Supplementary Information (SI) for Green Chemistry.

Light-driven Newman Kwart Rearrangement under Ambient Conditions with Cysteine Quantum Dots

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Supplementary Information

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1. General considerations:

All chemicals were procured from commercial suppliers and used without further purification: Spectrochem, Avra, SRL, TCI, BLD Pharm, Finar and Sigma Aldrich. The solvents were purchased from SD Fine Chemicals Limited (SDFCL), India. For column chromatography, hexane was distilled to remove the grease. For extraction/workup, standard laboratory grade solvents procured from SDFCL India were used. For the purpose of the reaction, acetonitrile was procured from Finar (HPLC grade) and distilled to dryness using P_2O_5. The distilled solvent was collected and stored over activated 4 Å molecular sieves. For column chromatography, silica gel (100-200 mesh) was taken from Isochem and thin layer chromatography (TLC) was carried out on silica gel

60 F_{254} precoated plates (0.25 mm), obtained from Sigma Aldrich (Supelco). The nanomaterial synthesis was done in distilled water.

All the reactions were carried out in oven-dried glassware (120°C). Dry reaction conditions were maintained (wherever mentioned) using standard Schlenck line techniques with an Argon atmosphere. NMR spectra was recorded in $CDCl_3$ solvent (procured from Cambridge Isotopes Limited and used as obtained). NMR yields were obtained using Dibromomethane as the reference.

The LEDs, CFLs and Kessil Lamp (PR160L) for photo-irradiation were procured commercially.

The data was normalized/smoothed/deconvoluted/fit (as required) in GraphPad/OriginPro 9.1.

All the images were processed in Adobe Illustrator CS6 software.

2. Instrumentation:

NMR spectroscopy: Bruker Ultrashield spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C); NMR spectra were processed on TopSpin 3.6.4; chemical shifts have been reported in parts per million (ppm), while coupling constants (*J*) have been reported in Hz. For ^{1}H-NMR, data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration.

HRMS: Waters XEVO G2-XS QTof instrument.

UV-visible spectroscopy: UV-3600 Shimadzu UV-Vis-NIR Spectrophotometer from Japan Analytical Instruments (1 mL quartz cuvette with a 10 mm optical path).

Fluorescence spectroscopy: Varian Cary Eclipse Fluorescence Spectrophotometer.

FT-IR spectroscopy: CaF_2 cell in Bruker alfa FT-IR instrument.

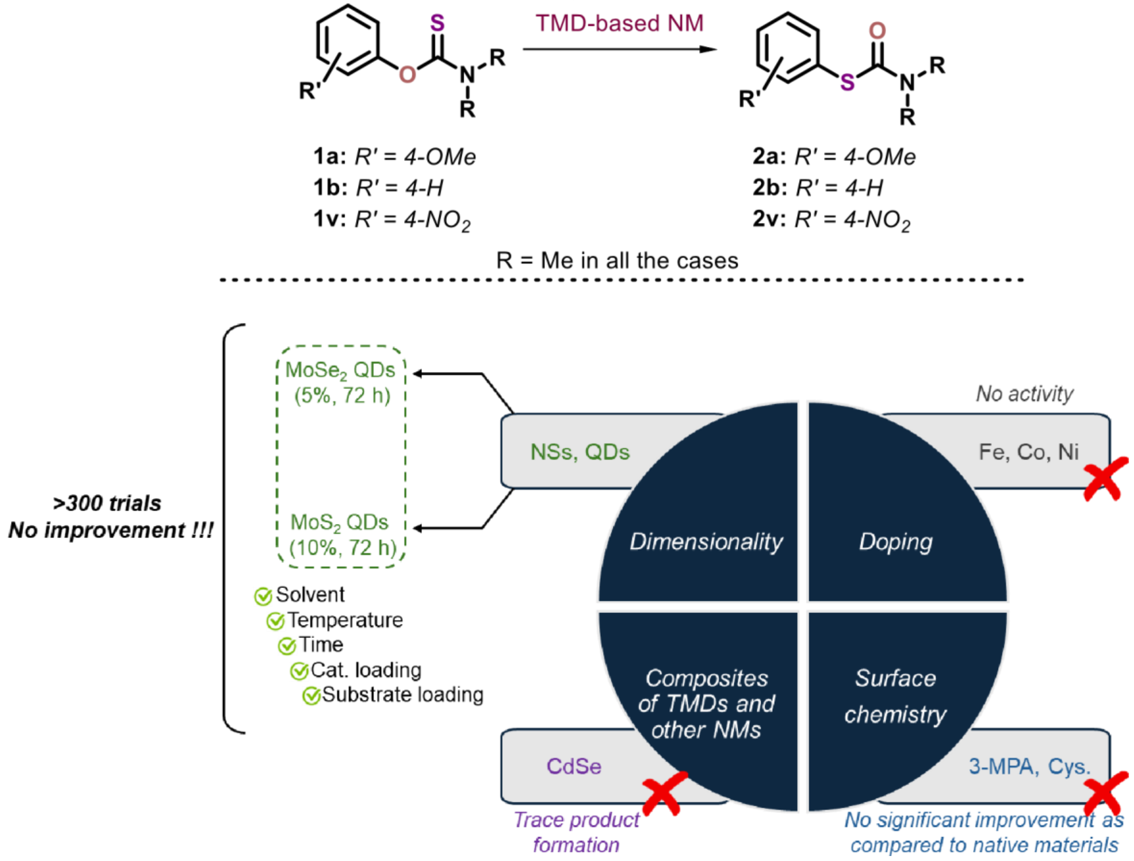
TEM: JOEL JEM-2100F with an accelerating voltage of 200 kV.

XPS: ESCALAB 250 (Thermo Electron) instrument with monochromatic Al Kα (1486.6 eV) as the X-ray source.

CV: Electrochemical Analyser (HCH Instruments CHI604E); platinum (glossy carbon) working electrode, platinum wire counter electrode and Ag/AgCl reference electrode were procured from CH Instruments, Inc.

Zeta Potential, Dynamic Light Scattering (DLS) and Molecular Weight calculation: Malvern Zetasizer Nano ZS System.

3. Initial attempts for photocatalytic NKR:



Scheme S1: Initial attempts to mediate NKR using TMDs bearing various dimensionality, functionality, dopant or composition.

The nanosheets (NSs) and quantum dots (QDs) of TMDs, MoS_2 and $MoSe_2$ were prepared using solvent exfoliation and hydrothermal routes respectively, as per our previous reports.[1-3] The doping with Fe/Co/Ni was done following documented protocols.[4, 5] For functionalization on the surface, the nanomaterial was stirred with the ligand 3-mercaptopropionic acid or L-cysteine.[6] CdSe[7] and

CdS[8] QDs were also prepared using bottom-up approaches, with the reaction conditions maintained so as to furnish QDs having absorption maxima in the range 350-420 nm. As NKR could proceed via the anionic or cationic pathway, we chose three different substrates for the trial, such that the substituents on the aryl ring could range from electron-donating (**1a**: R’ = 4-OMe) or withdrawing (**1v**: R’ = 4-NO_2) to electronically neutral groups (**1b**: R’ = H) (**Scheme S1**).

Since the NKR of **1a** with MoS_2 QDs gave a minimal yield of 10% (which could not be improved further by tuning the surface chemistry, dimensionality, composition or incorporation of metal dopant), the reaction parameters were modulated sequentially, *vide infra*:

a) Solvents: H_2O, MeCN, EtOH, THF, DMF (individual as well as mixture of solvents in different ratios).
b) Temperature: 25-70°C.
c) Time: 1-96 h.
d) Catalyst loading: 1-20 wt% of the catalyst, relative to the *O*-arylcarbamothioate.
e) Substrate loading: 0.1-0.25 mmol.

4. Experimental section:

4.1 Procedure for optical/microscopic characterization and sample preparation:

TEM (Transmission Electron Microscopy): The samples for TEM imaging were prepared on a Formvar/carbon 200 mesh copper grid loaded with a dilute solution of the sample and dried under vacuum.

UV-Visible (absorption) and Fluorescence (emission) spectroscopy: A 1 mL quartz cuvette having a 10 mm optical path was taken and the diluted sample was added to it. Scanning was done from 200 to 800 nm with a step duration of 0.5 nm. For the fluorescence spectrum, the sample was excited at different wavelengths from 250-450 nm (at intervals of 10 nm) and the emission profile was recorded.

Zeta Potential and hydrodynamic diameter measurement: For measuring surface charge and hydrodynamic diameter, the aqueous solution of the sample was used.

Molecular weight measurement: Toluene was used as the standard while water was used as the solvent. The measurements were done at variable concentrations of the nanomaterial.

FT-IR (Fourier transform InfraRed) spectroscopy: The FT-IR spectrum of CQDs was recorded by dissolving the lyophilized sample in MeOH and spreading it on a CaF_2 cell. The residual solvent was removed by drying. The spectrum was recorded from 4000 to 500 cm^{-1}.

XPS (X-ray Photoelectron Spectroscopy): The samples were prepared by drop-casting a relatively concentrated solution of the nanomaterial on silicon wafers (size less than 1 cm X 1 cm; cleaned thrice by heating at 60°C in isopropanol followed by acetone wash and oven drying). The sample was dried in air, and then in vacuum for at least 24 h.

4.2 Characterization of CQDs:

DLS measurements revealed a large hydrodynamic diameter compared to the size of the individual domains of the CQDs, which confirmed the close proximity of these entities.

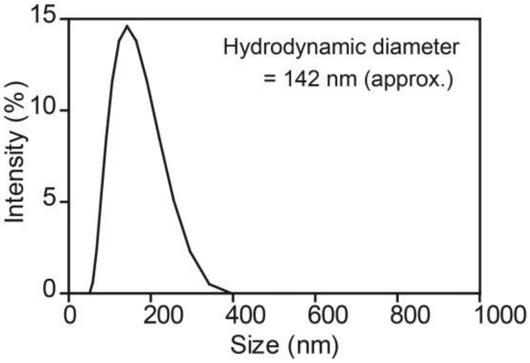


Figure S1: DLS measurement, showing the hydrodynamic diameter of the CQDs.

4.3 Calculation of molecular weight for the CQDs (reference given at the end):

The molecular weight was calculated using the Zetasizer equipment by the SLS (Static Light Scattering) method. The refractive index increment (dn/dc) was set as 0.1 mL/g, while the shape correction model was taken as that of a sphere. The temperature was kept as 25ºC throughout and the equilibration time was fixed to 100 seconds. First, the dark count measurement (laser turned off) was done for the background light level. Toluene was used as the scattering standard to establish the scattering intensity of the reference. Water was used as the solvent (first, a blank measurement was taken corresponding to zero sample concentration). The CQDs (homogeneous solution) were taken at different concentrations (diluted in water). The scattering intensity and concentration were ensured to be in accordance with the instrument quality criteria.

Finally, a plot of KC/R_θ (1/KDa) vs. concentration C (g/mL) was made (all the values were taken directly from the instrument) and the fitting was done using a linear regression model (K: optical constant; C: concentration; R_θ: Rayleigh ratio or the ratio of scattered light to incident light of the sample). The inverse of the intercept at the Y-axis gives the molecular weight in KDa. From this value, the mol% of the catalyst relative to the substrate **1** can be calculated.

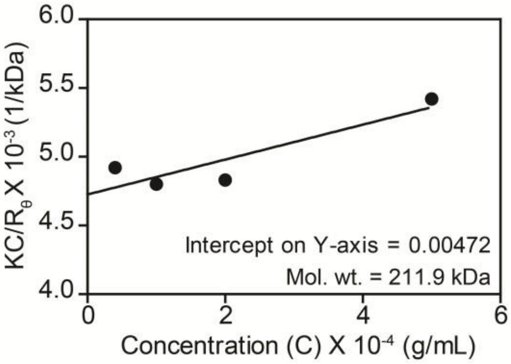
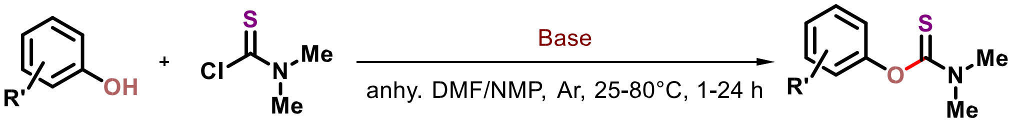


Figure S2: Molecular weight determination for the CQDs using the SLS method: plot of KC/R_θ vs. concentration.

4.4 Procedure for preparation of substrates:[9-18]

The substrates *O*-aryl carbamothioates **1** were prepared using one of the following methods (**Scheme S2** and **Scheme S3**), and characterized using ^{1}H and ^{13}C NMR as well as ESI-MS techniques:

4.4.1 General procedure for the preparation of substrates from *N*,*N*-dimethyl thiocarbamoyl chloride



Scheme S2: General scheme to access *O*-aryl carbamothioates from phenols starting from *N*,*N*-dimethyl thiocarbamoyl chloride.

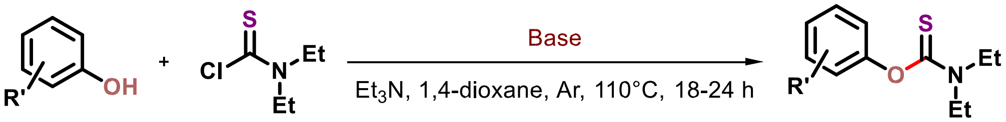
a) In a clean, dried round-bottom flask equipped with a magnetic stir-bar, *N*,*N*-dimethyl thiocarbamoyl chloride (1.5 equiv.) was dissolved in anhydrous DMF/NMP under Ar atmosphere. The phenol counterpart (1 equiv.) along with a suitable base (DABCO, 1.5 equiv.) was sequentially added. The reaction mixture was stirred for 16-24 h (monitored by TLC). Reaction temperature was maintained at 25-50°C, depending on the substrate. After the completion of the reaction, cold H_2O was added to the reaction mixture. The work-up and purification was achieved in one of the following ways:

    i) If addition of water results in the formation of a precipitate, the latter was collected via filtration. If required, recrystallization can be done using EtOH or EtOH/H_2O mixture. In case the washing with water gives precipitate of phenol and the desired *O*-aryl carbamothioate together, a suitable base (such as 0.3 M NaOH) can be used to remove the excess phenol derivative (provided no base sensitive functionalities are present) by first dissolving the precipitate in Et_2O prior to workup. The *O*-aryl carbamothioate can be retrieved post workup by concentrating the organic phase under reduced pressure.

ii) If no precipitation was observed upon addition of cold H_2O, the reaction mixture was extracted with EtOAc (3 × 20 mL). The combined organic phases were washed with brine and dried over anhydrous sodium sulphate. The solvent was removed by rotary evaporation. The *O*-aryl carbamothioate was obtained by purification using column chromatography with silica gel (100-200 mesh) using EtOAc/Hexane solvent. If the phenol derivative and *O*-aryl carbamothioate eluted together under the column conditions, the excess phenol counterpart was removed by dissolving the mixture in in Et_2O, followed by washing with a suitable base (such as 0.3 M NaOH), provided no base sensitive functionalities are present. The *O*-aryl carbamothioate was retrieved post workup by concentrating the organic phase under reduced pressure.

b) A clean, dried round-bottom flask equipped with a magnetic stir-bar was purged with Ar. NaH (1.2 equiv.) was taken in the flask. Anhydrous DMF was added slowly with stirring after placing the flask in ice. The phenol derivative (1 equiv.), dissolved in anhydrous DMF, was added dropwise to the flask over 5-10 mins. Then, the *N*,*N*-dimethyl thiocarbamoyl chloride (1.2 equiv.) was added in a single portion. The flask was gradually heated to 50-80°C with stirring for 1-3 h. The setup was allowed to come to room temperature, followed by gradual transfer to a separatory funnel containing Et_2O. The workup was done with H_2O and the organic layer was collected over anhydrous sodium sulphate. The solvent was removed under the effect of vacuum. The crude reaction mixture was finally purified through column chromatography on silica gel (100200 mesh) using EtOAc/Hexane eluent. If the phenol analogue and *O*-aryl carbamothioate eluted together under the column conditions, the excess phenol moiety was removed by dissolving the mixture in in Et_2O, followed by washing with a suitable base (such as 0.3 M NaOH), provided no base sensitive functionalities are present. The *O*-aryl carbamothioate was retrieved post workup by concentrating the organic phase under reduced pressure.

4.4.2 General procedure for the preparation of substrates from *N*,*N*-diethyl thiocarbamoyl chloride



Scheme S3: General scheme to access *O*-aryl carbamothioates from phenols starting from *N*,*N*-diethylthiocarbamoyl chloride.

In a clean, dried round-bottom flask equipped with a magnetic stir-bar, the phenol derivative (1 equiv.), *N*,*N*-diethylthiocarbamoyl chloride (1.1 equiv.), DMAP (0.1 equiv.) and triethylamine (2 equiv.) were taken. The flask was purged with Ar and 1,4-dioxane was added. The reaction mixture was refluxed for 18-24 h. The setup was cooled to room temperature, poured on a mixture of 12 N HCl and ice. The extraction was done with Et_2O and the combined organic phases were washed with 1 N HCl and 1 N NaOH, followed by collection over Na_2CO_3. The solvent was removed with a rotary evaporator. If required, further purification was done using column chromatography with silica gel (100-200 mesh) in EtOAc/Hexane solvent system to obtain the *O*-aryl carbamothioate derivative.

4.5 General procedure for the cyclic voltammetry (CV) studies:

The Ag/AgCl electrode was taken as the reference and cleaned with distilled water. Glassy carbon electrode was chosen as the working electrode and cleaned by rubbing on alumina sheet followed by rinsing with water. The Pt wire electrode was selected as the counter electrode and cleaned by dipping in conc. HCl, followed by heating over a burner flame and finally rinsing with distilled water.

Distilled water was used to prepare the solutions. A total of 40 mL of 5 mM $K_4[Fe(CN)_6]$ in 0.1 M KCl was taken with and without the CQDs, and CV studies were carried out. The scan rate was kept constant at 0.05 V/s throughout the experiment. The voltammograms were recorded in static mode, with stirring between successive experiments to prevent deposition of any analyte or material on the disc of the working electrode.

4.6 General procedure for the crossover experiments:

A clean, dried reaction tube equipped with a magnetic stir-bar was taken and cooled under the effect of Ar flow. 0.125 mmol of the *O*-aryl carbamothioates **1t** and **1j** were taken in the reaction tube. The tube was sealed with a septum and degassed under the effect of vacuum, followed by purging with Ar. The CQDs (2.5 wt% relative to **1t** and 2.5 wt% relative to **1j**, dissolved in 50 μL of H_2O) along with 4 mL of anhydrous MeCN (distilled to dryness with P_2O_5 and stored over activated 4 Å MS) were added. The reaction mixture was ultra-sonicated (if required) and subsequently irradiated for the stated time using a Kessil Lamp (370 nm, PR160L). Post irradiation, the reaction mixture may be extracted with EtOAc (3 X 10 mL) (removal of MeCN under reduced pressure is sufficient otherwise). The combined organic phases were washed with brine and dried over anhydrous sodium sulphate. The solvent was removed by rotary evaporation. The products formed in the reaction were quantified using ^{1}H-NMR, taking Dibromomethane as the reference in $CDCl_3$ solvent.

5. Measurement of quantum yield:[1]

7-hydroxycoumarin was taken as the reference to measure the quantum yield (QY) of the CQDs. The UV-visible absorption and fluorescence emission spectra was recorded for the reference as well as the sample in H_2O. QY was determined using the following general formula:

$$QY_{sample} = QY_{ref.} \text{ X } \left(\frac{\eta_{sample}}{\eta_{ref.}}\right)^2 \text{ X } \left(\frac{A_{ref.}}{A_{sample}}\right) \text{ X } \left(\frac{I_{sample}}{I_{ref.}}\right)$$

where:

$QY_{ref.}$ = QY of reference

QY_{sample} = QY of sample (in this case, CQDs) $\eta = \eta_{ref.} = 1.33$

(refractive index of medium; in this case H_2O)

$A_{ref.}$ = Absorbance of reference at λ_{max}

A_{sample} = Absorbance of sample at λ_{max}

$I_{ref.}$ = Integrated intensity of reference

I_{sample} = Integrated intensity of sample

6. Spectra of the crude reaction mixture:

We present the ^{1}H-NMR spectrum of the crude reaction mixture, recorded in $CDCl_3$, ruling out the formation of any side products. For this, the reaction was done as per the optimal conditions (Primary Manuscript: Table 1, Entry 9) and the reaction mixture may be subjected to EtOAc/H_2O workup. The organic layer was collected, concentrated and $CDCl_3$ was added along with Dibromomethane (δ (ppm) = 4.93) as the reference. The resultant spectrum clearly indicates the absence of any side product (**Figure S3**).

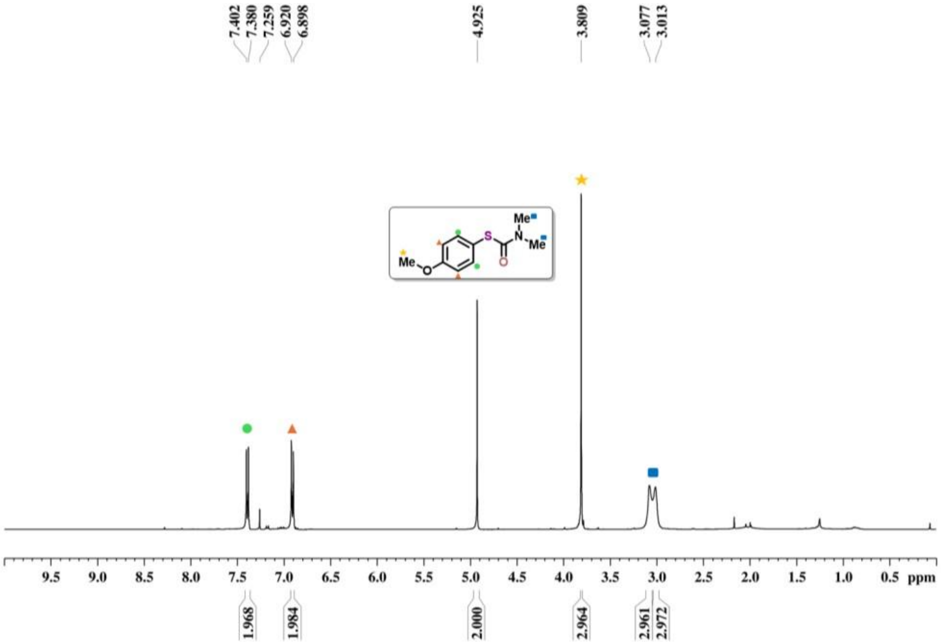


Figure S3: NMR spectrum of the crude reaction mixture, recorded in $CDCl_3$ solvent with Dibromomethane as the reference.

