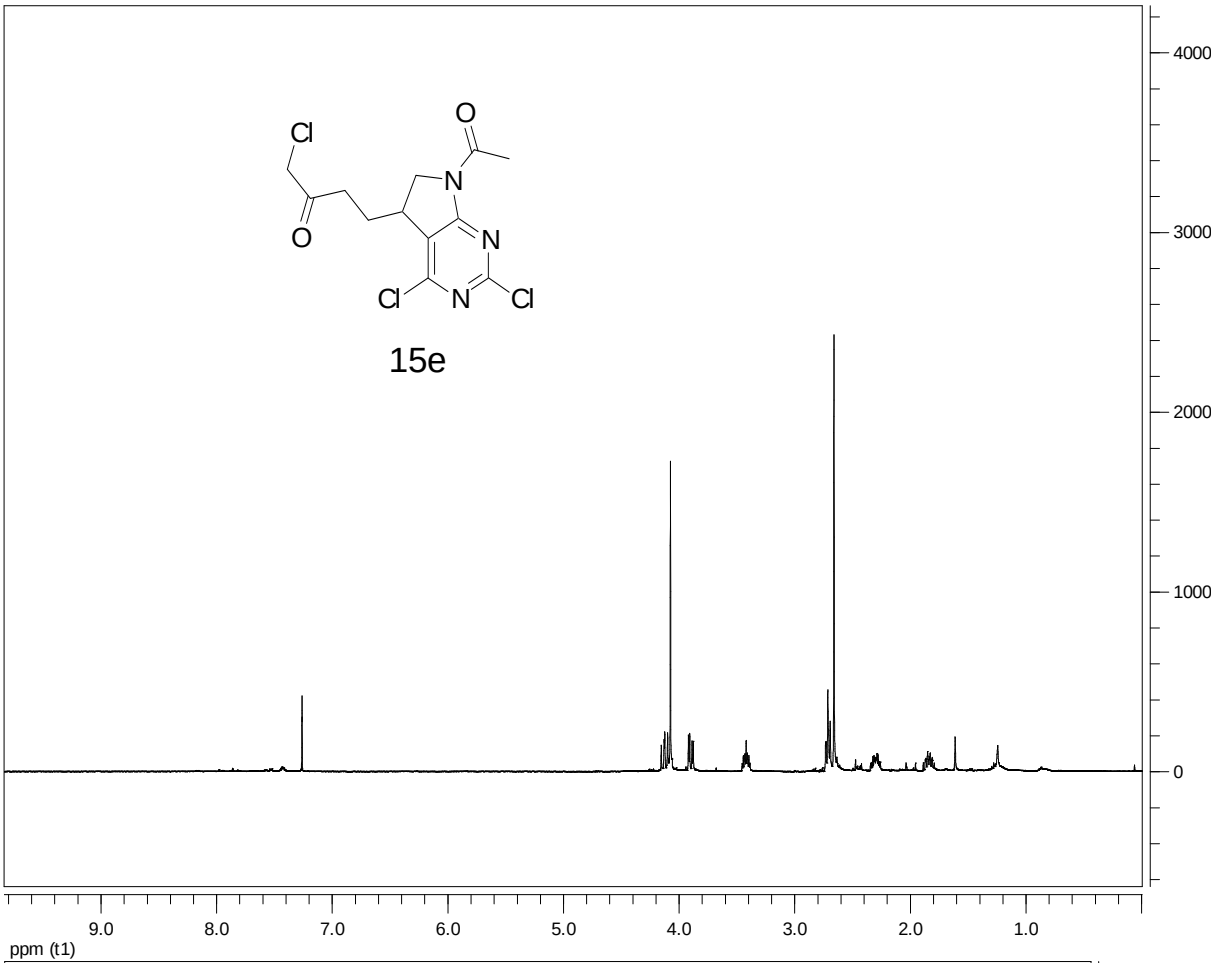

O
N
O
N
Cl
N
Cl
15c
600
500
400
300
200
100
0
200
150
100
50
0
ppm (t1)

