Supporting Information

Photocatalyzed Thiocarbamylation of Alkenyl Radicals *via* Thiophene Salts

Bai-Xi He [1], Xin-Yu Lin [1], Ru-An Chi [2], Qing-Wen Han [2], Jing-Jing Cui [1,2], Zhi-Peng Guan [1,2,3] and Zhi-Bing Dong [1,2,3,4,5,6,*]

[1] School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Wuhan 430205, China; 598325989@qq.com (B.-X.H.); 1120286258@qq.com (X.-Y.L.); 17061701@wit.edu.cn (J.-J.C.); 23071108@wit.edu.cn (Z.-P.G.)

[2] Hubei Three Gorges Laboratory, Yichang 443007, China; rac@wit.edu.cn (R.-A.C.); hanqingwen1989@xingfagroup.com (Q.-W.H.)

[3] State Key Laboratory of Green and Efficient Development of Phosphorus Resource, Wuhan Institute of Technology, Wuhan 430205, China

[4] School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, China

[5] Key Laboratory of Danjiangkou Reservoir Area's Aquatic Eco-Environment and Health, Hanjiang Normal University, Shiyan 442000, China

[6] Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou 213164, China

* Corresponding author. E-mail: dzb04982@ wit.edu.cn (Z.-B.D.)

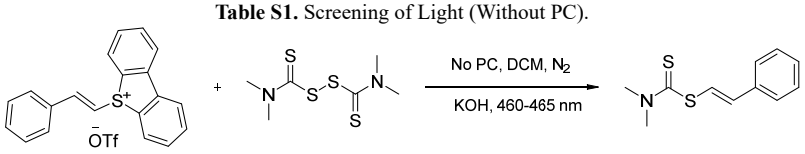
S1. General Informations

All reagents were obtained from commercial suppliers and used without further purification. Yields for all compounds were determined by the column chromatography which was generally performed on silica gel (200-300 mesh) using petroleum ether PE/EA or DCM/MeOH as eluent, and reactions were monitored by thin layer chromatography (TLC) on a glass pate coated with silica gel with fluorescent indicator (GF254) using UV light. The ^{1}H, ^{13}C and ^{19}F nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ADNANCE III 500 MHz using $CDCl_3$ as solvent with TMS as internal standard. Chemical shifts are given in ppm (δ) referenced to $CDCl_3$ with 7.26 for ^{1}H and 77.16 for ^{13}C. Signals are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, or combinations thereof, and coupling constants are expressed in hertz. High-resolution mass spectrometric data (HRMS) were obtained using Agilent 7200 Q-TOF and Bruker MicroTOF-Qll (APCI, or Electrospray ionization, ESI). Gas Chromatography-Mass Spectrometry (GC-MS) was performed on Agilent 7820A with FID detection.

Our bulbs and slides are purchased from Taobao. The lamp has a power of 30 W and a peak intensity wavelength of 460 nm. The distance from the light source to the irradiation vessel is about 1 cm. The reaction temperature is maintained at room temperature using a fan connected to the device.

S2. Additional Optimization of Reaction Conditions with TMTD

Table S1. Screening of Light (Without PC).

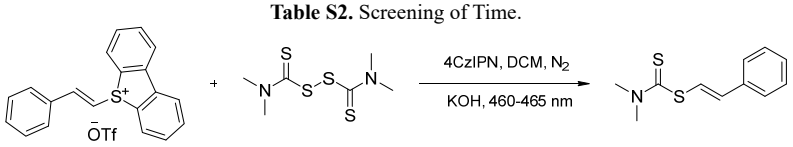


1a **2a** **3a**

Entry	Light(nm)	Yield [a]
1	395	Trace
2	425	32%
3	445	35%
4	465	40%

Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2a** (0.6 mmol, 3 equiv.), KOH (2 equiv.), in DCM (2 mL), room temperature, 12 h, Light (x nm). [a] Isolated yield of products.

Table S2. Screening of Time.

