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Electronic Supplementary Information

Metal-free g-C_3N_4 nanosheets as a highly visible-light-active photocatalyst for thiol-ene reactions

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Experimental

Chemicals

Urea, acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2), N,N-dimethyl formamide (DMF) and ethyl alcohol (EtOH) were obtained from Tianjin Kermel Chemical Reagent Co. Styrene, benzyl mercaptan, pentyl mercaptan and 4-chlorobenzyl mercaptan were purchased from Aladdin Reagent Co. Cyclohexanethiol was obtained from TCI. Cyclohexene was purchased from Sigma-Aldrich. Acrylonitrile, acrylyl chloride and 4-methoxybenzyl mercaptan were purchased from Energy Chemical. All chemicals were analytical reagents and used directly without further purification.

Characterization

The prepared g-C_3N_4 nanosheets and reaction products were characterized by the following methods. The diffuse-reflectance absorption spectra were measured on a Hitachi U-4100 ultraviolet/visible/near-infrared spectrophotometer equipped with an integration sphere accessory using $BaSO_4$ as a reference. The X-ray diffraction patterns were recorded on a

Bruker D8 Advance diffractometer using Cu Kα radiation. The Fourier-transform infrared (FTIR) spectra were taken on a Thermo Scientific Nicolet iS5 FTIR spectrometer. The sample for the FTIR measurement was mixed together with KBr power, following the standard method. Scanning electron microscopy (SEM) imaging was carried out on an FEI Quanta 250 with an FEG at a voltage of 20 kV. Transmission electron microscopy (TEM) imaging was performed on an FEI Tecnai G^2 20 microscope operated at 200 kV. The atomic force microscopy (AFM) images were acquired on a Veeco Metrology system (Model No. 920-006-101) operated in the contact mode using super-sharp silicon nitride tips. The samples for the AFM measurement were deposited on silicon substrates. The nitrogen adsorption-desorption isotherm was measured at -196 °C using a Micromeritics ASAP 2020HD88 system. The specific surface area and pore size distribution were evaluated according to the Brunauer-Emmett-Teller (BET) method, with the Barrett-Joyner-Halenda (BJH) formula applied to the adsorption branch. The electron spin resonance (ESR) spectra were recorded on a Bruker A300 ESR spectrometer. The gas chromatography-mass spectrometry (GC-MS) and high-performance liquid chromatography (HPLC) analyses of the organic products were carried out on a Thermo DSQ II spectrometer with an EI ion source and a Shimadzu LC-20A chromatograph, respectively. The ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker Avance III 400 MHz spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as an internal reference. The chemical shifts (δ) were reported in parts per million (ppm) from tetramethylsilane (TMS). The multiplicities of the peaks were abbreviated as follows: s, singlet; d, doublet; t, triplet; m, multiplet. The coupling constants (J) were reported in Hz. The thiol-ene reactions were carried out using a Xe lamp (CEL-HXF300) with UVCUT420 filter as the light source. The optical density was ~270 mW cm^{-2}. The amount of the evolved H_2 in the reaction system was measured by gas chromatography (GC-7806, Shiweipx) with high-purity N_2 as the carrier gas.

Energy band calculation

The bandgap energy of the prepared semiconductor can be determined according to the equation below

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \tag{1}$$

where A, α, ν, E_g and h represent a proportionality constant, the absorption coefficient, light frequency, bandgap energy and Planck constant, respectively. The value of n is determined by the type of optical transitions, where $n = 1$ is for direct transitions and $n = 4$ is for indirect transitions. The bandgap energy of the g-C_3N_4 nanosheets was estimated to be ~2.83 eV according to the Tauc plot of $(\alpha h\nu)^2$ *versus* the photon energy ($h\nu$).[1–3]

The band edge position of the conduction band (E^0_{CB}) of a semiconductor can be determined using eqn (2), and the valence band position (E^0_{VB}) can be calculated from eqn (3), as given below

$$E^0_{\mathrm{CB}} = X - E^c - \frac{1}{2}E_g \tag{2}$$

$$E^0_{\mathrm{VB}} = E^0_{\mathrm{CB}} + E_g \tag{3}$$

where X represents the absolute electronegativity of the semiconductor. Its value for g-C_3N_4 is 4.72 eV. E^c is the energy of free electrons on the hydrogen scale. It is ~4.5 eV *versus* the normal hydrogen electrode (NHE) for g-C_3N_4. Based on the measured results, the top of the valence band (VB) and the bottom of the conduction band (CB) were determined to be +1.63 eV and -1.20 eV, respectively.

Preparation of the g-C_3N_4 nanosheets

The g-C_3N_4 nanosheets were synthesized following a reported approach with slight modification.[4,5] In a muffle furnace, urea powder (15 g) was placed into an alumina crucible with a lid, heated to 550 °C at a heating rate of 1 $°C \cdot min^{-1}$ and then kept for another 3 h at the final temperature in air atmosphere. The furnace was subsequently cooled down to room temperature naturally to obtain the desired g-C_3N_4 nanosheets.

General procedure for the g-C_3N_4-catalyzed radical thiol-ene reactions

The radical thiol-ene reaction was conducted in a transparent vessel with CH_3CN (1 mL) as the solvent in air atmosphere. The g-C_3N_4 nanosheets were used to catalyze the reaction under visible-light illumination ($\lambda > 420$ nm) with a Xe lamp equipped with a UVCUT420 filter. The thiol (0.5 mmol) and alkene (0.25 mmol) were added in sequence to the solution of g-C_3N_4 (4.6 mg) in CH_3CN. The resultant mixture solution was illuminated under the visible light in air for 5 h at room temperature. After the reaction, the mixture was centrifuged immediately. The obtained supernatant was then concentrated under reduced pressure and purified by column chromatography with an appropriate eluent to give the final adduct. The obtained product was analyzed by HPLC, ^1H NMR and ^{13}C NMR.

Control reactions

In one control experiment, the reaction was performed following the general procedure in a vessel under nitrogen atmosphere. The CH_3CN solvent was degassed with continuous nitrogen bubbling before use.

In another control experiment, the reaction was performed in dark according to the general procedure without light illumination. The reaction vessel was wrapped by tin foil sheet.

Scaled-up experiment

The scaled-up reaction was carried out following the general procedure by use of more benzyl mercaptan (10 mmol) and styrene (5 mmol) reactants. The reaction was catalyzed by the g-C_3N_4 nanosheets (50 mg) in CH_3CN (20 mL).

Determination of the quantum yield

For the determination of the quantum yield, benzyl mercaptan (0.5 mmol) and styrene (0.25 mmol) were added in sequence to a solution of g-C_3N_4 (4.6 mg) in CH_3CN (1 mL). The resultant mixture was illuminated under 420 nm monochromatic light in air for 0.5 h (1800 s) for photocatalytic reaction. The product yield was measured by HPLC. The quantum yield was calculated according to

$$\eta = \frac{N_{reacted}}{N_{ph}} = \frac{N_A \times n_{reacted}}{\frac{E_{light}}{E_{ph}}} = \frac{N_A \times n_{reacted}}{\frac{P_{absorbed} \times t}{\frac{h \times c}{\lambda}}} = \frac{h \times c \times N_A \times n_{reacted}}{\lambda \times P_{absorbed} \times t} \quad (4)$$

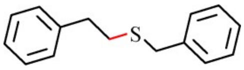
$$= \frac{6.626 \times 10^{-34} J \cdot s \times 2.998 \times 10^{8} m \cdot s^{-1} \times 6.022 \times 10^{23} mole^{-1} \times 8.32 \times 10^{-5} \mathrm{mole}}{4.20 \times 10^{-7} m \times 0.0107 J \cdot s^{-1} \times 1800\, s}$$

$$= 1.230$$

In the equation above, η is the quantum yield, N_{reacted} is the number of consumed styrene molecules, N_{ph} is the number of absorbed photons, N_{A} is Avogadro's constant, n_{reacted} is the molar amount of consumed styrene molecules, E_{light} is the energy of absorbed light, E_{ph} is the energy of a single photon, P_{absorbed} is the absorbed light power, t is the illumination time, h is Planck's constant, c is the velocity of light in free space, and λ is the wavelength of the illumination light (420 nm).

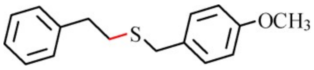
Synthetic procedure and analysis of the compounds 3a to 3j

Benzyl(phenethyl)sulfane (**3a**)



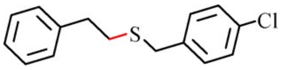
This compound was obtained following the general procedure using styrene (0.25 mmol) and benzyl mercaptan (0.5 mmol). The crude product was purified by column chromatography with hexane/ethyl acetate (40:1, v/v) as the eluent to afford **3a** as colourless oil (56.5 mg, 99%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.40–7.37 (m, 4H), 7.35–7.30 (m, 3H), 7.29–7.25 (m, 1H), 7.22–7.20 (m, 2H), 3.78 (s, 2H), 2.92–2.88 (m, 2H), 2.74–2.71 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 140.6, 138.4, 128.9, 128.5, 128.4, 127.0, 126.3, 36.5, 36.1, 32.8. MS (EI): *m*/*z* = 228.08 [M$^+$].

Phenylethyl(4-methoxybenzyl)sulfane (**3b**)



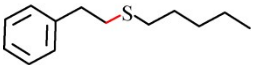
This compound was obtained following the general procedure using styrene (0.25 mmol) and 4-methoxybenzyl mercaptan (0.5 mmol). The crude product was purified by column chromatography with hexane/ethyl acetate (30:1, v/v) as the eluent to afford **3b** as colourless oil (62.6 mg, 97%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.22–7.18 (m, 2H), 7.17–7.10 (m, 3H), 7.08–7.06 (d, 2H), 6.78–6.76 (d, 2H), 3.71 (s, 3H), 3.59 (s, 2H), 2.78–2.74 (t, 2H), 2.59–2.56 (t, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 158.7, 140.6, 130.4, 129.9, 128.5, 128.4, 126.3, 114.0, 55.3, 36.1, 35.9, 32.7.

