

Supporting Information

Palladium-Catalyzed C–S Bond Cleavage with Allenates: Synthesis of Tetrasubstituted 2-Alkenylfuran Derivatives

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Experimental procedures and analytical data

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1. General considerations

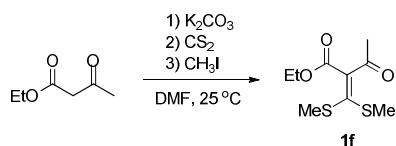
The solvents were dried and distilled prior to use by the literature methods. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker DRX-400 spectrometer and all chemical shift values refer to $\delta_{\text{TMS}} = 0.00$ ppm or CDCl_3 ($\delta(^1\text{H})$, 7.26 ppm and $\delta(^{13}\text{C})$, 77.16 ppm). The HRMS analysis was obtained on a Waters GC-TOF CA156 mass spectrometer. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. Known compounds **1a**,¹ **1b**,² **1c**,¹ **1d**,³ **1e** and **1f**,¹ **1i-k**,¹ **1l**,⁴ **1m** and **1n**,¹ **1s**,⁵ **1z6**,¹ **2c-g**,⁶ **2h** and **2i**,⁷ **5**,⁴ **7b**⁸ and **9a**,⁹ were prepared by the literature procedures, and their spectroscopic features are in good agreement with those reported in the literatures.

References

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2. Experimental procedures

2.1 Preparation of α -oxo ketene dithioacetals (**1**)



A typical procedure for the synthesis of α -oxo ketene dithioacetals 1 –
Synthesis of ethyl 2-(bis(methylthio)methylene)-3-oxobutanoate (1f): Iodomethane (3.1 g, 22 mmol) was added dropwise to a stirred mixture of ethyl acetoacetate (1.3 g, 10 mmol), K₂CO₃ (3.5 g, 25 mmol), and CS₂ (0.9 g, 12 mmol) in 10 mL DMF at 0 °C. The reaction was continued at 25 °C for 24 h. The resulting mixture was poured into 50 mL water, separated, and the aqueous phase was extracted with 10 mL CH₂Cl₂. The combined organic phase was washed with H₂O (3×10 mL), dried over anhydrous MgSO₄, filtered, and evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc = 20:1, v/v) to afford **1f** as a yellow oil (2.1 g, 88%).

2.2 General procedure for the C–S cleavage of α -oxo ketene dithioacetals 1

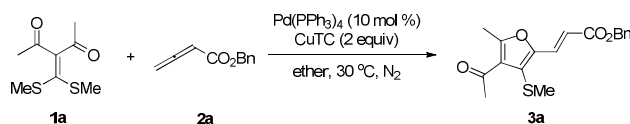
Screening of the reaction conditions: By means of the reaction of α,α -diacetyl ketene di(methylthio)acetal (**1a**) with benzyl buta-2,3-dienoate (**2a**) the reaction conditions were optimized as follows.

Table S1. Screening of reaction conditions.^a

entry	CuTC (equiv)	base (2 equiv)	time (h)	temp. (°C)	yield ^b (%)
1	2	Cs ₂ CO ₃	12	25	71
2	2	Cs ₂ CO ₃	12	30	76
3	2	CsOAc	12	30	76
4	2	NaHCO ₃	12	30	76
5	2		12	30	76
6	2		8	30	71
7	2		16	30	75
8	1		12	30	68
9	0.5		12	30	62
10	0		12	30	trace
11 ^c	2		12	30	n.d.
12 ^d	2		12	30	77 (74)

^a Conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), Pd(PPh₃)₄ (0.02 mmol), ether (2 mL), 0.1 MPa N₂. ^b Determined by ¹H NMR analysis with 1,3,5-trimethyloxylbenzene as the internal standard. Isolated yield given in the parentheses. ^c Without Pd(PPh₃)₄. ^d **1a** (0.3 mmol), **2a** (0.9 mmol), Pd(PPh₃)₄ (0.03 mmol), ether (3 mL), 0.1 MPa N₂.

2.3 Reactions of α -oxo ketene dithioacetals (**1**) with allenates **2**

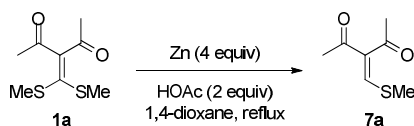


A typical procedure for the synthesis of tetrasubstituted 2-alkenylfurans (**3**)

– Synthesis of (*E*)-benzyl 3-(4-acetyl-5-methyl-3-(methylthio)furan-2-yl)acrylate (**3a**):

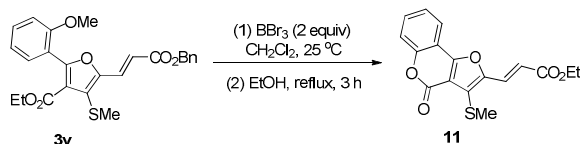
Under a nitrogen atmosphere, a mixture of α -oxo ketene dithioacetal **1a** (61 mg, 0.3 mmol), benzyl buta-2,3-dienoate (**2a**) (157 mg, 0.9 mmol), $\text{Pd(PPh}_3)_4$ (35 mg, 0.03 mmol), and CuTC (114 mg, 0.6 mmol) in diethyl ether (3 mL) was stirred at 30 °C for 12 h. The resultant mixture was filtered through a short pad of celite. The filtrate was evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc = 40:1, v/v) to afford **3a** as a yellow oil (73 mg, 74%).

2.4 Preparation of compound **7a**



Synthesis of 3-((methylthio)methylene)pentane-2,4-dione (7a**):** A mixture of α -oxo ketene dithioacetal **1a** (410 mg, 2 mmol), Zn powder (523 mg, 8 mmol), and HOAc (240 mg, 4 mmol) in 1,4-dioxane (10 mL) was stirred at reflux for 1 h. The reaction mixture was cooled to ambient temperature and the filtrate was evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether/EtOAc = 4/1, v/v) to afford **7a** as a white solid (105 mg, 33%).

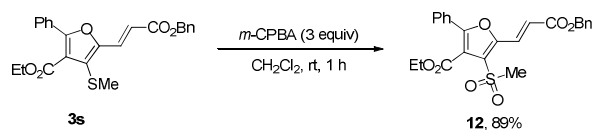
2.5 Intramolecular cyclization of tetrasubstituted furan **3v**



A general procedure for the lactonization of product **3v – Synthesis of (*E*)-ethyl 3-(3-(methylthio)-4-oxo-4H-furo[3,2-*c*]chromen-2-yl)acrylate (**11**):** Under a

nitrogen atmosphere, BBr₃ (400 μ L, 0.4 mmol, 0.1 M in CH₂Cl₂) was added to a stirred mixture of **3v** (90 mg, 0.2 mmol) in 2 mL of dry CH₂Cl₂ at 0 °C. Then, the reaction was stirred at 25 °C overnight. After quenching the reaction with EtOH (1 mL), the volatiles were removed under reduced pressure, and the residue was dissolved in EtOH (4 mL). The resulting mixture was heated at reflux for 3 h, cooled to ambient temperature, and filtered. The filtrate was evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc/CH₂Cl₂ = 20/1/2, v/v/v) to afford **11** as a yellow solid (39 mg, 59%).

2.6 Oxidation of tetrasubstituted furan **3s**



A general procedure for the product **12 – Synthesis of (*E*)-ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-4-(methylsulfonyl)-2-phenylfuran-3-carboxylate (**12**):** a mixture of **3s** (42 mg, 0.1 mmol) and *m*-CPBA (52 mg, 0.3 mmol) in 1 mL of CH₂Cl₂ at room temperature for 1 h. The resulting mixture was poured into 10 mL saturated aq. Na₂CO₃, extracted with dichloromethane (3×5 mL). The combined organic phase was washed with water (2×5 mL), dried over anhydrous Na₂SO₄, filtered, and evaporated all the volatiles under reduced pressure. The resultant residue was purified by silica gel column chromatography (eluent: petroleum ether (60-90 °C)/EtOAc = 5/1, v/v) to afford **12** as a yellow solid (40 mg, 89%).

3. X-Ray crystallographic studies

Single crystal X-ray diffraction studies for compounds **3e** and **4g** were carried out on a SMART APEX diffractometer with graphite-monochromated Mo K α radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2 . All non-hydrogen atoms were refined

anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 1813518 for **3e**, CCDC 1842016 for **4g**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

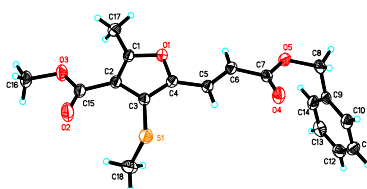


Figure S1. Molecular structure of **3e**.

Table S2. Crystal data and structure refinement for **3e**.

Identification code	w9n-994w	
Empirical formula	C ₁₈ H ₁₈ O ₅ S	
Formula weight	346.38	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /c	
Unit cell dimensions	$a = 18.2680(14)$ Å	$\alpha = 90^\circ$.
	$b = 8.0504(6)$ Å	$\beta = 97.173(7)^\circ$.
	$c = 11.7056(8)$ Å	$\gamma = 90^\circ$.
Volume	$1708.0(2)$ Å ³	
Z	4	
Density (calculated)	1.347 Mg/m ³	
Absorption coefficient	0.214 mm ⁻¹	
F(000)	728	
Crystal size	0.20 x 0.16 x 0.11 mm ³	
Theta range for data collection	2.769 to 25.999°.	
Index ranges	$-22 \leq h \leq 17$, $-9 \leq k \leq 9$, $-13 \leq l \leq 14$	
Reflections collected	8921	
Independent reflections	3355 [R(int) = 0.0198]	
Completeness to theta = 25.242°	99.9 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8629
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3355 / 0 / 221
Goodness-of-fit on F ²	1.040
Final R indices [I>2sigma(I)]	R1 = 0.0373, wR2 = 0.0940
R indices (all data)	R1 = 0.0532, wR2 = 0.1056
Extinction coefficient	0.0016(6)
Largest diff. peak and hole	0.217 and -0.233 e.Å ⁻³

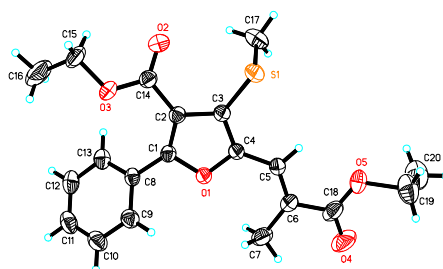


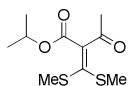
Figure S2. Molecular structure of **4g**.

Table S3. Crystal data and structure refinement for **4g**.

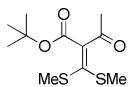
Identification code	WQN-1150W		
Empirical formula	C20 H22 O5 S		
Formula weight	374.43		
Temperature	293(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P -1		
Unit cell dimensions	a = 10.0038(6) Å	α = 86.152(4)°.	
	b = 10.8197(6) Å	β = 79.111(5)°.	
	c = 18.6560(10) Å	γ = 86.870(5)°.	
Volume	1976.7(2) Å ³		
Z	4		
Density (calculated)	1.258 Mg/m ³		
Absorption coefficient	0.190 mm ⁻¹		
F(000)	792		
Crystal size	0.200 x 0.170 x 0.130 mm ³		
Theta range for data collection	2.972 to 25.499°.		
Index ranges	-12<=h<=12, -12<=k<=13, -22<=l<=22		
Reflections collected	17768		
Independent reflections	7351 [R(int) = 0.0258]		
Completeness to theta = 25.242°	99.7 %		

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.7887
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7351 / 80 / 516
Goodness-of-fit on F ²	1.046
Final R indices [I > 2σ(I)]	R1 = 0.0594, wR2 = 0.1577
R indices (all data)	R1 = 0.1012, wR2 = 0.1921
Largest diff. peak and hole	0.590 and -0.271 e.Å ⁻³

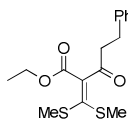
4. Analytical data



Isopropyl 2-(bis(methylthio)methylene)-3-oxobutanoate (1g): 2.1 g, 83% yield; yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 5.14 (hept, *J* = 6.3 Hz, 1 H, CH(CH₃)₂), 2.41 (s, 6 H, 2×SCH₃), 2.30 (s, 3 H, CH₃CO), 1.29 (d, *J* = 6.3 Hz, 6 H, CH(CH₃)₂). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 195.2 (Cq, C=O), 164.9 (Cq, CO₂CH), 156.8 and 135.9 (Cq), 69.34 (CO₂CH), 29.9 (CH₃CO), 21.7 (CH(CH₃)₂), 18.6 (2×SCH₃). HRMS Calcd for C₁₀H₁₆O₃S₂ [M+H]⁺: 249.0619, found: 249.0620.

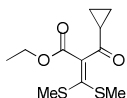


tert-Butyl 2-(bis(methylthio)methylene)-3-oxobutanoate (1h): 2.1 g, 81% yield; yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 2.40 (s, 6 H, 2×SCH₃), 2.31 (s, 3 H, CH₃CO), 1.51 (s, 9 H, C(CH₃)₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 195.6 (Cq, C=O), 164.3 (Cq, CO₂C), 155.4 and 137.2 (Cq), 82.6 (Cq, C(CH₃)₃), 29.9 (CH₃CO), 28.1 (C(CH₃)₃), 18.5 (2×SCH₃). HRMS Calcd for C₁₁H₁₈O₃S₂ [M+H]⁺: 263.0776, found: 263.0778.

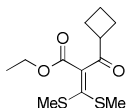


Ethyl 2-(bis(methylthio)methylene)-3-oxo-5-phenylpentanoate (1o): 1.4 g, 88% yield; yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.32 (m, 2 H, aromatic CH), 7.23 (m, 3 H, aromatic CH), 4.28 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂), 3.01 (m, 4 H, PhCH₂CH₂), 2.46 (s, 6 H, 2×SCH₃), 1.32 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃). ¹³C{¹H}

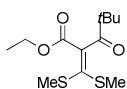
NMR (100 MHz, CDCl₃) δ 197.5 (Cq, C=O), 164.6 (Cq, CO₂CH₂), 156.9, 141.0, and 135.2 (Cq), 128.5, 128.4, and 126.1 (aromatic CH), 61.5 (CO₂CH₂), 44.2 and 29.9 (PhCH₂CH₂), 18.5 (2×SCH₃), 14.1 (CO₂CH₂CH₃). HRMS Calcd for C₁₆H₂₀O₃S₂ [M+H]⁺: 325.0932, found: 325.0931.



Ethyl 2-(cyclopropanecarbonyl)-3,3-bis(methylthio)acrylate (1p): 280 mg, 74% yield; yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 4.26 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂CH₃), 2.41 (s, 6 H, 2×SCH₃), 2.06 (m, 1 H, COCH), 1.29 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃), 1.15 and 0.94 (m each, 2:2 H, CH₂CHCH₂). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 198.5 (Cq, C=O), 165.1 (Cq, CO₂CH₂), 156.7 and 135.4 (Cq), 61.5 (CO₂CH₂), 21.4 (COCH), 18.6 (2×SCH₃), 14.1 (CO₂CH₂CH₃), 12.3 (CH₂CHCH₂). HRMS Calcd for C₁₁H₁₆O₃S₂ [M+H]⁺: 261.0619, found: 261.0621.

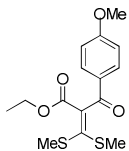


Ethyl 2-(cyclobutanecarbonyl)-3,3-bis(methylthio)acrylate (1q): 185 mg, 56% yield; yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 4.24 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂CH₃), 3.49 (p, *J* = 8.5 Hz, 1 H, COCH), 2.41 (s, 6 H, 2×SCH₃), 2.33 and 2.09 (m each, 2:2 H, CH₂CHCH₂), 1.93 and 1.83 (m each, 1:1 H, CH₂CH₂CH₂), 1.29 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 199.5 (Cq, C=O), 165.1 (Cq, CO₂CH₂), 157.0 and 134.8 (Cq), 61.5 (CO₂CH₂), 45.4 (COCH), 25.2 (CH₂CHCH₂), 18.7 and 18.6 (2×SCH₃), 17.9 (CH₂CH₂CH₂), 14.2 (CO₂CH₂CH₃). HRMS Calcd for C₁₂H₁₈O₃S₂ [M+H]⁺: 275.0776, found: 275.0775.

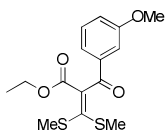


Ethyl 2-(bis(methylthio)methylene)-4,4-dimethyl-3-oxopentanoate (1r): 2.6 g, 95% yield; colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 4.18 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂CH₃), 2.42 (s, 3 H, SCH₃), 2.31 (s, 3 H, SCH₃), 1.24 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃), 1.20 (s, 9 H, C(CH₃)₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 208.7 (Cq, C=O), 162.7 (Cq, CO₂CH₂), 152.7 and 135.4 (Cq), 61.3 (CO₂CH₂), 44.7 (C(CH₃)₃),

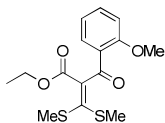
28.0 (C(CH₃)₃), 18.9 (SCH₃), 17.2 (SCH₃), 14.2 (CO₂CH₂CH₃). HRMS Calcd for C₁₂H₂₀O₃S₂ [M+H]⁺: 277.0932, found: 277.0935.



Ethyl 2-(4-methoxybenzoyl)-3,3-bis(methylthio)acrylate (1t): 274 mg, 80% yield; yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.7 Hz, 2 H, aromatic CH), 6.89 (d, *J* = 8.7 Hz, 2 H, aromatic CH), 4.08 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂CH₃), 3.81 (s, 3 H, OCH₃), 2.46 (s, 3 H, SCH₃), 2.19 (s, 3 H, SCH₃), 1.06 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 190.2 (Cq, C=O), 163.7 (Cq, CO₂CH₂), 163.3, 155.9, and 132.8 (Cq), 131.4 (aromatic CH), 129.9 (Cq), 113.8 (aromatic CH), 61.0 (CO₂CH₂), 55.5 (OCH₃), 19.3 (SCH₃), 17.2 (SCH₃), 14.0 (CO₂CH₂CH₃). HRMS Calcd for C₁₅H₁₈O₄S₂ [M+H]⁺: 327.0725, found: 327.0722.

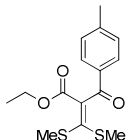


Ethyl 2-(3-methoxybenzoyl)-3,3-bis(methylthio)acrylate (1u): 424 mg, 81% yield; white solid; m.p. 84-86 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.47 (s, 1 H, aromatic CH), 7.35 (m, 2 H, aromatic CH), 7.10 (m, 1 H, aromatic CH), 4.12 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂), 3.84 (s, 3 H, OCH₃), 2.50 (s, 3 H, SCH₃), 2.22 (s, 3 H, SCH₃), 1.09 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 191.4 (Cq, C=O), 163.3 (CO₂CH₂), 156.0, 157.1, 138.5, and 132.6 (Cq), 129.6, 122.1, 120.1, and 112.7 (aromatic CH), 61.2 (CO₂CH₂), 55.5 (OCH₃), 19.5 (SCH₃), 17.3 (SCH₃), 14.1 (CO₂CH₂CH₃). HRMS Calcd for C₁₅H₁₈O₄S₂ [M+H]⁺: 327.0725, found: 327.0725.

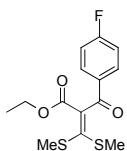


Ethyl 2-(2-methoxybenzoyl)-3,3-bis(methylthio)acrylate (1v): 384 mg, 65% yield; yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 7.7 Hz, 1 H, aromatic CH), 7.43 (t, *J* = 7.8 Hz, 1 H, aromatic CH), 6.97 (t, *J* = 7.5 Hz, 1 H, aromatic CH), 6.89 (d, *J* = 8.3 Hz, 1 H, aromatic CH), 4.07 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂), 3.76 (s, 3

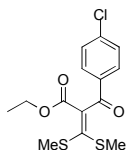
H, OCH₃), 2.41 (s, 3 H, SCH₃), 2.12 (s, 3 H, SCH₃), 1.02 (t, J = 7.1 Hz, 3 H, CO₂CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 190.1 (Cq, C=O), 163.5 (CO₂CH₂), 159.1, 154.3, and 136.1 (Cq), 134.3 and 131.6 (aromatic CH), 127.3 (Cq), 120.8 and 111.9 (aromatic CH), 60.80 (CO₂CH₂), 55.9 (OCH₃), 19.3 (SCH₃), 17.5 (SCH₃), 14.0 (CO₂CH₂CH₃). HRMS Calcd for C₁₅H₁₈O₄S₂ [M+H]⁺: 327.0725, found: 327.0724.



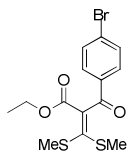
Ethyl 2-(4-methylbenzoyl)-3,3-bis(methylthio)acrylate (1w): 370 mg, 71% yield; yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (m, 2 H, aromatic CH), 7.25 (t, J = 5.9 Hz, 2 H, aromatic CH), 4.12 (q, J = 7.1 Hz, 2 H, CO₂CH₂), 2.50 (s, 3 H, SCH₃), 2.40 (s, 3 H, CH₃), 2.21 (s, 3 H, SCH₃), 1.08 (t, J = 7.1 Hz, 3 H, CO₂CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 191.3 (Cq, C=O), 163.4 (CO₂CH₂), 156.5, 144.3, 134.6, and 132.9 (Cq), 129.4 and 129.3 (aromatic CH), 61.2 (CO₂CH₂), 21.8 (CH₃), 19.5 (SCH₃), 17.3 (SCH₃), 14.0 (CO₂CH₂CH₃). HRMS Calcd for C₁₅H₁₈O₃S₂ [M+H]⁺: 311.0776, found: 311.0776.



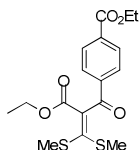
Ethyl 2-(4-fluorobenzoyl)-3,3-bis(methylthio)acrylate (1x): 841 mg, 67% yield; yellow solid; m.p. 63-65 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.90 (dd, J = 8.6, 5.5 Hz, 2 H, aromatic CH), 7.11 (t, J = 8.5 Hz, 2 H, aromatic CH), 4.12 (q, J = 7.1 Hz, 2 H, CO₂CH₂), 2.50 (s, 3 H, SCH₃), 2.23 (s, 3 H, SCH₃), 1.09 (t, J = 7.1 Hz, 3 H, CO₂CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 190.2 (Cq, C=O), 165.9 (d, J = 255.4 Hz, CF), 163.2 (CO₂CH₂), 157.3 (Cq), 133.6 (d, J = 2.9 Hz, Cq), 132.3 (Cq), 131.8 (d, J = 9.4 Hz, aromatic CH), 115.9 (d, J = 22.0 Hz, aromatic CH), 61.3 (CO₂CH₂), 19.5 (SCH₃), 17.4 (SCH₃), 14.1 (CO₂CH₂CH₃). HRMS Calcd for C₁₄H₁₅FO₃S₂ [M+H]⁺: 315.0525, found: 315.0525.



Ethyl 2-(4-chlorobenzoyl)-3,3-bis(methylthio)acrylate (1y): 817 mg, 75% yield; yellow solid; m.p. 80-82 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.82 (d, $J = 7.6$ Hz, 2 H, aromatic CH), 7.42 (d, $J = 7.6$ Hz, 2 H, aromatic CH), 4.13 (q, $J = 6.8$ Hz, 2 H, CO_2CH_2), 2.51 (s, 3 H, SCH₃), 2.23 (s, 3 H, SCH₃), 1.09 (t, $J = 6.9$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 190.5 (Cq, C=O), 163.2 (CO_2CH_2), 157.7, 139.8, 135.6, and 132.1 (Cq), 130.6 and 129.1 (aromatic CH), 61.4 (CO_2CH_2), 19.6 (SCH₃), 17.4 (SCH₃), 14.1 ($\text{CO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{14}\text{H}_{15}\text{ClO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 331.0229, found: 331.0227.

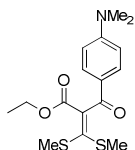


Ethyl 2-(4-bromobenzoyl)-3,3-bis(methylthio)acrylate (1z): 564 mg, 75% yield; yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.72 (m, 2 H, aromatic CH), 7.57 (m, 2 H, aromatic CH), 4.11 (q, $J = 7.1$ Hz, 2 H, CO_2CH_2), 2.49 (s, 3 H, SCH₃), 2.21 (s, 3 H, SCH₃), 1.08 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 190.6 (Cq, C=O), 163.0 (CO_2CH_2), 157.7 and 135.9 (Cq), 132.0 (aromatic CH), 131.8 (Cq), 130.6 (aromatic CH), 128.5 (Cq), 61.3 (CO_2CH_2), 19.5 (SCH₃), 17.3 (SCH₃), 14.0 ($\text{CO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{14}\text{H}_{15}\text{BrO}_3\text{S}_2$ $[\text{M}+\text{H}]^+$: 374.9724, found: 374.9723.

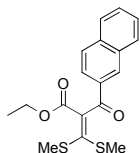


Ethyl 4-(2-(ethoxycarbonyl)-3,3-bis(methylthio)acryloyl)benzoate (1z1): 510 mg, 58% yield; yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (m, 2 H, aromatic CH), 7.91 (m, 2 H, aromatic CH), 4.37 (q, $J = 7.1$ Hz, 2 H, CO_2CH_2), 4.11 (q, $J = 7.1$ Hz, 2 H, CO_2CH_2), 2.50 (s, 3 H, SCH₃), 2.20 (s, 3 H, SCH₃), 1.38 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.06 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 190.9 (Cq, C=O), 165.8 (CO_2CH_2), 163.2 (CO_2CH_2), 158.2, 140.5, 134.3,

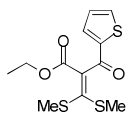
and 131.9 (Cq), 129.8 and 128.9 (aromatic CH), 61.5 (CO₂CH₂), 61.3 (CO₂CH₂), 19.5 (SCH₃), 17.4 (SCH₃), 14.3 (CO₂CH₂CH₃), 14.0 (CO₂CH₂CH₃). HRMS Calcd for C₁₇H₂₀O₅S₂ [M+H]⁺: 369.0830, found: 369.0831.



Ethyl 2-(4-(dimethylamino)benzoyl)-3,3-bis(methylthio)acrylate (1z2): 500 mg, 61% yield; yellow solid; m.p. 94-96 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.79 (m, 2 H, aromatic CH), 6.64 (m, 2 H, aromatic CH), 4.14 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂), 3.06 (s, 6 H, N(CH₃)₂), 2.49 (s, 3 H, SCH₃), 2.24 (s, 3 H, SCH₃), 1.13 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 190.0 (Cq, C=O), 163.8 (CO₂CH₂), 154.4, 153.7, and 134.0 (Cq), 131.7 (aromatic CH), 124.8 (Cq), 110.8 (aromatic CH), 61.2 (CO₂CH₂), 40.1 (N(CH₃)₂), 19.4 (SCH₃), 17.3 (SCH₃), 14.2 (CO₂CH₂CH₃). HRMS Calcd for C₁₆H₂₁NO₃S₂ [M+H]⁺: 340.1041, found: 340.1041.

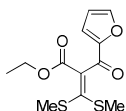


Ethyl 2-(2-naphthoyl)-3,3-bis(methylthio)acrylate (1z3): 300 mg, 69% yield; yellow solid; m.p. 90-92 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (s, 1 H, aromatic CH), 8.00 (dd, *J* = 8.6, 1.6 Hz, 1 H, aromatic CH), 7.87 (m, 3 H, aromatic CH), 7.52 (m, 2 H, aromatic CH), 4.11 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂), 2.50 (s, 3 H, SCH₃), 2.18 (s, 3 H, SCH₃), 1.04 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 191.4 (Cq, C=O), 163.3 (CO₂CH₂), 157.1, 135.6, 134.4, 132.5, and 132.4 (Cq), 131.0, 129.5, 128.5, 127.7, 126.7, and 124.3 (aromatic CH), 61.1 (CO₂CH₂), 19.4 (SCH₃), 17.2 (SCH₃), 13.9 (CO₂CH₂CH₃). HRMS Calcd for C₁₈H₁₈O₃S₂ [M+H]⁺: 347.0776, found: 347.0776.

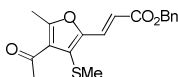


Ethyl 3,3-bis(methylthio)-2-(thiophene-2-carbonyl)acrylate (1z4): 571 mg, 70% yield; pale yellow solid; m.p. 60-62 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.66 (dd,

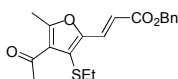
$J = 4.9, 1.1$ Hz, 1 H, aromatic CH), 7.56 (dd, $J = 3.8, 1.2$ Hz, 1 H, aromatic CH), 7.10 (dd, $J = 4.9, 3.8$ Hz, 1 H, aromatic CH), 4.15 (q, $J = 7.1$ Hz, 2 H, CO_2CH_2), 2.51 (s, 3 H, SCH₃), 2.28 (s, 3 H, SCH₃), 1.13 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 184.0 (Cq, C=O), 163.1 (CO_2CH_2), 158.1 and 144.5 (Cq), 134.5 and 133.5 (aromatic CH), 132.3 (Cq), 128.2 (aromatic CH), 61.3 (CO_2CH_2), 19.8 (SCH₃), 17.5 (SCH₃), 14.10 ($\text{CO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3\text{S}_3$ $[\text{M}+\text{H}]^+$: 303.0183, found: 303.0185.



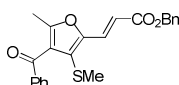
Ethyl 2-(furan-2-carbonyl)-3,3-bis(methylthio)acrylate (1z5): 810 mg, 75% yield; pale yellow solid; m.p. 51-53 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.59 (dd, $J = 1.6, 0.7$ Hz, 1 H, aromatic CH), 7.11 (dd, $J = 3.6, 0.6$ Hz, 1 H, aromatic CH), 6.53 (dd, $J = 3.6, 1.7$ Hz, 1 H, aromatic CH), 4.16 (q, $J = 7.1$ Hz, 2 H, CO_2CH_2), 2.50 (s, 3 H, SCH₃), 2.28 (s, 3 H, SCH₃), 1.13 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 179.2 (Cq, C=O), 163.3 (CO_2CH_2), 159.7 and 152.8 (Cq), 147.0 (aromatic CH), 131.1 (Cq), 118.8 and 112.6 (aromatic CH), 61.3 (CO_2CH_2), 19.8 (SCH₃), 17.6 (SCH₃), 14.1 ($\text{CO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_4\text{S}_2$ $[\text{M}+\text{H}]^+$: 287.0412, found: 287.0410.



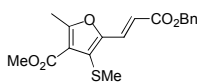
(E)-Benzyl 3-(4-acetyl-5-methyl-3-(methylthio)furan-2-yl)acrylate (3a): 73 mg, 74% yield; white solid; m.p. 84-86 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 7.37 (m, 5 H, aromatic CH), 6.45 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 5.25 (s, 2 H, $\text{CO}_2\text{CH}_2\text{Ph}$), 2.66 (s, 3 H, CH_3CO), 2.57 (s, 3 H, Furan-CH₃), 2.31 (s, 3 H, SCH₃). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 194.7 (Cq, C=O), 166.7 ($\text{CO}_2\text{CH}_2\text{Ph}$), 161.1, 151.2, and 136.1 (Cq), 128.8 ($\text{CH}=\text{CH}$), 128.7 and 128.3 (aromatic CH), 125.4 and 122.1 (Cq), 117.5 ($\text{CH}=\text{CH}$), 66.5 ($\text{CO}_2\text{CH}_2\text{Ph}$), 30.4 (CH_3CO), 21.0 (SCH₃), 15.2 (Furan-CH₃). HRMS Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 331.1004, found: 331.1005.



(E)-Benzyl 3-(4-acetyl-3-(ethylthio)-5-methylfuran-2-yl)acrylate (3b): 61 mg, 59% yield; white solid; m.p. 55-57 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 15.8 Hz, 1 H, CH=CH), 7.37 (m, 5 H, aromatic CH), 6.46 (d, *J* = 15.8 Hz, 1 H, CH=CH), 5.25 (s, 2 H, CO₂CH₂Ph), 2.71 (q, *J* = 7.3 Hz, 2 H, SCH₂CH₃), 2.65 (s, 3 H, CH₃CO), 2.57 (s, 3 H, Furan-CH₃), 1.19 (t, *J* = 7.3 Hz, 3 H, SCH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 195.0 (Cq, C=O), 166.7 (CO₂CH₂Ph), 161.1, 152.2, and 136.1 (Cq), 128.9 (CH=CH), 128.7, 128.3, and 128.3 (aromatic CH), 125.9 and 119.9 (Cq), 117.5 (CH=CH), 66.5 (CO₂CH₂Ph), 31.6 (SCH₂CH₃), 30.7 (CH₃CO), 15.2 (Furan-CH₃), 14.7 (SCH₂CH₃). HRMS Calcd for C₁₉H₂₀O₄S [M+H]⁺: 345.1161, found: 345.1159.

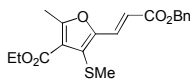


(E)-Benzyl 3-(4-benzoyl-5-methyl-3-(methylthio)furan-2-yl)acrylate (3c): 79 mg, 67% yield; colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 7.6 Hz, 2 H, aromatic CH), 7.75 (d, *J* = 15.8 Hz, 1 H, CH=CH), 7.61 (t, *J* = 7.3 Hz, 1 H, aromatic CH), 7.40 (m, 7 H, aromatic CH), 6.47 (d, *J* = 15.8 Hz, 1 H, CH=CH), 5.26 (s, 2 H, CO₂CH₂Ph), 2.29 (s, 3 H, Furan-CH₃), 2.20 (s, 3 H, SCH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 191.4 (Cq, C=O), 166.7 (CO₂CH₂Ph), 158.1, 150.4, 137.9, and 136.2 (Cq), 133.6 and 129.7 (aromatic CH), 128.8 (CH=CH), 128.7, 128.6, and 128.3 (aromatic CH), 125.5 and 123.9 (Cq), 116.9 (CH=CH), 66.5 (CO₂CH₂Ph), 20.1 (SCH₃), 14.2 (Furan-CH₃). HRMS Calcd for C₂₃H₂₀O₄S [M+H]⁺: 393.1161, found: 393.1160.



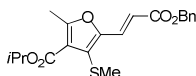
(E)-Methyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-2-methyl-4-(methylthio)furan-3-carboxylate (3e): 75 mg, 73% yield; white solid; m.p. 87-89 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 15.8 Hz, 1 H, CH=CH), 7.35 (m, 5 H, aromatic CH), 6.42 (d, *J* = 15.9 Hz, 1 H, CH=CH), 5.24 (s, 2 H, CO₂CH₂Ph), 3.88 (s, 3 H, CO₂CH₃), 2.59 (s, 3 H, Furan-CH₃), 2.37 (s, 3 H, SCH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.6 (CO₂CH₂Ph), 163.2 (CO₂CH₃), 162.2, 150.6, and 136.1 (Cq), 128.8 (CH=CH), 128.6 and 128.3 (aromatic CH), 123.5 and 117.1 (Cq), 116.8 (CH=CH), 66.4

(CO₂CH₂Ph), 51.6 (CO₂CH₃), 19.6 (SCH₃), 14.9 (Furan-CH₃). HRMS Calcd for C₁₈H₁₈O₅S [M+H]⁺: 347.0953, found: 347.0950.



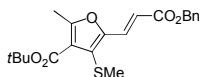
(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-2-methyl-4-(methylthio)

furan-3-carboxylate (3f): 86 mg, 80% yield; colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 15.8 Hz, 1 H, CH=CH), 7.36 (m, 5 H, aromatic CH), 6.42 (d, *J* = 15.8 Hz, 1 H, CH=CH), 5.24 (s, 2 H, CO₂CH₂Ph), 4.35 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂CH₃), 2.59 (s, 3 H, Furan-CH₃), 2.38 (s, 3 H, SCH₃), 1.38 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.7 (CO₂CH₂Ph), 162.8 (CO₂CH₂CH₃), 162.0, 150.6, and 136.1 (Cq), 128.8 (CH=CH), 128.6, 128.3, and 128.2 (aromatic CH), 123.6 and 117.3 (Cq), 116.7 (CH=CH), 66.4 (CO₂CH₂Ph), 60.7 (CO₂CH₂CH₃), 19.7 (SCH₃), 14.9 (Furan-CH₃), 14.3 (CO₂CH₂CH₃). HRMS Calcd for C₁₉H₂₀O₅S [M+H]⁺: 361.1110, found: 361.1107.



(E)-Isopropyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-2-methyl-4-(methylthio)

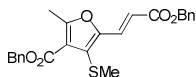
furan-3-carboxylate (3g): 91 mg, 81% yield; colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 15.8 Hz, 1 H, CH=CH), 7.36 (m, 5 H, aromatic CH), 6.42 (d, *J* = 15.8 Hz, 1 H, CH=CH), 5.22 (m, 3 H, CO₂CH₂Ph and CO₂CH(CH₃)₂), 2.58 (s, 3 H, Furan-CH₃), 2.38 (s, 3 H, SCH₃), 1.36 (d, *J* = 6.3 Hz, 6 H, CO₂CH(CH₃)₂). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.7 (CO₂CH₂Ph), 162.3 (CO₂CH(CH₃)₂), 161.8, 150.5, and 136.1 (Cq), 128.8 (CH=CH), 128.6, 128.2, and 128.2 (aromatic CH), 123.6, and 117.6 (Cq), 116.6 (CH=CH), 68.3 (CO₂CH(CH₃)₂), 66.3 (CO₂CH₂Ph), 22.0 (CO₂CH(CH₃)₂), 19.7 (SCH₃), 14.9 (Furan-CH₃). HRMS Calcd for C₂₀H₂₂O₅S [M+H]⁺: 375.1266, found: 375.1261.



(E)-tert-Butyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-2-methyl-4-(methylthio)

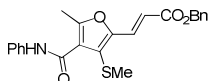
furan-3-carboxylate (3h): 88 mg, 76% yield; colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, *J* = 15.8 Hz, 1 H, CH=CH), 7.35 (m, 5 H, aromatic CH), 6.41 (d, *J* = 15.8 Hz, 1 H, CH=CH), 5.24 (s, 2 H, CO₂CH₂Ph), 2.56 (s, 3 H, Furan-CH₃), 2.37 (s,

3 H, SCH₃), 1.58 (s, 9 H, CO₂C(CH₃)₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.7 (CO₂CH₂Ph), 162.0 (CO₂C(CH₃)₃), 161.4, 150.2, and 136.1 (Cq), 128.9 (CH=CH), 128.6, 128.2, and 128.2 (aromatic CH), 123.7, and 118.3 (Cq), 116.4 (CH=CH), 81.6 (CO₂C(CH₃)₃), 66.3 (CO₂CH₂Ph), 28.3 (CO₂C(CH₃)₃), 19.7 (SCH₃), 14.9 (Furan-CH₃). HRMS Calcd for C₂₁H₂₄O₅S [M+H]⁺: 389.1423, found: 389.1420.



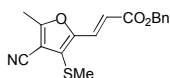
(E)-Benzyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-2-methyl-4-(methylthio)

furan-3-carboxylate (3i): 90 mg, 71% yield; white solid; m.p. 88-90 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 15.8 Hz, 1 H, CH=CH), 7.38 (m, 10 H, aromatic CH), 6.44 (d, *J* = 15.8 Hz, 1 H, CH=CH), 5.35 (s, 2 H, CO₂CH₂Ph), 5.26 (s, 2 H, CO₂CH₂Ph), 2.59 (s, 3 H, Furan-CH₃), 2.32 (s, 3 H, SCH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.7 (CO₂CH₂Ph), 162.6 (CO₂CH₂Ph), 162.4, 150.7, 136.1, and 135.7 (Cq), 128.8 (CH=CH), 128.7, 128.6, 128.4, and 128.3 (aromatic CH), 123.57 and 117.13 (Cq), 116.91 (CH=CH), 66.5 (CO₂CH₂Ph), 66.4 (CO₂CH₂Ph), 19.7 (SCH₃), 15.1 (Furan-CH₃). HRMS Calcd for C₂₄H₂₂O₅S [M+H]⁺: 423.1266, found: 423.1263.



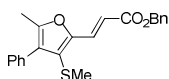
(E)-Benzyl 3-(5-methyl-3-(methylthio)-4-(phenylcarbamoyl)furan-2-yl)

acrylate (3j): 31 mg, 25% yield; pale yellow solid; m.p. 124-126 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.86 (s, 1 H, CONH), 7.76 (d, *J* = 15.8 Hz, 1 H, CH=CH), 7.66 (d, *J* = 8.0 Hz, 2 H, aromatic CH), 7.37 (m, 7 H, aromatic CH), 7.15 (t, *J* = 7.4 Hz, 1 H, aromatic CH), 6.52 (d, *J* = 15.8 Hz, 1 H, CH=CH), 5.27 (s, 2 H, CO₂CH₂Ph), 2.73 (s, 3 H, Furan-CH₃), 2.35 (s, 3 H, SCH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.6 (CO₂CH₂Ph), 162.4 (CONH), 160.6, 151.4, 138.1, and 136.1 (Cq), 129.2, 128.7, 128.4, 128.4, and 128.3 (aromatic CH), 124.6 (CH=CH), 120.1 (aromatic CH), 118.5 (Cq), 118.1 (CH=CH), 118.0 (Cq), 66.7 (CO₂CH₂Ph), 20.9 (SCH₃), 14.9 (Furan-CH₃). HRMS Calcd for C₂₃H₂₁NO₄S [M+H]⁺: 408.1270, found: 408.1267.

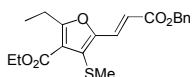


(E)-Benzyl 3-(4-cyano-5-methyl-3-(methylthio)furan-2-yl)acrylate (3k): 32

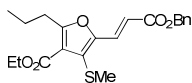
mg, 34% yield; white solid; m.p. 82-84 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, J = 15.9 Hz, 1 H, $\text{CH}=\text{CH}$), 7.36 (m, 5 H, aromatic CH), 6.44 (d, J = 15.9 Hz, 1 H, $\text{CH}=\text{CH}$), 5.25 (s, 2 H, $\text{CO}_2\text{CH}_2\text{Ph}$), 2.52 (s, 3 H, Furan- CH_3), 2.46 (s, 3 H, SCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.3 ($\text{CO}_2\text{CH}_2\text{Ph}$), 163.6, 150.4, and 136.0 (Cq), 128.7, 128.5, and 128.4 (aromatic CH), 127.7 ($\text{CH}=\text{CH}$), 123.7 (Cq), 118.3 ($\text{CH}=\text{CH}$), 112.6 and 101.1 (Cq), 66.7 ($\text{CO}_2\text{CH}_2\text{Ph}$), 18.5 (SCH_3), 13.9 (Furan- CH_3). HRMS Calcd for $\text{C}_{17}\text{H}_{15}\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 314.0851, found: 314.0851.



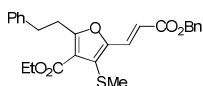
(E)-Benzyl 3-(5-methyl-3-(methylthio)-4-phenylfuran-2-yl)acrylate (3l): 84 mg, 77% yield; colourless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, J = 15.7 Hz, 1 H, $\text{CH}=\text{CH}$), 7.40 (m, 10 H, aromatic CH), 6.44 (d, J = 15.8 Hz, 1 H, $\text{CH}=\text{CH}$), 5.27 (s, 2 H, $\text{CO}_2\text{CH}_2\text{Ph}$), 2.35 (s, 3 H, SCH_3), 1.95 (s, 3 H, Furan- CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 167.2 ($\text{CO}_2\text{CH}_2\text{Ph}$), 152.1 (s), 149.8 (s), 136.4 (s), and 131.9 (Cq), 129.4, 129.3, 128.7, 128.6, 128.3, and 128.2 (aromatic CH), 127.6 ($\text{CH}=\text{CH}$), 126.0 and 124.4 (Cq), 115.0 ($\text{CH}=\text{CH}$), 66.3 ($\text{CO}_2\text{CH}_2\text{Ph}$), 18.9 (SCH_3), 13.0 (Furan- CH_3). HRMS Calcd for $\text{C}_{22}\text{H}_{20}\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 365.1211, found: 365.1209.



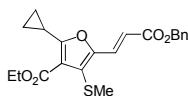
(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-2-ethyl-4-(methylthio)furan-3-carboxylate (3m): 82 mg, 73% yield; white solid; m.p. 61-63 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, J = 15.8 Hz, 1 H, $\text{CH}=\text{CH}$), 7.37 (m, 5 H, aromatic CH), 6.43 (d, J = 15.8 Hz, 1 H, $\text{CH}=\text{CH}$), 5.25 (s, 2 H, $\text{CO}_2\text{CH}_2\text{Ph}$), 4.35 (q, J = 7.1 Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 3.01 (q, J = 7.5 Hz, 2 H, CH_2CH_3), 2.39 (s, 3 H, SCH_3), 1.38 (t, J = 7.1 Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.27 (t, J = 7.5 Hz, 3 H, CH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.8 and 166.7 ($\text{CO}_2\text{CH}_2\text{Ph}$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 162.9, 150.6, and 136.2 (Cq), 129.0 ($\text{CH}=\text{CH}$), 128.7, 128.4, and 128.3 (aromatic CH), 123.6 (Cq), 116.8 ($\text{CH}=\text{CH}$), 116.5 (Cq), 66.5 ($\text{CO}_2\text{CH}_2\text{Ph}$), 60.7 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 22.3 (CH_2CH_3), 19.7 (SCH_3), 14.3 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 12.0 (CH_2CH_3). HRMS Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_5\text{S}$ $[\text{M}+\text{H}]^+$: 375.1266, found: 375.1268.



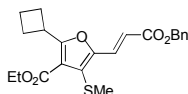
(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-4-(methylthio)-2-propylfuran-3-carboxylate (3n): 86 mg, 74% yield; white solid; m.p. 55-57 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 7.35 (m, 5 H, aromatic CH), 6.42 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 5.24 (s, 2 H, $\text{CO}_2\text{CH}_2\text{Ph}$), 4.34 (q, $J = 7.1$ Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.96 (t, $J = 7.5$ Hz, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 2.39 (s, 3 H, SCH_3), 1.72 (m, 2 H, $\text{CH}_2\text{CH}_2\text{CH}_3$), 1.38 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 0.97 (t, $J = 7.4$ Hz, 3 H, $\text{CH}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.7 and 165.7 ($\text{CO}_2\text{CH}_2\text{Ph}$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 162.8, 150.6, and 136.1 (Cq), 128.9 ($\text{CH}=\text{CH}$), 128.6, 128.23, and 128.2 (aromatic CH), 123.5 and 117.0 (Cq), 116.7 ($\text{CH}=\text{CH}$), 66.4 ($\text{CO}_2\text{CH}_2\text{Ph}$), 60.6 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 30.5 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 21.4 ($\text{CH}_2\text{CH}_2\text{CH}_3$), 19.6 (SCH_3), 14.2 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 13.8 ($\text{CH}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_5\text{S}$ $[\text{M}+\text{H}]^+$: 389.1423, found: 389.1426.



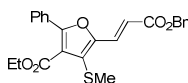
(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-4-(methylthio)-2-phenylethylfuran-3-carboxylate (3o): 101 mg, 75% yield; white solid; m.p. 64-66 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 7.31 (m, 5 H, aromatic CH), 7.22 (m, 2 H, aromatic CH), 7.13 (m, 3 H, aromatic CH), 6.35 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 5.20 (s, 2 H, $\text{CO}_2\text{CH}_2\text{Ph}$), 4.27 (q, $J = 7.1$ Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 3.24 (m, 2 H, PhCH_2CH_2), 2.93 (m, 2 H, PhCH_2CH_2), 2.32 (s, 3 H, SCH_3), 1.32 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.7 and 164.4 ($\text{CO}_2\text{CH}_2\text{Ph}$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 162.6, 150.8, 140.4, and 136.1 (Cq), 128.9 ($\text{CH}=\text{CH}$), 128.7, 128.6, 128.4, 128.3, and 126.5 (aromatic CH), 123.5 and 117.4 (Cq), 117.0 ($\text{CH}=\text{CH}$), 66.5 ($\text{CO}_2\text{CH}_2\text{Ph}$), 60.7 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 34.2 (PhCH_2CH_2), 30.7 (PhCH_2CH_2), 19.7 (SCH_3), 14.4 ($\text{CO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{26}\text{H}_{26}\text{O}_5\text{S}$ $[\text{M}+\text{H}]^+$: 451.1579, found: 451.1575.



(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-2-cyclopropyl-4-(methylthio)furan-3-carboxylate (3p): 96 mg, 83% yield; white solid; m.p. 103-105 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 15.8 Hz, 1 H, CH=CH), 7.35 (m, 5 H, aromatic CH), 6.27 (d, *J* = 15.8 Hz, 1 H, CH=CH), 5.23 (s, 2 H, CO₂CH₂Ph), 4.37 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂CH₃), 2.80 (m, 1 H, CH₂CHCH₂), 2.38 (s, 3 H, SCH₃), 1.39 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃), 1.11 (m, 4 H, CH₂CHCH₂). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.7 and 166.1 (CO₂CH₂Ph and CO₂CH₂CH₃), 163.2, 149.2, and 136.1 (Cq), 128.8 (CH=CH), 128.6, 128.3, and 128.3 (aromatic CH), 124.0 and 116.8 (Cq), 116.0 (CH=CH), 66.4 (CO₂CH₂Ph), 60.6 (CO₂CH₂CH₃), 19.7 (SCH₃), 14.3 (CH₂CHCH₂), 10.0 and 9.8 (CH₂CHCH₂). HRMS Calcd for C₂₁H₂₂O₅S [M+H]⁺: 387.1266, found: 387.1265.

