

Supporting Information

Visible-Light Driven C–S Bond Formation Based on Electron Donor-Acceptor Excitation and Hydrogen Atom Transfer Combined System

Tatsuhiko Uchikura, Yurina Hara, Kazushi Tsubono and Takahiko Akiyama*

Department of Chemistry, Faculty of Science, Gakushuin University, Mejiro, Toshima-ku, Tokyo 171-8588, Japan

Contents	Page
1. General Methods	S2
2. Additional data	
2-1. Screening of aryl halide	S3
2-2. Screening of base	S4
2-3. Screening of solvent using 20 equiv of THF	S5
3. Synthetic Procedures and Characterization of New Compounds	S6
4. 1 mmol scale experiment	S16
5. UV–Vis spectra	S16
6. Job plot	S17
7. Comparison with dark conditions	S18
8. References	S19
9. NMR spectra	S20

1. General Methods

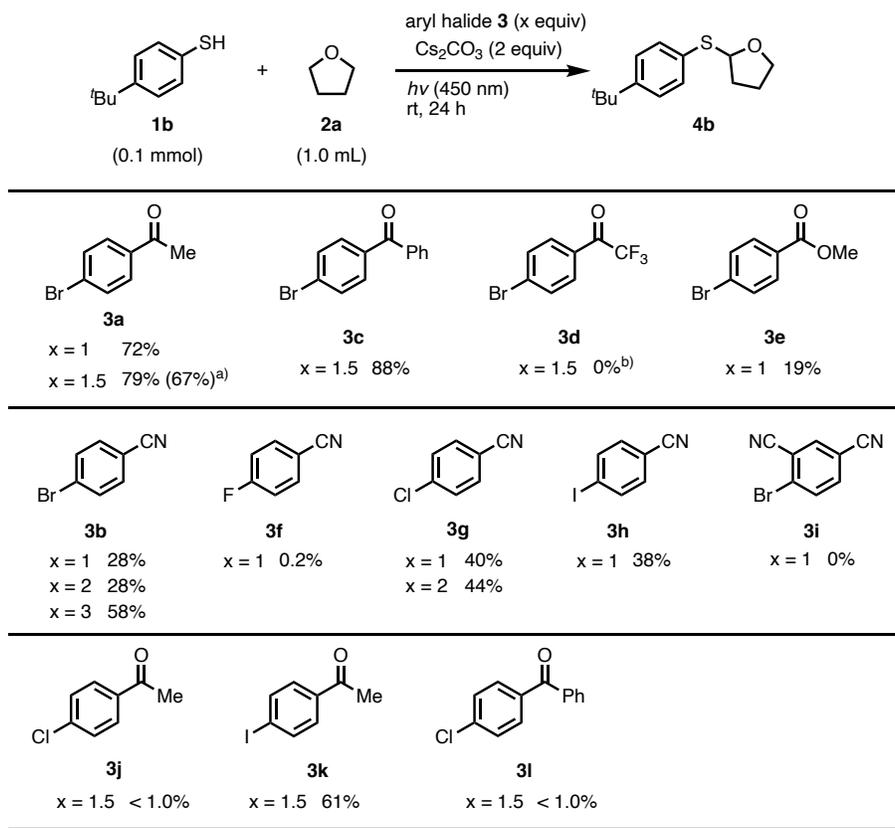
All operations were performed under nitrogen unless otherwise noted. NMR spectra for products data (^1H and ^{13}C) were recorded on a Bruker AVANCE-III (400 MHz for ^1H , 100 MHz for ^{13}C , 376 MHz for ^{19}F) and JEOL ECZ-400 (400 MHz for ^1H , 100 MHz for ^{13}C , 376 MHz for ^{19}F) spectrometer using CDCl_3 [tetramethylsilane (0 ppm) served as an internal standard in ^1H NMR and CDCl_3 (77.0 ppm) in ^{13}C NMR, hexafluorobenzene (-163.9 ppm) or benzotrifluoride (-63.7 ppm) served as an internal or external standard in ^{19}F NMR]. Chemical shifts are expressed in parts per million (ppm). ESI mass analyses were performed on Bruker micrOTOF mass spectrometer. UV-Vis spectra were recorded on a V-670 UV-VIS-NIR spectrometer (JASCO Co., Ltd.). Visible light irradiation was performed with LED450-100STND (Optcode Co., Ltd.).

THF was purchased from Kanto Chemical Co., Inc. and other solvents were distilled according to the usual procedures and stored over molecular sieves unless otherwise noted. All of the substrates were purified by distillation (for liquid) or recrystallization (for solid). *p*-Methoxycarbonylbenzenethiol (**1k**)^{S1} and *p*-cyanobenzenethiol (**1m**)^{S2} were synthesized according to the literature procedures. Other chemicals were purchased and used as received.

2. Additional data

2-1. Screening of aryl halide

Table S1. Screening of aryl halides



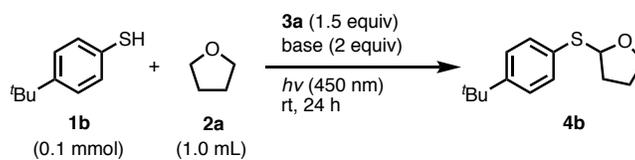
a) Isolated yield.

b) Unknown product was obtained.

A range of aryl halides were screened by use of *p*-*tert*-butylthiophenol (**1b**), *p*-Bromoacetophenone (**3a**) and *p*-bromobenzophenone (**3c**) gave **4b** in about 80% yields. 4-Bromophenyl trifluoromethyl ketone (**3d**) and methyl 4-bromobenzoate (**3e**) were not suitable. Benzonitrile derivatives **3b-3i** gave **4b** in lower yields in comparison with **3a** due to the stability of radical anion species. *p*-Chloroacetophenone (**3j**) and *p*-chlorobenzophenone (**3l**) almost did not give **4b**. *p*-Iodoacetophenone (**3k**) slightly decreased the yield of **4b**.

2-2. Screening of base

Table S2. Screening of base.



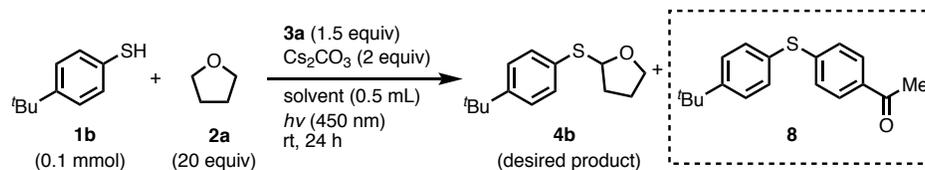
entry	base	yield ^{a)}
1	Cs ₂ CO ₃	78%
2	K ₂ CO ₃	0%
3	AcOK	0%
4	DBU	5%
5	NaOMe	0%

a) Determined by ¹H NMR.

Cesium carbonate was the base of choice for the C–S bond formation. Potassium carbonate did not give **4b** due to low solubility. Other inorganic and organic bases were not suitable.

2-3. Screening of solvent using 20 equivalents of THF

Table S3. Screening of solvents



entry	solvent	yield ^{a)}		ratio (4b / 8)
		4b	8	
1	acetone	51%	51%	1.00
2	CH ₃ CN	20%	64%	0.31
3	DCM	0%	0%	–
4 ^{b)}	AcOEt	51%	14%	3.64

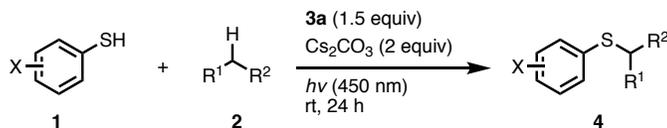
a) Determined by ¹H NMR.

b) 1.0 mL of AcOEt was used.

For the reaction of other alkanes, optimal solvent was screened by use of 20 equiv of THF. Although the desired product **4b** was obtained in 51% yield in acetone, undesired C(sp²)-S bond formation occurred to give **8** in comparative yield. Use of a more polar solvent such as acetonitrile preferentially gave **8** (entry 2). In contrast, both **4b** and **8** were not obtained in dichloromethane due to the low solubility of cesium carbonate (entry 3). Finally, ethyl acetate was found to be the solvent of choice and gave **4b** in 51% yield accompanied by **8** in 14%.

3. Synthetic Procedures and Characterization of New Compounds

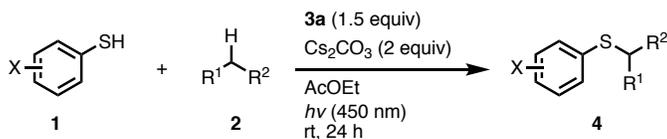
Using solvent amount of alkanes (Procedure I)



In a dried test tube, cesium carbonate (65.2 mg, 0.2 mmol), thiol **1** (0.1 mmol), and 4'-bromoacetophenone (**3a**) (29.9 mg, 0.15 mmol) were mixed in alkanes (1.0 mL), and degassed three times by the freeze-pump-thaw. The mixture was irradiated with 450 nm blue LED for 24 h. After the irradiation, water and ethyl acetate was added to the mixture, and the inorganic phase was extracted by ethyl acetate three times. The combined organic phase was dried over Na_2SO_4 and the solvent was removed in vacuo by rotary evaporator. The crude mixture was purified by preparative TLC on SiO_2 (hexane: ethyl acetate = 9 : 1) to give **4**.

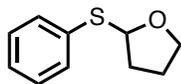
The reactions using other thiols in Figure 1 were performed based on this Procedure I.

Using 20 equiv of alkanes (Procedure II)



In a dried test tube, cesium carbonate (65.2 mg, 0.2 mmol), thiophenol **1a** (0.1 mmol), alkanes (2 mmol), and 4'-bromoacetophenone (**3a**) (29.9 mg, 0.15 mmol) or 4'-bromobenzophenone (39.2 mg, 0.15 mmol) were mixed in ethyl acetate (1.0 mL), and degassed three times by the freeze-pump-thaw. The mixture was irradiated with 450 nm blue LED for 24 h. After the irradiation, water and ethyl acetate was added to the mixture, and the inorganic phase was extracted by ethyl acetate three times. The combined organic phase was dried over Na_2SO_4 and the solvent was removed by rotary evaporator. The crude mixture was purified by preparative TLC on SiO_2 (hexane: ethyl acetate = 9 : 1) to give **4**.

Data of products

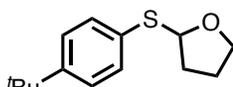


4a

Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.54 – 7.48 (m, 2H), 7.33 – 7.27 (m, 2H), 7.25 – 7.19 (m, 1H), 5.65 (dd, $J = 7.1$, 3.9 Hz, 1H), 4.09 – 3.90 (m, 2H), 2.46 – 2.31 (m, 1H), 2.12 – 1.79 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 135.6, 131.0, 128.8, 126.8, 87.1, 67.3, 32.6, 24.8.^{S3}

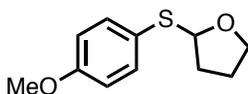


4b

Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.44 (d, $J = 8.7$ Hz, 2H), 7.32 (d, $J = 8.6$ Hz, 2H), 5.61 (dd, $J = 7.3$, 4.1 Hz, 1H), 4.06 – 4.00 (m, 1H), 3.98 – 3.93 (m, 1H), 2.40 – 2.31 (m, 1H), 2.07 – 1.83 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 150.1, 131.8, 131.3, 125.9, 87.4, 67.2, 34.5, 32.6, 31.2, 24.8 ppm.^{S3}

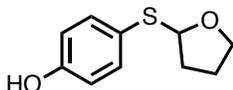


4c

Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, $J = 8.9$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 5.47 (dd, $J = 7.1$, 3.8 Hz, 1H), 4.07 – 3.88 (m, 2H), 3.79 (s, 3H), 2.39 – 2.26 (m, 1H), 2.04 – 1.80 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 159.4, 134.6, 125.5, 114.4, 88.2, 67.2, 55.3, 32.4, 24.8.^{S3}



4d

Colorless oil.

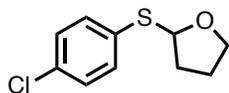
^1H NMR (400 MHz, CDCl_3) δ 7.43 – 7.34 (m, 2H), 6.75 – 6.64 (m, 2H), 5.49 (dd, $J = 7.2$, 3.8 Hz, 1H), 5.35 (brs,

1H), 4.09 – 4.00 (m, 1H), 3.99 – 3.90 (m, 1H), 2.42 – 2.23 (m, 1H), 2.09 – 1.80 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 155.7, 135.0, 125.2, 116.0, 88.3, 67.1, 32.4, 24.8.

LRMS (ESI): *m/z* = 235 [M+K].

HRMS (ESI): Calcd for C₁₀H₁₂O₂SK: 235.0190. Found 235.0198.

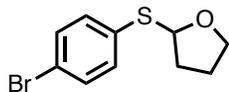


4e

Colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 5.60 (dd, *J* = 7.2, 3.8 Hz, 1H), 4.09 – 3.88 (m, 2H), 2.46 – 2.26 (m, 1H), 2.14 – 1.78 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 134.2, 132.9, 132.4, 128.9, 87.2, 67.3, 32.6, 24.8.^{S3}

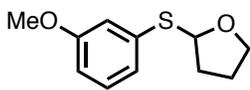


4f

Colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 5.61 (dd, *J* = 7.2, 3.8 Hz, 1H), 4.08 – 3.88 (m, 2H), 2.45 – 2.30 (m, 1H), 2.16 – 1.74 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 134.9, 132.5, 131.8, 120.9, 87.1, 67.3, 32.6, 24.8.^{S3}



4g

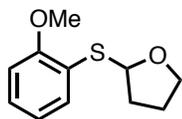
Colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.24 – 7.17 (m, 1H), 7.13 – 7.02 (m, 2H), 6.77 (td, *J* = 8.3, 2.5 Hz, 1H), 5.68 (dd, *J* = 7.2, 3.9 Hz, 1H), 4.09 – 3.90 (m, 2H), 3.80 (s, 3H), 2.45 – 2.30 (m, 1H), 2.12 – 1.77 (m, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 159.7, 137.0, 129.6, 123.0, 116.0, 112.7, 87.0, 67.3, 55.3, 32.6, 24.8.

LRMS (ESI): *m/z* = 249 [M+K].

