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Supporting Information

Copper-Catalyzed Synthesis of Thiazol-2-yl Ethers from Oxime Acetates and Xanthates under Redox-Neutral Conditions

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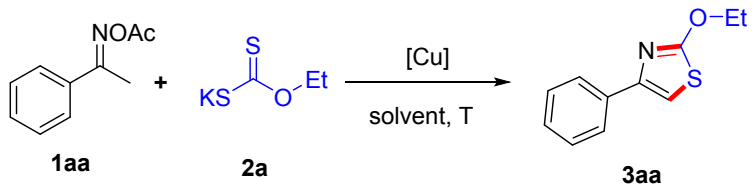
General methods

Melting points were measured with a melting point instrument and were uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and chloroform is solvent with TMS as the internal standard. GC-MS was obtained using electron ionization. TLC was performed by using commercially prepared 100-400 mesh silica gel plates and visualization was effected at 254 nm. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with an infrared Fourier spectrometer. High-resolution mass spectra (ESI) were obtained with a LCMS-IT-TOF mass spectrometer.

Screening reaction conditions

Table 1. Optimization of reaction conditions [a]



1aa **2a** **3aa**

entry	[Cu] (mol %)	**2a** (equiv)	T (°C)	solvent	yield (%)[b]
1	CuCl (20)	1.0	120	DCE	32
2	CuBr (20)	1.0	120	DCE	30
3	$Cu(OAc)_2$(20)	1.0	120	DCE	34
4	$Cu(OTf)_2$(20)	1.0	120	DCE	32
5	$CuCl_2$ (20)	1.0	120	DCE	35
6	$CuBr_2$ (20)	1.0	120	DCE	44
7	$CuBr_2$ (20)	1.2	120	DCE	53
8	$CuBr_2$ (20)	1.5	120	DCE	53
9	$CuBr_2$ (20)	1.2	120	toluene	42
10	$CuBr_2$ (20)	1.2	120	DMSO	n. d.
11	$CuBr_2$ (20)	1.2	120	CH3CN	12
12	$CuBr_2$ (20)	1.2	120	DCM	78
13	$CuBr_2$ (20)	1.2	115	DCM	85 (83) [c]
14	$CuBr_2$ (20)	1.2	110	DCM	75
15	$CuBr_2$ (10)	1.0	115	DCM	76
16	$CuBr_2$ (5)	1.0	115	DCM	52
17 [d]	$CuBr_2$ (20)	1.2	115	DCM	83
18	-	1.2	115	DCM	n. d.

[a] Reaction conditions: All reactions were performed with **1aa** (0.3 mmol), **2a**, catalyst, solvent (2.0 mL) in a sealed tube for 6 h. [b] GC-MS yield using *n*-dodecane as an internal standard. n. d. = not detected. [c] Isolated yield. [d] Under N_2 atmosphere.

Typical procedure for preparation of oxime acetates

General Procedure for oximes：To a solution of aromatic ketones (2 mmol) in the mixture of C_2H_5OH/H_2O (v/v = 1:1) was added hydroxylamine hydrochloride (2.2 mmol), NaOAc (3 mmol) in one portion, and the reaction mixture was stirred at 100 ^oC (when the substrates are aromatic ketones) or at room temperature (when the substrates are aromatic aldehydes) for 6-8 h. Upon completion of the reaction as indicated by TLC, the reaction mixture was diluted with water, extracted with ethyl acetate, and dried over anhydrous Na_2SO_4. The solvent was removed and concentrated under reduced pressure to give oximes.

General Procedure for oxime acetates: The mixture of ketoximes (2.0 mmol), anhydride (4.0 mmol, 2.0 equiv) was stirred in CH_2Cl_2 (10 mL) at room temperature for 24 h. Upon completion of the reaction as indicated by TLC, the reaction mixture was diluted with EtOAc (25 mL), washed with H_2O (20 mL) and aq. $NaHCO_3$ (10 mL). Neutralization with $NaHCO_3$ and dried over anhydrous Na_2SO_4 and evaporated in vacuo. The crude residue was purified by column chromatography using silica gel with hexanes as the eluent to give ketoxime acetates.

Typical procedure for the preparation of potassium xanthates 2

A mixture of alcohol (15 mmol), KOH (560 mg, 10 mmol) was stirred in 10 mL of dry diethyl

ether at room temperature for 1 h. Then carbon disulfide (12 mmol) was added and stirred at room temperature for 1 h to afford the corresponding potassium xanthates **2** as white or yellow precipitate. After that, the precipitate was washed and filtered with diethyl ether twice and dried under vacuum to provide the pure compounds.

Typical procedure for the preparation 3 and 4

Oximes acetates **1** (0.3 mmol), potassium xanthates **2** (0.36 mmol), CuBr (13.4 mg, 0. 06 mmol), and 2 mL of dry CH_2Cl_2 were added to a 10 mL screw-capped tube (F891410 reaction tube, purchased from beijing synthware glass). The reaction mixture was stirred at 115 ^oC (oil bath) for 6 h . The crude product was cooled to room temperature and filtered to obtain a filtrate. Then, the filtrate was concentrated in vacuum to give a mixture, which was purified by flash column chromatography to afford the target product. This operation is potentially dangerous and the screw-capped tube must be intact.

Characterization data for all products

2-Ethoxy-4-phenylthiazole (3aa): as a gray oil (51.1 mg, 83% yield); R_f = 0.5 (petroleum ether); IR (KBr): 2967, 2925, 1613, 1450, 1343, 945, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.87-7.85 (m, 2H), 7.43-7.39 (m, 2H), 7.36-7.28 (m, 1H), 6.85 (s, 1H), 4.57 (q, J = 7.1 Hz, 2H), 1.49 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 149.2, 134.8, 128.6, 127.8, 125.9, 104.4, 67.8, 14.6; HRMS (ESI) m/z: calcd for $C_{11}H_{12}NOS$ $[M+H]^+$ 206.0634; found 206.0633.

2-Ethoxy-4-(*p*-tolyl)thiazole (3ab): as a yellow solid (55.8 mg, 85% yield); mp 51.3-52.3 ^oC; R_f = 0.5 (petroleum ether); IR (KBr): 3114, 2961, 2925, 1650, 1525, 1230, 1018, 819, 730 cm^{-1}; ^1H

NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.2 Hz, 2H), 7.22 (t, J = 13.0 Hz, 2H), 6.79 (s, 1H), 4.55 (q, J = 7.1 Hz, 2H), 2.38 (s, 3H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 149.3, 137.6, 132.1, 129.3, 125.8, 103.5, 67.8, 21.3, 14.5; HRMS (ESI) m/z: calcd for $C_{12}H_{14}NOS$ $[M+H]^+$ 220.0791; found 220.0787.

2-Ethoxy-4-(4-ethylphenyl)thiazole (3ac): as a yellow oil (53.1 mg, 76% yield); R_f = 0.5 (petroleum ether); IR (KBr): 2965, 2928, 1526, 1231, 1021, 837, 745; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.71 (m, 2H), 7.24-7.19 (m, 2H), 6.77 (d, J = 2.1 Hz, 1H), 4.55-4.49 (m, 2H), 2.75-2.57 (m, 2H), 1.45 (td, J = 7.1, 2.2 Hz, 3H), 1.24 (td, J = 7.6, 2.3 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 149.3, 144.0, 132.3, 128.1, 125.9, 103.5, 67.7, 28.7, 15.6, 14.5; HRMS (ESI) m/z: calcd for $C_{13}H_{16}NOS$ $[M+H]^+$ 234.0947; found 234.0950.

2-Ethoxy-4-(4-methoxyphenyl)thiazole (3ad): as a yellow soild (45.8 mg, 65% yield); mp 49.1-50.0 ^{o}C;R_f = 0.3 (petroleum ether); IR (KBr): 2932, 1609, 1528, 1488, 1245, 1174, 1026, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 159.4, 149.0, 127.8, 127.2, 114.0, 102.4, 67.7, 55.3, 14.5; HRMS (ESI) m/z: calcd for $C_{12}H_{14}NO_2S$ $[M+H]^+$ 236.0740; found 236.0738.

2-Ethoxy-4-(4-(methylthio)phenyl)thiazole (3ae): as a gray oil (46.6 mg, 62% yield); R_f = 0.4 (petroleum ether); IR (KBr): 3113, 2982, 2923, 1596, 1526, 1475, 1231, 1018, 829, 741 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.6 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 6.78 (s, 1H), 4.53 (d, J = 7.1 Hz, 2H), 2.49 (s, 3H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 154.3, 146.4, 137.7, 129.0, 123.2, 122.6, 121.6, 114.3, 55.5, 18.5; HRMS (ESI) m/z: calcd for $C_{12}H_{14}NOS_2$ $[M+H]^+$ 252.0511; found 252.0507.

2-Ethoxy-4-(4-fluorophenyl)thiazole (3af): as a yellow solid (46.8 mg, 67% yield); mp 56.5-57.5 ^{o}C; R_f = 0.5 (petroleum ether); IR (KBr): 3112, 2981, 2823, 1679, 1525, 1473, 1229, 1018, 826, 739 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.78 (m, 2H), 7.09-7.05(m, 2H), 6.76 (s, 1H), 4.54 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 163.7, 161.3, 148.2, 131.0, 131.0, 127.6, 127.6, 115.6, 115.4, 103.9, 67.8, 14.5; HRMS (ESI) m/z: calcd for $C_{11}H_{11}FNOS$ $[M+H]^+$ 224.0540; found 224.0537.

4-(4-Chlorophenyl)-2-ethoxythiazole (3ag): as a light yellow solid (50.9 mg, 71% yield); mp 60.5-61.5 ^{o}C; R_f = 0.6 (petroleum ether); IR (KBr): 2982, 2925, 1681, 1526, 1233, 1020, 745, 665 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 6.82 (s, 1H), 4.53 (d, J = 7.1 Hz, 2H), 1.46 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 148.0, 133.5, 133.2, 128.7, 127.1, 104.7, 67.9, 14.5; HRMS (ESI) m/z: calcd for $C_{11}H_{11}ClNOS$ $[M+H]^+$ 240.0244; found 240.0235.

4-(4-Bromophenyl)-2-ethoxythiazole (3ah): as a yellow solid (49.9 mg, 59% yield); mp 70.1-71.0 ^{o}C; R_f = 0.5 (petroleum ether); IR (KBr): 2982, 2927, 1640, 1523, 1233, 1019, 739, 664; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.6 Hz, 2H), 7.58-7.42 (m, 2H), 6.82 (s, 1H), 4.53 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 148.0, 133.6, 131.7, 127.5, 121.7, 104.9, 67.9, 14.5; HRMS (ESI) m/z: calcd for $C_{11}H_{11}BrNOS$ $[M+H]^+$ 283.9739; found 283.9731.

2-Ethoxy-4-(4-iodophenyl)thiazole (3ai): as a light yellow solid (51.4 mg, 51% yield); mp 81.1-81.9 ^{o}C; R_f = 0.5 (petroleum ether); IR (KBr): 2982, 2923, 1525, 1229, 1013, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.69 (m, 2H), 7.55 (d, J = 8.6 Hz, 2H), 6.86 (s, 1H), 4.53 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 148.1, 137.7, 134.2, 131.0,

127.7, 105.0, 67.9, 14.5; HRMS (ESI) m/z: calcd for $C_{11}H_{11}INOS$ $[M+H]^+$ 331.9601; found 331.9596.

2-Ethoxy-4-(4-(trifluoromethyl)phenyl)thiazole (3aj): as a white solid (61.4 mg, 75% yield); mp 148-149 ^oC; R_f = 0.6 (petroleum ether); IR (KBr): 2982, 2930, 1686, 1529, 1323, 1235, 1020, 820 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.8 Hz, 2H), 7.63 (d, J = 7.7 Hz, 2H), 6.94 (d, J = 1.7 Hz, 1H), 4.58-4.52 (m, 2H), 1.50-1.46 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 147.7, 137.9, 129.5 (q, J = 32.1 Hz), 126.0, 125.6 (q, J = 3.6 Hz), 124.3 (q, J = 270.2 Hz), 106.4, 68.0, 14.4; HRMS (ESI) m/z: calcd for $C_{12}H_{11}F_3NOS$ $[M+H]^+$ 274.0508; found 274.0507.

2-Ethoxy-4-(4-nitrophenyl)thiazole (3ak): as a yellow solid (56.2 mg, 75% yield); mp 143-144 ^oC; R_f = 0.3 (petroleum ether); IR (KBr): 3100, 2987, 1595, 1526, 1335, 1230, 852, 731 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.5 Hz, 2H), 7.92 (d, J = 8.5 Hz, 2H), 7.05 (s, 1H), 4.54 (dd, J = 13.9, 6.9 Hz, 2H), 1.46 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 146.9, 146.8, 140.4, 126.3, 124.0, 108.4, 68.2, 14.5; HRMS (ESI) m/z: calcd for $C_{11}H_{11}N_2O_3S$ $[M+H]^+$ 251.0485; found 251.0478.

2-Ethoxy-4-(*o*-tolyl)thiazole (3al): as a yellow oil (53.3 mg, 81% yield); R_f = 0.4 (petroleum ether); IR (KBr): 2927, 1682, 1526, 1322, 1233, 1020, 755 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 4.9 Hz, 1H), 7.26-7.20 (m, 3H), 6.60 (s, 1H), 4.51 (q, J = 7.1 Hz, 2H), 2.46 (s, 3H), 1.45 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 136.2, 134.9, 130.9, 129.5, 127.9, 125.8, 107.5, 67.7, 21.2, 14.5; HRMS (ESI) m/z: calcd for $C_{12}H_{14}NOS$ $[M+H]^+$ 220.0791; found 220.0787.

4-(2-Chlorophenyl)-2-ethoxythiazole (3am): as a yellow oil (40.1 mg, 56% yield); R_f = 0.5 (petroleum ether); IR (KBr): 2923, 1596, 1527, 1230, 1018, 751, 694 cm^{-1}; ^1H NMR (400 MHz,

$CDCl_3$) δ 7.93-7.90 (m, 1H), 7.44-7.42 (m, 1H), 7.33-7.29 (m, 1H), 7.24-7.20 (m, 2H), 4.54 (q, J = 7.1 Hz, 2H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 145.5, 133.3, 131.8, 131.4, 130.5, 128.6, 126.8, 110.1, 67.8, 14.5; HRMS (ESI) m/z: calcd for $C_{11}H_{11}ClNOS$ $[M+H]^+$ 240.0244; found 240.0242.

2-Ethoxy-4-(*m*-tolyl)thiazole (3an): as a yellow oil (53.1 mg, 81% yield); R_f = 0.5 (petroleum ether); IR (KBr): 2926, 1685, 1527, 1232, 1117, 1020, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.13 (d, J = 7.5 Hz, 1H), 6.84 (s, 1H), 4.56 (q, J = 7.1 Hz, 2H), 2.41 (s, 3H), 1.49 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 149.3, 138.2, 134. 7, 128.6, 128.5, 126.6, 123. 0, 104.2, 67.8, 21.5, 14.6; HRMS (ESI) m/z: calcd for $C_{12}H_{14}NOS$ $[M+H]^+$ 220.0791; found 220.0790.

2-Ethoxy-4-(3-fluorophenyl)thiazole (3ao): as a yellow oil (44.2 mg, 66% yield); R_f = 0.6 (petroleum ether); IR (KBr) 2983, 1588, 1529, 1445, 1233, 753, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.53 (m, 2H), 7.38-7.28 (m, 1H), 7.01-6.97 (m, 1H), 6.86 (s, 1H), 4.55 (q, J = 7.1 Hz, 2H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 163.2 (d, J = 243.3 Hz), 147.9, 136.9 (d, J = 8.1 Hz), 130.1(d, J = 8.3 Hz), 121.3, 121.3, 114.5 (d, J = 21.2 Hz), 112.9 (d, J = 22.8 Hz), 105.4, 67.9, 14.5; HRMS (ESI) m/z: calcd for $C_{11}H_{11}FNOS$ $[M+H]^+$ 224.0540; found 224.0541.

4-(3-Chlorophenyl)-2-ethoxythiazole (3ap): as a yellow oil (45.2 mg, 63% yield); R_f = 0.4 (petroleum ether); IR (KBr): 3115, 2983, 1595, 1527, 1233, 1018, 725 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (t, J = 1.7 Hz, 1H), 7.71-7.60 (m, 1H), 7.31-7.20 (m, 2H), 6.88-6.66 (m, 1H), 4.56-4.49 (m, 2H), 1.46 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 147.7, 136.4, 134.6,

129.8, 127.7, 126.1, 123.8, 105.5, 67.9, 14.5; HRMS (ESI) m/z: calcd for $C_{11}H_{11}ClNOS$ $[M+H]^+$, 240.0244; found 240.0246.

4-(3,4-Dimethylphenyl)-2-ethoxythiazole (3aq): as a gray oil (57.2 mg, 82% yield); R_f = 0.5 (petroleum ether); IR (KBr): 3115, 2980, 1643, 1527, 1394, 1232, 737 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.60-7.58 (m, 1H), 7.18 (d, J = 7.8 Hz, 1H), 6.80 (s, 1H), 4.58 (q, J = 7.1 Hz, 2H), 2.35 (s, 3H), 2.32 (s, 3H), 1.51 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 149.4, 136.7, 136.3, 132.5, 129.9, 127.2, 123.4, 103.4, 67.8, 19. 9, 19.6, 14.6; HRMS (ESI) m/z: calcd for $C_{13}H_{16}NOS$ $[M+H]^+$ 234.0947; found 234.0948.

2-Ethoxy-5-methyl-4-phenylthiazole (**3ar**): as a yellow oil (51.9 mg, 79% yield); R_f = 0.5 (petroleum ether); IR (KBr): 3405, 3030, 2923, 1646, 1598, 1218, 819 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66-7.59 (m, 2H), 7.44-7.40 (m, 2H), 7.32 (d, J = 7.4 Hz, 1H), 4.48 (q, J = 7.1 Hz, 2H), 2.44 (s, 3H), 1.45 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 144.3, 135.3, 128.4, 128.3, 127.2, 119.4, 67.1, 14.5, 12.7; HRMS (ESI) m/z: calcd for $C_{12}H_{14}NOS$ $[M+H]^+$ 220.0791; found 220.0789.

2-Ethoxy-5-ethyl-4-phenylthiazole (3as): as a yellow oil (47.5 mg, 68% yield); R_f = 0.4 (petroleum ether); IR (KBr): 2971, 2930, 1530, 1233, 1020, 850, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62-7.57 (m, 2H), 7.43-7.40 (m, 2H), 7.33 (d, J = 7.4 Hz, 1H), 4.49 (q, J = 7.1 Hz, 2H), 2.86 (q, J = 7.5 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H), 1.29 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 143.6, 135.4, 128.5, 128.3, 127.8, 127.3, 67.1, 20.9, 16.6, 14.6; HRMS (ESI) m/z: calcd for $C_{13}H_{16}NOS$ $[M+H]^+$ 234.0947; found 234.0949.

2-Ethoxy-4,5-diphenylthiazole (3at): as a light yellow solid (51.3 mg, 61% yield); mp 96-97 ^oC; R_f = 0.4 (petroleum ether); IR (KBr): 2928, 1599, 1524, 1240, 1018, 837, 753 cm^{-1}; ^1H NMR (400

MHz, $CDCl_3$) δ 7.45-7.36 (m, 2H), 7.26-7.12 (m, 8H), 4.45 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 143.6, 135.1, 132.5, 129.6, 128.9, 128.7, 128.2, 127.7, 127.6, 124.3, 67.4, 14.6; HRMS (ESI) m/z: calcd for $C_{17}H_{16}NOS$ $[M+H]^+$ 282.0947; found 282.0942.

2-Ethoxy-4,5-dihydronaphtho[1,2-*d*]thiazole (3au): as a gray oil (58.2 mg, 84% yield); R_f = 0.35 (petroleum ether); IR (KBr): 3397, 2927, 1643, 1505, 1227, 1031, 831, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.6 Hz, 1H), 7.26-7.19 (m, 1H), 7.16-7.07 (m, 2H), 4.49 (q, J = 7.1 Hz, 2H), 3.00 (t, J = 7.9 Hz, 2H), 2.87-2.79 (m, 2H), 1.44 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 143.4, 134.3, 131.6, 127.7, 127.0, 126.8, 122.9, 121.4, 67.5, 28.9, 21.8, 14.6; HRMS (ESI) m/z: calcd for $C_{13}H_{14}NOS$ $[M+H]^+$ 232.0791; found 232.0789.

2-Ethoxy-4-(furan-2-yl)thiazole (3av): as a white oil (44.5 mg, 76% yield); R_f = 0.4 (petroleum ether); IR (KBr): 2925, 1686, 1523, 1239, 1016, 752, 492 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.39 (m, 1H), 6.79 (s, 1H), 6.67 (d, J = 3.1 Hz, 1H), 6.44-6.43 (m, 1H), 4.50 (q, J = 7.1 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 150.4, 141.9, 140.9, 111.4, 106.7, 103.8, 68.0, 14.5; HRMS (ESI) m/z: calcd for $C_9H_9NNaO_2S$ $[M+Na]^+$ 218.0246; found 218.0242.

2-Ethoxy-4-(thiophen-2-yl)thiazole (3aw): as a gray oil (46.2 mg, 73% yield); R_f = 0.4 (petroleum ether); IR (KBr): 3016, 2981, 1522, 1233, 1018, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 3.5 Hz, 1H), 7.23 (d, J = 5.0 Hz, 1H), 7.08-6.96 (m, 1H), 6.71 (s, 1H), 4.53 (q, J = 7.1 Hz, 2H), 1.46 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 143.8, 138.9, 127.6, 124.8, 123.7, 103.2, 68.0, 14.5; HRMS (ESI) m/z: calcd for $C_9H_9NNaOS_2$ $[M+Na]^+$ 234.0018; found 234.0020.

2-Ethoxy-4-(thiophen-3-yl)thiazole (3ax): as a light gray oil (45.5 mg, 72% yield); R_f = 0.4 (petroleum ether); IR (KBr): 3108, 2926, 1522, 1233, 1017, 789, 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67-7.66 (m, 1H), 7.39-7.38 (m, 1H), 7.32-7.30 (m, 1H), 6.68 (s, 1H), 4.53 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 145.3, 136.9, 126.1, 125.4, 121.8, 104.0, 67.8, 14.5; HRMS (ESI) m/z: calcd for $C_9H_9NNaOS_2$ $[M+Na]^+$ 234.0018; found 234.0020.

2-Ethoxy-4-(pyridin-2-yl)thiazole (3ay): as a blue oil (33.4 mg, 54% yield); R_f = 0.3 (petroleum ether; IR (KBr): 2926, 1528, 1229, 1020, 746, 677 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.63-8.47 (m, 1H), 7.96 (d, J = 7.9 Hz, 1H), 7.72-7.68 (m, 1H), 7.47 (s, 1H), 7.17-7.14 (m, 1H), 4.53 (q, J = 7.1 Hz, 2H), 1.45 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 152.6, 149.3, 148.8, 136.9, 122.4, 120.9, 108.9, 67.8, 14.5; HRMS (ESI) m/z: calcd for $C_{10}H_{10}N_2NaOS$ $[M+H]^+$ 229.0406; found 229.0411.

4-(Benzo[*b*]thiophen-2-yl)-2-ethoxythiazole (3az): as a yellow solid (50.8 mg, 65% yield); mp 87.0-88.0 °C; R_f = 0.4 (petroleum ether); IR (KBr): 3058, 2982, 1525, 1465, 1234, 1019, 717 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.7 Hz, 1H), 7.80-7.71 (m, 1H), 7.64 (s, 1H), 7.40-7.29 (m, 2H), 4.58 (q, J = 7.1 Hz, 2H), 1.50 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 143. 9, 140.4, 139.5, 138.5, 124.6, 123.8, 122.3, 120.4, 105.7, 68.1; HRMS (ESI) m/z: calcd for $C_{13}H_{11}NNaOS_2$ $[M+Na]^+$, 284.0174; found 284.0170.

2-Ethoxy-4-(naphthalen-2-yl)thiazole (3ba): as a yellow solid (49.2 mg, 64% yield); mp 95.0-96.0 °C; R_f = 0.35 (petroleum ether); IR (KBr): 3054, 2982, 1599, 1527, 1233, 1018, 748, 472 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.98-7.91 (m, 2H), 7.87 (d, J = 8.7 Hz, 2H), 7.56-7.51 (m, 2H), 6.94 (s, 1H), 4.63 (q, J = 7.1 Hz, 2H), 1.54 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 174.1, 149.2, 133.8, 133.1, 132.1, 128.5, 128.3, 127.8, 126.4, 126.1, 125.1, 123.9, 105.0, 68.0, 14.7; HRMS (ESI) m/z: calcd for $C_{15}H_{13}NNaOS$ $[M+Na]^+$ 278.0610; found 278.0612.

2-Ethoxy-4-ethyl-5-methylthiazole (3bb) as a gray oil (32.3 mg, 63% yield); R_f = 0.5 (petroleum ether); IR (KBr): 2923, 2854, 1595, 1455, 1259, 1023, 753, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.35 (q, J = 7.1 Hz, 2H), 2.49 (q, J = 7.5 Hz, 2H), 2.20 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H), 1.17 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 147.2, 116.3, 66.8, 22.2, 14.5, 13.8, 10.9; HRMS (ESI) m/z: calcd for $C_8H_{13}NNaOS$ $[M+Na]^+$, 194.0610; found 194.0609.

2-Ethoxy-5-ethyl-4-propylthiazole (3bc): as a light gray oil (40.7 mg, 68% yield); R_f = 0.5 (petroleum ether); IR (KBr): 2924, 1724, 1594, 1522, 1232, 1021, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.27 (q, J = 7.1 Hz, 2H), 2.54 (q, J = 7.5 Hz, 2H), 2.36 (t, J = 7.5 Hz, 2H), 1.55 (dd, J = 14.9, 7.4 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H), 1.11 (t, J = 7.5 Hz, 3H), 0.84 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 144.9, 125.2, 66.9, 31.0, 22.8, 19.7, 16.6, 14.5, 13.8; HRMS (ESI) m/z: calcd for $C_{10}H_{18}NOS$ $[M+H]^+$, 200.1104; found 200.1101.

4-butyl-2-ethoxy-5-propylthiazole (3bd): as a gray oil (49.0 mg, 72% yield); R_f = 0.45 (petroleum ether); IR (KBr): 2926, 1808, 1594, 1452, 1021, 753, 488 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.38-4.21 (m, 2H), 2.53 (t, J = 7.4 Hz, 2H), 2.47-2.38 (m, 2H), 1.61-1.50 (m, 4H), 1.39-1.29 (m, 5H), 0.95-0.88 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 145.7, 123.1, 66.8, 31.7, 28.8, 28.2, 25.1, 22.4, 14.5, 13.9, 13.6; HRMS (ESI) m/z: calcd for $C_{11}H_{22}NOS$ $[M+H]^+$, 228.1417; found 228.1420.

2-Ethoxy-4,5,6,7-tetrahydrobenzo[*d*]thiazole (3be): as a yellow oil (44.3 mg, 81% yield); R_f = 0.4 (petroleum ether); IR (KBr): 3780, 2928, 2857, 1721, 1669, 1447, 1263, 751, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.38 (q, J = 7.1 Hz, 2H), 2.70-2.51 (m, 4H), 1.81 (dd, J = 4.0, 2.1 Hz,

4H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 143.6, 119.8, 67.0, 26.6, 23.3, 23.2, 23.0, 14.5; HRMS (ESI) m/z: calcd for $C_9H_{13}NNaOS$ $[M+Na]^+$ 206.0610; found 206.0620.

2-Ethoxy-5,6,7,8-tetrahydro-4*H*-cyclohepta[*d*]thiazole (3bf): as a gray oil (44.7 mg, 76% yield); R_f = 0.4 (petroleum ether); IR (KBr): 2923, 2847, 1520, 1442, 1235, 1023, 854 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.30 (q, J = 7.1 Hz, 2H), 2.74-2.65 (m, 2H), 2.63-2.49 (m, 2H), 1.75 (d, J = 5.2 Hz, 2H), 1.70-1.59 (m, 4H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 148.2, 122.9, 66.7, 31.9, 31.3, 28.1, 26.6, 26.2, 14.5; HRMS (ESI) m/z: calcd for $C_{10}H_{15}NNaOS$ $[M+Na]^+$, 220.0767; found 220.0766.

2-Ethoxy-4,5,6,7,8,9-hexahydrocycloocta[*d*]thiazole (3bg): as a yellow oil (49.3 mg, 78% yield); R_f = 0.35 (petroleum ether); IR (KBr): 2924, 2851, 1714, 1518, 1233, 1023, 753 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.37 (q, J = 7.1 Hz, 2H), 2.71-2.67 (m, 4H), 1.65-1.68 (m, 4H), 1.46-1.43 (m, 4H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 146.4, 121.6, 66.9, 31.2, 29.5, 28.1, 26.1, 25.5, 24.4, 14.5; HRMS (ESI) m/z: calcd for $C_{11}H_{17}NOS$ $[M+H]^+$ 212.1104; found 212.1102.

2-Ethoxy-6,7-dihydrobenzo[*d*]thiazole (3bh): as a yellow oil (28.7 mg, 53% yield); R_f = 0.55 (petroleum ether); IR (KBr): 2930, 1667, 1526, 1446, 1233, 1021, 861 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (d, J = 9.8 Hz, 1H), 5.92-5.73 (m, 1H), 4.44-4.32 (m, 2H), 2.75 (t, J = 9.4 Hz, 2H), 2.41 (td, J = 9.6, 4.2 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 143.0, 125.6, 122.7, 118.8, 67.3, 23.5, 21.2, 14.5; HRMS (ESI) m/z: calcd for $C_9H_{12}NOS$ $[M+H]^+$, 182.0634; found 182.0631.

(*E*)-2-Ethoxy-4-styrylthiazole (3bi): as a yellow oil (29.1 mg, 42% yield); R_f = 0.5 (petroleum ether); IR (KBr): 2927, 2857, 1667, 1530, 1228, 961, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.49 (d, J = 7.3 Hz, 2H), 7.38-7.33 (m, 2H), 7.31 (d, J = 4.8 Hz, 1H), 7.25 (t, J = 3.0 Hz, 1H), 6.87 (d, J = 15.8 Hz, 1H), 6.53 (s, 1H), 4.53 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 148.5, 137.2, 130.7, 128.6, 127.6, 126.6, 121.8, 107.9, 67.8, 14.5; HRMS (ESI) m/z: calcd for $C_{13}H_{14}NOS[M+H]^+$, 232.0791; found 232.0788.

2-Ethoxy-4-ethyl-5-methylthiazole (3bj): as a yellow oil (26.2 mg, 51% yield); R_f = 0.5 (petroleum ether); IR (KBr): 2926, 2857, 1670, 1595, 1507, 1460, 1238, 1018, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.33 (d, J = 7.1 Hz, 2H), 2.57 (q, J = 7.5 Hz, 2H), 2.12 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H), 1.16 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 140.1, 124.9, 66.8, 19.8, 16.1, 14.7, 14.5; HRMS (ESI) m/z: calcd for $C_8H_{14}NOS$ $[M+H]^+$, 172.0791; found 172.0793.

2-Ethoxy-4-isopropyl-5-methylthiazole (3bk): as a yellow oil (35.0 mg, 63% yield); R_f = 0.5 (petroleum ether); IR (KBr): 2974, 2928, 1722, 1529, 1229, 1019, 753, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.33 (q, J = 7.1 Hz, 2H), 3.11-3.00 (m, 1H), 2.14 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H), 1.19 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 138.9, 131.0, 66.8, 27.2, 24.7, 14.9, 14.5; HRMS (ESI) m/z: calcd for $C_9H_{15}NNaOS$ $[M+Na]^+$, 208.0767; found 208.0765.

4-Butyl-2-ethoxy-5-methylthiazole (3bl): as a yellow oil (36.5 mg, 61% yield); R_f = 0.6 (petroleum ether); IR (KBr): 2924, 2856, 1719, 1671, 1596, 1456, 1262, 754 cm^{-1}; ^{1}H NMR (400 MHz, CDCl3) δ 4.36 (q, J = 7.1 Hz, 2H), 2.57 (t, J = 7.5 Hz, 2H), 2.15 (s, 3H), 1.51 (dd, J = 15.1, 7.6 Hz, 2H), 1.41-1.29 (m, 5H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 140.6, 123.3, 66.8, 33.7, 26.0, 22.1, 14.8, 14.5, 13.8; HRMS (ESI) m/z: calcd for $C_{10}H_{18}NOS$ $[M+H]^+$, 200.1104; found 200.1103.

2-Ethoxy-4-hexyl-5-methylthiazole (3bm): as a yellow oil (46.3 mg, 68% yield); R_f = 0.55 (petroleum ether); IR (KBr): 2982, 2923, 1521, 1383, 1232, 1021, 698 cm^{-1}; ^{1}H NMR (400 MHz,

$CDCl_3$) δ 4.35 (q, J = 7.1 Hz, 2H), 2.55 (t, J = 7.5 Hz, 2H), 2.14 (s, 3H), 1.57-1.46 (m, 2H), 1.39 (t, J = 7.1 Hz, 3H), 1.32-1.25 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 140.6, 123.4, 66.8, 31.5, 31.5, 28.6, 26.3, 22.6, 14.8, 14.5, 14.0; HRMS (ESI) m/z: calcd for $C_{12}H_{22}NOS$ $[M+H]^+$, 228.1417; found 228.1420.

4-Benzyl-2-ethoxy-5-methylthiazole (3bn): as a yellow oil (51.0 mg, 73% yield); R_f = 0.5 (petroleum ether); IR (KBr): 2982, 2924, 1521, 1383, 1232, 1021, 869, 752, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, J = 7.3 Hz, 2H), 7.24-7.21 (m, 2H), 4.39 (q, J = 7.1 Hz, 2H), 3.95 (s, 2H), 2.26 (s, 3H), 1.42 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 141.8, 140.0, 128.6, 128.2, 126.6, 121.6, 67.0, 32.3, 15.0, 14.5; HRMS (ESI) m/z: calcd for $C_{13}H_{15}NNaOS$ $[M+Na]^+$, 256.0767; found 256.0768.

2-Ethoxy-4-ethyl-5-pentylthiazole (3bo): as a yellow oil (27.9 mg, 41% yield); R_f = 0.45 (petroleum ether); IR (KBr): 2925, 2857, 1527, 1459, 1235, 1023, 802 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35 (q, J = 7.1 Hz, 2H), 2.60-2.52 (m, 2H), 2.48 (q, J = 7.5 Hz, 2H), 1.57-1.48 (m, 2H), 1.39 (t, J = 7.1 Hz, 3H), 1.35-1.28 (m, 4H), 1.16 (t, J = 7.5 Hz, 3H), 0.92-0.84 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 146.8, 122.9, 66.9, 31.6, 31.2, 26.1, 22.4, 14.5, 14.2, 14.0; HRMS (ESI) m/z: calcd for $C_{11}H_{22}NOS$ $[M+H]^+$, 228.1417; found 228.1414.

2-Ethoxy-5-hexyl-4-methylthiazole (3bo'): as a yellow oil (14.5 mg, 22% yield); R_f = 4.5 (petroleum ether); IR (KBr): 2924, 2856, 1526, 1458, 1235, 1023, 757 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.32 (q, J = 7.1 Hz, 2H), 2.43 (t, J = 7.5 Hz, 2H), 2.17 (s, 3H), 1.58-1.53 (m, 2H), 1.36 (t, J = 7.1 Hz, 3H), 1.31-1.23 (m, 6H), 0.86 (t, J = 6.6 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$) δ 170.4, 146.1, 116.7, 66.8, 31.7, 29.3, 28.9, 28.9, 22.6, 14.4, 14.0, 11.0; HRMS (ESI) m/z: calcd for $C_{11}H_{22}NOS$ $[M+H]^+$, 228.1417; found 228.1414.

(*E*)-2-ethoxy-4-(2-(2,6,6-trimethylcyclohex-1-en-1-yl)vinyl)thiazole (3ap): as a yellow oil (55.6 mg, 67% yield); R_f = 0.4 (petroleum ether); IR (KBr): 2924, 1668, 1526, 1446, 1233, 1021, 861 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.91 (d, J = 15.9 Hz, 1H), 6.44-6.24 (m, 1H), 6.17 (t, J = 15.5 Hz, 1H), 4.48 (q, J = 7.1 Hz, 2H), 2.03 (t, J = 6.0 Hz, 2H), 1.76 (s, 3H), 1.65-1.60 (m, 2H), 1.49 (d, J = 6.1 Hz, 2H), 1.43 (d, J = 7.0 Hz, 3H), 1.06 (d, J = 7.9 Hz, 6H); ^{13}C NMR (100MHz, $CDCl_3$) δ 173.7, 149.1, 137.4, 129.9, 129.7, 125.9, 105.7, 67.7, 39.7, 34.2, 33.1, 28.9, 21.7, 19.3, 14.5; HRMS (ESI) m/z: calcd for $C_{16}H_{24}NOS$ $[M+H]^+$, 278.1573; found 278.1574.

