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SUPPORTING INFORMATION

Synthesis of thiazoles from vinyl azides and xanthates under the action of Mn(III)-oxidant

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General

NMR spectra were registered on a Bruker Avance II 300 MHz instrument. Chemical shifts were measured relative to residual solvent peaks as an internal standard set to δ 7.26 and δ 77.0 (CDCl₃) or δ 2.50 and δ 39.0 (DMSO-d6). HRMS spectra were registered on Bruker maXis mass spectrometer. The TLC analyses were carried out on standard silica gel chromatography plates. The melting points were determined on a Kofler hot-stage apparatus. Column chromatography was performed on silica gel (60-200 mesh). 1,4-Dinitrobenzene, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), Na₂SO₄, MgSO₄, Na₂S₂O₃, Mn(OAc)₂·4H₂O, Mn(acac)₃, Fe(ClO₄)₃·8H₂O, Phl(OAc)₂, H₂O₂ (35% wt in Et₂O), petroleum ether (PE, 40/70), ethyl acetate (EA), THF, DMSO, MeCN, EtOH, DCM were purchased from commercial sources and were used without further purification. Vinylazides **1a-o** ¹ and xanthates **2a-j** ² synthesized in accordance with the slightly modified literary procedures.

Optimization of the reaction conditions for the synthesis of thiazole 3aa

(Experimental procedure for Table 1, entries 1-5, 8-16)

To a solution of vinyl azide **1a** (1-1.5 mmol, 145-217 mg) and xanthates **2a** (1-1.5 mmol, 174-261 mg) in 10 ml of THF-DMSO (1:1), DMSO, THF-H₂O (1:1), MeCN- H₂O (1:1), DMF-MeCN (1:1), DMF-H₂O (1:1) or MeCN-DMSO (1:1), Mn(OAc)₃·2H₂O (0.5-1.5 mmol, 134-402 mg) was added, and the mixture was stirred at 0-40°C for 30 min. The reaction mixture was transferred to a separation funnel and diluted with water (50 ml). The aqueous layer was extracted with ethyl acetate (5×10 ml). The combined organic layer was washed with brine (10 ml), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The yield of **3aa** was determined by ¹H NMR using 1,4-dinitrobenzene as an internal standard.

(Experimental procedure for Table 1, entries 6,7)

To a solution of vinyl azide **1a** (1 mmol, 145 mg) and xanthates **2a** (1 mmol, 174 mg) in 10 ml of EtOH-H₂O (1:1), or EtOH, Mn(OAc)₃·2H₂O (1 mmol, 268 mg) was added, and the mixture was stirred at 20°C for 30 min. The reaction mixture was transferred to a separation funnel and diluted with water (50 ml). The aqueous layer was extracted with ethyl acetate (5×10 ml). The combined organic layer was washed with

brine (10 ml), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The yield of **3aa** was determined by ¹H NMR using 1,4-dinitrobenzene as an internal standard.

(Experimental procedure for Table 1, entries 17-20)

To a solution of vinyl azide **1a** (1 mmol, 145 mg) and xanthates **2a** (1.5 mmol, 261 mg) in 10 ml of MeCN-DMSO (1:1) Mn(acac)₃, Fe(ClO₄)₃·8H₂O, H₂O₂ (35% wt in Et₂O) or PhI(OAc)₂ (1.5 mmol) was added, and the mixture was stirred at 20°C for 30 min. The reaction mixture was transferred to a separation funnel and diluted with water (50 ml). The aqueous layer was extracted with ethyl acetate (5×10 ml). The combined organic layer was washed with brine (10 ml), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The yield of **3aa** was determined by ¹H NMR using 1,4-dinitrobenzene as an internal standard.

(Experimental procedure for Table 1, entry 21)

To a solution of vinyl azide **1a** (1 mmol, 145 mg), xanthates **2a** (1.5 mmol, 261 mg) and Mn(OAc)₃·2H₂O (20 mol%, 80 mg) in 10 ml of MeCN-DMSO (1:1) Phl(OAc)₂ (1.5 mmol) was added, and the mixture was stirred at 20°C for 30 min. The reaction mixture was transferred to a separation funnel and diluted with water (50 ml). The aqueous layer was extracted with ethyl acetate (5×10 ml). The combined organic layer was washed with brine (10 ml), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The yield of **3aa** was determined by ¹H NMR using 1,4-dinitrobenzene as an internal standard.

(Experimental procedure for Table 1, entire 22)

A solution of vinyl azide **1a** (1 mmol,145 mg) and xanthates **2a** (1.5 mmol, 261 mg) in 10 ml of MeCN-DMSO (1:1), was stirred at 20°C for 30 min. The reaction mixture was transferred to a separation funnel and diluted with water (50 ml). The aqueous layer was extracted with ethyl acetate (5×10 ml). The combined organic layer was washed with brine (10 ml), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The yield of **3aa** was determined by ¹H NMR using 1,4-dinitrobenzene as an internal standard.

Procedure for synthesis of thiazoles 3aa-3oc

To a solution of vinyl azide **1a-o** (1 mmol) and xanthates **2a-j** (1.5 mmol) in 10 ml of MeCN-DMSO (1:1), $Mn(OAc)_3 \cdot 2H_2O$ (1.5 mmol, 402 mg) was added, and the mixture was stirred at 20°C for 30 min. The reaction mixture was transferred to a separation funnel and diluted with water (50 ml). The aqueous layer was extracted with ethyl acetate (5×10 ml). The combined organic layer was washed with brine (10 ml), dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. Product **3aa-3oc** was isolated by chromatography on SiO_2 (PE:EA = from 60:1 to 20:1).

The characterization data of the synthesized thiazoles

2-*iso*-**Propoxy-4-phenylthiazole (3aa)**.² Yellow oil. 149 mg (yield 68%). R_f = 0.61 (PE:EA 20:1). ¹H NMR (CDCl₃), δ : 7.84 (d, J = 7.1 Hz, 2H), 7.40 (t, J = 7.4 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 6.84 (s, 1H), 5.30 (hept, J = 6.2 Hz, 1H), 1.47 (d, J = 6.2 Hz, 6H). ¹³C NMR (CDCl₃), δ : 173.6, 149.2, 134.9, 128.7, 127.8, 126.0, 104.2, 75.8, 22.0.

2-Propoxy-4-phenylthiazole (3ab).² Yellow oil. 166 mg (yield 76%). $R_f = 0.60$ (PE:EA 20:1). ¹H NMR (CDCl₃), δ : 7.84 (d, J = 7.1 Hz, 2H), 7.44-7.36 (m, 2H), 7.34-7.27 (m, 1H), 6.85 (s, 1H), 4.45 (t, J = 6.6 Hz, 2H), 1.88 (h, J = 7.3 Hz, 2H), 1.07 (t, J = 7.4 Hz, 3H). ¹³C NMR (CDCl₃), δ : 174.3, 149.3, 134.9, 128.7, 127.9, 126.0, 104.4, 73.6, 22.4, 10.5.

2-Ethoxy-4-phenylthiazole (3ac).² Yellow oil. 156 mg (yield 76%). $R_f = 0.64$ (PE:EA 20:1). ¹H NMR (CDCl₃), δ : 7.84 (d, J = 7.7 Hz, 2H), 7.40 (d, J = 15.0 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 6.85 (s, 1H), 4.56 (q, J = 7.1 Hz, 2H), 1.48 (t, J = 7.1 Hz, 3H). ¹³C NMR (CDCl₃), δ : 174.1, 149.2, 134.8, 128.7, 127.9, 126.0, 104.4, 67.9, 14.6.

2-Butoxy-4-phenylthiazole (**3ad**).² Yellow oil. 177 mg (yield 78%). $R_f = 0.60$ (PE:EA 20:1). ¹H NMR (CDCl₃), δ : 7.83 (d, J = 7.3 Hz, 2H), 7.40 (t, J = 7.4 Hz, 2H), 7.32-7.28 (m, 1H), 6.85 (s, 1H), 4.50 (t, J = 6.6 Hz, 2H), 1.89-1.78 (m, 2H), 1.52 (h, J = 7.4 Hz, 2H), 1.00 (t, J = 7.4 Hz, 3H). ¹³C NMR (CDCl₃), δ : 174.3, 149.3, 134.8, 128.7, 127.9, 126.0, 104.4, 71.9, 31.1, 19.2, 13.9.

2-iso-Butoxy-4-phenylthiazole (3ae). Yellow oil. 210 mg (yield 90%). R_f = 0.55 (PE:EA 20:1). ¹H NMR (CDCl₃), δ : 7.82 (d, J = 7.4 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 6.85 (s, 1H), 4.26 (d, J = 6.6 Hz, 2H), 2.24-2.11 (m, 1H), 1.05 (d, J = 6.7 Hz, 6H). ¹³C NMR (CDCl₃), δ : 135.0, 128.7, 127.9, 126.0, 123.5, 104.5, 71.3, 27.1, 20.8, 14.3. HRMS (ESI) m/z: calcd for C₁₃H₁₅NOS [M+H]⁺ 234.0947, found 234.0947.

2-Nonyloxy-4-phenylthiazole (3af). Yellow oil. 222 mg (yield 73%). $R_f = 0.52$ (PE:EA 20:1). ¹H NMR (CDCl₃), δ : 7.83 (d, J = 7.4 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 6.85 (s, 1H), 4.48 (t, J = 6.6 Hz, 2H), 1.89-1.80 (m, 2H), 1.47-1.25 (m, 12H), 0.89 (t, J = 6.6 Hz, 3H). ¹³C NMR (CDCl₃), δ : 174.3, 149.3, 134.8, 128.7, 127.9, 126.0, 104.4, 72.2, 32.0, 29.6, 29.4, 29.4, 29.0, 26.0, 22.8, 14.2. HRMS (ESI) m/z: calcd for $C_{18}H_{25}NOS$ [M+H]⁺ 304.1729, found 304.1730.

2-tert-Butoxy-4-phenylthiazole (3ag). Yellow oil. 49 mg (yield 21%). $R_f = 0.55$ (PE:EA 20:1). ¹H NMR (CDCl₃), δ : 7.78 (d, J = 7.3 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.22 (d, J = 7.6 Hz, 1H), 6.81 (s, 1H), 1.61 (s, 9H). ¹³C NMR (CDCl₃), δ : 172.2, 149.3, 135.1, 129.4, 128.7, 127.8, 126.0, 125.0, 104.7, 85.3, 28.3. HRMS (ESI) m/z: calcd for $C_{13}H_{15}NOS$ [M+H]⁺ 234.0947, found 234.0947.

2-Benzyloxy-4-phenylthiazole (3ah). Yellow oil. 182 mg (yield 68%). R_f = 0.49 (PE:EA 20:1). ¹H NMR (CDCl₃), δ : 7.87 (d, J = 7.9 Hz, 2H), 7.52 (d, J = 7.3 Hz, 2H), 7.45-7.37 (m, 5H), 7.34 (d, J = 7.4 Hz, 1H), 6.89 (s, 1H), 5.56 (s, 2H). ¹³C NMR (CDCl₃), δ :

173.8, 149.1, 135.8, 134.8, 128.8, 128.7, 128.7, 128.6, 128.0, 126.0, 104.9, 73.3. HRMS (ESI) m/z: calcd for C₁₆H₁₃NOS [M+H]⁺ 268.0790, found 268.0791.

2-(Allyloxy)-4-phenylthiazole (3ai). Yellow oil. 178 mg (yield 82%). $R_f = 0.51$ (PE:EA 20:1). 1 H NMR (CDCl₃), δ : 7.84 (d, J = 7.4 Hz, 2H), 7.40 (d, J = 15.0 Hz, 1H), 7.32 (d, J = 7.2 Hz, 1H), 6.87 (s, 1H), 6.14 (ddt, J = 16.5, 11.2, 5.8 Hz, 1H), 5.49 (d, J = 17.2 Hz, 1H), 5.35 (d, J = 10.4 Hz, 1H), 5.02 (d, J = 5.8 Hz, 2H). 13 C NMR (CDCl₃), δ : 173.7, 149.2, 134.8, 132.1, 128.7, 127.9, 126.0, 119.3, 104.8, 72.2. HRMS (ESI) m/z: calcd for $C_{12}H_{11}NOS$ [M+H] $^+$ 218.0639, found 218.0634.

(Z)-2-(Hex-3-en-1-yloxy)-4-phenylthiazole (3aj). Yellow oil. 208 mg (yield 80%). R_f = 0.51 (PE:EA 20:1). ¹H NMR (CDCl₃), δ: 7.83 (d, J = 7.3 Hz, 2H), 7.39 (t, J = 7.4 Hz, 2H), 7.33-7.25 (m, 1H), 6.85 (s, 1H), 5.63-5.51 (m, 1H), 5.48-5.37 (m, 1H), 4.49 (t, J = 7.0 Hz, 2H), 2.61 (q, J = 7.0 Hz, 2H), 2.12 (p, J = 7.1 Hz, 2H), 1.00 (t, J = 7.5 Hz, 3H). ¹³C NMR (CDCl₃), δ: 174.1, 149.2, 135.0, 128.7, 127.9, 126.0, 123.5, 104.5, 71.3, 27.1, 20.8, 14.3. HRMS (ESI) m/z: calcd for C₁₅H₁₇NOS [M+H]⁺ 260.1109, found 260.1104.

2-Ethoxy-4-(4-tolyl)thiazole (3bc).² Yellow solid. 173 mg (yield 79%). R_f = 0.51 (PE:EA 20:1). mp = $50.5-51.2^{\circ}$ C (lit.² mp = $51.3-52.3^{\circ}$ C). ¹H NMR (CDCl₃), δ : 7.72 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.79 (s, 1H), 4.54 (q, J = 7.1 Hz, 2H), 2.37 (s, 3H), 1.47 (t, J = 7.1 Hz, 3H). ¹³C NMR (CDCl₃), δ : 174.0, 149.4, 137.7, 132.2, 129.4, 125.9, 103.6, 67.9, 21.4, 14.6.

2-Ethoxy4-(4-(*tert*-butyl)**phenyl)thiazole (3cc).** Yellow oil. 209 mg (yield 80%). R_f = 0.49 (PE:EA 20:1). 1 H NMR (CDCl₃), δ : 7.75 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 6.80 (s, 1H), 4.55 (q, J = 7.1 Hz, 2H), 1.48 (t, J = 7.1 Hz, 3H), 1.34 (s, 9H). 13 C NMR

(CDCl₃), δ : 174.0, 150.9, 149.3, 132.1, 125.7, 125.6, 103.7, 67.9, 34.7, 31.4, 14.6. HRMS (ESI) m/z: calcd for C₁₅H₁₉NOS [M+H]⁺ 262.1260, found 262.1260.

2-Ethoxy-4-(4-methoxyphenyl)thiazole (3dc).² Yellow solid. 165 mg (yield 70%). R_f = 0.51 (PE:EA 20:1). mp = 49.4-50.2°C (lit.² mp = 49.1-50.0°C). ¹H NMR (CDCl₃), δ : 7.76 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 6.70 (s, 1H), 4.53 (q, J = 7.1 Hz, 2H), 3.83 (s, 3H), 1.47 (t, J = 7.1 Hz, 3H). ¹³C NMR (CDCl₃), δ : 174.0, 159.5, 149.0, 127.8, 127.2, 114.0, 102.5, 67.8, 55.4, 14.6.

2-Ethoxy-4-(2-methoxyphenyl)thiazole (3ec). Yellow oil. 167 mg (yield 71%). $R_f = 0.51$ (PE:EA 20:1). ¹H NMR (CDCl₃), δ : 8.17 (dd, J = 7.7, 1.7 Hz, 1H), 7.35 (s, 1H), 7.26 (dd, J = 15.6, 1.7 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.96 (d, J = 8.3 Hz, 1H), 4.54 (q, J = 7.1 Hz, 2H), 3.93 (s, 3H), 1.47 (t, J = 7.1 Hz, 3H). ¹³C NMR (CDCl₃), δ : 172.4, 157.1, 145.0, 130.1, 128.5, 123.5, 120.9, 111.2, 109.4, 67.6, 55.5, 14.6. HRMS (ESI) m/z: calcd for $C_{12}H_{13}NO_2S$ [M+H]⁺ 236.0739, found 236.0740.

2-Ethoxy-4-(4-fluorophenyl)thiazole (3fc).² Yellow solid. 183 mg (yield 82%). R_f = 0.51 (PE:EA 20:1). mp = 55.8-56.6°C (lit.² mp = 56.5.3-57.5°C). ¹H NMR (CDCl₃), δ : 7.84-7.70 (m, 2H), 7.07 (t, J = 8.7 Hz, 2H), 6.77 (s, 1H), 4.54 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H). ¹³C NMR (CDCl₃), δ : 174.2, 162.7 (d, J = 246.9 Hz), 148.3, 131.1 (d, J = 3.0 Hz), 127.7 (d, J = 8.1 Hz), 115.6 (d, J = 21.7 Hz), 104.0, 68.0, 14.6.

2-Ethoxy-4-(4-chlorophenyl)thiazole (3gc).² Light yellow solid. 197 mg (yield 81%). R_f= 0.51 (PE:EA 20:1). mp = 60.2-61.4°C (lit.² mp = 60.5-61.5°C). ¹H NMR (CDCl₃), δ : 7.75 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 6.84 (s, 1H), 4.54 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H). ¹³C NMR (CDCl₃), δ : 174.3, 148.2, 133.7, 133.3, 128.9, 127.3, 104.8, 68.1, 14.6.

2-Ethoxy-4-(3-bromophenyl)thiazole (3hc). Yellow oil. 219 mg (yield 77%). $R_f = 0.51$ (PE:EA 20:1). ¹H NMR (CDCl₃), δ : 8.03 (s, 1H), 7.77 (d, J = 7.7 Hz, 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.29 (t, J = 7.2 Hz, 1H), 6.91 (s, 1H), 4.60 (q, J = 7.0 Hz, 2H), 1.52 (t, J = 7.1 Hz, 3H). ¹³C NMR (CDCl₃), δ : 174.2, 147.7, 136.7, 130.7, 130.2, 129.1, 124.4, 122.9, 105.5, 68.0, 14.6. HRMS (ESI) m/z: calcd for $C_{11}H_{10}BrNOS$ [M+H]⁺ 283.9739, found 283.9739.

2-Ethoxy-4-(4-(azidomethyl)phenyl)thiazole (3ic). Yellow oil. 177 mg (yield 68%). R_f = 0.51 (PE:EA 20:1). ¹H NMR (CDCl₃), δ : 7.84 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 6.87 (s, 1H), 4.55 (q, J = 7.1 Hz, 2H), 4.35 (s, 2H), 1.48 (t, J = 7.1 Hz, 3H). ¹³C NMR (CDCl₃), δ : 174.1, 148.7, 134.9, 128.6, 126.4, 104.9, 67.9, 54.7, 14.6. HRMS (ESI) m/z: calcd for $C_{12}H_{12}N_4OS$ [M+H]⁺ 261.0804, found 261.0805.

