Supporting Information
Silver-Catalyzed Three-Component Reaction of Uracils, Arylboronic acids, and Selenium: Synthesis of 5-arylselanyluracils

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1. General Information

All chromatographic separations were accomplished with Silica Gel 60N (Kanto Chemical Co., Inc.). Thin-layer chromatography (TLC) was performed with Macherey-Nagel Sil G25 UV_{254} pre-coated TLC plates. Reagents were used without further purification unless otherwise specified. Melting points were recorded on a Yanagimoto micro melting point hot-stage apparatus (MP-S3) and are not corrected. IR spectra were recorded on a SHIMADZU FTIR-8400S spectrophotometer and are reported in frequency of absorption (cm^{-1}). Only selected IR peaks are reported. ^{1}H NMR (TMS: δ = 0.00 ppm as an internal standard), ^{13}C NMR ($CDCl_3$: δ = 77.00 ppm and DMSO-d_6: δ = 39.52 ppm as an internal standard), ^{19}F NMR (trifluoromethylbenzene: δ = –64.0 ppm as an external standard) and ^{77}Se NMR (Ph_2Se_2: δ = 436.15 ppm as an internal standard) spectra were recorded on a JEOL ECZ-400S (400 MHz, 100 MHz, 376 MHz and 76 MHz) spectrometer in $CDCl_3$ and DMSO-d_6 unless otherwise stated. GC-MS (EI) spectra were recorded on Agilent 5977E Diff-SST MSD-230V spectrometer. HRMS (ESI) spectra were recorded on Agilent 6230 Accurate-Mass TOF LC/MS system. The X-ray diffraction measurements carried out using a Rigaku XtaLAB Synergy, Single source at home/near, HyPix3000 diffractometer. Spectroscopic data of 5-arylselanyluracils **5a**, **p**, **q** and **s** are in accordance with the literature.[1-3]

2. General procedure for the synthesis of 5-arylselanyluracil

Aryl boronic acid (**2**) (0.5 mmol, 1.0 eq.), Se powder (40 mg, 0.5 mmol, 1.0 eq.), $AgNO_3$ (8.5 mg, 0.05 mmol, 10 mol%), and 1,3-dimethyluracil derivative (**1**) (0.5 mmol) were added to dimethylsulfoxide (3 mL) in around-bottom flask. After stirring at 120 °C for 5-24 h, the mixture was cooled to room temperature and evaporated to dryness under reduced pressure. The crude product was purified on a silica gel column chromatography to give the desired product **5a**, **p**, **q** and **s**.

1,3-Dimethyl-5-(phenylselanyl)pyrimidine-2,4-(1*H*,3*H*)-dione (5a)[1]

Colorless prisms (143 mg, 96%). R_f = 0.5 (EtOAc/hexane 1:1). mp 112–114 °C (CH_2Cl_2-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.51 (m, 2H, Ar-H), 7.41 (s, 1H, H-6), 7.30–7.28 (m, 3H, Ar-H), 3.39 (s, 3H, *N*-CH_3) 3.38 (s, 3H, *N*-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.9 (s, C), 151.6 (s, C), 129.3 (s, C), 103.2(s, C), 146.1 (s, CH), 132.6 (s, CH), 129.4 (s, CH), 127.8 (s, CH), 37.1 (s, CH_3), 28.7 (s, CH_3). ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 330.4 (s). IR (KBr): ν_{max}/cm^{-1} 1712vs (C=O), 1645vs cm^{-1} (C=O). HRMS (ESI): *m/z* calcd for $C_{12}H_{12}N_2O_2Se+H^+$; 297.0142 $[M+H]^+$: found: 297.0140.

5-(Phenylselanyl)-2′,3′,5′-triacetate-uridine (5p)[2]

Colorless oil (85 mg, 32%). R_f = 0.5 (EtOAc/hexane 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.29 (s, 1H, NH), 7.76 (s, 1H, H-6), 7.52–7.48 (m, 2H, Ar-H), 7.31–7.26 (m, 3H, Ar-H), 6.09 (d, *J* = 5.5 Hz, 1H, H-1′), 5.33–5.27 (m, 2H, CH_2-5′), 4.35 (q, *J* = 3.2 Hz, 1H, H-2′), 4.29 (dd, *J* = 12.3, 3.2 Hz, 1H,

H-3′), 4.24 (dd, *J* = 12.6, 3.0 Hz, 1H, H-4′), 2.14 (s, 3H, OAc), 2.12 (s, 3H, OAc), 2.10 (s, 3H, OAc). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.1 (s, C), 169.6 (s, C), 161.0 (s, C), 150.2 (s, C), 143.0 (s, CH), 132.1 (s, CH), 129.5 (s, CH), 129.0 (s, C), 127.8 (s, CH), 105.4 (s, C), 87.0 (s, CH), 80.1 (s, CH), 72.9 (s, CH), 70.3 (s, CH), 63.2 (s, CH_2), 20.8 (s, CH_3), 20.5 (s, CH_3), 20.4 (s, CH_3). ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 325.4 (s). IR (KBr): ν_{max}/cm^{-1} 1748vs (C=O), 1694vs (C=O). HRMS (ESI): *m/z* calcd for $C_{21}H_{22}N_2O_9Se$+H+; 527.0565 $[M+H]^+$: found: 527.0550.

5-(Phenylselanyl)pyrimidine-2,4-(1*H*,3*H*)-dione (5q)[1]

Pale yellow needles (113 mg, 84%). R_f = 0.6 (EtOAc/hexane 4:1). mp 250–253 °C (CH_2Cl_2-hexane). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.4 (s, 1H, N-H), 11.2 (s, 1H, N-H), 7.77 (s, 1H, H-6), 7.36 (dt, *J* = 6.9, 1.4 Hz, 2H, Ar-H), 7.28 (tt, *J* = 6.6, 1.4 Hz, 2H, Ar-H), 7.23 (tt, *J* = 7.3, 1.4 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.5 (s, C), 151.4 (s, C), 148.2 (s, CH), 131.2 (s, C), 129.8 (s, CH), 129.3 (s, CH), 126.6 (s, CH), 99.6 (s, C). ^{77}Se NMR (76 MHz, DMSO-d_6): δ = 301.2 (s). IR (KBr): ν_{max}/cm^{-1} 1771vs (C=O), 1734vs (C=O). HRMS (ESI): *m/z* calcd for $C_{10}H_8N_2O_2Se$+Na^+; 290.9649 $[M+Na]^+$: found: 290.9649.

6-Chloro-1,3-dimethyl-5-(phenylselanyl)pyrimidine-2,4-(1*H*,3*H*)-dione (5s)[3]

Colorless plates (143 mg, 87%). R_f = 0.5 (EtOAc/hexane 1:2). mp 88−90 °C (CH_2Cl_2-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50 (dd, *J* = 7.8, 1.8 Hz, 2H, Ar-H), 7.27−7.24 (m, 3H, Ar-H), 3.67 (s, 3H, *N*-CH_3), 3.38 (s, 3H, *N*-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.4 (s, C), 151.7 (s, C), 150.8 (s, C), 132.0 (s, CH), 130.1 (s, C), 129.3 (s, CH), 127.6 (s, CH), 104.3 (s, C), 35.7 (s, CH_3), 29.6 (s, CH_3). ^{77}Se NMR (76 MHz, $CDCl_3$): δ = 356.8 (s). IR (KBr): ν_{max}/cm^{-1} 1701s (C=O), 1651vs (C=O). HRMS (ESI): *m/z* calcd for $C_{12}H_{11}N_2O_2Se$+H^+; 330.9753 $[M+H]^+$: found: 330.9755.

3. Single crystal X-ray diffraction experiment

The X-ray diffraction measurements of compounds **5a** was carried out using an XtaLAB Synergy, Single source at home/near, HyPix3000 diffractometer. The crystal was kept at 100 K during data collection. Using Olex2[4], the structure was solved with the SHELXT[5] structure solution program using Intrinsic Phasing and refined with the SHELXL[6] refinement package using Least Squares minimisation.

Crystal Data for **5a**. $C_{12}H_{12}N_2O_2Se$ (*M* = 295.20 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 12.30260(10) Å, *b* = 10.19280(10) Å, *c* = 56.9658(4) Å, β = 94.7340(10)°, *V* = 7119.03(10) Å^3, *Z* = 24, *T* = 100 K, μ(Cu Kα) = 4.228 mm^{-1}, D_{calc} = 1.653 g/cm^3, 38140 reflections measured (6.228° ≤ 2Θ ≤ 136.808°), 12880 unique (R_{int} = 0.0346, R_{sigma} = 0.0332) which were used in all calculations. The final R_1 was 0.0424 (I > 2σ(I)) and wR_2 was 0.1006 (all data).

The experimental and refinement details of the X-ray crystallographic structures of compound can be

obtained free of charge from the Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk), CCDC 2093049.

4. Reference

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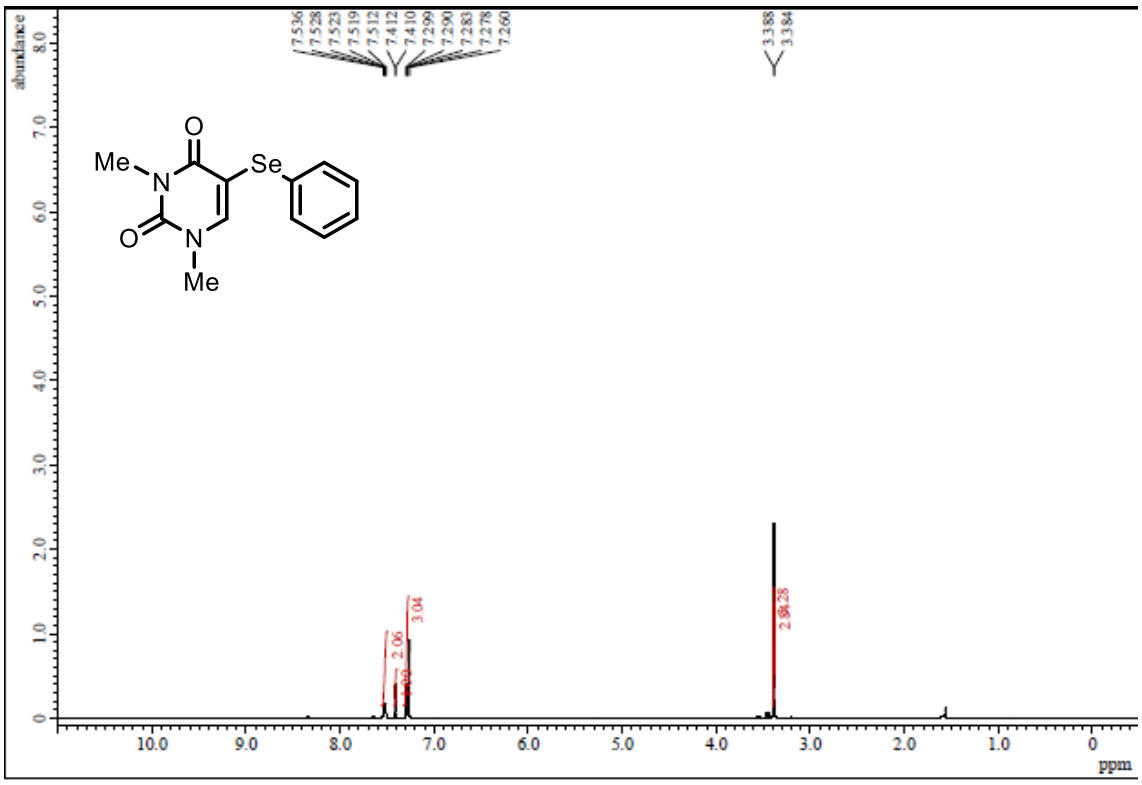
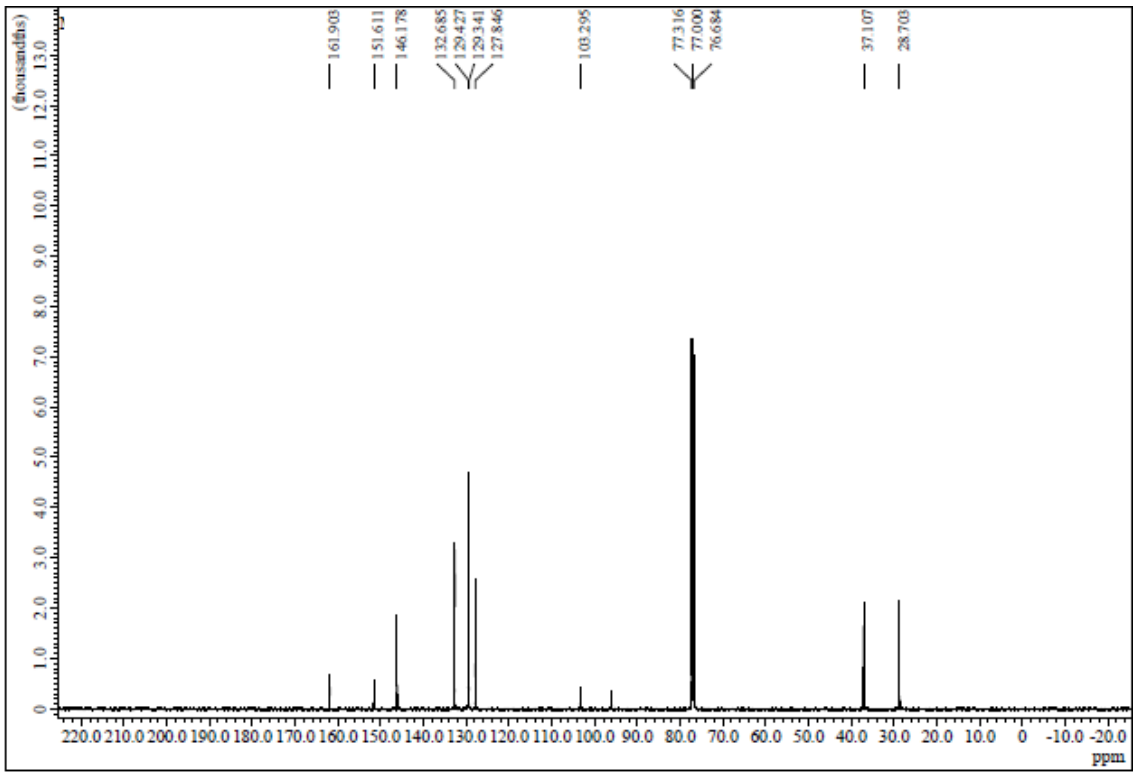
6 G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3–8.