HRMS (ESI): Calcd for C₁₁H₁₄O₂SK: 249.0346. Found 249.0353.



4h

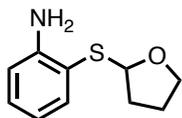
Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.58 (dd, $J = 7.7, 1.6$ Hz, 1H), 7.21 (td, $J = 8.2, 1.7$ Hz, 1H), 6.94 (td, $J = 7.6, 1.2$ Hz, 1H), 6.86 (dd, $J = 8.2, 1.2$ Hz, 1H), 5.78 (dd, $J = 7.0, 3.8$ Hz, 1H), 4.09 – 3.91 (m, 2H), 3.89 (s, 3H), 2.50 – 2.29 (m, 1H), 2.15 – 1.97 (m, 2H), 1.96 – 1.81 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 157.3, 131.4, 127.8, 123.9, 121.2, 110.5, 85.0, 67.3, 55.8, 32.6, 24.8.

LRMS (ESI): $m/z = 249$ [M+K].

HRMS (ESI): Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2\text{SK}$: 249.0346. Found 249.0352.



4j

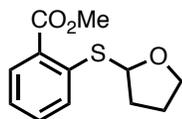
Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.41 (dd, $J = 7.7, 1.6$ Hz, 1H), 7.13 (td, $J = 7.7, 1.6$ Hz, 1H), 6.79 – 6.61 (m, 2H), 5.41 (dd, $J = 7.0, 3.8$ Hz, 1H), 4.47 (brs, 2H), 4.02 (q, $J = 8.3$ Hz, 1H), 3.91 (td, $J = 8.2, 4.3$ Hz, 1H), 2.39 – 2.22 (m, 1H), 2.11 – 1.75 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 148.9, 136.9, 130.2, 118.4, 116.9, 115.0, 88.1, 67.6, 32.8, 24.9.

LRMS (ESI): $m/z = 218$ [M+Na].

HRMS (ESI): Calcd for $\text{C}_{10}\text{H}_{13}\text{NOSNa}$: 218.0610. Found 218.0612.

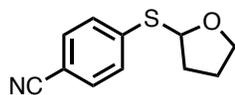


4l

Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.93 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.86 (dd, $J = 8.3, 1.1$ Hz, 1H), 7.46 (td, $J = 8.1, 1.6$ Hz, 1H), 7.24 – 7.14 (m, 1H), 5.76 (dd, $J = 7.5, 4.2$ Hz, 1H), 4.08 – 3.95 (m, 2H), 3.91 (s, 3H), 2.55 – 2.32 (m, 1H), 2.19 – 1.80 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 167.0, 141.1, 132.5, 130.9, 128.1, 128.0, 124.6, 84.4, 67.6, 52.1, 32.4, 25.1.^{S4}

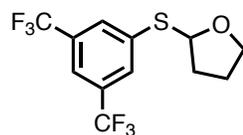


4m

Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, $J = 0.7$ Hz, 4H), 5.79 (dd, $J = 7.1, 3.8$ Hz, 1H), 4.01 (dd, $J = 7.9, 5.4$ Hz, 2H), 2.55 – 2.32 (m, 1H), 2.19 – 1.80 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 144.0, 132.2, 128.8, 118.9, 109.0, 85.7, 67.6, 32.5, 24.7.^{S3}



4o

Colorless oil.

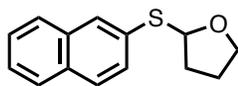
^1H NMR (400 MHz, CDCl_3) δ 7.92 (s, 2H), 7.67 (s, 1H), 5.75 (dd, $J = 7.3, 3.7$ Hz, 1H), 4.02 (dd, $J = 8.0, 5.3$ Hz, 2H), 2.47 – 2.38 (m, 1H), 2.10-1.88 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 139.9, 131.9 (q, $J = 30.3$ Hz), 129.6, 123.1 (q, $J = 273.9$ Hz), 119.9, 86.6, 67.6, 32.6, 24.7.

^{19}F NMR (376 MHz, CDCl_3) δ -61.4 (s, 6F).

LRMS (ESI): $m/z = 339$ [M+Na].

HRMS (ESI): Calcd for $\text{C}_{12}\text{H}_{10}\text{F}_6\text{OSNa}$: 339.0249. Found 339.0256.

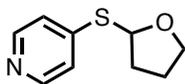


4p

Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 8.03 – 7.96 (m, 1H), 7.84 – 7.72 (m, 3H), 7.57 (dd, $J = 8.6, 1.8$ Hz, 1H), 7.51 – 7.39 (m, 2H), 5.77 (dd, $J = 7.1, 3.7$ Hz, 1H), 4.13 – 3.95 (m, 2H), 2.51 – 2.31 (m, 1H), 2.15 – 1.80 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 133.7, 133.2, 132.1, 129.3, 128.7, 128.3, 127.7, 127.4, 126.4, 125.8, 87.1, 67.4, 32.7, 24.9.^{S3}



4q

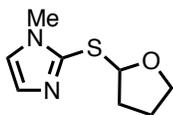
Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 8.46 – 8.32 (m, 2H), 7.40 – 7.30 (m, 2H), 5.87 (dd, $J = 7.2, 3.8$ Hz, 1H), 4.06 – 3.96 (m, 2H), 2.56 – 2.34 (m, 1H), 2.18 – 1.83 (m, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 149.3, 148.4, 122.1, 84.5, 67.6, 32.4, 24.7.

LRMS (ESI): $m/z = 220$ [M+K].

HRMS (ESI): Calcd for $\text{C}_9\text{H}_{11}\text{NOSK}$: 220.0193. Found 220.0191.



4r

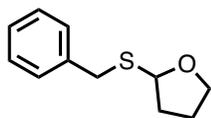
Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 6.77 (d, $J = 2.5$ Hz, 1H), 6.68 (d, $J = 2.5$ Hz, 1H), 6.30 (dd, $J = 6.4, 3.1$ Hz, 1H), 4.22 (td, $J = 8.0, 4.5$ Hz, 1H), 3.98 (td, $J = 8.3, 6.8$ Hz, 1H), 3.60 (s, 3H), 2.49 – 2.38 (m, 1H), 2.25 – 2.16 (m, 1H), 2.12 – 1.87 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 125.3, 117.8, 113.3, 88.2, 69.8, 34.4, 32.6, 23.9.

LRMS (ESI): $m/z = 185$ [M+H].

HRMS (ESI): Calcd for $\text{C}_8\text{H}_{13}\text{N}_2\text{OS}$: 185.0743. Found 185.0748.

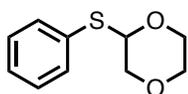


4s

Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.38 – 7.28 (m, 4H), 7.26 – 7.19 (m, 1H), 5.22 (dd, $J = 7.2, 3.6$ Hz, 1H), 4.04 – 3.86 (m, 3H), 3.75 (d, $J = 13.3$ Hz, 1H), 2.28 – 2.13 (m, 1H), 2.08 – 1.94 (m, 1H), 1.91 – 1.71 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 138.6, 128.9, 128.5, 126.8, 82.9, 66.8, 35.0, 32.0, 24.8.^{S5}

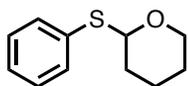


6b

Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.54 – 7.48 (m, 2H), 7.36 – 7.24 (m, 3H), 5.12 (dd, $J = 5.7, 3.0$ Hz, 1H), 4.33 – 4.14 (m, 1H), 3.99 (dd, $J = 11.7, 3.0$ Hz, 1H), 3.82 – 3.61 (m, 4H)..

^{13}C NMR (101 MHz, CDCl_3) δ 133.9, 131.6, 129.0, 127.4, 83.2, 69.9, 66.5, 63.8.^{S3}

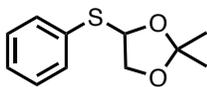


6c

Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.47 (m, 2H), 7.31 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 5.21 (dd, $J = 5.7, 3.9$ Hz, 1H), 4.21 – 4.15 (m, 1H), 3.60 (q, $J = 5.5$ Hz, 1H), 2.05 – 2.00 (m, 1H), 1.87 – 1.80 (m, 2H), 1.68 – 1.61 (m, 3H)

^{13}C NMR (101 MHz, CDCl_3) δ 135.4, 130.8, 128.8, 126.7, 85.3, 64.6, 31.6, 25.5, 21.7.^{S3}



6d

Colorless oil.

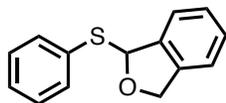
^1H NMR (400 MHz, CDCl_3) δ 7.56 – 7.48 (m, 2H), 7.36 – 7.24 (m, 3H), 5.56 (dd, $J = 6.3, 5.6$ Hz, 1H), 4.36 (dd,

$J = 9.2, 6.3$ Hz, 1H), 3.96 (dd, $J = 9.2, 5.5$ Hz, 1H), 1.51 (s, 3H), 1.42 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 134.2, 131.7, 129.0, 127.4, 111.4, 83.7, 69.5, 26.24, 26.16.

LRMS (ESI): $m/z = 231$ [M+K].

HRMS (ESI): Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2\text{SK}$: 231.0782. Found 231.0783.



6e

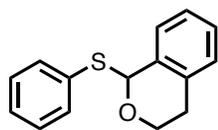
Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.57 – 7.50 (m, 2H), 7.45 – 7.38 (m, 1H), 7.36 – 7.13 (m, 6H), 6.80 (d, $J = 2.4$ Hz, 1H), 5.18 (dd, $J = 12.5, 1.8$ Hz, 1H), 5.08 (d, $J = 12.4$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 139.1, 138.2, 134.5, 132.1, 128.8, 128.6, 127.6, 127.4, 122.6, 120.9, 92.6, 72.6.

LRMS (ESI): $m/z = 229$ [M+H].

HRMS (ESI): Calcd for $\text{C}_{14}\text{H}_{13}\text{OS}$: 229.0682. Found 229.0678.

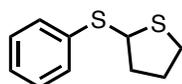


6f

Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 8.7$ Hz, 2H), 7.33 (t, $J = 7.3$ Hz, 3H), 7.27 (d, $J = 7.3$ Hz, 1H), 7.20 (dt, $J = 9.3, 4.0$ Hz, 2H), 7.14 – 7.09 (m, 1H), 6.48 (s, 1H), 4.54 (td, $J = 11.9, 3.2$ Hz, 1H), 4.00 (dd, $J = 11.3, 6.5$ Hz, 1H), 3.14 – 3.05 (m, 1H), 2.69 (dd, $J = 16.7, 3.0$ Hz, 1H) ppm.

^{13}C NMR (101 MHz, CDCl_3) δ 136.0, 133.84, 133.76, 131.2, 128.9, 128.8, 127.7, 127.13, 127.07, 126.0, 85.9, 58.2, 27.7 ppm.^{S6}

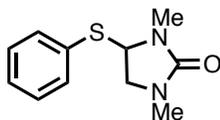


6h

Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.39 (m, 2H), 7.35 – 7.28 (m, 2H), 7.28 – 7.22 (m, 1H), 4.86 (t, $J = 4.5$ Hz, 1H), 3.11 – 3.05 (m, 1H), 2.96 – 2.80 (m, 1H), 2.31 – 2.00 (m, 4H).

^{13}C NMR (101 MHz, CDCl_3) δ 136.2, 131.3, 129.0, 127.1, 55.6, 38.3, 33.1, 28.7.^{S7}



6i

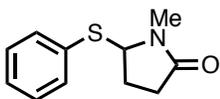
Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.46 – 7.39 (m, 2H), 7.37 – 7.30 (m, 3H), 4.80 (dd, $J = 8.4, 3.7$ Hz, 1H), 3.71 (dd, $J = 10.2, 8.4$ Hz, 1H), 3.34 (dd, $J = 10.2, 3.7$ Hz, 1H), 2.95 (s, 3H), 2.53 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 159.2, 134.8, 130.9, 129.1, 128.7, 65.4, 51.8, 30.3, 28.8.

LRMS (ESI): $m/z = 245$ [M+Na].

HRMS (ESI): Calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{OSNa}$: 245.0719. Found 245.0723.

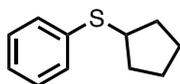


6j

Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.45 – 7.42 (m, 2H), 7.38 – 7.32 (m, 3H), 4.81 (dd, $J = 8.2, 2.3$ Hz, 1H), 2.99 (s, 3H), 2.54 – 2.44 (m, 1H), 2.23 – 2.16 (m, 1H), 2.13 – 2.06 (m, 1H), 1.73 – 1.64 (m, 1H)

^{13}C NMR (101 MHz, CDCl_3) δ 174.5, 135.3, 130.5, 129.3, 129.1, 69.5, 29.1, 28.0, 26.5.^{S8}



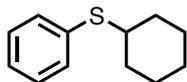
6k

Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.39 – 7.33 (m, 2H), 7.31 – 7.24 (m, 2H), 7.21 – 7.13 (m, 1H), 3.66 – 3.53 (m, 1H),

2.13 – 1.96 (m, 2H), 1.87 – 1.70 (m, 1H), 1.70 – 1.52 (m, 4H), 0.97 – 0.73 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 137.2, 129.9, 128.7, 125.8, 45.8, 33.5, 24.8.^{S9}



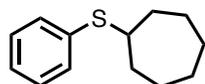
6i

Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.36 (m, 2H), 7.32 – 7.26 (m, 2H), 7.25 – 7.15 (m, 1H), 3.18 – 3.00 (m, 1H),

2.07 – 1.89 (m, 2H), 1.88 – 1.68 (m, 2H), 1.70 – 1.58 (m, 1H), 1.45 – 1.13 (m, 5H).