2-Ethoxy-5,7,7-trimethyl-6,7-dihydrobenzo[*d*]thiazole (3bq): as a yellow oil (52.2 mg, 78% yield); R_f = 0.5 (petroleum ether: ethyl acetate = 50: 1); IR (KBr):2959, 2865, 1665, 1522, 1232, 1022, 705, 702, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.17 (d, J = 1.4 Hz, 1H), 4.39 (q, J = 7.1 Hz, 2H), 2.17 (s, 2H), 1.86 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H), 1.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 142.7, 134.9, 127.9, 116.9, 67.1, 45.2, 33.5, 29.2, 23.4, 14.5; HRMS (ESI) m/z: calcd for $C_{12}H_{17}NOS$ $[M + H]^+$ 224.1104, found 224.1105.

2-Ethoxy-4-phenyl-4*H*-chromeno[4,3-*d*]thiazole (3br): as a yellow oil (75.1 mg, 81%); R_f = 0.3 (petroleum ether: ethyl acetate = 50: 1); IR (KBr): 3062, 2978, 1742, 1693, 1525, 1462, 1025, 1221, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71-7.66 (m, 1H), 7.45 (dd, J = 7.4, 1.7 Hz, 2H), 7.39-7.32 (m, 3H), 7.16-7.10 (m, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.89 (d, J = 8.0 Hz, 1H), 6.40 (s, 1H), 4.50 (q, J = 7.1 Hz, 2H), 1.43 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.9, 152.9, 140.6, 140.2, 129.1, 129.0, 128.8, 127.2, 123.1, 121.9, 119.9, 118.2, 116.5, 77.0, 62.6, 14.5; HRMS (ESI) m/z: calcd for $C_{18}H_{16}NO_2S$ [M +H]+ 310.0896, found 310.0894.

(7*R*,8a*S*,9*S*)-2-Ethoxy-8a,9-dimethyl-7-(prop-1-en-2-yl)-5,6,7,8,8a,9-hexahydronaphtho[2,3-*d*]thiazole (3bs): as a yellow oil (47.1 mg, 52%); R_f = 0.3 (petroleum ether: ethyl acetate = 20: 1);

Specific rotation $[a]_D^{22}$ +133.9 deg (0.1, CH_2Cl_2); IR (KBr): 2967, 2929, 1644, 1518, 1218, 1019, 884 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.09 (s, 1H), 4.72 (s, 2H), 4.38 (q, J = 7.2 Hz, 2H), 2.88 (q, J = 7.1 Hz, 2H), 2.39-2.36 (m, 2H), 2.20-2.14 (m, 1H), 1.94 (d, J = 12.8 Hz, 1H), 1.85-1.79 (m, 1H), 1.74 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H), 1.34-1.29 (m, 1H), 1.24 (s, 1H), 1.20 (d, J = 7.1 Hz, 3H), 0.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 149.9, 145.0, 142.2, 123.6, 116.4, 108.8, 67.1, 45.2, 41.3, 41.2, 40.5, 31.7, 31.3, 20.9, 15.3, 14.5, 13.6; HRMS (ESI) m/z: calcd for $C_{18}H_{26}NOS$ $[M+H]^+$ 304.1730, found 304.1728.

1-((3b*S*,10a*R*,12a*S*)-8-ethoxy-10a,12a-dimethyl-2,3,3a,3b,4,5,10,10a,10b,11,12,12a-dodecahydro-1H-cyclopenta[7,8]phenanthro[2,3-*d*]thiazol-1-yl)ethan-1-one (3bt): as a yellow oil (74.1 mg, 62%); R_f = 0.3 (petroleum ether: ethyl acetate = 20: 1); Specific rotation $[a]_D^{22}$ +189.6 deg (0.1, CH_2Cl_2);IR (KBr): 2931, 2903, 1701, 1519, 1229, 1020, 754, 586 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.02 (s, 1H), 4.37 (q, J = 7.0 Hz, 2H), 2.72 (d, J = 16.1 Hz, 1H), 2.62-2.47 (m, 2H), 2.36-2.24 (m, 2H), 2.19-2.14 (m, 1H), 2.09 (s, 3H), 2.03 (d, J = 12.0 Hz, 1H), 1.73 (d, J = 9.7 Hz, 2H), 1.68-1.62 (m, 1H), 1.55-1.45 (m, 2H), 1.42 (d, J = 9.8 Hz, 2H), 1.37 (t, J = 7.0 Hz, 3H), 1.26-1.22 (m, 2H), 1.18-1.10 (m, 2H), 1.00 (s, 3H), 0.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.4, 172.2, 145.5, 142.3, 115.8, 115.5, 67.2, 63.7, 56.2, 54.3, 44.0, 40.1, 38.9, 36.5, 36.4, 31.4, 31.4, 31.4, 24.5, 22.9, 21.6, 18.1, 14.5, 13.3; HRMS (ESI) m/z: calcd for $C_{24}H_{33}NO_2S$ $[M+H]^+$ 400.2305, found 400.2311.

2-Methoxy-4-phenylthiazole (3bu): as a yellow oil (47.6 mg, 83% yield); R_f = 0.5 (petroleum ether); IR (KBr): 3472, 2930, 1531, 1420, 1237, 1065, 979, 714 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90-7.78 (m, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.32 (d, J = 7.4 Hz, 1H), 6.87 (s, 1H), 4.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 149.2, 134.7, 128.6, 127.9, 125.9, 104.7, 58.5; HRMS (ESI)

m/z: calcd for $C_{10}H_{10}NOS$ $[M+H]^+$, 192.0478; found 192.0475.

4-phenyl-2-propoxythiazole (3bv): as a yellow oil (49.3 mg, 75% yield); R_f = 0.5 (petroleum ether); IR (KBr): 2966, 1599, 1527, 1473, 1229, 713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95-7.73 (m, 2H), 7.42-7.38 (m, 2H), 7.32-7.28 (m, 1H), 6.85 (s, 1H), 4.46 (t, J = 6.6 Hz, 2H), 1.96-1.76 (m, 2H), 1.07 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 149.2, 134.7, 128.6, 127.8, 125.9, 104.3, 73.5, 22.3, 10.4; HRMS (ESI) m/z: calcd for $C_{12}H_{13}NNaOS$ $[M+Na]^+$, 242.0610; found 242.0611.

2-Butoxy-4-phenylthiazole (3bw): as a yellow oil (43.3 mg, 62% yield); R_f = 0.45 (petroleum ether); IR (KBr): 2956, 1597, 1527, 1471, 1228, 1062, 711 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93-7.76 (m, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.30 (s, 1H), 6.85 (s, 1H), 4.49 (t, J = 6.6 Hz, 2H), 1.95-1.74 (m, 2H), 1.51 (dd, J = 15.0, 7.5 Hz, 2H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 149.2, 134.7, 128.6, 127.8, 125.9, 104.3, 71.8, 31.0, 19.1, 13.8; HRMS (ESI) m/z: calcd for $C_{13}H_{15}NNaOS$ $[M+Na]^+$, 256.0767; found 256.0764.

2-Isopropoxy-4-phenylthiazole (3bx): as a yellow oil (34.2 mg, 52% yield); R_f = 0. 5 (petroleum ether); IR (KBr): 2960, 2872, 1595, 1495, 1389, 819, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91-7.77 (m, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.30 (t, J =7.3, 1H), 6.84 (s, 1H), 5.30 (dt, J = 12.4, 6.2 Hz, 1H), 1.47 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 149.1, 134.8, 128.6, 127.8, 125.9, 104.1, 75.7, 21.9; HRMS (ESI) m/z: calcd for $C_{12}H_{13}NNaOS$ $[M + Na]^+$, 242.0610, found 242.0606.

2-(Cyclohexyloxy)-4-phenylthiazole (3by): as a blue oil (43.5 mg, 56% yield); R_f = 0.5 (petroleum ether); IR (KBr): 2935, 2857, 1601, 1520, 1447, 1227, 1010, 713 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 7.7 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.28 (d, J = 7.2 Hz, 1H), 6.81 (s,

1H), 5.07-4.93 (m, 1H), 2.18-2.02 (m, 2H), 1.82-1.79 (m, 2H), 1.58-1.54 (m, 3H), 1.47-1.34 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 149.1, 134.8, 128.6, 127.8, 125.9, 104.1, 80.6, 31.6, 25.5, 23.7; HRMS (ESI) m/z: calcd for $C_{15}H_{17}NNaOS$ $[M + Na]^+$ 282.0923, found 282.0910.

2-((3-Methylbut-3-en-1-yl)oxy)-4-phenylthiazole (3bz): as a white oil (44.3 mg, 64% yield); R_f = 0.5 (petroleum ether); IR (KBr): 3074, 2931, 1601, 1528, 1230, 1062, 715 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.75 (m, 2H), 7.40 (t, J = 7.5 Hz, 2H), 7.32 (d, J = 7.3 Hz, 1H), 6.86 (s, 1H), 4.87 (d, J = 14.2 Hz, 2H), 4.63 (t, J = 6.8 Hz, 2H), 2.58 (t, J = 6.8 Hz, 2H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 149.1, 141.5, 134.7, 128.6, 127.8, 125.9, 112.6, 104.5, 70.0, 36.9, 22.7; HRMS (ESI) m/z: calcd for $C_{13}H_{14}NOS$ $[M + H]^+$ 232.0791, found 232.0787.

2-Ethoxy-5,5-dimethyl-4-(propan-2-ylidene)-4,5-dihydrothiazole (4a): as a yellow oil (45.3 mg, 76% yield); R_f = 0.5 (petroleum ether); IR (KBr): 2924, 2854, 1725, 1596, 1458, 1375, 1261, 747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.34 (q, J = 7.1 Hz, 2H), 1.92 (s, 3H), 1.81 (s, 3H), 1.78 (s, 6H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 150.3, 118.9, 66.4, 63.2, 30.4, 23.0, 19.1, 14.4; HRMS (ESI) m/z: calcd for $C_{10}H_{18}NOS$ $[M+H]^+$, 200.1104; found 200.1103.

4-Cyclohexylidene-2-ethoxy-1-thia-3-azaspiro[4.5]dec-2-ene (4b): as a yellow oil (51.1 mg, 61% yield); R_f = 0.45 (petroleum ether); IR (KBr): 2928, 2854, 1709, 1599, 1447, 1259, 1066, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.33 (q, J = 7.1 Hz, 2H), 2.52 (d, J = 5.3 Hz, 2H), 2.36 (s, 2H), 2.15-2.11 (m, 2H), 1.82-1.75 (m, 3H), 1.72-1.69 (m, 1H), 1.58-1.56 (m, 6H), 1.44-1.40 (m, 2H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 147.9, 127.9, 72.7, 66.3, 38.6, 33.1, 30.6, 28.5, 28.1, 26.9, 25.5, 25.1, 14.5; HRMS (ESI) m/z: calcd for $C_{16}H_{26}NOS$ $[M+H]^+$, 280.1730; found 280.1712.

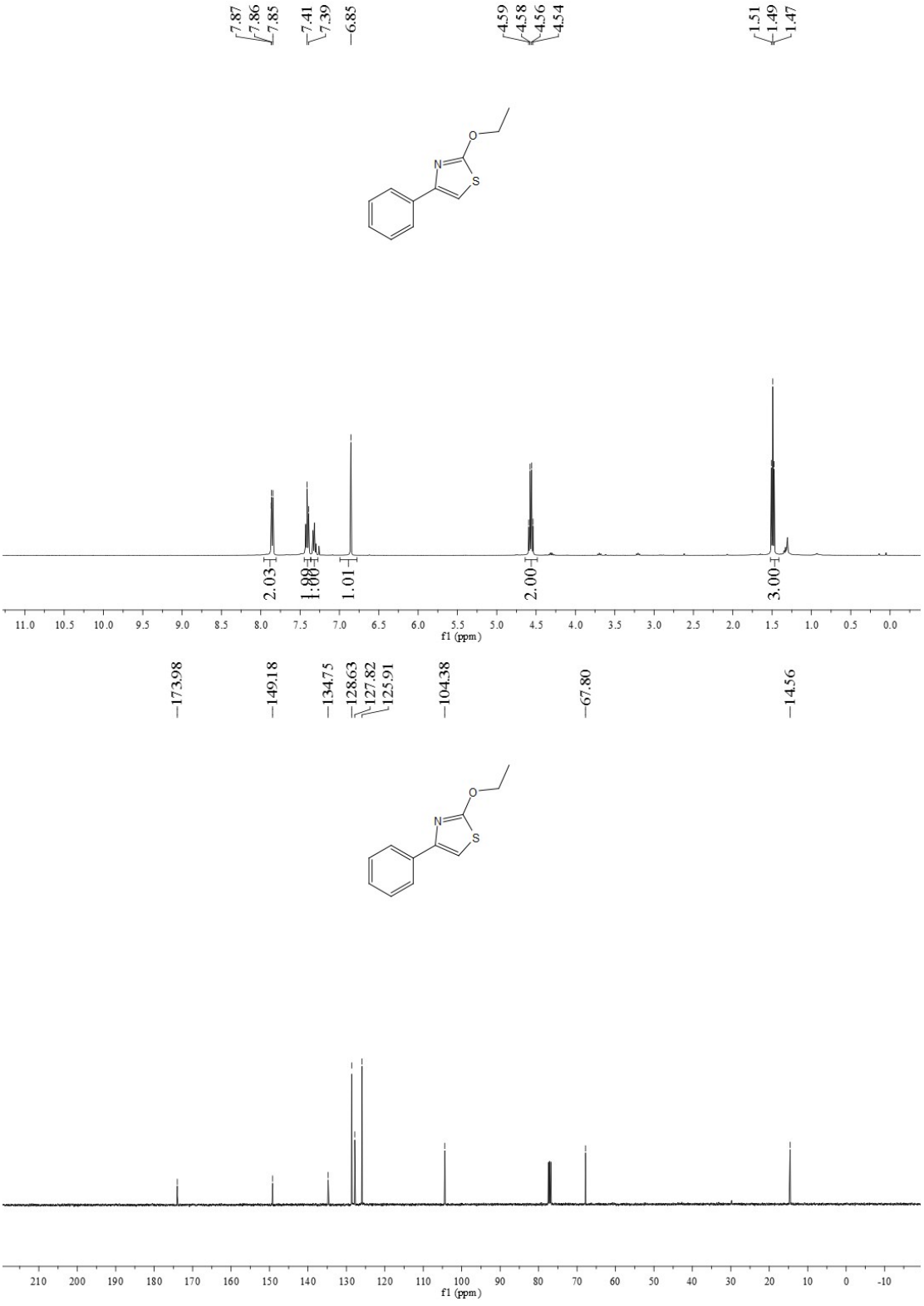
(*E*)-*S*-(Ethoxycarbonothioyl)-*N*-(1-phenylethylidene)thiohydroxylamine (5a): as a yellow oil

(37.2 mg, 52% yield); R_f = 0.3 (petroleum ether: ethyl acetate = 20: 1); IR (KBr): 2923, 1767, 1521, 1462, 1376, 1199, 928, 761 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.91-7.83 (m, 2H), 7.45-7.38 (m, 3H), 4.84 (q, J = 7.1 Hz, 2H), 2.42 (s, 3H), 1.55 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 162.7, 138.7, 130.4, 128.5, 126.8, 69.8, 20.5, 13.8; HRMS (ESI) m/z: calcd for $C_{11}H_{13}NNaOS_2$ $[M+Na]^+$, 262.0331; found 262.0329.

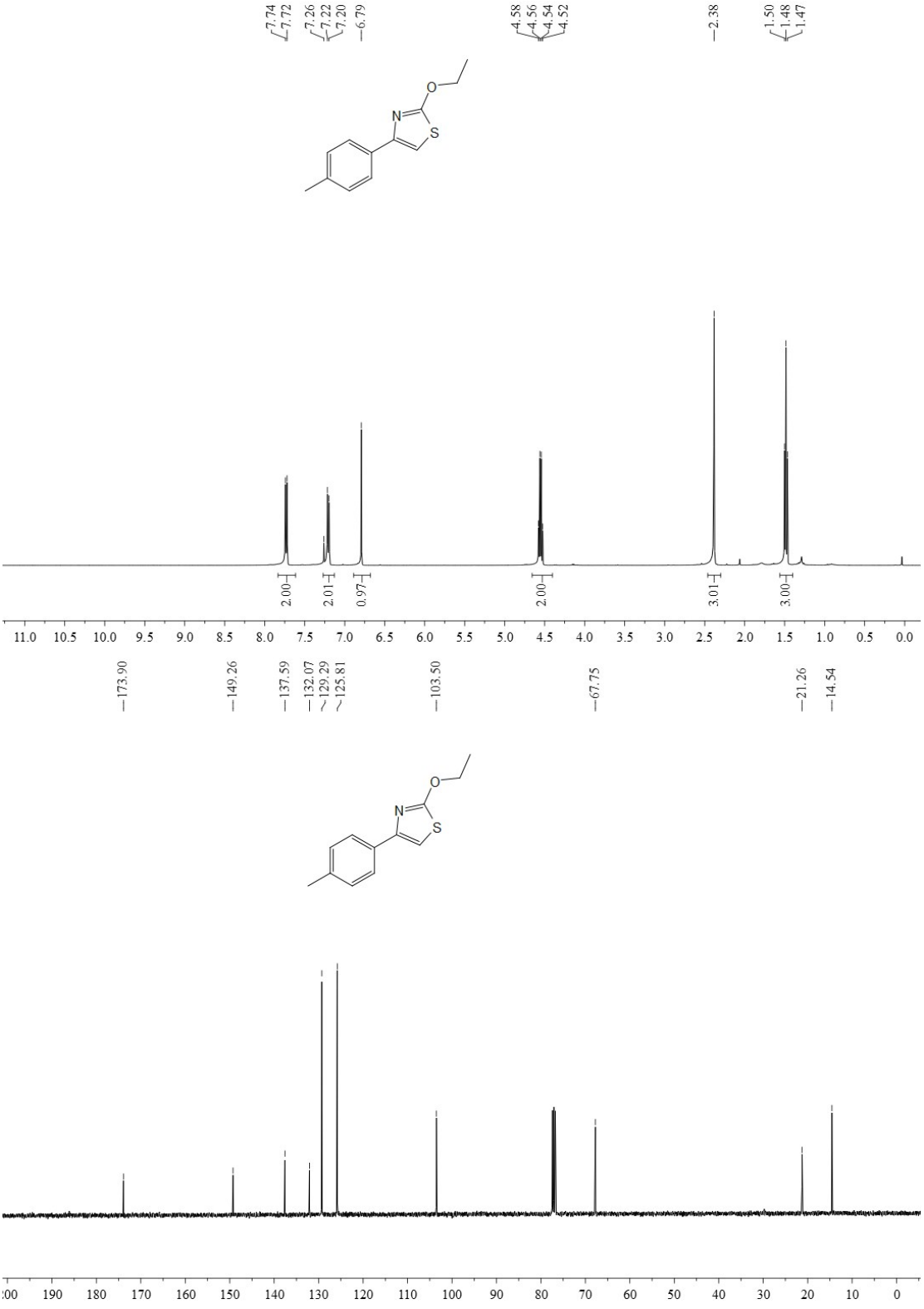
(*E*)-*S*-(ethoxycarbonothioyl)-*N*-(1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)thiohydroxylamine (5b): as a white oil (68.4 mg, 78% yield); R_f = 0.4 (petroleum ether: ethyl acetate = 20: 1); IR (KBr): 2932, 2865, 1769, 1523, 1464, 1376, 1227, 1027, 694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.60-4.47 (m, 2H), 2.71-2.61 (m, 1H), 2.01-1.97 (m, 2H), 1.90-1.85 (m, 1H), 1.79-1.67 (m, 1H), 1.56-1.50 (m, 1H), 1.40 (t, J = 7.2, 3H), 1.34-1.29 (m, 1H), 0.99 (d, J = 6.0 Hz, 3H), 0.96 (s, 3H), 0.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.2, 185.8, 68.1, 54.4, 48.1, 43.6, 34.9, 31.3, 27.0, 19.5, 19.0, 13.8, 10.6; HRMS (ESI) m/z: calcd for $C_{13}H_{21}NOS_2$ $[M+H]^+$ 294.0957, found 294.0961.

NMR Spectra for all the compounds

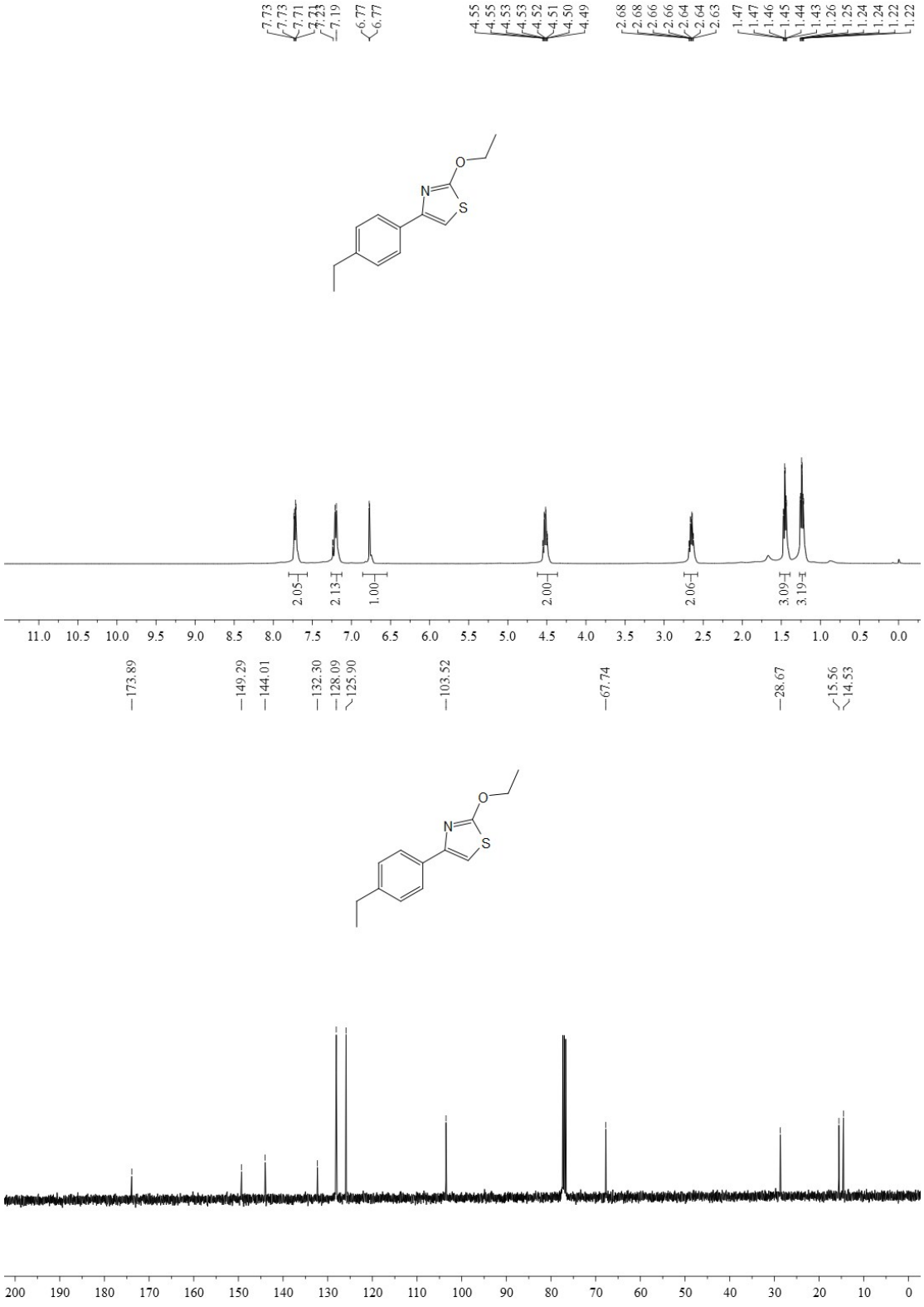
^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-phenylthiazole (3aa)



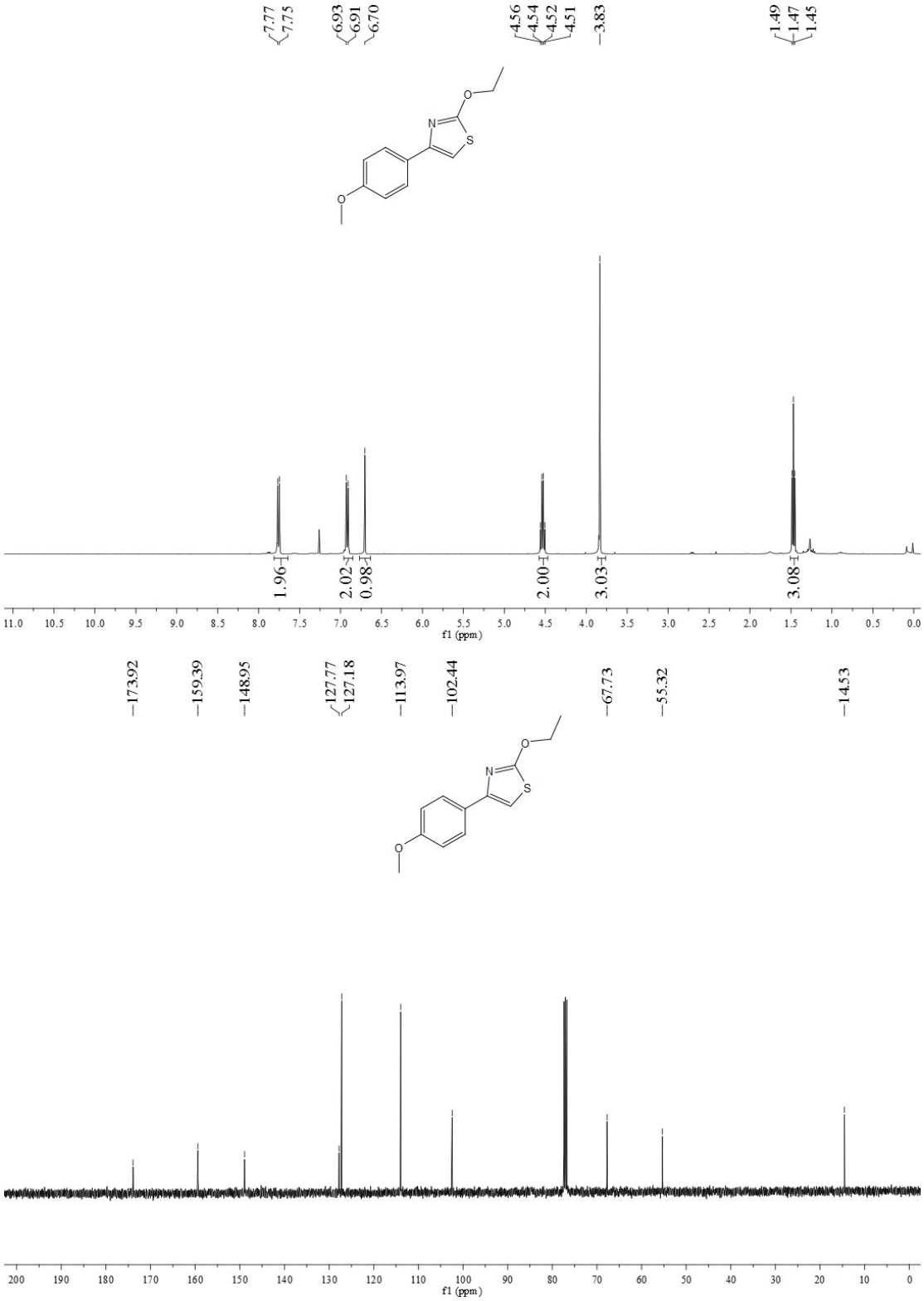
^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-(*p*-tolyl)thiazole (3ab)



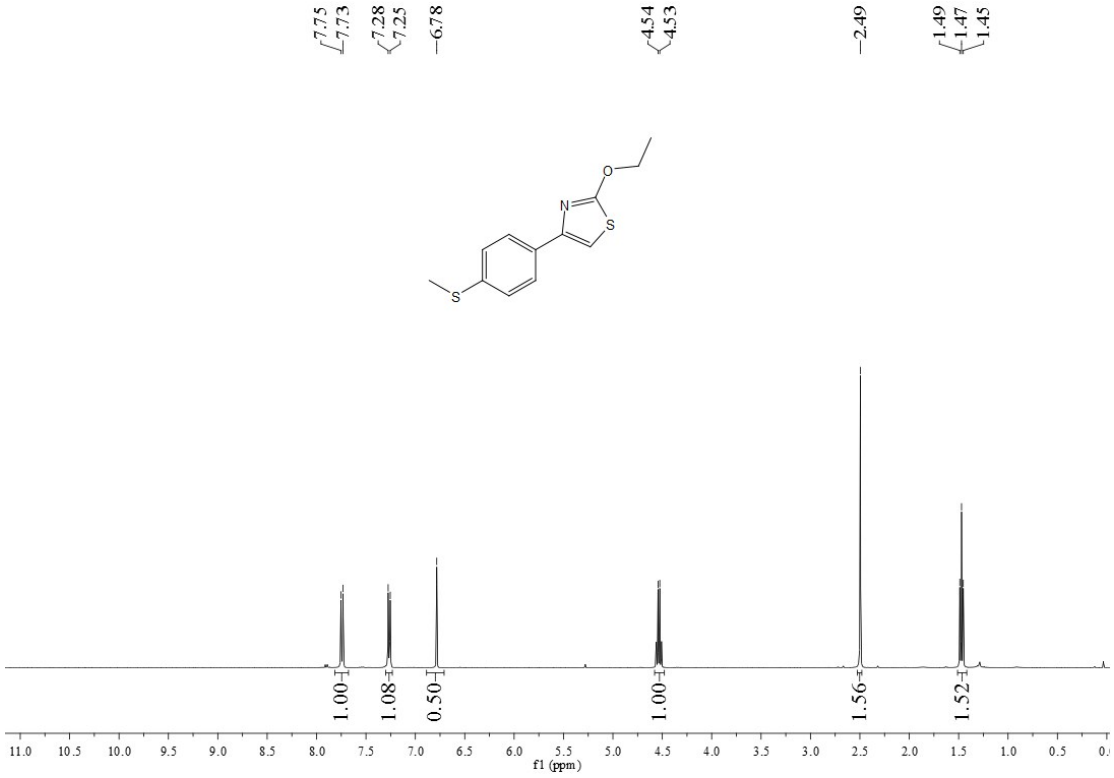
^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-(4-ethylphenyl)thiazole (3ac)

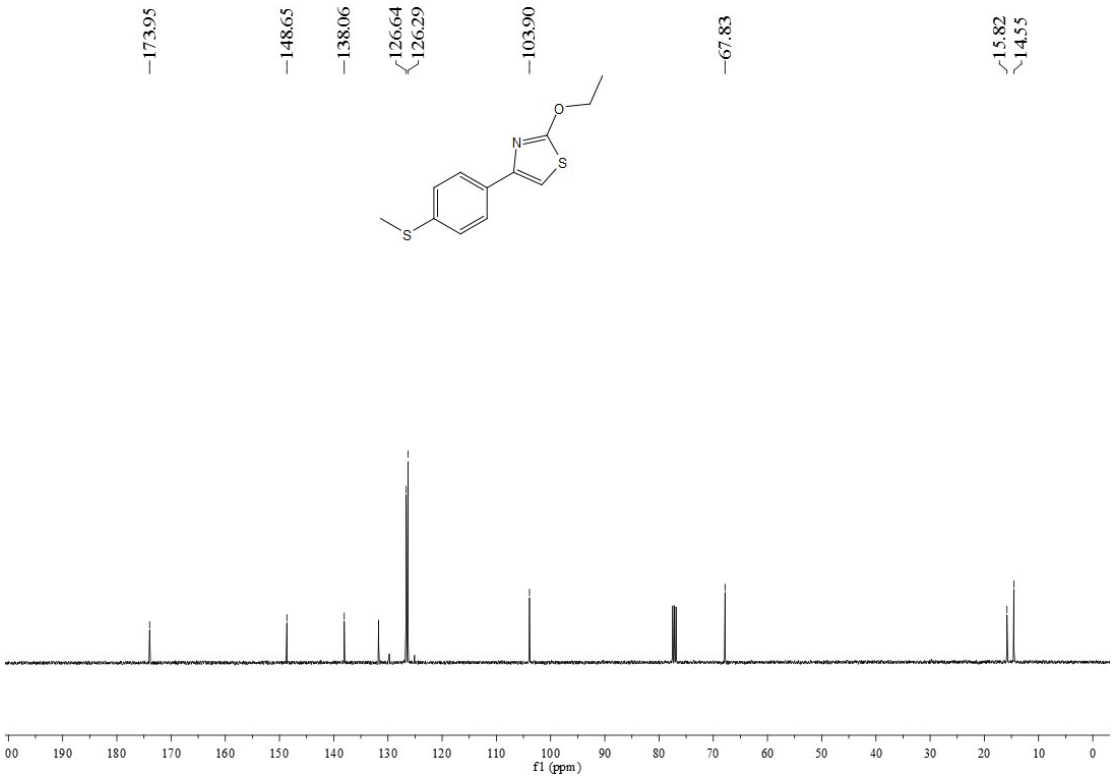


^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-(4-methoxyphenyl)thiazole (3ad)

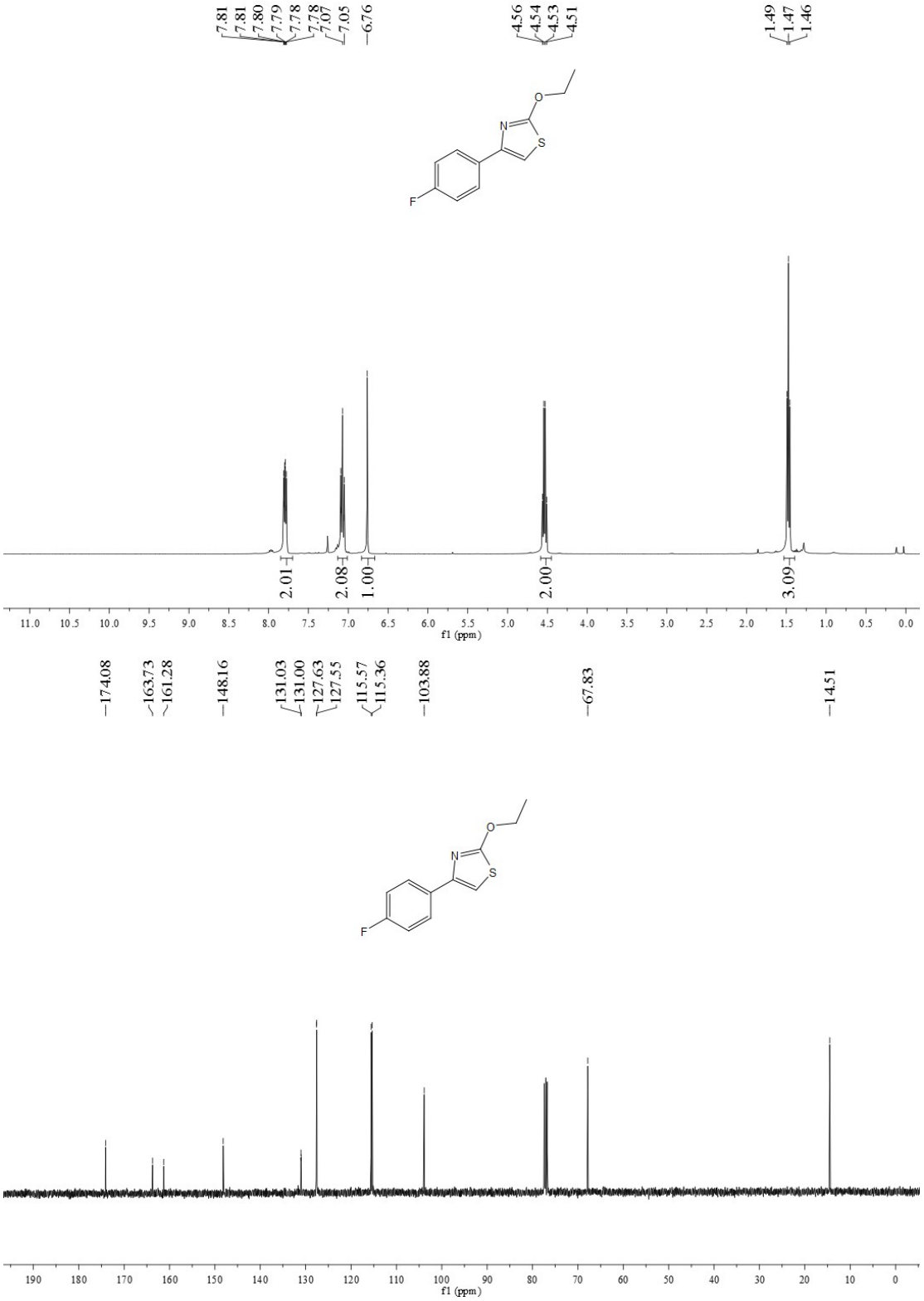


^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-(4-(methylthio)phenyl)thiazole (3ae)