7. Stern-Volmer quenching experiment:[19]

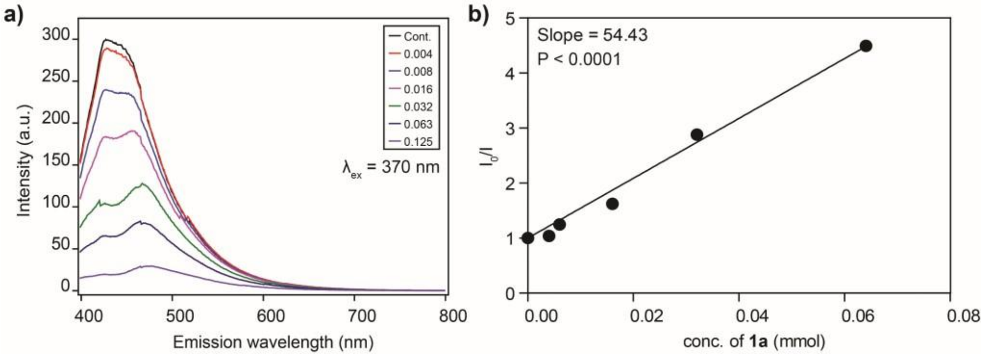


Figure S4: Stern-Volmer quenching experiment using CQDs: a) reduction in the fluorescence intensity upon increasing concentration of **1a** (the numbers represent the concentration in mmol) and b) calculation of the SternVolmer quenching constant.

8. Characterization of the recycled CQDs:

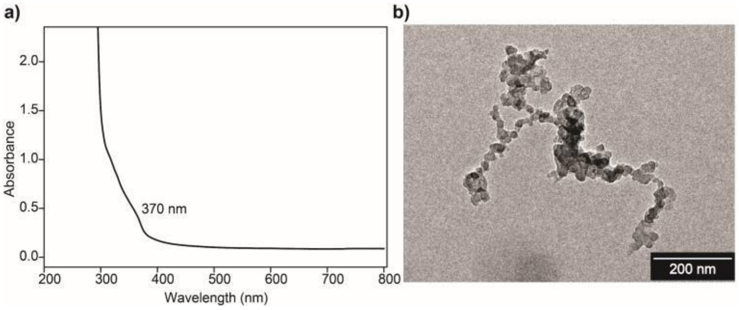


Figure S5: Characterization of the CQD post 10 runs of the NKR: a) UV-visible absorption profile and b) TEM image of the recycled catalyst.

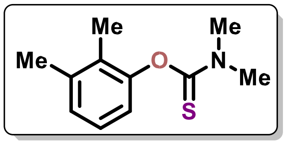
9. Estimation of EcoScale value (considering the model substrate 1a):

Parameter	**Penalty Points**	**Explanation**
Yield	1	(100 – % yield)/2
Price of reaction components (to obtain 10 mmol of end product)	0	Inexpensive reagents
Safety	5	Highly flammable
Technical setup	1	Inert gas
Temp./Time	0	Room temp./<1 h
Workup and purification	0	Removal of solvent with bp < 150°C
Workup and purification	10	Classical chromatography
TOTAL	**17**	
EcoScale (= 100 – Penalty Points)	**83**	

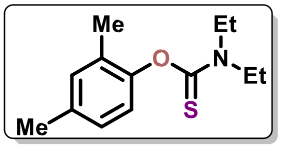
10. Characterization data:[9-11, 13-16, 20-24]

The substrates prepared by any of the methods from **Section 4.3** were characterized subsequently by ^{1}H and ^{13}C NMR spectroscopy, as well as ESI-MS technique. The data was verified from literature reports to confirm the formation of the pure *O*-aryl carbamothioate. The data for those substrates that have not been reported in literature, are presented below:

***O*-(2,3-dimethylphenyl) dimethylcarbamothioate:** Light orange solid; isolated using silica gel (100-200 mesh) column chromatography in 3-4% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.14-7.10 (t, *J* = 7.7 Hz, 1H), 7.07-7.05 (d, *J* = 7.4 Hz, 1H), 6.86-6.84 (d, *J* = 7.9 Hz, 1H), 3.47 (s, 3H), 3.37 (s, 3H), 2.31 (s, 3H), 2.08 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 187.96, 152.94, 138.77, 129.91, 127.96, 126.26, 120.96, 43.70, 38.99, 20.53, 13.04; **HRMS (ESI+):** Calculated for $C_{11}H_{15}NOS$ $[M+H]^+$: 210.0953, Found $[M+H]^+$: 210.0950.

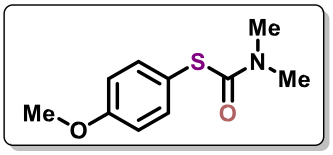


***O*-(2,4-dimethylphenyl) diethylcarbamothioate:** Orange solid; precipitated as per the procedure stated in section 6.5.3.2; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.04-7.01 (m, 2H), 6.87-6.85 (m, 1H), 3.94-3.88 (q, *J* = 7.1 Hz, 2H), 3.73-3.67 (q, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 2.17 (s, 3H), 1.35-1.31 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 186.91, 150.72, 135.96, 132.10, 130.89, 127.76, 122.96, 48.71, 44.43, 21.35, 16.80, 13.95, 12.30; **HRMS (ESI+):** Calculated for $C_{13}H_{19}NOS$ $[M+H]^+$: 238.1266, Found $[M+H]^+$: 238.1274.

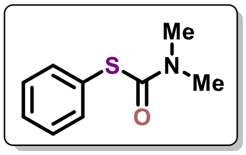


The data for the rearranged products are given below:

***S*-(4-methoxyphenyl) dimethylcarbamothioate:** Yellowish-white solid; isolated using silica gel (100-200 mesh) column chromatography in 3-4% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.41-7.38 (d, *J* = 8.8 Hz, 2H), 6.92-6.90 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 3.05 (br s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 168.11, 160.99, 137.75, 119.86, 115.05, 55.77, 37.29; **HRMS (ESI+):** Calculated for $C_{10}H_{13}NO_2S$ $[M+H]^+$: 212.0745, Found $[M+H]^+$: 212.0741.

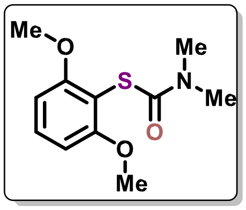


***S*-phenyl dimethylcarbamothioate:** Yellow liquid; isolated using silica gel (100-200 mesh)

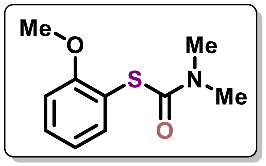


column chromatography in 3-4% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.52-7.48 (m, 2H), 7.39-7.37 (m, 3H), 3.08 (s, 3H), 3.04 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 136.27, 129.68, 129.45, 37.45; **HRMS (ESI+):** Calculated for $C_9H_{11}NOS$ $[M+H]^+$: 182.0640, Found $[M+H]^+$: 182.0642.

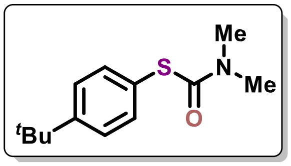
***S*-(2,6-dimethoxyphenyl) dimethylcarbamothioate:** White solid; isolated using silica gel (100-200 mesh) column chromatography in 13-14% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.38-7.34 (t, *J* = 8.4 Hz, 1H), 6.63-6.61 (d, *J* = 8.4 Hz, 2H), 3.86 (s, 6H), 3.18 (s, 3H), 2.99 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 166.24, 161.90, 132.22, 105.31, 104.73, 56.89, 37.65; **HRMS (ESI+):** Calculated for $C_{11}H_{15}NO_3S$ $[M+H]^+$: 242.0851, Found $[M+H]^+$: 242.0856.



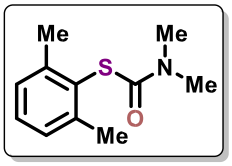
***S*-(2-methoxyphenyl) dimethylcarbamothioate:** White solid; isolated using silica gel (100-200 mesh) column chromatography in 4-5% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.47-7.45 (m, 1H), 7.42-7.38 (m, 1H), 6.99-6.95 (m, 2H), 3.87 (s, 3H), 3.13 (s, 3H), 3.01 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 166.77, 160.55, 138.59, 131.97, 121.42, 117.14, 111.91, 56.54, 37.42; **HRMS (ESI+):** Calculated for $C_{10}H_{13}NO_2S$ $[M+H]^+$: 212.0745, Found $[M+H]^+$: 212.0747.



***S*-(4-(*tert*-butyl)phenyl) dimethylcarbamothioate:** White solid; isolated using silica gel (100-200 mesh) column chromatography in 2-3% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.41-7.34 (m, 4H), 3.09 (s, 3H), 3.01 (s, 3H), 1.31 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 152.70, 149.52, 148.27, 135.79, 126.51, 126.47, 125.59, 121.42, 37.27, 35.09, 34.78, 31.82, 31.61, 31.33; **HRMS (ESI+):** Calculated for $C_{13}H_{19}NOS$ $[M+H]^+$: 238.1266, Found $[M+H]^+$: 238.1264.

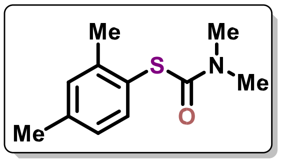


***S*-(2,6-dimethylphenyl) dimethylcarbamothioate:** White solid; isolated using silica gel (100-200 mesh)

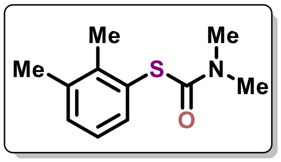


column chromatography in 2-3% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 7.22-7.18 (m, 1H), 7.15-7.13 (m, 2H), 3.16 (s, 3H), 3.02 (s, 3H), 2.42 (s, 6H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ (ppm) = 166.48, 144.15, 130.00, 128.59, 37.45, 22.52; **HRMS (ESI+):** Calculated for $C_{11}H_{15}NOS$ $[M+H]^+$: 210.0953, Found $[M+H]^+$: 210.0951.

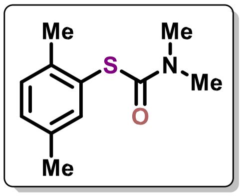
***S*-(2,4-dimethylphenyl) dimethylcarbamothioate:** White solid; isolated using silica gel (100200 mesh) column chromatography in 2-3% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 7.35-7.33 (d, *J* = 7.8 Hz, 1H), 7.12 (s, 1H), 7.02-7.00 (d, *J* = 7.8 Hz, 1H), 3.12 (s, 3H), 3.01 (s, 3H), 2.37 (s, 3H), 2.32 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ (ppm) = 166.90, 142.79, 140.06, 137.02, 131.50, 127.29, 124.70, 36.94, 21.25, 20.97; **HRMS (ESI+):** Calculated for $C_{11}H_{15}NOS$ $[M+H]^+$: 210.0953, Found $[M+H]^+$: 210.0952.



***S*-(2,3-dimethylphenyl) dimethylcarbamothioate:** White solid; isolated using silica gel (100200 mesh) column chromatography in 2-3% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 7.36-7.34 (d, *J* = 7.6 Hz, 1H), 7.21-7.19 (d, *J* = 7.6 Hz, 1H), 7.11-7.07 (t, *J* = 7.6 Hz, 1H), 3.13 (s, 3H), 3.02 (s, 3H), 2.36 (s, 3H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ (ppm) = 167.23, 141.92, 138.14, 135.21, 131.95, 128.55, 126.13, 37.30, 21.43, 17.92; **HRMS (ESI+):** Calculated for $C_{11}H_{15}NOS$ $[M+H]^+$: 210.0953, Found $[M+H]^+$: 210.0949.

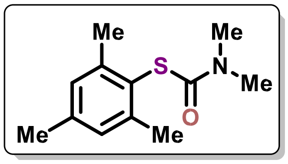


***S*-(2,5-dimethylphenyl) dimethylcarbamothioate:** White solid; isolated using silica gel (100-



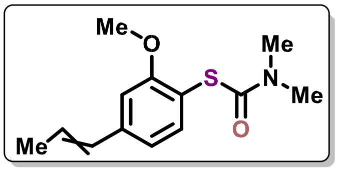
200 mesh) column chromatography in 2-3% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.30 (s, 1H), 7.19-7.17 (d, *J* = 7.8 Hz, 1H), 7.12-7.10 (d, *J* = 7.6 Hz, 1H), 3.12 (s, 3H), 3.02 (s, 3H), 2.36 (s, 3H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 166.78, 139.86, 137.58, 135.97, 130.78, 130.63, 130.40, 127.68, 126.23, 122.78, 36.97, 20.75, 20.56; **HRMS (ESI+):** Calculated for $C_{11}H_{15}NOS$ $[M+H]^+$: 210.0953, Found $[M+H]^+$: 210.0956.

***S*-mesityl dimethylcarbamothioate:** White solid; isolated using silica gel (100-200 mesh)



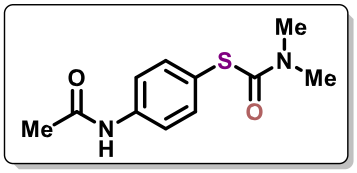
column chromatography in 7-8% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 6.97 (s, 2H), 3.15 (s, 3H), 3.02 (s, 3H), 2.38 (s, 6H), 2.28 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 166.79, 143.85, 139.95, 129.51, 125.06, 37.40, 22.36, 21.57; **HRMS (ESI+):** Calculated for $C_{12}H_{17}NOS$ $[M+H]^+$: 224.1109, Found $[M+H]^+$: 224.1107.

***S*-(2-methoxy-4-(prop-1-en-1-yl)phenyl) dimethylcarbamothioate:** Yellowish-white solid;

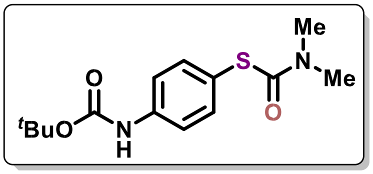


isolated using silica gel (100-200 mesh) column chromatography in 1-2% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, $CDCl_3$): δ (ppm) = 7.36-7.34 (d, *J* = 7.9 Hz, 1H), 6.94-6.92 (d, *J* = 7.6 Hz, 1H), 6.89 (s, 1H), 6.41-6.37 (d, *J* = 15.5 Hz, 1H), 6.32-6.23 (m, 1H), 3.87 (s, 3H), 3.12 (s, 3H), 3.00 (s, 3H), 1.89-1.88 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ (ppm) = 166.79, 160.46, 141.88, 138.40, 131.08, 127.73, 119.01, 114.96, 109.17, 56.38, 37.31, 18.87; **HRMS (ESI+):** Calculated for $C_{13}H_{17}NO_2S$ $[M+H]^+$: 252.1058, Found $[M+H]^+$: 252.1053.

***S*-(4-acetamidophenyl) dimethylcarbamothioate:** White solid; isolated using silica gel (100200 mesh) column chromatography in 35-37% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 7.82 (br s, 1H), 7.42-7.40 (d, *J* = 8.5 Hz, 2H), 7.36-7.34 (d, *J* = 8.3 Hz, 2H), 3.10 (s, 3H), 3.04 (s, 3H), 2.09 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ (ppm) = 168.94, 168.46, 139.85, 136.72, 122.76, 120.67, 37.38, 24.75; **HRMS (ESI+):** Calculated for $C_{11}H_{14}N_2O_2S$ [M+Na]$^+$: 261.0674, Found [M+Na]$^+$: 261.0677.

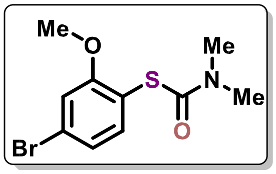


***tert*-butyl (4-((dimethylcarbamoyl)thio)phenyl)carbamate:** White solid; isolated using silica gel (100-200 mesh) column chromatography in 32-33% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 7.38 (s, 4H), 6.56 (s, 1H), 3.08 (s, 3H), 3.00 (s, 3H), 1.51 (s, 9H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ (ppm) = 139.95, 137.10, 122.63, 119.08, 37.37, 28.77; **HRMS (ESI+):** Calculated for $C_{14}H_{20}N_2O_3S$ [M+Na]$^+$: 319.1092, Found [M+Na]$^+$: 319.1096.

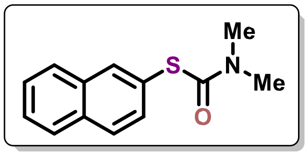


Product decomposes during the course of purification.

***S*-(4-bromo-2-methoxyphenyl) dimethylcarbamothioate:** White solid; isolated using silica gel (100-200 mesh) column chromatography in 3-4% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 7.32-7.30 (d, J = 8.0, 1H), 7.12-7.10 (dd, *J* = 8.2 Hz, *J* = 1.5 Hz, 1H), 7.08-7.07 (d, *J* = 1.8 Hz, 1H), 3.86 (s, 3H), 3.12 (s, 3H), 3.00 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ (ppm) = 166.11, 161.00, 139.36, 125.66, 124.57, 116.55, 115.62, 56.84, 37.45; **HRMS (ESI+):** Calculated for $C_{10}H_{12}BrNO_2S$ [M+H]$^+$: 289.9850, Found [M+H]$^+$: 289.9856.



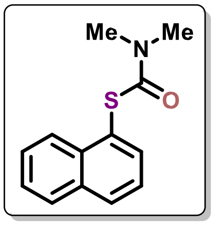
***S*-(naphthalen-2-yl) dimethylcarbamothioate:** Yellowish-white solid; isolated using silica gel



(100-200 mesh) column chromatography in 3-4% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 8.02 (s, 1H), 7.85-7.77 (m, 3H), 7.57-7.43 (m, 3H), 3.16 (s, 3H), 3.05 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ (ppm) = 167.50, 135.76, 133.91, 133.72, 132.71 128.90, 128.40, 128.16, 127.37, 126.76, 126.48, 37.39;

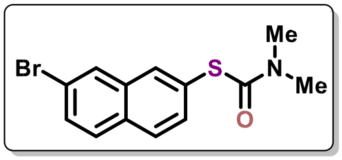
HRMS (ESI+): Calculated for $C_{13}H_{13}NOS$ [M+H]$^+$: 232.0796, Found [M+H]$^+$: 232.0797.

***S*-(naphthalen-1-yl) dimethylcarbamothioate:** Yellowish-white solid; isolated using silica gel



(100-200 mesh) column chromatography in 3-4% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 8.33-8.31 (d, *J* = 8.2 Hz, 1H), 7.95-7.93 (d, *J* = 8.2 Hz, 1H), 7.88-7.86 (d, *J* = 8.2 Hz, 1H), 7.79-7.77 (d, *J* = 7.2 Hz, 1H), 7.59-7.55 (t, *J* = 7.5 Hz, 1H), 7.52-7.47 (q, *J* = 7.8 Hz, 2H), 3.24 (s, 3H), 3.02 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ (ppm) = 167.04, 136.61, 135.65, 134.63, 131.27, 129.01, 127.50, 126.67, 126.57, 126.18, 126.00, 37.59; **HRMS (ESI+):** Calculated for $C_{13}H_{13}NOS$ [M+H]$^+$: 232.0796, Found [M+H]$^+$: 232.0799.

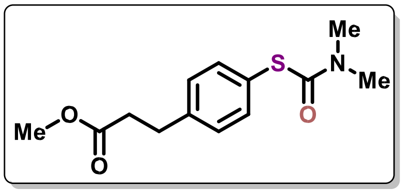
***S*-(7-bromonaphthalen-2-yl) dimethylcarbamothioate:** White solid; isolated using silica gel



(100- 200 mesh) column chromatography in 5-6% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 7.97-7.91 (m, 1H), 7.83-7.78 (m, 1H), 7.72-7.68 (m, 1H), 7.59-7.54 (m, 1H), 7.52-7.48 (m, 1H), 7.30-7.27 (m, 1H), 3.15 (s, 3H), 3.04 (s, 3H); **HRMS (ESI+):** Calculated for $C_{13}H_{12}BrNOS$ [M+H]$^+$: 309.9901, Found [M+H]$^+$: 309.9905.

Product decomposes very rapidly, hence ^{13}C-NMR spectrum could not be recorded.

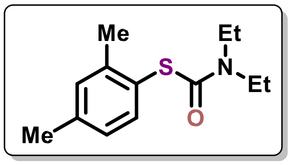
methyl 3-(4-((dimethylcarbamoyl)thio)phenyl)propanoate: White solid; isolated using silica



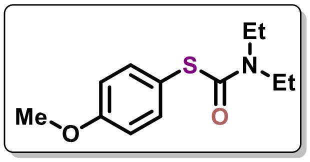
gel (100- 200 mesh) column chromatography in 3-5% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) =

7.41-7.39 (d, *J* = 8.3 Hz, 2H), 7.23-7.21 (d, *J* = 8.2 Hz, 2H), 3.67 (s, 3H), 3.08 (s, 3H), 3.03 (s, 3H), 2.98-2.94 (t, *J* = 7.9 Hz, 2H), 2.65-2.61 (t, *J* = 7.8 Hz, 2H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ (ppm) = 173.58, 142.20, 136.31, 129.38, 126.81, 52.08, 37.31, 35.78, 31.05; **HRMS (ESI+):** Calculated for $C_{13}H_{17}NO_3S$ [M+H]$^+$: 268.1007, Found [M+H]$^+$: 268.1007.

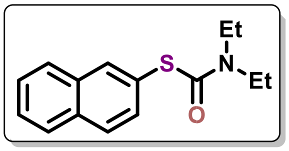
***S*-(2,4-dimethylphenyl) diethylcarbamothioate:** White solid; isolated using silica gel (100- 200 mesh) column chromatography in 6-8% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 7.37-7.35 (d, *J* = 7.7 Hz, 1H), 7.11 (s, 1H), 7.01-6.99 (d, *J* = 7.7 Hz, 1H), 3.44 (br s, 4H), 2.36 (s, 3H), 2.31 (s, 3H), 1.28 (s, 3H), 1.15 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ (ppm) = 166.10, 143.22, 140.37, 137.52, 131.92, 127.69, 125.30, 42.95, 42.88, 21.69, 21.42, 14.33, 14.03; **HRMS (ESI+):** Calculated for $C_{13}H_{19}NOS$ [M+H]$^+$: 238.1266, Found [M+H]$^+$: 238.1268.