Phenylethyl(4-chlorobenzyl)sulfane (**3c**)



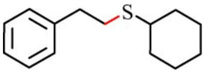
This compound was obtained following the general procedure using styrene (0.25 mmol) and 4-chlorobenzyl mercaptan (0.5 mmol). The crude product was purified by column chromatography with hexane as the eluent to afford **3c** as colourless oil (63.1 mg, 96%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.26–7.23 (m, 4H), 7.20–7.18 (m, 3H), 7.13–7.11 (m, 2H), 3.61 (s, 2H), 2.82–2.79 (m, 2H), 2.64–2.60 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 140.5, 137.1, 132.8, 130.3, 128.7, 128.6, 126.5, 36.1, 35.9, 32.9.

Phenylethyl(pentyl)sulfane (**3d**)



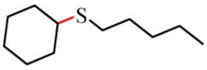
This compound was obtained following the general procedure using styrene (0.25 mmol) and pentyl mercaptan (0.5 mmol). The crude product was purified by column chromatography with hexane/ethyl acetate (35:1) as the eluent to afford **3d** as pale yellow oil (47.9 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.29–7.25 (m, 2H), 7.20–7.17 (m, 3H), 2.89–2.85 (m, 2H), 2.77–2.72 (m, 2H), 2.51 (t, *J* = 7.4 Hz, 2H), 1.58 (quint, *J* = 7.3 Hz, 2H), 1.39–1.26 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 140.8, 128.6, 128.5, 126.3, 36.5, 33.8, 32.4, 31.2, 29.4, 22.4, 14.1.

Phenylethyl(cyclohexyl)sulfane (**3e**)



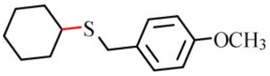
This compound was obtained following the general procedure using styrene (0.25 mmol) and cyclohexyl mercaptan (0.5 mmol). The crude product was purified by column chromatography with hexane/ethyl acetate (40:1, v/v) as the eluent to afford **3e** as pale yellow oil (31.4 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.29–7.25 (m, 2H), 7.21–7.17 (m, 3H), 2.88–2.83 (m, 2H), 2.80–2.75 (m, 2H), 2.66–2.60 (m, 1H), 1.98–1.95 (m, 2H), 1.77–1.73 (m, 2H), 1.60–1.58 (m, 1H), 1.36–1.20 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 140.9, 128.5, 128.4, 126.3, 43.7, 36.8, 33.8, 31.7, 26.2, 25.9.

Cyclohexyl(pentyl)sulfane (**3f**)



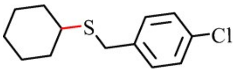
This compound was obtained following the general procedure using cyclohexene (0.25 mmol) and pentyl mercaptan (0.5 mmol). The crude product was purified by column chromatography with hexane as the eluent to afford **3f** as colourless oil (39.5 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 2.63–2.62 (m, 1H), 2.54–2.50 (t, 2H), 1.95 (m, 2H), 1.76 (m, 2H), 1.82–1.54 (m, 3H), 1.37–1.28 (m, 9H), 0.91–0.88 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 43.5, 33.8, 31.3, 30.1, 29.8, 26.2, 25.9, 22.3, 14.0.

Cyclohexyl(4-methoxybenzyl)sulfane (**3g**)



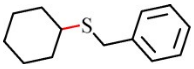
This compound was obtained following the general procedure using cyclohexene (0.25 mmol) and 4-methoxybenzyl mercaptan (0.5 mmol). The crude product was purified by column chromatography with hexane/ethyl acetate (35:1, v/v) as the eluent to afford **3g** as colorless oil (55.4 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 3.78 (s, 3H), 3.69 (s, 2H), 2.58–2.51 (m, 1H), 1.95–1.92 (m, 2H), 1.75–1.72 (m, 2H), 1.59–1.57 (m, 1H), 1.36–1.22 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.5, 130.9, 129.8, 113.9, 55.3, 42.9, 34.0, 33.4, 26.0, 25.9.

Cyclohexyl(4-chlorobenzyl)sulfane (**3h**)



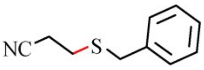
This compound was obtained following the general procedure using cyclohexene (0.25 mmol) and 4-chlorobenzyl mercaptan (0.5 mmol). The crude product was purified by column chromatography with hexane as the eluent to afford **3h** as colorless oil (54.8 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (s, 4H), 3.70 (s, 2H), 2.56–2.49 (m, 1H), 1.93–1.90 (m, 2H), 1.75–1.72 (m, 2H), 1.59–1.58 (m, 1H), 1.36–1.22 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 132.5, 130.1, 128.6, 43.0, 33.9, 33.4, 26.0, 25.9.

Cyclohexyl(benzyl)sulfane (**3i**)



This compound was obtained following the general procedure using cyclohexene (0.25 mmol) and benzyl mercaptan (0.5 mmol). The crude product was purified by column chromatography with hexane/ethyl acetate (50:1) as the eluent to afford **3i** as colorless oil (48.9 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.29 (m, 4H), 7.24–7.20 (m, 1H), 3.74 (s, 2H), 2.59–2.52 (m, 1H), 1.96–1.94 (m, 2H), 1.75–1.72 (m, 2H), 1.59–1.58 (m, 1H), 1.38–1.23 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.0, 128.8, 128.4, 126.8, 43.0, 34.6, 33.4, 26.0, 25.9.

3-(Benzylthio)propionitrile (**3j**)



This compound was obtained following the general procedure using acrylonitrile (0.25 mmol) and benzyl mercaptan (0.5 mmol). The crude product was purified by column chromatography with hexane/ethyl acetate (30:1, v/v) as the eluent to afford **3j** as colorless oil (13.3 mg, 30%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.28 (m, 4H), 7.27–7.23 (m, 1H), 3.77 (s, 2H), 2.62 (t, J = 7.0 Hz, 2H), 2.46 (t, J = 7.0 Hz, 2H), ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 128.9, 128.8, 127.5, 118.5, 36.3, 26.7, 18.6.

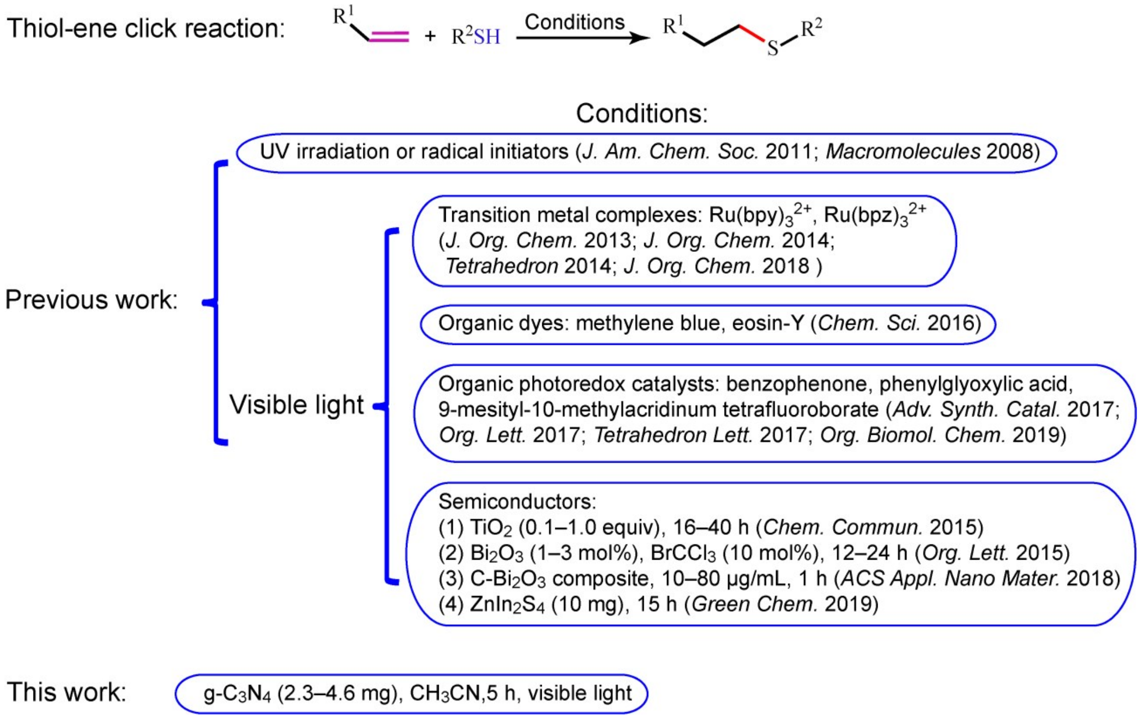


Fig. S1 Previous works on radical thiol-ene reactions and this work.

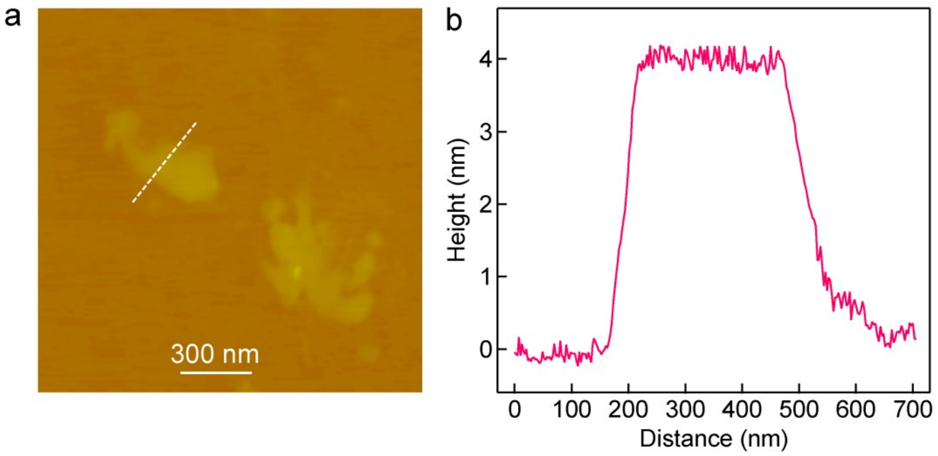


Fig. S2 AFM characterization of the g-C_3N_4 nanosheets. (a) AFM image of a representative g-C_3N_4 nanosheet. (b) Height profile taken along the white dashed line indicated in (a).

