

Supporting Information

**Synthesis of α -Heterofunctionalized Carbonyl Compounds
via Brønsted Acid-Catalyzed
Oxygenative Coupling of Ynamides**

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Table of Contents

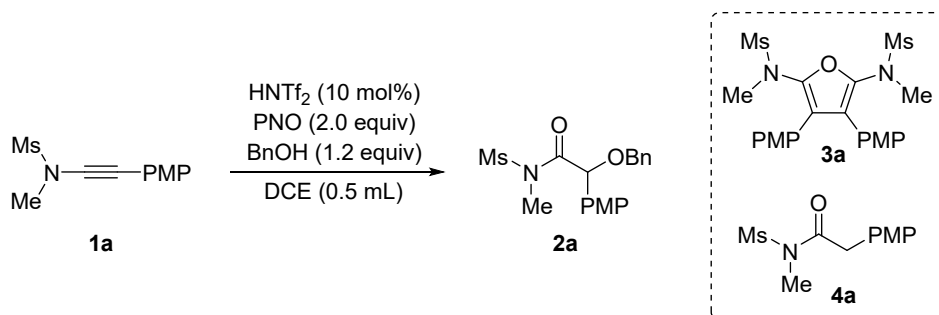
1. General Information-----	S2
2. Optimization Study-----	S3
3. General Procedure-----	S11
4. Characterization of Substrates-----	S13
5. Synthetic Applications-----	S38
Appendix: Copies of ¹ H and ¹³ C spectra	

1. General Information

All solvents were dried and distilled according to standard methods before use.¹ All the chemicals used for the synthesis of substrates were commercially available from Tokyo Chemical Industry, Sigma Aldrich and Alfa Aesar and were used as received, unless otherwise noted. TLC (thin-layer chromatography) analyses were carried out on Merck silica gel 60 F254 TLC plates and was visualized with UV lamp, phosphomolybdic acid and KMnO₄ solution. Flash chromatography was performed on Kieselgel 60 (230-400 mesh). ¹H and ¹³C NMR spectra were recorded on a Bruker (400 MHz) spectrometer with TMS as an internal standard. High-resolution mass spectra (HRMS) were recorded on Bruker compact UHR-MS (QTOF) machine by ESI source in Organic Chemistry Research Center (OCRC) in Sogang University. Infrared Spectroscopy (IR) were recorded on a Bruker LUMOS FT-IR spectrometer equipped with a microscope and mercury cadmium telluride (MCT) detector.

2. Optimization Study

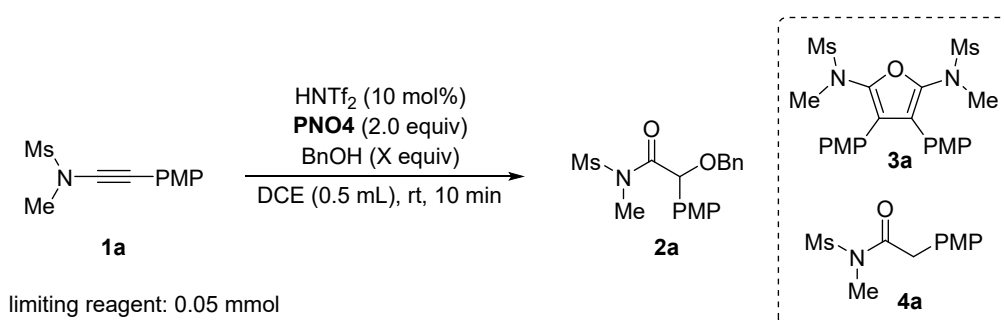
2.1. Oxidant screening (O-nucleophile)^a



entry	PNO	conditions	2a / 3a / 4a (%) ^b
1	pyridine- <i>N</i> -oxide (PNO1)	60 °C, 1 h	No reaction
2	quinolone- <i>N</i> -oxide (PNO2)	60 °C, 1 h	No reaction
3	2-Cl-pyridine- <i>N</i> -oxide (PNO3)	60 °C, 1 h	59 / 17 / -
4	2,6-Cl ₂ - pyridine- <i>N</i> -oxide (PNO4)	rt, 10 min	65 / 34 / -
5	2,6-Br ₂ - pyridine- <i>N</i> -oxide (PNO5)	rt, 10 min	56 / 35 / -
6	2-CF ₃ - pyridine- <i>N</i> -oxide (PNO6)	rt, 10 min	47 / 29 / -
7	2-Me- pyridine- <i>N</i> -oxide (PNO7)	60 °C, 1 h	No reaction
8	2,6-Me ₂ - pyridine- <i>N</i> -oxide (PNO8)	60 °C, 1 h	No reaction

^a**1a** (0.05 mmol) used. ^bYield was determined by ¹H NMR using CH₂Br₂ as the internal standard.

2.2. Variation of the equivalents (O-nucleophile)

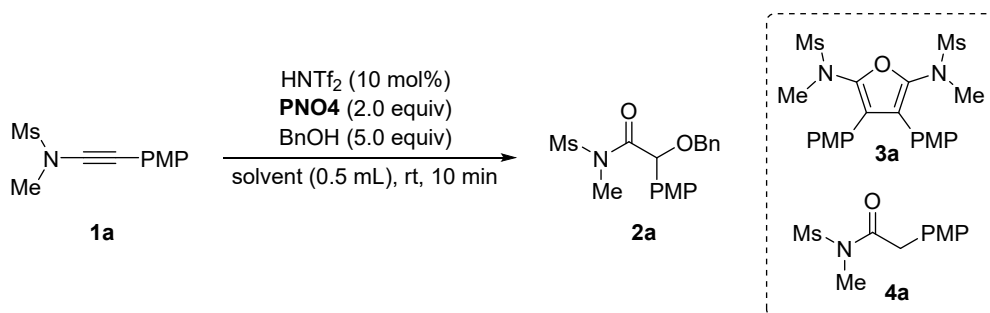


entry	BnOH (X equiv)	2a / 3a / 4a (%) ^a
1	1.2	61 / 29 / -
2	2	67 / 20 / -
3	3	69 / 15 / -

4	5	74 / 11 / -
5	10	70 / 6 / -

^aYield was determined by ¹H NMR using CH₂Br₂ as the internal standard

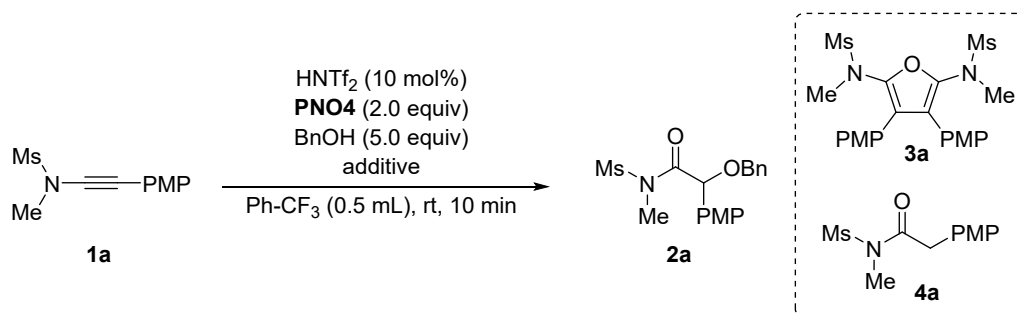
2.3. Variation of the solvents (O-nucleophile)^a



entry	solvent	2a / 3a / 4a (%) ^b
1	DCE	76 / 10 / -
2	DCM	77 / 10 / 10
3	CHCl ₃	73 / 7 / 15
4	Et ₂ O	43 / 14 / 20
5	MTBE	48 / 26 / 26
6	THF	67 / 15 / 19
7	1,4-dioxane	64 / 8 / 7
8	toluene	68 / 7 / 20
9	<i>m</i> -xylene	64 / 8 / 20
10	mesitylene	64 / 7 / 20
11	Ph-CF ₃	76 / 5 / 19
12	HFIP	16 / 67 / -
13	TFE	25 / 52 / 8
14	CH ₃ NO ₂	42 / 57 / 7
15	DMF	S.M decomposed
16	DMSO	S.M decomposed
17	H ₂ O	S.M decomposed

^a**1a** (0.05 mmol) used. ^bYield was determined by ¹H NMR using CH₂Br₂ as the internal standard.

2.4. Additive screening (O-nucleophile)^a

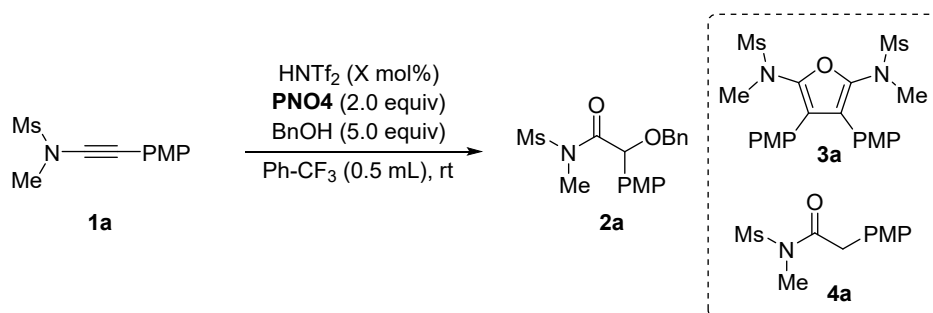


entry	additive	2a / 3a / 4a (%) ^b
1	-	76 / 5 / 19
2	4 Å M.S (100 mg)	40 - / -
3	4 Å M.S (100 mg)	23 - / -
4	5 Å M.S (50 mg)	74 / 5 / 4
5	5 Å M.S (100 mg)	83 / 5 / 5
6	5 Å M.S (200 mg)	84 (83) / 4 / 6 ^c
7	MgSO ₄ (100 mg)	70 / - / 24

^a**1a** (0.05 mmol) used. ^bYield was determined by ¹H NMR using CH₂Br₂ as the internal standard.

^cIsolated yield in parenthesis.

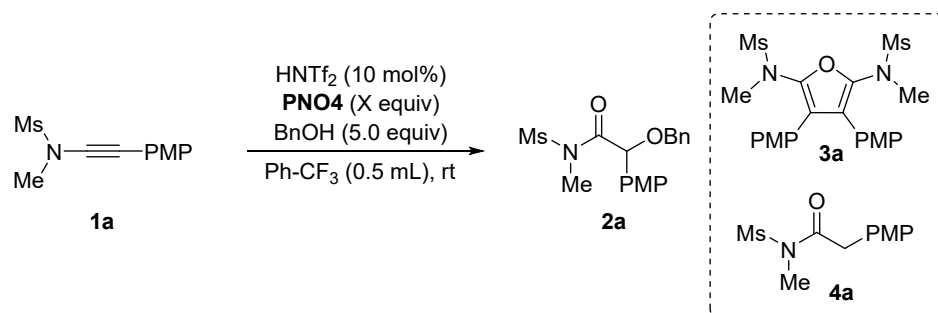
2.5. Variation of the amount of catalyst loading (O-nucleophile)^a



entry	HNTf ₂ (mol%)	time	2a / 3a / 4a (%) ^b
1	10	10 min	75 / 5 / 15
2	5	30 min	76 / 5 / 18
3	2.5	30 min	74 / 5 / 15
4	1	1 h	64 / 6 / 12

^a**1a** (0.05 mmol) used. ^bYield was determined by ¹H NMR using CH₂Br₂ as the internal standard.

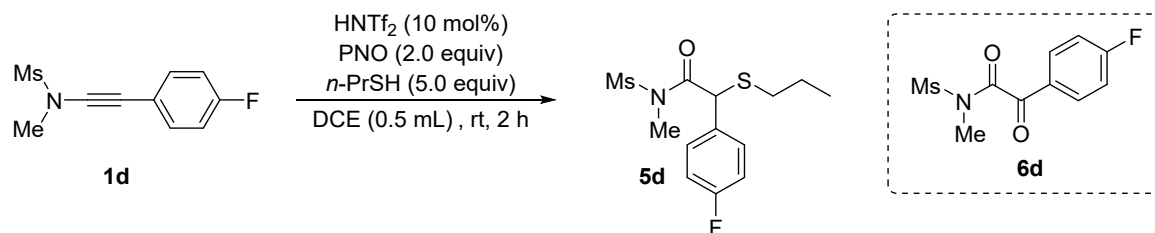
2.6. Variation of the amount of 2,6-Cl₂-pyridine-*N*-oxide PNO4 (O-nucleophile)^{a,b}



entry	PNO4 (equiv)	time	2a / 3a / 4a (%) ^c
1	2	10 min	81 / 8 / 7
2	1.5	10 min	79 / 13 / 6
3	1.2	10 min	72 / 18 / 7

^a1a (0.05 mmol) used. ^b5 Å molecular sieve was used. ^cYield was determined by ¹H NMR using CH₂Br₂ as the internal standard.

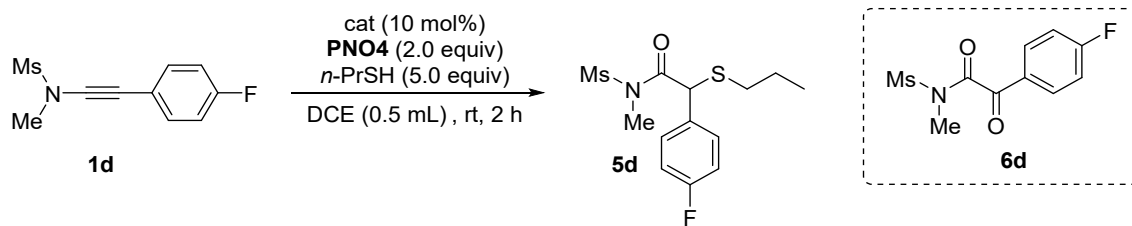
2.7. Oxidant screening (S-nucleophile)^a

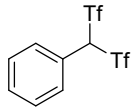
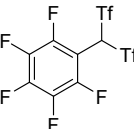


entry	PNO	5d / 6d (%) ^b
1	quinolone- <i>N</i> -oxide (PNO2)	10 / -
2	2-Cl-pyridine- <i>N</i> -oxide (PNO3)	5 / 13
3	2,6-Cl ₂ -pyridine- <i>N</i> -oxide (PNO4)	58 / 23
4	2,6-Cl ₂ -pyridine- <i>N</i> -oxide (PNO4)	57 / 19
5	2,6-Br ₂ -pyridine- <i>N</i> -oxide (PNO5)	45 / 28
6	3,5-Cl ₂ -pyridine- <i>N</i> -oxide (PNO9)	No reaction

^a1d (0.05 mmol) used. ^bYield was determined by ¹H NMR using CH₂Br₂ as the internal standard.