***S*-(4-methoxyphenyl) diethylcarbamothioate:** White solid; isolated using silica gel (100- 200 mesh) column chromatography in 4-5% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 7.42-7.40 (d, J = 8.8 Hz, 2H), 6.92-6.90 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H), 3.45-3.39 (q, J = 7.3 Hz, 4H), 1.25 (s, 3H), 1.15 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ (ppm) = 166.91, 160.92, 137.84, 119.94, 115.02, 55.80, 42.74, 14.31, 13.61; **HRMS (ESI+):** Calculated for $C_{12}H_{17}NO_2S$ [M+H]$^+$: 240.1058, Found [M+H]$^+$: 240.1060.



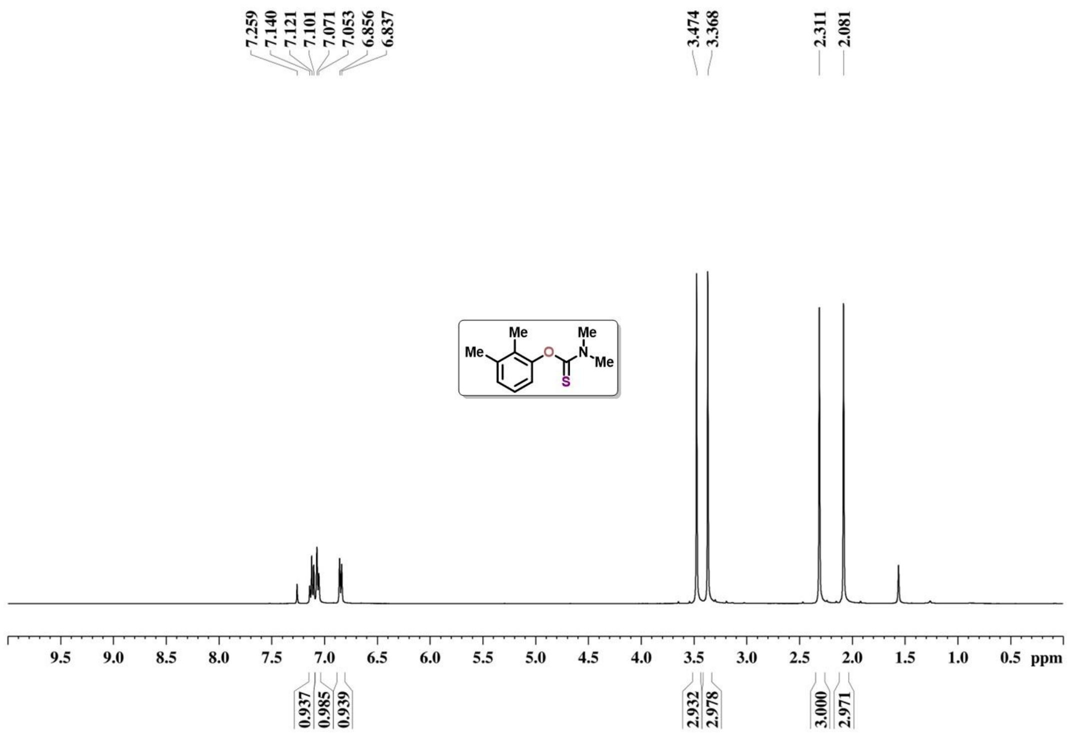
***S*-(naphthalen-2-yl) diethylcarbamothioate:** White solid; isolated using silica gel (100- 200 mesh) column chromatography in 4-6% EtOAc/Hexane eluent; **^{1}H NMR** (400 MHz, CDCl$_3$): δ (ppm) = 8.03 (s, 1H), 7.85-7.81 (m, 3H), 7.57-7.41 (m, 3H), 3.47 (br s, 4H), 1.32-1.28 (t, *J* = 6.9 Hz, 3H), 1.25-1.21 (m, 3H); **^{13}C NMR**

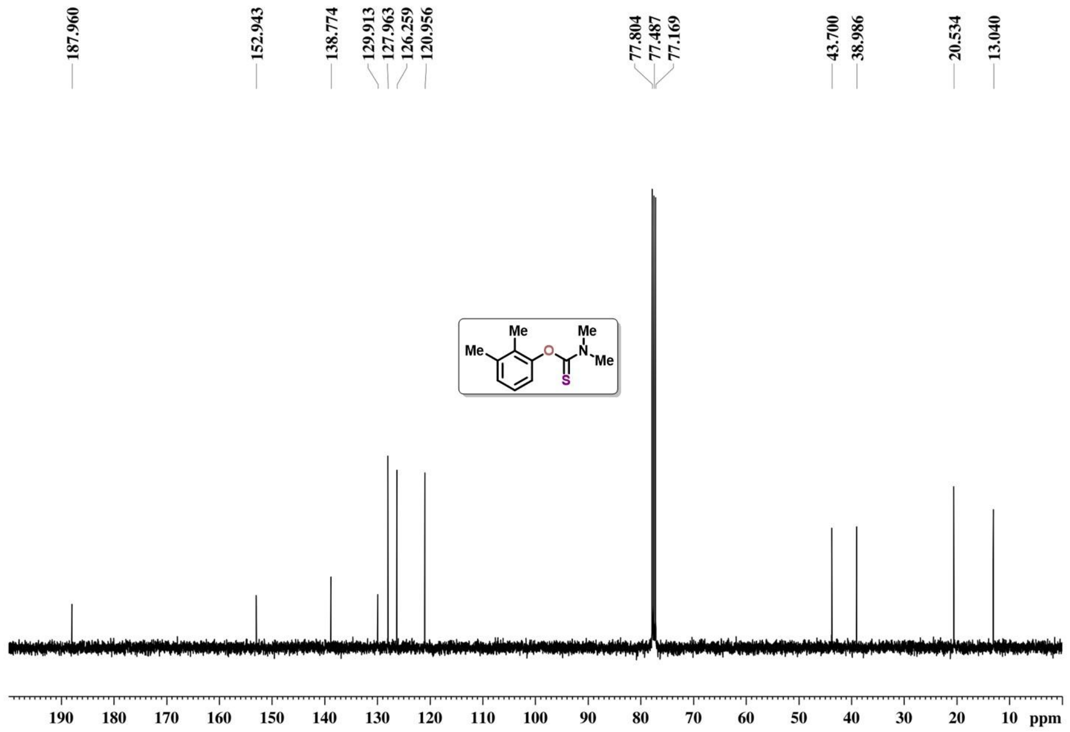


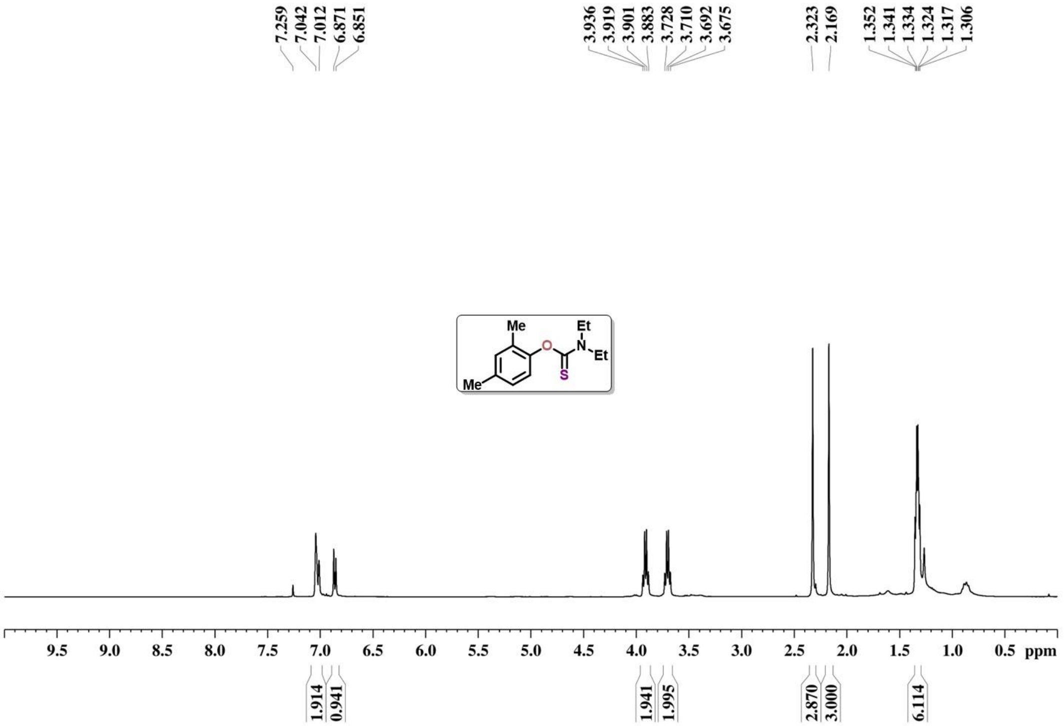
(100 MHz, $CDCl_3$): δ (ppm) = 166.29, 135.76, 133.99, 133.74, 132.87, 128.84, 128.44, 128.18, 127.33, 126.73, 126.69, 42.87, 14.32, 13.90; **DEPT-135** (100 MHz, $CDCl_3$): δ (ppm) = 135.77, 132.88, 128.85, 128.44, 128.18, 127.34, 126.74, 42.88, 14.34, 13.90; **HRMS (ESI+):** Calculated for $C_{15}H_{17}NOS$ $[M+H]^+$: 260.1109, Found $[M+H]^+$: 260.1112.

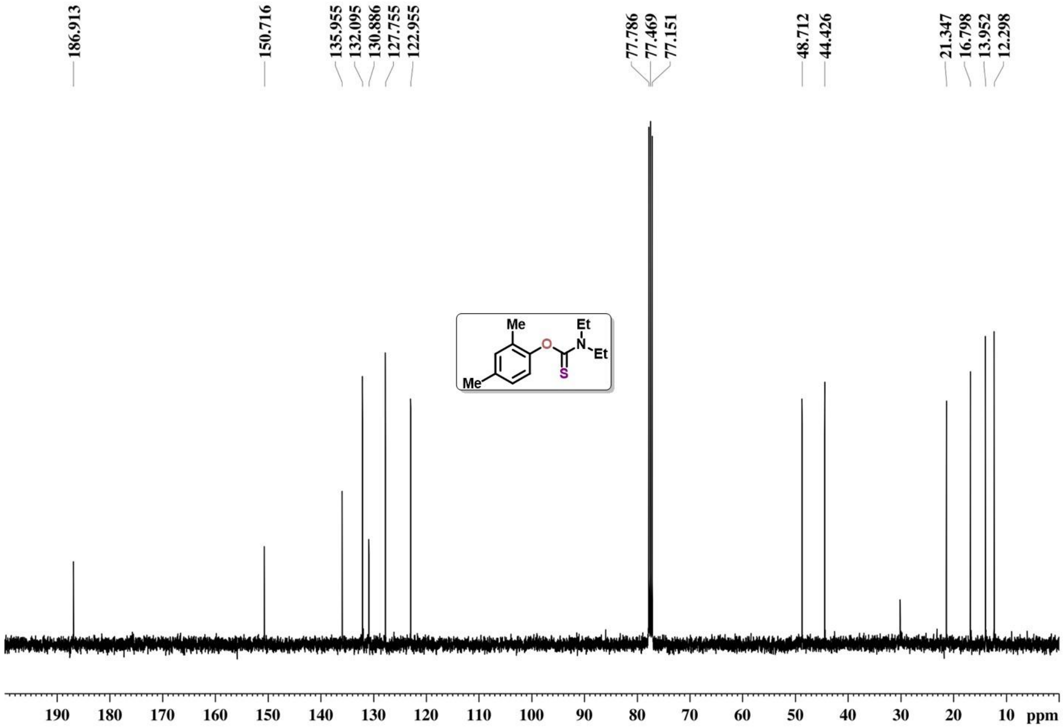
Additional peaks appear in the ^{13}C-NMR spectrum due to the rapid decomposition of the compound, possibly via oxidation.[25, 26]

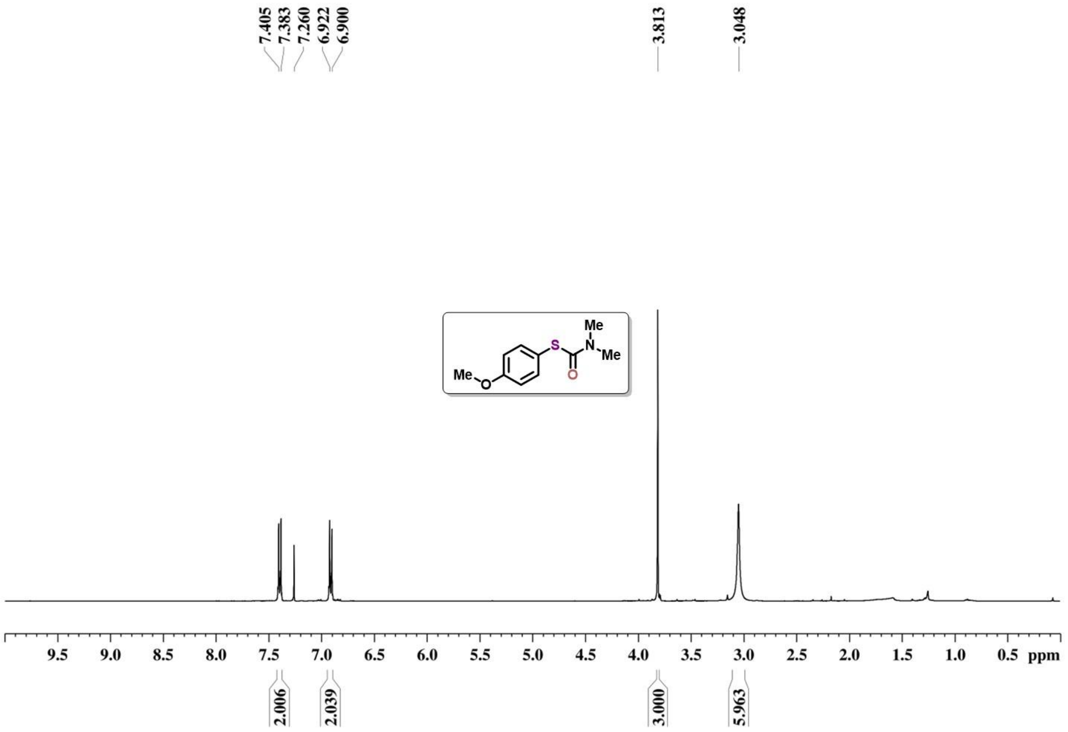
11. NMR Spectra:

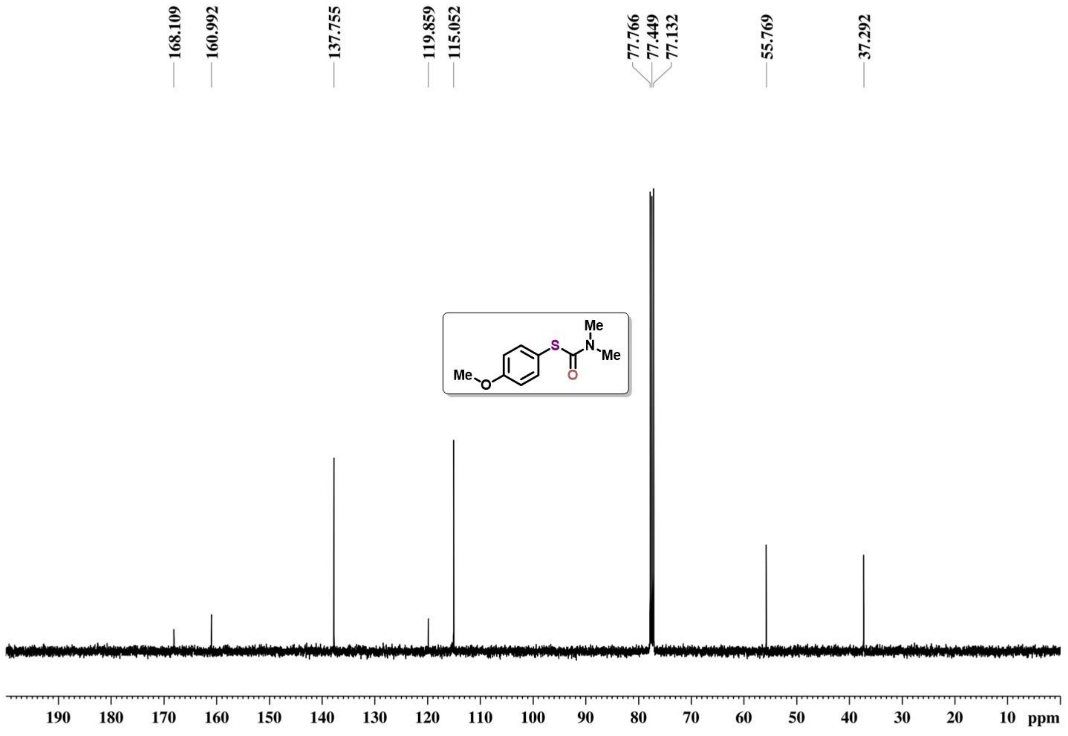

7.259
7.140
7.121
7.101
7.071
7.053
6.856
6.837
3.474
3.368
2.311
2.081
Me
Me
Me
N
Me
O
S
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.937
0.985
0.939
2.932
2.978
3.000
2.971

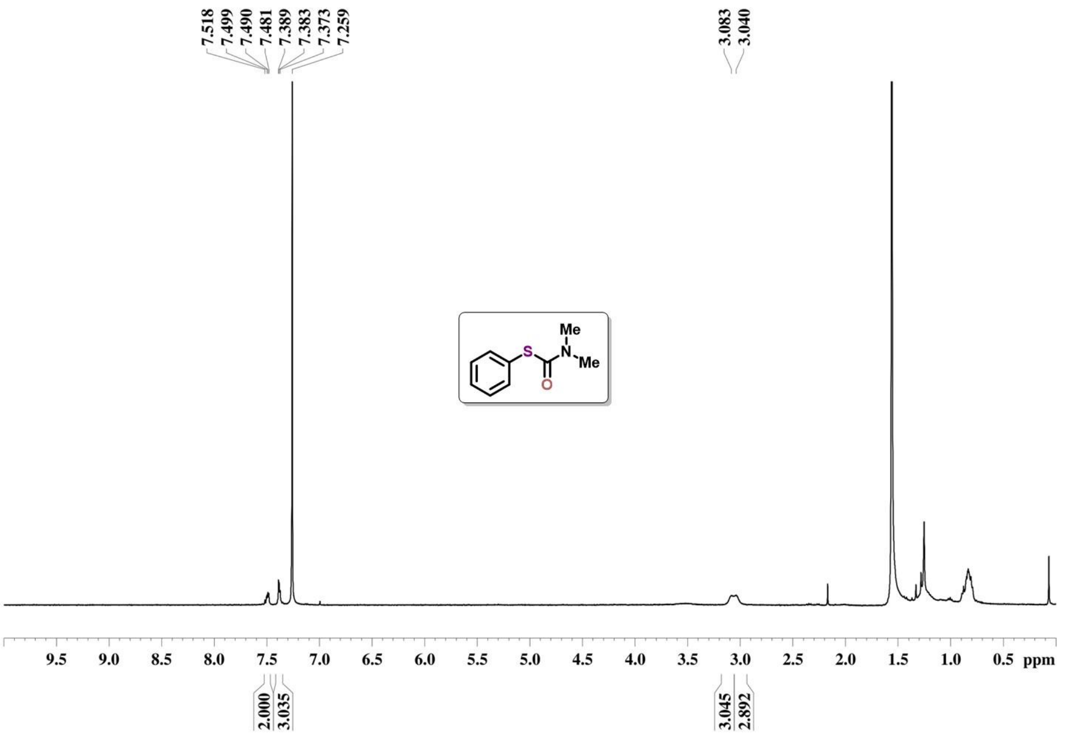

187.960
152.943
138.774
129.913
127.963
126.259
120.956
77.804
77.487
77.169
43.700
38.986
20.534
13.040
Me
Me
Me
N
Me
O
S
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

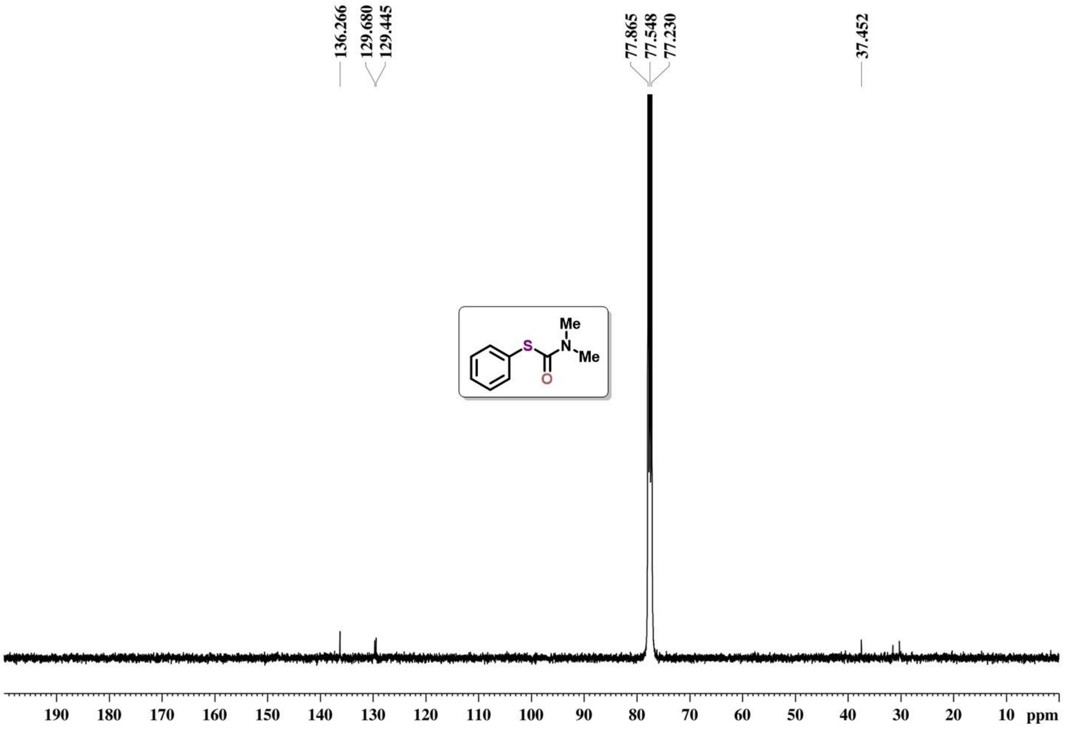

7.259
7.042
7.012
6.871
6.851
3.936
3.919
3.901
3.883
3.728
3.710
3.692
3.675
2.323
2.169
1.352
1.341
1.334
1.324
1.317
1.306
Me
Me
O
S
N
Et
Et
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.914
0.941
1.941
1.995
2.870
3.000
6.114