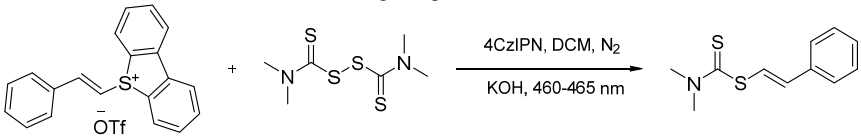


1a **2a** **3a**

Entry	Time (h)	Yield [a]
1	3	36%
2	6	47%
3	9	58%
4	15	62%

Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2a** (0.6 mmol, 3 equiv.), 4CzIPN (5 mol%), KOH (2 equiv.), in DCM (2 mL), room temperature, x h, Blue LED (460 nm). [a] Isolated yield of products.

Table S3. Screening of equivalence ratio of **1a:2a**.



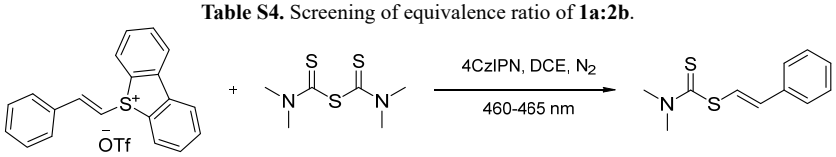
1a **2a** **3a**

Entry	Equivalence Ratio (1a:2a)	Yield [a]
1	2:1	trace
2	1:1	trace
3	1:2	54%
4	1:2.5	61%
5	1:3	70%
6	1:3.5	58%

Reaction conditions: **1a** (x equiv.), **2a** (x equiv.), 4CzIPN (5 mol%), KOH (2 equiv.), in DCM (2 mL), room temperature, 12 h, Blue LED (460 nm). [a] Isolated yield of products.

S3. Additional Optimization of Reaction Conditions with TMTM

Table S4. Screening of equivalence ratio of **1a:2b**.

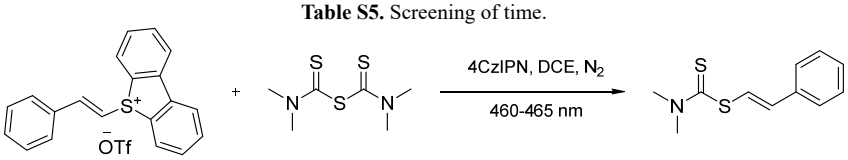


1a **2b** **3a**

Entry	Ratio (1a:2b)	Yield [a]
1	1:3	17%
2	1:2	15%
3	1:1	N.R.
4	2:1	N.R.
5	1:3.5	76%
6	1:4.5	77%
7	1:5	79%

Reaction conditions: **1a** (x equiv.), **2b** (x equiv.), 4CzIPN (5 mol%), in DCE (2 mL), room temperature, 12 h, Blue LED (460 nm). [a] Isolated yield of products.

Table S5. Screening of time.

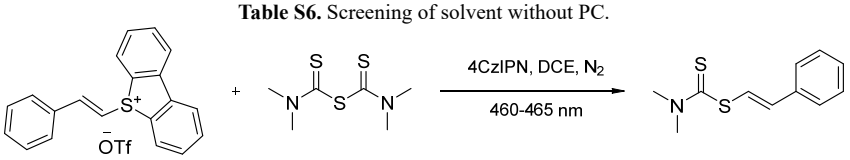


1a **2b** **3a**

Entry	Time (h)	Yield [a]
1	3	15%
2	6	20%
3	9	41%
4	15	52%

Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2b** (0.6 mmol, 3 equiv.), 4CzIPN (5 mol%), in DCE (2 mL), room temperature, x h, Blue LED (460 nm). [a] Isolated yield of products.

Table S6. Screening of solvent without PC.

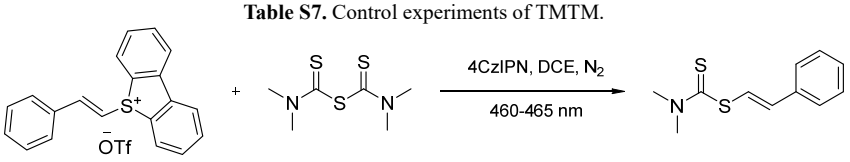


1a **2b** **3a**

Entry	Solvent (mL)	Yield [a]
1	MeCN	54%
2	DCE	60%
3	DCM	59%
4	THF	57%
5	MeOH	trace
6	DMAc	30%
7	DMSO	26%
8	DMF	49%
9	Acetone	59%

Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2b** (0.6 mmol, 3 equiv.), 4CzIPN (5 mol%), in solvent (2 mL), room temperature, 12 h, Blue LED (460 nm). [a] Isolated yield of products.