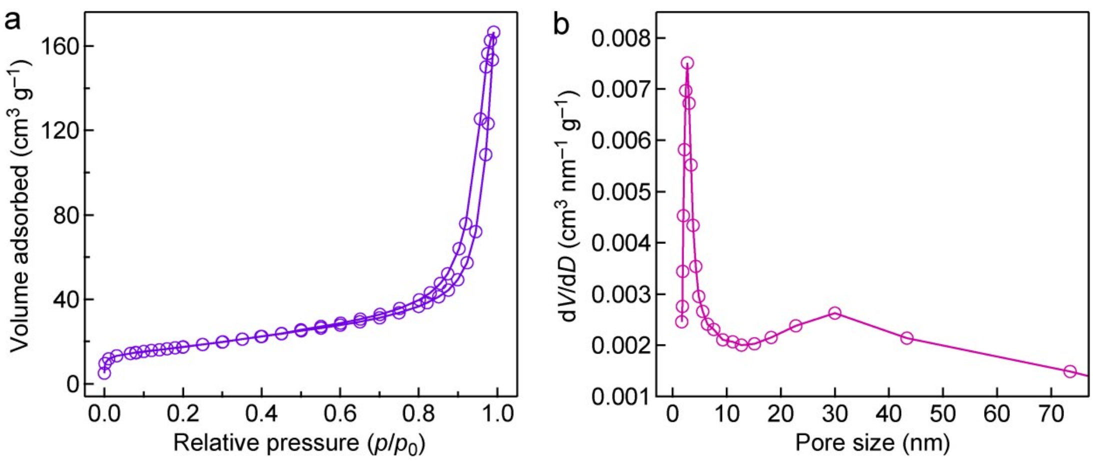


Fig. S3 Specific surface area characterization of the g-C_3N_4 nanosheets. (a) Nitrogen adsorption-desorption isotherm. (b) Corresponding pore size distribution curve.

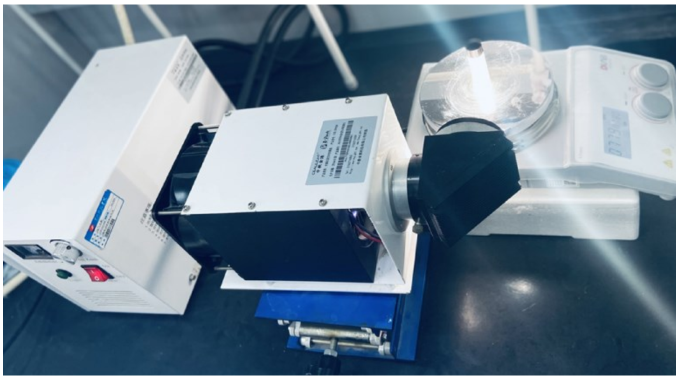


Fig. S4 Photograph of the photocatalytic reactor for thiol-ene reactions.

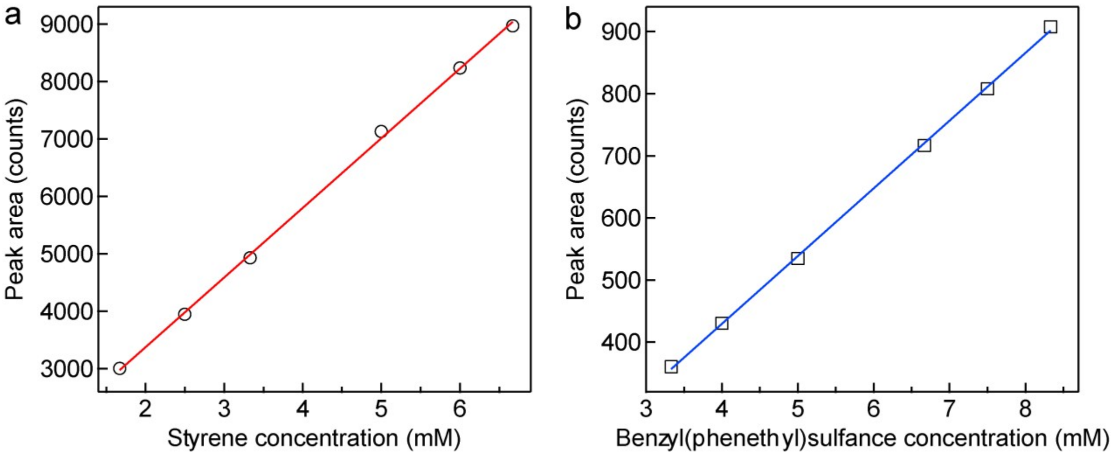


Fig. S5 Calibrated linear relationships between the peak area and concentration in the HPLC measurements. (a) For styrene. The circles represent the styrene concentrations of 1.67, 2.50, 3.33, 5.0, 6.0 and 6.67 mM in CH_3CN, respectively. The equation obtained from linear fitting is $y = (1211 \pm 17)\, x + (955 \pm 78)$. The coefficient of determination is $R^2 = 0.9990$. (b) For benzyl(phenethyl)sulfane. The squares represent the benzyl(phenethyl)sulfane concentrations of 3.33, 4.0, 5.0, 6.67, 7.50 and 8.33 mM in CH_3CN, respectively. The equation obtained from linear fitting is $y = (109.0 \pm 1.1)\, x - (6.4 \pm 6.6)$. The coefficient of determination is $R^2 = 0.9995$.

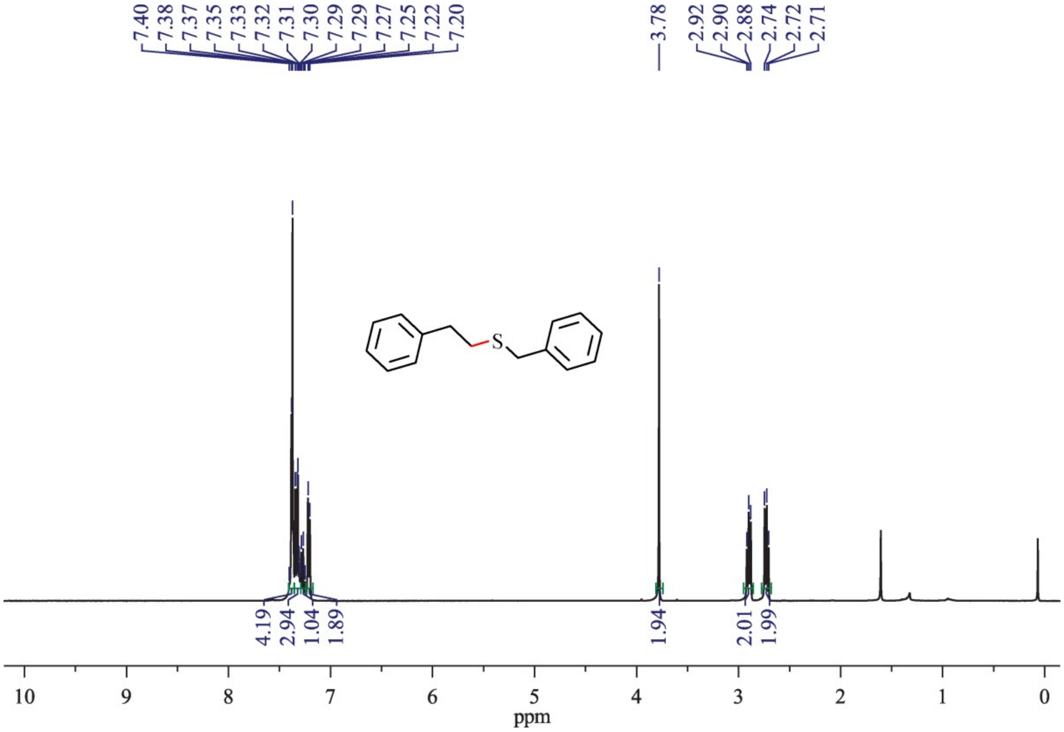


Fig. S6 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **3a**.

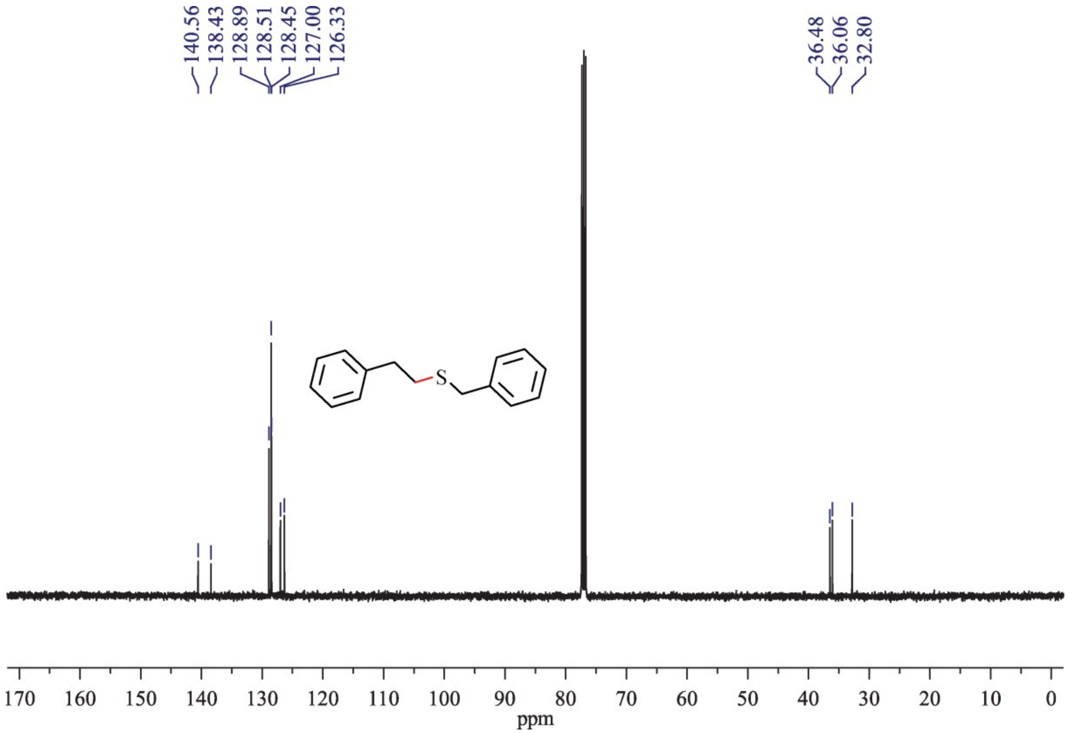


Fig. S7 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **3a**.

