Supplementary Information (SI) for Journal of Materials Chemistry A.

Naphthalenediimide-based donor-acceptor COFs with low exciton binding energy toward sunlight-driven synthesis of multisubstituted olefins and sulfoxides

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Supplementary Methods:

General methods

All air- and moisture-sensitive solutions and chemicals were handled under an argon atmosphere. Anhydrous solvents were purchased from Sigma-Aldrich and used without further purification. Unless otherwise stated, all reagents were commercially available and used as received without further purification. Chemicals were obtained from Sigma-Aldrich, Acros, TCI and Alfa-Aesar. TLC was performed with Merck TLC Silica gel60 F_{254} plates with detection under UV light at 254 nm. Silica gel (200-300 mesh, Qingdao) was used for flash chromatography. Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Bruker Avance III 400 at 400 MHz. Carbon-13 nuclear magnetic resonance (^{13}C-NMR) was recorded on Bruker Avance III 400 spectrometer at 100 MHz. Chemical shifts were reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants were reported in hertz.

Powder X-ray diffraction (XRD) measurements was recorded on a Bruker D8 ADVANCE X-Ray diffractometer at room temperature using a graphite monochromator Cu-target tube. UV-Vis spectra were performed on a Varian Cary 500 UV–Vis spectrophotometer. Thermostability of materials were performed on a Mettler Toledo TGA2 thermogravimetric system at N_2 atmosphere from 30 to 800 °C with a ramp rate of 10 °C/min. The electrochemical measurements were carried out using a Princeton 2273 electrochemical workstation. Fourier transform infrared (IR) spectra have been recorded on a Nicolet iS50 spectrometer using KBr disks dispersed with material powder. Scanning electron microscopy (SEM) images were obtained using an Thermo Fisher Quattro S. Transmission electron microscopy (TEM) images were obtained using a JEM-1400 with the accelerating voltage of 100 kV. BET surface area was measured at 77 K with a Micromeritics ASAP 2020 adsorption instrument. Photoluminescence spectra and photoluminescence lifetime were made with an Edinburgh Instrument FLS 980 luminescence spectrometer.

Electrochemical Measurements

COF powder (10 mg) was ground with poly(vinylidene fluoride) (4 mg) and then ultrasonically dispersed in 3 mL of acetone. The resultant slurry was then drop-casted onto indium tin oxide (ITO) glass with an area of 0.5 × 0.5 cm^2. A Pt wire (counter electrode), a Ag/AgCl electrode (reference electrode), and a coated ITO conductive glass (working electrode) were assembled into a three-electrode system with 0.2 M Na_2SO_4 aqueous solution used as the electrolyte. The Mott-Schottky plots were collected in dark at different frequencies. The photocurrent measurements were conducted under the irradiation of a 300 W xenon lamp with a 420 nm cut-off filter under a nitrogen- or oxygen-saturated atmosphere.

Structural modeling of SF-COF-1 and SF-COF-2

Structural modeling of COFs were generated using the Materials Studio (ver. 7.0) suite of programs. Optimization of molecular geometry was performed with MS DMol3 module. The initial lattice was created by starting with the space group P6/m. The a and b lattice parameters were estimated according to the center to center distance between the opposite sides hexagon of the COFs. The constructed model were optimized using the Forcite module (Universal force fields, Ewald summations). Then the calculated PXRD pattern was generated with the Reflex Plus module. Finally, Pawley refinement was applied for profile fitting, producing the refined PXRD profile. A staggered arrangement of COFs were also constructed using similar to the above method wherein the stacked units were offset by a/2 and b/2. Comparison of the observed and the simulated PXRD patterns suggested that the preferable structures of COFs are the eclipsed arrangement.

DFT Computational details

All of the calculations were investigated with the Gaussian 16 software package. Structural optimizations and electronic properties were performed using the B3LYP functional with 6-311G(d, p) basis set (empirical dispersion correction GD3(BJ)). Calculations of frequency were accomplished at the parallel level of the theory (no imaginary frequency) to confirm the optimized-geometries as true minima.

Procedure and characterization for the oxidation of sulfides to sulfoxides and photocatalytic synthesis of multisubstituted olefins.

General Procedure A: the oxidation of sulfides to sulfoxides.

An oven-dried 10 mL Schlenk tube equipped with a stir bar was charged with sulfides (0.4 mmol), SF-COF (16.0 mg), and methanol (4 mL). The reaction system was then exposed to O_2 and stirred at room temperature for a period of 24 - 48 hours, while being irradiated by a 60 W white LED at a distance of 15 cm. Once the reaction was complete, the mixture was filtered and concentrated *in vacuo*. The crude products were purified by column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10:1→3:1) to give the corresponding sulfoxide products **2a-2m**.

General Procedure B: synthesis of multisubstituted olefins.

In a dry 10 mL Schlenk tube equipped with a stirring bar, β-dicarbonyl compounds (0.4 mmol), ammonium thiocyanate (1.2 mmol), SF-COF (10 mg), and acetonitrile (4 mL) were added under an oxygen atmosphere. The mixture was subsequently irradiated under a 60 W blue LED at a distance of 10 cm while being stirred for 3 hours at room temperature. Once the reaction had been completed, the mixture was diluted with water and ethyl acetate. The layers were subsequently separated, and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with saturated brine solution (20 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude products were purified by column chromatography on silica gel (eluting with petroleum ether : ethyl acetate = 10:1→7:1) to give the corresponding multisubstituted olefins **5a-5q**.

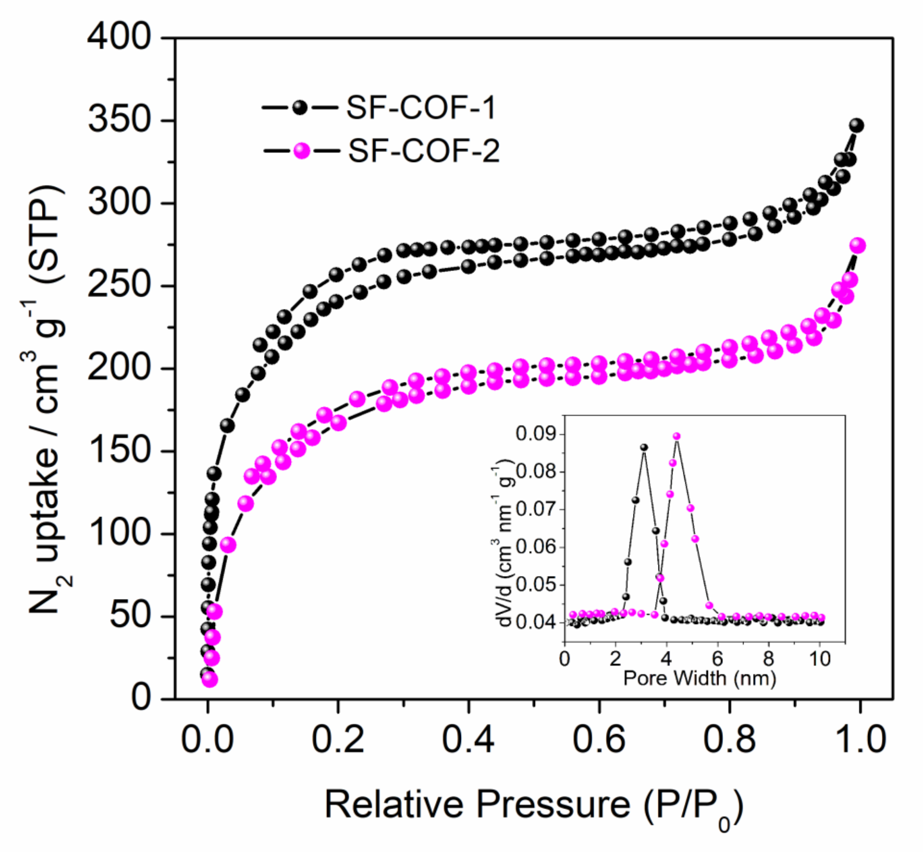


Figure S1. nitrogen adsorption-desorption isotherm curves for SF-COF-1 and SF-COF-2 measured at 77 K (the pore size distribution profile is presented in the inset).

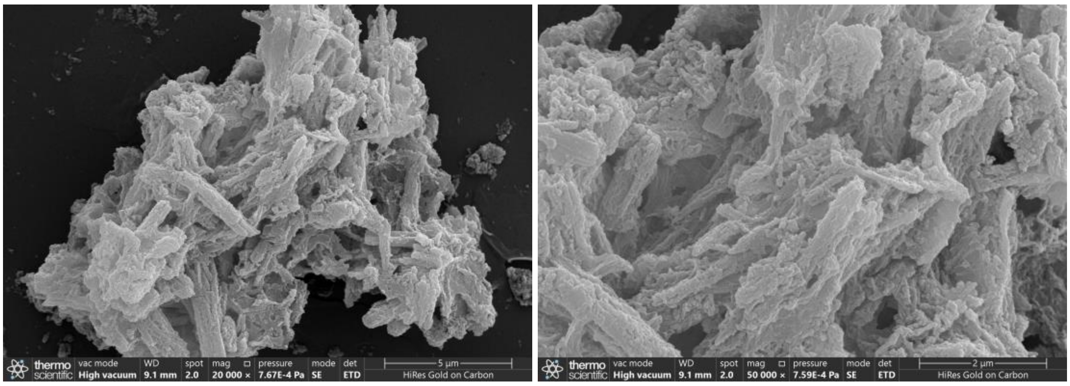


Figure S2. SEM images of the SF-COF-1.

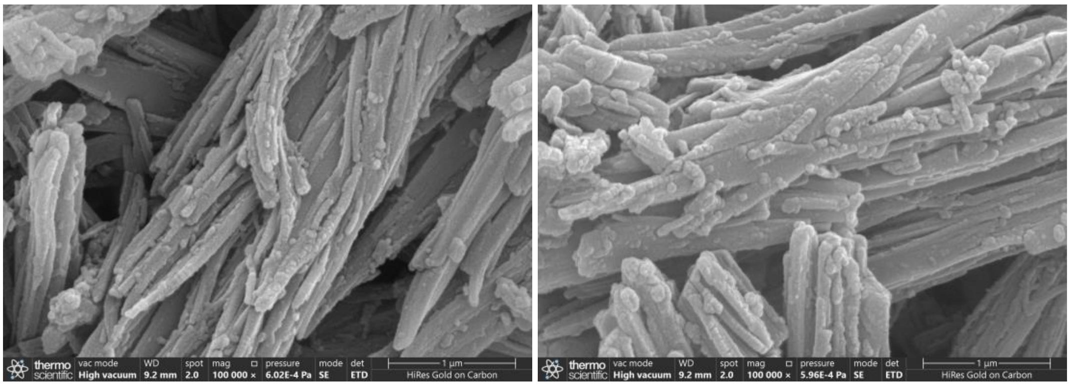


Figure S3. SEM images of the SF-COF-2.

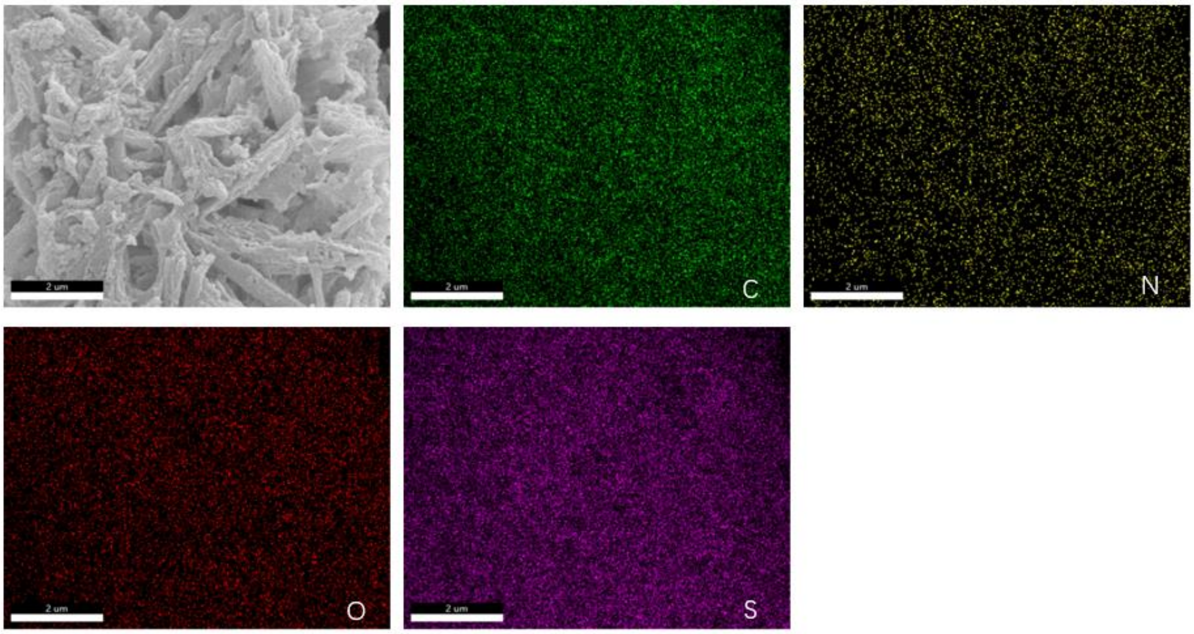


Figure S4. Elemental mapping images of SF-COF-1.

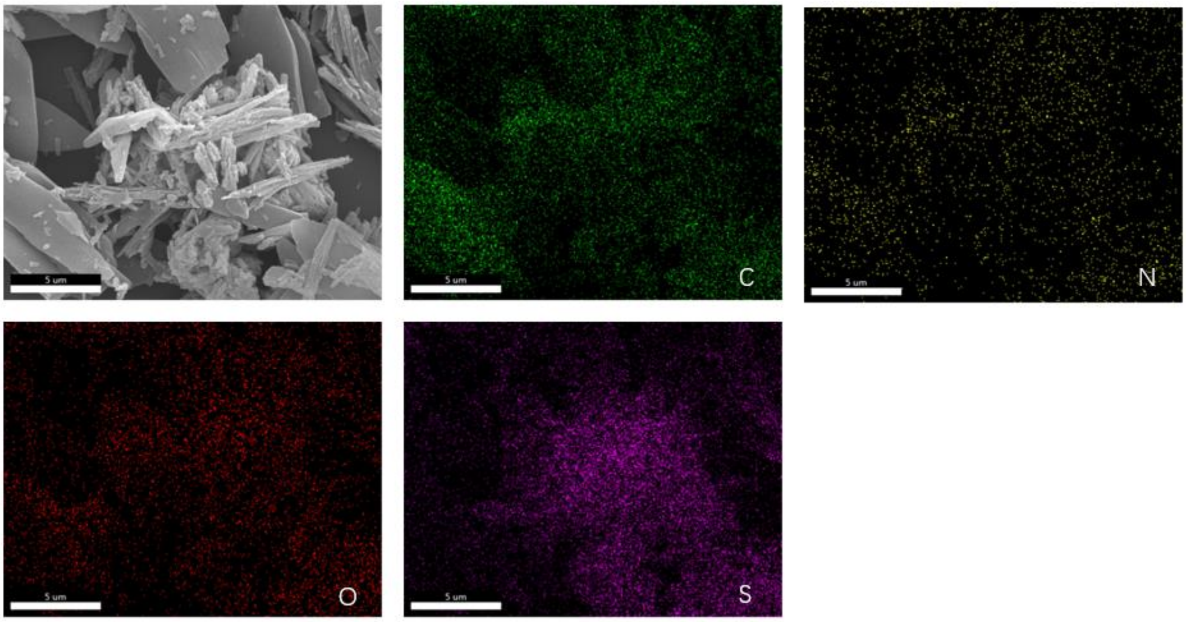


Figure S5. Elemental mapping images of SF-COF-2.

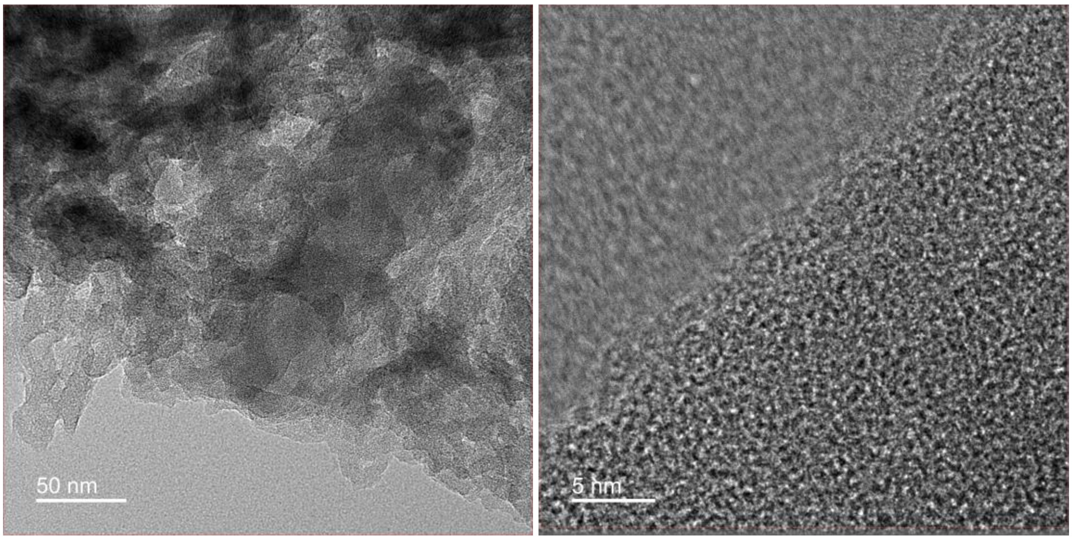


Figure S6. TEM images of the SF-COF-1.

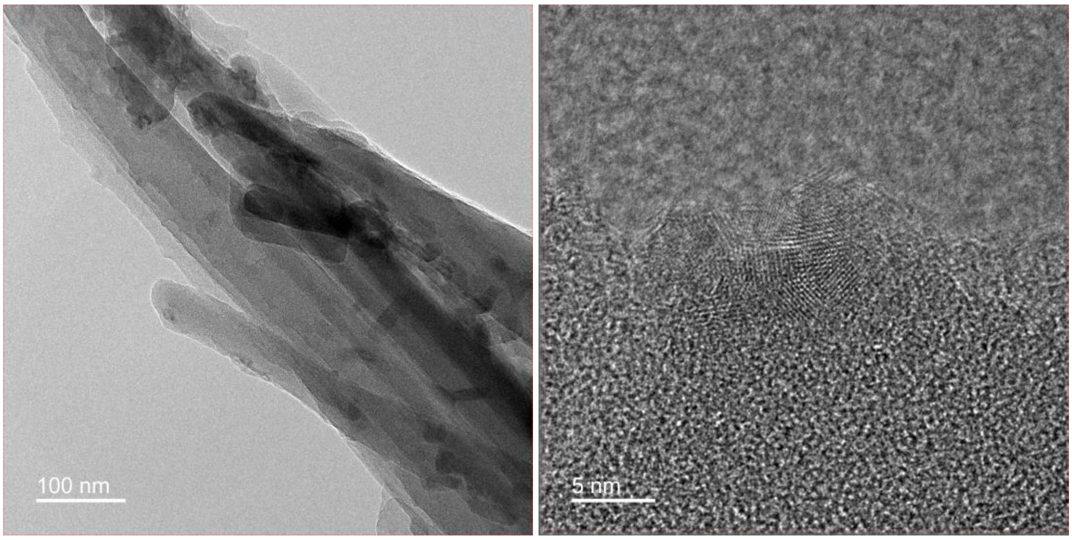


Figure S7. TEM images of the SF-COF-2.

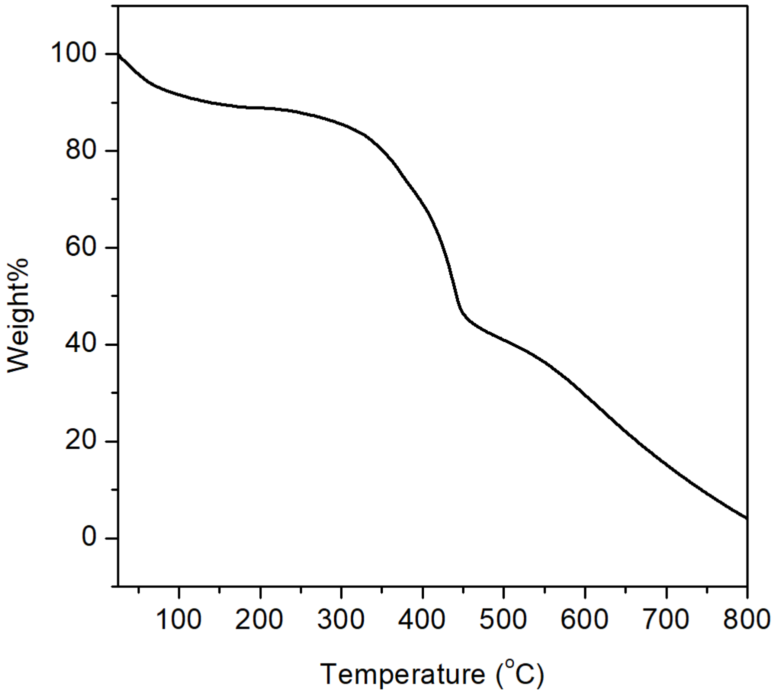


Figure S8. TGA curve of SF-COF-1.

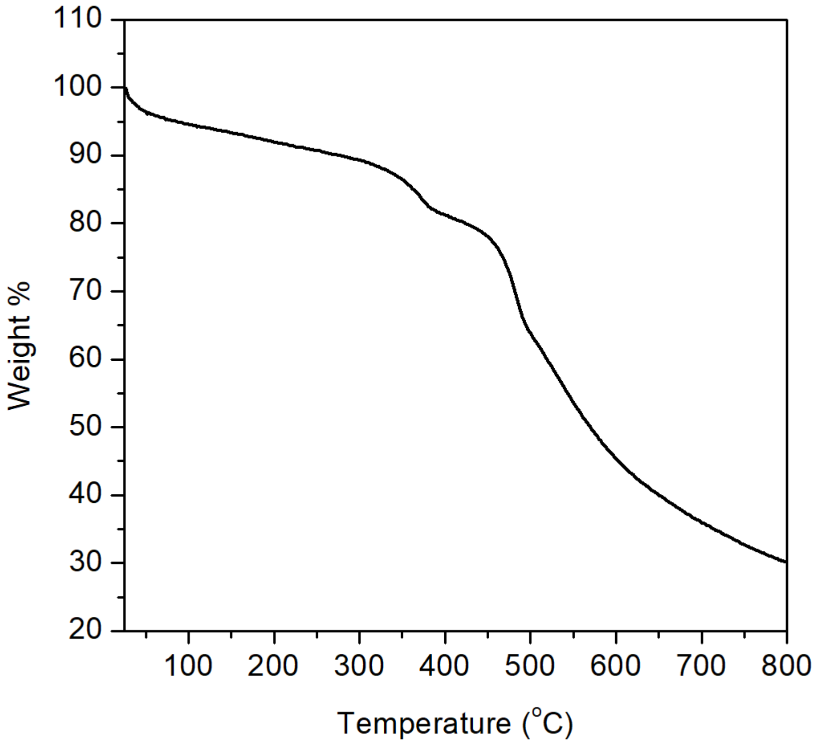


Figure S9. TGA curve of SF-COF-2

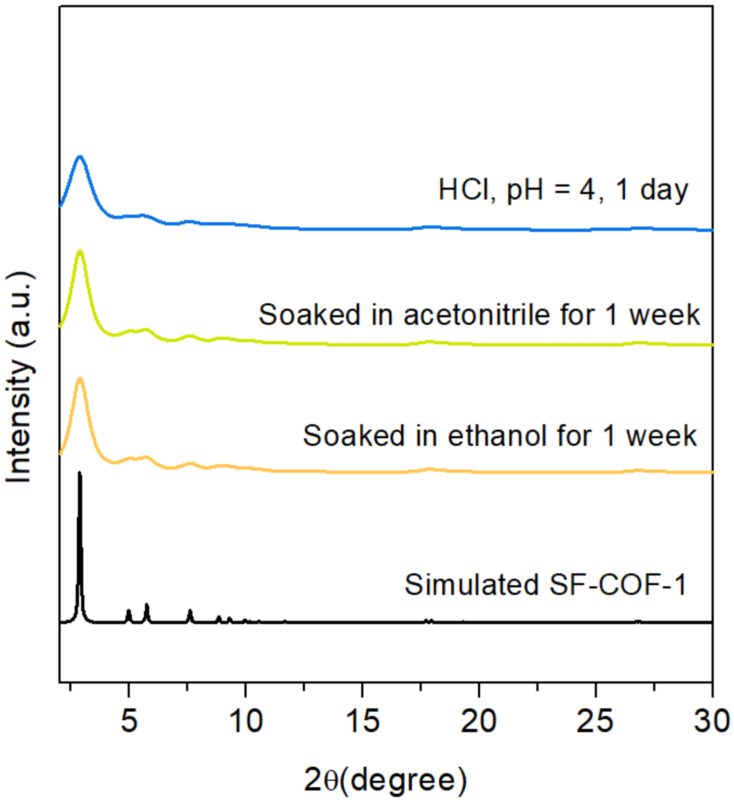


Figure S10. PXRD patterns of SF-COF-1 after being treated in different conditions.

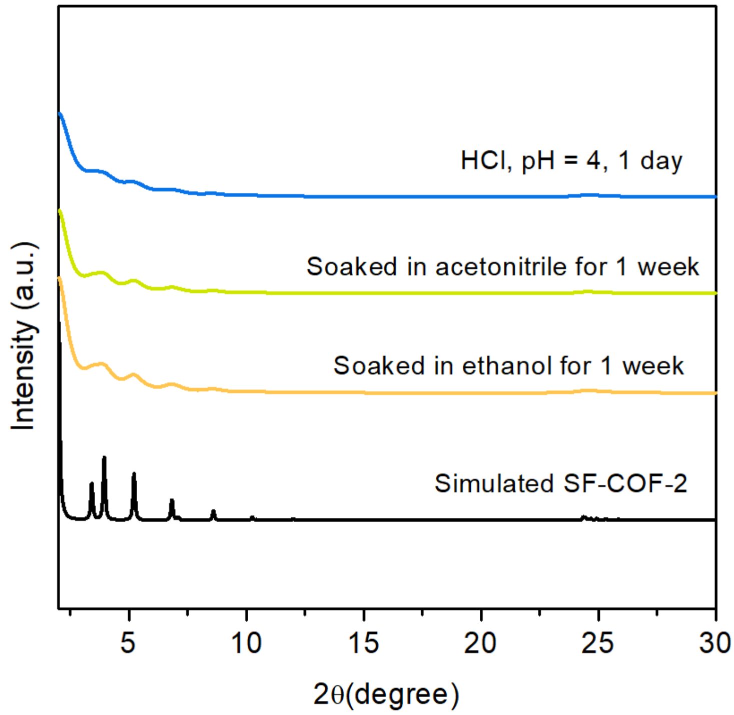


Figure S11. PXRD patterns of SF-COF-2 after being treated in different conditions.

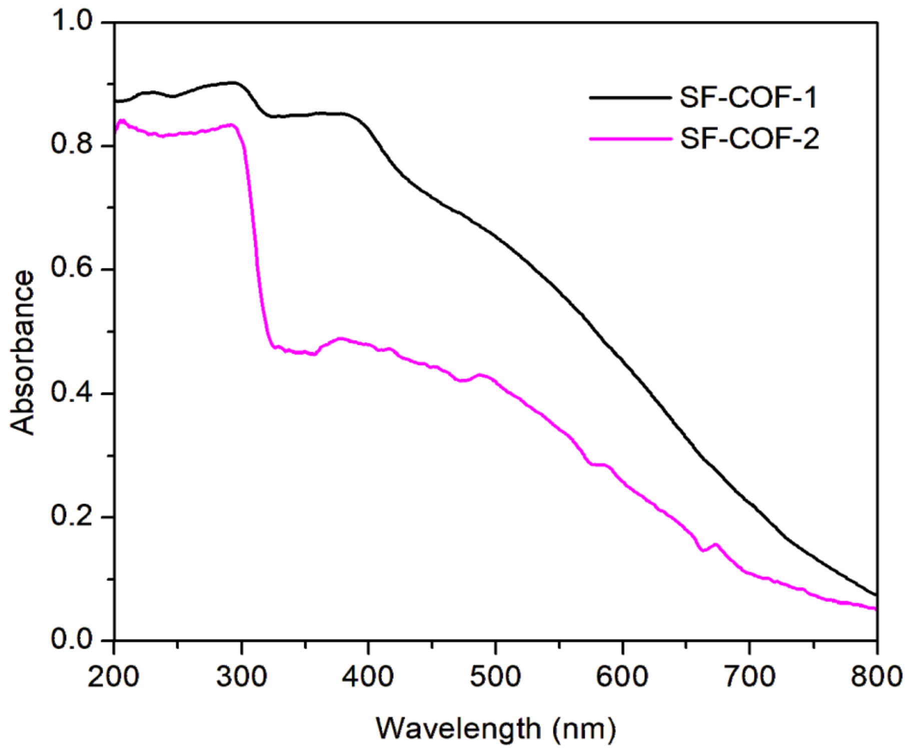


Figure S12. Solid state UV−Vis spectra of SF-COF-1 and SF-COF-2.

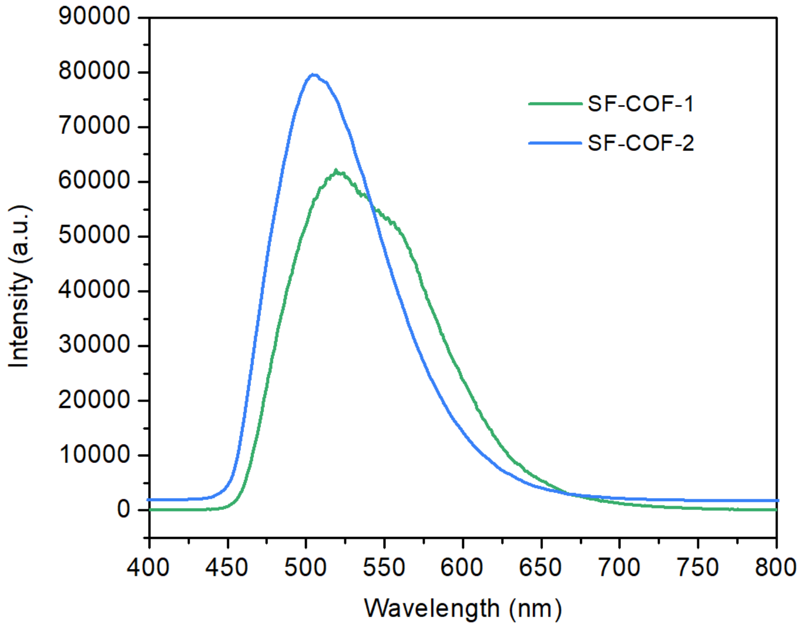


Figure S13. Solid-state fluorescent emission spectra of SF-COF-1 and SF-COF-2.