2-Ethoxy-4-(naphthalen-2-yl)thiazole (3jc).² Yellow oil. 217 mg (yield 85%). R_f = 0.51 (PE:EA 20:1). ¹H NMR (CDCl₃), δ : 8.37 (s, 1H), 7.82-7.92 (m, 4H), 7.45-7.52 (m, 2H), 6.97 (s, 1H), 4.61 (q, J = 7.1 Hz, 2H), 1.52 (t, J = 7.1 Hz, 3H). ¹³C NMR (CDCl₃), δ : 174.2, 149.2, 133.8, 133.2, 132.1, 128.5, 128.3, 127.8, 126.4, 126.1, 125.1, 123.9, 105.0, 68.1, 14.7.

2-Ethoxy-5-methyl-4-phenylthiazole (3kc).² Yellow oil. 77 mg (yield 35%). R_f = 0.51 (PE:EA 20:1). ¹H NMR (CDCl₃), δ : 7.62-7.59 (m, 2H), 7.40 (t, J = 7.4 Hz, 2H), 7.31 (d, J = 7.3 Hz, 1H), 4.47 (q, J = 7.1 Hz, 2H), 2.43 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H). ¹³C NMR (CDCl₃), δ : 170.2, 144.4, 135.4, 128.5, 128.4, 127.3, 119.5, 67.2, 14.7, 12.8.

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2-Ethoxy-4-octylthiazole (3lc). Yellow oil. 198 mg (yield 82%). R_f = 0.51 (PE:EA 20:1). ¹H NMR (CDCl₃), δ : 6.19 (s, 1H), 4.41 (d, J = 7.1 Hz, 2H), 2.55 (s, 2H), 1.42 (t, J = 7.1 Hz, 3H), 1.35-1.22 (m, 12H), 0.87 (t, J = 6.3 Hz, 4H). ¹³C NMR (CDCl₃), δ : 173.7, 151.5, 103.4, 67.3, 31.8, 31.6, 29.1, 29.0, 28.8, 28.3, 22.4, 14.2, 13.8. HRMS (ESI) m/z: calcd for C₁₃H₂₃NOS [M+H]⁺ 242.1569, found 242.1573.

2-Ethoxy-4-decylthiazole (3mc). Yellow oil. 197 mg (yield 73%). R_f = 0.51 (PE:EA 20:1). ¹H NMR (CDCl₃), δ : 6.19 (s, 1H), 4.41 (q, J = 7.1 Hz, 2H), 2.55 (t, J = 7.6 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H), 1.23-1.26 (m, J = 11.1 Hz, 16H), 0.85-0.90 (m, 3H). ¹³C NMR (CDCl₃), δ : 174.1, 151.8, 103.8, 67.7, 32.1, 32.0, 29.7, 29.7, 29.5, 29.4, 29.3, 28.7, 22.8, 14.6, 14.2. HRMS (ESI) m/z: calcd for $C_{15}H_{27}NOS$ [M+H]⁺ 270.1892, found 270.1886.

2-Ethoxy-4,5,6,7,8,9-hexahydrocycloocta[d]thiazole (3nc).² Yellow oil. 148 mg (yield 70%). R_f = 0.51 (PE:EA 20:1). ¹H NMR (CDCl₃), δ : 4.35 (q, J = 7.1 Hz, 2H), 2.70-2.64 (m, 4H), 1.68-1.61 (m, 4H), 1.44-1.37 (m, 7H). ¹³C NMR (CDCl₃), δ : 170.8, 146.6, 121.8, 67.1, 31.3, 29.6, 28.3, 26.2, 25.6, 24.6, 14.6.

Ethyl 2-ethoxythiazole-4-carboxylate (3oc). Yellow oil. 111 mg (yield 55%). R_f = 0.51 (PE:EA 20:1). ¹H NMR (CDCl₃), δ: 7.55 (s, 1H), 4.55 (q, J = 7.1 Hz, 2H), 4.35 (q, J = 7.1 Hz, 2H), 1.39 (dt, J = 17.0, 7.1 Hz, 6H). ¹³C NMR (CDCl₃), δ: 174.0, 161.3, 141.3,

120.1, 68.5, 61.3, 14.5, 14.4. HRMS (ESI) m/z: calcd for $C_8H_{11}NO_3S$ [M+K]⁺ 240.0097, found 240.0091.

Scale up experiment for synthesis of 2-ethoxy-4-phenylthiazole 3ac

To a solution of vinyl azide 1a (10 mmol,1.45 g) and xanthates 2c (15 mmol, 2.4 g) in 40 ml of MeCN-DMSO (1:1), Mn(OAc)₃·2H₂O (15 mmol, 4,02 g) was added, and the mixture was stirred at 20°C for 30 min. The reaction mixture was transferred to a separation funnel and diluted with water (250 ml). The aqueous layer was extracted with ethyl acetate (5×50 ml). The combined organic layer was washed with brine (50 ml), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. Product 3aa was isolated by chromatography on SiO₂ (PE:EA = from 60:1 to 20:1). Yield 65% (1.33 g).

Experimental details for control experiments

To a solution of vinyl azide **1a** (1 mmol,145 mg), xanthates **2c** (1.5 mmol, 240 mg) and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (3 mmol, 469 mg) in 10 ml of MeCN-DMSO (1:1), Mn(OAc)₃·2H₂O (1.5 mmol, 402 mg) was added, and the mixture was stirred at 20°C for 30 min. The reaction mixture was transferred to a separation funnel and diluted with water (50 ml). The aqueous layer was extracted with ethyl acetate (5×10 ml). The combined organic layer was washed with brine (10 ml), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The yield of **3ac** was determined by ¹H NMR using 1,4-dinitrobenzene as an internal standard. Additionally, reaction mixture was analyzed as is with HRMS to detect key intermediates.

Argon was bubbled through the solution of vinyl azide **1a** (1 mmol,145 mg) and xanthates **2c** (1.5 mmol, 240 mg) in 10 ml of MeCN-DMSO (1:1), Mn(OAc)₃·2H₂O (1.5 mmol, 402 mg) was added, and the mixture was stirred at 20°C for 30 min with argon bubbling. The reaction mixture was transferred to a separation funnel and diluted with water (50 ml). The aqueous layer was extracted with ethyl acetate (5×10 ml). The combined organic layer was washed with brine (10 ml), dried over Na₂SO₄, filtered, and

concentrated under reduced pressure. The yield of **3ac** was determined by ¹H NMR using 1,4-dinitrobenzene as an internal standard.

To a solution of vinyl azide **1a** (1 mmol,145 mg) and xanthates **2c** (1.5 mmol, 240 mg) in 10 ml of MeCN-DMSO (1:1), Mn(OAc)₂·4H₂O (1.5 mmol, 368 mg) was added, and the mixture was stirred at 20°C for 30 min. The reaction mixture was transferred to a separation funnel and diluted with water (50 ml). The aqueous layer was extracted with ethyl acetate (5×10 ml). The combined organic layer was washed with brine (10 ml), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The yield of **3ac** was determined by ¹H NMR using 1,4-dinitrobenzene as an internal standard.

Argon was bubbled through the solution of vinyl azide **1a** (1 mmol,145 mg) and xanthates **2c** (1.5 mmol, 240 mg) in 10 ml of MeCN-DMSO (1:1), Mn(OAc)₂·4H₂O (1.5 mmol, 368 mg) was added, and the mixture was stirred at 20°C for 30 min with argon bubbling. The reaction mixture was transferred to a separation funnel and diluted with water (50 ml). The aqueous layer was extracted with ethyl acetate (5×10 ml). The combined organic layer was washed with brine (10 ml), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The yield of **3ac** was determined by ¹H NMR using 1,4-dinitrobenzene as an internal standard.

To a solution of vinyl azide 1a (0.5 mmol, 72.5 mg) and xanthates 2c (0.75 mmol, 120 mg) in 10 ml of MeCN-DMSO (1:1), Mn(OAc)₃·2H₂O (0.75 mmol, 201 mg) was added, and the mixture was stirred at 20°C for 15 min. After that, vinyl azide 1a (0.5 mmol,

72.5 mg) and xanthate **2c** (0.75 mmol, 120 mg) were added to the reaction mixture and it was stirred at 20°C for 15 min. The reaction mixture was transferred to a separation funnel and diluted with water (50 ml). The aqueous layer was extracted with ethyl acetate (5×10 ml). The combined organic layer was washed with brine (10 ml), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The yield of **3ac** was determined by ¹H NMR using 1,4-dinitrobenzene as an internal standard. Additionally, reaction mixture was analyzed as is with HRMS to detect key intermediates.

Growth inhibition of the mycelium of the pathogenic fungi by thiazoles 3

Nº	Compound	Mycelium growth inhibition at 30 mol/L concentration, %						
		V. i.	R. s.	F. o.	F. m.	B. s.	S. s.	
*	Triadimefon	70	59	64	86	71	71	
3aa	O N= S	69	93	48	78	79	48	
3ab	N= S	15	41	16	45	39	16	
3ac	N=S	79	100	55	90	78	53	
3ad	N= N= S	61	68	32	66	67	28	
3ae	N= N= S	75	100	36	59	74	19	
3af	N O n C 9 H 19	13	30	11	34	45	9	
3ag	N=S	38	65	18	57	45	12	

3ah		28	40	25	61	53	11
	N S						
3aj	N _S O	28	45	23	53	46	14
3bc	N S	75	100	35	71	66	40
3cc	N S	28	41	25	66	47	18
3dc	N S	80	100	42	86	68	52
3ec	N S	74	95	44	75	75	48
3fc	N S	100	100	61	86	83	64
3gc	O N S	34	48	21	45	40	16

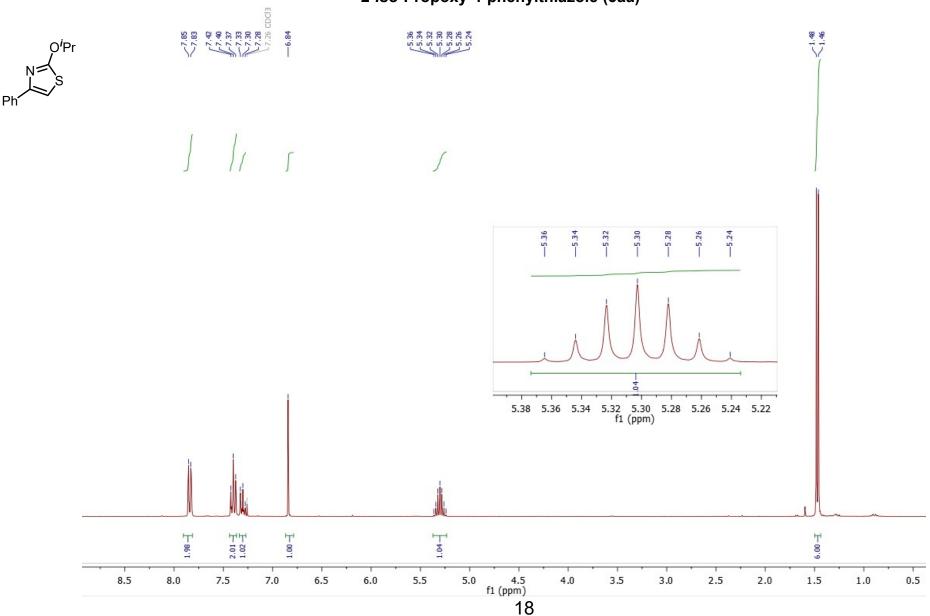
3hc	0-/	44	67	33	70	62	37
	N=S Br						
3ic	N= $N=$ $N=$ $N=$ $N=$	56	99	32	58	53	38
3jc	Ny O	30	41	21	53	42	24
3kc	N=S	79	100	46	73	88	42
3lc	O N N N C ₈ H ₁₇	28	50	16	35	8	24
3mc	O N C 10 H 21	24	35	10	34	10	14
3nc	N O S	56	87	45	72	52	29
Зос	0 N S	30	36	6	26	38	17

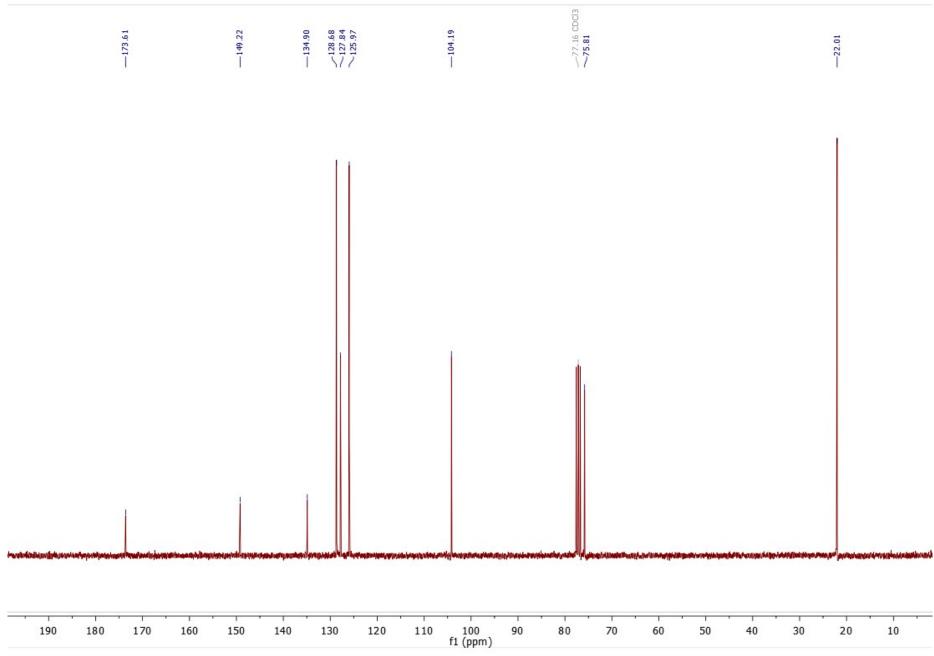
References

- 1. M. M. Doronin, A. S. Klikushin, O. M. Mulina, M. G. Medvedev, V. A. Vil', L.-N. He and A. O. Terent'ev, *Org. Chem. Front.*, 2025, DOI: 10.1039/D5QO00508F.
- 2. Z. Zhu, X. Tang, J. Cen, J. Li, W. Wu and H. Jiang, *Chem. Commun.*, 2018, **54**, 3767–3770.

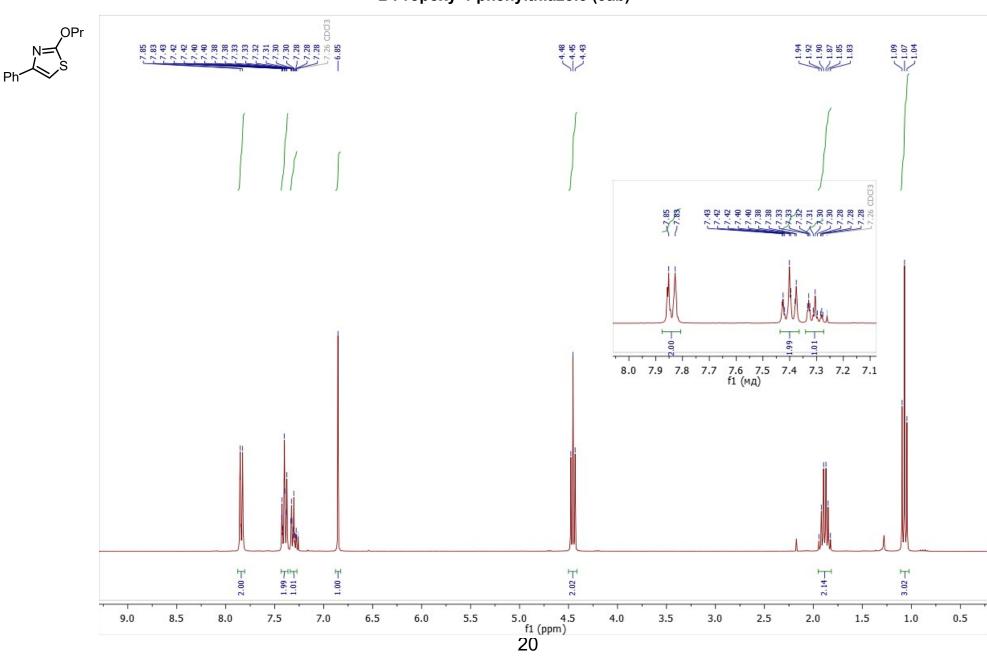
NMR spectra of the synthesized compounds

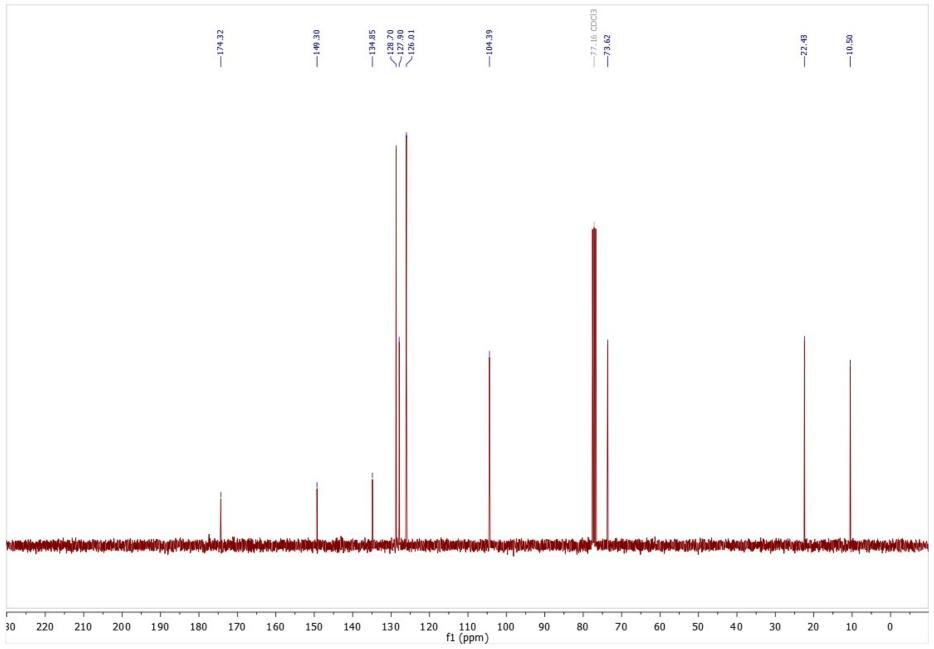
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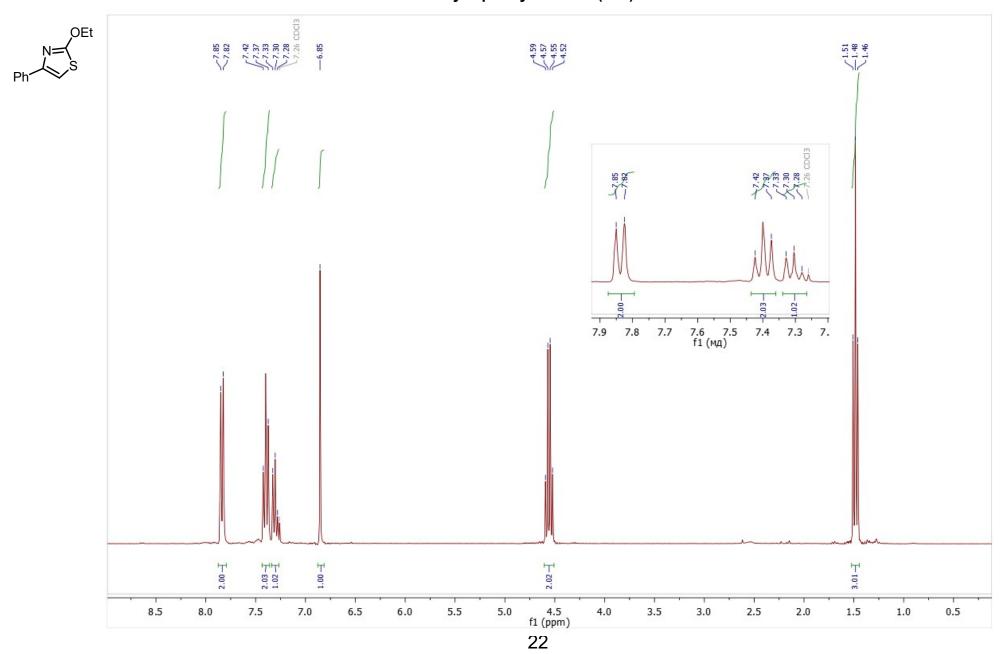


