

Supporting Information

Pd-Catalyzed Intramolecular C-H Addition to Cyano-Group: Construction of Functionalized Fused Thiophene Scaffolds

*Lang Zhao and Wei-Wei Liao**

Department of Organic Chemistry, College of Chemistry, Jilin University, Changchun 130012, China

E-mail: wliao@jlu.edu.cn

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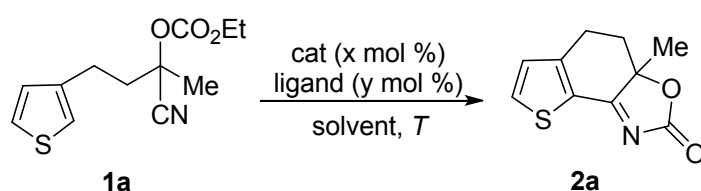
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I. General Information

All reactions were carried out under inert atmospheric condition unless otherwise noted, and solvents were dried according to established procedures. Reactions were monitored by thin layer chromatography (TLC) visualizing with ultraviolet light (UV), KMnO_4 , p-anisaldehyde stain, and phosphomolybdic acid (PMA) stain; column chromatography purifications were carried out using silica gel. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a 300 or 500 MHz spectrometer in CDCl_3 , and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on 125 MHz spectrometer in CDCl_3 unless otherwise noted. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane (TMS) and are referenced to residual protium in the NMR solvent ($\text{CHCl}_3 = \delta$ 7.26 ppm). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane (TMS) and are referenced to the carbon resonances of the solvent residual peak ($\text{CDCl}_3 = \delta$ 77.16 ppm). NMR data are presented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz), integration. Mass spectra were recorded on the Bruker MicrOTOF Q II.

II. Reaction Condition Screening

1) Table S1. Optimization of the Reaction Conditions ^a

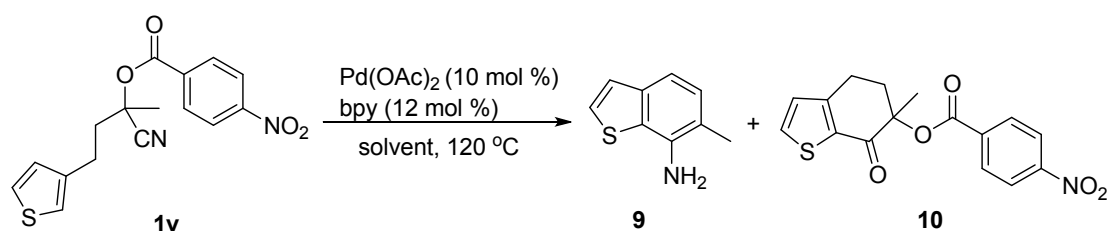


Entry	Cat.	Ligand	Solvent	T(°C)	t(h)	Yield(%) ^b	Con.(%) ^c
3	$\text{Pd}(\text{OAc})_2$	bpy	NMA	120	5	10	26
1 ^d	$\text{Pd}(\text{OAc})_2$	bpy	NMA/HOAc=3:1	120	5	46	99
2	$\text{Pd}(\text{OAc})_2$	bpy	NMA/HOAc=3:1	120	5	65	99
4 ^e	$\text{Pd}(\text{OAc})_2$	bpy	NMA/D-CSA	120	5	Trace	12
5 ^e	$\text{Pd}(\text{OAc})_2$	Bpy	NMA/ PhCO_2H	120	5	26	62
6	$\text{Pd}(\text{OAc})_2$	Bpy	NMA/TFA=3:1	120	5	0	16
7	$\text{Pd}(\text{OAc})_2$	Bpy	NMA/PA=3:1	120	5	59	74
8	$\text{Pd}(\text{OAc})_2$	Bpy	NMA/HFIP=3:1	120	5	12	22
9	$\text{Pd}(\text{OAc})_2$	bpy	NMA/HOAc=5:1	120	5	46	--
10	$\text{Pd}(\text{OAc})_2$	bpy	HOAc	120	5	7	76
11	$\text{Pd}(\text{OAc})_2$	bpy	DMF/HOAc=3:1	120	5	26	29
12	$\text{Pd}(\text{OAc})_2$	bpy	DMA/HOAc=3:1	120	5	6	20
13	$\text{Pd}(\text{OAc})_2$	bpy	DMSO/HOAc=3:1	120	5	12	69
14	$\text{Pd}(\text{OAc})_2$	bpy	Dioxane/HOAc=3:1	120	5	6	13
15	$\text{Pd}(\text{OAc})_2$	bpy	THF/HOAc=3:1	120	5	Trace	7
16	$\text{Pd}(\text{TFA})_2$	Bpy	NMA/HOAc=3:1	120	5	58	65
17	$\text{Pd}(\text{acac})_2$	Bpy	NMA/HOAc=3:1	120	12	48	80

18	Pd(OH) ₂	Bpy	NMA/HOAc=3:1	120	5	21	41
19 ^f	PdCl ₂	Bpy	NMA/HOAc=3:1	120	5	24	100
20	Pd(OAc) ₂	Phen	NMA/HOAc=3:1	120	5	64	99
21	Pd(OAc) ₂	L-1	NMA/HOAc=3:1	120	5	17	99
22	Pd(OAc) ₂	-	NMA/HOAc=3:1	120	5	0	35
23 ^g	Pd(OAc) ₂	Bpy	NMA/HOAc=3:1	120	3.5	41	--
24	Pd(OAc) ₂	Bpy	NMA/HOAc=3:1	120	3.5	61	73
25	Pd(OAc) ₂	Bpy	NMA/HOAc=3:1	100	15	63	88
26	Pd(OAc) ₂	Bpy	NMA/HOAc=3:1	80	20	34	58
27	Pd(OAc) ₂	Bpy	NMA/HOAc=3:1	140	3	10	--

^a Reactions were performed with **1a** (0.2 mmol), Pd(OAc)₂ (5 mol %), and ligand (6 mol %) in solvent (c = 0.1 M). ^b Isolated yields. ^c Based on recovered starting material **1a**. ^d c = 0.4 M. ^e Acid (1.5 equiv.). ^f PdCl₂ (10 mol %), bpy (12 mol %), AgSbF₆ (30 mol %). ^g Pd(OAc)₂ (10 mol %), bpy (12 mol %). bpy: 2,2'-bipyridine; phen: 1,10-phenanthroline; L-1: 4,4'-Dimethyl-2,2'-bipyridyl; PA: Pivalic acid; D-CSA: D-(+)-camphorsulfonic acid; DMA: N,N-dimethylacetamide; NMA: N-methylacetamide.

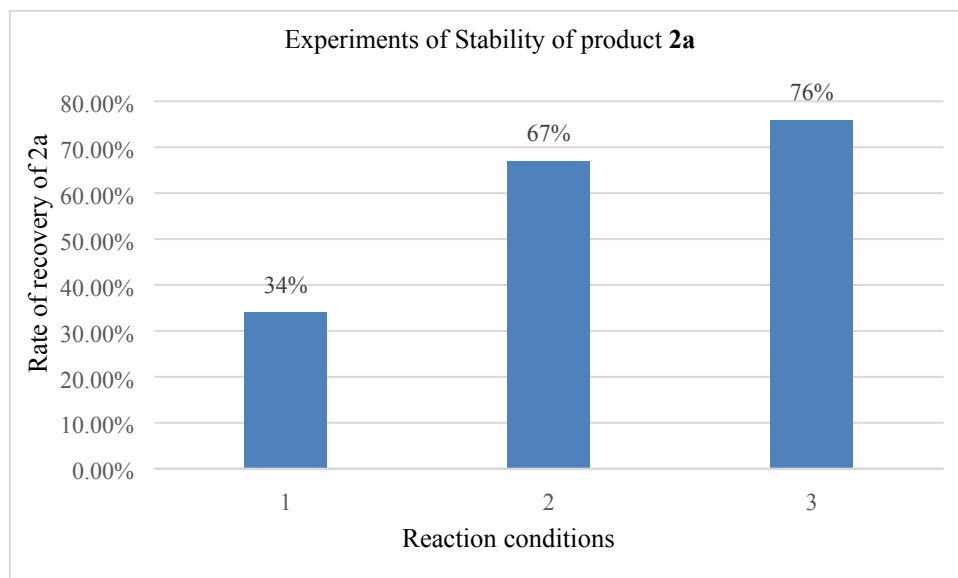
2) Table S2. Optimization of the Reaction Conditions for Compound **9**^a



Entry	Solvent	t(h)	9 Yield (%) ^b	10 Yield (%) ^b	Conv (%) ^c
1	HOAc	16	-	60	100
2	NMA/TFA=3:1	20	-	30	37
3	NMA/HOAc=3:1	16	-	55	85
4	PhMe /HOAc=3:1	16	-	44	60
5	DMSO/HOAc=3:1	16	27	trace	47
6	Dioxane/HOAc=3:1	16	28	21	50
7	DMF/HOAc=3:1	16	25	12	64
8	THF/HOAc=3:1	18	21	33	68
9	DCE/HOAc=3:1	16	3	20	44

^a Reactions were performed with **1v** (0.2 mmol), Pd(OAc)₂ (5 mol %), and bpy (6 mol %) in solvent (c = 0.1 M). ^b Isolated yields. ^c Based on recovered starting material **1v**.