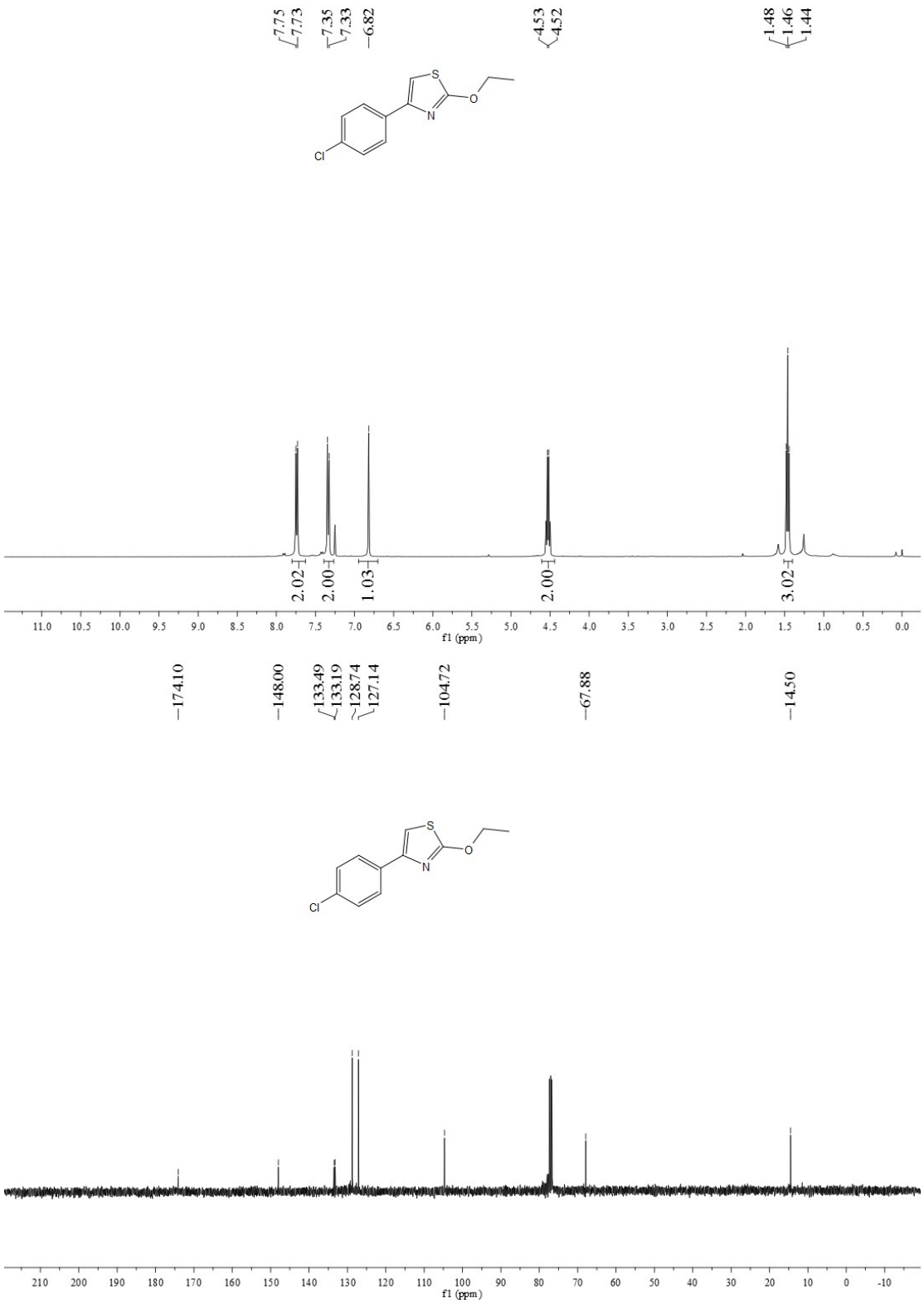




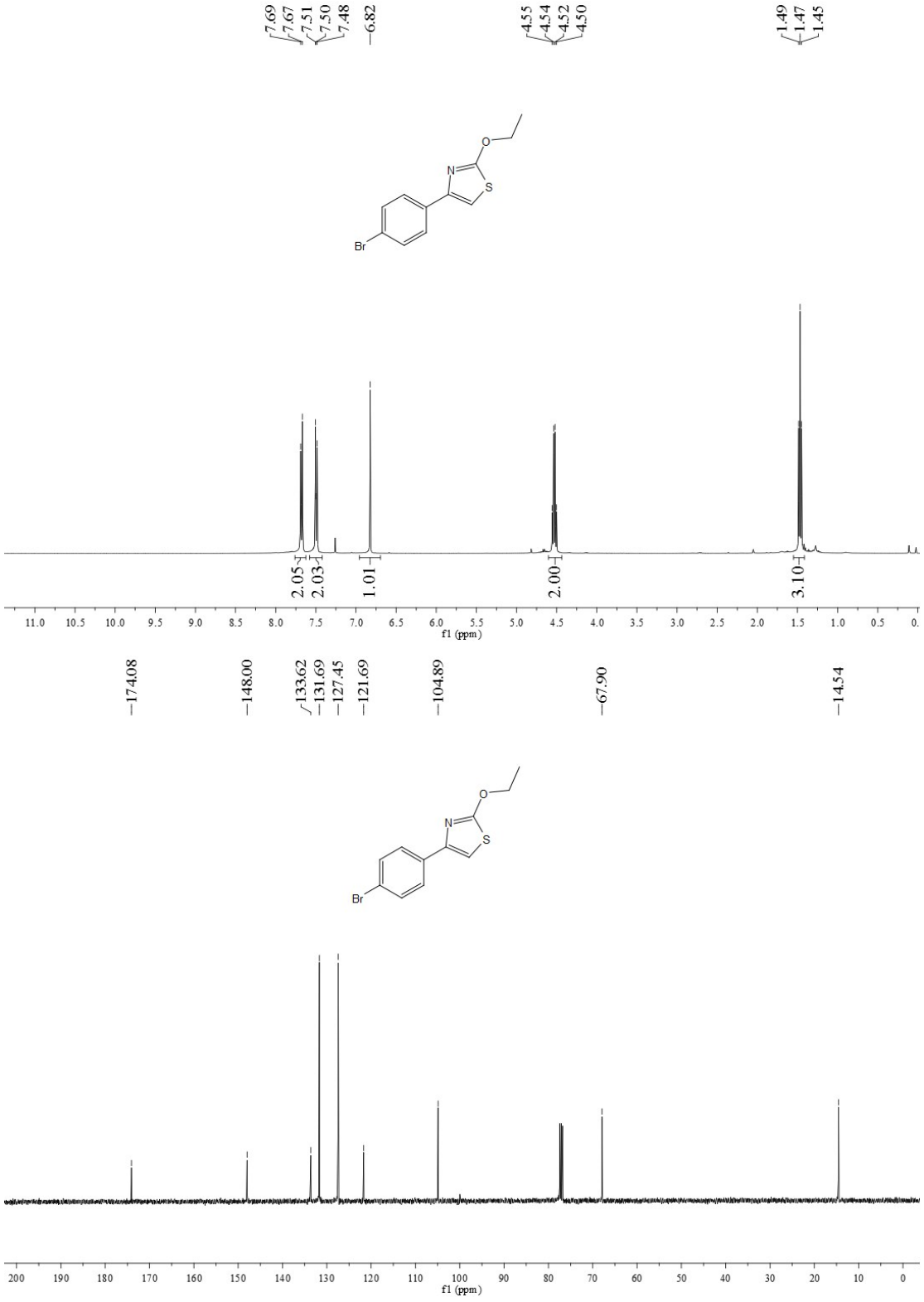
^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-(4-fluorophenyl)thiazole (3af)



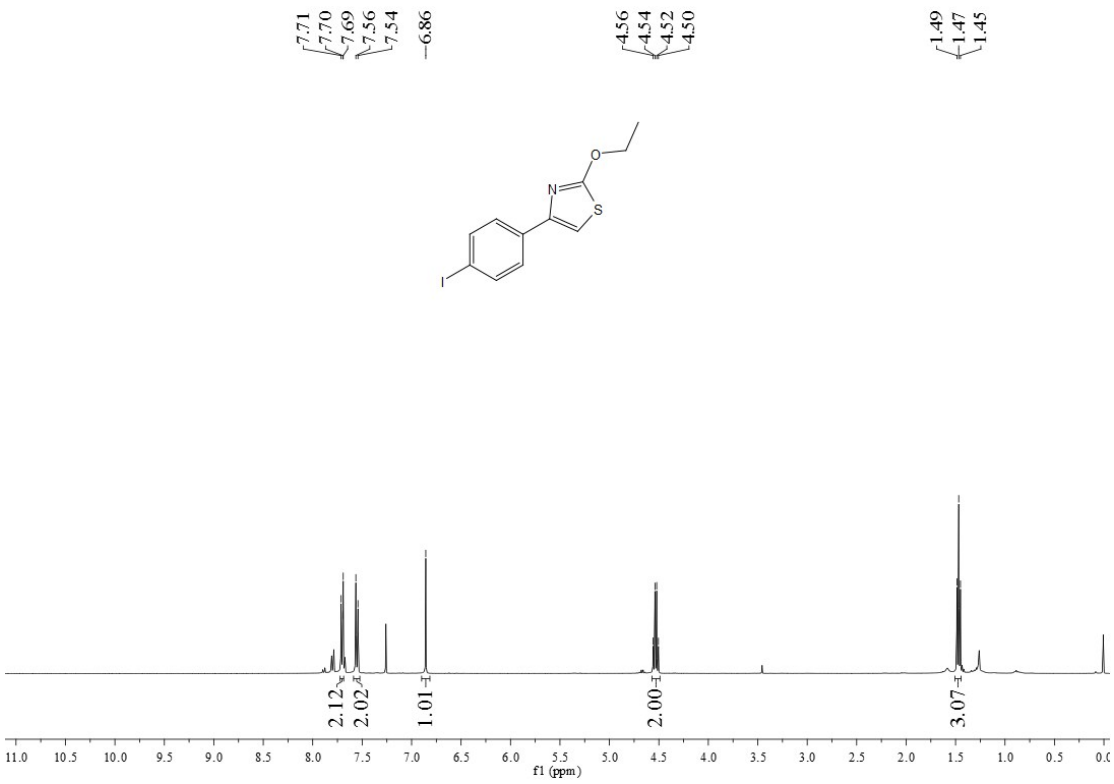
^{1}H NMR and ^{13}C NMR of 4-(4-chlorophenyl)-2-ethoxythiazole (3ag)

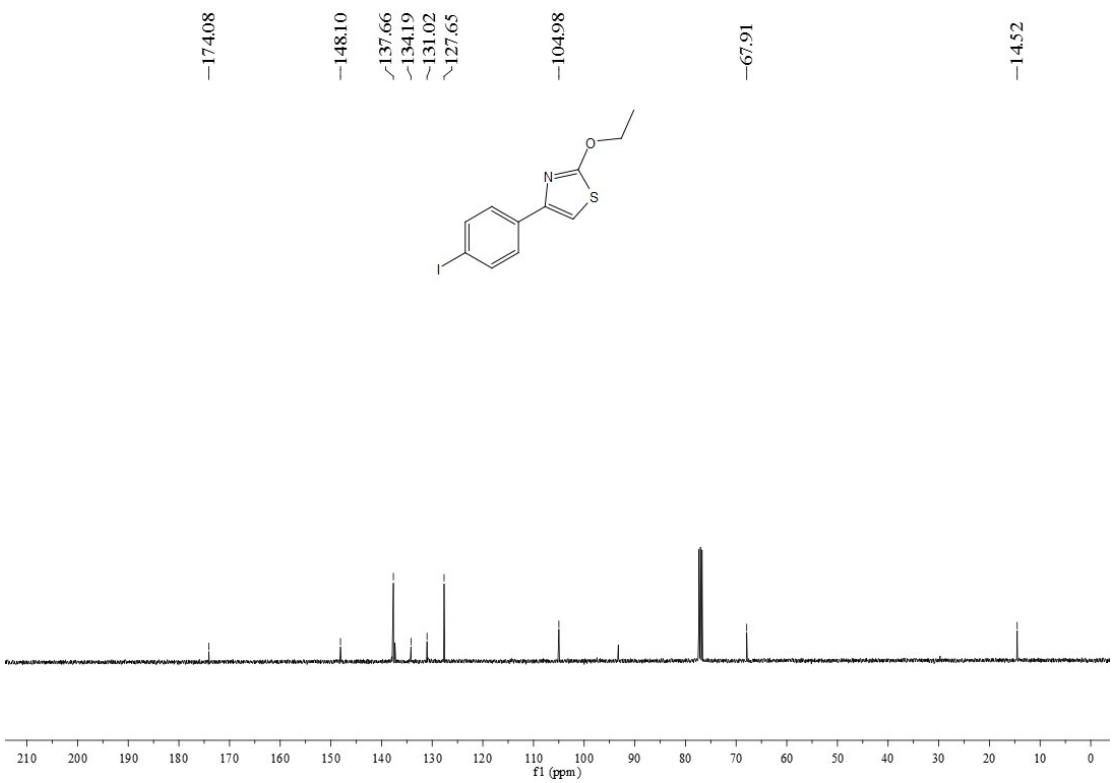


^{1}H NMR and ^{13}C NMR of 4-(4-bromophenyl)-2-ethoxythiazole (3ah)

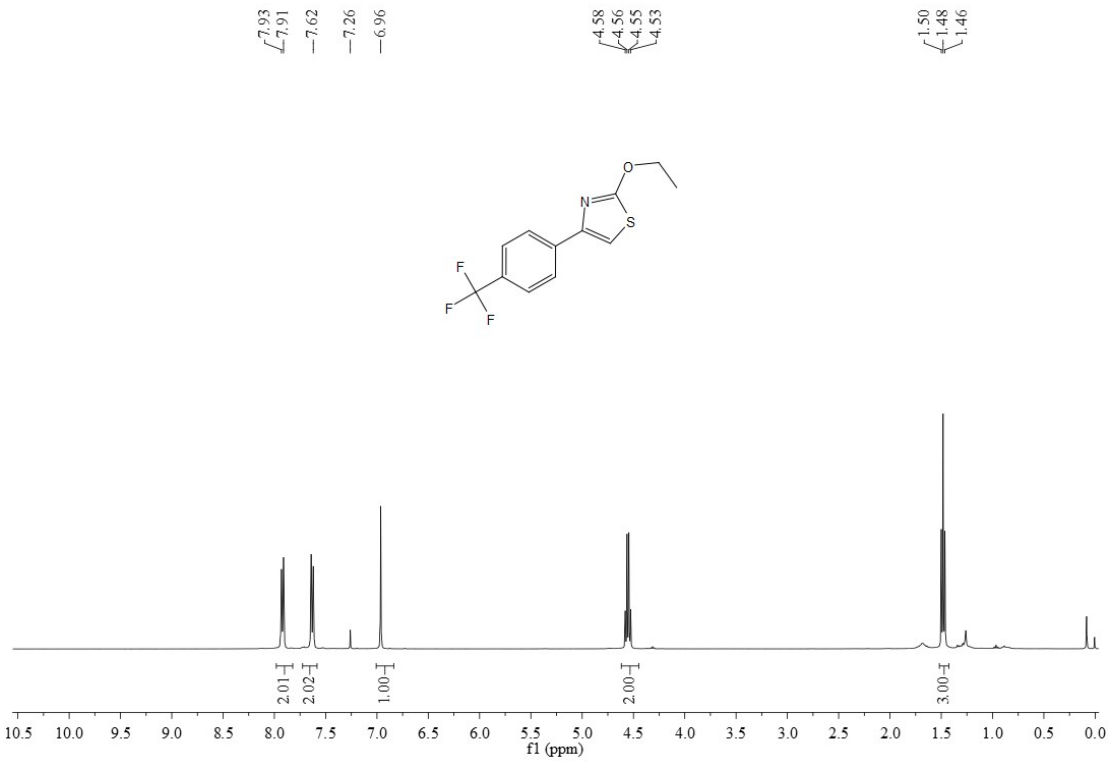


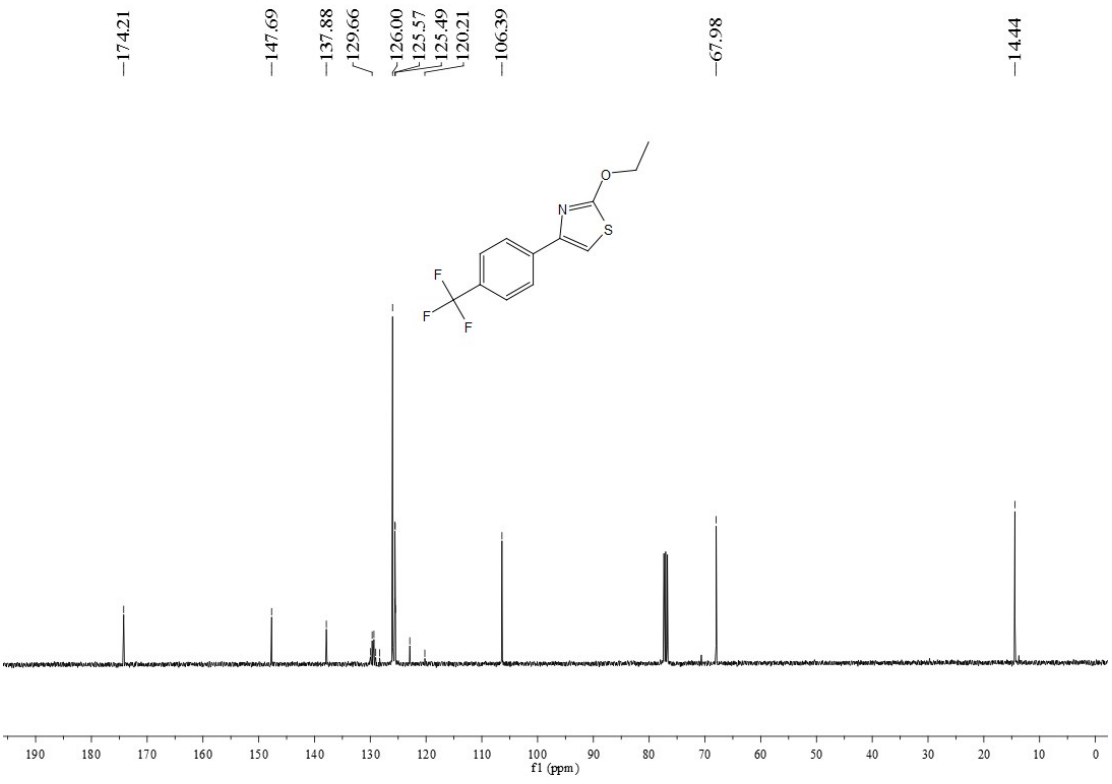
^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-(4-iodophenyl)thiazole (3ai)



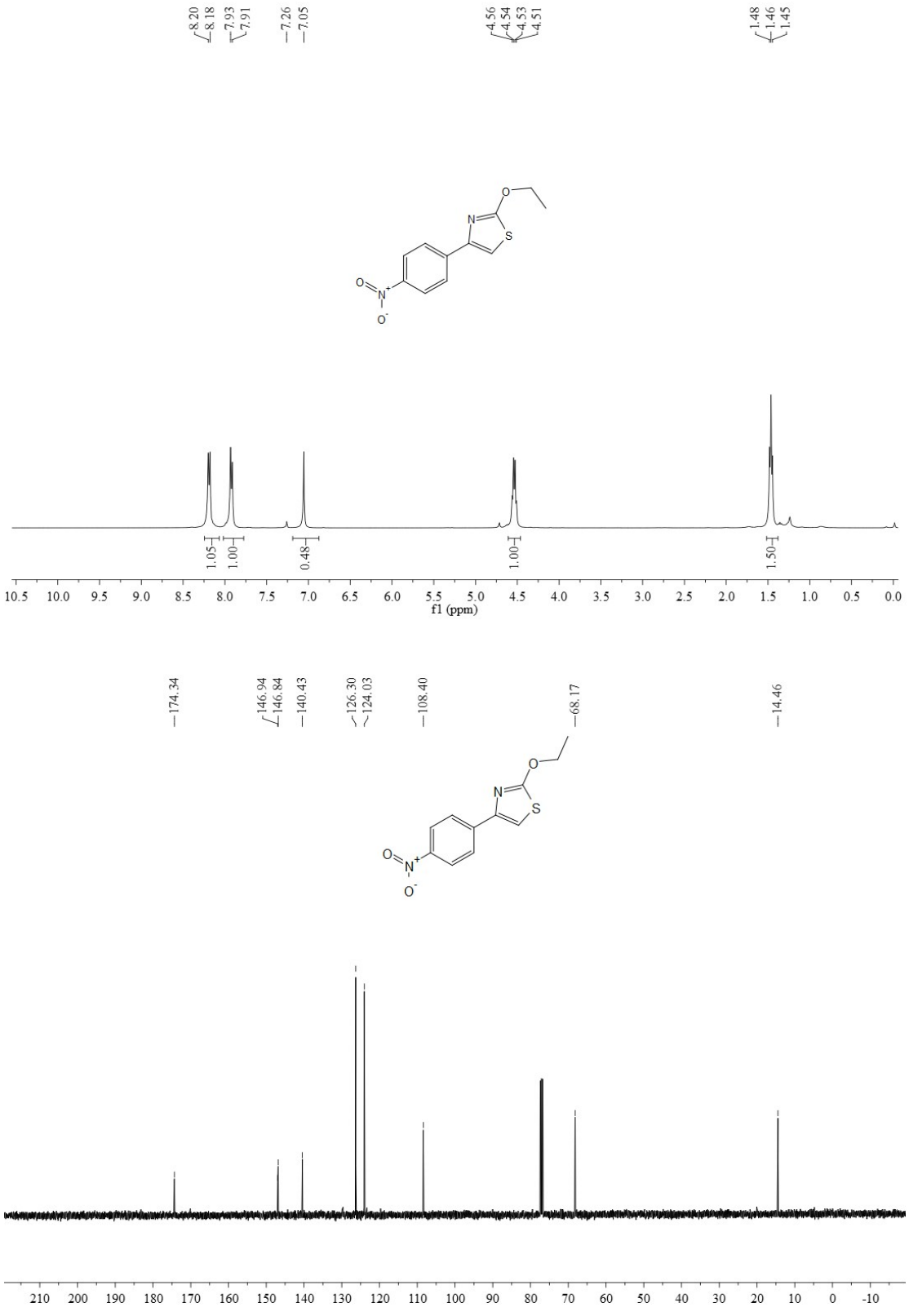


^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-(4-(trifluoromethyl)phenyl)thiazole (3aj)

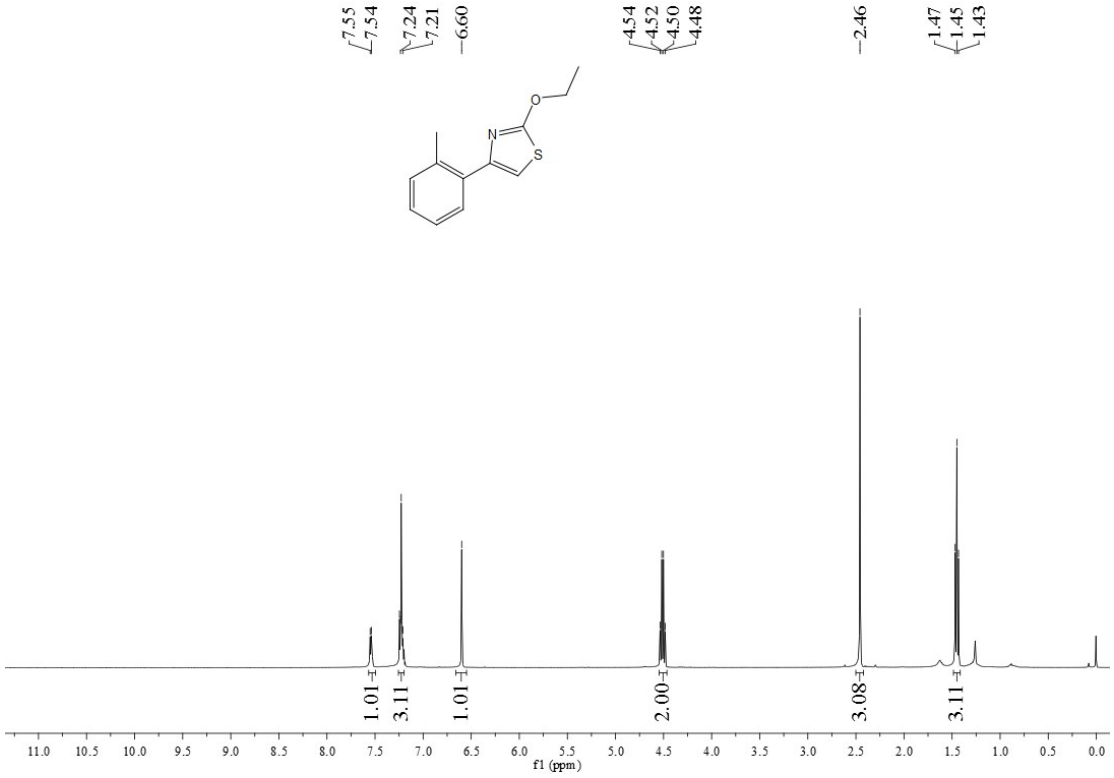


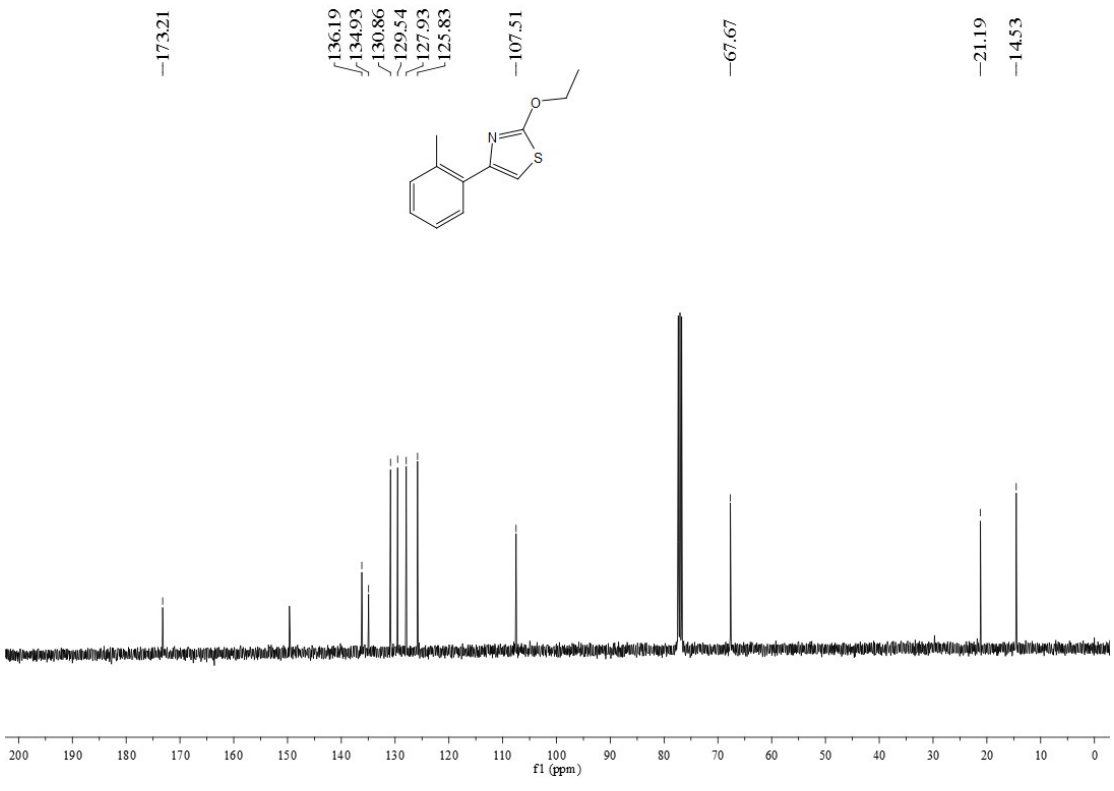


^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-(4-nitrophenyl)thiazole (3ak)

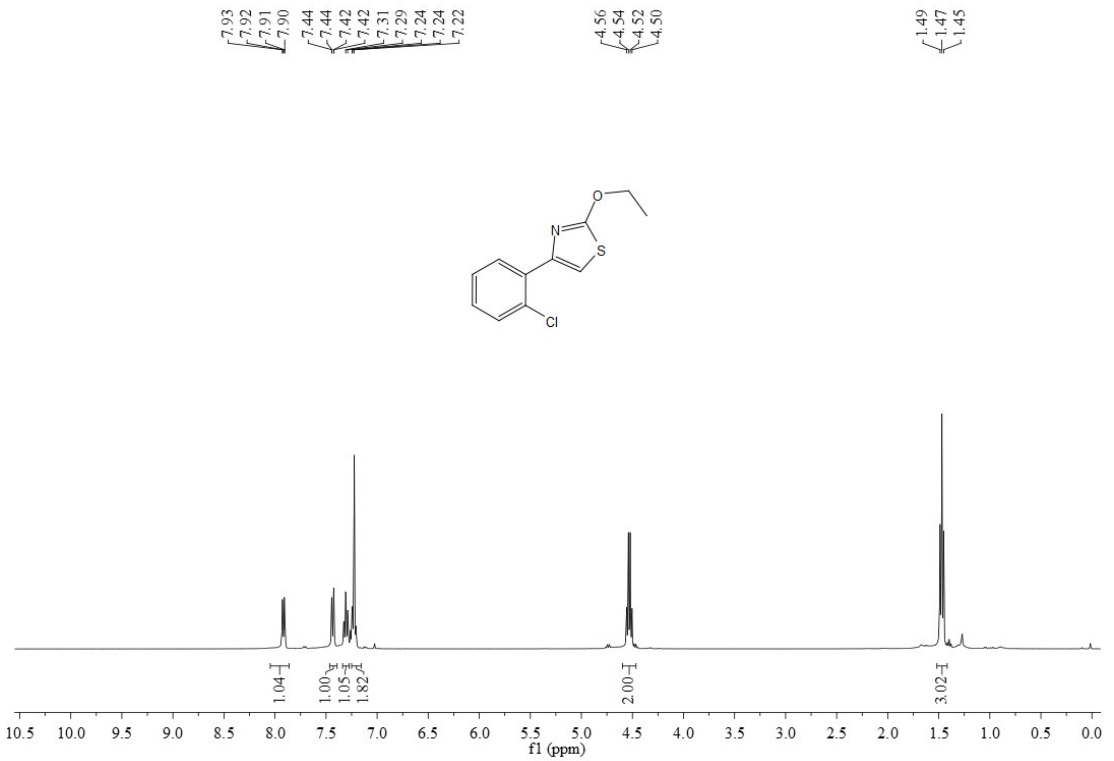


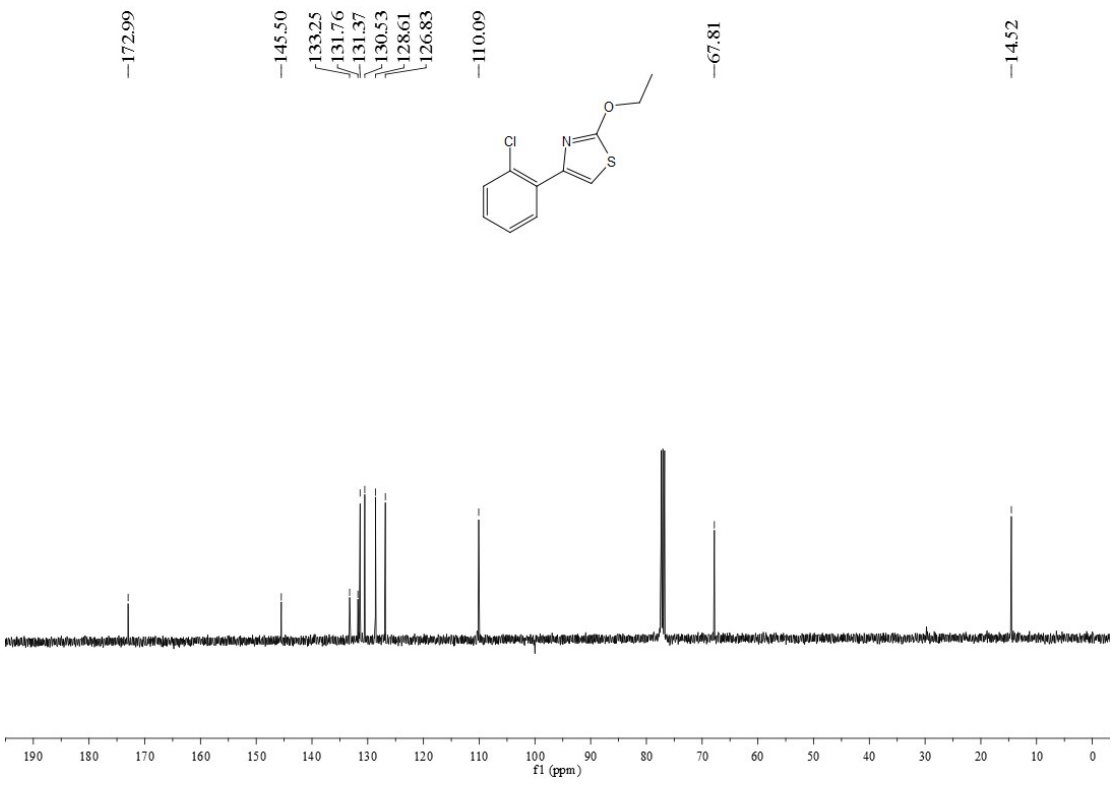
^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-(*o*-tolyl)thiazole (3al)



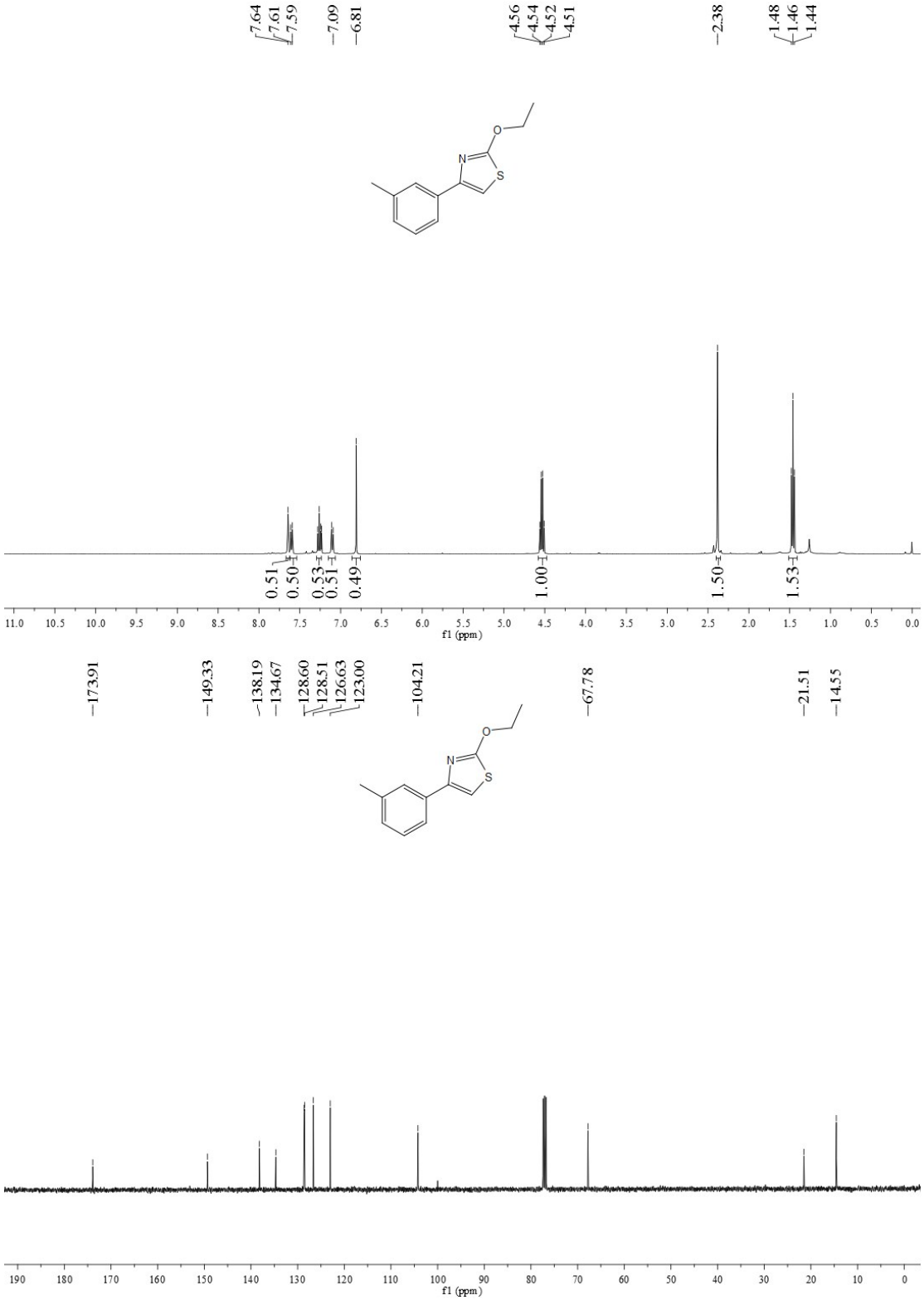


^{1}H NMR and ^{13}C NMR of 4-(2-chlorophenyl)-2-ethoxythiazole (3am)