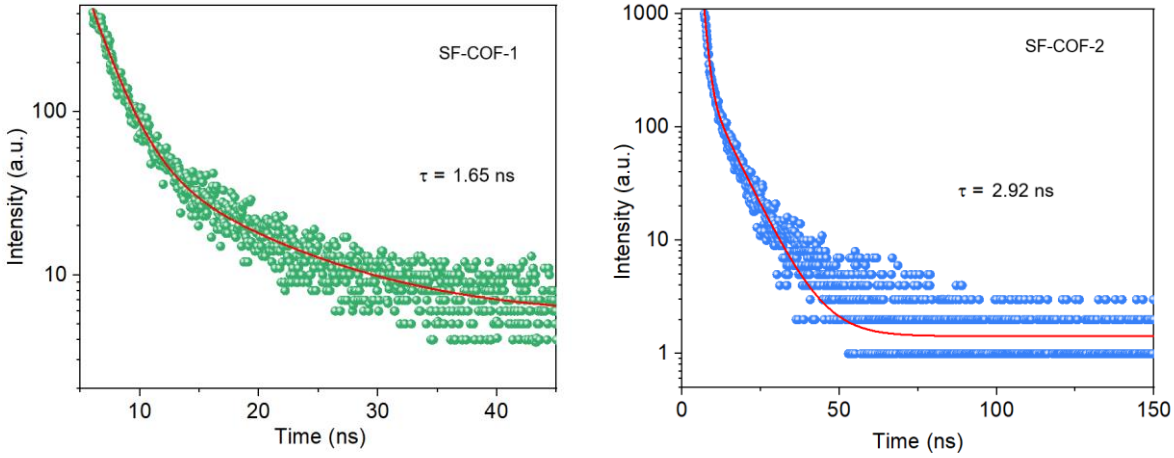


Figure S14. Fluorescence lifetime decay curves of SF-COF-1 and SF-COF-2.

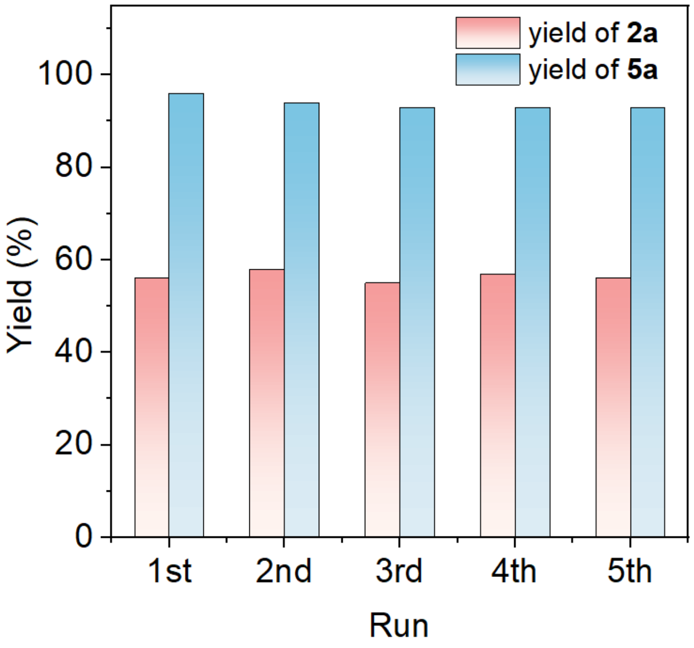


Figure S15. Cycle performance in synthesizing sulfoxide **2a** and multisubstituted olefin **5a** with photocatalyst SF-COF-2.

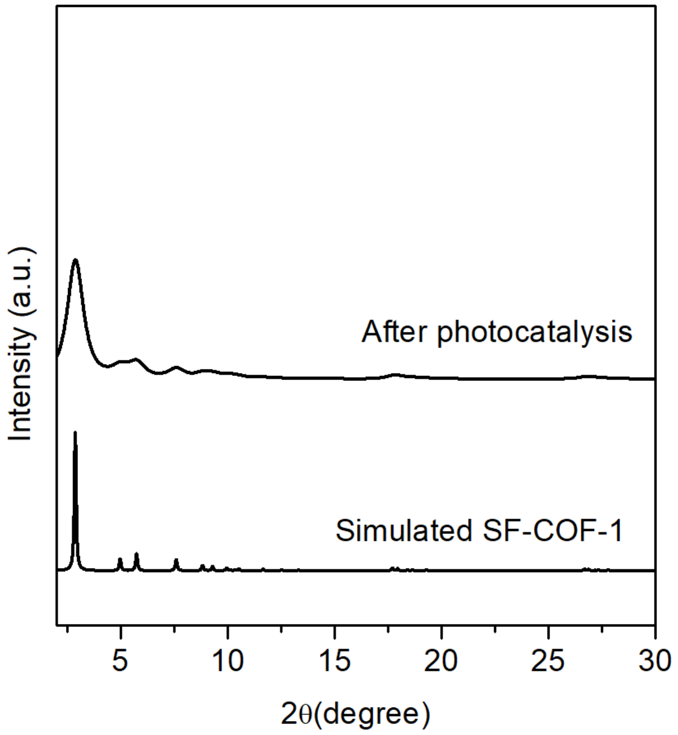


Figure S16. The PXRD patterns of SF-COF-1 after photocatalysis.

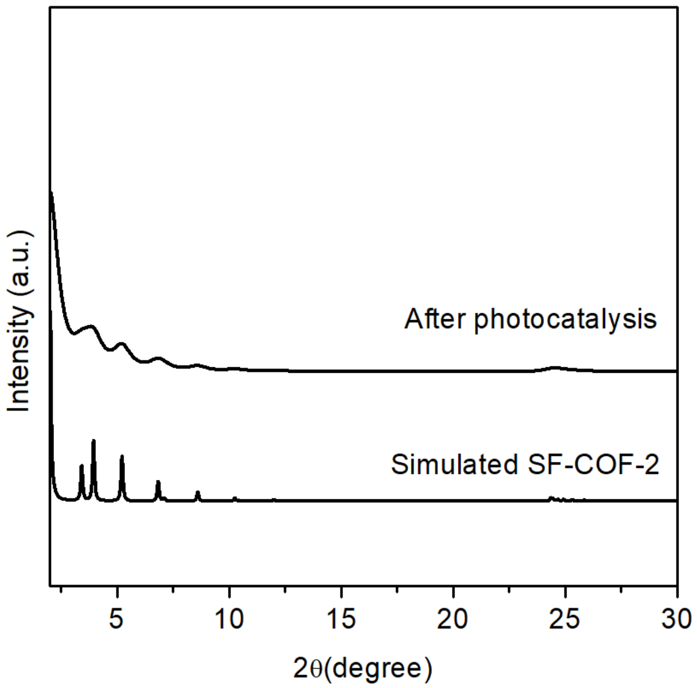


Figure S17. The PXRD patterns of SF-COF-2 after photocatalysis.

Figure S18. Experimental setup for photocatalytic oxidation of thioethers under outdoor

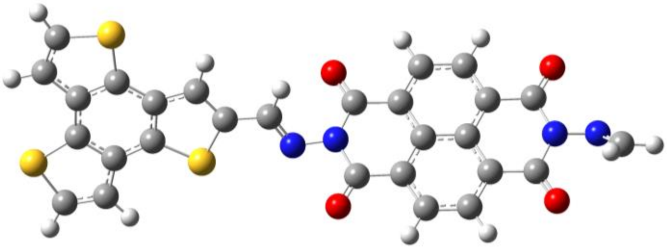


Figure S19. The optimized structural fragment of SF-COF-1. H: white; C: gray; N: blue; O: red; S: yellow.

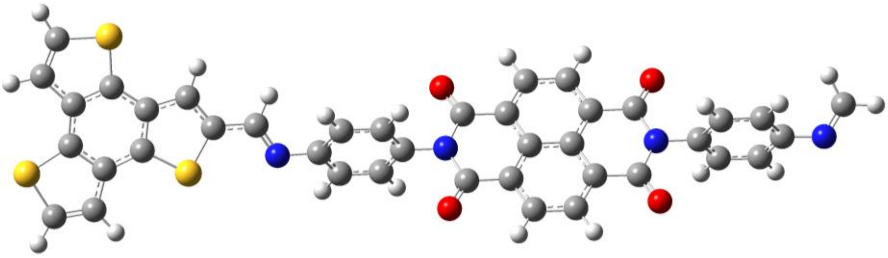
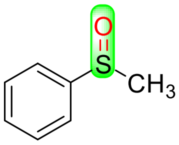


Figure S20. The optimized structural fragment of SF-COF-2. H: white; C: gray; N: blue; O: red; S: yellow.

Product Characterization:

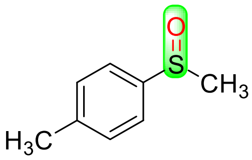
(methylsulfinyl)benzene (2a) :



The reaction was carried out in accordance with General Procedure A, using methyl phenyl sulfide (0.4 mmol) as the substrate, O_2 as a source of oxygen and methanol as the solvent. The crude material was purified by flash chromatography on silica gel (eluted with hexanes: ethyl acetate = 10:1→3:1) to give the product **2a** (53.28 mg, 95 % yield) as a yellow oil. The characterization data for this compound match the literature data.[1]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67-7.64 (m, 2H), 7.54 – 7.50 (m, 3H), 2.74 – 2.72 (m, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.2, 130.7, 129.0, 123.1, 43.6 ppm.

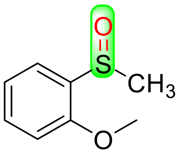
1-methyl-4-(methylsulfinyl)benzene (2b) :



The reaction was carried out in accordance with General Procedure A, using methyl *p*-tolyl sulphide (0.4 mmol) as the substrate, O_2 as a source of oxygen and methanol as the solvent. The crude material was purified by flash chromatography on silica gel (eluted with hexanes : ethyl acetate = 10:1 → 3:1) to give the product **2b** (56.14 mg, 91 % yield) as a colorless oil. The characterization data for this compound match the literature data.[1]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 7.2 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.68 (s, 3H), 2.39 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.5, 141.5, 130.0, 123.5, 44.0, 21.4 ppm.

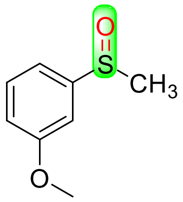
1-methoxy-2-(methylsulfinyl)benzene (2c) :



The reaction was carried out in accordance with General Procedure A, using 2-methoxythioanisol (0.4 mmol) as the substrate, O_2 as a source of oxygen and methanol as the solvent. The crude material was purified by flash chromatography on silica gel (eluted with hexanes : ethyl acetate = 10:1 → 3:1) to give the product **2c** (64.69 mg, 95 % yield) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 7.6 Hz, 1H), 7.18 (dd, *J* = 2.8, 1.6 Hz, 1H), 7.06 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.94 (ddd, *J* = 8.0, 3.6, 0.8 Hz, 1H), 3.80 (s, 3H), 2.65 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.6, 147.3, 130.4, 117.5, 115.6, 108.0, 55.7, 44.1 ppm.

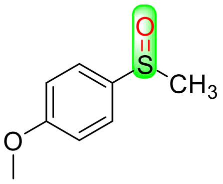
1-methoxy-3-(methylsulfinyl)benzene (2d) :



The reaction was carried out in accordance with General Procedure A, using 3-methoxythioanisole (0.4 mmol) as the substrate, O_2 as a source of oxygen and methanol as the solvent. The crude material was purified by flash chromatography on silica gel (eluted with hexanes : ethyl acetate = 10:1 → 3:1) to give the product **2d** (61.28 mg, 90 % yield) as a yellow oil. The characterization data for this compound match the literature data.[2]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.37 (m, 1H), 7.24 (dt, *J* = 4.4, 1.6 Hz, 1H), 7.12 (ddd, *J* = 7.6, 2.0, 0.8 Hz, 1H), 7.00 (ddd, *J* = 8.4, 3.6, 1.2 Hz, 1H), 3.85 (d, *J* = 1.2 Hz, 3H), 2.71 (d, *J* = 1.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.5, 147.2, 130.3, 117.4, 115.5, 108.0, 55.6, 44.0 ppm.

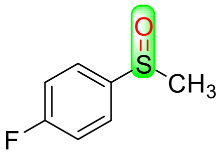
1-methoxy-4-(methylsulfinyl)benzene (2e) :



The reaction was carried out in accordance with General Procedure A, using 4-methoxythioanisole (0.4 mmol) as the substrate, O_2 as a source of oxygen and methanol as the solvent. The crude material was purified by flash chromatography on silica gel (eluted with hexanes : ethyl acetate = 10:1 → 3:1) to give the product **2e** (67.41 mg, 99 % yield) as a yellow oil. The characterization data for this compound match the literature data.[1]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.58 (m, 2H), 7.06 – 7.02 (m, 2H), 3.86 (s, 3H), 2.71 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.0, 136.5, 125.6, 114.9, 55.6, 44.0 ppm.

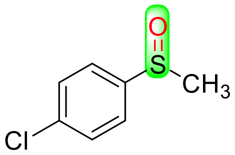
1-fluoro-4-(methylsulfinyl)benzene (2f) :



The reaction was carried out in accordance with General Procedure A, using 4-fluorothioanisole (0.4 mmol) as the substrate, O_2 as a source of oxygen and methanol as the solvent. The crude material was purified by flash chromatography on silica gel (eluted with hexanes : ethyl acetate = 10:1 → 3:1) to give the product **2f** (60.12 mg, 95 % yield) as a yellow oil.The characterization data for this compound match the literature data.[2]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (ddd, *J* = 8.8, 6.4, 1.6 Hz, 2H), 7.21 (td, *J* = 10.0, 1.2 Hz, 2H), 2.70 (d, *J* = 1.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.6, 163.1, 141.24, 141.20, 125.9, 125.8, 116.8, 116.6, 44.2 ppm.

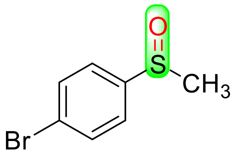
1-chloro-4-(methylsulfinyl)benzene (2g) :



The reaction was carried out in accordance with General Procedure A, using 4-chlorothioanisole (0.4 mmol) as the substrate, O_2 as a source of oxygen and methanol as the solvent. The crude material was purified by flash chromatography on silica gel (eluted with hexanes : ethyl acetate = 10:1 → 3:1) to give the product **2g** (58.68 mg, 84 % yield) as a yellow oil.The characterization data for this compound match the literature data.[2]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.50 (m, 2H), 7.45 – 7.42 (m, 2H), 2.65 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.3, 137.3, 129.7, 125.0, 44.1 ppm.

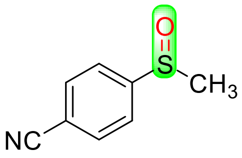
1-bromo-4-(methylsulfinyl)benzene (2h) :



The reaction was carried out in accordance with General Procedure A, using 4-bromothioanisole (0.4 mmol) as the substrate, O_2 as a source of oxygen and methanol as the solvent. The crude material was purified by flash chromatography on silica gel (eluted with hexanes : ethyl acetate = 10:1 → 10:1) to give the product **2h** (82.38 mg, 94 % yield) as a yellow oil. The characterization data for this compound match the literature data.[1]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 – 7.66 (m, 2H), 7.55 – 7.51 (m, 2H), 2.72 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.0, 132.7, 125.6, 125.2, 44.1 ppm.

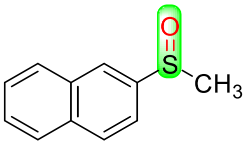
4-(methylsulfinyl)benzonitrile (2i) :



The reaction was carried out in accordance with General Procedure A, using 4-(methylthio)benzonitrile (0.4 mmol) as the substrate, O_2 as a source of oxygen and methanol as the solvent. The crude material was purified by flash chromatography on silica gel (eluted with hexanes : ethyl acetate = 10:1 → 3:1) to give the product **2i** (42.29 mg, 64 % yield) as a white solid. The characterization data for this compound match the literature data.[3]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.82 (m, 2H), 7.78 – 7.76 (m, 2H), 2.76 (d, *J* = 0.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.5, 133.0, 124.3, 117.7, 114.9, 43.8 ppm.

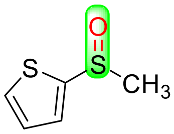
2-(methylsulfinyl)naphthalene (2j) :



The reaction was carried out in accordance with General Procedure A, using 2- (methylthio) naphthalene (0.4 mmol) as the substrate, O_2 as a source of oxygen and methanol as the solvent. The crude material was purified by flash chromatography on silica gel (eluted with hexanes : ethyl acetate = 10:1 → 3:1) to give the product **2j** (60.88 mg, 80 % yield) as a white solid. The characterization data for this compound match the literature data.[4]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (d, *J* = 1.6 Hz, 1H), 8.00 – 7.89 (m, 3H), 7.61 - 7.57(m , 3H), 2.79 (d, *J* = 1.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.9, 134.6, 133.1, 129.7, 128.7, 128.2, 127.9, 127.5, 124.2, 119.6, 43.9 ppm.

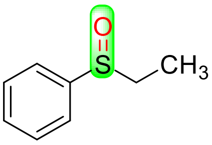
2-(methylsulfinyl)thiophene (2k) :



The reaction was carried out in accordance with General Procedure A, using 2-(methylthio)thiophene (0.4 mmol) as the substrate, O_2 as a source of oxygen and methanol as the solvent. The crude material was purified by flash chromatography on silica gel (eluted with hexanes : ethyl acetate = 10:1 → 3:1) to give the product **2k** (69.27 mg, 91 % yield) as a colorless oil. The characterization data for this compound match the literature data.[5]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.48 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.11 (dd, *J* = 4.8, 3.6 Hz, 1H), 2.92 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.3, 130.9, 129.4, 127.4, 44.5 ppm.

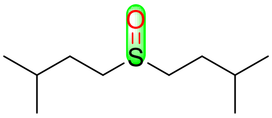
(ethylsulfinyl)benzene (2l) :



The reaction was carried out in accordance with General Procedure A, using ethyl phenyl sulfide (0.4 mmol) as the substrate, O_2 as a source of oxygen and methanol as the solvent. The crude material was purified by flash chromatography on silica gel (eluted with hexanes : ethyl acetate = 10:1 → 3:1) to give the product **2l** (66.97 mg, 88 % yield) as a yellow oil. The characterization data for this compound match the literature data.[4]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.57 (m, 2H), 7.52 – 7.45 (m, 3H), 2.93 - 2.84 (m , 1H), 2.79 - 2.70 (m , 1H), 1.17 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.4, 131.0, 129.2, 124.3, 50.4, 6.0 ppm.

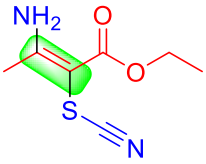
1-(isopentylsulfinyl)-3-methylbutane (2m) :



The reaction was carried out in accordance with General Procedure A, using isoamyl sulfide (0.4 mmol) as the substrate, O_2 as a source of oxygen and methanol as the solvent. The crude material was purified by flash chromatography on silica gel (eluted with hexanes : ethyl acetate = 10:1 → 3:1) to give the product **2m** (73.06 mg, 96 % yield) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.56 (dd, *J* = 12.4, 5.6 Hz, 4H), 1.67 – 1.45 (m, 6H), 0.84 (dd, *J* = 6.4, 4.0 Hz, 12H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 50.3, 31.0, 27.6, 22.3, 22.1 ppm.

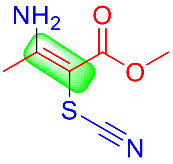
ethyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5a) :



The reaction was performed following the General Procedure B with ethyl acetoacetate (0.4 mmol), NH_4SCN (1.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 10:1 → 7:1) to give the product **5a** (67.79 mg, 91 % yield) as a yellow solid. The characterization data for this compound match the literature data.[6]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.27 (s, 1H), 5.70 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 1.34 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.6, 168.5, 113.7, 76.0, 61.0, 23.6, 14.5 . ppm.

methyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5b) :

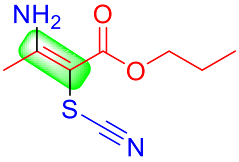


The reaction was performed following the General Procedure B with methyl acetoacetate (0.4 mmol), NH_4SCN (1.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 10:1 → 7:1) to give the product **5b**

(66.13 mg, 96 % yield) as a white solid. The characterization data for this compound match the literature data.[7]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.29 (s, 1H), 5.61 (s, 1H), 3.79 (s, 3H), 2.40 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.8, 168.5, 113.3, 76.0, 52.0, 23.5 ppm.

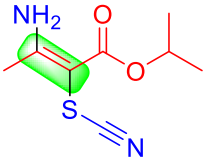
propyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5c) :



The reaction was performed following the General Procedure B with propyl acetoacetate (0.4 mmol), NH_4SCN (1.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 10:1 → 7:1) to give the product **5c** (75.30 mg, 94 % yield) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.21 (s, 1H), 5.58 (s, 1H), 4.06 (t, J = 6.8 Hz, 2H), 2.32 (s, 3H), 1.68 (dt, J = 13.2, 6.4 Hz, 2H), 0.95 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.6, 168.4, 113.6, 76.3, 66.5, 23.5, 22.3, 10.6 ppm.

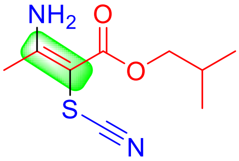
isopropyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5d) :



The reaction was performed following the General Procedure B with isopropyl acetoacetate (0.4 mmol), NH_4SCN (1.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 10:1 → 7:1) to give the product **5d** (77.70 mg, 97 % yield) as a white solid. The characterization data for this compound match the literature data.[8]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.27 (s, 1H), 5.61 (s, 1H), 5.08 - 4.99 (m , 1H), 2.37 (s, 3H), 1.33 (s, 3H), 1.31 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.12, 168.09, 113.6, 76.6, 68.4, 23.6, 22.1 ppm.

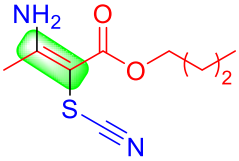
isobutyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5e) :



The reaction was performed following the General Procedure B with isobutyl 3-oxobutanoate (0.4 mmol), NH_4SCN (1.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 10:1 → 7:1) to give the product **5e** (84.00 mg, 98 % yield) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.27 (s, 1H), 5.65 (s, 1H), 3.94 (d, *J* = 6.8 Hz, 2H), 2.39 (s, 3H), 2.05 – 2.00 (m, 1H), 1.01 (d, *J* = 6.8 Hz, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.6, 168.4, 113.7, 76.3, 71.0, 28.0, 23.5, 19.3 ppm.

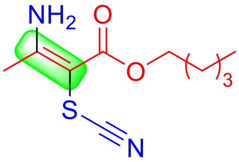
butyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5f) :



The reaction was performed following the General Procedure B with butyl 3-oxobutanoate (0.4 mmol), NH_4SCN (1.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 10:1 → 7:1) to give the product **5f** (77.14 mg, 90 % yield) as a yellow solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.27 (s, 1H), 5.69 (s, 1H), 4.16 (t, *J* = 6.4 Hz, 2H), 2.38 (s, 3H), 1.72 – 1.68 (m, 2H), 1.46 (d, *J* = 7.6 Hz, 1H), 0.95 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.6, 168.4, 113.7, 76.1, 64.8, 30.9, 23.6, 19.3, 13.9 ppm.

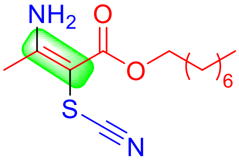
pentyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5g) :



The reaction was performed following the General Procedure B with pentyl 3-oxobutanoate (0.4 mmol), NH_4SCN (1.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 10:1 → 7:1) to give the product **5g** (89.50 mg, 98 % yield) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 5.84 (s, 1H), 4.13 (t, *J* = 6.4 Hz, 2H), 2.36 (s, 3H), 1.72 – 1.68 (m, 2H), 1.40 – 1.34 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.59, 168.55, 113.7, 75.8, 65.0, 28.5, 28.2, 23.4, 22.4, 14.1 ppm.

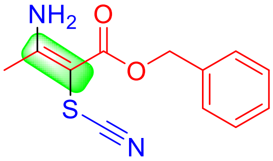
octyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5h) :



The reaction was performed following the General Procedure B with octyl 3-oxobutanoate (0.4 mmol), NH_4SCN (1.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 10:1 → 7:1) to give the product **5h** (97.34 mg, 90 % yield) as a yellow solid.The characterization data for this compound match the literature data.[7]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 5.82 (s, 1H), 4.13 (t, *J* = 6.8 Hz, 2H), 2.37 (s, 3H), 1.73 - 1.66 (m, 2H), 1.44 – 1.19 (m, 12H), 0.88 – 0.84 (m, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.6, 167.5, 112.7, 74.9, 64.1, 30.9, 28.30, 28.27, 27.8, 25.0, 22.4, 21.7, 13.2 ppm.

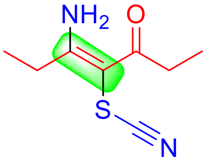
benzyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5i) :



The reaction was performed following the General Procedure B with benzyl 3-oxobutanoate (0.4 mmol), NH_4SCN (1.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 10:1 → 7:1) to give the product **5i** (92.33 mg, 92 % yield) as a colorless oil. The characterization data for this compound match the literature data.[7]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.29 (s, 1H), 7.44 (d, J = 8.0 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.34 – 7.29 (m, 1H), 5.62 (s, 1H), 5.24 (s, 2H), 2.41 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.8, 168.3, 136.4, 128.7, 128.1, 127.7, 113.5, 76.3, 66.5, 23.7 ppm.

(*E*)-5-amino-4-thiocyanatohept-4-en-3-one (5j) :

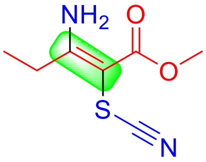


The reaction was performed following the General Procedure B with heptane-3,5-dione (0.4 mmol), NH_4SCN (1.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 10:1 → 7:1) to give the product **5j**

(69.80 mg, 88 % yield) as a white solid. The characterization data for this compound match the literature data.[6]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 11.14 (s, 1H), 6.04 (s, 1H), 2.89 (q, *J* = 7.2 Hz, 2H), 2.76 (q, *J* = 7.2 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 201.3, 173.8, 113.6, 86.1, 33.8, 29.9, 11.6, 9.0 ppm.

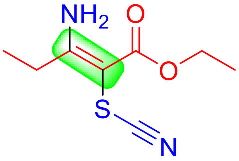
methyl (*E*)-3-amino-2-thiocyanatopent-2-enoate (5k) :



The reaction was performed following the General Procedure B with methyl 3-oxopentanoate (0.4 mmol), NH_4SCN (1.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 10:1 → 7:1) to give the product **5k** (70.03 mg, 94 % yield) as a yellow oil. The characterization data for this compound match the literature data.[8]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.32 (s, 1H), 5.66 (s, 1H), 3.73 (s, 3H), 2.69 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.3, 169.1, 113.9, 74.9, 52.1, 29.6, 11.9 ppm.

ethyl (*E*)-3-amino-2-thiocyanatopent-2-enoate (5l) :

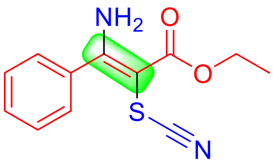


The reaction was performed following the General Procedure B with ethyl 3-oxopentanoate (0.4 mmol), NH_4SCN (1.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with petroleum ether: ethyl acetate = 10:1 → 7:1) to give the product **5l**

(76.90 mg, 96 % yield) as a white solid. The characterization data for this compound match the literature data.[6]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.36 (s, 1H), 5.72 (s, 1H), 4.22 (q, *J* = 6.8 Hz, 2H), 2.74 (q, *J* = 7.6 Hz, 2H), 1.34 (t, *J* = 6.8 Hz, 3H), 1.27 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.1, 168.8, 113.9, 75.2, 60.9, 29.7, 14.5, 12.0 ppm.

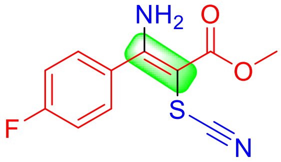
ethyl (*E*)-3-amino-3-phenyl-2-thiocyanatoacrylate (5m) :



The reaction was performed following the General Procedure B with ethyl 3-oxo-3-phenylpropanoate (0.4 mmol), NH_4SCN (1.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with petroleum ether: ethyl acetate = 10:1 → 7:1) to give the product **5m** (50.66 mg, 51 % yield) as awhite solid. The characterization data for this compound match the literature data.[9]

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.36 (s, 1H), 7.52 – 7.46 (m, 3H), 7.45 – 7.41 (m, 2H), 5.60 (s, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.7, 168.8, 136.9, 130.5, 128.9, 127.4, 114.2, 61.3, 14.5 ppm.

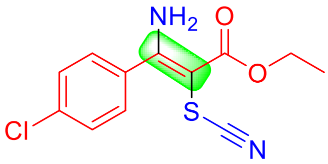
methyl (*E*)-3-amino-3-(4-fluorophenyl)-2-thiocyanatoacrylate (5n) :



The reaction was performed following the General Procedure B with methyl 3-(4-fluorophenyl)-3-oxopropanoate (0.4 mmol), NH_4SCN (1.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 10:1 → 7:1) to give the product **5n** (57.52 mg, 57 % yield) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.37 (s, 1H), 7.47 – 7.43 (m, 2H), 7.21 - 7.16 (m, 2H), 5.56 (s, 1H), 3.86 (d, *J* = 1.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.1, 168.9, 165.1, 162.6, 132.79, 132.76, 129.8, 129.7, 116.3, 116.1, 114.0, 52.5 ppm.