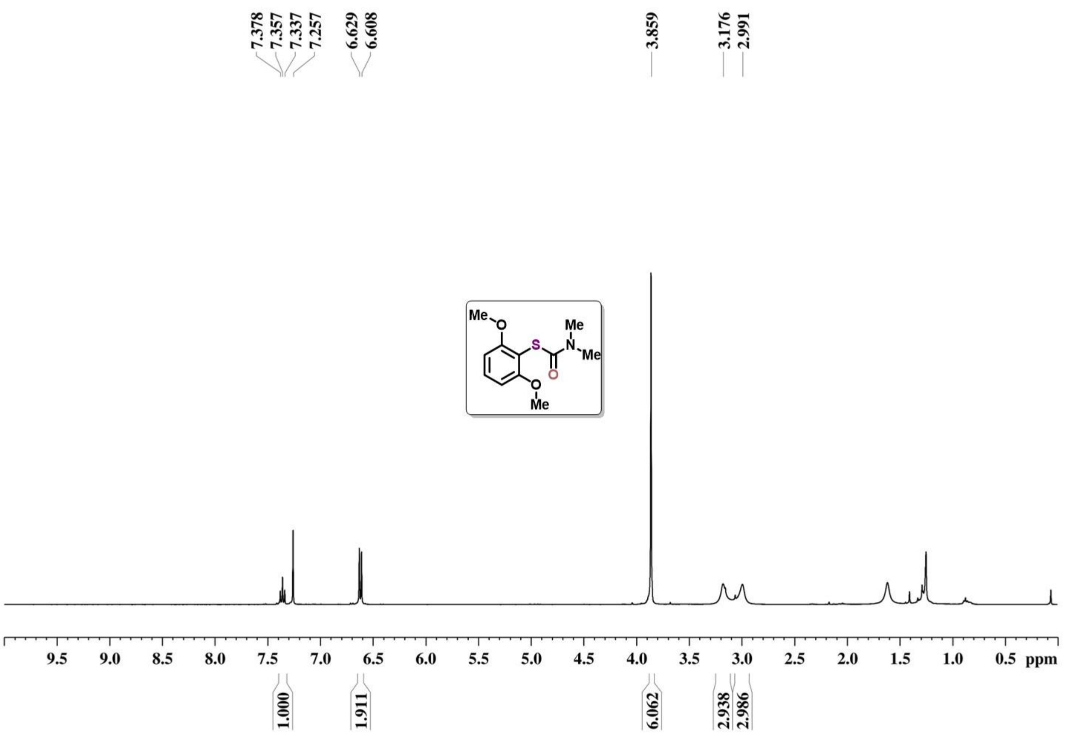

186.913
150.716
135.955
132.095
130.886
127.755
122.955
77.786
77.469
77.151
48.712
44.426
21.347
16.798
13.952
12.298
Me
Me
O
S
N
Et
Et
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

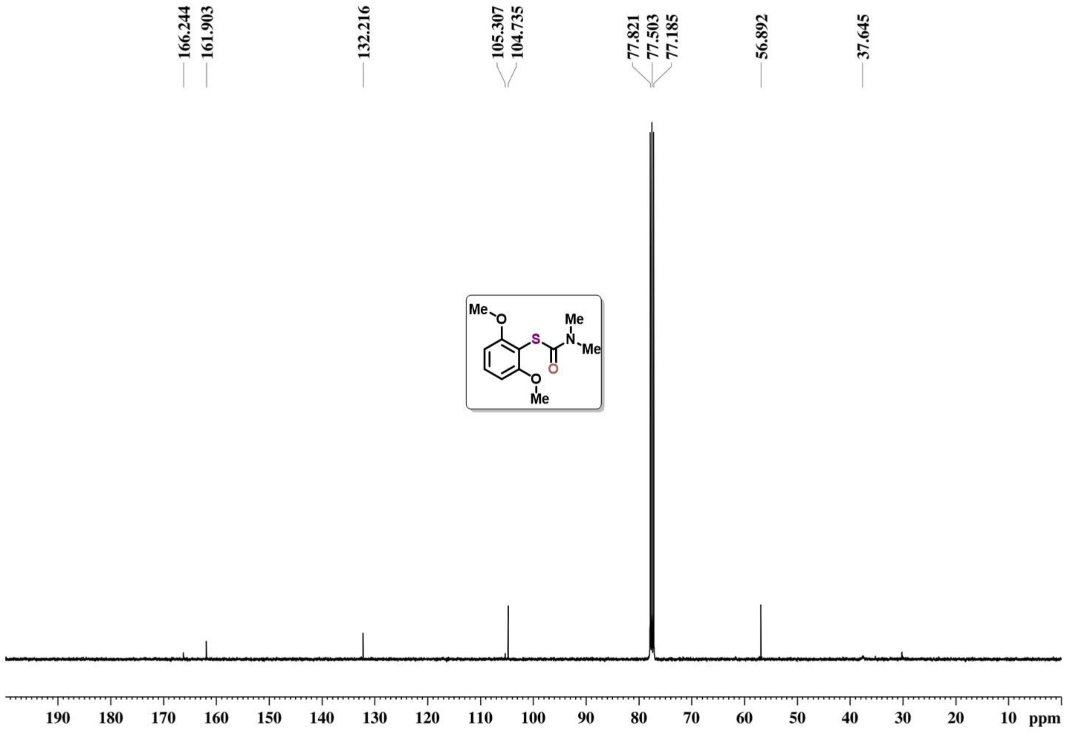

7.405
7.383
7.260
6.922
6.900
3.813
3.048
Me
S
N
Me
Me
O
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.006
2.039
3.000
5.963


168.109
160.992
137.755
119.859
115.052
77.766
77.449
77.132
55.769
37.292
Me
S
N
Me
Me
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.518
7.499
7.490
7.481
7.389
7.383
7.373
7.259
3.083
3.040
S
N
Me
Me
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
2.000
3.035
3.045
2.892


136.266
129.680
129.445
77.865
77.548
77.230
37.452
S
N
Me
Me
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


7.378
7.357
7.337
7.257
6.629
6.608
3.859
3.176
2.991
Me
O
S
N
Me
Me
O
O
Me
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.911
6.062
2.938
2.986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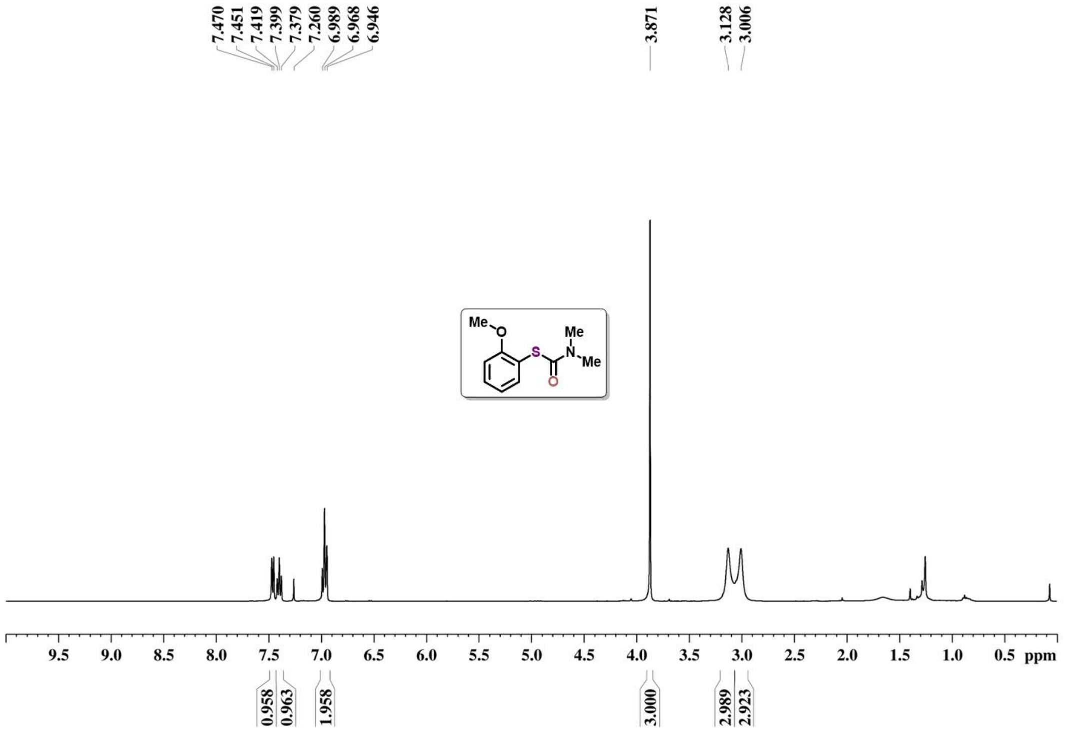
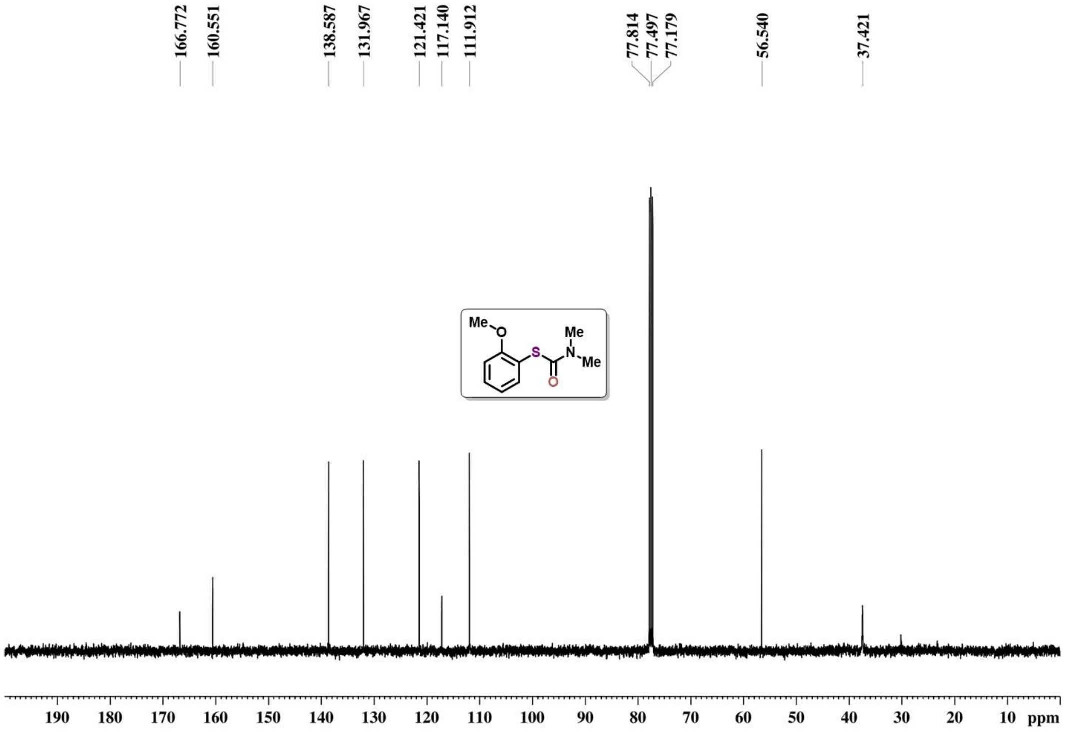
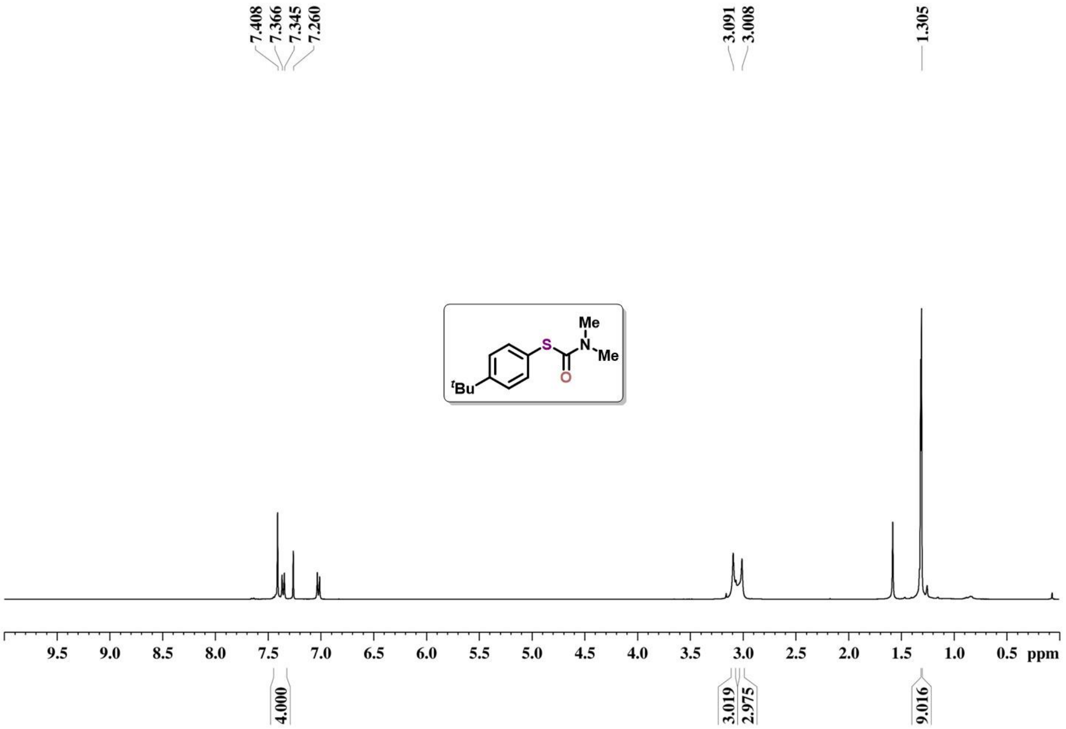
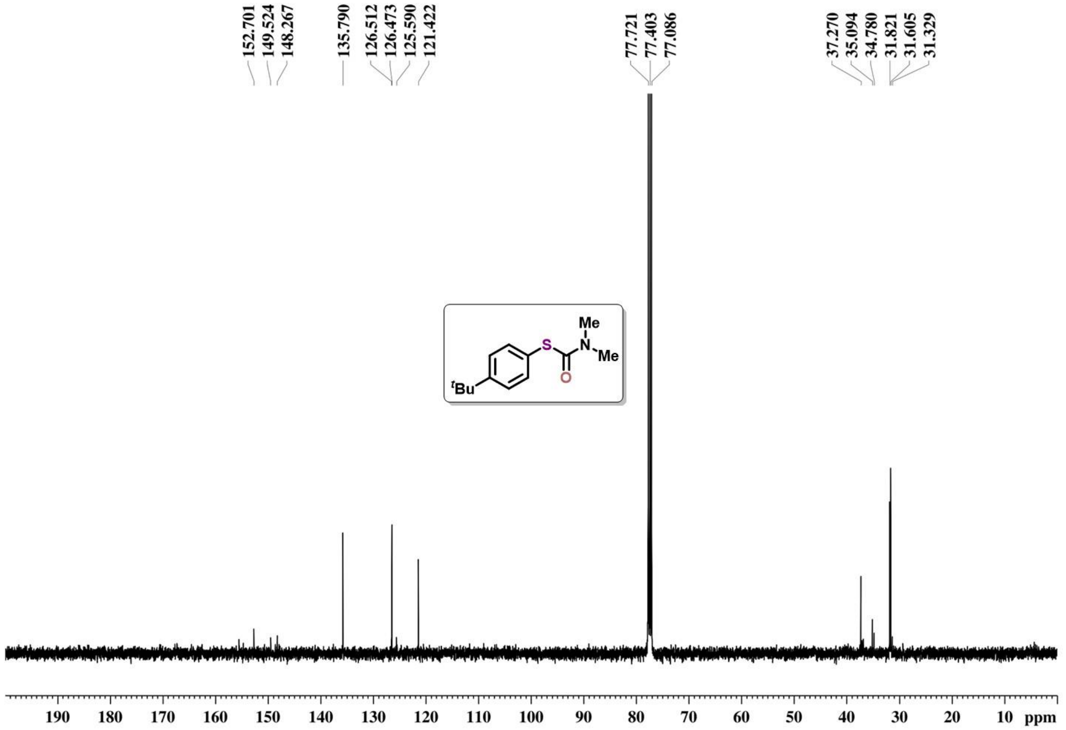
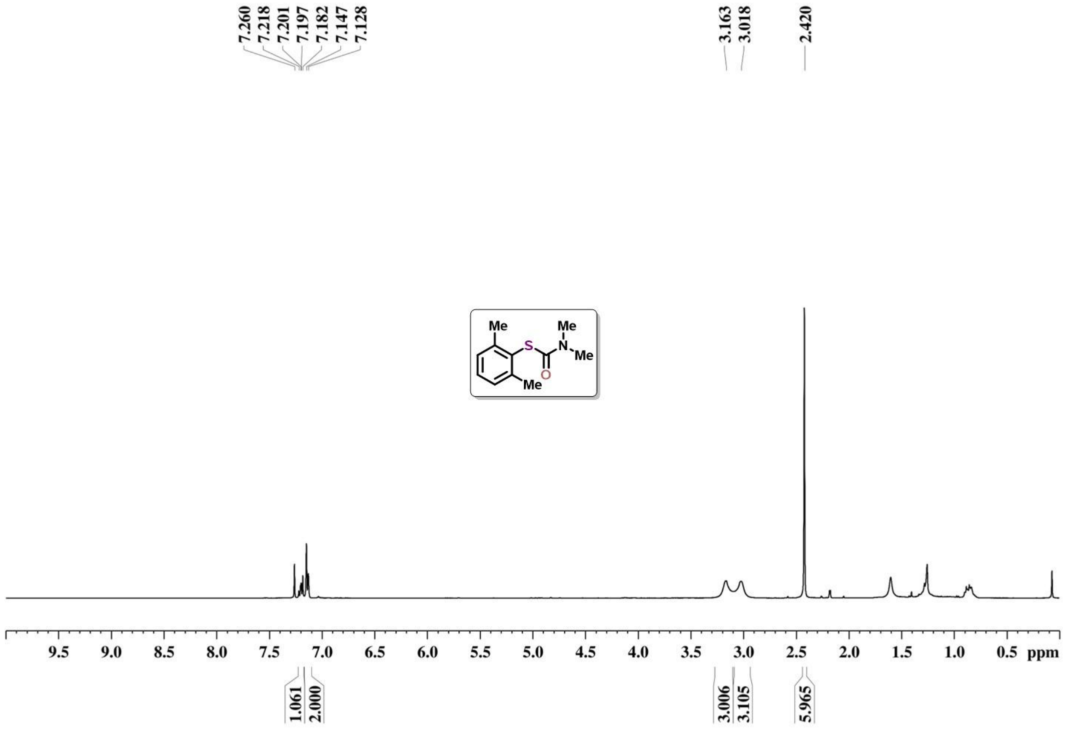
161.903
132.216
105.307
104.735
77.821
77.503
77.185
56.892
37.645
Me
O
S
N
Me
Me
O
O
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

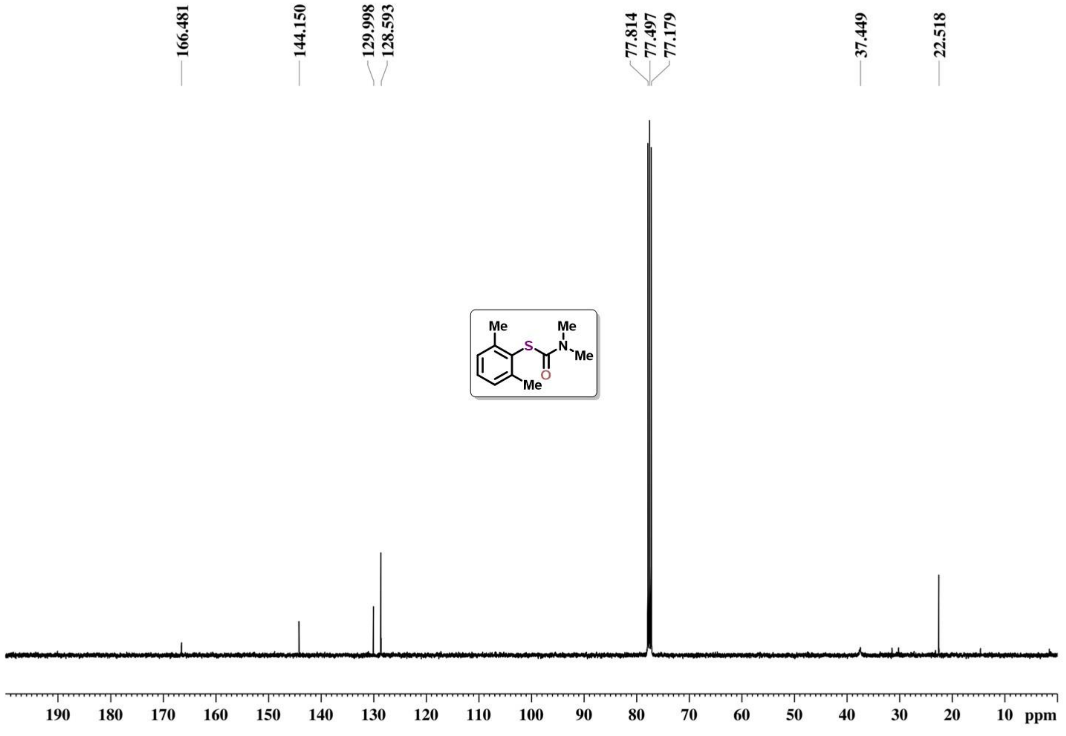

7.470
7.451
7.419
7.399
7.379
7.260
6.989
6.968
6.946
3.871
3.128
3.006
Me
O
Me
N
Me
S
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
0.958
0.963
1.958
3.000
2.989
2.923