3) Figure S-1. Experiments of Stability of **2a**

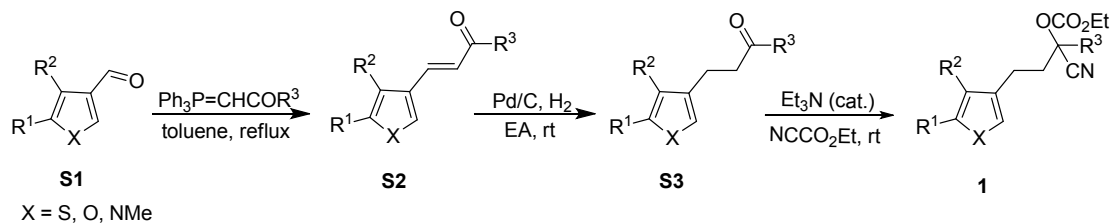


Reaction conditions:

1. **2a** (0.2 mmol), Pd(OAc)₂ (5 mol %), bpy (6 mol %) and NMA/HOAc=3:1 (c = 0.1 M), 120 °C, 3.5 h.
2. **2a** (0.2 mmol), NMA/HOAc=3:1 (c = 0.1 M), 120 °C, 3.5 h.
3. **2a** (0.2 mmol), NMA (c = 0.1 M), 120 °C, 3.5 h.

I. Preparation of Substrates

1)

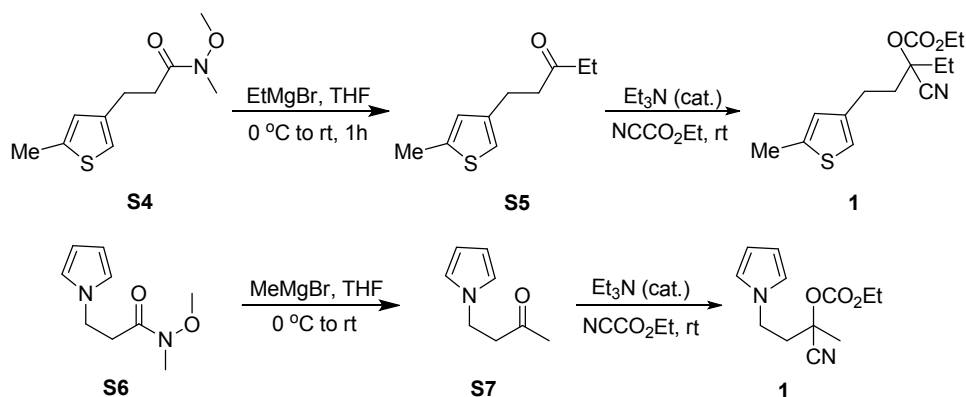


According to our previous work,¹ to a solution of **S1** (1.0 equiv.) in toluene (0.3 M) was added ylide (1.0 equiv.) The resulting mixture was heated to reflux and stirring was maintained until the reaction was completed (monitored by TLC). The solvent was evaporated *in vacuo* and the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether) to give **S2**.

The **S2** (1.0 equiv.) was dissolved in EtOAc (0.2 M), palladium on carbon (5% Pd) was added. The reaction was stirred for 2 hours under a H₂ atmosphere. Then the reaction was diluted with EtOAc and filtered through a short Celite® pad, and the filtrate was concentrated under reduced pressure, the residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether) to give **S3**.

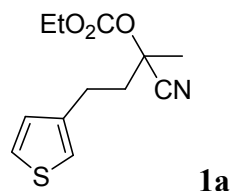
To a mixture of **S3** (1.0 equiv.) and Et₃N (10 mol%), ethyl carbonocyanidate (1.1 equiv.) was slowly added at rt.² Upon completion, the reaction was concentrated in vacuum. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether) to give product **1** (**1a-1l**, **1n-1s**, **3a**, **3b**). Compounds **1t-1u** were prepared according to previous procedure.¹

2)

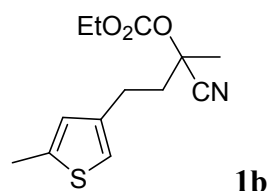


To a solution of **S4** or **S6** (1.0 equiv.) in dry THF (0.2 M) was added EtMgBr (1.1 equiv., 1.1 M in THF) dropwise at 0 °C. Then, the reaction mixture was stirred at rt for 2 h. After completion, the reaction was quenched with saturated ammonium chloride solution at 0 °C and the mixture was extracted with DCM. The combined organic phases were washed with brine before being dried over Na₂SO₄ and concentrated *in vacuo*. The residue was purified by column chromatography (silica gel, EtOAc/Petroleum ether) to give **S5** or **S7**.³

Compounds **1m** and **5** were prepared from compounds **S5** or **S7** according to the procedure for the synthesis of compound **1a**.

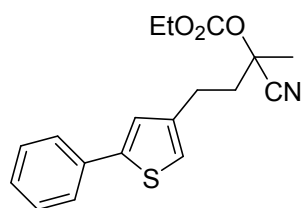


Colourless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.28 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.00 (m, 1H), 6.95 (dd, *J* = 4.9, 1.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.01 – 2.81 (m, 2H), 2.35 (ddd, *J* = 14.0, 11.7, 5.2 Hz, 1H), 2.24 (ddd, *J* = 14.0, 11.9, 5.3 Hz, 1H), 1.83 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 152.64, 139.90, 127.93, 126.07, 120.95, 118.29, 73.73, 65.03, 40.66, 24.79, 24.66, 14.24. HRMS (ESI): calcd. for C₁₂H₁₅NO₃S ([M+H]⁺): 254.0845, found 254.0851.

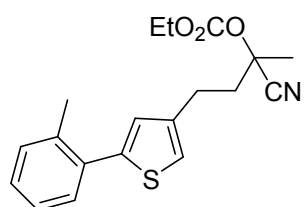


Colourless oil. ¹H NMR (500 MHz, CDCl₃) δ 6.73 (s, 1H), 6.61 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.91 – 2.73 (m, 2H), 2.45 (s, 3H), 2.32 (ddd, *J* = 13.9, 11.8, 5.2 Hz, 1H), 2.20 (ddd, *J* = 13.9, 12.0, 5.2 Hz, 1H), 1.82 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 152.65, 140.45, 139.75, 126.27, 118.57, 118.31, 73.76, 65.00,

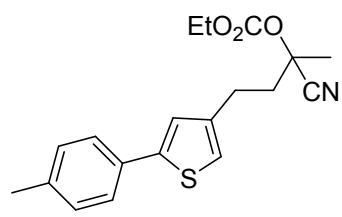
40.54, 25.00, 24.64, 15.39, 14.24. HRMS (ESI): calcd. for C₁₃H₁₇NO₃S ([M+H]⁺): 268.1102, found 268.1101.



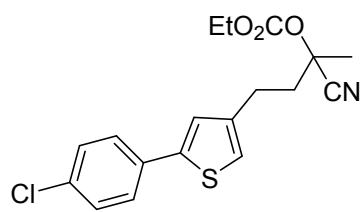
Colourless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.61 (d, *J* = 7.9 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.28 (m, 1H), 7.19 (s, 1H), 6.97 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.01 – 2.85 (m, 2H), 2.41 (ddd, *J* = 14.0, 11.7, 5.2 Hz, 1H), 2.30 (ddd, *J* = 14.0, 12.0, 5.3 Hz, 1H), 1.88 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 152.67, 145.03, 140.86, 134.36, 129.01, 127.72, 125.85, 124.03, 120.50, 118.31, 73.75, 65.07, 40.60, 25.17, 24.70, 14.25. HRMS (ESI): calcd. for C₁₈H₁₉NO₃S ([M+H]⁺): 330.1158, found 330.1159.



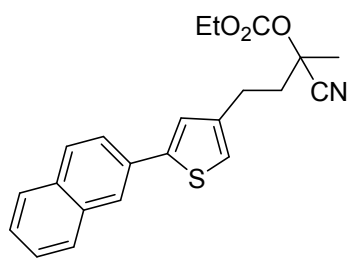
Colourless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.37 (d, *J* = 7.5 Hz, 1H), 7.27 – 7.18 (m, 3H), 6.99 (s, 1H), 6.90 (s, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.01 – 2.84 (m, 2H), 2.42 (s, 3H), 2.40 – 2.34 (m, 1H), 2.28 (ddd, *J* = 14.0, 12.0, 5.3 Hz, 1H), 1.85 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 152.69, 143.92, 139.90, 136.07, 134.21, 130.88, 130.40, 128.01, 127.36, 126.04, 120.78, 118.33, 73.79, 65.08, 40.63, 25.14, 24.72, 21.28, 14.27. HRMS (ESI): calcd. for C₁₉H₂₁NO₃S ([M+H]⁺): 344.1315, found 344.1319.



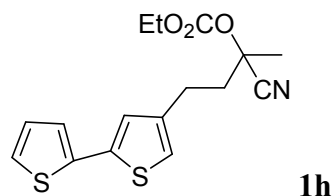
Yellow solid, mp: 55.6-56.9 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.46 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.11 (s, 1H), 6.90 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.97 – 2.81 (m, 2H), 2.43 – 2.32 (m, 4H), 2.27 (ddd, *J* = 14.0, 12.0, 5.3 Hz, 1H), 1.84 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 152.67, 145.18, 140.78, 137.61, 131.61, 129.68, 125.76, 123.53, 119.95, 118.32, 73.77, 65.06, 40.61, 25.17, 24.70, 21.28, 14.25. HRMS (ESI): calcd. for C₁₉H₂₁NO₃S ([M+H]⁺): 344.1315, found 344.1317.



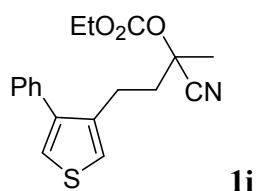
White solid, mp: 61.4-62.7 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.49 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 7.14 (s, 1H), 6.95 (s, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 2.98 – 2.81 (m, 2H), 2.37 (ddd, $J = 13.9, 11.7, 5.2$ Hz, 1H), 2.26 (ddd, $J = 14.0, 11.9, 5.3$ Hz, 1H), 1.84 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.67, 143.68, 141.06, 133.48, 132.91, 129.17, 127.04, 124.42, 120.92, 118.29, 73.72, 65.10, 40.62, 25.15, 24.72, 14.26. HRMS (ESI): calcd. for $\text{C}_{18}\text{H}_{18}\text{ClNO}_3\text{S}$ ($[\text{M}+\text{H}]^+$): 364.0769, found 364.0768.