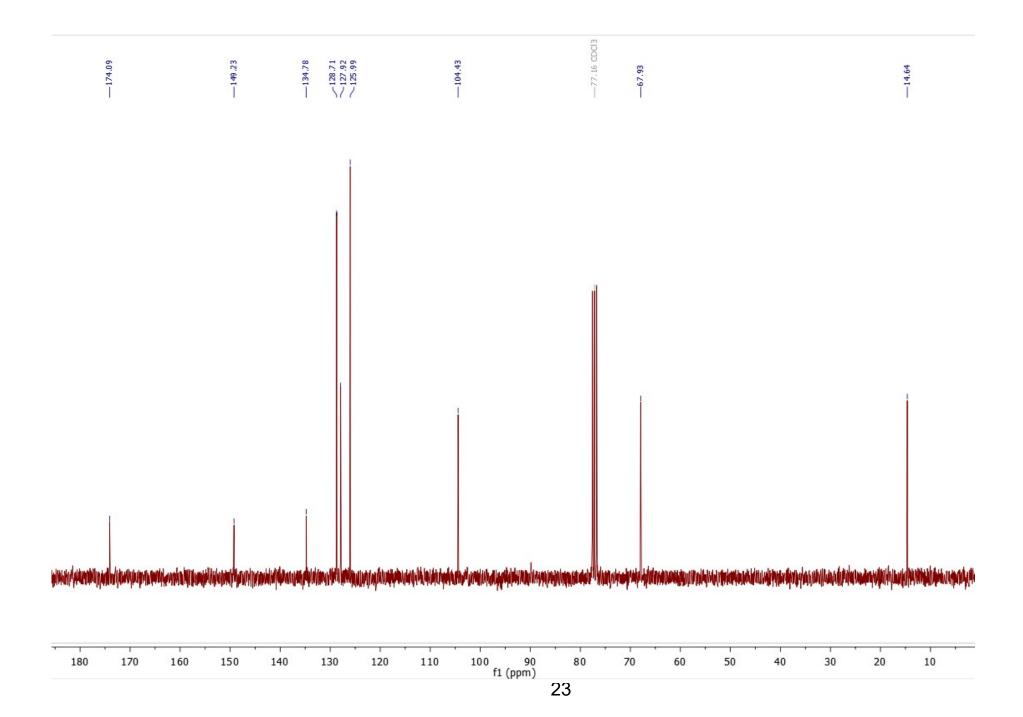
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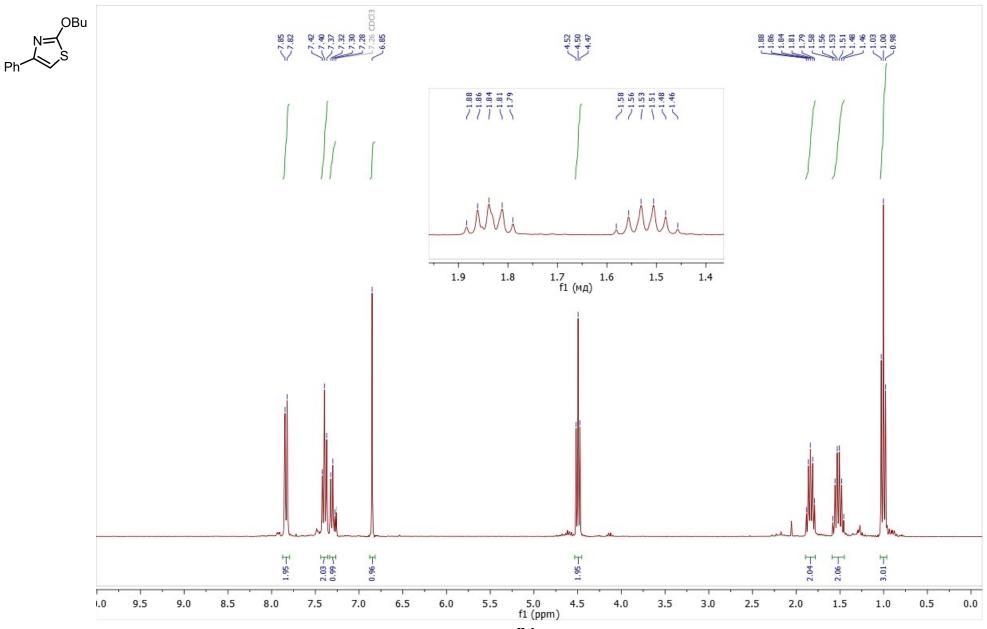


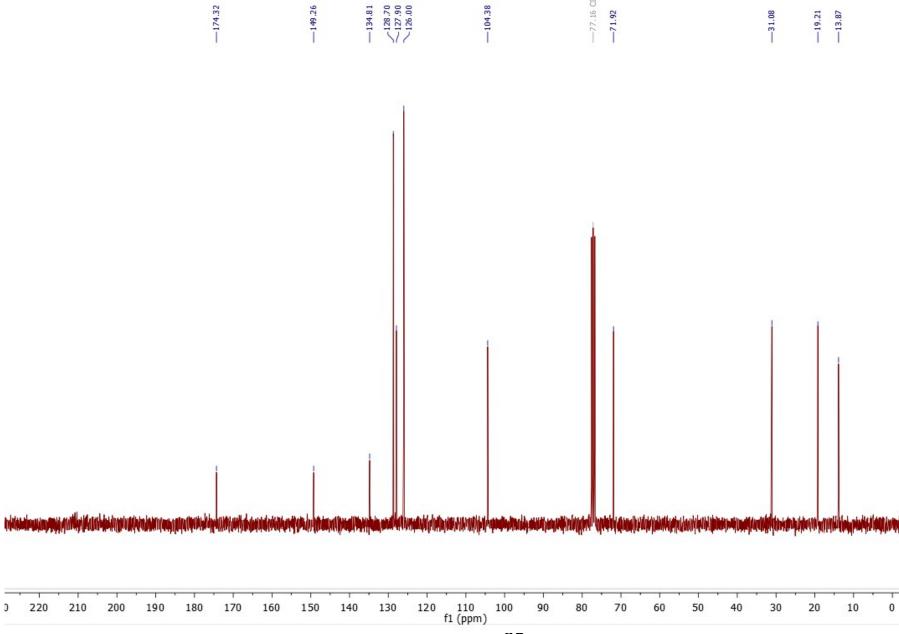
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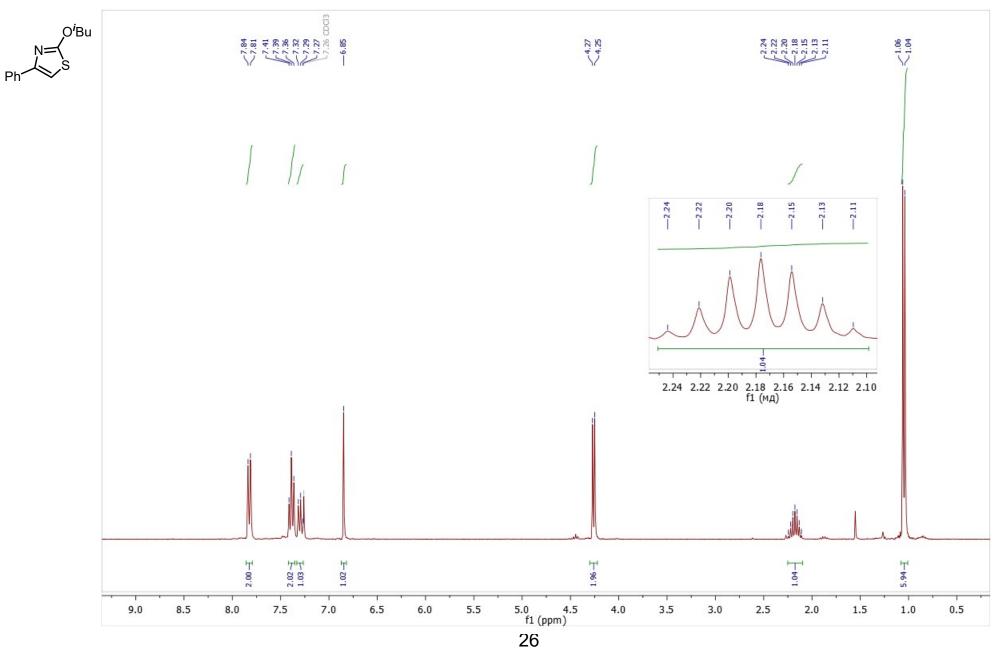


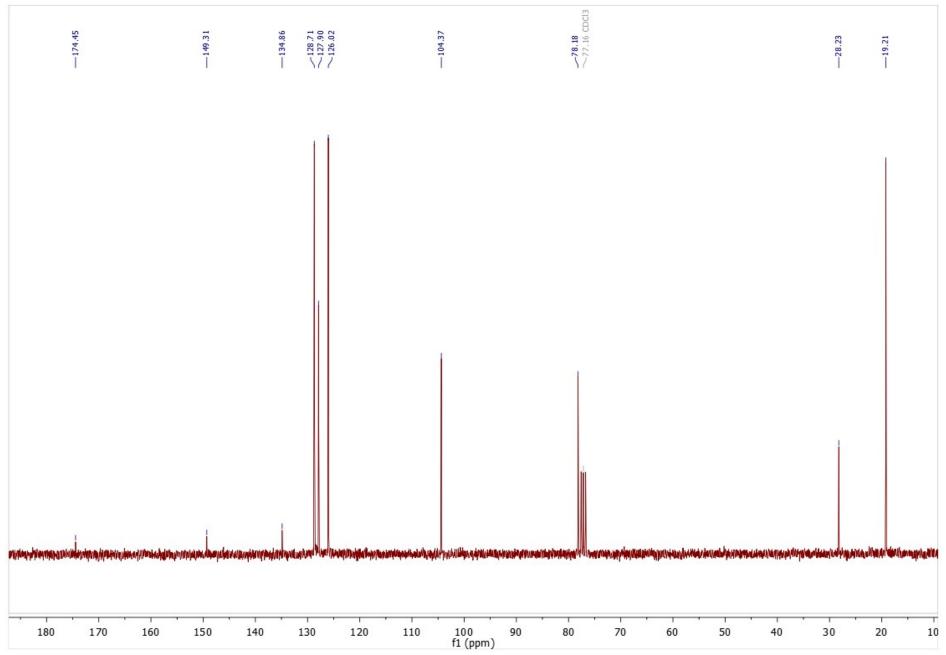
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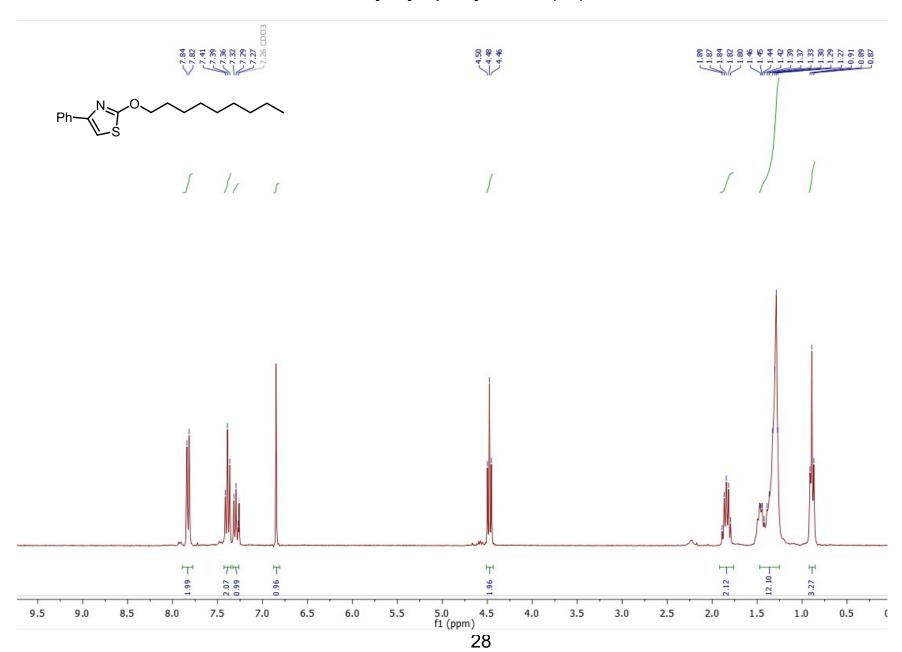


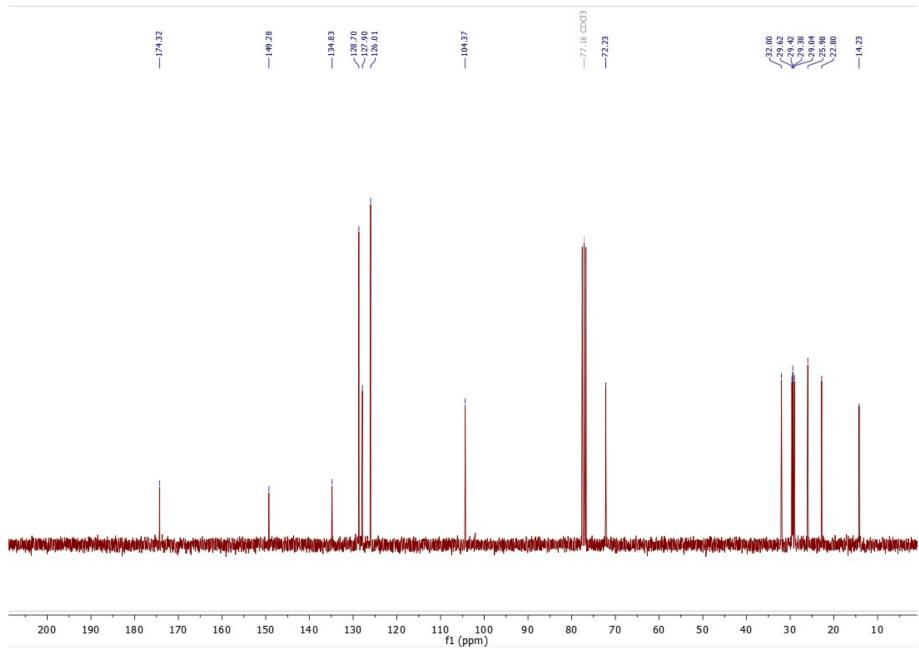
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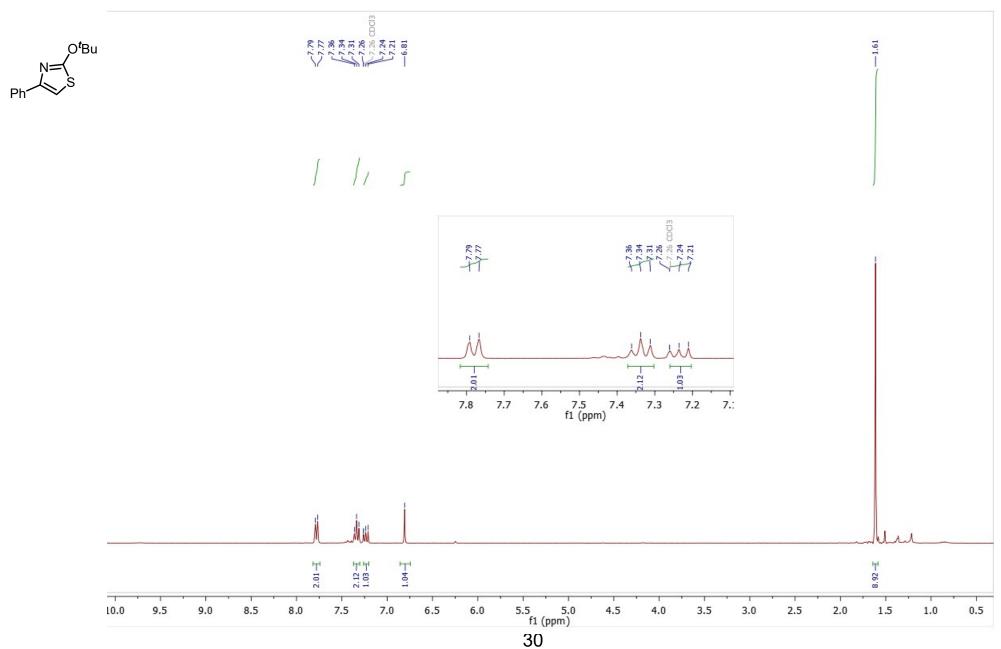