Table S7. Control experiments of TMTM.

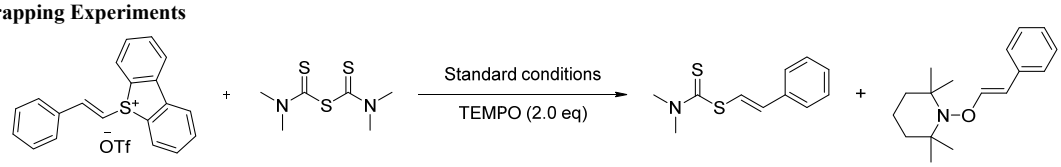


1a **2b** **3a**

Entry	Addition/Temp.	Yield [a]
1	TEMPO	N.D.
2	BHT	35%
3	No PC	40%
4	No Light	N.R.
5	Air	15%
6	RT	80%
7	50 ℃	N.R.
8	70 ℃	N.R.

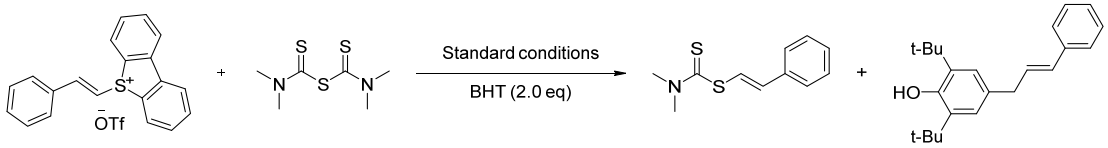
Reaction conditions: **1a** (0.2 mmol, 1 equiv.), **2b** (0.6 mmol, 3 equiv.), 4CzIPN (5 mol%), in DCE (2 mL), room temperature, 12 h, Blue LED (460 nm). [a] Isolated yield of products.

S4. Trapping Experiments



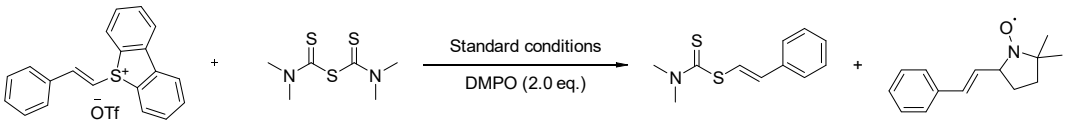
1a **2b** **3a,** N.D. Detected by GC-MS

In a 10 mL Schlenk flask equipped with a stirring rod and flame drying, sequentially add styrene thiophene salt (1.0 equivalent, 0.2 mmol), TMTM (5.0 equivalents, 1.0 mmol), 4CzIPN (5 mol%, 0.01 mmol), and TEMPO (2.0 equivalents, 0.4 mmol). Under nitrogen atmosphere, DCE (2.0 mL) was injected into the flask using a syringe. The mixture was stirred under 4×6 W blue LED irradiation at room temperature for 12 hours. Quantitative analysis by gas chromatography detected no formation of target compound **3a**. Simultaneous gas chromatography-mass spectrometry detected styrenyl radical capture products, indicating the generation of styrenyl radicals during the transformation.