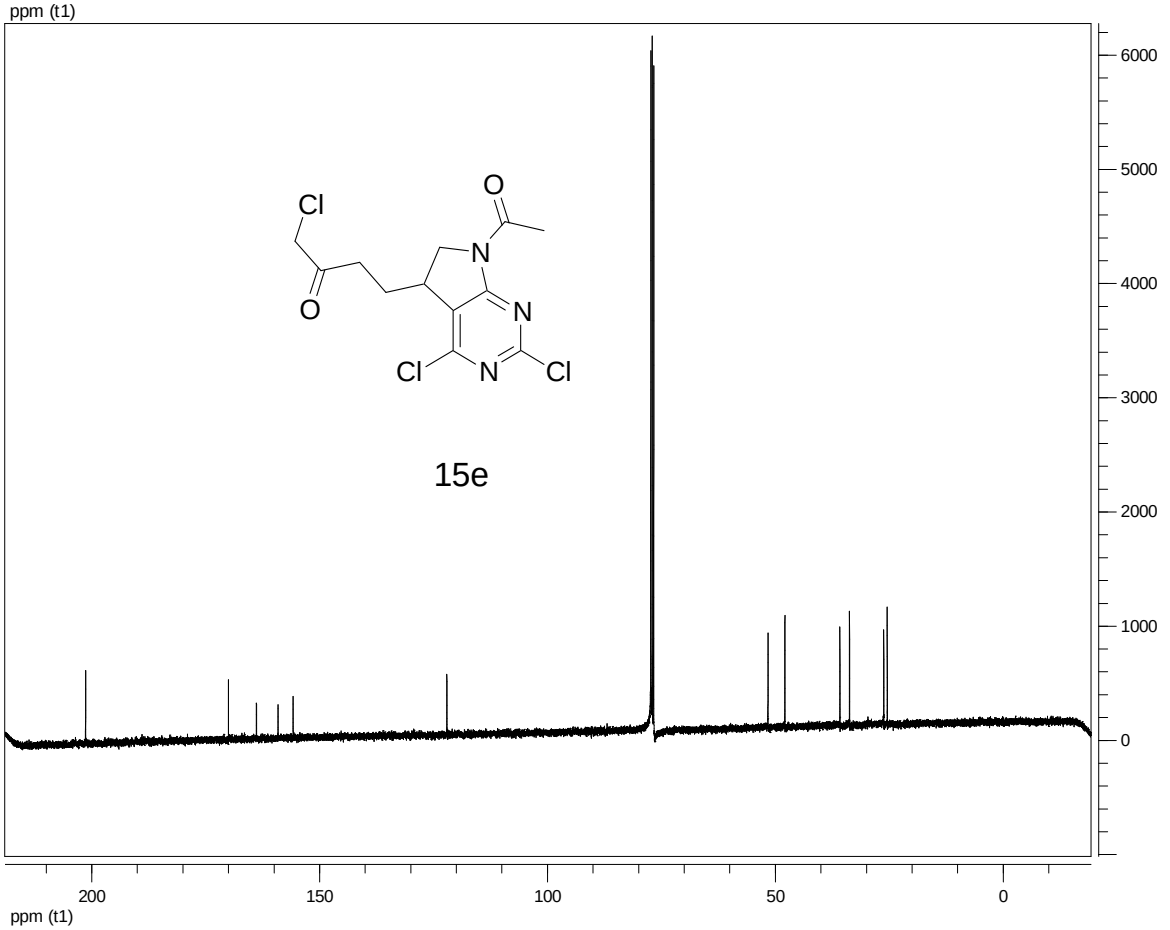

O
O
O
N
N
Cl
N
Cl
15d
1500
1000
500
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