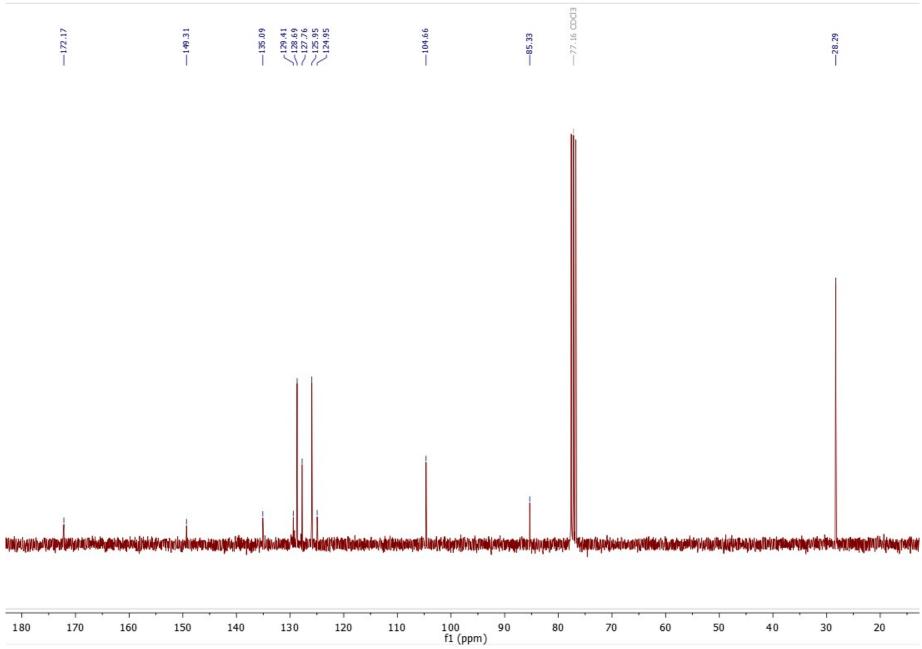
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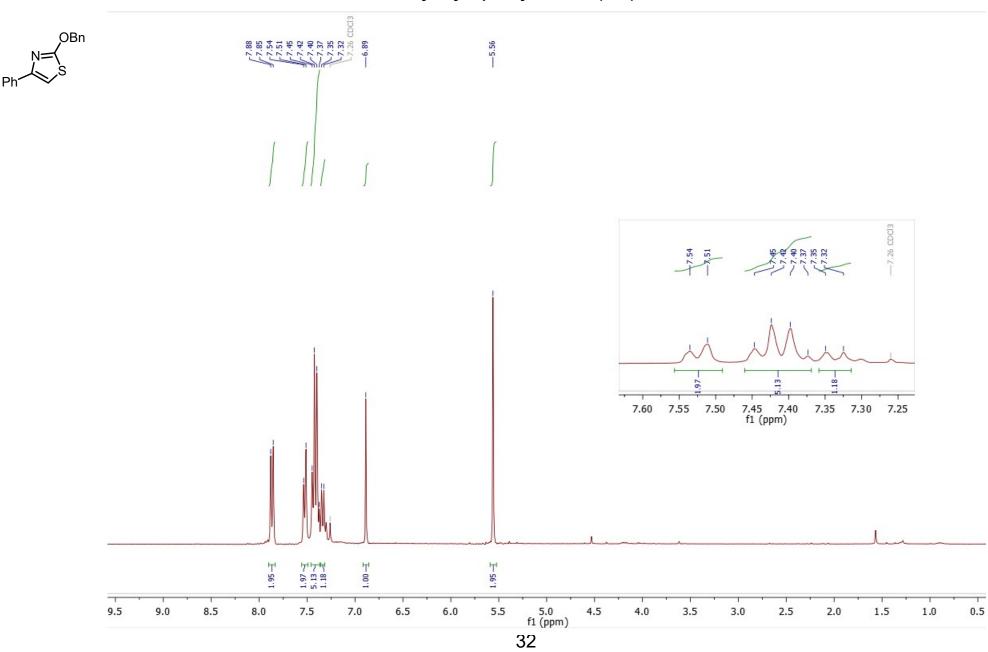


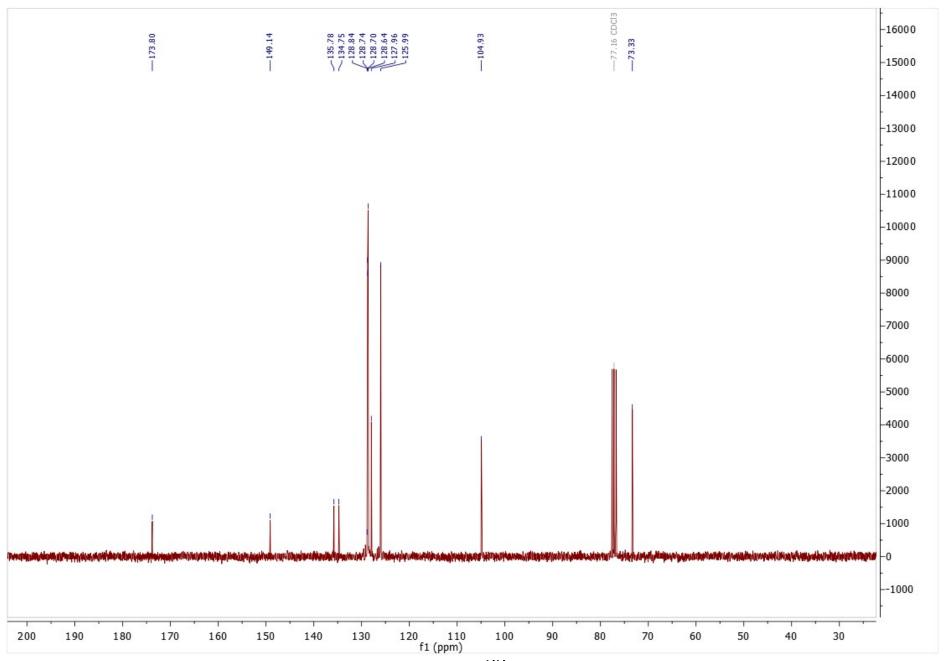


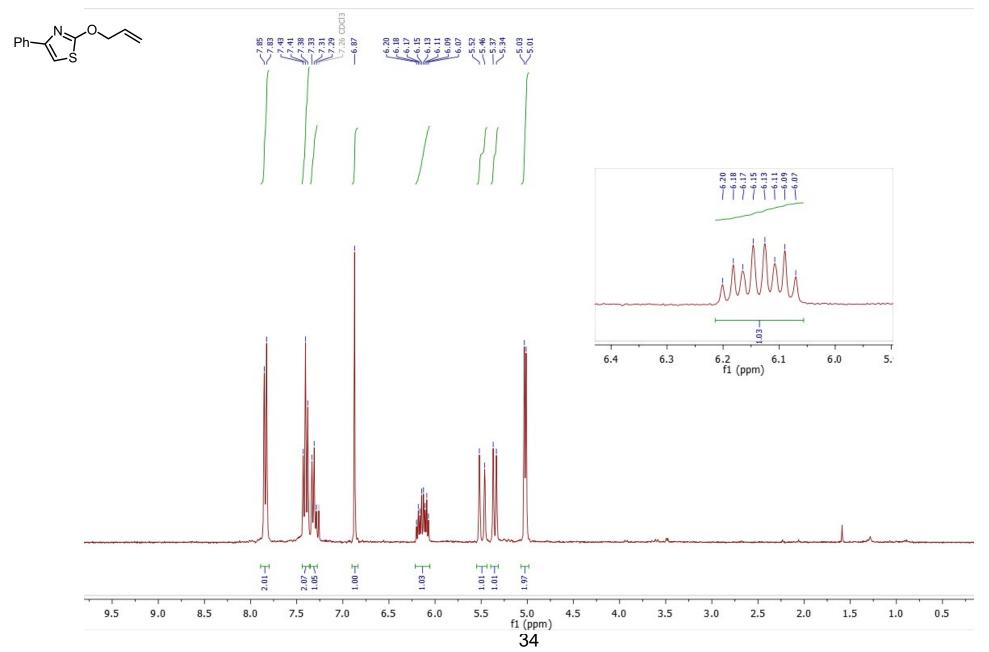
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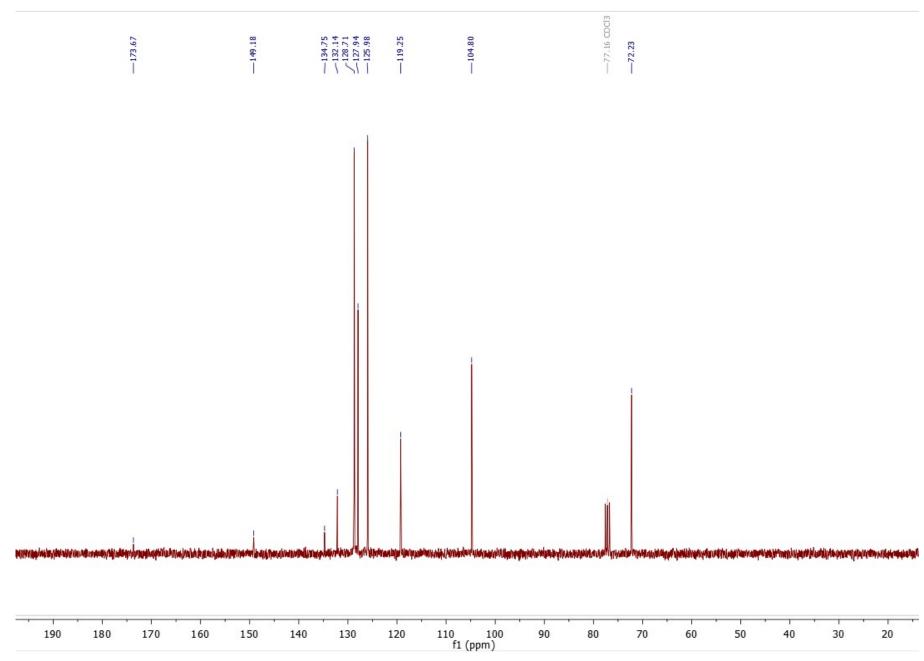




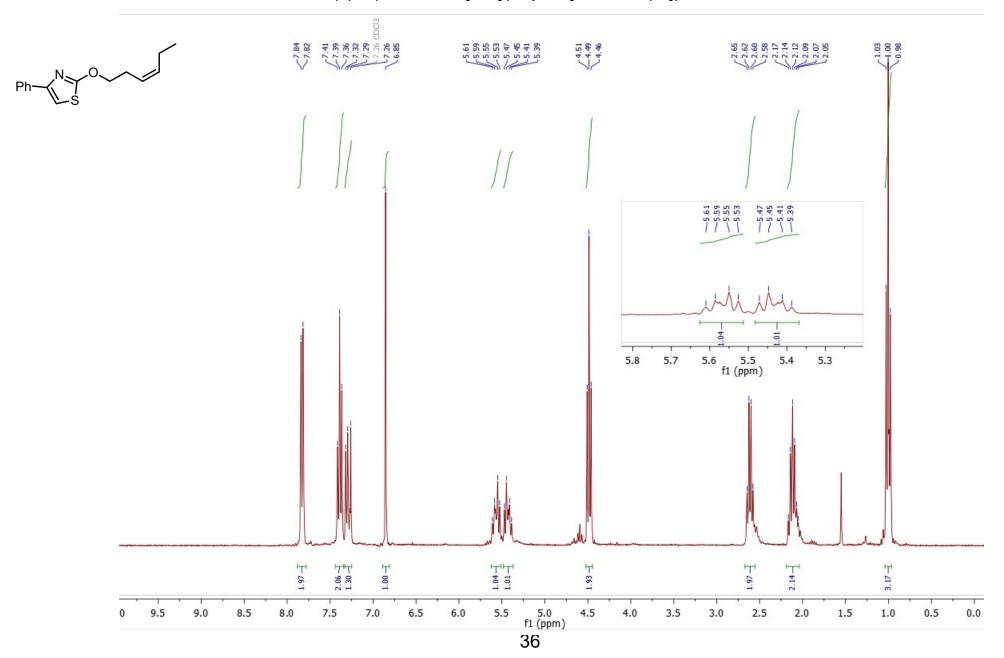


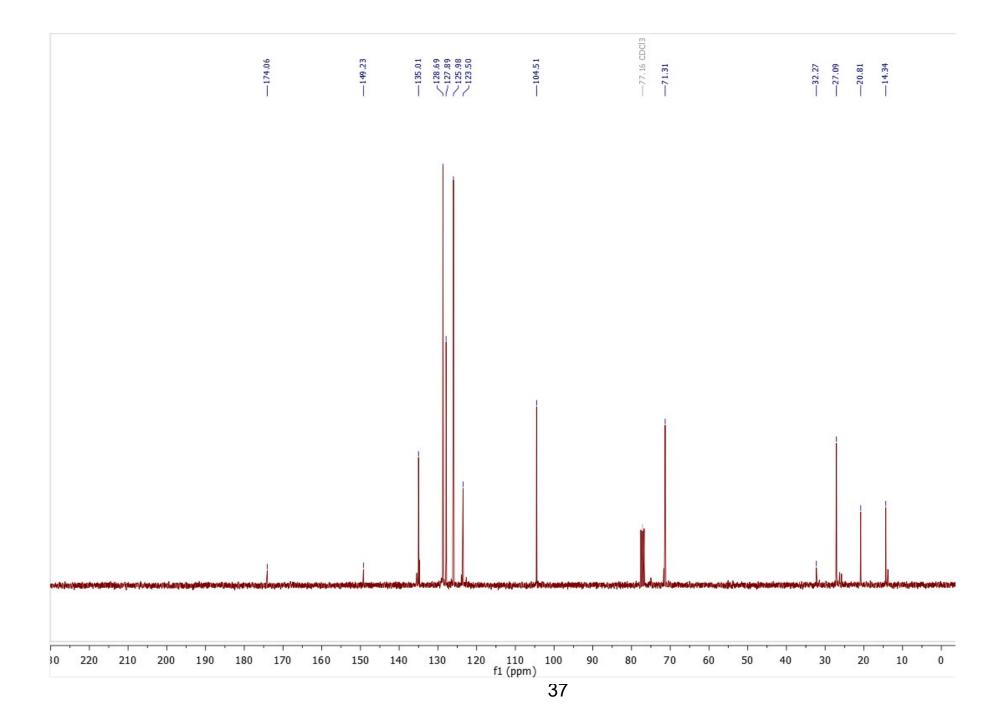


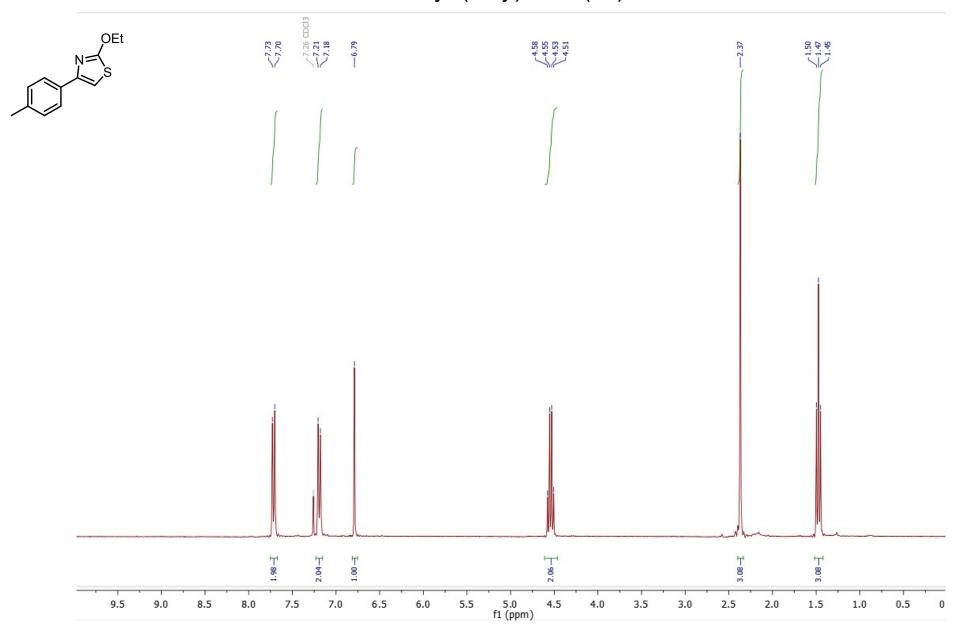


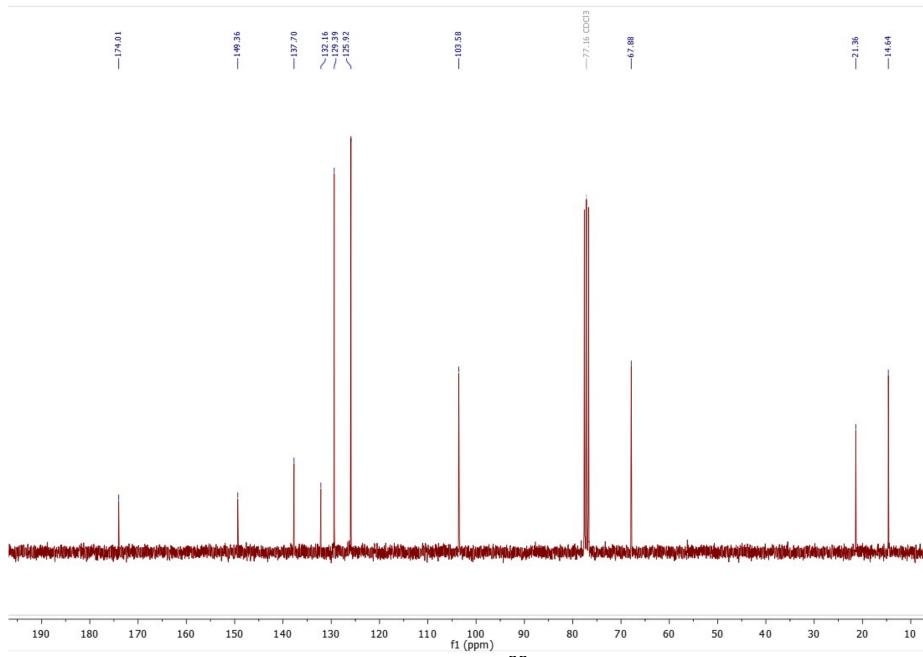


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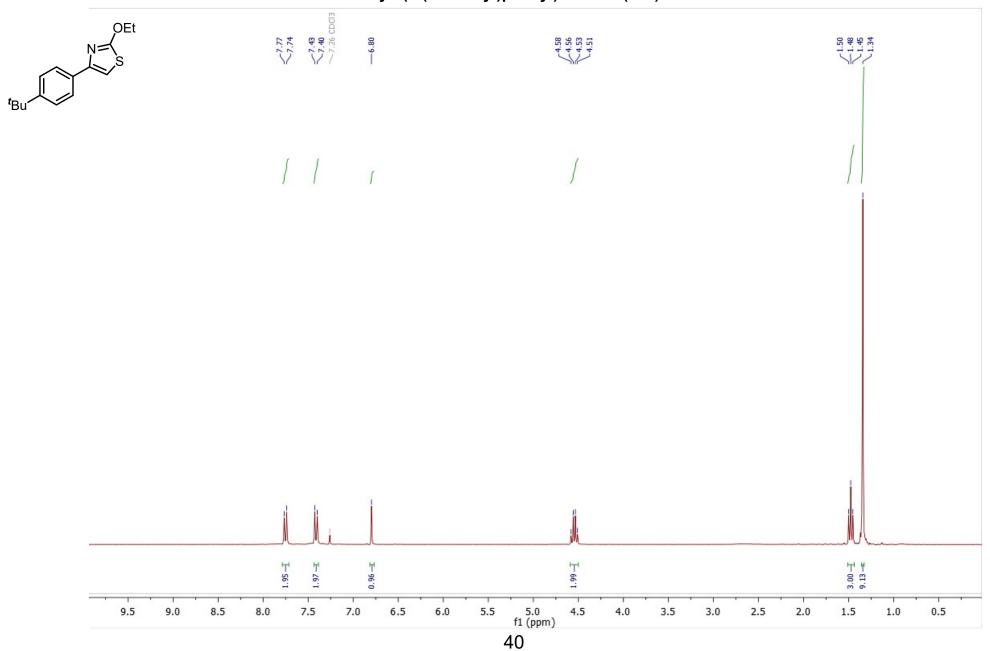