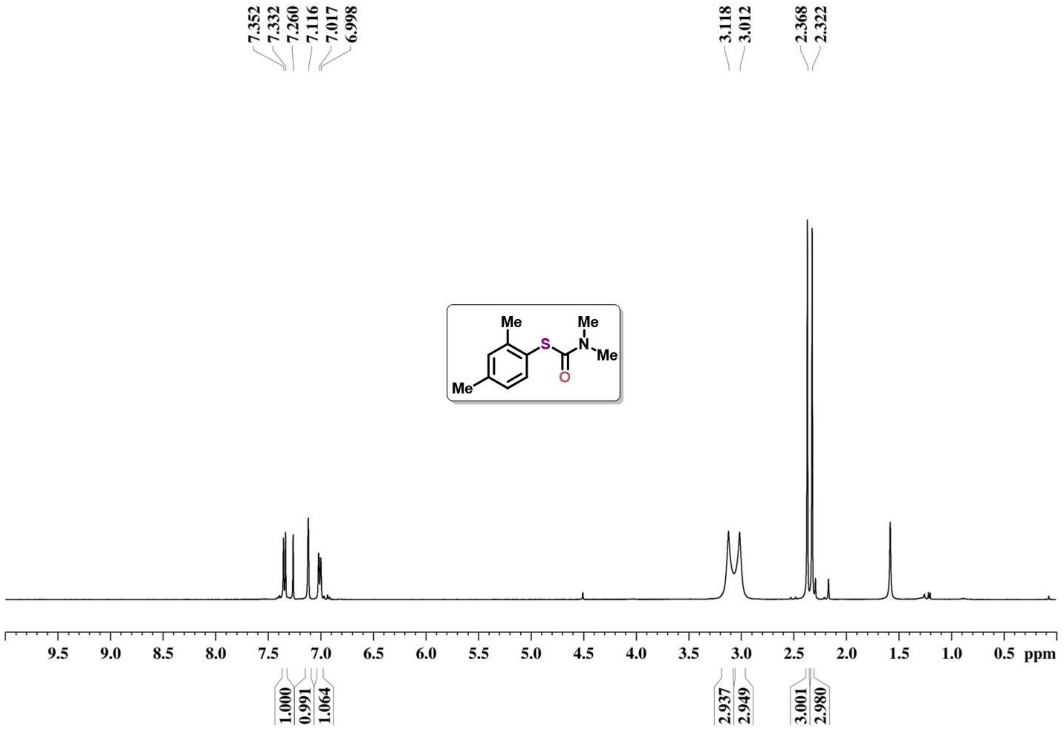

166.772
160.551
138.587
131.967
121.421
117.140
111.912
77.814
77.497
77.179
56.540
37.421
Me
O
Me
N
Me
S
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

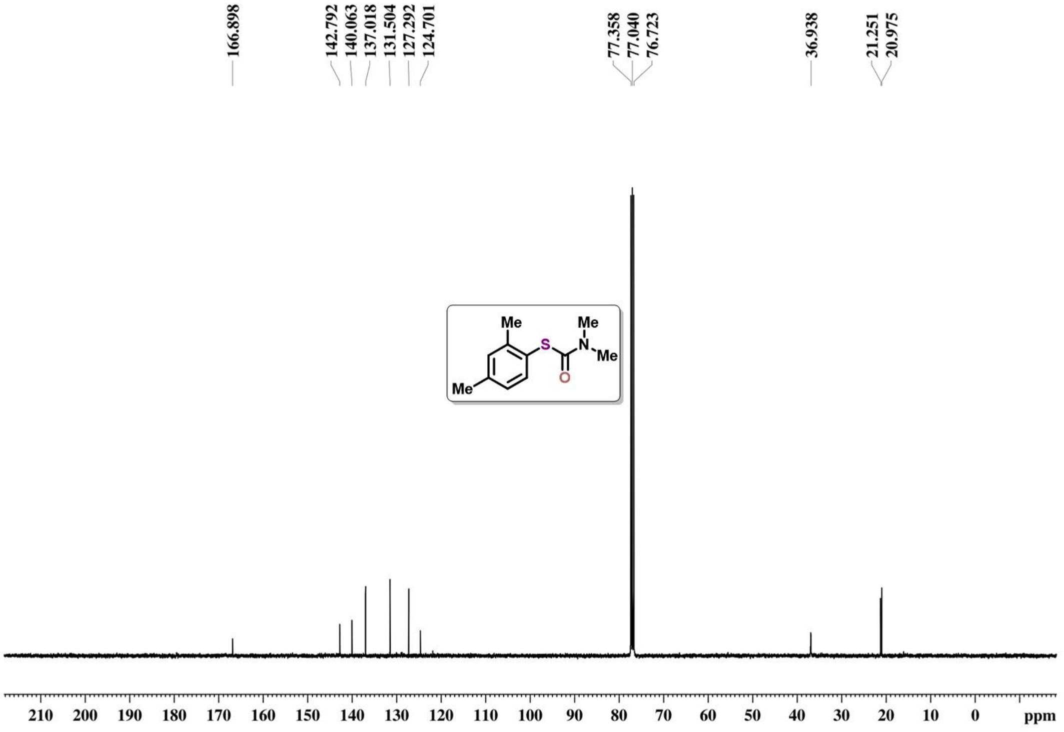

7.408
7.366
7.345
7.260
3.091
3.008
1.305
Me
N
Me
S
O
tBu
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
4.000
3.019
2.975
9.016

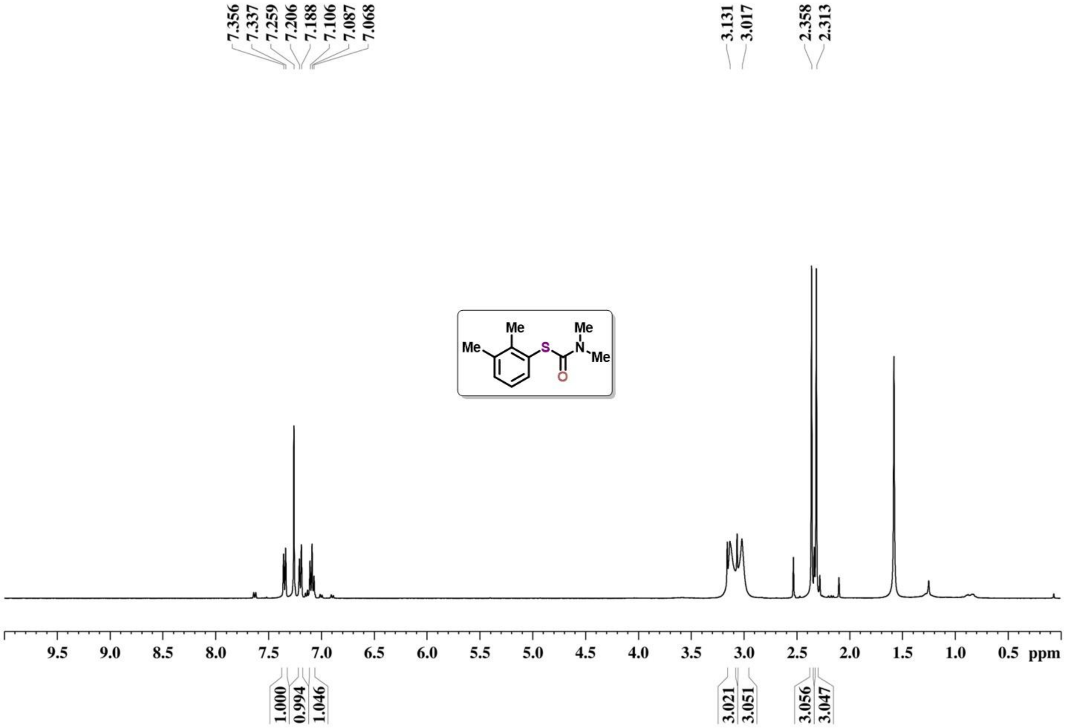

152.701
149.524
148.267
135.790
126.512
126.473
125.590
121.422
77.721
77.403
77.086
37.270
35.094
34.780
31.821
31.605
31.329
Me
N
Me
S
O
tBu
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

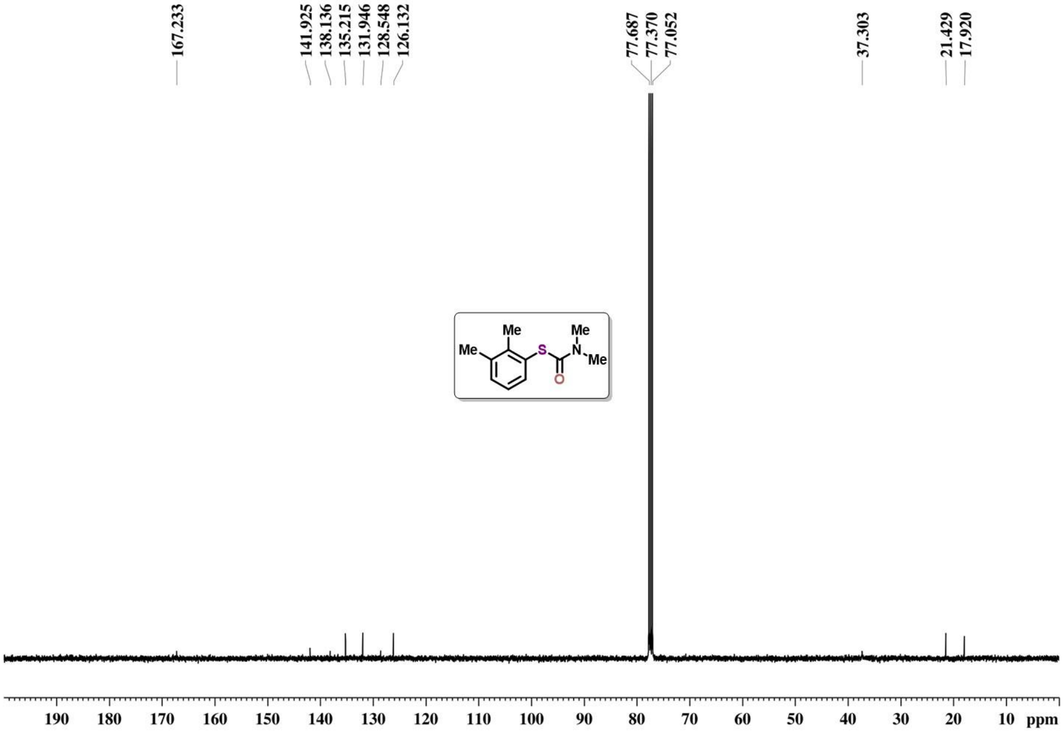

7.260
7.218
7.201
7.197
7.182
7.147
7.128
3.163
3.018
2.420
Me
Me
S
N
Me
O
Me
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.061
2.000
3.006
3.105
5.965

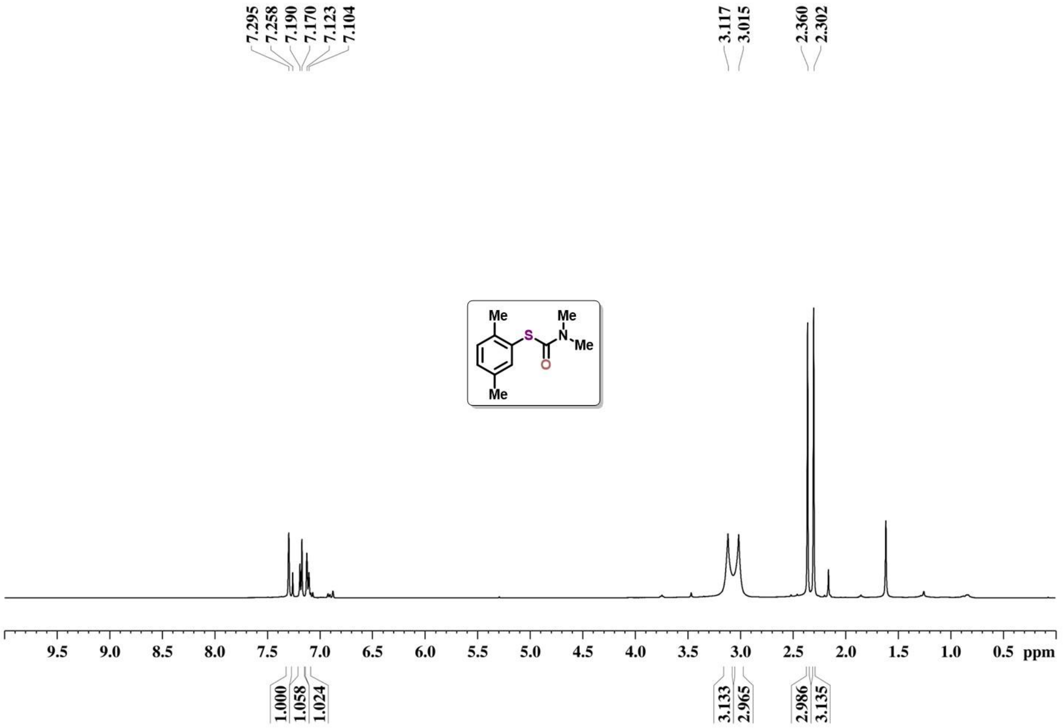

166.481
144.150
129.998
128.593
77.814
77.497
77.179
37.449
22.518
Me
Me
S
N
Me
O
Me
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

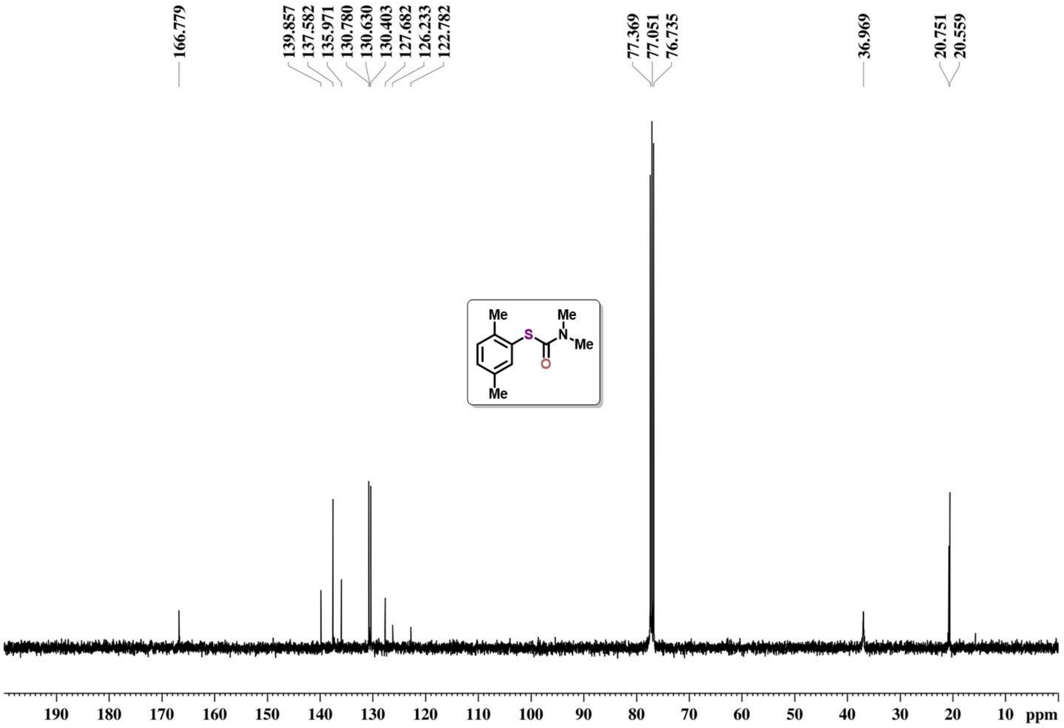

7.352
7.332
7.260
7.116
7.017
6.998
3.118
3.012
2.368
2.322
Me
S
Me
N
Me
O
Me
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
0.991
1.064
2.937
2.949
3.001
2.980

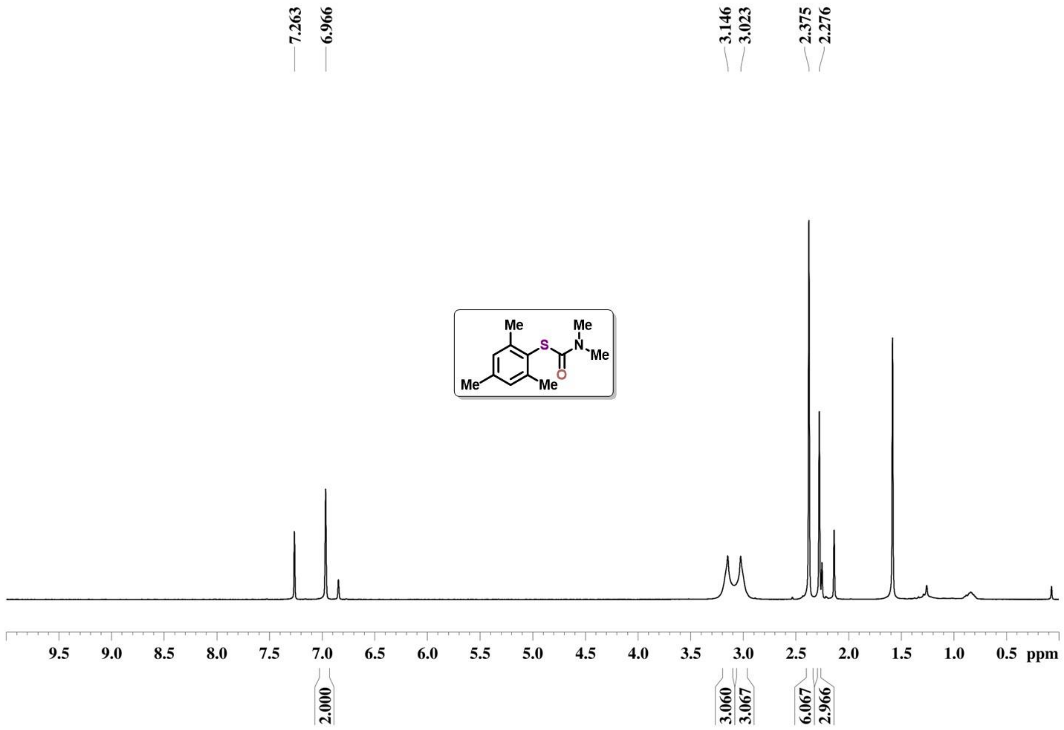

166.898
142.792
140.063
137.018
131.504
127.292
124.701
77.358
77.040
76.723
36.938
21.251
20.975
Me
S
Me
N
Me
O
Me
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

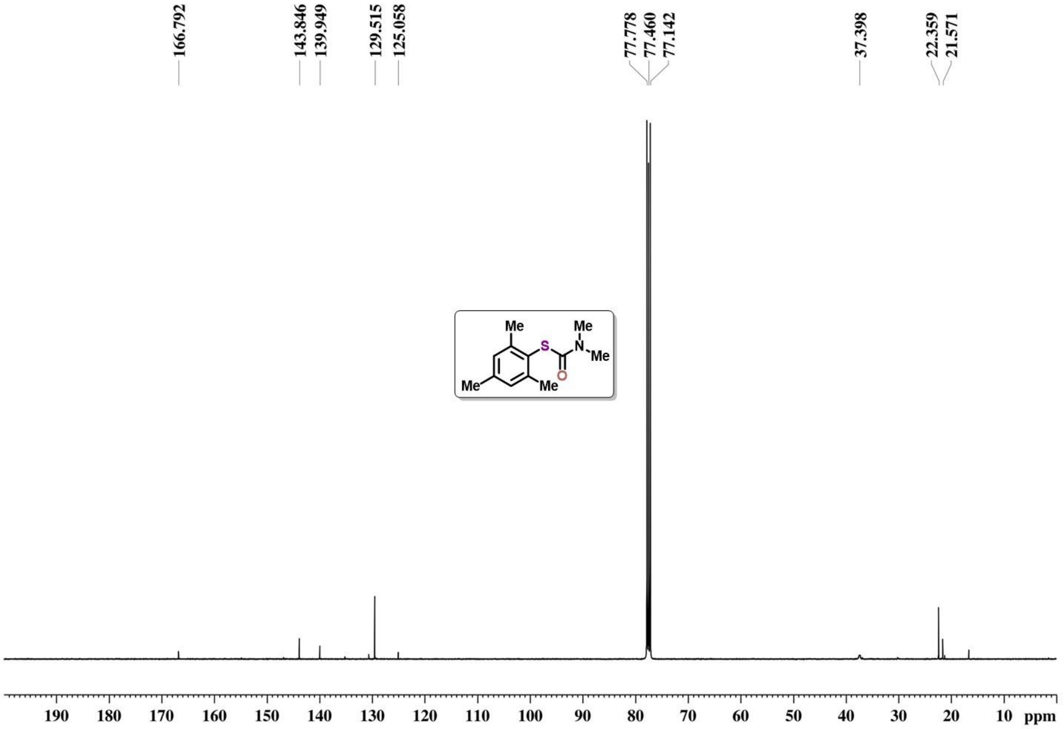

7.356
7.337
7.259
7.206
7.188
7.106
7.087
7.068
3.131
3.017
2.358
2.313
Me
Me
S
N
Me
Me
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
0.994
1.046
3.021
3.051
3.056
3.047