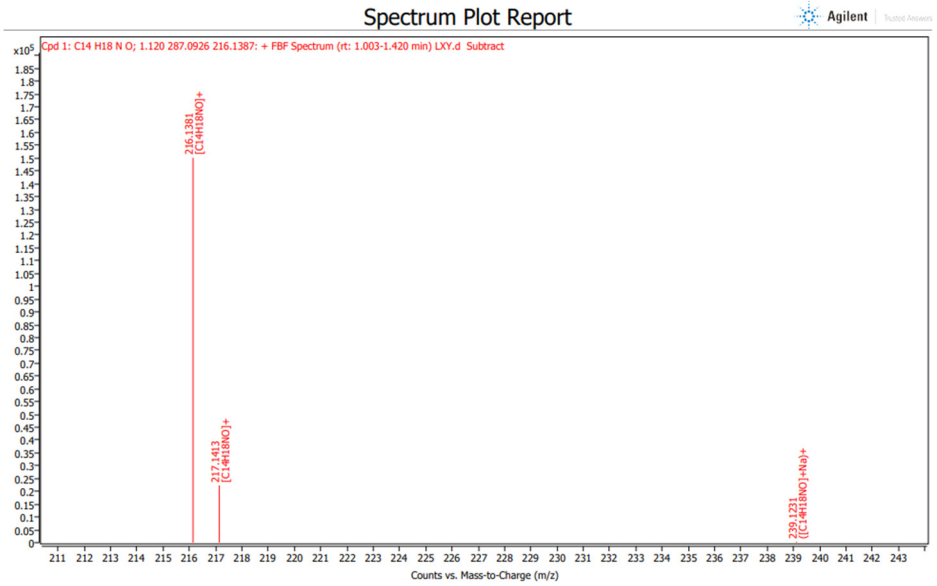
1a **2b** **3a,** 35% Detected by GC-MS

In a 10 mL Schlenk flask equipped with a stirring rod and flame drying, sequentially add styrene thiophene salt (1.0 equivalent, 0.2 mmol), TMTM (5.0 equivalents, 1.0 mmol), 4CzIPN (5 mol%, 0.01 mmol), and BHT (2.0 equivalents, 0.4 mmol). Under nitrogen atmosphere, DCE (2.0 mL) was injected into the flask using a syringe. The mixture was stirred under 4×6 W blue LED irradiation at room temperature for 12 hours. Quantitative analysis by gas chromatography detected the target compound **3a**, but the reaction was significantly inhibited. Simultaneously, styrenyl radical capture products were detected by gas chromatography-mass spectrometry, indicating the generation of styrenyl radicals during the transformation process.

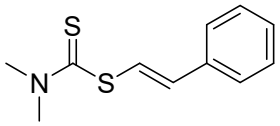


1a **2b** **3a**, N.D. Detected by GC-MS and HR-MS

In a 10 mL Schlenk flask equipped with a stirring rod and flame drying, sequentially add styrene thiophene salt (1.0 equivalent, 0.2 mmol), TMTM (5.0 equivalents, 1.0 mmol), 4CzIPN (5 mol%, 0.01 mmol), and TEMPO (2.0 equivalents, 0.4 mmol). Under nitrogen atmosphere, DCE (2.0 mL) was injected into the flask using a syringe. The mixture was stirred under 4×6 W blue LED irradiation at room temperature for 12 hours. Quantitative analysis by gas chromatography detected no formation of target compound **3a**. Simultaneous GC-MS and HR-MS spectrometry detected styrenyl radical capture products, indicating the generation of styrenyl radicals during the transformation.

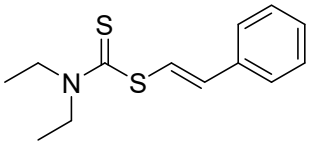


Analytical Data



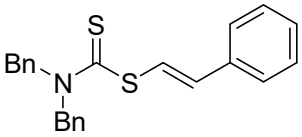
3a

(E)-styryl dimethylcarbamodithioate (3a). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (m, 3H), 7.36 (m, 2H), 7.27 (m, 1H), 6.79 (m, 1H), 3.57 (d, *J* = 12.0 Hz, 3H), 3.41 (d, *J* = 15.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 194.81, 193.55, 136.45, 136.30, 132.36, 128.90, 128.76, 128.60, 128.45, 128.20, 127.63, 126.67, 124.50, 123.16, 45.76, 45.15, 41.68.



