SUPPORTING INFORMATION

FOR

Diversified Syntheses of Multifunctionalized Thiazole Derivatives *via* Regioselective and Programmed C-H Activation

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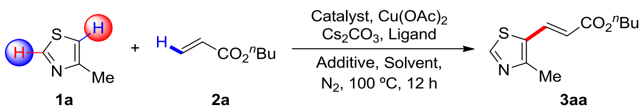
Table of Contents

1. General Information

Unless otherwise noted, all reactions were run under N_2 atmosphere. Prior to starting experiments, the parallel reactor was turned on, and was allowed to equilibrate to the desired temperature over 30 minutes. All starting materials were commercially available and were used as received. All reagents were handled in air. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV (400 MHz or 500 MHz and 125 MHz or 100 MHz, respectively) instrument internally referenced to $SiMe_4$ or chloroform signals. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet and m = multiplet. High resolution mass spectra (HRMS-ESI) were recorded at the Center for Mass Spectrometry, Peking University.

2. Experimental

Table S1. Regioselective 5-Alkenylation of 4-Methylthiaozle Under Various Conditions.[a]



Entry	Catalyst (mol%)	Solvent	Ligand (mol%)	Additive (equiv)	Yield (%)[b]
1	$Pd(OAc)_2$ (10)	toluene	-	-	2
2	$Pd(OAc)_2$ (10)	DCE	-	-	0
3	$Pd(OAc)_2$ (10)	^{t}AmylOH	-	-	18
4	$Pd(OAc)_2$ (10)	DMF	-	-	0
5	$Pd(OAc)_2$ (10)	^{t}AmylOH	**L1** (20)	-	23
6	$Pd(OAc)_2$ (10)	^{t}AmylOH	**L2** (10)	-	9
7	$Pd(OAc)_2$ (10)	^{t}AmylOH	**L3** (10)	-	15
8	$Pd(OAc)_2$ (10)	^{t}AmylOH	**L4** (10)	-	10
9	$Pd(OAc)_2$ (10)	^{t}AmylOH	**L5** (10)	-	51
10	$Pd(OPiv)_2$ (10)	^{t}AmylOH	**L5** (10)	-	44
11	$Pd(OTFA)_2$ (10)	^{t}AmylOH	**L5** (10)	-	48
12	$Pd(CH_3CN)_4(BF_4)_2$ (10)	^{t}AmylOH	**L5** (10)	-	47
13[c]	$Pd(OAc)_2$ (10)	^{t}AmylOH	**L5** (10)	-	0
14[d]	$Pd(OAc)_2$ (10)	^{t}AmylOH	**L5** (10)	-	5
15[e]	$Pd(OAc)_2$ (10)	^{t}AmylOH	**L5** (10)	-	6
16[f]	$Pd(OAc)_2$ (10)	^{t}AmylOH	**L5** (10)	-	2
17[g]	$Pd(OAc)_2$ (10)	^{t}AmylOH	**L5** (10)	-	0
18[h]	$Pd(OAc)_2$ (10)	^{t}AmylOH	**L5** (10)	DMSO	70 (60)[i]
19[h,j]	$Pd(OAc)_2$ (10)	^{t}AmylOH	**L5** (10)	DMSO	(70)[i]
20[h]	-	^{t}AmylOH	**L5** (10)	DMSO	0

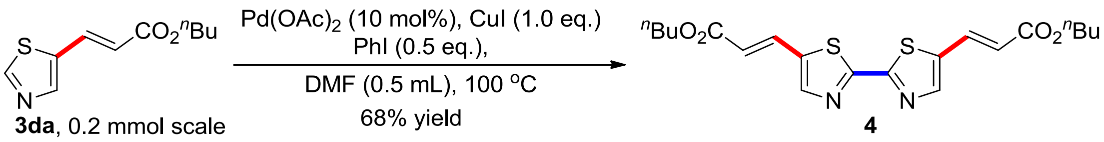
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Cs_2CO_3 (1.0 equiv), $Cu(OAc)_2$ (2.0 equiv), solvent (1.0 mL), 100 °C, 12 h. [b] Determined by GC analysis using tetradecane as the internal standard. [c] Na_2CO_3 (1.0 equiv) instead of Cs_2CO_3. [d] K_2CO_3 (1.0 equiv) instead of Cs_2CO_3. [e] NaOAc (1.0 equiv) instead of Cs_2CO_3. [f] CsOAc (1.0 equiv) instead of Cs_2CO_3. [g] LiO^{t}Bu (1.0 equiv) instead of Cs_2CO_3. [h] 6.0 equiv of DMSO was employed as additive. [i] Yield of isolated product in the parenthesis. [j] 2.5 equiv of **1a** was dissolved in 0.5 mL of ^{t}AmylOH and this solution was added to the reaction system in 0.1 mL portion every 1.0 h via syringe. **L1** = PPh_3,

L2 = 2,2'-bipyridine, **L3** = 1,10-phenanthroline, **L4** = 3,4,7,8-tetramethyl-1,10-phenanthroline, **L5** = 5-nitro-1,10-phenanthroline. DCE = 1,2-dichloroethane, DMF = *N*,*N*-dimethylformamide, DMSO = dimethylsulfoxide.

3. General Procedure for the Regioselective 5-Alkenylation of Thiazole Derivatives

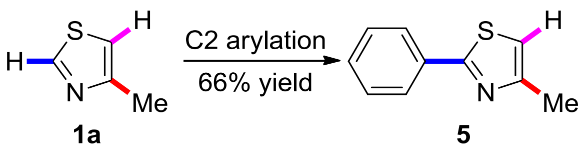
To a flame dried 25 mL Schlenk tube were added $Pd(OAc)_2$ (4.5 mg, 0.02 mmol; Acros), 5-nitro-1,10-phenanthroline (4.5 mg, 0.02 mmol; TCI), $Cu(OAc)_2$ (72.0 mg, 0.40 mmol; Acros) and Cs_2CO_3 (65.2 mg, 0.40 mmol; Ourchem), then the tube was capped with rubber stopper and alternatively extracted under vacuum pump and backfilled with nitrogen gas for three times. Then ^{t}AmylOH (1.0 mL or 2.0 mL, Alfa Aesar) was added *via* a syringe followed by sequential addition of DMSO (85.2 μL, 1.20 mmol, unpurified) and *n*-butyl acrylate (**2a**, 0.50 mmol). Finally, a solution of 4-methylthiazole (**1a**, 0.20 mmol, J&K) in ^{t}AmylOH (0.5 mL) was introduced intermittently (0.1 mL every hour) after the tube was placed on the preheated parallel reactor (100 ^{o}C). The reaction mixture was stirred at 100 ^{o}C for 12 h. After completion of the reaction, the reaction mixture was directly filtered by a short silica pad and further purified by flash column chromatography to afford (**3aa**, 31.5 mg, 70% yield) as colorless oil.

4. Procedure for the Homo-coupling of 5-Alkenylated Thiazole Derivative



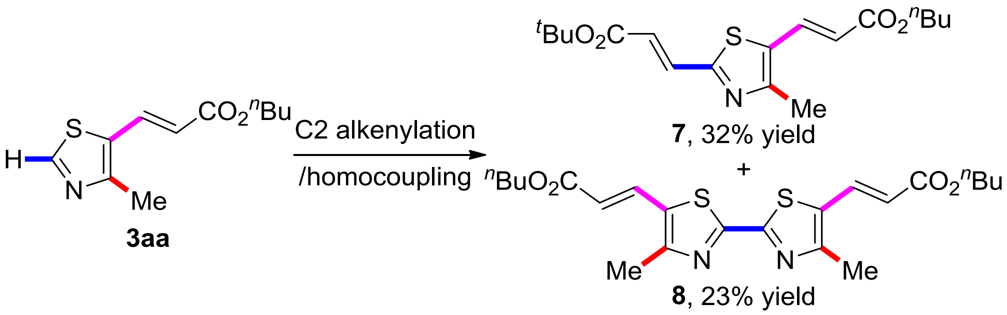
To a flame dried 25 mL Schlenk tube were added $Pd(OAc)_2$ (4.5 mg, 0.02 mmol; Acros), 5-alkenylated thiazole derivative **3da** (0.20 mmol), CuI (38.1 mg, 0.20 mmol), phenyl iodide (11.1 μL, 0.10 mmol) and *N*,*N*-dimethyl formamide (0.5 mL), then the tube was capped with rubber stopper and alternatively extracted under vacuum pump and backfilled with nitrogen gas for three times. After the tube was placed on the preheated parallel reactor (100 ^{o}C), the reaction mixture was stirred at 100 ^{o}C for 12 h. After completion of the reaction, the reaction mixture was directly filtered by a short silica pad and further purified by flash column chromatography to afford the homo-coupling product **4** (68% yield).

5. Procedure for the C-2 Arylation of 4-Methylthiazole

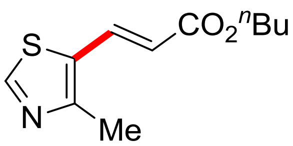


To a 25 mL Schlenk tube were added $Pd(OAc)_2$ (4.5 mg, 0.02 mmol; Acros), 4-methylthiazole **1a** (0.20 mmol), CuI (76.2 mg, 0.40 mmol) and *N*,*N*-dimethyl formamide (1.0 mL), then the tube was capped and placed on the preheated parallel reactor (140 ^{o}C), the reaction mixture was stirred at 140 ^{o}C for 24 h. After completion of the reaction, the mixture was directly filtered by a short silica pad and further purified by flash column chromatography to afford the homo-coupling product **5** (66% yield).

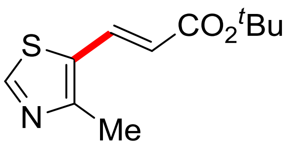
6. Procedure for the C-2 Alkenylation of 5-Alkenylated 4-Methyl Thiazole



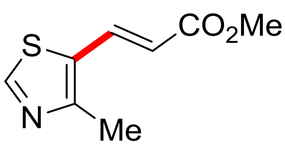
To a 25 mL Schlenk tube were added $Pd(OTFA)_2$ (6.6 mg, 0.02 mmol; Acros), 5-alkenylated 4-methylthiazole **3aa** (0.20 mmol), AgOTFA (88.4 mg, 0.40 mmol), 1,10-phenanthroline (54.1 mg, 0.3 mmol) and toluene (0.5 mL), then the tube was capped and placed on the preheated parallel reactor (100 °C), the reaction mixture was stirred at 100 °C for 24 h. After completion of the reaction, the mixture was directly filtered by a short silica pad and further purified by flash column chromatography to afford the 2-alkenylated product **7** (32% yield) and homo-coupling product **8** (23% yield).



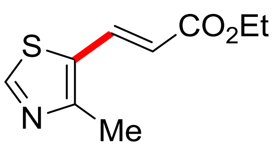
(*E*)-butyl 3-(4-methylthiazol-5-yl)acrylate (**3aa**)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.81 (d, *J* = 15.6 Hz, 1H), 6.16 (d, *J* = 15.6 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 2.57 (s, 3H), 1.72-1.65 (m, 2H), 1.48-1.39 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 155.7, 152.6, 133.6, 128.3, 119.9, 64.6, 30.7, 19.2, 15.6, 13.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{11}H_{16}NO_2S^+$: 226.0896 found 226.0889.



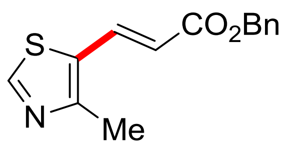
(*E*)-*tert*-butyl 3-(4-methylthiazol-5-yl)acrylate (**3ab**)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.72 (d, *J* = 15.5 Hz, 1H), 6.10 (d, *J* = 15.5 Hz, 1H), 2.55 (s, 3H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 155.3, 152.4, 132.7, 128.4, 121.8, 80.9, 28.2, 15.6. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{11}H_{16}NO_2S^+$: 226.0896 found 226.0895.



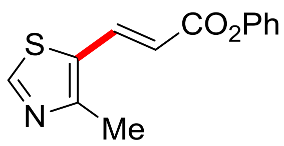
(*E*)-methyl 3-(4-methylthiazol-5-yl)acrylate (**3ac**)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.82 (d, *J* = 15.6 Hz, 1H), 6.16 (d, *J* = 15.6 Hz, 1H), 3.81 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 155.9, 152.7, 133.9, 128.2, 119.4, 51.8, 15.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_8H_{10}NO_2S^+$: 184.0427 found 184.0425.



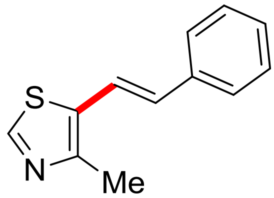
(*E*)-ethyl 3-(4-methylthiazol-5-yl)acrylate (**3ad**)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (s, 1H), 7.81 (d, *J* = 15.6 Hz, 1H), 6.16 (d, *J* = 15.6 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.57 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 155.7, 152.6, 133.6, 128.3, 119.9, 60.7, 15.6, 14.3. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_9H_{12}NO_2S^+$: 198.0583 found 198.0585.



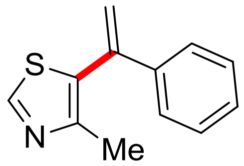
(*E*)-benzyl 3-(4-methylthiazol-5-yl)acrylate (**3ae**)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.85 (d, *J* = 15.5 Hz, 1H), 7.45-7.31 (m, 5H), 6.20 (d, *J* = 15.6 Hz, 1H), 5.24 (s, 2H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 156.0, 152.8, 135.9, 134.2, 128.6, 128.4, 128.3, 128.3, 119.4, 66.6, 15.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{14}H_{14}NO_2S^+$: 260.0740 found 260.0740.



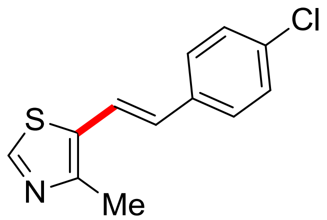
(*E*)-phenyl 3-(4-methylthiazol-5-yl)acrylate (**3af**)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.99 (dd, *J* = 15.5, 0.6 Hz, 1H), 7.42 (dd, *J* = 11.0, 4.8 Hz, 2H), 7.30-7.22 (m, 1H), 7.20-7.12 (m, 2H), 6.35 (d, *J* = 15.5 Hz, 1H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 156.6, 153.2, 150.7, 135.5, 129.5, 128.2, 125.9, 121.6, 118.8, 15.8. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{13}H_{12}NO_2S^+$: 246.0583 found 246.0584.



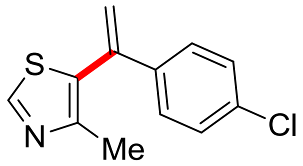
(*E*)-4-methyl-5-styrylthiazole (**3ag**)[1]
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.17 (d, *J* = 16.0 Hz, 1H), 6.82 (d, *J* = 16.0 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 149.5, 136.7, 131.3, 130.9, 128.8, 128.0, 126.4, 118.3, 15.4. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{12}H_{12}NS^+$: 202.0685 found 202.0684.



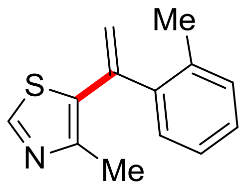
4-methyl-5-(1-phenylvinyl)thiazole (**3ag'**)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.33 (m, 5H), 5.74 (d, *J* = 0.8 Hz, 1H), 5.43 (d, *J* = 0.7 Hz, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 150.5, 140.2, 139.9, 131.4, 128.8, 128.6, 128.5, 128.3, 127.1, 118.6, 111.4, 16.3, 15.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{12}H_{12}NS^+$: 202.0685 found 202.0685.



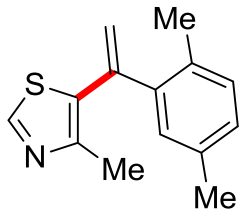
(*E*)-5-(4-chlorostyryl)-4-methylthiazole (**3ah**)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 15.9 Hz, 1H), 6.75 (d, *J* = 16.0 Hz, 1H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 149.7, 135.2, 133.6, 130.6, 129.9, 129.0, 127.5, 118.8, 15.5. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{12}H_{11}ClNS^+$: 236.0295 found 236.0293.



5-(1-(4-chlorophenyl)vinyl)-4-methylthiazole (**3ah'**)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 5.73 (s, 1H), 5.44 (s, 1H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 150.8, 150.7, 138.9, 138.7, 134.3, 130.9, 130.6, 130.2, 128.8, 128.7, 128.4, 120.4, 119.0, 16.3, 15.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{12}H_{11}ClNS^+$ 236.0295 found 236.0297.

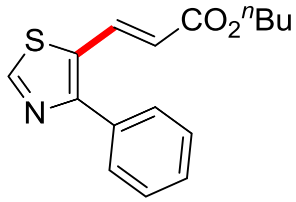


4-methyl-5-(1-(*o*-tolyl)vinyl)thiazole (**3ai**)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 7.28-7.16 (m, 4H), 5.61 (d, *J* = 0.9 Hz, 1H), 5.35 (d, *J* = 0.9 Hz, 1H), 2.24 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 149.5, 141.3, 140.9, 135.7, 132.9, 130.4, 129.2, 128.1, 126.0, 119.1, 19.8, 16.5. HRMS-ESI: m/z: $[M + H]^+$ calculated for Chemical Formula: $C_{13}H_{14}NS^+$ 216.0841 found 216.0845.



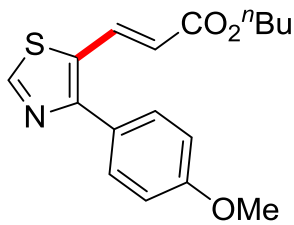
5-(1-(2,5-dimethylphenyl)vinyl)-4-methylthiazole (**3aj**)

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.56 (s, 1H), 7.06 (s, 1H), 7.06-7.03 (m, 2H), 5.59 (d, *J* = 1.1 Hz, 1H), 5.34 (d, *J* = 1.1 Hz, 1H), 2.33 (s, 3H) 2.25 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 150.1, 149.5, 141.2, 141.0, 135.4, 133.1, 132.5, 130.3, 129.8, 128.8, 118.9, 20.9, 19.4, 16.5. HRMS-ESI: m/z: [M + H]$^+$ calculated for $C_{14}H_{16}NS^+$: 230.0998 found 230.0999.



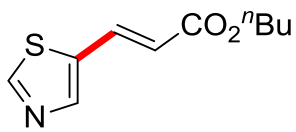
(*E*)-butyl 3-(4-phenylthiazol-5-yl)acrylate (**3ba**)

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.81 (s, 1H), 7.92 (d, *J* = 15.6 Hz, 1H), 7.65-7.63 (m, 2H), 7.52-7.43 (m, 3H), 6.29 (d, *J* = 15.6 Hz, 1H), 4.19 (t, *J* = 6.7 Hz, 2H), 1.70-1.63 (m, 2H), 1.46-1.37 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.3, 157.6, 152.8, 134.7, 133.8, 129.4, 129.1, 128.8, 121.5, 64.6, 30.7, 19.2, 13.7. HRMS-ESI: m/z: [M + H]$^+$ calculated for $C_{16}H_{18}NO_2S^+$: 288.1053 found 288.1053.



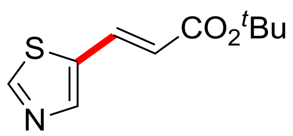
(*E*)-butyl 3-(4-(4-methoxyphenyl)thiazol-5-yl)acrylate (**3ca**)

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.79 (s, 1H), 7.91 (d, *J* = 15.6 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.26 (d, *J* = 15.6 Hz, 1H), 4.19 (t, *J* = 6.6 Hz, 2H), 1.70-1.63 (m, 2H), 1.47-1.38 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.4, 160.3, 157.4, 152.7, 135.0, 130.8, 127.9, 126.4, 120.9, 114.2, 64.6, 55.4, 30.7, 19.2, 13.7. HRMS-ESI: m/z: [M + H]$^+$ calculated for $C_{17}H_{20}NO_3S^+$: 318.1158 found 318.1160.



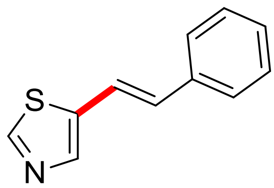
(*E*)-butyl 3-(thiazol-5-yl)acrylate (**3da**)

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.80 (s, 1H), 8.01 (s, 1H), 7.82 (d, *J* = 15.7 Hz, 1H), 6.27 (d, *J* = 15.7 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.72-1.65 (m, 2 H), 1.48-1.39 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 166.1, 154.5, 146.0, 134.9, 133.4, 121.1, 64.7, 30.7, 19.2, 13.7. HRMS-ESI: m/z: [M + H]$^+$ calculated for: $C_{10}H_{14}NO_2S^+$: 212.0740 found 212.0742.



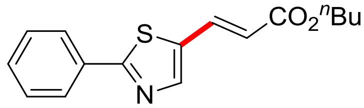
(*E*)-*tert*-butyl 3-(thiazol-5-yl)acrylate (**3db**)

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.78 (s, 1H), 7.98 (s, 1H), 7.72 (d, *J* = 15.7 Hz, 1H), 6.20 (d, *J* = 15.7 Hz, 1H), 1.53 (s, 9H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 165.3, 154.2, 145.7, 135.0, 132.4, 123.1, 81.0, 28.1. HRMS-ESI: m/z: [M + H]$^+$ calculated for: $C_{10}H_{14}NO_2S^+$: 212.0740 found 212.0743.



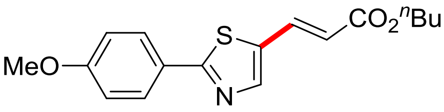
(*E*)-5-styrylthiazole (**3dg**)[2]

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.66 (s, 1H), 7.85 (s, 1H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 16.1 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 151.3, 141.8, 137.9, 136.3, 132.2, 128.8, 128.3, 126.5, 118.0. HRMS-ESI: m/z: [M + H]$^+$ calculated for: $C_{11}H_{10}NS^+$: 188.0528 found 188.0529.



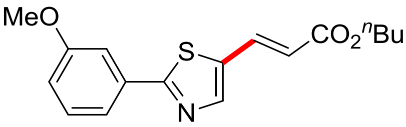
(*E*)-butyl 3-(2-phenylthiazol-5-yl)acrylate (**3ea**)

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00-7.94 (m, 2H), 7.93 (s, 1H), 7.79 (d, *J* = 15.6 Hz, 1H), 7.46 (dd, *J* = 6.5, 3.6 Hz, 3H), 6.23 (d, *J* = 15.6 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.72-1.65 (m, 2H), 1.49-1.39 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 169.8, 166.3, 146.9, 134.8, 133.8, 133.1, 130.9, 129.1, 126.8, 120.2, 64.7, 30.8, 19.2, 13.8. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{16}H_{18}NO_2S^+$: 288.1053 found 288.1054.



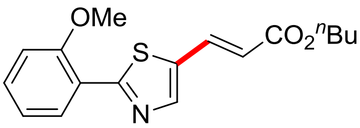
(*E*)-butyl 3-(2-(4-methoxyphenyl)thiazol-5-yl)acrylate (**3fa**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.9 Hz, 2H), 7.86 (s, 1H), 7.77 (d, *J* = 15.6 Hz, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.18 (d, *J* = 15.5 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 2H), 3.86 (s, 3H), 1.72-1.65 (m, 2H), 1.48-1.39 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 166.5, 161.9, 146.9, 134.0, 133.9, 128.4, 126.0, 119.6, 114.5, 64.6, 55.5, 30.8, 19.2, 13.8. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{17}H_{20}NO_3S^+$: 318.1158 found 318.1160.



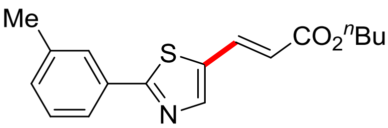
(*E*)-butyl 3-(2-(3-methoxyphenyl)thiazol-5-yl)acrylate (**3ga**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.79 (d, *J* = 15.6 Hz, 1H), 7.55-7.48 (m, 2H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.03- 6.98 (m, 1H), 6.23 (d, *J* = 15.6 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 3.88 (s, 3H), 1.73-1.65 (m, 2H), 1.49-1.39 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 166.3, 160.1, 146.7, 134.9, 134.3, 133.8, 130.1, 120.2, 119.4, 117.3, 111.3, 64.7, 55.5, 30.8, 19.2, 13.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{17}H_{20}NO_3S^+$: 318.1158 found 318.1166.



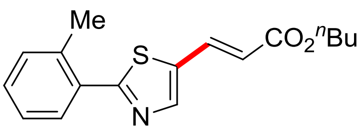
(*E*)-butyl 3-(2-(2-methoxyphenyl)thiazol-5-yl)acrylate (**3ha**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.96 (s, 1H), 7.83 (d, *J* = 15.7 Hz, 1H), 7.45-7.38 (m, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.28 (d, *J* = 15.7 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 4.04 (s, 3H), 1.72-1.65 (m, 2H), 1.49-1.40 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 164.1, 156.6, 145.3, 134.9, 134.5, 131.5, 128.5, 121.9, 121.2, 118.9, 111.4, 64.5, 55.6, 30.8, 19.2, 13.8. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{17}H_{20}NO_3S^+$: 318.1158 found 318.1166.



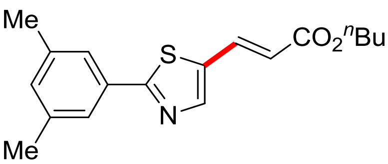
(*E*)-butyl 3-(2-(*m*-tolyl)thiazol-5-yl)acrylate (**3ia**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.79 (s, 1H), 7.78 (d, *J* = 15.6 Hz, 1H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 6.22 (d, *J* = 15.6 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 2.42 (s, 3H), 1.72-1.65 (m, 2H), 1.49-1.39 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 166.3, 146.8, 138.9, 134.7, 133.9, 133.0, 131.7, 129.0, 127.3, 124.1, 120.1, 64.6, 30.8, 21.3, 19.2, 13.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{17}H_{20}NO_2S^+$: 302.1209 found 302.1207.



(*E*)-butyl 3-(2-(*o*-tolyl)thiazol-5-yl)acrylate (**3ja**)

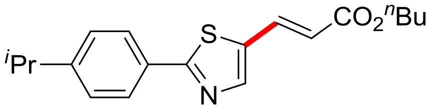
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.81 (d, *J* = 15.6 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.37-7.28 (m, 3H), 6.25 (d, *J* = 15.6 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 2.62 (s, 3H), 1.73-1.65 (m, 2H), 1.49-1.39 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 166.3, 146.2, 136.9, 135.2, 133.9, 132.4, 131.8, 130.1, 130.0, 126.3, 120.2, 64.6, 30.8, 21.7, 19.2, 13.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{17}H_{20}NO_2S^+$: 302.1209 found 302.1209.



(*E*)-butyl 3-(2-(3,5-dimethylphenyl)thiazol-5-yl)acrylate (**3ka**)

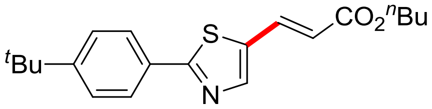
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.77 (d, *J* = 15.6

Hz, 1H), 7.56 (s, 2H), 7.08 (s, 1H), 6.21 (d, *J* = 15.6 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 2.37 (s, 6H), 1.72-1.65 (m, 2H), 1.48-1.39 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 166.3, 146.7, 138.8, 134.5, 133.9, 132.9, 132.7, 124.6, 119.9, 64.6, 30.8, 21.2, 19.2, 13.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{18}H_{22}NO_2S^+$: 316.1366 found 316.1371.



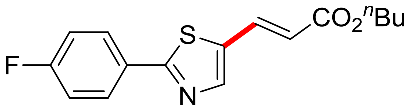
(*E*)-butyl 3-(2-(4-*iso*propylphenyl)thiazol-5-yl)acrylate (**3la**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.88 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 15.6 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 2H), 6.21 (d, *J* = 15.6 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 3.01-2.91 (m, 1H), 1.72-1.69 (m, 2H), 1.48-1.39 (m, 2H), 1.28 (d, *J* = 6.9 Hz, 6H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 166.4, 152.3, 146.9, 134.3, 134.0, 130.8, 127.2, 126.9, 119.9, 64.6, 34.1, 30.8, 23.7, 19.2, 13.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{19}H_{24}NO_2S^+$: 330.1522 found 330.1514.



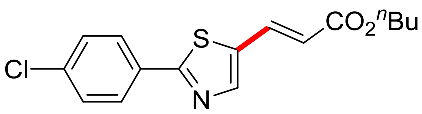
(*E*)-butyl 3-(2-(4-(*tert*-butyl)phenyl)thiazol-5-yl)acrylate (**3ma**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.89 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 15.6 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 2H), 6.22 (d, *J* = 15.6 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.72-1.65 (m, 2H), 1.49-1.41 (m, 2H), 1.35 (s, 9H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 166.4, 154.5, 146.9, 134.4, 134.0, 130.4, 126.6, 126.1, 119.9, 64.6, 35.0, 31.2, 30.8, 19.2, 13.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{20}H_{26}NO_2S^+$: 344.1679 found 344.1678.



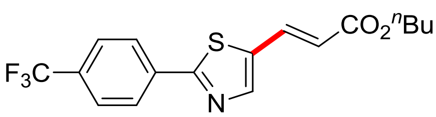
(*E*)-butyl 3-(2-(4-fluorophenyl)thiazol-5-yl)acrylate (**3na**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.93 (m, 2H), 7.91 (s, 1H), 7.78 (d, *J* = 15.6 Hz, 1H), 7.15 (t, *J* = 8.6 Hz, 2H), 6.22 (d, *J* = 15.6 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.73-1.65 (m, 2H), 1.49-1.39 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 166.3, 164.3 (d, *J* = 250.5 Hz), 146.8, 134.9, 133.7, 129.5 (d, *J* = 3.3 Hz), 128.8 (d, *J* = 8.7 Hz), 120.3, 116.3 (d, *J* = 22.2 Hz, 1H), 64.7, 30.7, 19.2, 13.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{16}H_{17}FNO_2S^+$: 306.0959 found 306.0961.



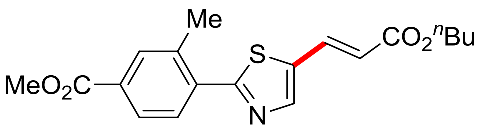
(*E*)-butyl 3-(2-(4-chlorophenyl)thiazol-5-yl)acrylate (**3oa**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.88 (d, *J* = 8.6 Hz, 2H), 7.78 (d, *J* = 15.6 Hz, 1H), 7.43 (d, *J* = 8.6 Hz, 2H), 6.23 (d, *J* = 15.6 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.73-1.65 (m, 2H), 1.49-1.39 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 166.2, 146.8, 136.9, 135.1, 133.6, 131.6, 129.4, 127.9, 120.5, 64.7, 30.7, 19.2, 13.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{16}H_{17}ClNO_2S^+$: 322.0663 found 322.0664.

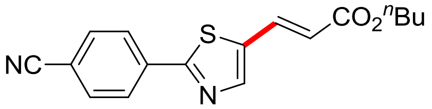


(*E*)-butyl 3-(2-(4-(trifluoromethyl)phenyl)thiazol-5-yl) acrylate (**3pa**)

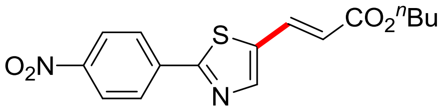
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.1 Hz, 2H), 7.98 (s, 1H), 7.80 (d, *J* = 15.7 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 6.28 (d, *J* = 15.6 Hz, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 1.73-1.66 (m, 2H), 1.49-1.40 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 166.1, 146.9, 136.1, 136.1(q, *J* = 1.1 Hz), 135.9, 133.4, 132.8, 132.3 (q, *J* = 32.6 Hz), 127.0, 126.1 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 270.6 Hz), 121.0, 64.8, 30.7, 19.2, 13.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{17}H_{17}F_3NO_2S^+$: 356.0927 found 356.0930.



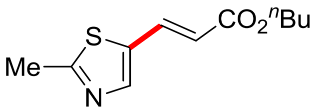
(*E*)-methyl 4-(5-(3-butoxy-3-oxoprop-1-en-1-yl) thiazol-2-yl)-3-methylbenzoate (**3qa**)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 8.00 (s, 1H), 7.94 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 15.7 Hz, 1H), 6.28 (d, *J* = 15.7 Hz, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 3.95 (s, 3H), 2.68 (s, 3H), 1.73-1.65 (m, 2H), 1.49-1.40 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 166.5, 166.2, 146.2, 137.0, 136.2, 136.0, 133.5, 132.9, 131.1, 130.0, 127.3, 120.8, 64.7, 52.3, 30.7, 21.8, 19.2, 13.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{19}H_{22}NO_4S^+$: 360.1264 found 360.1264.



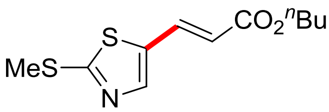
(*E*)-butyl 3-(2-(4-cyanophenyl)thiazol-5-yl)acrylate (**3ra**)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.2 Hz, 2H), 8.00 (s, 1H), 7.80 (d, *J* = 15.7 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 2H), 6.29 (d, *J* = 15.7 Hz, 1H), 4.23 (t, *J* = 6.7 Hz, 2H), 1.73-1.66 (m, 2H), 1.49-1.40 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 166.0, 147.0, 136.8, 136.5, 133.2, 132.9, 127.1, 121.4, 118.2, 114.0, 64.8, 30.7, 19.2, 13.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{17}H_{17}N_2O_2S^+$: 313.1005 found 313.1005.



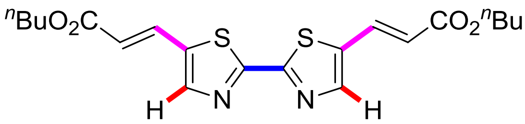
(*E*)-butyl 3-(2-(4-nitrophenyl)thiazol-5-yl)acrylate (**3sa**)
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.9 Hz, 2H), 8.13 (d, *J* = 8.9 Hz, 2H), 8.03 (s, 1H), 7.81 (d, *J* = 15.7 Hz, 1H), 6.31 (d, *J* = 15.7 Hz, 1H), 4.23 (t, *J* = 6.7 Hz, 2H), 1.74-1.66 (m, 2H), 1.49-1.40 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 166.0, 148.8, 147.1, 138.5, 136.9, 133.1, 127.4, 124.5, 121.6, 64.9, 30.7, 19.2 13.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{16}H_{17}N_2O_4S^+$: 333.0904 found 333.0909.



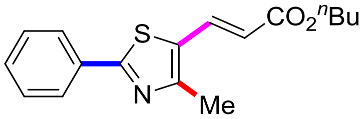
(*E*)-butyl 3-(2-methylthiazol-5-yl)acrylate (**3ta**)[3]
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.72 (d, *J* = 15.6 Hz, 1H), 6.12 (d, *J* = 15.7 Hz, 1H), 4.19 (t, *J* = 6.7 Hz, 2H), 2.72 (s, 3H), 1.71-1.64 (m, 2H), 1.47-1.38 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 166.3, 145.5, 134.8, 134.0, 119.8, 64.6, 30.7, 19.7, 19.2, 13.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{11}H_{16}NO_2S^+$: 226.0896 found 226.0899.



(*E*)-butyl 3-(2-(methylthio)thiazol-5-yl)acrylate (**3ua**)[3]
^{1}H NMR (400 MHz, $CDCl_3$) δ7.71 (s, 1H), 7.70 (d, *J* = 15.6 Hz, 1H), 6.04 (d, *J* = 15.6 Hz, 1H), 4.19 (t, *J* = 6.6 Hz, 2H), 2.72 (s, 3H), 1.72-1.63 (m, 2H), 1.47-1.38 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 166.3, 145.8, 134.2, 133.4, 119.3, 64.6, 30.7, 19.2, 16.3, 13.7. In agreement with literature data.

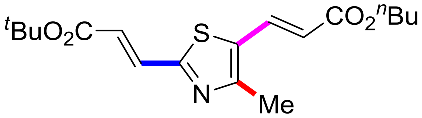


(2*E*, 2'*E*)-dibutyl 3, 3'-([2, 2'-bithiazole]-5, 5'-diyl) diacrylate (**4**)
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 2H), 7.79 (d, *J* = 15.7 Hz, 2H), 6.32 (d, *J* = 15.7 Hz, 2H), 4.22 (t, *J* = 6.7 Hz, 4H), 1.73-1.66 (m, 4H), 1.49-1.39 (m, 4H), 0.97 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 161.7, 146.8, 137.5, 133.0, 121.8, 64.9, 30.7, 19.2, 13.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{20}H_{25}N_2O_4S_2^+$: 421.1250 found 421.1250.