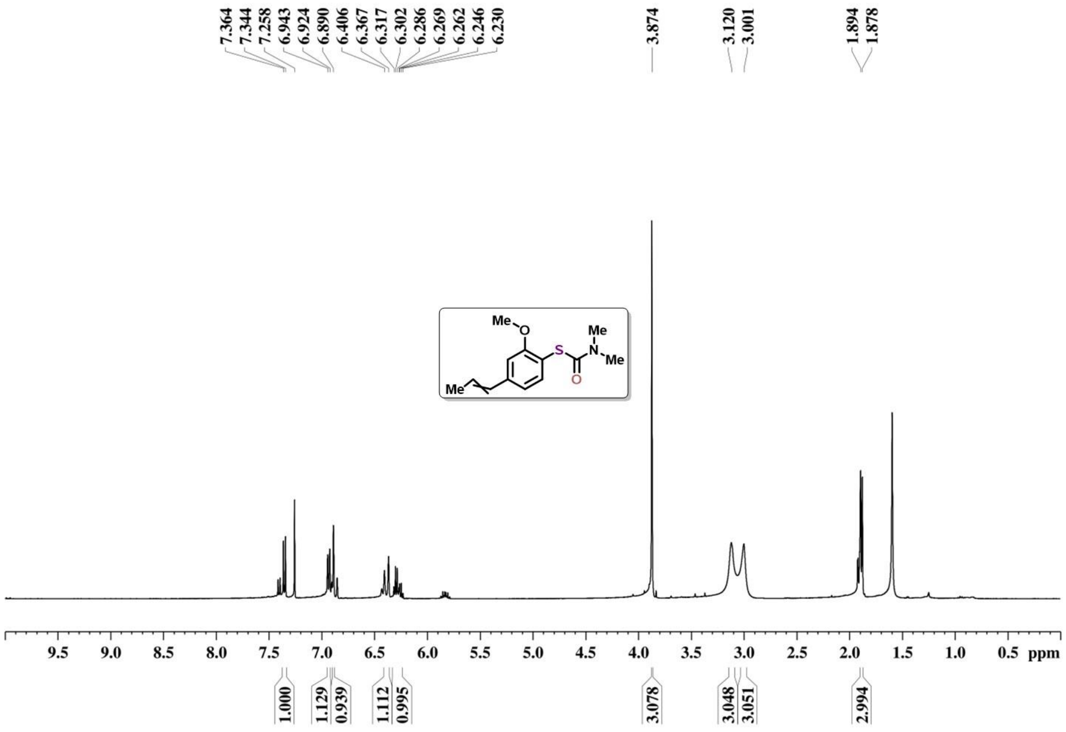

167.233
141.925
138.136
135.215
131.946
128.548
126.132
77.687
77.370
77.052
37.303
21.429
17.920
Me
Me
S
N
Me
Me
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

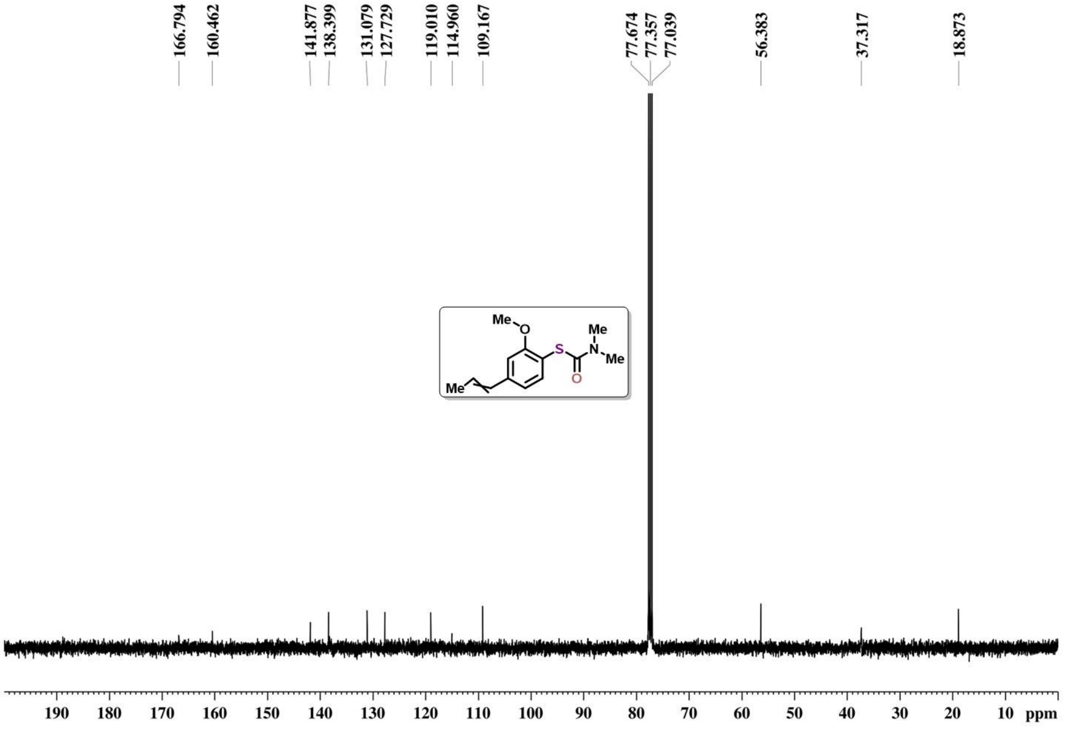

7.295
7.258
7.190
7.170
7.123
7.104
3.117
3.015
2.360
2.302
Me
S
Me
N
Me
O
Me
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
1.000
1.058
1.024
3.133
2.965
2.986
3.135


166.779
139.857
137.582
135.971
130.780
130.630
130.403
127.682
126.233
122.782
77.369
77.051
76.735
36.969
20.751
20.559
Me
S
Me
N
Me
O
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


7.263
6.966
3.146
3.023
2.375
2.276
Me
S
Me
N
Me
O
Me
Me
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
2.000
3.060
3.067
6.067
2.966


166.792
143.846
139.949
129.515
125.058
77.778
77.460
77.142
37.398
22.359
21.571
Me
S
Me
N
Me
O
Me
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


7.364
7.344
7.258
6.943
6.924
6.890
6.406
6.367
6.317
6.302
6.286
6.269
6.262
6.246
6.230
3.874
3.120
3.001
1.894
1.878
Me
O
S
N
Me
Me
O
Me
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.129
0.939
1.112
0.995
3.078
3.048
3.051
2.994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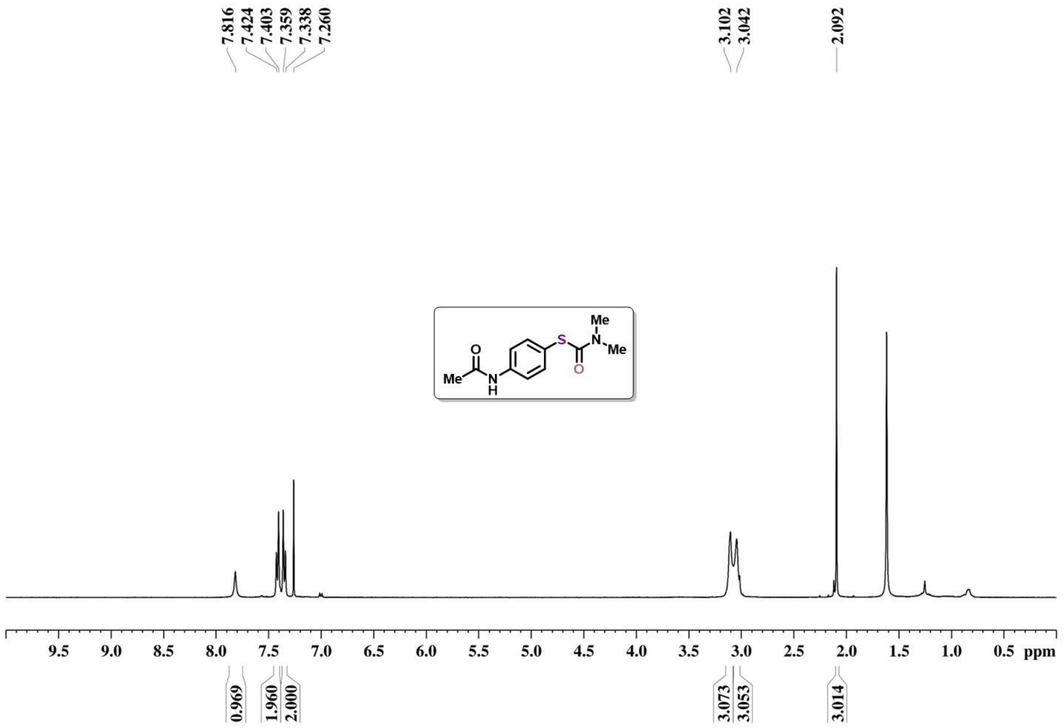
138.399
131.079
127.729
119.010
114.960
109.167
77.674
77.357
77.039
56.383
37.317
18.873
Me
O
S
N
Me
Me
O
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.816
7.424
7.403
7.359
7.338
7.260
3.102
3.042
2.092
Me
S
N
Me
O
Me
N
H
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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1.960
2.000
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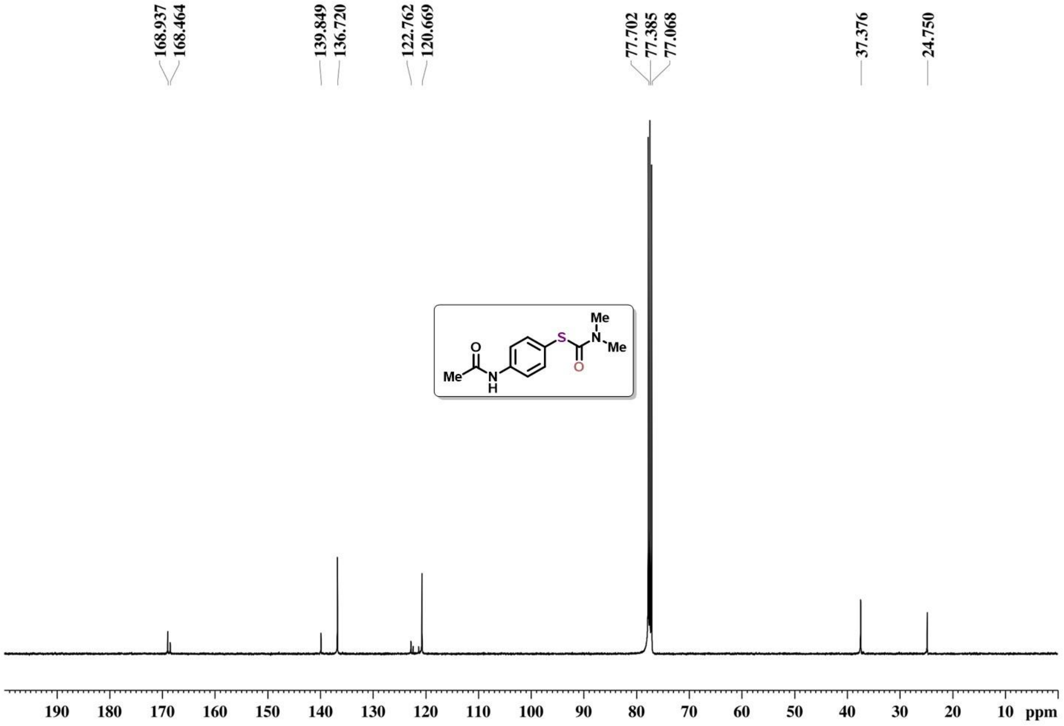
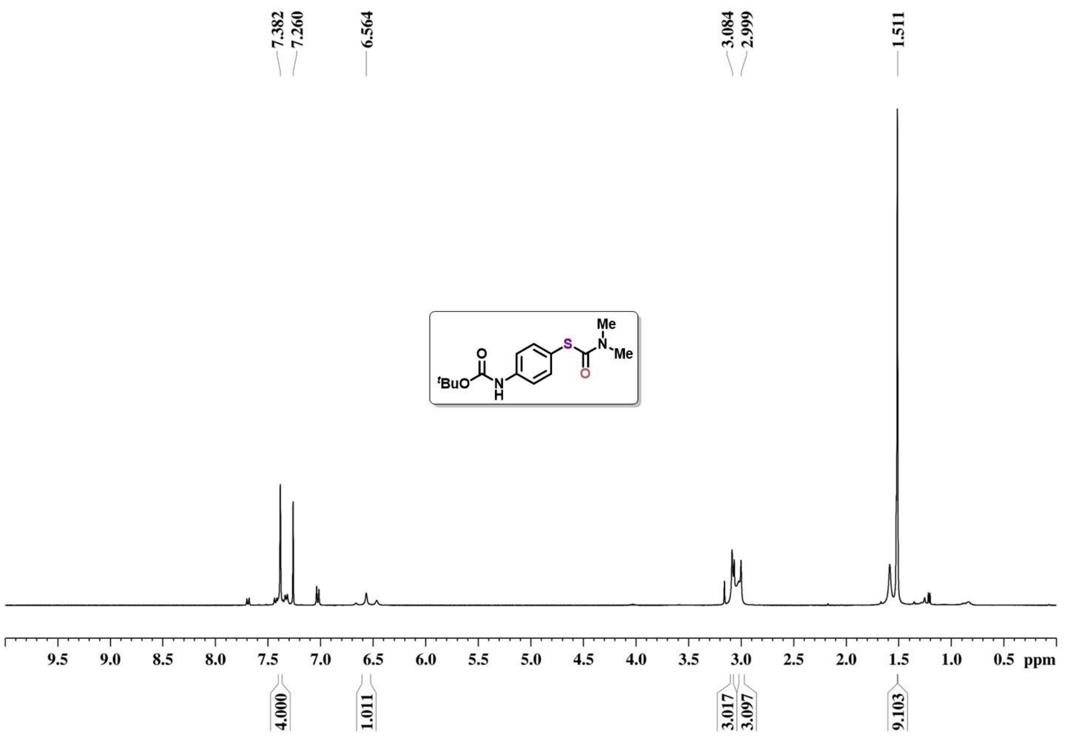
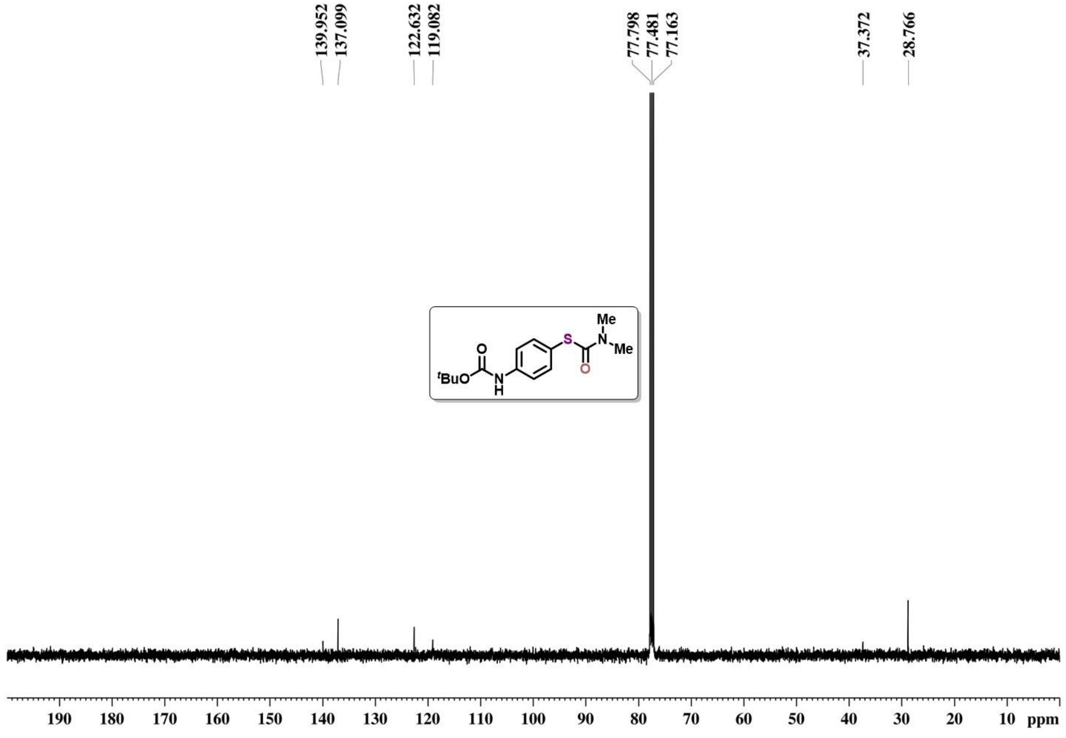
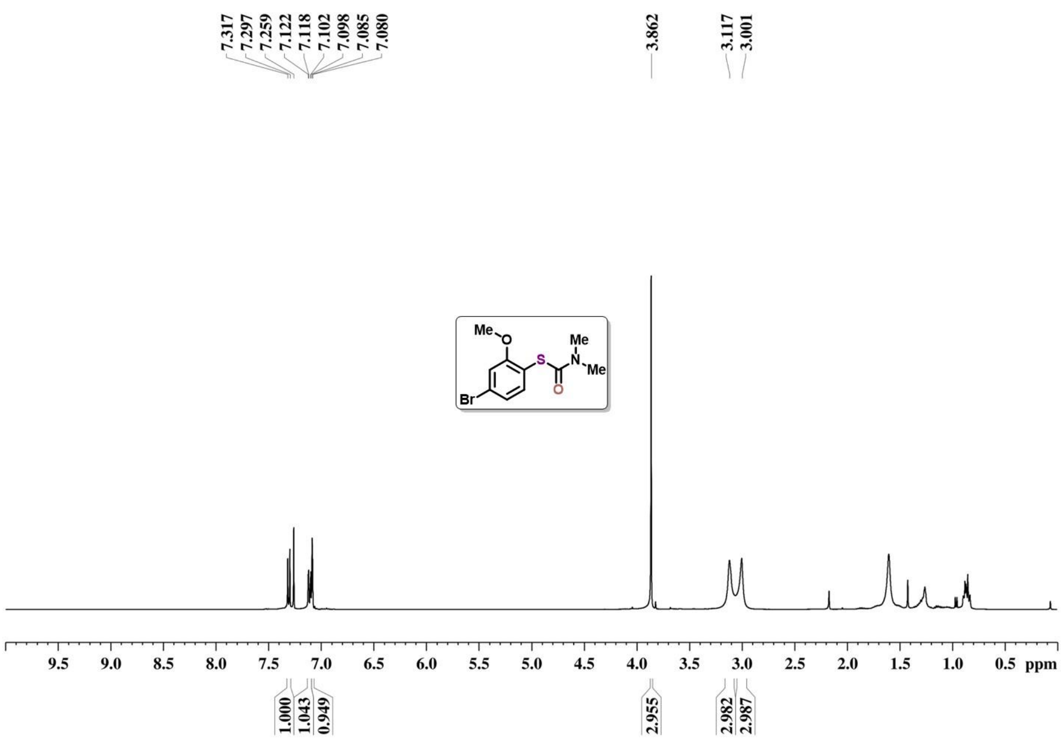
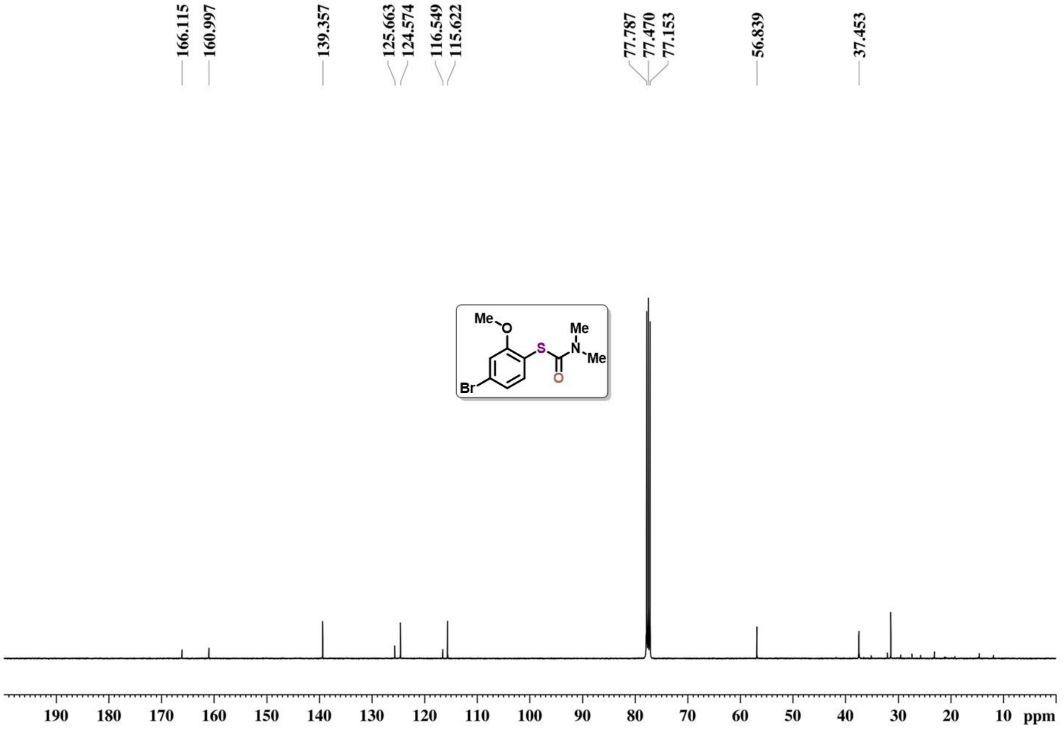
3.053
3.014

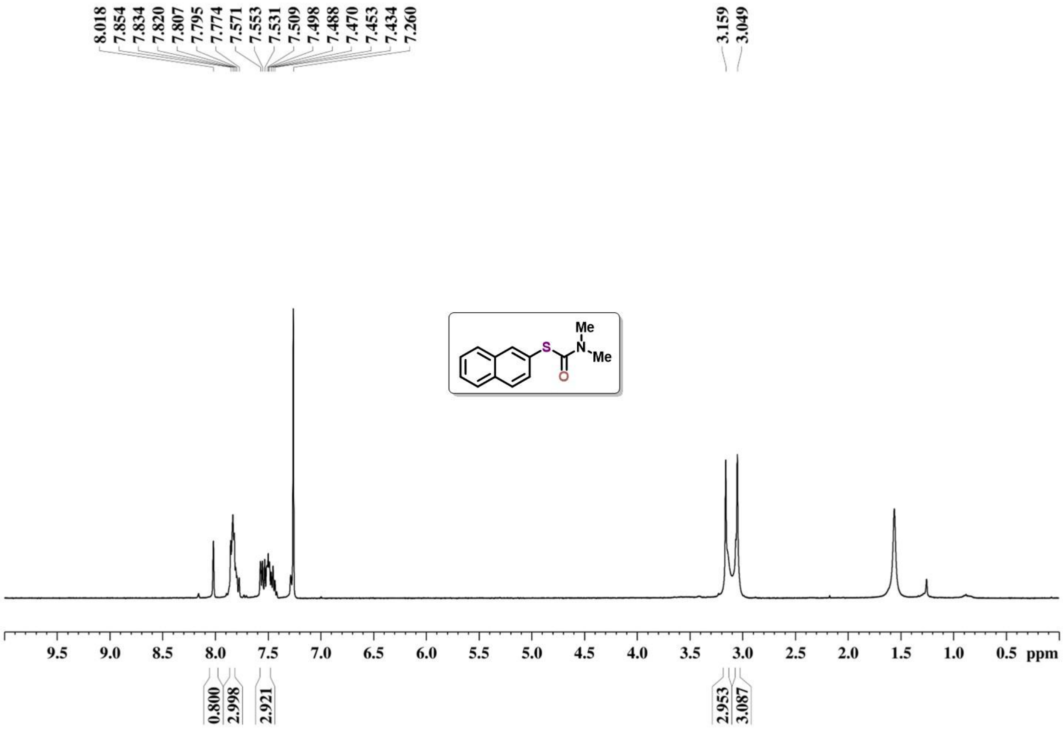

168.937
168.464
139.849
136.720
122.762
120.669
77.702
77.385
77.068
37.376
24.750
Me
S
N
Me
O
Me
N
H
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.382
7.260
6.564
3.084
2.999
1.511
Me
S
N
Me
O
O
ᵗBuO
N
H
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
4.000
1.011
3.017
3.097
9.103