3b

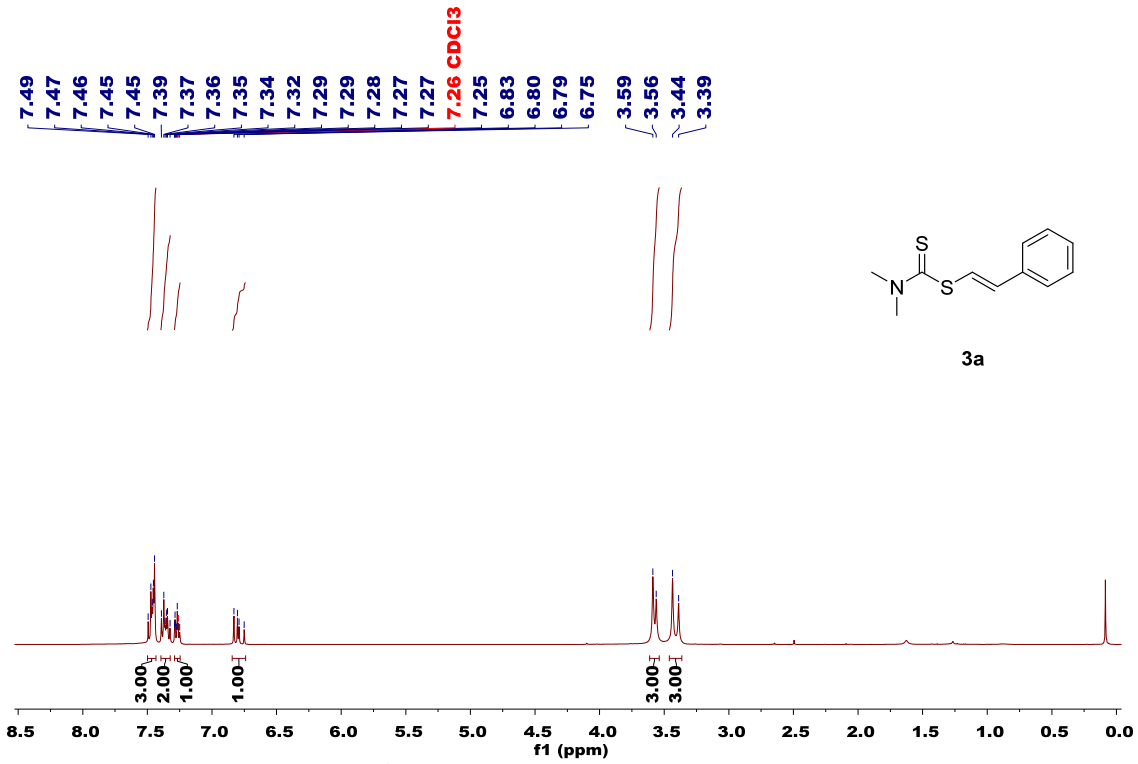
(E)-styryl diethylcarbamodithioate (3b). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 (m, 3H), 7.23 (m, 2H), 7.14 (m, 1H), 6.65 (m, 1H), 3.93 (m, 2H), 3.65 (m, 2H), 1.19 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ193.25, 191.97, 136.54, 136.42, 132.25, 128.91, 128.75, 128.44, 128.39, 128.14, 127.55, 126.67, 124.28, 122.94, 50.06, 49.43, 47.13, 46.99, 12.88, 12.75, 11.70, 11.61.



3c

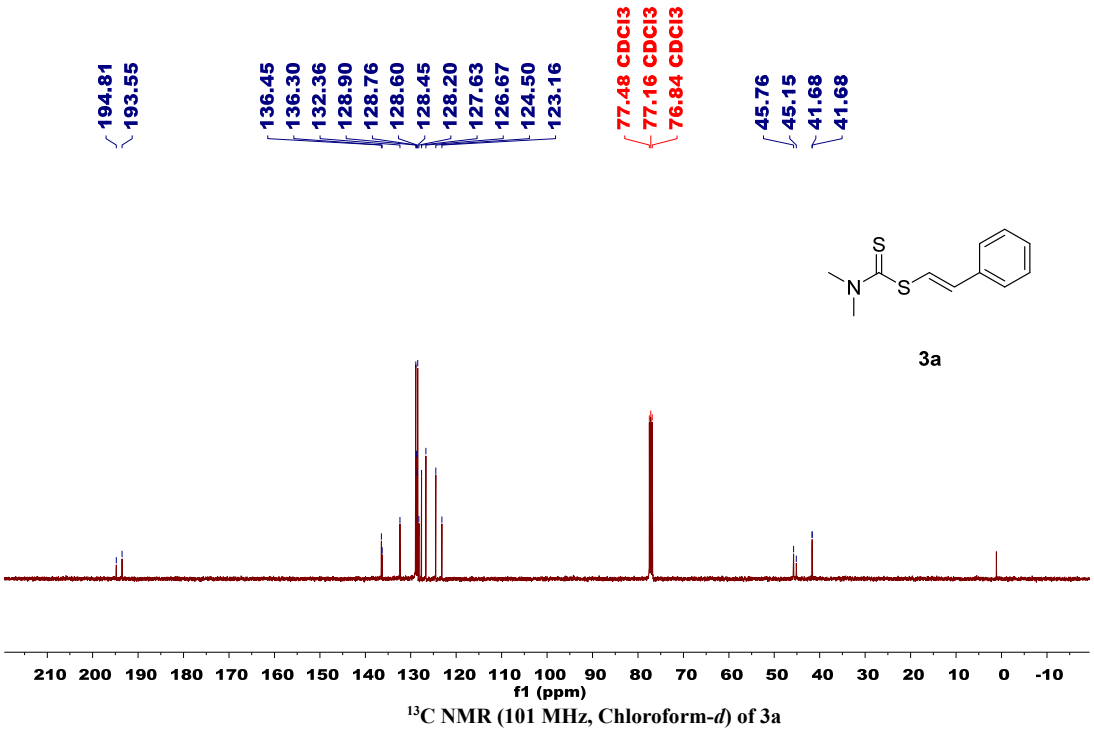
(E)-styryl dibenzylcarbamodithioate (3c). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (m, 16H), 6.85 (m, 1H), 5.37 (s, 2H), 4.95 (d, *J* = 24.0 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.92, 136.24, 132.92, 129.18, 129.08, 128.89, 128.73, 128.40, 128.25, 127.95, 127.65, 127.30, 126.69, 124.14, 122.76, 56.54, 54.15.