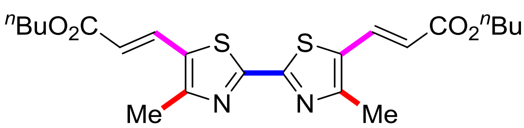
(E)-butyl 3-(4-methyl-2-phenylthiazol-5-yl)acrylate (**6**)[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 6.5, 3.0 Hz, 2H), 7.80 (d, J = 15.5 Hz, 1H), 7.44-7.42 (m, 3H), 6.13 (d, J = 15.5 Hz, 1H), 4.21 (t, J = 6.7 Hz, 2H), 2.56 (s, 3H), 1.73-1.65 (m, 2H), 1.48-1.39 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 166.7, 156.6, 133.9, 133.1, 130.7, 129.0, 128.6, 126.7, 118.9, 64.5, 30.8, 19.2, 15.8, 13.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{17}H_{20}NO_2S^+$: 302.1209 found 302.1205.



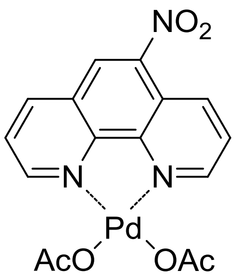
(E)-butyl 3-(2-((E)-3-(*tert*-butoxy)-3-oxoprop-1-en-1-yl) -4-methylthiazol-5-yl)acrylate (**7**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 15.5 Hz, 1H), 7.57 (d, J = 15.8 Hz, 1H), 6.61 (d, J = 15.8 Hz, 1H), 6.15 (d, J = 15.5 Hz, 1H), 4.21 (t, J = 6.7 Hz, 2H), 2.54 (s, 3H), 1.72 -1.65(m, 2H), 1.53 (s, 9H), 1.48-1.39 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 164.8, 162.8, 156.9, 134.5, 133.2, 130.6, 126.4, 120.5, 81.5, 64.7, 30.7, 28.1, 19.2, 15.7, 13.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{18}H_{26}NO_4S^+$: 352.1577 found 352.1582.



(2E,2'E)-dibutyl 3,3'-(4,4'-dimethyl-[2,2'-bithiazole]-5,5'-diyl)diacrylate (**8**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 15.6 Hz, 2H), 6.21 (d, J = 15.6 Hz, 2H), 4.22 (t, J = 6.7 Hz, 4H), 2.58 (s, 6H), 1.73-1.66 (m, 4H), 1.48-1.39 (m, 4H), 0.97 (t, J = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 159.5, 156.9, 133.2, 131.2, 120.4, 64.8, 30.7, 19.2, 15.7, 13.7. HRMS-ESI: m/z: $[M + H]^+$ calculated for $C_{22}H_{29}N_2O_4S_2^+$: 449.1563 found 449.1568.



Complex of $Pd(OAc)_2$ with 5-nitro-1,10-phenanthroline (**9**)

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 9.32 (dd, J = 8.7, 1.0 Hz, 1H), 9.18 (dd, J = 8.3, 1.0 Hz, 1H), 8.64 (ddd, J = 9.2, 5.2, 1.1 Hz, 2H), 8.21 (ddd, J = 10.3, 8.5, 5.3 Hz, 2H), 1.98 (s, 6H). ^{13}C NMR (125 MHz, DMSO) δ 175.7, 152.9, 147.8, 146.5, 143.8, 141.7, 136.6, 127.1, 127.0, 126.9, 126.9, 122.6, 23.3.

7. Determination of the Regiochemistry of This Alkenylation Reaction

The determination of the regiochemistry of this methodology was achieved by an X-ray diffraction technique using crystal of compound **3ea** as a representative. And the alkenylation reaction did occur at the C-5 position of thiazole moiety (Figure S1). The original crystallographic data (CCDC 1024929) for this compound can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

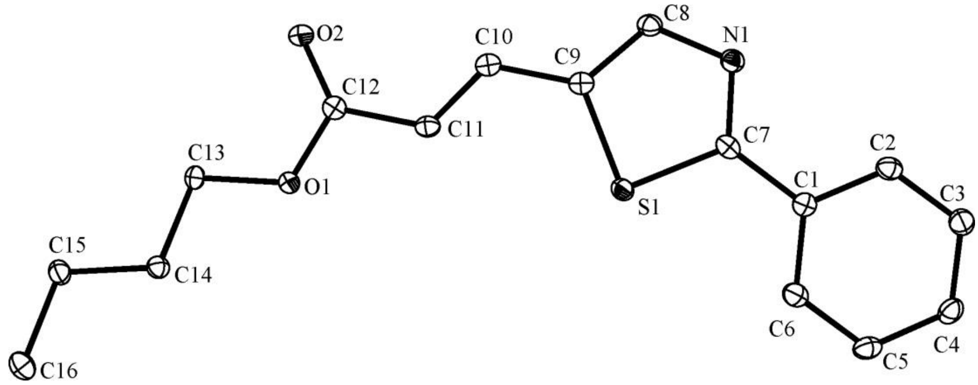


Figure S1 X-ray crystal structure of compound **3ea**.

++

\+ SHELXTL XLMP CRYSTAL STRUCTURE REFINEMENT - MULTI-CPU VERSION +

\+ Copyright(c) Bruker AXS Inc. 1993-2013 Version 2013/3 +

\+ exp_4110 started at 14:58:24 on 18-Sep-2014 +

++

Command line parameters: exp_4110 -a50000 -b3000 -c624 -t2

-a sets the approximate maximum number of atoms including hydrogens.

-b sets the maximum number of full-matrix parameters (leave unchanged for CGLS). For example -b9000 allows refinement of 1000 anisotropic atoms or 3000 with BLOC 1. For a 32-bit version, -b times the square root of the number of threads should not exceed about 65500. -c sets the reflection buffer size. This depends on the CPU cache size but will rarely need changing. -t sets the number of threads, otherwise the multi-CPU version sets this equal to the number of available CPUs. For optimal performance on systems with hyperthreading, usually the hyperthreading should be switched off or -t used to halve the number of threads; e.g. -t4 rather than -t8 for an Intel i7 processor.

Running 2 threads on 2 processors

```
TITL exp_4110 in P21/n #14
CELL 0.71073 14.34508 5.60237 19.17127 90 110.0102 90
ZERR 4 0.00137 0.00039 0.00197 0 0.0114 0
LATT 1
SYMM 0.5-X,0.5+Y,0.5-Z
SFAC C    H    N    O    S
UNIT 64 68 4 8 4
V  =         1447.72          F(000)  =          608.0          Mu  =      0.22  mm-1            Cell  Wt  =
1149.46        Rho =    1.318
L.S. 4
ACTA
BOND $H
FMAP 2
PLAN 1
SIZE 0.1 0.1 0.2
SHEL 999 0.81
WGHT    0.043600    0.220600
FVAR    4.859240
TEMP -93
C1          1      0.390919    0.569574    0.841005 11.000000    0.014460    0.019580 =
                   0.023700    0.001080    0.006280    0.004420
C2          1      0.424101    0.754658    0.892472 11.000000    0.020220    0.021940 =
                   0.029540    0.000410    0.009790 -0.000740
AFIX 43
H2          2      0.457711    0.887326    0.881226 11.000000 -1.200000
AFIX 0
C3          1      0.408319    0.745864    0.959630 11.000000    0.023620    0.029880 =
                   0.031600 -0.006240    0.011610 -0.002390
AFIX 43
H3          2      0.430906    0.872683    0.994221 11.000000 -1.200000
AFIX 0
C4          1      0.359922    0.553743    0.976604 11.000000    0.022520    0.034360 =
                   0.026570 -0.001370    0.012960    0.000480
AFIX 43
H4          2      0.349873    0.548056    1.023050 11.000000 -1.200000
AFIX 0
C5          1      0.325765    0.368353    0.926095 11.000000    0.023550    0.026250 =
                   0.034830    0.003810    0.015890    0.000620
AFIX 43
H5          2      0.291872    0.236693    0.937601 11.000000 -1.200000
AFIX 0
C6          1      0.341560    0.377398    0.859085 11.000000    0.021190    0.020750 =
                   0.031400 -0.001980    0.010220 -0.000210
AFIX 43
```

```
H6      2    0.318415    0.250482    0.824608 11.000000 -1.200000
AFIX 0
C7      1    0.409269    0.579650    0.770450 11.000000    0.015590    0.016260 =
             0.024920 -0.000520    0.003660    0.001660
C8      1    0.468226    0.702995    0.684763 11.000000    0.023450    0.019220 =
             0.022050    0.003410    0.006950 -0.001290
AFIX 43
H8      2    0.503771    0.806250    0.663524 11.000000 -1.200000
AFIX 0
C9      1    0.420448    0.504659    0.648377 11.000000    0.015810    0.020110 =
             0.021850    0.004180    0.004810    0.002360
C10     1    0.419377    0.408714    0.577932 11.000000    0.014850    0.020060 =
             0.022490    0.004400    0.005490    0.003790
AFIX 43
H10     2    0.447009    0.502787    0.548643 11.000000 -1.200000
AFIX 0
C11     1    0.381784    0.195731    0.551863 11.000000    0.017700    0.022300 =
             0.023500    0.002190    0.007570 -0.001340
AFIX 43
H11     2    0.354409    0.101297    0.581234 11.000000 -1.200000
AFIX 0
C12     1    0.380369    0.099541    0.480598 11.000000    0.015480    0.018690 =
             0.022210    0.001240    0.005380    0.004060
C13     1    0.313795 -0.220235    0.394831 11.000000    0.025010    0.020670 =
             0.019500 -0.004740    0.010980 -0.001120
AFIX 23
H13A    2    0.375302 -0.306409    0.397836 11.000000 -1.200000
H13B    2    0.298748 -0.102682    0.353902 11.000000 -1.200000
AFIX 0
C14     1    0.229249 -0.392572    0.381454 11.000000    0.020520    0.017270 =
             0.021670 -0.000760    0.008090    0.000210
AFIX 23
H14A    2    0.167950 -0.302578    0.376599 11.000000 -1.200000
H14B    2    0.243224 -0.500076    0.424821 11.000000 -1.200000
AFIX 0
C15     1    0.212505 -0.541172    0.312113 11.000000    0.025650    0.019880 =
             0.020800 -0.002740    0.006090 -0.001690
AFIX 23
H15A    2    0.275427 -0.620676    0.315197 11.000000 -1.200000
H15B    2    0.193243 -0.434522    0.268298 11.000000 -1.200000
AFIX 0
C16     1    0.132454 -0.729597    0.301548 11.000000    0.027470    0.021680 =
             0.030810 -0.004900    0.007290 -0.000580
AFIX 137
```

```
H16A      2      0.151968 -0.838423    0.344140 11.000000 -1.500000
H16B      2      0.124143 -0.819972    0.256044 11.000000 -1.500000
H16C      2      0.069688 -0.651763    0.297654 11.000000 -1.500000
AFIX 0
N1        3      0.462260    0.745444    0.753518 11.000000    0.024180    0.019790 =
                 0.021440    0.000470    0.006710 -0.001730
O1        4      0.325919 -0.100606    0.464613 11.000000    0.024210    0.020940 =
                 0.020640 -0.003850    0.009950 -0.005090
O2        4      0.421553    0.186203    0.440297 11.000000    0.025290    0.023190 =
                 0.024810    0.000740    0.011770 -0.003840
S1        5      0.362664    0.362916    0.702688 11.000000    0.019820    0.019710 =
                 0.023230 -0.002910    0.007770 -0.003090
HKLF 4
Covalent radii and connectivity table for    exp_4110 in P21/n #14
C       0.770
H       0.320
N       0.700
O       0.660
S       1.030
C1 - C6 C2 C7
C2 - C3 C1
C3 - C4 C2
C4 - C3 C5
C5 - C6 C4
C6 - C5 C1
C7 - N1 C1 S1
C8 - C9 N1
C9 - C8 C10 S1
C10 - C11 C9
C11 - C10 C12
C12 - O2 O1 C11
C13 - O1 C14
C14 - C13 C15
C15 - C14 C16
C16 - C15
N1 - C7 C8
O1 - C12 C13
O2 - C12
S1 - C9 C7
   h     k     l           Fo^2          Sigma          Why rejected

  -7     0    14         4475.65       809.09         observed but should be systematically absent
     6329    Reflections read, of which      915    rejected
-15 =< h =< 17,         -6 =< k =<    6,        -23 =< l =< 15,      Max. 2-theta =      52.03
```

1 Systematic absence violations

Inconsistent equivalents etc.

h	k	l	Fo^2	Sigma(Fo^2)	N	Esd of mean(Fo^2)
-11	3	5	2735.73	251.24	2	1358.55
-7	4	5	27652.03	623.45	2	8124.85
-11	2	10	87.83	28.43	3	149.31

3 Inconsistent equivalents

2828 Unique reflections, of which 0 suppressed

R(int) = 0.0393 R(sigma) = 0.0657 Friedel opposites merged

Maximum memory for data reduction = 1961 / 28147

Number of data for d > 0.810A (CIF: max) and d > 0.833A (CIF: full)

(ignoring systematic absences):

Unique reflections found (point group) 2828 2612

Unique reflections possible (point group) 2841 2624

Unique reflections found (Laue group) 2828 2612

Unique reflections possible (Laue group) 2841 2624

Default effective X-H and X-D distances for T = -93.0C

AFIX m = 1 2 3 4 4[N] 3[N] 15[B] 8[O] 9 9[N] 16

d(X-H) = 1.00 0.99 0.98 0.95 0.88 0.91 1.12 0.84 0.95 0.88 0.95

Note that these distances are chosen to give the best fit to the X-ray data and so avoid the introduction of systematic error. The true internuclear distances are longer and do not vary with temperature! The apparent variation with temperature is caused by libration.

Least-squares cycle 1 Maximum vector length = 623 Memory required = 2485 / 273070

wR2 = 0.1152 before cycle 1 for 2828 data and 182 / 182 parameters

GooF = S = 1.045; Restrained GooF = 1.045 for 0 restraints

Weight = 1 / [sigma^2(Fo^2) + (0.0436 * P)^2 + 0.22 * P] where P = (Max (Fo^2, 0) + 2 * Fc^2) / 3

N	value	esd	shift/esd	parameter
1	4.85928	0.01068	0.004	OSF

Mean shift/esd = 0.004 Maximum = -0.012 for x S1

Max. shift = 0.000 A for C5 Max. dU = 0.000 for C11

Least-squares cycle 2 Maximum vector length = 623 Memory required = 2485 / 273070

wR2 = 0.1152 before cycle 2 for 2828 data and 182 / 182 parameters

GooF = S = 1.045; Restrained GooF = 1.045 for 0 restraints

Weight = 1 / [sigma^2(Fo^2) + (0.0436 * P)^2 + 0.22 * P] where P = (Max (Fo^2, 0) + 2 * Fc^2) / 3

N	value	esd	shift/esd	parameter
1	4.85927	0.01067	-0.001	OSF

Mean shift/esd = 0.001 Maximum = -0.004 for x S1

Max. shift = 0.000 A for C2 Max. dU = 0.000 for C16

Least-squares cycle 3 Maximum vector length = 623 Memory required = 2485 /

273070
wR2 = 0.1152 before cycle 3 for 2828 data and 182 / 182 parameters
GooF = S = 1.045; Restrained GooF = 1.045 for 0 restraints
Weight = 1 / [sigma^2(Fo^2) + (0.0436 * P)^2 + 0.22 * P] where P = (Max (Fo^2, 0) + 2 * Fc^2) / 3

N	value	esd	shift/esd	parameter
1	4.85927	0.01067	0.000	OSF

Mean shift/esd = 0.000 Maximum = 0.000 for z C1
Max. shift = 0.000 A for H16A Max. dU = 0.000 for C6
Least-squares cycle 4 Maximum vector length = 623 Memory required = 2485 / 273070
wR2 = 0.1152 before cycle 4 for 2828 data and 182 / 182 parameters
GooF = S = 1.045; Restrained GooF = 1.045 for 0 restraints
Weight = 1 / [sigma^2(Fo^2) + (0.0436 * P)^2 + 0.22 * P] where P = (Max (Fo^2, 0) + 2 * Fc^2) / 3

N	value	esd	shift/esd	parameter
1	4.85927	0.01067	0.000	OSF

Mean shift/esd = 0.000 Maximum = 0.001 for z S1
Max. shift = 0.000 A for C5 Max. dU = 0.000 for C9
No correlation matrix elements larger than 0.500
Idealized hydrogen atom generation before cycle 5

Name	x	y	z	AFIX	d(X-H)	shift	Bonded to	Conformation determined by
H2	0.4577	0.8873	0.8812	43	0.950	0.000	C2	C3 C1
H3	0.4309	0.8727	0.9942	43	0.950	0.000	C3	C4 C2
H4	0.3499	0.5481	1.0230	43	0.950	0.000	C4	C3 C5
H5	0.2919	0.2367	0.9376	43	0.950	0.000	C5	C6 C4
H6	0.3184	0.2505	0.8246	43	0.950	0.000	C6	C5 C1
H8	0.5038	0.8062	0.6635	43	0.950	0.000	C8	C9 N1
H10	0.4470	0.5028	0.5486	43	0.950	0.000	C10	C11 C9
H11	0.3544	0.1013	0.5812	43	0.950	0.000	C11	C10 C12
H13A	0.3753	-0.3064	0.3978	23	0.990	0.000	C13	O1 C14
H13B	0.2987	-0.1027	0.3539	23	0.990	0.000	C13	O1 C14
H14A	0.1680	-0.3026	0.3766	23	0.990	0.000	C14	C13 C15
H14B	0.2432	-0.5001	0.4248	23	0.990	0.000	C14	C13 C15
H15A	0.2754	-0.6207	0.3152	23	0.990	0.000	C15	C14 C16
H15B	0.1932	-0.4345	0.2683	23	0.990	0.000	C15	C14 C16
H16A	0.1520	-0.8384	0.3441	137	0.980	0.000	C16	C15 H16A
H16B	0.1241	-0.8200	0.2560	137	0.980	0.000	C16	C15 H16A
H16C	0.0697	-0.6518	0.2977	137	0.980	0.000	C16	C15 H16A

exp_4110 in P21/n #14

ATOM	x	y	z	sof	U11	U22	U33	U23	U13	U12	Ueq
C1	0.39092	0.56957	0.84101	1.00000	0.01446	0.01958					

0.02370 0.00108 0.00629 0.00442 0.01931
0.00439 0.00015 0.00039 0.00013 0.00000 0.00105 0.00121
0.00134 0.00096 0.00096 0.00095 0.00052
C2 0.42410 0.75466 0.89247 1.00000 0.02022 0.02195
0.02954 0.00041 0.00980 -0.00074 0.02357
0.00469 0.00016 0.00043 0.00014 0.00000 0.00116 0.00127
0.00149 0.00103 0.00108 0.00101 0.00055
H2 0.45771 0.88732 0.88122 1.00000 0.02828
0.00000 0.00000
C3 0.40832 0.74586 0.95963 1.00000 0.02362 0.02986
0.03159 -0.00624 0.01161 -0.00240 0.02780
0.00490 0.00017 0.00044 0.00014 0.00000 0.00123 0.00144
0.00158 0.00111 0.00116 0.00114 0.00060
H3 0.43090 0.87268 0.99422 1.00000 0.03336
0.00000 0.00000
C4 0.35992 0.55374 0.97660 1.00000 0.02252 0.03436
0.02656 -0.00137 0.01296 0.00049 0.02664
0.00475 0.00016 0.00043 0.00014 0.00000 0.00120 0.00146
0.00142 0.00111 0.00108 0.00113 0.00057
H4 0.34987 0.54806 1.02305 1.00000 0.03196
0.00000 0.00000
C5 0.32576 0.36836 0.92610 1.00000 0.02355 0.02624
0.03482 0.00381 0.01590 0.00063 0.02668
0.00497 0.00017 0.00044 0.00014 0.00000 0.00124 0.00136
0.00155 0.00111 0.00116 0.00110 0.00058
H5 0.29187 0.23670 0.93760 1.00000 0.03202
0.00000 0.00000
C6 0.34156 0.37740 0.85909 1.00000 0.02119 0.02074
0.03140 -0.00198 0.01023 -0.00021 0.02413
0.00477 0.00016 0.00041 0.00014 0.00000 0.00116 0.00125
0.00148 0.00104 0.00109 0.00104 0.00055
H6 0.31842 0.25048 0.82461 1.00000 0.02895
0.00000 0.00000
C7 0.40927 0.57965 0.77045 1.00000 0.01559 0.01625
0.02493 -0.00053 0.00366 0.00166 0.01977
0.00432 0.00015 0.00038 0.00013 0.00000 0.00106 0.00115
0.00135 0.00095 0.00097 0.00096 0.00052
C8 0.46823 0.70299 0.68476 1.00000 0.02344 0.01922
0.02205 0.00342 0.00695 -0.00129 0.02179
0.00447 0.00016 0.00040 0.00013 0.00000 0.00120 0.00124
0.00138 0.00096 0.00107 0.00100 0.00054
H8 0.50377 0.80625 0.66352 1.00000 0.02614
0.00000 0.00000
C9 0.42045 0.50466 0.64838 1.00000 0.01581 0.02011

0.02184 0.00417 0.00482 0.00236 0.01967
0.00431 0.00015 0.00039 0.00012 0.00000 0.00106 0.00124
0.00129 0.00098 0.00097 0.00098 0.00052
C10 0.41938 0.40871 0.57793 1.00000 0.01485 0.02006
0.02249 0.00440 0.00548 0.00379 0.01937
0.00432 0.00015 0.00039 0.00012 0.00000 0.00107 0.00124
0.00133 0.00095 0.00098 0.00094 0.00052
H10 0.44701 0.50278 0.54865 1.00000 0.02324
0.00000 0.00000
C11 0.38178 0.19573 0.55186 1.00000 0.01769 0.02229
0.02350 0.00220 0.00757 -0.00133 0.02102
0.00444 0.00015 0.00039 0.00013 0.00000 0.00112 0.00128
0.00135 0.00101 0.00101 0.00100 0.00053
H11 0.35441 0.10130 0.58123 1.00000 0.02523
0.00000 0.00000
C12 0.38037 0.09954 0.48060 1.00000 0.01548 0.01869
0.02222 0.00124 0.00537 0.00406 0.01907
0.00441 0.00015 0.00039 0.00013 0.00000 0.00107 0.00122
0.00131 0.00096 0.00100 0.00097 0.00052
C13 0.31380 -0.22023 0.39483 1.00000 0.02501 0.02066
0.01950 -0.00474 0.01098 -0.00111 0.02085
0.00433 0.00016 0.00040 0.00013 0.00000 0.00120 0.00124
0.00134 0.00095 0.00105 0.00102 0.00053
H13A 0.37530 -0.30641 0.39784 1.00000 0.02503
0.00000 0.00000
H13B 0.29875 -0.10268 0.35390 1.00000 0.02503
0.00000 0.00000
C14 0.22925 -0.39258 0.38145 1.00000 0.02051 0.01726
0.02167 -0.00077 0.00808 0.00021 0.01959
0.00429 0.00016 0.00038 0.00013 0.00000 0.00112 0.00119
0.00131 0.00093 0.00101 0.00096 0.00052
H14A 0.16795 -0.30259 0.37660 1.00000 0.02351
0.00000 0.00000
H14B 0.24323 -0.50008 0.42482 1.00000 0.02351
0.00000 0.00000
C15 0.21250 -0.54117 0.31211 1.00000 0.02564 0.01988
0.02081 -0.00275 0.00609 -0.00169 0.02259
0.00428 0.00016 0.00040 0.00012 0.00000 0.00121 0.00122
0.00133 0.00097 0.00103 0.00103 0.00054
H15A 0.27543 -0.62068 0.31520 1.00000 0.02711
0.00000 0.00000
H15B 0.19324 -0.43452 0.26830 1.00000 0.02711
0.00000 0.00000
C16 0.13245 -0.72960 0.30155 1.00000 0.02746 0.02167

0.03080 -0.00490 0.00729 -0.00058 0.02734
0.00468 0.00017 0.00042 0.00014 0.00000 0.00128 0.00129
0.00151 0.00106 0.00114 0.00108 0.00058
H16A 0.15197 -0.83842 0.34414 1.00000 0.04101
0.00000 0.00000
H16B 0.12414 -0.81997 0.25605 1.00000 0.04101
0.00000 0.00000
H16C 0.06969 -0.65176 0.29766 1.00000 0.04101
0.00000 0.00000
N1 0.46226 0.74544 0.75352 1.00000 0.02417 0.01980
0.02144 0.00047 0.00672 -0.00173 0.02209
0.00370 0.00013 0.00033 0.00011 0.00000 0.00101 0.00104
0.00118 0.00082 0.00089 0.00087 0.00046
O1 0.32592 -0.10061 0.46461 1.00000 0.02421 0.02093
0.02064 -0.00386 0.00994 -0.00509 0.02134
0.00290 0.00011 0.00026 0.00008 0.00000 0.00083 0.00086
0.00091 0.00066 0.00071 0.00069 0.00038
O2 0.42155 0.18620 0.44030 1.00000 0.02528 0.02320
0.02480 0.00074 0.01177 -0.00383 0.02360
0.00306 0.00011 0.00027 0.00009 0.00000 0.00086 0.00091
0.00098 0.00069 0.00077 0.00071 0.00040
S1 0.36266 0.36292 0.70269 1.00000 0.01982 0.01971
0.02323 -0.00291 0.00777 -0.00309 0.02082
0.00111 0.00004 0.00010 0.00003 0.00000 0.00031 0.00033
0.00035 0.00025 0.00025 0.00025 0.00019

Final Structure Factor Calculation for exp_4110 in P21/n #14

Total number of l.s. parameters = 182 Maximum vector length = 623 Memory required = 2303 / 29281

wR2 = 0.1152 before cycle 5 for 2828 data and 0 / 182 parameters

GooF = S = 1.045; Restrained GooF = 1.045 for 0 restraints

Weight = 1 / [sigma^2(Fo^2) + (0.0436 * P)^2 + 0.22 * P] where P = (Max (Fo^2, 0) + 2 * Fc^2) / 3

R1 = 0.0493 for 2136 Fo > 4sig(Fo) and 0.0741 for all 2828 data

wR2 = 0.1152, GooF = S = 1.045, Restrained GooF = 1.045 for all data

Occupancy sum of asymmetric unit = 20.00 for non-hydrogen and 17.00 for H and D atoms

Principal mean square atomic displacements U

0.0241 0.0221 0.0117 C1
0.0296 0.0222 0.0189 C2
0.0371 0.0245 0.0219 C3
0.0346 0.0283 0.0171 C4
0.0370 0.0254 0.0176 C5
0.0318 0.0207 0.0199 C6
0.0279 0.0172 0.0142 C7

0.0264	0.0225	0.0165	C8
0.0256	0.0192	0.0142	C9
0.0259	0.0195	0.0127	C10
0.0256	0.0211	0.0164	C11
0.0231	0.0214	0.0127	C12
0.0269	0.0221	0.0136	C13
0.0220	0.0198	0.0170	C14
0.0273	0.0231	0.0174	C15
0.0353	0.0272	0.0195	C16
0.0258	0.0213	0.0191	N1
0.0287	0.0185	0.0168	O1
0.0286	0.0249	0.0174	O2
0.0250	0.0208	0.0166	S1

0 atoms may be split and 0 atoms NPD

Analysis of variance for reflections employed in refinement K = Mean[Fo^2] / Mean[Fc^2] for group

Fc/Fc(max) 0.000 0.010 0.018 0.028 0.038 0.049 0.062
0.079 0.101 0.139 1.000

Number in group 314. 263. 284. 295. 274. 269. 281.
289. 275. 284.

GooF 0.884 1.103 1.197 1.079 1.081 1.018 0.960
0.992 1.076 1.050

K 1.749 1.028 0.986 1.042 1.005 1.023 1.023
1.033 1.016 0.993

Resolution(A) 0.81 0.84 0.88 0.91 0.96 1.02 1.10
1.21 1.38 1.73 inf

Number in group 284. 285. 282. 280. 282. 285. 280.
287. 279. 284.

GooF 1.086 0.982 1.026 1.038 0.952 1.029 0.955
0.947 1.159 1.238

K 1.054 1.067 1.097 1.048 1.005 1.005 0.985
1.005 1.025 0.983

R1 0.174 0.150 0.132 0.112 0.079 0.067 0.052
0.039 0.040 0.031

Recommended weighting scheme: WGHT 0.0435 0.2208

Note that in most cases convergence will be faster if fixed weights (e.g. the default WGHT 0.1) are retained until the refinement is virtually complete, and only then should the above recommended values be used.

Most Disagreeable Reflections (* if suppressed or used for Rfree).

Error/esd is calculated as sqrt(wD^2/<wD^2>) where w is given by the weight formula, D = Fo^2-Fc^2 and <> refers to the average over all reflections.

h	k	l	Fo^2	Fc^2	Error/esd	Fc/Fc(max)	Resolution(A)
-5	3	14	1.07	22.17	4.26	0.022	1.10
4	2	1	21.83	45.81	4.26	0.032	2.09

-12	4	15	-6.10	61.11	4.19	0.037	0.82
-3	0	9	2480.91	1975.91	4.00	0.212	2.12
12	0	0	65.75	0.12	3.86	0.002	1.12
-4	0	10	186.00	91.86	3.82	0.046	1.88
6	3	3	506.95	373.53	3.82	0.092	1.33
-1	0	9	750.08	535.35	3.72	0.110	2.09
-3	2	2	45.40	73.55	3.61	0.041	2.41
1	1	10	34.68	62.26	3.58	0.038	1.64
10	3	10	-3.21	32.66	3.51	0.027	0.84
-13	3	8	25.83	69.65	3.50	0.040	0.94
-5	2	4	13.48	27.31	3.45	0.025	1.97
-6	1	2	6.23	16.65	3.37	0.019	2.19
-5	3	2	91.86	132.35	3.29	0.055	1.56
-10	2	19	923.68	583.60	3.25	0.115	0.89
-6	2	9	105.65	136.07	3.21	0.056	1.54
0	6	1	1798.99	1416.81	3.05	0.179	0.93
-15	1	5	-5.95	12.50	2.99	0.017	0.94
-8	4	8	176.63	238.13	2.95	0.073	1.07
0	2	7	521.79	434.76	2.94	0.099	1.90
2	1	9	10.14	23.80	2.93	0.023	1.68
-2	3	4	759.67	643.11	2.87	0.121	1.73
-2	5	4	252.79	177.99	2.83	0.063	1.09
9	2	0	65.27	108.49	2.81	0.050	1.32
-11	4	14	-11.09	41.65	2.81	0.031	0.86
-4	1	4	88.26	113.04	2.79	0.051	2.84
-5	1	10	530.62	439.39	2.76	0.100	1.72
-4	2	17	415.62	515.43	2.72	0.108	1.05
-6	0	12	705.72	548.57	2.66	0.111	1.51
-11	4	13	-11.07	31.08	2.65	0.027	0.88
-7	0	9	3466.50	3041.55	2.63	0.262	1.71
-3	3	16	49.08	79.03	2.62	0.042	1.01
1	3	12	151.74	218.31	2.58	0.070	1.14
4	3	1	-0.24	7.43	2.58	0.013	1.60
-14	4	8	7.65	50.07	2.56	0.034	0.82
0	2	2	64.17	86.34	2.56	0.044	2.67
0	6	3	49.79	10.94	2.56	0.016	0.92
-7	2	17	598.85	707.57	2.55	0.127	1.02
-5	2	11	66.80	45.23	2.54	0.032	1.44
-8	1	5	141.33	112.76	2.54	0.051	1.69
-4	1	8	378.53	315.84	2.52	0.085	2.10
-14	0	12	1422.63	1161.59	2.52	0.162	0.98
8	3	12	35.89	5.48	2.50	0.011	0.86
-8	6	3	32.15	79.17	2.47	0.042	0.83
-3	2	16	187.73	242.44	2.42	0.074	1.10

3	6	9	-7.75	22.93	2.40	0.023	0.81
6	3	12	2.62	26.27	2.38	0.024	0.94
-10	2	7	120.90	156.24	2.38	0.059	1.26
-12	0	14	-9.52	24.22	2.36	0.023	1.04

Bond lengths and angles

C1 -	Distance	Angles	
C6	1.3959 (0.0032)		
C2	1.3978 (0.0032)	118.43 (0.22)	
C7	1.4649 (0.0032)	121.72 (0.21)	119.85 (0.20)
	C1 -	C6	C2

C2 -	Distance	Angles	
C3	1.3824 (0.0034)		
C1	1.3978 (0.0032)	120.41 (0.22)	
H2	0.9500	119.79	119.79
	C2 -	C3	C1

C3 -	Distance	Angles	
C4	1.3787 (0.0034)		
C2	1.3824 (0.0034)	120.25 (0.23)	
H3	0.9500	119.87	119.87
	C3 -	C4	C2

C4 -	Distance	Angles	
C3	1.3787 (0.0034)		
C5	1.3898 (0.0034)	120.33 (0.24)	
H4	0.9500	119.84	119.84
	C4 -	C3	C5

C5 -	Distance	Angles	
C6	1.3797 (0.0033)		
C4	1.3898 (0.0034)	119.35 (0.23)	
H5	0.9500	120.32	120.32
	C5 -	C6	C4

C6 -	Distance	Angles	
C5	1.3797 (0.0033)		
C1	1.3959 (0.0032)	121.22 (0.22)	
H6	0.9500	119.39	119.39
	C6 -	C5	C1

C7 -	Distance	Angles	
N1	1.3095 (0.0028)		
C1	1.4649 (0.0032)	124.00 (0.20)	
S1	1.7362 (0.0023)	114.72 (0.18)	121.27 (0.16)
	C7 -	N1	C1

C8 -	Distance	Angles	
C9	1.3652 (0.0031)		
N1	1.3706 (0.0029)	116.55 (0.20)	
H8	0.9500	121.73	121.73

	C8 -	C9	N1	
C9 -	Distance	Angles		
C8	1.3652 (0.0031)			
C10	1.4487 (0.0031)	128.43 (0.21)		
S1	1.7299 (0.0023)	109.04 (0.17)	122.44 (0.17)	
	C9 -	C8	C10	
C10 -	Distance	Angles		
C11	1.3341 (0.0030)			
C9	1.4487 (0.0031)	123.71 (0.21)		
H10	0.9500	118.14	118.14	
	C10 -	C11	C9	
C11 -	Distance	Angles		
C10	1.3341 (0.0030)			
C12	1.4623 (0.0032)	123.66 (0.21)		
H11	0.9500	118.17	118.17	
	C11 -	C10	C12	
C12 -	Distance	Angles		
O2	1.2223 (0.0025)			
O1	1.3407 (0.0026)	123.88 (0.20)		
C11	1.4623 (0.0032)	126.08 (0.21)	110.03 (0.19)	
	C12 -	O2	O1	
C13 -	Distance	Angles		
O1	1.4526 (0.0026)			
C14	1.5020 (0.0030)	106.80 (0.17)		
H13A	0.9900	110.36	110.36	
H13B	0.9900	110.36	110.36	108.59
	C13 -	O1	C14	H13A
C14 -	Distance	Angles		
C13	1.5020 (0.0030)			
C15	1.5164 (0.0030)	112.27 (0.18)		
H14A	0.9900	109.15	109.15	
H14B	0.9900	109.15	109.15	107.87
	C14 -	C13	C15	H14A
C15 -	Distance	Angles		
C14	1.5164 (0.0030)			
C16	1.5215 (0.0031)	112.55 (0.19)		
H15A	0.9900	109.09	109.09	
H15B	0.9900	109.09	109.09	107.83
	C15 -	C14	C16	H15A
C16 -	Distance	Angles		
C15	1.5215 (0.0031)			
H16A	0.9800	109.47		
H16B	0.9800	109.47	109.47	
H16C	0.9800	109.47	109.47	109.47

C16 - C15 H16A H16B

N1 - Distance Angles

C7 1.3095 (0.0028)

C8 1.3706 (0.0029) 110.36 (0.19)

N1 - C7

O1 - Distance Angles

C12 1.3407 (0.0026)

C13 1.4526 (0.0026) 118.24 (0.17)

O1 - C12

O2 - Distance Angles

C12 1.2223 (0.0025)

O2 -

S1 - Distance Angles

C9 1.7299 (0.0023)

C7 1.7362 (0.0023) 89.32 (0.11)

S1 - C9

FMAP and GRID set by program

FMAP 2 3 25

GRID -1.136 -2 -2 1.136 2 2

R1 = 0.0738 for 2828 unique reflections after merging for Fourier

Electron density synthesis with coefficients Fo-Fc

Highest peak 0.34 at 0.9201 0.1189 0.1790 [0.91 A from C9]

Deepest hole -0.33 at 0.8590 0.2159 0.1715 [0.73 A from S1]

Mean = 0.00, Rms deviation from mean = 0.06, Highest memory used = 2223 / 17938

Fourier peaks appended to .res file

x y z sof U Peak Distances to nearest atoms (including eq.)