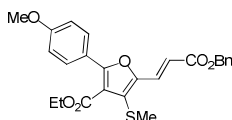


(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-2-cyclobutyl-4-(methylthio)furan-3-carboxylate (3q): 96 mg, 80% yield; white solid; m.p. 74-76 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 15.8 Hz, 1 H, CH=CH), 7.37 (m, 5 H, aromatic CH), 6.49 (d, *J* = 15.8 Hz, 1 H, CH=CH), 5.26 (s, 2 H, CO₂CH₂Ph), 4.34 (q, *J* = 7.0 Hz, 2 H, CO₂CH₂CH₃), 4.18 (p, *J* = 8.7 Hz, 1 H, CH₂CHCH₂), 2.35 (m, 7 H, SCH₃ and CH₂CHCH₂), 2.04 and 1.93 (m each, 1:1 H, CH₂CH₂CH₂), 1.38 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.8 and 166.6 (CO₂CH₂Ph and CO₂CH₂CH₃), 162.9, 150.5, and 136.1 (Cq), 129.1 (CH=CH), 128.7, 128.4, and 128.4 (aromatic CH), 123.8 (Cq), 116.7 (CH=CH), 115.9 (Cq), 66.5 (CO₂CH₂Ph), 60.7 (CO₂CH₂CH₃), 33.5 (CH₂CHCH₂), 27.5 (CH₂CHCH₂), 19.7 (SCH₃), 18.4 (CH₂CH₂CH₂), 14.3 (CO₂CH₂CH₃). HRMS Calcd for C₂₂H₂₄O₅S [M+H]⁺: 401.1423, found: 401.1416.



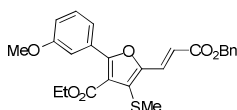
(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-4-(methylthio)-2-phenylfuran-3-carboxylate (3s): 106 mg, 84% yield; white solid; m.p. 68-70 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, *J* = 15.8 Hz, 1 H, CH=CH), 7.76 (m, 2 H, aromatic CH),

7.47 (m, 8 H, aromatic CH), 6.57 (d, $J = 15.8$ Hz, 1 H, CH=CH), 5.28 (s, 2 H, CO₂CH₂Ph), 4.37 (q, $J = 7.1$ Hz, 2 H, CO₂CH₂CH₃), 2.45 (s, 3 H, SCH₃), 1.32 (t, $J = 7.1$ Hz, 3 H, CO₂CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.6 and 163.3 (CO₂CH₂Ph and CO₂CH₂CH₃), 157.5, 151.5, and 136.1 (Cq), 130.1 (aromatic CH), 129.0 (Cq), 128.7 (CH=CH), 128.7, 128.4, 128.4, and 128.1 (aromatic CH), 124.5 and 118.8 (Cq), 117.8 (CH=CH), 66.6 (CO₂CH₂Ph), 61.4 (CO₂CH₂CH₃), 20.1 (SCH₃), 14.1 (CO₂CH₂CH₃). HRMS Calcd for C₂₄H₂₂O₅S [M+H]⁺: 423.1266, found: 423.1263.



(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-2-(4-methoxyphenyl)-4-

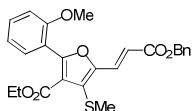
(methylthio)furan-3-carboxylate (3t): 96 mg, 71% yield; pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, $J = 15.8$ Hz, 1 H, CH=CH), 7.74 (d, $J = 8.8$ Hz, 2 H, aromatic CH), 7.37 (m, 5 H, aromatic CH), 6.95 (d, $J = 8.8$ Hz, 2 H, aromatic CH), 6.53 (d, $J = 15.8$ Hz, 1 H, CH=CH), 5.27 (s, 2 H, CO₂CH₂Ph), 4.36 (q, $J = 7.1$ Hz, 2 H, CO₂CH₂CH₃), 3.85 (s, 3 H, OCH₃), 2.42 (d, $J = 10.2$ Hz, 3 H, SCH₃), 1.34 (t, $J = 7.1$ Hz, 3 H, CO₂CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.7 and 163.4 (CO₂CH₂Ph and CO₂CH₂CH₃), 161.1, 158.0, 151.0, and 136.1 (Cq), 129.9 (aromatic CH), 128.8 (CH=CH), 128.7, 128.3, and 128.3 (aromatic CH), 124.7, 121.5, and 117.4 (Cq), 117.2 (CH=CH), 113.8 (aromatic CH), 66.5 (CO₂CH₂Ph), 61.2 (CO₂CH₂CH₃), 55.4 (OCH₃), 20.1 (SCH₃), 14.1 (CO₂CH₂CH₃). HRMS Calcd for C₂₅H₂₄O₆S [M+H]⁺: 453.1372, found: 453.1372.



(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-2-(3-methoxyphenyl)-4-

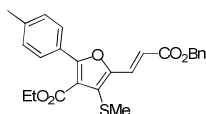
(methylthio)furan-3-carboxylate (3u): 102 mg, 75% yield; colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, $J = 15.8$ Hz, 1 H, CH=CH), 7.37 (m, 8 H, aromatic CH), 6.98 (m, 1 H, aromatic CH), 6.57 (d, $J = 15.8$ Hz, 1 H, CH=CH), 5.27 (s, 2 H, CO₂CH₂Ph), 4.37 (q, $J = 7.1$ Hz, 2 H, CO₂CH₂CH₃), 3.85 (s, 3 H, OCH₃), 2.44 (s, 3 H, SCH₃), 1.33 (t, $J = 7.1$ Hz, 3 H, CO₂CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ

166.6 and 163.4 (CO₂CH₂Ph and CO₂CH₂CH₃), 159.5, 156.9, 151.4, 136.0, and 130.1 (Cq), 129.5 (CH=CH), 128.7, 128.4, and 128.3 (aromatic CH), 124.5 (Cq), 120.5 (aromatic CH), 119.1 (Cq), 117.8 (CH=CH), 115.9 and 113.4 (aromatic CH), 66.6 (CO₂CH₂Ph), 61.4 (CO₂CH₂CH₃), 55.4 (OCH₃), 20.1 (SCH₃), 14.1 (CO₂CH₂CH₃). HRMS Calcd for C₂₅H₂₄O₆S [M+H]⁺: 453.1372, found: 453.1367.



(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-2-(2-methoxyphenyl)-4-

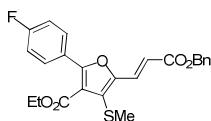
(methylthio)furan-3-carboxylate (3v): 95 mg, 70% yield; pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 15.8 Hz, 1 H, CH=CH), 7.54 (d, *J* = 7.6 Hz, 1 H, aromatic CH), 7.36 (m, 6 H, aromatic CH), 7.05 (t, *J* = 7.5 Hz, 1 H, aromatic CH), 6.95 (d, *J* = 8.3 Hz, 1 H, aromatic CH), 6.53 (d, *J* = 15.8 Hz, 1 H, CH=CH), 5.26 (s, 2 H, CO₂CH₂Ph), 4.24 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂CH₃), 3.79 (s, 3 H, OCH₃), 2.47 (s, 3 H, SCH₃), 1.17 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 166.6 and 163.4 (CO₂CH₂Ph and CO₂CH₂CH₃), 156.8, 154.5, 151.3, and 136.1 (Cq), 131.5 and 129.9 (aromatic CH), 128.8 (CH=CH), 128.6, 128.3, and 128.3 (aromatic CH), 123.9 and 121.1 (Cq), 120.6 (aromatic CH), 118.7 (Cq), 117.2 (CH=CH), 110.9 (aromatic CH), 66.4 (CO₂CH₂Ph), 60.7 (CO₂CH₂CH₃), 55.4 (OCH₃), 19.9 (SCH₃), 13.9 (CO₂CH₂CH₃). HRMS Calcd for C₂₅H₂₄O₆S [M+H]⁺: 453.1372, found: 453.1367.



(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-4-(methylthio)-2-(p-tolyl)

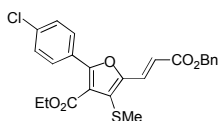
furan-3-carboxylate (3w): 100 mg, 76% yield; pale yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 15.8 Hz, 1 H, CH=CH), 7.63 (d, *J* = 8.2 Hz, 2 H, aromatic CH), 7.34 (m, 5 H, aromatic CH), 7.22 (d, *J* = 8.1 Hz, 2 H, aromatic CH), 6.53 (dd, *J* = 15.8, 7.9 Hz, 1 H, CH=CH), 5.24 (s, 2 H, CO₂CH₂Ph), 4.33 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂CH₃), 2.41 (s, 3 H, SCH₃), 2.37 (s, 3 H, CH₃), 1.30 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 166.6 and 163.4 (CO₂CH₂Ph and CO₂CH₂CH₃), 157.8, 151.2, 140.5, and 136.1 (Cq), 129.1 (aromatic CH), 128.8

(CH=CH), 128.7, 128.4, 128.3, and 128.1 (aromatic CH), 126.2, 124.6, and 118.2 (Cq), 117.5 (CH=CH), 66.5 (CO₂CH₂Ph), 61.3 (CO₂CH₂CH₃), 21.6 (CH₃), 20.1 (SCH₃), 14.1 (CO₂CH₂CH₃). HRMS Calcd for C₂₅H₂₄O₅S [M+H]⁺: 437.1423, found: 437.1422.



(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-2-(4-fluorophenyl)-4-

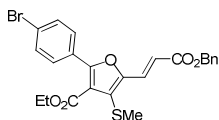
(methylthio)furan-3-carboxylate (3x): 101 mg, 77% yield; colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 15.8 Hz, 1 H, CH=CH), 7.78 (dd, *J* = 8.5, 5.4 Hz, 2 H, aromatic CH), 7.38 (m, 5 H, aromatic CH), 7.13 (t, *J* = 8.6 Hz, 2 H, aromatic CH), 6.55 (d, *J* = 15.8 Hz, 1 H, CH=CH), 5.27 (s, 2 H, CO₂CH₂Ph), 4.36 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂CH₃), 2.44 (s, 3 H, SCH₃), 1.33 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.5 (CO₂CH₂Ph), 163.7 (d, *J* = 251.5 Hz, CF), 163.1 (CO₂CH₂CH₃), 156.7, 151.5, and 136.0 (Cq), 130.4 (d, *J* = 8.6 Hz, aromatic CH), 128.7 (aromatic CH), 128.7 (CH=CH), 128.4 (aromatic CH), 125.27 (d, *J* = 3.4 Hz, Cq), 124.5 and 118.5 (Cq), 117.9 (CH=CH), 115.6 (d, *J* = 22.0 Hz, aromatic CH), 66.6 (CO₂CH₂Ph), 61.4 (CO₂CH₂CH₃), 20.1 (SCH₃), 14.1 (CO₂CH₂CH₃). HRMS Calcd for C₂₄H₂₁FO₅S [M+H]⁺: 441.1172, found: 441.1169.



(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-2-(4-chlorophenyl)-4-

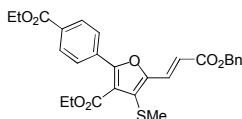
(methylthio)furan-3-carboxylate (3y): 108 mg, 79% yield; colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, *J* = 15.8 Hz, 1 H, CH=CH), 7.72 (m, 2 H, aromatic CH), 7.41 (m, 5 H, aromatic CH), 7.35 (m, 2 H, aromatic CH), 6.56 (d, *J* = 15.8 Hz, 1 H, CH=CH), 5.27 (s, 2 H, CO₂CH₂Ph), 4.37 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂CH₃), 2.43 (s, 3 H, SCH₃), 1.34 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.4 and 163.1 (CO₂CH₂Ph and CO₂CH₂CH₃), 156.2, 151.7, 136.2, and 136.0 (Cq), 129.4, 128.7, 128.7 (aromatic CH), 128.6 (CH=CH), 128.4 (aromatic CH), 127.4, 124.6, and 119.0 (Cq), 118.1 (CH=CH), 66.6 (CO₂CH₂Ph), 61.5 (CO₂CH₂CH₃), 20.1 (SCH₃), 14.1 (CO₂CH₂CH₃). HRMS Calcd for C₂₄H₂₁ClO₅S [M+H]⁺: 457.0876,

found: 457.0869.



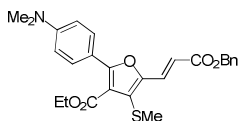
(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-2-(4-bromophenyl)-4-

(methylthio)furan-3-carboxylate (3z): 119 mg, 79% yield; pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 7.65 (m, 2 H, aromatic CH), 7.56 (m, 2 H, aromatic CH), 7.37 (m, 5 H, aromatic CH), 6.55 (d, $J = 15.9$ Hz, 1 H, $\text{CH}=\text{CH}$), 5.27 (s, 2 H, $\text{CO}_2\text{CH}_2\text{Ph}$), 4.37 (q, $J = 7.1$ Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.43 (s, 3 H, SCH_3), 1.34 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.5 and 163.1 ($\text{CO}_2\text{CH}_2\text{Ph}$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 156.3, 151.8, and 136.0 (Cq), 131.7, 129.6, and 128.7 (aromatic CH), 128.6 ($\text{CH}=\text{CH}$), 128.4 (aromatic CH), 127.9, 124.7, 124.6, and 119.1 (Cq), 118.2 ($\text{CH}=\text{CH}$), 66.7 ($\text{CO}_2\text{CH}_2\text{Ph}$), 61.5 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 20.1 (SCH_3), 14.1 ($\text{CO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{24}\text{H}_{21}\text{BrO}_5\text{S}$ $[\text{M}+\text{H}]^+$: 501.0371, found: 501.0372.

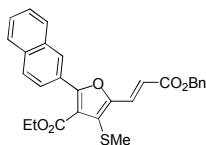


(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-2-(4-(ethoxycarbonyl)-

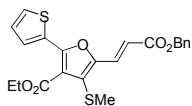
phenyl)-4-(methylthio)furan-3-carboxylate (3z1): 120 mg, 81% yield; yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 8.5$ Hz, 2 H, aromatic CH), 7.83 (m, 3 H, $\text{CH}=\text{CH}$ and aromatic CH), 7.37 (m, 5 H, aromatic CH), 6.59 (d, $J = 15.9$ Hz, 1 H, $\text{CH}=\text{CH}$), 5.26 (s, 2 H, $\text{CO}_2\text{CH}_2\text{Ph}$), 4.38 (m, 4 H, $2\times\text{CO}_2\text{CH}_2\text{CH}_3$), 2.43 (s, 3 H, SCH_3), 1.40 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.32 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.3, 165.9, and 163.0 ($\text{CO}_2\text{CH}_2\text{Ph}$ and $2\times\text{CO}_2\text{CH}_2\text{CH}_3$), 155.6, 152.1, 135.9, 132.7, and 131.4 (Cq), 129.5 and 128.6 (aromatic CH), 128.4 ($\text{CH}=\text{CH}$), 128.3 and 127.7 (aromatic CH), 124.6 and 120.2 (Cq), 118.4 ($\text{CH}=\text{CH}$), 66.6 ($\text{CO}_2\text{CH}_2\text{Ph}$), 61.6 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 61.3 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 20.1 (SCH_3), 14.3 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 14.0 ($\text{CO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{27}\text{H}_{26}\text{O}_7\text{S}$ $[\text{M}+\text{H}]^+$: 495.1477, found: 495.1469.



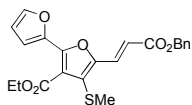
(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-2-(4-(dimethylamino)phenyl)-4-(methylthio)furan-3-carboxylate (3z2): 96 mg, 69% yield; yellow solid; m.p. 105-107 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 7.71 (d, $J = 9.0$ Hz, 2 H, aromatic CH), 7.37 (m, 5 H, aromatic CH), 6.70 (d, $J = 9.0$ Hz, 2 H, aromatic CH), 6.50 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 5.27 (s, 2 H, $\text{CO}_2\text{CH}_2\text{Ph}$), 4.37 (q, $J = 7.1$ Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 3.03 (s, 6 H, $\text{N}(\text{CH}_3)_2$), 2.43 (s, 3 H, SCH_3), 1.36 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.9 and 163.8 ($\text{CO}_2\text{CH}_2\text{Ph}$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 159.2, 151.4, 150.2, and 136.2 (Cq), 129.5, 129.0, 128.6, and 128.3 (aromatic CH), 128.3 ($\text{CH}=\text{CH}$), 125.0 (Cq), 116.3 ($\text{CH}=\text{CH}$), 115.9 (Cq), 111.3 (aromatic CH), 66.4 ($\text{CO}_2\text{CH}_2\text{Ph}$), 61.1 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 40.2 ($\text{N}(\text{CH}_3)_2$), 20.1 (SCH_3), 14.2 ($\text{CO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{26}\text{H}_{27}\text{NO}_5\text{S}$ $[\text{M}+\text{H}]^+$: 466.1688, found: 466.1686.



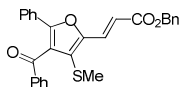
(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-4-(methylthio)-2-(naphthalen-2-yl)furan-3-carboxylate (3z3): 104 mg, 74% yield; pale yellow solid; m.p. 101-103 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.30 (s, 1 H, aromatic CH), 7.86 (m, 5 H, aromatic CH and $\text{CH}=\text{CH}$), 7.54 (m, 2 H, aromatic CH), 7.40 (m, 5 H, aromatic CH), 6.64 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 5.30 (s, 2 H, $\text{CO}_2\text{CH}_2\text{Ph}$), 4.41 (q, $J = 7.1$ Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.48 (s, 3 H, SCH_3), 1.34 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.6 and 163.4 ($\text{CO}_2\text{CH}_2\text{Ph}$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 157.3, 151.6, 136.0, 133.8, and 132.8 (Cq), 128.8, 128.7, 128.7, 128.4, 128.3, 128.2, 128.0, and 127.8 (aromatic CH), 127.4 ($\text{CH}=\text{CH}$), 126.8 (aromatic CH), 126.2 (Cq), 124.9 (aromatic CH), 124.7 and 119.1 (Cq), 117.8 ($\text{CH}=\text{CH}$), 66.6 ($\text{CO}_2\text{CH}_2\text{Ph}$), 61.4 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 20.1 (SCH_3), 14.1 ($\text{CO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{28}\text{H}_{24}\text{O}_5\text{S}$ $[\text{M}+\text{H}]^+$: 473.1423, found: 473.1420.



(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-4-(methylthio)-2-(thiophen-2-yl)furan-3-carboxylate (3z4): 97 mg, 76% yield; pale yellow solid; m.p. 79-81 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.91 (dd, $J = 3.8, 1.1$ Hz, 1 H, aromatic CH), 7.83 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 7.49 (dd, $J = 5.1, 1.1$ Hz, 1 H, aromatic CH), 7.38 (m, 5 H, aromatic CH), 7.12 (dd, $J = 5.0, 3.9$ Hz, 1 H, aromatic CH), 6.55 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 5.27 (s, 2 H, $\text{CO}_2\text{CH}_2\text{Ph}$), 4.44 (q, $J = 7.1$ Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.41 (s, 3 H, SCH_3), 1.43 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.6 and 162.8 ($\text{CO}_2\text{CH}_2\text{Ph}$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 153.7, 150.8, 136.1, and 130.7 (Cq), 130.0, 129.5, and 128.7 (aromatic CH), 128.5 ($\text{CH}=\text{CH}$), 128.4, 128.4, and 127.6 (aromatic CH), 124.7 (Cq), 117.8 ($\text{CH}=\text{CH}$), 116.5 (Cq), 66.6 ($\text{CO}_2\text{CH}_2\text{Ph}$), 61.4 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 20.1 (SCH_3), 14.3 ($\text{CO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{22}\text{H}_{20}\text{O}_5\text{S}_2$ $[\text{M}+\text{H}]^+$: 429.0830, found: 429.0827.

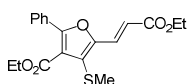


(E)-Ethyl -(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-4-(methylthio)-[2,2'-bifuran]-3-carboxylate (3z5): 92 mg, 74% yield; white solid; m.p. 85-86 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 7.56 (s, 1 H, aromatic CH), 7.36 (m, 6 H, aromatic CH), 6.59 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 6.54 (dd, $J = 3.1, 1.4$ Hz, 1 H, aromatic CH), 5.26 (s, 2 H, $\text{CO}_2\text{CH}_2\text{Ph}$), 4.42 (q, $J = 7.1$ Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.41 (s, 3 H, SCH_3), 1.41 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.6 and 162.5 ($\text{CO}_2\text{CH}_2\text{Ph}$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 151.2 and 149.4 (Cq), 144.4 (aromatic CH), 143.8 and 136.1 (Cq), 128.7 (aromatic CH), 128.5 ($\text{CH}=\text{CH}$), 128.3 (aromatic CH), 124.3 (Cq), 118.0 ($\text{CH}=\text{CH}$), 116.9 (Cq), 114.4 and 112.2 (aromatic CH), 66.6 ($\text{CO}_2\text{CH}_2\text{Ph}$), 61.3 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 20.1 (SCH_3), 14.3 ($\text{CO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{22}\text{H}_{20}\text{O}_6\text{S}$ $[\text{M}+\text{H}]^+$: 413.1059, found: 413.1056.



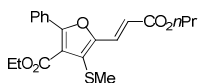
(E)-Benzyl 3-(4-benzoyl-3-(methylthio)-5-phenylfuran-2-yl)acrylate (3z6):

105 mg, 77% yield; white solid; m.p. 89-91 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 7.9$ Hz, 2 H, aromatic CH), 7.76 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 7.48 (m, 3 H, aromatic CH), 7.32 (m, 7 H, aromatic CH), 7.20 (m, 3 H, aromatic CH), 6.59 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 5.22 (s, 2 H, $\text{CO}_2\text{CH}_2\text{Ph}$), 2.19 (s, 3 H, SCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 192.4 (PhCO), 166.6 ($\text{CO}_2\text{CH}_2\text{Ph}$), 153.6, 151.2, 136.9, and 136.1 (Cq), 134.1 and 130.0 (aromatic CH), 129.6 ($\text{CH}=\text{CH}$), 128.8, 128.7, 128.5, 128.5, 128.4, and 126.6 (aromatic CH), 125.7 and 124.9 (Cq), 117.7 ($\text{CH}=\text{CH}$), 66.6 ($\text{CO}_2\text{CH}_2\text{Ph}$), 20.3 (SCH_3). HRMS Calcd for $\text{C}_{28}\text{H}_{22}\text{O}_4\text{S}$ $[\text{M}+\text{H}]^+$: 455.1317, found: 455.1315.



(E)-Ethyl 5-(3-ethoxy-3-oxoprop-1-en-1-yl)-4-(methylthio)-2-phenylfuran

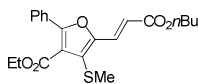
-3-carboxylate (4a): 79 mg, 73% yield; white solid; m.p. 76-78 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.76 (m, 3 H, aromatic CH and $\text{CH}=\text{CH}$), 7.43 (m, 3 H, aromatic CH), 6.50 (d, $J = 15.9$ Hz, 1 H, $\text{CH}=\text{CH}$), 4.35 and 4.27 (q each, $J = 7.1$ Hz, 2:2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CH}=\text{CHCO}_2\text{CH}_2\text{CH}_3$), 2.43 (s, 3 H, SCH_3), 1.33 and 1.31 (t each, $J = 7.1$ Hz, 3:3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CH}=\text{CHCO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.8 ($\text{CH}=\text{CHCO}_2$), 163.4 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 157.3 and 151.6 (Cq), 130.1 (aromatic CH), 129.1 (Cq), 128.4 (aromatic CH), 128.2 ($\text{CH}=\text{CH}$), 128.2 (aromatic CH), 124.2 and 118.8 (Cq), 118.3 ($\text{CH}=\text{CH}$), 61.4 and 60.8 ($\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CH}=\text{CHCO}_2\text{CH}_2\text{CH}_3$), 20.1 (SCH_3), 14.4 and 14.1 ($\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CH}=\text{CHCO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{19}\text{H}_{20}\text{O}_5\text{S}$ $[\text{M}+\text{H}]^+$: 361.1110, found: 361.1112.



(E)-Ethyl 4-(methylthio)-5-(3-oxo-3-propoxyprop-1-en-1-yl)-2-phenylfuran

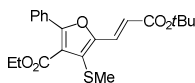
-3-carboxylate (4b): 85 mg, 76% yield; white solid; m.p. 52-54 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.76 (m, 3 H, aromatic CH and $\text{CH}=\text{CH}$), 7.43 (m, 3 H, aromatic CH), 6.51 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 4.35 (q, $J = 7.1$ Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 4.17 (t, $J = 6.7$ Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_2$), 2.44 (s, 3 H, SCH_3), 1.73 (m, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_2$), 1.31 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 0.99 (t, $J = 7.4$ Hz, 3 H, $\text{CH}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR

(100 MHz, CDCl₃) δ 166.9 (CO₂CH₂CH₂), 163.4 (CO₂CH₂CH₃), 157.4 and 151.7 (Cq), 130.1 (aromatic CH), 129.1 (Cq), 128.4 (aromatic CH), 128.2 (CH=CH), 128.2 (aromatic CH), 124.2 and 118.8 (Cq), 118.3 (CH=CH), 66.4 (CO₂CH₂CH₂), 61.4 (CO₂CH₂CH₃), 22.2 (CO₂CH₂CH₂), 20.1 (SCH₃), 14.1 (CO₂CH₂CH₃), 10.5 (CH₂CH₂CH₃). HRMS Calcd for C₂₀H₂₂O₅S [M+H]⁺: 375.1266, found: 375.1262.



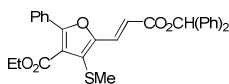
(E)-Ethyl 5-(3-butoxy-3-oxoprop-1-en-1-yl)-4-(methylthio)-2-phenylfuran

-3-carboxylate (4c): 88 mg, 76% yield; colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.76 (m, 3 H, aromatic CH and CH=CH), 7.42 (m, 3 H, aromatic CH), 6.50 (d, *J* = 15.8 Hz, 1 H, CH=CH), 4.35 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂CH₃), 4.21 (t, *J* = 6.7 Hz, 2 H, CO₂CH₂CH₂), 2.43 (s, 3 H, SCH₃), 1.69 (m, 2 H, CH₂CH₂CH₂CH₃), 1.43 (m, 2 H, CH₂CH₂CH₂CH₃), 1.30 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃), 0.96 (t, *J* = 7.4 Hz, 3 H, CH₂CH₂CH₂CH₃). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 166.8 (CO₂CH₂CH₂), 163.4 (CO₂CH₂CH₃), 157.3 and 151.6 (Cq), 130.1 (aromatic CH), 129.0 (Cq), 128.4 (aromatic CH), 128.2 (CH=CH), 128.1 (aromatic CH), 124.1 and 118.7 (Cq), 118.3 (CH=CH), 64.7 (CO₂CH₂CH₂), 61.3 (CO₂CH₂CH₃), 30.8 (CO₂CH₂CH₂), 20.1 (SCH₃), 19.3 (CH₂CH₂CH₂CH₃), 14.0 (CO₂CH₂CH₃), 13.8 (CH₂CH₂CH₂CH₃). HRMS Calcd for C₂₁H₂₄O₅S [M+H]⁺: 389.1423, found: 389.1422.

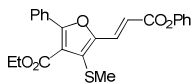


(E)-Ethyl-(3-(tert-butoxy)-3-oxoprop-1-en-1-yl)-4-(methylthio)-2-phenylfuran-3-carboxylate (4d):

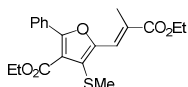
84 mg, 72% yield; colourless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.74 (m, 3 H, aromatic CH and CH=CH), 7.42 (m, 3 H, aromatic CH), 6.44 (d, *J* = 15.8 Hz, 1 H, CH=CH), 4.34 (q, *J* = 7.1 Hz, 2 H, CO₂CH₂CH₃), 2.42 (s, 3 H, SCH₃), 1.53 (s, 9 H, C(CH₃)₃), 1.30 (t, *J* = 7.1 Hz, 3 H, CO₂CH₂CH₃). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 166.0 (CO₂C), 163.4 (CO₂CH₂CH₃), 157.1 and 151.8 (Cq), 130.0 (aromatic CH), 129.1 (Cq), 128.3 and 128.1 (aromatic CH), 127.4 (CH=CH), 123.6 (Cq), 120.2 (CH=CH), 118.6 (Cq), 80.8 (C(CH₃)₃), 61.3 (CO₂CH₂CH₃), 28.2 (C(CH₃)₃), 20.1 (SCH₃), 14.0 (CO₂CH₂CH₃). HRMS Calcd for C₂₁H₂₄O₅S [M+H]⁺: 389.1423, found: 389.1419.



(E)-Ethyl 5-(3-(benzhydryloxy)-3-oxoprop-1-en-1-yl)-4-(methylthio)-2-phenylfuran-3-carboxylate (4e): 104 mg, 70% yield; pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 7.80 (dd, $J = 6.7, 2.9$ Hz, 2 H, aromatic CH), 7.39 (m, 13 H, aromatic CH), 7.07 (s, 1 H, CO_2CH), 6.69 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 4.39 (q, $J = 7.1$ Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.47 (s, 3 H, SCH_3), 1.34 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 165.8 (CO_2CH), 163.3 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 157.5 and 151.5 (Cq), 140.3 and 130.2 (aromatic CH), 129.0 ($\text{CH}=\text{CH}$), 129.0 (Cq), 128.6, 128.4, 128.2, 128.0, and 127.2 (aromatic CH), 124.7 and 118.8 (Cq), 117.8 ($\text{CH}=\text{CH}$), 77.3 (CO_2CH), 61.4 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 20.1 (SCH_3), 14.0 ($\text{CO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{30}\text{H}_{26}\text{O}_5\text{S}$ $[\text{M}+\text{H}]^+$: 499.1579, found: 499.1582.

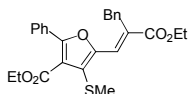


(E)-Ethyl 4-(methylthio)-5-(3-oxo-3-phenoxyprop-1-en-1-yl)-2-phenylfuran-3-carboxylate (4f): 61 mg, 50% yield; pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 7.78 (m, 2 H, aromatic CH), 7.43 (m, 5 H, aromatic CH), 7.24 (dd, $J = 7.9, 6.9$ Hz, 1 H, aromatic CH), 7.18 (m, 2 H, aromatic CH), 6.68 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 4.36 (q, $J = 7.1$ Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.46 (s, 3 H, SCH_3), 1.32 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 165.2 (CO_2Ph), 163.3 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 157.9, 151.4, and 150.9 (Cq), 130.3, 129.8, and 129.5 (aromatic CH), 129.0 (Cq), 128.5 and 128.2 (aromatic CH), 125.9 ($\text{CH}=\text{CH}$), 125.4 (Cq), 121.7 (aromatic CH), 118.9 (Cq), 117.2 ($\text{CH}=\text{CH}$), 61.5 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 20.2 (SCH_3), 14.1 ($\text{CO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{23}\text{H}_{20}\text{O}_5\text{S}$ $[\text{M}+\text{H}]^+$: 409.1110, found: 409.1109.

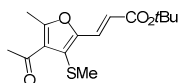


(E)-Ethyl 5-(3-ethoxy-2-methyl-3-oxoprop-1-en-1-yl)-4-(methylthio)-2-phenylfuran-3-carboxylate (4g): 56 mg, 50% yield; white solid; m.p. 55-57 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.75 (m, 3 H, aromatic CH and $\text{CH}=\text{C}$), 7.43 (m, 3 H,

aromatic CH), 4.37 (q, $J = 7.1$ Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 4.29 (q, $J = 7.1$ Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.43 (s, 3 H, SCH_3), 2.36 (d, $J = 1.0$ Hz, 3 H, $\text{CH}=\text{CCH}_3$), 1.34 (dt, $J = 14.4, 7.1$ Hz, 6 H, $\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 168.6 and 163.8 ($\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 156.5 and 153.1 (Cq), 129.8 (aromatic CH), 129.3 (Cq), 128.5 (aromatic CH), 127.9 (Cq), 127.8 (aromatic CH), 123.8 (Cq), 122.0 ($\text{CH}=\text{C}$), 118.4 (Cq), 61.4 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 61.2 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 20.3 (SCH_3), 14.5 ($\text{CH}=\text{CCH}_3$), 14.4 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 14.1 ($\text{CO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_5\text{S} [\text{M}+\text{H}]^+$: 375.1266, found: 375.1265.

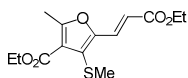


(E)-Ethyl 5-(2-benzyl-3-ethoxy-3-oxoprop-1-en-1-yl)-4-(methylthio)-2-phenylfuran-3-carboxylate (4h): 60 mg, 44% yield; colourless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.99 (s, 1 H, $\text{CH}=\text{C}$), 7.57 (d, $J = 6.6$ Hz, 2 H, aromatic CH), 7.35 (m, 7 H, aromatic CH), 7.21 (d, $J = 6.0$ Hz, 1 H, aromatic CH), 4.41 (q, $J = 7.1$ Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 4.28 (m, 4 H, PhCH_2 and $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.49 (s, 3 H, SCH_3), 1.34 (dd, $J = 16.1, 7.2$ Hz, 6 H, $\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 168.1 and 163.7 ($\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 156.9, 152.4, 139.9, and 130.1 (Cq), 130.0 (aromatic CH), 129.0 (Cq), 128.4, 127.9, and 126.1 (aromatic CH), 125.0 (Cq), 123.0 ($\text{CH}=\text{C}$), 118.6 (Cq), 61.5 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 61.3 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 33.7 (PhCH_2), 20.3 (SCH_3), 14.4 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 14.1 ($\text{CO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{26}\text{H}_{26}\text{O}_5\text{S} [\text{M}+\text{H}]^+$: 451.1579, found: 451.1578.



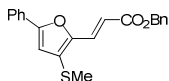
(E)-tert-Butyl 3-(4-acetyl-5-methyl-3-(methylthio)furan-2-yl)acrylate (4i): 62 mg, 70% yield; colourless oil. ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 6.32 (d, $J = 15.8$ Hz, 1 H, $\text{CH}=\text{CH}$), 2.64 (s, 3 H, CH_3CO), 2.54 (s, 3 H, Furan- CH_3), 2.29 (s, 3 H, SCH_3), 1.50 (s, 9 H, $\text{C}(\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 194.8 (CH_3CO), 166.1 (CO_2C), 160.7 and 151.5 (Cq), 127.4 ($\text{CH}=\text{CH}$), 125.3 and 121.1 (Cq), 119.9 ($\text{CH}=\text{CH}$), 80.8 ($\text{C}(\text{CH}_3)_3$), 30.4 (CH_3CO), 28.3 ($\text{C}(\text{CH}_3)_3$), 21.0 (SCH_3), 15.1 (Furan- CH_3). HRMS Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_4\text{S} [\text{M}+\text{H}]^+$:

297.1161, found: 297.1159.

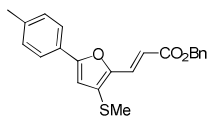


(E)-Ethyl 5-(3-ethoxy-3-oxoprop-1-en-1-yl)-2-methyl-4-(methylthio)furan

-3-carboxylate (4j): 60 mg, 67% yield; pale yellow solid; m.p. 54-56 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, J = 15.9 Hz, 1 H, $\text{CH}=\text{CH}$), 6.33 (d, J = 15.9 Hz, 1 H, $\text{CH}=\text{CH}$), 4.32 (q, J = 7.1 Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 4.22 (q, J = 7.1 Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.57 (s, 3 H, Furan- CH_3), 2.36 (s, 3 H, SCH_3), 1.36 (t, J = 7.1 Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 1.29 (t, J = 7.1 Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.8 and 162.9 ($\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 161.9 and 150.7 (Cq), 128.3 ($\text{CH}=\text{CH}$), 123.1 and 117.3 (Cq), 117.2 ($\text{CH}=\text{CH}$), 60.7 and 60.6 ($\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 19.7 (SCH_3), 14.9 (Furan- CH_3), 14.4 and 14.3 ($\text{CO}_2\text{CH}_2\text{CH}_3$ and $\text{CO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_5\text{S}$ $[\text{M}+\text{H}]^+$: 299.0953, found: 299.0951.

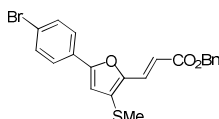


(E)-Benzyl 3-(3-(methylthio)-5-phenylfuran-2-yl)acrylate (6a): 61 mg, 58% yield; pale yellow solid; m.p. 73-75 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.69 (m, 3 H, aromatic CH and $\text{CH}=\text{CH}$), 7.39 (m, 8 H, aromatic CH), 6.76 (s, 1 H, aromatic CH), 6.46 (d, J = 15.7 Hz, 1 H, $\text{CH}=\text{CH}$), 5.28 (s, 2 H, $\text{CO}_2\text{CH}_2\text{Ph}$), 2.46 (s, 3 H, SCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 167.1 ($\text{CO}_2\text{CH}_2\text{Ph}$), 155.8, 147.9, 136.3, and 129.3 (Cq), 129.0 (aromatic CH), 128.9 ($\text{CH}=\text{CH}$), 128.7, 128.3, and 128.3 (aromatic CH), 127.5 (Cq), 124.5 (aromatic CH), 114.6 ($\text{CH}=\text{CH}$), 109.3 (aromatic CH), 66.4 ($\text{CO}_2\text{CH}_2\text{Ph}$), 18.1 (SCH_3). HRMS Calcd for $\text{C}_{21}\text{H}_{18}\text{O}_3\text{S}$ $[\text{M}+\text{H}]^+$: 351.1055, found: 351.1056.



(E)-Benzyl 3-(3-(methylthio)-5-(p-tolyl)furan-2-yl)acrylate (6b): 60 mg, 55% yield; pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, J = 15.6 Hz, 1 H, $\text{CH}=\text{CH}$), 7.59 (d, J = 8.2 Hz, 2 H, aromatic CH), 7.39 (m, 5 H, aromatic CH), 7.22 (d, J = 8.0 Hz, 2 H, aromatic CH), 6.70 (s, 1 H, aromatic CH), 6.44 (d, J = 15.6 Hz, 1 H, $\text{CH}=\text{CH}$), 5.28 (s, 2 H, $\text{CO}_2\text{CH}_2\text{Ph}$), 2.45 (s, 3 H, SCH_3), 2.38 (s, 3 H, CH_3). $^{13}\text{C}\{^1\text{H}\}$

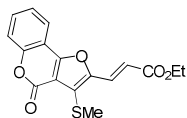
NMR (100 MHz, CDCl₃) δ 167.1 (CO₂CH₂Ph), 156.1, 147.5, 139.1, and 136.3 (Cq), 129.6 (aromatic CH), 128.9 (CH=CH), 128.6, 128.3, and 128.2 (aromatic CH), 127.7 and 126.6 (Cq), 124.4 (aromatic CH), 114.1 (CH=CH), 108.5 (aromatic CH), 66.3 (CO₂CH₂Ph), 21.5 (CH₃), 18.0 (SCH₃). HRMS Calcd for C₂₂H₂₀O₃S [M+H]⁺: 365.1211, found: 365.1217.



(E)-Benzyl 3-(5-(4-bromophenyl)-3-(methylthio)furan-2-yl)acrylate (6c): 64 mg, 50% yield; yellow solid; m.p. 64-66 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 15.7 Hz, 1 H, CH=CH), 7.53 (s, 4 H, aromatic CH), 7.38 (m, 5 H, aromatic CH), 6.75 (s, 1 H, aromatic CH), 6.44 (d, *J* = 15.7 Hz, 1 H, CH=CH), 5.26 (s, 2 H, CO₂CH₂Ph), 2.44 (s, 3 H, SCH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 167.0 (CO₂CH₂Ph), 154.6, 148.1, and 136.3 (Cq), 132.2 (aromatic CH), 128.7 (CH=CH), 128.7, 128.5, and 128.4 (aromatic CH), 128.2 and 127.6 (Cq), 125.9 (aromatic CH), 123.0 (Cq), 115.0 (CH=CH), 109.7 (aromatic CH), 66.4 (CO₂CH₂Ph), 18.1 (SCH₃). HRMS Calcd for C₂₁H₁₇BrO₃S [M+H]⁺: 429.0160, found: 429.0160.

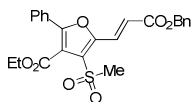


3-((Methylthio)methylene)pentane-2,4-dione (7a): 105 mg, 33% yield; white solid; m.p. 40-42 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.13 (s, 1 H, C=CH), 2.45 (s, 3 H, CH₃CO), 2.41 (s, 3 H, CH₃CO), 2.35 (s, 3 H, SCH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 197.5 (CH₃CO), 194.5 (CH₃CO), 164.4 (C=CH), 134.0 (C=CH), 30.9 (CH₃CO), 27.7 (CH₃CO), 21.3 (SCH₃). HRMS Calcd for C₇H₁₀O₂S [M+H]⁺: 159.0480, found: 159.0480.



(E)-Ethyl 3-(3-(methylthio)-4-oxo-4H-furo[3,2-c]chromen-2-yl)acrylate (11): 39 mg, 59% yield; yellow solid; m.p. 191-193 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.87 (dd, *J* = 7.8, 1.2 Hz, 1 H, aromatic CH), 7.77 (d, *J* = 15.8 Hz, 1 H, CH=CH), 7.56 (m, 1 H, aromatic CH), 7.38 (m, 2 H, aromatic CH), 6.59 (d, *J* = 15.8 Hz, 1 H, CH=CH),

4.29 (q, $J = 7.1$ Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 2.58 (s, 3 H, SCH_3), 1.35 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 166.3 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 158.9, 156.6, 153.4, and 152.5 (Cq), 132.2, 127.5, and 124.9 (aromatic CH), 122.7 (Cq), 121.4, 119.6, and 117.5 (aromatic CH), 112.9 and 120.0 (Cq), 61.0 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 18.9 (SCH_3), 14.4 ($\text{CO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{17}\text{H}_{14}\text{O}_5\text{S}$ $[\text{M}+\text{H}]^+$: 331.0640, found: 331.0646.



(E)-Ethyl 5-(3-(benzyloxy)-3-oxoprop-1-en-1-yl)-4-(methylsulfonyl)-2-phenylfuran-3-carboxylate (12): 40 mg, 89% yield; Colourless liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, $J = 15.9$ Hz, 1 H, $\text{CH}=\text{CH}$), 7.70 (m, 2 H, aromatic CH), 7.40 (m, 8 H, aromatic CH), 6.72 (d, $J = 15.9$ Hz, 1 H, $\text{CH}=\text{CH}$), 5.27 (s, 2 H, $\text{CO}_2\text{CH}_2\text{Ph}$), 4.38 (q, $J = 7.1$ Hz, 2 H, $\text{CO}_2\text{CH}_2\text{CH}_3$), 3.39 (s, 3 H, SO_2CH_3), 1.31 (t, $J = 7.1$ Hz, 3 H, $\text{CO}_2\text{CH}_2\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 165.5 and 162.4 ($\text{CO}_2\text{CH}_2\text{Ph}$ and $\text{CO}_2\text{CH}_2\text{CH}_3$), 155.8, 151.3, and 135.7 (Cq), 130.8, 128.8, 128.7, 128.5, 128.4, 128.2, and 127.8 (aromatic CH), 127.8 and 127.3 (Cq), 123.2 (aromatic CH), 115.1 (Cq), 66.9 ($\text{CO}_2\text{CH}_2\text{Ph}$), 62.5 ($\text{CO}_2\text{CH}_2\text{CH}_3$), 45.5 (SO_2CH_3), 13.9 ($\text{CO}_2\text{CH}_2\text{CH}_3$). HRMS Calcd for $\text{C}_{24}\text{H}_{22}\text{O}_7\text{S}$ $[\text{M}+\text{H}]^+$: 455.1164, found: 455.1158.

5. Copies of NMR spectra

WQN-1003W

PROTON CDC13 {D:\NMR400\203} nmr 21

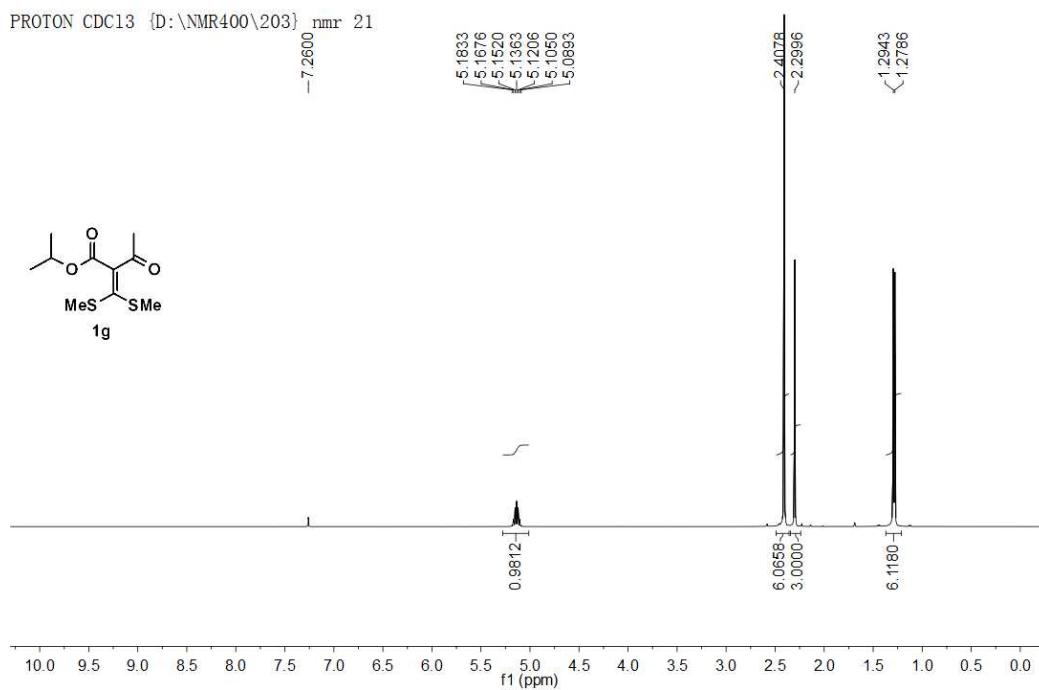


Figure S3. ¹H NMR spectrum of compound **1g** (CDCl₃, 25 °C, 400 MHz).

WQN-1003W

¹³C NMR in CDC13 (100 MHz)

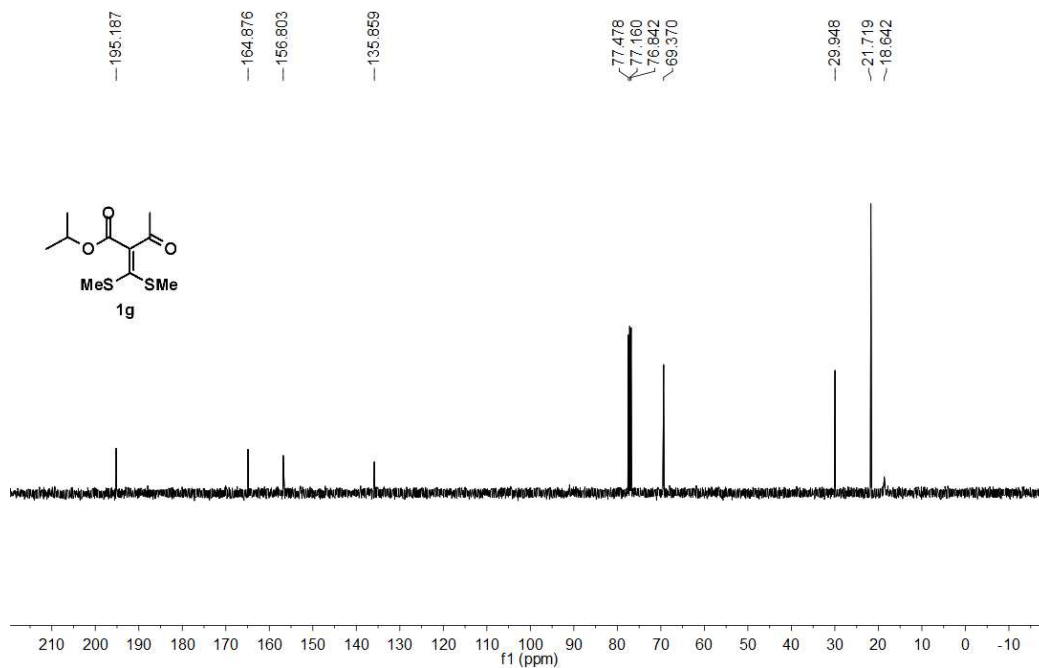


Figure S4. ¹³C{¹H} NMR spectrum of compound **1g** (CDCl₃, 25 °C, 100 MHz).