^{13}C NMR (101 MHz, CDCl_3) δ 135.1, 131.8, 128.7, 126.6, 46.5, 33.3, 26.1, 25.7.^{S9}



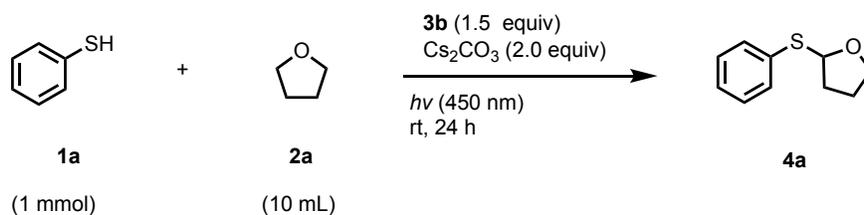
6m

Colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.34 (m, 2H), 7.32 – 7.25 (m, 2H), 7.23 – 7.16 (m, 1H), 3.34 (tt, $J = 9.2, 4.2$ Hz, 1H), 2.09 – 1.95 (m, 2H), 1.80 – 1.66 (m, 1H), 1.65 – 1.39 (m, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 136.2, 131.1, 128.8, 126.3, 47.9, 34.6, 28.2, 25.9.^{S9}

4. 1 mmol scale experiment



In a dried test tube, cesium carbonate (652 mg, 2 mmol), benzenethiol **1** (110.2 mg, 1 mmol), 4'-bromoacetophenone (**3a**) (299 mg, 1.5 mmol) were mixed in THF (10 mL), and degassed three times by the freeze-pump-thaw. The mixture was irradiated with 450 nm blue LED for 24 h. After the irradiation, water and ethyl acetate was added to the mixture, and the inorganic phase was extracted by ethyl acetate three times. The combined organic phase was dried over Na_2SO_4 and the solvent was removed by rotary evaporator. The crude mixture was purified by silica gel column chromatography to give **4a** (149.6 mg, 83%).

5. UV-Vis spectra

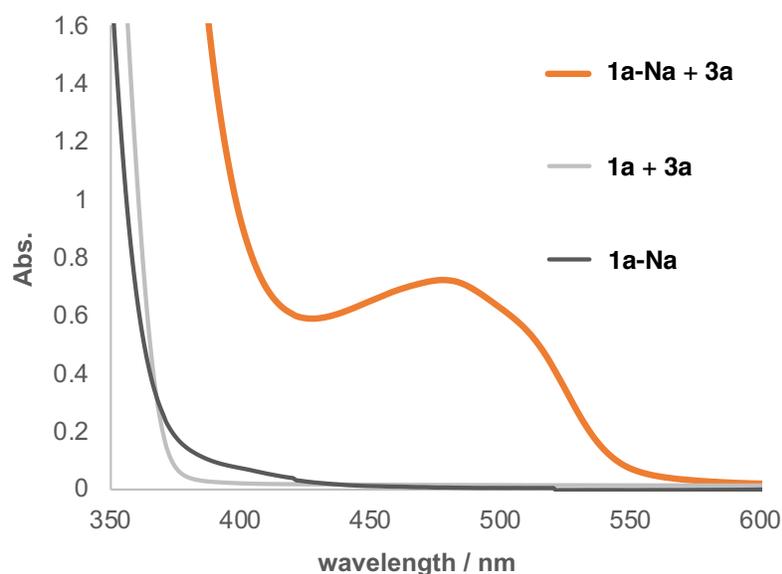


Figure S1. UV-Vis spectra of the EDA complex.

In screw-capped quartz cell ($l = 1$ cm), **1a-Na** (44.3 mg, 0.3 mmol) or **1a** (30.6 μL , 0.3 mmol) and **3a** (89.7 mg, 0.45 mmol) were mixed in acetonitrile (3 mL). Then UV-Vis spectra were measured by V-670 UV-VIS-NIR spectrometer (JASCO Co., Ltd.).

6. Job plot

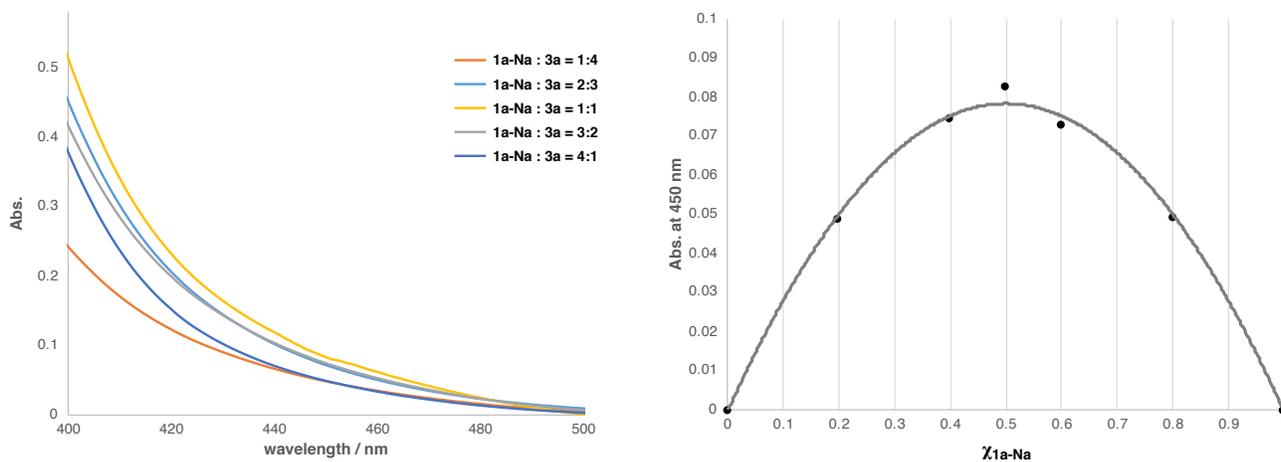
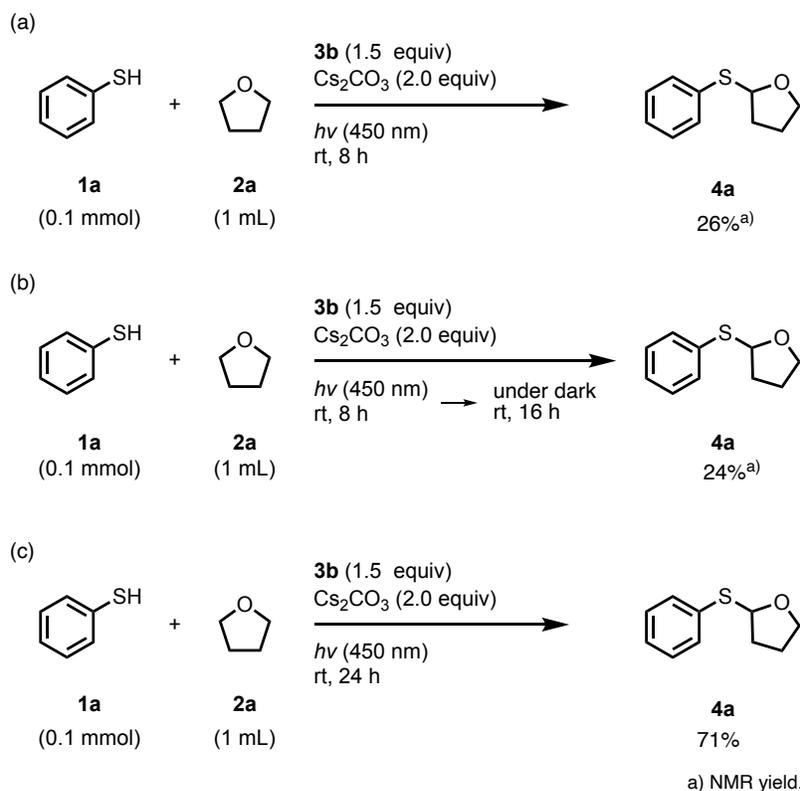


Figure S2. Job plot by the method of continuous variation.

In screw-capped quartz cell ($l = 1$ cm), various ratio (1:4, 2:3, 1:1, 3:2, 4:1) of **1a-Na** and **3a** ($[\mathbf{1a-Na}] + [\mathbf{3a}] = 0.25$ M) were mixed in DMSO (3 mL). Then UV-Vis spectra were measured by V-670 UV-VIS-NIR spectrometer (JASCO Co., Ltd.). The Job plot ($\chi_{1a-Na} = [\mathbf{1a-Na}] / ([\mathbf{1a-Na}] + [\mathbf{3a}])$) supported 1;1 complex of **1a-Na** and **3a** as EDA complex.^{S9}

7. Comparison with dark conditions



In order to clarify whether the reaction proceeded by radical chain mechanism, we attempted to measure the quantum yield, or track the reaction under light ON/OFF conditions by NMR experiment. But we failed to achieve those experiments because of the insolubility of the base and the generated thiolate. Instead of these experiments, we tried to confirm that the reaction did not proceed without irradiation after irradiating for 8 h. After the irradiation for 8 h, **4a** was obtained in 26% (Scheme S1a). After irradiating for 8 h, irradiation was stopped and stirred for 16 h (totally 24 h), **4a** was obtained in 24% yield, which is almost same as the reaction of Scheme S1a (Scheme S1b). Based on the results, the reactions are considered not to proceed by radical chain mechanism.

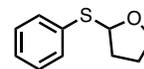
8. References

- S1) Graßl, S.; Hamze, C.; Koller, T.; Knochel, P. *Chem. Eur. J.* **2019**, *25*, 3752–3755.
- S2) Heine, N. B.; Studer, A. *Org. Lett.* **2017**, *19*, 4150–4153.
- S3) Zhu, X.; Xie, X.; Li, P.; Guo, J.; Wang, L. *Org. Lett.* **2016**, *18*, 1546–1549.
- S4) Yu, Y.-P.; Tang, R.-Y. *Synth. Commun.* **2014**, *44*, 2045–2050.
- S5) Dong, Y.; Mengliang, T. *Chem. J. Chin. Univ.* **2016**, *37*, 269–273.
- S6) Birch, S. F.; McAllan, D. T. *J. Chem. Soc.* **1952**, 233–234.
- S7) Tang, R.-Y.; Xie, Y.-X.; Xie, Y.-L.; Xiang, J.-N.; Li, J.-H. *Chem. Commun.* **2011**, *47*, 12867–12869.
- S8) Zhao, J.; Fang, H.; Han, J.; Pan, Y.; Li, G. *Adv. Synth. Catal.* **2014**, *356*, 2719–2724.
- S9) Renny, J. S.; Tomasevich, L. L.; Tallmadge, E. H.; Collum, D. B. *Angew. Chem. Int. Ed.* **2013**, *52*, 11998–12013.

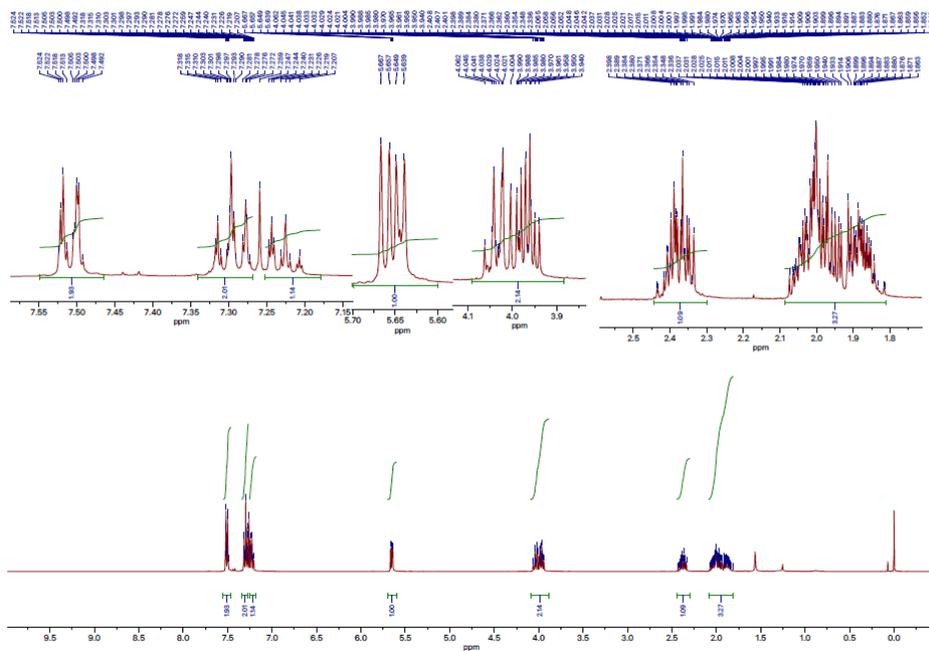
9. NMR spectra

4a

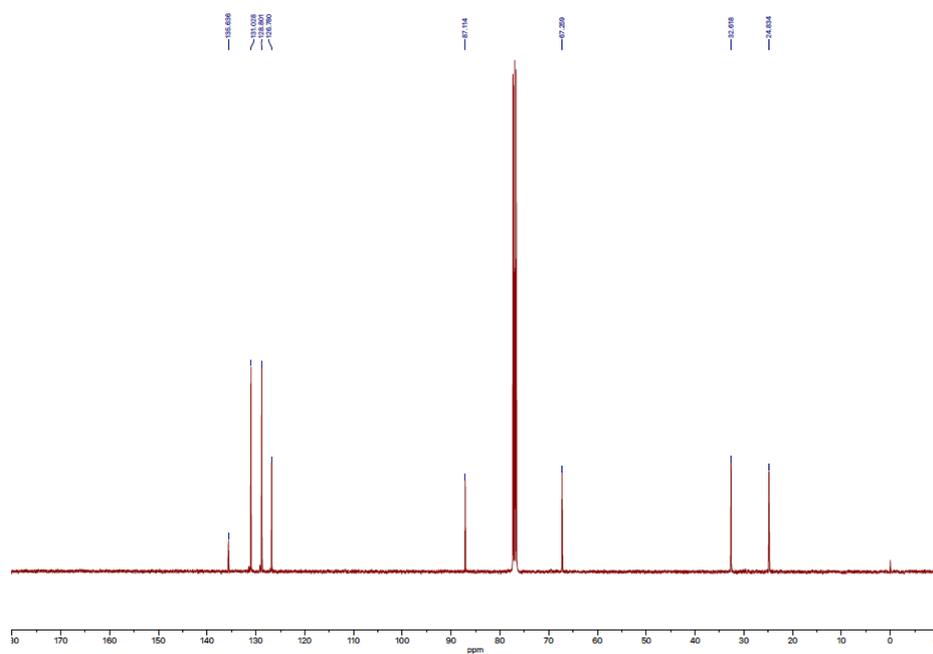
^1H NMR (400 MHz, CDCl_3)