S5. NMR Spectra



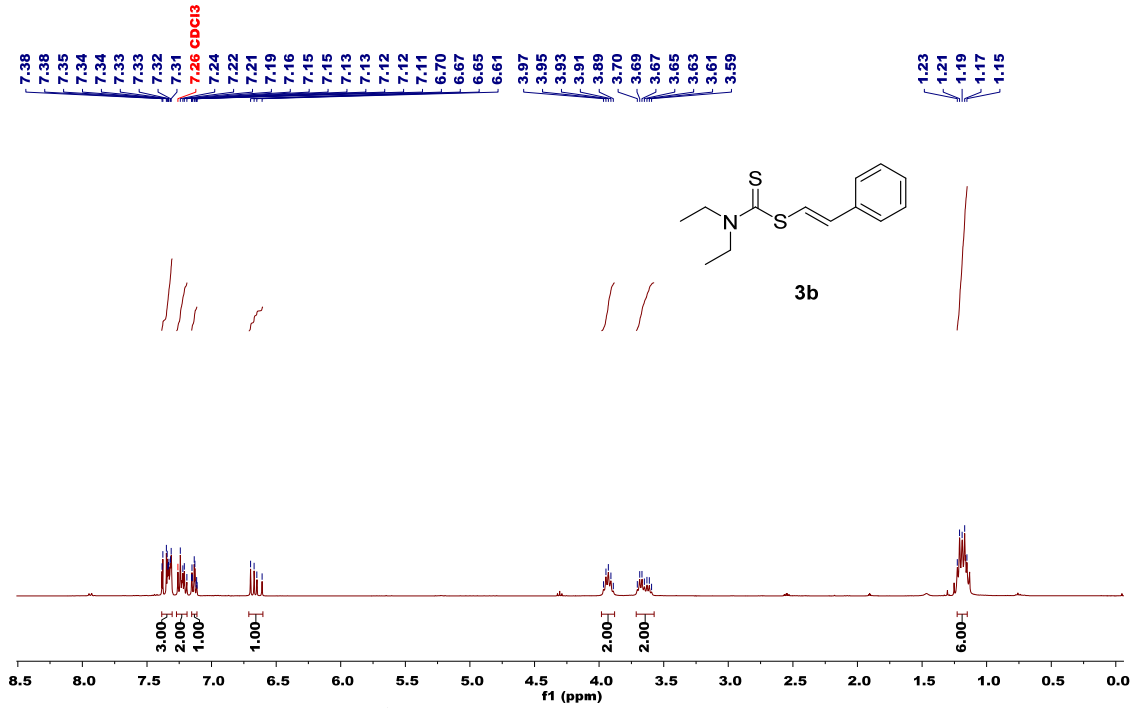
3a

^{1}H NMR (400 MHz, Chloroform-*d*) of 3a