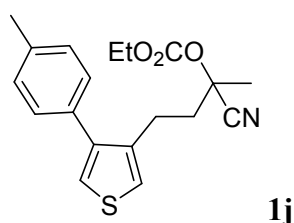
Yellow solid, mp: 72.4-72.6 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.02 (s, 1H), 7.86 – 7.78 (m, 3H), 7.70 (d, $J = 8.5$ Hz, 1H), 7.51 – 7.42 (m, 2H), 7.29 (s, 1H), 6.98 (s, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 3.01 – 2.85 (m, 2H), 2.44 – 2.36 (m, 1H), 2.33 – 2.26 (m, 1H), 1.85 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.69, 145.07, 141.02, 133.72, 132.90, 131.75, 128.70, 128.14, 127.84, 126.72, 126.15, 124.42, 124.29, 124.16, 120.77, 118.33, 73.77, 65.09, 40.64, 25.22, 24.72, 14.26. HRMS (ESI): calcd. for $\text{C}_{22}\text{H}_{21}\text{NO}_3\text{S}$ ($[\text{M}+\text{H}]^+$): 380.1315, found 380.1313.



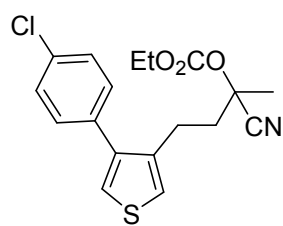
Yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.20 (dd, $J = 5.1, 1.0$ Hz, 1H), 7.15 (dd, $J = 3.5, 0.9$ Hz, 1H), 7.04 – 6.99 (m, 2H), 6.87 (s, 1H), 4.27 (q, $J = 7.2$ Hz, 2H), 2.95 – 2.78 (m, 2H), 2.36 (ddd, $J = 13.9, 11.7, 5.2$ Hz, 1H), 2.25 (ddd, $J = 14.0, 11.9, 5.3$ Hz, 1H), 1.84 (s, 3H), 1.34 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.66, 140.66, 138.05, 137.39, 127.92, 124.60, 124.59, 123.86, 120.03, 118.28, 73.70, 65.08, 40.57, 25.06, 24.70, 14.25. HRMS (ESI): calcd. for $\text{C}_{16}\text{H}_{17}\text{NO}_3\text{S}_2$ ($[\text{M}+\text{H}]^+$): 336.0723, found 336.0721.



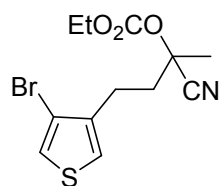
Colourless oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.43 – 7.40 (m, 2H), 7.36 – 7.33 (m, 3H), 7.19 (d, $J = 3.2$ Hz, 1H), 7.09 (d, $J = 3.2$ Hz, 1H), 4.22 (q, $J = 7.1$ Hz, 2H), 2.97 – 2.80 (m, 2H), 2.17 (ddd, $J = 13.9, 11.7, 5.1$ Hz, 1H), 2.06 (ddd, $J = 13.9, 11.9, 5.2$ Hz, 1H), 1.66 (s, 3H), 1.31 (q, $J = 7.5$ Hz, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 152.56, 142.81, 138.23, 136.73, 128.74, 128.70, 127.50, 123.92, 122.33, 118.18, 73.59, 64.95, 39.81, 24.40, 23.84, 14.23. HRMS (ESI): calcd. for $\text{C}_{18}\text{H}_{19}\text{NO}_3\text{S}$ ($[\text{M}+\text{H}]^+$): 330.1158, found 330.1157.



White solid, mp: 73.4-74.7 °C. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.27 – 7.19 (m, 4H), 7.16 (d, $J = 3.1$ Hz, 1H), 7.07 (d, $J = 3.0$ Hz, 1H), 4.22 (q, $J = 7.1$ Hz, 2H), 2.97 – 2.80 (m, 2H), 2.39 (s, 3H), 2.19 (ddd, $J = 13.8, 11.8, 5.1$ Hz, 1H), 2.08 (ddd, $J = 13.9, 12.0, 5.3$ Hz, 1H), 1.67 (s, 3H), 1.32 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 152.55, 142.76, 138.26, 137.17, 133.75, 129.38, 128.56, 123.60, 122.16, 118.19, 73.61, 64.92, 39.75, 24.39, 23.84, 21.29, 14.21. HRMS (ESI): calcd. for $\text{C}_{19}\text{H}_{21}\text{NO}_3\text{S}$ ($[\text{M}+\text{H}]^+$): 344.1315, found 344.1313.

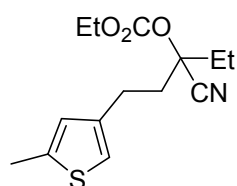


Yellow oil. $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.39 (d, $J = 8.5$ Hz, 2H), 7.29 (d, $J = 8.5$ Hz, 2H), 7.19 (d, $J = 3.2$ Hz, 1H), 7.10 (d, $J = 3.2$ Hz, 1H), 4.23 (q, $J = 7.1$ Hz, 2H), 2.95 – 2.80 (m, 2H), 2.18 (ddd, $J = 14.0, 11.6, 5.2$ Hz, 1H), 2.08 (ddd, $J = 14.0, 11.8, 5.3$ Hz, 1H), 1.70 (s, 3H), 1.33 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 152.54, 141.51, 138.03, 135.13, 133.55, 130.03, 128.91, 124.25, 122.64, 118.13, 73.50, 65.03, 39.90, 24.49, 23.77, 14.24. HRMS (ESI): calcd. for $\text{C}_{18}\text{H}_{18}\text{ClNO}_3\text{S}$ ($[\text{M}+\text{H}]^+$): 364.0769, found 364.0766.



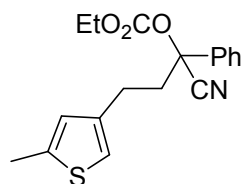
1l

Yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.26 (s, 1H), 7.05 (s, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 2.95 – 2.76 (m, 2H), 2.39 – 2.20 (m, 2H), 1.86 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.64, 138.60, 123.66, 122.05, 118.22, 112.40, 73.58, 65.08, 39.39, 24.61, 24.60, 14.28. HRMS (ESI): calcd. for $\text{C}_{12}\text{H}_{14}\text{BrNO}_3\text{S}$ ($[\text{M}+\text{H}]^+$): 331.9951, found 331.9949.



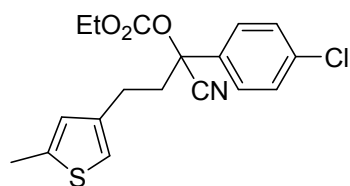
1m

Yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 6.72 (s, 1H), 6.61 (s, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 2.84 – 2.68 (m, 2H), 2.45 (s, 3H), 2.37 – 2.22 (m, 2H), 2.17 (dq, $J = 14.9, 7.5$ Hz, 1H), 2.07 (dq, $J = 14.7, 7.4$ Hz, 1H), 1.34 (t, $J = 7.1$ Hz, 3H), 1.10 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.65, 140.45, 139.88, 126.29, 118.57, 117.76, 78.01, 64.96, 37.08, 30.09, 24.80, 15.40, 14.25, 8.17. HRMS (ESI): calcd. for $\text{C}_{14}\text{H}_{19}\text{NO}_3\text{S}$ ($[\text{M}+\text{H}]^+$): 282.1158, found 282.1159.



1n

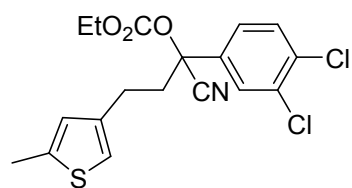
Colourless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.54 (d, $J = 7.5$ Hz, 2H), 7.46 – 7.37 (m, 3H), 6.66 (s, 1H), 6.54 (s, 1H), 4.24 – 4.11 (m, 2H), 2.87 (td, $J = 13.3, 4.2$ Hz, 1H), 2.68 – 2.59 (m, 1H), 2.54 (td, $J = 13.0, 4.2$ Hz, 1H), 2.41 (s, 3H), 2.33 (td, $J = 13.1, 4.3$ Hz, 1H), 1.28 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.35, 140.36, 139.59, 136.84, 129.60, 129.17, 126.26, 124.84, 118.51, 117.12, 79.15, 65.25, 43.44, 25.38, 15.37, 14.19. HRMS (ESI): calcd. for $\text{C}_{18}\text{H}_{19}\text{NO}_3\text{S}$ ($[\text{M}+\text{H}]^+$): 330.1158, found 330.1151.



1o

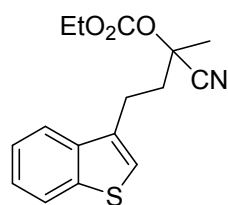
Yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.48 (d, $J = 8.5$ Hz, 2H), 7.41 (d, $J = 8.6$ Hz, 2H), 6.66 (s, 1H), 6.53 (s, 1H), 4.25 – 4.13 (m, 2H), 2.86 (td, $J = 13.4, 3.9$ Hz, 1H), 2.67 – 2.58 (m, 1H), 2.57 – 2.47 (m, 1H), 2.42 (s, 3H), 2.31 (td, $J = 13.5, 4.3$ Hz, 1H),

1.29 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.30, 140.51, 139.30, 135.74, 135.43, 129.45, 126.42, 126.19, 118.63, 116.77, 78.57, 65.44, 43.25, 25.34, 15.39, 14.21. HRMS (ESI): calcd. for $\text{C}_{18}\text{H}_{18}\text{ClNO}_3\text{S}$ ($[\text{M}+\text{H}]^+$): 364.0769, found 364.0767.