Q1 1 0.4201 0.3811 0.6790 1.00000 0.05 0.34 0.91 C9 1.07 S1 1.92 C8 1.94 C10

No peaks closer than 4 Angstroms to each other

Time profile in seconds

0.08: Read and process instructions

0.00: Fit rigid groups

0.00: Interpret restraints etc.

0.00: Generate connectivity array

0.00: Analyse DFIX and DANG restraints

0.00: Analyse SAME and SADI restraints

0.00: Generate CHIV restraints

0.00: Check if bonds in residues restrained

0.00: Generate DELU and RIGU restraints

0.00: Generate SIMU restraints

0.00: Generate ISOR restraints

0.00: Generate NCSY restraints
0.00: Analyse other restraints etc.
0.05: Read intensity data, sort/merge etc.
0.00: Set up constraints
0.02: OSF, H-atoms from difference map
0.03: Set up l.s. refinement
0.00: Generate idealized H-atoms
0.08: Structure factors and derivatives
0.17: Sum l.s. matrices
0.00: Generate and apply antibumping restraints
0.00: Apply other restraints
0.03: Solve l.s. equations
0.00: Generate HTAB table
0.28: Other dependent quantities, CIF, tables
0.03: Analysis of variance
0.11: Merge reflections for Fourier and .fcf
0.02: Fourier summations
0.00: Peaksearch
0.00: Analyse peaklist

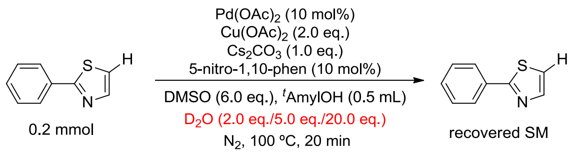
** WARNING: These times are only approximate for multiple threads.
To get better estimates run with -t1 **

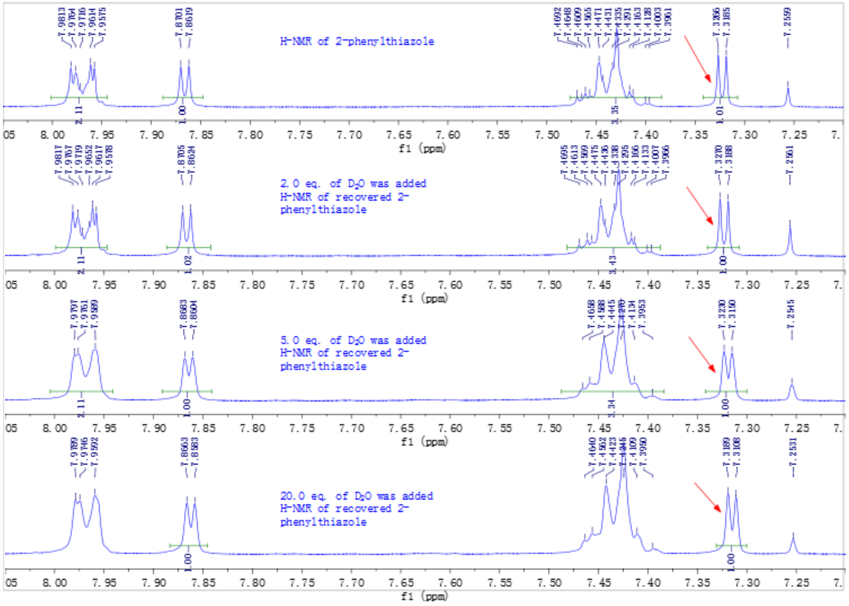
++

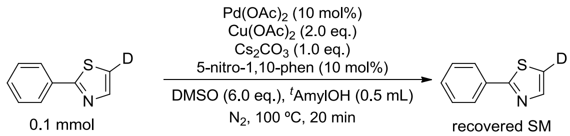
+ exp_4110 finished at 14:58:25 Total elapsed time: 0.89 secs +

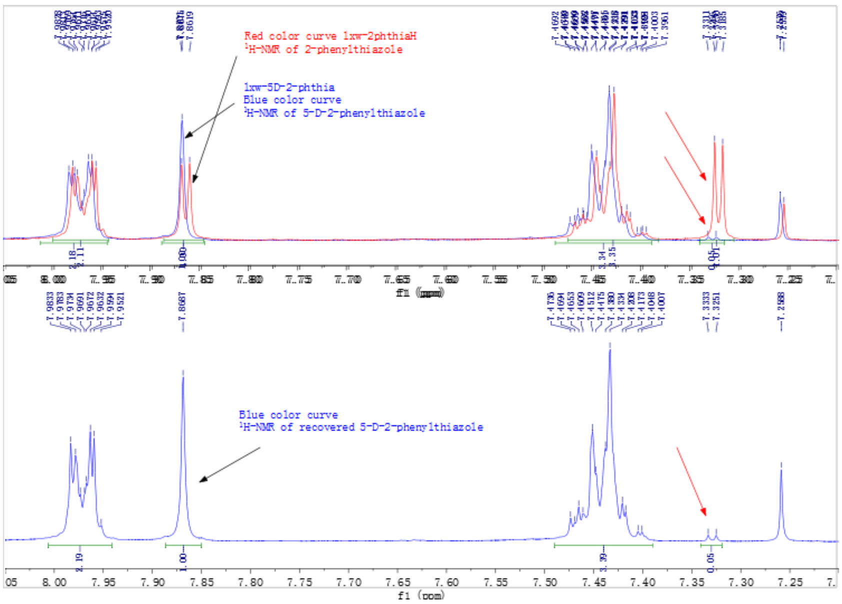
++

8. Spectra for the D/H and H/D Exchange Experiments









9. Proposed Plausible Reaction Mechanism

Based on these preliminary results, we proposed a plausible mechanism (Figure S2). C-H activation occurred *via* electrophilic palladation of **1a** with **I-0** to form the **I-1**, then reversible coordination of **I-1** with the alkene partner **2** to generate **I-2** which undergoes following migratory insertion to form **I-3**, then *β*-hydride elimination of **I-3** to deliver the desired alkenylated product **3** and **I-4**, further reductive elimination of **I-4** to form Pd(0) species **I-5** and acetic acid which is neutralized by the presence of Cs_2CO_3, following oxidation of the Pd(0) species by the copper(II) to regenerate the catalyst species **I-0**. Additionally, preliminary H/D exchange experiments suggested that the C-H bond activation step is probably irreversible. Furthermore, a synthesized precatalyst of **9** was applied to the model reaction to deliver the desired 5-alkenylated product **3aa** in 24% yield, This indicated that such a complex **9** was possibly formed under the standard conditions.

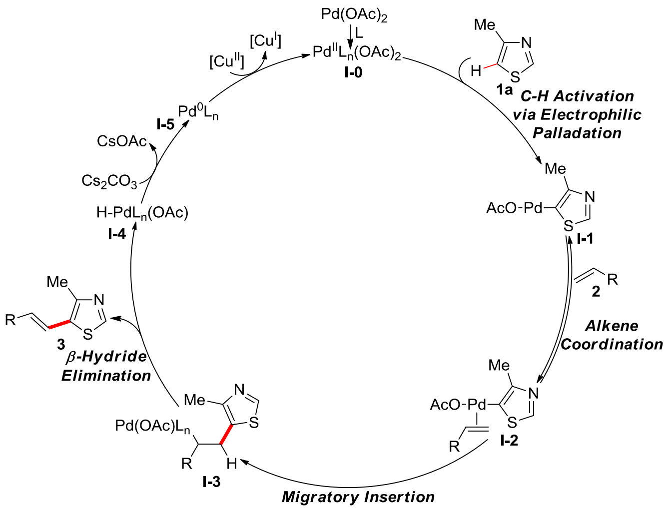


Figure S2 Plausible Reaction Mechanism.

10.References

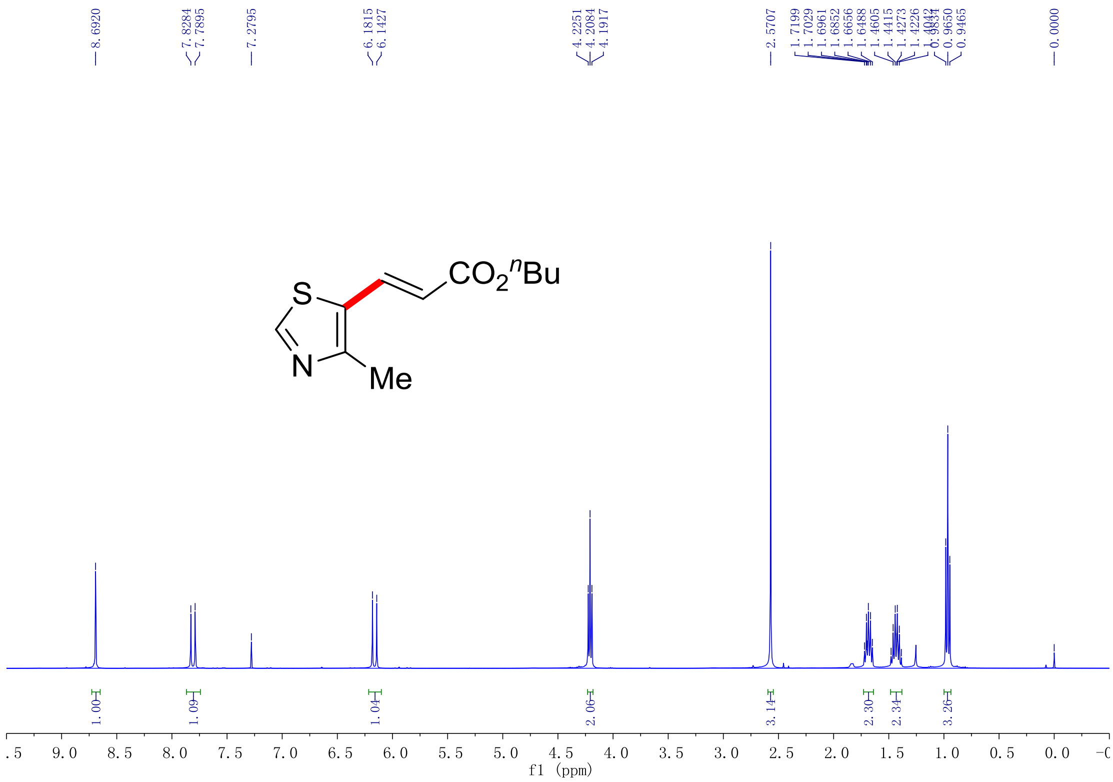
[1] a) M. Annapurna, P. Vishnuvardhan Reddy, S. P. Singh, M. L. Kantam, *Tetrahedron* **2013**, *69*, 10940-10945; b) J. P. Parrish, Y. C. Jung, S. I. Shin, K. W. Jung, *J. Org. Chem.* **2002**, *67*, 7127-7130.

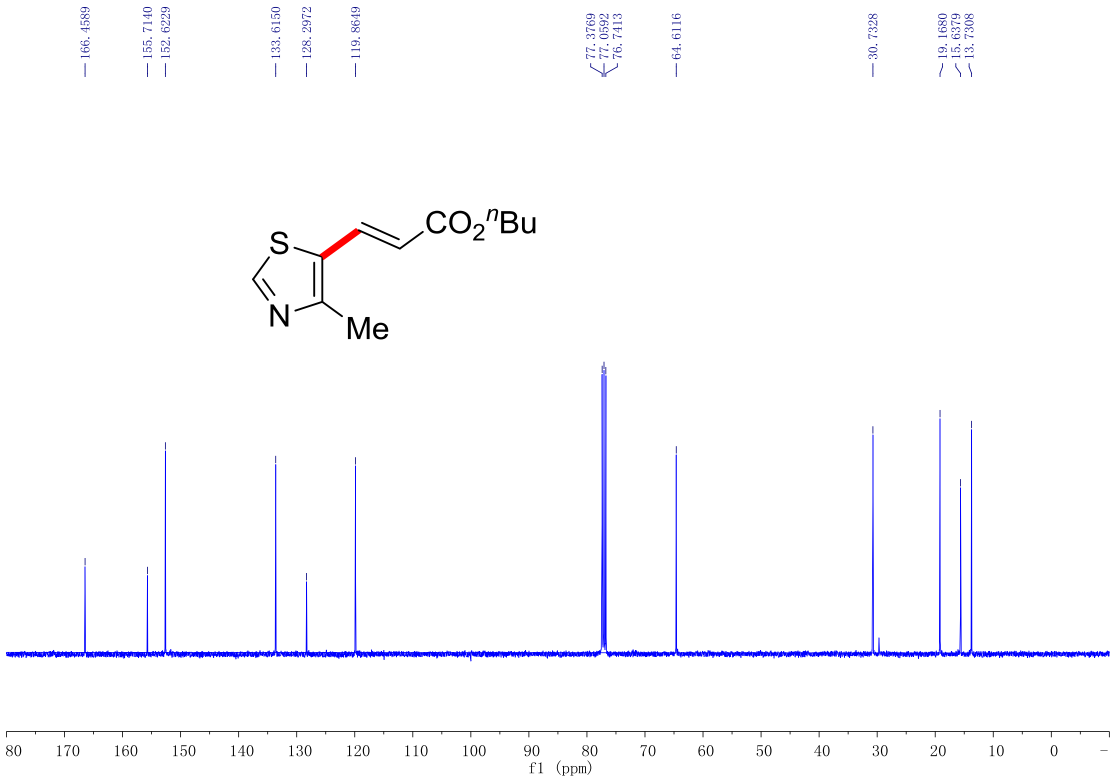
[2] Y. Kanda, H. Araki, K. Hayashi, N. Omori, N. Kuroda, S. Kida, PCT Int. Appl. WO 2009123164 A1, 08 Oct 2009

[3] M. Miyasaka, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2010**, *75*, 5421-5424.

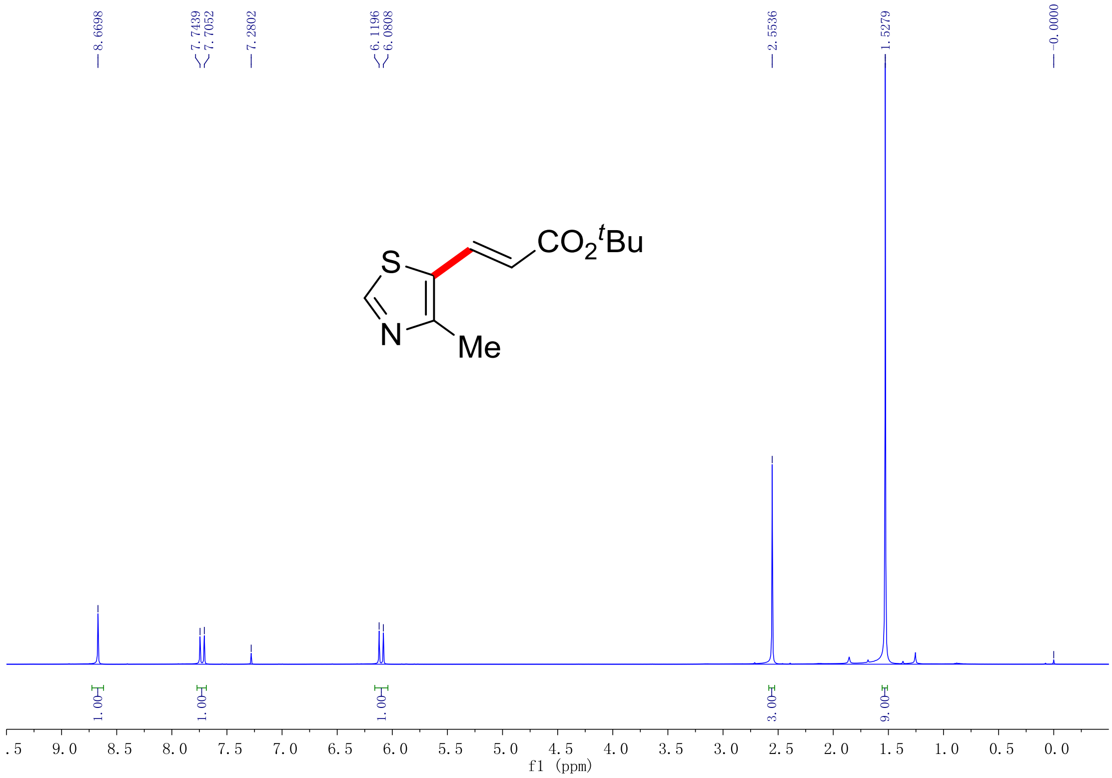
11. ^{1}H and ^{13}C NMR Spectral Scopies Obtained in the Study.

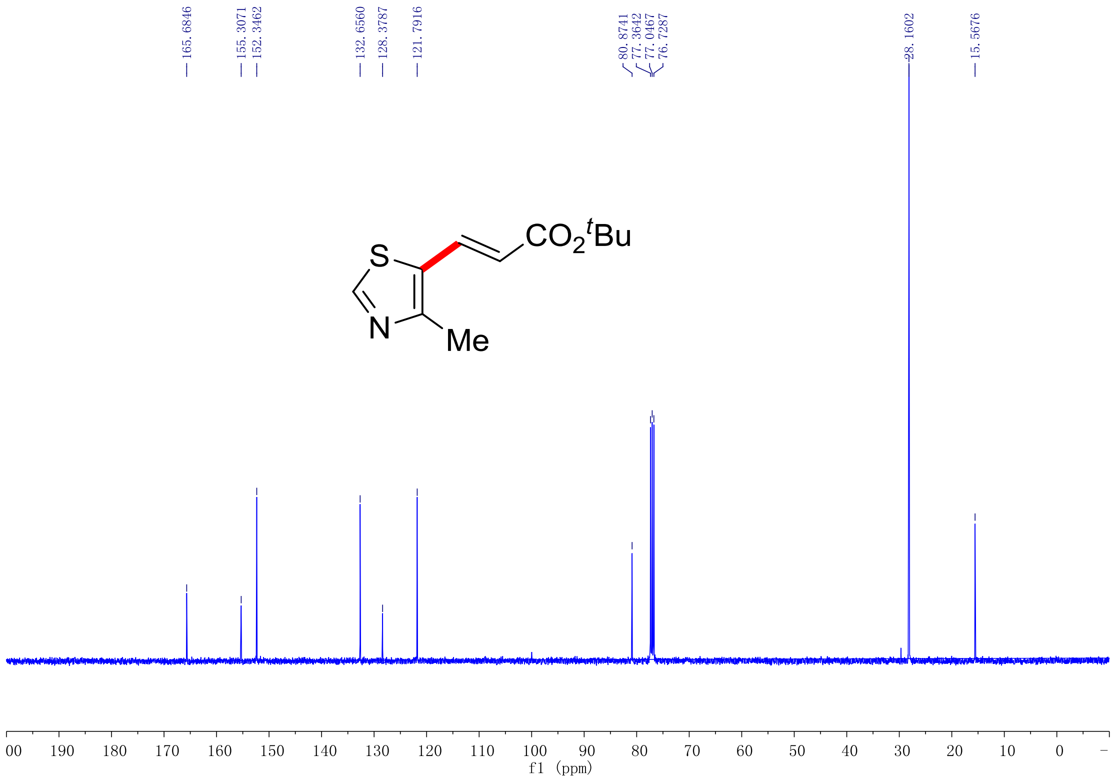
(*E*)-butyl 3-(4-methylthiazol-5-yl)acrylate (**3aa**)



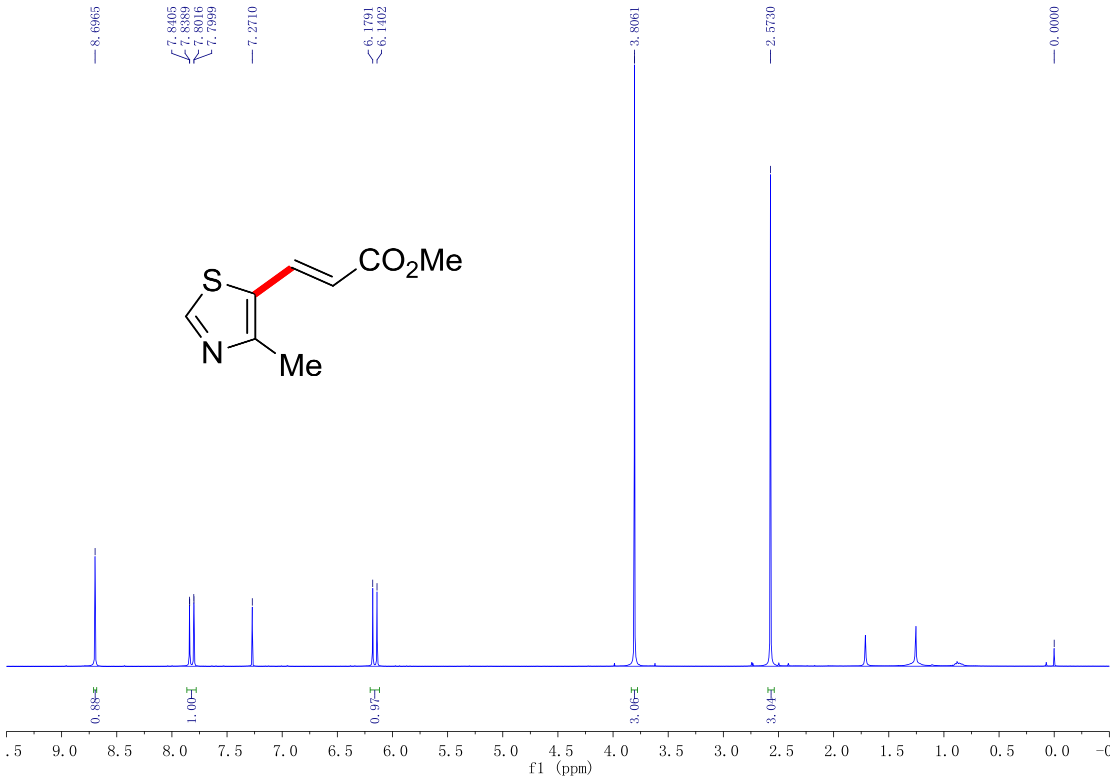


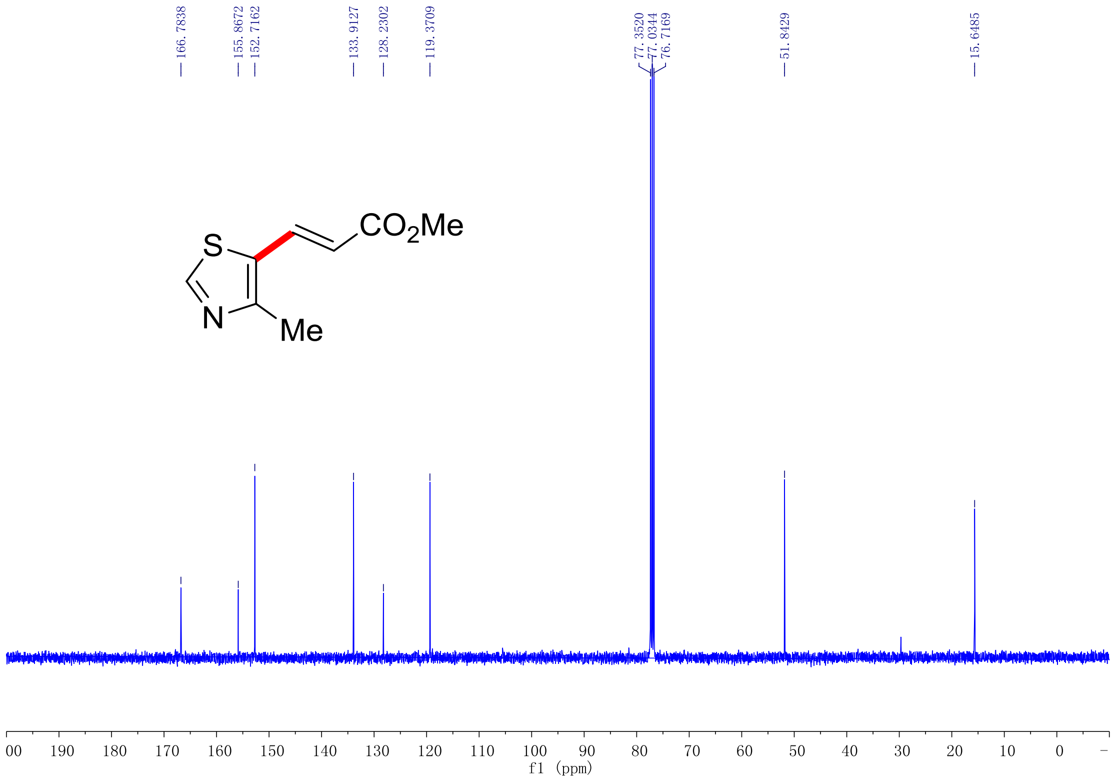
(*E*)-tert-butyl 3-(4-methylthiazol-5-yl)acrylate (**3ab**)



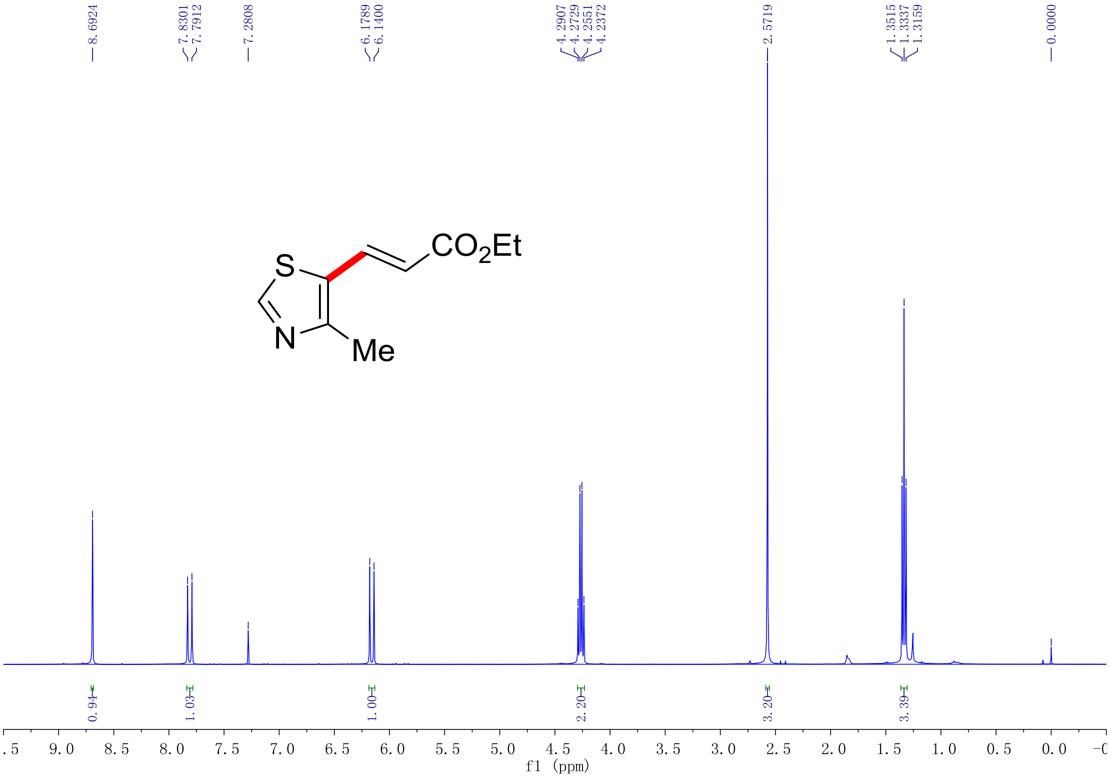


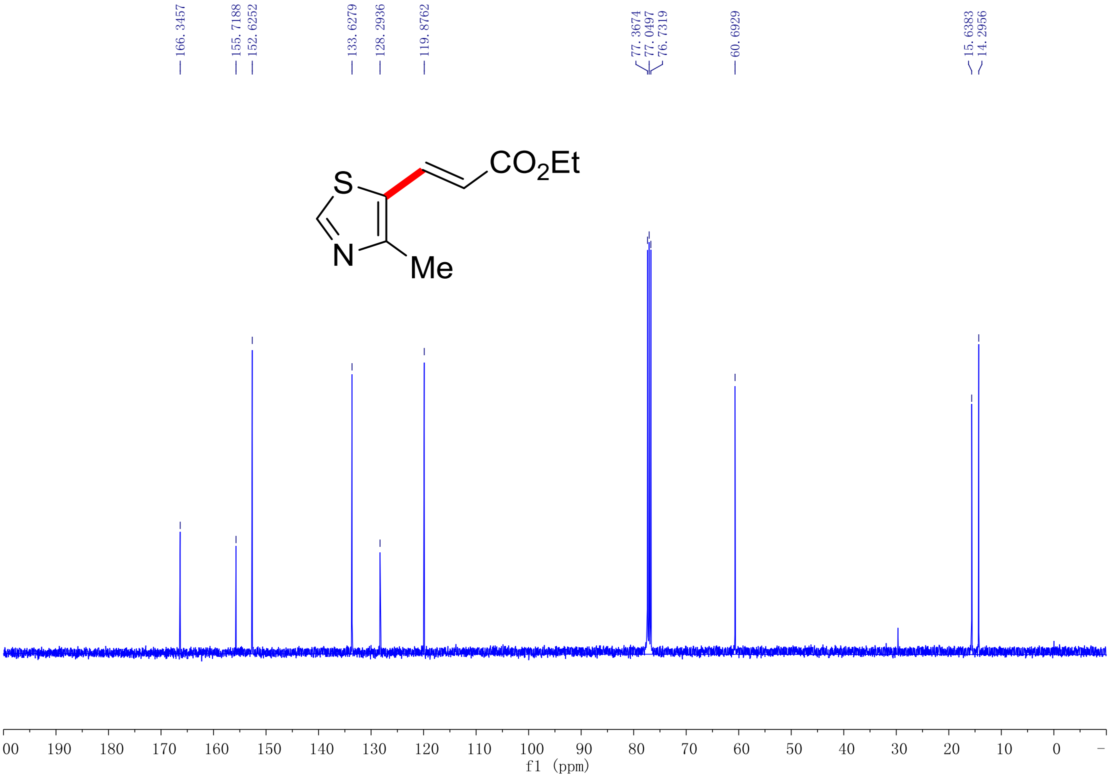
(*E*)-methyl 3-(4-methylthiazol-5-yl)acrylate (**3ac**)



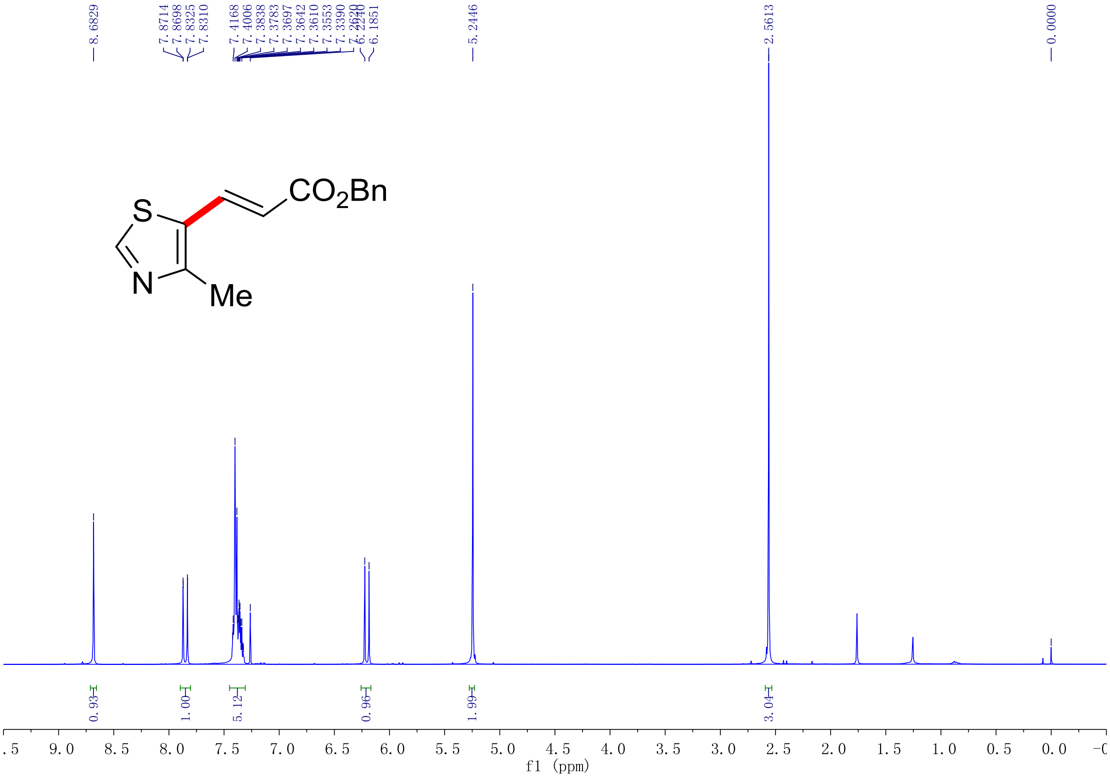


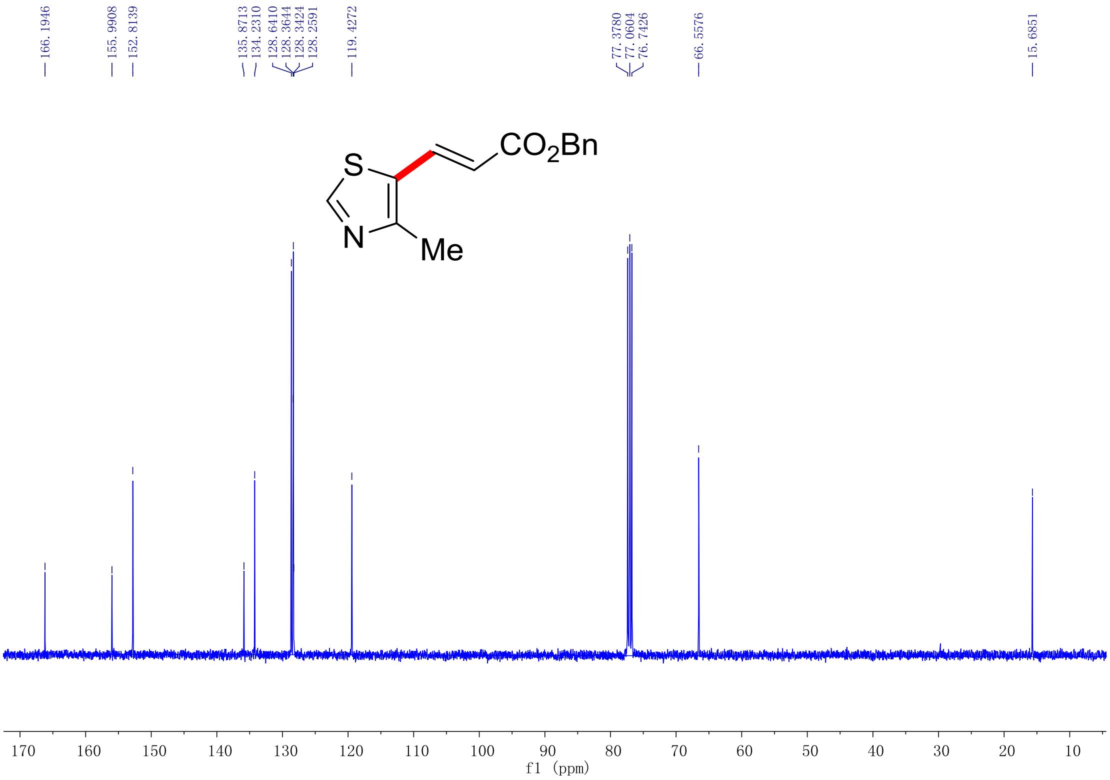
(*E*)-ethyl 3-(4-methylthiazol-5-yl)acrylate (**3ad**)