WQN-1009W

^1H NMR in CDCl_3 (400 MHz)

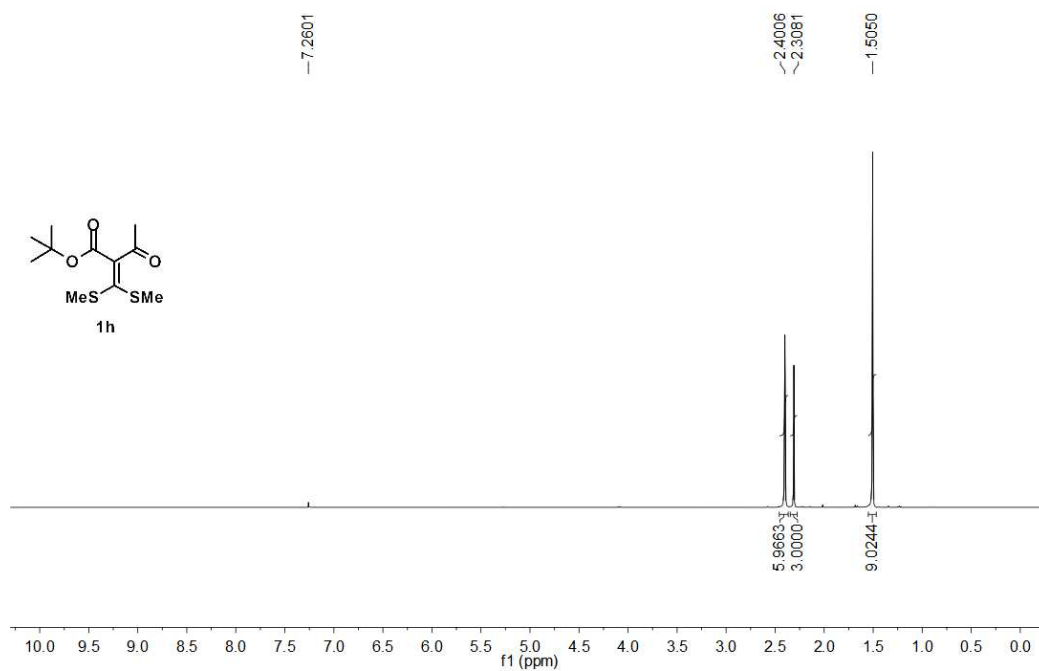


Figure S5. ^1H NMR spectrum of compound **1h** (CDCl_3 , 25 $^\circ\text{C}$, 400 MHz).

WQN-1009W

^{13}C NMR in CDCl_3 (100 MHz)

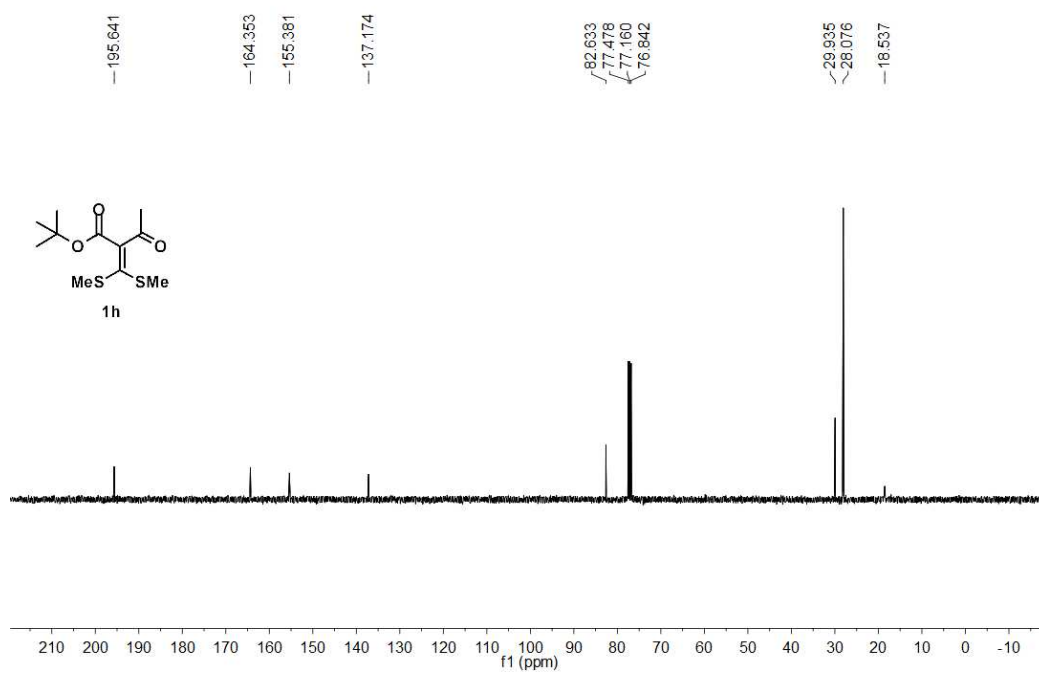


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **1h** (CDCl_3 , 25 $^\circ\text{C}$, 100 MHz).

WQN-1098W

^1H NMR in CDCl_3 (400 MHz)

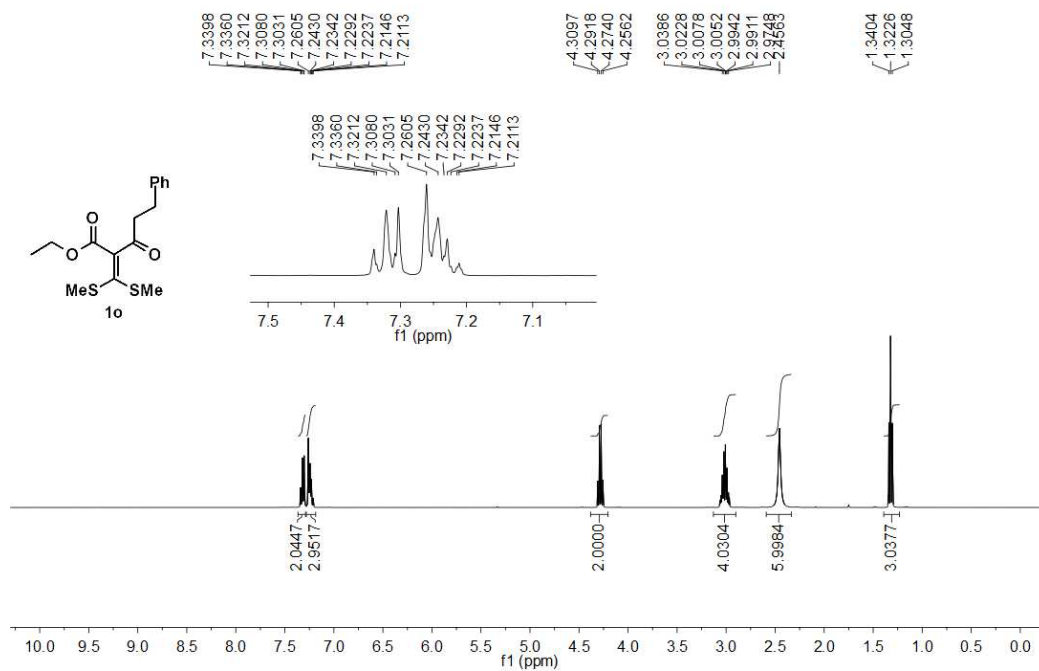


Figure S7. ^1H NMR spectrum of compound **1o** (CDCl_3 , 25 °C, 400 MHz).

WQN-1098W

^{13}C NMR in CDCl_3 (100 MHz)

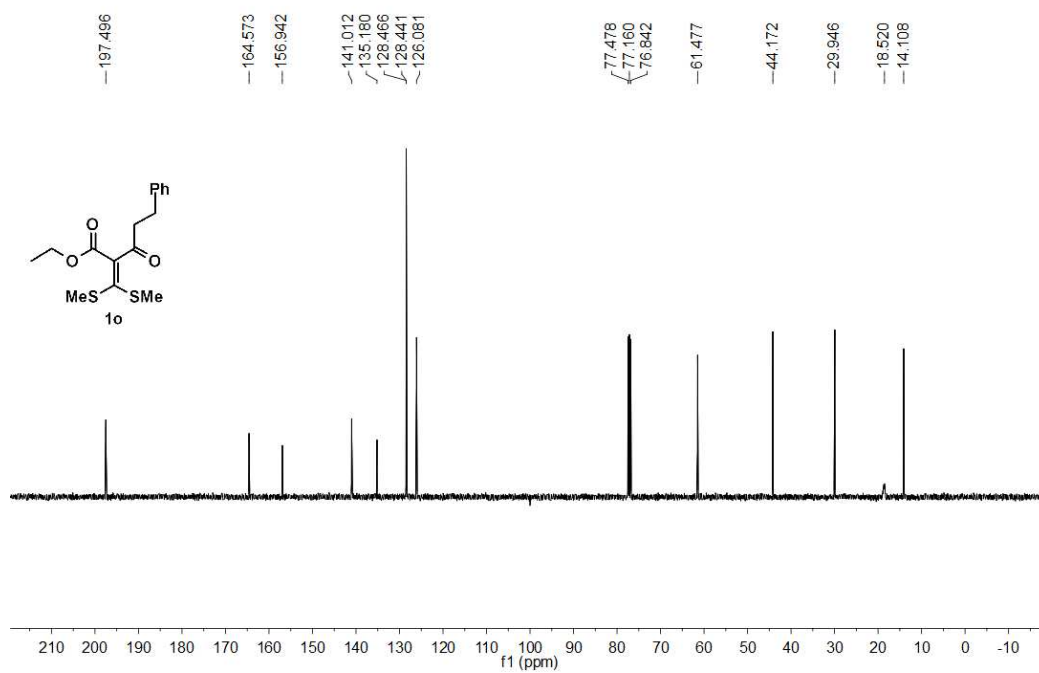


Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **1o** (CDCl_3 , 25 °C, 100 MHz).

WQN-1021W
¹H NMR in CDCl₃ (400 MHz)

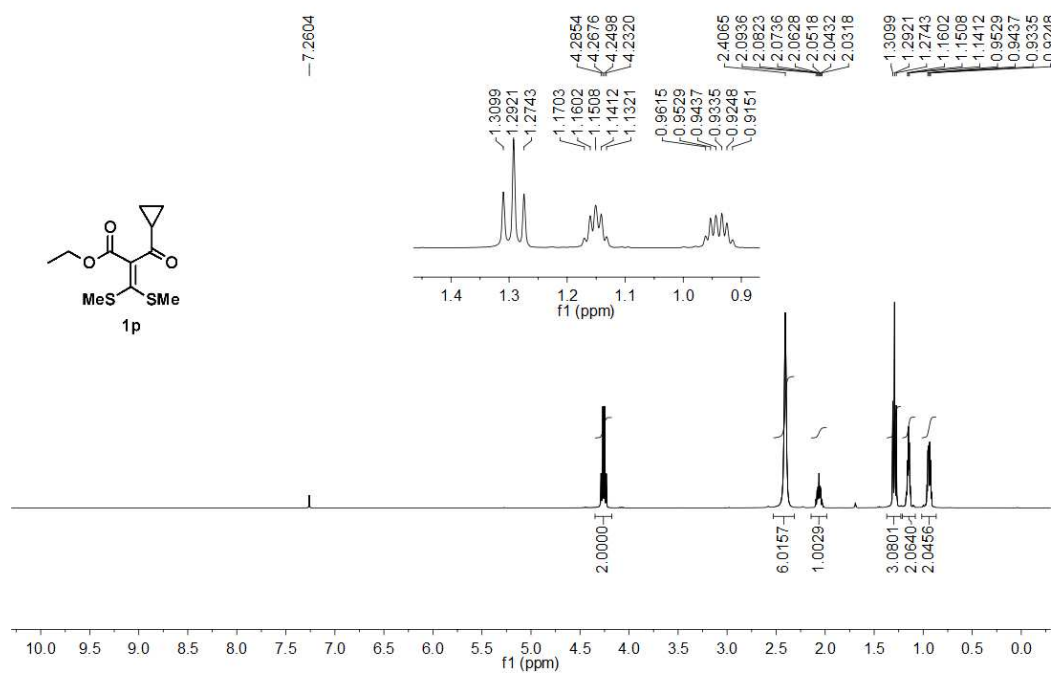


Figure S9. ¹H NMR spectrum of compound **1p** (CDCl₃, 25 °C, 400 MHz).

WQN-1021W
¹³C NMR in CDCl₃ (100 MHz)

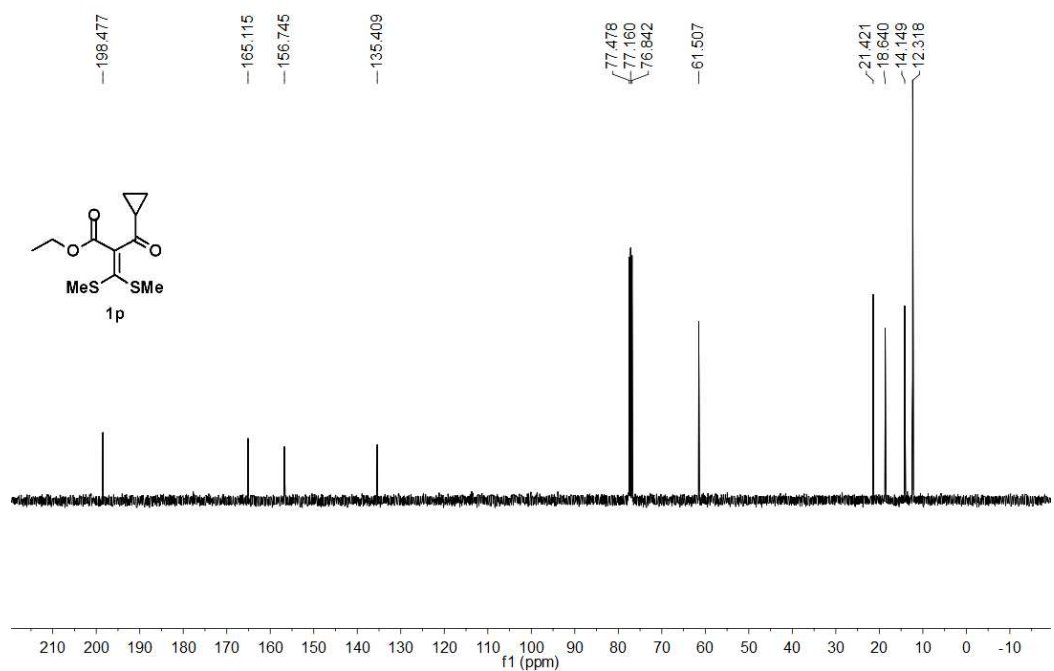


Figure S10. ¹³C{¹H} NMR spectrum of compound **1p** (CDCl₃, 25 °C, 100 MHz).

WQN-1055W
¹H NMR in CDCl₃ (400 MHz)

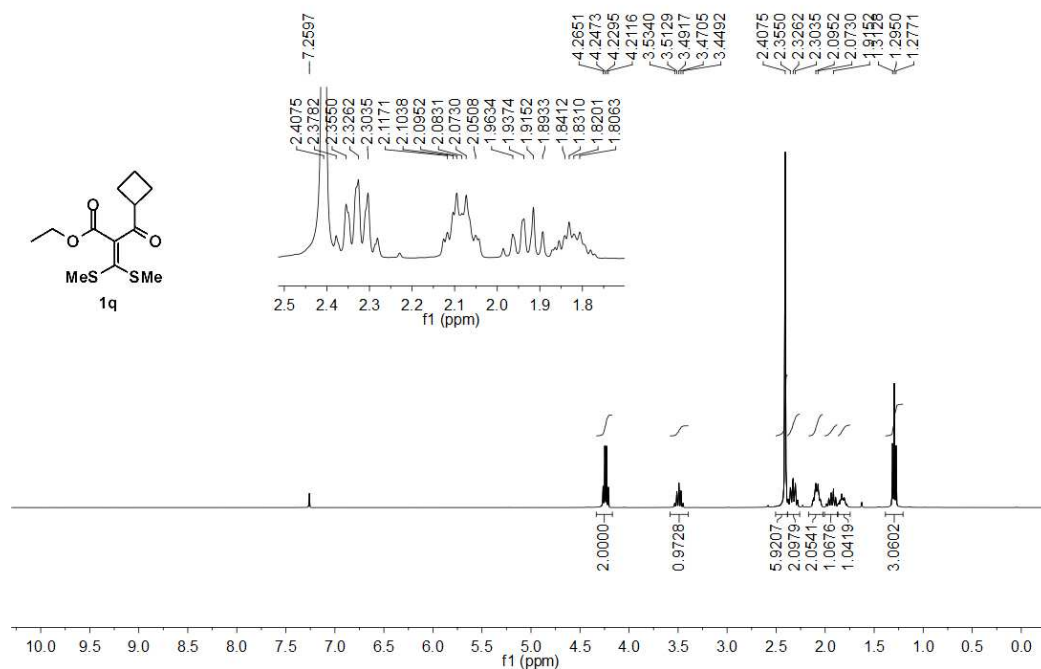


Figure S11. ¹H NMR spectrum of compound **1q** (CDCl₃, 25 °C, 400 MHz).

WQN-1055W
¹³C NMR in CDCl₃ (100 MHz)

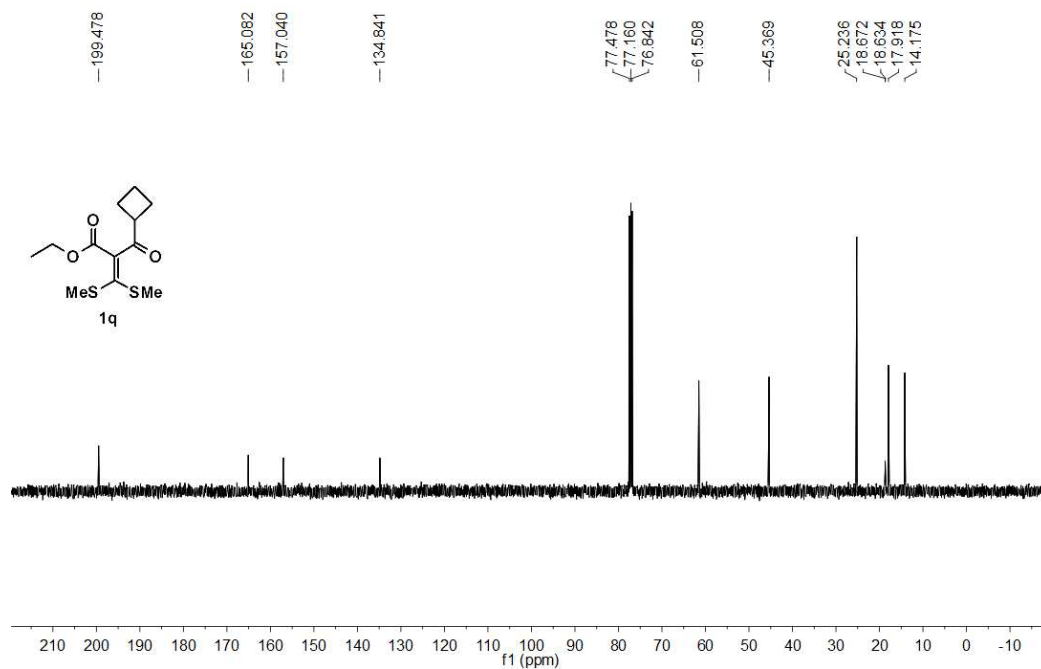


Figure S12. ¹³C{¹H} NMR spectrum of compound **1q** (CDCl₃, 25 °C, 100 MHz).

WQN-1062W
¹H NMR in CDCl₃ (400 MHz)

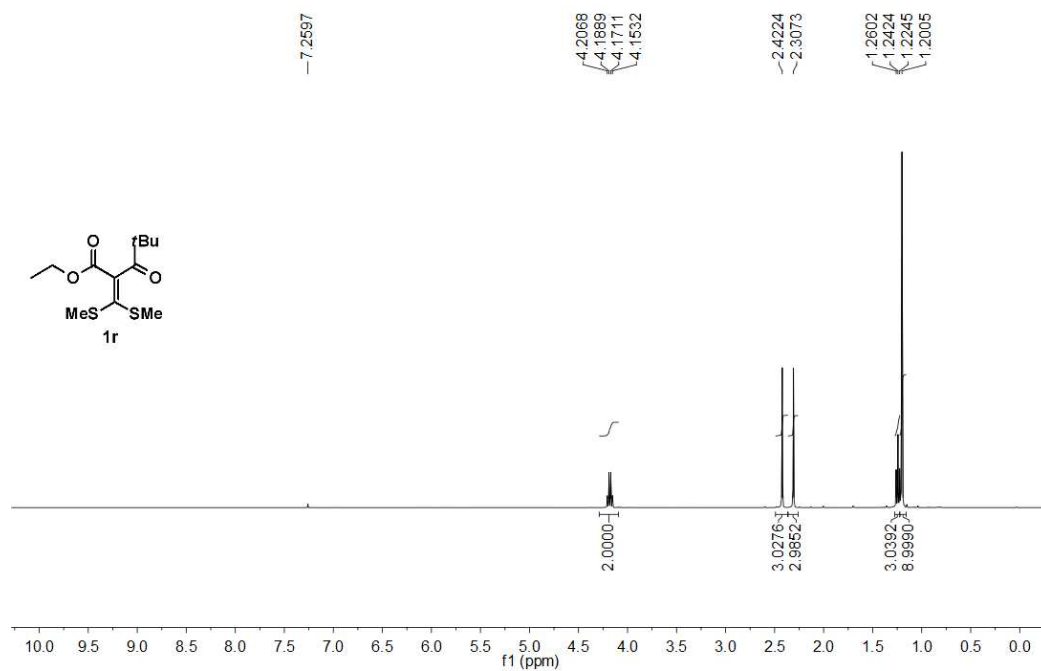


Figure S13. ¹H NMR spectrum of compound **1r** (CDCl₃, 25 °C, 400 MHz).

WQN-1062W
¹³C NMR in CDCl₃ (100 MHz)

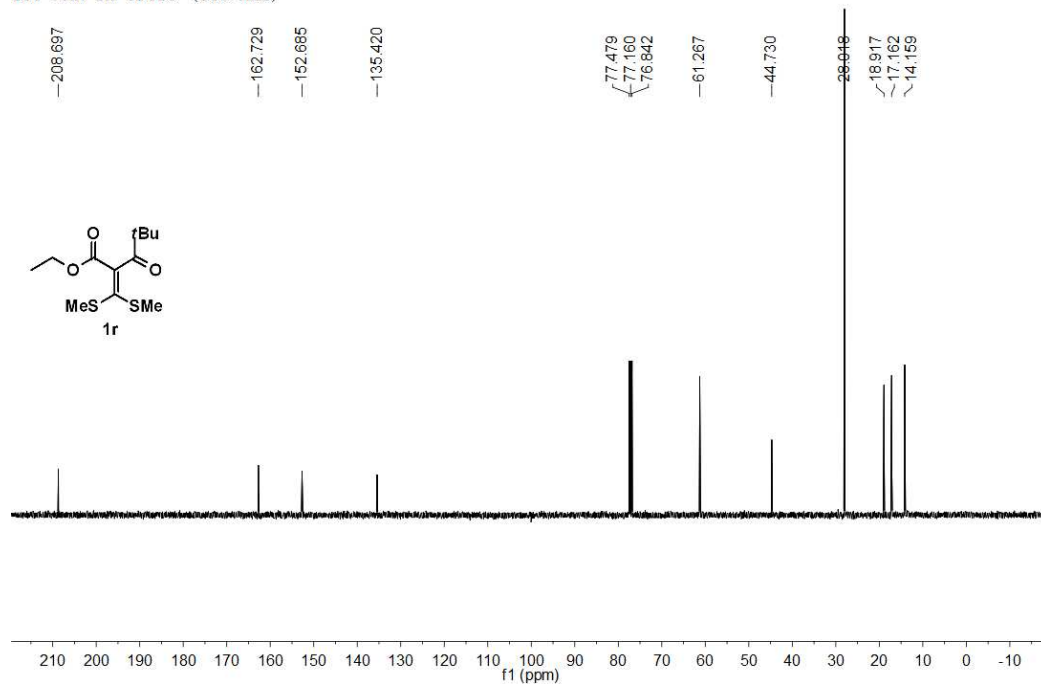


Figure S14. ¹³C{¹H} NMR spectrum of compound **1r** (CDCl₃, 25 °C, 100 MHz).

WQN-1044W
¹H NMR in CDCl₃ (400 MHz)

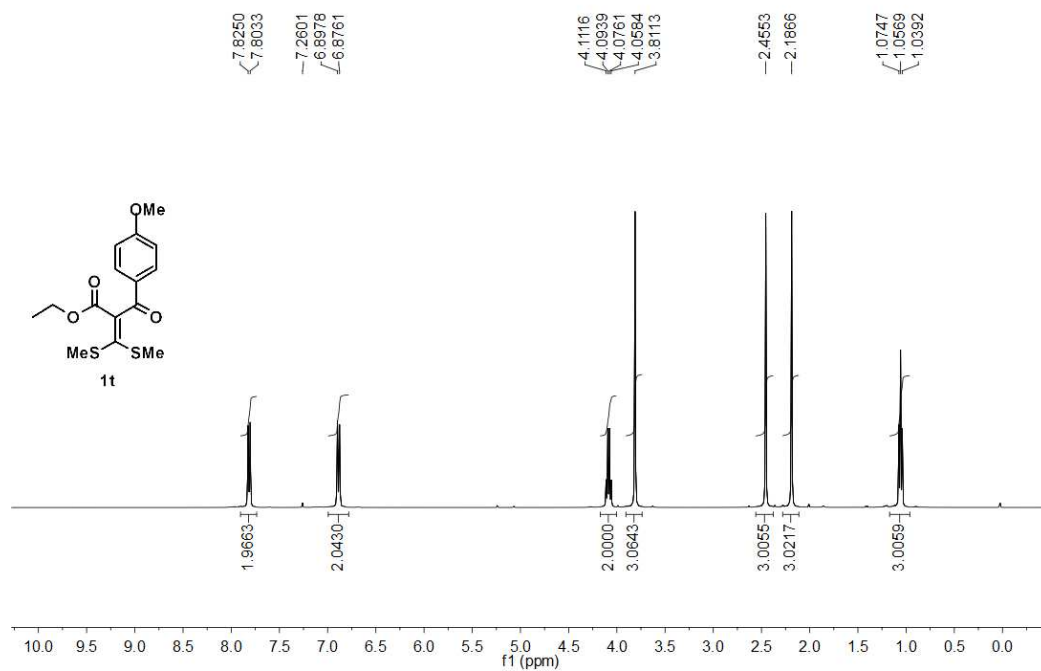


Figure S15. ¹H NMR spectrum of compound **1t** (CDCl₃, 25 °C, 400 MHz).

WQN-1044W
¹³C NMR in CDCl₃ (100 MHz)

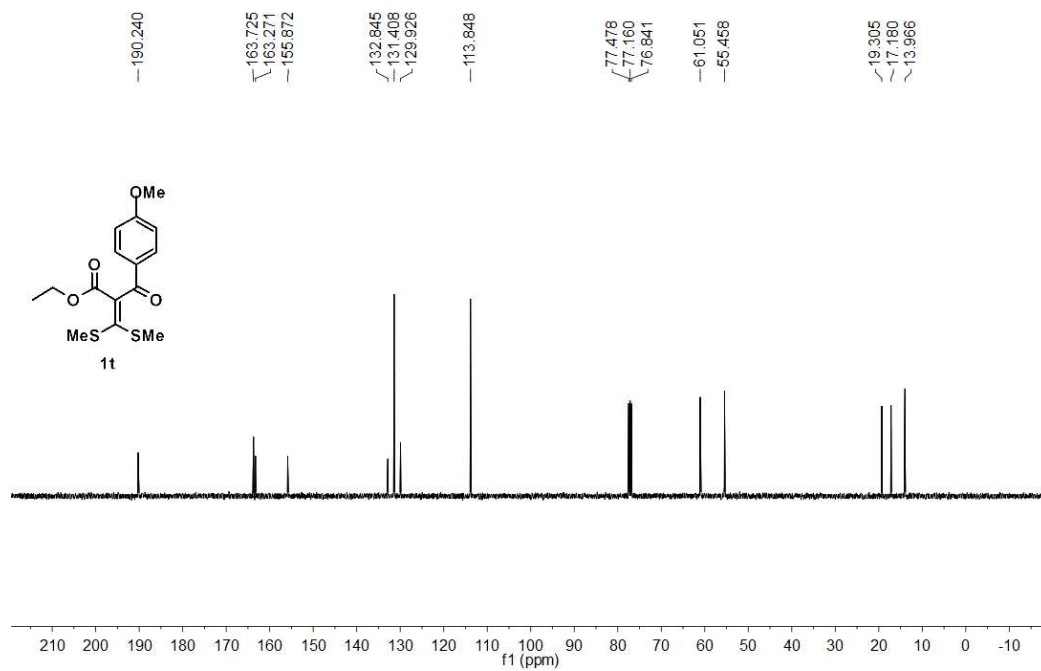


Figure S16. ¹³C{¹H} NMR spectrum of compound **1t** (CDCl₃, 25 °C, 100 MHz).

WQN-1047W
¹H NMR in CDCl₃ (400 MHz)

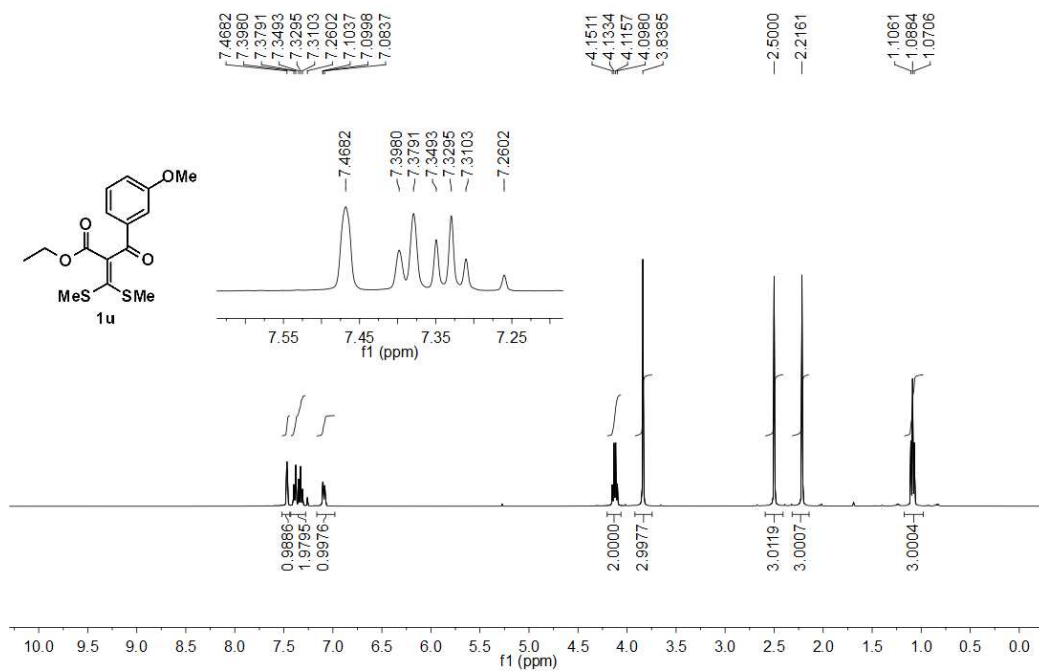


Figure S17. ¹H NMR spectrum of compound **1u** (CDCl₃, 25 °C, 400 MHz).

WQN-1047W
¹³C NMR in CDCl₃ (100 MHz)

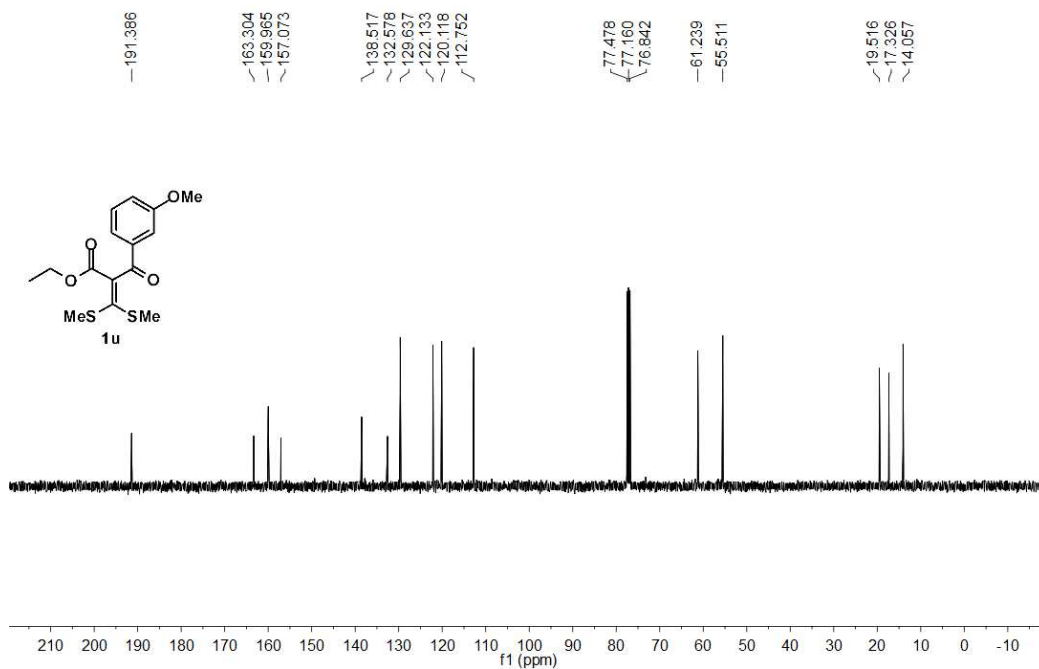


Figure S18. ¹³C{¹H} NMR spectrum of compound **1u** (CDCl₃, 25 °C, 100 MHz).

WQN-1075W
¹H NMR in CDCl₃ (400 MHz)

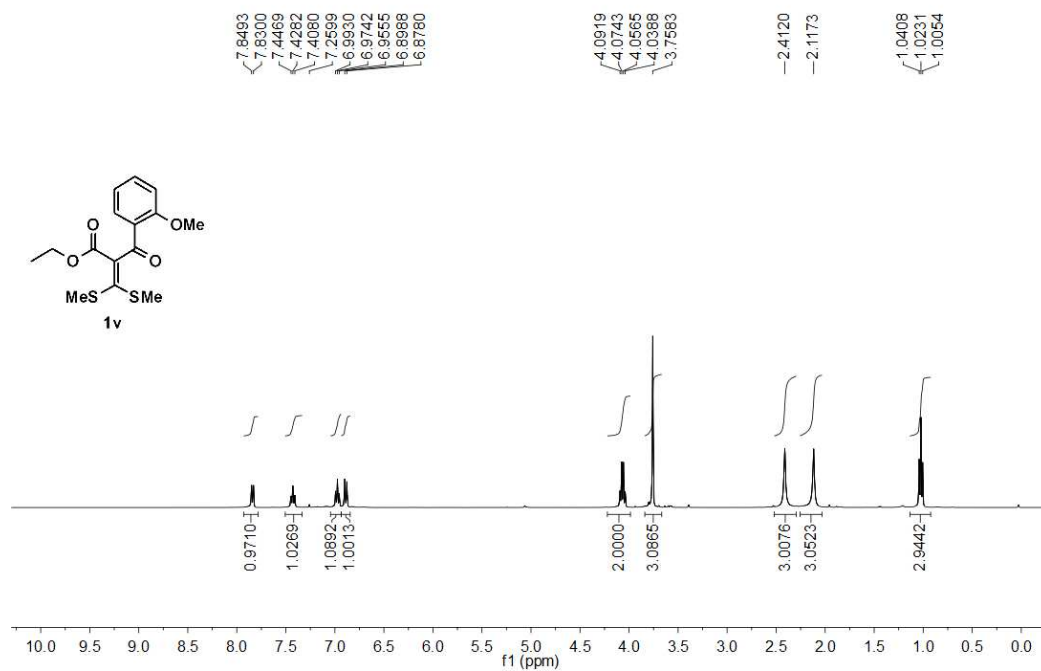


Figure S19. ¹H NMR spectrum of compound **1v** (CDCl₃, 25 °C, 400 MHz).

WQN-1075W
¹³C NMR in CDCl₃ (100 MHz)

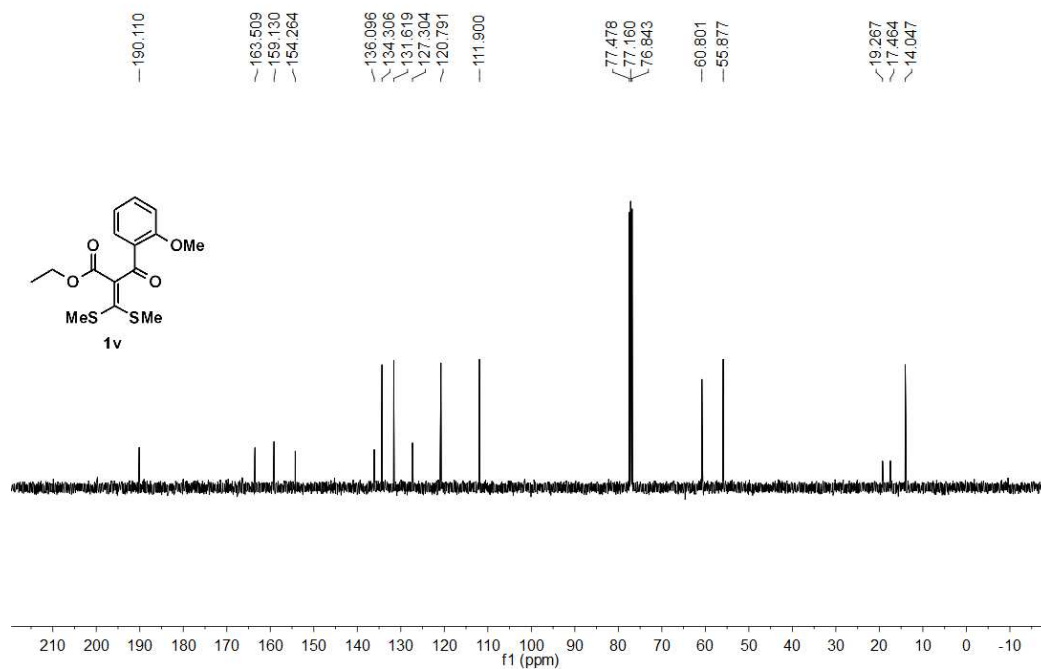


Figure S20. ¹³C{¹H} NMR spectrum of compound **1v** (CDCl₃, 25 °C, 100 MHz).

WQN-1392W

^1H NMR in CDCl_3 (400 MHz)

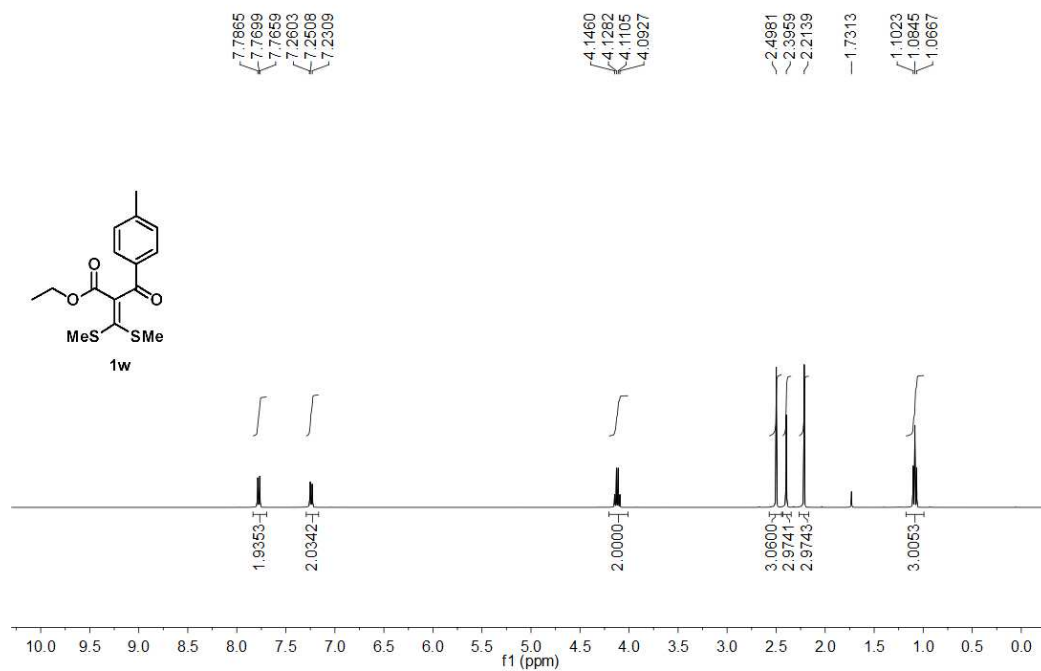


Figure S21. ^1H NMR spectrum of compound **1w** (CDCl_3 , 25 $^\circ\text{C}$, 400 MHz).

WQN-1392W

^{13}C NMR in CDCl_3 (100 MHz)

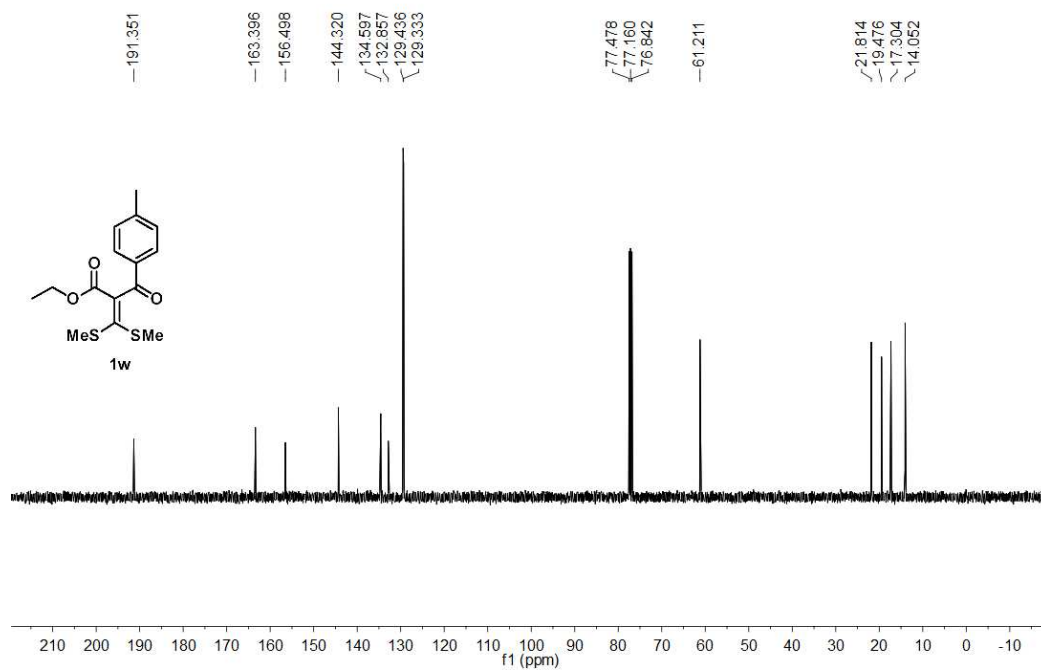


Figure S22. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **1w** (CDCl_3 , 25 $^\circ\text{C}$, 100 MHz).

WQN-1077W

^1H NMR in CDCl_3 (400 MHz)

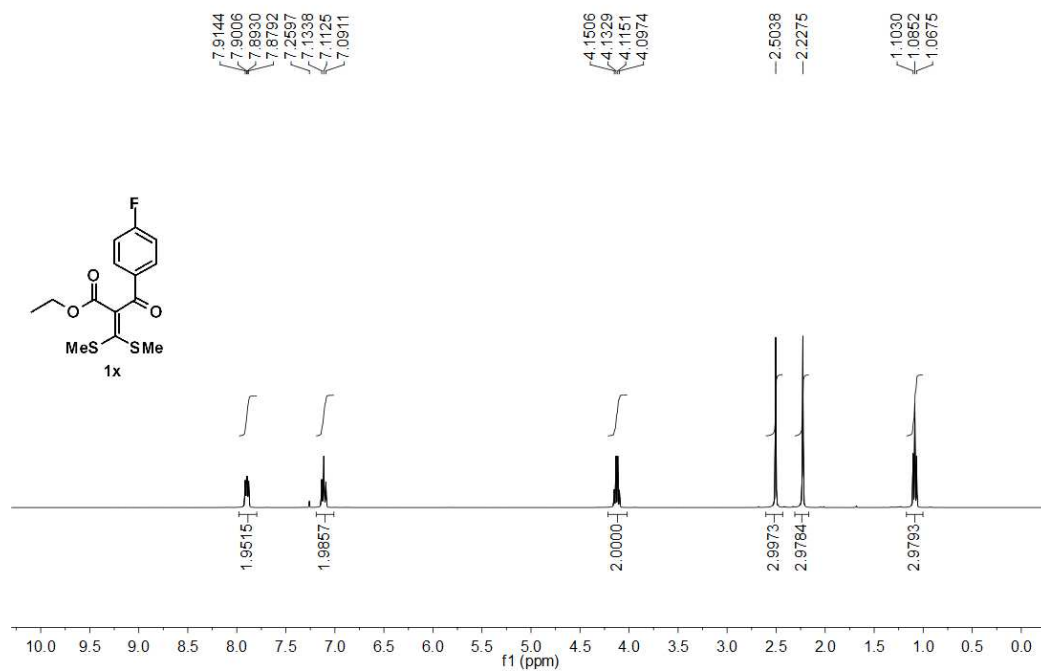


Figure S23. ^1H NMR spectrum of compound **1x** (CDCl_3 , 25 °C, 400 MHz).

WQN-1077W

^{13}C NMR in CDCl_3 (100 MHz)

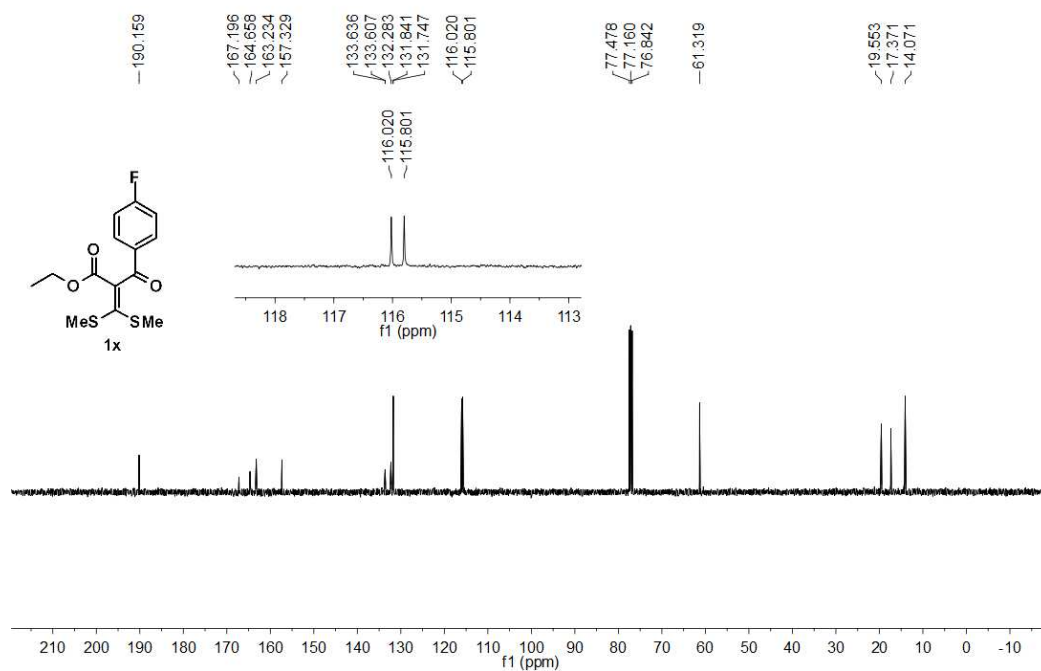


Figure S24. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **1x** (CDCl_3 , 25 °C, 100 MHz).

WQN-1079W

^1H NMR in CDCl_3 (400 MHz)

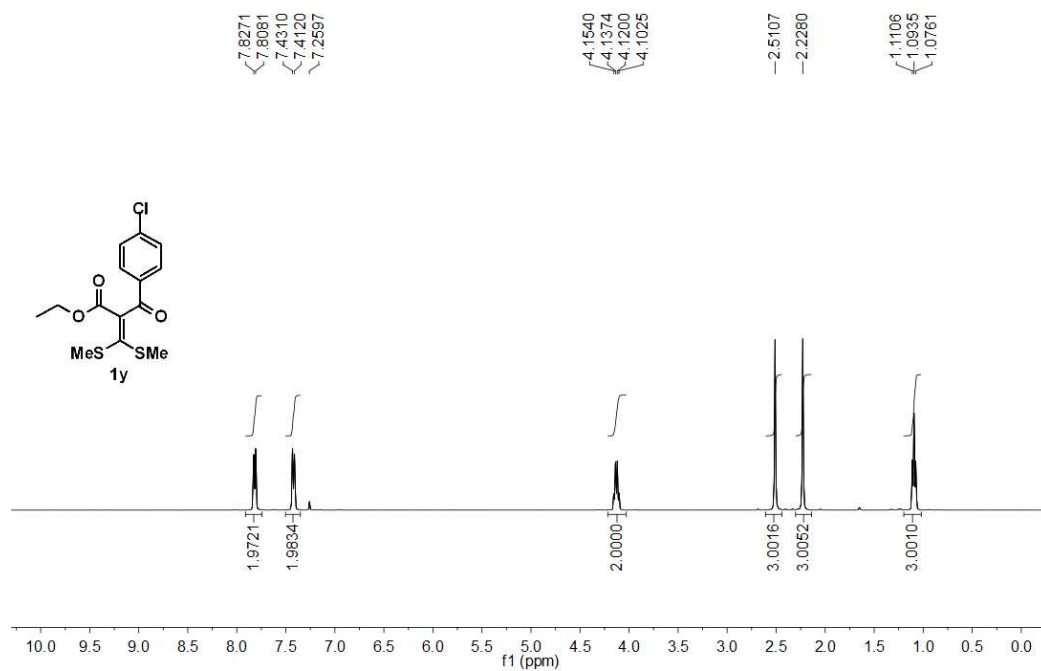


Figure S25. ^1H NMR spectrum of compound **1y** (CDCl_3 , 25 °C, 400 MHz).