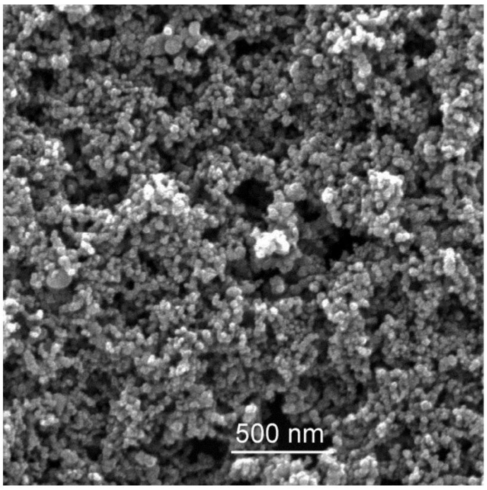


Fig. S8 SEM image of the TiO_2 nanoparticles (P25).

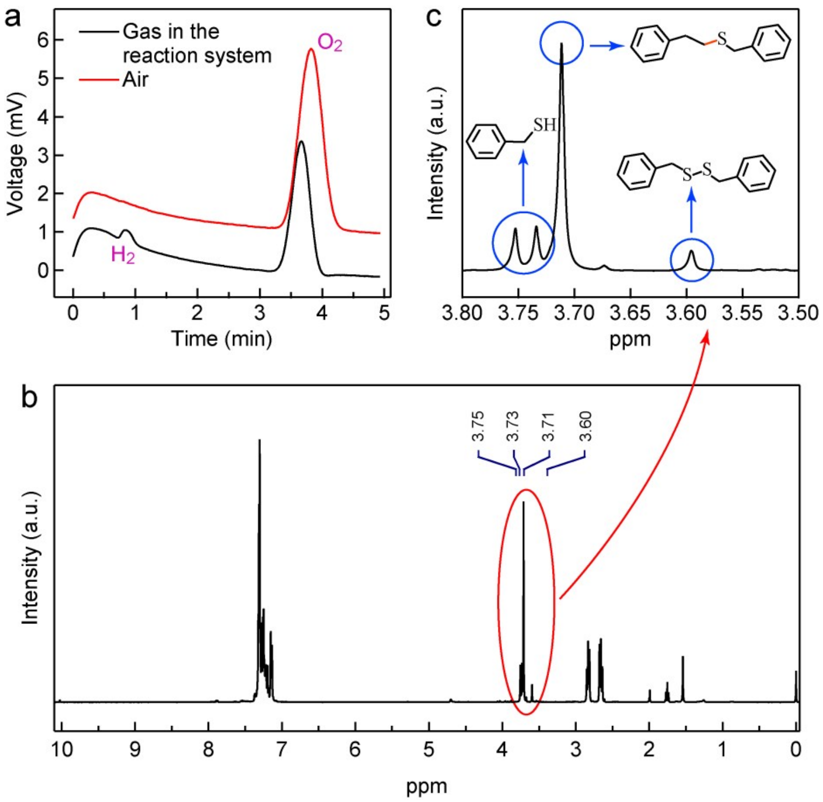


Fig. S9 Products of the thiol-ene reaction catalyzed by the g-C_3N_4 nanosheets. (a) H_2 evolution. The slight time difference of O_2 was caused by manual GC injection. (b) ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the mixture (crude product) in $CDCl_3$ after the reaction of styrene and benzyl mercaptan catalyzed by the g-C_3N_4 nanosheets. (c) Zoomed-in spectrum in the region indicated by the red circle in (b).

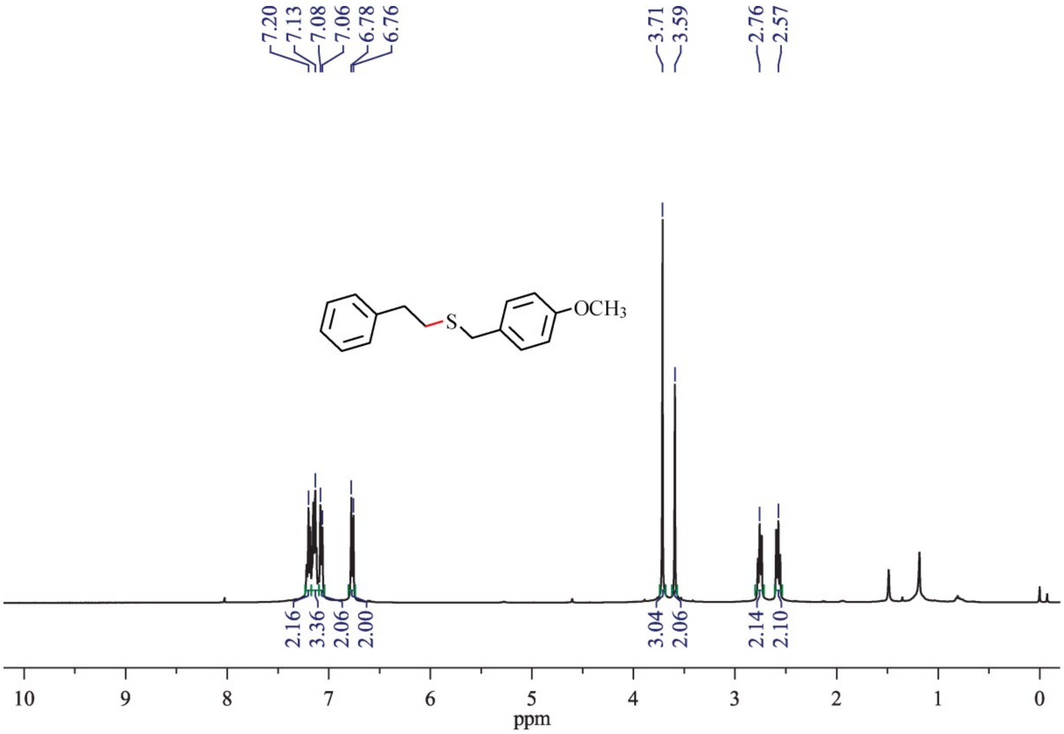


Fig. S10 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **3b**.

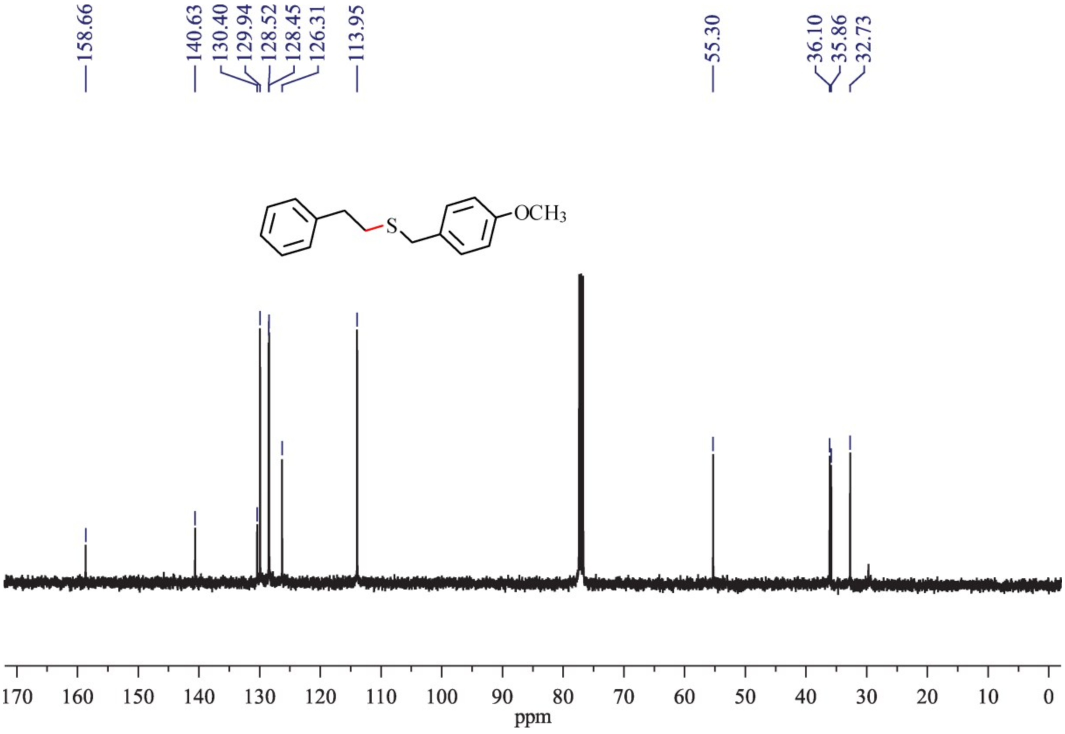


Fig. S11 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **3b**.