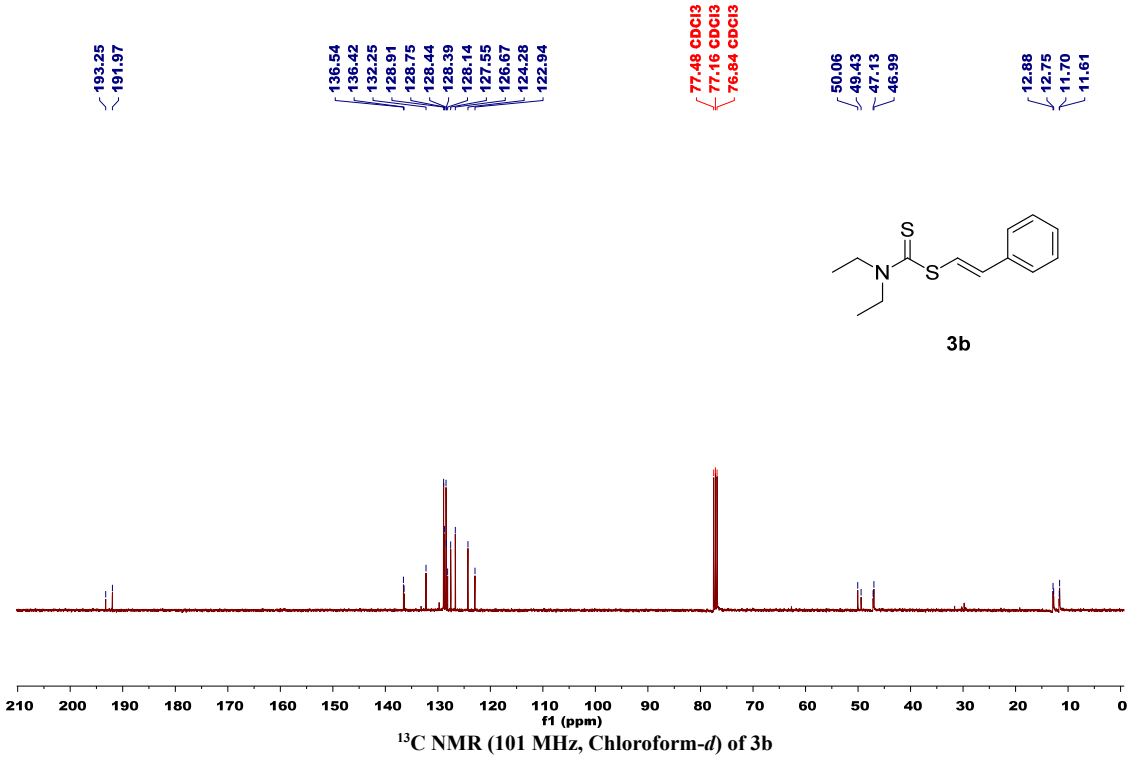


3a

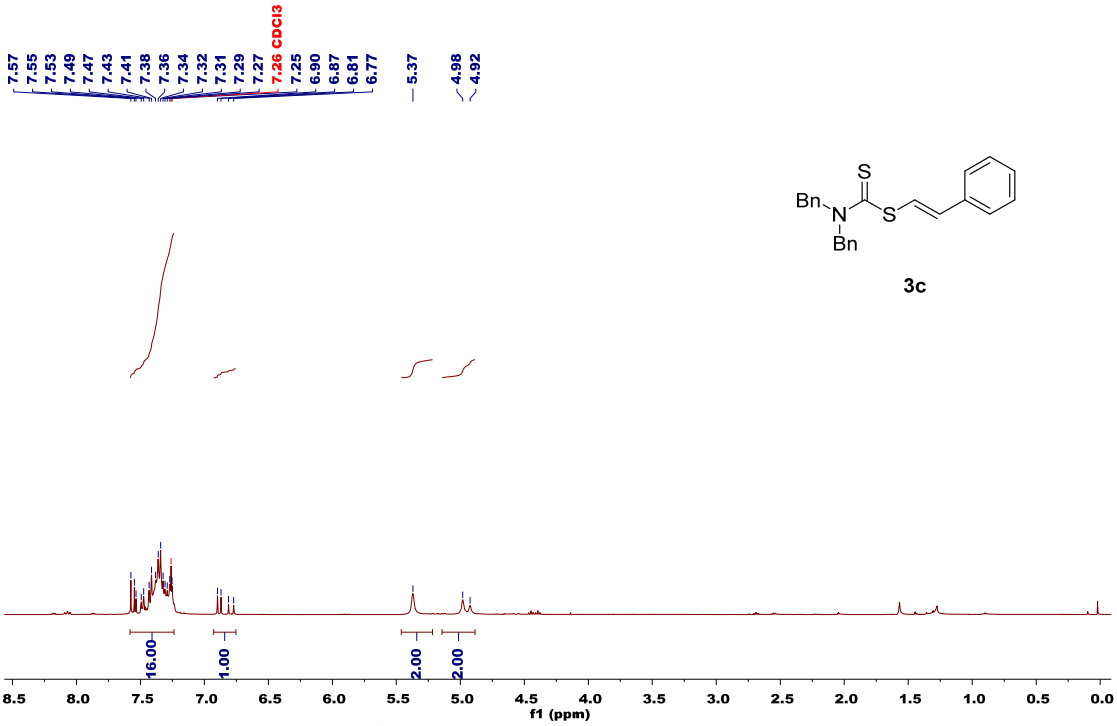
^{13}C NMR (101 MHz, Chloroform-*d*) of 3a