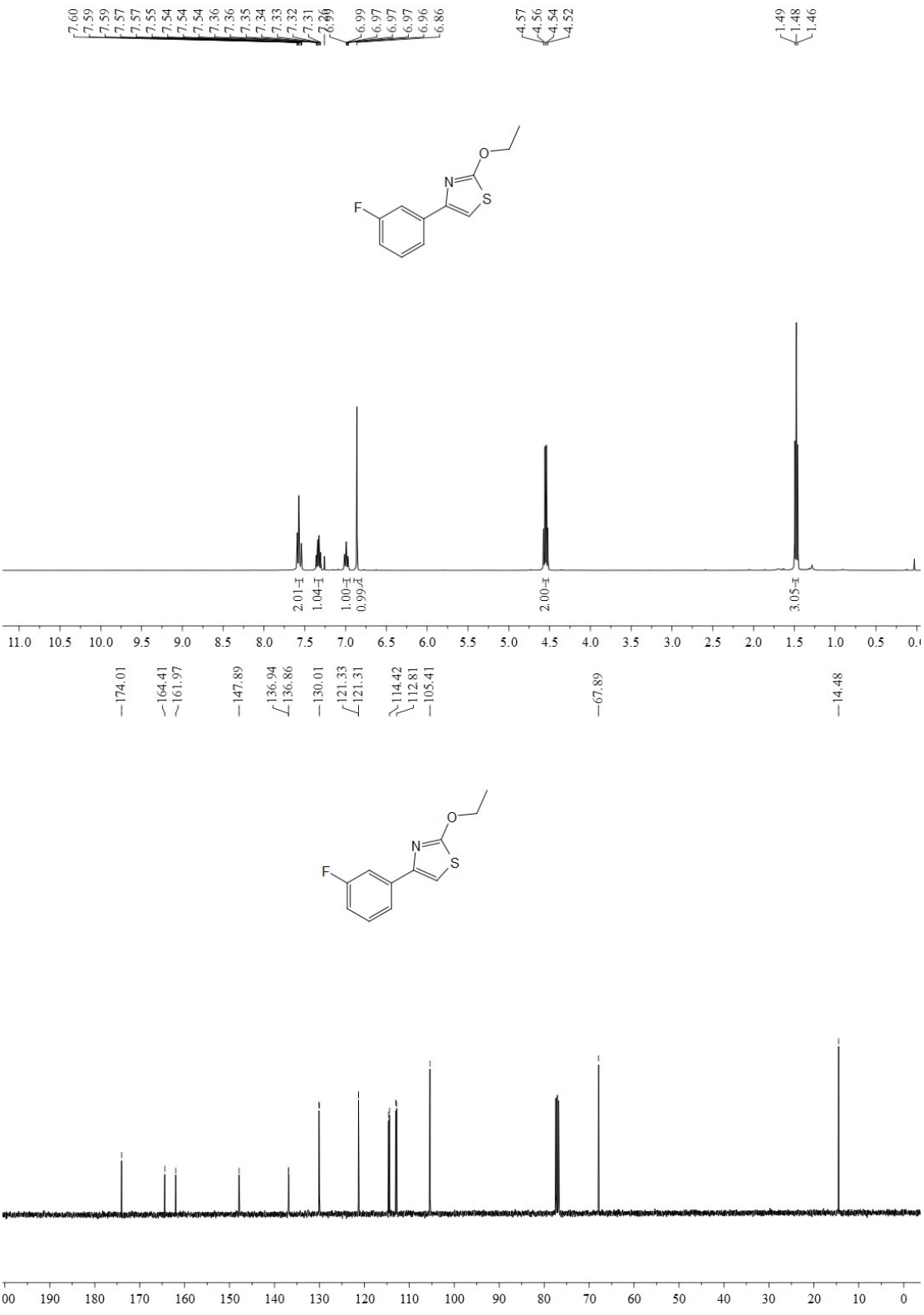




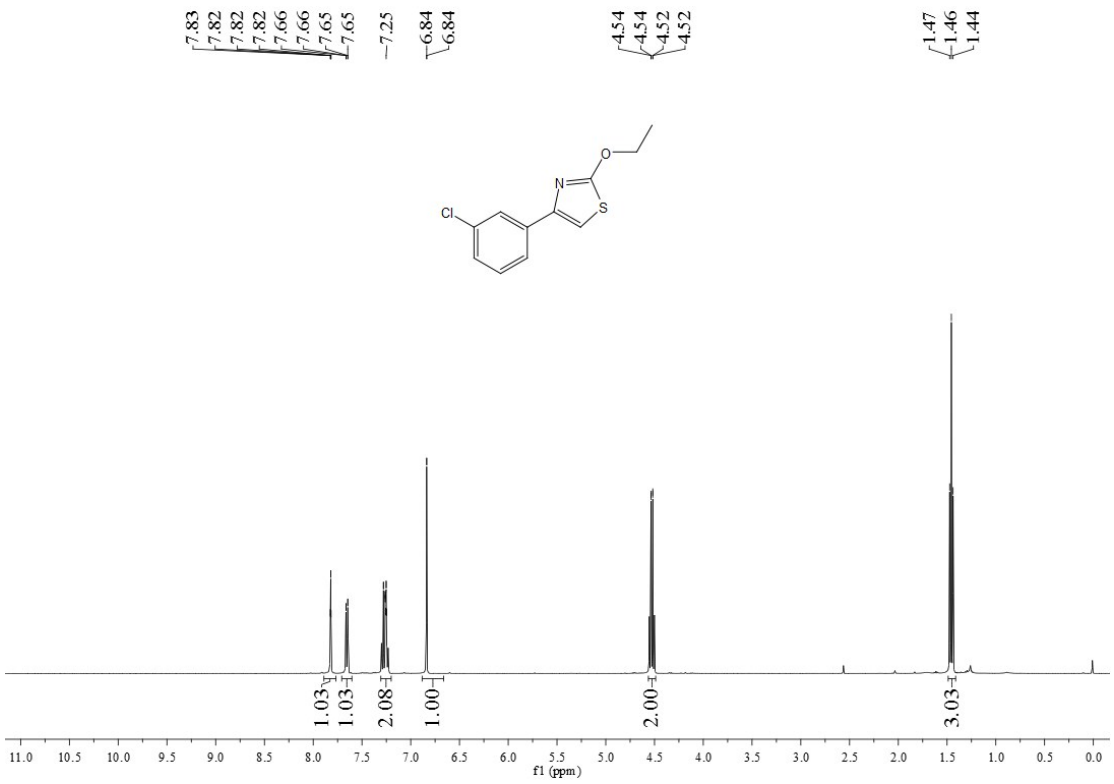
^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-(*m*-tolyl)thiazole (3an)

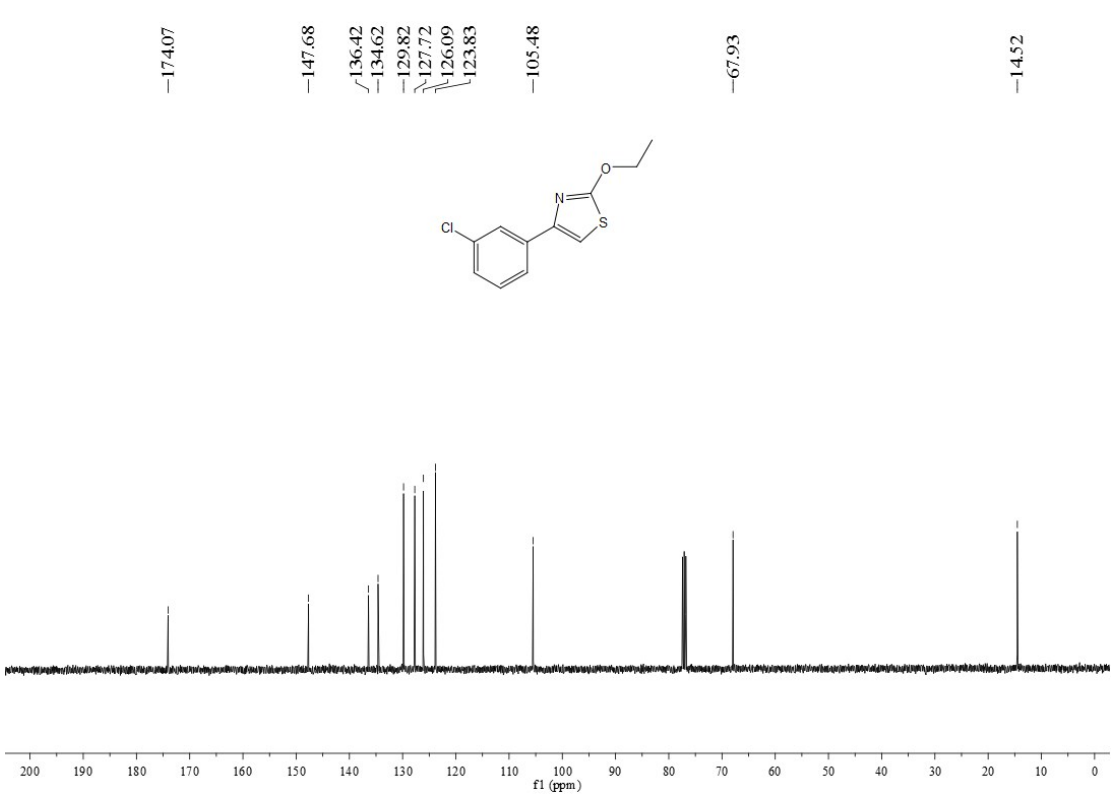


^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-(3-fluorophenyl)thiazole (3ao)

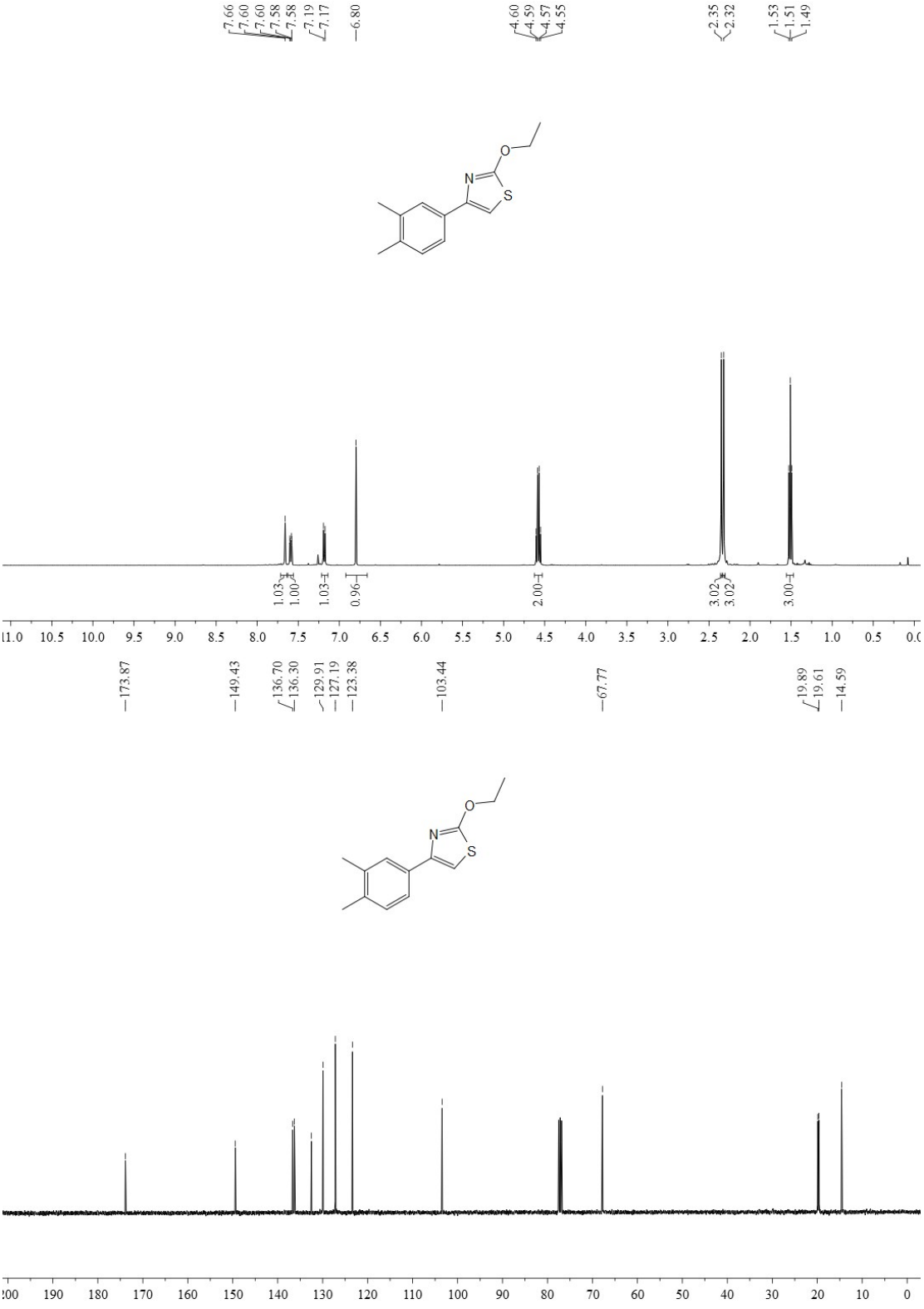


^{1}H NMR and ^{13}C NMR of 4-(3-chlorophenyl)-2-ethoxythiazole (3ap)

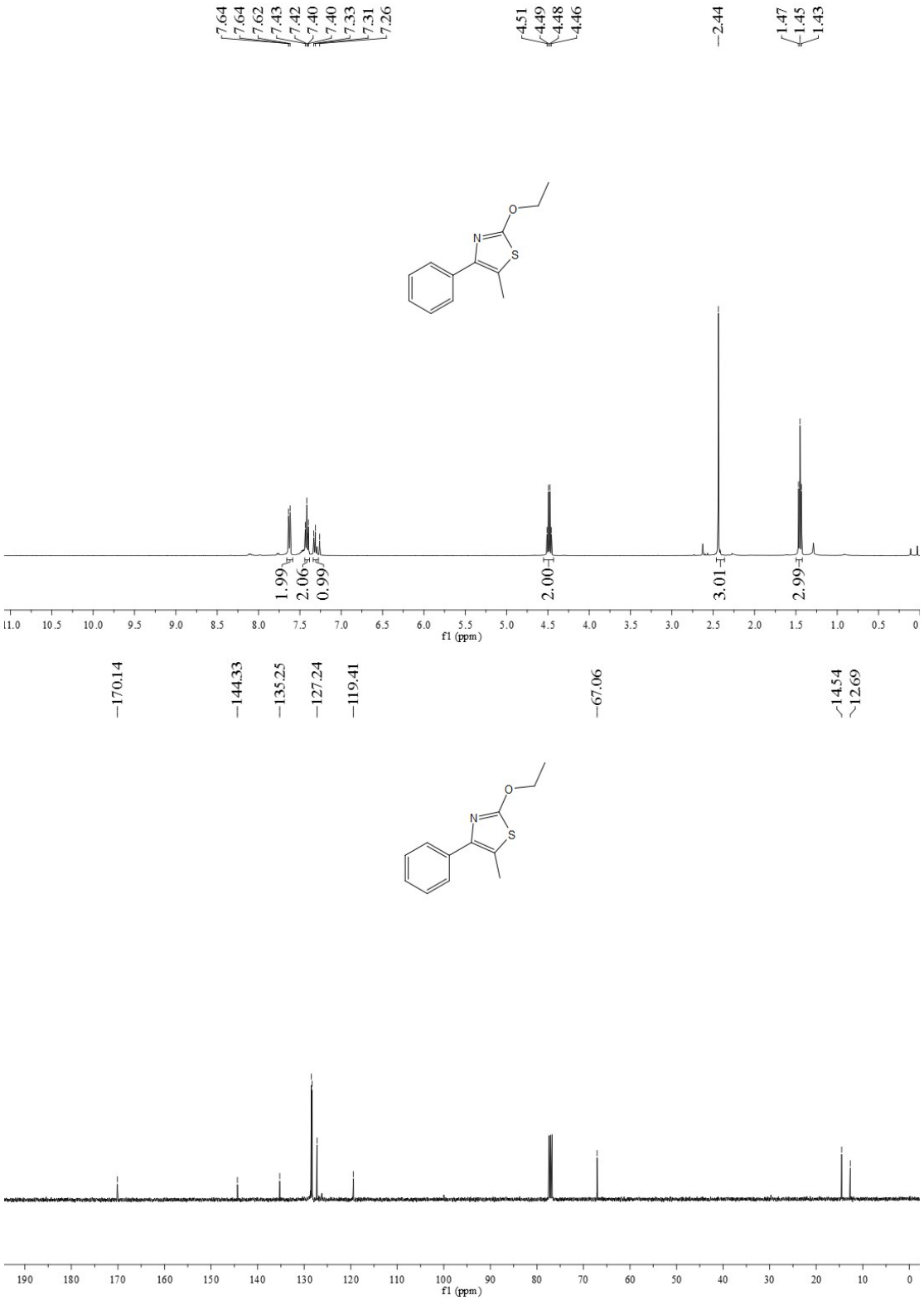




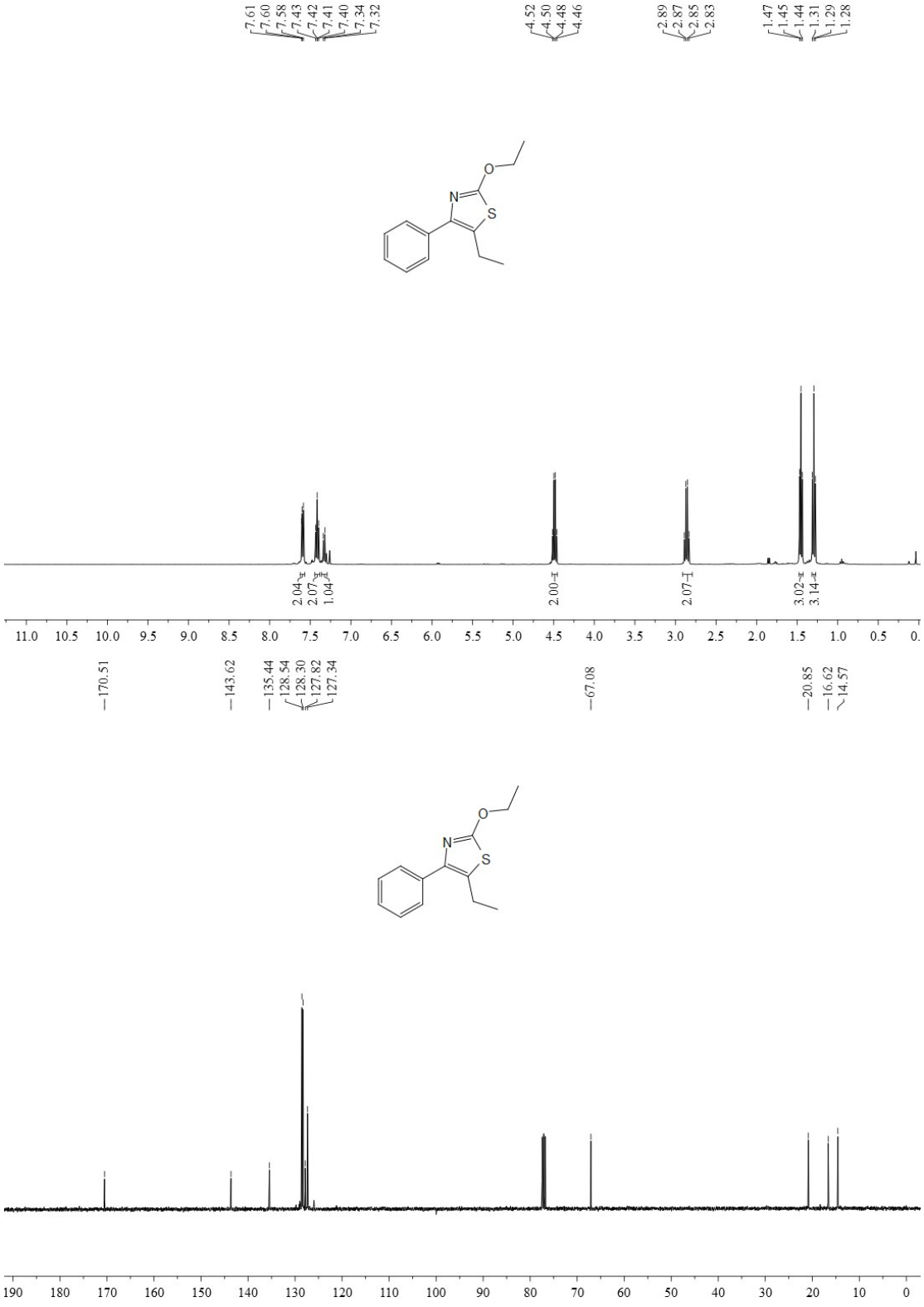
^{1}H NMR and ^{13}C NMR of 4-(3,4-dimethylphenyl)-2-ethoxythiazole (3aq)



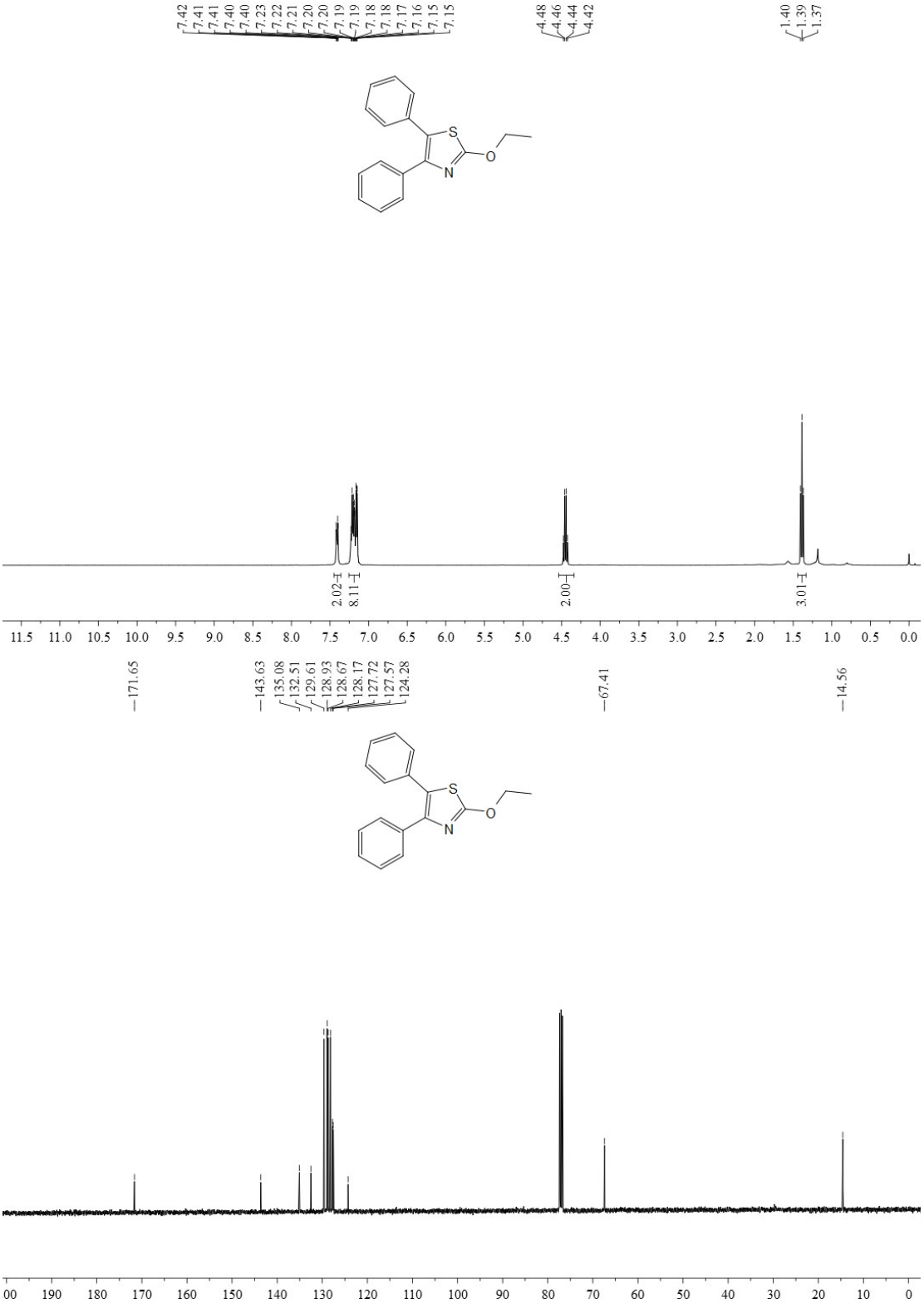
^{1}H NMR and ^{13}C NMR of 2-ethoxy-5-methyl-4-phenylthiazole (3ar)



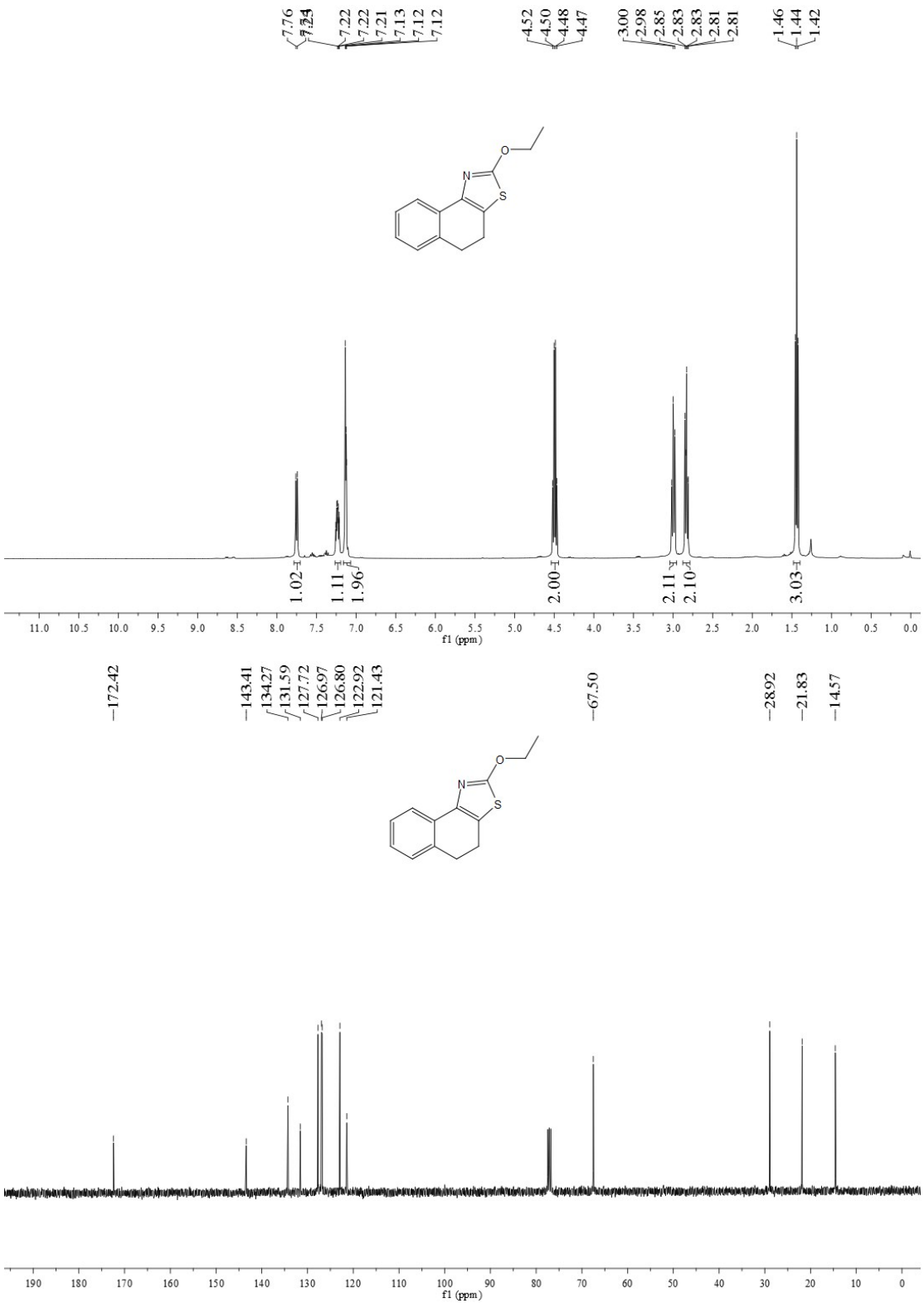
^{1}H NMR and ^{13}C NMR of 2-ethoxy-5-ethyl-4-phenylthiazole (3as)



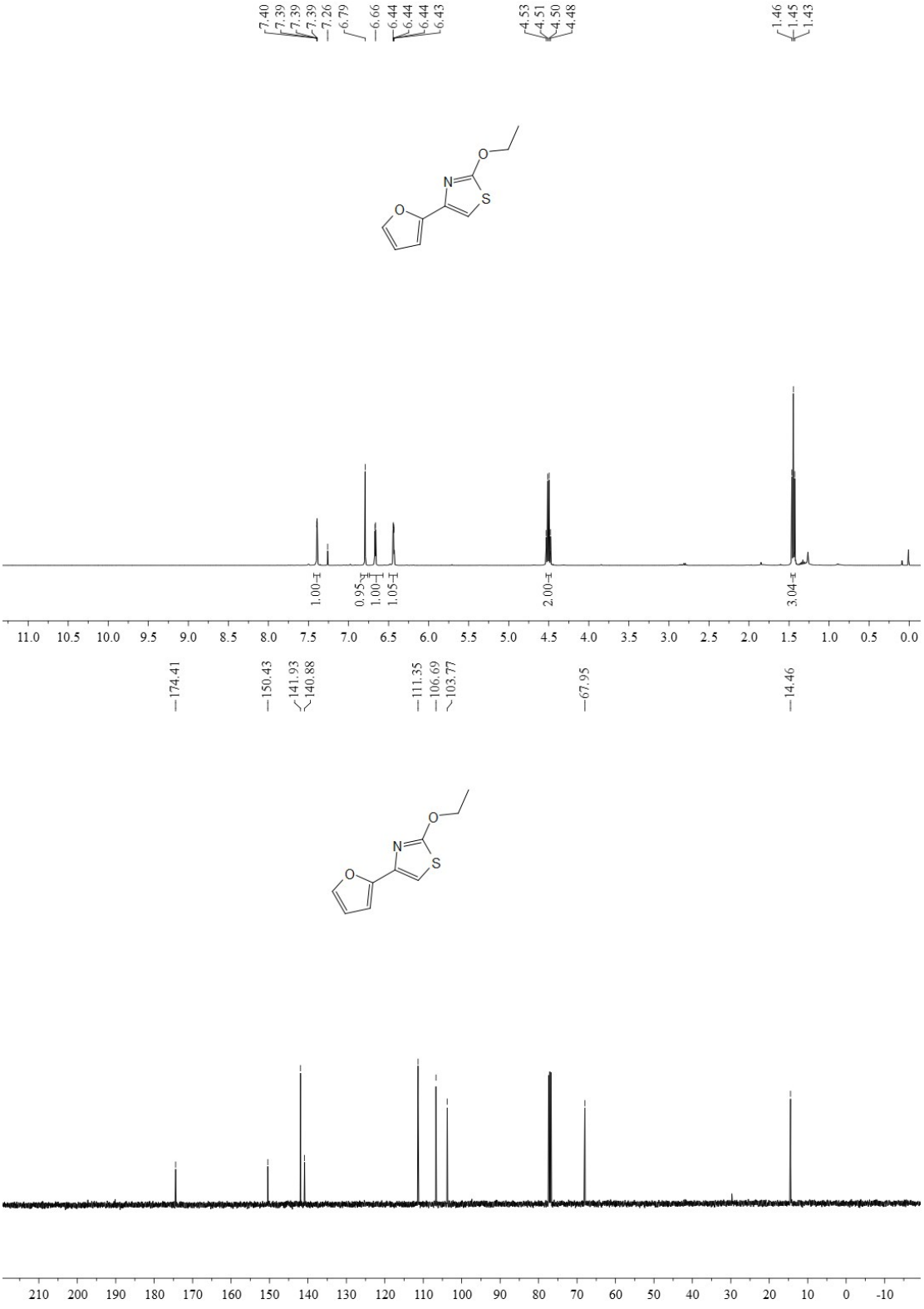
^{1}H NMR and ^{13}C NMR of 2-ethoxy-4,5-diphenylthiazole (3at)



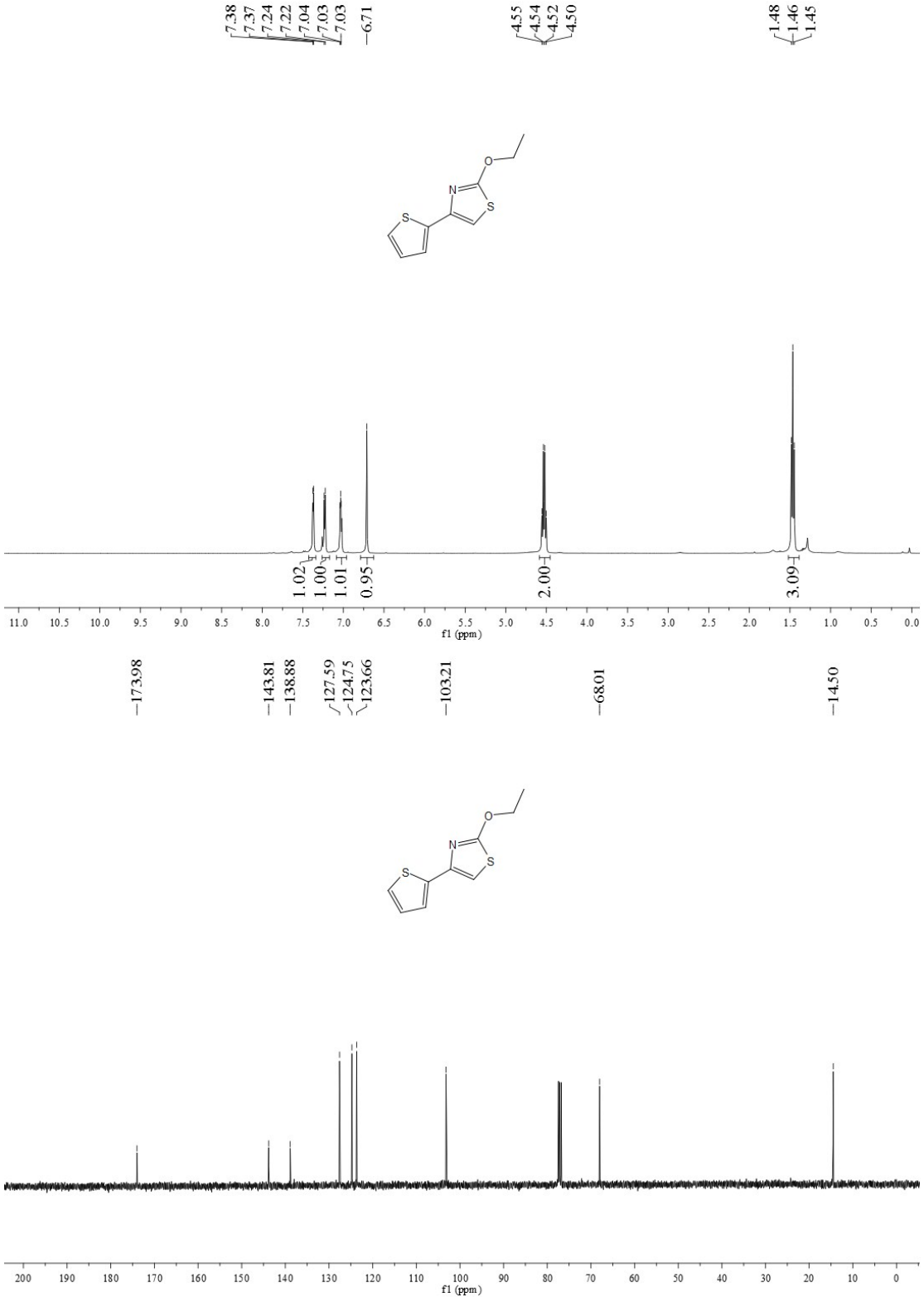
^{1}H NMR and ^{13}C NMR of 2-ethoxy-4,5-dihydronaphtho[1,2-*d*]thiazole (3au)