4a

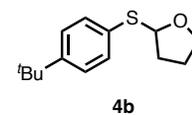
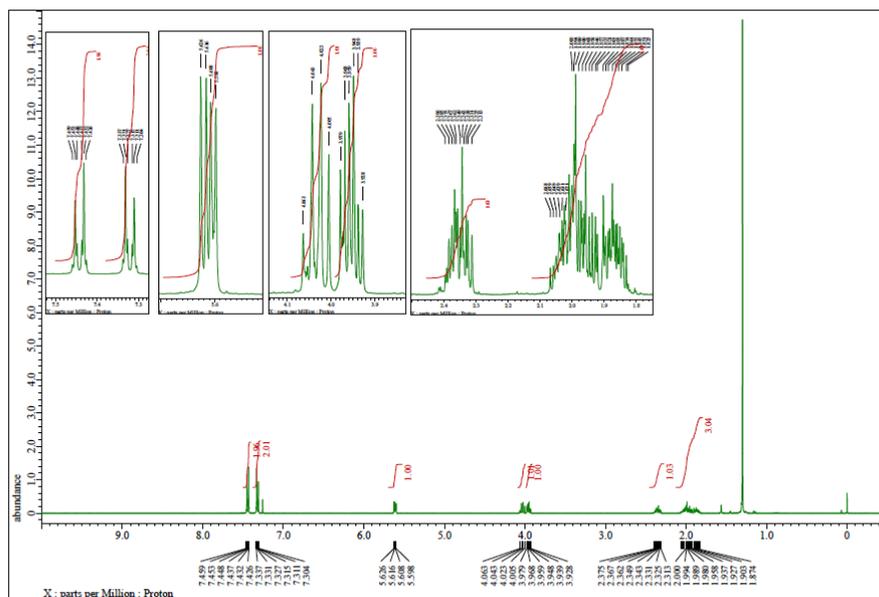


^{13}C NMR (101 MHz, CDCl_3)

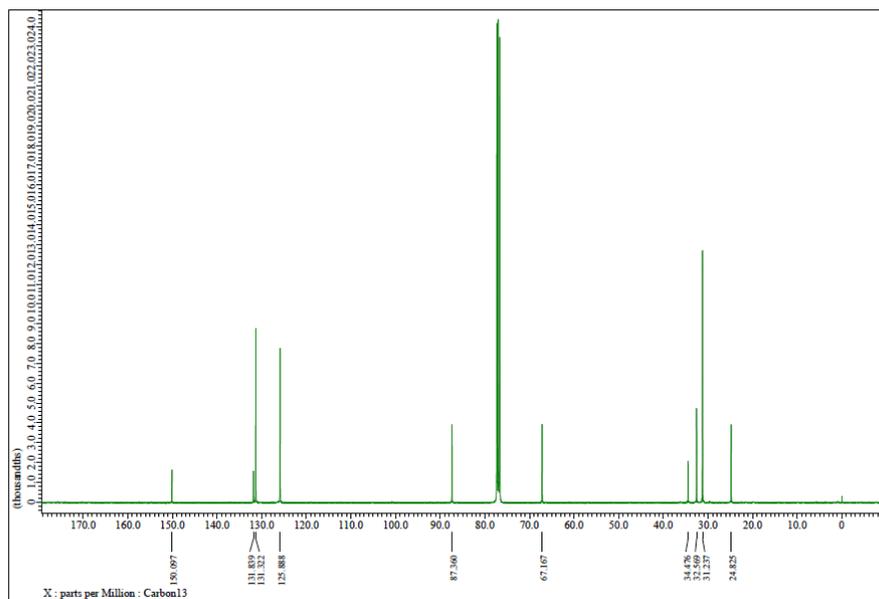


4b

^1H NMR (400 MHz, CDCl_3)

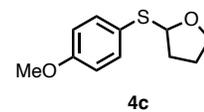
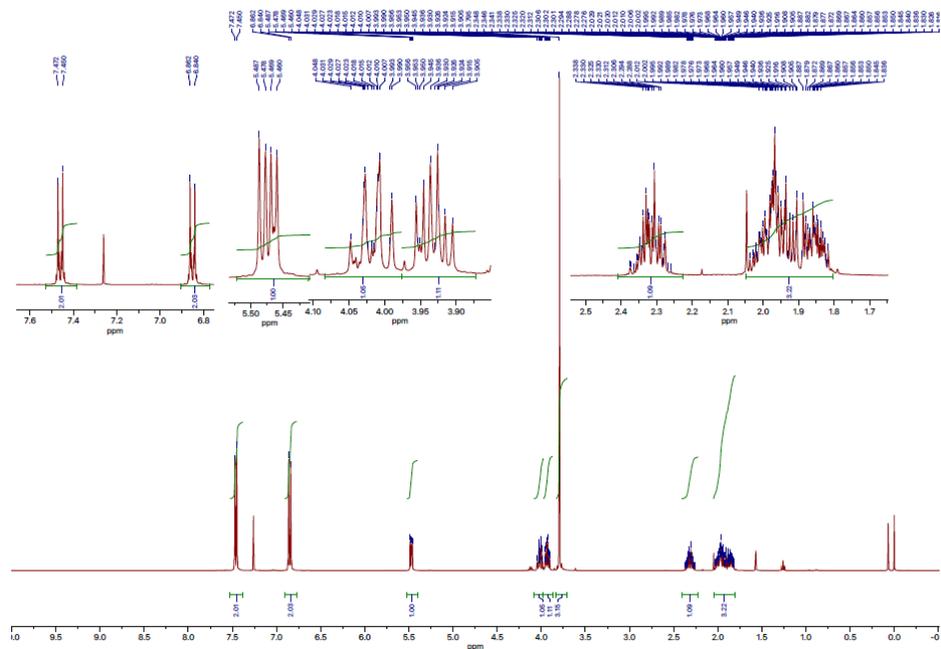


^{13}C NMR (101 MHz, CDCl_3)

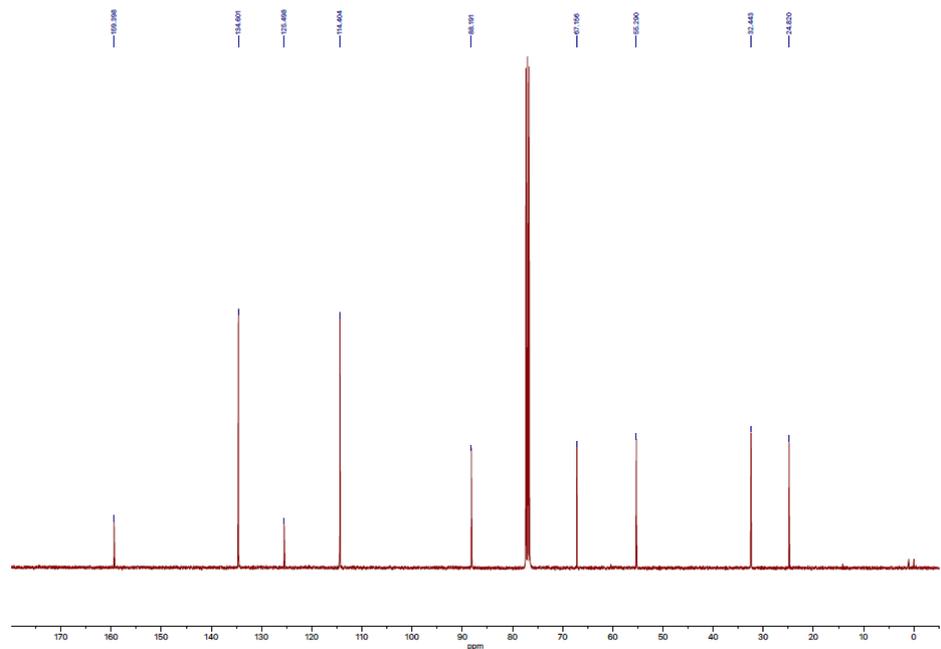


4c

¹H NMR (400 MHz, CDCl₃)

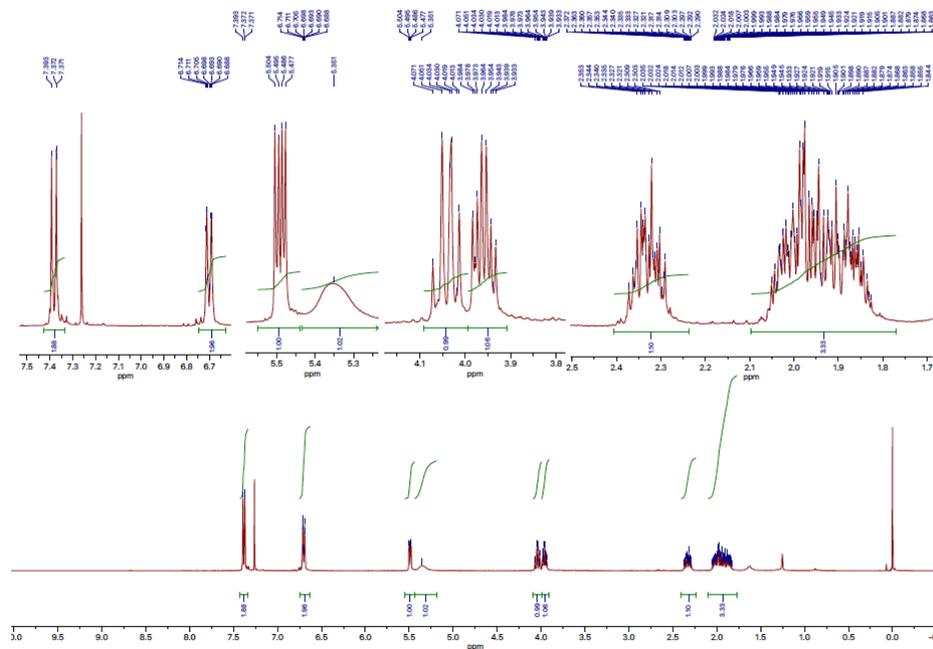
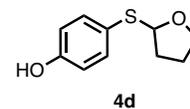


¹³C NMR (101 MHz, CDCl₃)



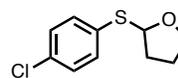
4d

¹H NMR (400 MHz, CDCl₃)

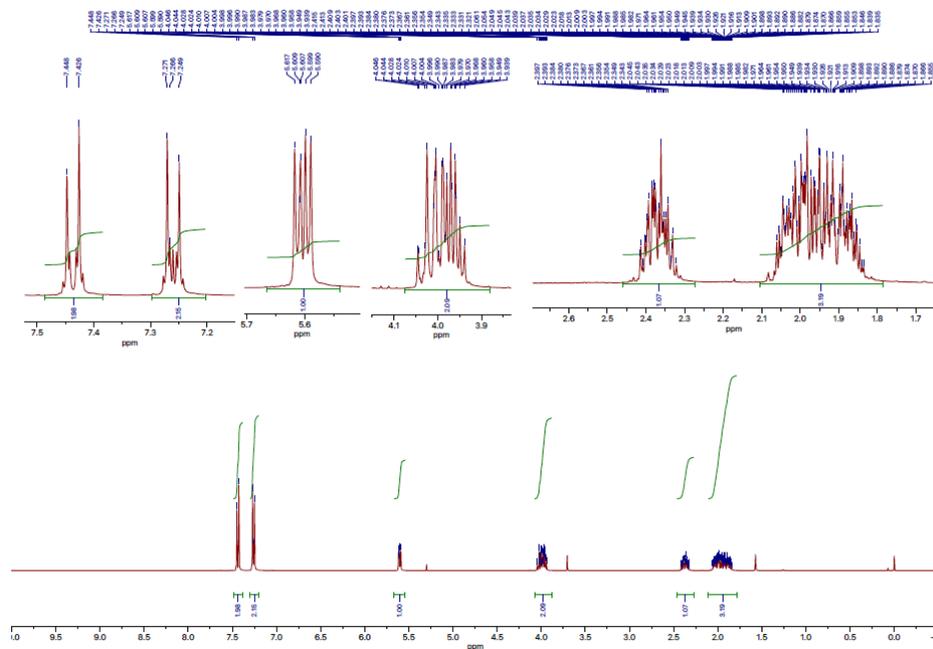


4e

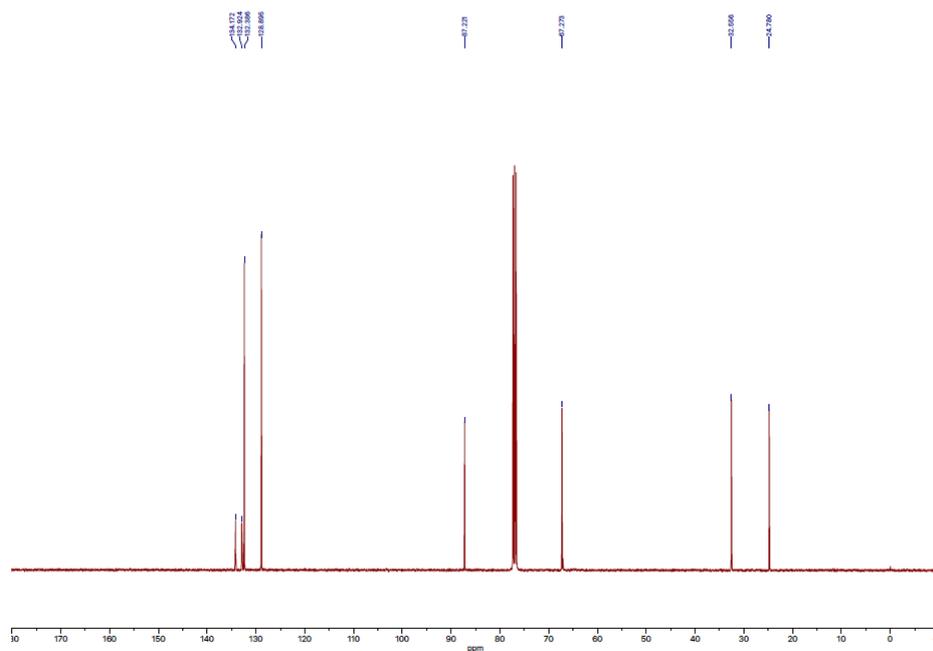
^1H NMR (400 MHz, CDCl_3)