5. ^{1}H NMR and ^{13}C NMR spectra

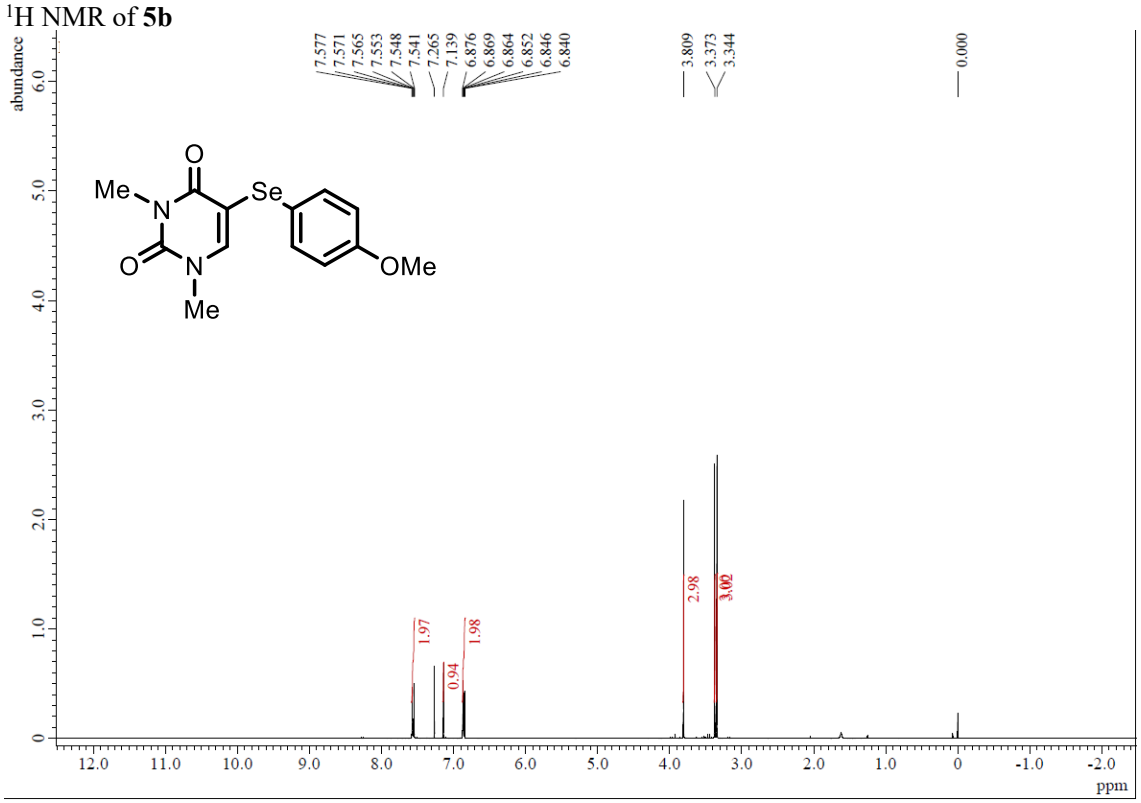
^{1}H NMR of **5a**



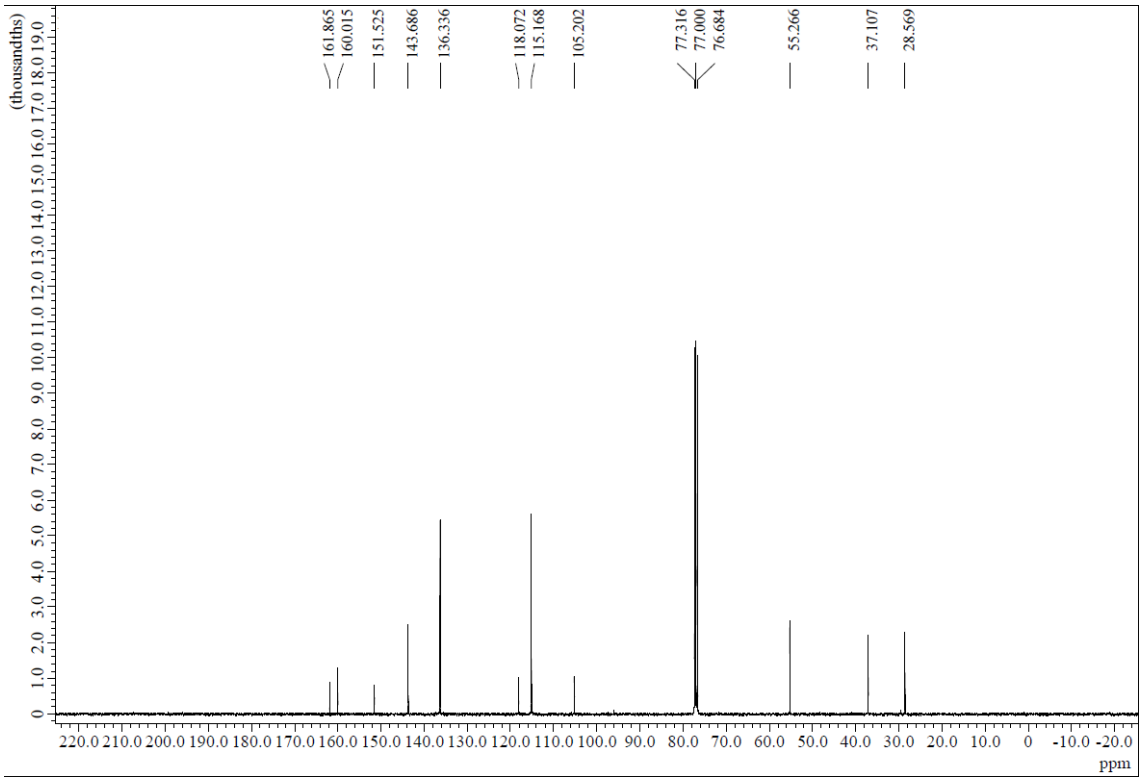
^{13}C NMR of **5a**



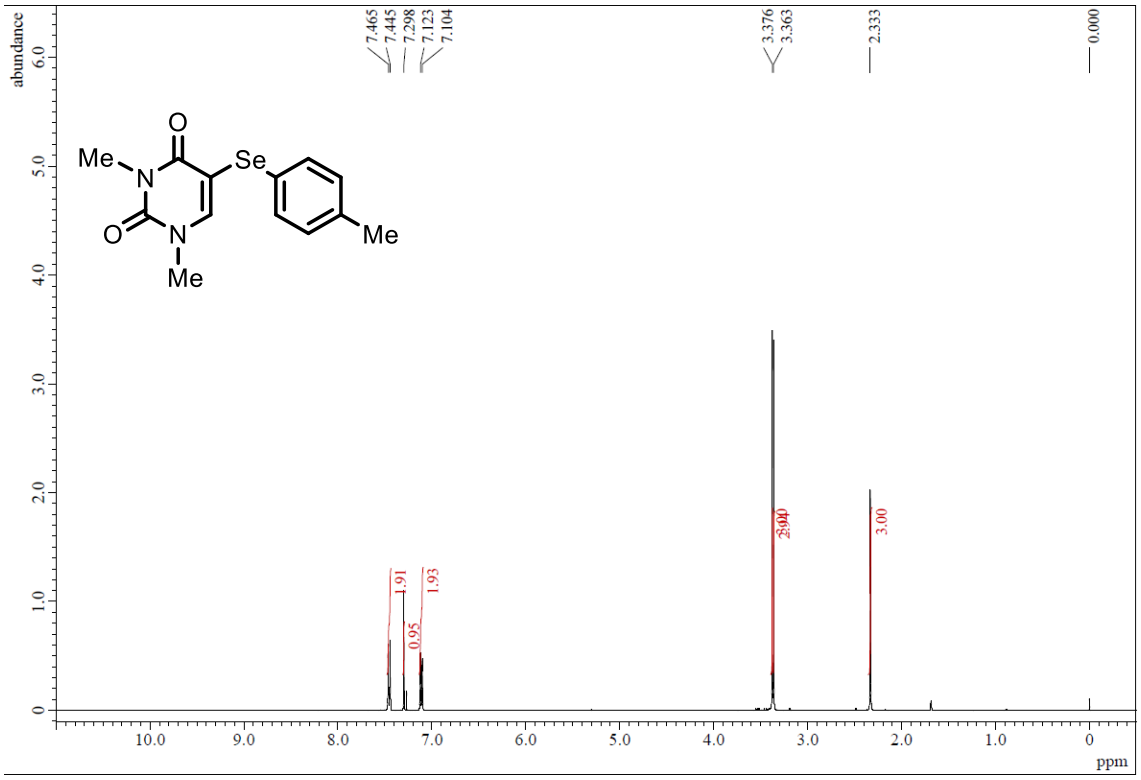
^{1}H NMR of **5b**



^{13}C NMR of **5b**



^{1}H NMR of **5c**



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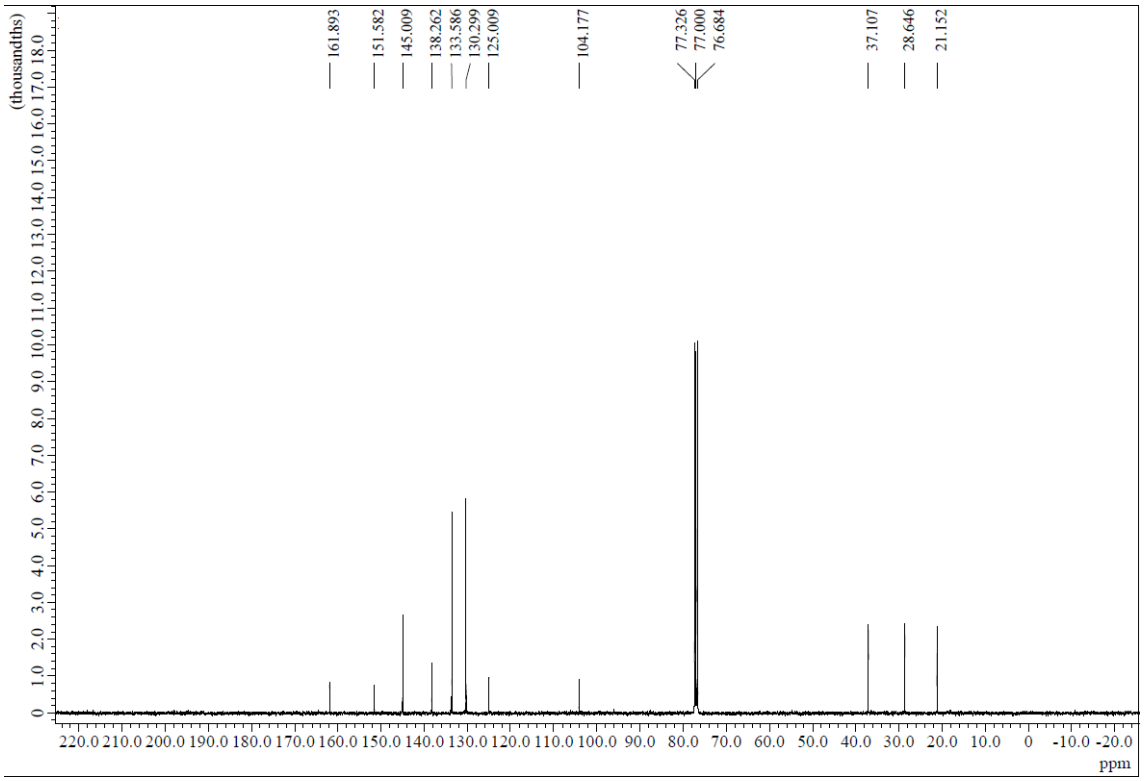