139.952
137.099
122.632
119.082
77.798
77.481
77.163
37.372
28.766
Me
S
N
Me
O
O
ᵗBuO
N
H
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


7.317
7.297
7.259
7.122
7.118
7.102
7.098
7.085
7.080
3.862
3.117
3.001
Me
O
S
Me
N
Me
O
Br
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
1.000
1.043
0.949
2.955
2.982
2.987


166.115
160.997
139.357
125.663
124.574
116.549
115.622
77.787
77.470
77.153
56.839
37.453
Me
O
S
Me
N
Me
O
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


8.018
7.854
7.834
7.820
7.807
7.795
7.774
7.571
7.553
7.531
7.509
7.498
7.488
7.470
7.453
7.434
7.260
3.159
3.049
Me
S
N
Me
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
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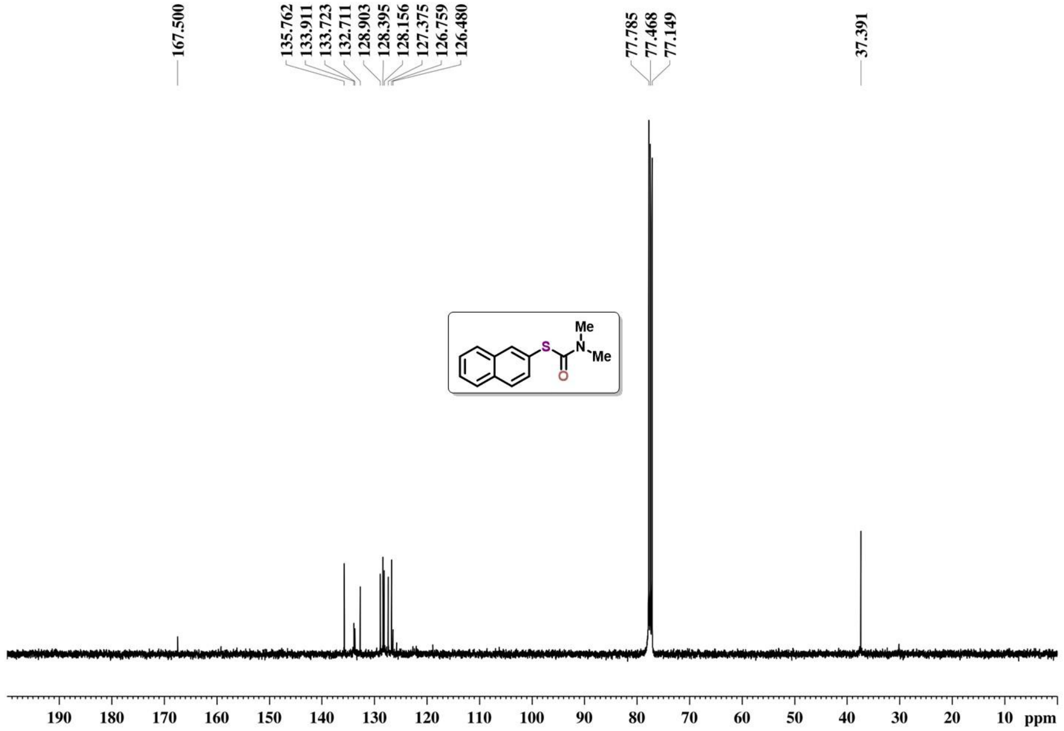
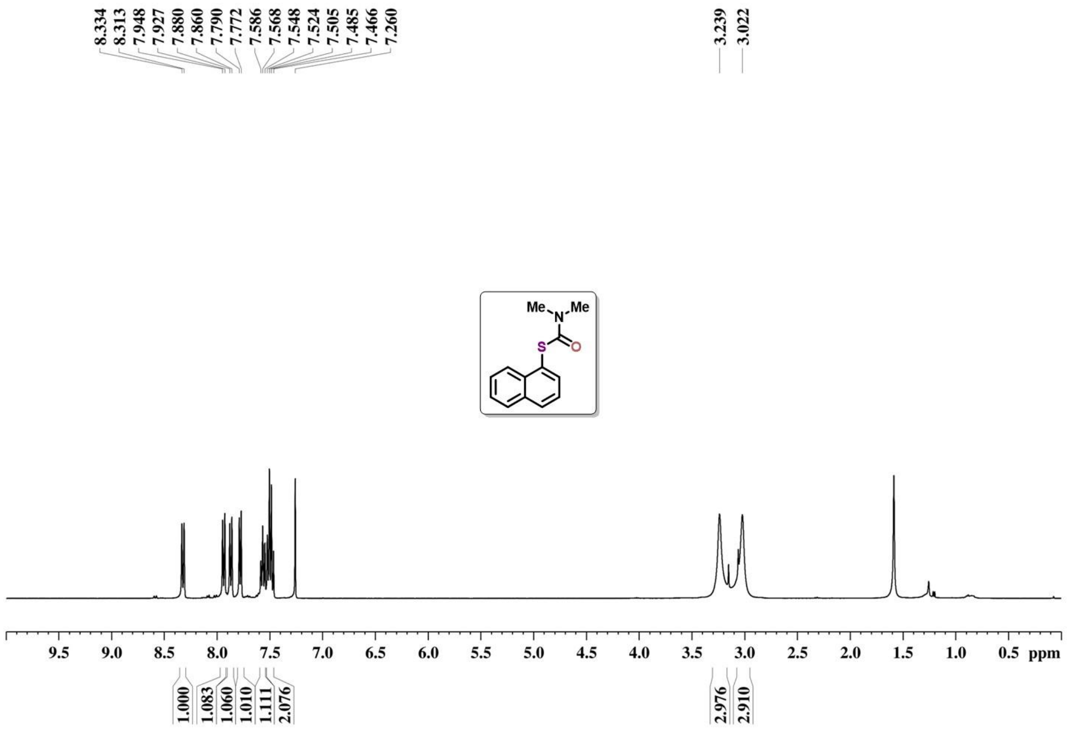
2.998
2.921
2.953
3.087


167.500
135.762
133.911
133.723
132.711
128.903
128.395
128.156
127.375
126.759
126.480
77.785
77.468
77.149
37.391
Me
S
N
Me
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


8.334
8.313
7.948
7.927
7.880
7.860
7.790
7.772
7.586
7.568
7.548
7.524
7.505
7.485
7.466
7.260
3.239
3.022
Me
N
Me
S
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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ppm
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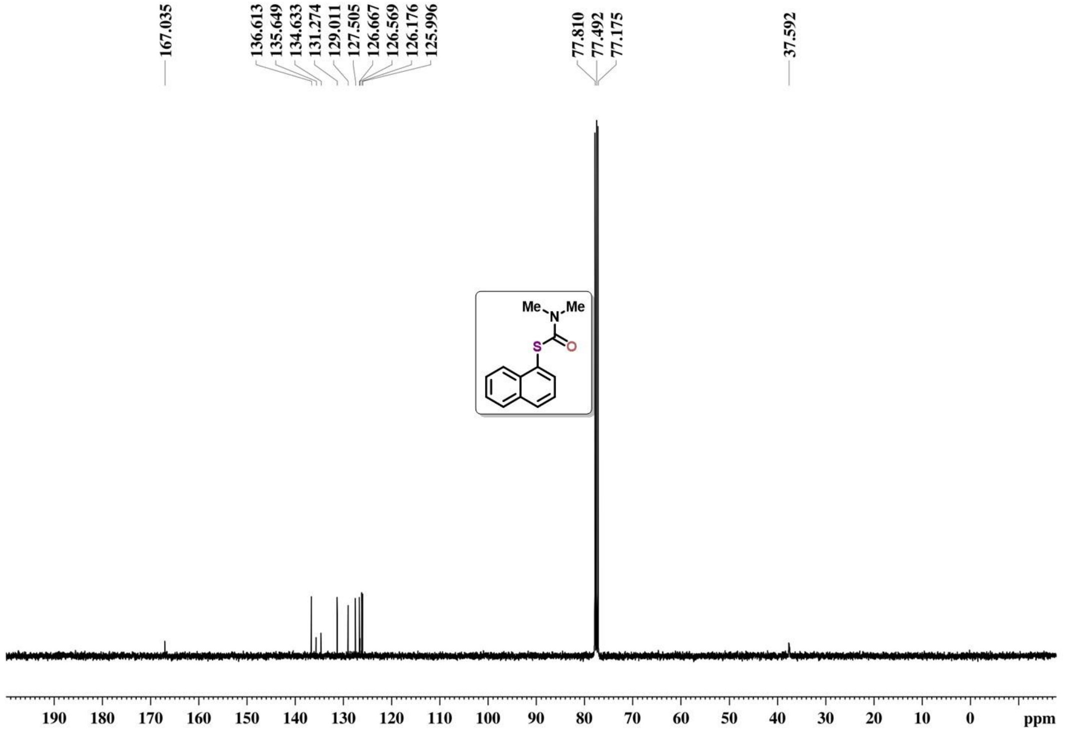
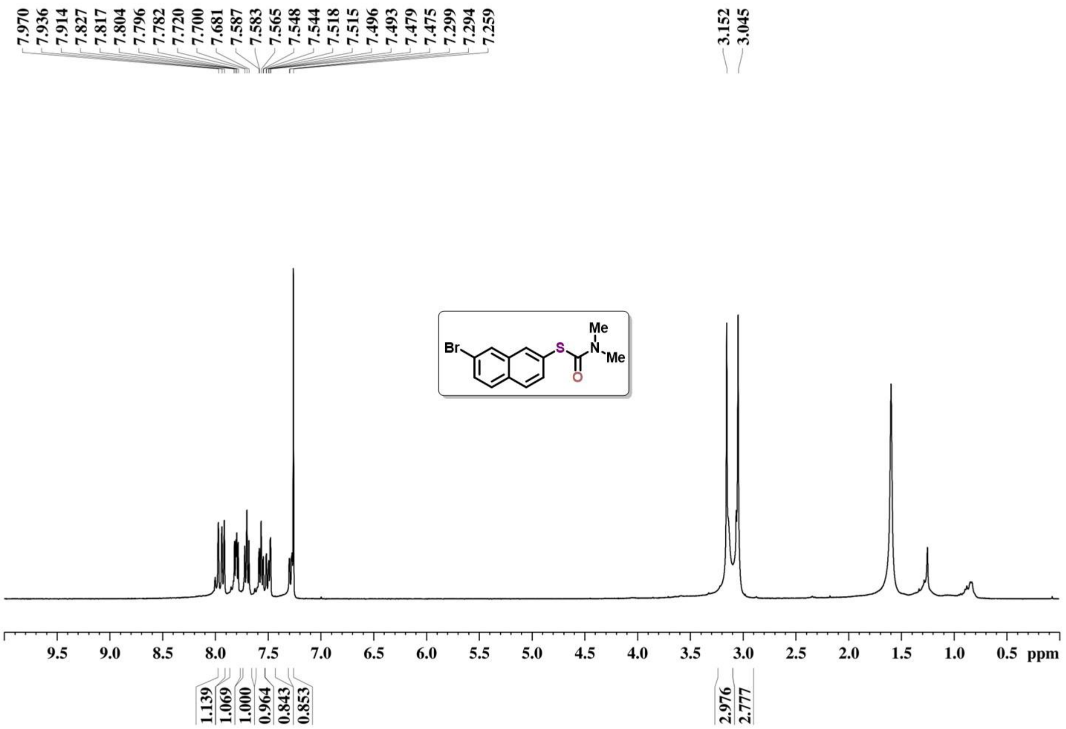
1.083
1.060
1.010
1.111
2.076
2.976
2.910


167.035
136.613
135.649
134.633
131.274
129.011
127.505
126.667
126.569
126.176
125.996
77.810
77.492
77.175
37.592
Me
N
Me
S
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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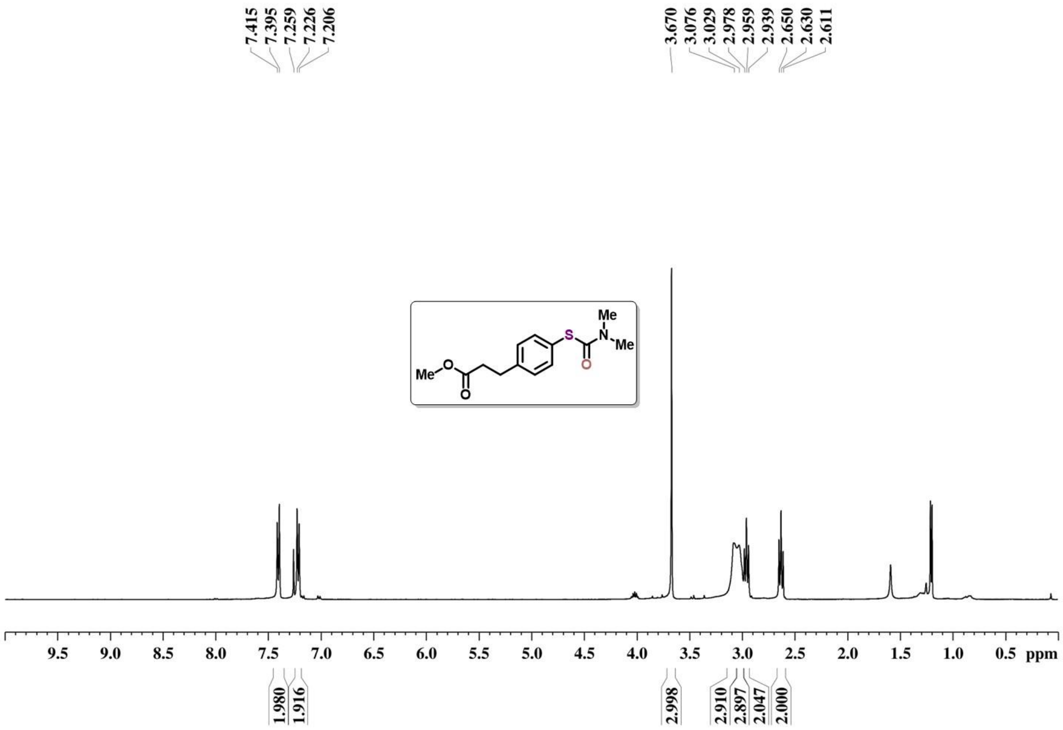
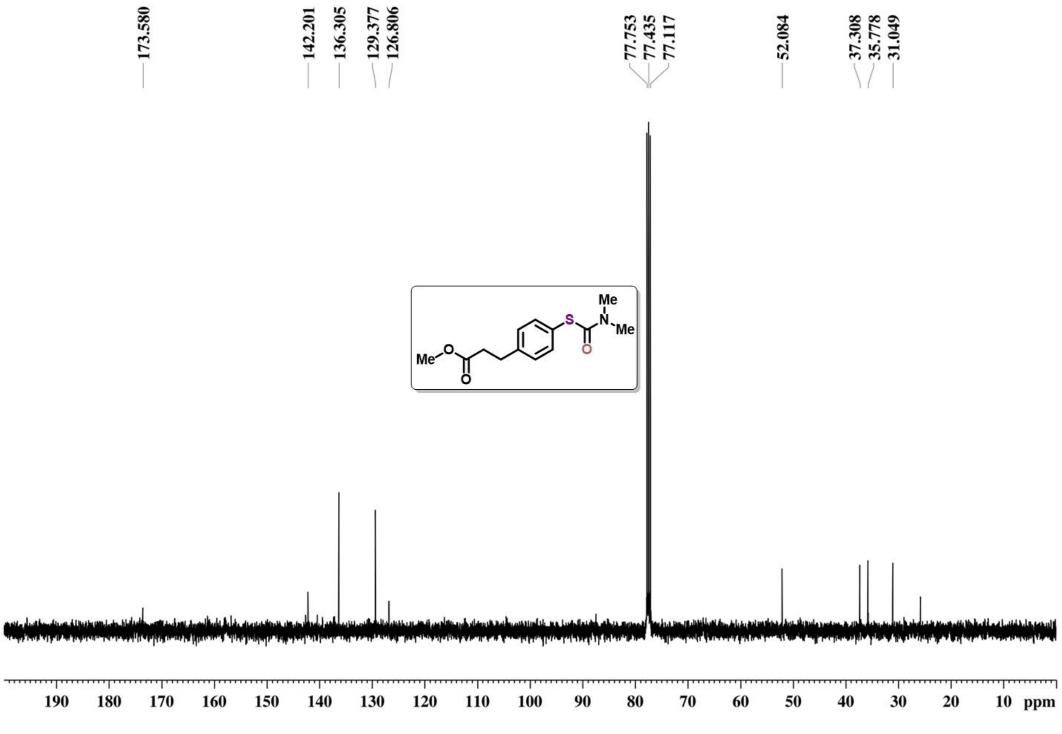
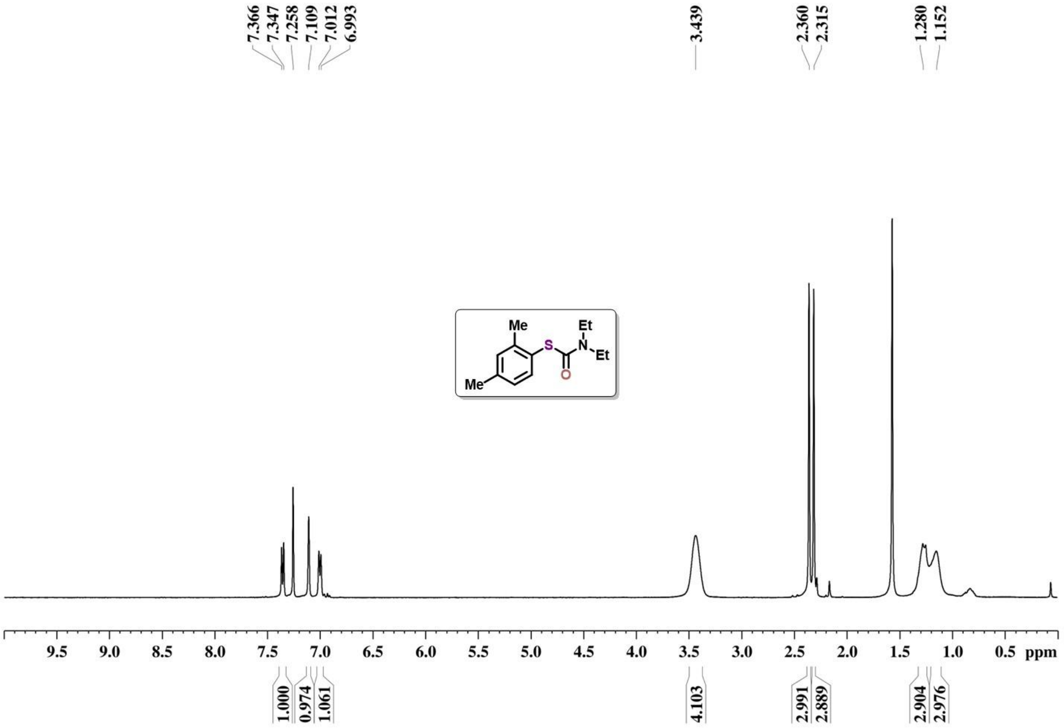
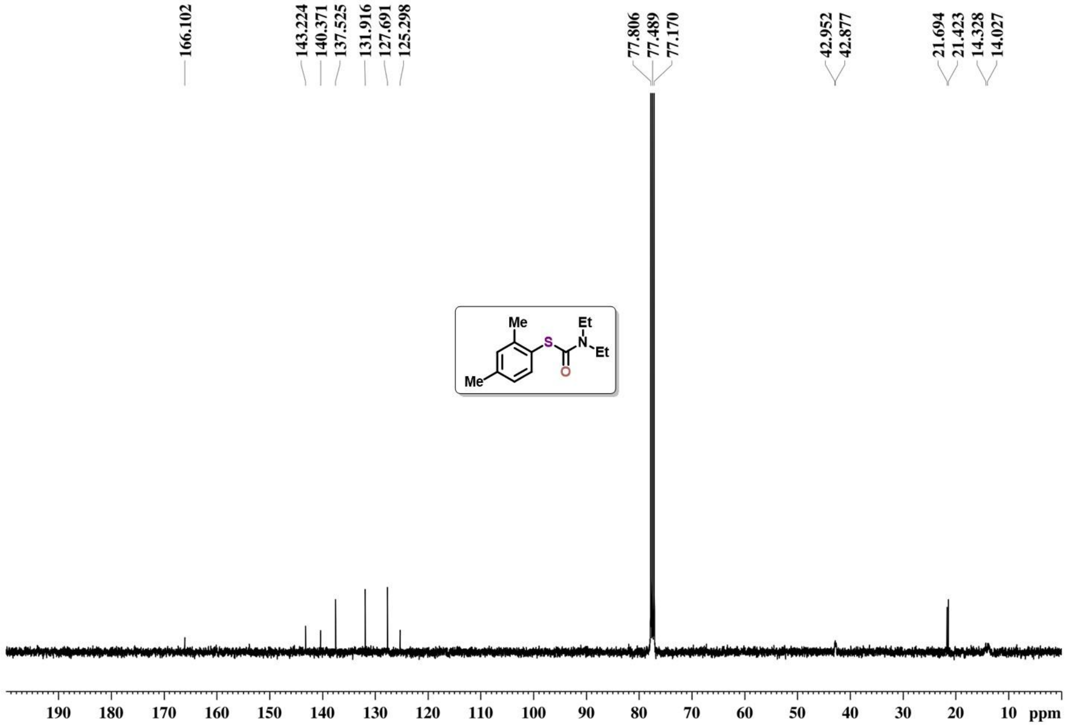
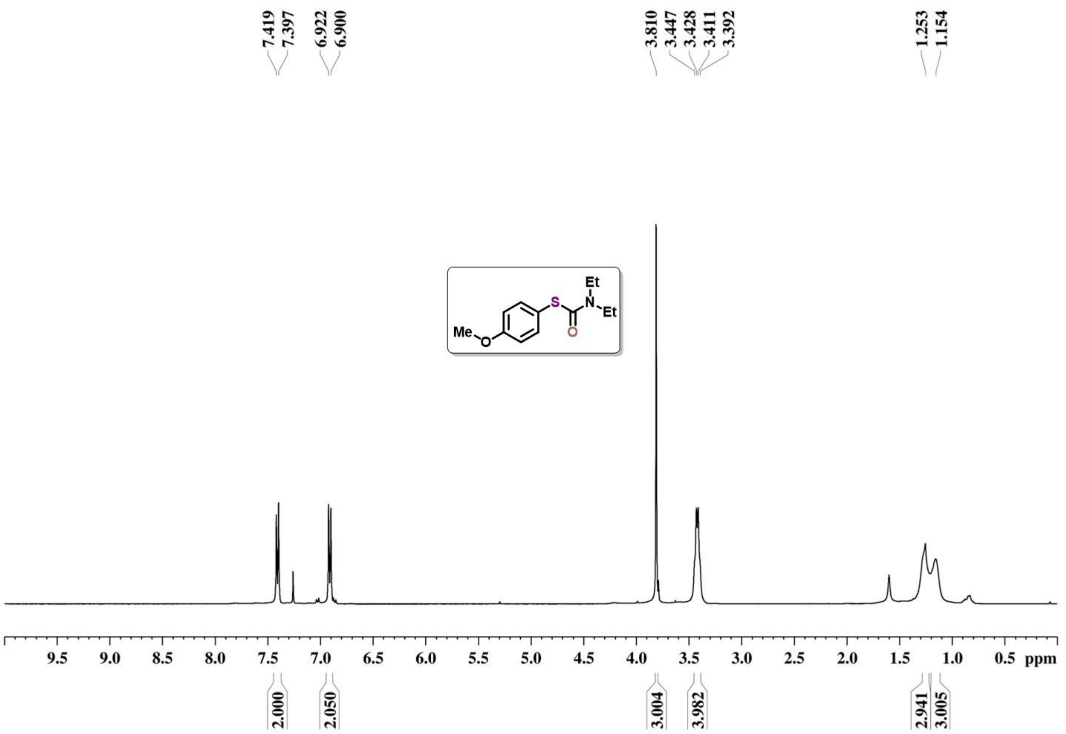
7.914
7.827
7.817
7.804
7.796
7.782
7.720
7.700
7.681
7.587
7.583
7.565
7.548
7.544
7.518
7.515
7.496
7.493
7.479
7.475
7.299
7.294
7.259
3.152
3.045
Br
S
N
Me
Me
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.139
1.069
1.000
0.964
0.843
0.853
2.976
2.777