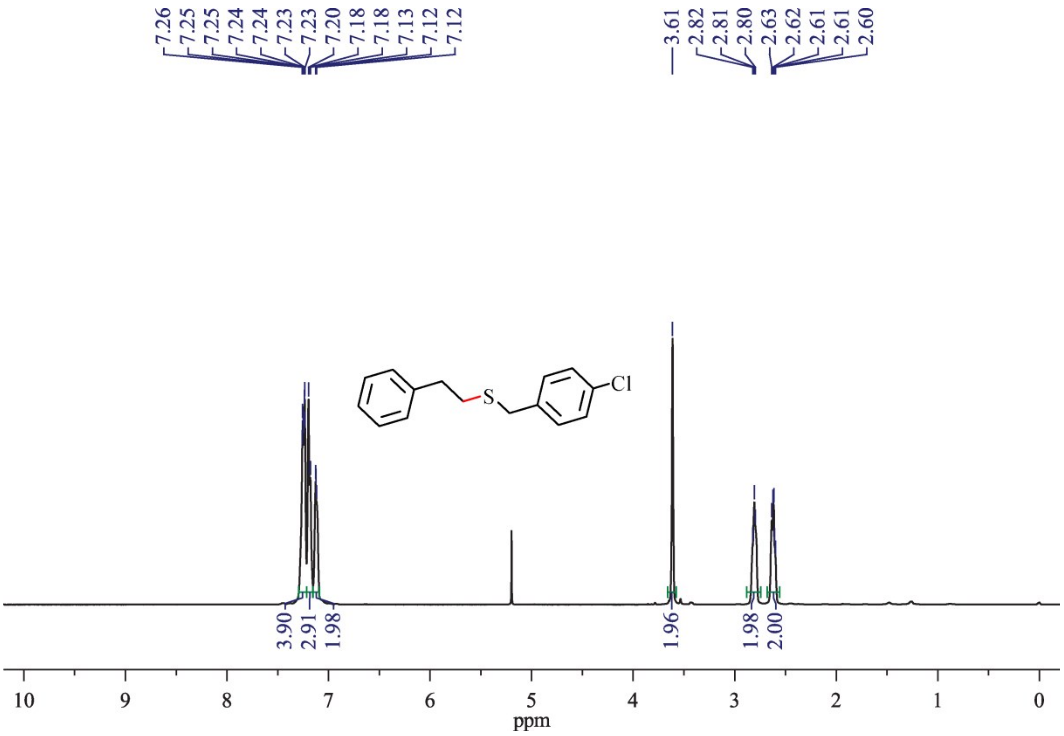


Fig. S12 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **3c**.

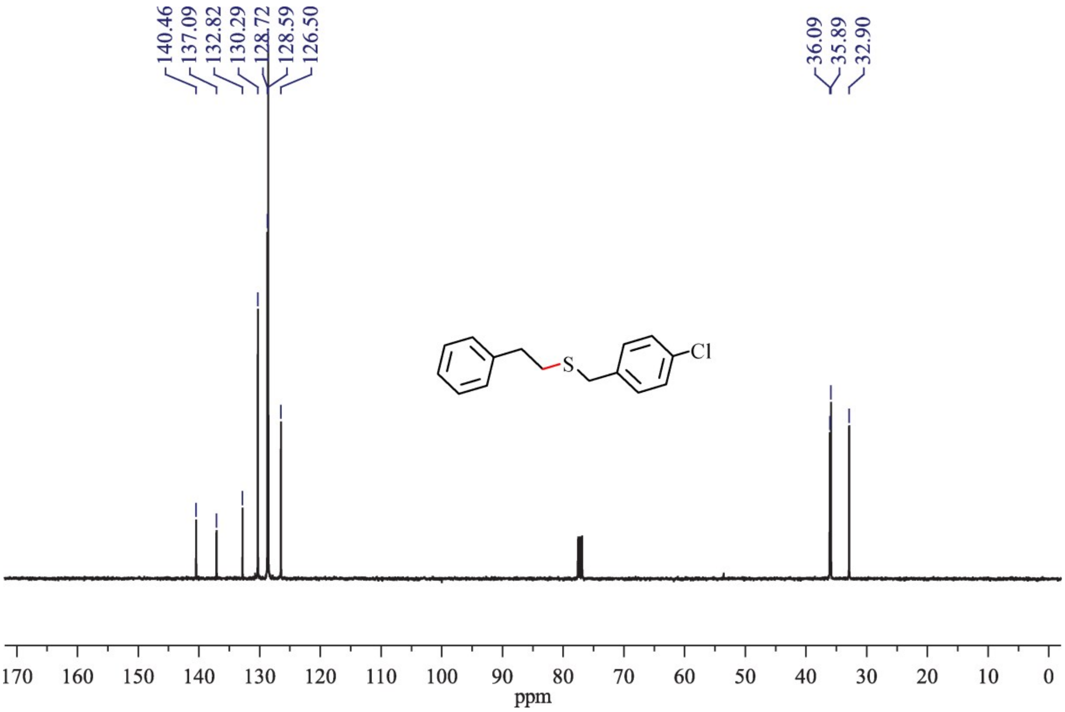


Fig. S13 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **3c**.

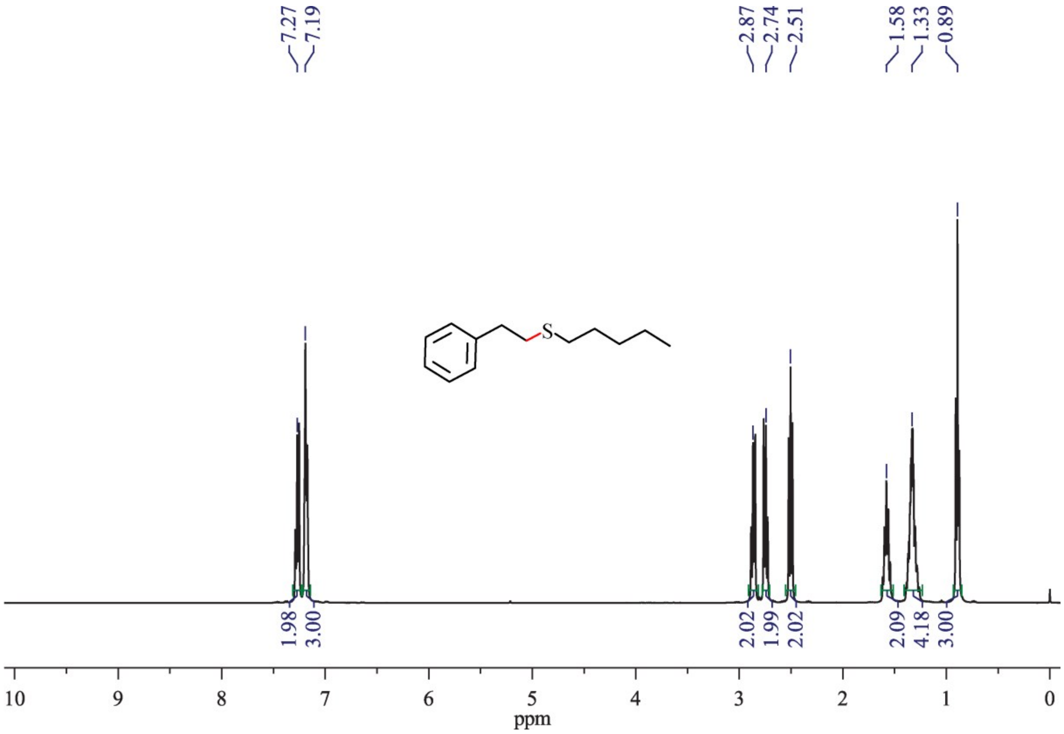


Fig. S14 ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of the compound **3d**.

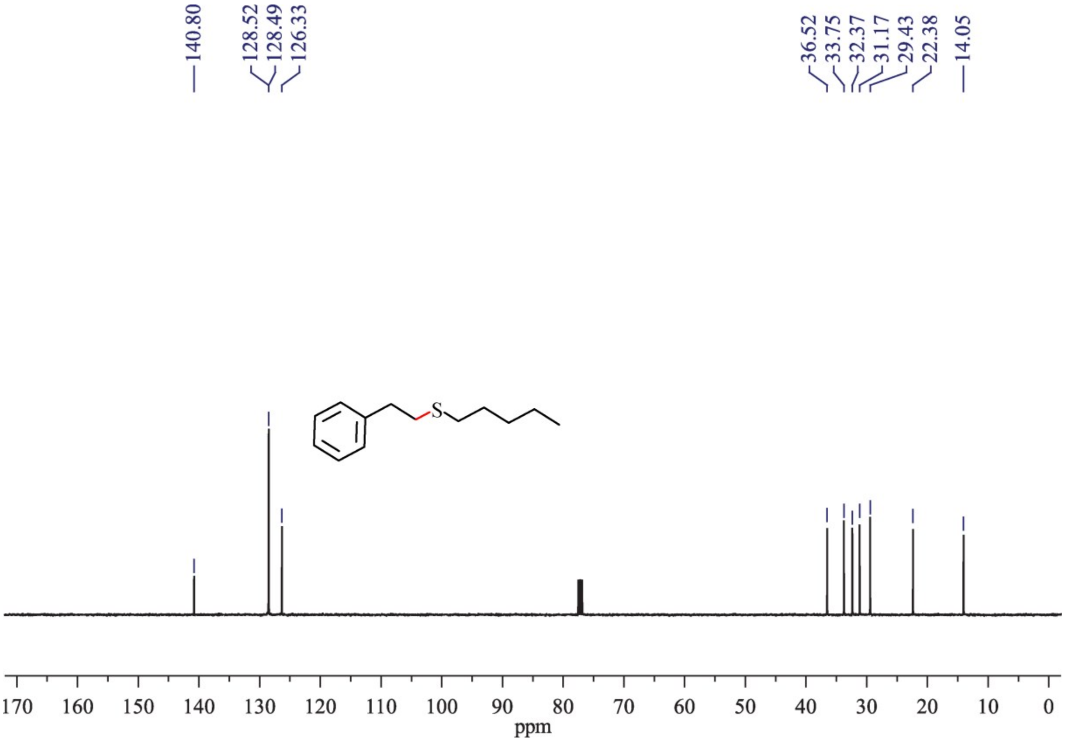


Fig.S15 ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of the compound **3d**.