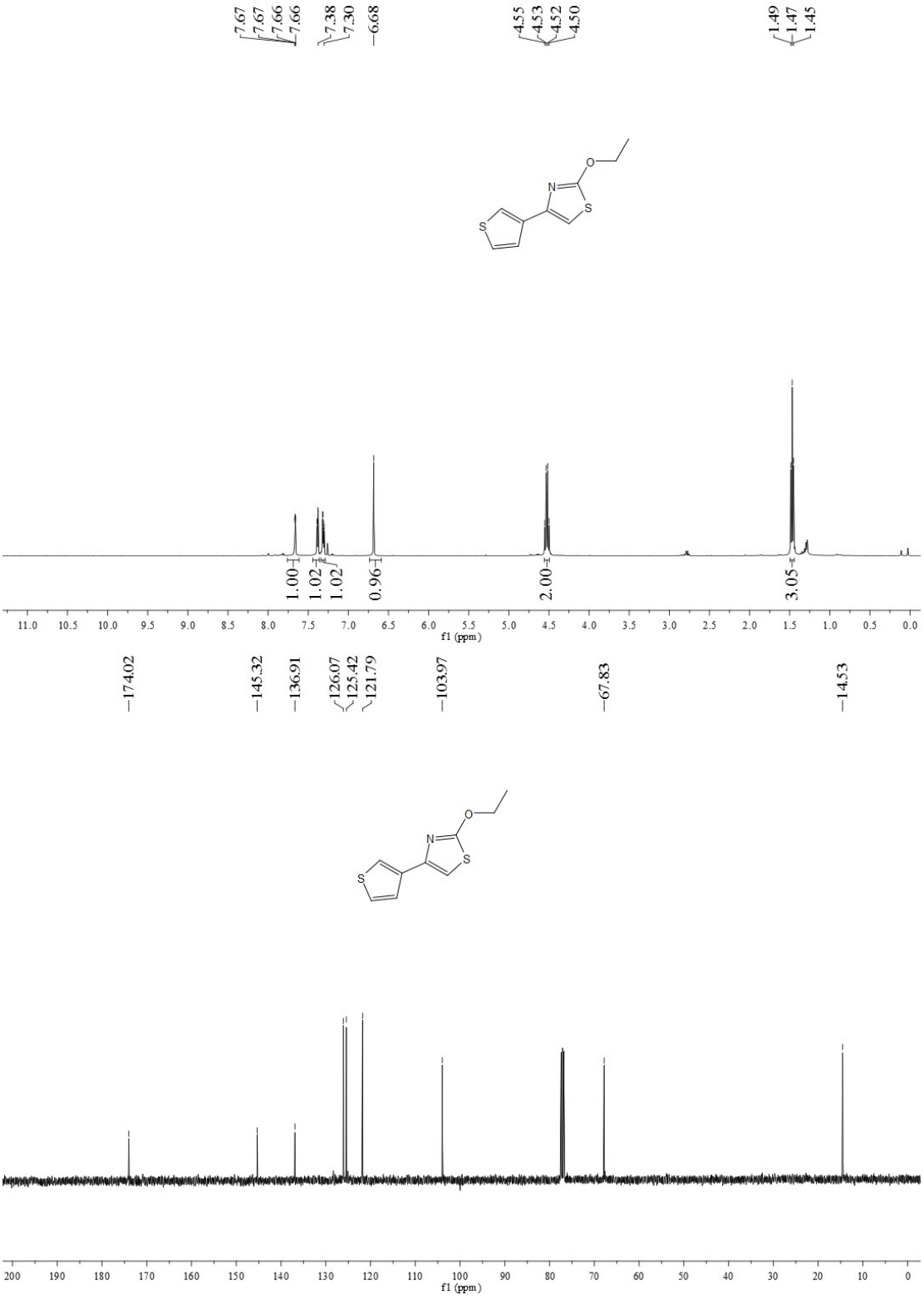
^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-(furan-2-yl)thiazole (3av)



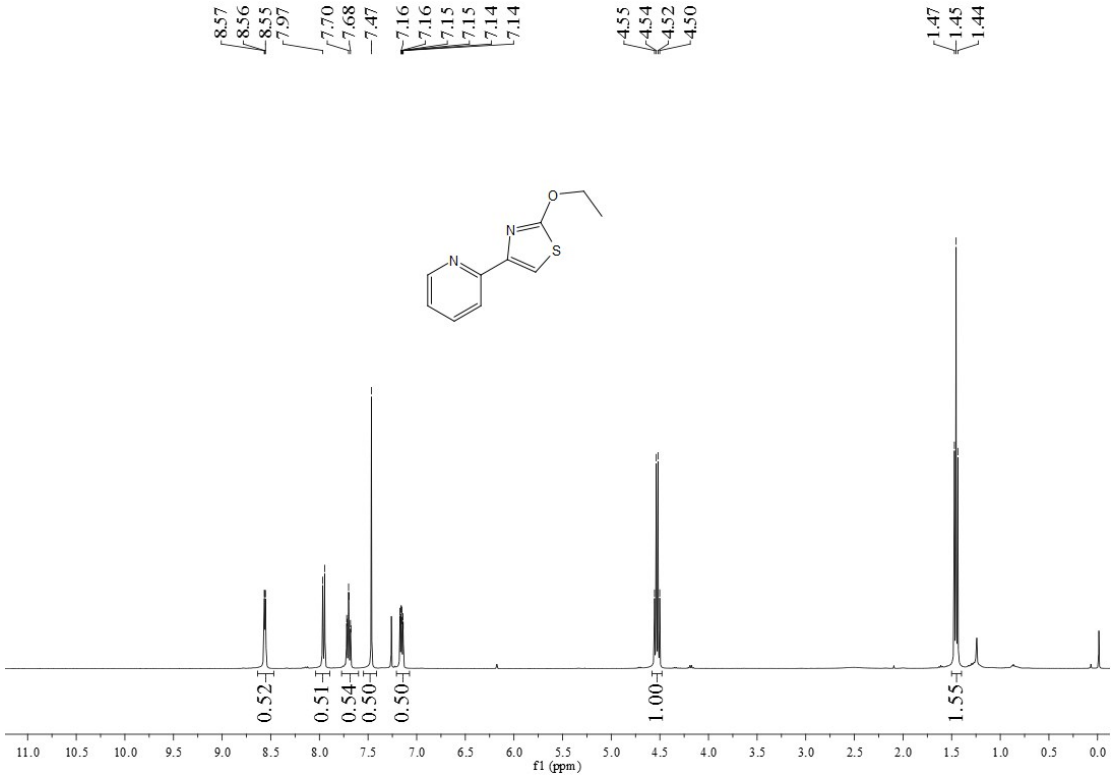
^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-(thiophen-2-yl)thiazole (3aw)

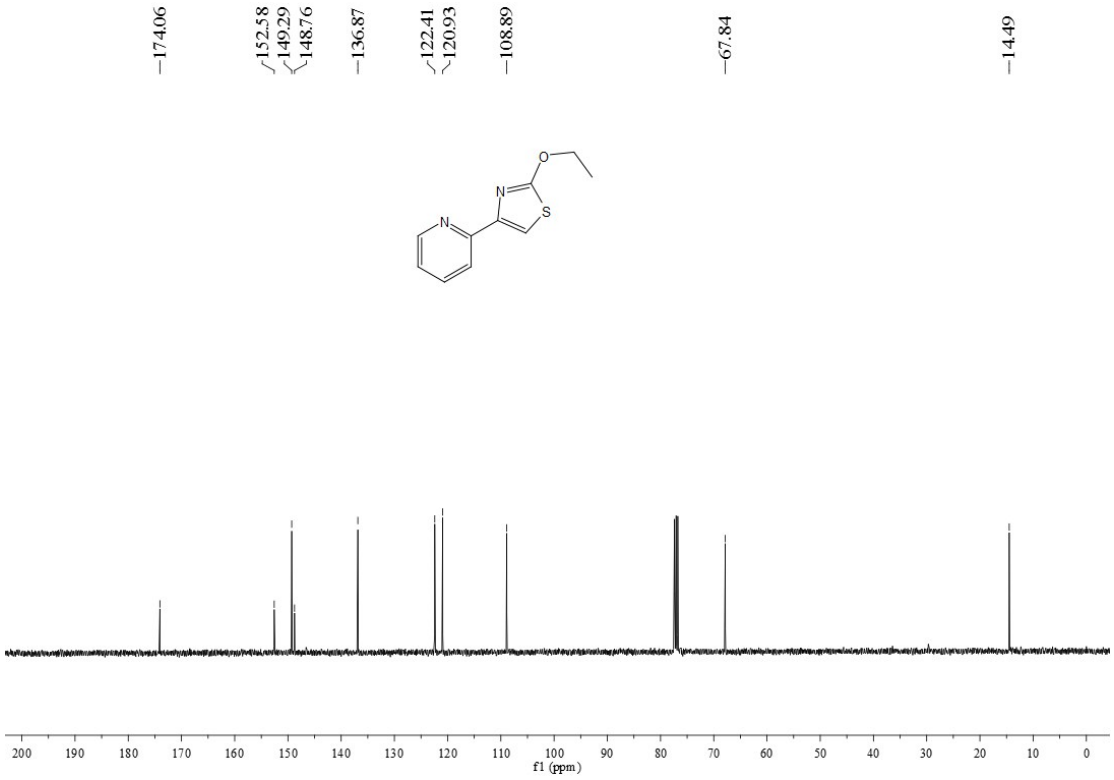


^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-(thiophen-3-yl)thiazole (3ax)

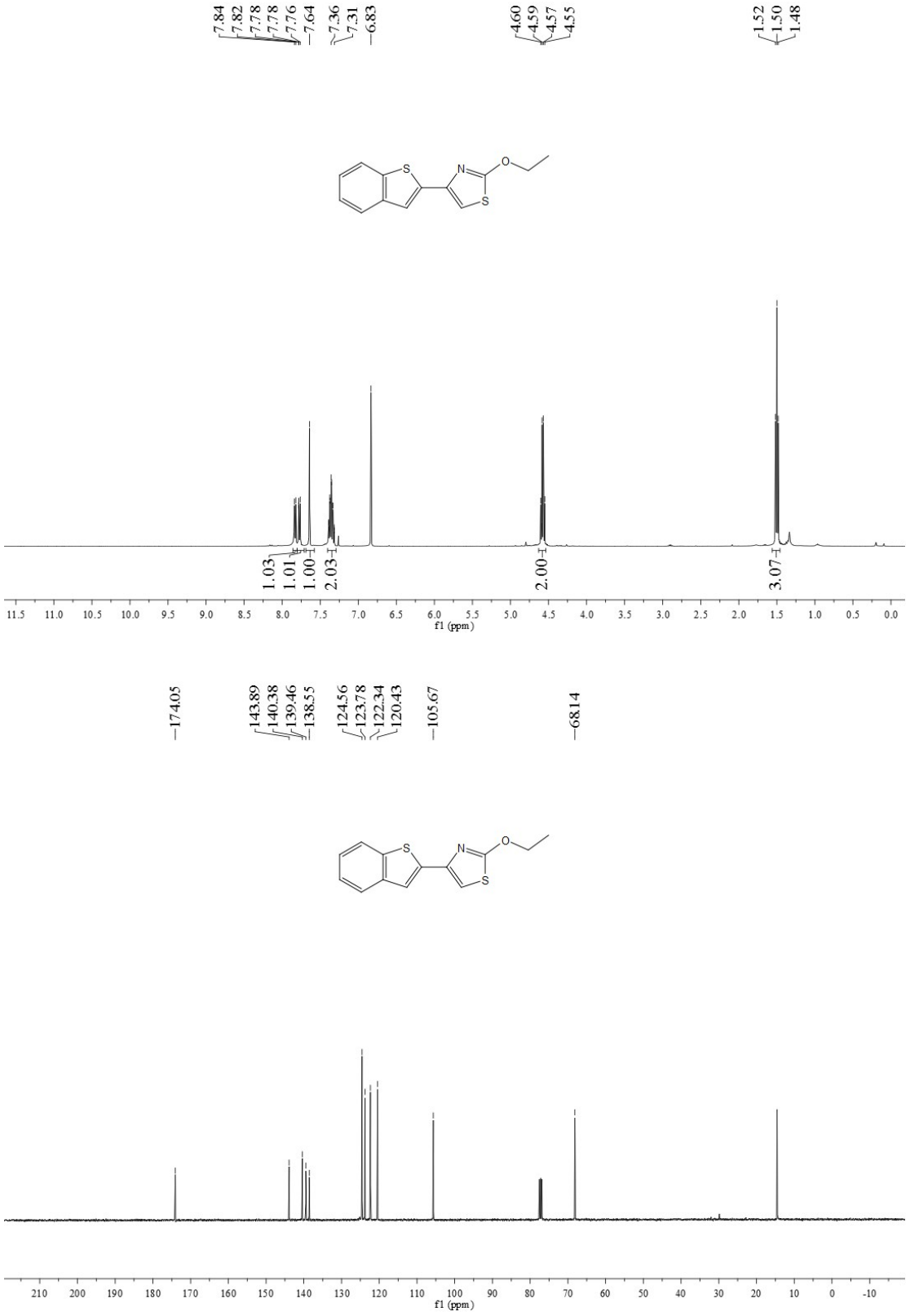


^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-(pyridin-2-yl)thiazole (3ay)

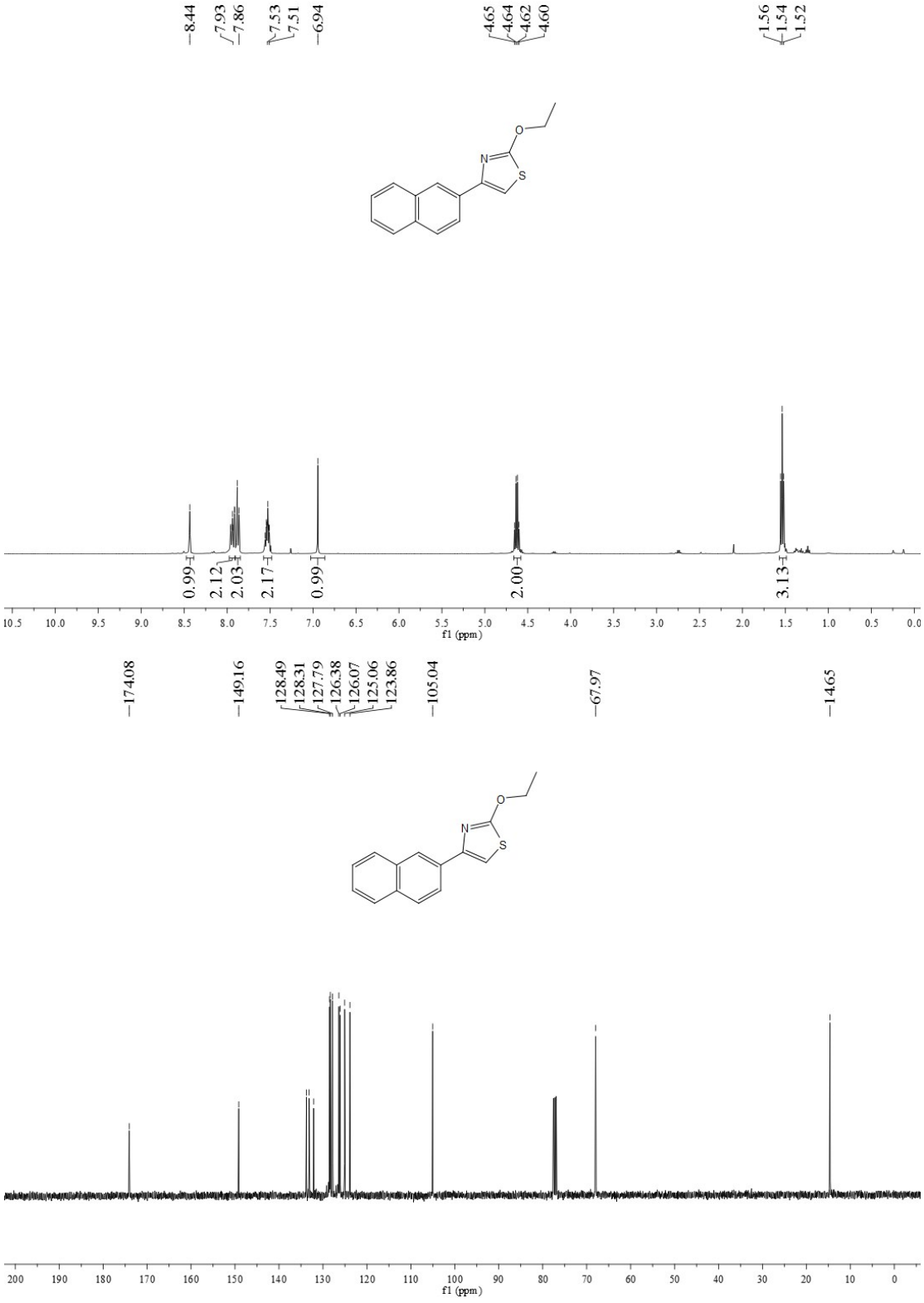




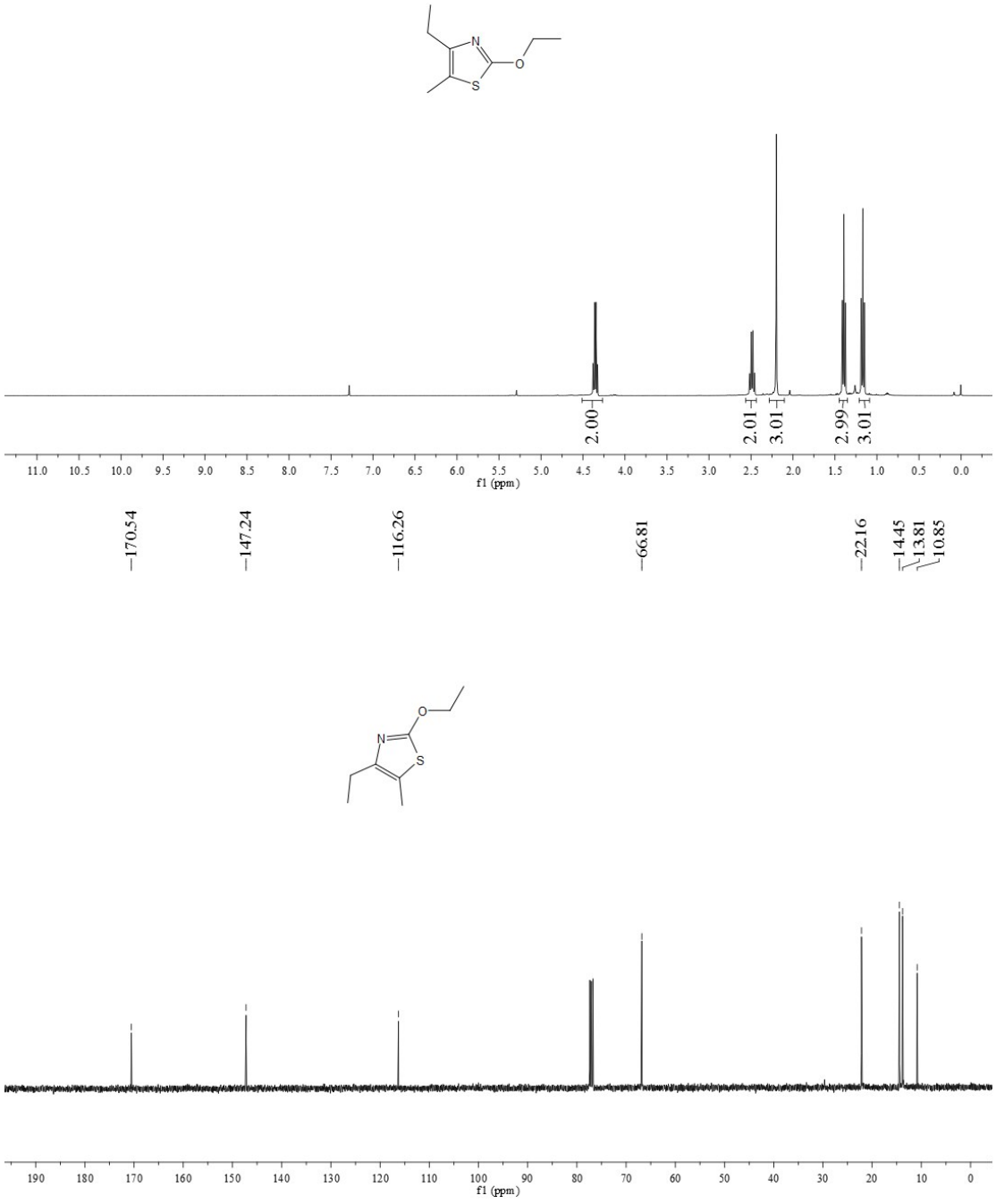
^{1}H NMR and ^{13}C NMR of 4-(benzo[b]thiophen-2-yl)-2-ethoxythiazole (3az)



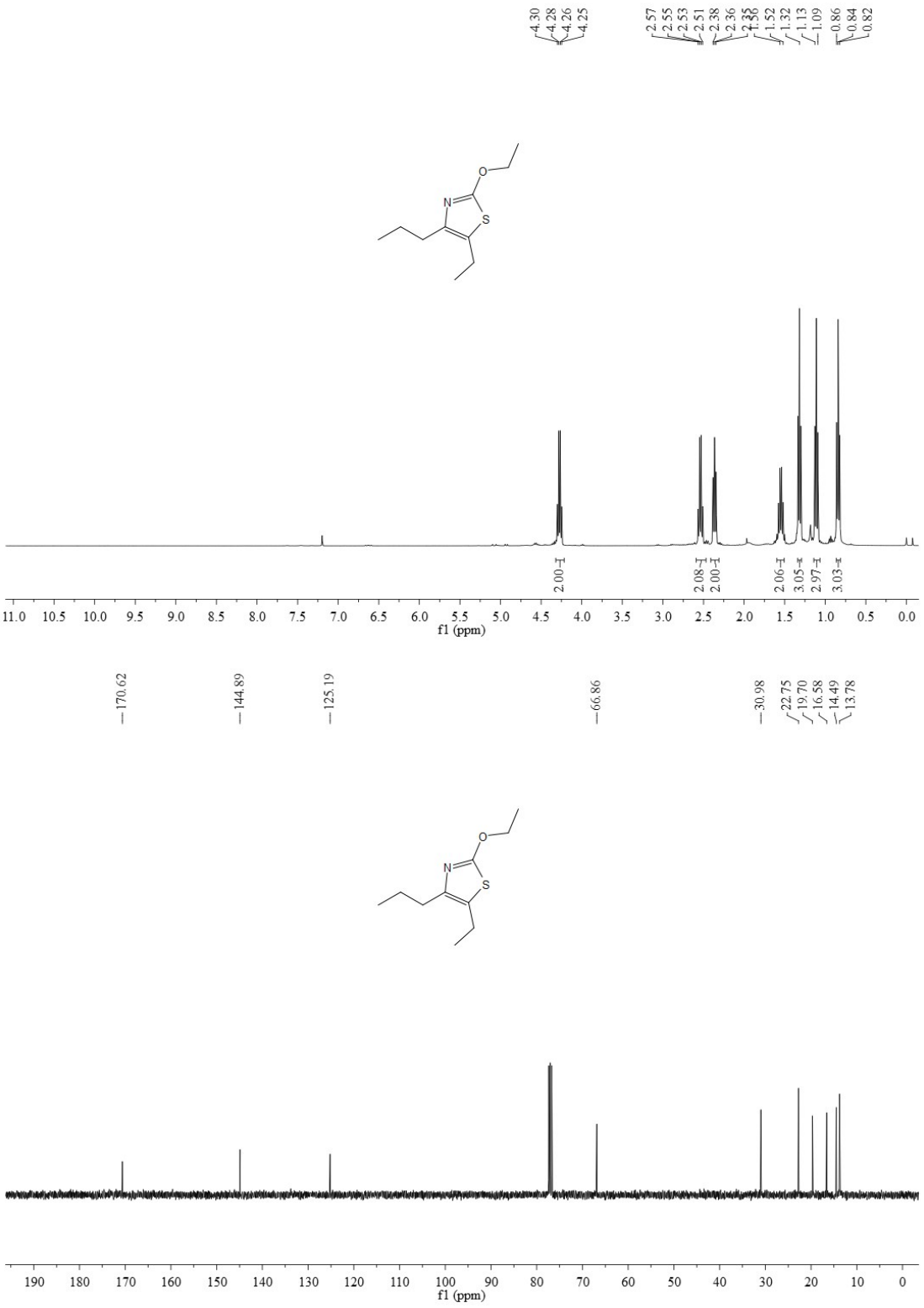
^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-(naphthalen-2-yl)thiazole (3ba)



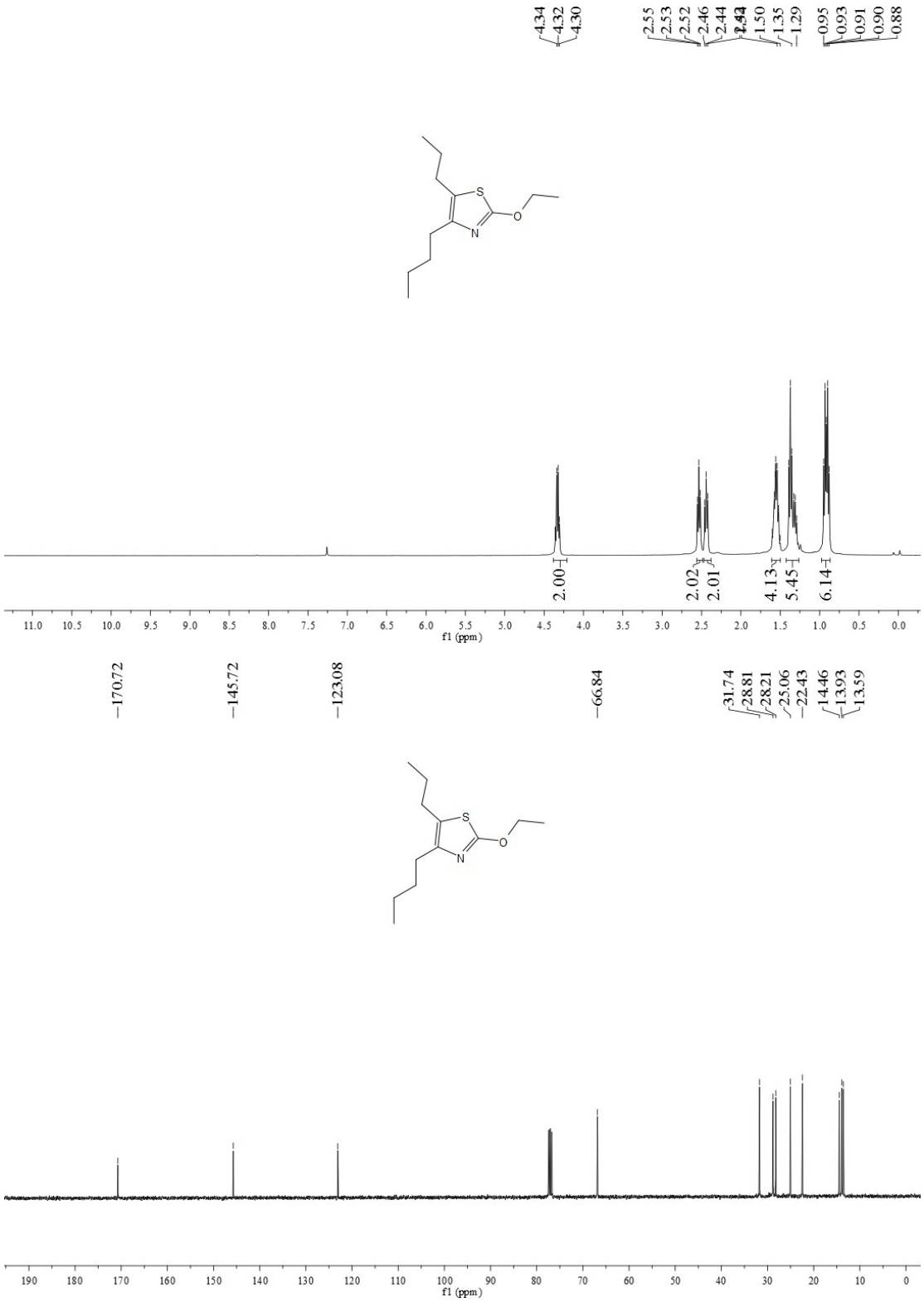
^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-ethyl-5-methylthiazole (3bb)



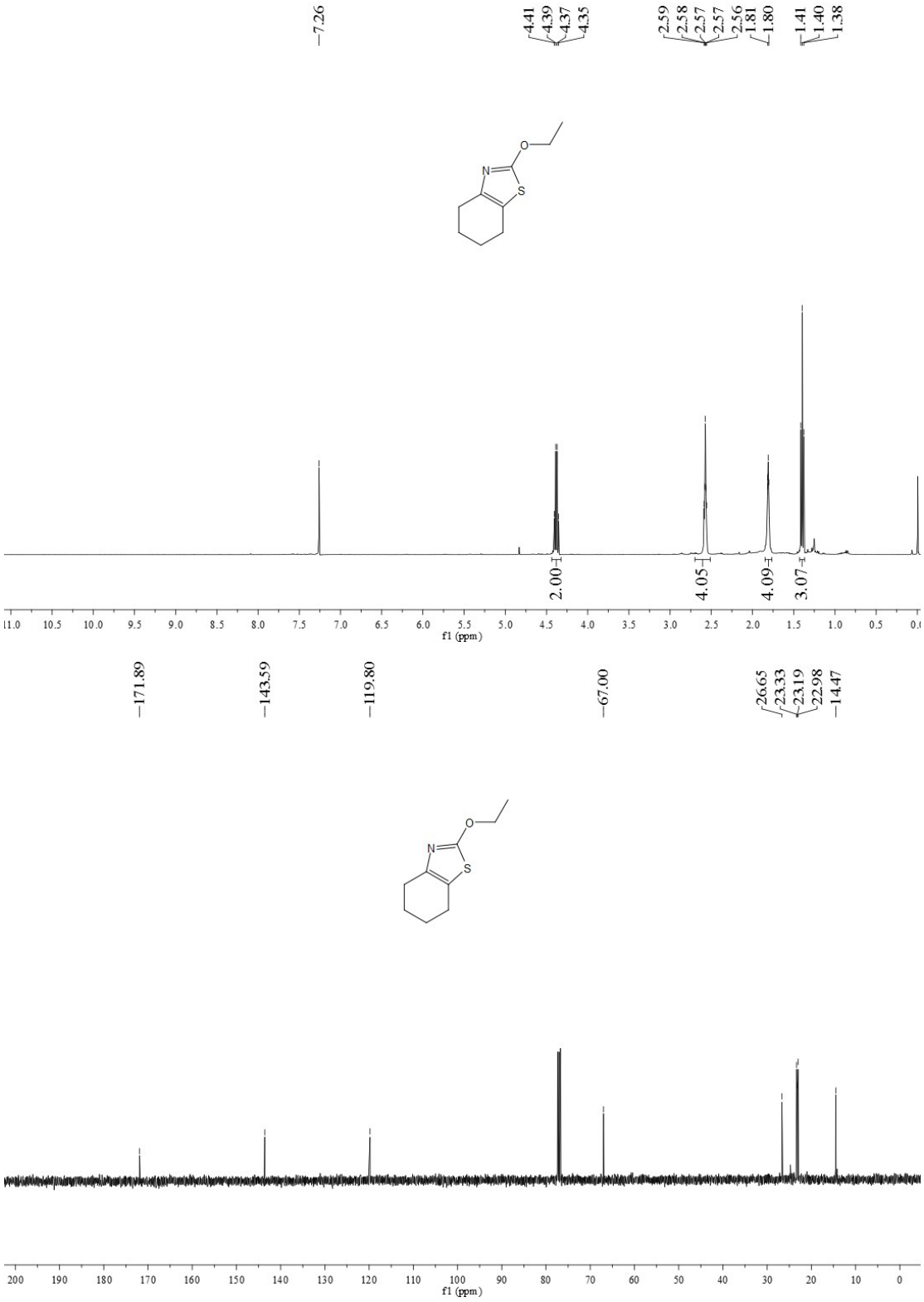
^{1}H NMR and ^{13}C NMR of 2-ethoxy-5-ethyl-4-propylthiazole (3bc)



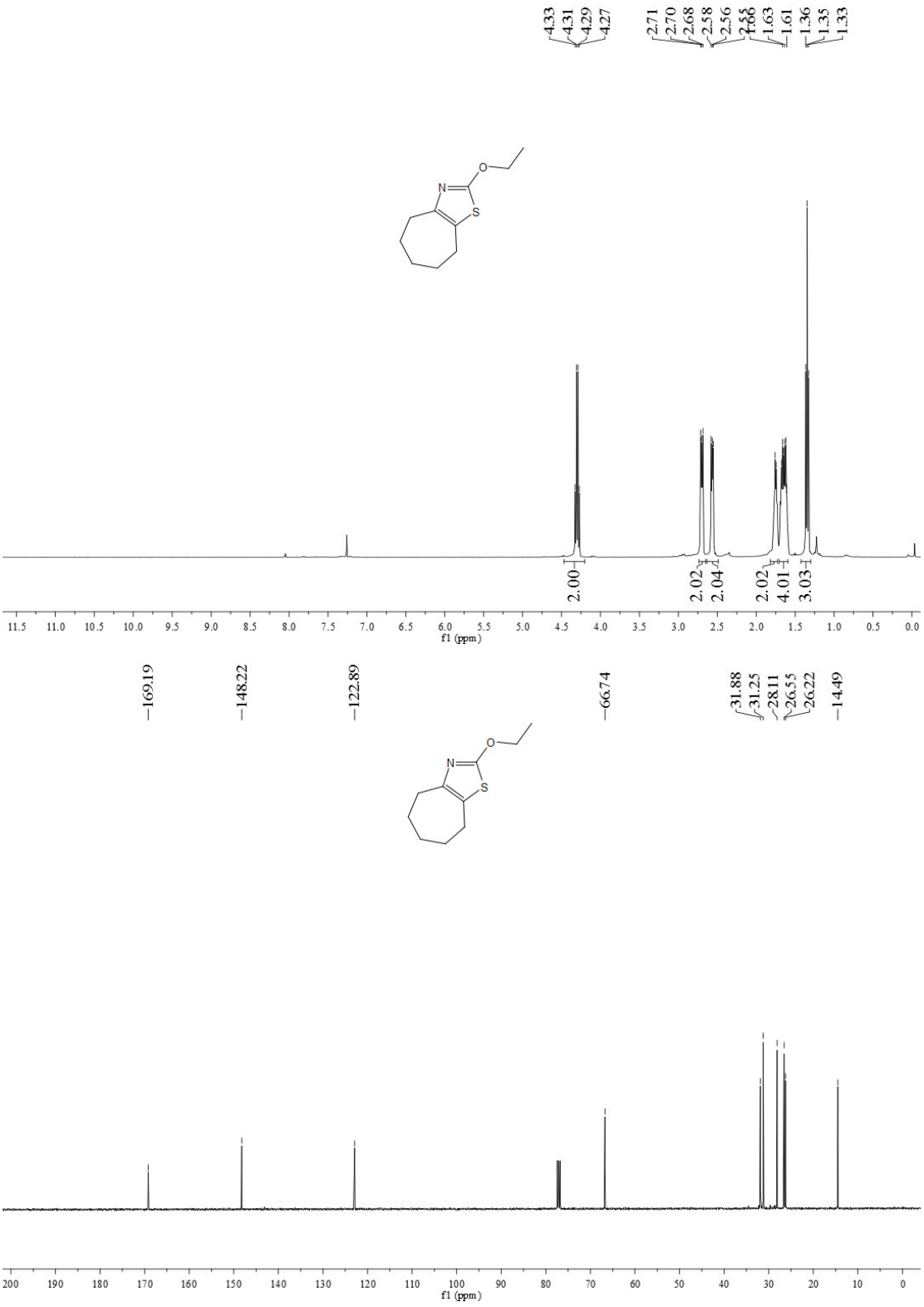
^{1}H NMR and ^{13}C NMR of 4-butyl-2-ethoxy-5-propylthiazole (3bd)



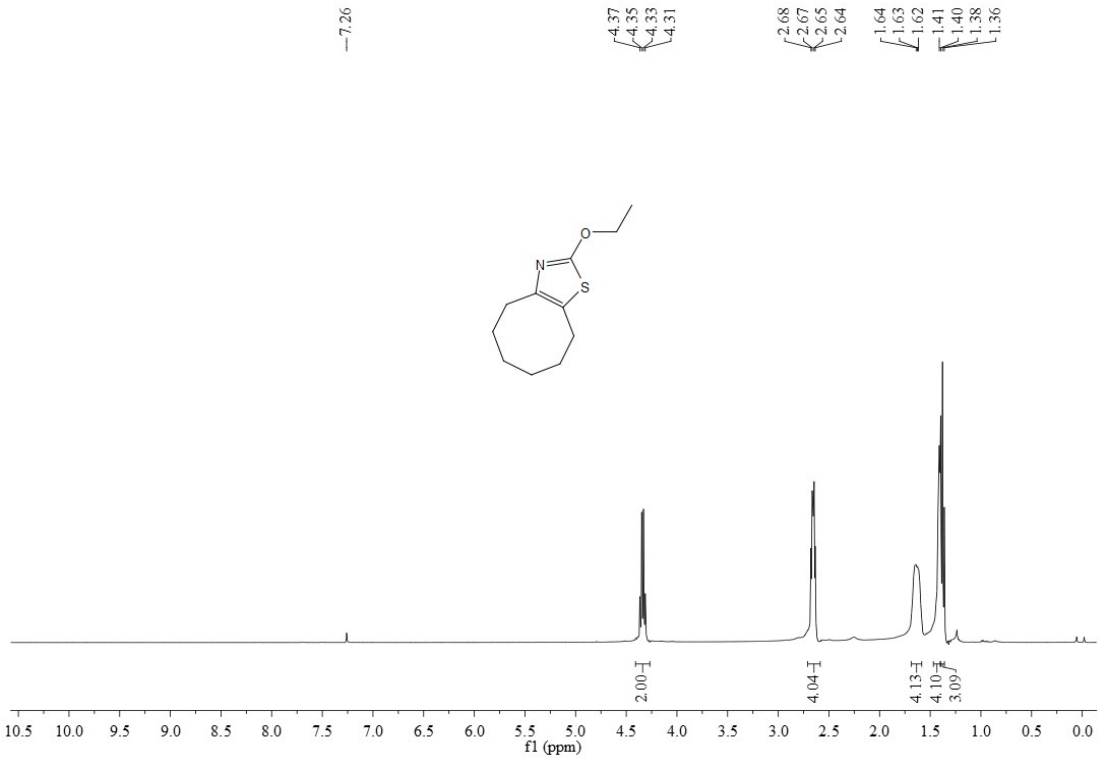
^{1}H NMR and ^{13}C NMR of 2-ethoxy-4,5,6,7-tetrahydrobenzo[*d*]thiazole (3be)