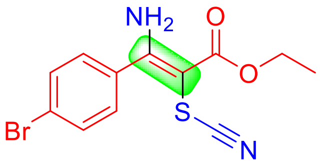
ethyl (*E*)-3-amino-3-(4-chlorophenyl)-2-thiocyanatoacrylate (5o) :



The reaction was performed following the General Procedure B with ethyl 3-(4-chlorophenyl)-3-oxopropanoate (0.4 mmol), NH_4SCN (1.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with petroleum ether: ethyl acetate = 10:1 → 7:1) to give the product **5o** (55.42 mg, 49 % yield) as a white solid.

1H NMR (400 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 7.48 – 7.46 (m, 2H), 7.38 (dd, *J* = 8., 1.6 Hz, 2H), 5.57 (s, 1H), 4.33 - 4.27 (m, 2H), 1.39 (td, *J* = 8.0, 1.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.6, 168.5, 136.7, 135.2, 129.3, 128.9, 113.9, 77.9, 61.4, 14.5 ppm.

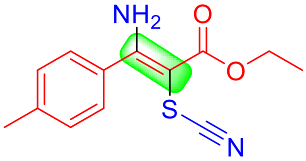
ethyl (*E*)-3-amino-3-(4-bromophenyl)-2-thiocyanatoacrylate (5p) :



The reaction was performed following the General Procedure B with ethyl 3-(4-bromophenyl)-3-oxopropanoate (0.4 mmol), NH_4SCN (1.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 10:1 → 7:1) to give the product **5p** (35.34 mg, 27 % yield) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.32 (s, 1H), 7.64 – 7.61 (m, 2H), 7.32 – 7.29 (m, 2H), 5.63 (s, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.6, 168.5, 135.6, 132.2, 129.1, 124.9, 113.9, 77.7, 61.4, 14.5 ppm.

ethyl (*E*)-3-amino-2-thiocyanato-3-(p-tolyl)acrylate (5q) :



The reaction was performed following the General Procedure B with ethyl 3-oxo-3-(*p*-tolyl)propanoate (0.4 mmol), NH_4SCN (1.2 mmol). The crude material was purified by flash chromatography on silica gel (eluted with petroleum ether : ethyl acetate = 10:1 → 7:1) to give the product **5q** (49.32 mg, 47 % yield) as a yellow oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 7.34 – 7.26 (m, 4H), 5.61 (s, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.38 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.9, 168.8, 140.8, 134.0, 129.5, 127.4, 114.3, 77.1, 61.2, 21.6, 14.5 ppm.

Supplementary references

[1] Maitra P K, Bhattacharyya S, Hickey N, et al. Self-Assembly of a Water-Soluble Pd16 Square Bicupola Architecture and Its Use in Aerobic Oxidation in Aqueous Medium[J]. *Journal of the American Chemical Society*, 2024, 146(22): 15301-15308.

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[5] Dai W, Shang S, Lv Y, et al. Highly chemoselective and enantioselective catalytic oxidation of heteroaromatic sulfides via high-valent manganese (IV)–Oxo cation radical oxidizing intermediates[J]. *ACS Catalysis*, 2017, 7(7): 4890-4895.

[6] Xu H, Xia S, Li C, et al. Programming tetrathiafulvalene-based covalent organic frameworks for promoted photoinduced molecular oxygen activation[J]. *Angewandte Chemie*, 2024, 136(29): e202405476.

[7] An W K, Xu X, Zheng S J, et al. EDOT-decorated covalent organic polymers as versatile metal-free photocatalysts for organic transformations[J]. *ACS Catalysis*, 2023, 13(14): 9845-9856.

[8] Bagad P K, Darole R S, Krishna G R, et al. Highly Selective C–N and C–S Dual Functionalization of 1, 3-Dicarbonyl Derivatives Using TBHP as an Oxidant[J]. *The Journal of Organic Chemistry*, 2024, 89(13): 9371-9380.

[9] Ali D, Panday A K, Choudhury L H. Hydrogen peroxide-mediated rapid room temperature metal-free C (sp^2)-H thiocyanation of amino pyrazoles, amino uracils, and enamines[J]. *The Journal of Organic Chemistry*, 2020, 85(21): 13610-13620.

NMR Spectra

Figure S21. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of (methylsulfinyl)benzene (2a) :

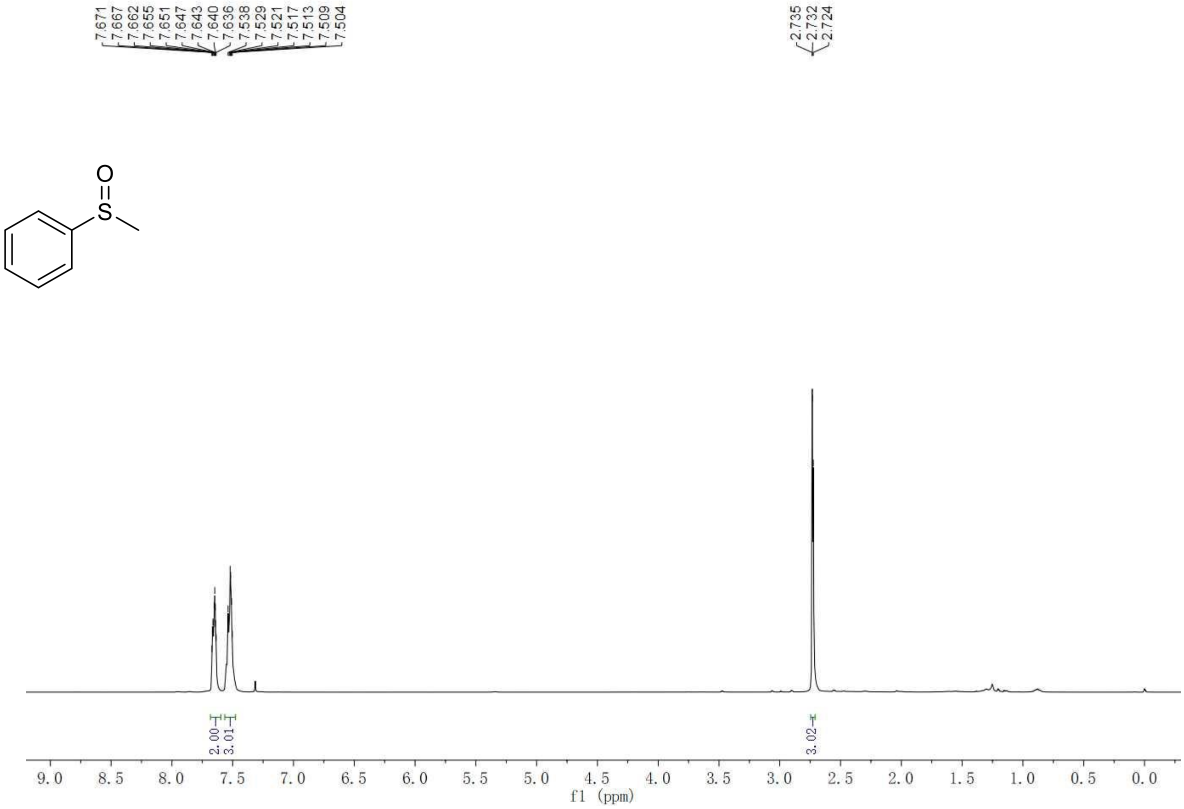

Figure S22. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of (methylsulfinyl)benzene (2a) :

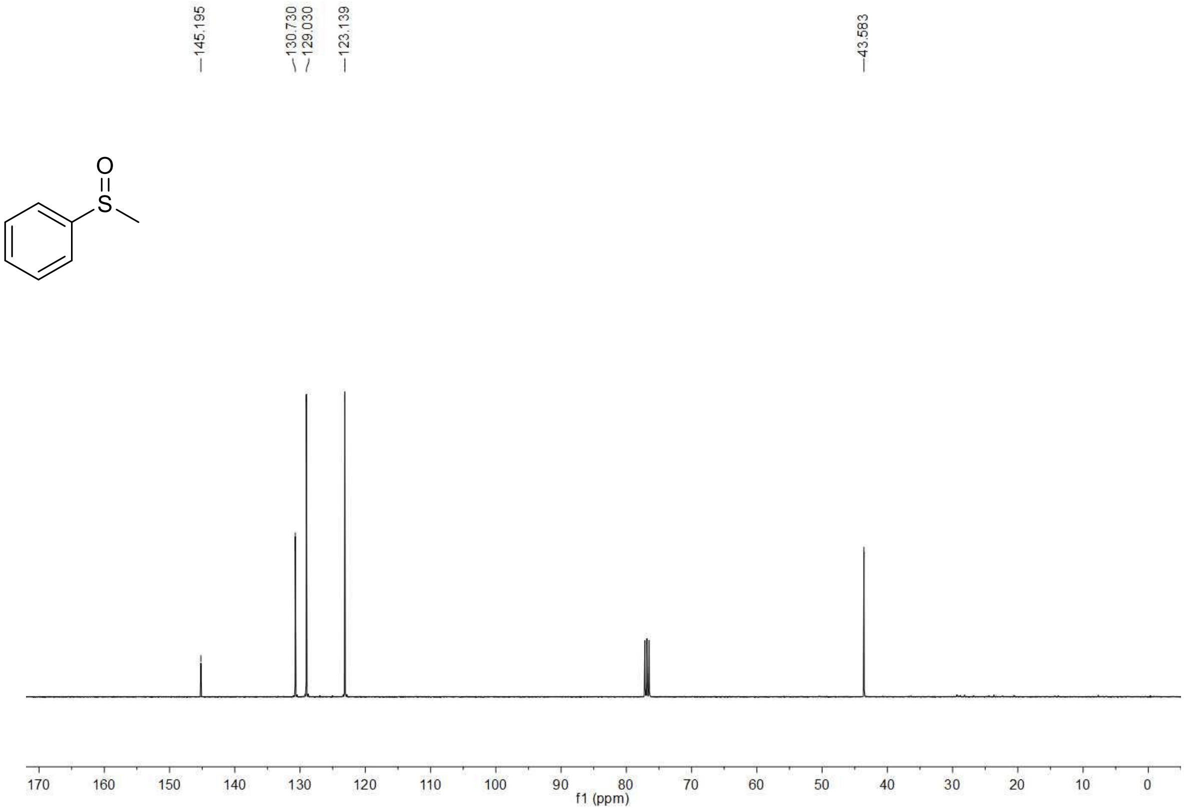

Figure S23. **^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 1-methyl-4-(methylsulfinyl)benzene (2b):**

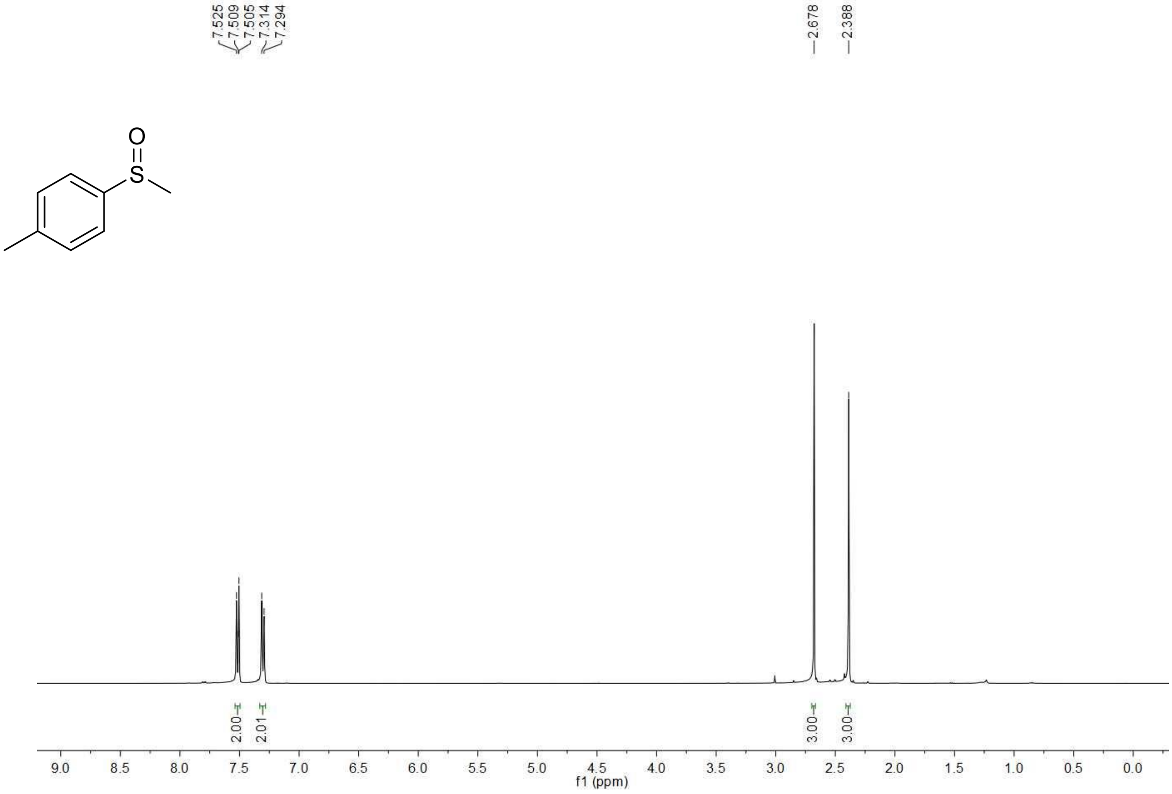

Figure S24. **^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 1-methyl-4-(methylsulfinyl)benzene (2b) :**

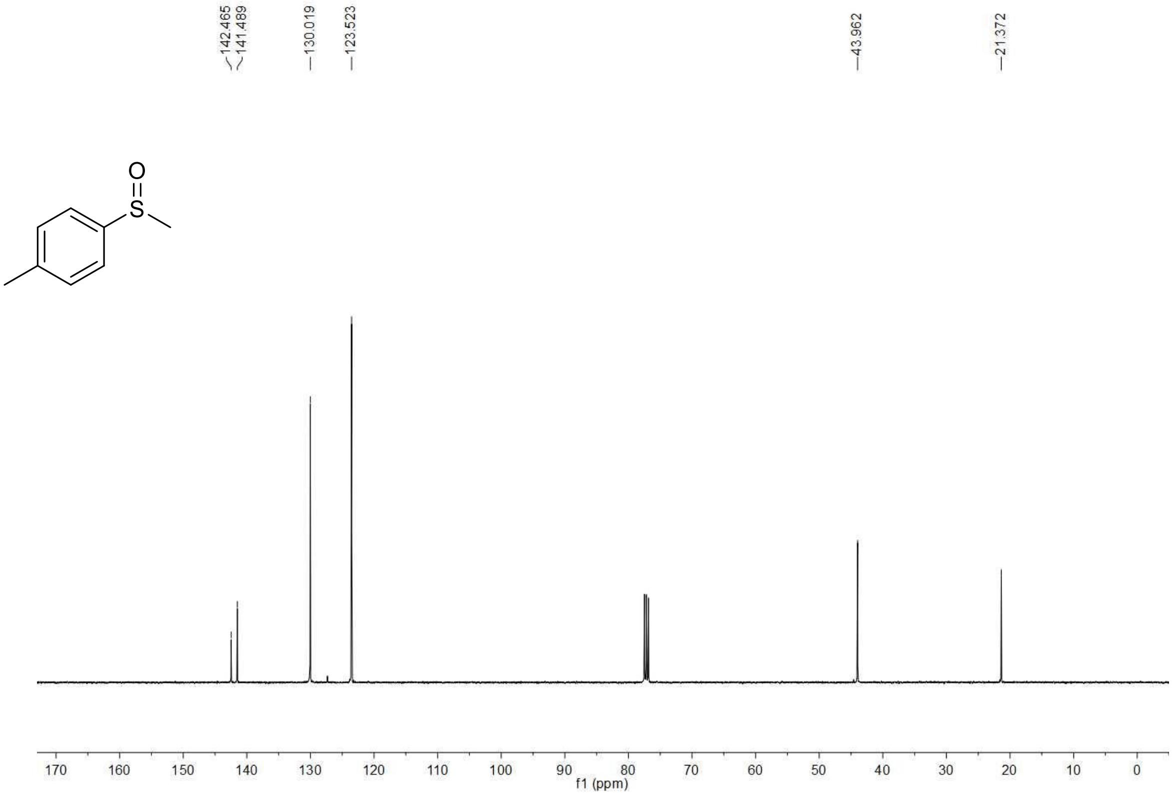

Figure S25. **^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 1-methoxy-2-(methylsulfinyl)benzene (2c):**

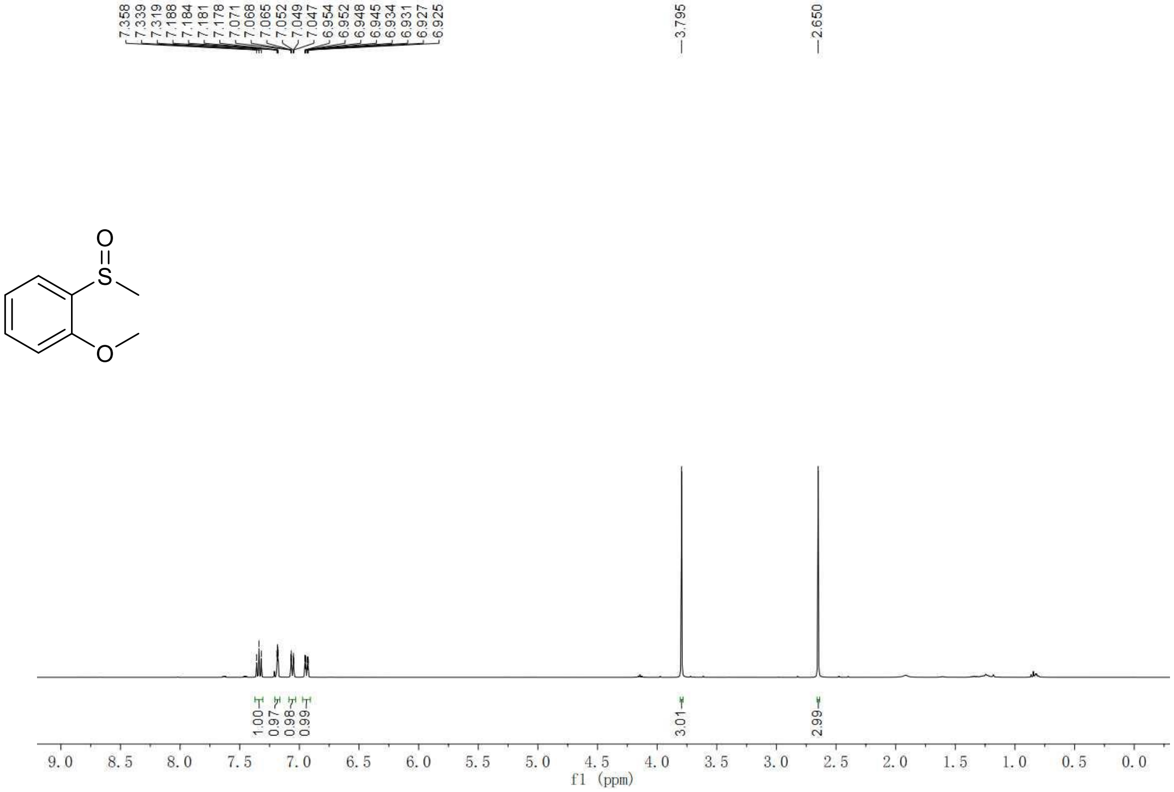

Figure S26. **^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 1-methoxy-2-(methylsulfinyl)benzene (2c) :**

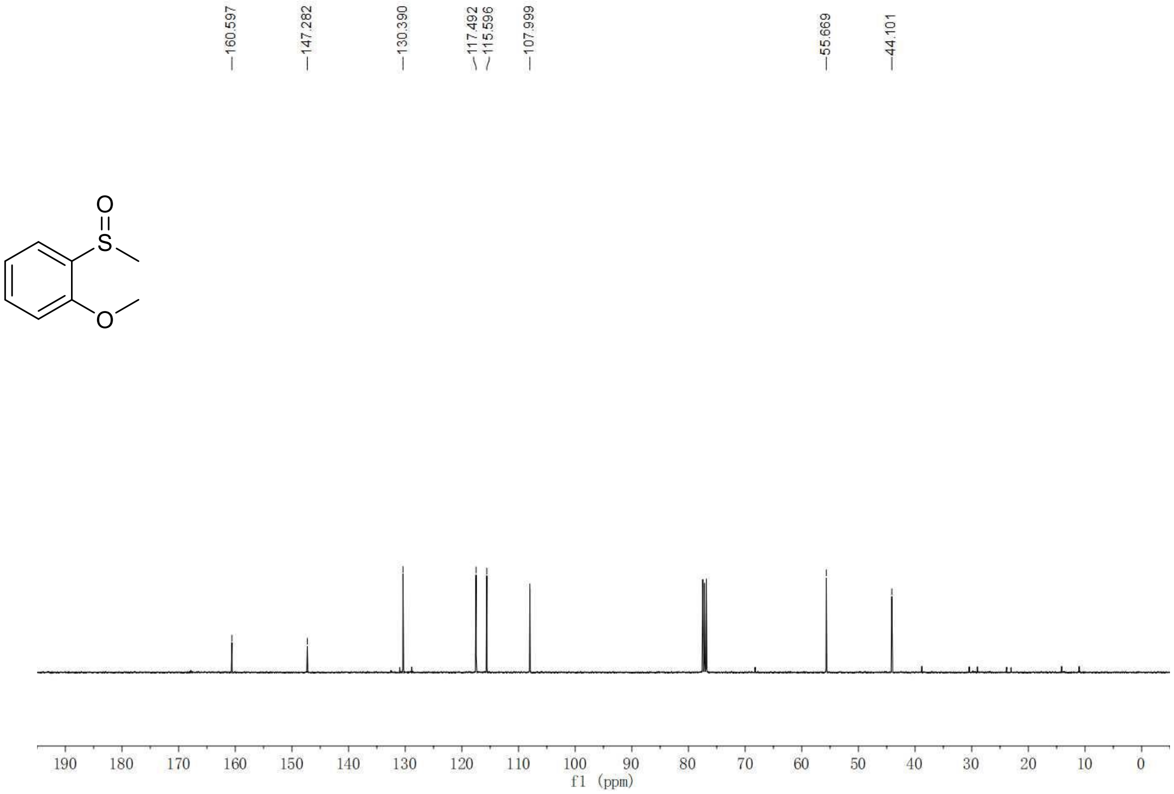

Figure S27. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 1-methoxy-3-(methylsulfinyl)benzene (2d) :

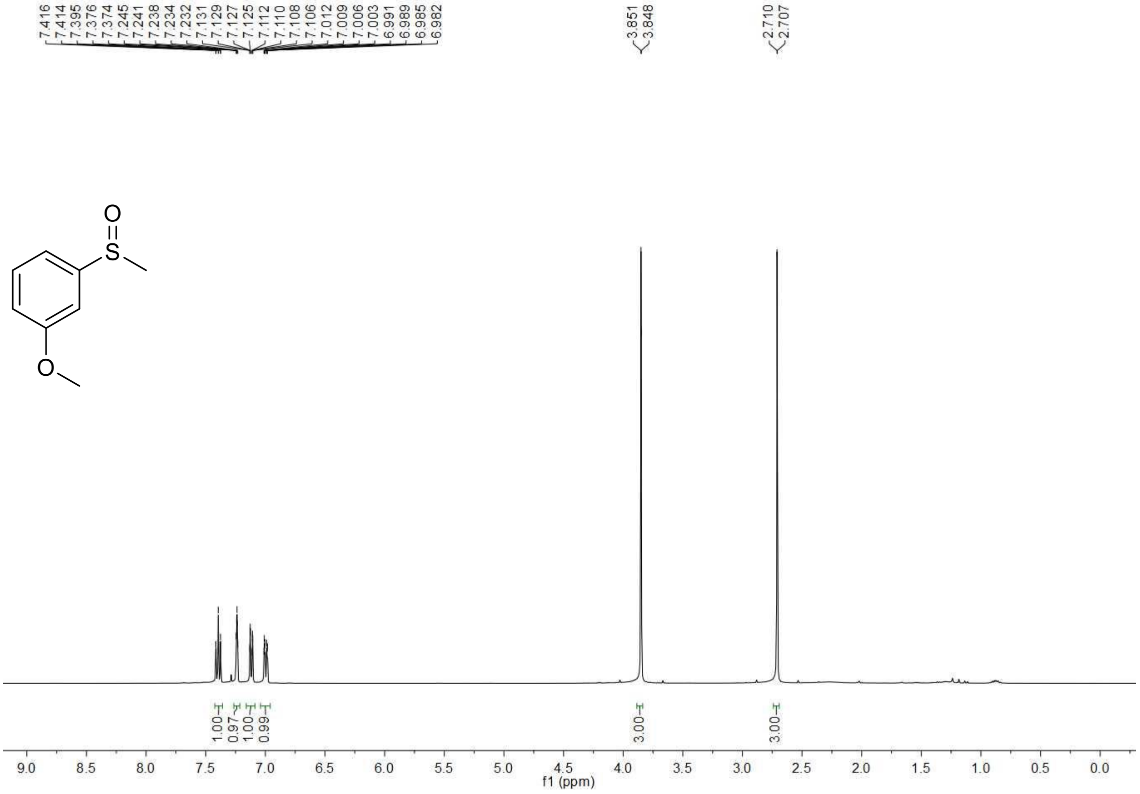

Figure S28. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 1-methoxy-3-(methylsulfinyl)benzene (2d) :

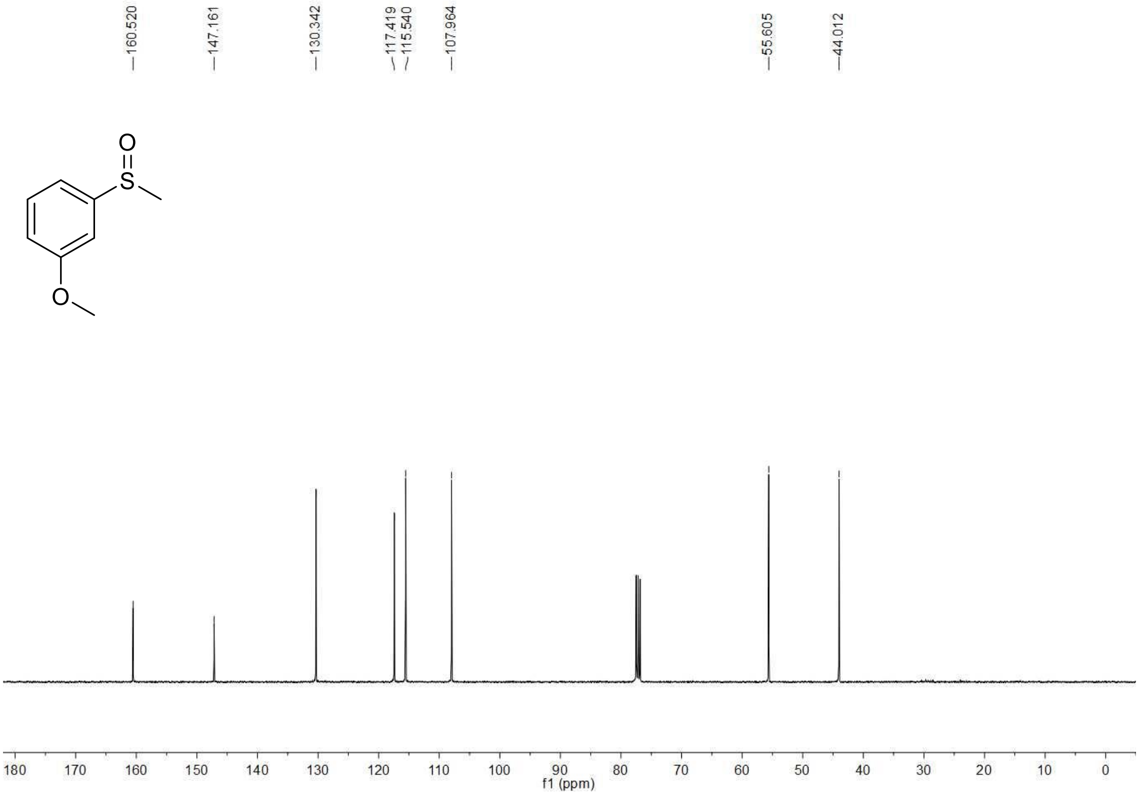

Figure S29. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 1-methoxy-4-(methylsulfinyl)benzene (2e) :

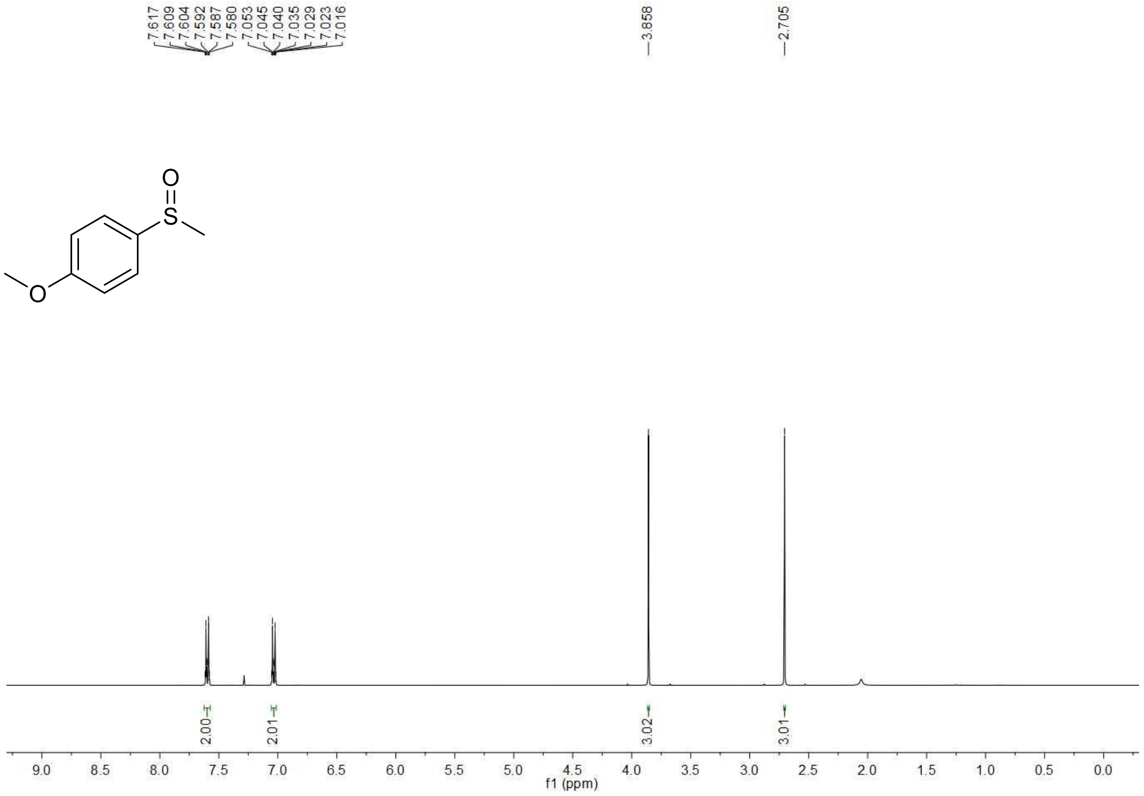

Figure S30. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 1-methoxy-4-(methylsulfinyl)benzene (2e) :

