Supplementary Information for:

Three-component Formal Metathesis via Remote Activating Strategy Enabled (RASE) Domino Activation of Two (sp^3)-O Bonds in Alkyl Ethers

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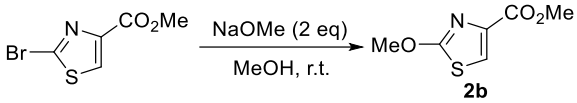
1. General Remarks

All commercially available compounds were purchased from Sigma-Aldrich, Alfa-Aesar, Acros, J&K Chemicals, Adamas-beta, Accela ChemBio and Aladdin Chemicals. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Benzyl alkyl ethers **1** and their alkyl benzene precursors **7** were prepared according to the methods reported in our recently published remote activating strategy enabled benzylic C(sp^3)-H alkoxylation.[1] Products were purified by flash chromatography on silica gel using petroleum ether, ethyl acetate and dichloromethane as the eluents. ^{1}H-NMR spectra were recorded on JNM-ECZ400S/L1 spectrometers. Chemical shifts (in ppm) were referenced with TMS in $CDCl_3$ (0 ppm). ^{13}C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with $CDCl_3$ (δ = 77.00 ppm) or DMSO-d_6 (δ = 39.50 ppm). Single-crystal X-ray diffraction intensity data of **6a** were collected on a Bruker D8 Venture diffractometer. High resolution mass spectra were obtained from an Agilent 6520B Q-TOF mass spectrometer with electron spray ionization (ESI) as the ion source.

2. General Procedure and Characterization Data

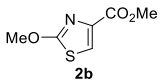
2.1 General Procedure and Characterization Data for the Preparation of 2-Alkoxythiazoles 2



2b

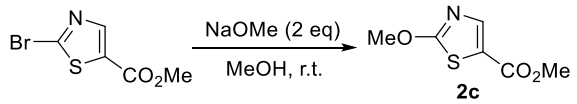
To a solution of methyl 2-bromothiazol-4-carboxylate (2.21 g, 10 mmol, 1 eq) in methanol (20 mL) was added sodium methoxide (0.54 g, 20 mmol, 2 equiv) in five batches, and the reaction mixture was stirred for 12 hours at room temperature. After quenched with NH_4Cl (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was washed with water and brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (3:1, *v*/*v*) on silica gel to afford 1.14 g of methyl 2-methoxythiazol-4-carboxylate **2b** (66%).

Methyl 2-methoxythiazole-4-carboxylate (2b):



2b

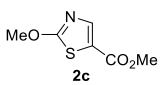
Light yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.61 (s, 1H), 4.16 (s, 3H), 3.90 (s, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 174.5, 161.6, 140.7, 120.7, 59.0, 52.3 ppm. **HRMS (ESI)** *m/z* calcd for $C_6H_8NO_3S$ $[M+H]^+$: 174.0219, found 174.0222.



2c

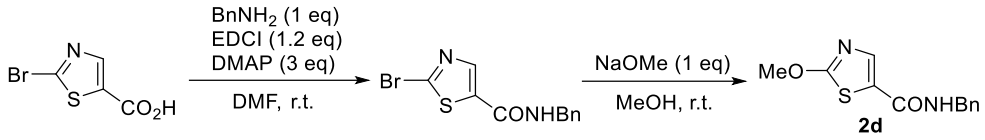
To a solution of methyl 2-bromothiazol-5-carboxylate (2.21 g, 10 mmol, 1 eq) in methanol (20 mL) was added sodium methoxide (0.54 g, 20 mmol, 2 equiv) in five batches, and the reaction mixture was stirred for 12 hours at room temperature. After quenched with NH_4Cl (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was washed with water and brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (3:1, *v*/*v*) on silica gel to afford 1.04 g of methyl 2-methoxythiazol-5-carboxylate **2c** (60%).

Methyl 2-methoxythiazole-5-carboxylate (2c):



2c

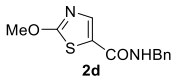
Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.83 (s, 1H), 4.13 (s, 3H), 3.86 (s, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 178.7, 161.8, 144.3, 121.0, 58.7, 52.0 ppm. **HRMS (ESI)** *m/z* calcd for $C_6H_8NO_3S$ $[M+H]^+$: 174.0219, found 174.0222.



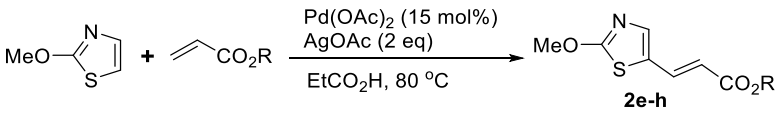
To a solution of 2-bromothiazol-5-carboxylic acid (1.03 g, 5 mmol, 1 eq) and DMAP (1.83 g, 15 mmol, 3 eq) in DMF (15 mL) was added EDCI (1.15 g, 6 mmol, 1.2 equiv). After stirring for 15 minutes, benzylamine (0.54 g, 5 mmol, 1 eq) was added, and the reaction mixture was stirred for 12 hours at room temperature. After quenched with NH_4Cl (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was washed with water and brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The generated residue was employed directly in the next step.

To a solution of the above residue in methanol (10 mL) was added sodium methoxide (0.27 g, 5 mmol, 1 equiv) in three batches, and the reaction mixture was stirred for 4 hours at room temperature. After quenched with NH_4Cl (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was washed with water and brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (15:1, *v*/*v*) on silica gel to afford 0.58 g of *N*-benzyl-2-methoxythiazole-5-carboxamide **2d** (47% for two steps).

***N*-Benzyl-2-methoxythiazole-5-carboxamide (2d):**



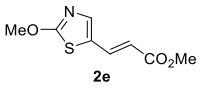
Light yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.59 (s, 1H), 7.29-7.20 (m, 5H), 7.15 (t, *J* = 5.9 Hz, 1H), 4.45 (d, *J* = 5.8 Hz, 2H), 4.03 (s, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 177.2, 160.9, 138.5, 137.8, 128.5, 127.6, 127.3, 126.7, 58.5, 43.6 ppm. **HRMS (ESI)** *m/z* calcd for $C_{12}H_{13}N_2O_2S$ $[M+H]^+$: 249.0692, found 249.0690.



To a reaction tube charged with a solution of 2-methoxythiazole (**2a**, 1.15 g, 10 mmol, 1 eq), palladium diacetate (340 mg, 1.5 mmol, 15 mol%) and silver acetate (3.34 g, 20 mmol, 2 eq) in propionic acid (30 mL) was added acylate (20 mmol, 2 equiv) at room temperature, and the reaction mixture was stirred at 80 °C (oil temperature) for 12 hours. After filtered over celite, the

mixture was extracted with ethyl acetate. The combined organic phase was washed with Na_2CO_3 (aq.), water and brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (6:1, *v*/*v*) on silica gel to afford 2-methoxythiazole-5-arylates **2e-h**.

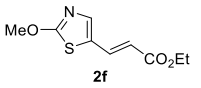
Methyl (*E*)-3-(2-methoxythiazol-5-yl)acrylate (2e):



2e

Yield 62%. Light yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.65 (d, *J* = 15.6 Hz, 1H), 7.29 (s, 1H), 5.93 (d, *J* = 15.6 Hz, 1H), 4.11 (s, 3H), 3.77 (s, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 176.0, 166.8, 141.6, 135.1, 127.8, 116.7, 58.6, 51.6 ppm. **HRMS (ESI)** *m/z* calcd for $C_8H_{10}NO_3S$ $[M+H]^+$: 200.0376, found 200.0374.

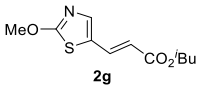
Ethyl (*E*)-3-(2-methoxythiazol-5-yl)acrylate (2f):



2f

Yield 60%. Light yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.65 (d, *J* = 15.5 Hz, 1H), 7.29 (s, 1H), 5.93 (d, *J* = 15.6 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.11 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 175.9, 166.3, 141.4, 134.8, 127.8, 117.1, 60.3, 58.5, 14.1 ppm. **HRMS (ESI)** *m/z* calcd for $C_9H_{12}NO_3S$ $[M+H]^+$: 214.0533, found 214.0535.

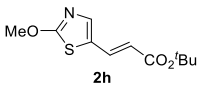
Isobutyl (*E*)-3-(2-methoxythiazol-5-yl)acrylate (2g):



2g

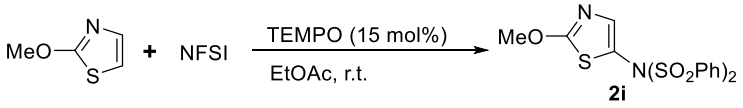
Yield 65%. Light yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.64 (d, *J* = 15.6 Hz, 1H), 7.30 (s, 1H), 5.95 (d, *J* = 15.6 Hz, 1H), 4.11 (s, 3H), 3.96 (d, *J* = 6.7 Hz, 2H), 1.99 (sept, *J* = 6.7 Hz, 1H), 0.97 (d, *J* = 6.8 Hz, 6H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 176.0, 166.5, 141.4, 134.8, 127.9, 117.2, 70.6, 58.6, 27.7, 19.0 ppm. **HRMS (ESI)** *m/z* calcd for $C_{11}H_{16}NO_3S$ $[M+H]^+$: 242.0845, found 242.0843.

***Tert*-butyl (*E*)-3-(2-methoxythiazol-5-yl)acrylate (2h):**



2h

Yield 54%. Light yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.53 (d, *J* = 15.5 Hz, 1H), 7.26 (s, 1H), 5.87 (d, *J* = 15.6 Hz, 1H), 4.10 (s, 3H), 1.51 (s, 9H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 175.8, 165.7, 140.9, 133.8, 128.1, 119.4, 80.6, 58.5, 28.1 ppm. **HRMS (ESI)** *m/z* calcd for $C_{11}H_{16}NO_3S$ $[M+H]^+$: 242.0845, found 242.0842.

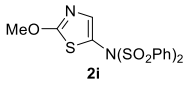


2i

To a reaction tube charged with NFSI (2.52 g, 8 mmol, 4 eq) was added a solution of

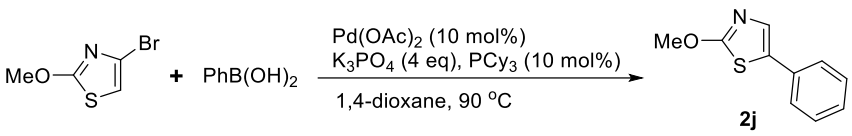
2-methoxythiazole (**2a**, 230 mg, 2 mmol, 1 eq) and TEMPO (46.9 mg, 0.3 mmol, 0.15 eq) in ethyl acetate (5 mL) under argon (1 atm). After stirring at room temperature for 24 hours, the reaction mixture was concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (4:1, *v*/*v*) on silica gel to afford 551.4 mg of thiazole **2i** (67%).

***N*-(2-Methoxythiazol-5-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (2i):**



2i

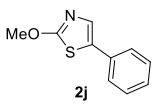
Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.00-7.97 (m, 4H), 7.71-7.67 (m, 2H), 7.58-7.54 (m, 4H), 6.76 (s, 1H), 4.06 (s, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 175.4, 141.1, 138.4, 134.5, 129.2, 128.6, 121.6, 57.9 ppm. **HRMS (ESI)** *m/z* calcd for $C_{16}H_{15}N_2O_5S_3$ $[M+H]^+$: 411.0138, found 411.0135.



2j

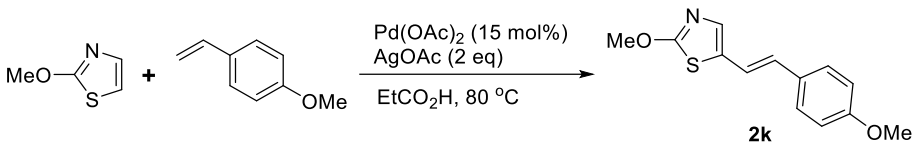
To a reaction tube charged with phenylboronic acid (1.83 g, 15 mmol, 1.5 eq), palladium diacetate (227 mg, 1 mmol, 10 mol%), tricyclohexyl phosphine (280 mg, 1 mmol, 10 mol%) and potassium phosphate (8.49 g, 40 mmol, 4 eq) was added a solution of 2-methoxythiazole (**2a**, 1.15 g, 10 mmol, 1 eq) in 1,4-dioxane (30 mL) under argon (1 atm), and the reaction mixture was stirred at 90 °C (oil temperature) for 16 hours. After filtered over celite, the mixture was extracted with ethyl acetate. The combined organic phase was washed with water and brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (20:1, *v*/*v*) on silica gel to afford 1.38 g of thiazole **2j** (72%).

2-Methoxy-5-phenylthiazole (2j):



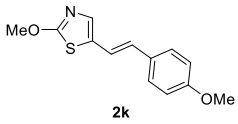
2j

Light brown oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.44-7.42 (m, 2H), 7.37-7.32 (m, 3H), 7.29-7.25 (m, 1H), 4.09 (s, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 174.1, 131.8, 131.8, 131.2, 128.9, 127.5, 125.8, 58.1 ppm. **HRMS (ESI)** *m/z* calcd for $C_{10}H_{10}NOS$ $[M+H]^+$: 192.0478, found 192.0477.

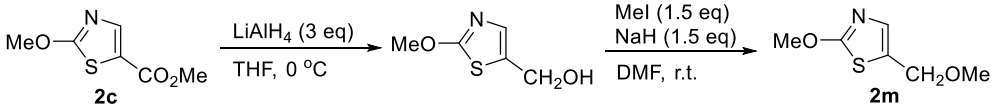


To a reaction tube charged with a solution of 2-methoxythiazole (**2a**, 1.15 g, 10 mmol, 1 eq), palladium diacetate (340 mg, 1.5 mmol, 15 mol%) and silver acetate (3.34 g, 20 mmol, 2 eq) in propionic acid (20 mL) was added 4-methoxystyrene (2.01 g, 15 mmol, 1.5 equiv) at room temperature, and the reaction mixture was stirred at 80 °C (oil temperature) for 12 hours. After filtered over celite, the mixture was extracted with ethyl acetate. The combined organic phase was washed with Na_2CO_3 (aq.), water and brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (20:1, *v*/*v*) on silica gel to afford 1.41 g of thiazole **2k** (57%).

(*E*)-2-Methoxy-5-(4-methoxystyryl)thiazole (2k):



Light yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.33 (d, *J* = 8.8 Hz, 2H), 7.03 (s, 1H), 6.90 (d, *J* = 16.0 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 16.0 Hz, 1H), 4.06 (s, 3H), 3.80 (s, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 173.1, 159.3, 134.9, 131.1, 129.4, 128.4, 127.3, 117.1, 114.1, 58.1, 55.2 ppm. **HRMS (ESI)** *m/z* calcd for $C_{13}H_{14}NO_2S$ $[M+H]^+$: 248.0740, found 248.0737.

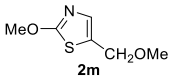


To a solution of thiazle **2c** (520 mg, 3 mmol, 1 eq) in THF (8 mL) was added lithium aluminum hydride (342 mg, 9 mmol, 3 equiv) in five batches at 0 °C (iced water bath temperature). After stirring for 6 hours, the reaction mixture was carefully quenched with iced water at 0 °C, and extracted with ethyl acetate. The combined organic phase was washed with water and brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The generated residue was employed directly in the next step.

To a solution of the above residue in DMF (10 mL) was added sodium hydride (180 mg, 4.5 mmol, 1.5 equiv) in three batches at 0 °C (iced water bath temperature). The reaction mixture was stirred for 15 minutes and iodomethane (640 mg, 4.5 mmol, 3 eq) was added. After strring at room

temperature for 3 hours, the reaction mixture was quenched with NH_4Cl (aq.) and extracted with ethyl acetate. The combined organic phase was washed with water and brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent (8:1, *v*/*v*) on silica gel to afford 195.9 mg of thiazole **2m** (41% for two steps).

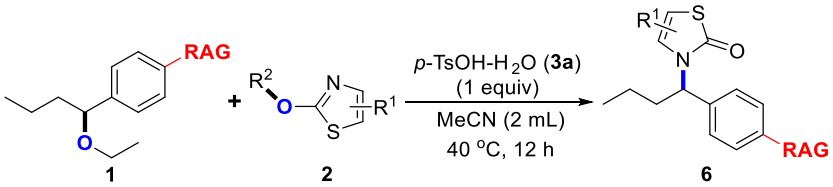
2-Methoxy-5-(methoxymethyl)thiazole (2m):



2m

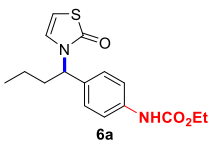
Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.02 (t, *J* = 0.88 Hz, 1H), 4.47 (d, *J* = 0.88 Hz, 2H), 4.06 (s, 3H), 3.35 (s, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 175.8, 135.6, 127.2, 67.0, 58.1, 57.4 ppm. **HRMS (ESI)** *m/z* calcd for $C_6H_{10}NO_2S$ $[M+H]^+$: 160.0427, found 160.0426.

2.2 General Procedure and Characterization Data for the Three-component Formal Metathesis Using Benzyl Alkyl Ether 1 (Results Shown in Table 2)



To a reaction tube charged with *p*-TsOH-H_2O (**3a**, 57.1 mg, 0.3 mmol, 1 equiv) was added a solution of **1** (0.3 mmol, 1 equiv) and **2** (0.45 mmol, 1.5 equiv) in anhydrous MeCN (2 mL, 0.15 M of **1**) via a syringe under argon (1 atm), and the reaction mixture was stirred for 12 hours at 40 °C (oil bath temperature). After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent on silica gel to afford corresponding thiazol-2(3*H*)-one products **6a-p**.

Ethyl (4-(1-(2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6a):



6a

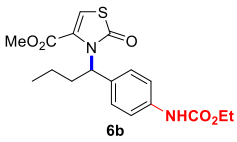
The three-component formal metathesis of 0.3 mmol of ethyl (4-(1-ethoxybutyl)phenyl)carbamate (**1a**, 79.6 mg), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL,

51.8 mg) afforded 84.8 mg of **6a** (88%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

In another three-component formal metathesis of 0.3 mmol of ethyl (4-(1-ethoxybutyl)phenyl)carbamate (**1a**, 79.6 mg), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of 2-ethoxythiazole (**2a'**, 51 μL, 58.1 mg) afforded 73.5 mg of **6a** (76%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

White solid, m.p. 78-80 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.38 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 6.98 (s, 1H), 6.53 (d, *J* = 5.5 Hz, 1H), 6.07 (d, *J* = 5.5 Hz, 1H), 5.43 (dd, *J* = 6.7 Hz, 2.5 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.09-1.97 (m, 2H), 1.38-1.32 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 172.1, 153.6, 137.9, 134.1, 127.9, 121.7, 118.8, 101.4, 61.2, 56.6, 35.4, 19.4, 14.5, 13.6 ppm. **HRMS (ESI)** *m/z* calcd for $C_{16}H_{21}N_2O_3S$ $[M+H]^+$: 321.1267, found 321.1262.

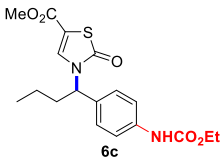
Methyl 3-(1-(4-((ethoxycarbonyl)amino)phenyl)butyl)-2-oxo-2,3-dihydrothiazole-4-carboxylate (6b):



6b

The three-component formal metathesis of 0.3 mmol of ethyl (4-(1-ethoxybutyl)phenyl)carbamate (**1a**, 79.6 mg), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of methyl 2-methoxythiazole-4-carboxylate (**2b**, 77.9 mg) did not afford any **6b**.

Methyl 3-(1-(4-((ethoxycarbonyl)amino)phenyl)butyl)-2-oxo-2,3-dihydrothiazole-5-carboxylate (6c):



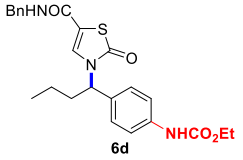
6c

The three-component formal metathesis of 0.3 mmol of ethyl (4-(1-ethoxybutyl)phenyl)carbamate (**1a**, 79.6 mg), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of methyl 2-methoxythiazole-5-carboxylate (**2c**, 77.9 mg) afforded 108.7 mg of **6c** (96%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.43-7.40 (m, 3H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.06 (s, 1H), 5.44 (t, *J* = 7.9 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.12-2.01 (m, 2H), 1.37-1.33 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100**

MHz): δ = 171.3, 161.2, 153.5, 138.4, 133.1, 130.3, 127.9, 119.0, 108.5, 61.2, 57.4, 52.2, 35.4, 19.4, 14.4, 13.5 ppm. **HRMS (ESI)** *m/z* calcd for $C_{18}H_{23}N_2O_5S$ $[M+H]^+$: 379.1322, found 379.1320.

Ethyl (4-(1-(5-(benzylcarbamoyl)-2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6d):

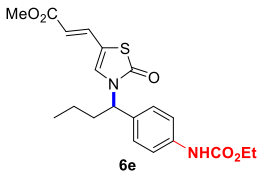


6d

The three-component formal metathesis of 0.3 mmol of ethyl (4-(1-ethoxybutyl)phenyl)carbamate (**1a**, 79.6 mg), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of *N*-benzyl-2-methoxythiazole-5-carboxamide (**2d**, 111.7 mg) afforded 118.6 mg of **6d** (87%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.45 (s, 1H), 7.39 (s, 1H), 7.30 (d, *J* = 8.3 Hz, 2H), 7.25-7.18 (m, 5H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.06 (t, *J* = 5.7 Hz, 1H), 5.36 (dd, *J* = 6.8 Hz, 1.8 Hz, 1H), 4.43-4.32 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.00-1.89 (m, 2H), 1.29-1.26 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 170.9, 160.3, 153.8, 138.2, 137.5, 133.1, 128.4, 127.7, 127.4, 126.1, 119.1, 112.8, 61.1, 57.2, 43.7, 35.3, 19.3, 14.4, 13.4 ppm. **HRMS (ESI)** *m/z* calcd for $C_{24}H_{28}N_3O_4S$ $[M+H]^+$: 454.1795, found 454.1791.

Methyl (*E*)-3-(3-(1-(4-((ethoxycarbonyl)amino)phenyl)butyl)-2-oxo-2,3-dihydrothiazol-5-yl) acrylate (6e):



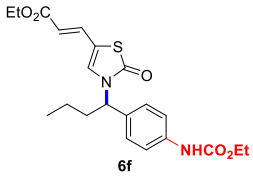
6e

The three-component formal metathesis of 0.3 mmol of ethyl (4-(1-ethoxybutyl)phenyl)carbamate (**1a**, 79.6 mg), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of methyl (*E*)-3-(2-methoxythiazol-5-yl)acrylate (**2e**, 89.6 mg) afforded 110.8 mg of **6e** (91%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

Light yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.44-7.41 (m, 3H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.14 (s, 1H), 6.86 (s, 1H), 5.77 (d, *J* = 15.4 Hz, 1H), 5.42 (t, *J* = 7.9 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.74 (s, 3H), 2.12-1.97 (m, 2H), 1.42-1.31 (m, 2H), 1.29 (t, *J* = 7.4 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 169.9, 166.7, 153.6, 138.3, 135.0, 133.1, 127.8,

126.5, 118.9, 116.0, 115.6, 61.2, 57.2, 51.6, 35.3, 19.4, 14.4, 13.5 ppm. **HRMS (ESI)** *m/z* calcd for $C_{20}H_{25}N_2O_5S$ $[M+H]^+$: 405.1479, found 405.1473.

Ethyl (*E*)-3-(3-(1-(4-((ethoxycarbonyl)amino)phenyl)butyl)-2-oxo-2,3-dihydrothiazol-5-yl) acrylate (6f):

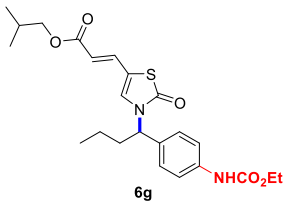


6f

The three-component formal metathesis of 0.3 mmol of ethyl (4-(1-ethoxybutyl)phenyl)carbamate (**1a**, 79.6 mg), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of ethyl (*E*)-3-(2-methoxythiazol-5-yl)acrylate (**2f**, 96.0 mg) afforded 103.4 mg of **6f** (82%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.44-7.40 (m, 3H), 7.25 (d, *J* = 8.6 Hz, 2H), 7.13 (s, 1H), 6.84 (s, 1H), 5.77 (d, *J* = 15.3 Hz, 1H), 5.42 (dd, *J* = 6.9 Hz, 2.0 Hz, 1H), 4.34-4.17 (m, 4H), 2.12-1.97 (m, 2H), 1.40-1.27 (m, 8H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 170.0, 166.3, 153.6, 138.3, 134.8, 133.2, 127.9, 126.3, 118.9, 116.6, 115.7, 61.2, 60.4, 57.2, 35.3, 19.4, 14.4, 14.1, 13.5 ppm. **HRMS (ESI)** *m/z* calcd for $C_{21}H_{27}N_2O_5S$ $[M+H]^+$: 419.1635, found 419.1635.

Isobutyl (*E*)-3-(3-(1-(4-((ethoxycarbonyl)amino)phenyl)butyl)-2-oxo-2,3-dihydrothiazol-5-yl) acrylate (6g):



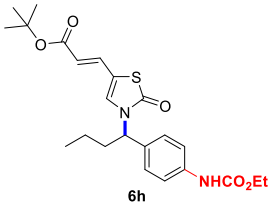
6g

The three-component formal metathesis of 0.3 mmol of ethyl (4-(1-ethoxybutyl)phenyl)carbamate (**1a**, 79.6 mg), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of isobutyl (*E*)-3-(2-methoxythiazol-5-yl)acrylate (**2g**, 108.6 mg) afforded 120.9 mg of **6g** (90%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

Light yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.44-7.40 (m, 3H), 7.29-7.24 (m, 3H), 6.87 (s, 1H), 5.79 (d, *J* = 15.4 Hz, 1H), 5.43 (t, *J* = 7.9 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.94 (d, *J* = 6.6 Hz, 2H), 2.11-1.92 (m, 3H), 1.40-1.32 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.99-0.94 (m, 9H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 169.9, 166.3, 153.6, 138.3, 134.7, 133.1, 127.8, 126.4, 118.9,

116.5, 115.6, 70.6, 61.1, 57.2, 35.3, 27.6, 19.4, 18.9, 14.4, 13.5 ppm. **HRMS (ESI)** *m/z* calcd for $C_{23}H_{31}N_2O_5S$ $[M+H]^+$: 447.1948, found 447.1949.

***Tert*-Butyl (*E*)-3-(3-(1-(4-((ethoxycarbonyl)amino)phenyl)butyl)-2-oxo-2,3-dihydrothiazol-5-yl)acrylate (6h):**

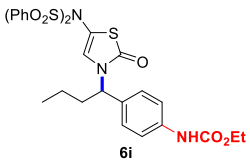


6h

The three-component formal metathesis of 0.3 mmol of ethyl (4-(1-ethoxybutyl)phenyl)carbamate (**1a**, 79.6 mg), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of *tert*-butyl (*E*)-3-(2-methoxythiazol-5-yl)acrylate (**2h**, 108.6 mg) afforded 95.6 mg of **6h** (71%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

Light yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.41 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 15.4 Hz, 1H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.02 (s, 1H), 6.79 (s, 1H), 5.71 (d, *J* = 15.4 Hz, 1H), 5.42 (dd, *J* = 6.9 Hz, 2.0 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.10-1.98 (m, 2H), 1.48 (s, 9H), 1.38-1.32 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 170.0, 165.5, 153.6, 138.3, 133.7, 133.3, 127.9, 125.7, 119.0, 118.8, 115.9, 80.6, 61.2, 57.1, 35.4, 28.1, 19.4, 14.4, 13.5 ppm. **HRMS (ESI)** *m/z* calcd for $C_{23}H_{31}N_2O_5S$ $[M+H]^+$: 447.1948, found 447.1944.

Ethyl (4-(1-(2-oxo-5-(*N*-(phenylsulfonyl)phenylsulfonamido)thiazol-3(2*H*)-yl)butyl)phenyl) carbamate (6i):



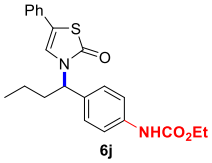
6i

The three-component formal metathesis of 0.3 mmol of ethyl (4-(1-ethoxybutyl)phenyl)carbamate (**1a**, 79.6 mg), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of *N*-(2-methoxythiazol-5-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (**2i**, 184.7 mg) afforded 175.1 mg of **6i** (95%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

White solid, m.p. 68-69 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.91 (d, *J* = 7.3 Hz, 4H), 7.67 (t, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.9 Hz, 4H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.12-7.10 (m, 3H), 6.26 (s, 1H), 5.43 (dd, *J* = 6.7 Hz, 2.4 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.99-1.80 (m, 2H), 1.32-1.25 (m, 5H),

0.95 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 169.8, 153.5, 138.1, 138.0, 134.5, 133.2, 129.1, 128.4, 127.6, 127.3, 118.8, 109.9, 61.2, 56.7, 35.4, 19.2, 14.4, 13.5 ppm. **HRMS (ESI)** *m/z* calcd for $C_{28}H_{30}N_3O_7S_3$ $[M+H]^+$: 616.1240, found 616.1237.

Ethyl (4-(1-(2-oxo-5-phenylthiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6j):

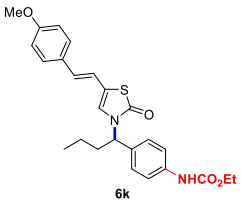


6j

The three-component formal metathesis of 0.3 mmol of ethyl (4-(1-ethoxybutyl)phenyl)carbamate (**1a**, 79.6 mg), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of 2-methoxy-5-phenylthiazole (**2j**, 86.1 mg) afforded 112.1 mg of **6j** (94%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.43 (d, *J* = 8.3 Hz, 2H), 7.33-7.21 (m, 8H), 6.79 (s, 1H), 5.51 (dd, *J* = 6.8 Hz, 2.1 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.14-2.03 (m, 2H), 1.43-1.34 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 171.0, 153.6, 138.0, 133.7, 131.3, 128.8, 127.8, 127.6, 124.7, 118.8, 116.4, 61.1, 56.6, 35.2, 19.4, 14.4, 13.6 ppm. **HRMS (ESI)** *m/z* calcd for $C_{22}H_{25}N_2O_3S$ $[M+H]^+$: 397.1580, found 397.1575.

Ethyl (*E*)-(4-(1-(5-(4-methoxystyryl)-2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6k):

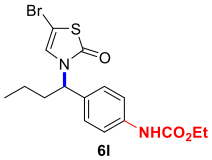


6k

The three-component formal metathesis of 0.3 mmol of ethyl (4-(1-ethoxybutyl)phenyl)carbamate (**1a**, 79.6 mg), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of (*E*)-2-methoxy-5-(4-methoxystyryl)thiazole (**2k**, 111.3 mg) afforded 117.8 mg of **6k** (87%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

Light brown oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.39 (d, *J* = 8.3 Hz, 2H), 7.29-7.24 (m, 4H), 7.02 (s, 1H), 6.83 (d, *J* = 8.3 Hz, 2H), 6.69 (d, *J* = 15.8 Hz, 1H), 6.51 (s, 1H), 6.38 (d, *J* = 15.8 Hz, 1H), 5.44 (dd, *J* = 7.0 Hz, 2.0 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 2.10-1.96 (m, 2H), 1.42-1.34 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 170.1, 159.3, 153.6, 138.0, 133.9, 129.2, 127.8, 127.8, 127.3, 119.3, 118.9, 118.9, 117.2, 114.1, 61.2, 56.6, 55.2, 35.3, 19.4, 14.4, 13.6 ppm. **HRMS (ESI)** *m/z* calcd for $C_{25}H_{29}N_2O_4S$ $[M+H]^+$: 453.1843, found 453.1832.

Ethyl (4-(1-(5-bromo-2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6l):

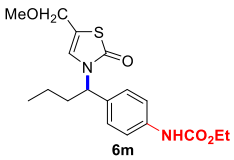


6l

The three-component formal metathesis of 0.3 mmol of ethyl (4-(1-ethoxybutyl)phenyl)carbamate (**1a**, 79.6 mg), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of 5-bromo-2-methoxythiazole (**2l**, 87.3 mg) afforded 111.0 mg of **6l** (93%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.42 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.12 (s, 1H), 6.55 (s, 1H), 5.43 (dd, *J* = 6.8 Hz, 2.3 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.09-1.94 (m, 2H), 1.38-1.31 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 170.9, 153.6, 138.1, 133.3, 127.9, 122.2, 118.8, 88.9, 61.2, 56.9, 35.1, 19.4, 14.4, 13.5 ppm. **HRMS (ESI)** *m/z* calcd for $C_{16}H_{19}BrN_2O_3S$ $[M+H]^+$: 399.0373, found 399.0372.

Ethyl (4-(1-(5-(methoxymethyl)-2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6m):

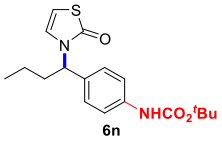


6m

The three-component formal metathesis of 0.3 mmol of ethyl (4-(1-ethoxybutyl)phenyl)carbamate (**1a**, 79.6 mg), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of 2-methoxy-5-(methoxymethyl)thiazole (**2m**, 71.6 mg) afforded 55.4 mg of **6m** (51%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.38 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.02 (s, 1H), 6.47 (s, 1H), 5.42 (dd, *J* = 6.7 Hz, 2.4 Hz, 1H), 4.22 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.31 (s, 3H), 2.10-1.94 (m, 2H), 1.36-1.28 (m, 5H), 0.96 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 172.0, 153.6, 137.9, 133.9, 127.9, 119.9, 118.8, 115.4, 68.0, 61.2, 57.7, 56.4, 35.3, 19.4, 14.5, 13.6 ppm. **HRMS (ESI)** *m/z* calcd for $C_{18}H_{25}N_2O_4S$ $[M+H]^+$: 365.1530, found 365.1526.

***Tert*-Butyl (4-(1-(2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6n):**



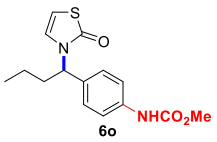
6n

The three-component formal metathesis of 0.3 mmol of *tert*-butyl (4-(1-ethoxybutyl)phenyl)carbamate (**1b**, 88.0 mg), 0.3 mmol of

p-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 74.9 mg of **6n** (72%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.36 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.81 (s, 1H), 6.51 (d, *J* = 5.5 Hz, 1H), 6.06 (d, *J* = 5.5 Hz, 1H), 5.43 (dd, *J* = 6.7 Hz, 2.4 Hz, 1H), 2.10-1.94 (m, 2H), 1.50 (s, 9H), 1.38-1.29 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 172.0, 152.7, 138.2, 133.7, 127.8, 121.7, 118.7, 101.3, 80.5, 56.5, 35.3, 28.2, 19.4, 13.6 ppm. **HRMS (ESI)** *m/z* calcd for $C_{18}H_{25}N_2O_3S$ $[M+H]^+$: 349.1580, found 349.1577.

Methyl (4-(1-(2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6o):

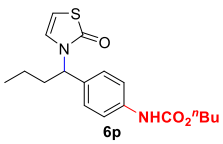


6o

The three-component formal metathesis of 0.3 mmol of methyl (4-(1-ethoxybutyl)phenyl)carbamate (**1c**, 75.4 mg), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 60.9 mg of **6o** (66%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

White solid, m.p. 165-166 °C. **^{1}H NMR (DMSO-d_6, 400 MHz):** δ = 9.69 (s, 1H), 7.43 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.15 (d, *J* = 5.5 Hz, 1H), 6.44 (d, *J* = 5.4 Hz, 1H), 5.22 (dd, *J* = 6.3 Hz, 3.4 Hz, 1H), 3.65 (s, 3H), 2.14-1.95 (m, 2H), 1.25-1.15 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR (DMSO-d_6, 100 MHz):** δ = 171.0, 154.0, 138.7, 134.0, 127.5, 123.4, 118.3, 101.1, 56.5, 51.6, 34.6, 19.1, 13.3 ppm. **HRMS (ESI)** *m/z* calcd for $C_{15}H_{19}N_2O_3S$ $[M+H]^+$: 307.1111, found 307.1107.

Butyl (4-(1-(2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6p):



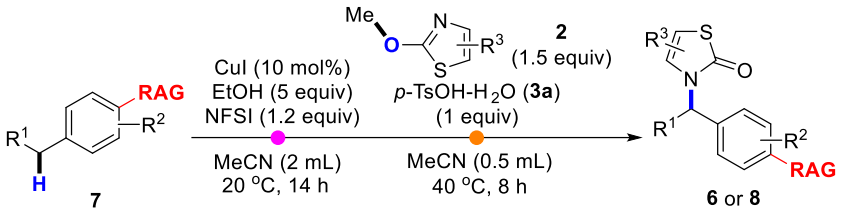
6p

The three-component formal metathesis of 0.3 mmol of butyl (4-(1-ethoxybutyl)phenyl)carbamate (**1d**, 88.0 mg), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 73.6 mg of **6p** (70%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.39 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 2H),

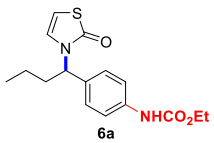
7.05 (s, 1H), 6.53 (d, J = 5.5 Hz, 1H), 6.07 (d, J = 5.5 Hz, 1H), 5.43 (dd, J = 6.8 Hz, 2.4 Hz, 1H), 4.15 (t, J = 6.7 Hz, 2H), 2.11-1.94 (m, 2H), 1.67-1.60 (m, 2H), 1.45-1.26 (m, 4H), 0.98-0.92 (m, 6H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 172.1, 153.7, 137.9, 134.0, 127.8, 121.7, 118.8, 101.4, 65.1, 56.6, 35.4, 30.9, 19.4, 19.0, 13.6, 13.6 ppm. **HRMS (ESI)** *m/z* calcd for $C_{18}H_{25}N_2O_3S$ $[M+H]^+$: 349.1580, found 349.1576.

2.3 General Procedure and Characterization Data for the One-pot Direct Benzylic C(sp^3)-N Coupling of Alkyl Benzene 7 and 2-Alkoxythiazole 2 (Results Shown in Table 3)



To a reaction tube charged with CuI (5.7 mg, 0.03 mmol, 10 mol%) and NFSI (113.5 mg, 0.36 mmol, 1.2 equiv) was added a solution of alkyl benzene (**7**, 0.3 mmol, 1 equiv) and ethanol (88 μL, 1.5 mmol, 5 equiv) in anhydrous MeCN (2 mL, 0.15 M of **7**) via a syringe under argon (1 atm) at 20 °C (oil bath temperature), and the reaction mixture was stirred for 14 hours at 20 °C (oil bath temperature). Then a solution of 2-alkoxythiazole (**2**, 0.45 mmol, 1.5 equiv) and *p*-TsOH-H_2O (**3a**, 57.1 mg, 0.3 mmol, 1 equiv) in anhydrous MeCN (0.5 mL) via a syringe was added, and the reaction temperature was elevated to 40 °C (oil bath temperature). After stirring for another 8 hours at this temperature, the reaction mixture was quenched with Na_2CO_3 (aq.) and extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent on silica gel to afford corresponding thiazol-2(3*H*)-one products **6a**, **6c-l**, **6n-p** and **8a-h**.

Ethyl (4-(1-(2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6a):

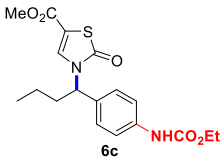


6a

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (4-butylphenyl)carbamate (**7a**, 66.4 mg) with 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 64.7 mg of **6a** (67%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

See **Section 2.2** for characterization data of **6a**.

Methyl 3-(1-(4-((ethoxycarbonyl)amino)phenyl)butyl)-2-oxo-2,3-dihydrothiazole-5-carboxylate (6c):

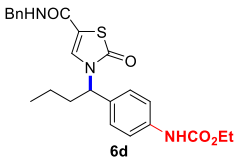


6c

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (4-butylphenyl)carbamate (**7a**, 66.4 mg) with 0.45 mmol of methyl 2-methoxythiazole-5-carboxylate (**2c**, 77.9 mg) afforded 84.4 mg of **6c** (74%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

See **Section 2.2** for characterization data of **6c**.

Ethyl (4-(1-(5-(benzylcarbamoyl)-2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6d):

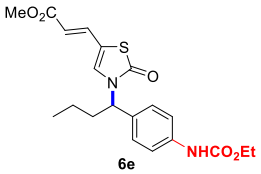


6d

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (4-butylphenyl)carbamate (**7a**, 66.4 mg) with 0.45 mmol of *N*-benzyl-2-methoxythiazole-5-carboxamide (**2d**, 111.7 mg) afforded 84.4 mg of **6d** (78%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

See **Section 2.2** for characterization data of **6d**.

Methyl (*E*)-3-(3-(1-(4-((ethoxycarbonyl)amino)phenyl)butyl)-2-oxo-2,3-dihydrothiazol-5-yl) acrylate (6e):

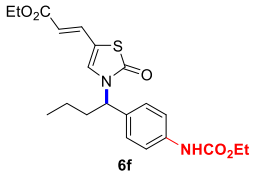


6e

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (4-butylphenyl)carbamate (**7a**, 66.4 mg) with 0.45 mmol of methyl (*E*)-3-(2-methoxythiazol-5-yl)acrylate (**2e**, 89.6 mg) afforded 93.1 mg of **6e** (77%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

See **Section 2.2** for characterization data of **6e**.

Ethyl (*E*)-3-(3-(1-(4-((ethoxycarbonyl)amino)phenyl)butyl)-2-oxo-2,3-dihydrothiazol-5-yl) acrylate (6f):

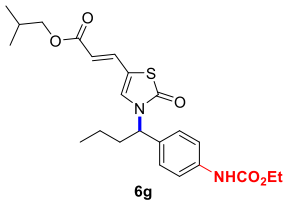


6f

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (4-butylphenyl)carbamate (**7a**, 66.4 mg) with 0.45 mmol of ethyl (*E*)-3-(2-methoxythiazol-5-yl)acrylate (**2f**, 96.0 mg) afforded 94.3 mg of **6f** (75%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

See **Section 2.2** for characterization data of **6f**.

Isobutyl (*E*)-3-(3-(1-(4-((ethoxycarbonyl)amino)phenyl)butyl)-2-oxo-2,3-dihydrothiazol-5-yl) acrylate (6g):

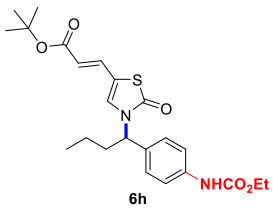


6g

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (4-butylphenyl)carbamate (**7a**, 66.4 mg) with 0.45 mmol of isobutyl (*E*)-3-(2-methoxythiazol-5-yl)acrylate (**2g**, 108.6 mg) afforded 105.5 mg of **6g** (79%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

See **Section 2.2** for characterization data of **6g**.

***Tert*-Butyl (*E*)-3-(3-(1-(4-((ethoxycarbonyl)amino)phenyl)butyl)-2-oxo-2,3-dihydrothiazol-5-yl)acrylate (6h):**

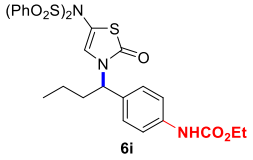


6h

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (4-butylphenyl)carbamate (**7a**, 66.4 mg) with 0.45 mmol of *tert*-butyl (*E*)-3-(2-methoxythiazol-5-yl)acrylate (**2h**, 108.6 mg) afforded 82.0 mg of **6h** (61%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

See **Section 2.2** for characterization data of **6h**.

Ethyl (4-(1-(2-oxo-5-(*N*-(phenylsulfonyl)phenylsulfonamido)thiazol-3(2*H*)-yl)butyl)phenyl) carbamate (6i):



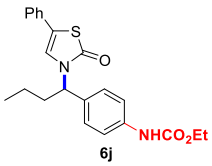
6i

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (4-butylphenyl)carbamate (**7a**, 66.4 mg) with 0.45 mmol of

N-(2-methoxythiazol-5-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (**2i**, 184.7 mg) afforded 129.6 mg of **6i** (70%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

See **Section 2.2** for characterization data of **6i**.

Ethyl (4-(1-(2-oxo-5-phenylthiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6j):

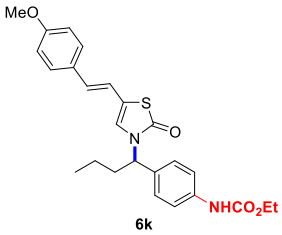


6j

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (4-butylphenyl)carbamate (**7a**, 66.4 mg) with 0.45 mmol of 2-methoxy-5-phenylthiazole (**2j**, 86.1 mg) afforded 87.8 mg of **6j** (74%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

See **Section 2.2** for characterization data of **6j**.

Ethyl (*E*)-(4-(1-(5-(4-methoxystyryl)-2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6k):

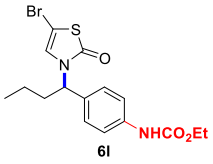


6k

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (4-butylphenyl)carbamate (**7a**, 66.4 mg) with 0.45 mmol of (*E*)-2-methoxy-5-(4-methoxystyryl)thiazole (**2k**, 111.3 mg) afforded 96.0 mg of **6k** (71%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

See **Section 2.2** for characterization data of **6k**.

Ethyl (4-(1-(5-bromo-2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6l):

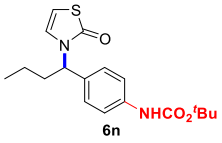


6l

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (4-butylphenyl)carbamate (**7a**, 66.4 mg) with 0.45 mmol of 5-bromo-2-methoxythiazole (**2l**, 87.3 mg) afforded 97.6 mg of **6l** (81%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

See **Section 2.2** for characterization data of **6l**.

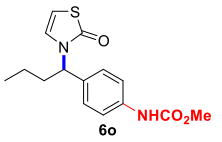
***Tert*-Butyl (4-(1-(2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6n):**



6n

The one-pot direct benzylic C-N coupling of 0.3 mmol of *tert*-butyl (4-butylphenyl)carbamate (**7b**, 74.8 mg) with 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 61.3 mg of **6n** (59%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent. See **Section 2.2** for characterization data of **6n**.

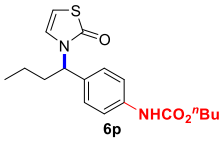
Methyl (4-(1-(2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6o):



6o

The one-pot direct benzylic C-N coupling of 0.3 mmol of methyl (4-butylphenyl)carbamate (**7c**, 62.2 mg) with 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 52.1 mg of **6o** (57%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent. See **Section 2.2** for characterization data of **6o**.

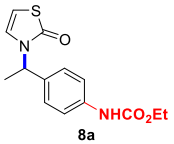
Butyl (4-(1-(2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6p):



6p

The one-pot direct benzylic C-N coupling of 0.3 mmol of butyl (4-butylphenyl)carbamate (**7d**, 74.8 mg) with 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 68.3 mg of **6p** (65%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent. See **Section 2.2** for characterization data of **6p**.

Ethyl (4-(1-(2-oxothiazol-3(2*H*)-yl)ethyl)phenyl)carbamate (8a):

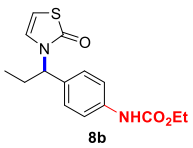


8a

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (4-ethylphenyl)carbamate (**7f**, 58.0 mg) with 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 65.9 mg of **8a** (75%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

Light yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.39 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.85 (s, 1H), 6.44 (d, *J* = 5.5 Hz, 1H), 6.07 (d, *J* = 5.5 Hz, 1H), 5.62 (q, *J* = 7.1 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.69 (d, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 171.8, 153.6, 137.9, 134.6, 127.5, 121.8, 118.8, 101.4, 61.3, 52.2, 19.2, 14.5 ppm. **HRMS (ESI)** *m/z* calcd for $C_{14}H_{17}N_2O_3S$ $[M+H]^+$: 293.0954, found 293.0950.

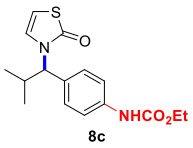
Ethyl (4-(1-(2-oxothiazol-3(2*H*)-yl)propyl)phenyl)carbamate (8b):



8b

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (4-propylphenyl)carbamate (**7g**, 62.2 mg) with 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 49.9 mg of **8b** (54%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent. White solid, m.p. 146-147 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.38 (d, *J* = 8.2 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 6.92 (s, 1H), 6.51 (d, *J* = 5.5 Hz, 1H), 6.08 (d, *J* = 5.5 Hz, 1H), 5.33 (dd, *J* = 6.6 Hz, 2.5 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.20-1.97 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 172.2, 153.6, 137.9, 133.9, 127.9, 121.7, 118.9, 101.4, 61.2, 58.4, 26.5, 14.5, 10.8 ppm. **HRMS (ESI)** *m/z* calcd for $C_{15}H_{19}N_2O_3S$ $[M+H]^+$: 307.1111, found 307.1106.

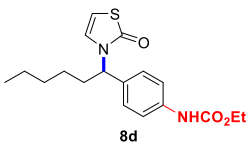
Ethyl (4-(2-methyl-1-(2-oxothiazol-3(2*H*)-yl)propyl)phenyl)carbamate (8c):



8c

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (4-isobutylphenyl)carbamate (**7h**, 66.4 mg) with 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 49.2 mg of **8c** (51%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent. Light yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.38 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 6.91 (s, 1H), 6.65 (d, *J* = 5.5 Hz, 1H), 6.07 (d, *J* = 5.5 Hz, 1H), 4.99 (d, *J* = 11.3 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.45 (d-spet, *J* = 11.4 Hz, 6.6 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J* = 6.5 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 172.1, 153.6, 137.9, 133.4, 128.6, 121.7, 118.9, 101.5, 63.9, 61.3, 30.8, 20.3, 19.5, 14.5 ppm. **HRMS (ESI)** *m/z* calcd for $C_{16}H_{21}N_2O_3S$ $[M+H]^+$: 321.1267, found 321.1264.

Ethyl (4-(1-(2-oxothiazol-3(2*H*)-yl)hexyl)phenyl)carbamate (8d):



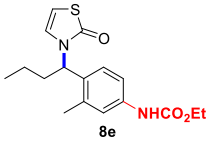
8d

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (4-hexylphenyl)carbamate (**7i**, 74.8 mg) with 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 75.0 mg of **8d** (72%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the

eluent.

Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.39 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.6 Hz, 2H), 7.04 (s, 1H), 6.53 (d, *J* = 5.5 Hz, 1H), 6.07 (d, *J* = 5.5 Hz, 1H), 5.41 (dd, *J* = 6.7 Hz, 2.4 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.12-1.94 (m, 2H), 1.33-1.26 (m, 9H), 0.86 (t, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 172.1, 153.6, 137.9, 134.1, 127.8, 121.7, 118.8, 101.4, 61.2, 56.9, 33.3, 31.3, 25.8, 22.3, 14.5, 13.9 ppm. **HRMS (ESI)** *m/z* calcd for $C_{18}H_{24}N_2O_3SNa$ $[M+Na]^+$: 371.1400, found 371.1396.

Ethyl (3-methyl-4-(1-(2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (8e):

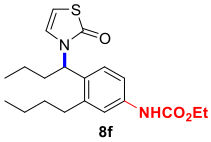


8e

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (4-butyl-3-methylphenyl)carbamate (**7j**, 70.6 mg) with 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 81.8 mg of **8e** (82%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

Light yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.38 (dd, *J* = 8.5 Hz, 2.3 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 2.3 Hz, 1H), 7.13 (s, 1H), 6.37 (d, *J* = 5.5 Hz, 1H), 6.02 (d, *J* = 5.5 Hz, 1H), 5.54 (t, *J* = 7.7 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.25 (s, 3H), 2.05-1.98 (m, 2H), 1.44-1.35 (m, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 171.7, 153.6, 138.6, 137.9, 131.6, 126.6, 122.1, 120.9, 116.0, 101.2, 61.1, 53.5, 35.8, 19.4, 19.3, 14.4, 13.7 ppm. **HRMS (ESI)** *m/z* calcd for $C_{17}H_{23}N_2O_3S$ $[M+H]^+$: 335.1424, found 335.1421.

Ethyl (3-butyl-4-(1-(2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (8f):



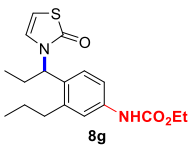
8f

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (3,4-dibutylphenyl)carbamate (**7k**, 83.2 mg) with 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 94.4 mg of **8f** (84%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.37-7.32 (m, 2H), 7.23 (d, *J* = 2.1 Hz, 1H), 6.99 (s, 1H), 6.38 (d, *J* = 5.5 Hz, 1H), 6.01 (d, *J* = 5.5 Hz, 1H), 5.62 (t, *J* = 7.7 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.69-2.50 (m, 2H), 2.09-1.93 (m, 2H), 1.49-1.28 (m, 9H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 171.5, 153.6, 143.7, 138.0, 130.9, 126.9,

122.1, 120.0, 116.0, 101.1, 61.1, 52.9, 36.0, 33.5, 31.9, 22.7, 19.5, 14.5, 13.9, 13.7 ppm. **HRMS (ESI)** *m/z* calcd for $C_{20}H_{29}N_2O_3S$ $[M+H]^+$: 377.1893, found 377.1896.

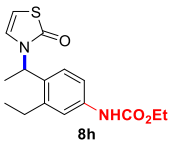
Ethyl (4-(1-(2-oxothiazol-3(2*H*)-yl)propyl)-3-propylphenyl)carbamate (8g):



8g

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (3,4-dipropylphenyl)carbamate (**7l**, 74.8 mg) with 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 77.1 mg of **8g** (74%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent. Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.37 (d, *J* = 8.5 Hz, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 7.23 (s, 1H), 7.04 (s, 1H), 6.38 (d, *J* = 5.5 Hz, 1H), 6.01 (d, *J* = 5.5 Hz, 1H), 5.52 (t, *J* = 7.7 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.67-2.47 (m, 2H), 2.10-2.02 (m, 2H), 1.56-1.34 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 171.6, 153.6, 143.5, 138.0, 130.7, 126.9, 122.1, 120.1, 116.0, 101.1, 61.1, 54.7, 34.1, 26.9, 24.4, 14.5, 14.0, 11.0 ppm. **HRMS (ESI)** *m/z* calcd for $C_{18}H_{25}N_2O_3S$ $[M+H]^+$: 349.1580, found 349.1576.

Ethyl (3-ethyl-4-(1-(2-oxothiazol-3(2*H*)-yl)ethyl)phenyl)carbamate (8h):

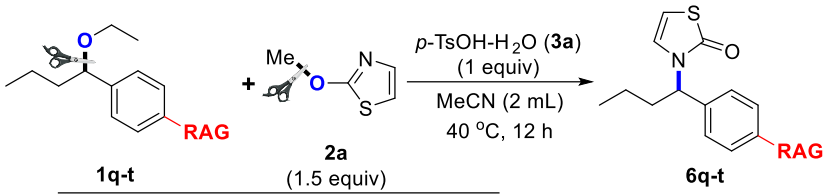


8h

The one-pot direct benzylic C-N coupling of 0.3 mmol of ethyl (3,4-diethylphenyl)carbamate (**7m**, 66.4 mg) with 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 74.5 mg of **8h** (78%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent. Light yellow solid, m.p. 144-145 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.39-7.35 (m, 2H), 7.24 (s, 1H), 7.00 (s, 1H), 6.29 (d, *J* = 5.5 Hz, 1H), 6.01 (d, *J* = 5.5 Hz, 1H), 5.73 (q, *J* = 7.0 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.67-2.44 (m, 2H), 1.66 (d, *J* = 7.0 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 171.2, 153.6, 144.3, 138.4, 131.4, 126.6, 122.1, 119.2, 116.0, 101.2, 61.2, 49.2, 24.7, 19.4, 14.6, 14.5 ppm. **HRMS (ESI)** *m/z* calcd for $C_{16}H_{21}N_2O_3S$ $[M+H]^+$: 321.1267, found 321.1268.

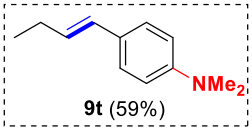
3. Control Experiments for Mechanistic Studies

3.1 Control Experiments Demonstrating the Significance of the Remote Activating Strategy in the Three-component Formal Metathesis (Results Shown in Scheme 1)



1q-t + 2a (1.5 equiv) → 6q-t (1)

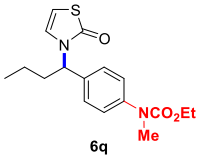
Entry	Ether 1	RAG	Yield of 6
1	1q	$N(Me)CO_2Et$	**6q** (23%)
2	1r	NHAc	**6r** (53%)
3	1s	OMe	**6s** (68%)
4	1t	NMe_2	**6t** (trace)



9t (59%)

To a reaction tube charged with *p*-TsOH-H_2O (**3a**, 57.1 mg, 0.3 mmol, 1 equiv) was added a solution of **1q-t** (0.3 mmol, 1 equiv) and 2-methoxythiazole (**2a**, 43 μL, 51.8 mg, 0.45 mmol, 1.5 equiv) in anhydrous MeCN (2 mL, 0.15 M of **1**) via a syringe under argon (1 atm), and the reaction mixture was stirred for 12 hours at 40 °C (oil bath temperature). After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent on silica gel to afford corresponding thiazol-2(3*H*)-one products **6q-t**.

Ethyl methyl(4-(1-(2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6q):

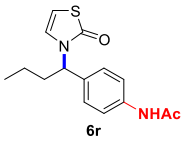


6q

The three-component formal metathesis of 0.3 mmol of ethyl methyl(4-(1-ethoxybutyl)phenyl)carbamate (**1q**, 83.8 mg), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 22.8 mg of **6q** (23%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:1, *v*/*v*) as the eluent.

Light yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.29-7.23 (m, 4H), 6.56 (d, *J* = 5.2 Hz, 1H), 6.10 (d, *J* = 5.2 Hz, 1H), 5.46 (t, *J* = 8.1 Hz, 1H), 4.18 (q, *J* = 7.0 Hz, 2H), 3.29 (s, 3H), 2.13-1.97 (m, 2H), 1.41-1.34 (m, 2H), 1.25 (t, *J* = 7.3 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 172.1, 155.5, 143.0, 136.8, 127.5, 125.6, 121.7, 101.5, 61.8, 56.5, 37.3, 35.5, 19.5, 14.6, 13.6 ppm. **HRMS (ESI)** *m/z* calcd for $C_{17}H_{23}N_2O_3S$ $[M+H]^+$: 335.1424, found 335.1421.

Ethyl methyl(4-(1-(2-oxothiazol-3(2*H*)-yl)butyl)phenyl)carbamate (6r)

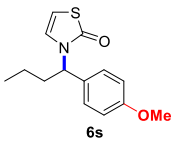


6r

The three-component formal metathesis of 0.3 mmol of *N*-(4-(1-ethoxybutyl)phenyl)acetamide (**1r**, 70.6 mg, 0.3 mmol, 1 equiv), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 45.9 mg of **6r** (53%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (3:2, *v*/*v*) as the eluent.

Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.32 (s, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.57 (d, *J* = 5.5 Hz, 1H), 6.11 (d, *J* = 5.5 Hz, 1H), 5.40 (dd, *J* = 6.8 Hz, 2.6 Hz, 1H), 2.15 (s, 3H), 2.09-1.95 (m, 2H), 1.38-1.29 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 172.3, 168.9, 138.0, 134.9, 127.5, 121.9, 120.2, 101.6, 56.9, 35.5, 24.3, 19.4, 13.6 ppm. **HRMS (ESI)** *m/z* calcd for $C_{15}H_{19}N_2O_2S$ $[M+H]^+$: 291.1162, found 291.1159.

3-(1-(4-Methoxyphenyl)butyl)thiazol-2(3*H*)-one (6s)

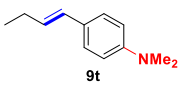


6s

The three-component formal metathesis of 0.3 mmol of 1-(1-ethoxybutyl)-4-methoxybenzene (**1s**, 62.5 mg, 0.3 mmol, 1 equiv), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 53.9 mg of **6s** (68%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (5:1, *v*/*v*) as the eluent.

Light yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.25 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.52 (d, *J* = 5.5 Hz, 1H), 6.05 (d, *J* = 5.5 Hz, 1H), 5.43 (dd, *J* = 6.8 Hz, 2.2 Hz, 1H), 3.78 (s, 3H), 2.10-1.95 (m, 2H), 1.40-1.30 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 171.9, 159.1, 131.4, 128.3, 121.7, 114.0, 101.2, 56.5, 55.1, 35.4, 19.4, 13.6 ppm. **HRMS (ESI)** *m/z* calcd for $C_{14}H_{18}NO_2S$ $[M+H]^+$: 264.1053, found 264.1061.

(*E*)-1-(But-1-en-1-yl)-*N*,*N*-dimethylaniline (9t)

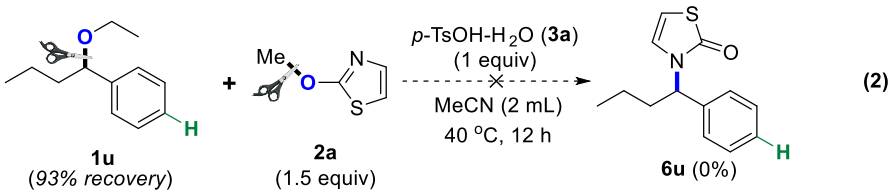


9t

The three-component formal metathesis of 0.3 mmol of 4-(1-ethoxybutyl)-*N*,*N*-dimethylaniline (**1t**, 62.5 mg, 0.3 mmol, 1 equiv), 0.3 mmol of *p*-TsOH-H_2O (**3a**, 57.1 mg) and 0.45 mmol of 2-methoxythiazole (**2a**, 43 μL, 51.8 mg) afforded 30.8 mg of **9t** (59%) after flash chromatography on silica gel using petroleum ether and ethyl acetate (15:1, *v*/*v*) as the eluent, while no thiazol-2(3*H*)-one **6t** could be acquired.

Yellow oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.24 (d, *J* = 8.8 Hz, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 6.29 (d, *J* = 15.8 Hz, 1H), 6.06 (dt, *J* = 15.8 Hz, 6.5 Hz, 1H), 2.93 (s, 3H), 2.19 (quintet, *J* = 7.2

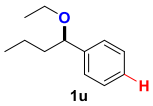
Hz, 2H), 1.07 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 149.6, 128.6, 128.4, 126.7, 126.7, 112.7, 40.7, 26.1, 14.0 ppm. **HRMS (ESI)** *m/z* calcd for $C_{12}H_{18}N$ $[M+H]^+$: 176.1434, found 176.1433.



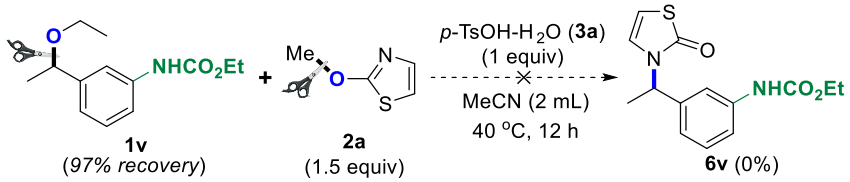
(2)

To a reaction tube charged with *p*-TsOH-H_2O (**3a**, 57.1 mg, 0.3 mmol, 1 equiv) was added a solution of (1-ethoxybutyl)benzene (**1u**, 53.5 mg, 0.3 mmol, 1 equiv) and 2-methoxythiazole (**2a**, 43 μL, 51.8 mg, 0.45 mmol, 1.5 equiv) in anhydrous MeCN (2 mL, 0.15 M of **1u**) via a syringe under argon (1 atm), and the reaction mixture was stirred for 12 hours at 40 °C (oil bath temperature). After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent on silica gel to recover 49.9 mg of **1u** (93%) while no thiazol-2(3*H*)-one **6u** was generated.

(1-Ethoxybutyl)benzene (1u)[1a]:



Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.34-7.23 (m, 5H), 4.20 (dd, *J* = 7.5 Hz, 1.7 Hz, 1H), 3.40-3.26 (m, 2H), 1.84-1.75 (m, 1H), 1.63-1.54 (m, 1H), 1.47-1.38 (m, 1H), 1.32-1.23 (m, 1H), 1.17 (t, *J* = 7.0 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 143.3, 128.2, 127.2, 126.5, 81.9, 64.0, 40.5, 19.1, 15.3, 13.9 ppm.

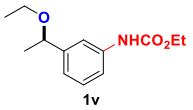


(3)

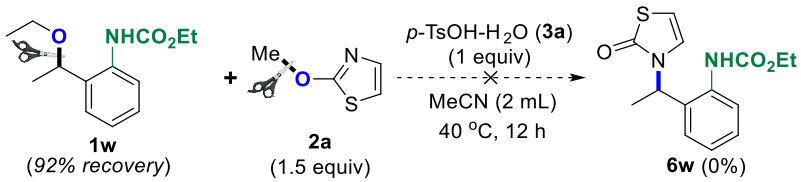
To a reaction tube charged with *p*-TsOH-H_2O (**3a**, 57.1 mg, 0.3 mmol, 1 equiv) was added a solution of ethyl (3-(1-ethoxyethyl)phenyl)carbamate (**1v**, 71.2 mg, 0.3 mmol, 1 equiv) and 2-methoxythiazole (**2a**, 43 μL, 51.8 mg, 0.45 mmol, 1.5 equiv) in anhydrous MeCN (2 mL, 0.15 M of **1v**) via a syringe under argon (1 atm), and the reaction mixture was stirred for 12 hours at 40

°C (oil bath temperature). After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent on silica gel to recover 68.8 mg of **1v** (97%) while no thiazol-2(3*H*)-one **6v** was generated.

Ethyl (3-(1-ethoxyethyl)phenyl)carbamate (1v):



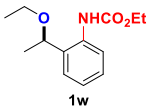
Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.37-7.33 (m, 2H), 7.27 (t, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.89 (s, 1H), 4.39 (q, *J* = 6.5 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.36 (q, *J* = 7.1 Hz, 2H), 1.42 (d, *J* = 6.5 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 153.6, 145.3, 138.1, 129.1, 120.9, 117.5, 116.2, 77.6, 63.9, 61.1, 24.1, 15.3, 14.5 ppm. **HRMS (ESI)** *m/z* calcd for $C_{13}H_{20}NO_3$ $[M+H]^+$: 238.1438, found 238.1434.



(4)

To a reaction tube charged with *p*-TsOH-H_2O (**3a**, 57.1 mg, 0.3 mmol, 1 equiv) was added a solution of ethyl (2-(1-ethoxyethyl)phenyl)carbamate (**1w**, 71.2 mg, 0.3 mmol, 1 equiv) and 2-methoxythiazole (**2a**, 43 μL, 51.8 mg, 0.45 mmol, 1.5 equiv) in anhydrous MeCN (2 mL, 0.15 M of **1w**) via a syringe under argon (1 atm), and the reaction mixture was stirred for 12 hours at 40 °C (oil bath temperature). After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate as the eluent on silica gel to recover 65.7 mg of **1w** (92%) while no thiazol-2(3*H*)-one **6w** was generated.