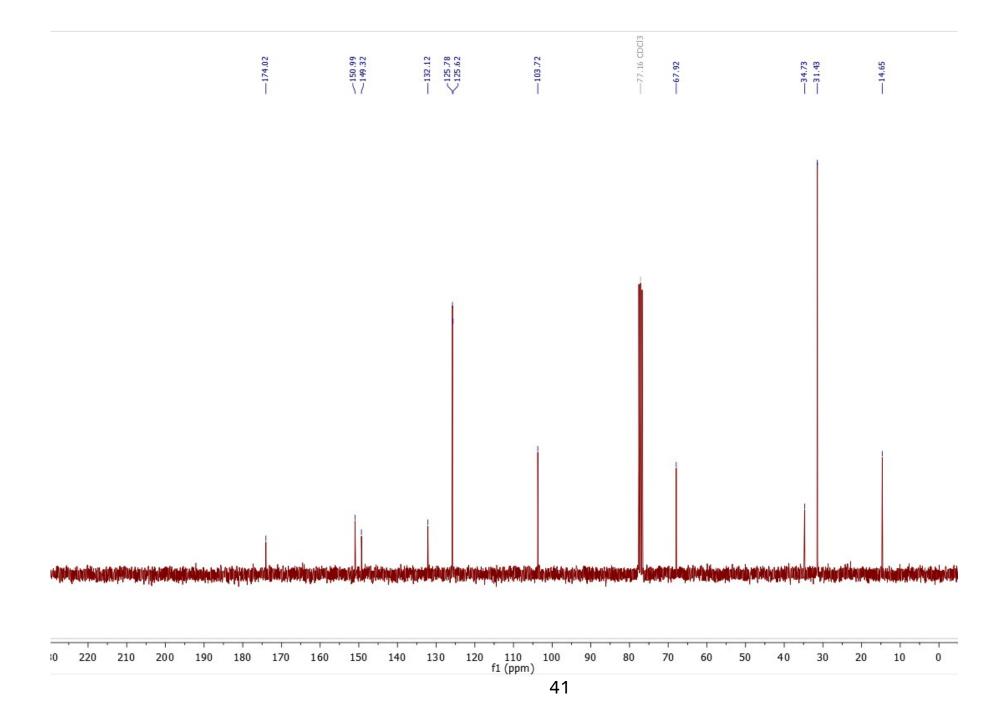




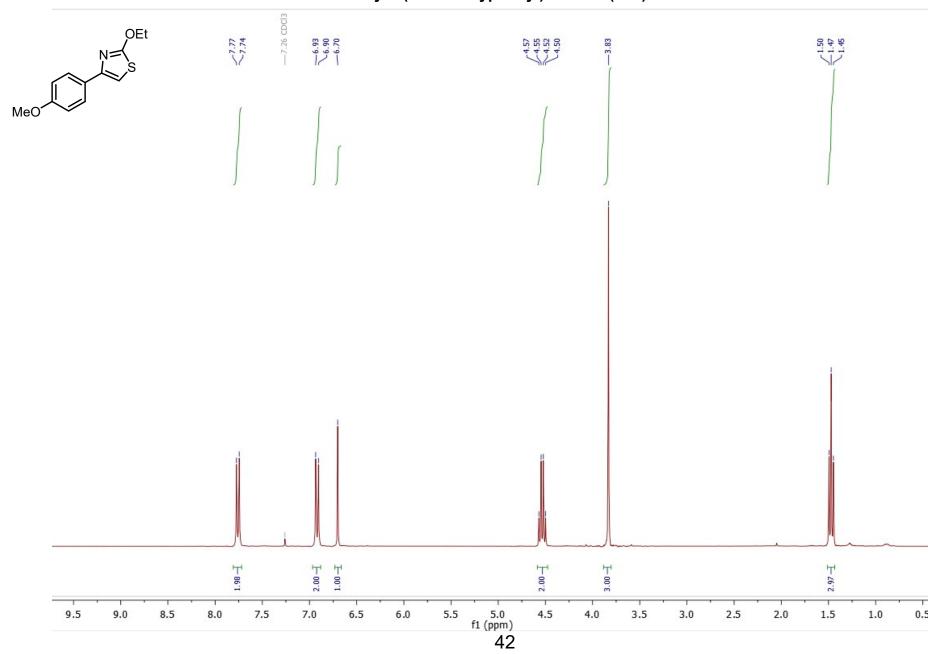


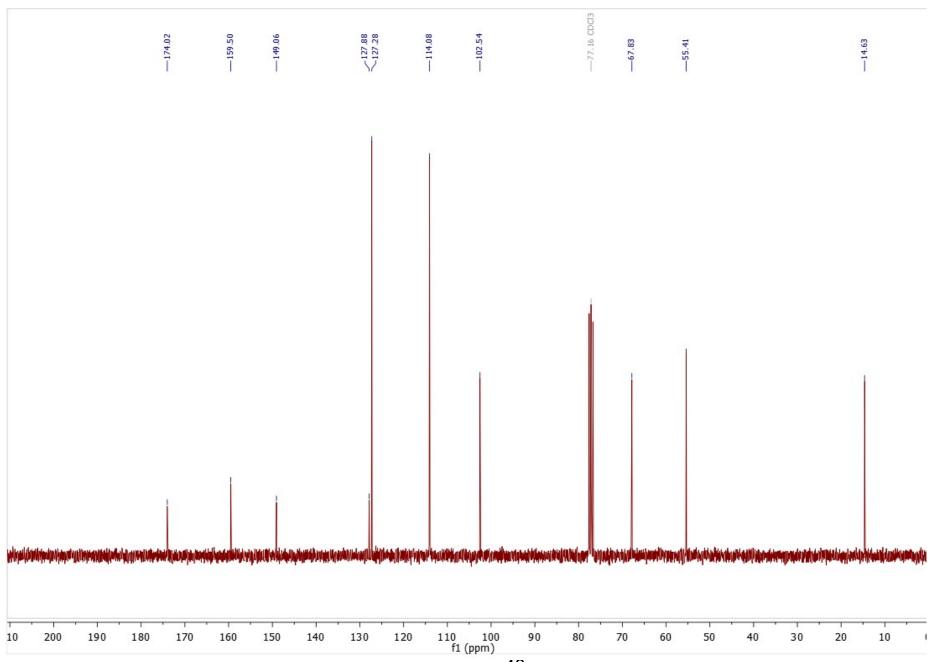
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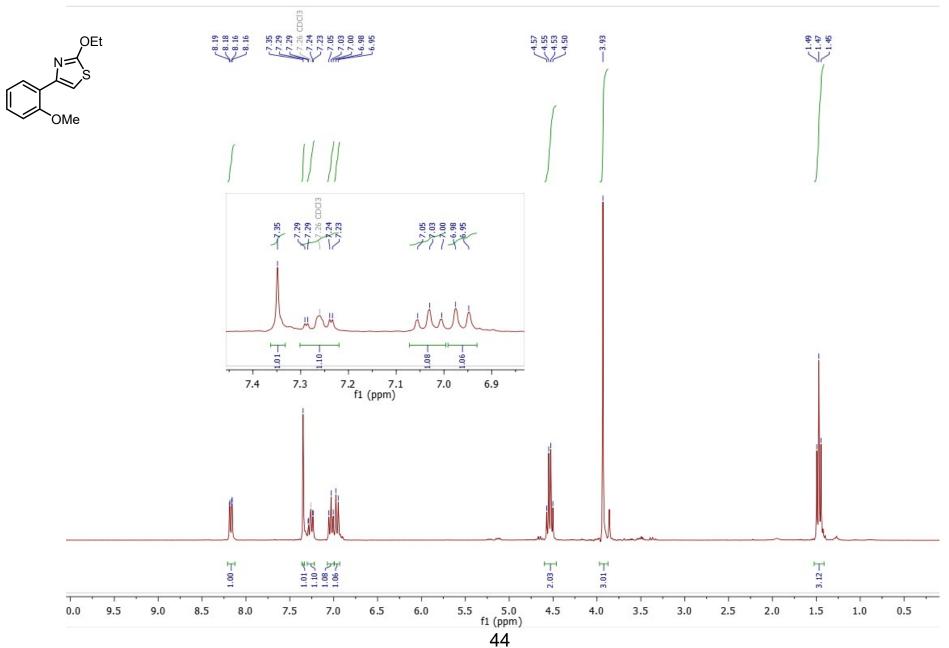


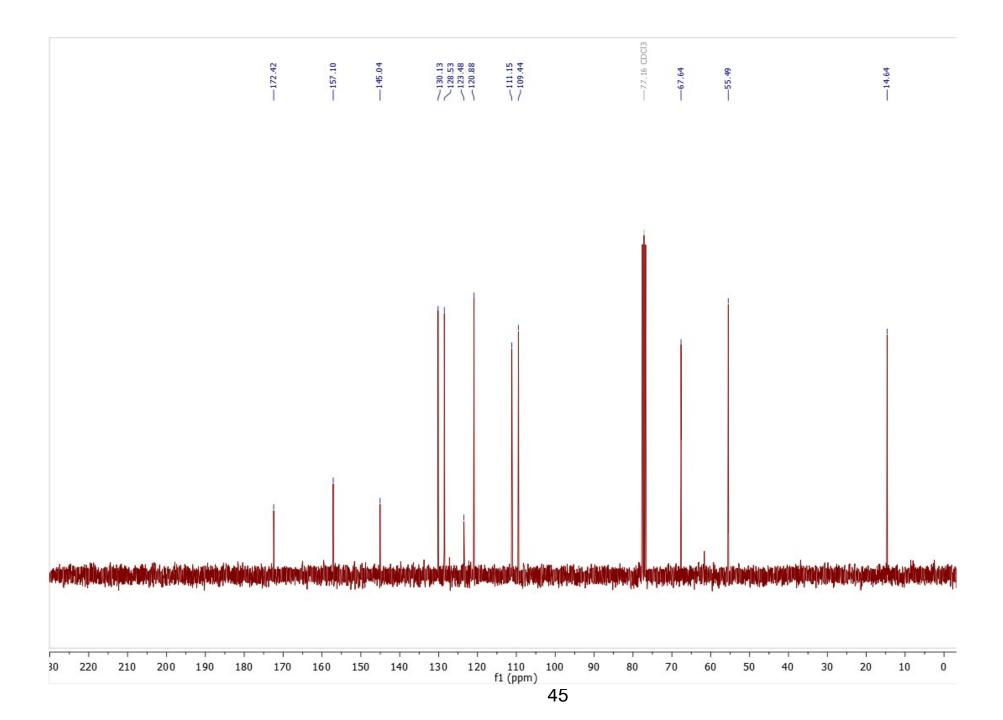
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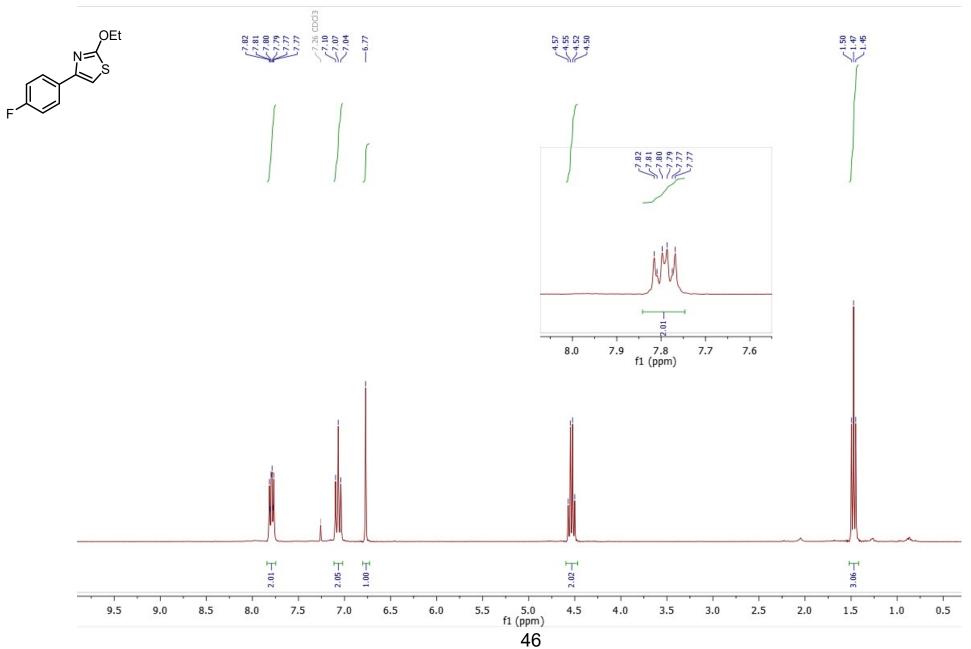


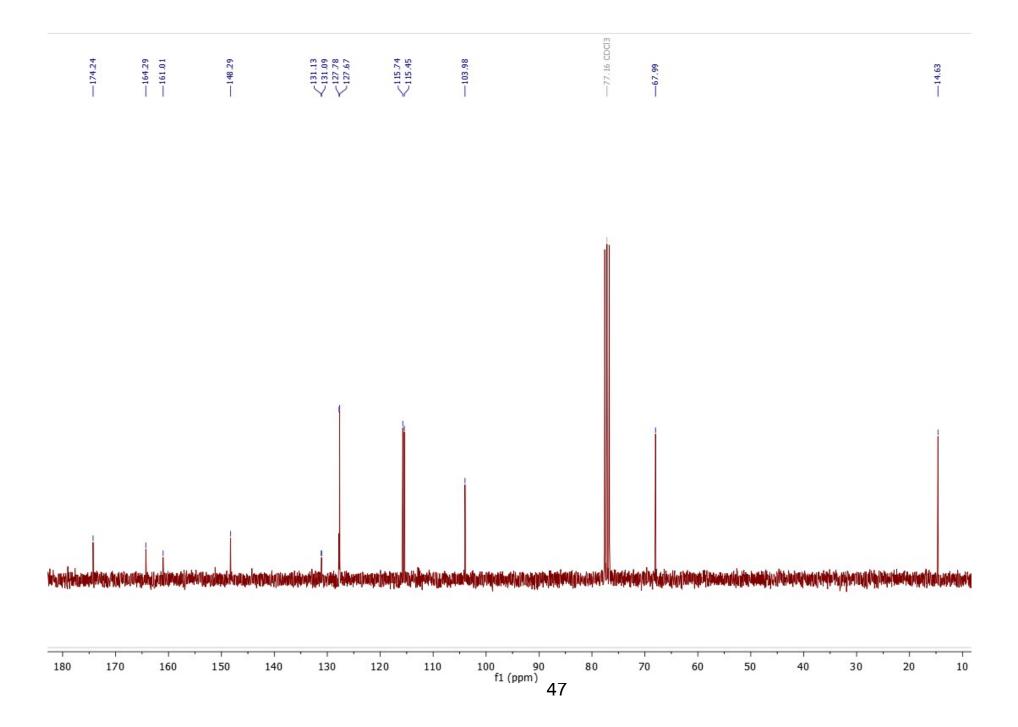
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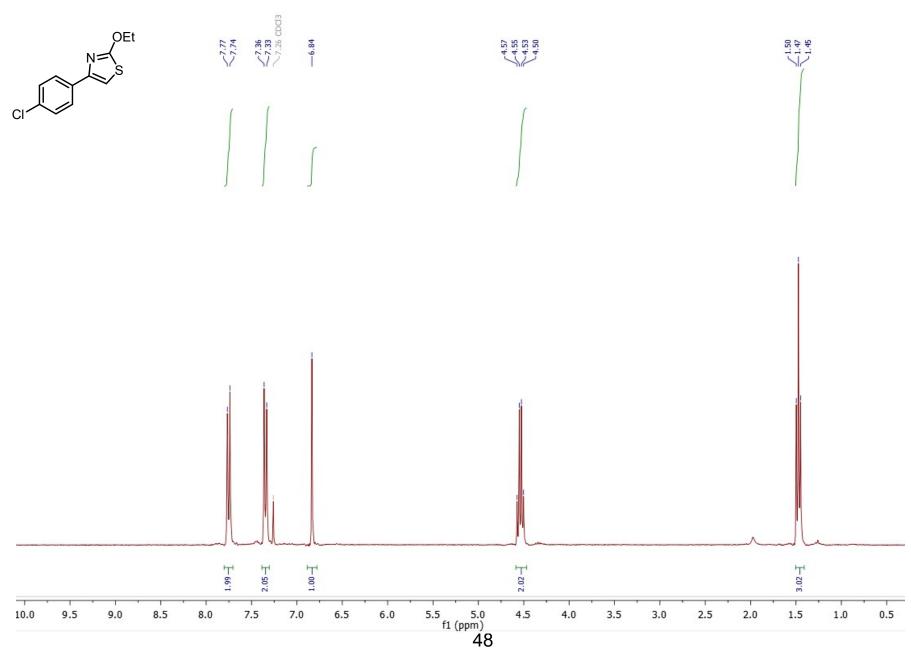