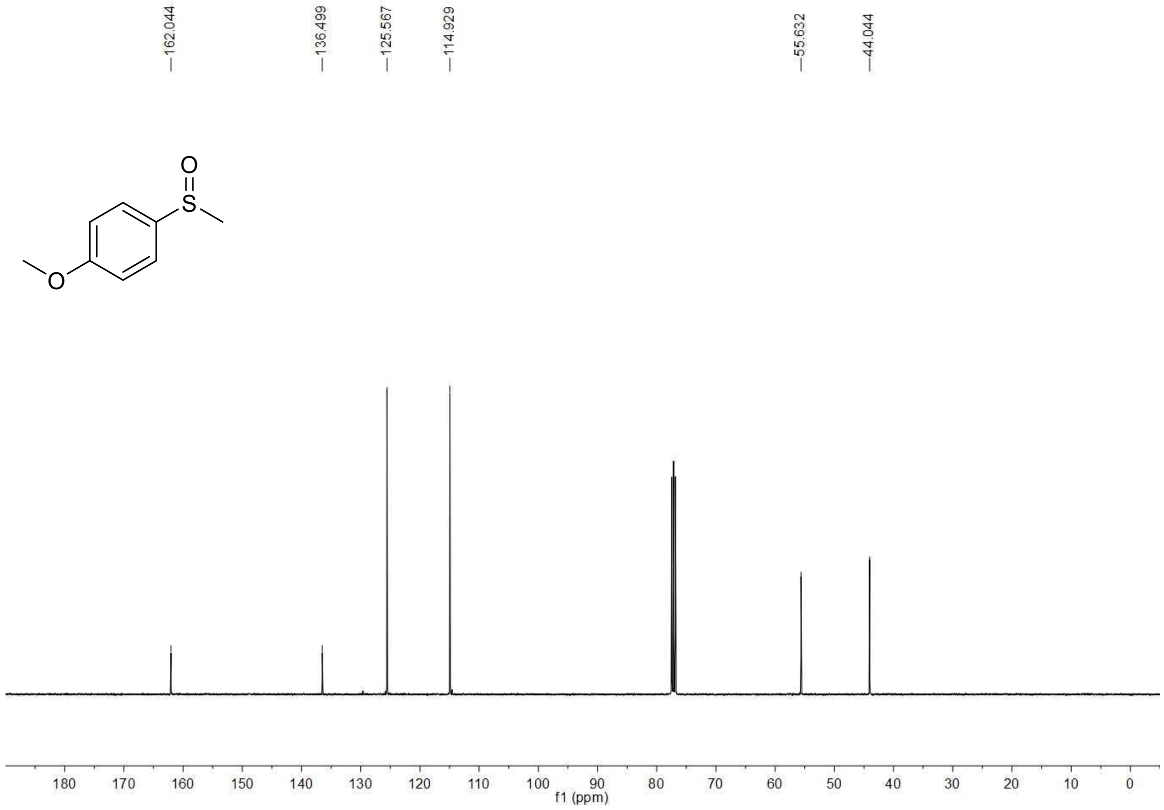

Figure S31. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 1-fluoro-4-(methylsulfinyl)benzene (2f) :

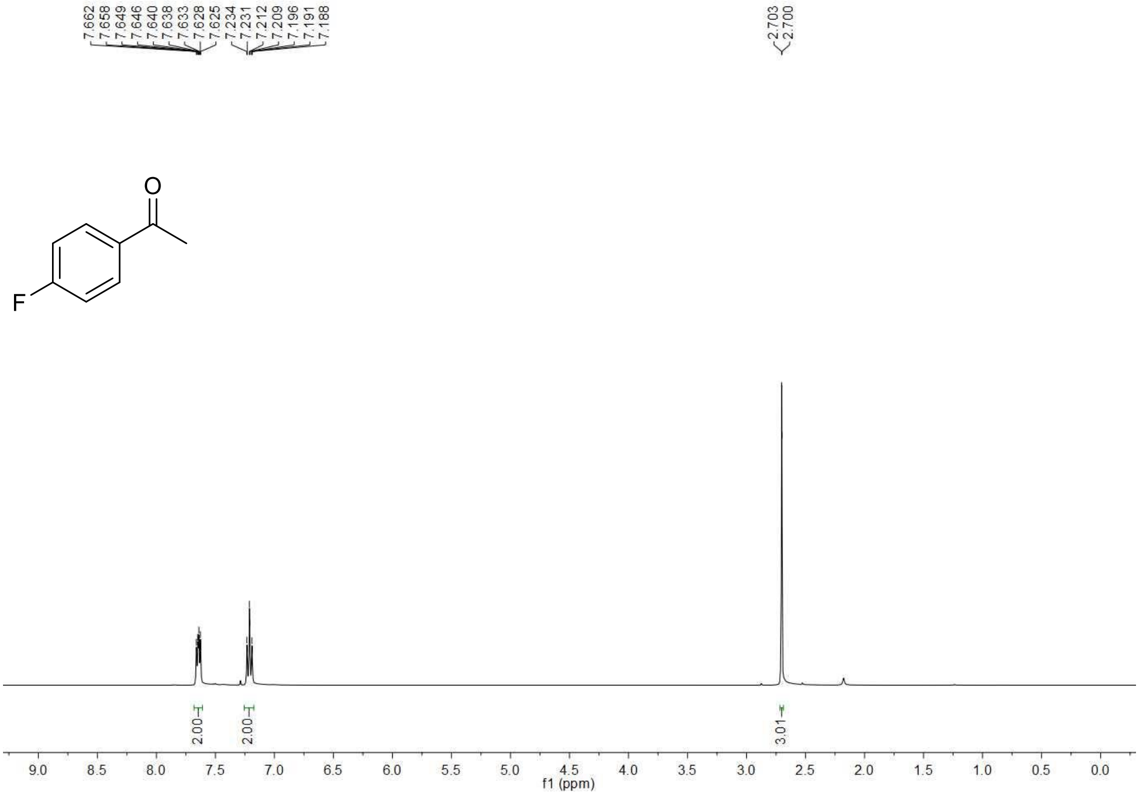

Figure S32. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 1-fluoro-4-(methylsulfinyl)benzene (2f) :

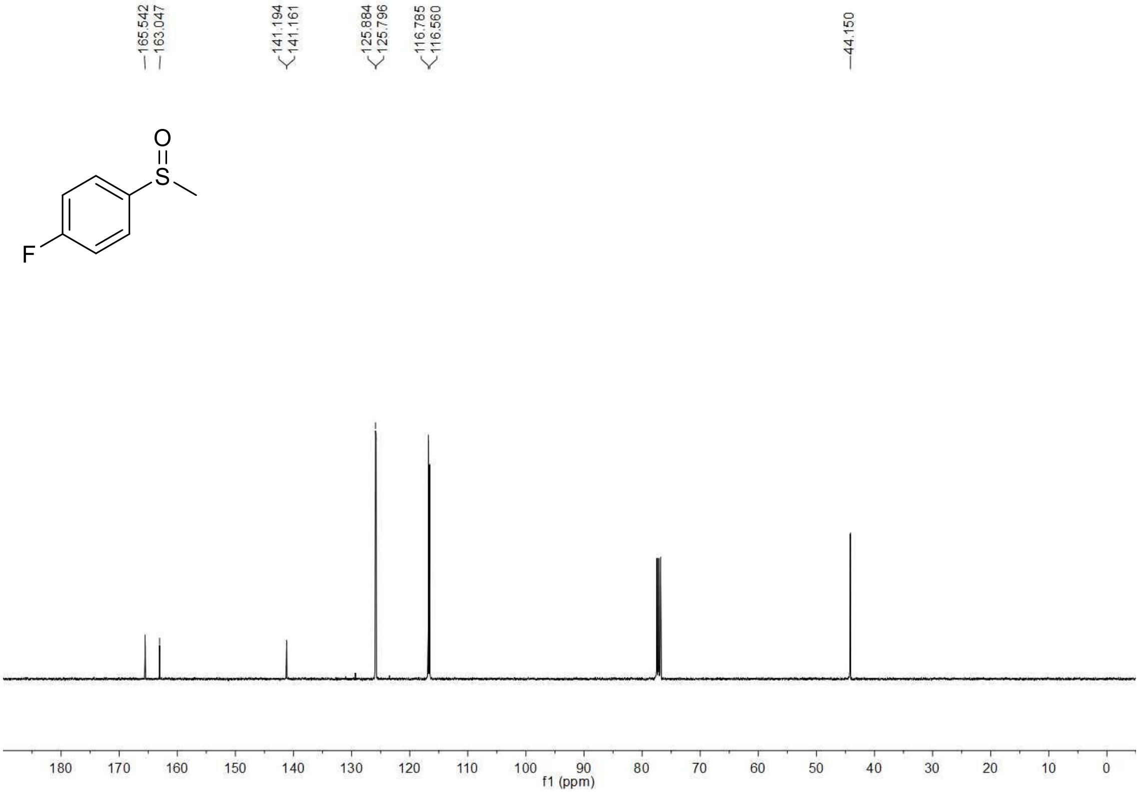

Figure S33. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 1-chloro-4-(methylsulfinyl)benzene (2g) :

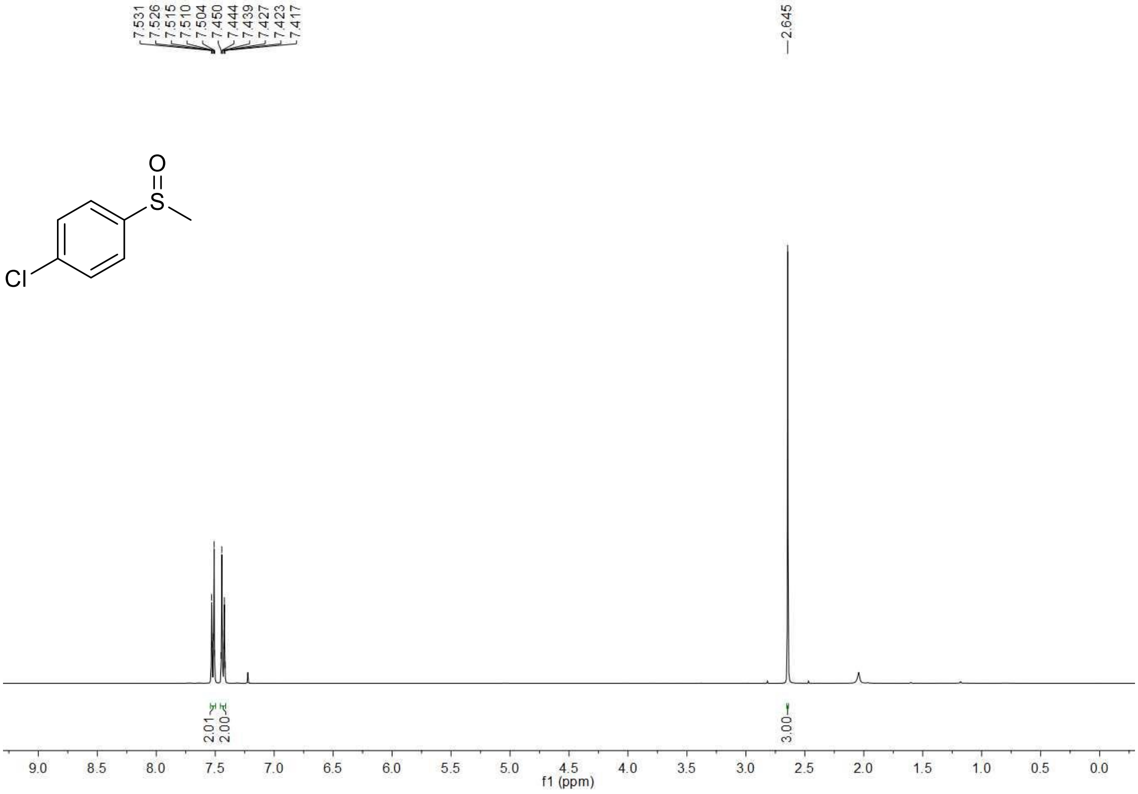

Figure S34. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 1-chloro-4-(methylsulfinyl)benzene (2g) :

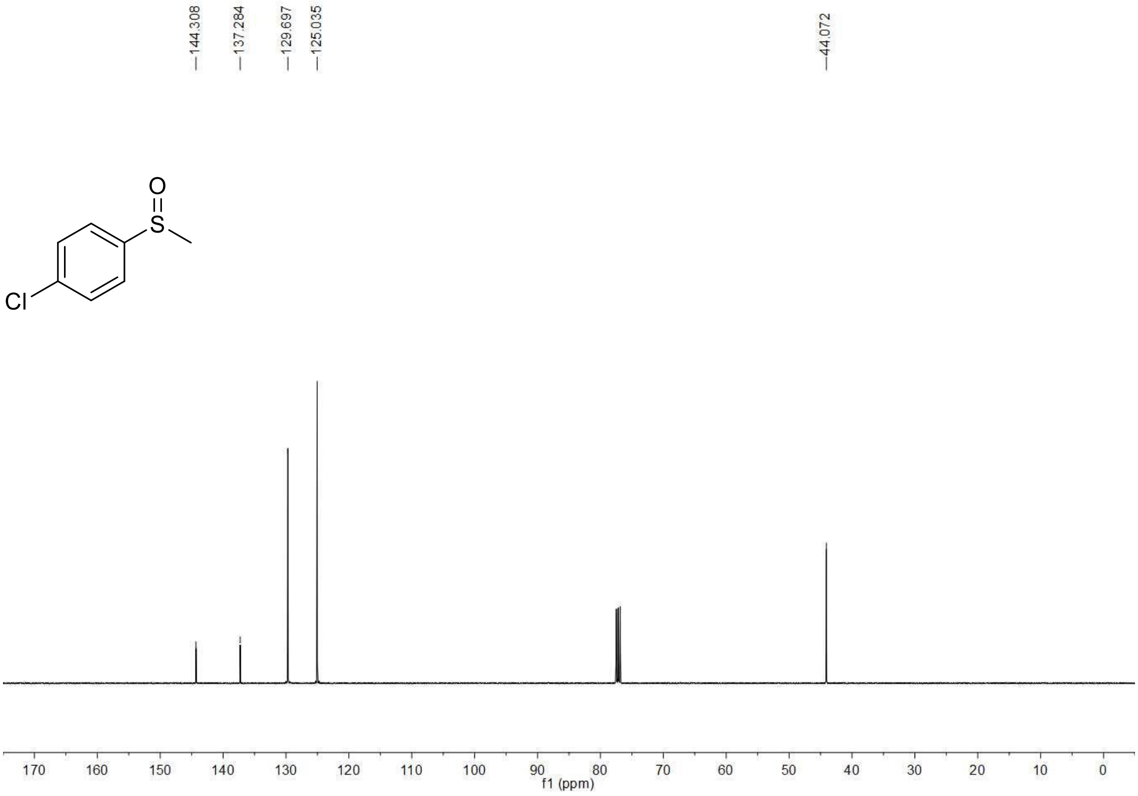

Figure S35. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 1-bromo-4-(methylsulfinyl)benzene (2h) :

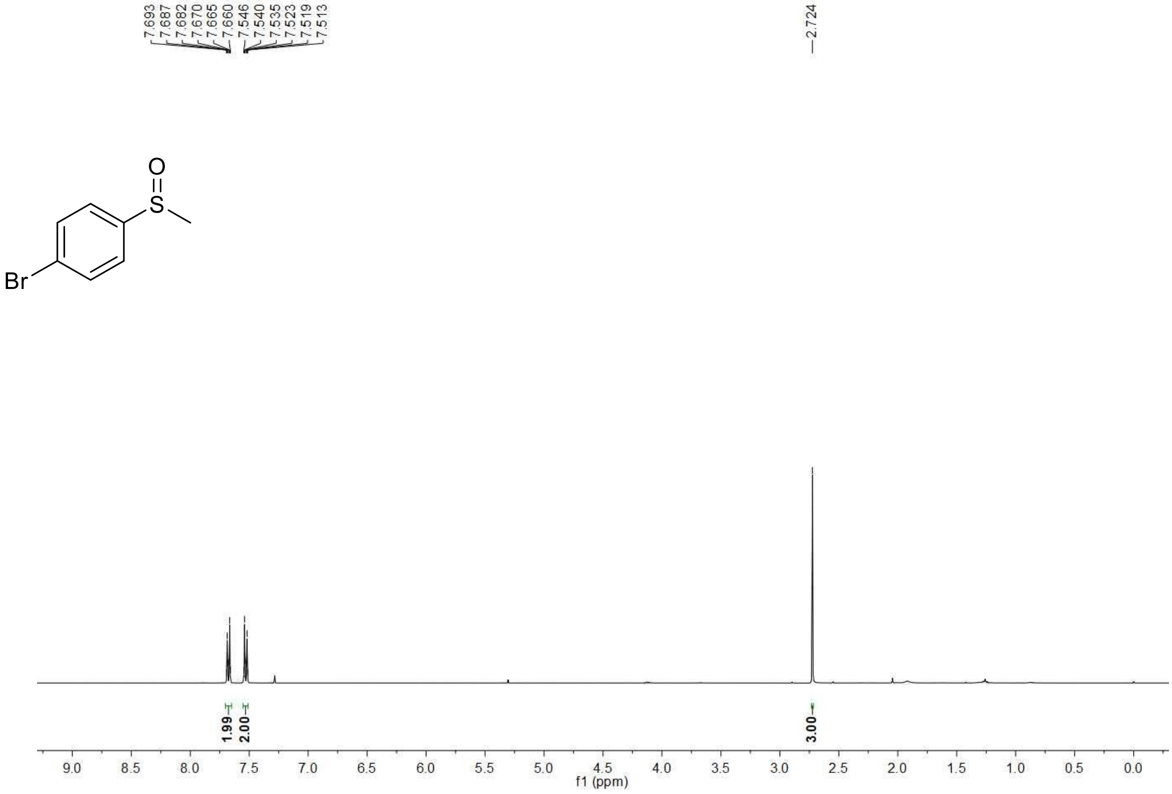

Figure S36. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 1-bromo-4-(methylsulfinyl)benzene (2h) :

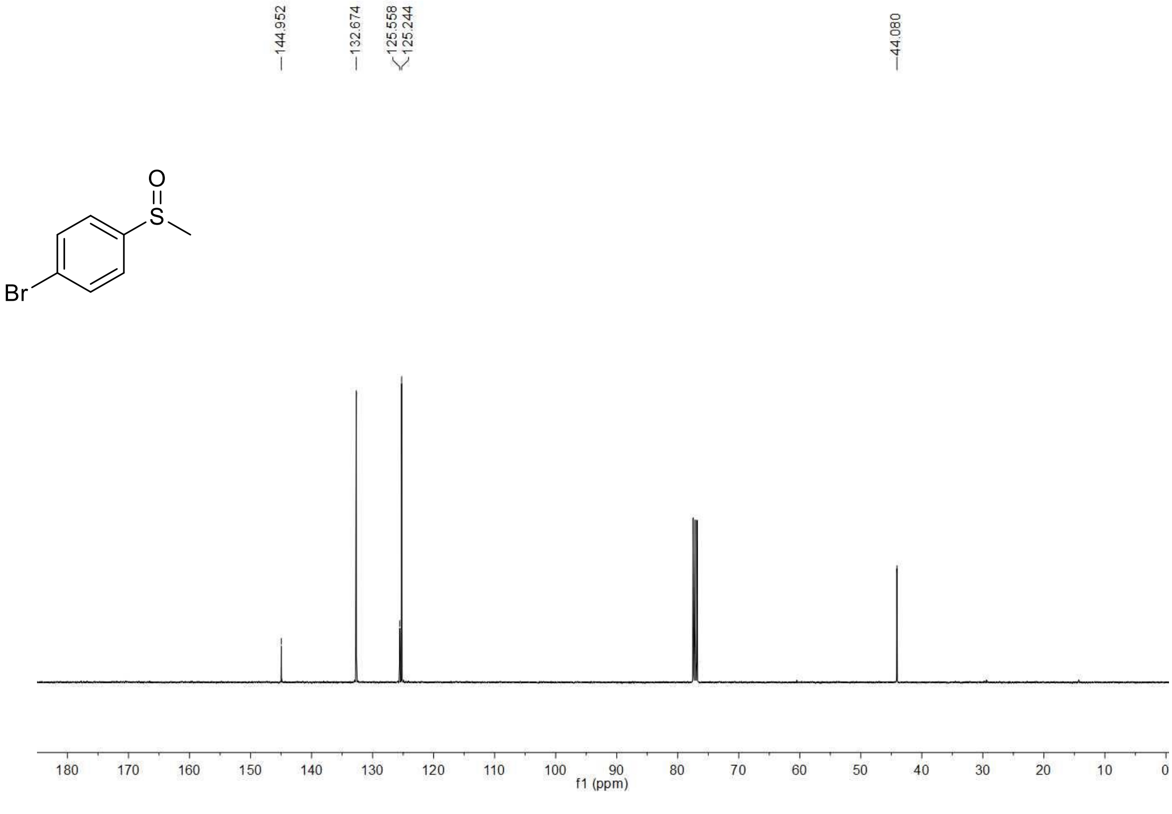

Figure S37. ^{1}H NMR spectra (400 MHz, Chloroform-d) of 4-(methylsulfinyl)benzonitrile (2i) :

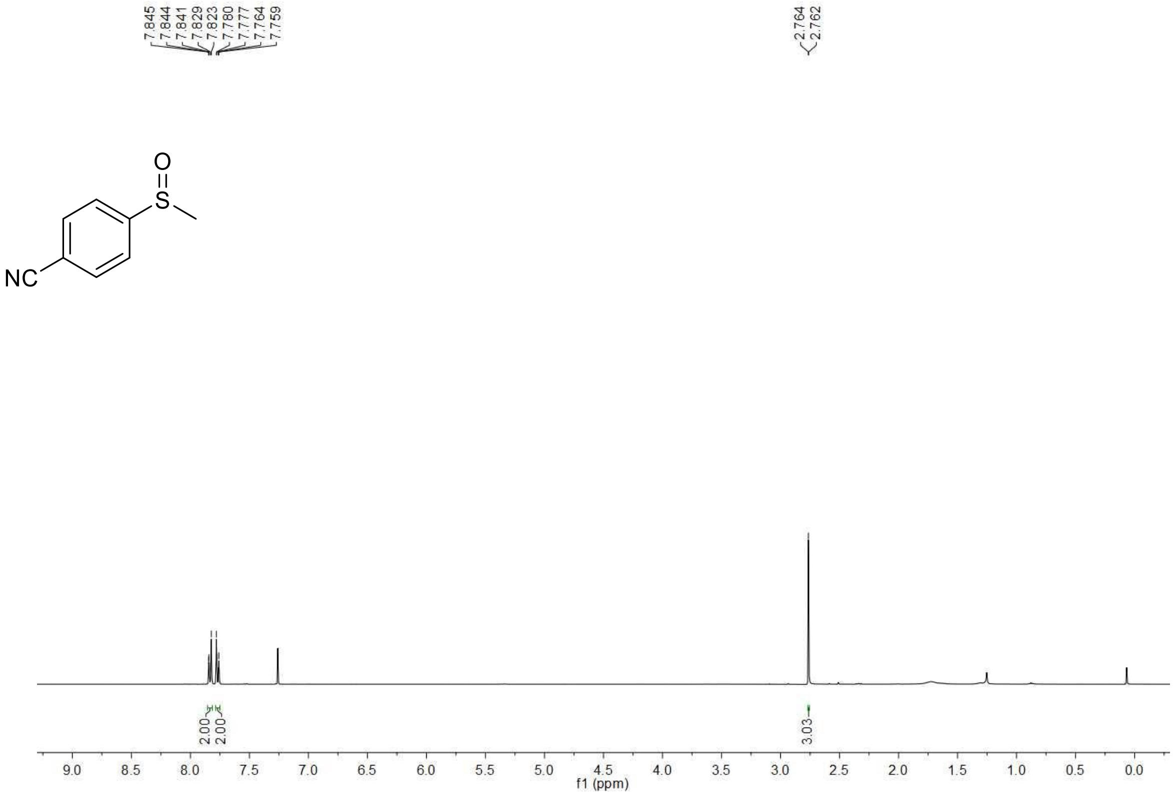

Figure S38. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 4-(methylsulfinyl)benzonitrile (2i) :

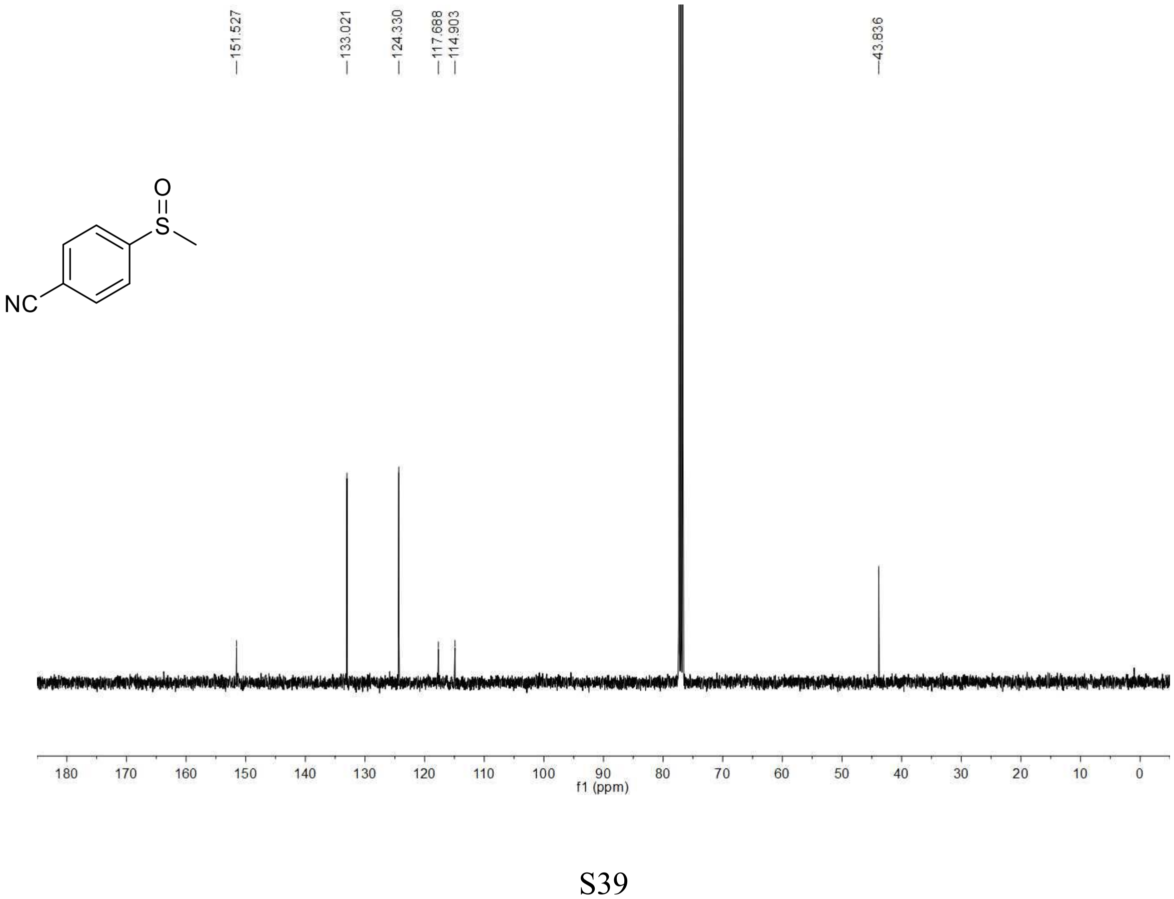

Figure S39. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 2-(methylsulfinyl)naphthalene (2j) :

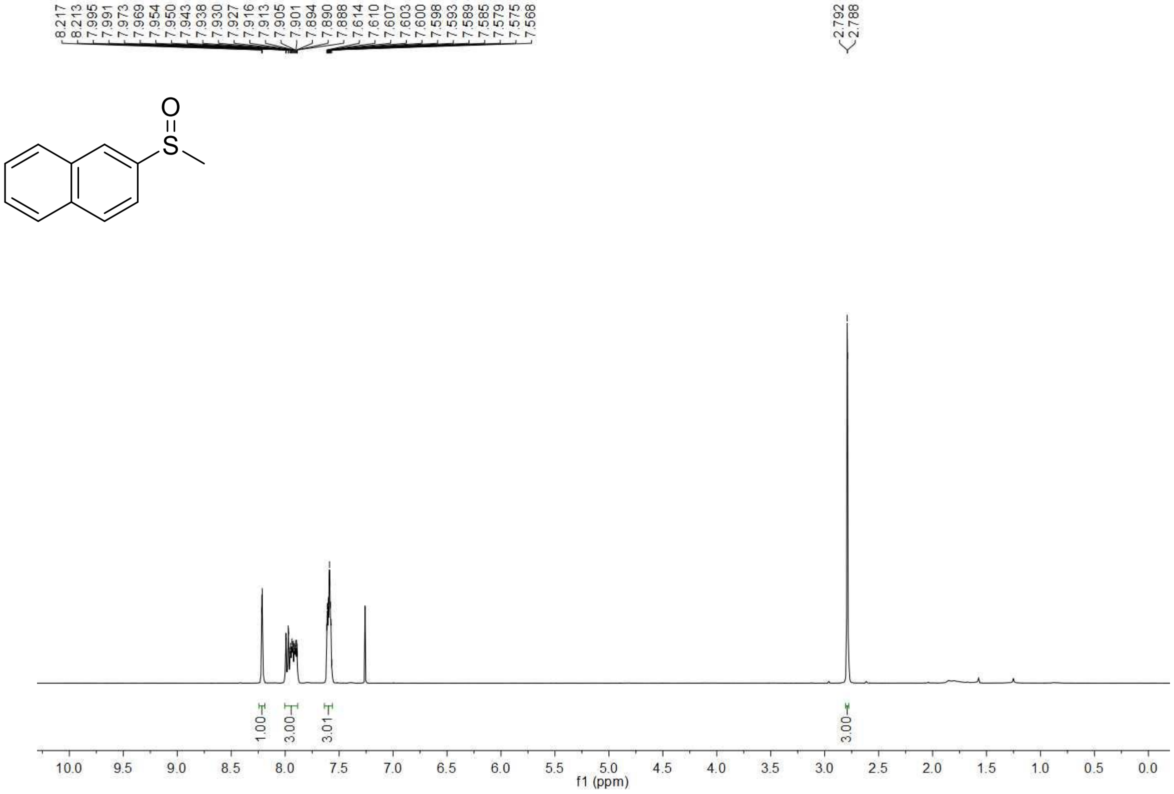

Figure S40. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 2-(methylsulfinyl)naphthalene (2j) :