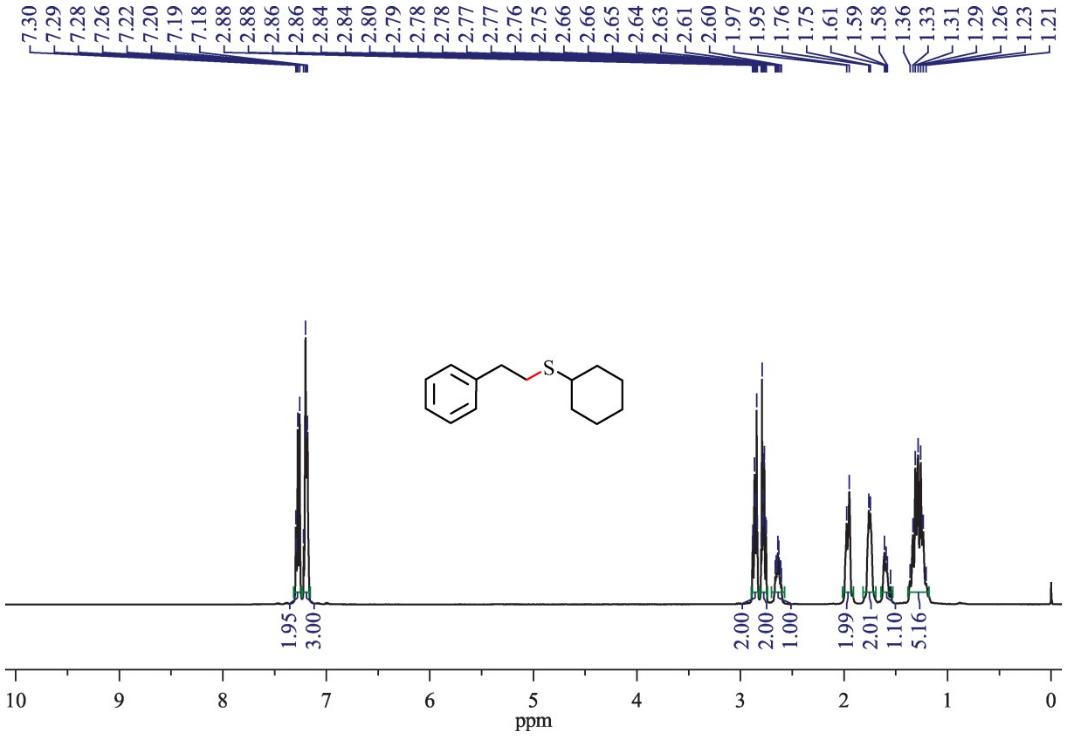


Fig. S16 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **3e**.

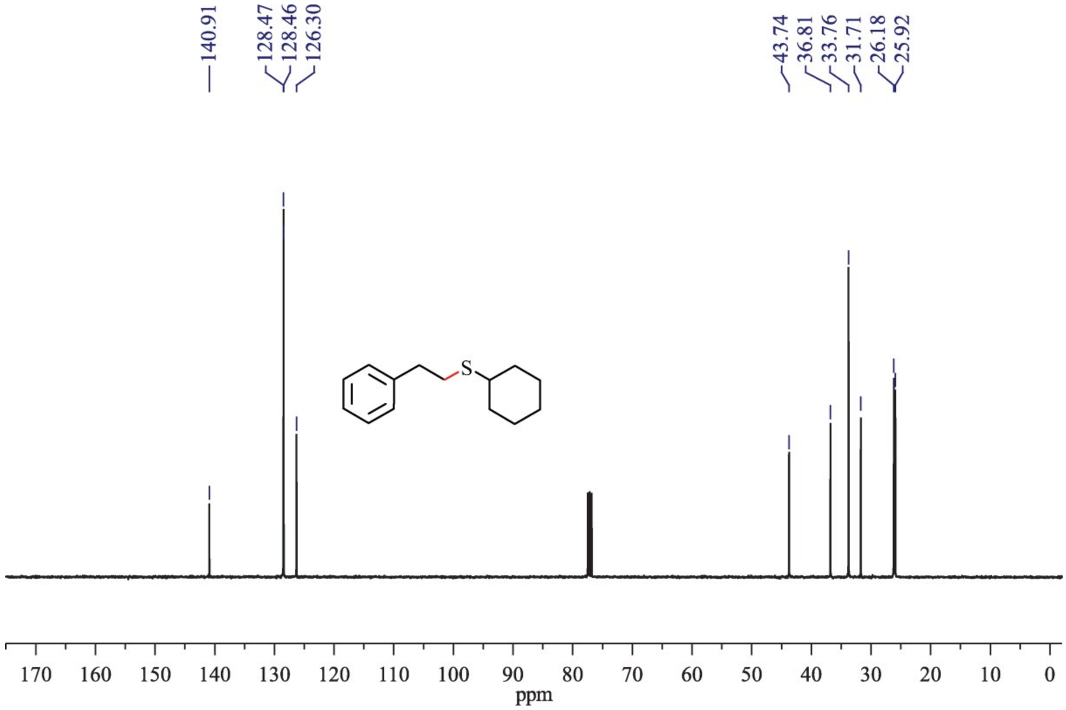


Fig. S17 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **3e**.

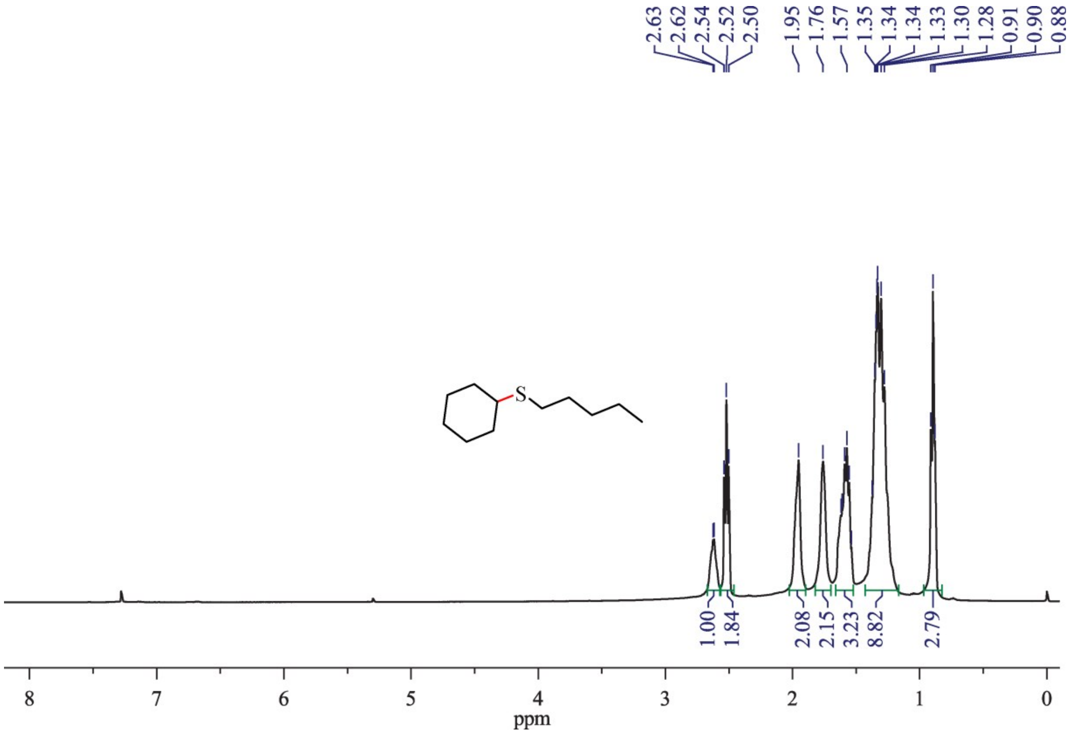


Fig. S18 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **3f**.

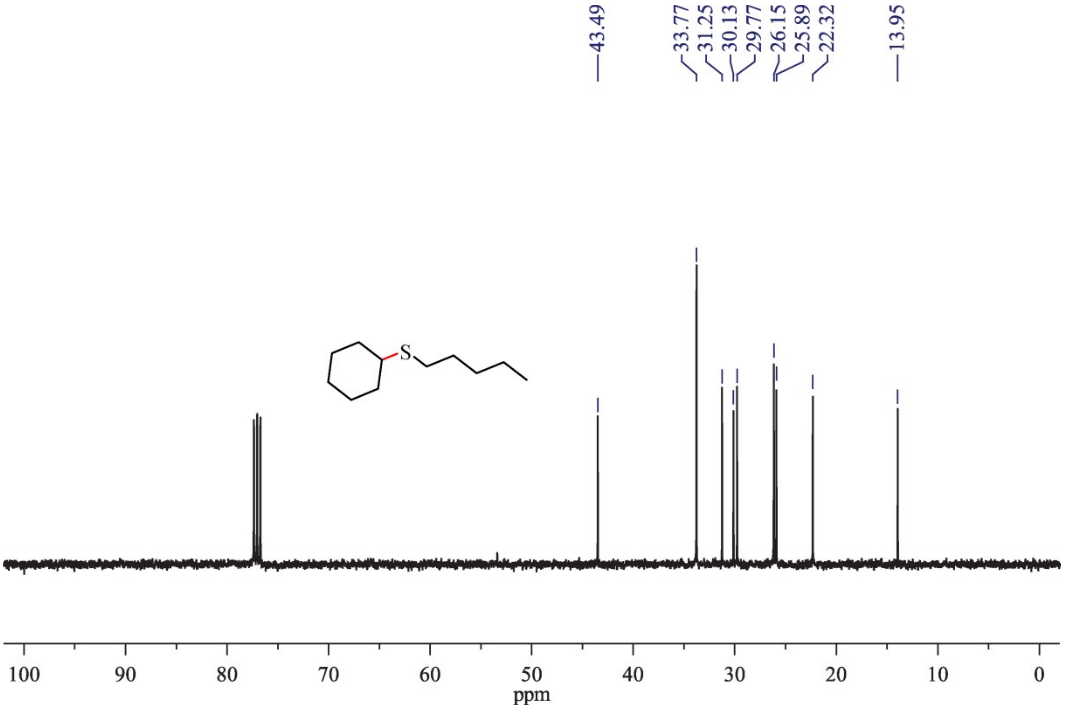


Fig. S19 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **3f**.