WQN-1079W

^{13}C NMR in CDCl_3 (100 MHz)

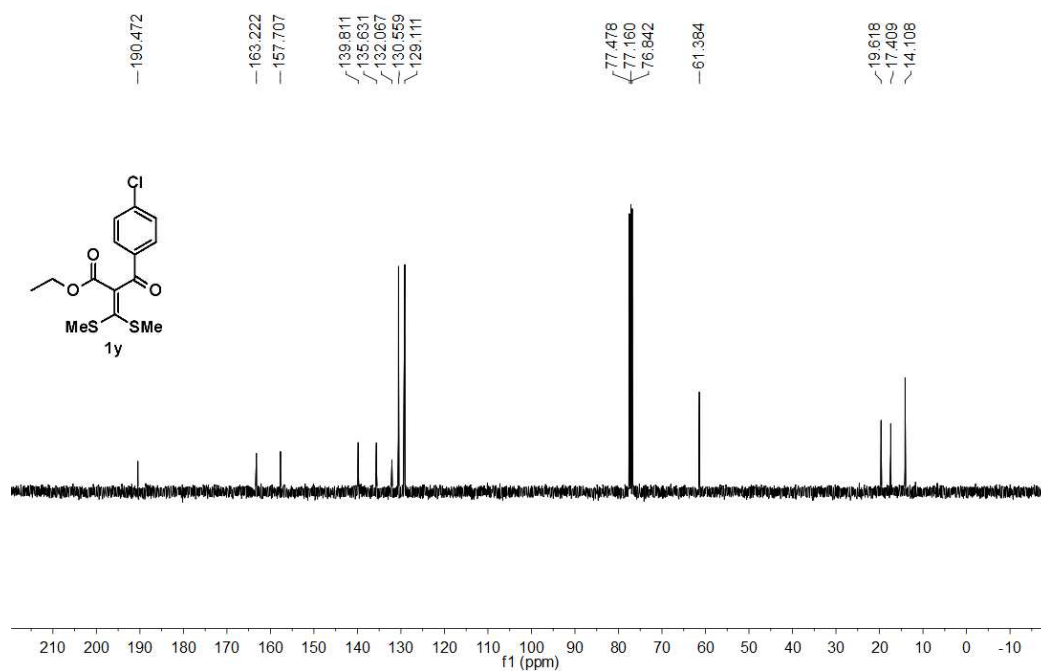


Figure S26. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **1y** (CDCl_3 , 25 °C, 100 MHz).

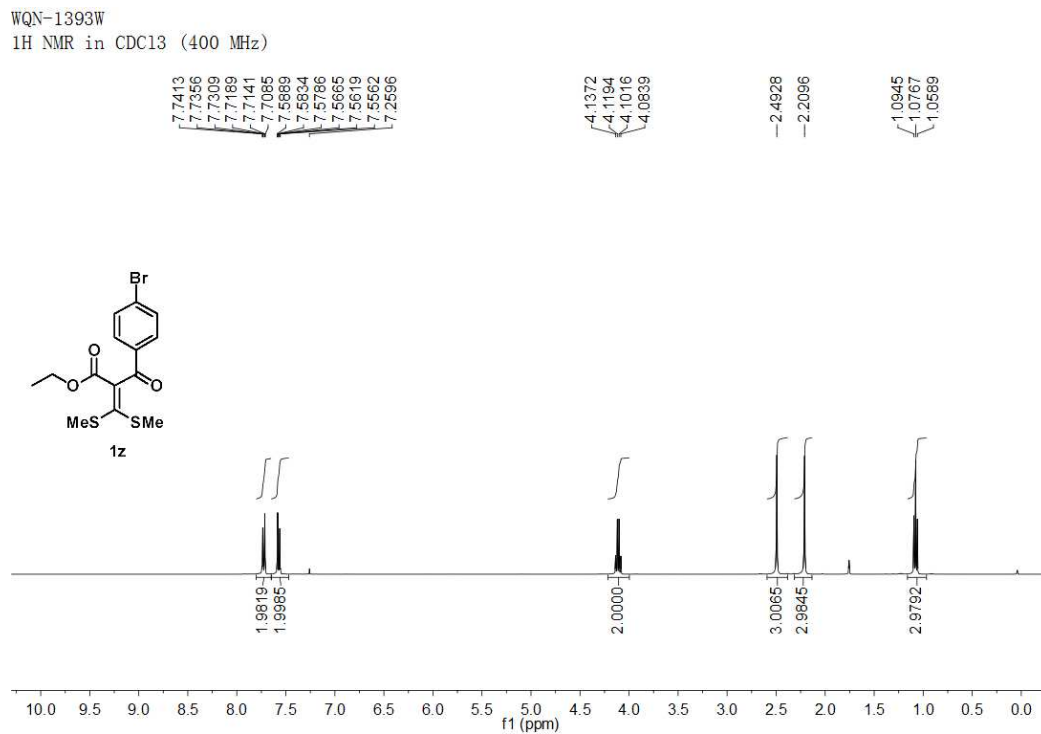


Figure S27. ¹H NMR spectrum of compound **1z** (CDCl₃, 25 °C, 400 MHz).

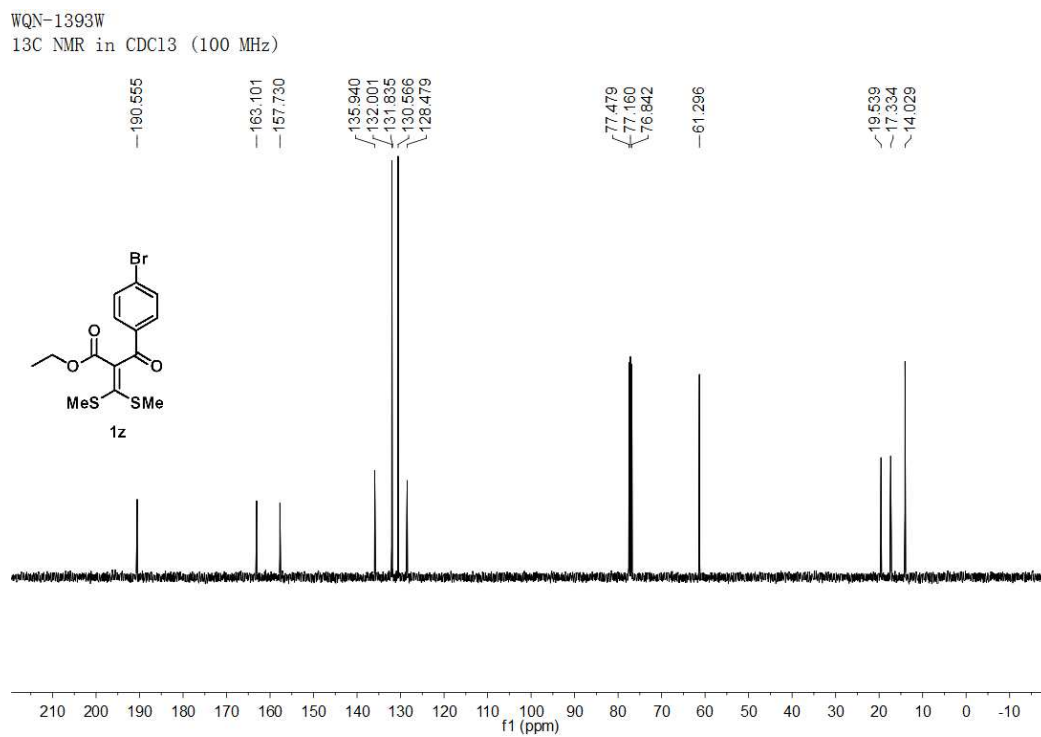


Figure S28. ¹³C{¹H} NMR spectrum of compound **1z** (CDCl₃, 25 °C, 100 MHz).

WQN-1417W-2

¹H NMR in CDCl₃ (400 MHz)

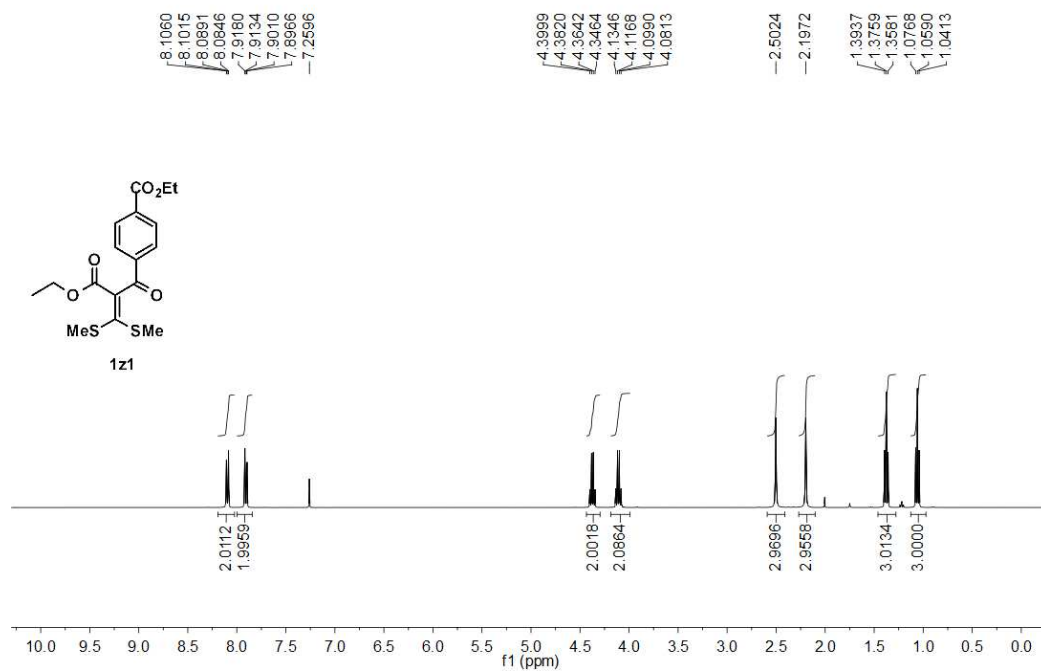


Figure S29. ¹H NMR spectrum of compound **1z1** (CDCl₃, 25 °C, 400 MHz).

WQN-1417W-2

¹³C NMR in CDCl₃ (100 MHz)

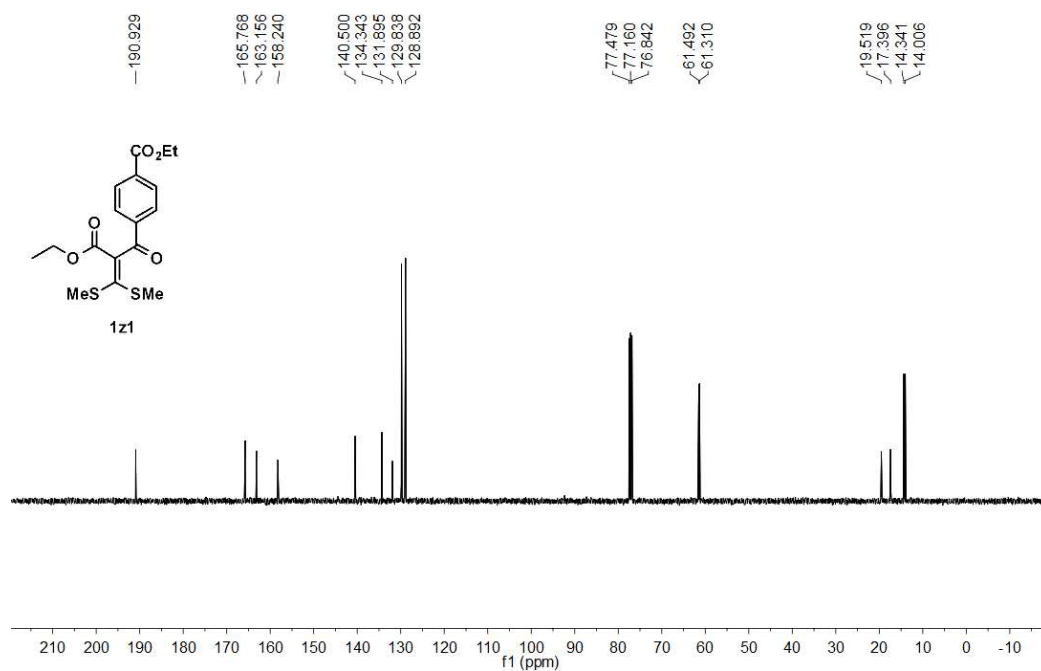


Figure S30. ¹³C{¹H} NMR spectrum of compound **1z1** (CDCl₃, 25 °C, 100 MHz).

WQN-1475W

^1H NMR in CDCl_3 (400 MHz)

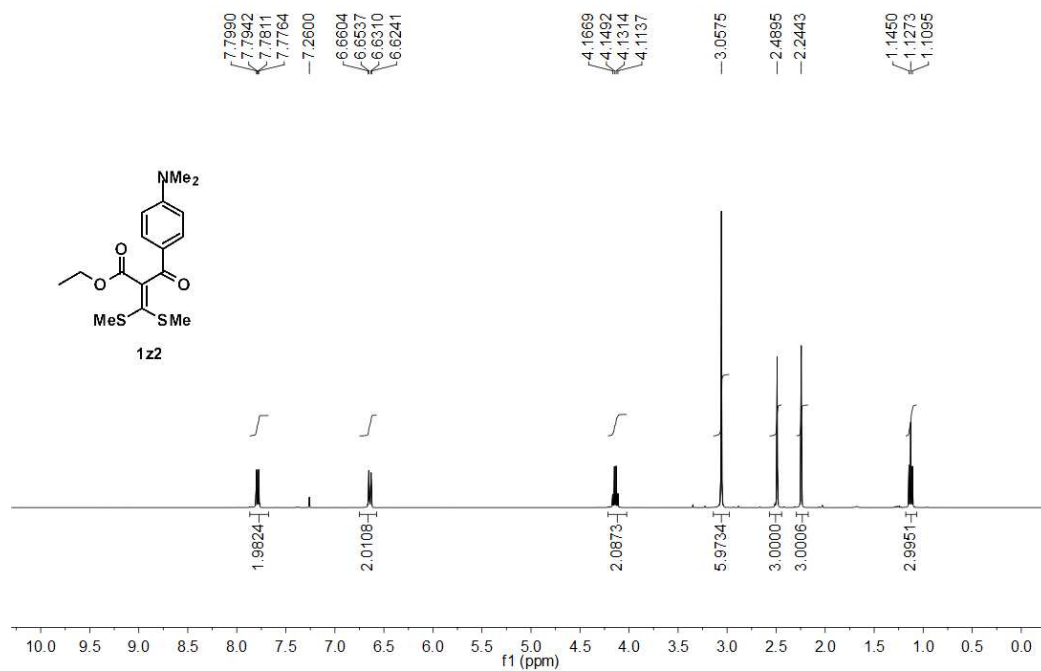


Figure S31. ^1H NMR spectrum of compound **1z2** (CDCl_3 , 25 °C, 400 MHz).

WQN-1475W

^{13}C NMR in CDCl_3 (100 MHz)

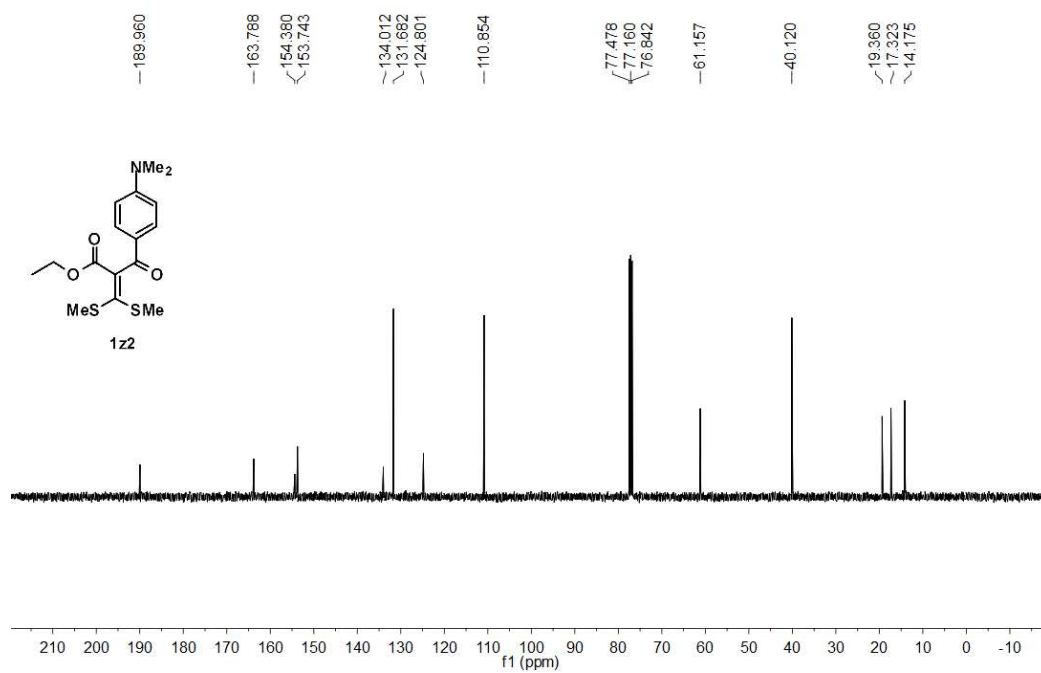


Figure S32. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **1z2** (CDCl_3 , 25 °C, 100 MHz).

WQN-1081W

^1H NMR in CDCl_3 (400 MHz)

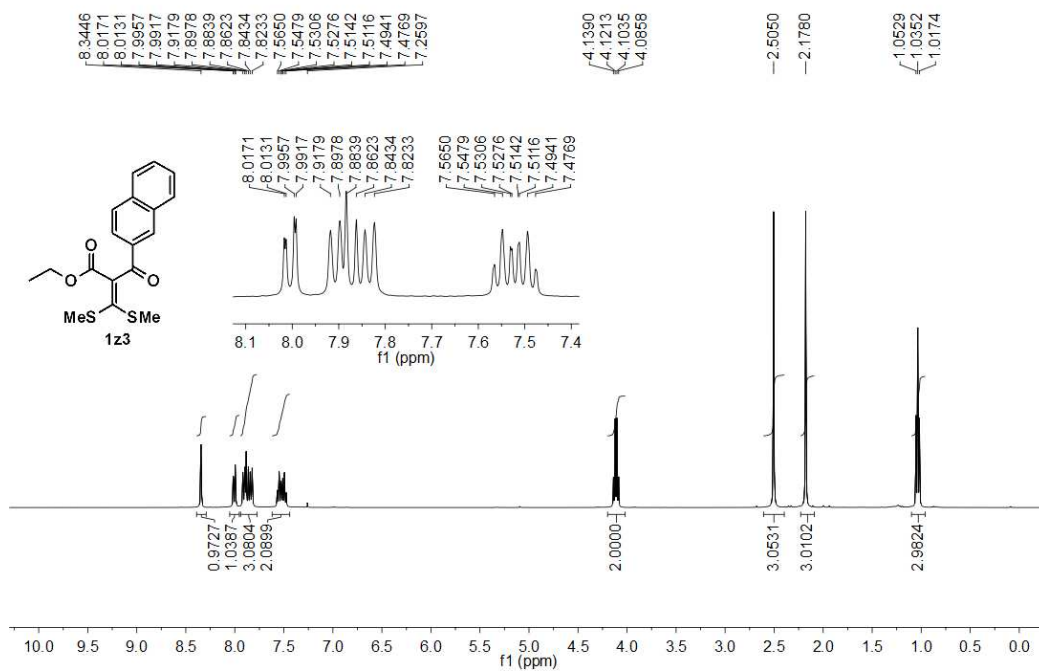


Figure S33. ^1H NMR spectrum of compound **1z3** (CDCl_3 , 25 °C, 400 MHz).

WQN-1081W

^{13}C NMR in CDCl_3 (100 MHz)

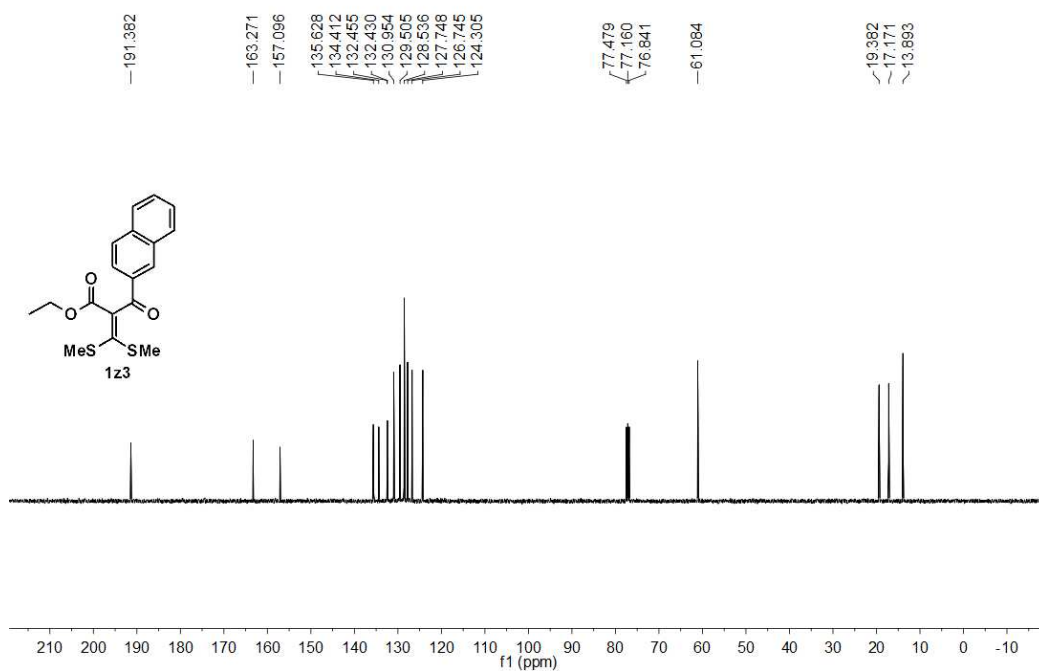


Figure S34. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **1z3** (CDCl_3 , 25 °C, 100 MHz).

WQN-1087W

^1H NMR in CDCl_3 (400 MHz)

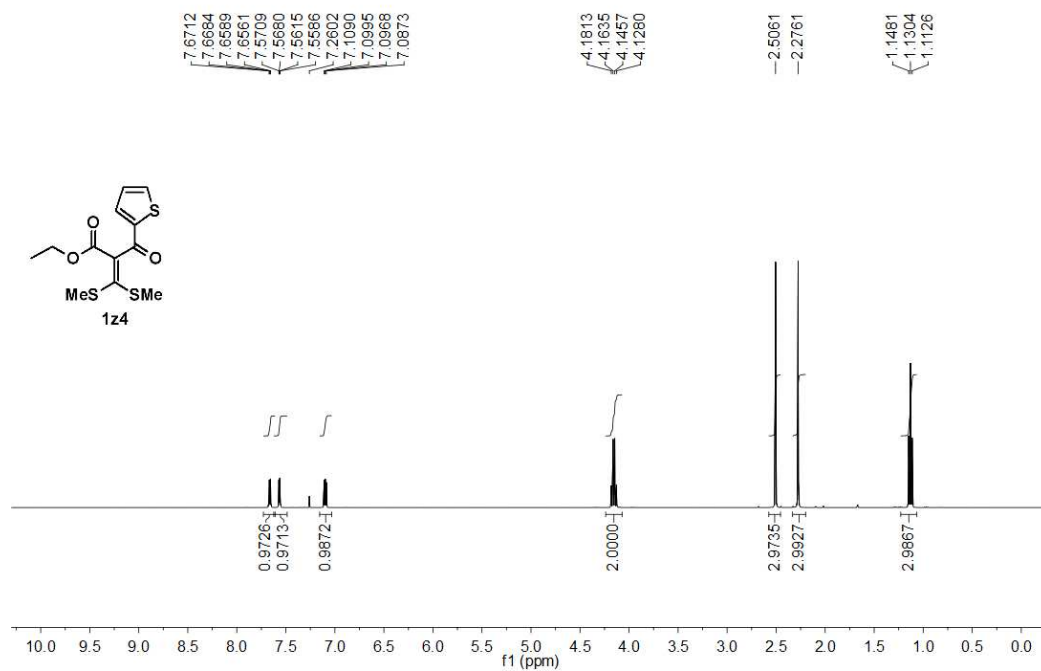


Figure S35. ^1H NMR spectrum of compound **1z4** (CDCl_3 , 25 $^\circ\text{C}$, 400 MHz).

WQN-1087W

^{13}C NMR in CDCl_3 (100 MHz)

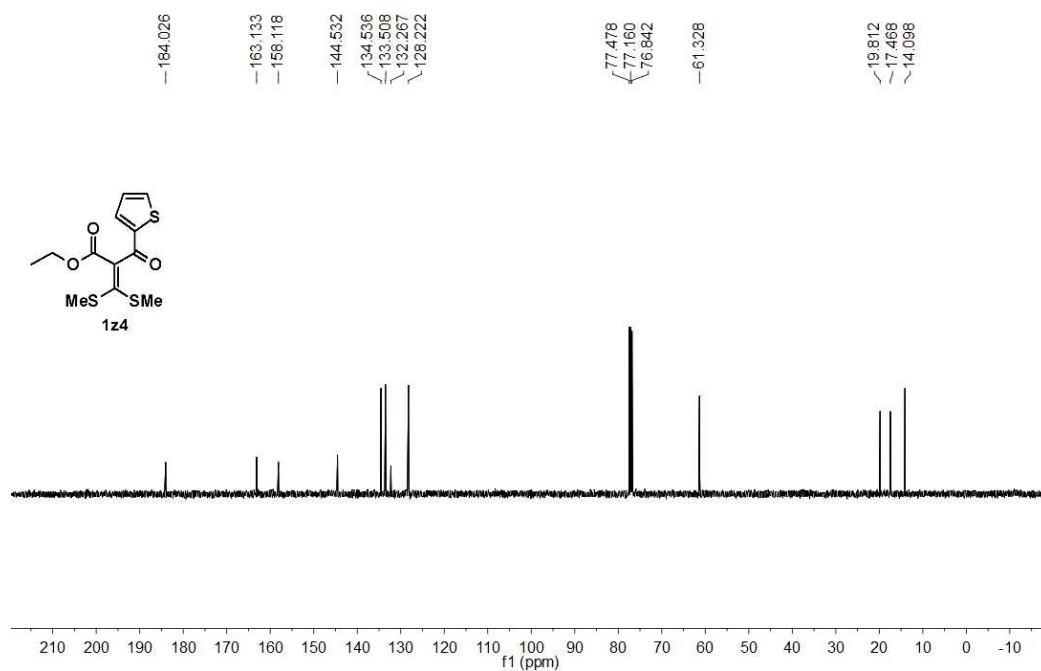


Figure S36. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **1z4** (CDCl_3 , 25 $^\circ\text{C}$, 100 MHz).

WQN-1085W

^1H NMR in CDCl_3 (400 MHz)

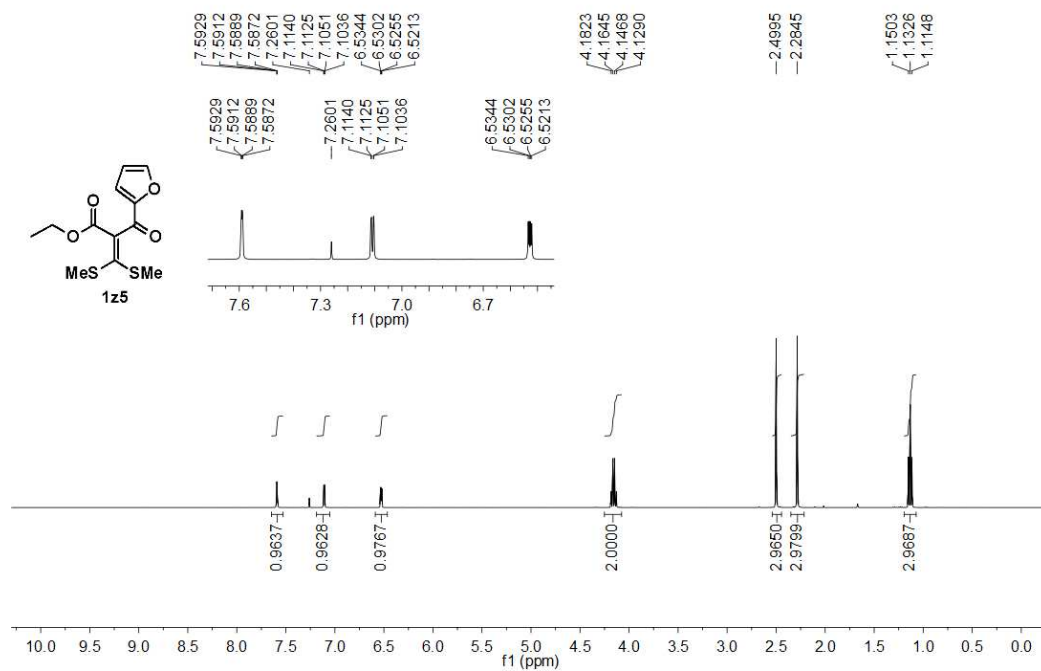


Figure S37. ^1H NMR spectrum of compound **1z5** (CDCl_3 , 25 °C, 400 MHz).

WQN-1085W

^{13}C NMR in CDCl_3 (100 MHz)

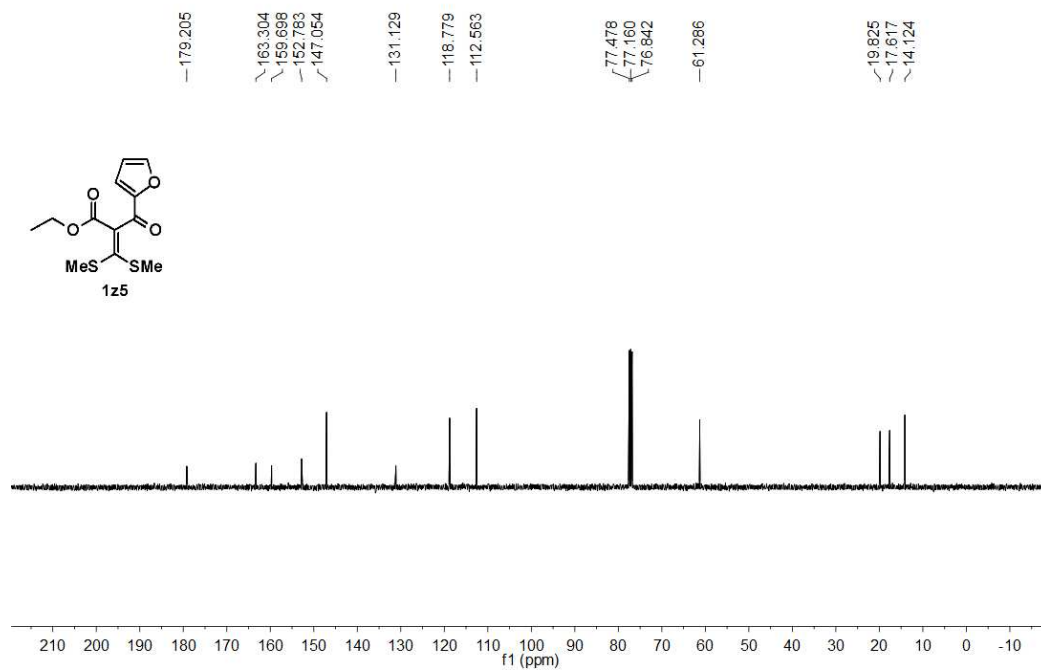


Figure S38. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **1z5** (CDCl_3 , 25 °C, 100 MHz).

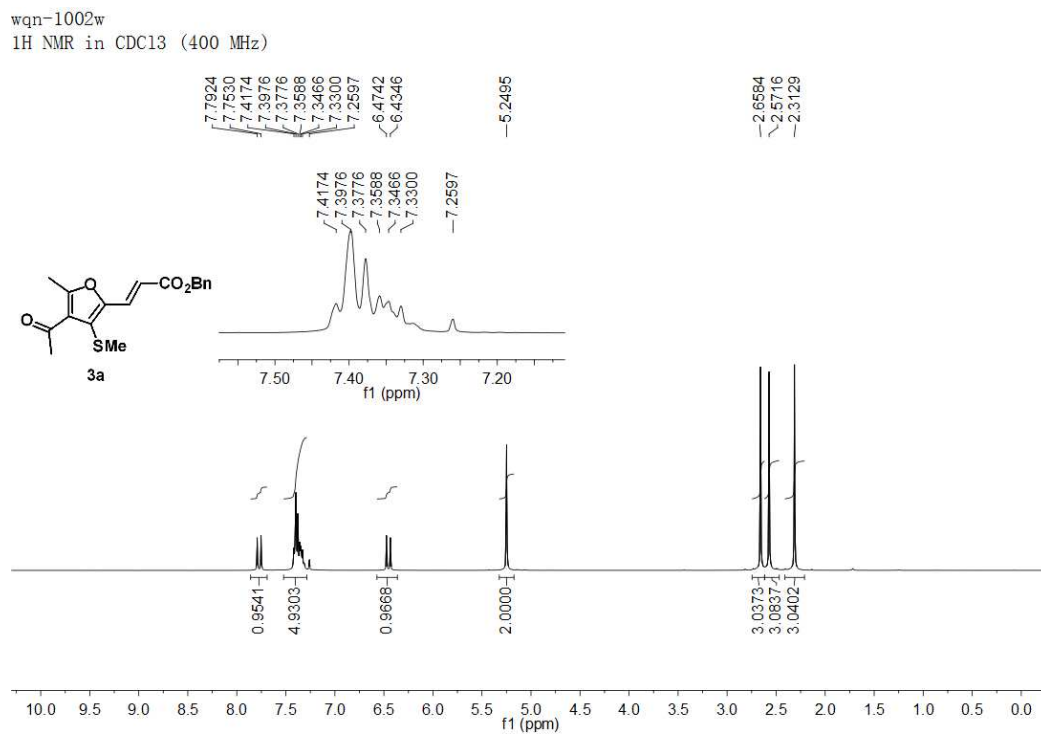


Figure S39. ¹H NMR spectrum of compound **3a** (CDCl₃, 25 °C, 400 MHz).

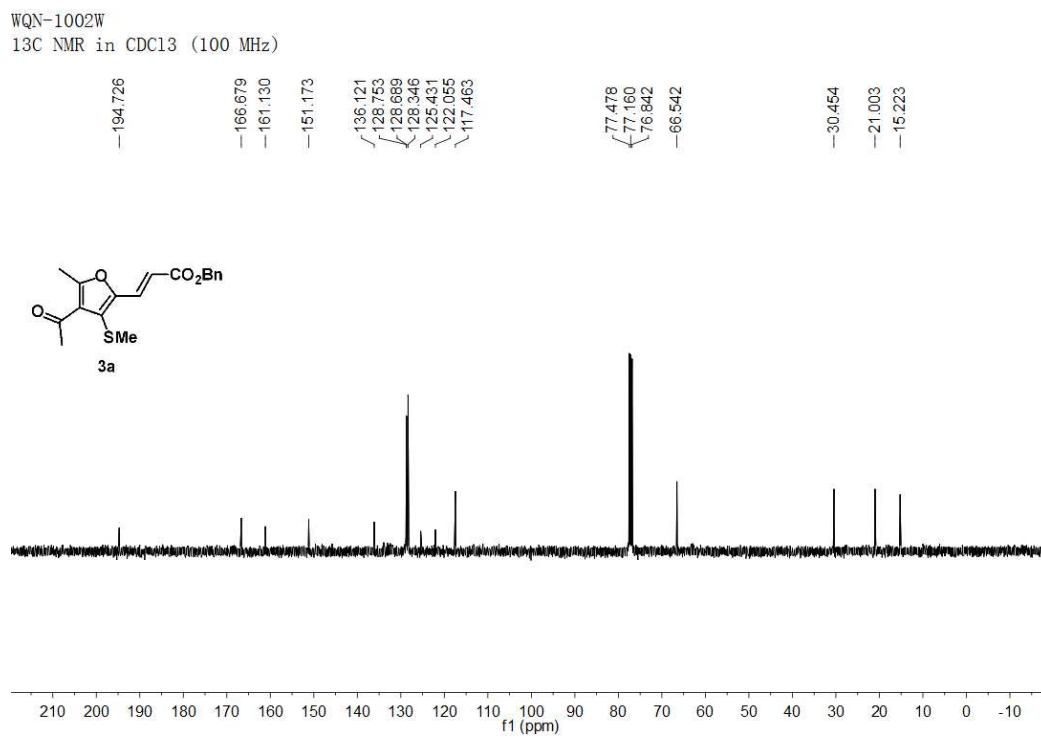


Figure S40. ¹³C{¹H} NMR spectrum of compound **3a** (CDCl₃, 25 °C, 100 MHz).

WQN-1030W-3
¹H NMR in CDCl₃ (400 MHz)

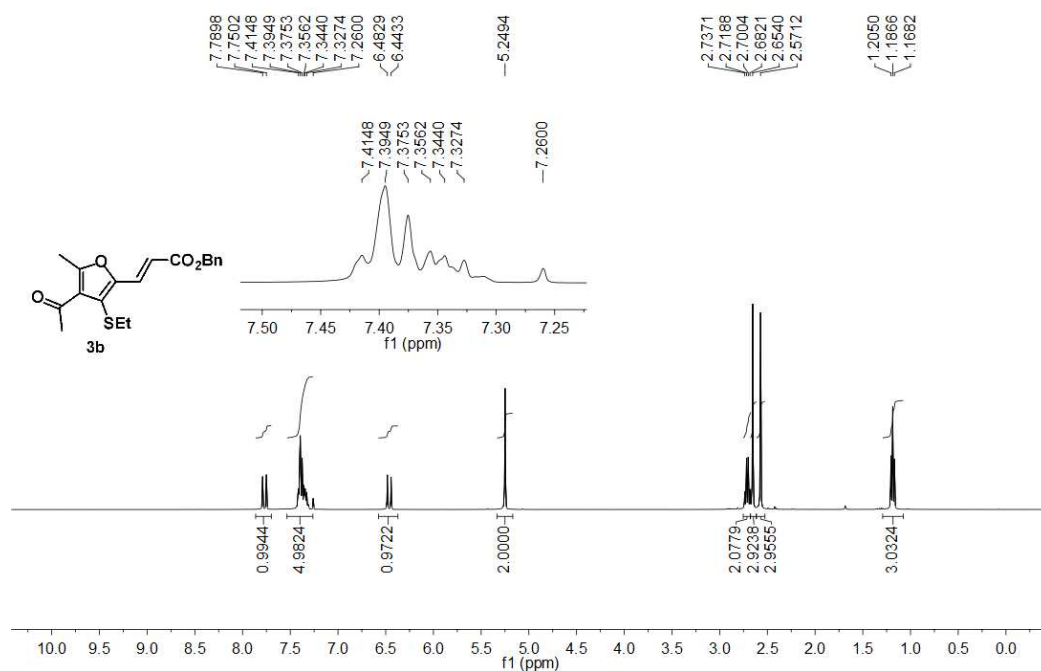


Figure S41. ¹H NMR spectrum of compound **3b** (CDCl₃, 25 °C, 400 MHz).

WQN-1030W-3
¹³C NMR in CDCl₃ (100 MHz)

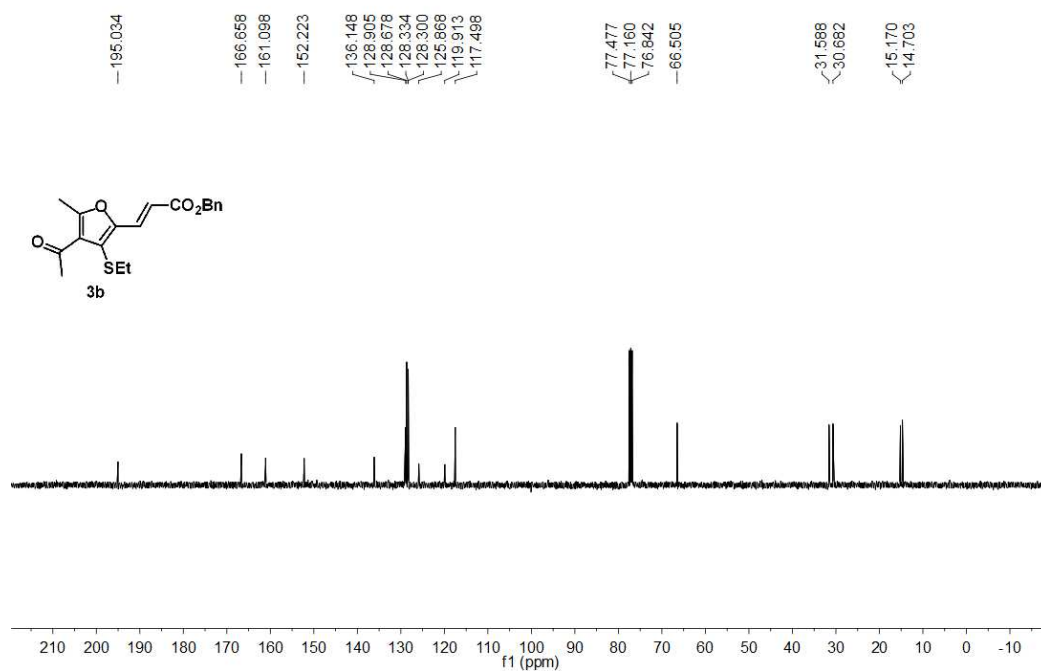


Figure S42. ¹³C{¹H} NMR spectrum of compound **3b** (CDCl₃, 25 °C, 100 MHz).

WQN-1045W

^1H NMR in CDCl_3 (400 MHz)

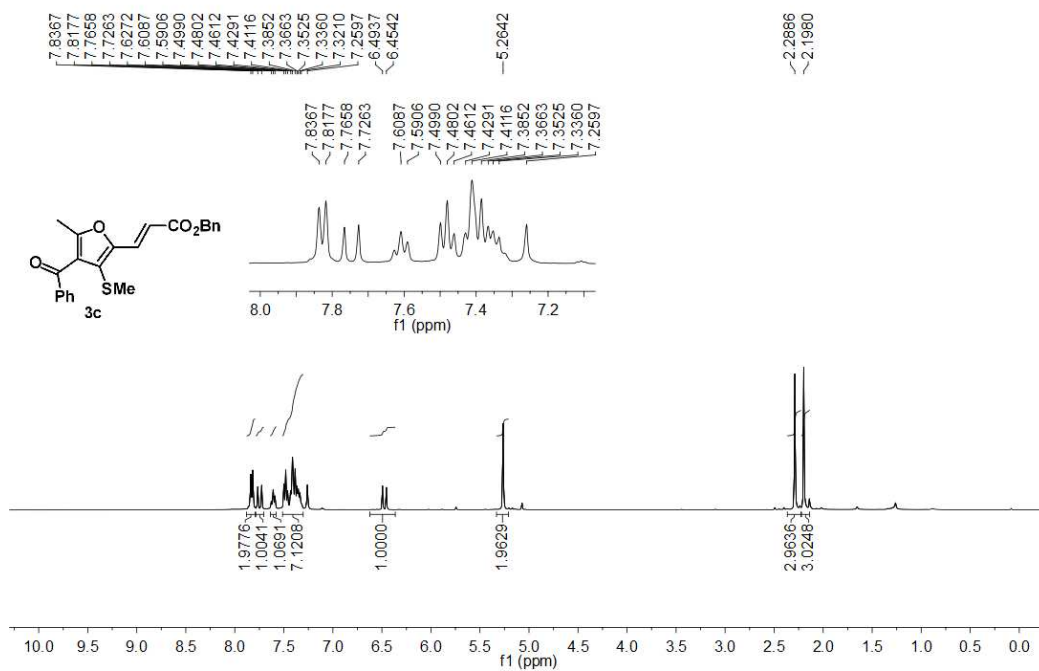


Figure S43. ^1H NMR spectrum of compound **3c** (CDCl_3 , 25 °C, 400 MHz).

WQN-1045W

^{13}C NMR in CDCl_3 (100 MHz)

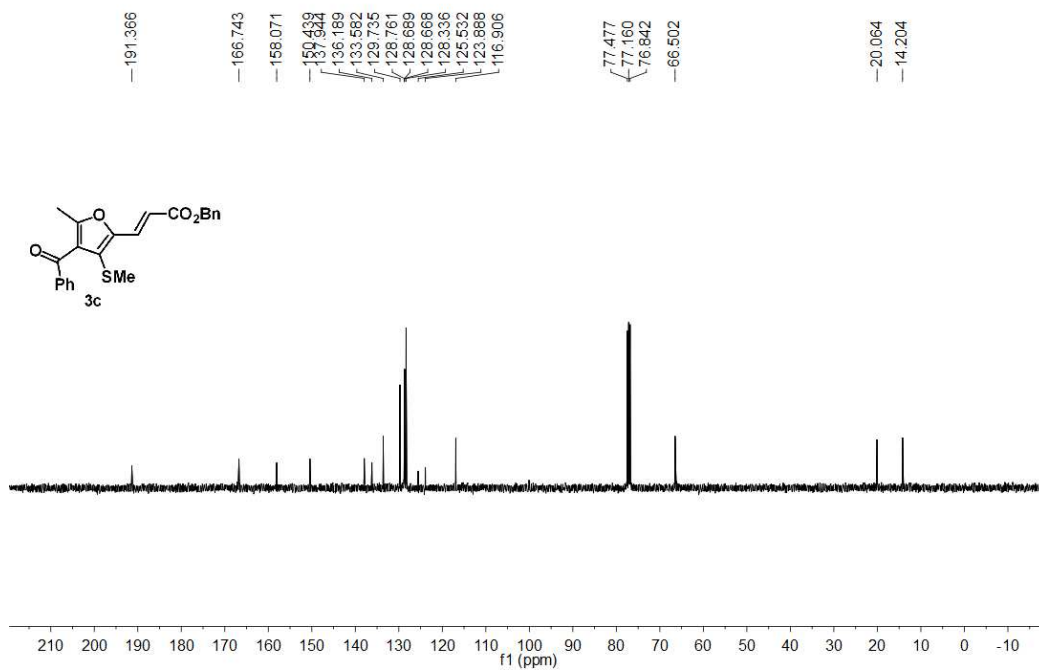


Figure S44. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3c** (CDCl_3 , 25 °C, 100 MHz).

wqn-994w

^1H NMR in CDCl_3 (400 MHz)

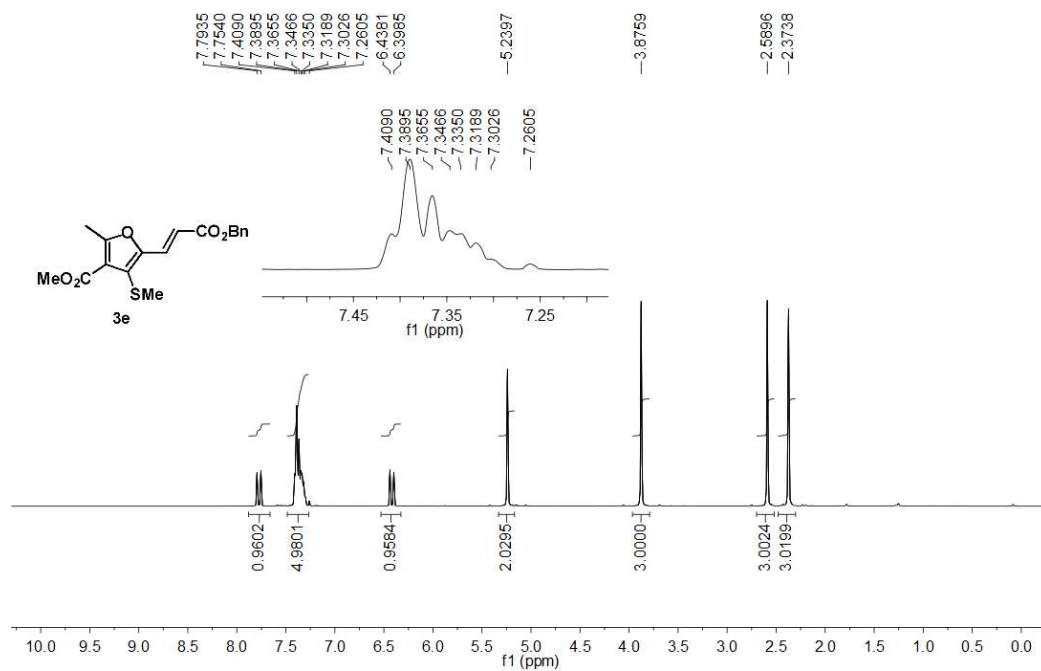


Figure S45. ^1H NMR spectrum of compound **3e** (CDCl_3 , 25 °C, 400 MHz).