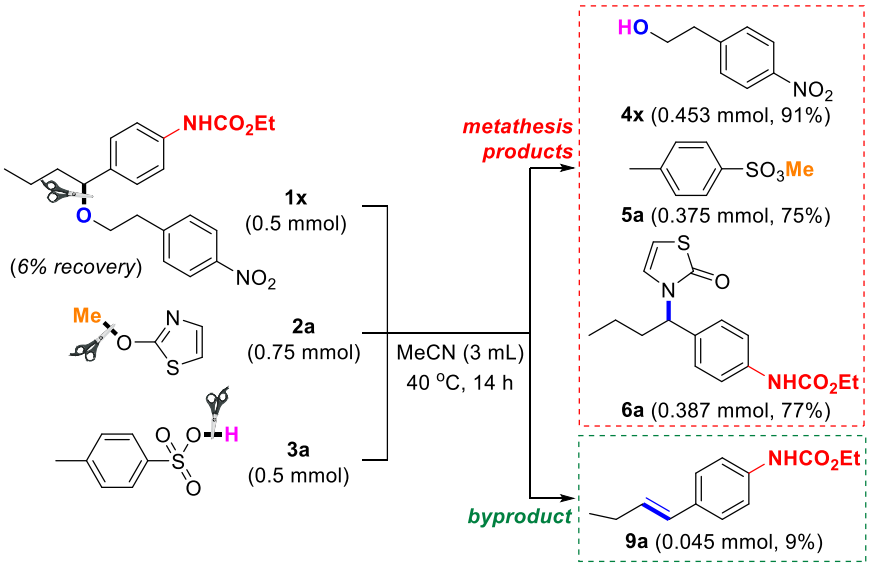
Ethyl (2-(1-ethoxyethyl)phenyl)carbamate (1w):



Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.62 (s, 1H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.4 Hz, 1H), 4.51 (q, *J* = 6.7 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.42 (q, *J* = 7.1 Hz, 2H), 1.50 (d, *J* = 6.8 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.0 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ =

153.8, 136.9, 129.3, 128.4, 128.2, 122.6, 119.9, 79.6, 64.2, 60.9, 21.4, 15.2, 14.6 ppm. **HRMS (ESI)** *m/z* calcd for $C_{13}H_{19}NO_3Na$ $[M+Na]^+$: 260.1257, found 260.1265.

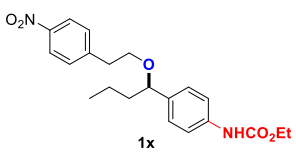
3.2 Control Experiments to Support the Proposed Mechanism (Results Shown in Scheme 2)



(5)

To a reaction tube charged with *p*-TsOH-H_2O (**3a**, 95.2 mg, 0.5 mmol, 1 equiv) was added a solution of ethyl (4-(1-(4-nitrophenethoxy)butyl)phenyl)carbamate (**1x**, 193.2 mg, 0.5 mmol, 1 equiv) and 2-methoxythiazole (**2a**, 72 μL, 86.4 mg, 0.75 mmol, 1.5 equiv) in anhydrous MeCN (3 mL, 0.167 M of **1x**) via a syringe under argon (1 atm), and the reaction mixture was stirred for 14 hours at 40 °C (oil bath temperature). After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (10:1 to 6:1 to 3:1 to 2:1, *v*/*v*) as the eluent on silica gel to recover 11.9 mg of ether **1x** (0.031 mmol, 6%) while obtain 75.7 mg of alcohol **4x** (0.453 mmol, 91%), 69.8 mg of sulfonate **5a** (0.375 mmol, 75%), 124.0 mg of thiazol-2(3*H*)-one **6a** (0.387 mmol, 77%) and 9.8 mg of alkene **9a** (0.045 mmol, 9%). All of the above yields were calculated according to their maximum theoretical yields (0.5 mmol = 100%).

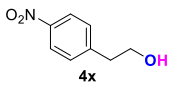
Ethyl (4-(1-(4-nitrophenethoxy)butyl)phenyl)carbamate (1x):



Light brown oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.11 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 4H), 7.12 (d, *J* = 8.6 Hz, 2H), 6.85 (s,

1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.13 (t, *J* = 7.5 Hz, 1H), 3.57-3.45 (m, 2H), 2.92 (t, *J* = 6.5 Hz, 2H), 1.79-1.70 (m, 1H), 1.58-1.49 (m, 1H), 1.38-1.28 (m, 4H), 1.24-1.15 (m, 1H), 0.85 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 153.7, 147.5, 146.4, 137.3, 137.3, 129.7, 127.2, 123.3, 118.6, 81.9, 68.2, 61.1, 40.1, 36.2, 18.8, 14.4, 13.8 ppm. **HRMS (ESI)** *m/z* calcd for $C_{21}H_{27}N_2O_5$ $[M+H]^+$: 387.1915, found 387.1912.

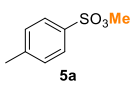
2-(4-Nitrophenyl)ethan-1-ol (4x)[2]:



4x

Yellow solid. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 8.14 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 3.91 (t, *J* = 6.5 Hz, 2H), 2.97 (q, *J* = 6.5 Hz, 2H), 2.23 (s, 1H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 146.9, 146.5, 129.8, 123.5, 62.7, 38.7 ppm.

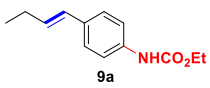
Methyl 4-methylbenzenesulfonate (5a)[3]:



5a

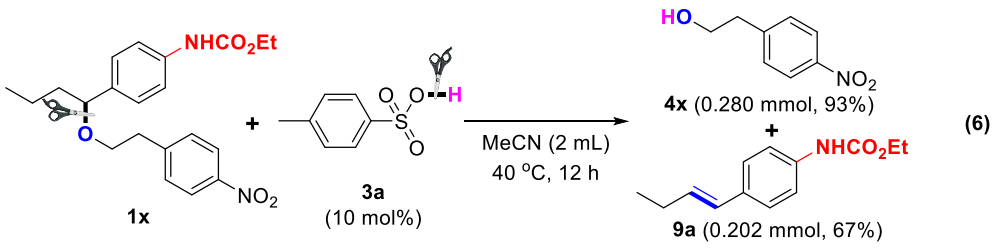
Colorless oil. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.79 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 3.73 (s, 3H), 2.45 (s, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 144.9, 132.0, 129.8, 128.0, 56.1, 21.5 ppm.

Ethyl (*E*)-(4-(but-1-en-1-yl)phenyl)carbamate (9a)[1a]:



9a

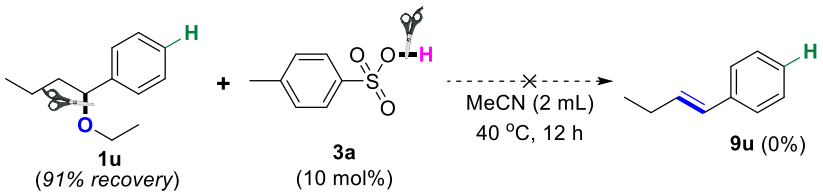
White solid, m.p. 69-70 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 7.32-7.25 (m, 4H), 6.72 (s, 1H), 6.31 (dt, *J* = 15.8 Hz, 1.5 Hz, 1H), 6.17 (dt, *J* = 15.8 Hz, 6.4 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.21 (quint-d, *J* = 7.5 Hz, 1.5 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.5 Hz, 3H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 153.6, 136.6, 133.2, 131.5, 128.0, 126.4, 118.6, 61.1, 26.0, 14.5, 13.6 ppm.



(6)

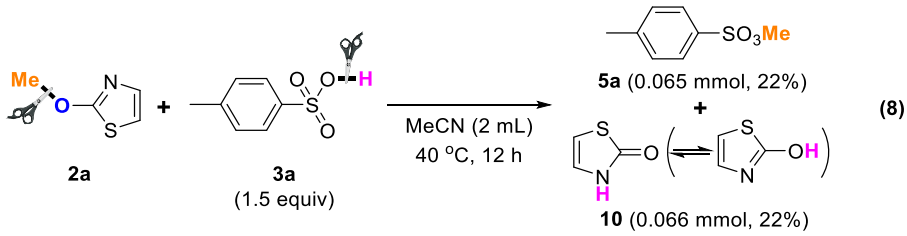
To a reaction tube charged with *p*-TsOH-H_2O (**3a**, 5.7 mg, 0.03 mmol, 10 mol%) was added a solution of ethyl (4-(1-(4-nitrophenethoxy)butyl)phenyl)carbamate (**1x**, 115.9 mg, 0.3 mmol, 1 equiv) in anhydrous MeCN (2 mL, 0.15 M of **1x**) via a syringe under argon (1 atm), and the reaction mixture was stirred for 12 hours at 40 °C (oil bath temperature). After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was

concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (10:1 to 6:1 to 3:1, *v*/*v*) as the eluent on silica gel to afford 46.8 mg of **4x** (0.280 mmol, 93%) and 44.3 mg of **9a** (0.202 mmol, 67%). Both yields were calculated according to their maximum theoretical yields (0.3 mmol = 100%).



(7)

To a reaction tube charged with *p*-TsOH-H_2O (**3a**, 5.7 mg, 0.03 mmol, 10 mol%) was added a solution of (1-ethoxybutyl)benzene (**1u**, 53.5 mg, 0.3 mmol, 1 equiv) in anhydrous MeCN (2 mL, 0.15 M of **1u**) via a syringe under argon (1 atm), and the reaction mixture was stirred for 12 hours at 40 °C (oil bath temperature). After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (10:1 to 6:1, *v*/*v*) as the eluent on silica gel to recover 48.5 mg of **1u** (91%) while no alkene **9a** was generated.

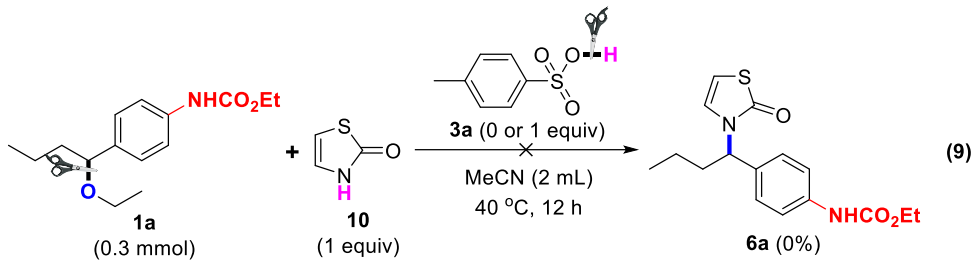


(8)

To a reaction tube charged with *p*-TsOH-H_2O (**3a**, 85.6 mg, 0.45 mmol, 1.5 equiv) was added a solution of 2-methoxythiazole (**2a**, 29 μL, 34.5 mg, 0.3 mmol, 1 equiv) in anhydrous MeCN (2 mL, 0.15 M of **2a**) via a syringe under argon (1 atm), and the reaction mixture was stirred for 12 hours at 40 °C (oil bath temperature). After quenched with Na_2CO_3 (aq.), the mixture was extracted with ethyl acetate. The combined organic phase was concentrated *in vacuo* to give dark residue, which was then purified by flash chromatography using petroleum ether and ethyl acetate (10:1 to 6:1 to 3:1 to 2:1, *v*/*v*) as the eluent on silica gel to afford 12.1 mg of **5a** (0.065 mmol, 22%) and 6.7 mg of **10** (0.066 mmol, 22%).

Thiazol-2(3*H*)-one (10)[4]:

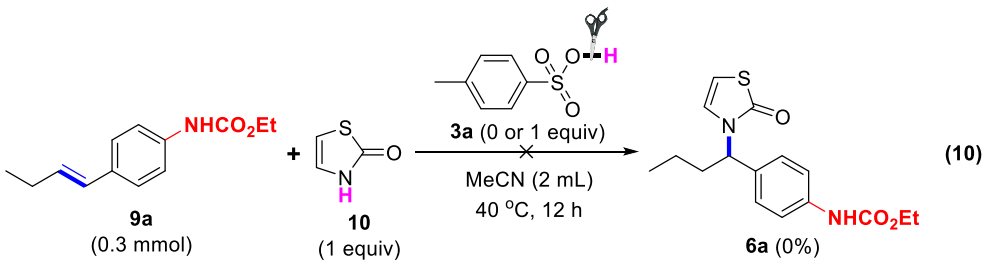
Yellow solid. **^{1}H NMR (DMSO-d_6, 400 MHz):** δ = 11.16 (s, 1H), 6.81 (dd, *J* = 5.4 Hz, 2.7 Hz, 1H), 6.34 (dd, *J* = 5.4 Hz, 1.6 Hz, 1H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 176.6, 121.0, 103.7 ppm.



(9)

To a reaction tube without any *p*-TsOH-H_2O was added a solution of ethyl (4-(1-ethoxybutyl)phenyl)carbamate (**1a**, 79.6 mg, 0.3 mmol, 1 equiv) and thiazol-2(3*H*)-one (**10**, 30.3 mg, 0.3 mmol, 1 equiv) in anhydrous MeCN (2 mL, 0.15 M of **1a**) via a syringe under argon (1 atm). Then the reaction mixture was stirred for 12 hours at 40 °C (oil bath temperature), and no thiazol-2(3*H*)-one **6a** could be observed on TLC.

To another reaction tube charged with *p*-TsOH-H_2O (**3a**, 57.1 mg, 0.3 mmol, 1 equiv) was added a solution of ethyl (4-(1-ethoxybutyl)phenyl)carbamate (**1a**, 79.6 mg, 0.3 mmol, 1 equiv) and thiazol-2(3*H*)-one (**10**, 30.3 mg, 0.3 mmol, 1 equiv) in anhydrous MeCN (2 mL, 0.15 M of **1a**) via a syringe under argon (1 atm). Then the reaction mixture was stirred for 12 hours at 40 °C (oil bath temperature), and no thiazol-2(3*H*)-one **6a** could be observed on TLC, either.

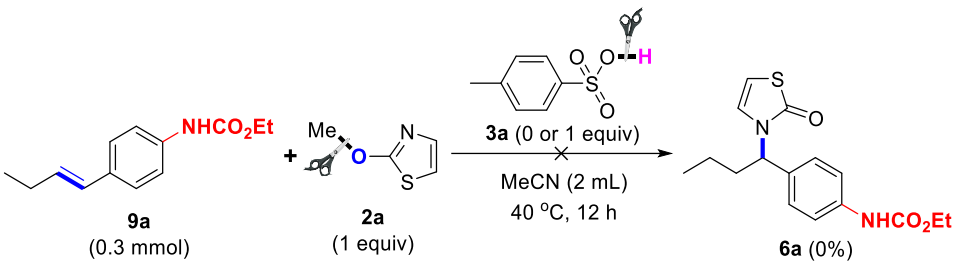


(10)

To a reaction tube without any *p*-TsOH-H_2O was added a solution of ethyl (*E*)-(4-(but-1-en-1-yl)phenyl)carbamate (**9a**, 65.8 mg, 0.3 mmol, 1 equiv) and thiazol-2(3*H*)-one (**10**, 30.3 mg, 0.3 mmol, 1 equiv) in anhydrous MeCN (2 mL, 0.15 M of **9a**) via a syringe under

argon (1 atm). Then the reaction mixture was stirred for 12 hours at 40 °C (oil bath temperature), and no thiazol-2(3*H*)-one **6a** could be observed on TLC.

To another reaction tube charged with *p*-TsOH-H_2O (**3a**, 57.1 mg, 0.3 mmol, 1 equiv) was added a solution of ethyl (*E*)-(4-(but-1-en-1-yl)phenyl)carbamate (**9a**, 65.8 mg, 0.3 mmol, 1 equiv) and thiazol-2(3*H*)-one (**10**, 30.3 mg, 0.3 mmol, 1 equiv) in anhydrous MeCN (2 mL, 0.15 M of **9a**) via a syringe under argon (1 atm). Then the reaction mixture was stirred for 12 hours at 40 °C (oil bath temperature), and no thiazol-2(3*H*)-one **6a** could be observed on TLC, either.



(11)

To a reaction tube without any *p*-TsOH-H_2O was added a solution of ethyl (*E*)-(4-(but-1-en-1-yl)phenyl)carbamate (**9a**, 65.8 mg, 0.3 mmol, 1 equiv) and 2-methoxythiazole (**2a**, 29 μL, 34.5 mg, 0.3 mmol, 1 equiv) in anhydrous MeCN (2 mL, 0.15 M of **9a**) via a syringe under argon (1 atm). Then the reaction mixture was stirred for 12 hours at 40 °C (oil bath temperature), and no thiazol-2(3*H*)-one **6a** could be observed on TLC.

To another reaction tube charged with *p*-TsOH-H_2O (**3a**, 57.1 mg, 0.3 mmol, 1 equiv) was added a solution of ethyl (*E*)-(4-(but-1-en-1-yl)phenyl)carbamate (**9a**, 65.8 mg, 0.3 mmol, 1 equiv) and 2-methoxythiazole (**2a**, 29 μL, 34.5 mg, 0.3 mmol, 1 equiv) in anhydrous MeCN (2 mL, 0.15 M of **9a**) via a syringe under argon (1 atm). Then the reaction mixture was stirred for 12 hours at 40 °C (oil bath temperature), and no thiazol-2(3*H*)-one **6a** could be observed on TLC, either.

4. Crystal Structure of 6a

Sample Preparation for Crystal Growth: The compound **6a** was dissolved in a solvent combined by petroleum ether and ethyl acetate (2:1, *v*/*v*), and kept for slow evaporation (7 days).

Crystal Structure of 6a: The crystal structure of **6a** (CDCC 2330166) with the ellipsoids drawn at the 30% probability level is shown in Figure S1.

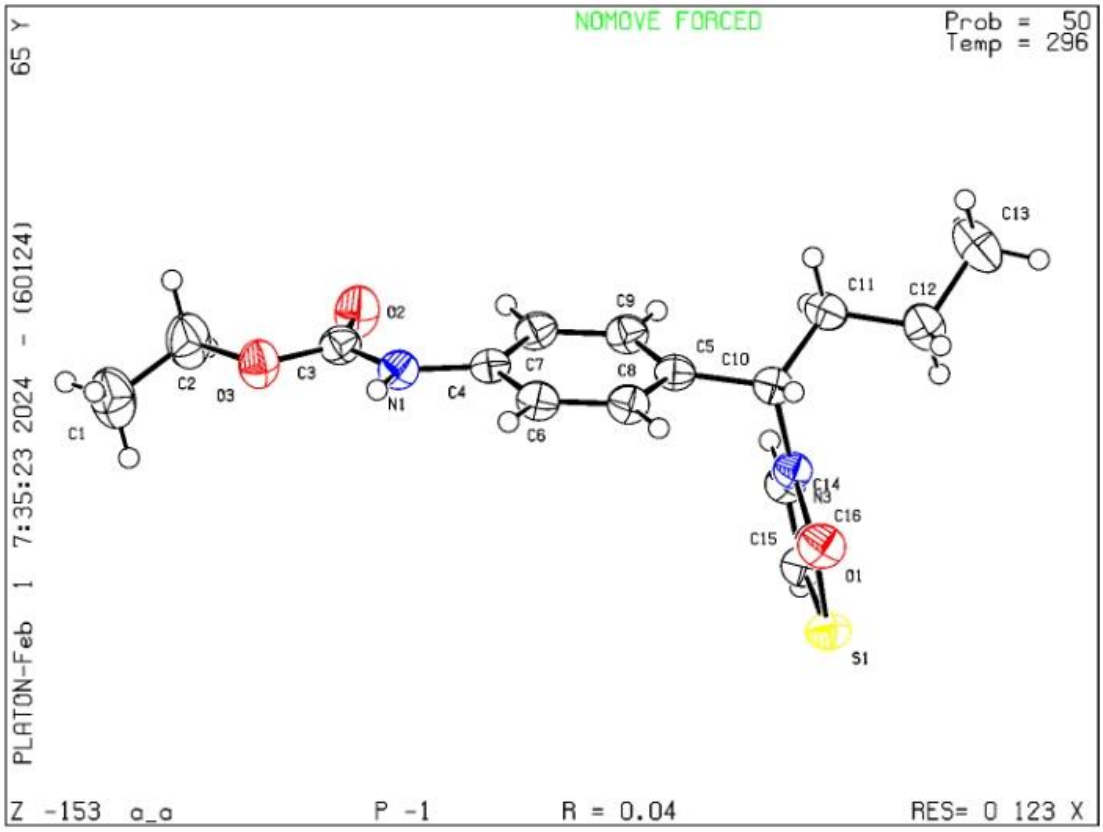


Figure S1. Crystal structure of 6a (CDCC 2330166).

Table S1. Crystal data and structure refinement for 6a.

Identification code	a_a	
Empirical formula	C16 H20 N2 O3 S	
Formula weight	320.40	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.3337(6) Å	α= 89.680(3)°.
	b = 8.9410(6) Å	β= 75.307(2)°.

	c = 11.3827(8) Å γ = 81.963(3)°.
Volume	811.95(10) $Å^3$
Z	2
Density (calculated)	1.311 Mg/m^3
Absorption coefficient	0.213 mm^{-1}
F(000)	340
Theta range for data collection	2.302 to 27.553°.
Index ranges	-10<=h<=10, -11<=k<=10, -14<=l<=14
Reflections collected	7501
Independent reflections	3664 [R(int) = 0.0391]
Completeness to theta = 25.242°	98.1 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3664 / 0 / 201
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0422, wR2 = 0.1146
R indices (all data)	R1 = 0.0470, wR2 = 0.1191
Extinction coefficient	n/a
Largest diff. peak and hole	0.235 and -0.211 $e.Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 6a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	5662(1)	2623(1)	3609(1)	42(1)
O(1)	8842(1)	2954(1)	2598(1)	45(1)
O(3)	8520(1)	10530(1)	8080(1)	47(1)
O(2)	6739(2)	11100(1)	6889(1)	51(1)
N(3)	6799(1)	5032(1)	2790(1)	32(1)
N(1)	8917(2)	9151(1)	6408(1)	36(1)
C(14)	5080(2)	5439(2)	3262(1)	35(1)
C(4)	8681(2)	8524(2)	5348(1)	32(1)
C(16)	7375(2)	3549(2)	2915(1)	34(1)
C(5)	8271(2)	7028(2)	3292(1)	34(1)
C(6)	9784(2)	7233(2)	4828(1)	37(1)
C(7)	7424(2)	9097(2)	4792(1)	37(1)
C(8)	9572(2)	6501(2)	3825(1)	37(1)
C(10)	7986(2)	6100(2)	2273(1)	35(1)

C(15)	4291(2)	4285(2)	3728(1)	39(1)
C(3)	7946(2)	10332(2)	7097(1)	38(1)
C(9)	7231(2)	8354(2)	3782(1)	38(1)
C(11)	7426(2)	6995(2)	1262(1)	40(1)
C(12)	7266(2)	5990(2)	235(2)	51(1)
C(13)	7044(3)	6871(3)	-875(2)	64(1)
C(2)	7625(3)	11763(2)	8908(2)	62(1)
C(1)	7838(3)	11441(3)	10130(2)	71(1)

Table S3. Bond lengths [Å] and angles [°] for 6a.

S(1)-C(15)	1.7264(15)
S(1)-C(16)	1.7597(15)
O(1)-C(16)	1.2269(17)
O(3)-C(3)	1.3449(19)
O(3)-C(2)	1.4437(19)
O(2)-C(3)	1.2107(18)
N(3)-C(16)	1.3652(17)
N(3)-C(14)	1.3931(17)
N(3)-C(10)	1.4832(17)
N(1)-C(3)	1.3546(18)
N(1)-C(4)	1.4027(19)
N(1)-H(1)	0.8600
C(14)-C(15)	1.336(2)
C(14)-H(14)	0.9300
C(4)-C(7)	1.394(2)
C(4)-C(6)	1.4007(19)
C(5)-C(9)	1.3936(19)
C(5)-C(8)	1.398(2)
C(5)-C(10)	1.516(2)
C(6)-C(8)	1.381(2)
C(6)-H(6)	0.9300
C(7)-C(9)	1.386(2)
C(7)-H(7)	0.9300
C(8)-H(8)	0.9300
C(10)-C(11)	1.529(2)
C(10)-H(10)	0.9800

C(15)-H(15)	0.9300
C(9)-H(9)	0.9300
C(11)-C(12)	1.522(2)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(13)	1.522(2)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(2)-C(1)	1.469(3)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(1)-H(1A)	0.9600
C(1)-H(1B)	0.9600
C(1)-H(1C)	0.9600

C(15)-S(1)-C(16)	91.36(7)
C(3)-O(3)-C(2)	116.23(13)
C(16)-N(3)-C(14)	114.65(12)
C(16)-N(3)-C(10)	120.47(11)
C(14)-N(3)-C(10)	124.72(11)
C(3)-N(1)-C(4)	127.09(12)
C(3)-N(1)-H(1)	116.5
C(4)-N(1)-H(1)	116.5
C(15)-C(14)-N(3)	113.45(13)
C(15)-C(14)-H(14)	123.3
N(3)-C(14)-H(14)	123.3
C(7)-C(4)-C(6)	118.56(14)
C(7)-C(4)-N(1)	124.27(12)
C(6)-C(4)-N(1)	117.18(12)
O(1)-C(16)-N(3)	125.84(14)
O(1)-C(16)-S(1)	125.41(11)
N(3)-C(16)-S(1)	108.75(10)
C(9)-C(5)-C(8)	117.55(14)
C(9)-C(5)-C(10)	123.06(13)
C(8)-C(5)-C(10)	119.28(12)

C(8)-C(6)-C(4)	120.54(13)
C(8)-C(6)-H(6)	119.7
C(4)-C(6)-H(6)	119.7
C(9)-C(7)-C(4)	120.16(13)
C(9)-C(7)-H(7)	119.9
C(4)-C(7)-H(7)	119.9
C(6)-C(8)-C(5)	121.33(13)
C(6)-C(8)-H(8)	119.3
C(5)-C(8)-H(8)	119.3
N(3)-C(10)-C(5)	109.49(11)
N(3)-C(10)-C(11)	110.69(12)
C(5)-C(10)-C(11)	116.01(12)
N(3)-C(10)-H(10)	106.7
C(5)-C(10)-H(10)	106.7
C(11)-C(10)-H(10)	106.7
C(14)-C(15)-S(1)	111.75(11)
C(14)-C(15)-H(15)	124.1
S(1)-C(15)-H(15)	124.1
O(2)-C(3)-O(3)	124.13(14)
O(2)-C(3)-N(1)	126.61(15)
O(3)-C(3)-N(1)	109.26(12)
C(7)-C(9)-C(5)	121.73(13)
C(7)-C(9)-H(9)	119.1
C(5)-C(9)-H(9)	119.1
C(12)-C(11)-C(10)	113.02(13)
C(12)-C(11)-H(11A)	109.0
C(10)-C(11)-H(11A)	109.0
C(12)-C(11)-H(11B)	109.0
C(10)-C(11)-H(11B)	109.0
H(11A)-C(11)-H(11B)	107.8
C(11)-C(12)-C(13)	112.90(16)
C(11)-C(12)-H(12A)	109.0
C(13)-C(12)-H(12A)	109.0
C(11)-C(12)-H(12B)	109.0
C(13)-C(12)-H(12B)	109.0
H(12A)-C(12)-H(12B)	107.8
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5

H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
O(3)-C(2)-C(1)	109.39(16)
O(3)-C(2)-H(2A)	109.8
C(1)-C(2)-H(2A)	109.8
O(3)-C(2)-H(2B)	109.8
C(1)-C(2)-H(2B)	109.8
H(2A)-C(2)-H(2B)	108.2
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 6a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	45(1)	33(1)	46(1)	7(1)	-9(1)	-4(1)
O(1)	38(1)	41(1)	51(1)	3(1)	-12(1)	8(1)
O(3)	49(1)	42(1)	46(1)	-8(1)	-18(1)	9(1)
O(2)	50(1)	44(1)	61(1)	-9(1)	-24(1)	14(1)
N(3)	31(1)	30(1)	34(1)	2(1)	-8(1)	0(1)
N(1)	32(1)	33(1)	41(1)	2(1)	-12(1)	1(1)
C(14)	32(1)	34(1)	37(1)	1(1)	-8(1)	2(1)
C(4)	30(1)	30(1)	38(1)	5(1)	-8(1)	-4(1)
C(16)	38(1)	32(1)	33(1)	1(1)	-11(1)	1(1)
C(5)	31(1)	34(1)	37(1)	5(1)	-7(1)	-5(1)
C(6)	31(1)	37(1)	42(1)	5(1)	-12(1)	2(1)
C(7)	34(1)	30(1)	45(1)	3(1)	-11(1)	1(1)
C(8)	33(1)	34(1)	40(1)	2(1)	-8(1)	2(1)
C(10)	31(1)	35(1)	36(1)	3(1)	-6(1)	-2(1)

C(15)	35(1)	40(1)	40(1)	2(1)	-7(1)	-2(1)
C(3)	37(1)	34(1)	43(1)	3(1)	-12(1)	-2(1)
C(9)	34(1)	35(1)	44(1)	5(1)	-14(1)	-1(1)
C(11)	42(1)	42(1)	37(1)	9(1)	-10(1)	-8(1)
C(12)	58(1)	58(1)	40(1)	2(1)	-14(1)	-9(1)
C(13)	62(1)	90(2)	40(1)	12(1)	-14(1)	-10(1)
C(2)	76(1)	52(1)	52(1)	-14(1)	-19(1)	16(1)
C(1)	83(2)	73(1)	53(1)	-13(1)	-21(1)	12(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for 6a.

	x	y	z	U(eq)
H(1)	9772	8740	6647	43
H(14)	4533	6418	3252	42
H(6)	10667	6866	5161	44
H(7)	6712	9980	5100	44
H(8)	10309	5639	3497	44
H(10)	9061	5487	1892	42
H(15)	3144	4367	4075	47
H(9)	6386	8750	3422	45
H(11A)	6352	7606	1606	48
H(11B)	8230	7674	933	48
H(12A)	6313	5456	527	62
H(12B)	8262	5244	-2	62
H(13A)	6058	7611	-648	96
H(13B)	6928	6189	-1487	96
H(13C)	8006	7370	-1190	96
H(2A)	6444	11889	8925	75
H(2B)	8054	12694	8635	75
H(1A)	7381	10535	10405	107
H(1B)	7263	12269	10678	107
H(1C)	9009	11306	10106	107

5. Density Functional Theory (DFT) Calculations

Computational details

All of the DFT calculations were performed with the Gaussian 09 program package.[5] The geometry optimization of all the minima involved were performed at the B3LYP level of theory[6] with Grimme's dispersion correction with Becke-Johnson Damping (D3-BJ)[7] and def2-SVP basis set for all atoms.[8] The structures of the reactants, intermediates, transition states, and products were fully optimized without any restriction. The vibrational frequencies were computed at the same level to check whether each optimized structure is an energy minimum or a transition state and to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298 K. IRC calculations[9] were used to confirm that the transition states found from the optimization calculations connect the related reactants and products. Single-point solvent calculations were performed at the B3LYP-D3BJ level of theory and def2-TZVP basis set[8] at the optimized geometries for all the intermediates and transition states. Solvation effects were taken into account by applying the SMD[10] solvation model with acetonitrile solvent in both geometry optimization and single-point energy calculations. The reported energies are Gibbs free energies in acetonitrile solution (ΔG_{sol}). In addition, single-point solvent calculations were also performed at the M06-2X level of theory[11] with Grimme's D3 empirical dispersion correction[12] and def2-TZVP basis set[8] at the optimized geometries for all the intermediates and transition states.

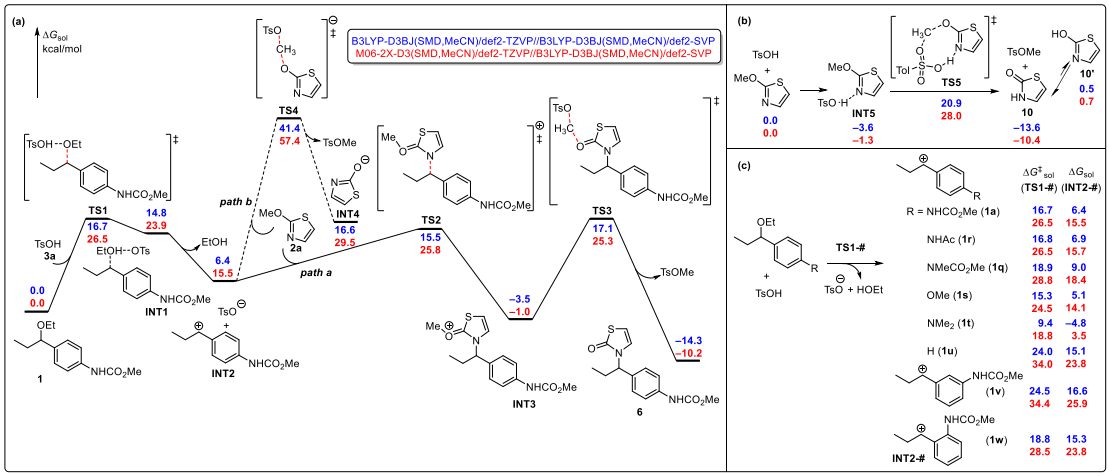


Figure S1 Free energy profiles for the three-component formal metathesis.

DFT-Computed Energies of All Stationary Points

Table S6. Sum of electronic and thermal Free Energies (*G*, in Hartree), thermal correction to Gibbs free energy (*CGFE*, in Hartree), electronic energy in single-point calculations in acetonitrile at the B3LYP level of theory ($E_{sol(B3LYP)}$, in Hartree), and free energies in acetonitrile at the B3LYP level of theory ($G_{sol(B3LYP)}$, in Hartree), electronic energy in single-point calculations in acetonitrile at the M06-2X level of theory ($E_{sol(M06-2X)}$, in Hartree), and free energies in acetonitrile at the M06-2X level of theory ($G_{sol(M06-2X)}$, in Hartree). For transition state structures, one imaginary frequency (Ifreq) was observed and given below. For all minimum structures, no imaginary frequency was observed.

Structure	G^a	$CGFE^a$	$E_{sol(B3LYP)}{}^b$	$G_{sol(B3LYP)}{}^b$	$E_{sol(M06-2X)}{}^c$	$G_{sol(M06-2X)}{}^c$	Ifreq[a]
1	-786.527049	0.257429	-787.662933	-787.405504	-787.259431	-787.002002	--
TsOH(**3a**)	-894.829016	0.104223	-895.702209	-895.597986	-895.422746	-895.318523	--
TS1	-1681.330663	0.386321	-1683.363153	-1682.976832	-1682.664567	-1682.278246	-57.28
INT1	-1681.333463	0.383833	-1683.363778	-1682.979945	-1682.666242	-1682.282409	--
INT2	-632.05936	0.191706	-632.953676	-632.76197	-632.619646	-632.42794	--
EtOH	-154.882109	0.05404	-155.122705	-155.068665	-155.03352	-154.97948	--
TsO^-	-894.375991	0.093201	-895.255839	-895.162638	-894.98159	-894.888389	--
2a	-683.229084	0.057104	-683.750607	-683.693503	-683.580284	-683.52318	--
TS2	-1315.27965	0.269861	-1316.710911	-1316.44105	-1316.204619	-1315.934758	-44.19
INT3	-1315.313658	0.274438	-1316.745632	-1316.471194	-1316.251922	-1315.977484	--
TS3	-2209.66848	0.386715	-2211.98772	-2211.601005	-2211.210698	-2210.823983	-551.06
6	-1275.646373	0.236053	-1276.997765	-1276.761712	-1276.532777	-1276.296724	--
TsOMe	-934.080711	0.12923	-935.018604	-934.889374	-934.712986	-934.583756	--
TS4	-1577.559545	0.164236	-1578.96456	-1578.800324	-1578.509004	-1578.344768	-548.41
INT4	-643.519005	0.018159	-643.968673	-643.950514	-643.823717	-643.805558	--
INT5	-1578.067317	0.180347	-1579.477523	-1579.297176	-1579.024199	-1578.843852	--
TS5	-1578.026042	0.182732	-1579.440974	-1579.258242	-1578.979874	-1578.797142	-553.18
10	-644.002428	0.031518	-644.455308	-644.42379	-644.306072	-644.274554	--
10'	-643.978824	0.031164	-644.43251	-644.401346	-644.287928	-644.256764	--
1r	-711.36358	0.253344	-712.407063	-712.153719	-712.026946	-711.773602	--
TS1-r	-1606.166765	0.381584	-1608.106547	-1607.724963	-1607.431475	-1607.049891	-66.69
INT2-r	-556.895543	0.187995	-557.69737	-557.509375	-557.387255	-557.19926	--
1q	-825.777833	0.283047	-826.981129	-826.698082	-826.553606	-826.270559	--
TS1-q	-1720.579043	0.413307	-1722.679307	-1722.266	-1721.956524	-1721.543217	-56.76
INT2-q	-671.306377	0.218811	-672.269268	-672.050457	-671.910755	-671.691944	--
1s	-617.936297	0.235025	-618.858055	-618.62303	-618.52322	-618.288195	--
TS1-s	-1512.740006	0.360093	-1514.556794	-1514.196701	-1513.927753	-1513.56766	-27.73
INT2-s	-463.469947	0.169077	-464.150609	-463.981532	-463.885444	-463.716367	--
1t	-637.34325	0.271444	-638.314763	-638.043319	-637.955029	-637.683585	--
TS1-t	-1532.155795	0.401311	-1534.027581	-1533.62627	-1533.373384	-1532.972073	-168.9

INT2-t	-482.892049	0.208397	-483.626004	-483.417607	-483.337064	-483.128667	--
1u	-503.520013	0.205799	-504.280456	-504.074657	-503.99624	-503.790441	--
TS1-u	-1398.308251	0.329324	-1399.963674	-1399.63435	-1399.384069	-1399.054745	-15.89
INT2-u	-349.037715	0.139539	-349.556752	-349.417213	-349.34263	-349.203091	--
1v	-786.527935	0.257022	-787.663273	-787.406251	-787.259899	-787.002877	--
TS1-v	-1681.318902	0.383924	-1683.349045	-1682.965121	-1682.650447	-1682.266523	-26.71
INT2-v	-632.043619	0.190968	-632.937428	-632.74646	-632.60323	-632.412262	--
1w	-786.530237	0.258716	-787.66465	-787.405934	-787.260072	-787.001356	--
TS1-w	-1681.328198	0.384984	-1683.358935	-1682.973951	-1682.659387	-1682.274403	-22.63
INT2-w	-632.046802	0.192525	-632.940741	-632.748216	-632.606583	-632.414058	--

[a] B3LYP-D3(BJ)(SMD, MeCN)/def2-SVP.

[b] B3LYP-D3(BJ)(SMD, MeCN)/def2-TZVP//B3LYP-D3(BJ)(SMD, MeCN)/def2-SVP.

[c] M06-2X-D3(SMD, MeCN)/def2-TZVP//B3LYP-D3(BJ)(SMD, MeCN)/def2-SVP.

The coordinates of all stationary points (Å)

1

C	1.24638200	0.33255600	0.07601500
C	0.80078800	-0.49064400	-0.96856800
C	-0.55723100	-0.72630800	-1.16561600
C	-1.51730900	-0.13774300	-0.32045100
C	-1.08138100	0.68819400	0.73019300
C	0.28603600	0.90814500	0.91507000
H	1.53401600	-0.96095600	-1.62748500
H	-0.89018300	-1.37422700	-1.98127200
H	-1.81195200	1.14354400	1.39425600
H	0.61058400	1.54735000	1.74157300
C	2.72550500	0.63036600	0.25275800
H	2.89888000	0.90134500	1.31399100
C	3.17481800	1.80628800	-0.62050200
H	2.51907400	2.66340600	-0.39593900
H	2.99182200	1.53880500	-1.67596500
C	4.63759200	2.18628900	-0.41303900
H	5.29752100	1.33587700	-0.64104200
H	4.92637600	3.02936300	-1.06115400
H	4.82568100	2.48579300	0.63200700
N	-2.86600600	-0.42125100	-0.58039400
H	-3.05035300	-1.03217400	-1.37116300
C	-3.97056100	0.01934300	0.09416600
O	-3.98832400	0.75336500	1.06269900
O	-5.07717300	-0.49147500	-0.48405200
C	-6.32327400	-0.12254600	0.10714400
H	-7.09984900	-0.62197300	-0.48582000
H	-6.37933800	-0.45808600	1.15406900
H	-6.47019500	0.96780600	0.07212500
O	3.53604800	-0.48235800	-0.08516300
C	3.51496400	-1.53732700	0.85842200
H	2.48281300	-1.91278200	0.99921600
H	3.85726200	-1.16438900	1.84506500
C	4.41622700	-2.65077400	0.36710400
H	5.44871100	-2.28874300	0.23491900
H	4.42980800	-3.48044300	1.09151800
H	4.06162600	-3.04203300	-0.60019100

TsOH(**3a**)

S	1.90026100	-0.00739300	-0.12278300
C	0.12566800	-0.00496200	-0.09162700
C	-0.55008200	1.21750200	-0.05690000
C	-0.56341300	-1.22189100	-0.08070500
C	-1.94356400	1.21284900	-0.00404000
H	0.00523000	2.15658200	-0.07548400
C	-1.95532300	-1.20398200	-0.02960900
H	-0.01558200	-2.16455500	-0.11844300
C	-2.66711000	0.00851300	0.01202500
H	-2.48176300	2.16337700	0.02202400
H	-2.50341500	-2.14963800	-0.02412800
O	2.38319900	1.20085600	-0.78027900
O	2.37592400	-1.32921100	-0.53102000
O	2.29796300	0.21472400	1.44763000
H	2.17365800	-0.62567100	1.93362100
C	-4.16993700	0.00404300	0.06676900
H	-4.57559900	1.02414400	0.12135900

H	-4.59255100	-0.48941900	-0.82430200
H	-4.52827400	-0.55991700	0.94374600

TS1

C	-1.37473100	-2.10514000	-0.03218200
C	-0.97478800	-1.66172400	-1.32752700
C	0.34852800	-1.42749600	-1.60743300
C	1.34029900	-1.61300800	-0.60993500
C	0.96839700	-2.08024300	0.67670900
C	-0.36260900	-2.31019800	0.94854700
H	-1.72146600	-1.47969200	-2.09709200
H	0.64791400	-1.05160600	-2.58684200
H	1.73108500	-2.22814400	1.43544500
H	-0.65867400	-2.64320400	1.94593800
C	-2.72258100	-2.26484100	0.32658200
H	-2.91566200	-2.65975600	1.32704900
C	-3.86772900	-2.18207200	-0.61434200
H	-3.64136500	-2.86473500	-1.45520100
N	2.63031700	-1.29907700	-0.95767500
H	2.76087700	-0.91067800	-1.88936000
C	3.76199900	-1.30871400	-0.16054200
O	3.83534800	-1.73411000	0.97085800
O	4.77584100	-0.77237600	-0.84737000
O	-2.97224500	-0.19540400	1.35677800
S	-1.29475900	1.90571700	-1.31664900
O	-0.84168900	1.72634200	-2.71655400
O	-1.80678700	3.26095600	-0.98934400
O	-2.26909000	0.82768700	-0.89903200
H	-2.59177300	0.21680700	0.52863900
C	0.16756400	1.68719300	-0.28137200
C	0.04629100	1.38067300	1.07809900
C	1.42799600	1.91913000	-0.83584400
C	1.19081900	1.30512300	1.87146800
H	-0.93067600	1.17434500	1.51607500
C	2.56646400	1.84763100	-0.02911800
H	1.50948100	2.14543500	-1.90018200
C	2.46949600	1.54155300	1.33674500
H	1.09149700	1.05376700	2.93118600
H	3.55053700	2.02230100	-0.47154700
H	-3.87063600	-1.17753100	-1.07267100
C	-4.18670500	0.50123000	1.60469800
H	-4.86703600	0.41179600	0.73691800
H	-4.67866900	0.00824400	2.45925400
C	3.69520000	1.43714400	2.20511500
H	4.56937300	1.89972500	1.72358900
H	3.53708100	1.92441600	3.18030400
H	3.94018200	0.38044100	2.40124400
C	6.04046200	-0.70948400	-0.17588600
H	6.36249000	-1.71162900	0.14241400
H	6.74746000	-0.30006700	-0.90724400
H	5.98002100	-0.04771700	0.69993000
C	-5.21672800	-2.53360200	0.00271900
H	-6.02062400	-2.43806200	-0.74262800
H	-5.22045600	-3.57094600	0.37389800
H	-5.45788900	-1.87311700	0.84814300
C	-3.93457500	1.97275800	1.90557800
H	-3.42610900	2.45964600	1.05819600
H	-4.88876900	2.49487300	2.08725200
H	-3.30368400	2.08690800	2.80226000

INT1

C	1.39473600	2.19436300	-0.08493600
C	0.98341600	1.66734500	-1.35199000
C	-0.33541200	1.39507900	-1.59726500
C	-1.31676400	1.61520500	-0.59179300
C	-0.93964600	2.17741200	0.65941600
C	0.38492900	2.45233500	0.89559700
H	1.72330000	1.45296700	-2.11938800
H	-0.64033900	0.95015900	-2.54492400
H	-1.69655900	2.35416000	1.41767300
H	0.68901000	2.85619600	1.86388400
C	2.73077300	2.37808700	0.25010900
H	2.93291600	2.78649800	1.24487100
C	3.88635200	2.13791700	-0.64401700
H	3.75417600	2.78684300	-1.53177900
N	-2.59463000	1.24022700	-0.89308600
H	-2.73098900	0.79703800	-1.79984100
C	-3.72732000	1.29708500	-0.09022200
O	-3.79552800	1.79484400	1.00990800
O	-4.73683000	0.71329100	-0.73868400
O	2.97992700	0.11912500	1.54468000
S	1.33397500	-1.81189200	-1.33281500
O	0.92683100	-1.55643200	-2.73660900
O	1.82719500	-3.18808200	-1.06825000
O	2.29322900	-0.76324800	-0.82388400
H	2.63042900	-0.20933000	0.67697800
C	-0.16592400	-1.64620700	-0.34140000
C	-0.11535300	-1.22910500	0.99217400

C	-1.38505600	-2.02187900	-0.91186500
C	-1.28912000	-1.19001300	1.74513300
H	0.82737700	-0.91059200	1.43859500
C	-2.55162600	-1.98729300	-0.14437300
H	-1.41585300	-2.32742100	-1.95925900
C	-2.52436100	-1.57608600	1.19699500
H	-1.24728100	-0.84796800	2.78308900
H	-3.50365000	-2.27407500	-0.59837000
H	3.79921900	1.11111400	-1.04251900
C	4.10617000	-0.69084600	1.83402700
H	4.86461500	-0.60573700	1.03042600
H	4.56982600	-0.29076500	2.75216900
C	-3.77768800	-1.52872800	2.03017600
H	-4.64948400	-1.89289100	1.46777000
H	-3.67305700	-2.14621400	2.93771400
H	-3.98820100	-0.49973000	2.36271900
C	-6.01233900	0.72198700	-0.08269600
H	-6.34117700	1.75413700	0.10737900
H	-6.70531000	0.22573100	-0.77226900
H	-5.96482100	0.17047500	0.86628400
C	5.24289500	2.38320500	0.00619400
H	6.05846700	2.16993500	-0.70099900
H	5.34233900	3.43058100	0.33345300
H	5.37832200	1.73911300	0.88764900
C	3.73324800	-2.15599400	2.02379900
H	3.26288800	-2.55832400	1.11222600
H	4.62956900	-2.75860000	2.24823500
H	3.02304200	-2.27381900	2.85919100

INT2

C	-2.11774800	0.24720100	0.20885800
C	-1.65454100	-1.11509600	0.18307400
C	-0.31942200	-1.39553100	0.11542300
C	0.64520500	-0.33990100	0.06735400
C	0.21199000	1.01832000	0.09158300
C	-1.12893100	1.29088500	0.15850800
H	-2.37319500	-1.93431800	0.21543900
H	0.03398300	-2.42853900	0.09631600
H	0.94690000	1.81725100	0.05440200
H	-1.46862200	2.32880100	0.17547700
N	1.95023800	-0.70745500	-0.00274100
H	2.14115200	-1.70919400	-0.02378000
C	3.08435100	0.11141200	-0.05218100
O	3.08458400	1.31822700	-0.04040500
O	4.16005100	-0.66846200	-0.11314100
C	5.43133000	-0.00268300	-0.16908700
H	6.18360600	-0.79882300	-0.21180200
H	5.49498800	0.62962000	-1.06655800
H	5.58121900	0.61493700	0.72829200
C	-3.45339100	0.59568000	0.27786400
H	-3.67512100	1.67019200	0.27624100
C	-4.62980700	-0.29057700	0.34149800
C	-5.62676100	0.00613700	-0.79374100
H	-5.12909400	-0.06340700	1.30453000
H	-4.35618500	-1.35362000	0.35632200
H	-6.52341600	-0.61903200	-0.66982600
H	-5.93829100	1.06233200	-0.78763700
H	-5.18032000	-0.21722600	-1.77476700

EtOH

O	-1.15358100	-0.39751200	0.00000200
H	-1.98416200	0.09923000	-0.00001200
C	-0.08844700	0.53995600	0.00000100
C	1.22336300	-0.21899000	-0.00000100
H	-0.13689800	1.20050200	0.88963900
H	-0.13689900	1.20050400	-0.88963500
H	2.07673900	0.47774400	-0.00001400
H	1.30019300	-0.86183100	0.89234100
H	1.30017700	-0.86184700	-0.89233200

TsO^-

S	-1.97630800	-0.00114400	0.00917500
C	-0.16424800	0.00367700	-0.05208900
C	0.53537500	1.21189000	-0.04173000
C	0.53914000	-1.20606900	-0.04189100
C	1.93349700	1.20896500	-0.01335800
H	-0.02304000	2.14995600	-0.06649600
C	1.93387500	-1.20076300	-0.01331500
H	-0.01742600	-2.14534800	-0.06768700
C	2.65655300	0.00615500	0.00396200
H	2.47516200	2.15933500	-0.00813200
H	2.47778600	-2.15028000	-0.00837500
O	-2.38980400	1.27158000	-0.64578100
O	-2.29623900	-0.05518800	1.46351100
O	-2.38448300	-1.22503300	-0.73643200
C	4.16307700	-0.00412000	0.03155300
H	4.57256400	1.01604300	0.06990900
H	4.54181900	-0.55777100	0.90709800

H	4.57465600	-0.50290700	-0.86229200

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C	0.37761200	-0.08390100	-0.00007000
C	-1.24571400	1.40459900	0.00007500
C	-2.03194200	0.29003600	-0.00001400
S	-1.02938400	-1.14169800	0.00004000
H	-1.62788600	2.42742300	0.00011200
H	-3.11870300	0.21724600	-0.00003700
N	0.11799700	1.18847200	-0.00011700
O	1.57684100	-0.64705900	-0.00011600
C	2.70069900	0.24196800	0.00010900
H	3.59193600	-0.39726700	0.00113600
H	2.69070600	0.87975000	-0.89717800
H	2.68945700	0.88098400	0.89647500

TS2

C	-2.04121400	1.63818100	-0.75631600
H	-2.47727200	0.98653300	-1.52008500
O	-3.40992300	-1.48398300	-0.93036300
C	-3.26485900	-2.72758500	-1.62335900
H	-3.93448000	-2.67762500	-2.48991100
H	-2.22610300	-2.86139600	-1.96679000
H	-3.56292300	-3.56825900	-0.97581700
C	-2.70474400	-1.28405200	0.17014900
C	-1.91917900	-0.16829700	1.91537000
C	-1.19828000	-1.30968800	2.09691200
H	-1.85904300	0.71418300	2.55408900
H	-0.48460700	-1.55360400	2.88254100
N	-2.76083500	-0.15837800	0.82519000
S	-1.58574200	-2.46769200	0.84715800
C	-2.90591300	2.72623300	-0.25748700
H	-2.66664100	3.57791700	-0.93177500
H	-2.59276300	3.05904500	0.74371200
C	-0.67028200	1.47881600	-0.51909200
C	0.03165700	0.44051100	-1.20177800
C	0.05643400	2.26973400	0.42195900
C	1.36693100	0.19452700	-0.97637600
H	-0.51475000	-0.17771200	-1.91772900
C	1.38942200	2.03658400	0.65084900
H	-0.44788200	3.06503400	0.97183600
C	2.07128000	0.99247200	-0.03651200
H	1.88540000	-0.60327200	-1.50030600
H	1.94280600	2.64056600	1.37320000
N	3.39478000	0.81401700	0.26351200
H	3.79383200	1.44942500	0.95259800
C	-4.40251600	2.43928000	-0.32034000
H	-4.97723200	3.33344500	-0.03674300
H	-4.70701700	2.14559700	-1.33768300
H	-4.66272000	1.61826500	0.36273900
C	4.27479100	-0.13579400	-0.24365900
O	4.01197400	-0.98114000	-1.06713500
O	5.46604000	0.03846300	0.33230500
C	6.50774400	-0.85952400	-0.07386900
H	6.70416700	-0.76222700	-1.15175600
H	7.39556500	-0.56777000	0.49955400
H	6.23356600	-1.89966200	0.15572600

INT3

C	1.72369700	1.15035900	0.40604100
H	1.94442600	0.92027900	1.45482000
O	3.50832000	-0.76736000	1.48081700
C	4.39366800	-1.75562600	2.05523300
H	4.40869800	-1.55069000	3.13076500
H	3.99630500	-2.76422000	1.86618000
H	5.40311300	-1.63962400	1.63271800
C	3.28796200	-0.77881100	0.20156200
C	2.35114000	-0.05671000	-1.74567500
C	3.09847000	-1.07174700	-2.23087100
H	1.69892800	0.61024600	-2.30499800
H	3.19313600	-1.40805000	-3.26210700
N	2.46289400	0.10036200	-0.36847500
S	3.97786900	-1.87329400	-0.95219200
C	2.31437700	2.52487900	0.07875500
H	2.14553700	2.76557400	-0.98310400
H	3.40567700	2.45240400	0.21280200
C	0.23516800	0.96779300	0.18627200
C	-0.45004200	0.00676900	0.94224800
C	-0.48696700	1.69083900	-0.77405100
C	-1.80912700	-0.24221200	0.75815500
H	0.09429300	-0.56818400	1.69690200
C	-1.84571300	1.45820500	-0.96840500
H	0.00619400	2.45056500	-1.38290100
C	-2.52544900	0.48729400	-0.20910900
H	-2.32103500	-0.99186900	1.35611000
H	-2.39578900	2.03303800	-1.71789100
N	-3.88786100	0.30706900	-0.46442500
H	-4.28984900	0.89588600	-1.18876700

C	1.75569200	3.62580600	0.97481200
H	2.24663400	4.58592000	0.75281200
H	0.67279400	3.76102900	0.83220000
H	1.92870500	3.39589300	2.03890900
C	-4.75480800	-0.56811100	0.13562800
O	-4.49181300	-1.35775100	1.02015600
O	-5.97689600	-0.42479100	-0.41136200
C	-7.00410600	-1.27059200	0.10936100
H	-7.16272500	-1.08330400	1.18230700
H	-7.91400800	-1.02173600	-0.45096000
H	-6.75282900	-2.33205700	-0.03706000

TS3

C	1.50268500	-2.43409100	-0.12341300
H	1.15780300	-2.53692800	0.91287100
O	-0.91722700	-1.53447100	1.08786000
C	-0.69008700	-1.26931300	-0.11762600
C	0.46756300	-1.25216300	-2.11749800
C	-0.60808500	-0.53658700	-2.50561600
H	1.33162500	-1.52089300	-2.72193200
H	-0.80890700	-0.10559700	-3.48490600
N	0.42087400	-1.65876300	-0.78736800
S	-1.74702900	-0.34216700	-1.18937300
C	1.59562200	-3.83363900	-0.73880400
H	1.90348800	-3.76279300	-1.79471300
H	0.57858100	-4.25810300	-0.73987000
C	2.77967100	-1.61309800	-0.11241900
C	2.96369600	-0.64968500	0.88895000
C	3.77272200	-1.73827000	-1.09459400
C	4.08944100	0.17268000	0.92412800
H	2.20226100	-0.53511200	1.66567700
C	4.90465400	-0.92716400	-1.07463800
H	3.67239200	-2.47720100	-1.89178100
C	5.07856800	0.04024700	-0.06776900
H	4.21114800	0.91161100	1.71221800
H	5.67096000	-1.03908800	-1.84628700
N	6.24159500	0.81642300	-0.11446900
H	6.88206900	0.61771100	-0.87820800
C	2.53941500	-4.75320600	0.03009400
H	2.53262800	-5.76511100	-0.40422200
H	3.57702900	-4.38602300	0.00846600
H	2.23622400	-4.83771800	1.08670400
C	6.62756900	1.81850900	0.73496800
O	6.01989900	2.22182600	1.70633500
O	7.81431300	2.31017900	0.32878000
C	8.35897100	3.37138000	1.11482000
H	8.53507600	3.04483700	2.15105800
H	9.31173200	3.64026000	0.64177200
H	7.68617000	4.24245500	1.12218100
S	-5.33639000	0.06056700	1.72028700
O	-5.62210400	-1.31314800	1.23899300
O	-4.12630000	0.09402400	2.65565300
O	-6.47268500	0.78880100	2.31816800
C	-2.47261800	-0.78698600	1.83618900
H	-3.13756200	-1.40151300	1.23486700
H	-2.19880000	0.21788900	1.53323900
H	-2.21145400	-1.12550200	2.83384000
C	-4.79766000	0.98827600	0.27494200
C	-5.14721700	0.54693800	-1.00152000
C	-4.03859100	2.15257000	0.43843900
C	-4.72151500	1.26733900	-2.12015900
H	-5.72853700	-0.36968800	-1.11237800
C	-3.61616800	2.86023200	-0.68557500
H	-3.76481700	2.48800600	1.44082200
C	-3.94191500	2.42629500	-1.98332900
H	-4.98782300	0.91420100	-3.12003600
H	-3.01057200	3.76165000	-0.55747900
C	-3.42616300	3.16361500	-3.18988100
H	-2.37712200	2.88396100	-3.39247400
H	-4.01169600	2.92606000	-4.09033000
H	-3.44498900	4.25364400	-3.03533000

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C	0.39363800	0.77309600	0.15672500
C	-0.01595200	0.34996400	-1.11931600
C	-1.34617800	0.02879600	-1.37098700
C	-2.31719000	0.12455500	-0.35541200
C	-1.91964700	0.54961700	0.92326100
C	-0.57895300	0.86356600	1.16009500
H	0.71983600	0.25614600	-1.91863900
H	-1.64931500	-0.30242300	-2.36794200
H	-2.65661700	0.62955500	1.71853100
H	-0.28475100	1.19007900	2.16157700
C	1.83429500	1.13402200	0.46815300
H	1.86682900	1.45348300	1.51801900
C	2.38318500	2.29708900	-0.37102400
H	1.70417300	3.14767300	-0.19721400
H	2.32025900	2.04994600	-1.43948200

C	3.81194700	2.68496600	-0.00268800
H	4.52259100	1.87062800	-0.21632900
H	4.13683700	3.56679100	-0.57723500
H	3.89828700	2.93059700	1.06908400
N	-3.63405600	-0.21529000	-0.69040000
H	-3.78937400	-0.50621800	-1.65159700
C	-4.74187800	-0.20758200	0.11232400
O	-4.78692600	0.10171300	1.28654300
O	-5.81241800	-0.60435700	-0.60477400
C	-7.05690000	-0.64927000	0.09421100
H	-7.80255100	-0.98767500	-0.63615000
H	-7.01183500	-1.35623600	0.93671900
H	-7.33218300	0.34597700	0.47545700
N	2.72044100	-0.05845900	0.43505300
C	3.20403900	-0.61799600	-0.72815700
C	3.09817800	-0.70568000	1.60674100
C	3.89633700	-1.77819100	1.43131700
H	2.73695200	-0.31202700	2.55584600
H	4.31324500	-2.42412100	2.20213800
O	3.00708200	-0.25331300	-1.87217300
S	4.22321800	-2.04187400	-0.27209900

TsOMe

S	-1.55132700	0.00875500	-0.44042600
C	0.20376500	0.00691900	-0.21840200
C	0.87925800	-1.21552600	-0.14204900
C	0.87782500	1.22519800	-0.11659500
C	2.25875700	-1.20594800	0.04504000
H	0.33087900	-2.15419200	-0.23423100
C	2.26033000	1.21196900	0.07062700
H	0.33010300	2.16596800	-0.18865600
C	2.97050300	0.00324900	0.15577800
H	2.79856300	-2.15449100	0.10426200
H	2.79937000	2.15900800	0.15020700
O	-1.98671400	-1.24127800	-1.06849600
O	-1.99139700	1.28155900	-1.01729700
O	-1.98913900	-0.02419800	1.13823500
C	4.46102800	-0.01203600	0.35377900
H	4.73066500	-0.58585000	1.25572400
H	4.96303000	-0.50154000	-0.49748000
H	4.86669200	1.00457400	0.45495500
C	-3.40876600	-0.03101600	1.38317300
H	-3.87537900	-0.92558200	0.94323100
H	-3.52277500	-0.05137600	2.47437000
H	-3.87812100	0.87788400	0.97680600

TS4

S	-1.03454700	-0.05288500	0.55115500
O	-0.83865200	-0.99045800	1.67935500
O	-0.49738100	-0.63948500	-0.76689000
O	-0.54824000	1.32835600	0.76810900
C	1.41837400	-0.94645800	-0.67550900
H	1.29737500	-1.73657000	0.05708700
H	1.40206400	-1.18929800	-1.73226600
O	3.37570400	-1.33613000	-0.66567000
H	1.62453700	0.06947200	-0.35346400
C	4.10196700	-0.35343100	-0.34322700
C	4.81719500	1.68266900	0.25908000
C	6.05708100	1.11400100	0.21685400
H	4.64270500	2.73032600	0.52144900
H	7.02198500	1.57608200	0.42307300
N	3.74137800	0.88499700	-0.04722200
S	5.91197400	-0.57157300	-0.24143500
C	-2.79486700	0.04339600	0.22785100
C	-3.61068800	-1.04982900	0.52279400
C	-3.32997500	1.19948300	-0.34841600
C	-4.97557200	-0.98288300	0.23315600
H	-3.17777400	-1.93987700	0.98283000
C	-4.69393200	1.25252900	-0.63180500
H	-2.67790700	2.04842500	-0.56139300
C	-5.53905300	0.16423800	-0.34797400
H	-5.61704000	-1.83700900	0.46590400
H	-5.11588000	2.15662200	-1.07966900
C	-7.01087500	0.24297500	-0.65506600
H	-7.18166100	0.47241900	-1.71995300
H	-7.52403700	-0.70070400	-0.41967700
H	-7.49221200	1.04806000	-0.07453700

INT4

C	-0.95339400	0.23799100	0.00005600
C	1.09949600	1.19289800	0.00010600
C	1.59265800	-0.08194700	0.00036900
S	0.26786200	-1.23124500	-0.00018800
H	1.74865300	2.07625700	-0.00012700
H	2.63886500	-0.38957100	0.00052200
N	-0.25743900	1.37981200	-0.00041100
O	-2.16297400	0.03261200	0.00028800

INT5

S	0.54971700	-2.01558200	0.06573600
O	1.26374000	-3.27818700	-0.19361600
O	-0.23182900	-1.93882800	1.32663900
O	-0.31999300	-1.62410700	-1.13415900
O	-3.69996900	-0.45653500	0.37700300
C	-2.92345900	0.50403400	-0.02592100
C	-1.17710400	1.62242500	-0.93962600
C	-1.91680900	2.68647100	-0.54905900
H	-0.20843800	1.63789800	-1.43618200
H	-1.69307300	3.74629000	-0.65996900
N	-1.75779500	0.39833600	-0.64204000
S	-3.39478900	2.15849900	0.22372700
H	-1.18345700	-0.55050900	-0.85577200
C	1.77844800	-0.71006100	0.15394600
C	1.51824800	0.43554200	0.90805600
C	2.95466200	-0.81787000	-0.59476800
C	2.44248000	1.48335200	0.90526700
H	0.59992100	0.50198200	1.49356700
C	3.86870600	0.23464100	-0.58777200
H	3.14744100	-1.72417400	-1.17176500
C	3.62841300	1.40290600	0.15863200
H	2.23839200	2.38089100	1.49511300
H	4.78965300	0.15132400	-1.17163100
C	4.63203500	2.52492100	0.16127100
H	4.89716000	2.82340600	-0.86610700
H	4.24851300	3.40903000	0.69093100
H	5.56849200	2.21309700	0.65455600
C	-3.30487800	-1.83283500	0.14405400
H	-2.36682500	-2.04231800	0.67707700
H	-4.12883400	-2.43809200	0.53675700
H	-3.18326900	-2.00375000	-0.93510000

TS5

S	-1.03993500	-1.81840300	0.38146200
O	-1.85279000	-2.86777500	1.01378200
O	-0.64980800	-2.20249300	-1.04828400
O	0.16117900	-1.38170000	1.16399300
C	1.09528400	-1.31830500	-1.53607300
H	1.50918400	-1.94913500	-0.76287600
H	1.08191800	-1.68689300	-2.55974200
O	2.77988300	-0.39580300	-1.68902100
H	0.61534800	-0.37011900	-1.33075500
C	3.10204400	0.16065400	-0.61613700
C	3.05021500	0.82788400	1.60403800
C	4.17620300	1.47486200	1.23613800
H	2.58253700	0.82044200	2.58752100
H	4.81987800	2.10273600	1.84956300
N	2.46078900	0.10483800	0.57713900
S	4.53685300	1.18596800	-0.45718800
H	1.59543000	-0.45311300	0.74120400
C	-2.07352300	-0.36481400	0.20501800
C	-1.51799900	0.91336000	0.28630000
C	-3.43609100	-0.53410100	-0.06565700
C	-2.33649100	2.02932500	0.09164700
H	-0.45753600	1.04059700	0.50922100
C	-4.23925800	0.58806900	-0.25700300
H	-3.85980600	-1.53875800	-0.11582700
C	-3.70518800	1.88789900	-0.18231600
H	-1.90226000	3.03013700	0.15933300
H	-5.30481700	0.45674100	-0.46457500
C	-4.59196800	3.08798900	-0.37890200
H	-5.35490600	3.14659200	0.41581400
H	-4.01442600	4.02358600	-0.36632200
H	-5.13382800	3.02753000	-1.33700000

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C	0.94399200	0.12977400	-0.00019500
C	-1.17636800	1.15408700	0.00004200
C	-1.60136300	-0.12709300	-0.00004500
S	-0.24239600	-1.24490800	0.00016100
H	-1.79434800	2.05123900	0.00011500
H	-2.63009500	-0.48326700	-0.00002300
N	0.20223600	1.28585400	-0.00005900
O	2.15191600	0.02762100	-0.00012800
H	0.67423200	2.18800400	-0.00004800

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C	0.79403600	0.18315600	0.00003800
C	-1.16383700	1.18911600	0.00006400
C	-1.62618900	-0.09421900	0.00012300
S	-0.27789100	-1.20678000	-0.00012600
H	-1.80274700	2.07444100	0.00010000
H	-2.65397900	-0.45478600	0.00019100
N	0.20866300	1.34020900	-0.00000100
O	2.10842800	-0.02573500	0.00003500
H	2.55085800	0.84492400	0.00010400