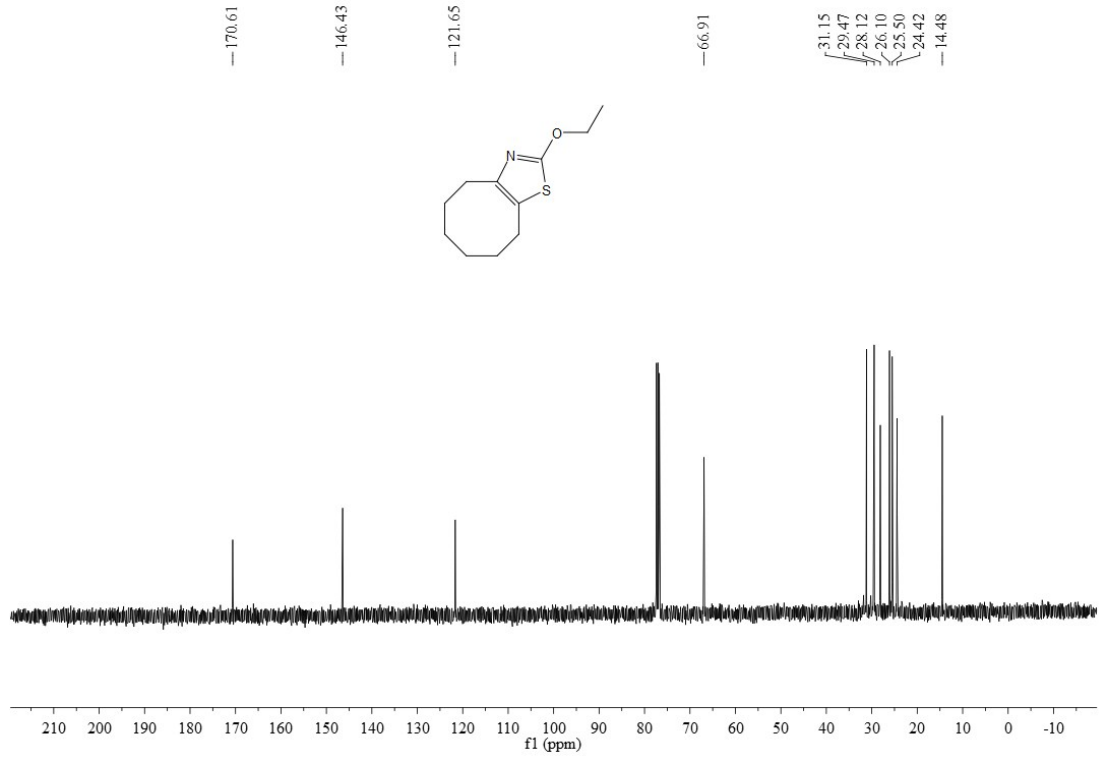


^{1}H NMR and ^{13}C NMR of 2-ethoxy-5,6,7,8-tetrahydro-4*H*-cyclohepta[*d*]thiazole (3bf)

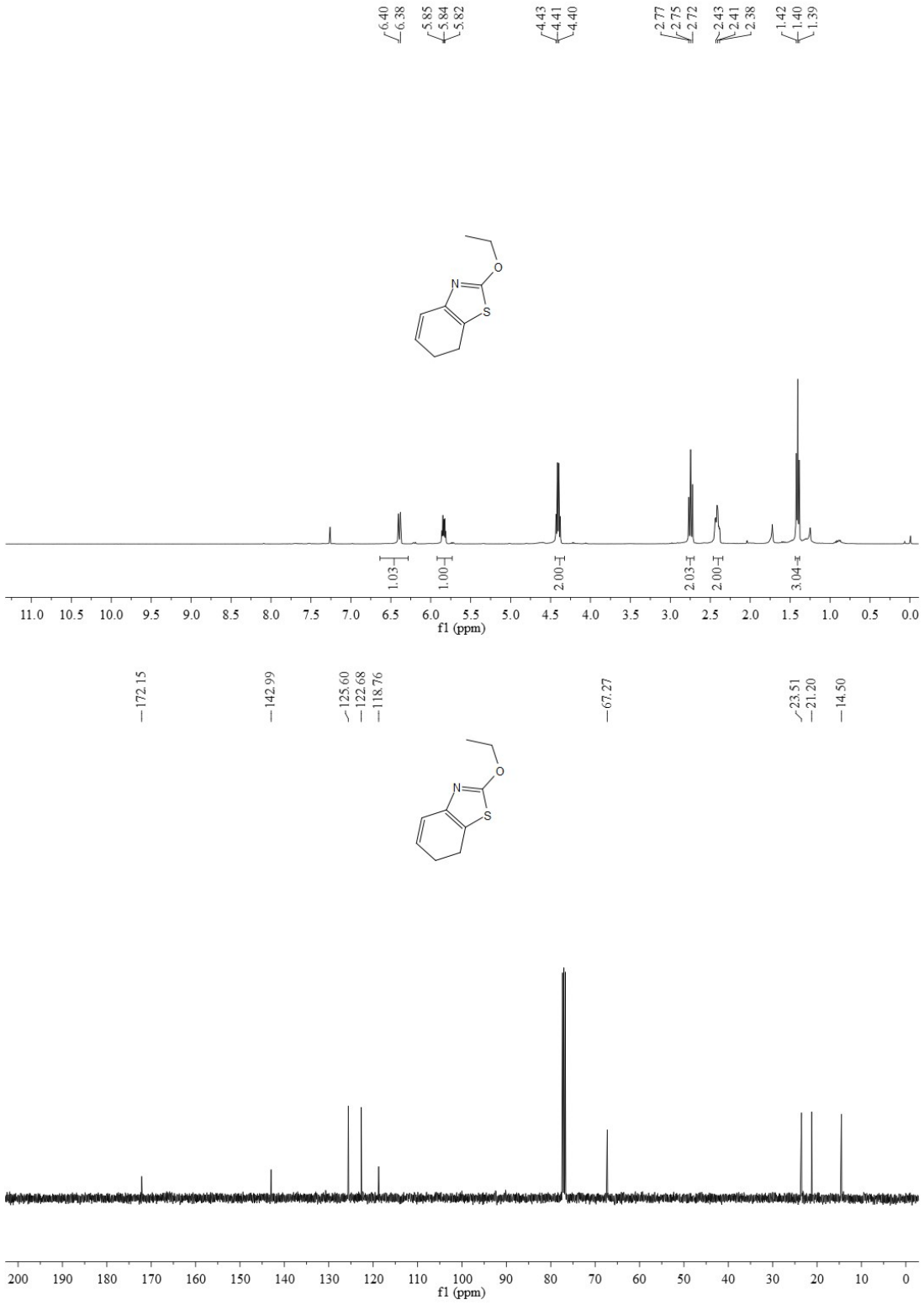


^{1}H NMR and ^{13}C NMR of 2-ethoxy-4,5,6,7,8,9-hexahydrocycloocta[*d*]thiazole (3bg)

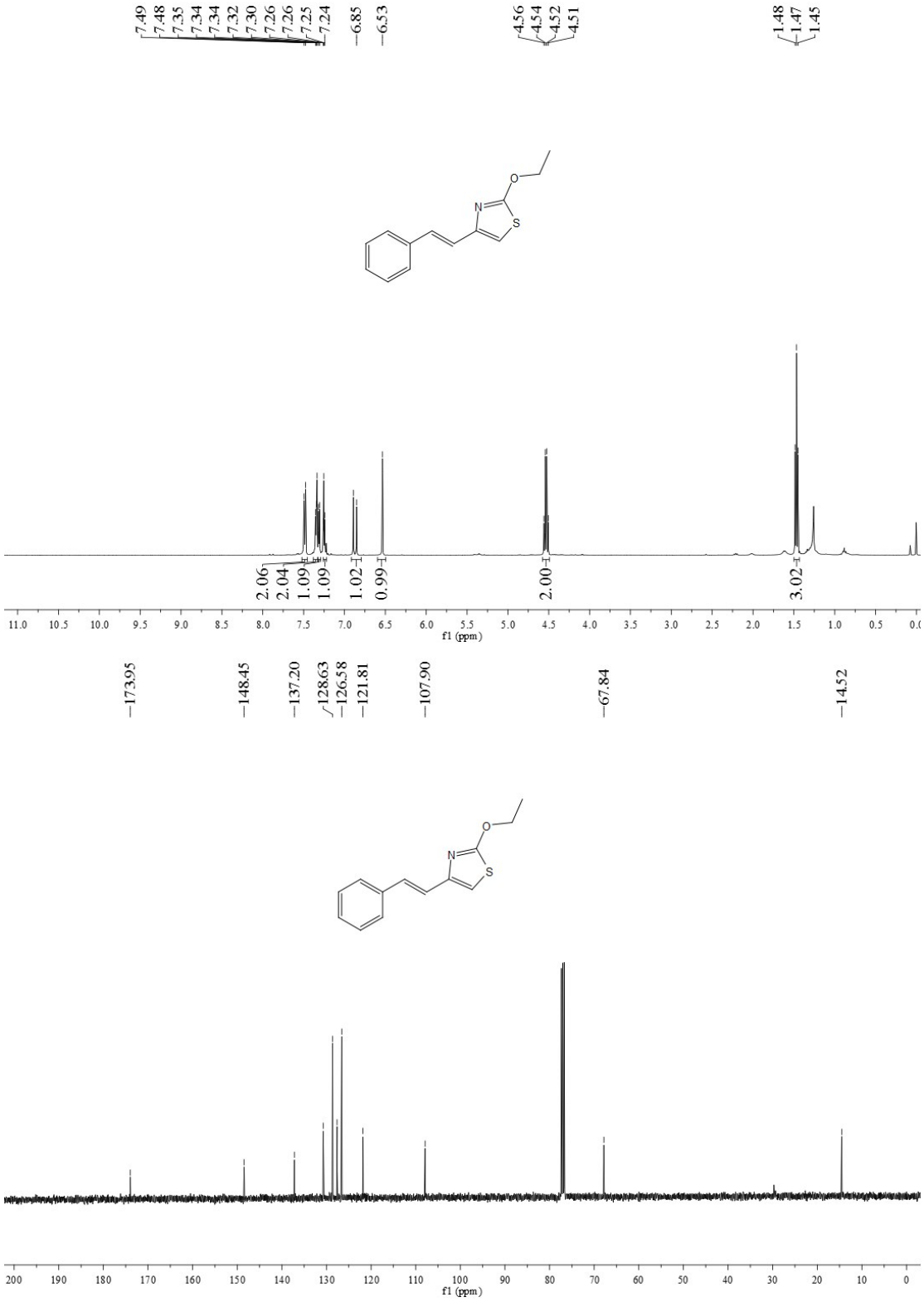




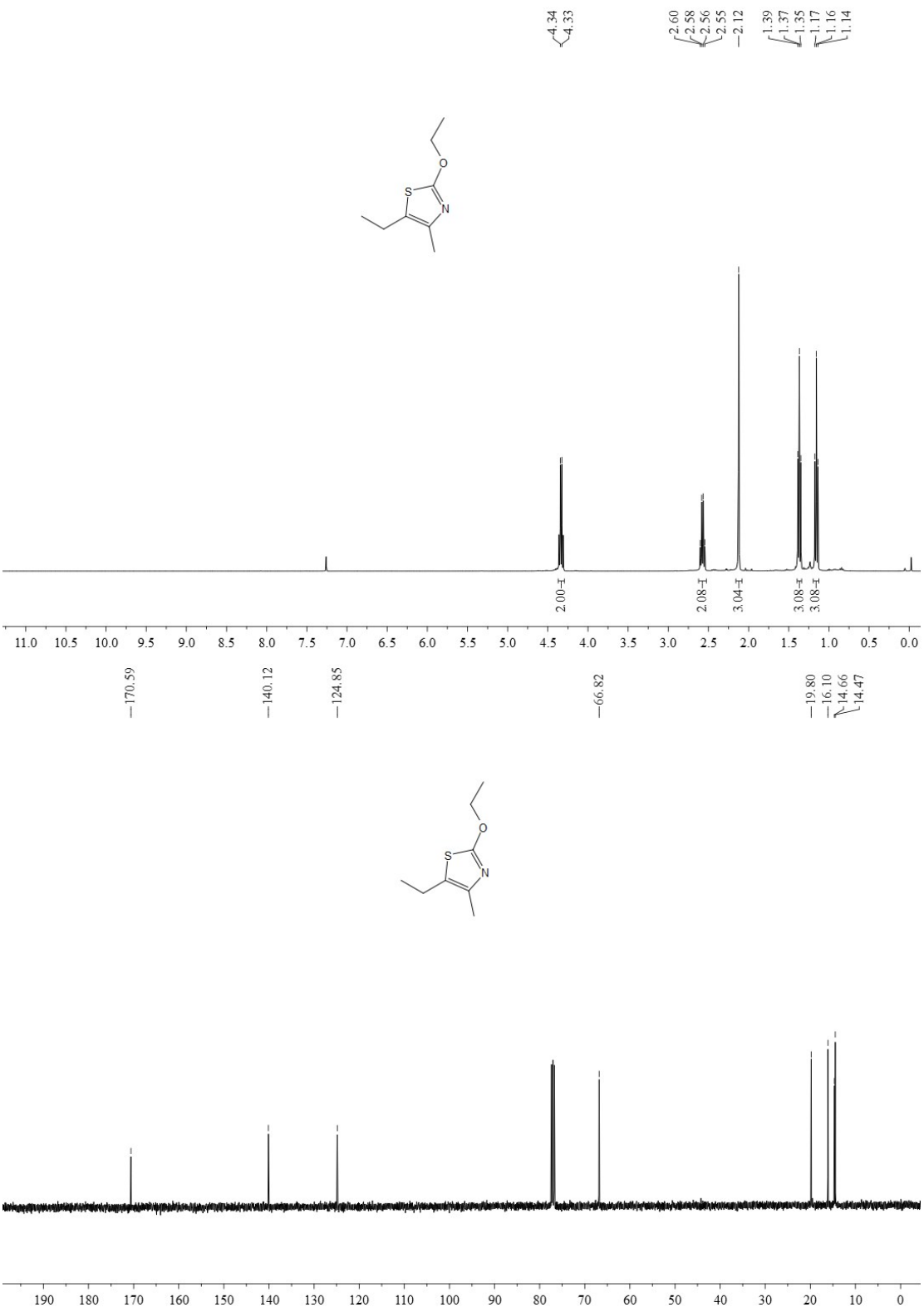
^{1}H NMR and ^{13}C NMR of 1-(3,4-dihydroquinolin-1(2*H*)-yl)-*N*-phenylethan-1-imine (3bh)



^{1}H NMR and ^{13}C NMR of (*E*)-2-ethoxy-4-styrylthiazole (3bi)

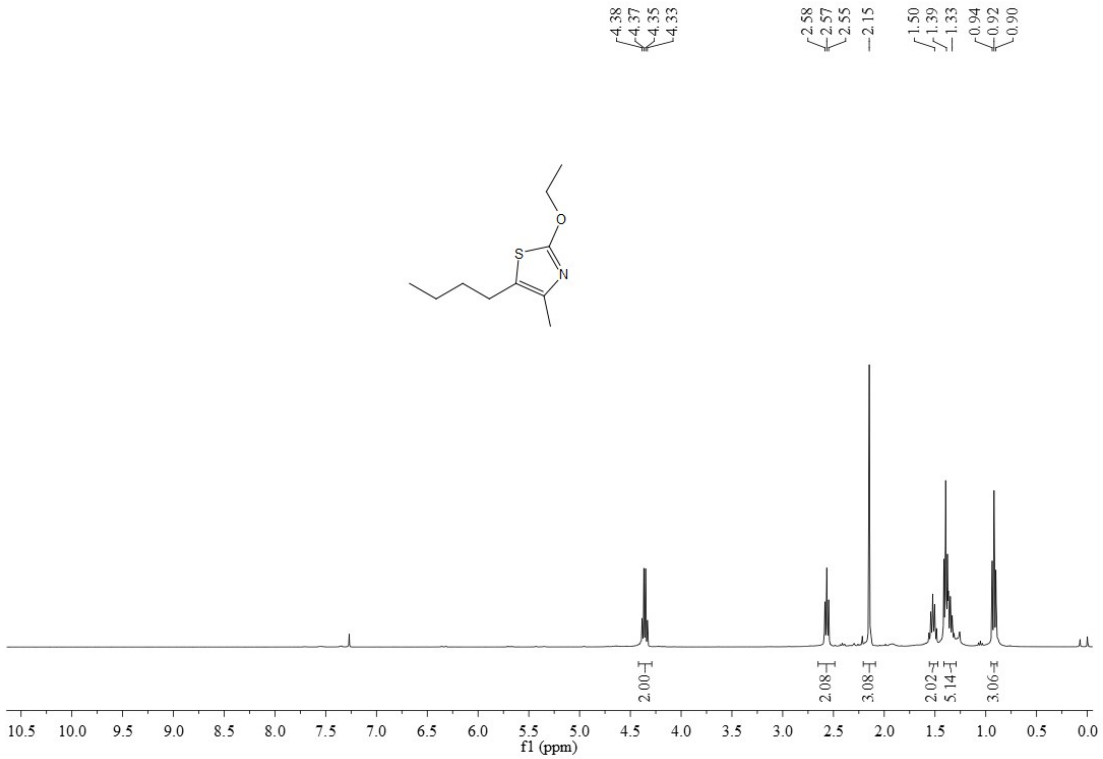


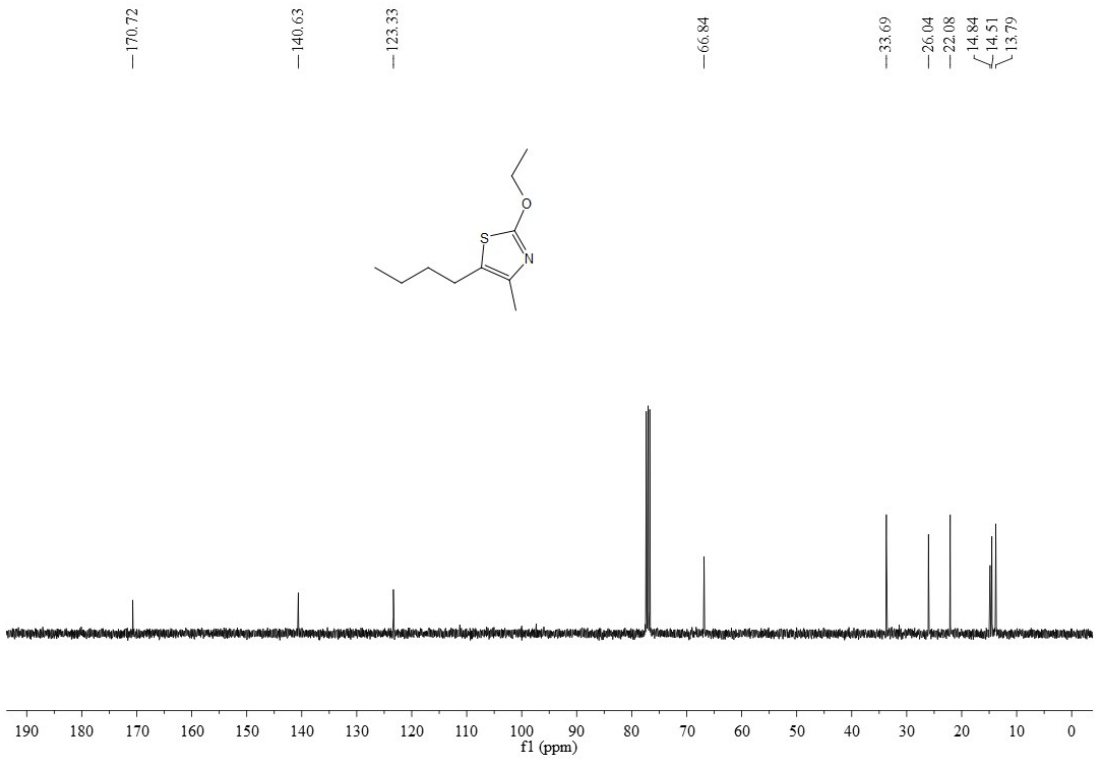
^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-ethyl-5-methylthiazole (3bj)



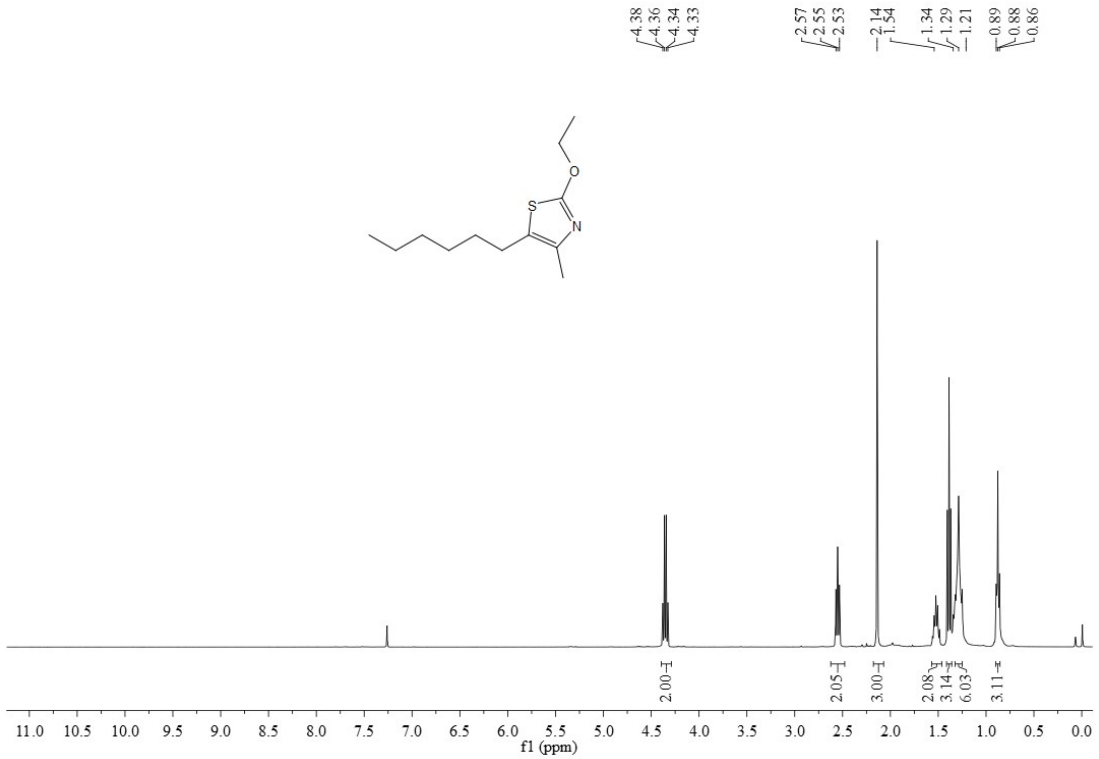
^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-isopropyl-5-methylthiazole (3bk)

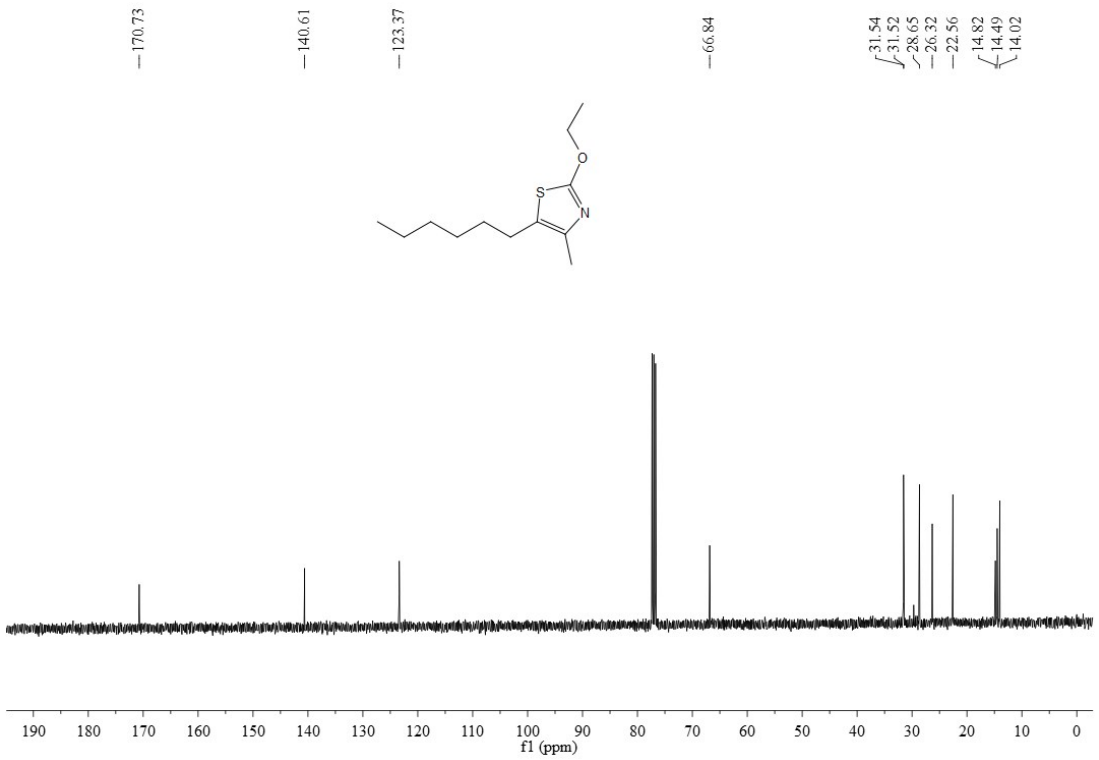
^{1}H NMR and ^{13}C NMR of 4-butyl-2-ethoxy-5-methylthiazole (3bl)



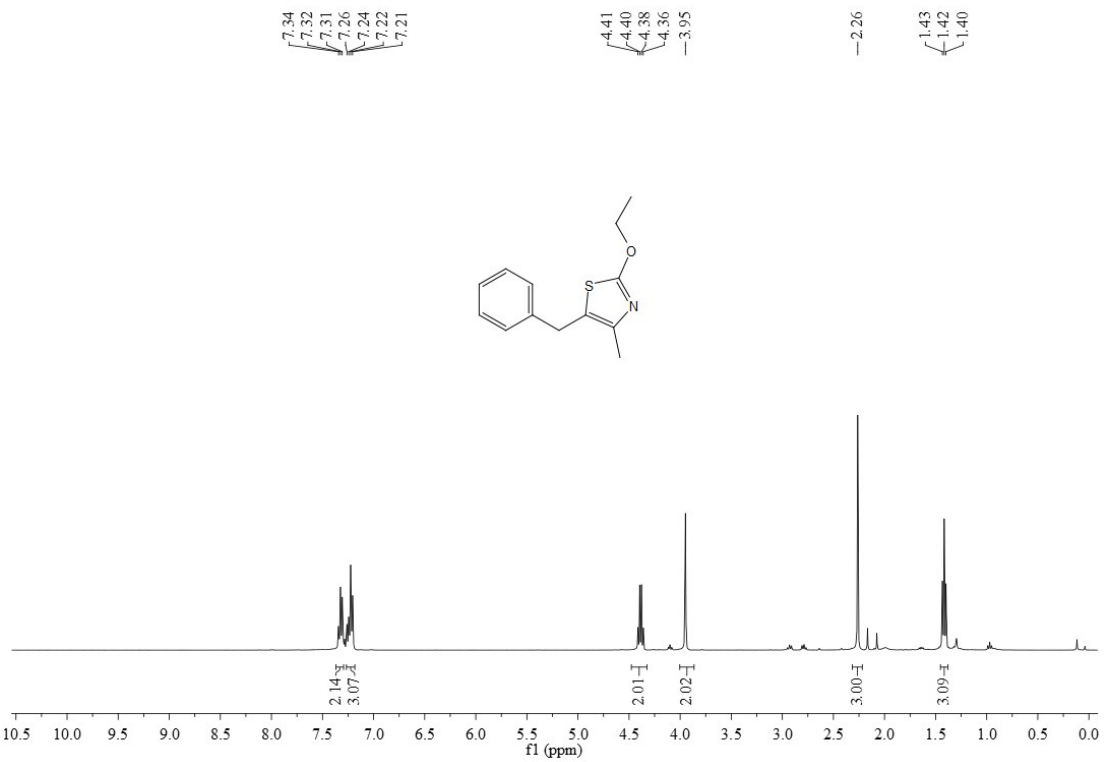


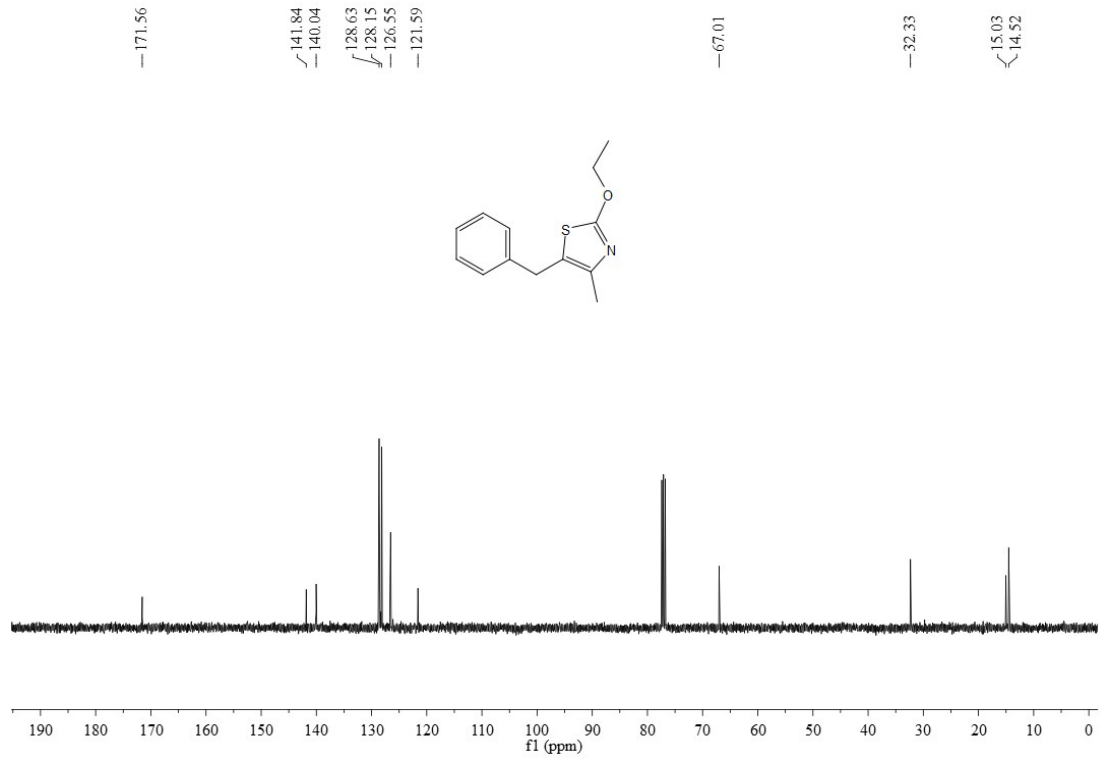
^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-hexyl-5-methylthiazole (3bm)



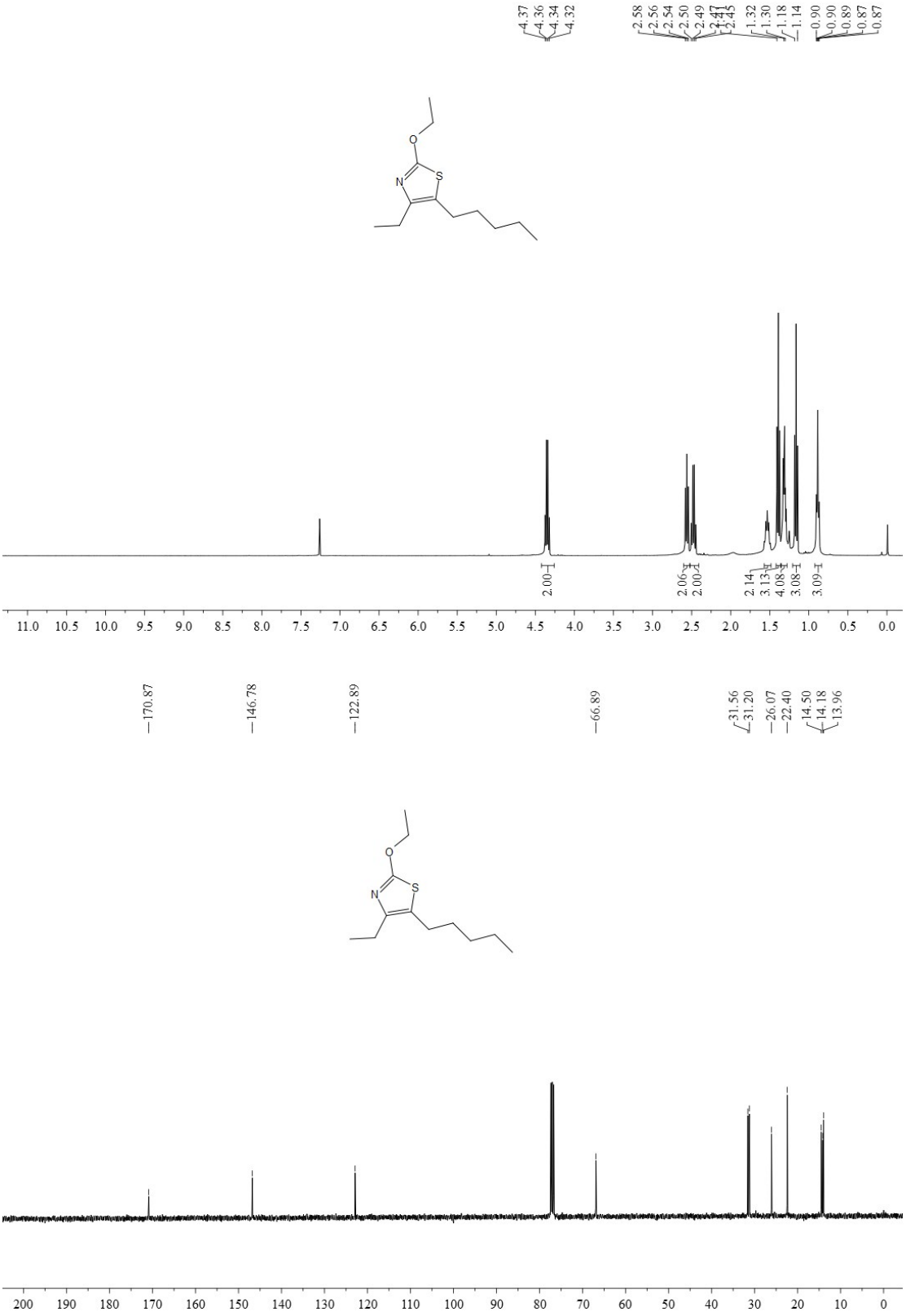


^{1}H NMR and ^{13}C NMR of 4-benzyl-2-ethoxy-5-methylthiazole (3bn)