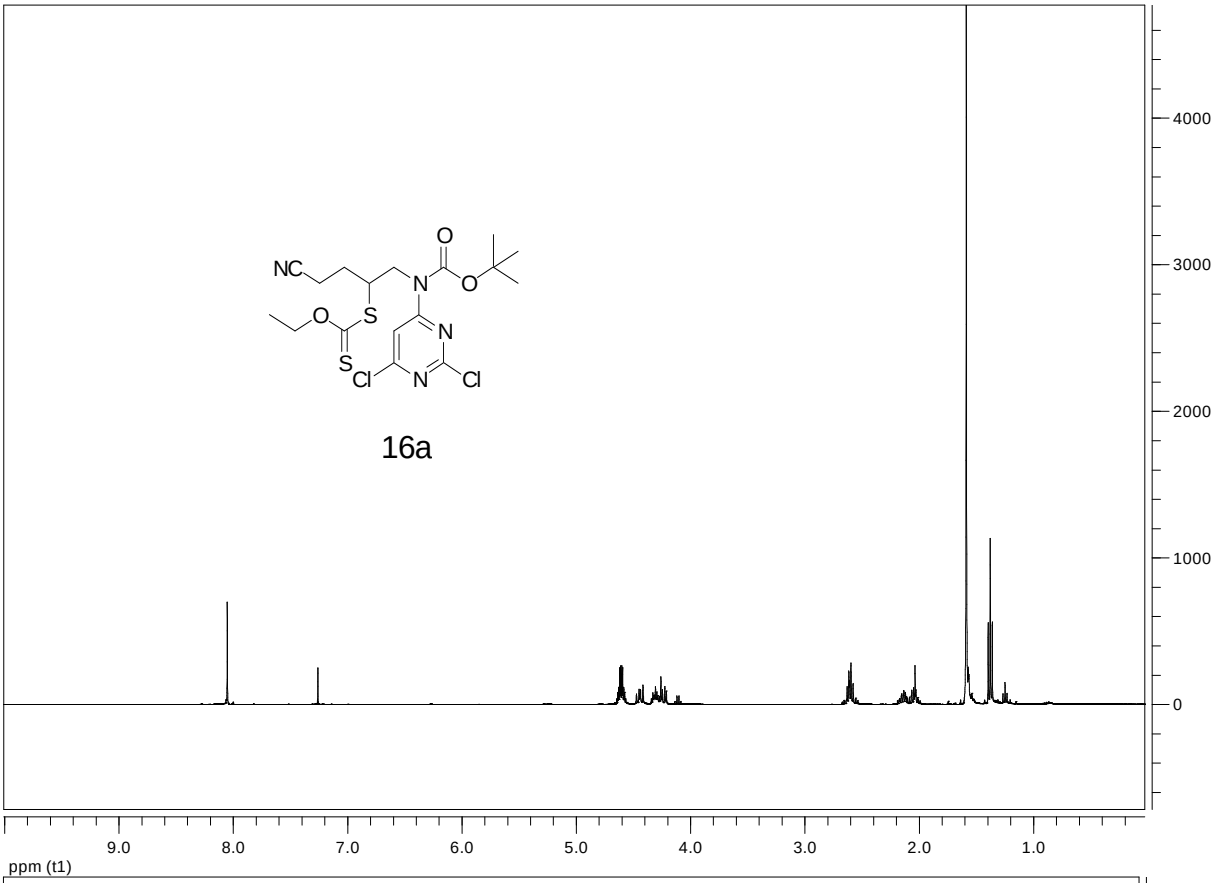

O
O
O
N
N
Cl
N
Cl
15d
300
250
200
150
100
50
0
-50
200
150
100
50
0
ppm (t1)


14e
1000
500
0
5.0
ppm (t1)