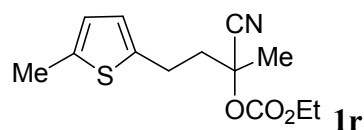
1p

Yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.62 (d, $J = 2.1$ Hz, 1H), 7.50 (d, $J = 8.4$ Hz, 1H), 7.39 (dd, $J = 8.4, 2.2$ Hz, 1H), 6.67 (s, 1H), 6.53 (s, 1H), 4.27 – 4.15 (m, 2H), 2.87 (td, $J = 14.0, 4.3$ Hz, 1H), 2.70 – 2.61 (m, 1H), 2.56 – 2.47 (m, 1H), 2.42 (s, 3H), 2.36 – 2.27 (m, 1H), 1.31 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.23, 140.60, 139.02, 137.07, 134.14, 133.73, 131.19, 127.10, 126.11, 124.38, 118.75, 116.36, 77.96, 65.64, 43.13, 25.31, 15.37, 14.19. HRMS (ESI): calcd. for $\text{C}_{18}\text{H}_{17}\text{Cl}_2\text{NO}_3\text{S}$ ($[\text{M}+\text{H}]^+$): 397.0379, found 397.0385.



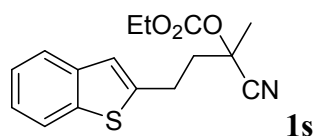
1q

White solid. mp: 65.6-67.7 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.86 (d, $J = 7.9$ Hz, 1H), 7.77 (d, $J = 7.8$ Hz, 1H), 7.43 – 7.33 (m, 2H), 7.15 (s, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 3.21 – 3.04 (m, 2H), 2.45 (ddd, $J = 14.0, 11.8, 5.2$ Hz, 1H), 2.33 (ddd, $J = 14.0, 11.9, 5.2$ Hz, 1H), 1.87 (s, 3H), 1.35 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.71, 140.62, 138.51, 134.06, 124.59, 124.28, 123.11, 122.15, 121.49, 118.35, 73.80, 65.10, 39.56, 24.71, 23.26, 14.26. HRMS (ESI): calcd. for $\text{C}_{16}\text{H}_{17}\text{NO}_3\text{S}$ ($[\text{M}+\text{H}]^+$): 304.1002, found 304.1004.

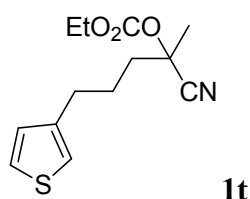


1r

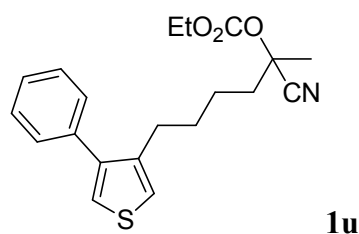
Colourless oil. ^1H NMR (500 MHz, CDCl_3) δ 6.61 (d, $J = 3.2$ Hz, 1H), 6.55 (d, $J = 3.2$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 3.09 – 2.94 (m, 2H), 2.43 (s, 3H), 2.36 (ddd, $J = 14.0, 11.7, 5.2$ Hz, 1H), 2.25 (ddd, $J = 14.0, 11.9, 5.3$ Hz, 1H), 1.83 (s, 3H), 1.35 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.64, 139.86, 138.33, 124.97, 124.71, 118.19, 73.51, 65.08, 41.80, 24.75, 24.67, 15.40, 14.26. HRMS (ESI): calcd. for $\text{C}_{13}\text{H}_{17}\text{NO}_3\text{S}$ ($[\text{M}+\text{H}]^+$): 268.1002, found 268.1005.



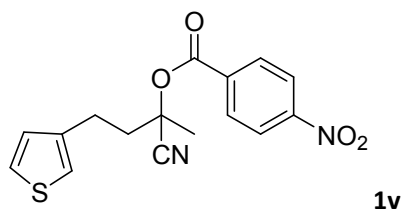
White solid. mp: 48.6-49.8 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.34 – 7.24 (m, 2H), 7.06 (s, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.26 – 3.10 (m, 2H), 2.46 (ddd, *J* = 14.0, 11.5, 5.3 Hz, 1H), 2.36 (ddd, *J* = 14.0, 11.7, 5.4 Hz, 1H), 1.85 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 152.59, 143.10, 140.02, 139.40, 124.43, 124.01, 123.09, 122.27, 121.52, 118.10, 73.45, 65.12, 41.13, 25.46, 24.67, 14.21. HRMS (ESI): calcd. for C₁₆H₁₇NO₃S ([M+H]⁺): 304.1002, found 304.1003.



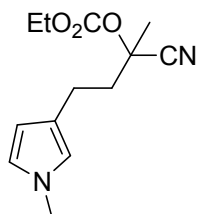
Colourless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.27 – 7.26 (m, 1H), 6.97 – 6.96 (m, 1H), 6.95 – 6.93 (m, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.71 (t, *J* = 6.2 Hz, 2H), 2.09 – 2.01 (m, 1H), 1.98 – 1.82 (m, 3H), 1.77 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 152.68, 141.38, 128.04, 125.83, 120.70, 118.51, 74.06, 64.96, 39.34, 29.64, 24.82, 24.58, 14.26. HRMS (ESI): calcd. for C₁₃H₁₇NO₃S ([M+H]⁺): 268.1002, found 268.1001.



Colourless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.43 – 7.38 (m, 2H), 7.35 – 7.32 (m, 3H), 7.16 (d, *J* = 3.1 Hz, 1H), 7.03 (d, *J* = 3.0 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.68 – 2.62 (m, 2H), 1.98 – 1.90 (m, 1H), 1.83 (dd, *J* = 15.6, 9.1 Hz, 1H), 1.71 (s, 3H), 1.61 – 1.43 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 152.66, 143.02, 140.62, 137.30, 128.87, 128.49, 127.24, 123.42, 121.43, 118.52, 74.09, 64.91, 39.52, 29.63, 29.00, 24.51, 23.63, 14.25. HRMS (ESI): calcd. for C₂₀H₂₃NO₃S ([M+H]⁺): 358.1471, found 358.1473.

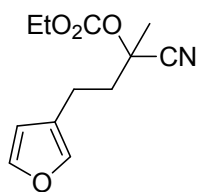


Colourless oil. ^1H NMR (500 MHz, CDCl_3) δ 8.29 (d, $J = 8.7$ Hz, 2H), 8.10 (d, $J = 8.7$ Hz, 2H), 7.31 – 7.28 (m, 1H), 7.04 (s, 1H), 7.00 (d, $J = 4.7$ Hz, 1H), 3.09 – 2.92 (m, 2H), 2.55 (ddd, $J = 14.3, 10.5, 5.9$ Hz, 1H), 2.43 (ddd, $J = 14.2, 10.7, 5.7$ Hz, 1H), 1.97 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 162.68, 151.06, 139.79, 134.37, 131.05, 127.90, 126.31, 123.81, 121.06, 118.05, 73.36, 40.44, 25.07, 24.80. HRMS (ESI): calcd. for $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_4\text{S}$ ($[\text{M}+\text{H}]^+$): 331.0747, found 331.0750.



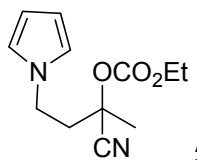
4a

Colourless oil. ^1H NMR (500 MHz, CDCl_3) δ 6.52 (t, $J = 2.2$ Hz, 1H), 6.42 (s, 1H), 5.98 (t, $J = 1.9$ Hz, 1H), 4.26 (q, $J = 7.1$ Hz, 2H), 3.60 (s, 3H), 2.80 – 2.62 (m, 2H), 2.39 – 2.25 (m, 1H), 2.21 – 2.12 (m, 1H), 1.81 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.75, 121.96, 121.85, 119.42, 118.55, 108.12, 74.04, 64.94, 41.56, 36.19, 24.66, 21.62, 14.28. HRMS (ESI): calcd. for $\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}_3$ ($[\text{M}+\text{H}]^+$): 251.1390, found 251.1395.



4b

Colourless oil. ^1H NMR (500 MHz, CDCl_3) δ 7.37 (t, $J = 1.4$ Hz, 1H), 7.26 (s, 1H), 6.29 (s, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 2.79 – 2.63 (m, 2H), 2.28 (ddd, $J = 13.9, 11.7, 5.2$ Hz, 1H), 2.17 (ddd, $J = 14.0, 11.9, 5.3$ Hz, 1H), 1.83 (s, 3H), 1.35 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.66, 143.31, 139.18, 122.86, 118.29, 110.76, 73.74, 65.06, 40.32, 24.66, 19.64, 14.25. HRMS (ESI): calcd. for $\text{C}_{12}\text{H}_{15}\text{NO}_4$ ($[\text{M}+\text{H}]^+$): 238.1074, found 238.1073.

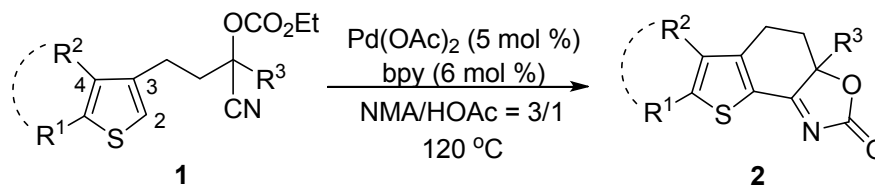


5

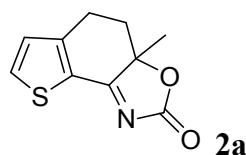
Yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 6.67 (brs, 2H), 6.16 (brs, 2H), 4.27 (q, $J = 7.1$ Hz, 2H), 4.22 – 4.11 (m, 2H), 2.52 – 2.45 (m, 1H), 2.44 – 2.35 (m, 1H), 1.74 (s, 3H), 1.35 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 152.45, 120.56, 117.73, 109.00, 72.28, 65.24, 44.54, 41.46, 24.62, 14.22. HRMS (ESI): calcd. for $\text{C}_{12}\text{H}_{16}\text{N}_2\text{O}_3$ ($[\text{M}+\text{H}]^+$): 237.1234, found 237.1238.