WQN-994W

^{13}C NMR in CDCl_3 (100 MHz)

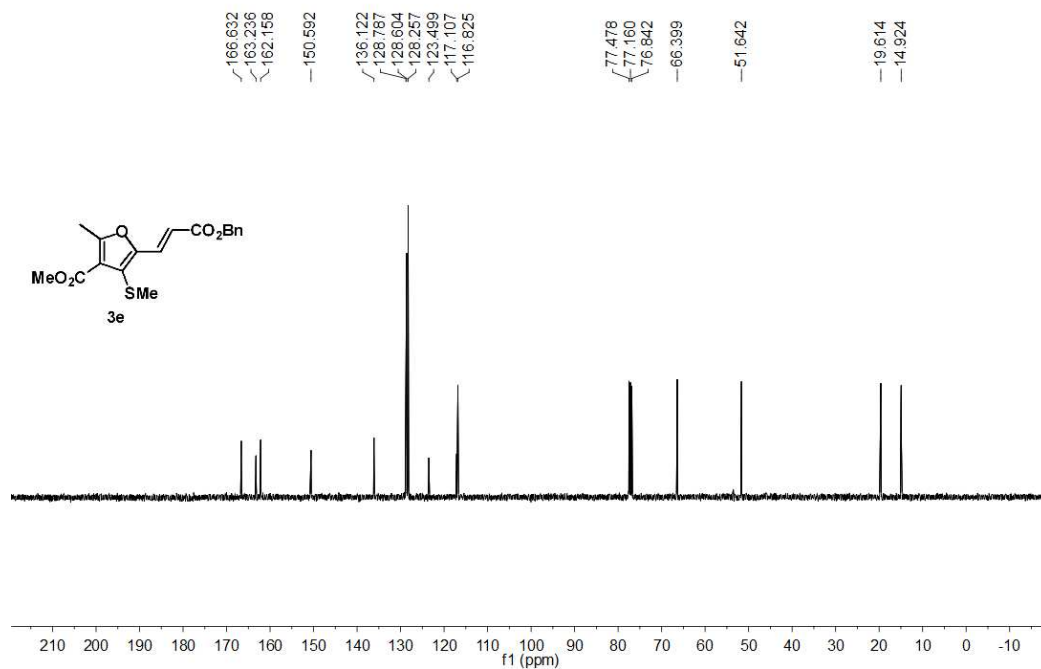


Figure S46. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3e** (CDCl_3 , 25 °C, 100 MHz).

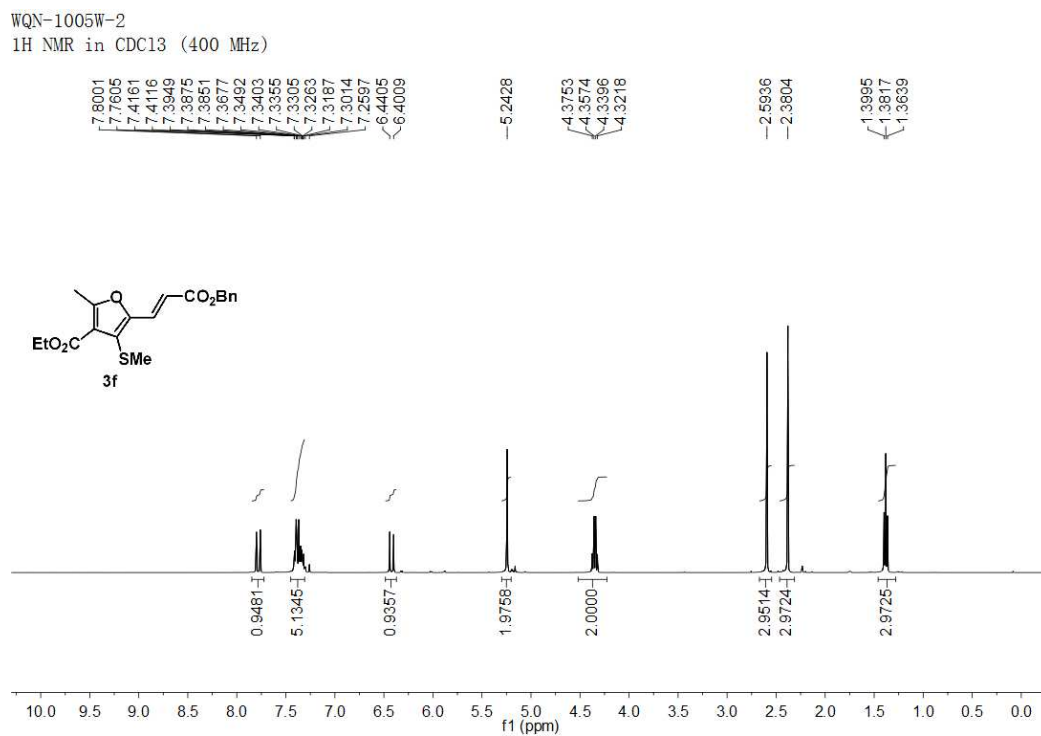


Figure S47. ¹H NMR spectrum of compound **3f** (CDCl₃, 25 °C, 400 MHz).

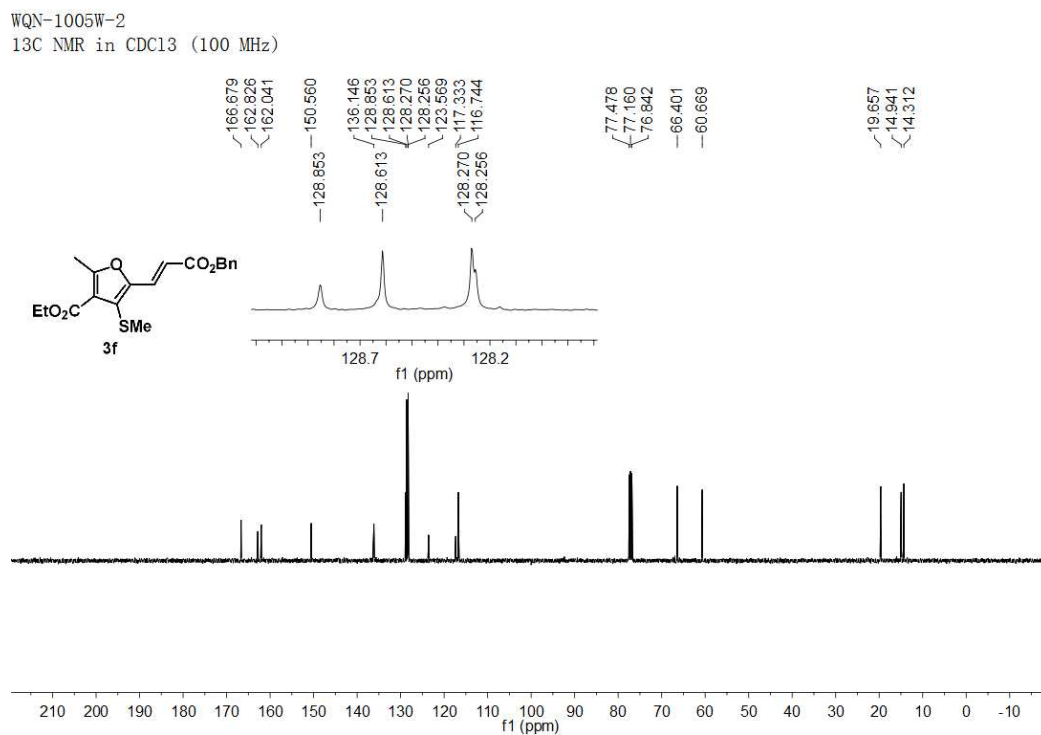


Figure S48. ¹³C{¹H} NMR spectrum of compound **3f** (CDCl₃, 25 °C, 100 MHz).

WQN-1014W

^1H NMR in CDCl_3 (400 MHz)

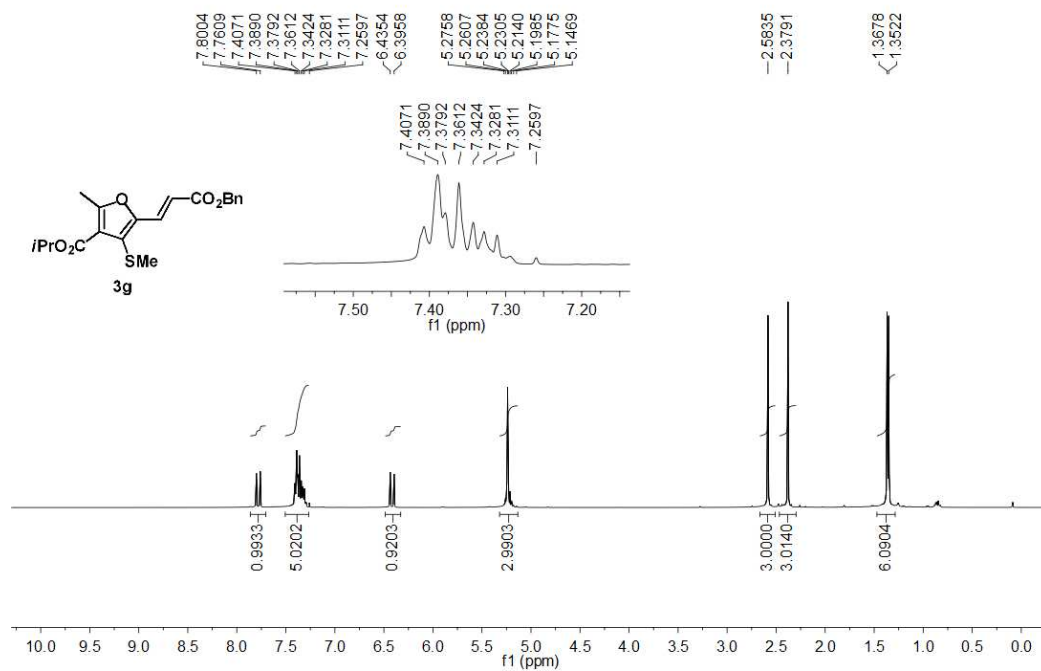


Figure S49. ^1H NMR spectrum of compound **3g** (CDCl_3 , 25 °C, 400 MHz).

WQN-1014W

^{13}C NMR in CDCl_3 (100 MHz)

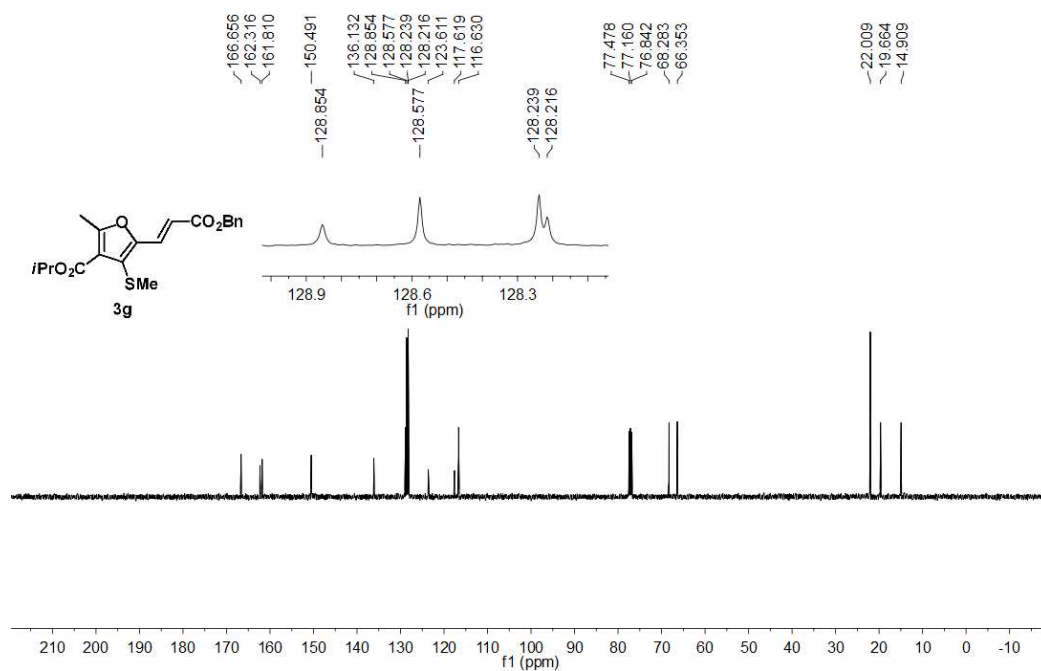


Figure S50. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3g** (CDCl_3 , 25 °C, 100 MHz).

WQN-1020W-1

PROTON CDC13 {D:\NMR400\203} nmr 49

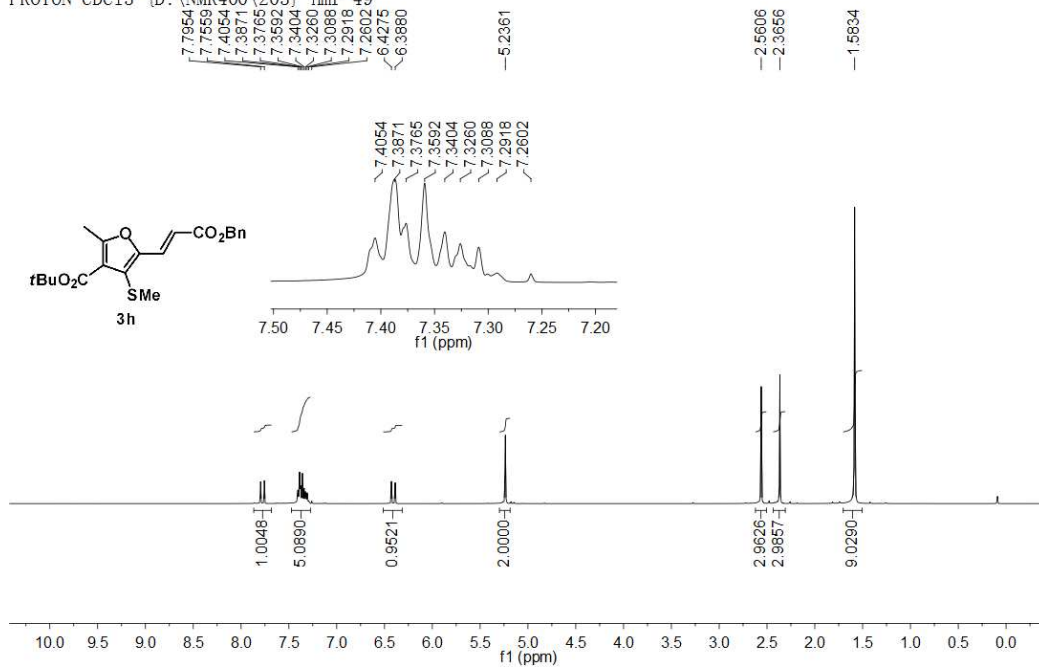


Figure S51. ¹H NMR spectrum of compound **3h** (CDCl₃, 25 °C, 400 MHz).

WQN-1020W-1

¹³C NMR in CDCl3 (100 MHz)

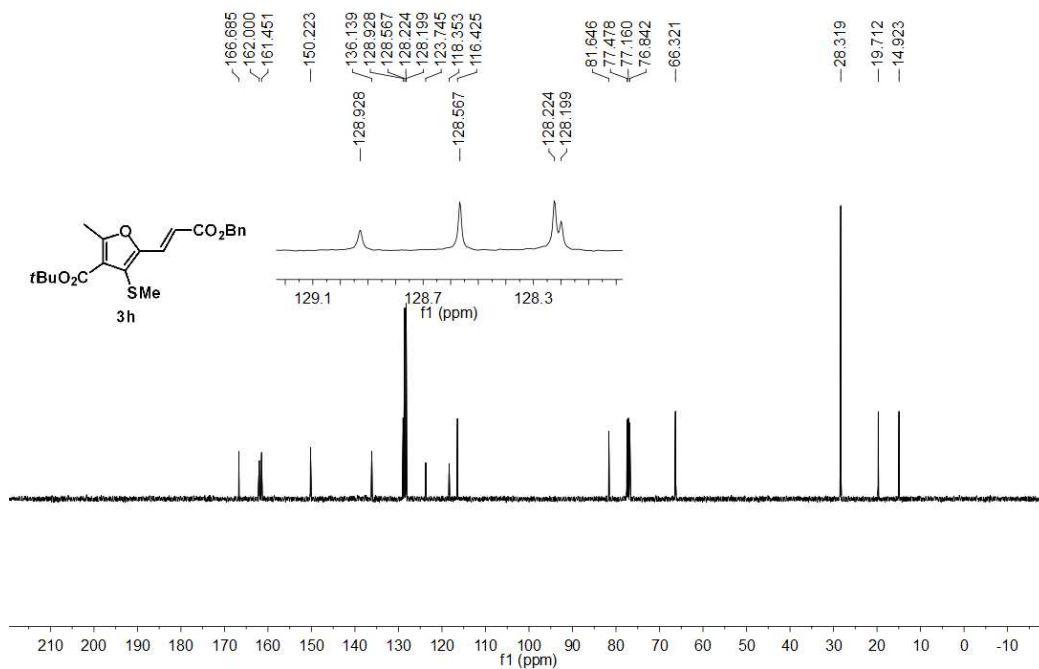


Figure S52. ¹³C{¹H} NMR spectrum of compound **3h** (CDCl₃, 25 °C, 100 MHz).

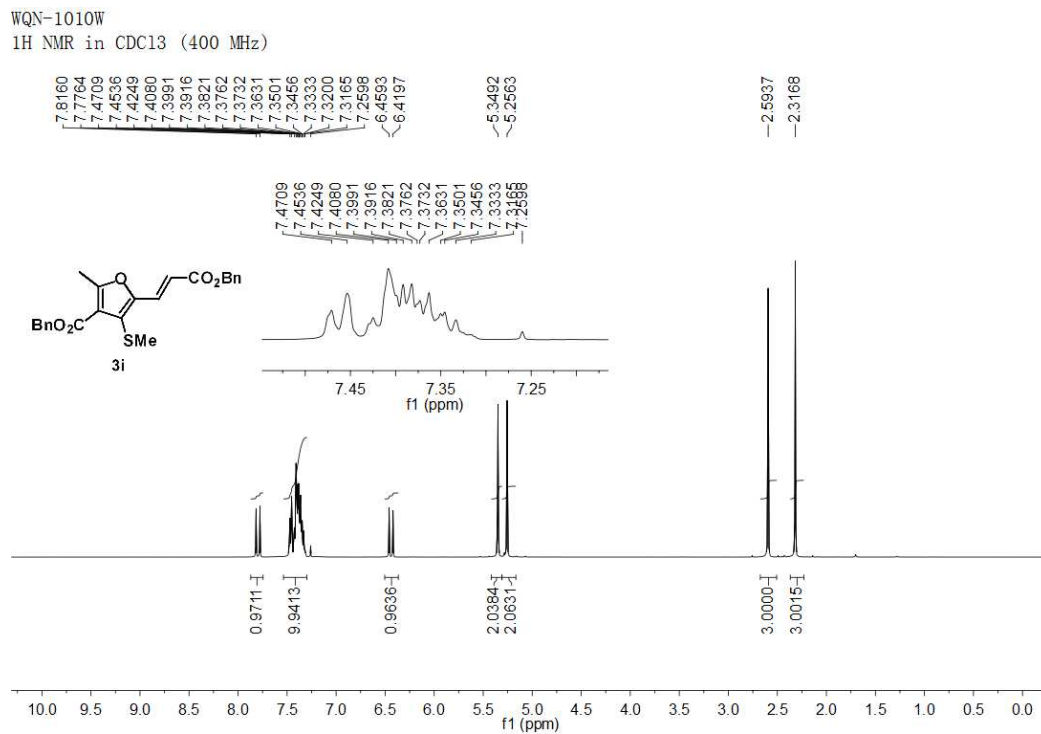


Figure S53. ¹H NMR spectrum of compound **3i** (CDCl₃, 25 °C, 400 MHz).

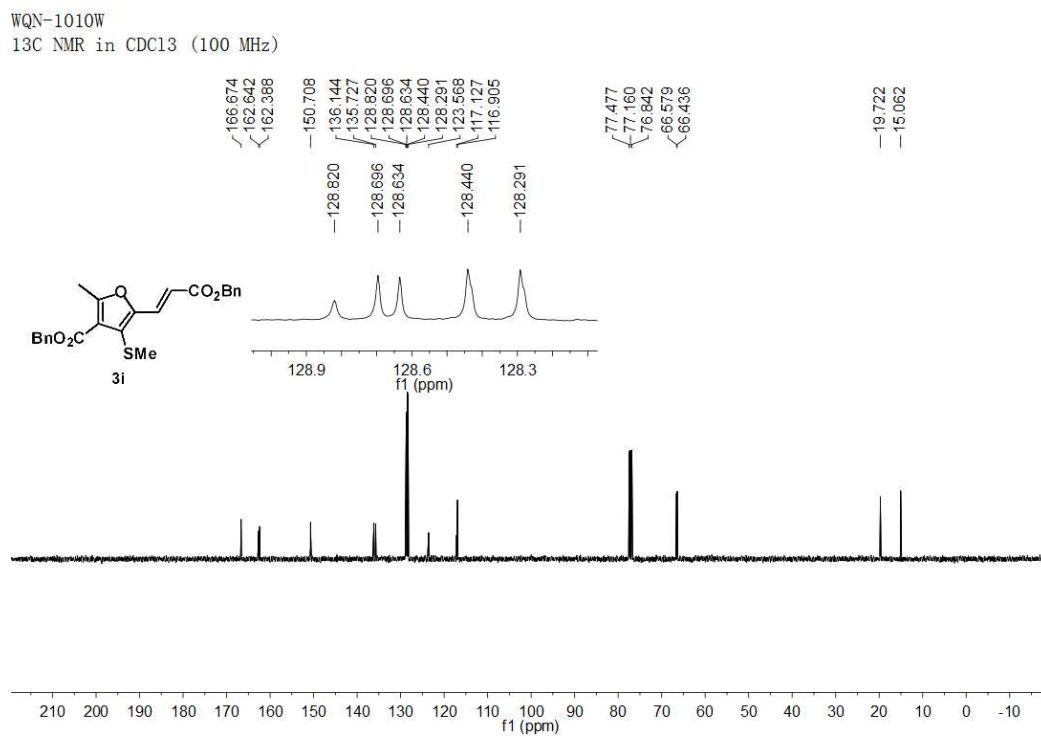


Figure S54. ¹³C{¹H} NMR spectrum of compound **3i** (CDCl₃, 25 °C, 100 MHz).

WQN-908W

^1H NMR in CDCl_3 (400 MHz)

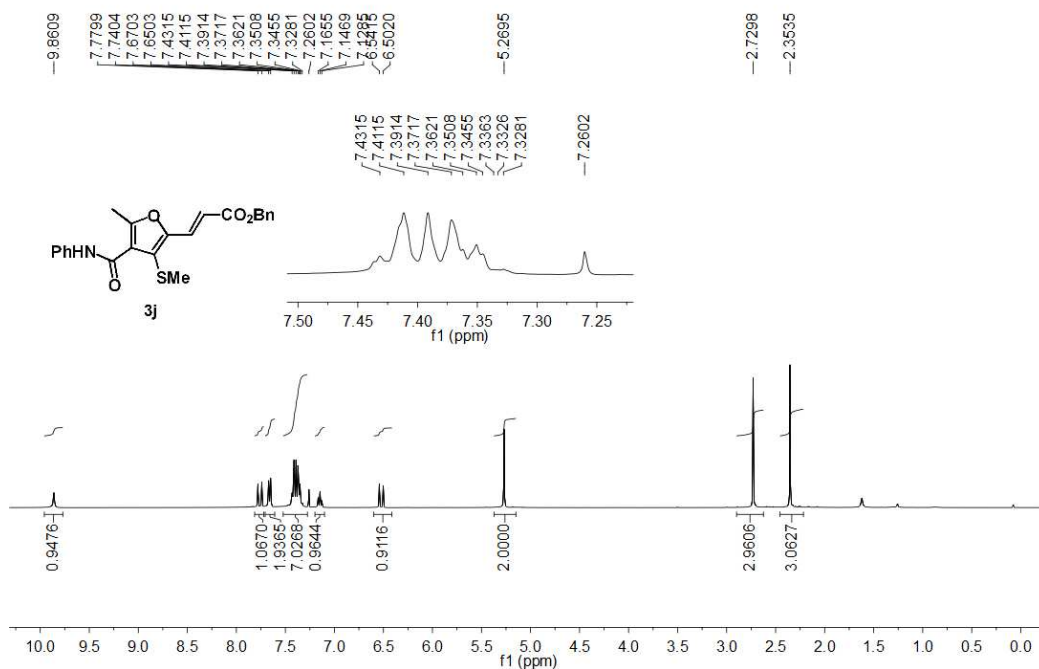


Figure S55. ^1H NMR spectrum of compound **3j** (CDCl_3 , 25 °C, 400 MHz).

WQN-908W

^{13}C NMR in CDCl_3 (100 MHz)

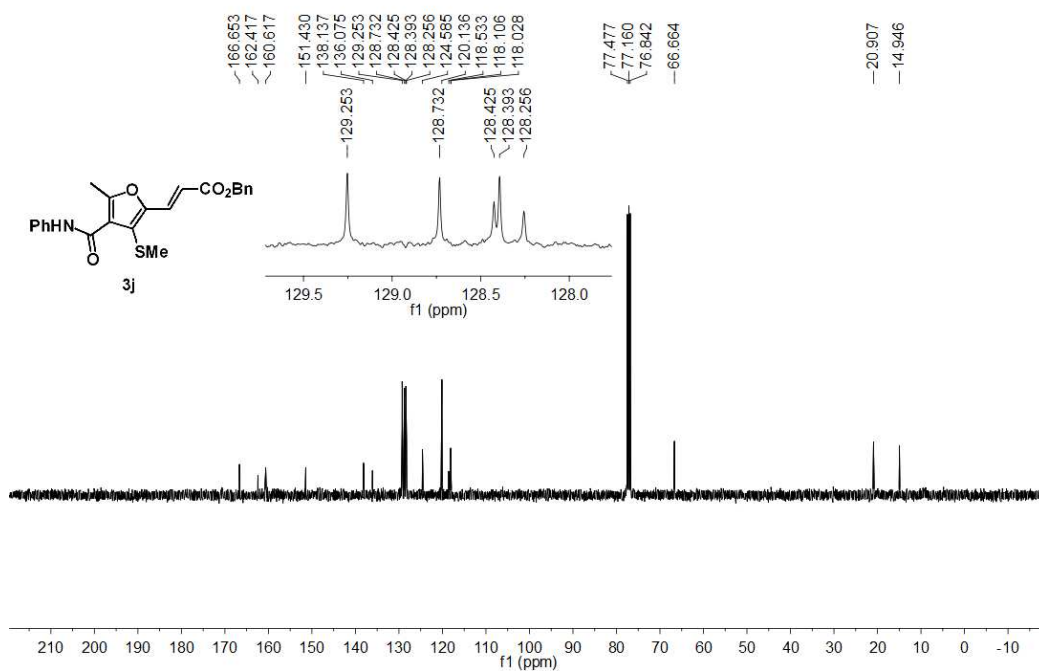


Figure S56. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3j** (CDCl_3 , 25 °C, 100 MHz).

WQN-1032W-3

¹H NMR in CDCl₃ (400 MHz)

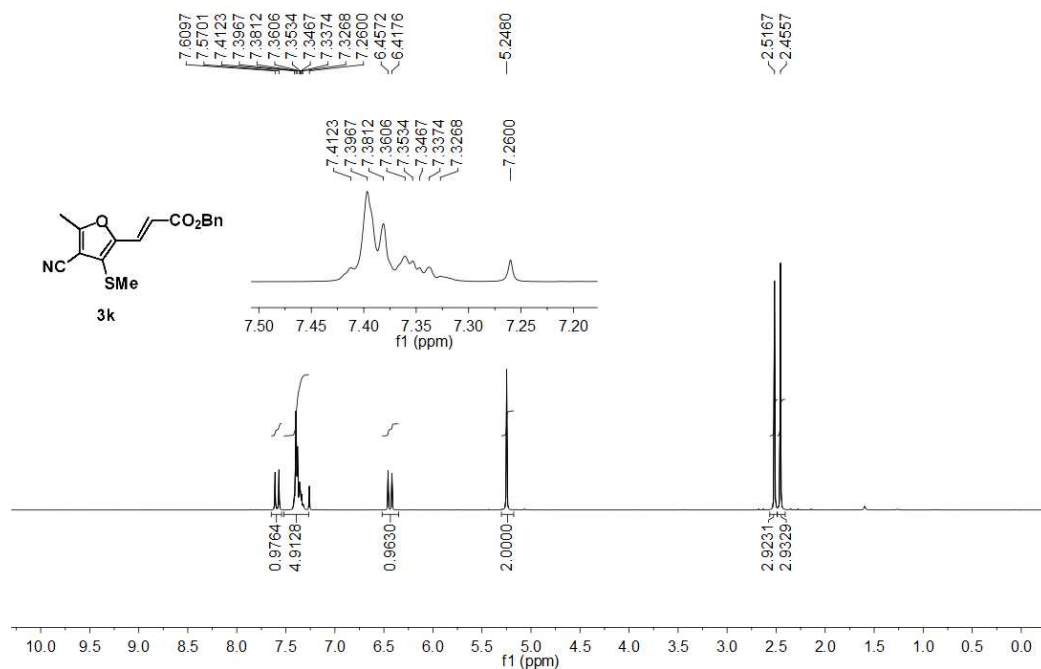


Figure S57. ¹H NMR spectrum of compound **3k** (CDCl₃, 25 °C, 400 MHz).

WQN-1032W-3

¹³C NMR in CDCl₃ (100 MHz)

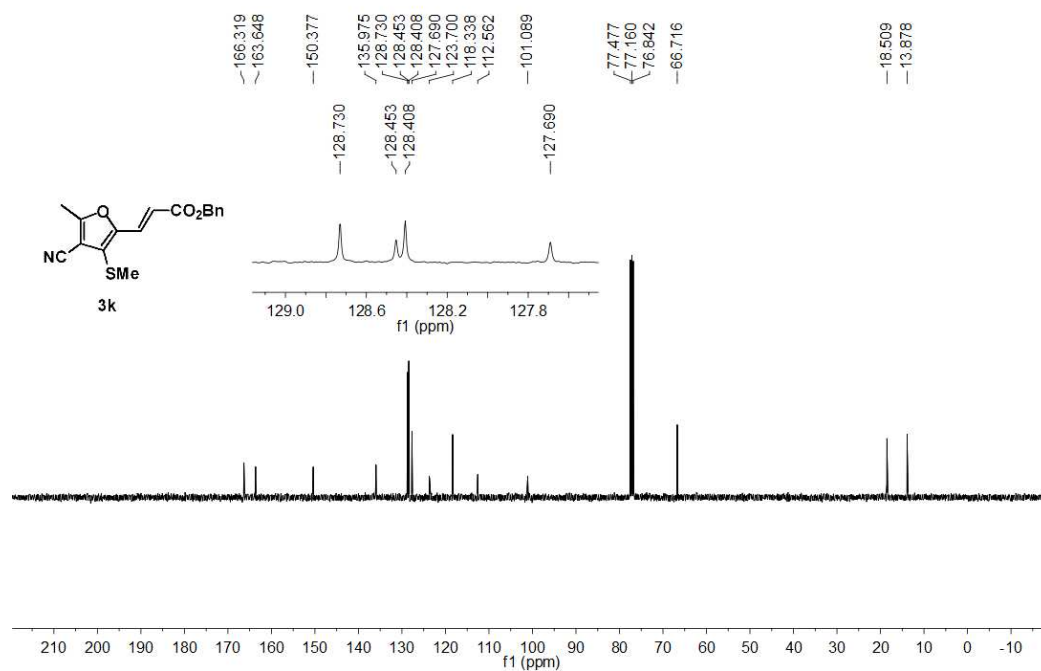


Figure S58. ¹³C{¹H} NMR spectrum of compound **3k** (CDCl₃, 25 °C, 100 MHz).

wqn-1076w
¹H NMR in CDCl₃ (400 MHz)

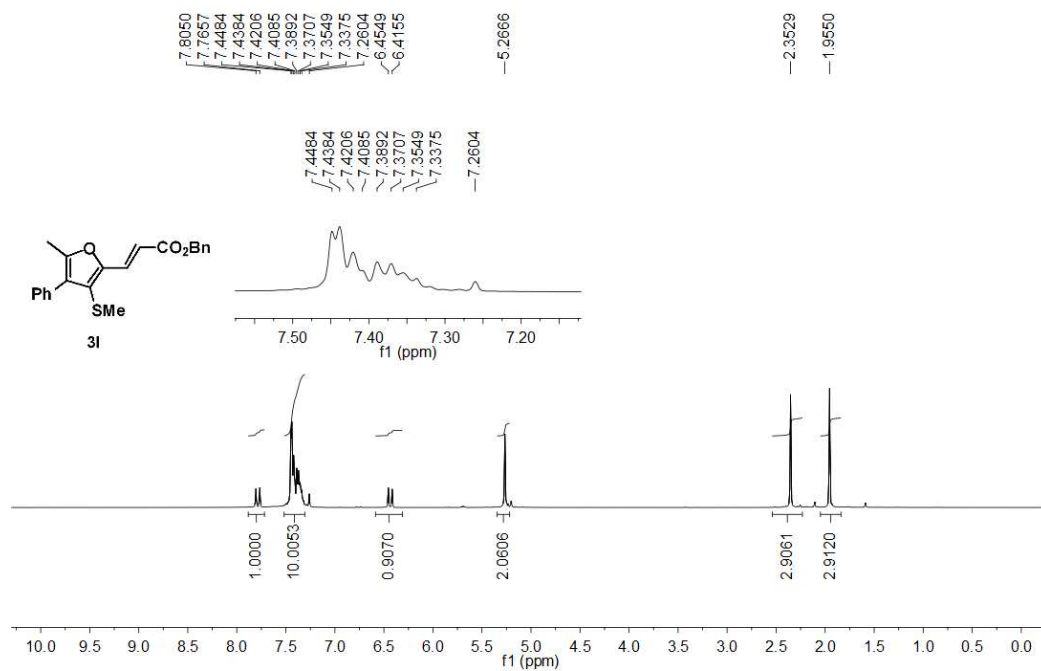


Figure S59. ¹H NMR spectrum of compound **3I** (CDCl₃, 25 °C, 400 MHz).

wqn-1076w
¹³C NMR in CDCl₃ (100 MHz)

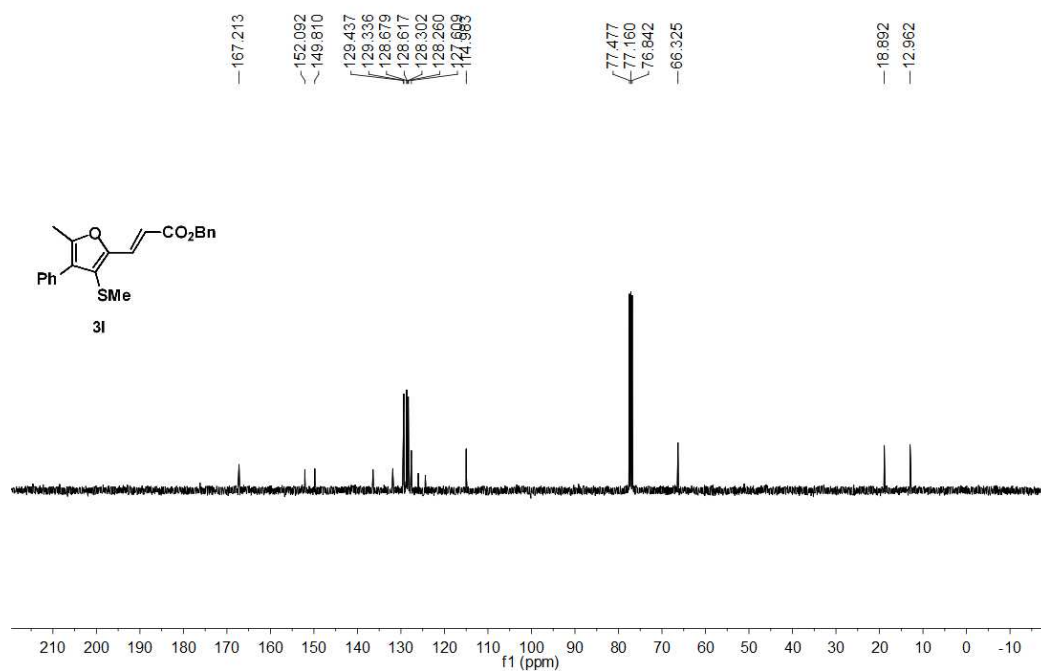


Figure S60. ¹³C{¹H} NMR spectrum of compound **3I** (CDCl₃, 25 °C, 100 MHz).

WQN-1046W

^1H NMR in CDCl_3 (400 MHz)

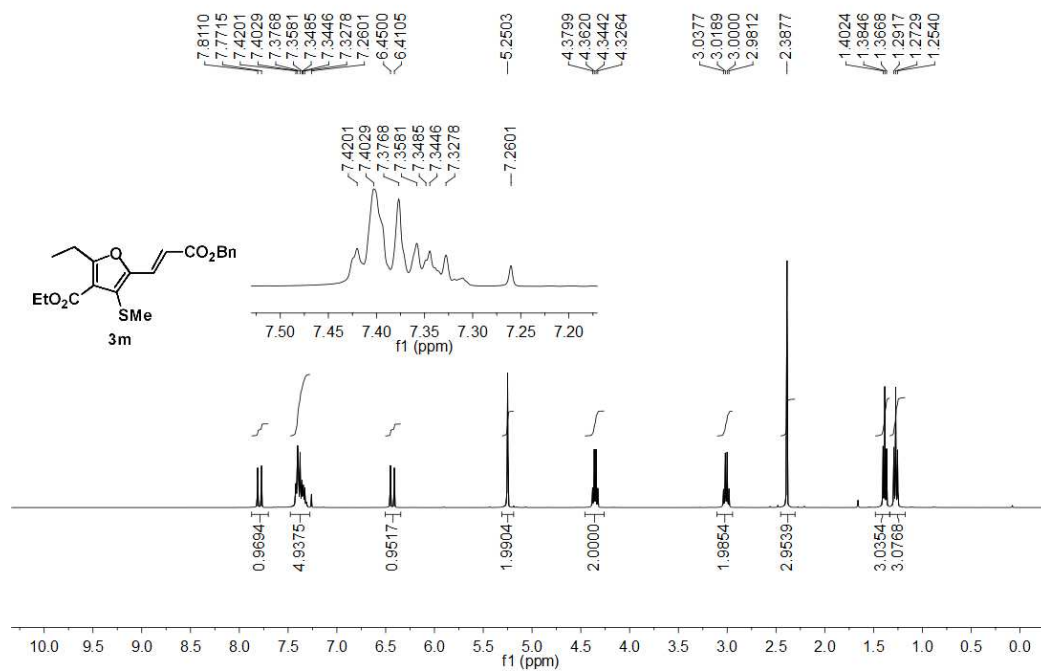


Figure S61. ^1H NMR spectrum of compound **3m** (CDCl_3 , 25 $^\circ\text{C}$, 400 MHz).

WQN-1046W

^{13}C NMR in CDCl_3 (100 MHz)

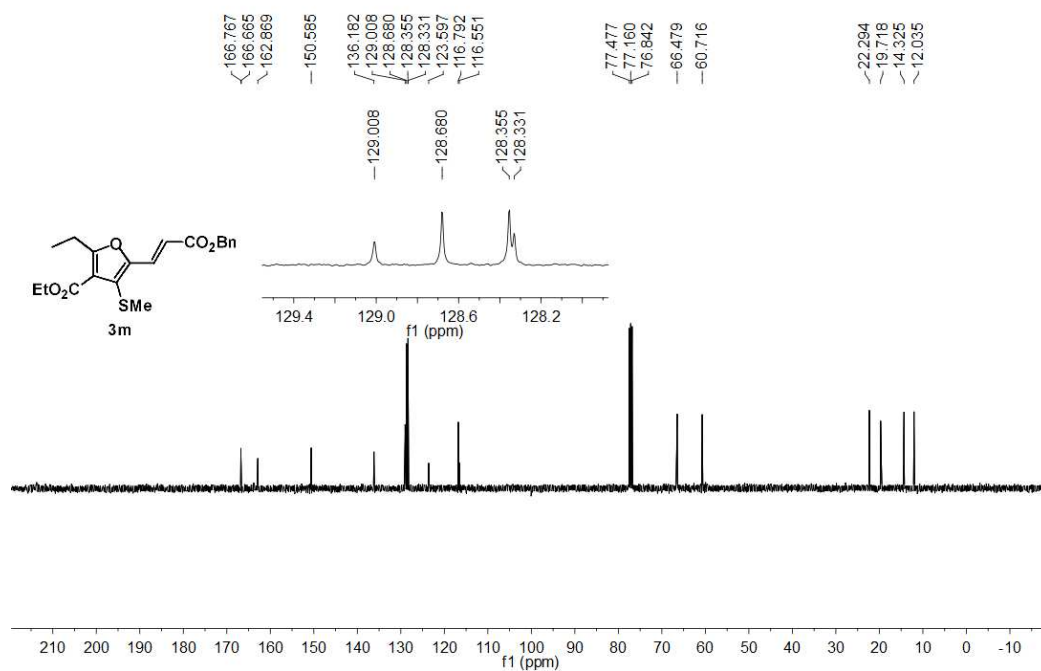


Figure S62. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3m** (CDCl_3 , 25 $^\circ\text{C}$, 100 MHz).

WQN-1048W

¹H NMR in CDCl₃ (400 MHz)

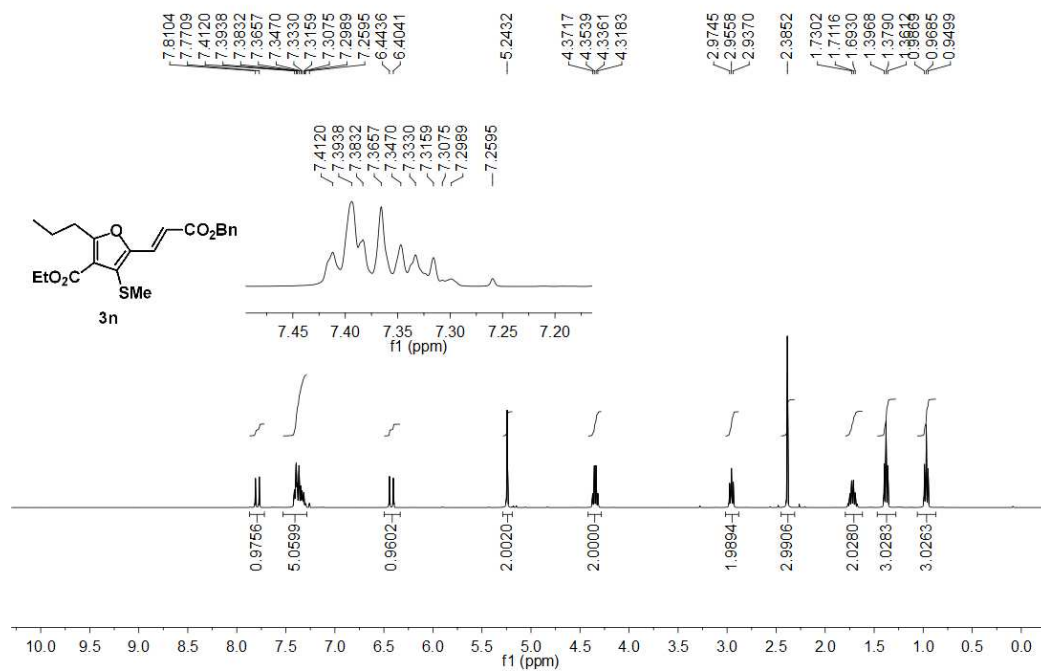


Figure S63. ¹H NMR spectrum of compound **3n** (CDCl₃, 25 °C, 400 MHz).

WQN-1048W

¹³C NMR in CDCl₃ (100 MHz)

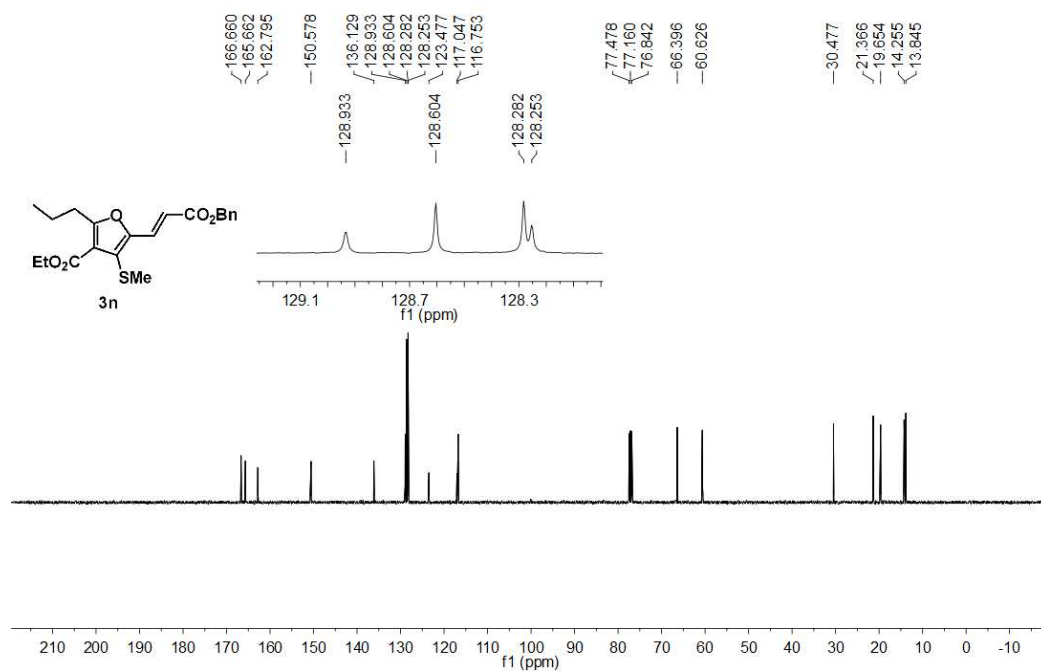


Figure S64. ¹³C{¹H} NMR spectrum of compound **3n** (CDCl₃, 25 °C, 100 MHz).

WQN-1162W

^1H NMR in CDCl_3 (400 MHz)

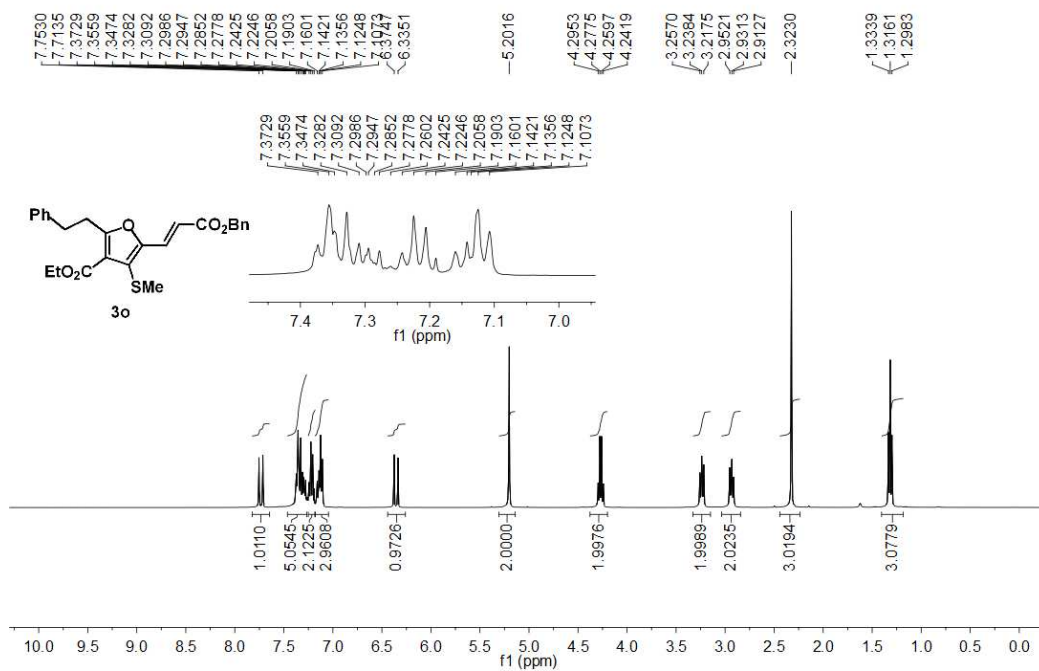


Figure S65. ^1H NMR spectrum of compound **3o** (CDCl_3 , 25 °C, 400 MHz).