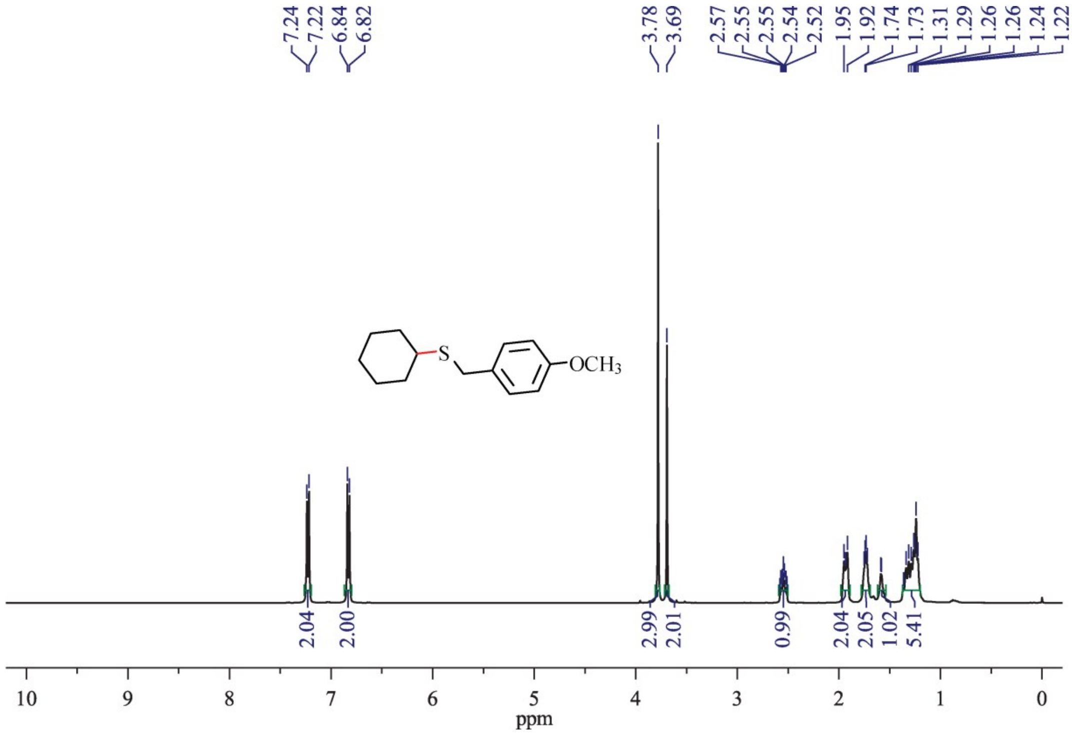


Fig. S20 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **3g**.

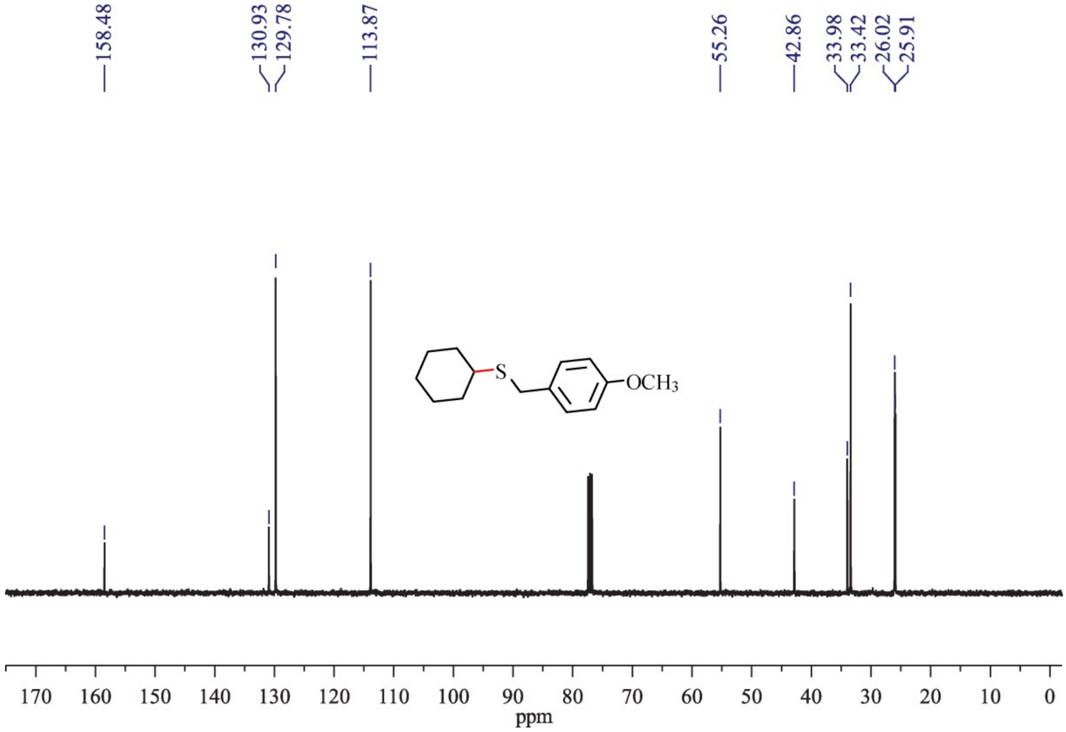


Fig. S21 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **3g**.

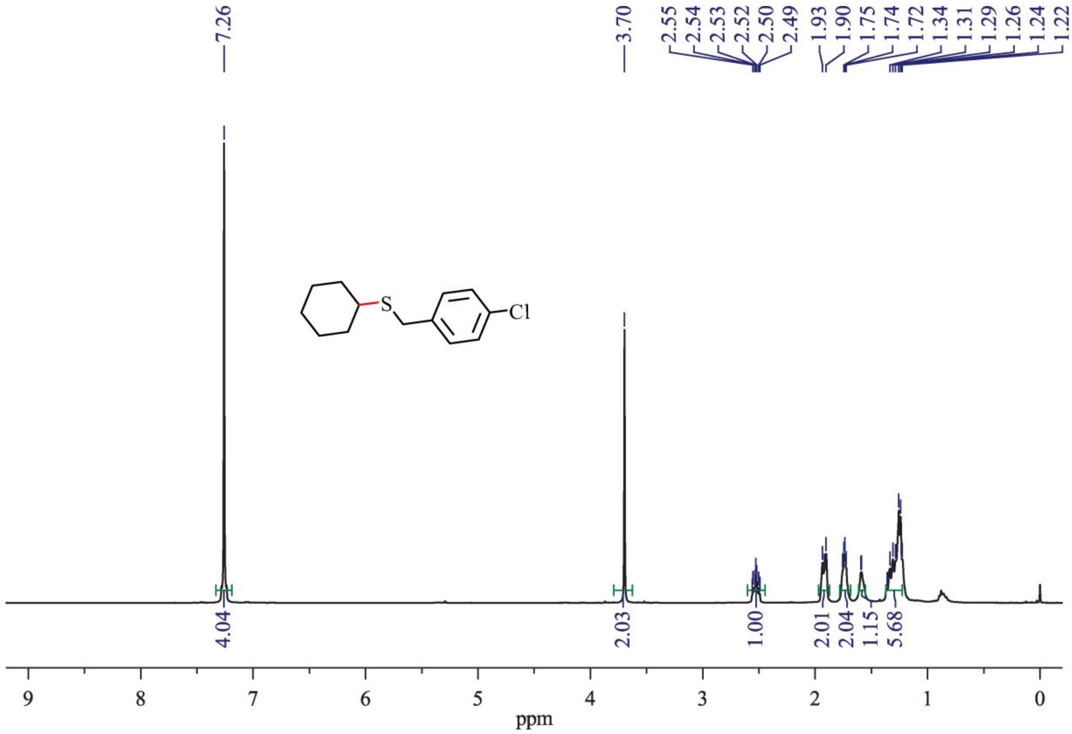


Fig. S22 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **3h**.

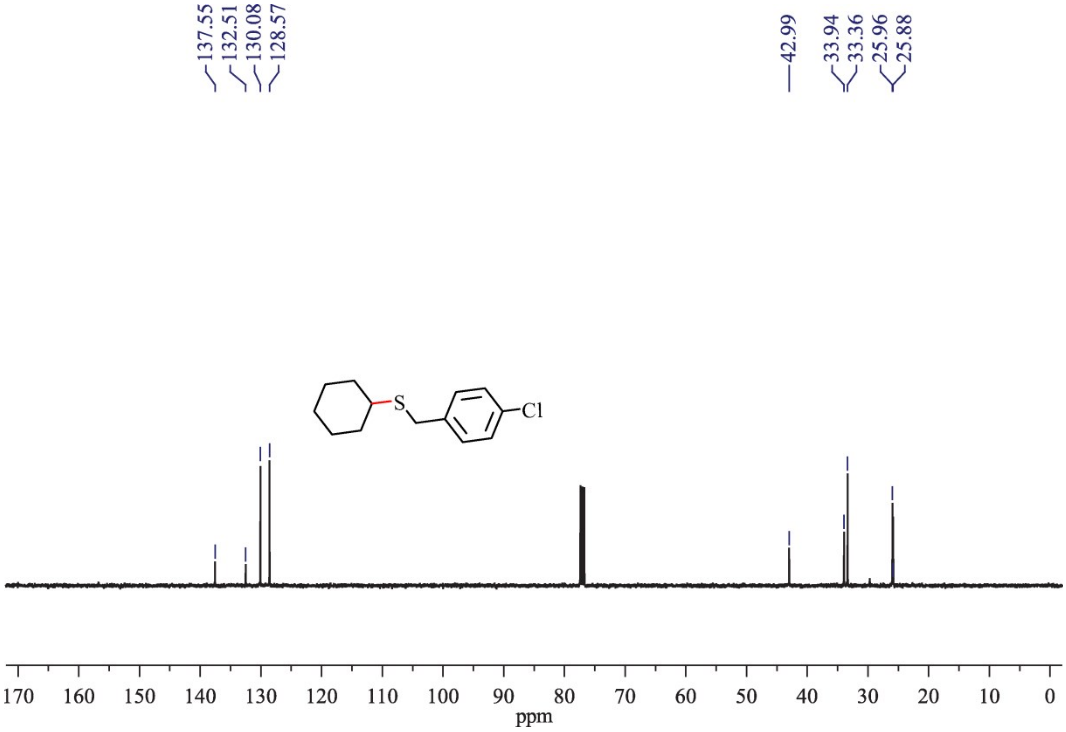


Fig. S23 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **3h**.