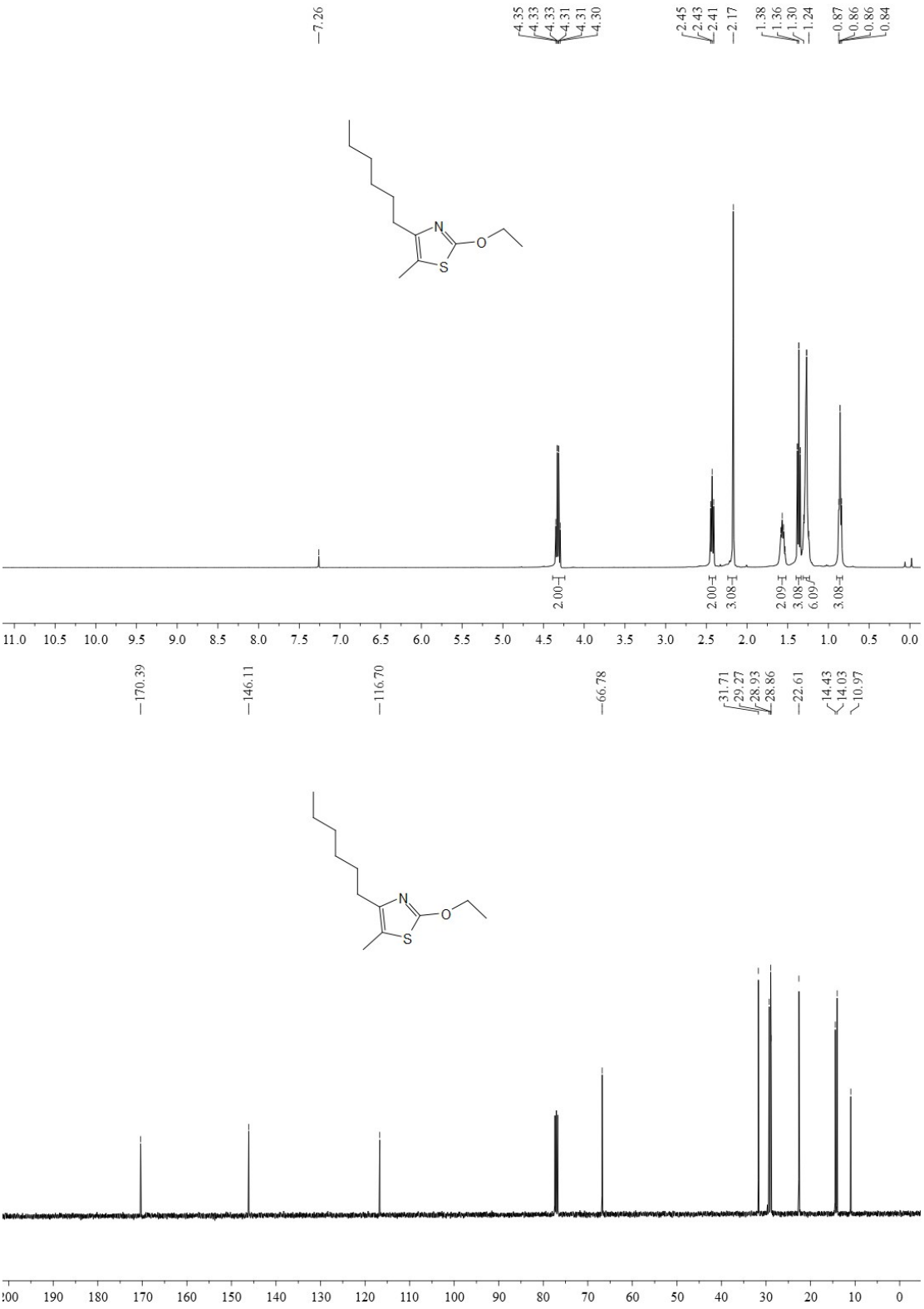




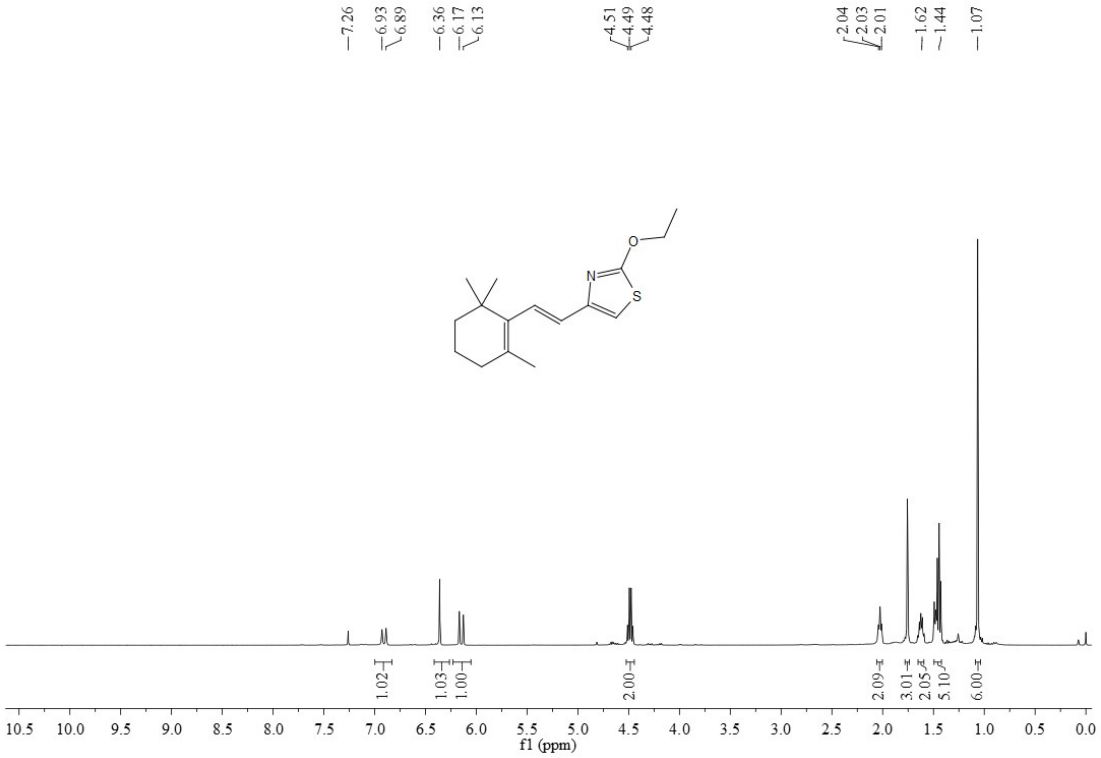
^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-ethyl-5-pentylthiazole (3bo)

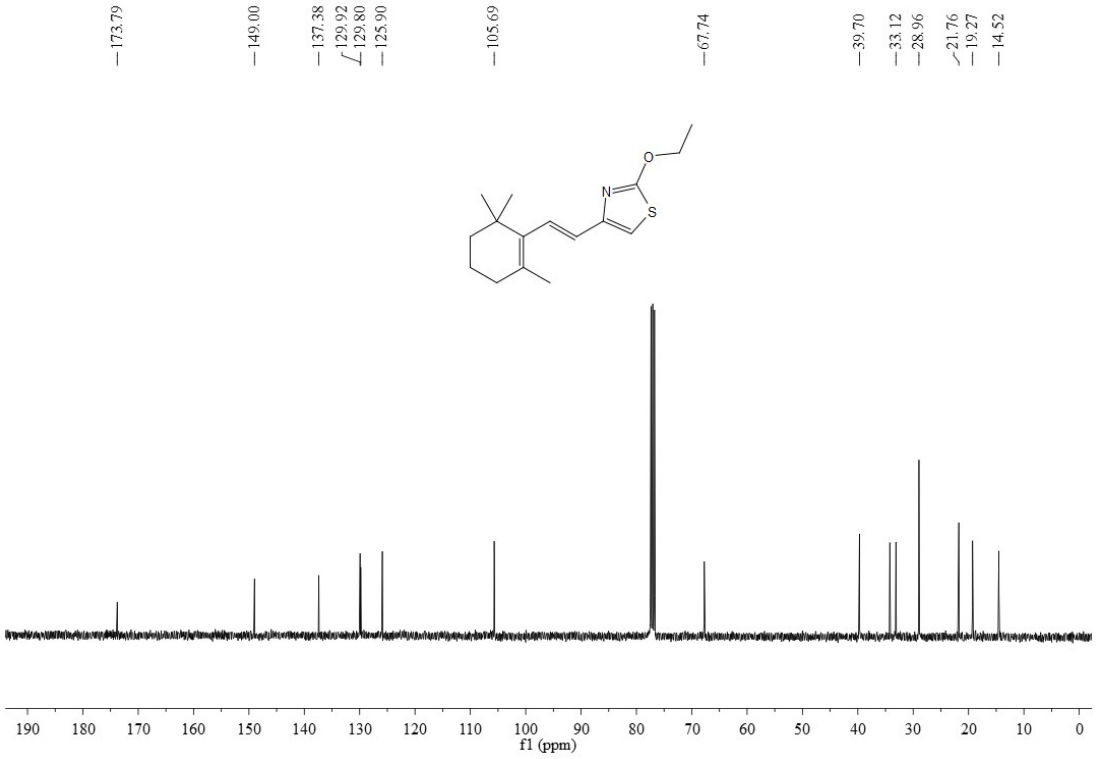


^{1}H NMR and ^{13}C NMR of hyl-1-(*o*-tolyl)-1*H*-benzo[*d*]imidazole (3bo')

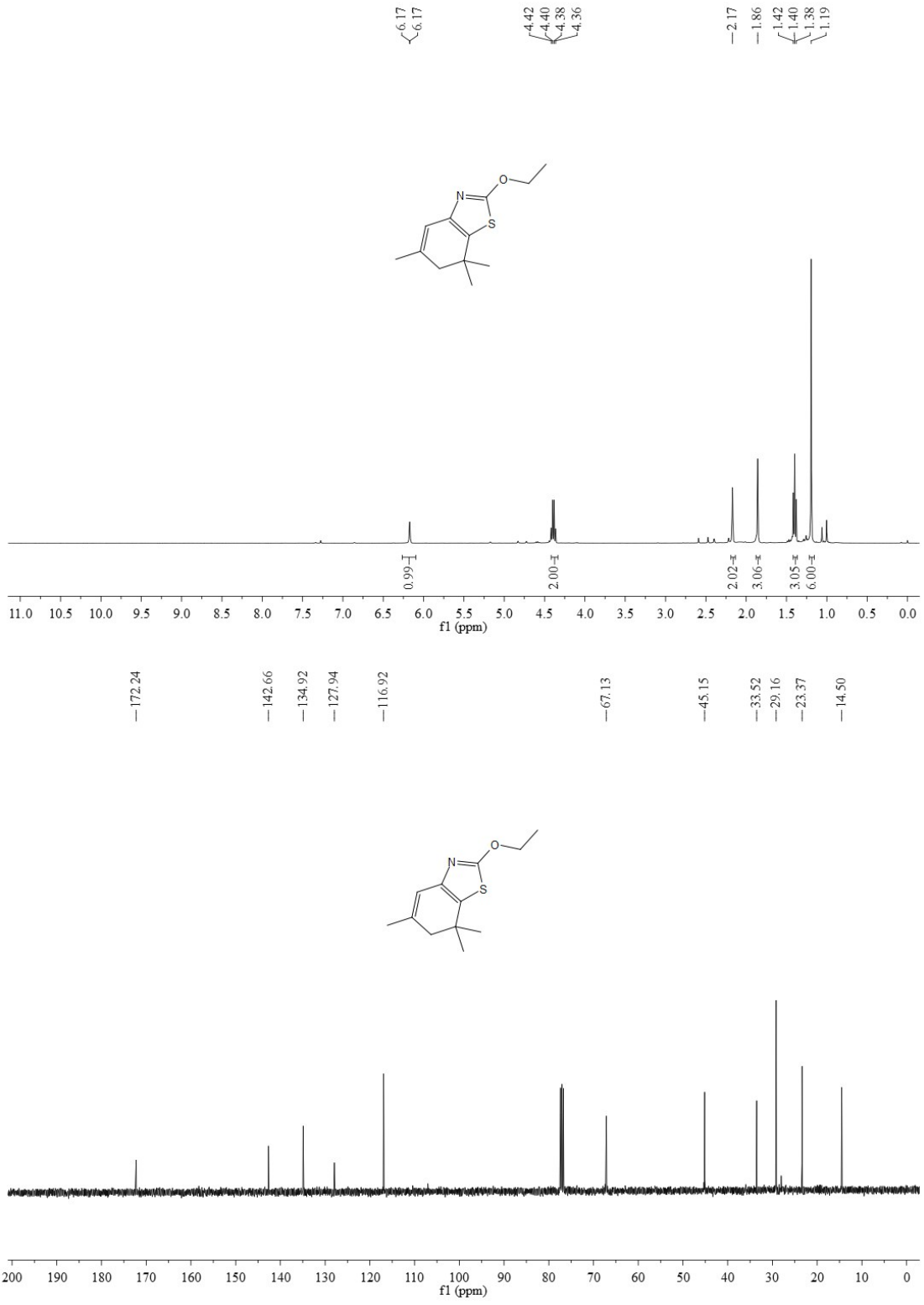


^{1}H NMR and ^{13}C NMR of (*E*)-2-ethoxy-4-(2-(2,6,6-trimethylcyclohex-1-en-1-yl)vinyl)thiazole (3bp)

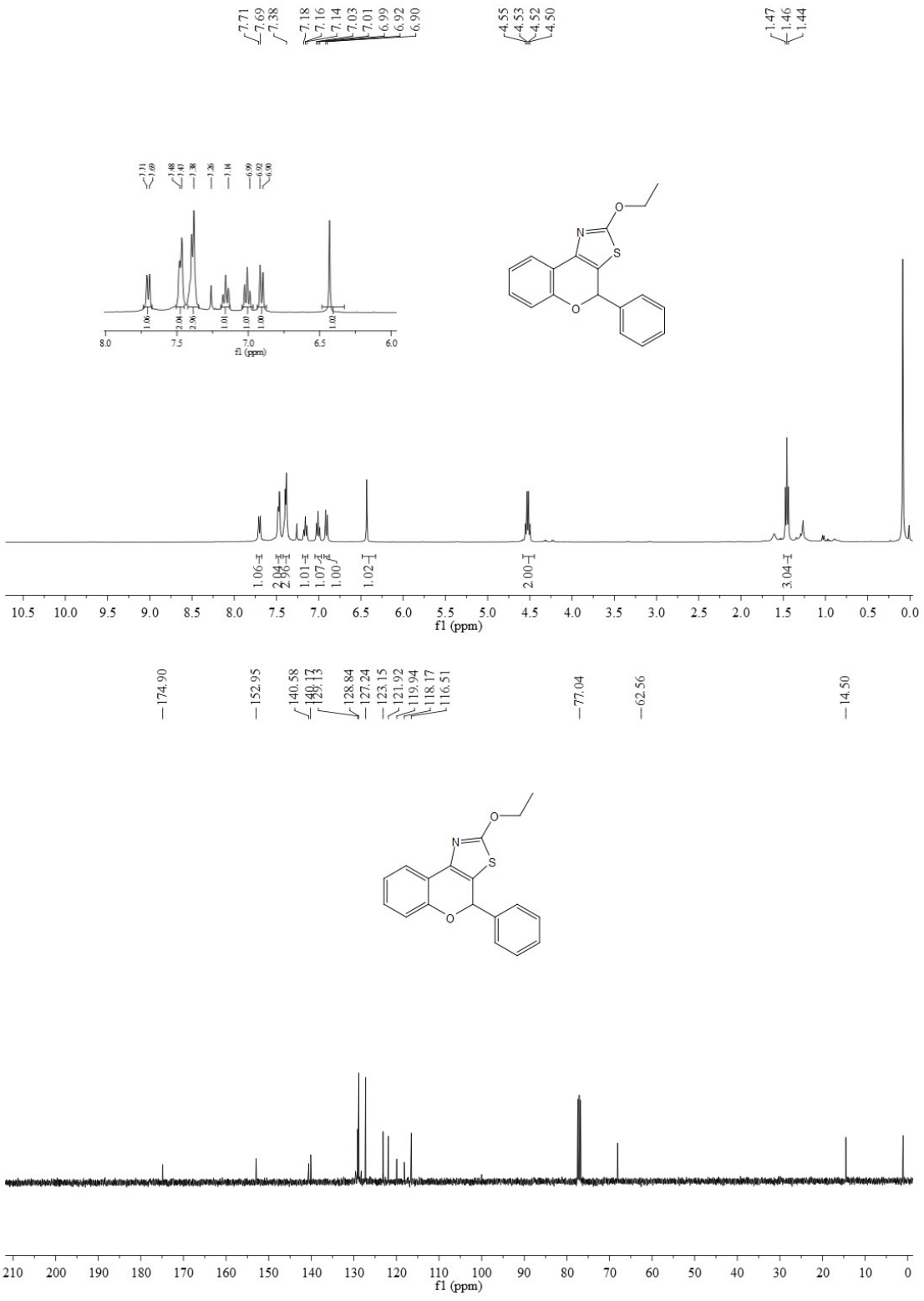




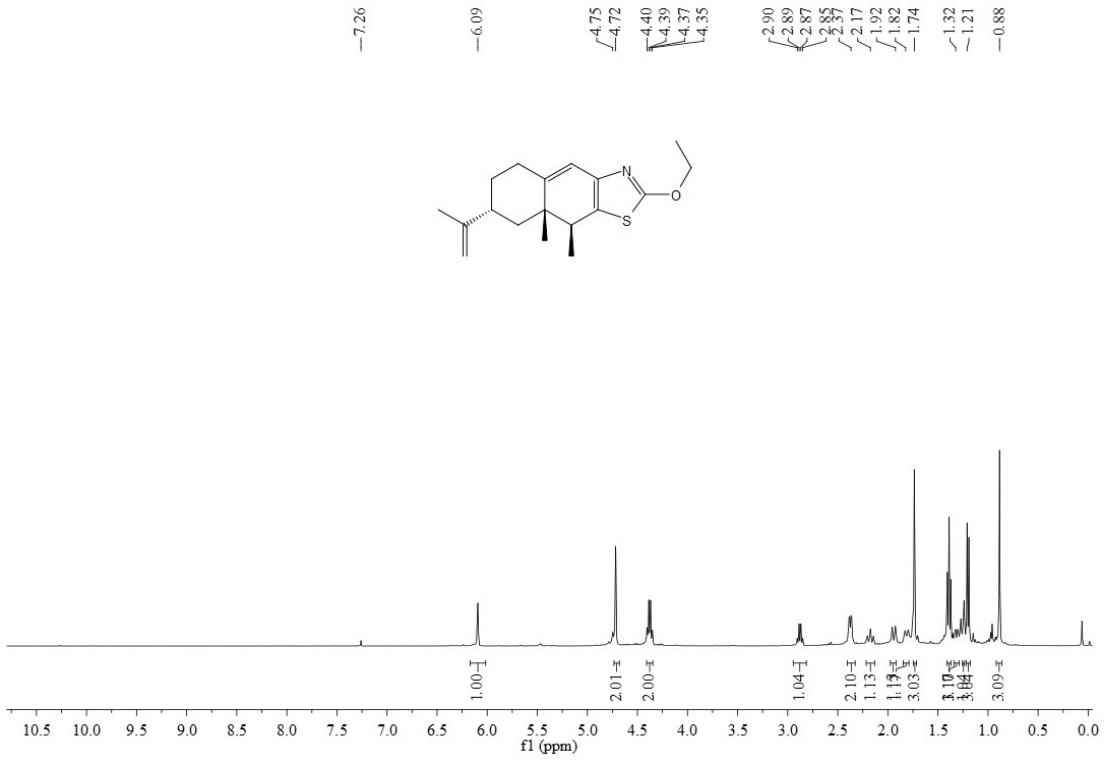
^{1}H NMR and ^{13}C NMR of 2-ethoxy-5,7,7-trimethyl-6,7-dihydrobenzo[*d*]thiazole (3bq)

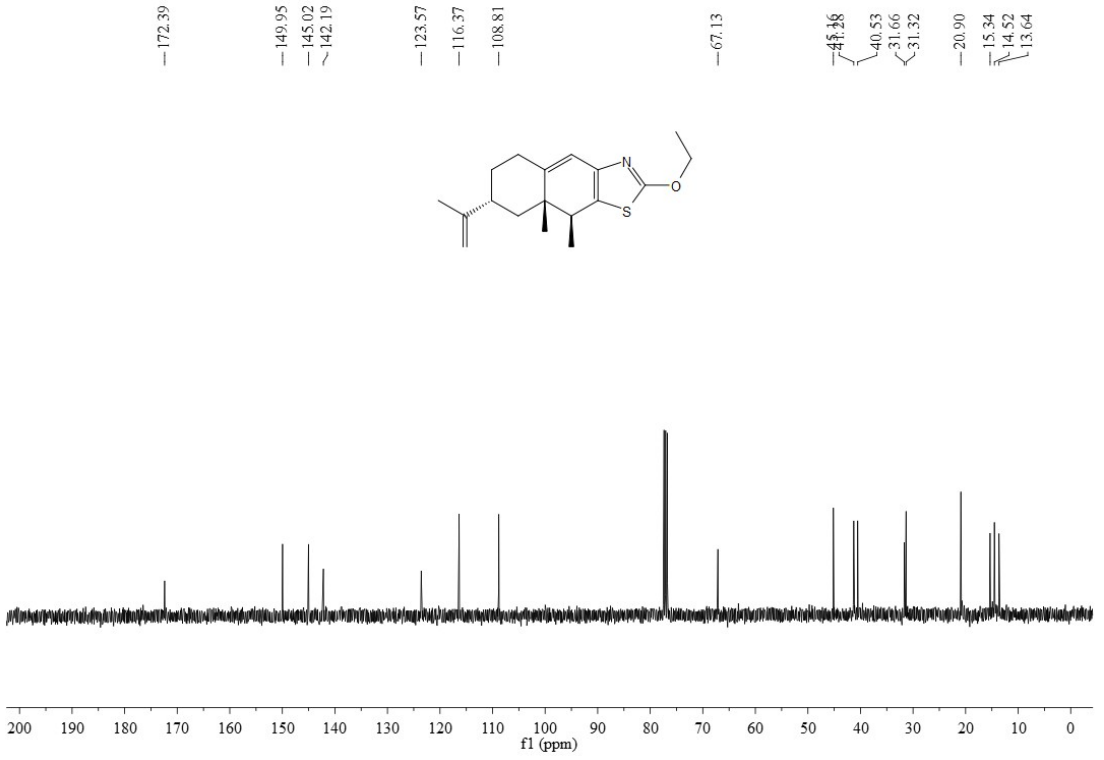


^{1}H NMR and ^{13}C NMR of 2-ethoxy-4-phenyl-4*H*-chromeno[4,3-*d*]thiazole (3br)

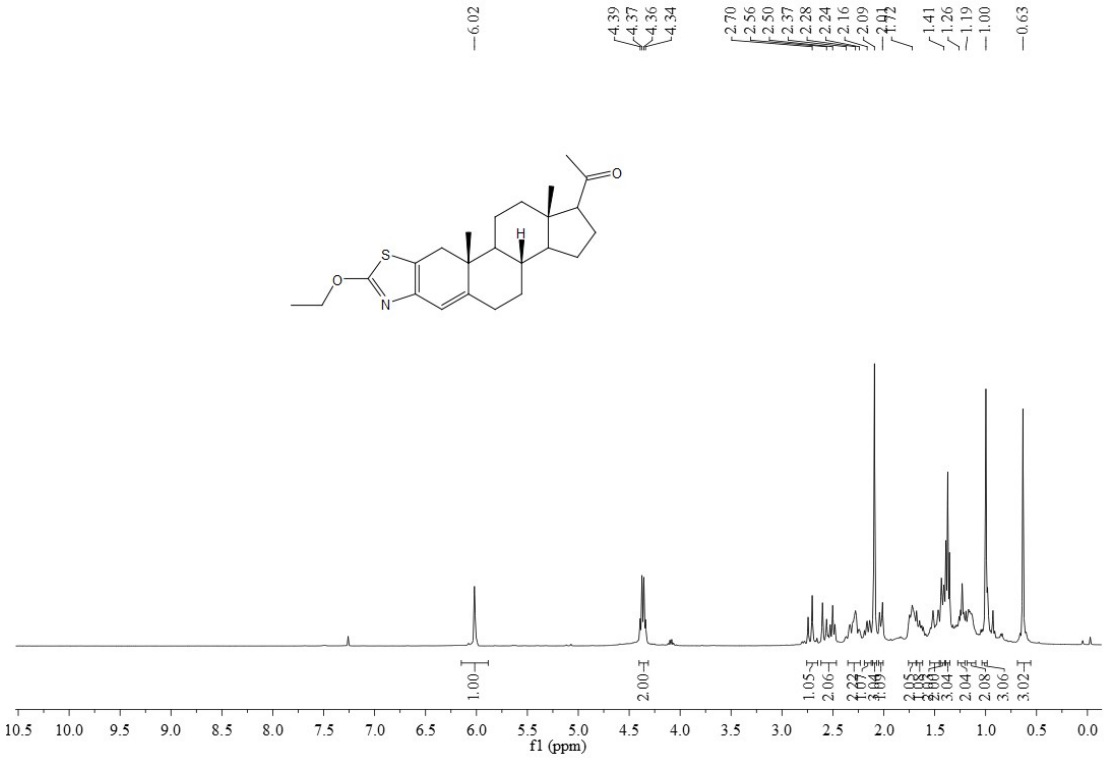


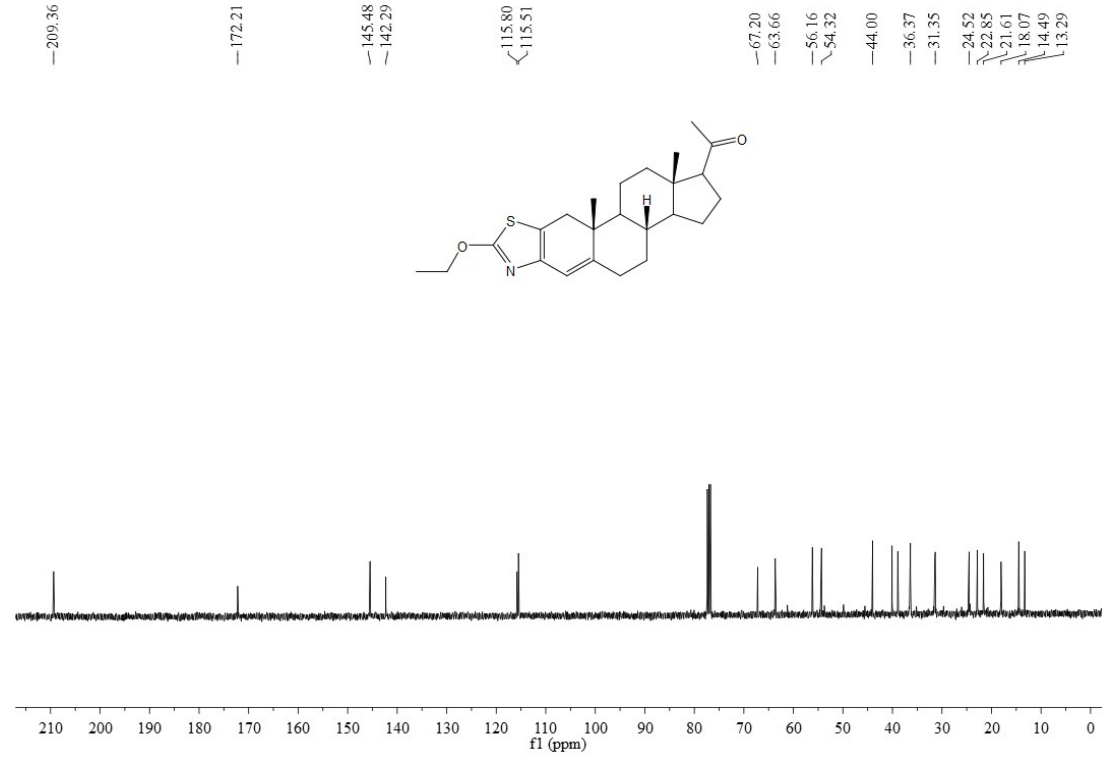
^{1}H NMR and ^{13}C NMR of (7*R*,8a*S*,9*S*)-2-ethoxy-8a,9-dimethyl-7-(prop-1-en-2-yl)-5,6,7,8,8a,9-hexahydronaphtho[2,3-*d*]thiazole (3bs)



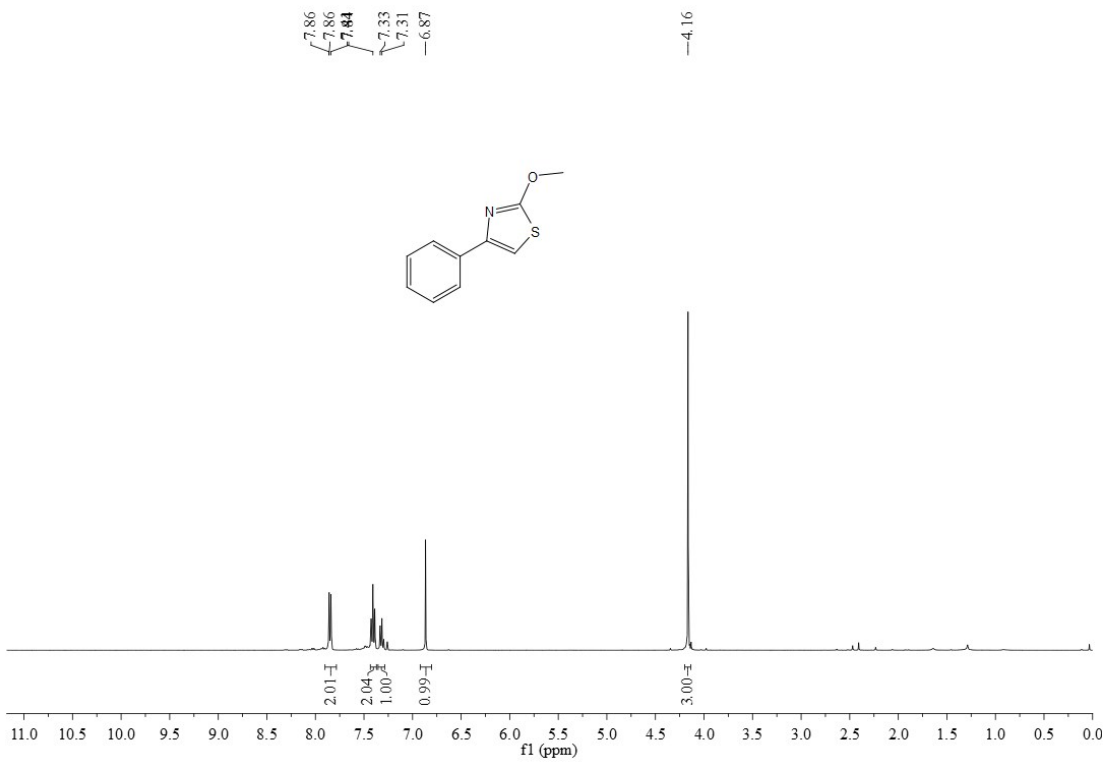


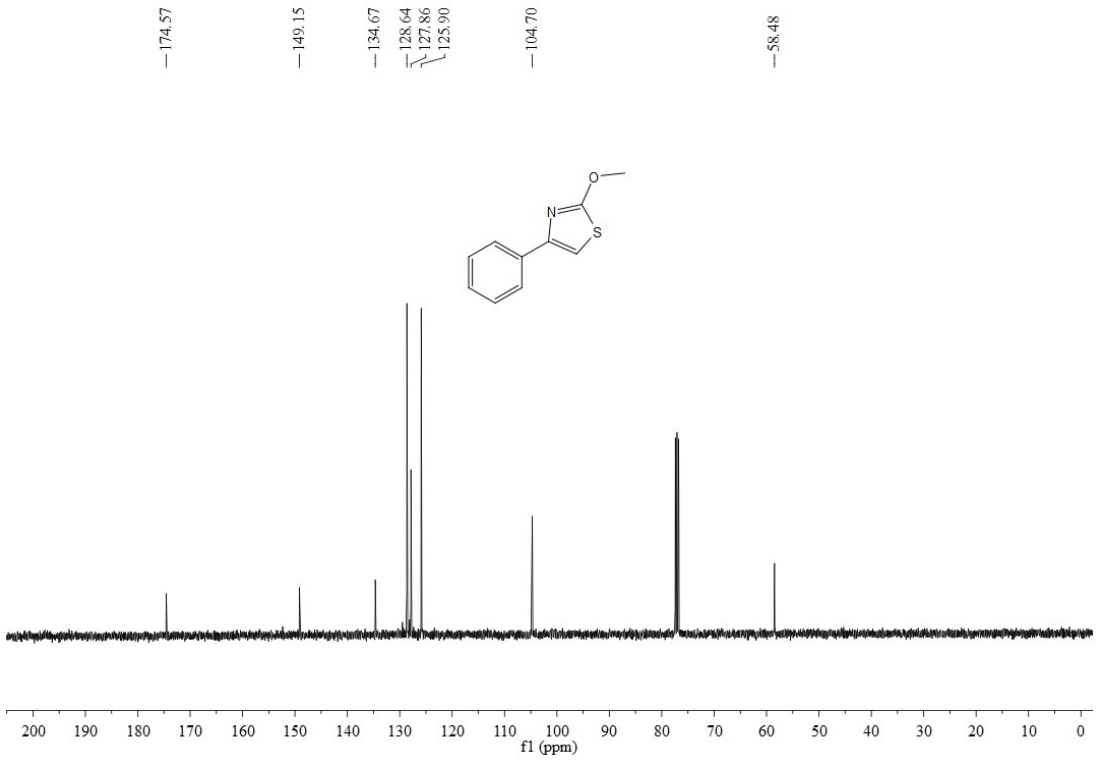
^{1}H NMR and ^{13}C NMR of 1-((3b*S*,10a*R*,12a*S*)-8-ethoxy-10a,12a-dimethyl-2,3,3a,3b,4,5,10,10a ,10b,11,12,12a-dodecahydro-1H-cyclopenta[7,8]phenanthro[2,3-*d*]thiazol-1-yl)ethan-1-one (3bt)



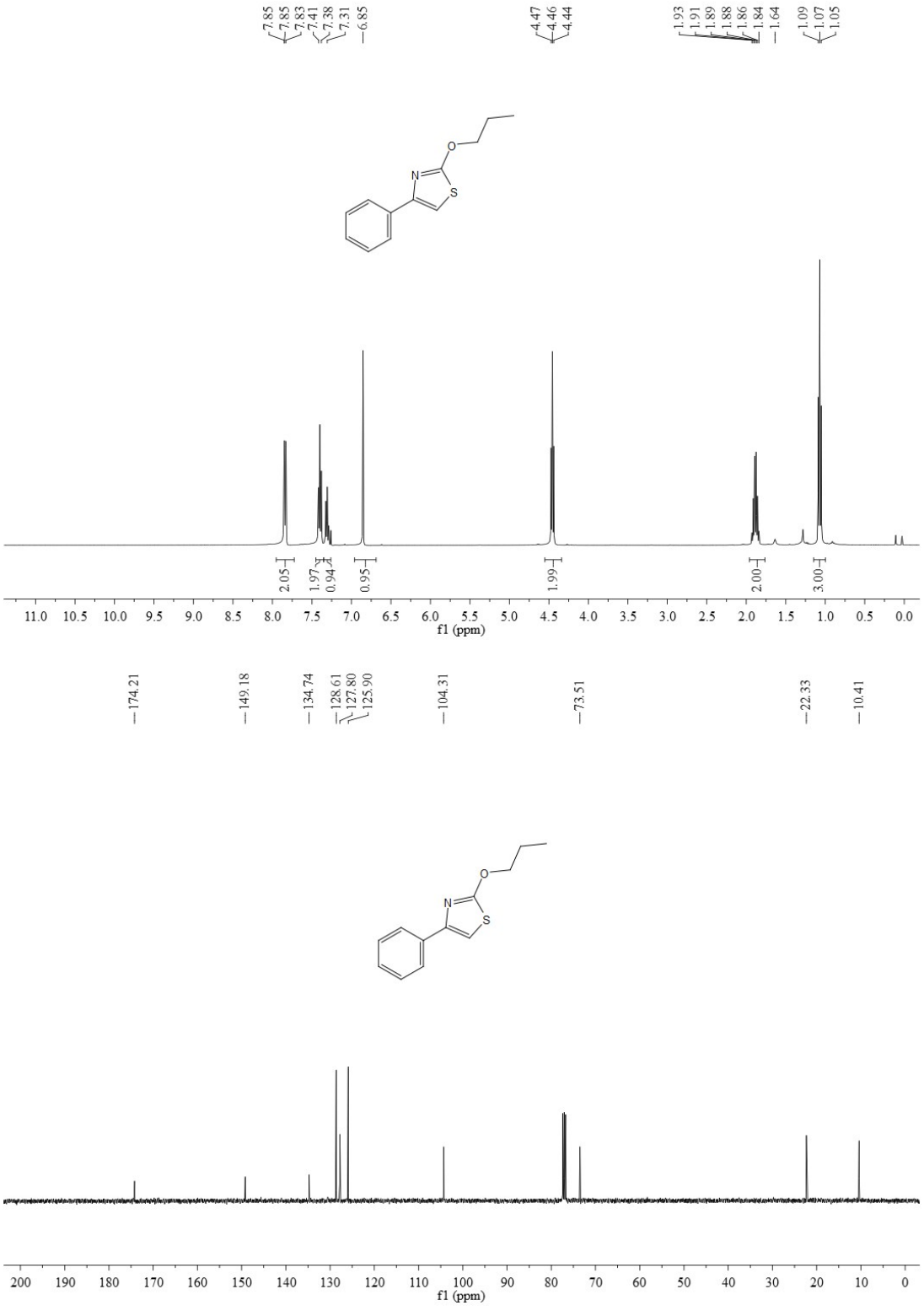


^{1}H NMR and ^{13}C NMR of 2-methoxy-4-phenylthiazole (3bu)