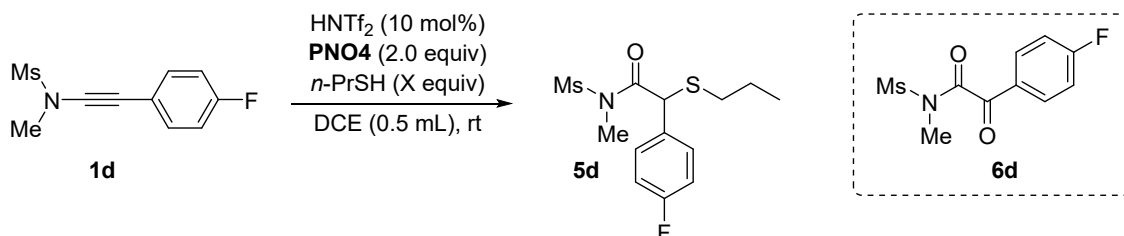
2.8. Brønsted acid catalyst screening (S-nucleophile)^a



entry	catalyst	5d / 6d (%) ^b
1	HNTf ₂	59 / 20
2	TfOH	49 / 28
3		55 / 30
4		45 / 24

^a**1d** (0.05 mmol) used. ^bYield was determined by ¹H NMR using CH₂Br₂ as the internal standard.

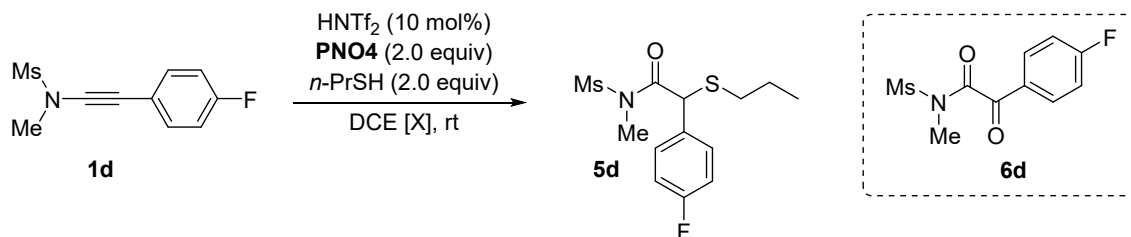
2.9. Variation of the equivalents (S-nucleophile)^a



entry	<i>n</i> -PrSH (equiv)	time	5d / 6d (%) ^b
1	1.2	6 h	46 / 10
2	2.0	2 h	53 / 13
3	3.0	2 h	53 / 15
4	5.0	2 h	56 / 18

^a**1d** (0.05 mmol) used. ^bYield was determined by ¹H NMR using CH₂Br₂ as the internal standard.

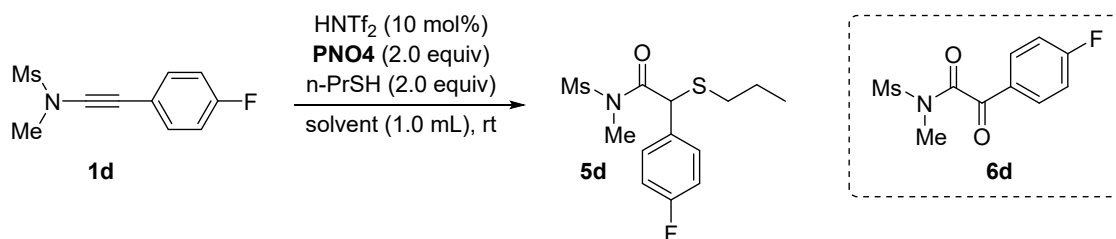
2.10. Solvent concentration screening (S-nucleophile)^a



entry	DCE (vol)	time	5d / 6d (%) ^b
1	0.1 M (0.5 mL)	2 h	53 / 20
2	0.05 M (1.0 mL)	2 h	47 / 10
3	0.025 M (2.0 mL)	2 h	51 / 10

^a**1d** (0.05 mmol) used. ^bYield was determined by ¹H NMR using CH₂Br₂ as the internal standard.

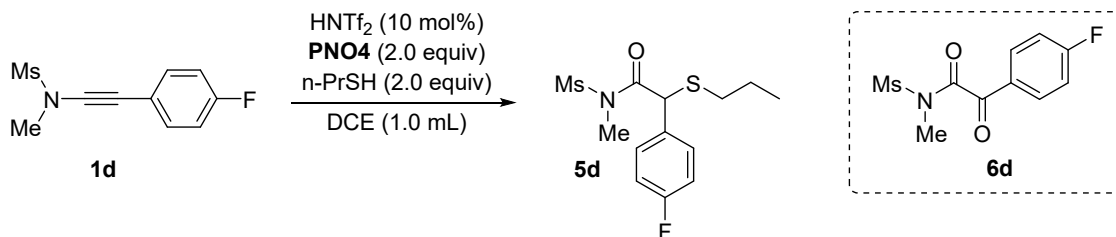
2.11. H₂O solvent effect (S-nucleophile)^a



entry	solvent	time	5d / 6d (%) ^b
1	DCE	2 h	57 / 10
2	DCE/H ₂ O (0.5 mL/0.5mL)	2 h	42 / 7
3	H ₂ O	2 h	32 / 2

^a**1d** (0.05 mmol) used. ^bYield was determined by ¹H NMR using CH₂Br₂ as the internal standard.

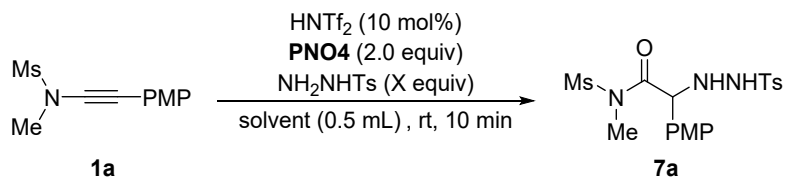
2.12. Temperature effect (S-nucleophile)^a



entry	Temp	time	5d / 6d (%) ^b
1	0 °C	5 h	26 / 47
2	rt	2 h	47 / 10
3	40 °C	2 h	51 / 7
4	60 °C	2 h	82 / 2

^a**1d** (0.05 mmol) used. ^bYield was determined by ¹H NMR using CH₂Br₂ as the internal standard.

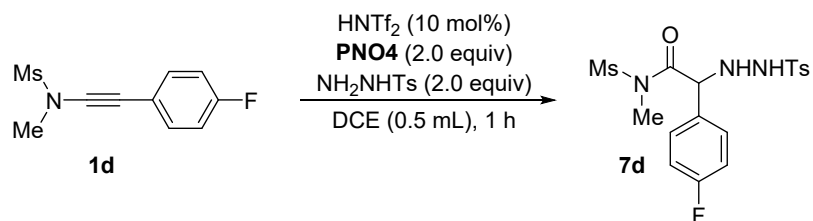
2.13. Solvent and equivalent screening (N-nucleophile)^a



entry	solvent	NH ₂ NHTs (equiv)	7a (%) ^b
1	Ph-CF ₃	1.2	17
2	DCE	1.2	74
3	DCE	2	81
4	DCE	3	74
5	DCE	5	57

^a**1a** (0.05 mmol) used. ^bYield was determined by ¹H NMR using CH₂Br₂ as the internal standard.

2.14. Temperature effect (N-nucleophile)^a

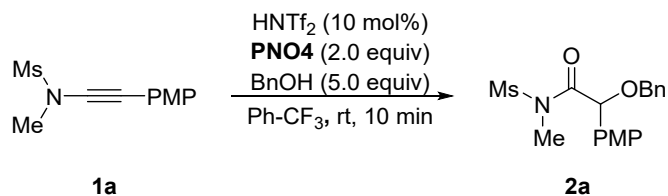


entry	Temp	7d (%) ^b
1	rt	31
2	60 °C	62
3	80 °C	55

^a**1d** (0.05 mmol) used. ^bYield was determined by ¹H NMR using CH₂Br₂ as the internal standard.

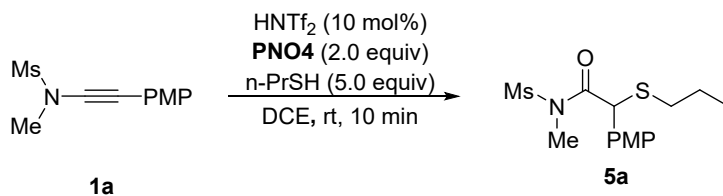
3. General Procedure

3.1. Representative procedure for the synthesis of **2a**



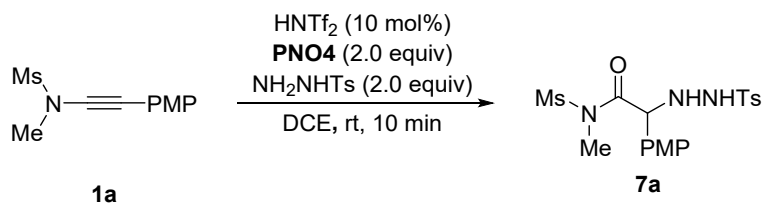
In a 4 mL vial, ynamide **1a** (23.9 mg, 0.10 mmol), 2,6-dichloropyridine-N-oxide **PNO4** (32.8 mg, 0.20 mmol) and benzyl alcohol (54.1 mg, 0.50 mmol) was dissolved in trifluoromethyl benzene (1.0 mL) at room temperature. To this mixture was added HNTf₂ (2.8 mg, 0.01 mmol) and was capped under air. The resulting mixture was stirred at room temperature until TLC indicated complete consumption (usually 10 minutes). The reaction mixture was poured onto a silica gel column and was eluted with EtOAc:Hex (1:4~1:2) to yield 30.6 mg (83%) of **2a** as a sticky colorless oil.

3.2. Representative procedure for the synthesis of **5a**



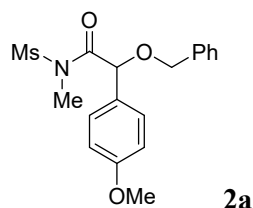
In a 4 mL vial, ynamide **1a** (23.9 mg, 0.10 mmol), 2,6-dichloropyridine-N-oxide **PNO4** (32.8 mg, 0.20 mmol) and propyl mercaptan (15.2 mg, 0.20 mmol) was dissolved in 1,2-dichloroethane (1.0 mL) at room temperature. To this mixture was added HNTf₂ (2.8 mg, 0.01 mmol) and was capped under air. The resulting mixture was stirred at room temperature until TLC indicated complete consumption (usually 10 minutes). The reaction mixture was poured onto a silica gel column and was eluted with EtOAc:Hex (1:4~1:2) to yield 30.6 mg (92%) of **5a** as a sticky colorless oil.

3.3. Representative procedure for the synthesis of **7a**

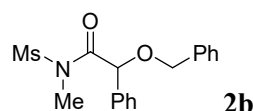


In a 4 mL vial, ynamide **1a** (23.9 mg, 0.10 mmol), 2,6-dichloropyridine-N-oxide **PNO4** (32.8 mg, 0.20 mmol) and *p*-toluenesulfonyl hydrazide (37.2 mg, 0.20 mmol) was dissolved in 1,2-dichloroethane (1.0 mL) at room temperature. To this mixture was added HNTf₂ (2.8 mg, 0.01 mmol) and was capped under air. The resulting mixture was stirred at room temperature until TLC indicated complete consumption (usually 10 minutes). The reaction mixture was poured onto a silica gel column and was eluted with EtOAc:Hex (1:4~1:1) to yield 37.0 mg (84%) of **7a** as a white solid.

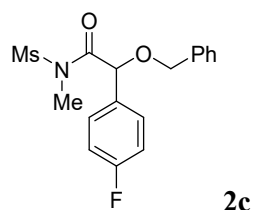
4. Characterization of Substrates



Sticky colorless oil (30.6 mg, 83%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 7.42-7.27 (m, 7H), 6.93 (d, *J* = 8.6 Hz, 2H), 5.49 (s, 1H), 4.58 (d of ABq, *J* = 11.8 Hz, 1H), 4.55 (d of ABq, *J* = 11.6 Hz, 1 H), 3.82 (s, 3H), 3.16 (s, 3H), 2.96 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.3, 160.2, 137.0, 129.6, 128.6, 128.4, 128.2, 126.7, 114.4, 80.2, 71.6, 55.3, 40.8, 32.6; **IR** (ATR): $\tilde{\nu}$ = 3025, 2940, 2338, 1702, 1609, 1512, 1455, 1349, 1249, 1165, 1067, 965, 700 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₈H₂₁NNaO₅S⁺ 386.1033, found 386.1038.

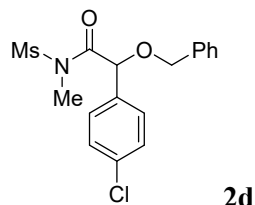


Sticky colorless oil (23.0 mg, 70%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 7.51-7.27 (m, 10H), 5.54 (s, 1H), 4.61 (d of ABq, *J* = 11.4 Hz, 1H), 4.58 (d of ABq, *J* = 11.4 Hz, 1H), 3.16 (s, 3H), 2.98 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.2, 136.9, 134.8, 129.2, 129.0, 128.6, 128.4, 128.2, 128.0, 81.0, 72.0, 40.8, 32.6; **IR** (ATR): $\tilde{\nu}$ = 2989, 2320, 1705, 1352, 1275, 1161, 971, 764 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₇H₁₉NNaO₄S⁺ 356.0927, found 356.0933.

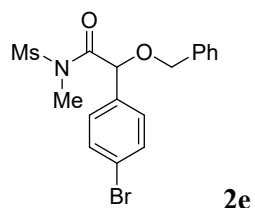


Sticky colorless oil (22.3mg, 64%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 7.42 (dd, *J* = 7.6, 5.4 Hz, 2H), 7.39-7.29 (m, 5H), 7.10 (t, *J* = 8.6 Hz, 2H), 5.56 (s, 1H), 4.58 (d of ABq, *J* = 11.4 Hz, 1H), 4.54 (d of ABq, *J* = 11.4 Hz, 1H), 3.17 (s, 3H), 2.99 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.9, 163.1 (d, *J* = 247.2 Hz), 136.7, 130.8 (d, *J* = 3.4 Hz), 130.0 (d, *J* = 8.2 Hz), 128.6, 128.43, 128.36, 115.9 (d, *J* = 21.7 Hz), 80.2, 72.0, 40.9, 32.7; **IR** (ATR): $\tilde{\nu}$ = 3009, 2334, 1701, 1604, 1509, 1352, 1260,

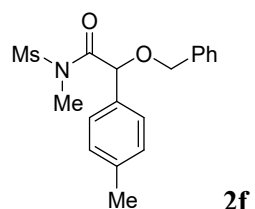
1157, 1068, 964, 835 cm^{-1} ; **HRMS** (ESI) m/z : $[M+\text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{18}\text{FNNaO}_4\text{S}^+$ 374.0833, found 374.0834.