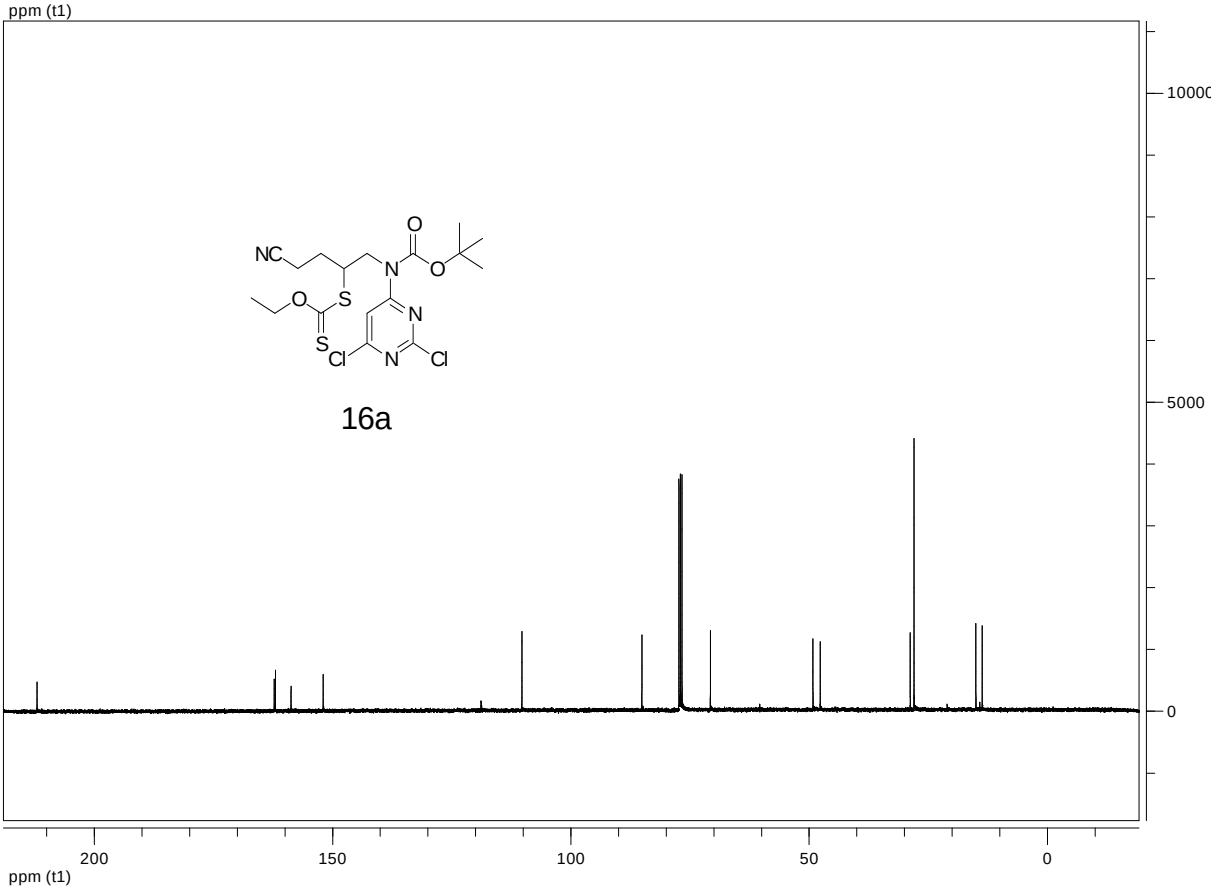

14e
800
700
600
500
400
300
200
100
0
-100
200
150
100
50
0
ppm (t1)


Cl
O
N
O
N
Cl
N
Cl
15e
4000
3000
2000
1000
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

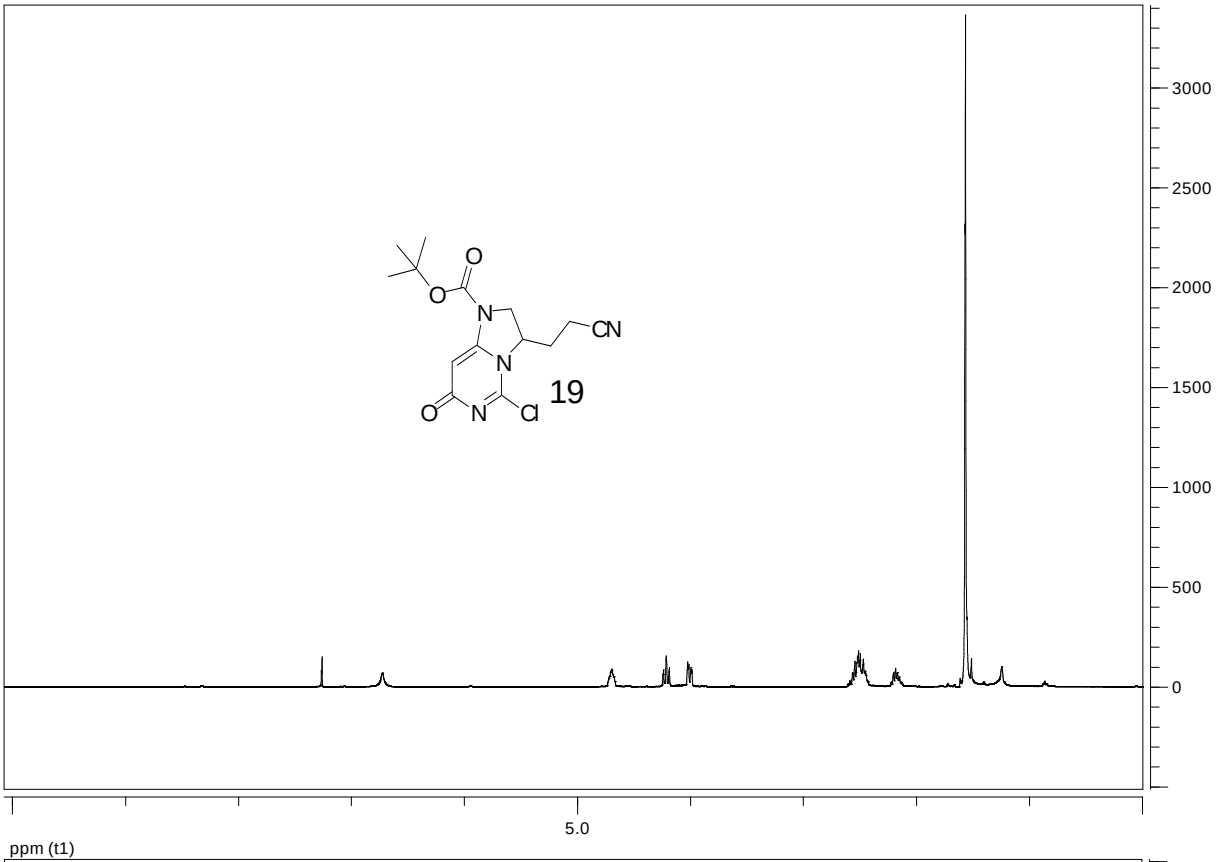

Cl
O
N
O
N
Cl
N
Cl
15e
6000
5000
4000
3000
2000
1000
0
200
150
100
50
0
ppm (t1)