1r

C	-0.83084500	-0.33407100	0.07990200
C	-0.37106300	0.50604400	-0.94506800
C	0.99012100	0.73866400	-1.12313200
C	1.93996500	0.13094300	-0.27906400
C	1.48829100	-0.71324400	0.75143500
C	0.11807400	-0.92975200	0.91806400
H	-1.09556600	0.99130600	-1.60280300
H	1.33340500	1.40001900	-1.92381700
H	2.21344500	-1.18244000	1.41081200
H	-0.21847200	-1.58236400	1.72923900
C	-2.31278500	-0.62924600	0.23710000
H	-2.49872100	-0.90848300	1.29406200
C	-2.75458400	-1.79745200	-0.65039600
H	-2.10206200	-2.65715700	-0.42647200
H	-2.56100400	-1.52134100	-1.70173000
C	-4.21971200	-2.17748800	-0.46013300
H	-4.87665400	-1.32462200	-0.68765000
H	-4.50313000	-3.01508900	-1.11763100
H	-4.41799800	-2.48505800	0.58067300
N	3.29414700	0.41353600	-0.51810400
C	4.40472500	-0.03436000	0.15132200
O	4.36485400	-0.81036900	1.09719300
O	-3.11707600	0.48780800	-0.10077500
C	-3.10581600	1.53451800	0.85227200
H	-2.07520900	1.90875500	1.00682000
H	-3.45797300	1.15282800	1.83204000
C	-4.00224400	2.65205700	0.36152000
H	-5.03333300	2.29118800	0.21606400
H	-4.02306700	3.47560500	1.09268800
H	-3.63820200	3.05151800	-0.59889700
C	5.70841700	0.54571500	-0.35670600
H	5.65678000	0.86313800	-1.40812600
H	5.97021500	1.42385200	0.25766000
H	6.50365200	-0.20183000	-0.23127400
H	3.46737700	1.05193900	-1.28897000

TS1-r

C	-1.21557300	-2.11471500	-0.12876700
C	-0.77294700	-1.60266200	-1.38441000
C	0.56487200	-1.40678800	-1.62486000
C	1.53027500	-1.70138500	-0.62634900
C	1.11240100	-2.24065300	0.61787700
C	-0.23202600	-2.43132000	0.85096200
H	-1.49652400	-1.33778200	-2.15220400
H	0.89745300	-0.98334700	-2.57436200
H	1.85492300	-2.47225600	1.37467000
H	-0.56143900	-2.81950400	1.81750900
C	-2.57489400	-2.23634500	0.20164200
H	-2.79979700	-2.69165400	1.16950800
C	-3.70119700	-2.03053000	-0.74223500
H	-3.49208400	-2.65612000	-1.63070300
N	2.84190700	-1.42231900	-0.92724800
C	3.97560400	-1.54657300	-0.13065500
O	3.95220900	-2.02981600	0.98697800
O	-2.72958000	-0.23322200	1.37666200
S	-1.08505900	2.00815700	-1.18974400
O	-0.70622400	1.97244600	-2.62183700
O	-1.57601500	3.32258600	-0.70201500
O	-2.03742300	0.88928800	-0.83308400
H	-2.35878600	0.22053200	0.56563700
C	0.42973400	1.69237300	-0.26077100
C	0.38646700	1.21274600	1.05213600
C	1.65379900	2.03204200	-0.84157900
C	1.57223900	1.07583900	1.77419300
H	-0.56191800	0.92439600	1.50726900
C	2.83295300	1.90097700	-0.10400000
H	1.67451000	2.39316400	-1.87112900
C	2.81454800	1.42515700	1.21601900
H	1.53424500	0.68804100	2.79599700
H	3.78671200	2.17404300	-0.56318300
H	-3.65124700	-0.99484500	-1.12192700
C	-3.91548200	0.47900600	1.70541300
H	-4.61695600	0.47500100	0.84986300
H	-4.40401000	-0.06222800	2.53235900
C	4.08335000	1.26769400	2.01182700
H	4.93950200	1.73279400	1.50187600
H	3.98604900	1.72507900	3.00979100
H	4.31708100	0.20159100	2.16495700
C	-5.07321900	-2.36679300	-0.16903000
H	-5.86123100	-2.17965600	-0.91396800
H	-5.12805200	-3.42791300	0.12251900
H	-5.29779600	-1.76161400	0.72131000
C	-3.60950500	1.91516100	2.10853200
H	-3.10696200	2.44984200	1.28668400
H	-4.54183700	2.45020900	2.35487500
H	-2.95307700	1.94200300	2.99378300
H	2.99341200	-1.00122600	-1.84101600

C	5.22250300	-0.99217500	-0.76930500
H	5.30495200	-1.29101800	-1.82535000
H	5.18366100	0.10895000	-0.73292900
H	6.09965500	-1.33735400	-0.20866800

INT2-r

C	1.67012400	0.24764300	-0.21410400
C	1.18778500	-1.10821200	-0.19278200
C	-0.15089200	-1.36933400	-0.11874500
C	-1.10233100	-0.30142200	-0.05726000
C	-0.64796600	1.05092700	-0.07786900
C	0.69631800	1.30469300	-0.15298900
H	1.89486800	-1.93714700	-0.23331800
H	-0.51745000	-2.39786200	-0.10198600
H	-1.37240200	1.85806500	-0.03176100
H	1.05078500	2.33776500	-0.16777600
N	-2.41313400	-0.64967800	0.02212300
C	-3.55653000	0.17046300	0.10169000
O	-3.49255400	1.38038800	0.09943200
C	3.01004000	0.57813100	-0.28721000
H	3.24624100	1.64950800	-0.28247000
C	4.17415000	-0.32401900	-0.35667000
C	5.17534900	-0.04621500	0.77970800
H	4.67627100	-0.09980200	-1.31882800
H	3.88536900	-1.38298100	-0.37569200
H	6.06281800	-0.68393000	0.65359000
H	5.50222800	1.00534500	0.77753400
H	4.72563900	-0.26658500	1.75993200
H	-2.59891600	-1.65235000	0.02916500
C	-4.83543600	-0.61503700	0.19187000
H	-5.68415000	0.07805600	0.22777200
H	-4.93413200	-1.28512700	-0.67749500
H	-4.82846100	-1.24401800	1.09717000

1q

C	1.42052000	-0.39395400	-0.15905000
C	0.92961000	0.26499000	0.97439700
C	-0.44183000	0.34111900	1.22421500
C	-1.36056900	-0.25717800	0.34664100
C	-0.87353500	-0.92720300	-0.78811700
C	0.49785100	-0.98136100	-1.03521100
H	1.63407600	0.73962100	1.66068500
H	-0.79782500	0.87837500	2.10462500
H	-1.57127800	-1.39841300	-1.47810200
H	0.85872900	-1.50254000	-1.92670600
C	2.91570900	-0.52282400	-0.39926100
H	3.08566900	-0.58919800	-1.49295200
C	3.48129700	-1.79010300	0.25062800
H	2.89160000	-2.64812600	-0.11114700
H	3.30490800	-1.72341900	1.33844800
C	4.96410400	-2.00302800	-0.03725600
H	5.55757500	-1.14987800	0.32425400
H	5.33850500	-2.91542600	0.45413100
H	5.14800100	-2.10458000	-1.12031200
N	-2.75247600	-0.20375800	0.63546200
C	-3.65406100	0.08723800	-0.36287400
O	-3.38659500	0.24790100	-1.53851600
O	-4.90618200	0.18405200	0.12802800
C	-5.93188700	0.46701200	-0.82354000
H	-6.86944700	0.50720800	-0.25468100
H	-5.75410300	1.43258600	-1.32077500
H	-5.99105800	-0.32269300	-1.58791200
O	3.63614800	0.57973600	0.12155400
C	3.52483200	1.77085600	-0.63641600
H	2.46392800	2.07216600	-0.73394400
H	3.90451600	1.59726400	-1.66356900
C	4.31958600	2.86244000	0.04916100
H	5.37886100	2.57378200	0.14476900
H	4.26610500	3.79698600	-0.53134900
H	3.92348400	3.05921600	1.05853900
C	-3.18568100	-0.26612100	2.03201100
H	-3.30452900	0.73531000	2.47814700
H	-4.14471700	-0.79231100	2.10013400
H	-2.43830800	-0.82442100	2.60898500

TS1-q

C	-1.37581500	-2.07433400	0.12607500
C	-0.97120900	-1.70810600	-1.18801900
C	0.34832000	-1.45729400	-1.48098700
C	1.35790500	-1.55295300	-0.48099200
C	0.96190000	-1.92148700	0.83748500
C	-0.36292700	-2.16494800	1.12135400
H	-1.71263900	-1.59244200	-1.97529000
H	0.59285600	-1.13139600	-2.48636800
H	1.70755500	-2.00541400	1.61827700
H	-0.65010900	-2.43041600	2.14140300
C	-2.71915300	-2.27708500	0.47723800
H	-2.90926700	-2.60731100	1.50154200

C	-3.85165200	-2.31487300	-0.48127400
H	-3.57905500	-3.03632700	-1.27448900
N	2.67033100	-1.26485900	-0.83660300
C	3.71017200	-1.17568800	0.10199900
O	3.67614900	-1.59486300	1.23833600
O	4.77417500	-0.55808400	-0.41761800
O	-3.11920200	-0.14642300	1.36268000
S	-1.44554600	1.82803700	-1.39131200
O	-0.93539700	1.58178300	-2.76144400
O	-2.00472700	3.18473600	-1.16219800
O	-2.40623100	0.74826600	-0.94693700
H	-2.74262200	0.22316400	0.51311300
C	-0.01878200	1.70691900	-0.29335300
C	-0.18365200	1.48526000	1.07787900
C	1.25693000	1.92022200	-0.81831200
C	0.93336400	1.47336000	1.91228800
H	-1.17217600	1.29329700	1.49526300
C	2.36853300	1.90746300	0.02794600
H	1.37152300	2.08437000	-1.89070100
C	2.22743700	1.68690700	1.40616700
H	0.80028500	1.28872500	2.98200900
H	3.36582600	2.06054200	-0.39190100
H	-3.89668200	-1.34219300	-1.00206400
C	-4.37581800	0.49603500	1.53224300
H	-5.02829200	0.30560500	0.65905600
H	-4.86233700	0.03910800	2.40975300
C	3.42195500	1.65186100	2.32174200
H	4.32075300	2.04589000	1.82543200
H	3.24242000	2.24182500	3.23469300
H	3.63727200	0.61794500	2.63715500
C	5.94454300	-0.49559300	0.40823100
H	6.27476600	-1.50660300	0.68768200
H	6.71078500	-0.00214300	-0.20137300
H	5.74907400	0.09037600	1.31609100
C	-5.19092700	-2.69396500	0.14055600
H	-5.98766100	-2.68364200	-0.61838300
H	-5.14969700	-3.70574000	0.57468700
H	-5.47587400	-1.99606300	0.94101400
C	-4.21297300	1.99752800	1.73005800
H	-3.70471100	2.44902100	0.86316500
H	-5.19863700	2.47806400	1.84696900
H	-3.61659100	2.21153400	2.63209200
C	2.95938400	-0.96163500	-2.24664100
H	2.54660500	-1.75471100	-2.88279500
H	2.52097900	0.00360400	-2.53766500
H	4.03871200	-0.92212500	-2.39381200

INT2-q

C	-2.26484900	-0.36793700	-0.14200800
C	-1.80448900	0.97775200	-0.33788400
C	-0.47373800	1.28790800	-0.26347600
C	0.50896400	0.27498100	-0.01371000
C	0.06379800	-1.07077200	0.18673100
C	-1.27031800	-1.36929800	0.13159200
H	-2.52057700	1.77023400	-0.55576300
H	-0.16701500	2.31765800	-0.42696900
H	0.78199000	-1.85435300	0.40032000
H	-1.60014700	-2.39505900	0.31093700
N	1.82939900	0.63944700	0.06577900
C	2.87186700	-0.31435900	-0.06501900
O	2.71775500	-1.44771300	-0.45178300
O	4.04388000	0.20960200	0.27244100
C	5.18856800	-0.64718000	0.13264600
H	6.04867600	-0.04676300	0.45057900
H	5.08315600	-1.53465200	0.77268200
H	5.30717900	-0.96004400	-0.91467700
C	-3.59675800	-0.73368200	-0.19258400
H	-3.81644800	-1.79261100	-0.00689600
C	-4.77206700	0.12004000	-0.44720000
C	-5.78161300	0.05198500	0.71427700
H	-5.26126800	-0.29334600	-1.35102700
H	-4.49684100	1.16007400	-0.66594700
H	-6.67792500	0.63668200	0.45918500
H	-6.09108100	-0.98553100	0.91530600
H	-5.34582100	0.46754700	1.63569800
C	2.17466800	2.06801400	0.18108700
H	3.21191000	2.15839000	0.50550100
H	2.05449000	2.57320400	-0.78872800
H	1.52665500	2.54262000	0.92737000

1s

C	0.11456000	-0.32523700	-0.12348000
C	-0.33921500	0.43567700	0.96724700
C	-1.69543500	0.68362800	1.15430400
C	-2.64343500	0.16863300	0.25072400
C	-2.20479900	-0.59330200	-0.84317600
C	-0.83505400	-0.82647000	-1.01795100
H	0.39063300	0.84733800	1.66815200

H	-2.05007700	1.28050600	1.99787000
H	-2.91408700	-0.99986500	-1.56391100
H	-0.50414700	-1.41440800	-1.87932100
C	1.59305600	-0.63261700	-0.29152200
H	1.78390100	-0.83658300	-1.36483600
C	2.01376100	-1.86764400	0.51125900
H	1.35244000	-2.70027300	0.22064300
H	1.81542700	-1.66646300	1.57860400
C	3.47570600	-2.25130400	0.30415100
H	4.14047200	-1.42448800	0.59593900
H	3.74486100	-3.13693100	0.90205300
H	3.67832800	-2.48638200	-0.75459800
O	2.41138500	0.44504900	0.13245900
C	2.41573100	1.56226500	-0.73633700
H	1.38968200	1.95738100	-0.86729700
H	2.77066400	1.25483800	-1.74101300
C	3.31922600	2.62993300	-0.15546500
H	4.34601100	2.24903700	-0.03216300
H	3.35244600	3.50724400	-0.82068700
H	2.95260700	2.95763500	0.83081100
O	-3.94120300	0.46164400	0.50875900
C	-4.93939800	-0.02065900	-0.37222800
H	-4.95216400	-1.12395100	-0.41111100
H	-5.90165900	0.33353000	0.02173100
H	-4.80502300	0.37086800	-1.39576500

TS1-s

C	-1.03404800	1.93052600	-0.83637000
C	-0.75903200	2.28444500	0.52692400
C	0.52601200	2.40054200	0.98772100
C	1.60710800	2.14176500	0.10582500
C	1.36929100	1.83590300	-1.26460800
C	0.08498500	1.71185500	-1.71535200
H	-1.58679400	2.45314700	1.21363600
H	0.70957300	2.63462200	2.03300100
H	2.22850400	1.65476900	-1.91033400
H	-0.11139200	1.43819400	-2.75402000
C	-2.32023700	1.79276800	-1.32472300
H	-2.40652700	1.50236700	-2.37862300
C	-3.58576500	2.07678800	-0.60893300
H	-3.65583400	3.18322100	-0.55087100
O	-2.75051000	-0.94089800	-0.50068800
S	0.18195200	-1.03000200	1.86237000
O	1.03533600	-0.19828700	2.75281000
O	-0.04094000	-2.41405900	2.35561900
O	-1.10730800	-0.34039000	1.49890800
H	-2.11038900	-0.67958500	0.20739700
C	1.10487700	-1.20402300	0.32150400
C	0.45130200	-1.53980900	-0.87007200
C	2.49140000	-1.04920400	0.33879300
C	1.19419700	-1.70720300	-2.03773600
H	-0.63514900	-1.63316900	-0.89952000
C	3.22415300	-1.21390600	-0.83986900
H	2.99124100	-0.78396800	1.27116900
C	2.59094500	-1.54260000	-2.04717400
H	0.67810800	-1.95733400	-2.96928200
H	4.30864100	-1.07584200	-0.82172300
H	-3.51511200	1.74221600	0.43769800
C	-3.66017800	-1.84433400	0.09896000
H	-4.11956100	-1.39321400	1.00211600
H	-4.48173200	-2.00932200	-0.62004000
C	3.37004300	-1.68956800	-3.32735700
H	4.45454500	-1.67819000	-3.14442500
H	3.11548500	-2.62832800	-3.84569500
H	3.13692300	-0.86652600	-4.02491300
C	-4.82843900	1.51524000	-1.29242900
H	-5.73475000	1.78076200	-0.72764100
H	-4.93479600	1.91605600	-2.31332900
H	-4.76455400	0.41997200	-1.35666800
C	-3.01349700	-3.17418900	0.46697000
H	-2.17300900	-3.02051000	1.16283600
H	-3.74716700	-3.84528400	0.94555900
H	-2.62502800	-3.68007100	-0.43313100
C	3.20517400	2.27624400	1.87412500
H	2.96721200	3.28693800	2.23954300
H	2.66398800	1.51577100	2.45587000
H	4.28705400	2.10866200	1.93243000
O	2.86836400	2.15453800	0.48258000

INT2-s

C	-0.88587100	-0.26835400	-0.21339600
C	-0.41228600	1.09181500	-0.17723600
C	0.92276100	1.36032600	-0.07008100
C	1.86524900	0.29079100	0.01021100
C	1.42905300	-1.06273200	-0.02683200
C	0.08716600	-1.32488000	-0.13366800
H	-1.12476500	1.91530400	-0.23200000
H	1.30309000	2.38236200	-0.03810900

H	2.14688300	-1.87942700	0.03290600
H	-0.26473500	-2.35851800	-0.16011500
C	-2.22247900	-0.60555200	-0.31447300
H	-2.45364600	-1.67802000	-0.31518600
C	-3.38860500	0.29140100	-0.40345700
C	-4.39163700	0.02649300	0.73529900
H	-3.88740500	0.05030200	-1.36288300
H	-3.10312800	1.35082600	-0.43605300
H	-5.28107300	0.65866100	0.59608900
H	-4.71407200	-1.02627700	0.74898700
H	-3.94508900	0.26477500	1.71269200
O	3.12251600	0.64936700	0.12069100
C	4.16780300	-0.33205200	0.21919800
H	5.10023100	0.23690600	0.30751900
H	4.02279000	-0.95736600	1.11233900
H	4.19385800	-0.95801300	-0.68509900

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C	-0.48134700	-0.39517200	0.17179400
C	0.08648600	0.43274200	-0.80702100
C	1.46318800	0.63039700	-0.89299600
C	2.35188100	-0.00526900	0.01427400
C	1.77279600	-0.84613500	0.99998100
C	0.39100400	-1.02204800	1.06989800
H	-0.57112300	0.94406700	-1.51477000
H	1.85033200	1.28682200	-1.67147200
H	2.40369000	-1.36004500	1.72411900
H	-0.01843800	-1.67165500	1.85010700
C	-1.97786300	-0.64618800	0.21387500
H	-2.24714500	-0.96323700	1.24243100
C	-2.40202100	-1.75726800	-0.75195000
H	-1.79603200	-2.64958800	-0.52425100
H	-2.12837100	-1.44503000	-1.77512100
C	-3.88882700	-2.09142500	-0.67756900
H	-4.50002100	-1.20747700	-0.91408200
H	-4.15452900	-2.89251700	-1.38613500
H	-4.16930300	-2.43127100	0.33401000
O	-2.72503400	0.51208200	-0.12621400
C	-2.72360300	1.52763500	0.85807000
H	-1.68984600	1.86327800	1.06989300
H	-3.13119300	1.12947200	1.80984600
C	-3.56153200	2.68892000	0.36462600
H	-4.59650500	2.36773000	0.16385200
H	-3.58767500	3.49102900	1.11914800
H	-3.14330900	3.10417500	-0.56665900
C	4.59626000	-0.56168400	0.81400200
H	4.50741000	-1.65476700	0.66397700
H	5.63541100	-0.27507900	0.61064100
H	4.39401400	-0.35712800	1.88032900
N	3.71440000	0.18866400	-0.05619400
C	4.27728300	0.98998300	-1.12335100
H	4.07945300	0.56268600	-2.12540200
H	3.87592500	2.01850700	-1.11773900
H	5.36449800	1.05580100	-0.99145300

TS1-t

C	-0.52460000	-2.15846800	-0.18340300
C	0.07139700	-1.47149800	-1.27834700
C	1.42550500	-1.23880400	-1.32924700
C	2.28919700	-1.67390600	-0.27326800
C	1.69048300	-2.34944400	0.83747600
C	0.33329100	-2.56936300	0.87375800
H	-0.55709100	-1.09944800	-2.08721200
H	1.83634700	-0.70458600	-2.18321000
H	2.30548300	-2.69241300	1.66678800
H	-0.10440100	-3.08119100	1.73461600
C	-1.91364100	-2.41096600	-0.09616800
H	-2.22795600	-3.04909600	0.73403200
C	-2.84675400	-2.31158400	-1.26142700
H	-2.36371100	-2.85652600	-2.09276000
O	-2.48081400	-0.75308600	1.03593400
S	-1.56561900	2.25183900	-0.73603000
O	-1.44969600	2.95844000	-2.02976900
O	-2.27511600	2.99574200	0.33537000
O	-2.12589400	0.85126900	-0.91141000
H	-2.29301000	-0.06643500	0.31360000
C	0.11102300	2.00053200	-0.12582700
C	0.31836400	1.31041000	1.07282400
C	1.19521000	2.51191800	-0.84052500
C	1.61740600	1.14119000	1.55251300
H	-0.52552700	0.88586300	1.61920700
C	2.49065600	2.33888200	-0.34765100
H	1.01373700	3.04101400	-1.77725600
C	2.72414300	1.65778700	0.85795600
H	1.77806300	0.59201700	2.48366900
H	3.33770100	2.74412100	-0.90821300
H	-2.89510500	-1.26300500	-1.59723400
C	-3.79304300	-0.50647100	1.53874500

H	-4.49759400	-0.34627700	0.70391200
H	-4.11229300	-1.41303000	2.07787600
C	4.12254100	1.50431500	1.39279800
H	4.82069000	1.18468200	0.60424000
H	4.49824100	2.46584700	1.78374900
H	4.16346200	0.77240000	2.21160200
C	-4.23675400	-2.89074400	-1.01470600
H	-4.85085200	-2.81800700	-1.92547100
H	-4.17623200	-3.95481700	-0.73395700
H	-4.76706700	-2.36172400	-0.21050200
C	-3.79200100	0.70277100	2.46024800
H	-3.44290200	1.59399500	1.91497500
H	-4.81000600	0.89312000	2.83915300
H	-3.12727600	0.53420600	3.32318300
C	4.49414100	-1.95476500	0.72951600
H	4.47474600	-3.05676800	0.78282500
H	5.52175800	-1.63538600	0.52504000
H	4.20055600	-1.55669500	1.71264700
N	3.62262100	-1.45757100	-0.32626000
C	4.22088600	-0.81141500	-1.48626000
H	4.06948700	-1.40657900	-2.40267600
H	3.79224300	0.18913200	-1.64916300
H	5.29753200	-0.70203400	-1.31819800

INT2-t

C	1.28285600	0.36450500	-0.22629800
C	0.68416600	-0.95071700	-0.24125000
C	-0.66262100	-1.12329400	-0.14278200
C	-1.55050900	0.01111600	-0.01980900
C	-0.96572500	1.33161100	-0.01561400
C	0.38288600	1.49008500	-0.11264600
H	1.32449300	-1.82908300	-0.33051400
H	-1.07149400	-2.13122100	-0.15543500
H	-1.60297300	2.20883100	0.07125900
H	0.81223700	2.49469000	-0.10321100
C	2.63617600	0.58713700	-0.30437100
H	2.96039200	1.63426600	-0.26461700
C	3.72639100	-0.41125100	-0.40766600
C	4.69852400	-0.31288900	0.78080100
H	4.28622400	-0.18154100	-1.33421300
H	3.34068900	-1.43504700	-0.50471800
H	5.53252400	-1.01780700	0.64336900
H	5.11792900	0.70164200	0.87211100
H	4.18940000	-0.55948800	1.72555100
C	-3.76586100	0.99289000	0.20720100
H	-4.79746100	0.63285500	0.26511600
H	-3.54119100	1.57083000	1.11645500
H	-3.67022900	1.65403100	-0.66693200
N	-2.86781000	-0.15782700	0.08928700
C	-3.45849600	-1.49813200	0.10242800
H	-3.25741100	-2.02339200	-0.84360800
H	-3.05372700	-2.09441700	0.93359800
H	-4.54145100	-1.40672700	0.23081700

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C	-0.71808100	0.23713700	0.14001100
C	-1.12718700	-0.59217800	-0.91433000
C	-2.47648300	-0.91790600	-1.07971800
C	-3.43562000	-0.41439600	-0.19395300
C	-3.03525600	0.41238000	0.86118100
C	-1.68410300	0.73204700	1.02696100
H	-0.37431800	-0.98836000	-1.59933400
H	-2.78149400	-1.56852000	-1.90378500
H	-3.77731700	0.80476700	1.56157100
H	-1.37262200	1.37259200	1.85736200
C	0.74158500	0.63927700	0.28418600
H	0.93724300	0.85040500	1.35492200
C	1.05332200	1.90640700	-0.51885500
H	0.33649900	2.68567300	-0.21278200
H	0.85240400	1.69426600	-1.58348900
C	2.48562800	2.39737800	-0.33381900
H	3.20563600	1.62427200	-0.64145300
H	2.67684600	3.30280100	-0.93193200
H	2.68782600	2.64288200	0.72254600
O	1.62221100	-0.37589800	-0.16187400
C	1.73926000	-1.48305800	0.71350000
H	0.74994200	-1.95024200	0.88379800
H	2.10645800	-1.14074400	1.70213800
C	2.69690400	-2.48680100	0.10668400
H	3.68663500	-2.03142500	-0.05941100
H	2.82094900	-3.35119300	0.77795200
H	2.31846300	-2.85226600	-0.86165000
H	-4.49065800	-0.66945200	-0.32255500

TS1-u

C	0.00080800	2.50014500	0.10891700
C	-0.48477200	1.91468300	-1.10218800
C	-1.84152100	1.70724700	-1.26632200

C	-2.73229900	2.03122000	-0.23047000
C	-2.27814100	2.59169300	0.97704100
C	-0.92889500	2.83115600	1.14738200
H	0.20654500	1.60622100	-1.88495500
H	-2.21697700	1.25863500	-2.18592500
H	-2.98927600	2.83008400	1.76958700
H	-0.54884300	3.27158700	2.07169000
C	1.35274500	2.76803300	0.32708500
H	1.59695700	3.22527300	1.29512100
C	2.47532500	2.54845200	-0.58879000
H	2.53254800	3.49498500	-1.17411300
O	2.52235100	-0.46018600	1.83038500
S	0.84514300	-1.28152800	-1.50124200
O	0.51683700	-0.69772600	-2.82907600
O	1.27236400	-2.70335500	-1.54784100
O	1.79857200	-0.40662700	-0.72988400
H	2.26880200	-0.45608500	0.87546500
C	-0.69621300	-1.25160700	-0.56530200
C	-0.71686600	-0.89231800	0.78627600
C	-1.88323600	-1.57848400	-1.22512000
C	-1.93525100	-0.83926400	1.46268200
H	0.20967900	-0.63813700	1.30191600
C	-3.09538700	-1.52343400	-0.53589400
H	-1.85911300	-1.84124000	-2.28440200
C	-3.14476600	-1.14331100	0.81564800
H	-1.95137900	-0.53669500	2.51339400
H	-4.02449700	-1.76391300	-1.05980700
H	2.24432800	1.74690300	-1.30377200
C	3.20179200	-1.67490900	2.07967200
H	4.11035600	-1.75517000	1.44678800
H	3.55427100	-1.64044400	3.12598900
C	-4.45136100	-1.04777900	1.55674700
H	-4.47858400	-1.75088500	2.40628200
H	-4.59480600	-0.03769500	1.97552400
H	-5.30550200	-1.27197700	0.90136300
C	3.80585000	2.30448900	0.12661000
H	4.60905600	2.15677500	-0.61029600
H	4.07874900	3.15853800	0.76681300
H	3.73584800	1.40578500	0.75711400
C	2.33271500	-2.90857400	1.86712600
H	1.98985400	-2.97319000	0.82194400
H	2.89974200	-3.82590400	2.10113000
H	1.44519300	-2.88006700	2.52136100
H	-3.79939300	1.83959800	-0.36360800

INT2-u

C	0.07263200	-0.23287600	-0.11257400
C	0.54910100	1.11549100	-0.05382400
C	1.90326000	1.35980300	0.06812800
C	2.80610200	0.28188000	0.13692200
C	2.36423800	-1.05023500	0.08704300
C	1.01156200	-1.31085600	-0.03375100
H	-0.15616800	1.94576400	-0.09996100
H	2.27659900	2.38411000	0.11499000
H	3.08421400	-1.86828600	0.14418200
H	0.63878000	-2.33645600	-0.07547300
C	-1.27999600	-0.55137000	-0.24970900
H	-1.52337100	-1.62162200	-0.25988200
C	-2.41851600	0.35427700	-0.40846700
C	-3.60807700	-0.01526700	0.49361900
H	-2.73048800	0.19582700	-1.46519000
H	-2.14138200	1.41163500	-0.31126200
H	-4.46300200	0.63365000	0.25528000
H	-3.91332400	-1.06240300	0.34472300
H	-3.34879100	0.12508000	1.55375800
H	3.87509200	0.48762100	0.23451800

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C	-1.32873200	1.60717700	-0.79285400
C	-0.35255400	2.58042200	-1.02545600
C	0.99645800	2.29891200	-0.81617500
C	1.38905200	1.02596300	-0.36083100
C	0.40688300	0.04972800	-0.12210800
C	-0.94544800	0.33803000	-0.34122000
H	-0.64351400	3.57473500	-1.37435600
H	1.75716500	3.06286400	-0.99739500
H	0.70473200	-0.93313000	0.23721500
C	-1.98529800	-0.75411600	-0.13812300
H	-1.60804200	-1.45125200	0.63689900
C	-2.21691800	-1.55079700	-1.42632100
H	-1.23901800	-1.91989600	-1.77583700
H	-2.58464000	-0.85306500	-2.19878300
C	-3.19143900	-2.71053800	-1.24768700
H	-4.17145000	-2.34695800	-0.90404500
H	-3.33927800	-3.25594700	-2.19361100
H	-2.81914100	-3.43003700	-0.49878000
N	2.75988000	0.80840200	-0.16008400
H	3.37086200	1.59625800	-0.35688600

C	3.38531300	-0.33109100	0.26520400
O	2.85854700	-1.38879100	0.54959300
O	4.71441300	-0.11121900	0.32825700
C	5.51494900	-1.21319600	0.75711200
H	6.55217200	-0.85531700	0.74951300
H	5.23708600	-1.53187200	1.77340500
H	5.41001300	-2.06827200	0.07194900
O	-3.23564400	-0.23107000	0.27082300
C	-3.28202600	0.20332700	1.61801100
H	-2.51496000	0.98022200	1.80252100
H	-3.04807900	-0.64478400	2.29276900
C	-4.66388000	0.75054600	1.90783400
H	-5.43347300	-0.01906900	1.73476500
H	-4.73285100	1.08018500	2.95655500
H	-4.88675000	1.61298900	1.25898700
H	-2.38668000	1.82596900	-0.94799600

TS1-v

C	0.52465800	1.77954300	-1.11091600
C	0.80551800	1.21759600	-2.39012500
C	-0.20467500	0.56468200	-3.06845000
C	-1.48463800	0.46327600	-2.50806800
C	-1.79163100	1.01263000	-1.24507800
C	-0.77514500	1.65413300	-0.53928800
H	1.80642500	1.28078400	-2.81215700
H	-0.01097300	0.10540300	-4.03873600
H	-0.96991400	2.07032600	0.44566300
C	1.50090000	2.43452900	-0.35159100
H	1.19149000	2.74784300	0.65271700
C	2.89144000	2.68759600	-0.73269300
H	2.94071200	3.05112000	-1.77439300
O	2.44518700	0.85381000	2.22777000
S	2.27097700	-1.56751800	-0.73250700
O	2.34792100	-1.60687700	-2.21348200
O	2.90648400	-2.72407200	-0.05007800
O	2.75156900	-0.24716000	-0.17618900
H	2.55551000	0.42193900	1.34649900
C	0.51960200	-1.66563000	-0.31296800
C	0.02546900	-1.11107400	0.86985600
C	-0.33263100	-2.37857200	-1.16147400
C	-1.31660300	-1.30262200	1.21446000
H	0.67510300	-0.51906200	1.51602800
C	-1.67127100	-2.55348000	-0.81187600
H	0.05803500	-2.78193200	-2.09719100
C	-2.18410400	-2.03028300	0.38865400
H	-1.70054200	-0.85418000	2.13354200
H	-2.33377600	-3.10891500	-1.48194900
H	3.31777700	1.65894200	-0.78586500
C	3.34959900	0.21449000	3.10899200
H	4.39536000	0.34788600	2.76200600
H	3.27582200	0.73092400	4.08223400
C	-3.62629800	-2.24871500	0.76168700
H	-4.30249500	-1.89321600	-0.03136800
H	-3.83545600	-3.32232300	0.90561200
H	-3.88691400	-1.72490300	1.69233000
C	3.67546000	3.55683200	0.24271400
H	4.72710700	3.63675100	-0.06973100
H	3.25788500	4.57449400	0.30029000
H	3.64471200	3.11066100	1.24856300
C	3.06253000	-1.27177200	3.28476800
H	3.11741700	-1.80008200	2.31893400
H	3.79362500	-1.72953000	3.97282000
H	2.05462900	-1.42927100	3.70417000
H	-2.27150100	-0.05949900	-3.05778600
N	-3.09294300	0.86074100	-0.77159100
C	-3.56977100	1.19752900	0.46905600
O	-2.93852500	1.72760100	1.36102700
O	-4.86364900	0.84929100	0.55817100
C	-5.49946000	1.09352400	1.81524100
H	-6.52917800	0.73133400	1.70760000
H	-4.99204500	0.54698100	2.62400600
H	-5.50182900	2.16822500	2.05111500
H	-3.74761500	0.38840200	-1.38885900

INT2-v

C	1.97744000	1.47367500	-0.04062100
C	1.93881500	0.04949600	-0.15059500
C	0.68337700	-0.62640400	-0.15493300
C	-0.51252500	0.08196200	-0.05266600
C	-0.44532800	1.49157700	0.05234000
C	0.78572100	2.16612500	0.05541300
H	0.66872200	-1.71499900	-0.23969200
H	-1.37283800	2.05489700	0.13444100
H	0.78732200	3.25416600	0.14071300
N	-1.70719300	-0.63105400	-0.05812000
H	-1.62889000	-1.64143000	-0.14226500
C	-2.98641300	-0.13459200	0.03215400
O	-3.29649000	1.03380600	0.13966000

O	-3.85669300	-1.15316100	-0.01693800
C	-5.24306700	-0.80850900	0.07050200
H	-5.79293900	-1.75558000	0.00933400
H	-5.46234800	-0.30782800	1.02544100
H	-5.53585200	-0.14943100	-0.76038300
C	3.09414600	-0.73213100	-0.25264700
H	2.93960500	-1.81702800	-0.31906800
H	2.92981700	2.00274600	-0.02921600
C	4.48742800	-0.29037100	-0.31103100
H	4.60306300	0.78335500	-0.11483800
H	4.76030100	-0.45244600	-1.37909800
C	5.43104000	-1.14257000	0.55168500
H	6.47061600	-0.83073500	0.37647100
H	5.20373300	-1.01121500	1.62035900
H	5.34169800	-2.21180000	0.30526300

1w

C	1.43486300	0.61860800	0.02828100
C	0.12013000	1.15158700	0.00268500
C	-0.07096000	2.53524100	0.16868700
C	1.02411200	3.38053900	0.35731400
C	2.32180100	2.86593700	0.39345500
C	2.50911100	1.49068600	0.23254900
H	-1.08259100	2.93297500	0.14353800
H	3.17926800	3.52485800	0.54797000
H	3.51930400	1.07229200	0.25972100
C	1.73033000	-0.85202700	-0.24171500
H	2.73744000	-1.07077600	0.15904100
C	1.72782700	-1.16962500	-1.74100300
H	2.44463800	-0.48542200	-2.22241900
H	0.73461900	-0.92494700	-2.15462000
C	2.08912900	-2.61972100	-2.04782100
H	1.37055500	-3.31109600	-1.58308900
H	2.09105400	-2.80504000	-3.13380800
H	3.09191100	-2.86867600	-1.66149700
N	-0.94589600	0.25585700	-0.16819600
H	-0.68705000	-0.73153000	-0.10337000
C	-2.27663700	0.52976700	-0.29606600
O	-2.80382200	1.62326100	-0.36223400
O	-2.96019700	-0.63553600	-0.34292800
C	-4.37609300	-0.52941200	-0.48609800
H	-4.75765000	-1.55811600	-0.50092300
H	-4.81934300	0.02096100	0.35792700
H	-4.64215300	-0.01949100	-1.42476200
O	0.79608000	-1.73213900	0.38323500
C	0.87524600	-1.78737800	1.80320000
H	0.78418300	-0.77154300	2.23124200
H	1.86839400	-2.17725900	2.09739500
C	-0.23572800	-2.68000400	2.31300500
H	-0.14814300	-3.69469200	1.89278100
H	-0.19022000	-2.75355000	3.41083400
H	-1.22119100	-2.27267200	2.03486300
H	0.85296500	4.45285300	0.48313400

TS1-w

C	-0.43285000	-0.35078900	-2.14432900
C	-0.77426800	0.82073200	-2.89665100
C	0.20920200	1.66051800	-3.35804200
C	1.56433900	1.36865300	-3.06518300
C	1.93489800	0.31470200	-2.24669900
C	0.93608600	-0.51121100	-1.69218800
H	-1.81776100	0.99293600	-3.16014100
H	-0.04192200	2.53006700	-3.96749300
H	2.97518000	0.15626600	-1.97847600
C	-1.34408100	-1.39099600	-1.97662600
H	-0.93735700	-2.36419200	-1.69562600
C	-2.79606700	-1.32498500	-2.25208800
H	-2.94416900	-0.94874100	-3.28064600
N	1.14715900	-1.40720200	-0.68500100
H	0.30677200	-1.65841500	-0.12118800
C	2.36483600	-1.76352400	-0.12477800
O	3.46281100	-1.50799300	-0.56708900
O	2.12991100	-2.45693400	0.99330800
O	-1.26933500	-1.62524200	0.57121300
S	-2.11296700	1.72915000	1.26532800
O	-2.59808900	3.03775900	0.77465300
O	-2.42808000	1.41828500	2.68211700
O	-2.52214800	0.59888200	0.33605300
H	-1.75178800	-0.74047100	0.54808400
C	-0.31462200	1.76596800	1.15024400
C	0.45179500	0.90128500	1.93851900
C	0.30418900	2.62283300	0.23920900
C	1.83798800	0.88395100	1.79363600
H	-0.03768400	0.24700400	2.65912400
C	1.69490300	2.60224100	0.11010700
H	-0.30540700	3.29931600	-0.36166100
C	2.48424500	1.73033500	0.87492900
H	2.43354200	0.20090300	2.40533800

H	2.17696100	3.26850600	-0.60954200
H	-3.19668000	-0.52491500	-1.60019100
C	-1.92470500	-2.51010200	1.46695400
H	-3.00544500	-2.54526700	1.23607300
H	-1.52014500	-3.51929600	1.28275400
C	3.97895500	1.67667500	0.70850500
H	4.33096800	2.42274500	-0.01887200
H	4.49442200	1.85904100	1.66609400
H	4.29122100	0.67956500	0.35780900
C	3.27997100	-2.89921100	1.72344400
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H	-0.64146400	-2.11325100	3.16921400
H	2.34578000	2.02171800	-3.46150700

INT2-w

C	1.38883600	0.22594500	0.10056700
C	2.39938800	1.25453800	0.02423900
C	2.06974700	2.57718400	-0.07540700
C	0.69973900	2.94226200	-0.10933300
C	-0.31943500	2.00733200	-0.06335800
C	-0.01959400	0.63175300	0.02202800
H	3.44591900	0.95512000	0.05540000
H	2.84267400	3.34514100	-0.12756600
H	-1.35752700	2.32218700	-0.10482700
C	1.75165000	-1.09475800	0.28408200
H	0.96473500	-1.85360200	0.35718700
C	3.10193500	-1.66951400	0.42584400
H	3.14382700	-2.04529800	1.46896200
N	-0.99580300	-0.31668800	0.03139200
H	-0.71877500	-1.29470100	0.04921200
C	-2.38303000	-0.14140500	-0.00043800
O	-2.97097800	0.91175500	-0.04059200
O	-2.94817200	-1.34723400	0.02051000
H	3.90139900	-0.92688600	0.31731000
C	-4.38309400	-1.38384600	-0.01498700
H	-4.75667000	-0.92041900	-0.93968600
H	-4.65523600	-2.44529400	0.01413500
H	-4.80314600	-0.85918600	0.85536500
C	3.31826000	-2.86358900	-0.51917900
H	4.29935700	-3.31820700	-0.31807700
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H	3.29449100	-2.53912700	-1.57059600
H	0.43213900	3.99931400	-0.18378000

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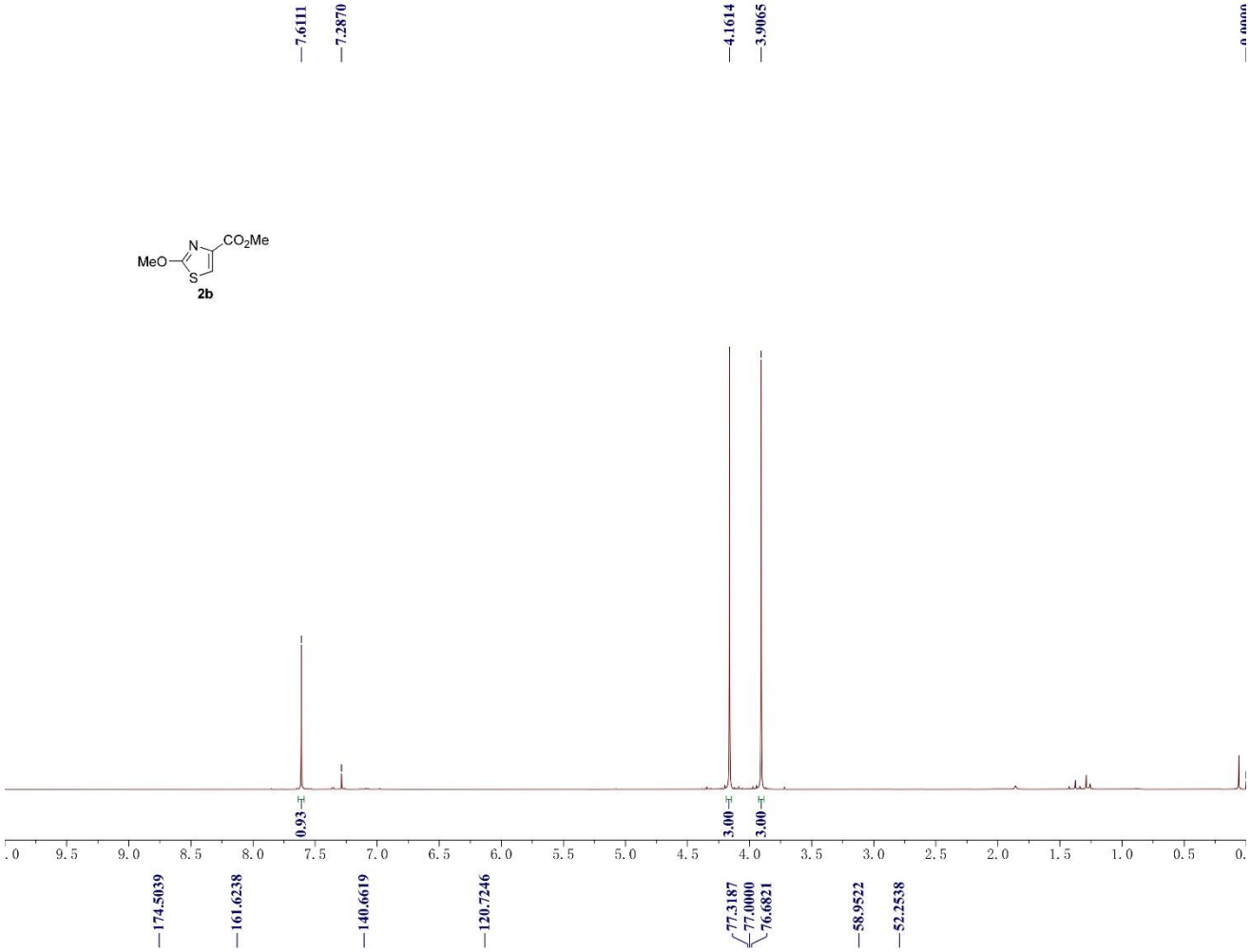
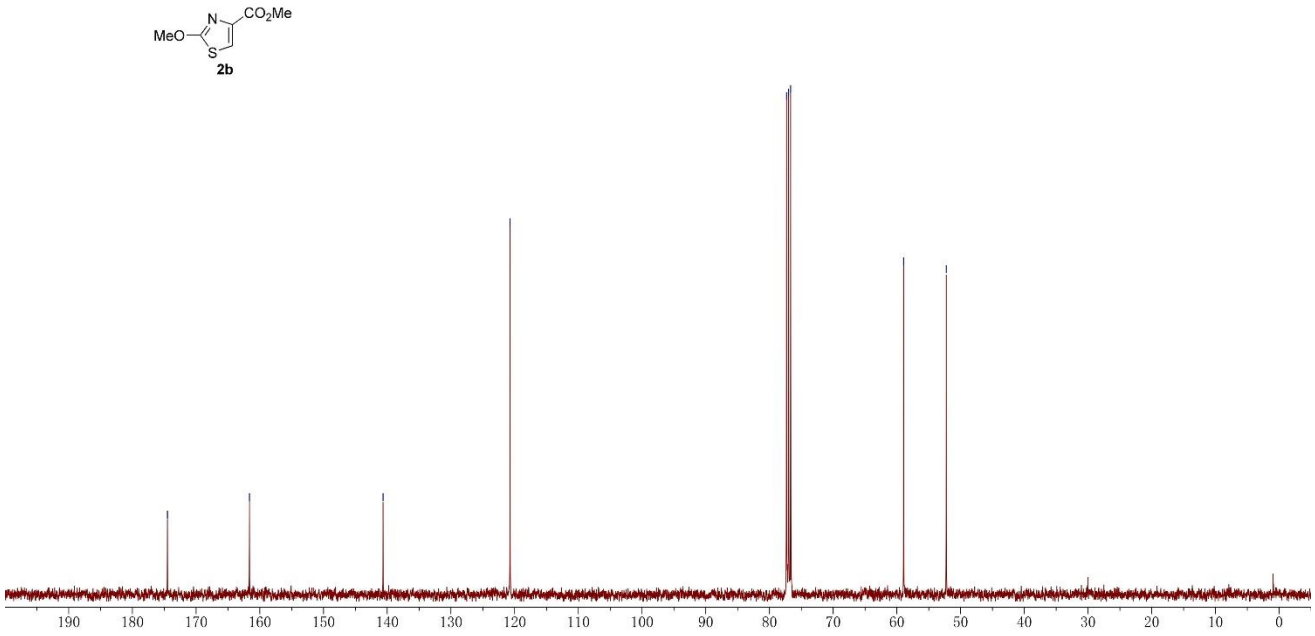
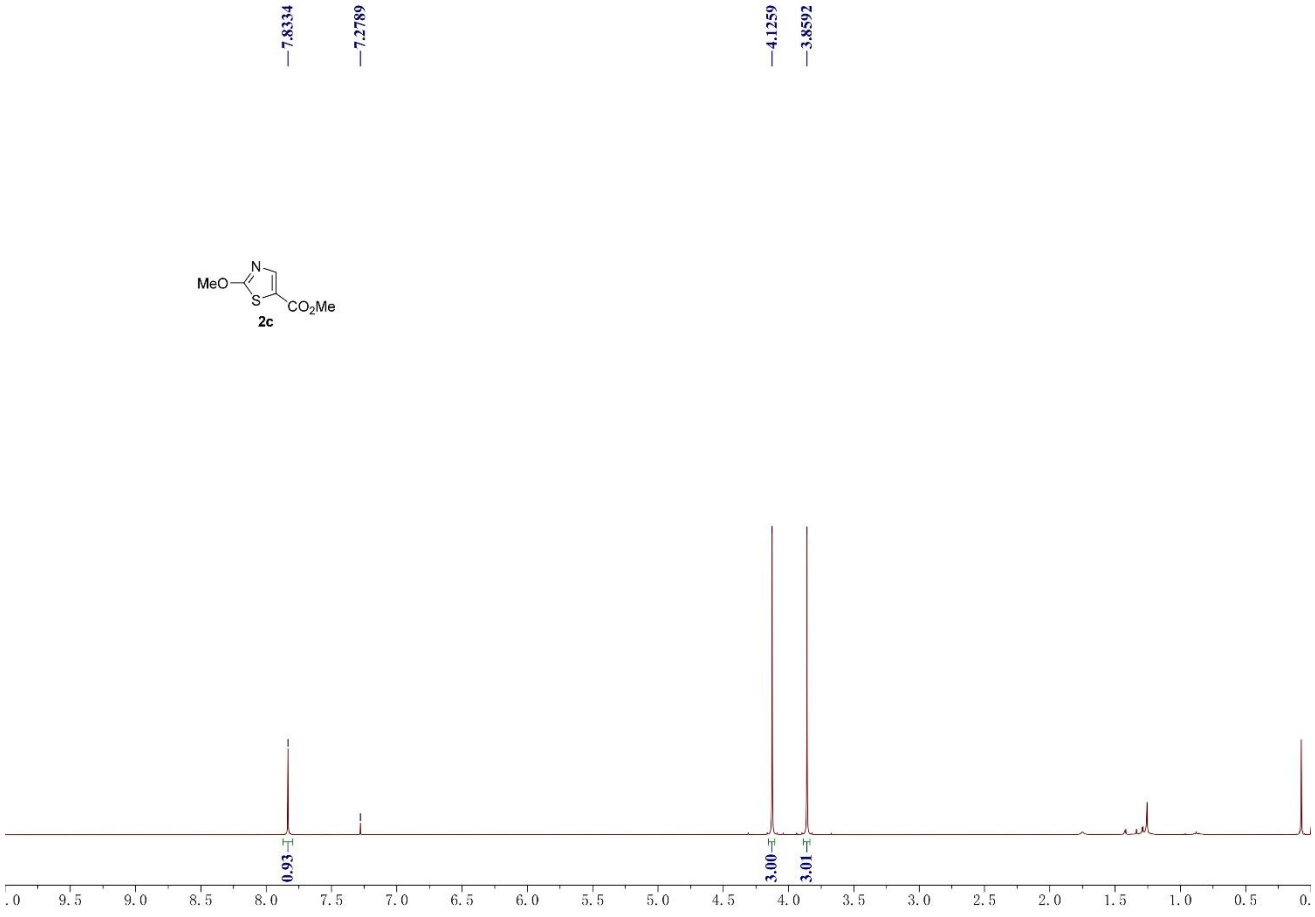
7. NMR Spectra