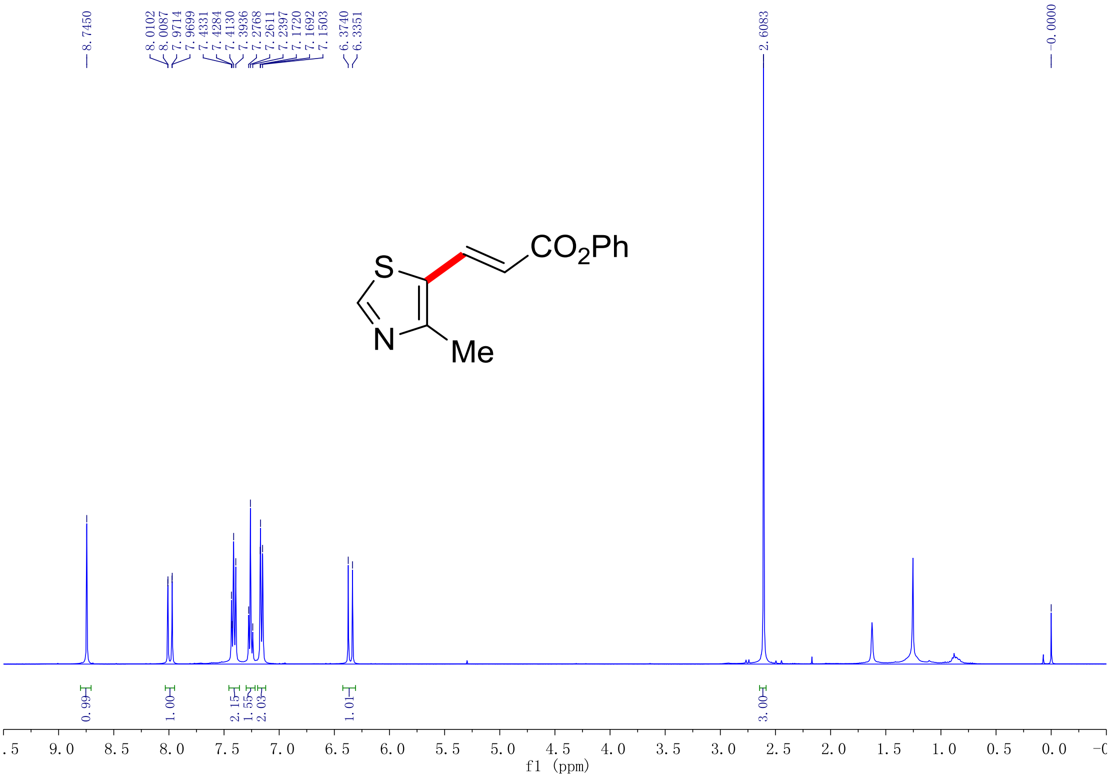


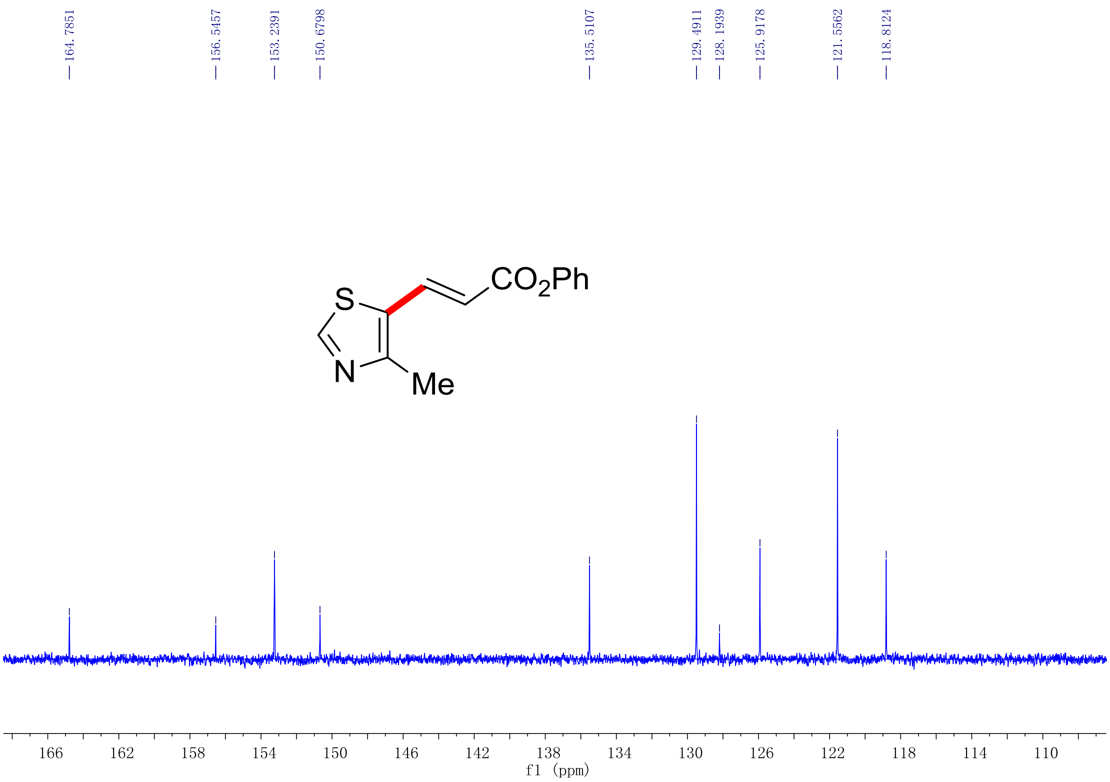
(*E*)-benzyl 3-(4-methylthiazol-5-yl)acrylate (**3ae**)



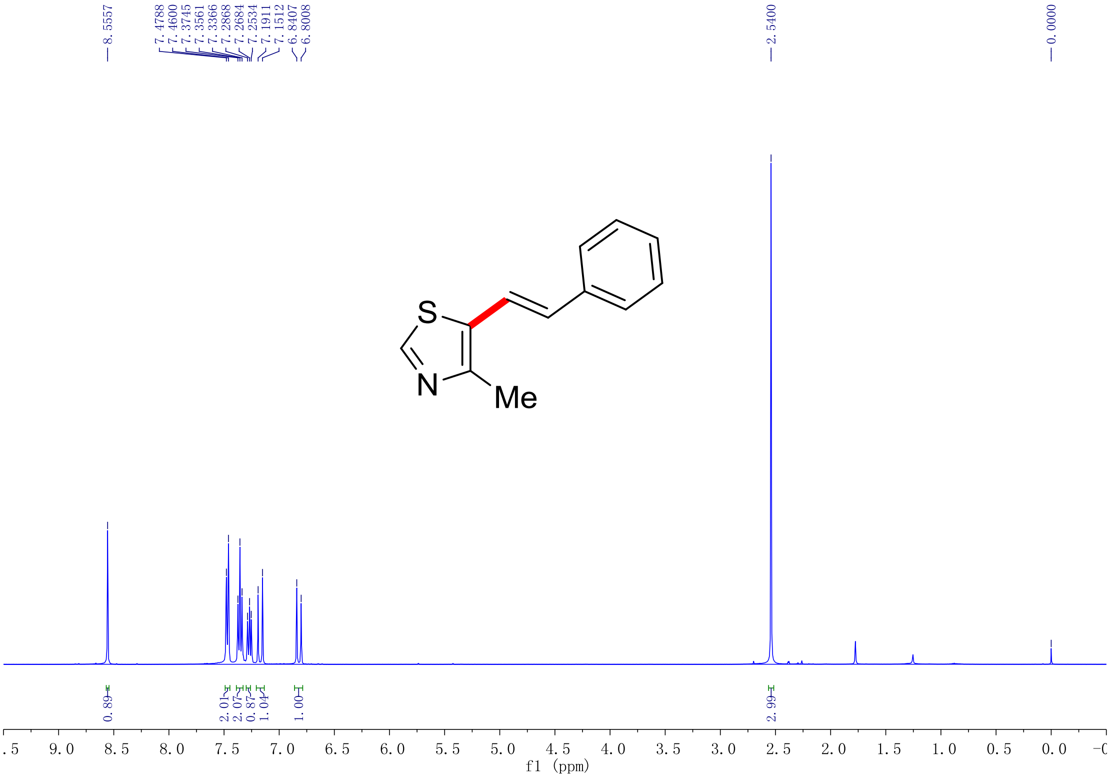


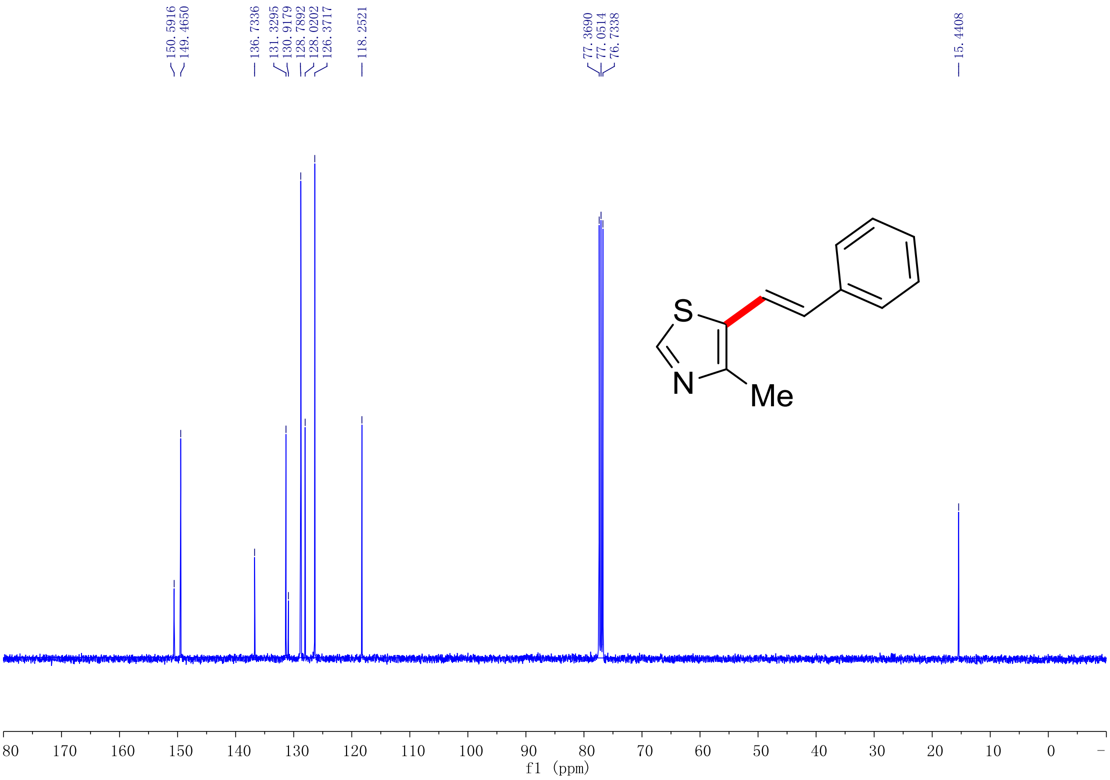
(*E*)-phenyl 3-(4-methylthiazol-5-yl)acrylate (**3af**)



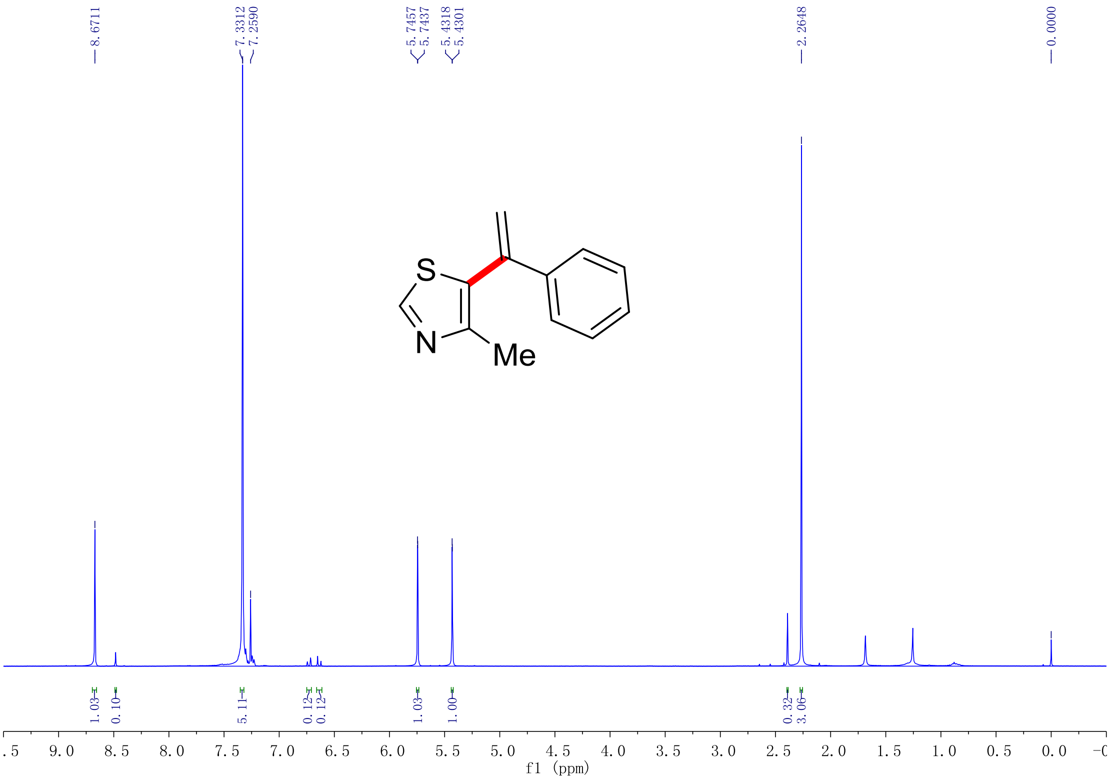


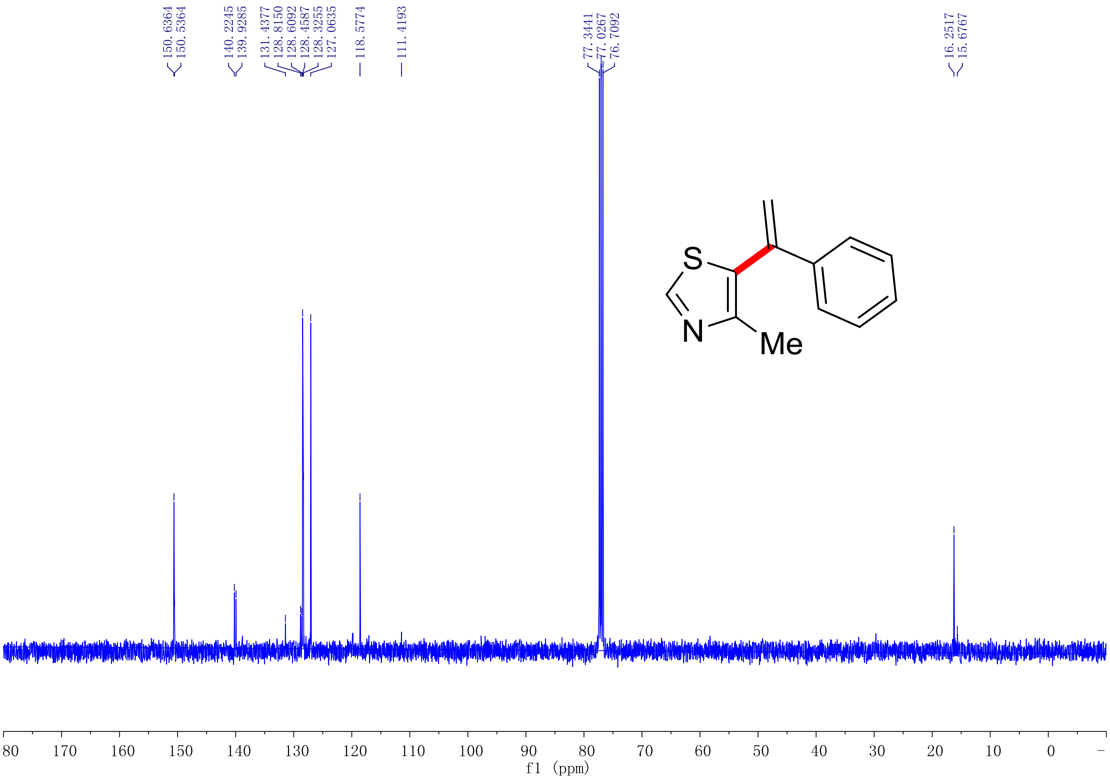
(*E*)-4-methyl-5-styrylthiazole (**3ag**)



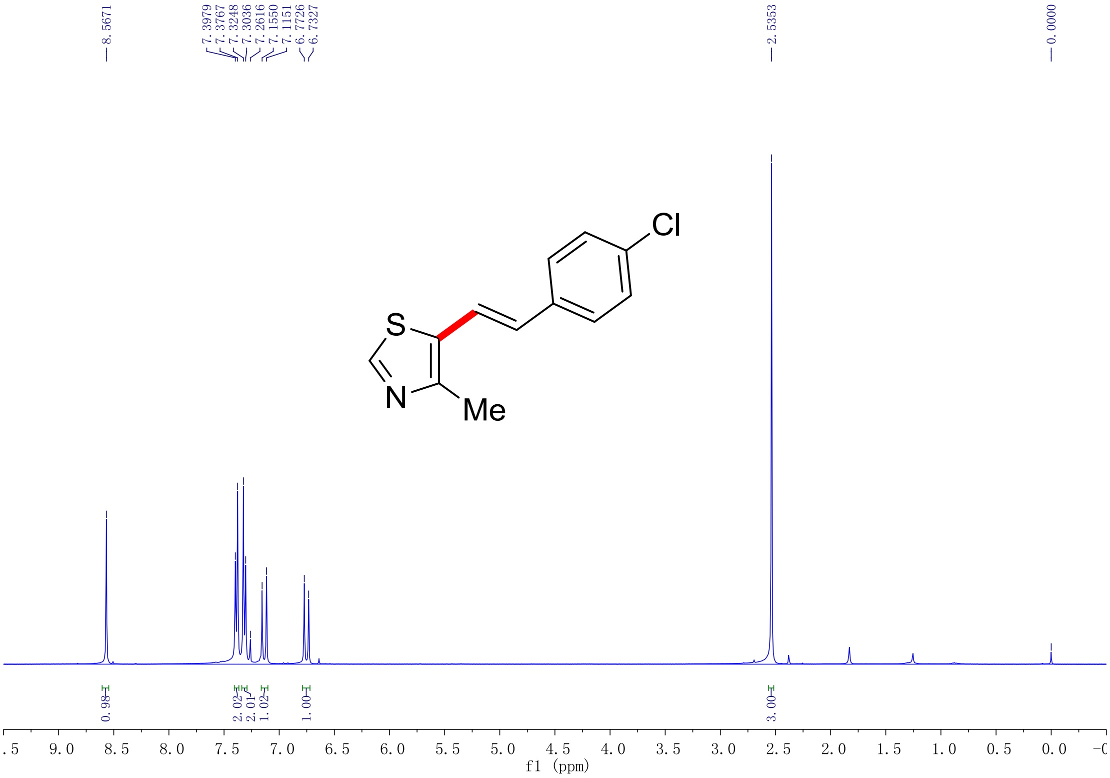


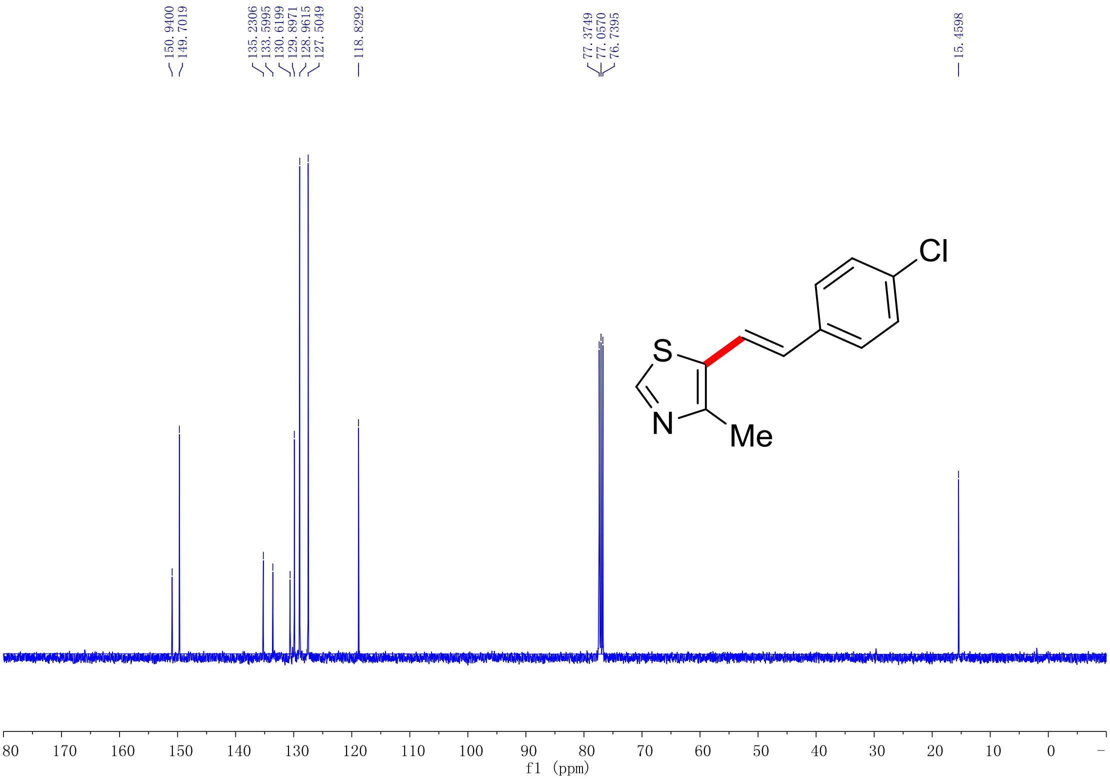
4-methyl-5-(1-phenylvinyl)thiazole (**3ag'**)



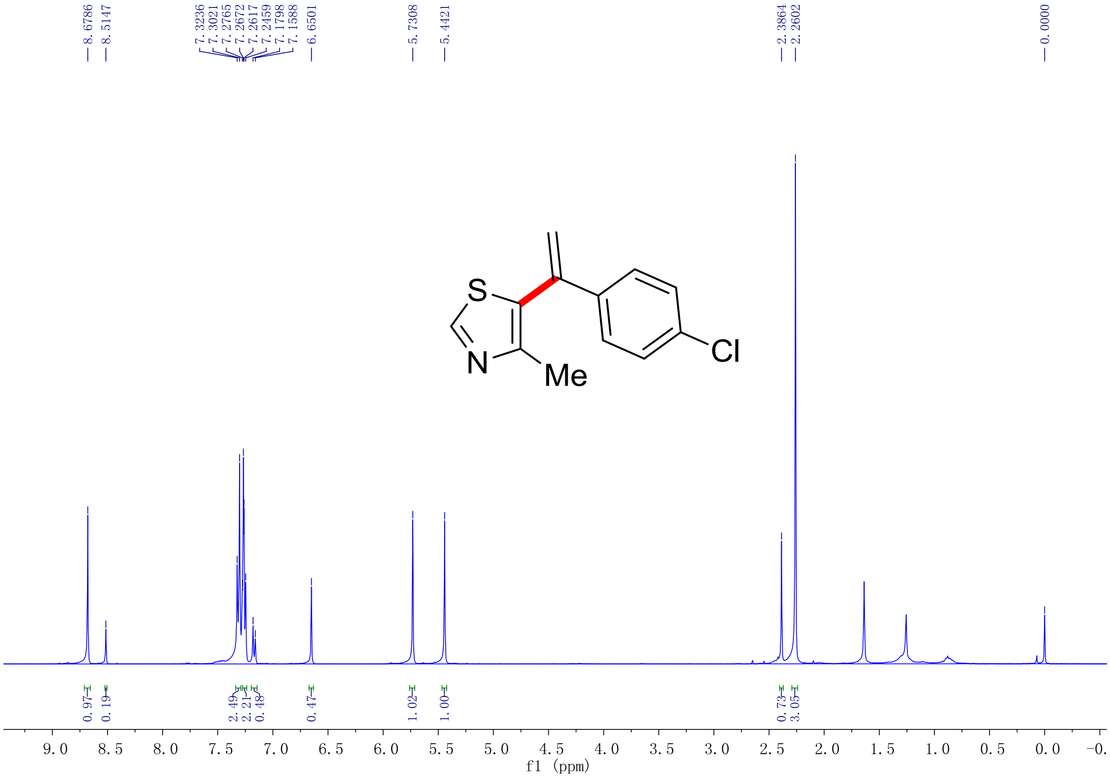


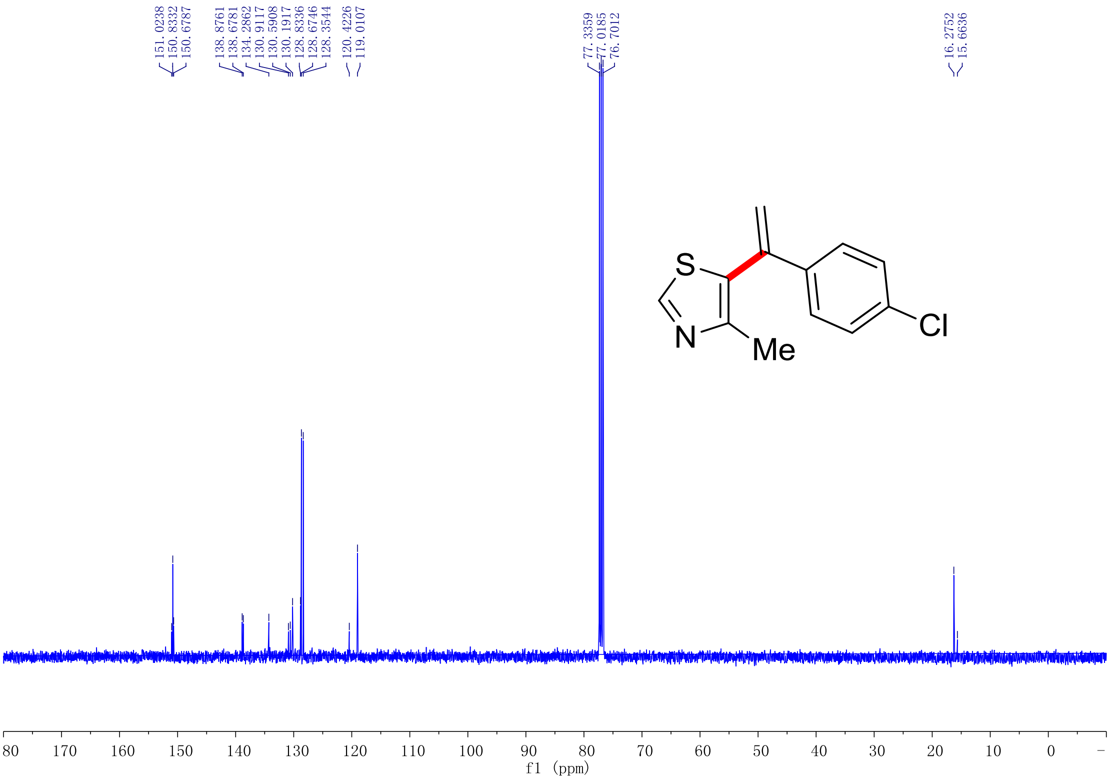
(*E*)-5-(4-chlorostyryl)-4-methylthiazole (**3ah**)



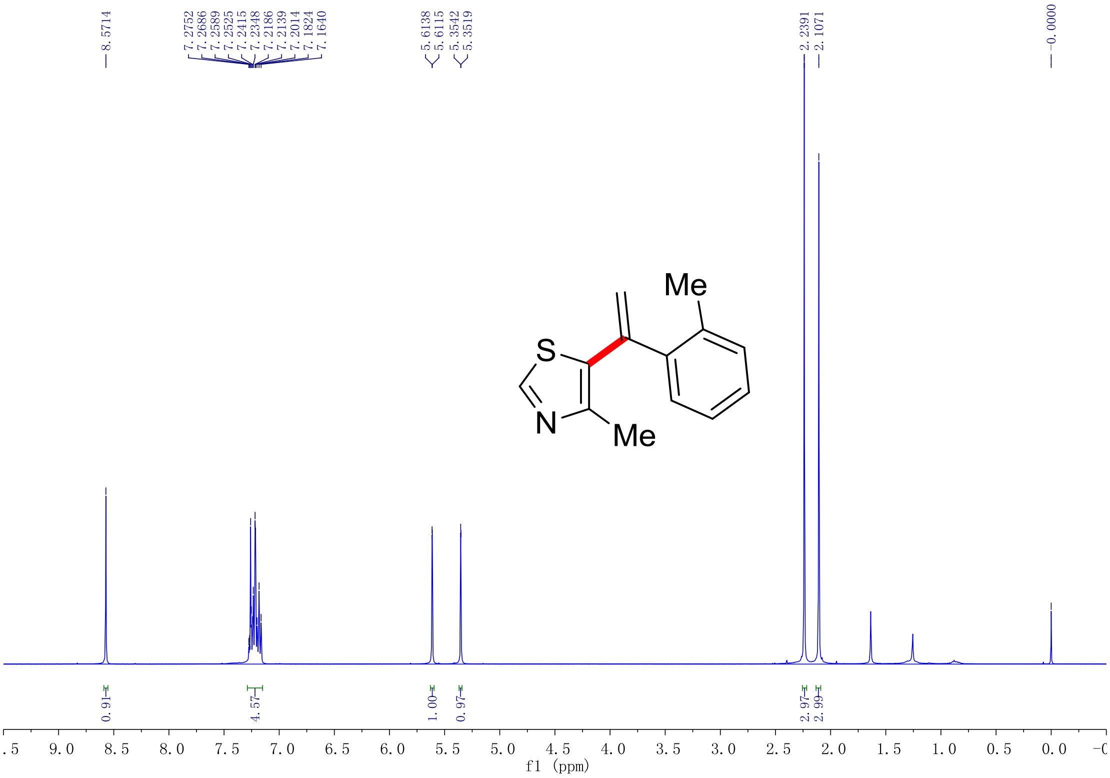


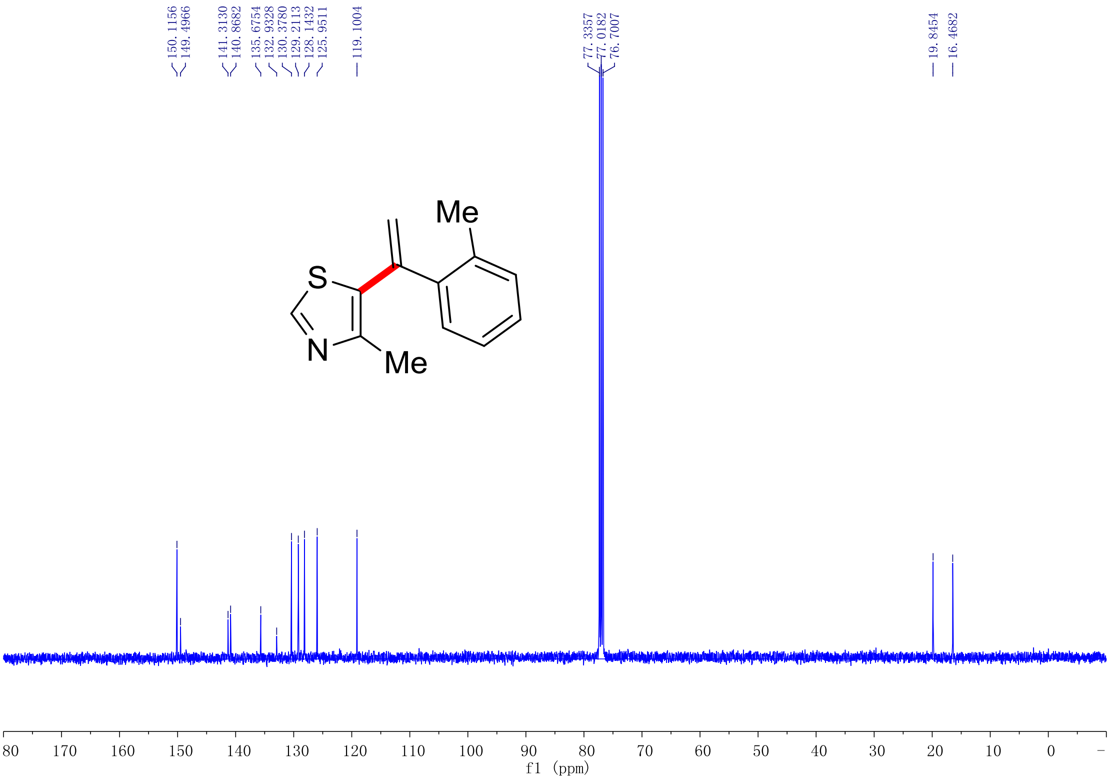
5-(1-(4-chlorophenyl)vinyl)-4-methylthiazole (**3ah'**)



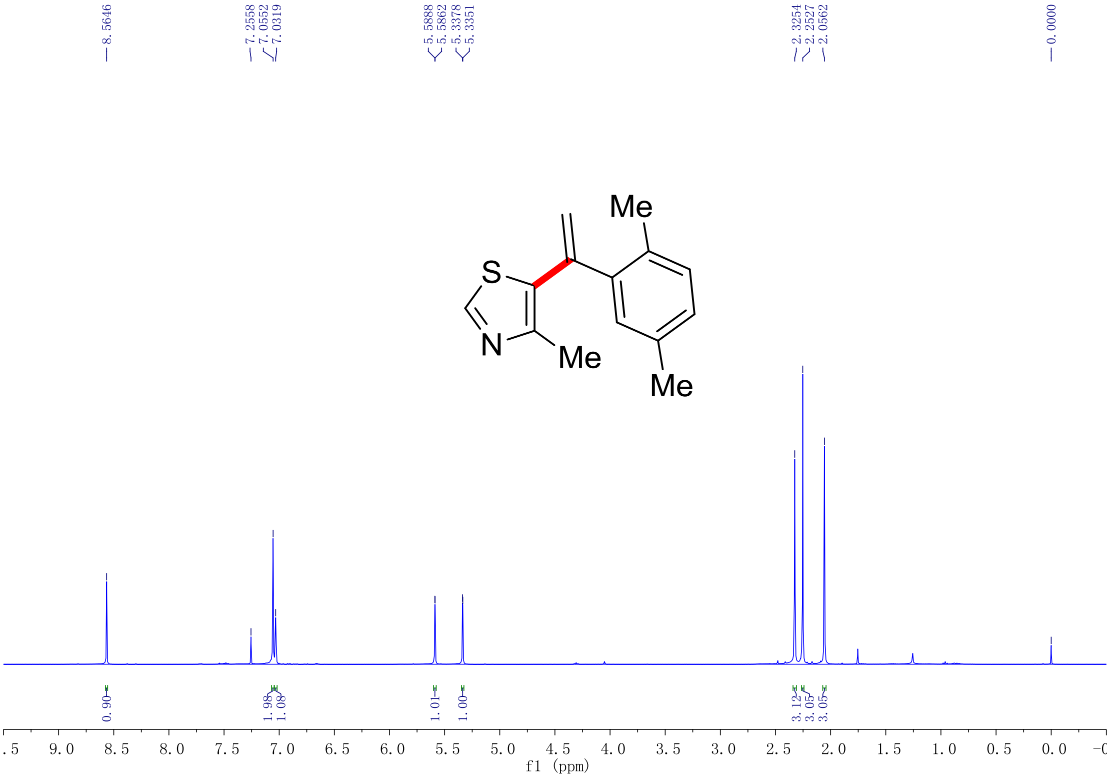


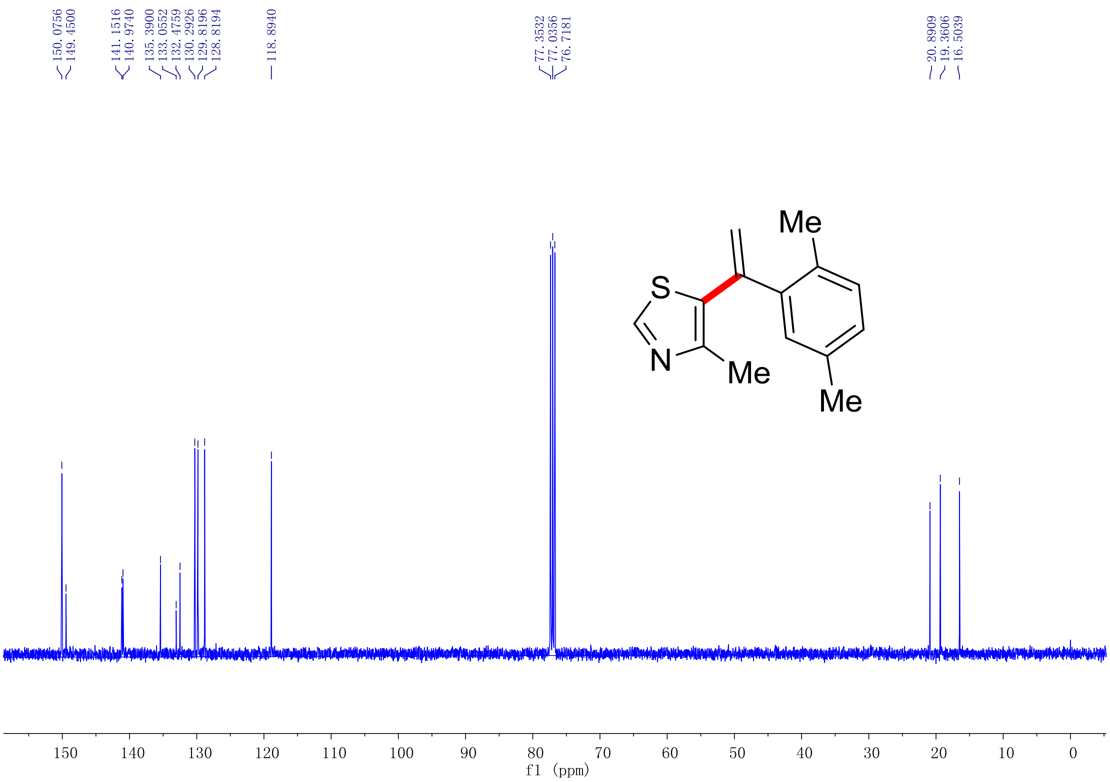
4-methyl-5-(1-(*o*-tolyl)vinyl)thiazole (**3ai**)