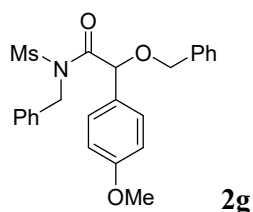
Sticky colorless oil (26.9 mg, 73%, EtOAc:Hex = 1:3); **^1H NMR** (400 MHz, CDCl_3): δ 7.43-7.28 (m, 9H), 5.55 (s, 1H), 4.58 (d of ABq, $J = 11.4$ Hz, 1H), 4.54 (d of ABq, $J = 11.4$ Hz, 1H), 3.17 (s, 3H), 3.00 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3): δ 170.7, 136.6, 135.1, 133.5, 129.4, 129.1, 128.7, 128.5, 128.4, 80.3, 72.1, 40.9, 32.7; **IR** (ATR): $\tilde{\nu} = 3002, 2348, 1702, 1491, 1351, 1157, 1088, 964, 823, 699$ cm^{-1} ; **HRMS** (ESI) m/z : $[M+\text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{18}\text{ClNNaO}_4\text{S}^+$ 390.0537, found 390.0535.



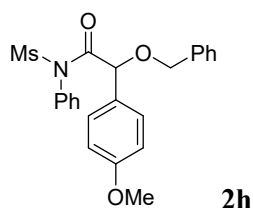
Sticky colorless oil (29.5 mg, 72%, EtOAc:Hex = 1:3); **^1H NMR** (400 MHz, CDCl_3): δ 7.55 (d, $J = 8.4$ Hz, 2H), 7.44-7.27 (m, 7H), 5.53 (s, 1H), 4.57 (d of ABq, $J = 11.2$ Hz, 1H), 4.54 (d of ABq, $J = 11.2$ Hz, 1H), 3.17 (s, 3H), 3.00 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3): δ 170.6, 136.6, 134.1, 132.1, 129.7, 128.7, 128.5, 128.4, 123.3, 80.4, 72.1, 40.9, 32.7; **IR** (ATR): $\tilde{\nu} = 3002, 2945, 2338, 1700, 1488, 1352, 1275, 1166, 1070, 964, 801, 750$ cm^{-1} ; **HRMS** (ESI) m/z : $[M+\text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{18}\text{BrNNaO}_4\text{S}^+$ 434.0032, found 434.0030.



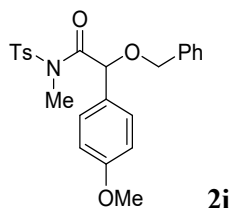
Sticky colorless oil (24.0 mg, 69%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 7.40-7.34 (m, 4H), 7.34-7.28 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 5.50 (s, 1H), 4.60 (d of ABq, *J* = 12.0 Hz, 1H), 4.57 (d of ABq, *J* = 11.6 Hz, 1H), 3.16 (s, 3H), 2.98 (s, 3H), 2.37 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.3, 139.1, 137.0, 131.7, 129.7, 128.6, 128.4, 128.2, 128.0, 80.7, 71.8, 40.9, 32.6, 21.3; **IR** (ATR): $\tilde{\nu}$ = 3027, 2926, 2332, 1702, 1348, 1164, 1066, 963 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₈H₂₁NNaO₄S⁺ 370.1084, found 370.1082.



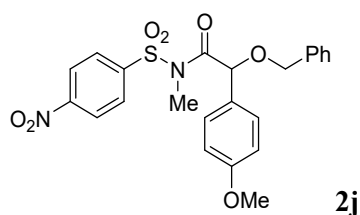
Sticky colorless oil (42.0 mg, 95%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 7.4 5-7.11 (m, 12H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.42 (s, 1H), 4.97 (d of ABq, *J* = 16.3 Hz, 1H), 4.85 (d of ABq, *J* = 16.3 Hz, 1H), 4.47 (d of ABq, *J* = 11.6 Hz, 1H), 4.42 (d of ABq, *J* = 11.6 Hz, 1H), 3.80 (s, 3H), 2.82 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.5, 160.4, 137.0, 136.0, 130.1, 128.9, 128.5, 128.4, 128.1, 128.0, 127.5, 126.7, 114.4, 79.4, 71.3, 55.4, 48.8, 42.4; **IR** (ATR): $\tilde{\nu}$ = 2936, 2496, 1701, 1610, 1512, 1347, 1246, 1164, 1063, 1030, 963 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₄H₂₅NNaO₅S⁺ 462.1346, found 462.1345.



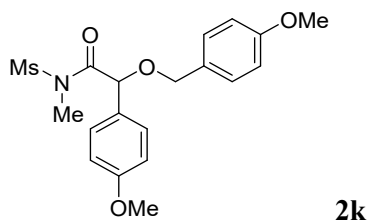
Sticky yellow oil (32.4 mg, 76%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 7.42 (t, *J* = 7.5 Hz, 1H), 7.37-7.25 (m, 7H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 7.6 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 4.67 (s, 1H), 4.52 (d of ABq, *J* = 11.8 Hz, 1H), 4.39 (d of ABq, *J* = 11.8 Hz, 1H), 3.83 (s, 3H), 3.46 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.3, 160.4, 137.0, 133.9, 130.4, 130.1, 130.0, 129.5, 128.5, 128.3, 128.1, 126.3, 114.2, 78.4, 70.8, 55.3, 42.1; **IR** (ATR): $\tilde{\nu}$ = 3043, 2926, 2312, 1709, 1609, 1512, 1454, 1354, 1248, 1153, 1075, 964 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₃H₂₃NNaO₅S⁺ 448.1189, found 448.1185.



Sticky colorless oil (31.9 mg, 72%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ **¹H NMR** (400 MHz, CDCl₃): 7.59 (d, *J* = 8.3 Hz, 2H), 7.42-7.30 (m, 5H), 7.30-7.20 (m, 4H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.59 (s, 1H), 4.54 (d of ABq, *J* = 11.9 Hz, 1H), 4.50 (d of ABq, *J* = 11.2 Hz, 1H), 3.84 (s, 3H), 3.15 (s, 3H), 2.45 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.9, 160.1, 144.9, 137.2, 135.4, 129.6, 128.5, 128.2, 128.0, 127.9, 127.0, 114.2, 79.7, 71.2, 55.4, 33.0, 21.7; **IR** (ATR): $\tilde{\nu}$ = 2987, 2368, 1699, 1611, 1517, 1355, 1275, 1267, 1169, 1056, 750 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₄H₂₅NNaO₅S⁺ 462.1346, found 462.1351.

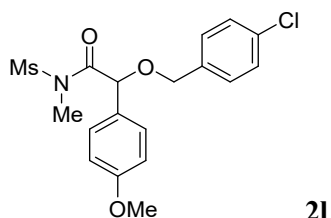


Yellow solid (22.1 mg, 47%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): 8.27 (d, *J* = 8.9 Hz, 2H), 7.95 (d, *J* = 8.9 Hz, 2H), 7.42-7.32 (m, 3H), 7.30 (d, *J* = 9.9 Hz, 2H), 7.20 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.36 (s, 1H), 4.55 (d of ABq, *J* = 12.1 Hz, 1H), 4.51 (d of ABq, *J* = 11.2 Hz, 1H), 3.83 (s, 3H), 3.24 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.7, 160.3, 150.5, 144.1, 136.7, 129.43, 129.36, 128.6, 128.2, 126.0, 124.0, 114.4, 79.9, 71.3, 55.4, 33.1; **IR** (ATR): $\tilde{\nu}$ = 3101, 3020, 2349, 1709, 1511, 1530, 1348, 1250, 1174, 1028, 1061, 763 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₃H₂₂N₂NaO₇S⁺ 493.1040, found 493.1037.

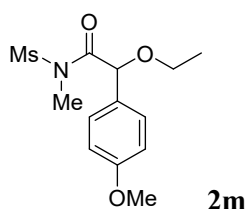


Sticky colorless oil (29.4 mg, 75%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 7.33 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 2H), 5.45 (s, 1H), 4.49

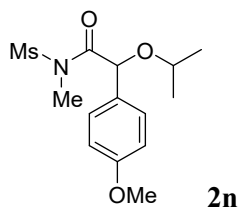
(s, 2H), 3.82 (s, 3H), 3.80 (s, 3H), 3.15 (s, 3H), 2.98 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 171.4, 160.2, 159.6, 130.1, 129.6, 129.0, 126.8, 114.3, 113.9, 79.9, 71.3, 55.34, 55.30, 40.9, 32.6; **IR** (ATR): $\tilde{\nu}$ = 2992, 2349, 1701, 1611, 1513, 1350, 1255, 1167, 1031, 964, 828 cm^{-1} ; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{23}\text{NNaO}_6\text{S}^+$ 416.1138, found 416.1134.



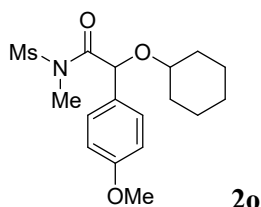
Sticky colorless oil (32.4 mg, 81%, EtOAc:Hex = 1:3); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.49-7.20 (m, 6H), 6.93 (d, J = 8.6 Hz, 2H), 5.51 (s, 1H), 4.54 (d of ABq, J = 11.5 Hz, 1H), 4.49 (d of ABq, J = 11.5 Hz, 1H), 3.82 (s, 3H), 3.17 (s, 3H), 2.94 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 171.2, 160.4, 135.6, 133.9, 129.8, 129.6, 128.7, 126.5, 114.4, 80.2, 70.7, 55.4, 40.8, 32.6; **IR** (ATR): $\tilde{\nu}$ = 3013, 2934, 2340, 1701, 1609, 1512, 1350, 1252, 1165, 1030, 964, 829 cm^{-1} ; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{20}\text{ClNNaO}_5\text{S}^+$ 420.0643, found 420.0650.



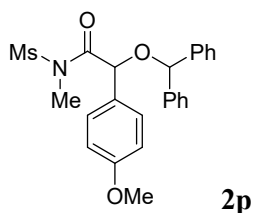
Sticky colorless oil (21.5 mg, 72%, EtOAc:Hex = 1:3); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.33 (d, J = 8.5 Hz, 2H), 6.92 (d, J = 8.5 Hz, 2H), 5.41 (s, 1H), 3.81 (s, 3H), 3.61 (quintet of ABq, J = 7.1 Hz, 1H), 3.52 (quintet of ABq, J = 7.1 Hz, 1H), 3.21 (s, 3H), 3.05 (s, 3H), 1.26 (t, J = 7.0 Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 171.7, 160.1, 129.3, 127.0, 114.3, 81.3, 65.6, 55.3, 40.9, 32.5, 15.2; **IR** (ATR): $\tilde{\nu}$ = 3004, 2990, 2348, 1613, 1517, 1463, 1365, 1275, 1167, 1037, 772 cm^{-1} ; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{19}\text{NNaO}_5\text{S}^+$ 324.0876, found 324.0869.



Sticky colorless oil (20.7 mg, 66%, EtOAc:Hex = 1:4); **¹H NMR** (400 MHz, CDCl₃): δ 7.33 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.50 (s, 1H), 3.81 (s, 3H), 3.73 (heptet, *J* = 6.1 Hz, 1H), 3.20 (s, 3H), 3.05 (s, 3H), 1.26 (d, *J* = 6.1 Hz, 3H), 1.21 (d, *J* = 6.1 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 172.5, 160.0, 128.8, 127.4, 114.3, 79.4, 71.5, 55.3, 40.9, 32.5, 22.14, 22.11; **IR** (ATR): $\tilde{\nu}$ = 2970, 2333, 1705, 1610, 1512, 1349, 1250, 1166, 1063, 965, 836, 774 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₄H₂₁NNaO₅S⁺ 338.1033, found 338.1035.

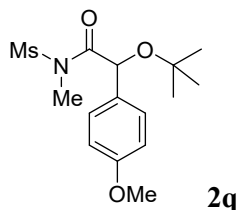


Sticky colorless oil (23.1 mg, 65%, EtOAc:Hex = 1:4); **¹H NMR** (400 MHz, CDCl₃): δ 7.33 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.53 (s, 1H), 3.81 (s, 3H), 3.55-3.35 (m, 1H), 3.19 (s, 3H), 3.05 (s, 3H), 2.10-1.81 (m, 2H), 1.82-1.65 (m, 2H), 1.59-1.46 (m, 1H), 1.46-1.32 (m, 2H), 1.32-1.12 (m, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 172.7, 159.9, 128.5, 127.6, 114.3, 79.4, 77.7, 55.3, 40.9, 32.42, 32.36, 32.1, 25.6, 24.1; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₇H₂₅NNaO₅S⁺ 378.1346, found 378.1350.

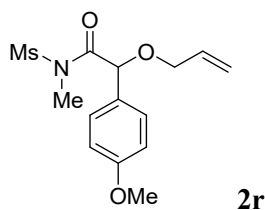


Sticky colorless oil (28.6 mg, 65%, EtOAc:Hex = 1:4); **¹H NMR** (400 MHz, CDCl₃): δ 7.48-7.18 (m, 12H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.51 (s, 1H), 5.39 (s, 1H), 3.80 (s, 3H), 3.07 (s, 3H), 2.95 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.7, 160.2, 141.1, 140.8, 129.3, 128.6, 128.5, 127.9, 127.9, 127.7, 127.4, 126.7, 114.5, 82.1, 78.6, 55.4, 41.0, 32.3; **IR** (ATR): $\tilde{\nu}$ = 3026, 2930, 1702, 1609, 1454, 1512,

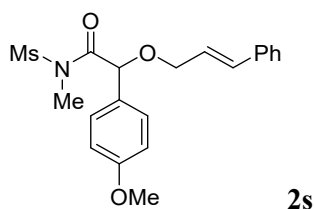
1351, 1280, 1166, 1059, 963, 832, 767 cm^{-1} ; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{24}\text{H}_{25}\text{NNaO}_5\text{S}^+$ 462.1346, found 462.1339.