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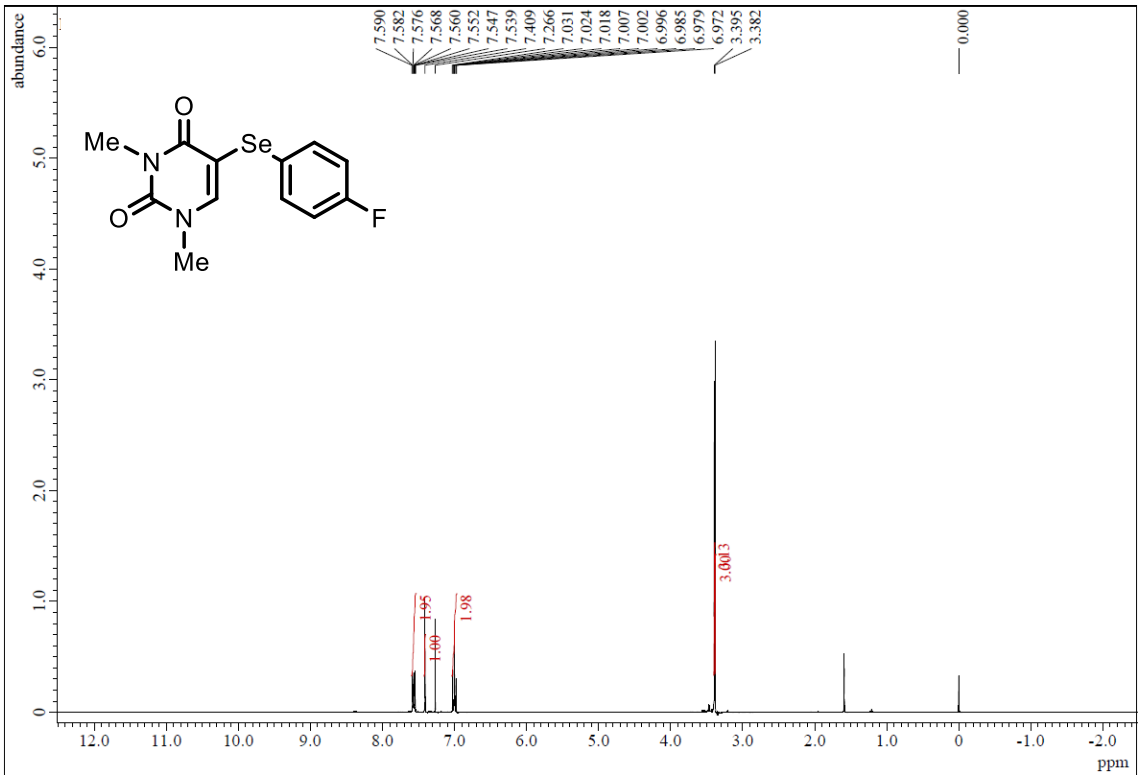

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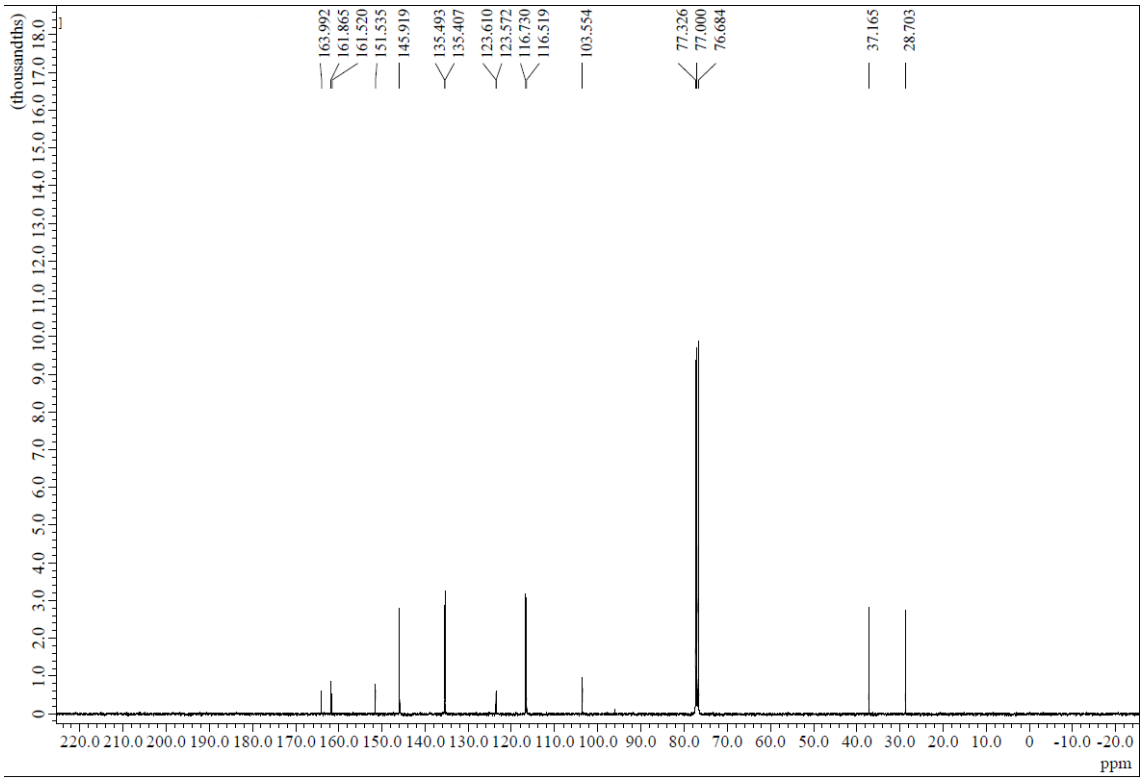

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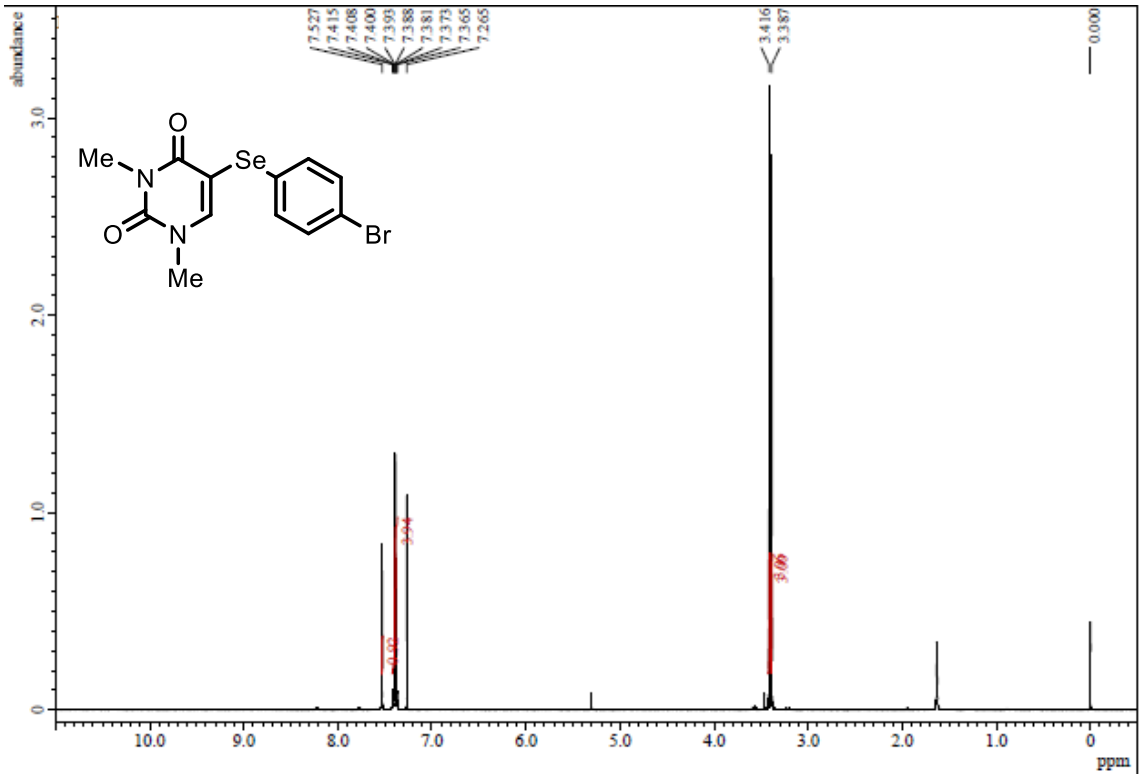

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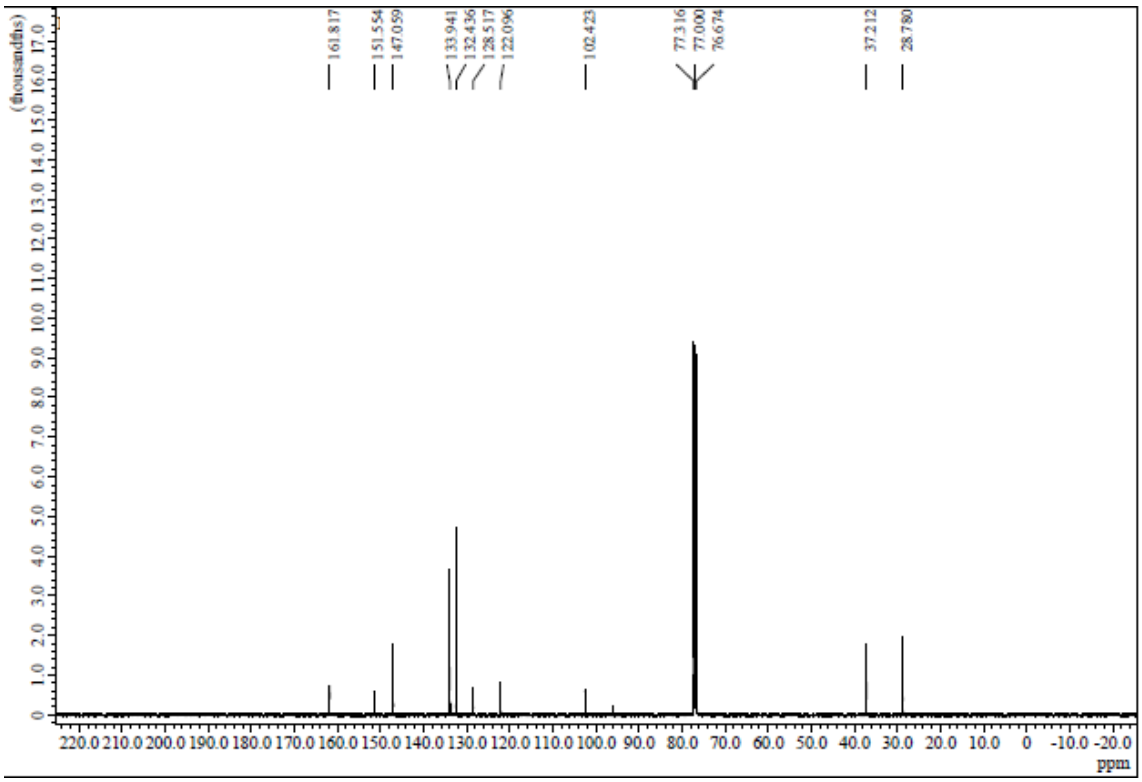