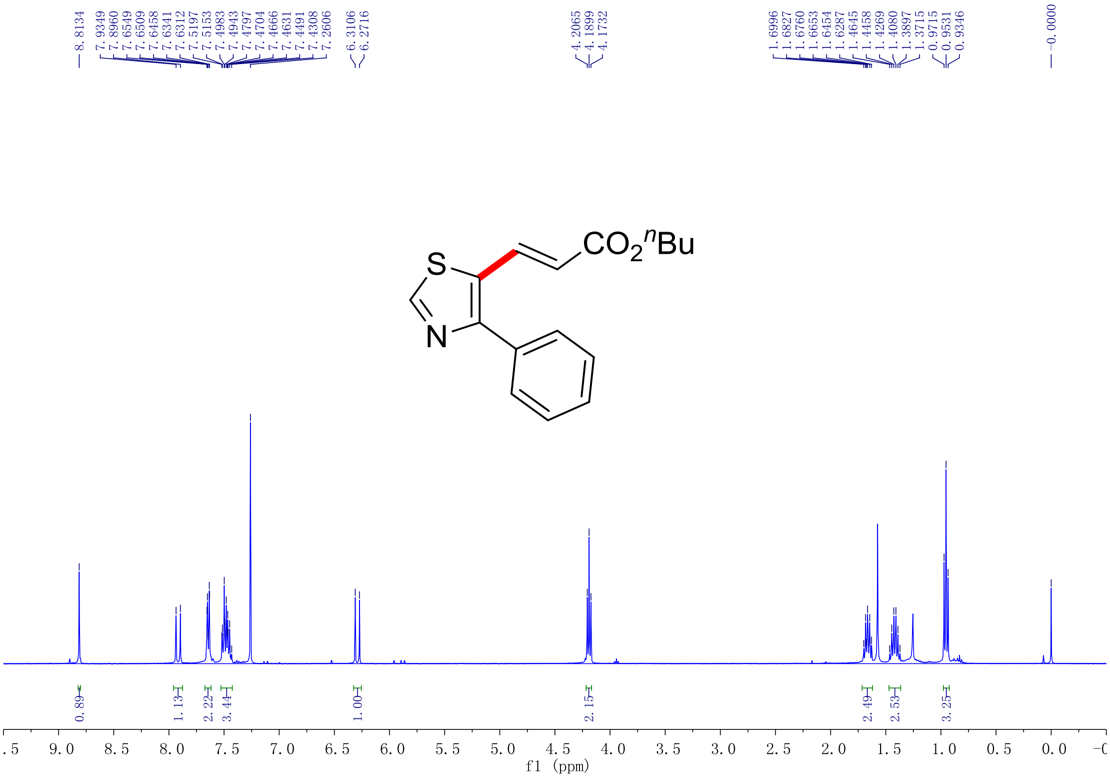


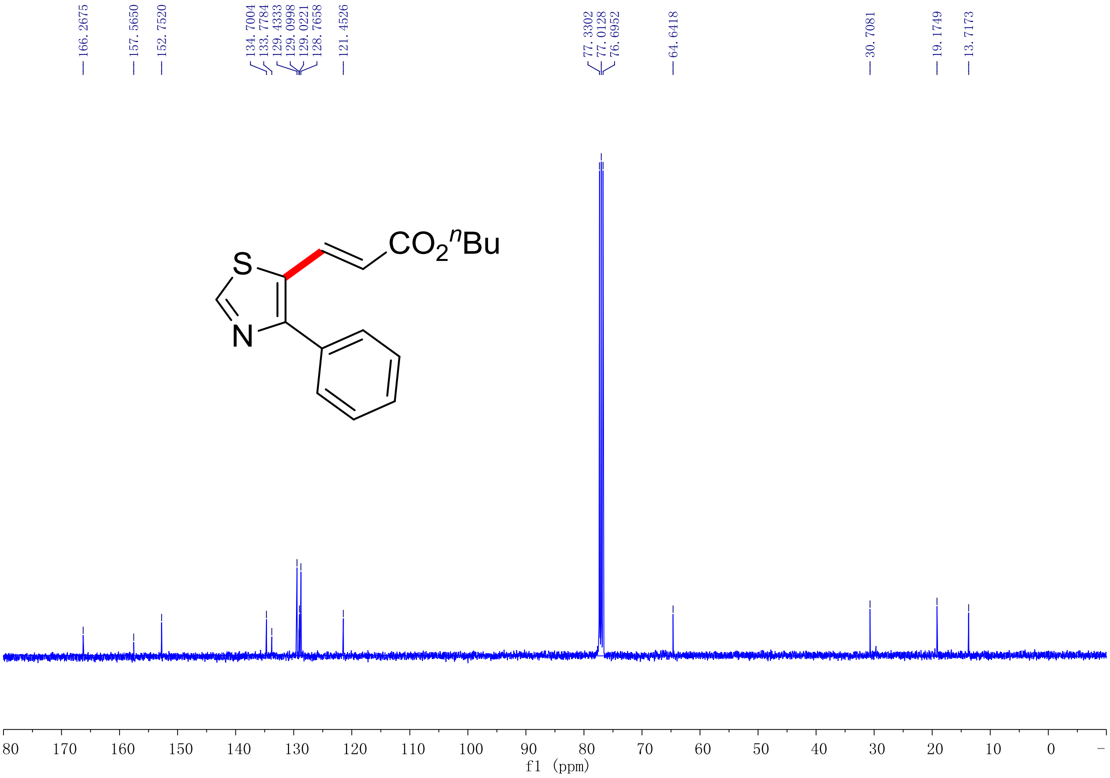
5-(1-(2,5-dimethylphenyl)vinyl)-4-methylthiazole (**3aj**)



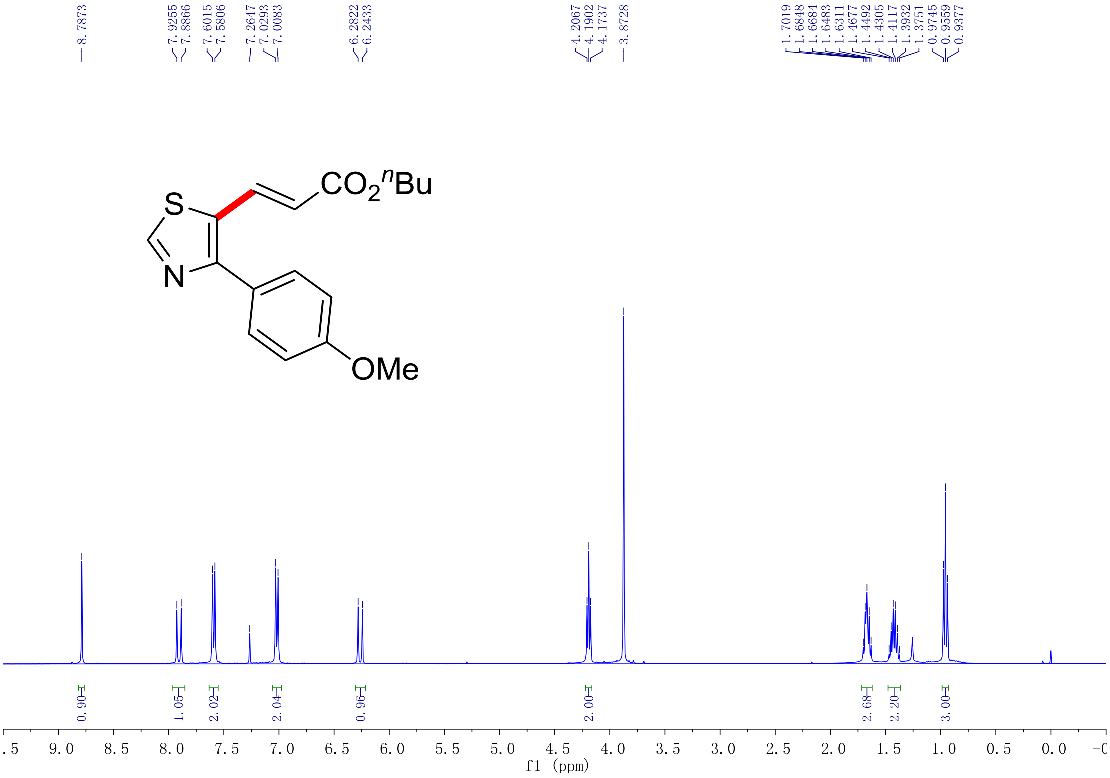


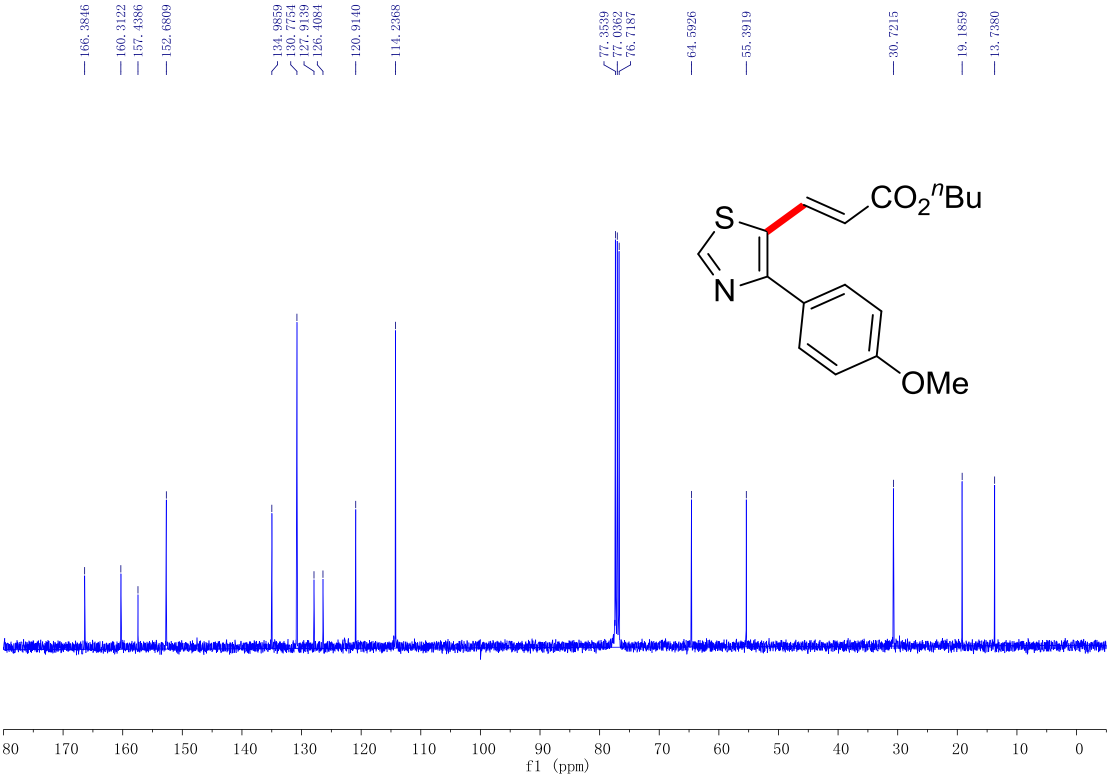
(*E*)-butyl 3-(4-phenylthiazol-5-yl)acrylate (**3ba**)



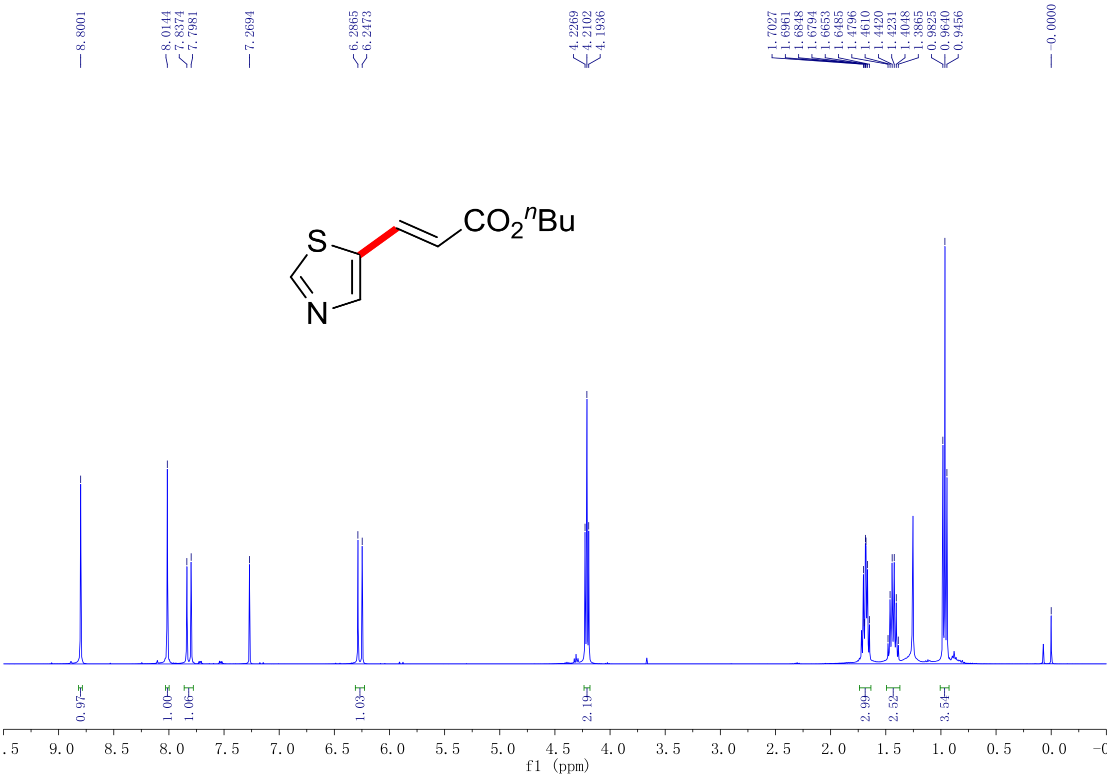


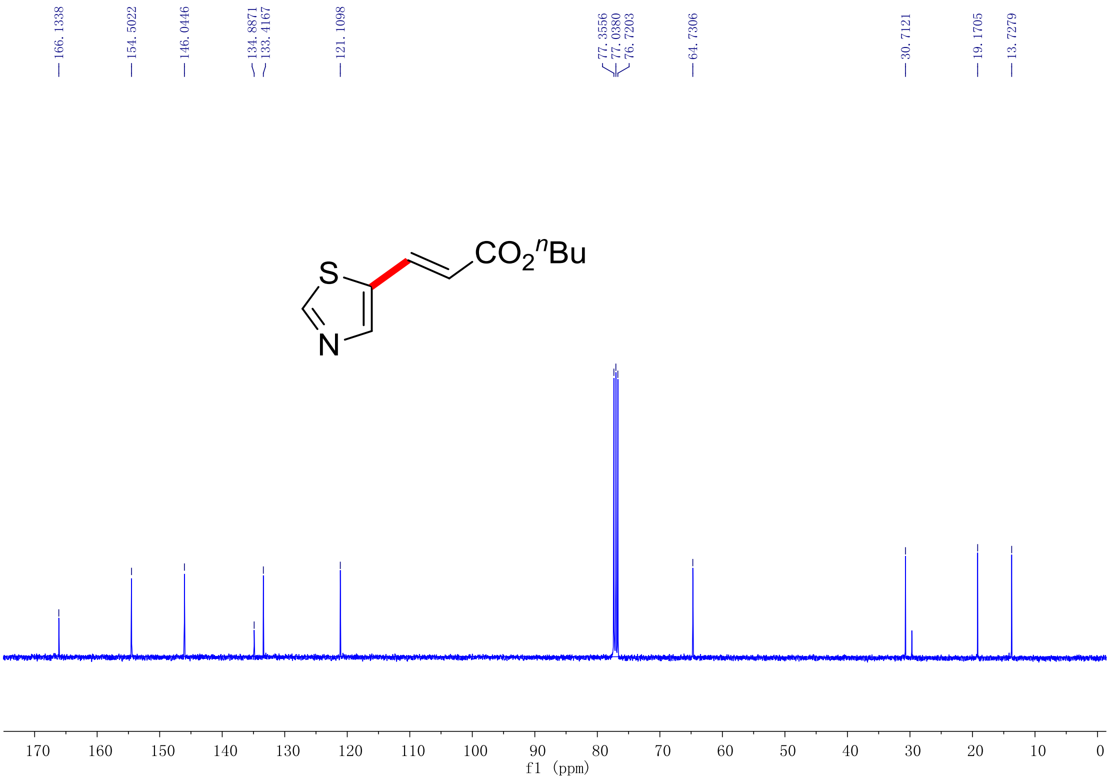
(*E*)-butyl 3-(4-(4-methoxyphenyl)thiazol-5-yl)acrylate (**3ca**)



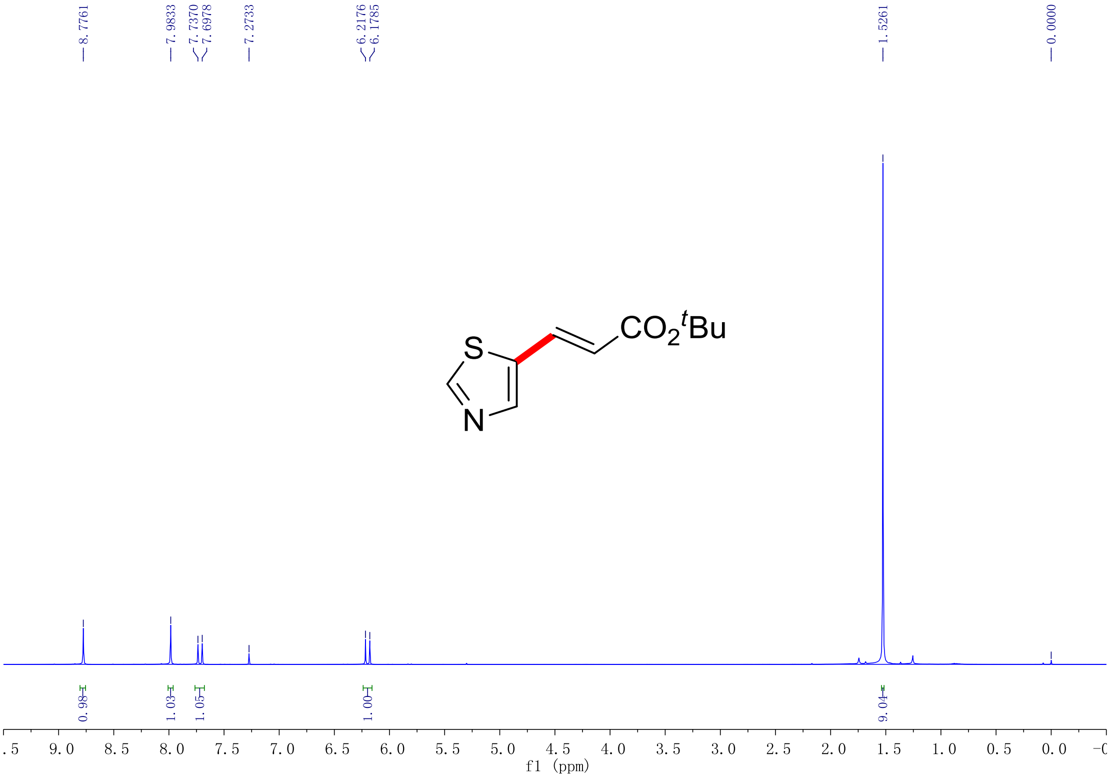


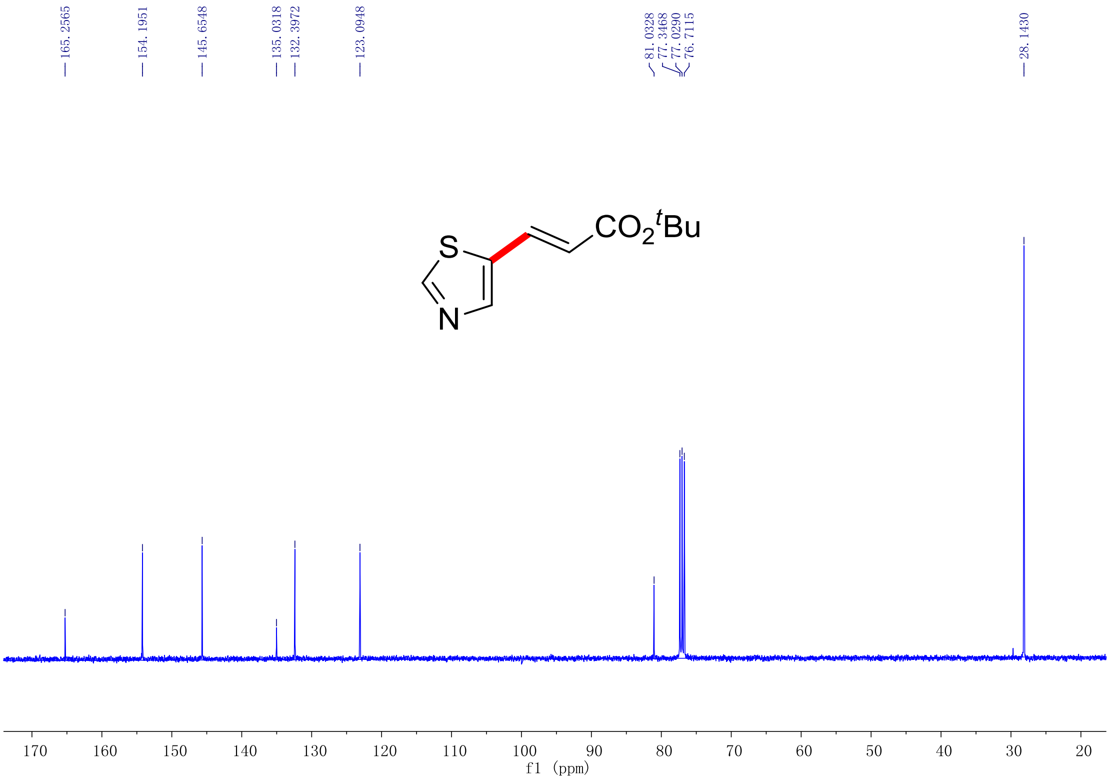
(*E*)-butyl 3-(thiazol-5-yl)acrylate (**3da**)



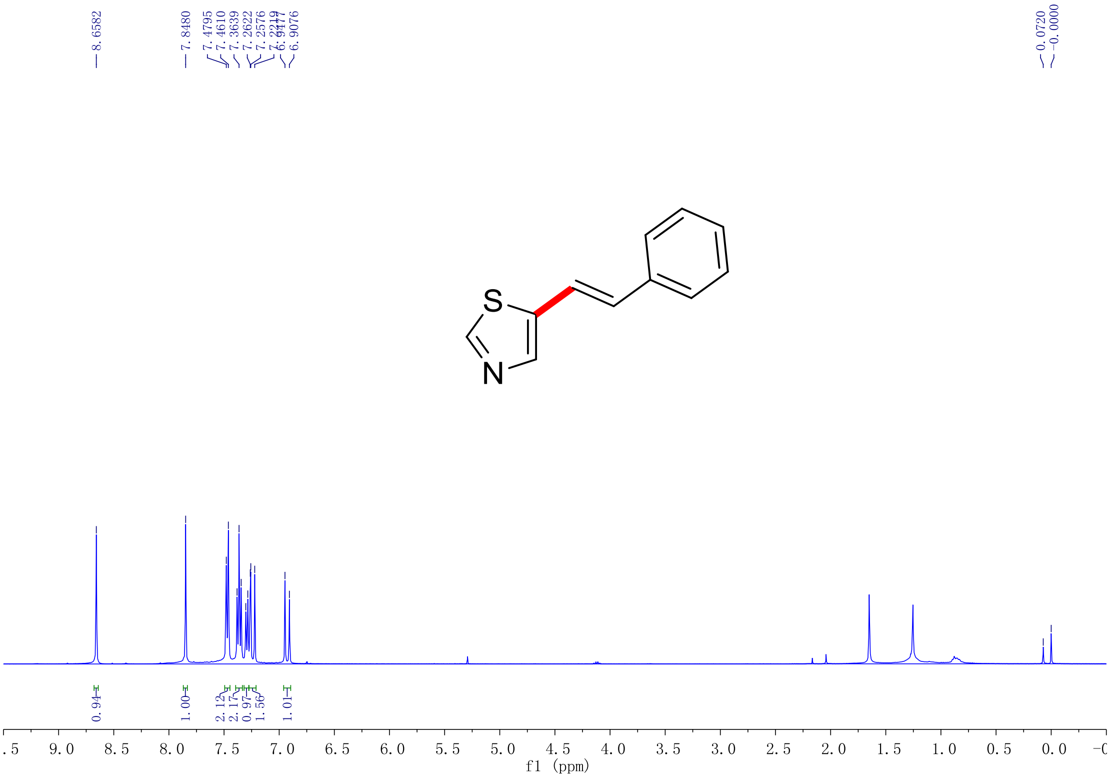


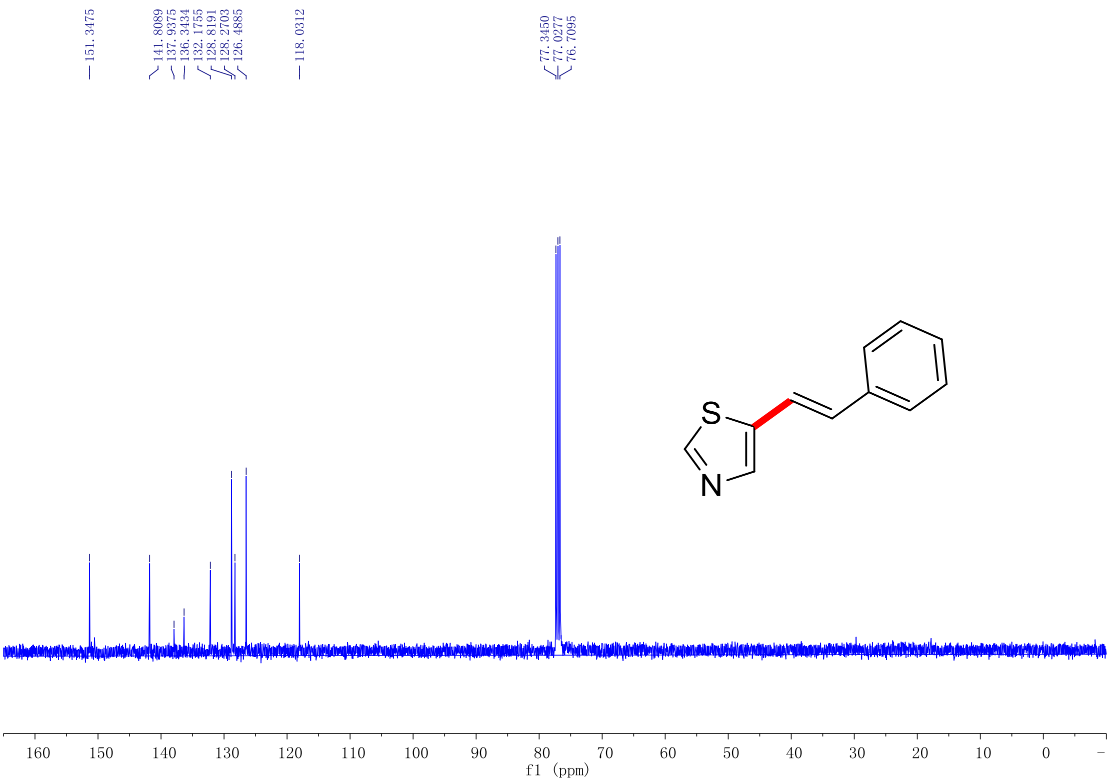
(*E*)-*tert*-butyl 3-(thiazol-5-yl)acrylate (**3db**)



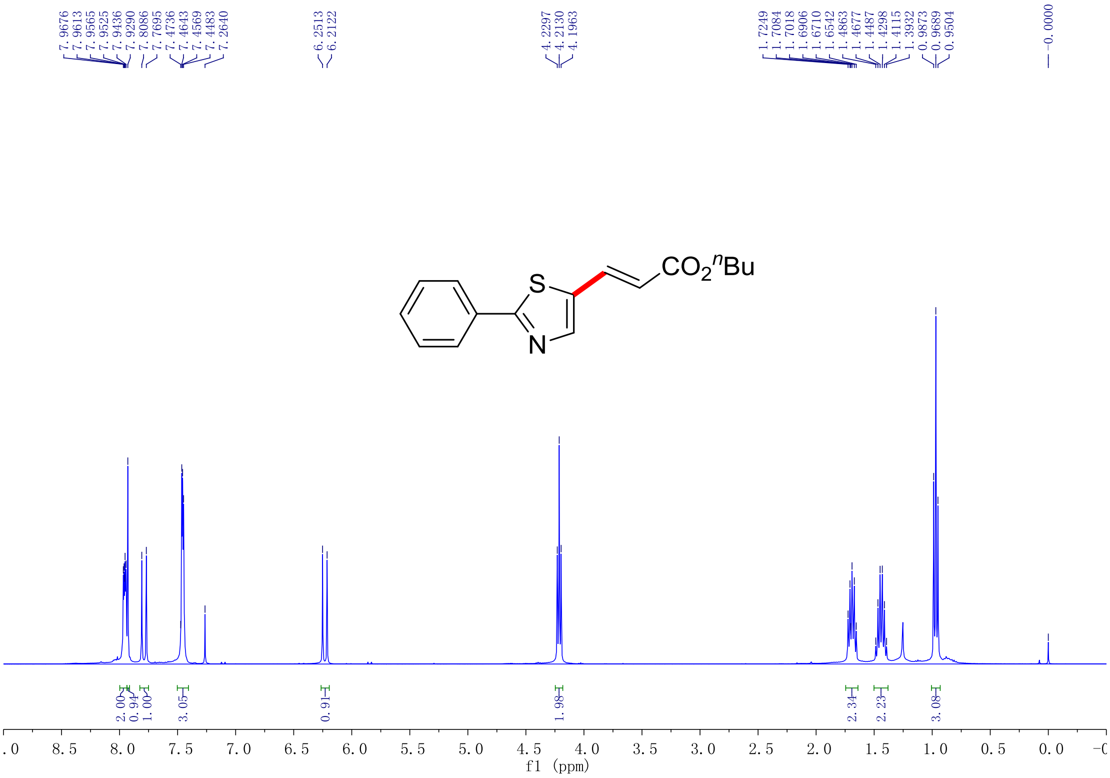


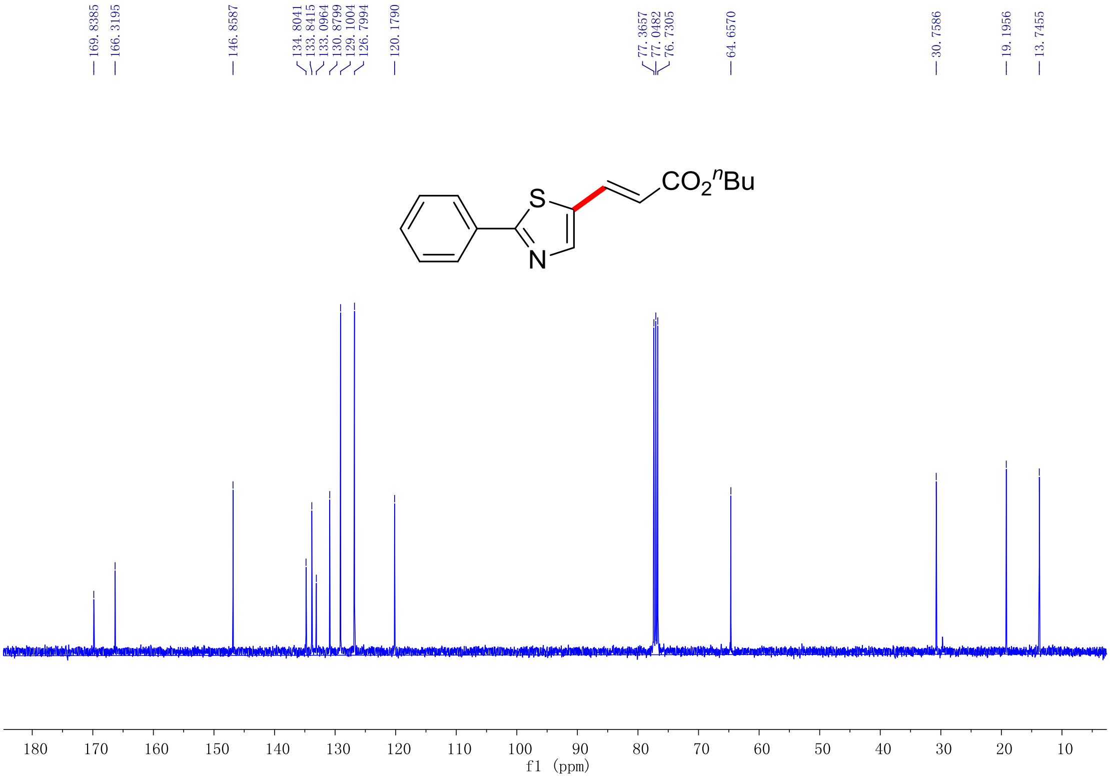
(*E*)-5-styrylthiazole (**3dg**)