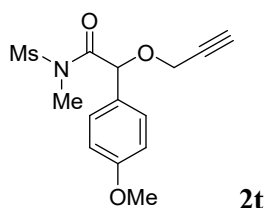
Sticky colorless oil (13.0 mg, 40%, EtOAc:Hex = 1:4); **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ 7.35 (d, $J = 8.2$ Hz, 2H), 6.90 (d, $J = 7.5$ Hz, 2H), 5.54 (s, 1H), 3.81 (s, 3H), 3.18 (s, 3H), 3.10 (s, 3H), 1.31 (s, 9H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3): δ 174.2, 159.6, 128.4, 127.4, 114.3, 76.5, 76.1, 55.3, 40.9, 32.4, 28.0; **IR** (ATR): $\tilde{\nu} = 2972, 2313, 1684, 1512, 1349, 1260, 1167, 1083, 749 \text{ cm}^{-1}$; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{23}\text{NNaO}_5\text{S}^+$ 352.1189, found 352.1194.



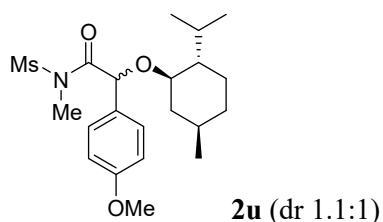
Sticky colorless oil (23.6 mg, 75%, EtOAc:Hex = 1:4); **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ 7.33 (d, $J = 8.7$ Hz, 2H), 6.92 (d, $J = 8.8$ Hz, 2H), 5.93 (ddt, $J = 17.2, 10.4, 5.8$ Hz, 1H), 5.48 (s, 1H), 5.31 (ddt, $J = 17.2, 1.6, 1.5$ Hz, 1H), 5.24 (ddt, $J = 10.4, 1.4, 1.1$ Hz, 1H), 4.12-3.97 (m, 2H), 3.81 (s, 3H), 3.20 (s, 3H), 3.04 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3): δ 171.4, 160.2, 133.7, 129.6, 126.7, 118.4, 114.3, 80.2, 70.6, 55.3, 40.8, 32.6; **IR** (ATR): $\tilde{\nu} = 3013, 2928, 2846, 2320, 1704, 1610, 1513, 1350, 1254, 1165, 1064, 964, 829 \text{ cm}^{-1}$; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{19}\text{NNaO}_5\text{S}^+$ 336.0876, found 336.0870.



Sticky colorless oil (25.0 mg, 64%, EtOAc:Hex = 1:4); **¹H NMR** (400 MHz, CDCl₃): δ 7.47-7.22 (m, 7H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.29 (dt, *J* = 15.9, 6.3 Hz, 1H), 5.54 (s, 1H), 4.27-4.16 (m, 2H), 3.81 (s, 3H), 3.20 (s, 3H), 3.02 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.5, 160.3, 136.3, 133.9, 129.7, 128.6, 128.0, 126.7, 126.6, 124.9, 114.4, 80.2, 70.4, 55.4, 40.9, 32.6; **IR** (ATR): $\tilde{\nu}$ = 2940, 2834, 2322, 1702, 1616, 1513, 1350, 1246, 1163, 963, 697 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₀H₂₃NNaO₅S⁺ 412.1189, found 412.1191.



Sticky colorless oil (19.3 mg, 62%, EtOAc:Hex = 1:4); **¹H NMR** (400 MHz, CDCl₃): δ 7.37 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 2H), 5.73 (s, 1H), 4.27 (dd of ABq, *J* = 15.9, 2.4 Hz, 1H), 4.14 (dd of ABq, *J* = 15.9, 2.4 Hz, 1H), 3.84 (s, 3H), 3.25 (s, 3H), 3.08 (s, 3H), 2.55 (t, *J* = 2.4 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.7, 160.5, 130.2, 125.6, 114.4, 78.7, 78.6, 76.0, 56.2, 55.4, 41.0, 32.6; **IR** (ATR): $\tilde{\nu}$ = 3016, 2325, 1701, 1616, 1518, 1358, 1463, 1275, 1154, 1059, 750 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₄H₁₇NNaO₅S⁺ 334.0720, found 334.0719.

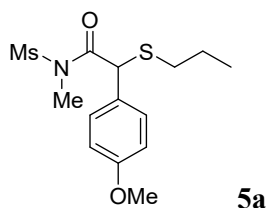


Sticky colorless oil (26.2 mg, 64%, EtOAc:Hex = 1:4)

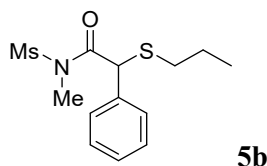
(diastereomeric mixture) **¹H NMR** (400 MHz, CDCl₃): δ 7.34 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 1H), 5.60 (s, 0.5H), 5.49 (s, 0.5H), 3.81 (s, 1.5H), 3.80 (s, 1.5H), 3.36 (td, *J* = 4.2, 10.5 Hz, 0.5H), 3.20 (s, 1.5H), 3.19 (td, *J* = 4.2, 10.6 Hz, 0.5H), 3.13 (s, 1.5H), 3.03 (s, 1.5H), 3.02 (s, 1.5H), 2.45-2.35 (m, 0.5H), 2.30-2.18 (m, 0.5H), 2.18-2.02 (m, 1H), 1.72-1.55 (m, 2H), 1.41-1.21 (m, 2H), 1.08-0.81 (m, 3H), 0.92 (d, *J* = 7.1 Hz, 3H), 0.90 (d, *J* = 7.1 Hz, 1.5H), 0.86 (d, *J* = 7.1 Hz, 1.5H), 0.81 (d, *J* = 6.9 Hz, 1.5H), 0.52 (d, *J* = 6.9 Hz, 1.5H).

(diastereomeric mixture) ^{13}C NMR (100 MHz, CDCl_3): δ 172.6, 172.5, 160.0, 159.9, 129.1, 128.2, 128.0, 127.2, 114.4, 114.3, 79.6, 79.4, 79.1, 78.8, 55.33, 55.32, 48.3, 40.9, 40.8, 40.4, 40.3, 34.4, 34.3, 32.5, 32.4, 31.6, 31.5, 25.3, 25.2, 22.9, 22.3, 21.2, 21.1, 16.0, 15.6.

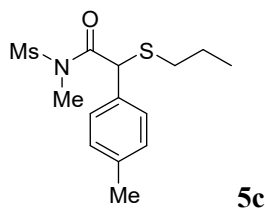
IR (ATR): $\tilde{\nu}$ = 3013, 2955, 2357, 1707, 1606, 1511, 1463, 1351, 1275, 1168, 1063, 1259, 1267, 963 cm^{-1} ; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{33}\text{NNaO}_5\text{S}^+$ 434.1972, found 434.1980.



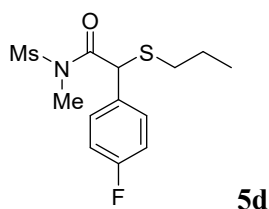
Sticky colorless oil (30.6 mg, 93%, EtOAc:Hex = 1:3); ^1H NMR (400 MHz, CDCl_3): δ 7.36 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 5.34 (s, 1H), 3.81 (s, 3H), 3.27 (s, 3H), 3.06 (s, 3H), 2.46 (t, J = 7.3 Hz, 2H), 1.55 (sextet of doublet, J = 7.7, 1.4 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 171.1, 159.6, 130.1, 127.2, 114.3, 55.3, 51.8, 41.0, 33.5, 33.1, 22.4, 13.5; **IR** (ATR): $\tilde{\nu}$ = 2926, 2873, 2326, 1688, 1605, 1463, 1511, 1350, 1256, 1164, 1032, 965, 764 cm^{-1} ; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{21}\text{NNaO}_4\text{S}_2^+$ 354.0804, found 354.0805.



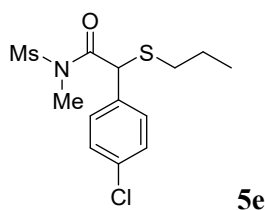
Sticky colorless oil (25.0 mg, 83%, EtOAc:Hex = 1:3); ^1H NMR (400 MHz, CDCl_3): δ 7.44 (d, J = 7.3 Hz, 2H), 7.41-7.28 (m, 3H), 5.38 (s, 1H), 3.27 (s, 3H), 3.05 (s, 3H), 2.47 (t, J = 6.9 Hz, 2H), 1.56 (sextet of doublet, J = 1.2, 7.7 Hz, 2H), 0.94 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.9, 135.5, 129.0, 128.8, 128.4, 52.4, 41.0, 33.5, 33.1, 22.4, 13.5; **IR** (ATR): $\tilde{\nu}$ = 2959, 2398, 1688, 1349, 1163, 1074, 964, 773 cm^{-1} ; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{19}\text{NNaO}_3\text{S}_2^+$ 324.0699, found 324.0703.



Sticky colorless oil (23.1 mg, 73%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 7.31 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 5.33 (s, 1H), 3.26 (s, 3H), 3.06 (s, 3H), 2.46 (t, *J* = 7.3 Hz, 2H), 2.34 (s, 3H), 1.56 (tq, *J* = 7.6, 7.2 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.0, 138.3, 132.3, 129.7, 128.7, 52.2, 41.0, 33.5, 33.1, 22.4, 21.2, 13.5; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₄H₂₁NNaO₃S₂⁺ 338.0855, found 338.0861.

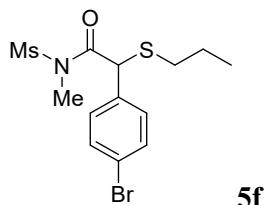


Sticky colorless oil (26.1 mg, 82%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 7.46 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.06 (t, *J* = 8.6 Hz, 2H), 5.41 (s, 1H), 3.29 (s, 3H), 3.13 (s, 3H), 2.46 (t, *J* = 7.2 Hz, 2H), 1.55 (sextet of doublet, *J* = 7.6, 1.2 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.7, 162.6 (d, *J* = 246.6 Hz), 131.4 (d, *J* = 3.2 Hz), 130.7 (d, *J* = 8.2 Hz), 115.8 (d, *J* = 21.7 Hz), 51.1, 41.1, 33.6, 33.1, 22.3, 13.5; **IR** (ATR): $\tilde{\nu}$ = 2997, 2968, 2326, 1694, 1598, 1509, 1354, 1226, 1160, 961, 778 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₃H₁₈FNNaO₃S₂⁺ 342.0604, found 342.0598.

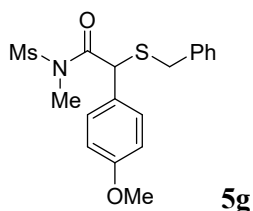


Sticky colorless oil (23.9 mg, 71%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 5.39 (s, 1H), 3.29 (s, 3H), 3.15 (s, 3H), 2.46 (t, *J* = 7.3 Hz, 2H), 1.56 (sextet of doublet, *J* = 7.6, 1.2 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.5, 134.4, 134.2, 130.3, 129.0, 51.1, 41.1, 33.6, 33.2, 22.3, 13.5; **IR** (ATR): $\tilde{\nu}$ = 3013, 2951, 2348, 1689,

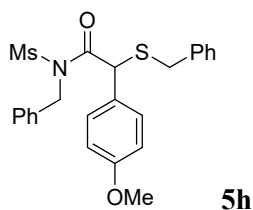
1490, 1351, 1275, 1164, 1075, 966, 750 cm^{-1} ; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{18}\text{ClNNaO}_3\text{S}_2^+$ 358.0309, found 358.0311.



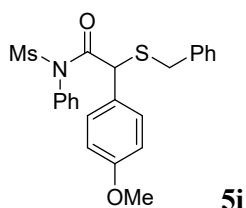
Sticky colorless oil (25.8 mg, 68%, EtOAc:Hex = 1:3); **^1H NMR** (400 MHz, CDCl_3): δ 7.49 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.4$ Hz, 2H), 5.38 (s, 1H), 3.29 (s, 3H), 3.15 (s, 3H), 2.46 (t, $J = 7.4$ Hz, 2H), 1.55 (sextet of doublet, $J = 7.6, 1.2$ Hz, 2H), 0.94 (t, $J = 7.3$ Hz, 3H); **^{13}C NMR** (100 MHz, CDCl_3): δ 170.4, 134.8, 132.0, 130.7, 122.5, 51.2, 41.1, 33.6, 33.2, 22.3, 13.5; **IR** (ATR): $\tilde{\nu} = 2999, 2965, 2342, 1688, 1352, 1275, 1163, 1072, 965, 750$ cm^{-1} ; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{18}\text{BrNNaO}_3\text{S}_2^+$ 401.9804, found 401.9810.



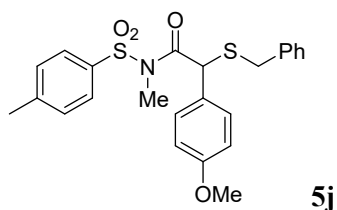
Sticky colorless oil (36.8 mg, 97%, EtOAc:Hex = 1:3); **^1H NMR** (400 MHz, CDCl_3): δ 7.46-7.17 (m, 7H), 6.89 (d, $J = 8.7$ Hz, 2H), 4.98 (s, 1H), 3.80 (s, 3H), 3.76 (d of ABq, $J = 13.5$ Hz, 1H), 3.55 (d of ABq, $J = 13.5$ Hz, 1H), 3.05 (s, 3H), 2.95 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3): δ 170.8, 159.8, 137.4, 130.3, 129.2, 128.7, 127.4, 126.5, 114.4, 55.4, 50.8, 41.2, 35.9, 32.6; **IR** (ATR): $\tilde{\nu} = 3016, 2934, 2345, 1688, 1606, 1510, 1350, 1252, 1163, 1076, 770, 704$ cm^{-1} ; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{21}\text{NNaO}_4\text{S}_2^+$ 402.0804, found 402.0801.



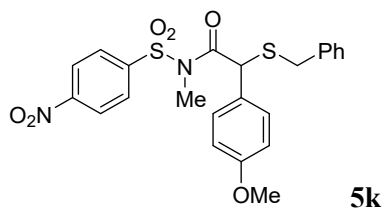
Sticky colorless oil (44.7 mg, 98%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 7.33-7.25 (m, 5H), 7.23-7.17 (m, 4H), 7.10-7.03 (m, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.00-4.88 (m, 2H), 4.78 (d of ABq, *J* = 16.6 Hz, 1H), 3.79 (s, 3H), 3.74 (d of ABq, *J* = 13.7 Hz, 1H), 3.41 (d of ABq, *J* = 13.7 Hz, 1H), 2.89 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.3, 159.8, 137.5, 136.2, 130.6, 129.2, 129.0, 128.9, 128.1, 127.6, 127.3, 126.7, 114.3, 55.4, 50.3, 49.0, 42.6, 35.8; **IR** (ATR): $\tilde{\nu}$ = 3009, 2349, 1692, 1606, 1510, 1353, 1255, 1164, 1030, 961, 702 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₄H₂₅NNaO₄S₂⁺ 478.1117, found 478.1118.