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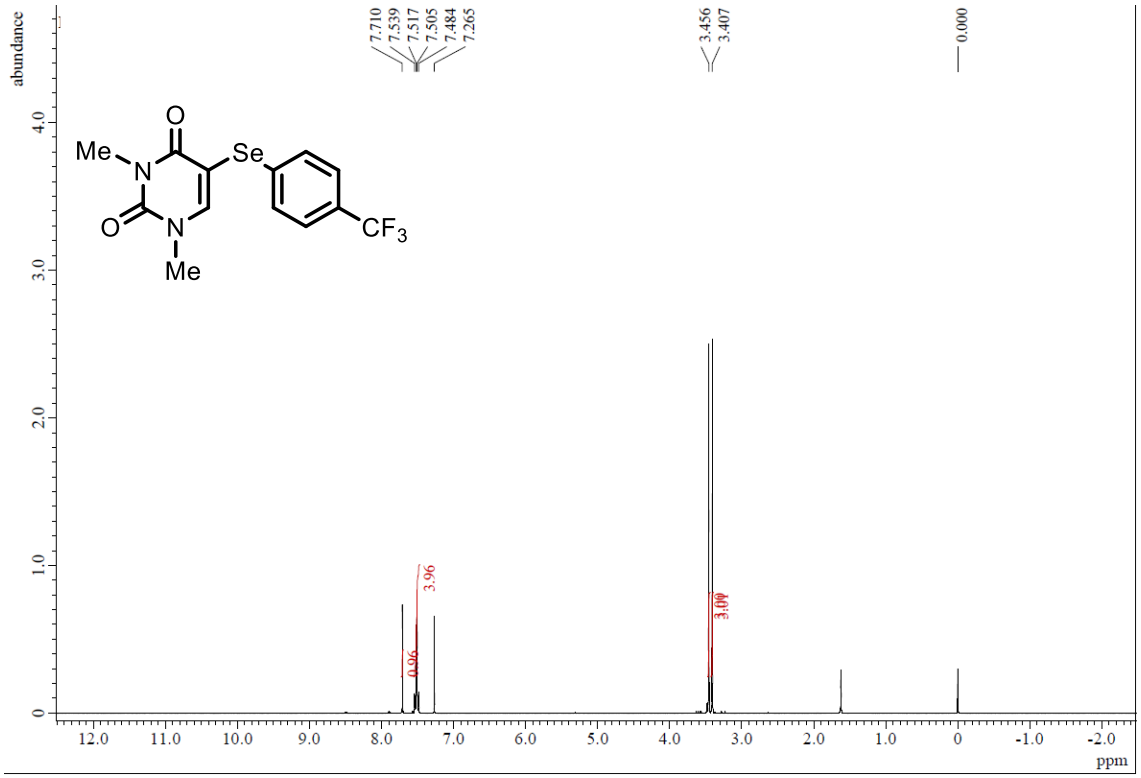
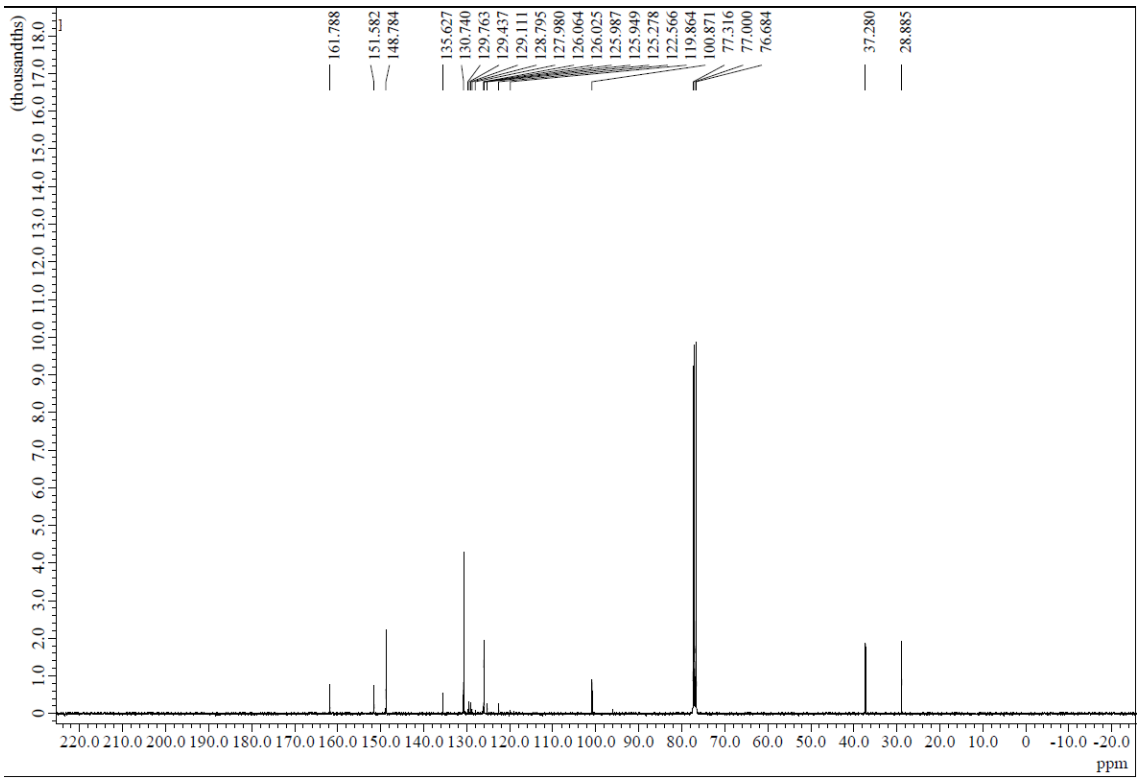
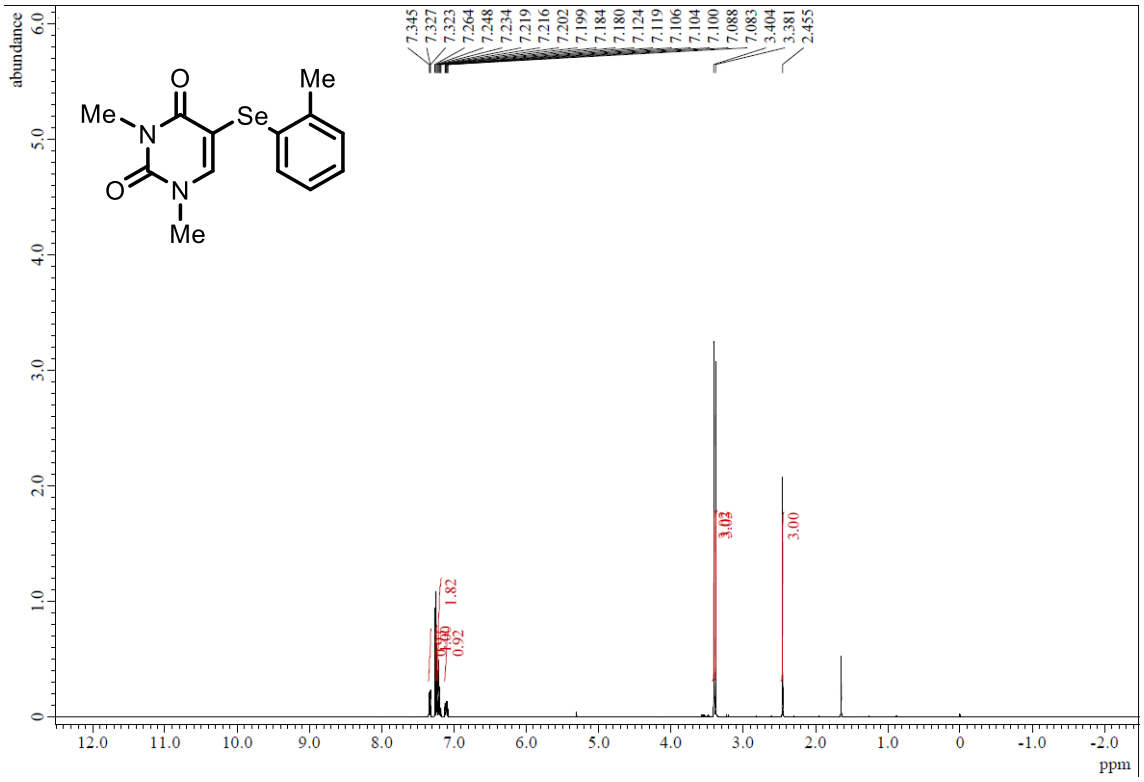


^{13}C NMR of **5f**



^{1}H NMR of **5g**



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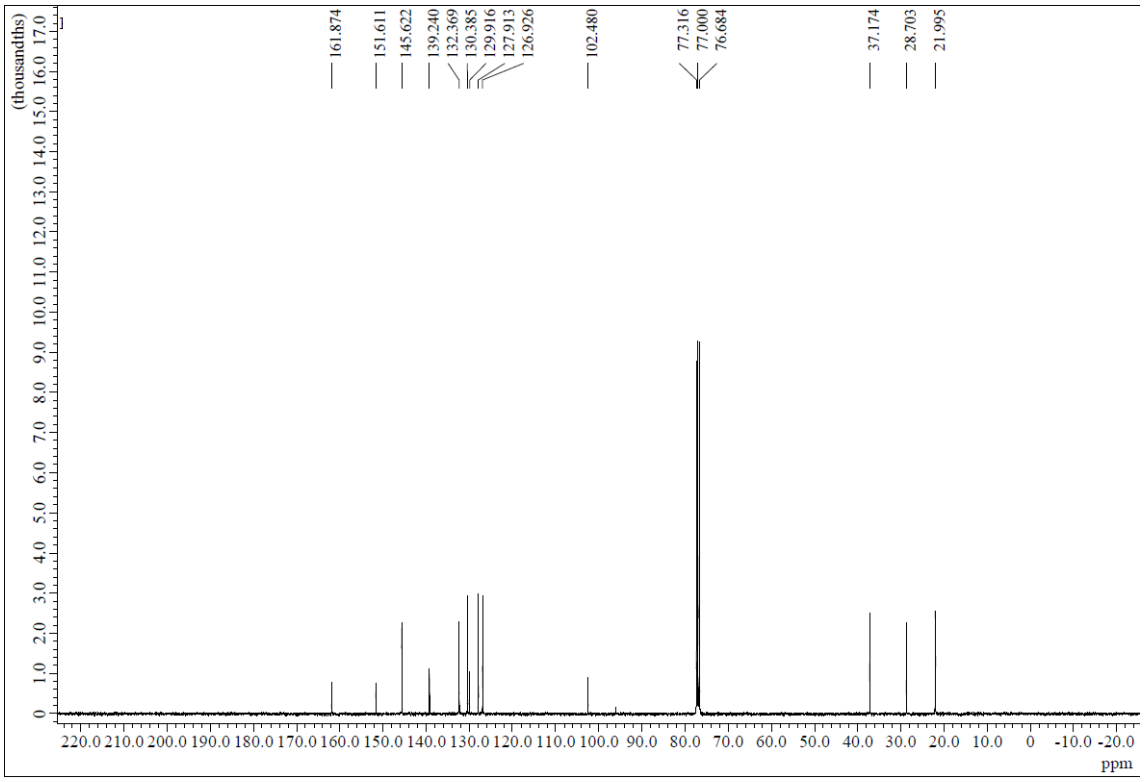

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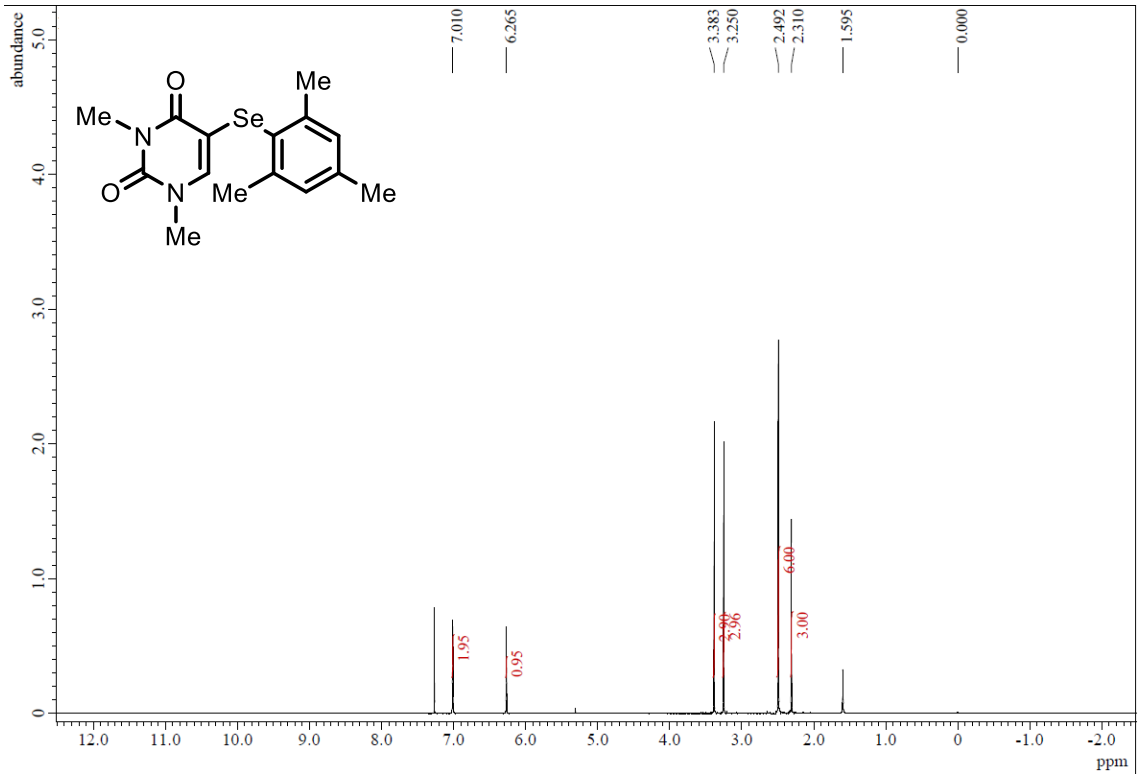