7.1 Spectra of 2-Alkoxythiazoles



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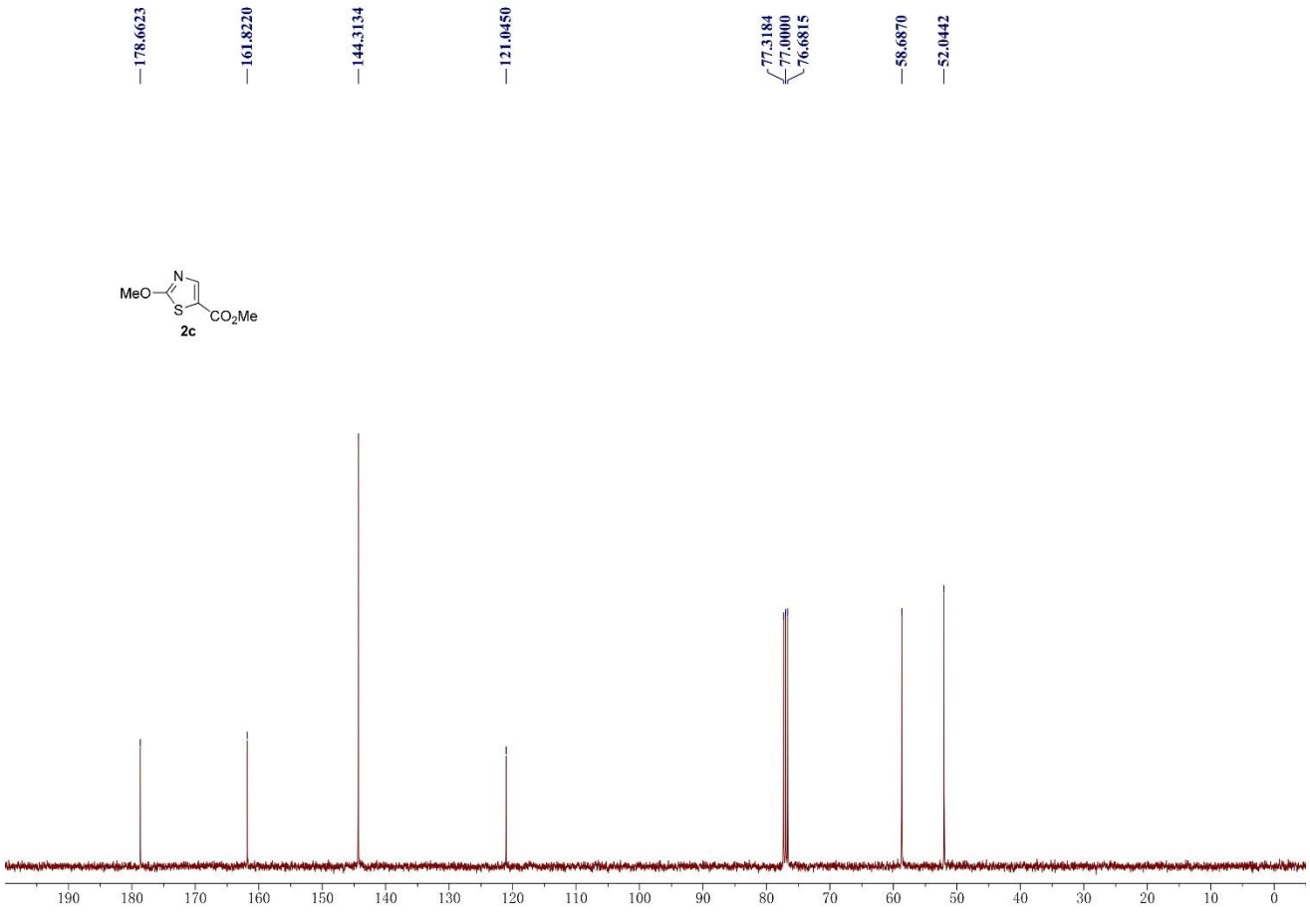
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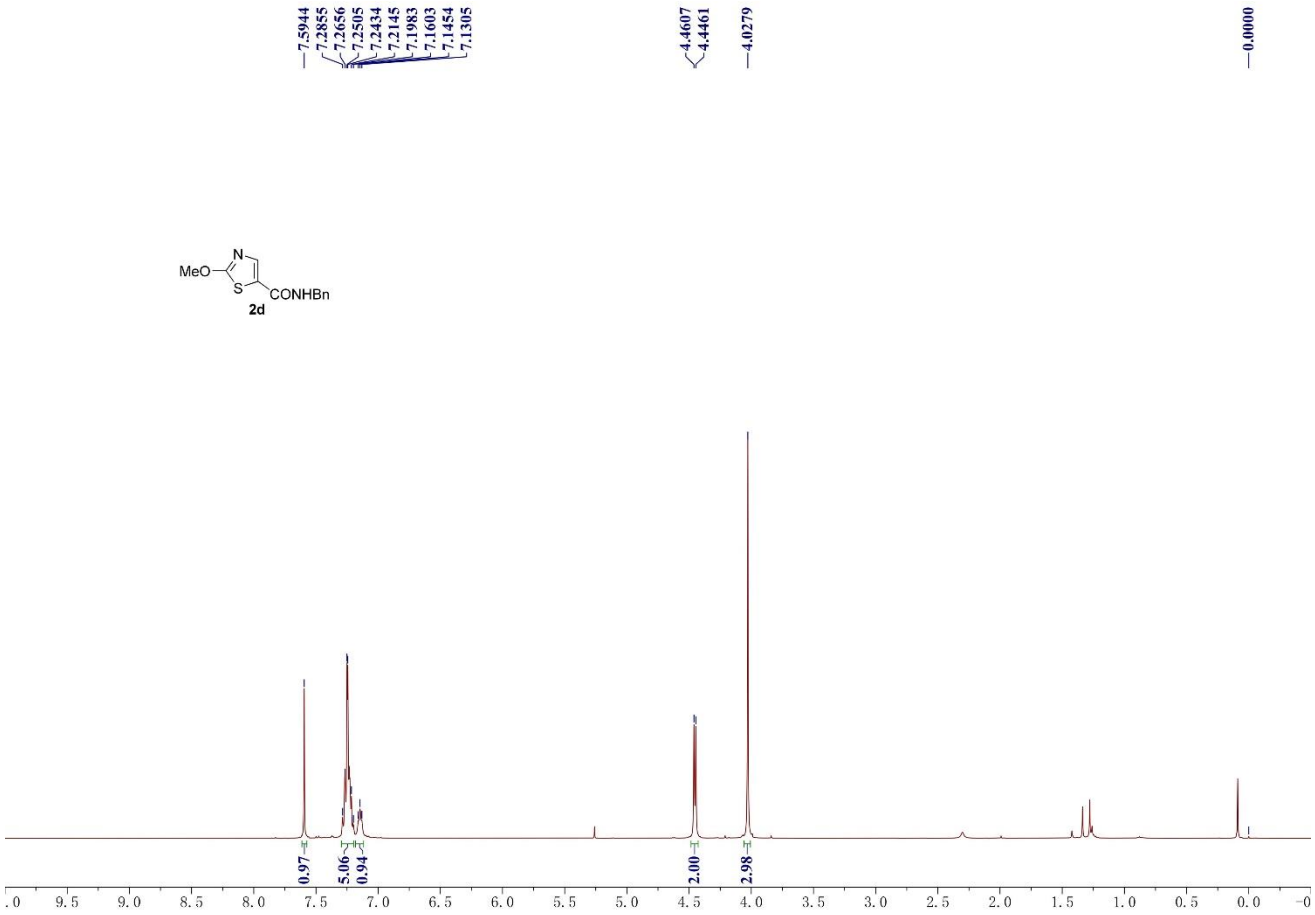
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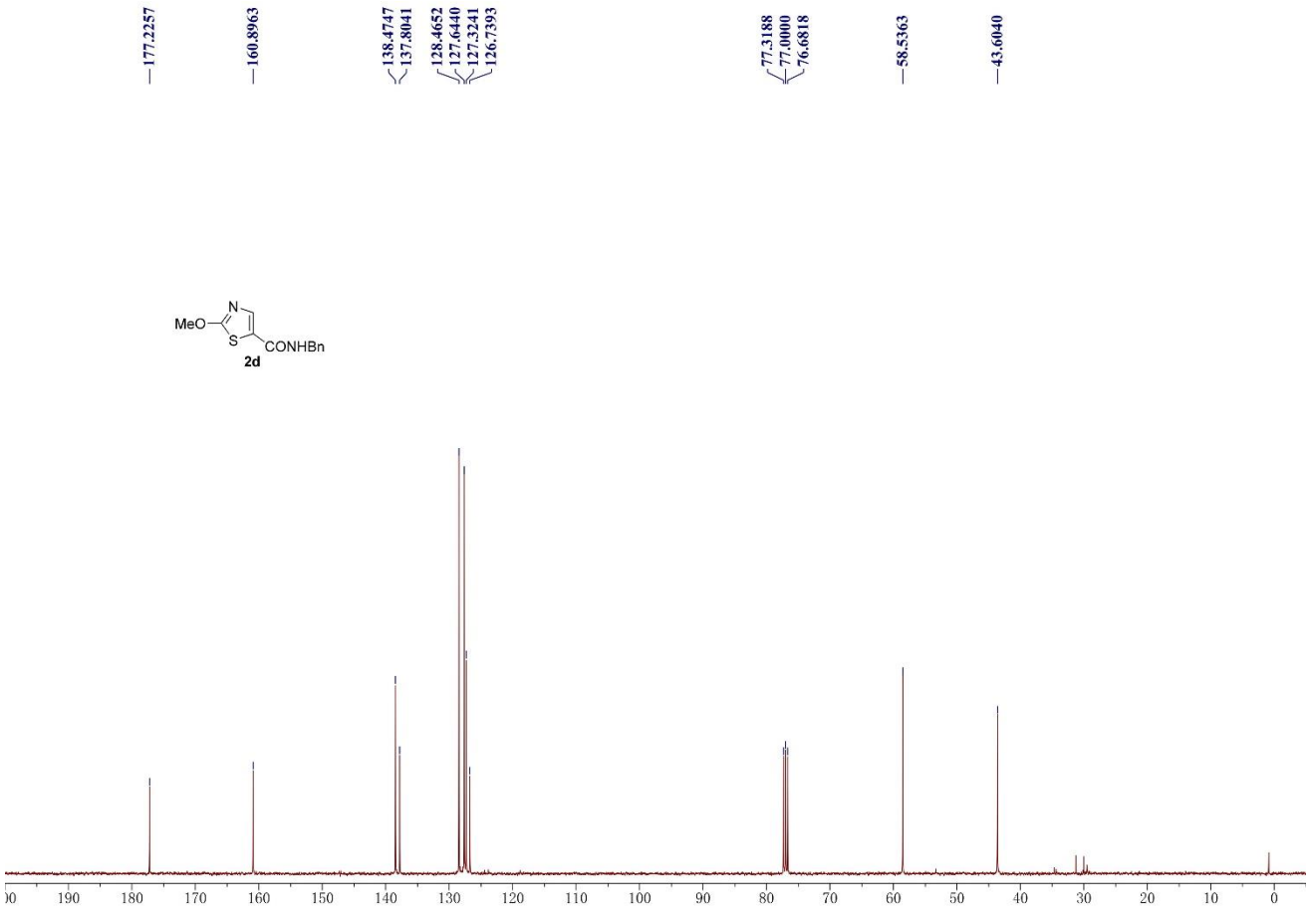
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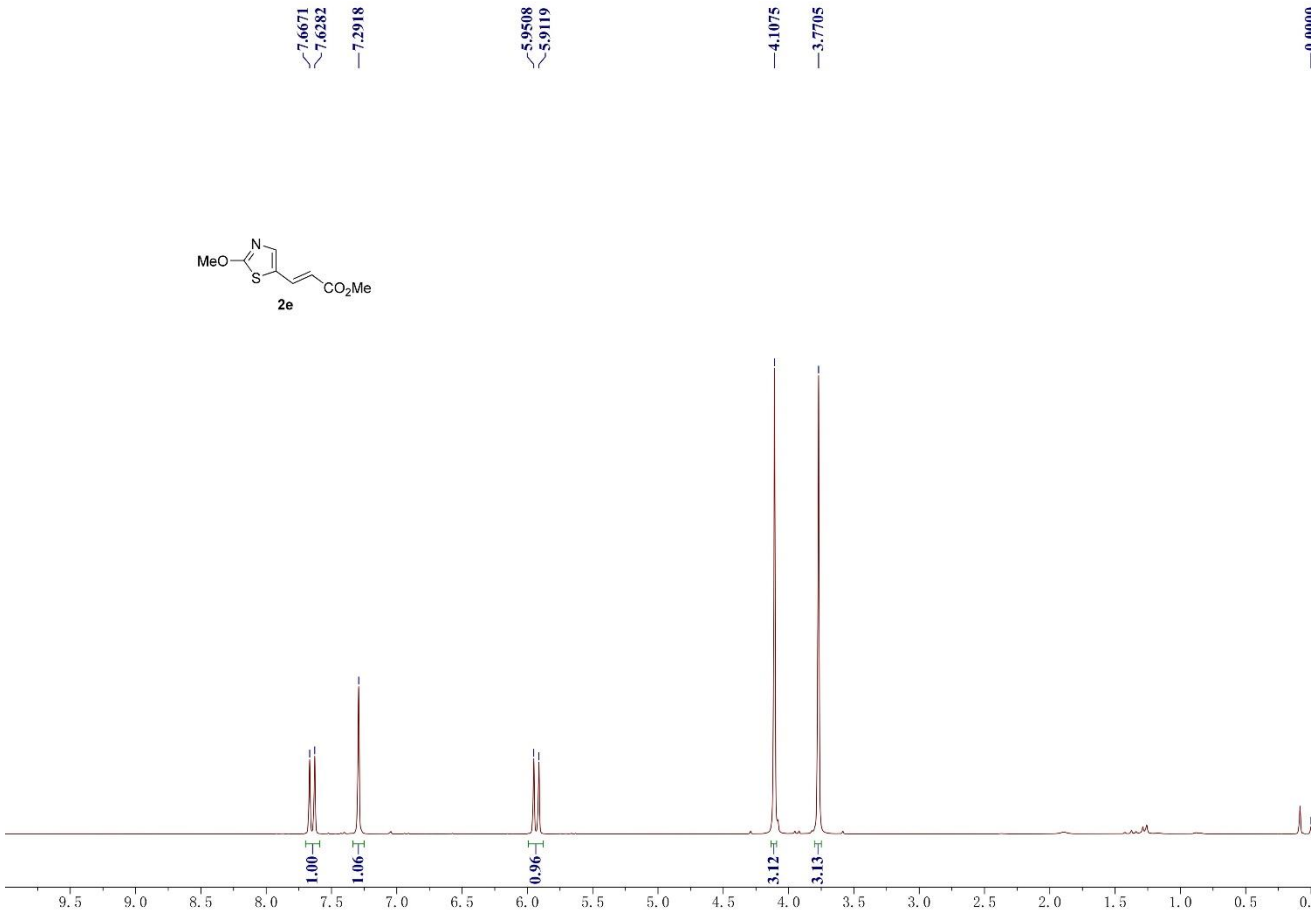
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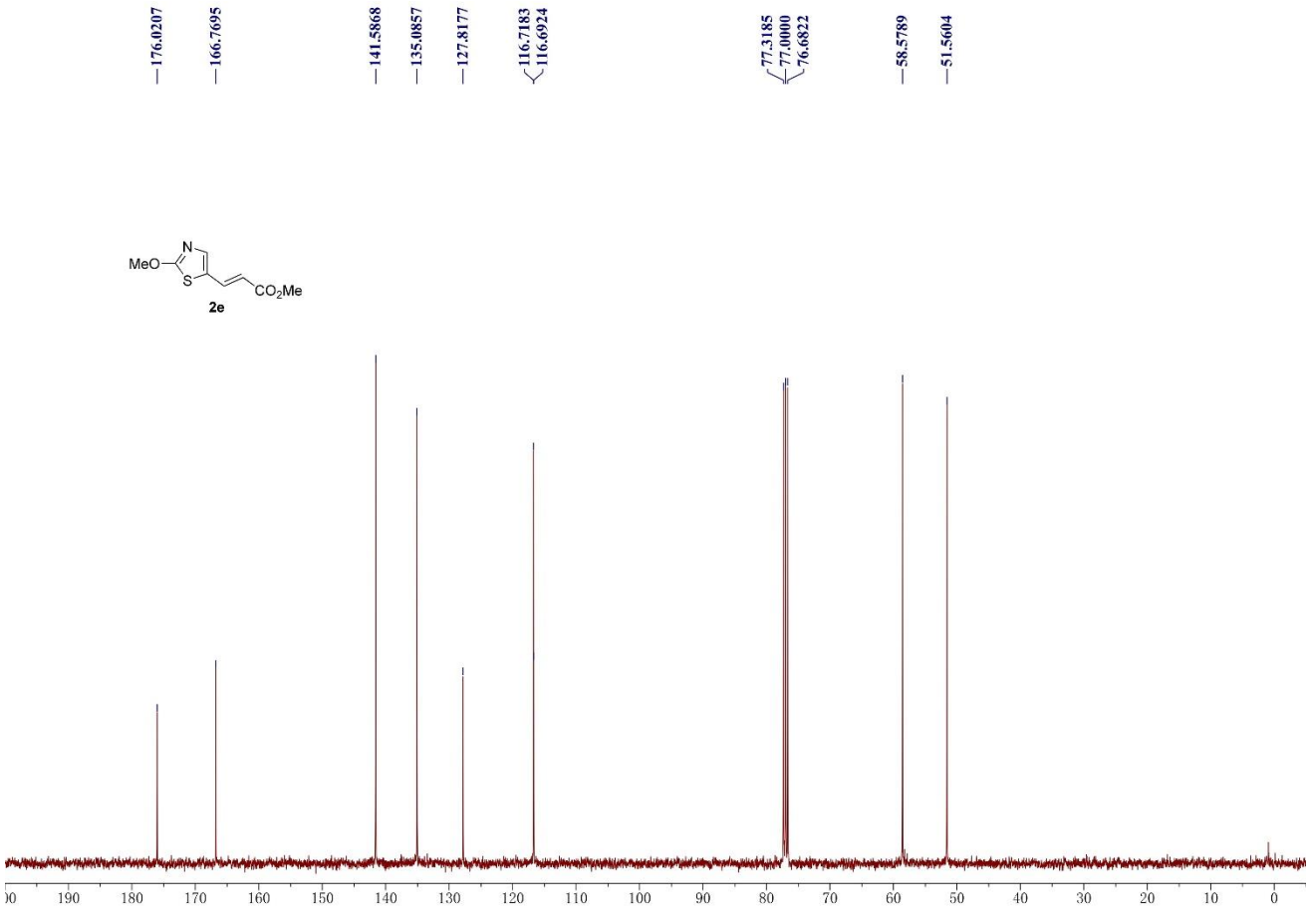
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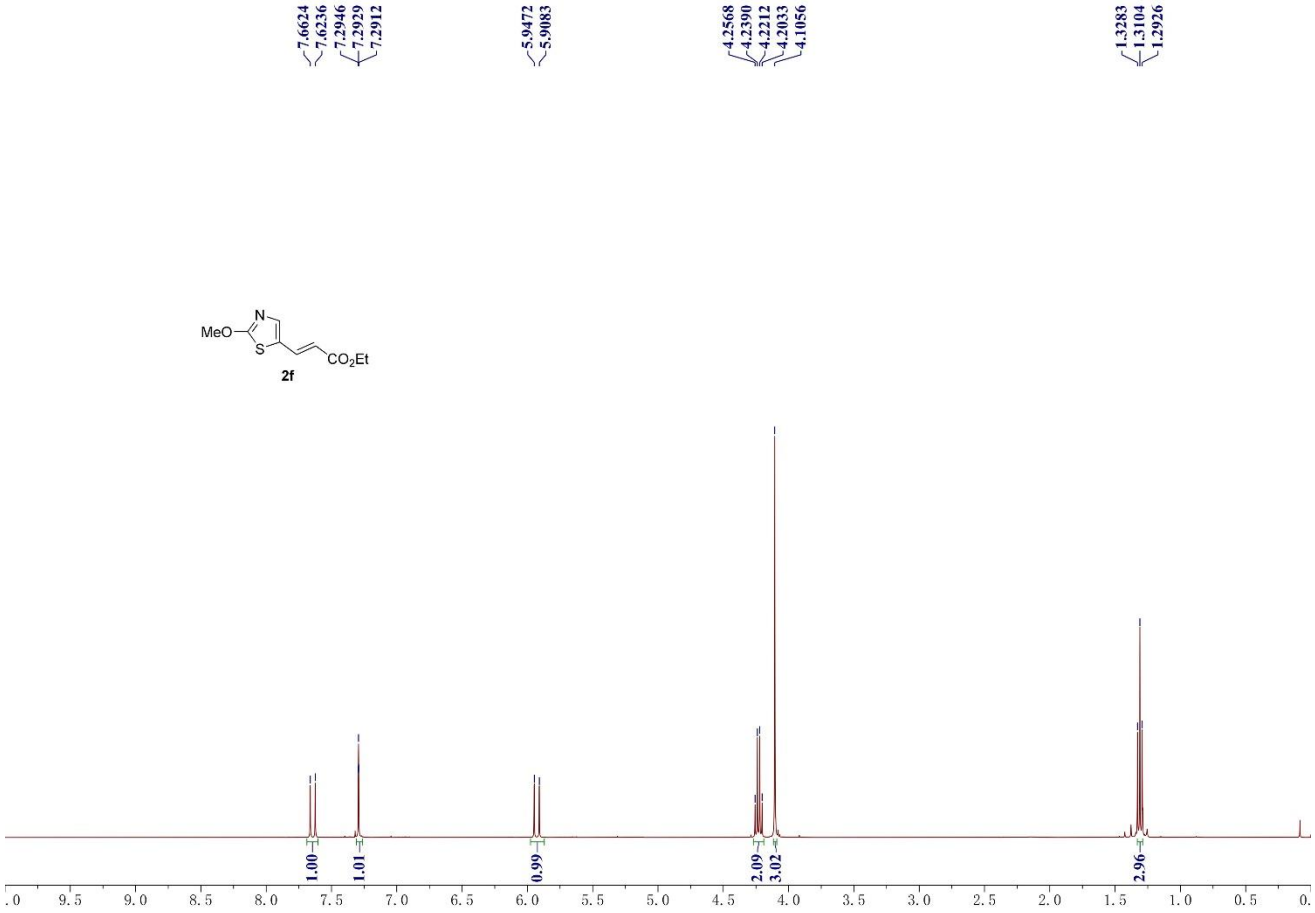
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5.9083
4.2568
4.2390
4.2212
4.2033
4.1056
1.3283
1.3104
1.2926
MeO
N
S
CO2Et
2f
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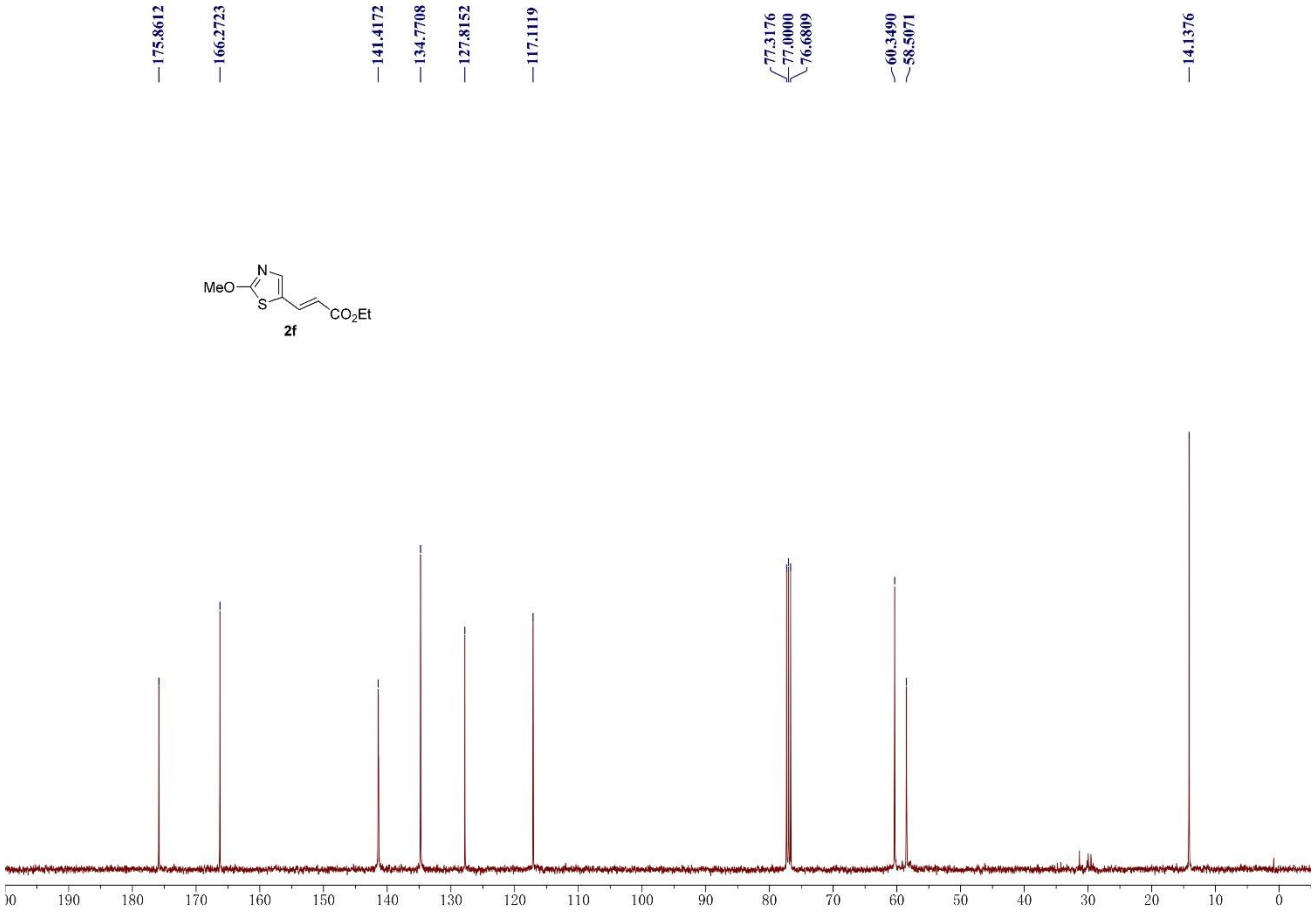
0.99
2.09
3.02
2.96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60.3490
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14.1376
MeO
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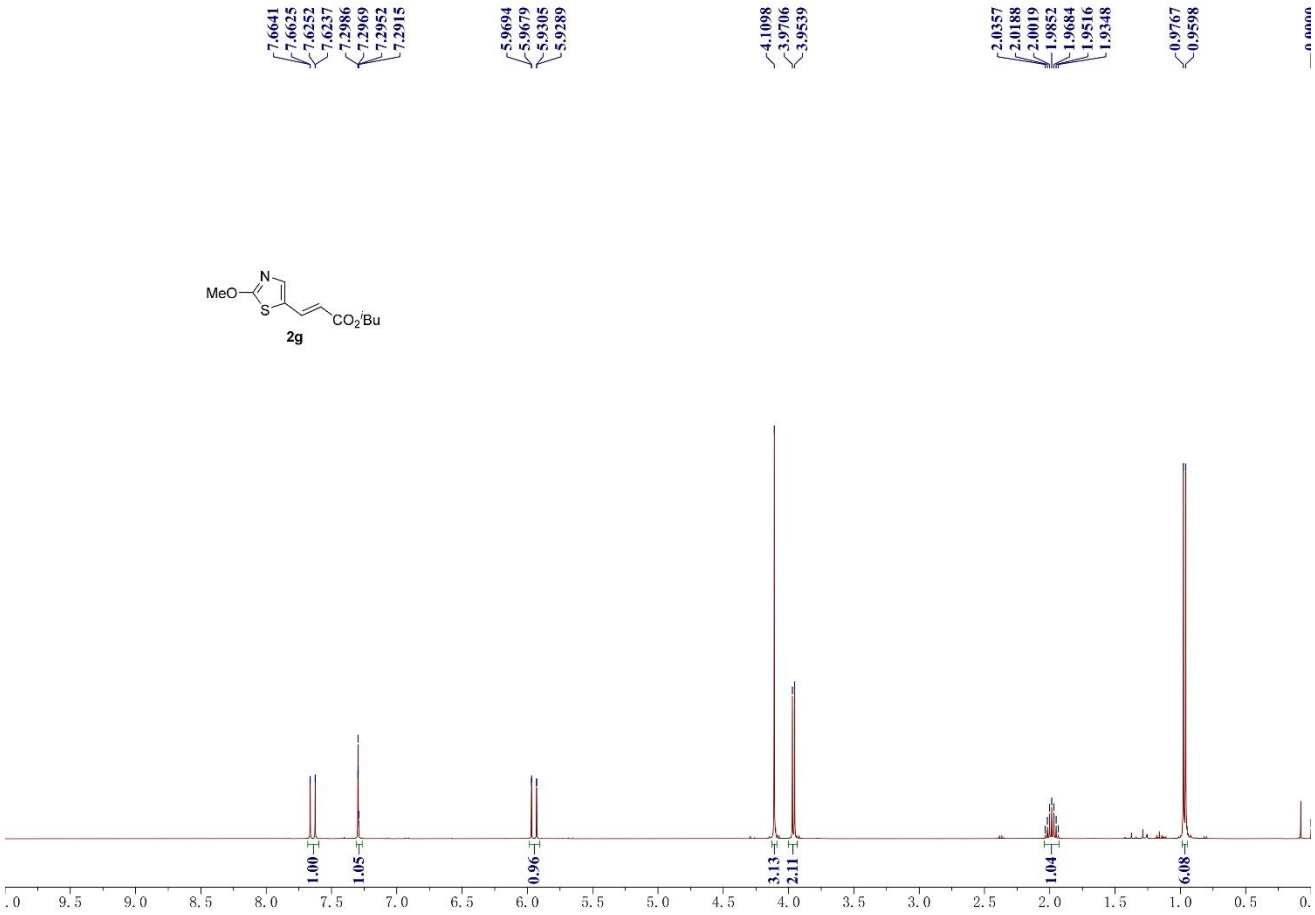
S
CO2Et
2f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5.9679
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5.9289
4.1098
3.9706
3.9539
2.0357
2.0188
2.0019
1.9852
1.9684
1.9516
1.9348
0.9767
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S
CO2tBu
2g
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1.05
0.96
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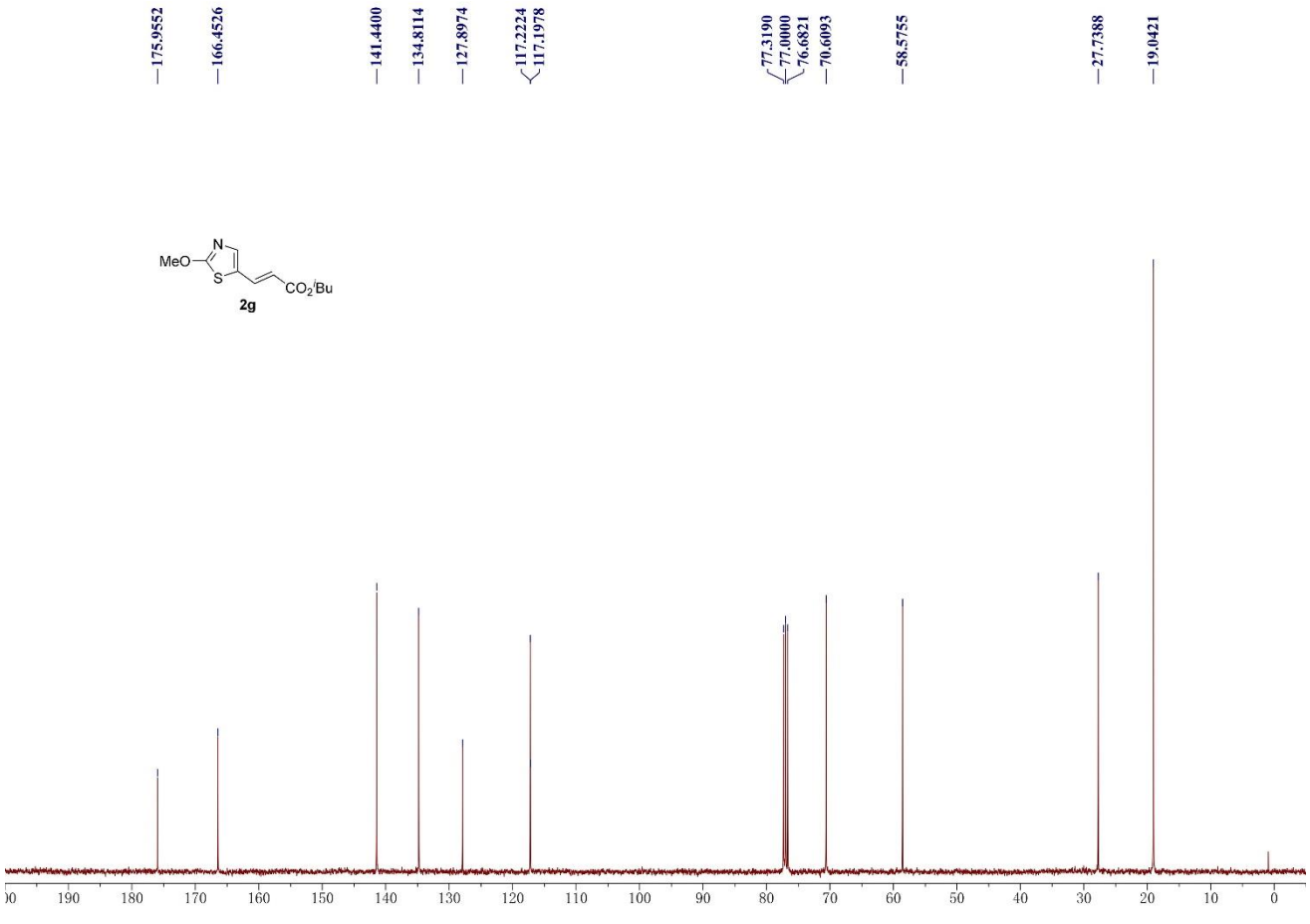
2.11
1.04
6.08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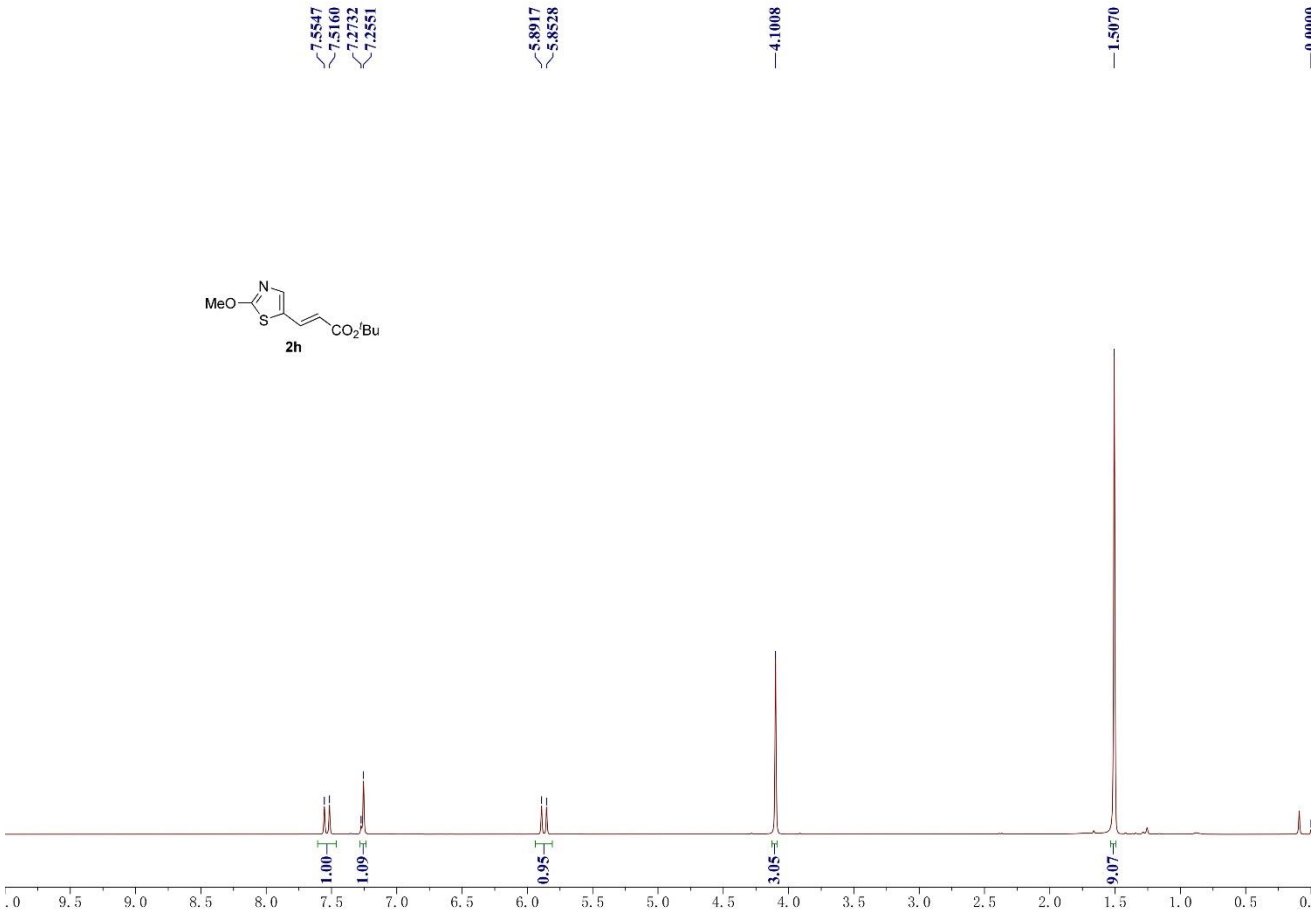
19.0421
MeO
N
S
CO2tBu
2g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4.1008
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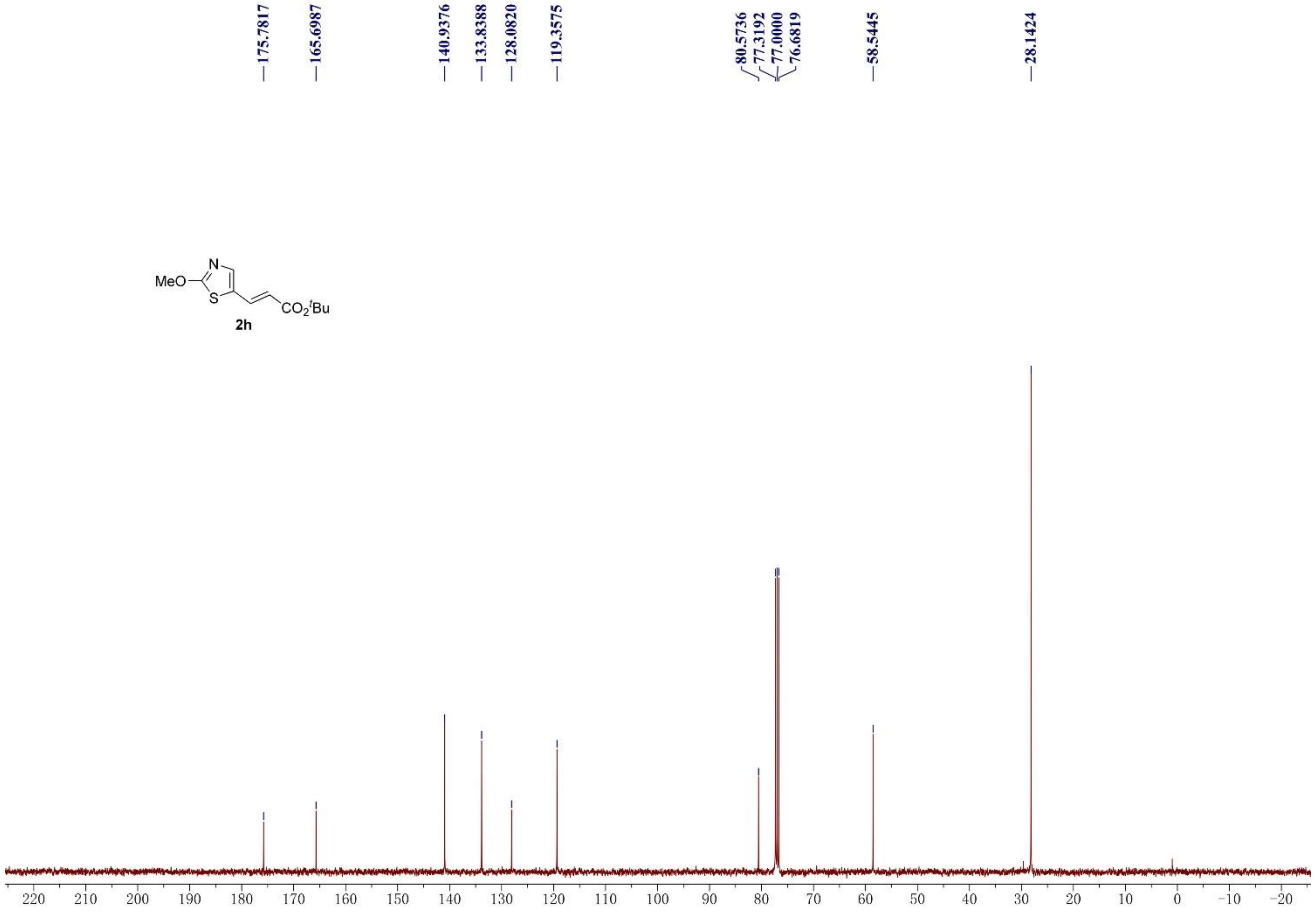
MeO
CO2tBu
2h
1.00
1.09
0.95
3.05
9.07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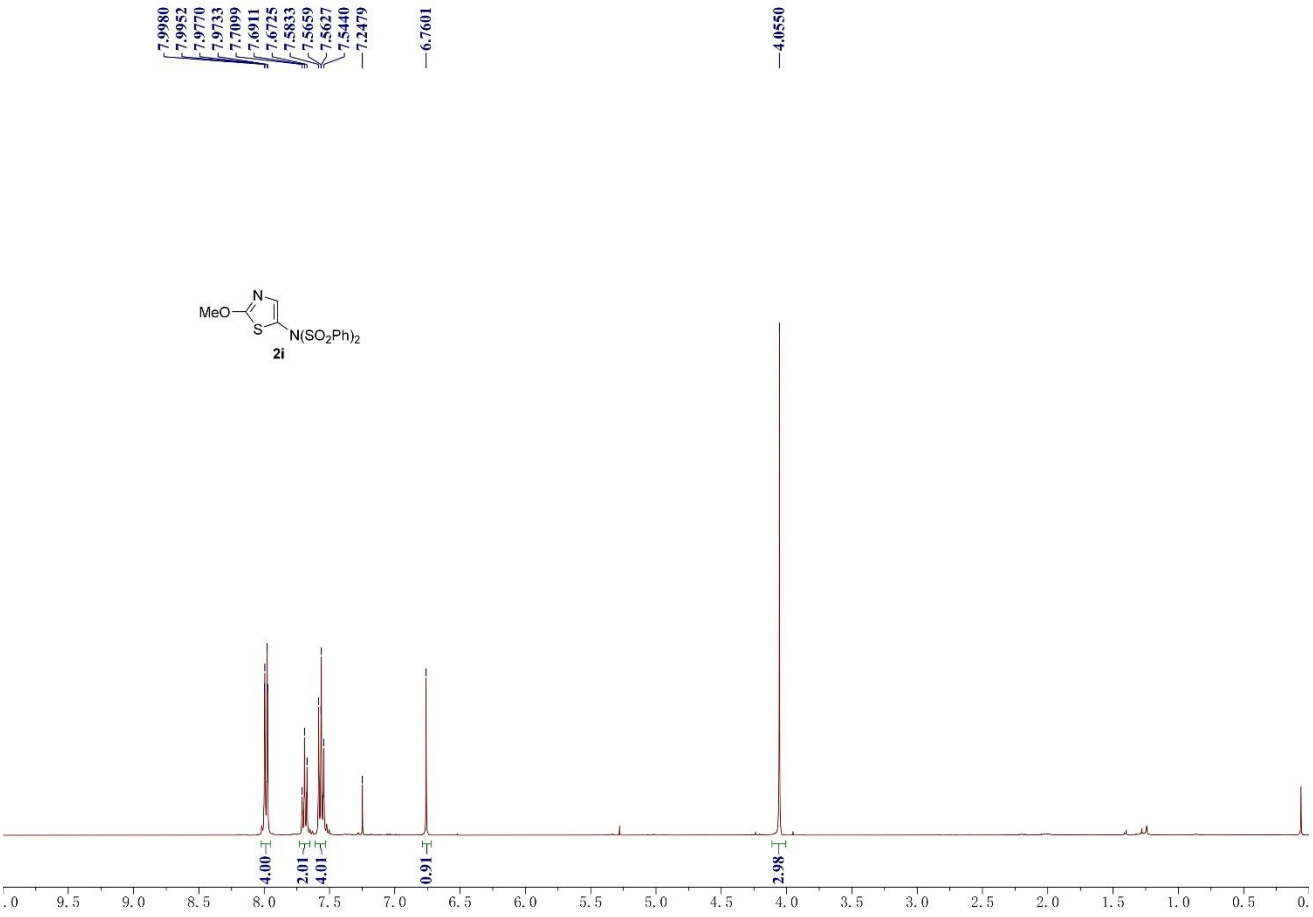
76.6819
58.5445
28.1424
MeO
CO2tBu
2h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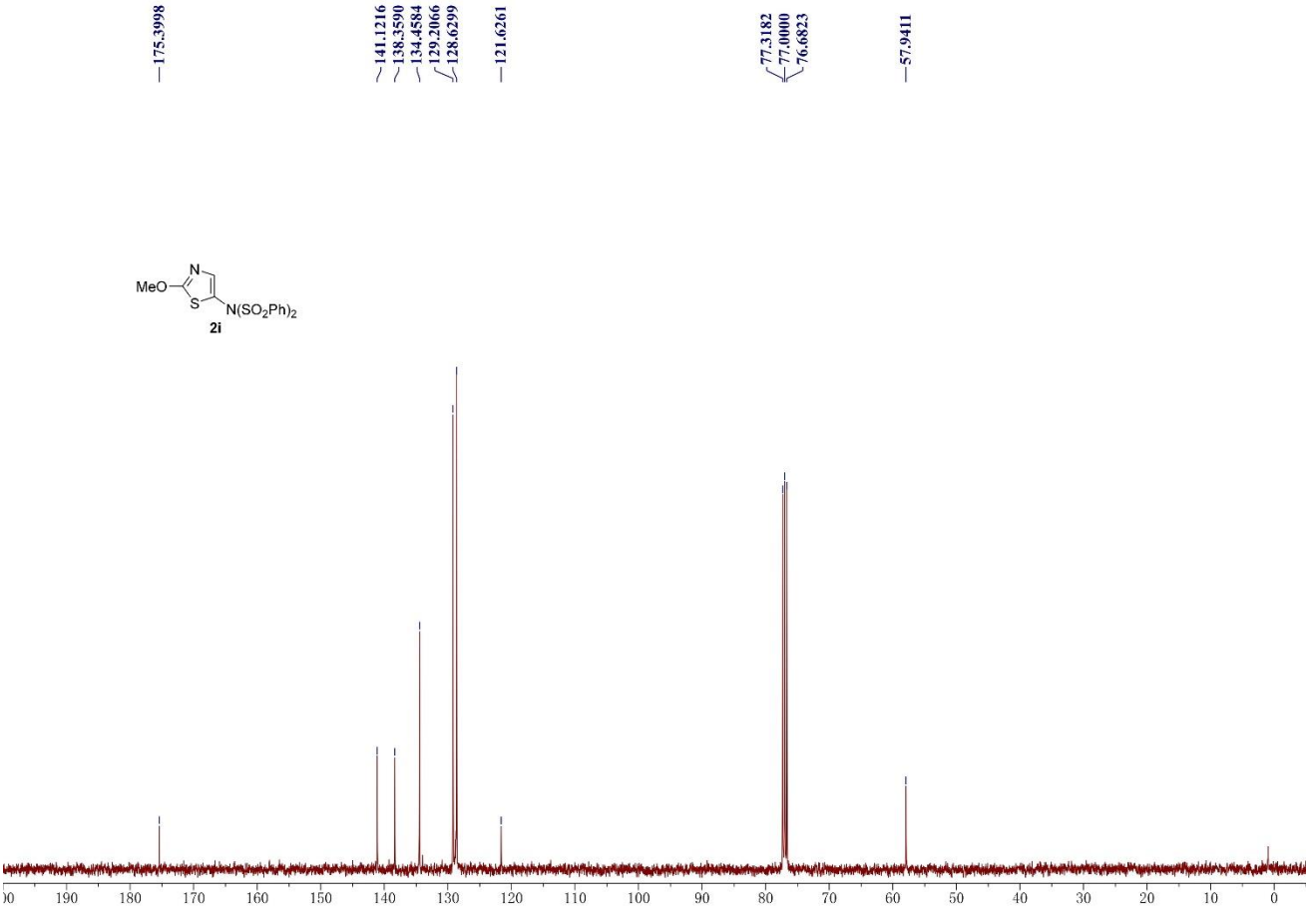
7.9770
7.9733
7.7099
7.6911
7.6725
7.5833
7.5659
7.5627
7.5440
7.2479
6.7601
4.0550
MeO
N
S
N(SO2Ph)2
2i
4.00
2.01
4.01
0.91
2.98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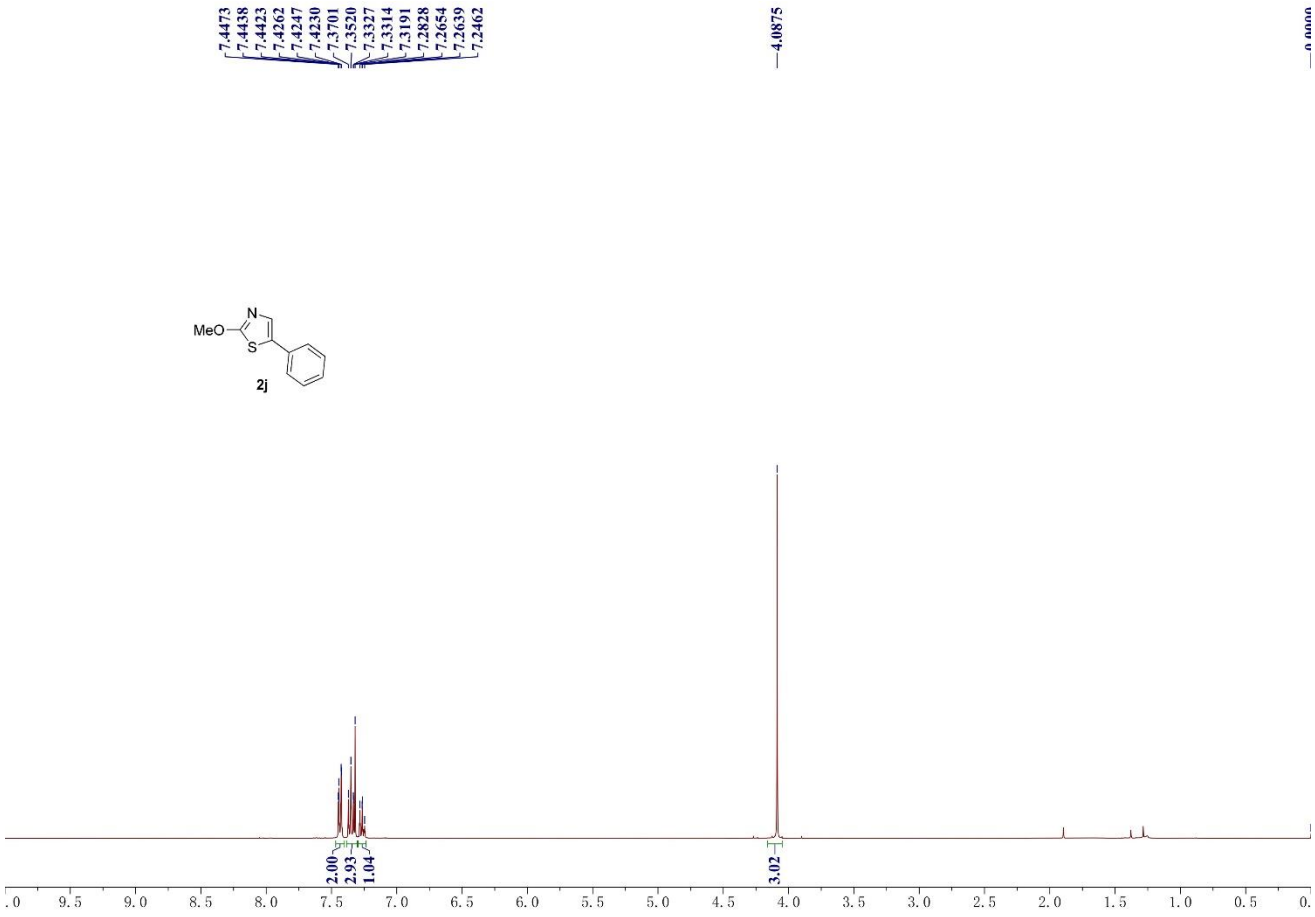
MeO
N
S
N(SO2Ph)2
2i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7.4423
7.4262
7.4247
7.4230
7.3701
7.3520
7.3327
7.3314
7.3191
7.2828
7.2654
7.2639
7.2462
4.0875
MeO
N
S
2j
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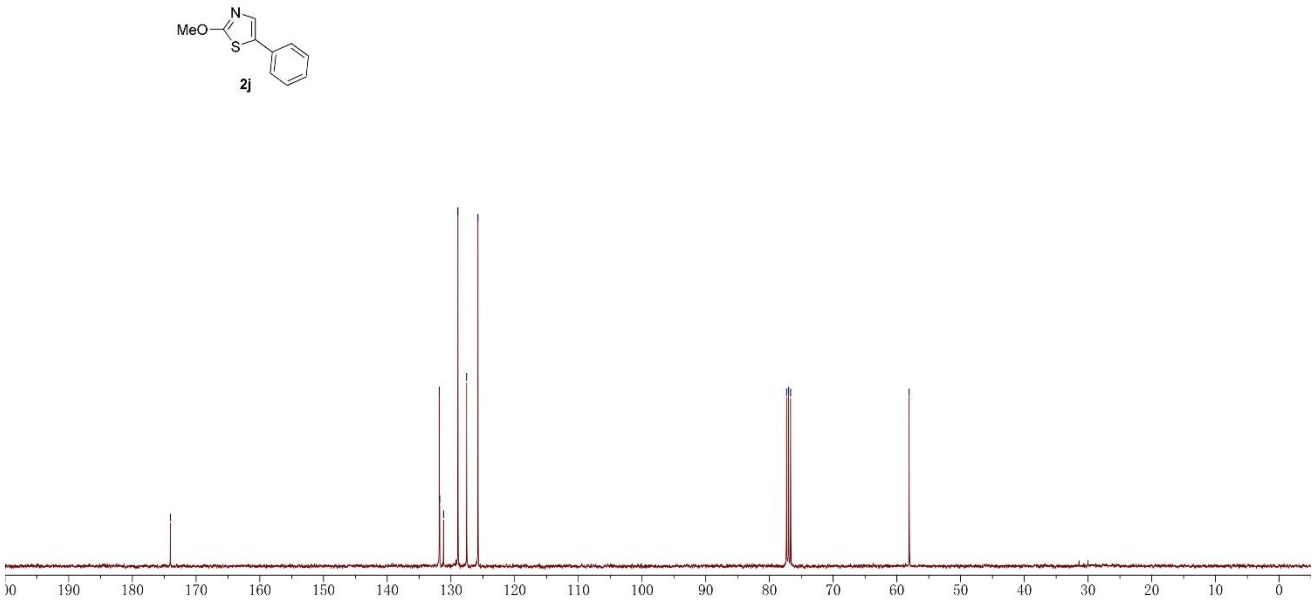
2.93
1.04
3.02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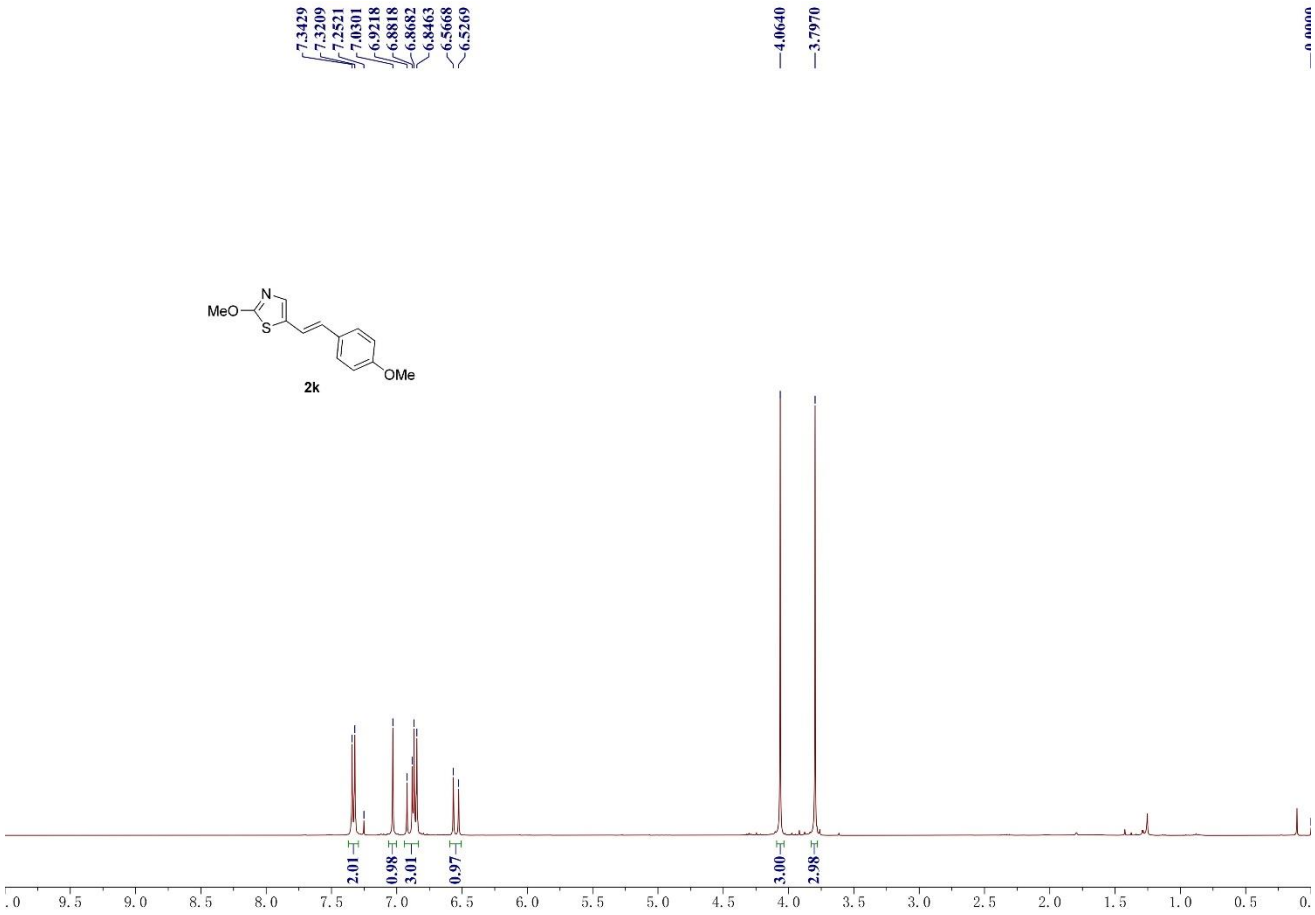
131.7663
131.1698
128.8980
127.5331
125.7578
77.3186
77.0000
76.6823
58.0615
MeO
N
S
2j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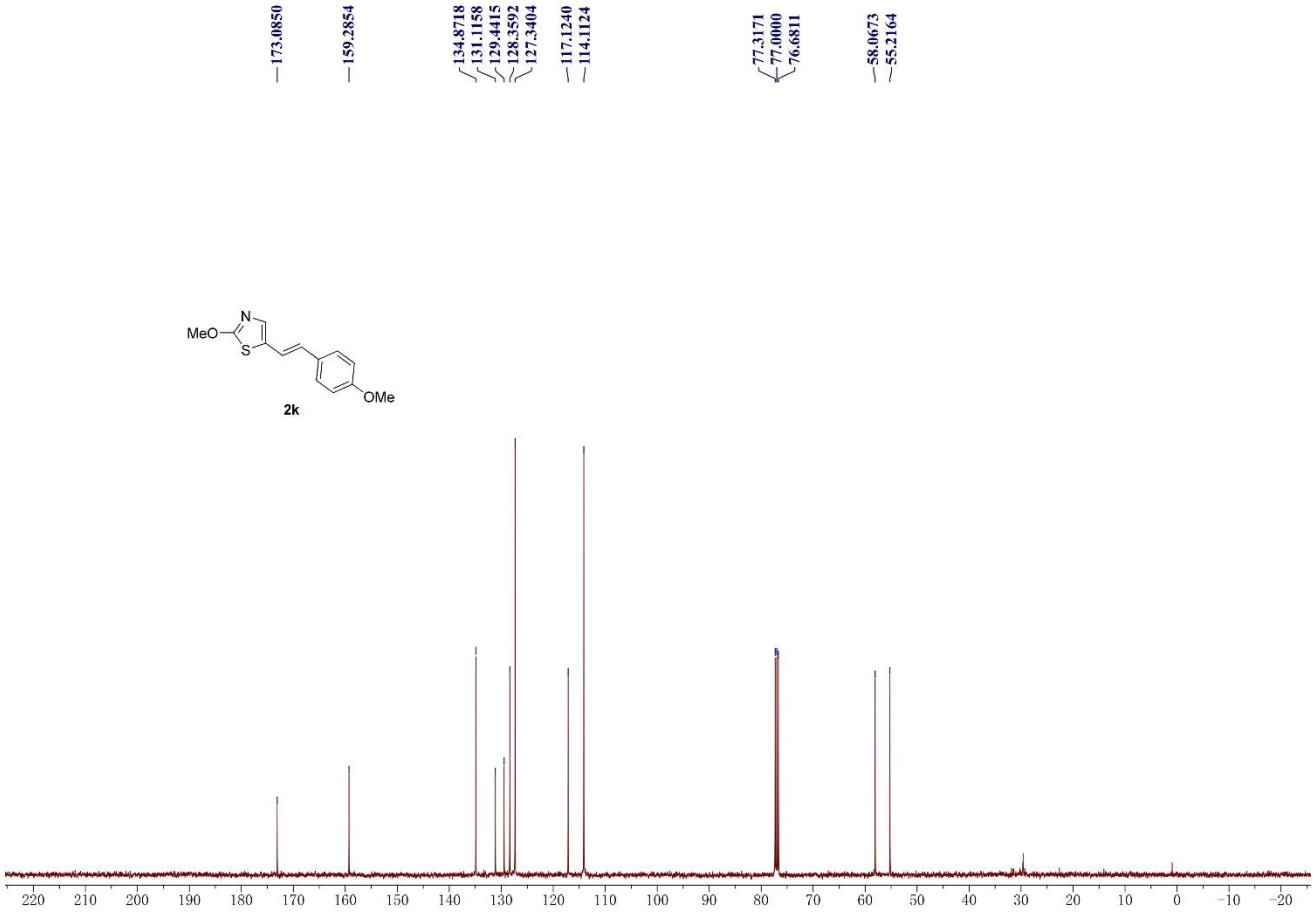
7.2521
7.0301
6.9218
6.8818
6.8682
6.8463
6.5668
6.5269
4.0640
3.7970
MeO
N
S
OMe
2k
2.01
0.98
3.01
0.97
3.00
2.98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159.2854
134.8718
131.1158
129.4415
128.3592
127.3404
117.1240
114.1124
77.3171
77.0000
76.6811
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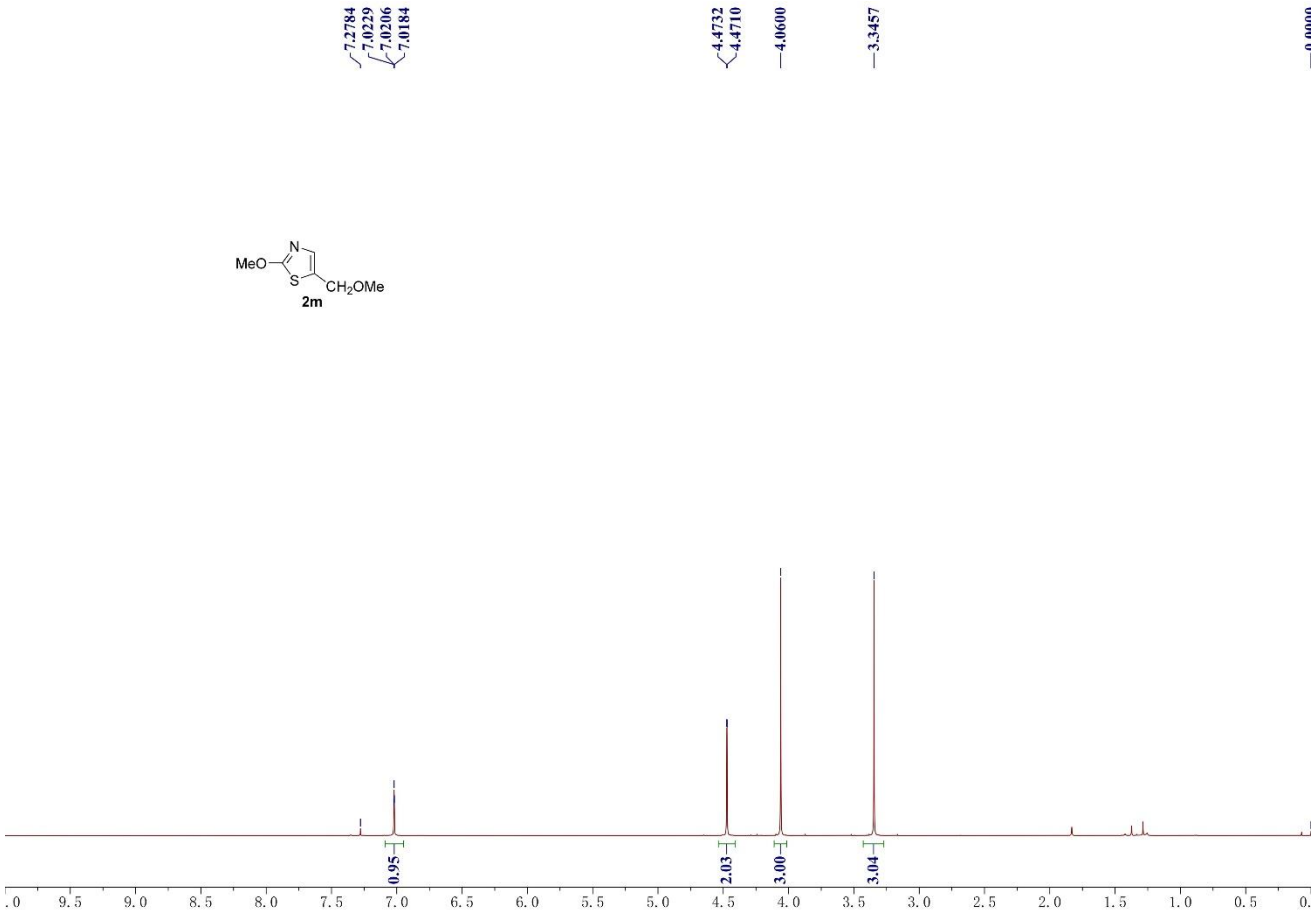
55.2164
MeO
N
S
OMe
2k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7.0206
7.0184
4.4732
4.4710
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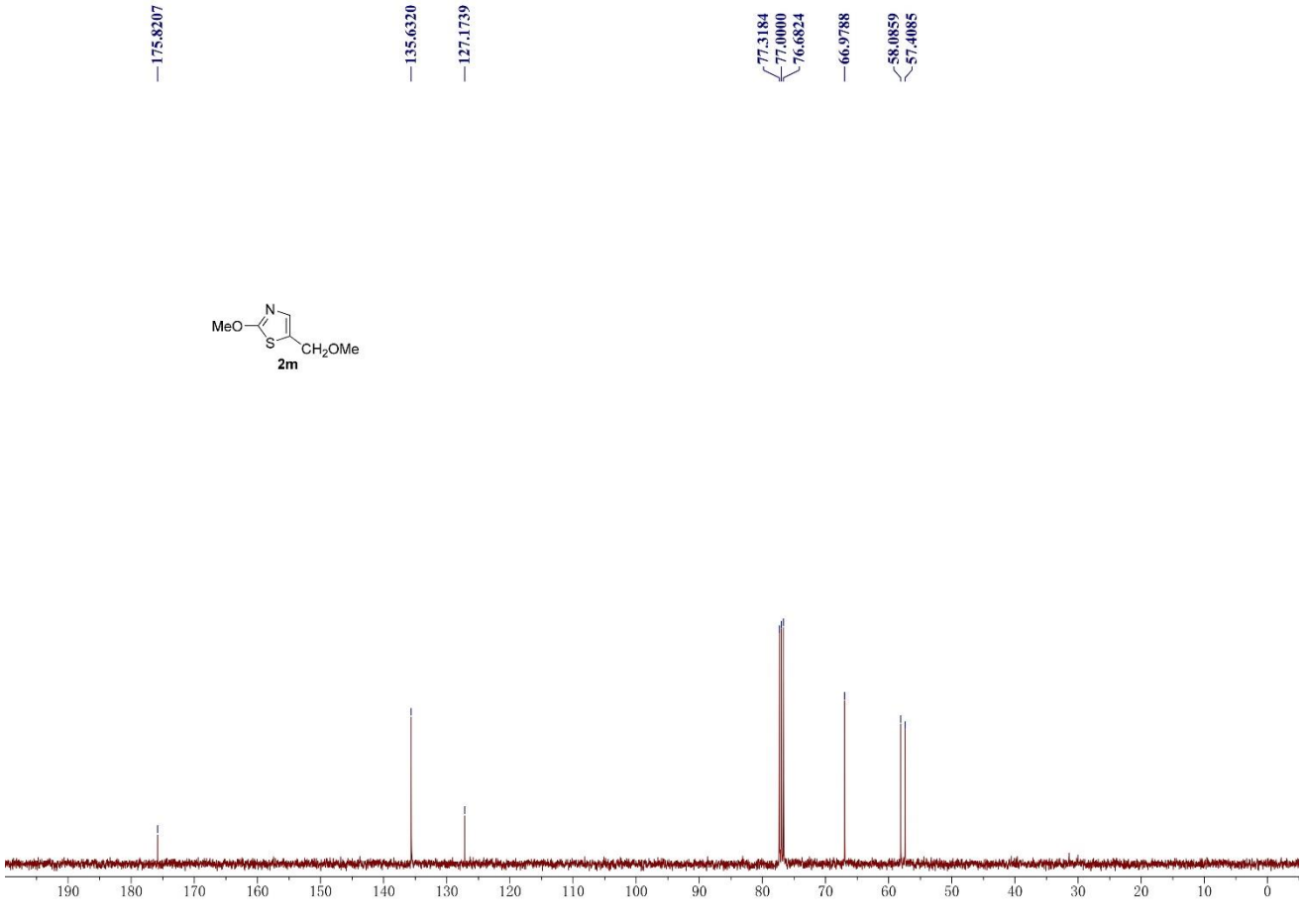
MeO
N
S
CH2OMe
2m
0.95
2.03
3.00
3.04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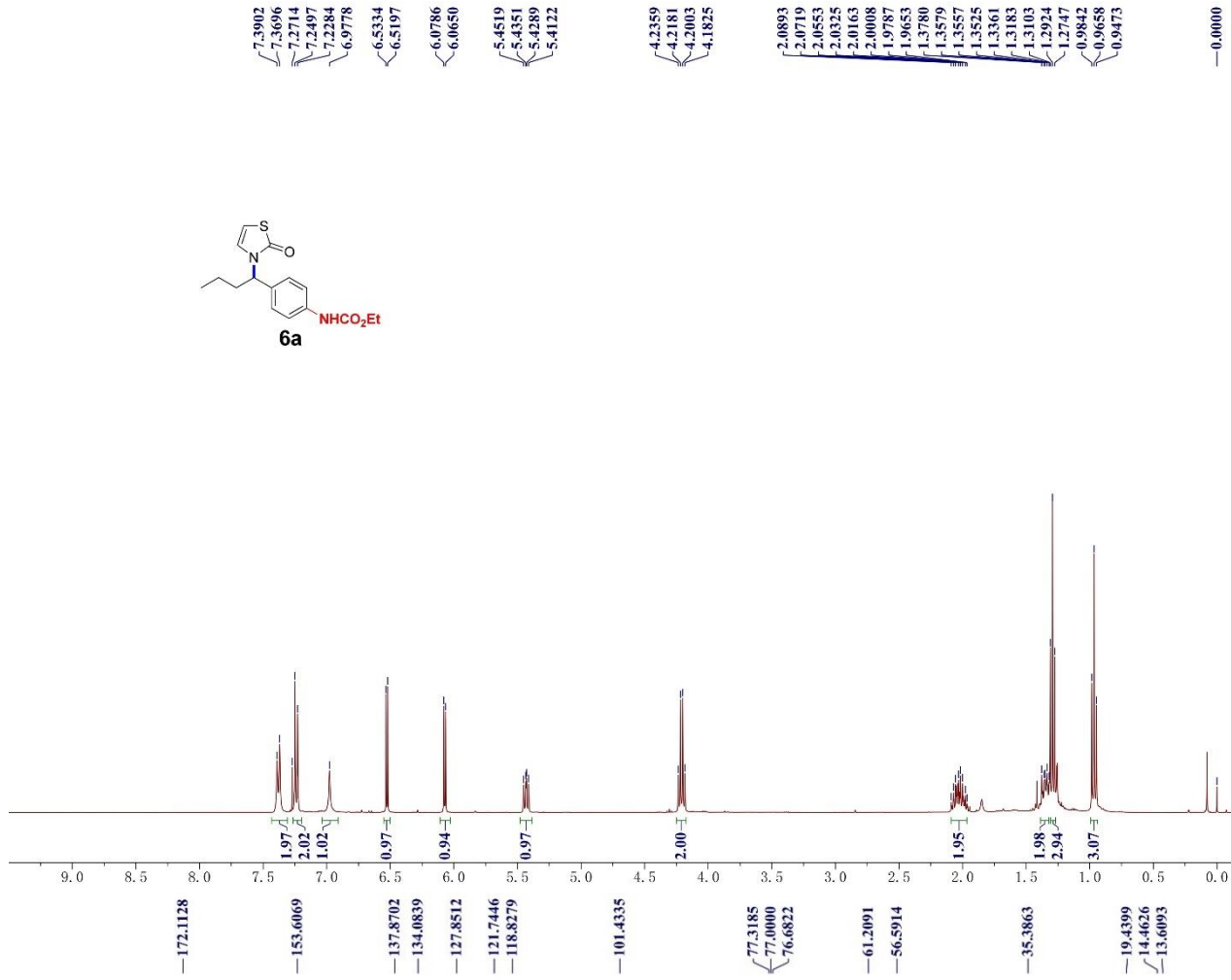
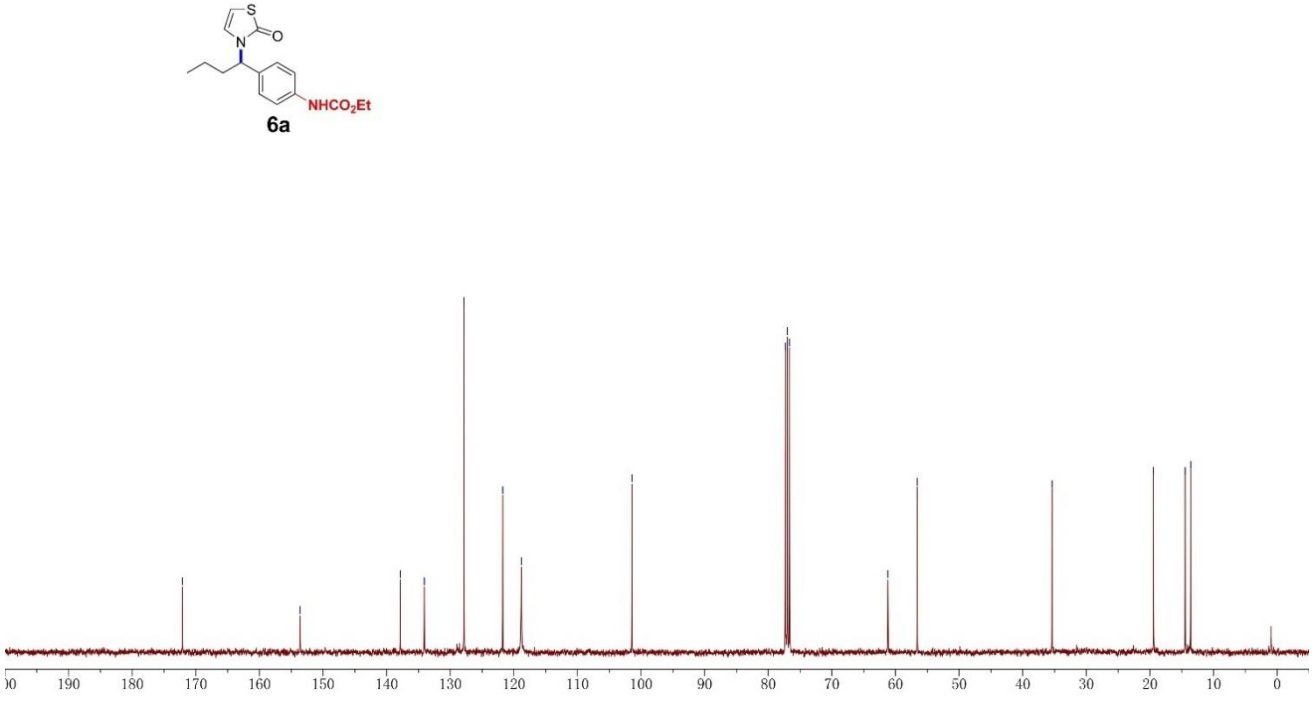
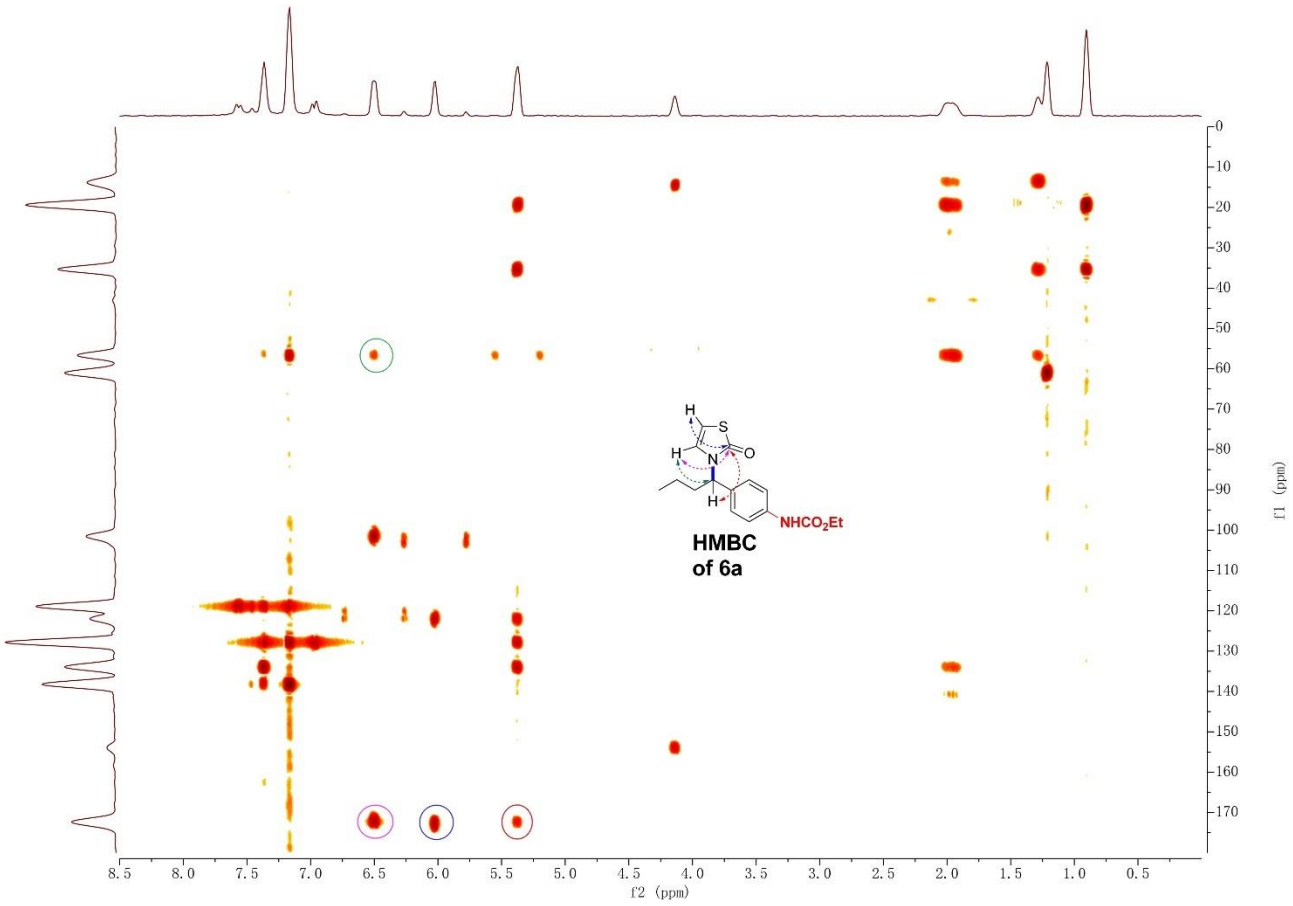
MeO
N
S
CH2OMe
2m