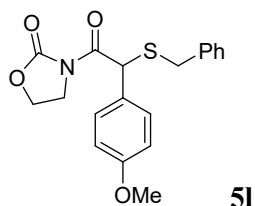
Sticky colorless oil (43.3 mg, 98%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 7.36 (t, *J* = 8.6 Hz, 1H), 7.32-7.15 (m, 7H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.81-6.73 (m, 4H), 4.15 (s, 1H), 3.78 (s, 3H), 3.75 (d of ABq, *J* = 13.7 Hz, 1H), 3.45 (d of ABq, *J* = 13.7 Hz, 1H), 3.41 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.8, 159.8, 137.2, 134.4, 130.2, 130.0, 129.6, 129.1, 128.8, 127.4, 126.5, 114.2, 55.4, 51.2, 42.1, 35.9; **IR** (ATR): $\tilde{\nu}$ = 3007, 2336, 1700, 1510, 1357, 1275, 1143, 1029, 963 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₃H₂₃NNaO₄S₂⁺ 464.0961, found 464.0955.



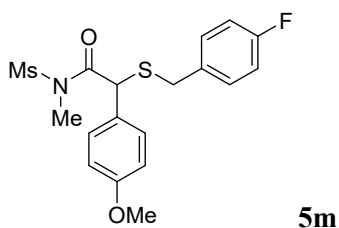
White solid (36.6 mg, 80%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.31-7.16 (m, 7H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.11 (s, 1H), 3.83 (s, 3H), 3.70 (d of ABq, *J* = 13.3 Hz, 1H), 3.53 (d of ABq, *J* = 13.3 Hz, 1H), 3.07 (s, 3H), 2.45 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.2, 159.5, 144.9, 137.4, 135.5, 130.2, 129.6, 129.1, 128.6, 127.9, 127.3, 126.8, 114.2, 55.3, 51.1, 35.9, 33.2, 21.7; **IR** (ATR): $\tilde{\nu}$ = 3011, 2342, 1702, 1608, 1510, 1456, 1355, 1275, 1258, 1167 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₄H₂₅NNaO₄S₂⁺ 478.1117, found 478.1110.



White solid (40.6 mg, 80%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 8.28 (d, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 7.2 Hz, 2H), 7.13 (d, *J* = 7.2 Hz, 2H), 6.82 (d, *J* = 7.2 Hz, 2H), 4.79 (s, 1H), 3.80 (s, 3H), 3.69 (d of ABq, *J* = 13.6 Hz, 1H), 3.51 (d of ABq, *J* = 13.2 Hz, 1H), 3.10 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.0, 159.8, 150.5, 144.1, 137.1, 130.1, 129.5, 129.1, 128.8, 127.5, 125.7, 124.1, 114.4, 55.4, 51.0, 35.8, 33.2; **IR** (ATR): $\tilde{\nu}$ = 2931, 1710, 1597, 1530, 1349, 1164, 1010, 746 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₃H₂₂N₂NaO₆S₂⁺ 509.0811, found 509.0804.

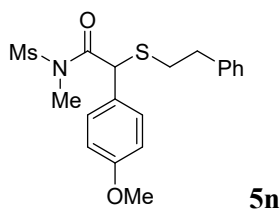


White solid (34.8 mg, 97%, EtOAc:Hex = 1:1); **¹H NMR** (400 MHz, CDCl₃): δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.34-7.16 (m, 5H), 6.85 (d, *J* = 7.6 Hz, 2H), 5.96 (s, 1H), 4.32-4.19 (m, 2H), 3.83 (t, *J* = 8.4 Hz, 2H), 3.79 (s, 3H), 3.75 (d of ABq, *J* = 12.0 Hz, 1H), 3.69 (d of ABq, *J* = 13.2 Hz, 1H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.7, 159.5, 152.8, 137.5, 130.4, 129.1, 128.5, 127.7, 127.2, 114.1, 61.8, 55.3, 48.8, 42.8, 36.5; **IR** (ATR): $\tilde{\nu}$ = 3004, 2985, 2320, 1775, 1697, 1606, 1509, 1386, 1259, 1030, 750 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₉H₁₉NNaO₄S⁺ 380.0927, found 380.0930.

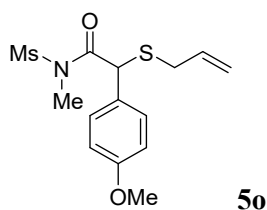


Sticky colorless oil (31.0 mg, 78%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 7.32 (d, *J* = 8.7 Hz, 2H), 7.25 (dd, *J* = 8.4, 5.0 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 5.04 (s, 1H),

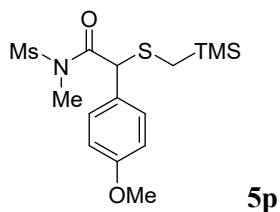
3.81 (s, 3H), 3.73 (d of ABq, $J = 13.4$ Hz, 1H), 3.55 (d of ABq, $J = 13.5$ Hz, 1H), 3.10 (s, 3H), 2.97 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.7, 162.0 (d, $J = 244.7$ Hz), 159.8, 133.0 (d, $J = 3.3$ Hz), 130.7 (d, $J = 8.0$ Hz), 130.2, 126.3, 115.5 (d, $J = 21.2$ Hz), 114.5, 55.4, 51.1, 41.1, 35.1, 32.8; IR (ATR): $\tilde{\nu} = 3393, 3030, 2916, 2852, 1687, 1461, 1346, 1159, 1085, 1020, 967, 875, 824, 752$ cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{20}\text{FNNaO}_4\text{S}_2^+$ 420.0710, found 420.0711.



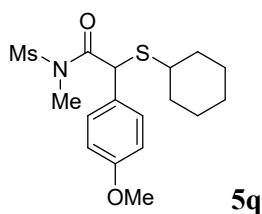
Sticky colorless oil (33.9 mg, 86%, EtOAc:Hex = 1:3); ^1H NMR (400 MHz, CDCl_3): δ 7.32 (d, $J = 8.7$ Hz, 2H), 7.28 (t, $J = 7.6$ Hz, 2H), 7.20 (t, $J = 7.4$ Hz, 1H), 7.15 (d, $J = 7.0$ Hz, 2H), 6.88 (d, $J = 8.7$ Hz, 2H), 5.25 (s, 1H), 3.80 (s, 3H), 3.18 (s, 3H), 3.02 (s, 3H), 2.87-2.65 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.9, 159.7, 140.1, 130.1, 128.6, 128.5, 127.0, 126.5, 114.4, 55.4, 52.0, 41.0, 35.8, 33.0, 32.7; IR (ATR): $\tilde{\nu} = 3023, 2931, 2413, 1691, 1607, 1510, 1351, 1254, 1164, 1029, 964, 749$ cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{23}\text{NNaO}_4\text{S}_2^+$ 416.0961, found 416.0959.



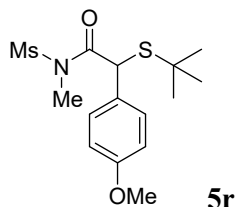
Sticky colorless oil (26.8 mg, 81%, EtOAc:Hex = 1:3); ^1H NMR (400 MHz, CDCl_3): δ 7.35 (d, $J = 8.5$ Hz, 2H), 6.89 (d, $J = 8.4$ Hz, 2H), 5.81 (ddt, $J = 16.8, 10.0, 6.8$ Hz, 1H), 5.22 (s, 1H), 5.17 (d, $J = 10.7$ Hz, 1H), 5.13 (d, $J = 17.0$ Hz, 1H), 3.81 (s, 3H), 3.25 (s, 3H), 3.18 (dd of ABq, $J = 13.8, 6.6$ Hz, 1H), 3.07 (s, 3H), 3.01 (dd of ABq, $J = 13.9, 7.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.9, 159.7, 133.7, 130.2, 126.6, 118.2, 114.4, 55.3, 50.8, 41.2, 34.5, 32.9; IR (ATR): $\tilde{\nu} = 2940, 2844, 2351, 1698, 1605, 1511, 1353, 1248, 1161, 961, 834, 505$ cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{19}\text{NNaO}_4\text{S}_2^+$ 352.0648, found 352.0640.



Sticky colorless oil (32.0 mg, 85%, EtOAc:Hex = 1:4); **¹H NMR** (400 MHz, CDCl₃): δ 7.37 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.23 (s, 1H), 3.82 (s, 3H), 3.29 (s, 3H), 3.10 (s, 3H), 1.75 (d of ABq, *J* = 11.6 Hz, 1H), 1.72 (d of ABq, *J* = 11.6 Hz, 1H), 0.07 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 172.6, 161.2, 131.9, 128.5, 115.9, 57.0, 56.1, 42.8, 34.7, 18.9, 0.0; **IR** (ATR): $\tilde{\nu}$ = 2992, 2956, 2325, 1690, 1607, 1511, 1350, 1252, 1163, 1076, 847, 765 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₅H₂₅NNaO₄S₂Si⁺ 398.0886, found 398.0880.

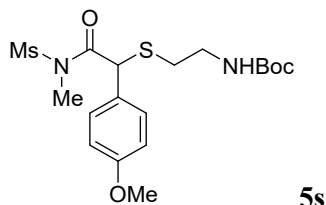


Sticky colorless oil (34.7 mg, 93%, EtOAc:Hex = 1:4); **¹H NMR** (400 MHz, CDCl₃): δ 7.37 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.45 (s, 1H), 3.80 (s, 3H), 3.27 (s, 3H), 3.07 (s, 3H), 2.69-2.56 (m, 1H), 2.03-1.90 (m, 1H), 1.86-1.62 (m, 3H), 1.62-1.50 (m, 1H), 1.44-1.15 (m, 5H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.2, 159.6, 130.0, 127.7, 114.3, 55.3, 50.3, 43.8, 41.0, 33.5, 33.3, 33.1, 25.9, 25.8, 25.7; **IR** (ATR): $\tilde{\nu}$ = 2931, 2860, 2420, 1693, 1511, 1351, 1255, 1164, 1074, 964, 765 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₇H₂₅NNaO₄S₂⁺ 394.1117, found 394.1114.

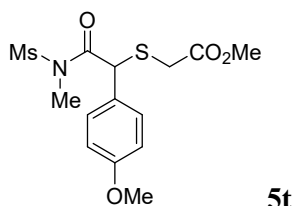


Sticky colorless oil (20.0 mg, 58%, EtOAc:Hex = 1:4); **¹H NMR** (400 MHz, CDCl₃): δ 7.40 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 5.57 (s, 1H), 3.81 (s, 3H), 3.29 (s, 3H), 3.05 (s, 3H), 1.33 (s, 9H); **¹³C NMR** (100 MHz, CDCl₃): δ 172.0, 159.5, 129.9, 128.2, 114.4, 55.3, 49.4, 45.2, 40.9, 33.2, 31.1; **IR**

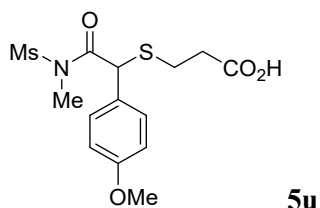
(ATR): $\tilde{\nu}$ = 2961, 2349, 1693, 1608, 1510, 1349, 1252, 1163, 1071, 964, 749 cm^{-1} ; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{23}\text{NNaO}_4\text{S}_2^+$ 368.0961, found 368.0963.



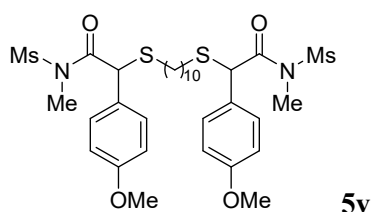
Sticky colorless oil (35.1 mg, 81%, EtOAc:Hex = 1:4); **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ 7.35 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 5.40 (s, 1H), 4.87 (s, 1H), 3.80 (s, 3H), 3.36-3.17 (m, 5H), 3.17 (s, 3H), 2.67-2.52 (m, 2H), 1.43 (s, 9H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3): δ 171.1, 159.8, 155.8, 130.1, 126.7, 114.5, 79.5, 55.3, 51.8, 41.1, 39.4, 33.0, 31.7, 28.4; **IR** (ATR): $\tilde{\nu}$ = 3376, 2989, 2348, 1690, 1511, 1350, 1257, 1163, 1078, 966, 750 cm^{-1} ; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{28}\text{N}_2\text{NaO}_6\text{S}_2^+$ 455.1281, found 455.1287.



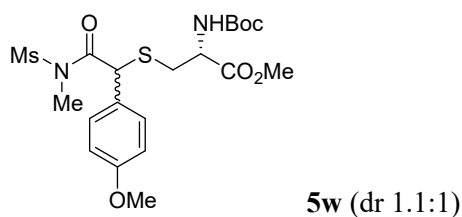
Sticky colorless oil (31.8 mg, 88%, EtOAc:Hex = 1:2); **$^1\text{H NMR}$** (400 MHz, CDCl_3): δ 7.39 (d, J = 7.7 Hz, 2H), 6.91 (d, J = 7.7 Hz, 2H), 5.62 (s, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 3.27 (s, 3H), 3.24 (d of ABq, J = 15.3 Hz, 1H), 3.12 (s, 3H), 3.06 (d of ABq, J = 15.1 Hz, 1H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3): δ 170.7, 170.6, 160.0, 130.4, 125.8, 114.6, 55.4, 52.5, 52.1, 41.1, 32.9, 32.1; **IR** (ATR): $\tilde{\nu}$ = 3007, 2324, 1689, 1607, 1511, 1349, 1257, 1163, 1029, 965, 765 cm^{-1} ; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{19}\text{NNaO}_6\text{S}_2^+$ 384.0546, found 384.0545.



Sticky colorless oil (35.4 mg, 98%, EtOAc:Hex = 1:0); **¹H NMR** (400 MHz, CDCl₃): δ 7.35 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 5.42 (s, 1H), 3.82 (s, 3H), 3.26 (s, 3H), 3.07 (s, 3H), 2.83-2.65 (m, 2H), 2.64-2.52 (m, 2H); **¹³C NMR** (100 MHz, CDCl₃): δ 177.6, 170.9, 159.8, 130.1, 126.6, 114.6, 55.4, 52.3, 41.0, 34.2, 33.1, 25.8; **IR** (ATR): $\tilde{\nu}$ = 3009, 2917, 2316, 1745, 1688, 1599, 1513, 1351, 1260, 1168, 1025, 750 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₄H₁₉NNaO₆S₂⁺ 384.0546, found 384.0547.