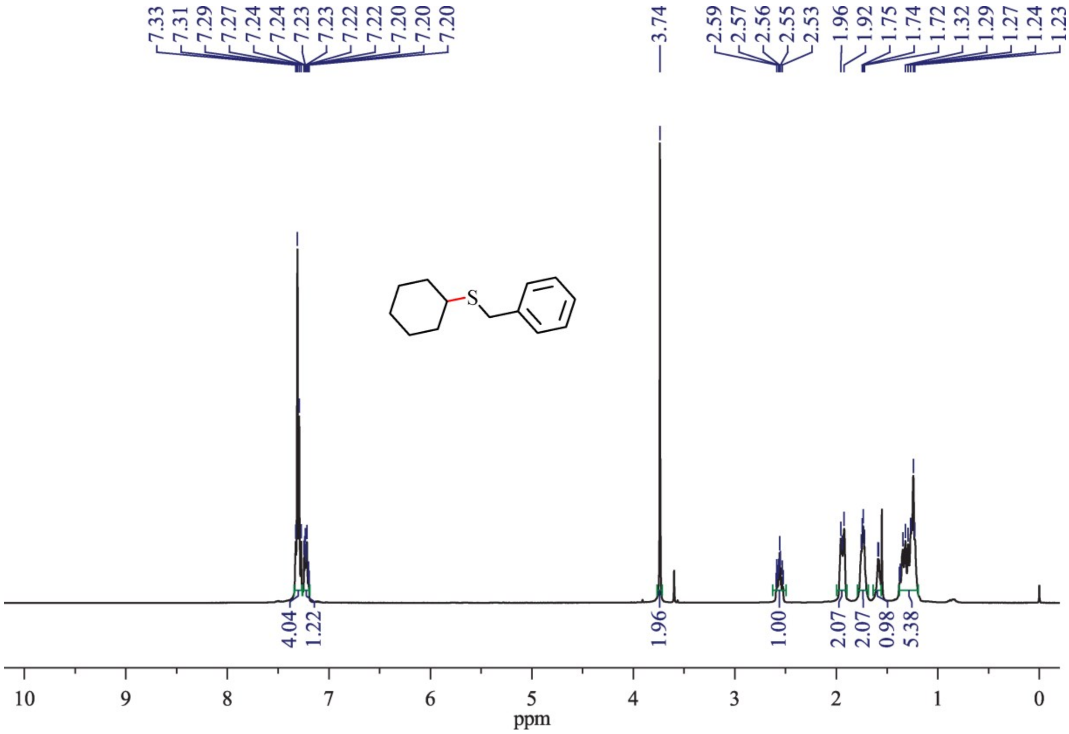


Fig. S24 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **3i**.

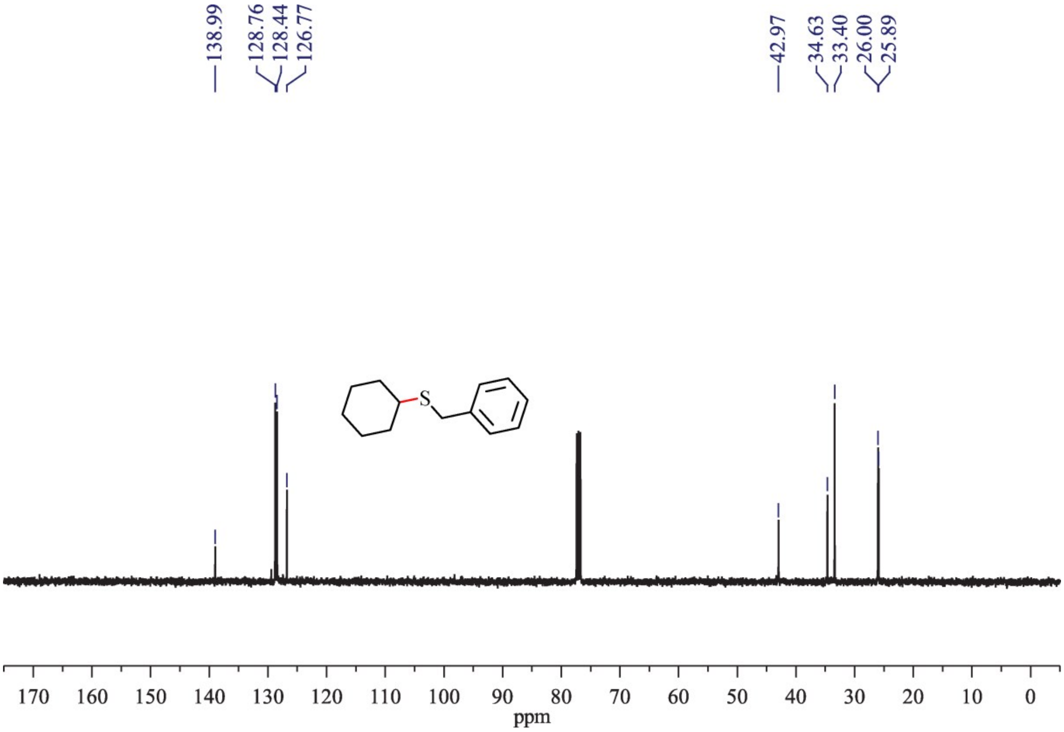


Fig. S25 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **3i**.

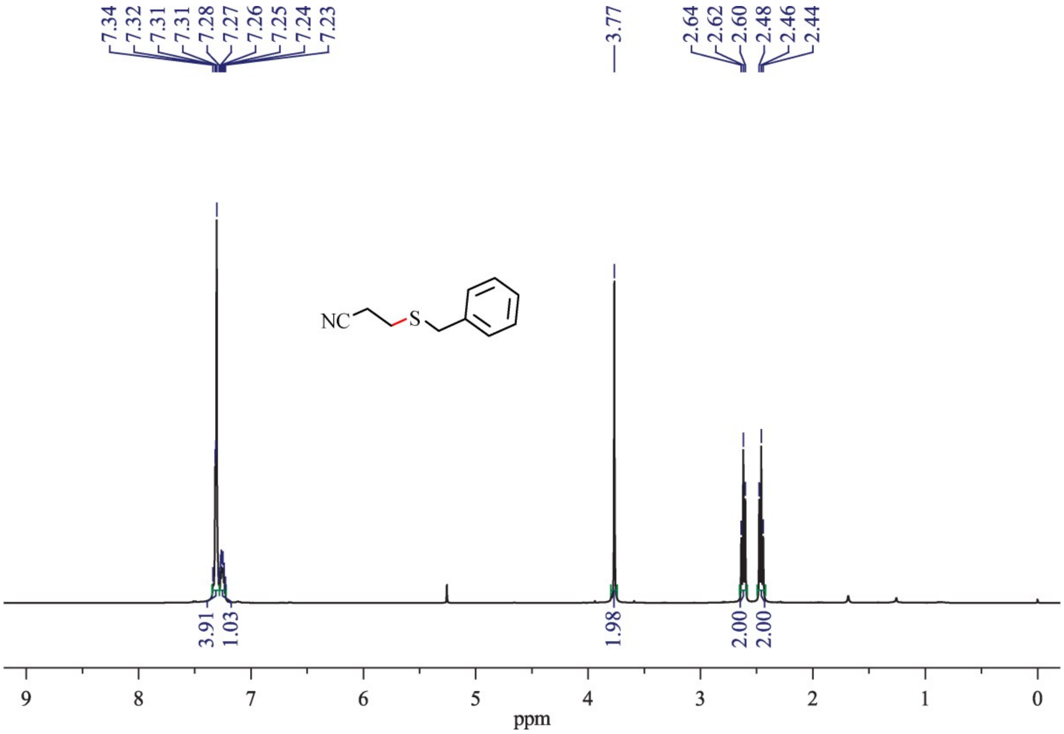


Fig. S26 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the compound **3j**.

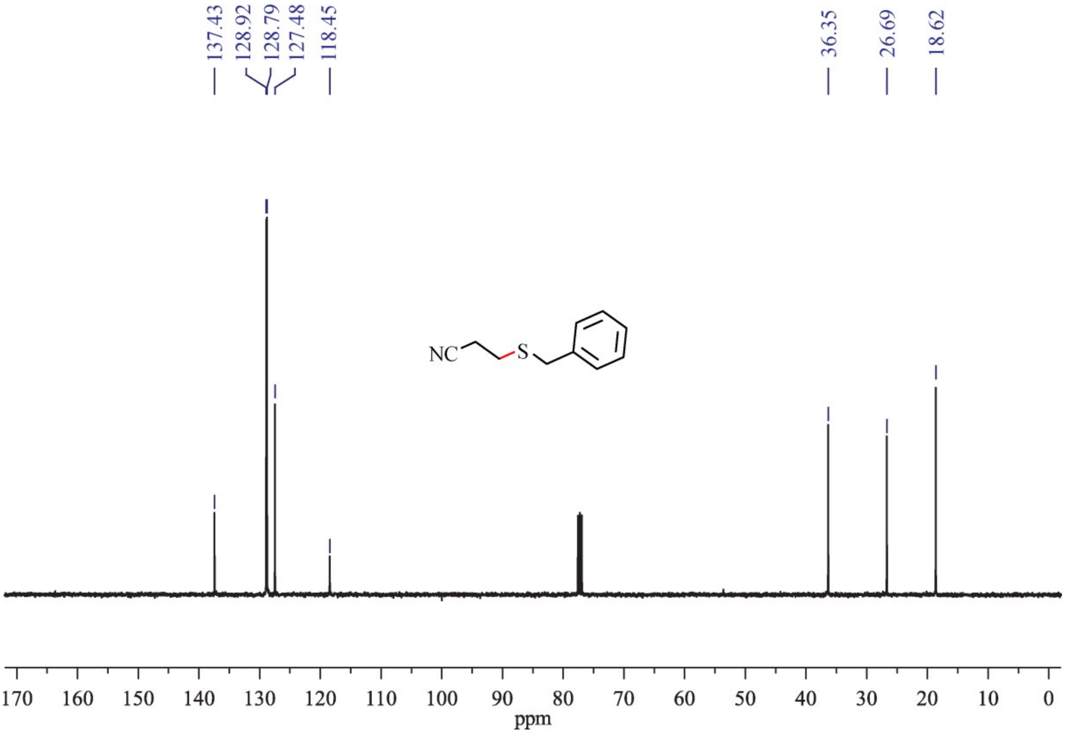


Fig. S27 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of the compound **3j**.

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