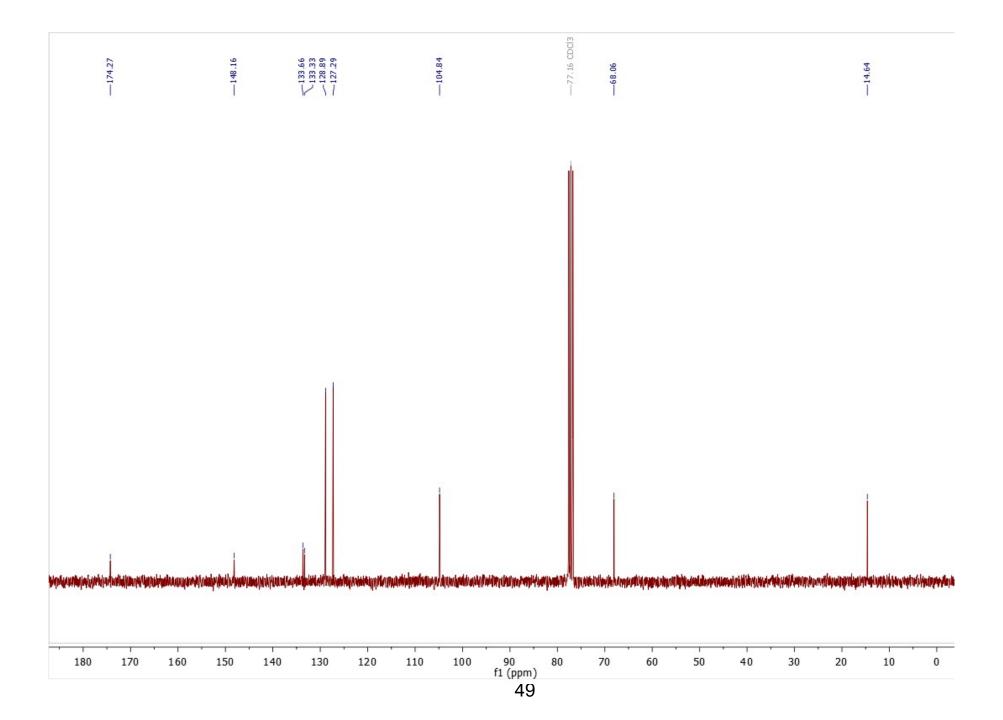
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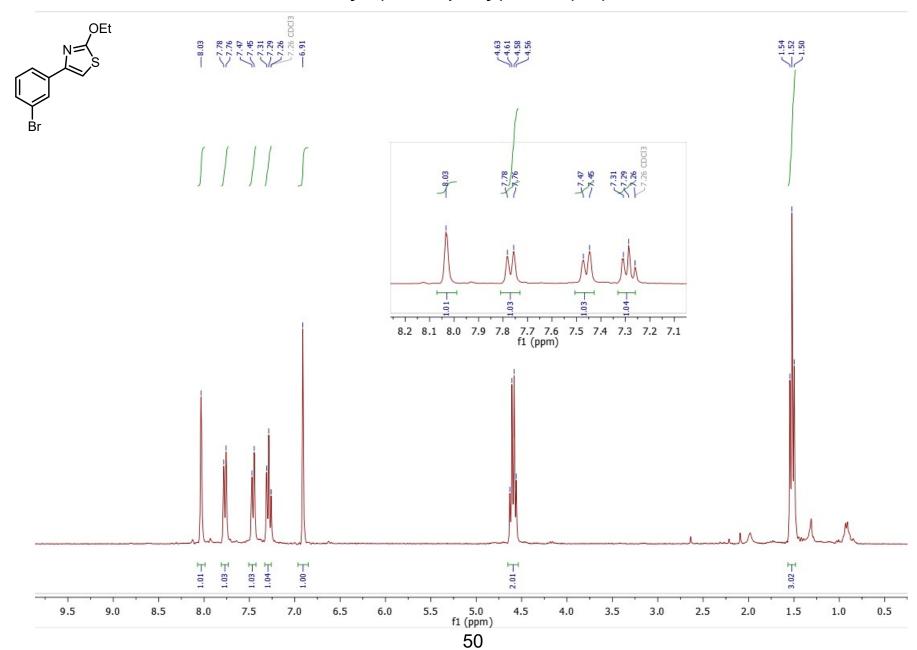


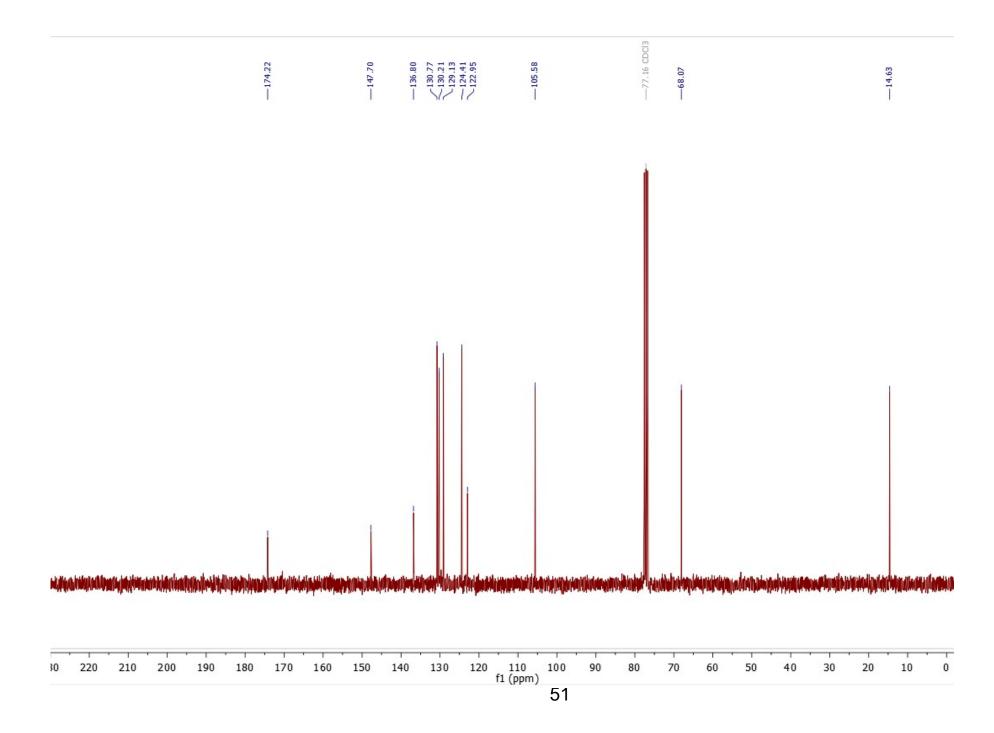
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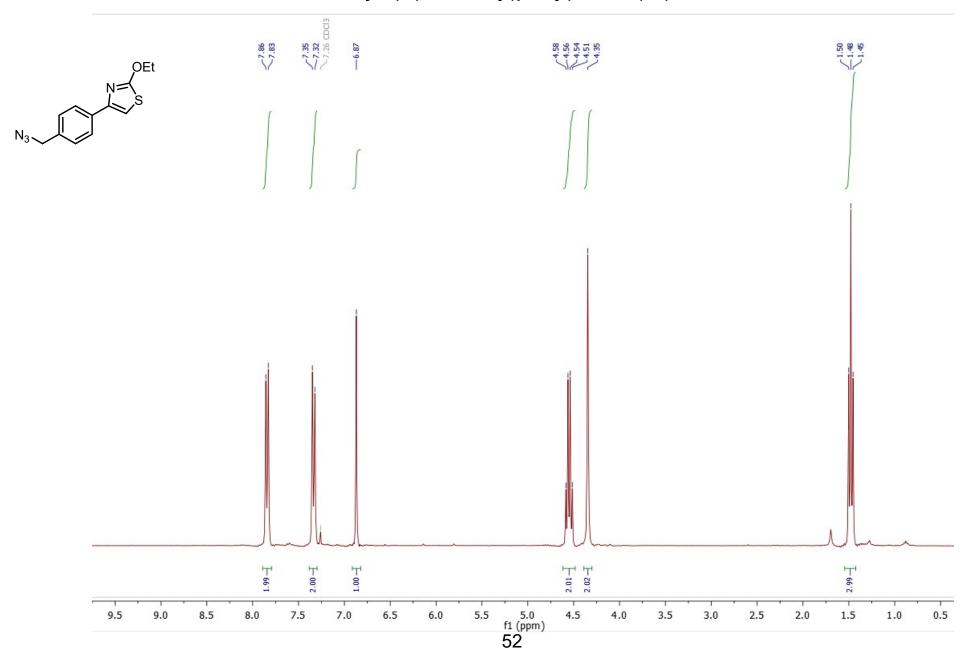


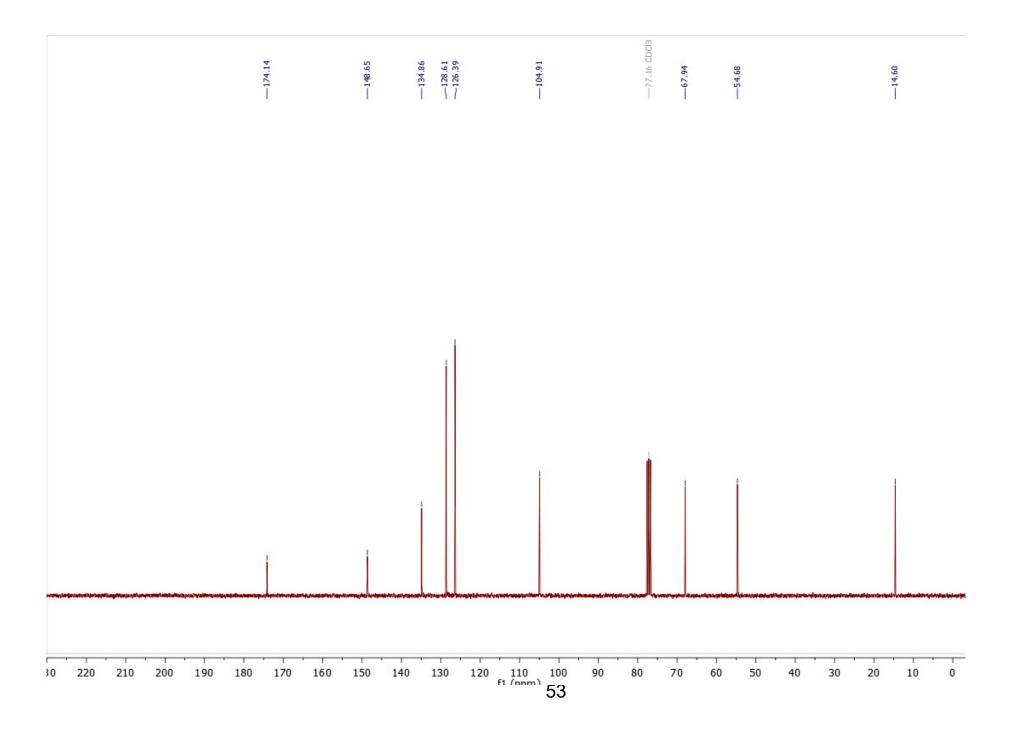
2-Ethoxy-4-(3-bromophenyl)thiazole (3hc)



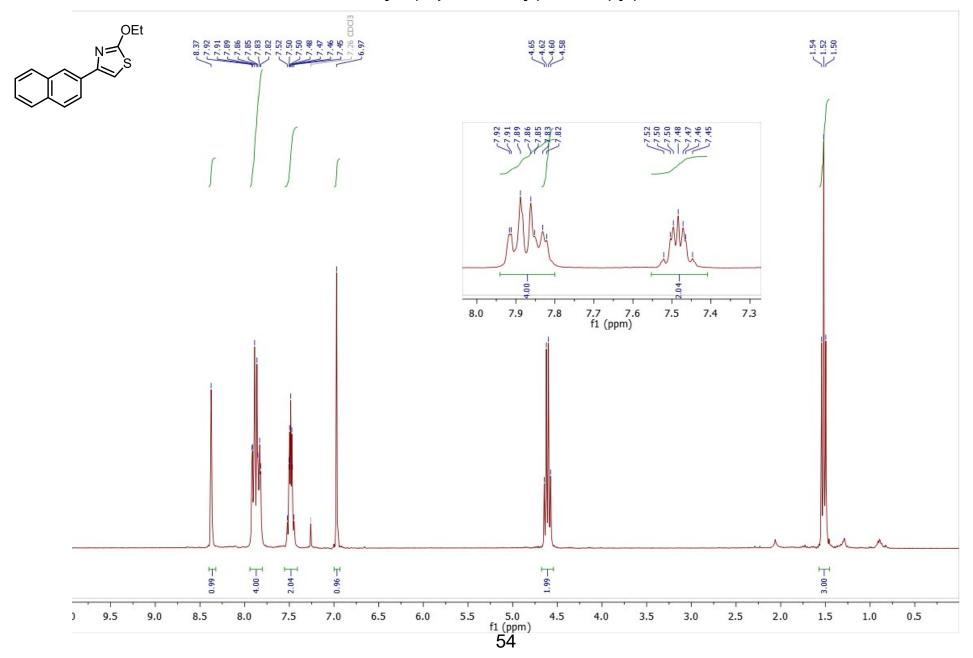


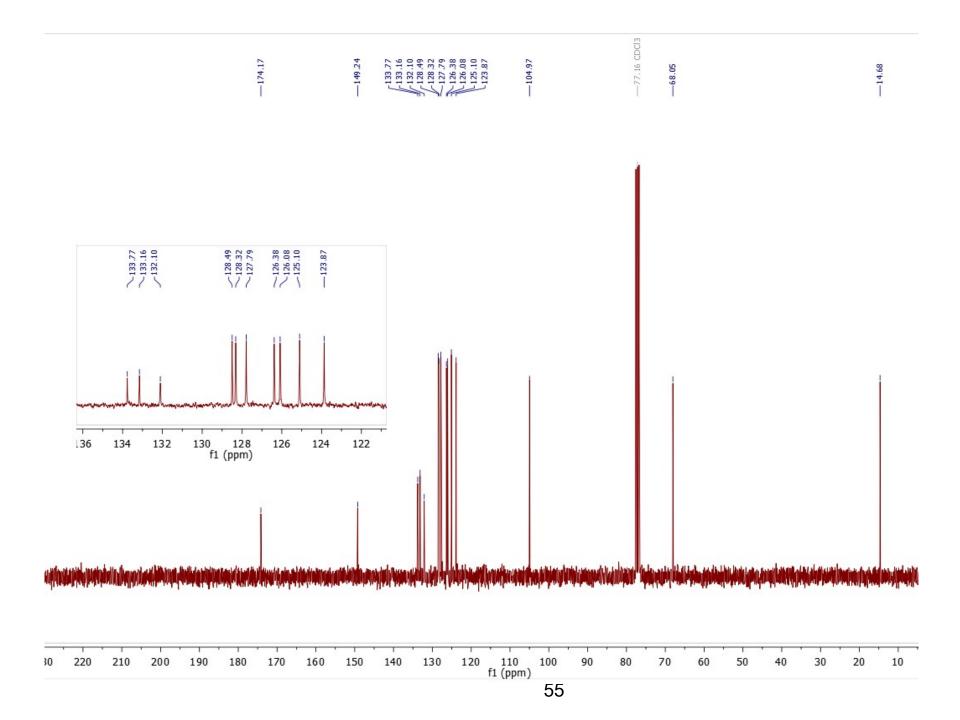
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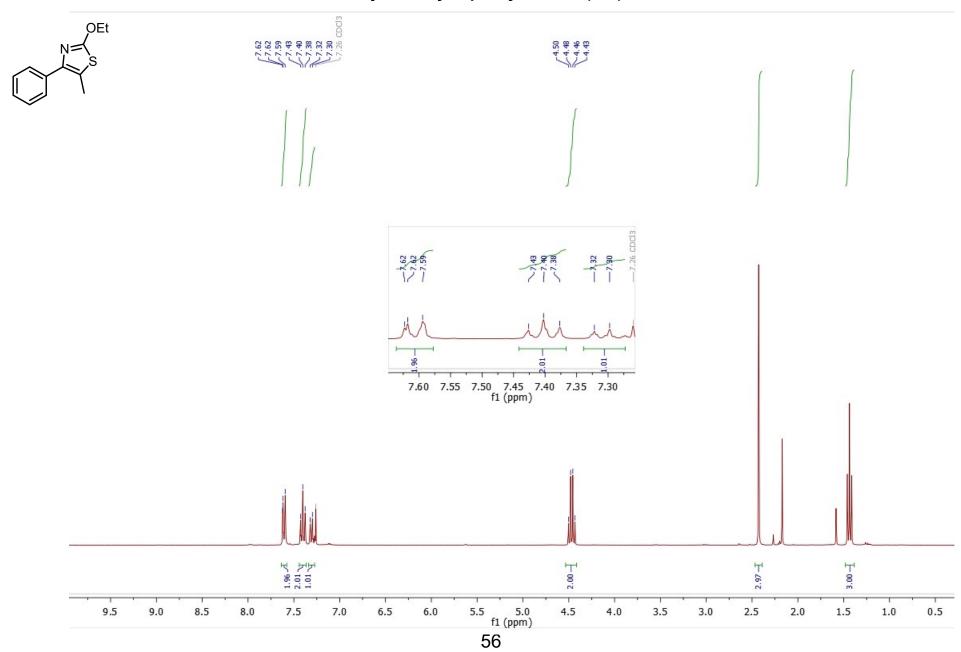


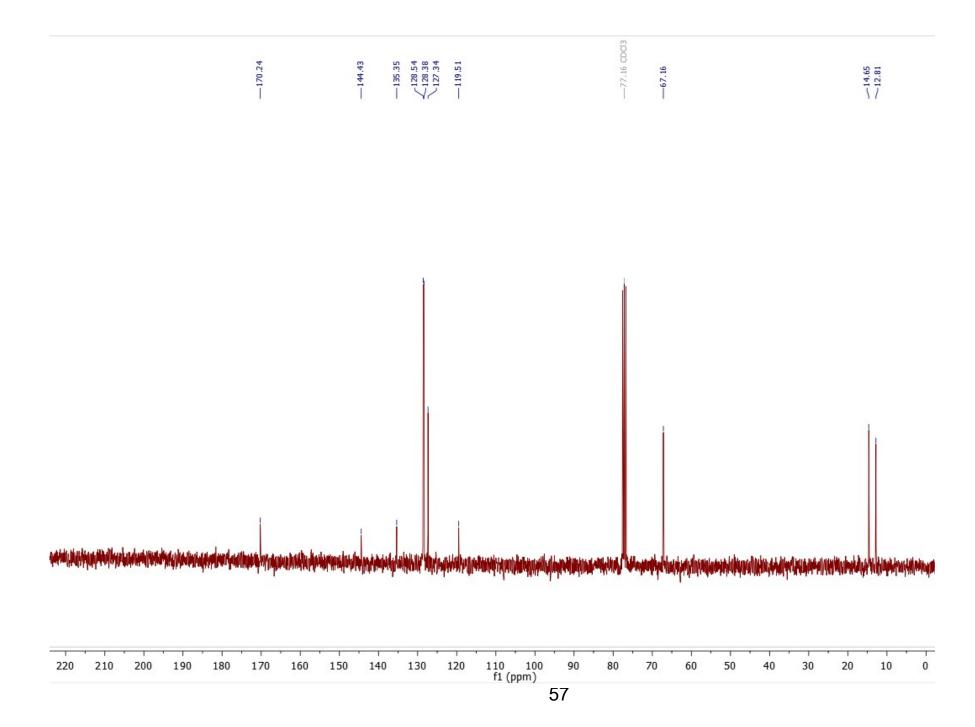
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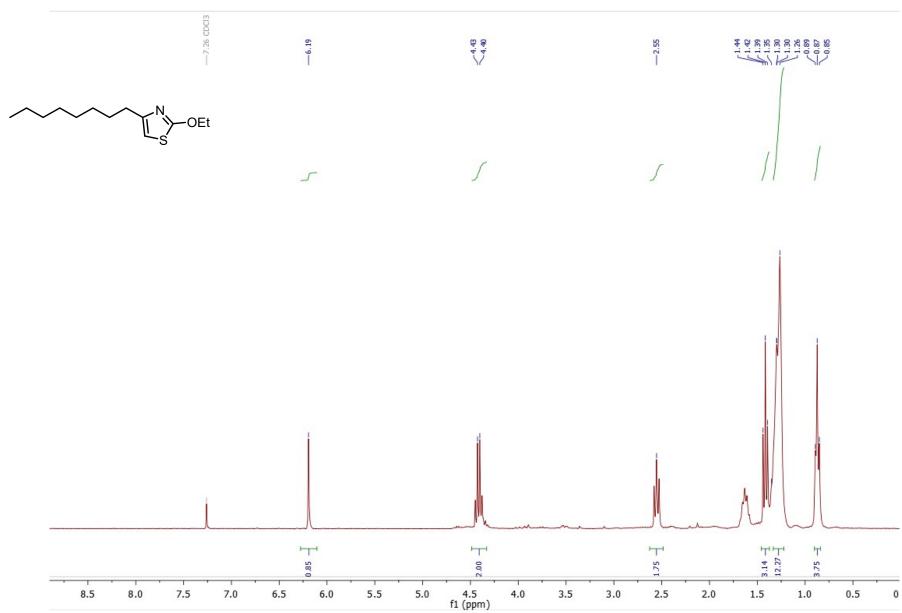