Sticky colorless oil (65.9 mg, 92%, EtOAc:Hex = 1:1); **¹H NMR** (400 MHz, CDCl₃): δ 7.35 (d, *J* = 8.6 Hz, 4H), 6.88 (d, *J* = 8.6 Hz, 4H), 5.32 (s, 2H), 3.80 (s, 6H), 3.26 (s, 6H), 3.06 (s, 6H), 2.46 (t, *J* = 7.3 Hz, 4H), 1.58-1.42 (m, 4H), 1.40-1.12 (m, 12H); **¹³C NMR** (100 MHz, CDCl₃): δ 171.1, 159.6, 130.0, 127.2, 114.3, 55.3, 51.8, 41.0, 33.1, 31.4, 29.3, 29.1, 28.9, 28.8; **IR** (ATR): $\tilde{\nu}$ = 3005, 2924, 2330, 1689, 1606, 1511, 1352, 1275, 1260, 1163, 764 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₂H₄₈N₂NaO₈S₄⁺ 739.2186, found 739.2194.

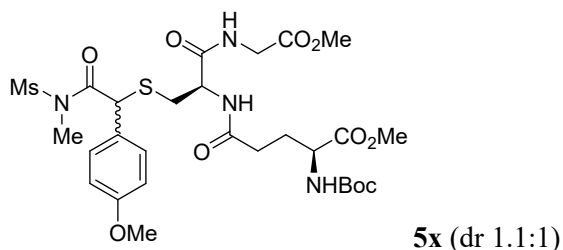


Sticky colorless oil (31.5 mg, 64%, EtOAc:Hex = 1:1)

(diastereomeric mixture) **¹H NMR** (400 MHz, CDCl₃): δ 7.34 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 2H), 5.44 (s, SCH, 0.5H), 5.43 (s, SCH, 0.5H), 5.37 (d, *J* = 6.8 Hz, Boc-NH, 0.5H), 5.32 (d, *J* = 6.8 Hz, Boc-NH 0.5H), 4.63-4.39 (m, cys- α -H, 1H), 3.80 (s, 3H), 3.76 (s, CO₂Me, 1.5H), 3.72 (s, CO₂Me, 1.5H), 3.25 (s, 1.5H), 3.24 (s, 1.5H), 3.05 (s, 1.5H), 3.03 (s, 1.5H), 2.95 (dd, *J* = 14.0, 5.1 Hz, SCH₂, 0.5H), 2.90-2.75 (m, SCH₂, 1.5H), 1.46 (s, 4.5H), 1.44 (s, 4.5H).

(diastereomeric mixture) ^{13}C NMR (100 MHz, CDCl_3): δ 171.4, 171.3, 170.8, 159.8, 155.3, 130.2, 130.1, 126.4, 114.55, 114.54, 80.3, 55.3, 53.2, 53.0, 52.72, 52.70, 52.3, 41.1, 41.0, 33.6, 33.3, 33.0, 32.9, 28.3.

IR (ATR): $\tilde{\nu}$ = 3377, 2979, 1750, 1714, 1505, 1366, 1164, 1064 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{30}\text{N}_2\text{NaO}_8\text{S}_2^+$ 513.1336, found 513.1339.

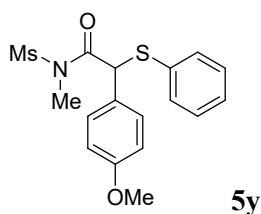


Sticky colorless oil (63.7 mg, 92%, CH_2Cl_2 :MeOH = 10:1)

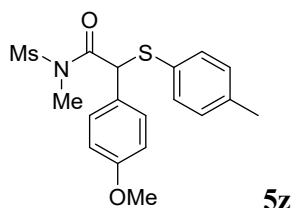
(diastereomeric mixture) ^1H NMR (400 MHz, CDCl_3): δ 7.38 (m, gly-NH, 0.5H), 7.35 (d, J = 8.4 Hz, 2H), 7.21 (m, gly-NH, 0.5H), 6.99 (d, J = 7.9 Hz, cys-NH, 1H), 6.90 (d, J = 8.6 Hz, 1H), 6.89 (d, J = 8.6 Hz, 1H), 5.41 (m, Boc-NH, 1H), 5.42 (s, SCH, 0.5H), 5.41 (s, SCH, 0.5H), 4.64 (m, cys- α -H, 1H), 4.32 (m, glu- α -H, 1H), 4.12-3.95 (m, gly- α -H, 2H), 3.80 (s, 3H), 3.73 (s, two CO_2Me , 6H), 3.25 (s, 1.5H), 3.22 (s, 1.5H), 3.20 (s, 1.5H), 3.12 (s, 1.5H), 3.05-2.94 (m, SCH_2 , 1H), 2.81-2.68 (m, SCH_2 , 1H), 2.35 (t, J = 7.0 Hz, γ -glu, 2H), 2.21-2.05 (m, β -glu, 1H), 2.05-1.90 (m, β -glu, 1H), 1.43 (s, 9H).

(diastereomeric mixture) ^{13}C NMR (100 MHz, CDCl_3): δ 172.9, 172.4, 172.3, 172.1, 171.4, 170.7, 170.6, 170.0, 169.9, 159.8, 155.6, 190.1, 129.9, 126.2, 126.1, 114.7, 80.1, 55.3, 53.5, 52.8, 52.5, 52.3, 51.9, 41.4, 41.3, 41.2, 41.1, 33.9, 32.88, 32.86, 31.9, 28.3.

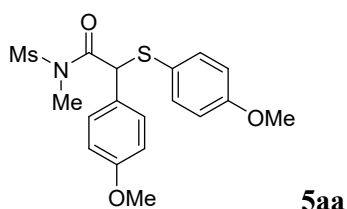
IR (ATR): $\tilde{\nu}$ = 3345, 2964, 2357, 1742, 1665, 1599, 1436, 1510, 1365, 1307, 1275, 1259, 1210, 1161, 1030 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{42}\text{N}_4\text{NaO}_{12}\text{S}_2^+$ 713.2133, found 713.2140.



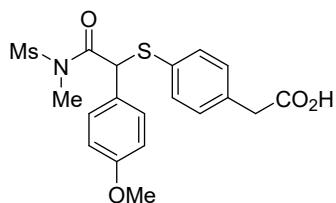
Sticky colorless oil (31.2 mg, 85%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 7.39-7.31 (m, 2H), 7.29-7.20 (m, 2H), 6.83 (d, *J* = 8.3 Hz, 2H), 5.65 (s, 1H), 3.79 (s, 3H), 3.22 (s, 3H), 2.89 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.7, 159.8, 133.6, 133.2, 130.1, 129.1, 128.4, 126.8, 114.3, 56.6, 55.3, 40.9, 33.1; **IR** (ATR): $\tilde{\nu}$ = 3023, 2325, 1693, 1511, 1351, 1258, 1164, 964, 764 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₇H₁₉NNaO₄S₂⁺ 388.0648, found 388.0645.



Sticky colorless oil (31.3 mg, 82%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 7.30-7.17 (m, 4H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.55 (s, 1H), 3.79 (s, 3H), 3.21 (s, 3H), 2.91 (s, 3H), 2.31 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.9, 159.7, 138.8, 134.2, 130.2, 129.9, 129.4, 127.0, 114.3, 56.8, 55.3, 41.0, 33.0, 21.2; **IR** (ATR): $\tilde{\nu}$ = 3016, 2928, 2356, 1692, 1607, 1510, 1350, 1255, 1164, 1075, 964, 765 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₈H₂₁NNaO₄S₂⁺ 402.0804, found 402.0800.

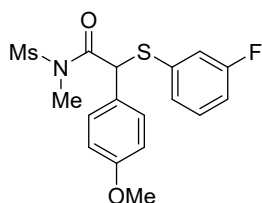


Sticky colorless oil (35.0 mg, 89%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 7.26 (d, *J* = 8.7 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 5.45 (s, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.20 (s, 3H), 2.93 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.9, 160.4, 159.7, 136.8, 130.2, 127.0, 123.2, 114.6, 114.2, 57.4, 55.33, 55.31, 41.0, 33.0; **IR** (ATR): $\tilde{\nu}$ = 3005, 2934, 2336, 1690, 1591, 1510, 1463, 1350, 1257, 1164, 1029, 830 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₈H₂₁NNaO₅S₂⁺ 418.0753, found 418.0750.



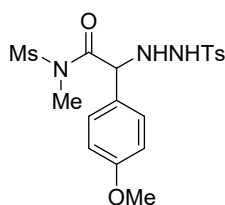
5ab

Sticky colorless oil (39.4 mg, 93%, EtOAc:Hex = 2:1); **¹H NMR** (400 MHz, CDCl₃): δ 10.94 (s, 1H), 7.30 (d, 2H, *J* = 8.7 Hz), 7.24 (d, 2H, *J* = 6.8 Hz), 7.17 (d, 2H, *J* = 8.2 Hz), 6.83 (d, 2H, *J* = 8.7 Hz), 5.63 (s, 1H), 3.78 (s, 3H), 3.61 (s, 2H), 3.20 (s, 3H), 2.87 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 177.3, 170.7, 159.8, 133.8, 133.7, 132.4, 130.2, 130.1, 126.6, 114.4, 56.6, 55.3, 40.9, 40.6, 33.1.; **IR** (ATR): $\tilde{\nu}$ = 2933, 1693, 1606, 1510, 1349, 1252, 1163, 809 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₉H₂₁NNaO₆S₂⁺ 446.0703, found 446.0706.



5ac

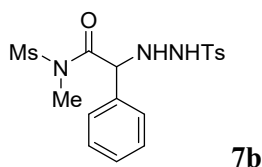
Sticky colorless oil (31.7 mg, 83%, EtOAc:Hex = 1:3); **¹H NMR** (400 MHz, CDCl₃): δ 7.30-7.17 (m, 3H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.8 Hz, 1H), 6.96 (dt, *J* = 8.4, 2.0 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.72 (s, 1H), 3.79 (s, 3H), 3.23 (s, 3H), 2.89 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 170.3, 162.5 (d, *J* = 248.2 Hz), 159.9, 135.5 (d, *J* = 8.0 Hz), 130.3 (d, *J* = 8.1 Hz), 130.1, 128.6 (d, *J* = 3.0 Hz), 126.3, 119.8 (d, *J* = 22.1 Hz), 115.3 (d, *J* = 21.1 Hz), 114.5, 56.5, 55.3, 40.8, 33.2; **IR** (ATR): $\tilde{\nu}$ = 3002, 2928, 2325, 1693, 1578, 1511, 1472, 1352, 1258, 1165, 881, 765 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₇H₁₈FNNaO₄S₂⁺ 406.0553, found 406.0551.



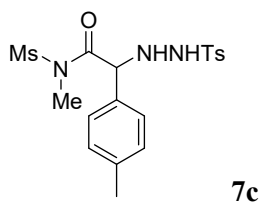
7a

Sticky colorless oil (37.0 mg, 84%, EtOAc:Hex = 1:2); **¹H NMR** (400 MHz, CDCl₃): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 7.8 Hz, 2H), 6.56 (s, 1H), 5.10 (d, *J* = 10.1 Hz, 1H), 4.27 (d, *J* = 10.2 Hz, 1H), 3.78 (s, 3H), 3.12 (s, 3H), 3.11 (s, 3H), 2.42 (s, 3H);

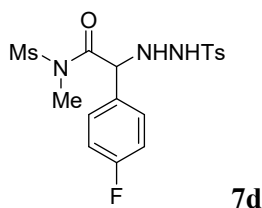
^{13}C NMR (100 MHz, CDCl_3): δ 173.4, 160.3, 144.1, 134.9, 129.9, 129.6, 128.2, 124.7, 114.7, 67.9, 55.4, 41.4, 32.2, 21.6; IR (ATR): $\tilde{\nu}$ = 3307, 3010, 1715, 1612, 1513, 1311, 1249, 1151, 1033, 750 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{23}\text{N}_3\text{NaO}_6\text{S}_2^+$ 464.0920, found 464.0925.



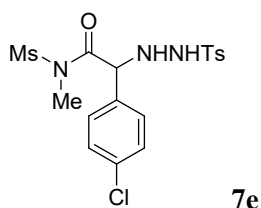
Sticky colorless oil (27.2 mg, 66%, EtOAc:Hex = 1:2); ^1H NMR (400 MHz, CDCl_3): δ 7.78 (d, J = 7.5 Hz, 2H), 7.42-7.32 (m, 3H), 7.32-7.18 (m, 4H), 6.32 (s, 1H), 5.19 (s, 1H), 4.23 (s, 1H), 3.13 (s, 3H), 3.10 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.2, 144.1, 134.8, 132.9, 129.6, 129.5, 129.40, 129.38, 128.6, 128.3, 68.6, 41.3, 32.2, 21.6; IR (ATR): $\tilde{\nu}$ = 3248, 2982, 1714, 1512, 1260, 1152, 1033, 749 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{21}\text{N}_3\text{NaO}_5\text{S}_2^+$ 434.0815, found 434.0821.



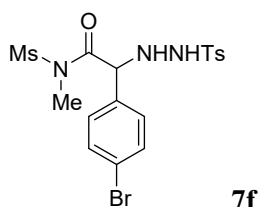
Sticky colorless oil (26.3 mg, 62%, EtOAc:Hex = 1:2); ^1H NMR (400 MHz, CDCl_3): δ 7.79 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 6.44 (d, J = 1.4 Hz, 1H), 5.14 (d, J = 10.2 Hz, 1H), 4.25 (dd, J = 2.0, 10.0 Hz, 1H), 3.24-3.02 (m, 6H), 2.43 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 173.3, 144.1, 139.5, 134.8, 130.1, 129.8, 129.6, 128.5, 128.2, 68.3, 41.4, 32.2, 21.6, 21.2; IR (ATR): $\tilde{\nu}$ = 3251, 2925, 1683, 1352, 1161, 749, 533 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{23}\text{N}_3\text{NaO}_5\text{S}_2^+$ 448.0971, found 448.0975.