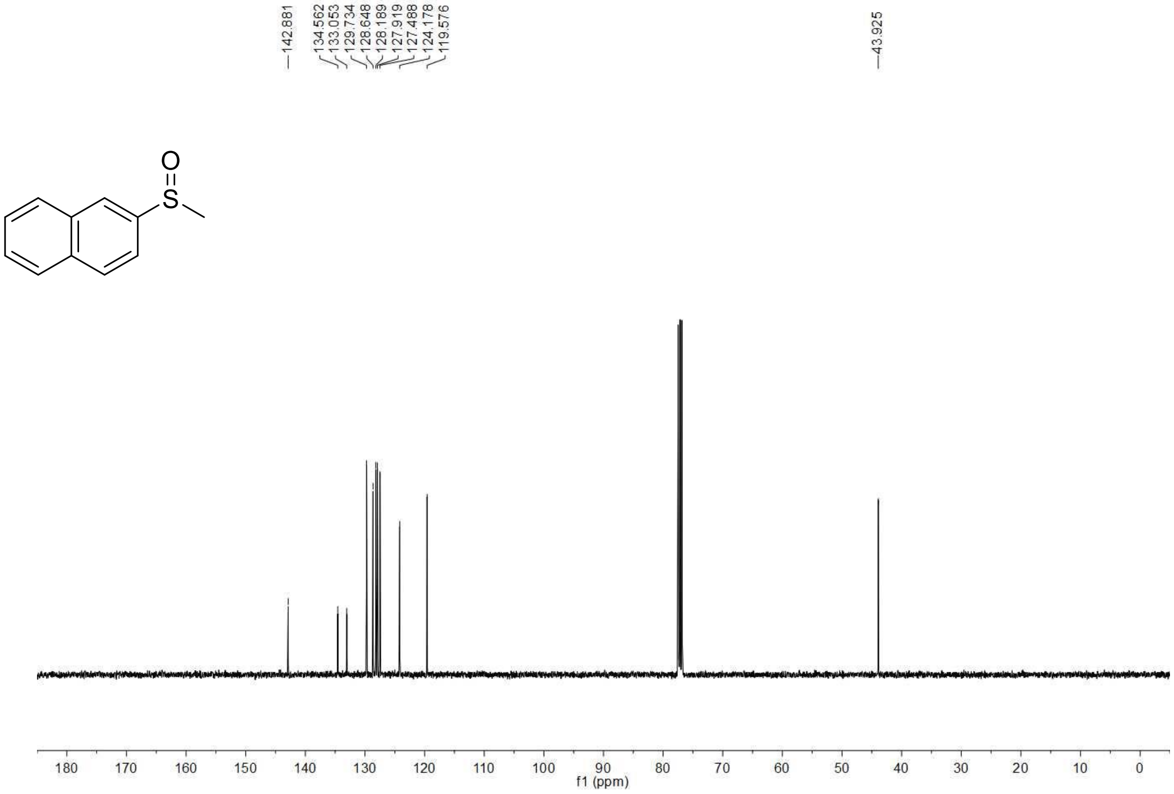

Figure S41. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 2-(methylsulfinyl)thiophene (2k) :

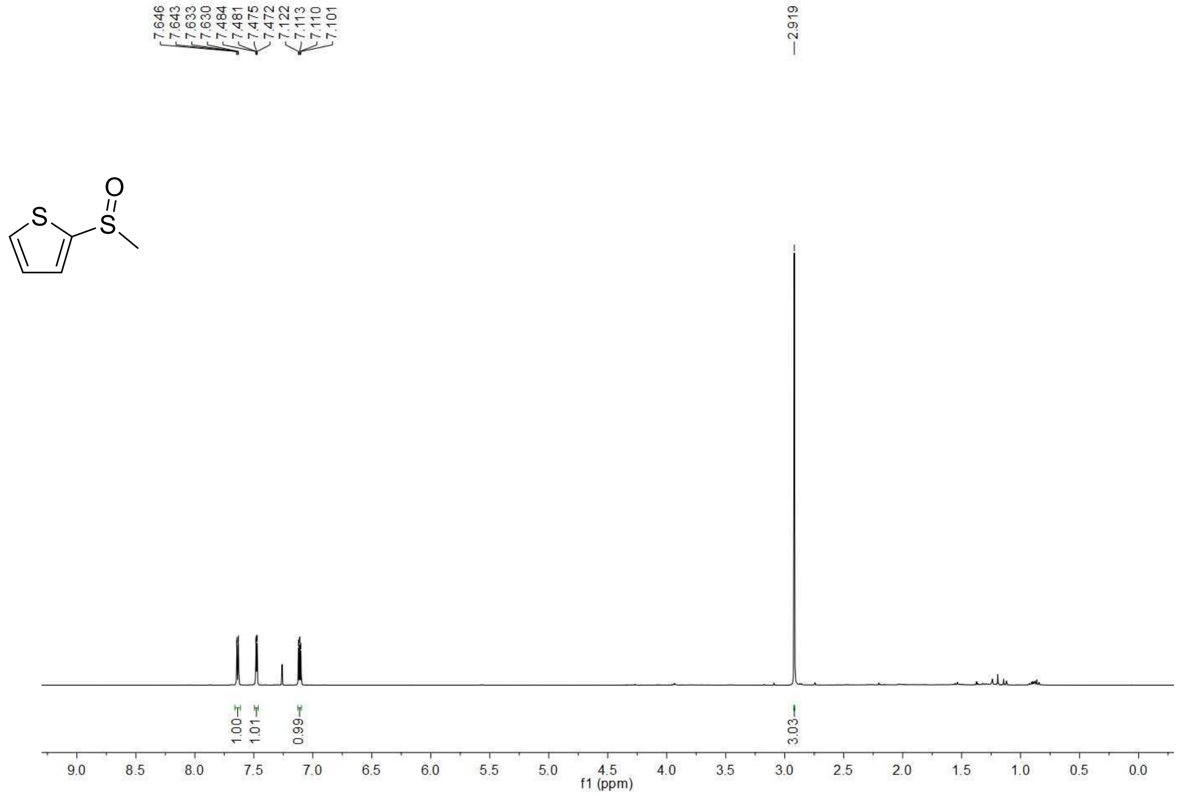

Figure S42. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of 2-(methylsulfinyl)thiophene (2k) :

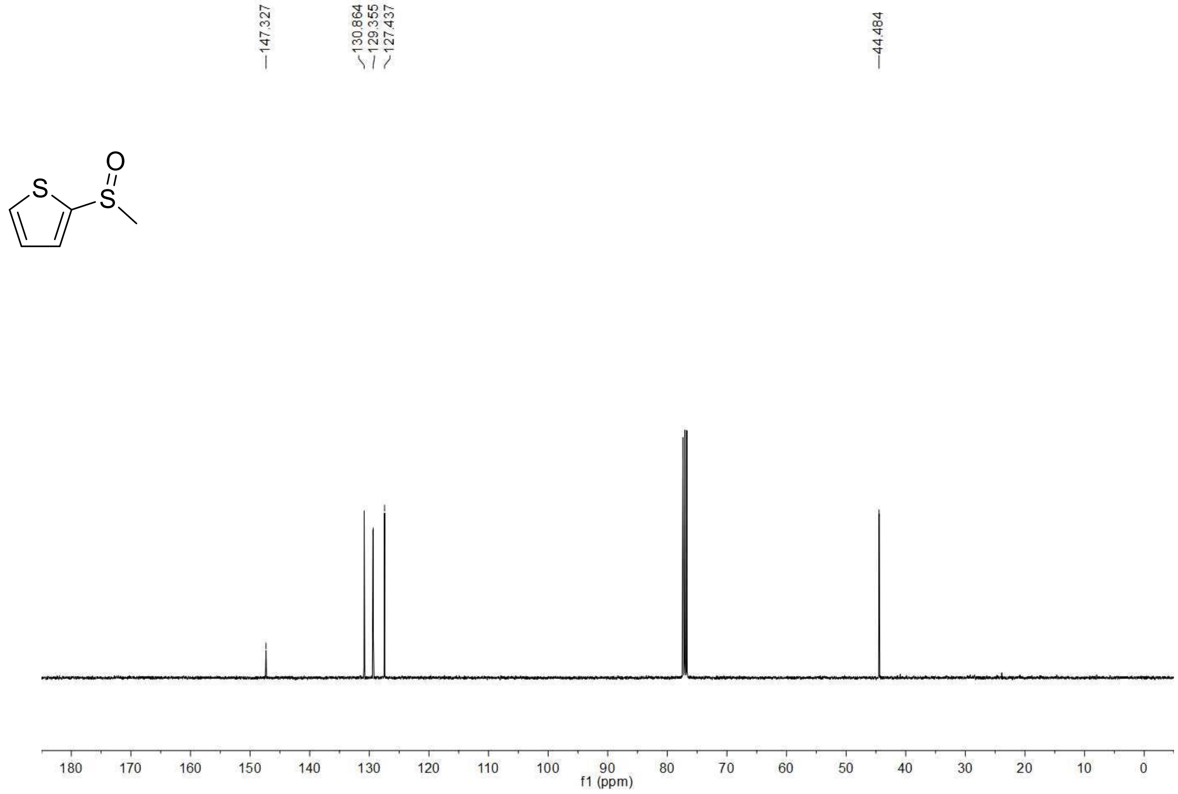

Figure S43. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of (ethylsulfinyl)benzene (2l) :

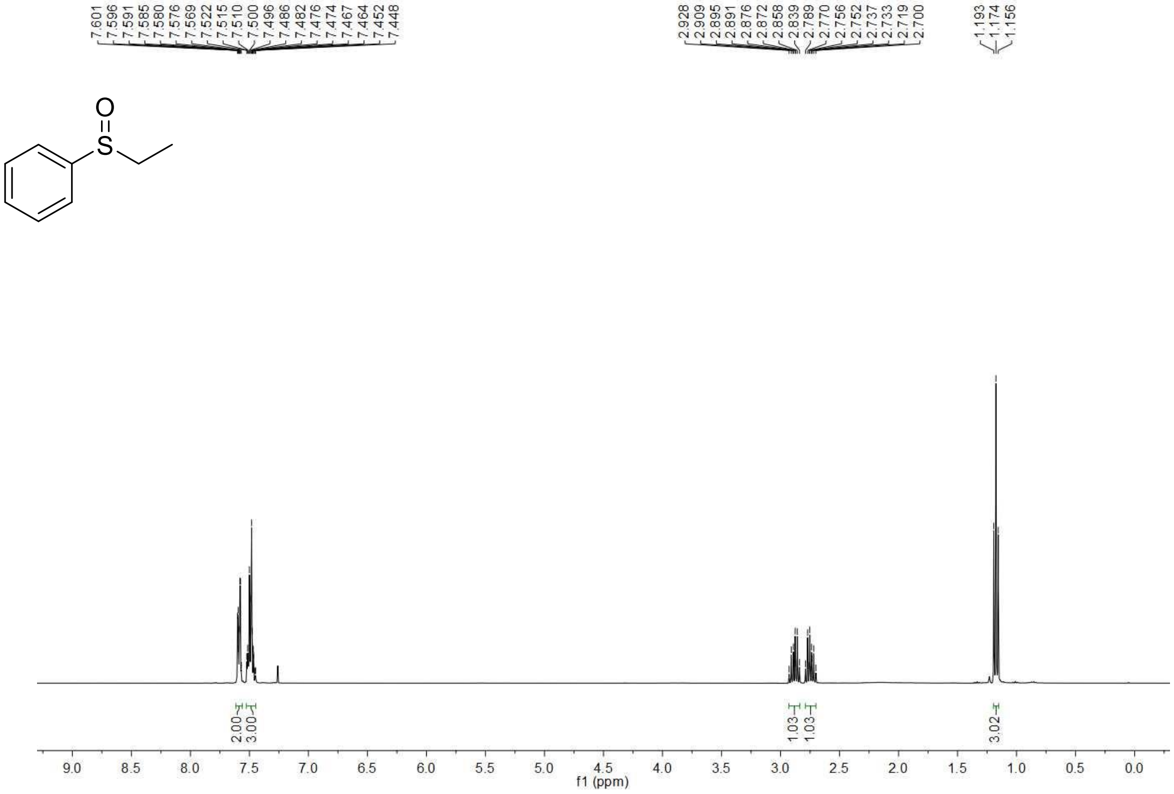

Figure S44. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of (ethylsulfinyl)benzene (2l) :

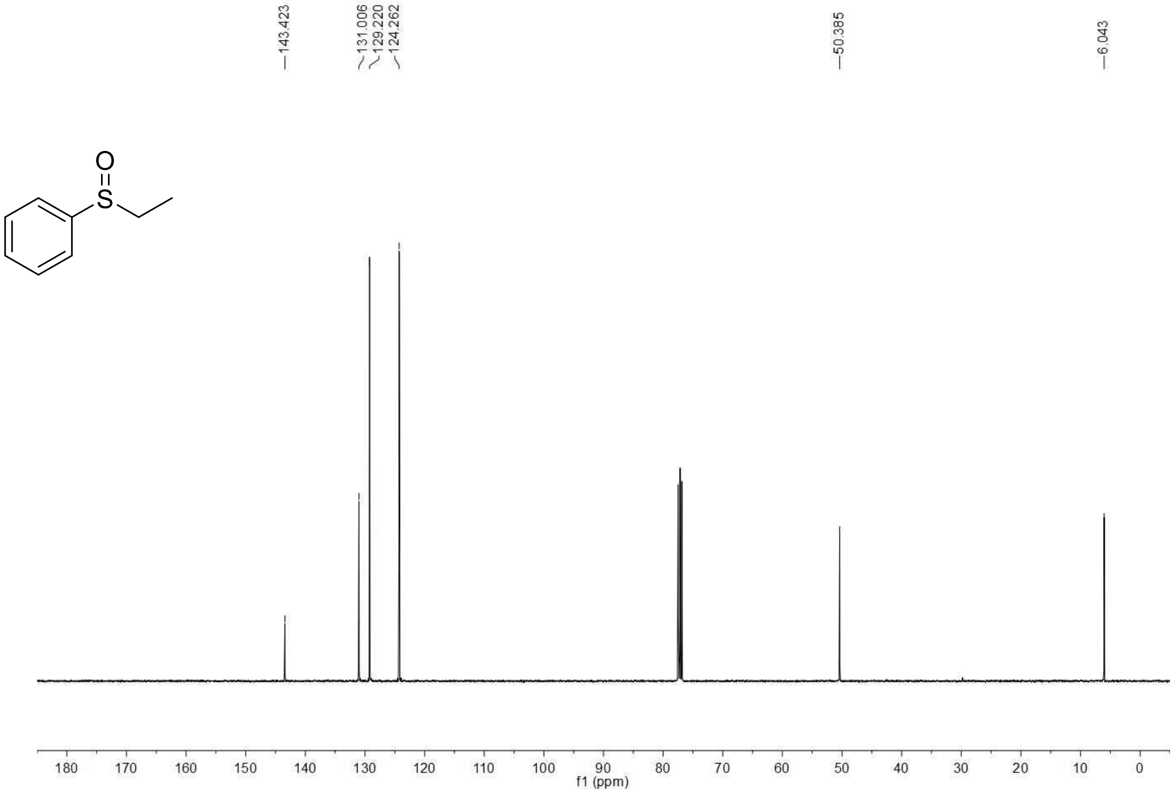

Figure S45. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of 1-(isopentylsulfinyl)-3-methylbutane (2m) :

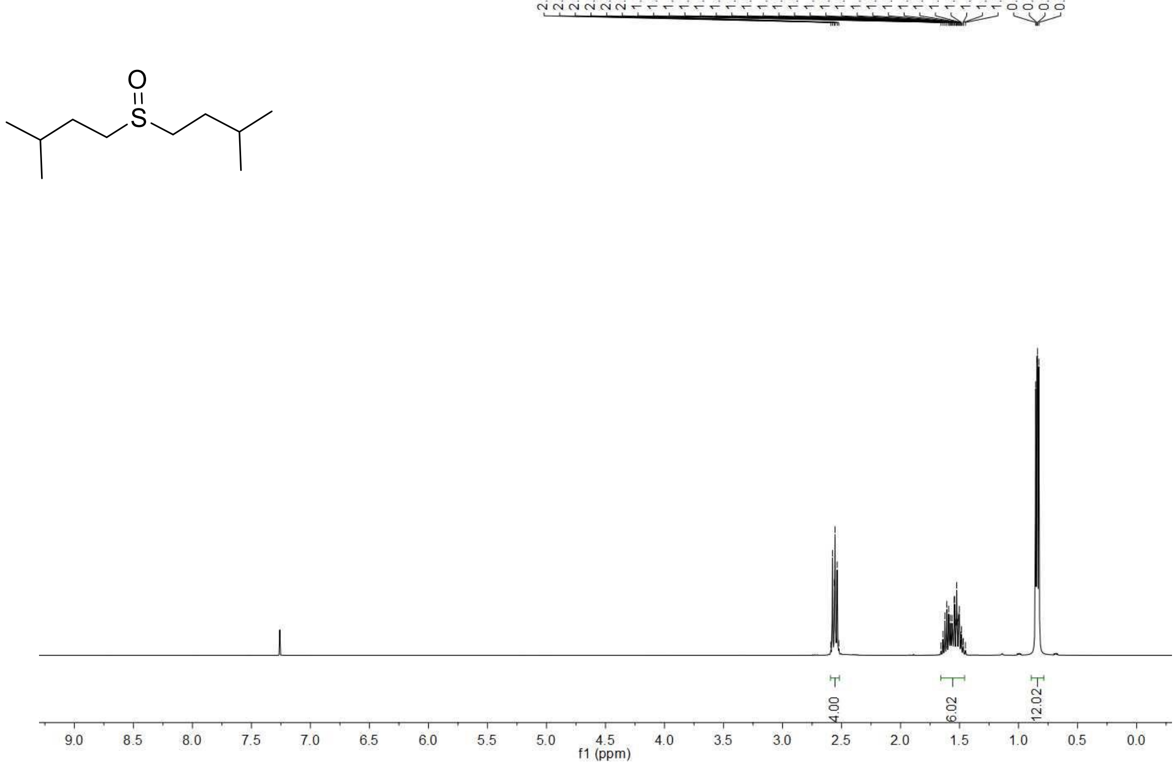

Figure S46. $^{13}C\{^1H\}$ NMR spectra (100 MHz, Chloroform-*d*) of 1-(isopentylsulfinyl)-3-methylbutane (2m) :

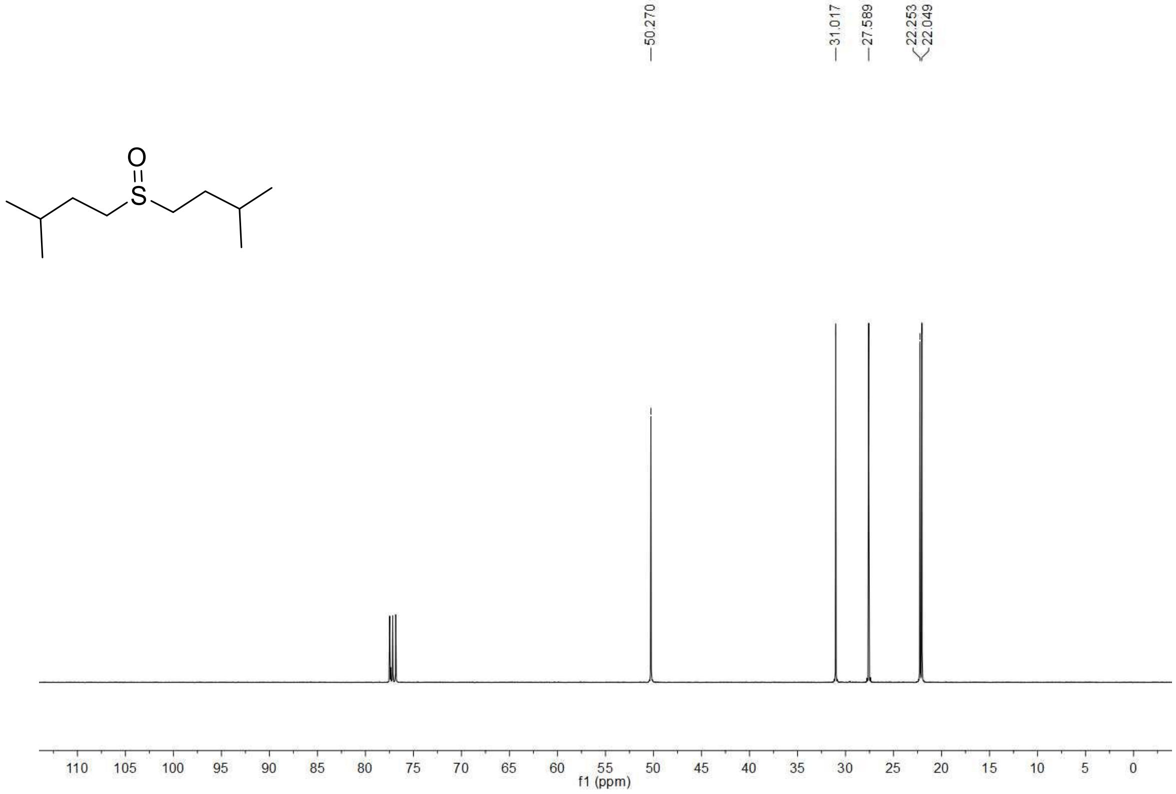

Figure S47. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of ethyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5a) :

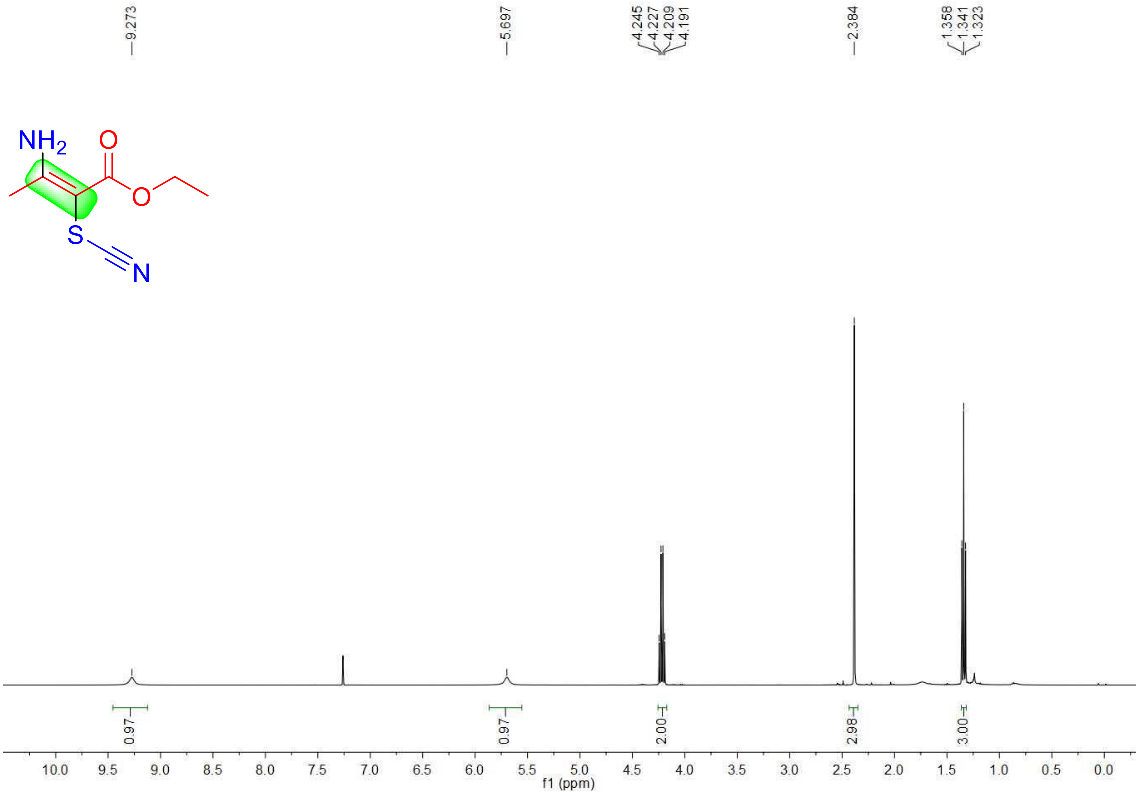

Figure S48. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of ethyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5a) :

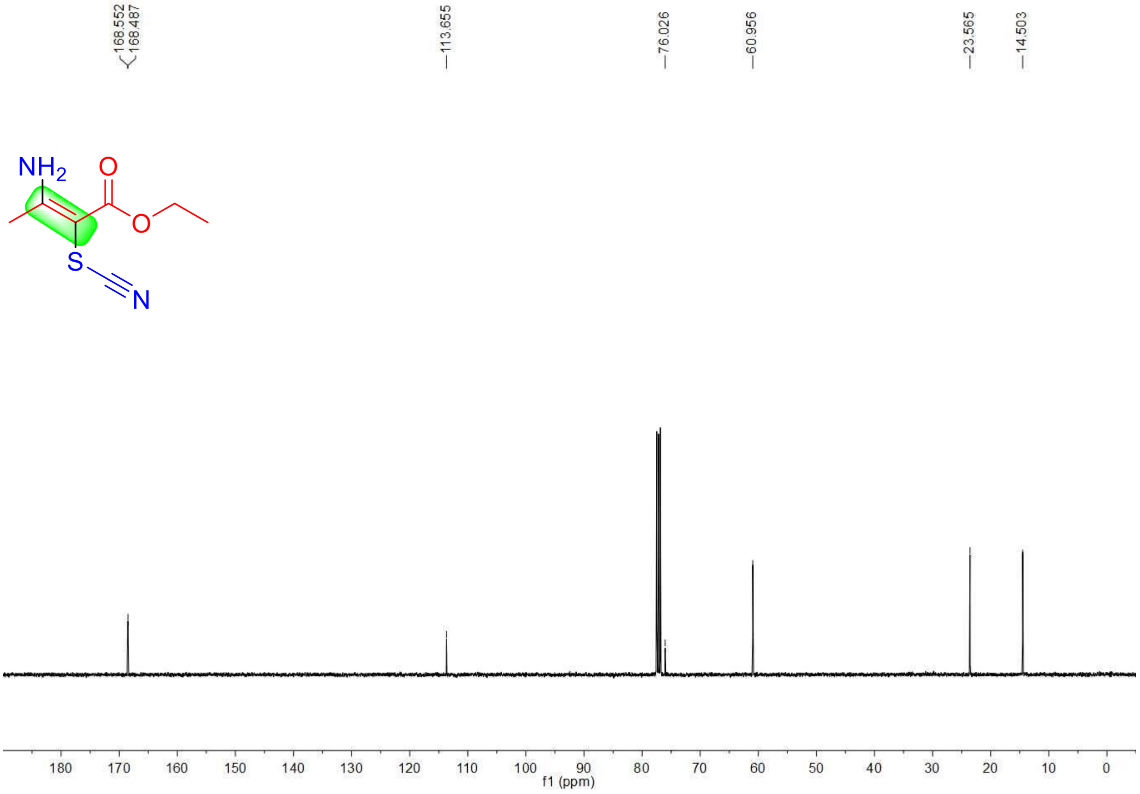

Figure S49. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of methyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5b) :

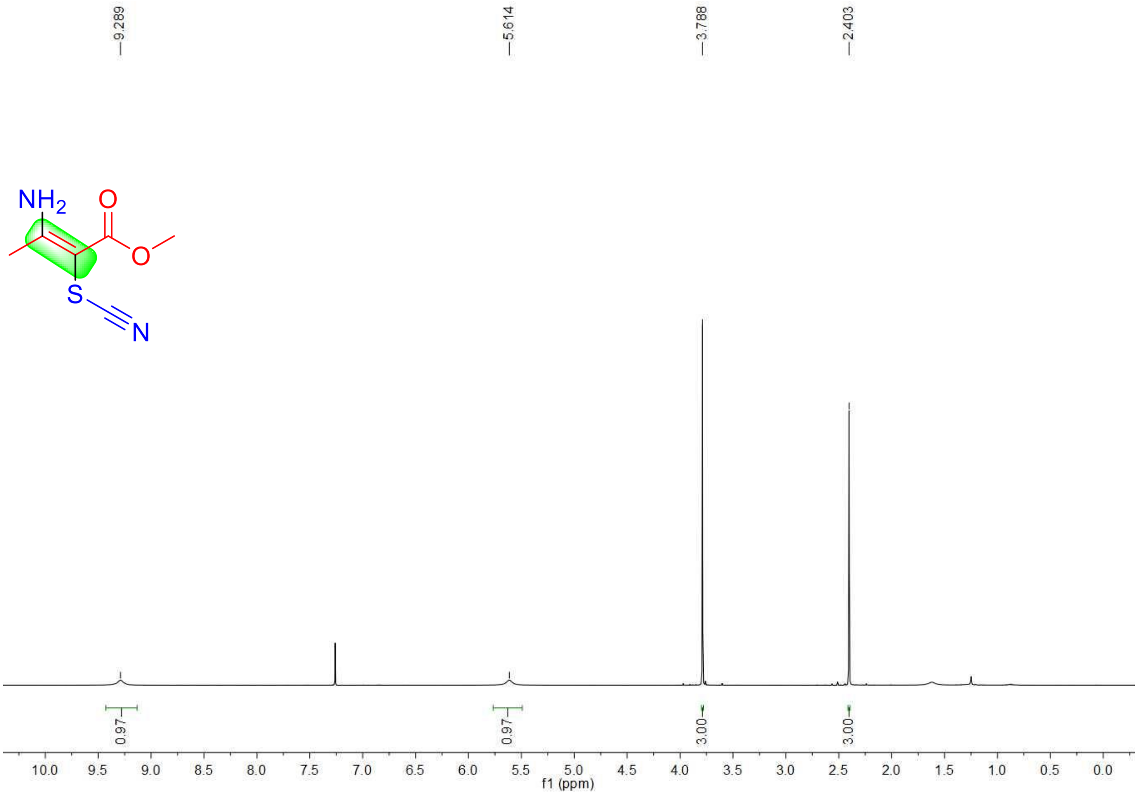

Figure S50. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of methyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5b) :