4e

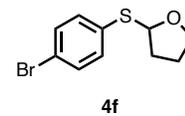
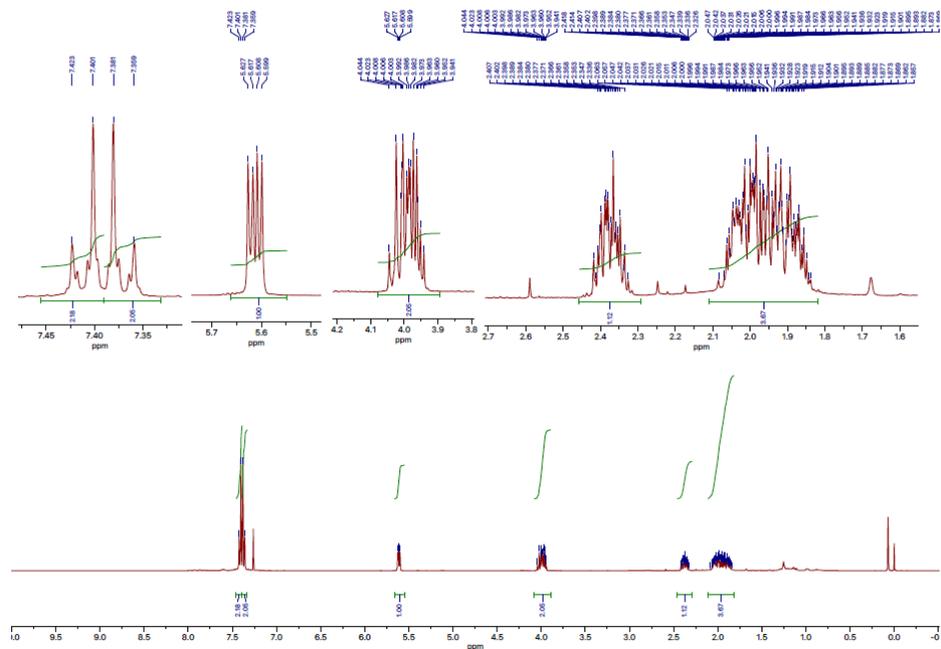


^{13}C NMR (101 MHz, CDCl_3)

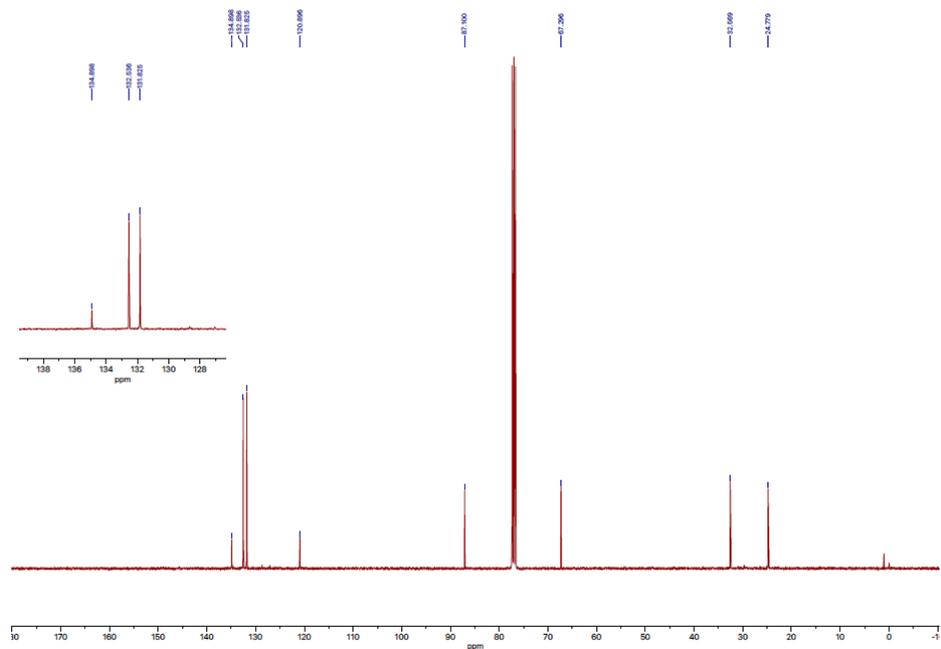


4f

¹H NMR (400 MHz, CDCl₃)

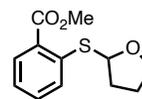
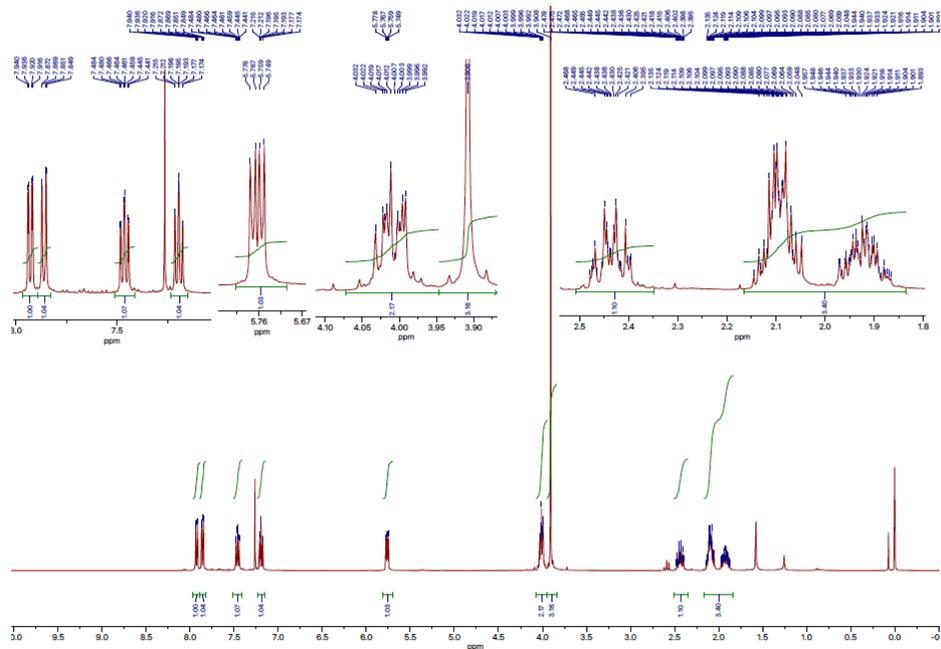


¹³C NMR (101 MHz, CDCl₃)



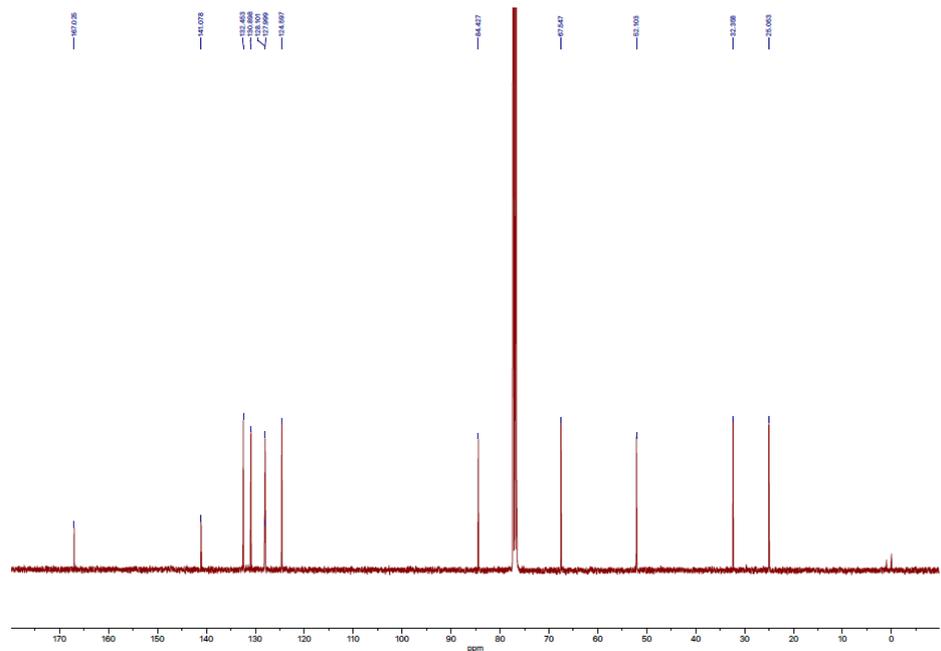
4I

^1H NMR (400 MHz, CDCl_3)



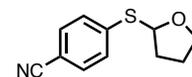
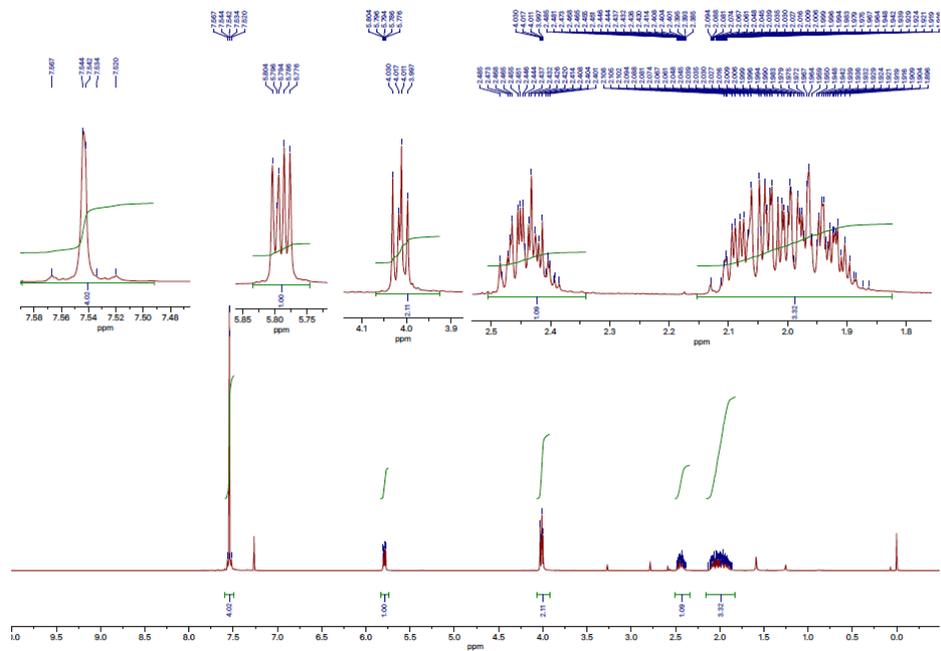
4I

^{13}C NMR (101 MHz, CDCl_3)



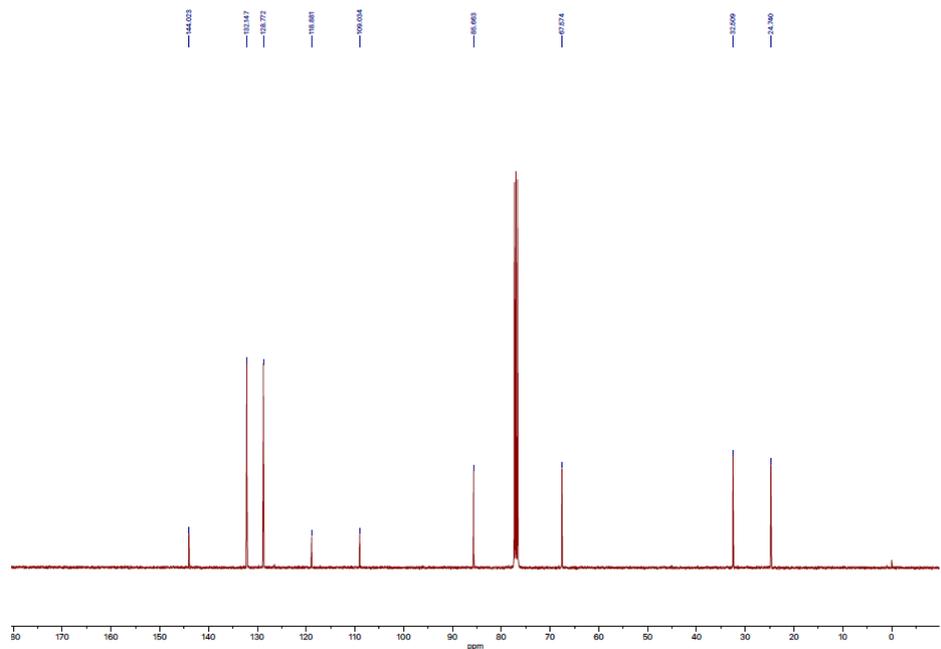
4m

^1H NMR (400 MHz, CDCl_3)



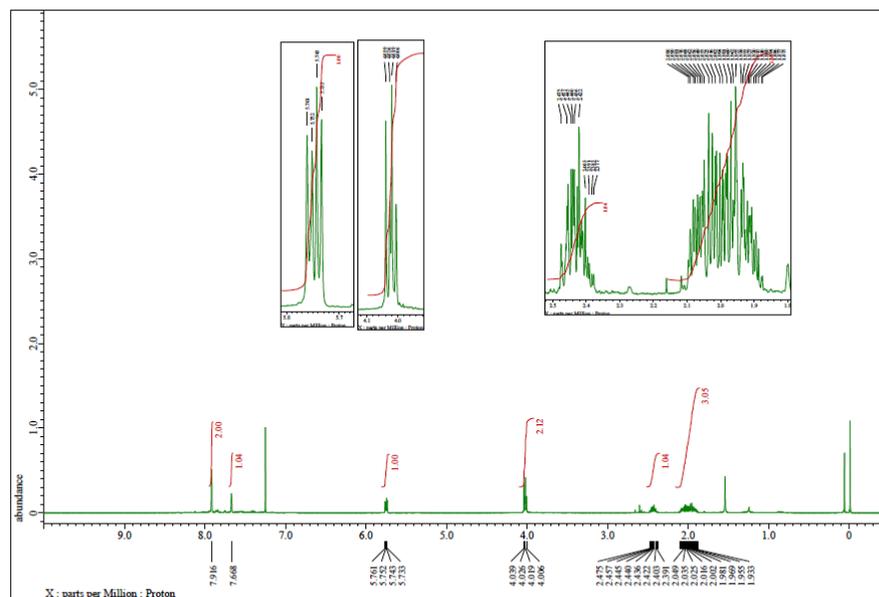
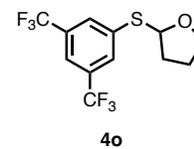
4m

^{13}C NMR (101 MHz, CDCl_3)