7.2 Spectra of Compounds in Table 2



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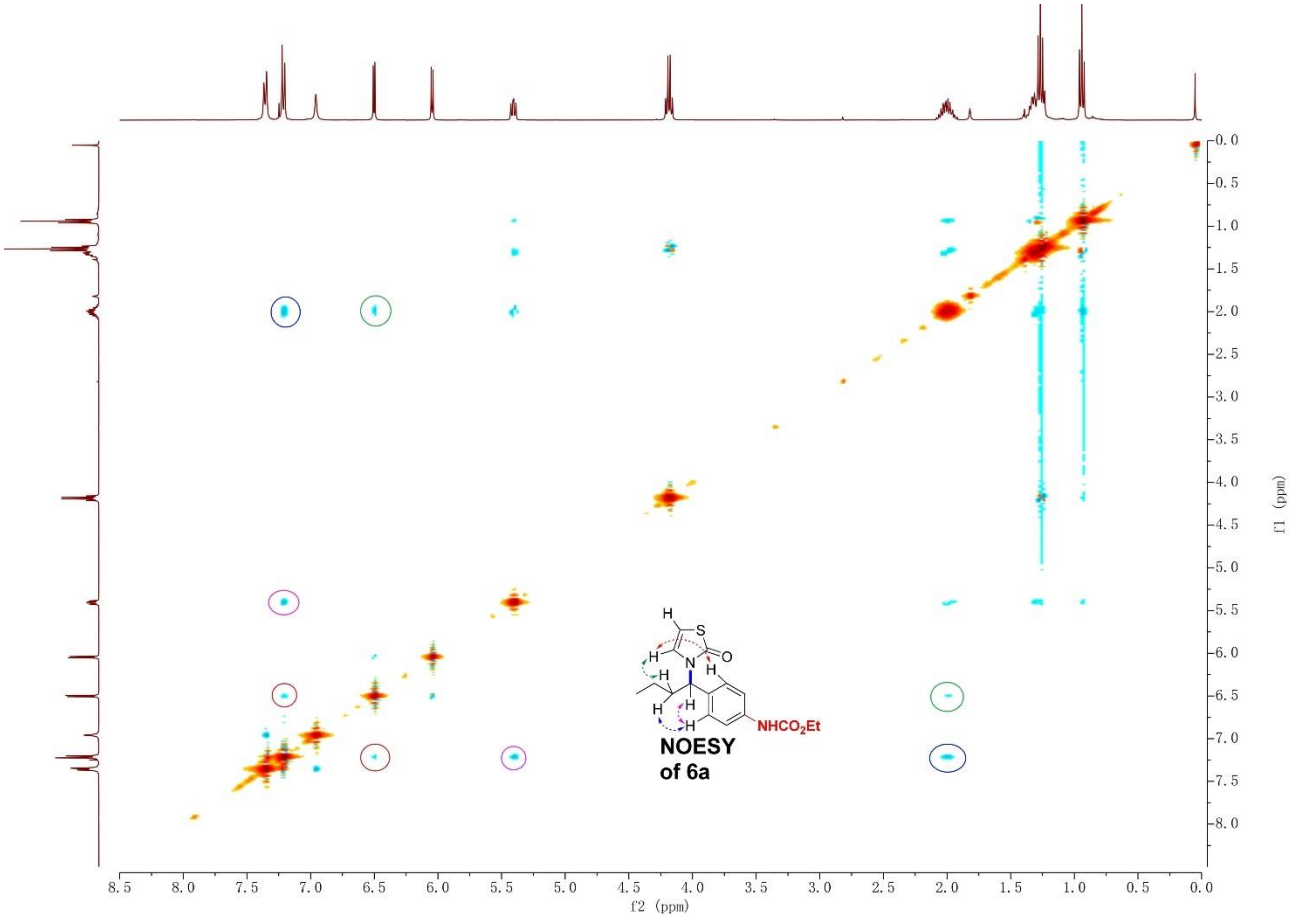
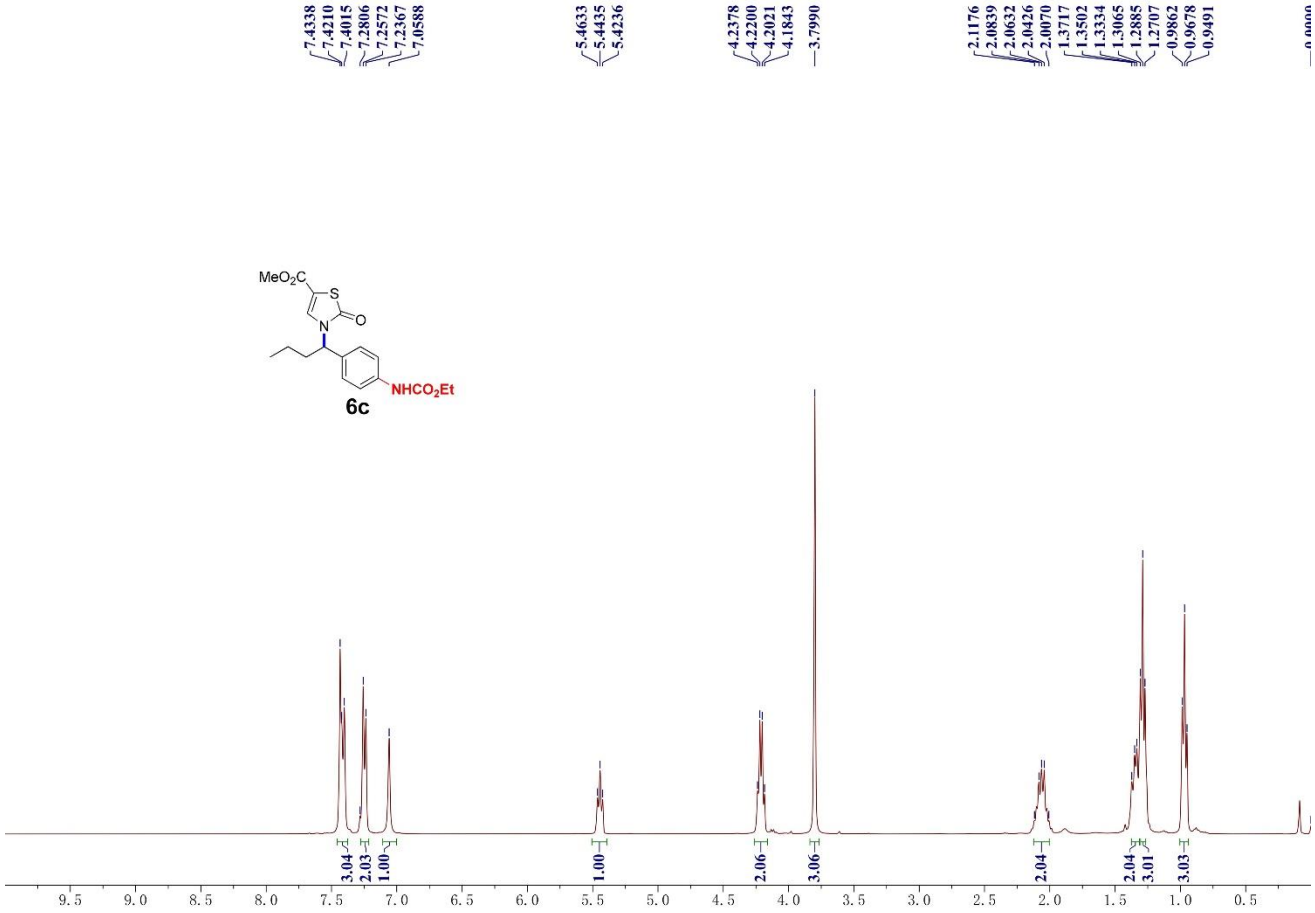
of 6a
NHCO2Et
f2 (ppm)
f1 (ppm)


NOESY
of 6a
NHCO2Et
f2 (ppm)
f1 (ppm)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7.0588
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5.4435
5.4236
4.2378
4.2200
4.2021
4.1843
3.7990
2.1176
2.0839
2.0632
2.0426
2.0070
1.3717
1.3502
1.3334
1.3065
1.2885
1.2707
0.9862
0.9678
0.9491
MeO2C
S
N
O
NHCO2Et
6c
3.04
2.03
1.00
1.00
2.06
3.06
2.04
2.04
3.01
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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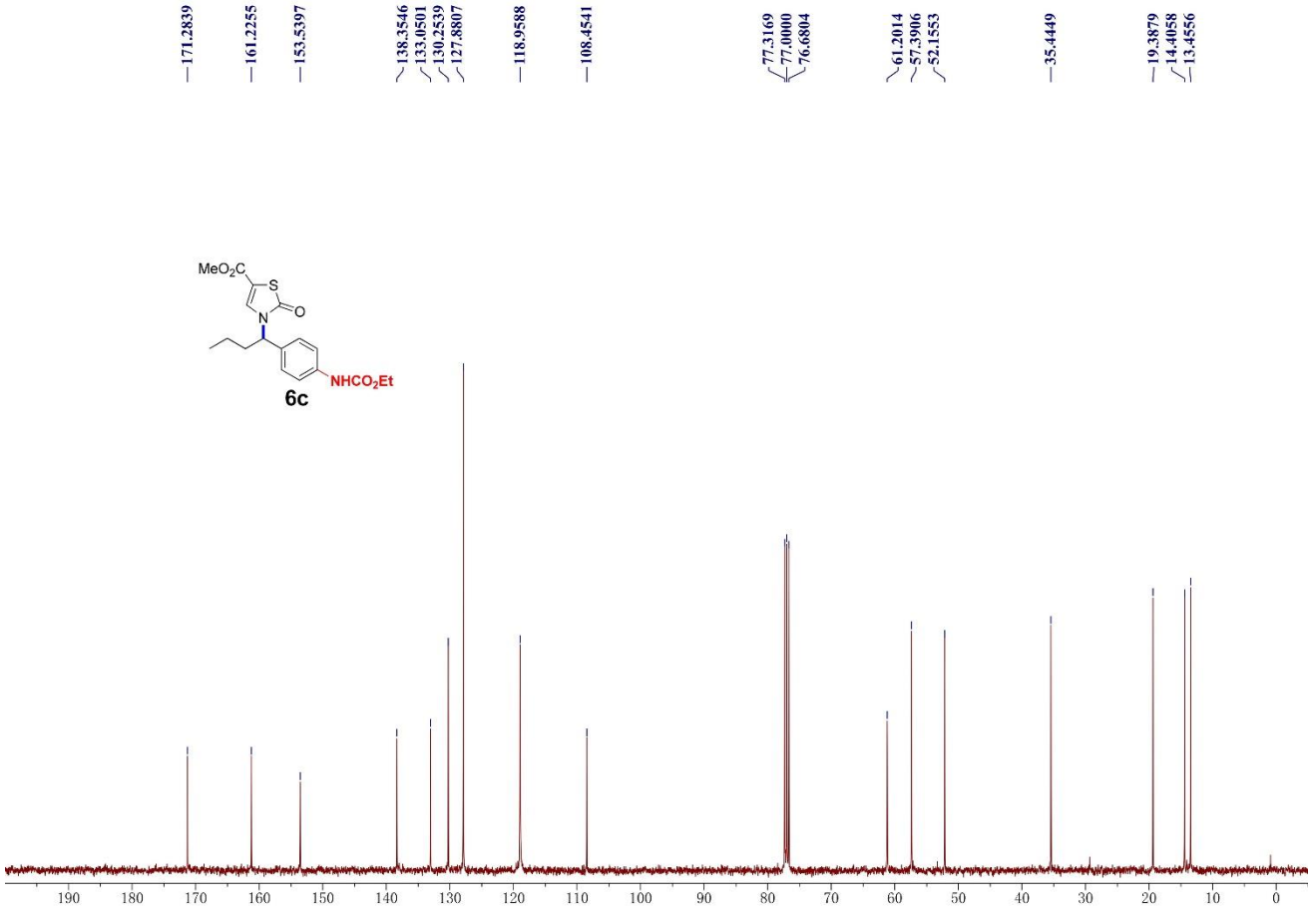
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5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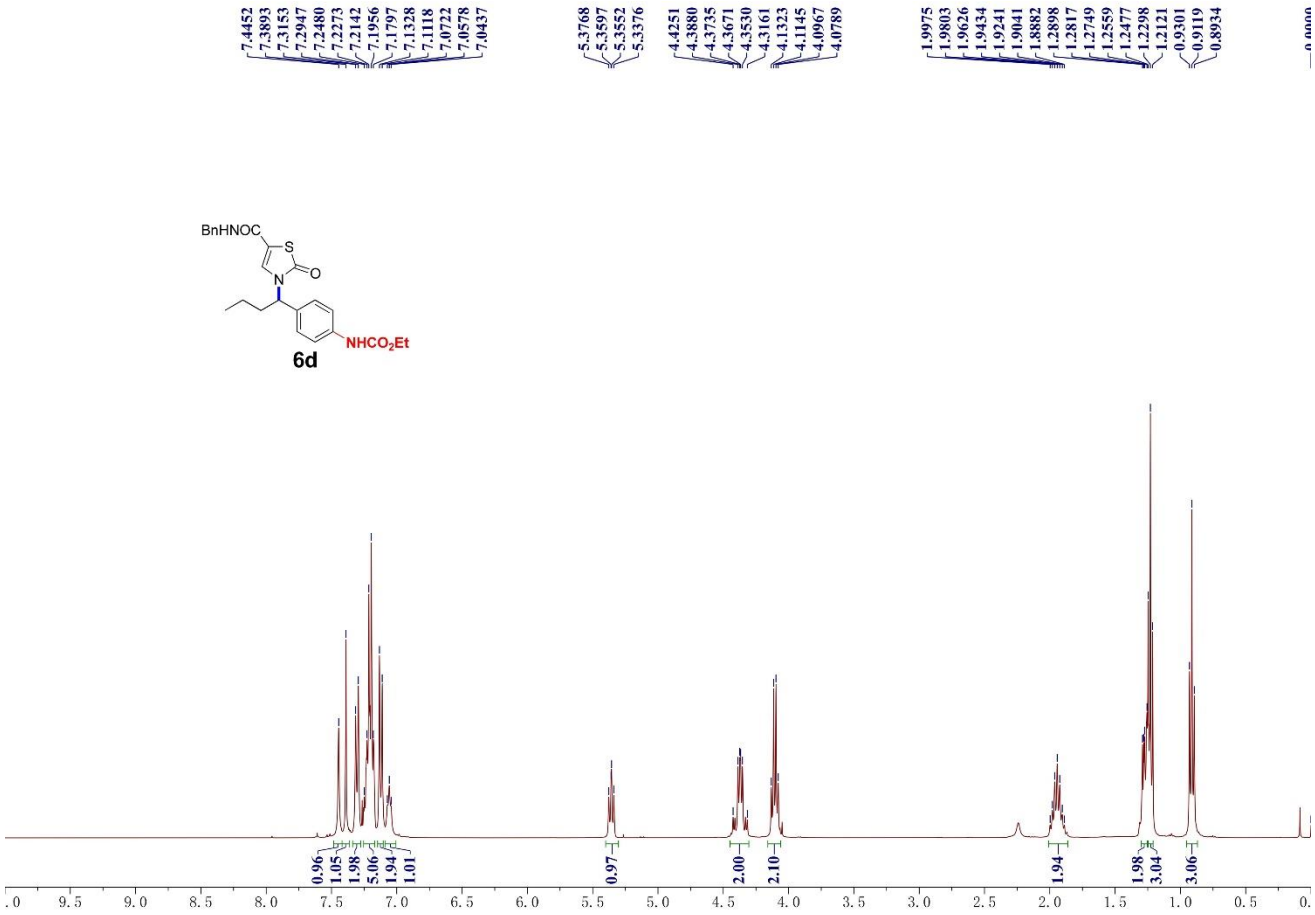
77.0000
76.6804
61.2014
57.3906
52.1553
35.4449
19.3879
14.4058
13.4556
MeO2C
S
N
O
NHCO2Et
6c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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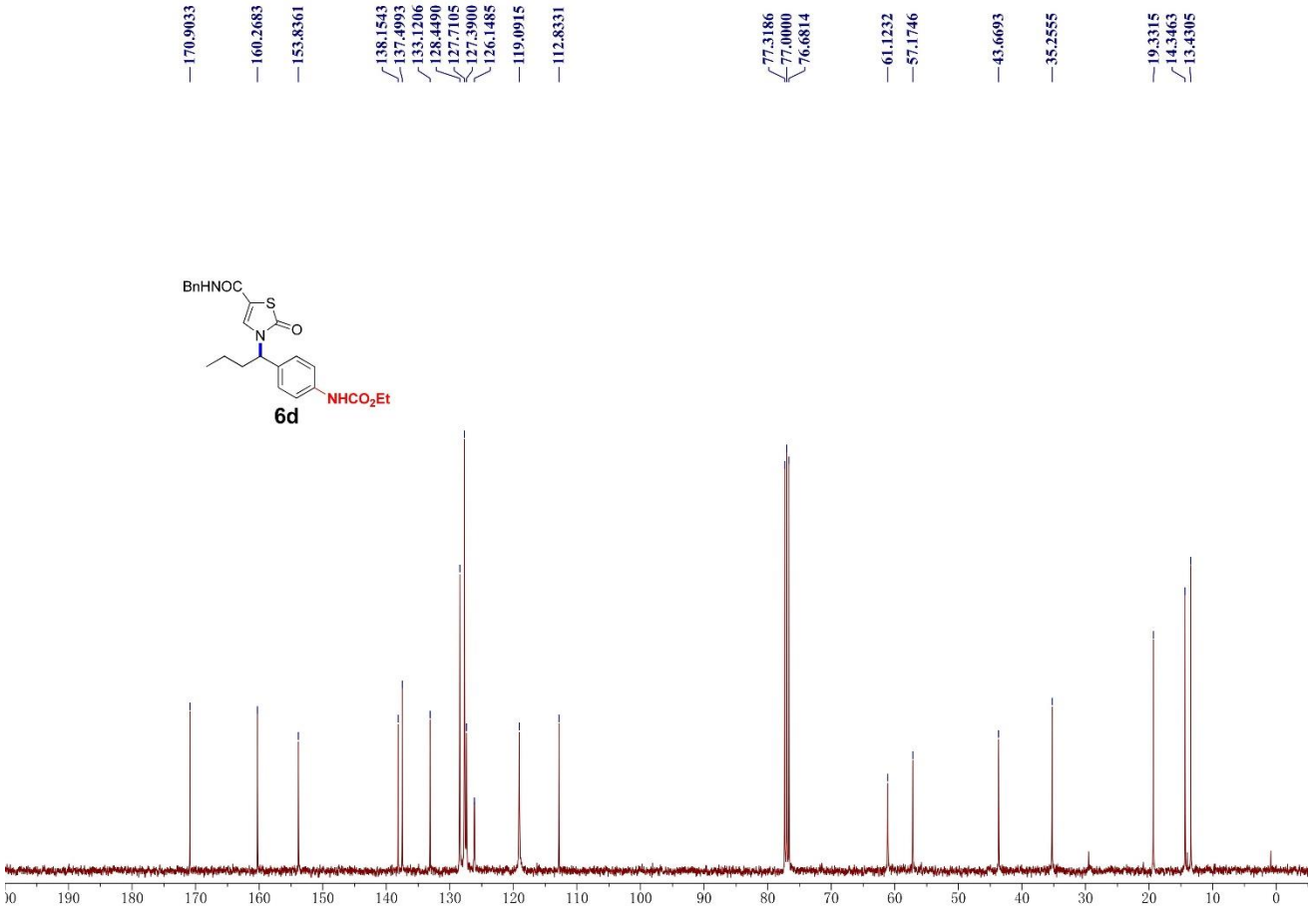
7.1118
7.0722
7.0578
7.0437
5.3768
5.3597
5.3552
5.3376
4.4251
4.3880
4.3735
4.3671
4.3530
4.3161
4.1323
4.1145
4.0967
4.0789
1.9975
1.9803
1.9626
1.9434
1.9241
1.9041
1.8882
1.2898
1.2817
1.2749
1.2559
1.2477
1.2298
1.2121
0.9301
0.9119
0.8934
BnHNOC
S
O
N
NHCO2Et
6d
0.96
1.05
1.98
5.06
1.94
1.01
0.97
2.00
2.10
1.94
1.98
3.04
3.06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77.0000
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14.3463
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BnHNOC
S
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N
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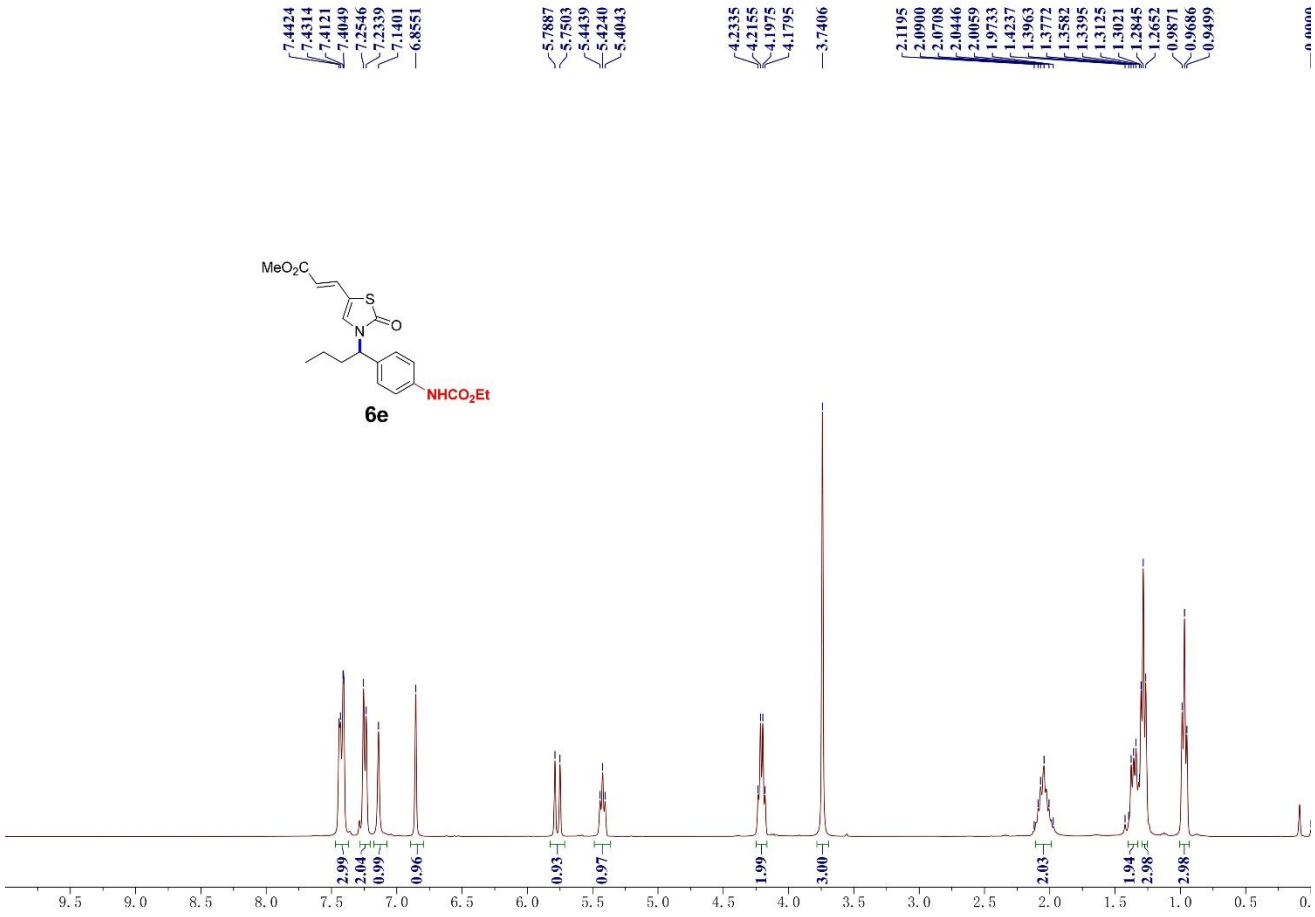
6d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5.4043
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4.2155
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4.1795
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2.0446
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1.3021
1.2845
1.2652
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0.9686
0.9499
MeO2C
S
N
O
NHCO2Et
6e
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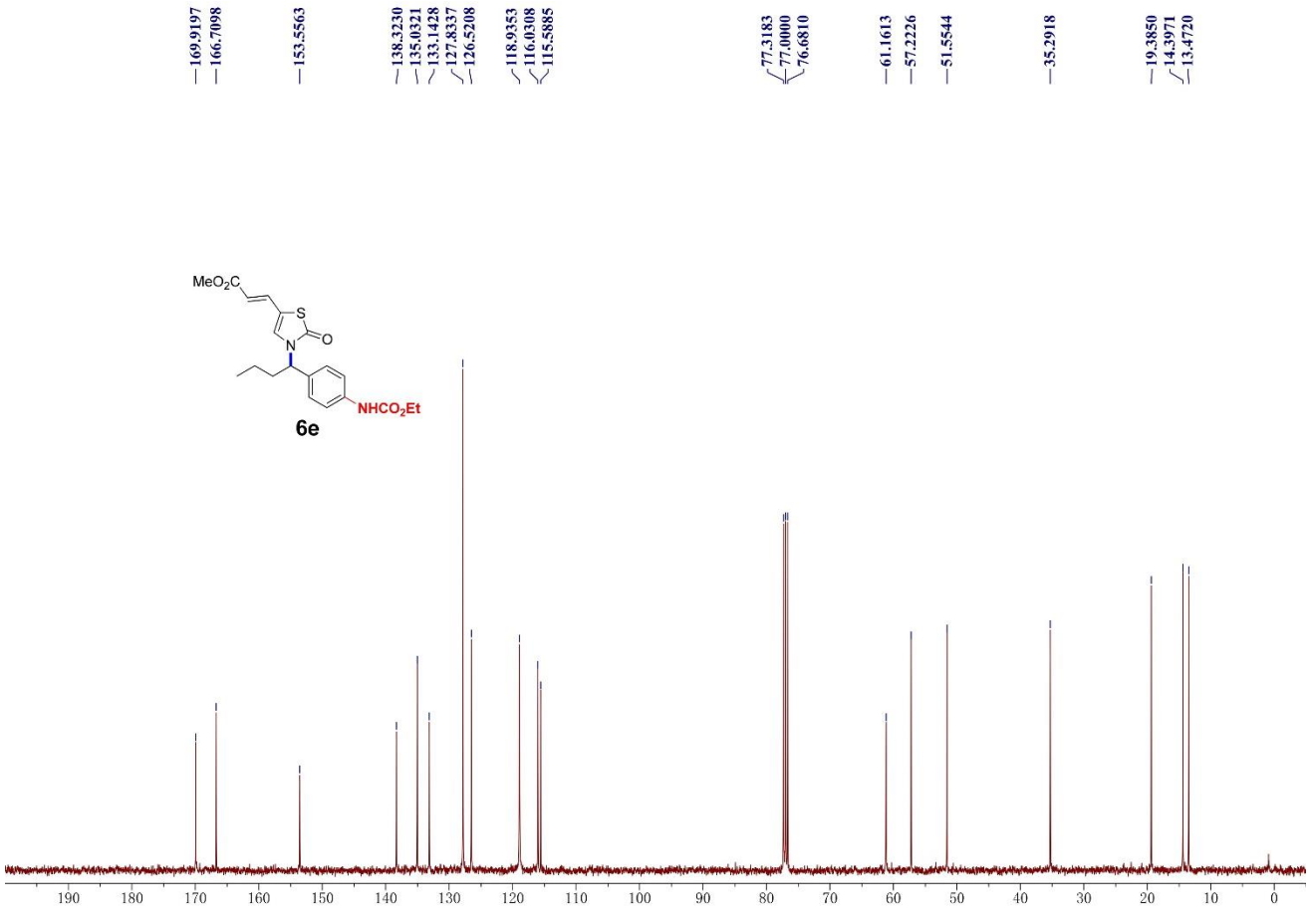
2.04
0.99
0.96
0.93
0.97
1.99
3.00
2.03
1.94
2.98
2.98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MeO2C
S
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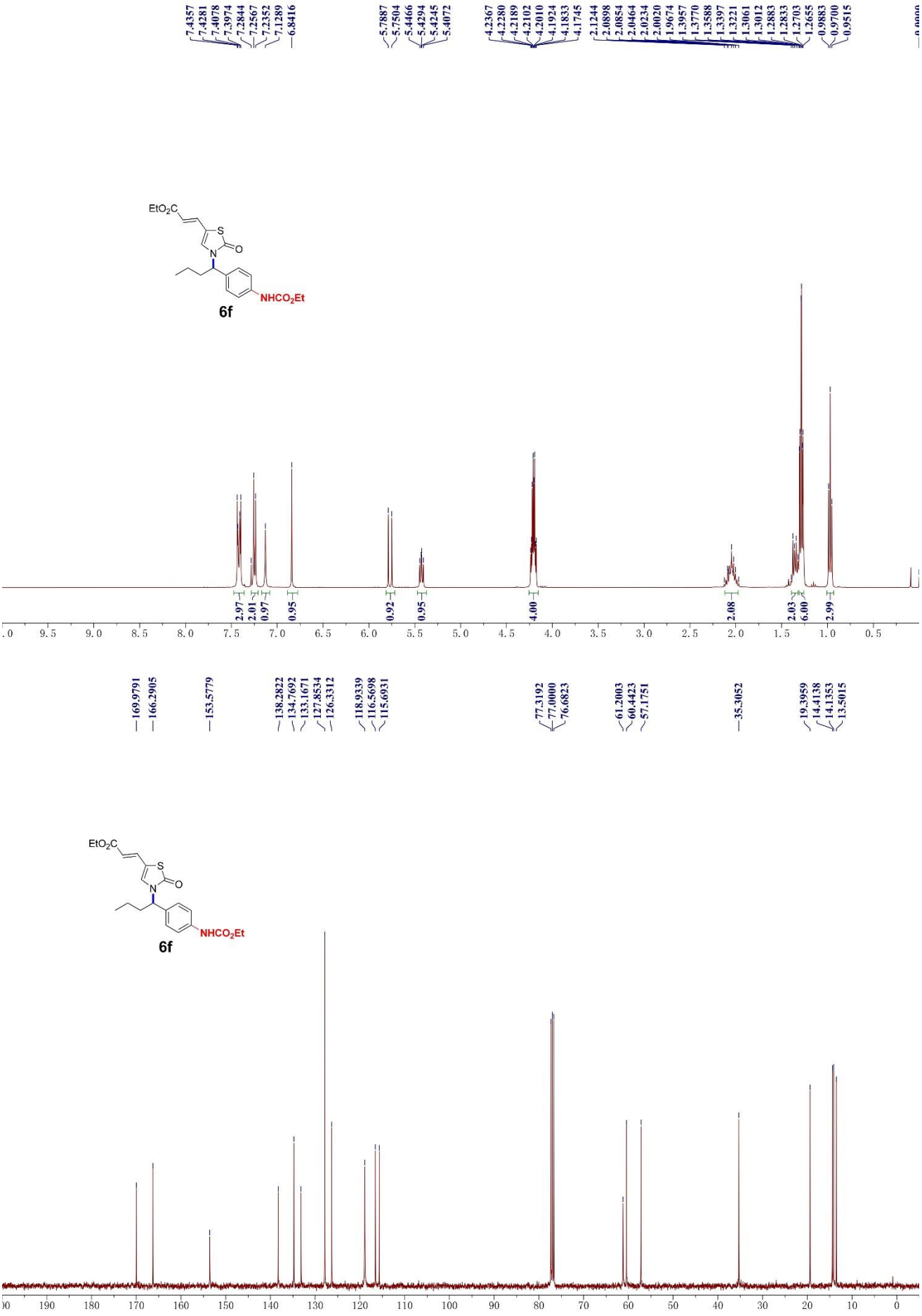
O
NHCO2Et
6e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0.9515
EtO2C
S
O
N
NHCO2Et
6f
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2.01
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0.95
0.92
0.95
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2.08
2.03
6.00
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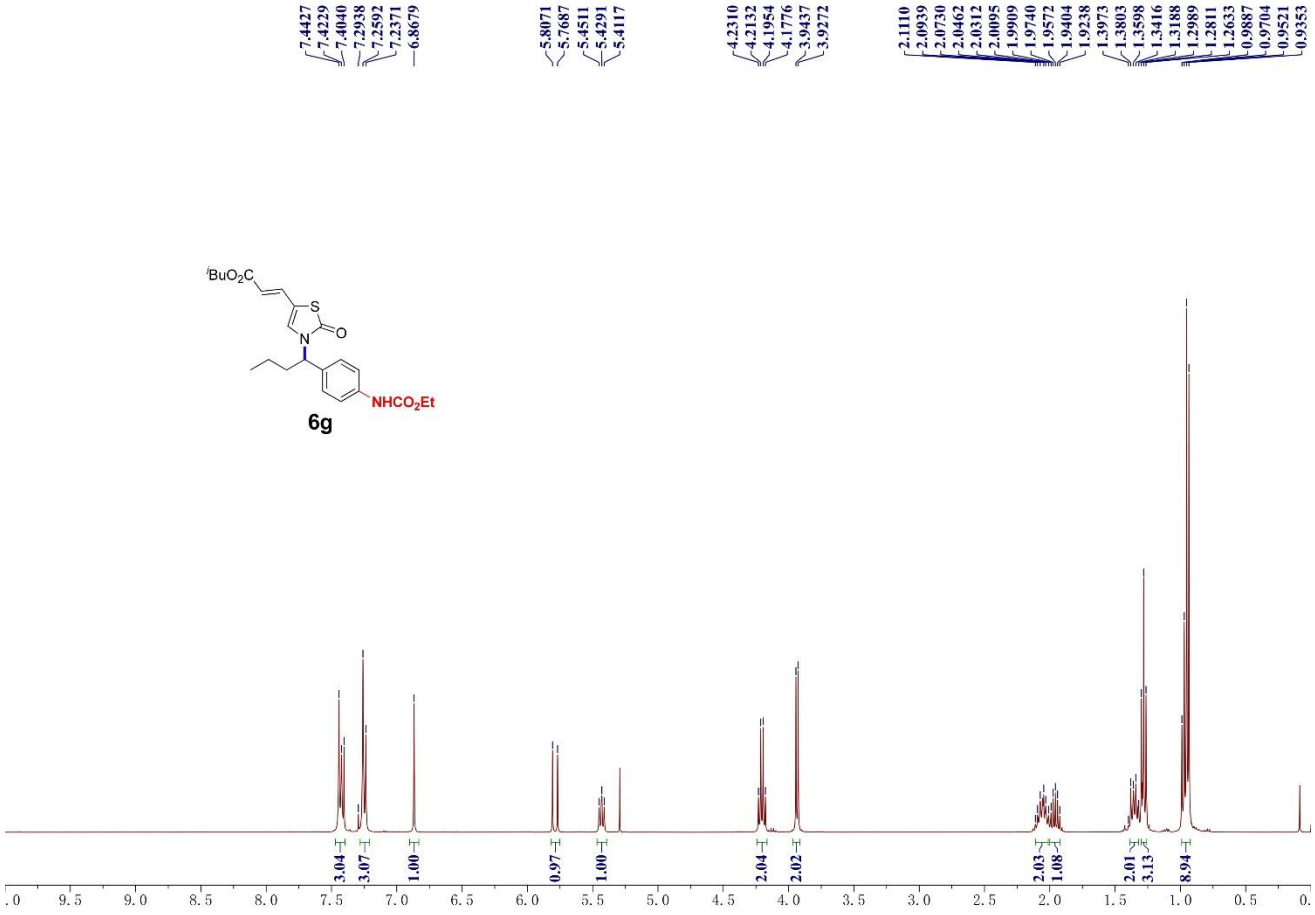
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5.4117
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4.1954
4.1776
3.9437
3.9272
2.1110
2.0939
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2.0462
2.0312
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1.9740
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1.3188
1.2989
1.2811
1.2633
0.9887
0.9704
0.9521
0.9353
tBuO2C
S
O
N
NHCO2Et
6g
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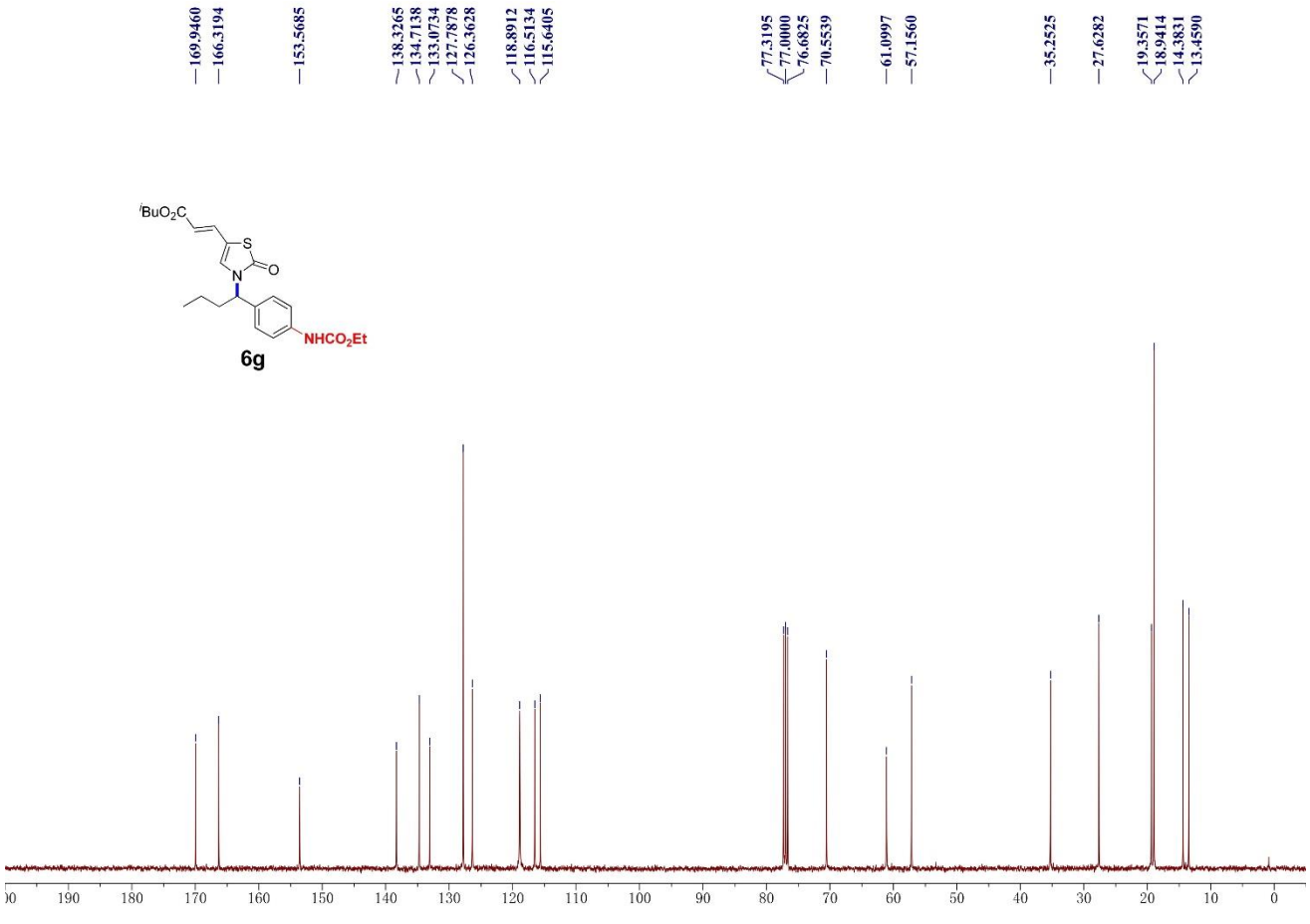
3.13
8.94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77.0000
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70.5539
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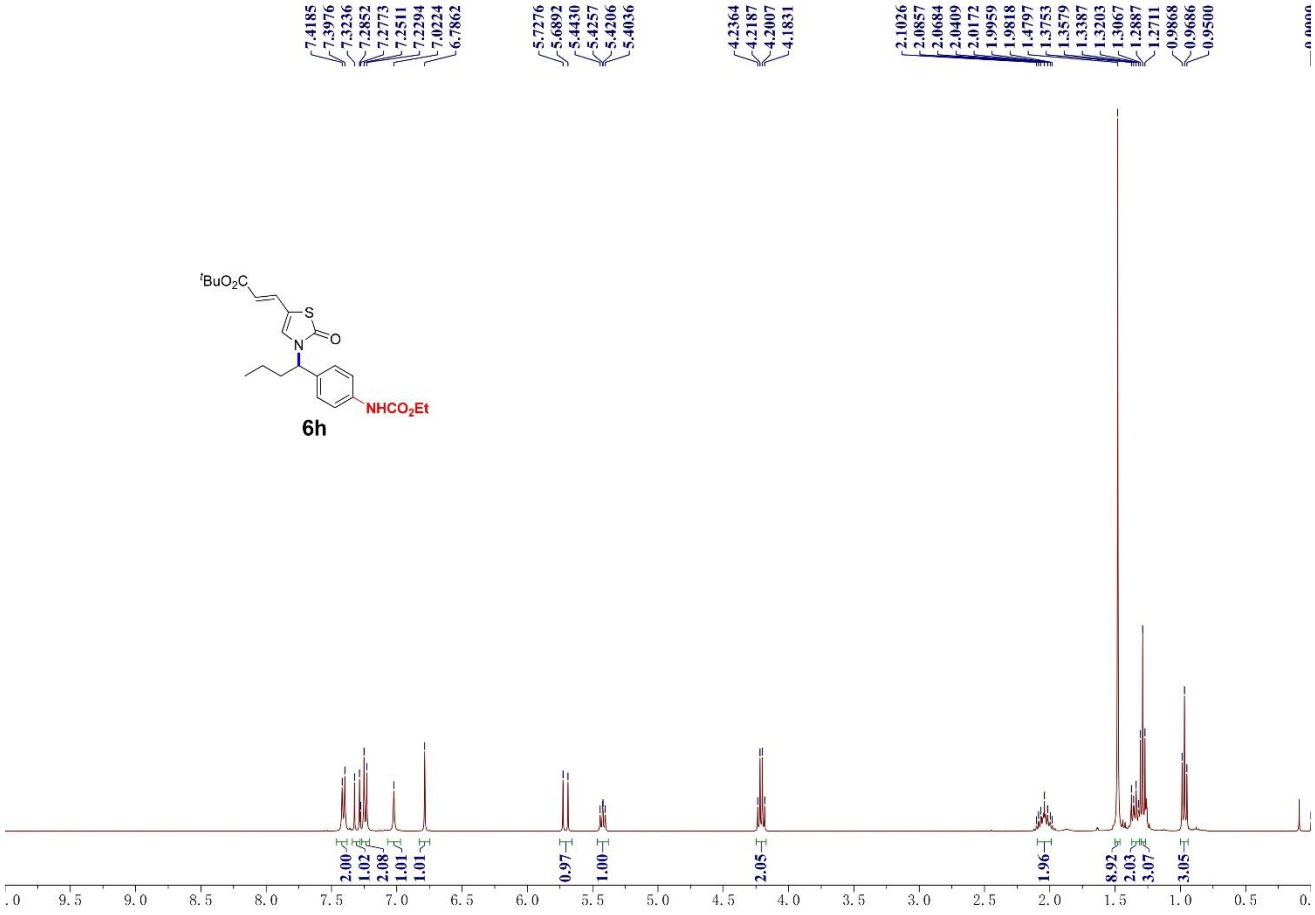
18.9414
14.3831
13.4590
tBuO2C
S
O
N
NHCO2Et
6g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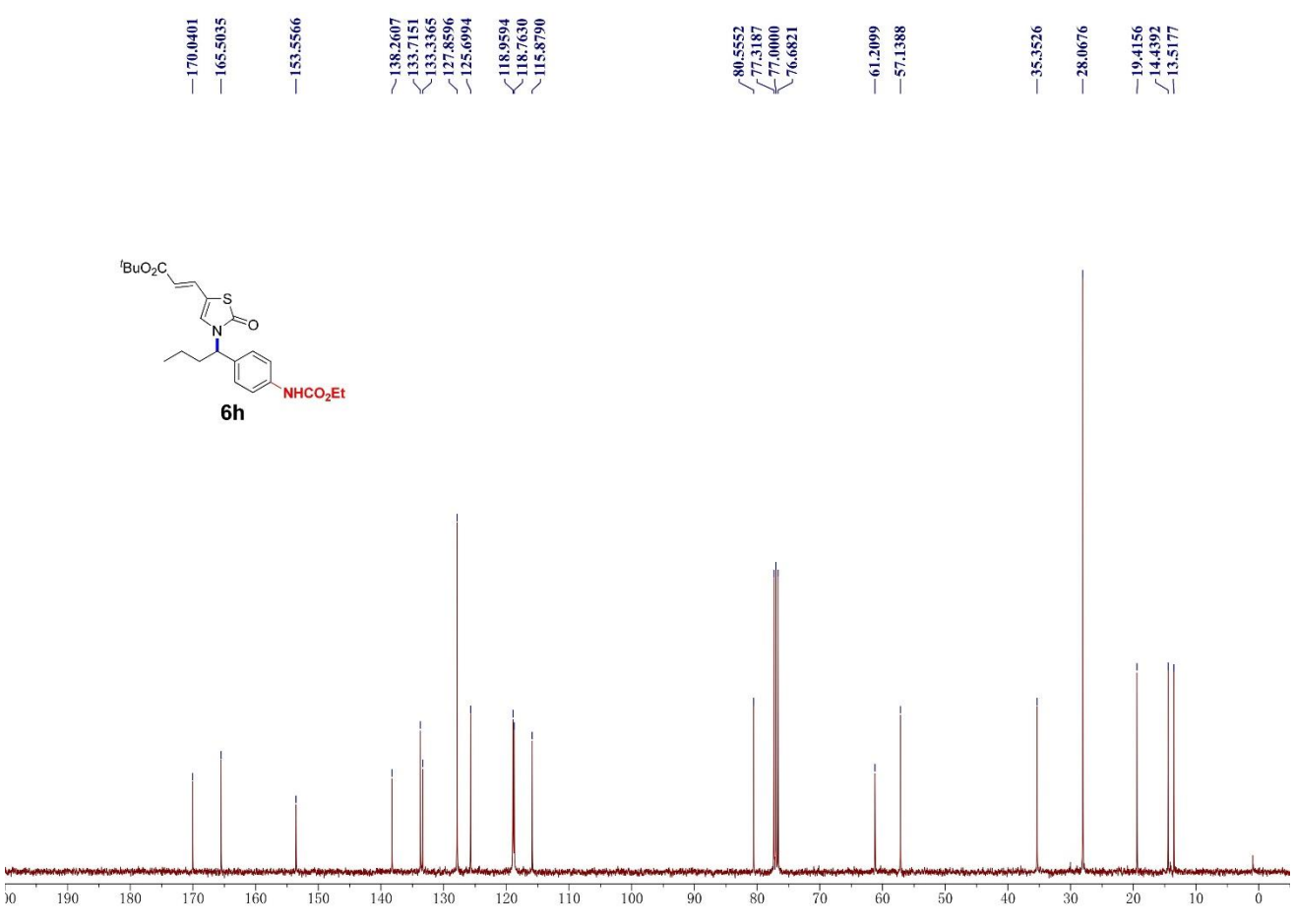
5.4257
5.4206
5.4036
4.2364
4.2187
4.2007
4.1831
2.1026
2.0857
2.0684
2.0409
2.0172
1.9959
1.9818
1.4797
1.3753
1.3579
1.3387
1.3203
1.3067
1.2887
1.2711
0.9868
0.9686
0.9500
2.00
1.02
2.08
1.01
1.01
0.97
1.00
2.05
1.96
8.92
2.03
3.07
3.05

tBuO2C
S
N
O
NHCO2Et

6h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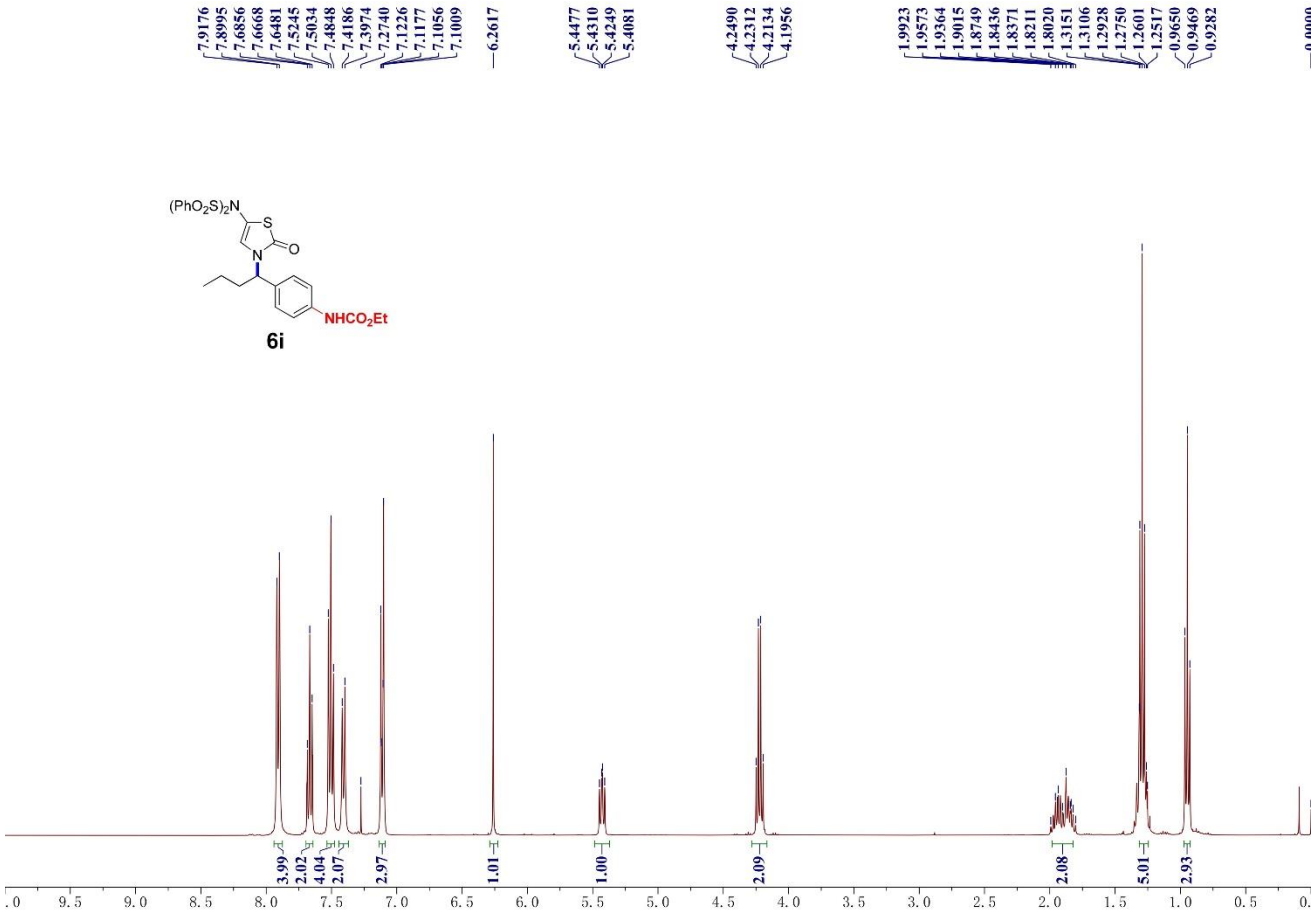
14.4392
13.5177