^{1}H NMR (400 MHz, Chloroform-*d*) of 3b

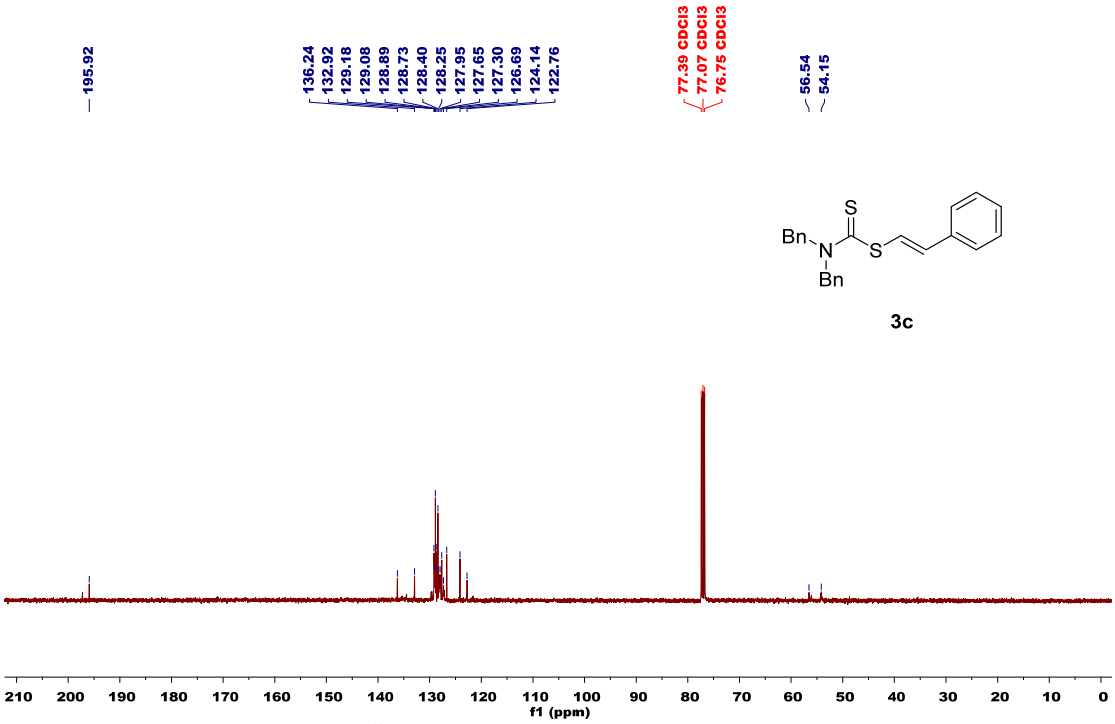


^{13}C NMR (101 MHz, Chloroform-*d*) of 3b



3c

^{1}H NMR (400 MHz, Chloroform-*d*) of 3c



3c

^{13}C NMR (101 MHz, Chloroform-*d*) of 3c