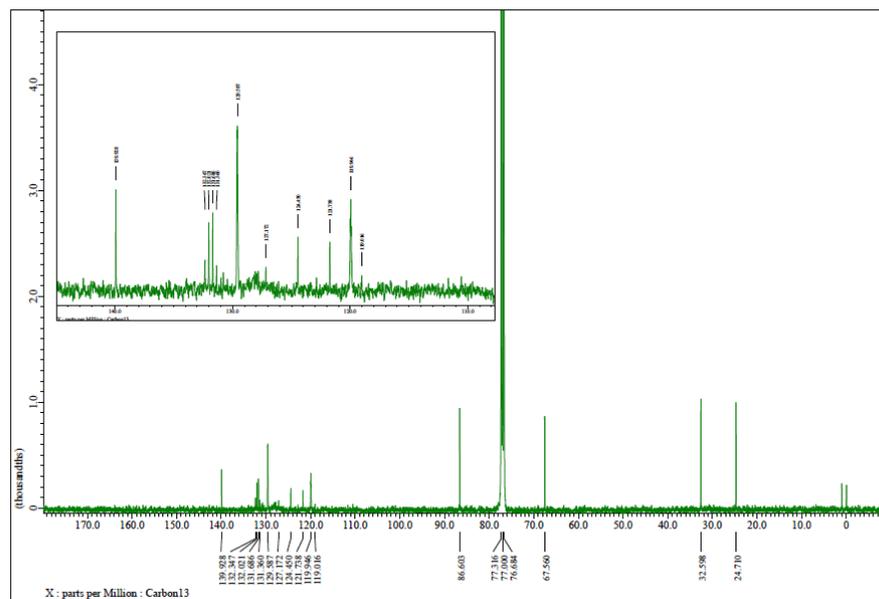


4o

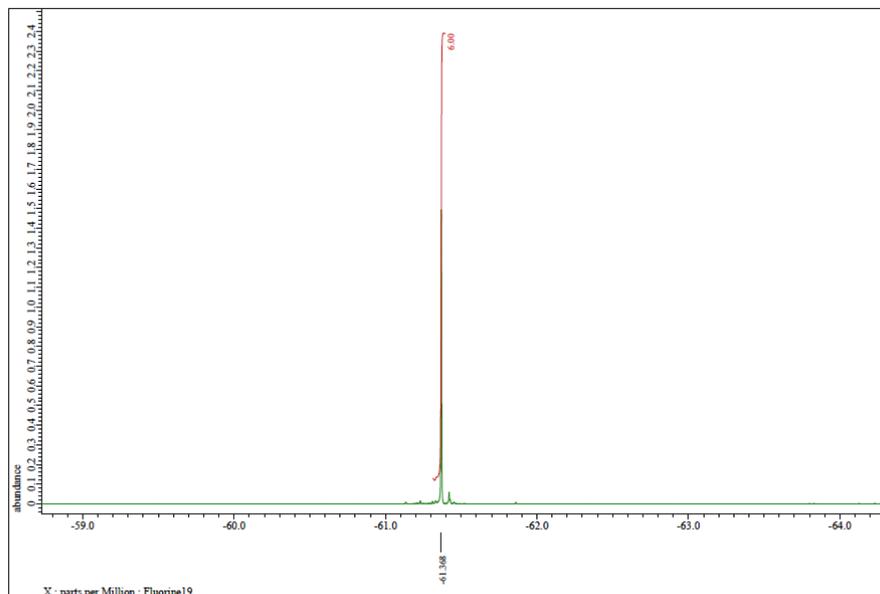
¹H NMR (400 MHz, CDCl₃)



¹³C NMR (101 MHz, CDCl₃)

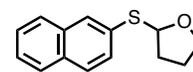


^{19}F NMR (376 MHz, CDCl_3)

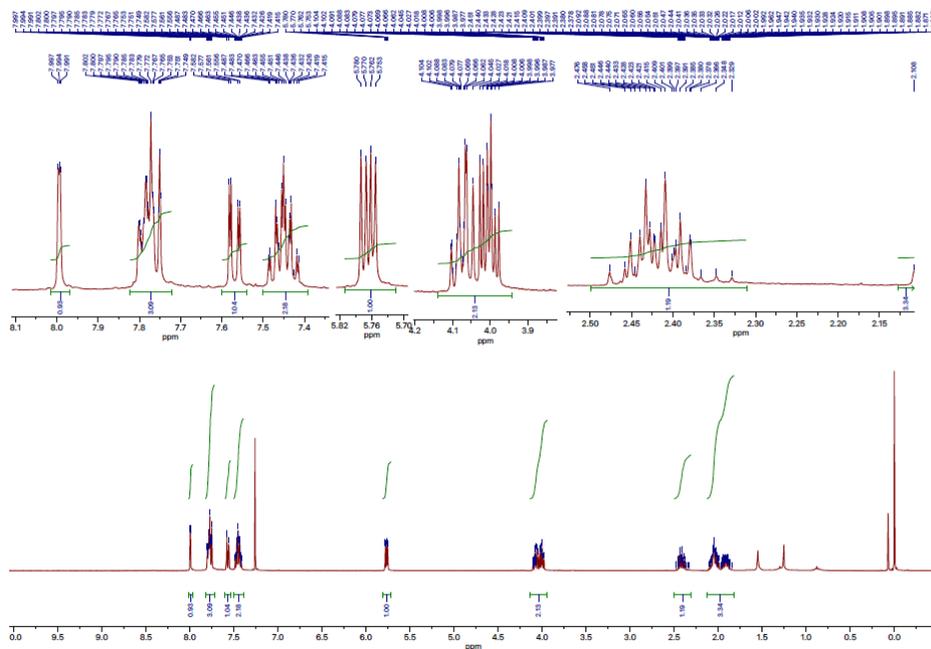


4p

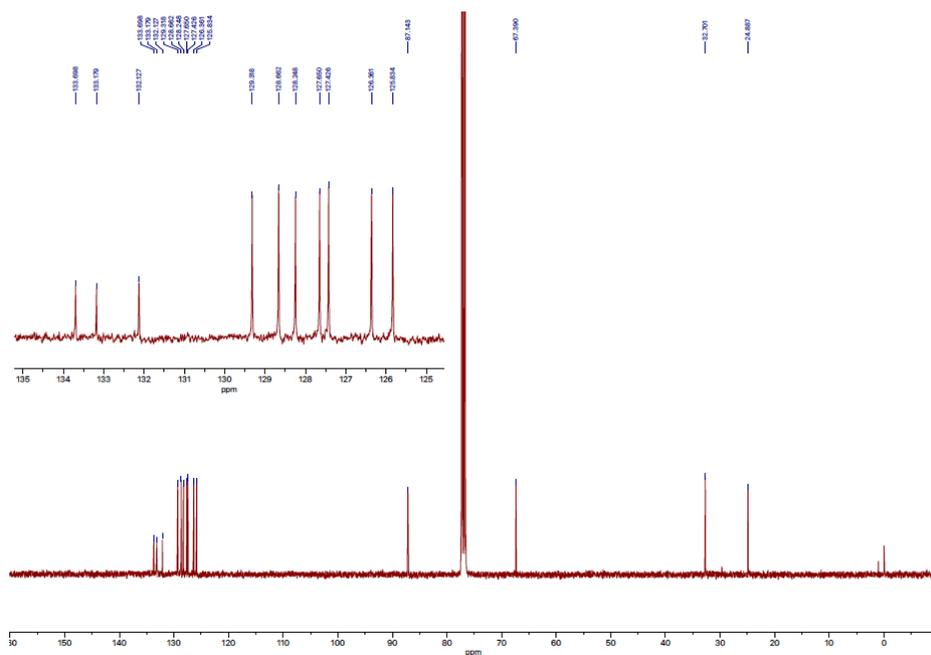
^1H NMR (400 MHz, CDCl_3)



4p

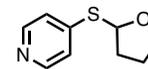
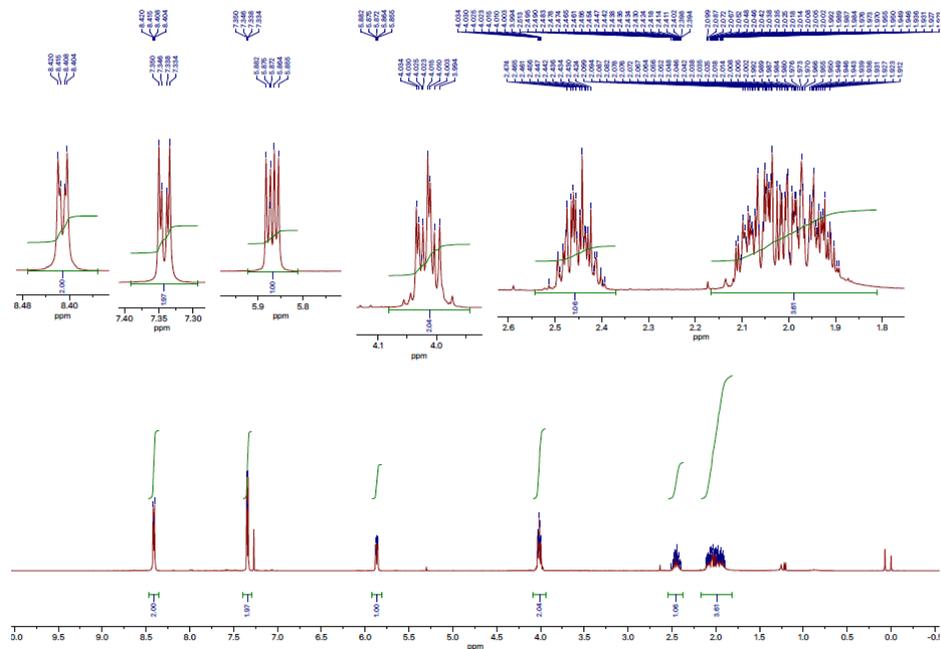


^{13}C NMR (101 MHz, CDCl_3)



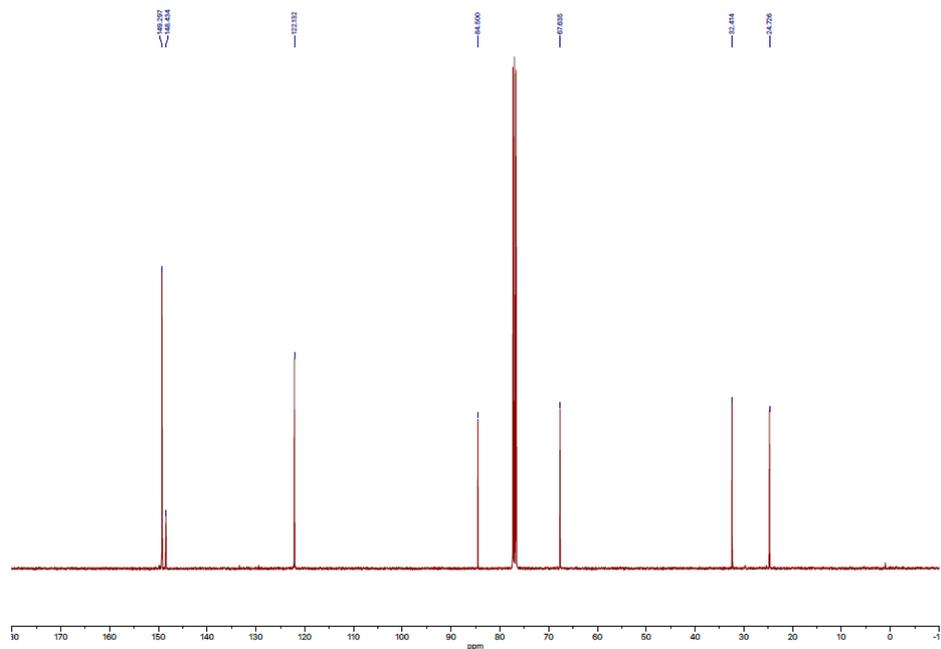
4q

^1H NMR (400 MHz, CDCl_3)



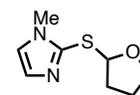
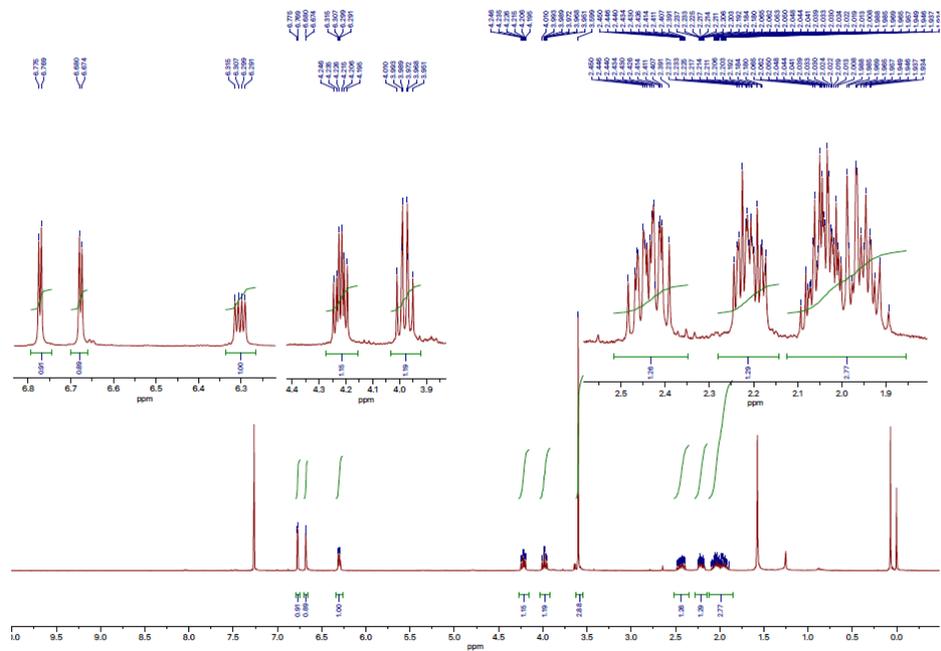
4q

^{13}C NMR (101 MHz, CDCl_3)