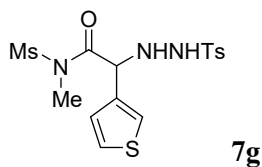
Sticky colorless oil (23.9 mg, 56%, EtOAc:Hex = 1:2); **¹H NMR** (400 MHz, CDCl₃): δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.22 (dd, *J* = 5.3, 8.5 Hz, 2H), 7.03 (t, *J* = 8.5 Hz, 2H), 6.61 (d, *J* = 1.1 Hz, 1H), 5.20 (d, *J* = 9.8 Hz, 1H), 4.33 (dd, *J* = 9.8, 2.2 Hz, 1H), 3.26-3.05 (m, 6H), 2.42 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 173.2, 163.0 (d, *J* = 249.2 Hz), 144.2, 134.6, 130.5 (d, *J* = 8.2 Hz), 129.6, 129.0 (d, *J* = 3.4 Hz), 128.2, 116.3 (d, 21.8 Hz), 67.8, 41.4, 32.3, 21.6; **IR** (ATR): $\tilde{\nu}$ = 3251, 2977, 1693, 1599, 1509, 1363, 1316, 1228, 1153, 969, 750 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₇H₂₀FN₃NaO₅S₂⁺ 452.0721, found 452.0723.



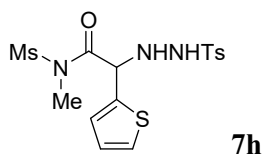
Sticky colorless oil (23.7 mg, 53%, EtOAc:Hex = 1:2); **¹H NMR** (400 MHz, CDCl₃): δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.39-7.25 (m, 4H), 7.19 (d, *J* = 8.3 Hz, 2H), 6.48 (s, 1H), 5.24 (d, *J* = 8.6 Hz, 1H), 4.31 (d, *J* = 8.3 Hz, 1H), 3.24-3.10 (m, 6H), 2.44 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 173.0, 144.3, 135.5, 134.5, 131.6, 129.9, 129.6, 129.5, 128.2, 67.9, 41.5, 32.3, 21.6; **IR** (ATR): $\tilde{\nu}$ = 3282, 2990, 1692, 1311, 1275, 1260, 1153, 1034, 1009, 764 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₇H₂₀ClN₃NaO₅S₂⁺ 468.0425, found 468.0431.



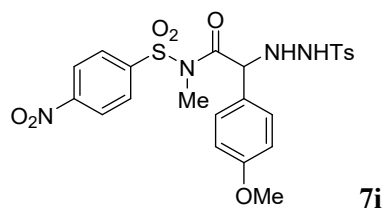
Sticky colorless oil (20.1 mg, 41%, EtOAc:Hex = 1:2); **¹H NMR** (400 MHz, CDCl₃): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.57 (s, 1H), 5.20 (s, 1H), 4.41 (s, 1H), 3.15 (s, 3H), 3.14 (s, 3H), 2.42 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 173.0, 144.3, 134.5, 132.5, 132.1, 130.2, 129.6, 128.2, 123.7, 67.9, 41.5, 32.4, 21.6; **IR** (ATR): $\tilde{\nu}$ = 3307, 2985, 1693, 1362, 1313, 1276, 1153, 1010, 750 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₇H₂₀BrN₃NaO₅S₂⁺ 511.9920, found 511.9922.



Brown oil (25.2 mg, 61%, EtOAc:Hex = 1:2); **¹H NMR** (400 MHz, CDCl₃): δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.37-7.26 (m, 3H), 7.20 (d, *J* = 1.6 Hz, 1H), 7.02 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.40 (s, 1H), 5.33 (d, *J* = 10.3 Hz, 1H), 4.26 (dd, *J* = 10.4, 3.1 Hz, 1H), 3.17 (s, 3H), 3.12 (s, 3H), 2.42 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 173.1, 144.2, 134.7, 133.4, 129.7, 128.2, 127.4, 127.3, 125.3, 63.8, 41.4, 32.3, 21.6; **IR** (ATR): $\tilde{\nu}$ = 3260, 2922, 1687, 1350, 1160, 1092, 963, 814 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₅H₁₉N₃NaO₅S₃⁺ 440.0379, found 440.0376.

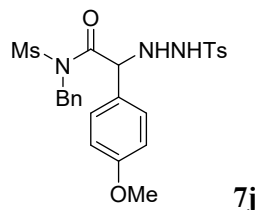


Sticky colorless oil (23.3 mg, 56%, EtOAc:Hex = 1:2); **¹H NMR** (400 MHz, CDCl₃): δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.36 (dd, *J* = 4.4, 2.4 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.04-6.93 (m, 2H), 6.33 (d, *J* = 3.0 Hz, 1H), 5.48 (d, *J* = 10.2 Hz, 1H), 4.35 (dd, *J* = 10.2, 3.1 Hz, 1H), 3.25 (s, 3H), 3.19 (s, 3H), 2.45 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 172.3, 144.3, 134.9, 134.5, 129.7, 128.3, 127.94, 127.86, 127.3, 63.3, 41.4, 32.4, 21.6; **IR** (ATR): $\tilde{\nu}$ = 3247, 2926, 1686, 1348, 1160, 1091, 963, 774 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₅H₁₉N₃NaO₅S₃⁺ 440.0379, found 440.0378.

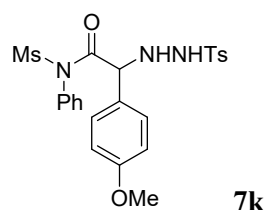


Sticky colorless oil (38.5 mg, 70%, EtOAc:Hex = 1:2); **¹H NMR** (400 MHz, CDCl₃): δ 8.32 (d, *J* = 8.6 Hz, 2H), 7.99 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 7.9 Hz, 2H), 6.20 (s, 1H), 5.14 (s, 1H), 4.07 (s, 1H), 3.79 (s, 3H), 3.22 (s, 3H), 2.40 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 172.7, 160.4, 150.7, 144.1, 143.9, 134.7, 129.8, 129.6, 128.1, 124.4, 124.2, 114.7, 68.1, 55.4, 32.9, 21.6; **IR** (ATR): $\tilde{\nu}$ = 3192, 2995, 1712, 1599, 1534, 1353,

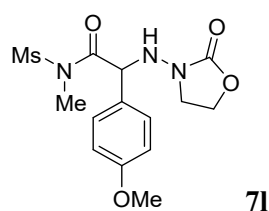
1169, 1075, 817, 749 cm^{-1} ; **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for $\text{C}_{23}\text{H}_{24}\text{N}_4\text{NaO}_8\text{S}_2^+$ 571.0928, found 571.0930.



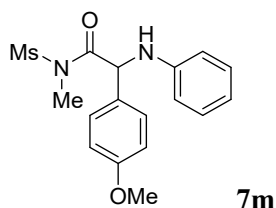
Sticky colorless oil (50.0 mg, 97%, EtOAc:Hex = 1:2); **^1H NMR** (400 MHz, CDCl_3): δ 7.70 (d, J = 8.2 Hz, 2H), 7.40-7.28 (m, 3H), 7.26-7.21 (m, 4H), 7.05 (d, J = 8.7 Hz, 2H), 6.81 (d, J = 8.7 Hz, 2H), 6.39 (s, 1H), 5.10 (s, 1H), 4.95 (d of ABq, J = 16.4 Hz, 1H), 4.75 (d of ABq, J = 16.6 Hz, 1H), 3.77 (s, 2H), 2.93 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3): δ 173.6, 160.3, 144.0, 135.4, 134.8, 129.9, 129.5, 129.0, 128.23, 128.20, 127.2, 124.7, 114.7, 67.7, 55.3, 48.8, 42.7, 21.6; **IR** (ATR): $\tilde{\nu}$ = 3232, 3003, 1708, 1598, 1512, 1495, 1325, 1256, 1148, 1033, 750 cm^{-1} ; **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for $\text{C}_{24}\text{H}_{27}\text{N}_3\text{NaO}_6\text{S}_2^+$ 540.1233, found 540.1237.



Yellow oil (45.2 mg, 90%, EtOAc:Hex = 1:1); **^1H NMR** (400 MHz, CDCl_3): δ 7.76 (d, J = 7.9 Hz, 2H), 7.56-7.17 (m, 5H), 7.28 (d, J = 7.7 Hz, 2H), 6.85-6.68 (m, 4H), 6.58 (s, 1H), 4.40 (s, 1H), 4.26 (s, 1H), 3.79 (s, 3H), 3.50 (s, 3H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, CDCl_3): δ 173.2, 160.2, 144.0, 134.8, 133.6, 130.2, 129.7, 129.6, 129.5, 128.2, 125.1, 124.9, 114.4, 67.7, 55.3, 42.2, 21.6; **IR** (ATR): $\tilde{\nu}$ = 3216, 2997, 1701, 1609, 1511, 1356, 1252, 1157, 1030, 964 cm^{-1} ; **HRMS** (ESI) m/z : $[M+Na]^+$ Calcd for $\text{C}_{23}\text{H}_{25}\text{N}_3\text{NaO}_6\text{S}_2^+$ 526.1077, found 526.1075.

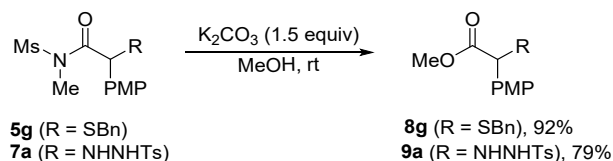


White solid (29.2 mg, 82%, EtOAc:Hex = 1:1); **¹H NMR** (400 MHz, CDCl₃): δ 7.34 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 5.35 (d, *J* = 4.0 Hz, 1H), 4.75 (d, *J* = 3.9 Hz, 1H), 4.27-4.21 (m, 2H), 3.81(s, 3H), 3.75 (ddd, *J* = 13.4, 11.5, 5.2 Hz, 1H), 3.89 (q, *J* = 8.4 Hz, 1H), 3.15 (s, 2H), 3.09 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 172.1, 160.4, 158.9, 130.2, 125.6, 114.7, 65.5, 61.8, 55.4, 47.6, 41.1, 32.4; **IR** (ATR): $\tilde{\nu}$ = 3280, 3011, 1748, 1692, 1512, 1346, 1250, 1163, 966, 770 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₄H₁₉N₃NaO₆S⁺ 380.0887, found 380.0882.



Sticky colorless oil (15.5 mg, 45%, EtOAc:Hex = 1:2); **¹H NMR** (400 MHz, CDCl₃): δ 7.38 (d, *J* = 8.7 Hz, 2H), 7.19 (t, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.77 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 7.7 Hz, 2H), 5.89 (s, 1H), 3.82 (s, 3H), 3.29 (s, 3H), 2.90 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃): δ 173.1, 156.0, 146.1, 129.6, 129.4, 127.9, 118.9, 114.8, 113.9, 59.9, 55.4, 40.8, 32.7; **IR** (ATR): $\tilde{\nu}$ = 3376, 3018, 2838, 1693, 1602, 1511, 1348, 1250, 1163, 963 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₇H₂₀N₂NaO₄S⁺ 371.1036, found 371.1032.

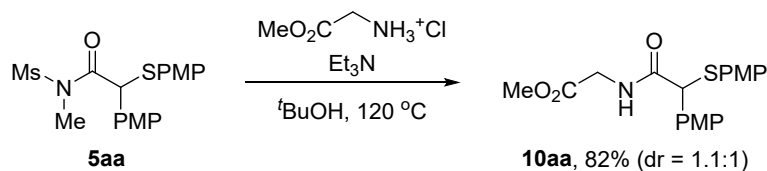
5. Synthetic applications



In a 4mL vial, imide **5g** (or **7a**) (0.10 mmol) was dissolved in methanol (1.0 mL) at room temperature. To this mixture was added K_2CO_3 (20.7 mg, 0.15 mmol) and was stirred at room temperature for 30 minutes. The reaction mixture was poured onto a silica gel column and was eluted with EtOAc:Hex.

8g: sticky colorless oil (27.8 mg, 92%, EtOAc:Hex = 1:10); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.42-7.18 (m, 7H), 6.85 (d, $J = 8.7$ Hz, 2H), 4.39 (s, 1H), 3.79 (s, 3H), 3.75 (d of ABq, $J = 13.5$ Hz, 1H), 3.67 (s, 3H), 3.60 (d of ABq, $J = 13.5$ Hz, 1H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 171.4, 159.5, 137.3, 129.8, 129.1, 128.6, 127.7, 127.3, 114.1, 55.3, 52.7, 50.9, 36.2; **IR** (ATR): $\tilde{\nu} = 3010, 2559, 1684, 1598, 1510, 1261, 1166, 1028, 750 \text{ cm}^{-1}$; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{18}\text{NaO}_3\text{S}^+$ 325.0869, found 325.0876.

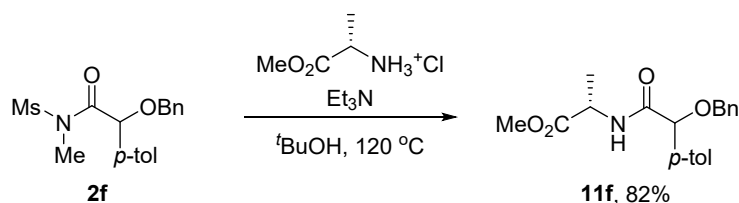
9a: sticky colorless oil (28.8 mg, 79%, EtOAc:Hex = 1:5); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.80 (d, $J = 8.2$ Hz, 2H), 7.31 (d, $J = 8.2$ Hz, 2H), 7.13 (d, $J = 8.6$ Hz, 2H), 6.86 (d, $J = 8.6$ Hz, 2H), 6.23 (d, $J = 2.0$ Hz, 1H), 4.63 (d, $J = 9.8$ Hz, 1H), 4.16 (dd, $J = 9.8, 2.3$ Hz, 1H), 3.81 (s, 3H), 3.73 (s, 3H), 2.45 (s, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 172.7, 160.0, 144.0, 135.1, 129.7, 129.2, 128.2, 126.5, 114.3, 66.8, 55.3, 52.5, 21.6; **IR** (ATR): $\tilde{\nu} = 3257, 3003, 2207, 1723, 1596, 1513, 1275, 1260, 1168, 1032, 750 \text{ cm}^{-1}$; **HRMS** (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{20}\text{N}_2\text{NaO}_5\text{S}^+$ 387.0985, found 387.0981.