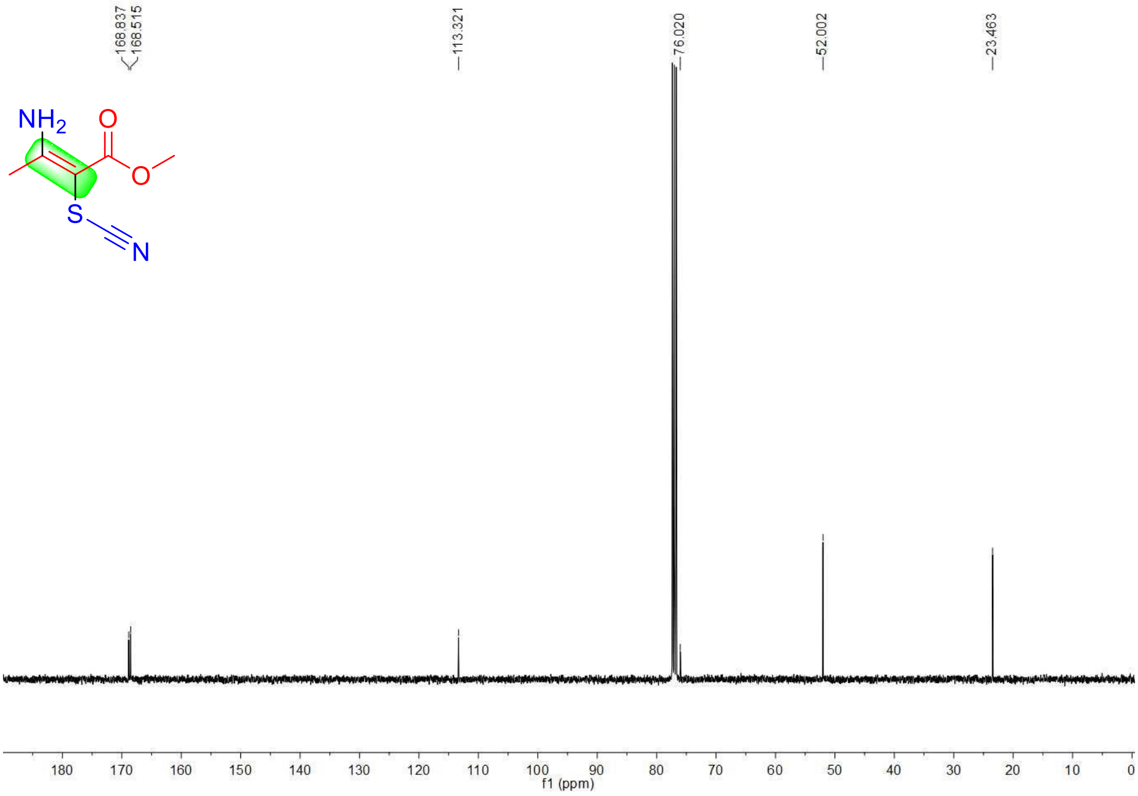

Figure S51. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of propyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5c) :

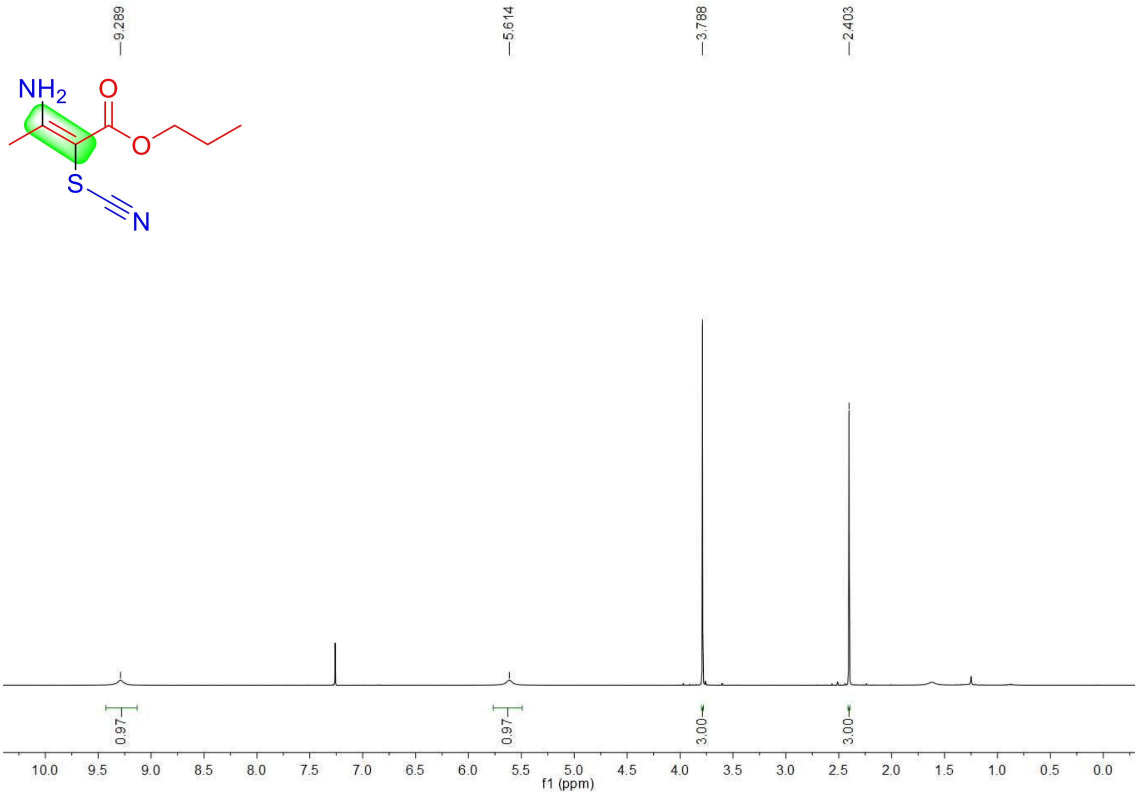

Figure S52. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of propyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5c) :

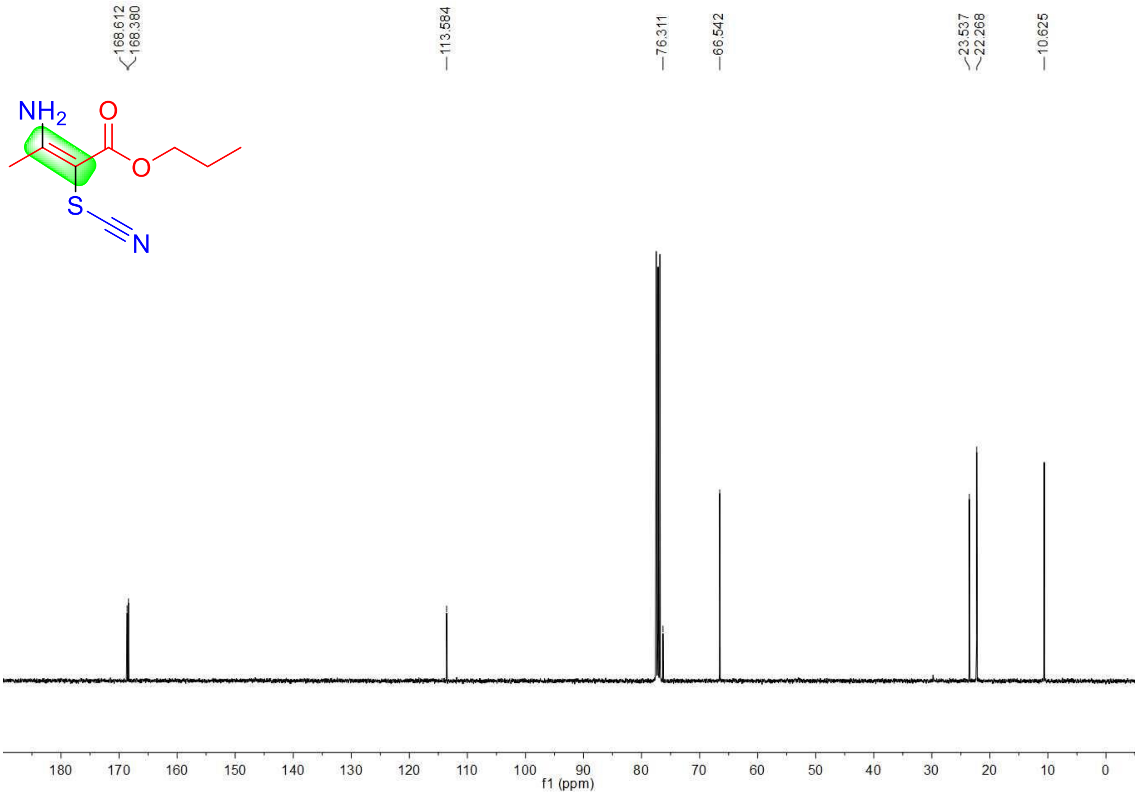

Figure S53. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of isopropyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5d) :

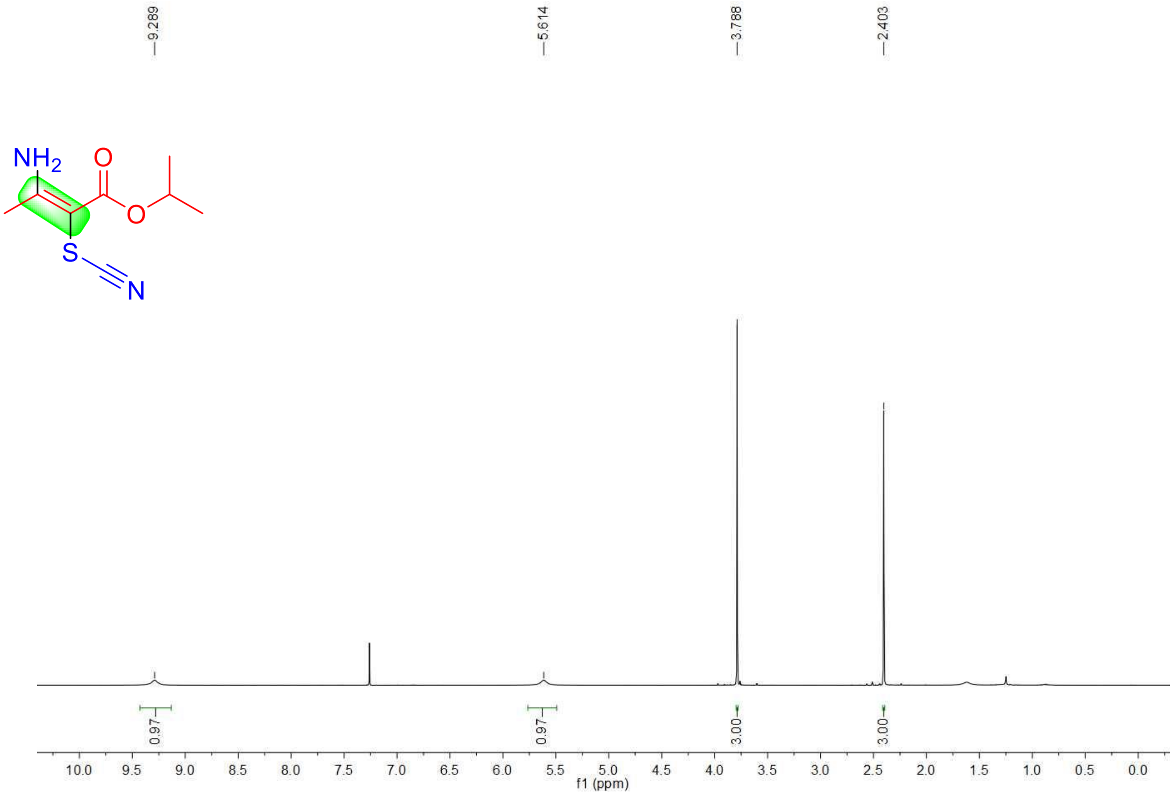

Figure S54. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of isopropyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5d) :

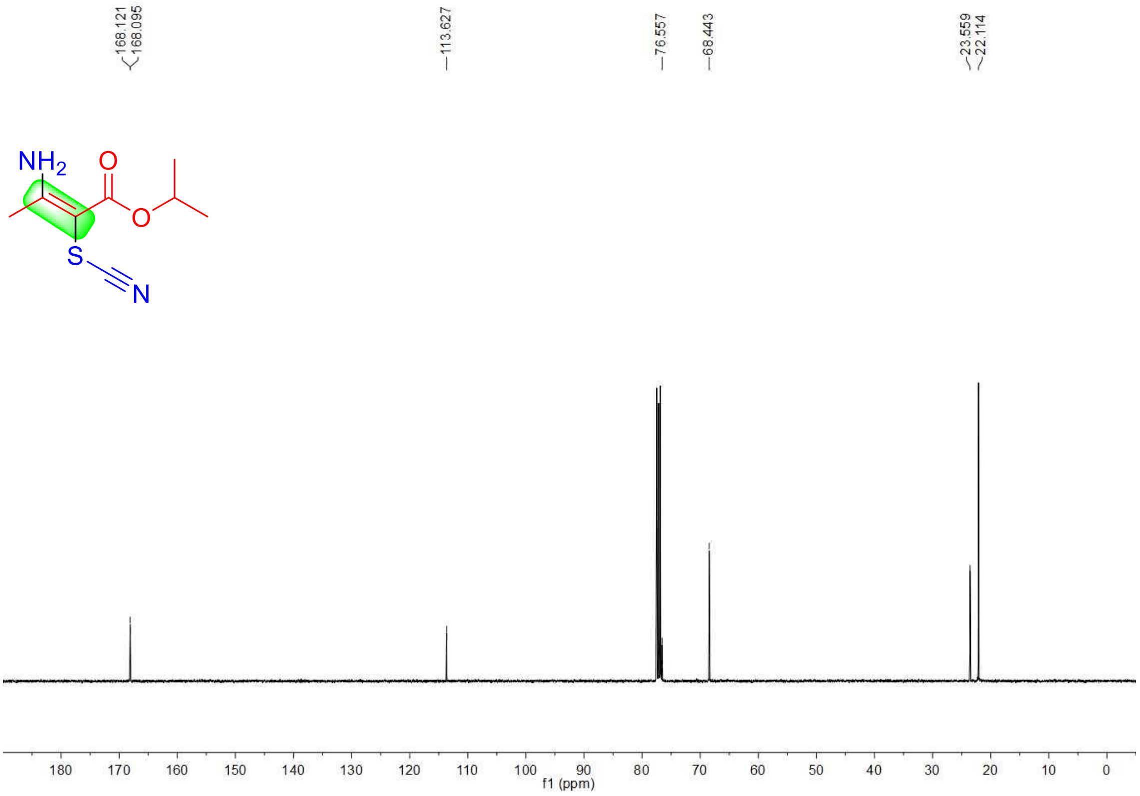

Figure S55. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of isobutyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5e) :

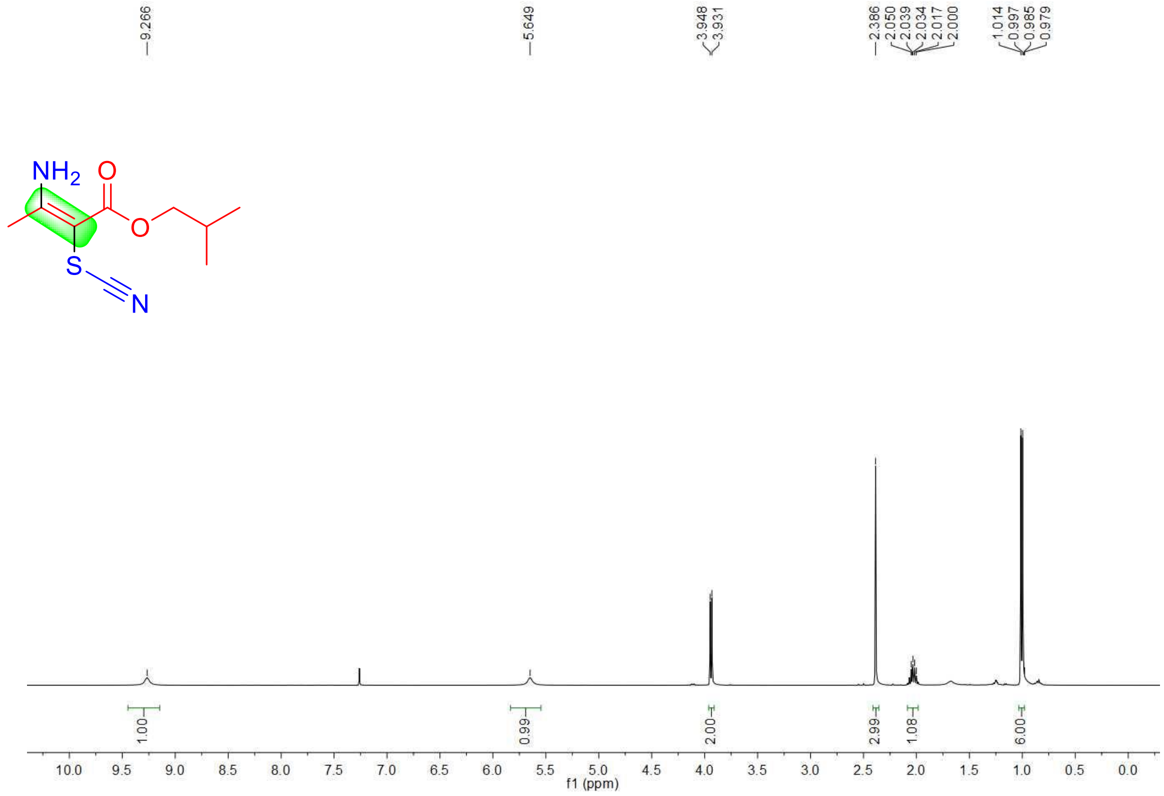

Figure S56. $^{13}C\{^1H\}$ NMR spectra (100 MHz, Chloroform-*d*) of isobutyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5e) :

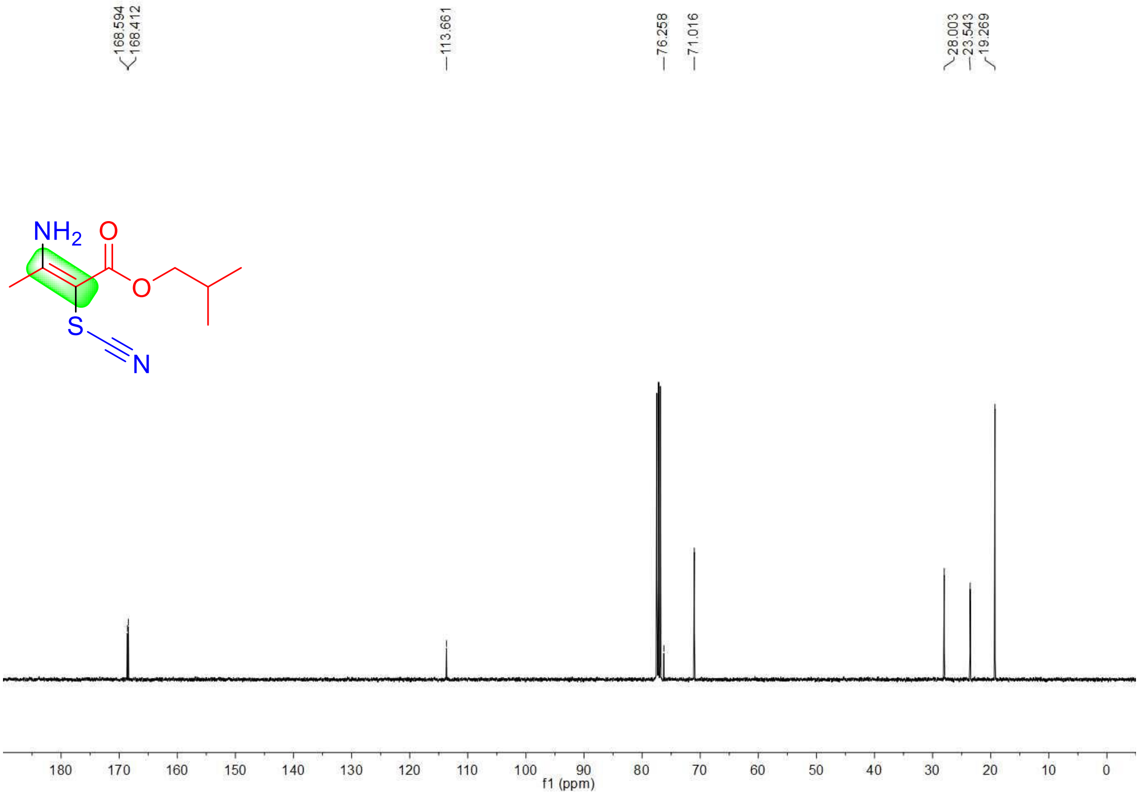

Figure S57. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of butyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5f) :

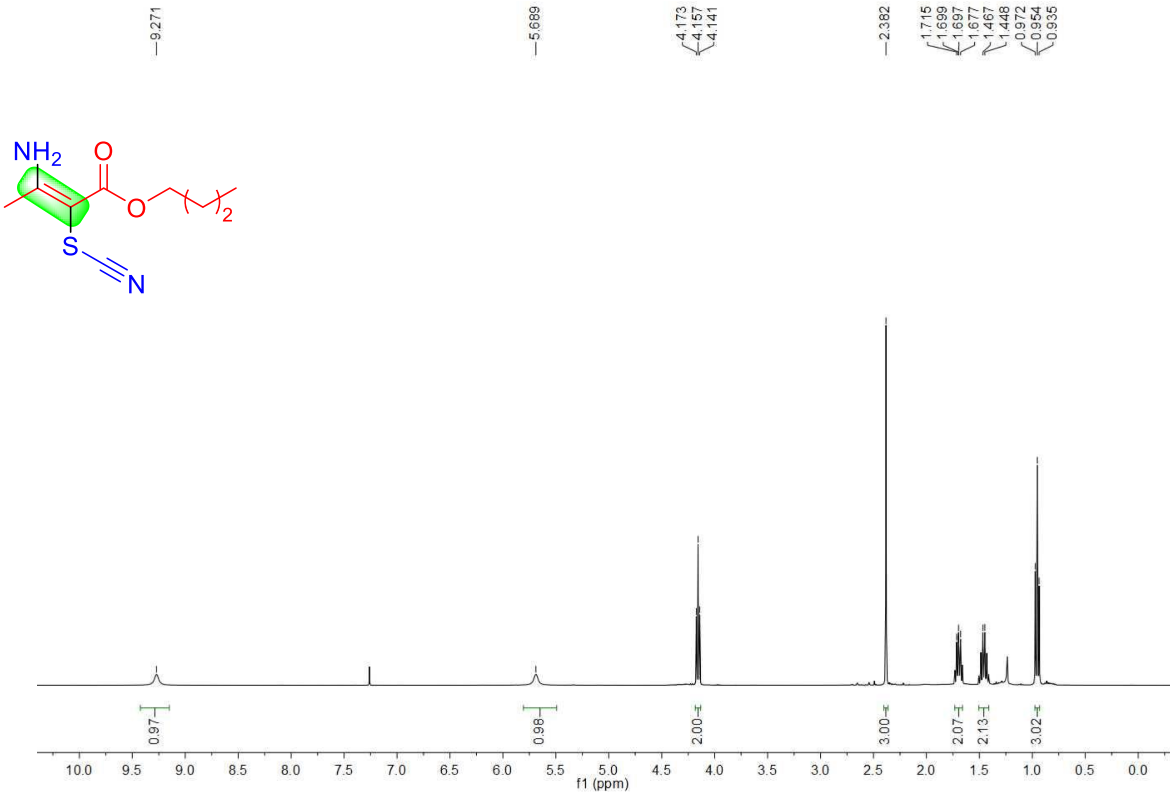

Figure S58. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of butyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5f) :

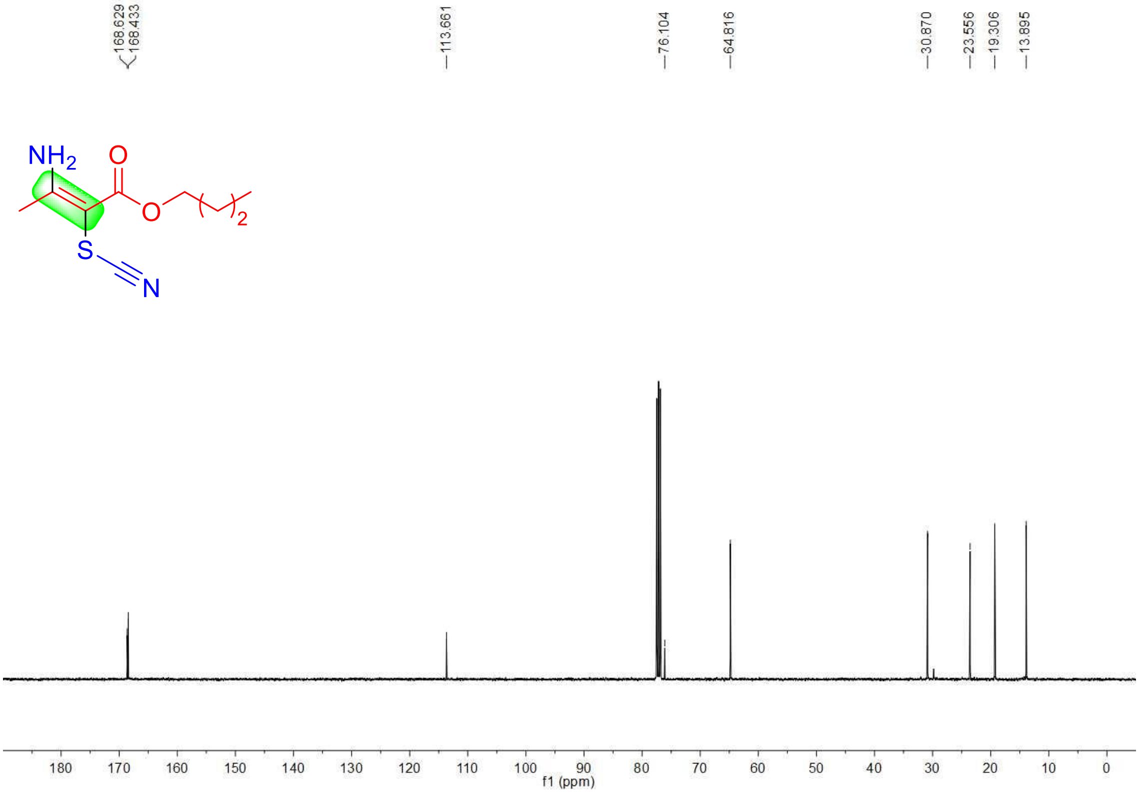

Figure S59. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of pentyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5g) :

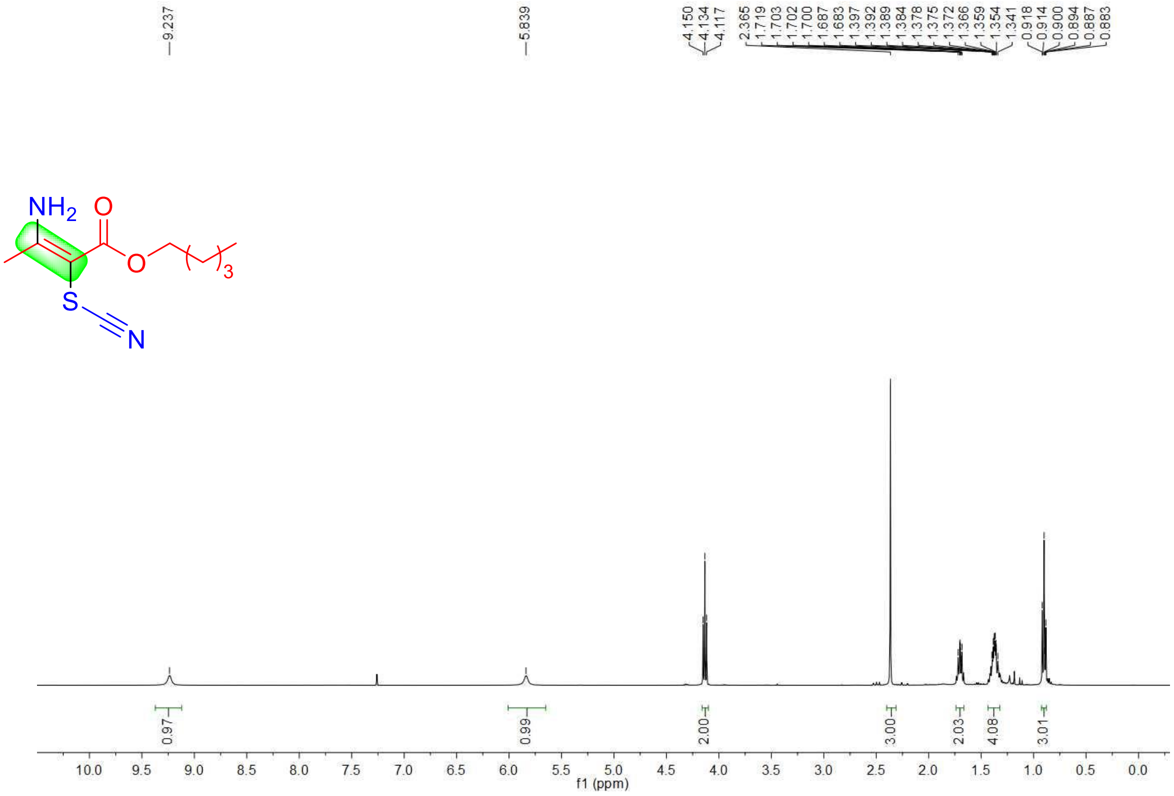

Figure S60. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of pentyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5g) :