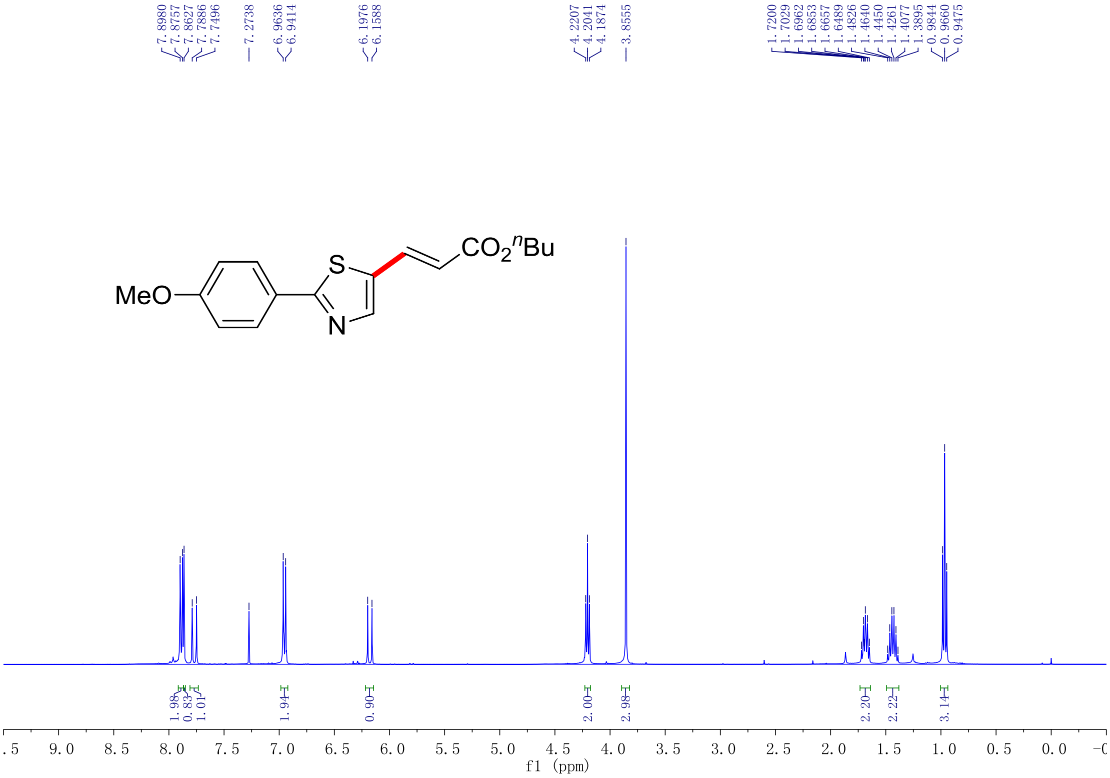


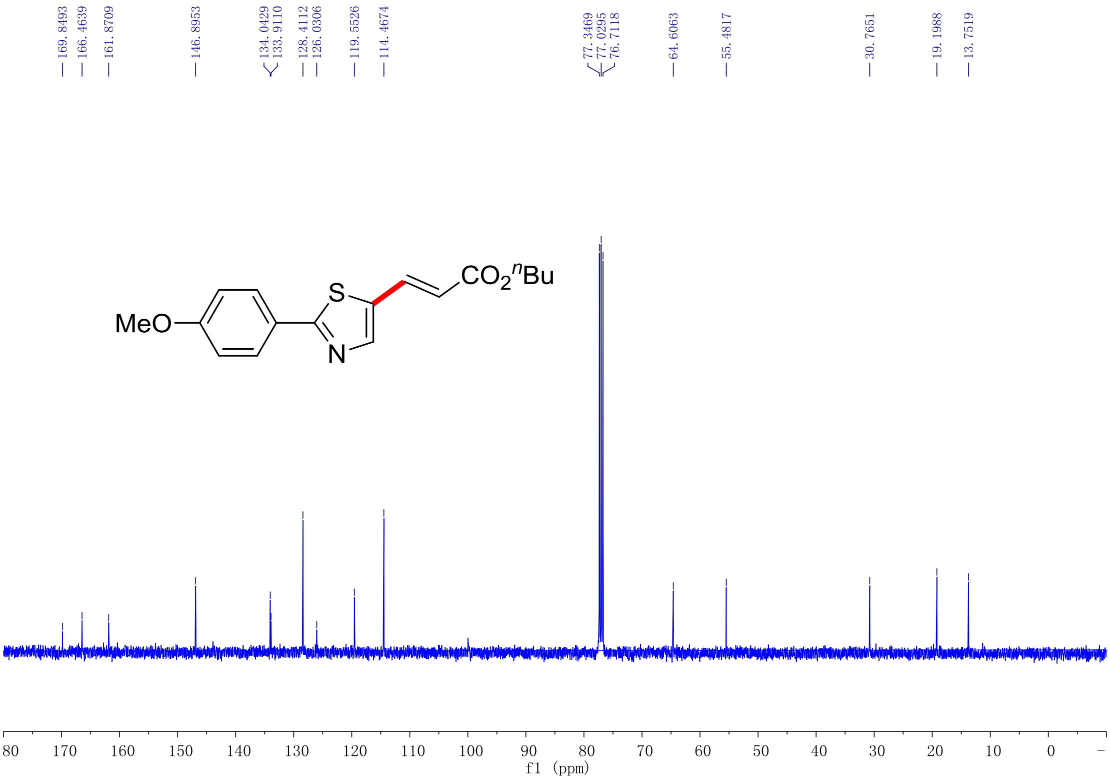
(*E*)-butyl 3-(2-phenylthiazol-5-yl)acrylate (**3ea**)



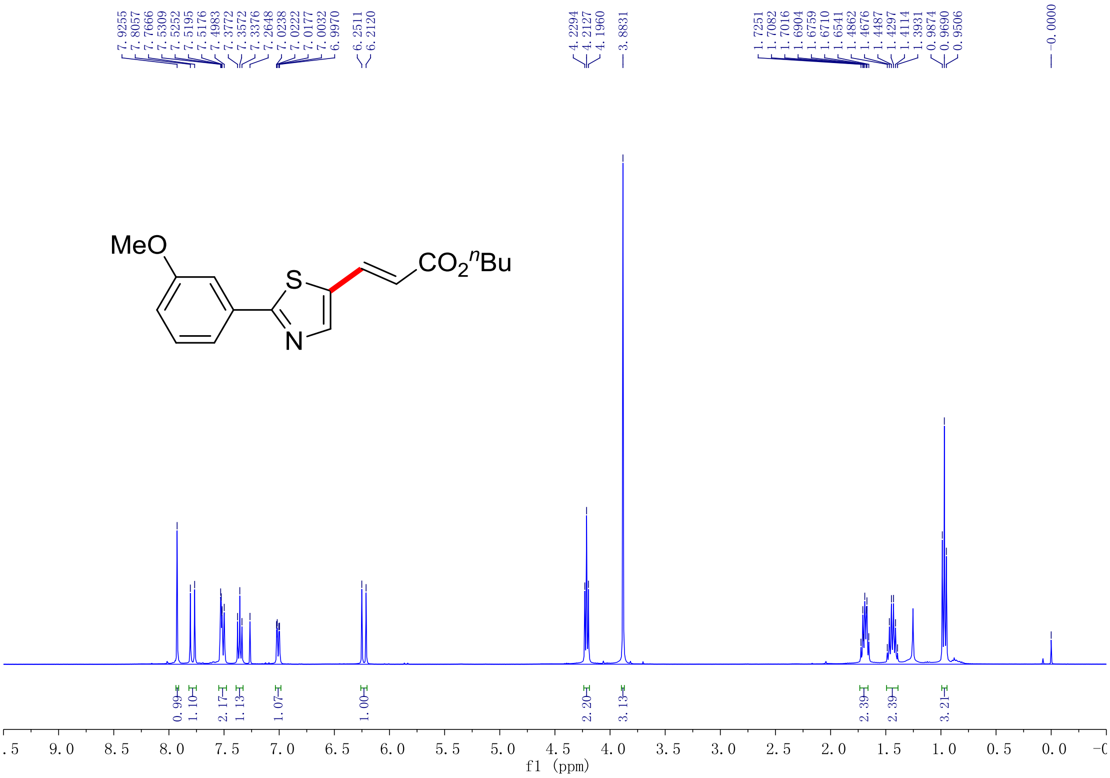


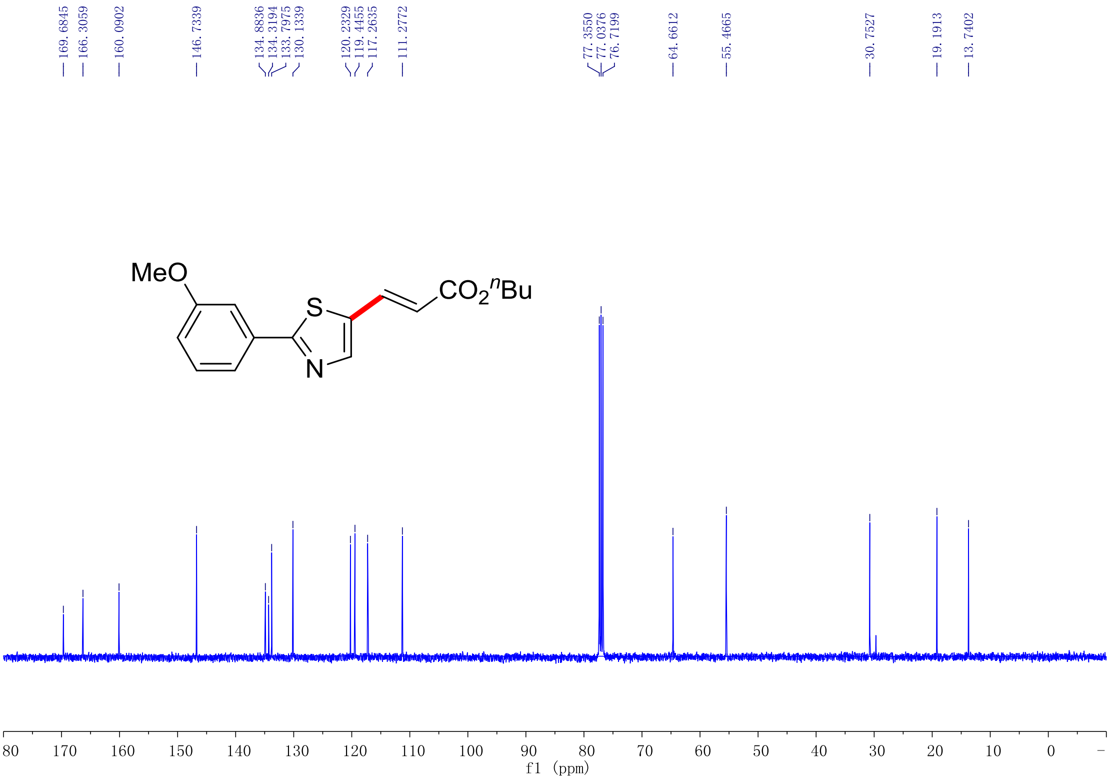
(*E*)-butyl 3-(2-(4-methoxyphenyl)thiazol-5-yl)acrylate (**3fa**)



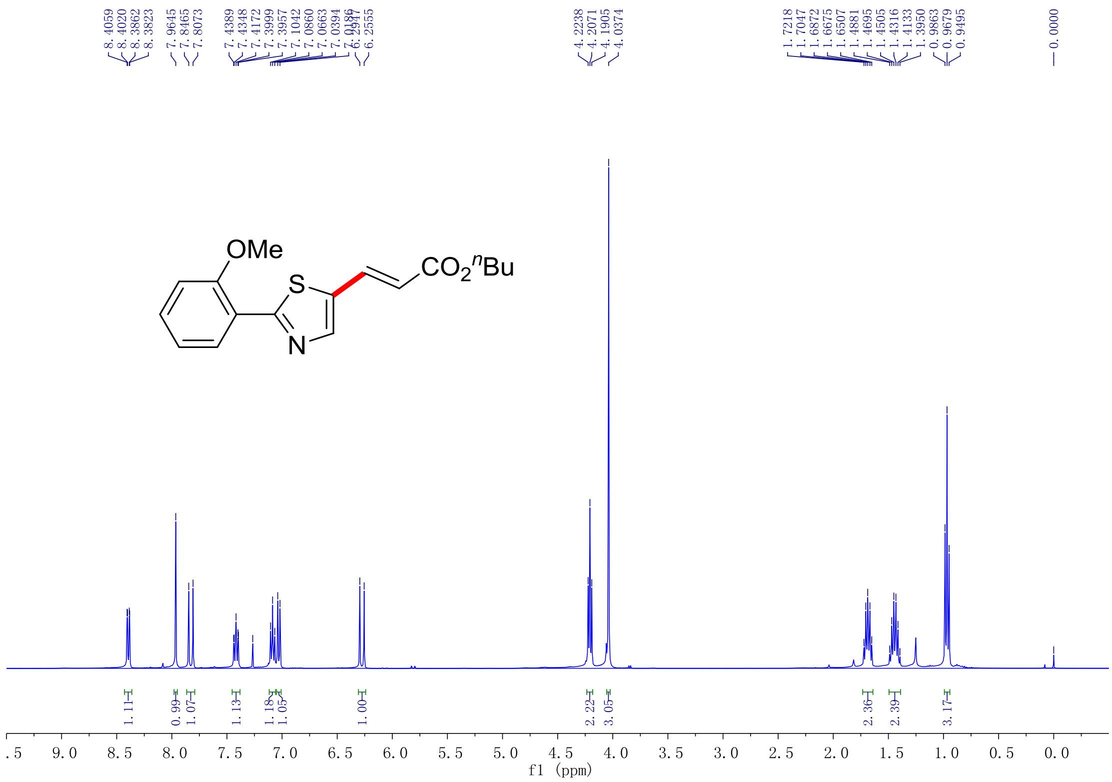


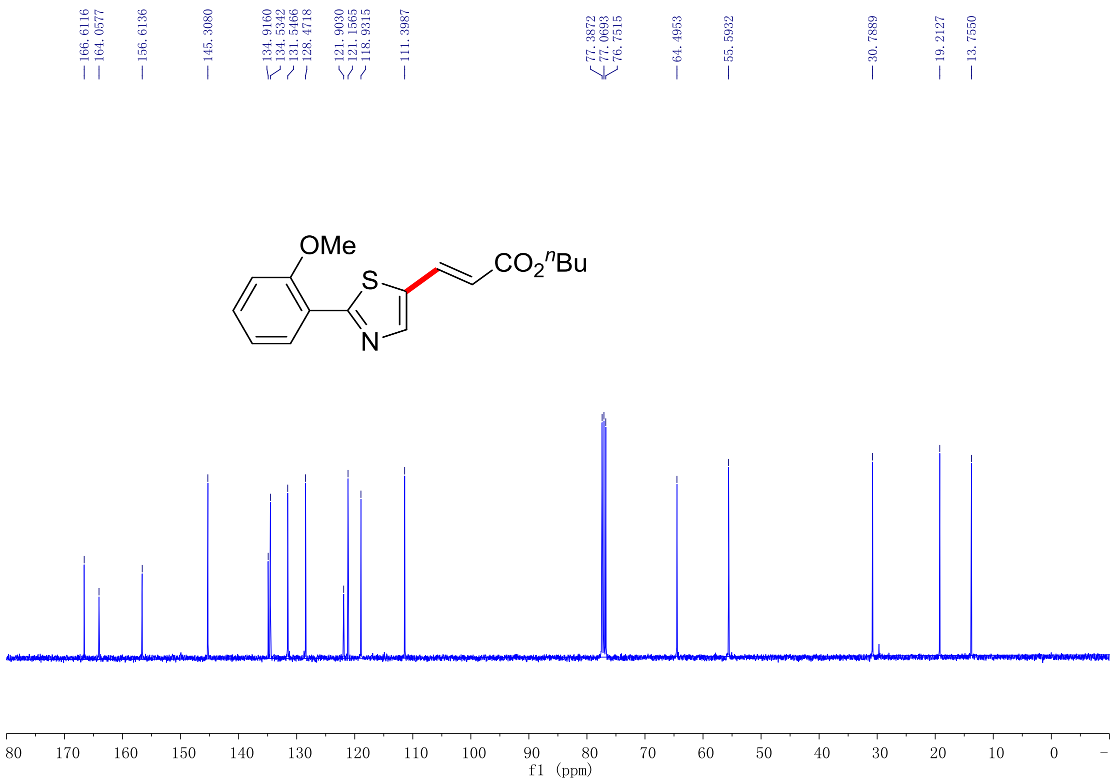
(*E*)-butyl 3-(2-(3-methoxyphenyl)thiazol-5-yl)acrylate (**3ga**)



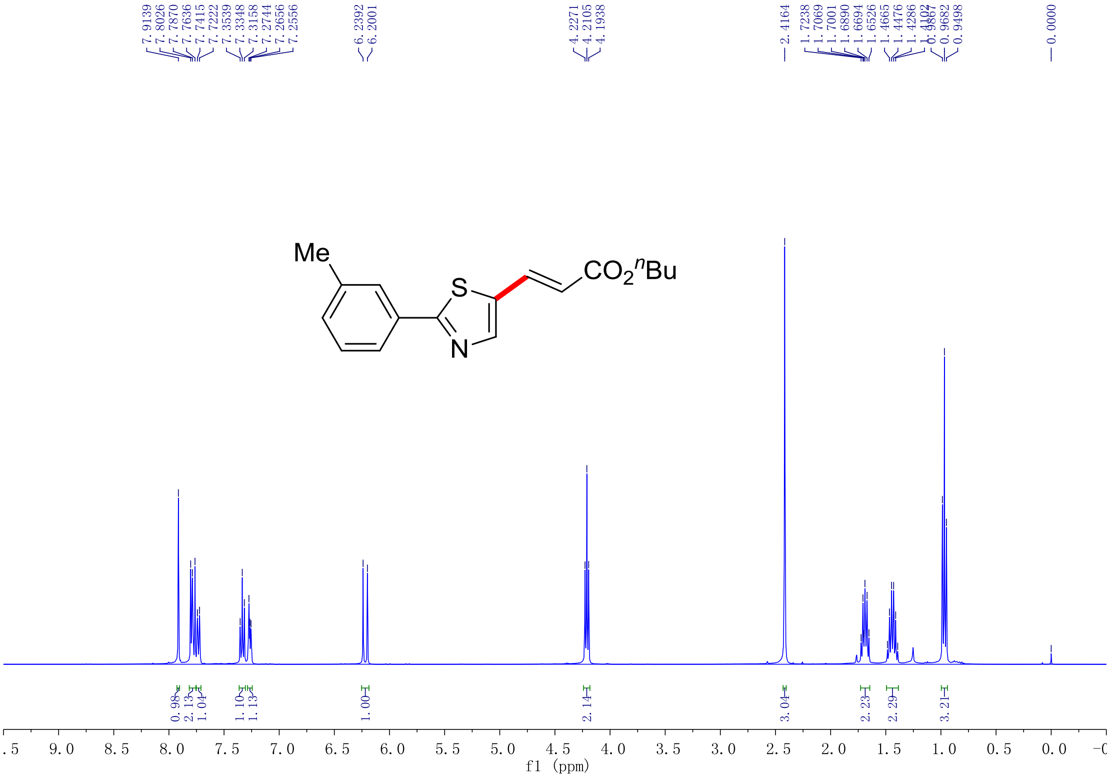


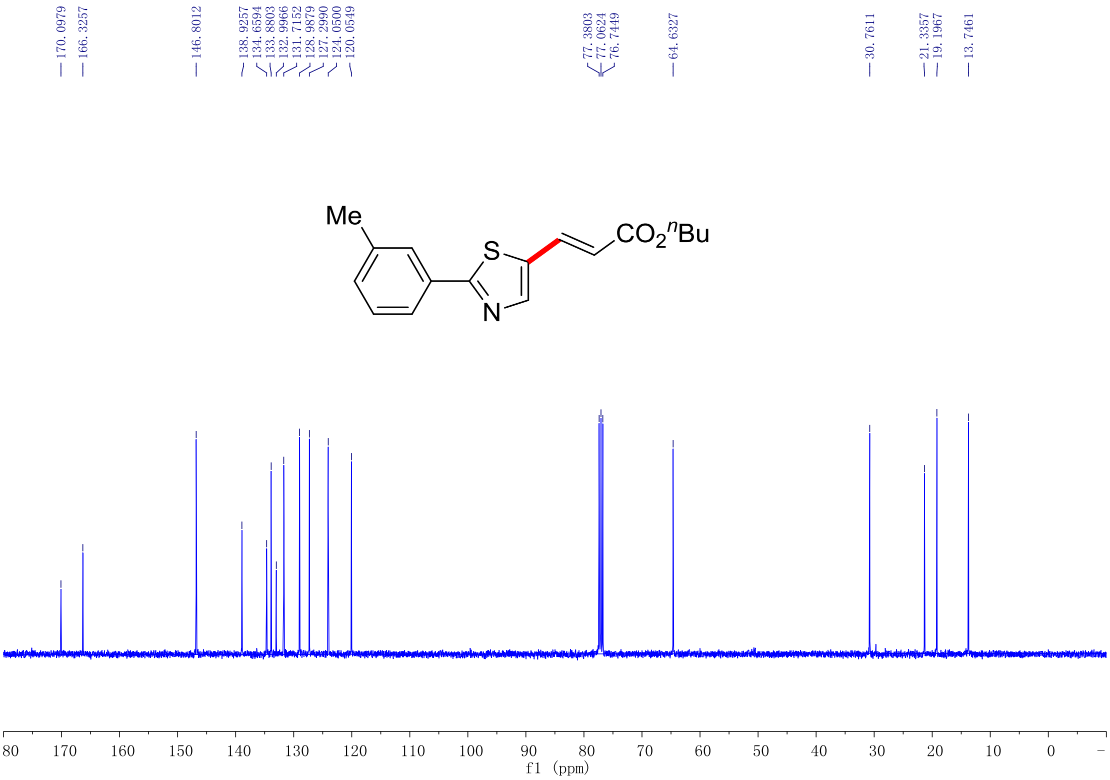
(*E*)-butyl 3-(2-(2-methoxyphenyl)thiazol-5-yl)acrylate (**3ha**)



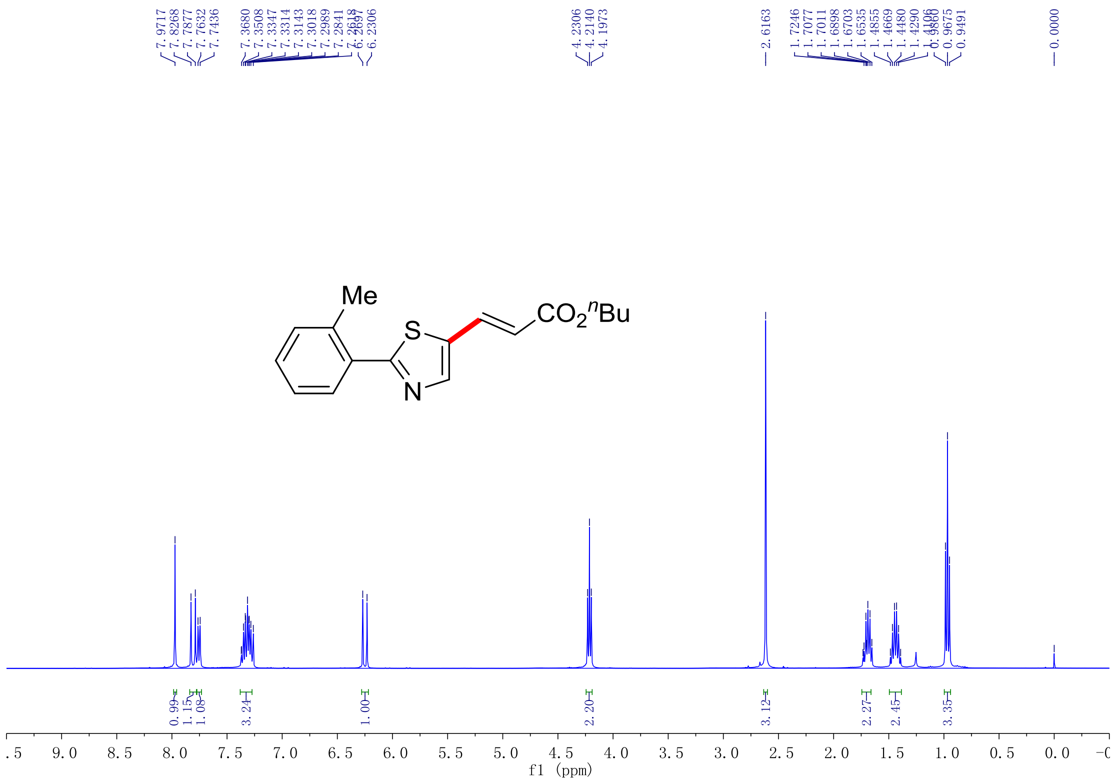


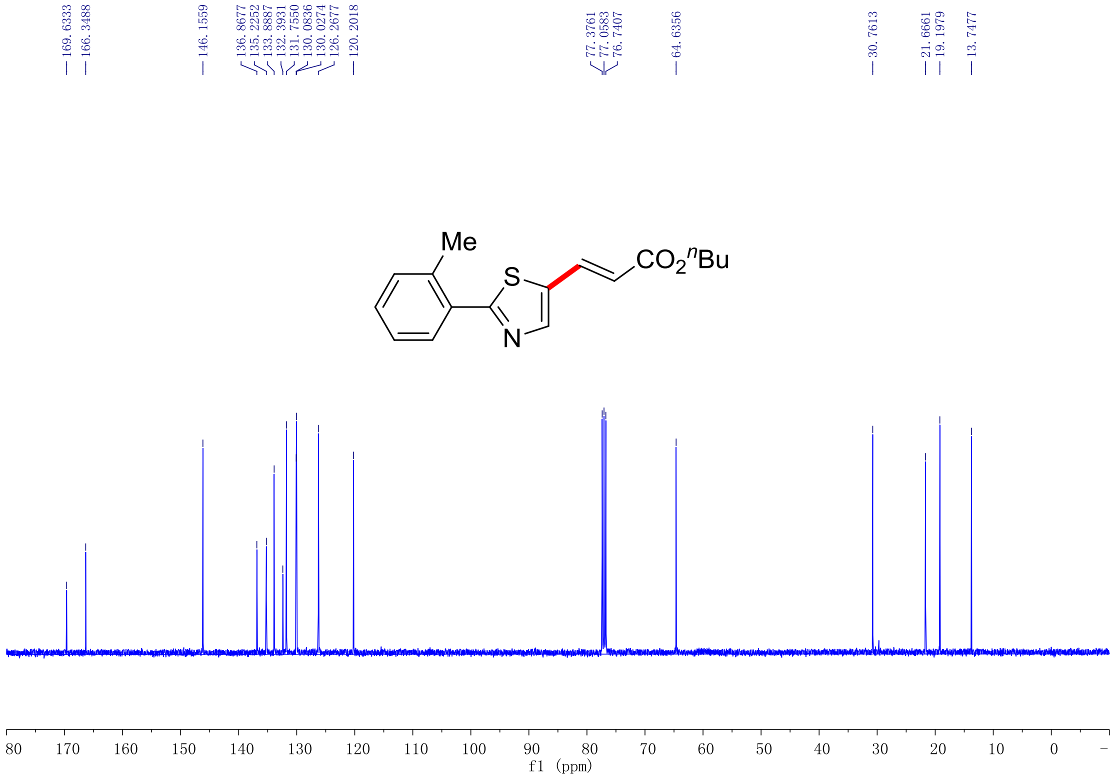
(*E*)-butyl 3-(2-(*m*-tolyl)thiazol-5-yl)acrylate (**3ia**)



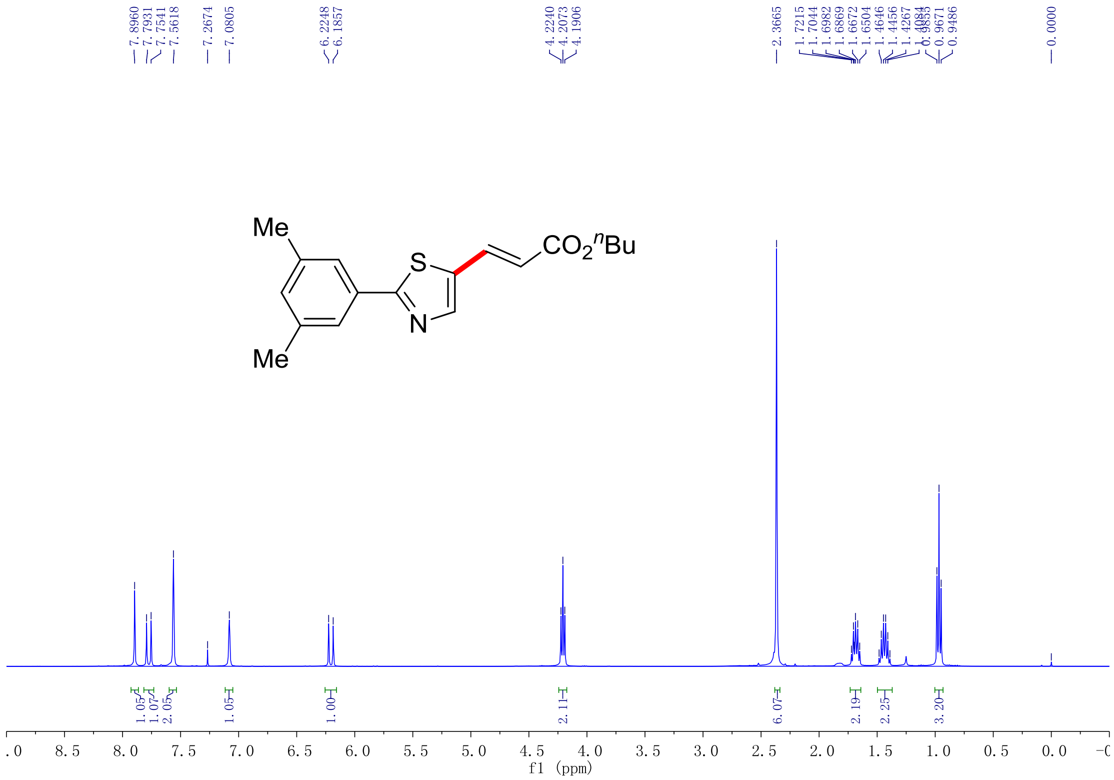


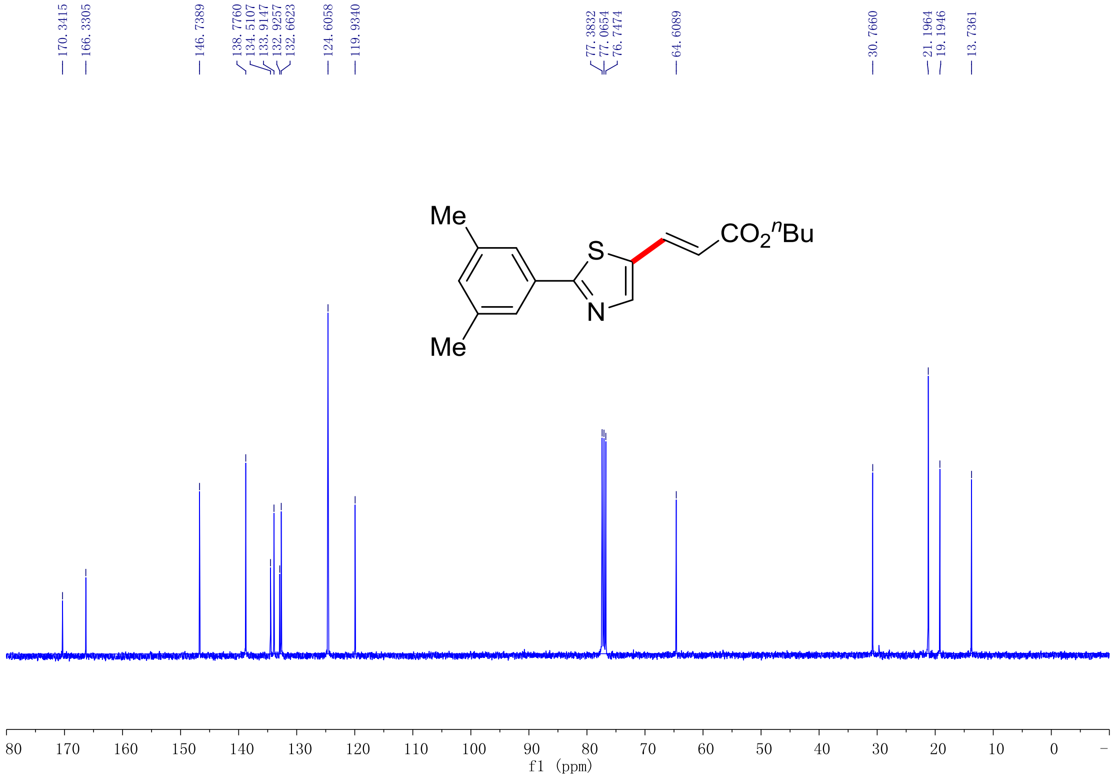
(*E*)-butyl 3-(2-(*o*-tolyl)thiazol-5-yl)acrylate (**3ja**)



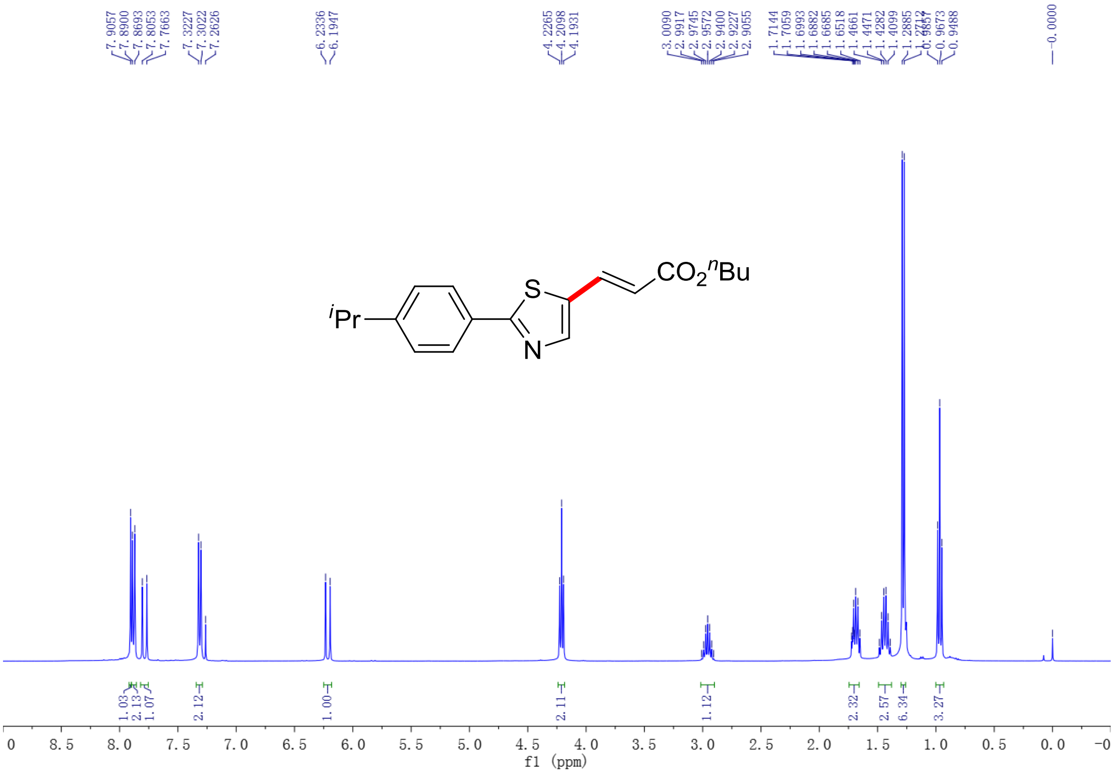


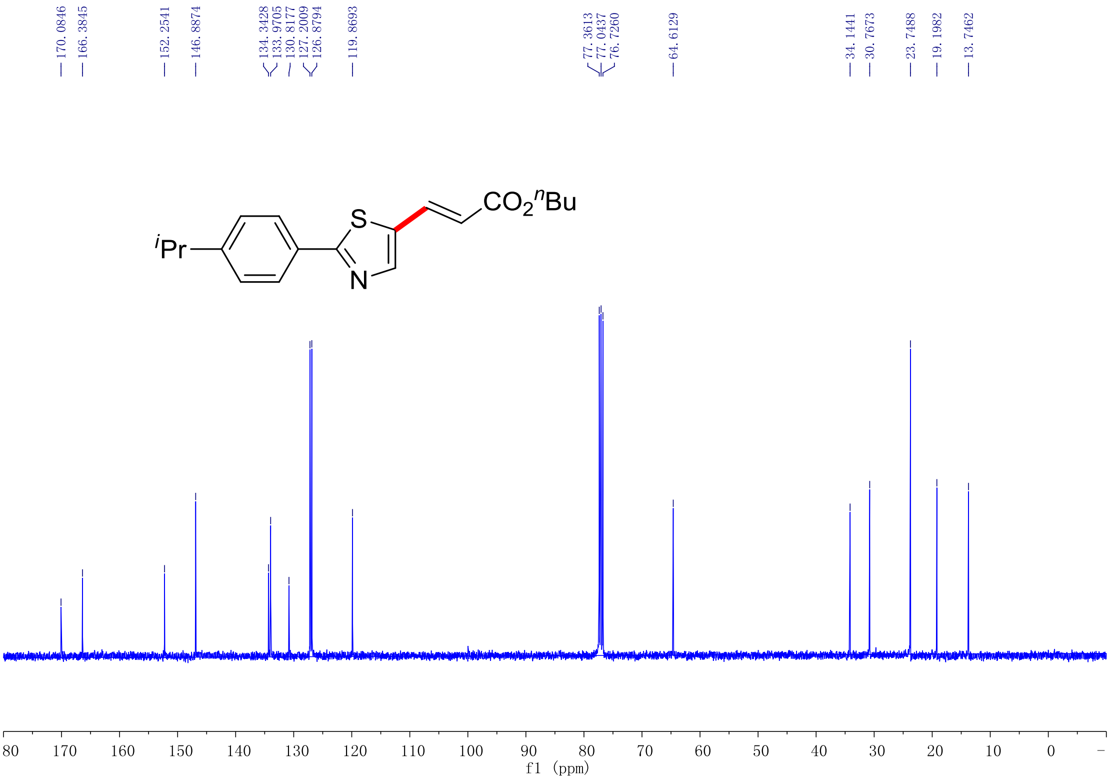
(*E*)-butyl 3-(2-(3,5-dimethylphenyl)thiazol-5-yl)acrylate (**3ka**)