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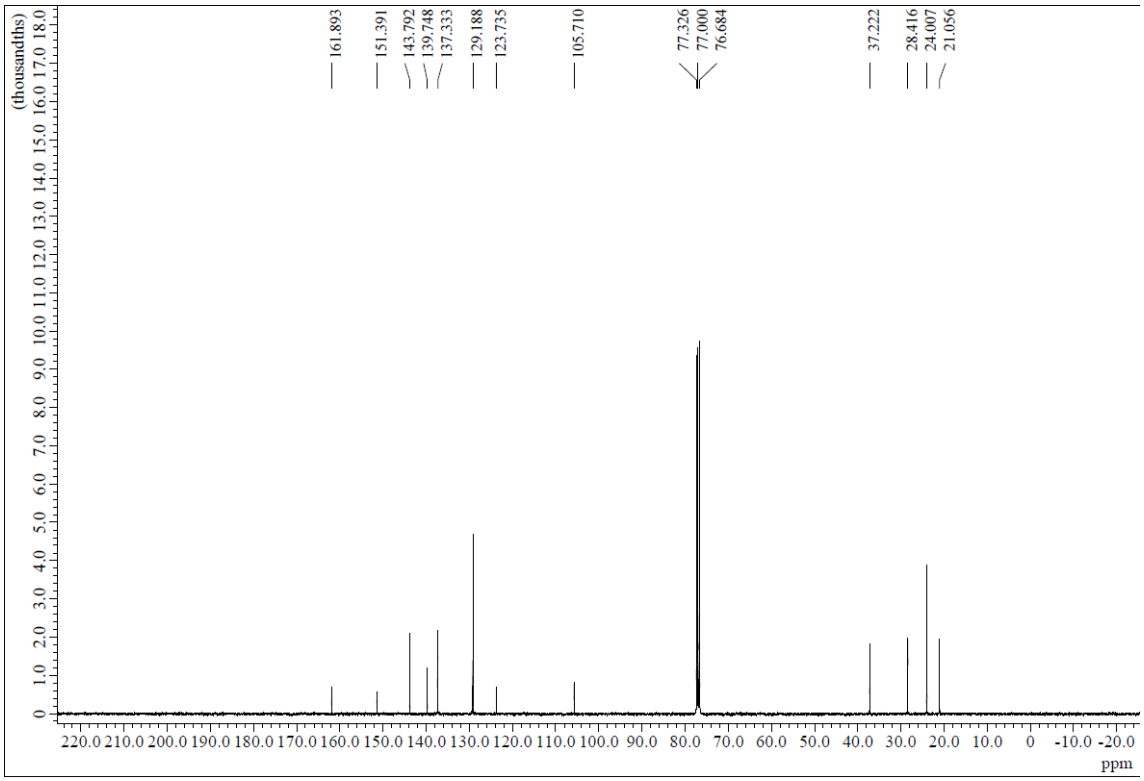

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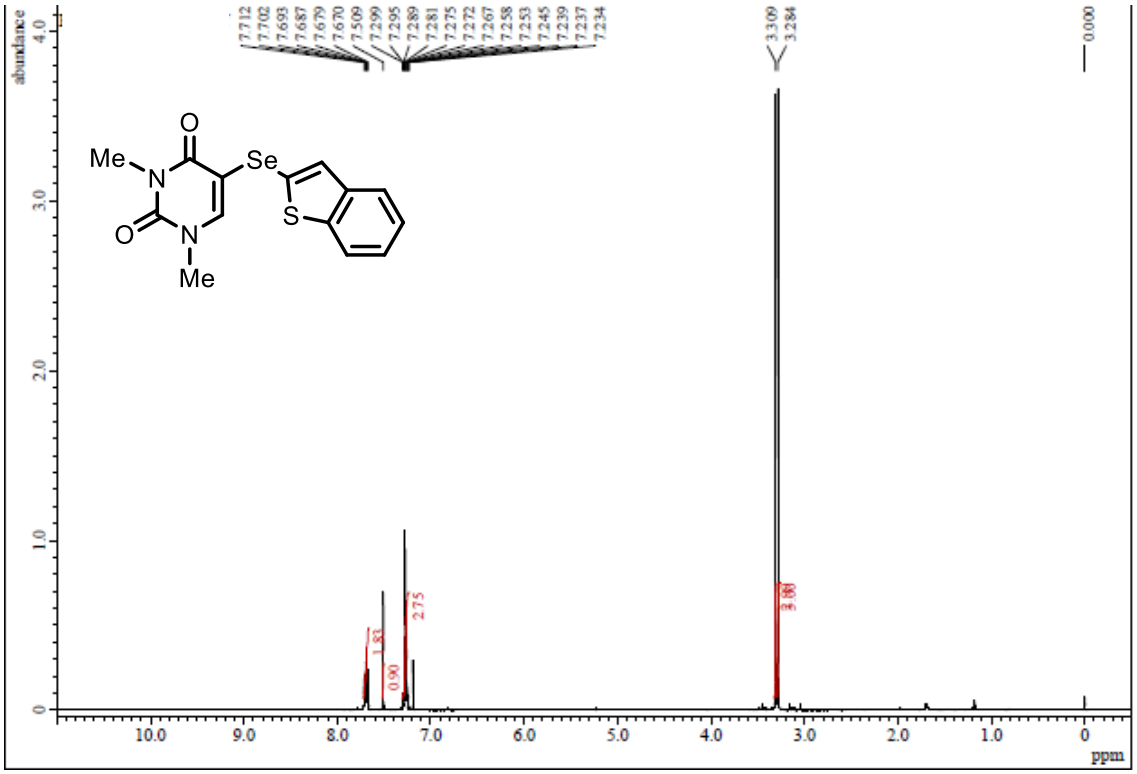

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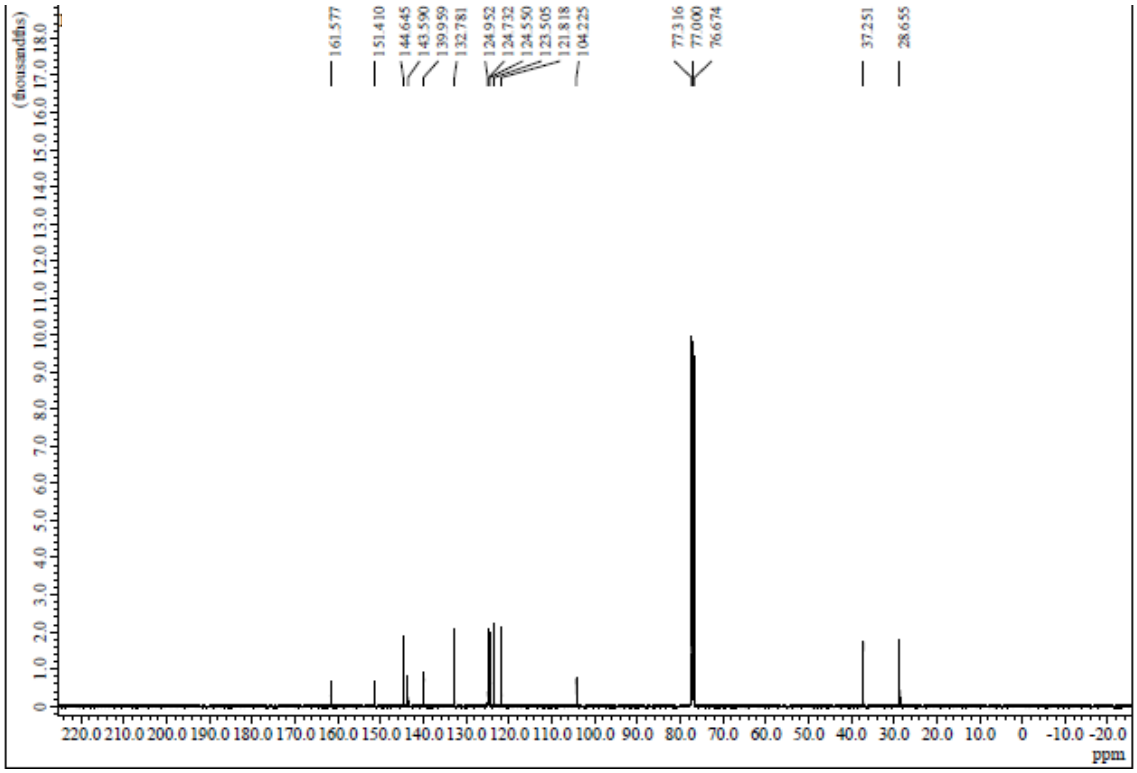

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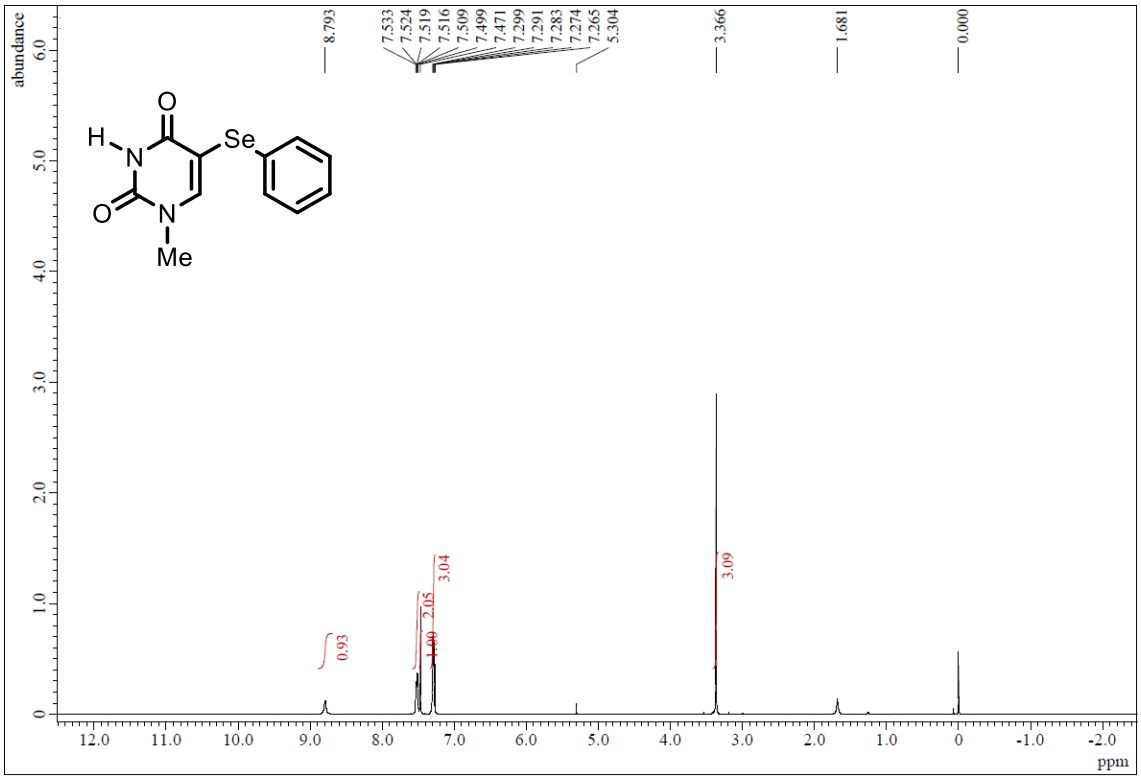