IV. General Procedure and Experimental Details of Palladium-Catalyzed

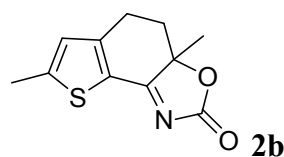
Intermolecular cyclization



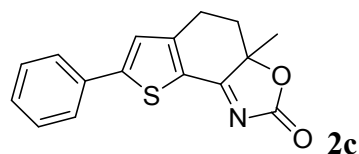
The **1** (0.2 mmol), Pd(OAc) (5 mol %), 2,2'-bipyridine (6 mol %), HOAc (0.5 ml) and *N*-methylacetamide (1.5 ml) were placed in a sealed tube under nitrogen atmosphere. The mixture was stirred at 120 °C for the desired time. After the reaction was finished, the reaction mixture was cooled to room temperature, and then NaHCO₃ was added to the sealed tube until no CO₂ bubbles were generated. The resulting mixture was extracted with CH₂Cl₂ three times. The combined organic layers were dried over anhydrous Na₂SO₄ and the solvent was evaporated under reduced pressure. The crude product **2** was purified by chromatography on a silica gel column.



Yellow solid, (27.1 mg, 65%) mp: 165.3-166.6 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, *J* = 4.9 Hz, 1H), 7.09 (d, *J* = 4.9 Hz, 1H), 3.18 (dd, *J* = 18.0, 5.0 Hz, 1H), 3.08 – 2.98 (m, 1H), 2.49 (dd, *J* = 12.7, 4.0 Hz, 1H), 2.21 (td, *J* = 12.2, 6.1 Hz, 1H), 1.59 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 191.59, 166.09, 151.60, 137.58, 128.85, 125.73, 86.46, 34.93, 24.91, 22.41. HRMS (ESI): calcd. for C₁₀H₉NO₂S ([M+H]⁺): 208.0427, found 208.0421.

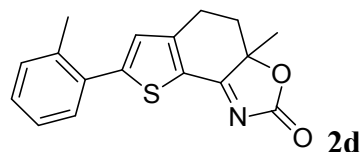


Yellow solid, (39.8 mg, 90%), mp: 105.1-106.3 °C. ¹H NMR (500 MHz, CDCl₃) δ 6.76 (s, 1H), 3.06 (dd, *J* = 18.0, 5.4 Hz, 1H), 2.99 – 2.88 (m, 1H), 2.59 (s, 3H), 2.44 (dd, *J* = 12.7, 4.3 Hz, 1H), 2.17 (td, *J* = 12.2, 6.1 Hz, 1H), 1.56 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 191.02, 166.36, 154.56, 152.57, 127.78, 123.73, 86.12, 34.92, 24.97, 22.65, 16.51. HRMS (ESI): calcd. for C₁₁H₁₁NO₂S ([M+H]⁺): 222.0583, found 222.0584.

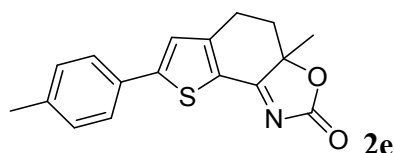


Yellow solid, (52.6 mg, 93%), mp: 190.4-191.8 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.65 (d, *J* = 7.2 Hz, 2H), 7.48 – 7.40 (m, 3H), 7.27 (s, 1H), 3.17 (dd, *J* = 17.9, 5.8 Hz, 1H),

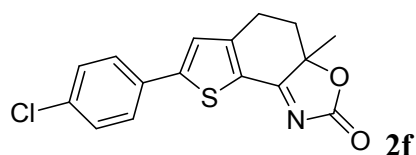
3.07 – 2.97 (m, 1H), 2.48 (dd, $J = 12.6, 4.9$ Hz, 1H), 2.20 (td, $J = 12.2, 6.1$ Hz, 1H), 1.60 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 191.01, 166.23, 156.88, 152.79, 132.58, 130.09, 129.42, 126.59, 124.58, 124.42, 86.19, 34.79, 25.07, 22.63. HRMS (ESI): calcd. for $\text{C}_{16}\text{H}_{13}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 284.0740, found 284.0747.



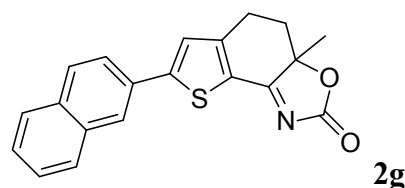
Yellow solid, (50.5 mg, 85%), mp: 130.1-131.5 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.41 (d, $J = 7.5$ Hz, 1H), 7.37 – 7.24 (m, 3H), 7.03 (s, 1H), 3.17 (dd, $J = 17.8, 5.7$ Hz, 1H), 3.09 – 2.99 (m, 1H), 2.50 (dd, $J = 12.6, 4.7$ Hz, 1H), 2.46 (s, 3H), 2.24 (td, $J = 12.2, 6.1$ Hz, 1H), 1.63 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 191.18, 166.22, 156.32, 151.79, 136.13, 132.47, 131.35, 130.24, 129.69, 128.12, 126.48, 125.23, 86.24, 35.00, 25.07, 22.63, 21.21. HRMS (ESI): calcd. for $\text{C}_{17}\text{H}_{15}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 298.0896, found 298.0898.



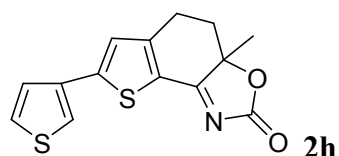
Yellow solid, (57.0 mg, 96%), mp: 188.2-189.4 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.54 (d, $J = 8.1$ Hz, 2H), 7.27 – 7.21 (m, 3H), 3.18 – 3.10 (m, 1H), 3.01 (td, $J = 12.1, 5.9$ Hz, 1H), 2.50 – 2.43 (m, 1H), 2.40 (s, 3H), 2.19 (td, $J = 12.2, 6.1$ Hz, 1H), 1.60 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 190.95, 166.31, 157.27, 152.88, 140.56, 130.10, 129.84, 126.48, 124.05, 123.90, 86.14, 34.81, 25.08, 22.68, 21.47. HRMS (ESI): calcd. for $\text{C}_{17}\text{H}_{15}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 298.0896, found 298.0898.



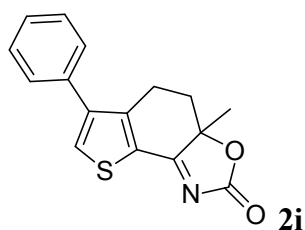
Yellow solid, (56.4 mg, 89%), mp: 181.4-182.6 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.59 (d, $J = 8.5$ Hz, 2H), 7.42 (d, $J = 8.5$ Hz, 2H), 7.24 (s, 1H), 3.17 (dd, $J = 17.9, 5.2$ Hz, 1H), 3.07 – 2.97 (m, 1H), 2.49 (dd, $J = 12.7, 4.2$ Hz, 1H), 2.21 (td, $J = 12.3, 6.1$ Hz, 1H), 1.61 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 190.94, 166.13, 155.22, 152.70, 136.14, 131.14, 129.69, 127.80, 124.85, 124.81, 86.20, 34.79, 25.08, 22.61. HRMS (ESI): calcd. for $\text{C}_{16}\text{H}_{12}\text{ClNO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 318.0350, found 318.0347.



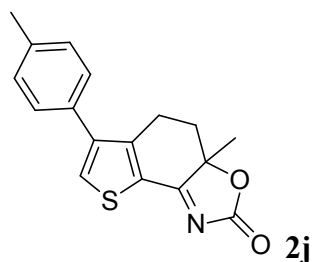
Yellow solid, (59.9 mg, 90%), mp: 221.3-222.7 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.13 (s, 1H), 7.94 – 7.83 (m, 3H), 7.72 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.57 – 7.52 (m, 2H), 7.37 (s, 1H), 3.17 (dd, *J* = 17.9, 4.7 Hz, 1H), 3.09 – 2.97 (m, 1H), 2.49 (dd, *J* = 12.6, 3.9 Hz, 1H), 2.21 (td, *J* = 12.2, 6.0 Hz, 1H), 1.62 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 190.95, 166.30, 156.95, 152.79, 133.92, 133.39, 129.94, 129.31, 128.60, 127.96, 127.48, 127.30, 126.04, 124.80, 124.58, 123.90, 86.21, 34.82, 25.12, 22.69. HRMS (ESI): calcd. for C₂₀H₁₅NO₂S ([M+H]⁺): 334.0896, found 334.0892.



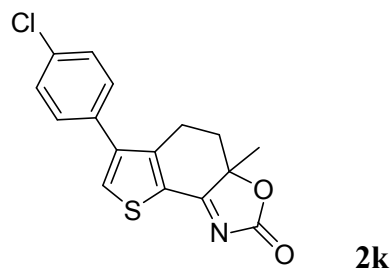
Yellow solid, (50.3 mg, 87%), mp: 196.5-197.7 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.41 (d, *J* = 4.7 Hz, 1H), 7.39 (d, *J* = 3.5 Hz, 1H), 7.13 – 7.08 (m, 2H), 3.13 (dd, *J* = 17.6, 5.5 Hz, 1H), 3.03 – 2.93 (m, 1H), 2.51 – 2.44 (m, 1H), 2.20 (td, *J* = 12.3, 6.1 Hz, 1H), 1.60 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 190.73, 166.21, 152.66, 149.63, 135.53, 128.71, 127.99, 126.97, 124.56, 123.63, 86.13, 34.73, 25.05, 22.69. HRMS (ESI): calcd. for C₁₄H₁₁NO₂S₂ ([M+H]⁺): 290.0304, found 290.0305.