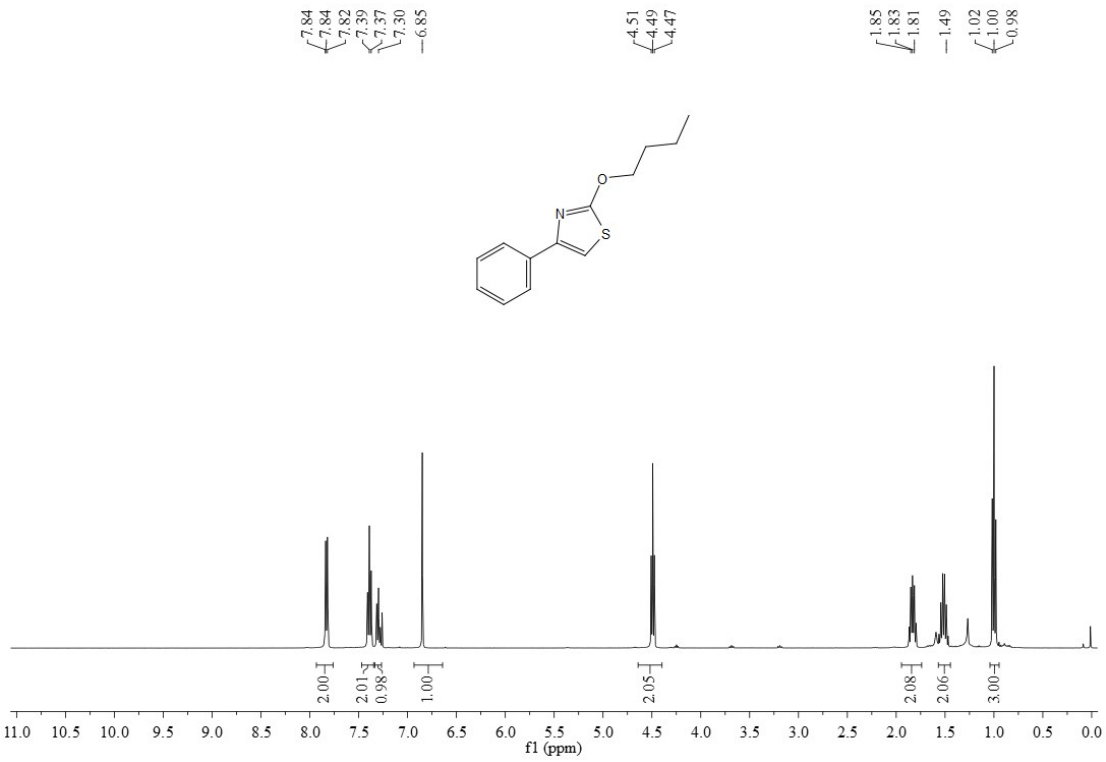


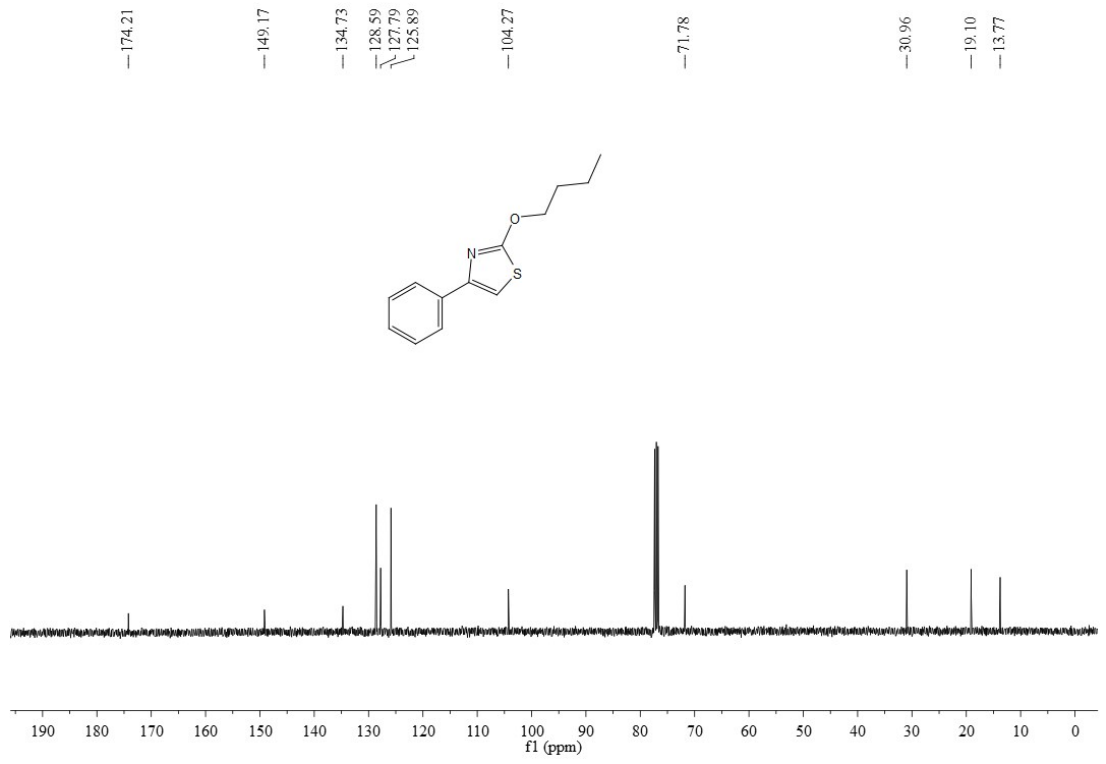


^{1}H NMR and ^{13}C NMR of 4-phenyl-2-propoxythiazole (3bv)

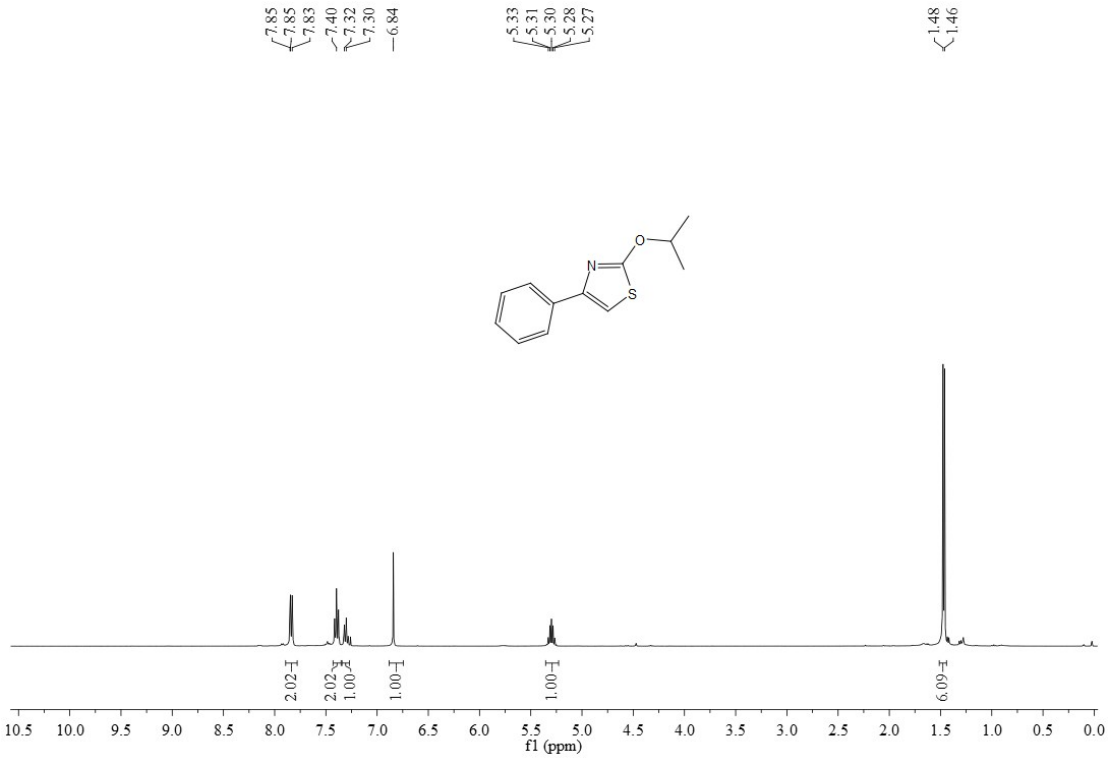


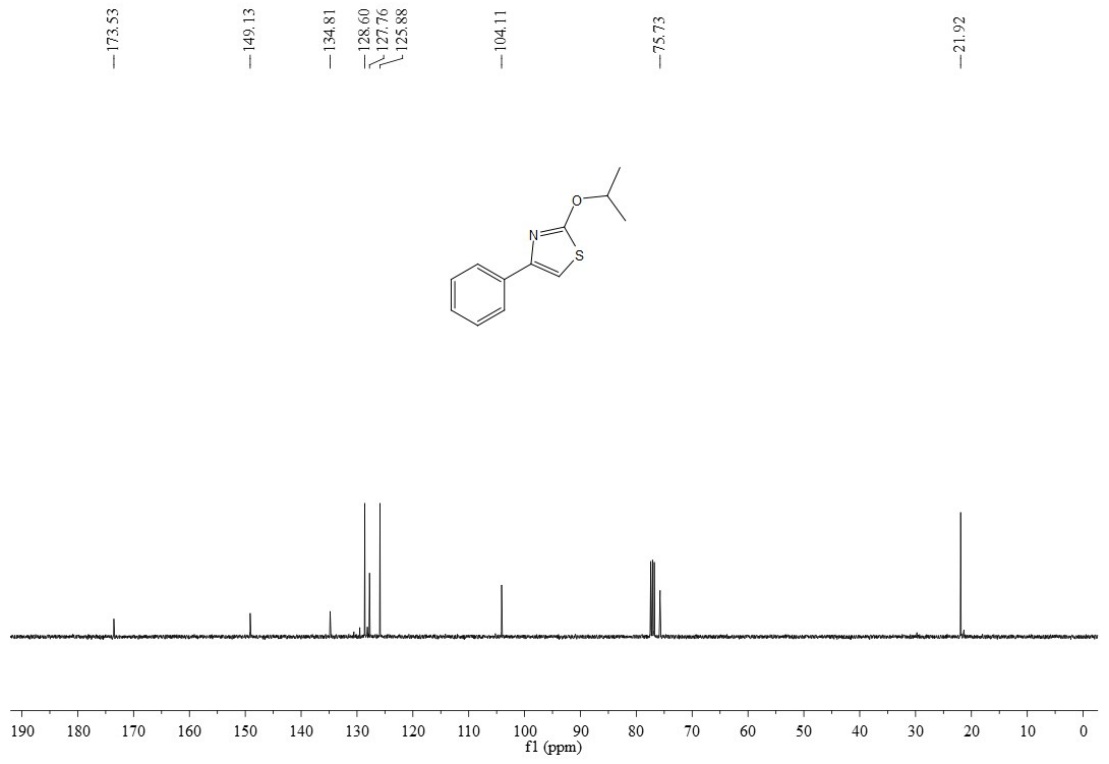
^{1}H NMR and ^{13}C NMR of 2-butoxy-4-phenylthiazole (3bw)



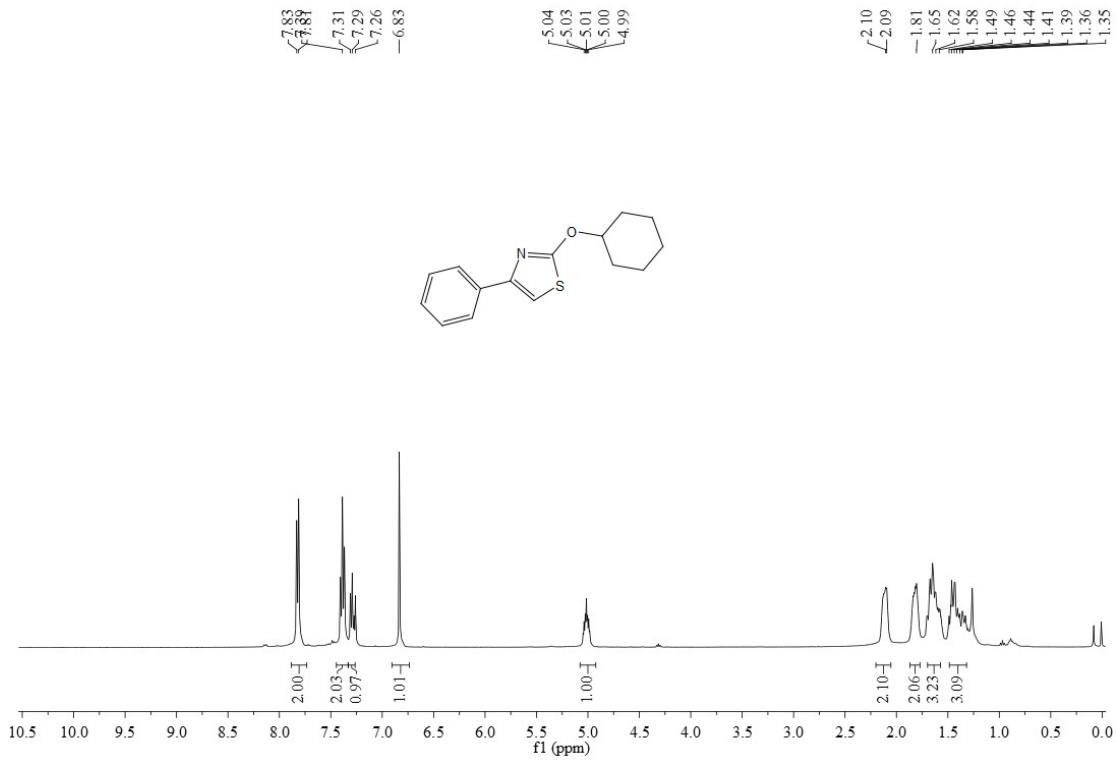


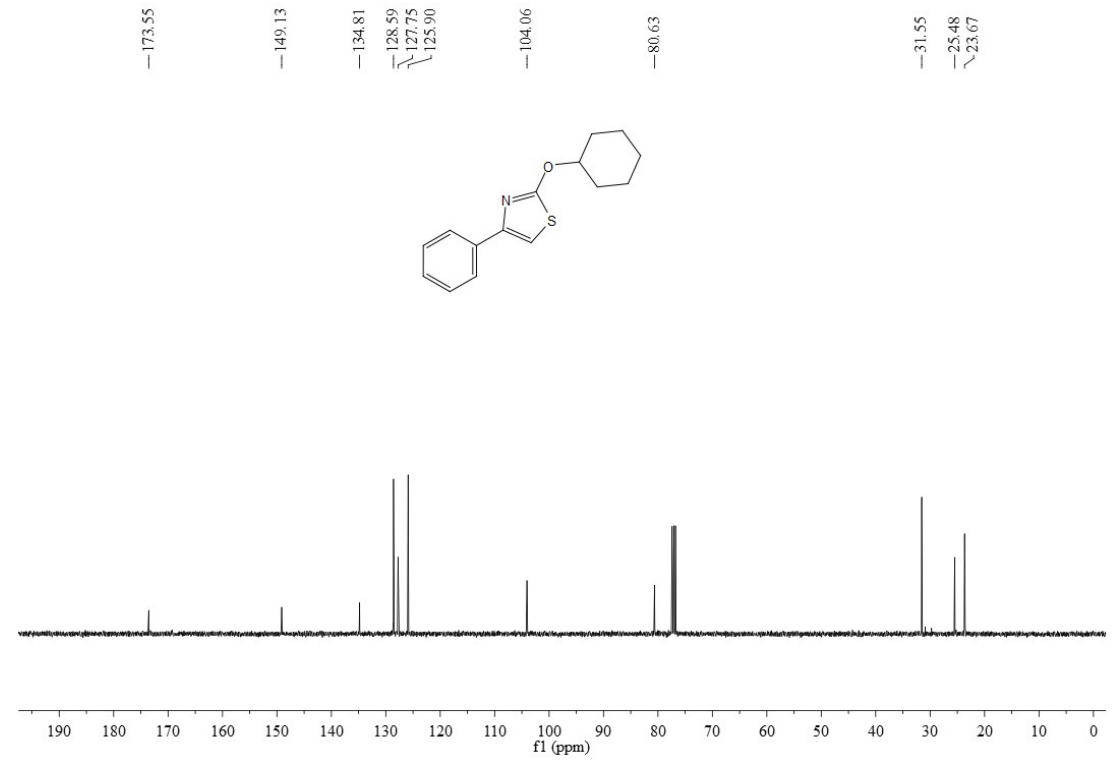
^{1}H NMR and ^{13}C NMR of 2-isopropoxy-4-phenylthiazole (3bx)



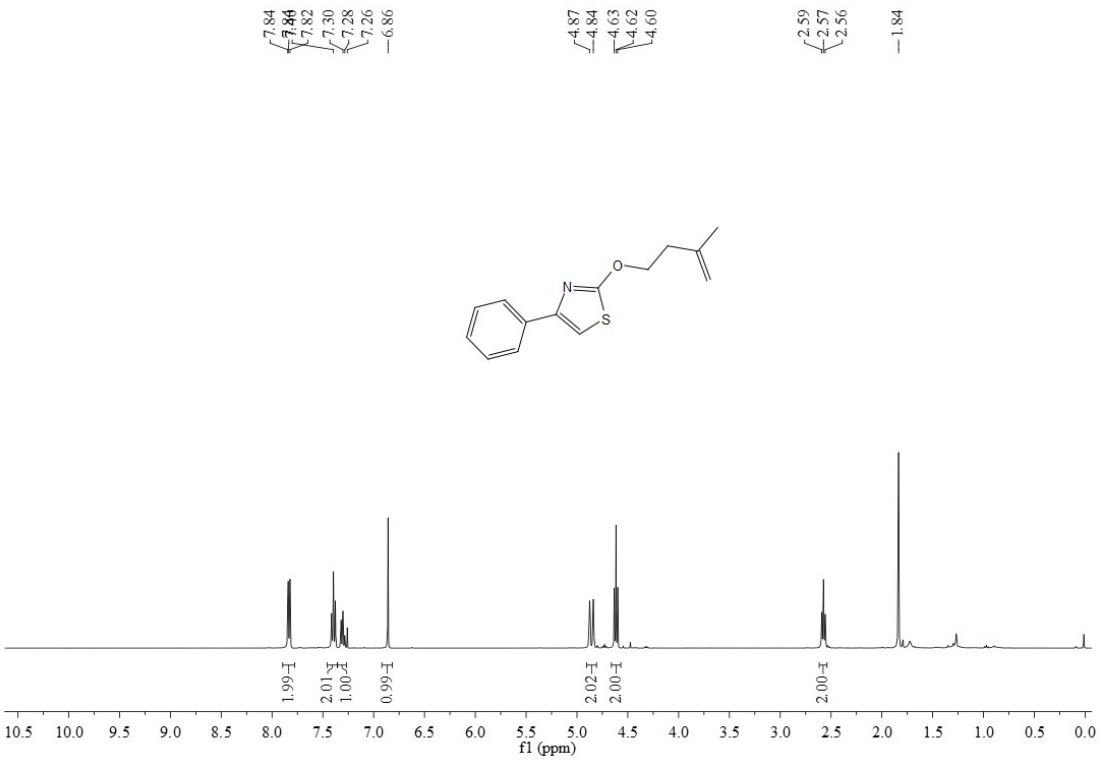


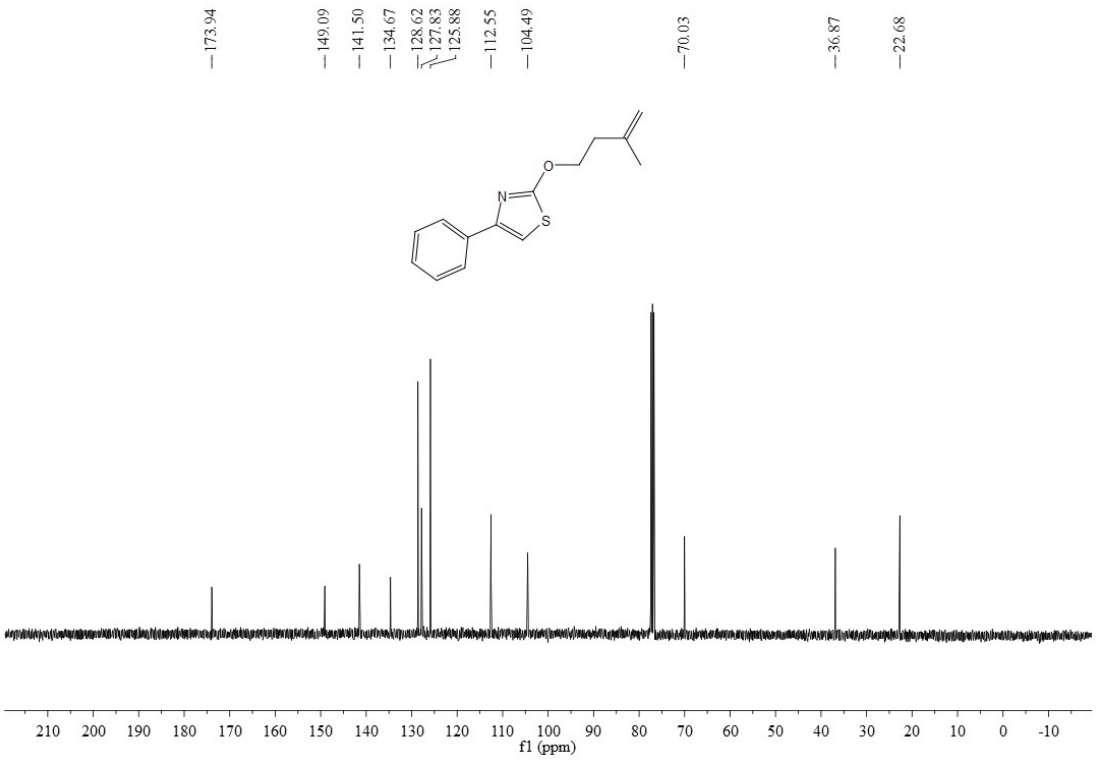
^{1}H NMR and ^{13}C NMR of 2-(cyclohexyloxy)-4-phenylthiazole (3by)



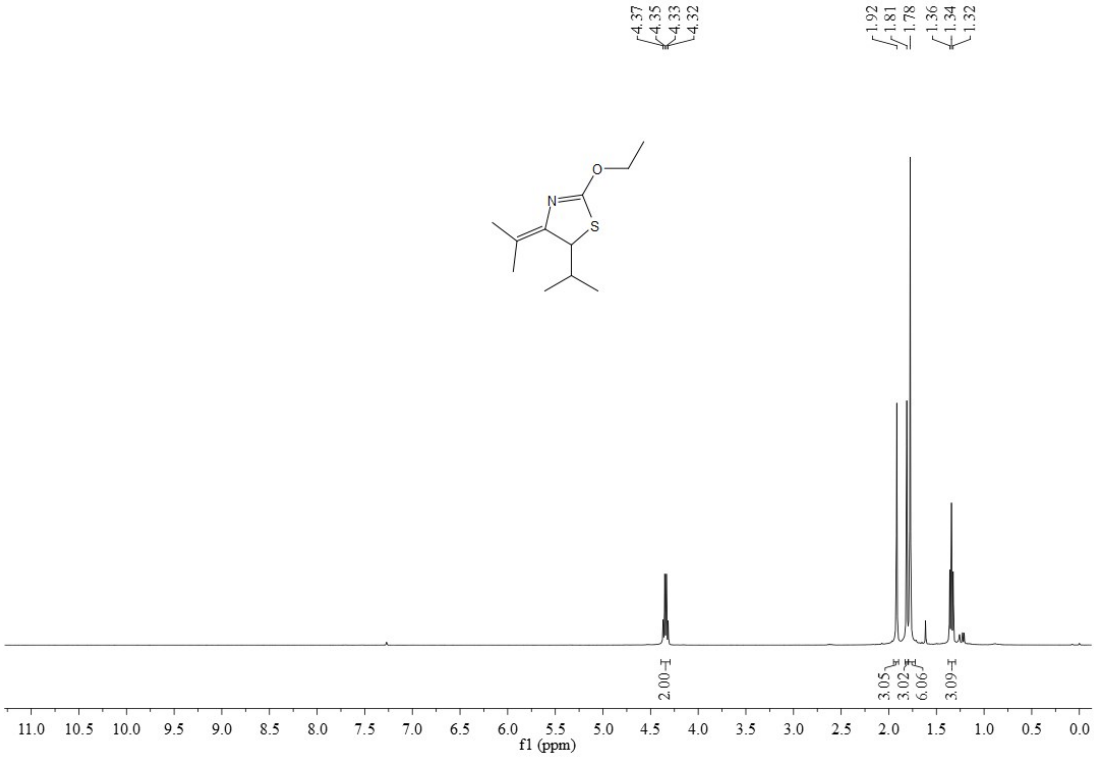


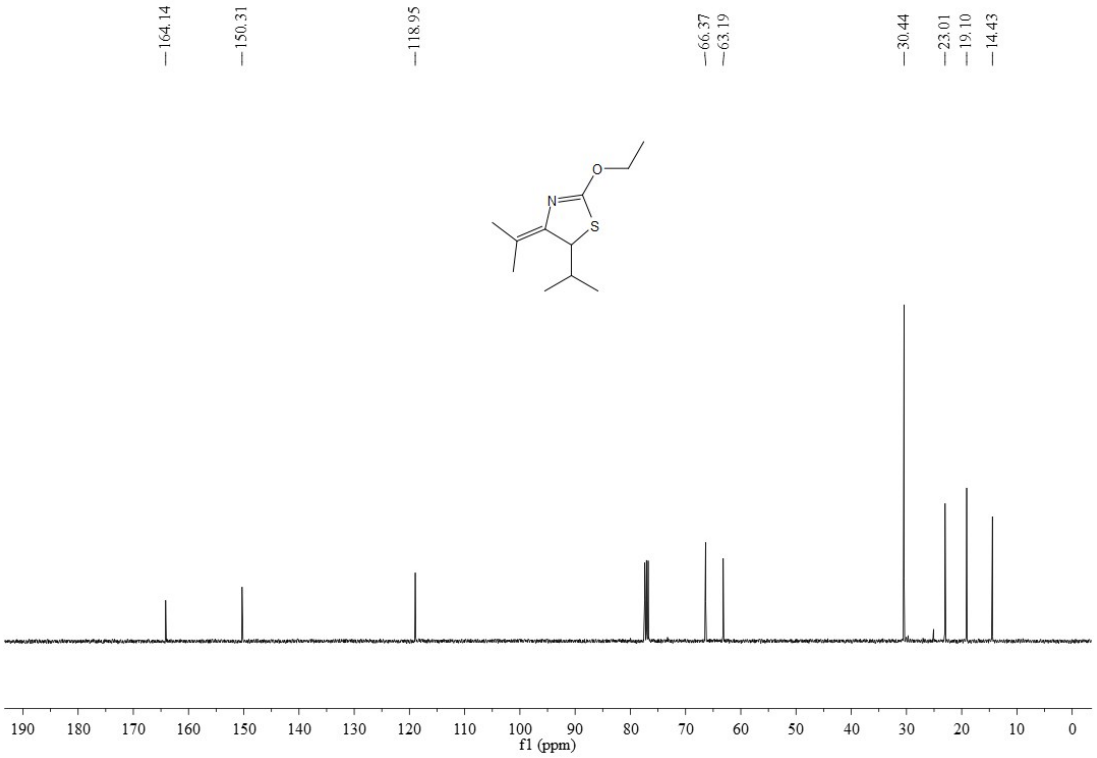
^{1}H NMR and ^{13}C NMR of 2-((3-methylbut-3-en-1-yl)oxy)-4-phenylthiazole (3bz)



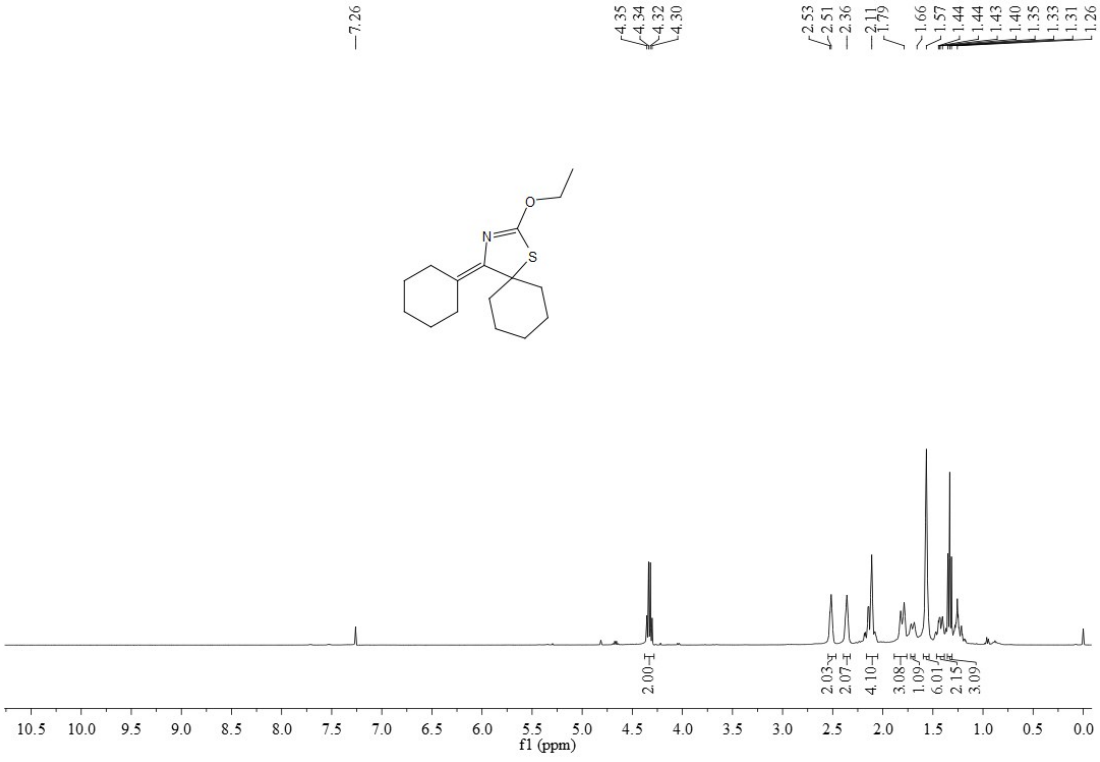


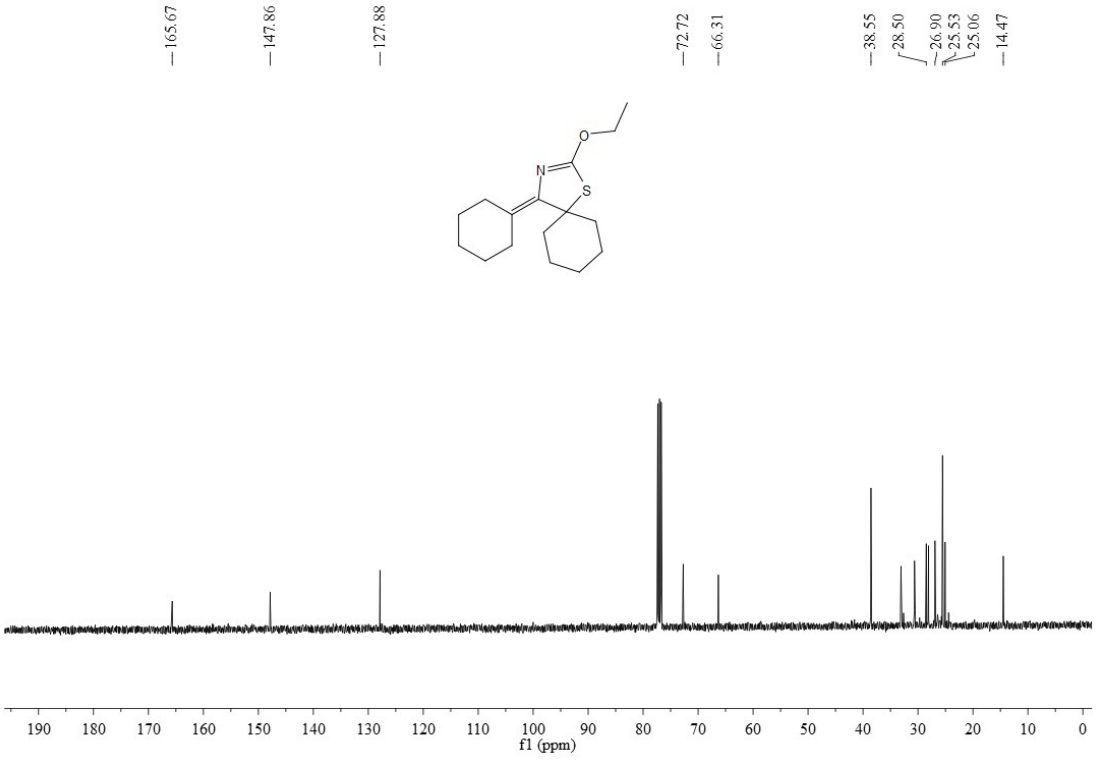
^{1}H NMR and ^{13}C NMR of 2-ethoxy-5,5-dimethyl-4-(propan-2-ylidene)-4,5-dihydrothiazole (4a)



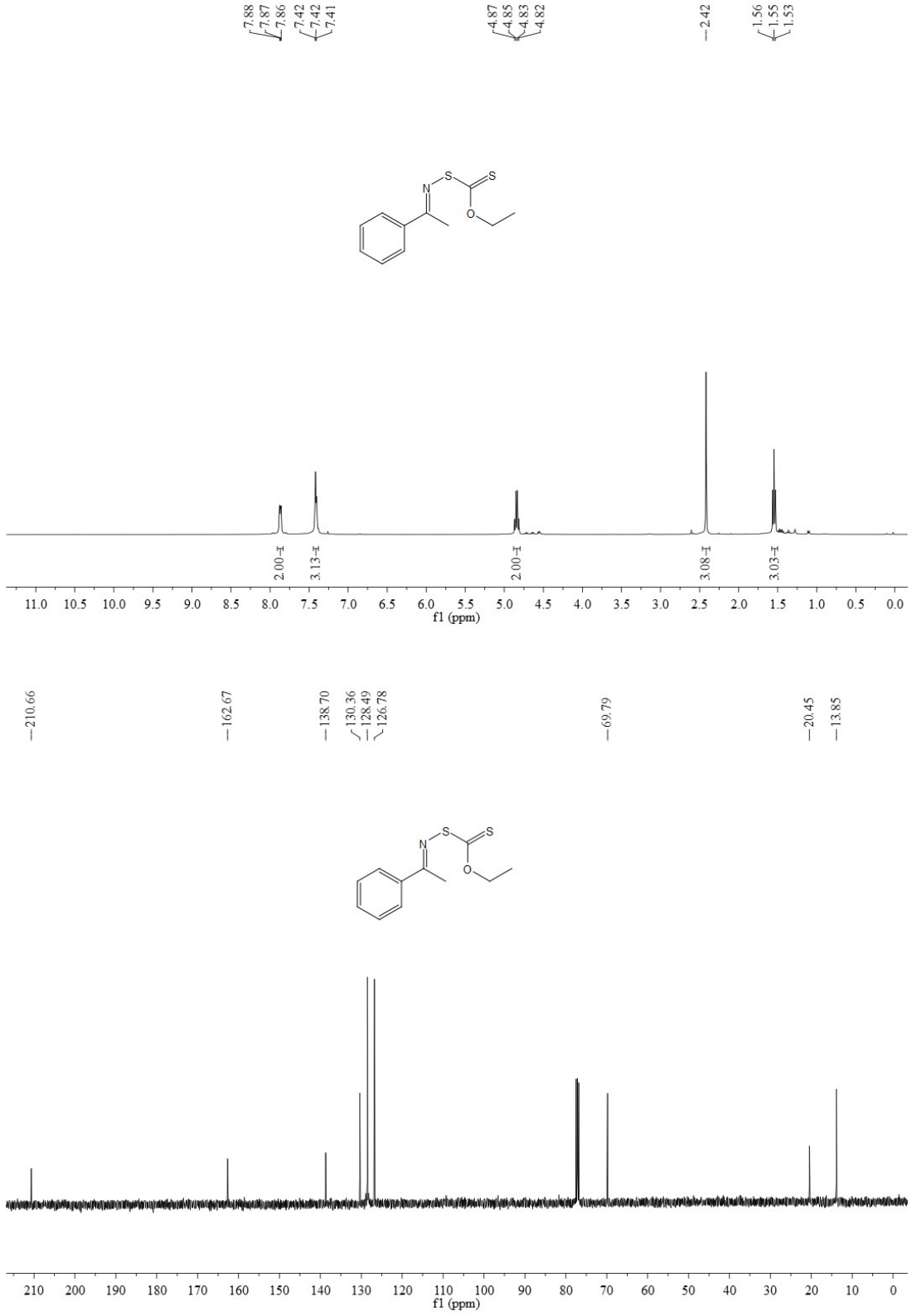


^{1}H NMR and ^{13}C NMR of 4-cyclohexylidene-2-ethoxy-1-thia-3-azaspiro[4.5]dec-2-ene (4b)





^{1}H NMR and ^{13}C NMR of (*E*)-*S*-(ethoxycarbonothioyl)-*N*- (1-phenylethylidene)thiohydroxylamine (5a)



^{1}H NMR and ^{13}C NMR of (*E*)-*S*-(ethoxycarbonothioyl)-*N*-(1,7,7-trimethylbicyclo[2.2.1] heptan-2-ylidene)thiohydroxylamine (5b)