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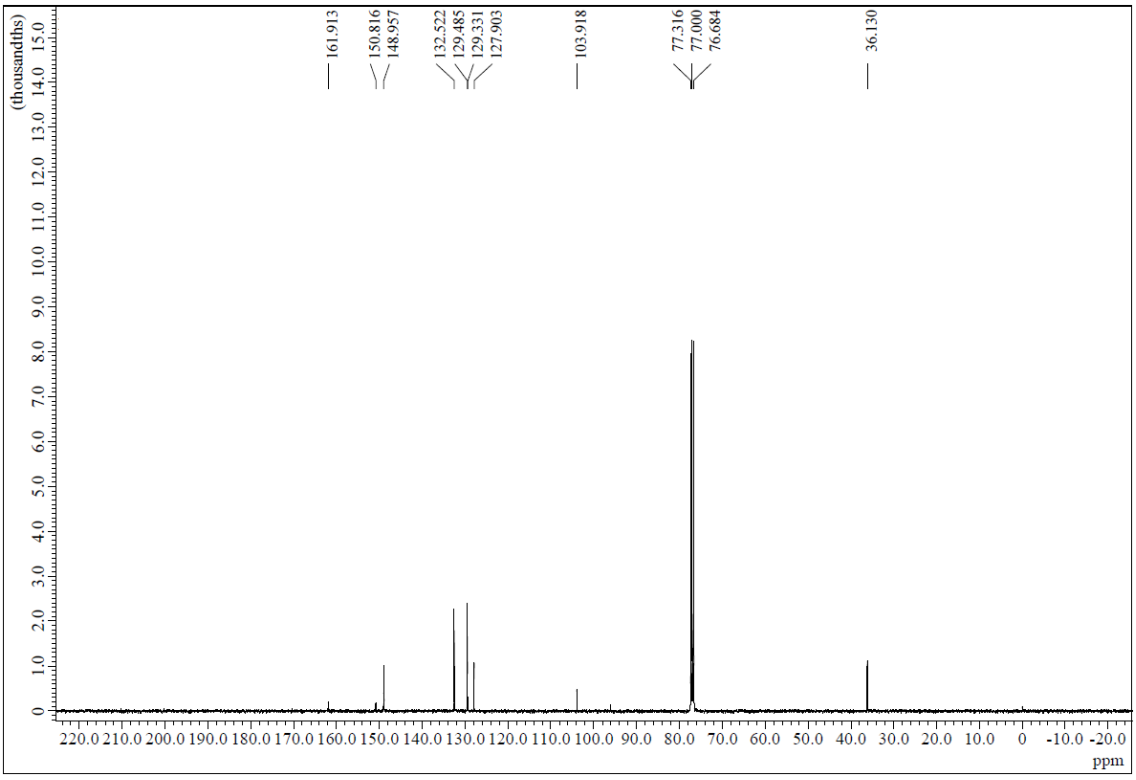

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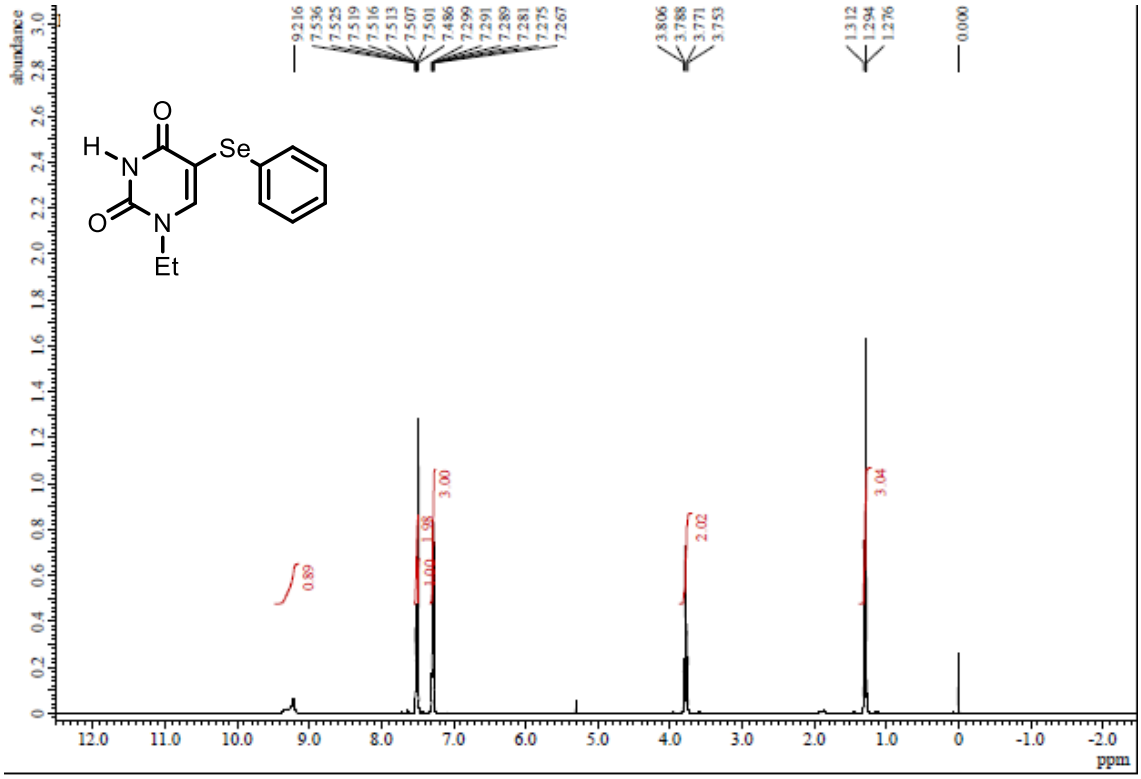

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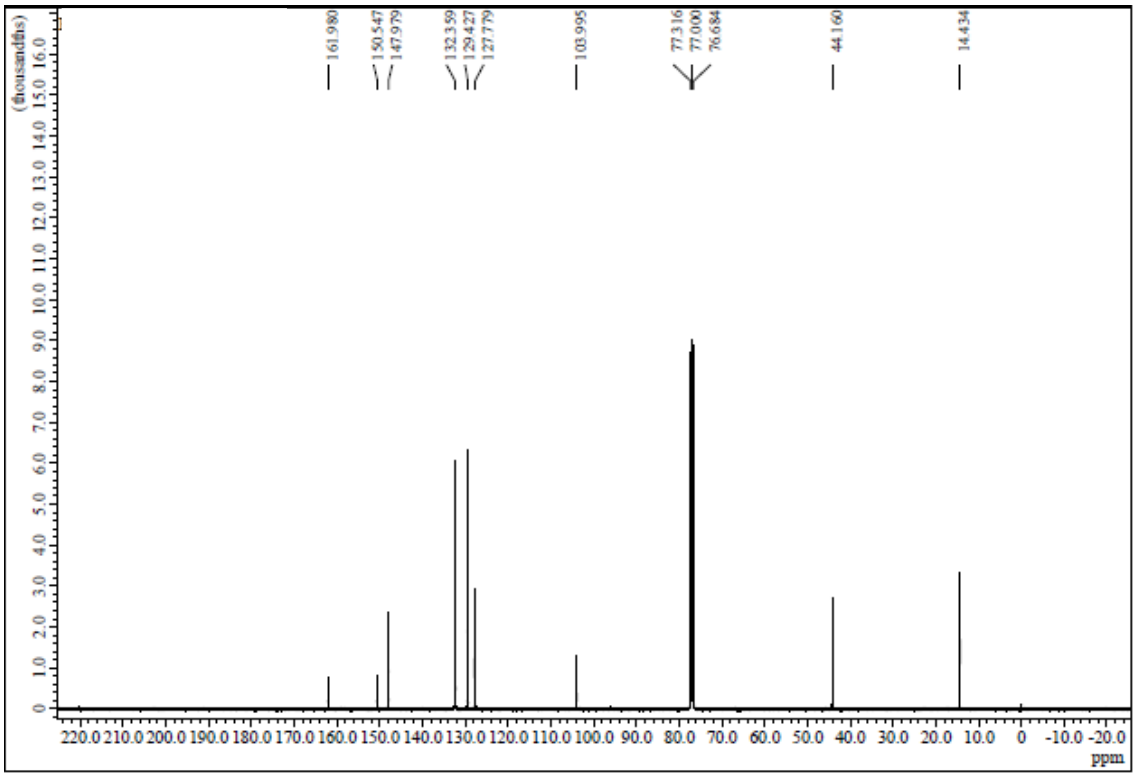

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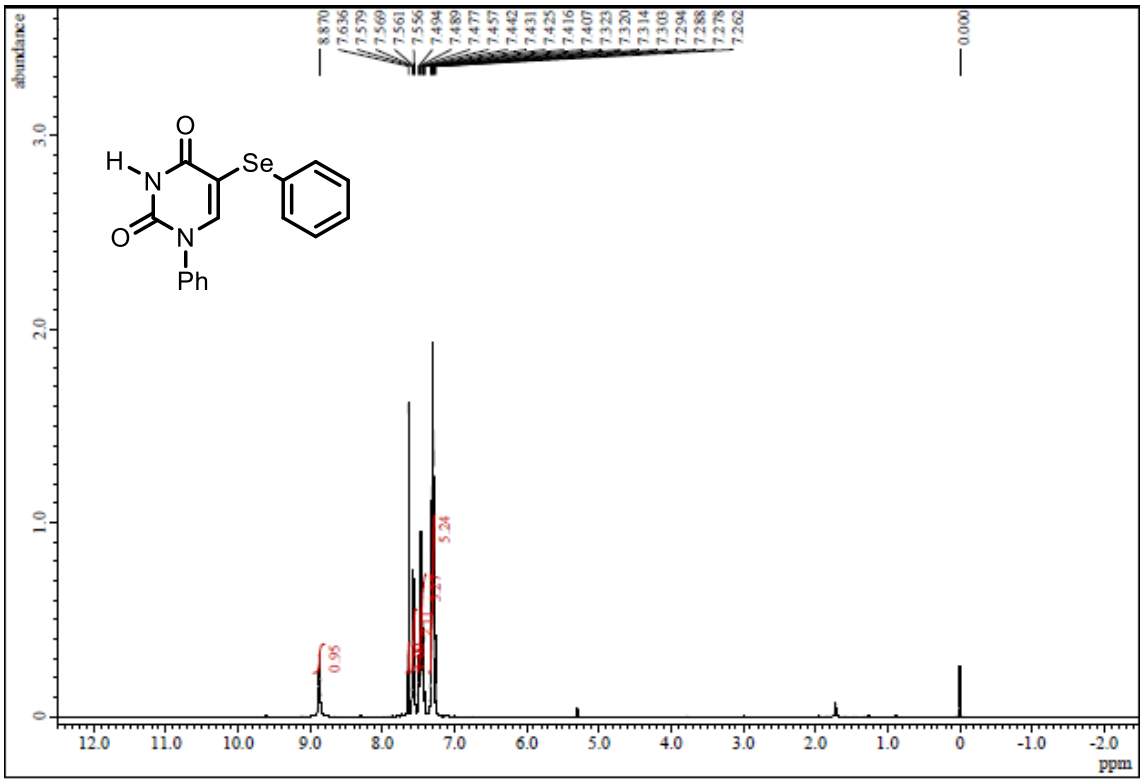

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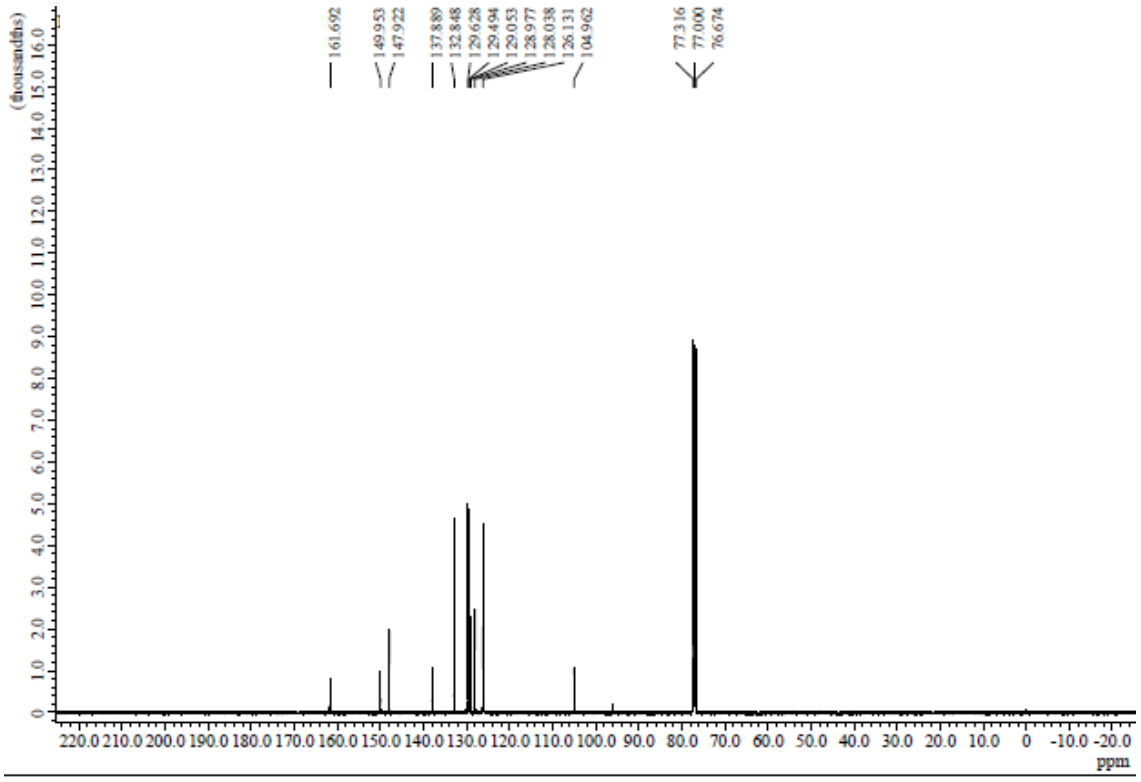