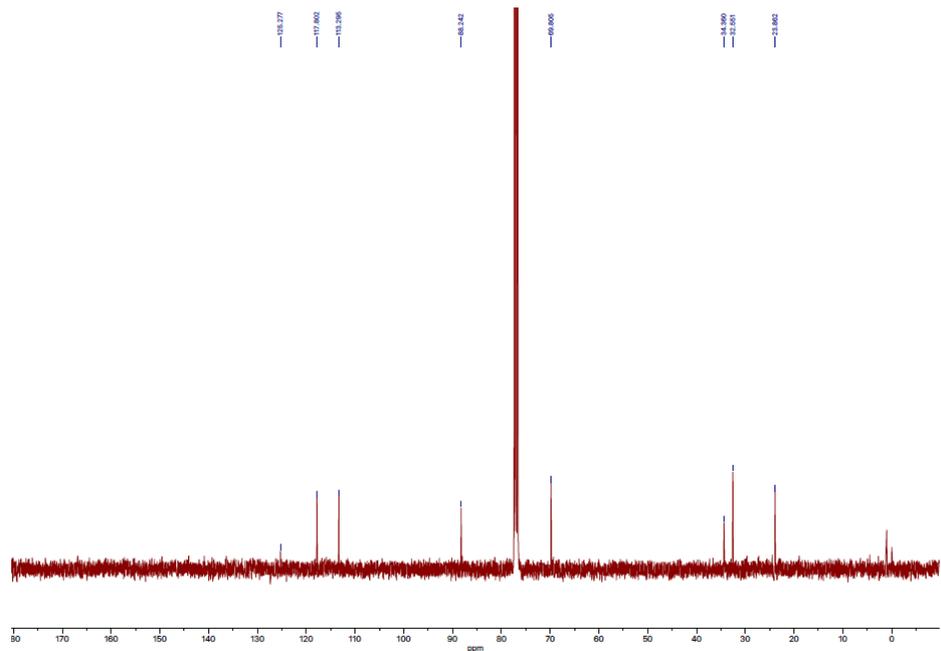
4r

¹H NMR (400 MHz, CDCl₃)



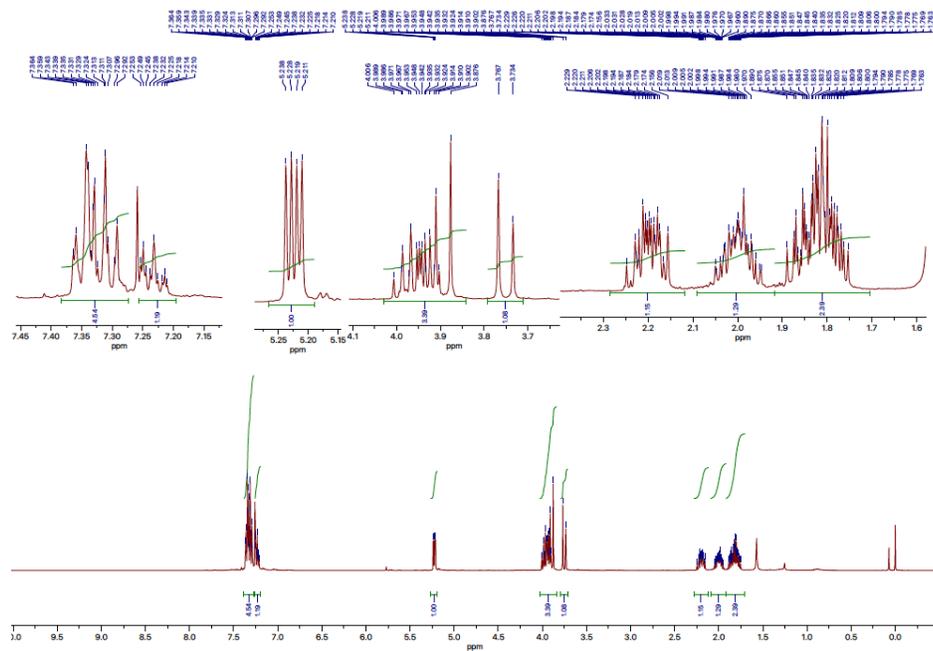
4r

¹³C NMR (101 MHz, CDCl₃)

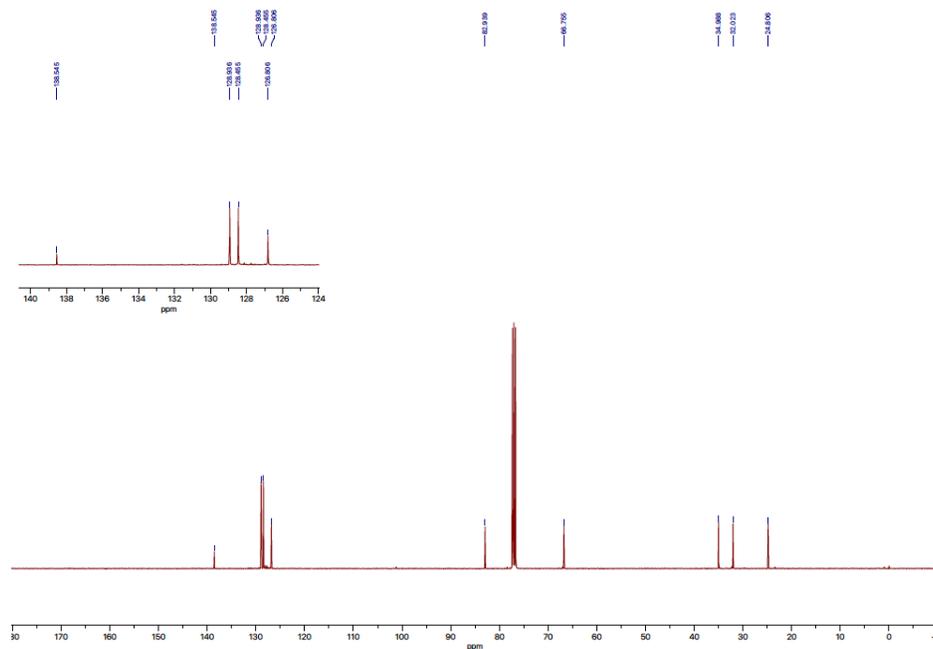


4s

^1H NMR (400 MHz, CDCl_3)

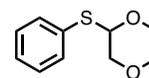
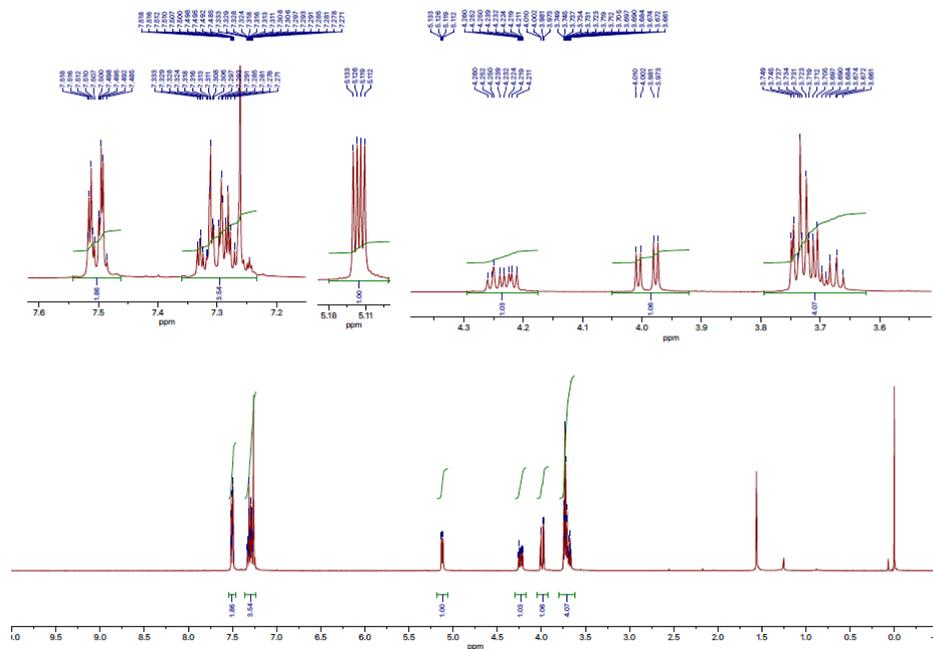


^{13}C NMR (101 MHz, CDCl_3)



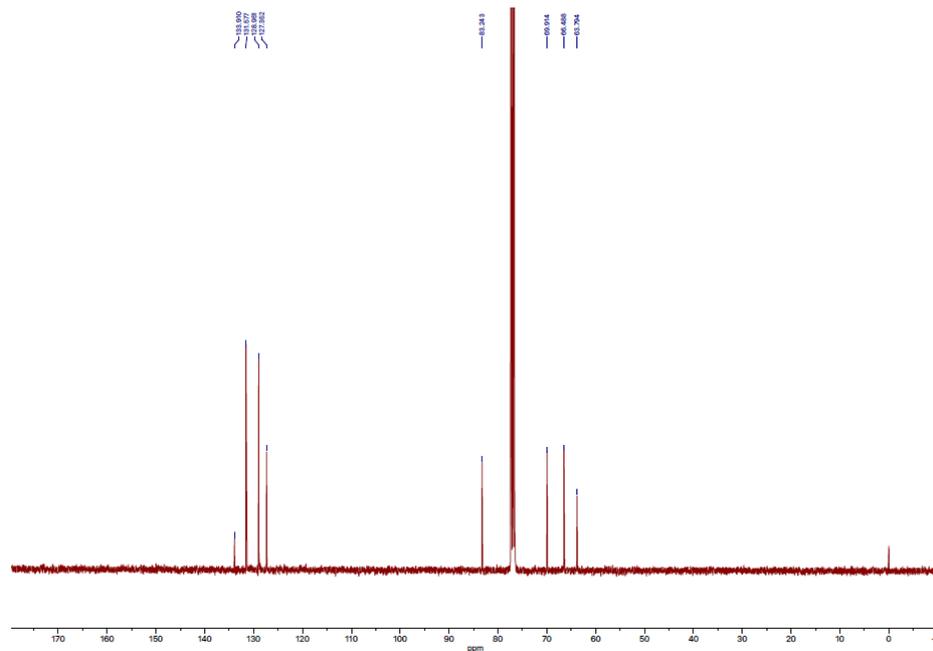
6b

^1H NMR (400 MHz, CDCl_3)



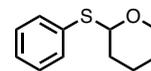
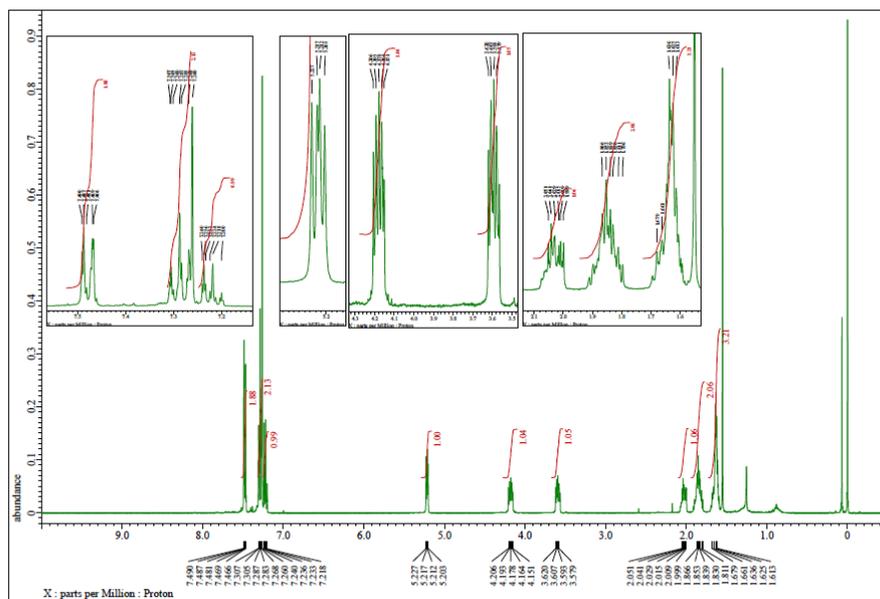
6b

^{13}C NMR (101 MHz, CDCl_3)



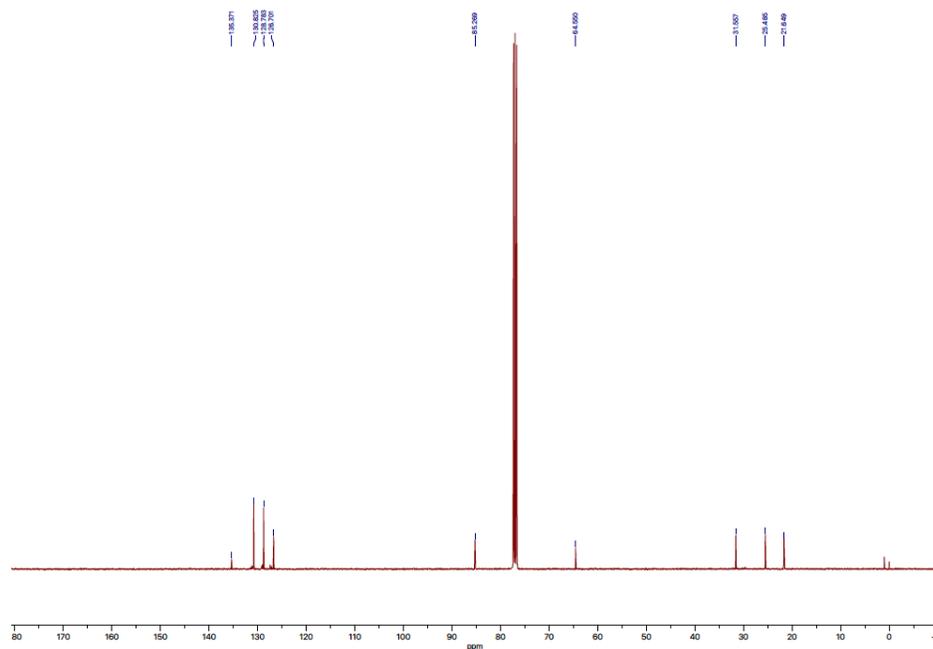
6c

^1H NMR (400 MHz, CDCl_3)