tBuO2C
S
N
O
NHCO2Et

6h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1.8371
1.8211
1.8020
1.3151
1.3106
1.2928
1.2750
1.2601
1.2517
0.9650
0.9469
0.9282
(PhO2S)2N
S
O
N
NHCO2Et
6i
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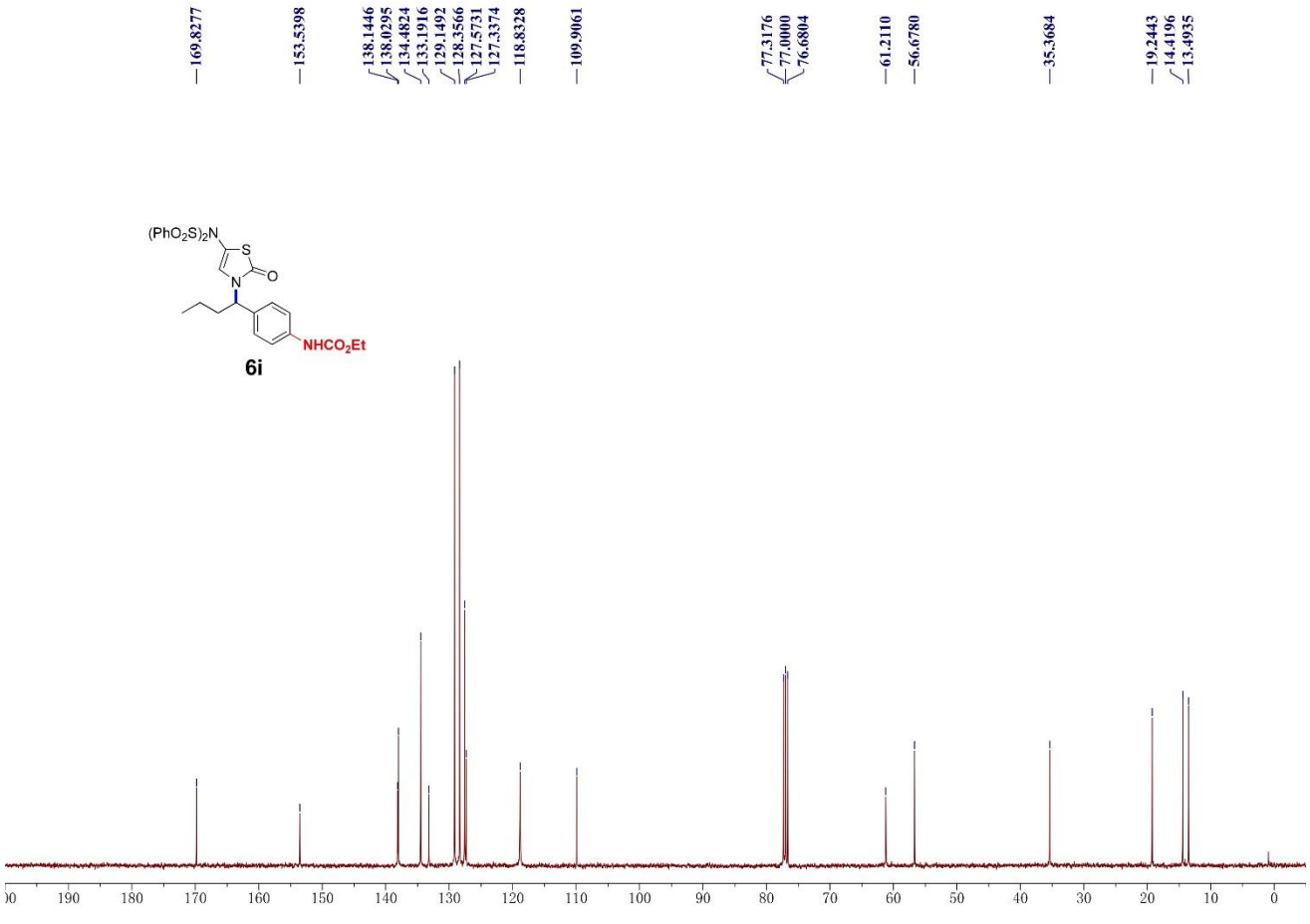
4.04
2.07
2.97
1.01
1.00
2.09
2.08
5.01
2.93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77.0000
76.6804
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O
N
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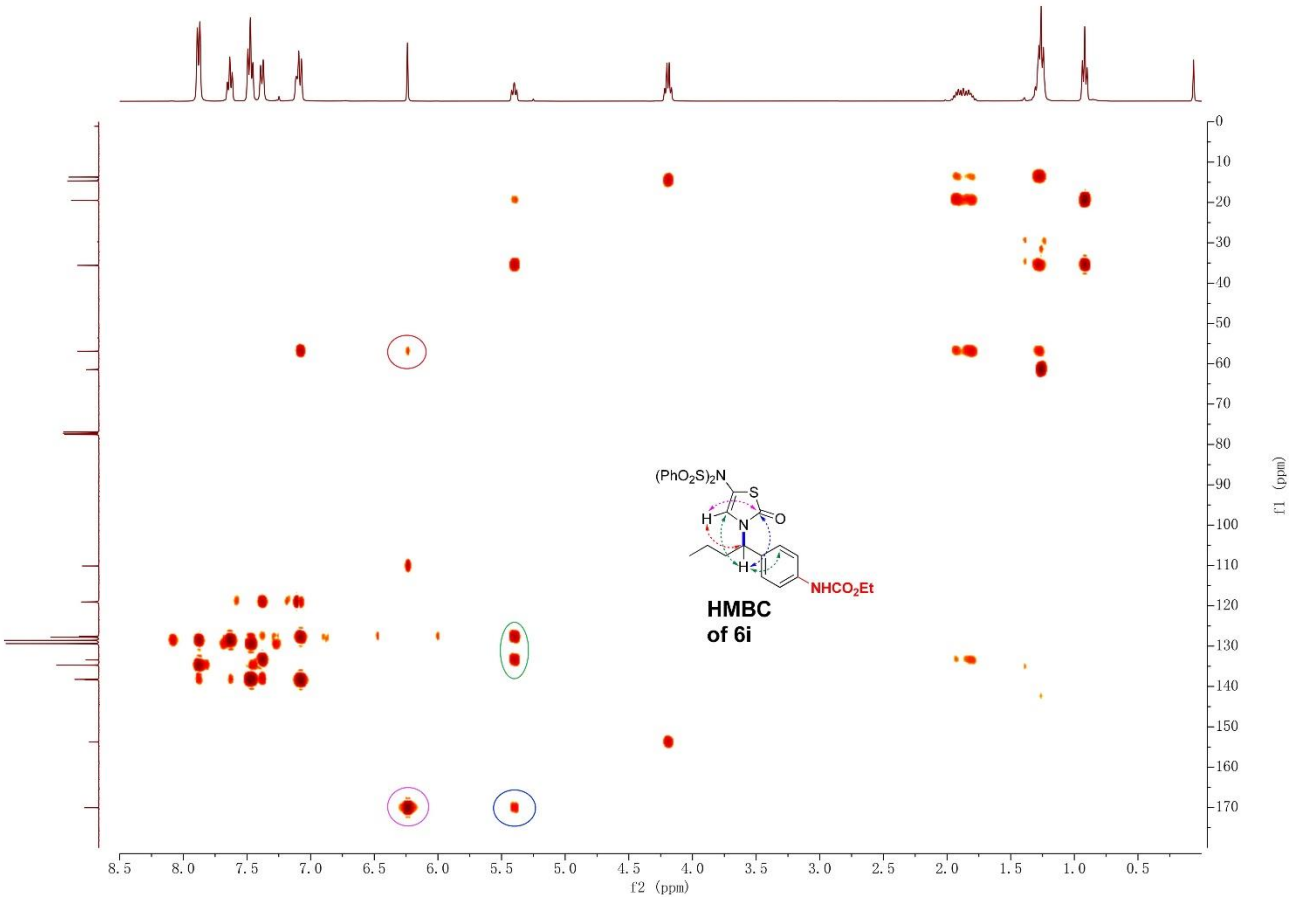
6i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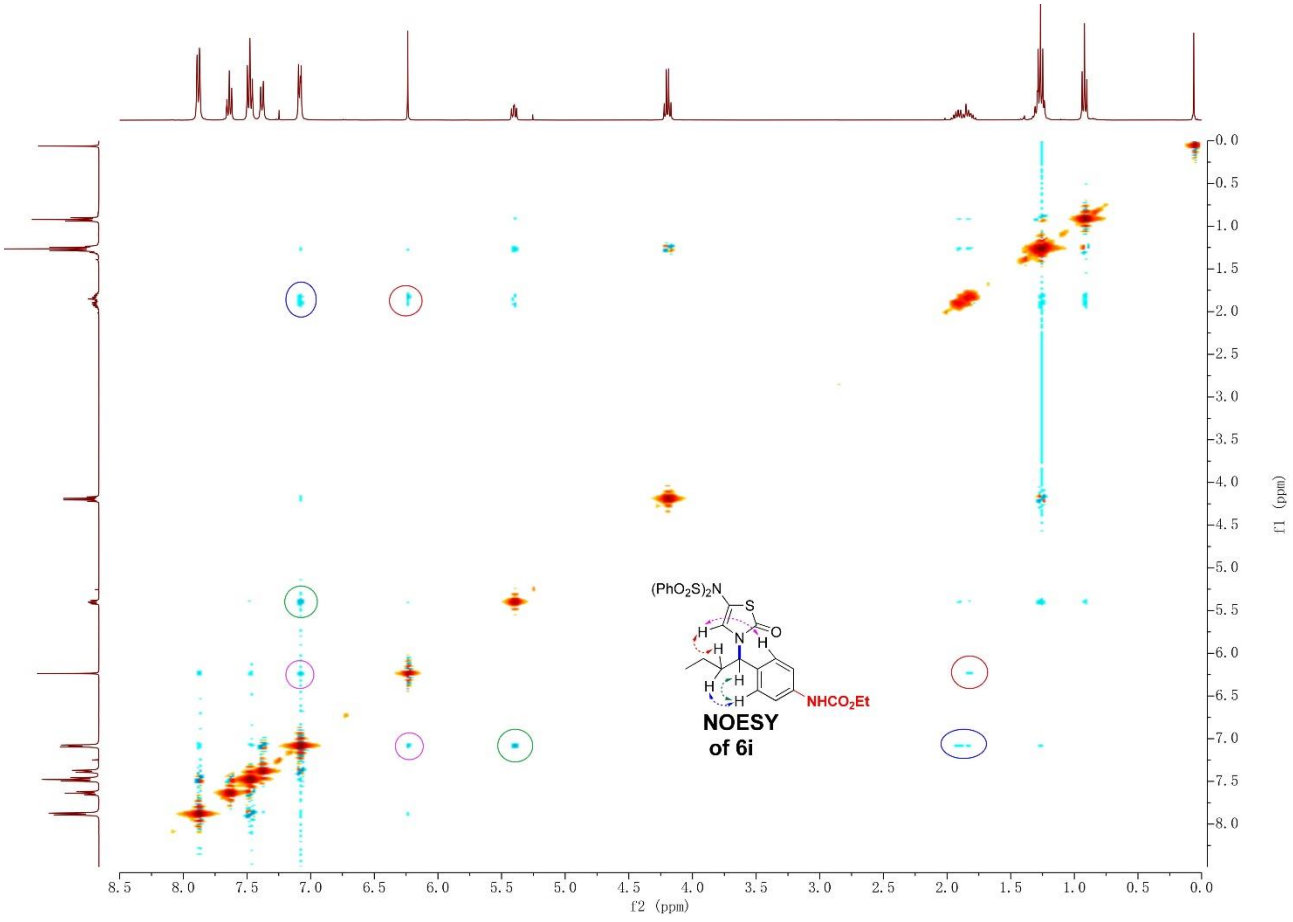
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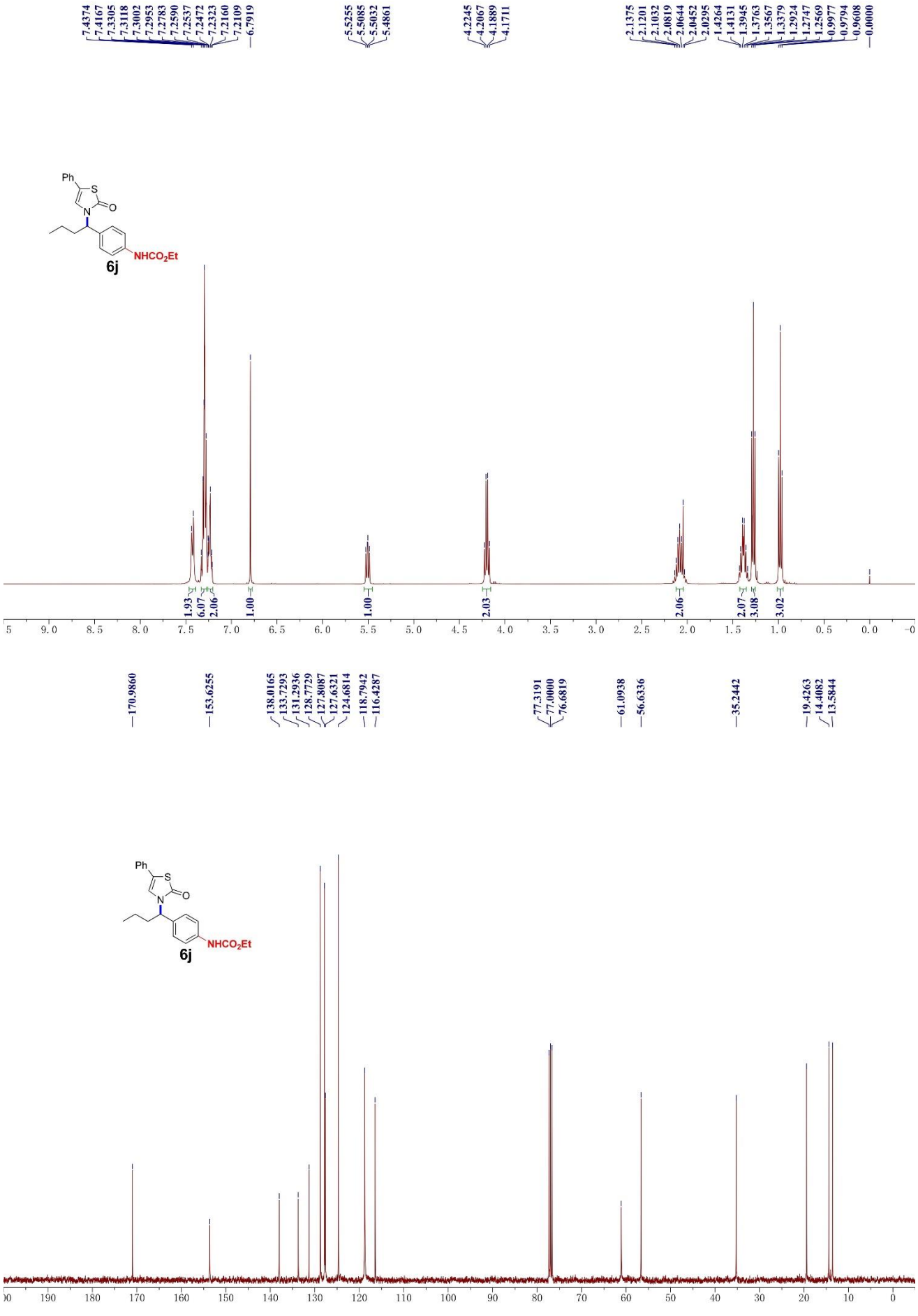
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7.2160
7.2109
6.7919
5.5255
5.5085
5.5032
5.4861
4.2245
4.2067
4.1889
4.1711
2.1375
2.1201
2.1032
2.0819
2.0644
2.0452
2.0295
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1.2747
1.2569
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0.9608
0.0000
Ph
S
O
N
NHCO2Et
6j
1.93
6.07
2.06
1.00
1.00
2.03
2.06
2.07
3.08
3.02
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128.7729
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127.6321
124.6814
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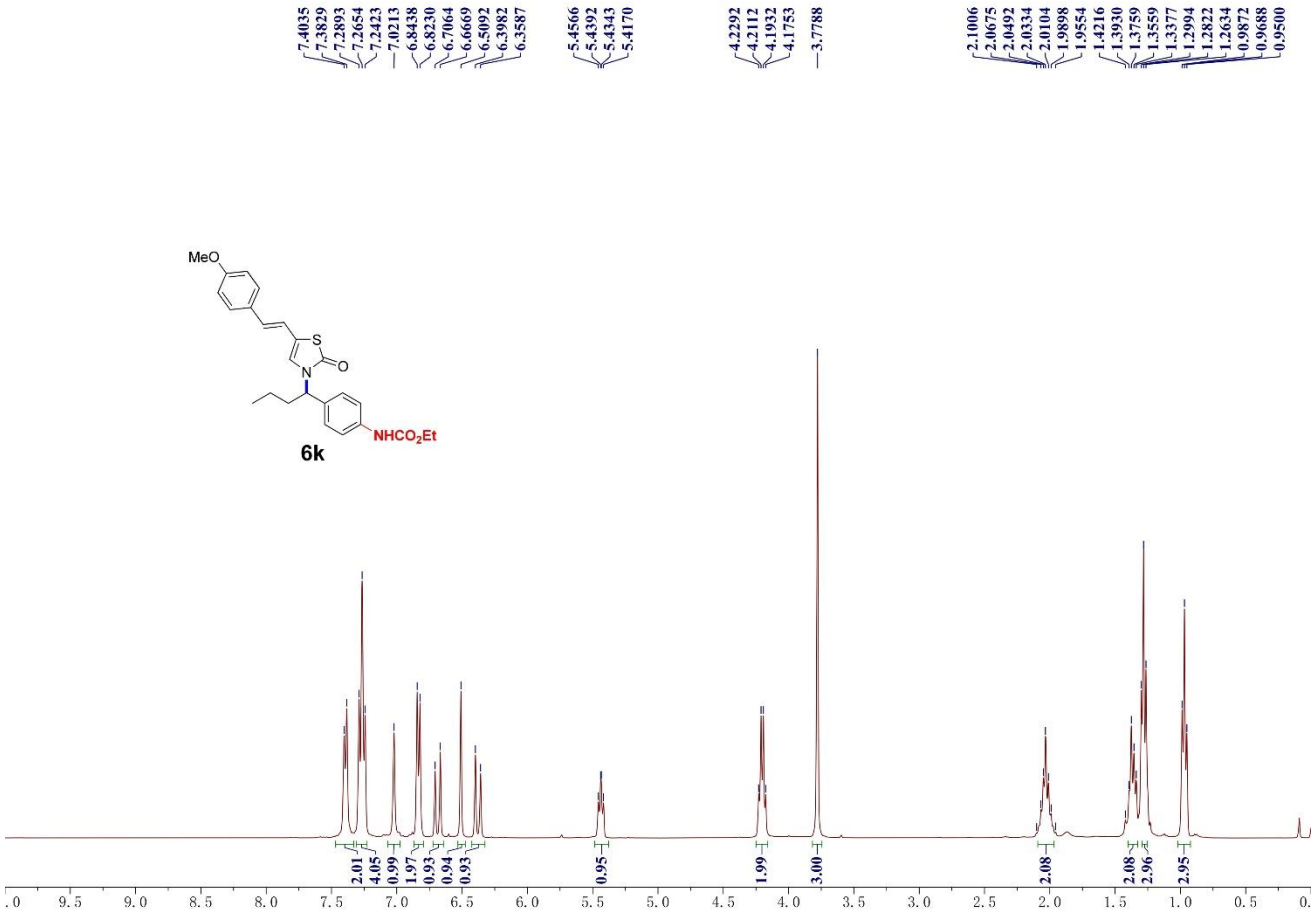
6j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6.3982
6.3587
5.4566
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5.4170
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4.2112
4.1932
4.1753
3.7788
2.1006
2.0675
2.0492
2.0334
2.0104
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1.9554
1.4216
1.3930
1.3759
1.3559
1.3377
1.2994
1.2822
1.2634
0.9872
0.9688
0.9500
MeO
S
O
N
NHCO2Et
6k
2.01
4.05
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0.94
0.93
0.95
1.99
3.00
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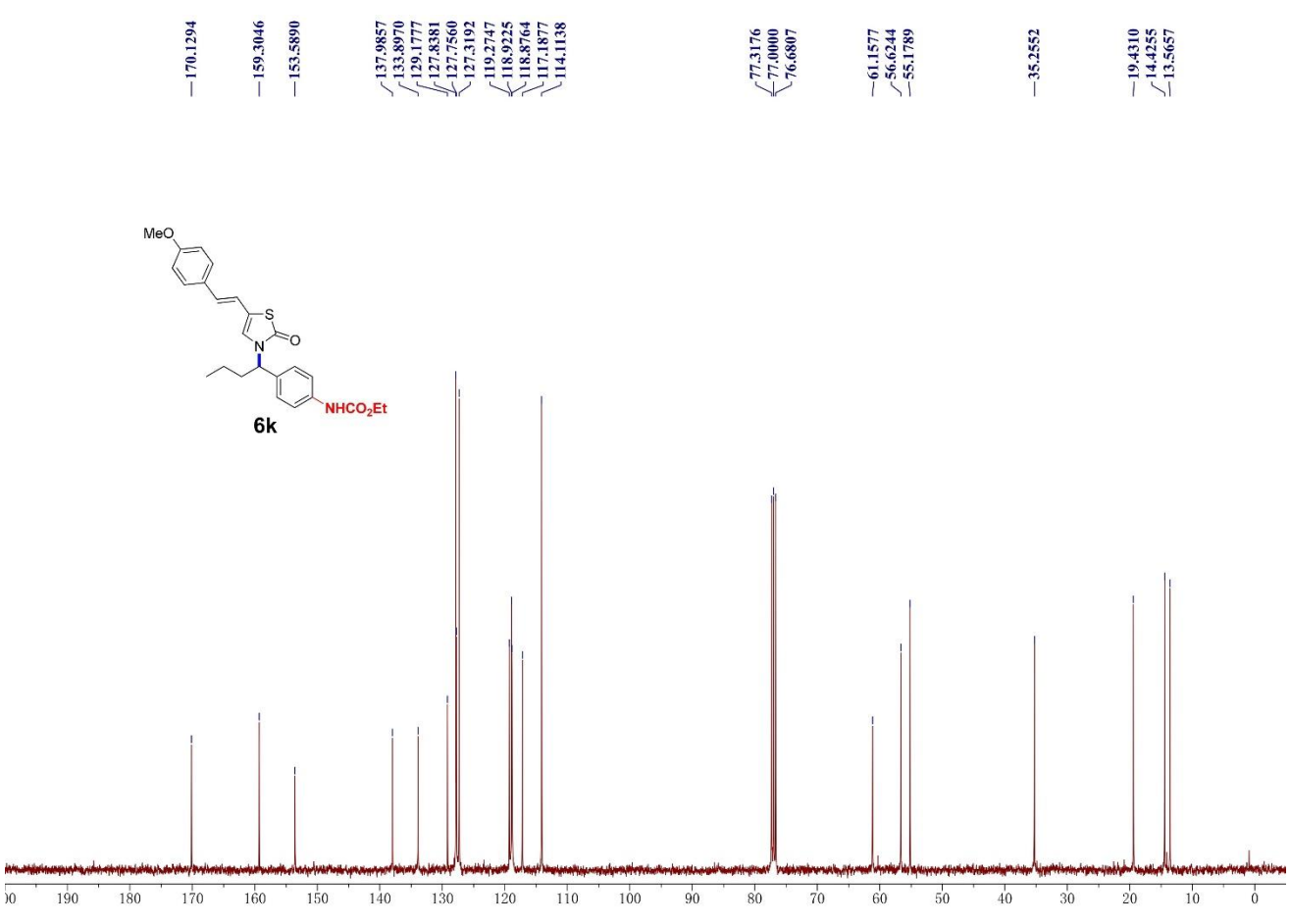
2.08
2.96
2.95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117.1877
114.1138
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77.0000
76.6807
61.1577
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35.2552
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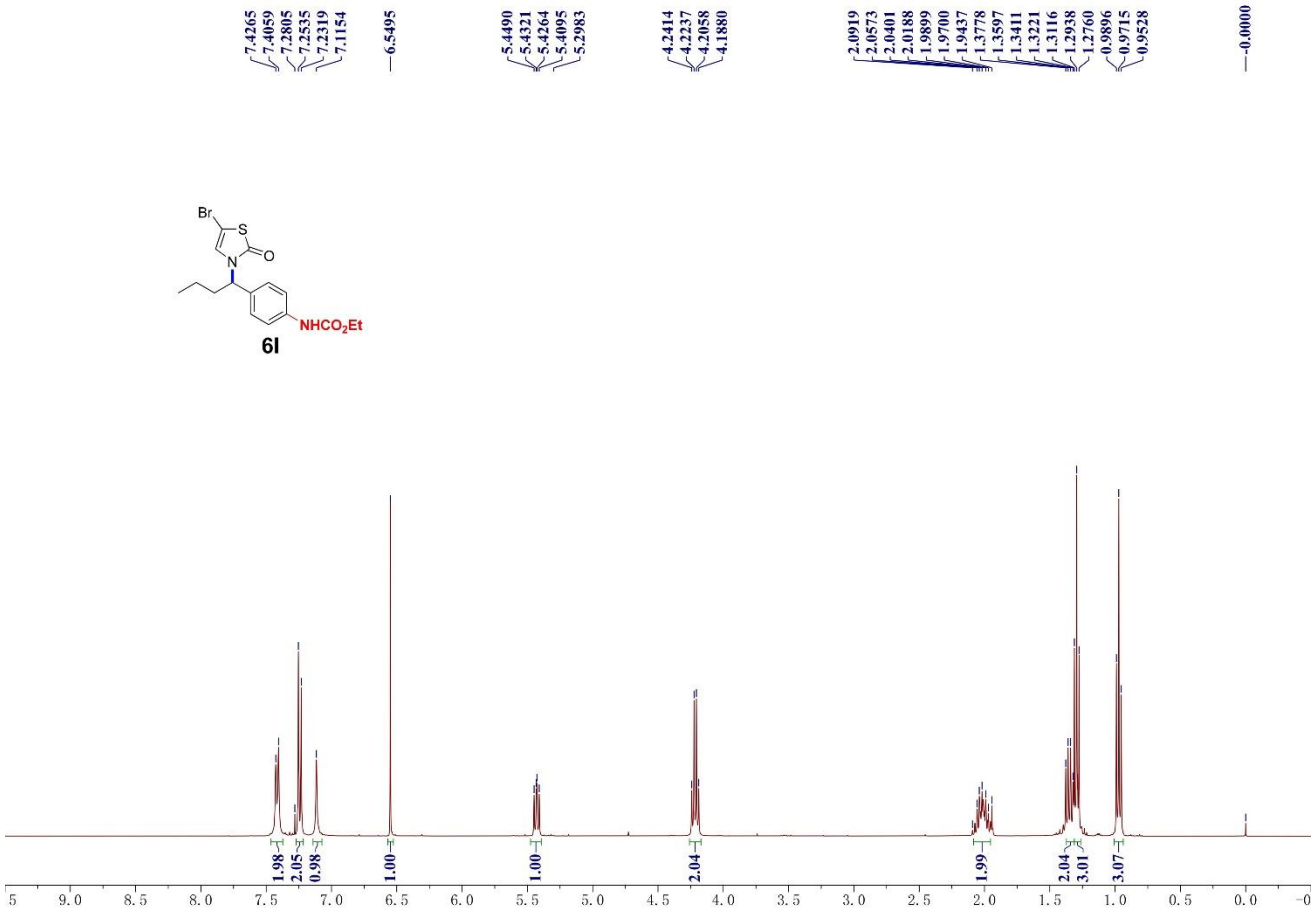
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5.2983
4.2414
4.2237
4.2058
4.1880
2.0919
2.0573
2.0401
2.0188
1.9899
1.9700
1.9437
1.3778
1.3597
1.3411
1.3221
1.3116
1.2938
1.2760
0.9896
0.9715
0.9528
0.0000
Br
S
O
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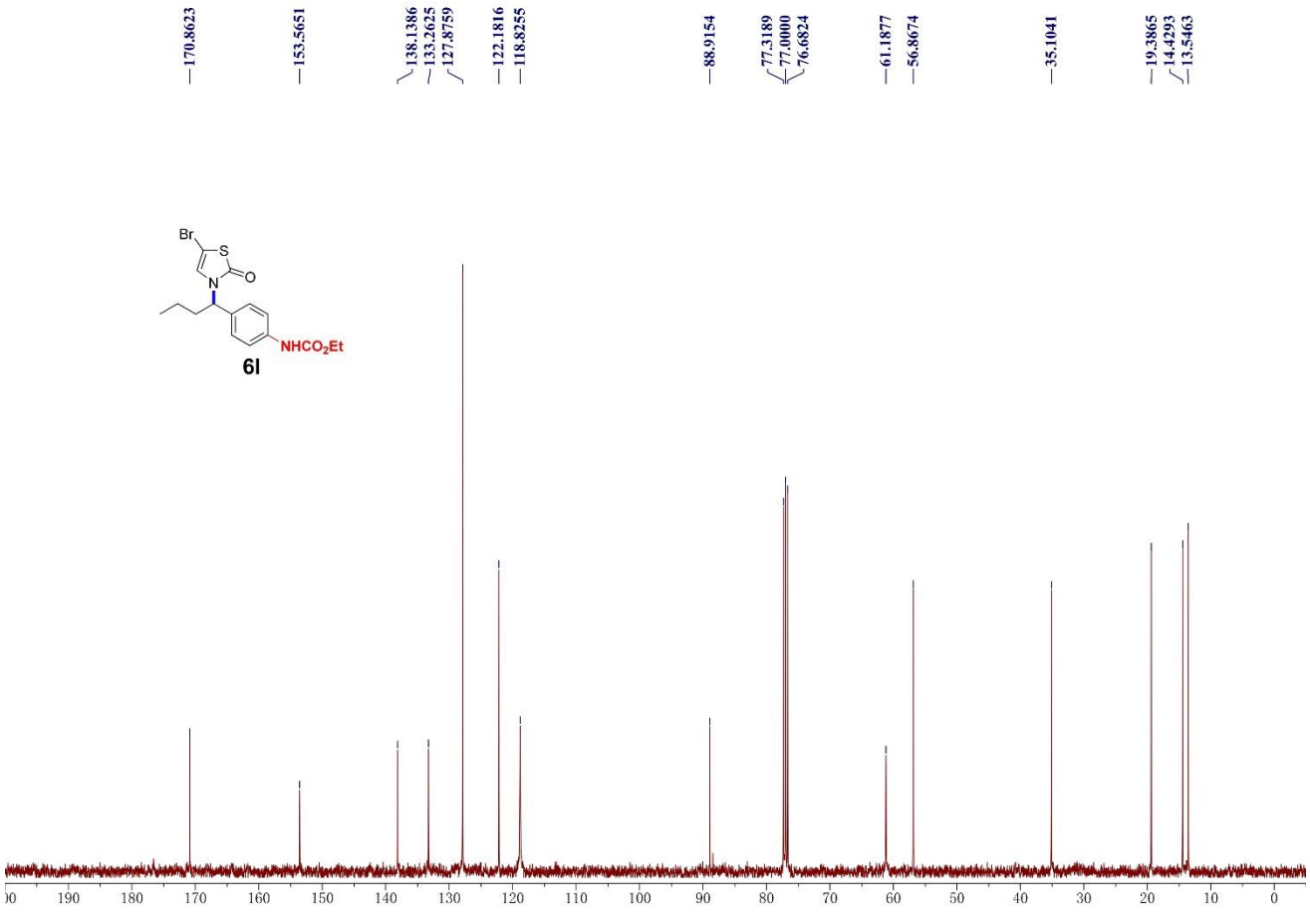
0.98
1.00
1.00
2.04
1.99
2.04
3.01
3.07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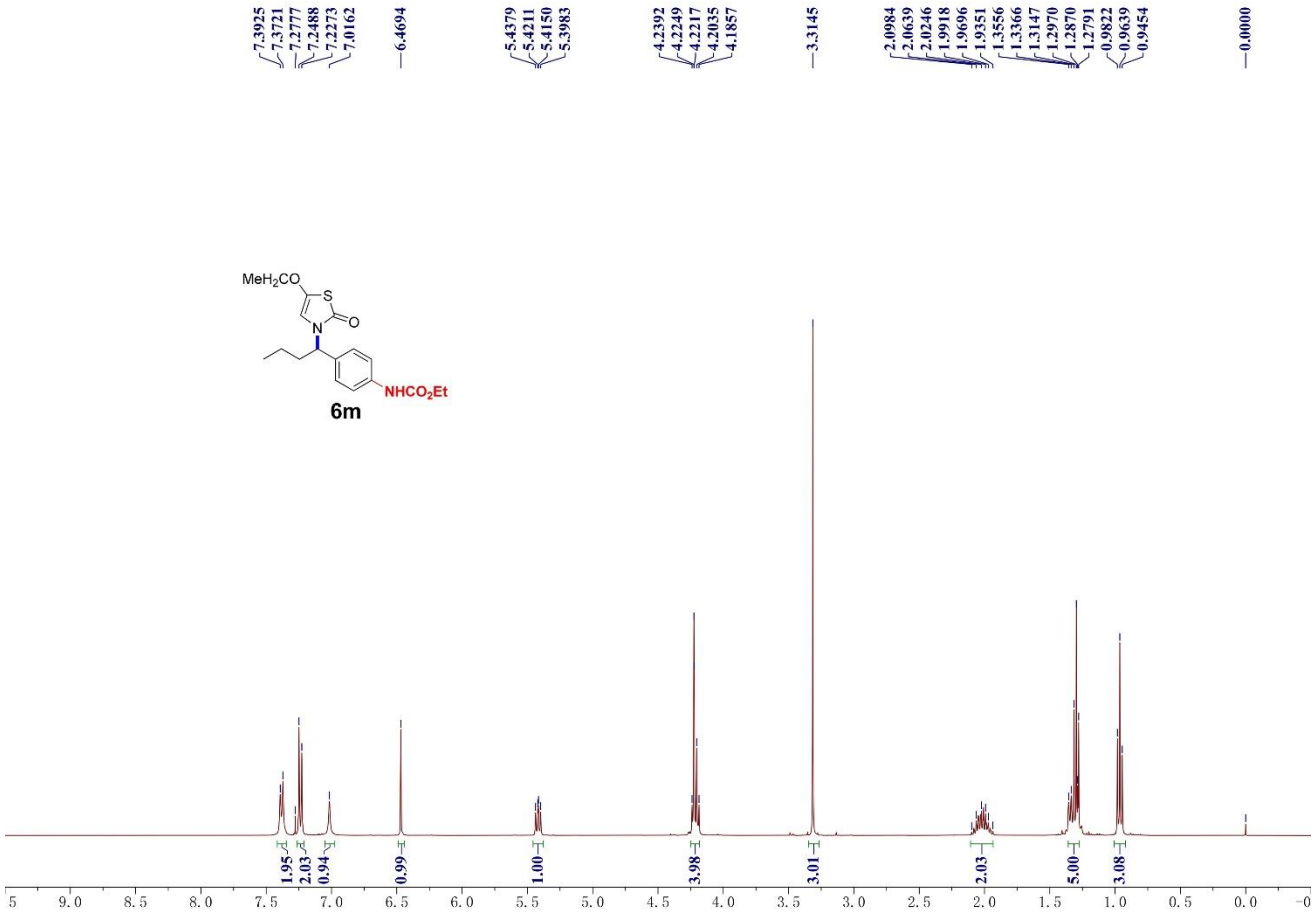
Br
S
O
N
NHCO2Et
6l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4.2249
4.2217
4.2035
4.1857
3.3145
2.0984
2.0639
2.0246
1.9918
1.9696
1.9351
1.3556
1.3366
1.3147
1.2970
1.2870
1.2791
0.9822
0.9639
0.9454
0.0000
MeH2CO
S
N
O
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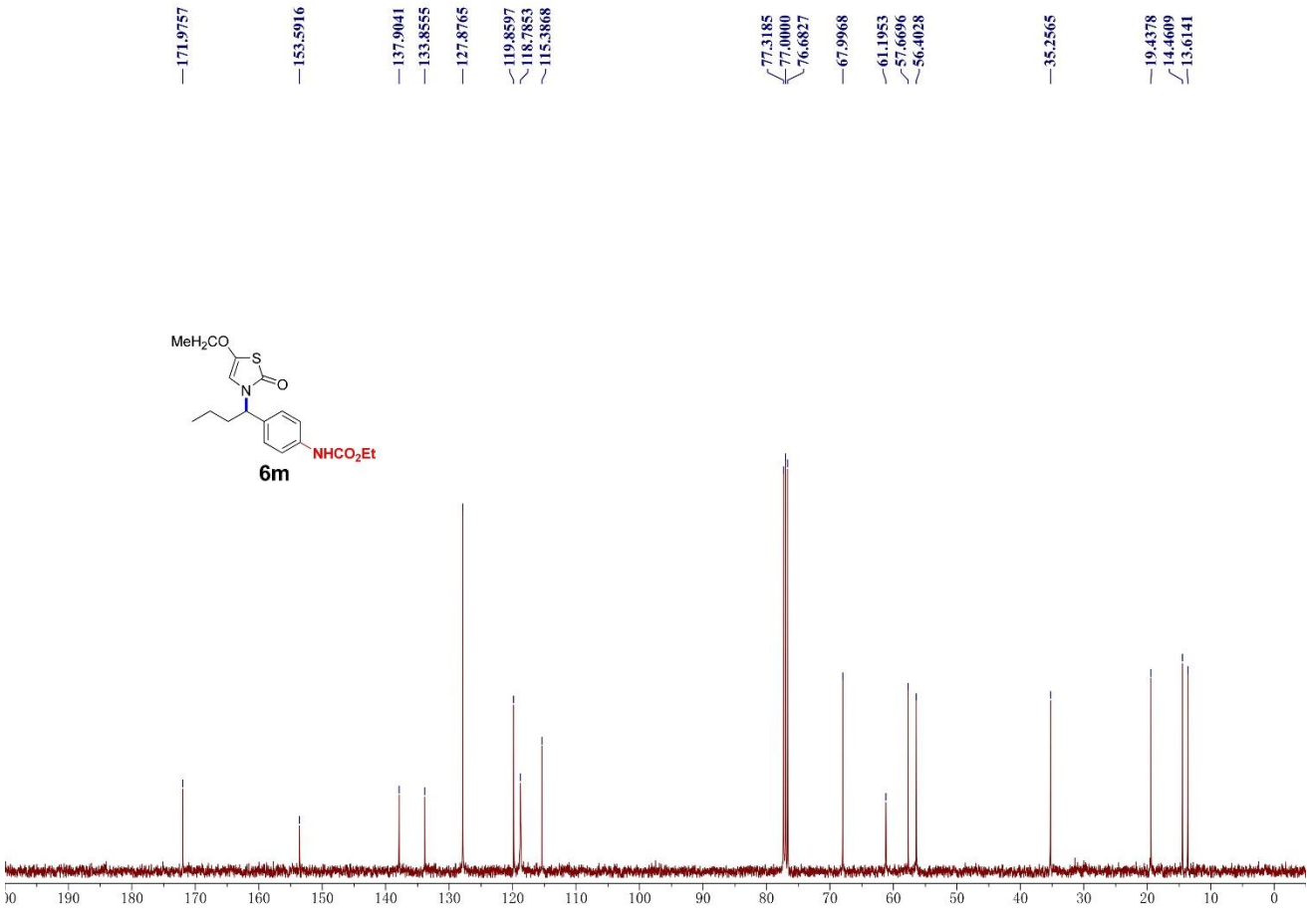
3.98
3.01
2.03
5.00
3.08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61.1953
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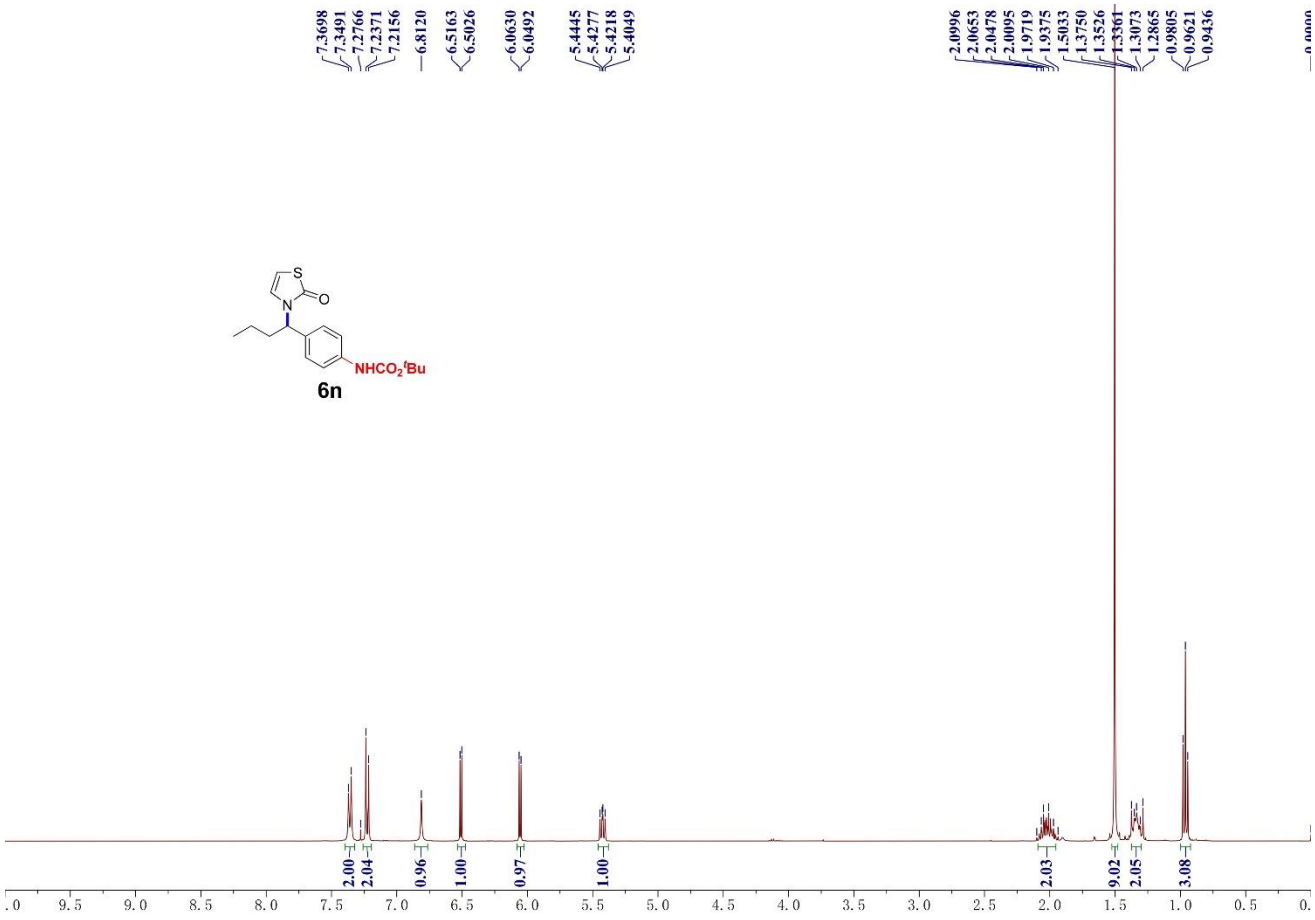
MeH2CO
S
N
O
NHCO2Et
6m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5.4277
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2.0478
2.0095
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1.5033
1.3750
1.3526
1.3361
1.3073
1.2865
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0.9621
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1.00
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2.05
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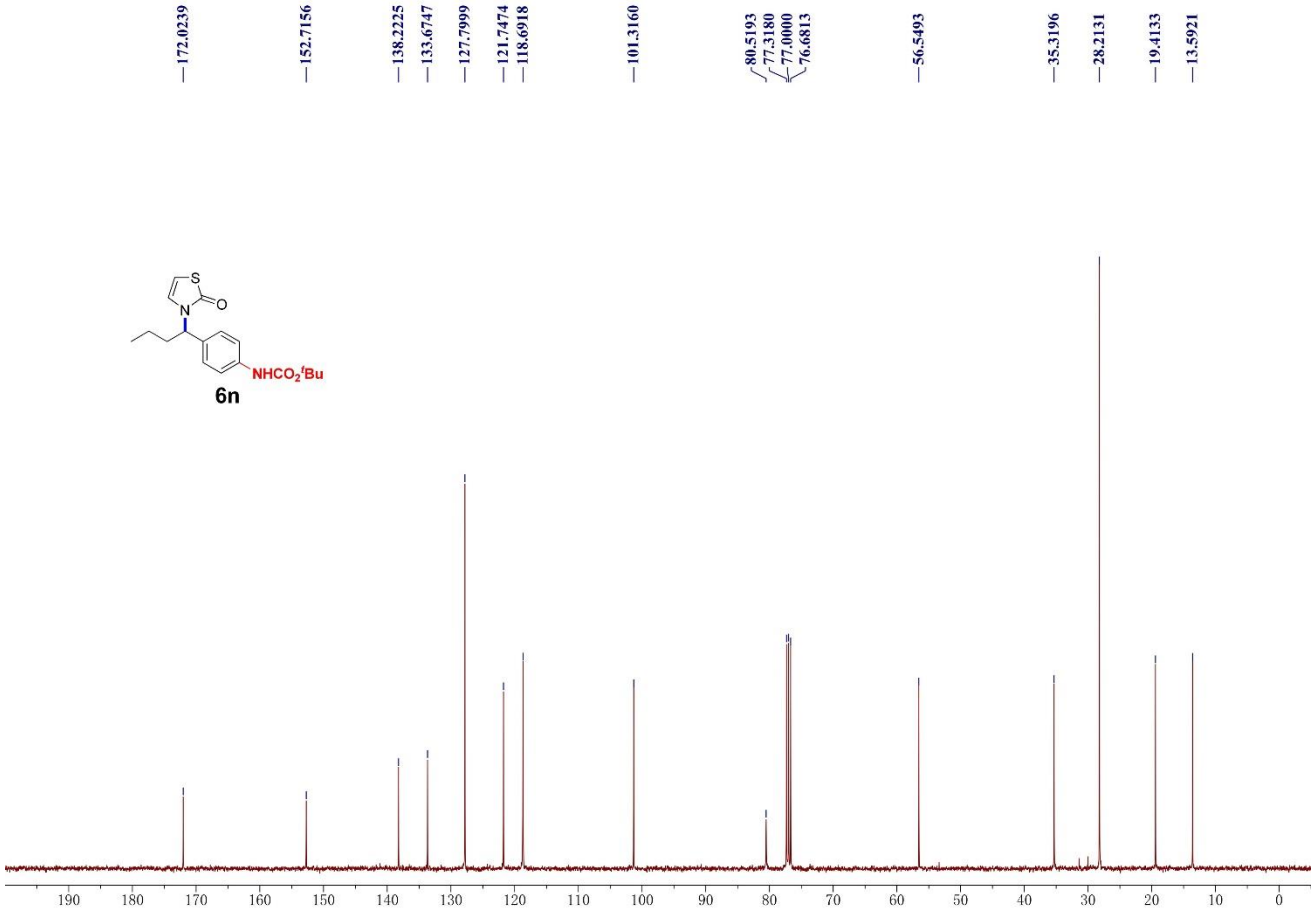
6n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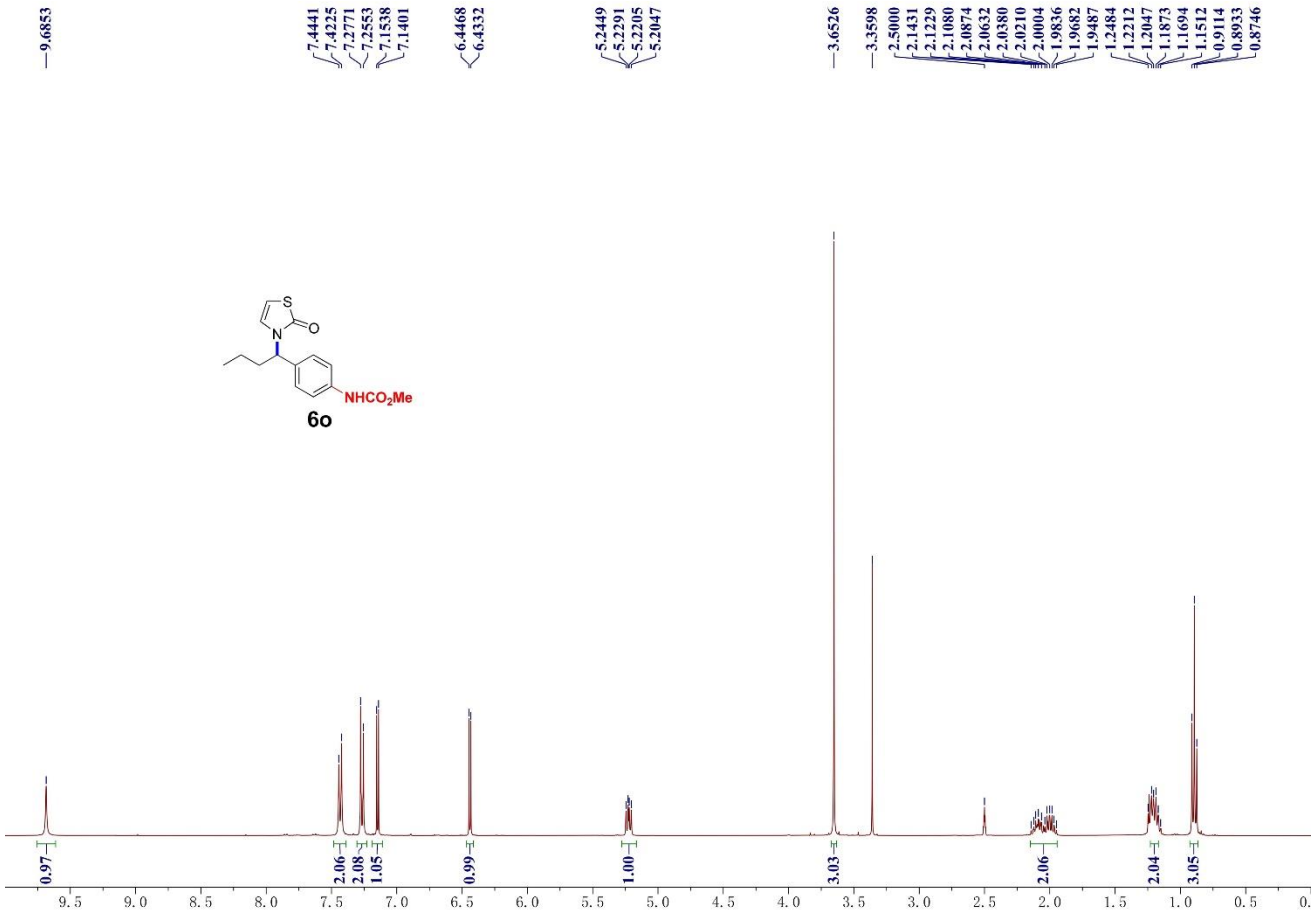
19.4133
13.5921
NHCO2tBu
6n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5.2047
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2.0874
2.0632
2.0380
2.0210
2.0004
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1.9487
1.2484
1.2212
1.2047
1.1873
1.1694
1.1512
0.9114
0.8933
0.8746
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1.00
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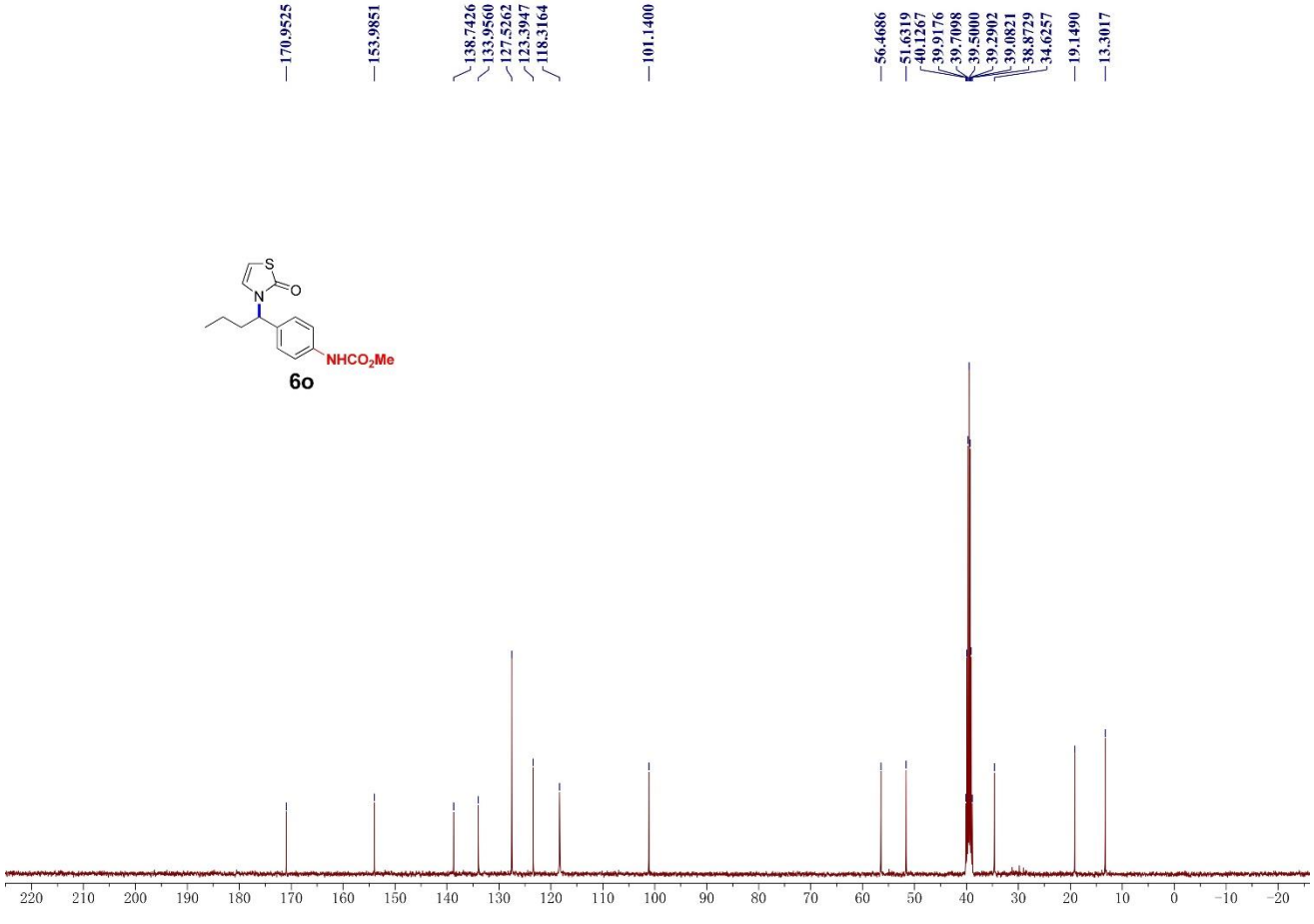
2.04
3.05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39.0821
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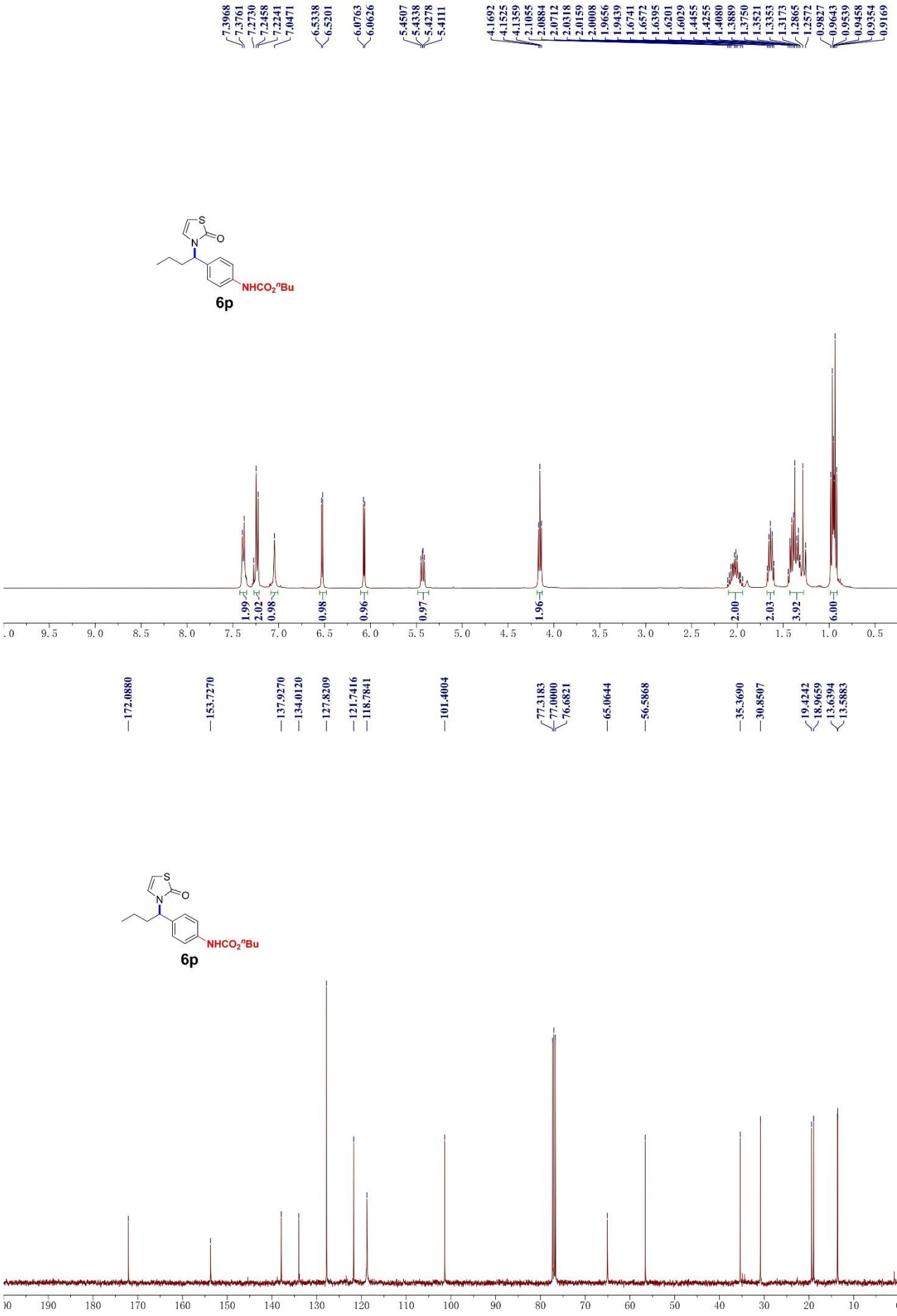
NHCO2Me
6o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4.1692
4.1525
4.1359
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2.0318
2.0159
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1.6201
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1.4255
1.4080
1.3889
1.3750
1.3521
1.3353
1.3173
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1.2572
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0.9643
0.9539
0.9458
0.9354
0.9169
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6p
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0.98
0.98
0.96
0.97
1.96
2.00
2.03
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6.00
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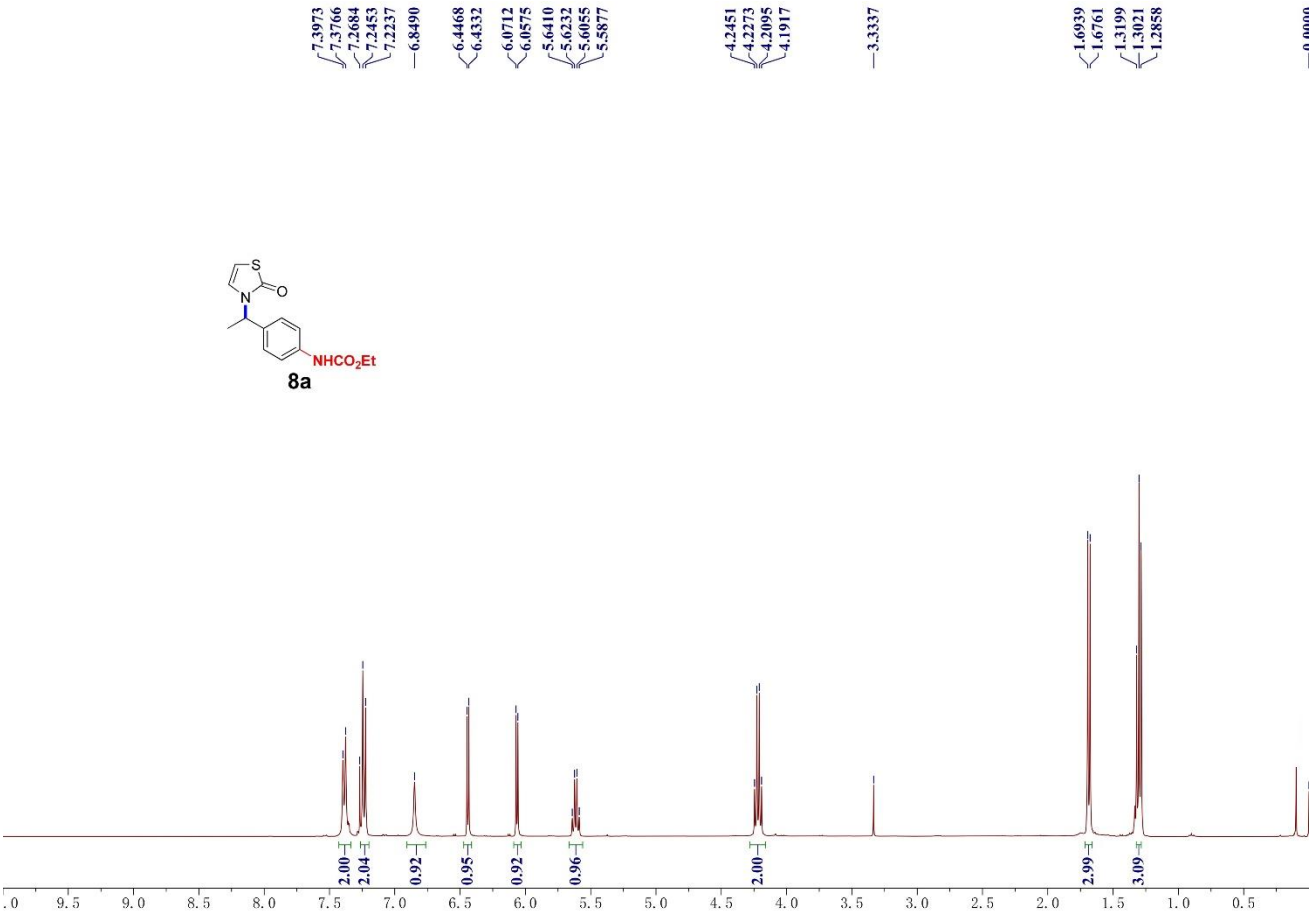
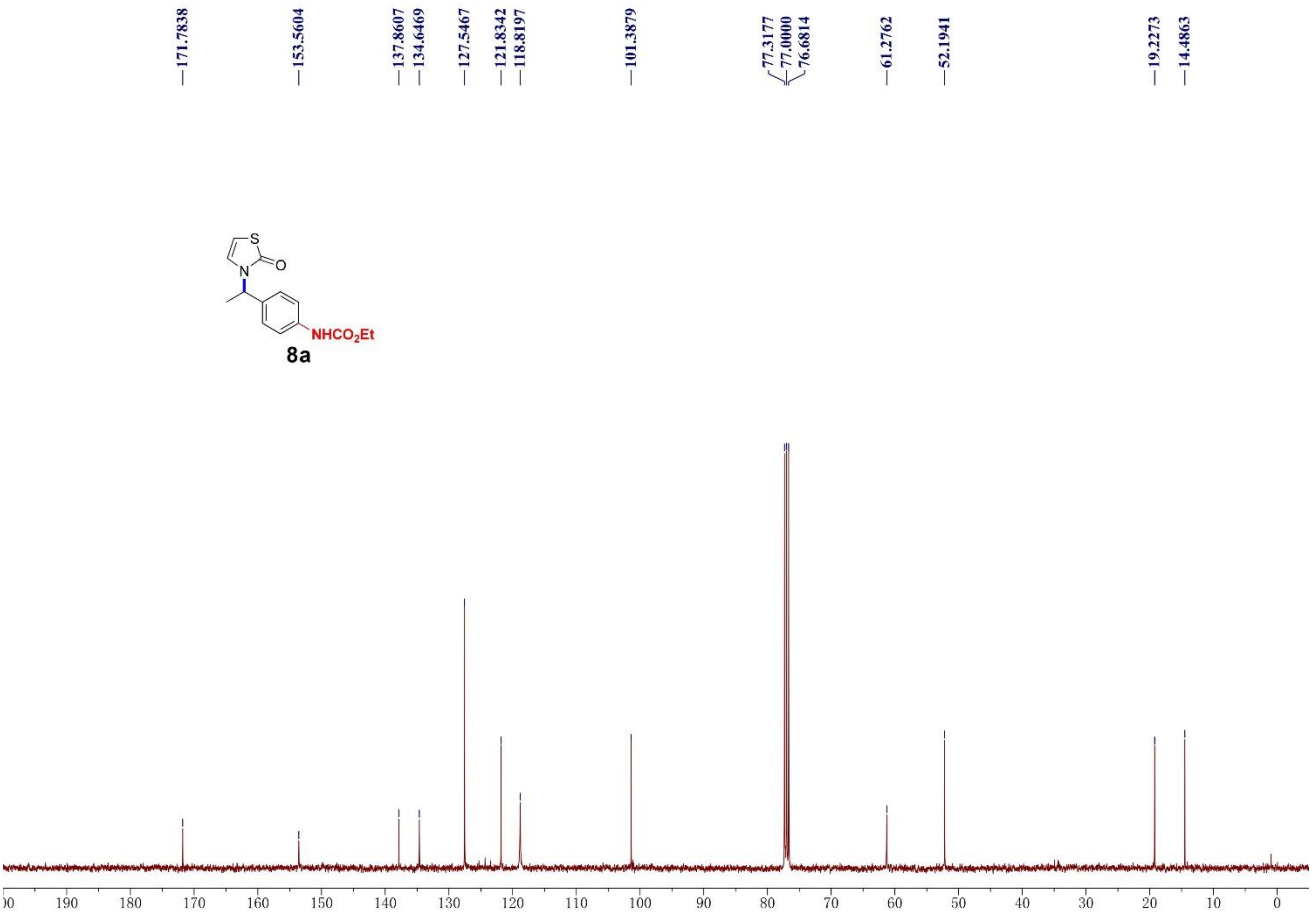
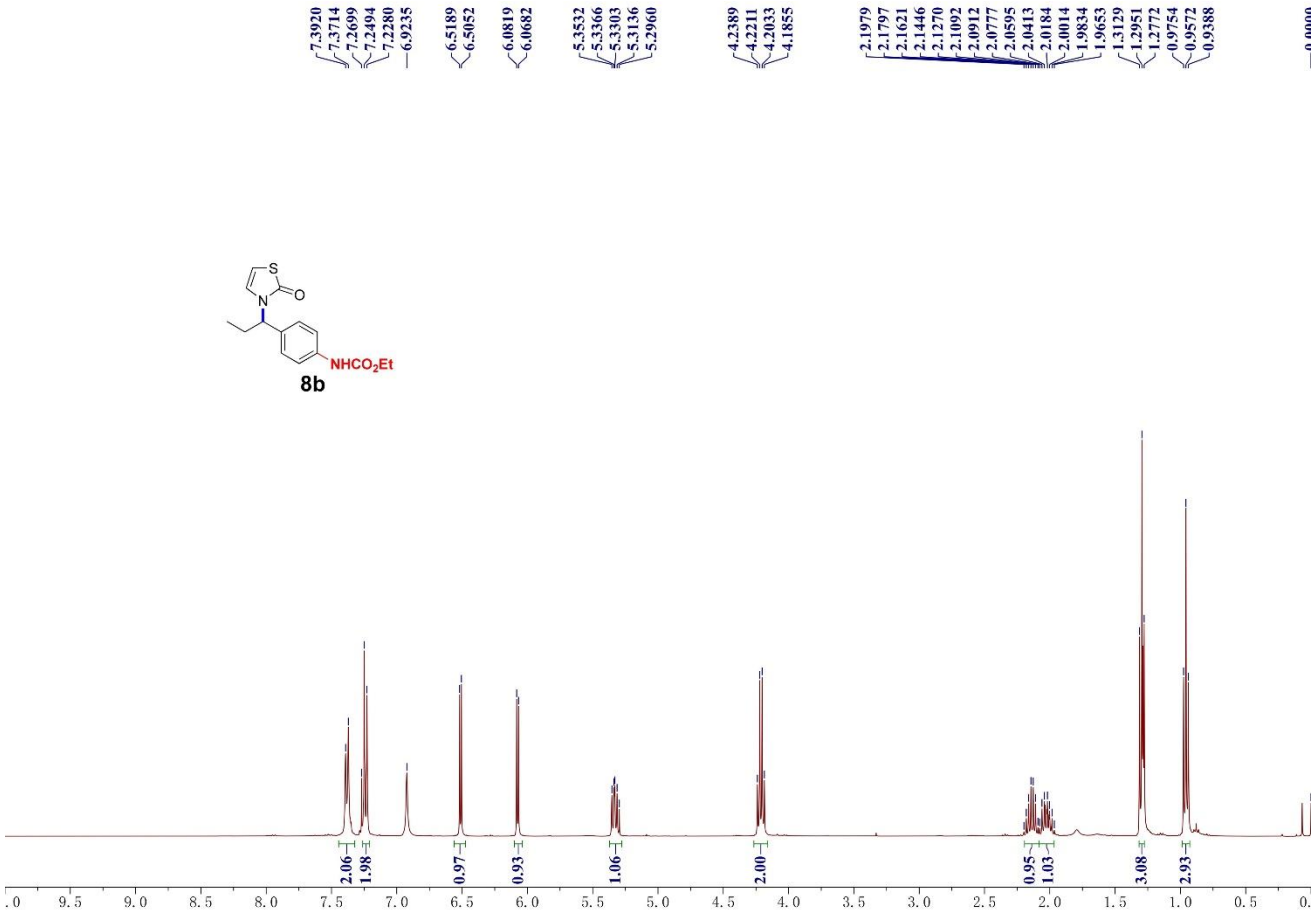
NHCO2nBu
6p