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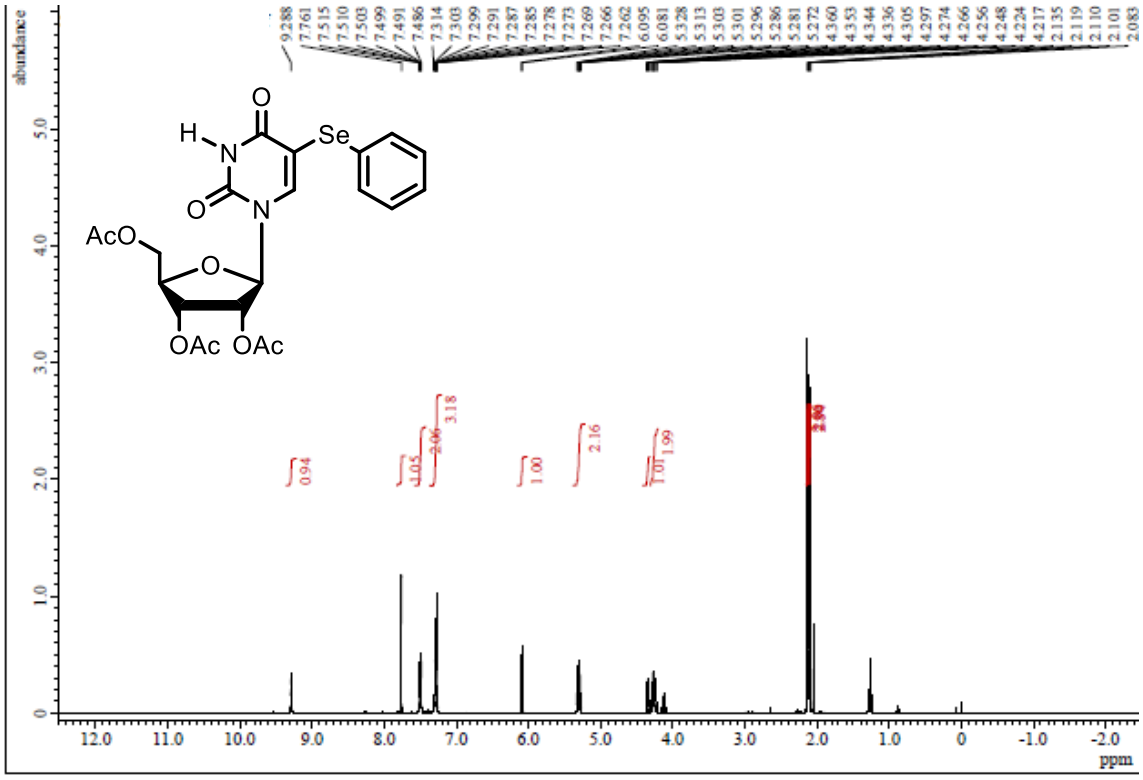

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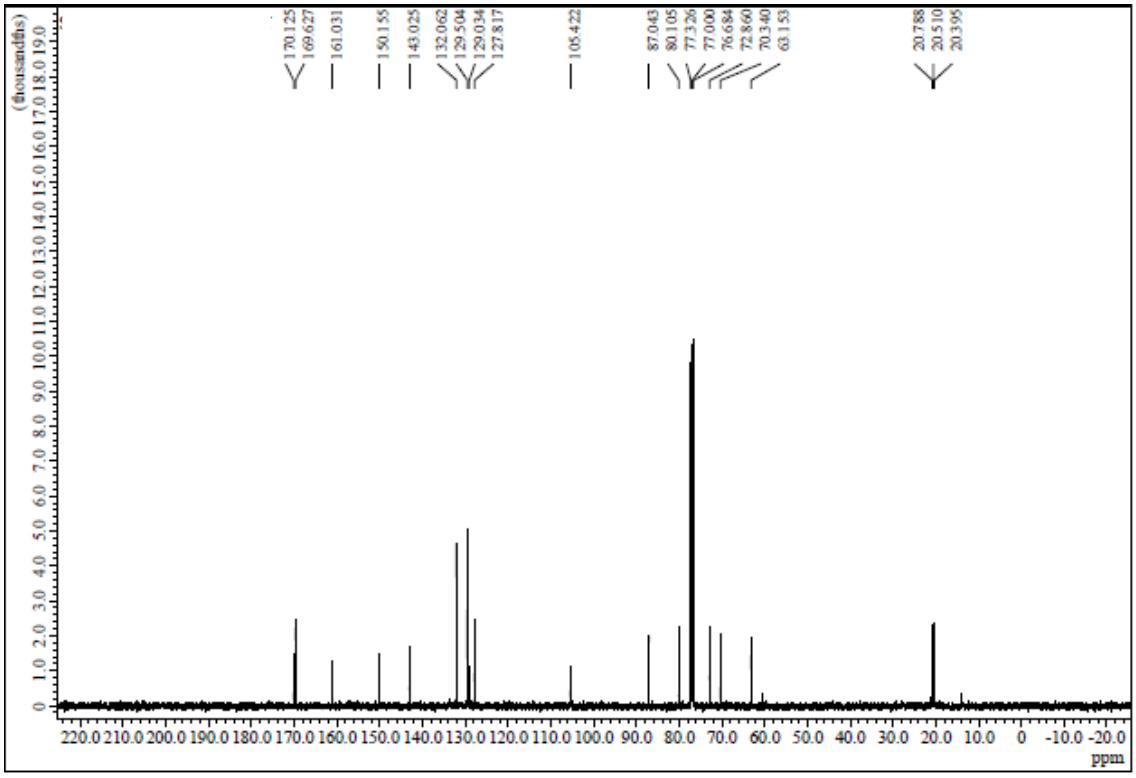

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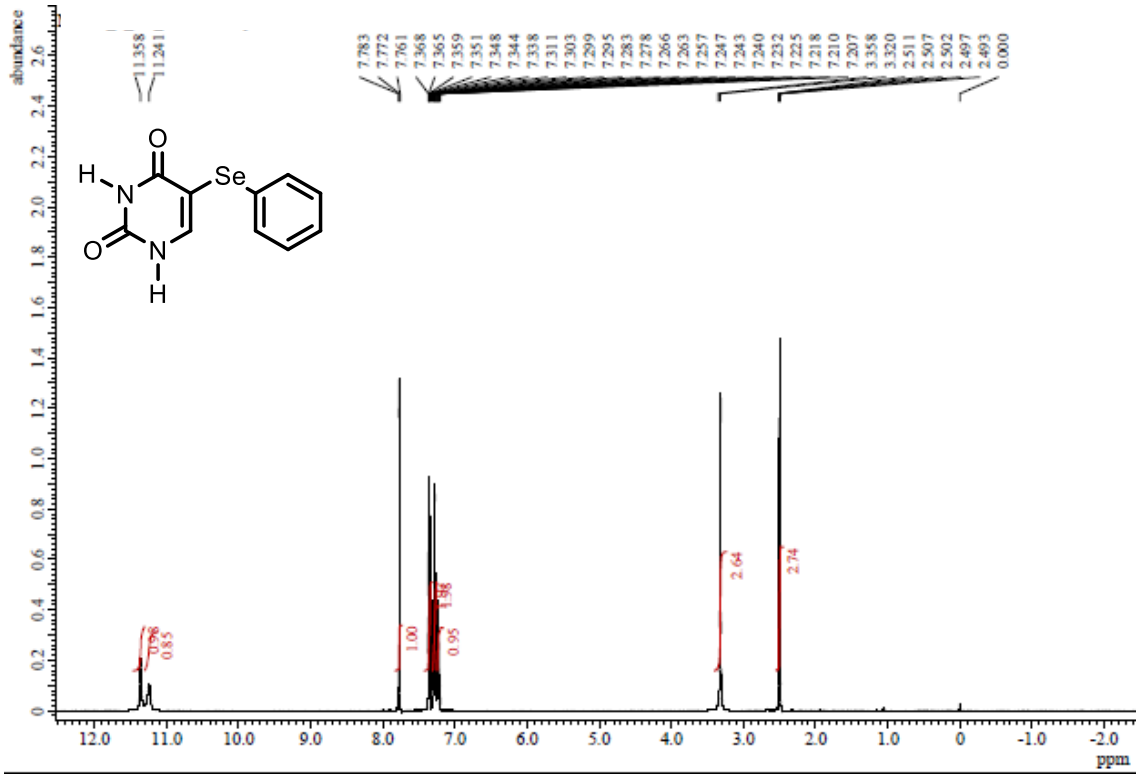

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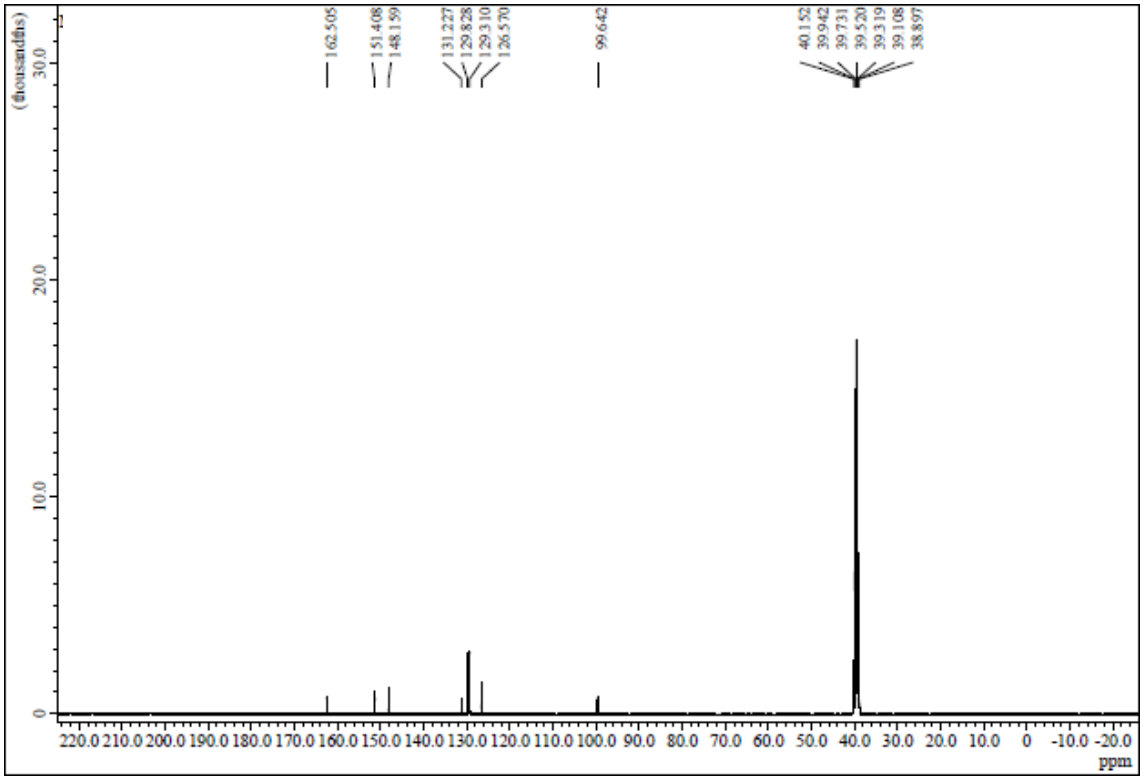