WQN-1162W

^{13}C NMR in CDCl_3 (100 MHz)

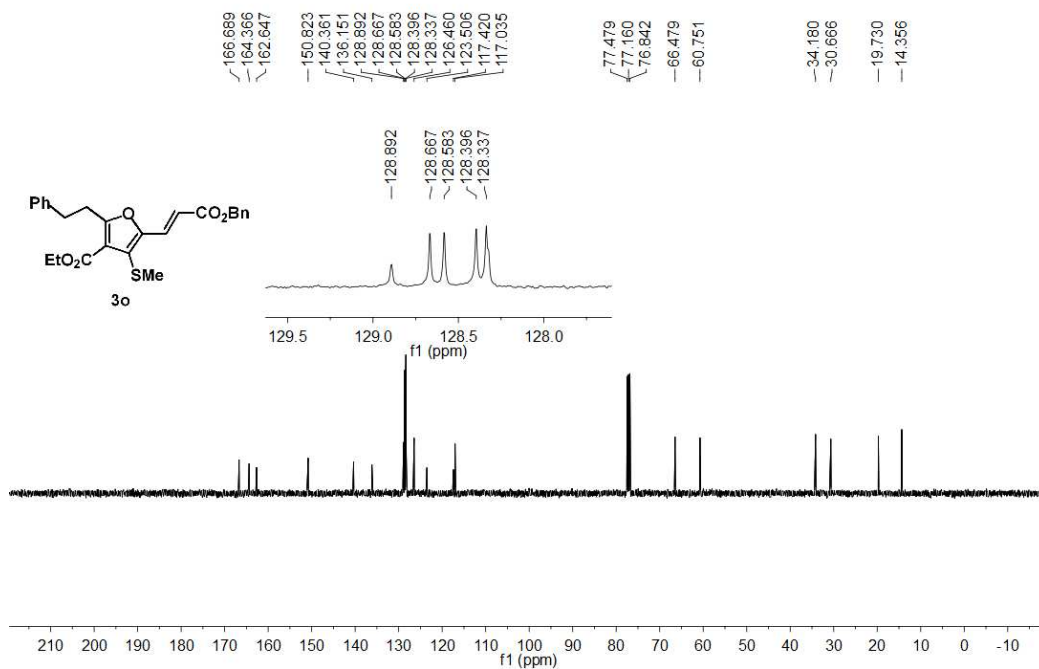


Figure S66. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3o** (CDCl_3 , 25 °C, 100 MHz).

WQN-1029W

^1H NMR in CDCl_3 (400 MHz)

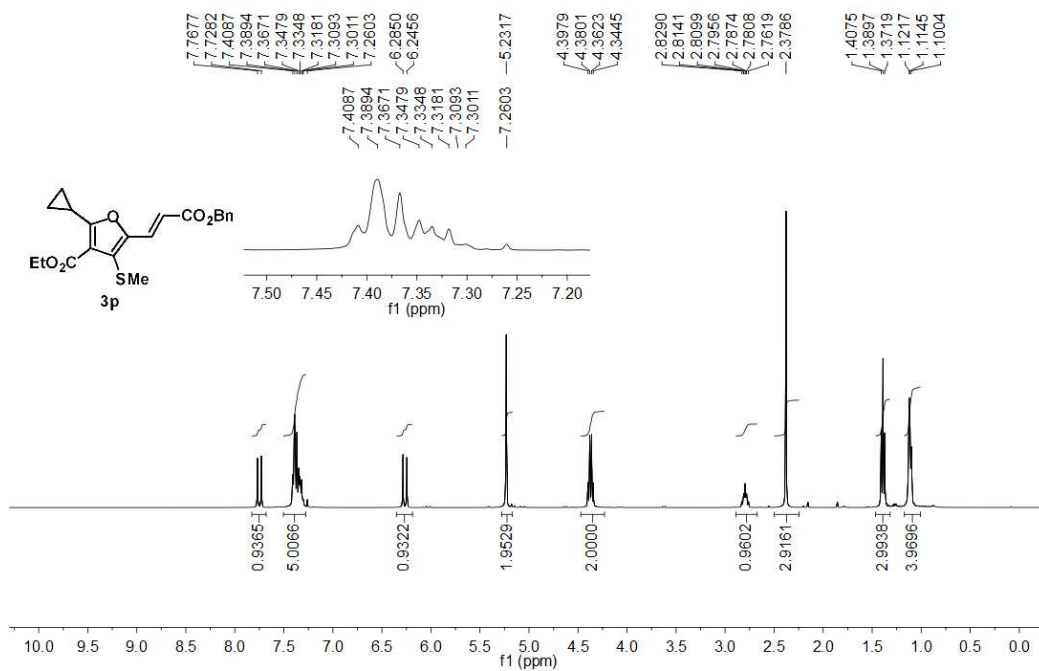


Figure S67. ^1H NMR spectrum of compound **3p** (CDCl_3 , 25 °C, 400 MHz).

WQN-1029W

^{13}C NMR in CDCl_3 (100 MHz)

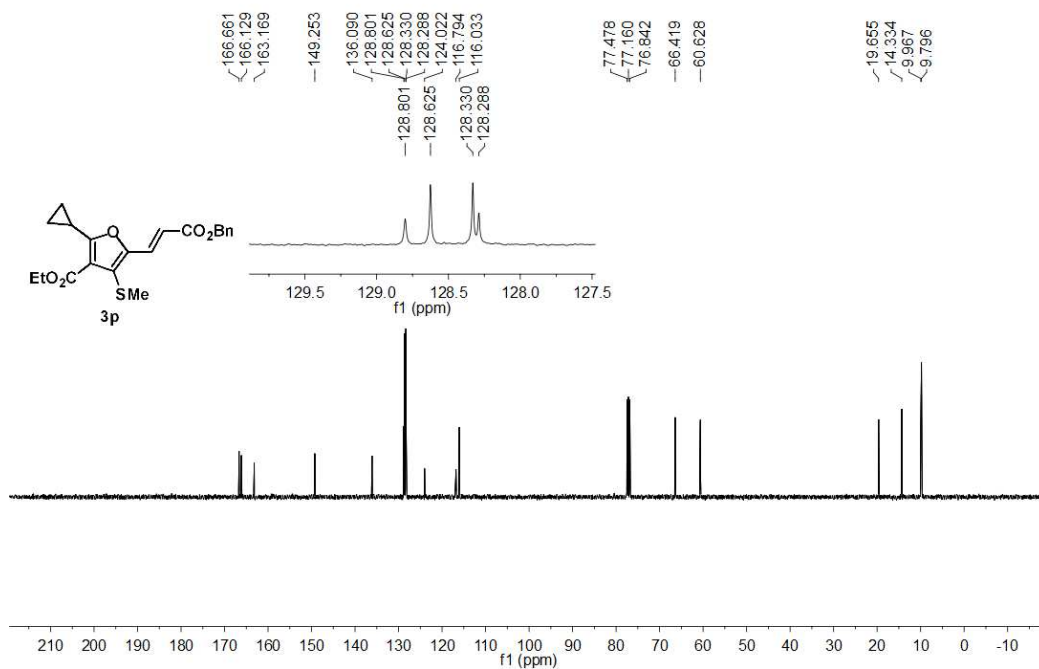


Figure S68. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3p** (CDCl_3 , 25 °C, 100 MHz).

WQN-1072W

^1H NMR in CDCl_3 (400 MHz)

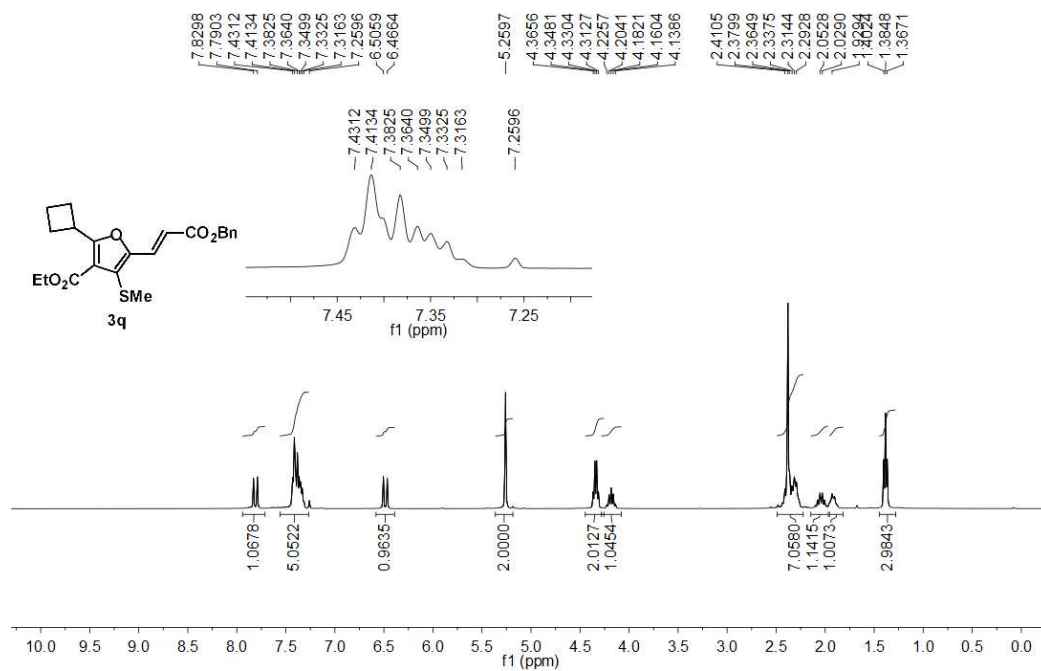


Figure S69. ^1H NMR spectrum of compound **3q** (CDCl_3 , 25 °C, 400 MHz).

WQN-1072W

^{13}C NMR in CDCl_3 (100 MHz)

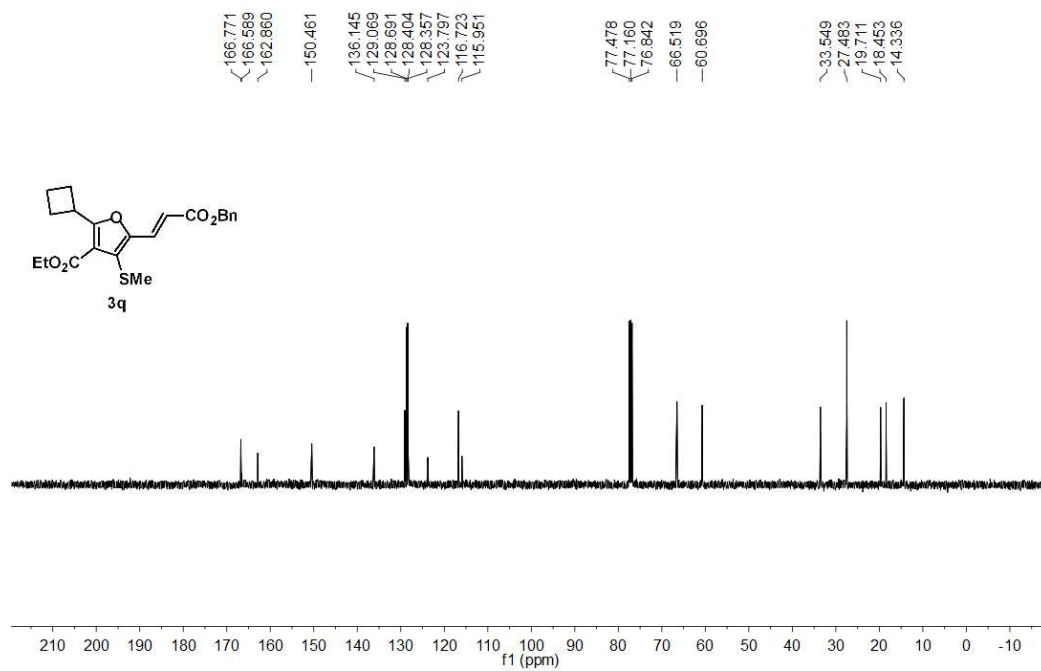


Figure S70. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3q** (CDCl_3 , 25 °C, 100 MHz).

WQN-1037W

^1H NMR in CDCl_3 (400 MHz)

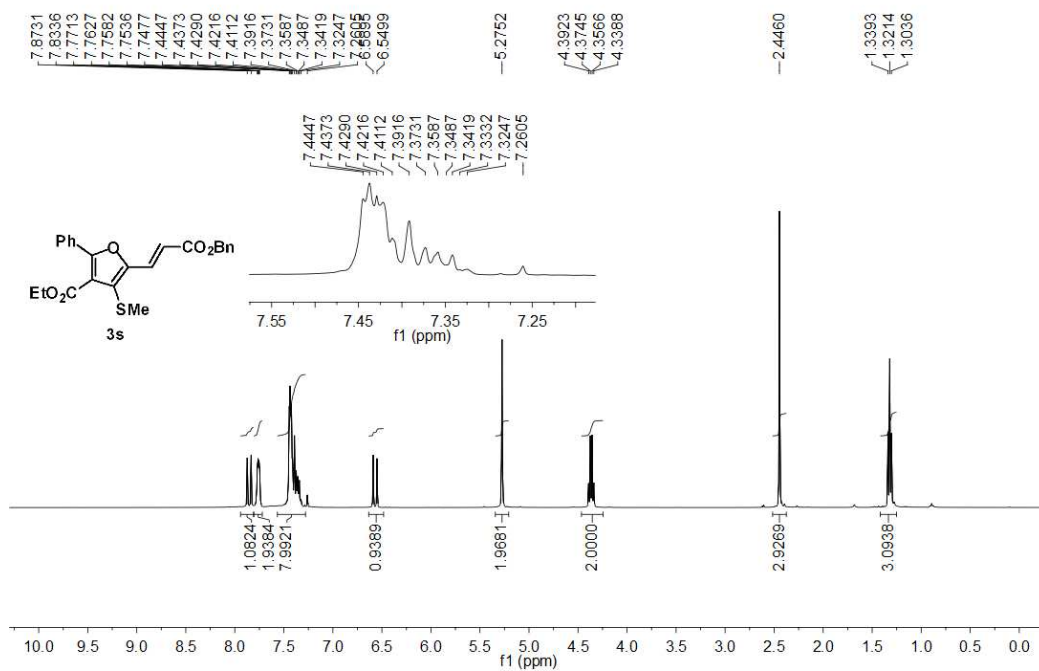


Figure S71. ^1H NMR spectrum of compound **3s** (CDCl_3 , 25 °C, 400 MHz).

WQN-1037W

^{13}C NMR in CDCl_3 (100 MHz)

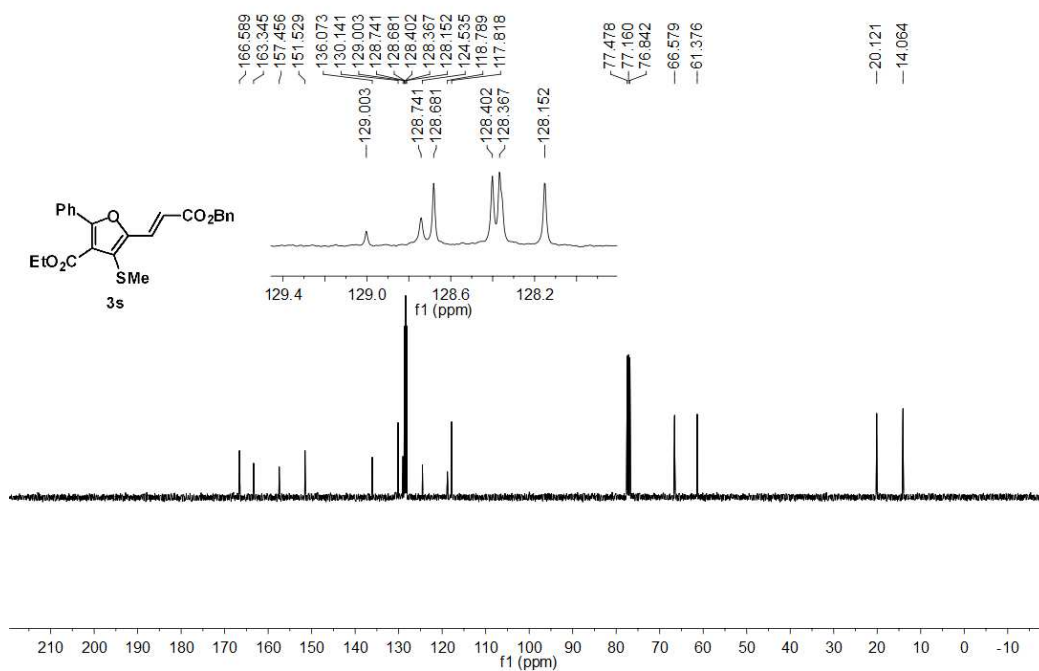


Figure S72. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3s** (CDCl_3 , 25 °C, 100 MHz).

WQN-1053W

^1H NMR in CDCl_3 (400 MHz)

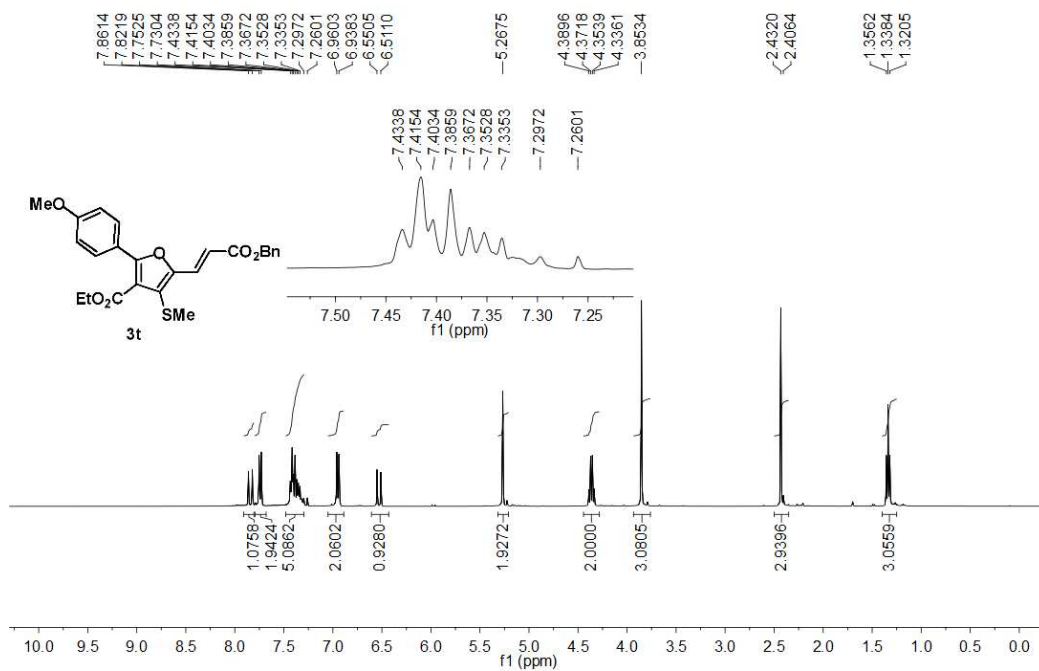


Figure S73. ^1H NMR spectrum of compound **3t** (CDCl_3 , 25 °C, 400 MHz).

WQN-1053W

^{13}C NMR in CDCl_3 (100 MHz)

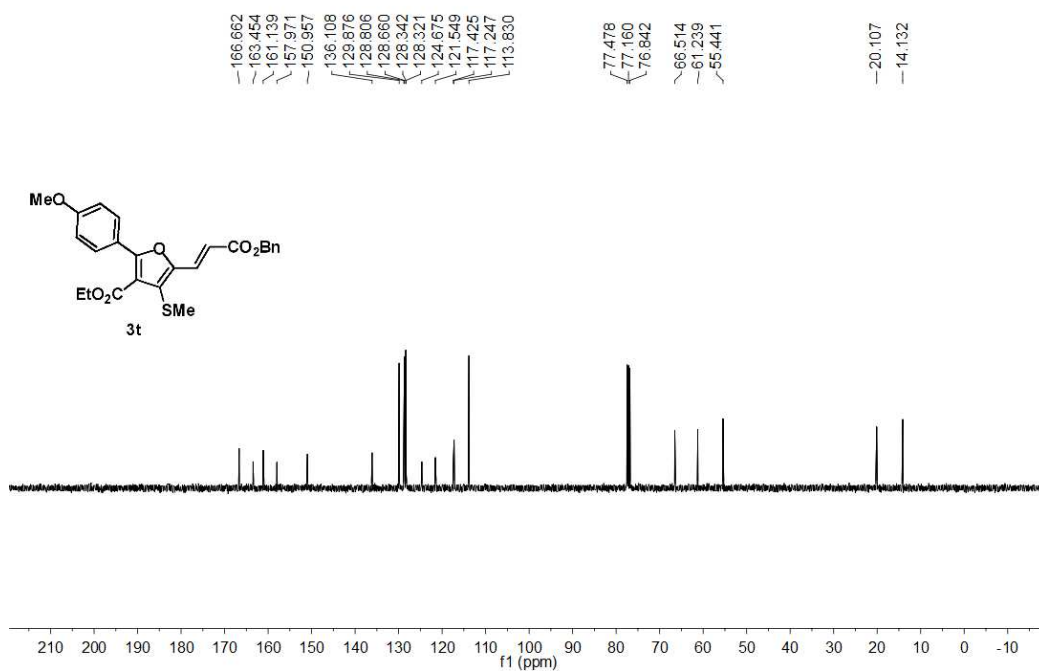


Figure S74. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3t** (CDCl_3 , 25 °C, 100 MHz).

WQN-1056W

^1H NMR in CDCl_3 (400 MHz)

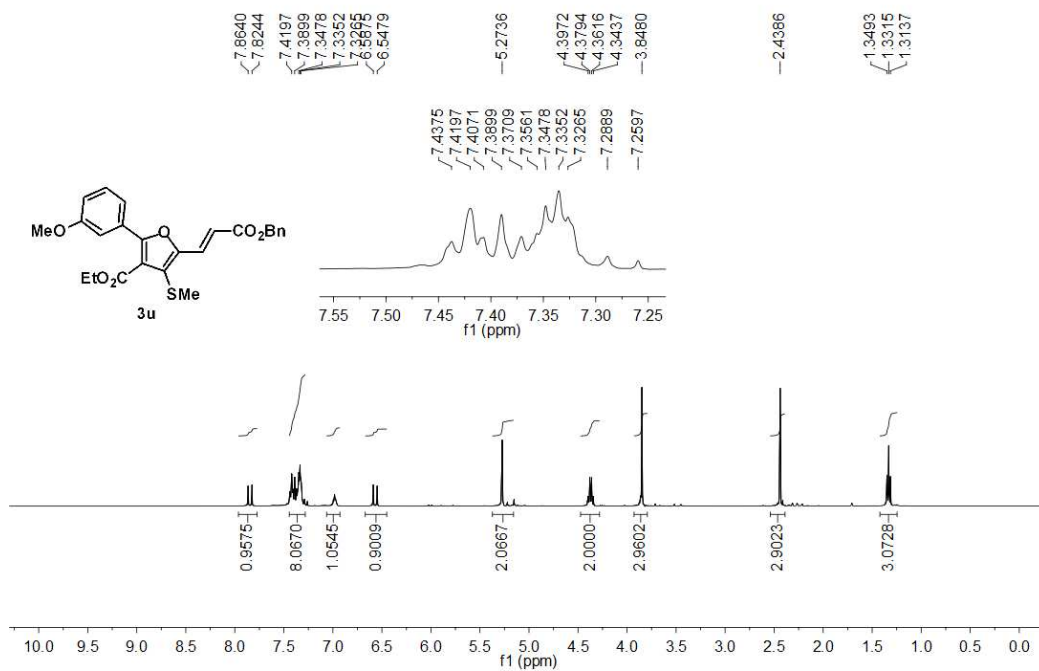


Figure S75. ^1H NMR spectrum of compound **3u** (CDCl_3 , 25 °C, 400 MHz).

WQN-1056W

^{13}C NMR in CDCl_3 (100 MHz)

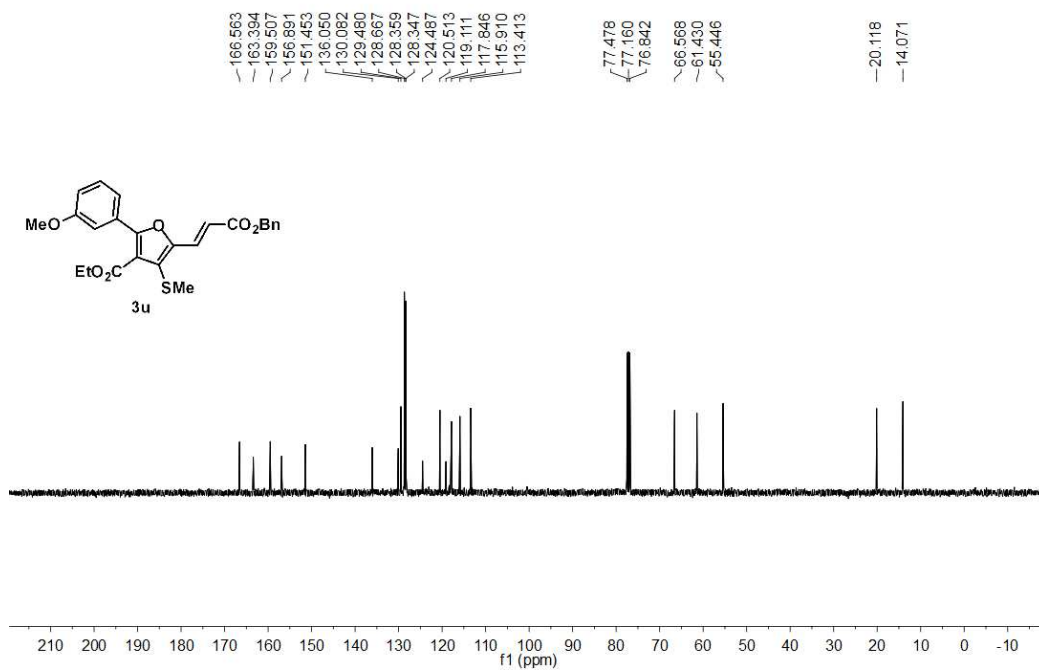


Figure S76. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3u** (CDCl_3 , 25 °C, 100 MHz).

WQN-1078W

^1H NMR in CDCl_3 (400 MHz)

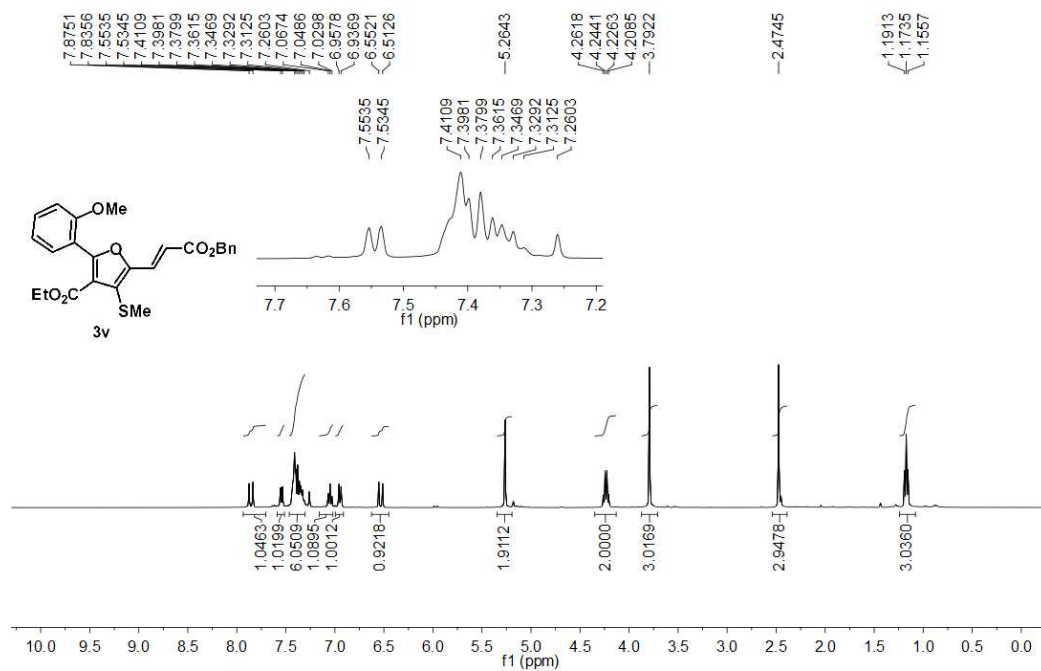


Figure S77. ^1H NMR spectrum of compound **3v** (CDCl_3 , 25 °C, 400 MHz).

WQN-1078W

^{13}C NMR in CDCl_3 (100 MHz)

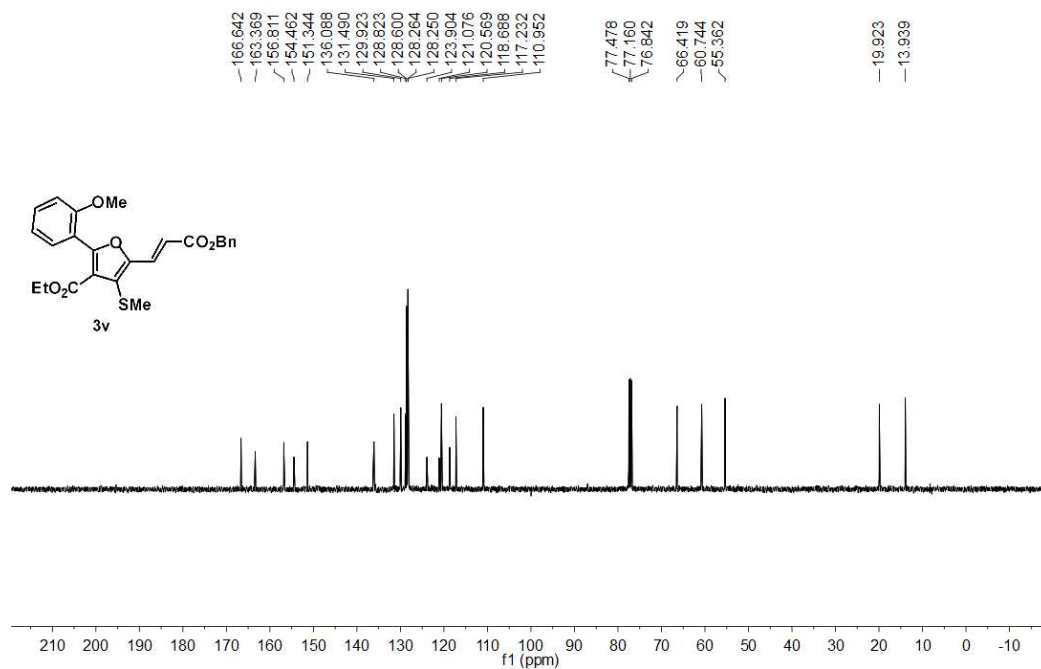


Figure S78. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3v** (CDCl_3 , 25 °C, 100 MHz).

WQN-1391W

^1H NMR in CDCl_3 (400 MHz)

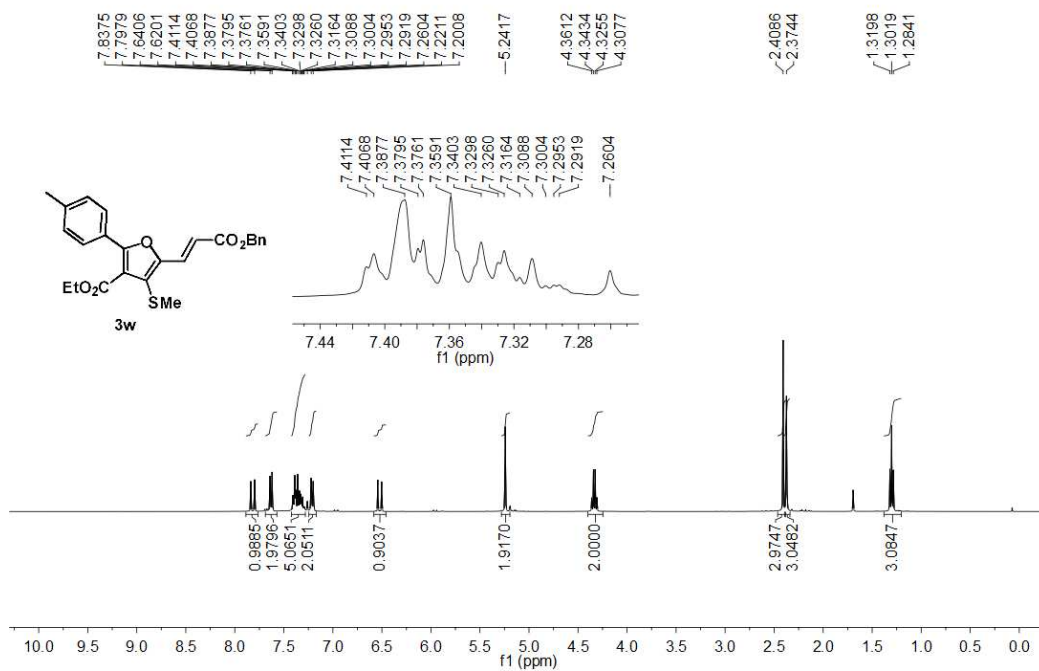


Figure S79. ^1H NMR spectrum of compound **3w** (CDCl_3 , 25 °C, 400 MHz).

WQN-1391W

^{13}C NMR in CDCl_3 (100 MHz)

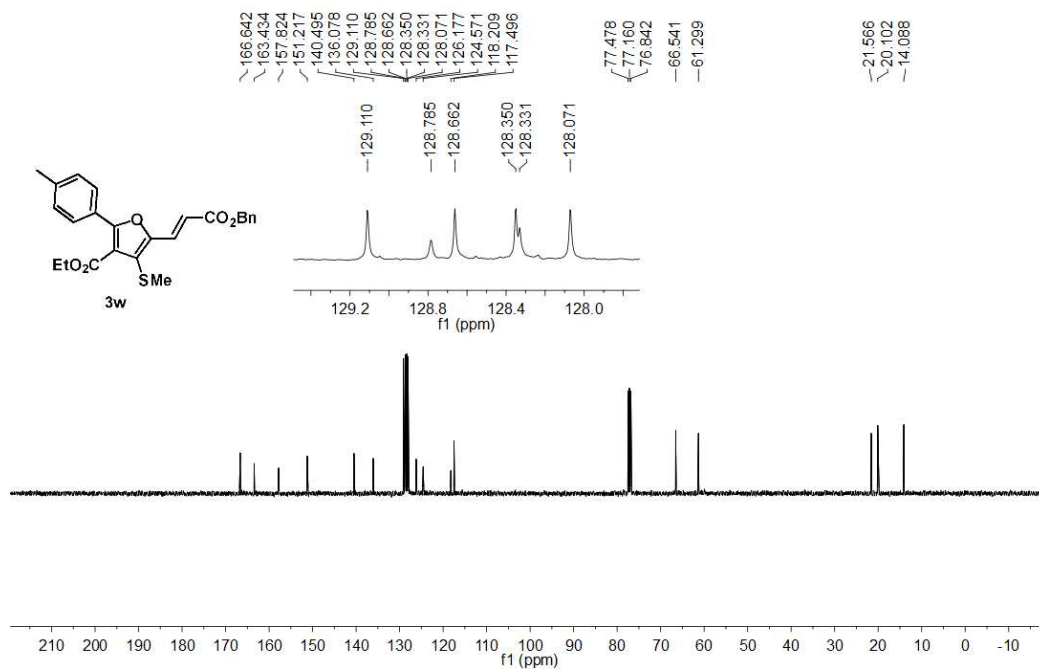


Figure S80. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3w** (CDCl_3 , 25 °C, 100 MHz).

WQN-1082W

^1H NMR in CDCl_3 (400 MHz)

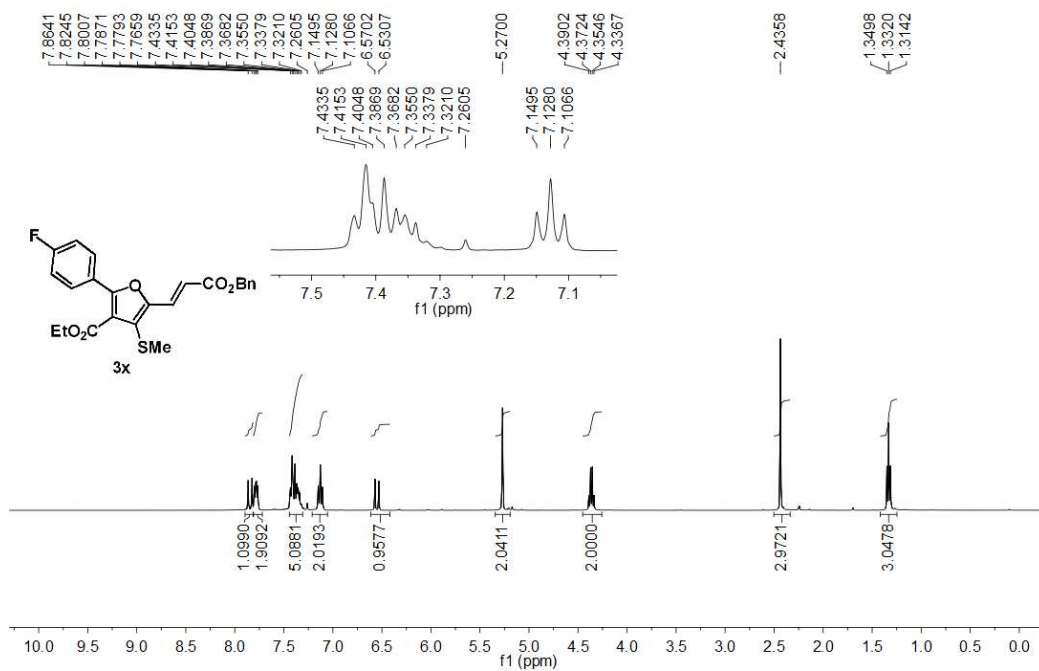


Figure S81. ^1H NMR spectrum of compound **3x** (CDCl_3 , 25 °C, 400 MHz).

WQN-1082W

^{13}C NMR in CDCl_3 (100 MHz)

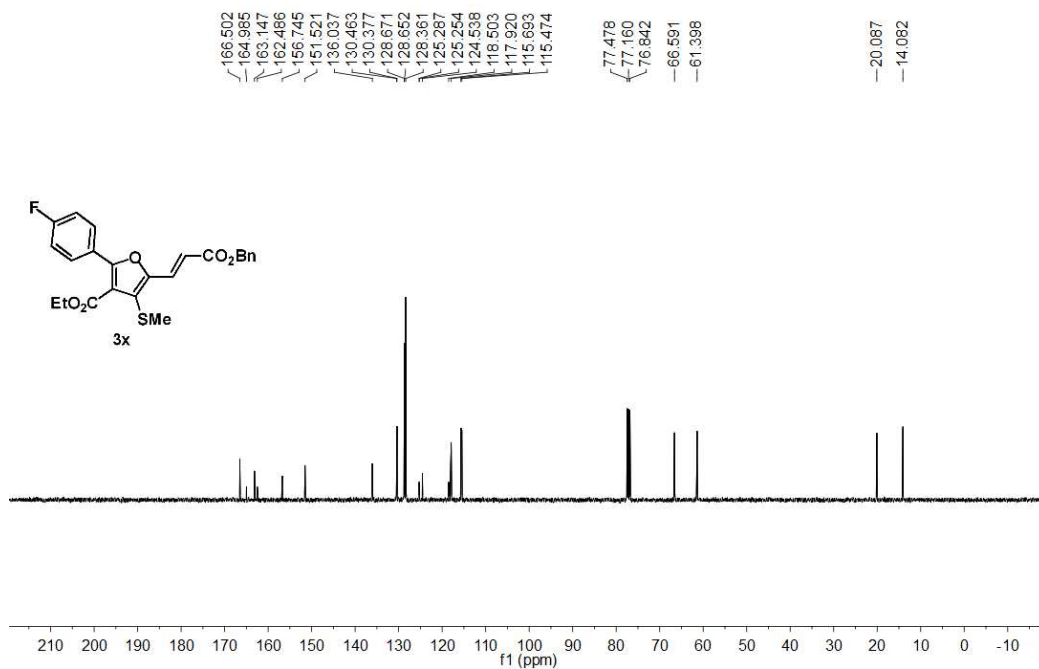


Figure S82. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3x** (CDCl_3 , 25 °C, 100 MHz).

WQN-1083W

^1H NMR in CDCl_3 (400 MHz)

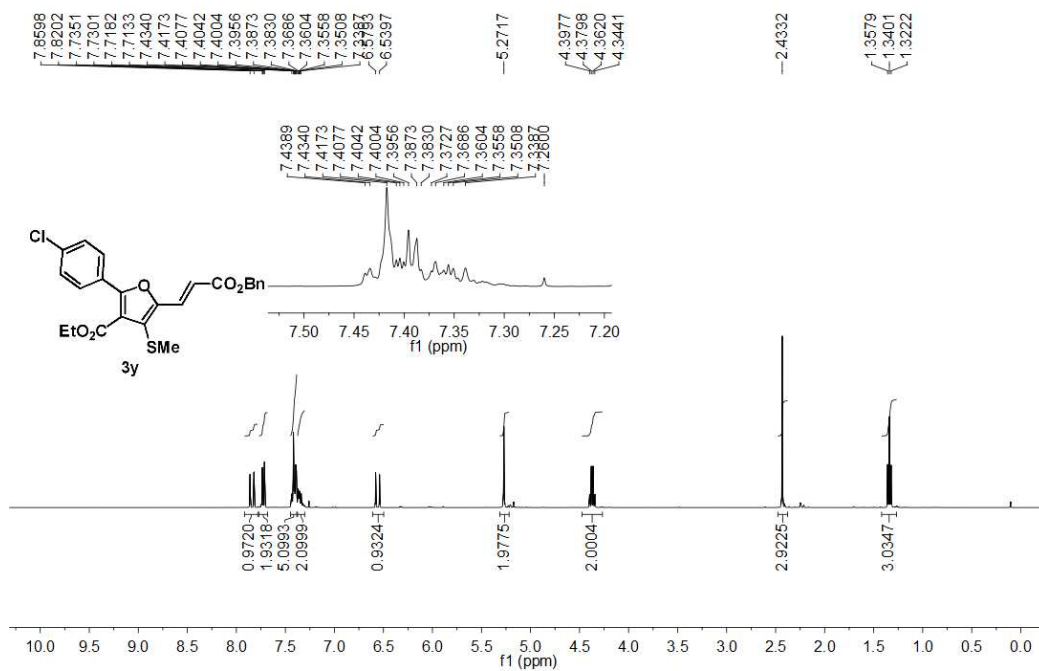


Figure S83. ^1H NMR spectrum of compound **3y** (CDCl_3 , 25 °C, 400 MHz).

WQN-1083W

^{13}C NMR in CDCl_3 (100 MHz)

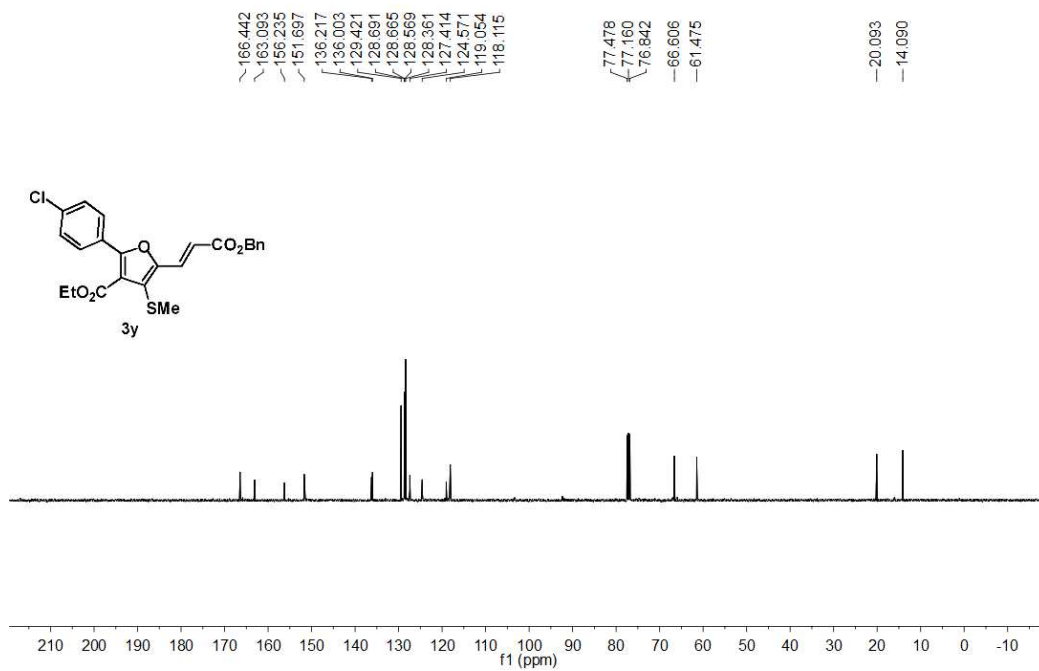


Figure S84. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3y** (CDCl_3 , 25 °C, 100 MHz).

WQN-1394W

^1H NMR in CDCl_3 (400 MHz)

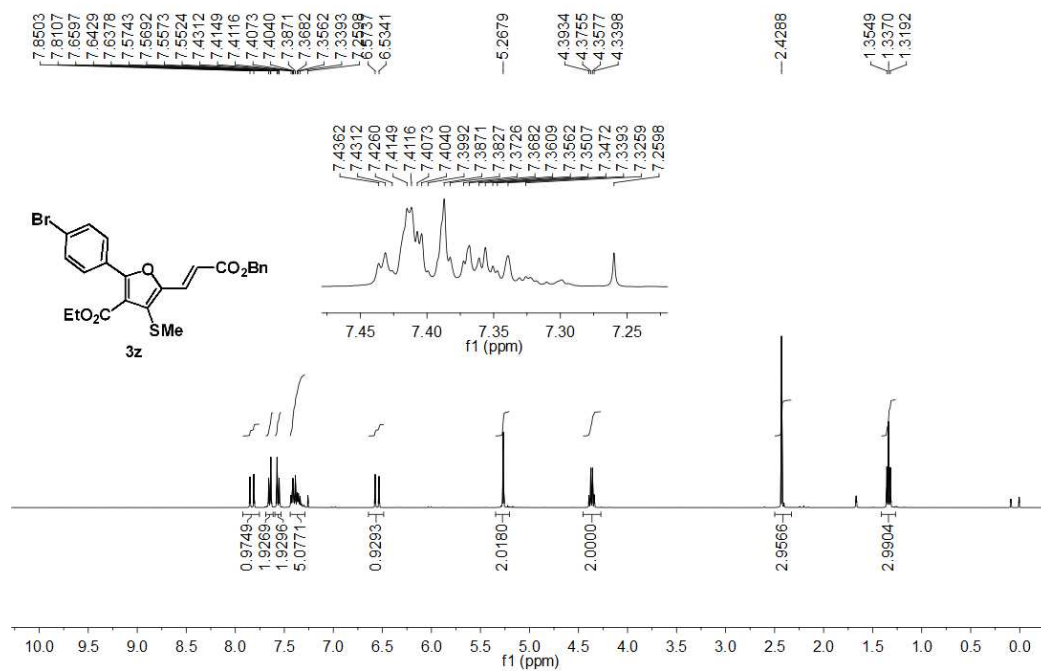


Figure S85. ^1H NMR spectrum of compound **3z** (CDCl_3 , 25 °C, 400 MHz).

WQN-1394W

^{13}C NMR in CDCl_3 (100 MHz)

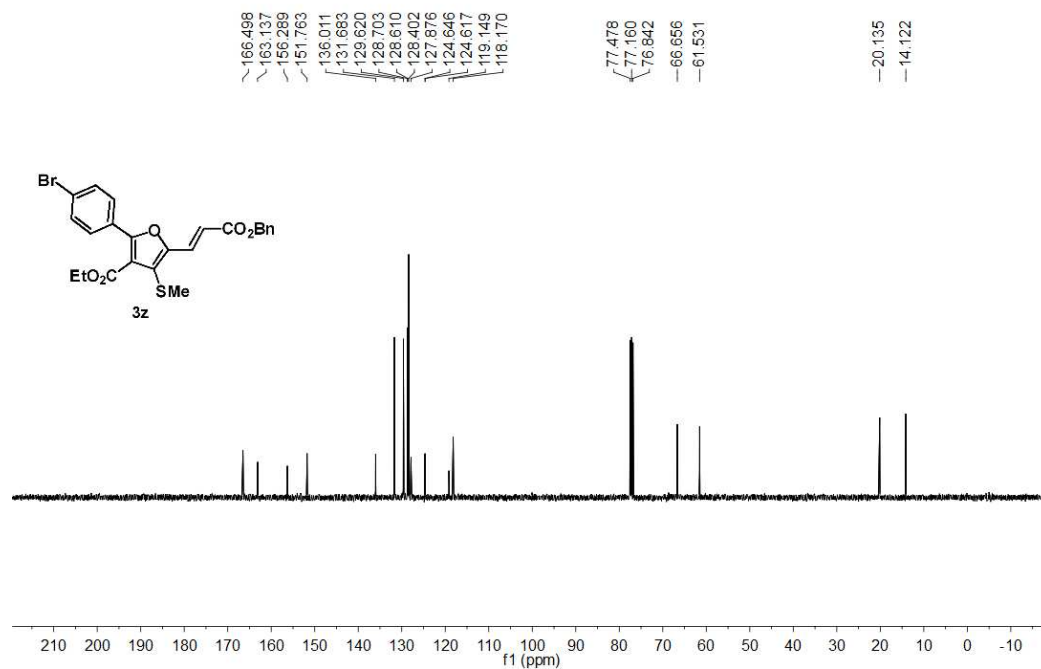


Figure S86. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3z** (CDCl_3 , 25 °C, 100 MHz).