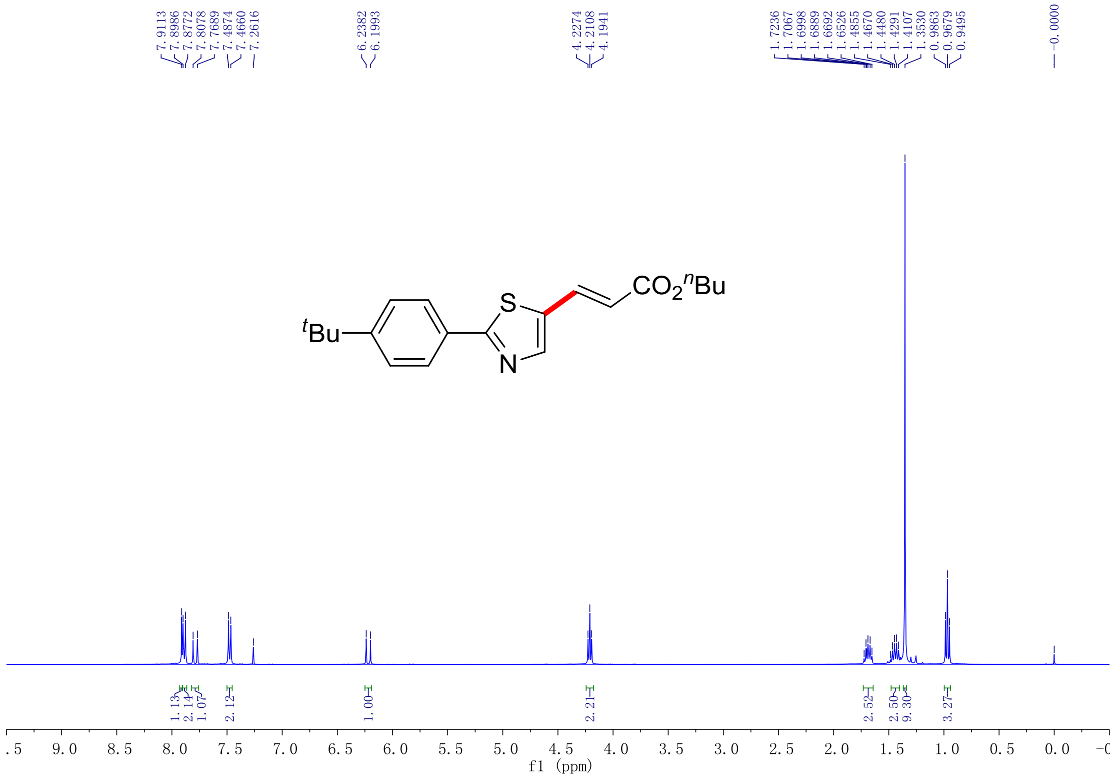


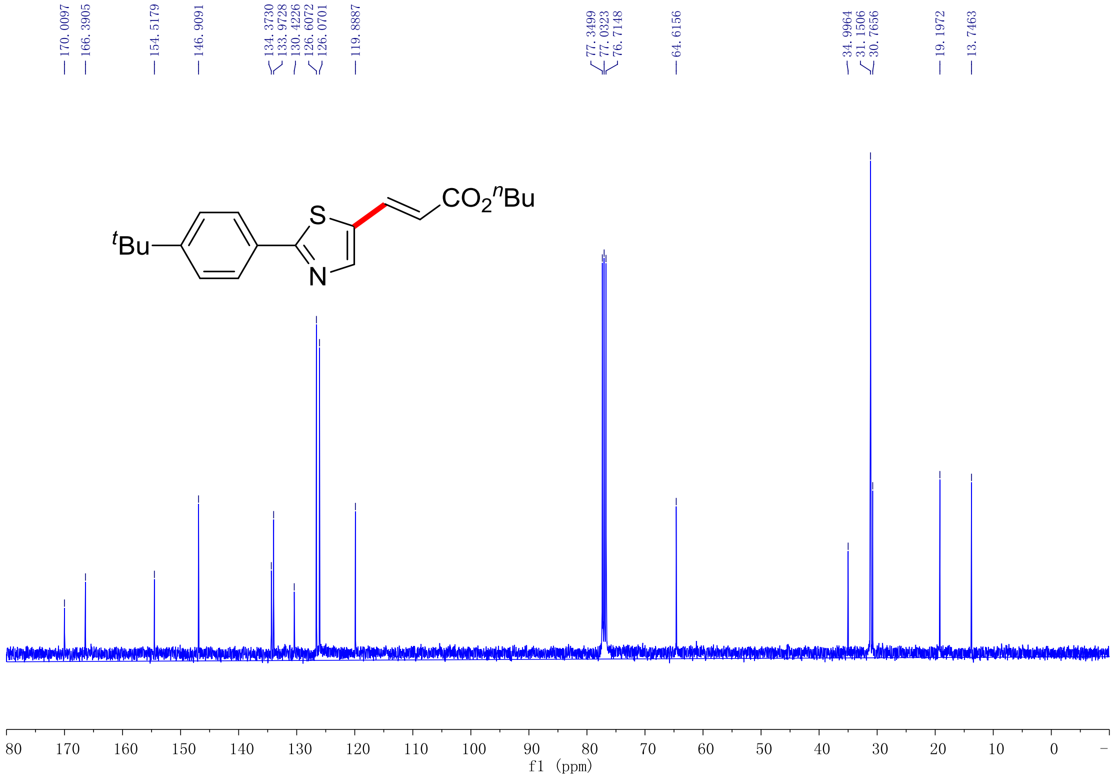
(*E*)-butyl 3-(2-(4-*iso*propylphenyl)thiazol-5-yl)acrylate (**3la**)



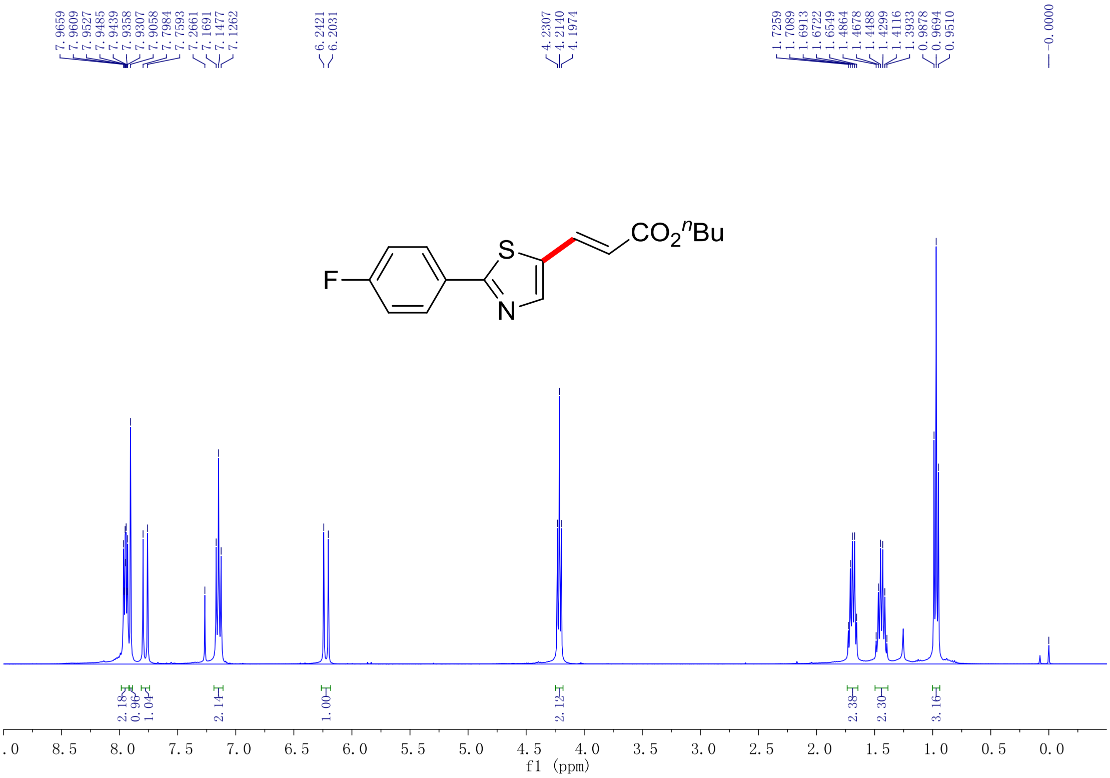


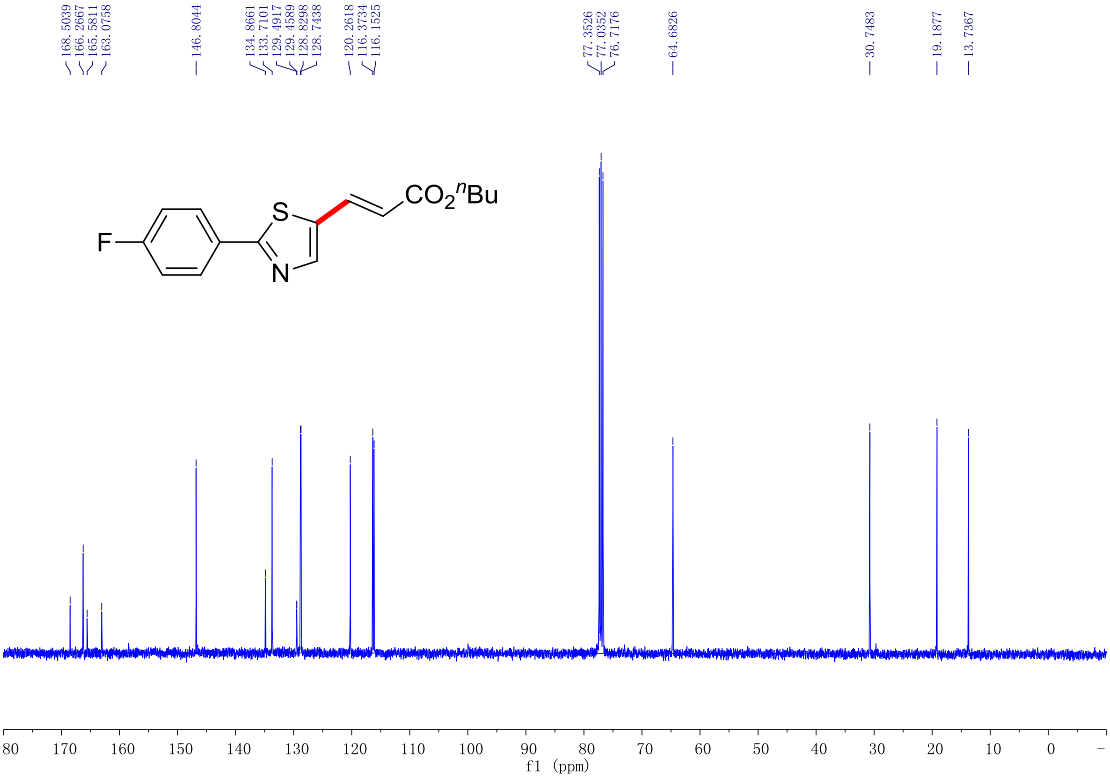
(*E*)-butyl 3-(2-(4-(*tert*-butyl)phenyl)thiazol-5-yl)acrylate (**3ma**)



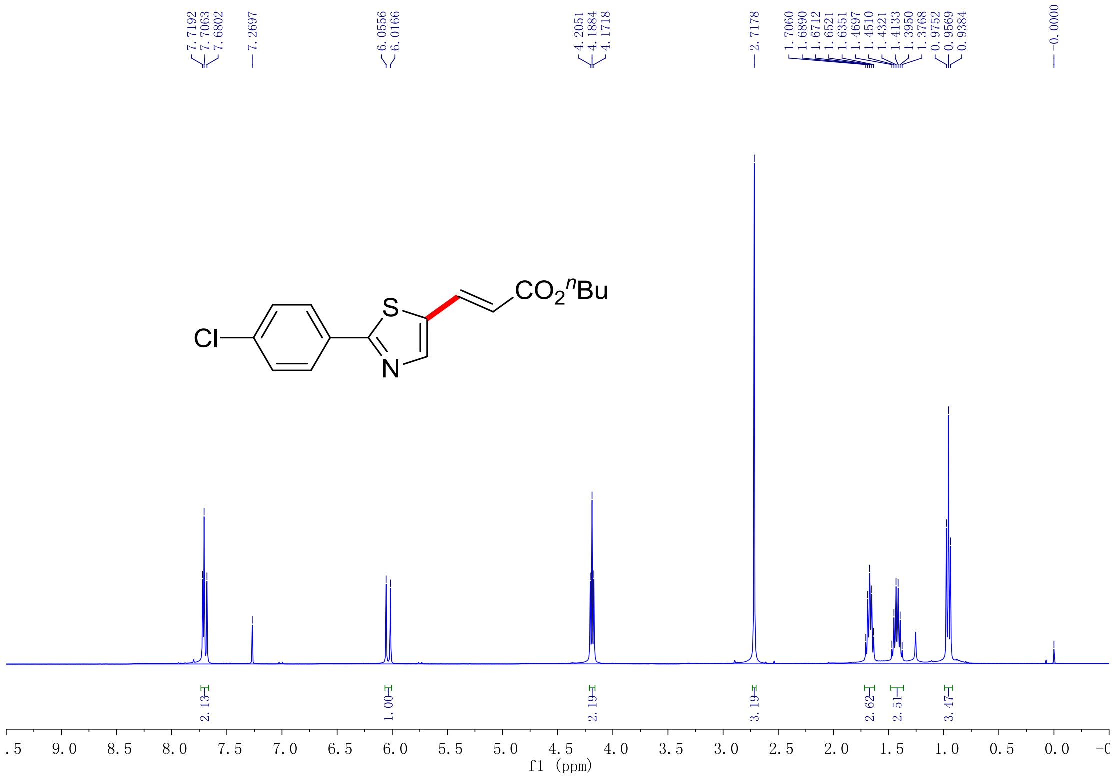


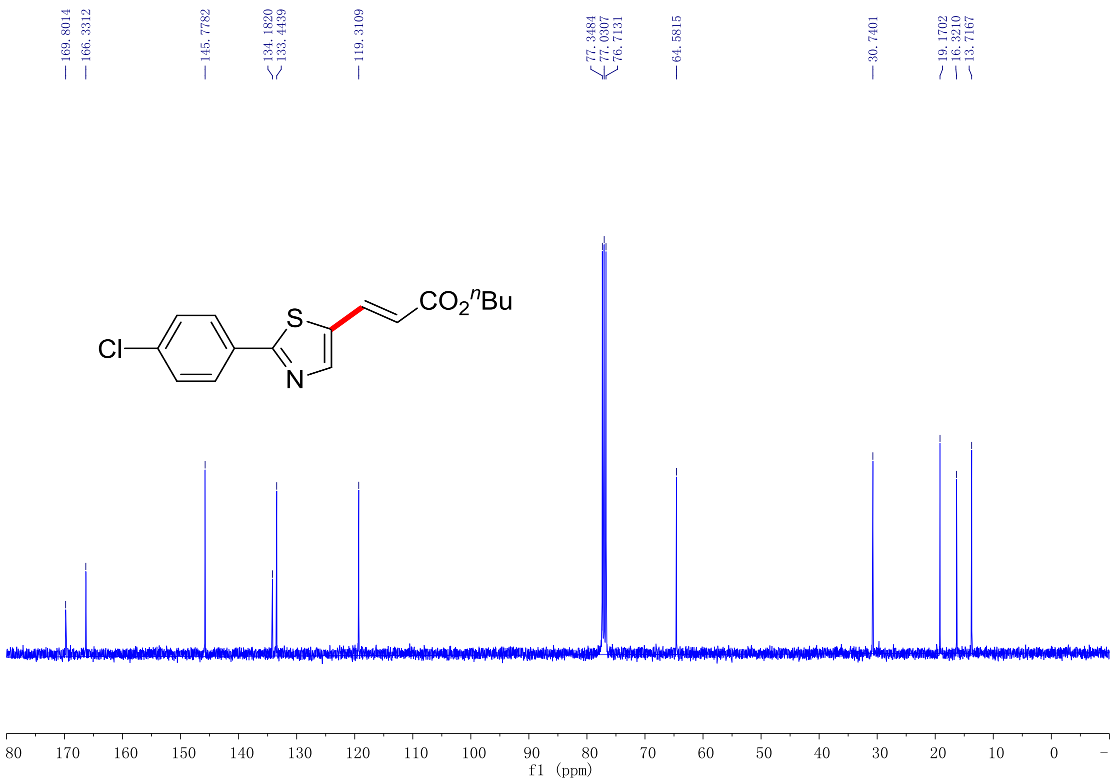
(*E*)-butyl 3-(2-(4-fluorophenyl)thiazol-5-yl)acrylate (**3na**)



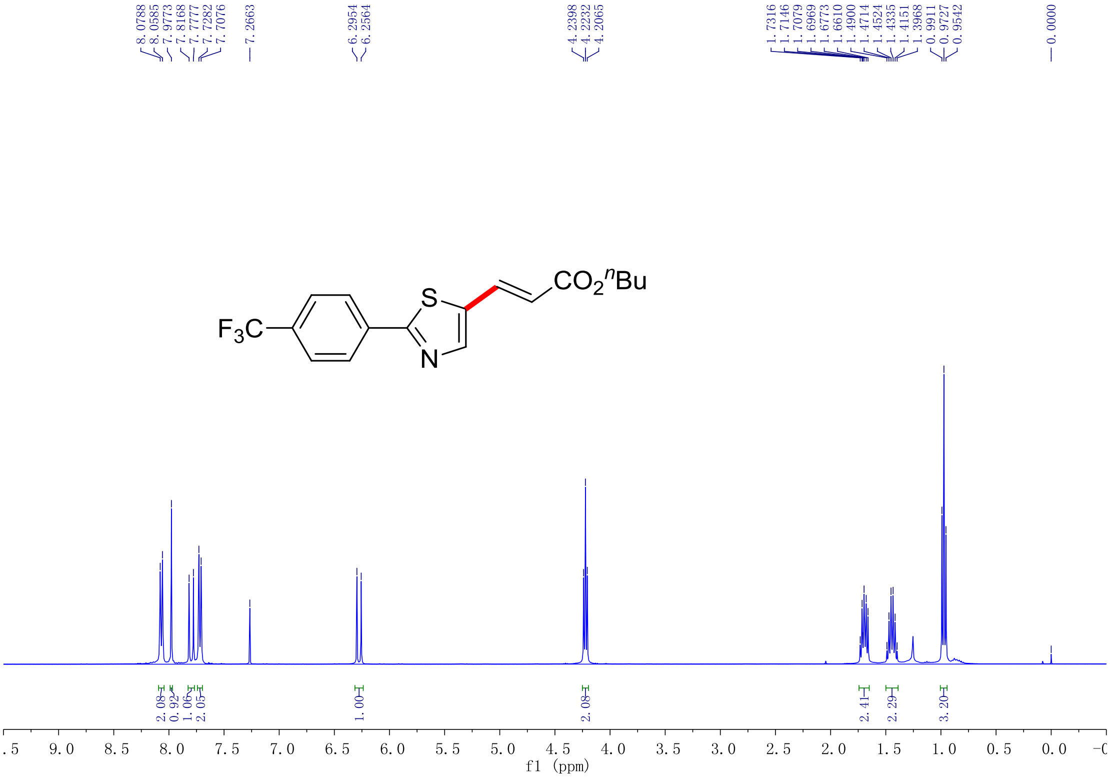


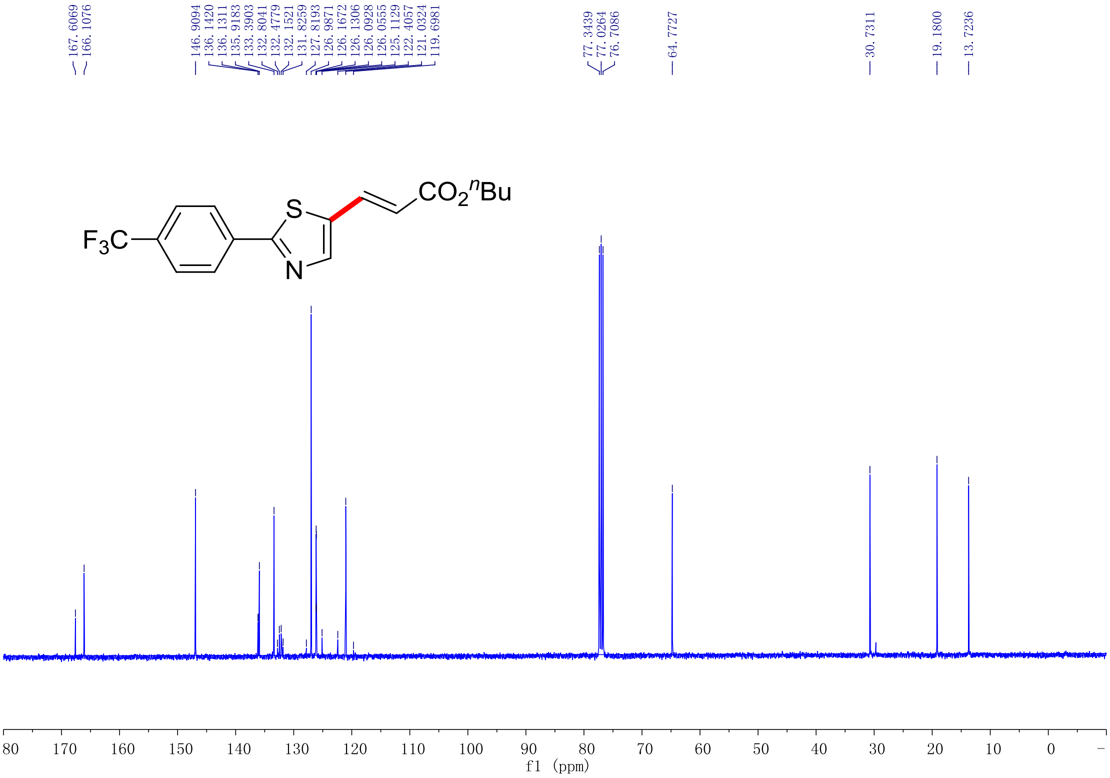
(*E*)-butyl 3-(2-(4-chlorophenyl)thiazol-5-yl)acrylate (**3oa**)



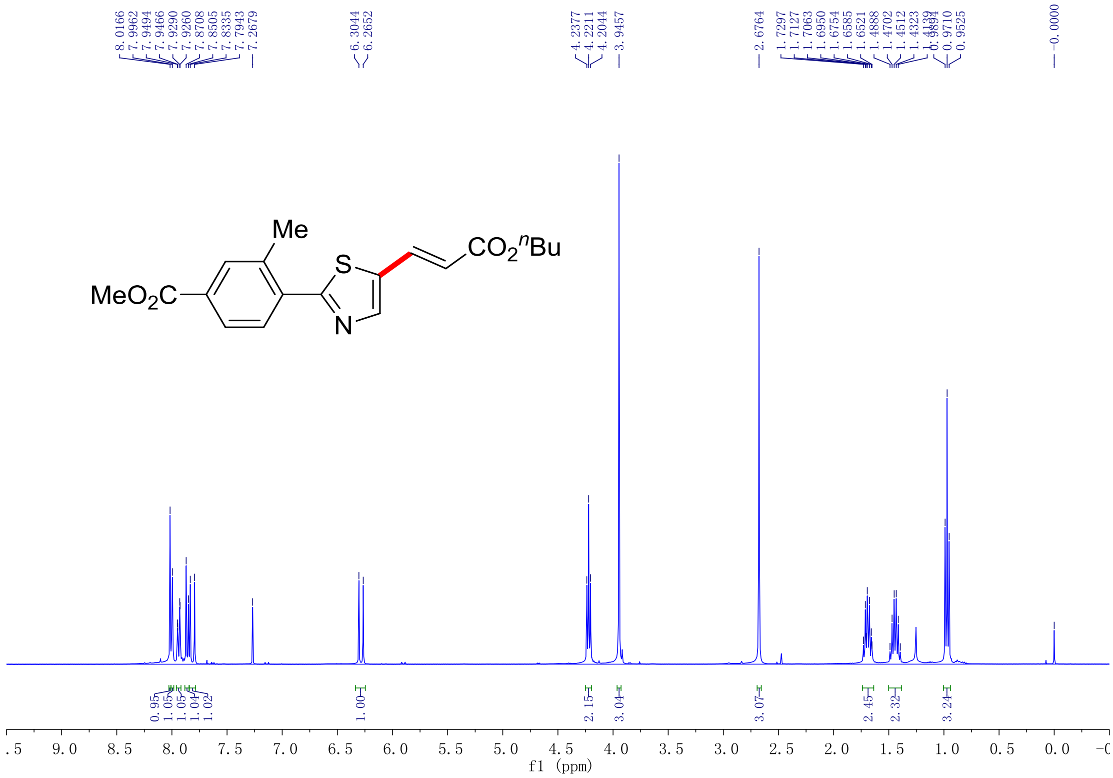


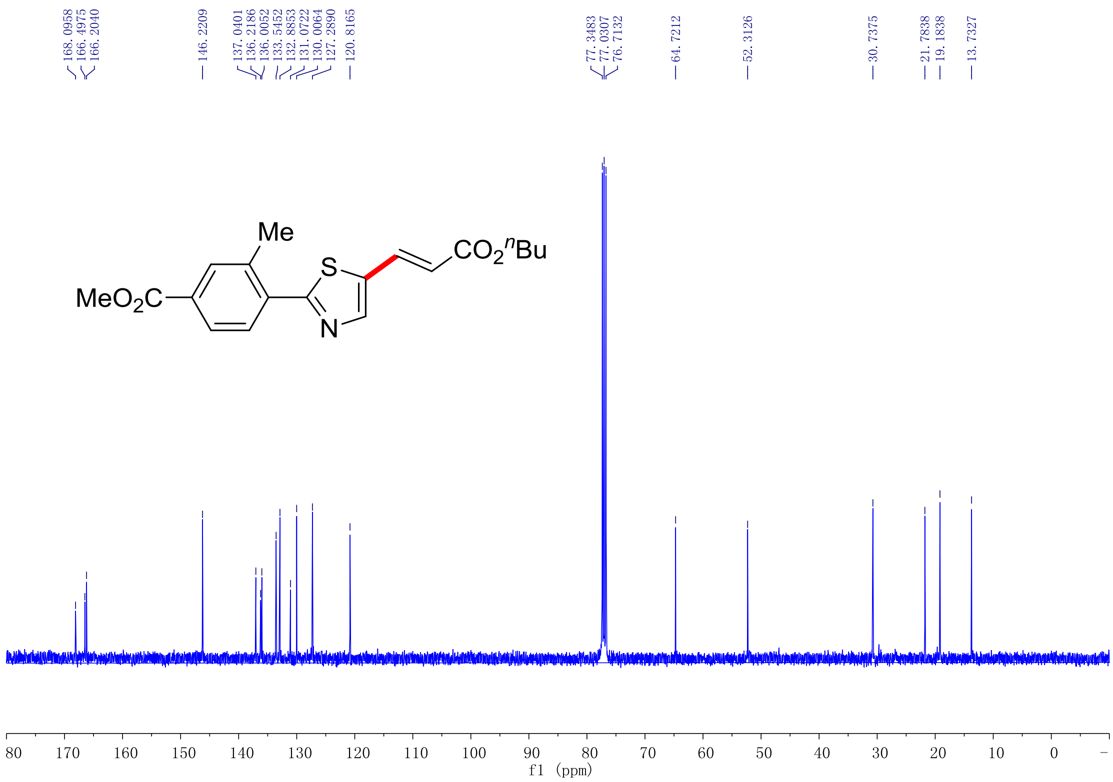
(*E*)-butyl 3-(2-(4-(trifluoromethyl)phenyl)thiazol-5-yl)acrylate (**3pa**)



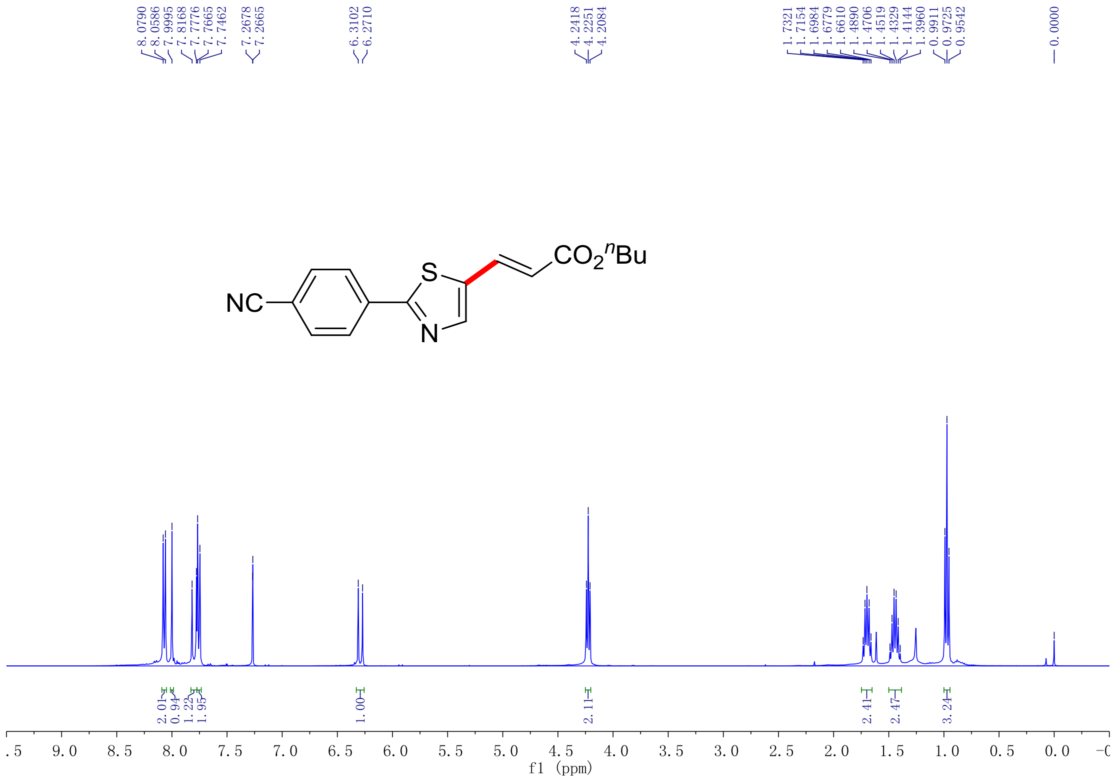


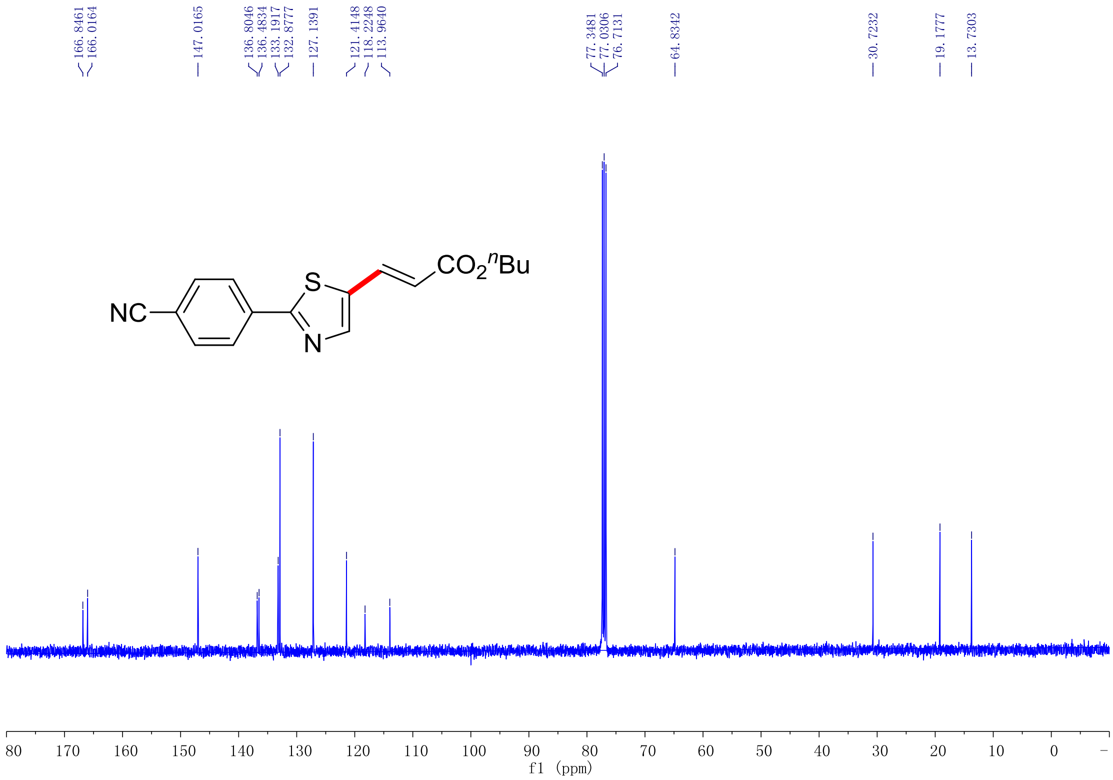
(*E*)-methyl 4-(5-(3-butoxy-3-oxoprop-1-en-1-yl)thiazol-2-yl)-3-methylbenzoate (**3qa**)