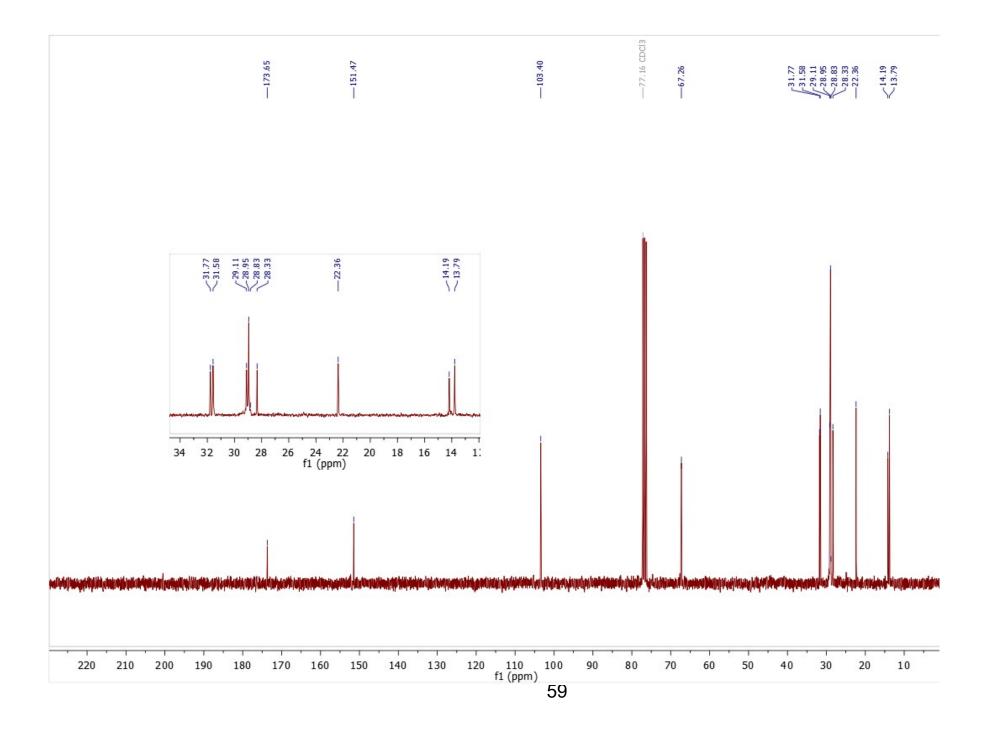
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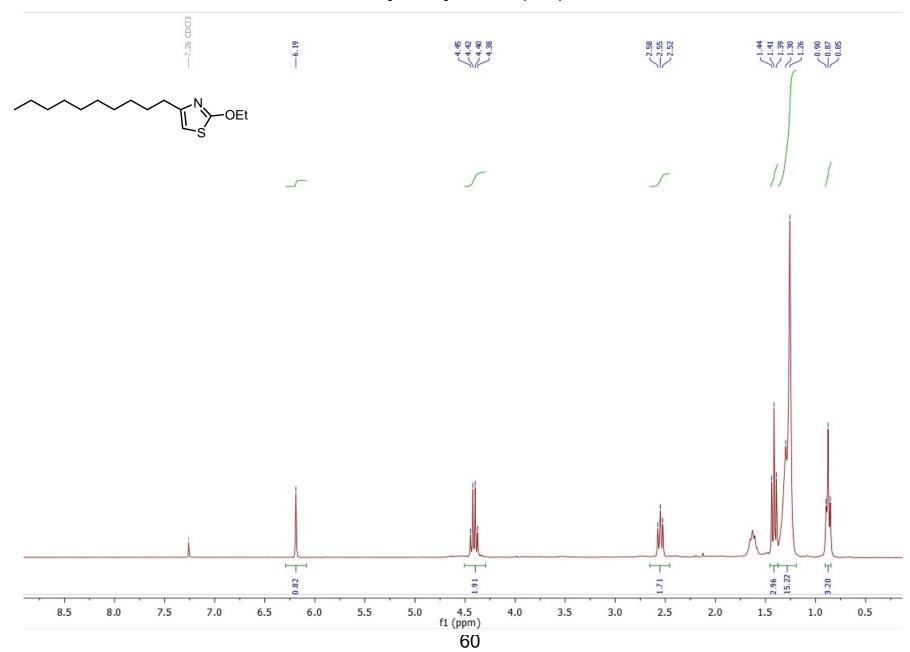


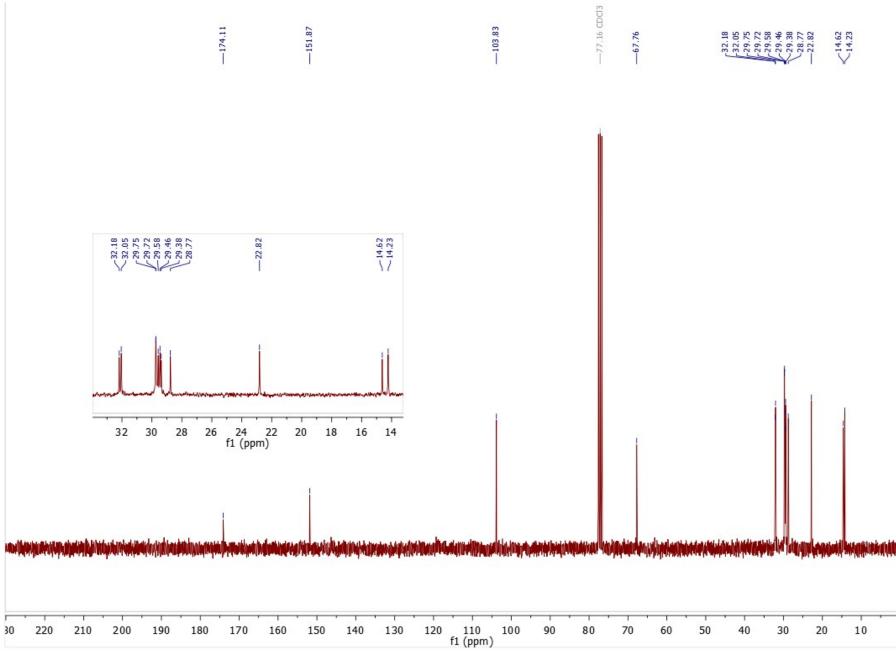
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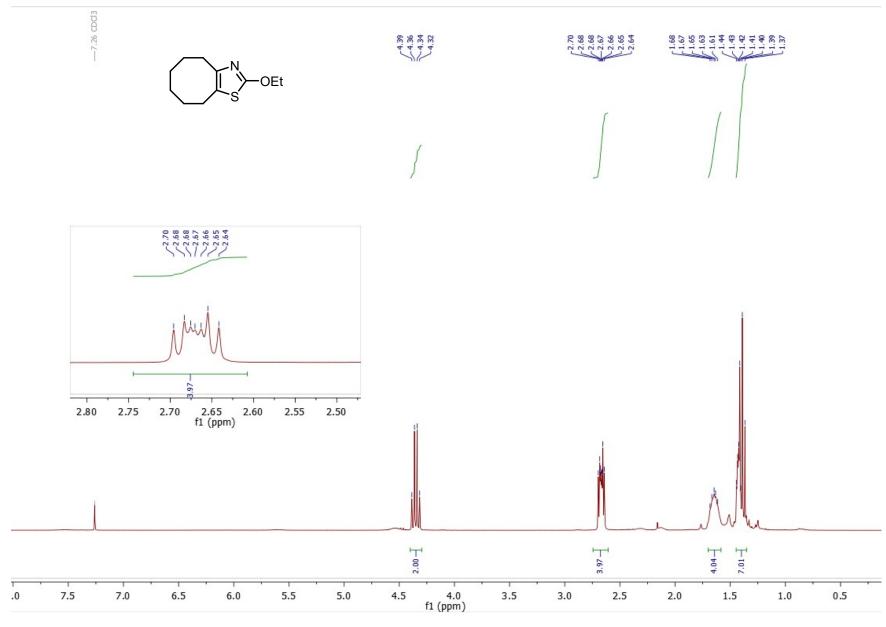


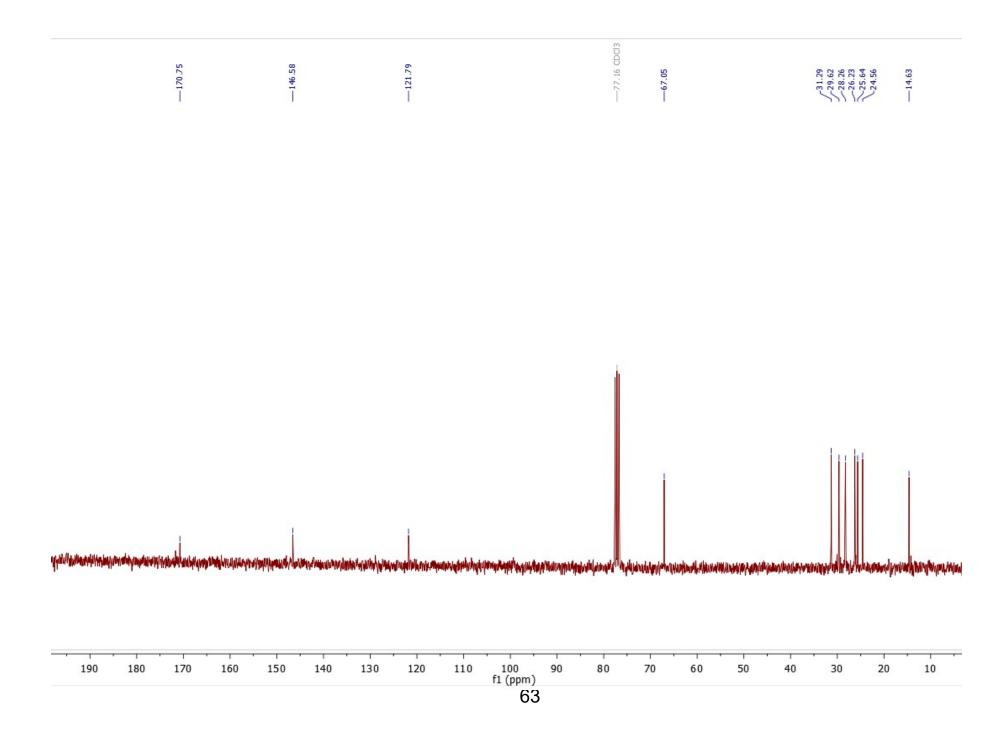
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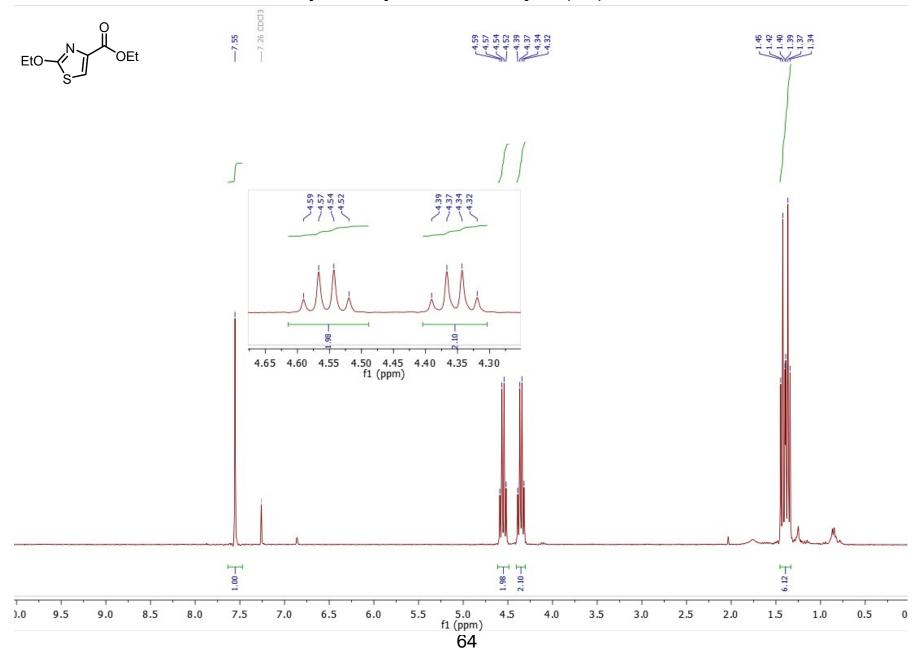


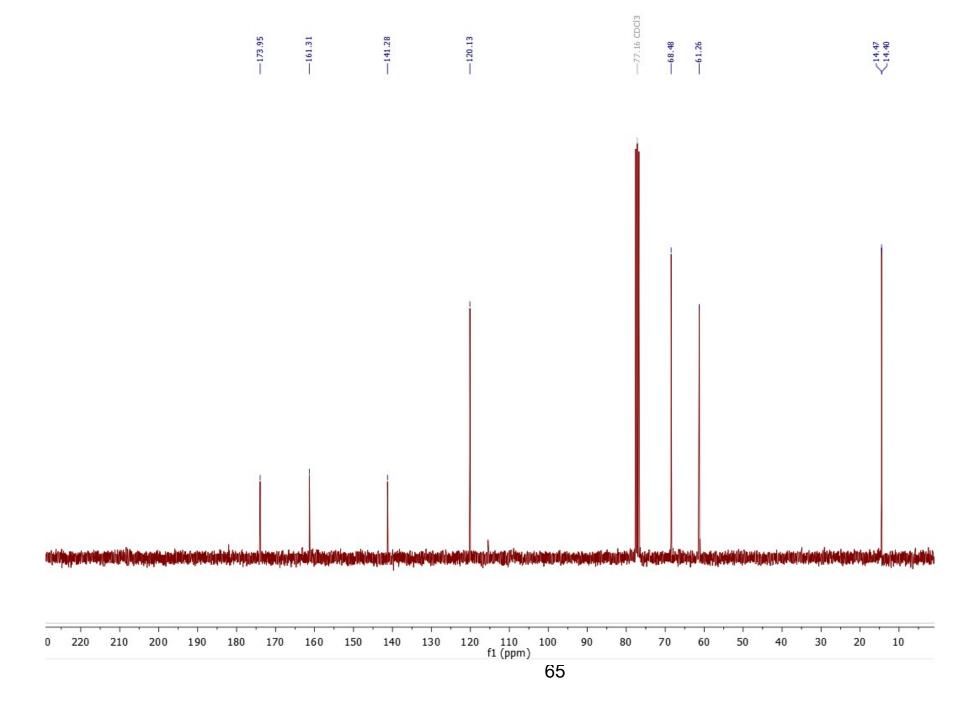


2-Ethoxy-4,5,6,7,8,9-hexahydrocycloocta[d]thiazole (3nc)



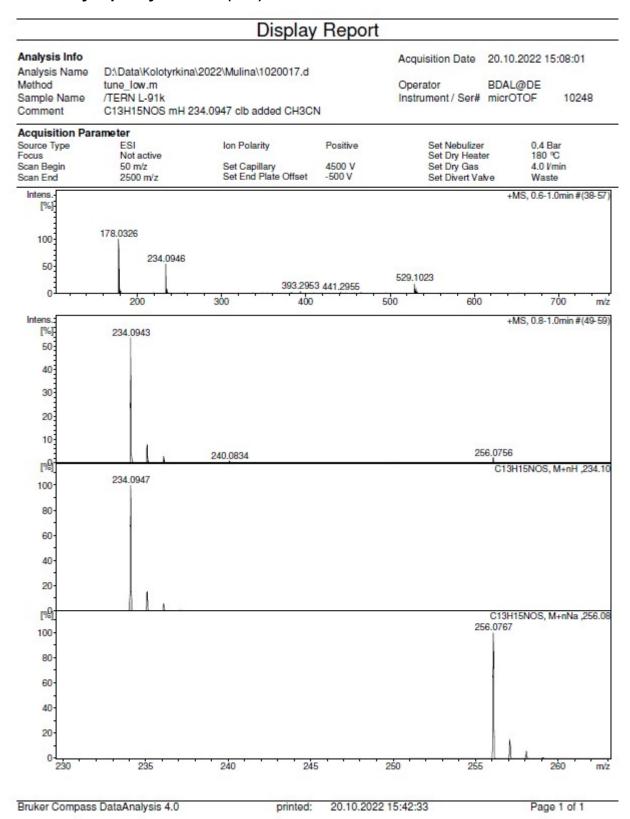




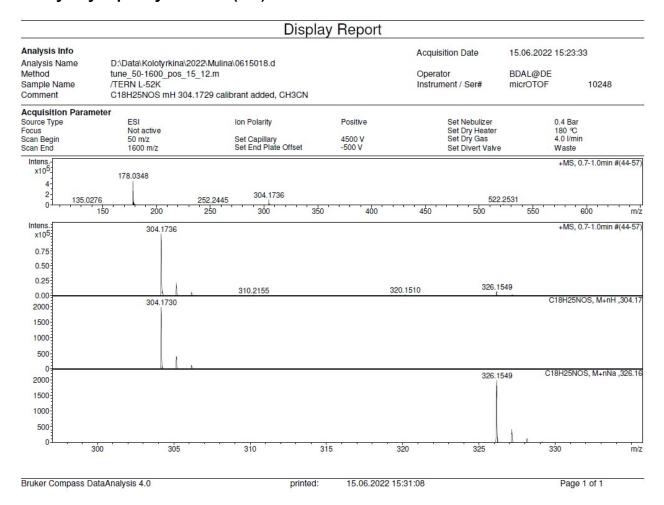


HRMS spectra of the synthesized compounds

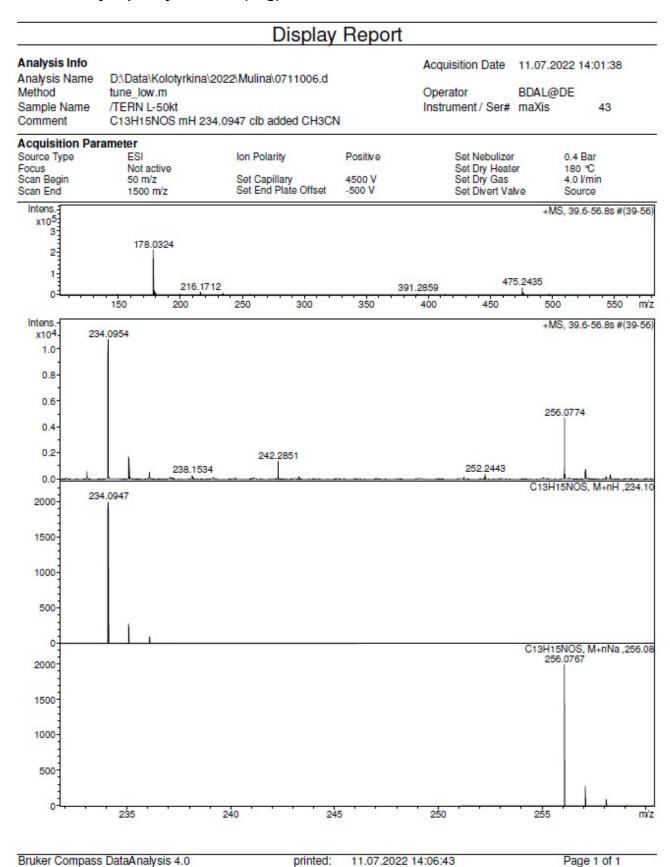
2-iso-Butoxy-4-phenylthiazole (3ae)