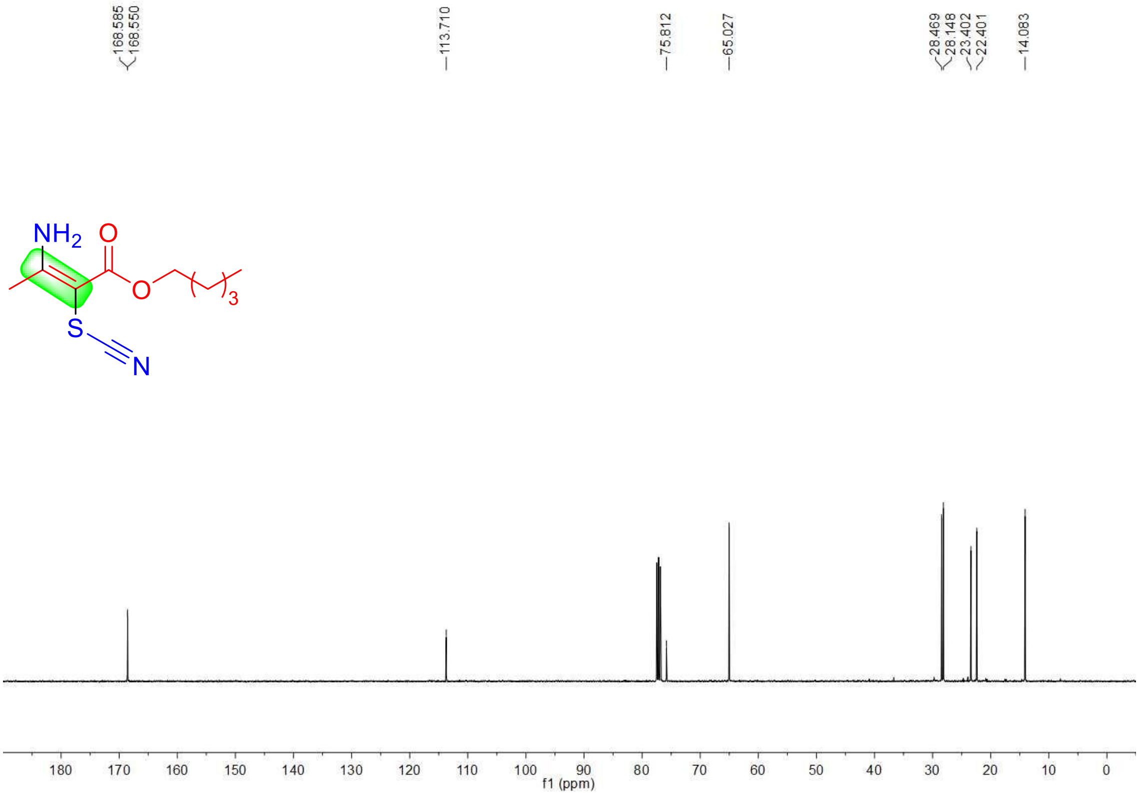

Figure S61. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of octyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5h) :

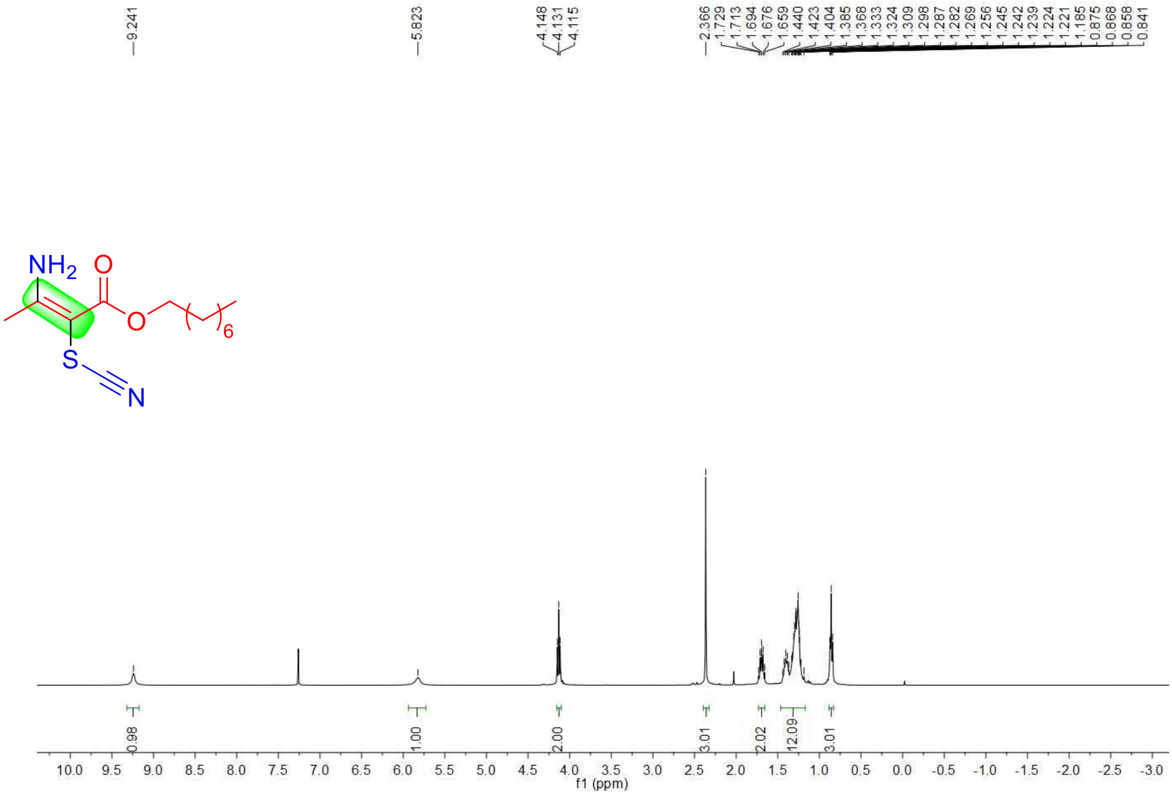

Figure S62. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of octyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5h) :

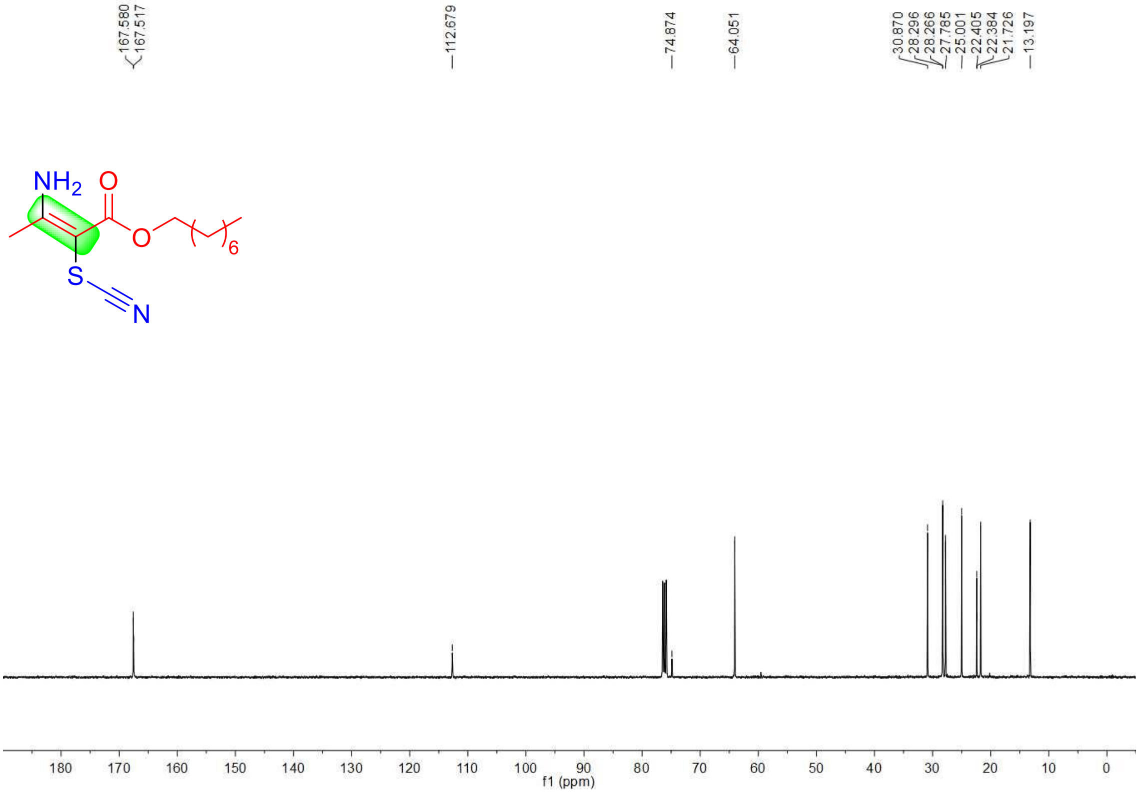

Figure S63. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of benzyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5i) :

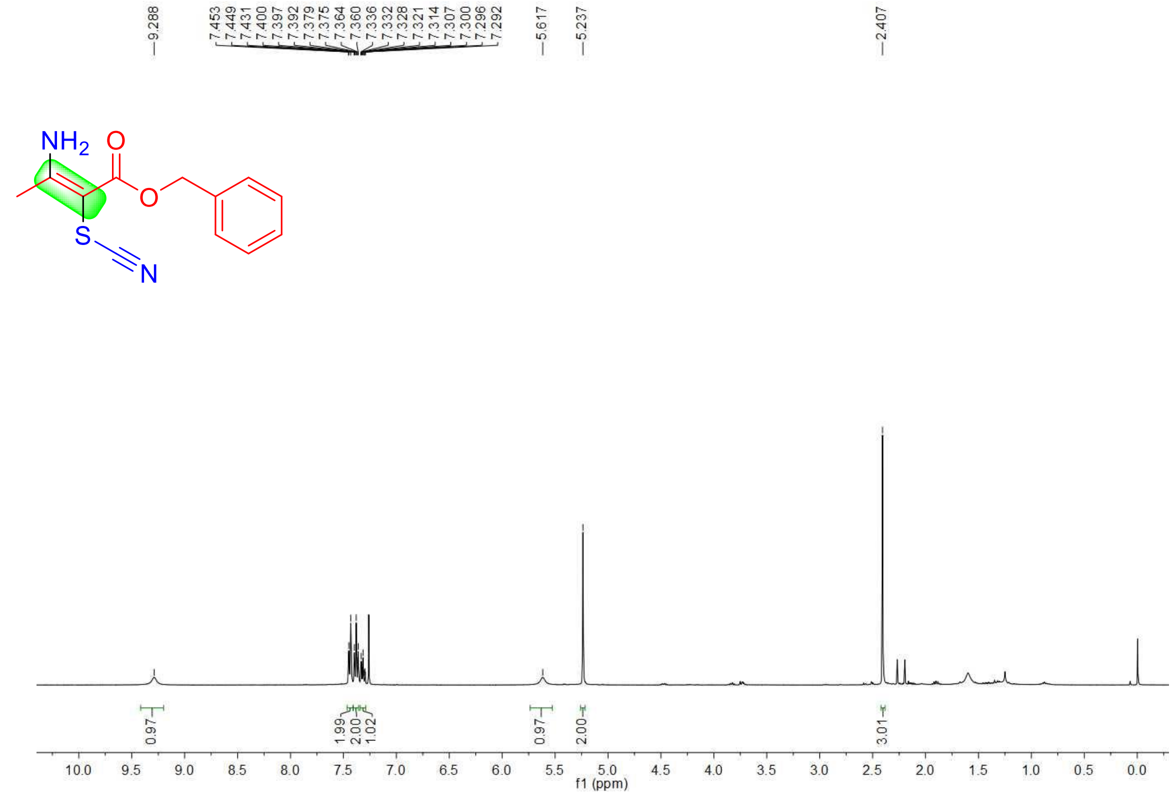

Figure S64. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of benzyl (*E*)-3-amino-2-thiocyanatobut-2-enoate (5i) :

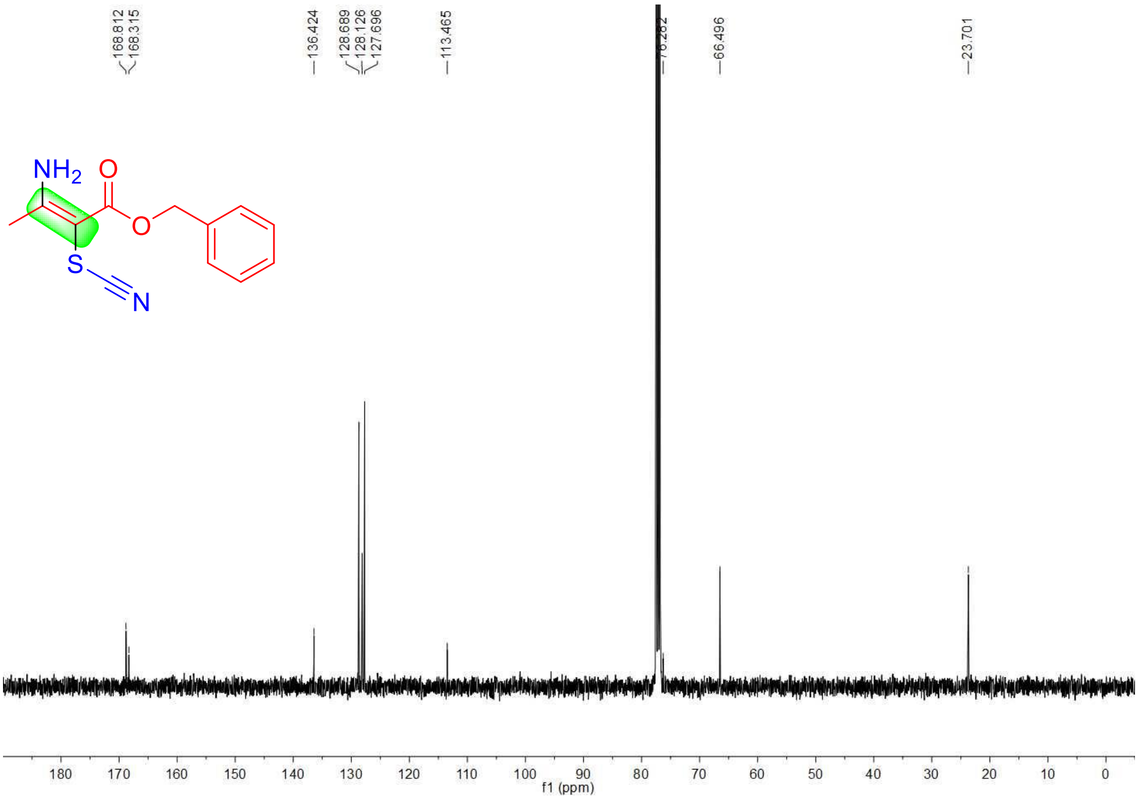

Figure S65. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of (*E*)-5-amino-4-thiocyanatohept-4-en-3-one (5j) :

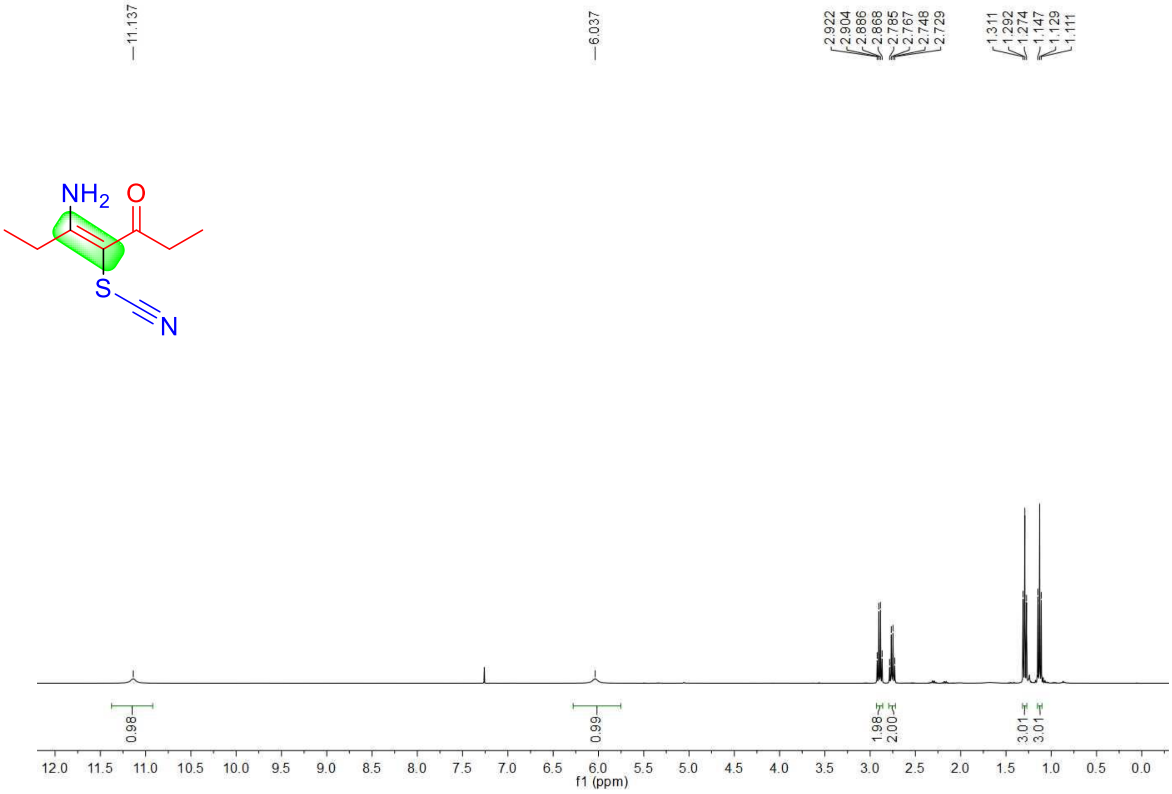

Figure S66. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of (*E*)-5-amino-4-thiocyanatohept-4-en-3-one (5j) :

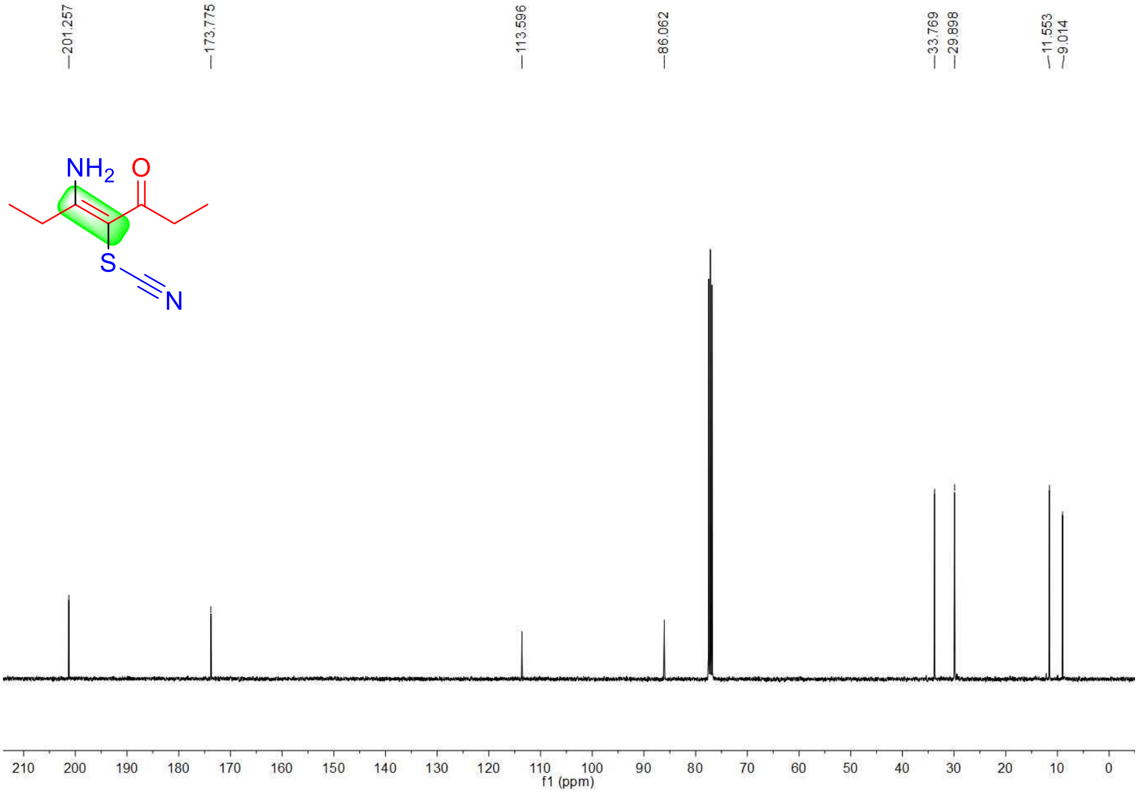

Figure S67. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of methyl (*E*)-3-amino-2-thiocyanatopent-2-enoate (5k) :

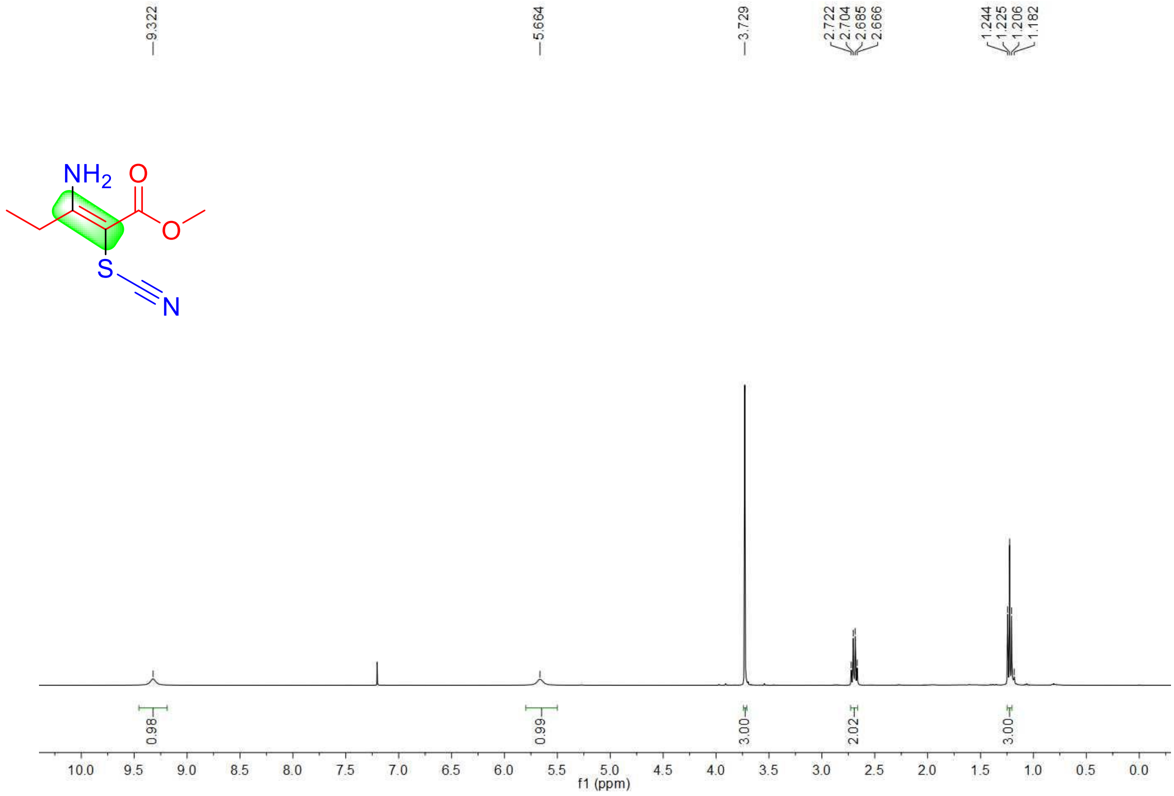

Figure S68. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of methyl (*E*)-3-amino-2-thiocyanatopent-2-enoate (5k) :

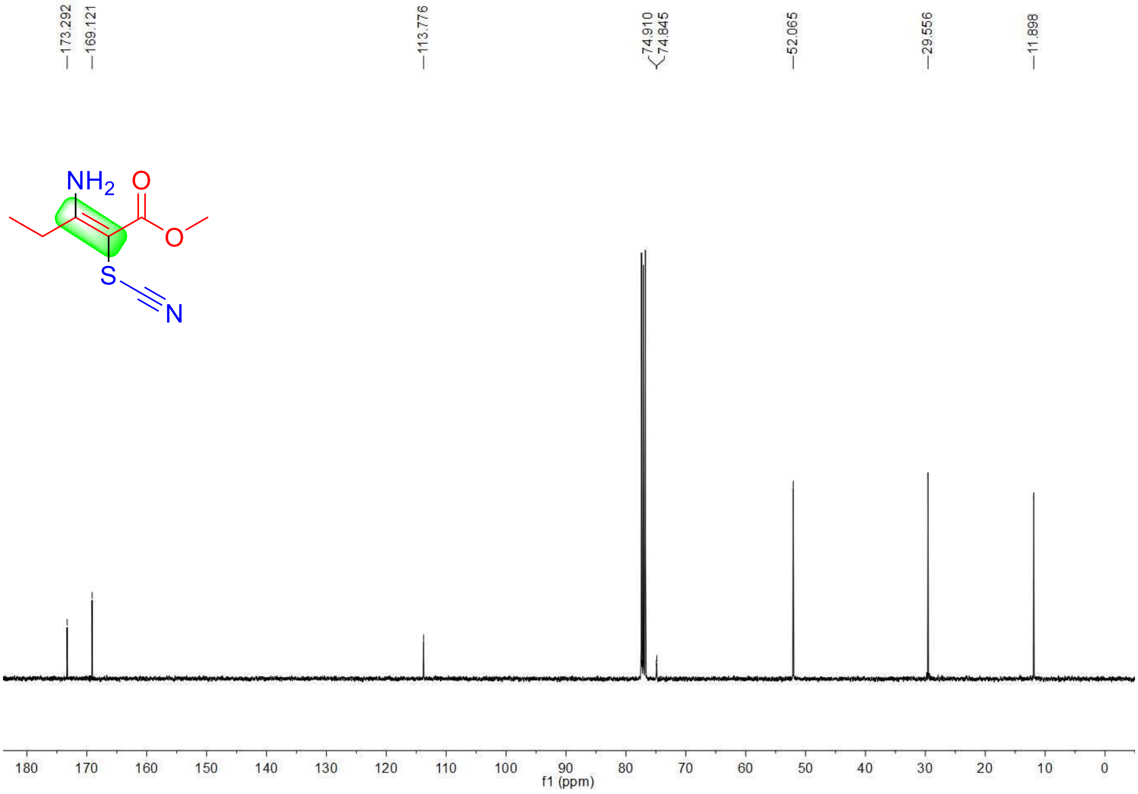

Figure S69. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of ethyl (*E*)-3-amino-2-thiocyanatopent-2-enoate (5l) :

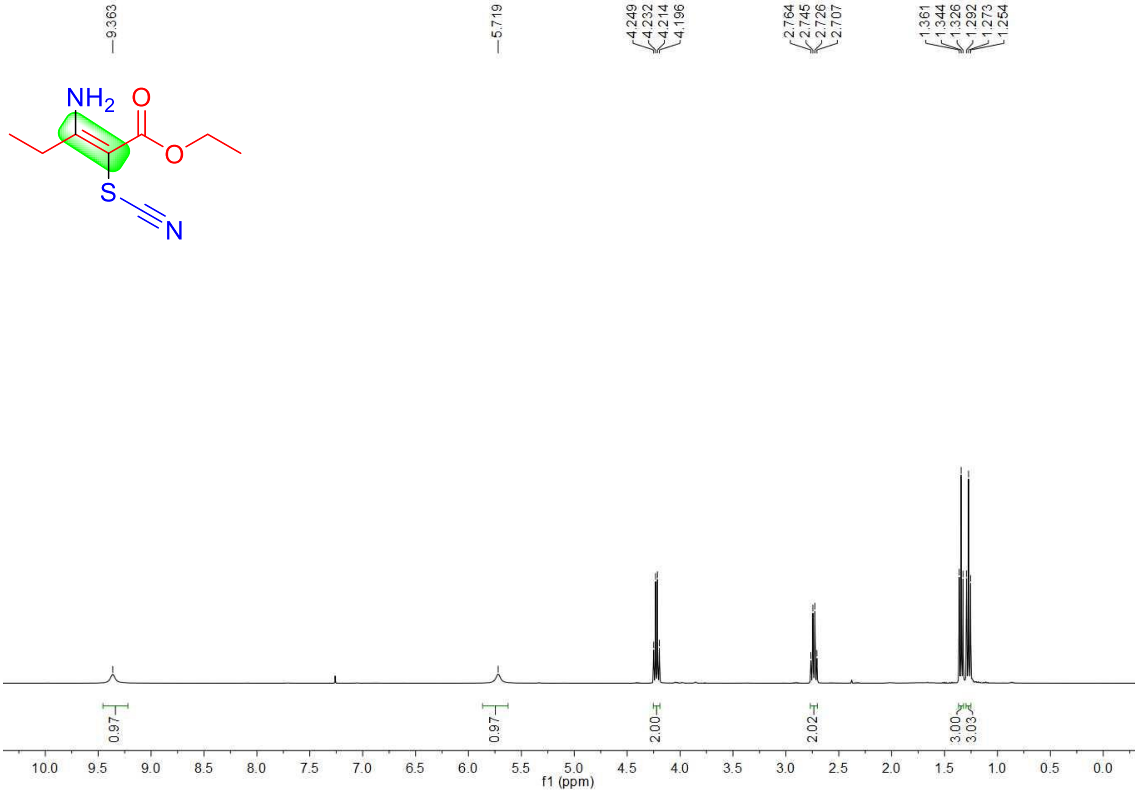

Figure S70. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of ethyl (*E*)-3-amino-2-thiocyanatopent-2-enoate (5l) :