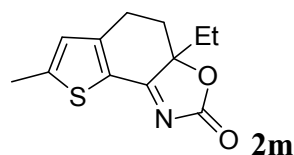
Yellow solid, (53.2 mg, 94%), mp: 191.4-192.7 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.79 (s, 1H), 7.50 – 7.33 (m, 5H), 3.06 – 3.03 (m, 2H), 2.51 – 2.45 (m, 1H), 2.22 – 2.13 (m, 1H), 1.67 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 191.88, 166.01, 149.38, 143.80, 134.41, 134.30, 128.99, 128.45, 126.73, 86.31, 35.19, 25.33, 22.30. HRMS (ESI): calcd. for C₁₆H₁₃NO₂S ([M+H]⁺): 284.0740, found 284.0749.



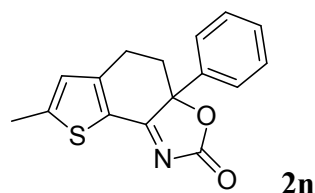
Yellow solid, (52.9 mg, 89%), mp: 190.4-191.7 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.76 (s, 1H), 7.27 (brs, 4H), 3.07 – 3.00 (m, 2H), 2.51 – 2.44 (m, 1H), 2.41 (s, 3H), 2.20 – 2.13 (m, 1H), 1.66 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 191.91, 166.06, 149.46, 143.83, 138.45, 134.11, 131.41, 129.69, 128.33, 126.66, 86.32, 35.22, 25.39, 22.32, 21.33. HRMS (ESI): calcd. for C₁₇H₁₅NO₂S ([M+H]⁺): 298.0896, found 298.0897.



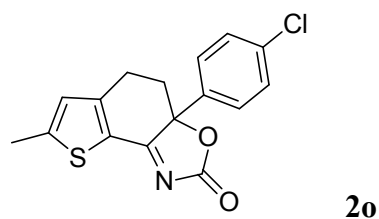
Yellow solid, (55.1 mg, 87%), mp: 183.4-184.8 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.81 (s, 1H), 7.44 (d, $J = 8.3$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 3.10 – 2.97 (m, 2H), 2.53 – 2.46 (m, 1H), 2.17 (td, $J = 11.9, 6.7$ Hz, 1H), 1.66 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 191.76, 165.91, 149.05, 142.49, 134.58, 134.55, 132.73, 129.75, 129.22, 126.97, 86.27, 35.14, 25.25, 22.26. HRMS (ESI): calcd. for $\text{C}_{16}\text{H}_{12}\text{ClNO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 318.0350, found 318.0345.



Yellow oil (42.8 mg, 90%). ^1H NMR (500 MHz, CDCl_3) δ 6.76 (s, 1H), 3.04 (dd, $J = 17.9, 5.8$ Hz, 1H), 2.99 – 2.88 (m, 1H), 2.59 (s, 3H), 2.56 – 2.48 (m, 1H), 2.16 (dt, $J = 18.1, 6.3$ Hz, 1H), 1.99 – 1.90 (m, 1H), 1.86 – 1.75 (m, 1H), 0.96 – 0.88 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 190.37, 166.70, 154.27, 152.55, 127.79, 123.80, 88.74, 32.97, 28.21, 24.73, 16.47, 7.62. HRMS (ESI): calcd. for $\text{C}_{12}\text{H}_{13}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 236.0740, found 236.0741.

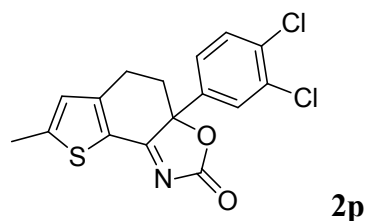


Yellow solid, (52.6 mg, 93%), mp: 151.2-152.5 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.37 – 7.28 (m, 5H), 6.71 (s, 1H), 3.01 – 2.85 (m, 2H), 2.60 (s, 3H), 2.55 – 2.39 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 188.52, 165.93, 154.86, 154.00, 135.92, 129.49, 128.99, 128.02, 126.27, 125.08, 89.60, 36.12, 24.78, 16.56. HRMS (ESI): calcd. for $\text{C}_{16}\text{H}_{13}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 284.0740, found 284.0747.

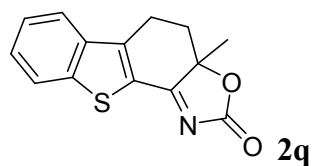


Yellow solid, (61.5 mg, 97%), mp: 158.2-159.5 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.32

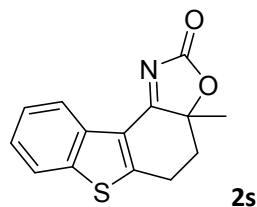
(d, $J = 8.7$ Hz, 2H), 7.26 (d, $J = 8.5$ Hz, 2H), 6.72 (s, 1H), 3.03 – 2.93 (m, 1H), 2.89 – 2.80 (m, 1H), 2.61 (s, 3H), 2.53 – 2.39 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 187.94, 165.67, 155.36, 153.95, 135.59, 134.53, 129.25, 128.08, 127.75, 124.92, 88.88, 36.09, 24.69, 16.61. HRMS (ESI): calcd. for $\text{C}_{16}\text{H}_{12}\text{ClNO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 318.0350, found 318.0351.



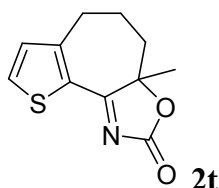
Yellow solid, (64.6 mg, 89%), mp: 191.4-192.7 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.44 – 7.40 (m, 2H), 7.13 (dd, $J = 8.4, 2.0$ Hz, 1H), 6.75 (s, 1H), 3.07 – 2.98 (m, 1H), 2.87 – 2.78 (m, 1H), 2.63 (s, 3H), 2.55 – 2.40 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 187.24, 165.39, 155.90, 154.07, 136.17, 133.99, 133.47, 130.96, 128.57, 128.19, 125.57, 124.73, 88.25, 36.01, 24.61, 16.66. HRMS (ESI): calcd. for $\text{C}_{16}\text{H}_{11}\text{Cl}_2\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 351.9960, found 351.9954.



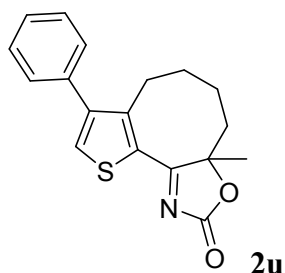
Yellow solid, (15.9 mg, 31%), mp: 236.4-237.7 °C. ^1H NMR (500 MHz, CDCl_3) δ 7.95 (d, $J = 8.1$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 7.57 (t, $J = 7.4$ Hz, 1H), 7.51 (t, $J = 7.4$ Hz, 1H), 3.42 (dd, $J = 18.1, 5.5$ Hz, 1H), 3.19 – 3.10 (m, 1H), 2.64 (dd, $J = 12.7, 4.8$ Hz, 1H), 2.31 (td, $J = 12.2, 6.2$ Hz, 1H), 1.64 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 192.39, 165.79, 146.94, 144.13, 137.52, 129.07, 125.90, 125.64, 123.78, 123.76, 86.77, 34.58, 23.50, 22.50. HRMS (ESI): calcd. for $\text{C}_{14}\text{H}_{11}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 258.0583, found 258.0585.



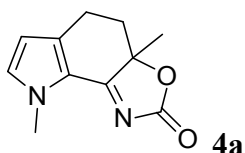
Yellow solid, (15.9 mg, 31%), mp: 183.3-184.5 °C. ^1H NMR (500 MHz, CDCl_3) δ 8.48 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.53 (t, $J = 7.5$ Hz, 1H), 7.45 (t, $J = 7.3$ Hz, 1H), 3.44 – 3.24 (m, 2H), 2.63 – 2.56 (m, 1H), 2.32 (td, $J = 12.1, 6.3$ Hz, 1H), 1.61 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 191.36, 166.93, 157.16, 138.91, 135.06, 126.49, 126.31, 124.60, 123.68, 122.34, 85.92, 35.08, 25.21, 22.41. HRMS (ESI): calcd. for $\text{C}_{14}\text{H}_{11}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 258.0583, found 258.0584.



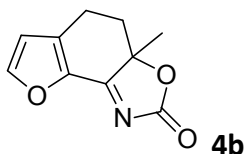
Yellow solid, (33.6 mg, 76%), mp: 136.4-137.8 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.68 (d, *J* = 4.9 Hz, 1H), 7.02 (d, *J* = 4.9 Hz, 1H), 3.14 – 3.04 (m, 1H), 3.02 – 2.93 (m, 1H), 2.43 – 2.36 (m, 1H), 2.21 – 2.09 (m, 2H), 2.04 – 1.92 (m, 1H), 1.61 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 192.95, 165.54, 151.43, 134.44, 132.13, 127.33, 90.34, 36.00, 30.51, 26.80, 23.70. HRMS (ESI): calcd. for C₁₁H₁₁NO₂S ([M+H]⁺): 222.0583, found 222.0584.



Yellow solid, (41.7 mg, 67%), mp: 176.2-177.5 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.63 (s, 1H), 7.48 – 7.39 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.09 – 3.01 (m, 1H), 2.75 – 2.69 (m, 1H), 2.47 (dd, *J* = 15.4, 8.7 Hz, 1H), 2.04 (dd, *J* = 15.4, 10.5 Hz, 1H), 1.86 – 1.76 (m, 5H), 1.63 – 1.58 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 192.06, 164.93, 146.82, 146.50, 135.82, 133.82, 131.05, 129.26, 128.79, 128.17, 92.89, 35.85, 28.26, 26.16, 25.68, 23.37. HRMS (ESI): calcd. for C₁₈H₁₇NO₂S ([M+H]⁺): 312.1053, found 312.1054.

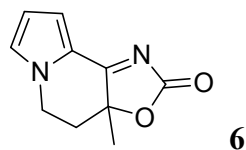


Yellow solid, (29.8 mg, 73%), mp: 176.4-177.6 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.06 (s, 1H), 6.14 (s, 1H), 3.97 (s, 3H), 2.99 – 2.80 (m, 2H), 2.37 (dd, *J* = 12.4, 3.8 Hz, 1H), 2.10 (td, *J* = 12.1, 6.2 Hz, 1H), 1.55 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 186.11, 167.49, 136.90, 134.66, 120.66, 109.71, 86.64, 36.13, 36.06, 23.26, 22.03. HRMS (ESI): calcd. for C₁₁H₁₂N₂O₂ ([M+H]⁺): 205.0972, found 205.0968.