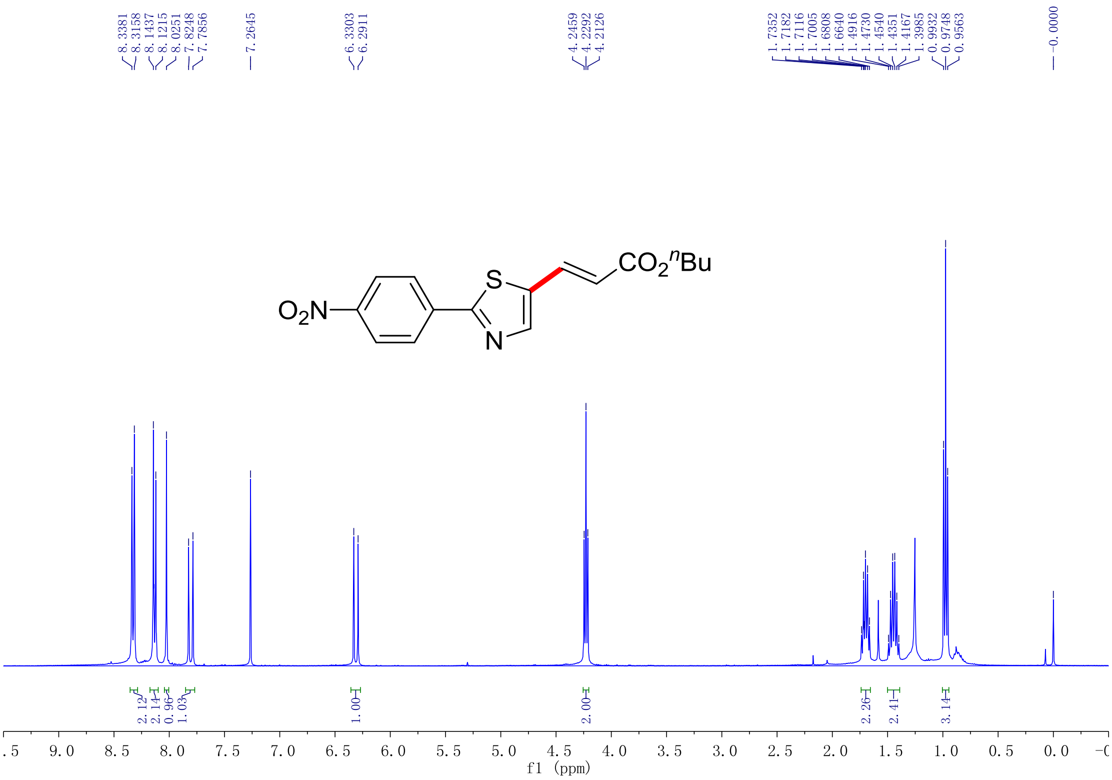


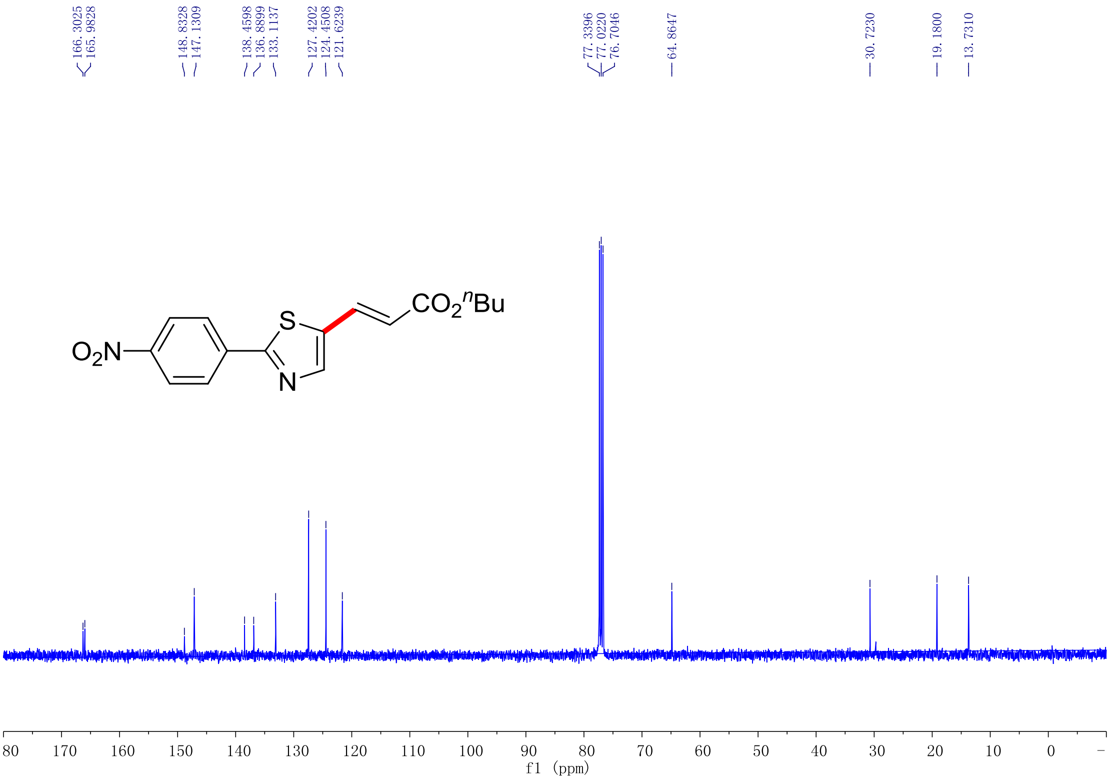
(*E*)-butyl 3-(2-(4-cyanophenyl)thiazol-5-yl)acrylate (**3ra**)



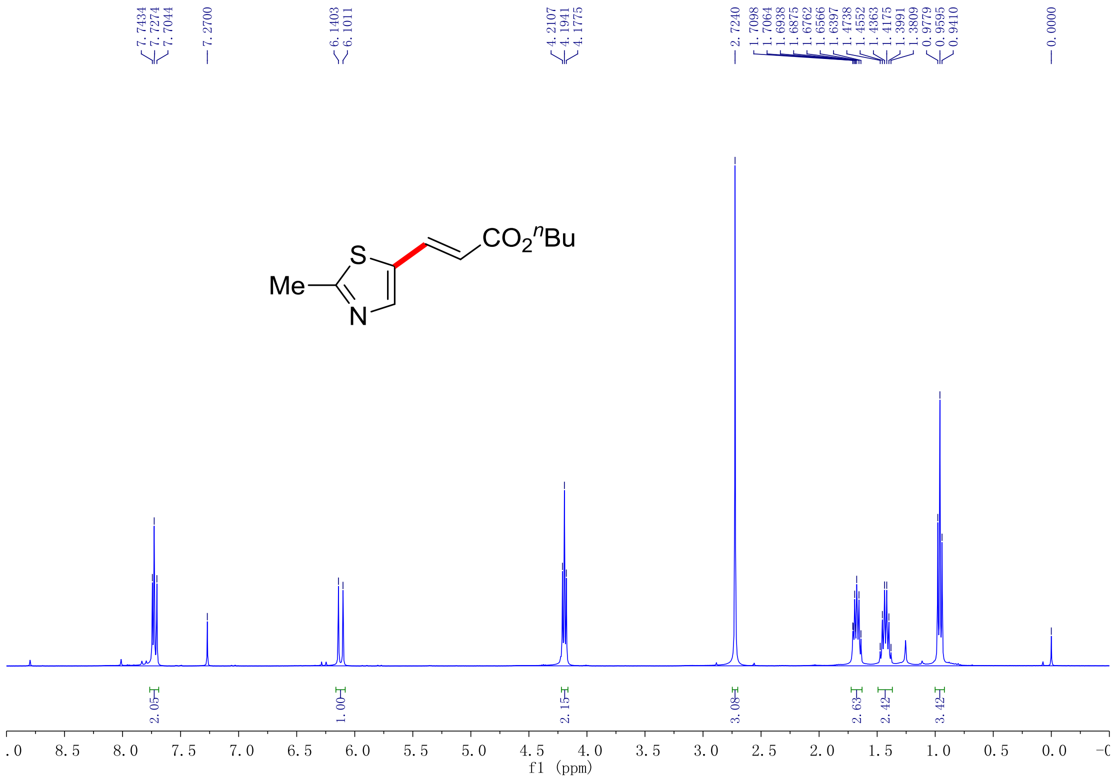


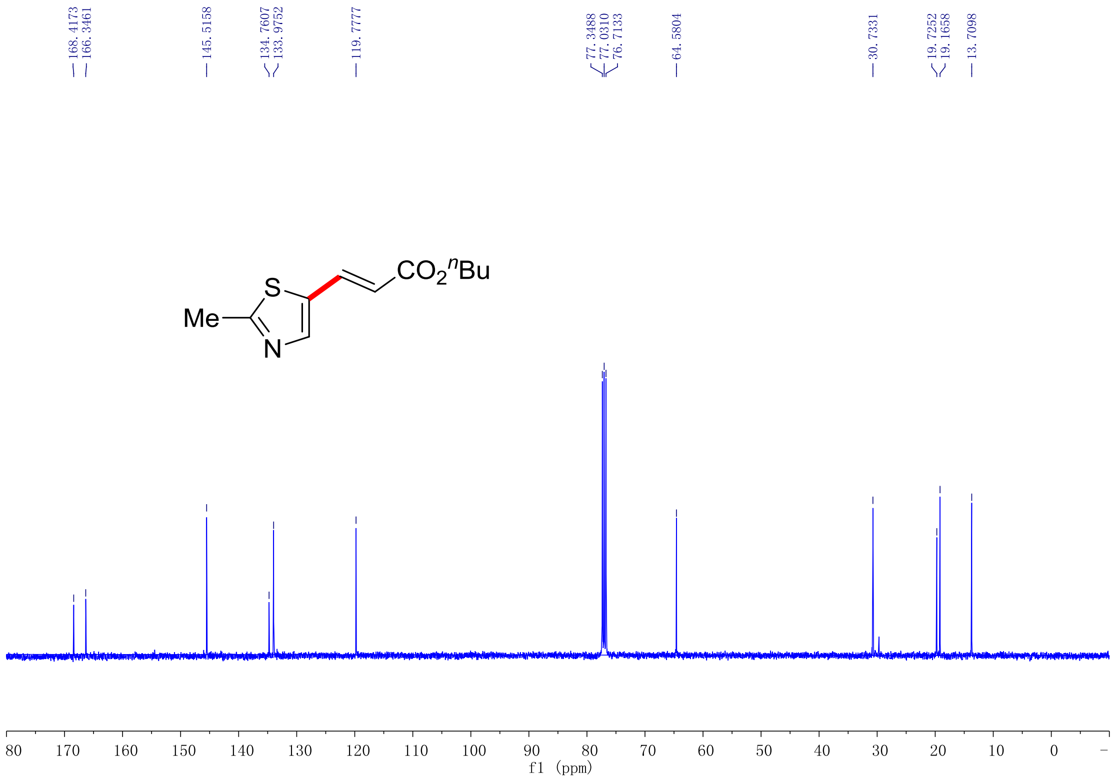
(*E*)-butyl 3-(2-(4-nitrophenyl)thiazol-5-yl)acrylate (**3sa**)



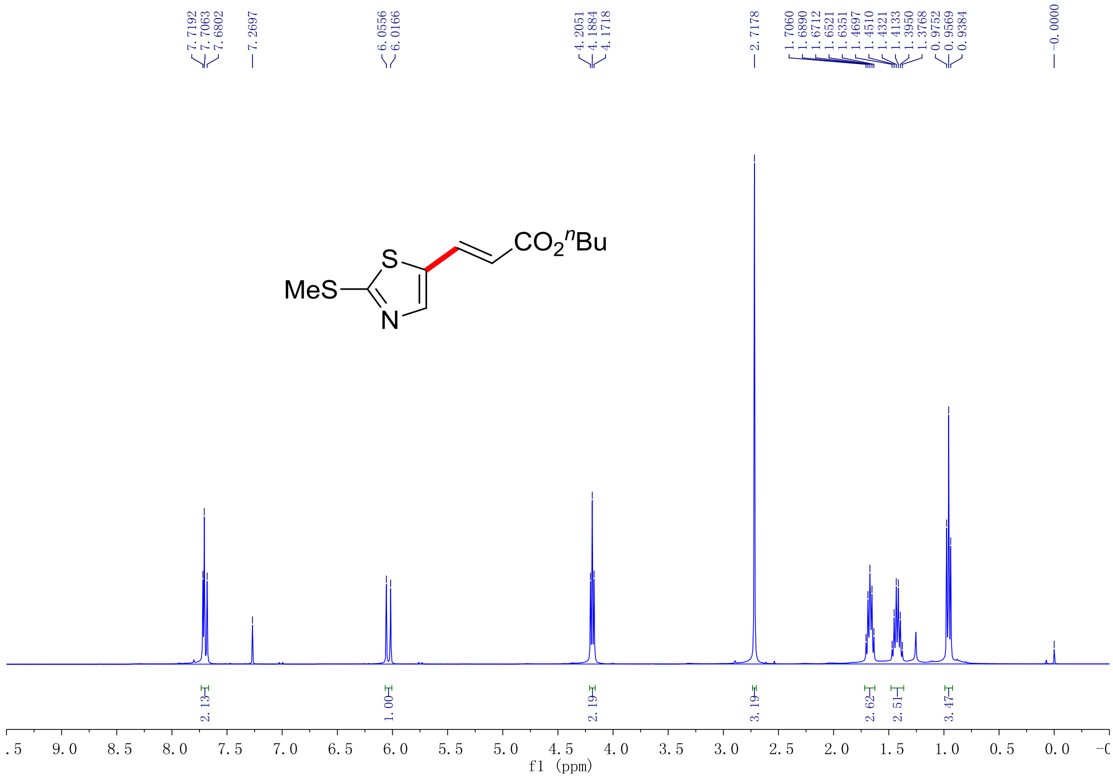


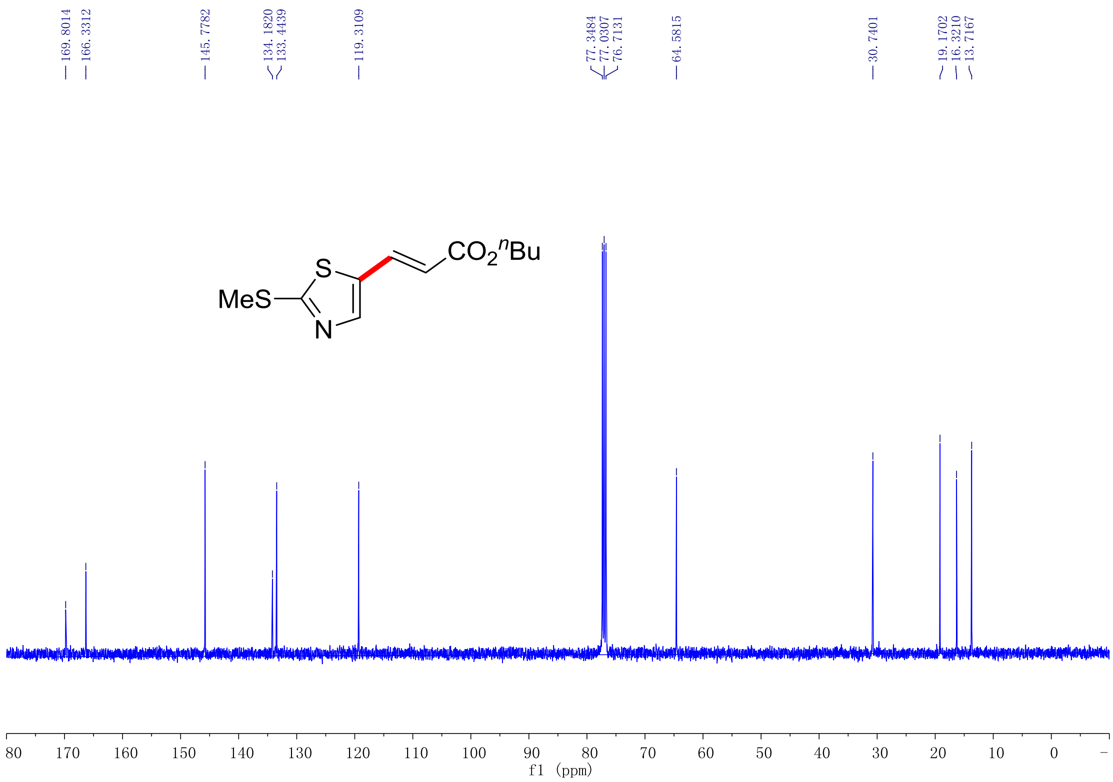
(*E*)-butyl 3-(2-methylthiazol-5-yl)acrylate (**3ta**)



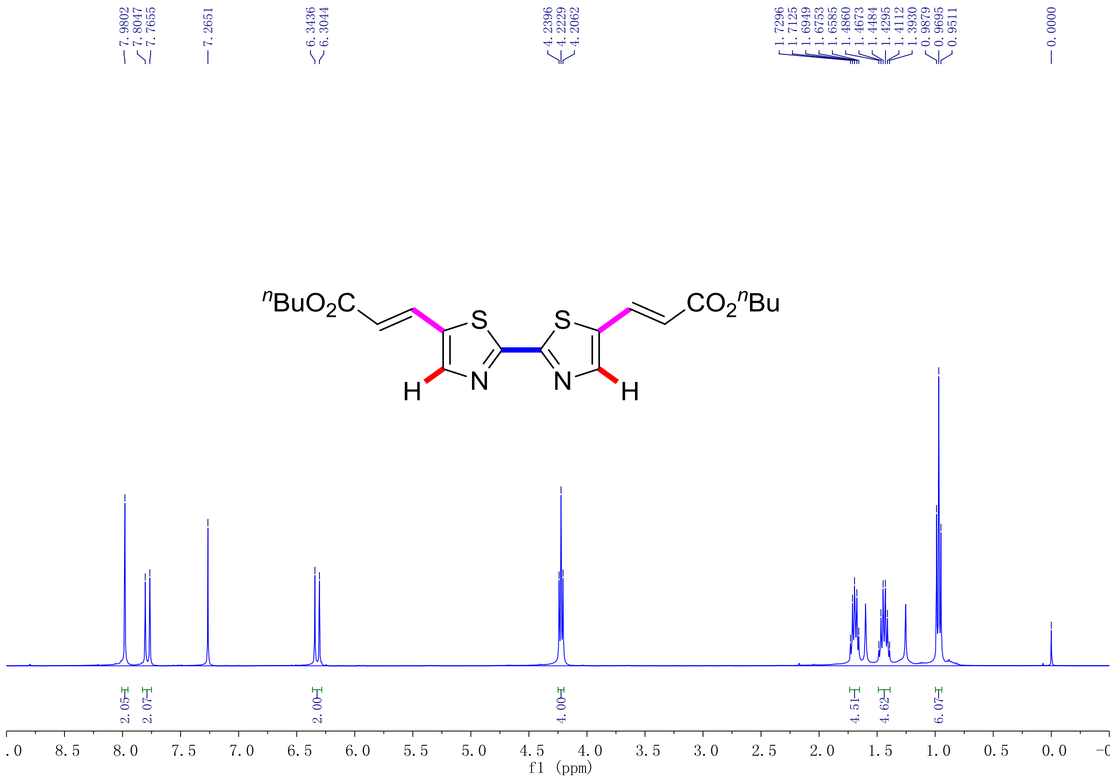


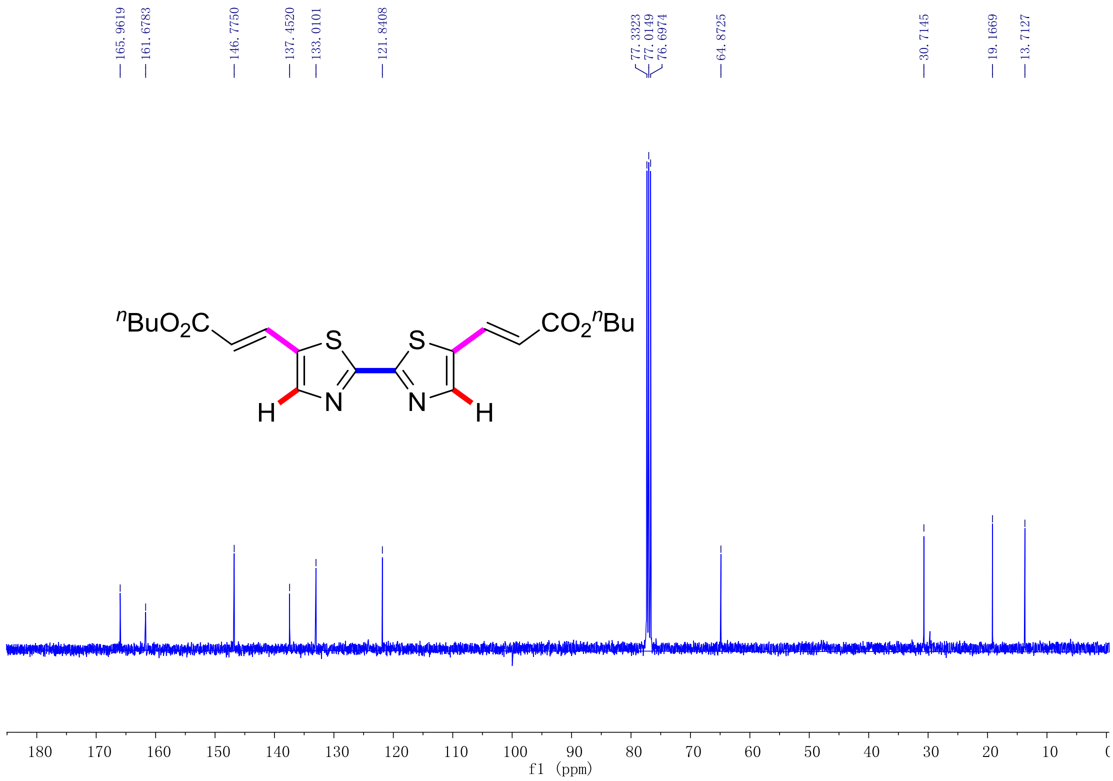
(*E*)-butyl 3-(2-(methylthio)thiazol-5-yl)acrylate (**3ua**)



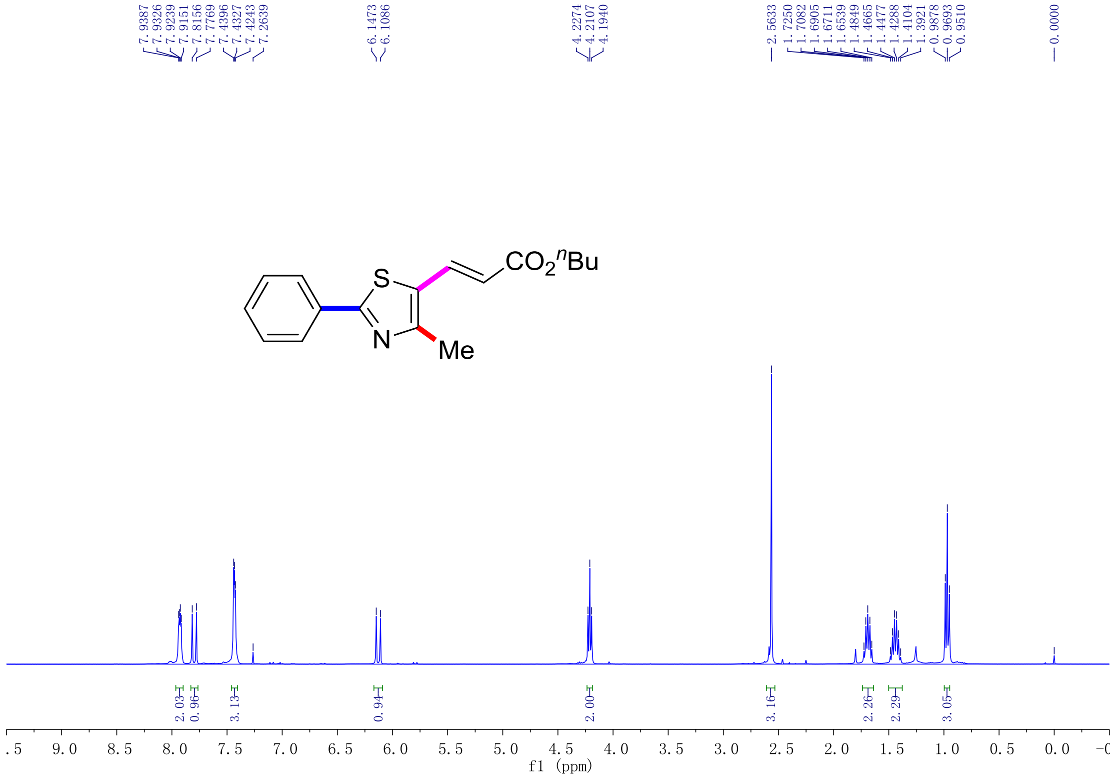


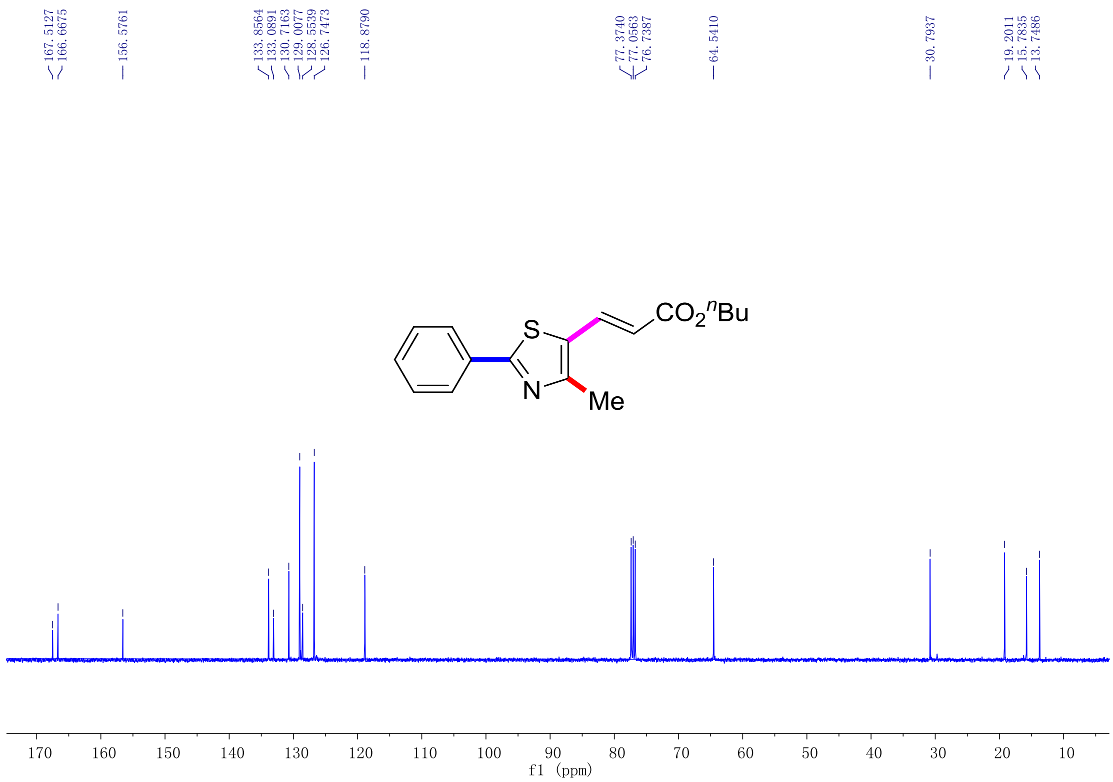
(2*E*,2'*E*)-dibutyl 3,3'-([2,2'-bithiazole]-5,5'-diyl)diacrylate (**4**)



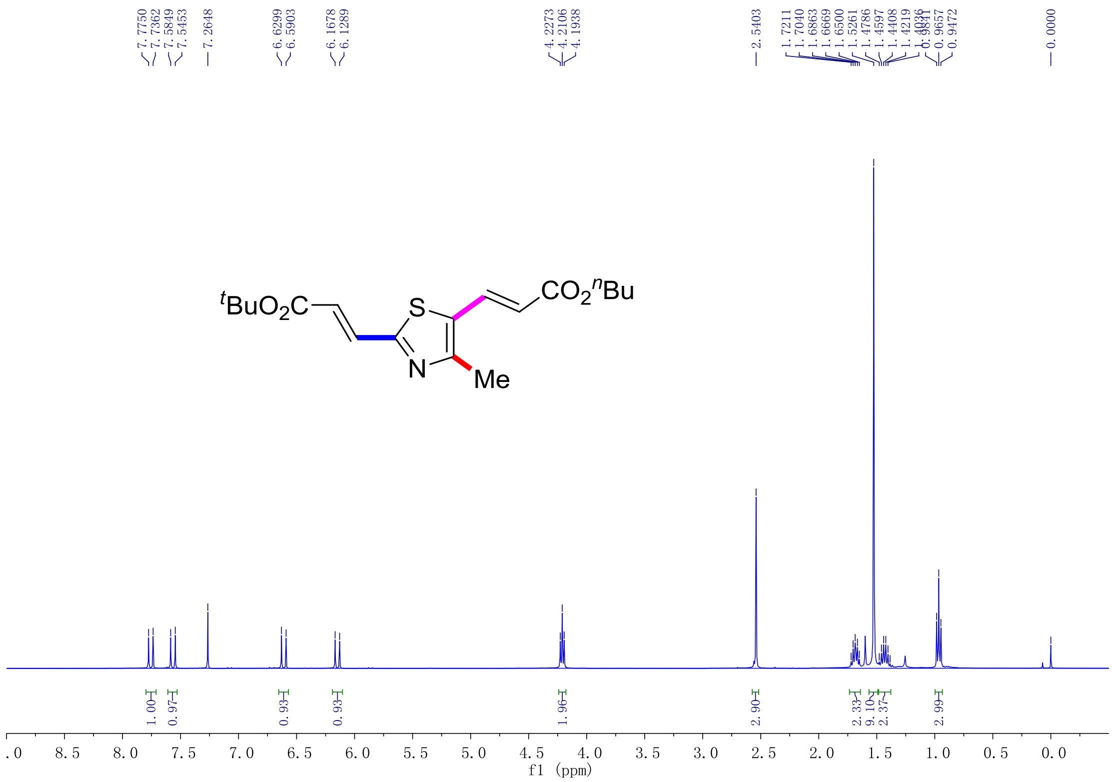


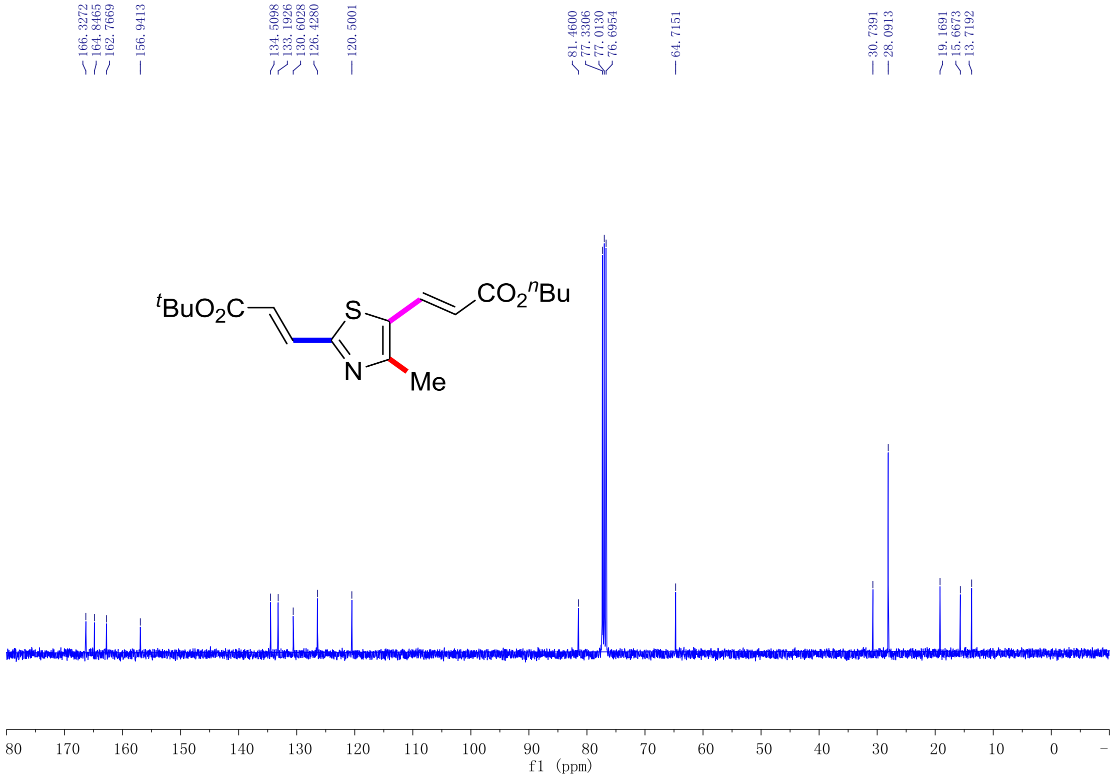
(*E*)-butyl 3-(4-methyl-2-phenylthiazol-5-yl)acrylate (**6**)



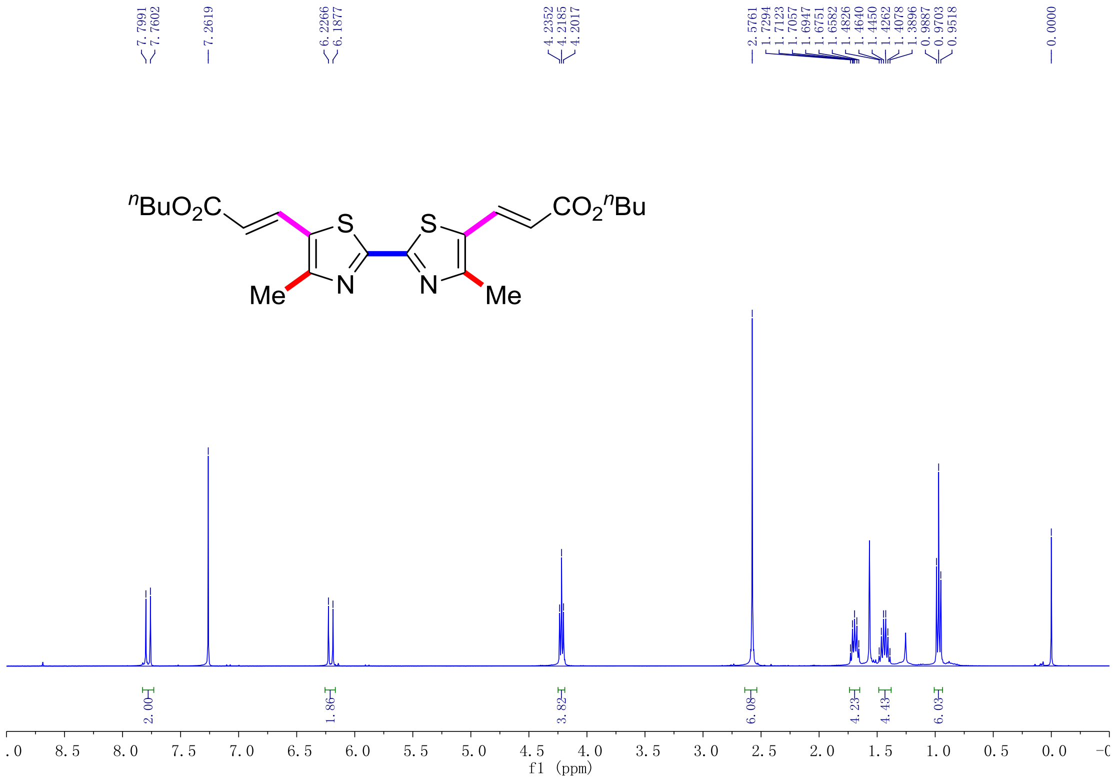


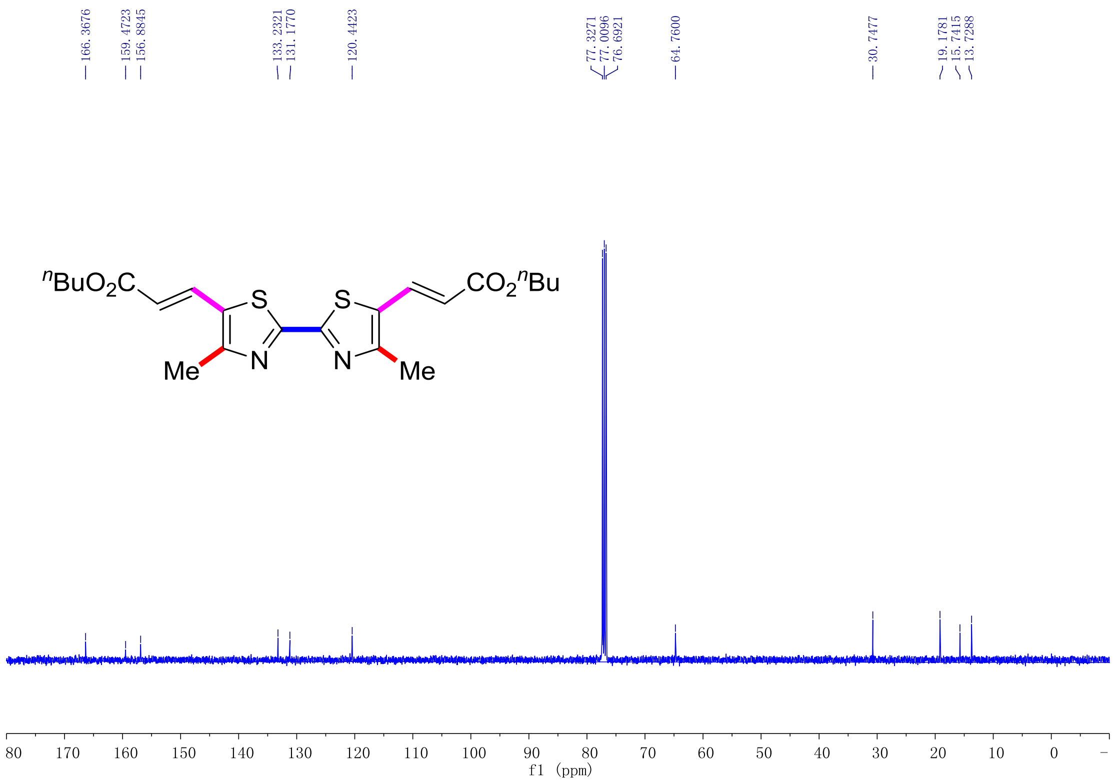
(*E*)-butyl 3-(2-((*E*)-3-(*tert*-butoxy)-3-oxoprop-1-en-1-yl)-4-methylthiazol-5-yl)acrylate (**7**)





(2*E*,2'*E*)-dibutyl 3,3'-(4,4'-dimethyl-[2,2'-bithiazole]-5,5'-diyl)diacrylate (**8**)





Pd(OAc)$_2$/5-nitro-1,10-phenanthroline complex (**9**)