7.3 Spectra of Compounds in Table 3



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5.3366
5.3303
5.3136
5.2960
4.2389
4.2211
4.2033
4.1855
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2.1797
2.1621
2.1446
2.1270
2.1092
2.0912
2.0777
2.0595
2.0413
2.0184
2.0014
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1.2951
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0.9572
0.9388
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2.00
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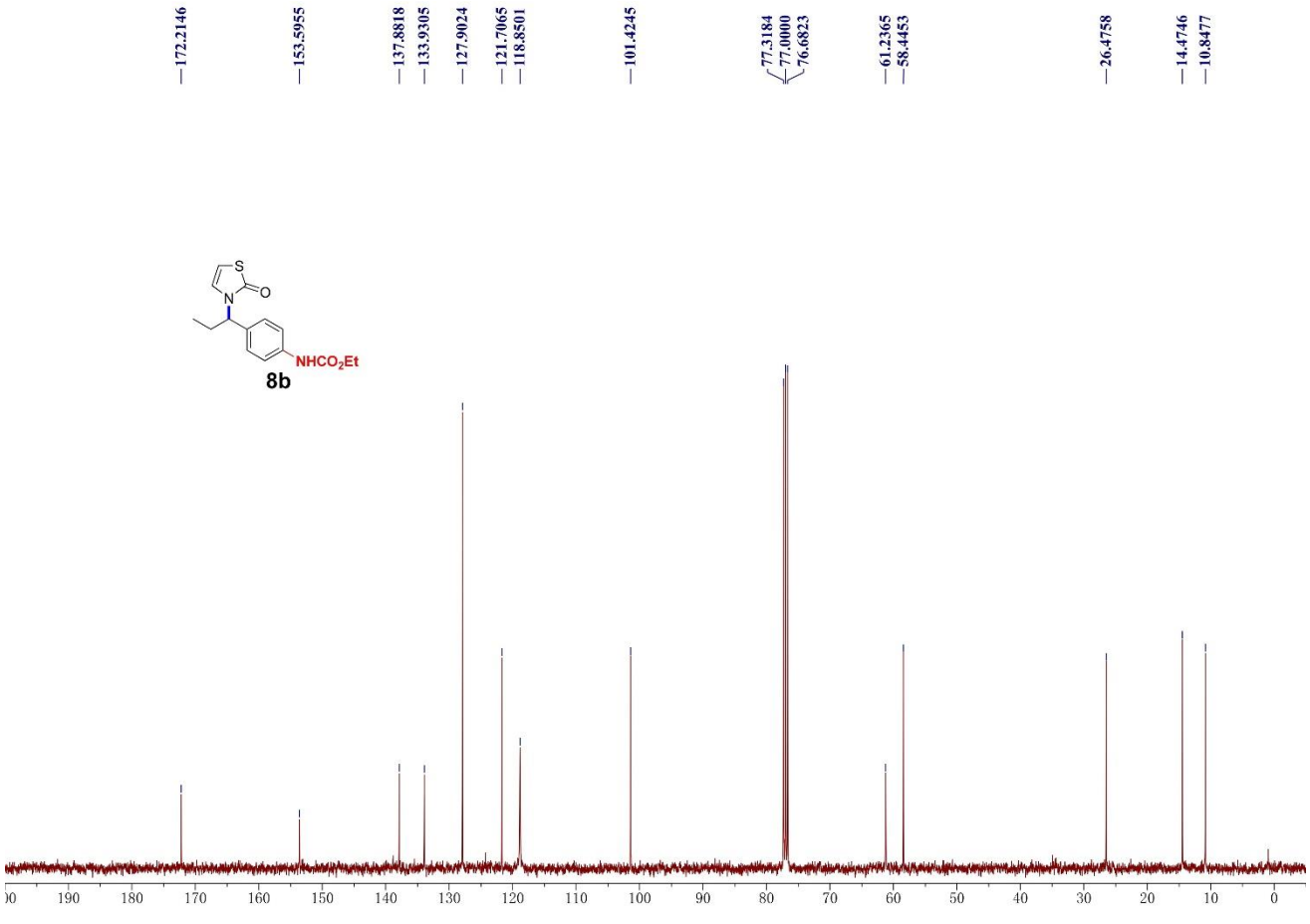
3.08
2.93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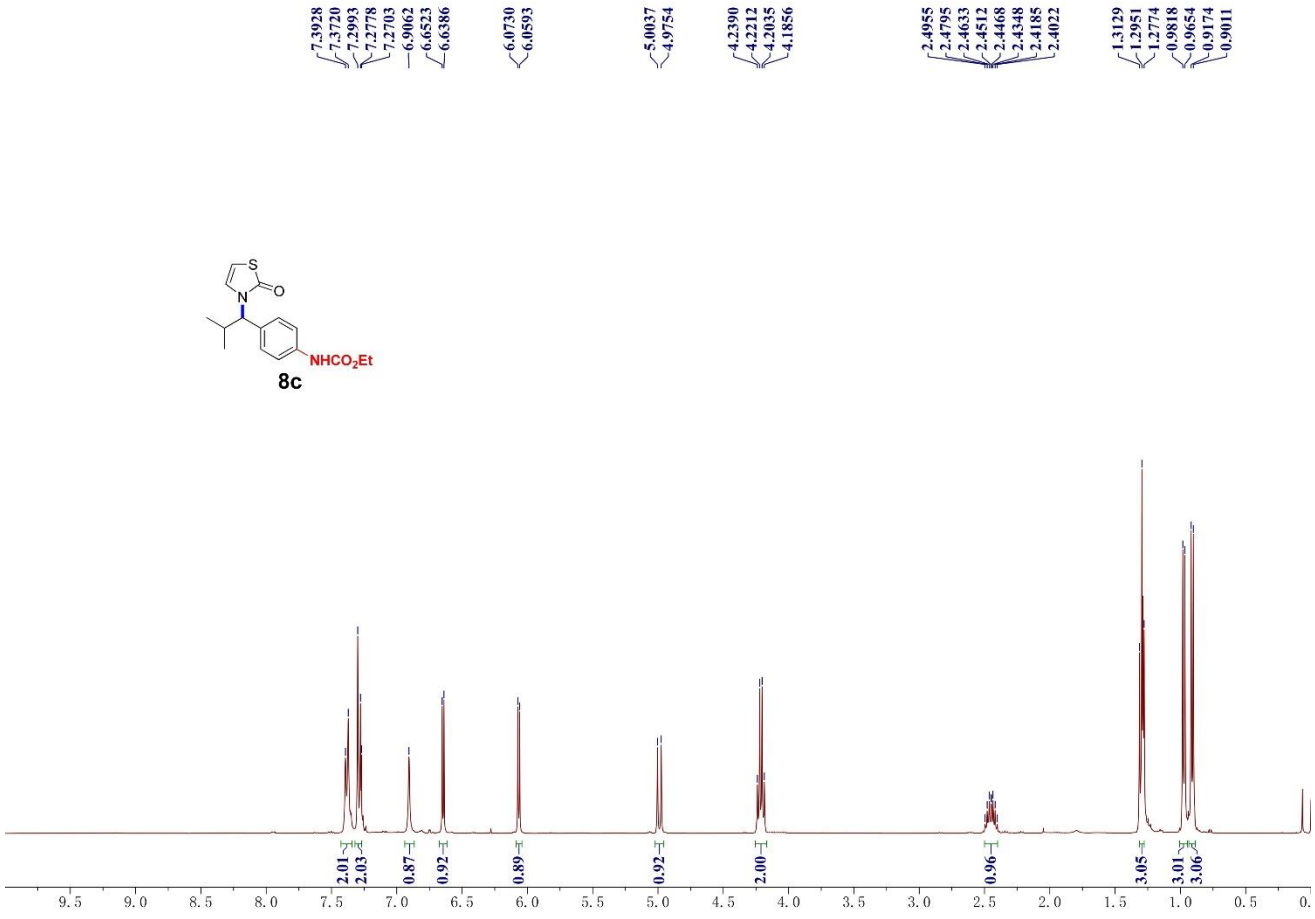
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2.4348
2.4185
2.4022
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1.2774
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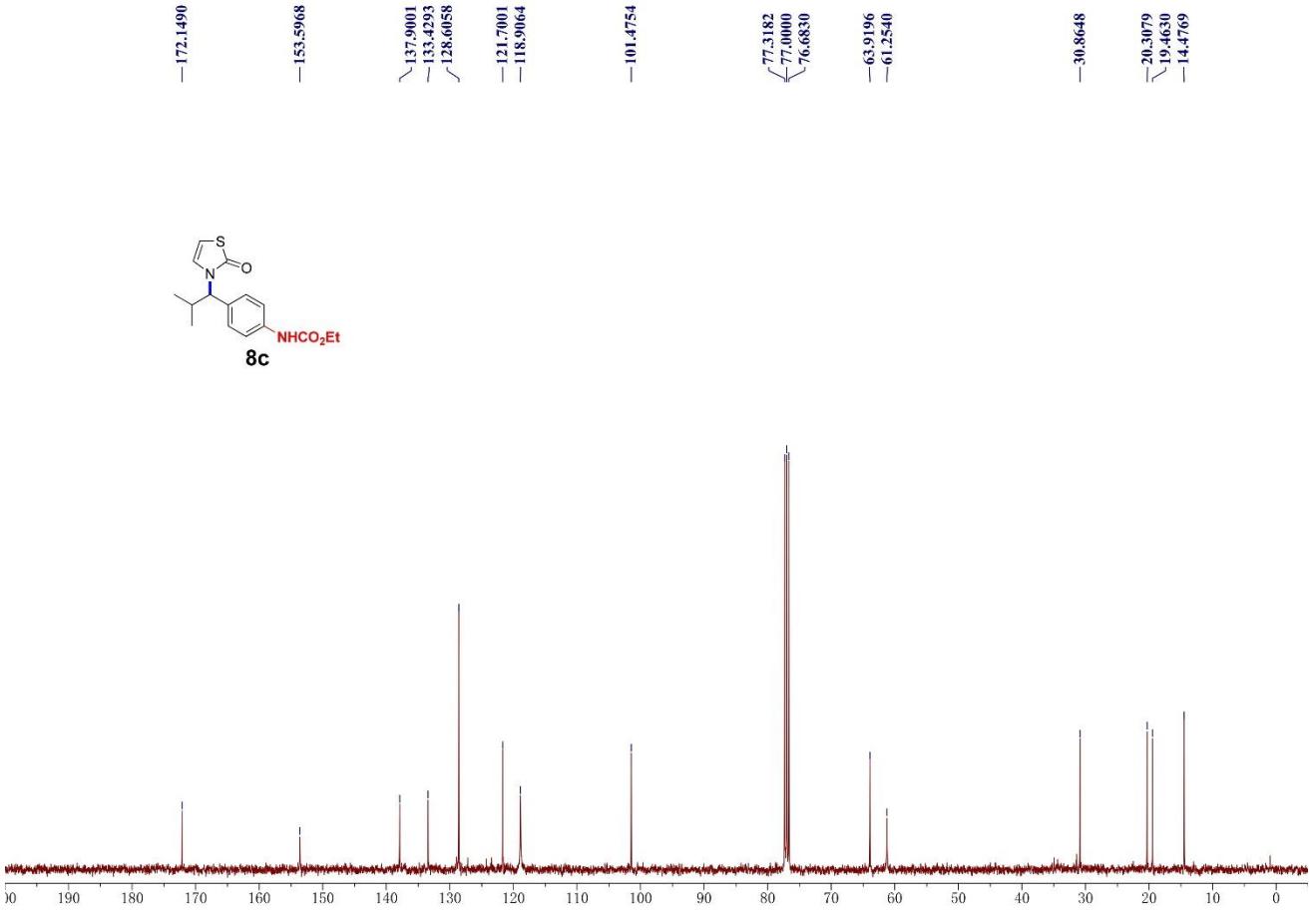
3.06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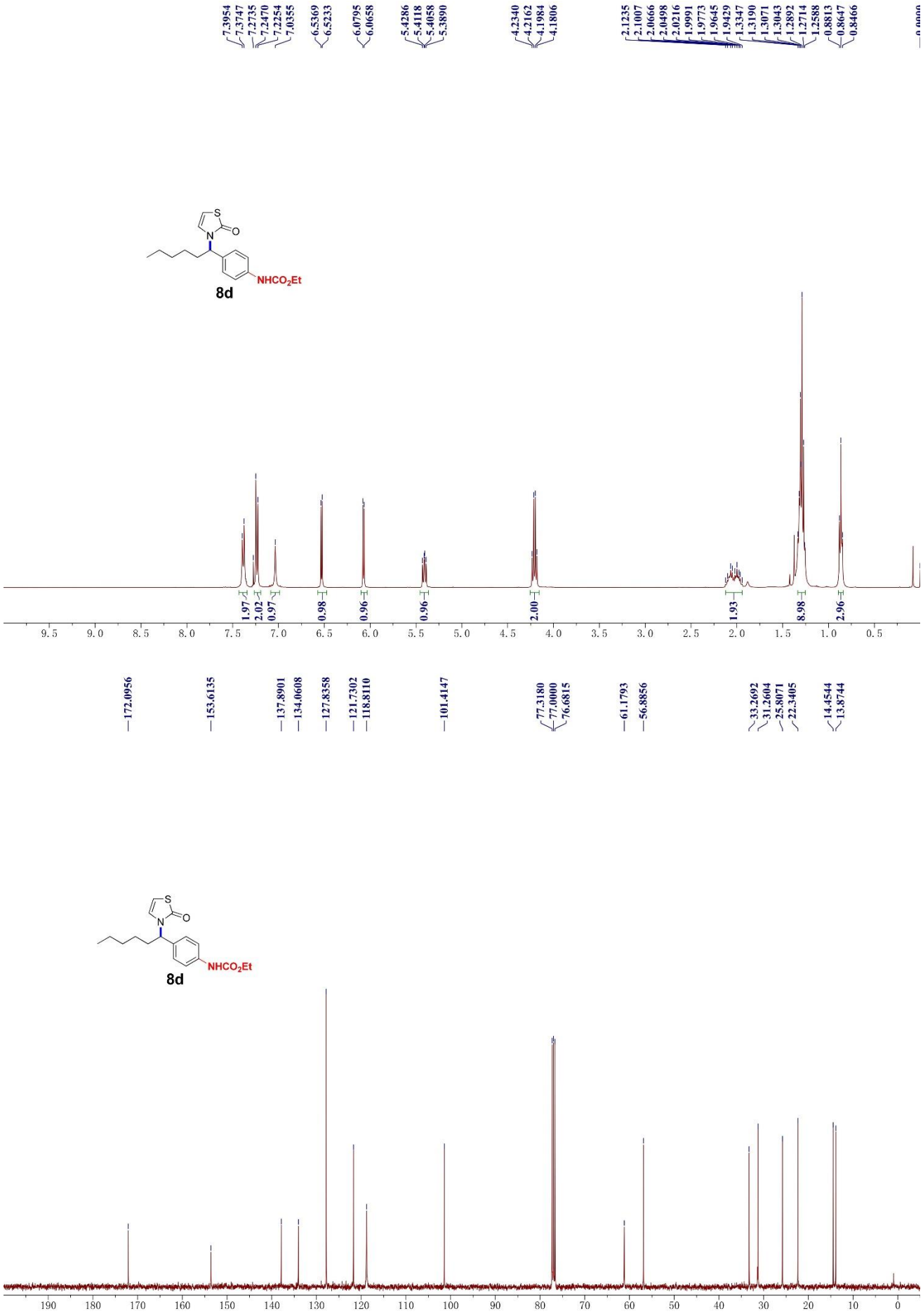
NHCO2Et
8c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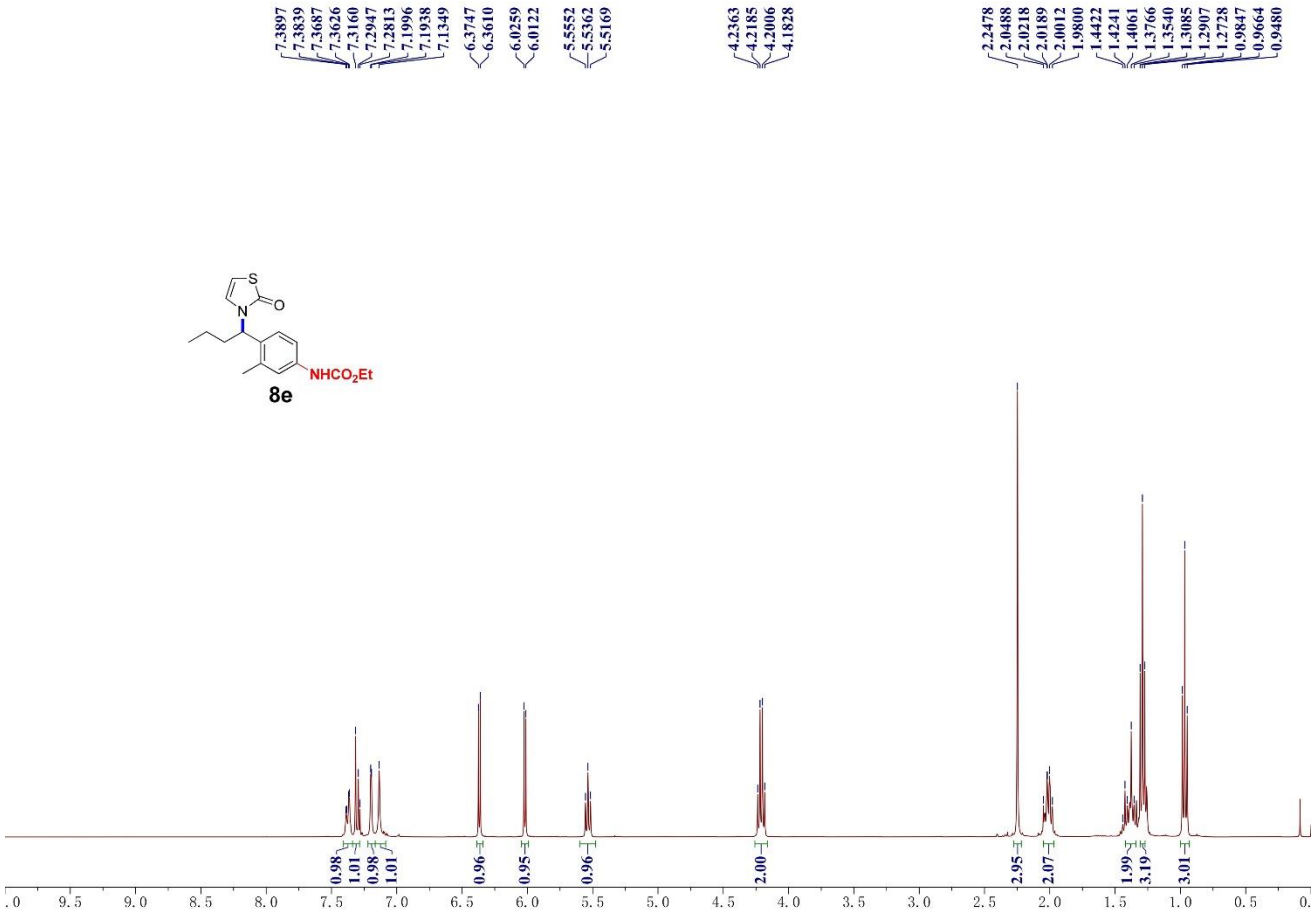
8d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NHCO2Et
8e
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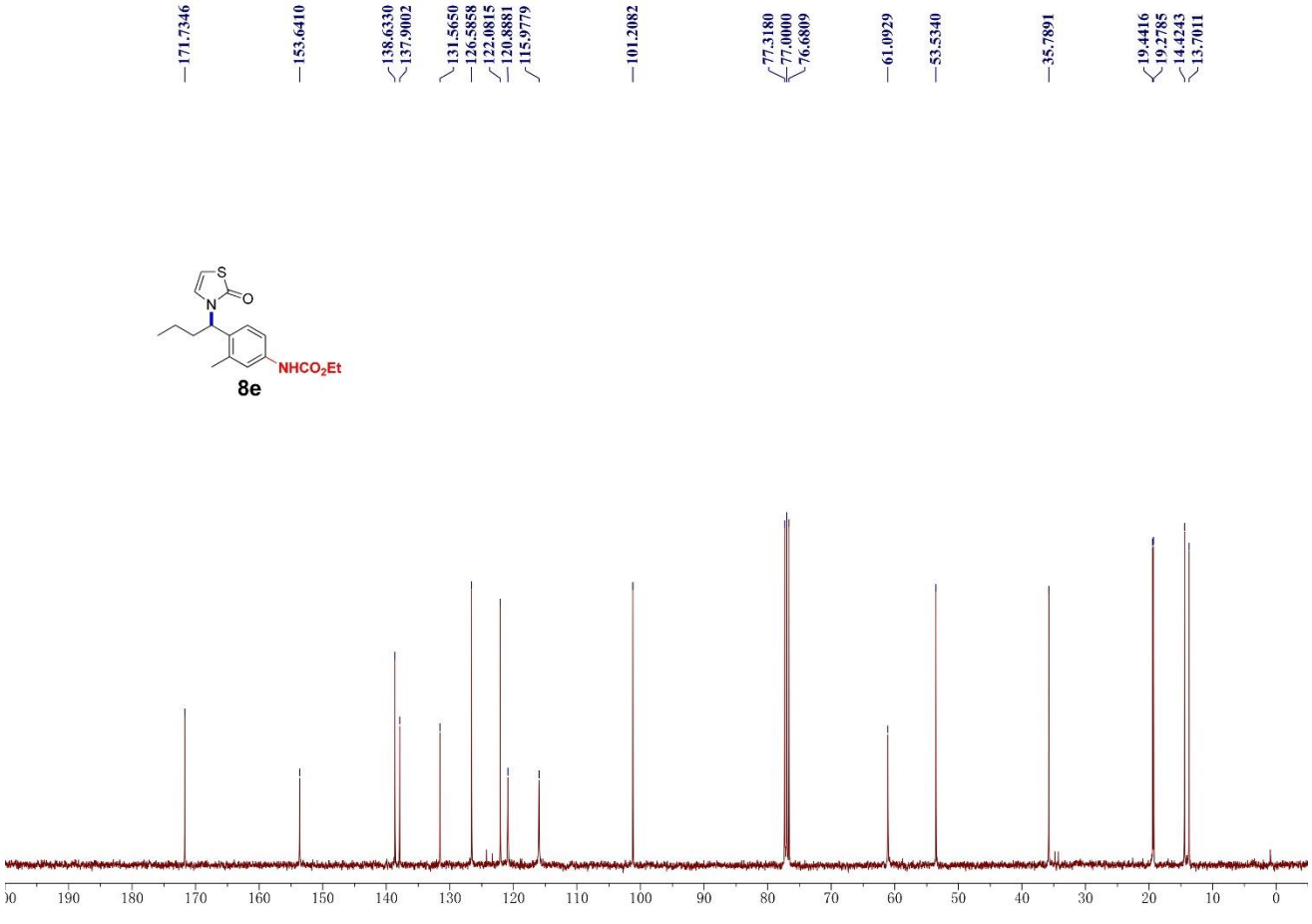
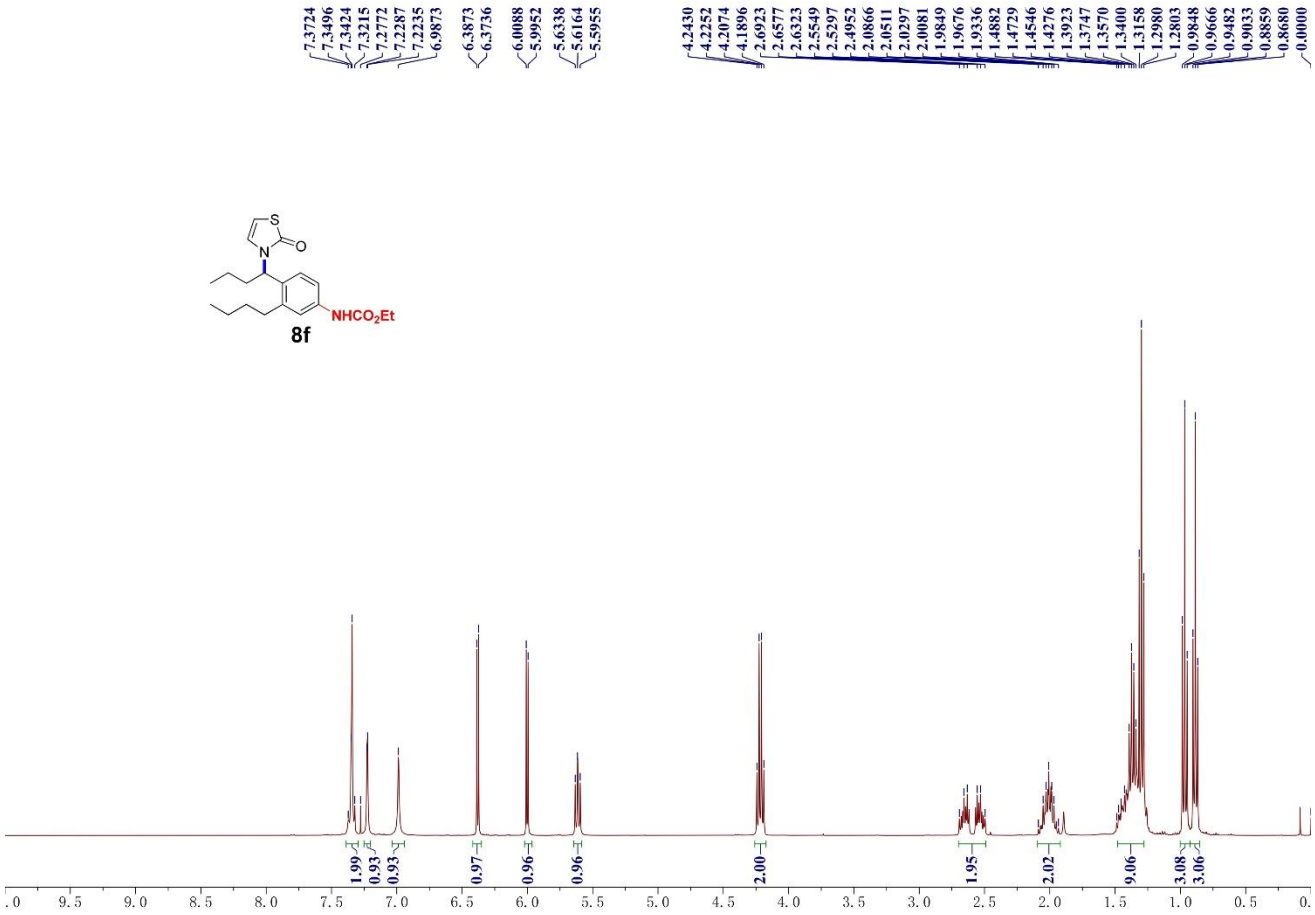
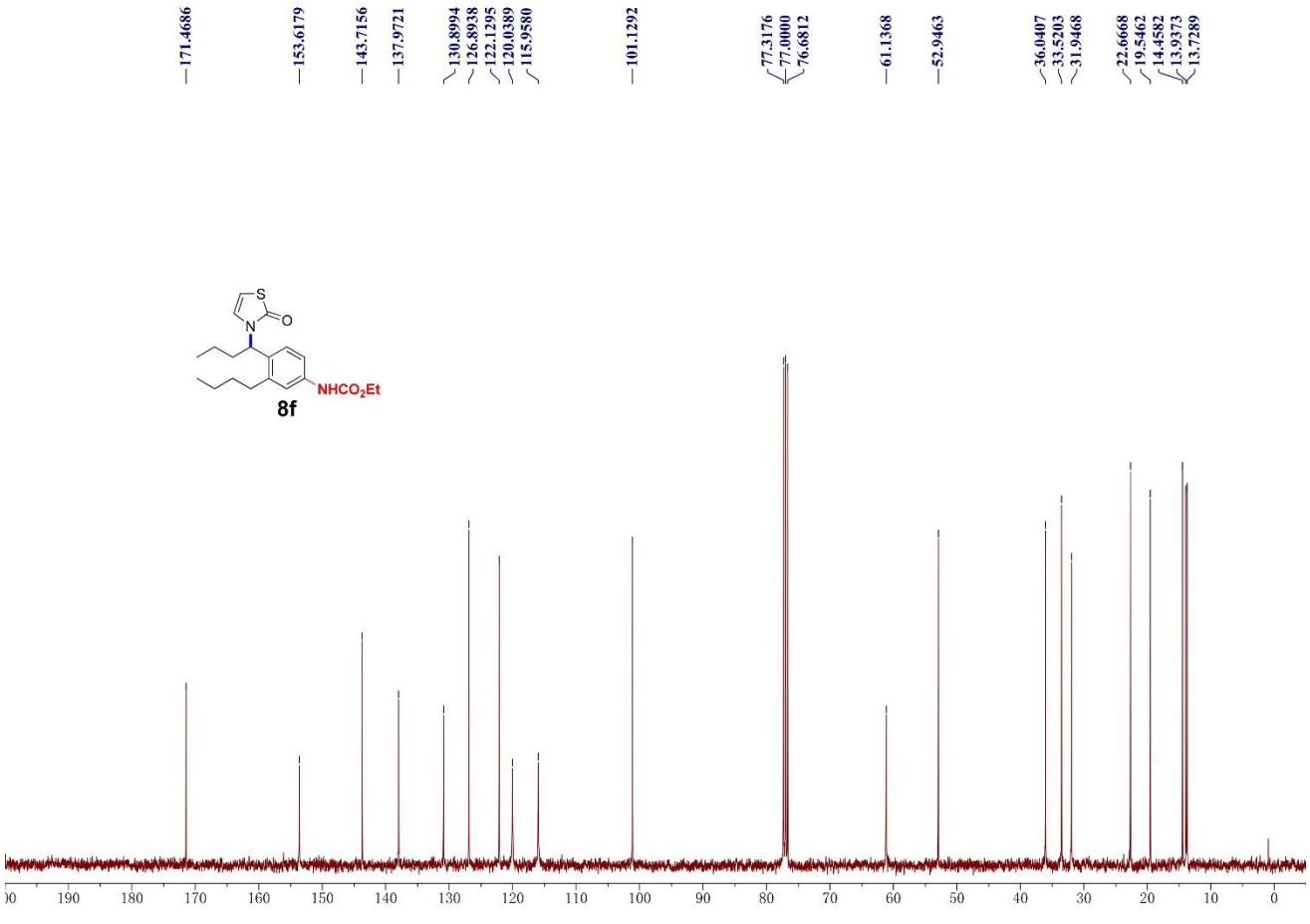
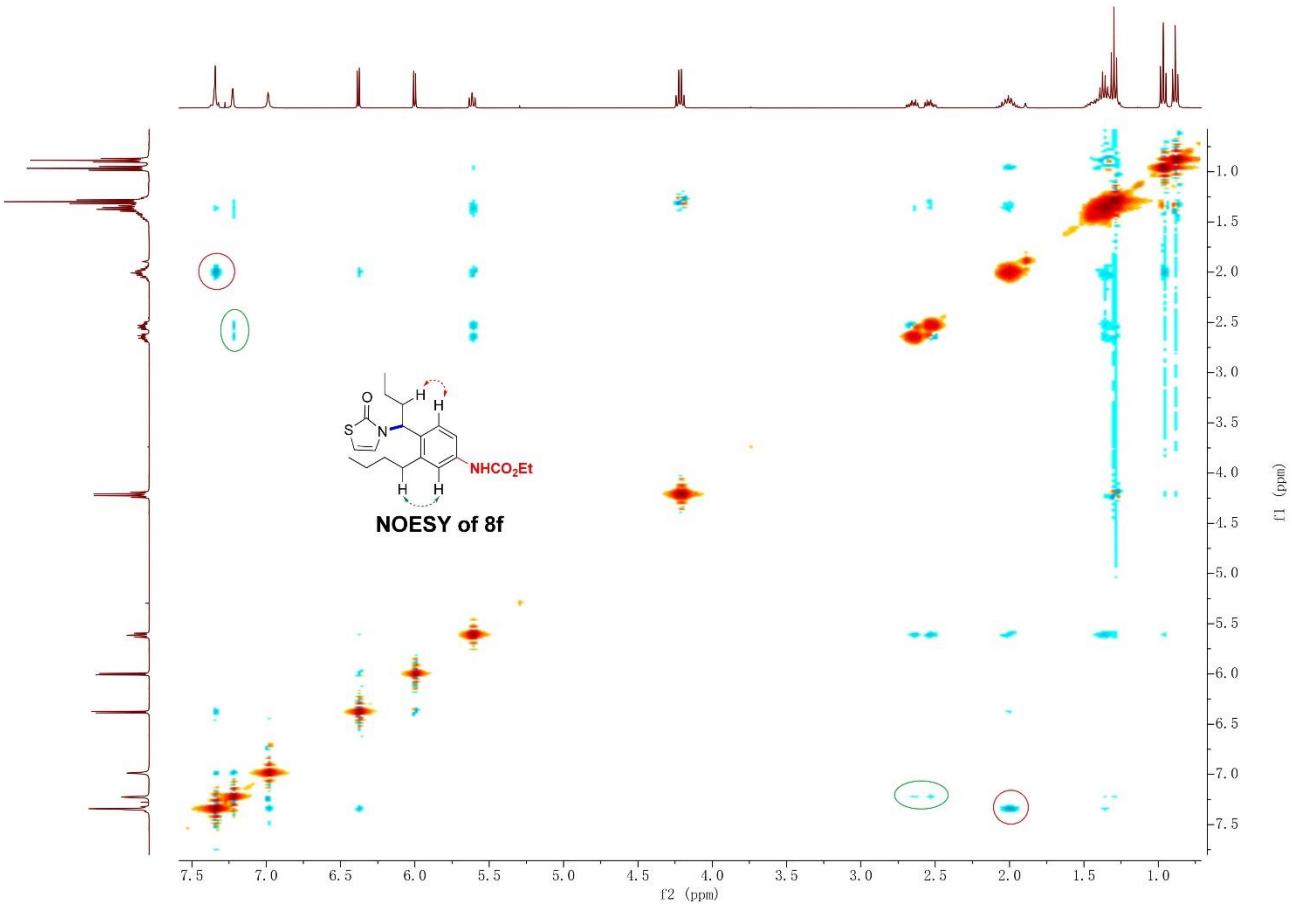
0.98
1.01
0.96
0.95
0.96
2.00
2.95
2.07
1.99
3.19
3.01


171.7346
153.6410
138.6330
137.9002
131.5650
126.5858
122.0815
120.8881
115.9779
101.2082
77.3180
77.0000
76.6809
61.0929
53.5340
35.7891
19.4416
19.2785
14.4243
13.7011
NHCO2Et
8e


7.3724
7.3496
7.3424
7.3215
7.2772
7.2287
7.2235
6.9873
6.3873
6.3736
6.0088
5.9952
5.6338
5.6164
5.5955
4.2430
4.2252
4.2074
4.1896
2.6923
2.6577
2.6323
2.5549
2.5297
2.4952
2.0866
2.0511
2.0297
2.0081
1.9849
1.9676
1.9336
1.4882
1.4729
1.4546
1.4276
1.3923
1.3747
1.3570
1.3400
1.3158
1.2980
1.2803
0.9848
0.9666
0.9482
0.9033
0.8859
0.8680
0.0000
NHCO2Et
8f
1.99
0.93
0.93
0.97
0.96
0.96
2.00
1.95
2.02
9.06
3.08
3.06

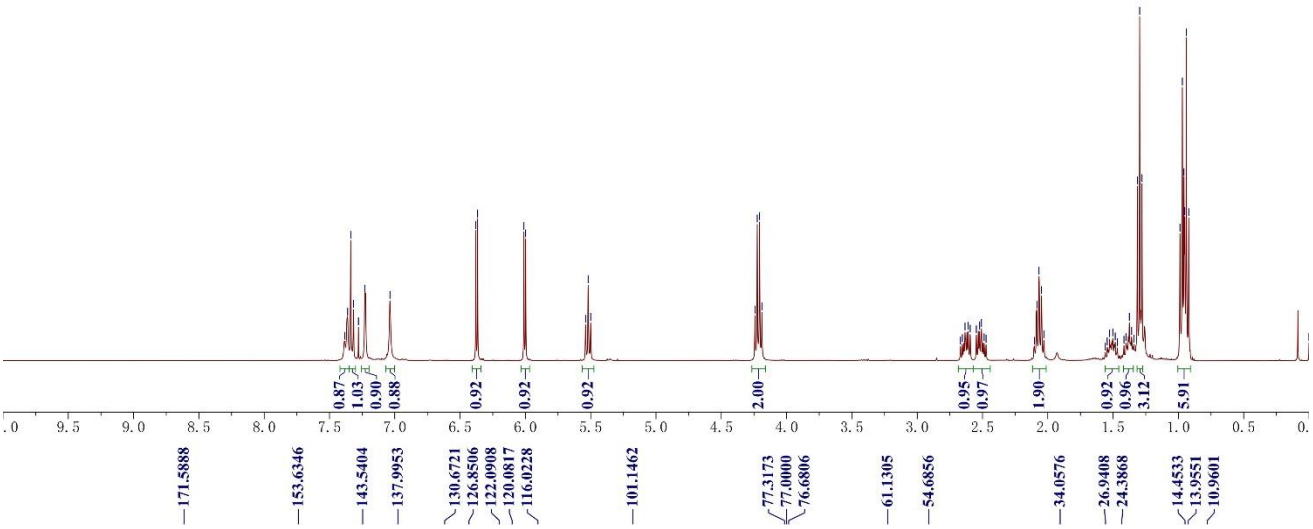

171.4686
153.6179
143.7156
137.9721
130.8994
126.8938
122.1295
120.0389
115.9580
101.1292
77.3176
77.0000
76.6812
61.1368
52.9463
36.0407
33.5203
31.9468
22.6668
19.5462
14.4582
13.9373
13.7289
NHCO2Et
8f


NHCO2Et
NOESY of 8f
f2 (ppm)
f1 (ppm)


7.3823
7.3611
7.3373
7.3162
7.2784
7.2295
7.0368
6.3796
6.3659
6.0117
5.9980
5.5388
5.5196
5.5002
4.2424
4.2246
4.2069
4.1890
2.6691
2.6541
2.6340
2.6091
2.5942
2.5468
2.5222
2.5079
2.4873
2.4727
2.1020
2.0838
2.0668
2.0482
2.0299
1.5600
1.5448
1.5265
1.5018
1.4835
1.4683
1.4165
1.4017
1.3759
1.3581
1.3403
1.3143
1.2965
1.2786
0.9879
0.9696
0.9573
0.9513
0.9389
0.9205
0.0000

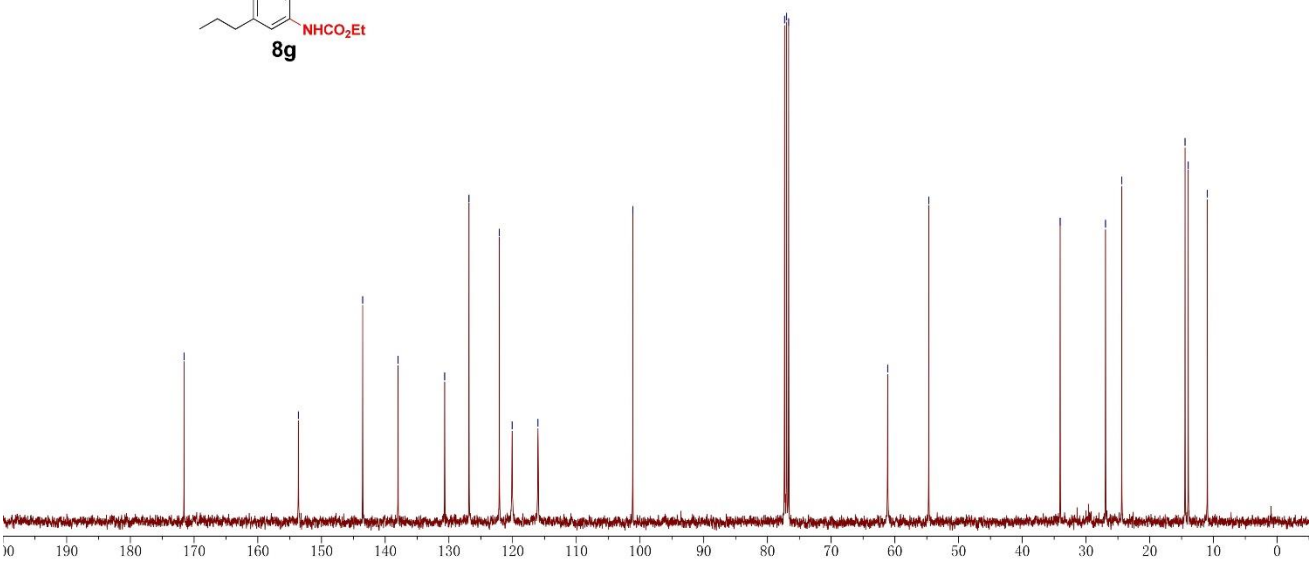

S
N
O
NHCO2Et

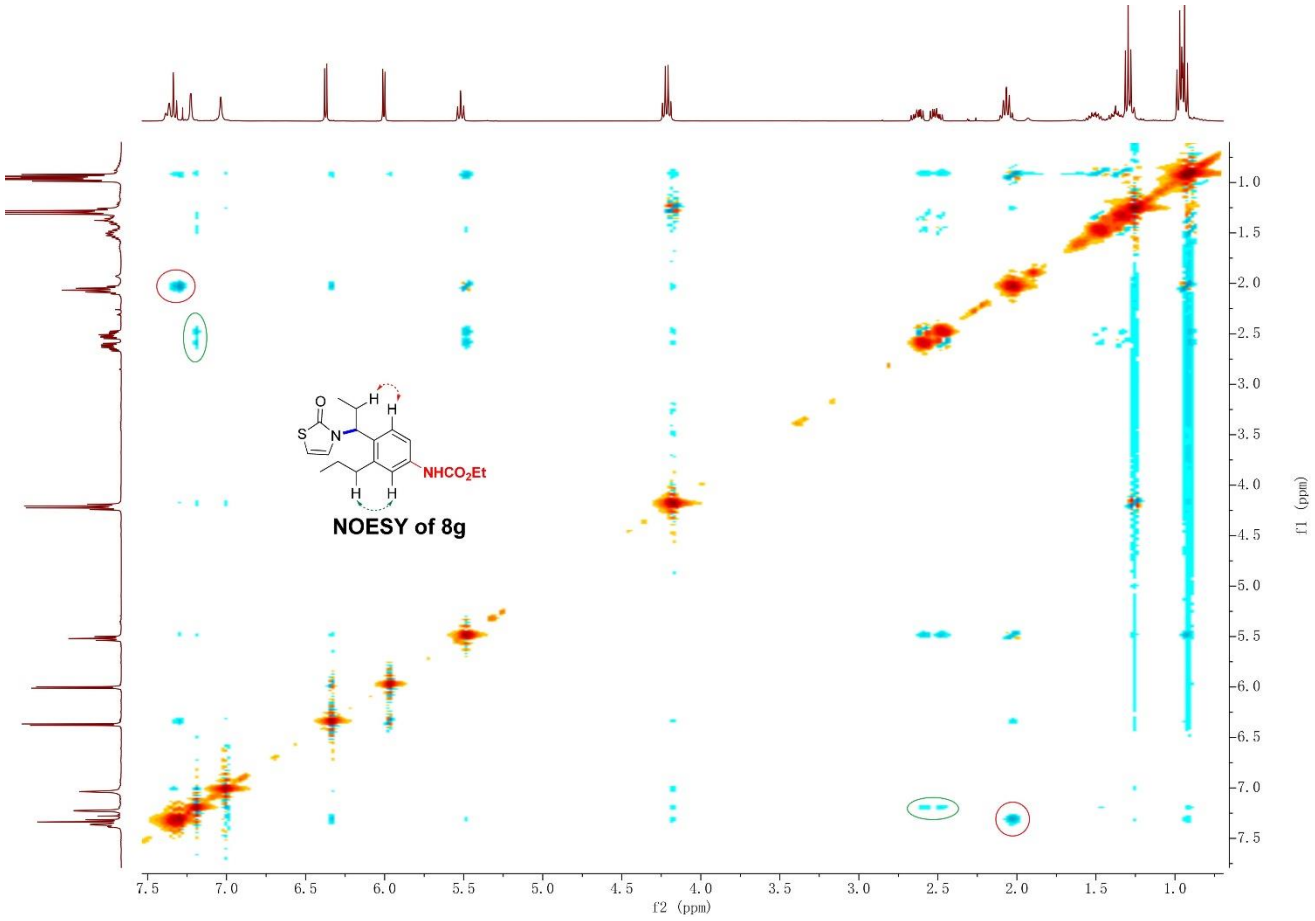
8g

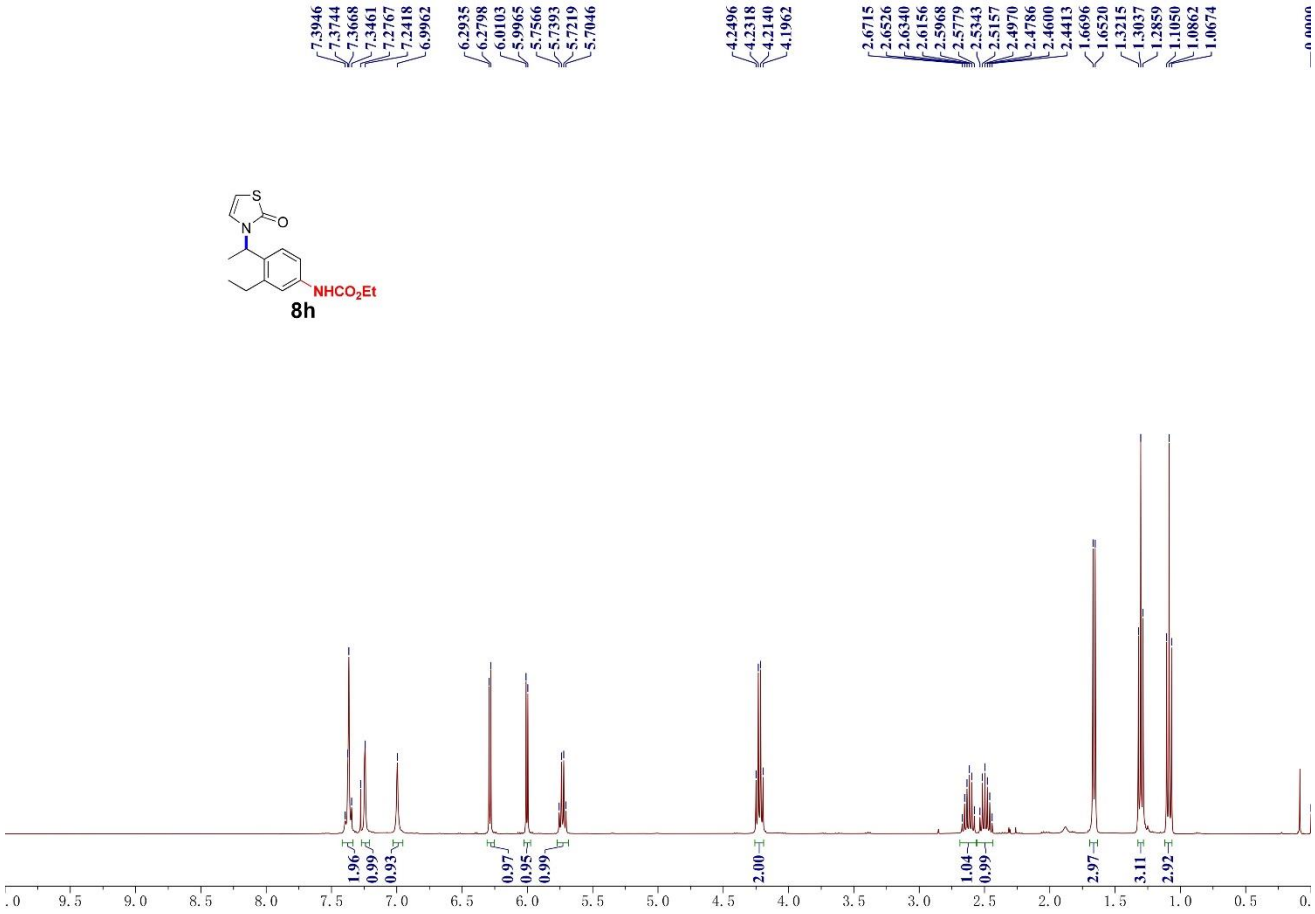

0.87
1.03
0.90
0.88
0.92
0.92
0.92
2.00
0.95
0.97
1.90
0.92
0.96
3.12
5.91
171.5888
153.6346
143.5404
137.9953
130.6721
126.8506
122.0908
120.0817
116.0228
101.1462
77.3173
77.0000
76.6806
61.1305
54.6856
34.0576
26.9408
24.3868
14.4533
13.9551
10.9601

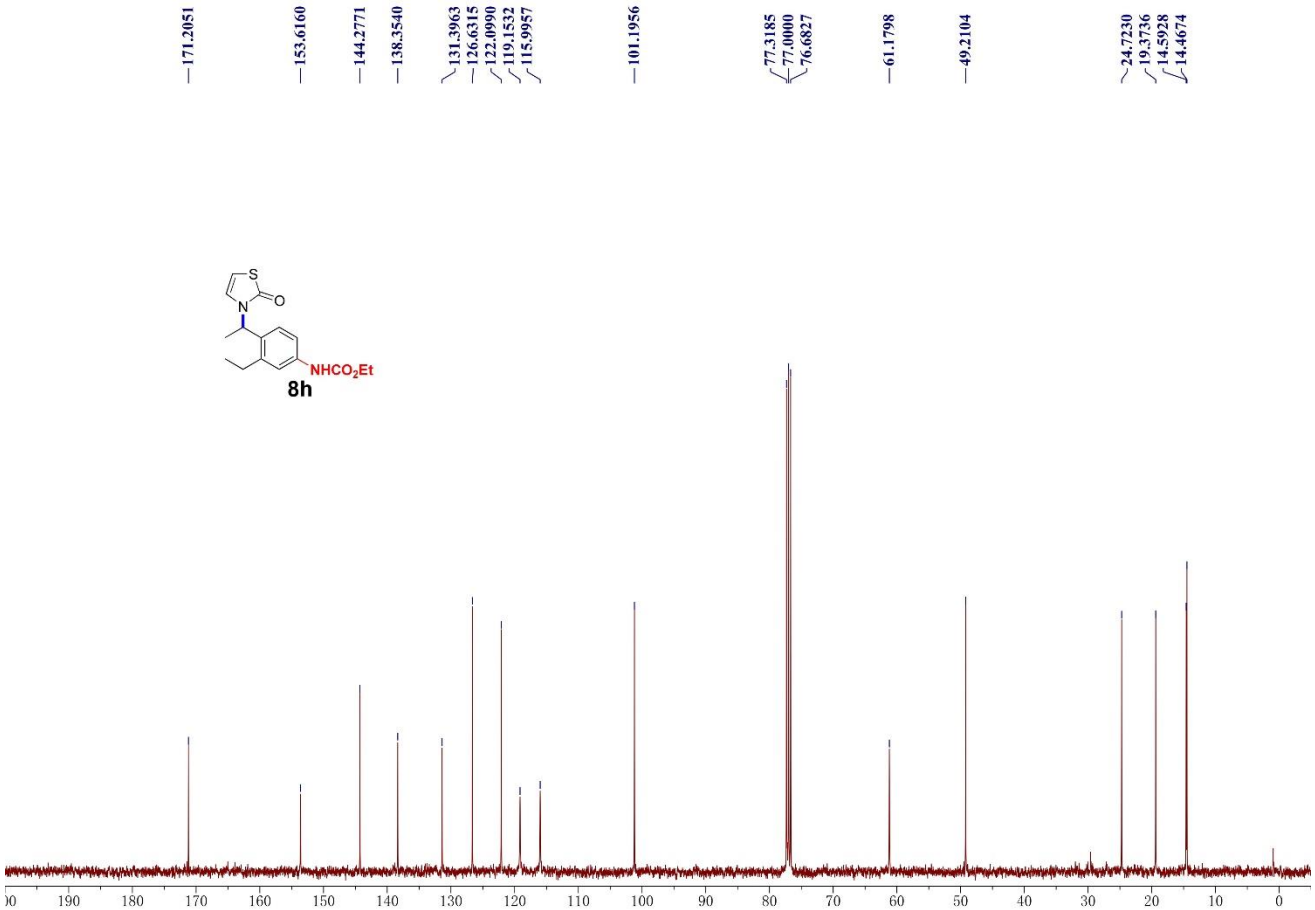

S
N
O
NHCO2Et

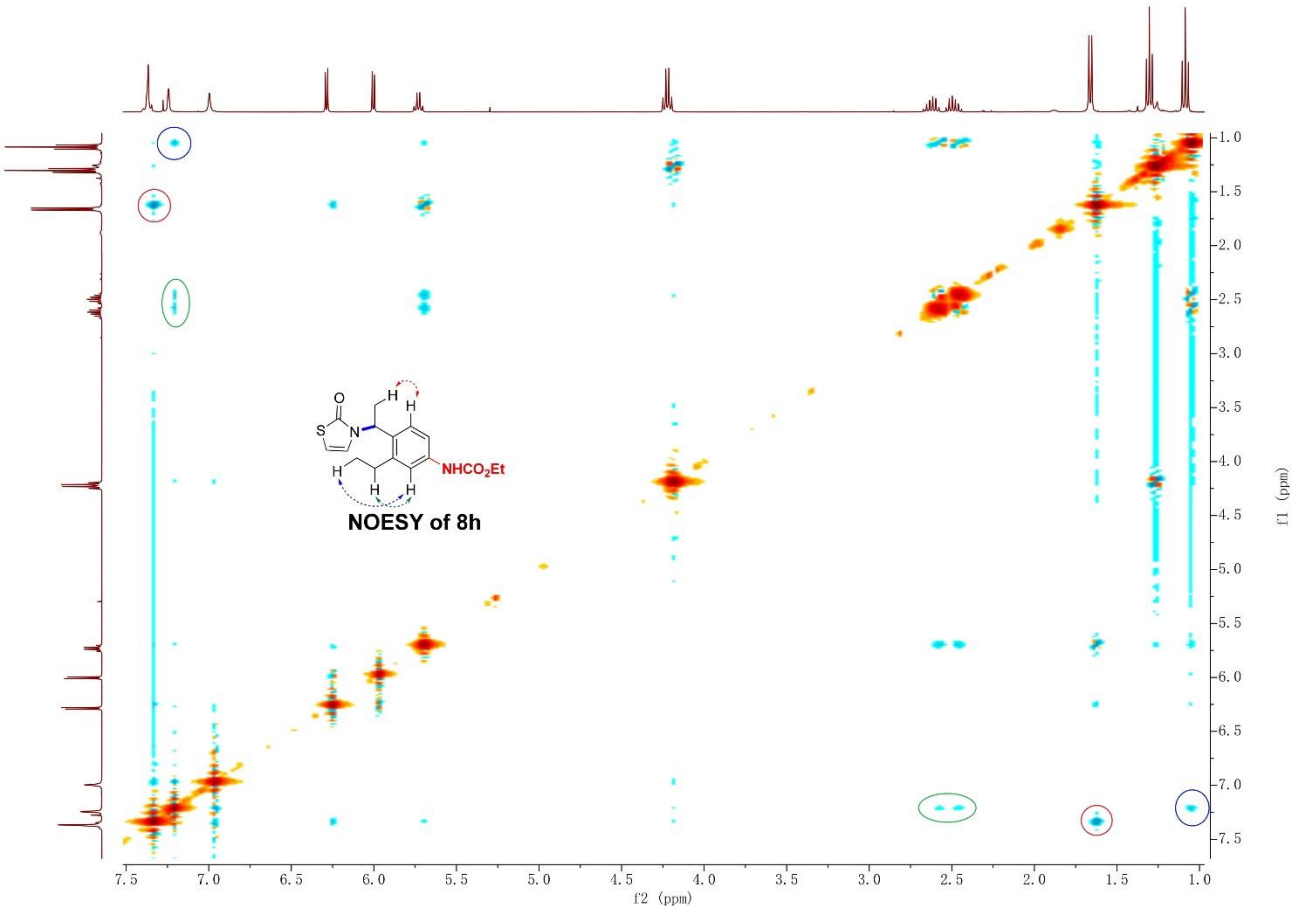
8g



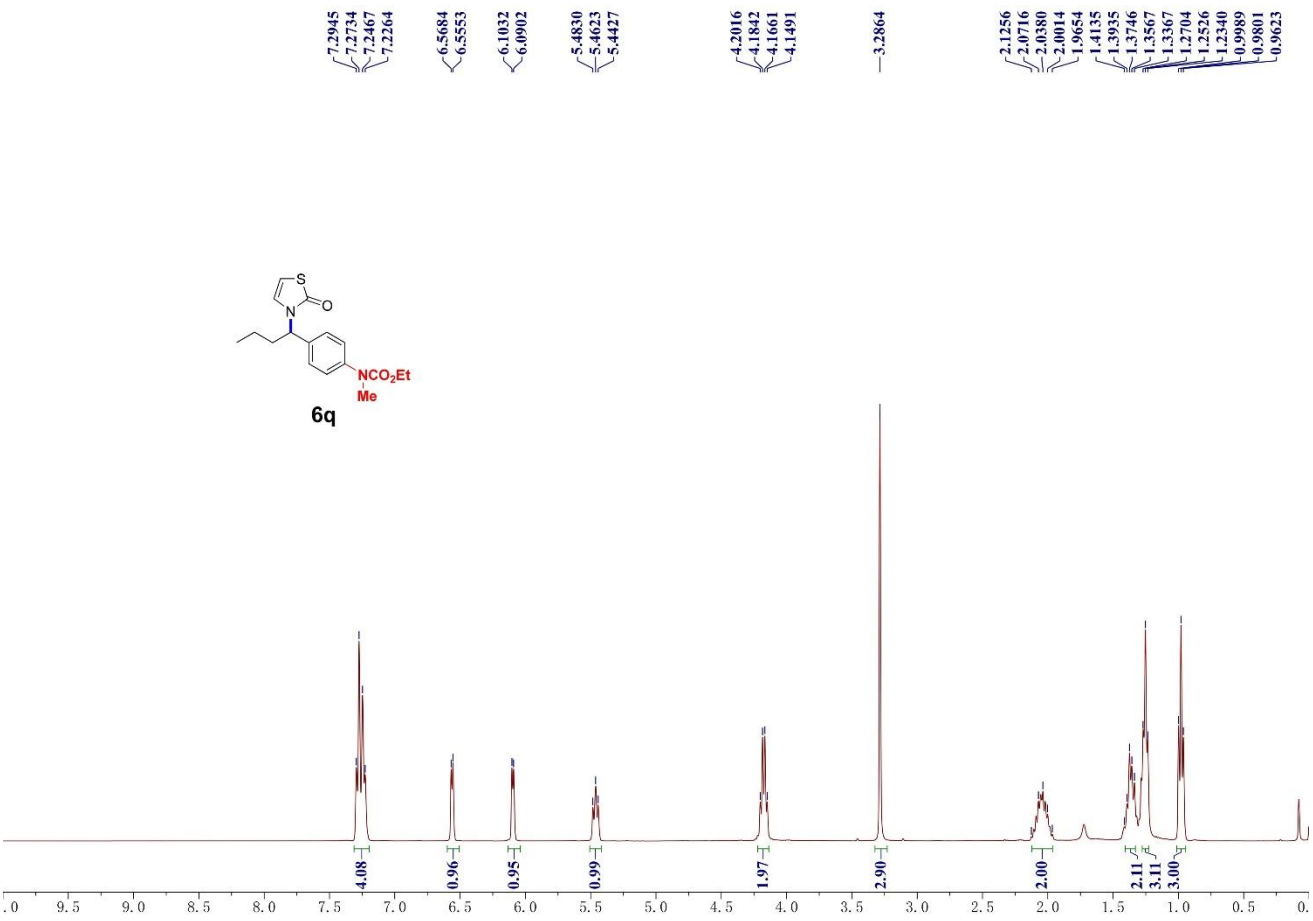

NHCO2Et
NOESY of 8g
f2 (ppm)
f1 (ppm)

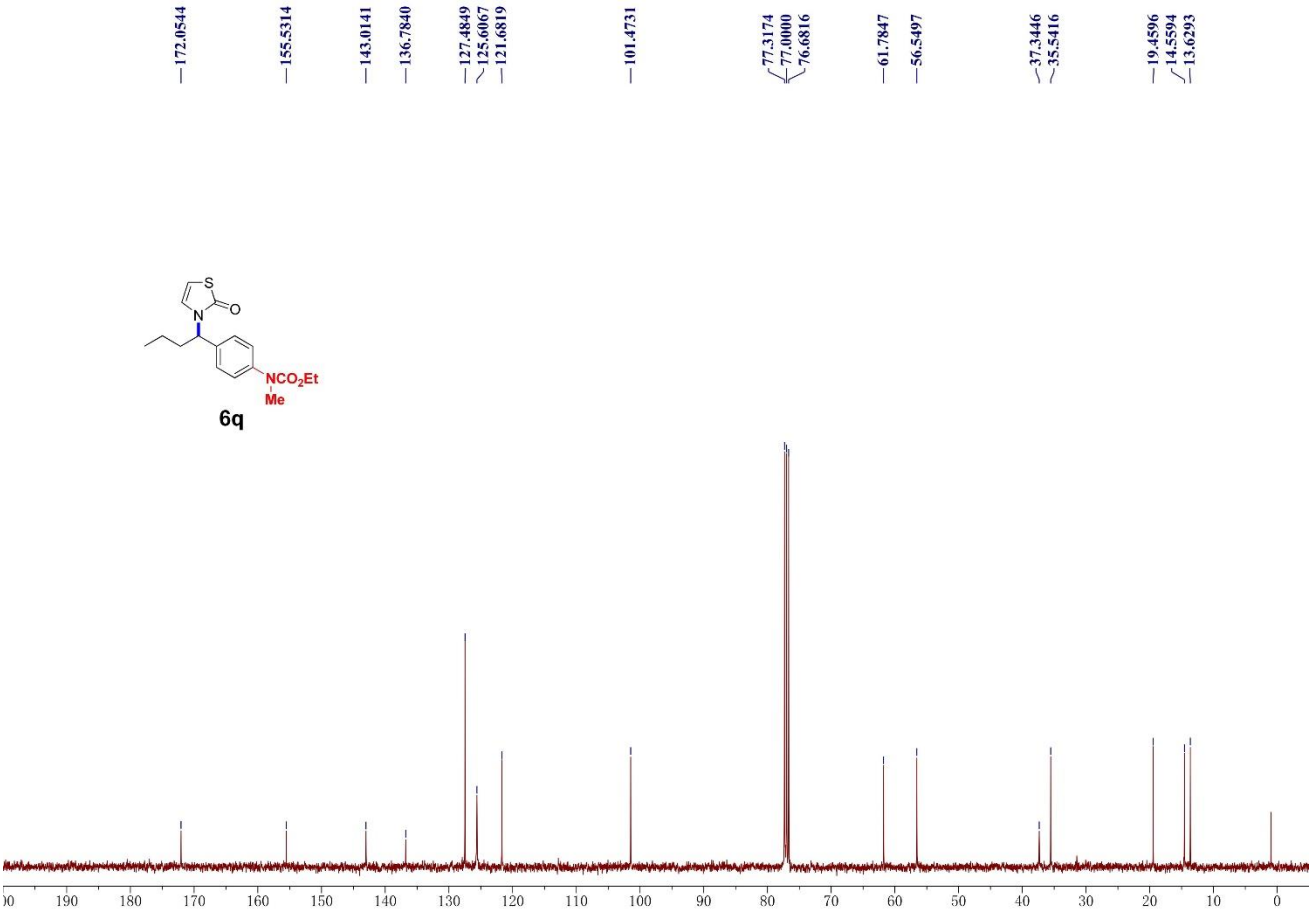

7.3946
7.3744
7.3668
7.3461
7.2767
7.2418
6.9962
6.2935
6.2798
6.0103
5.9965
5.7566
5.7393
5.7219
5.7046
4.2496
4.2318
4.2140
4.1962
2.6715
2.6526
2.6340
2.6156
2.5968
2.5779
2.5343
2.5157
2.4970
2.4786
2.4600
2.4413
1.6696
1.6520
1.3215
1.3037
1.2859
1.1050
1.0862
1.0674
NHCO2Et
8h
1.96
0.99
0.93
0.97
0.95
0.99
2.00
1.04
0.99
2.97
3.11
2.92

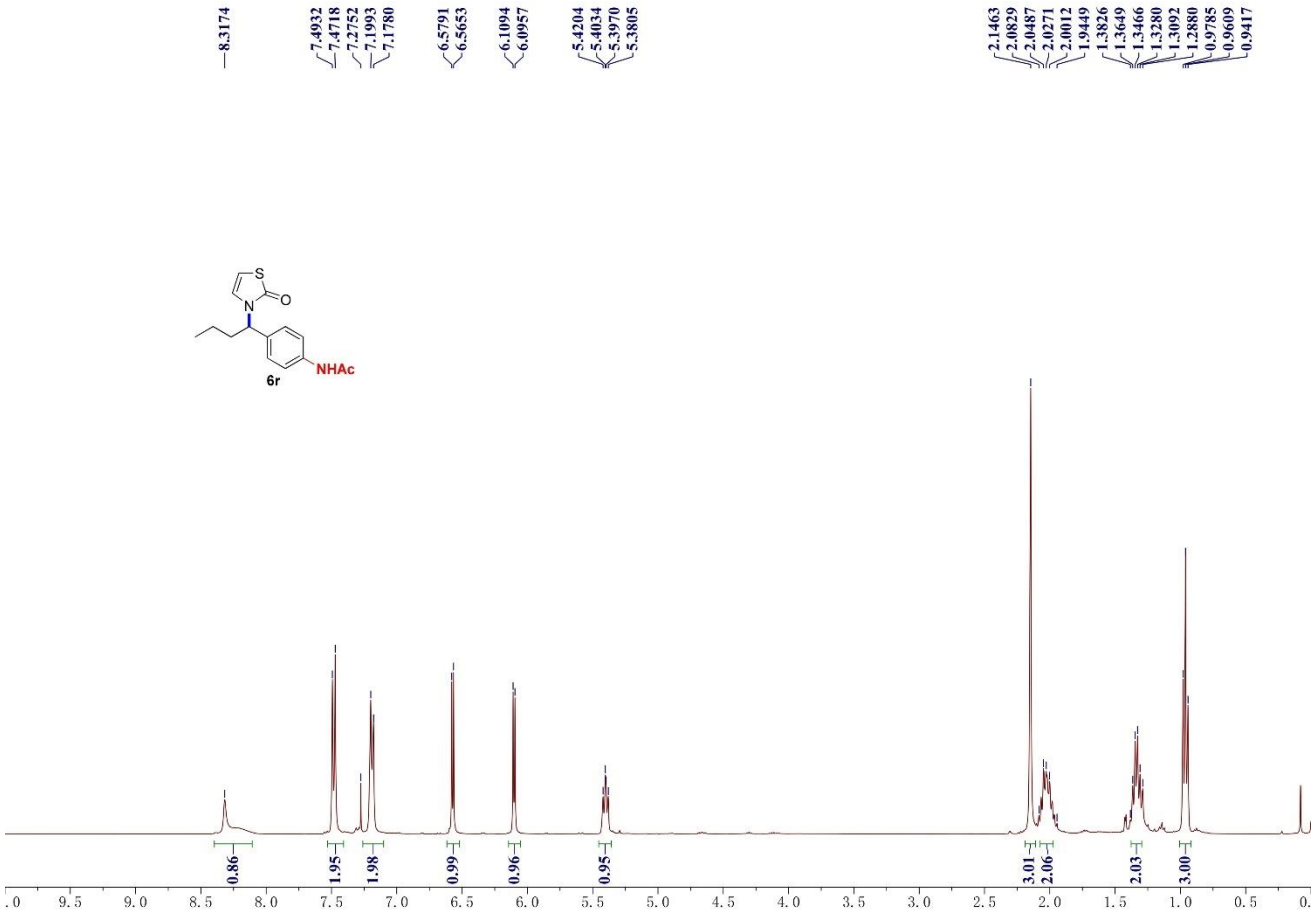

171.2051
153.6160
144.2771
138.3540
131.3963
126.6315
122.0990
119.1532
115.9957
101.1956
77.3185
77.0000
76.6827
61.1798
49.2104
24.7230
19.3736
14.5928
14.4674
NHCO2Et
8h

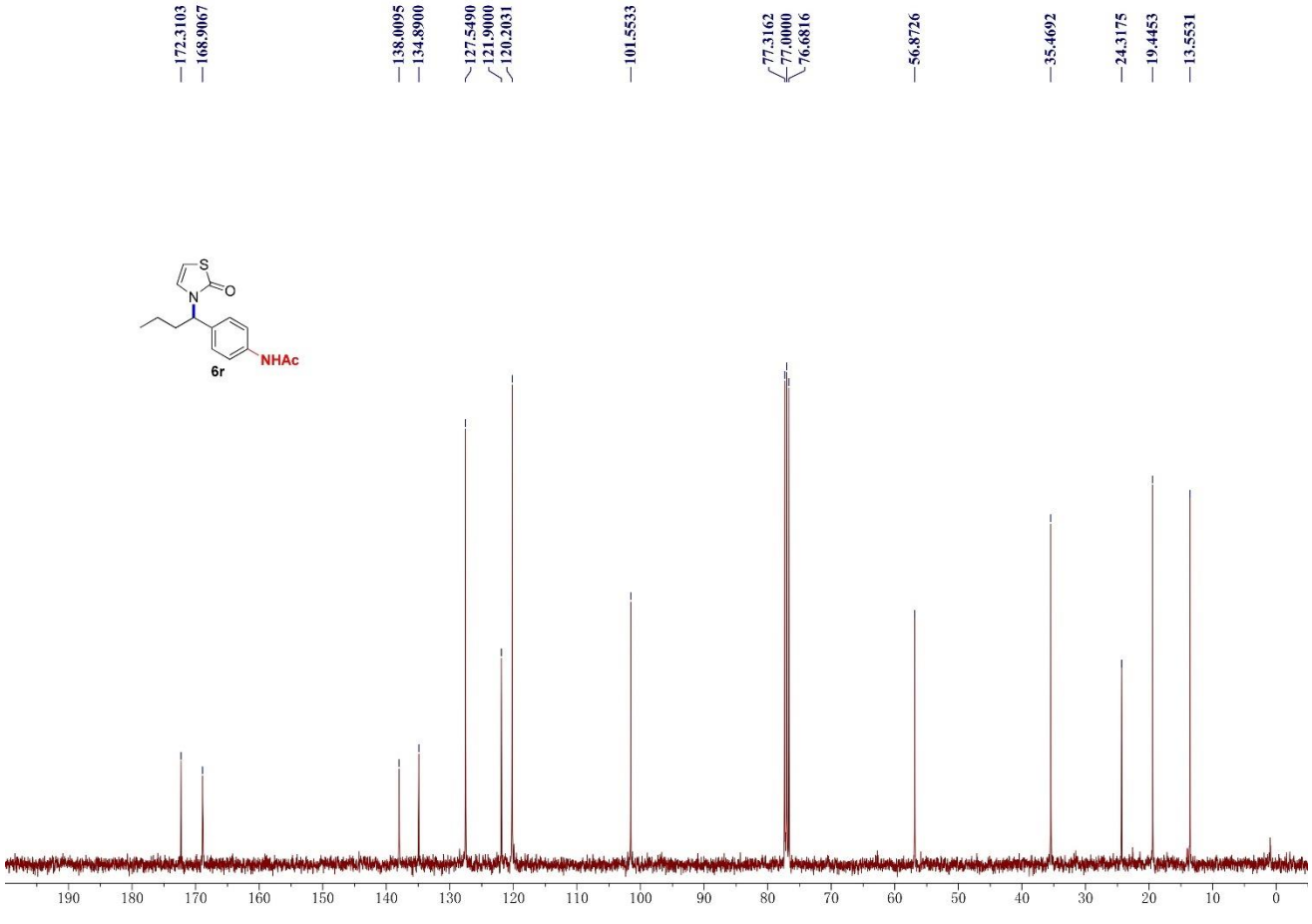

NHCO2Et
NOESY of 8h
f2 (ppm)
f1 (ppm)

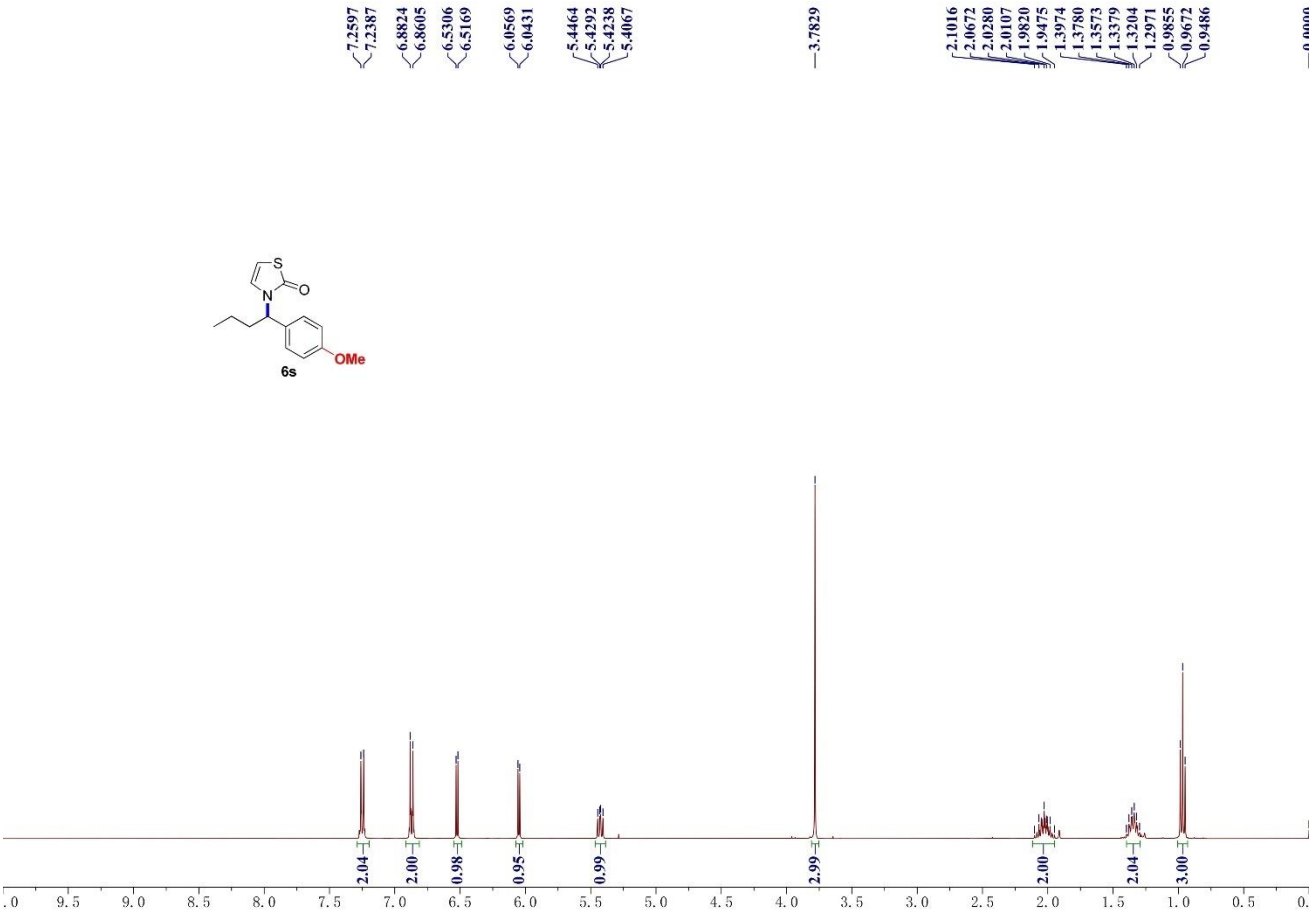
7.4 Spectra of Compounds in Scheme 1

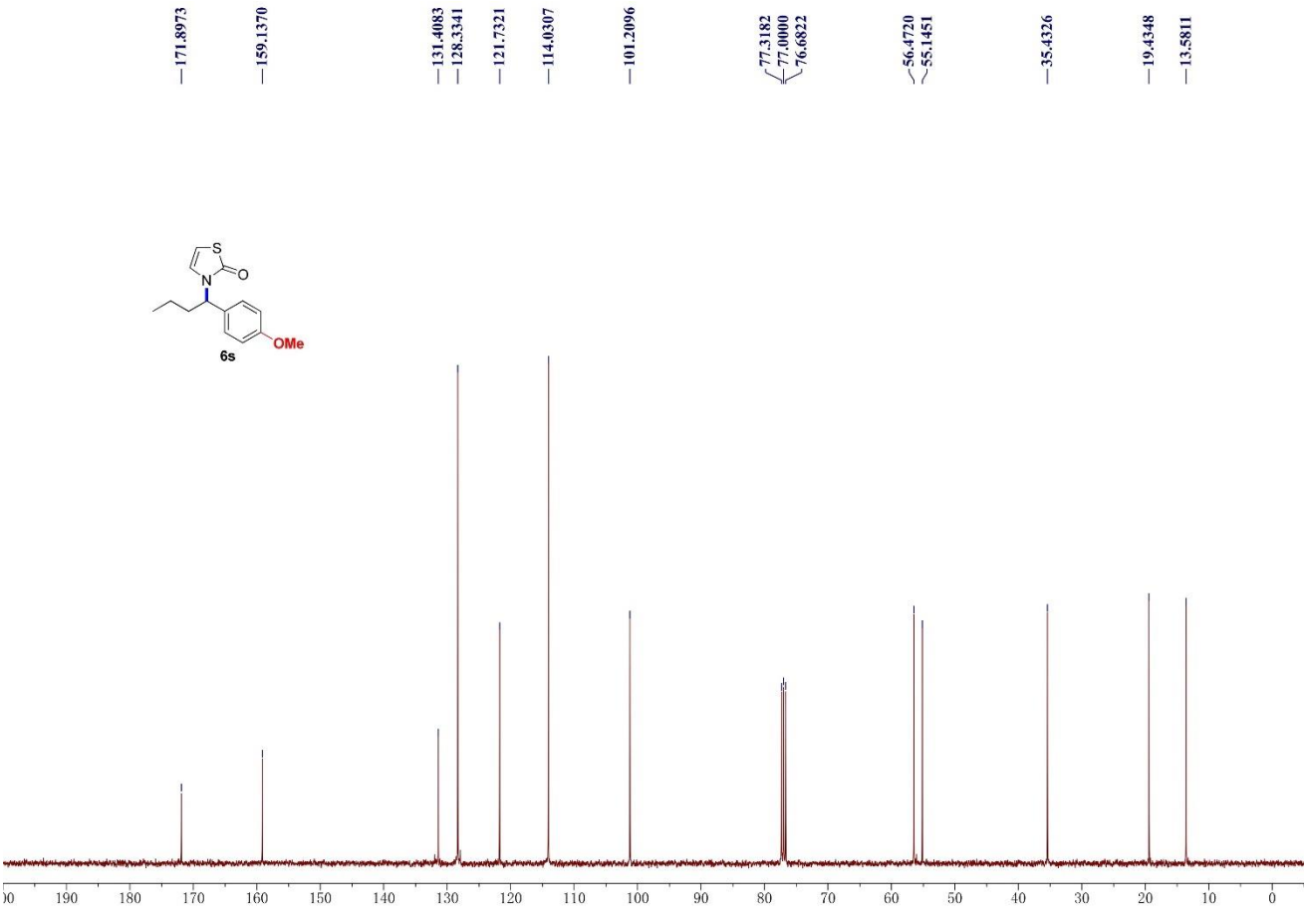


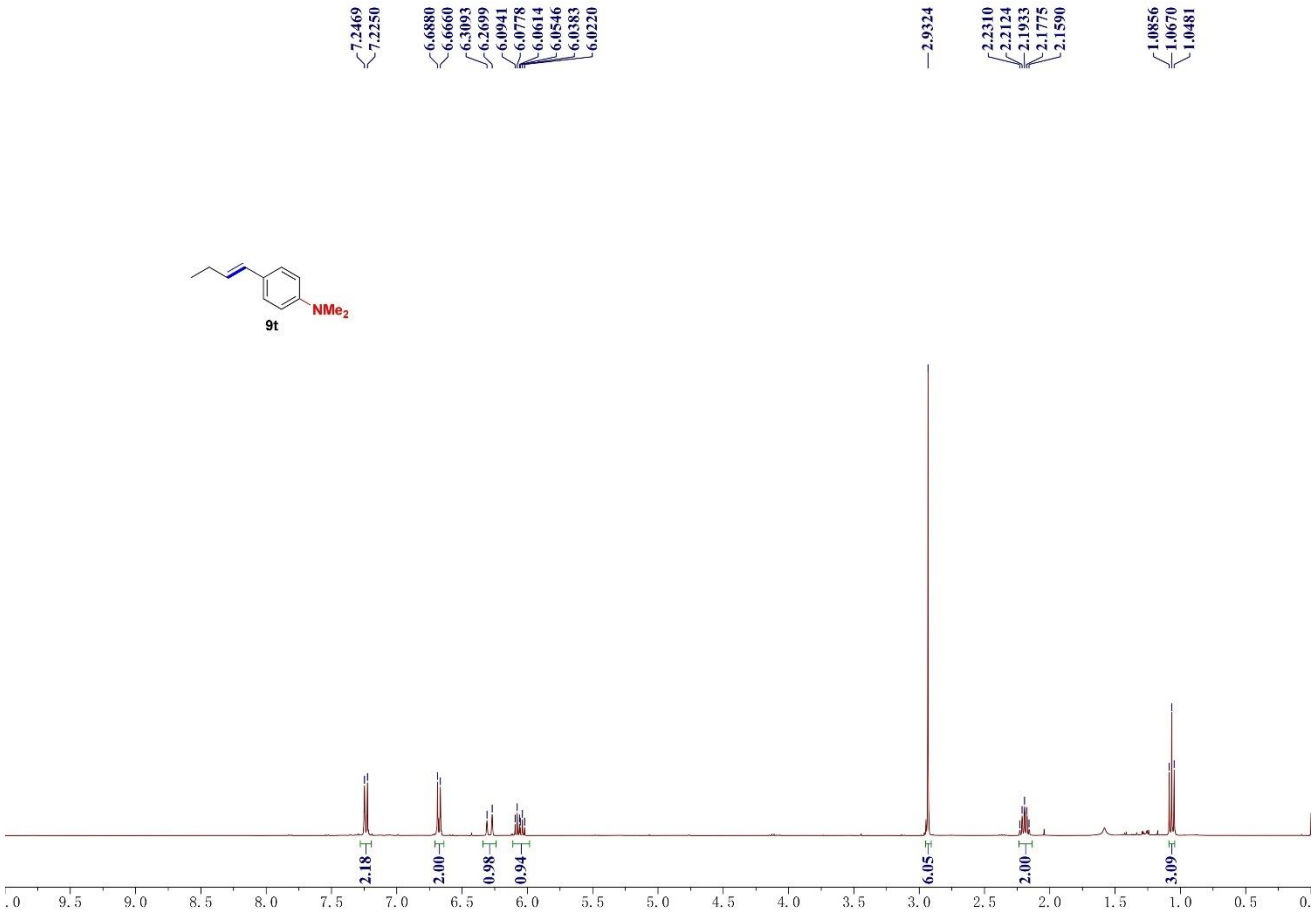


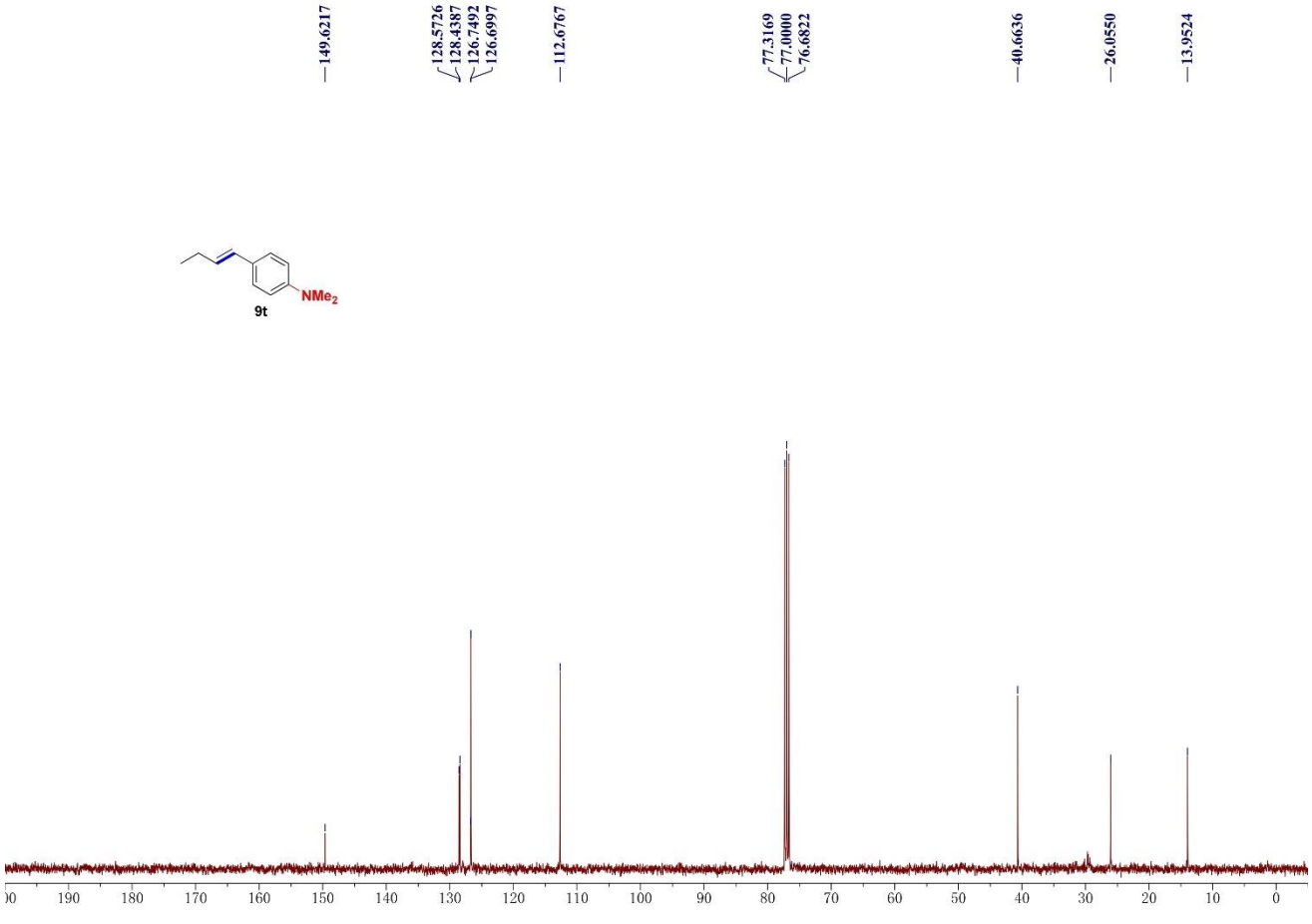

8.3174
7.4932
7.4718
7.2752
7.1993
7.1780
6.5791
6.5653
6.1094
6.0957
5.4204
5.4034
5.3970
5.3805
2.1463
2.0829
2.0487
2.0271
2.0012
1.9449
1.3826
1.3649
1.3466
1.3280
1.3092
1.2880
0.9785
0.9609
0.9417
S
N
O
NHAc
6r
0.86
1.95
1.98
0.99
0.96
0.95
3.01
2.06
2.03
3.00