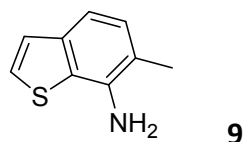


Yellow solid, (25.6 mg, 67%), mp: 53.3-54.5 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 1.5 Hz, 1H), 6.56 (d, *J* = 1.4 Hz, 1H), 3.02 – 2.84 (m, 2H), 2.45 (ddd, *J* = 12.7, 5.0, 1.4 Hz, 1H), 2.16 (td, *J* = 12.1, 6.2 Hz, 1H), 1.57 (s, 3H). ¹³C NMR (125 MHz,

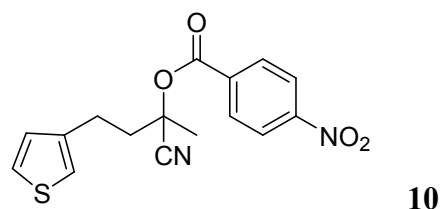
CDCl₃) δ 184.39, 166.19, 151.45, 141.04, 140.30, 113.07, 86.68, 35.67, 22.83, 21.47. HRMS (ESI): calcd. for C₁₀H₉NO₃ ([M+H]⁺): 192.0655, found 192.0656.



Yellow solid, (29.3 mg, 77%), mp: 156.3-157.5°C. ¹H NMR (500 MHz, CDCl₃) δ 7.20 – 7.17 (m, 1H), 7.15 (brs, 1H), 6.49 (dd, *J* = 4.1, 2.5 Hz, 1H), 4.41 (dd, *J* = 13.2, 6.2 Hz, 1H), 4.27 (td, *J* = 13.0, 4.5 Hz, 1H), 2.55 (dd, *J* = 12.9, 3.8 Hz, 1H), 2.38 (td, *J* = 12.8, 6.5 Hz, 1H), 1.61 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 186.78, 166.79, 130.18, 122.16, 117.18, 114.02, 83.50, 43.69, 33.86, 22.59. HRMS (ESI): calcd. for C₁₀H₁₀N₂O₂ ([M+H]⁺): 191.0815, found 191.0814.



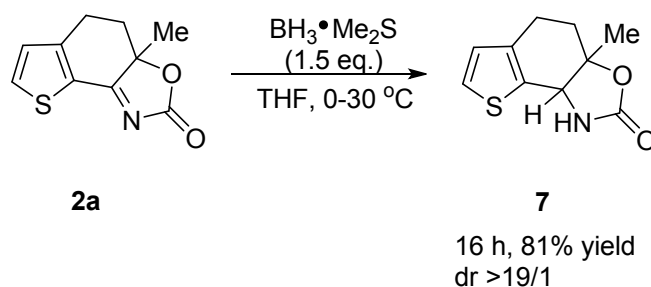
Brown solid, (9.4 mg, 28%), mp: 57.3-58.5 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.23 (m, 3H), 7.12 (d, *J* = 7.9 Hz, 1H), 3.82 (brs, 2H), 2.32 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 139.41, 138.53, 127.98, 126.98, 125.12, 124.24, 116.62, 114.27, 17.10. HRMS (ESI): calcd. for C₉H₉NS ([M+H]⁺): 164.0528, found 164.0530.



Brown solid, (40.2 mg, 60%), mp: 117.3-118.5 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.28 (d, *J* = 8.7 Hz, 2H), 8.22 (d, *J* = 8.7 Hz, 2H), 7.72 (d, *J* = 4.9 Hz, 1H), 6.99 (d, *J* = 4.9 Hz, 1H), 3.24 (td, *J* = 12.4, 5.5 Hz, 1H), 3.16 – 3.09 (m, 1H), 2.99 (ddd, *J* = 17.2, 12.2, 5.0 Hz, 1H), 2.26 – 2.19 (m, 1H), 1.75 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 188.23, 163.31, 150.72, 150.55, 136.11, 135.77, 134.94, 131.09, 128.19, 123.57, 83.41, 34.04, 24.12, 22.00. HRMS (ESI): calcd. for C₁₆H₁₃NO₅S ([M+H]⁺): 332.0587, found 332.0591.

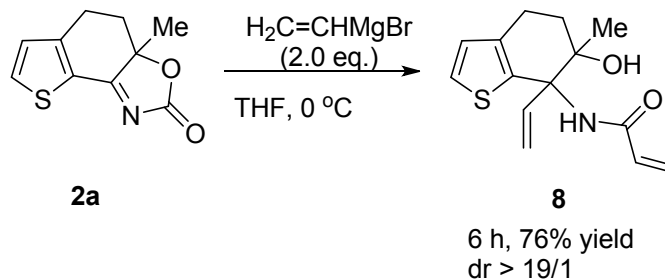
V. Synthetic Transformation

1)



To solution of **2a** (0.2 mmol) in THF (0.1 M) was added $\text{BH}_3 \cdot \text{Me}_2\text{S}$ (1.5 equiv.) dropwise at 0 °C.⁴ Then the reaction mixture was warmed to 30 °C and allowed to proceed for 24 h. The resulting mixture was cooled to 0 °C and quenched by dropwise addition of a 1:1 mixture of THF:H₂O. Solid K_2CO_3 was added until the aqueous and organic layers separated. The aqueous and organic layers were separated, and the aqueous layer was extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by chromatography on a silica gel column (EtOAc/petroleum ether) to afford **7** (33.4 mg, 80%). White solid, mp: 154.3-155.6 °C. ¹H NMR (500 MHz, CDCl_3) δ 7.22 (d, $J = 5.0$ Hz, 1H), 6.80 (d, $J = 5.0$ Hz, 1H), 6.24 (brs, 1H), 4.58 (s, 1H), 2.83 – 2.75 (m, 1H), 2.62 (dt, $J = 16.2, 4.7$ Hz, 1H), 2.28 (dt, $J = 14.0, 4.5$ Hz, 1H), 1.83 (ddd, $J = 14.8, 10.2, 4.9$ Hz, 1H), 1.60 (s, 3H). ¹³C NMR (125 MHz, CDCl_3) δ 158.77, 137.44, 133.55, 127.32, 125.64, 82.93, 55.74, 33.07, 26.28, 21.59. HRMS (ESI): calcd. for $\text{C}_{10}\text{H}_{11}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 210.0583, found 210.0582.

2)



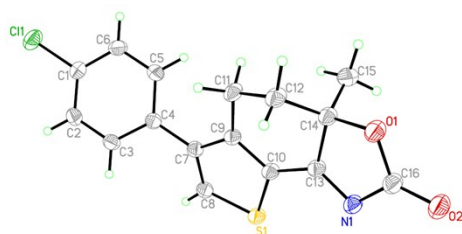
To solution of **2a** (0.2 mmol) in THF (0.1 M) was added $\text{H}_2\text{C}=\text{CHMgBr}$ (2.0 equiv.) at 0°C.⁵ Upon completion, the reaction was quenched with saturated ammonium chloride solution at 0 °C, and the mixture was extracted with DCM. The combined organic phases were washed with brine before being dried Na_2SO_4 and concentrated *in vacuo*. Purification by column chromatography on silica gel eluting with EtOAc/petroleum ether to afford **8** (40.1 mg, 76%). Yellow oil. ¹H NMR (500 MHz, CDCl_3) δ 7.27 – 7.25 (m, 1H), 6.76 (d, $J = 5.1$ Hz, 1H), 6.57 (dd, $J = 17.1, 10.5$ Hz, 1H), 6.39 (d, $J = 16.8$ Hz, 1H), 6.32 (s, 1H), 6.24 (dd, $J = 16.9, 10.2$ Hz, 1H), 6.18 (brs, 1H), 5.79 (d, $J = 10.3$ Hz, 1H), 5.20 (d, $J = 10.5$ Hz, 1H), 4.88 (d, $J = 17.1$ Hz, 1H), 2.75 (dd, $J = 17.0, 4.7$ Hz, 1H), 2.66 – 2.56 (m, 1H), 2.13 (td, $J = 13.0, 5.8$ Hz, 1H), 1.85 (dd, $J = 13.5, 4.2$ Hz, 1H), 1.24 (s, 3H). ¹³C NMR (125 MHz, CDCl_3) δ 166.93, 138.22, 138.17, 137.99, 130.42, 128.56, 127.62, 125.43, 115.12, 74.82, 69.35, 33.91, 23.76, 23.43. HRMS (ESI): calcd. for $\text{C}_{14}\text{H}_{17}\text{NO}_2\text{S}$ ($[\text{M}+\text{H}]^+$): 264.1053, found 264.1052.

VI. References

1. T.-T. Wang, L. Zhao, Y.-J. Zhang, W.-W. Liao, *Org. Lett.* **2016**, *18*, 5002.
2. A. Baeza, C. Nájera, M. G. Retamosa, J. M. Sansano *Synthesis* **2005**, *16*, 2787.
3. G. Zhan, Q. He, X. Yuan, Y.- C. Chen, *Org. Lett.* **2014**, *16*, 6000.
4. T. J. Montavon, Y. E. Turkmen, N. A. Shamsi, C. Miller, C. S. Sumaria, *Angew. Chem. Int. Ed.* **2013**, *51*, 13821.
5. G. Lesma, N. Landoni, T. Pilati, A. Sacchetti, *J. Org. Chem.* **2009**, *74*, 4537.

VII. Crystal Data and Structure Refinement

Compound **2a**



CCDC 1582236

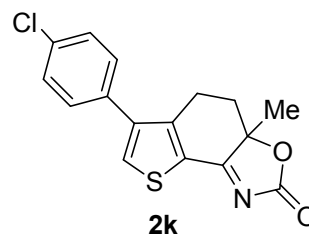


Table 1. Crystal data and structure refinement for **2k**.