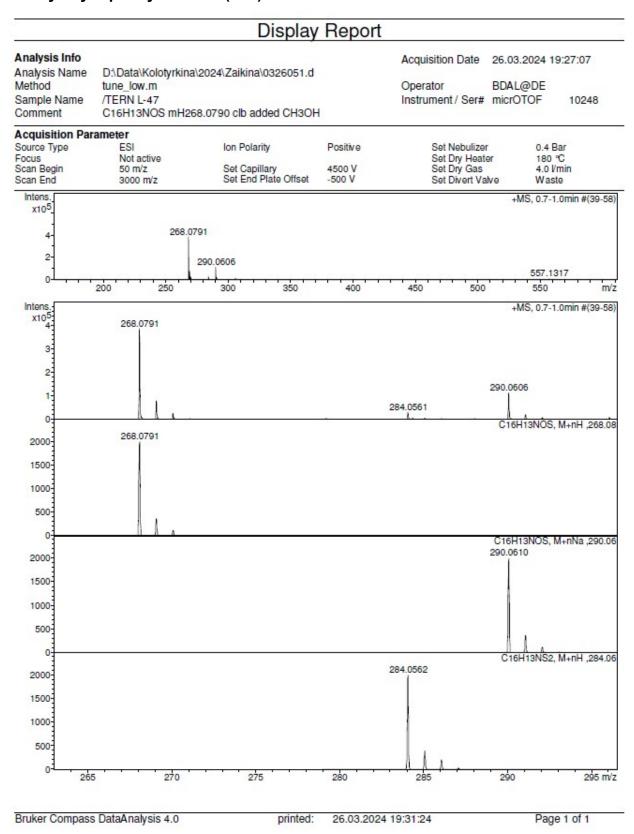
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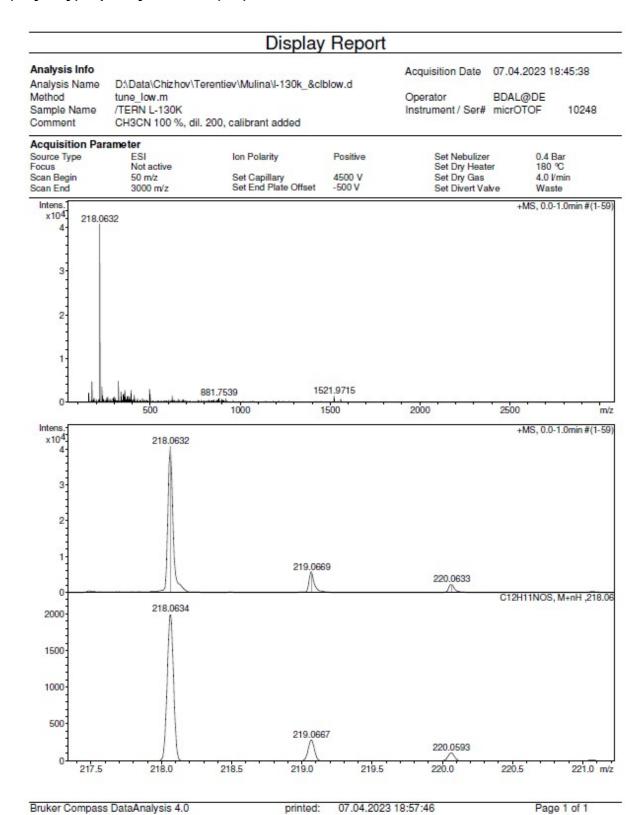
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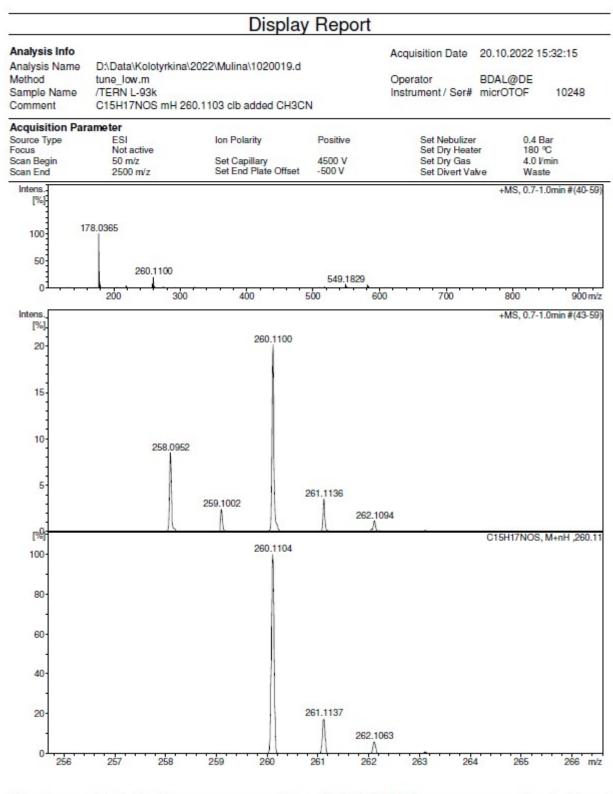
2-Benzyloxy-4-phenylthiazole (3ah)



2-(Allyloxy)-4-phenylthiazole (3ai)



(Z)-2-(Hex-3-en-1-yloxy)-4-phenylthiazole (3aj)



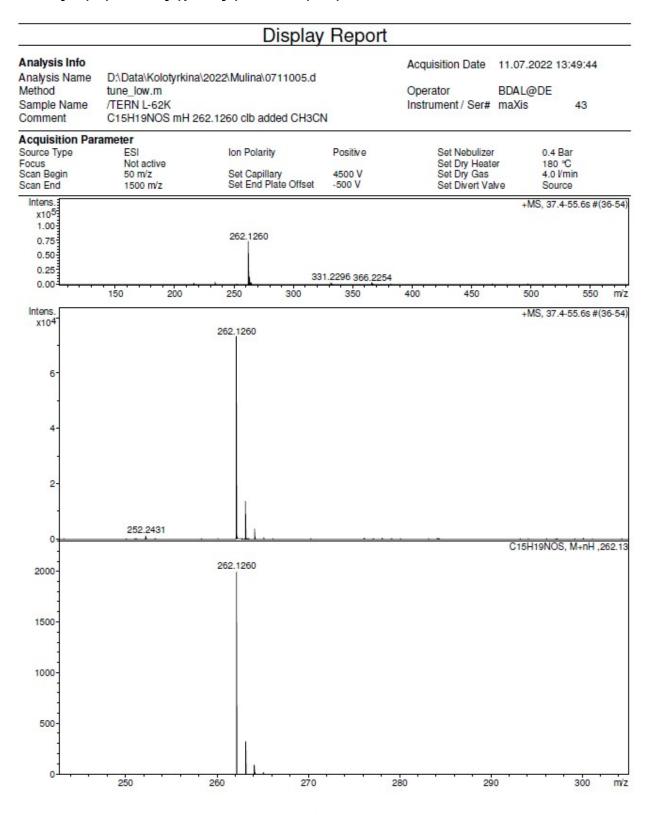
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2-Ethoxy4-(4-(tert-butyl)phenyl)thiazole (3cc)



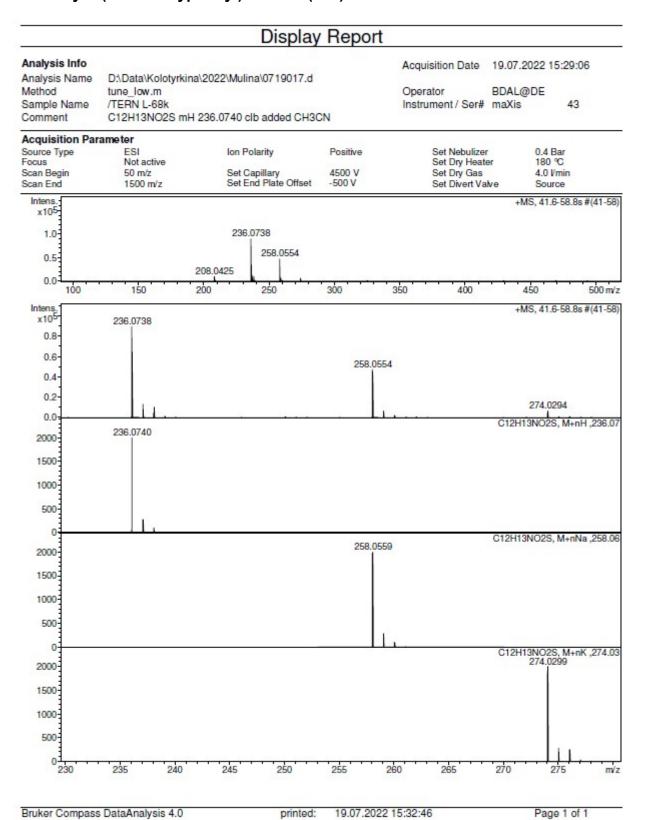
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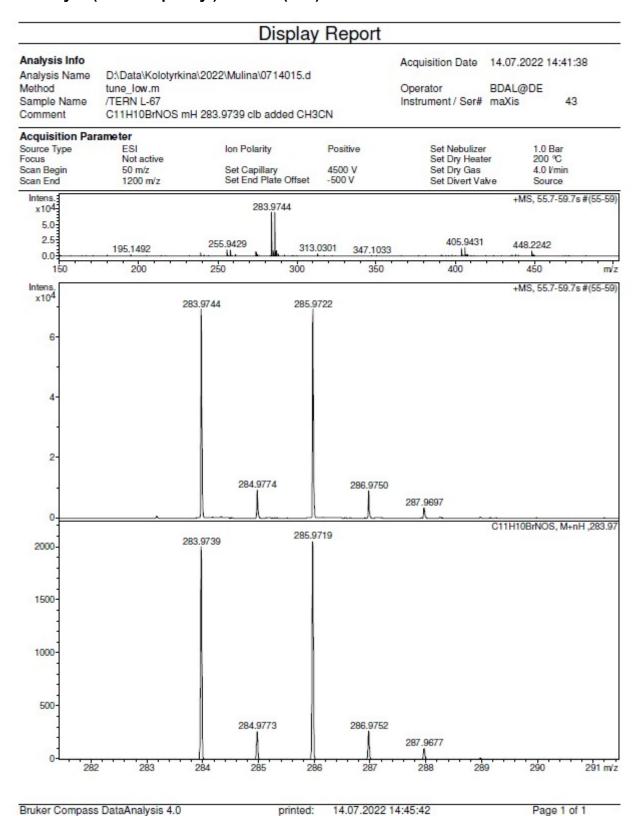
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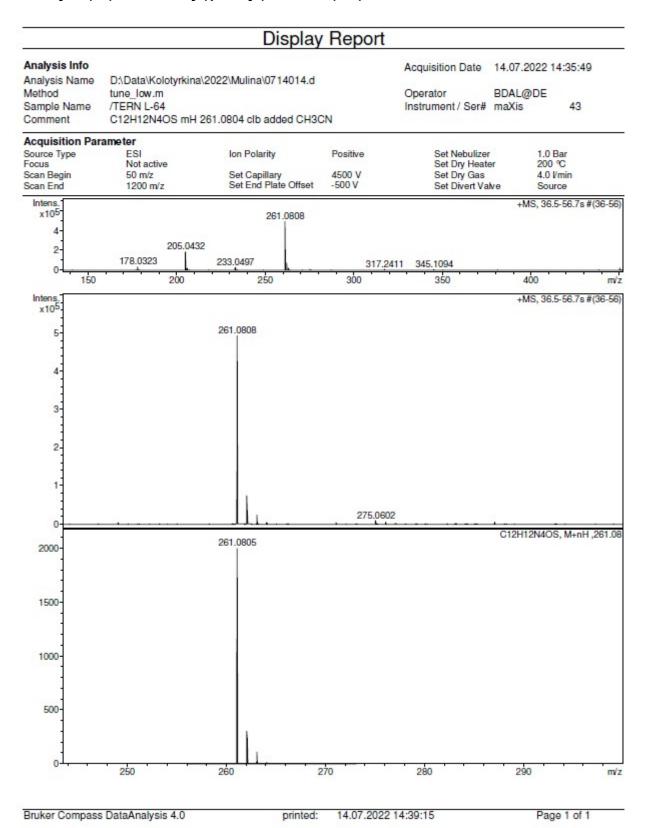
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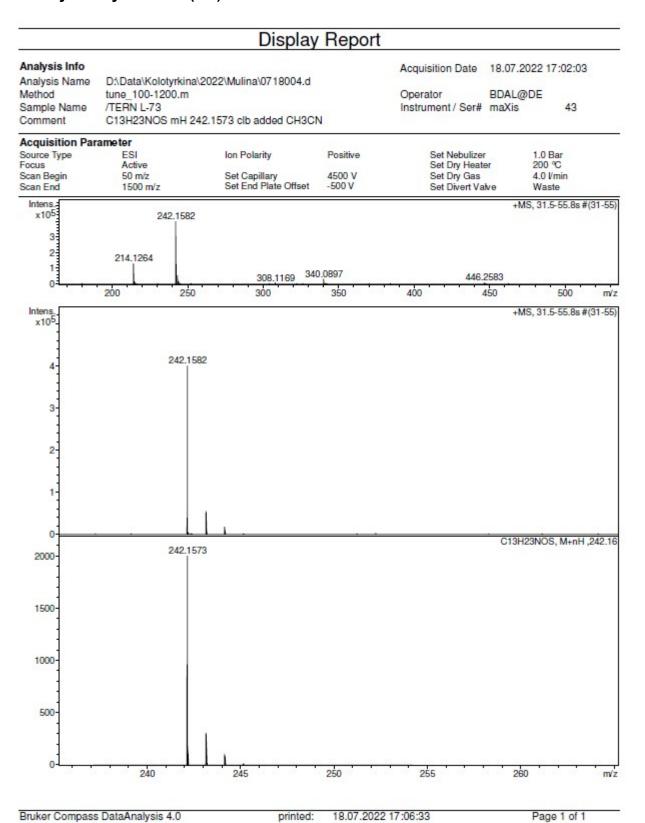
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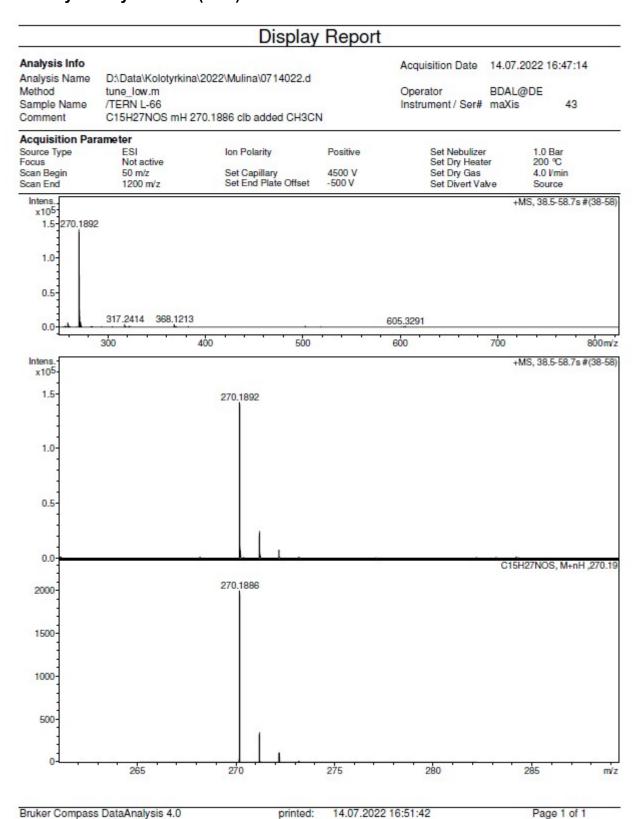
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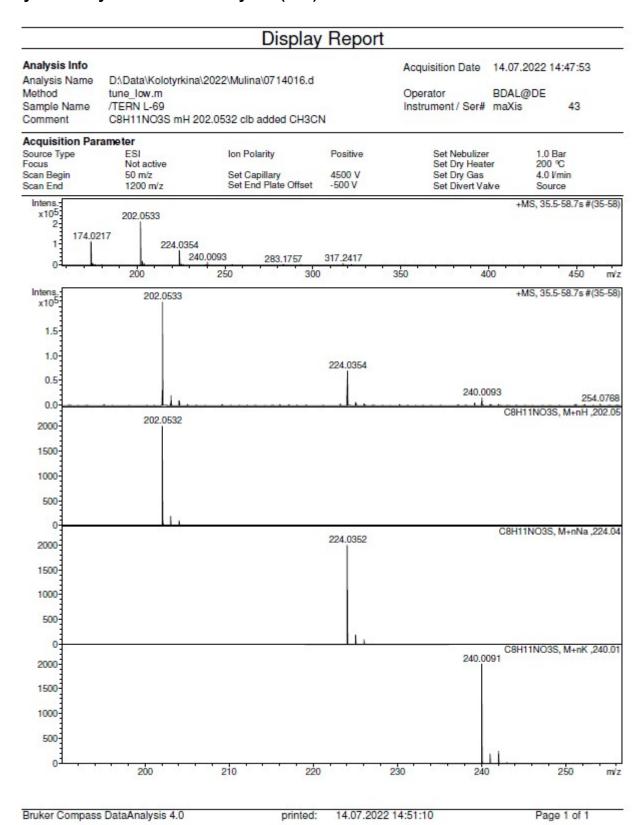
2-Ethoxy-4-octylthiazole (3lc)



2-Ethoxy-4-decylthiazole (3mc)



Ethyl 2-ethoxythiazole-4-carboxylate (3oc)



The control experiment using TEMPO