WQN-1473W

^1H NMR in CDCl_3 (400 MHz)

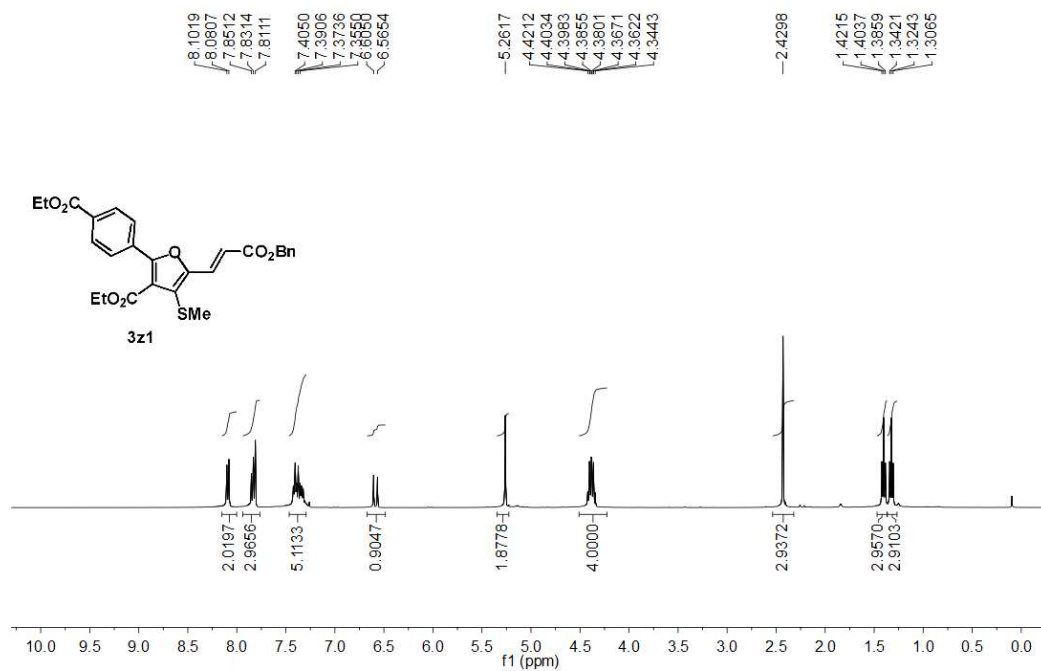


Figure S87. ^1H NMR spectrum of compound **3z1** (CDCl_3 , 25 °C, 400 MHz).

WQN-1473W

^{13}C NMR in CDCl_3 (100 MHz)

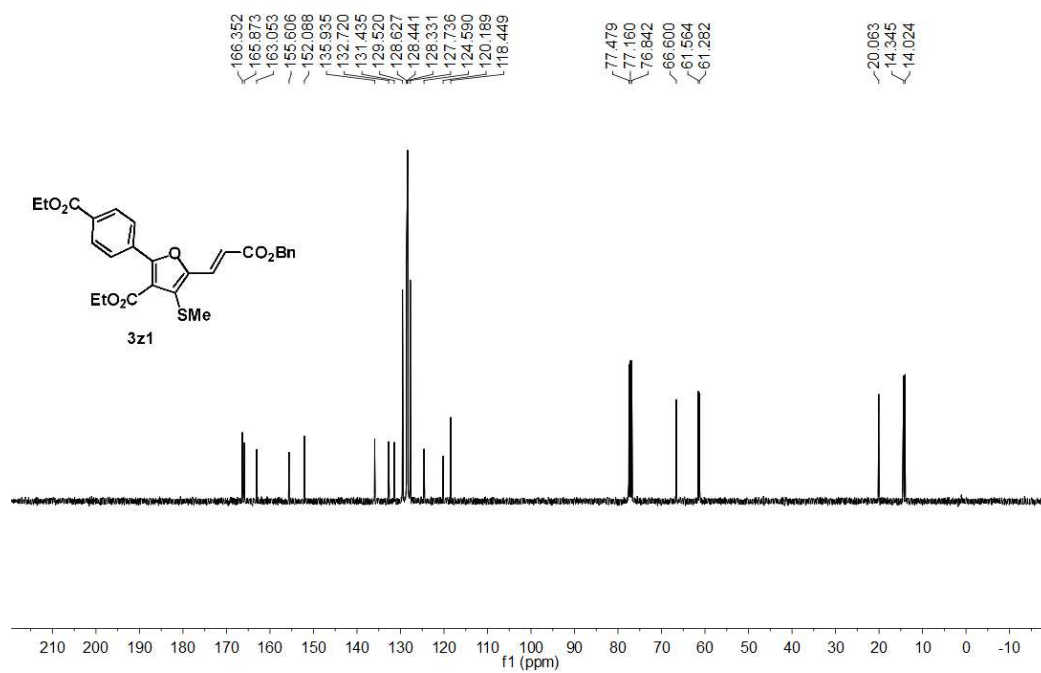
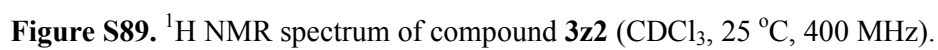
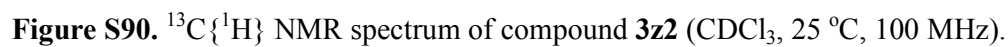


Figure S88. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3z1** (CDCl_3 , 25 °C, 100 MHz).

¹H NMR in CDCl₃ (400 MHz)



¹³C NMR in CDCl₃ (100 MHz)



WQN-1088W

¹H NMR in CDCl₃ (400 MHz)

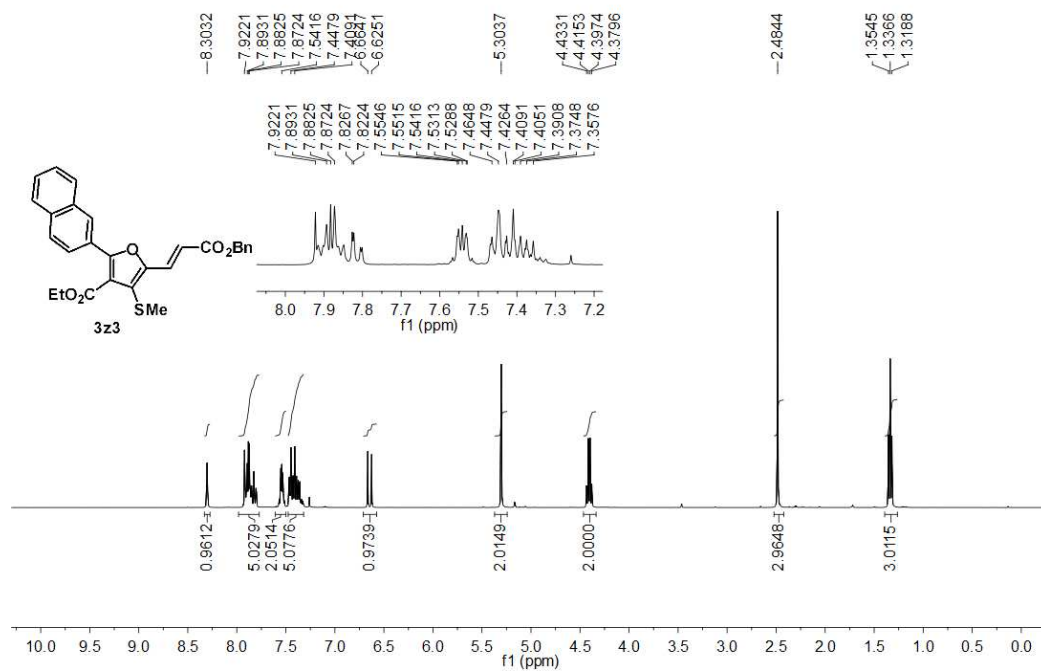


Figure S91. ¹H NMR spectrum of compound **3z3** (CDCl₃, 25 °C, 400 MHz).

WQN-1088W

¹³C NMR in CDCl₃ (100 MHz)

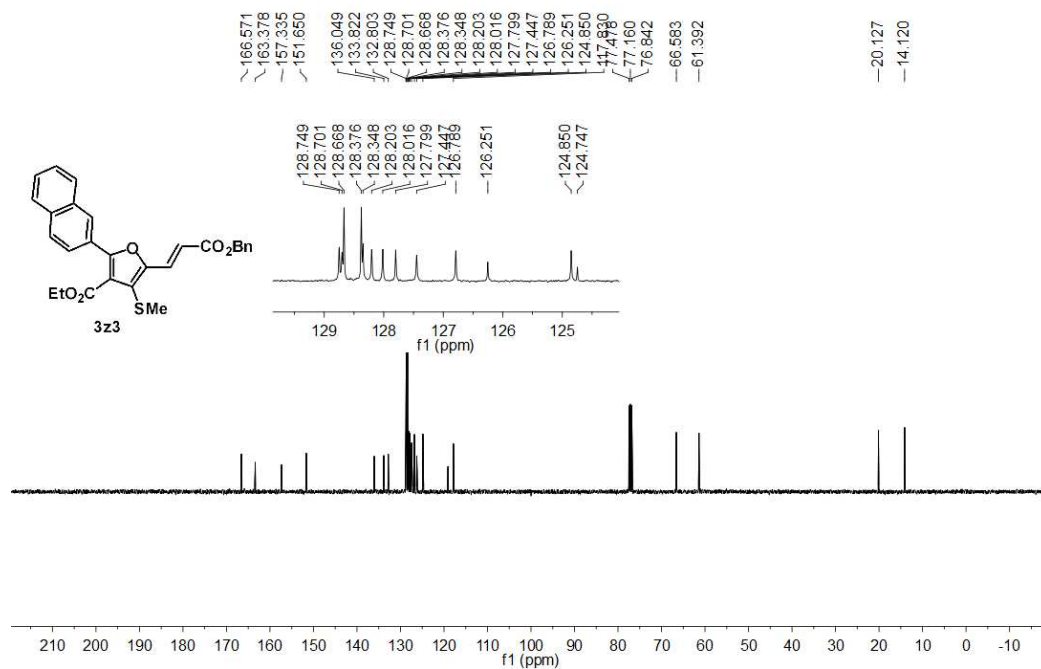


Figure S92. ¹³C{¹H} NMR spectrum of compound **3z3** (CDCl₃, 25 °C, 100 MHz).

WQN-1089W

^1H NMR in CDCl_3 (400 MHz)

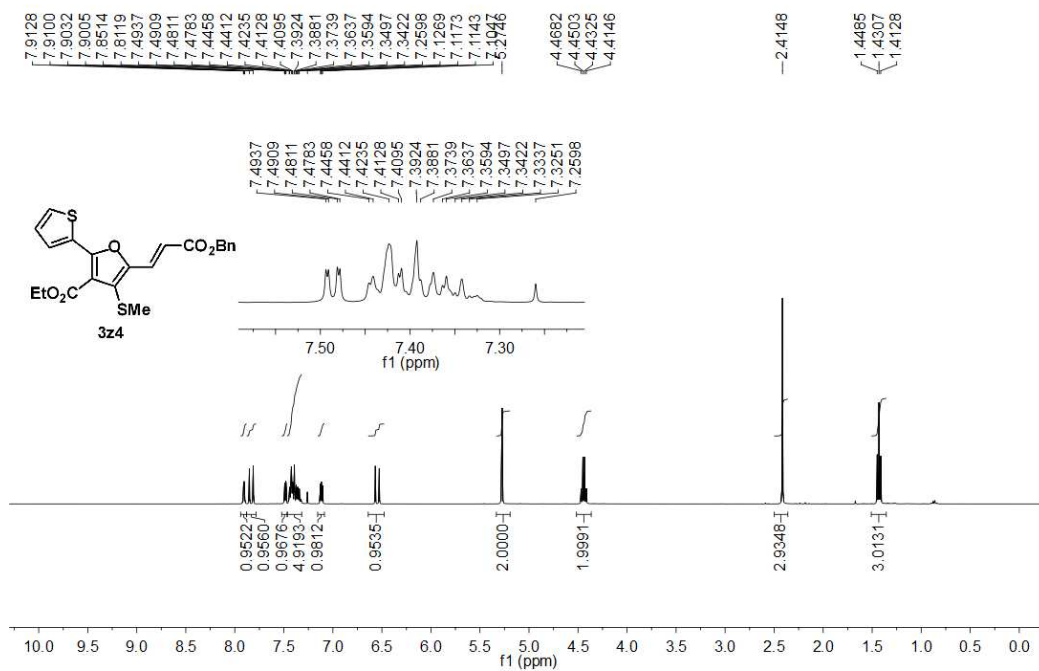


Figure S93. ^1H NMR spectrum of compound **3z4** (CDCl_3 , 25 °C, 400 MHz).

WQN-1089W

^{13}C NMR in CDCl_3 (100 MHz)

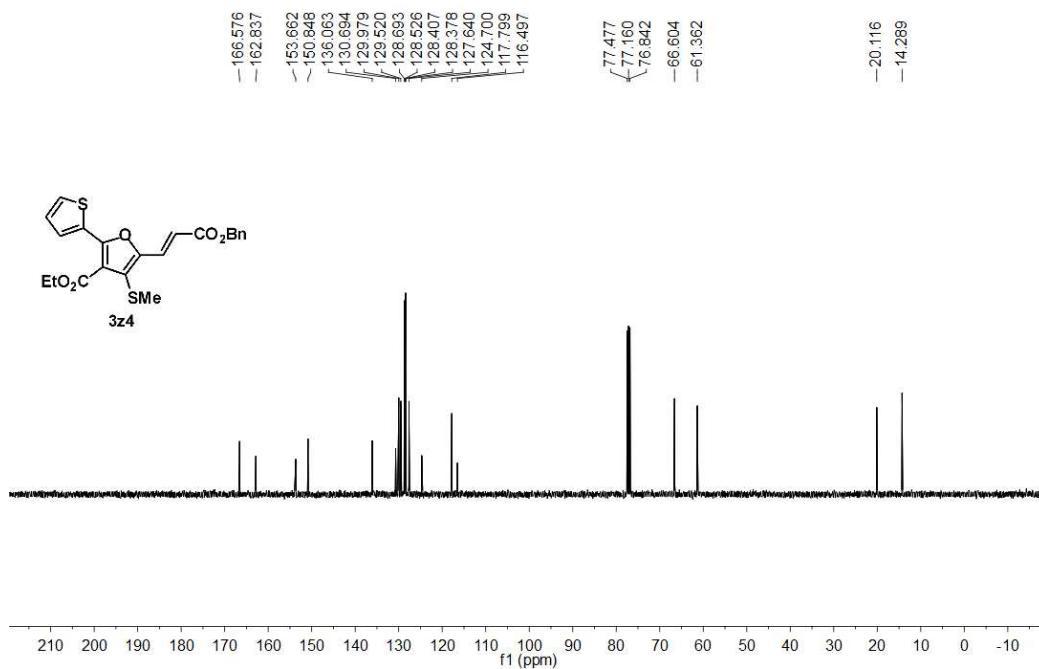


Figure S94. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3z4** (CDCl_3 , 25 °C, 100 MHz).

WQN-1090W

^1H NMR in CDCl_3 (400 MHz)

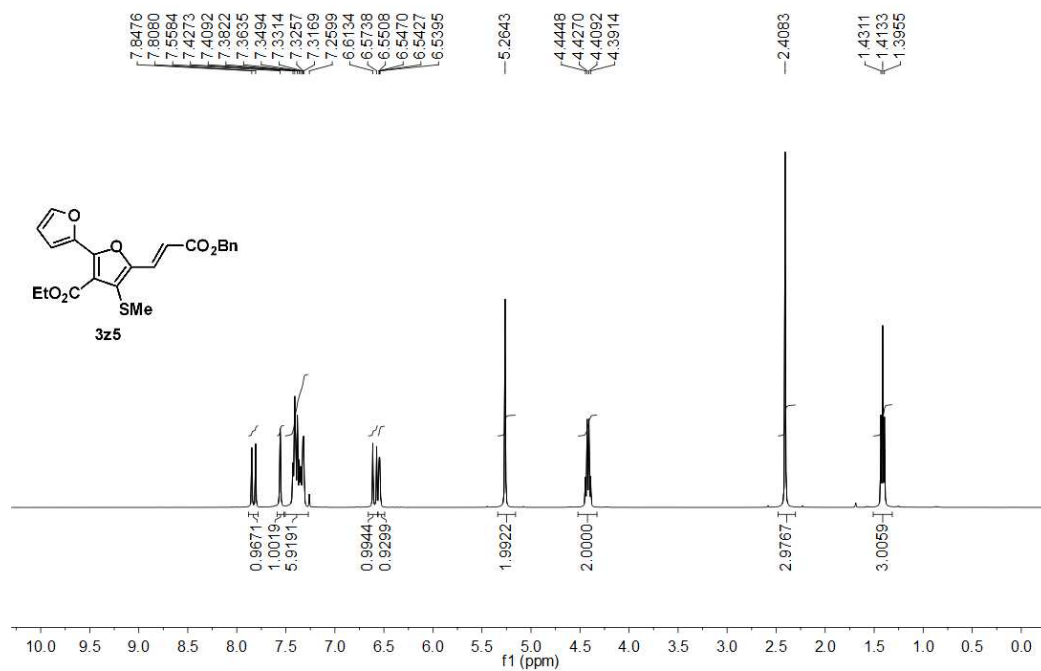


Figure S95. ^1H NMR spectrum of compound **3z5** (CDCl_3 , 25 °C, 400 MHz).

WQN-1090W

^{13}C NMR in CDCl_3 (100 MHz)

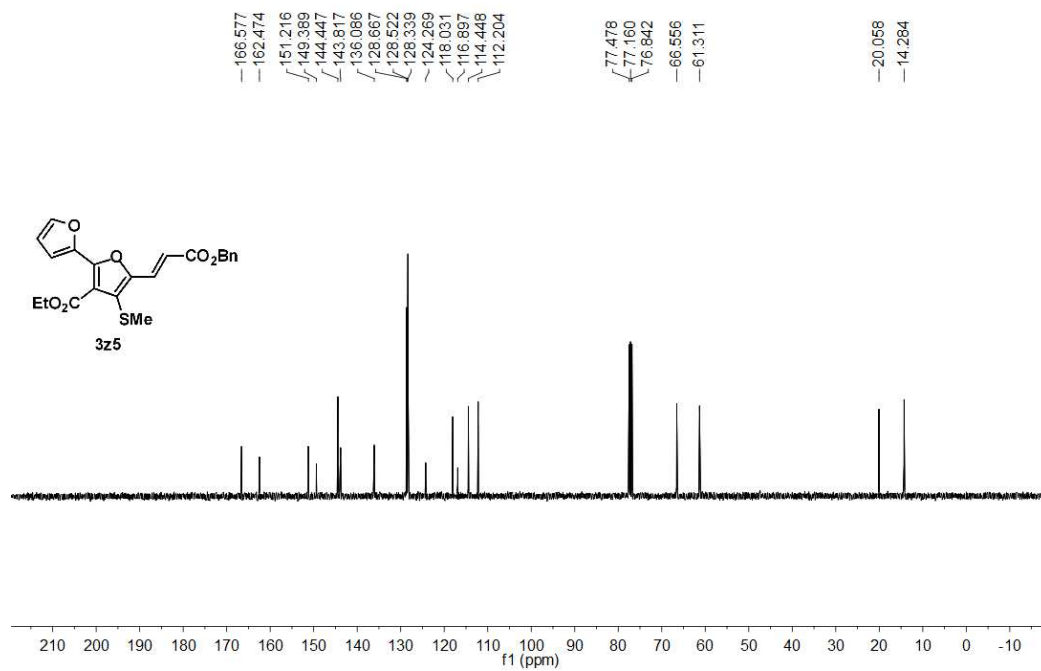


Figure S96. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3z5** (CDCl_3 , 25 °C, 100 MHz).

WQN-1026W-2

^1H NMR in CDCl_3 (400 MHz)

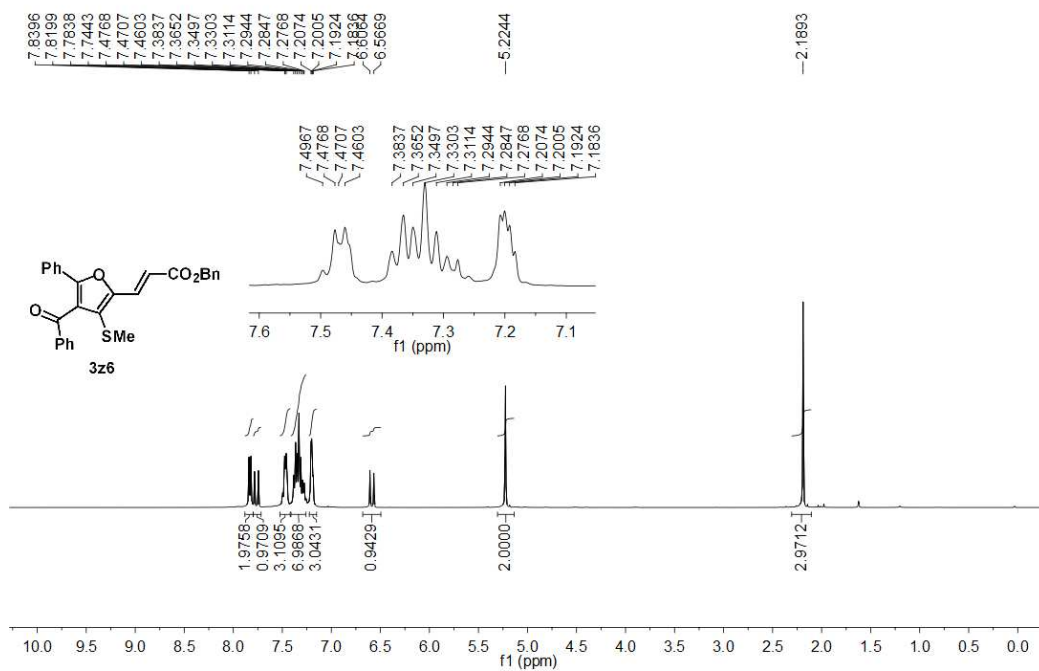


Figure S97. ^1H NMR spectrum of compound **3z6** (CDCl_3 , 25 °C, 400 MHz).

WQN-1026W-2

^{13}C NMR in CDCl_3 (100 MHz)

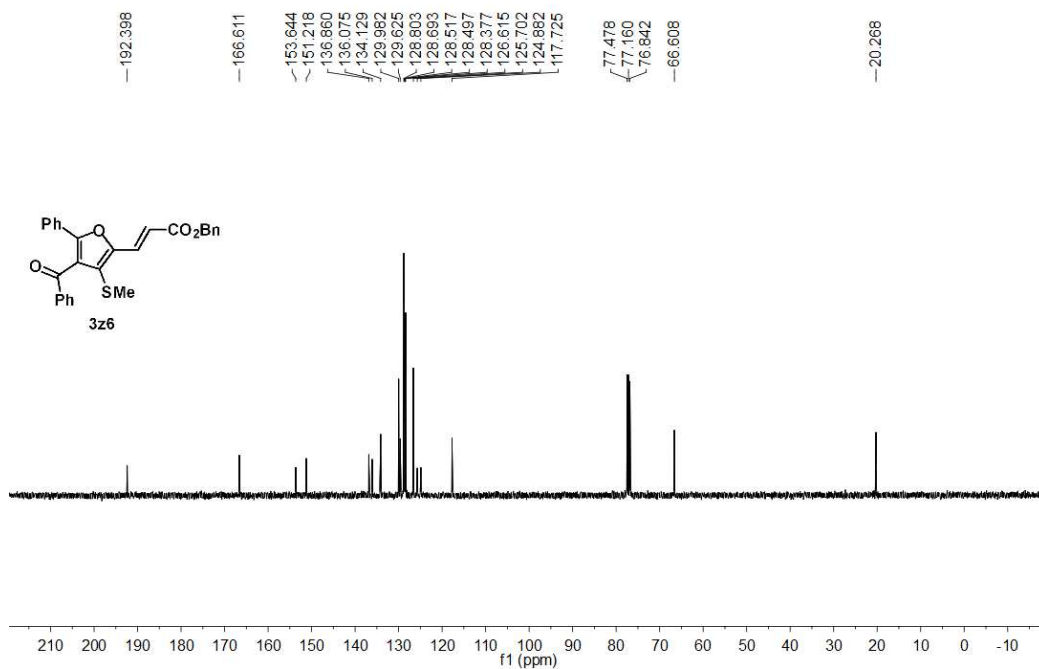


Figure S98. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **3z6** (CDCl_3 , 25 °C, 100 MHz).

WQN-1102W

^1H NMR in CDCl_3 (400 MHz)

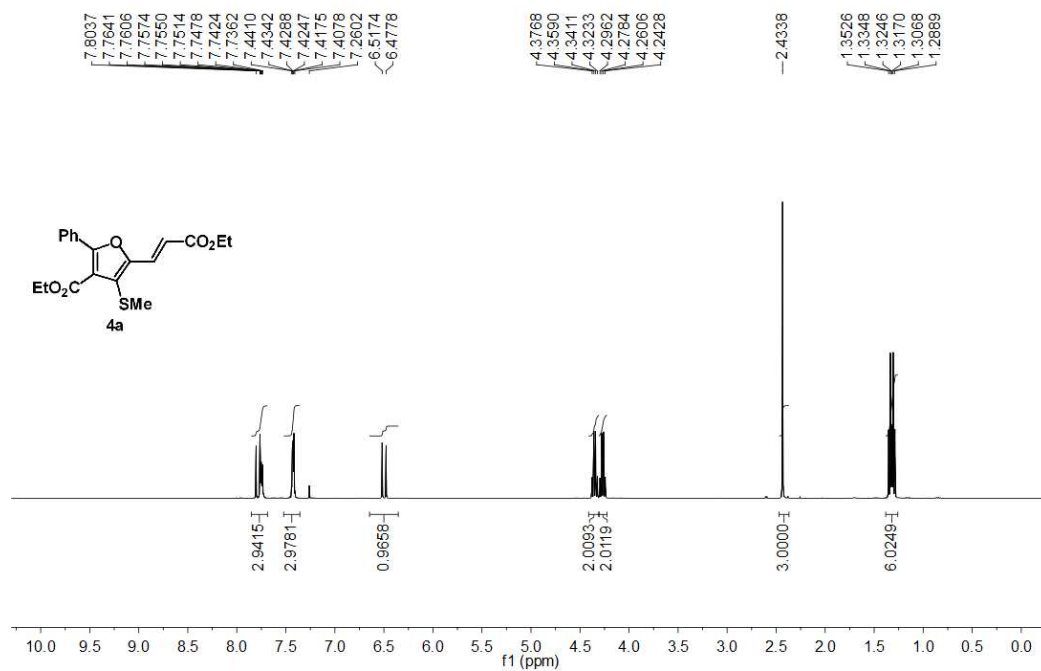


Figure S99. ^1H NMR spectrum of compound **4a** (CDCl_3 , 25 °C, 400 MHz).

WQN-1102W

^{13}C NMR in CDCl_3 (100 MHz)

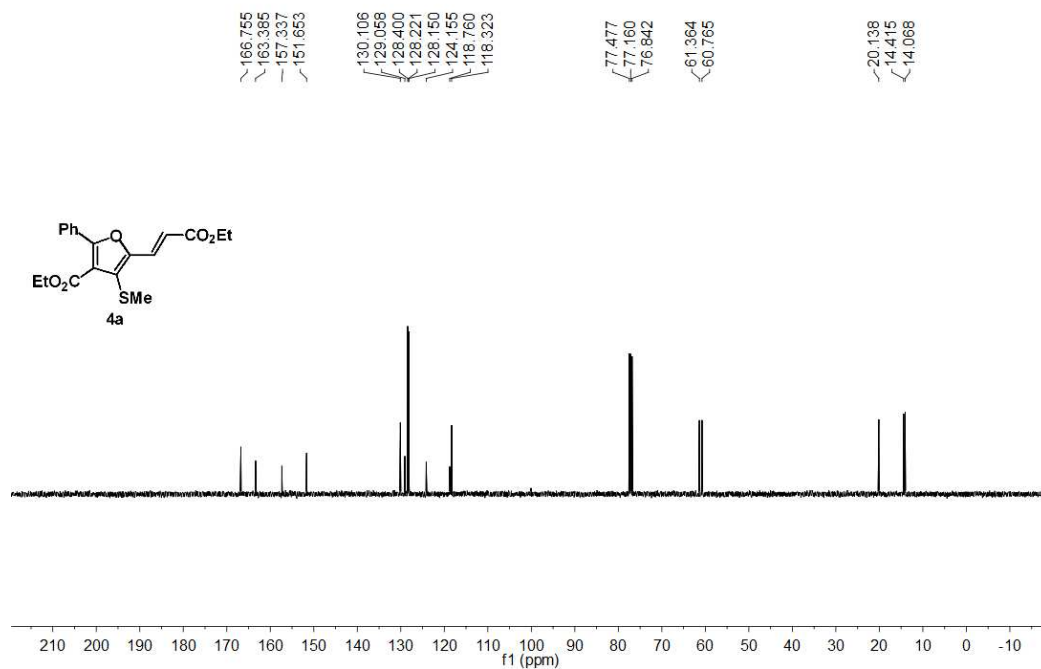


Figure S100. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **4a** (CDCl_3 , 25 °C, 100 MHz).

WQN-1121W

¹H NMR in CDCl₃ (400 MHz)

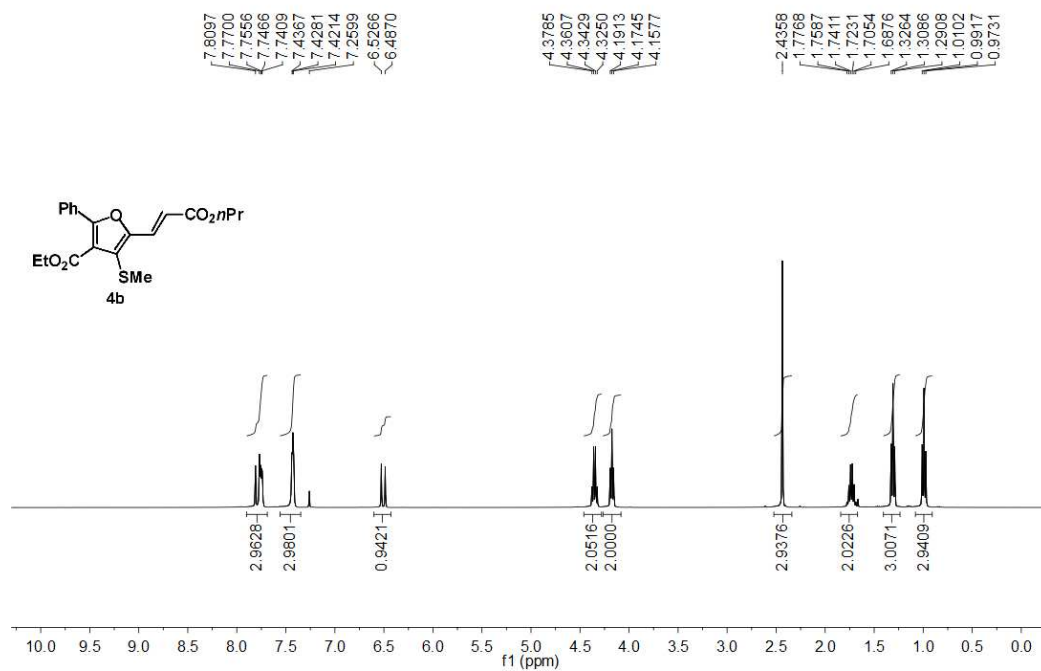


Figure S101. ¹H NMR spectrum of compound **4b** (CDCl₃, 25 °C, 400 MHz).

WQN-1121W

¹³C NMR in CDCl₃ (100 MHz)

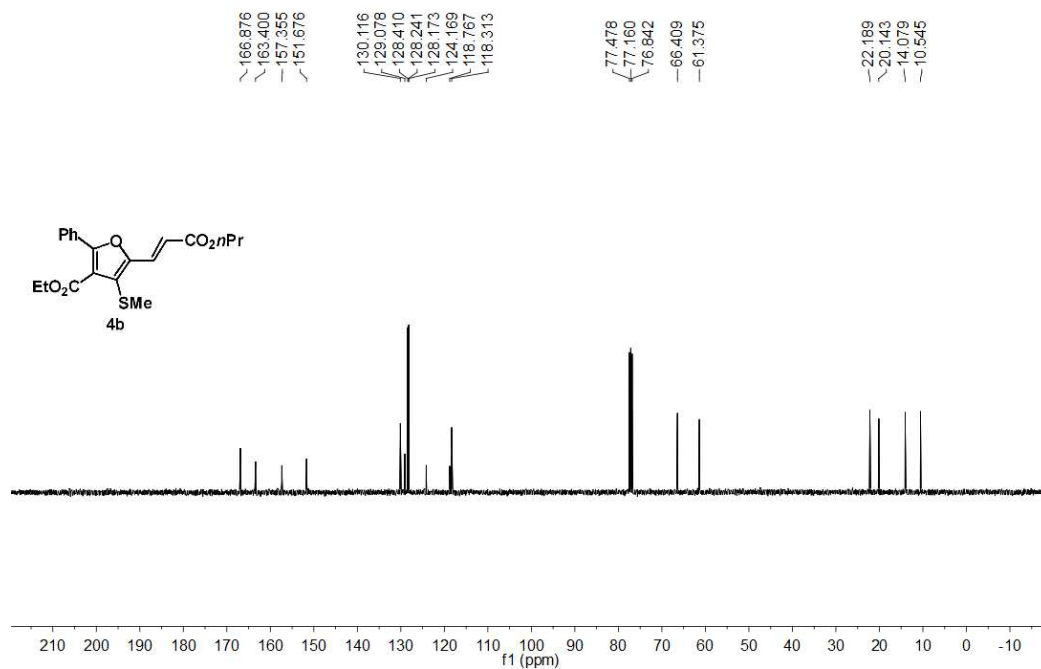


Figure S102. ¹³C{¹H} NMR spectrum of compound **4b** (CDCl₃, 25 °C, 100 MHz).

WQN-1125W
¹H NMR in CDCl₃ (400 MHz)

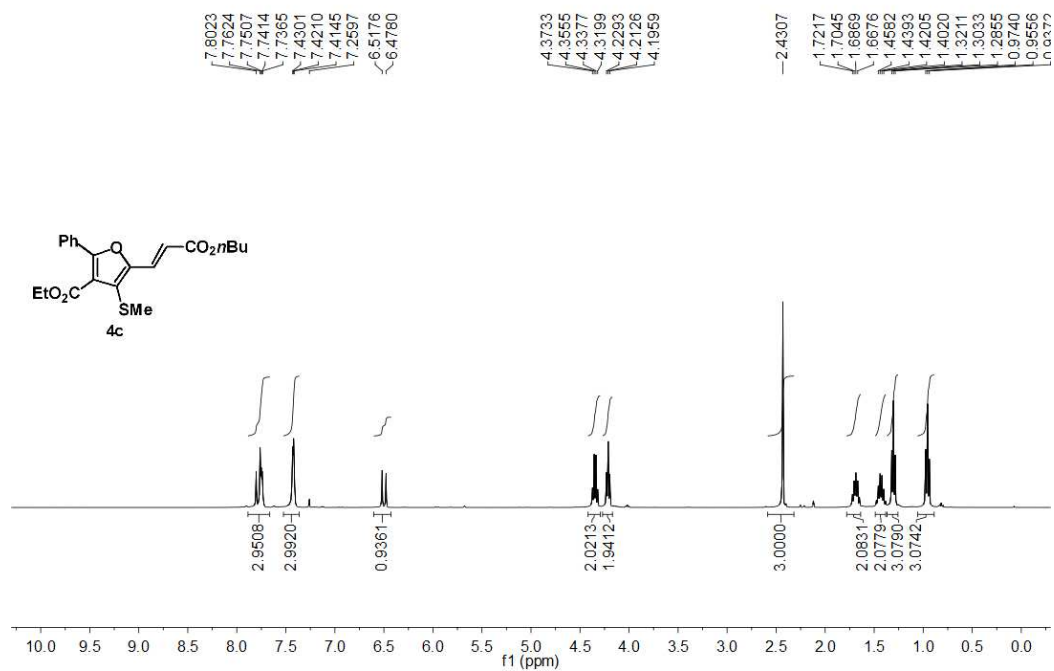


Figure S103. ¹H NMR spectrum of compound **4c** (CDCl₃, 25 °C, 400 MHz).

WQN-1125W
¹³C NMR in CDCl₃ (100 MHz)

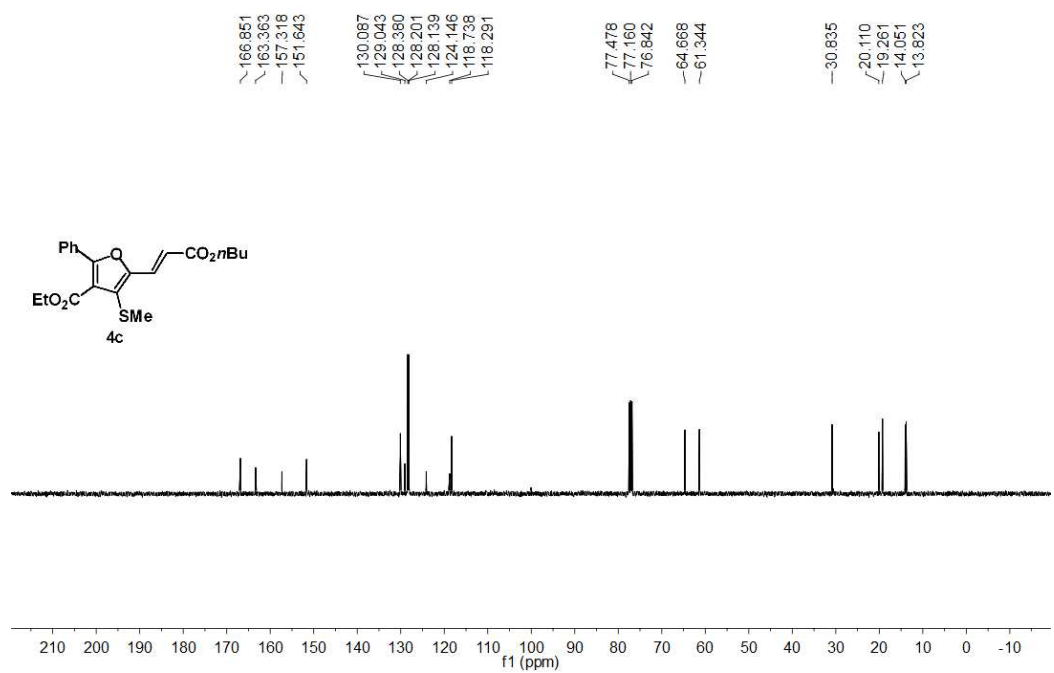


Figure S104. ¹³C{¹H} NMR spectrum of compound **4c** (CDCl₃, 25 °C, 100 MHz).

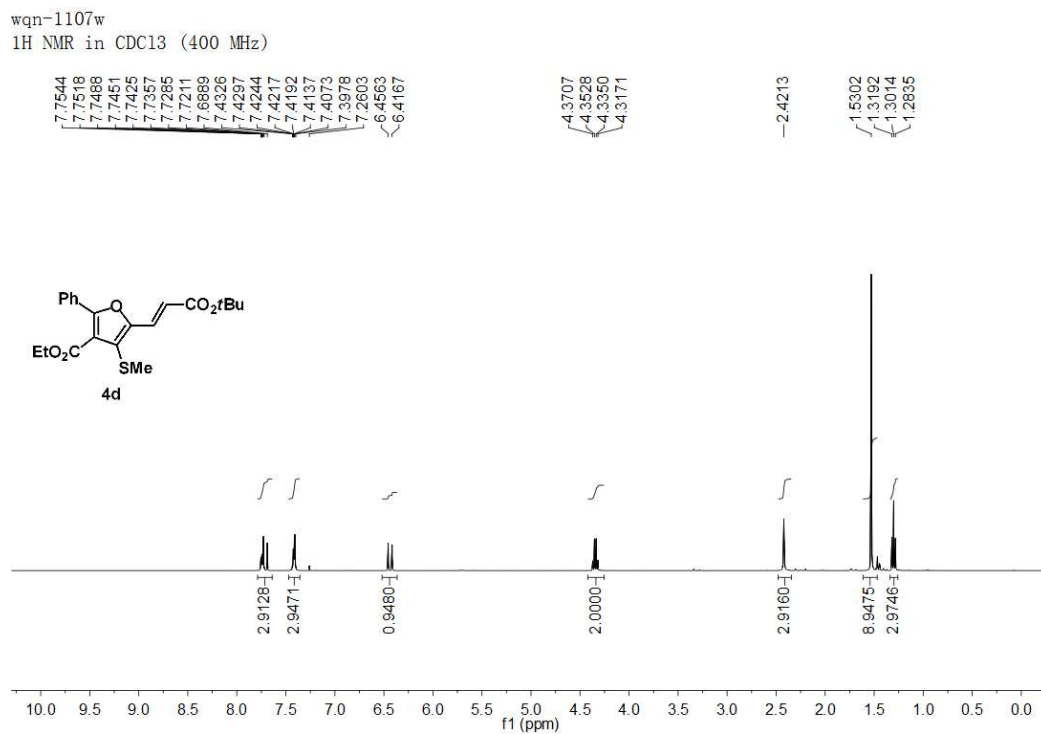


Figure S105. ¹H NMR spectrum of compound **4d** (CDCl₃, 25 °C, 400 MHz).

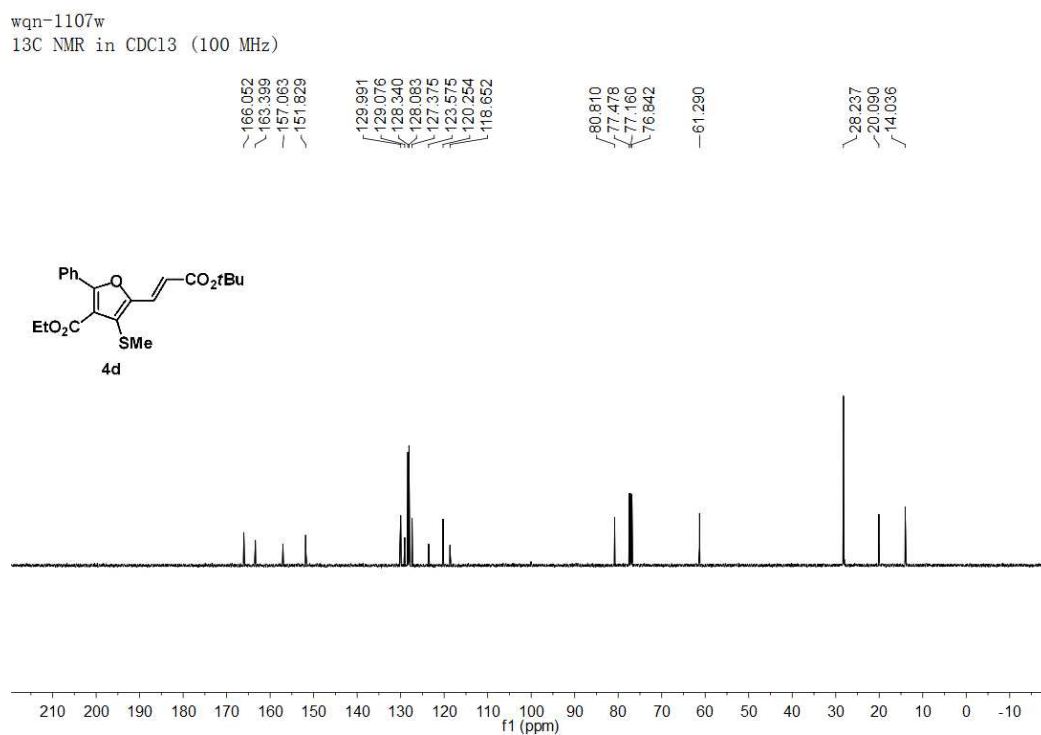


Figure S106. ¹³C{¹H} NMR spectrum of compound **4d** (CDCl₃, 25 °C, 100 MHz).

WQN-1148W

^1H NMR in CDCl_3 (400 MHz)

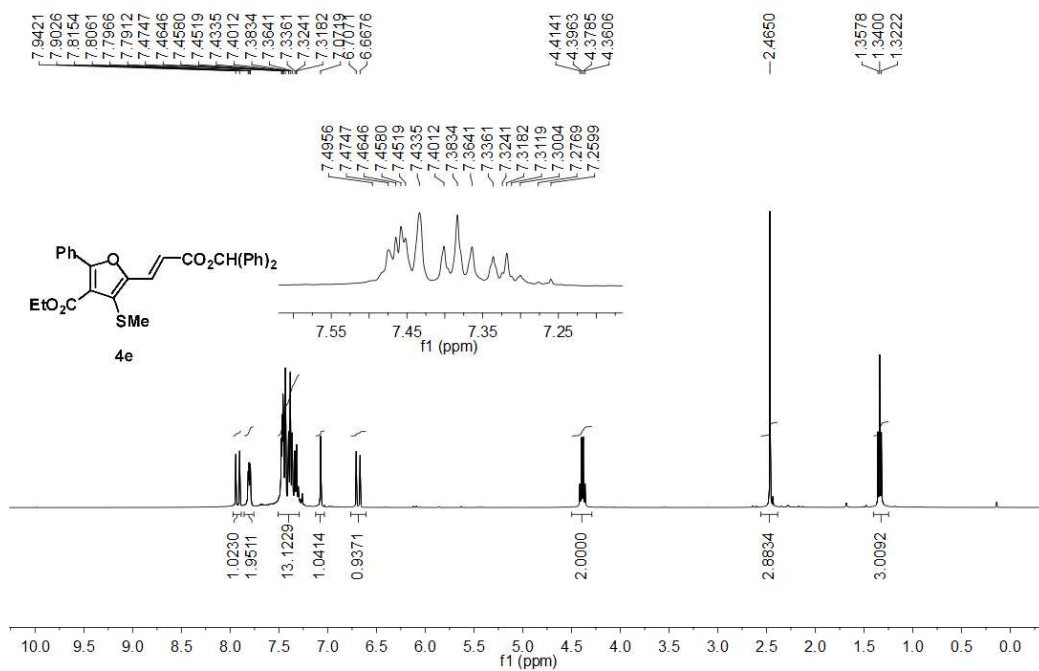


Figure S107. ^1H NMR spectrum of compound **4e** (CDCl_3 , 25 $^\circ\text{C}$, 400 MHz).

WQN-1148W

^{13}C NMR in CDCl_3 (100 MHz)

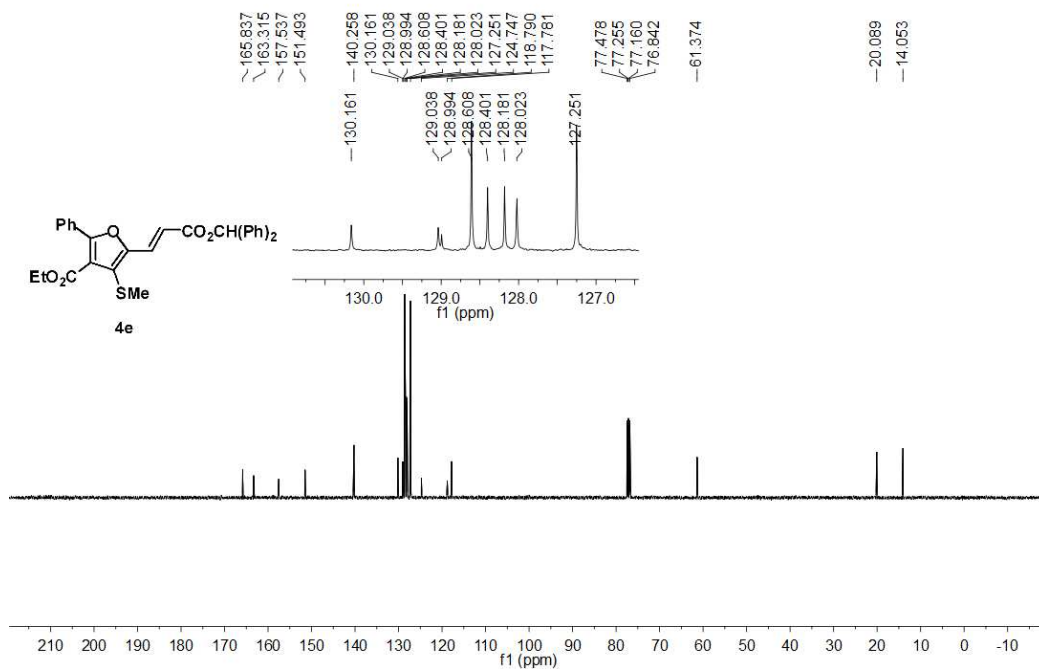


Figure S108. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **4e** (CDCl_3 , 25 $^\circ\text{C}$, 100 MHz).