Identification code	2k	
Empirical formula	C ₁₆ H ₁₂ Cl N O ₂ S	
Formula weight	317.79	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 24.908(3) Å	α = 90°.
	b = 13.4385(17) Å	β = 93.042(6)°.
	c = 8.7528(13) Å	γ = 90°.
Volume	2925.7(7) Å ³	
Z	8	
Density (calculated)	1.443 Mg/m ³	
Absorption coefficient	0.406 mm ⁻¹	
F(000)	1312	
Crystal size	0.21 x 0.20 x 0.18 mm ³	
Theta range for data collection	2.86 to 27.48°.	
Index ranges	-32 ≤ h ≤ 32, -17 ≤ k ≤ 17, -11 ≤ l ≤ 10	
Reflections collected	23376	
Independent reflections	3340 [R(int) = 0.0257]	
Completeness to theta = 27.48°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9304 and 0.9195	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3340 / 0 / 191	
Goodness-of-fit on F ²	1.021	
Final R indices [I > 2σ(I)]	R1 = 0.0406, wR2 = 0.0937	
R indices (all data)	R1 = 0.0507, wR2 = 0.1023	
Largest diff. peak and hole	0.494 and -0.499 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for y. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cl(1)	-10448(1)	-2867(1)	-19701(1)	66(1)
S(1)	-12314(1)	2171(1)	-17532(1)	42(1)
O(1)	-11365(1)	4903(1)	-20328(2)	49(1)
O(2)	-12020(1)	6004(1)	-19908(2)	58(1)
N(1)	-12075(1)	4391(1)	-18945(2)	42(1)
C(1)	-10789(1)	-1757(2)	-19369(2)	43(1)
C(2)	-11341(1)	-1759(2)	-19391(2)	44(1)
C(3)	-11607(1)	-875(1)	-19126(2)	42(1)
C(4)	-11328(1)	10(1)	-18844(2)	37(1)
C(5)	-10767(1)	-26(2)	-18801(3)	46(1)
C(6)	-10497(1)	-901(2)	-19072(3)	49(1)
C(7)	-11617(1)	951(1)	-18568(2)	37(1)
C(8)	-12070(1)	997(1)	-17740(2)	41(1)
C(9)	-11466(1)	1912(1)	-19078(2)	37(1)
C(10)	-11803(1)	2646(1)	-18566(2)	37(1)
C(11)	-11031(1)	2149(1)	-20165(2)	44(1)
C(12)	-11105(1)	3178(2)	-20920(2)	44(1)
C(13)	-11738(1)	3661(1)	-18985(2)	37(1)
C(14)	-11221(1)	3941(1)	-19701(2)	39(1)
C(15)	-10755(1)	4096(2)	-18526(3)	54(1)
C(16)	-11838(1)	5185(1)	-19730(2)	44(1)

Table 3. Selected bond lengths [\AA] and angles [$^\circ$] for y.

Symmetry transformations used to generate equivalent atoms:

Table 4. Bond lengths [\AA] and angles [$^\circ$] for y.

Cl(1)-C(1)	1.747(2)
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S(1)-C(8)	1.703(2)
S(1)-C(10)	1.7222(18)
O(1)-C(16)	1.369(2)
O(1)-C(14)	1.443(2)
O(2)-C(16)	1.197(2)
N(1)-C(13)	1.293(2)
N(1)-C(16)	1.415(2)
C(1)-C(2)	1.375(3)
C(1)-C(6)	1.379(3)
C(2)-C(3)	1.387(3)
C(2)-H(2)	0.9300
C(3)-C(4)	1.393(3)
C(3)-H(3)	0.9300
C(4)-C(5)	1.397(3)
C(4)-C(7)	1.482(3)
C(5)-C(6)	1.381(3)
C(5)-H(5)	0.9300
C(6)-H(6)	0.9300
C(7)-C(8)	1.375(2)
C(7)-C(9)	1.424(3)
C(8)-H(8)	0.9300
C(9)-C(10)	1.385(2)
C(9)-C(11)	1.514(2)
C(10)-C(13)	1.423(3)
C(11)-C(12)	1.540(3)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(14)	1.519(3)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-C(14)	1.510(2)
C(14)-C(15)	1.523(3)
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600
C(8)-S(1)-C(10)	90.61(9)
C(16)-O(1)-C(14)	107.75(14)

C(13)-N(1)-C(16)	105.80(15)
C(2)-C(1)-C(6)	121.45(18)
C(2)-C(1)-Cl(1)	119.35(16)
C(6)-C(1)-Cl(1)	119.20(16)
C(1)-C(2)-C(3)	118.92(18)
C(1)-C(2)-H(2)	120.5
C(3)-C(2)-H(2)	120.5
C(2)-C(3)-C(4)	121.44(17)
C(2)-C(3)-H(3)	119.3
C(4)-C(3)-H(3)	119.3
C(3)-C(4)-C(5)	117.76(18)
C(3)-C(4)-C(7)	121.00(16)
C(5)-C(4)-C(7)	121.24(17)
C(6)-C(5)-C(4)	121.34(18)
C(6)-C(5)-H(5)	119.3
C(4)-C(5)-H(5)	119.3
C(1)-C(6)-C(5)	119.07(18)
C(1)-C(6)-H(6)	120.5
C(5)-C(6)-H(6)	120.5
C(8)-C(7)-C(9)	111.22(16)
C(8)-C(7)-C(4)	122.93(17)
C(9)-C(7)-C(4)	125.85(16)
C(7)-C(8)-S(1)	113.88(14)
C(7)-C(8)-H(8)	123.1
S(1)-C(8)-H(8)	123.1
C(10)-C(9)-C(7)	111.76(16)
C(10)-C(9)-C(11)	121.39(16)
C(7)-C(9)-C(11)	126.63(16)
C(9)-C(10)-C(13)	121.27(16)
C(9)-C(10)-S(1)	112.50(14)
C(13)-C(10)-S(1)	126.06(14)
C(9)-C(11)-C(12)	112.61(15)
C(9)-C(11)-H(11A)	109.1
C(12)-C(11)-H(11A)	109.1
C(9)-C(11)-H(11B)	109.1
C(12)-C(11)-H(11B)	109.1
H(11A)-C(11)-H(11B)	107.8
C(14)-C(12)-C(11)	109.12(16)

C(14)-C(12)-H(12A)	109.9
C(11)-C(12)-H(12A)	109.9
C(14)-C(12)-H(12B)	109.9
C(11)-C(12)-H(12B)	109.9
H(12A)-C(12)-H(12B)	108.3
N(1)-C(13)-C(10)	129.56(17)
N(1)-C(13)-C(14)	113.04(16)
C(10)-C(13)-C(14)	117.21(15)
O(1)-C(14)-C(13)	100.42(14)
O(1)-C(14)-C(12)	112.99(16)
C(13)-C(14)-C(12)	108.77(16)
O(1)-C(14)-C(15)	107.42(16)
C(13)-C(14)-C(15)	112.94(16)
C(12)-C(14)-C(15)	113.60(16)
C(14)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
O(2)-C(16)-O(1)	122.13(18)
O(2)-C(16)-N(1)	126.40(18)
O(1)-C(16)-N(1)	111.45(16)

Symmetry transformations used to generate equivalent atoms:

Table 5. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for y. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	67(1)	50(1)	83(1)	-10(1)	15(1)	15(1)
S(1)	36(1)	43(1)	48(1)	-1(1)	16(1)	-2(1)
O(1)	50(1)	39(1)	59(1)	10(1)	23(1)	5(1)
O(2)	56(1)	41(1)	80(1)	9(1)	18(1)	9(1)
N(1)	39(1)	38(1)	50(1)	1(1)	13(1)	3(1)
C(1)	47(1)	41(1)	42(1)	0(1)	6(1)	6(1)

C(2)	46(1)	38(1)	48(1)	-1(1)	-3(1)	-4(1)
C(3)	35(1)	41(1)	50(1)	2(1)	0(1)	-3(1)
C(4)	37(1)	37(1)	37(1)	2(1)	4(1)	-2(1)
C(5)	38(1)	40(1)	62(1)	-2(1)	4(1)	-5(1)
C(6)	35(1)	49(1)	62(1)	1(1)	8(1)	2(1)
C(7)	36(1)	37(1)	38(1)	0(1)	5(1)	-2(1)
C(8)	38(1)	40(1)	45(1)	1(1)	8(1)	-5(1)
C(9)	34(1)	38(1)	39(1)	-1(1)	8(1)	0(1)
C(10)	36(1)	39(1)	38(1)	2(1)	13(1)	1(1)
C(11)	46(1)	38(1)	49(1)	0(1)	22(1)	4(1)
C(12)	47(1)	44(1)	43(1)	2(1)	21(1)	2(1)
C(13)	36(1)	40(1)	35(1)	-2(1)	10(1)	1(1)
C(14)	40(1)	36(1)	44(1)	4(1)	15(1)	3(1)
C(15)	42(1)	59(1)	62(1)	-8(1)	10(1)	0(1)
C(16)	43(1)	39(1)	50(1)	1(1)	11(1)	4(1)

Table 6. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for y.

	x	y	z	U(eq)
H(2)	-11533	-2344	-19580	53
H(3)	-11981	-872	-19137	50
H(5)	-10571	551	-18584	56
H(6)	-10123	-912	-19054	58
H(8)	-12229	438	-17330	49
H(11A)	-11032	1643	-20956	53
H(11B)	-10684	2127	-19608	53
H(12A)	-10781	3362	-21422	53
H(12B)	-11401	3156	-21686	53
H(15A)	-10448	4337	-19030	82
H(15B)	-10667	3475	-18030	82
H(15C)	-10856	4572	-17777	82

Table 7. Hydrogen bonds for y [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
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