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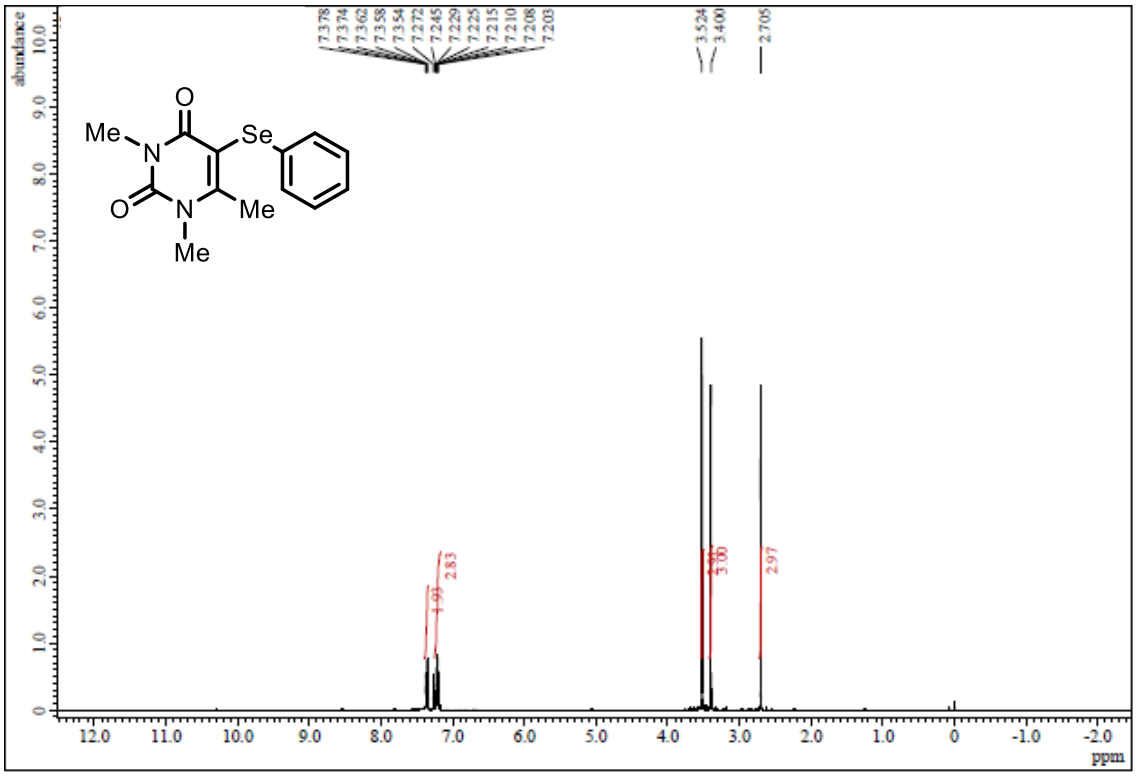

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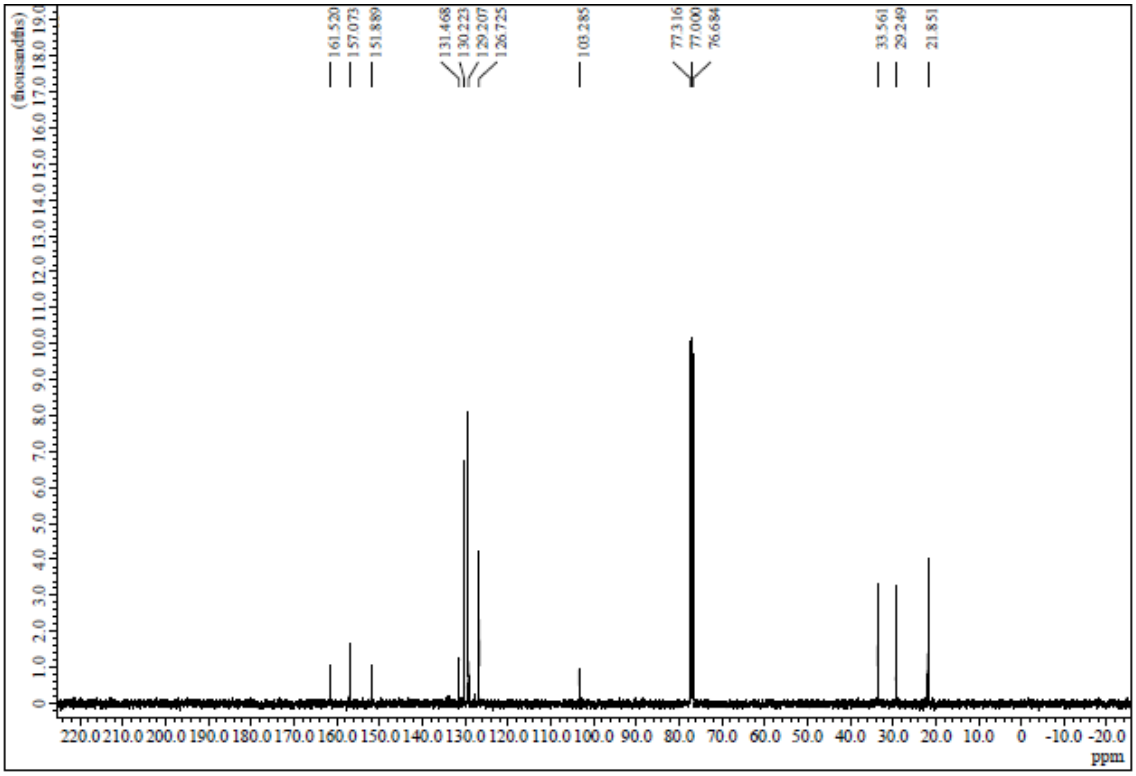

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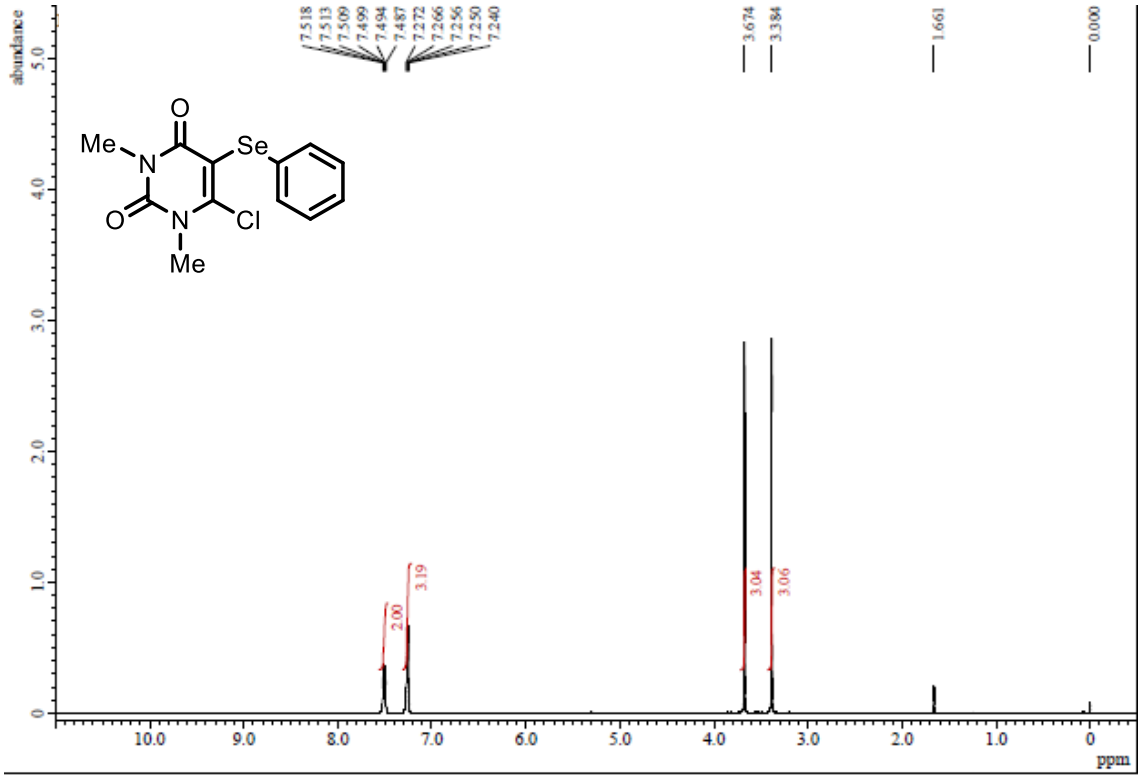
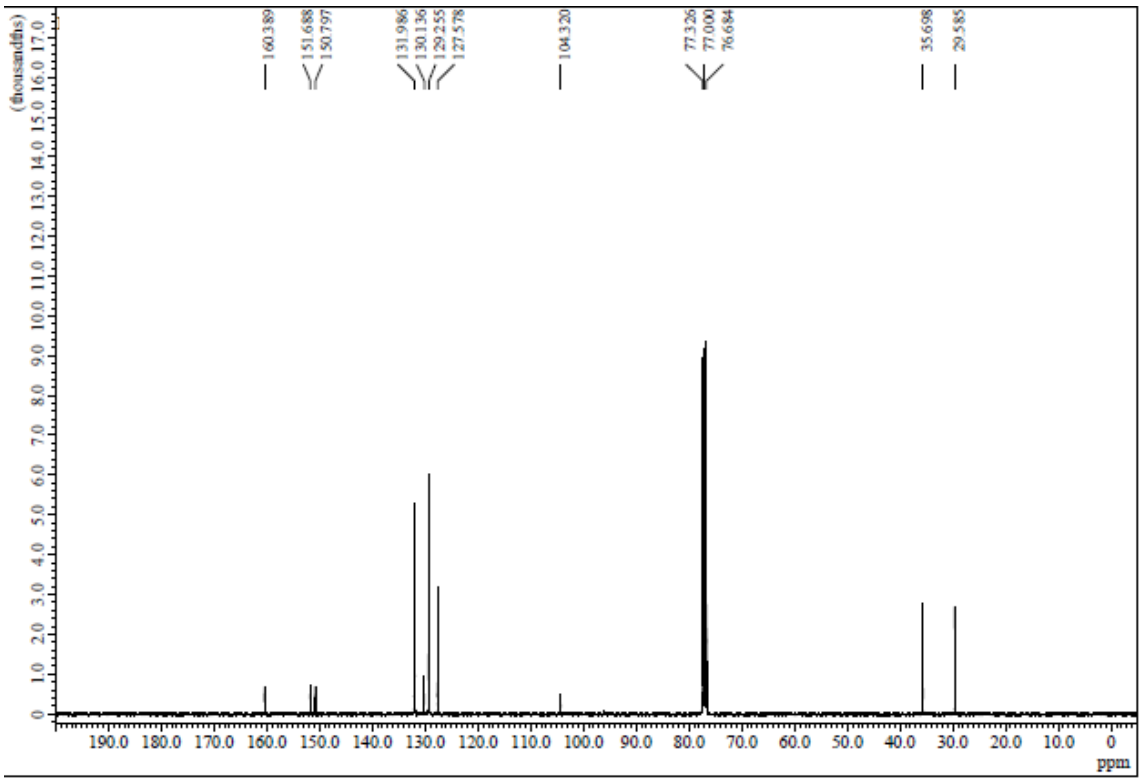
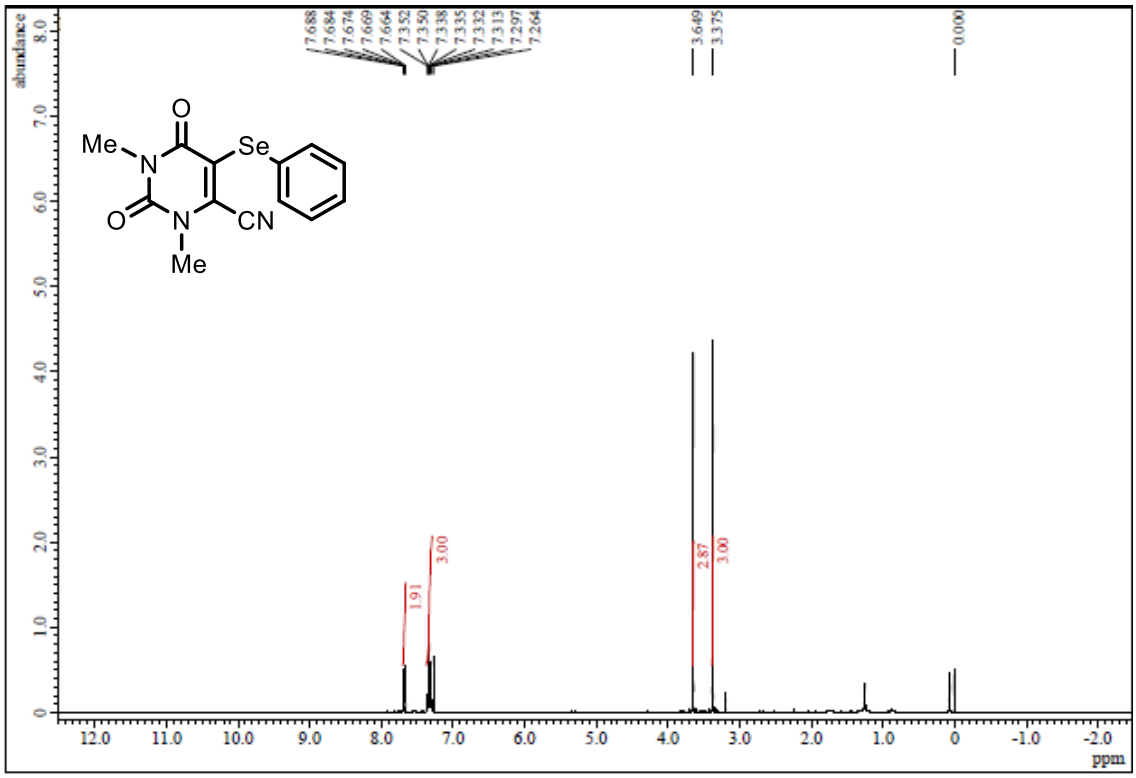


^{13}C NMR of **5s**



^{1}H NMR of **5t**



^{13}C NMR of **5t**