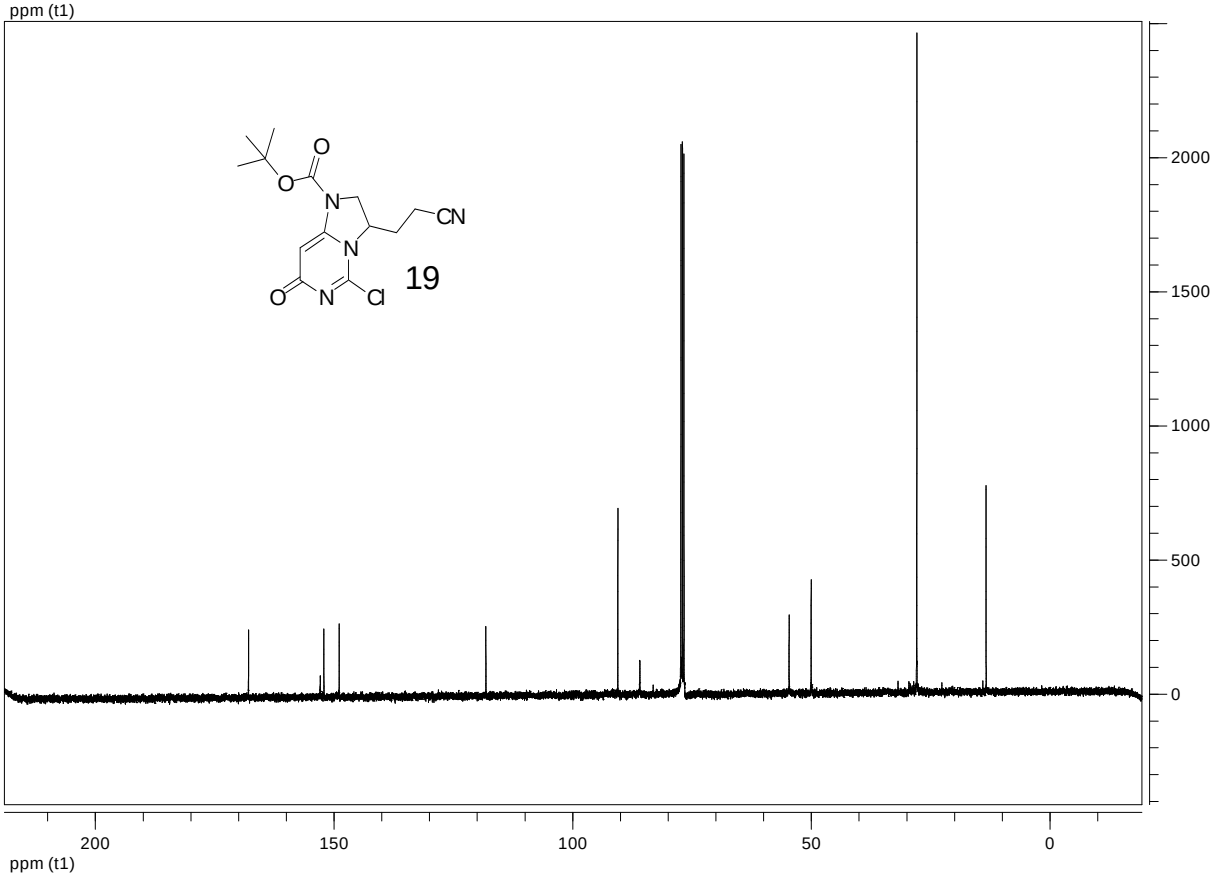

NC
O
N
O
O
S
N
S
Cl
N
Cl
4000
3000
2000
1000
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

16a


NC
O
N
O
O
S
N
S
Cl
N
Cl
10000
5000
0
200
150
100
50
0
ppm (t1)

16a


O
O
N
CN
N
19
O
N
Cl
3000
2500
2000
1500
1000
500
0
5.0
ppm (t1)


O
O
N
CN
N
19
O
N
Cl
2000
1500
1000
500
0
200
150
100
50
0
ppm (t1)