WQN-1129W

^1H NMR in CDCl_3 (400 MHz)

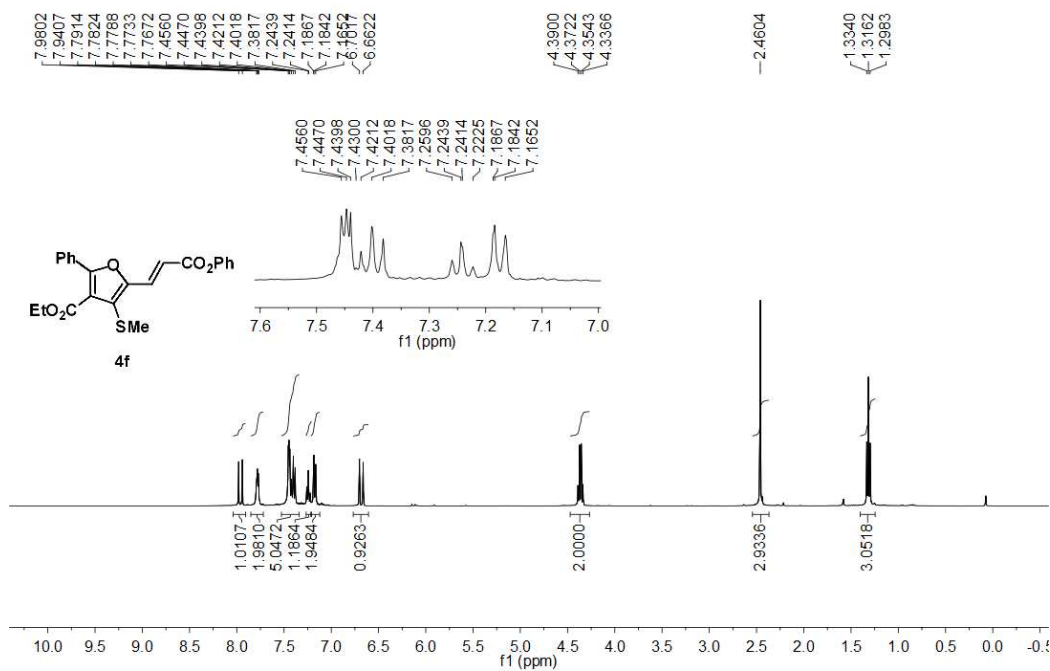


Figure S109. ^1H NMR spectrum of compound **4f** (CDCl_3 , 25 °C, 400 MHz).

WQN-1129W

^{13}C NMR in CDCl_3 (100 MHz)

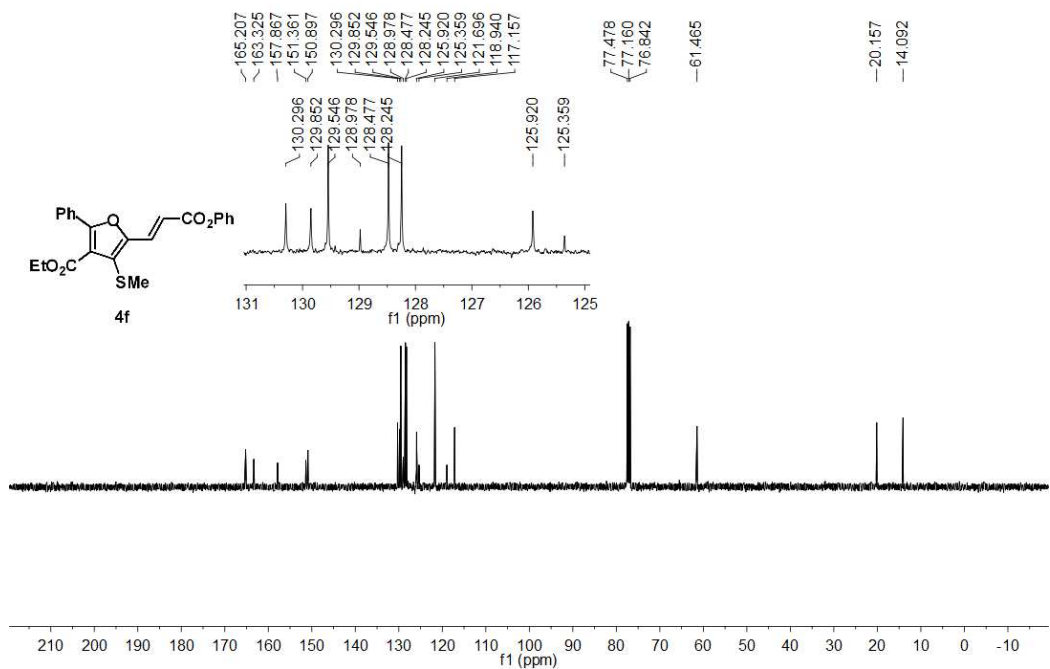


Figure S110. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **4f** (CDCl_3 , 25 °C, 100 MHz).

wqn-1150w
¹H NMR in CDCl₃ (400 MHz)

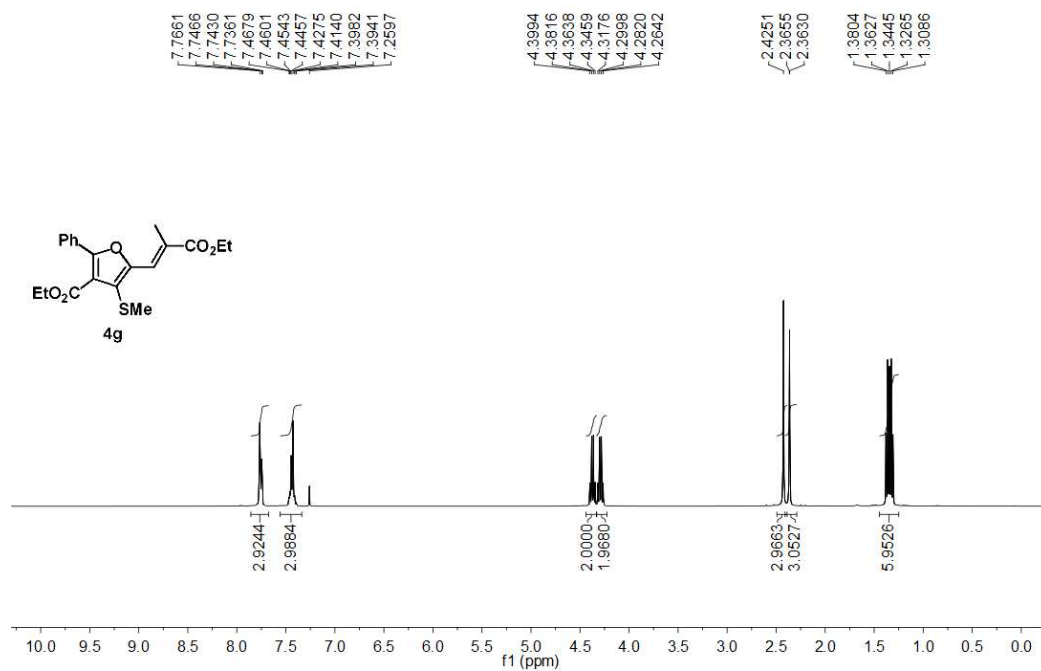


Figure S111. ¹H NMR spectrum of compound **4g** (CDCl₃, 25 °C, 400 MHz).

wqn-1150w
¹³C NMR in CDCl₃ (100 MHz)

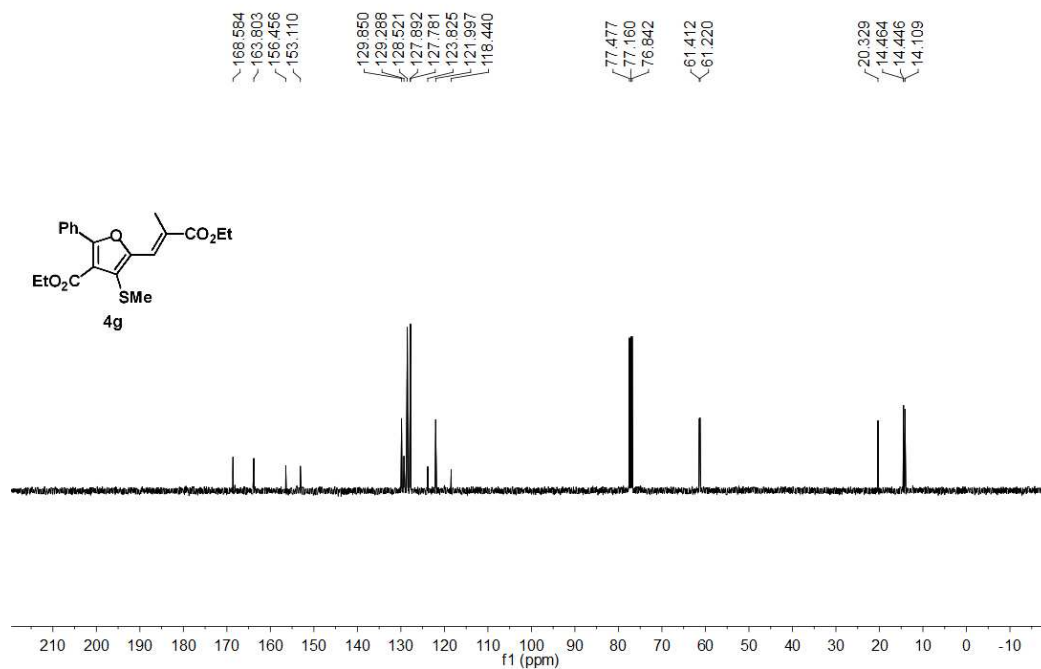


Figure S112. ¹³C{¹H} NMR spectrum of compound **4g** (CDCl₃, 25 °C, 100 MHz).

WQN-1124W

^1H NMR in CDCl_3 (400 MHz)

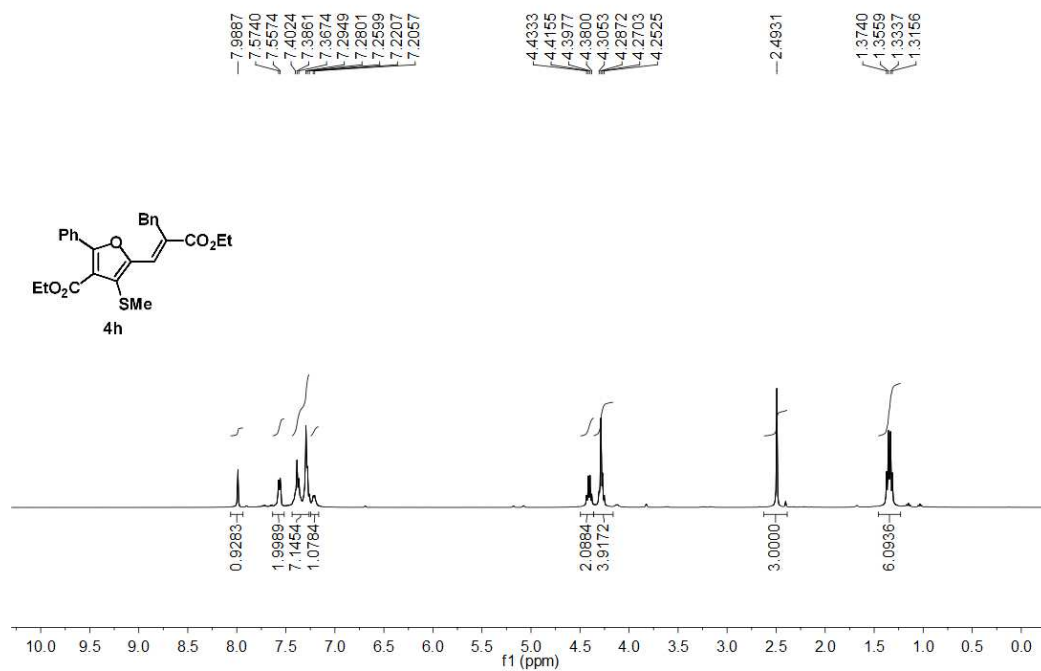


Figure S113. ^1H NMR spectrum of compound **4h** (CDCl_3 , 25 °C, 400 MHz).

WQN-1124W

^{13}C NMR in CDCl_3 (100 MHz)

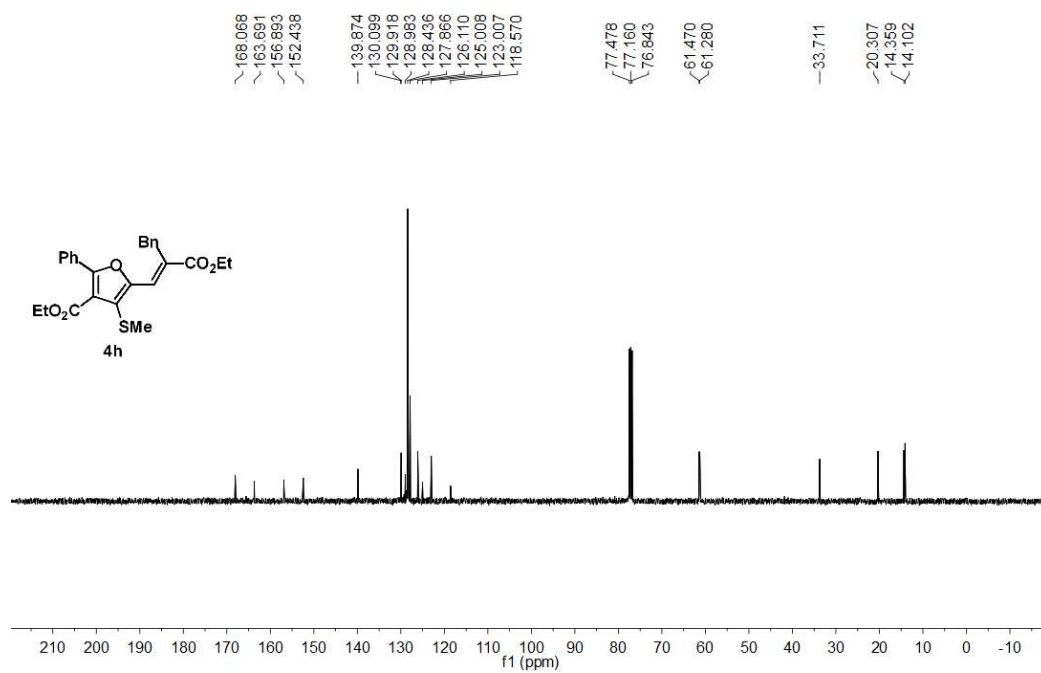


Figure S114. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **4h** (CDCl_3 , 25 °C, 100 MHz).

WQN-1019W

^1H NMR in CDCl_3 (400 MHz)

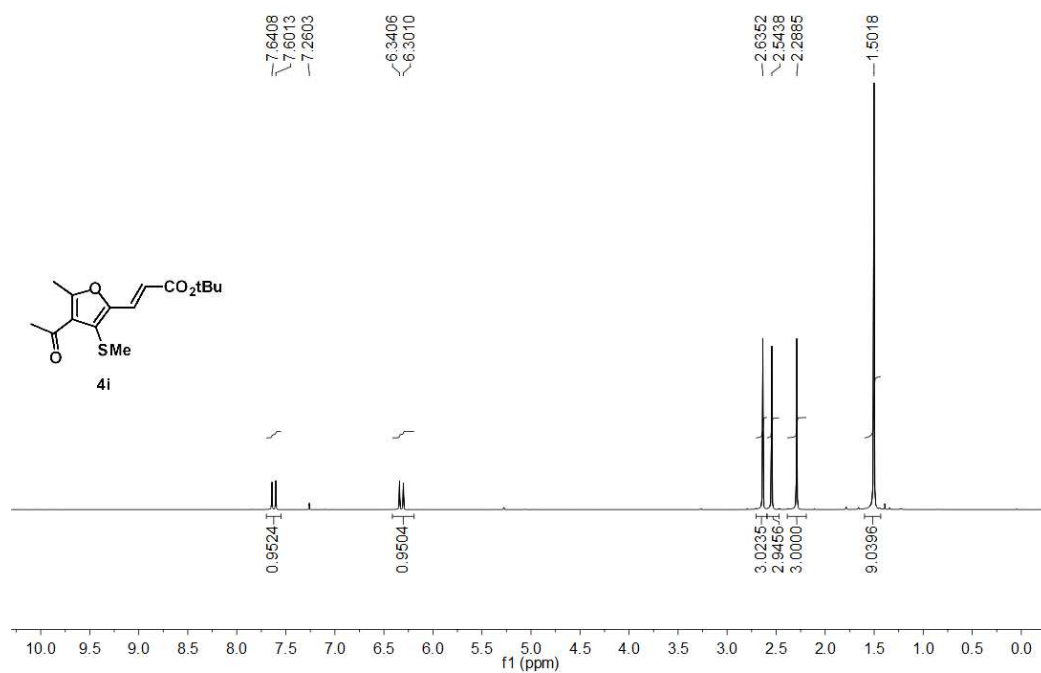


Figure S115. ^1H NMR spectrum of compound **4i** (CDCl_3 , 25 $^\circ\text{C}$, 400 MHz).

WQN-1019W

^{13}C NMR in CDCl_3 (100 MHz)

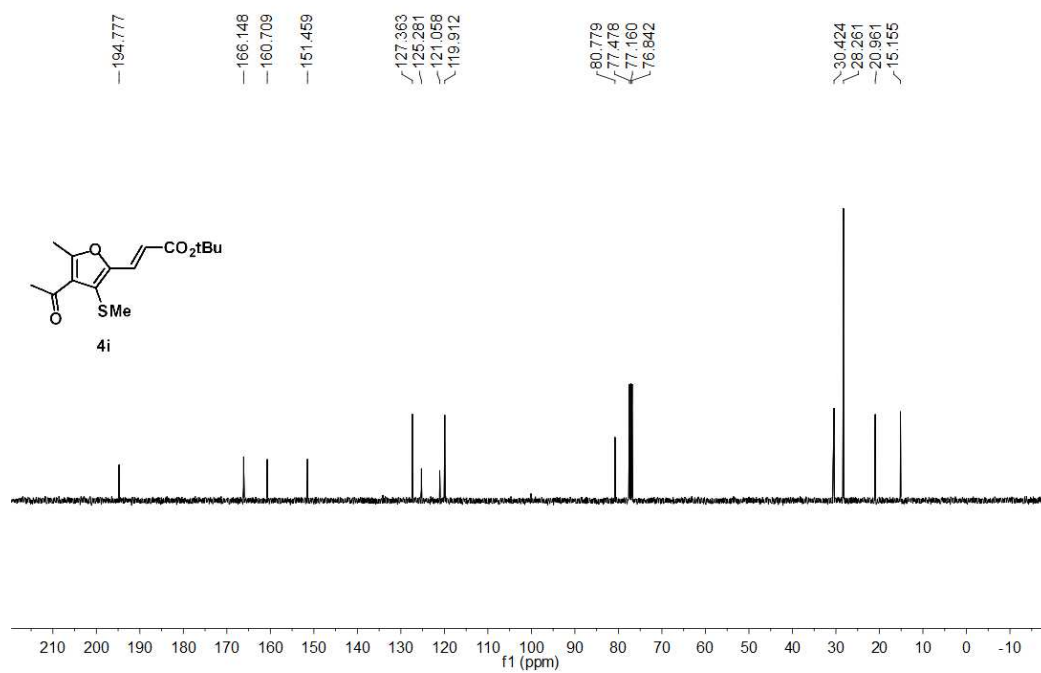


Figure S116. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **4i** (CDCl_3 , 25 $^\circ\text{C}$, 100 MHz).

wqn-1108w
¹H NMR in CDCl₃ (400 MHz)

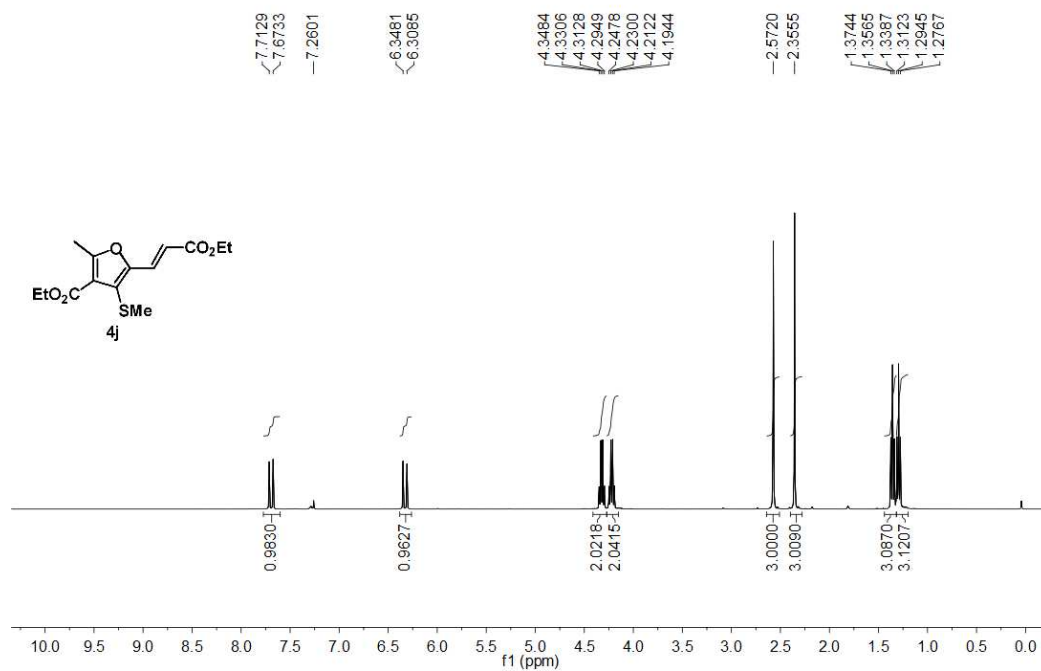


Figure S117. ¹H NMR spectrum of compound **4j** (CDCl₃, 25 °C, 400 MHz).

wqn-1108w
¹³C NMR in CDCl₃ (100 MHz)

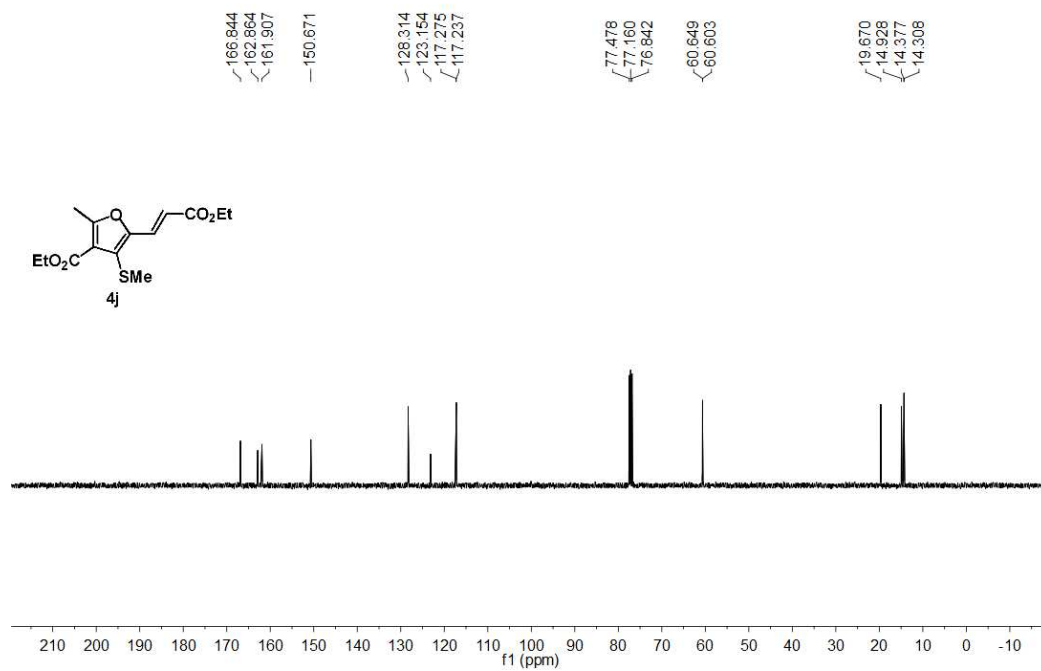


Figure S118. ¹³C{¹H} NMR spectrum of compound **4j** (CDCl₃, 25 °C, 100 MHz).

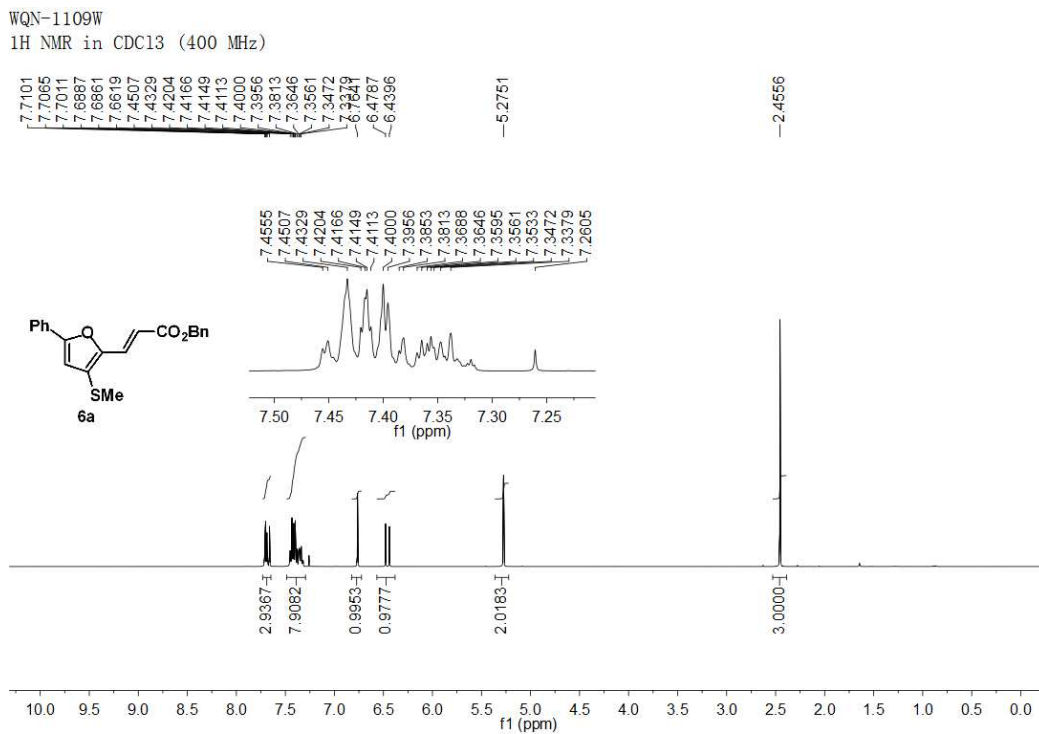


Figure S119. ¹H NMR spectrum of compound **6a** (CDCl₃, 25 °C, 400 MHz).

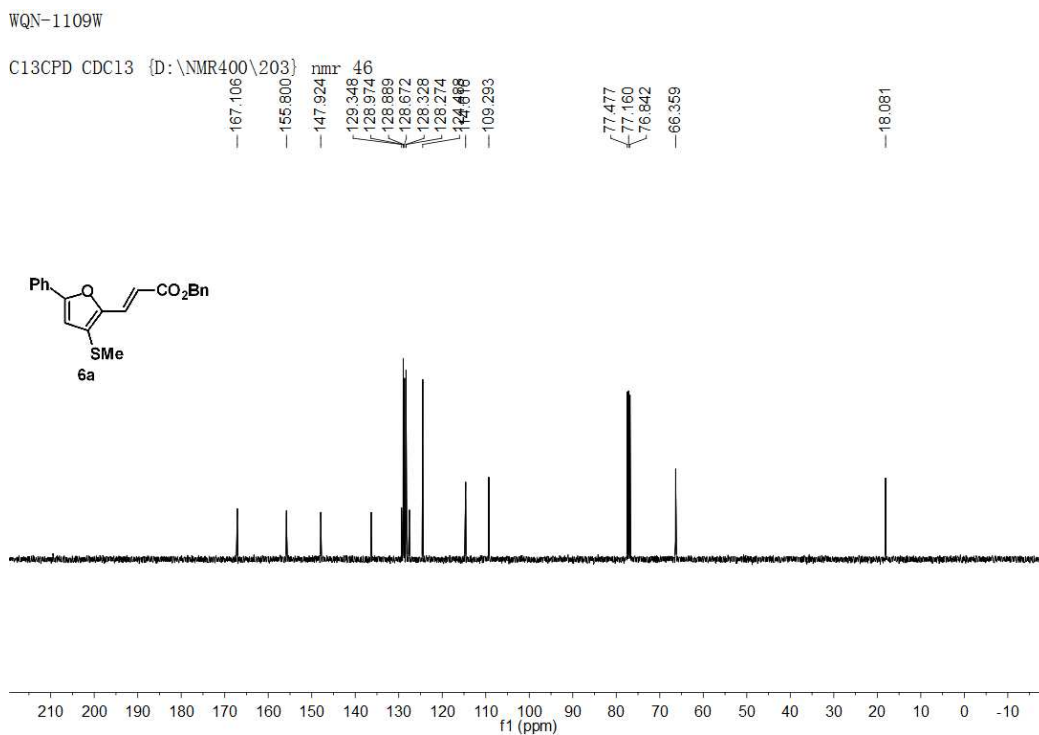


Figure S120. ¹³C{¹H} NMR spectrum of compound **6a** (CDCl₃, 25 °C, 100 MHz).

WQN-1358W

^1H NMR in CDCl_3 (400 MHz)

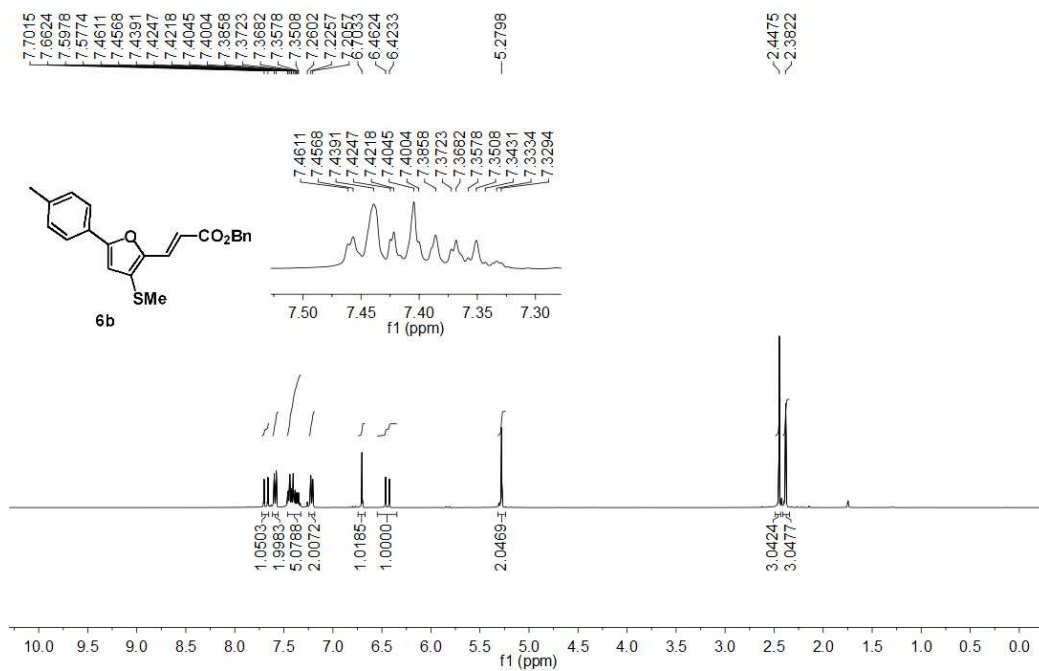


Figure S121. ^1H NMR spectrum of compound **6b** (CDCl_3 , 25 °C, 400 MHz).

WQN-1358W

^{13}C NMR in CDCl_3 (100 MHz)

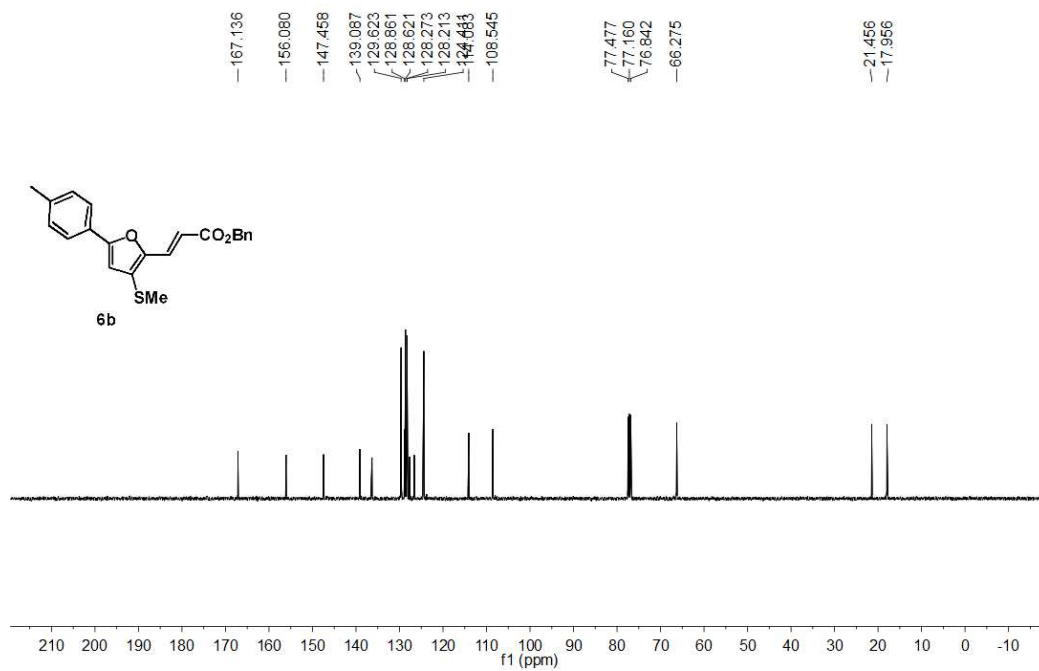
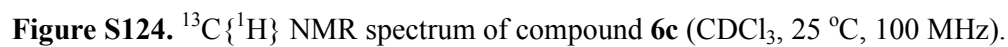


Figure S122. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **6b** (CDCl_3 , 25 °C, 100 MHz).

¹H NMR in CDCl₃ (400 MHz)



¹³C NMR in CDCl₃ (100 MHz)



WQN-1164W
¹H NMR in CDCl₃ (400 MHz)

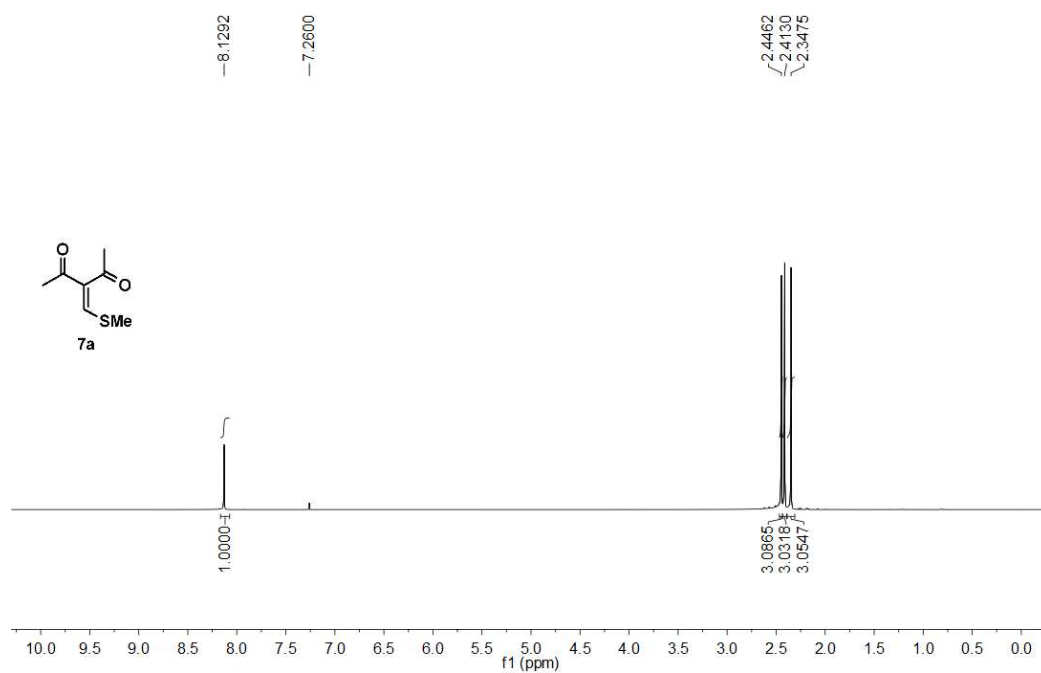


Figure S125. ¹H NMR spectrum of compound **7a** (CDCl₃, 25 °C, 400 MHz).

WQN-1164W
¹³C NMR in CDCl₃ (100 MHz)

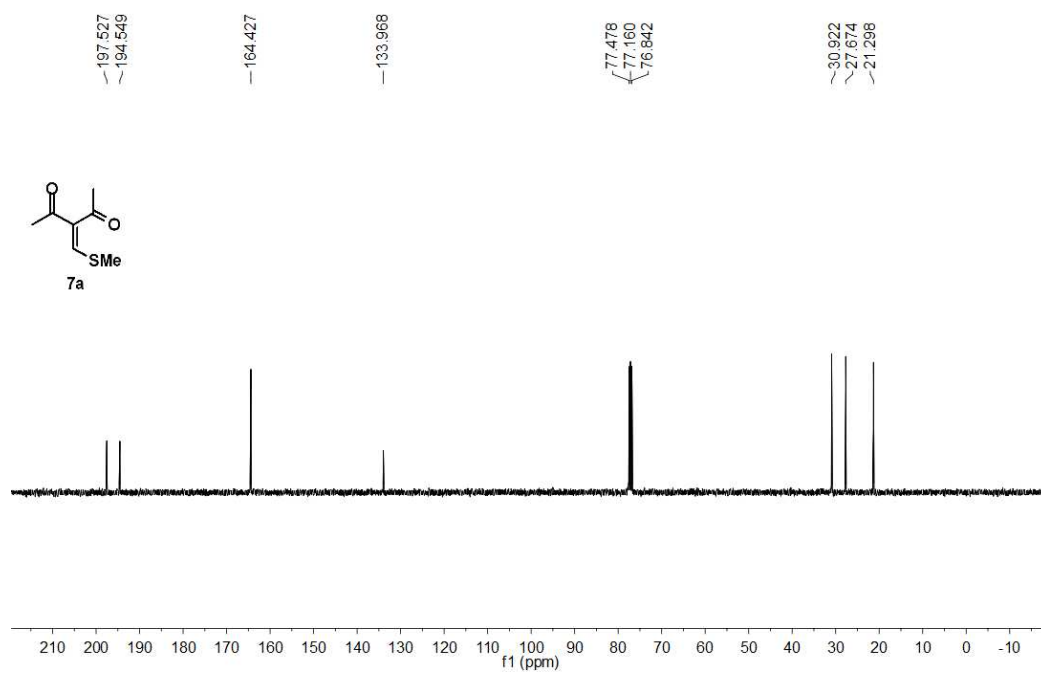


Figure S126. ¹³C{¹H} NMR spectrum of compound **7a** (CDCl₃, 25 °C, 100 MHz).

WQN-1220W

^1H NMR in CDCl_3 (400 MHz)

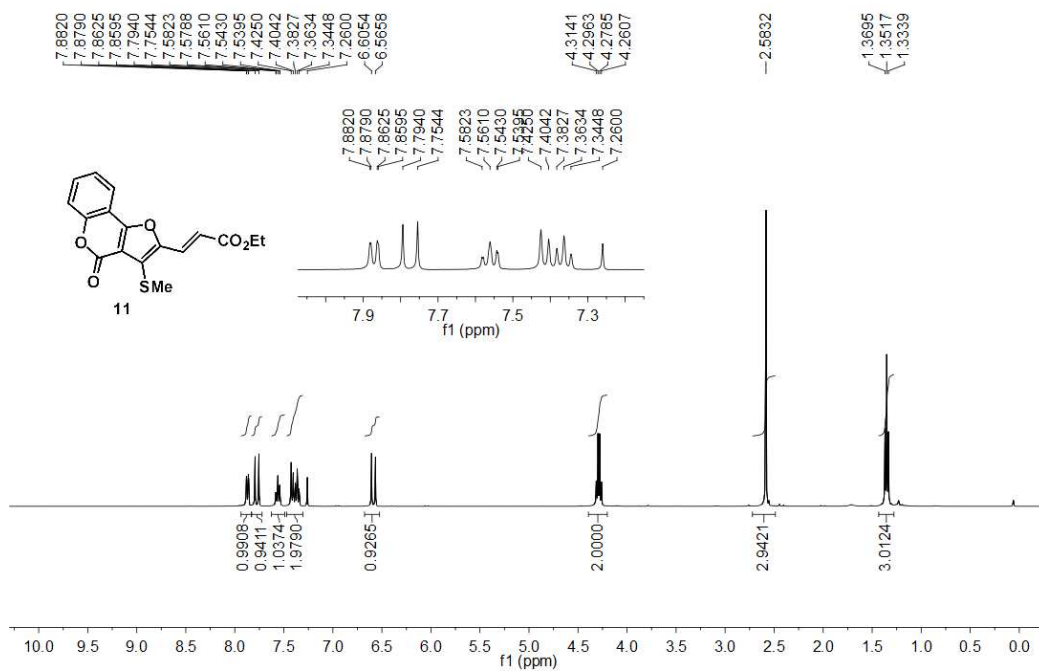


Figure S127. ^1H NMR spectrum of compound **11** (CDCl_3 , 25 °C, 400 MHz).

WQN-1220W

^{13}C NMR in CDCl_3 (100 MHz)

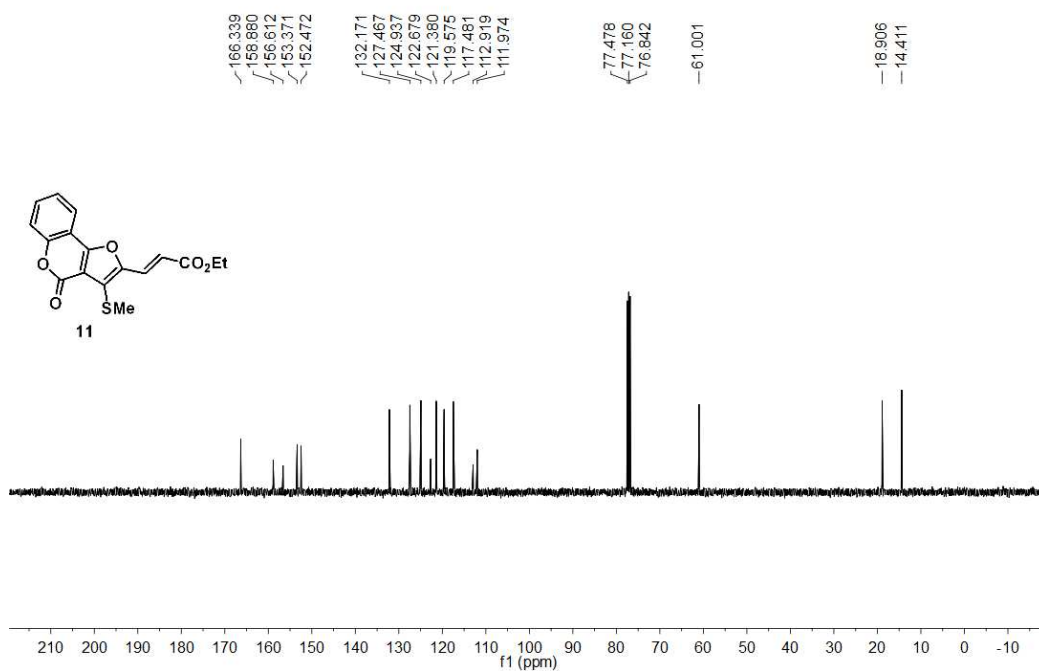


Figure S128. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **11** (CDCl_3 , 25 °C, 100 MHz).

wqn-1429w

^1H NMR in CDCl_3 (400 MHz)

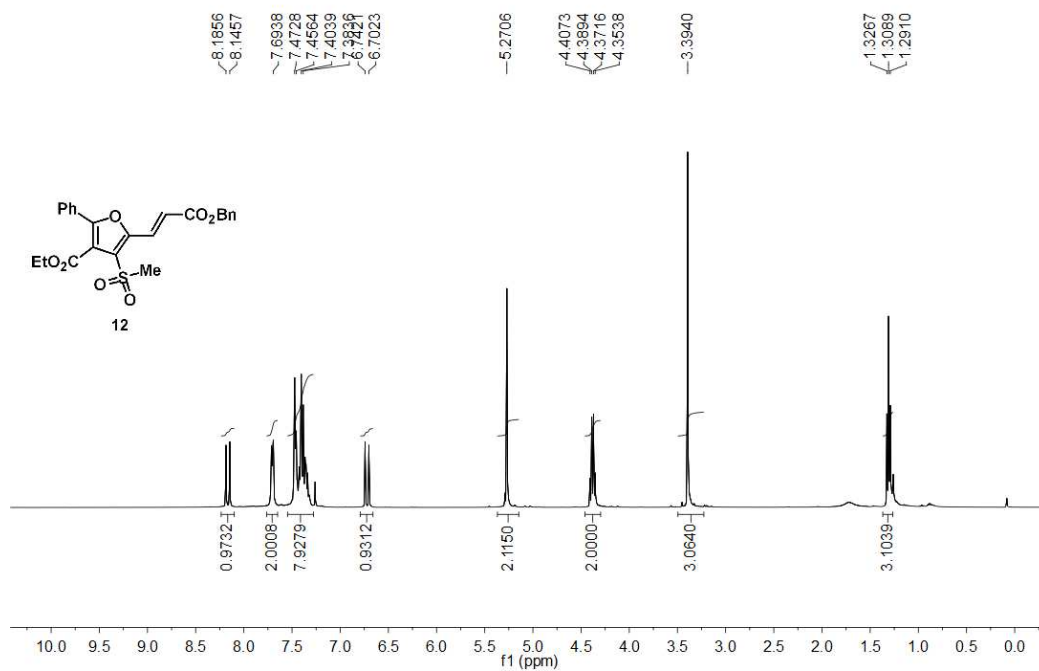


Figure S129. ^1H NMR spectrum of compound **12** (CDCl_3 , 25 °C, 400 MHz).

wqn-1429w

^{13}C NMR in CDCl_3 (100 MHz)

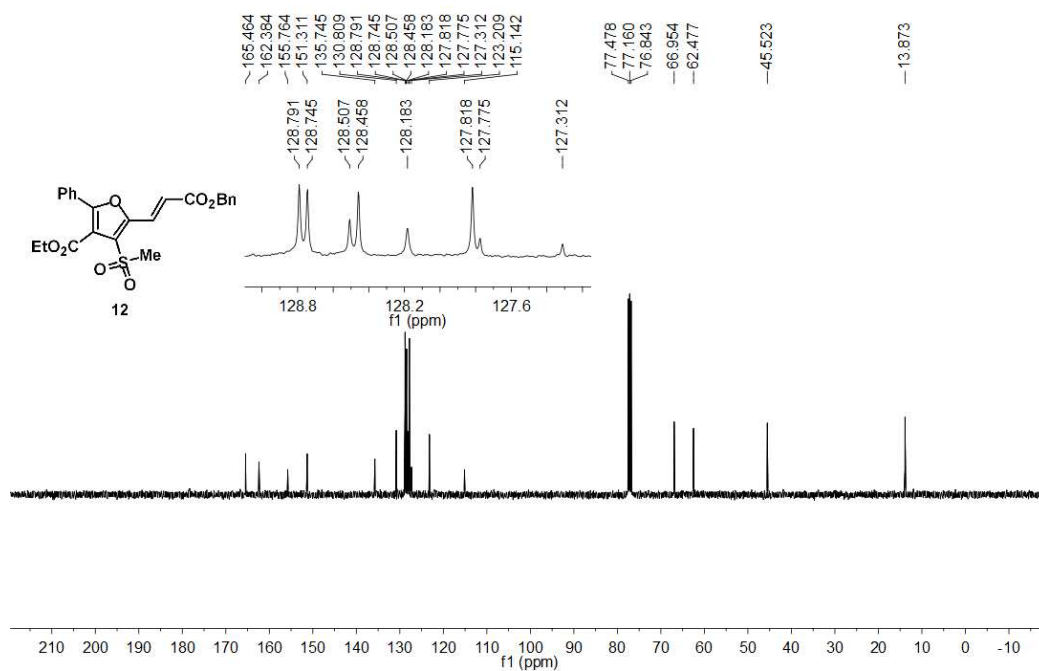


Figure S130. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **12** (CDCl_3 , 25 °C, 100 MHz).