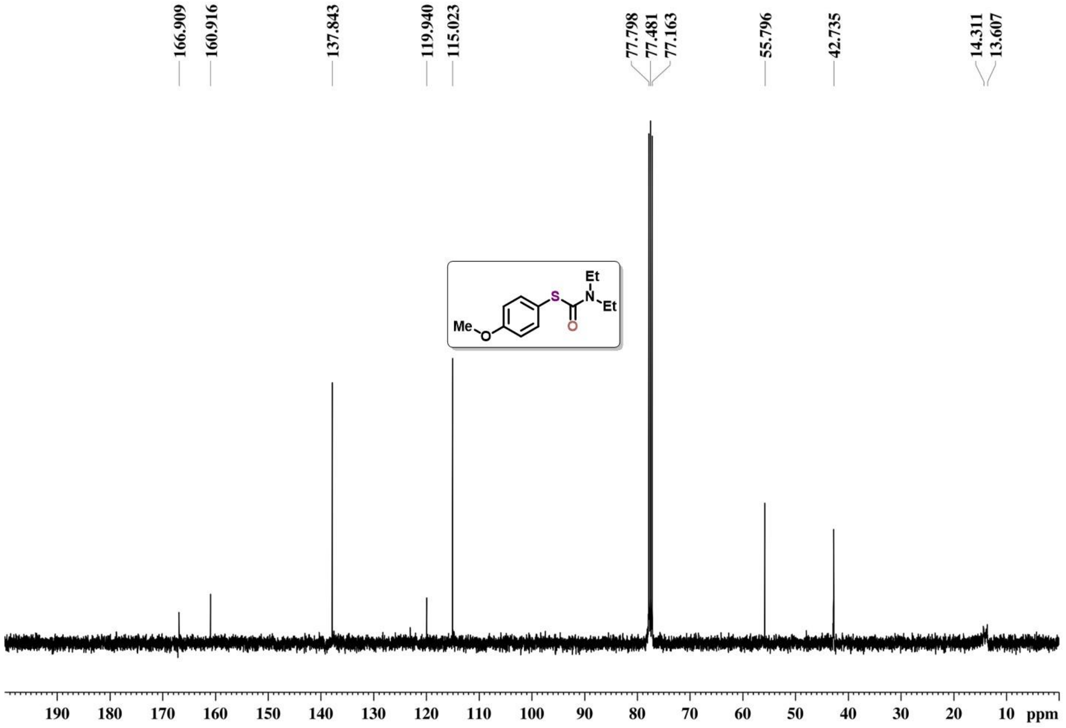

7.415
7.395
7.259
7.226
7.206
3.670
3.076
3.029
2.978
2.959
2.939
2.650
2.630
2.611
Me
S
N
Me
O
Me
O
O
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.980
1.916
2.998
2.910
2.897
2.047
2.000

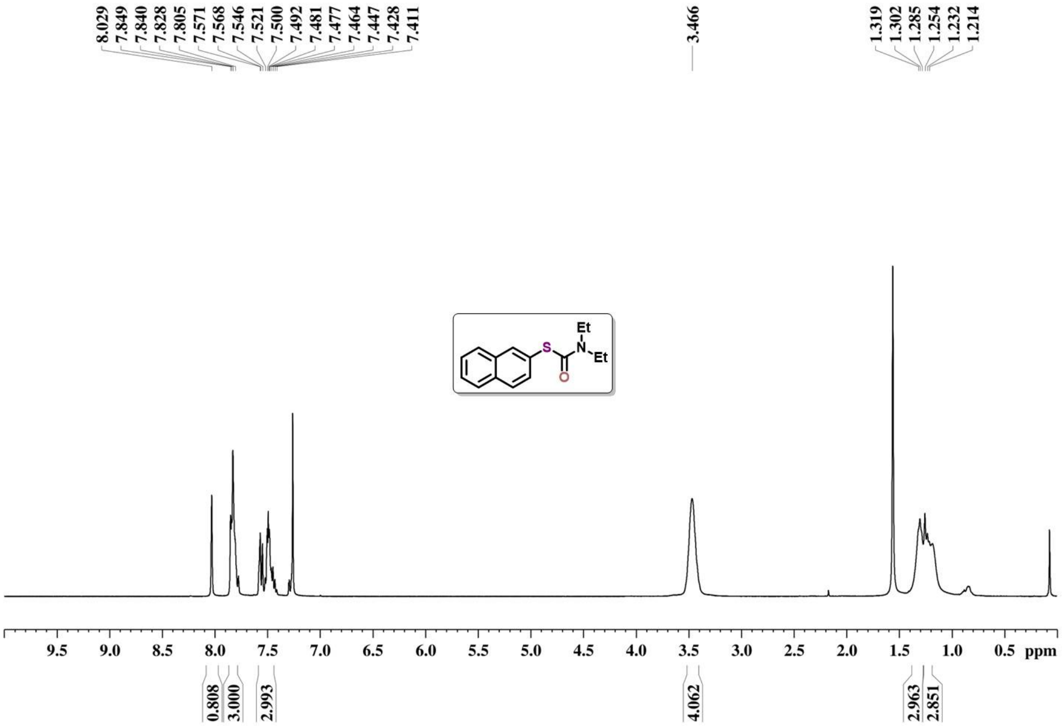

173.580
142.201
136.305
129.377
126.806
77.753
77.435
77.117
52.084
37.308
35.778
31.049
Me
S
N
Me
O
Me
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

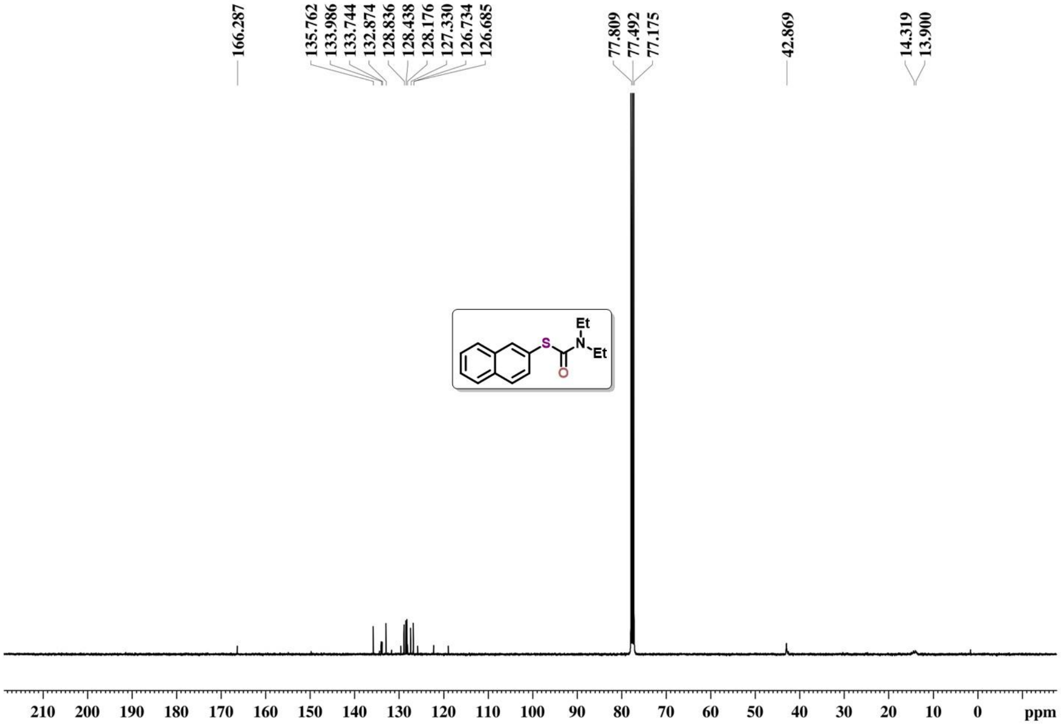

7.366
7.347
7.258
7.109
7.012
6.993
3.439
2.360
2.315
1.280
1.152
Me
S
O
N
Et
Et
Me
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
1.000
0.974
1.061
4.103
2.991
2.889
2.904
2.976


166.102
143.224
140.371
137.525
131.916
127.691
125.298
77.806
77.489
77.170
42.952
42.877
21.694
21.423
14.328
14.027
Me
S
O
N
Et
Et
Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm

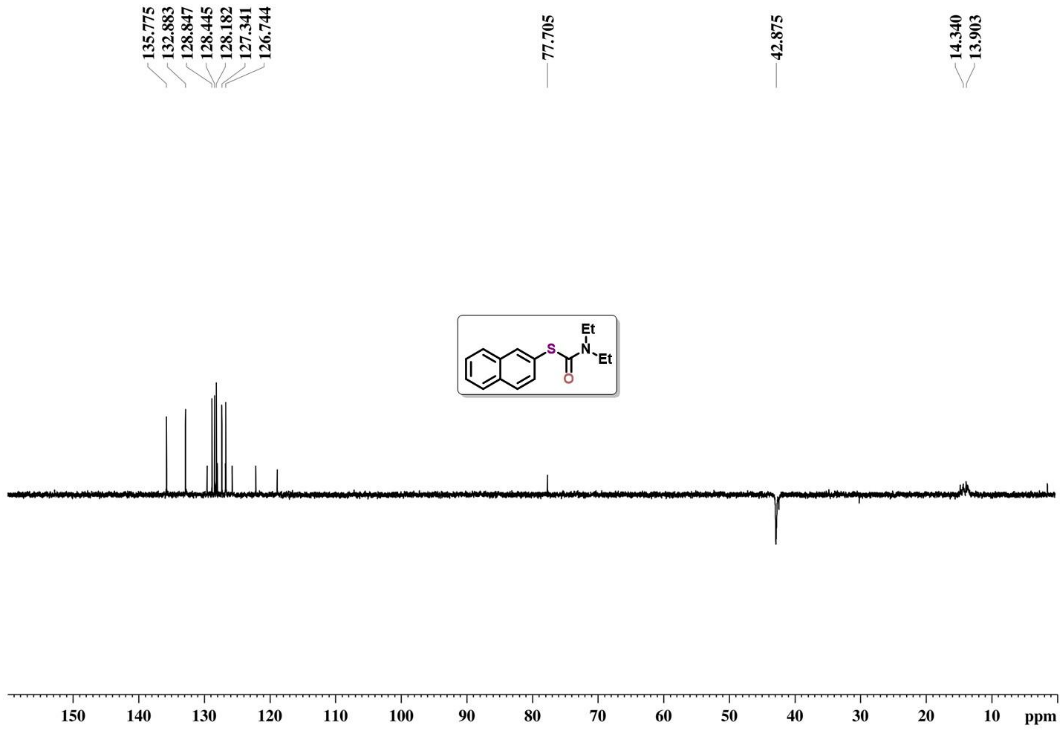

7.419
7.397
6.922
6.900
3.810
3.447
3.428
3.411
3.392
1.253
1.154
Et
S
N
Et
Me
O
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5 ppm
2.000
2.050
3.004
3.982
2.941
3.005


166.909
160.916
137.843
119.940
115.023
77.798
77.481
77.163
55.796
42.735
14.311
13.607
Et
S
N
Et
Me
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


8.029
7.849
7.840
7.828
7.805
7.571
7.568
7.546
7.521
7.500
7.492
7.481
7.477
7.464
7.447
7.428
7.411
3.466
1.319
1.302
1.285
1.254
1.232
1.214
S
N
Et
Et
O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.808
3.000
2.993
4.062
2.963
2.851


166.287
135.762
133.986
133.744
132.874
128.836
128.438
128.176
127.330
126.734
126.685
77.809
77.492
77.175
42.869
14.319
13.900
S
N
Et
Et
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

DEPT-135:


135.775
132.883
128.847
128.445
128.182
127.341
126.744
77.705
42.875
14.340
13.903
S
N
Et
Et
O
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

12. Supplemental references:

1. Jaiswal, K.; Girish, Y. R.; Behera, P.; De, M., Dual Role of MoS_2 Quantum Dots in a Cross-Dehydrogenative Coupling Reaction. *ACS Org. Inorg. Au* **2022,** *2*, 205-213.
2. Jaiswal, K.; Girish, Y. R.; De, M., Influence of a Tunable Band Gap on Photoredox Catalysis by Various Two-Dimensional Transition-Metal Dichalcogenides. *ACS Appl. Nano Mater.* **2020,** *3*, 84-93.
3. Behera, P.; Jaiswal, K.; De, M., Time-resolved fluorescence sensor array for the discrimination of phosphate anions using transition metal dichalcogenide quantum dots and Tb(III). *Luminescence* **2023,** *38*, 1339-1346.
4. Massey, A. T.; Gusain, R.; Kumari, S.; Khatri, O. P., Hierarchical Microspheres of MoS_2 Nanosheets: Efficient and Regenerative Adsorbent for Removal of Water-Soluble Dyes. *Ind. Eng. Chem. Res.* **2016,** *55*, 7124-7131.
5. Singh, P.; Ojha, R. P.; Kumar, S.; Singh, A. K.; Prakash, R., Fe-doped MoS_2 nanomaterials with amplified peroxidase mimetic activity for the colorimetric detection of glutathione in human serum. *Mater. Chem. Phys.* **2021,** *267*, 124684.
6. Karunakaran, S.; Pandit, S.; Basu, B.; De, M., Simultaneous Exfoliation and Functionalization of 2H-MoS_2 by Thiolated Surfactants: Applications in Enhanced Antibacterial Activity. *J. Am. Chem. Soc.* **2018,** *140*, 12634-12644.
7. Landry, M. L.; Morrell, T. E.; Karagounis, T. K.; Hsia, C.-H.; Wang, C.-Y., Simple Syntheses of CdSe Quantum Dots. *J. Chem. Educ.* **2014,** *91*, 274-279.
8. Aboulaich, A.; Billaud, D.; Abyan, M.; Balan, L.; Gaumet, J.-J.; Medjadhi, G.; Ghanbaja, J.; Schneider, R., One-Pot Noninjection Route to CdS Quantum Dots via Hydrothermal Synthesis. *ACS Appl. Mater. Interfaces* **2012,** *4*, 2561-2569.
9. Perkowski, A. J.; Cruz, C. L.; Nicewicz, D. A., Ambient-Temperature Newman–Kwart Rearrangement Mediated by Organic Photoredox Catalysis. *J. Am. Chem. Soc.* **2015,** *137*, 15684-15687.
10. Gendron, T.; Pereira, R.; Abdi, H. Y.; Witney, T. H.; Årstad, E., Iron(II)/Persulfate Mediated Newman–Kwart Rearrangement. *Org. Lett.* **2020,** *22*, 274-278.
11. Broese, T.; Roesel, A. F.; Prudlik, A.; Francke, R., An Electrocatalytic Newman–Kwarttype Rearrangement. *Org. Lett.* **2018,** *20*, 7483-7487.
12. Bera, S. S.; Maji, M. S., Carbamates: A Directing Group for Selective C–H Amidation and Alkylation under Cp*Co(III) Catalysis. *Org. Lett.* **2020,** *22*, 2615-2620.
13. Matter, M. E.; Čamdžić, L.; Stache, E. E., Photothermal Conversion by Carbon Black Facilitates Aryl Migration by Photon-Promoted Temperature Gradients. *Angew. Chem. Int. Ed.* **2023,** *62*, e202308648.
14. Zhao, Y.; Xie, Y.; Xia, C.; Huang, H., Palladium-Catalyzed Intramolecular Oxidative C⍰ H Sulfuration of Aryl Thiocarbamates. *Adv. Synth. Catal.* **2014,** *356*, 2471-2476.
15. NAOKI, Y.; YOSHINOR, S.; HIROSH, Y.; TATSUYA, K.; YASUHIRO, H. BENZOÝb¨THIOPHEN DERIVATIVE AND PROCESS FOR PRODUCTION THEREOF. 2008.

16. SHO, I.; RYO, M.; HIDEKI, E.; AYA, I. Organic compound, method for preparing same, organic semiconductor material containing same, and organic transistor containing same. 2024.

17. Novakova, V.; Miletin, M.; Filandrová, T.; Lenčo, J.; Růžička, A.; Zimcik, P., Role of Steric Hindrance in the Newman-Kwart Rearrangement and in the Synthesis and Photophysical Properties of Arylsulfanyl Tetrapyrazinoporphyrazines. *J. Org. Chem.* **2014,** *79*, 2082-2093.

Komal, Madhusmita and Mrinmoy/Organic Chemistry/ IISc

18. Davis, S. E.; Davis, A. O.; Kuyper, L. F., Regioselectivity in the Lithiation of O-(4Methoxyphenyl)-N,N-diethylthiocarbamate: Relative Directed Metalation Abilities of Methoxy and N,N-diethylthiocarbamate Functionalities. *Synth. Commun.* **1997,** *27*, 2487-2496.

19. Deore, J. P.; De, M., Semiconductor Quantum Dots Act as Photocatalysts for Carbon–Carbon Bond Formation: Selective Functionalization of Xanthene's 9H Position. *J. Org. Chem.* **2023,** *88*, 16292-16301.

20. Moseley, J. D.; Lenden, P., A high temperature investigation using microwave synthesis for electronically and sterically disfavoured substrates of the Newman–Kwart rearrangement. *Tetrahedron* **2007,** *63*, 4120-4125.

21. Chen, J.; Mao, J.; He, Y.; Shi, D.; Zou, B.; Zhang, G., $AlCl_3$-promoted thiolation of acyl C–H bonds with arylsulfonyl hydrazides. *Tetrahedron* **2015,** *71*, 9496-9500.

22. LTD, S. B.; W, B. C.; LAXMAN, E.; AYMAN, K.; SON, L.; BIN, L.; DINGGUO, L.; R, M. B.; SUKUMAR, S. POLYNUCLEOTIDE CONSTRUCTS HAVING DISULFIDE GROUPS. 2015.

23. Nishiyama, Y.; Kawamatsu, H.; Sonoda, N., A Facile Method for the Synthesis of Thiocarbamates: Palladium-Catalyzed Reaction of Disulfide, Amine, and Carbon Monoxide. *J. Org. Chem.* **2005,** *70*, 2551-2554.

24. Ghotbi, F.; Baradarani, M. M.; Sheikh, D., β-Naphthyl chlorothionoformate: an efficient, powerful and a new reagent for dealkylation tertiary amines. *J. Sulfur Chem.* **2012,** *33*, 397-402.

25. Bolt, R. R. A.; Raby-Buck, S. E.; Ingram, K.; Leitch, J. A.; Browne, D. L., TemperatureControlled Mechanochemistry for the Nickel-Catalyzed Suzuki–Miyaura-Type Coupling of Aryl Sulfamates via Ball Milling and Twin-Screw Extrusion. *Angew. Chem. Int. Ed.* **2022,** *61*, e202210508.

26. Bajo, S.; Laidlaw, G.; Kennedy, A. R.; Sproules, S.; Nelson, D. J., Oxidative Addition of Aryl Electrophiles to a Prototypical Nickel(0) Complex: Mechanism and Structure/Reactivity Relationships. *Organometallics* **2017,** *36*, 1662-1672.

Reference for molecular weight determination of CQDs by SLS technique in Zetasizer instrument:

https://www.chem.uci.edu/~dmitryf/manuals/Malvern%20Zetasizer%20ZS%20DLS%20user%20manual.pdf