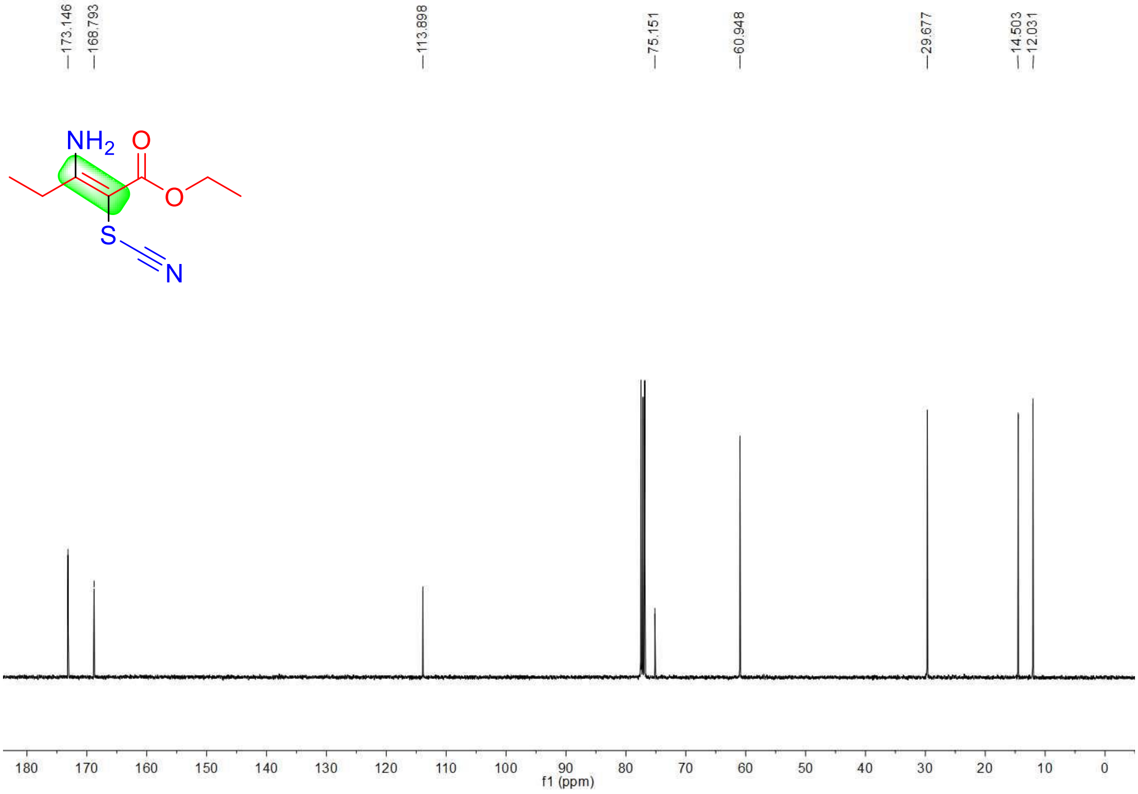

Figure S71. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of ethyl (*E*)-3-amino-3-phenyl-2-thiocyanatoacrylate (5m) :

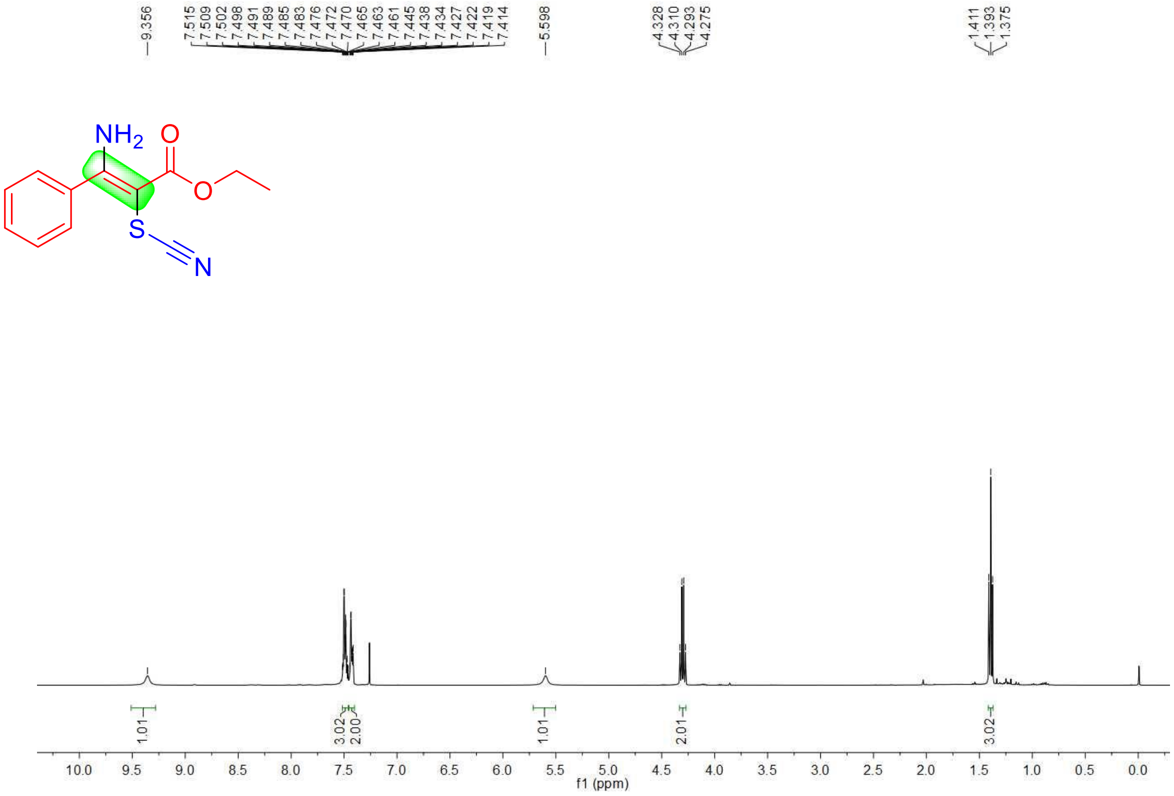

Figure S72. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of ethyl (*E*)-3-amino-3-phenyl-2-thiocyanatoacrylate (5m) :

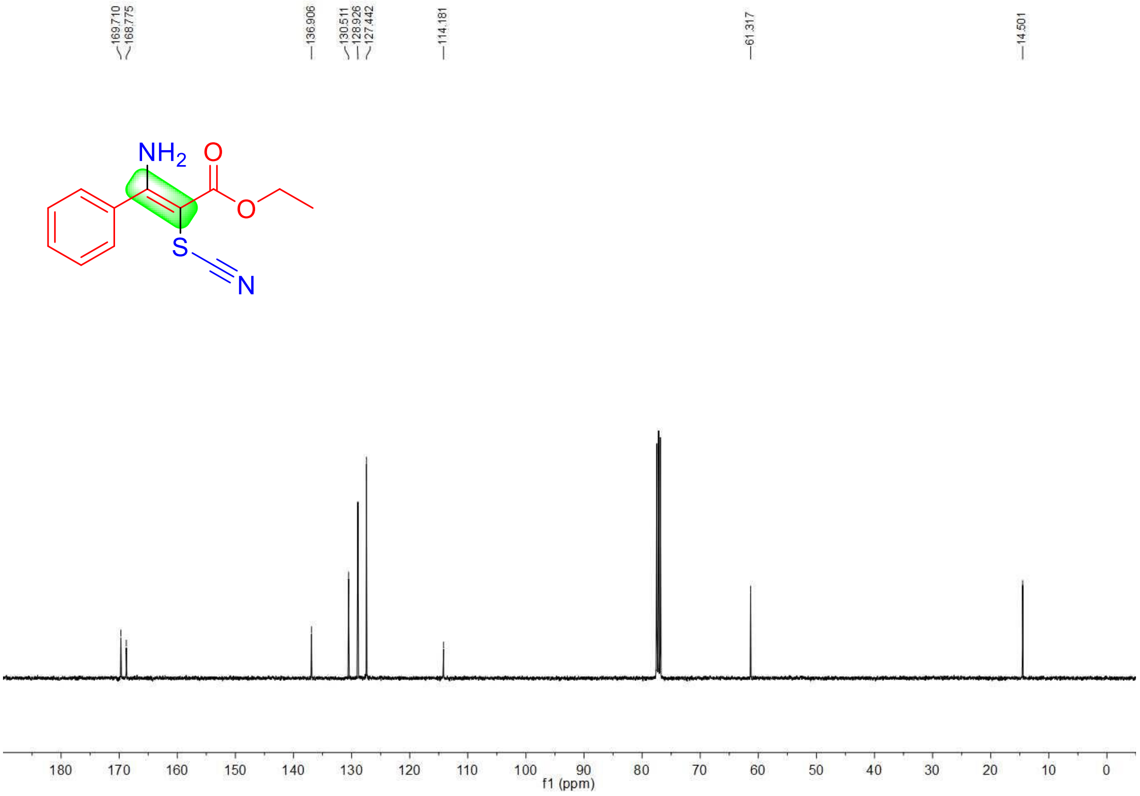

Figure S73. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of methyl (*E*)-3-amino-3-(4-fluorophenyl)-2-thiocyanatoacrylate (5n) :

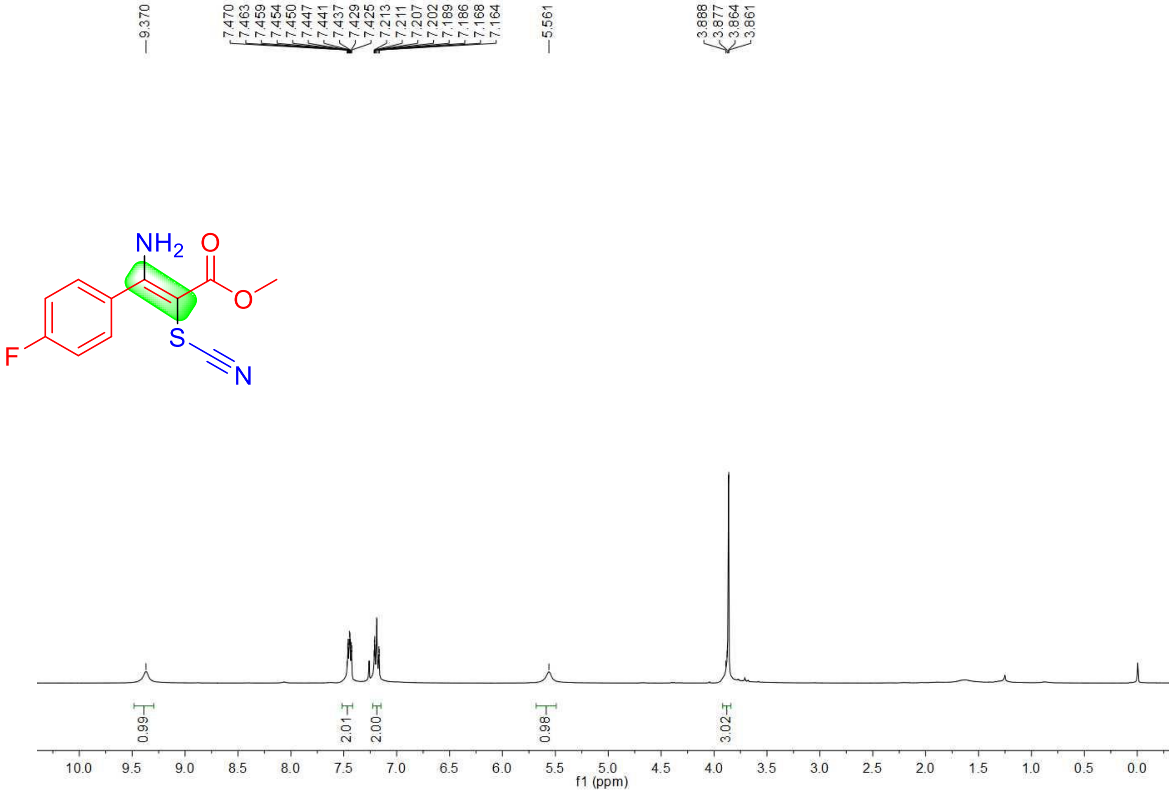

Figure S74. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of methyl (*E*)-3-amino-3-(4-fluorophenyl)-2-thiocyanatoacrylate (5n) :

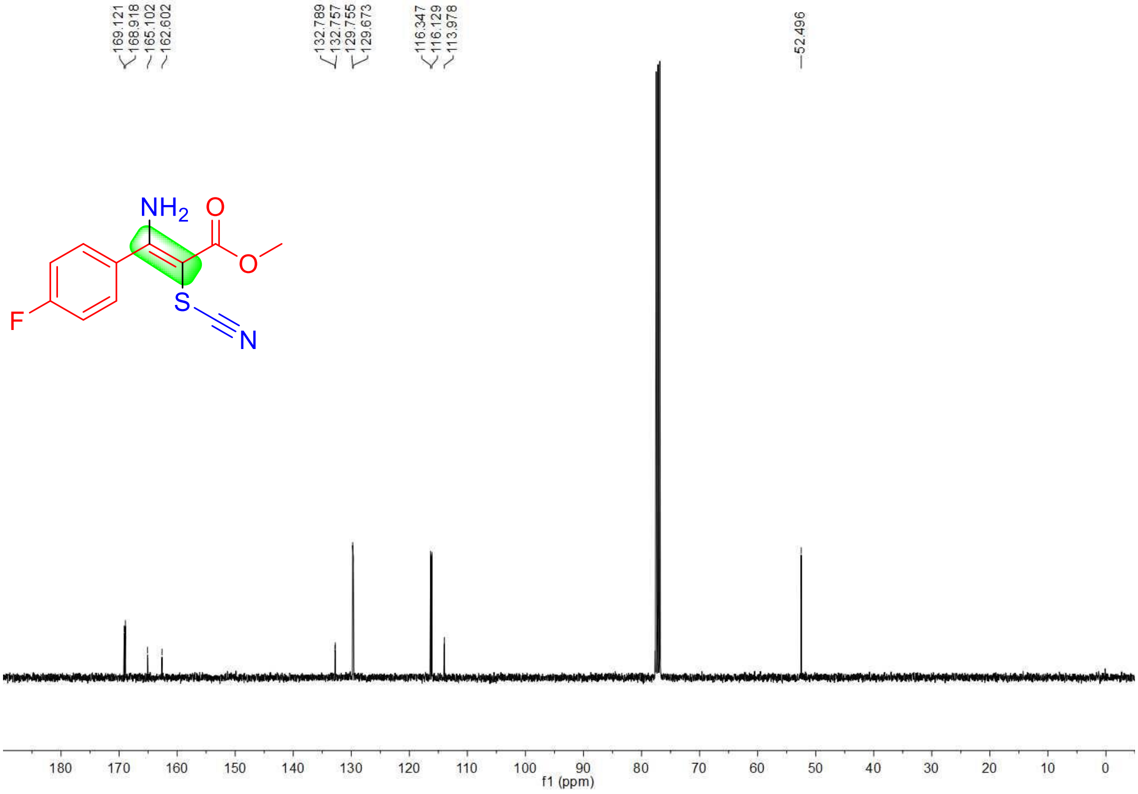

Figure S75. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of ethyl (*E*)-3-amino-3-(4-chlorophenyl)-2-thiocyanatoacrylate (5o) :

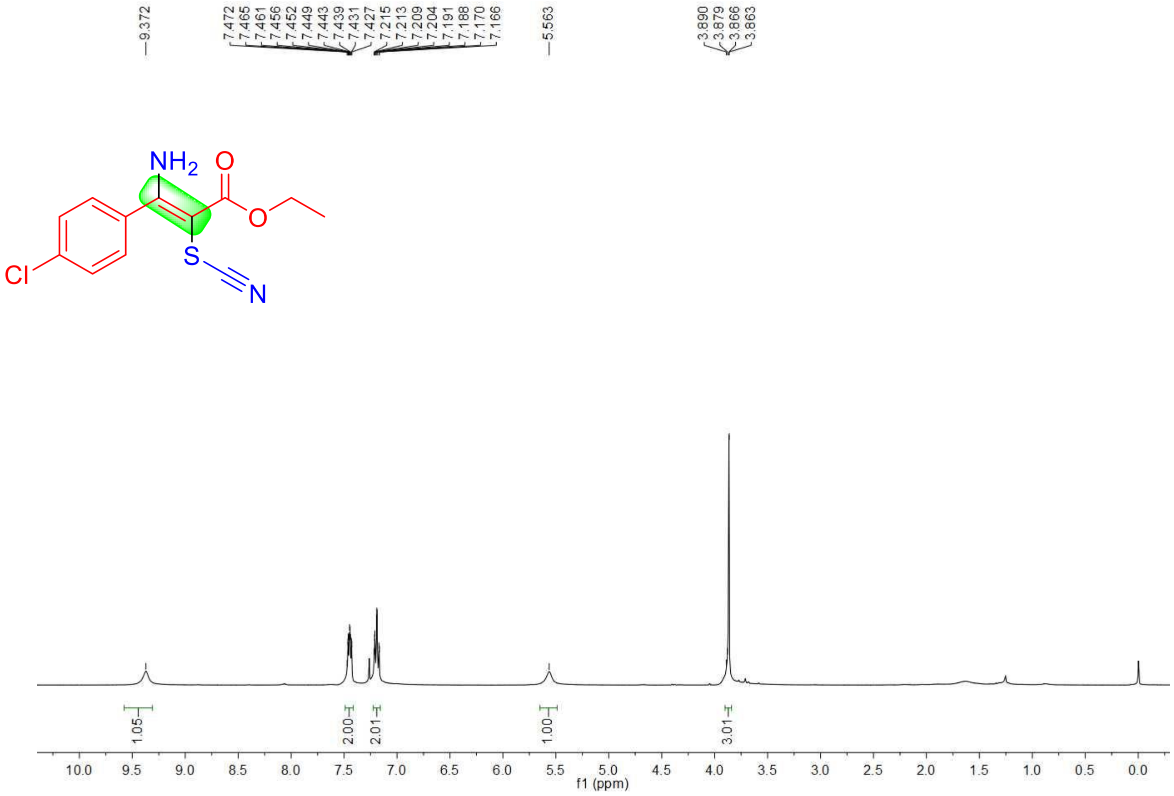

Figure S76. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of ethyl (*E*)-3-amino-3-(4-chlorophenyl)-2-thiocyanatoacrylate (5o) :

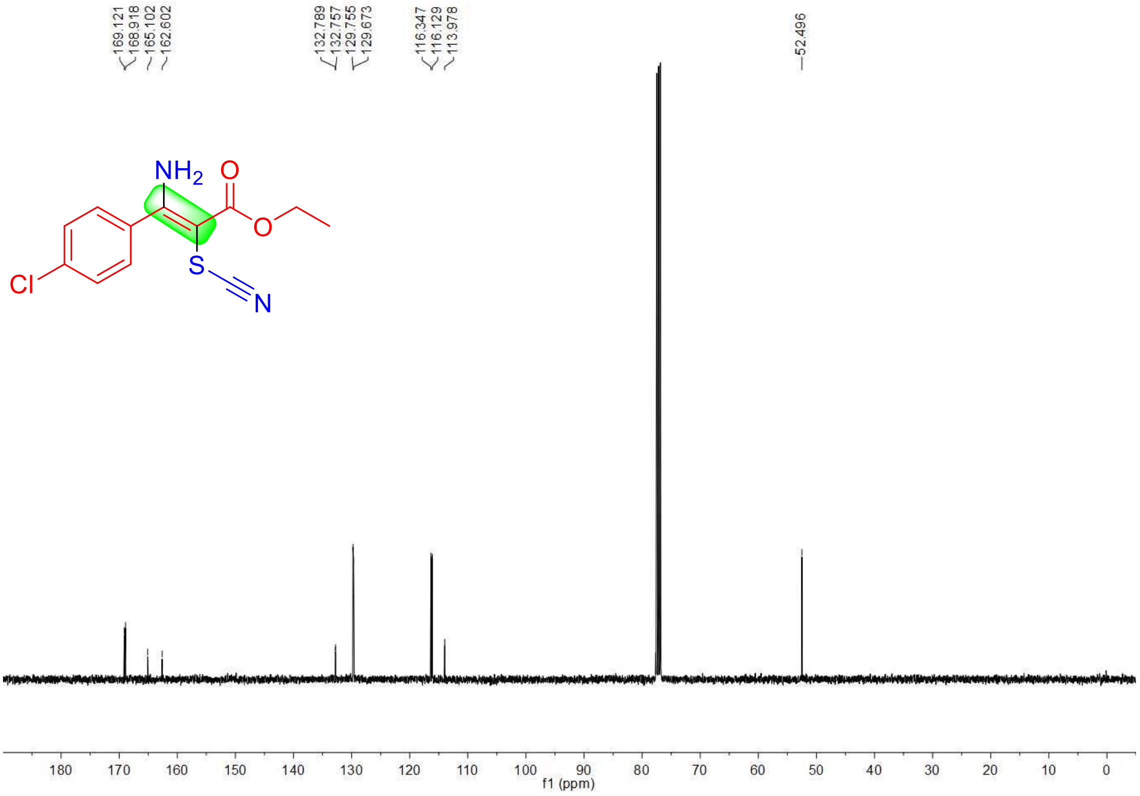

Figure S77. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of ethyl (*E*)-3-amino-3-(4-bromophenyl)-2-thiocyanatoacrylate (5p) :

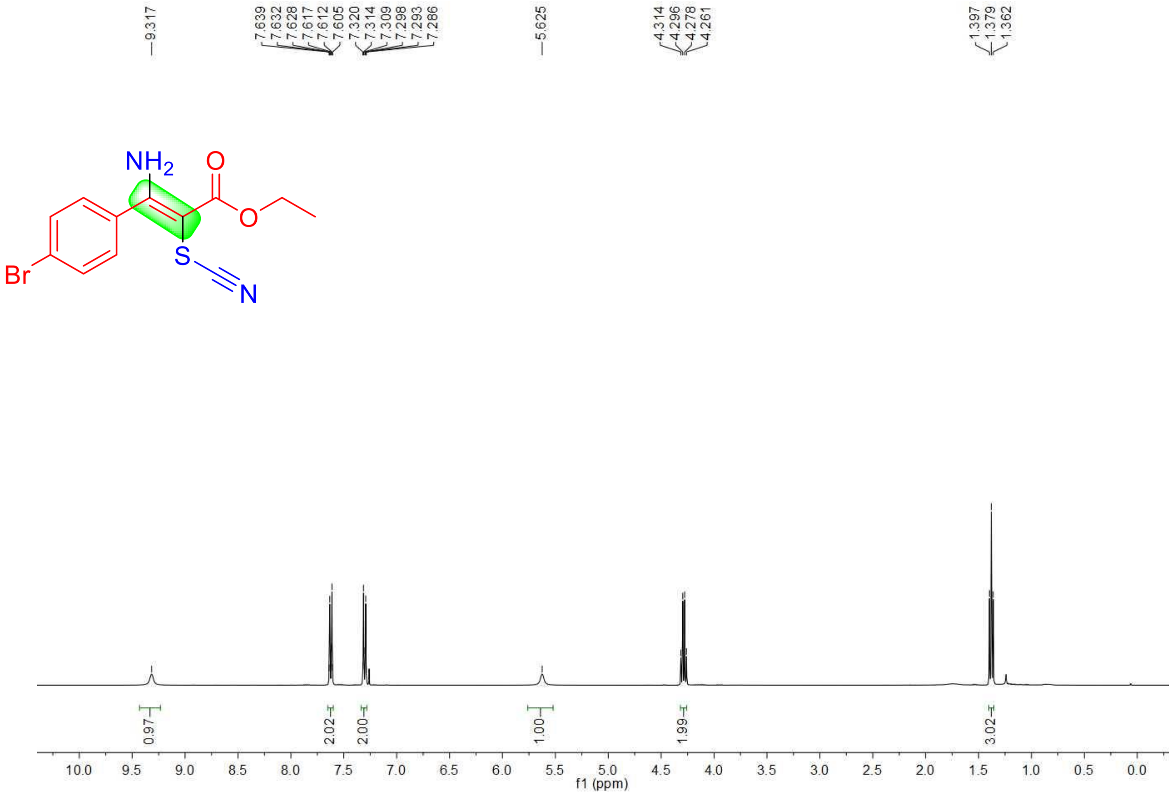

Figure S78. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of ethyl (*E*)-3-amino-3-(4-bromophenyl)-2-thiocyanatoacrylate (5p) :

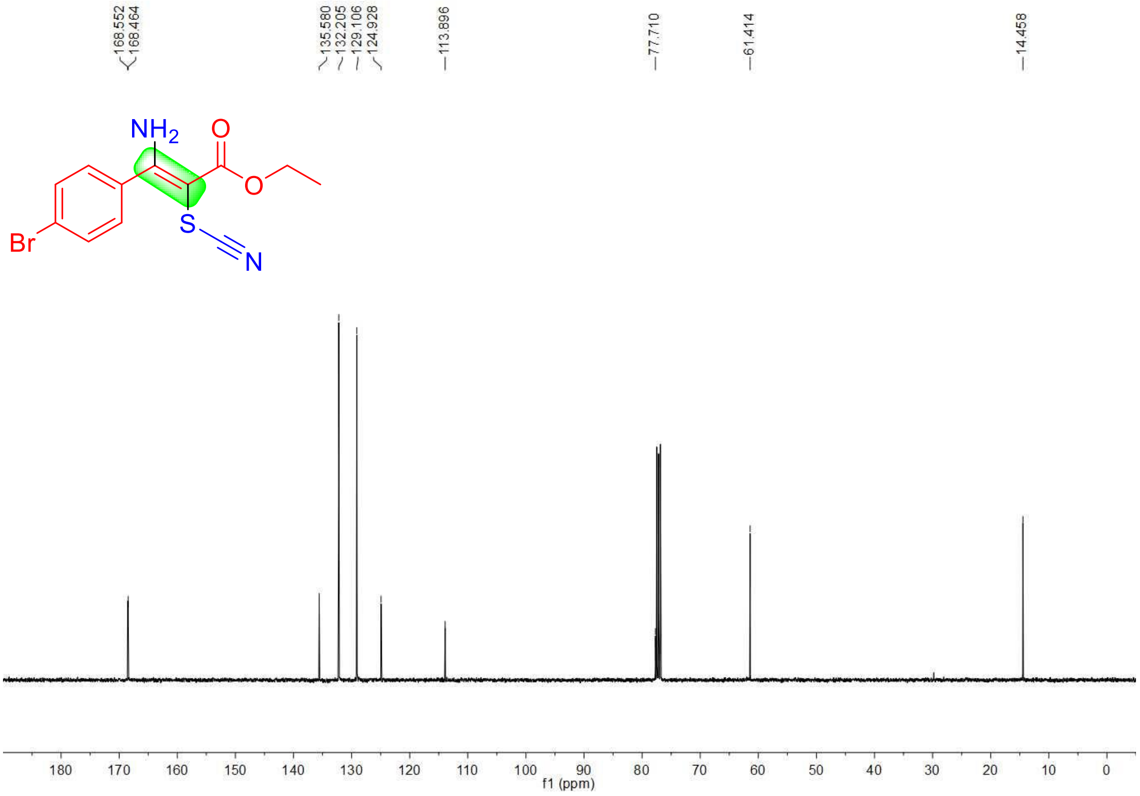

Figure S79. ^{1}H NMR spectra (400 MHz, Chloroform-*d*) of ethyl (*E*)-3-amino-2-thiocyanato-3-(*p*-tolyl)acrylate (5q) :

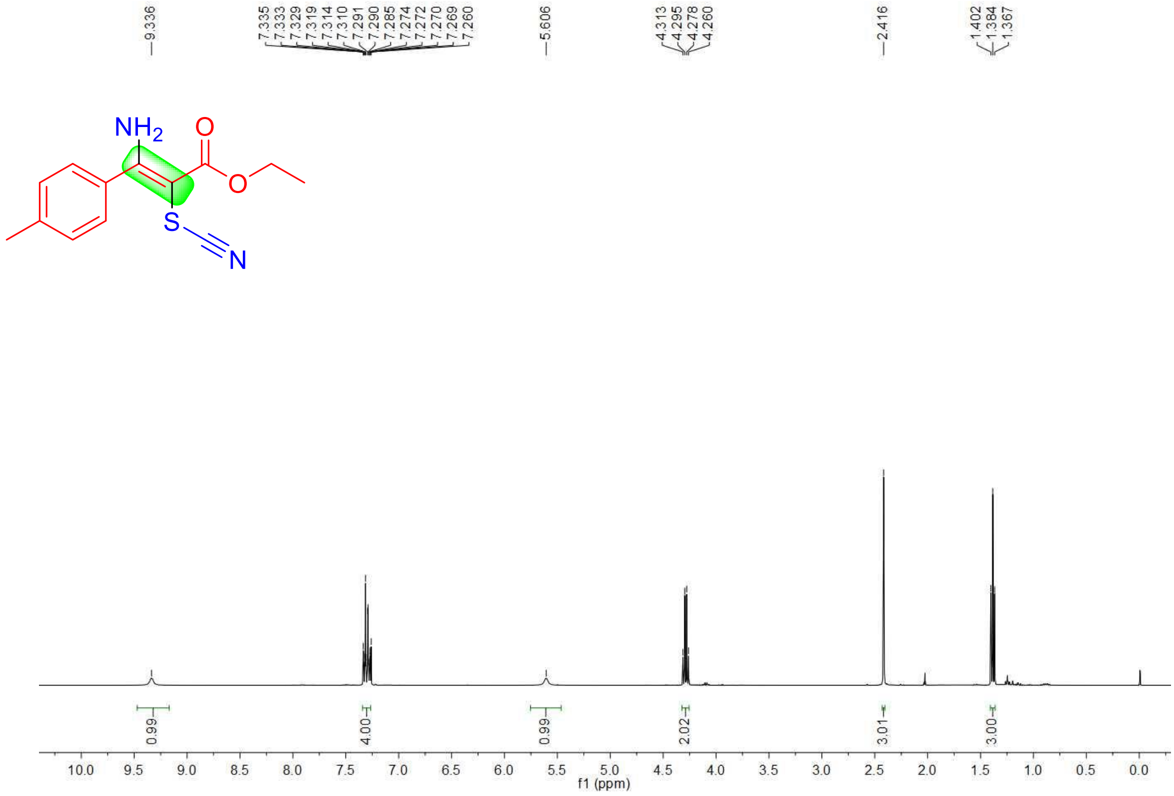

Figure 80. ^{13}C{^{1}H} NMR spectra (100 MHz, Chloroform-*d*) of ethyl (*E*)-3-amino-2-thiocyanato-3-(*p*-tolyl)acrylate (5q) :