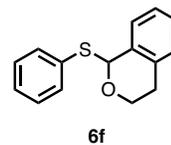
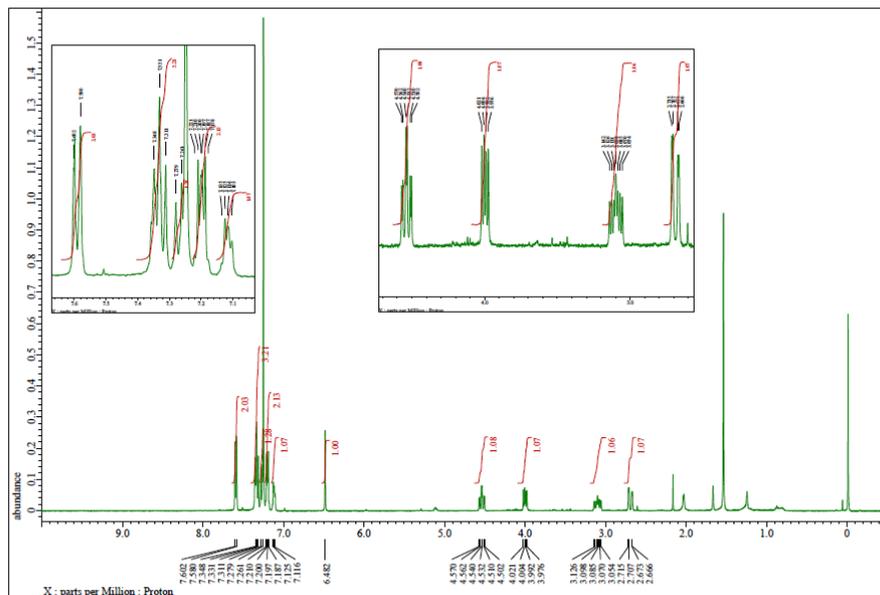
6c

^{13}C NMR (101 MHz, CDCl_3)

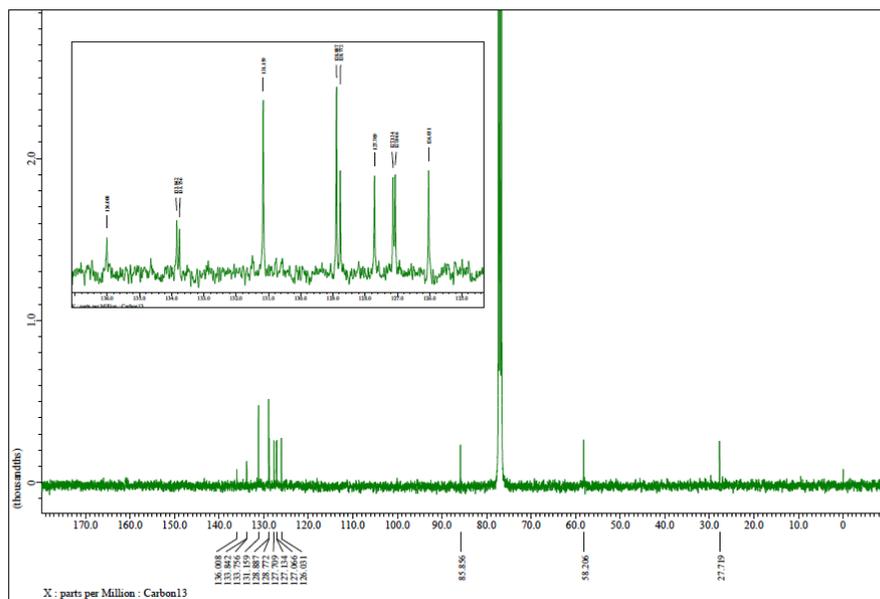


6f

^1H NMR (400 MHz, CDCl_3)

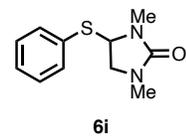
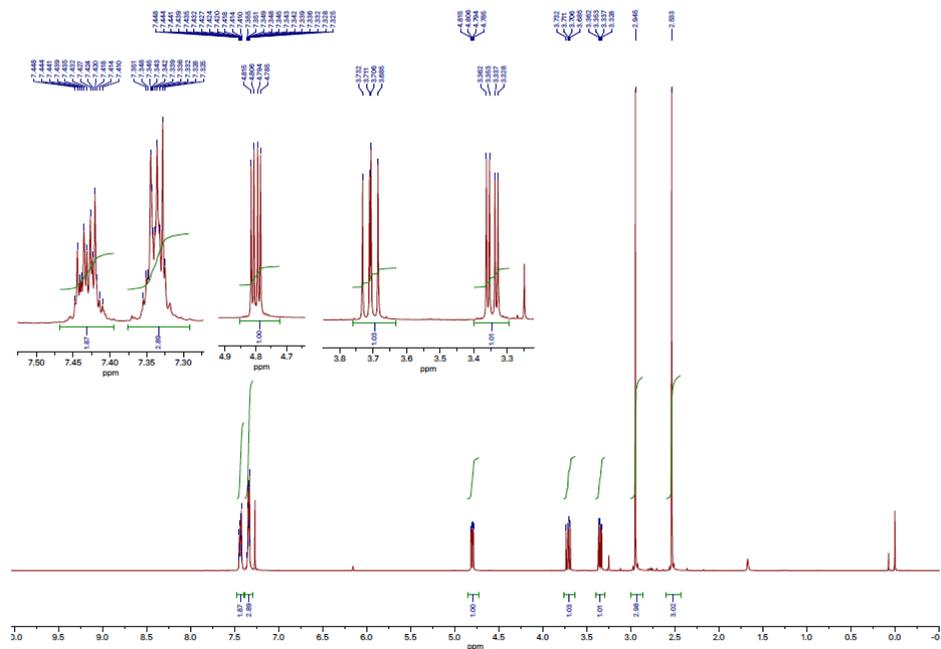


^{13}C NMR (101 MHz, CDCl_3)

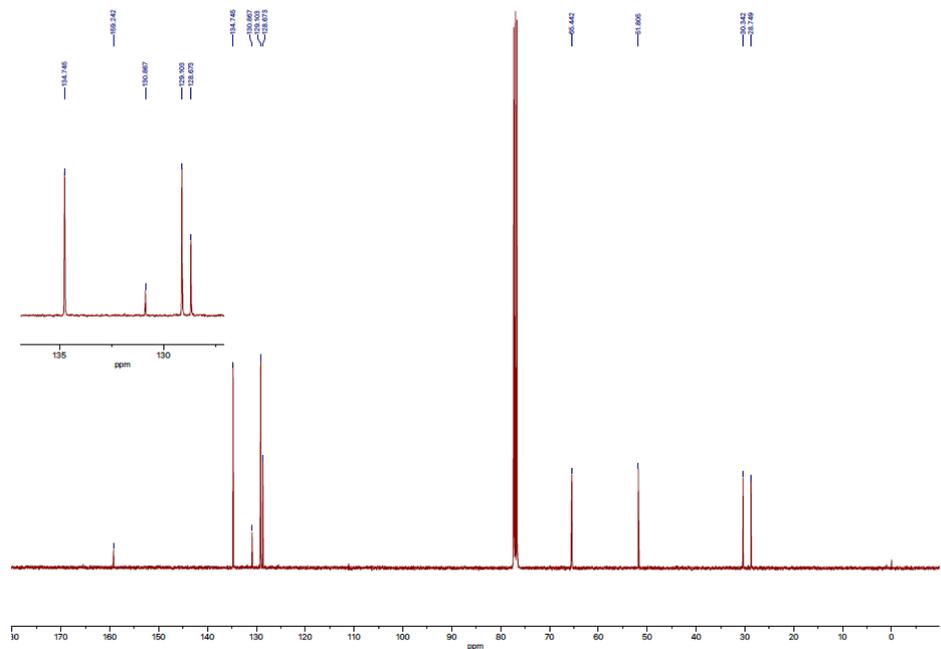


6i

^1H NMR (400 MHz, CDCl_3)

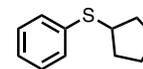


^{13}C NMR (101 MHz, CDCl_3)

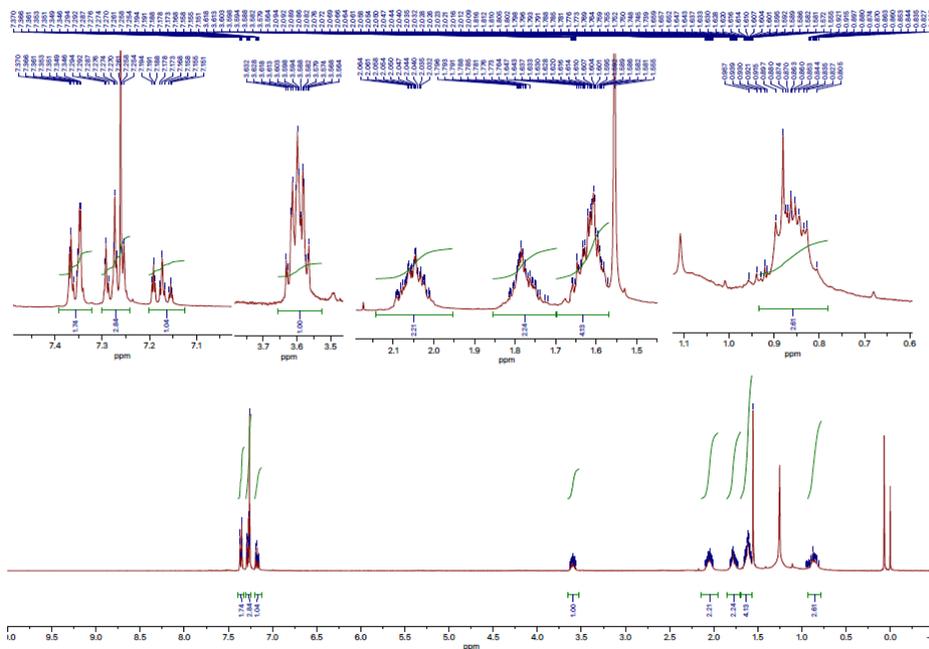


6k

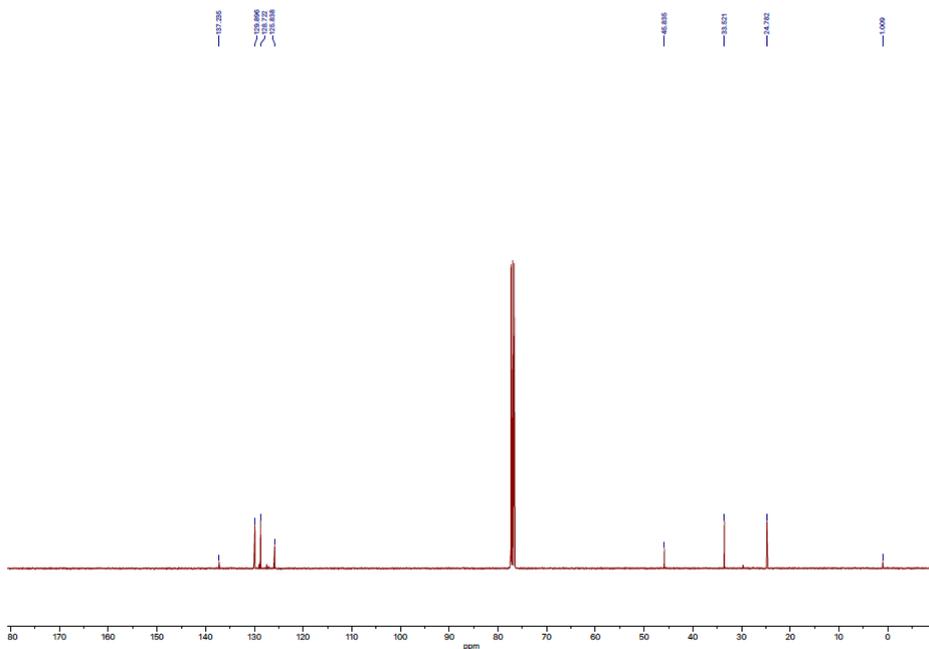
^1H NMR (400 MHz, CDCl_3)



6k

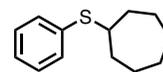
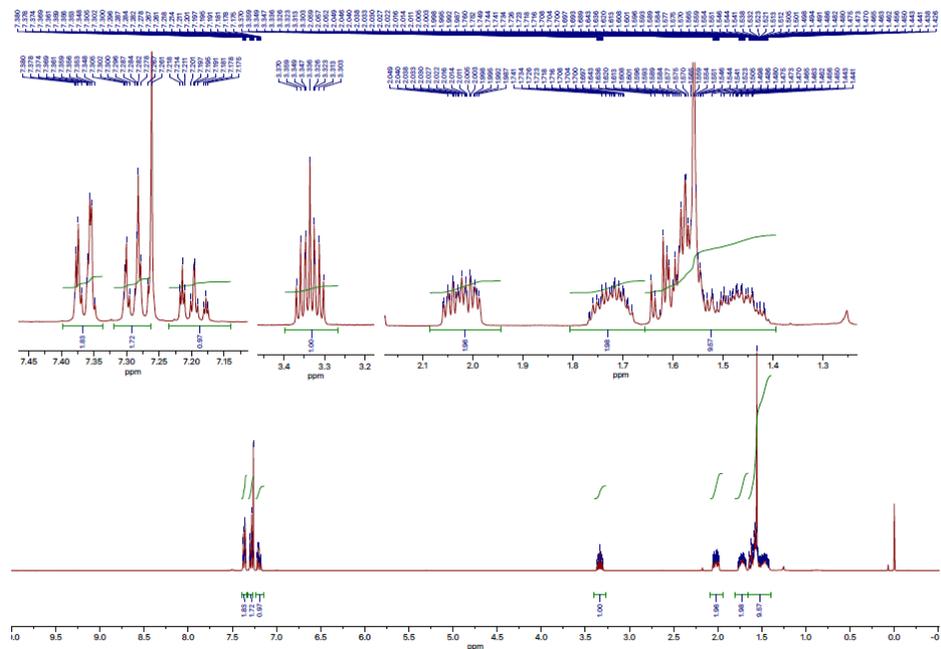


^{13}C NMR (101 MHz, CDCl_3)



6m

^1H NMR (400 MHz, CDCl_3)



6m

^{13}C NMR (101 MHz, CDCl_3)