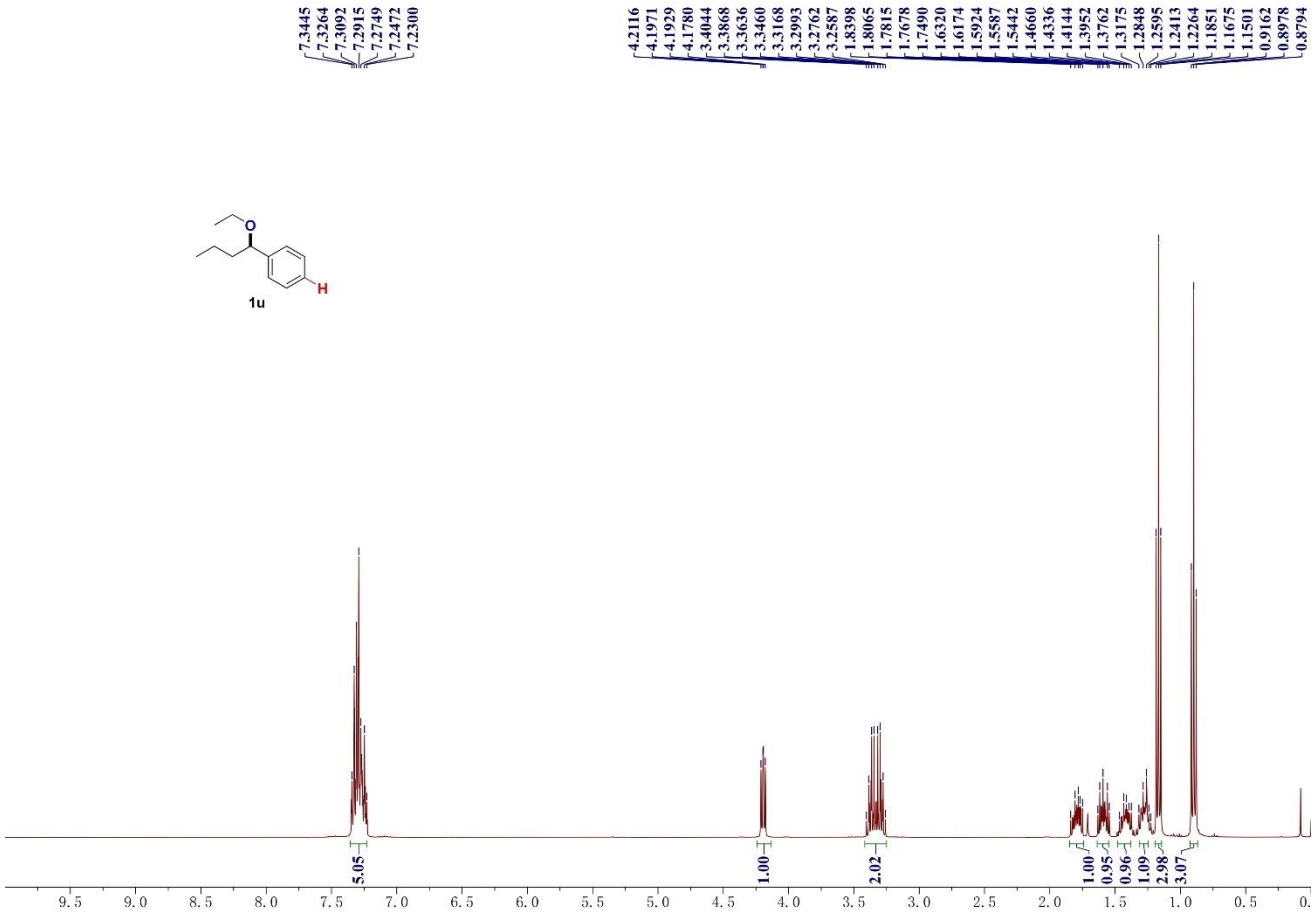

172.3103
168.9067
138.0095
134.8900
127.5490
121.9000
120.2031
101.5533
77.3162
77.0000
76.6816
56.8726
35.4692
24.3175
19.4453
13.5531
S
N
O
NHAc
6r

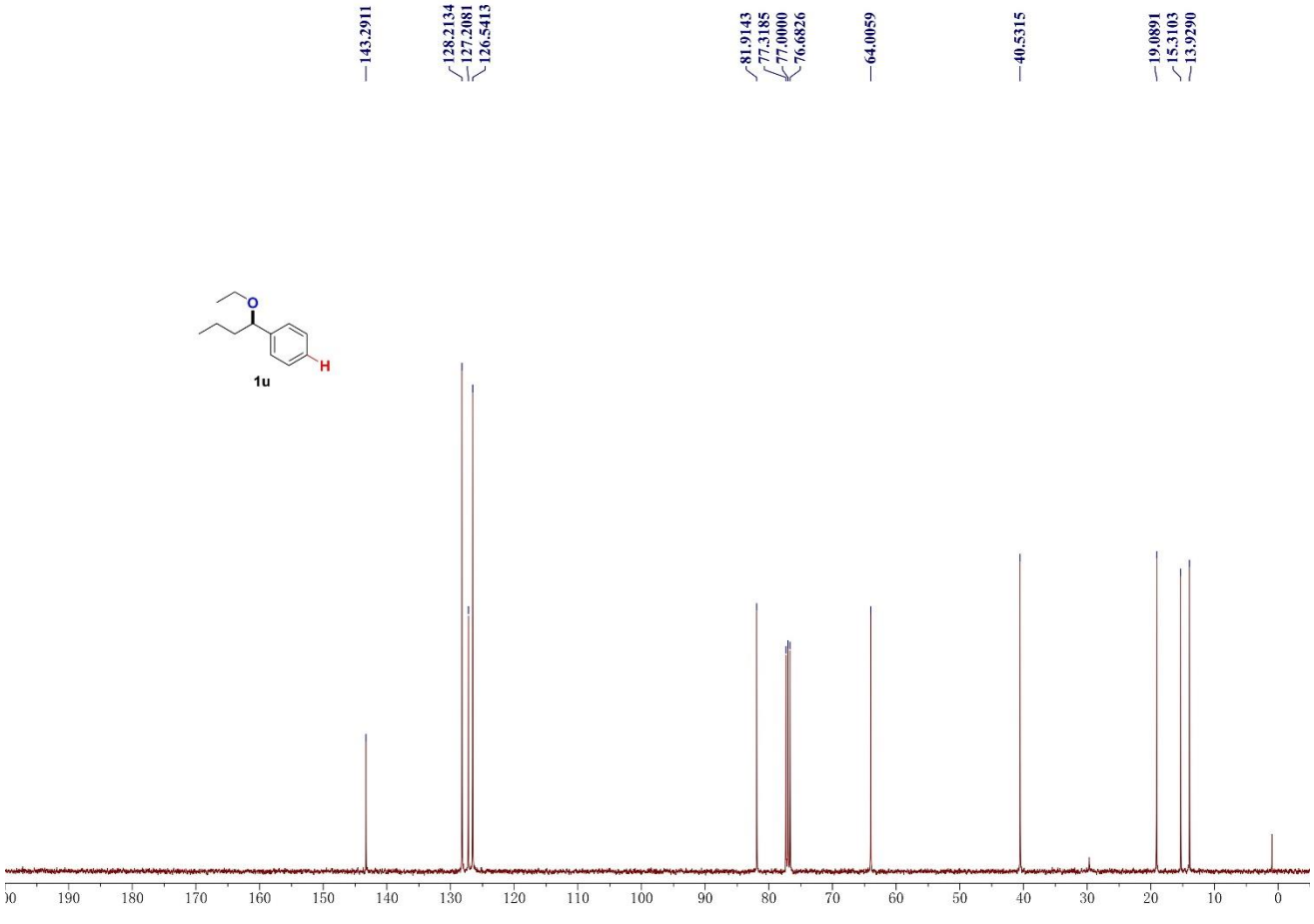

7.2597
7.2387
6.8824
6.8605
6.5306
6.5169
6.0569
6.0431
5.4464
5.4292
5.4238
5.4067
3.7829
2.1016
2.0672
2.0280
2.0107
1.9820
1.9475
1.3974
1.3780
1.3573
1.3379
1.3204
1.2971
0.9855
0.9672
0.9486
6s
2.04
2.00
0.98
0.95
0.99
2.99
2.00
2.04
3.00

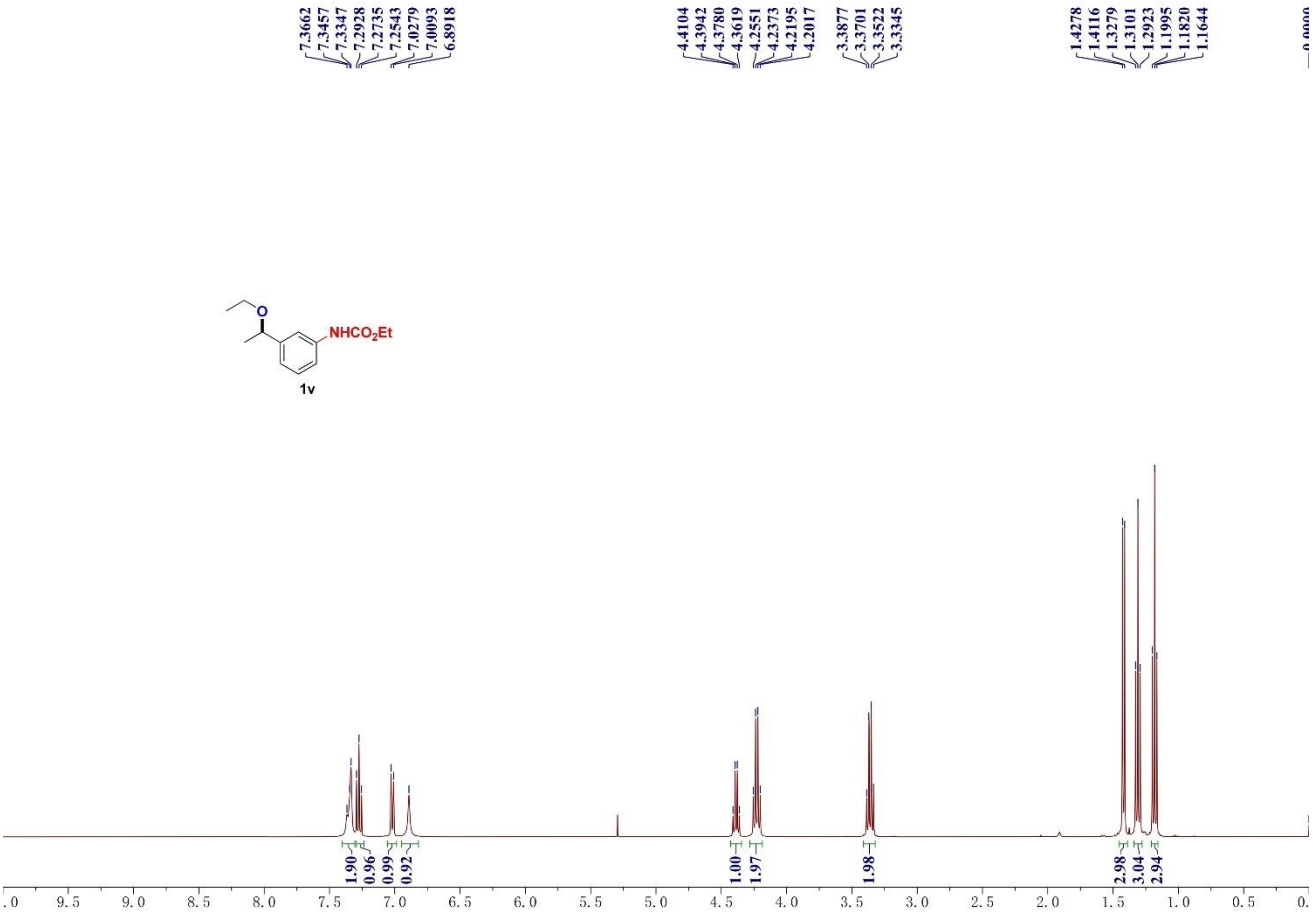

171.8973
159.1370
131.4083
128.3341
121.7321
114.0307
101.2096
77.3182
77.0000
76.6822
56.4720
55.1451
35.4326
19.4348
13.5811
6s

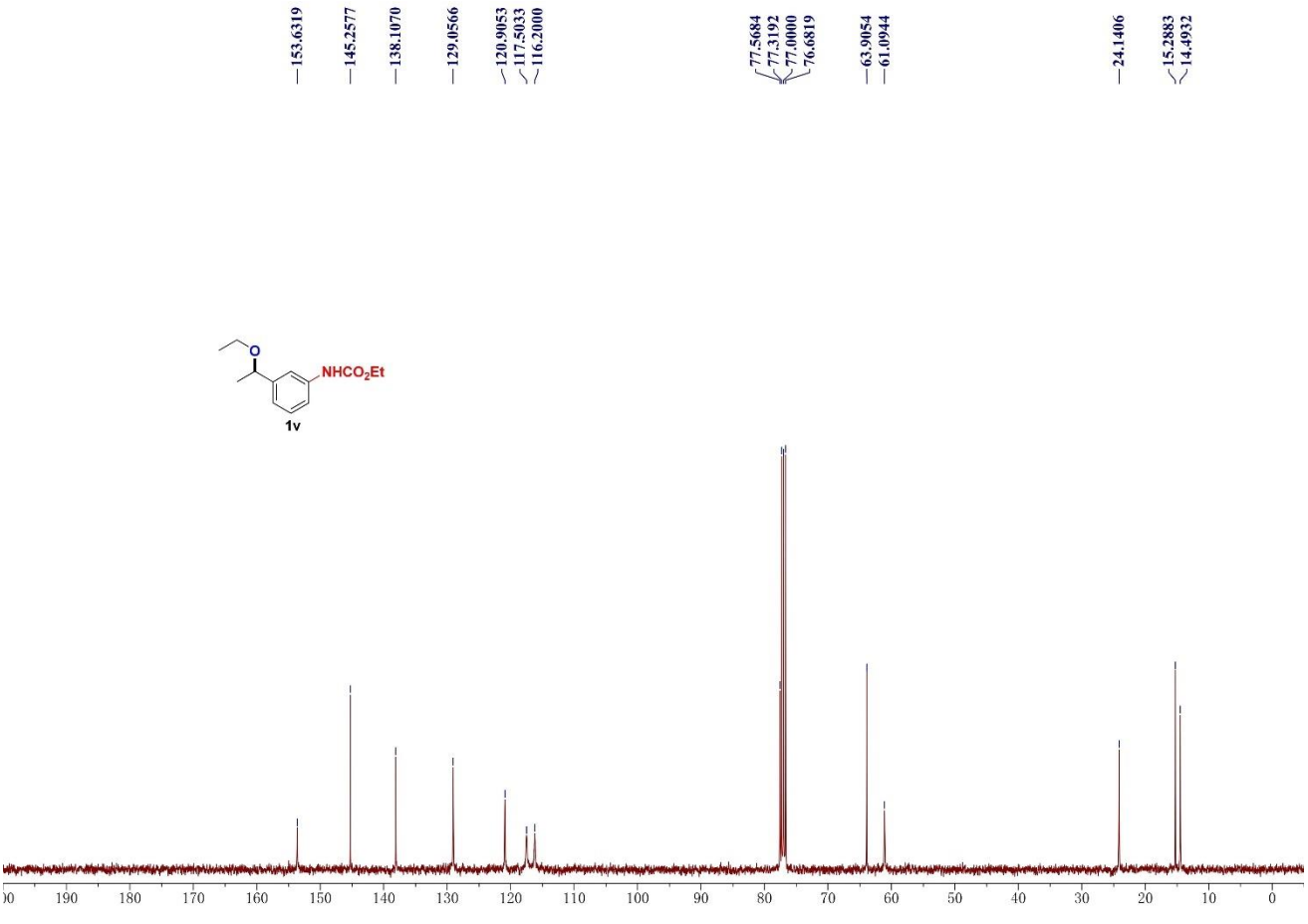

7.2469
7.2250
6.6880
6.6660
6.3093
6.2699
6.0941
6.0778
6.0614
6.0546
6.0383
6.0220
2.9324
2.2310
2.2124
2.1933
2.1775
2.1590
1.0856
1.0670
1.0481
NMe2
9t
2.18
2.00
0.98
0.94
6.05
2.00
3.09

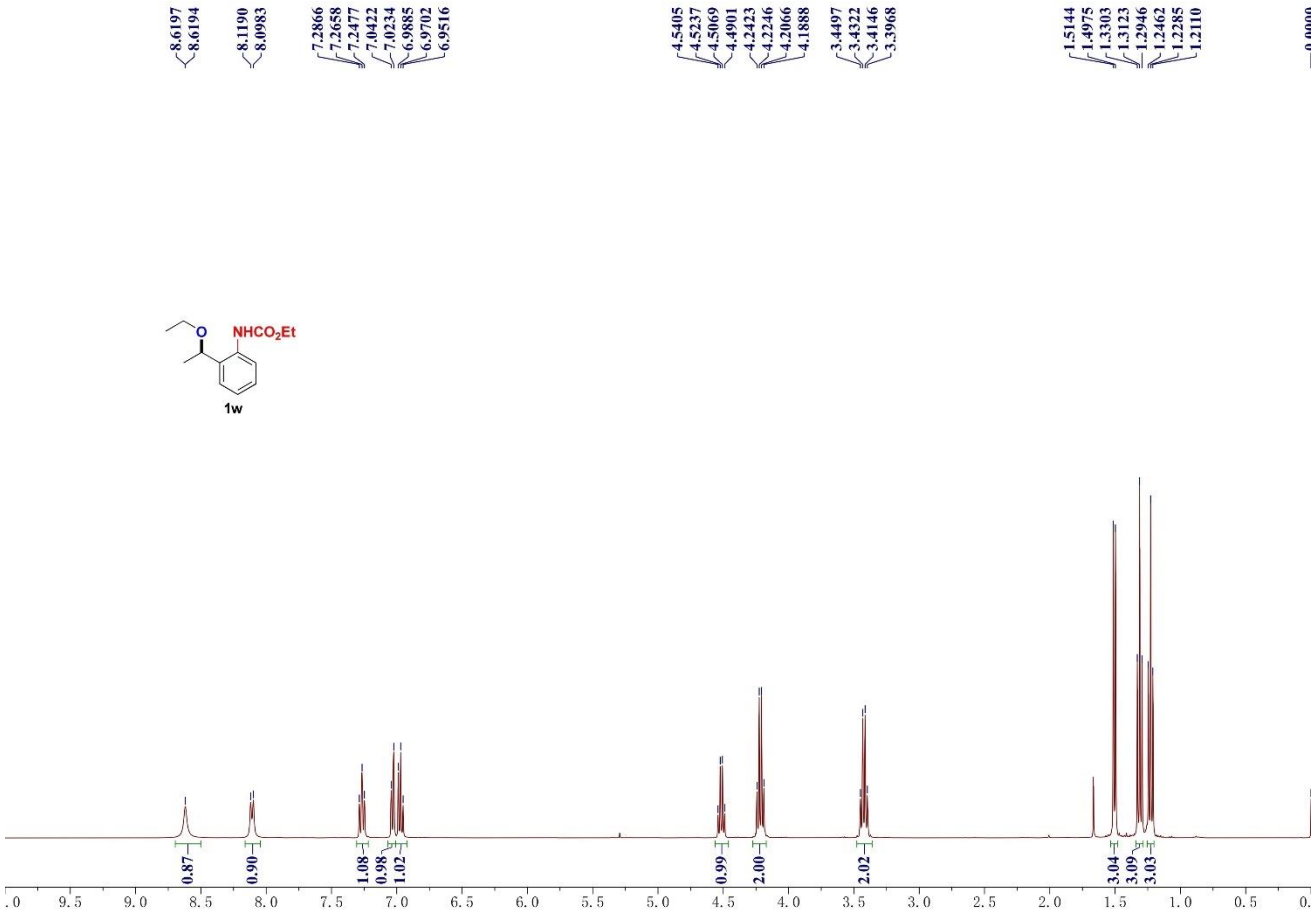

149.6217
128.5726
128.4387
126.7492
126.6997
112.6767
77.3169
77.0000
76.6822
40.6636
26.0550
13.9524
NMe2
9t

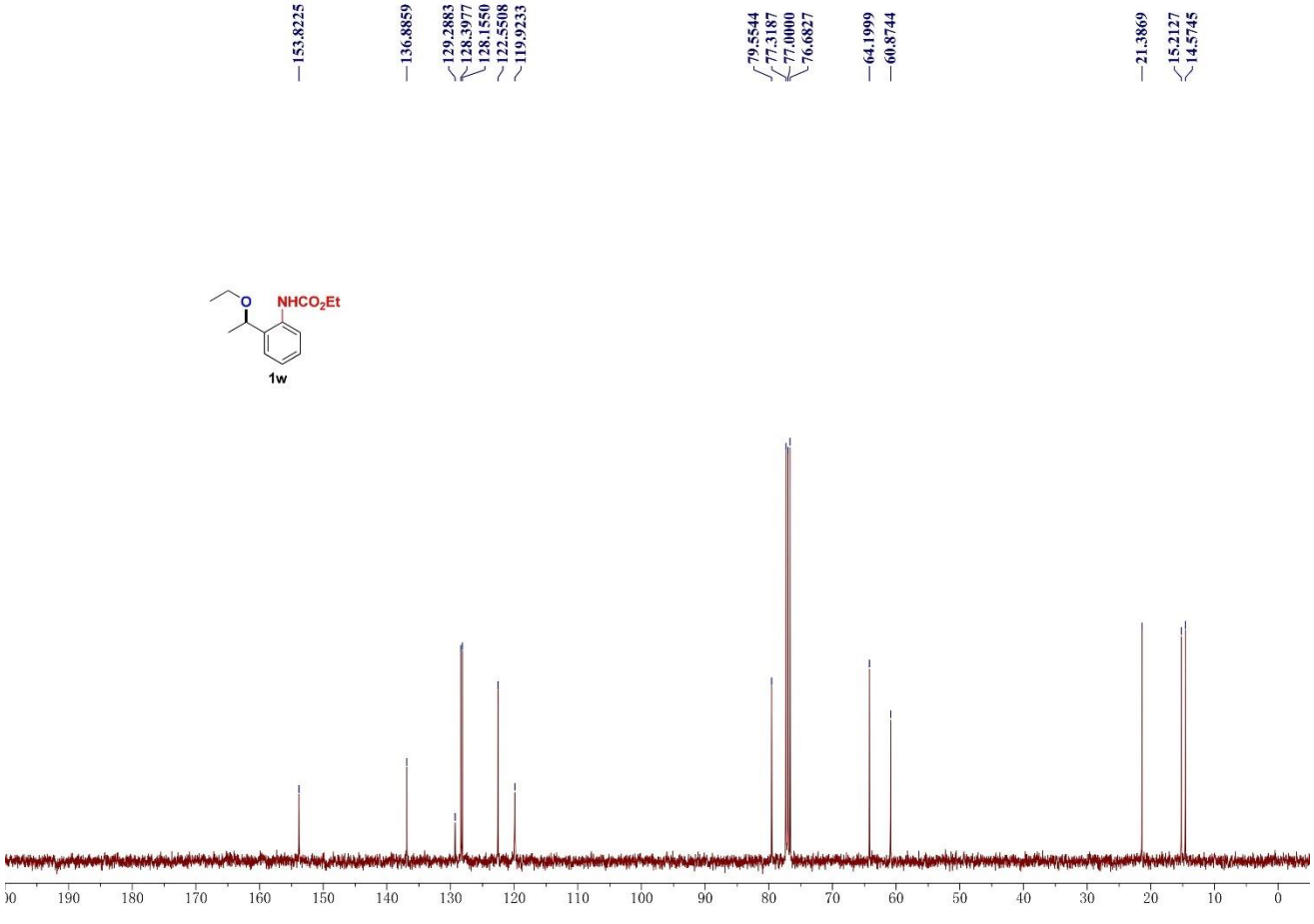

7.3445
7.3264
7.3092
7.2915
7.2749
7.2472
7.2300
4.2116
4.1971
4.1929
4.1780
3.4044
3.3868
3.3636
3.3460
3.3168
3.2993
3.2762
3.2587
1.8398
1.8065
1.7815
1.7678
1.7490
1.6320
1.6174
1.5924
1.5587
1.5442
1.4660
1.4336
1.4144
1.3952
1.3762
1.3175
1.2848
1.2595
1.2413
1.2264
1.1851
1.1675
1.1501
0.9162
0.8978
0.8794
O
H
1u
5.05
1.00
2.02
1.00
0.95
0.96
1.09
2.98
3.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


143.2911
128.2134
127.2081
126.5413
81.9143
77.3185
77.0000
76.6826
64.0059
40.5315
19.0891
15.3103
13.9290
O
H
1u
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

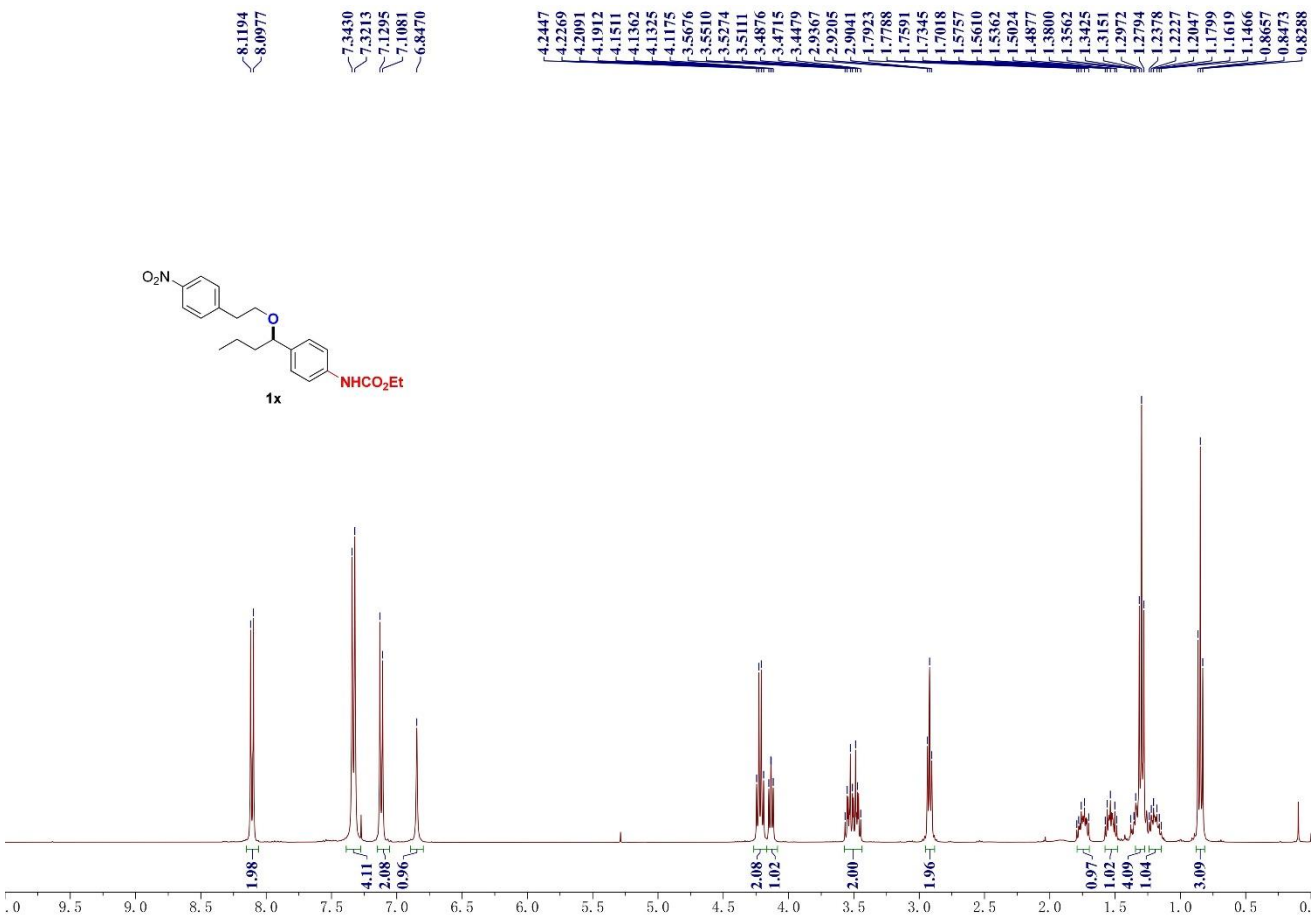

7.3662
7.3457
7.3347
7.2928
7.2735
7.2543
7.0279
7.0093
6.8918
4.4104
4.3942
4.3780
4.3619
4.2551
4.2373
4.2195
4.2017
3.3877
3.3701
3.3522
3.3345
1.4278
1.4116
1.3279
1.3101
1.2923
1.1995
1.1820
1.1644
NHCO2Et
1v
1.90
0.96
0.99
0.92
1.00
1.97
1.98
2.98
3.04
2.94

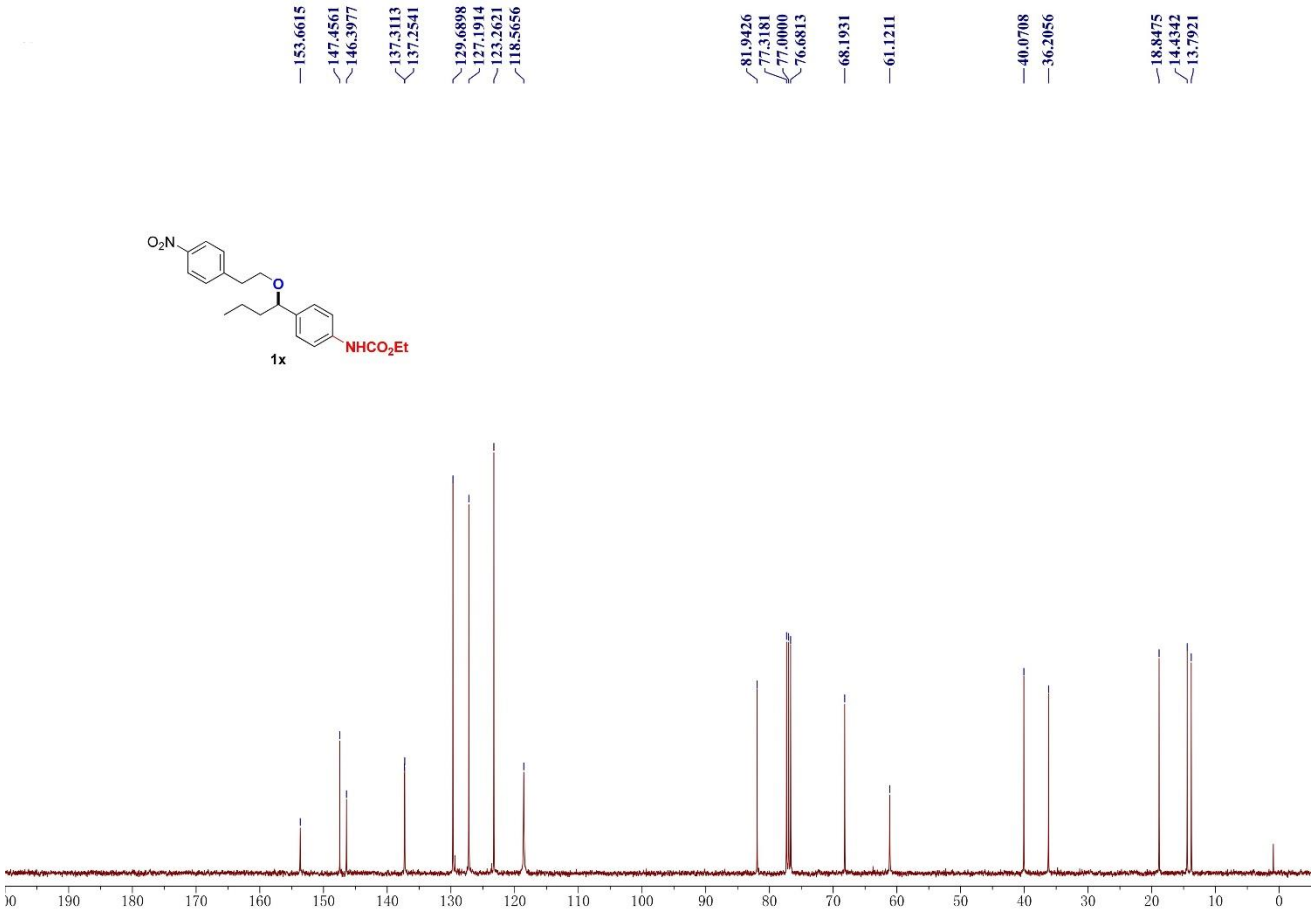

153.6319
145.2577
138.1070
129.0566
120.9053
117.5033
116.2000
77.5684
77.3192
77.0000
76.6819
63.9054
61.0944
24.1406
15.2883
14.4932
NHCO2Et
1v

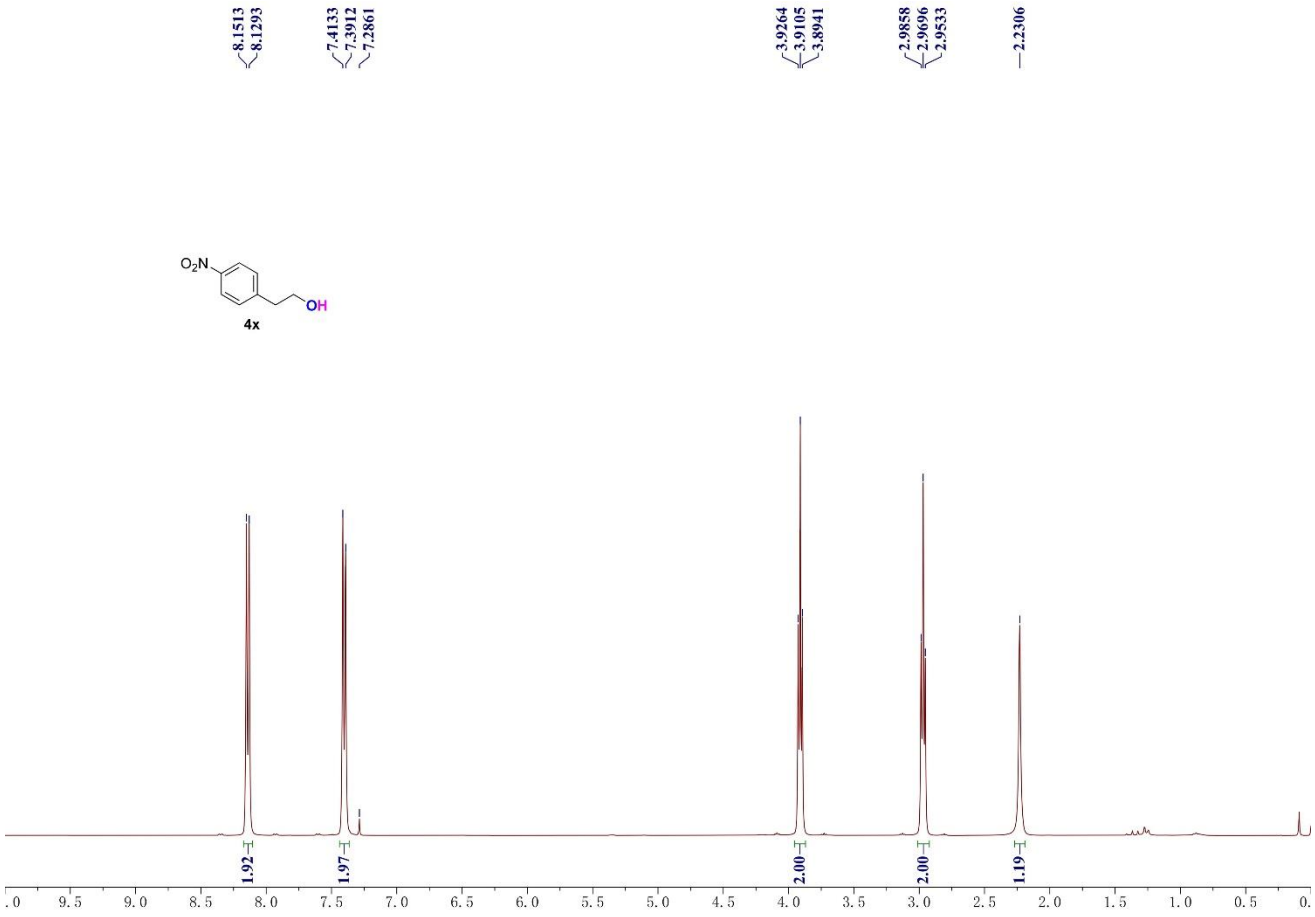

8.6197
8.6194
8.1190
8.0983
7.2866
7.2658
7.2477
7.0422
7.0234
6.9885
6.9702
6.9516
4.5405
4.5237
4.5069
4.4901
4.2423
4.2246
4.2066
4.1888
3.4497
3.4322
3.4146
3.3968
1.5144
1.4975
1.3303
1.3123
1.2946
1.2462
1.2285
1.2110
NHCO2Et
1w
0.87
0.90
1.08
0.98
1.02
0.99
2.00
2.02
3.04
3.09
3.03

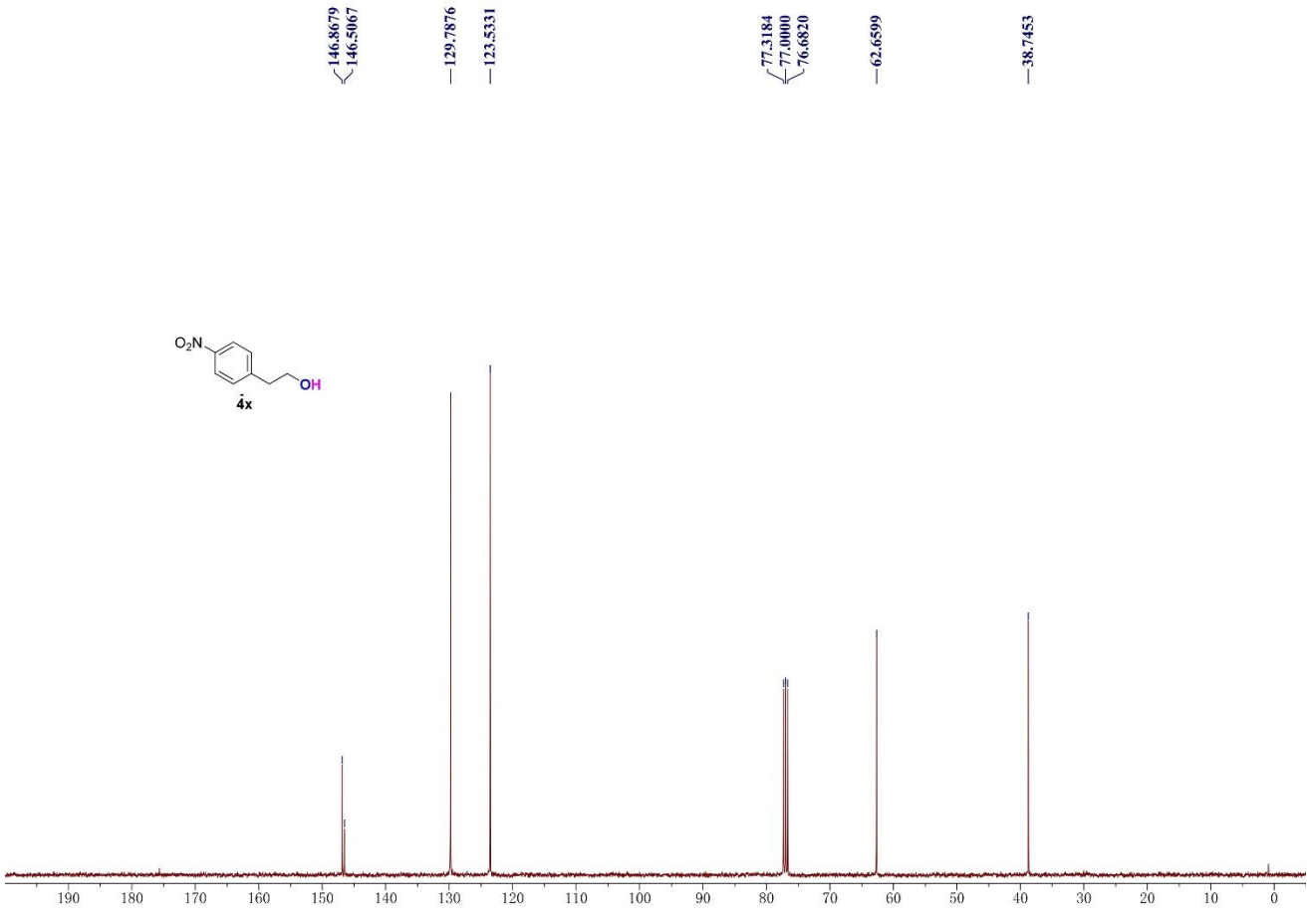

153.8225
136.8859
129.2883
128.3977
128.1550
122.5508
119.9233
79.5544
77.3187
77.0000
76.6827
64.1999
60.8744
21.3869
15.2127
14.5745
NHCO2Et
1w

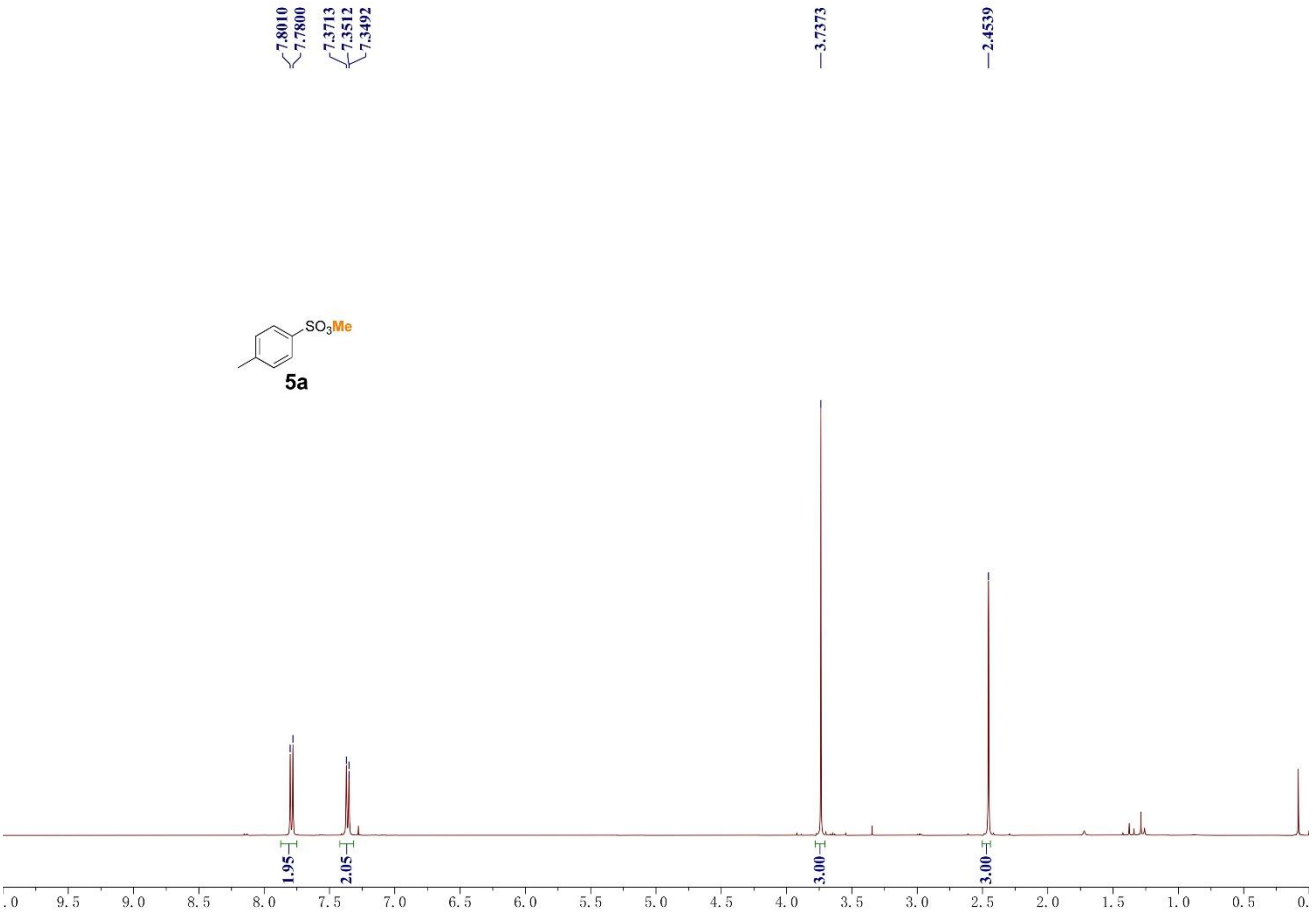
7.5 Spectra of Compounds in Scheme 2

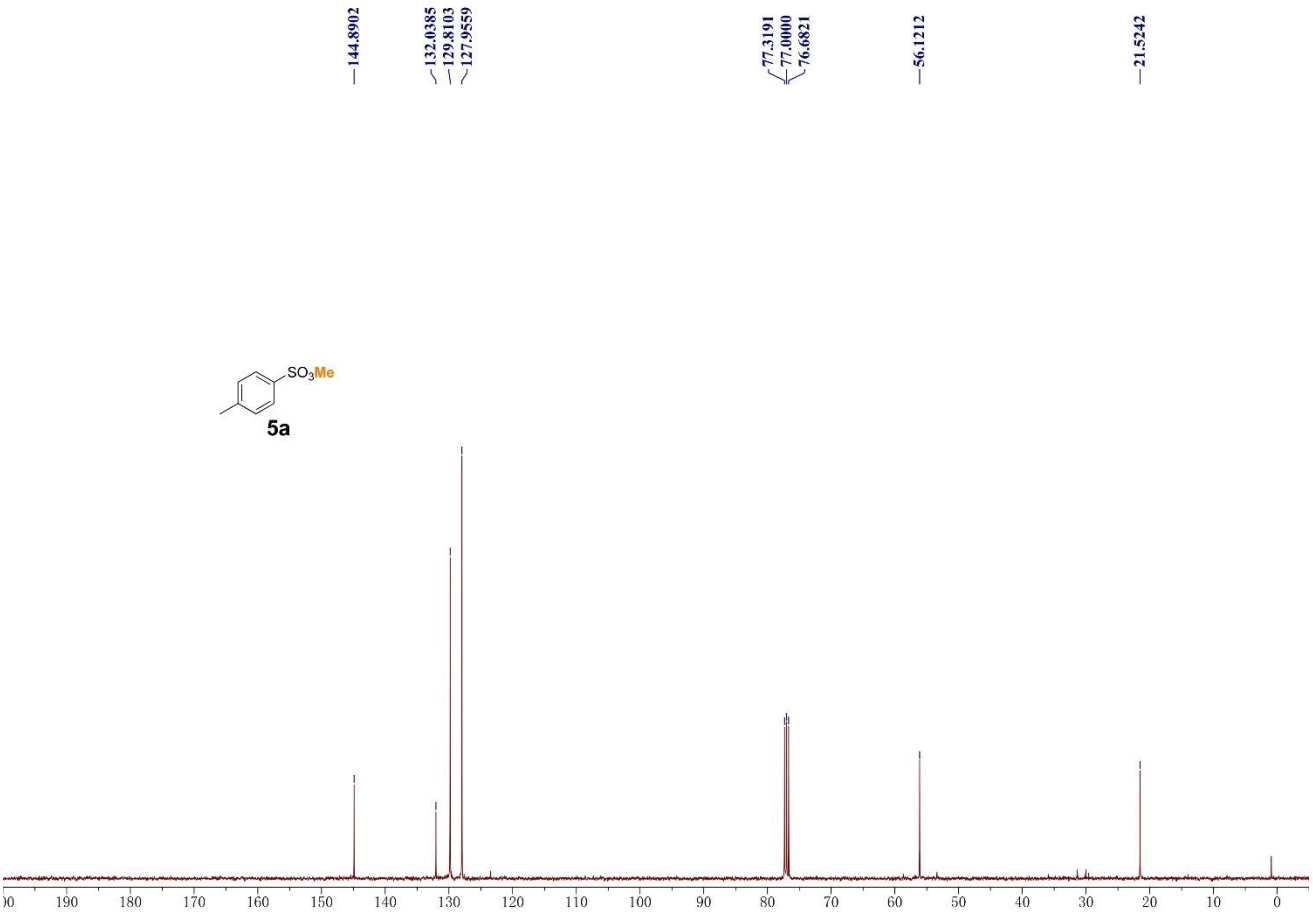


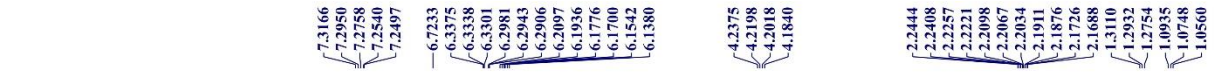



8.1513
8.1293
7.4133
7.3912
7.2861
3.9264
3.9105
3.8941
2.9858
2.9696
2.9533
2.2306
O2N
OH
4x
1.92
1.97
2.00
2.00
1.19


146.8679
146.5067
129.7876
123.5331
77.3184
77.0000
76.6820
62.6599
38.7453
O2N
OH
4x


7.8010
7.7800
7.3713
7.3512
7.3492
3.7373
2.4539
SO3Me
5a
1.95
2.05
3.00
3.00


144.8902
132.0385
129.8103
127.9559
77.3191
77.0000
76.6821
56.1212
21.5242
SO3Me
5a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6.1380
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4.2198
4.2018
4.1840
2.2444
2.2408
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2.2221
2.2098
2.2067
2.2034
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2.1876
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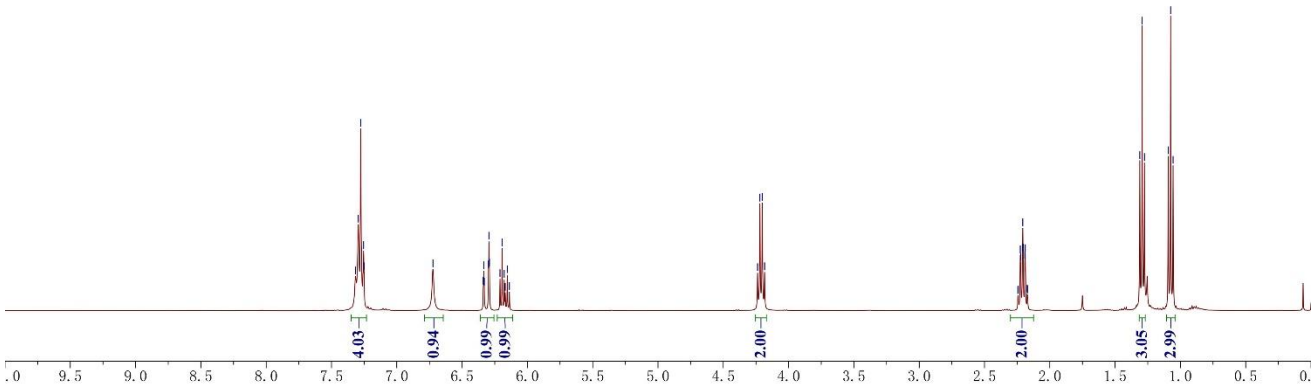
NHCO2Et

9a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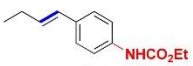
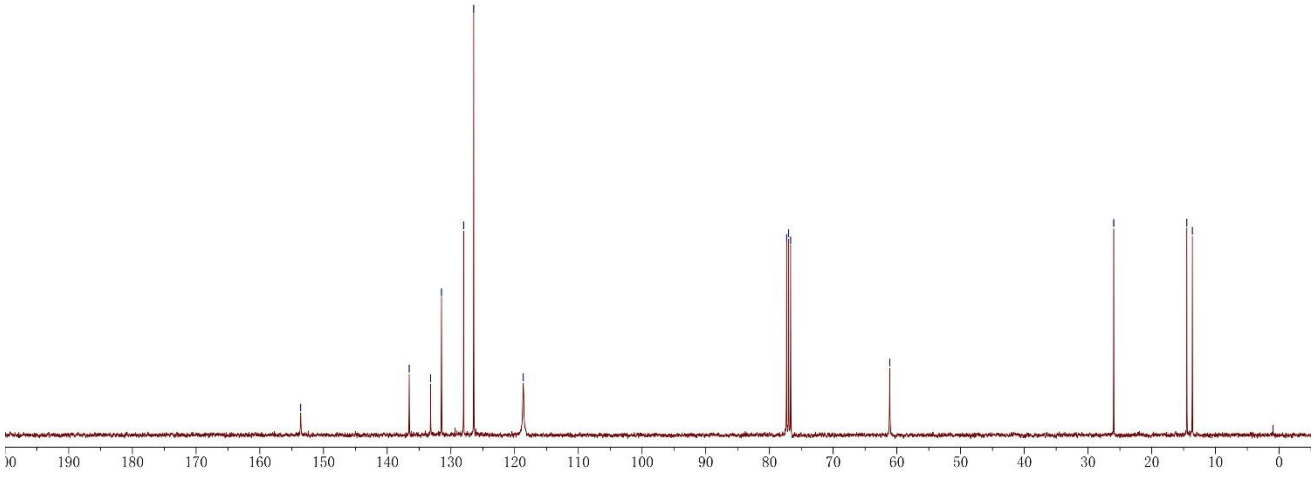
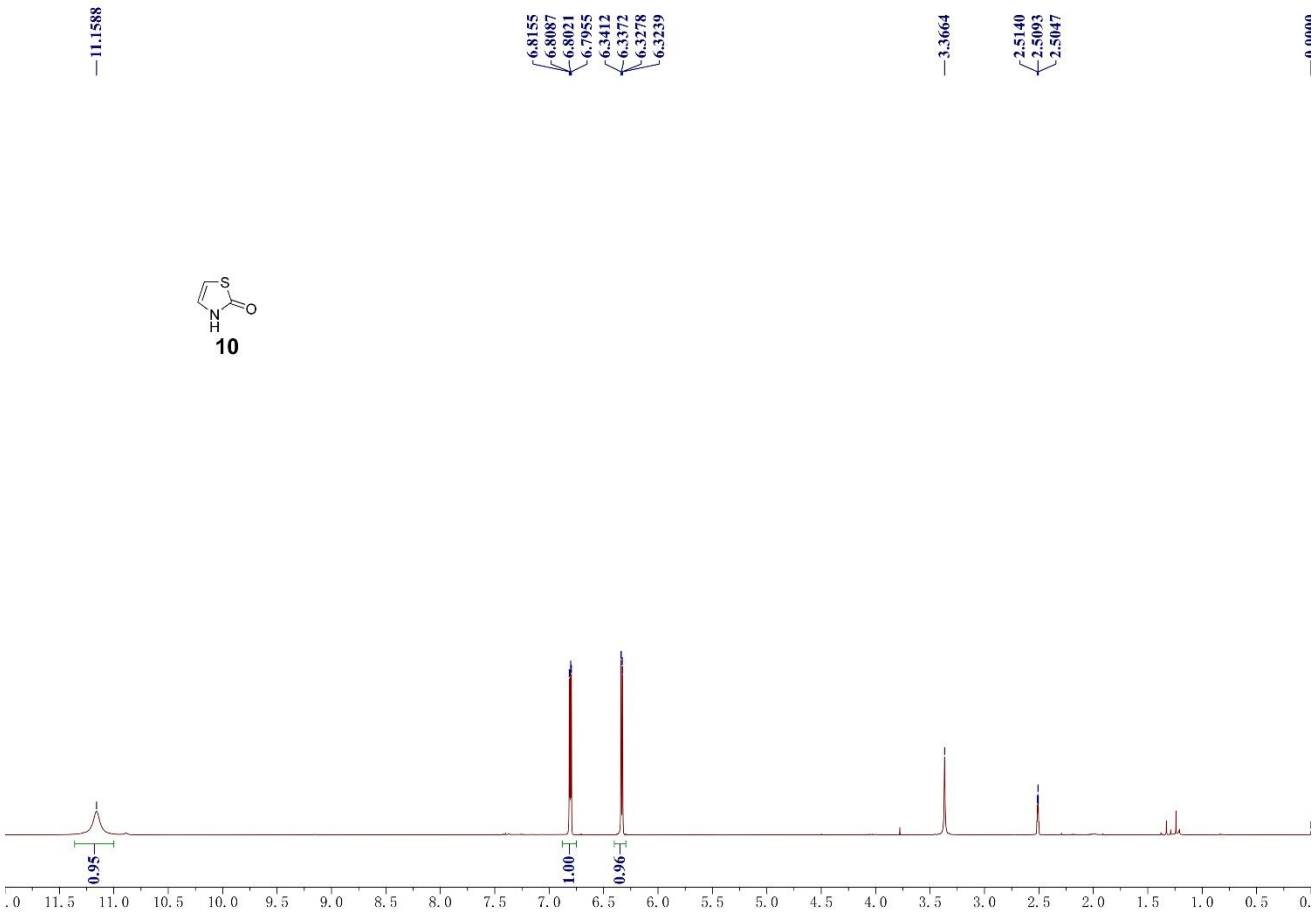

NHCO2Et

9a

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H
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1.00
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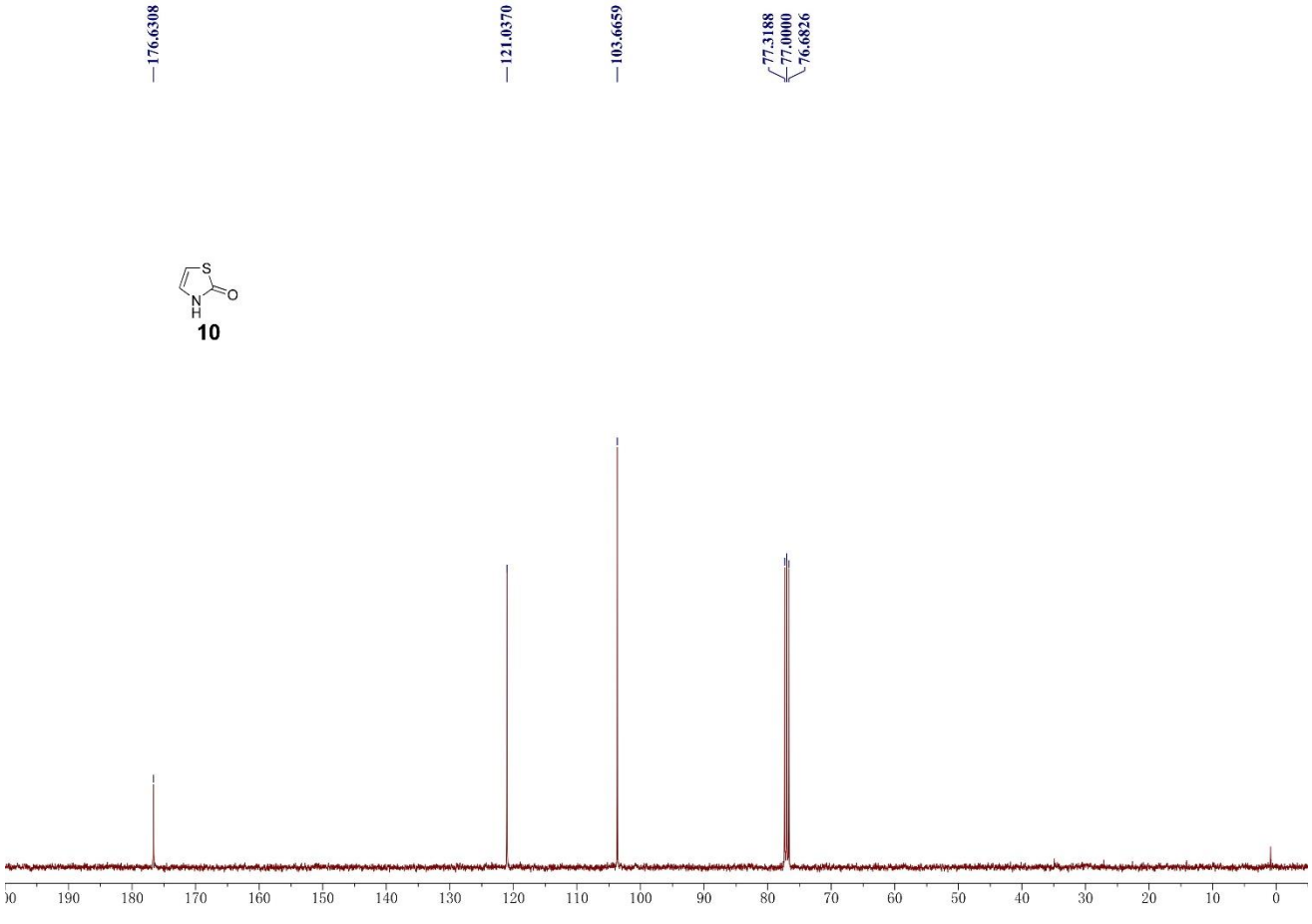
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