In a 4mL vial, imide **5aa** (19.8 mg, 0.05 mmol) and glycine methyl ester hydrochloride (31.4 mg, 0.25 mmol) was dissolved in $t\text{BuOH}$ (0.5 mL). To this mixture was added triethylamine (25.3 mg, 0.25 mmol) and was capped under air. The resulting mixture was stirred at 120°C for 13 h. When the reaction was judged to be complete by TLC, reaction mixture was extracted with DCM (3 x 1 mL). The combined organic layers were dried (MgSO_4) and concentrated in vacuo. The residue was poured onto

a silica gel column and was eluted with EtOAc:Hex (1:2~1:1) to afford **10aa** (15.4 mg, 82%) as yellow stick oil.

10aa: ¹H NMR (400 MHz, CDCl₃): δ 7.36 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.20 (t, *J* = 5.4 Hz, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 4.77 (s, 1H), 4.09 (dd of ABq, *J* = 18.5, 4.6 Hz, 1H), 4.02 (dd of ABq, *J* = 18.2, 5.1 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.76 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 170.1, 169.9, 159.8, 159.4, 134.5, 129.5, 128.4, 124.2, 114.7, 114.2, 58.7, 55.4, 55.3, 52.5, 41.6.; IR (ATR): $\tilde{\nu}$ = 3308, 3005, 2837, 2359, 1750, 1655, 1608, 1591, 1509, 1494, 1275, 1249, 1030, 829 cm⁻¹; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₉H₂₁NNaO₅S⁺ 398.1033, found 398.1040.

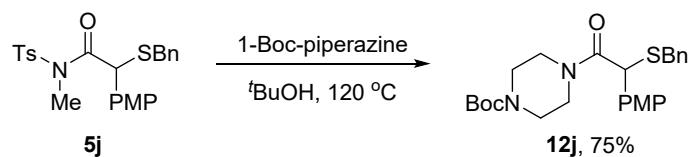


In a 4mL vial, imide **2f** (17.4 mg, 0.05 mmol) and alanine methyl ester hydrochloride (31.4 mg, 0.25 mmol) was dissolved in t-BuOH (0.5 mL). To this mixture was added triethylamine (25.3 mg, 0.25 mmol) and was capped under air. The resulting mixture was stirred at 120 °C for 13 h. When the reaction was judged to be complete by TLC, reaction mixture was extracted with DCM (3 x 1 mL). The combined organic layers were dried (MgSO₄) and concentrated in vacuo. The residue was poured onto a silica gel column and was eluted with EtOAc:Hex (1:3) to afford diastereomeric mixture of **11f** (dr = 1.1:1, 12.8 mg, 75%) as yellow sticky oil.

(diastereomeric mixture) **11f**: ¹H NMR (500 MHz, CDCl₃): δ 7.43-7.28 (m, 7H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 4.80 (s, 0.5H), 4.79 (s, 0.5H), 4.65-4.56 (m, 2H), 4.53 (d, *J* = 11.6 Hz, 1H), 4.43 (d, *J* = 11.8 Hz, 1H), 3.77 (s, 1.5H), 3.71 (s, 1.5H), 2.35 (s, 3H), 1.45 (d, *J* = 7.2 Hz, 1.5H), 1.39 (d, *J* = 7.2 Hz, 1.5H).

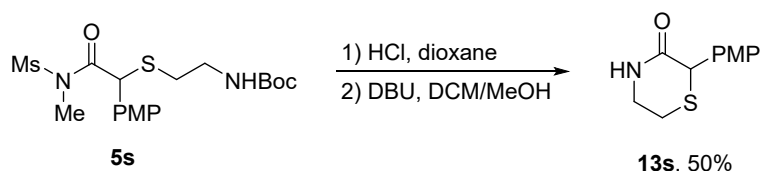
(diastereomeric mixture) ¹³C NMR (126 MHz, CDCl₃): δ ¹³C NMR (126 MHz, CDCl₃) δ 173.3, 173.1, 170.5, 170.3, 138.4, 138.3, 137.12, 137.08, 134.0, 133.9, 129.3, 128.6, 128.1, 128.0, 127.9, 127.4, 127.0, 81.0, 80.9, 71.3, 70.9, 52.44, 52.36, 47.6., 47.58, 21.21, 21.19, 18.44, 18.37.

IR (ATR): $\tilde{\nu}$ = 3404, 2927, 2450, 1743, 1680, 1512, 1453, 1212, 1157, 1067 cm⁻¹; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₀H₂₃NNaO₄⁺ 364.1519, found 364.1517.



In a 4mL vial, imide **5j** (22.8 mg, 0.05 mmol) and 1-Boc-piperazine (46.6 mg, 0.25 mmol) was dissolved in *t*BuOH (0.5 mL) and was capped under air. The resulting mixture was stirred at 120 °C for 13 h. When the reaction was judged to be complete by TLC, reaction mixture was extracted with DCM (3 x 1 mL). The combined organic layers were dried (MgSO₄) and concentrated in vacuo. The residue was poured onto a silica gel column and was eluted with EtOAc:Hex (1:2~1:1) to afford **12j** (17.0 mg, 75%) as colorless oil.

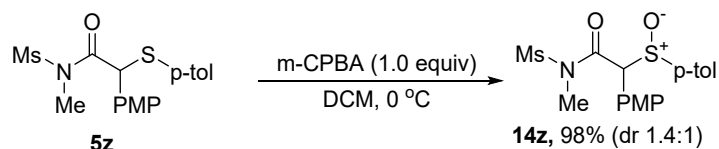
12j: ¹H NMR (400 MHz, CDCl₃): δ 7.40-7.18 (m, 7H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.50 (s, 1H), 3.81 (s, 3H), 3.73 (d of ABq, *J* = 13.6 Hz, 1H), 3.65-3.44 (m, 2H), 3.49 (d of ABq, *J* = 13.9 Hz, 1H), 3.43-3.33 (m, 1H), 3.32-3.24 (m, 1H), 3.23-3.15 (m, 1H), 3.14-3.04 (m, 2H), 3.02-2.84 (m, 1H), 1.43 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 168.2, 159.3, 154.5, 137.7, 129.9, 129.1, 128.6, 128.4, 127.3, 114.2, 80.3, 55.3, 45.5, 42.2, 35.7, 28.4 cm⁻¹; IR (ATR): $\tilde{\nu}$ = 3301, 2936, 2836, 1750, 1655, 1591, 1509, 1463, 1247, 1176, 1030, 829 cm⁻¹; HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₂₅H₃₂N₂NaO₄S⁺ 479.1975, found 479.1970.



In a 4mL vial, imide **5s** (21.6 mg, 0.05 mmol) was dissolved in 1,4-dioxane (0.5 mL). To the reaction mixture was added HCl (4 M in 1,4-dioxane, 0.2 mL) and the resulting mixture was stirred at room temperature for 1 h. When the reaction was judged to be complete by TLC, reaction mixture was diluted with sat. NaHCO₃ (1 mL) and then extracted with DCM (3 x 1 mL). The combined organic layers were dried (MgSO₄) and concentrated in vacuo. The residue was directly diluted with DCM/MeOH (1/1, 1 mL). To the reaction mixture was added DBU (7.6 mg, 0.05 mmol) and the resulting mixture was stirred at room temperature for 30 minutes. The residue was poured onto a silica gel column and was eluted with EtOAc:Hex (1:1~1:0) to afford **13s** (11.2 mg, 50%) as sticky colorless oil.

13s: ¹H NMR (400 MHz, CDCl₃): δ 7.35 (d, *J* = 8.7 Hz, 2H), 7.34 (s, 1H), 6.90 (d, *J* = 8.7 Hz, 2H),

4.63 (s, 1H), 3.81 (s, 3H), 3.73-3.54 (m, 2H), 2.97-2.78 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 170.2, 159.2, 129.9, 128.9, 114.0, 55.3, 45.8, 44.0, 25.7; IR (ATR): $\tilde{\nu}$ = 3195, 3076, 2930, 1660, 1610, 1514, 1246, 1178, 1028, 908 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{11}\text{H}_{13}\text{NNaO}_2\text{S}^+$ 246.0559, found 246.0562.



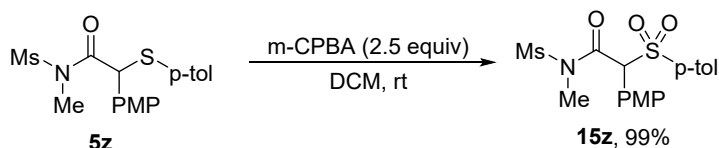
In a 4mL vial, imide **5z** (37.9 mg, 0.10 mmol) was dissolved in dichloromethane (1 mL) and the mixture was cooled to 0 °C. To the reaction mixture was added 3-chloroperbenzoic acid (22.4 mg, <77%wt., 0.1 mmol) and the resulting mixture was stirred at 0 °C for 10 minutes. When the reaction was judged to be complete by TLC, reaction mixture was diluted with sat. NaHCO_3 (1 mL) and then extracted with DCM (3 x 1 mL). The combined organic layers were dried (MgSO_4) and concentrated in vacuo. The residue was poured onto a silica gel column and was eluted with EtOAc:Hex (1:2) to afford **14z** (38.7 mg, 98%, d.r = 1.4:1) as white solid.

(major diastereomer) **14z**; ^1H NMR (400 MHz, CDCl_3): δ 7.17-7.06 (m, 4H), 7.02 (d, J = 8.1 Hz, 2H), 6.73 (d, J = 8.0 Hz, 2H), 5.55 (s, 1H), 3.77 (s, 3H), 3.31 (s, 3H), 3.23 (s, 3H), 2.35 (s, 3H).

(minor diastereomer) **14z'**; ^1H NMR (400 MHz, CDCl_3): δ 7.46 (d, J = 7.6 Hz, 2H), 7.27 (d, J = 7.7 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 8.0 Hz, 2H), 5.29 (s, 1H), 3.81 (s, 3H), 3.09 (s, 3H), 2.61 (s, 3H), 2.41 (s, 3H);

(diastereomeric mixture) **14z** and **14z'** ^{13}C NMR (100 MHz, CDCl_3): δ 169.2, 168.4, 160.8, 160.4, 142.4, 142.3, 139.5, 137.9, 131.6, 131.1, 129.7, 129.4, 125.43, 125.37, 120.0, 119.7, 114.4, 114.2, 77.8, 55.4, 55.3, 42.2, 40.5, 33.1, 32.8, 21.51, 21.50.

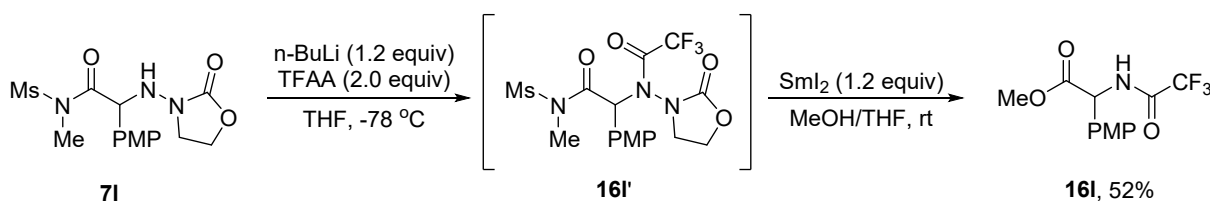
IR (ATR): $\tilde{\nu}$ = 3002, 1679, 1607, 1510, 1352, 1256, 1029, 965, 768 cm^{-1} ; HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{21}\text{NNaO}_5\text{S}_2^+$ 418.0753, found 418.0755.



In a 4 mL vial, imide **5z** (37.9 mg, 0.10 mmol) was dissolved in dichloromethane (1 mL) and the mixture was cooled to 0 °C. To the reaction mixture was added 3-chloroperbenzoic acid (56.0 mg,

<77%wt., 0.25 mmol) and the resulting mixture was stirred at room temperature for 30 minutes. When the reaction was judged to be complete by TLC, reaction mixture was diluted with sat. NaHCO₃ (1 mL) and then extracted with DCM (3 x 1 mL). The combined organic layers were dried (MgSO₄) and concentrated in vacuo. The residue was poured onto a silica gel column and was eluted with EtOAc:Hex (1:3) to afford **15z** (40.8 mg, 99%) as white solid.

15z: ¹H NMR (400 MHz, CDCl₃): δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.31-7.14 (m, 4H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.27 (s, 1H), 3.79 (s, 3H), 3.27 (s, 3H), 3.13 (s, 3H), 2.42 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 165.4, 160.8, 145.3, 133.2, 132.0, 130.2, 129.2, 119.5, 114.1, 73.3, 55.4, 41.2, 33.2, 21.7; **IR** (ATR): $\tilde{\nu}$ = 2931, 1694, 1607, 1511, 1355, 1256, 1147, 1079, 844 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₈H₂₁NNaO₆S₂⁺ 434.0703, found 434.0710.



In a flame-dried 4mL vial, imide **71** (17.9 mg, 0.05 mmol) was dissolved in THF (0.5 mL) and the mixture was cooled to -78°C under Ar. To the reaction mixture was added *n*-BuLi (1.6 M in hexane, 34 μL, 0.055 mmol) and the resulting mixture was stirred at -78 °C. After 30 minutes, TFAA (15.8 mg, 0.075 mmol) was added dropwise and the mixture was stirred at -78 °C. When the reaction was judged to be complete by TLC, reaction mixture was diluted with sat. NH₄Cl (1 mL) and was brought to room temperature. The mixture was extracted with DCM (3 x 1 mL). The combined organic layers were dried (MgSO₄) and concentrated in vacuo. The residue was poured onto a silica gel column and was eluted with EtOAc:Hex (1:4) to afford **161'**. The crude **161'** was re-dissolved in MeOH (100 μL) and the mixture was treated with SmI₂ (0.1 M in THF, 4 mL, 0.4 mmol) at room temperature. After stirring the mixture for 3 hours, solvent was evaporated, and the residue was poured onto a silica gel column and was eluted with EtOAc:Hex (1:2) to afford **161** (7.6 mg, 52%) as brown liquid.

161: ¹H NMR (400 MHz, CDCl₃): δ 7.45-7.21 (m, 3H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.80 (d, *J* = 8.0 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H); ¹³C NMR (100 MHz, Acetone D₆): δ 169.9, 158.0, 156.4 (d, *J* = 37.1 Hz), 129.5, 125.6, 116.0 (d, *J* = 285.2 Hz), 115.6, 56.6, 52.0, 29.7; **IR** (ATR): $\tilde{\nu}$ = 3195, 3076, 2930, 1660, 1610, 1514, 1246, 1178, 1028, 908 cm⁻¹; **HRMS** (ESI) *m/z*: [M+Na]⁺ Calcd for C₁₂H₁₂F₃NNaO₄⁺ 314.0611, found 314.0615.